*Electronic Supplementary Information*

# Hydrogen-Bonding Networks of Purine Derivatives and Their Bilayers for Guest Intercalation

Yoona Jang,[a] Seo Yeon Yoo,[b] Hye Rin Gu,[b] Yu Jin Lee,[b] Young Shin Cha,[b] Laekyeong You,[a] Kyungkyou Noh[a] and Jaheon Kim*[a]

[a] Department of Chemistry, Soongsil University, Seoul 06978, Korea. Fax: +82 2 824 4383; Tel: +82 2 820 0459; E-mail: jaheon@ssu.ac.kr

[b] Hankuk Academy of Foreign Studies, Yongin 17035, Korea.

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# 1. NMR and IR Spectra

## 6-Chloro-9-propyl-purin-2-amine (pr-GCl)

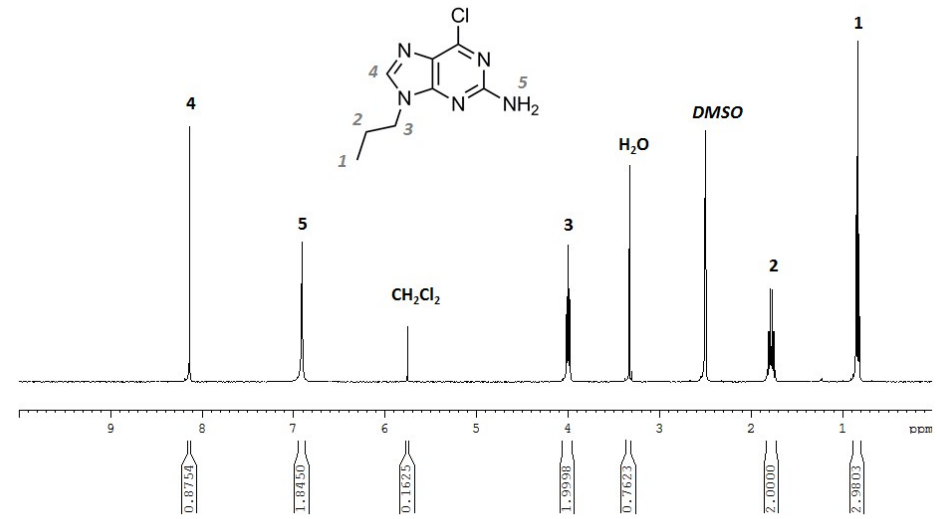



**Figure S1.** [1]H-NMR spectrum of pr-GCl dissolved in DMSO-$d_{6:}$.

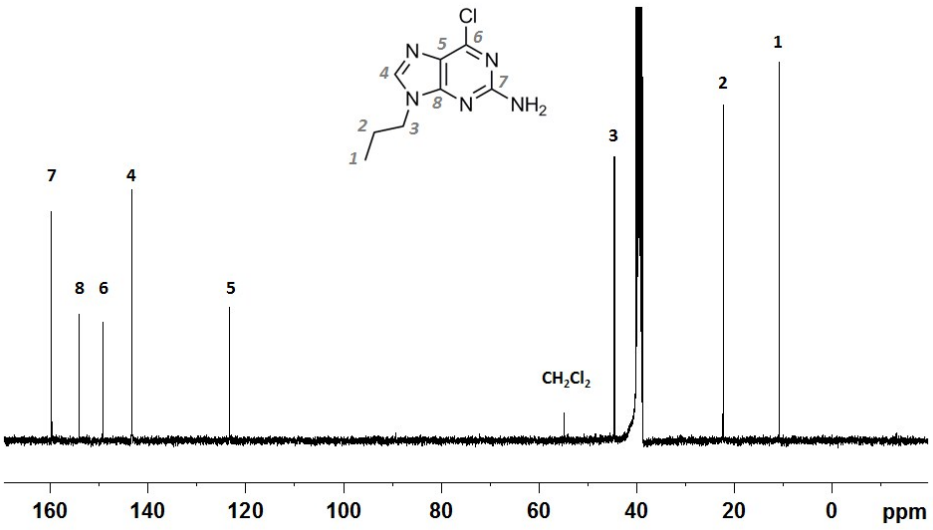



**Figure S2.** [13]C-NMR spectrum of pr-GCl in DMSO-$d_6$.

## 9-Propyl-Guanine (pr-G)

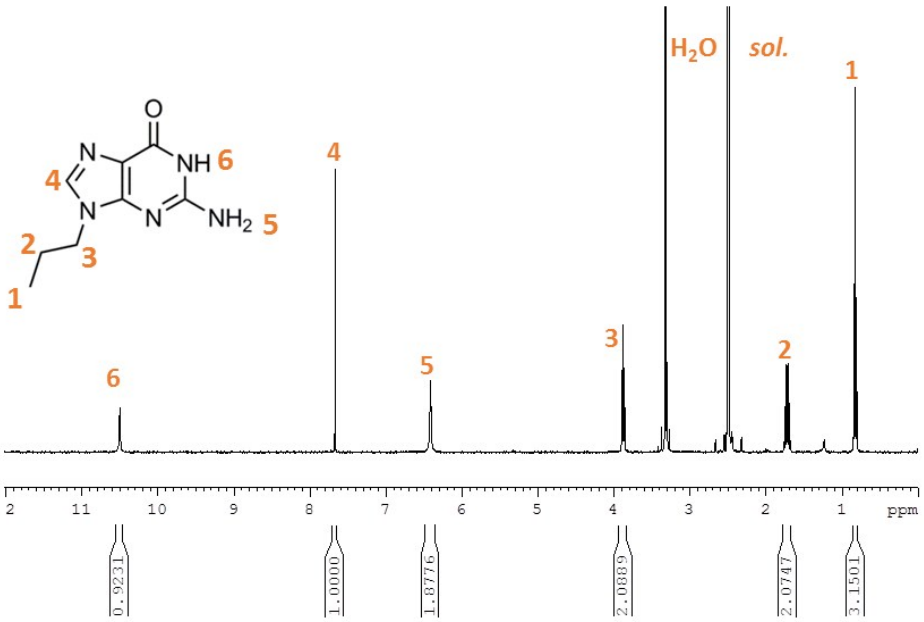



**Figure S3.** [1]H-NMR spectrum of pr-G in DMSO-$d_{6:}$.

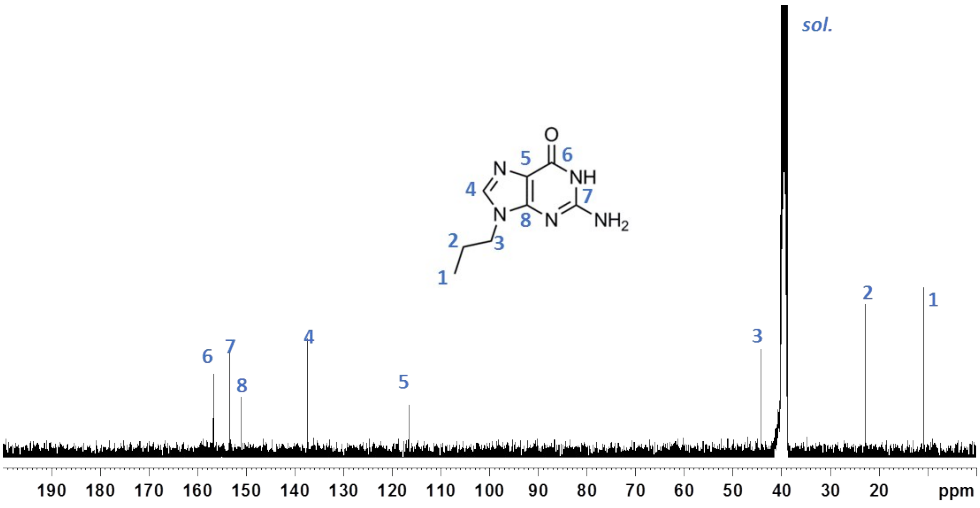



**Figure S4.** [13]C-NMR spectrum of pr-G in DMSO-$d_{6:}$.

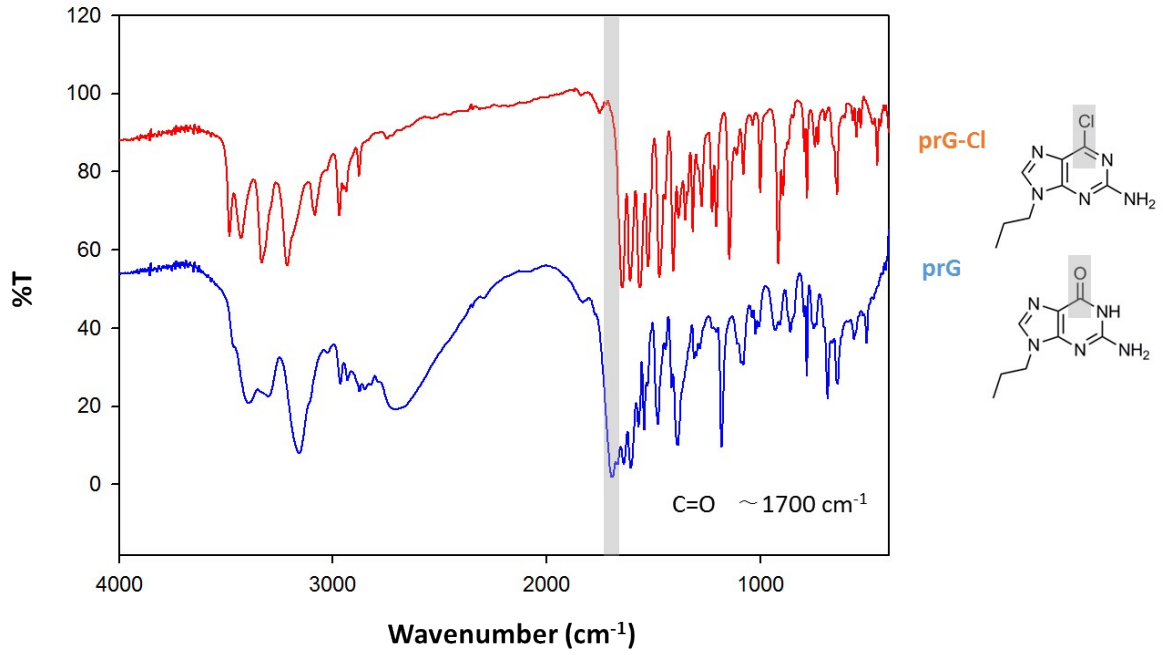



**Figure S5.** FT-IR spectra of pr-GCl and pr-G where the –C=O band for pr-G is highlighted.

## 6-Chloro-9-pentyl-purin-2-amine (pt-GCl)

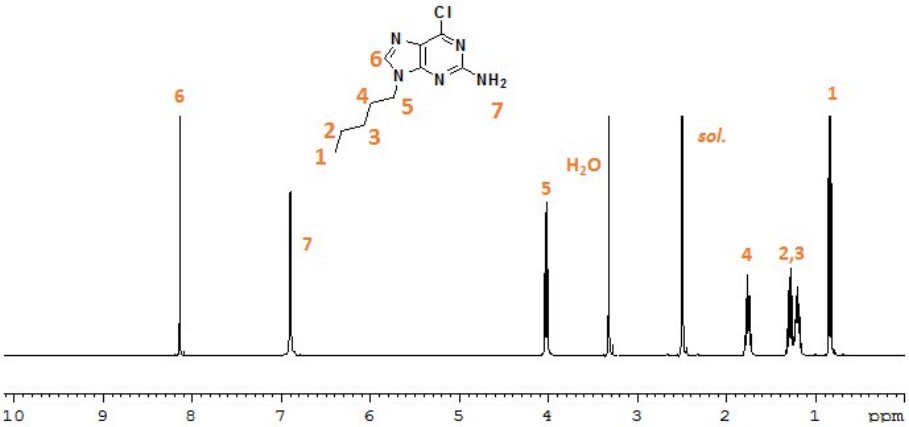



**Figure S6.** $^{1}$H-NMR spectrum of pt-GCl in DMSO-$d_6$.

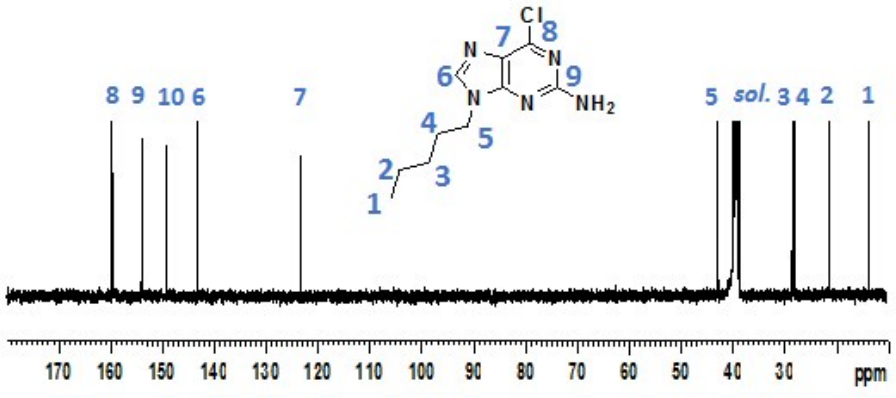



**Figure S7.** $^{13}$C-NMR spectrum of pt-GCl in DMSO-$d_6$.

## 9-Pentyl-Guanine (pt-G)

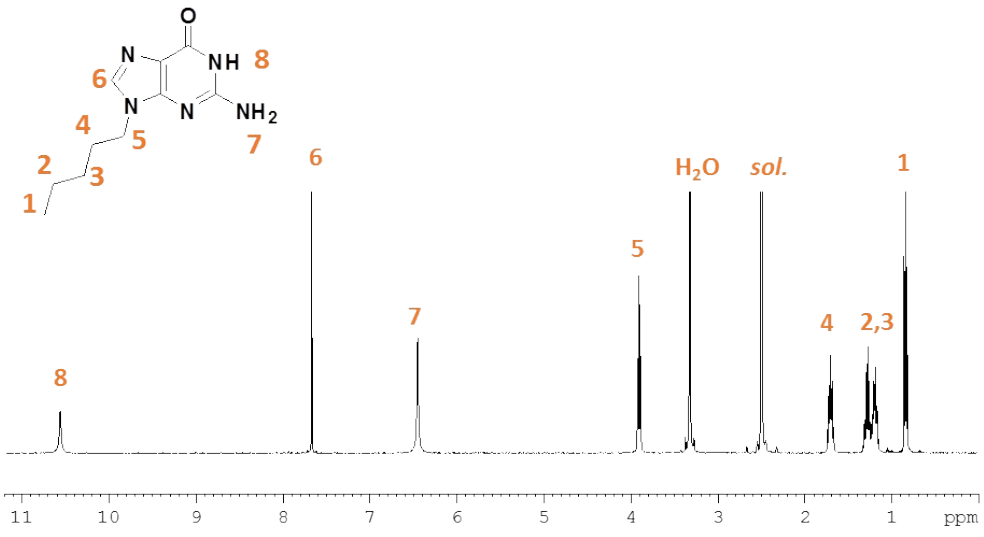



**Figure S8.** $^{1}$H-NMR spectrum of pt-G in DMSO-$d_6$.

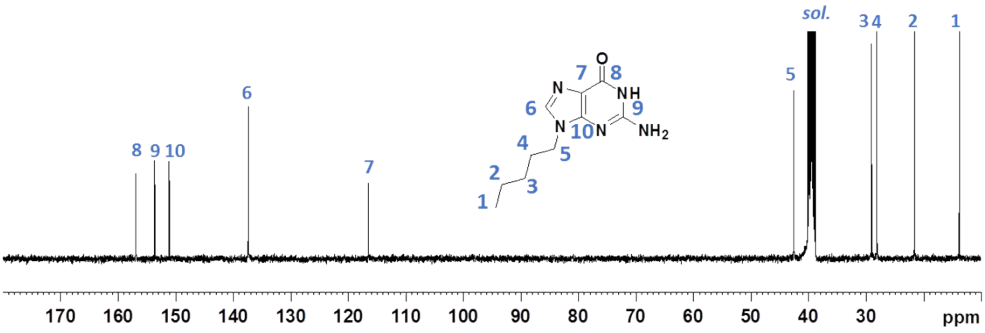



**Figure S9.** $^{13}$C-NMR spectrum of pt-G in DMSO-$d_6$.

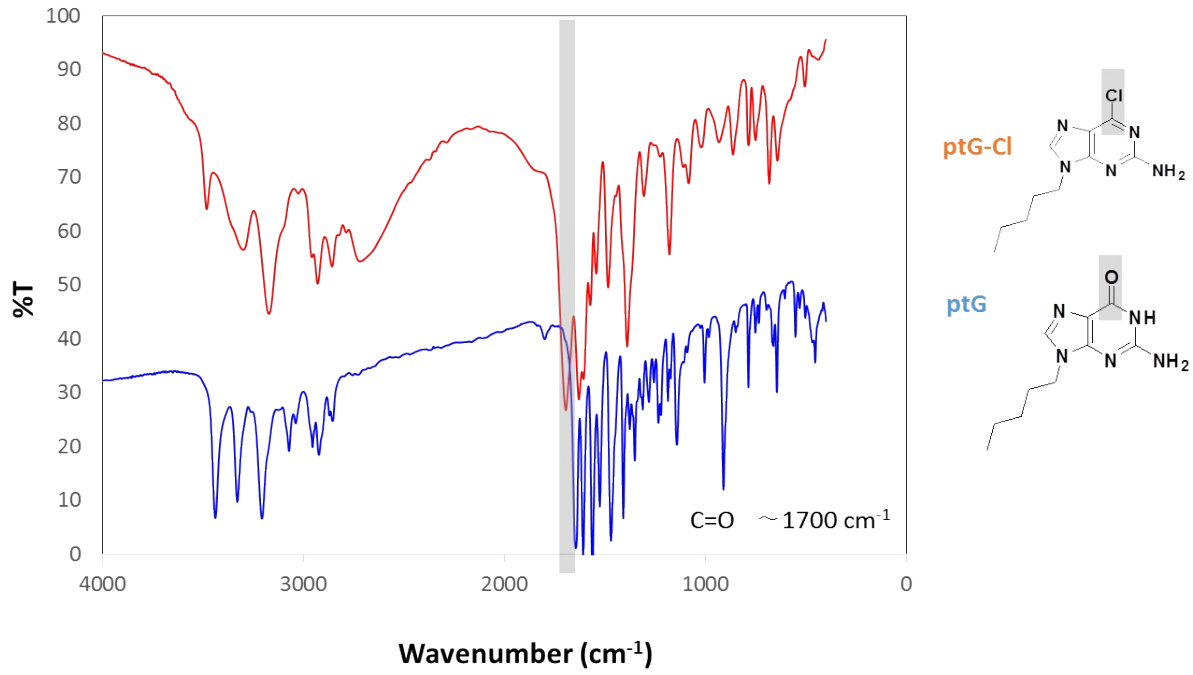



**Figure S10.** FT-IR spectra of pt-GCl and pt-G where the –C=O band for pr-G is highlighted.

## 2. Crystal Pictures

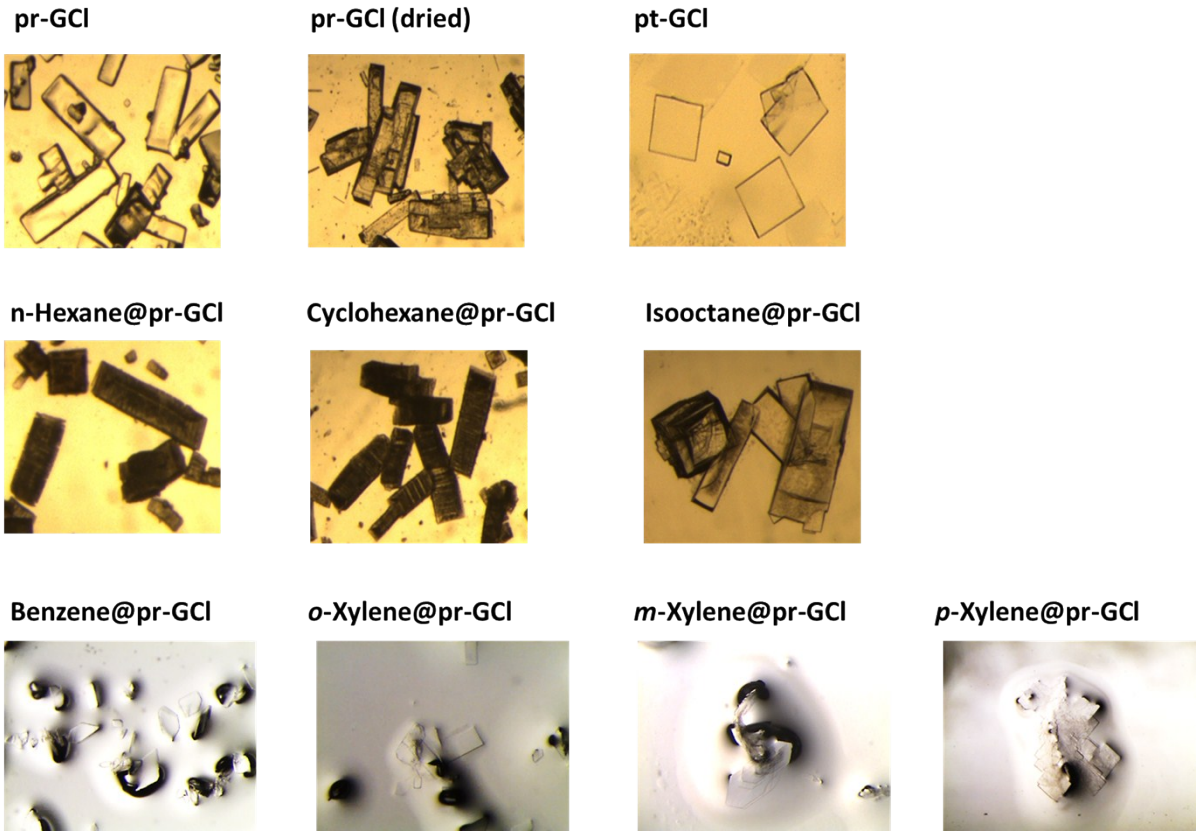



**Figure S11.** Crystal pictures seen under an optical microscope.

# 3. Single Crystal X-ray Diffraction Analyses

**Table S1.** Crystal data and structure refinement for pr-GCl
(Refined with intensity data treated with **SQUEEZE**).

| | | |
|---|---|---|
| Empirical formula | C8 H10 Cl N5 | |
| Formula weight | 211.66 | |
| Temperature | 173(2) K | |
| Wavelength | 0.71075 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | *a* = 14.916(7) Å | α= 64.365(8)°. |
| | *b* = 14.964(7) Å | β= 89.997(8)°. |
| | *c* = 15.309(7) Å | γ = 62.904(9)°. |
| Volume | 2659(2) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.058 $Mg/m^3$ | |
| Absorption coefficient | 0.263 $mm^{-1}$ | |
| F(000) | 880 | |
| Crystal size | 0.300 x 0.300 x 0.250 $mm^3$ | |
| Theta range for data collection | 3.025 to 26.373°. | |
| Index ranges | -18<=h<=17, -18<=k<=18, -19<=l<=17 | |
| Reflections collected | 21213 | |
| Independent reflections | 10218 [R(int) = 0.1238] | |
| Completeness to theta = 25.242° | 94.6 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 10218 / 0 / 506 | |
| Goodness-of-fit on $F^2$ | 0.865 | |
| Final R indices [I>2sigma(I)] | R1 = 0.0989, wR2 = 0.2552 | |
| R indices (all data) | R1 = 0.1766, wR2 = 0.3053 | |
| Extinction coefficient | 0.033(4) | |
| Largest diff. peak and hole | 0.442 and -0.434 $e.Å^{-3}$ | |

**Table S2.** Possible Hydrogen Bonds for pr-GCl

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

| D-H | d(D-H) | d(H..A) | <DHA | d(D..A) | A |
|---|---|---|---|---|---|
| C5-H5A | 0.950 | 2.283 | 159.12 | 3.189 | N6 |
| C6-H6B | 0.990 | 2.943 | 124.19 | 3.594 | Cl3 |
| C13-H13A | 0.950 | 2.313 | 159.41 | 3.220 | N1 [ x+1, y, z ] |
| C14-H14A | 0.990 | 2.961 | 123.74 | 3.606 | Cl4 [ x+1, y, z ] |
| C21-H21A | 0.950 | 2.294 | 159.29 | 3.200 | N16 [ x, y, z-1 ] |
| C22-H22A | 0.990 | 2.953 | 125.91 | 3.623 | Cl1 [ x, y, z-1 ] |
| C29-H29A | 0.950 | 2.304 | 158.94 | 3.208 | N11 [ x-1, y, z+1 ] |
| N3-H3A | 0.880 | 2.219 | 177.92 | 3.099 | N17 [ x, y, z-1 ] |
| N3-H3B | 0.880 | 2.541 | 170.52 | 3.412 | N9 [ x-1, y, z ] |
| N8-H8D | 0.880 | 2.197 | 171.43 | 3.070 | N12 [ x, y, z+1 ] |
| N8-H8E | 0.880 | 2.516 | 171.59 | 3.389 | N4 |
| N13-H13B | 0.880 | 2.223 | 174.84 | 3.100 | N7 [ x, y, z-1 ] |
| N13-H13C | 0.880 | 2.516 | 171.69 | 3.389 | N19 [ x+1, y, z-1 ] |
| N18-H18A | 0.880 | 2.222 | 178.25 | 3.101 | N2 [ x, y, z+1 ] |
| N18-H18B | 0.880 | 2.487 | 173.30 | 3.362 | N14 [ x, y, z+1 ] |

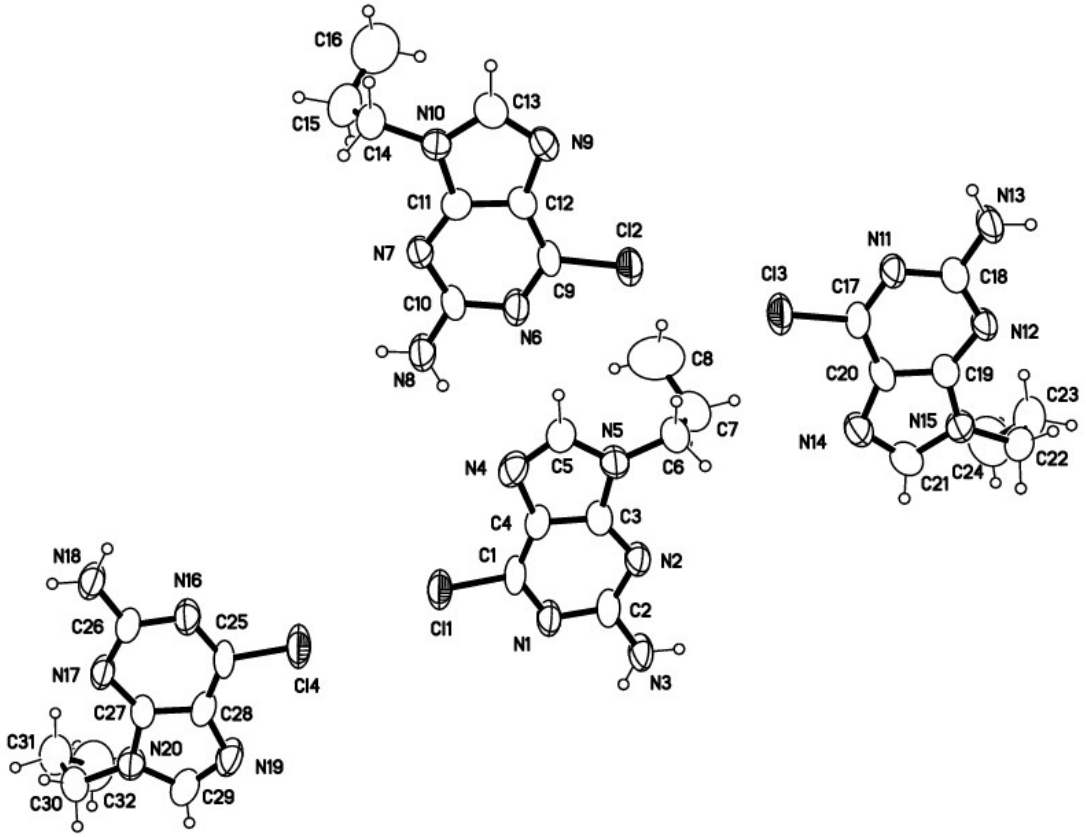



**Figure S12.** ORTEP view of four independent pr-GCl molecules in an asymmetric unit is displayed at 50% probability level.

**Table S3.** Crystal data and structure refinement for pt-GCl.

| | | |
|---|---|---|
| Empirical formula | C20 H28 Cl2 N10 | |
| Formula weight | 479.42 | |
| Temperature | 296(2) K | |
| Wavelength | 0.71075 Å | |
| Crystal system | Triclinic | |
| Space group | P -1 | |
| Unit cell dimensions | *a* = 15.078(3) Å | α= 81.61(3)°. |
| | *b* = 15.132(3) Å | β= 80.08(3)°. |
| | *c* = 21.864(4) Å | γ = 89.95(3)°. |
| Volume | 4860.0(18) $Å^3$ | |
| Z | 8 | |
| Density (calculated) | 1.310 $Mg/m^3$ | |
| Absorption coefficient | 0.296 $mm^{-1}$ | |
| F(000) | 2016 | |
| Crystal size | 0.300 x 0.200 x 0.100 $mm^3$ | |
| Theta range for data collection | 2.988 to 26.373°. | |
| Index ranges | -18<=h<=18, -18<=k<=18, -27<=l<=23 | |
| Reflections collected | 39215 | |
| Independent reflections | 18927 [R(int) = 0.1619] | |
| Completeness to theta = 25.242° | 96.2 % | |
| Absorption correction | None | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 18927 / 48 / 1153 | |
| Goodness-of-fit on $F^2$ | 0.992 | |
| Final R indices [I>2sigma(I)] | R1 = 0.1411, wR2 = 0.3251 | |
| R indices (all data) | R1 = 0.2303, wR2 = 0.3679 | |
| Largest diff. peak and hole | 0.572 and -0.705 $e.Å^{-3}$ | |

**Table S4.** Possible Hydrogen Bonds for pt-GCl

Hydrogen bonds with H..A < r(A) + 2.000 Angstroms and <DHA > 110 deg.

| D-H | d(D-H) | d(H..A) | <DHA | d(D..A) | A |
|---|---|---|---|---|---|
| N5A-H5A1 | 0.860 | 2.231 | 173.15 | 3.086 | N2F |
| N5A-H5A2 | 0.860 | 2.684 | 158.60 | 3.499 | N3B [ x+1, y, z ] |
| C5A-H5A | 0.930 | 2.434 | 157.86 | 3.314 | N1B [ x+1, y-1, z ] |
| C6A-H6A2 | 0.970 | 2.969 | 131.42 | 3.684 | Cl1E |
| N5B-H5B1 | 0.860 | 2.638 | 162.07 | 3.466 | N3A [ x-1, y+1, z ] |
| N5B-H5B2 | 0.860 | 2.284 | 171.46 | 3.137 | N2E [ x, y+1, z ] |
| C5B-H5B | 0.930 | 2.452 | 155.35 | 3.320 | N1A [ x-1, y, z ] |
| C6B-H6B1 | 0.970 | 2.939 | 130.84 | 3.648 | Cl1F |
| N5C-H5C1 | 0.860 | 2.221 | 176.11 | 3.080 | N2G [ -x, -y+2, -z+1 ] |
| N5C-H5C2 | 0.860 | 2.528 | 174.06 | 3.384 | N3D [ x-1, y, z ] |
| C5C-H5C | 0.930 | 2.365 | 160.83 | 3.258 | N1D |
| C6C-H6C2 | 0.970 | 2.951 | 128.25 | 3.632 | Cl1H [ x, y+1, z ] |
| N5D-H5D1 | 0.860 | 2.234 | 177.81 | 3.094 | N2H |
| N5D-H5D2 | 0.860 | 2.505 | 173.87 | 3.361 | N3C |
| C5D-H5D | 0.930 | 2.363 | 161.90 | 3.259 | N1C [ x+1, y, z ] |
| C6D-H6D1 | 0.970 | 2.944 | 128.13 | 3.624 | Cl1G [ -x+1, -y+1, -z+1 ] |
| N5E-H5E1 | 0.860 | 2.614 | 167.35 | 3.458 | N3F [ x, y-1, z ] |
| N5E-H5E2 | 0.860 | 2.224 | 170.71 | 3.076 | N2B [ x, y-1, z ] |
| C5E-H5E | 0.930 | 2.384 | 159.69 | 3.272 | N1F |
| N5F-H5F1 | 0.860 | 2.222 | 169.69 | 3.072 | N2A |
| N5F-H5F2 | 0.860 | 2.628 | 167.22 | 3.472 | N3E |
| C5F-H5F | 0.930 | 2.350 | 161.53 | 3.246 | N1E [ x, y+1, z ] |
| C6F-H6F2 | 0.970 | 2.973 | 130.69 | 3.680 | Cl1B [ x+1, y, z ] |
| N5G-H5G1 | 0.860 | 2.200 | 178.68 | 3.060 | N2C [ -x, -y+2, -z+1 ] |
| N5G-H5G2 | 0.860 | 2.549 | 173.66 | 3.405 | N3H [ -x, -y+1, -z+1 ] |
| C5G-H5G | 0.930 | 2.301 | 163.07 | 3.202 | N1H [ -x+1, -y+1, -z+1 ] |
| C6G-H6G1 | 0.970 | 2.917 | 125.22 | 3.566 | Cl1D [ -x+1, -y+2, -z+1 ] |
| N5H-H5H1 | 0.860 | 2.194 | 177.89 | 3.053 | N2D |
| N5H-H5H2 | 0.860 | 2.570 | 173.97 | 3.426 | N3G [ -x+1, -y+1, -z+1 ] |
| C5H-H5H | 0.930 | 2.311 | 163.11 | 3.213 | N1G [ -x, -y+1, -z+1 ] |
| C6H-H6H1 | | | 0.970 | 2.928 | 126.01 | 3.585 | Cl1C |

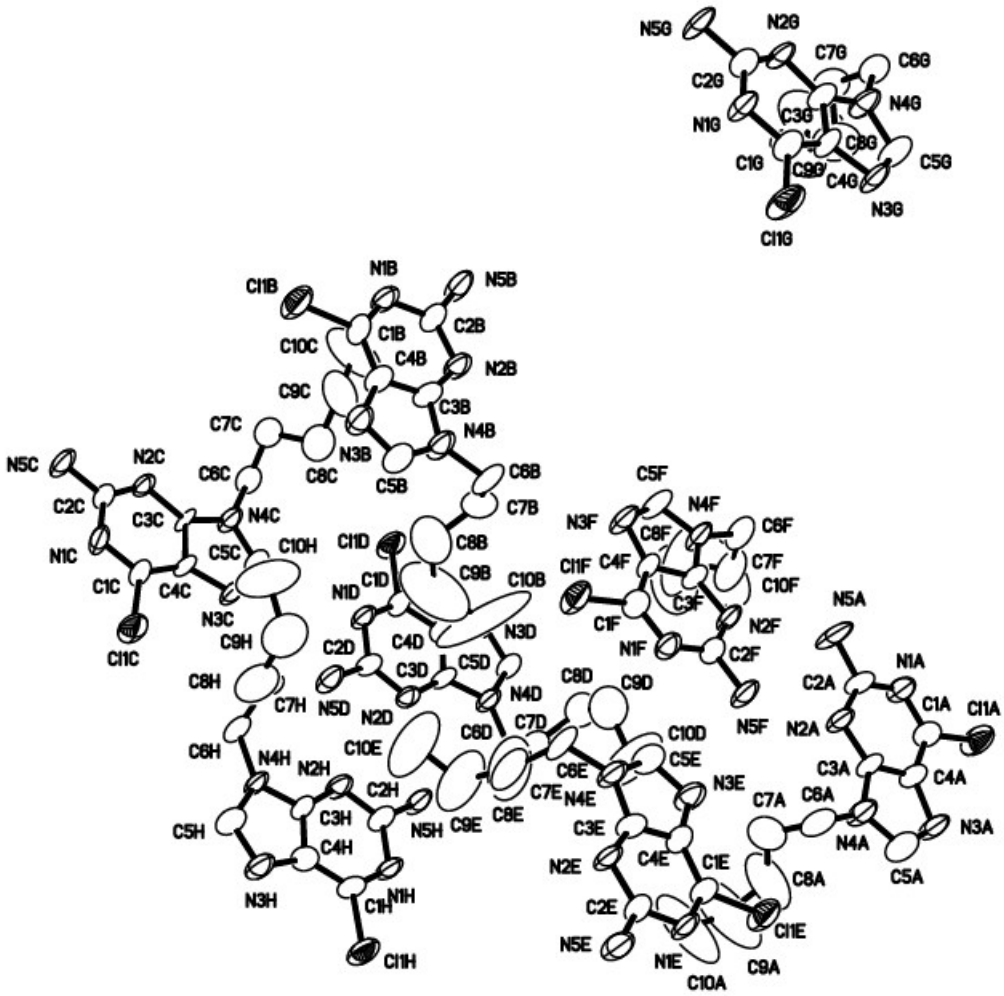



**Figure S13.** ORTEP view of eight independent pt-GCl molecules in an asymmetric unit is displayed at 50% probability level.

**Table S5.** Crystal data and structure refinement for p-Xylene@pr-GCl.

| | | |
|---|---|---|
| Empirical formula | C24 H30 Cl2 N10 | |
| Formula weight | 529.48 | |
| Temperature | 173(2) K | |
| Wavelength | 0.710 Å | |
| Crystal system | Orthorhombic | |
| Space group | *Ccca* | |
| Unit cell dimensions | *a* = 15.022(3) Å | α= 90°. |
| | *b* = 44.140(9) Å | β= 90°. |
| | *c* = 15.211(3) Å | γ = 90°. |
| Volume | 10086(3) $Å^3$ | |
| Z | 16 | |
| Density (calculated) | 1.395 $Mg/m^3$ | |
| Absorption coefficient | 0.293 $mm^{-1}$ | |
| F(000) | 4448 | |
| Crystal size | 0.30 x 0.20 x 0.02 $mm^3$ | |
| Theta range for data collection | 2.709 to 30.473°. | |
| Index ranges | 0<=h<=22, 0<=k<=62, 0<=l<=23 | |
| Reflections collected | 96254 | |
| Independent reflections | 7649 [R(int) = 0.534] | |
| Completeness to theta = 25.214° | 99.5 % | |
| Absorption correction | Empirical | |
| Refinement method | Full-matrix least-squares on $F^2$ | |
| Data / restraints / parameters | 7649 / 100 / 432 | |
| Goodness-of-fit on $F^2$ | 2.240 | |
| Final R indices [I>2sigma(I)] | R1 = 0.2602, wR2 = 0.5974 | |
| R indices (all data) | R1 = 0.3296, wR2 = 0.6304 | |
| Largest diff. peak and hole | 2.190 and -1.519 $e.Å^{-3}$ | |

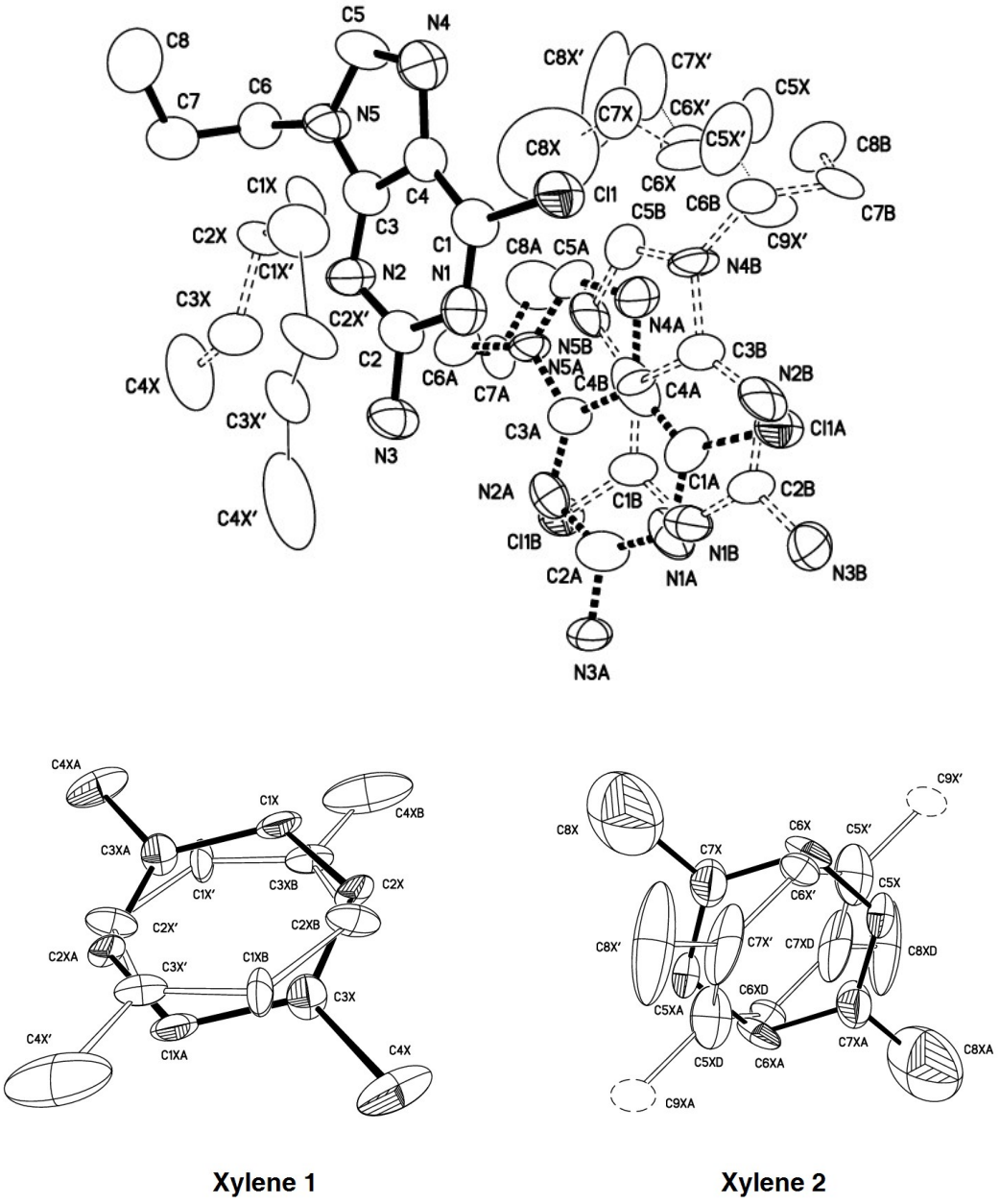
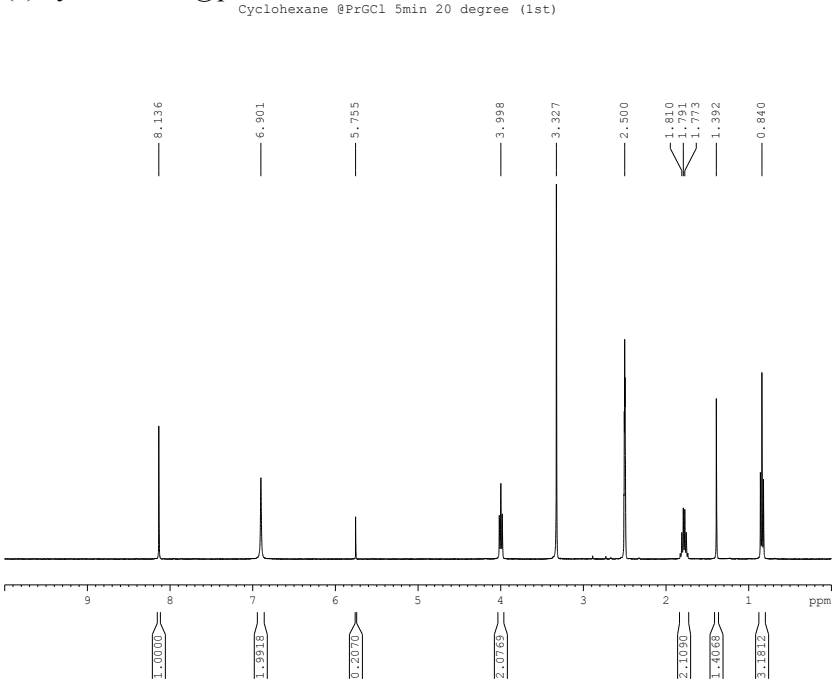



**Figure S14.** ORTEP view of *p*-xylene@pr-GCl molecules in an asymmetric unit is displayed at 50% probability level. One of two pr-GCl molecules is disordered over two sites with an equal probability. At the bottom, two independent and disorder *p*-xylene molecules are drawn separately at 20% probability level.

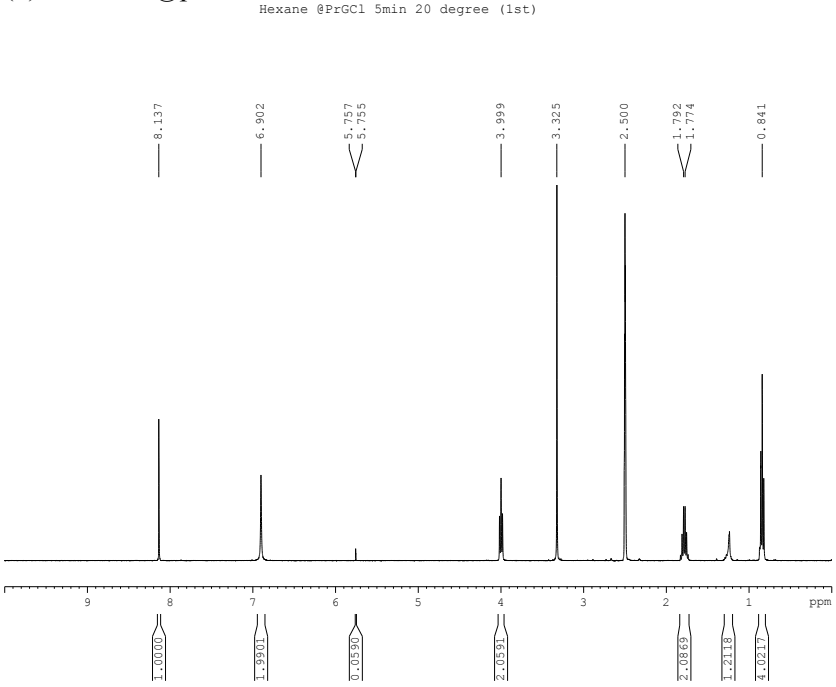
# 4. NMR Spectra for the Guest-Included pr-GCl Crystals

**Figure S15.** $^{1}$H-NMR spectra for the guest-included pr-GCl crystals: guest = (a) cyclohexane, (b) *n*-hexane, (c) isooctane, (d) benzene, (e) *o*-xylene, (f) *m*-xylene, and (g) *p*-xylene. Only the NMR spectra for the crystals immersed in each solvent for 5 min are shown for simplicity.

(a) cyclohexane@pr-GCl

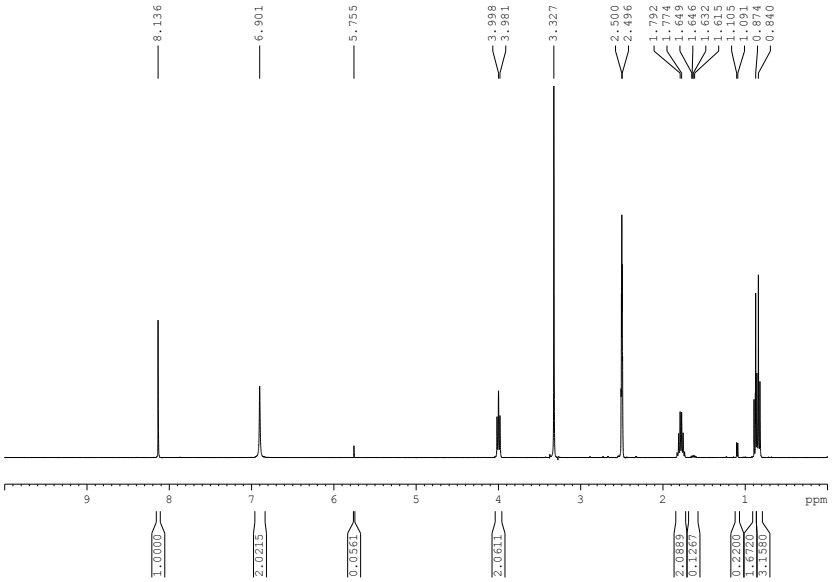



(b) *n*-hexane@pr-GCl



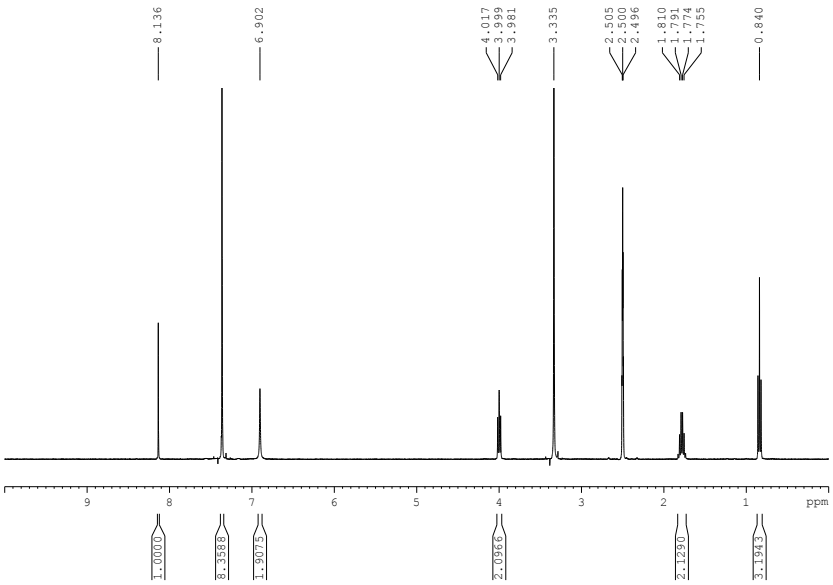
(c) isooctane@pr-GCl

Isooctane @PrGCl 5min 20 degree (1st)

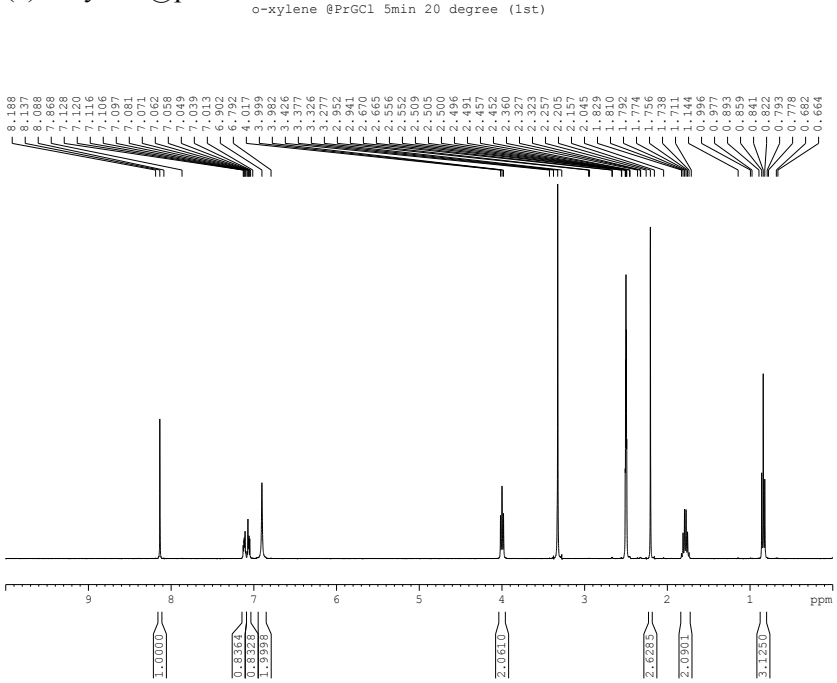



(d) benzene@pr-GCl

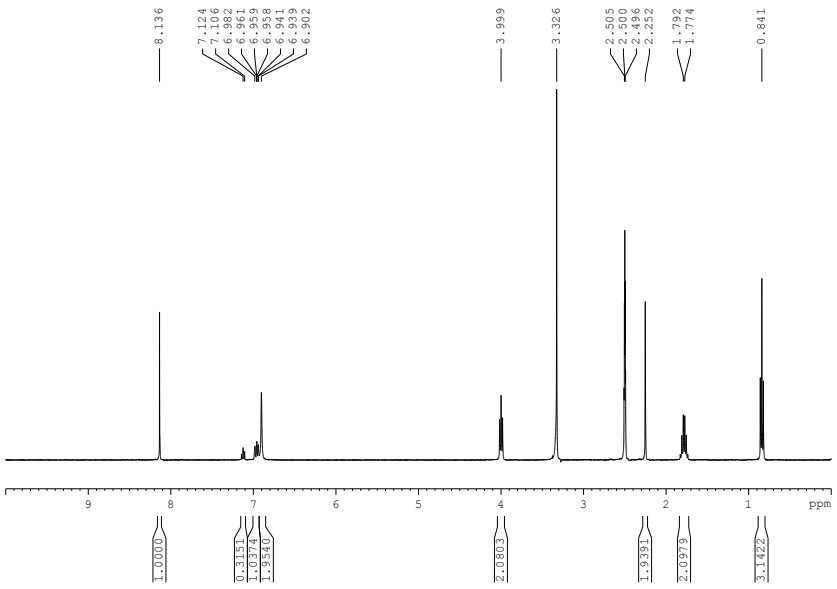
Benzene @PrGCl 5min 20 degree (2nd)



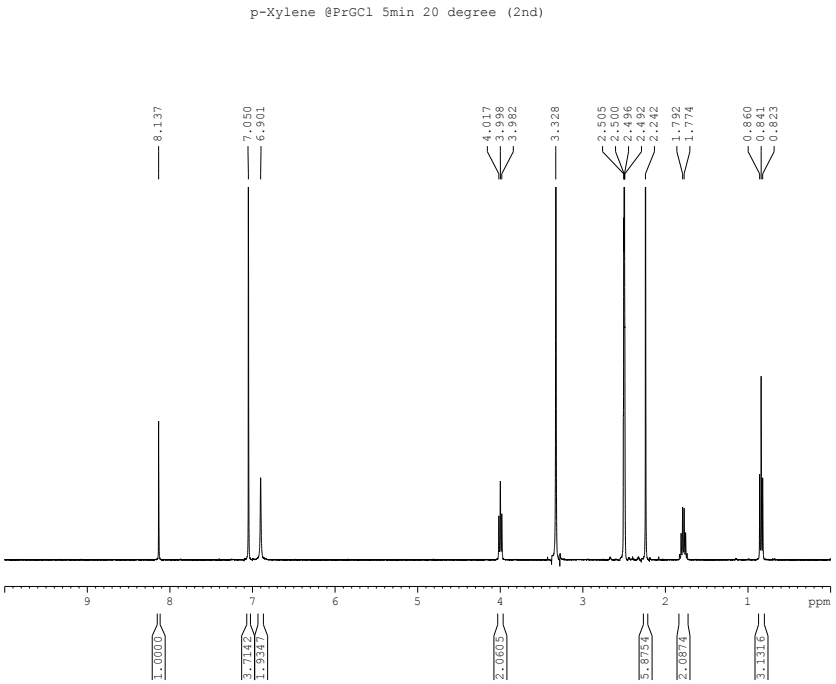
(e) *o*-xylene@pr-GCl




(f) *m*-xylene@pr-GCl



(g) *p*-xylene@pr-GCl



# 5. PXRD Patterns

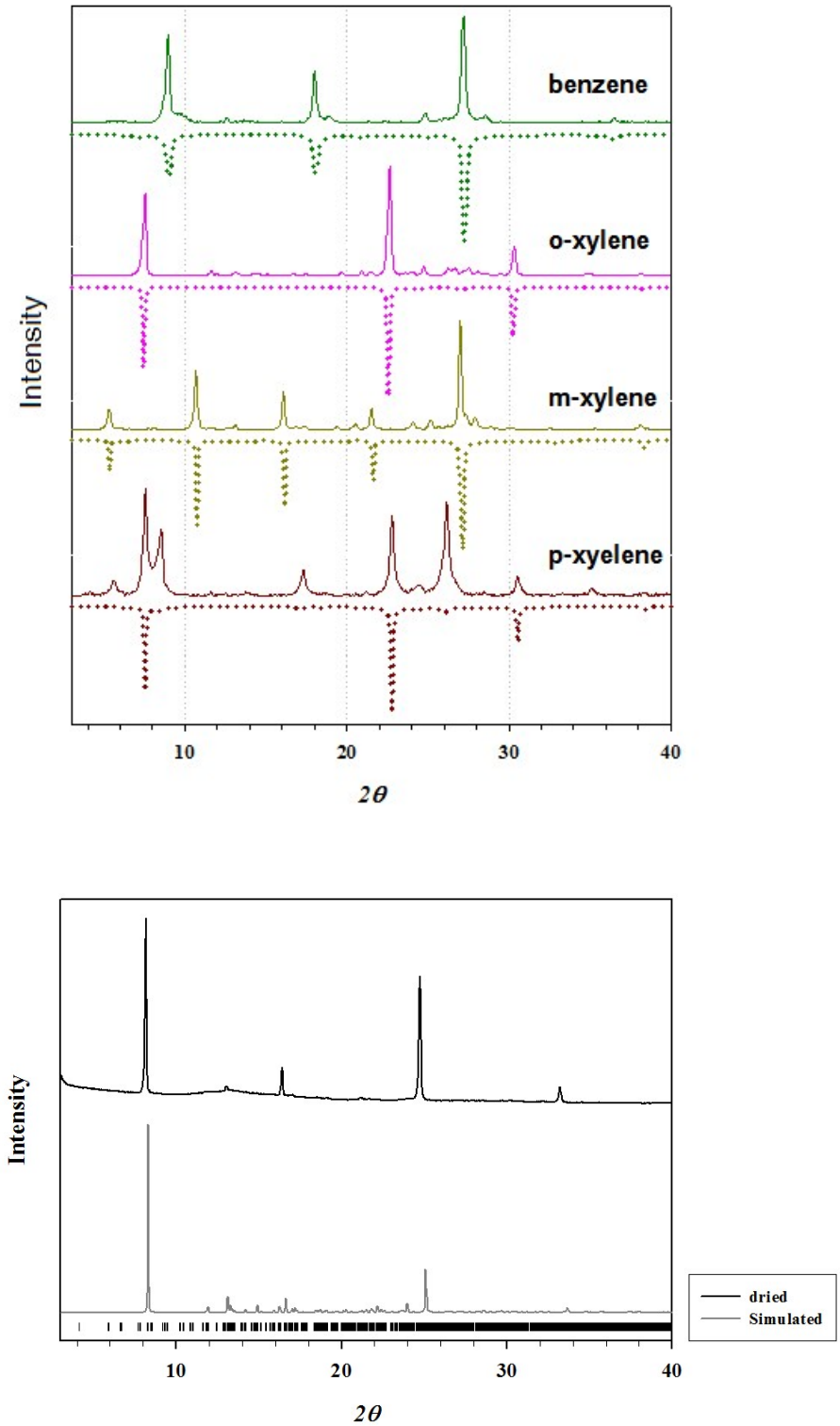



**Figure S16.** (**Top**) Comparison of the PXRD patterns measured for the pr-GCl crystals immersed in solvent (solid line) and those for the recrystallized pr-GCl in solvent (dotted and inverted lines). It is not certain why *p*-xylene gives different PXRD patterns for the samples prepared differently. (**Bottom**) Comparison of the measured PXRD pattern for dried pt-GCl crystals with the simulated one generated using a crystal structure.