

## Supplementary Material

### Ketenes from *N*-(2-Pyridyl)amides

Carsten Plüg,<sup>A</sup> Hussein Kanaani<sup>A</sup> and Curt Wentrup<sup>A,B</sup>

<sup>A</sup>School of Chemistry and Molecular Biosciences, The University of Queensland, Brisbane, Qld 4072, Australia

<sup>B</sup>Corresponding author. Email: [wentrup@uq.edu.au](mailto:wentrup@uq.edu.au)

#### Contents:

**Figure S1.** IR spectrum of *s-Z* and *s-E*-2-pyridylketene **4f**.

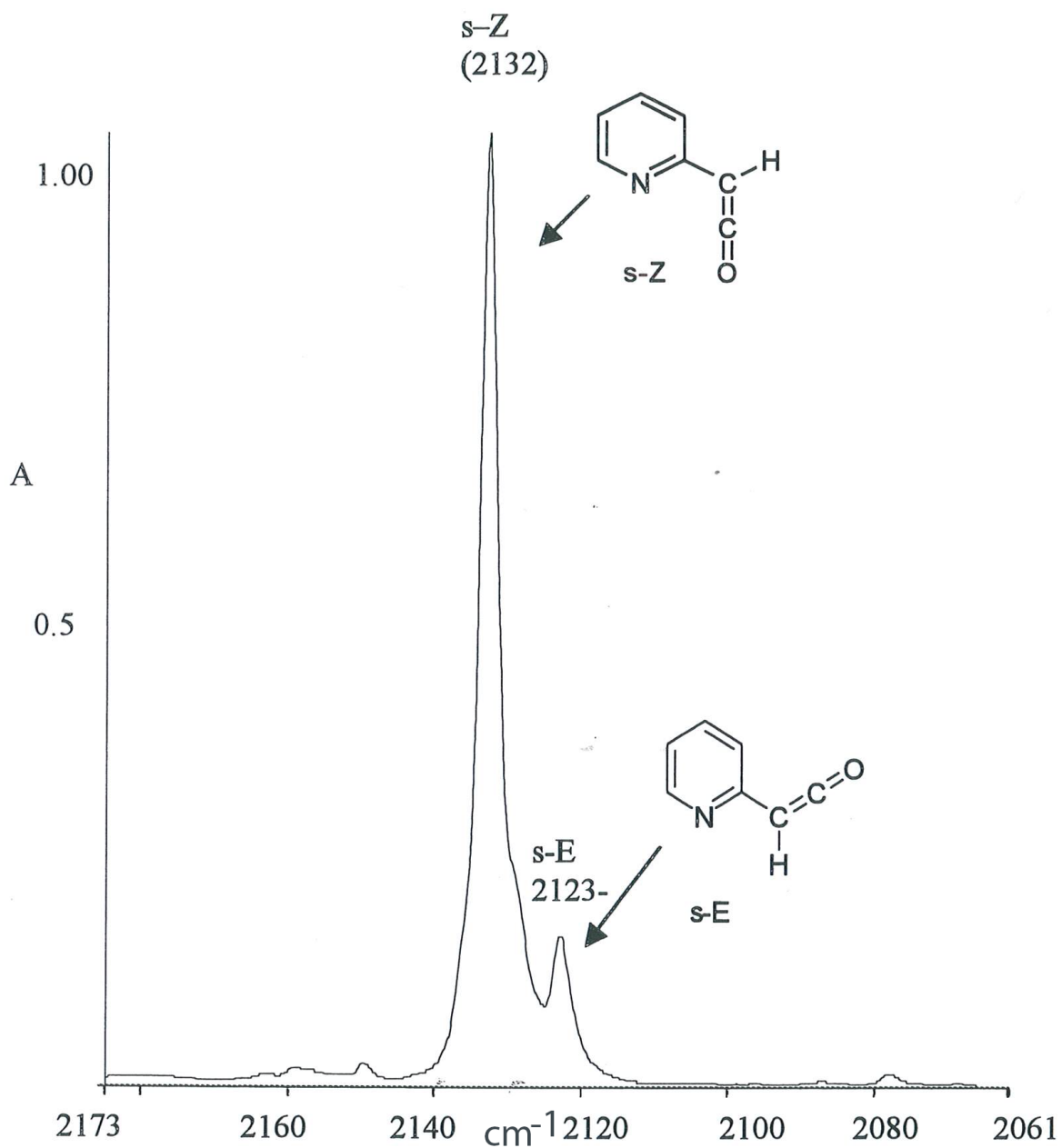
**Figure S2.** Changing structure of ketene peak of 2-pyridylketene **4f** on warm-up.

**Figure S3.** Matrix-IR spectrum of 2-aminopyridine

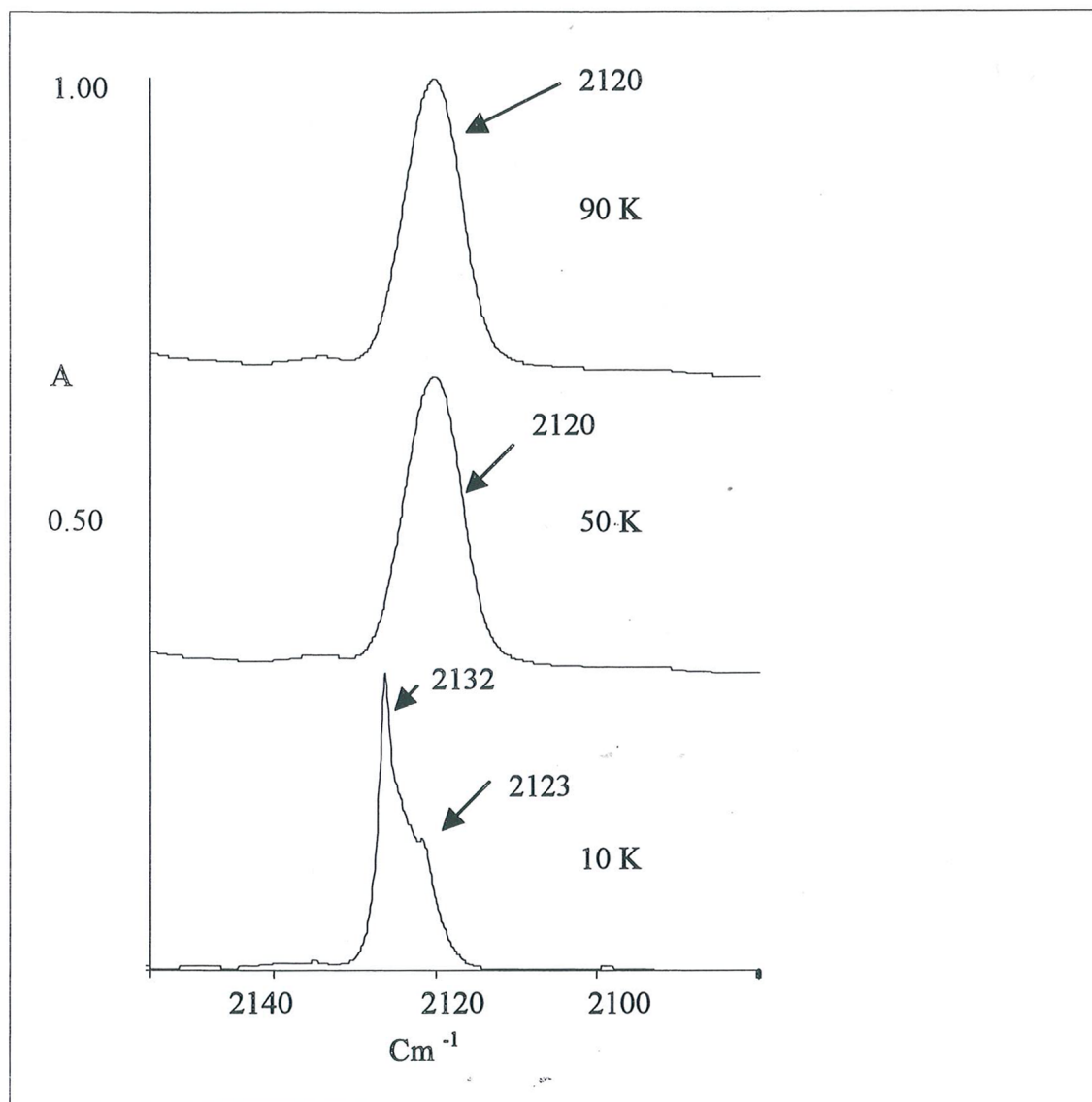
**Figure S4.** Matrix-IR spectrum of 2-(methylamino)pyridine

**Figure S5.** Matrix-IR spectrum of 2-picoline.

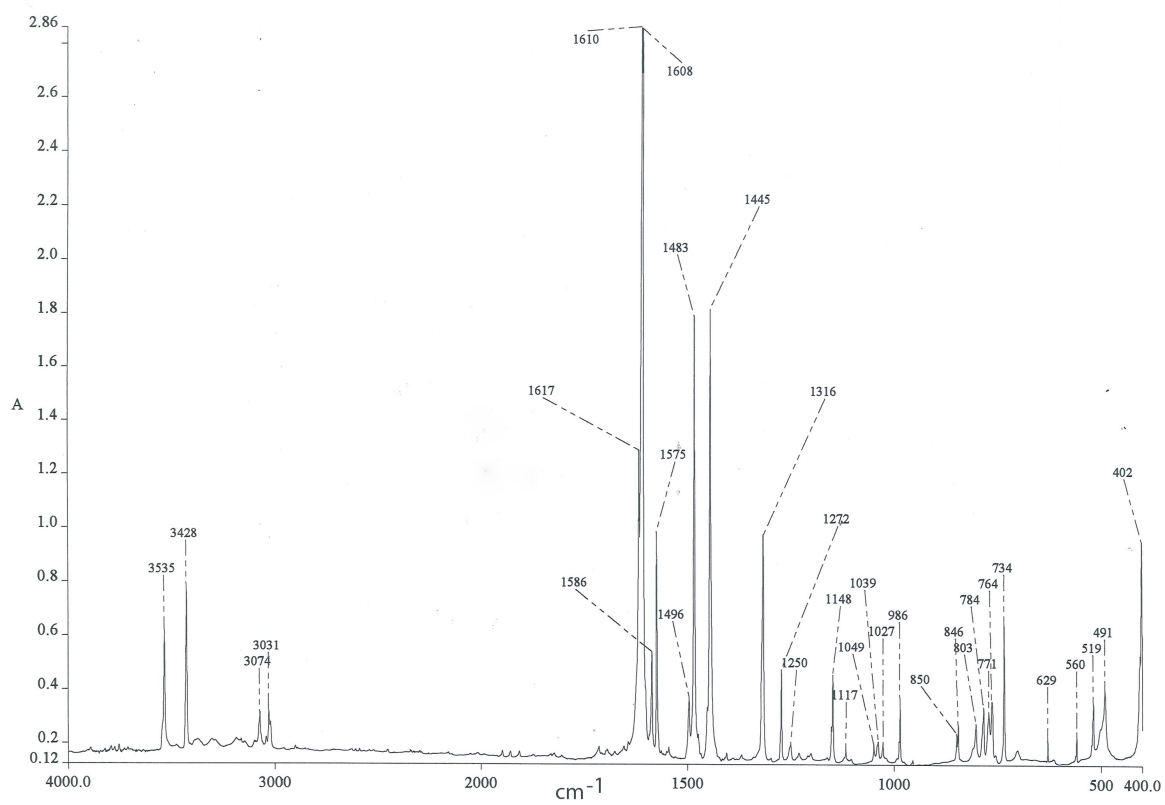
**Figures S6-S15:** <sup>1</sup>H and <sup>13</sup>C NMR spectra of starting materials **3**.



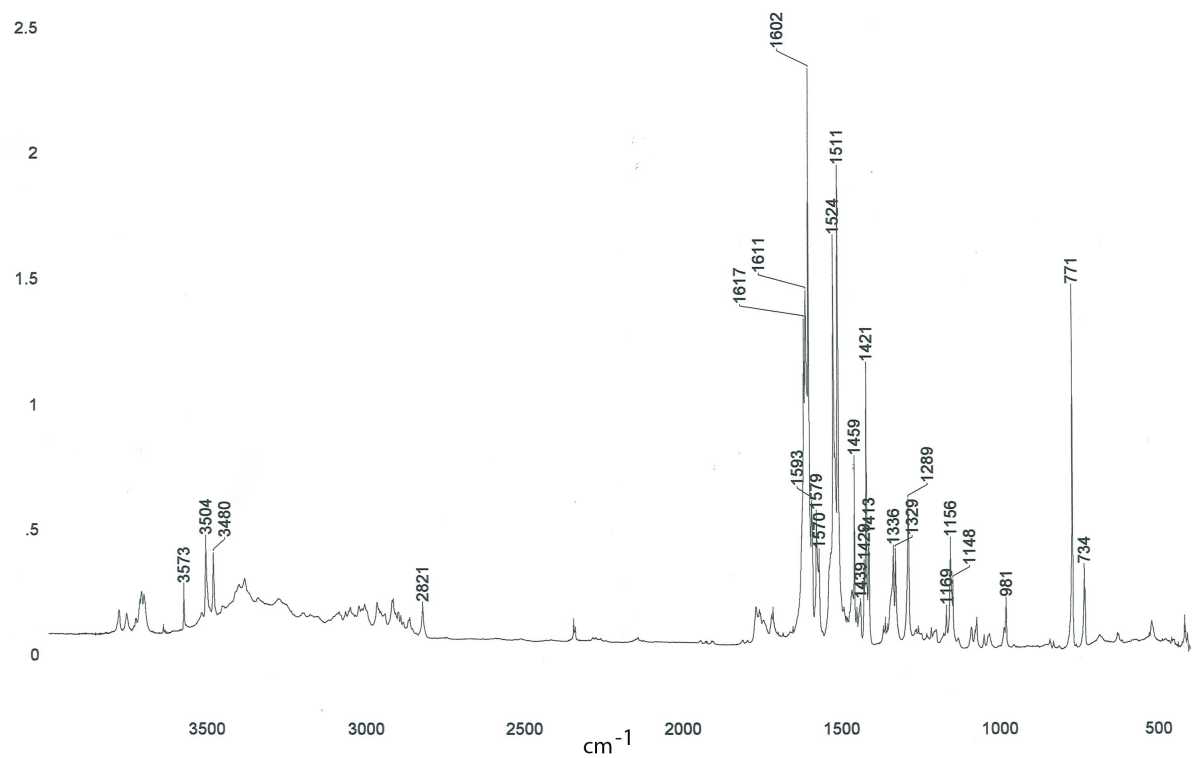
**Figure S1.** Detail of the IR spectrum of *s-Z* and *s-E*-2-pyridylketene **4f** from FVT of **3f** (Ar matrix, 10 K).



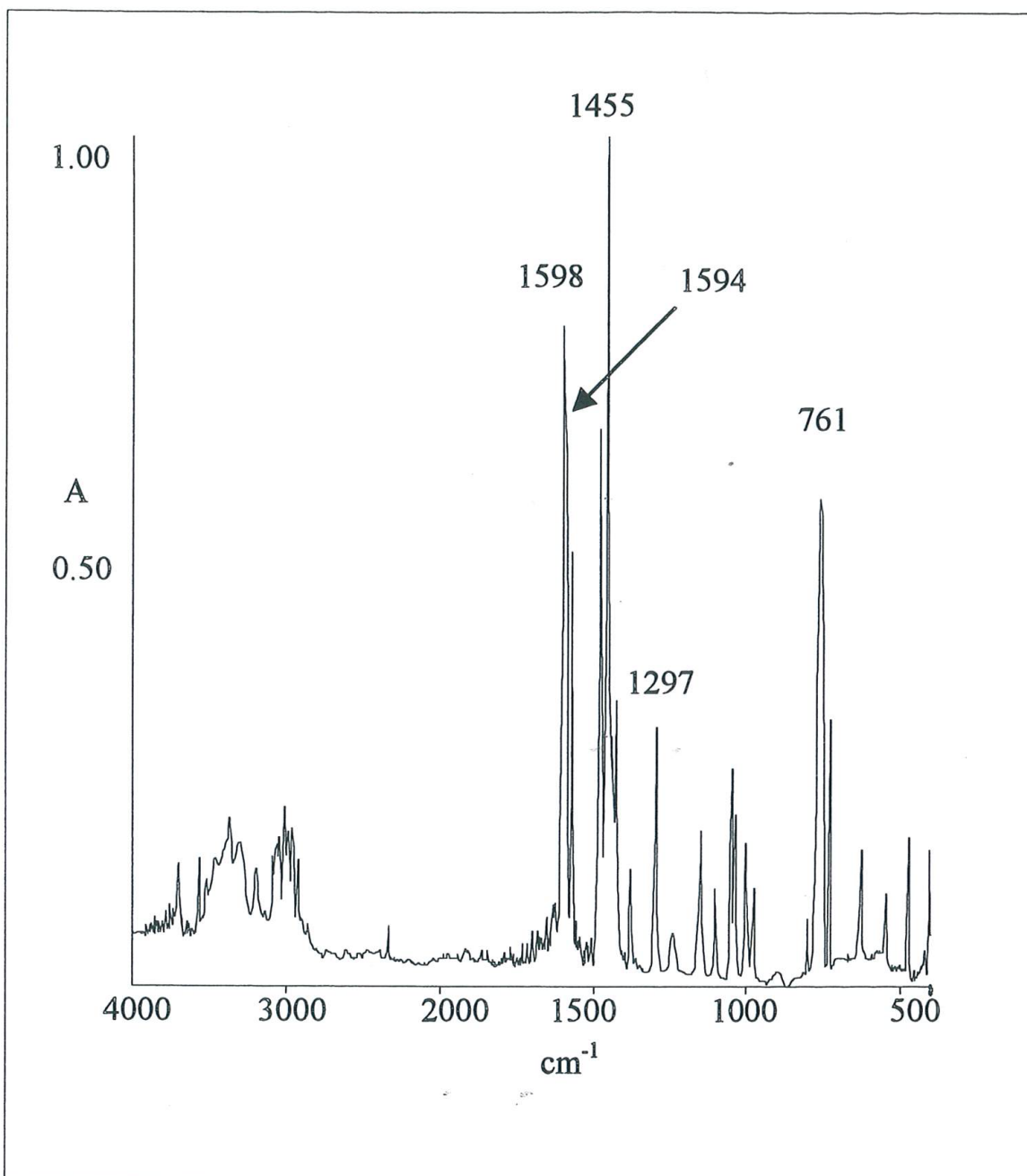
**Figure S2.** Changing structure of ketene peak of 2-pyridylketene **4f** on warm-up from 10 to 90 K. the *s-Z* and *s-E* peaks merge and blue-shift when Ar has been removed at 40 K.



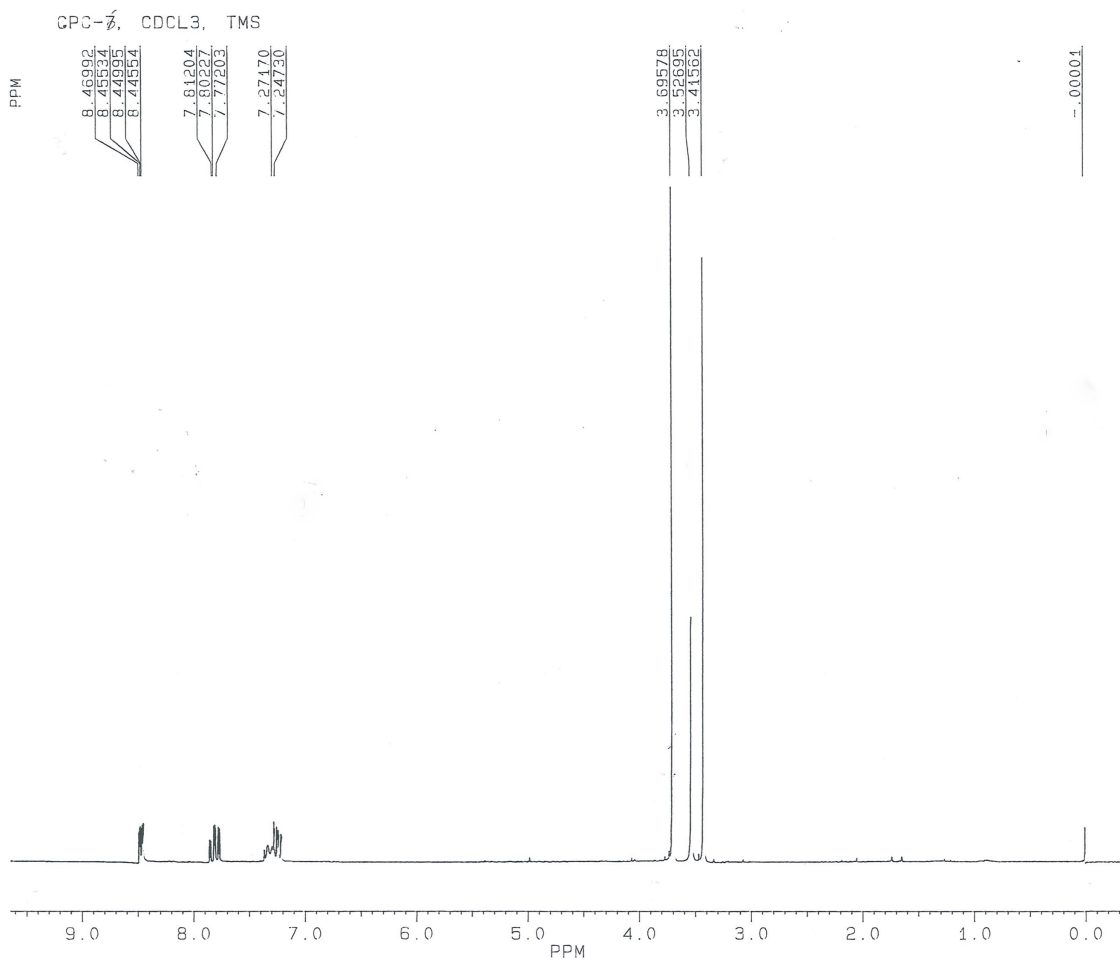
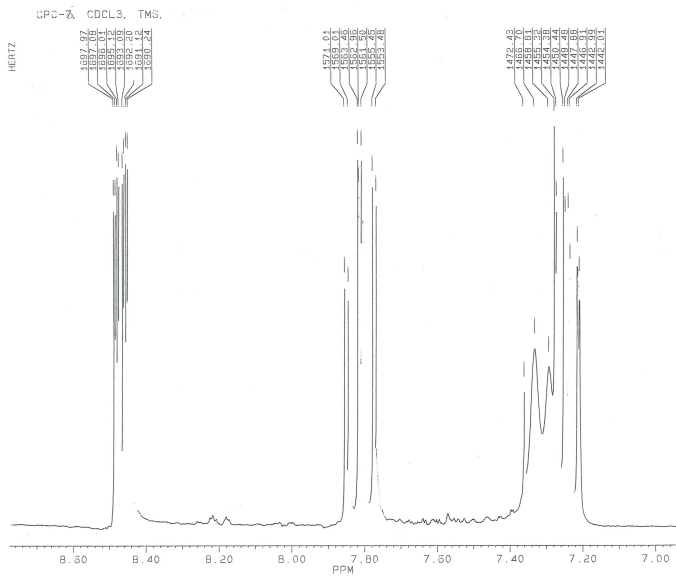
**Figure S3.** IR spectrum of 2-aminopyridine (Ar, 10 K).



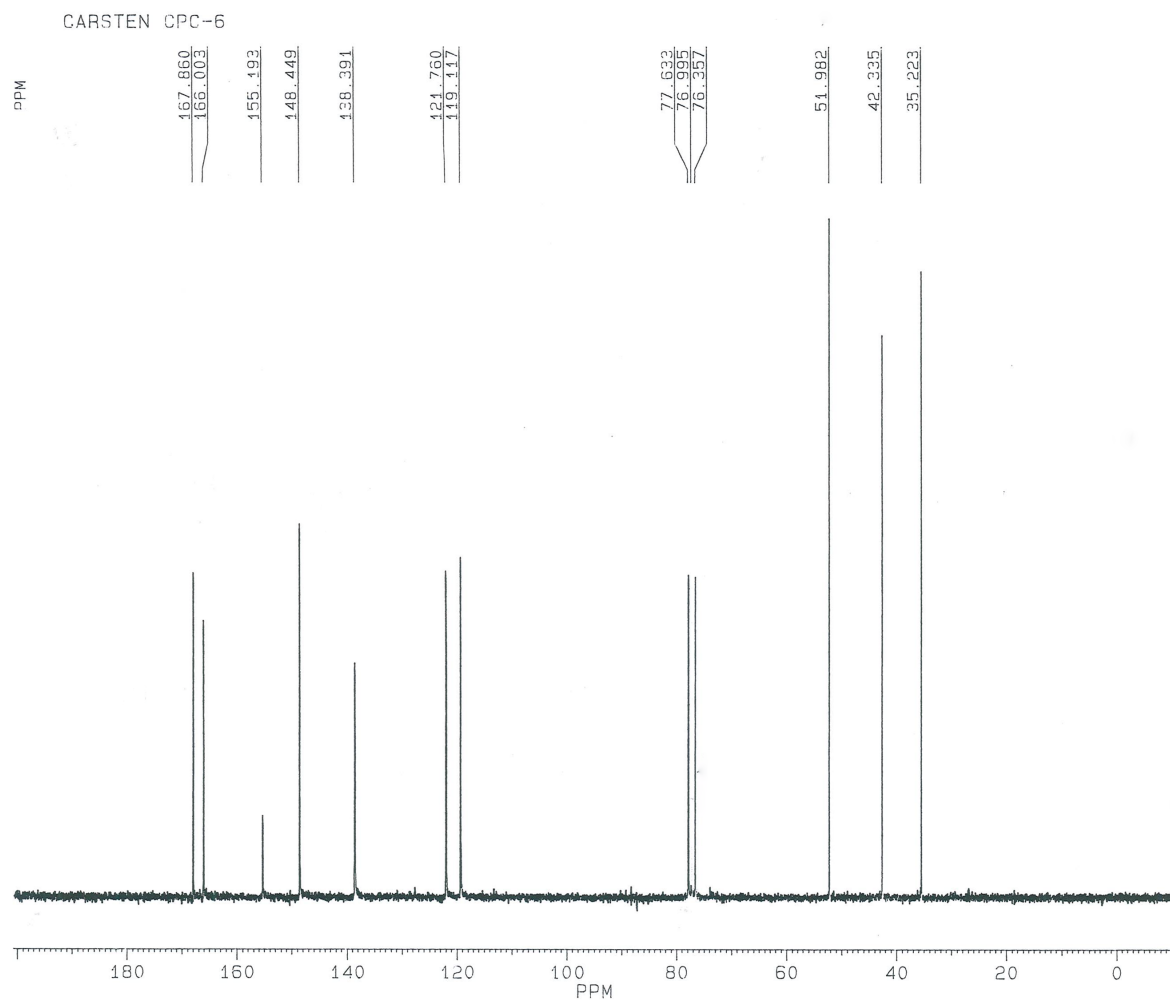
**Figure S4.** IR spectrum of 2-(methylamino)pyridine **1a** (Ar, 14 K). A small peak at 2340  $\text{cm}^{-1}$  is due to  $\text{CO}_2$ . The peak at 3573  $\text{cm}^{-1}$  is ascribed to the  $\text{H}_2\text{O}$  dimer. The band at 3504 and 3480  $\text{cm}^{-1}$  are due to the NH stretchings of the *s-Z* and *s-E* conformers, respectively. These absorptions have calculated intensities of 20 and 34  $\text{km/mol}$ , respectively, at the B3LYP/6-31G\* level. A peak at 1661  $\text{cm}^{-1}$  may be due to a 2-(methylimino)-1*H*-pyridine tautomer **9a** (see Chart 1). The spectrum was obtained from a commercial sample.



**Figure S5.** Matrix-IR spectrum of 2-picoline (Ar, 10 K). 3016w, 1598s, 1594s, 1571m, 1479s, 1455vs, 1437m, 1425m, 1378w, 1297m, 1244w, 1149m, 1102w, 1052m, 1038m, 1002m, 977w, 801w, 761s, 731m, 629w, 546w, 472m, 405m  $\text{cm}^{-1}$ . Bands due to water are seen in the region 3500-3700  $\text{cm}^{-1}$  and  $\text{CO}_2$  at 2340w  $\text{cm}^{-1}$ .

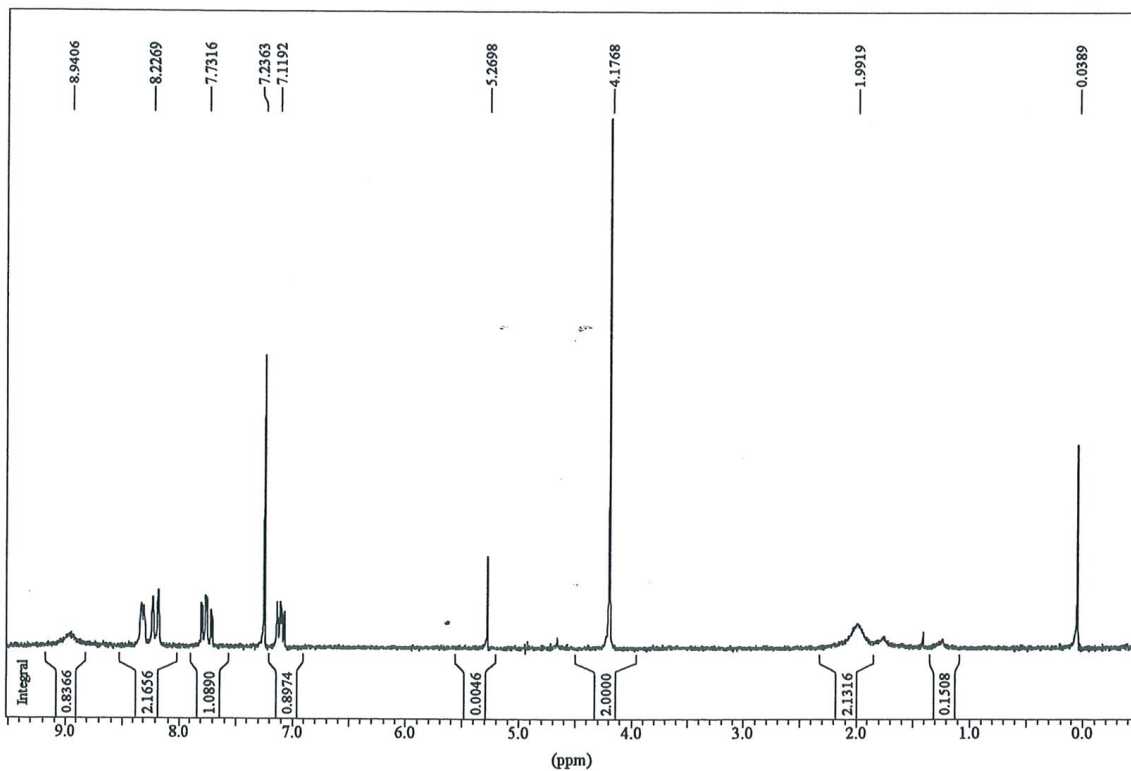


**Figure S6.** <sup>1</sup>H NMR spectrum of methyl *N*-methyl-*N*-(2-pyridyl)aminocarbonylacetate **3a** (CDCl<sub>3</sub>) with enlarged image of the aromatic region.

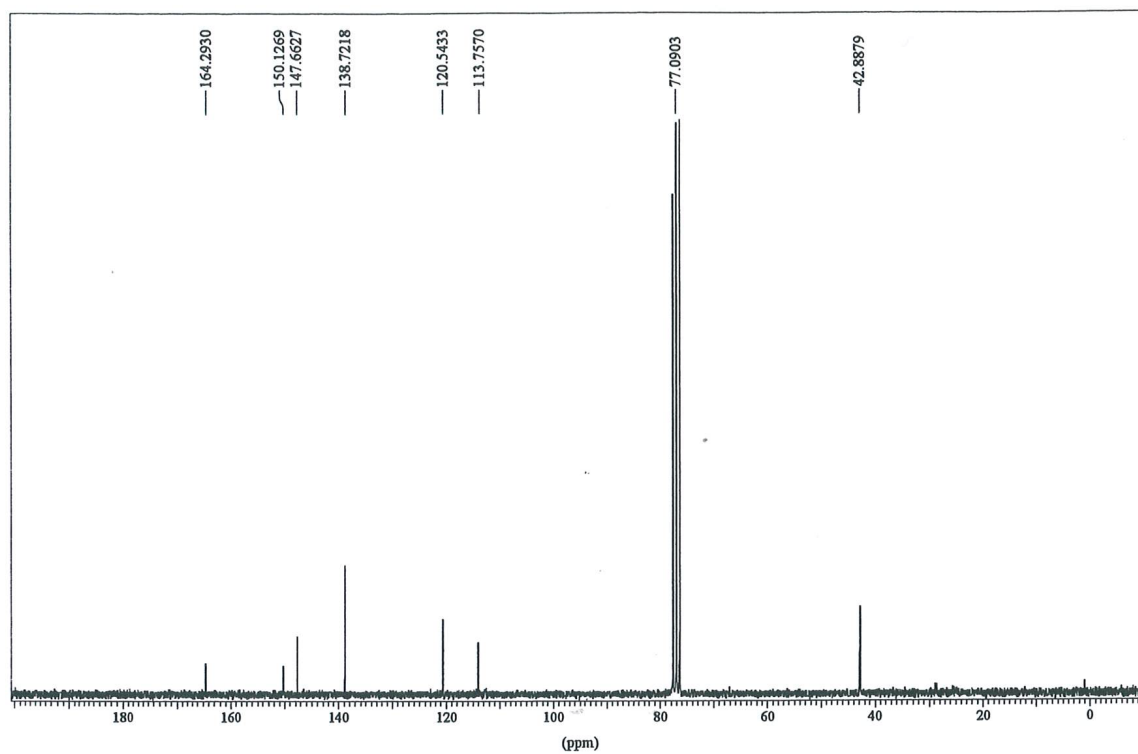


**Figure S7.**  $^{13}\text{C}$  NMR spectrum of methyl *N*-methyl-*N*-(2-pyridyl)aminocarbonylacetate **3a** ( $\text{CDCl}_3$ ).

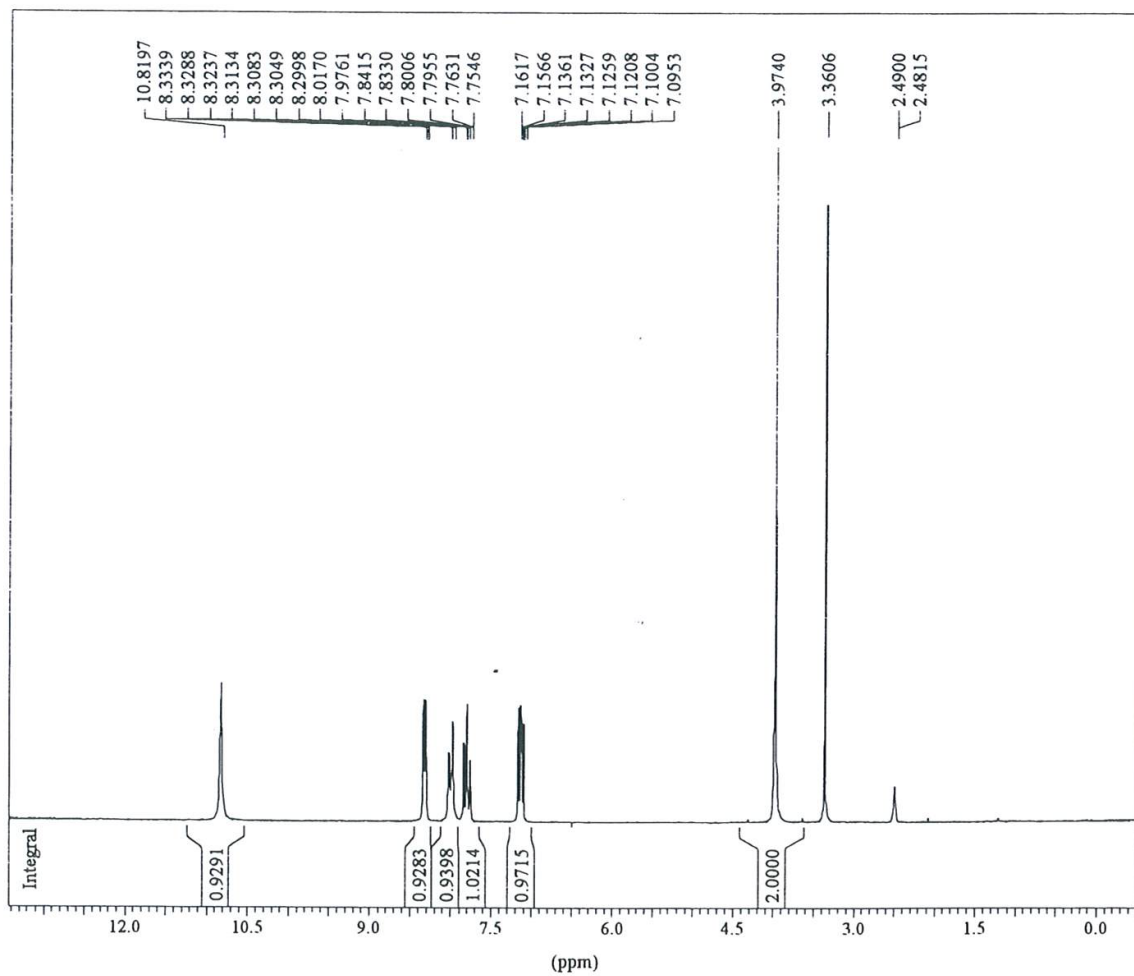




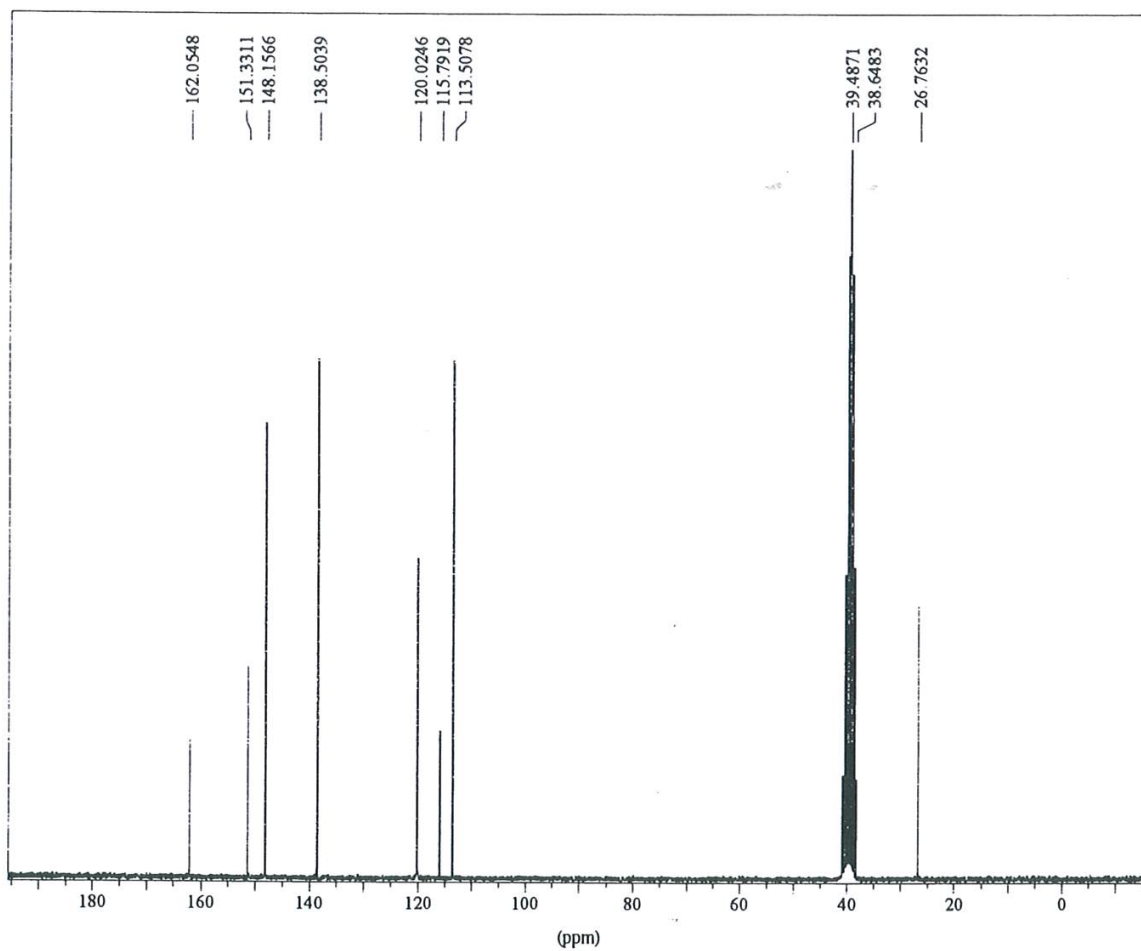
**Figure S8.**  $^1\text{H}$  NMR spectrum of *N*-(2-pyridyl)chloroacetamide **3c** ( $\text{CDCl}_3$ ). The peak at 7.23 ppm is due to  $\text{CHCl}_3$ .



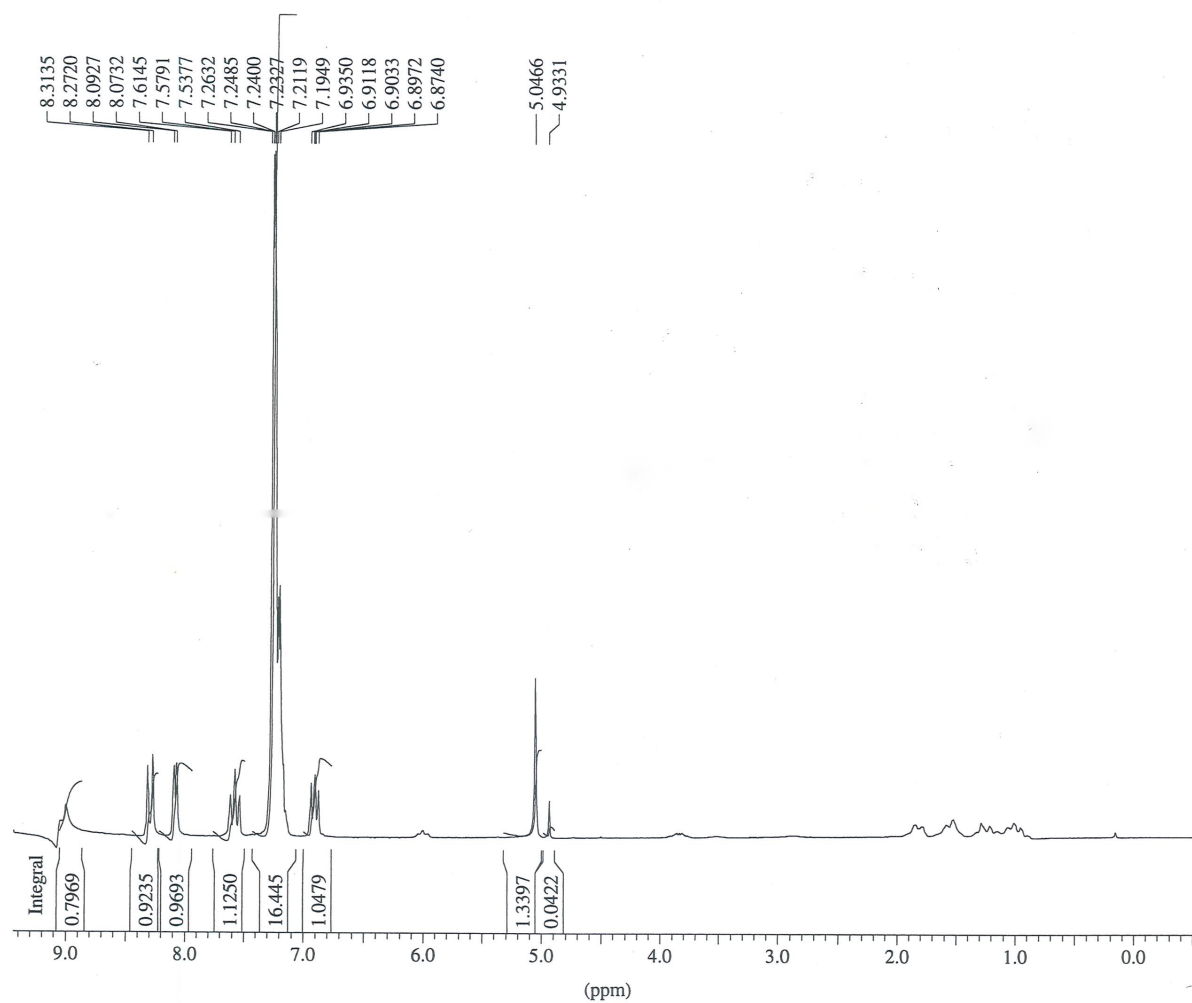
**Figure S9.**  $^{13}\text{C}$  NMR spectrum of *N*-(2-pyridyl)chloroacetamide **3c** ( $\text{CDCl}_3$ ).



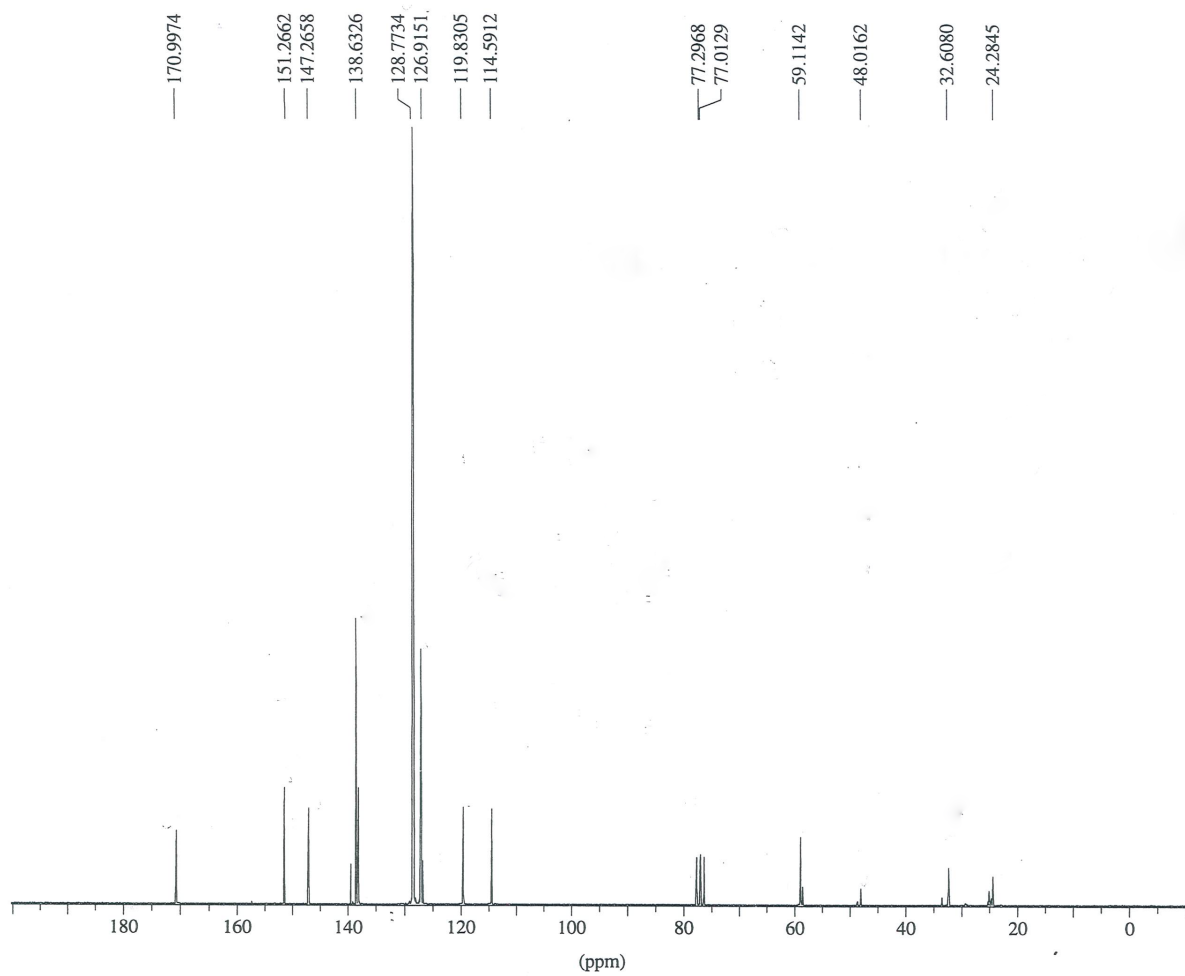
**Figure S10.**  $^1\text{H}$  NMR spectrum of *N*-(2-pyridyl)cyanoacetamide **3d** ( $\text{CDCl}_3$ )



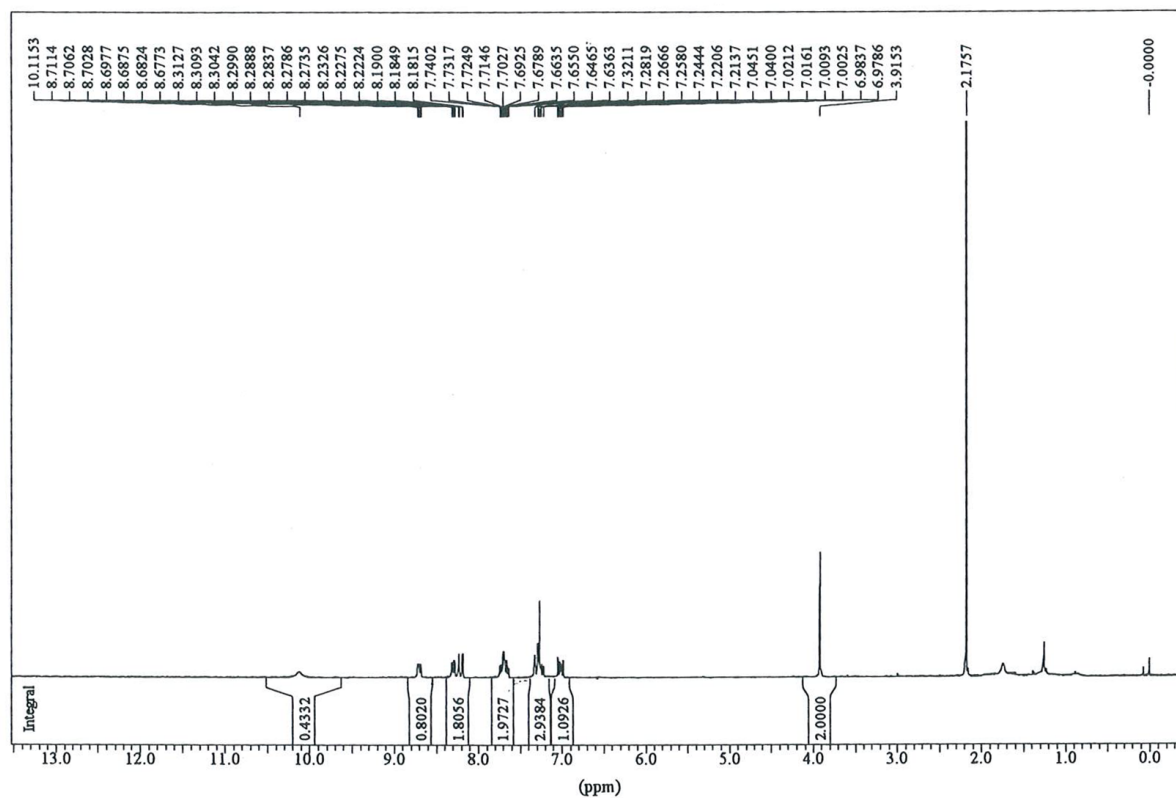
**Figure S11.**  $^{13}\text{C}$  NMR spectrum of *N*-(2-pyridyl)cyanoacetamide **3d** ( $\text{CDCl}_3$ ).



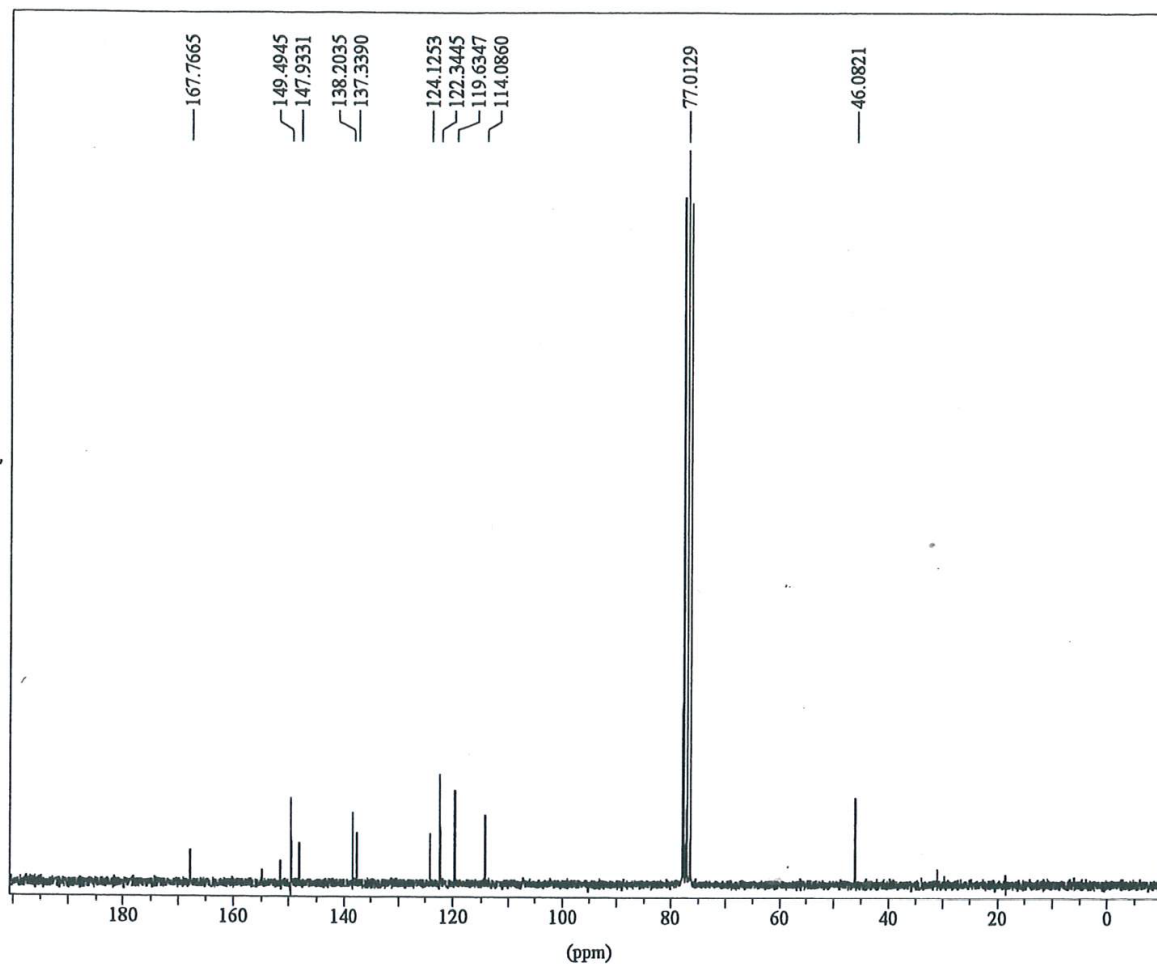
**Figure S12.**  $^1\text{H}$  NMR spectrum of *N*-(2-pyridyl)diphenylmethacetamide **3e** ( $\text{CDCl}_3$ ). The peak at 7.19–7.26 ppm corresponds to 10 aromatic protons plus  $\text{CHCl}_3$ .



**Figure S13.**  $^{13}\text{C}$  NMR spectrum of *N*-(2-pyridyl)diphenylmethacetamide **3e** ( $\text{CDCl}_3$ ). Peaks at 24.29, 32.61 and 77 correspond to ethyl acetate, acetone and  $\text{CHCl}_3$ , respectively.



**Figure S14.**  $^1\text{H}$  NMR spectrum of *N*-(2-pyridyl)-2-pyridylacetamide **3f** ( $\text{CDCl}_3$ ). The peak at 2.18 ppm corresponds to acetone.



**Figure S15.**  $^{13}\text{C}$  NMR spectrum of *N*-(2-pyridyl)-2-pyridylacetamide **3f** ( $\text{CDCl}_3$ ). The small peak at 30.9 ppm corresponds to acetone.