Electronic Supplementary Material (ESI) for ChemComm.

SUPPORTING INFORMATION

A G_4•K^+ hydrogel made from 5′-hydrazinoguanosine for remediation of α,β-unsaturated carbonyls

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General Experimental: Guanosine **1** was purchased from Sigma-Aldrich. The 5′-hydrazido guanosine **2,**[1] and the 5′-hydrazinoguanosine **3,**[2] were synthesized according to literature procedures and their ^{1}H and ^{13}C NMR spectra matched published results. NMR spectra were recorded on Bruker DRX-400, Bruker DRX-500, or Bruker AVIII-600 spectrometers. Chemical shifts are reported in ppm relative to the residual solvent peak. Deuterated solvents were purchased from Cambridge Isotope Labs. ESI-MS experiments were done with a JEOL AccuTOF spectrometer. Chemicals and solvents were purchased from Acros, Aldrich, Alfa Aesar, Fisher, Carbosynth, or Santa Cruz Biotechnology.

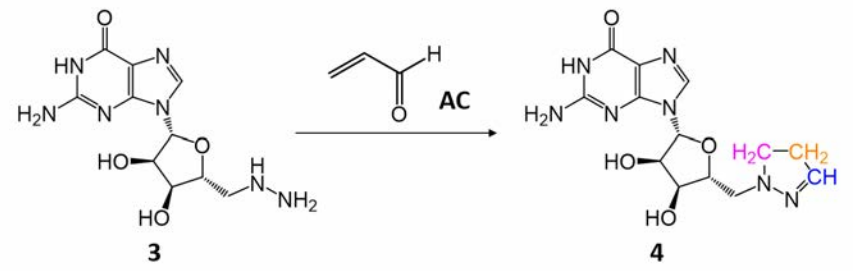
General Procedure for Preparation of G_4•K^+ hydrogels: The desired amount of guanosine derivatives **2** or **3** was weighed into a vial and the appropriate amount of deionized water was added (e.g. 2 wt% hydrazine **3** (68 mM), 0.5 eq KCl (34 mM)). The resulting suspension was sonicated until large aggregates were broken up to give a fine suspension. The suspension was then heated to boil with a heat gun until a clear solution resulted. The vial was removed from the heat and the appropriate amount of KCl was immediately added to the hot solution. The mixture was then vigorously shaken and heated to boil again. The mixture was then allowed to cool at room temperature.

Procedure for gas phase uptake of α,β-unsaturated carbonyls by G_4•K^+ hydrogels: A small vial, without a cap, containing 0.5 mL of a G_4•K^+ hydrogel made from either 5′-hydrazidoguanosine **2** or 5′-hydrazinoguanosine **3** (2 wt%, 0.5 eq KCl) was placed inside the larger vial, and 1.0 equiv of neat α,β-UC (either **AC**, **MVK** or **MA**) was added to the outside, larger vial (see **Fig. S1**). The large vial was immediately capped and sealed with parafilm and the reaction mixture was allowed to stand at RT. The small vial was removed after 2 days, the hydrogel was lyophilized to give a white powder, which was dissolved in 0.6 mL of DMSO-d_6 and analyzed by ^{1}H and ^{13}C NMR and by ESI-MS.

Figure S1: The experimental setup for gas phase uptake of α,β-UC by G_4•K^+ hydrogels.

Section on Acrolein (AC) Uptake

Preparation of 5′-deoxy-5′-pyrazolinoguanosine (4).



5′-deoxy-5′-pyrazolinoguanosine **4**. Using the experimental protocol for gas phase uptake described above, pyrazoline **4** was prepared from AC and 5′-deoxy-5′-hydrazinoguanosine **3**.[2] The lyophilized hydrogel, a white powder containing **4**, was analyzed by ^{1}H and ^{13}C NMR and by ESI-MS. ^{1}H NMR (DMSO-d_6) δ: 2.51-2.56 (2 H, m, CH_2), 2.84-2.98 (2 H, m, CH_2), 3.02-3.08 (1 H, dd, 5′-CH_2, J=6.5 Hz, J=6.7 Hz), 3.21-3.26 (1 H, dd, 5′′-CH_2, J=8.3 Hz, J=5.0 Hz), 4.07 (1 H, m, 4′-CH), 4.12 (1 H, m, 3′-CH), 4.50 (1 H, m, 2′-CH), 5.22 (1 H, d, J=5.0 Hz, 3′-OH), 5.45 (1 H, d, J=6.0 Hz, 2′-OH), 5.68 (1 H, d, J=6.0 Hz, 1′-CH), 6.61 (2 H, s, NH_2), 6.81 (1 H, t, J=1.6 Hz, CH), 7.91 (1 H, s, 8-CH), 10.77 (1 H, s, br, N1H); ^{13}C NMR (DMSO-d_6) δ: 33.90 (CH_2), 55.23 (CH_2), 58.36 (C5′), 71.55 (C4′), 72.73 (C2′), 82.51 (C3′), 86.35 (C1′), 116.69 (C5), 135.60 (C8), 142.81 (C3), 151.39 (C4), 153.75 (C2), 156.66 (C6); ESI-MS m/z=335.98 (MW of **4**: 335.32)

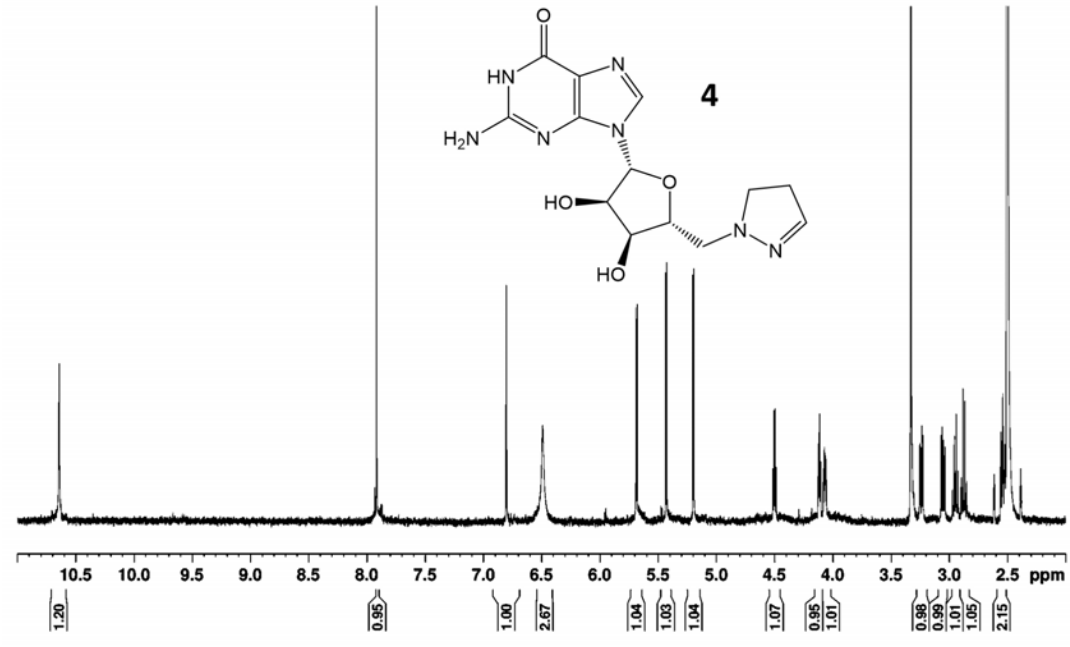


Figure S2: ^{1}H NMR spectrum of pyrazoline **4**

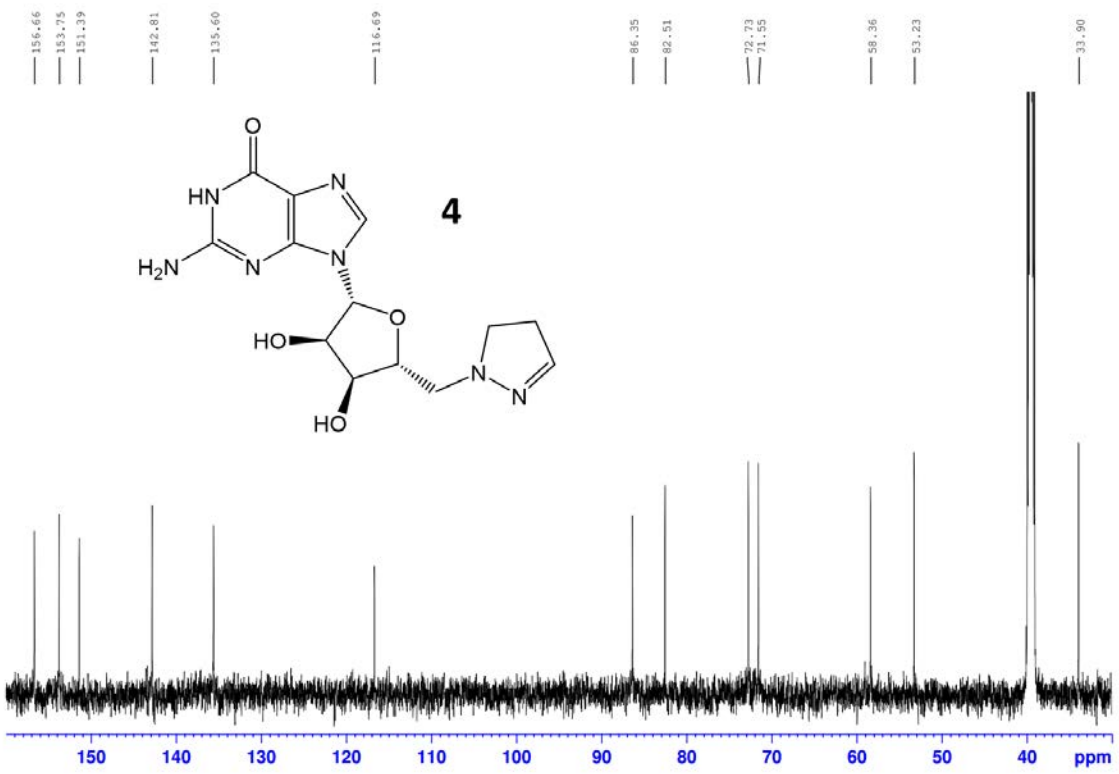


Figure S3: The ^{13}C NMR spectrum for pyrazoline **4** shows 13 peaks, consistent with the formation of an adduct between 5′-hydrazinoguanosine **3** and acrolein.

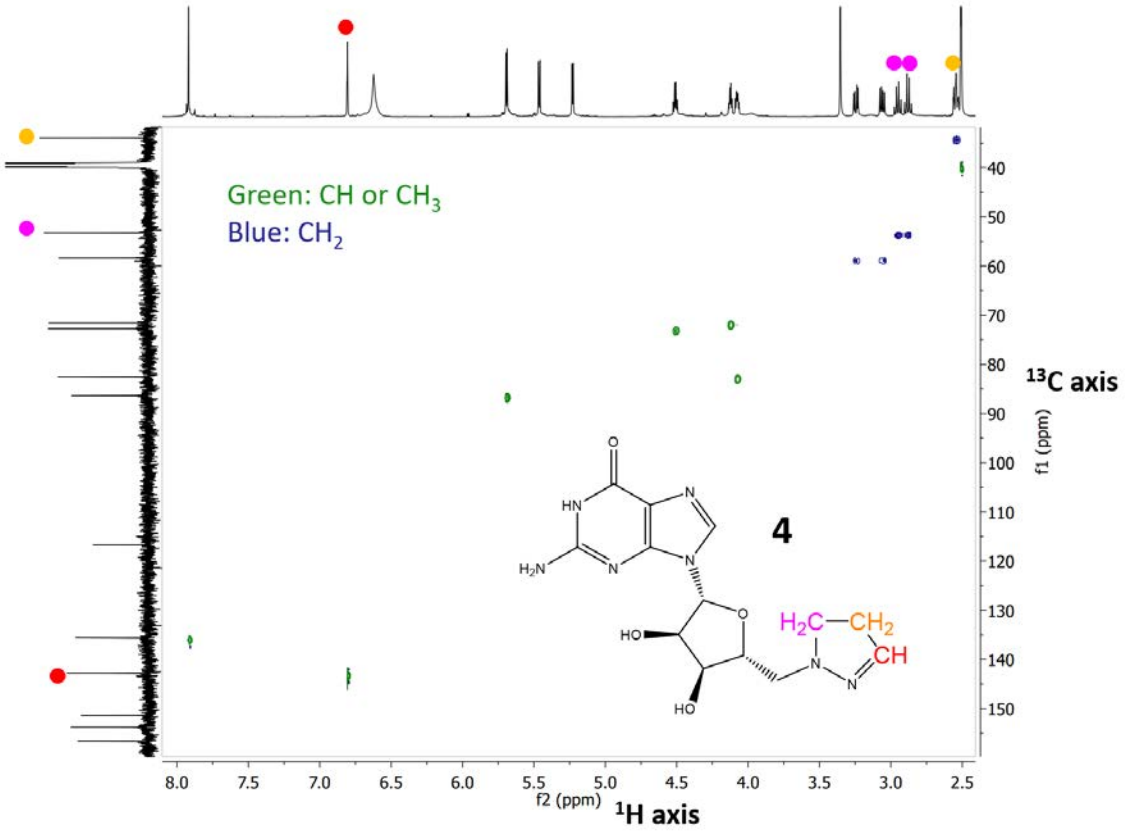


Figure S4: ^{1}H-^{13}C HSQC spectrum of **4**. NMR signals for the CH_2 and CH groups in the 5′-pyrazoline ring are indicated by colored dots (pink, orange and red).

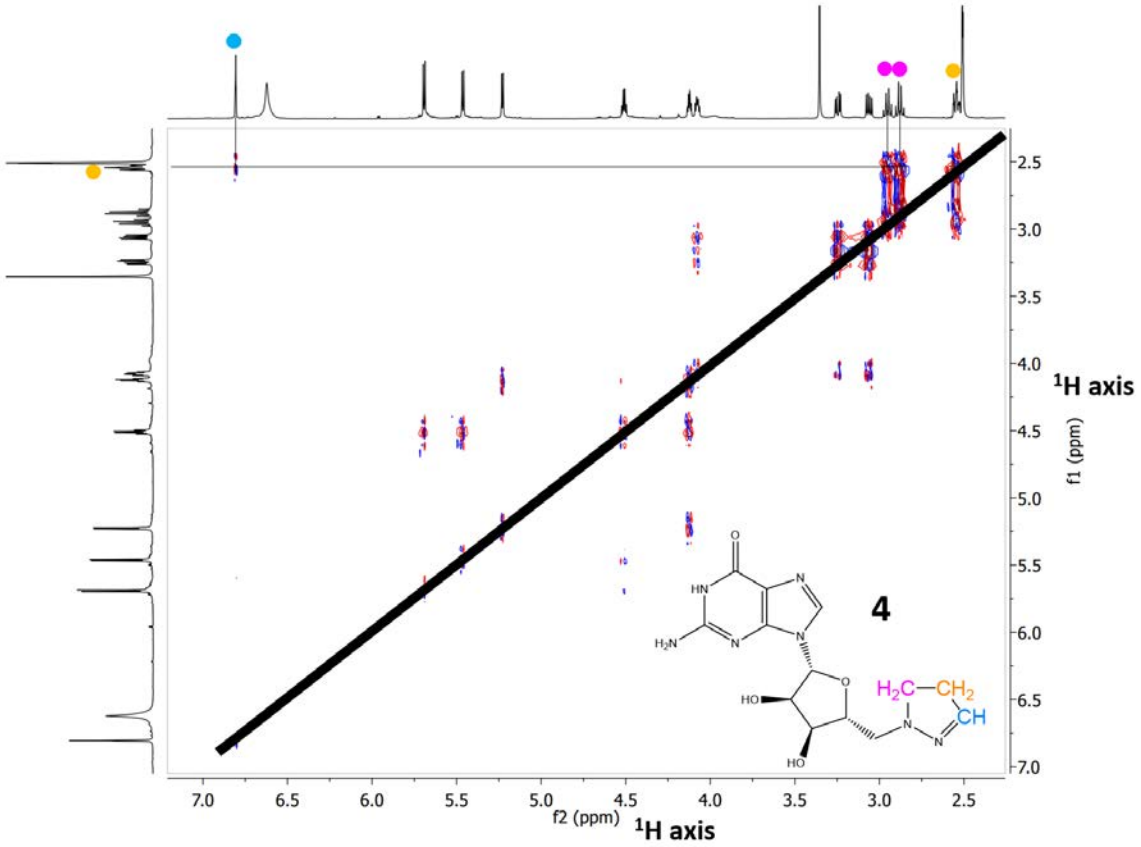


Figure S5: ^{1}H-^{1}H COSY spectrum of **4**. The signal for the CH_2 group at δ 2.51 ppm (orange dot) has correlation peaks with both the triplet at δ 6.81 ppm (blue dot) and the multiplet CH_2 at δ 2.90 ppm (pink dot). Combining this data with the HSQC spectrum in **Figure S4**, a CH_2-CH_2-CH linkage can be identified in pyrazoline **4**.

Mass Spectrometry Procedure: 0.1 mL DMSO-d_6 solution of the freeze-dried hydrazine **2** or hydrazide **3** hydrogel (2 wt%, 0.5 eq KCl) after uptake of electrophile was diluted with 0.5 mL H_2O and then injected into the JEOL AccuTOF-CS Spectrometer.

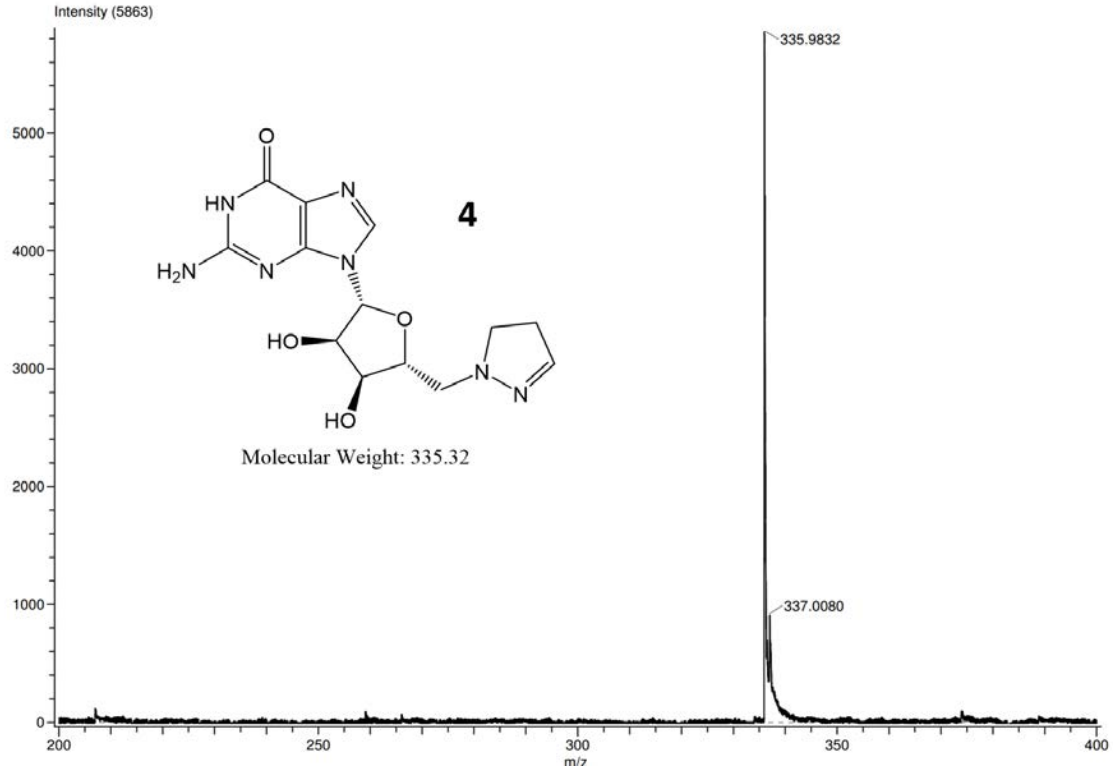


Figure S6: ESI-MS of pyrazoline **4**. No peak corresponding to the precursor hydrazine **3** (mw =297.28) was detected.

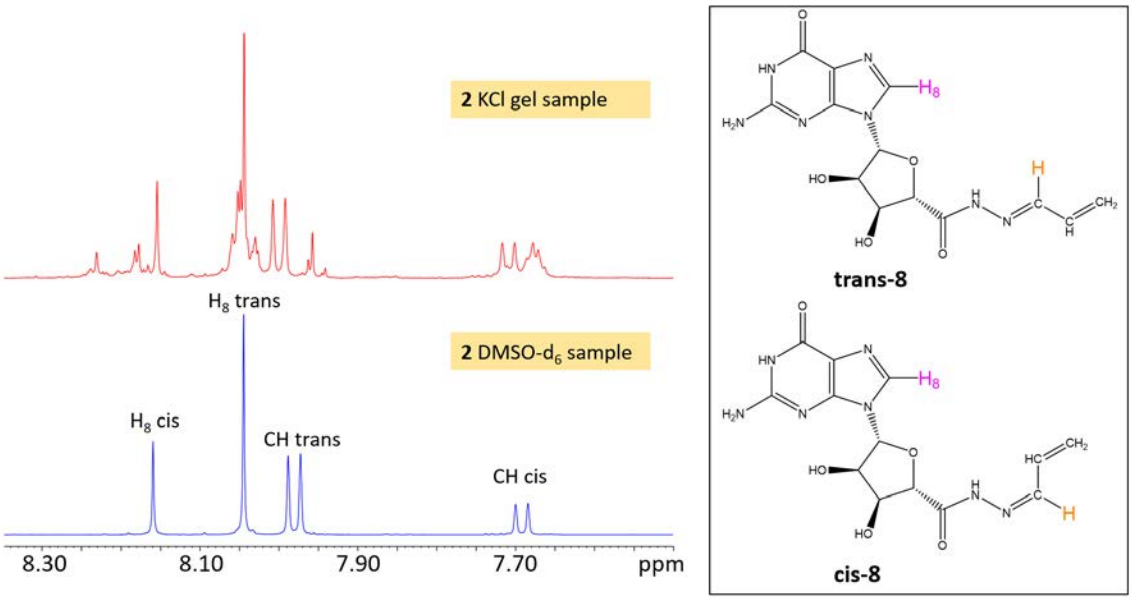


Figure S7: Top: A region of the ^{1}H NMR spectrum of reaction products formed by gas phase uptake of 1.0 eq of AC by the G_4•K^+ hydrogel made from 5′-hydrazidoguanosine **2** (2 wt%, 65 mM, 0.5 eq KCl) shows formation of a cis/trans mixture of acylhydrazones **8** and some cyclic adduct **9** (see also **Figure S8**). The region of the spectrum shown contains H_8 (pink) and the acylhydrazone CH (orange) in the acylhydrazones **8**. Bottom: The spectrum of a sample obtained by performing a gas phase uptake of 1.0 eq of AC with a 2 wt% solution of **2** in DMSO-d_6 for 2 days at RT. This sample gives a cleaner spectrum that shows formation of only cis/trans hydrazones **8**. All NMR signals were unambiguously assigned using 2D ^{1}H, ^{1}H-COSY and ^{1}H, ^{13}C-HSQC spectra (not shown).

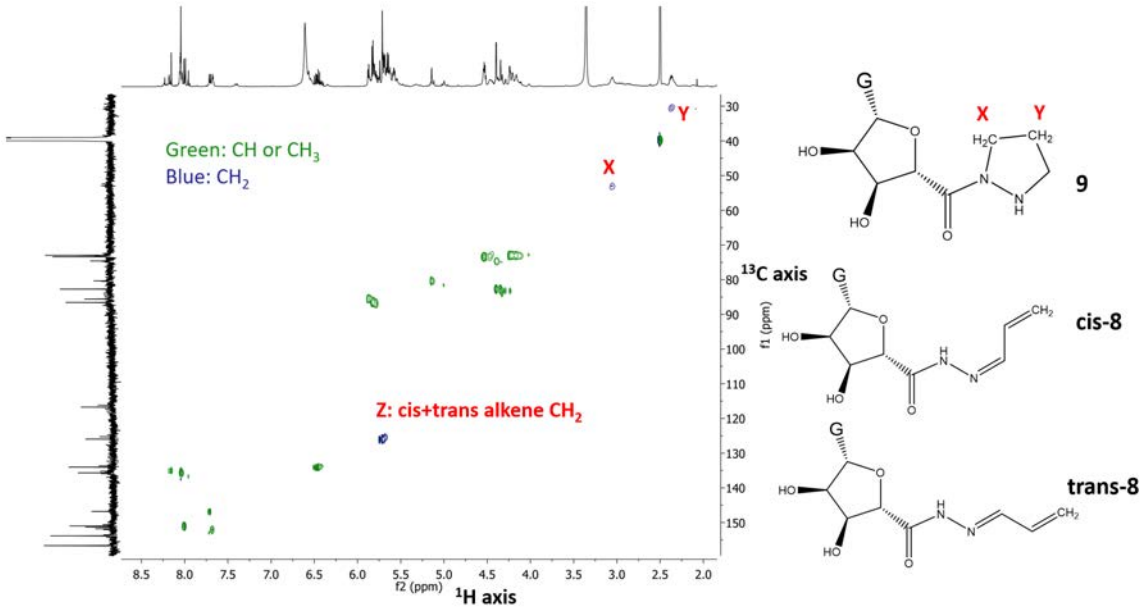


Figure S8: ^{1}H-^{13}C HSQC spectrum of reaction products formed by gas phase uptake of 1.0 eq of AC by the G_4•K^+ hydrogel made from 5′-hydrazidoguanosine **2** (2 wt%, 65 mM, 0.5 eq KCl) shows formation of a cis/trans mixture of acylhydrazones **8** and some cyclic adduct **9** (see also **Figure S8**). Blue crosspeaks represent CH_2 groups while green crosspeaks represent CH or CH_3 groups. Three CH_2 signals are identified: X and Y result from a CH_2-CH_2 linkage in the cyclic adduct **9** (a crosspeak is observed between X and Y in the ^{1}H, ^{1}H-COSY spectrum in **Figure S9**), while the crosspeak Z represents 2 different terminal alkenes, namely the acylhydrazones cis-**8** and trans-**8**, which show 2 separate ^{13}C signals peaks (f1) at δ ~126 ppm.

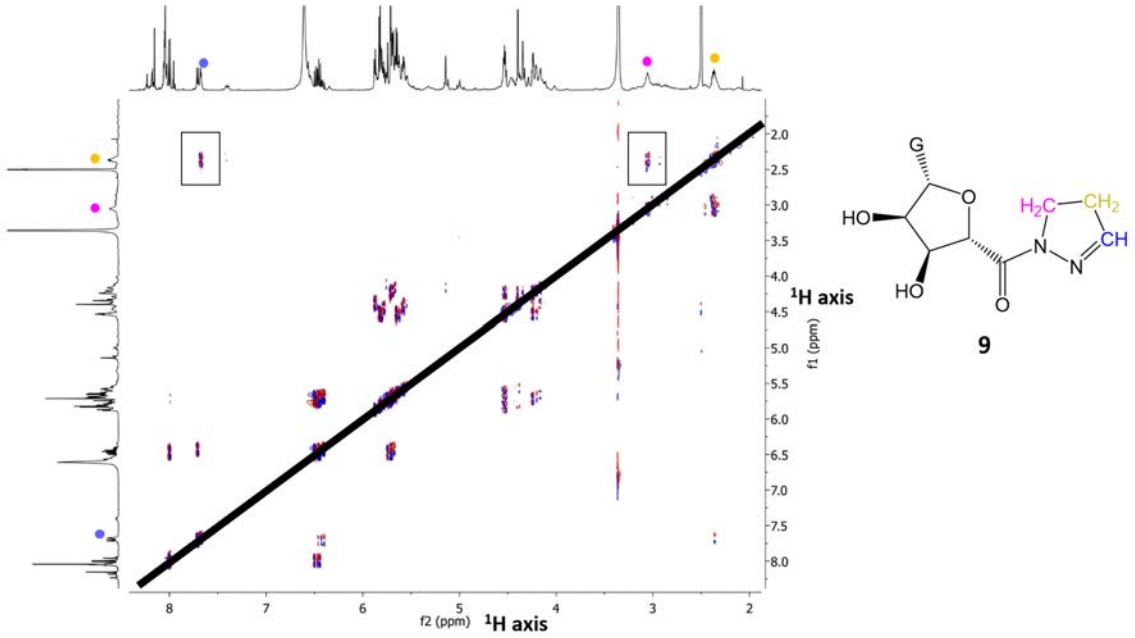


Figure S9: ^{1}H-^{1}H COSY spectrum of reaction products formed by gas phase uptake of 1.0 eq of AC by the G_4•K^+ hydrogel made from 5′-hydrazidoguanosine **2** (2 wt%, 65 mM, 0.5 eq KCl) shows a CH_2-CH_2-CH linkage (yellow CH_2 has crosspeaks with both pink CH_2 and blue CH), indicating formation of cyclic acylhydrazone **9**.

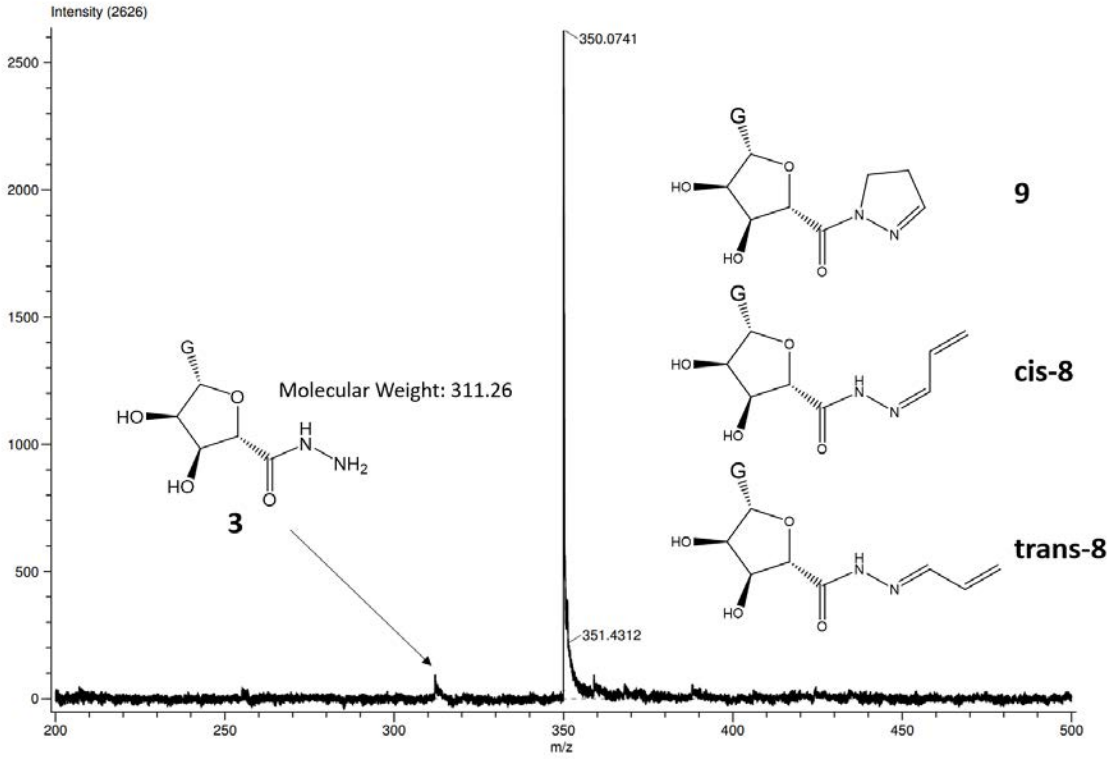


Figure S10: ESI-MS shows dehydration products formed between 1.0 eq of AC and the $G_4 \bullet K^+$ hydrogel made from 5′-hydrazidoguanosine **2** (2 wt%, 65 mM, 0.5 eq KCl). The major signal at m/z=350.07 is consistent with the structures of the 2 acyclic acylhydrazones (cis/trans-**8**) and the cyclic acylhydrazones **9**. A small amount of unreacted hydrazide **3** is also found at m/z=312.13.

This following experiment shows that AC in the solution is taken up ***from the solution***:

Procedure for aqueous phase uptake of AC by G_4•K^+ hydrogels: Hydrogels made from either 5′-hydrazidoguanosine **2** or 5′-hydrazinoguanosine **3** (2 wt%, 0.5 eq KCl) in D_2O were prepared according to the general preparation method. The G_4•K^+ hydrogel made from guanosine **1** (2 wt%, 72 mM) and $KB(OH)_4$ (0.5 equiv) was prepared according to literature procedure.[3] After heating the mixtures to boiling we then added 0.5 mL of the hot solutions into a parafilm-lined mold and allowed the solution to cool at RT for 1 h. The resulting hydrogels were then placed into a vial containing 5 mL of 155 mM KCl in D_2O that contained AC (3.37 mM, overall 0.5 eq of AC relative to the amount of nucleoside **1**-**3** in the hydrogel). Aliquots of the solution (0.6 mL) were removed periodically into a small vial and 10 μL of a 200 mM internal standard (3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt in D_2O) was added to each vial. These solutions were well mixed and transferred to NMR tubes after which ^{1}H NMR spectra were acquired (32 scans). The integration of the internal standard was set to 1.0 and the integration of the three olefin peaks in the AC (~ 6.5 ppm) was used for quantification. Experiments were done in triplicate. The amount of AC in solution at ***t*** hour was determined according to the following equation:

$$\frac{\text{AC } integration(\boldsymbol{t})}{\text{AC } integration(\boldsymbol{0\ h})} \times 100\%$$This following experiment shows that AC in the solution is ***taken up into the 3•KCl hydrogel:***

Procedure for AC Binding with 3•KCl Hydrogel in Aqueous Phase: 2 wt% hydrazine **3** (68 mM) hydrogels with 2.0 eq KCl were prepared according to the general gel preparation method in H_2O. 0.5 mL of the hot gels were then pipetted into a parafilm mold and allowed to cool at room temperature for 1 h. The hydrogels were then placed into a vial containing 5 mL of freshly prepared H_2O solution of AC (3.37 mM, overall 0.5 eq relative to the amount of hydrazine **3** in the gel) in 155 mM KCl. After 4 hours, the vial was gently shaken and the outside solution was removed. Then another 5 mL of 155 mM KCl solution was added to the vial in order to rinse the hydrogel. The solution was completely removed and the remaining hydrogel was lyophilized, dissolved in DMSO-d_6 and studied by ^{1}H NMR.

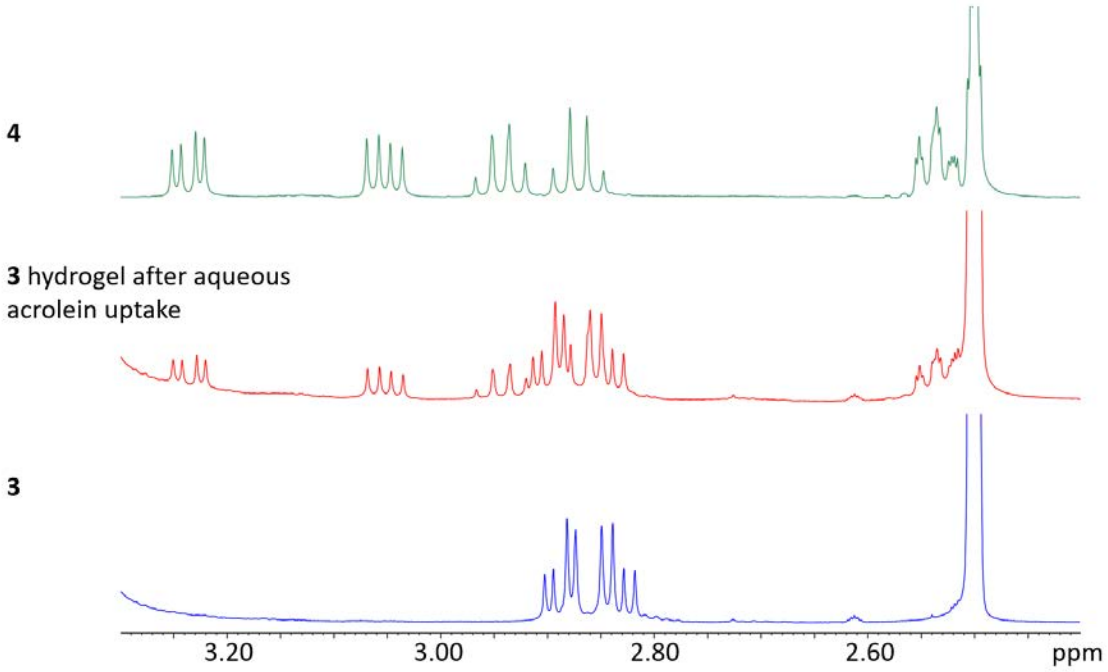


Figure S11: Acrolein reacts with the G_4•K^+ hydrogel containing hydrazine **3** (2 wt%, 68 mM, 2 eq KCl) in aqueous solution by forming the cyclic pyrazoline **4**. ^{1}H NMR of the lyophilized gel (middle) shows peaks for both pyrazoline **4** (top) and unreacted hydrazine **3** (bottom). This experiment shows that AC is taken up from the solution into the hydrogels.

Section on Methyl Vinyl Ketone (MVK) Uptake

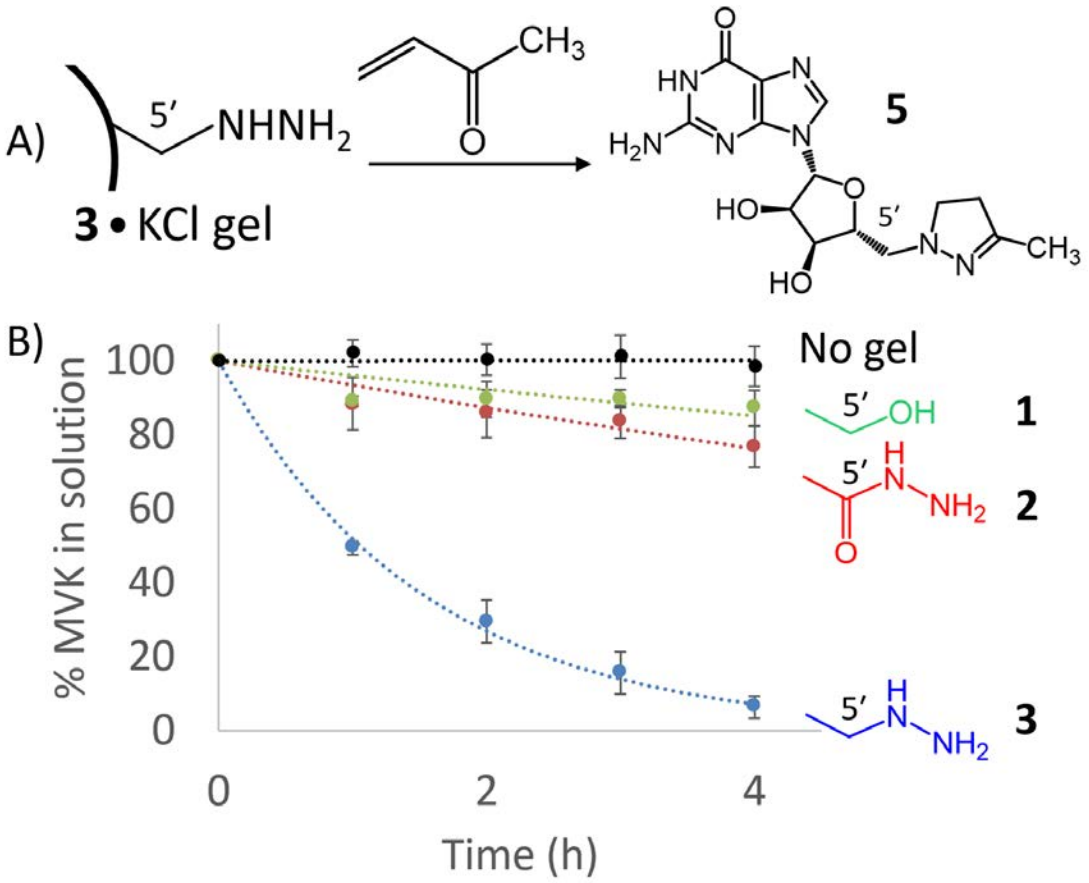
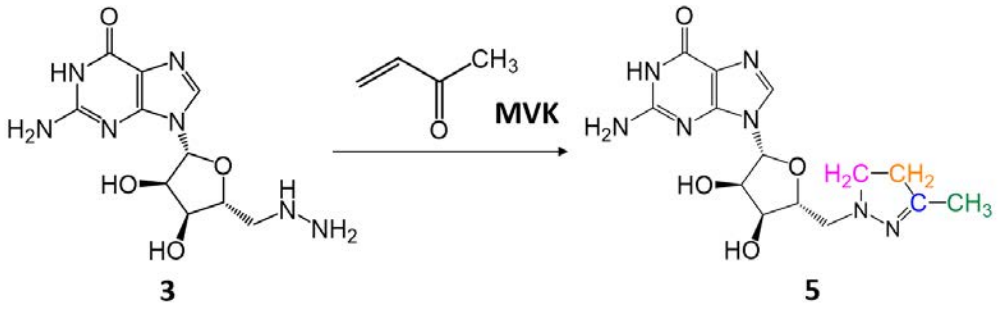


Fig. S12. A) Pyrazoline **5** from Michael addition/cyclization of **MVK** with hydrazine **3** $G_4•K^+$ hydrogel. B) % **MVK** (3.37 mM) in 5 mL solution of 155 mM KCl in D_2O, pD 6.3 after addition of hydrogels (0.5 mL, 68 mM) made from **1-3**.



5′-deoxy-5′-methylpyrazolinoguanosine **5**. ^{1}H NMR (DMSO-d_6): δ 1.86 (3 H, s, CH_3), 2.45-2.50 (2 H, m, CH_2), 2.84-2.98 (2 H, m, CH_2), 2.91-2.98 (1 H, dd, 5′-CH_2), 3.10-3.16 (1 H, dd, 5″-CH_2, J=7.7 Hz, J=5.3 Hz), 4.05 (1 H, m, 4′-CH), 4.11 (1 H, m, 3′-CH), 4.50 (1 H, m, 2′-CH), 5.20 (1 H, d, J=5.0 Hz, 3′-OH), 5.43 (1 H, d, J=6.0 Hz, 2′-OH), 5.67 (1 H, d, J=6.0 Hz, 1′-CH), 6.60 (2 H, s, NH_2), 7.91 (1 H, s, 8-CH), 10.76 (1 H, s, br, N1H), ^{13}C NMR (DMSO-d_6) δ: 15.70, 36.61 (CH_2), 55.00 (CH_2), 58.84 (C5′), 71.61 (C4′), 72.74 (C2′), 82.59 (C3′), 86.23 (C1′), 116.68 (C5), 135.63 (C8), 151.44 (C4), 151.45 (C4), 153.75 (C2), 156.69 (C6); ESI-MS m/z=350.13 (MW of **5**: 349.35)

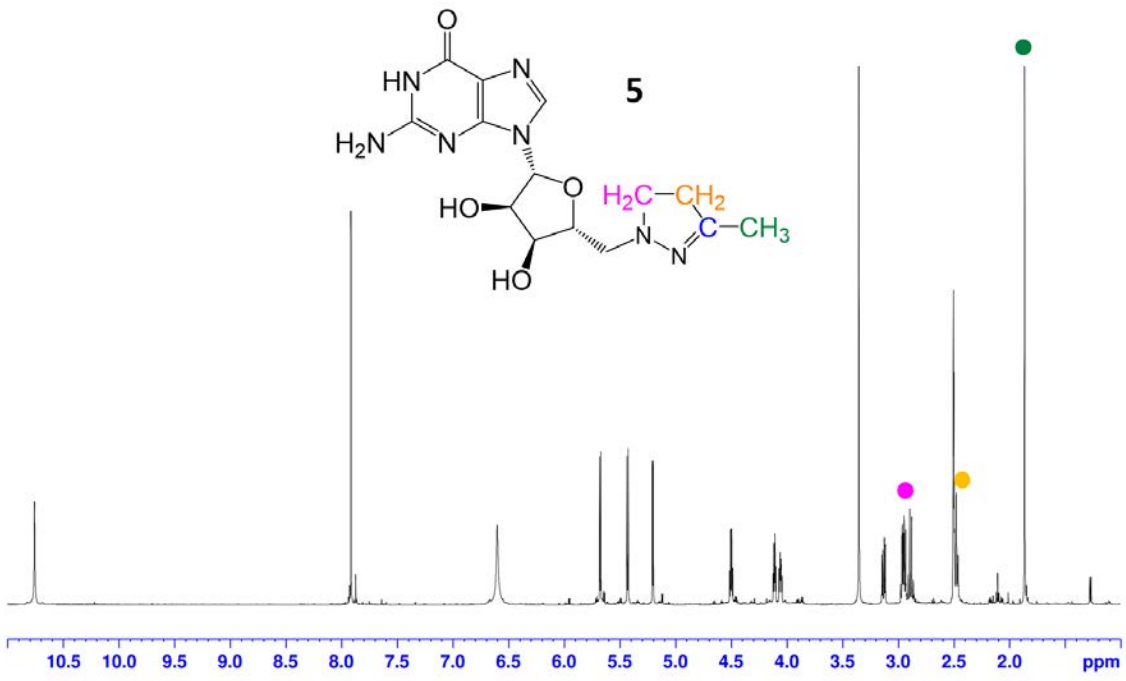


Figure S13: ^{1}H NMR spectrum of methylpyrazoline **5**.

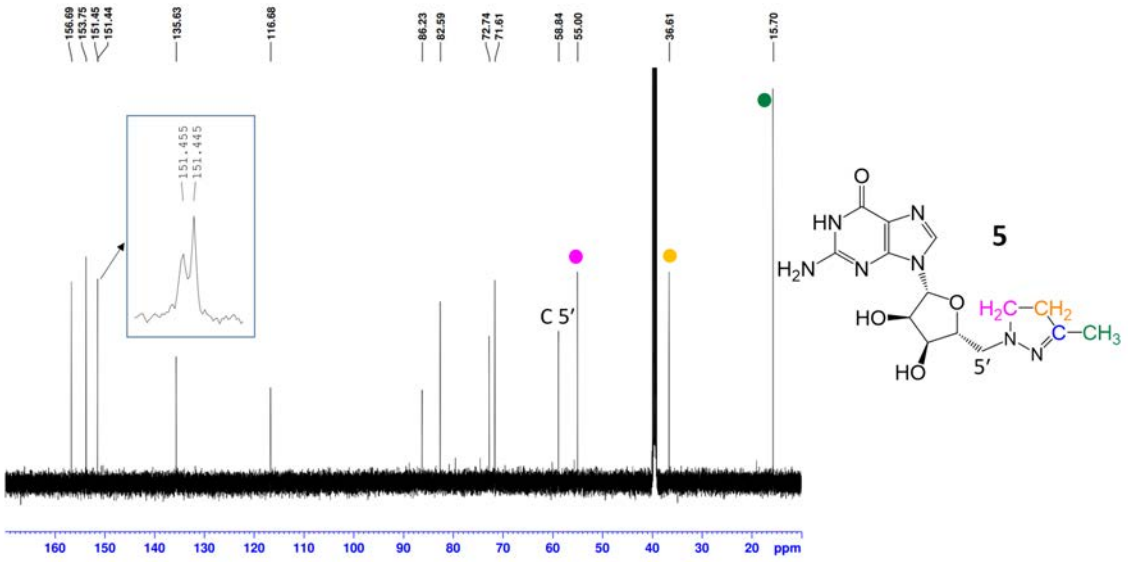


Figure S14: The ^{13}C NMR spectrum for methylpyrazoline **5** shows 14 peaks, consistent with the formation of an adduct between 5′-hydrazinoguanosine **3** and MVK. Inset shows two overlapping peaks at δ 151.45.

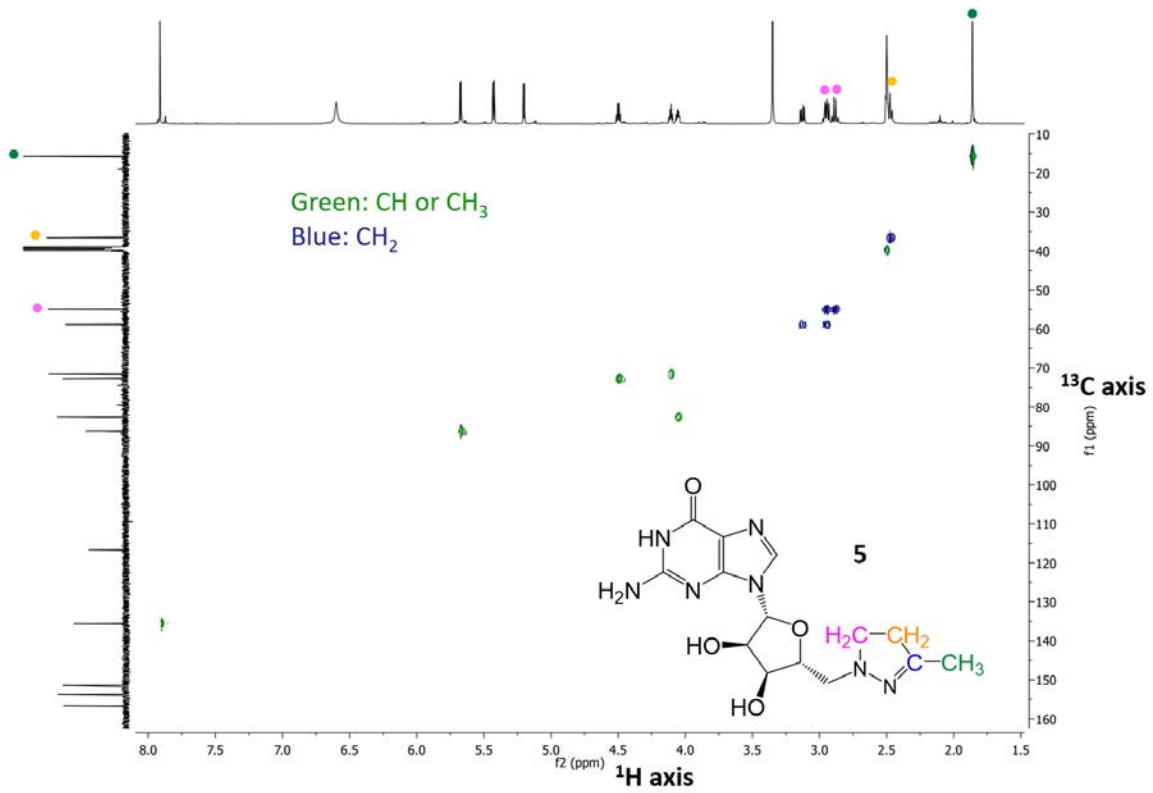


Figure S15: ^{1}H-^{13}C HSQC spectrum of methylpyrazoline **5**. The blue crosspeaks represent CH_2 groups while green crosspeaks represent CH or CH_3 groups. NMR signals for the CH_2 groups in the 5′-pyrazoline ring are indicated by colored dots (pink and orange).

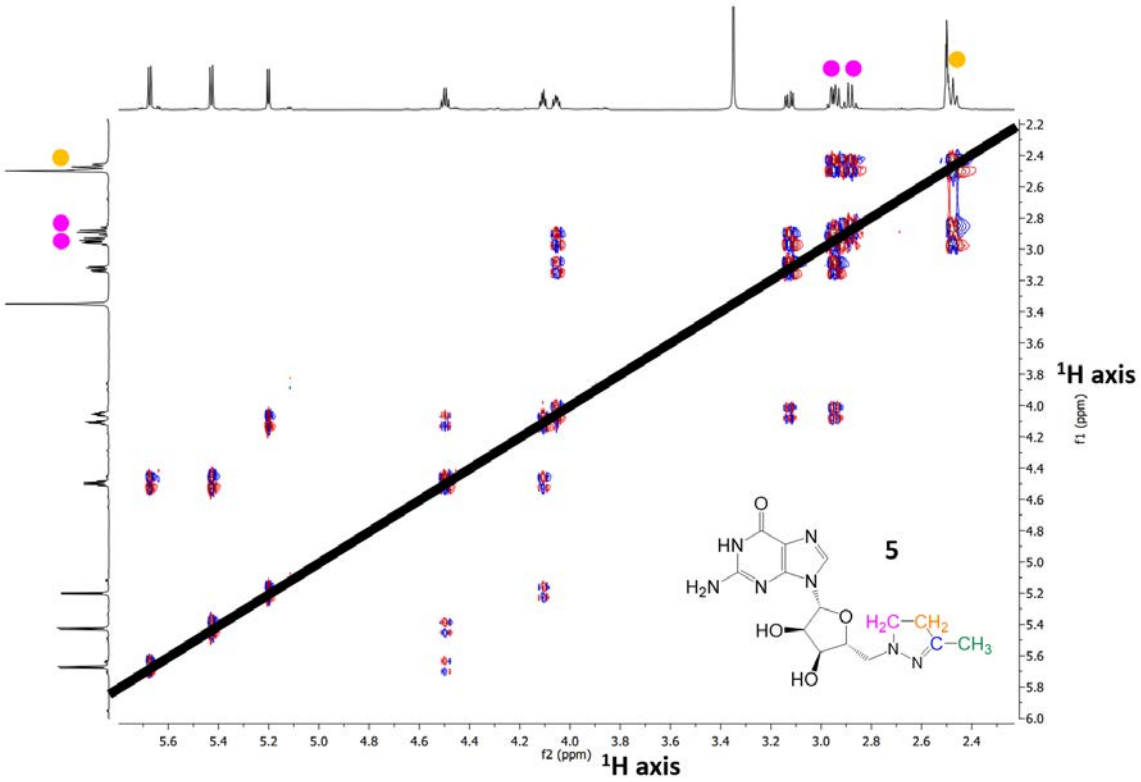


Figure S16: ^{1}H-^{1}H COSY spectrum of methylpyrazoline **5**. Combining this data with the HSQC spectrum in **Figure S14**, a CH_2-CH_2 linkage (pink and yellow) for the pyrazoline ring can be identified.

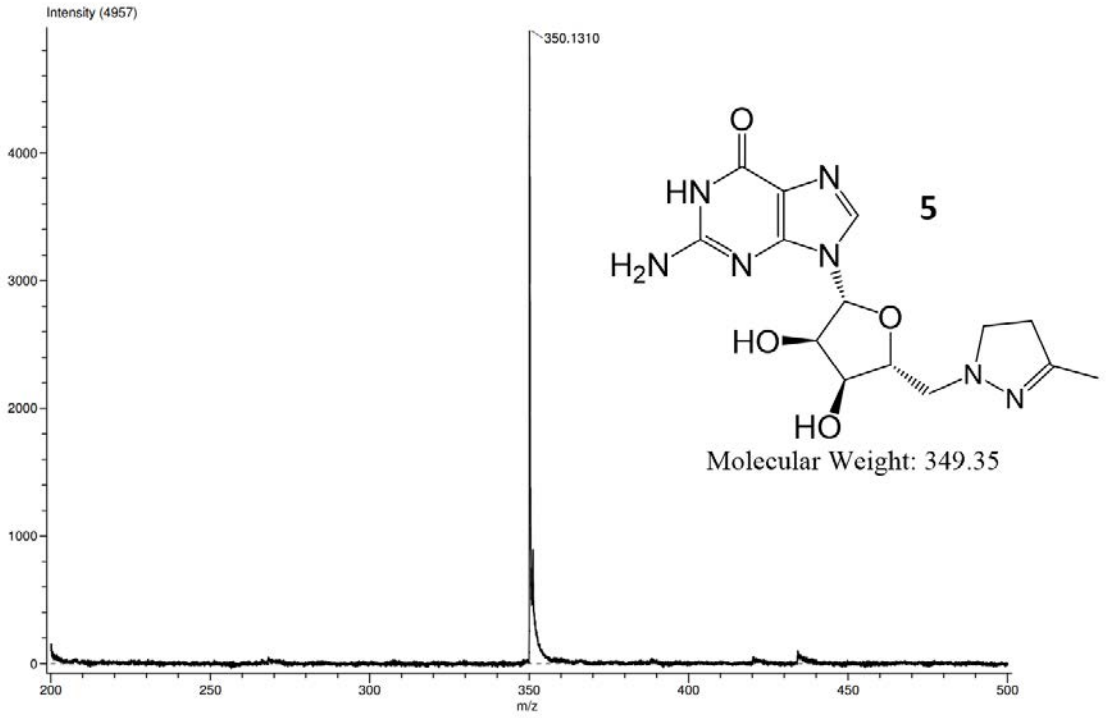


Figure S17: ESI-MS spectrum of methylpyrazoline **5**. No peak corresponding to hydrazine **2** (MW=297.28) was detected.

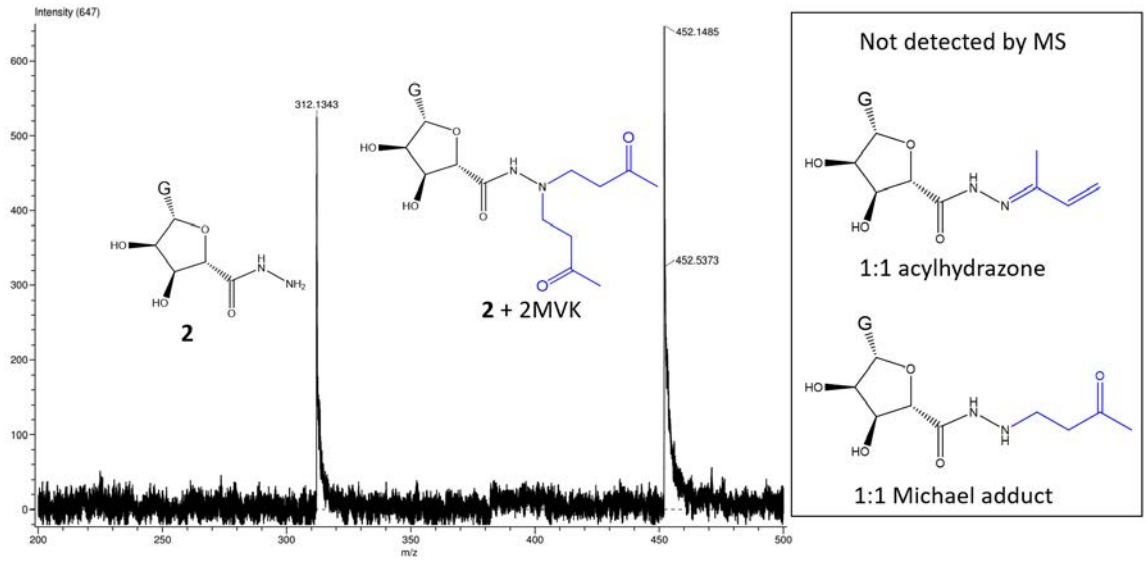


Figure S18: ESI-MS of gas-phase uptake reaction between 1.0 eq of MVK and the $G_4 \bullet K^+$ hydrogel containing hydrazide **2** (2 wt%, 65 mM, 0.5 eq KCl). Only peaks for unreacted **2** (m/z=312.13) and 1:2 Michael adduct (m/z=452.15) are observed. Signals for the 1:1 Michael adduct and 1:1 acylhydrazone adduct are not observed. A putative structure is shown for the 1:2 adduct. Addition of the first MVK molecule would likely increase the nucleophilicity of the terminal nitrogen, leading to a second Michael addition.

This following experiment shows that MVK in the solution is taken up ***from the solution***:

Procedure for aqueous phase uptake of MVK by G_4•K^+ hydrogels: Hydrogels made from either 5′-hydrazidoguanosine **2** or 5′-hydrazinoguanosine **3** (2 wt%, 0.5 eq KCl) in D_2O were prepared according to the general preparation method. The G_4•K^+ hydrogel made from guanosine **1** (2 wt%, 72 mM) and $KB(OH)_4$ (0.5 equiv) was prepared according to literature procedure.[3] After heating the mixtures to boiling we then added 0.5 mL of the hot solutions into a parafilm-lined mold and allowed the solution to cool at RT for 1 h. The resulting hydrogels were then placed into a vial containing 5 mL of 155 mM KCl in D_2O that contained MVK (3.37 mM, overall 0.5 eq of MVK relative to the amount of nucleoside **1-3** in the hydrogel). Aliquots of the solution (0.6 mL) were removed periodically into a small vial and 10 μL of a 200 mM internal standard (3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt in D_2O) was added to each vial. These solutions were well mixed and transferred to NMR tubes after which ^{1}H NMR spectra were acquired (32 scans). The integration of the internal standard was set to 1.0 and the integration of the three olefin peaks in the MVK (~ 6.5 ppm) was used for quantification. Experiments were done in triplicate. The amount of MVK in solution at ***t*** hour was determined according to the following equation:

$$\frac{\text{MVK } integration(\boldsymbol{t})}{\text{MVK } integration(\boldsymbol{0\ h})} \times 100\%$$

This following experiment shows that MVK in the solution is taken up ***into 3•KCl hydrogel***:

Procedure for MVK Binding with 3•KCl Hydrogel in Aqueous Phase: 2 wt% hydrazine **3** (68 mM) hydrogels with 2.0 eq KCl were prepared according to the general gel preparation method in H_2O. 0.5 mL of the hot gels were then pipetted into a parafilm mold and allowed to cool at room temperature for 1 h. The hydrogels were then placed into a vial containing 5 mL of freshly prepared H_2O solution of MVK (3.37 mM, overall 0.5 eq relative to the amount of hydrazine **3** in the gel) in 155 mM KCl. After 4 hours, the vial was gently shaken and the outside solution was removed. Then another 5 mL of 155 mM KCl solution was added to the vial in order to rinse the hydrogel. The solution was completely removed and the remaining hydrogel was lyophilized, dissolved in DMSO-d_6 and studied by ^{1}H NMR.

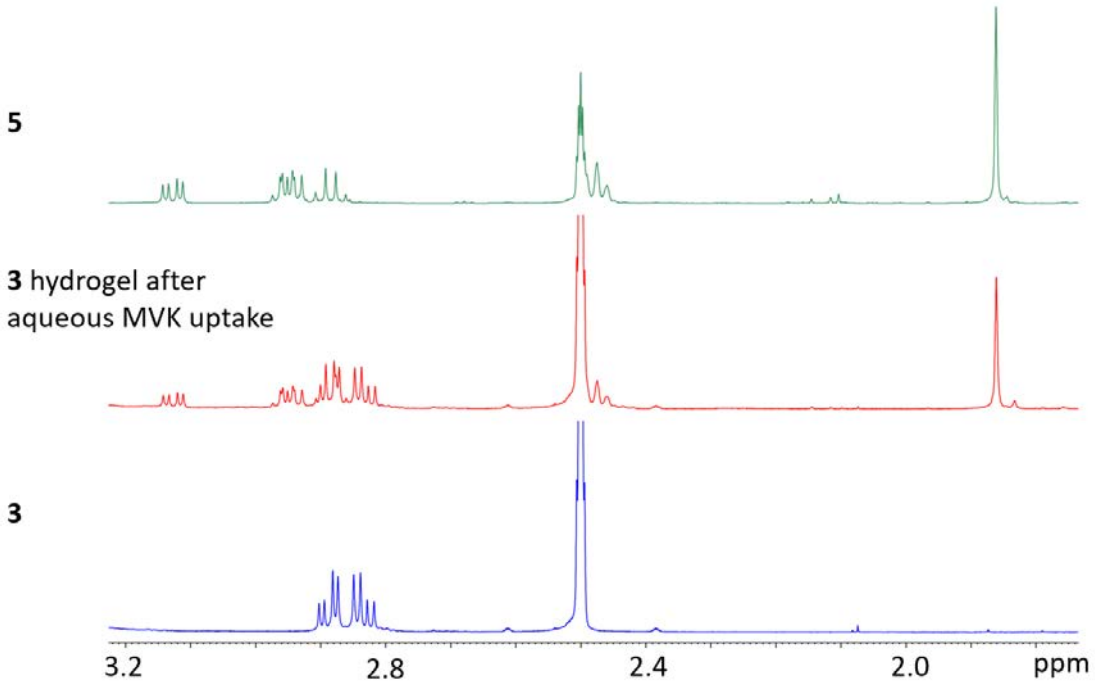


Figure S19: Methyl vinyl ketone (MVK) reacts with the G_4•K^+ hydrogel containing hydrazine **3** (2 wt%, 68 mM, 2 eq KCl) in aqueous solution by forming the cyclic pyrazoline **4**. ^{1}H NMR of the lyophilized gel (middle) shows peaks for both methylpyrazoline **5** (top) and unreacted hydrazine **3** (bottom).

Section on Methyl Acrylate (MA) Uptake

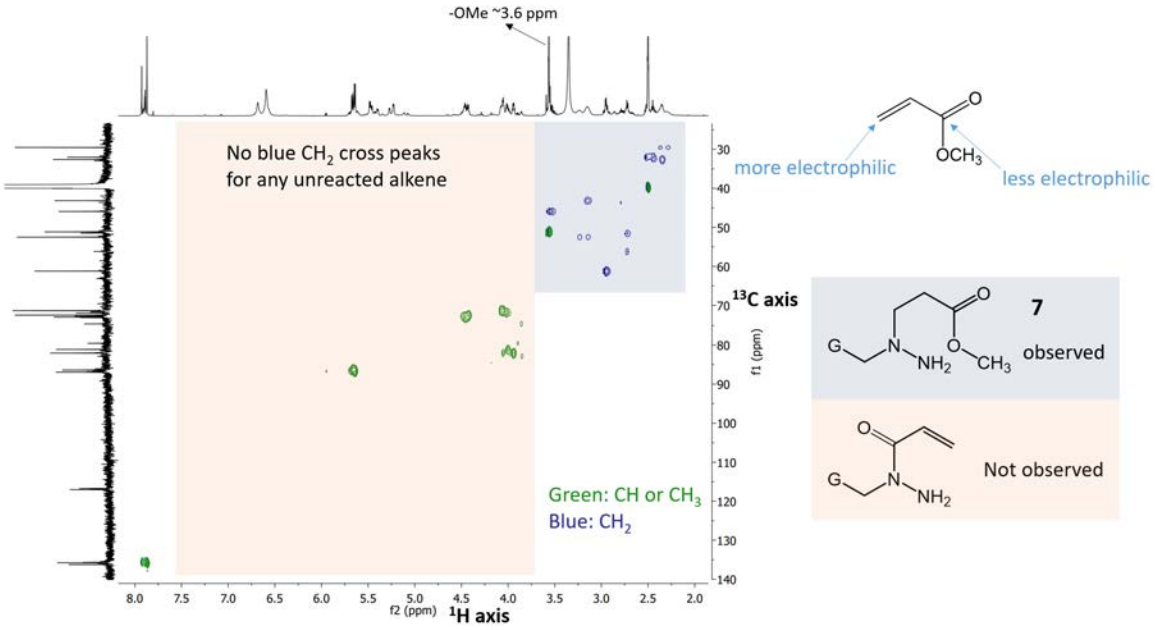


Figure S20: ^{1}H-^{13}C HSQC spectrum of reaction products formed by gas phase uptake of 1.0 eq of MA by the $G_4 \bullet K^+$ hydrogel made from 5′-hydrazinoguanosine **3** (2 wt%, 68 mM, 0.5 eq KCl) shows that the Michael acceptor end of MA has all reacted to form **7**. Blue crosspeaks represent CH_2 groups while green crosspeaks represent CH or CH_3 groups. In the pink region (from δ 3.7-7.5 ppm) where alkene protons are expected, no CH_2 crosspeaks for unreacted terminal alkene (-CH=CH_2) are found. Meanwhile, multiple CH_2 crosspeaks are identified in the blue region (from δ 2.0-3.7 ppm), indicating different sp^3 CH_2 groups in the resulting adducts. Also, the -OMe peaks around δ 3.6 ppm shows that cyclization must be a slower step than Michael addition. This result indicates that the Michael acceptor of MA is more electrophilic than the ester end (inset) toward hydrazine **3**.

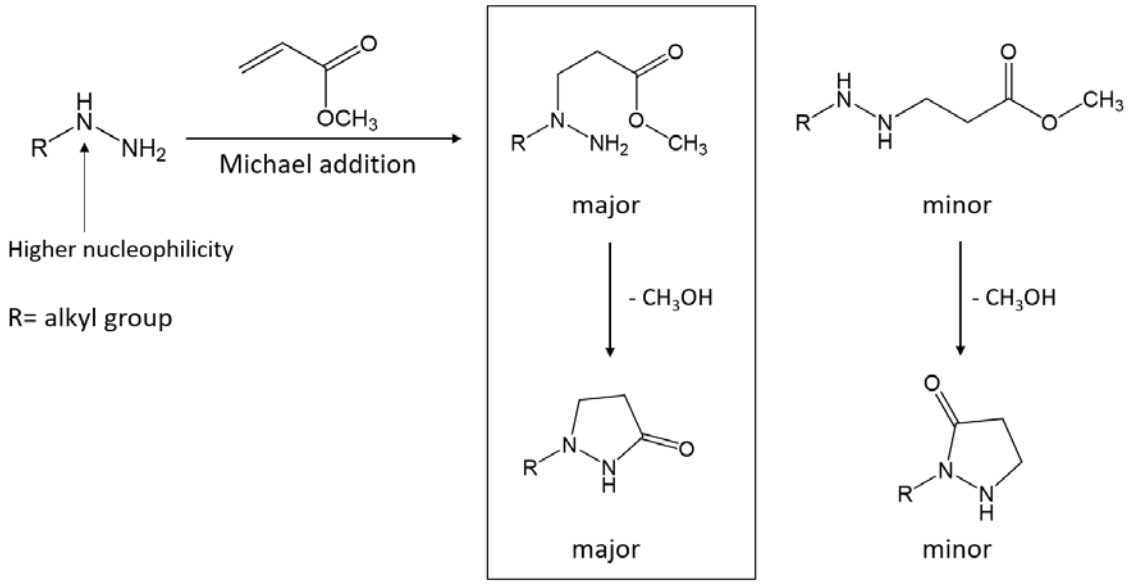


Figure S21: Proposed product distribution of 1:1 adduct between hydrazine **3** and MA. Due to the higher nucleophilicity of the alkylated nitrogen of hydrazine,[4] the 1,1-dialkyl hydrazine product (in the box) is favored during absorption, which influences the regioselectivity of linear and cyclic products.

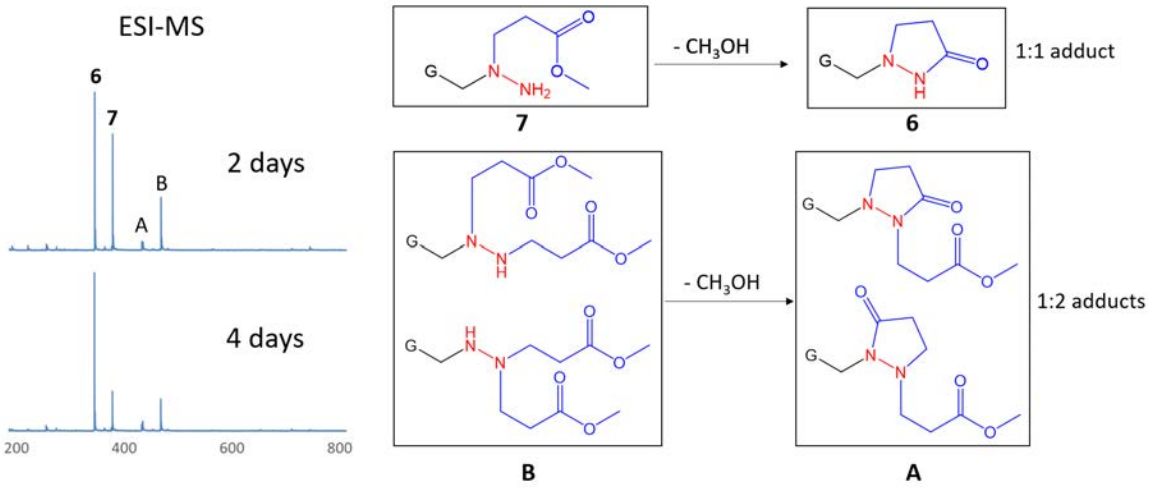


Figure S22: (left) ESI-MS spectra of hydrazine **3** hydrogel (2 wt%, 0.5 eq KCl) after 2 and 4 days of MA uptake (1.0 eq) from the gas phase at room temperature. (right) Structures of adducts formed in this reaction. MS shows that 1:1 acyclic adduct **7** (m/z=384.01) is slowly converted into cyclic adducts **6** (m/z=352.00), by losing a molecule of methanol (mw=32). Small amounts of 1:2 adducts, labeled **A** and **B**, were also observed (**A**: m/z=438.02; **B**: m/z=470.06).

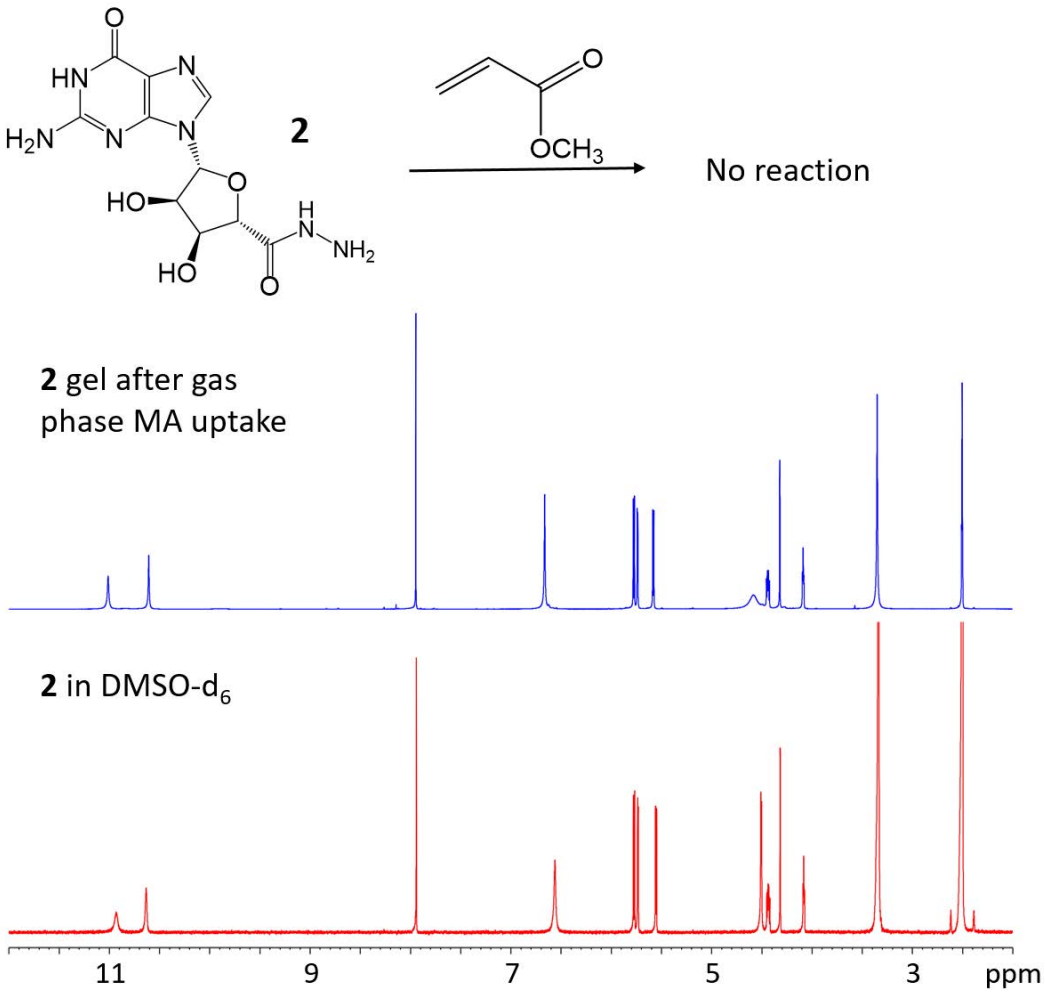


Figure S23: ^{1}H NMR shows no reaction of MA with hydrazide **2** gel (2 wt%, 0.5 eq KCl) after 2 days at RT. The gel was lyophilized and dissolved in DMSO-d_6. This result shows that hydrazide **2** hydrogel is far less reactive toward MA than it is toward AC or MVK.

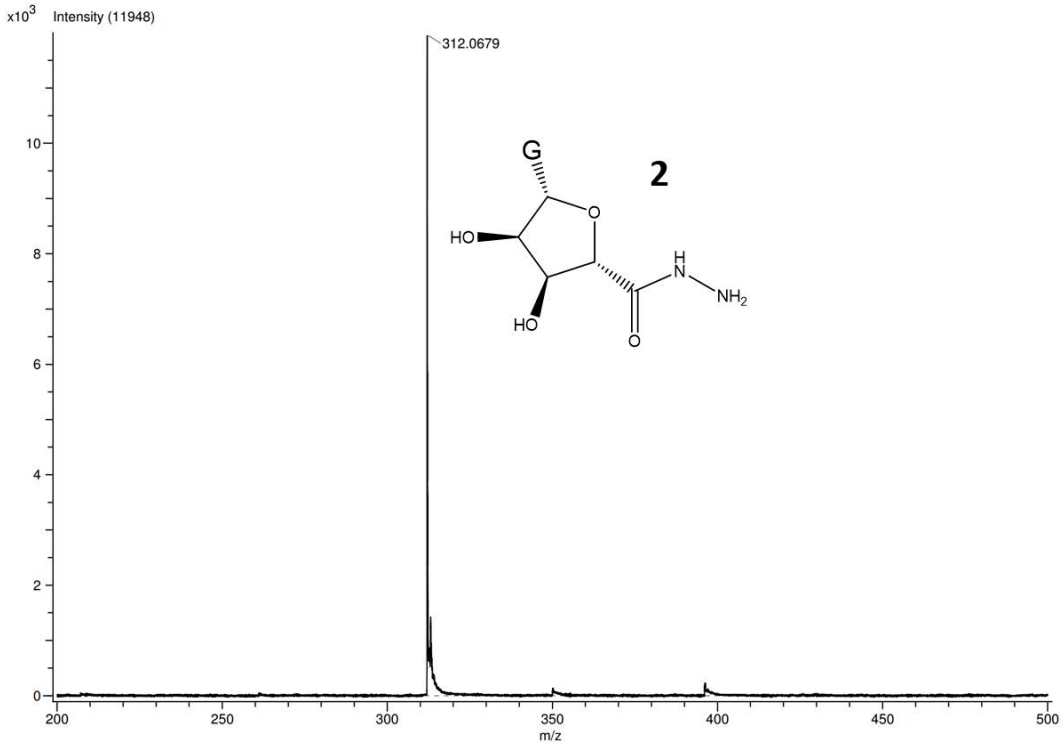


Figure S24: ESI-MS shows no covalent adduct formation between hydrazide **2** hydrogel (2 wt%, 0.5 eq KCl) and MA in gas phase uptake experiments after 2 days at RT.

Procedure for aqueous phase uptake of MA by G_4•K^+ hydrogels: 2 wt% G **3** (68 mM) and G **2** (65 mM) hydrogels with 2.0 eq KCl were prepared according to the general gel preparation method in D_2O. 0.5 mL of the hot gels were then pipetted into a parafilm lined mold and allowed to cool at room temperature for 1 h. A MA solution in 155 mM D_2O solution without any hydrogels served as a blank control. The hydrogels were then placed into a vial containing 5.5 mL of freshly prepared D_2O solution of MA (3.37 mM, overall 0.5 eq relative to the amount of G **3** in the gel) in 155 mM KCl. Before the addition of hydrogels (t=0 h), 0.5 mL of MA solution was pipetted into a vial which was used for NMR experiments at t=0 h. After 24 h of incubation at room temperature, the vials were gently shaken before 0.5 mL of the outside solution (0.5 mL) were removed into a small vial and 10 μL of a 200 mM internal standard (3-(trimethylsilyl)propionic-2,2,3,3-d_4 acid sodium salt in D_2O) was added to each vial. The solutions were well mixed and transferred to NMR tubes after which ^{1}H NMR spectra were acquired (16 scans). The integration of internal standard was set to 1.0 and the integration of three olefin peaks (~ 6.5 ppm) was used for quantification. Experiments were done in triplicates. The amount of MA in solution at 24 h was determined according to the following equation:

$$\frac{\text{MA } integration(\mathbf{24}\ \boldsymbol{h})}{\text{MA } integration(\mathbf{0}\ \boldsymbol{h})} \times 100\%$$

The % MA that disappeared in the blank is subtracted from samples containing G **3** and G **2** hydrogels.

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