

Supporting Information

Condensation of cyclohexanediones with pyrrole under acidic conditions: Unusual products and interesting structural features

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Instrumentation and reagents:

NMR spectra were recorded on a Bruker Avance-400 MHz FT NMR spectrometer at room temperature. Mass spectral determinations were carried out by Shimadzu-LCMS-2010 mass spectrometer and elemental analyses were obtained through Thermo Finnigan Flash EA 1112 analyzer. Melting points were determined on MR-Vis+ visual melting point range apparatus from LABINDIA instruments private limited. IR spectra were recorded on a JASCO-FT-IR model 5300 and NICOLET 5700 FT-IR spectrometer.

Crystallographic data for Compound-4 (polymorph-1, polymorph-2), Compound-5, Compound-6, Compound-7, and Compound-8 was collected on Oxford Gemini A Ultra diffractometer with dual source. Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation was used to collect the X-ray reflections of the crystal. Data reduction was performed using CrysAlis^{Pro} 171.33.55 software.^{S1} Structures were solved and refined using SHELXL-97^{S2} with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on N were located from the Fourier map in all of the crystal structures. All C-H atoms were fixed geometrically. Empirical absorption correction was done using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. A check of the final CIF file using PLATON^{S3} did not show any missed symmetry.

Crystallographic data for compound-2 were collected on BRUKER SMART-APEX CCD diffractometer. Mo-K α ($\lambda = 0.71073 \text{ \AA}$) radiation was used to collect X-ray reflections on the single crystal. Data reduction was performed using Bruker SAINT^{S4} software. Intensities for absorption were corrected using SADABS^{S5} and refined using SHELXL-97^{S2} with anisotropic displacement parameters for non-H atoms. Hydrogen atoms on O and N were experimentally located in difference electron density maps. All C-H atoms were fixed geometrically using HFIX command in SHELX-TL. A check of the final CIF file using PLATON^{S3} did not show any missed symmetry.

Crystallographic data (excluding the structure factor) for structures compound-2, compound-4 (polymorph-1 and polymorph-2), compound-5, compound-6, Compound-7 and Compound-8 in this paper have been deposited in the Cambridge Crystallographic Data Centre as supplementary publication

number CCDC 903469-903473, 914173 and 914174. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

^{S1} Oxford Diffraction (2008). CrysAlis CCD and CrysAlis RED. Versions 1.171.33.55. Oxford Diffraction Ltd, Yarnton, Oxfordshire, England.

^{S2} Sheldrick, G. M.; *SHELXS-97* and *SHELXL-97*, Programs for the Solution and Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

^{S3} (a) Spek, A. L.; *PLATON, A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 2002; (b) Spek, A. L. *J. Appl. Cryst.* 2003, 36, 7-13.

^{S4} SAINT, version 6.45 /8/6/03, Bruker AXS, 2003.

^{S5} Sheldrick, G. M.; *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, University of Göttingen, Germany, 1997.

NMR Spectra: All the NMR spectra were collected using CDCl₃ as solvent at 20 °C.

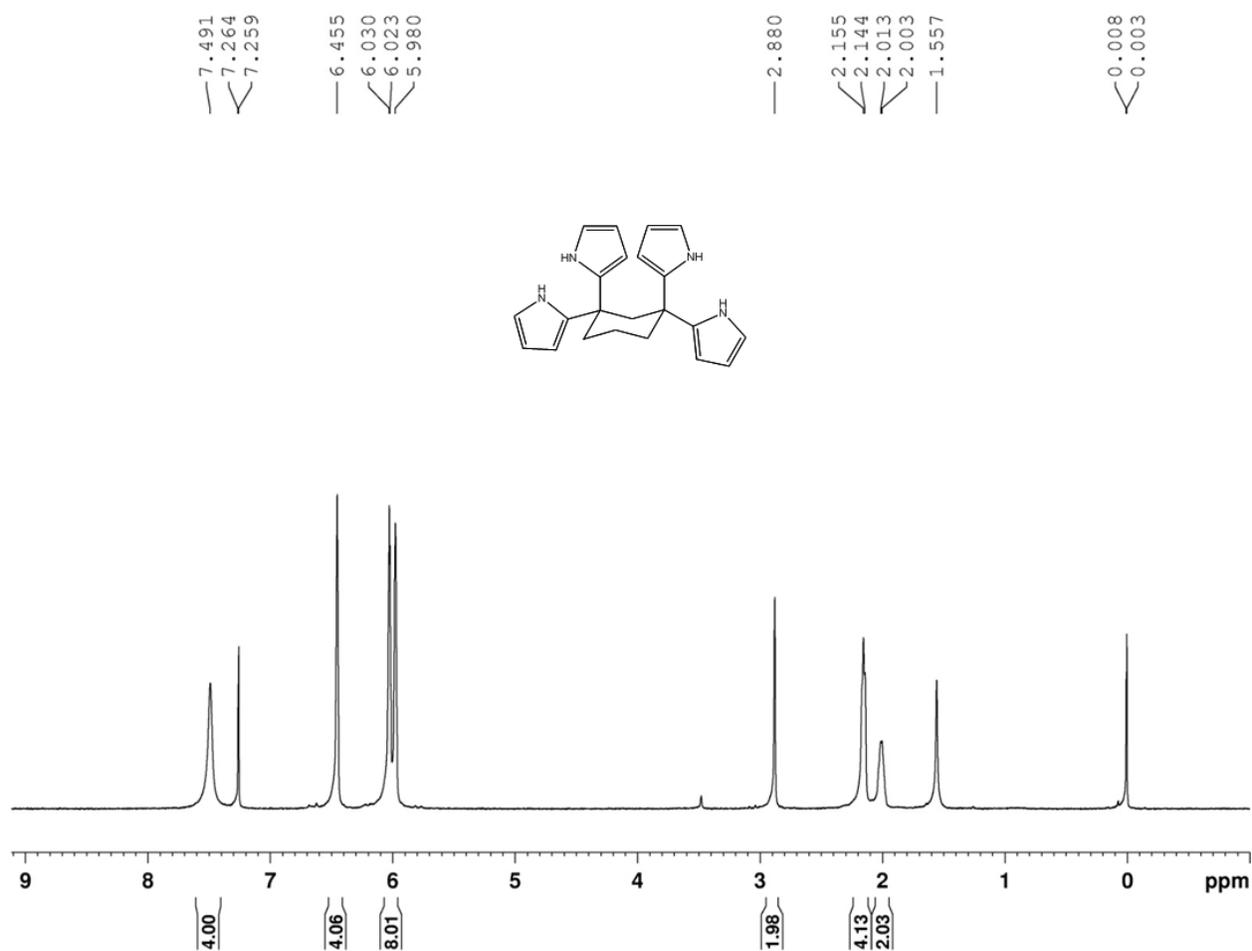


Fig. S1. ¹H NMR spectrum of compound 2.

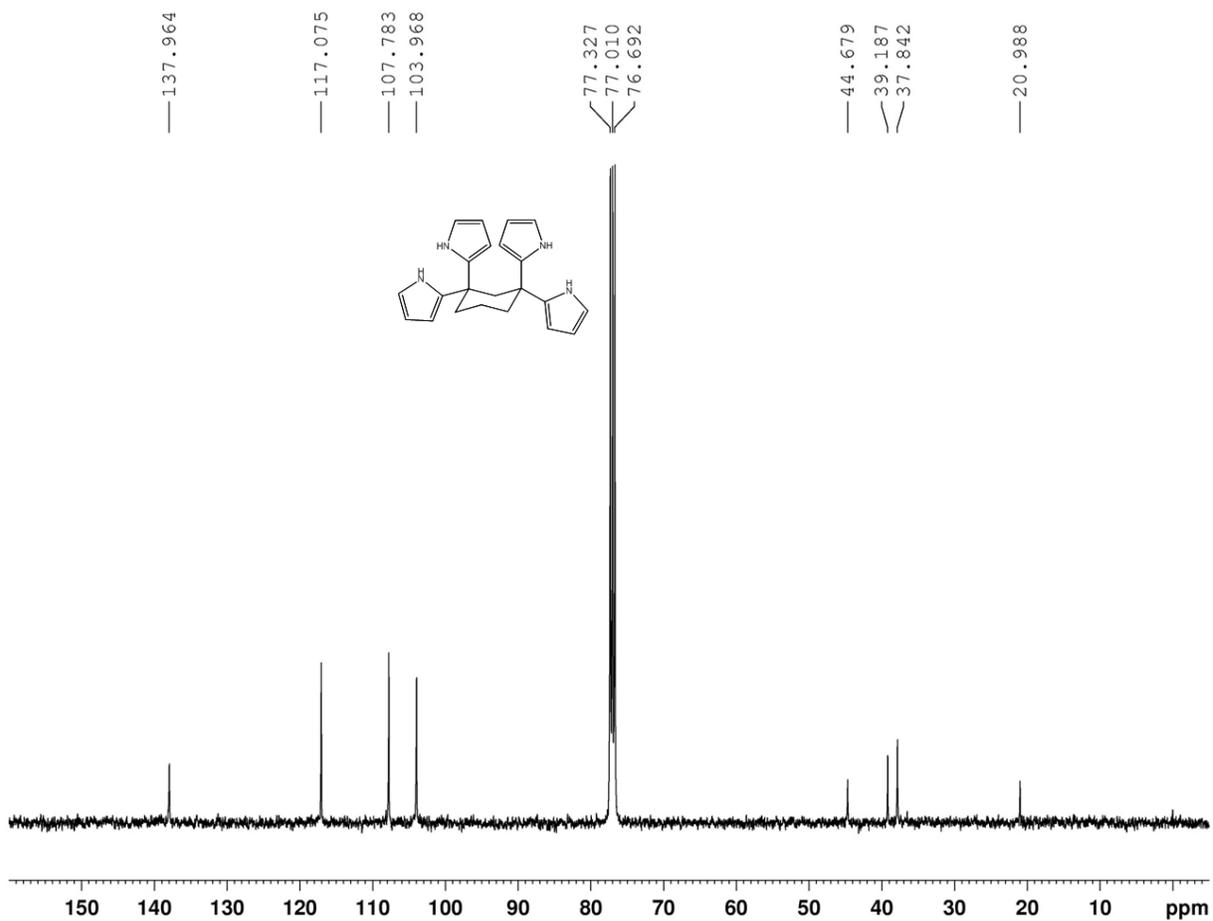


Fig. S2. ^{13}C NMR spectrum of compound 2.

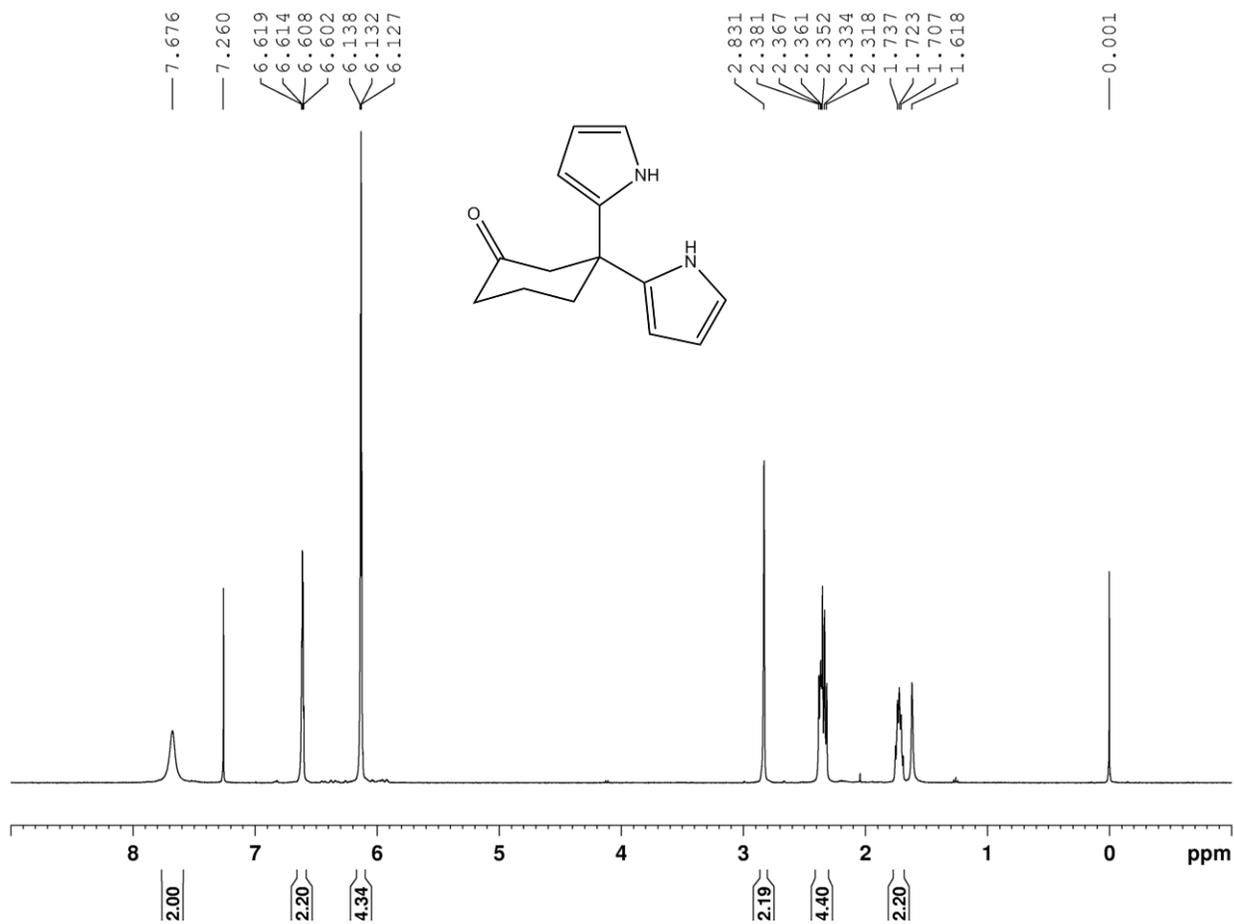


Fig. S3. ¹H NMR spectrum of compound 4.

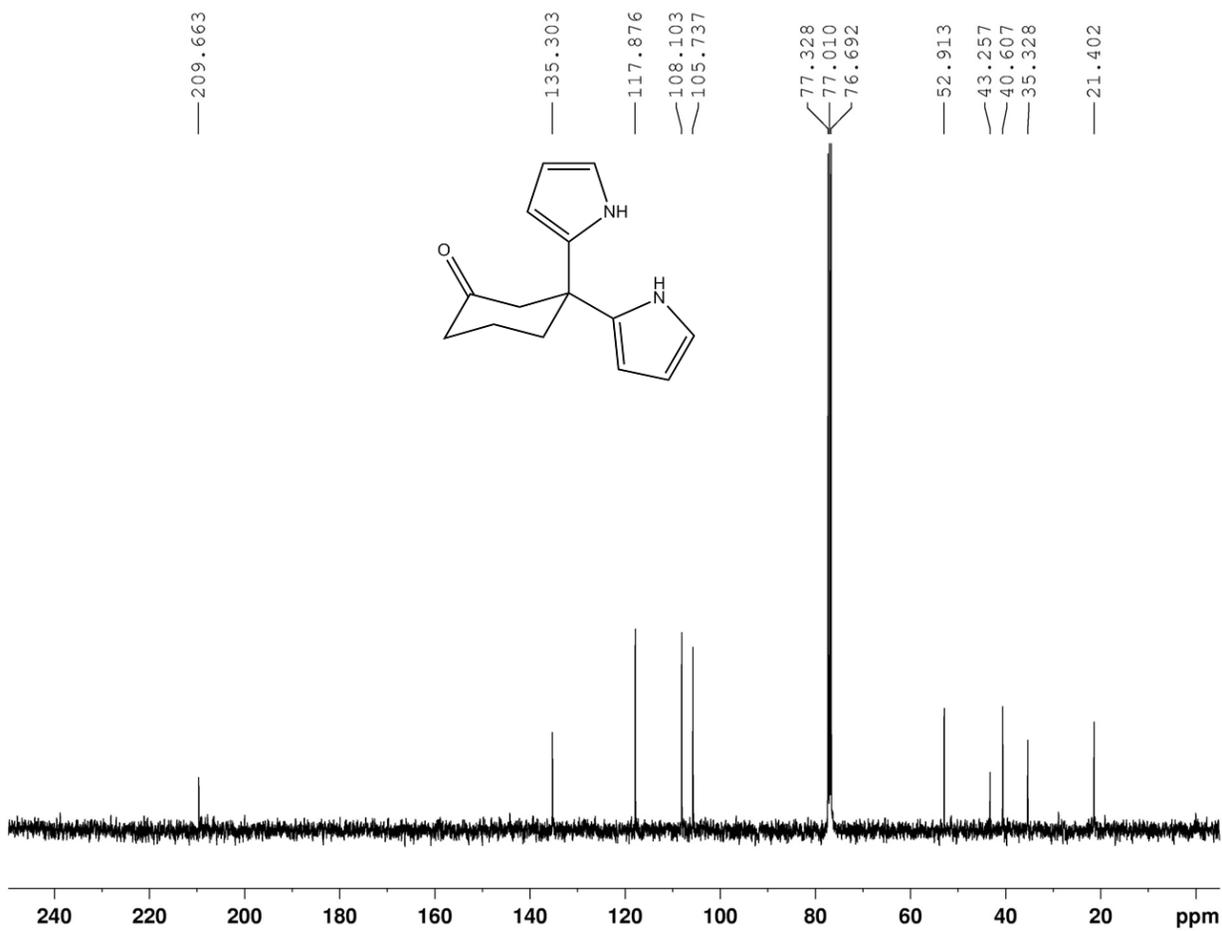


Fig. S4. ^{13}C NMR spectrum of compound 4.

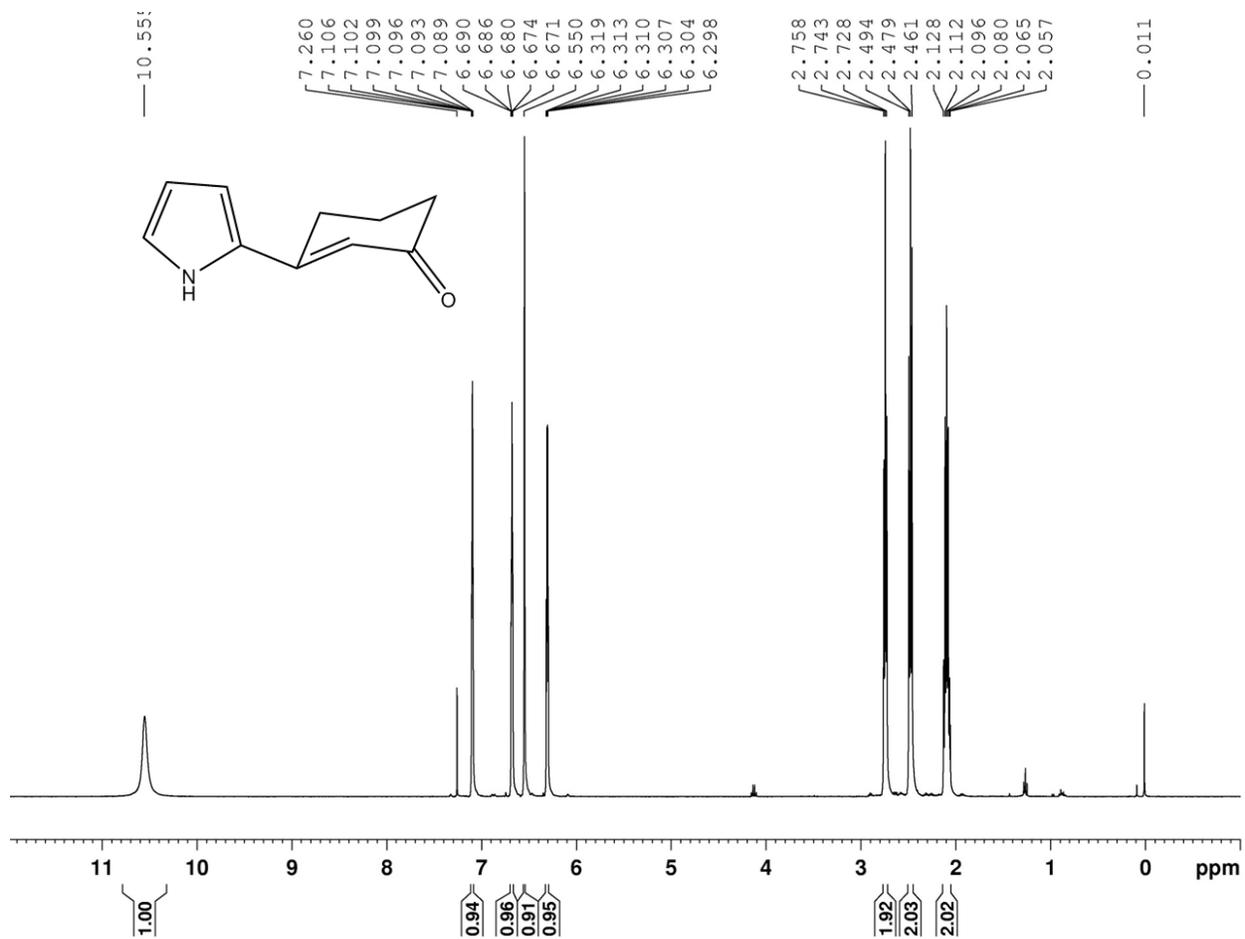


Fig. S5. ¹H NMR spectrum of compound 5.

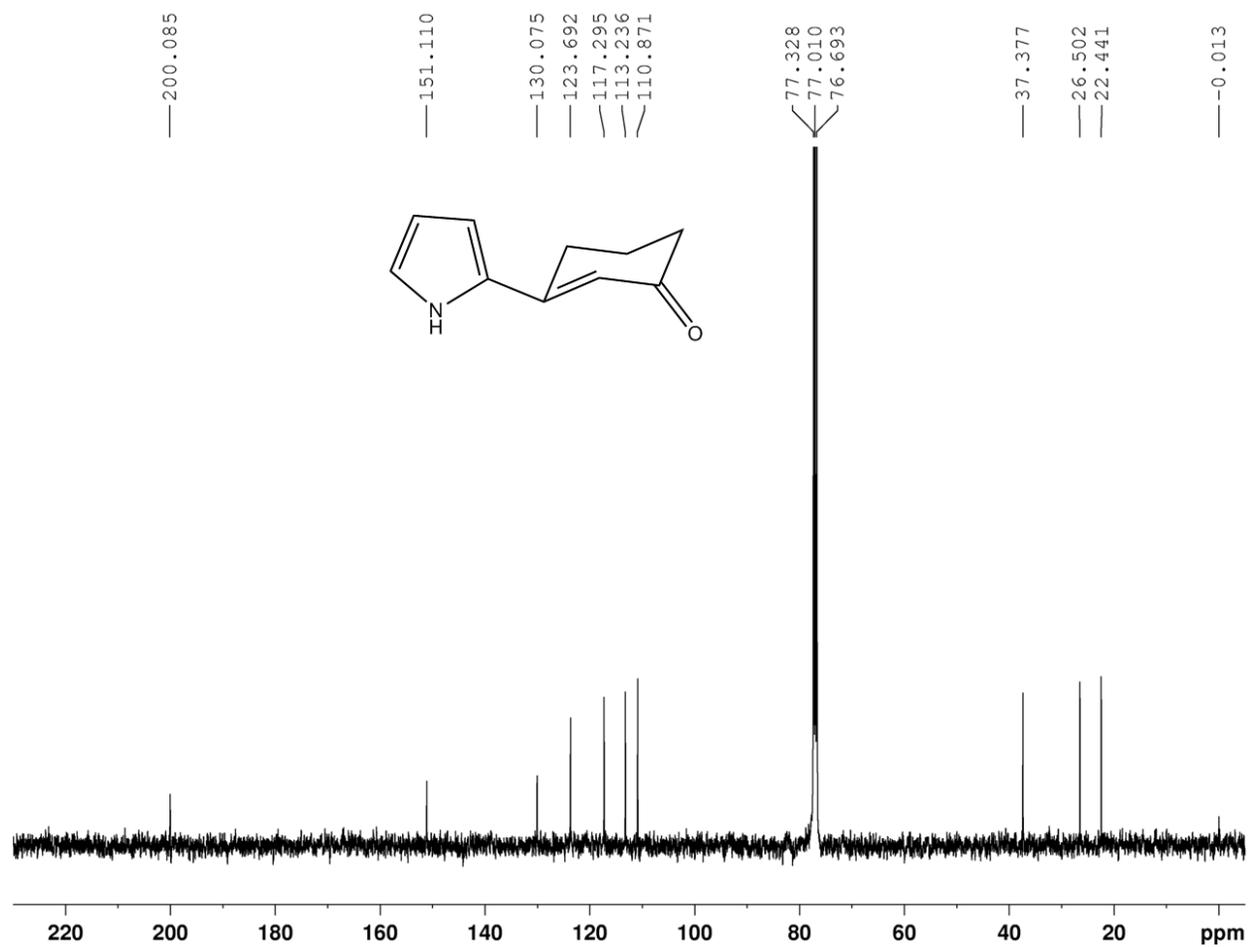


Fig. S6. ^{13}C NMR spectrum of compound 5.

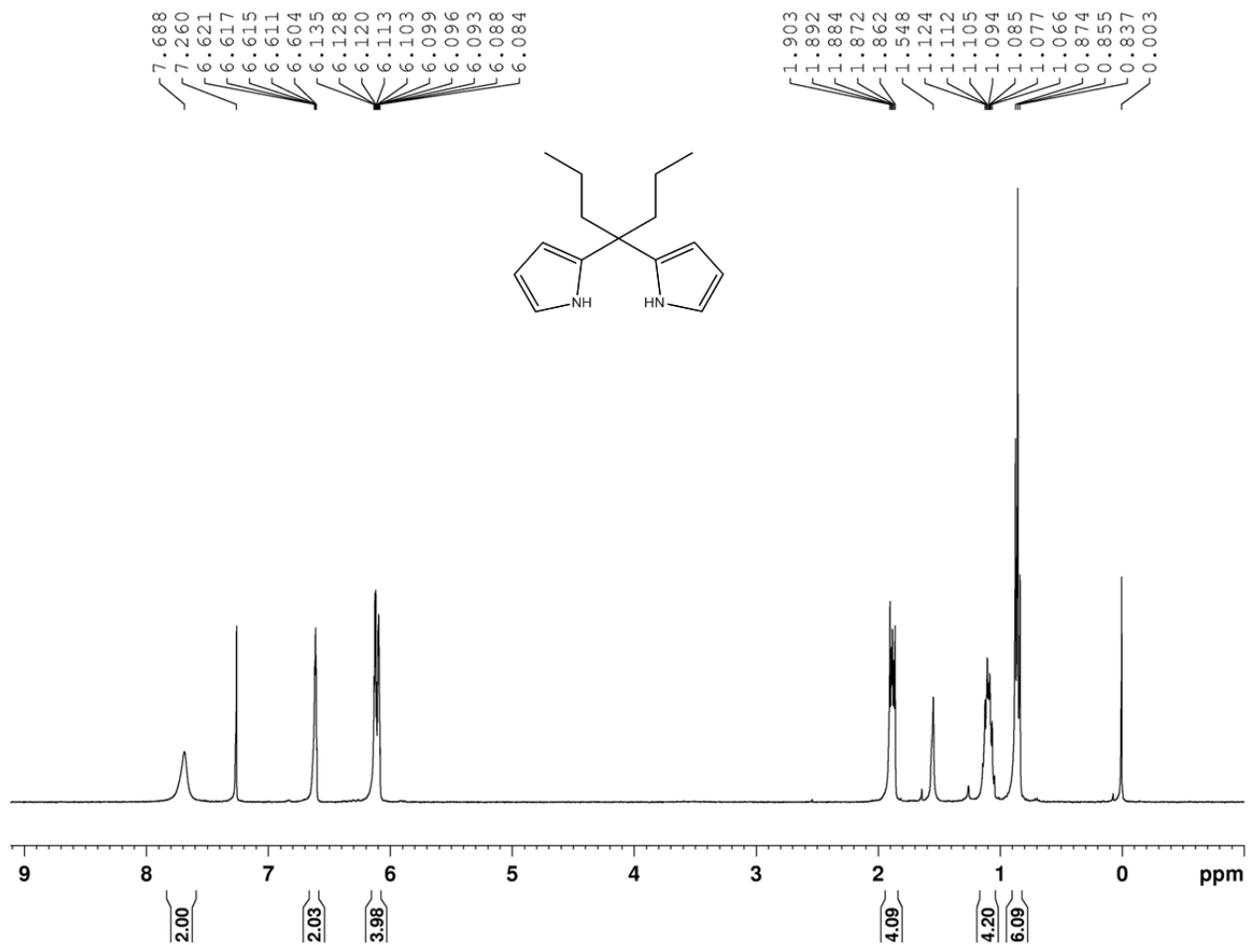


Fig. S7. ¹H NMR spectrum of compound 6.

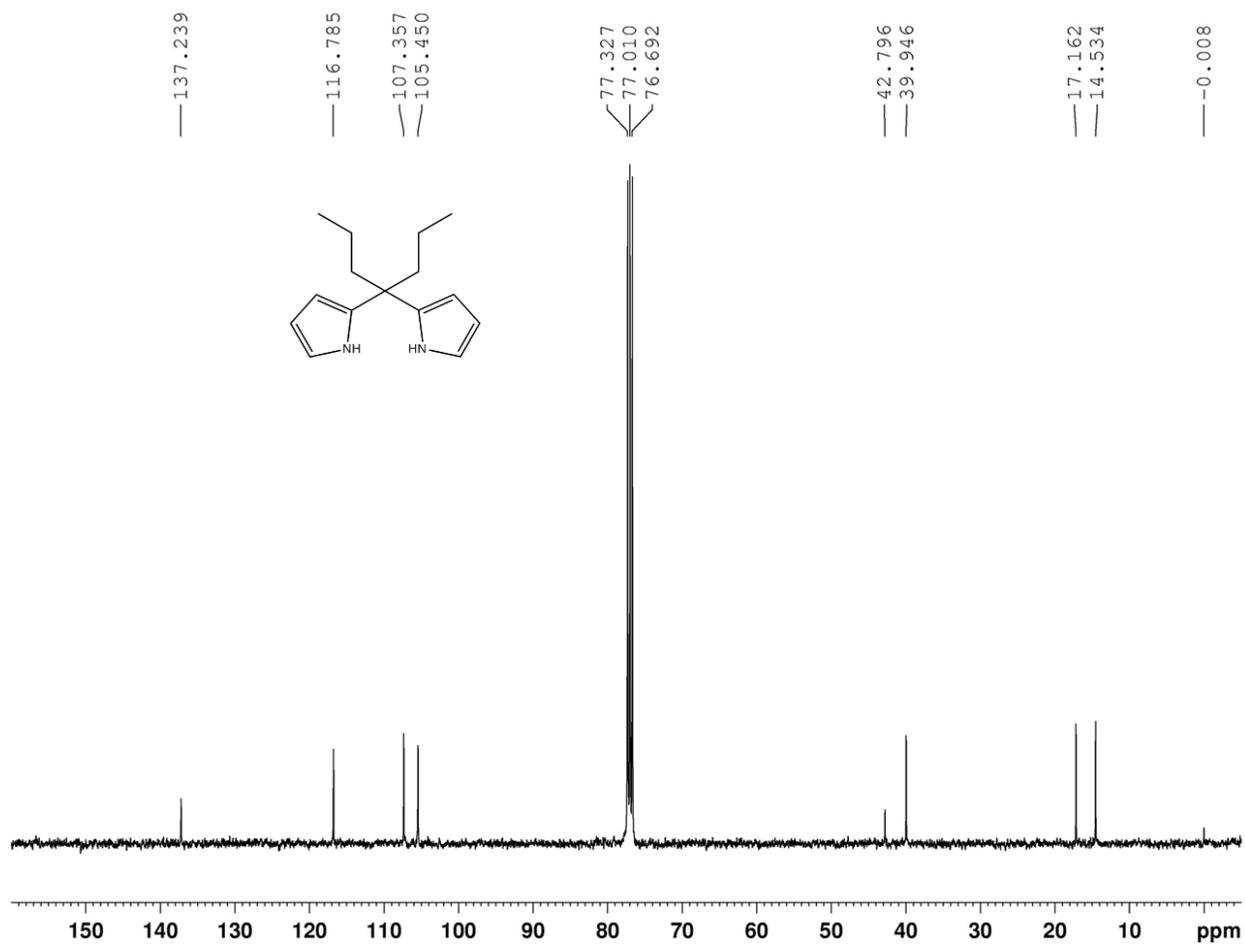


Fig. S8. ^{13}C NMR spectrum of compound **6**.

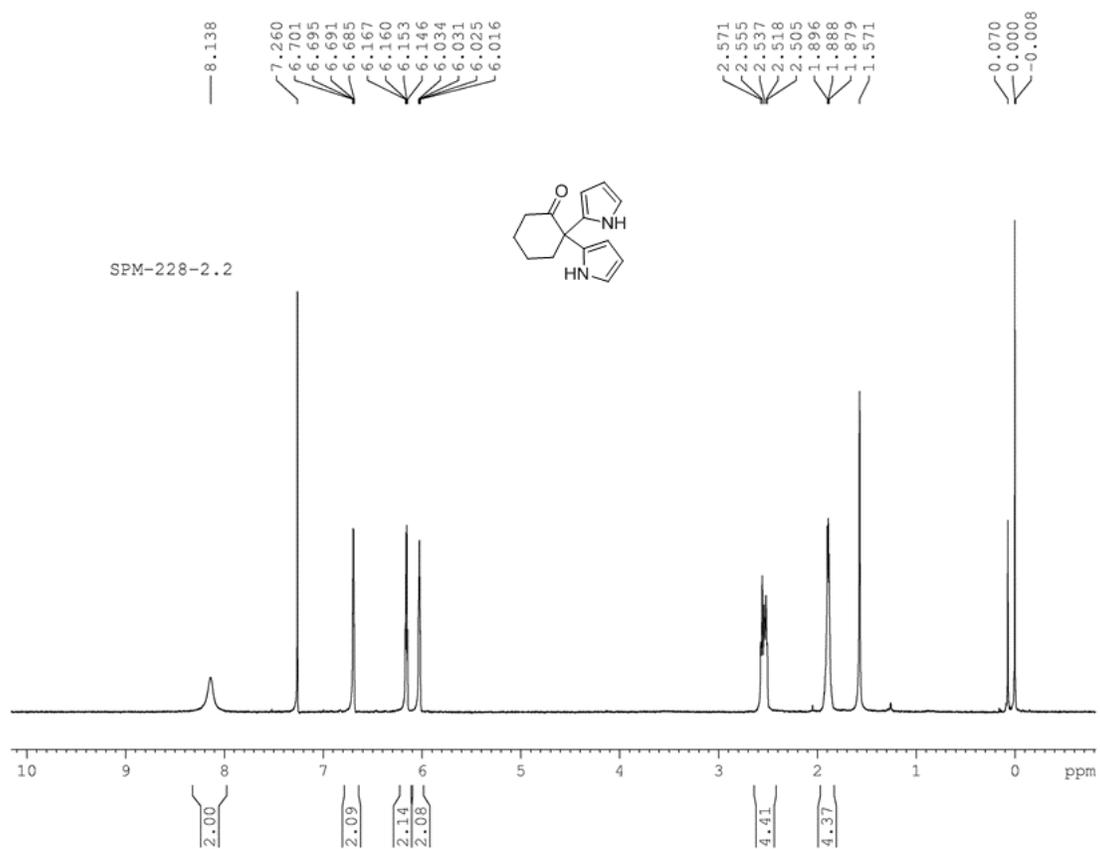


Fig. S9. ^1H NMR spectrum of compound 7.

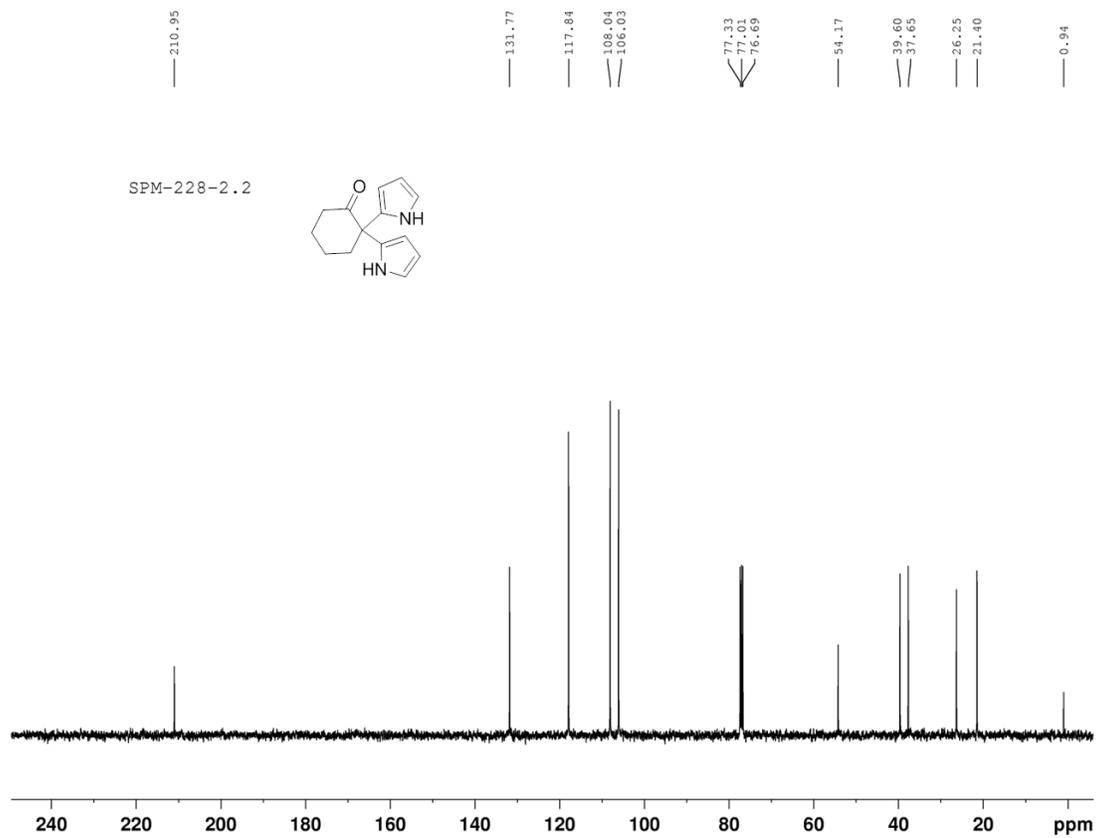


Fig. S10: ^{13}C NMR spectrum of compound 7.

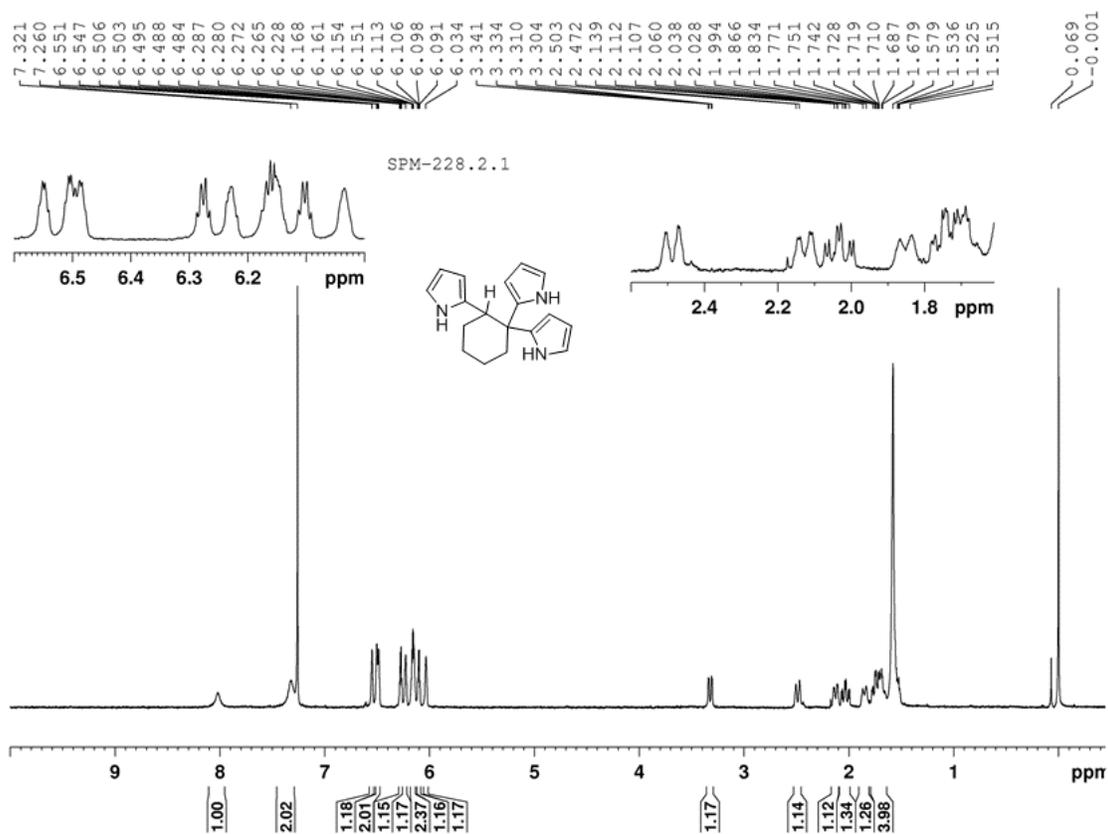


Fig. S11. ^1H NMR spectrum of compound 8.

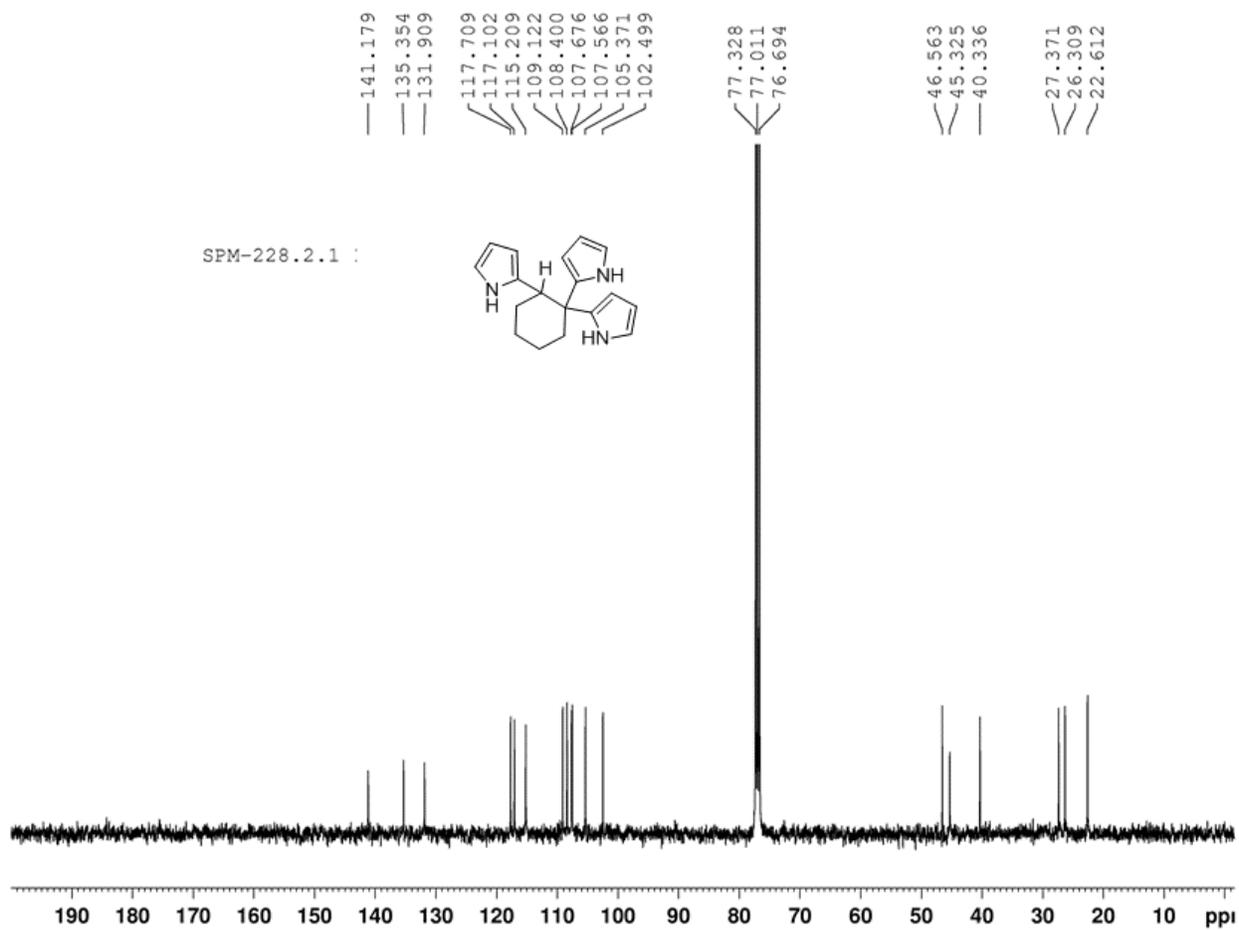


Fig. S12. ¹³C NMR spectrum of compound 8.

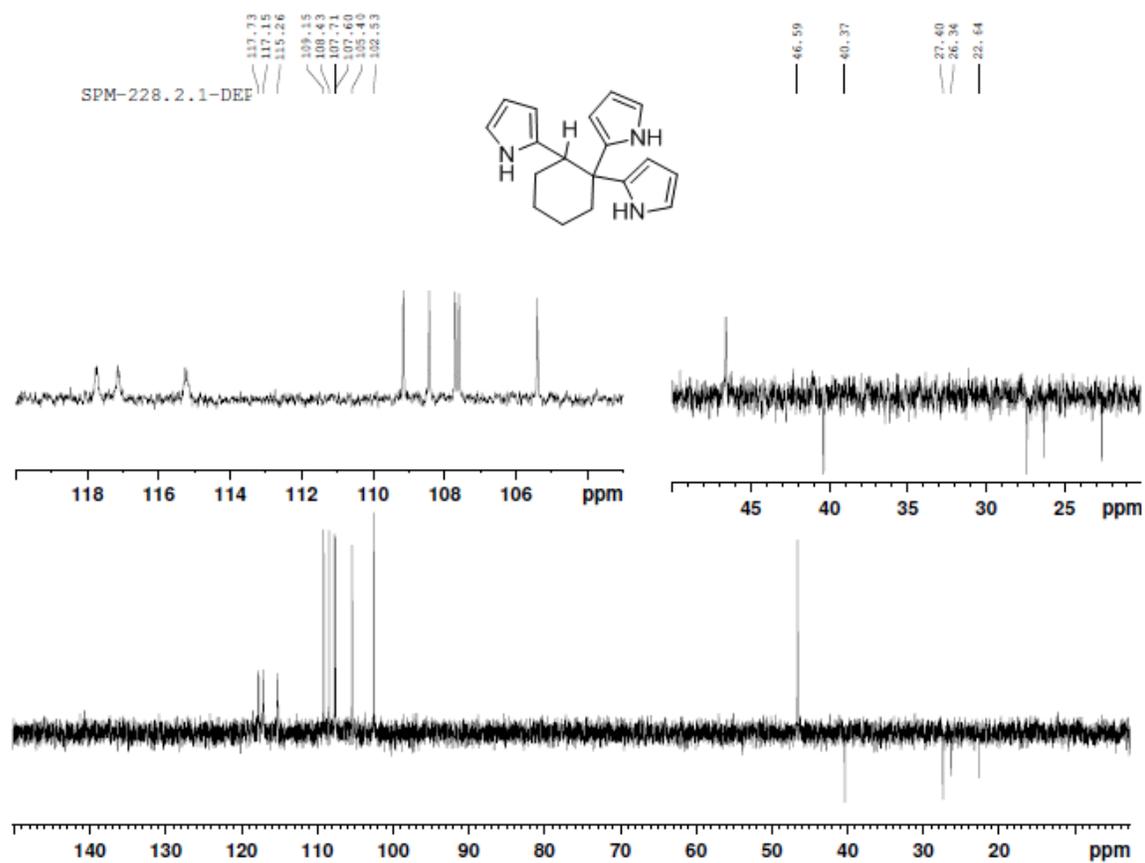


Fig. S13. DEPT-135 spectrum of compound **8**.

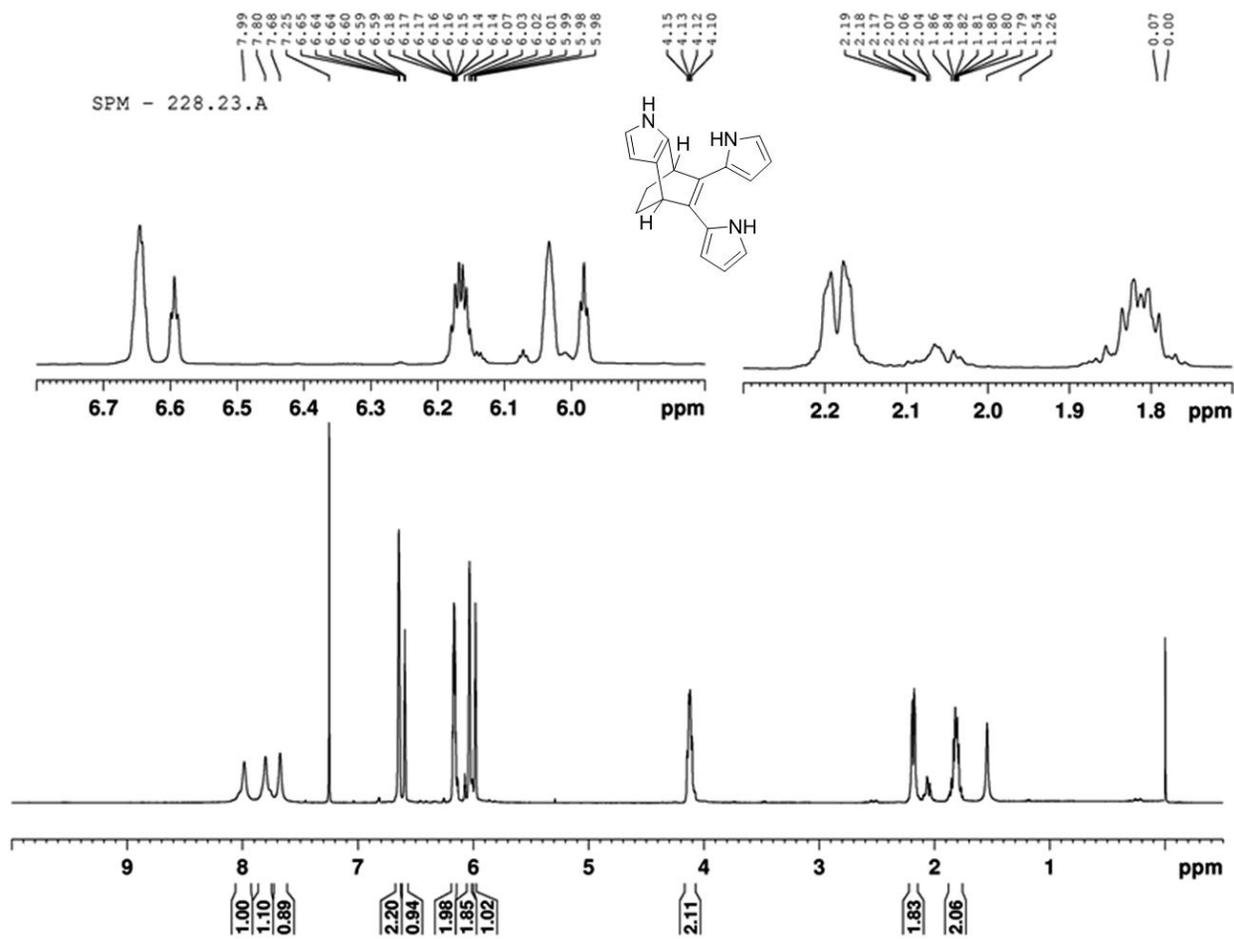


Fig. S14. ¹H NMR spectrum of compound 9.

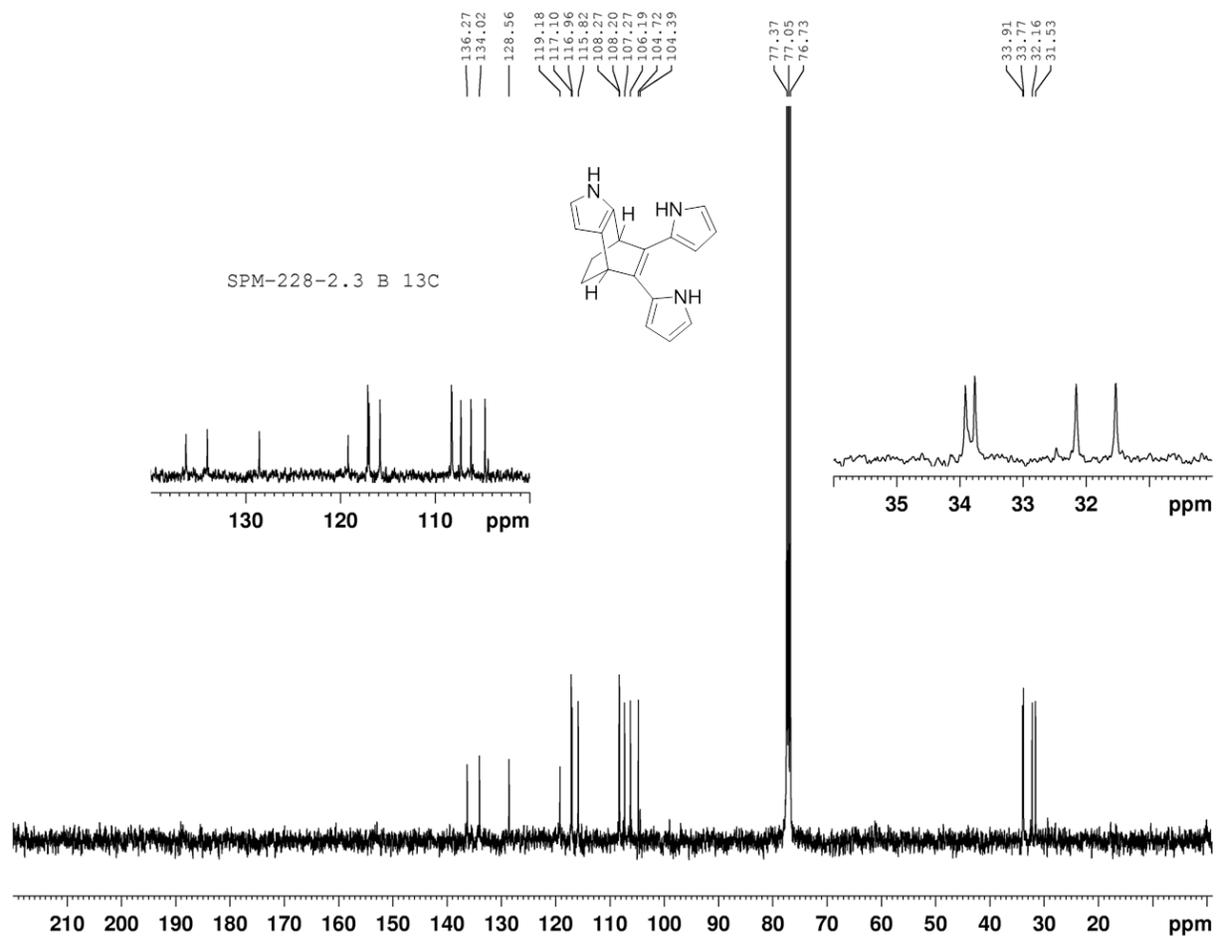


Fig. S15. ^{13}C NMR spectrum of compound 9.

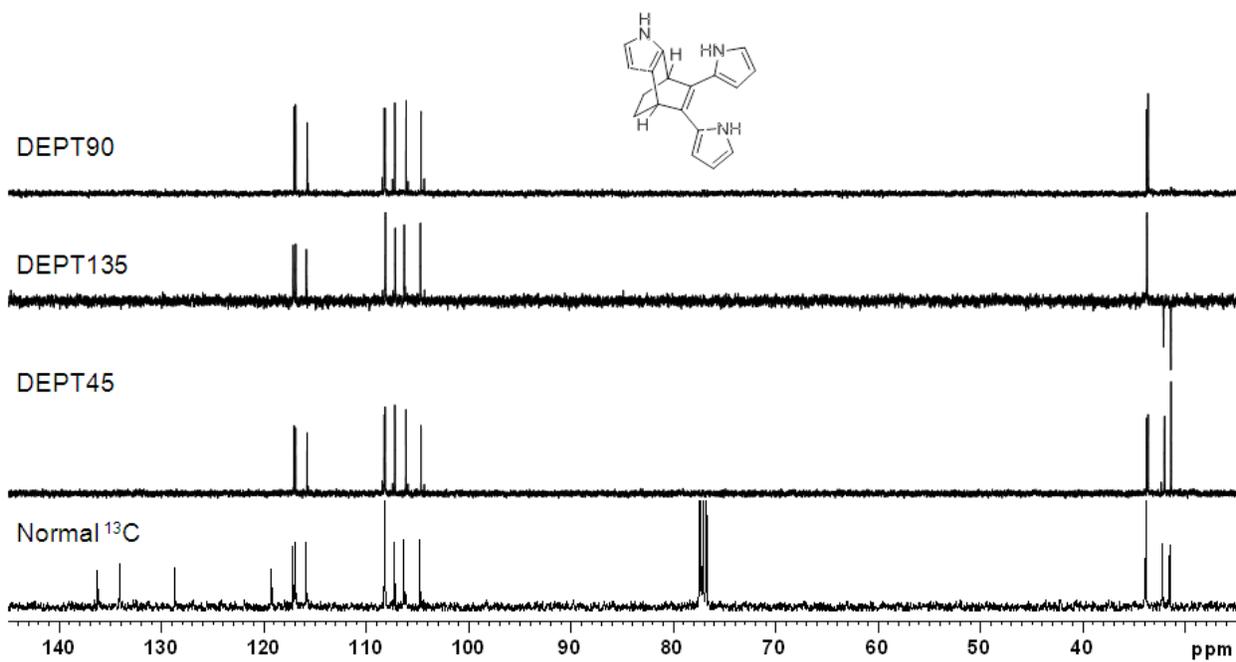


Fig. S16. DEPT-135 spectra of compound **9**.

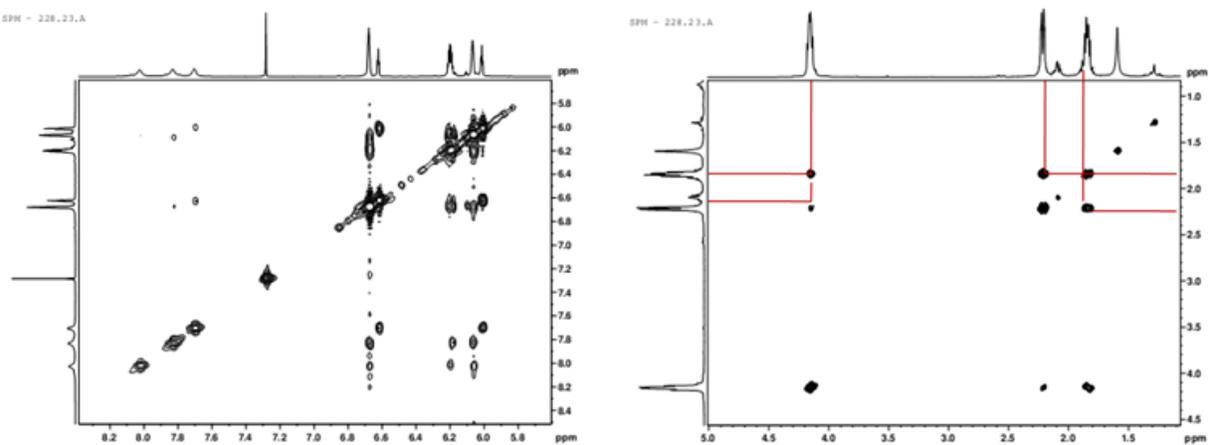


Fig. S17. ^1H - ^1H COSY spectrum of compound **9**.

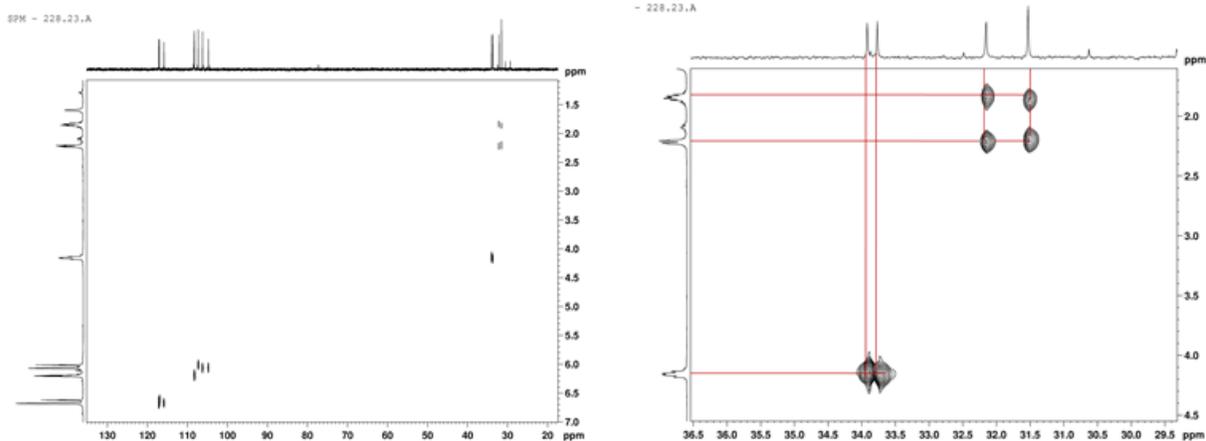


Fig. S18. ^1H - ^{13}C COSY spectrum of compound **9**.

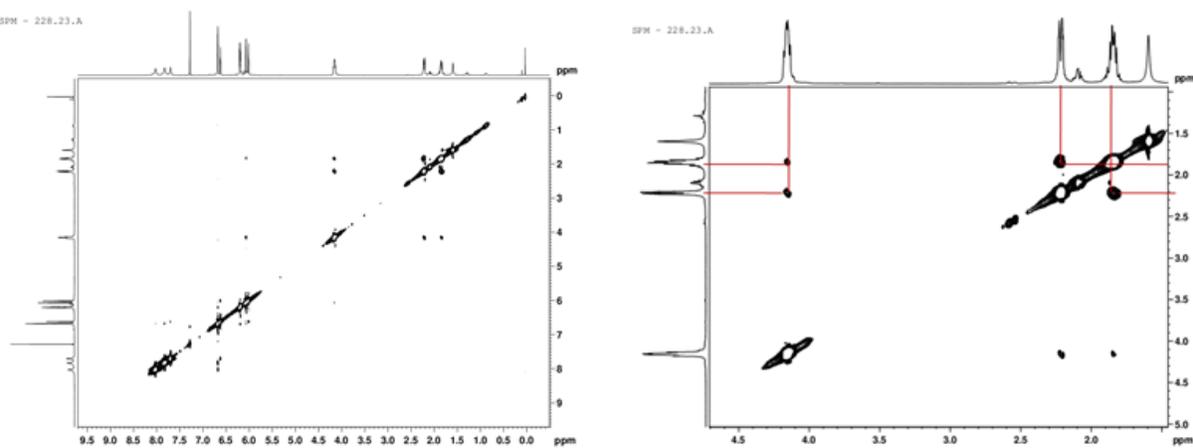


Fig. S19. ^1H - ^{13}C COSY spectrum of compound **9**.

Single crystal X-Ray diffraction analysis:

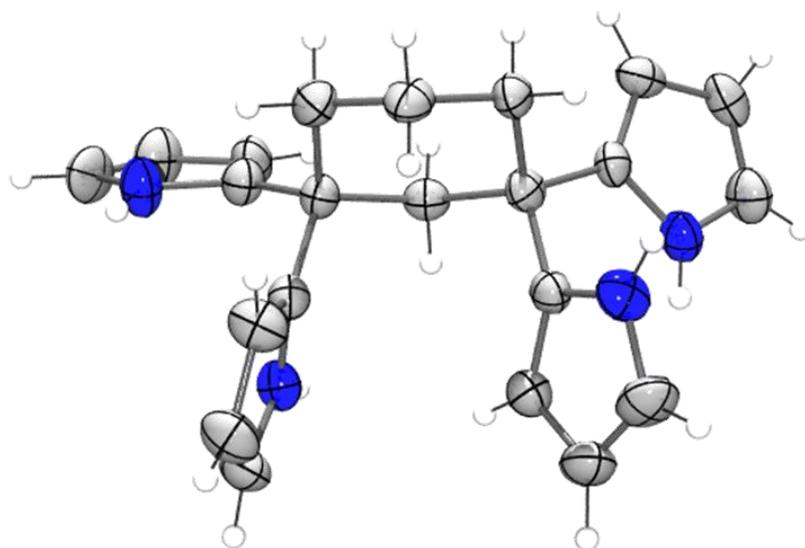


Fig. S20. ORTEP-POVray diagram of compound **2**. Thermal ellipsoids are scaled upto 25% probability level.

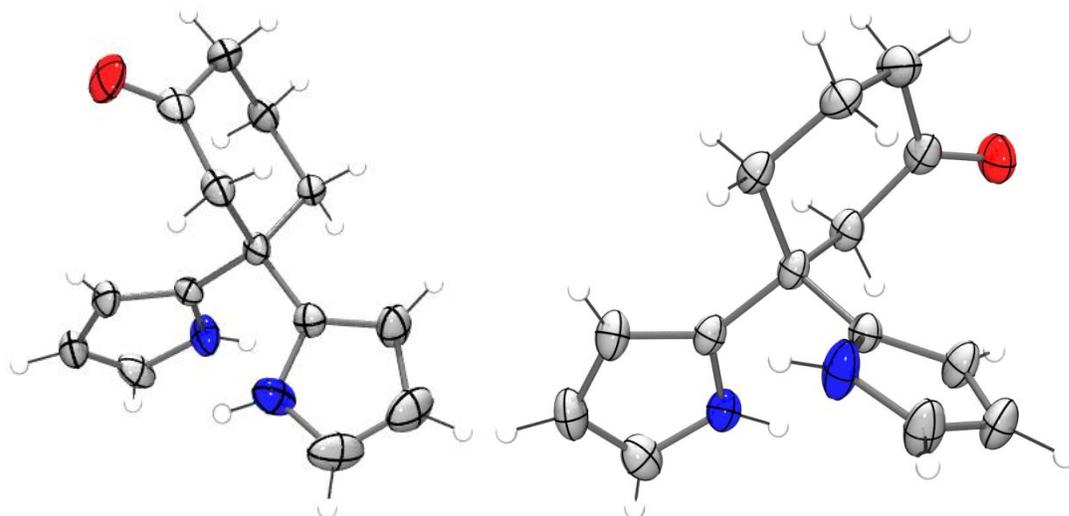


Fig. S21. ORTEP-POVray diagram of compound **4** (Left: Polymorph-1, Right: Polymorph-2). Thermal ellipsoids are scaled upto 25% probability level.

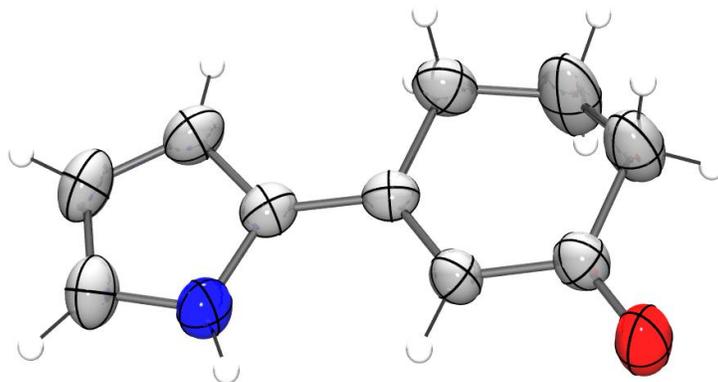


Fig. S22. ORTEP-POVray diagram of compound **5**. Thermal ellipsoids are scaled upto 25% probability level.

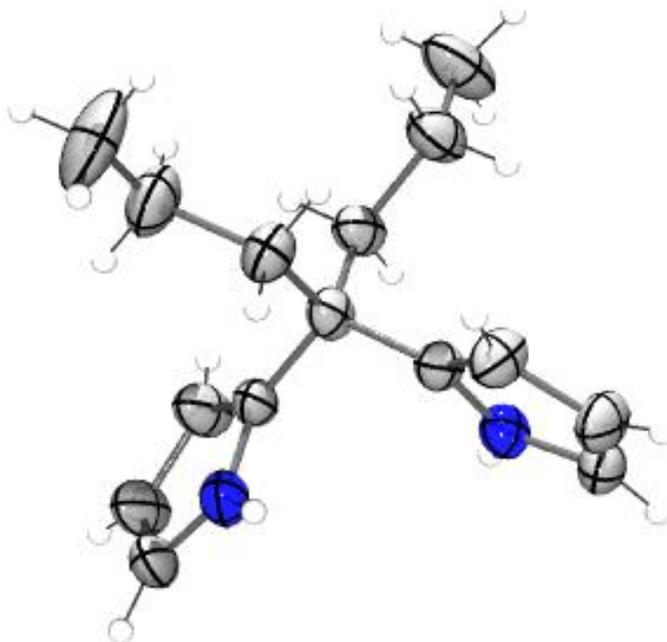


Fig. S23. ORTEP-POVray diagram of compound **6**. Thermal ellipsoids are scaled upto 25% probability level.

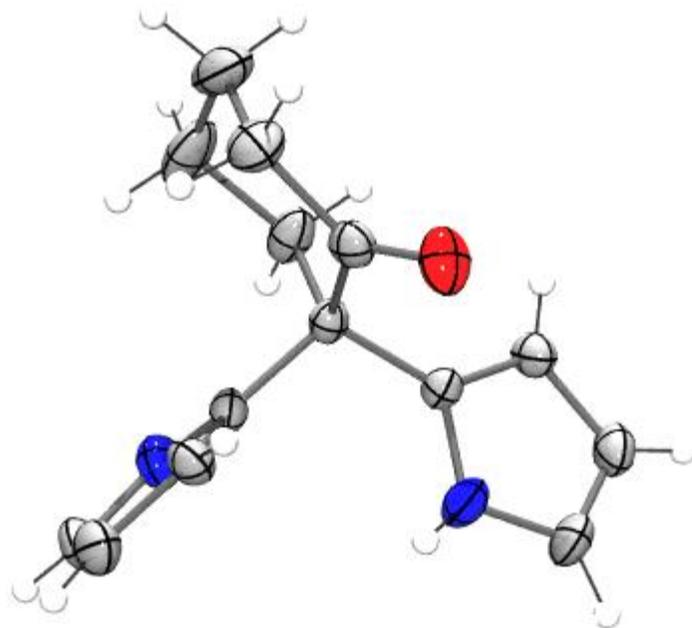


Fig. S24. ORTEP-POVray diagram of compound **7**. Thermal ellipsoids are scaled up to 25% probability level.

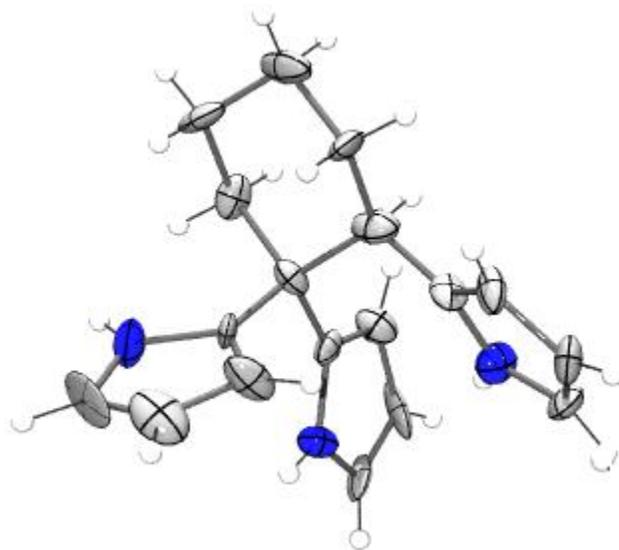


Fig. S25. ORTEP-POVray diagram of compound **8**. Thermal ellipsoids are scaled up to 25% probability level.

Author's comment on IUCR check .cif alert:

Compound 2:

RINTA01_ALERT_3_A The value of Rint is greater than 0.25 Rint given 0.397

PLAT020_ALERT_3_A The value of Rint is greater than 0.120.397

PLAT026_ALERT_3_A Ratio Observed / Unique Reflections too Low25 Perc.

Compound 4:

Polymorph-1:

PLAT026_ALERT_3_A Ratio Observed/Unique Reflections too Low.... 28 Perc.

PLAT222_ALERT_3_A Large Non-Solvent H Uiso(max)/Uiso(min) .. 10.0 Ratio

Polymorph-2:

PLAT029_ALERT_3_A diffrn_measured_fraction_theta_full Low 0.868

Compound 5:

REFLT03_ALERT_3_A Reflection count < 85% complete (theta max?)

From the CIF: diffrn_reflns_theta_max 28.99

From the CIF: diffrn_reflns_theta_full 28.99

From the CIF: reflns_number_total 1942

TEST2: Reflns within _diffrn_reflns_theta_max

Count of symmetry unique reflns 2294

Completeness (_total/calc) 84.66%

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full Low 0.847

Compound 6:

PLAT029_ALERT_3_A _diffrn_measured_fraction_theta_full Low0.865

Compound 7:

PLAT029_ALERT_3_A diffrn_measured_fraction_theta_full Low 0.854

Compound 8:

REFLT03 ALERT 3 A Reflection count < 85% complete (theta max?)

From the CIF: `_diffn_refl_theta_max` 28.97

From the CIF: `_diffn_refl_theta_full` 28.97

From the CIF: `_reflns_number_total` 5382

TEST2: Reflns within `_diffn_refl_theta_max`

Count of symmetry unique reflns 8040

Completeness (`_total/calc`) 66.94%

PLAT026 ALERT 3 A Ratio Observed / Unique Reflections too Low.... 16 Perc.

PLAT029 ALERT 3 A `diffn_measured_fraction_theta_full` Low 0.669

PLAT213 ALERT 2 A Atom C18 has ADP max/min Ratio 5.6 prola

Author Response: The compounds reported here contain one or more pyrrole moieties so these compounds are relatively unstable in crystallization conditions. So we carried out fast crystallization such that compound retains its integrity. The data reported here is the best one among the collected. Again, in case of compound **8**, one carbon atom has disorder which we are unable to model..

Packing analysis of the two polymorphs of compound **4**:

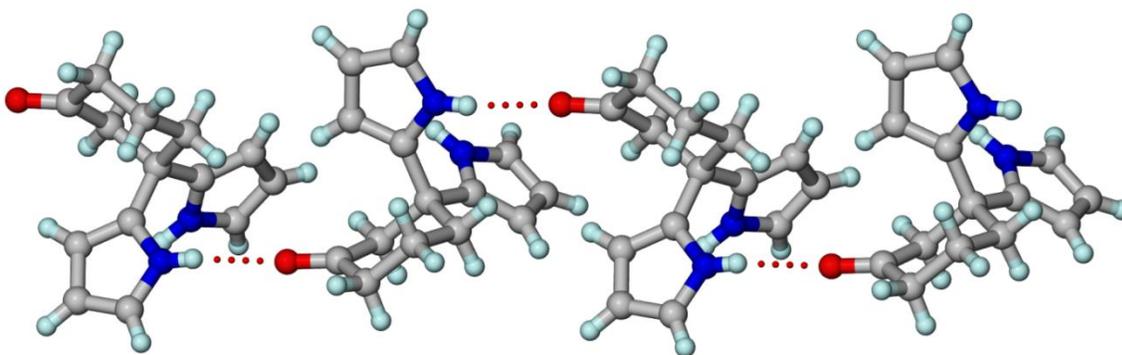


Fig. S26. 1-D linear chain present in polymorph-1.

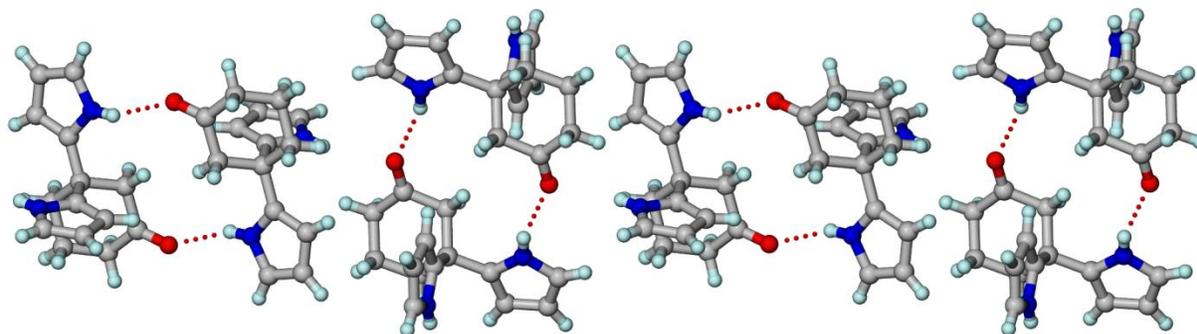


Fig. S27. Dimeric motif present in polymorph-1.

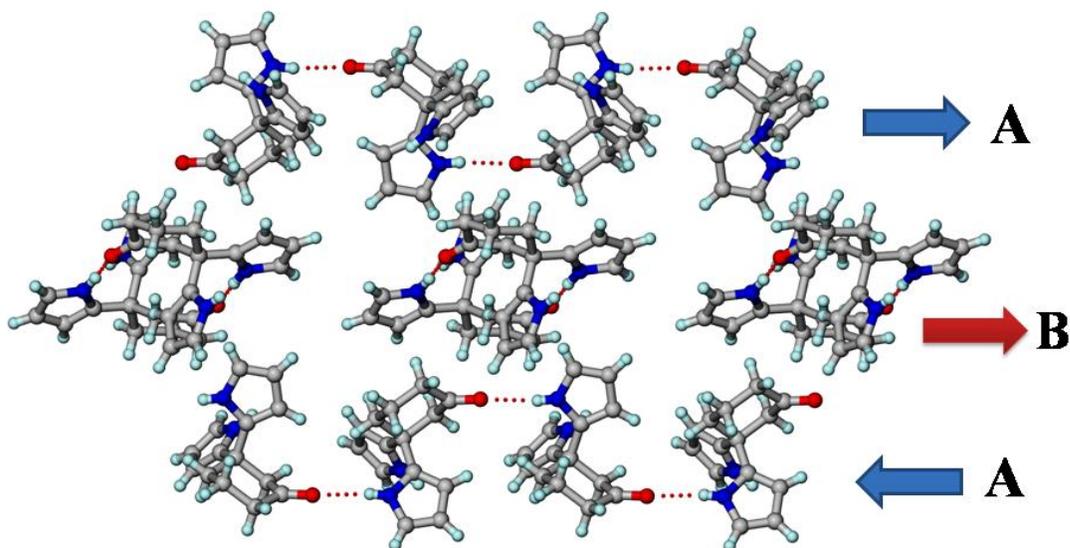


Fig. S28. The overall packing pattern of polymorph-1 showing ABAB stacks.

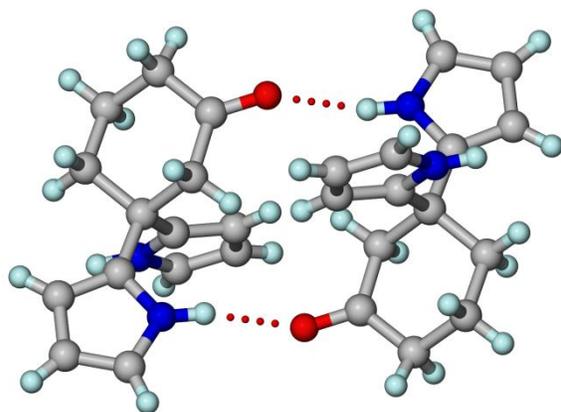


Fig. S29. Dimeric motif present in polymorph-2.

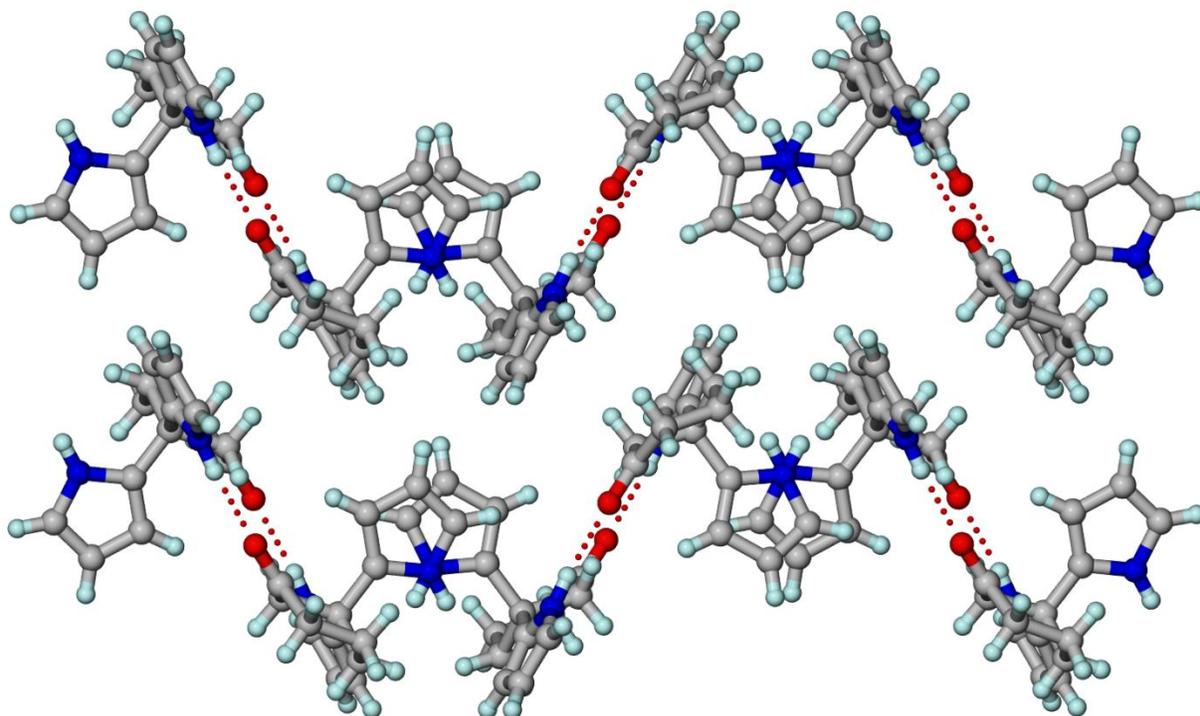


Fig. S30. The overall packing pattern of polymorph-2 showing Herringbone pattern.