Figure 1-S. Calculated Powder Patterns of 1 (red = monoclinic, blue = orthorhombic) using 120K data
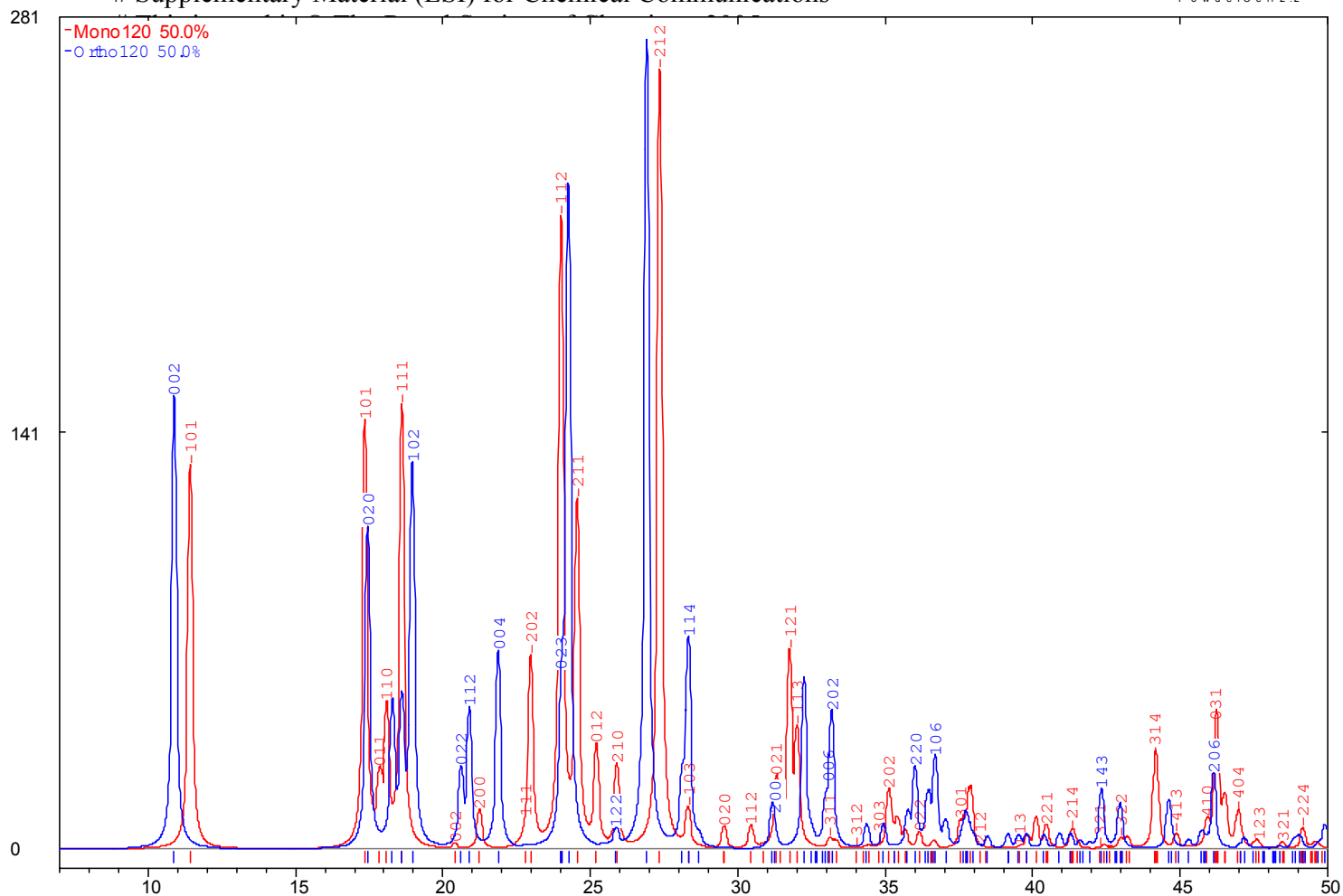
Figure 2-S. Calculated Powder Patterns of 1 (red = monoclinic, blue = orthorhombic) with indices, using 120K data
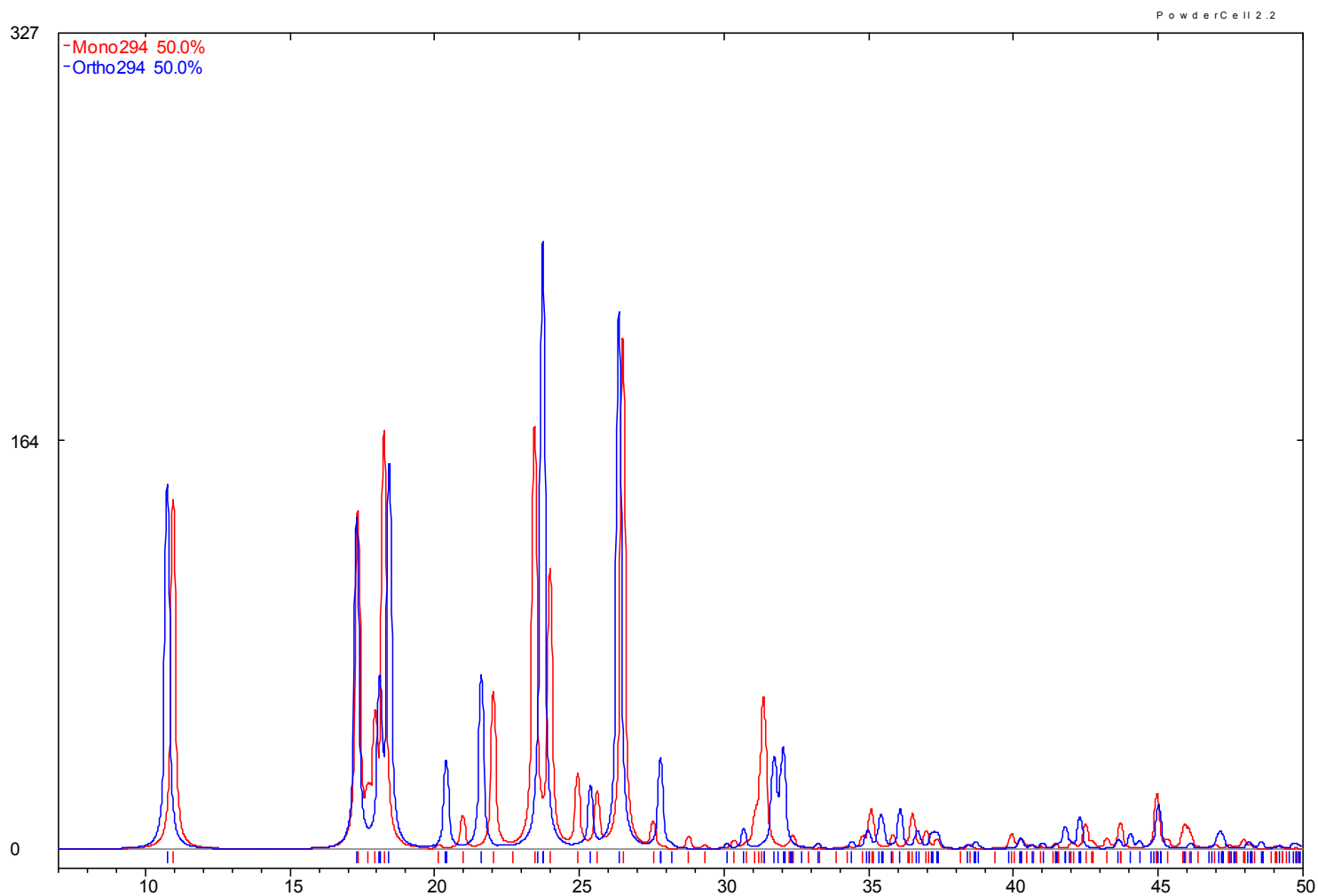
PowderCell 2.2

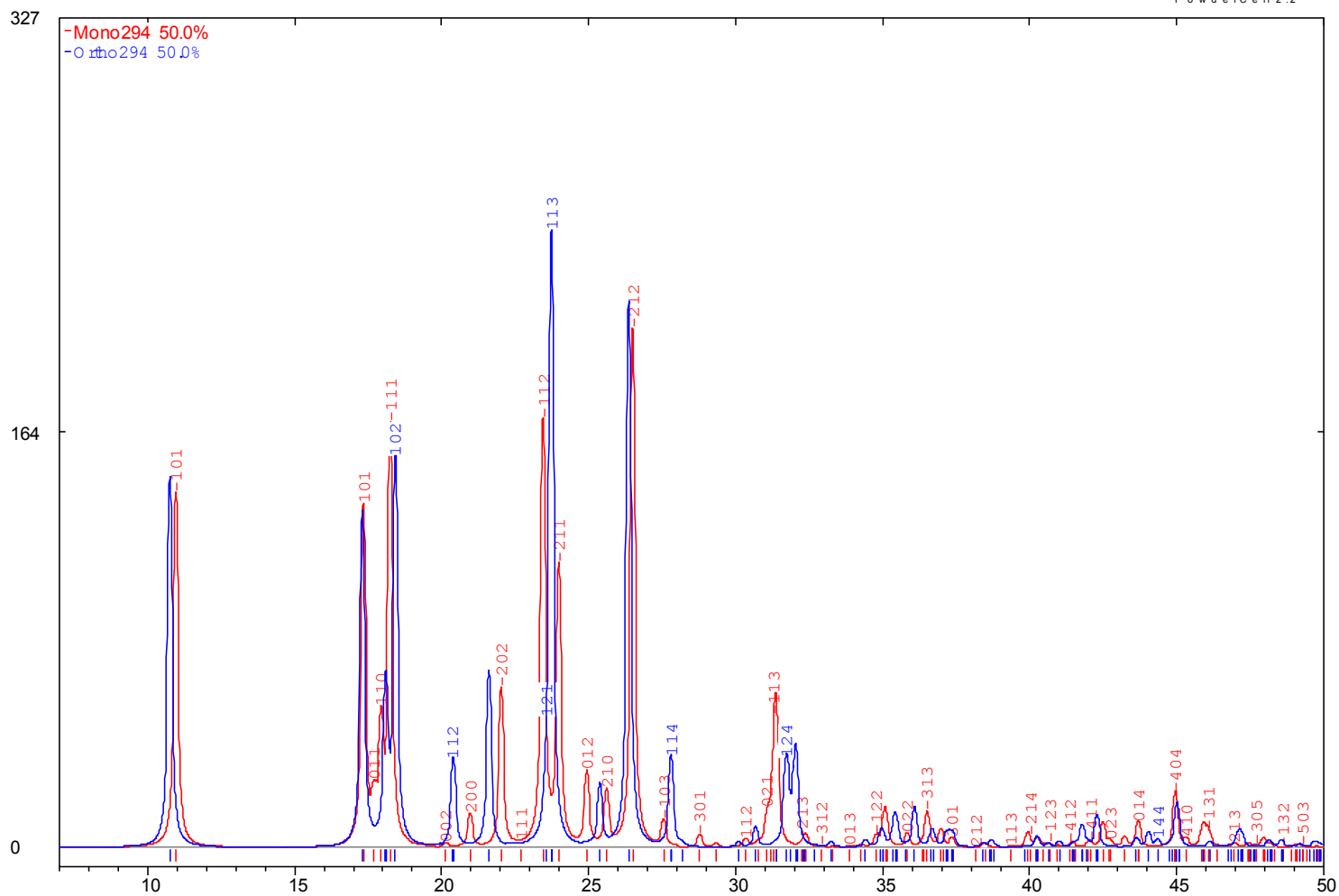**Figure 3-S. Calculated Powder Patterns of 1 (red = monoclinic, blue = orthorhombic), using 294K data**

Figure 4-S. Calculated Powder Patterns of 1 (red = monoclinic, blue = orthorhombic) with indices, using 294K data
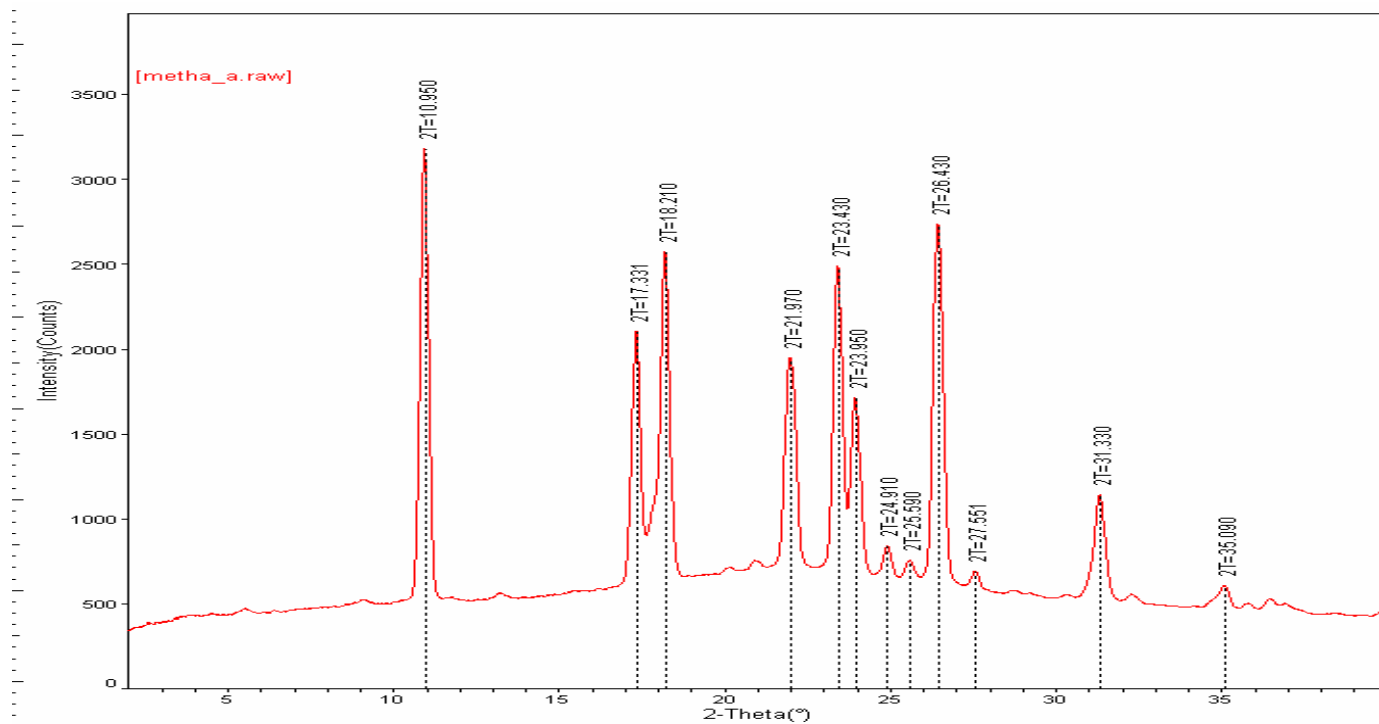
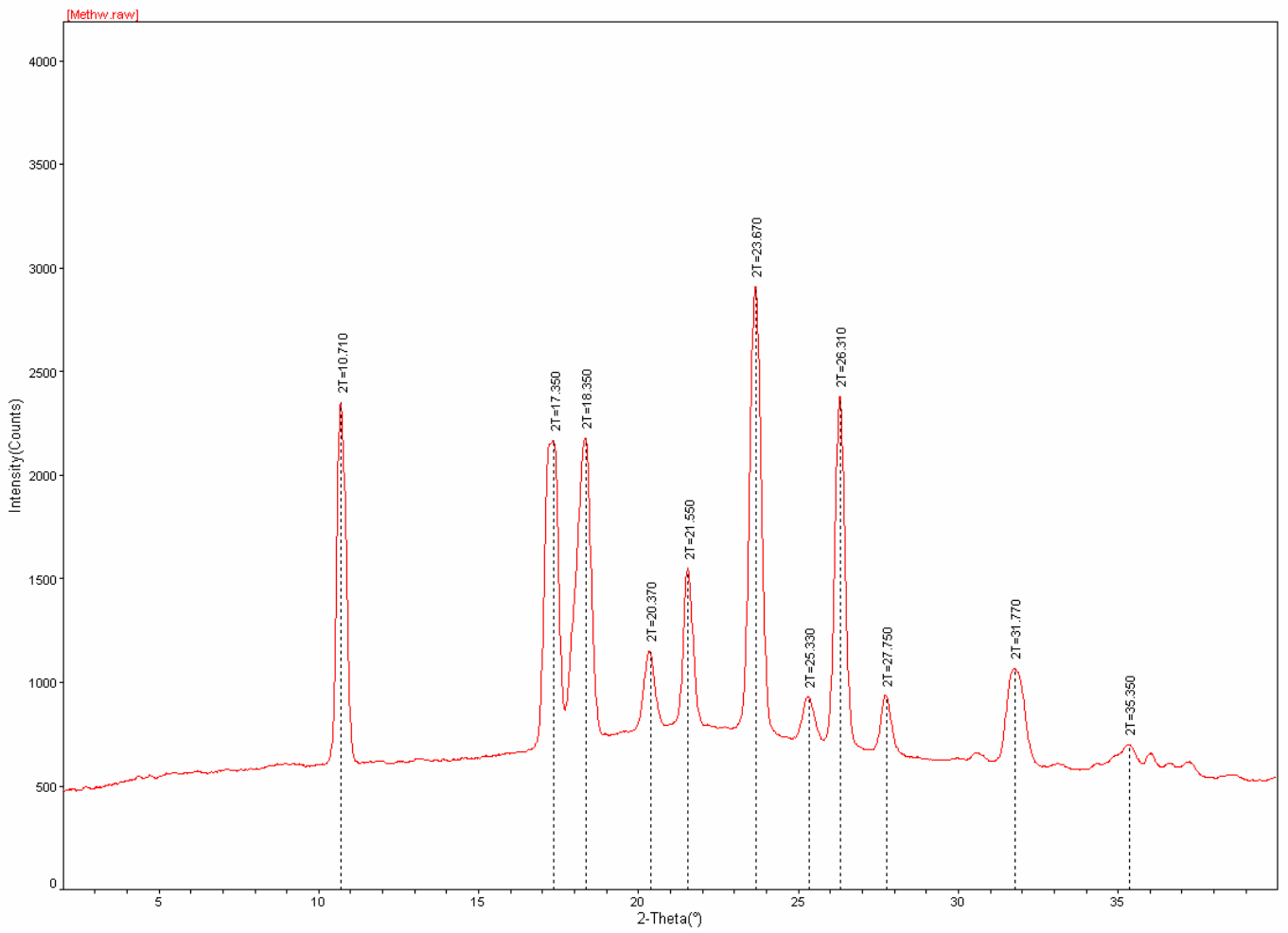**Figure S-5. Experimental Powder Diffraction Pattern of Form I**

Figure S-6. Experimental Powder Diffraction Pattern of Form II

For the structure of 2-carbamoyl-1-phenyl thiolato-ethenyl acetate, (R. L. Beddoes, D. MacLeod, D. Moorcraft, P. Quayle. Y. Zhao and G. M. Davies, *Tetrahedron Lett.*, 1992, **33**, 417-420, CSD refcode KOVROC), the data in CSD *strongly suggest an incorrect structure*, with a calculated C–NH$_2$ distance of 1.197 Å and C=O distance of 1.355 Å. Switching the identity of the N and O atoms, and moving the misplaced H atoms to the "new" N atom produces a chemically appropriate structure, with an *s-cis* conformation, and a reasonable hydrogen bonding pattern compared to that derived from the published coordinates.

PLATON reports the following (not very sensible) hydrogen bond patterns for KOVROC:

```
===============================================================================
Donor --- H....Acceptor [   ARU  ]    D - H      H...A     D...A  D - H...A

N(1)  --H(2)    .. ?                   0.94
N(1)  --H(3)    ..S(1)  [         ]    0.95       2.03      2.8340      142
N(1)  --H(3)    ..O(2)  [  8554.01]    0.95       2.36      2.8238      110

C(11) --H(11)   ..O(1)  [         ]    0.95       2.56      2.9105      102

Translation of ARU-code to Equivalent Position Code
===================================================
   [  8554. ]  = x,1/2-y,-1/2+z
```

If the amide N and O atoms are simply switched, the H atoms on the "old" N atom removed, and H atoms placed in calculated positions on the "new" N atom, PLATON reports a quite reasonable H-bonding pattern:

```
===============================================================================
Donor --- H....Acceptor [   ARU  ]    D - H      H...A     D...A  D - H...A

N(2)  --H(21)   ..O(3)  [  4655.01]    0.88       2.18      3.0607      176
N(2)  --H(22)   ..O(4)  [  8555.01]    0.88       1.96      2.8238      168

C(11) --H(11)   ..O(1)  [         ]    0.95       2.56      2.9105      102

Translation of ARU-code to Equivalent Position Code
===================================================
   [  4655. ]  = 1-x,1/2+y,1/2-z
   [  8555. ]  = x,1/2-y,1/2+z
```

The hydrogen bonds for the revised assignment are shown in the Figure on the following page:
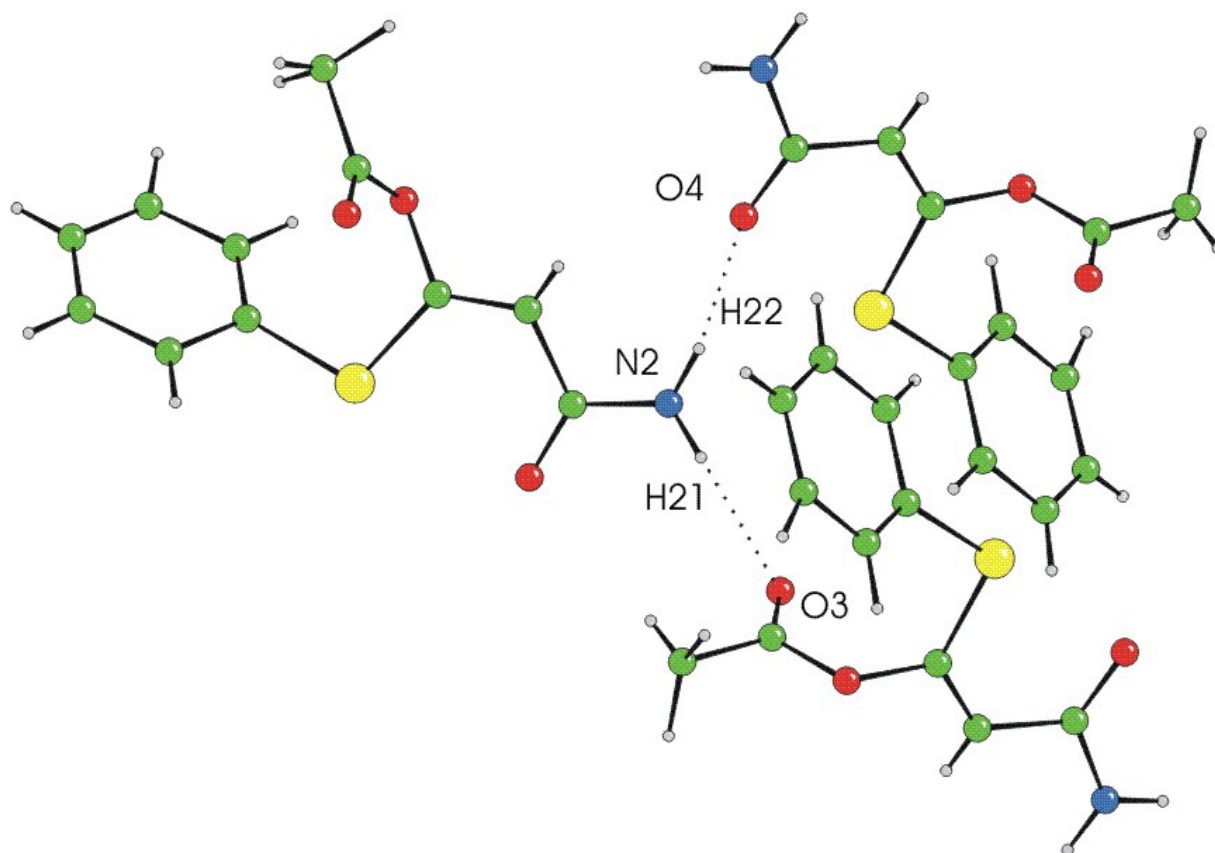
Figure S-7. Hydrogen bonds for the *revised* (*s-trans*) structure of KOVROC

A CIF file for the revised structure follows:

```
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_audit_creation_method CRYSTALS_ver_12.51

_oxford_structure_analysis_title   'CSD_CIF_KOVROC_revised'
_chemical_name_systematic          ?
_chemical_melting_point            ?

_cell_length_a                     15.8100(10)
_cell_length_b                     16.2630(10)
_cell_length_c                     9.4360(10)
_cell_angle_alpha                  90
_cell_angle_beta                   90
_cell_angle_gamma                  90
_cell_volume                       2426.2(3)

_symmetry_cell_setting             'Orthorhombic'
_symmetry_space_group_name_H-M     'P b c a '
_symmetry_space_group_name_Hall    '?'
loop_
 _symmetry_equiv_pos_as_xyz
 'x,y,z'
```

```
 '-x,-y,-z'
 '-x+1/2,y+1/2,z'
 'x+1/2,-y+1/2,-z'
 'x,-y+1/2,z+1/2'
 '-x,y+1/2,-z+1/2'
 '-x+1/2,-y,z+1/2'
 'x+1/2,y,-z+1/2'

loop_
_atom_type_symbol
_atom_type_scat_dispersion_real
_atom_type_scat_dispersion_imag
_atom_type_scat_Cromer_Mann_a1
_atom_type_scat_Cromer_Mann_b1
_atom_type_scat_Cromer_Mann_a2
_atom_type_scat_Cromer_Mann_b2
_atom_type_scat_Cromer_Mann_a3
_atom_type_scat_Cromer_Mann_b3
_atom_type_scat_Cromer_Mann_a4
_atom_type_scat_Cromer_Mann_b4
_atom_type_scat_Cromer_Mann_c
_atom_type_scat_source
 C      0.0033   0.0016   2.3100 20.8439   1.0200 10.2075   1.5886   0.5687
   0.8650 51.6512   0.2156 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
 H      0.0000   0.0000   0.4930 10.5109   0.3229 26.1257   0.1402   3.1424
   0.0408 57.7998   0.0030 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
 N      0.0061   0.0033 12.2126   0.0057   3.1322   9.8933   2.0125 28.9975
   1.1663   0.5826 -11.5290 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
 O      0.0106   0.0060   3.0485 13.2771   2.2868   5.7011   1.5463   0.3239
   0.8670 32.9089   0.2508 'International Tables Vol C 4.2.6.8 and 6.1.1.4'
 S      0.1246   0.1234   6.9053   1.4679   5.2034 22.2151   1.4379   0.2536
   1.5863 56.1720   0.8669 'International Tables Vol C 4.2.6.8 and 6.1.1.4'


_cell_formula_units_Z                    8

# Given Formula = C11 H11 N1 O3 S1
# Dc =       1.30 Fooo =    992.00 Mu =     2.58 M =    237.28
# Found Formula = C11 H11 N1 O3 S1
# Dc =       1.30 FOOO =    992.00 Mu =     2.58 M =    237.28

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_chemical_compound_source              ?
_chemical_formula_weight           237.28


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_cell_measurement_theta_min             0
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_cell_measurement_temperature           0

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_exptl_crystal_colour             'colorless'
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_exptl_crystal_size_mid           ?
_exptl_crystal_size_max           ?

_exptl_crystal_density_diffrn     1.299
_exptl_crystal_density_meas       ?
# Non-dispersive F(000):
_exptl_crystal_F_000              992
_exptl_absorpt_coefficient_mu     0.258
```

```
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_exptl_absorpt_correction_T_max     1.0000
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_diffrn_radiation_type              'Mo K\a'
_diffrn_radiation_wavelength             0.71073
_diffrn_measurement_method          \w/2\q

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_computing_data_reduction           'USER DEFINED DATA REDUCTION'
_computing_cell_refinement          'USER DEFINED CELL REFINEMENT'
_computing_structure_solution       'USER DEFINED STRUCTURE SOLUTION'
_computing_structure_refinement     'CRYSTALS (Betteridge et al., 2003)'
_computing_publication_material     'CRYSTALS (Betteridge et al., 2003)'
_computing_molecular_graphics       'CAMERON (Watkin et al., 1996)'

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_reflns_number_total                0
_diffrn_reflns_av_R_equivalents     0.000
# Number of reflections with Friedels Law is 0
# Number of reflections without Friedels Law is 0


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_diffrn_reflns_theta_max            0.000
_diffrn_measured_fraction_theta_max NaN

_diffrn_reflns_theta_full           0.000
_diffrn_measured_fraction_theta_full 1.000


_diffrn_reflns_limit_h_min**********
_diffrn_reflns_limit_h_max**********
_diffrn_reflns_limit_k_min**********
_diffrn_reflns_limit_k_max**********
_diffrn_reflns_limit_l_min**********
_diffrn_reflns_limit_l_max**********

_oxford_diffrn_Wilson_B_factor      0.00
_oxford_diffrn_Wilson_scale         0.00

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# _atom_sites_solution_secondary  difmap
_atom_sites_solution_hydrogens      geom

_refine_diff_density_min            ?
_refine_diff_density_max            ?


_refine_ls_number_reflns            0
_refine_ls_number_restraints        0
_refine_ls_number_parameters        0

#_refine_ls_R_factor_ref 0.0006
```

```
_refine_ls_wR_factor_ref          0.0000
_refine_ls_goodness_of_fit_ref    0.0000

#_reflns_number_all 0
_refine_ls_R_factor_all           0.0000
_refine_ls_wR_factor_all          0.0000

# The I/u(I) cutoff below was used for refinement as
# well as the _gt R-factors:
_reflns_threshold_expression      I>0.00u(I)
_reflns_number_gt                 0
_refine_ls_R_factor_gt            0.0000
_refine_ls_wR_factor_gt           0.0000

_refine_ls_shift/su_max           0.000000

# choose from: rm (reference molecule of known chirality),
# ad (anomolous dispersion - Flack), rmad (rm and ad),
# syn (from synthesis), unk (unknown) or . (not applicable).
_chemical_absolute_configuration  '.'


_refine_ls_structure_factor_coef  F
_refine_ls_matrix_type            full
_refine_ls_hydrogen_treatment     noref          # none, undef, noref, refall,
                                                 # refxyz, refU, constr or mixed

# WARNING. The IUCr will not accept Unit Weights
_refine_ls_weighting_scheme       calc
_refine_ls_weighting_details
;
 Method= Quasi-Unit weights
 W = 1.0 or 1./2F
;


loop_
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_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_U_iso_or_equiv
_atom_site_occupancy
_atom_site_adp_type
_atom_site_refinement_flags_posn
_atom_site_refinement_flags_adp
_atom_site_refinement_flags_occupancy
_atom_site_disorder_assembly
_atom_site_disorder_group
_atom_site_attached_hydrogens
S1 S 0.3722 0.0756 0.0853 0.0500 1.0000 Uiso . . . . . . .
O1 O 0.3686 0.0244 0.3559 0.0500 1.0000 Uiso . . . . . . .
N2 N 0.4666 0.2960 0.3246 0.0500 1.0000 Uiso . . . . . . .
O3 O 0.4923 -0.0399 0.3185 0.0500 1.0000 Uiso . . . . . . .
O4 O 0.4447 0.2339 0.1171 0.0500 1.0000 Uiso . . . . . . .
C1 C 0.3927 0.0888 0.2675 0.0500 1.0000 Uiso . . . . . . .
C2 C 0.4222 0.1565 0.3248 0.0500 1.0000 Uiso . . . . . . .
C3 C 0.4457 0.2302 0.2438 0.0500 1.0000 Uiso . . . . . . .
C4 C 0.4245 -0.0392 0.3706 0.0500 1.0000 Uiso . . . . . . .
C5 C 0.3840 -0.1028 0.4640 0.0500 1.0000 Uiso . . . . . . .
C6 C 0.3318 -0.0264 0.0749 0.0500 1.0000 Uiso . . . . . . .
C7 C 0.3725 -0.0773 -0.0200 0.0500 1.0000 Uiso . . . . . . .
```

```
C8 C 0.3405 -0.1553 -0.0410 0.0500 1.0000 Uiso . . . . . . .
C9 C 0.2720 -0.1814 0.0290 0.0500 1.0000 Uiso . . . . . . .
C10 C 0.2303 -0.1307 0.1210 0.0500 1.0000 Uiso . . . . . . .
C11 C 0.2615 -0.0526 0.1430 0.0500 1.0000 Uiso . . . . . . .
H1 H 0.4310 0.1560 0.4050 0.0500 1.0000 Uiso . . . . . .
H4 H 0.3200 -0.1140 0.4000 0.0500 1.0000 Uiso . . . . . .
H5 H 0.4020 -0.1420 0.4400 0.0500 1.0000 Uiso . . . . . .
H6 H 0.3890 -0.0760 0.5700 0.0500 1.0000 Uiso . . . . . .
H7 H 0.4200 -0.0590 -0.0700 0.0500 1.0000 Uiso . . . . . . .
H8 H 0.3550 -0.1860 -0.1100 0.0500 1.0000 Uiso . . . . . .
H9 H 0.2400 -0.2290 0.0170 0.0500 1.0000 Uiso . . . . . . .
H10 H 0.1760 -0.1370 0.1840 0.0500 1.0000 Uiso . . . . . . .
H11 H 0.2380 -0.0180 0.2140 0.0500 1.0000 Uiso . . . . . . .
H21 H 0.4814 0.3426 0.2841 0.0600 1.0000 Uiso . . . . . . .
H22 H 0.4653 0.2922 0.4176 0.0600 1.0000 Uiso . . . . . .


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_oxford_refine_ls_scale 1.000
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 _geom_bond_site_symmetry_1
 _geom_bond_atom_site_label_2
 _geom_bond_site_symmetry_2
 _geom_bond_distance
 _geom_bond_publ_flag
S1 . C1 . 1.763    yes
S1 . C6 . 1.780    yes
O1 . C1 . 1.392    yes
O1 . C4 . 1.368    yes
N2 . C3 . 1.355    yes
N2 . H21 . 0.880   no
N2 . H22 . 0.880   no
O3 . C4 . 1.179    yes
O4 . C3 . 1.197    yes
C1 . C2 . 1.312    yes
C2 . C3 . 1.469    yes
C2 . H1 . 0.769    no
C4 . C5 . 1.502    yes
C5 . H4 . 1.192    no
C5 . H5 . 0.734    no
C5 . H6 . 1.094    no
C6 . C7 . 1.379    yes
C6 . C11 . 1.353    yes
C7 . C8 . 1.380    yes
C7 . H7 . 0.935    no
C8 . C9 . 1.338    yes
C8 . H8 . 0.852    no
C9 . C10 . 1.367    yes
C9 . H9 . 0.932    no
C10 . C11 . 1.378    yes
C10 . H10 . 1.049    no
C11 . H11 . 0.951    no
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 _geom_angle_publ_flag
C1 . S1 . C6 . 103.487    yes
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C1  . O1  . C4  . 116.932    yes
C3  . N2  . H21 . 120.000    no
C3  . N2  . H22 . 120.000    no
H21 . N2  . H22 . 120.000    no
S1  . C1  . O1  . 116.263    yes
S1  . C1  . C2  . 124.709    yes
O1  . C1  . C2  . 118.791    yes
C1  . C2  . C3  . 124.053    yes
C1  . C2  . H1  . 117.426    no
C3  . C2  . H1  . 118.326    no
C2  . C3  . N2  . 114.409    yes
C2  . C3  . O4  . 123.859    yes
N2  . C3  . O4  . 121.702    yes
O1  . C4  . O3  . 123.533    yes
O1  . C4  . C5  . 107.748    yes
O3  . C4  . C5  . 128.708    yes
C4  . C5  . H4  . 99.773     no
C4  . C5  . H5  . 104.582    no
H4  . C5  . H5  . 92.297     no
C4  . C5  . H6  . 103.374    no
H4  . C5  . H6  . 125.823    no
H5  . C5  . H6  . 126.883    no
S1  . C6  . C7  . 115.326    yes
S1  . C6  . C11 . 124.202    yes
C7  . C6  . C11 . 120.189    yes
C6  . C7  . C8  . 118.296    yes
C6  . C7  . H7  . 120.742    no
C8  . C7  . H7  . 120.952    no
C7  . C8  . C9  . 121.171    yes
C7  . C8  . H8  . 123.355    no
C9  . C8  . H8  . 114.160    no
C8  . C9  . C10 . 120.845    yes
C8  . C9  . H9  . 130.037    no
C10 . C9  . H9  . 108.452    no
C9  . C10 . C11 . 118.618    yes
C9  . C10 . H10 . 134.076    no
C11 . C10 . H10 . 107.306    no
C10 . C11 . C6  . 120.850    yes
C10 . C11 . H11 . 120.784    no
C6  . C11 . H11 . 118.003    no
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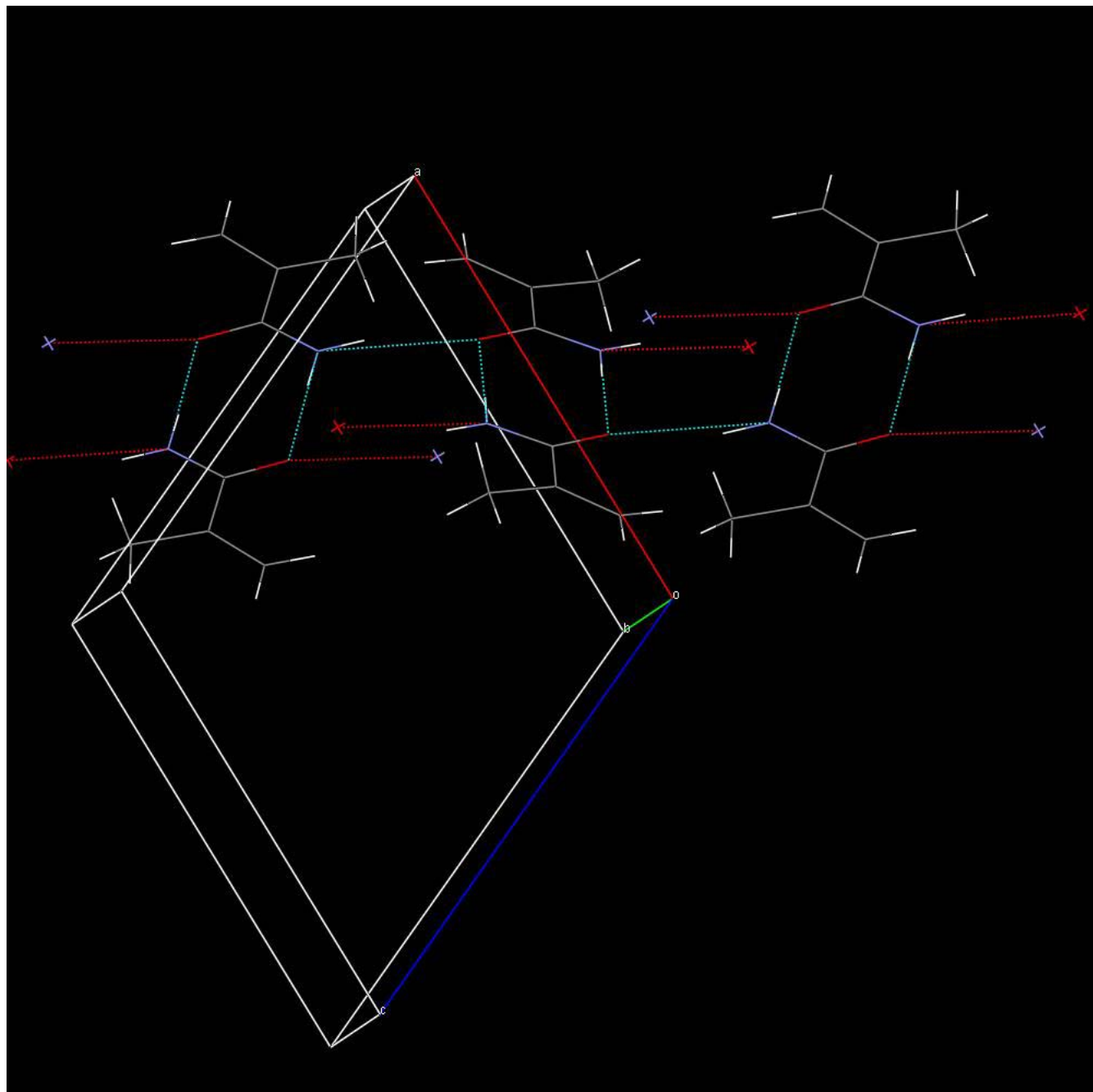
**Figure 8-S. Packing Diagram of Form I showing spiralling nature of C(4)
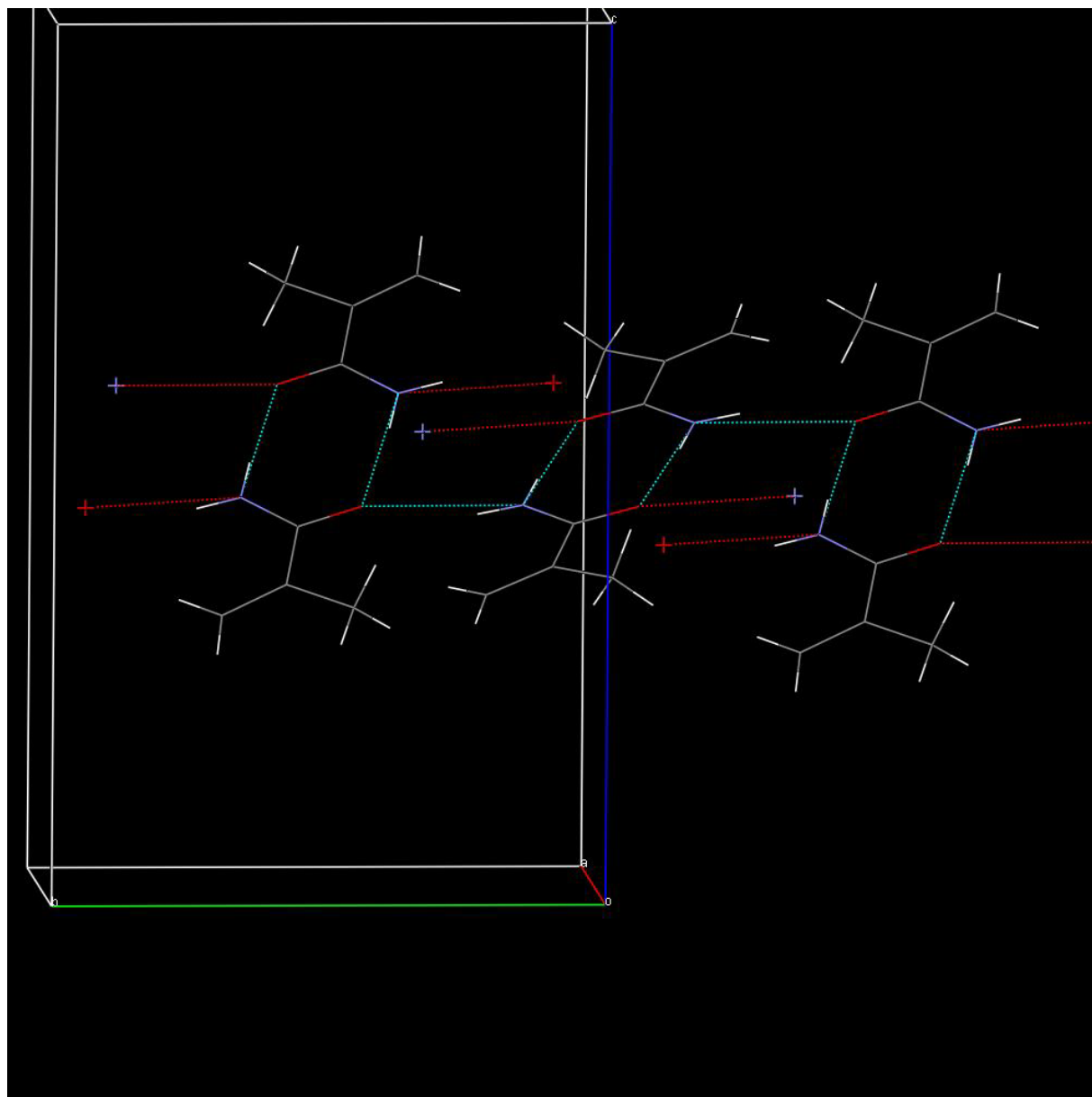chains along 2_1 axis (upper and lower chains are truncated for clarity).**

Figure 9-S. Packing Diagram for Form II showing spiralling nature of C(4) chains along 2₁ axis (upper and lower chains are truncated for clarity).