Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Are Pyridinium Ylides Radicals?

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SUPPORTING INFORMATION

1. Materials and Methods

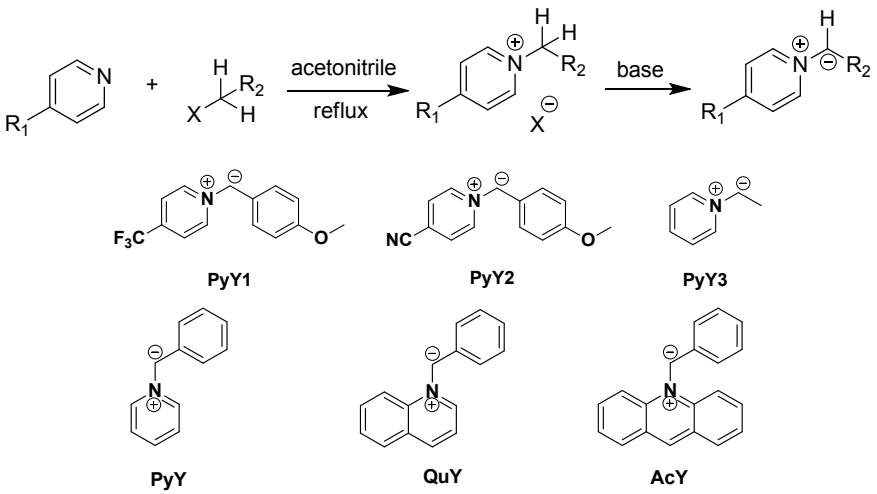
1.1 Materials

All reagents and solvents and were obtained from Energy Chemicals and were used as received. Water was deionized with a Milli-Q SP reagent water system (Millipore) to a specific resistivity of 18.2 MΩ. Analytical thin layer chromatography (TLC) was performed using glass plates pre-coated with silica gel and zinc phosphate (0.25 mm).TLC plates were visualized by exposure to UV light (UV) at 254 nm. Flash column chromatography was performed using silica gel 60 (230-400 mesh, Merck) with the indicated solvents.

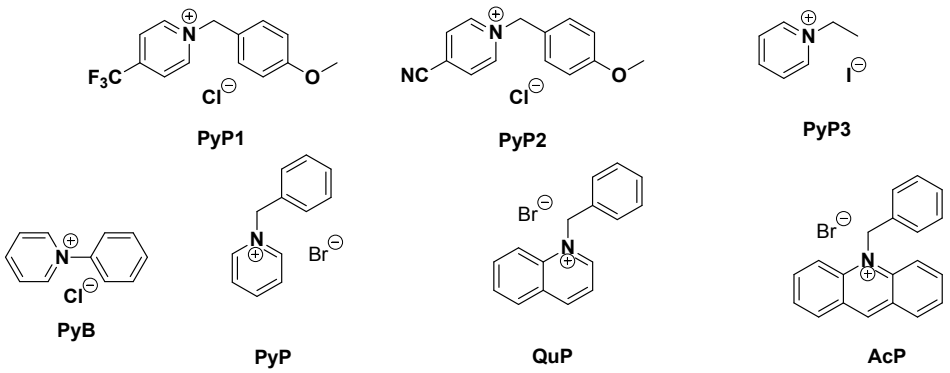
1.2 Methods

^{1}H-NMR spectra were recorded on a Bruker AV400 NMR spectrometer operated in the Fourier transform mode, NMR spectra were recorded at 400 MHz for ^{1}H and 101 MHz for ^{13}C. ^{1}H NMR spectra are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), integration, and coupling constant (*J*) in Hertz (Hz). ^{1}H NMR spectra were referenced to the signal for residual chloroform at 7.26 ppm or DMSO at 2.50 ppm. Electrospray ionization (ESI) mass spectra were recorded on an Acquity UPLC-Xevo G2 QT of mass spectrometer. EPR spectra were recorded on a JEOL JES-FA200 ESR spectrometer (300 K, 9.063 GHz, X-band) and a Bruker EMX plus 10/12 (equipped with Oxford ESR910 Liquid Helium cryostat). FT-IR spectra were recorded in the range of 400-4000 cm^{-1} on a BRUKER TENSOR II spectrophotometer. EasySpin were used for spectral simulations of EPR.

2. Synthesis



Scheme S1. Synthetic routes and structures of pyridinium yldies.



Scheme S2. Structures of N-alkyl substituted pyridinium salts.

General Procedures for the synthesis of the precursor of pyridinium ylide (PyP) derivatives represented by 1-(4-methoxybenzyl)-4-(trifluoromethyl)pyridin-1-ium chloride (PyP1).

4-(trifluoromethyl)pyridine (1.47 g, 10 mmol) and 1-(chloromethyl)-4- methoxybenzene (1.57 g, 10 mmol) were added to a round-bottomed flask containing 10 mL acetonitrile and the solution was stirred at 80 °C overnight. The mixture was cooled to room temperature, and then the acetonitrile solvent was removed in vacuum. The resulting solid was washed with ethyl acetate to give the final product[1] (2.64 g, 87%). ^{1}H NMR (400 MHz, DMSO) δ 9.57 (d, *J* = 6.3 Hz, 2H), 8.67 (d, *J* = 6.5 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 7.07 – 6.96 (m, 2H), 5.94 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 160.17, 146.96, 142.93 (q, $J^{2}_{C\text{-}F}$ = 36 Hz), 131.14, 125.74, 125.24 (q, $J^{3}_{C\text{-}F}$ = 3 Hz), 121.36 (q, $J^{1}_{C\text{-}F}$ = 273 Hz) , 114.54, 63.31, 55.31. ^{19}F NMR (377 MHz, DMSO) δ = -63.88. HRMS (ESI+) m/z 268.0940 [M^+, calculated mass for $C_{14}H_{13}F_3NO^+$: 268.0944 amu].

4-cyano-1-(4-methoxybenzyl)pyridin-1-ium chloride (PyP2). Synthesized according to the above method for **PyP1**. Yield 2.16 g, 88%. ^{1}H NMR (400 MHz, DMSO) δ 9.66 (d, J = 6.6 Hz, 2H), 8.73 (d, *J* = 6.4 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 5.96 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 160.19, 145.98, 131.33, 131.11, 127.25, 125.68, 114.85, 114.57, 63.58, 55.32. HRMS (ESI+) m/z 225.1023 [M^+, calculated mass for $C_{14}H_{13}N_2O^+$: 225.1022 amu].

1-ethylpyridin-1-ium iodide (PyP3). Synthesized according to the above method for **PyP1**. Yield 2.02 g, 86%. ^{1}H NMR (400 MHz, DMSO) δ 9.14 (d, *J* = 5.7 Hz, 2H), 8.62 (t, *J* = 7.8 Hz, 1H), 8.18 (t, *J* = 7.0 Hz, 2H), 4.66 (q, *J* = 7.3 Hz, 2H), 1.55 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ = 145.41, 144.53, 128.08, 56.37, 16.35. HRMS (ESI+) m/z 108.0804 [M^+, calculated mass for $C_7H_{10}N^+$: 108.0808 amu].

1-benzylpyridin-1-ium bromide (PyP). Synthesized according to the above method for **PyP1**. Yield 2.20 g, 88%. ^{1}H NMR (400 MHz, DMSO) δ 9.28 (d, *J* = 6.6 Hz, 2H), 8.65 (tt, *J* = 7.9, 1.3 Hz, 1H), 8.21 (dd, *J* = 7.7, 6.8 Hz, 2H), 7.66 – 7.51 (m, 2H), 7.53 – 7.33 (m, 3H), 5.92 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 146.10 (s), 134.35 (s), 129.40 (s), 128.83 (s), 128.52 (s), 63.19 (s). HRMS (ESI+) m/z 170.0962 [M^+, calculated mass for $C_{12}H_{12}N^+$: 170.0964 amu].

1-benzylquinolin-1-ium bromide (QuP). Synthesized according to the above method for **PyP1**. Yield 2.40 g, 80%. ^{1}H NMR (400 MHz, DMSO) δ 9.80 (d, *J* = 5.7 Hz, 1H), 9.40 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.7 Hz, 2H), 8.32 (dd, *J* = 8.3, 5.8 Hz, 1H), 8.23 (t, *J* = 8.0 Hz, 1H), 8.03 (t, *J* = 7.7 Hz, 1H), 7.48 – 7.27 (m, 5H), 6.41 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 150.47 (s), 148.20 (s), 137.53 (s), 135.76 (s), 133.93 (s), 130.89 (s), 130.00 (s), 129.93 (s), 129.12 (s), 128.79 (s), 127.35 (s), 122.50 (s), 119.33 (s), 59.84 (s). HRMS (ESI+) m/z 220.1121 [M^+, calculated mass for $C_{16}H_{14}N^+$: 220.1121 amu].

Preparation of 10-benzylacridin-10-ium bromide (AcP). 0.5 g (2.8 mmol) of acridine was melted at 130 °C in a dried flask using an oil bath. Then 0.6 mL (5.0 mmol) of benzyl bromide were added dropwise under stirring at 130 °C which continued for additional 30 min. After cooling to rt, diethyl ether (100 mL) was added and the suspension was stirred again for 1 h. Then the mixture was filtered, the resulting solid product was washed with diethyl ether and recrystallized from methanol/diethyl ether. The compound was then kept dried over phosphorus pentoxide.[2] Yield 0.4 g (41%); ^{1}H NMR (400 MHz, DMSO) δ 10.35 (s, 1H), 8.72 (d, *J* = 7.5 Hz, 2H), 8.63 (d, *J* = 9.3 Hz, 2H), 8.49 – 8.39 (m, 2H), 8.12 – 7.99 (m, 2H), 7.40 – 7.25 (m, 3H), 7.23 – 7.08 (m, 2H), 6.78 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 152.44 (s), 141.41 (s), 139.91 (s), 134.49 (s), 132.23 (s), 129.08 (s), 128.12 (s), 127.94 (s), 126.68 (s), 125.99 (s), 118.70 (s), 53.19 (s). HRMS (ESI+) m/z 270.1279 [M^+, calculated mass for $C_{20}H_{16}N^+$: 270.1277 amu].

Synthesis of 1-phenylpyridin-1-ium (PyB). Synthesized according to the literature method.[3] Yield 44%. ^{1}H NMR (400 MHz, DMSO) δ 9.43 – 9.34 (m, 2H), 8.81 (tt, *J* = 7.9, 1.3 Hz, 1H), 8.37 – 8.27 (m, 2H), 7.96 – 7.87 (m, 2H), 7.81 – 7.72 (m, 3H). HRMS (ESI+) m/z 156.0808 [M^+, calculated mass for $C_{11}H_{10}N^+$: 156.0808 amu].

General Procedure for the preparation of pyridinium ylide (PyY) derivatives represented by (4-methoxyphenyl)(4-(trifluoromethyl)pyridin-1-ium-1-yl)methanide (PyY1).

There are two strategies for preparing **PyY1** derivatives. The first method is to dissolve **PyP1** in DMF (0.01 M), and then add potassium tert-butoxide (20 eq.) to it to obtain **PyY1** in solution. In the second

way, **PyP1** in H_2O treated with aqueous sodium hydroxide (20 eq.) gave a yellow solid, which was then centrifuged, washed with water, and lyophilized to obtain **PyY1** in solid state. HRMS (ESI+) m/z 268.0933 [$(M+H)^{\bullet+}$, calculated mass for $C_{14}H_{13}F_3NO^{\bullet+}$: 268.0944 amu].

(4-cyanopyridin-1-ium-1-yl)(4-methoxyphenyl)methanide (PyY2) . HRMS (ESI+) m/z 225.1022 [$(M+H)^{\bullet+}$, calculated mass for $C_{14}H_{13}N_2O^{\bullet+}$: 225.1022 amu].

1-(pyridin-1-ium-1-yl)ethan-1-ide (PyY3). HRMS (ESI+) m/z 108.0806 [$(M+H)^{\bullet+}$, calculated mass for $C_7H_{10}N^{\bullet+}$: 108.0808 amu].

Phenyl(pyridin-1-ium-1-yl)methanide (PyY). Obtained by the first method for **PyY1**. HRMS (ESI+) m/z 170.0965 [$(M+H)^{\bullet+}$, calculated mass for $C_{12}H_{12}N^{\bullet+}$: 170.0964 amu].

Phenyl(quinolin-1-ium-1-yl)methanide (QuY). Obtained by the first method for **PyY1**. HRMS (ESI+) m/z 220.1123 [$(M+H)^{\bullet+}$, calculated mass for $C_{16}H_{14}N^{\bullet+}$: 220.1121 amu].

Acridin-10-ium-10-yl(phenyl)methanide (AcY). Obtained by the first method for **PyY1**.

3. Supplementary Figures and Table

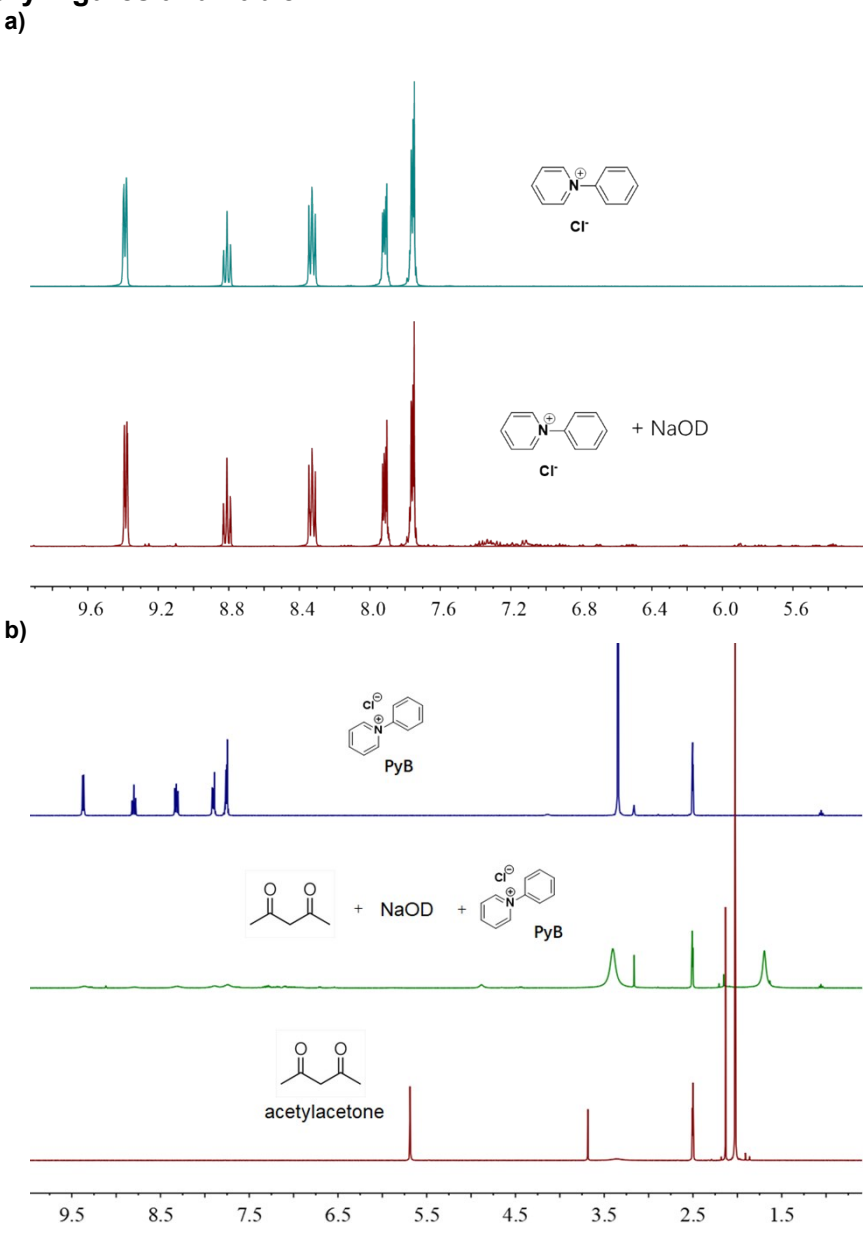


Fig. S1. ^{1}H-NMR spectra of a) **PyB** and **PyB** with NaOD (5 eq.) in DMSO-d_6 and b) **PyB** with the acetylacetone anion generated from NaOD and acetylacetone.

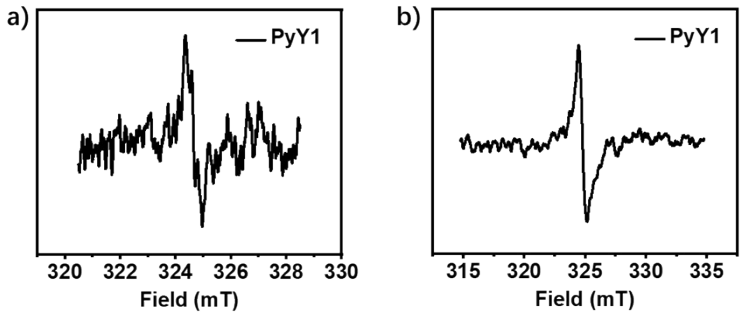


Fig. S2. EPR spectra of a) **PyY1** in DMF (0.01 M) after 1 min and b) after 7 days of storage in a capped vial at room temperature with no other special treatments.

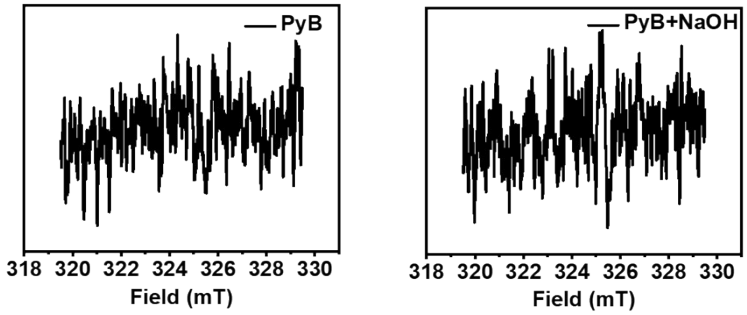
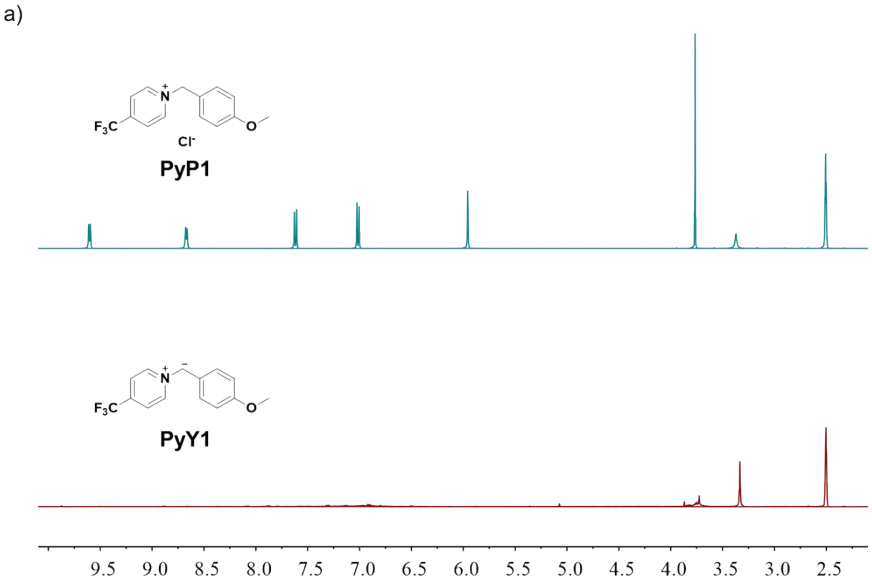


Fig. S3. EPR spectra of **PyB** and **PyB** with NaOH (5 eq.) in DMSO (0.01 M)**.**



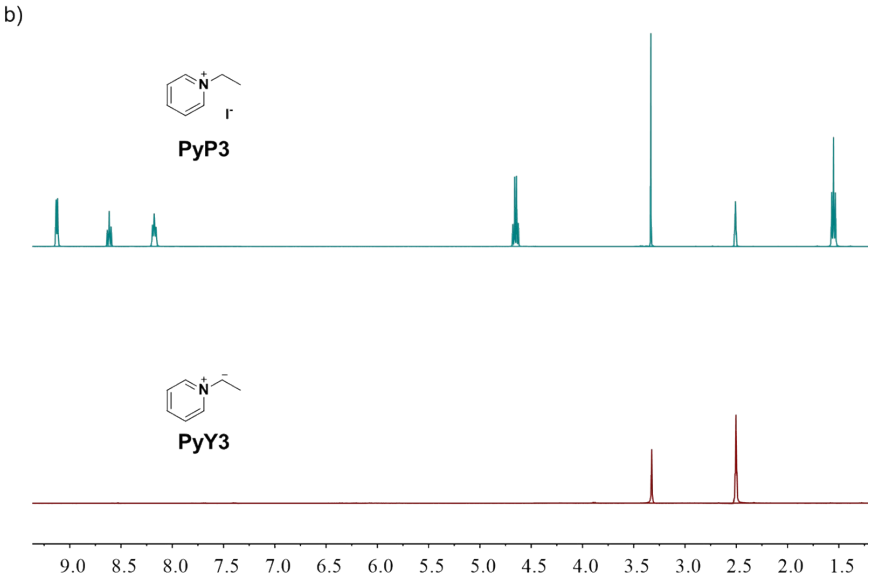


Fig. S4. ^{1}H-NMR spectra of a) **PyP1** and **PyY1** (precipitation from aqueous solutions of **PyP1** by addition of NaOH); and b) **PyP3** and **PyY3** (precipitation from aqueous solutions of **PyP3** by addition of NaOH) in DMSO-d_6.

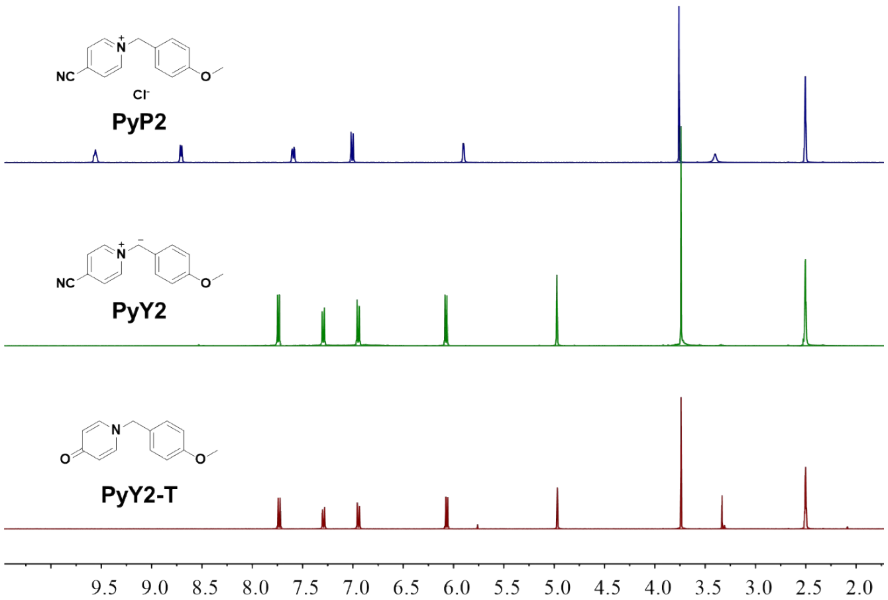


Fig. S5. ^{1}H NMR spectra of **PyP2**, **PyY2** (precipitation from aqueous solutions of **PyP2** by addition of NaOH) and **PyP2-T** (isolated from **PyY2** by flash column chromatography) in DMSO-d_6.

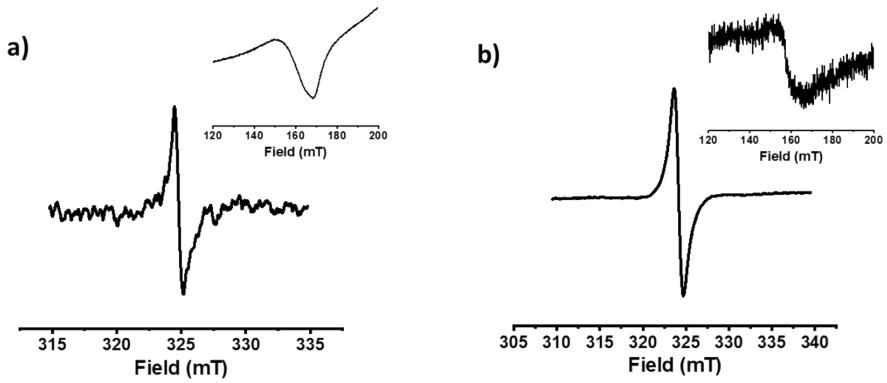


Fig. S6. EPR spectra of **PyY1** in a) DMF solution (inset: a half-field peak was also noted in solution at 10 K), and b) the solid state (inset: a half-field peak was also noted in the solid state at 10 K) at room temperature.

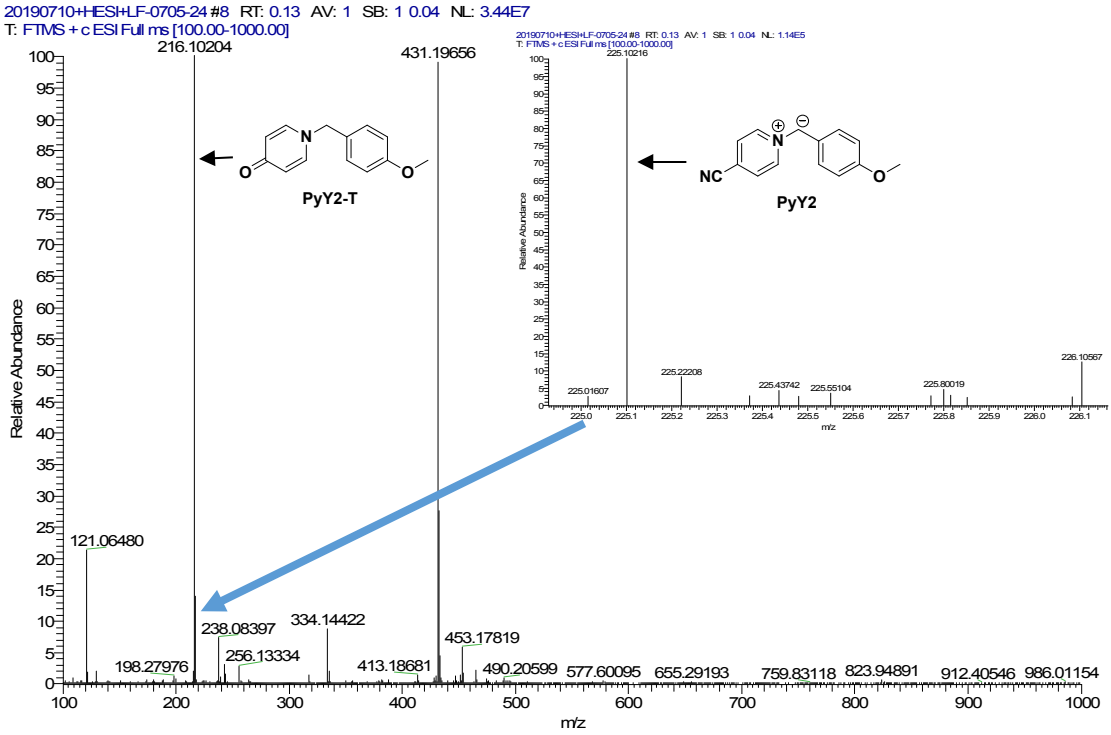


Fig. S7. ESI mass spectra of **PyY2**.

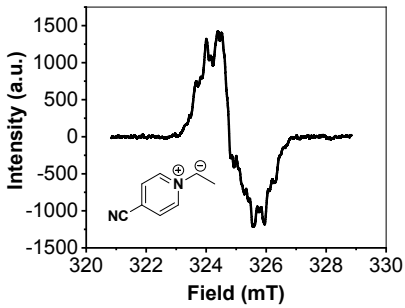


Fig. S8. EPR spectrum of another CN-substituted pyridinium ylide (DMSO, 0.01 M) at room temperature.

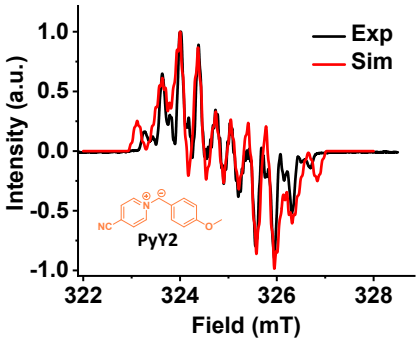


Fig. S9. Experimental (Exp) and simulated (Sim) EPR spectra spetra of **PyY1** (DMSO, 0.01 M, RT). Simulation parameters: S = 1, g = 2.00009, D = 41.8 MHz, E = 4.17 MHz, line width: LWPP = 0.035 mT, hyperfine splitting a(^{14}N) = 3.68 (1N), a(^{14}N) = 0.28 (1N), a(^{1}H) = 0.74 (1H), a(^{1}H) = 0.74 (2H) [G].

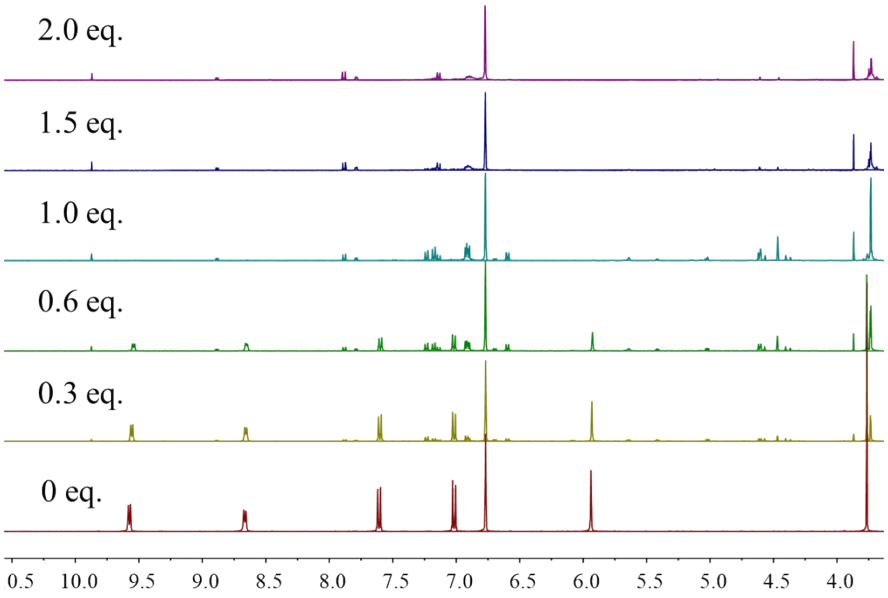


Fig. S10. ^{1}H NMR spectra of **PyP1** with NaOD (0~2.0 eq.) in DMSO-d_6 (Internal standard: mesitylene).

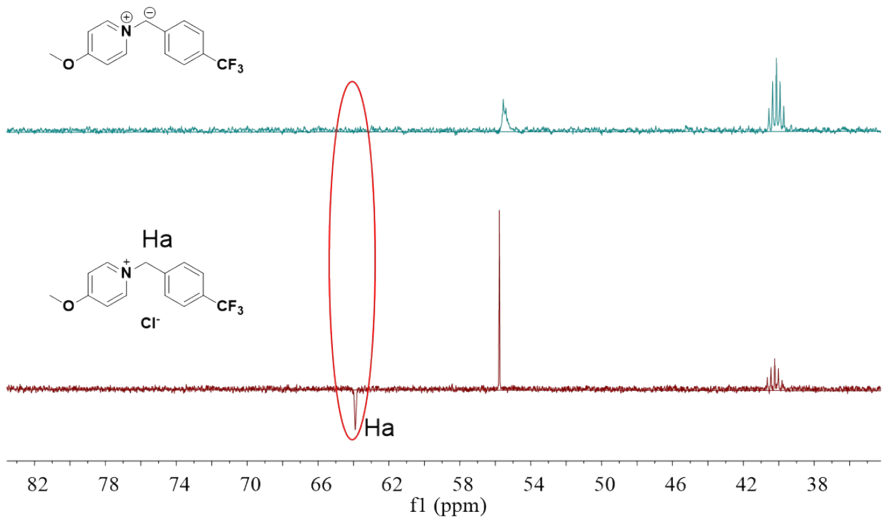


Fig. S11. DEPT 135° NMR spectra of **PyP1** and **PyY1** in DMSO-d_6.

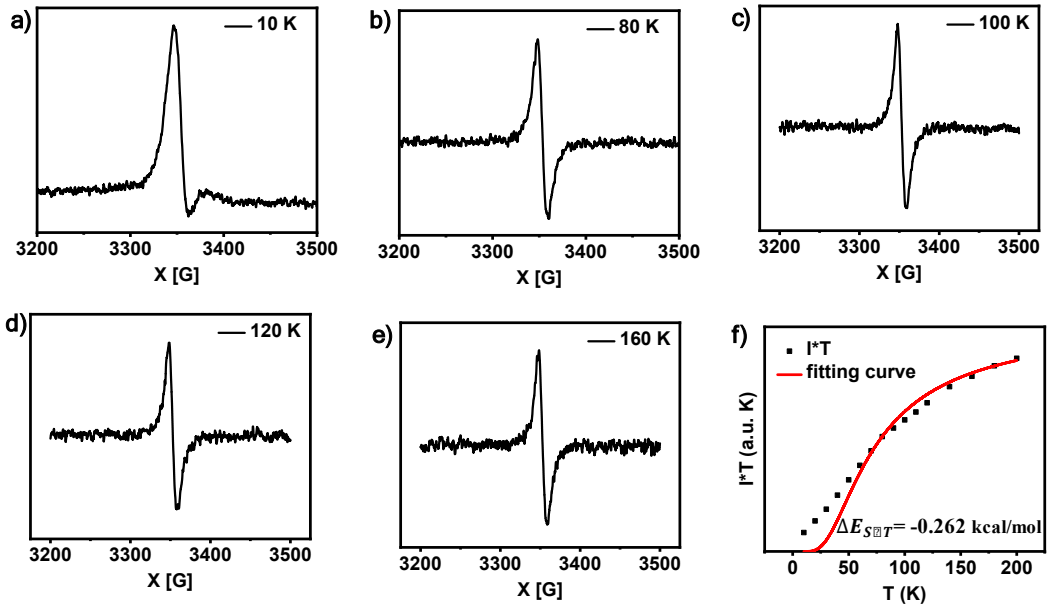


Fig. S12. a)- e) EPR spectra of **PyY1** in solid state at different temperatures, f) the T vs. I×T curve of **PyY1**.

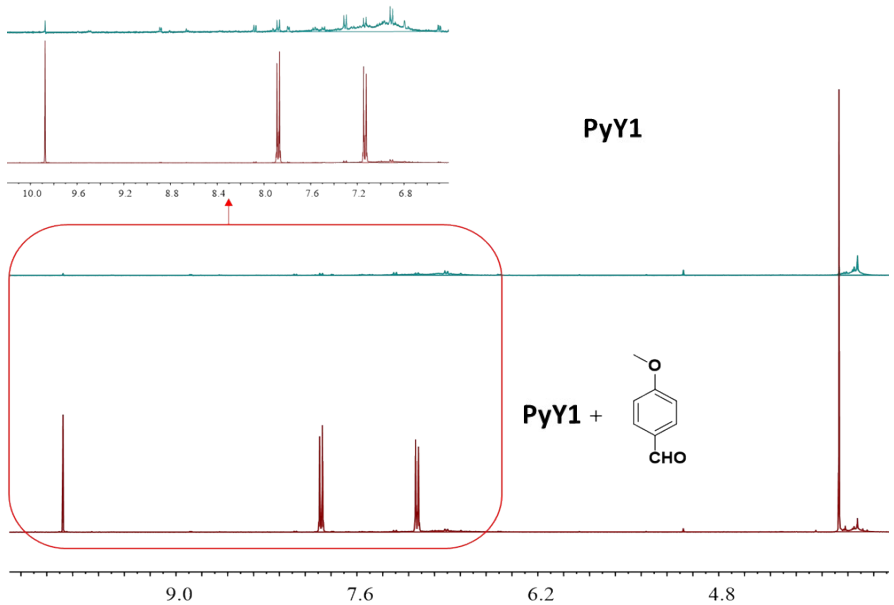


Fig. S13. ^{1}H NMR spectra of **PyY1** and **PyY1 +** 4-methoxybenzaldehyde in DMSO-d_6 (Inset: the signal intensity of **PyY1** is amplified by 5 times for comparison, indicating that there is a small amount of corresponding impurity in **PyY1**).

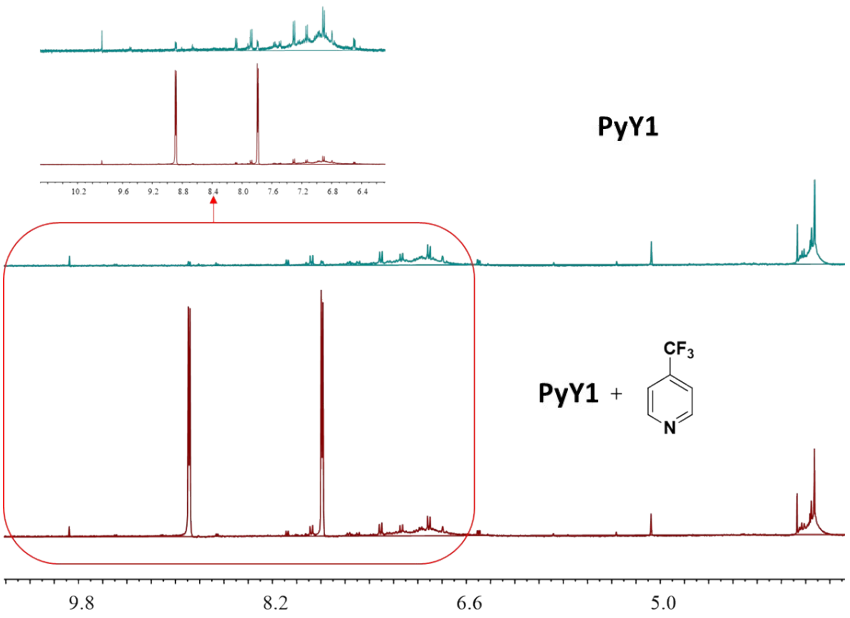


Fig. S14. ^{1}H NMR spectra of **PyY1** and **PyY1 +** 4-(trifluoromethyl)pyridine in DMSO-d_6 (Inset: the signal intensity of **PyY1** is amplified by 5 times for comparison, indicating that there is a small amount of corresponding impurity in **PyY1**).

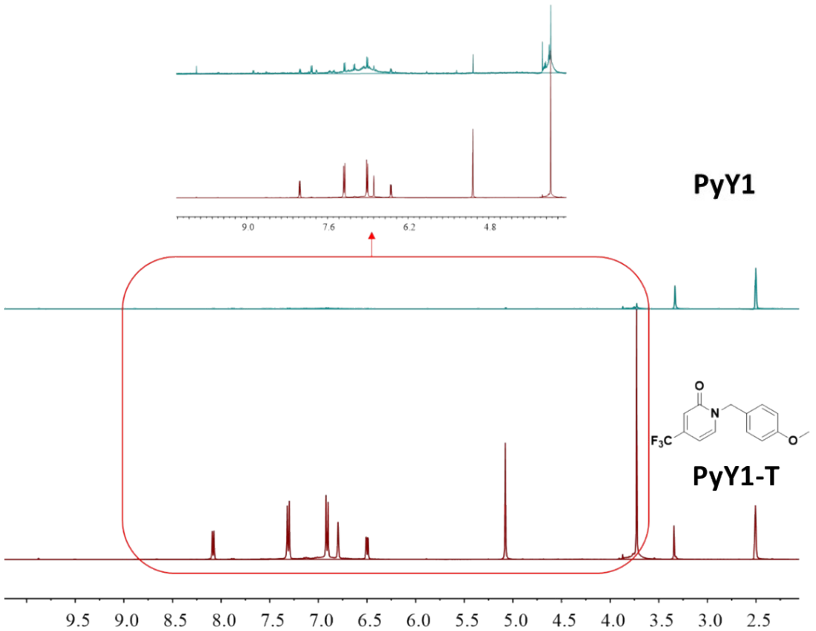


Fig. S15. ^{1}H NMR spectra of **PY1** and **PyY1-T** (1-(4-methoxybenzyl)-4-(trifluoromethyl)pyridin-2(1H)-one) (isolated from **PyY1** by TLC with a yield of 12%) in DMSO-d_6 (Inset: the signal intensity of **PyY1** is amplified by 20 times for comparison, indicating that there is a small amount of corresponding impurity in **PyY1**).

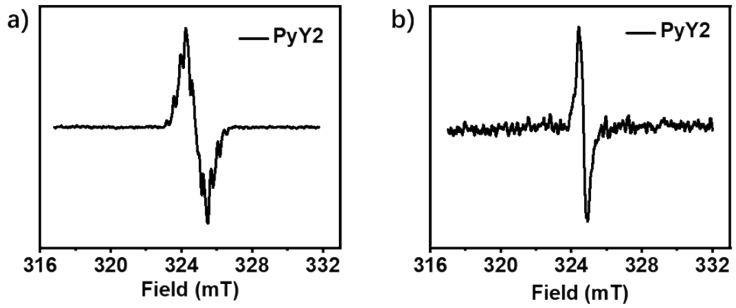


Fig. S16. EPR spectra of a) **PyY2** in DMF (0.01 M) and b) its EPR spectra after 8 days of storage in a capped vial in the solid state at room temperature in air.

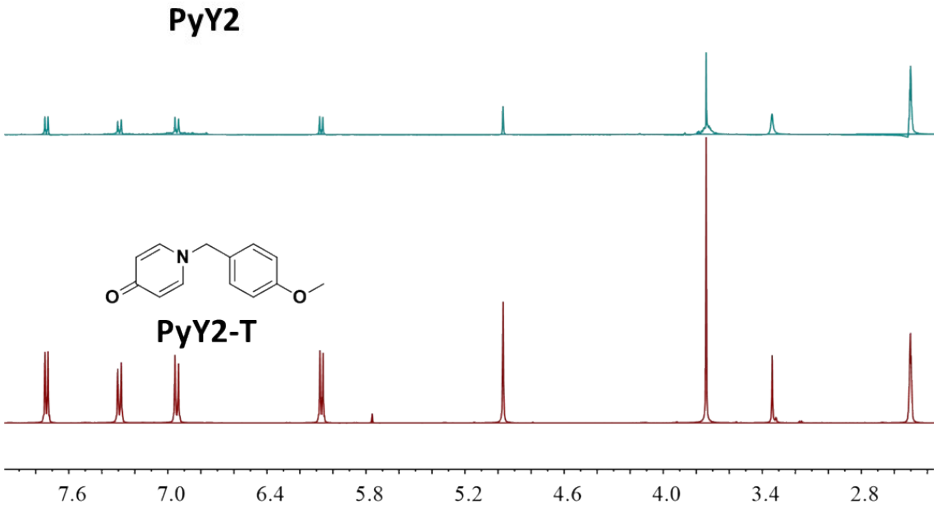


Fig. S17. ^{1}H NMR spectra of **PyY2** and **PyY2-T** (1-(4-methoxybenzyl)pyridin-4(1H)-one) (isolated from **PyY2** by TLC with a yield of 42%) in DMSO-d_6.

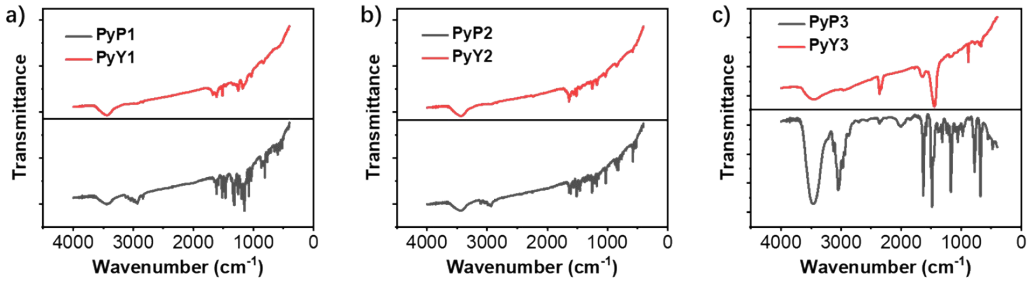


Fig. S18. The FT-IR spectra of a) **PyP1** and **PyY1**, b) **PyP2** and **PyY2**, c) **PyP3** and **PyY3** cast on NaCl showing diminshed CH_2 vibrations.

4. Nuclear Magnetic Resonance (NMR) and High-Resolution Mass (HRM) Spectra

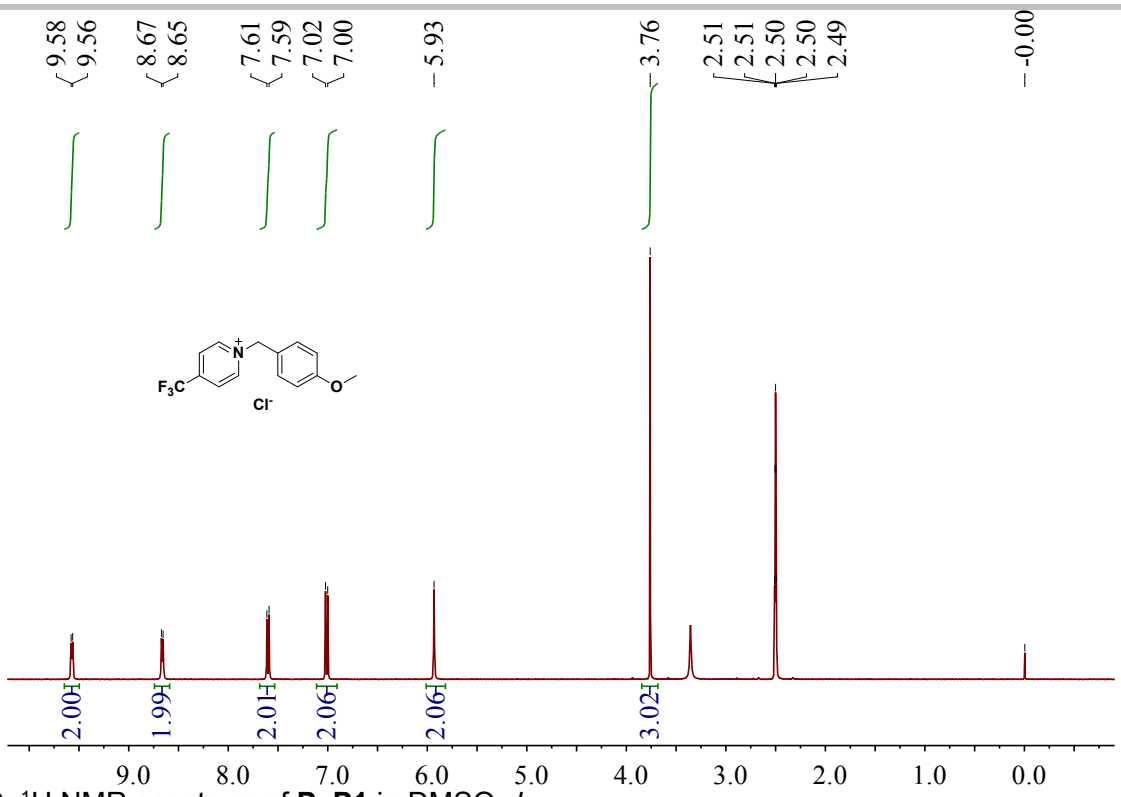


Fig. S19. ^{1}H NMR spectrum of **PyP1** in DMSO-d_6.

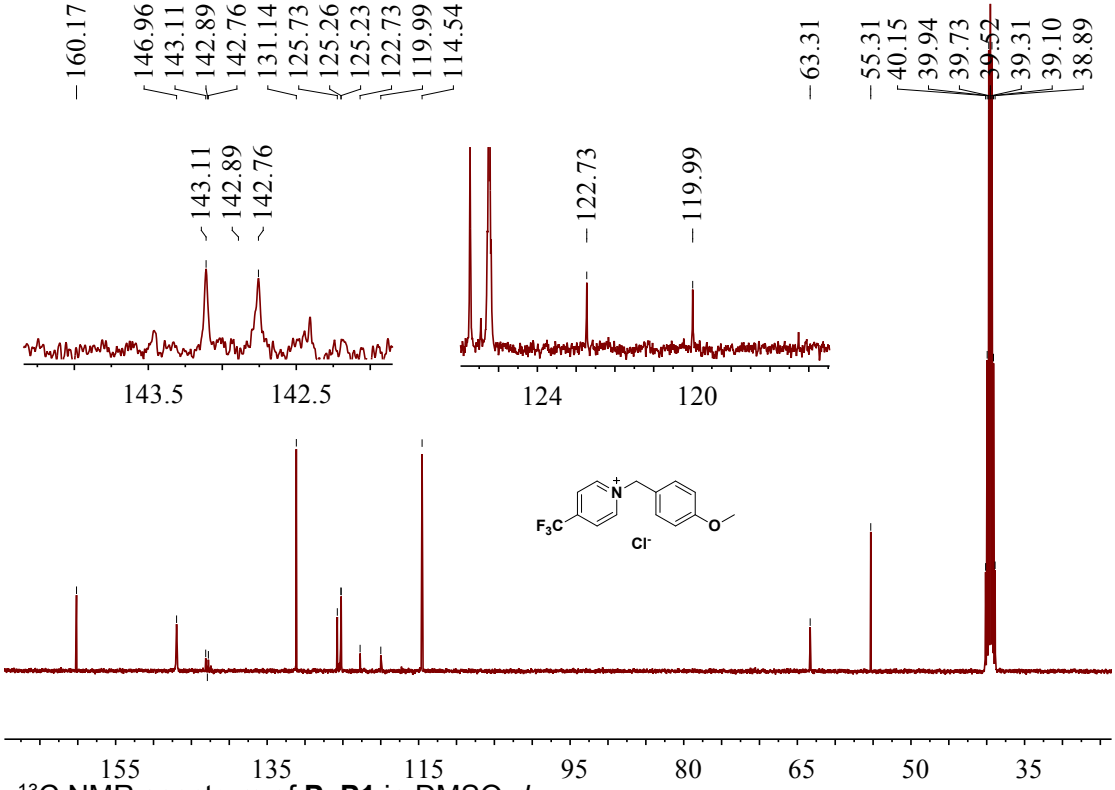


Fig. S20. ^{13}C NMR spectrum of **PyP1** in DMSO-d_6.

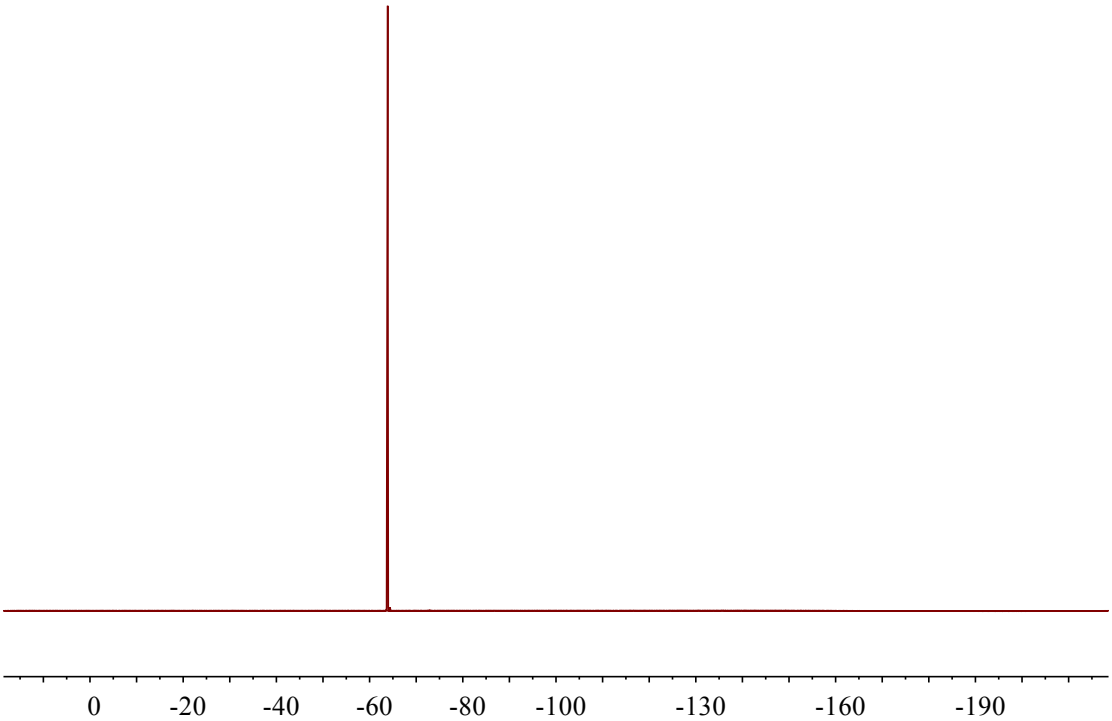


Fig. S21. ^{19}F NMR spectrum of **PyP1** in DMSO-d_6.

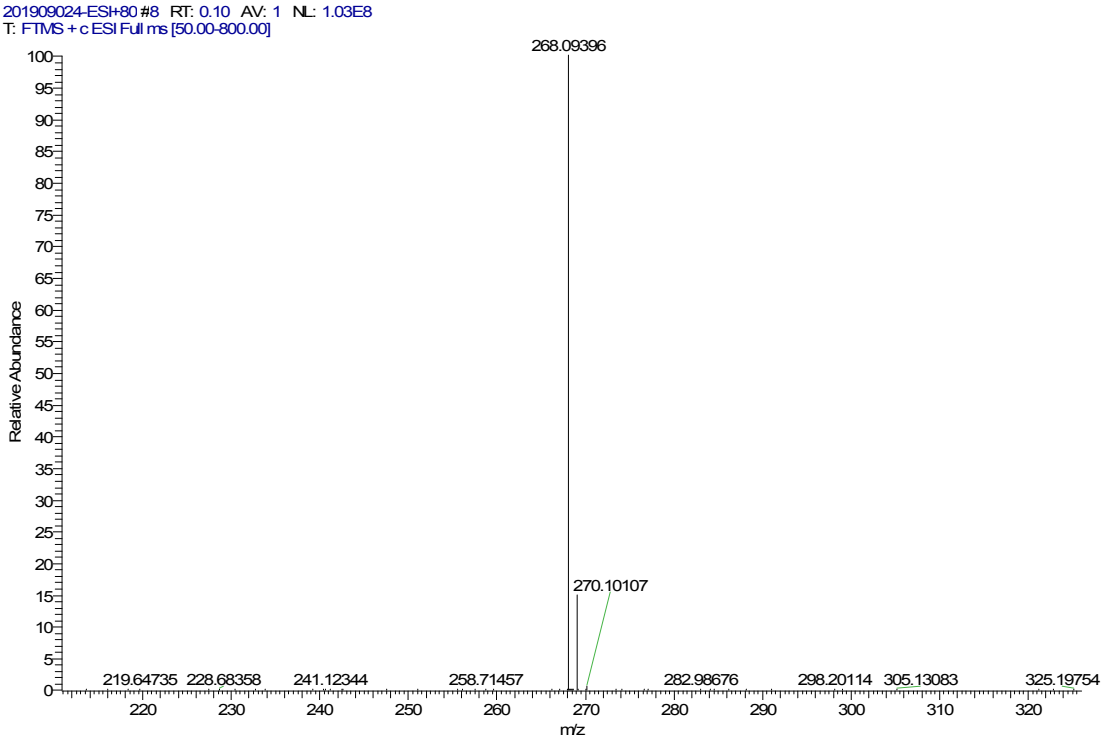


Fig. S22. ESI mass spectrum of **PyP1**.

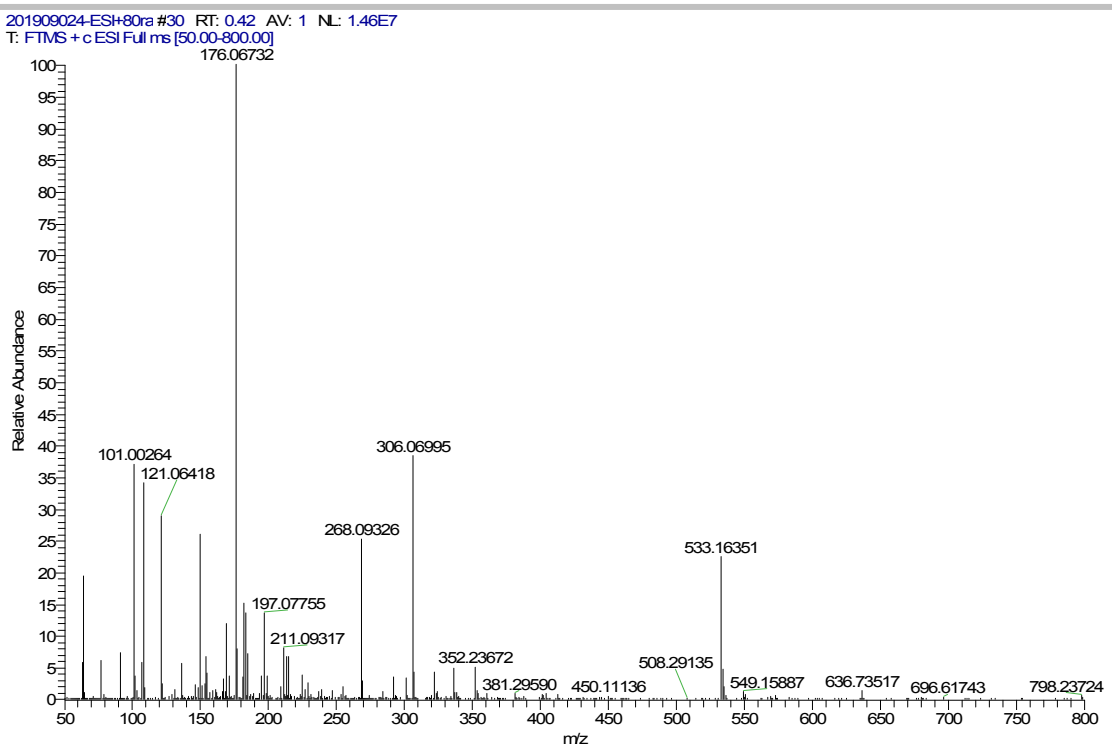


Fig. S23. ESI mass spectrum of **PyY1**.

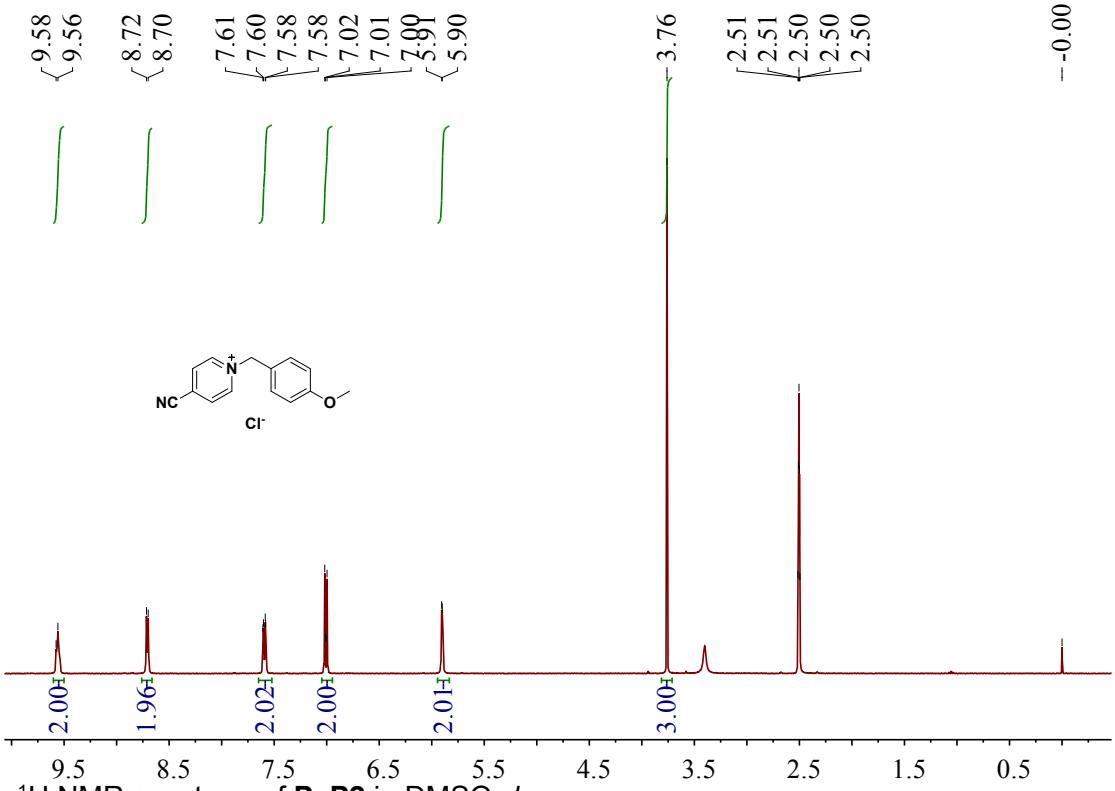


Fig. S24. ^{1}H NMR spectrum of **PyP2** in DMSO-d_6.

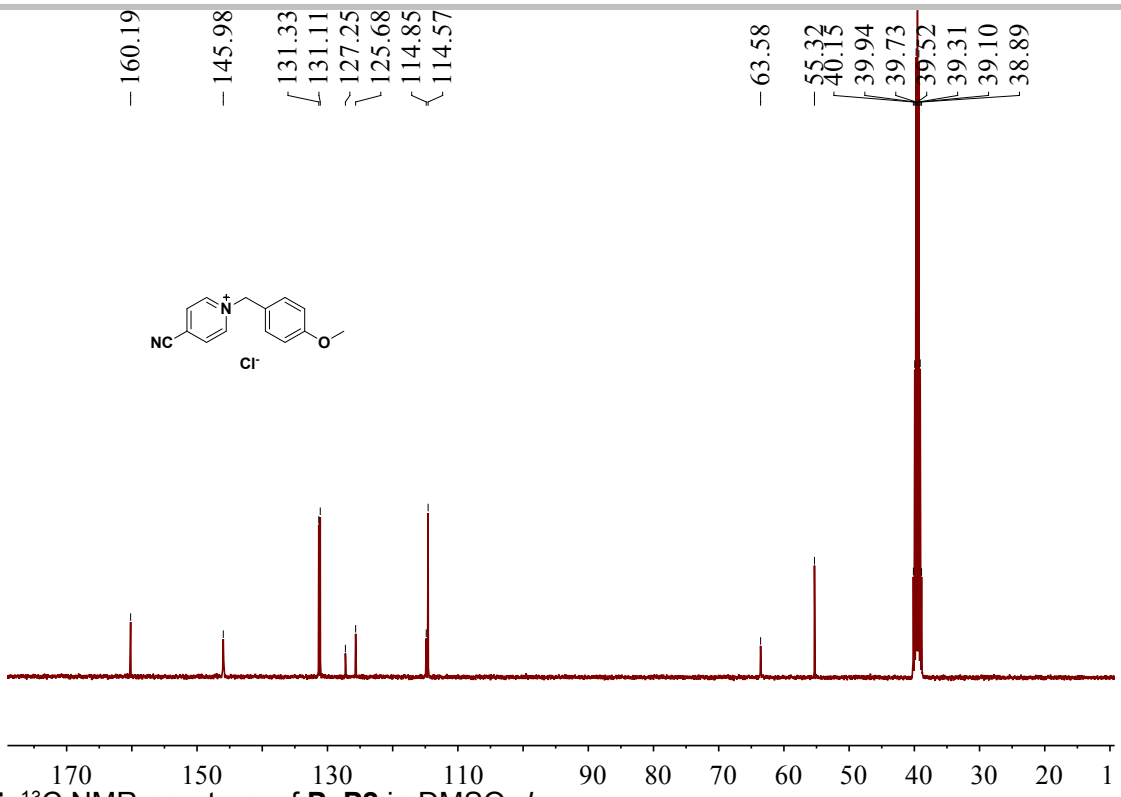


Fig. S25. ^{13}C NMR spectrum of **PyP2** in DMSO-d_6.

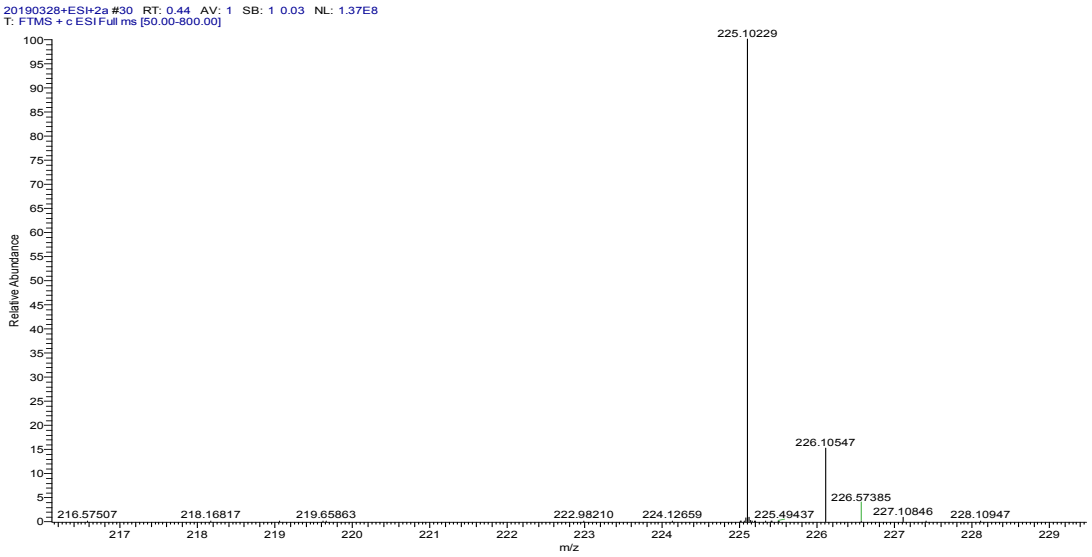


Fig. S26. ESI mass spectrum of **PyP2**.

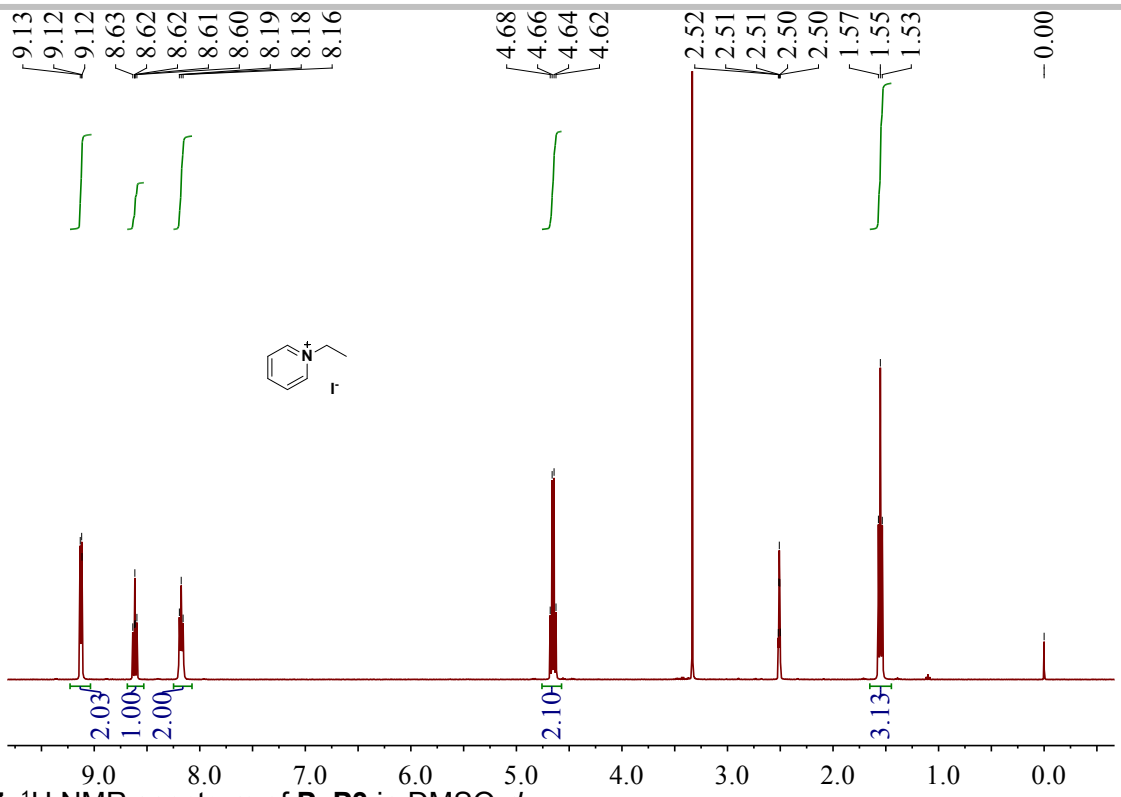


Fig. S27. ^{1}H NMR spectrum of **PyP3** in DMSO-d_6.

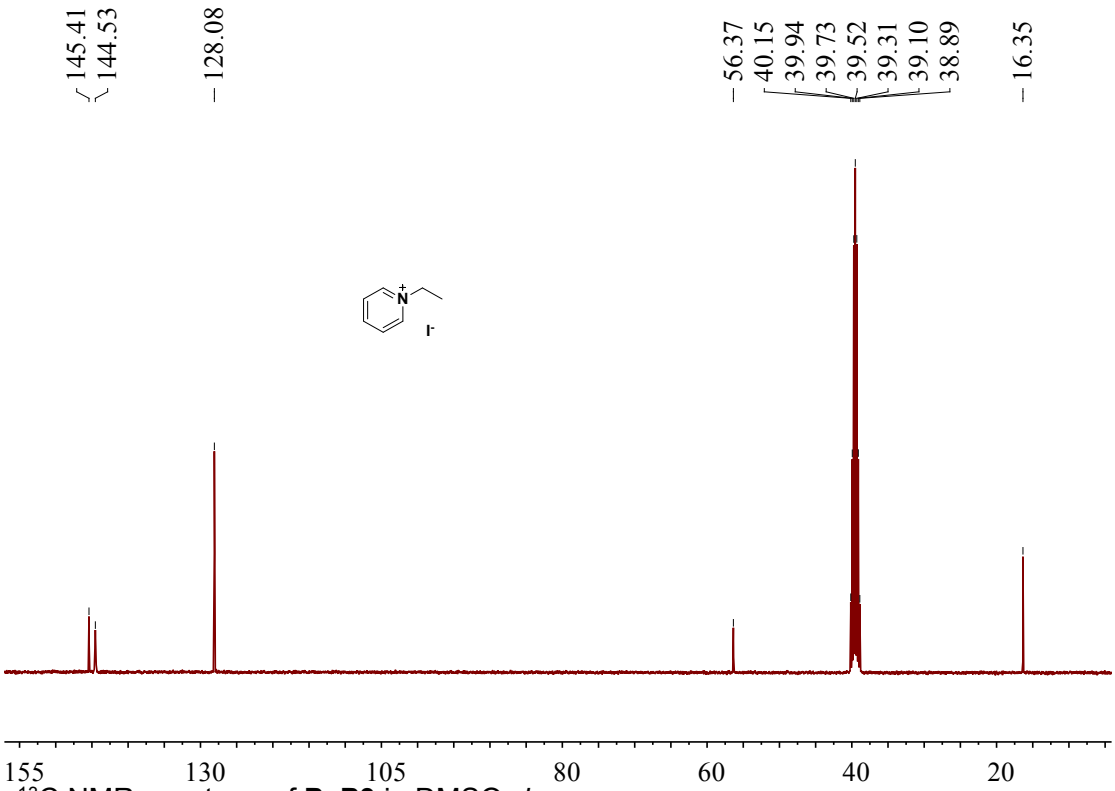


Fig. S28. ^{13}C NMR spectrum of **PyP3** in DMSO-d_6.

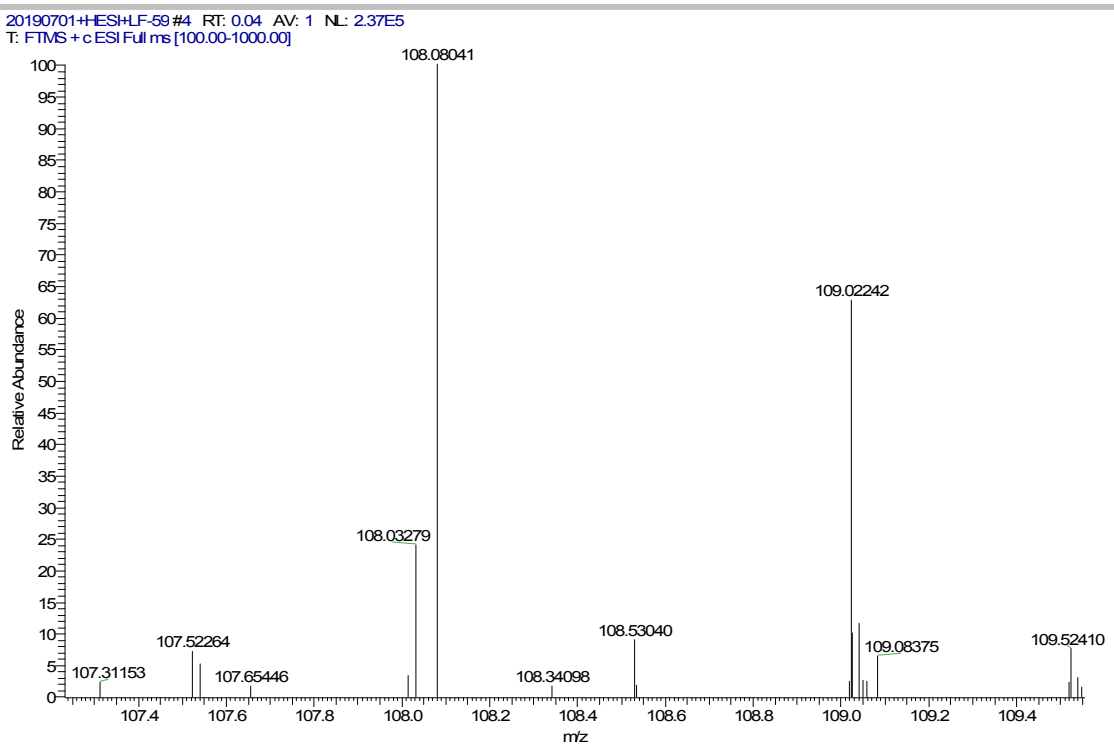


Fig. S29. ESI mass spectrum of **PyP3.**

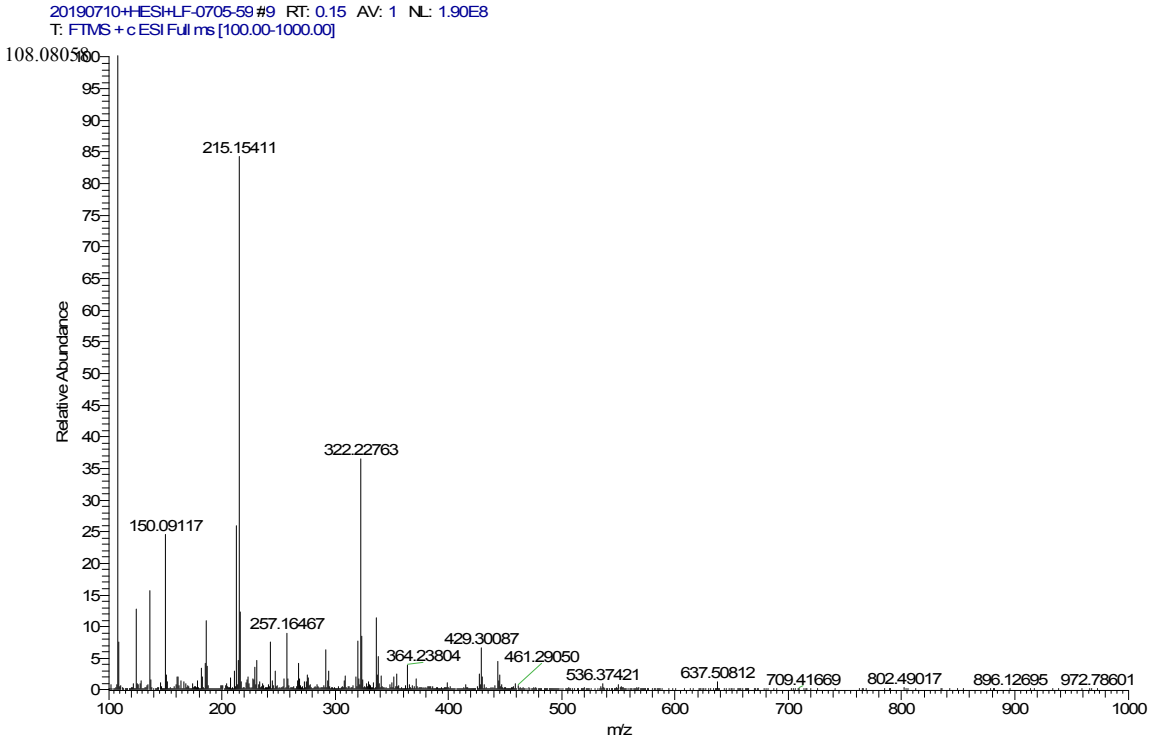


Fig. S30. ESI mass spectrum of **PyY3**.

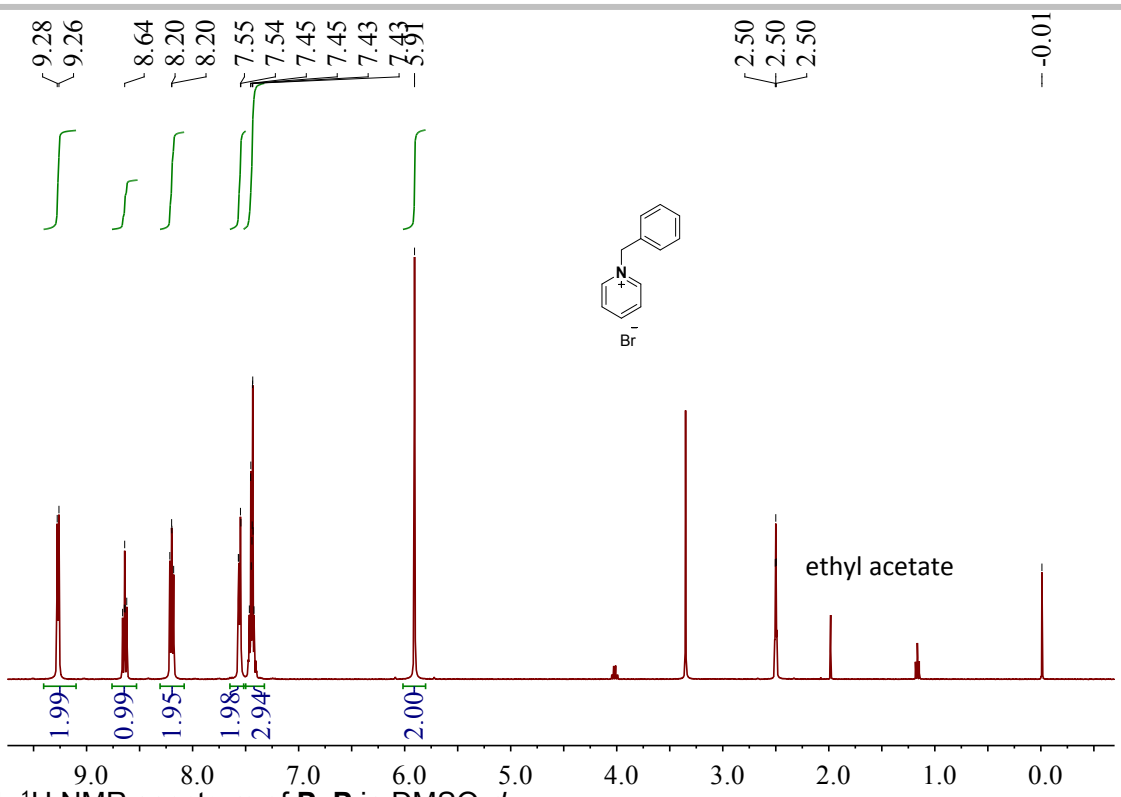


Fig. S31. ^{1}H NMR spectrum of **PyP** in DMSO-d_6.

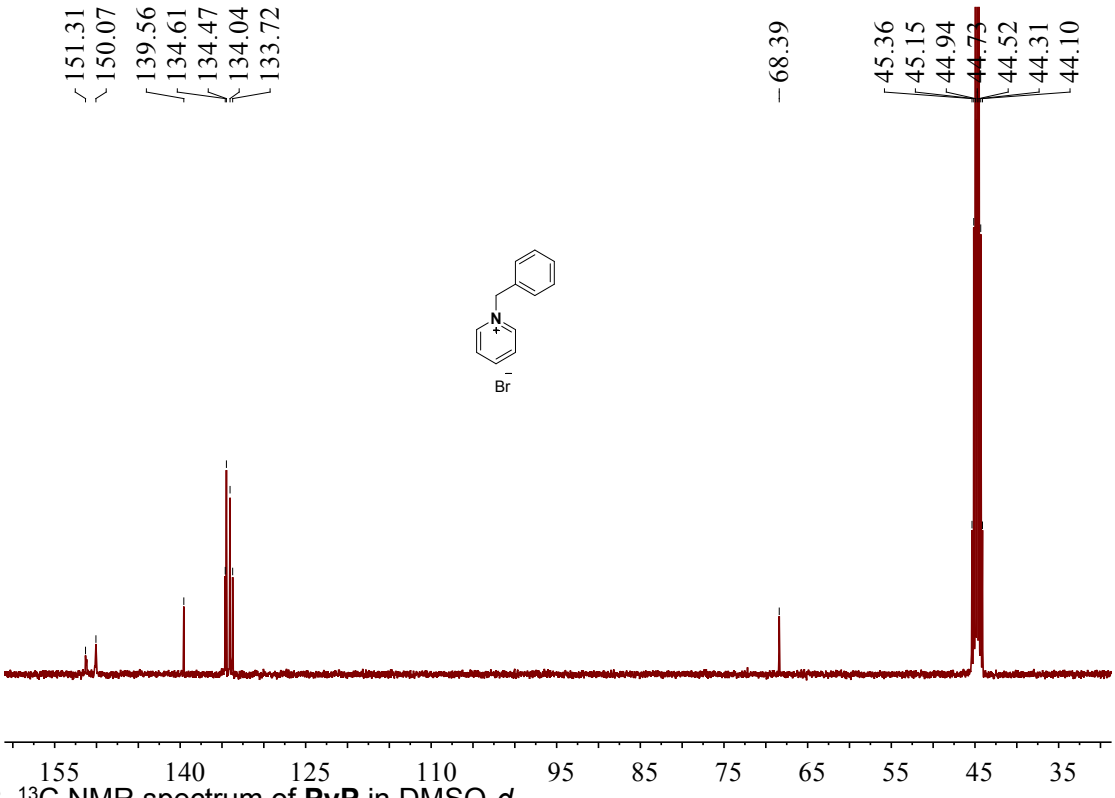


Fig. S32. ^{13}C NMR spectrum of **PyP** in DMSO-d_6.

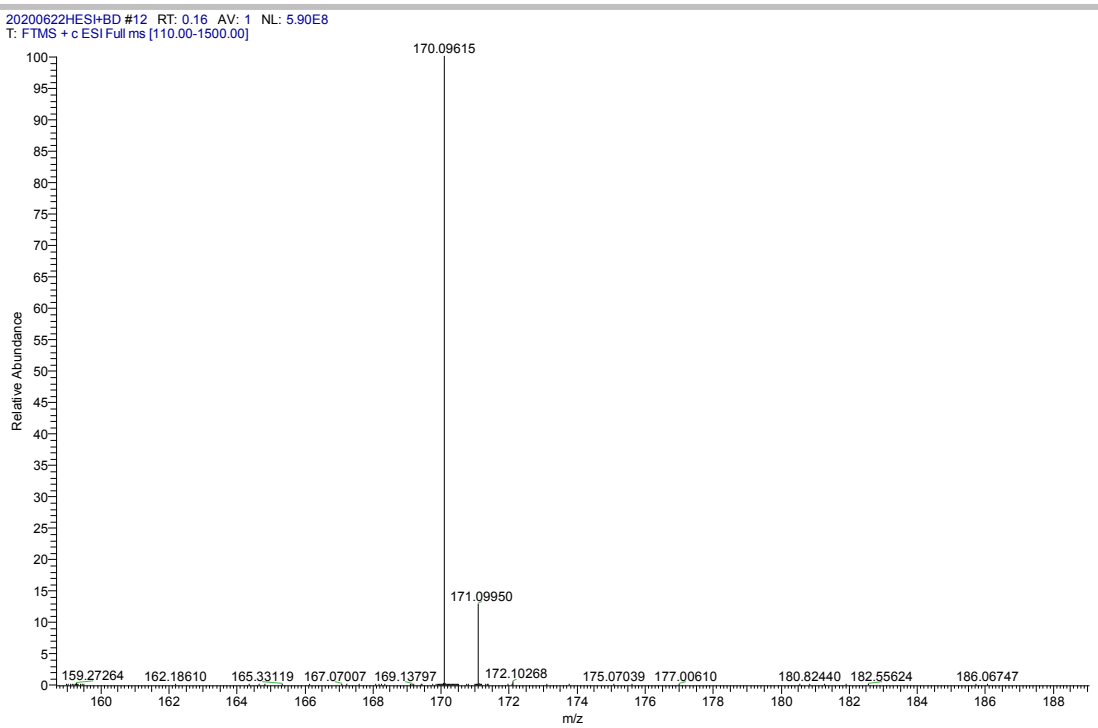


Fig. S33. ESI mass spectrum of **PyP**.

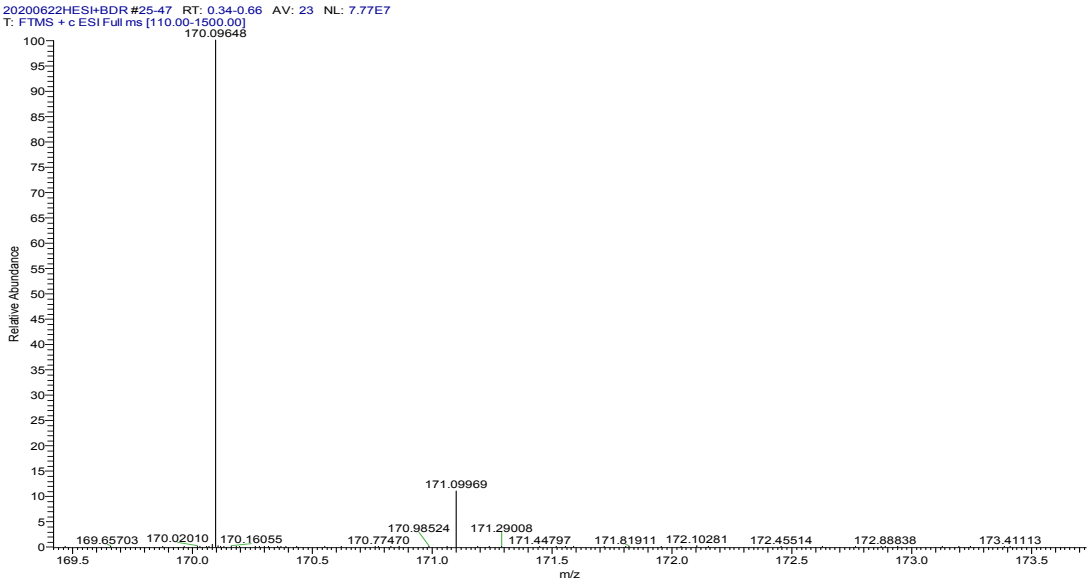


Fig. S34. ESI mass spectrum of **PyY**.

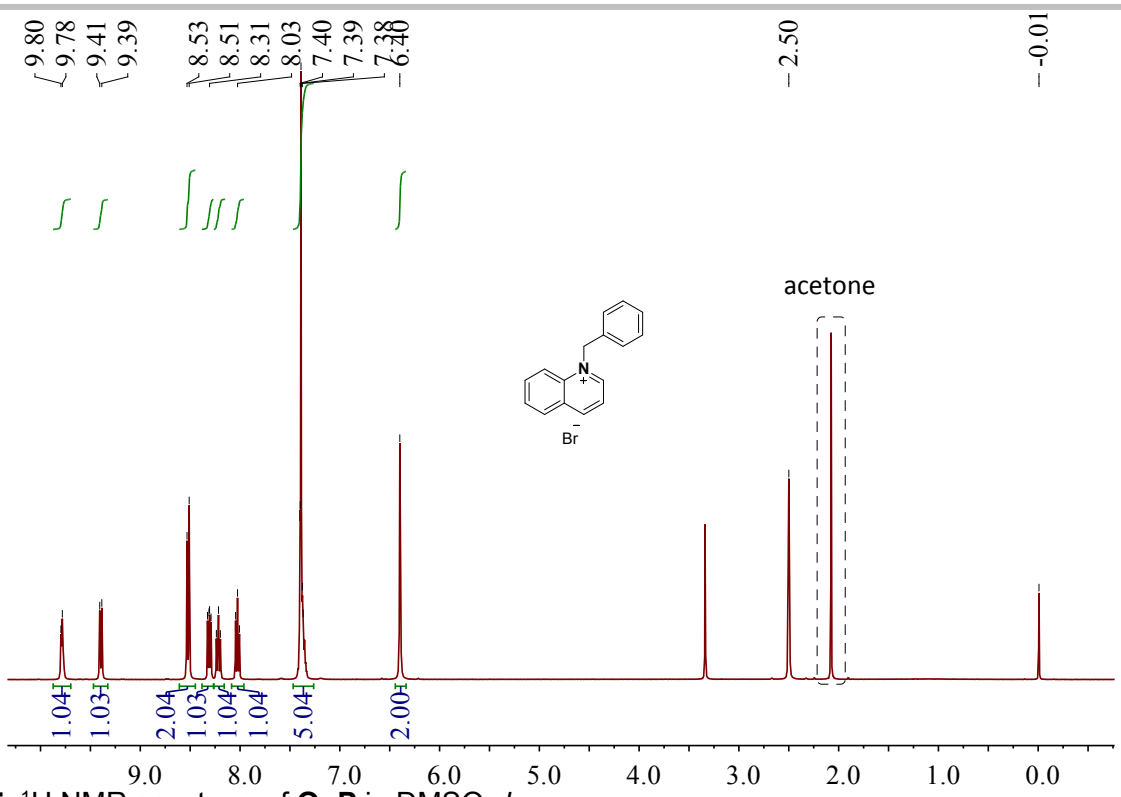


Fig. S35. ^{1}H NMR spectrum of **QuP** in DMSO-d_6.

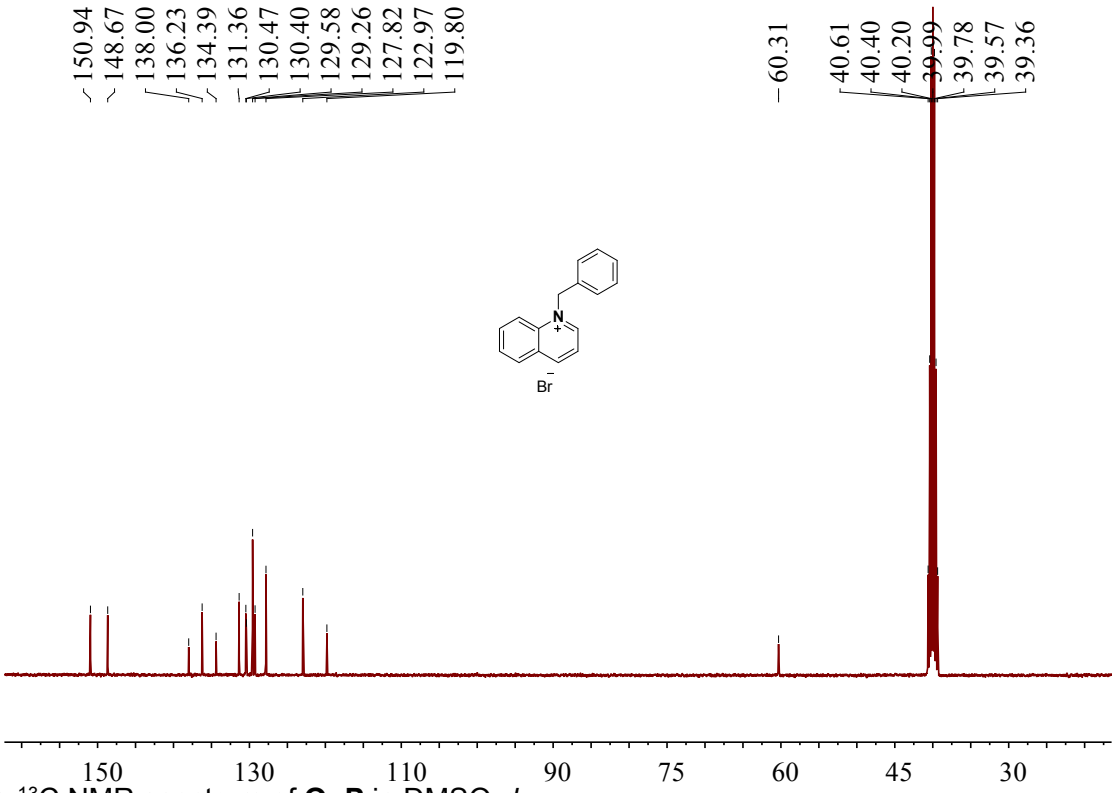


Fig. S36. ^{13}C NMR spectrum of **QuP** in DMSO-d_6.

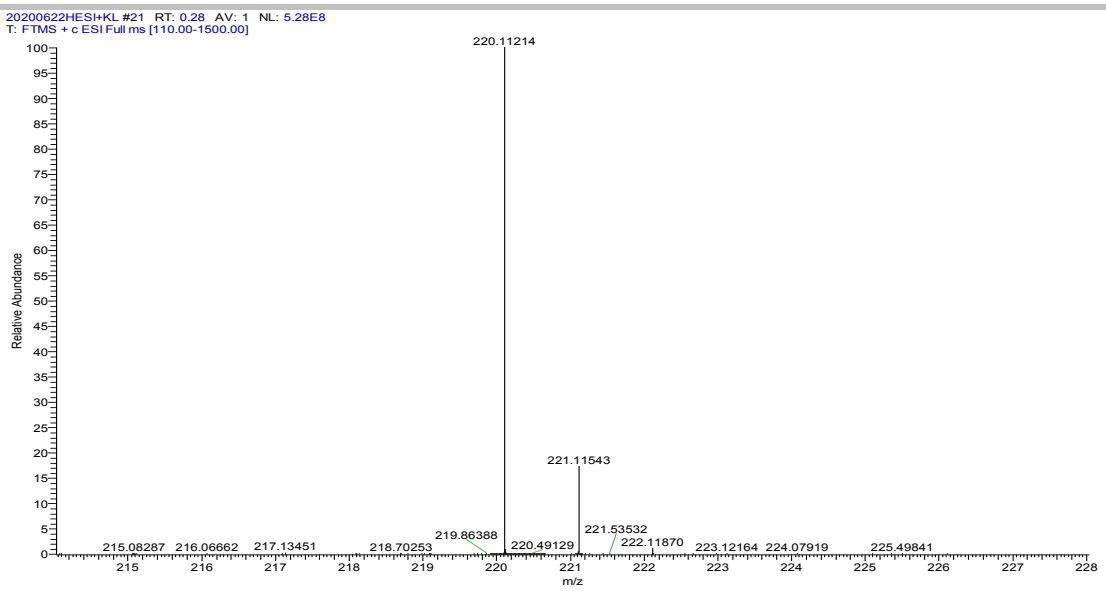


Fig. S37. ESI mass spectrum of **QuP**.

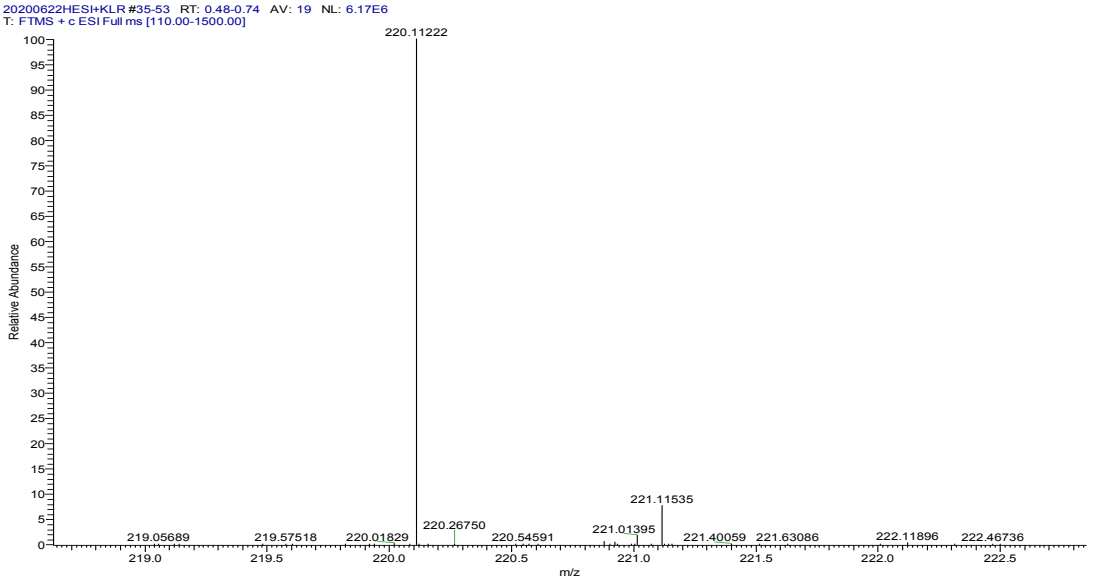


Fig. S38. ESI mass spectrum of **QuY**.

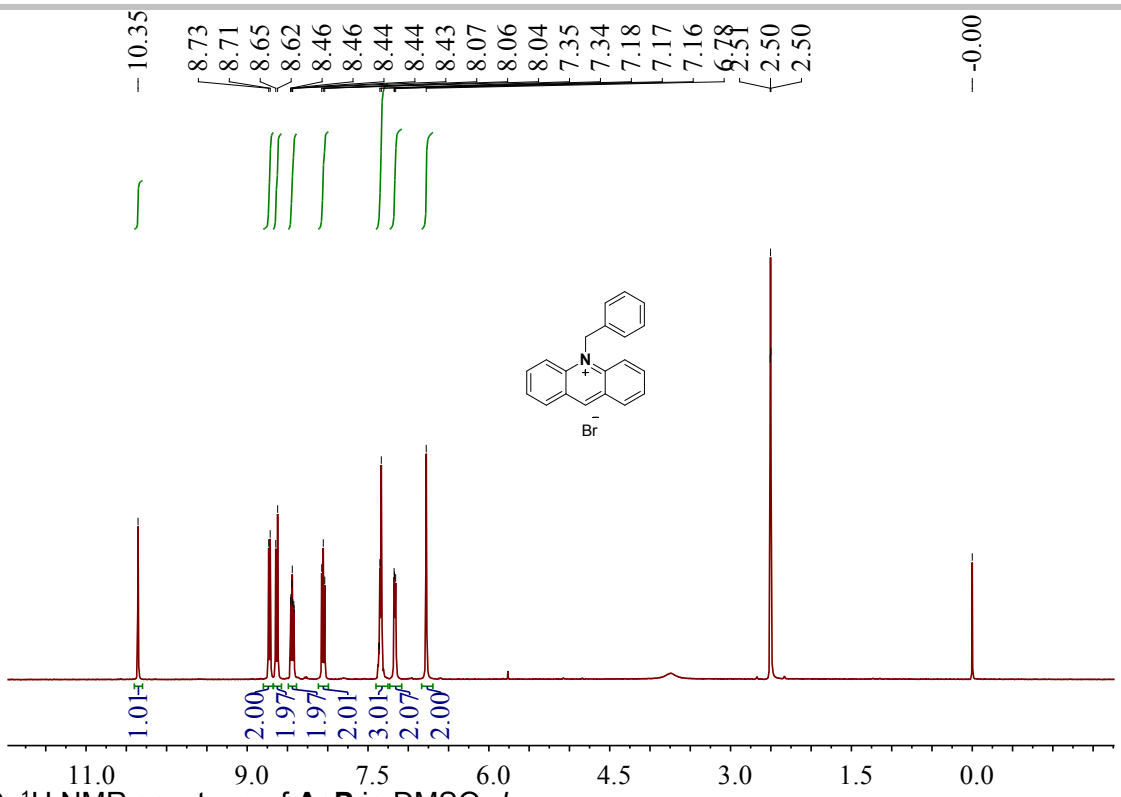


Fig. S39. ^{1}H NMR spectrum of **AcP** in DMSO-d_6.

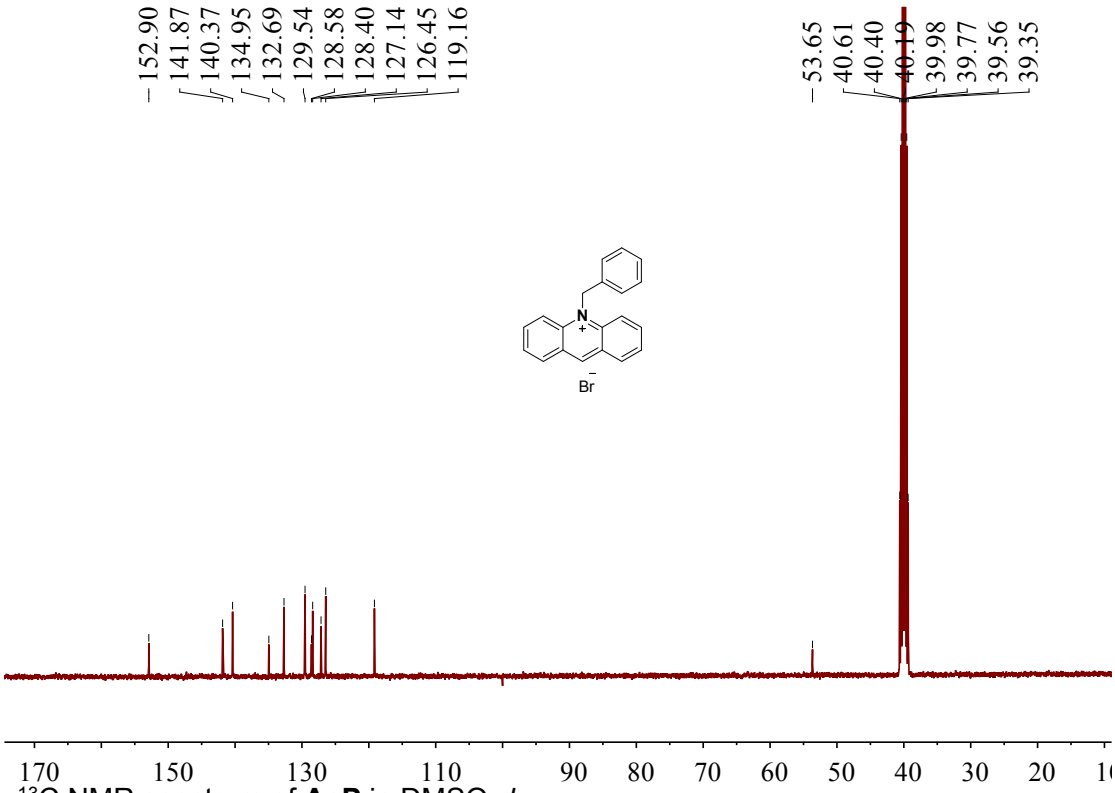


Fig. S40. ^{13}C NMR spectrum of **AcP** in DMSO-d_6.

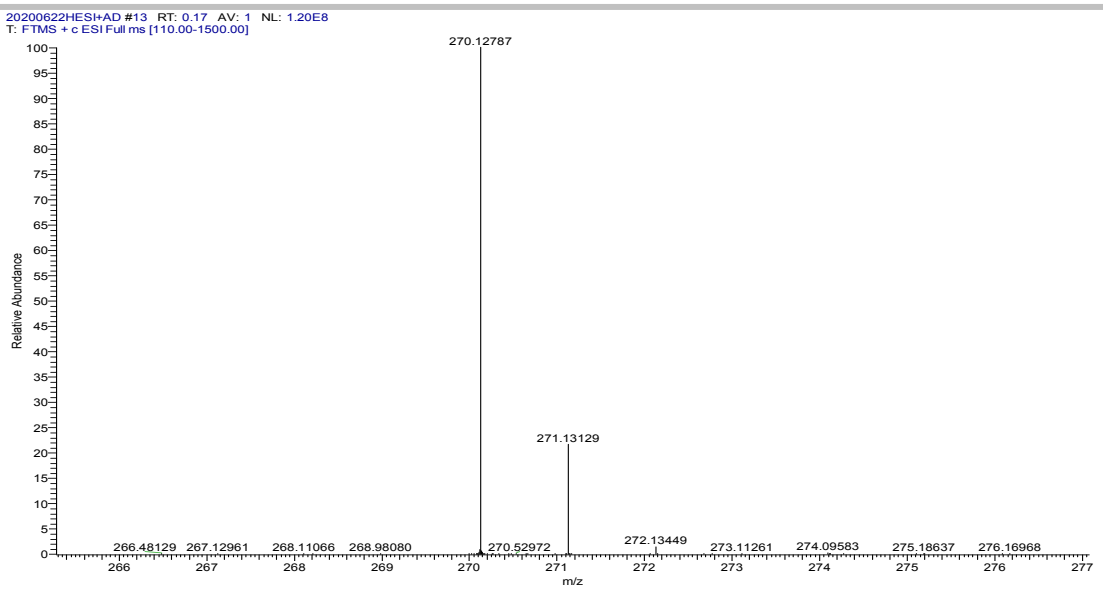


Fig. S41. ESI mass spectrum of **AcP**.

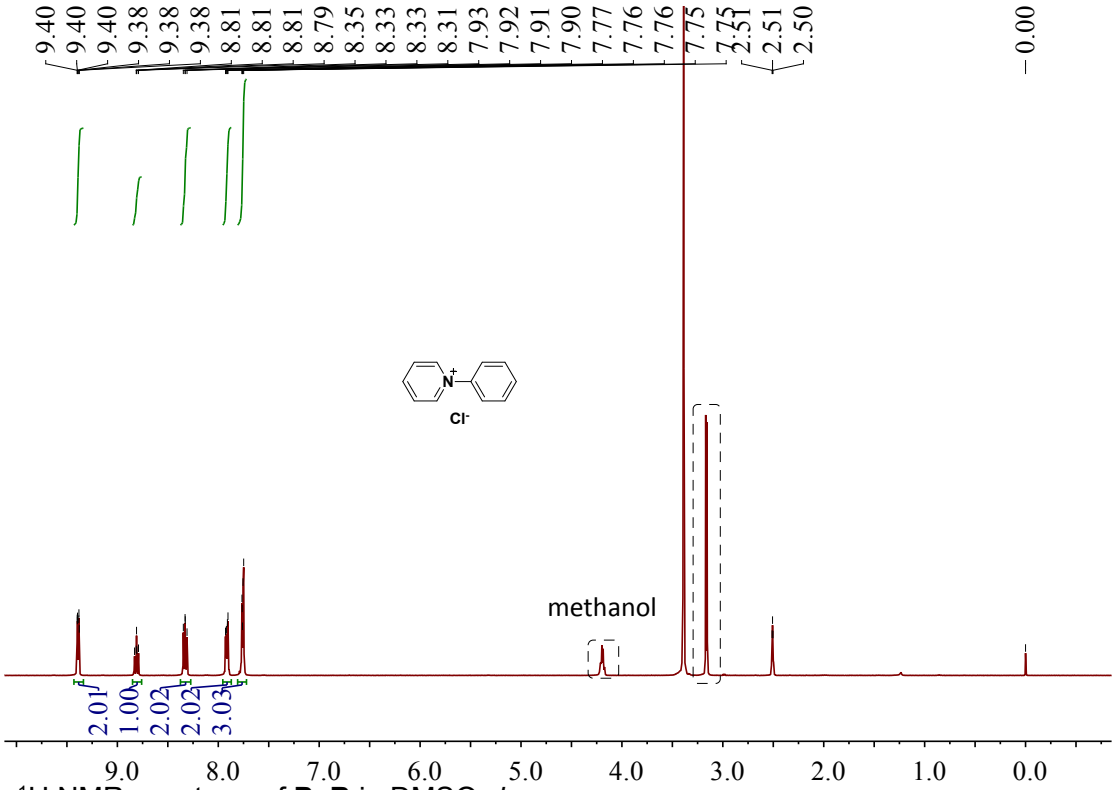


Fig. S42. ^{1}H NMR spectrum of **PyB** in DMSO-d_6.

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