

## Supporting Information

### **Metal-Ligand Cooperative Activation of Nitriles by a Ruthenium Complex with a De-Aromatized PNN Pincer Ligand**

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#### **Contents**

NMR spectra of 1 + cinnamitrile.....	2
NMR spectra of 1 + 4-pentenenitrile .....	4
NMR spectra of 1 + acetonitrile.....	9
NMR spectra of 1 + benzonitrile .....	14
NMR spectra of 1 + benzyl cyanide .....	17
Analysis of equilibria in 1 + 4-pentenenitrile .....	22
Dependence on 4-pentenenitrile concentration .....	22
Temperature dependence (Van 't Hoff analysis).....	23
DFT calculations.....	24

# NMR spectra of **1** + cinnamitrile

**1** + cinnamitrile, 1:1

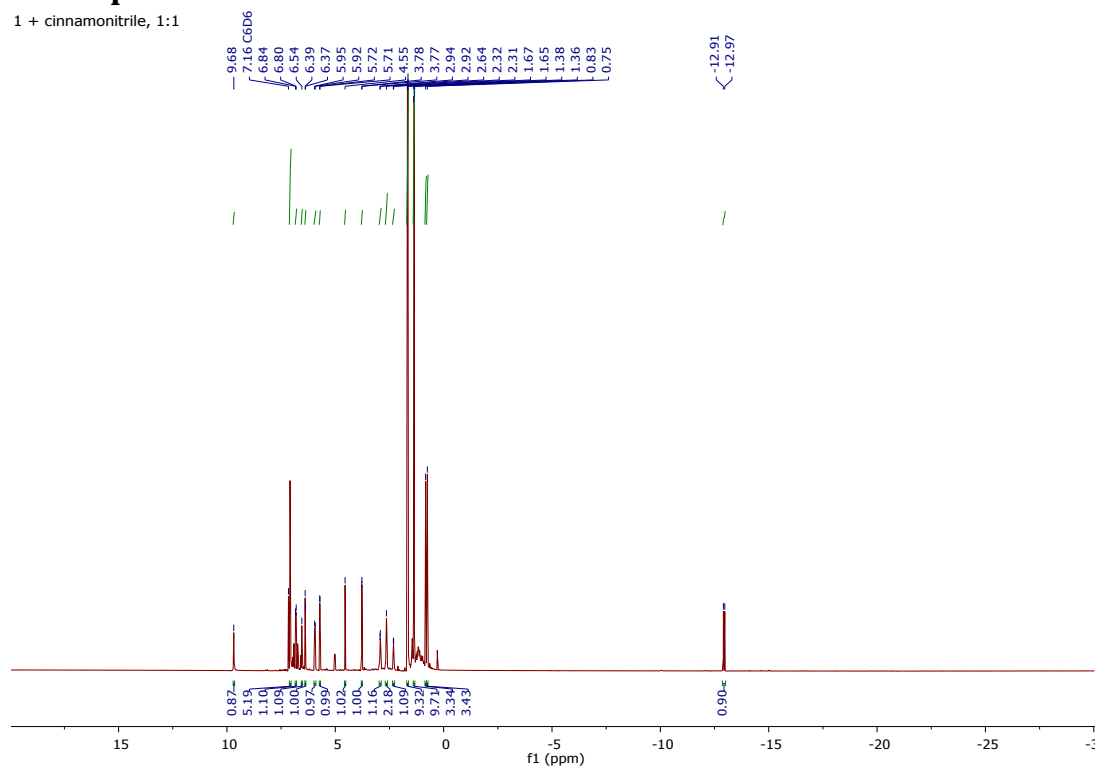


Figure S1a. <sup>1</sup>H NMR spectrum of **1** + cinnamitrile (**4a**; full range)

**1** + cinnamitrile, 1:1

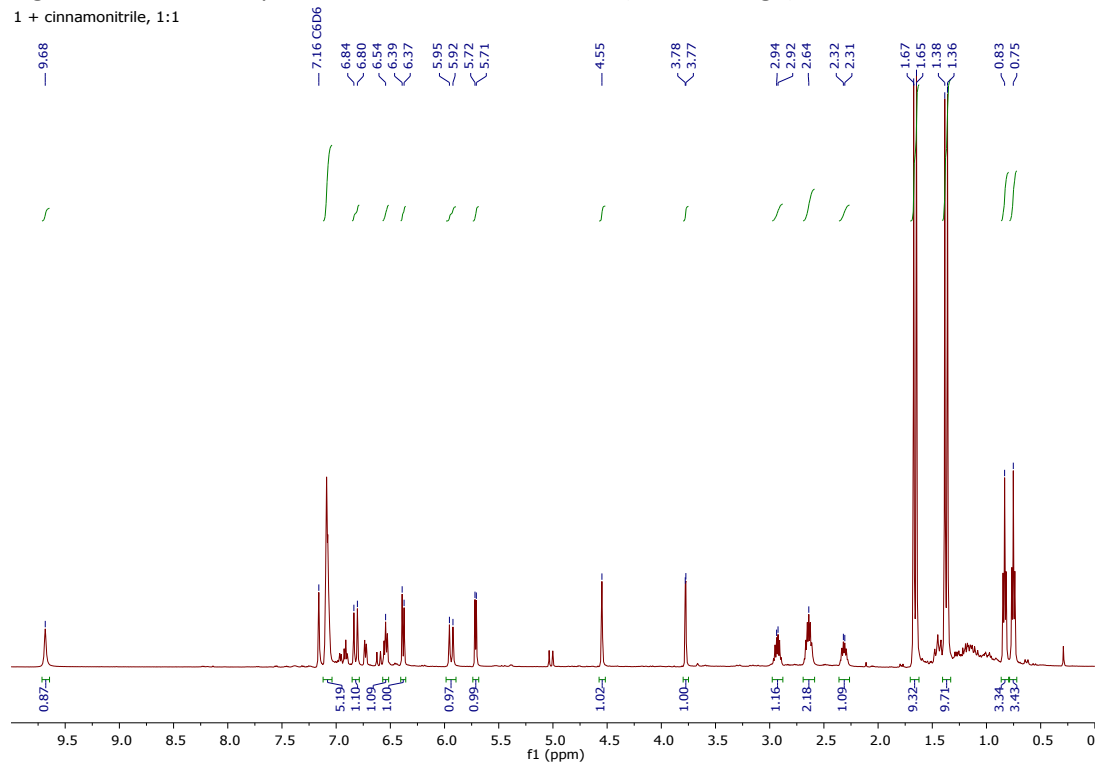


Figure S1b. <sup>1</sup>H NMR spectrum of **1** + cinnamitrile (**4a**; between 0 and 10 ppm)

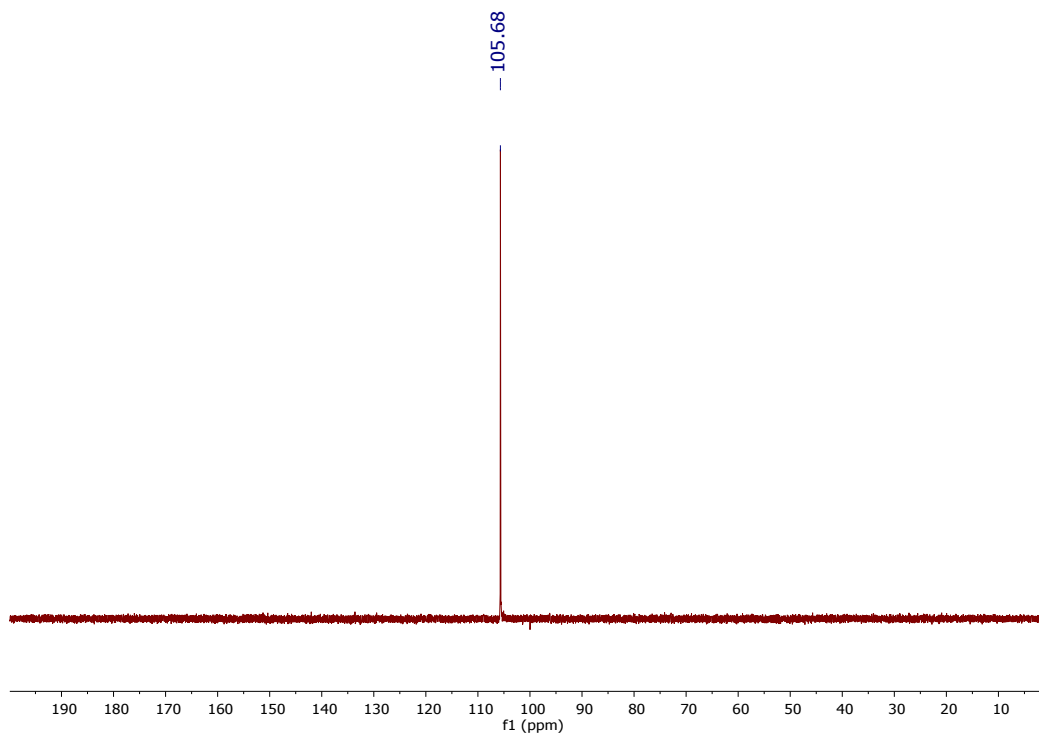


Figure S1c.  $^{31}\text{P}$  NMR spectrum of **1** + cinnamionitrile

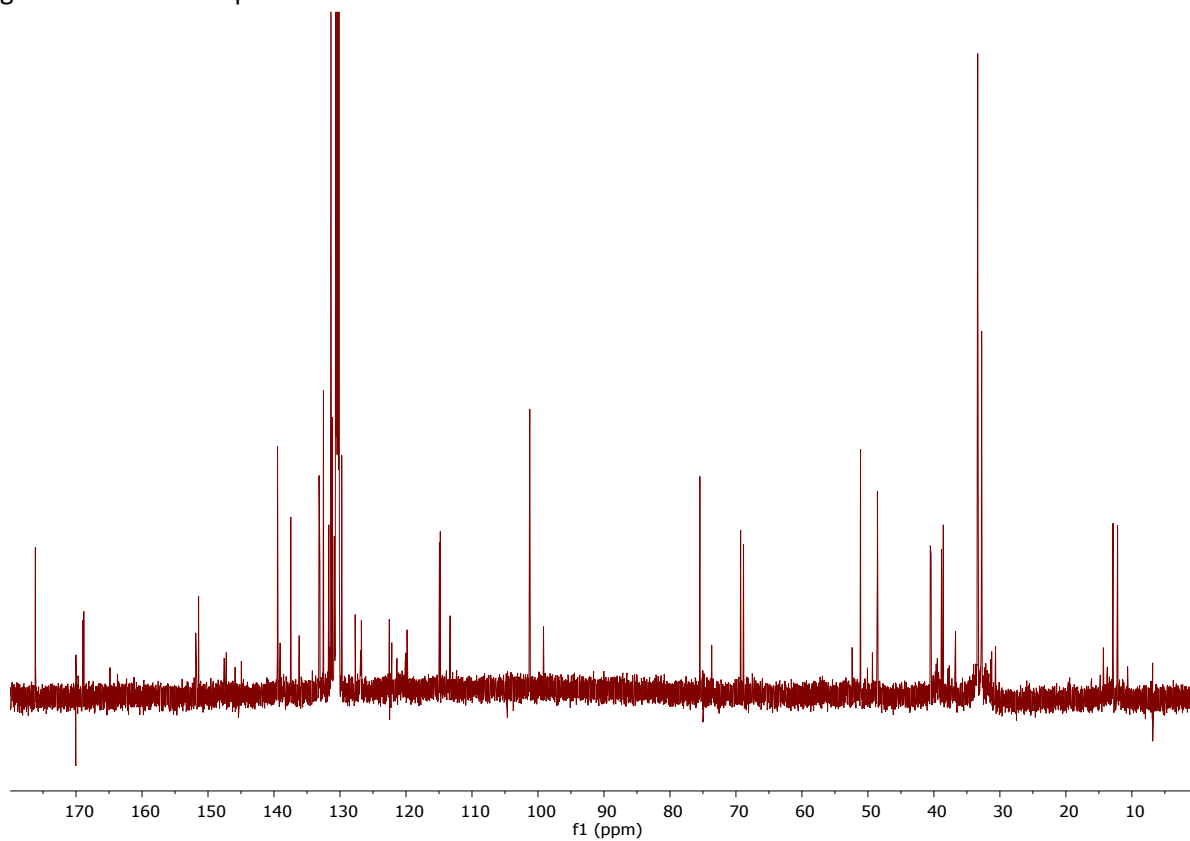


Figure S1d.  $^{13}\text{C}$  NMR spectrum of **1** + cinnamionitrile (**4a**; decomposition starts to occur during acquisition of NMR data; assignments are corroborated by HSQC and HMBC NMR experiments )

# NMR spectra of 1 + 4-pentenitrile

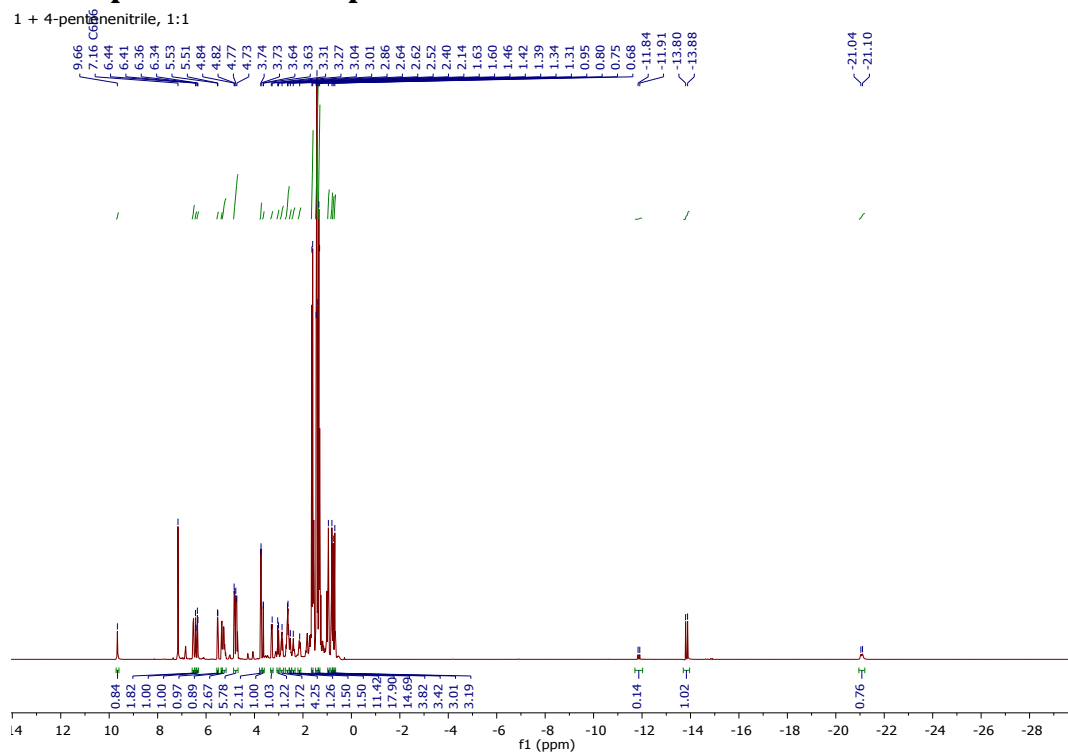


Figure S2a.  $^1\text{H-NMR}$  spectrum of **1** + 4-pentenitrile  $\rightleftharpoons$  **2b**  $\rightleftharpoons$  **3b**  $\rightleftharpoons$  **4b** (full range)

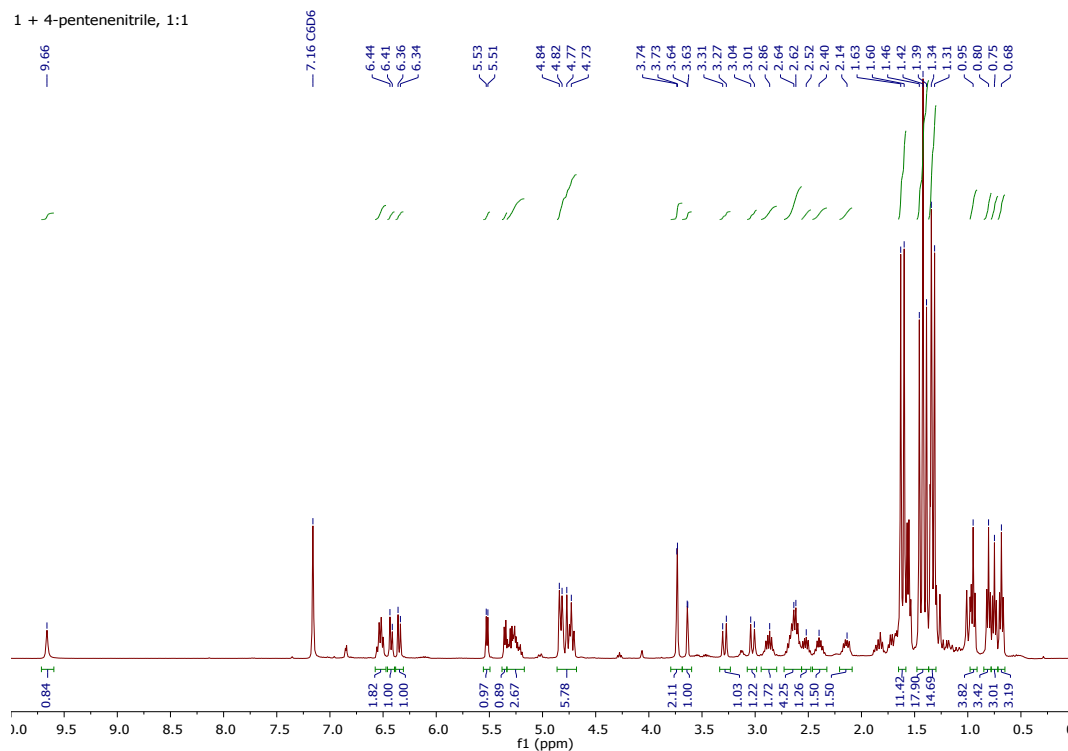


Figure S2b.  $^1\text{H-NMR}$  spectrum of **1** + 4-pentenitrile  $\rightleftharpoons$  **2b**  $\rightleftharpoons$  **3b**  $\rightleftharpoons$  **4b** (between 0 and 10 ppm)

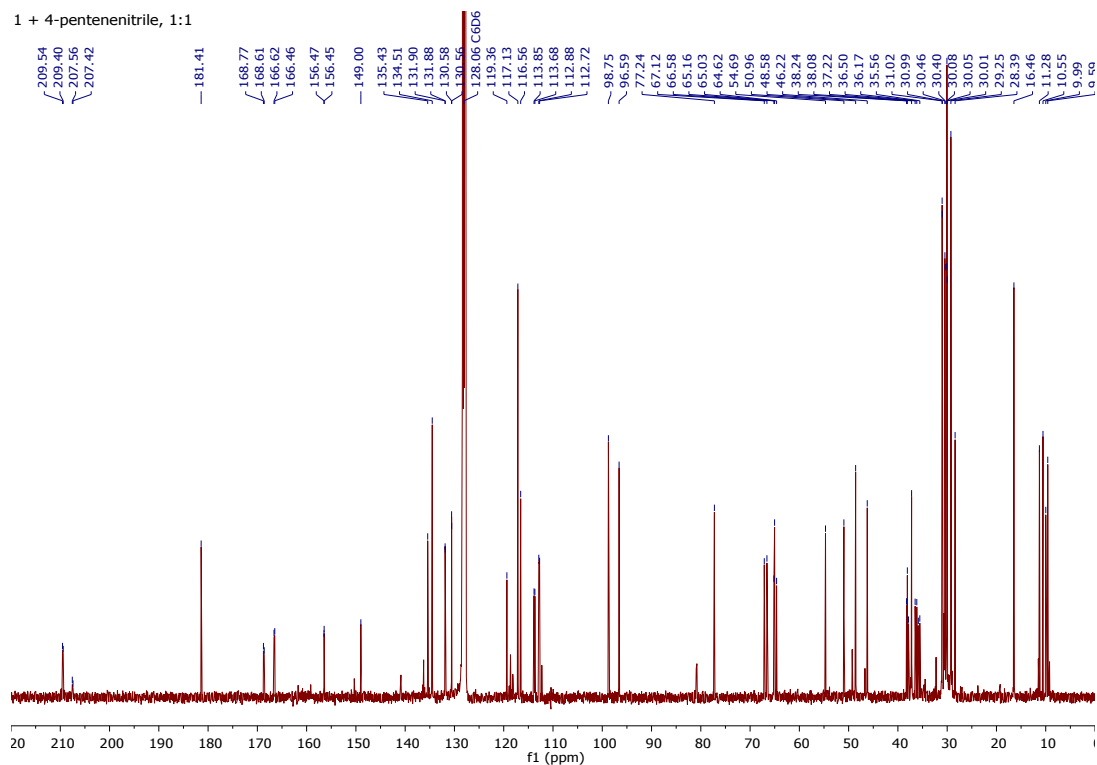


Figure S2c. <sup>13</sup>C-NMR spectrum of **1** + 4-pentenenitrile ⇌ **2b** ⇌ **3b** ⇌ **4b**

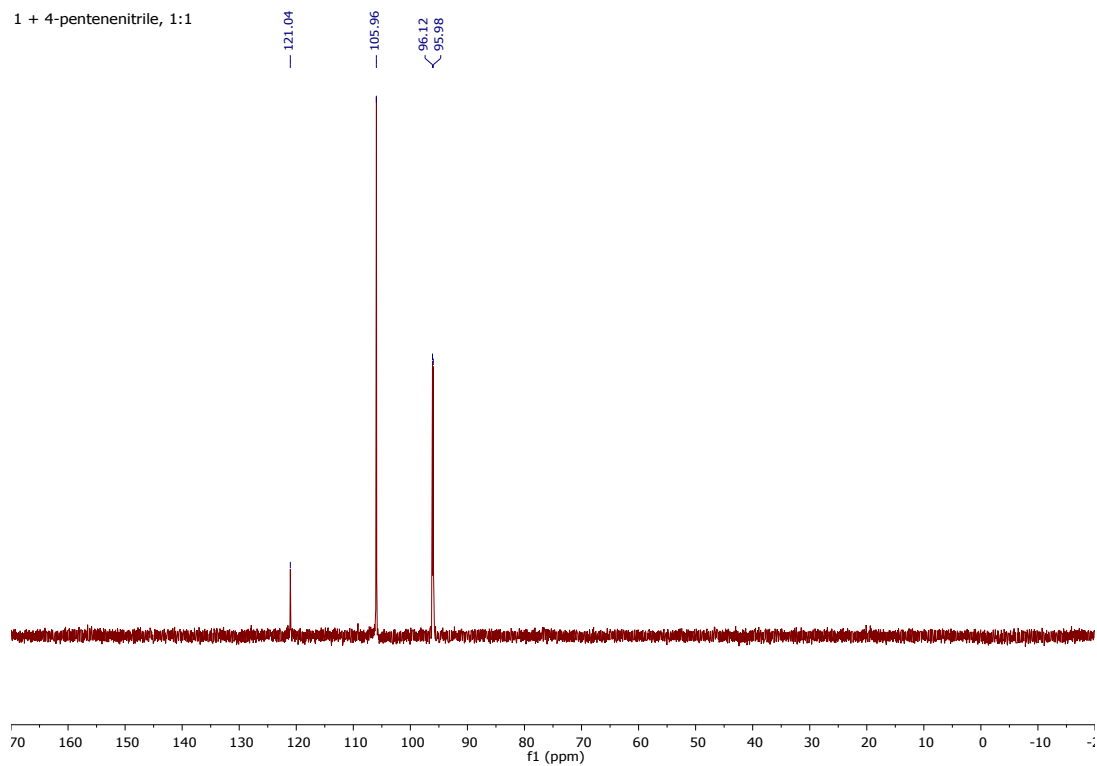


Figure S2d. <sup>31</sup>P-NMR spectrum of **1** + 4-pentenenitrile ⇌ **2b** ⇌ **3b** ⇌ **4b**

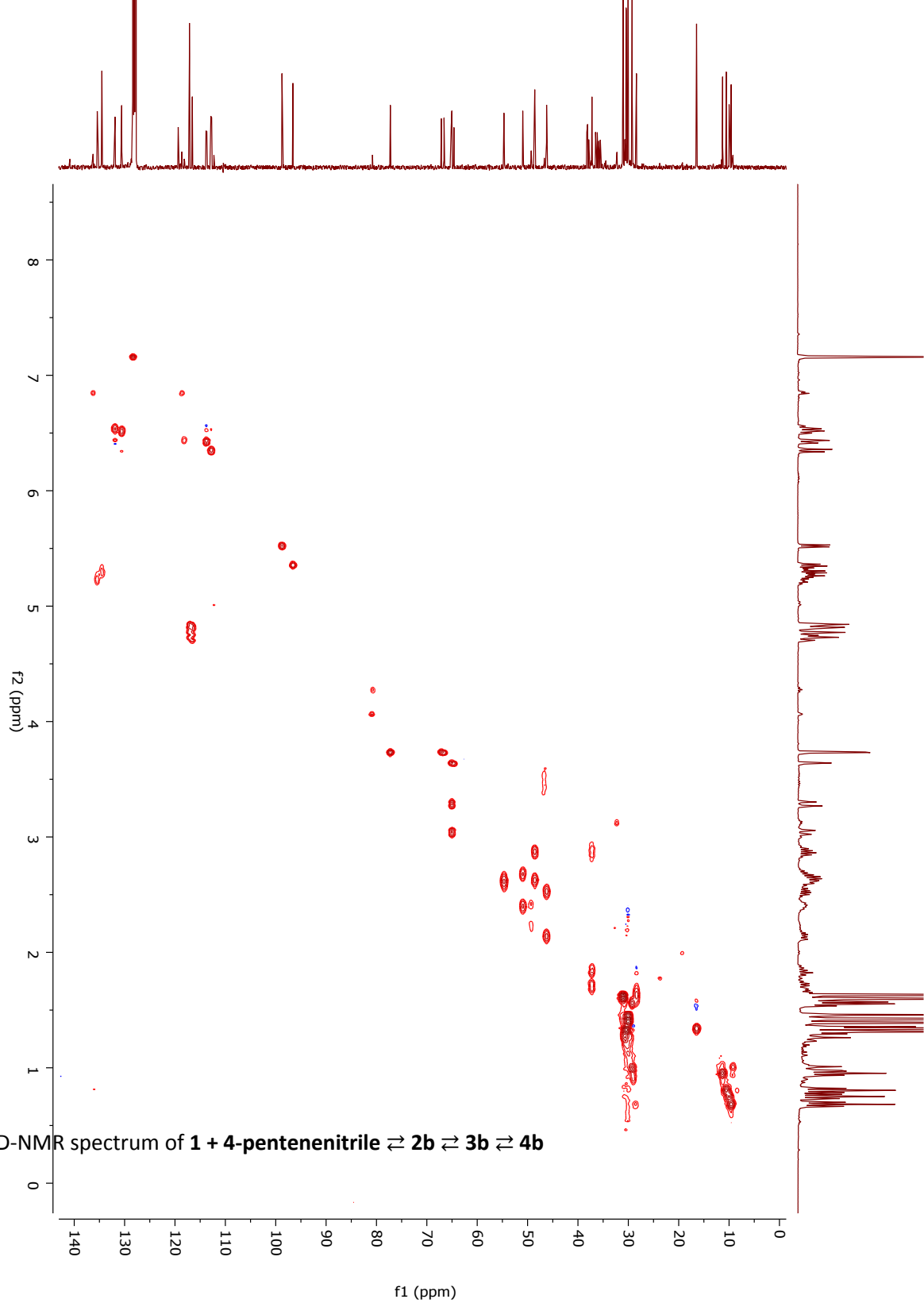


Figure S2e. gHSQCAD-NMR spectrum of **1** + **4-pentenitrile** ⇌ **2b** ⇌ **3b** ⇌ **4b**

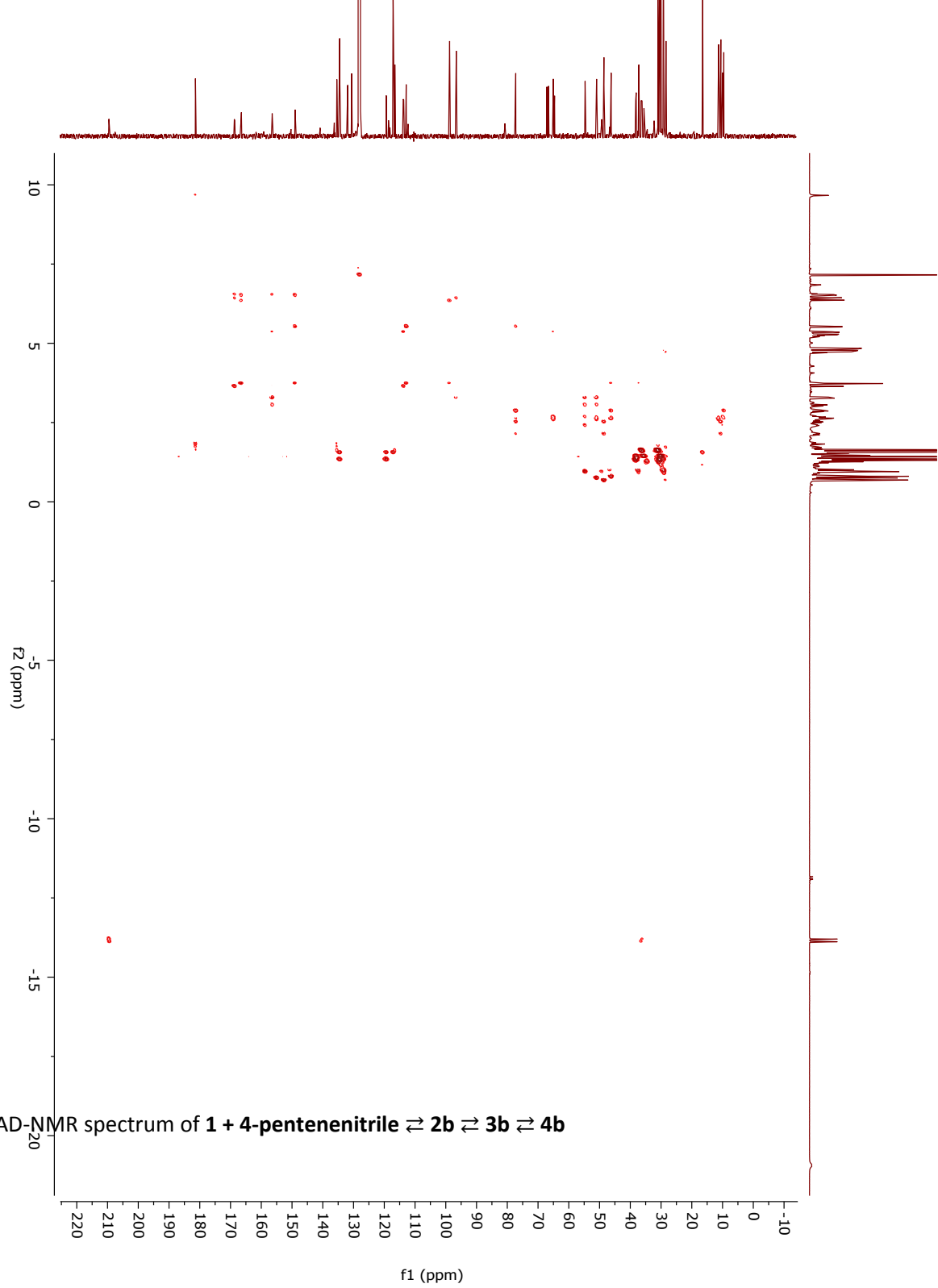


Figure S2f. gHSMBCAD-NMR spectrum of **1** + **4-pentenenitrile**  $\leftrightarrow$  **2b**  $\leftrightarrow$  **3b**  $\leftrightarrow$  **4b**

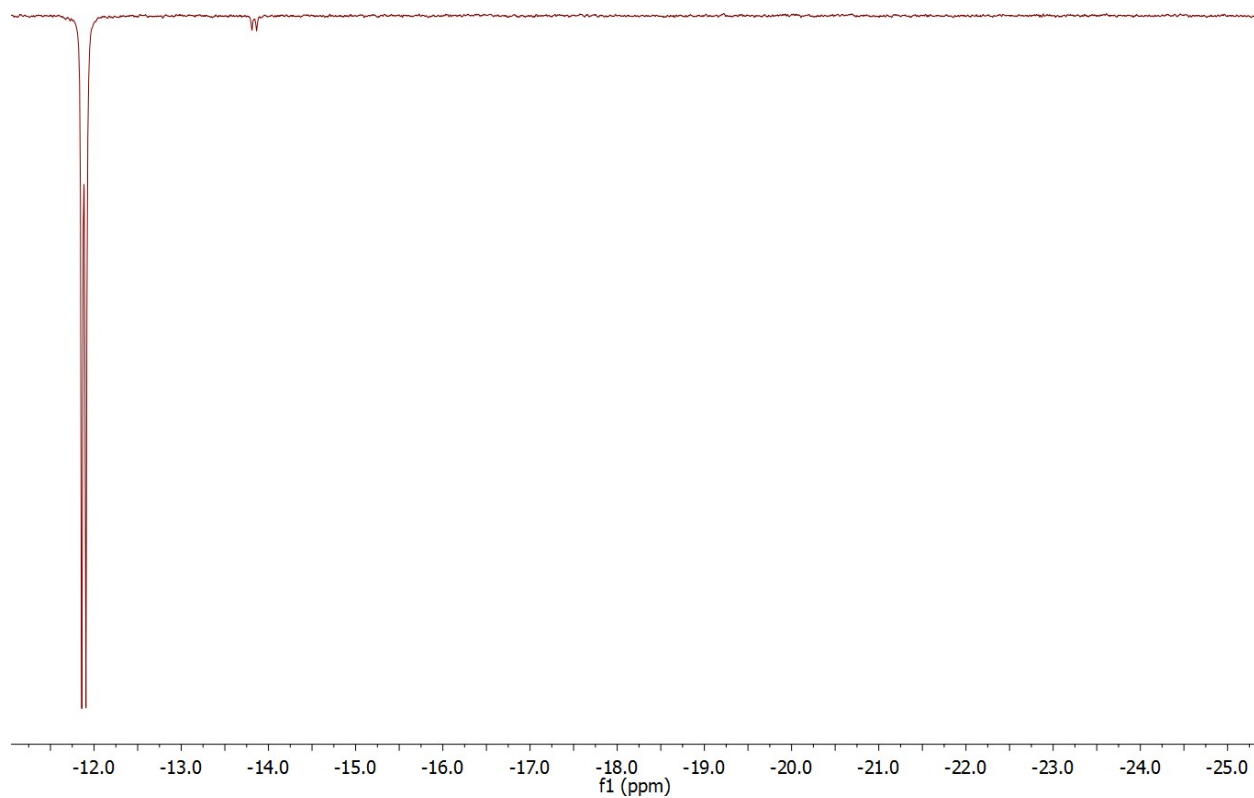


Figure S2g. 1D-NOESY spectrum of **1** + 4-pentenenitrile  $\rightleftharpoons$  **2b**  $\rightleftharpoons$  **3b**  $\rightleftharpoons$  **4b**, irradiated at the Ru-H resonance of compound **3b** (mixing time 1.0 s).



# NMR spectra of 1 + acetonitrile

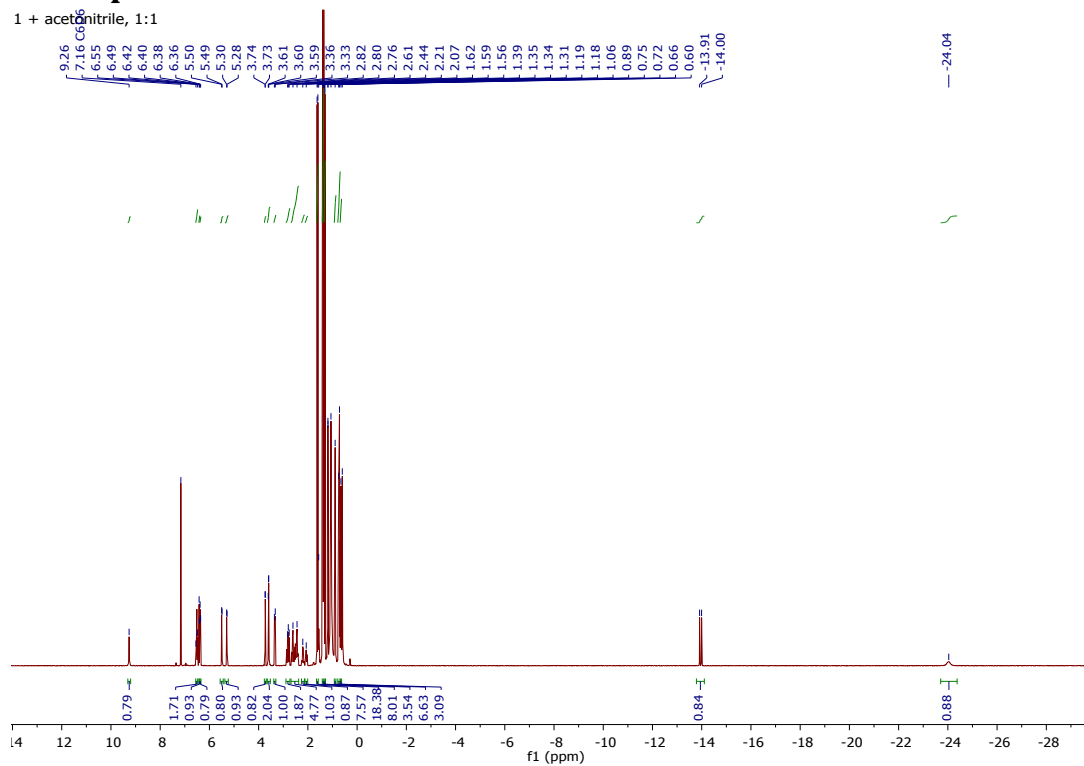


Figure S3a.  $^1\text{H-NMR}$  spectrum of **1** + acetonitrile  $\rightleftharpoons$  **2c**  $\rightleftharpoons$  **4c** (full range)

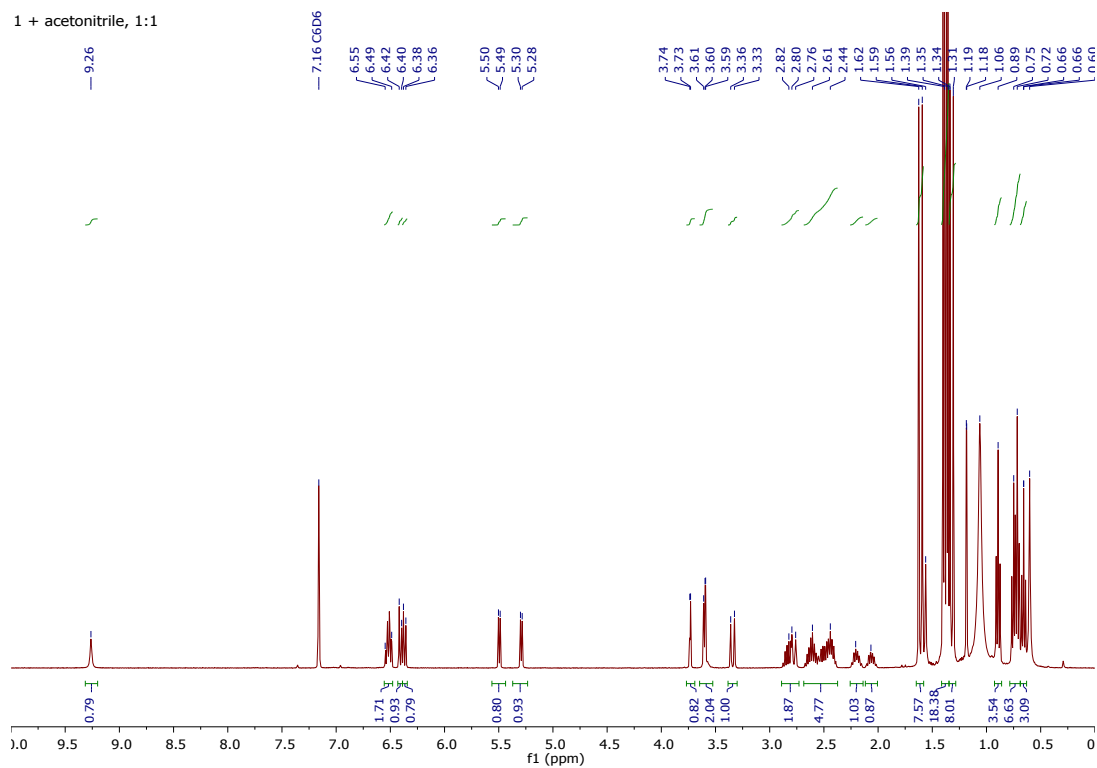


Figure S3b.  $^1\text{H-NMR}$  spectrum of **1** + acetonitrile  $\rightleftharpoons$  **2c**  $\rightleftharpoons$  **4c** (between 0 and 10 ppm)

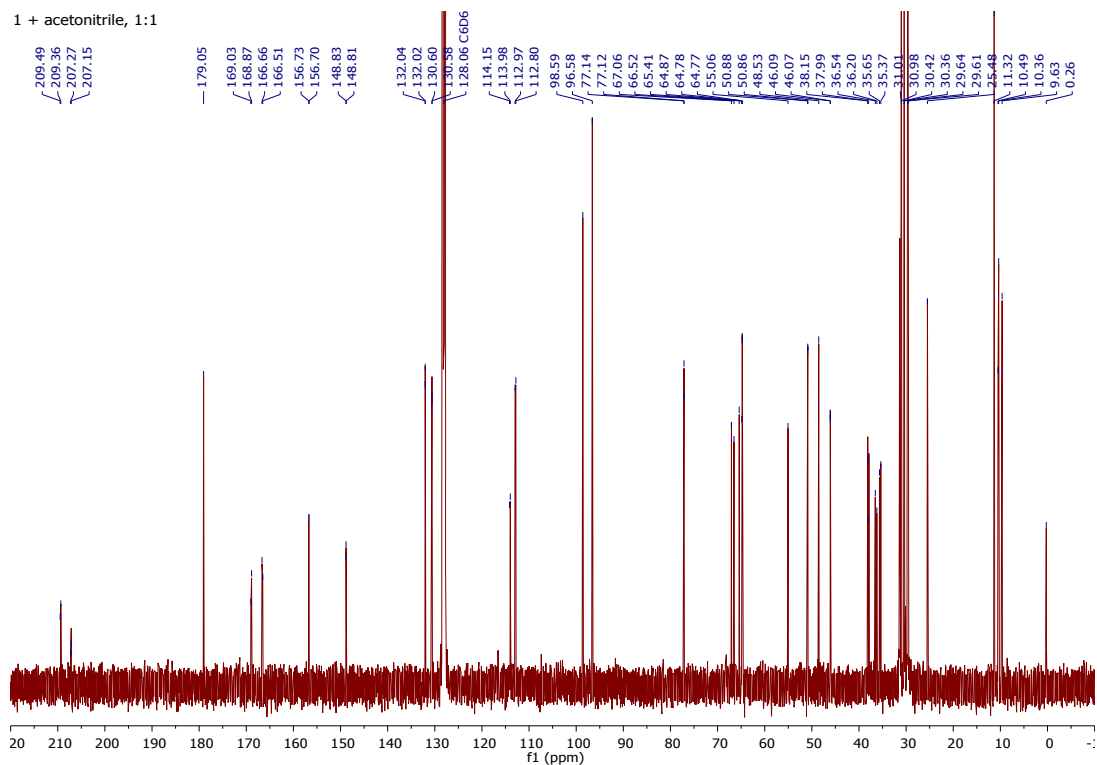


Figure S3c. <sup>13</sup>C-NMR spectrum of **1** + acetonitrile ⇌ **2c** ⇌ **4c**

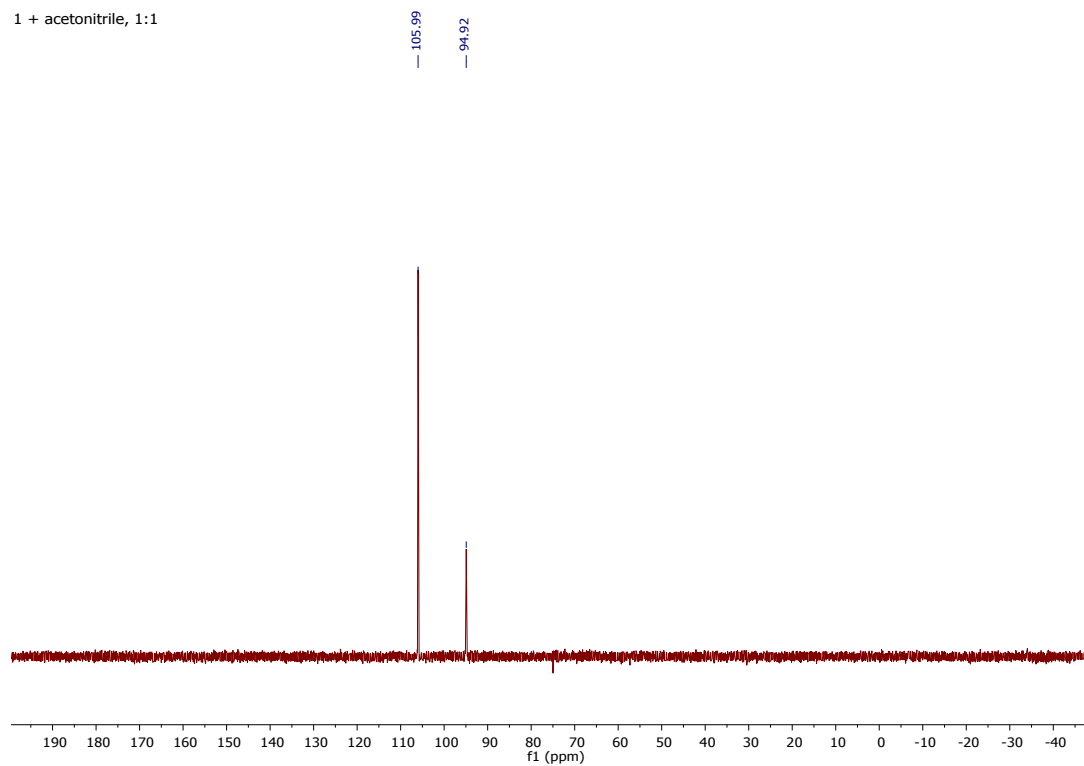


Figure S3d. <sup>31</sup>P-NMR spectrum of **1** + acetonitrile ⇌ **2c** ⇌ **4c**

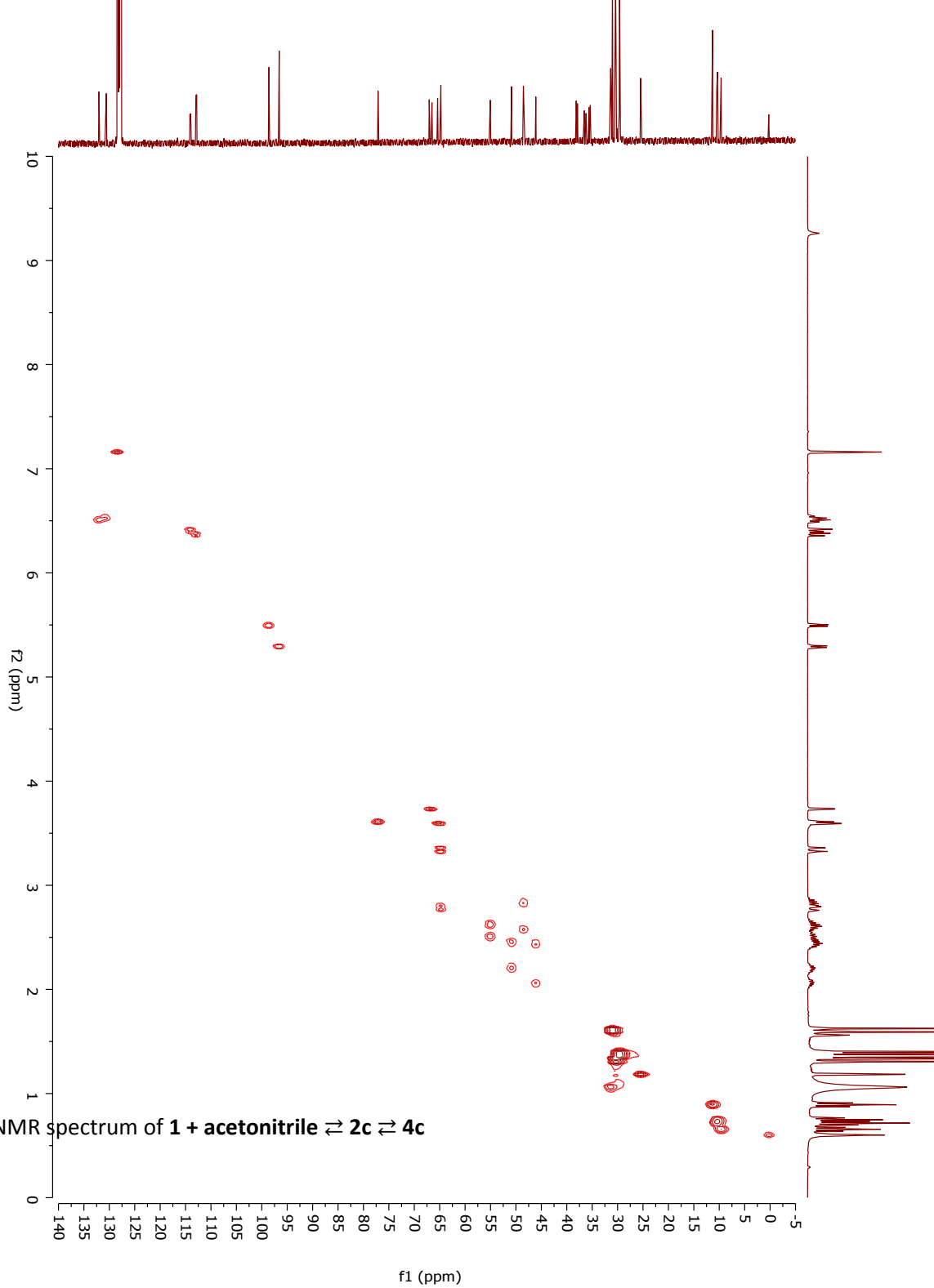


Figure S3e. gHSQC-NMR spectrum of **1** + acetonitrile  $\rightleftharpoons$  **2c**  $\rightleftharpoons$  **4c**

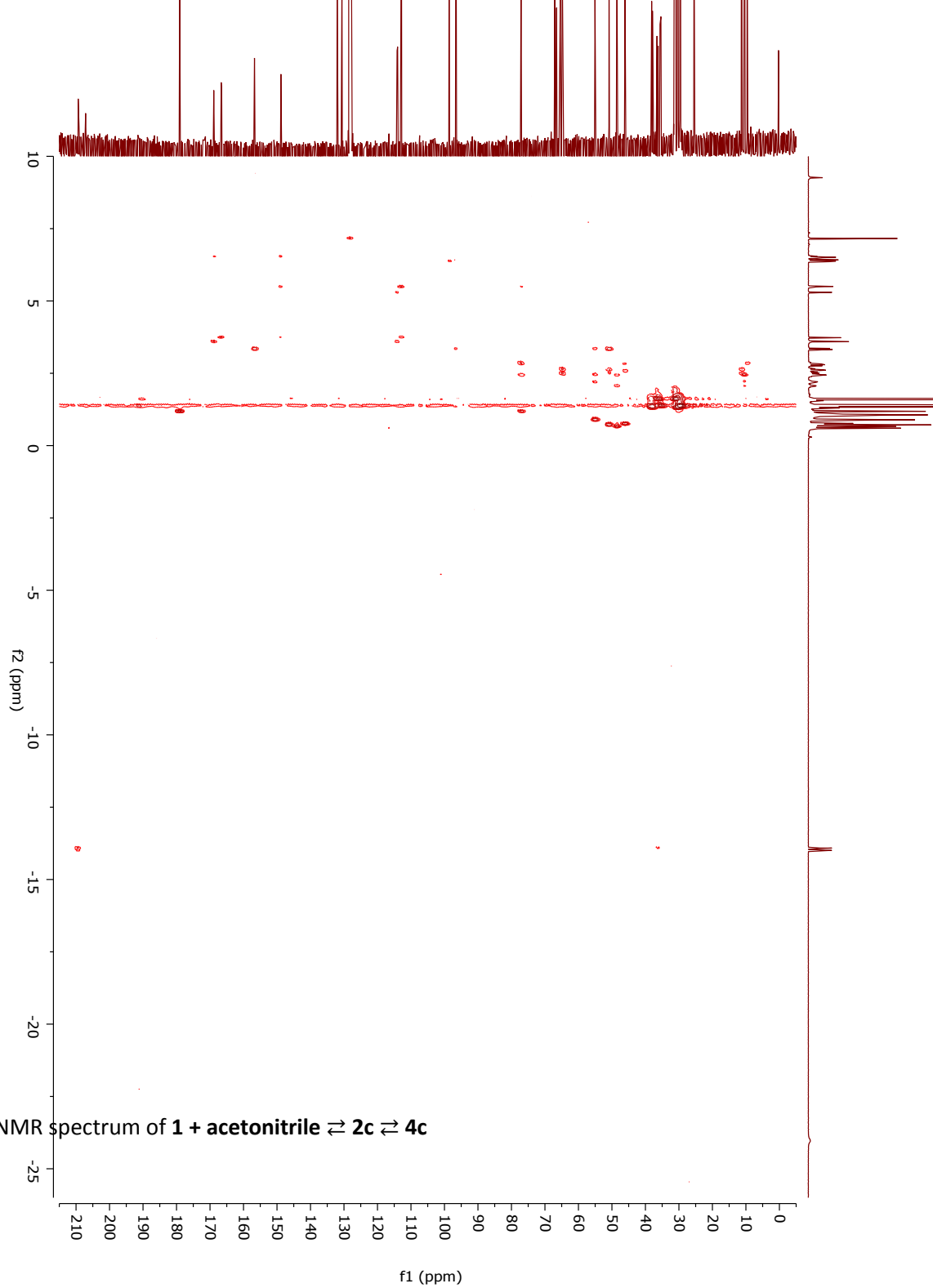


Figure S3f. gHMBC-NMR spectrum of **1** + acetonitrile  $\leftrightarrow$  **2c**  $\leftrightarrow$  **4c**

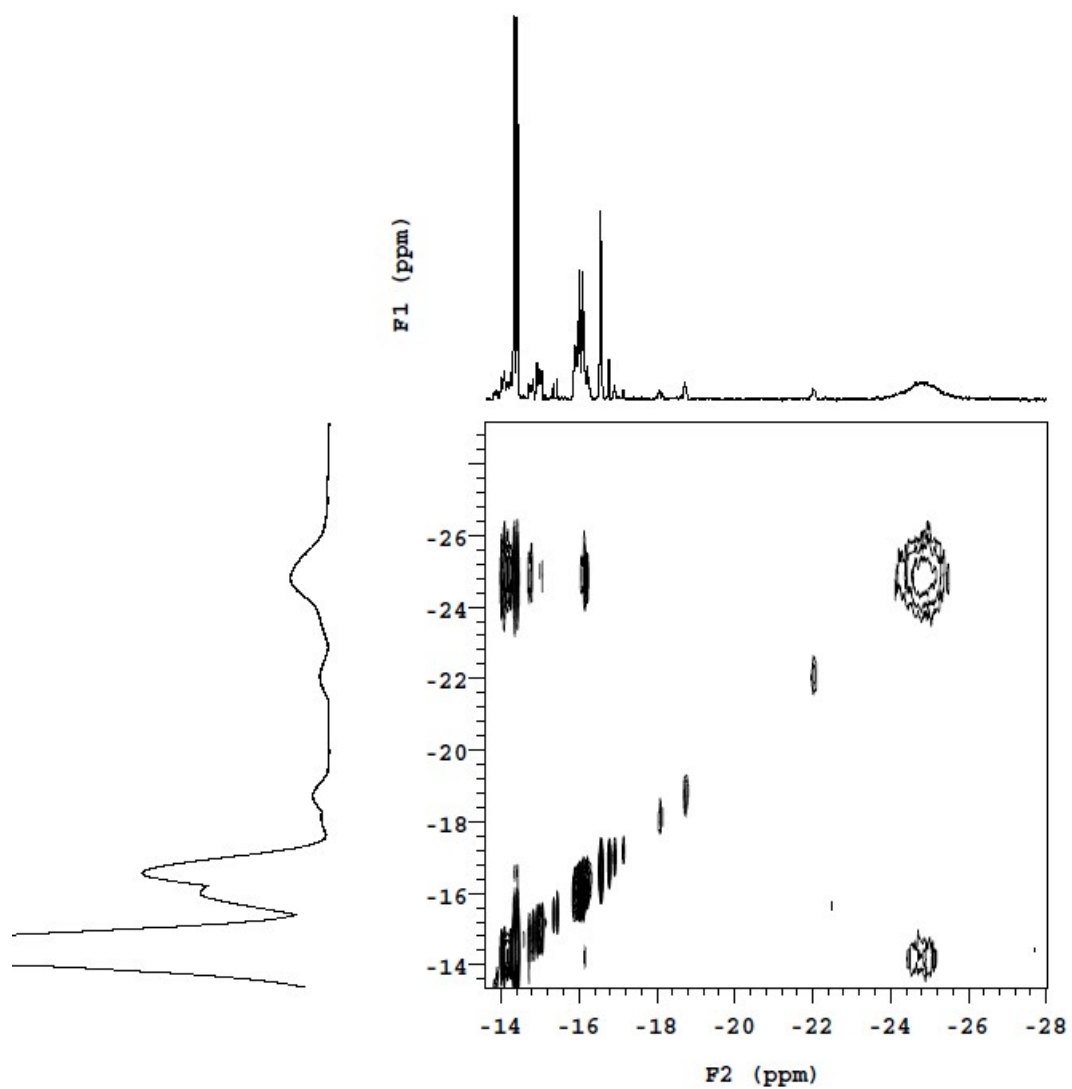


Figure S3g. NOESY spectrum of **1** + acetonitrile  $\rightleftharpoons$  **2c**  $\rightleftharpoons$  **4c** at 50 °C (mixing time 0.8 s), showing chemical exchange between the Ru-H of **2c** and **4c**.

# NMR spectra of 1 + benzonitrile

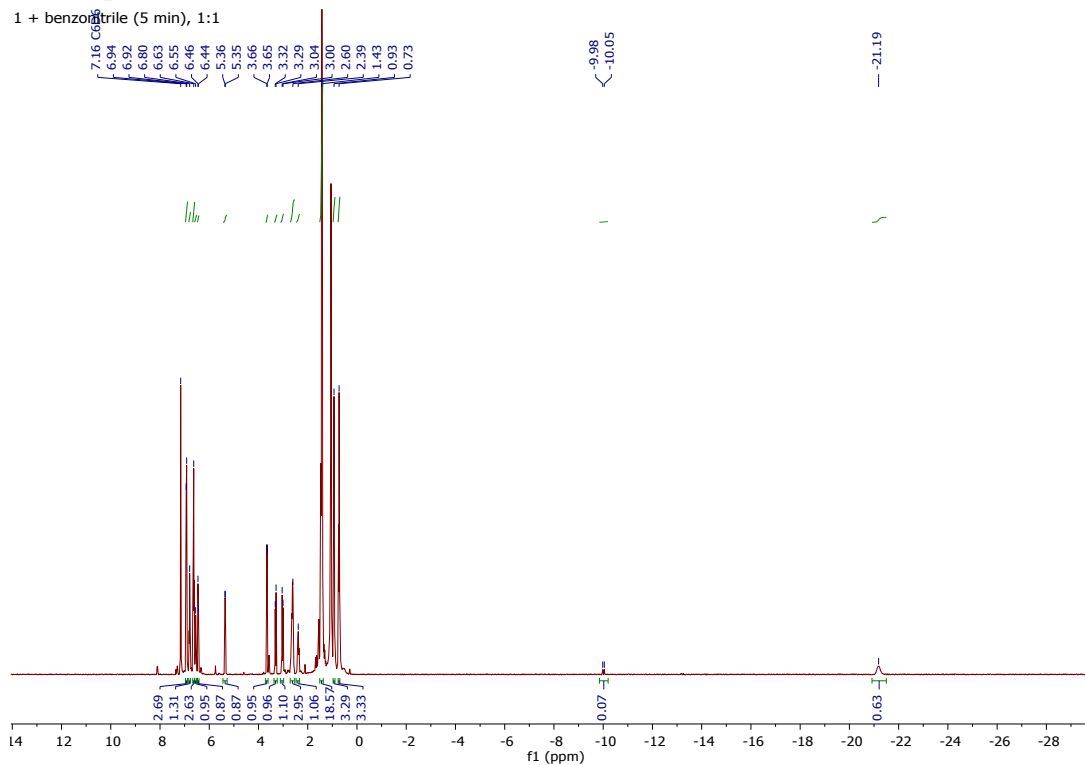


Figure S4a.  $^1\text{H-NMR}$  spectrum of **1** + benzonitrile  $\rightleftharpoons$  **2d**  $\rightleftharpoons$  **3d** (after 5 minutes, full range)

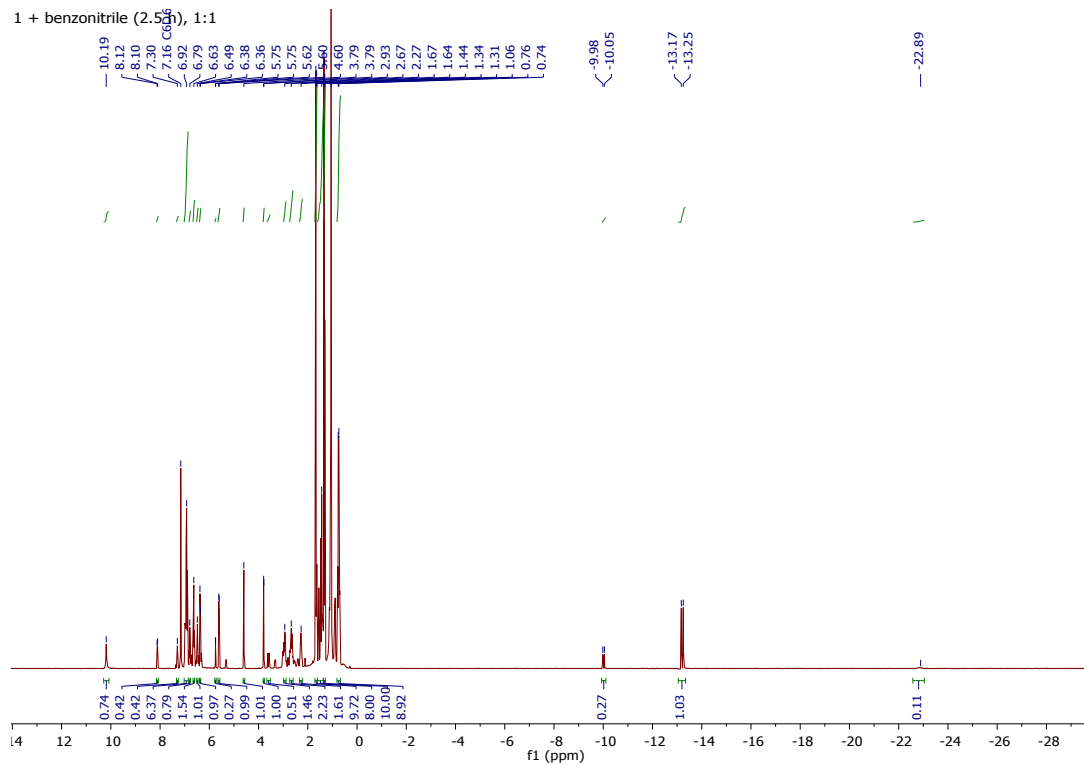


Figure S4b.  $^1\text{H-NMR}$  spectrum of **3d** + **4d** (after 2.5 hours, full range)

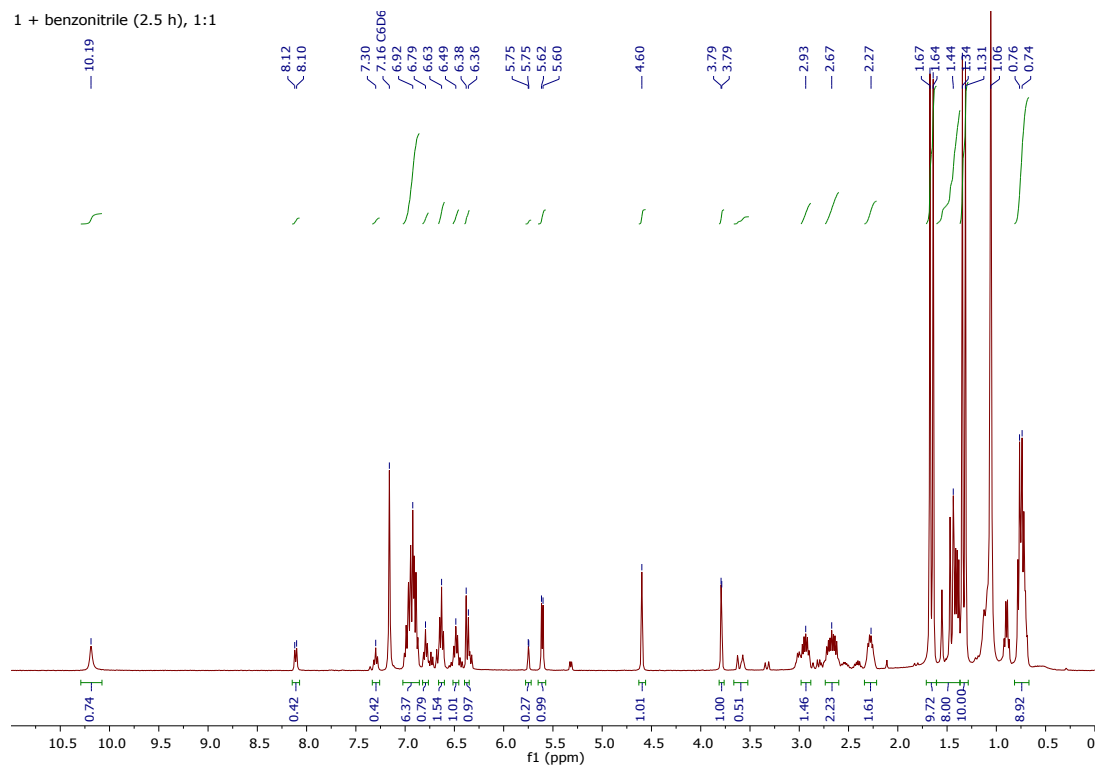


Figure S4c.  $^1\text{H}$ -NMR spectrum of **3d** + **4d** (after 2.5 hours, between 0 and 11 ppm)

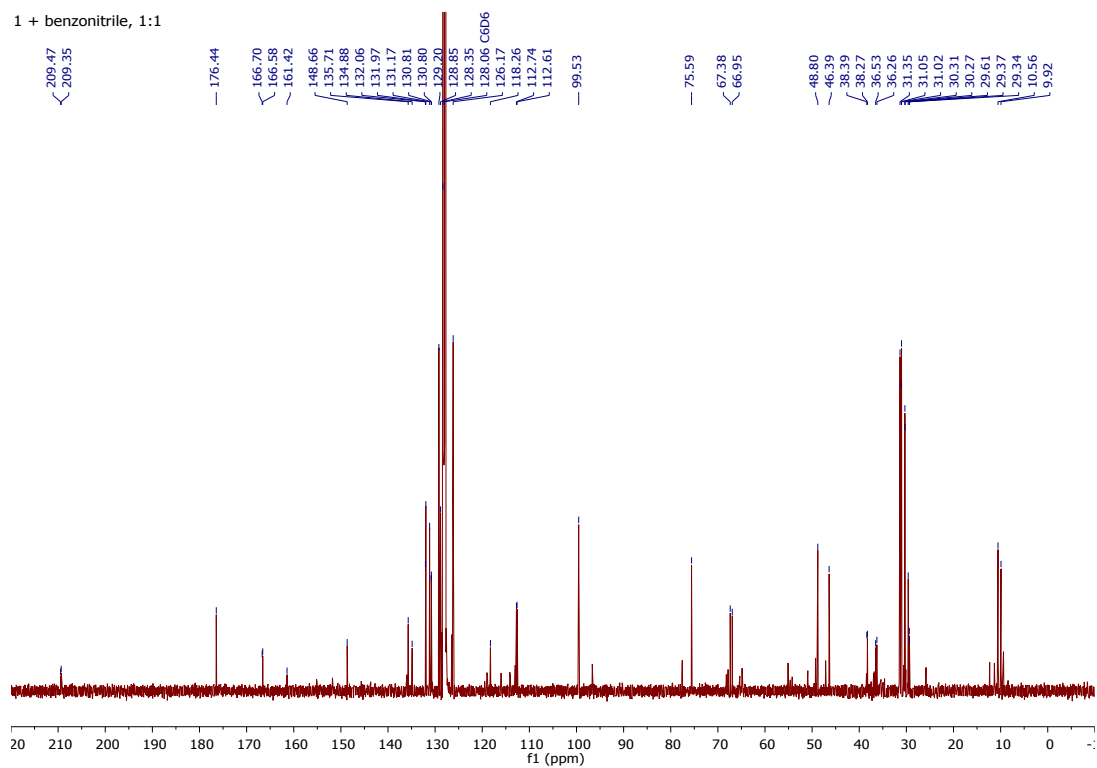


Figure S4d.  $^{13}\text{C}$ -NMR spectrum of **3d** + **4d**

1 + benzonitrile (2.5 h), 1:1

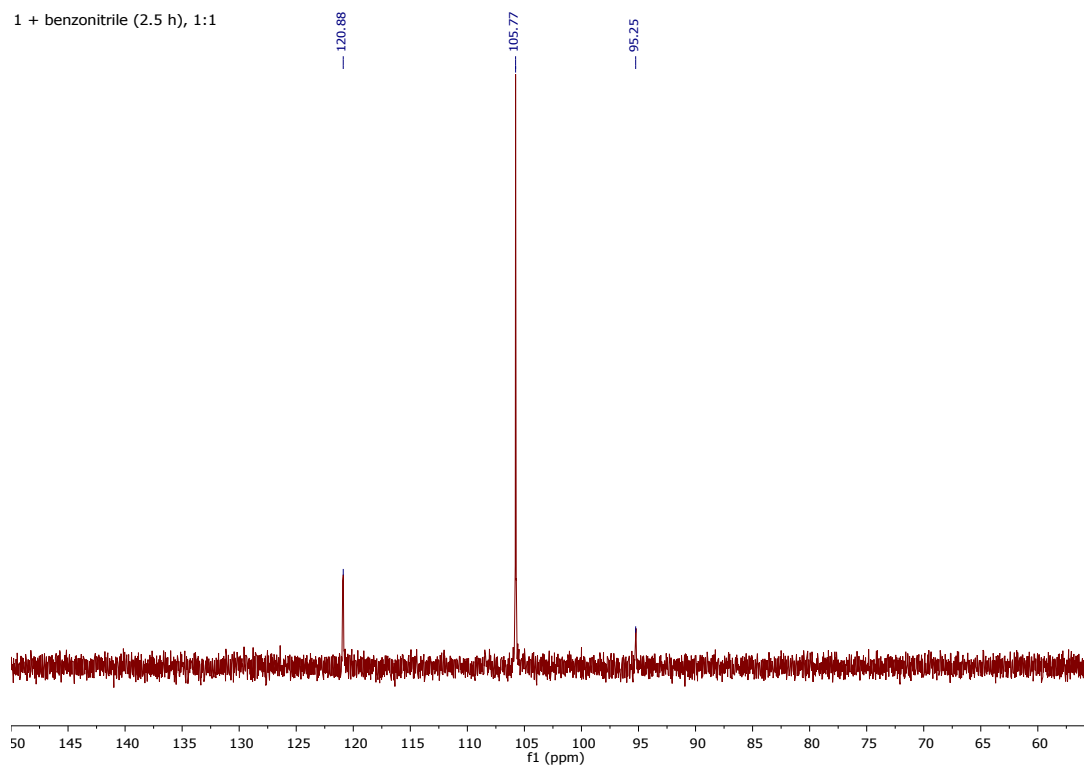


Figure S4e.  $^{31}\text{P}$ -NMR spectrum of **3d + 4d**



# NMR spectra of 1 + benzyl cyanide

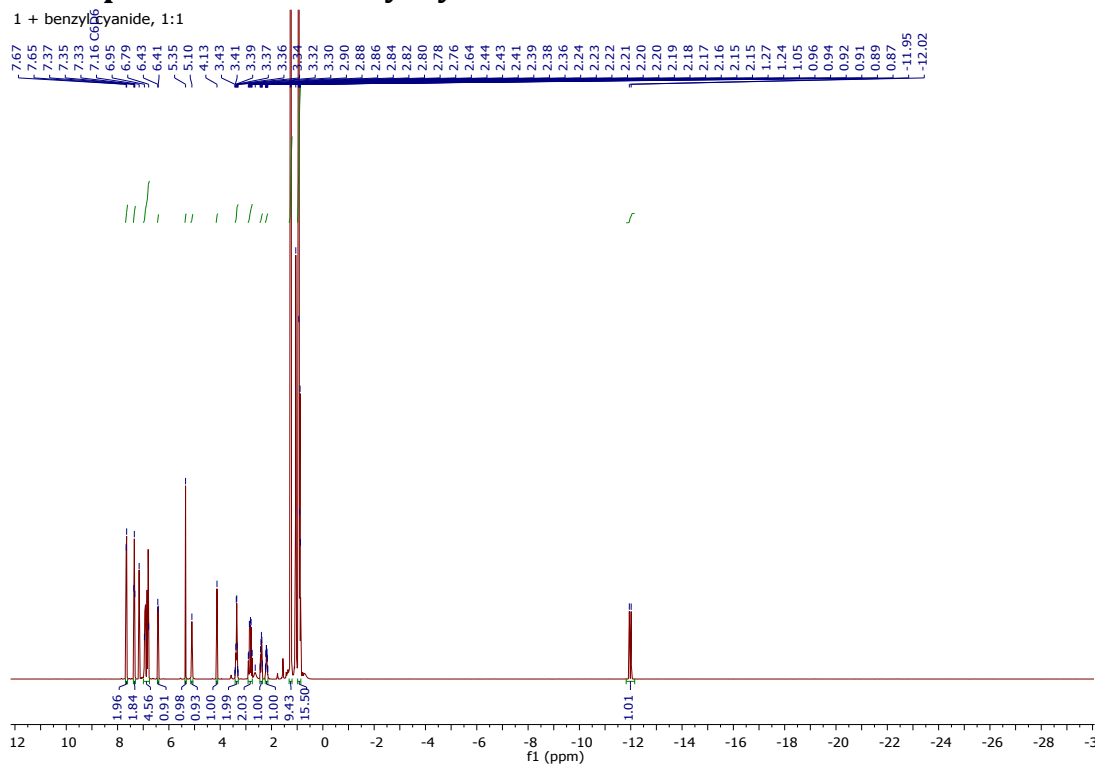


Figure S5a. <sup>1</sup>H-NMR spectrum of 5e (full range)

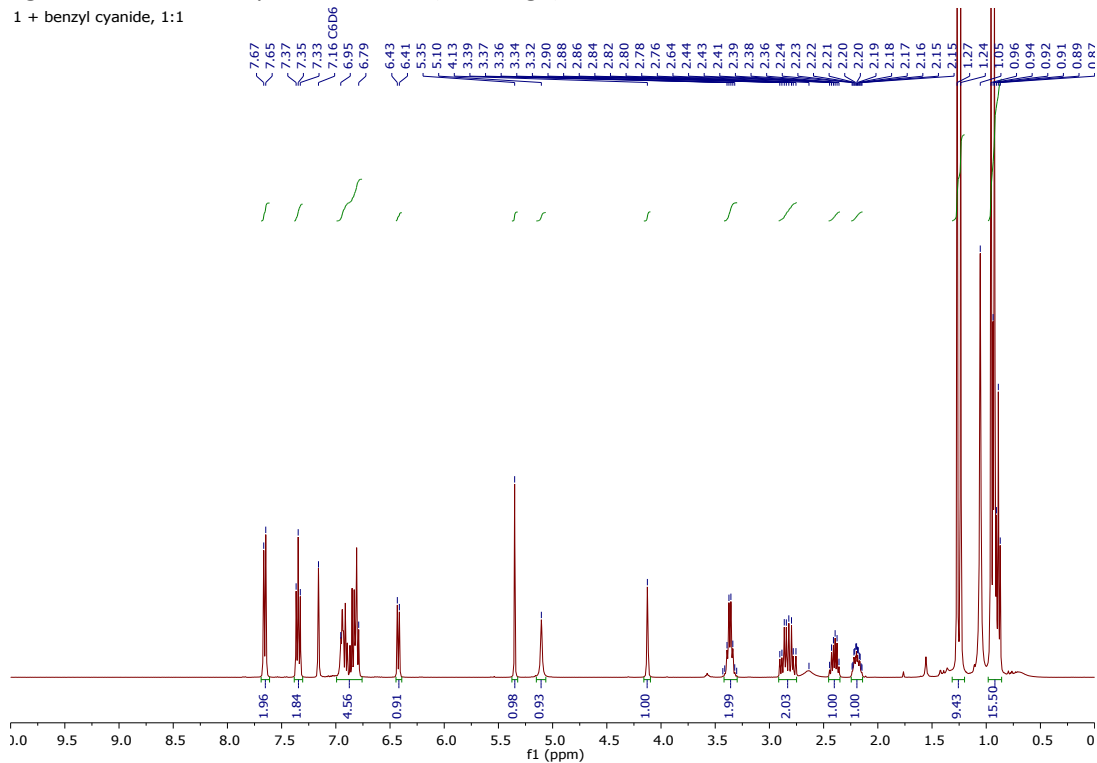


Figure S5b. <sup>1</sup>H-NMR spectrum of 5e (between 0 and 10 ppm)

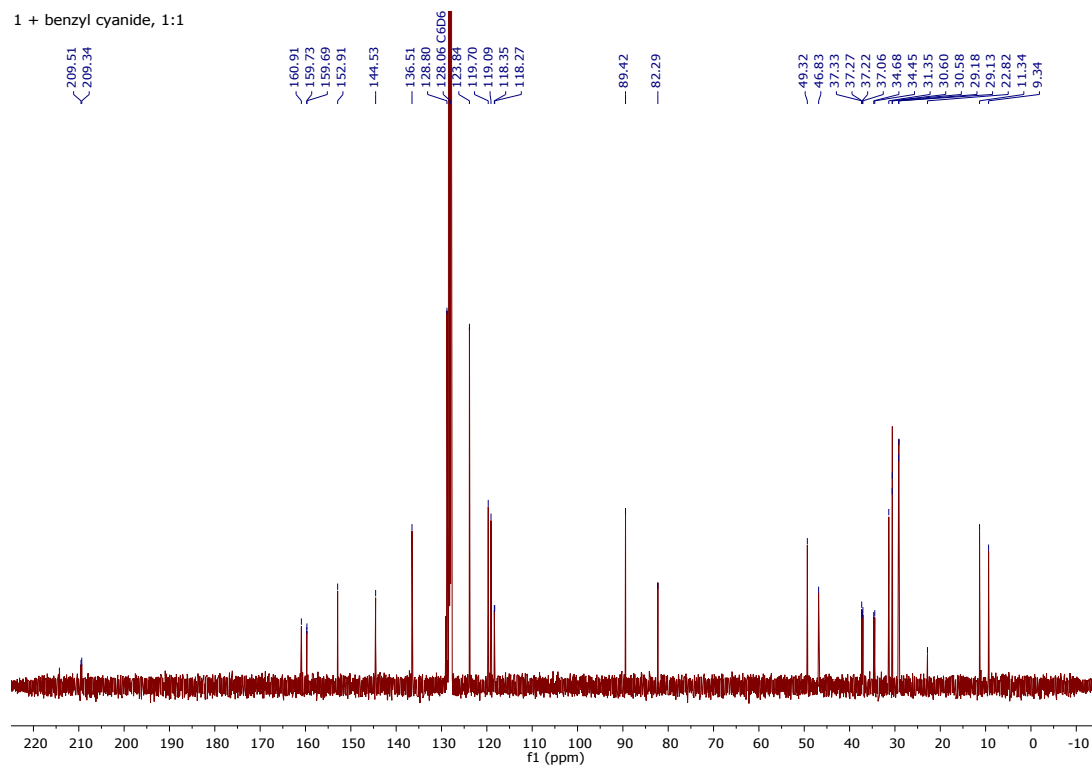


Figure S5c.  $^{13}\text{C}$ -NMR spectrum of **5e**

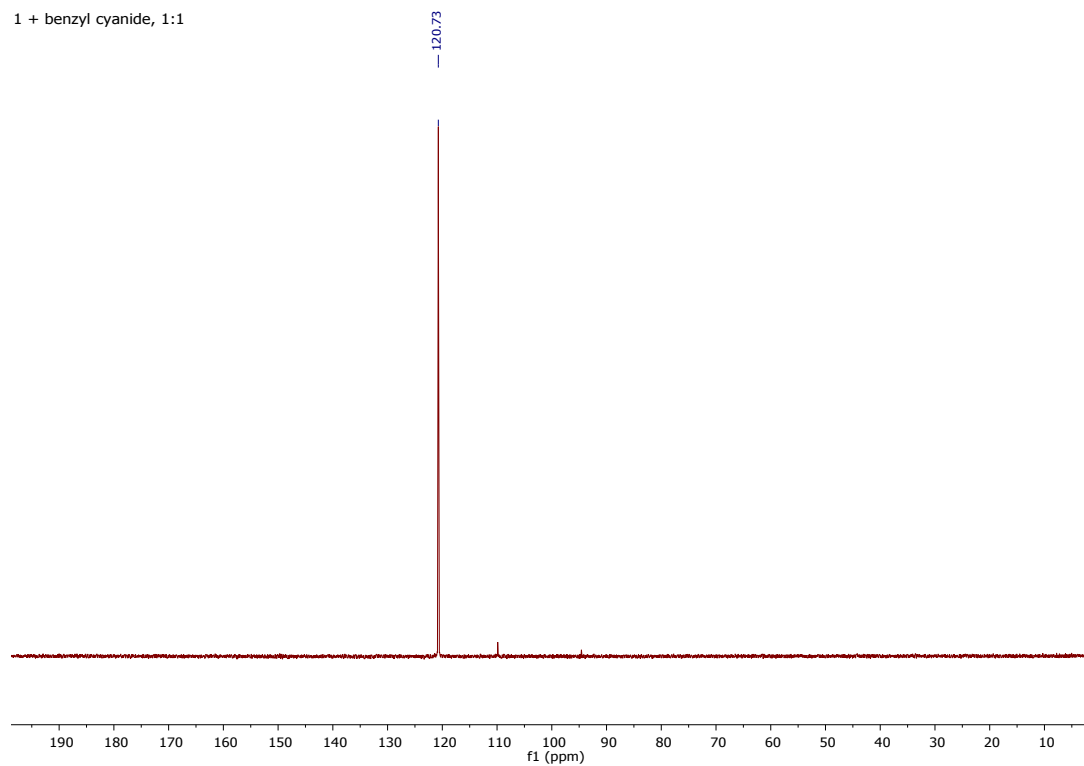


Figure S5d.  $^{31}\text{P}$ -NMR spectrum of **5e**

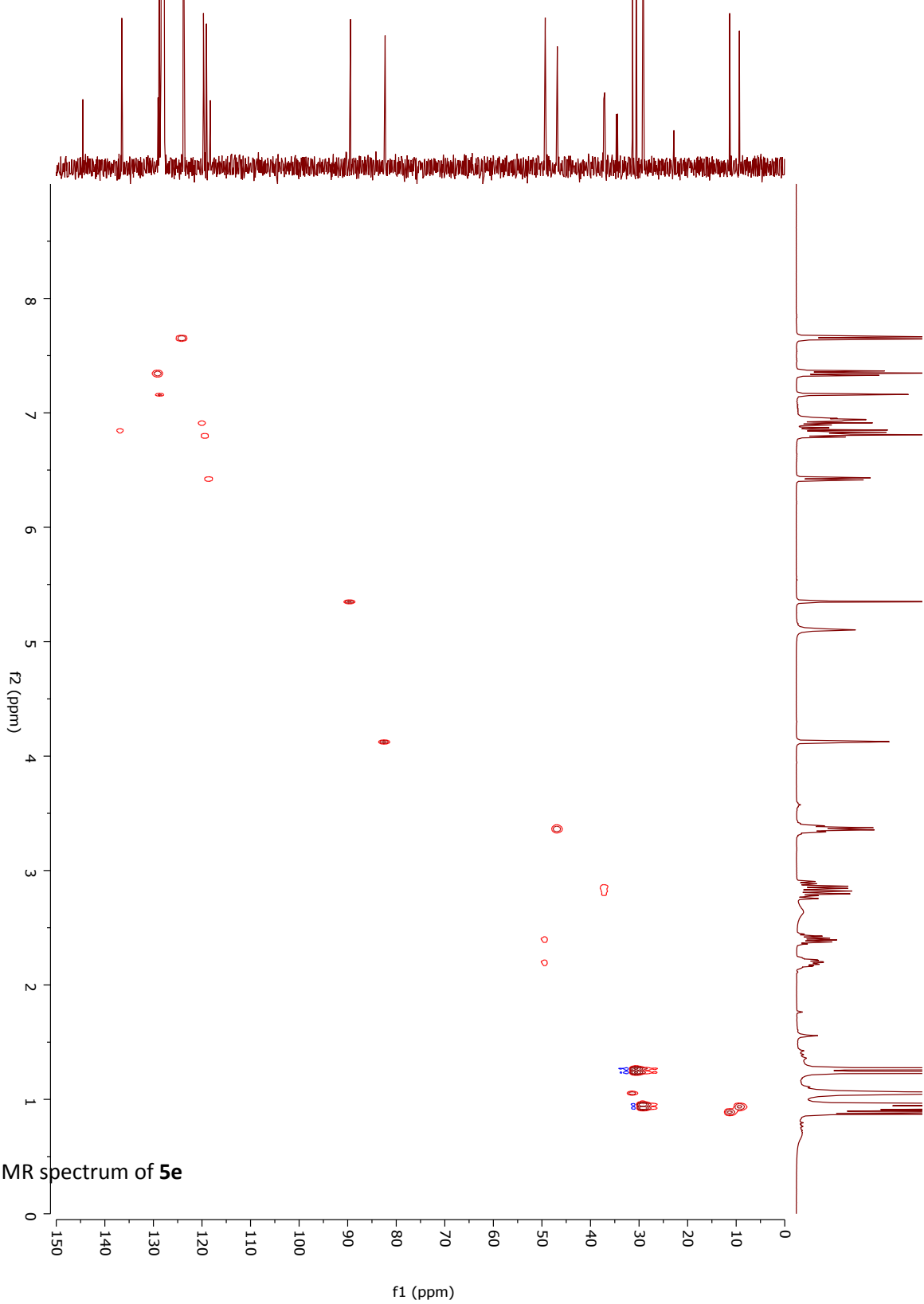
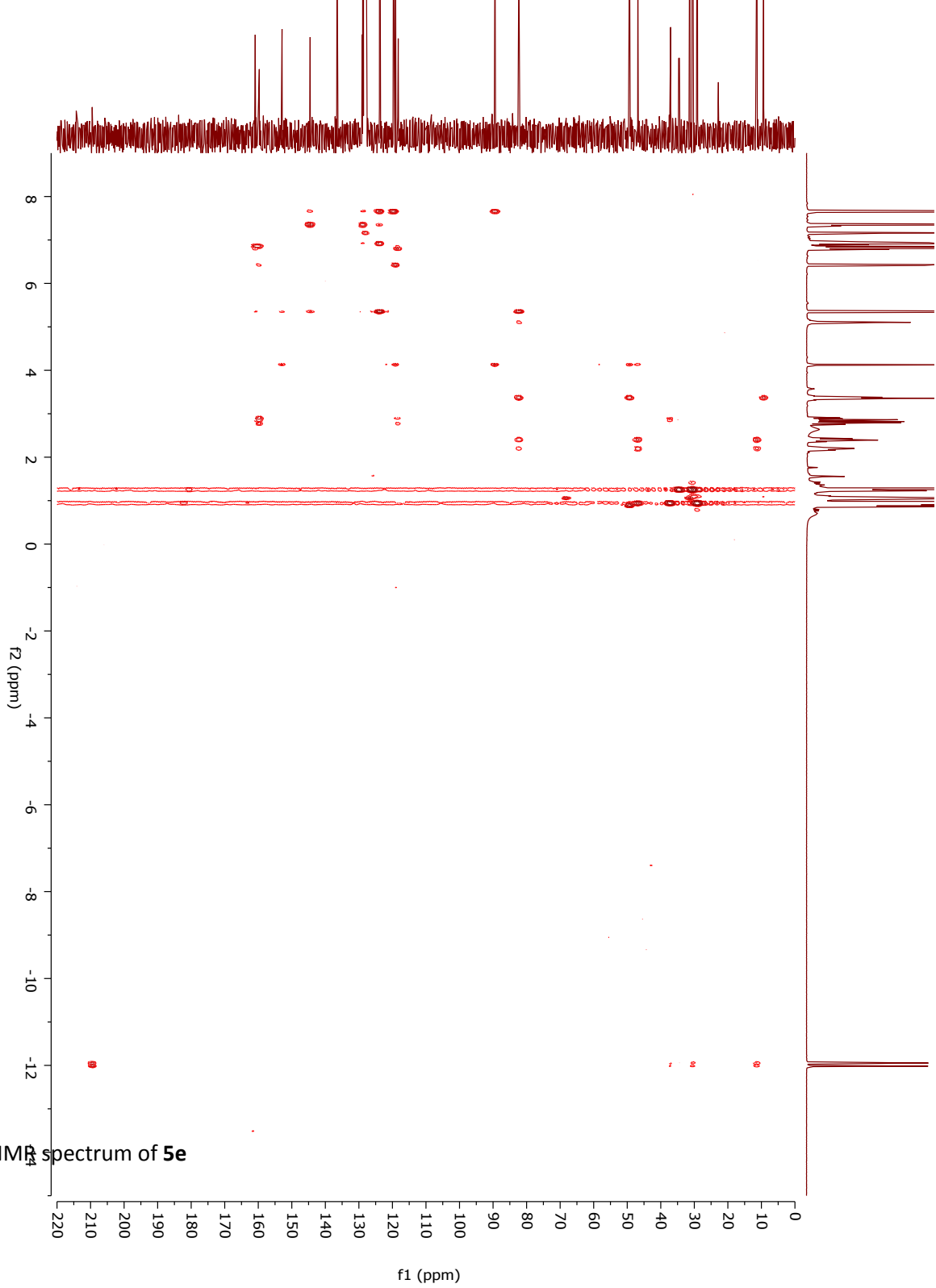


Figure S5e. gHSQC-NMR spectrum of **5e**



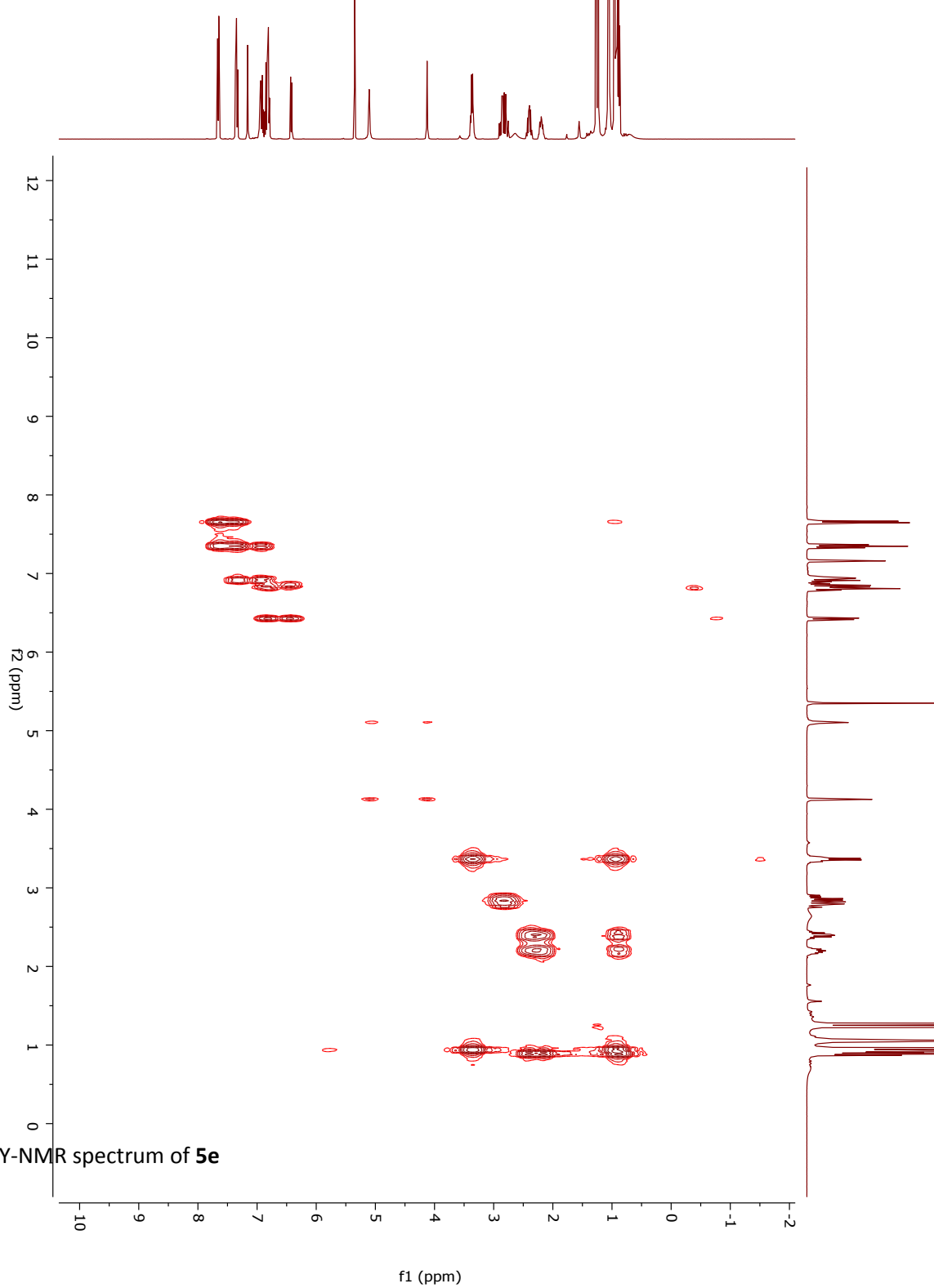


Figure S5g. DQFCOSY-NMR spectrum of **5e**

## Analysis of equilibria in 1 + 4-pentenenitrile

### Dependence on 4-pentenenitrile concentration

The dependence of the  $^1\text{H}$  NMR shift as a function of 4-pentenenitrile concentrations was evaluated using the MatLab code developed by Thordarson (see for details: P. Thordarson, *Chem. Soc. Rev.*, 2011, **40**, 1305). Analysis was performed using the Ru-H resonance and 3 other resonances in the aliphatic region that show shifts as a function of 4-pentenenitrile concentration. Experimental and predicted  $^1\text{H}$  NMR shifts for the Ru-H resonance are shown in Figure S6.

The best fit parameters are obtained for  $K = 41 (\pm 20\%) \text{ M}^{-1}$

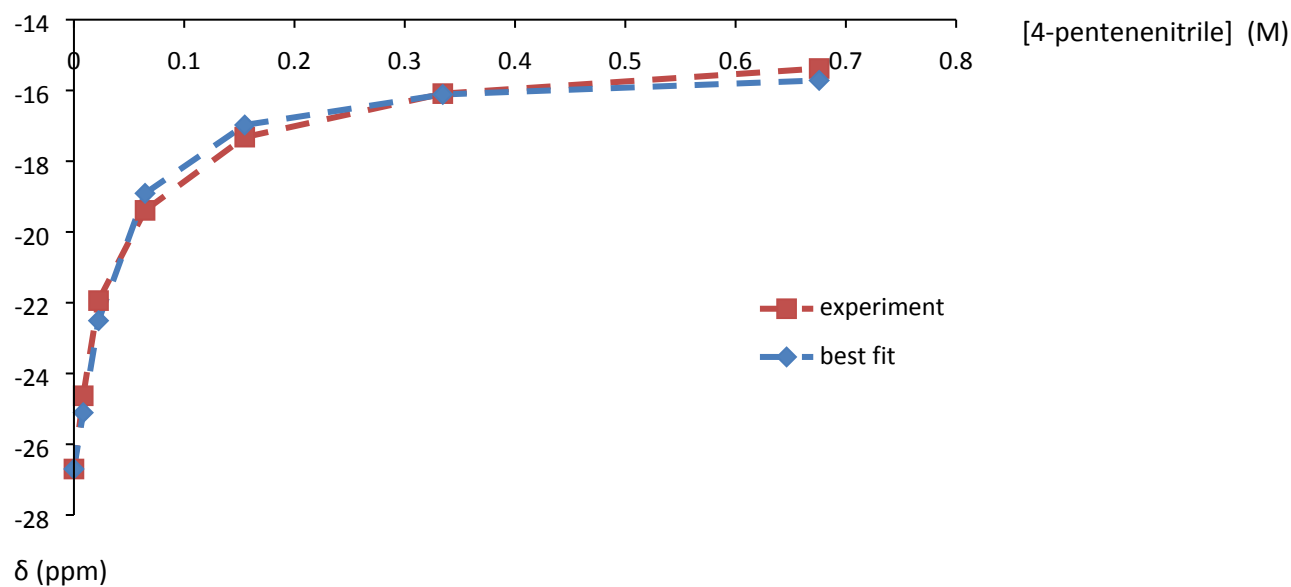


Figure S6. Experimental and predicted Ru-H NMR shifts as a function of 4-pentenenitrile concentration (dashed line is only a guide to the eye).

### Temperature dependence (Van 't Hoff analysis)

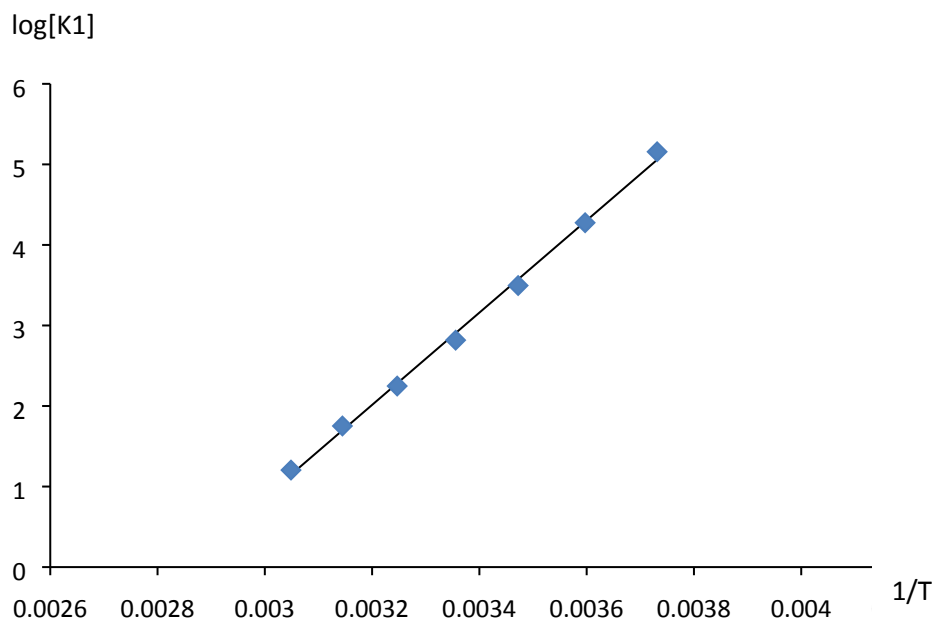


Figure S7. Van 't Hoff plot for the temperature dependence of K1

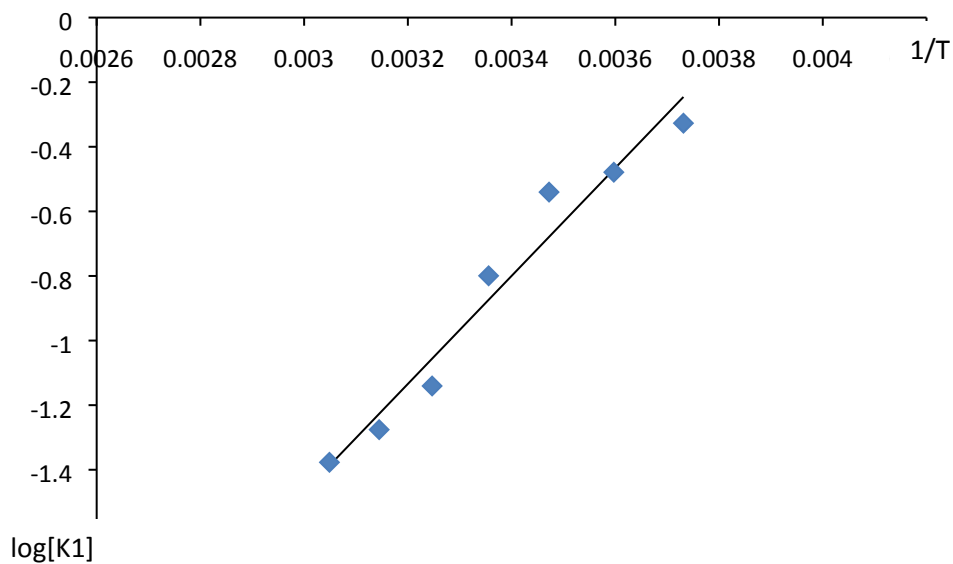


Figure S8. Van 't Hoff plot for the temperature dependence of K2

## DFT calculations

Geometry optimizations were carried out using Gaussian09 at the DFT/TPSSSTPSS level of theory with the LANL2DZ basis set with effective core potential on Ru and the 6-31G(d,p) basis set on all other atoms. Subsequent frequency analyses confirmed the resulting structures to be minima on the potential energy surface (no imaginary frequencies)

The energies of these geometries was evaluated using a better basis set (Def2TZVP on all atoms) and with the inclusion of dispersion correction (D3). A comparison of these data is given in Table S1.

	<b>3<sup>a</sup></b> 6- 31G(d,p) LANL2DZ	<b>3<sup>a</sup></b> TZVP	<b>3</b> (%) <sup>b</sup>	<b>4<sup>a</sup></b> 6- 31G(d,p) LANL2DZ	<b>4<sup>a</sup></b> TZVP	<b>4</b> (%) <sup>b</sup>	<b>5<sup>a</sup></b> 6- 31G(d,p) LANL2DZ	<b>5<sup>a</sup></b> TZVP	<b>5 (%)<sup>b</sup></b>
(a) cinnamitrile	1.3	1.8	0	0	0	100	-	-	-
(b) 4-pentenitrile	0	0.5	9	1.1	1.0	48	1.5	0	0
(c) acetonitrile	0	0.5	0	0.1	0	49	3.6	1.0	0
(d) benzonitrile	0	0	20	0.8	0.3	76	-	-	-
(e) benzyl cyanide	6.0	7.9	0	4.6	5.7	0	0	0	100

<sup>a</sup> Gibbs free energies in kcal/mol relative to the lowest energy isomer.

<sup>b</sup> Relative amount of each component as determined by <sup>1</sup>H NMR integration of 1:1 mixture **1** + nitrile at room temperature (remainder is **1** + **2**).