Supporting Information

Targetable Mechanical Properties by Switching between Self-Sorting and Co-assembly with In Situ Formed Tripodal Ketoenamine Supramolecular Hydrogels

Jamie S. Foster, Andrew W. Prentice, Ross S. Forgan, Martin J. Paterson, and Gareth O. Lloyd*

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Targetable mechanical properties by switching between self-sorting and co-assembly with \textit{in-situ} formed tripodal ketoenamine supramolecular hydrogels

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1.0 Technical Details

All references in this SI document refer to the reference list of the main manuscript.

1.1 Chemical list

Chemicals were obtained from the following and used as supplied.

Trifluoroacetic acid – Fluorochem

Hexamethylenetetramine, Glucono-\(\delta\)-lactone (GdL), 4-amino-2-methoxybenzoic acid, 5-amino-2-chlorobenzoic acid, 4-amino-2-methylbenzoic acid, 4-amino-3-hydroxybenzoic acid – Alfa Aesar

Phloroglucinol, 6-aminohexanoic acid, 4-aminobenzoic acid, 3-amino-2-methoxybenzoic acid, 3-amino-4-hydroxybenzoic acid, 4-aminophenol – Sigma Aldrich

4-amino-2-fluorobenzoic acid, 3-amino-5-(trifluoromethyl)benzoic acid – Apollo Scientific

Deuterium oxide (D\(_2\)O), d\(_6\)-dimethylsulfoxide (d\(_6\)-DMSO) – Cambridge isotope laboratories

Dichloromethane (DCM), ethanol. sodium hydroxide pellets, hydrochloric acid – Fisher Chemical

1.2 Powder X-Ray Diffraction:

PXRD patterns were collected at room temperature using a Bruker D8 Advance powder diffractometer in reflectance mode. Lynxeye super speed detector was used with the radiation being monochromated Cu K\(\alpha\)1, with a characteristic wavelength of 1.541 Å. 30 minute scans over the range 5° ≤ 2θ ≤ 60° (stepsize = 0.014481°/counting time = 0.5 s/steps).

1.3 NMR:

NMR spectra were recorded on a Bruker AV 400 operating at 400.1 MHz for \(^1\)H, 282.4 MHz for \(^{19}\)F and 100.6 MHz for \(^{13}\)C experiments. All spectra were recorded using 10 -15 mg of sample in 0.6 ml of solvent. Spectra recorded in D\(_2\)O also feature the addition of NaOH (approximately 5 mg) to dissolve the sample unless otherwise stated.

1.4 SEM:

SEM images were produced using a Philips XL30 LaB6 ESEM equipped with an Oxford Instrument X-max 80 EDX detector at 3 kV. Wet gel samples were placed on carbon sticky tabs mounted on aluminium SEM stubs. Once mounted, samples were dried under dynamic vacuum (< 10 mBar) in a desiccator for 48 hours. These dried samples were given a thin coating of gold, to prevent charging effects during SEM imaging, by placing samples in a sputter coater for two minutes at 12 μA.

1.5 IR:

IR spectra were recorded on a Nicolet is5 instrument using 24 scans at a resolution of 1 cm\(^{-1}\) and data spacing of 0.964 cm\(^{-1}\).
1.6 Rheology:

Rheological experiments were performed on a Bohlin nano II rheometer. A 40 mm aluminium cone at 4° was used with an operating gap of 300 μm gap and a solvent trap. For all gels 5 ml of the solution was prepared and added to the plate with a syringe in the operating gap so the gel could form in contact with the cone.

1.6.1 Time sweep experiments: Commenced immediately upon addition and dissolution of the appropriate amount of GdL to the gelator solutions. All samples were recorded over 15 h at 20 °C with a torque of 100 μNm and a frequency of 1 Hz, data was taken every 30 s for a sampling time of 3 s. Some of the time sweeps show unusual abrupt changes; this was due to syneresis and partial drying of samples, which could not be removed experimentally by varying instrumental parameters.

1.6.2 Frequency sweep experiment: Performed immediately after the time sweep at 20 °C. The torque was kept constant at 100 μNm. Data was obtained for the Frequency sweep from 0.01 Hz to 100 Hz, as a log scale. We have chosen to plot the Frequency sweeps’ x axes not as log scales in this paper as the data overlapped too significantly at lower frequencies (which are always noisier) to convey clear differences in the materials’ properties.

1.6.3 Stress sweep experiments: Recorded after frequency sweep experiments. All samples were recorded at 20 °C and at a frequency of 1 Hz.

1.8 pH meter:

The pH meter used was a Mettler Toledo FiveEasy, a two point calibration was performed each morning.

1.9 Mass Spectrometry:

Mass spectrometry data were recorded using electrospray ionization (ESI) in negative mode using a Bruker micrOTOF instrument.
2.0 Synthetic Details and Compound Analysis

2.1 Synthesis of 1,3,5-triformylphloroglucinol (A)

![Figure S1. 1,3,5-triformylphloroglucinol (A).](image)

To a mixture of hexamethylenetetramine (22.2 g, 157.5 mmol, 2.2 equiv.) and phloroglucinol (9 g, 71.4 mmol, 1 equiv) trifluoroacetic acid (135 ml) was added, the solution was then heated to 100 °C and stirred under nitrogen for 2.5 h. To the reaction mixture 3 M HCl (300 ml) was slowly added with continued heating at 100 °C and stirred for 1 h. After being allowed to cool to room temperature the reaction mixture was filtered and the filtrate obtained was extracted with dichloromethane (5 × 100 ml) before being dried with MgSO₄. Once dry the dichloromethane was removed by rotary evaporation yielding an orange solid. This solid was washed with hot ethanol (3 × 100 ml) to yield a pale yellow free flowing powder. This powder was dried in the oven overnight to yield the final product I. The synthesis is a scaled up version of the synthesis presented by Chong et al.

2.1.1 Yield: 19%, 2.96 g (210.14 gmol⁻¹)

2.1.2 ¹H NMR(d₆-DMSO, J/Hz, δ/ppm): 14.13 (s, 3H, Ar-OH), 10.85 (s, 3H, CHO)

2.1.3 ¹³C NMR (CDCl₃, δ/ppm): 189.07 (-CHO), 178.43 (C-OH), 105.23 (C-aldehyde)

2.1.4 Elemental analysis: Calculated %C = 51.44, %H = 2.88 Found %C = 51.17, %H = 2.92

2.1.5 Melting point: 198-199 °C (literature mp: 198 – 200 °C)
2.2 *Ex Situ* Synthesis of gelators R₁ to R₉ inclusively

To a suspension of A (.250 mg, 1.19 mmol) in ethanol (50 ml) the appropriate amine was added (3.69 mmol, 3.1 molar equivalents) and the resultant suspension was refluxed for 16 hours. Once complete the reflux was cooled to room temperature then cooled to 0 °C, before the reaction mixture was filtered to obtain a yellow precipitate. The precipitate was washed with hot ethanol (5 × 50 ml) then dried overnight at 80 °C this produced the desired product at good yields and purity.

**Table S1 Reaction details for gelators R₁ to R₉ inclusively**

| Gelator | Amine                                | Mass of amine used (mg) | Mass yield (mg) | % yield | Molecular weight of gelator (g/mol⁻¹) |
|---------|--------------------------------------|-------------------------|-----------------|---------|---------------------------------------|
| R₁      | 4-aminobenzoic acid                  | 506                     | 561             | 83      | 567.50                                |
| R₂      | 5-amino-2-chlorobenzoic acid         | 633                     | 679             | 85      | 670.84                                |
| R₃      | 4-amino-2-methoxybenzoic acid        | 617                     | 618             | 79      | 657.58                                |
| R₄      | 4-amino-3-hydroxybenzoic acid        | 565                     | 659             | 90      | 615.50                                |
| R₅      | 3-amino-4-hydroxybenzoic acid        | 565                     | 645             | 88      | 615.50                                |
| R₆      | 3-amino-5-(trifluoromethyl)benzoic acid | 757                 | 725             | 79      | 771.50                                |
| R₇      | 3-amino-2-methoxybenzoic acid        | 617                     | 571             | 73      | 657.58                                |
| R₈      | 4-amino-2-methylbenzoic acid         | 558                     | 638             | 88      | 609.58                                |
| R₉      | 4-aminophenol                        | 403                     | 512             | 89      | 483.47                                |
2.3 Analysis of *ex situ* prepared gelators R₁ to R₉ inclusively

2.3.1 Gelator R₁

![Chemical structures of gelator R₁ showing both conformers C₁ (left) and C₂ (right).]

**Figure S2.** Gelator R₁ showing both conformers C₁ (left) and C₂ (right).

2.3.1.1 \(^{1}H\) NMR (d₆-DMSO, J/Hz, δ/ppm): 13.33 (d, J = 12.70, =CNH), 12.86 (dd, J = 11.47, 8.83, =CNH), 8.74 (d, J = 12.76, 3H, HC-N), 7.99 (d, J = 2.41, 6H, Ar-H), 7.58 (dd, J= 16.88, 8.16, 6H, Ar-H).

2.3.1.2 \(^{13}C\) NMR (D₂O, δ/ppm): 187.94, 187.58, 186.93, 175.75, 171.97, 149.75, 130.88, 130.58, 126.21, 116.75, 115.10, 112.05, 111.87, 107.32.

2.3.1.3 IR (cm\(^{-1}\)): 3065, 1712, 1623, 1595, 1570, 1455, 1427, 1304, 1229, 1175, 1100, 1034, 995, 847, 764, 686, 649, 635, 578.

2.3.1.4 HRMS: Calculated for [M-H] \(^{566.1205}\), C\(_{30}\)H\(_{20}\)N\(_{3}\)O\(_{9}\) found 566.1191.

2.3.1.5 Melting point: Compound decomposes upon heating (>300 °C).
2.3.2 Gelator R₂

Figure S3. Gelator R₂ showing both conformers C₁ (left) and C₅ (right).

2.3.2.1 \(^1\)H NMR (d₂-D₂O, J/Hz, δ/ppm): 9.51 (s, 3H, HC-N), 7.29 (s, 6H, Ar-H), 7.02 (s, 3H, Ar-H).

2.3.2.2 \(^{13}\)C NMR (D₂O, δ/ppm): 187.93, 187.42, 186.94, 175.88, 173.73, 147.88, 145.00, 139.76, 139.45, 138.06, 135.85, 131.22, 130.16, 126.68, 118.47, 117.35, 116.17, 114.87, 112.08, 106.01.

2.3.2.3 IR (cm⁻¹): 2987, 2589, 1725, 1605, 1568, 1548, 1444, 1409, 1340, 1294, 1270, 1228, 1121, 1037, 985, 890, 816, 763, 695, 665.

2.3.1.4 HRMS: Calculated for [M-H] - 668.0036, C₃₀H₁₇Cl₃N₃O₉ found 668.1007.

2.3.1.5 Melting point: Compound decomposes upon heating (>300 °C).
2.3.3 Gelator R₃

![Diagram of Gelator R₃ showing both conformers C₁ (left) and C₄ (right).](image)

**Figure S4.** Gelator R₃ showing both conformers C₁ (left) and C₄ (right).

### 2.3.3.1 H NMR (d₆-DMSO, J/Hz, δ/ppm):
- 13.92 (d, J = 13.00, −CNH),
- 13.29 (dd, J = 24.67, 13.41, −CNH),
- 8.80 (m, 3H, HC-N),
- 7.22 (m, 6H, Ar-H),
- 3.90 (d, J = 3.63, 9H, OCH₃).

### 2.3.3.2 C NMR (D₂O, δ/ppm):
- 187.44, 187.0, 175.87, 158.56, 149.82, 131.56, 117.71, 112.12, 107.33, 99.50, 55.22.

### 2.3.3.3 IR (cm⁻¹):
- 3010, 1725, 1627, 1565, 1468, 1446, 1296, 1216, 1153, 1075, 1024, 948, 871, 796, 763, 645, 560.

### 2.3.3.4 HRMS:
- Calculated for [M-H] - 656.1522, C₃₃H₂₆N₃O₁₂ found 668.1581.

### 2.3.3.5 Melting point:
- Compound decomposes upon heating (>300 °C).
2.3.4 Gelator R₄

![Chemical Structure](image)

Figure S5. Gelator R₄ showing both conformers C₃ (left) and C₅ (right).

2.3.4.1 H NMR (d₆-DMSO, J/Hz, δ/ppm): 13.99 (d, J = 13.29, =CNH), 13.50 (dd, J = 28.00, 13.31, =CNH), 12.81 (s, 3H-OH), 8.78 (m, 3H, HC-N), 7.74 (dt, J = 8.57, 4.52, 3H, Ar-H), 7.48 (t, J = 7.49, 6H, Ar-H)

2.3.4.2 C NMR (D₂O, δ/ppm): 188.04, 187.4, 187.13, 176.63, 176.02, 156.77, 154.26, 147.19, 140.64, 133.65, 132.50, 127.79, 119.50, 117.67, 116.45, 115.46, 114.70, 113.79, 111.96, 106.41.

2.3.4.3 IR (cm⁻¹): 3394, 3263, 1662, 1575, 1530, 1429, 1353, 1277, 1196, 1142, 1092, 988, 949, 884, 841, 816, 758, 721, 672, 635, 570.

2.3.4.4 HRMS: Calculated for [M-H]- 614.1052, C₃₀H₂₀N₃O₁₂ found 614.1233.

2.3.4.5 Melting point: Compound decomposes upon heating (>.>300 °C).
2.3.5 Gelator R₅

Figure S6. Gelator R₅ showing both conformers C₃ (left) and C₅ (right).

2.3.5.1 ¹H NMR (d₆-DMSO, J/Hz, δ/ppm): 13.29 (dd, J = 18.92, 13.56, =CNH), 12.83 (dd, J = 13.59, 8.14, =CNH), 11.36 (s, 3H, =–OH), 8.74 (dd, J = 13.37, 2.88, 3H, HC-N), 8.01 (d, J = 16.78, 3H Ar-H), 7.69 (d, J = 8.36, 3H, Ar-H), 7.08 (m, 3H, Ar-H).

2.3.5.2 ¹³C NMR (D₂O, δ/ppm): 176.51, 175.81, 162.17, 148.35, 135.76, 129.25, 128.96, 128.61, 123.52, 121.28, 118.70, 117.29, 116.59, 105.97.

2.3.5.3 IR (cm⁻¹): 3076, 1693, 1580, 1450, 1320, 1250, 1121, 1093, 941, 820, 761, 614, 562.

2.3.5.4 HRMS: Calculated for [M-H] 614.1052, C₃₀H₂₀N₃O₁₂ found 614.1759.

2.3.5.5 Melting point: Compound decomposes upon heating (>300 °C).
2.3.6 Gelator R₆

![Chemical structures]

**Figure S7.** Gelator R₆ showing both conformers C₃ (left) and Cₛ (right).

2.3.6.1 **¹H NMR** (d₂-D₂O, J/Hz, δ/ppm): 9.45 (s, 3H, HC-N), 7.36 (s, 3H, Ar-H), 7.11 (s, 6H, Ar-H).

2.3.6.2 **¹³C NMR** (D₂O, δ/ppm): 187.22, 173.94, 147.12, 138.25, 131.19, 130.81, 130.28, 129.93, 129.86, 129.35, 125.75, 122.13, 119.39, 115.69, 114.40, 111.99.

2.3.6.3 **IR** (cm⁻¹): 3079, 2577, 1715, 1621, 1586, 1471, 1355, 1274, 1172, 1124, 1042, 946, 870, 829, 768, 734, 675, 607, 571, 562.

2.3.6.4 **HRMS:** Calculated for [M-H]⁻ 770.0827, C₃₃H₁₇F₉N₃O₇ found 770.0495.

2.3.6.5 **Melting point:** Compound decomposes upon heating (>300 °C).
2.3.7 Gelator R₇

![Figure S8. Gelator R₇ showing both conformers C₇ (left) and C₅ (right).](image)

2.3.7.1 ^1^H NMR (d₂-D₂O, J/Hz, δ/ppm): 9.57 (s, 3H, HC-N), 7.40 (s, 3H, Ar-H), 7.04 (s, 3H, Ar-H), 6.70 (s, 3H, Ar-H).

2.3.7.2 ^1^C NMR (D₂O, δ/ppm): 188.34, 187.91, 187.09, 178.68, 177.46, 148.41, 147.79, 147.01, 139.26, 138.45, 137.76, 137.24, 137.07, 135.84, 129.97, 129.26, 128.47, 118.91, 117.74, 114.10, 113.01, 111.83, 106.87, 106.18, 20.17, 19.82.

2.3.7.3 IR (cm⁻¹): 2973, 2613, 1698, 1623, 1563, 1448, 1344, 1284, 1217, 1143, 1039, 984, 821, 770, 751, 688, 648, 567.

2.3.7.4 HRMS: Calculated for [M-H] -656.1522, C₃₅H₂₆N₃O₁₂ found 668.1085.

2.3.7.5 Melting point: Compound decomposes upon heating (>300 °C).
2.3.8 Gelator R₈

![Gelator R₈ showing both conformers C₃ (left) and C₅ (right).](image)

2.3.8.1 H NMR (d₂-D₂O, J/Hz, δ/ppm): 9.43 (d, J = 11.43, 3H, HC-N), 7.32 (s, 3H, Ar-H), 7.04 (s, 3H, Ar-H), 6.61 (s, 3H, Ar-H).

2.3.8.2 13C NMR (D₂O, δ/ppm): 187.93, 187.47, 186.97, 176.47, 173.75, 146.46, 144.01, 139.06, 133.37, 131.45, 130.40, 126.09, 124.53, 124.23, 118.60, 117.84, 114.45, 112.02, 106.25, 61.81, 60.92.

2.3.8.3 IR (cm⁻¹): 3079, 1705, 1623, 1566, 1454, 1420, 1221, 1170, 1113, 1091, 1034, 985, 846, 764, 688, 634.

2.3.8.4 HRMS: Calculated for [M-H] 608.1675, C₃₃H₂₆N₉O₉ found 608.1752.

2.3.8.5 Melting point: Compound decomposes upon heating (>300 °C).
2.3.9 Gelator R₉

Figure S10. Gelator R₉ showing both conformers C₁ (left) and C₅ (right).

2.3.9.1 H NMR (d₆-DMSO, J/Hz, δ/ppm): 13.36 (t, J = 13.11, =CNH), 12.77 (dd, J = 13.50, 4.15, =CNH), 9.61 (s, 3H, Ar-OH), 8.53 (m, 3H, HC-N), 7.28 (dd, J = 7.71, 5.45, 6H, Ar-H), 6.84 (d, J = 8.39, 6H, Ar-H).

2.3.9.2 ¹³C NMR (D₂O, δ/ppm): 187.78, 185.80, 184.00, 165.22, 159.52, 148.51, 147.89, 133.32, 126.51, 126.17, 119.36, 118.85, 111.92, 104.85.

2.3.9.3 IR (cm⁻¹): 3079, 1705, 1623, 1566, 1454, 1420, 1221, 1170, 1113, 1091, 1034, 985, 846, 764, 688, 634.

2.3.9.4 HRMS: Calculated for [M-H]⁻ 482.1358, C₂₇H₂₀N₃O₆ found 482.1731.

2.3.9.5 Melting point: Compound decomposes upon heating (>300 °C).
2.4 Synthesis of compound R₁₀

To a suspension of A (.250 mg, 1.19 mmol) in ethanol (50 ml) 6-aminohexanoic acid was added (3.69 mmol, 3.1 molar equivalents) and the resulting solution was refluxed for 16 hours. Once complete the reflux was cooled to room temperature and rotary evaporation was used to remove all the ethanol resulting in a dark orange oil. After a week at 5 °C the oil had solidified to give a dark orange solid. The solid ground to a fine powder and washed with hot ethanol (5 × 50 ml) then dried overnight at 80 °C this produced the desired product at good yields (71 %) and purity.

![Figure S11. Compound R₁₁ showing both conformers C₁ (left) and C₅ (right).](image)

2.5.1 ¹H NMR (d₆-DMSO, J/Hz, δ/ppm): 11.31 (m, =CNH), 10.87 (m, =CNH), 8.06 (m, 3H, HC-N), 3.40 (m, 6H, N-CH₂-), 2.18 (t, J = 6.96, 6H, -CH₂-), 1.52 (dt, J = 15.06, 7.47, 12H, -CH₂-), 1.30 (m, 6H, -CH₂-).

2.5.2 ¹³C NMR (d₆-DMSO, δ/ppm): 187.19, 184.26, 181.25, 175.20, 157.78, 157.31, 157.16, 156.55, 104.26, 104.07, 49.62, 49.42, 34.47, 30.49, 27.36, 26.07, 24.75.

2.5.3 IR (cm⁻¹): 2932, 2860, 1716, 1601, 1525, 1450, 1306, 1160, 1105, 1074, 1021, 832, 776, 732, 655.

2.5.4 HRMS: Calculated for [M-H]⁻ 548.2608 C₂₇H₃₈N₃O₉ found 548.2588.

2.5.5 Melting point: 128 – 132 °C.
2.5 Chemical Analysis notes

Ligands R₃, R₆, R₇ and R₈ proved too insoluble in any solvent to obtain a ¹H spectra of the pure compounds. This resulted in proton data experiments having to be run in D₂O with the addition of NaOH in order to solubilise the ligand. To obtain chemical information for the ligands the spectra were recorded between 5 and 15 ppm in order to remove the H₂O signal which would have otherwise suppressed the signals for the ligand ¹H nuclei. Due to deprotonation and exchange, the –NH- and –COOH signals were lost.

All ¹³C NMR spectra with the exception of R₁₀ were recorded in the manner described above. Due to the two distinct conformations of the ligands and the overlapping of the subsequent signals exact assignment of signals proved impossible.
3.0 Methods for hydrogel Preparation.

Nine hydrogels could be prepared with two preparation methods attributed to each individual hydrogel. The ‘ex situ’ preparation method describes the use of the previously prepared compounds R₁ to R₉ to form the corresponding hydrogel. The ‘in situ’ preparation method relates to the mixing and subsequent reaction of the amine and aldehyde component of the gelator in the volume of water that is to be gelled.

3.1 Setting gel using In situ gel preparation method (gels R₁ to R₈ inclusively):

This procedure describes the method used in a typical in situ setting of the hydrogels using a solution of 1,3,5-triformylglucinol and the appropriate aminobenzoic acid.

1,3,5-triformylglucinol (0.082g, 0.39 mmol) was suspended in water (5 ml), to this suspension sodium hydroxide (0.05 g, 1.25 mmol) was added and sonication and gentle heating was used to produce a clear pale yellow solution. To a separate portion of water (5 ml) the appropriate aminobenzoic acid was added (1.17 mmol) along with sodium hydroxide (0.016 g, 0.4 mmol) to ensure the complete dissolution of the aminobenzoic acid. These two aqueous solutions were then mixed together vigorously shaken before being allowed to react at room temperature for 4 hours. After this reaction period glucono delta-lactone (GdL) (0.08 g, 0.45 mmol) was added and the solution was shaken until the GdL had completely dissolved, this resulted in the formation of the gel after approximately 2 hours.

3.2 In situ R₉ gel formation:

This procedure describes the method used in a typical in situ setting of the hydrogel R₉ using a solution of 1,3,5-triformylglucinol and the 4-aminophenol.

1,3,5-triformylglucinol (0.082g, 0.39 mmol) was suspended in water (5 ml), to this suspension sodium hydroxide (0.05 g, 1.25 mmol) was added and sonication and gentle heating was used to produce a clear pale yellow solution. To a separate portion of water (5 ml) the 4-aminophenol was added (0.13 g, 1.17 mmol) along with sodium hydroxide (0.016 g, 0.4 mmol) to ensure the complete dissolution of the 4-aminophenol. These two aqueous solutions were then mixed together vigorously shaken before being allowed to react at room temperature for 4 hours. After this reaction period conc. Hydrochloric acid (0.8 ml) was rapidly added to the solution instantly producing a bright orange gel.
3.3 Setting gel using the *ex situ* prepared compound (gels R$_1$ to R$_8$ inclusively):

This procedure describes the method used in a typical setting of the hydrogel at 2 wt% using the previously prepared synthesised compound.

The gel ligand (0.1 g) was suspended in water, to this suspension sodium hydroxide was added (0.05 g, 1.25 mmol). Sonication and gentle heating was used to ensure the ligand had completely dissolved giving a solution with a pH of 9 – 10. To this solution glucono delta-lactone (GdL) (0.08 g, 0.45 mmol) was added and the solution was shaken until the GdL had completely dissolved, this resulted in the formation of the gel after approximately 2 hours.

3.4 Setting gel R9 using the *ex situ* prepared compound:

This procedure describes the method used in a typical setting of the hydrogel R$_9$ at 2 wt% using the previously prepared synthesised compound R$_9$.

The synthesised compound R9 (0.1 g, 0.21 mmol) was suspended in water (5 ml), to this suspension sodium hydroxide was added (0.05 g, 1.25 mmol). Sonication and gentle heating was used to ensure the ligand had completely dissolved giving a solution with a pH of 9 – 10. To this solution conc. Hydrochloric acid (0.4 ml) was rapidly added instantly producing a bright orange gel.

3.5 Critical gel concentration (CGC):

Critical gel concentration was determined using the inverted vial method in 2 ml sample vials using 0.5 ml of water. This method can often give lower CGC values than are determined using a rheometer due to the low volume of solution and the high surface tension within the vials.
4.0 Morphology determination of single amine Gels

The morphology of the gels could be determined using SEM images. The gels were prepared by both the \textit{ex situ} and \textit{in situ} in vials before being mounted on carbon covered SEM stubs. The gels were then dried under vacuum for 72 hours before being gold coated.

4.1 Gel R₁

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure12.png}
\caption{SEM images of gel R₁ \textit{ex situ} preparation method (left) \textit{in situ} preparation method (right).}
\end{figure}

4.2 Gel R₂

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure13.png}
\caption{SEM images of gel R₂ \textit{ex situ} preparation method (left) \textit{in situ} preparation method (right).}
\end{figure}
4.3 Gel R₃

Figure S14. SEM images of gel R₃ ex situ preparation method (left) in situ preparation method (right).

4.4 Gel R₄

Figure S15. SEM images of gel R₄ ex situ preparation method (left) in situ preparation method (right).

4.5 Gel R₅

Figure S16. SEM images of gel R₅ ex situ preparation method (left) in situ preparation method (right).
4.6 Gel $R_6$

Figure S17. SEM images of gel $R_6$ ex situ preparation method (left) in situ preparation method (right).

4.7 Gel $R_7$

Figure S18. SEM images of gel $R_7$ ex situ preparation method (left) in situ preparation method (right).

4.8 Gel $R_8$

Figure S19 SEM images of gel $R_8$ ex situ preparation method (left) in situ preparation method (right).
4.9 Gel R9

Figure S20. SEM images of gel R9 ex situ preparation method (left) in situ preparation method (right).
5.0 Rheological studies of single amine gels

5.1 Rheological characterisation of *in situ* and *ex situ* prepared gel R₁

**Figure S21.** Time sweep rheometry of gel R₁ *ex situ* preparation method (empty □) and *in situ* preparation method (filled □).

**Figure S22.** Frequency sweep rheometry of gel R₁ showing *ex situ* preparation method (*G'*= empty ○, *G''*= empty □) and the *in situ* preparation method (*G'*= filled ○, *G''*= filled □).

**Figure S23.** Stress sweep rheometry of gel R₁ showing *ex situ* preparation method (empty □) and *in situ* preparation method (filled □) (line has been added to guide the eye).
5.2 Rheological characterisation of *in situ* and *ex situ* prepared gel R$_2$

![Figure S24](image1.png)

**Figure S24.** Time sweep rheometry of gel R$_2$ *ex situ* preparation method (empty □) and *in situ* preparation method (filled □).

![Figure S25](image2.png)

**Figure S25.** Frequency sweep rheometry of gel R$_1$ showing *ex situ* preparation method ($G'$ = empty ○, $G''$ = empty □) and the *in situ* preparation method ($G'$ = filled ○, $G''$ = filled □).

![Figure S26](image3.png)

**Figure S26.** Stress sweep rheometry of gel R$_2$ showing *ex situ* preparation method (empty ○) and *in situ* preparation method (filled □) (line has been added to guide the eye).
5.3 Rheological characterisation of *in situ* and *ex situ* prepared gel R₃

**Figure S27.** Time sweep rheometry of gel R₃ *ex situ* preparation method (empty □) and *in situ* preparation method (filled □).

**Figure S28.** Frequency sweep rheometry of gel R₃ showing *ex situ* preparation method ($G' =$ empty ○, $G'' =$ empty □) and the *in situ* preparation method ($G' =$ filled ○, $G'' =$ filled □).

**Figure S29.** Stress sweep rheometry of gel R₃ showing *ex situ* preparation method (empty □) and *in situ* preparation method (filled □) (line has been added to guide the eye).
5.4 Rheological characterisation of *in situ* and *ex situ* prepared gel R₄

**Figure S30.** Time sweep rheometry of gel R₄ *ex situ* preparation method (empty □) and *in situ* preparation method (filled □).

**Figure S31.** Frequency sweep rheometry of gel R₄ showing *ex situ* preparation method ($G' =$ empty ○, $G'' =$ empty □) and the *in situ* preparation method ($G' =$ filled ○, $G'' =$ filled □).

**Figure S32.** Stress sweep rheometry of gel R₄ showing *ex situ* preparation method (empty □) and *in situ* preparation method (filled □) (line has been added to guide the eye).
5.5 Rheological characterisation of *in situ* and *ex situ* prepared gel R$_5$

**Figure S33.** Time sweep rheometry of gel R$_5$ *ex situ* preparation method (empty □) and *in situ* preparation method (filled □).

**Figure S34.** Frequency sweep rheometry of gel R$_5$ showing *ex situ* preparation method ($G'$ = empty ○, $G''$ = empty □) and the *in situ* preparation method ($G'$ = filled ○, $G''$ = filled □).

**Figure S35.** Stress sweep rheometry of gel R$_5$ showing *ex situ* preparation method (empty □) and *in situ* preparation method (filled □) (line has been added to guide the eye).
5.6 Rheological characterisation of in situ and ex situ prepared gel R₆

Figure S36. Time sweep rheometry of gel R₆ ex situ preparation method (empty □) and in situ preparation method (filled □).

Figure S37. Frequency sweep rheometry of gel R₆ showing ex situ preparation method (\(G' = \) empty ○, \(G'' = \) empty □) and the in situ preparation method (\(G' = \) filled ○, \(G'' = \) filled □).

Figure S38 Stress sweep rheometry of gel R₆ showing ex situ preparation method (empty □) and in situ preparation method (filled □) (line has been added to guide the eye).

5.7 Rheological characterisation of *in situ* and *ex situ* prepared gel R<sub>7</sub>

*Figure S39.* Time sweep rheometry of gel R<sub>7</sub> *ex situ* preparation method (empty □) and *in situ* preparation method (filled □).

*Figure S40.* Frequency sweep rheometry of gel R<sub>7</sub> showing *ex situ* preparation method ($G'$ = empty ○, $G''$ = empty □) and the *in situ* preparation method ($G'$ = filled ○, $G''$ = filled □).

*Figure S41.* Stress sweep rheometry of gel R<sub>7</sub> showing *ex situ* preparation method (empty □) and *in situ* preparation method (filled □) (line has been added to guide the eye).
5.8 Rheological characterisation of *in situ* and *ex situ* prepared gel R$_8$

**Figure S42.** Time sweep rheometry of gel R$_8$ *ex situ* preparation method (empty □) and *in situ* preparation method (filled ○).

**Figure S43.** Frequency sweep rheometry of gel R$_8$ showing *ex situ* preparation method ($G'$ = empty ○, $G''$ = empty □) and the *in situ* preparation method ($G'$ = filled ○, $G''$ = filled □).

**Figure S44.** Stress sweep rheometry of gel R$_8$ showing *ex situ* preparation method (empty □) and *in situ* preparation method (filled □) (line has been added to guide the eye).
5.9 Rheological characterisation of *in situ* and *ex situ* prepared gel R9

**Figure S45.** Frequency sweep rheometry of gel R9 showing *ex situ* preparation method ($G' =$ empty ○, $G'' =$ empty □) and the *in situ* preparation method ($G' =$ filled ○, $G'' =$ filled □).

**Figure S46.** Stress sweep rheometry of gel R9 showing *ex situ* preparation method (empty □) and *in situ* preparation method (filled □) (line has been added to guide the eye).
The conversion of the initial solution to each of the gels could be observed by monitoring the growth of $G$' over time after the addition of GdL. The results of these time sweep experiments make it possible to determine the Avrami constants for the formation of the gels. The Avrami constants for gels $R_1$ to $R_9$ were calculated to be 1.7, 1.6, 1.9, 1.7, 1.8, 1.7, 2.0, 1.6, respectively.

By performing a time sweep, the data acquired allowed determination of the Avrami constant for gelation sample. The Avrami constant is a useful method of quantifying the kinetics of a phase change.\(^\text{22}\) More recently it has been used to describe the sol to gel transition for supramolecular gelation systems.\(^\text{22}\) The use of the Avrami equation, which is used to determine the Avrami constant, relies on the general sigmoidal profile for the extent of transformation from one phase to another.

\[ \ln(1 - X_{cr}) = -kt^D \]

(equation 1.)

The work of Avrami is generally thought of as relating to the formation of bulk crystals, it describes how phase and ordered growth kinetics relate to physical properties such as temperature and concentration. This also means that different morphologies can arise from different growth rates.\(^\text{22}\) Liu used the foundations laid by Avrami to develop a method where by the growth of the fibres involved in the formation of the three-dimensional supramolecular gel networks could be characterised in situ. The work of Liu describes the Avrami constant as the fractal dimension, however, throughout this work the term Avrami constant will be used.\(^\text{22}\) The general form of the Avrami constant (equation 1.) where $k$ = constant, $t$ = time and $X_{cr}$ = the systems crystallinity which is equal to $\phi(t)/\phi(\infty)$, where $\phi(t)$ is the volume fraction of crystal materials $t$, and $\phi(\infty)$ is $\phi(t)$ at $t \to \infty$. $D$ describes the dimensions in which the bulk crystal grows, with rod-like growth described by $D$ = 1, plate like crystals described by $D$ = 2 and spherulite growth described by $D$ = 3. By considering the relationship proposed by Einstein between relative viscosity and volume concentration of suspension of spheres\(^\text{22}\) it is possible to relate $X_{cr}$ to specific viscosity $\eta_{sp}$. Equation 2 describes specific viscosity of a system in terms of the complex viscosity $\eta^*$, and the viscosity of the medium in which the phase change is taking place, $\eta_0$.

\[ \eta_{sp} = \frac{\eta^* - \eta_0}{\eta_0} \]

(equation 2.)

It is possible to define the crystallinity of the solution in terms of $\eta^*$ and $\eta_0$ with respect to time as can be seen in equation 3.

\[ X_{cr}(t) = \frac{\phi(t)}{\phi(\infty)} = \frac{\eta_{sp}(t)}{\eta_{sp}(\infty)} = \frac{\eta^*(t) - \eta_0}{\eta^*(\infty) - \eta_0} \]

(equation 3.)

With equation 3 it is possible to observe how the viscosity of the solution as a function of time can be used to determine $X_{cr}$. Viscosity is a rheological property, with this in mind it is possible to use other rheological material properties to determine $X_{cr}$. Although gels do exhibit a relatively high degree of long-range order, they are not strictly crystalline, in most cases. With this in mind, from now on $X_{cr}$
will be discussed as $X$, which represents gelation as opposed to crystallinity. With a supramolecular gel’s rheological characterisation the elastic modulus $G'$ is representative of the materials elastic, solid-like behaviour.

$$X = \frac{G'(t)}{G'_{\infty}}$$

*(equation 4.)*

Equation 4 shows the relationship between the elastic modulus at time $t$, $G'(t)$ and it as $t \rightarrow \infty$, $G'_{\infty}$. The information required to solve for $X$ can be obtained from the time sweep experiments that were performed on the gel as it set. $G'_{\infty}$ is defined as the average value for the last 20 measurements of $G'$. The values of $G'(t)$ used are up to $t \sim 10$ Pa, where generally the rate of increase in $G'$ is less than 0.1 Pa per measurement. The rate of increase in $G'$ is important, as below 0.1 Pa per measurement, fibre growth is the key factor in the increase in $G'$. When this rate exceeds 0.1 Pa per measurement the branching and entangling of the existing fibres becomes an increasingly significant factor, as this marks the point at which the system moves from fibre growth to the onset of gelation.\(^{22}\) With these factors in mind, the Avrami constant can be determined from equation 5.

$$\ln\left(\ln\left(\frac{1}{1-X}\right)\right) = \ln(K) + DLn(t)$$

*(equation 5.)*

$X$ can be replaced with equation 4, $K$ represents a constant that is related to temperature, $t$ is time and $D$ is the Avrami constant itself. The *in situ* reaction system discussed here relies on the addition of GdL to set the gel meaning that the term $K$ does not have to be considered. A plot of $\ln(\ln(1/1-X))$ against $\ln(t)$ will result in a straight line with a gradient equal to $D$.

Reference 22 refers to references in main paper.
6.0 Apparent pKas for synthesised gelators R₁ – R₉

In order to determine the apparent pKa of gelators R₁ to R₉ a series of titration experiments were performed. 1 mmol of gelator was dispersed in 15 ml of water and dissolved with the addition of NaOH. Further NaOH was added until the pH of the solution had been adjusted to approximately 10. Before aliquots of HCl\textsubscript{(aq)} were added and the resulting pH recorded.

![Figure S47](image)

**Figure S47.** Apparent pKa determination of gelator R₁ showing an apparent pKa of 6.1-5.8 as taken to be the observed plateau region shown in the shaded area.

![Figure S48](image)

**Figure S48.** Apparent pKa determination of gelator R₂ showing an apparent pKa of 5.8-5.5 as taken to be the observed plateau region shown in the shaded area.
**Figure S49.** Apparent $pK_a$ determination of gelator $R_3$ showing an apparent $pK_a$ of 6.1-5.7 as taken to be the observed plateau region shown in the shaded area.

**Figure S50.** Apparent $pK_a$ determination of gelator $R_4$ showing an apparent $pK_a$ of 6.5-6.2 as taken to be the observed plateau region shown in the shaded area.
Figure S51. Apparent $pK_a$ determination of gelator $R_5$ showing an apparent $pK_a$ of 6.1-5.8 as taken to be the observed plateau region shown in the shaded area.

Figure S52. Apparent $pK_a$ determination of gelator $R_6$ showing an apparent $pK_a$ of 5.2-5.0 as taken to be the observed plateau region shown in the shaded area.
Figure S53. Apparent $pK_a$ determination of gelator $R_7$ showing an apparent $pK_a$ of 6.5-6.3 as taken to be the observed plateau region shown in the shaded area.

Figure S54. Apparent $pK_a$ determination of gelator $R_8$ showing an apparent $pK_a$ of 6.4-6.0 as taken to be the observed plateau region shown in the shaded area.
Figure S55. Apparent $pK_a$ determination of gelator R9 showing an apparent $pK_a$ of 9.9-9.0 as taken to be the observed plateau region shown in the shaded area.
7.0 PXRD Patterns for dried gel samples R₁ – R₉

**Figure S56.** PXRD patterns for samples produced from dried gels R₁, R₂, R₃, R₄ and R₅ recorded between 5 – 60° for 30 minutes.

**Figure S57.** PXRD patterns for samples produced from dried gels R₆, R₇, R₈ and R₉ recorded between 5 – 60° for 30 minutes.
7.1 PXRD pattern of non gelator R$_{10}$

![Graph showing PXRD pattern](image)

**Figure S58.** PXRD patterns for samples produced from precipitate collected from an attempted gelation of R$_{10}$ using GdL. Recorded between 5 – 60° for 30 minutes.
8.0 Analysis of mixed gelators systems.

8.1 UV-vis transmission data recorded for various gels of $R_1$ and $R_6$ mixtures

Figure S59. UV-vis transmission data showing a decrease in transmission with a reduction in $R_6$ relative to the total concentration of gelator ($R_1 + R_6$) from 100 - 20 % $R_6$ in 20 % steps.
8.2 PXRD analysis gels of $R_1$ and $R_6$ mixtures

Figure S60. PXRD patterns for samples produced from dried mix gel systems (100 % $R_1$, 75 % $R_1$ : 25 % $R_6$, 50 % $R_1$ : 50 % $R_6$) recorded between 5 – 60 ° for 30 minutes.

Figure S61. Expansion of Figure S60. between 22 ° and 29 °.
Table S2. Analysis of PXRD data for mixed (R₁ and R₆) gel systems.

| Gel                  | Angle (°) | d spacing |
|----------------------|-----------|-----------|
| 100 % R₁             | 25.2435   | 3.53      |
| 75 % R₁ : 25 % R₆    | 25.6055   | 3.47      |
| 50 % R₁ : 50 % R₆    | 26.0544   | 3.42      |
| 25 % R₁ : 75 % R₆    | 26.4743   | 3.36      |
| 100 % R₆             | 26.8652   | 3.32      |

As can be seen in table S2 the d spacing decreases with increasing concentration of R₆ relative to the total concentration of the gelator.
8.3 Morphology determined by SEM for gels of R₁ and R₆ mixtures.

Figure S62. SEM analysis showing the consistency of morphology for gels set using various molar ratios of R₁ and R₆. a) R₁ 100 : 0 R₆. b) R₁ 75 : 25 R₆. c) R₁ 50 : 50 R₆. d) R₁ 25 : 75 R₆. e) R₁ 0 : 100 R₆.
8.4 Apparent pKa of R₁ and R₆ mixtures.

Figure S63. Apparent pKₐ determination for mixtures of R₁ and R₆ from 100% R₁ to 100% R₆ in 20% increments relative to the total concentration of gelator molecule 80 mg in 20 ml of water. Apparent pKₐ was determined with constant rapid stirring to prevent gelation.

The apparent pKₐ is defined as the plateau region where the change in the pH of the solution is minimal. As can be seen for the R₁ : R₆ mixtures there is a gradual and constant reduction in the apparent pKₐ from the value of 100% R₁ to that of 100% R₆. This shows that both gelators influence the apparent pKₐ region collectively allowing co-assembly to occur given the correct gelation conditions.
8.5 NMR of R₁ : R₆ gelator co-assembly process

A solution was created by dissolving 25 µmol of R₁ and 25 µmol of R₆ in D₂O with the addition of NaOH and a spectra was obtained. 10 µmol of GdL was then added and a spectra was recorded every five minutes for a total of two hours and over a range of 6 – 9 ppm. Examination of the integrations of peaks (determined against the internal standard of 4-aminobenzoic acid) that relate to the aromatic protons of both R₁ and R₆ allowed the plot shown in Figure S64 to be produced. The initial measurement at time zero (before the addition of GdL) was used as the reference with which to normalise the data.

![Figure S64](image-url)  
*Figure S64. Co-assembly over time of gelators R₁ and R₆ as determined by ¹H NMR.*
8.6 PXRD analysis of xerogels of R₁ and R₁₀ 50:50 mixture

Figure S65. PXRD pattern of R₁ : R₁₀ (50 : 50) xerogel.

Figure S66. Pure R₁₀ compound as synthesised (green). Pure R₁ xerogel (red). R₁ : R₁₀ (50 : 50) xerogel (blue) highlights the self-sorting ability of the 50:50 R₁ : R₁₀ gel into gel phase R₁ and precipitate R₁₀.
8.7 Apparent $pK_a$ of $R_1$ and $R_{10}$ mixture

Figure S67. Apparent $pK_a$ determination for mixtures of $R_1$ and $R_{10}$ (50 : 50) mix (red), Pure $R_1$ (blue), Pure $R_{10}$ (green). Step in the plateau of $R_1$ and $R_{10}$ (50 : 50) mix shows a stepwise self-sorting co-assembly process.
8.8 NMR of $R_1 : R_{10}$ gelator self-sorting process

A solution was created by dissolving 25 µmol of $R_1$ and 25 µmol of $R_{10}$ in $D_2O$ with the addition of NaOH and a spectra was obtained. 10 µmol of GdL was then added and a spectra was recorded every five minutes. The same procedure described for the $R_1$ and $R_8$ mixed samples, section 7.5, was utilised.

![Figure S68](attachment:image.png)

**Figure S68.** Self-sorting experiment of gelators $R_1$ and $R_{10}$ over time as determined by $^1H$ NMR. The two compounds are not disappearing through self-assembly at the same rate as the pH is changing, nor have they had the same initiation point (5 mins vs 15mins).
8.9 HPLC of R₁ : R₆ gelator process

**Figure S69.** From left to right, HPLC trace for *ex situ* synthesised compound R₁, with a retention time of 323 seconds recorded; *ex situ* synthesised compound R₆, with a retention time of 391 seconds recorded; and *in situ* reaction mixture containing R₁ amine, R₆ amine and II. All components were dissolved in water at pH 8, with the HPLC analysis performed after 16 hours.

**Figure S70.** All possible reaction products for the *in situ* R₁ + R₆ + II, including the gelators R₁, R₆, and products composed of mixed amines R₁₁,₂₆ and R₁₁,₂₆₂. 

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9.0 Computational Calculations

**Figure S71.** All possible reaction products for the *in situ* \( R_1 + R_{10} + II \), including the known molecules \( R_1 \) and \( R_{10} \), and products composed of mixed amines \( R_1^1 R_{10}^1 \) and \( R_1^2 R_{10}^2 \). Chemical analyses highlight a chemical self-sorting of these compounds resulting in only the pure \( R_{10} \) and \( R_1 \) species during *in situ* reactions. \( R_{11} \) variants would be the methyl derivatives of the four compounds shown above.

Table S3. Computed electronic and zero point corrected energy differences between the C\(_3\) and C\(_5\) conformations of various tripodal ketoenamine molecules. All energies are in kcal mol\(^{-1}\).

| Structure | B3LYP Electronic | B3LYP Zero Point Correct. | B97-D Electronic | B97-D Zero Point Correct. |
|-----------|------------------|---------------------------|------------------|---------------------------|
| 3\(R_1\)  | 1.041            | 1.170                     | 1.032            | 1.199                     |
| 2\(R_1^1\) : 1\(R_{10}^1\) | 1.145            | 1.296                     | 1.146            | 1.227                     |
| 1\(R_1^1\) : 2\(R_{10}^1\) | 0.875            | 0.981                     | 0.939            | 0.950                     |
Table S4. Computed electronic and zero point corrected reaction energetics, using the B3LYP functional, for the formation of various tripodal keto-enamine systems. All values reported pertain to the C$_3$ conformation and in terms of kcal mol$^{-1}$. R$_{11}$ being the methyl derivative to allow for reduction of the conformational flexibility of the calculated compounds.

| Structure  | Electronic | Zero Point Corrected |
|------------|------------|----------------------|
|            | 1$^{st}$   | 2$^{nd}$  | 3$^{rd}$  | 1$^{st}$   | 2$^{nd}$  | 3$^{rd}$  |
| 3R$_{10}$  | 0.911      | 1.158     | 0.916     | 1.178      |
| 2R$_1$: 1R$_{11}$ | 1.156    | 1.313     | 1.076     | 1.302      |
| 1R$_1$: 2R$_{11}$ | 0.942    | 1.041     | 0.943     | 1.115      |
| 3R$_{11}$  | 1.034      | 1.091     | 1.029     | 1.046      |
| 2R$_1$: 1R$_6$ | 1.061    | 1.242     | 1.031     | 1.304      |
| 1R$_1$: 2R$_6$ | 1.232    | 1.461     | 1.241     | 1.547      |
| 3R$_6$     | 1.321      | 1.568     | 1.326     | 1.684      |

Table S5. Computed electronic and zero point corrected reaction energetics, using the B97-D functional, for the formation of various tripodal keto-enamine systems. All values reported pertain to the C$_3$ conformation and are in kcal mol$^{-1}$.

| Structure  | Electronic | Zero Point Corrected |
|------------|------------|----------------------|
|            | 1$^{st}$   | 2$^{nd}$  | 3$^{rd}$  | 1$^{st}$   | 2$^{nd}$  | 3$^{rd}$  |
| 3R$_1$     | 4.801      | 4.986     | 5.128     | 2.625      | 2.784     | 2.714     |
| 2R$_1$: 1R$_{11}$ | 4.801    | 4.986     | -0.031    | 2.625      | 2.784     | -1.940    |
| 1R$_1$: 2R$_{11}$ | -0.834   | 0.284     | 5.555     | -2.780     | -1.526    | 3.452     |
| 3R$_{11}$  | -0.834     | 0.284     | 1.258     | -2.780     | -1.526    | -0.540    |
| 2R$_1$: 1R$_6$ | 4.801    | 4.986     | 4.764     | 2.625      | 2.784     | 2.375     |
| 1R$_1$: 2R$_6$ | 4.542    | 4.602     | 5.049     | 2.373      | 2.342     | 2.771     |
| 3R$_6$     | 4.542      | 4.602     | 4.697     | 2.373      | 2.342     | 2.434     |
Table S6. Computed electronic and zero point corrected energy for the keto-enol tautomerisation for the three-subunit systems in the $C_3$ conformation. All values are in kcal mol$^{-1}$.

| Structure | B3LYP Electronic | B3LYP Zero Point Correct. | B97-D Electronic | B97-D Zero Point Correct. |
|-----------|-------------------|---------------------------|-------------------|---------------------------|
| 3R$_1$    | -14.289           | -12.181                   | -14.937           | -11.546                   |
| 2R$_1$: 1R$_{11}$ | -13.986           | -11.972                   | -14.519           | -11.417                   |
| 1R$_{11}$: 2R$_{11}$ | -13.507           | -11.505                   | -13.973           | -11.037                   |
| 3R$_{11}$ | -12.742           | -10.725                   | -13.101           | -10.111                   |
| 2R$_1$: 1R$_6$ | -13.374           | -11.472                   | -14.159           | -10.987                   |
| 1R$_1$: 2R$_6$ | -12.609           | -10.762                   | -13.405           | -10.439                   |
| 3R$_6$    | -11.852           | -9.965                    | -12.758           | -9.855                    |