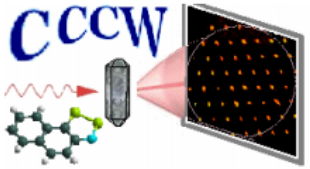

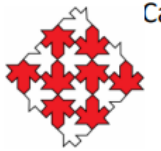

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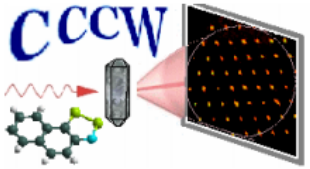
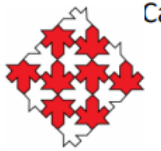
OLEX2 – Modeling disorder: Fixed positions

Louise Dawe
Wilfrid Laurier University

and

Jamie Ritch
University of Winnipeg





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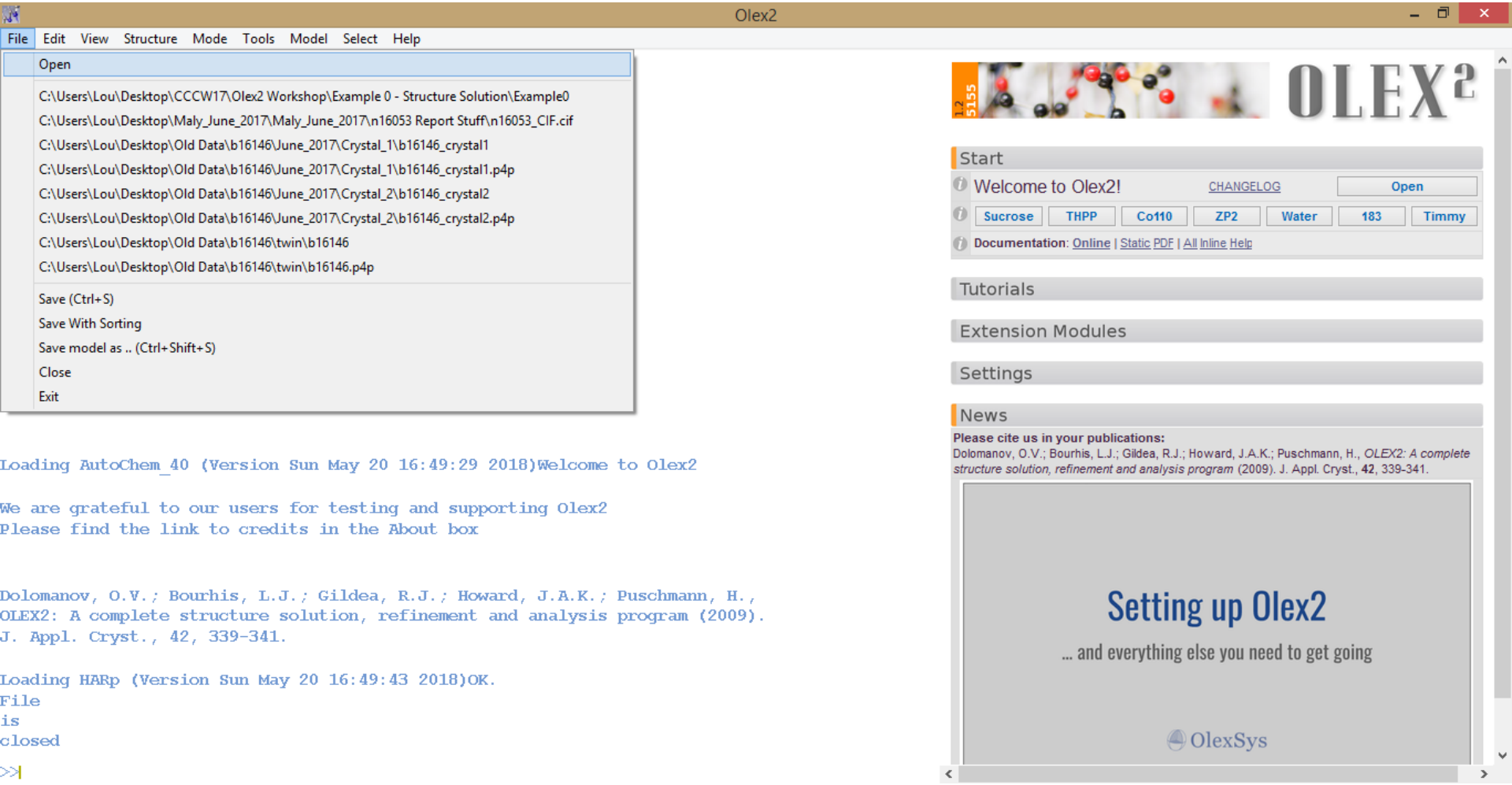
Data from Charlotte Stern

Check out the OLEX2 youtube channel for an alternate way to tackle this:
https://www.youtube.com/watch?v=LklP0s-KEFQ

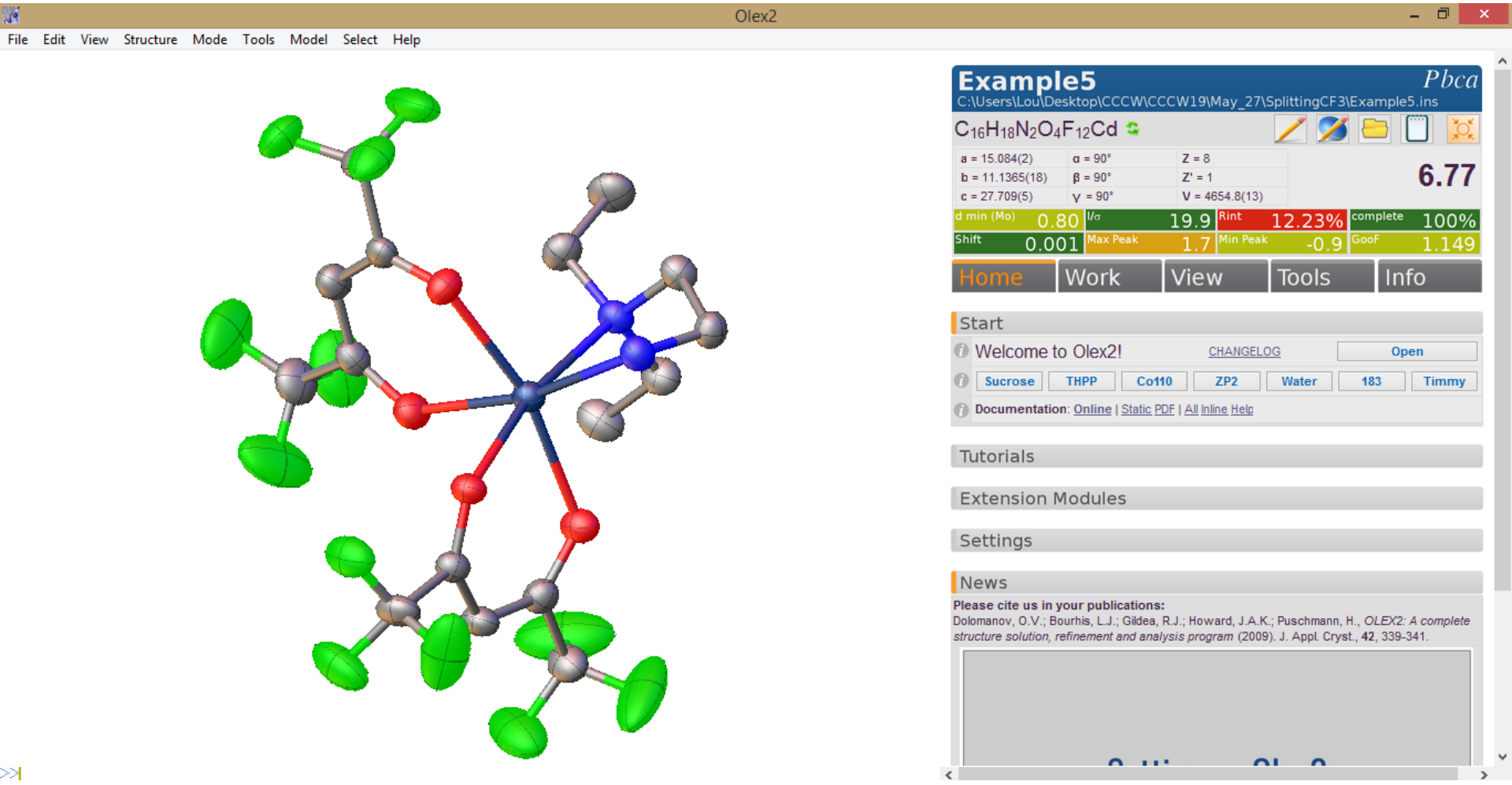
Another good resource:
http://web.mit.edu/pmueller/www/ACA2007/WK01/Disorder.pdf

Navigate to SplittingCF3 folder.
File → Open “Example5.ins”

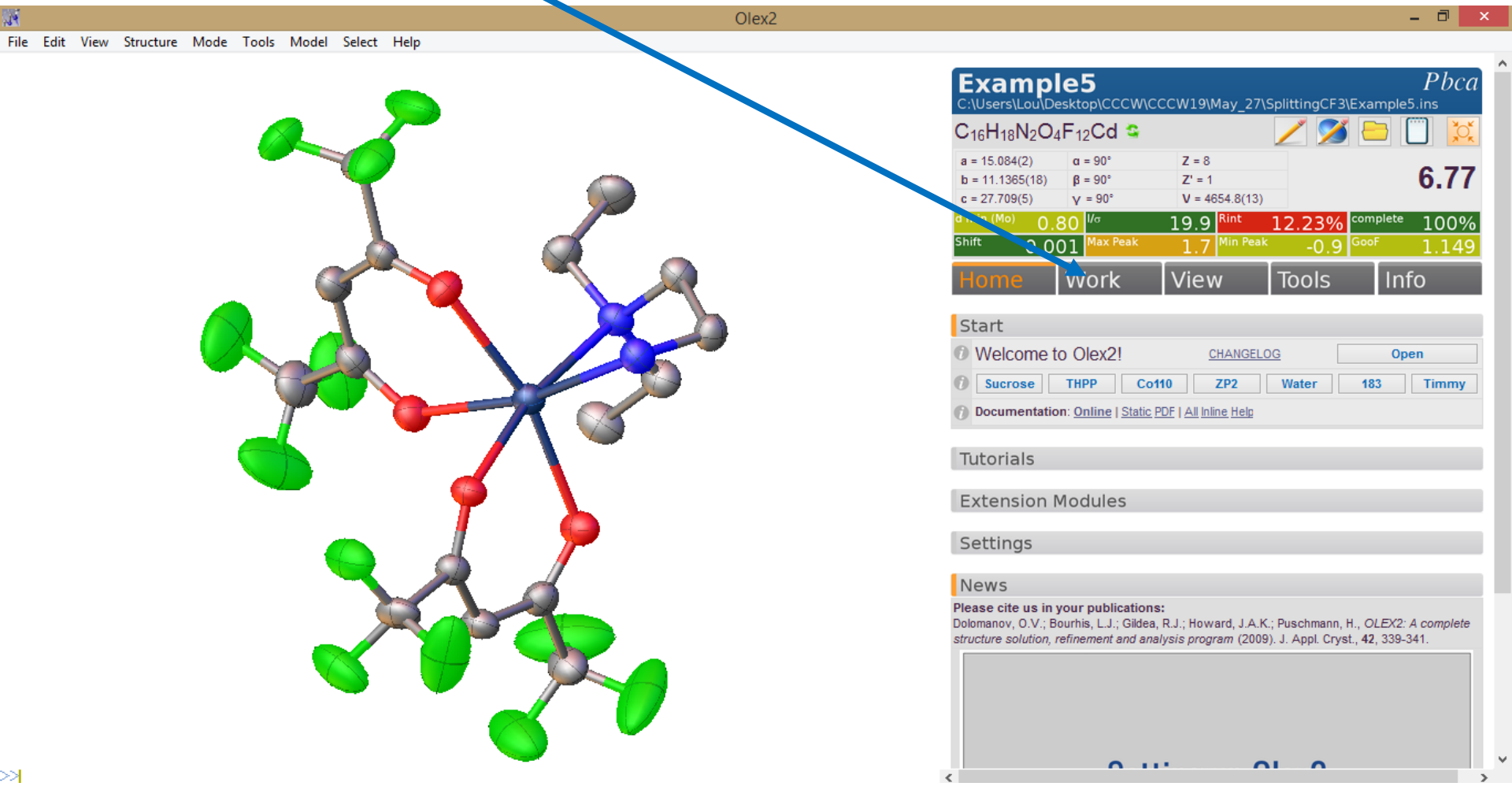


Looks like all of our work is done! Coffee?

No hydrogens = No coffee

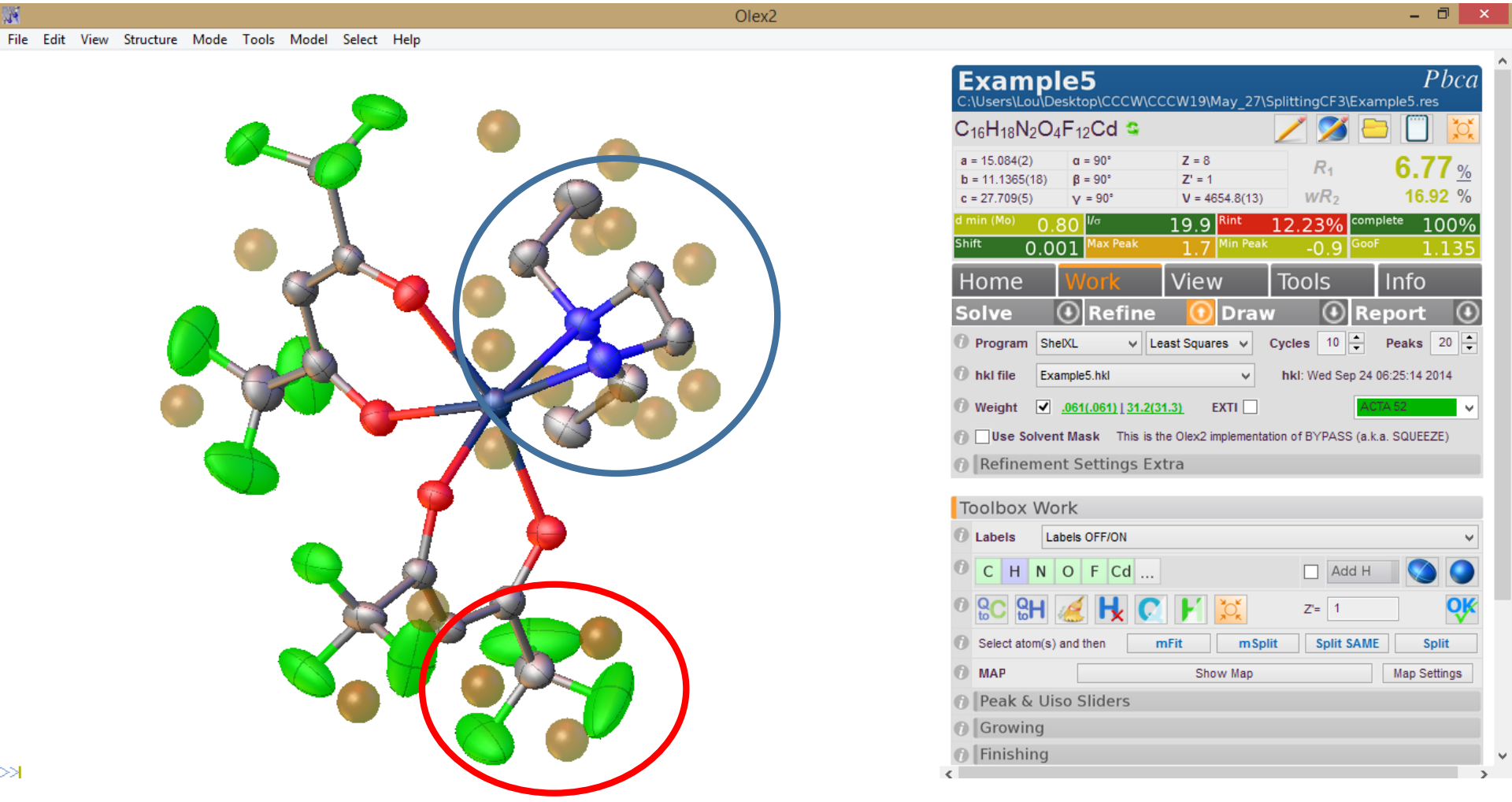


Go to:
Work
Refine dropdown
Refine with Shelxl



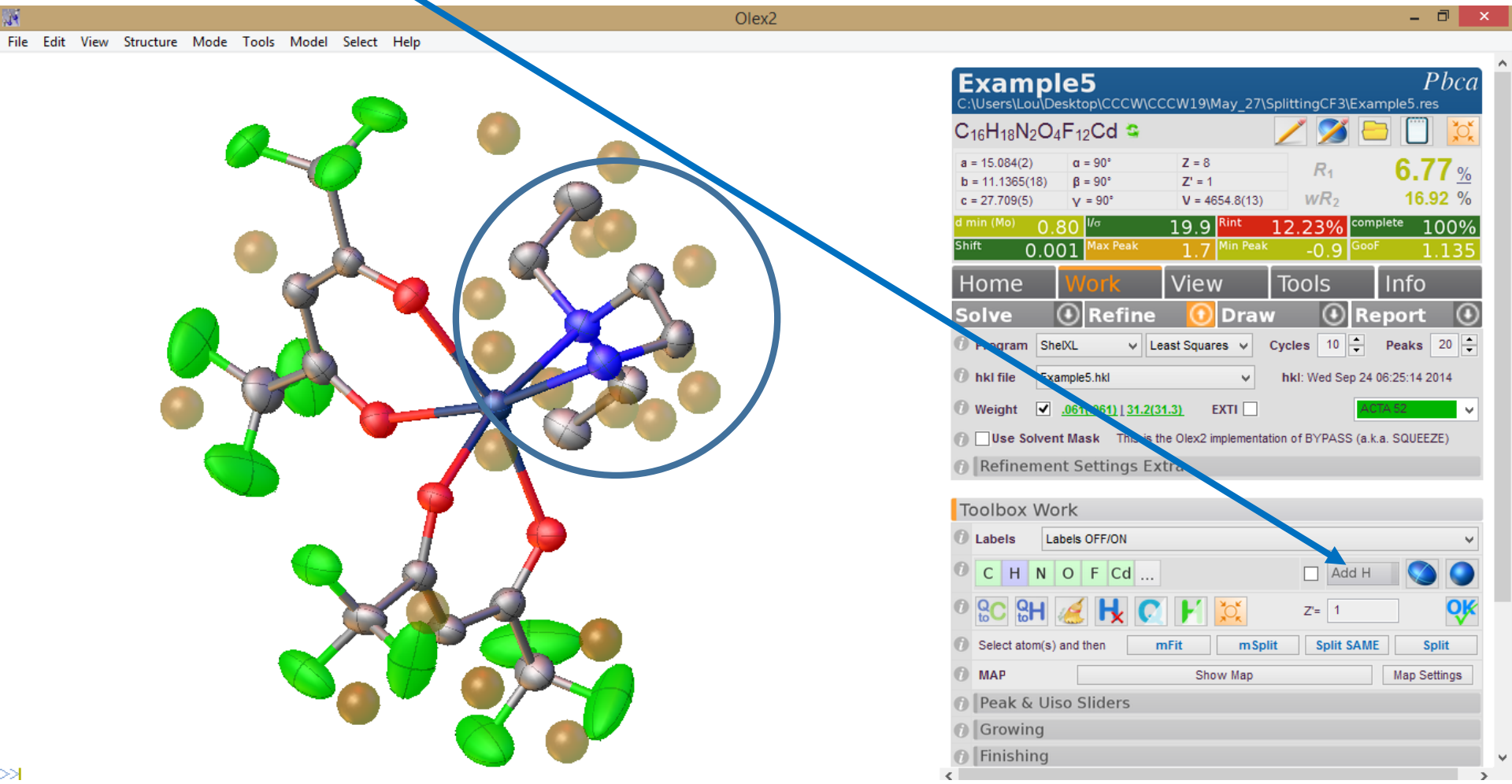
Notice two things here

1. Yes, we missed a bunch of hydrogens
2. There are three residual peaks directly between the F-atoms of this -CF_3 group



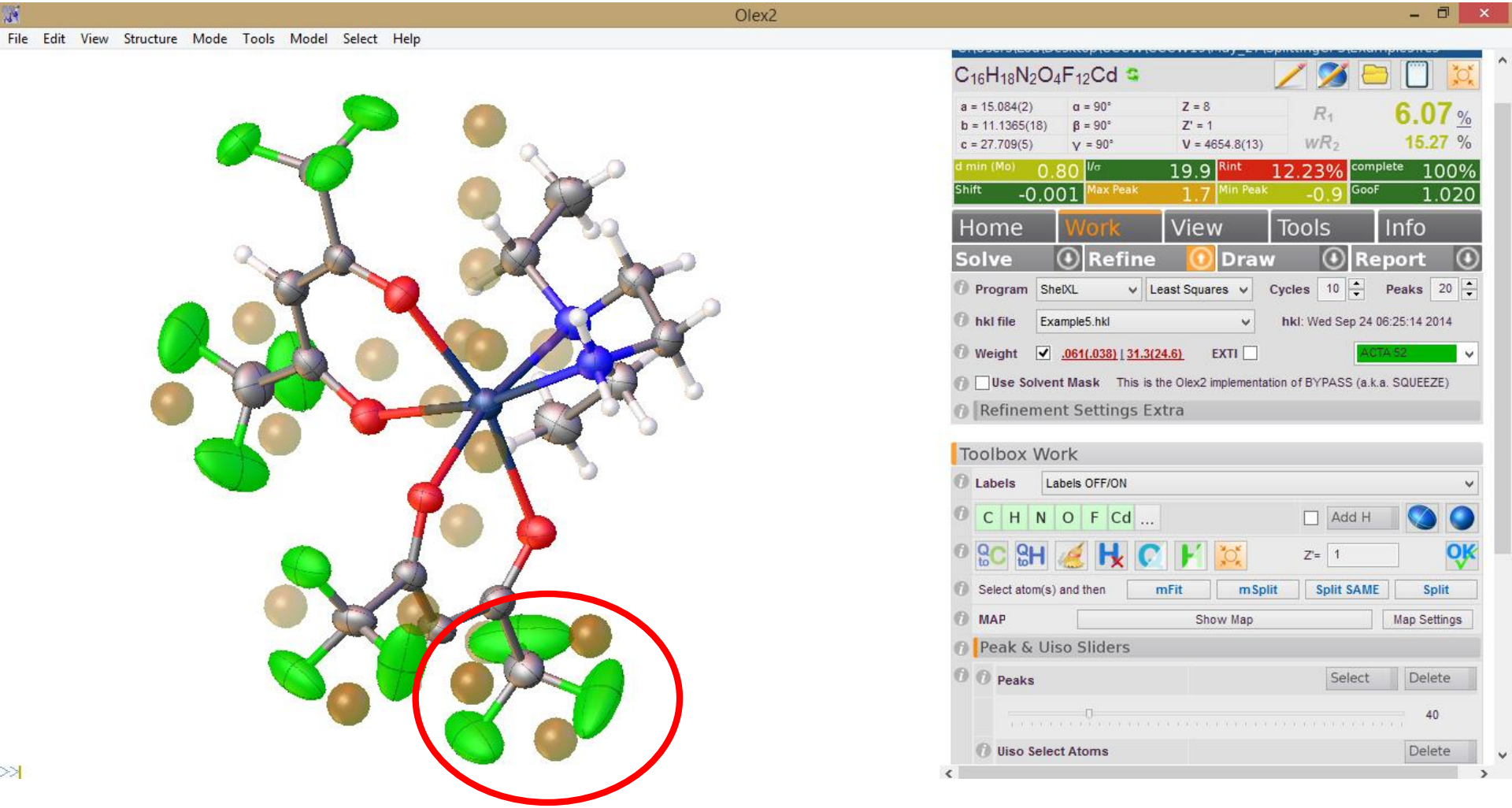
Now:

1. Add H; then Refine

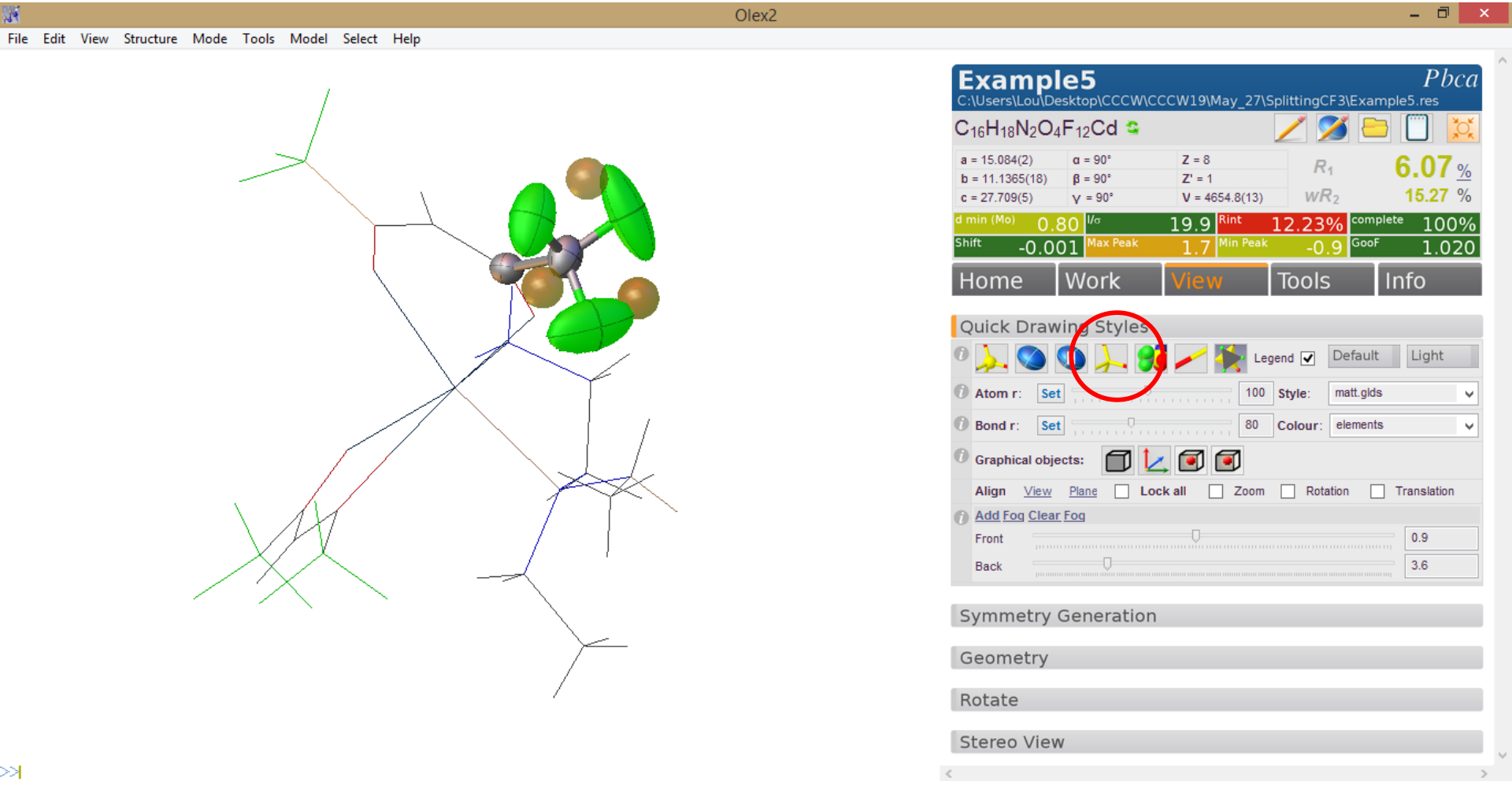


1. Looks good, but
2. Now there are residual peaks between F-atoms in multiple -CF_3 groups!

Let's deal with one of these groups; the highest residual peaks (Q1, Q2, Q4) are associated with the group comprised of C10, F10, F11, F12.



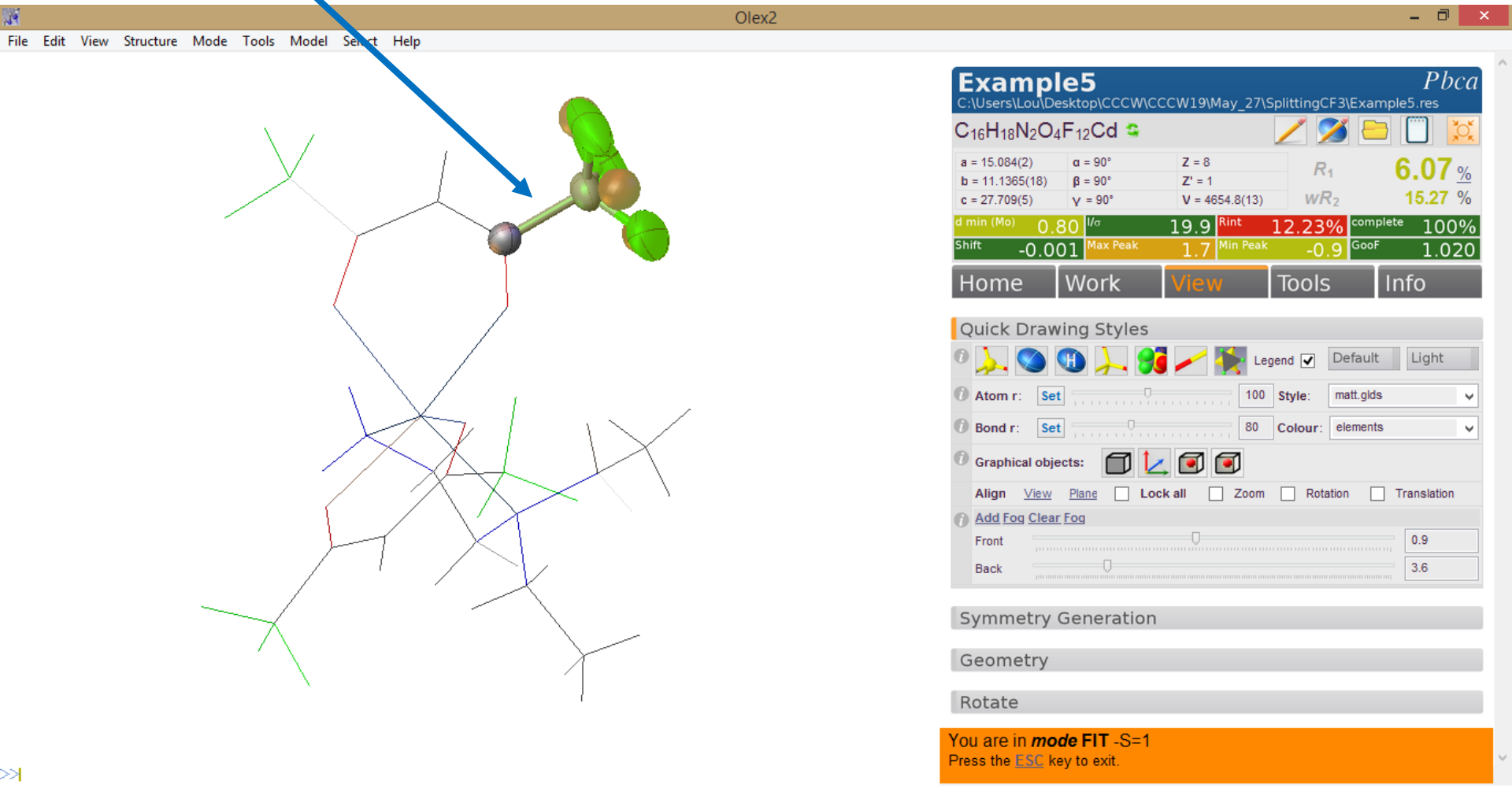
I'm going to tidy my display to work on this (mouse scroll down, or "Peak & Uiso Sliders" workbar, to show only the top four peaks and reorient my molecule to carefully inspect this group.)
Also, "Ctrl A", then select C8, C10, F10, F11, F12, then "View" and "Quick Drawing Styles" to convert everything else to a line
(You don't have to do this, but it makes my slide look better!)



Next, select C10, F10, F11, F12 in this order (or at least, C10 first, and then the three F atoms.) Then type:

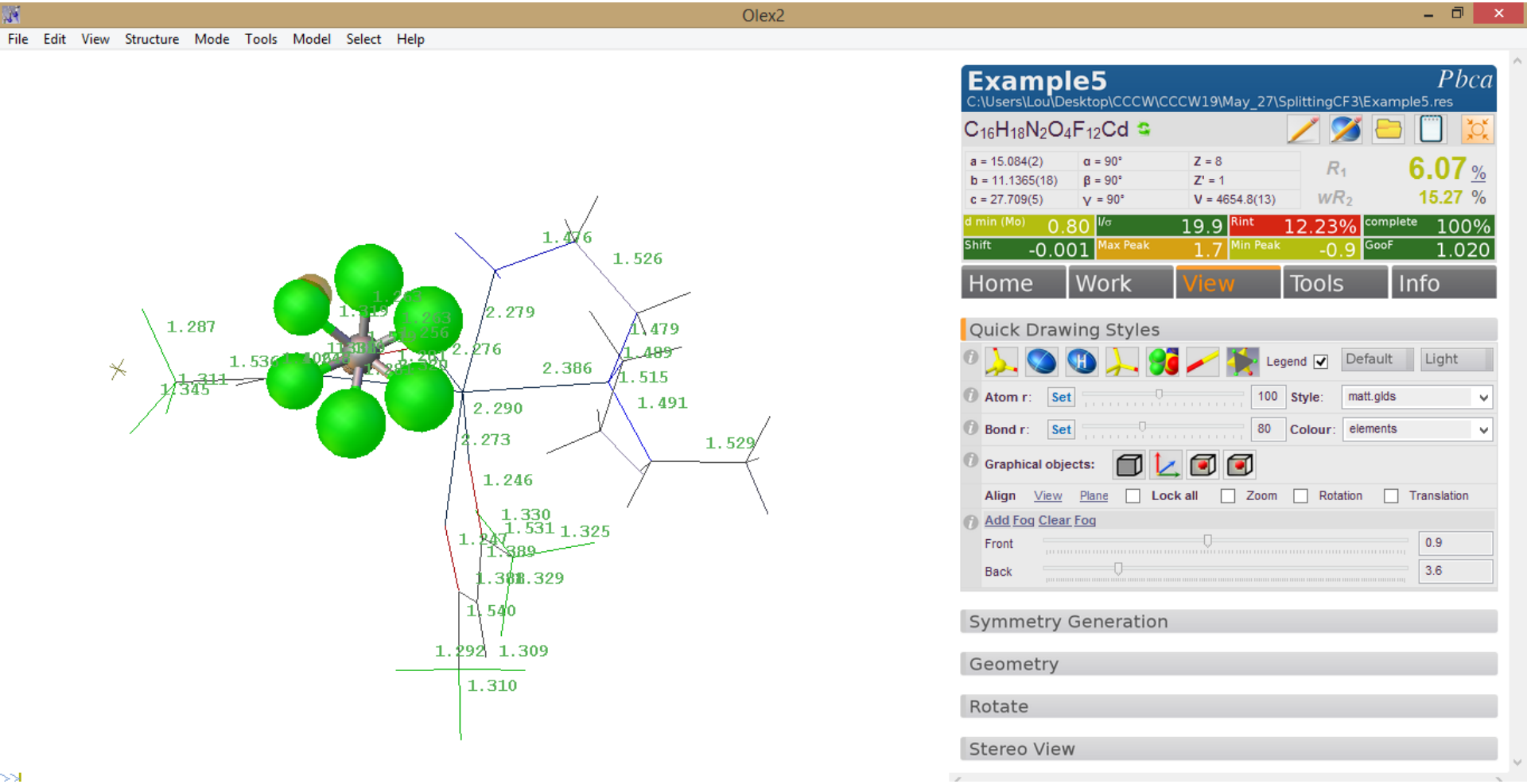
mode fit -s=1

Note that the C8-C10 bond is now selected as well (even though we didn't select C8.)



Right click on the C8-C10 bond once, and then use your left mouse key to rotate around this bond until the second set of F-atoms match up with your residual electron density peaks. Then hit esc

Only C8 has remained anisotropic. (You can use “Fn F3” to remove the distance labels.)



Go back to your Work menu and Sort your atoms.
Then type “edit ins” at the prompt
Notes: Global RIGU (I’m deleting it), second free variable of 0.75, and two parts at bottom of the file with occupancies tied to the second free variable
Close your .ins

File Edit Format View Help

```
TITL disorder1 in Pbca
REM Solution 1 R1 0.144 Rweak 0.004, Alpha = 0.0755 in Pbca
CELL 0.71073 15.0844 11.1365 27.7091 90 90 90
ZERR 8 0.0024 0.0018 0.0045 0 0 0
LATT 1
SYMM 0.5-X,-Y,0.5+Z
SYMM -X,0.5+Y,0.5-Z
SYMM 0.5+X,0.5-Y,-Z
SFAC C H N O F Cd
UNIT 128 144 16 32 96 8
RIGU

L.S. 10
PLAN  20
TEMP -120
BOND
LIST 6
MORE -1
CONF
fmap 2
acta 52
WGHT 0.0613 31.275499
FVAR 0.183 0.75
REM <olex2.extras>
REM <HklSrc "%.\\Example5.hkl">
REM </olex2.extras>
```

```
H15A  2     0.63802  0.68612  0.39892  11.00000 -1.20000
H15B  2     0.71711  0.63780  0.36572  11.00000 -1.20000
AFIX 0
C16   1     0.69784  0.53366  0.42679  11.00000  0.02955  0.03732  0.03
 0.00103 -0.00146  0.00142
AFIX 23
H16A  2     0.72548  0.46001  0.41360  11.00000 -1.20000
H16B  2     0.74321  0.57731  0.44572  11.00000 -1.20000
AFIX 0
PART 1
F10   5     0.54794  0.10701  0.30649  21.00000  0.13570
F11   5     0.62770  0.02720  0.35801  21.00000  0.13234
F12   5     0.49989 -0.02748  0.34778  21.00000  0.09000
PART 0
PART 2
F10a  5     0.48980  0.04404  0.31955 -21.00000  0.13570
F11a  5     0.62024  0.09781  0.32720 -21.00000  0.13234
F12a  5     0.56930 -0.03864  0.36784 -21.00000  0.09000
HKLF 4

END
```

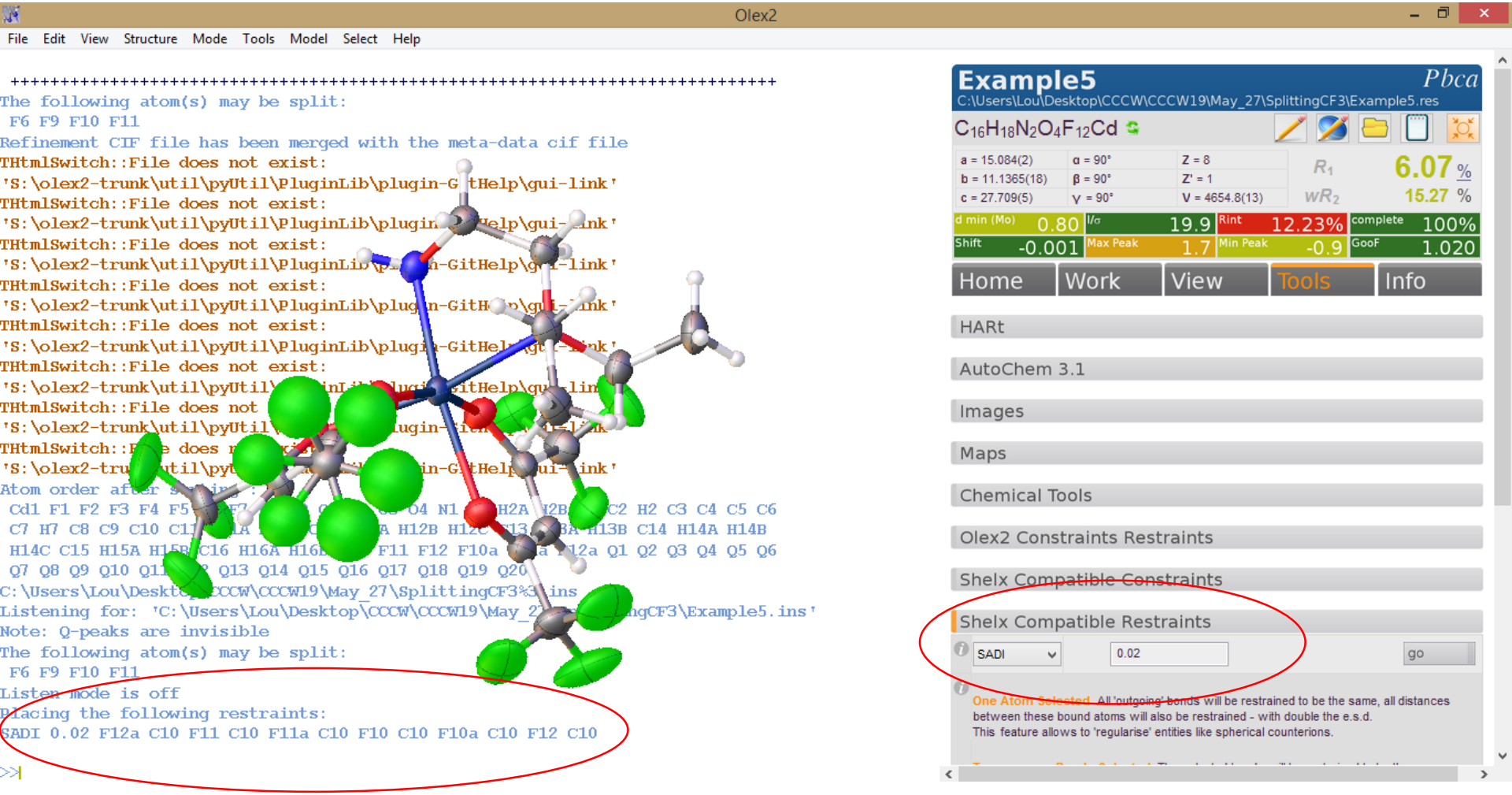
Next, let's apply restraints

To to Tools → Shelx Compatible Restraints → SADI

Select all C-F bonds in the group we are modelling and "GO"

(I switched back to the default view with "Fn F2" for white background and "Ctrl T" to see text in background)

Note the formatting of the restraint; each sequential pair is restrained to have the same distance



Note the formatting of the restraint; each sequential pair is restrained to have the same distance

We can select individual atoms in a pairwise manner and apply the same restraint. Let's do this with each of the 1,4 pairs in our disorder group.

If we want to do this with the 1,3 pairs we encounter a problem with using a GUI!

We can add these by editing our .ins (note that shelx doesn't "do" angle restraints, so we get around this with SADI)

File Edit Format View Help

```
TITL disorder1 in Pbca
REM Solution 1 R1 0.144 Rweak 0.004, Alpha = 0.0755 in Pbca
CELL 0.71073 15.0844 11.1365 27.7091 90 90 90
ZERR 8 0.0024 0.0018 0.0045 0 0 0
LATT 1
SYMM 0.5-X,-Y,0.5+Z
SYMM -X,0.5+Y,0.5-Z
SYMM 0.5+X,0.5-Y,-Z
SFAC C H N O F Cd
UNIT 128 144 16 32 96 8
SADI F12a C10 F11 C10 F11a C10 F10 C10 F10a C10 F12 C10
SADI F12 F11a F10a F11 F10 F12a
SADI F10 F11 F11 F12 F12 F10 F10a F11a F11a F12a F12a F10a

L.S. 10
PLAN  20
TEMP -120
BOND
```

CF distance restraints

1,4 distance restraints

1,3 distance restraints

I'm still not ready to hit "Refine"
Let's think about how those 1,4 displacements should "look".
Select the 1,4 F-atoms, one pair at a time, and introduce "Shelx Compatible Constraints" EADP after each selection.

(WHOA! Just noticed that there is a LIST 6 instructions in this ins! This instructs the kind of structure factor output that is generated. LIST 6 is not compatible with many things; let's edit this to LIST 4)
Displacements, distances and effectively angles, are now managed. Let's hit "Refine".

Example5.

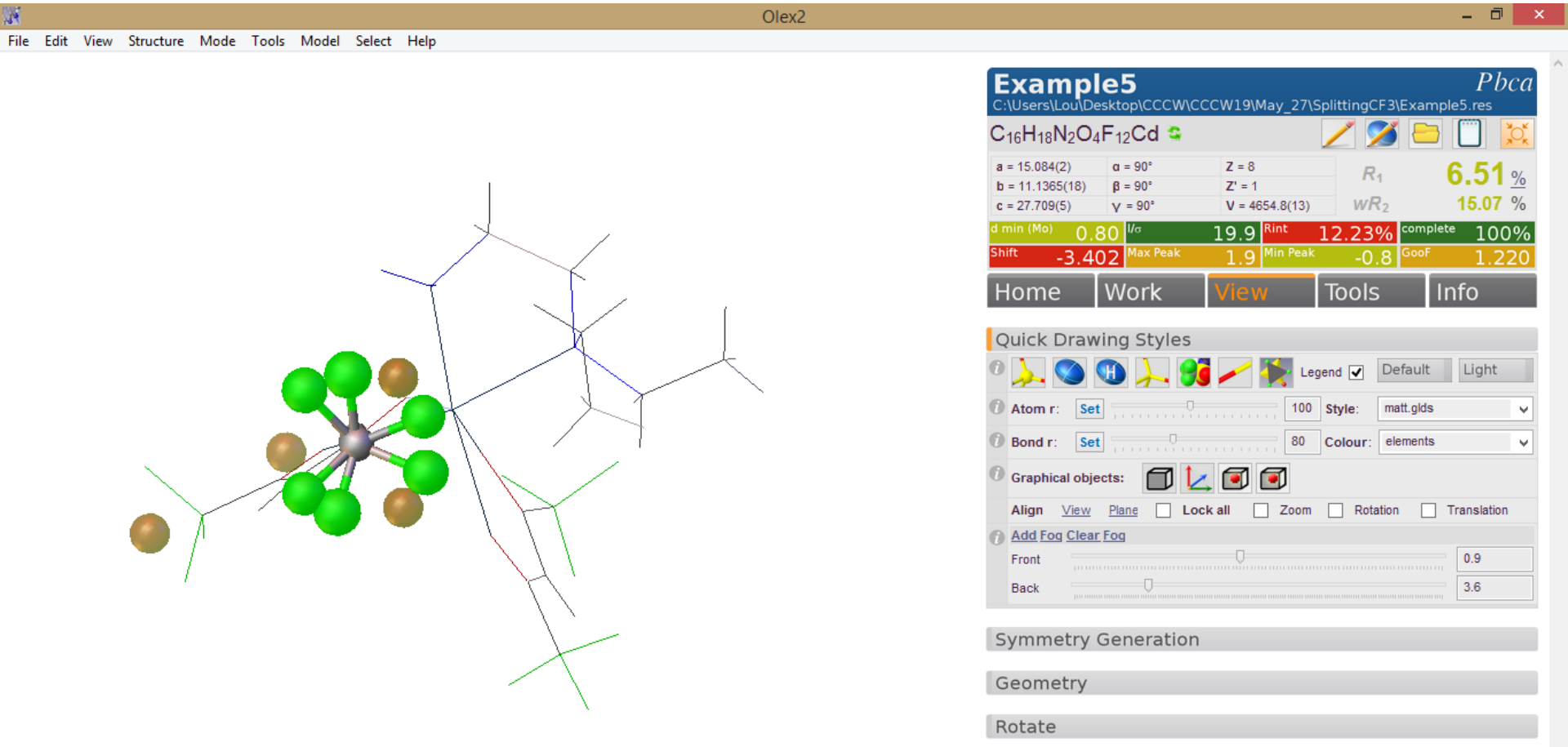
File Edit Format View Help

```
TITL disorder1 in Pbca
REM Solution 1 R1 0.144 Rweak 0.004, Alpha = 0.0755 in Pbca
CELL 0.71073 15.0844 11.1365 27.7091 90 90 90
ZERR 8 0.0024 0.0018 0.0045 0 0 0
LATT 1
SYMM 0.5-X,-Y,0.5+Z
SYMM -X,0.5+Y,0.5-Z
SYMM 0.5+X,0.5-Y,-Z
SFAC C H N O F Cd
UNIT 128 144 16 32 96 8
SADI F12a C10 F11 C10 F11a C10 F10 C10 F10a C10 F12 C10
SADI F12 F11a F10a F11 F10 F12a
SADI F10 F11 F11 F12 F12 F10 F10a F11a F11a F12a F12a F10a
EADP F10a F11
EADP F12 F11a
EADP F12a F10

L.S. 10
PLAN  20
TEMP -120
BOND
LIST 6
MORE -1
CONF
fmap 2
```

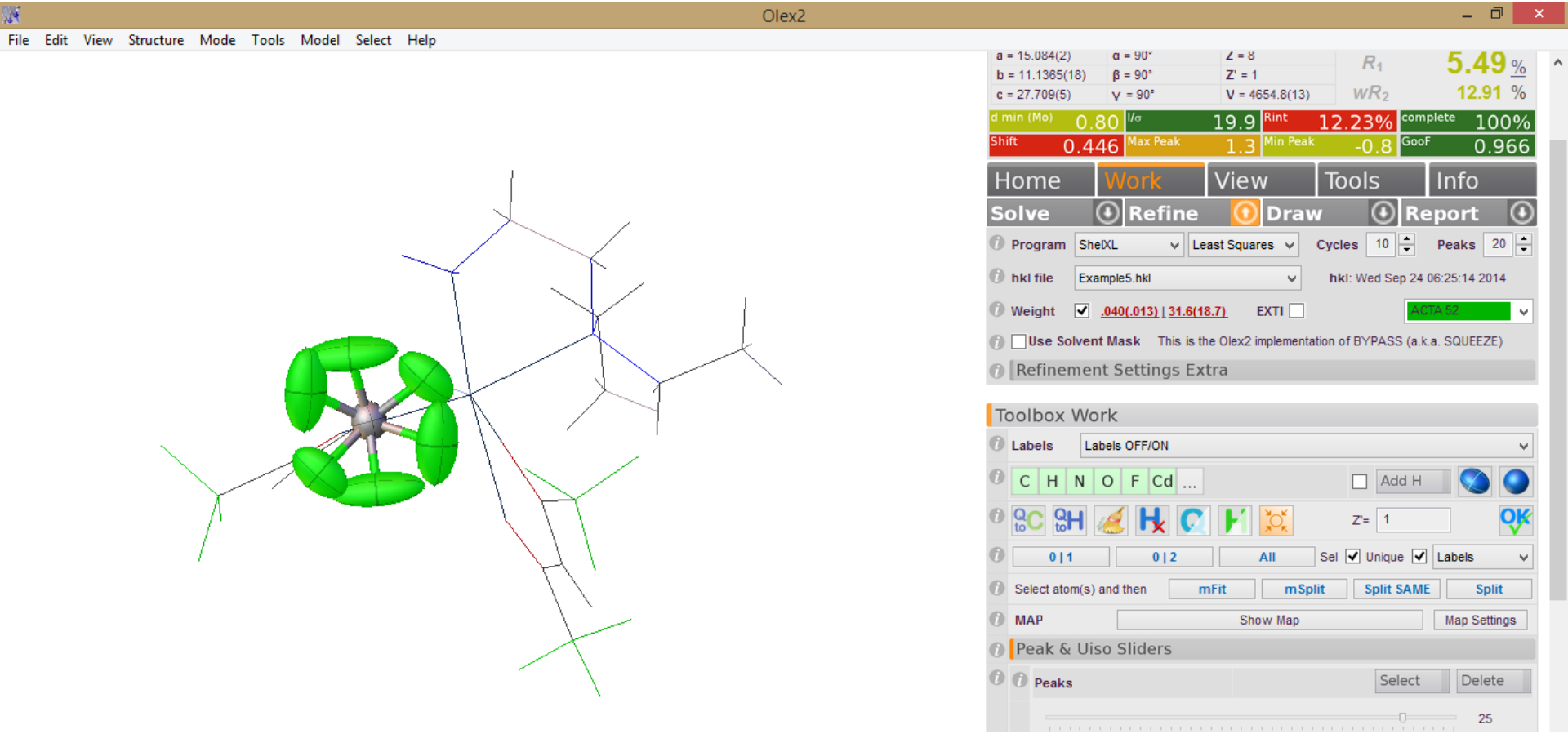
Sigh…those 1,4 restraints…and those new residual density peaks…

If only Mike Katz was here…

In the meantime, change the isotropic atoms to anisotropic, and refine again.

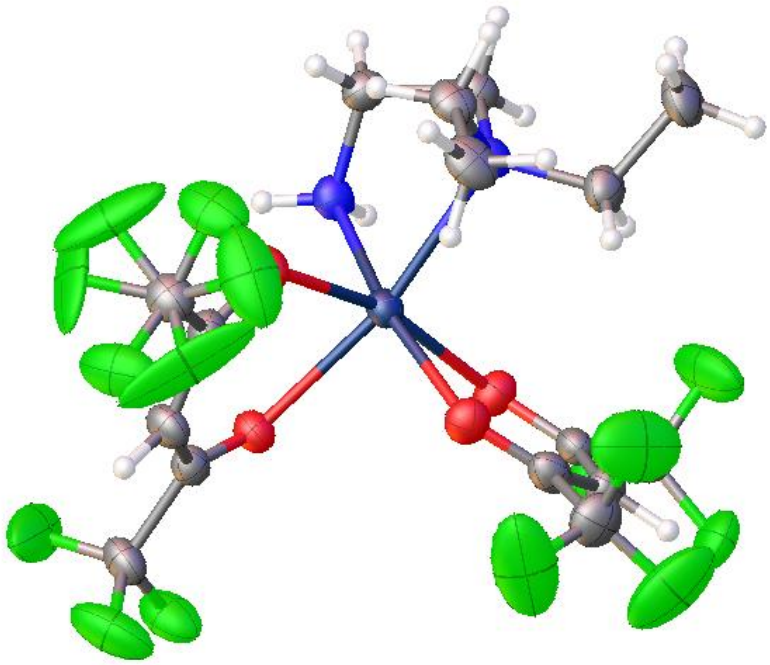


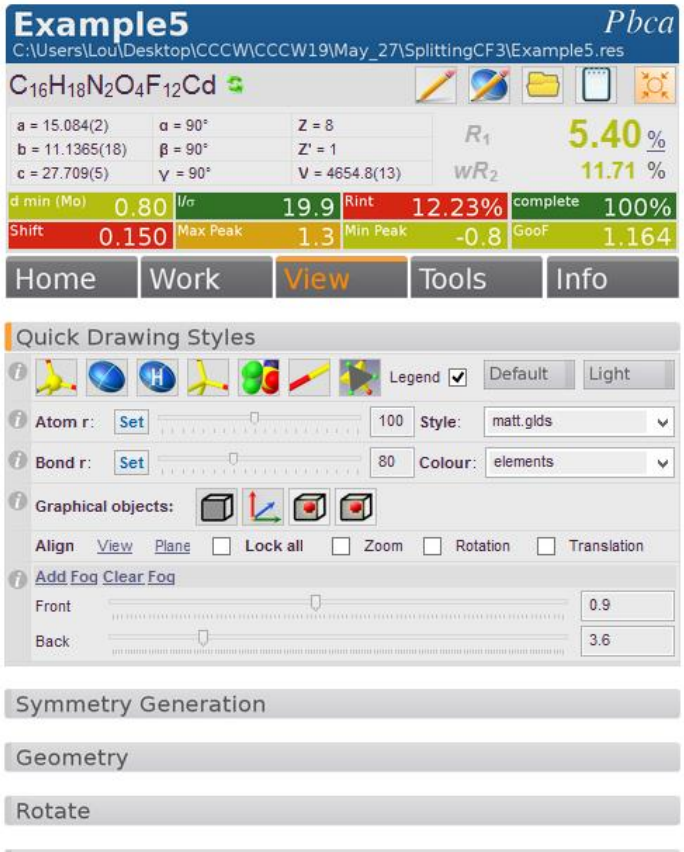
Well, anisotropic refinement dealt with those residual peaks, but is this a good model for what is taking place here?



We are done with this example, but here are a few things to consider:

1. I went in and manually changed the EADP constraints to RIGU restraints but this does not really improve the model.
2. You could go in and further model this with a third (and fourth, and fifth) orientation, tying the occupancies to a SUMP instruction (there is no convenient way to do this in OLEX2; you have to directly edit your ins.)
3. What about the other -CF_3 groups?
4. Everything would have been tidier if I had rotated my original second component by 180° instead of 60°.





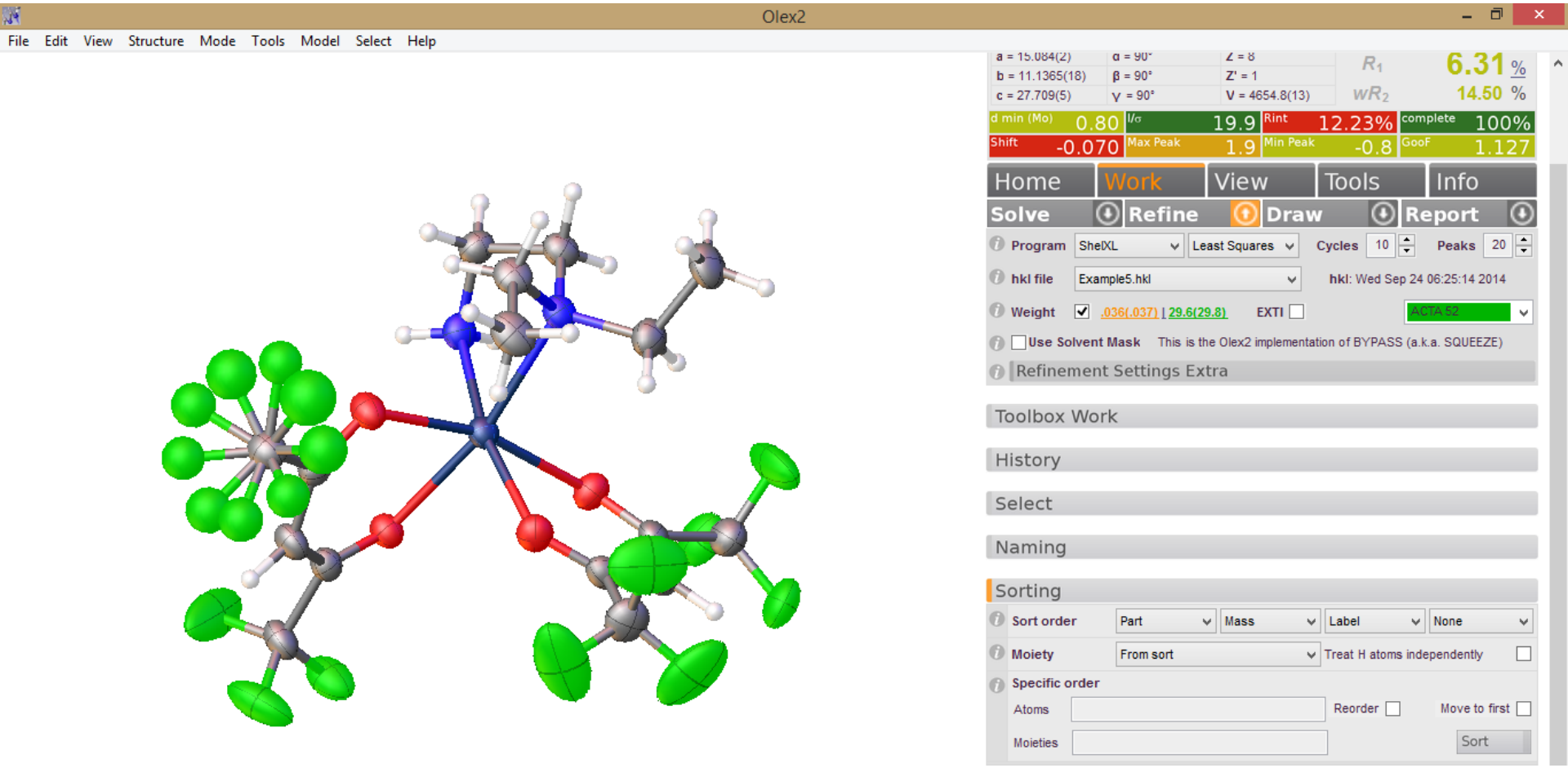
If I was going to split this into three components:

1. Go back to isotropic refinement. Run a round of least squares. Bring back those third component residual electron density peaks.
2. I introduced the next component by directly converting the three peaks to F atoms, and manually named them to F10B, F11B, F12B.
3. “Sort” and then edit ins.
4. Delete the 1,4 SADI restraints. Introduce a new set of C-F and 1,3 F-F SADI restraints for the B component (carry on to the next line using =). Combine all F atoms into a single RIGU line.
5. Find F10B, F11B, F12B, and move them to the bottom of the .cif, under a PART 3.
6. For PART 2, change all of the “-21.000” to “31.000”; for PART 3 change all of the “11.0000” to “41.000”
7. Go back to your FVAR line and change the second FVAR to 0.5, then add in a third with 0.3 and fourth with 0.2
8. Finally, add in the following line with your other instructions (this requires that the sum of the free variables add up to one.)

SUMP 1.0 0.001 1.0 2 1.0 3 1.0 4

9. Hit save. Close the .ins. Hit Refine. Good luck to you. History is still there in case of disaster!

This is before I hit refine. The next slide is what my .ins looks like, just before I hit refine.

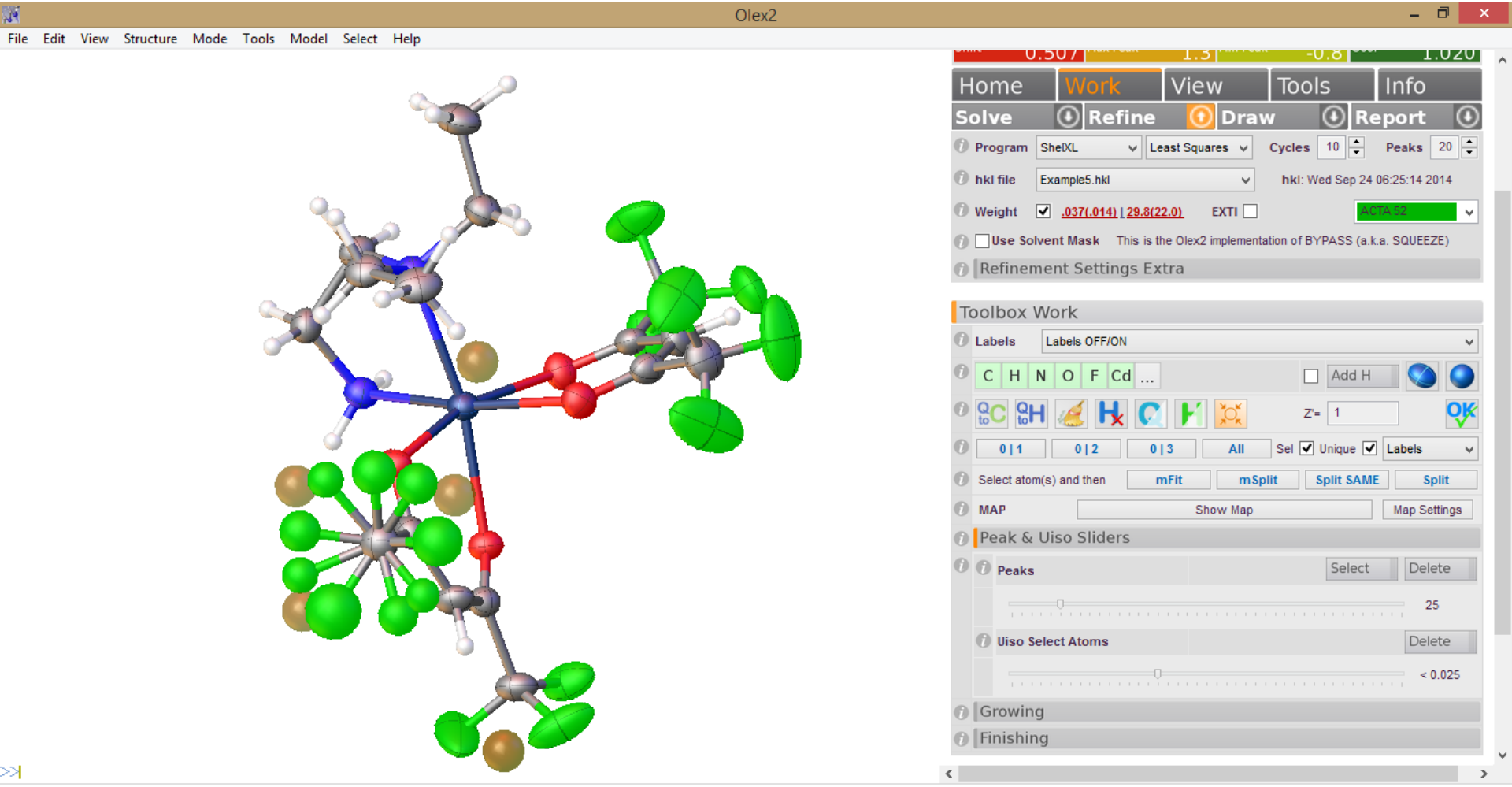


File Edit Format View Help

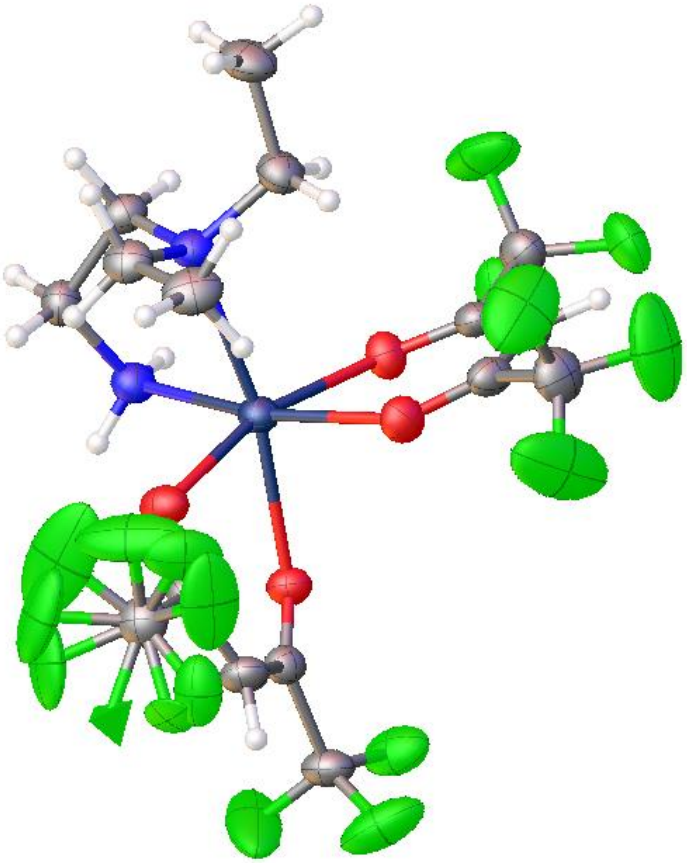
```
SYMM -X,0.5+Y,0.5-Z
SYMM 0.5+X,0.5-Y,-Z
SFAC C H N O F Cd
UNIT 128 144 16 32 96 8
SADI F12A C10 F11 C10 F11A C10 F10 C10 F10A C10 F12 C10 =
F10B C10 F11B C10 F12B C10
SADI F10 F11 F11 F12 F12 F10 F10A F11A F11A F12A F12A F10A =
F10B F11B F11B F12B F12B F10B
RIGU F10 F10A F10B F11 F11A F11B F12 F12A F12B
SUMP 1.0 0.001 1.0 2 1.0 3 1.0 4

L.S. 10
PLAN  20
TEMP -120
BOND
LIST 4
MORE -1
CONF
fmap 2
acta 52
WGHT 0.0359 29.634201
FVAR 0.18368 0.5 0.3 0.2
REM <olex2.extras>
REM <HklSrc "%.\\Example5.hkl">
REM </olex2.extras>
```

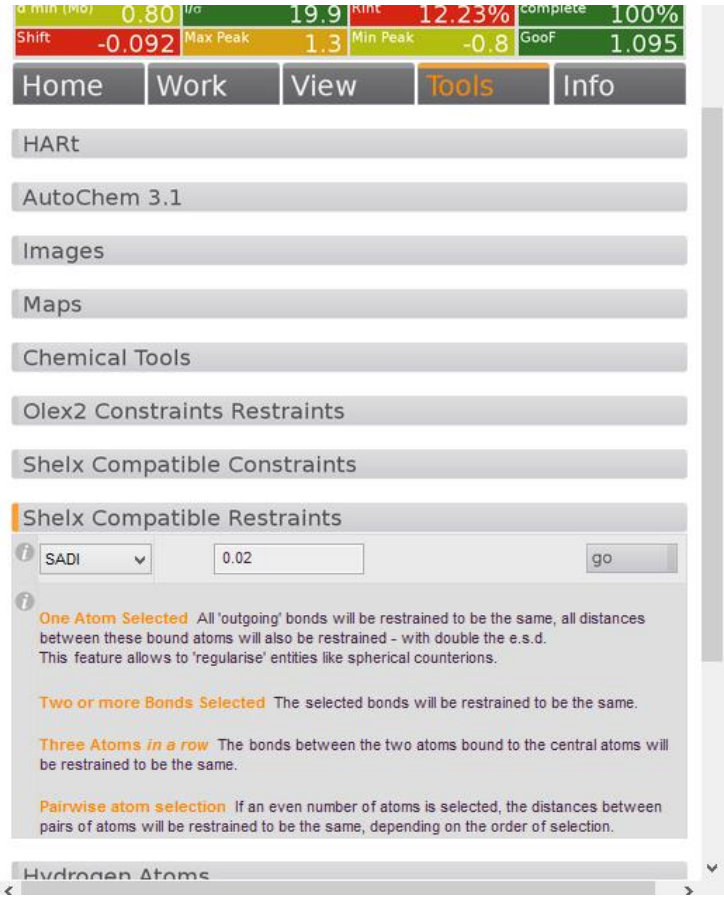
```
AFIX 23
H16A  2     0.72559  0.46002  0.41364  11.00000 -1.20000
H16B  2     0.74317  0.57743  0.44573  11.00000 -1.20000
AFIX 0
PART 1
F10   5     0.52945  0.10426  0.30518  21.00000  0.06323
F11   5     0.63609  0.05060  0.34907  21.00000  0.06735
F12   5     0.50936 -0.03925  0.35458  21.00000  0.05607
PART 2
F10A  5     0.48861 -0.01254  0.33930 31.00000  0.05231
F11A  5     0.58560  0.11146  0.30990 31.00000  0.08463
F12A  5     0.61935  0.00110  0.36795 31.00000  0.05323
PART 3
F10B  5     0.49590  0.04800  0.32080  41.00000  0.05000
F11B  5     0.63050  0.10340  0.32540  41.00000  0.05000
F12B  5     0.56990 -0.03840  0.36780  41.00000  0.05000
PART 0
HKLF 4

END
```

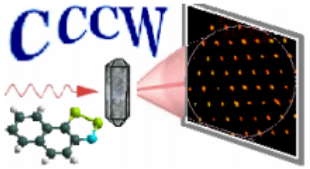
Post refine. Still some peaks.
Hover over the atoms to see their occupancies.
Let’s go anisotropic.

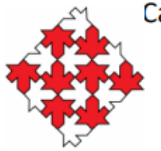


Ugh. Let's go home.
(No, seriously, I could probably "fix" this with some ISOR restraints, or EADP constraints, or changing the default RIGU esd to something much smaller. But that doesn't make it "right".)









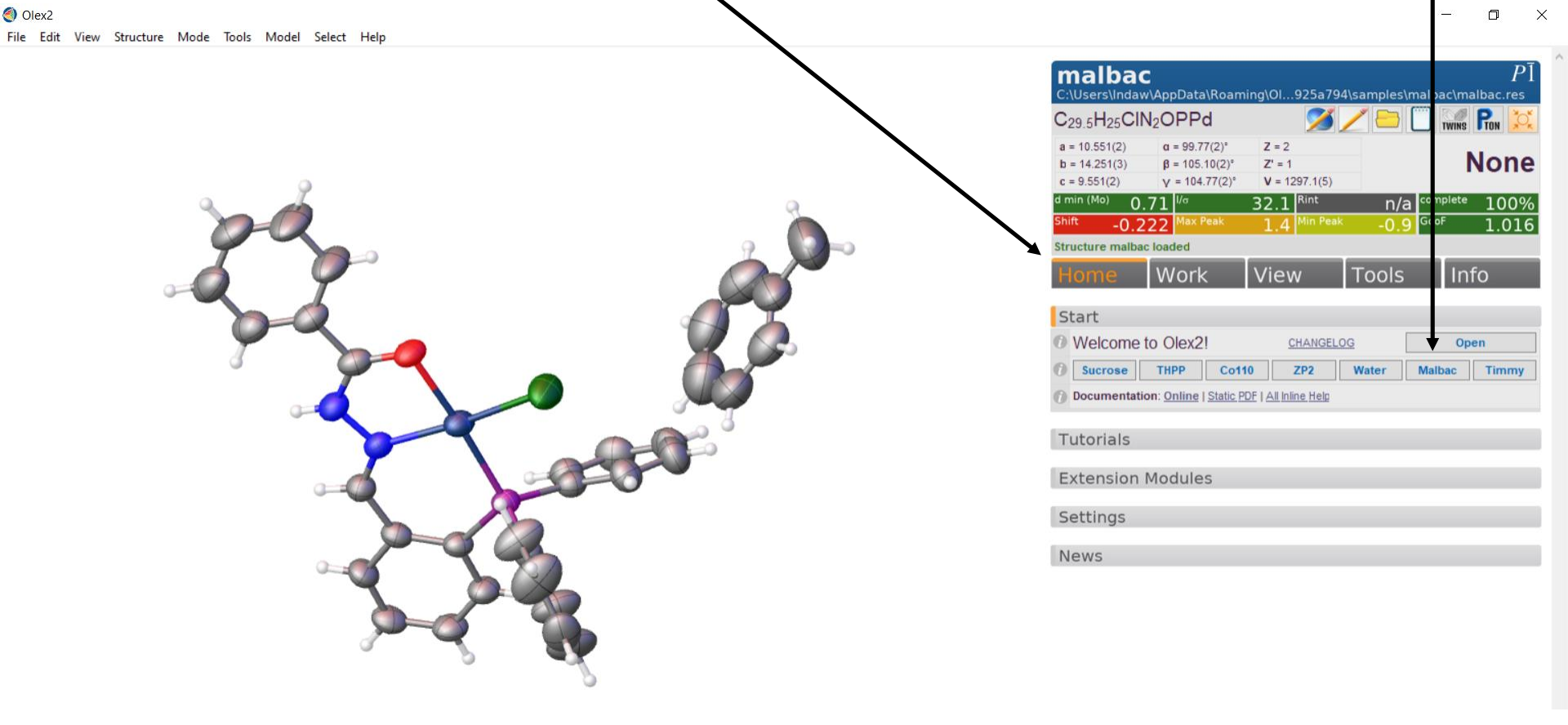
Canadian National Committee
for Crystallography
http://xtallography.ca/

Solvent or Anion Disorder: Fixed Positions

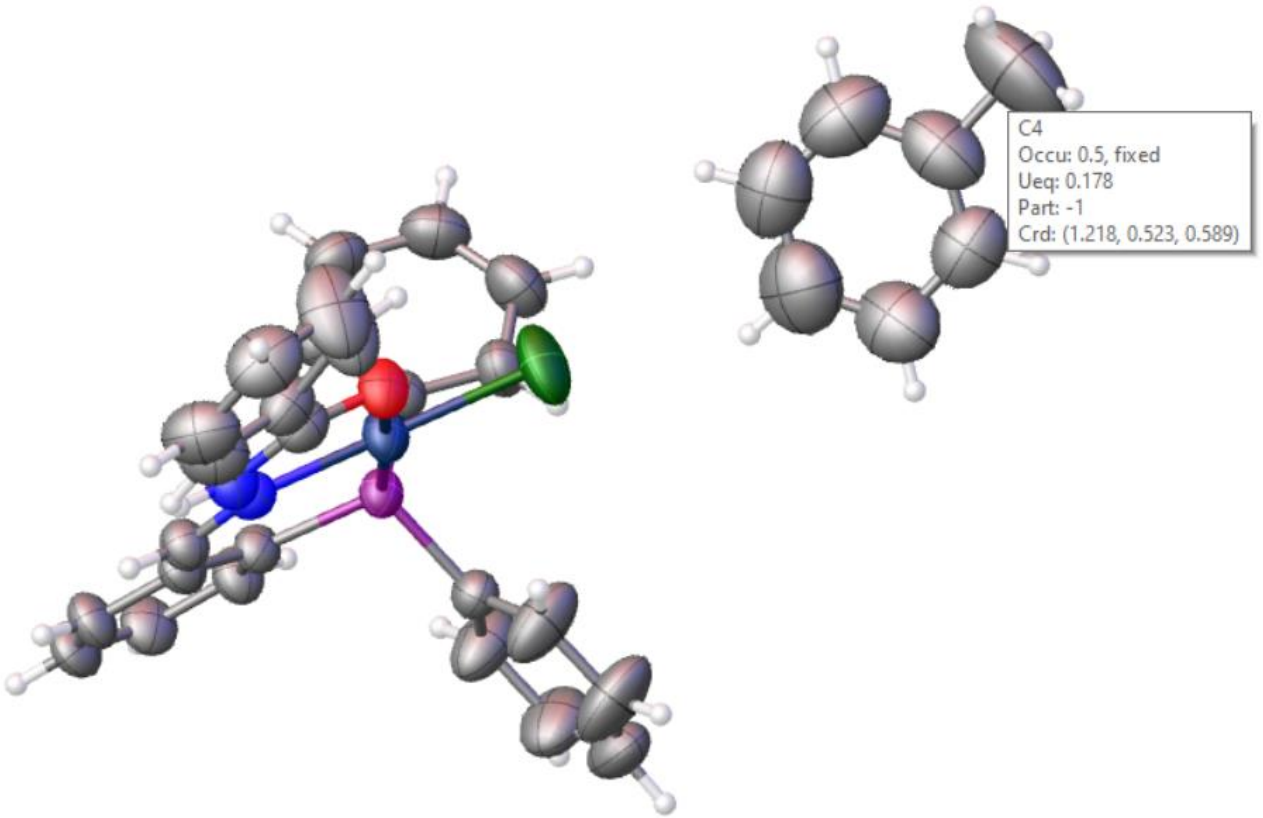
Check out the OLEX2 youtube channel for a similar example:
https://www.youtube.com/watch?v=hCI4VdQ8iBg&list=PLJgQksgBIpeAMDW5PVOI0r9EqFZ8p-Y4_&index=7&t=0s

Navigate to Home.

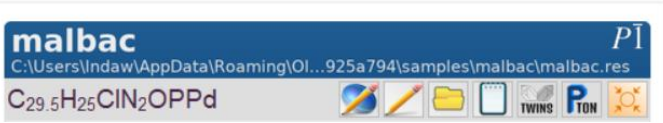
Under Start, select “Malbec”



This is the finished structure.
Toluene looks disordered.
Hover over any atom; occupancy is 0.5, and it is is PART -1
Why?

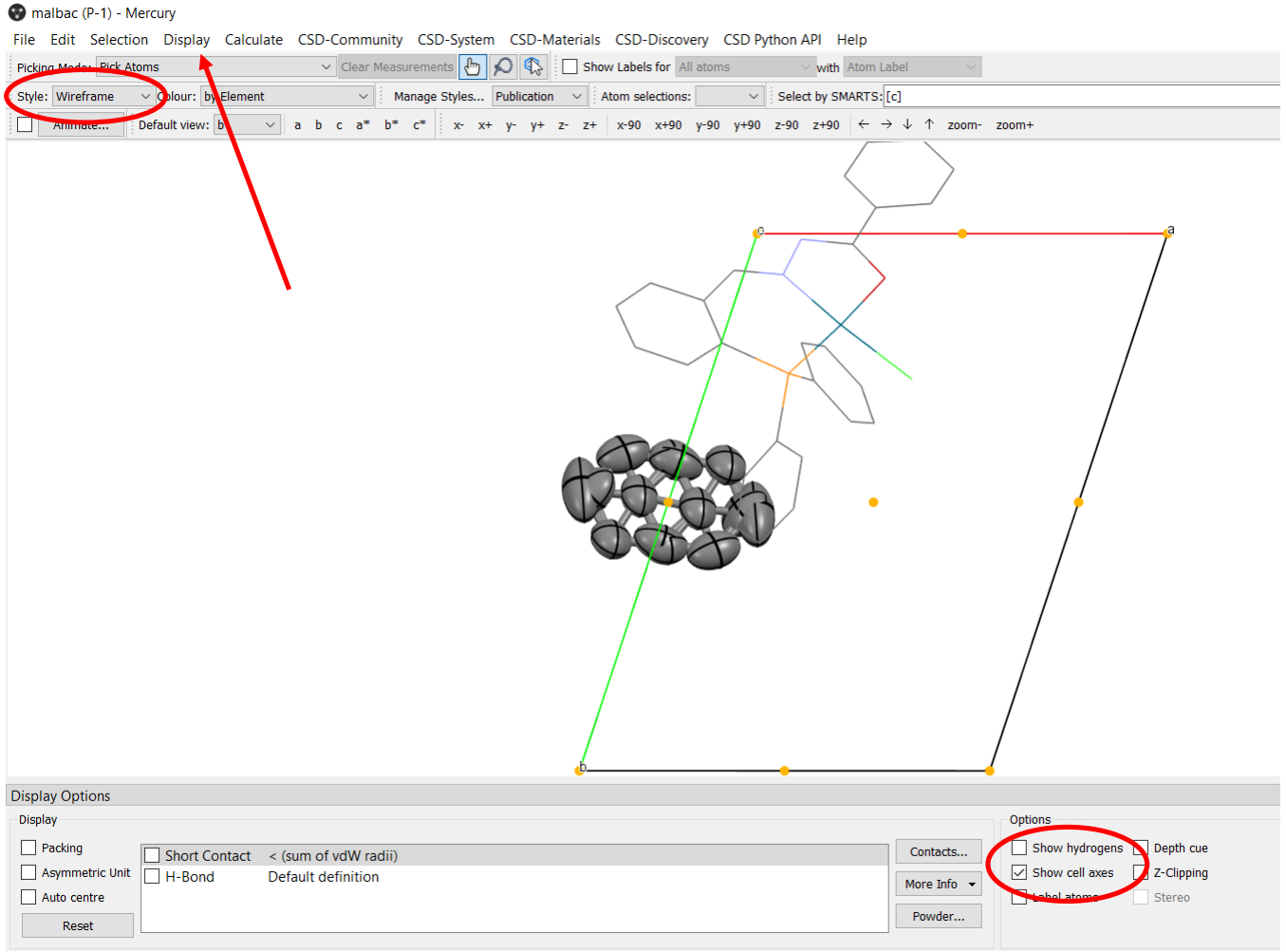


Open the .cif in Mercury; I got my file path by looking here:



Right click on the main molecule (not toluene): Selection → Select Molecule

I then changed my style to “Wireframe”, deselected “Show hydrogen”, selected “Show cell axes”, and the went to: Display → Symmetry Elements…→ OK

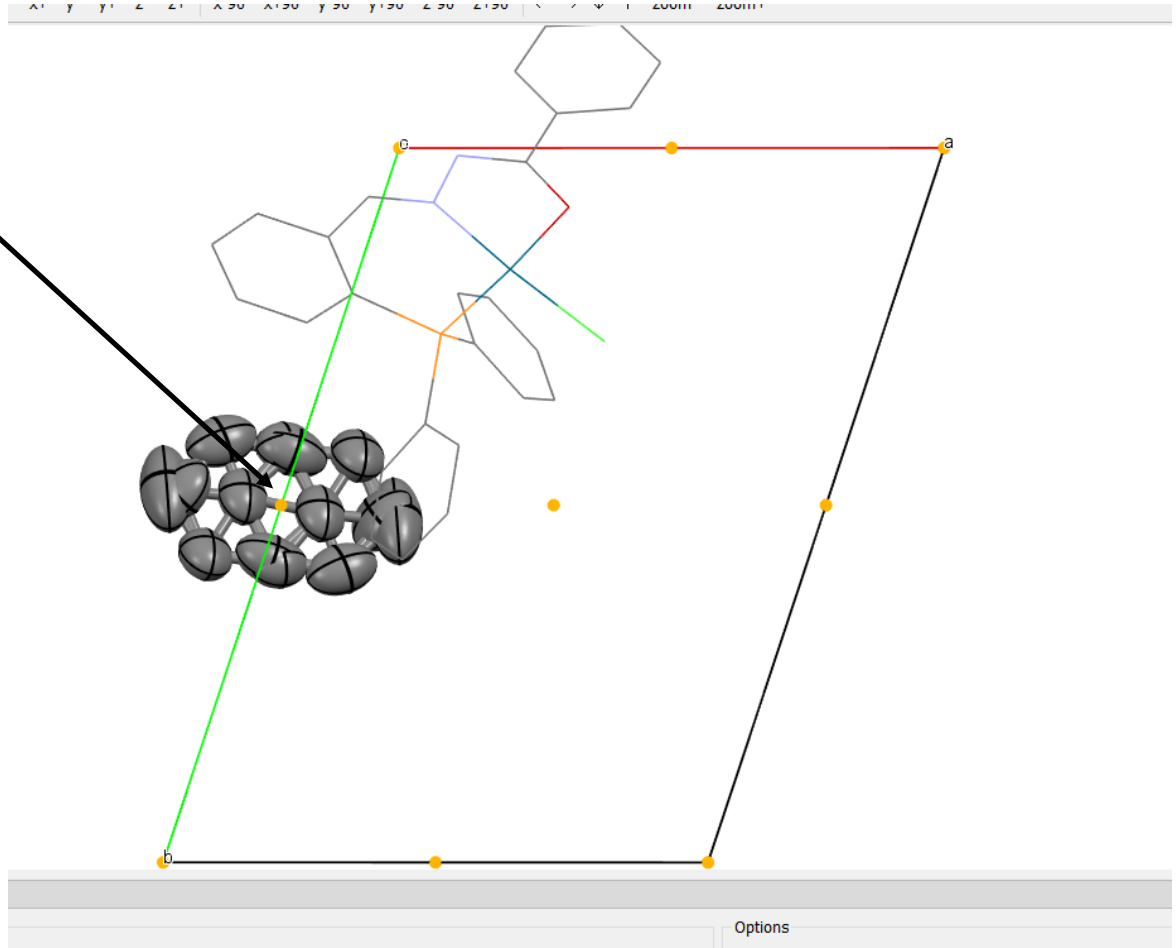


Looking at this structure in Mercury:

Space group is P-1
The only symmetry is inversion

Toluene is “sitting on” an inversion centre, yet its molecular symmetry does not exhibit inversion.

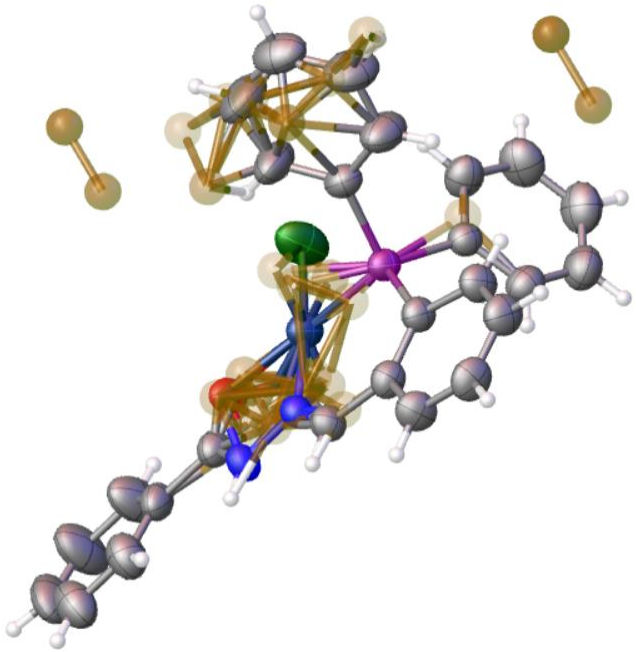
How do we model this?



Back in OLEX2

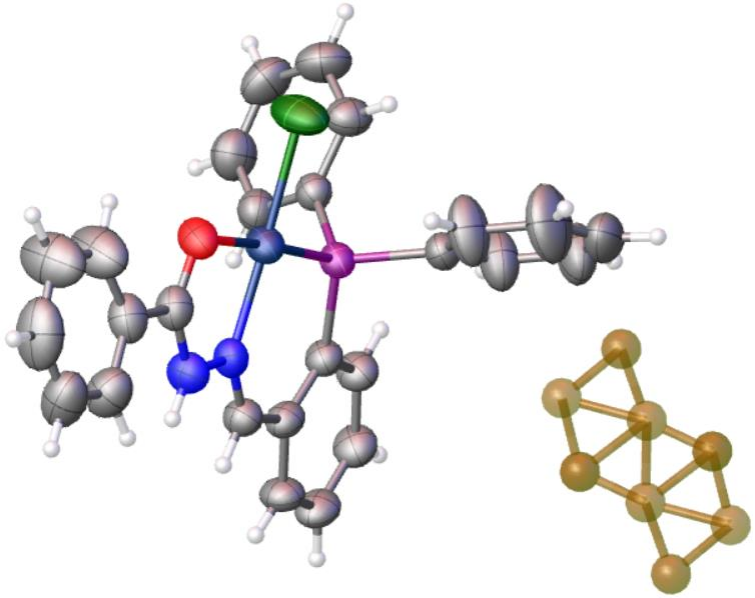
1. Delete toluene, set your rounds of least squares to five, set your peaks to 25, and refine.
2. Assemble your fragments.
3. Display only your top four peaks, and type “grow”.

1.



2.

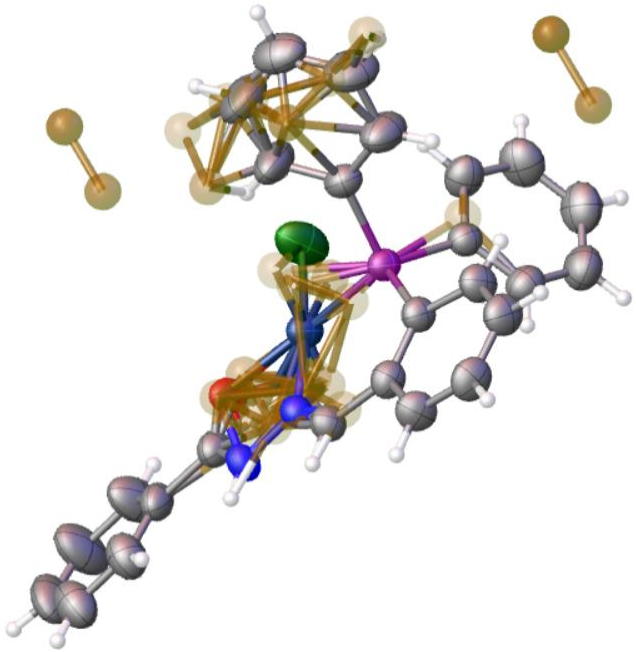
3.



Back in OLEX2

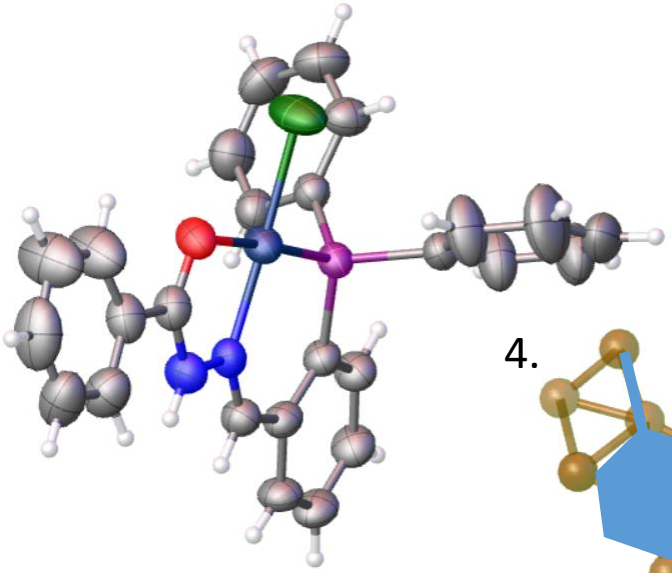
1. Delete toluene, set your rounds of least squares to five, set your peaks to 25, and refine.
2. Assemble your fragments.
3. Display only your top four peaks, and type “grow”.
4. Imagination!

1.



2.

3.

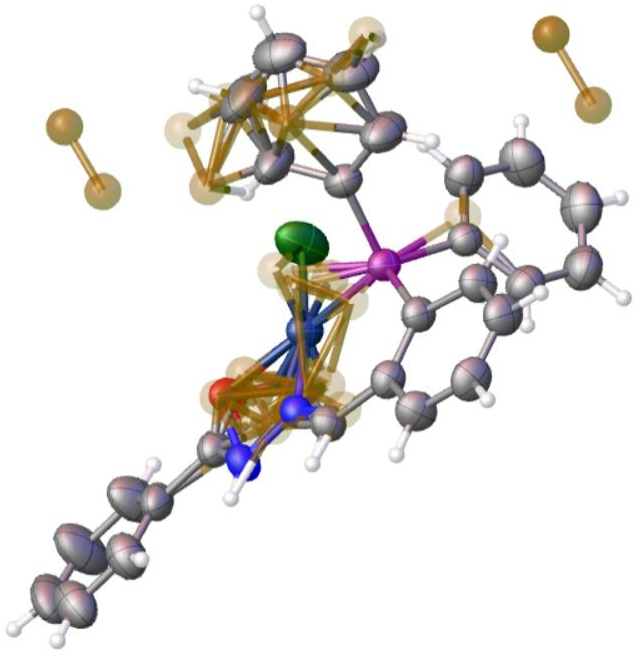


4.

Back in OLEX2

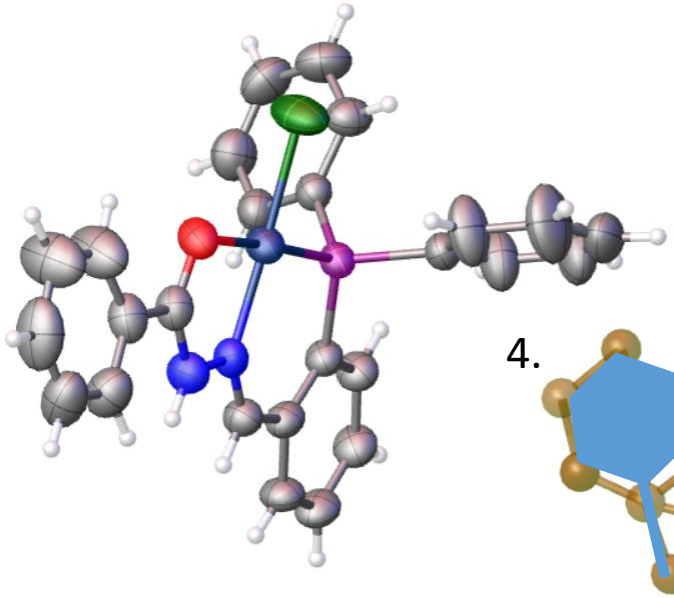
1. Delete toluene, set your rounds of least squares to five, set your peaks to 25, and refine.
2. Assemble your fragments.
3. Display only your top four peaks, and type “grow”.
4. Imagination! (No seriously now, how do I make it do that?)

1.



2.

3.



4.

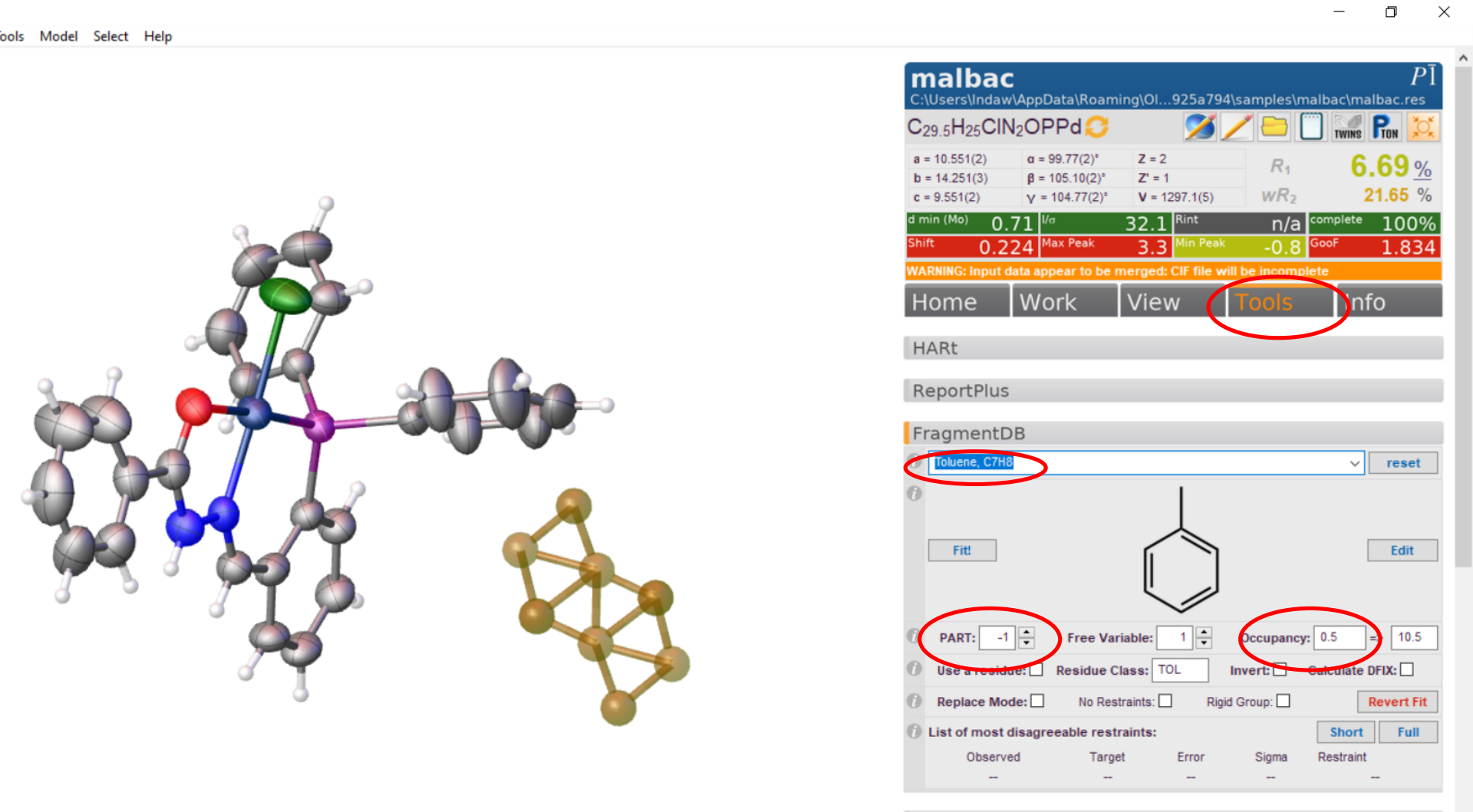
OLEX2 makes FRAG/FEND “simple”

From the shelx manual:

FRAG code[17] a[1] b[1] c[1] α[90] β[90] γ[90] Enables a fragment to be input using a cell and coordinates taken from the literature. Orthogonal coordinates may also be input in this way. Such a fragment may be fitted to the set of atoms following an AFIX instruction with m=code (code must be greater than 16); there must be the same number of atoms in this set as there are following FRAG, and they must be in the same order. Atoms with zero coordinates are not fitted, but new coordinates are generated for these atoms. The atom names, sfac numbers, sof and Uij of the FRAG fragment are ignored, only the coordinates are used. A FRAG fragment may be given anywhere between UNIT and HKLF or END or in an 'include' file, and must be terminated by a FEND instruction, but must precede any AFIX instruction which refers to it. This rigid fit is often a preliminary to a rigid group refinement (AFIX 6).

Tools → FragmentDB → Find toluene from the list

Next: PART = -1; Occupancy = 0.5 (Why?)



Tools → FragmentDB → Find toluene from the list

Next: PART = -1; Occupancy = 0.5 (Why?)

Directly from Peter Mueller: http://web.mit.edu/pmueller/www/ACA2007/WK01/Disorder.pdf

Disorder Involving Special Positions

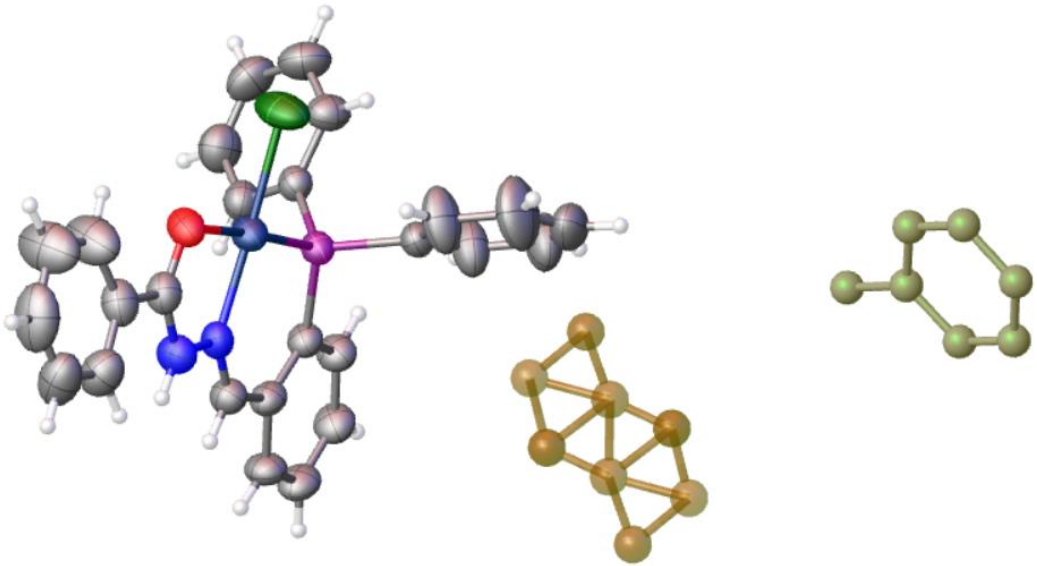
Imagine a molecule sitting on or near a special position without fulfilling the geometry of that symmetry element (*e.g.* toluene on inversion center).

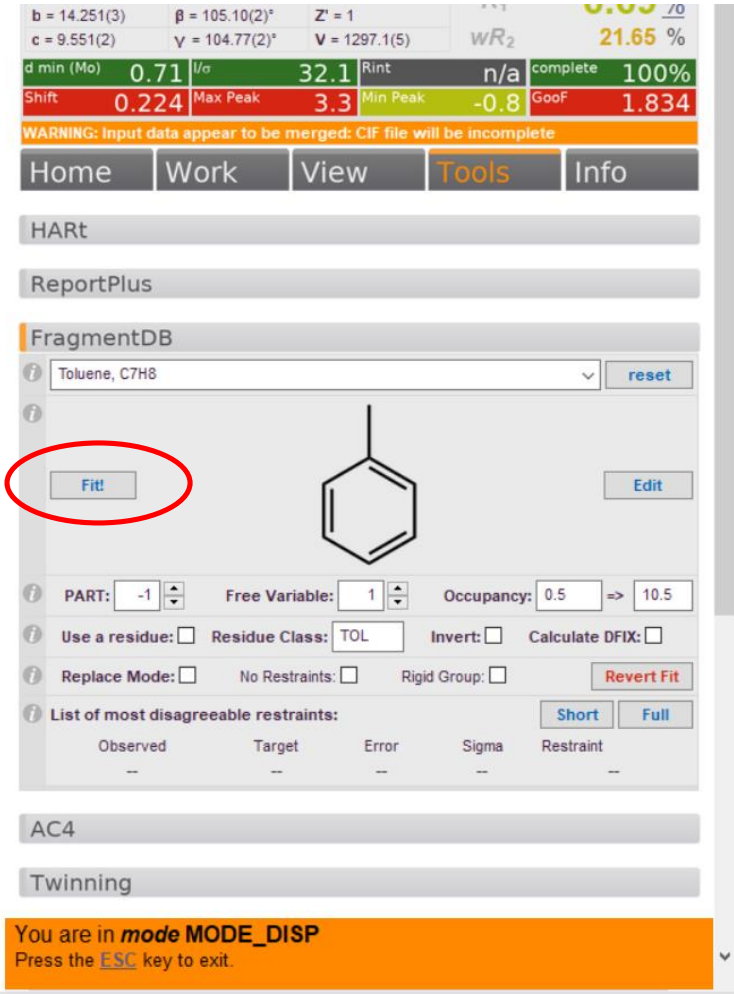
Two possible ways of describing: either use different space group without the symmetry element(s) in question or refine a disorder about the special position.

Refinement is easy: you need only one set of coordinates, as the second one can be generated from the first by means of the symmetry operator(s) corresponding to the special position in question. Therefore instead of **`PART 1`** and **`PART 2`** you only need one component, which has to be placed in **`PART -1`**.

The ratio does not need to be refined as it corresponds to the multiplicity of the symmetry operator (0.5 for an inversion center, mirror and twofold axis; 0.3333 for a threefold, 0.25 for a fourfold and 0.1667 for a sixfold). Combinations of symmetry operators are possible, of course.

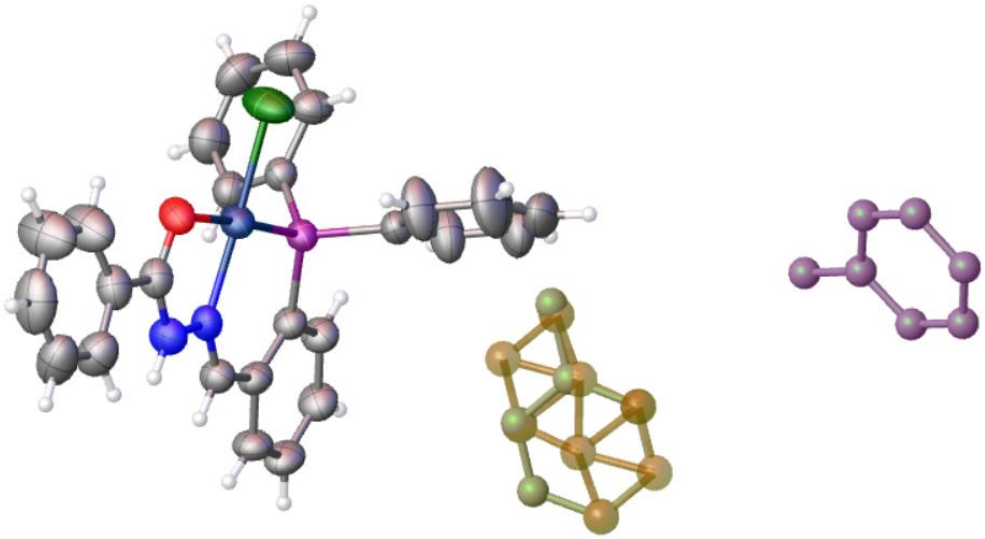
Once you have selected toluene from the list, hit “Fit”
A “shadow” toluene will appear.
Click on one atom in the shadow, and then click on one of your electron density peaks that you want to line up with the shadow.

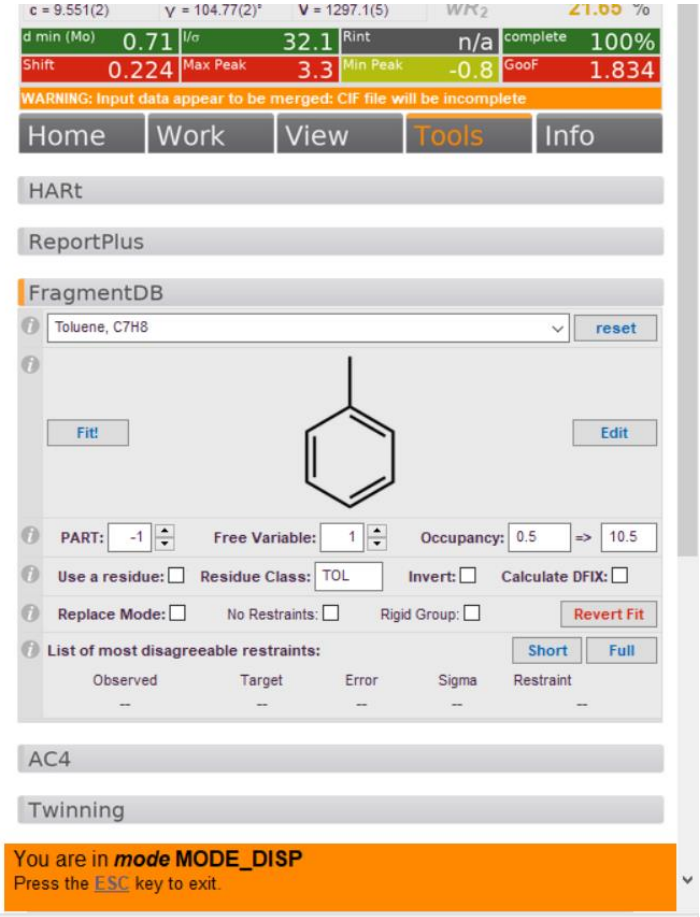




Once you have selected toluene from the list, hit “Fit”
A “shadow” toluene will appear.
Click on one atom in the shadow, and then click on one of your electron density peaks that you want to line up with the shadow.

Keep selecting one shadow peak (green) and one electron density peak (orange) until you get a reasonable fit. This took me three clicks.

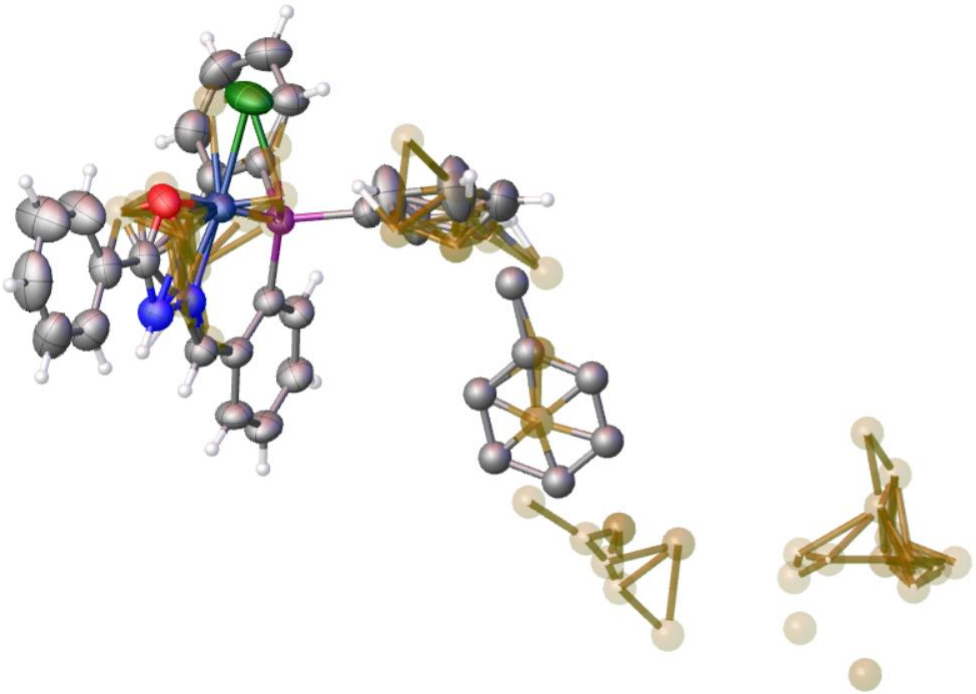


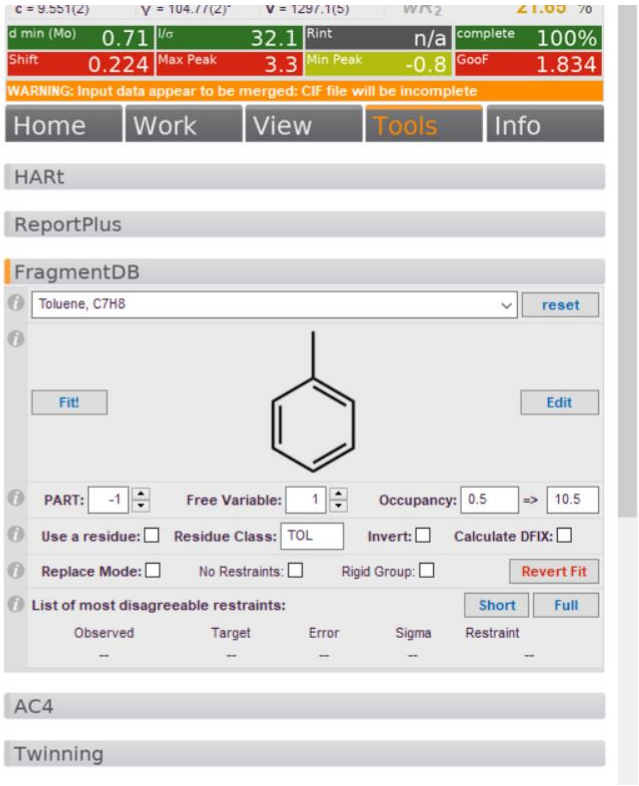


Once you have selected toluene from the list, hit “Fit”
A “shadow” toluene will appear.
Click on one atom in the shadow, and then click on one of your electron density peaks that you want to line up with the shadow.

Keep selecting one shadow peak (green) and one electron density peak (orange) until you get a reasonable fit. This took me three clicks.

Then hit “Esc”





To keep things ordered, I then named the tolune C50 – C56, and sorted my atoms, so that I could see what all this clicking did in my instruction file.

malbac.ins - Notepad

File Edit Format View Help

```
TITL r26
REM r26
REM 384 parameters refined using 6 restraints
CELL 0.71078 10.551 14.251 9.551 99.77 105.1 104.77
ZERR 2 0.002 0.003 0.002 0.02 0.02 0.02
LATT 1
SFAC C H Cl N O P Pd
UNIT 59 50 2 4 2 2 2
DFIX 1.51 C50 C51
DANG 2.42 C51 C53
FLAT C50 C51 C52 C53 C54 C55 C56
DFIX 1.39 C51 C52 C51 C56 C53 C54
DANG 2.39 C52 C54
DFIX 1.38 C52 C53 C54 C55 C55 C56
RIGU C50 > C56
SADI C51 C52 C52 C53 C53 C54 C54 C55 C55 C56 C56 C51
DANG 2.41 C51 C55
SADI 0.04 C51 C55 C51 C53 C56 C54 C52 C56 C53 C55 C52 C54
DANG 2.4 C53 C55 C54 C56
SIMU C50 > C56
SADI 0.04 C50 C56 C50 C52
DANG 2.52 C50 C52 C50 C56
```

```
PART -1
C50    1     0.22881  0.51794 -0.40920  10.50000  0.05000
C51    1     0.07692  0.50459 -0.47142  10.50000  0.05000
C52    1     0.03148  0.57907 -0.52536  10.50000  0.05000
C53    1    -0.10717  0.56792 -0.58177  10.50000  0.05000
C54    1    -0.20480  0.48040 -0.58520  10.50000  0.05000
C55    1    -0.16180  0.40549 -0.53257  10.50000  0.05000
C56    1    -0.02268  0.41731 -0.47593  10.50000  0.05000
HKLF 4

END
```

Close your .ins and Refine.

Make your toluene anisotropic, and Refine.

Add your hydrogen atoms, and Refine.

If you “grow”, OLEX2 does not show you the other “half”, but if you open your structure in Mercury, or if you go to “View → Symmetry Generation → Packing → Pack to limits” (for example), your full disorder model will be visible.