

***N*-Vinylolation of lactams with calcium carbide water system**

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**S1. General information**

Granulated calcium carbide  $\text{CaC}_2$  of technical grade ( $\geq 75\%$  purity) was purchased from Sigma Aldrich. Cyclic lactams were purchased from a local chemical company. The purity of the reagents was verified by GS-MS and NMR. Uracil (97+% purity) was purchased from Alfa Aesar. Solvents (hexane, diethyl ether, DMSO) were used without further purification.

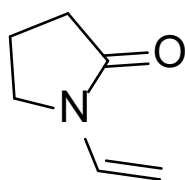
NMR spectra were recorded on a Bruker Avance 400 spectrometer (400 MHz for  $^1\text{H}$ ; 101 MHz for  $^{13}\text{C}$ ). Chemical shifts  $\delta$  are given in ppm using residual protons of deuterated solvents as internal standards  $\text{CDCl}_3$  ( $^1\text{H}$ ,  $\delta$  7.26 ppm;  $^{13}\text{C}$ ,  $\delta$  77.00 ppm) and  $\text{D}_2\text{O}$  ( $^1\text{H}$ ,  $\delta$  4.79 ppm). High resolution mass spectra (HRMS) were recorded on a Bruker MaXis spectrometer using electrospray ionization (ESI). Column chromatography was performed using Merck Silica gel 60 (60-200 mesh) preliminarily neutralized with  $\text{Et}_3\text{N}$ . Merck silica gel 60 uv-254 plates were used for thin-layer chromatography (TLC); a 5% aqueous solution of  $\text{KMnO}_4$  was used for visualization.

## S2. Synthetic procedure and spectral data

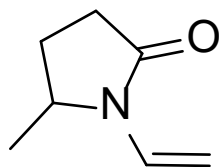
**Caution!** Gaseous acetylene is a flammable gas with explosive nature. The authors recommend using protective screens for reaction set ups.

*Vinylation procedure.* A lactam (1 mmol),  $K_2CO_3$  or  $Cs_2CO_3$  (1 mmol), KF (116 mg, 2 mmol),  $CaC_2$  (192 mg, 3 mmol), DMSO (3 mL) were placed in a tube with a screw cap. Then, water (110  $\mu$ L, 6 mmol) was added and the tube was immediately capped. The mixture was heated at 110-140  $^{\circ}C$  for 4 hours. Then, the reaction mixture was cooled to room temperature, filtered and extracted alternately with diethyl ether and methyl *tert*-butyl ether. The organic layer was washed with water and brine, dried over  $Na_2SO_4$ , the residue was chromatographed. Eluents for chromatography are indicated in the spectral characteristics of the compounds. The reaction mixture from uracil vinylation was not extracted and was directly chromatographed on silica gel.

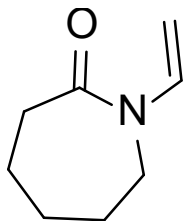
### Spectral data of synthesized compounds



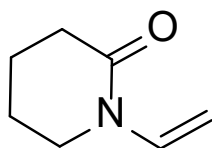
*1-Vinylpyrrolidin-2-one 2a:* yellow oil, yield 93% (eluent – hexane, then hexane– $Et_2O$ , 2:1).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 7.07 (dd,  $J$  16.0, 9.1 Hz, 1H), 4.49–4.27 (m, 2H), 3.55–3.47 (m, 2H), 2.48 (t,  $J$  8.2 Hz, 2H), 2.17–2.01 (m, 2H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$ : 173.3, 129.3, 94.3, 44.5, 31.3, 17.3. HRMS (ESI),  $m/z$ : 112.0758 [ $M+H$ ] $^+$ , (calc. for  $C_6H_9NO^+$ ,  $m/z$ : 112.0757).



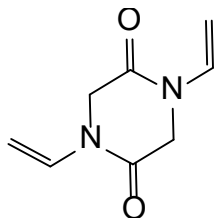
*5-Methyl-1-vinylpyrrolidin-2-one 2b:* yellow oil, yield 83% (eluent – hexane, then hexane– $Et_2O$ , 2:1).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$ : 6.94 (dd,  $J$  16.3, 9.4 Hz, 1H), 4.44 (t,  $J$  12.0 Hz, 2H), 4.45 (d,  $J$  8.3 Hz, 1H), 4.42 (d,  $J$  15.8 Hz, 1H), 4.09–3.98 (m, 1H), 2.62–2.48 (m, 1H), 2.37 (ddd,  $J$  17.3, 9.6, 2.1 Hz, 1H), 2.20 (dt,  $J$  20.6, 10.0 Hz, 1H), 1.77–1.67 (m, 1H), 1.24 (d,  $J$  6.3 Hz, 3H).  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$ : 172.9, 127.9, 94.7, 51.8, 29.7, 26.0, 17.9. HRMS (ESI),  $m/z$ : 126.0914 [ $M+H$ ] $^+$ , (calc. for  $C_7H_{11}NO^+$ ,  $m/z$ : 126.0913).



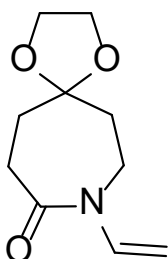
*1-Vinylazepan-2-one 2c*: yellow oil, yield 97% (eluent – hexane, then pentane–Et<sub>2</sub>O, 2:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.37 (dd, *J* 16.1, 9.4 Hz, 1H), 4.52–4.32 (m, 2H), 4.45 (d, *J* 8.3 Hz, 1H), 4.42 (d, *J* 15.8 Hz, 1H), 3.61–3.51 (m, 2H), 2.66–2.56 (m, 2H), 1.80–1.59 (m, 6H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 174.3, 132.1, 92.6, 44.1, 37.2, 29.4, 27.2, 23.4. HRMS (ESI), *m/z*: 140.1073 [M+H]<sup>+</sup>, (calc. for C<sub>8</sub>H<sub>13</sub>NO<sup>+</sup>, *m/z*: 140.1070).



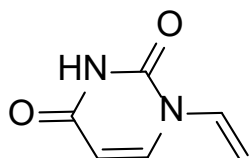
*1-Vinylpiperidin-2-one 2d*: white powder, yield 16% (hexane, then hexane–Et<sub>2</sub>O, 1:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.60 (dd, *J* 16.2, 9.4 Hz, 1H), 4.50–4.33 (m, 2H), 3.38 (t, *J* 6.2 Hz, 2H), 2.47 (t, *J* 6.6 Hz, 2H), 1.95–1.72 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 168.6, 132.4, 93.4, 44.2, 32.9, 22.5, 20.5. HRMS (ESI), *m/z*: 126.0914 [M+H]<sup>+</sup>, (calc. for C<sub>7</sub>H<sub>11</sub>NO<sup>+</sup>, *m/z*: 126.0913).



*1,4-Divinylpiperazine-2,5-dione 2e*: yellow powder, yield 39% (hexane, then chloroform). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.48 (dd, *J* 16.2, 9.3 Hz, 2H), 4.65–4.45 (m, 4H), 4.12 (s, 4H). HRMS (ESI), *m/z*: 167.0817 [M+H]<sup>+</sup>, (calc. for C<sub>8</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub><sup>+</sup>, *m/z*: 167.0815). Spectral characteristics correspond to those described in literature.<sup>1</sup>



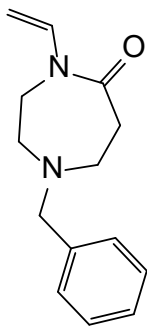
*8-Vinyl-1,4-dioxaspiro[4.6]undecan-9-one 2f*: yellow oil, yield 87% (hexane, then hexane–Et<sub>2</sub>O, 1:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.36 (dd, *J* 16.1, 9.4 Hz, 1H), 4.56–4.35 (m, 2H), 3.97 (s, 4H), 3.66–3.58 (m, 2H), 2.71–2.63 (m, 2H), 1.89–1.75 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 173.5, 131.8, 108.7, 93.1, 64.7 (2C), 39.3, 37.2, 33.3, 32.1. HRMS (ESI), *m/z*: 198.1126 [M+H]<sup>+</sup>, (calc. for C<sub>10</sub>H<sub>15</sub>NO<sub>3</sub><sup>+</sup>, *m/z*: 198.1125).



*1-Vinylpyrimidine-2,4(1H,3H)-dione 2g*: white powder, yield 87%. <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O) δ: 7.92 (d, *J* 8.1 Hz, 1H), 7.10 (dd, *J* 15.8, 8.9 Hz, 1H), 5.96 (d, *J* 8.1 Hz, 1H), 5.40 (dd, *J* 15.8, 2.2 Hz, 1H), 5.18 (dd, *J* 8.9, 2.2 Hz, 1H). <sup>13</sup>C NMR (101 MHz, D<sub>2</sub>O) δ: 166.4, 150.9, 142.3, 129.7, 104.9, 102.5. The compound characteristics correspond to those described in literature.<sup>2</sup>

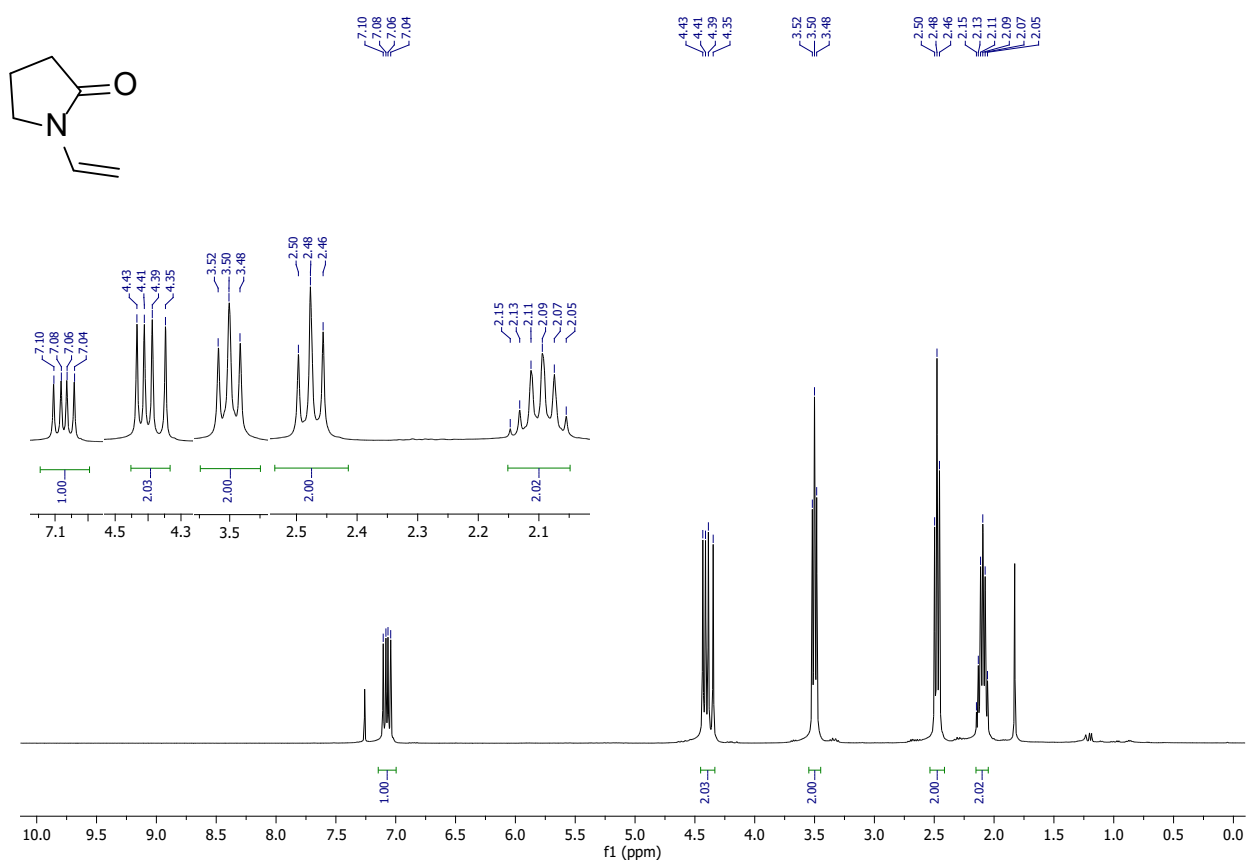
<sup>1</sup> E. Semina, P. Tuzina, F. Bienewald, A. S. K. Hashmi and T. Schaub, *Chem. Commun.*, 2020, **56**, 5977.

<sup>2</sup> R. Dalpozzo, A. D. Nino, L. Maiuolo, A. Procopio, R. Romeo and G. Sindona, *Synthesis*, 2002, **2002**, 0172.



*1-Benzyl-4-vinyl-1,4-diazepan-5-one* **2h**: yellow powder, yield 90% (hexane, then hexane–Et<sub>2</sub>O, 5:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 7.42–7.23 (m, 6H), 4.46–4.37 (m, 2H), 3.67 (dd, *J* 5.4, 3.6 Hz, 2H), 3.58 (s, 2H), 2.78 (dd, *J* 6.5, 4.0 Hz, 2H), 2.68–2.55 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ: 173.2, 137.9, 132.1, 128.9, 128.4, 127.3, 93.0, 62.8, 55.0, 50.7, 44.2, 38.7. HRMS (ESI), *m/z*: 231.1490 [M+H]<sup>+</sup>, (calc. for C<sub>14</sub>H<sub>18</sub>N<sub>2</sub>O<sup>+</sup>, *m/z*: 231.1492).

### S3. NMR spectra of synthesized compounds



**Figure S1.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 1-vinylpyrrolidin-2-one (**2a**).

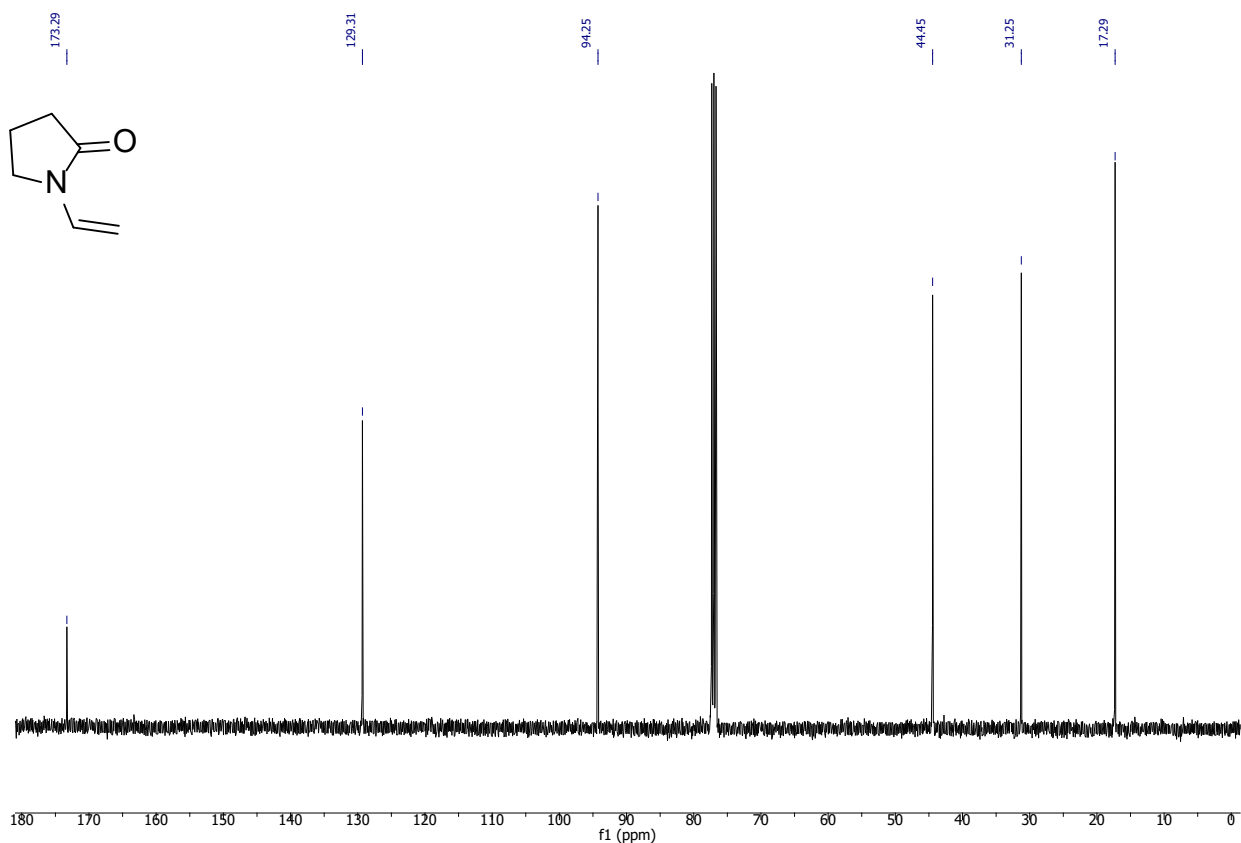


Figure S2.  $^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-vinylpyrrolidin-2-one (2a).

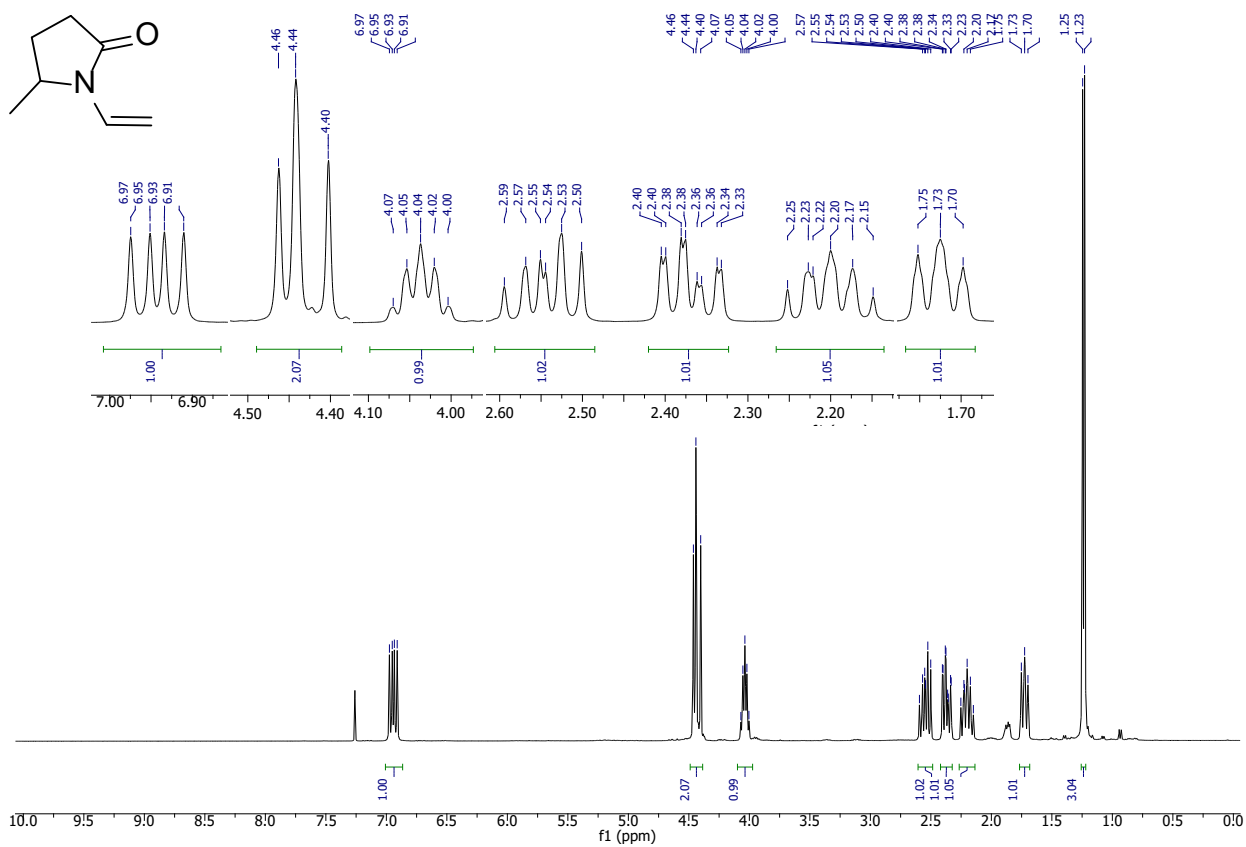


Figure S3.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 5-methyl-1-vinylpyrrolidin-2-one (2b).

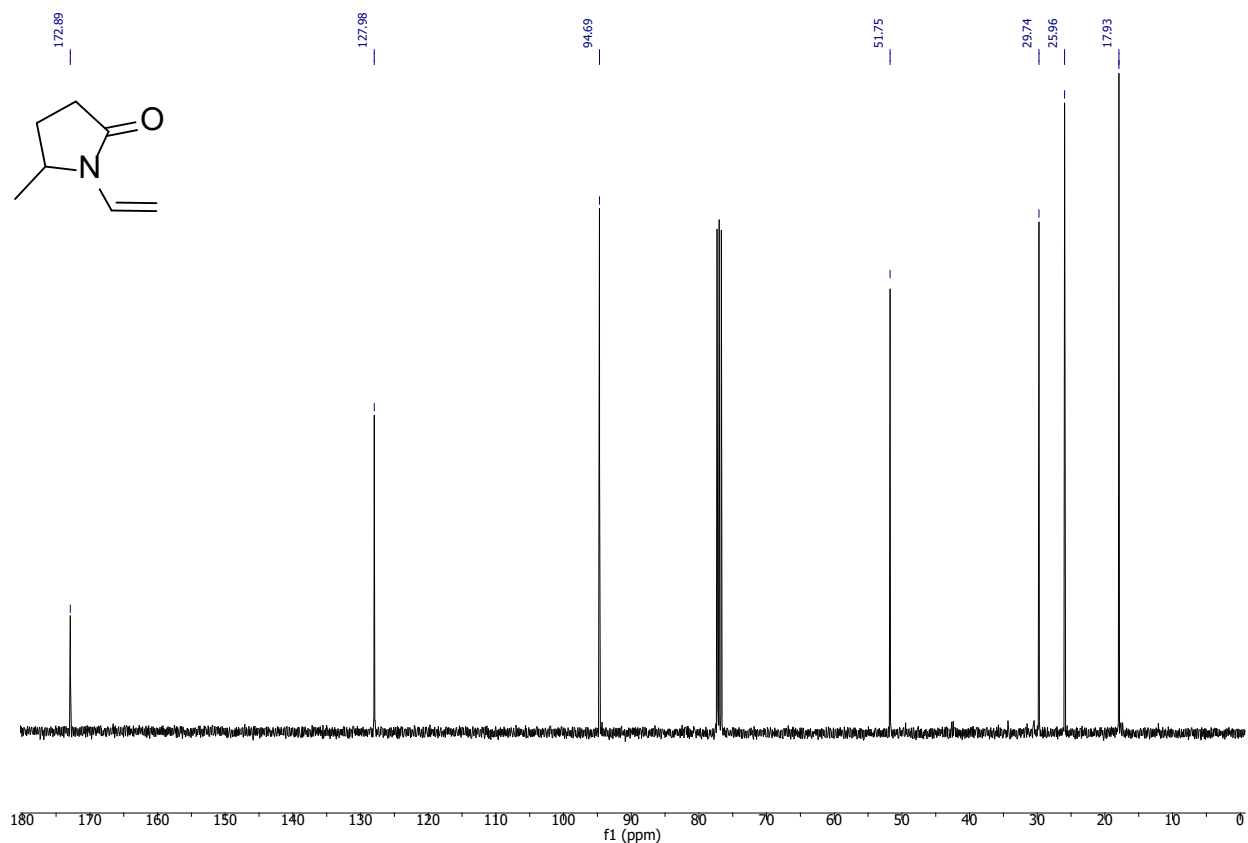


Figure S4.  $^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 5-methyl-1-vinylpyrrolidin-2-one (2b).

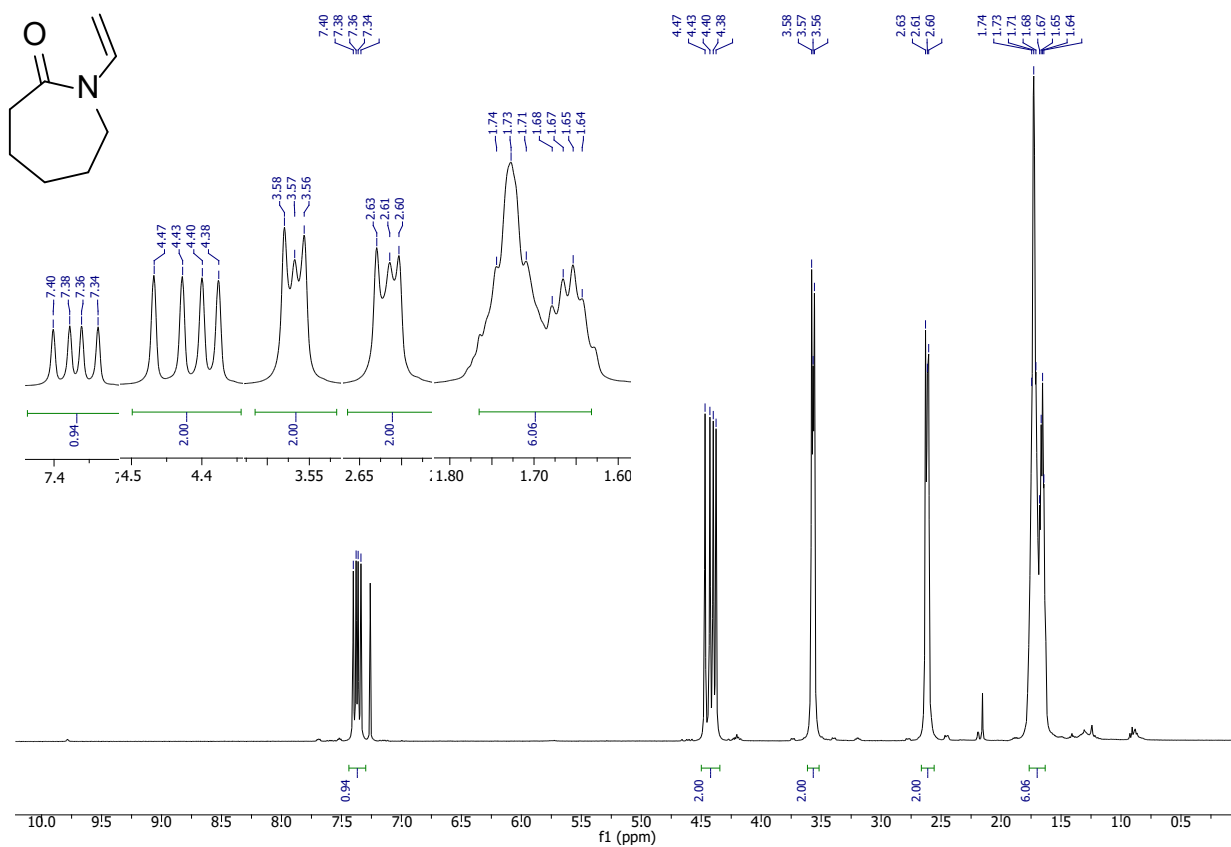
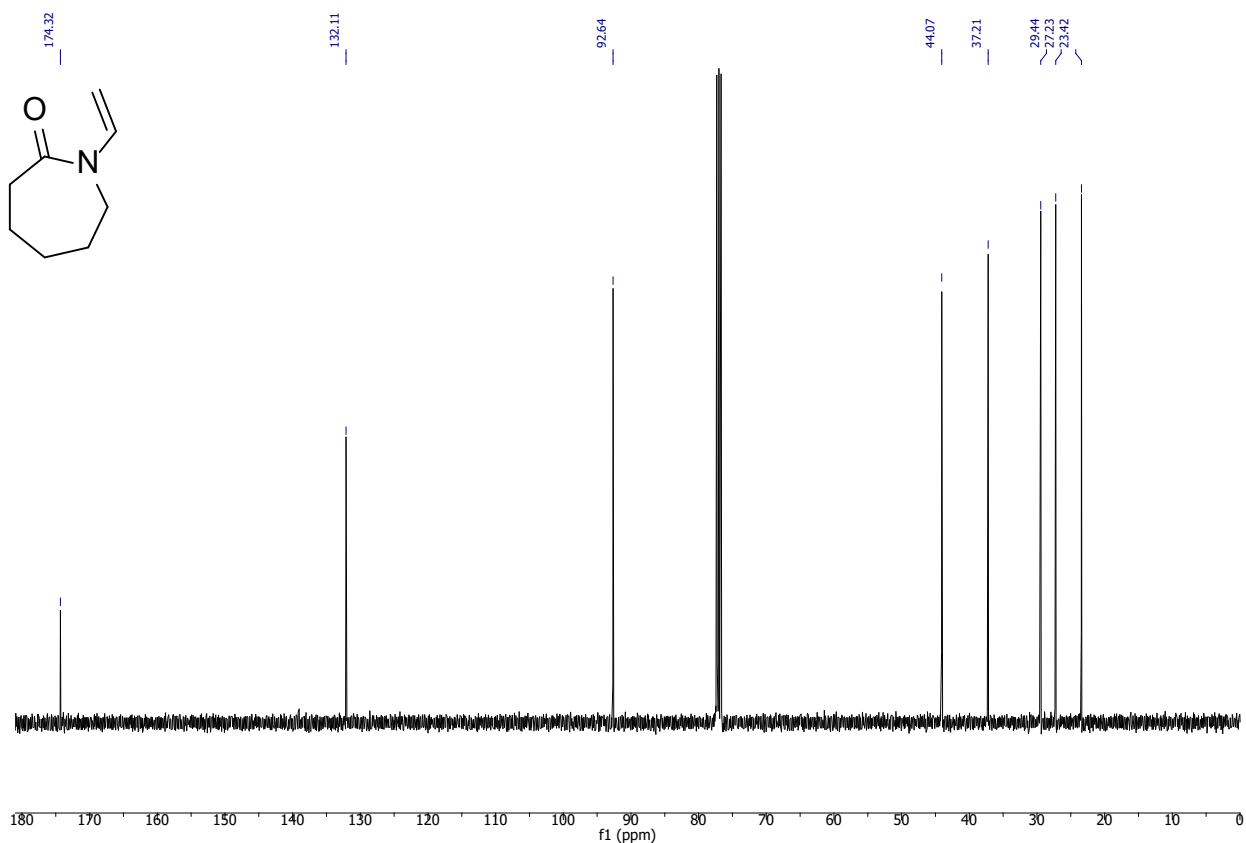
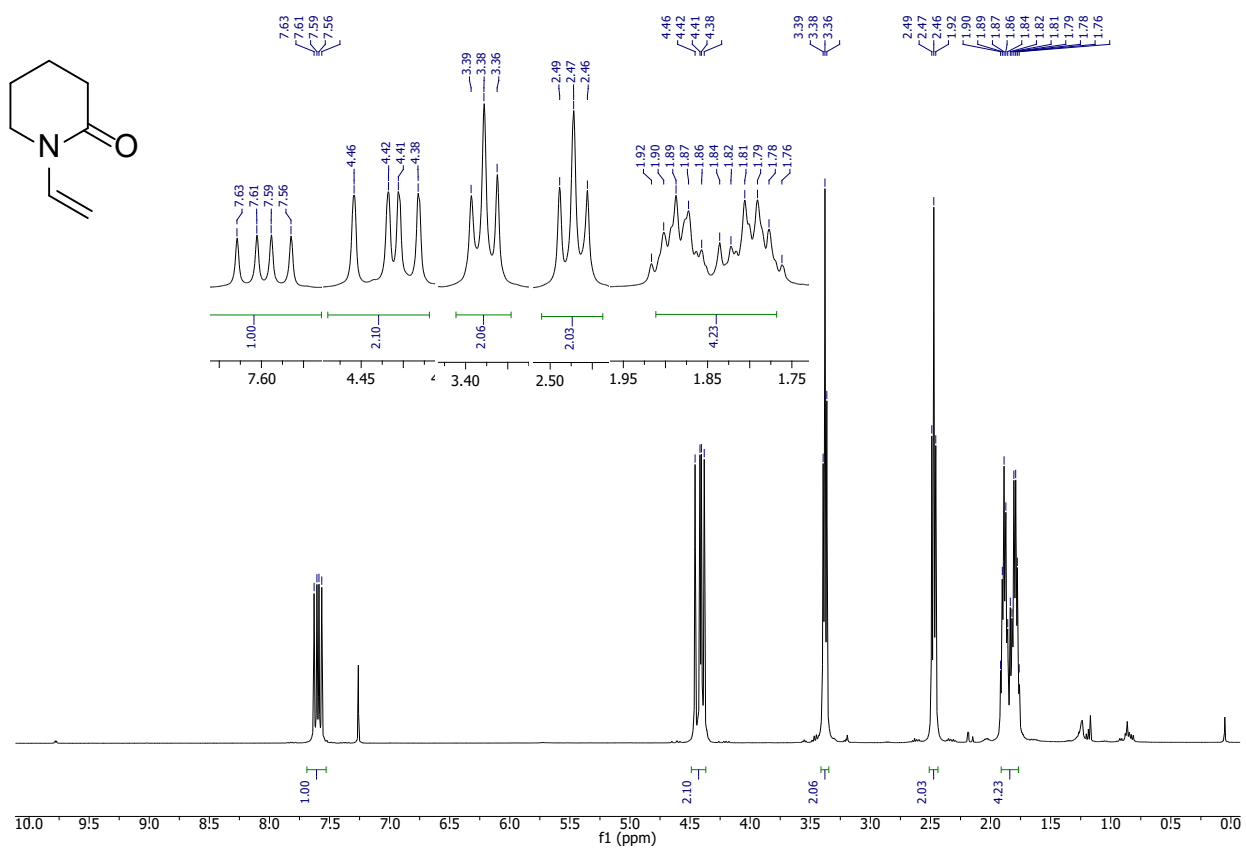


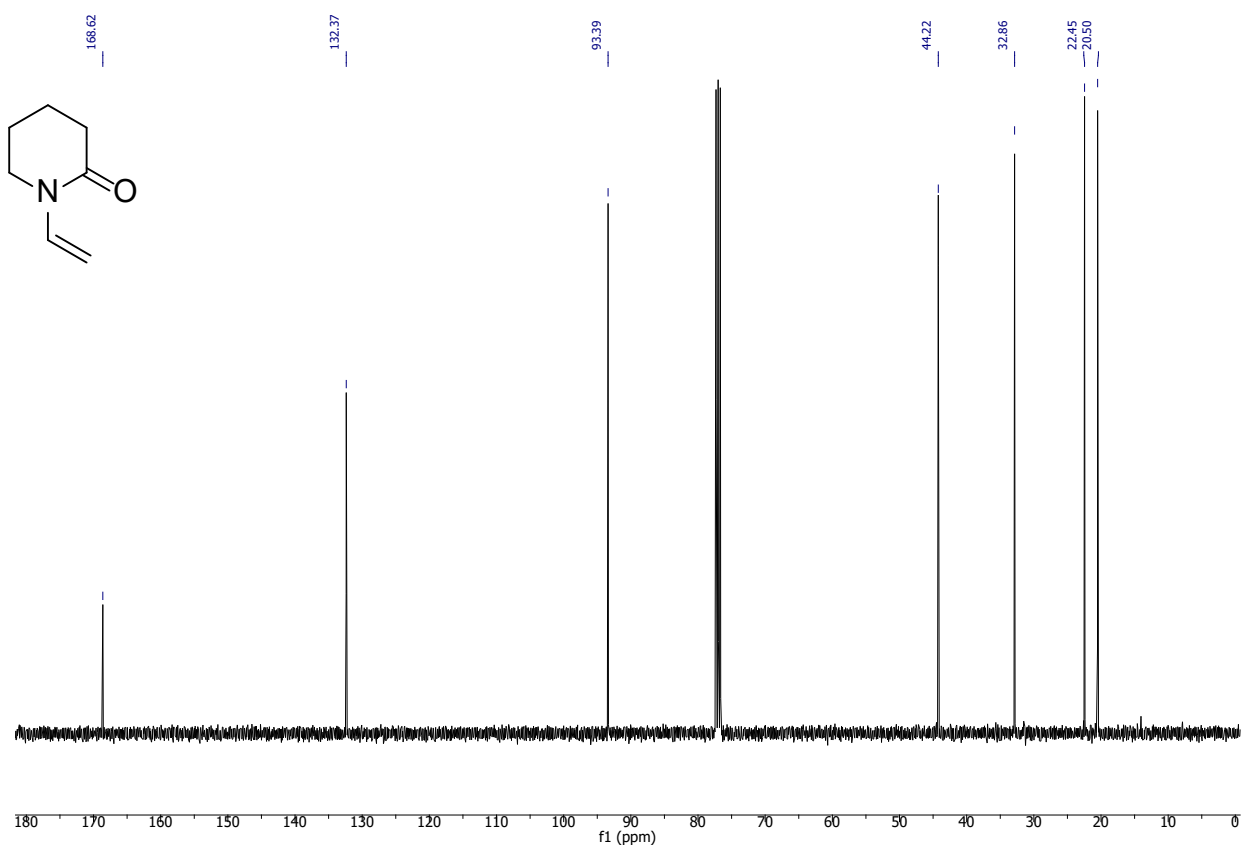
Figure S5.  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-vinylazepan-2-one (2c).



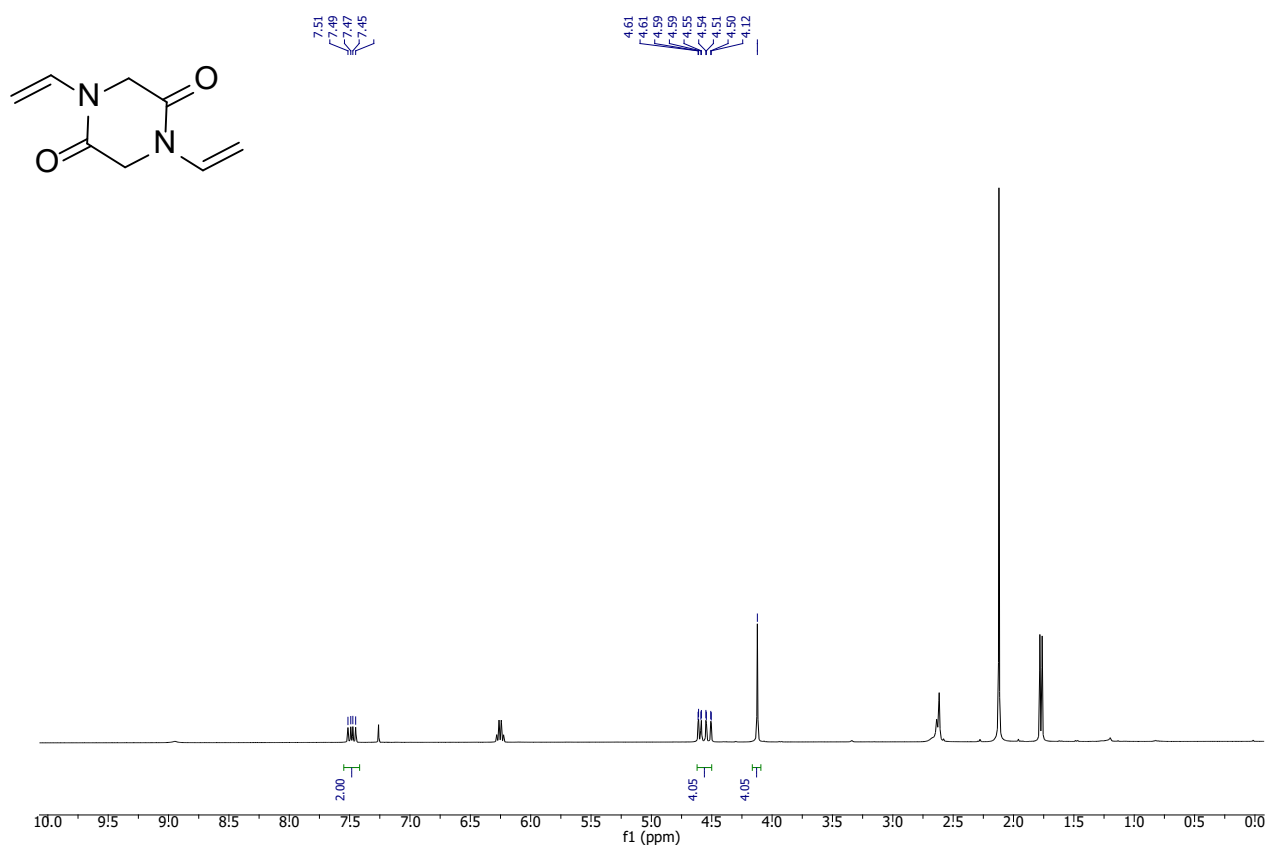
**Figure S6.**  $^{13}\text{C}$  NMR spectrum (101 MHz,  $\text{CDCl}_3$ ) of 1-vinylazepan-2-one (2c).



**Figure S7.**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ ) of 1-vinylpiperidin-2-one (2d).

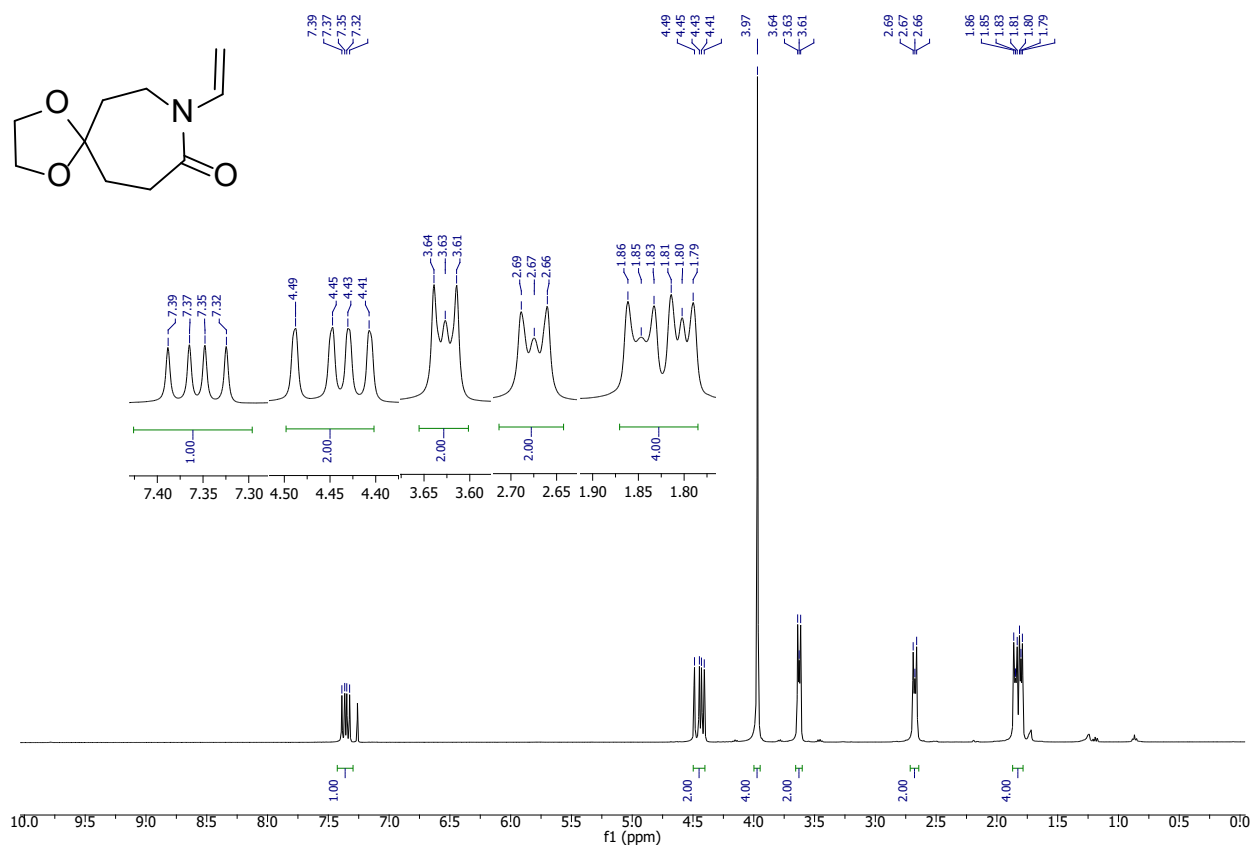


**Figure S8.** <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of 1-vinylpiperidin-2-one (2d).

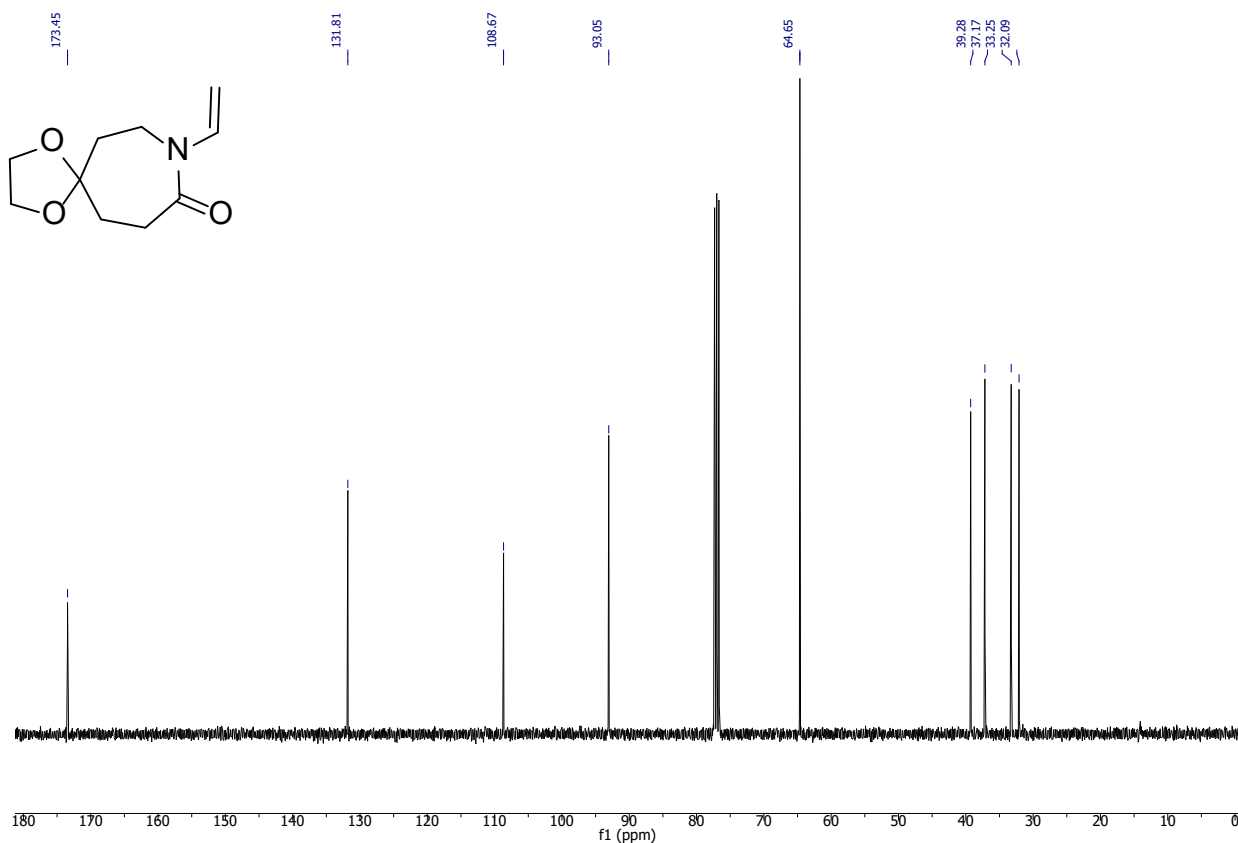


**Figure S9.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 1,4-divinylpiperazine-2,5-dione (2e) reaction mixture.

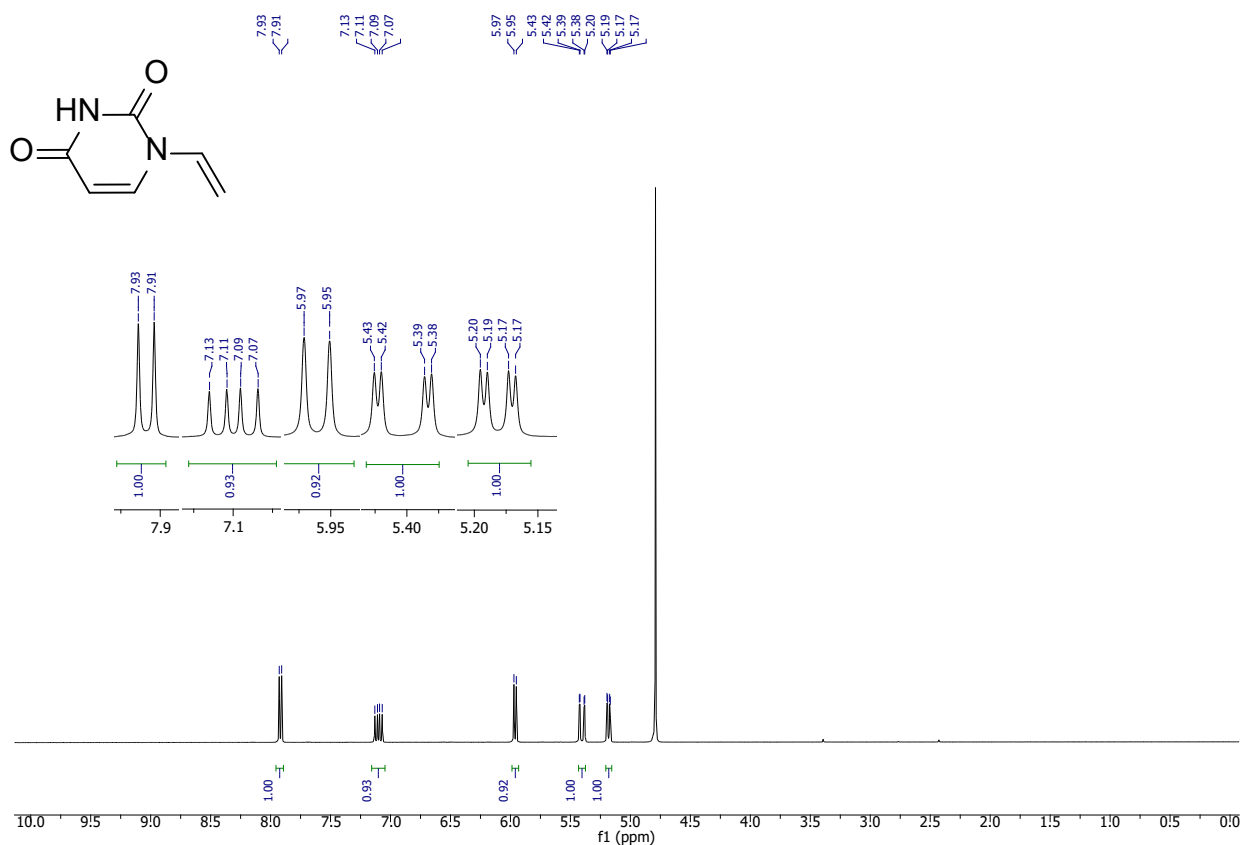




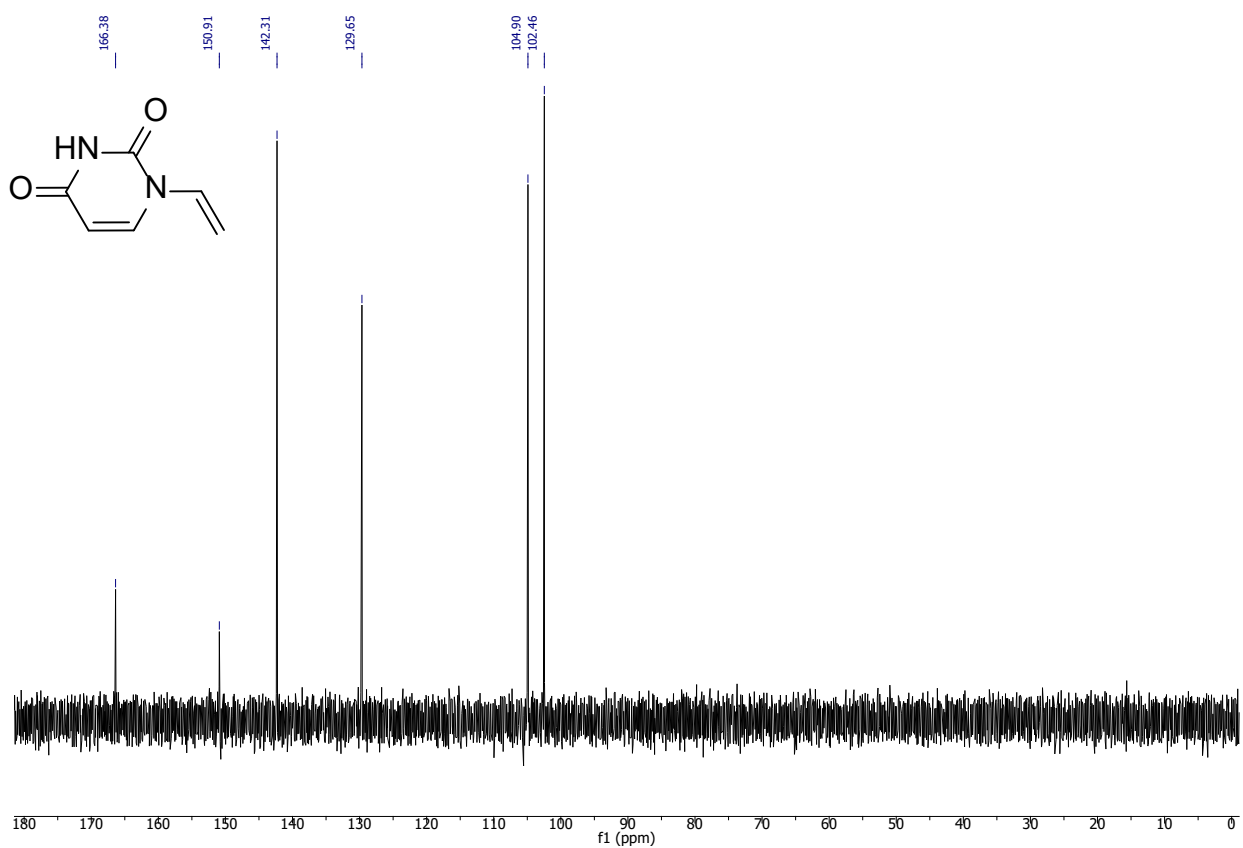
**Figure S10.** <sup>1</sup>H NMR spectrum (400 MHz, CDCl<sub>3</sub>) of 8-vinyl-1,4-dioxo-8-azaspiro[4.6]undecan-9-one (2f).



**Figure S11.** <sup>13</sup>C NMR spectrum (101 MHz, CDCl<sub>3</sub>) of 8-vinyl-1,4-dioxo-8-azaspiro[4.6]undecan-9-one (2f).



**Figure S12.** <sup>1</sup>H NMR spectrum (400 MHz, D<sub>2</sub>O) of 1-vinylpyrimidine-2,4(1*H*,3*H*)-dione (**2g**).



**Figure S13.** <sup>13</sup>C NMR spectrum (101 MHz, D<sub>2</sub>O) of 1-vinylpyrimidine-2,4(1*H*,3*H*)-dione (**2g**).

