**Pseudo-polymorphism in 2-pyridylmethoxy cone derivatives of**

***p*-*tert*-butylcalix[4]arene and *p*-*tert*-butylhomooxacalix[*n*]arenes**

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Table S1a: Summary of the various crystalline forms of **PyC4, PyHOC4** and **PyH3OC3** obtained under various crystallisation conditions.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **PyC4** | | | | | | | | |
| **PyC4-MeOH-α** | **PyC4-H2O-α** | | **PyC4-MeOH-β** | **PyC4⸦ACN-MeOH** | | **PyC4⸦ACN-H2O** | **PyC4** | |
| MeOH + a/d | MeOH + d | | MeOH + CHCl3 + c | MeOH + MeCN + a/b | | DMSO + MeCN + b | MeOH + Toluene + f | |
| MeOH + CHCl3 + b |  | | MeOH + Hexane + e | MeOH+MeCN+THF+e | |  | MeOH + Hexane + a | |
| MeOH + Hexane + b/c |  | |  |  | |  |  | |
|  |  | |  |  | |  |  | |
| **PyHOC4** | | | | | | | |
| **PyHOC4-DMSO** | | **PyHOC4-MeCN-MeOH** | | | **PyHOC4-Hexane** | | |
| DMSO + f | | MeOH + MeCN + b | | | MeOH + Hexane + f | | |

|  |  |
| --- | --- |
| **PyH3OC3** | |
| **PyHO3C3** | **PyHO3C3-H2O-MeOH** |
| MeOH + CHCl3 + a/c/d/e | MeOH + CHCl3 + b |
| MeCN + b/c |  |
| MeOH + b |  |
| MeOH + MeCN + a |  |
| DMSO + b |  |

a La(NO3)3.6H2O; b Er(NO3)3.5H2O; c La(triflate); d Gd(NO3)3.6H2O; e Yb(triflate; f Tb(triflate)

Table S2. Crystal data and structure refinements for **PyC4** pseudo-polymorphs.

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | **PyC4-MeOH-α** | **PyC4-H2O-α** | **PyC4-MeOH-β** | **PyC4⸦MeCN-MeOH** | **PyC4⸦MeCN-H2O** | **PyC4** |
| Empirical formula | C68.2 H76.8 O4.2 N4 | C68 H76.8 O4.4 N4 | C68.75 H79 O4.75 N4 | C71 H83 O5 N5 | C70 H79.4 N5 O4.2 | C68 H76 O4 N4 |
| Formula weight | 1019.73 | 1020.53 | 1037.35 | 1086.42 | 1057.99 | 1013.32 |
| Temp. (K) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) | 100(2) |
| Wavelength (Ǻ) | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 | 0.7 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic | Triclinic | Monoclinic |
| Space group | P 21/c | P 21/c | P -1 | P21 | P -1 | P 21/n |
| Unit cell  Dimensions (Ǻ. °) | a = 12.004(4)  b = 12.090(8)  c = 40.691(5)  = 90  = 95.857(13)  = 90 | a = 12.005(5)  b = 12.121(1)  c = 40.565(2)  = 90  = 95.98(2)  = 90 | a = 10.410(4)  b = 23.014(9)  c = 24.874(10)  = 95.813(8)  = 90.17(3)  = 97.56(3) | a = 13.936(2)  b = 15.260(1)  c = 14.125(2)  = 90  = 92.794(19)  = 90 | a = 13.239(2)  b = 14.358(1)  c = 18.297(2)  = 95.419(8)  = 100.656(11)  = 117.079(9) | a  b  c  = 90  = 108.878(12)  = 90 |
| Volume (Ǻ3) | 5875(2) | 5871(2) | 5876(4) | 3000.3(6) | 2979.3(6) | 5815(4) |
| Z | 4 | 4 | 4 | 2 | 2 | 4 |
| ** calcd (g/cm3) | 1.153 | 1.155 | 1.173 | 1.203 | 1.179 | 1.157 |
| ** (mm–1) | 0.068 | 0.069 | 0.070 | 0.072 | 0.070 | 0.071 |
| F(000) | 2190 | 2192 | 2230 | 1168 | 1136 | 2176 |
| Reflections collected | 92155 | 108677 | 26719 | 53761 | 55796 | 106058 |
| Independent reflections | 16083 | 15795 | 14199 | 16697 | 15954 | 16910 |
| parameters/ restr. | 747/8 | 747/0 | 1465/0 | 751/1 | 748/0 | 698/0 |
| GOOF | 1.0072 | 1.049 | 1.032 | 1.043 | 1.043 | 1.047 |
| *R* all data | 0.0633 | 0.0535 | 0.1459 | 0.0417 | 0.0522 | 0.0631 |
| *R* [I>2σ(I)] | 0.0616 | 0.0444 | 0.0966 |  | 0.0479 | 0.0585 |
| *wR* all data | 0.1664 | 0.1238 | 0.2930 | 0.1131 | 0.1333 | 0.1666 |
| *wR* [I>2σ(I)] | 0.1646 | 0.1171 | 0.2538 | 0.1119 | 0.1295 | 0.1614 |
| Largest Diff. peak (e Å-3) | 0.633/-0.350 | 0.351/-0.276 | 0.450/-0.357 | 0.336/-0.319 | 0.674/-0.358 | 0.592/-0.402 |
| CCDC code | 2331929 | 2331930 | 2331931 | 2331932 | 2331933 | 2331934 |

Table S3. Crystal data and structure refinements for **PyHOC4** pseudo-polymorphs.

|  |  |  |  |
| --- | --- | --- | --- |
|  | **PyHOC4-DMSO** | **PyHOC4⸦MeCN-MeOH** | **PyHOC4-Hexane** |
| Empirical formula | C70.72 H81.68 N4 O5.86 S0.86 | C71.80 H84.20 N5 O5.80 | C78 H99 N4 O5 |
| Formula weight | 1110.73 | 1110.04 | 1172.61 |
| Temperature (K) | 100(2) | 100(2) | 100(2) |
| Wavelength (Ǻ) | 0.7 | 0.7 | 0.7 |
| Crystal system | Triclinic | Triclinic | Triclinic |
| Space group | P -1 | P -1 | P -1 |
| Unit cell  Dimensions (Ǻ. °) | a = 20.98(2)  b = 22.476(18)  c = 28.52(3)  = 72.25(2)  = 81.425(15)  = 89.765(16) | a = 13.969 (11)  b = 14.823(8)  c = 15.292(5)  = 84.06(3)  = 83.01(4)   = 87.134(16) | a = 11.686 (5)  b = 16.604(2)  c = 17.957(3)  = 88.99(3)  = 86.252(5)   = 77.253(5) |
| Volume (Ǻ3) | 12655(22) | 3124(3) | 3391.1(15) |
| Z | 8 | 2 | 2 |
| ** calcd (g/cm3) | 1.164 | 1.18 | 1.148 |
| ** (mm–1) | 0.098 | 0.075 | 0.068 |
| F(000) | 4758 | 1193 | 1272 |
| Reflections collected | 101598 | 20556 | 123826 |
| Independent reflections | 29067 | 6399 | 19724 |
| parameters/ restr. | 2802/2286 | 714/0 | 801/0 |
| GOOF | 1.025 | 1.062 | 1.032 |
| *R* all data | 0.2285 | 0.1568 | 0.0673 |
| *R* [I>2σ(I)] | 0.1659 | 0.1326 | 0.0643 |
| *wR* all data | 0.5018 | 0.4251 | 0.1891 |
| *wR* [I>2σ(I)] | 0.4387 | 0.3876 | 0.1857 |
| Largest Diff. peak/ hole (e Å-3) | 0.841/-0.646 | 0.517/-0.325 | 1.047/-0.598 |
| CCDC code | 2331935 | 2331936 | 2331937 |

Table S4. Crystal data and structure refinements for **PyHO3C3** pseudo-polymorphs

|  |  |  |
| --- | --- | --- |
|  | **PyHO3C3** | **PyHO3C3-H2O-MeOH** |
| Empirical formula | C54 H63 N3 O6 | C55 H75 N3 O11 |
| Formula weight | 850.07 | 954.18 |
| Temperature (K) | 100(2) | 100(2) |
| Wavelength (Ǻ) | 0.7 | 0.7 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | P 21/c | P 21/c |
| Unit cell  Dimensions (Ǻ. °) | a = 24.022(3)  b = 10.7210(14)  c = 19.415(5)  = 90  = 111.667(7)  = 90 | a = 19.430(19)  b = 14.376(3)  c = 19.605(8)  = 90  = 106.84(5)  = 90 |
| Volume (Ǻ3) | 4646.9(14) | 5241(6) |
| Z | 4 | 4 |
| ** calcd (g/cm3) | 1.215 | 1.209 |
| ** (mm–1) | 0.075 | 0.080 |
| F(000) | 1824 | 2056 |
| Reflections collected | 85480 | 96321 |
| Independent reflections | 13548 | 15397 |
| Data/parameters/ restr. | 712/1570 | 659/0 |
| GOOF | 1.091 | 1.020 |
| *R* all data | 0.1104 | 0.0816 |
| *R* [I>2σ(I)] | 0.0883 | 0.0567 |
| *wR* all data | 0.2571 | 0.1605 |
| *wR* [I>2σ(I)] | 0.2376 | 0.1434 |
| Largest Diff. peak/ hole (e Å-3) | 0.699/-0.630 | 0.515/-0.296 |
| CCDC code | 2331938 | 2331939 |

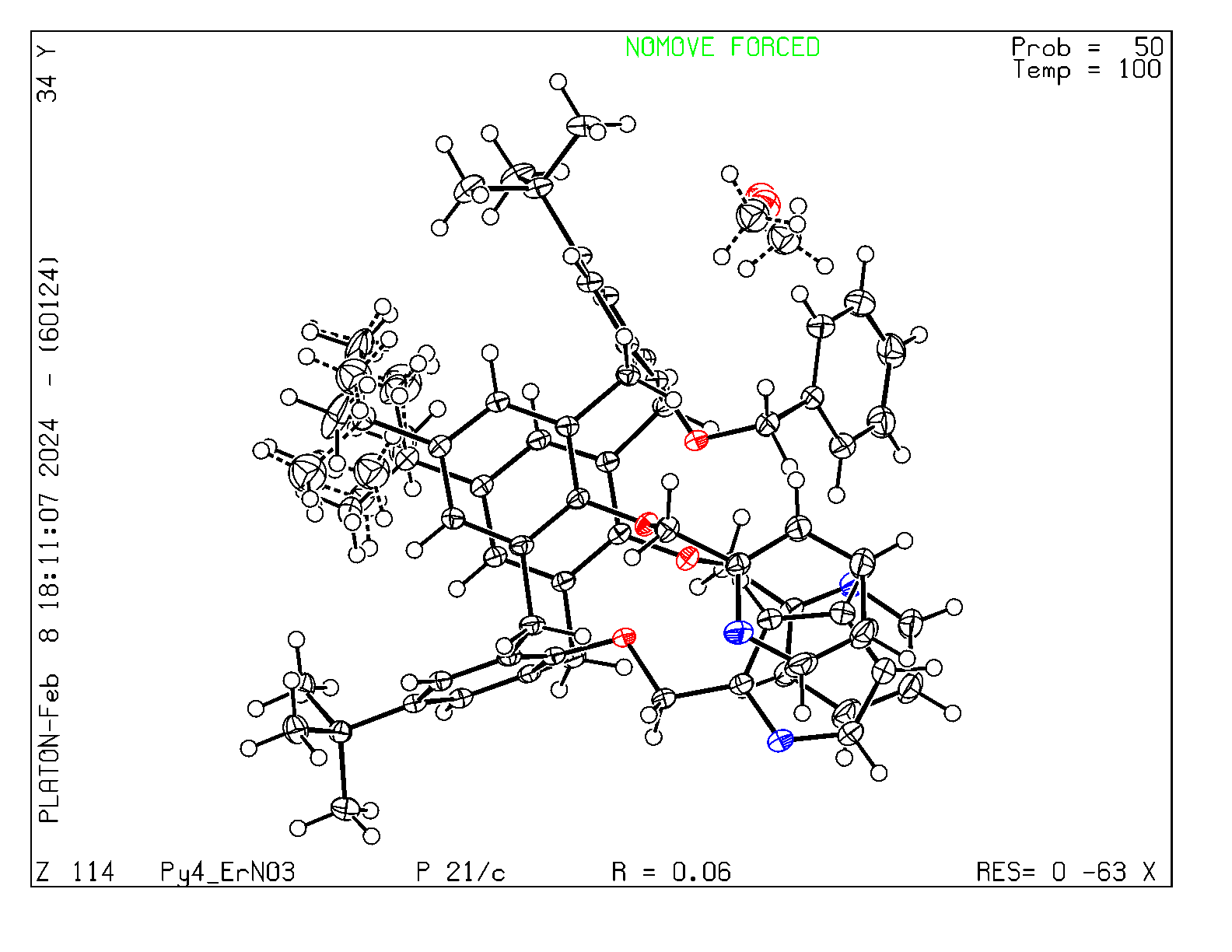


Figure S1. ORTEP drawing of the asymmetric unit for the **PyC4-MeOH-α** crystal form.

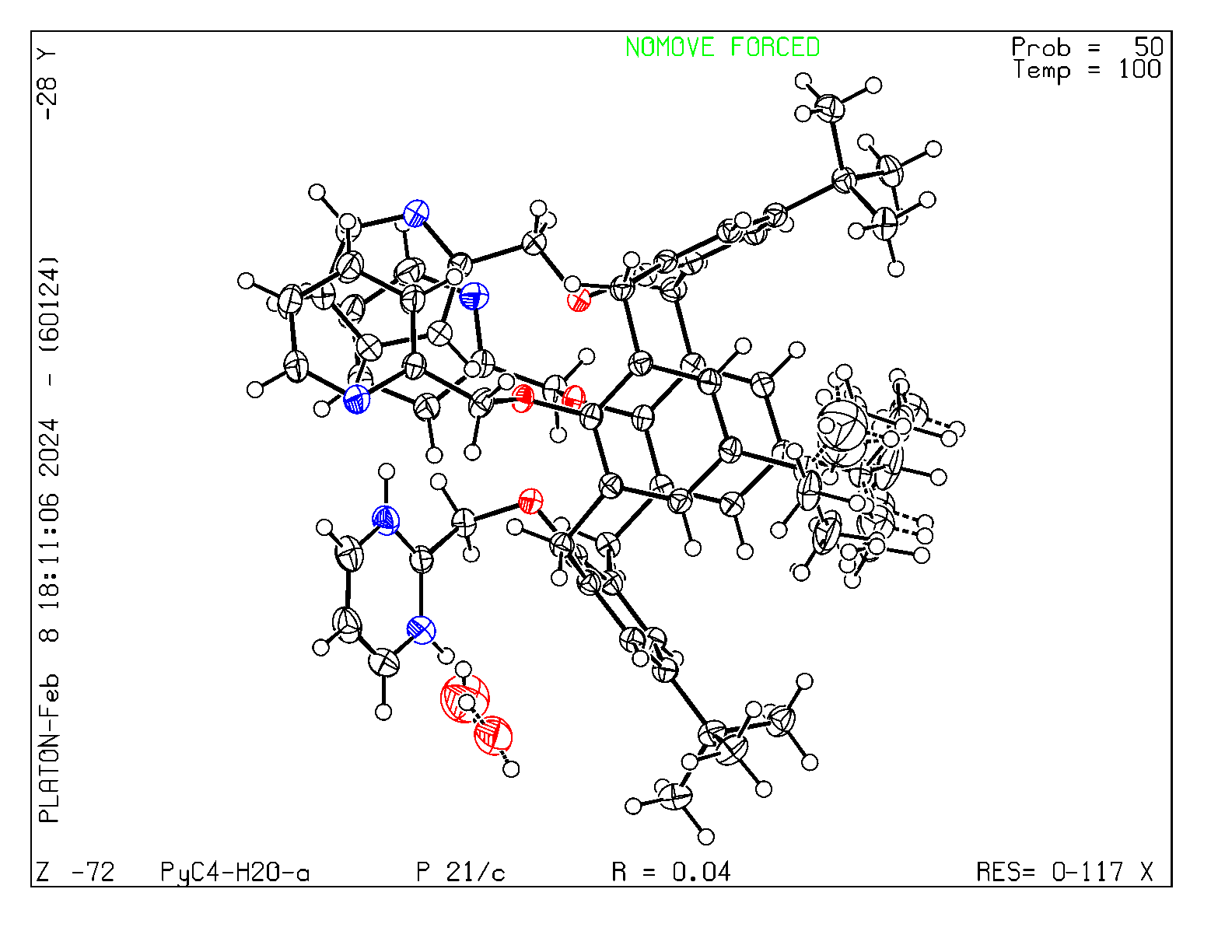


Figure S2. ORTEP drawing of the asymmetric unit for the **PyC4-H2O-α** crystal form.

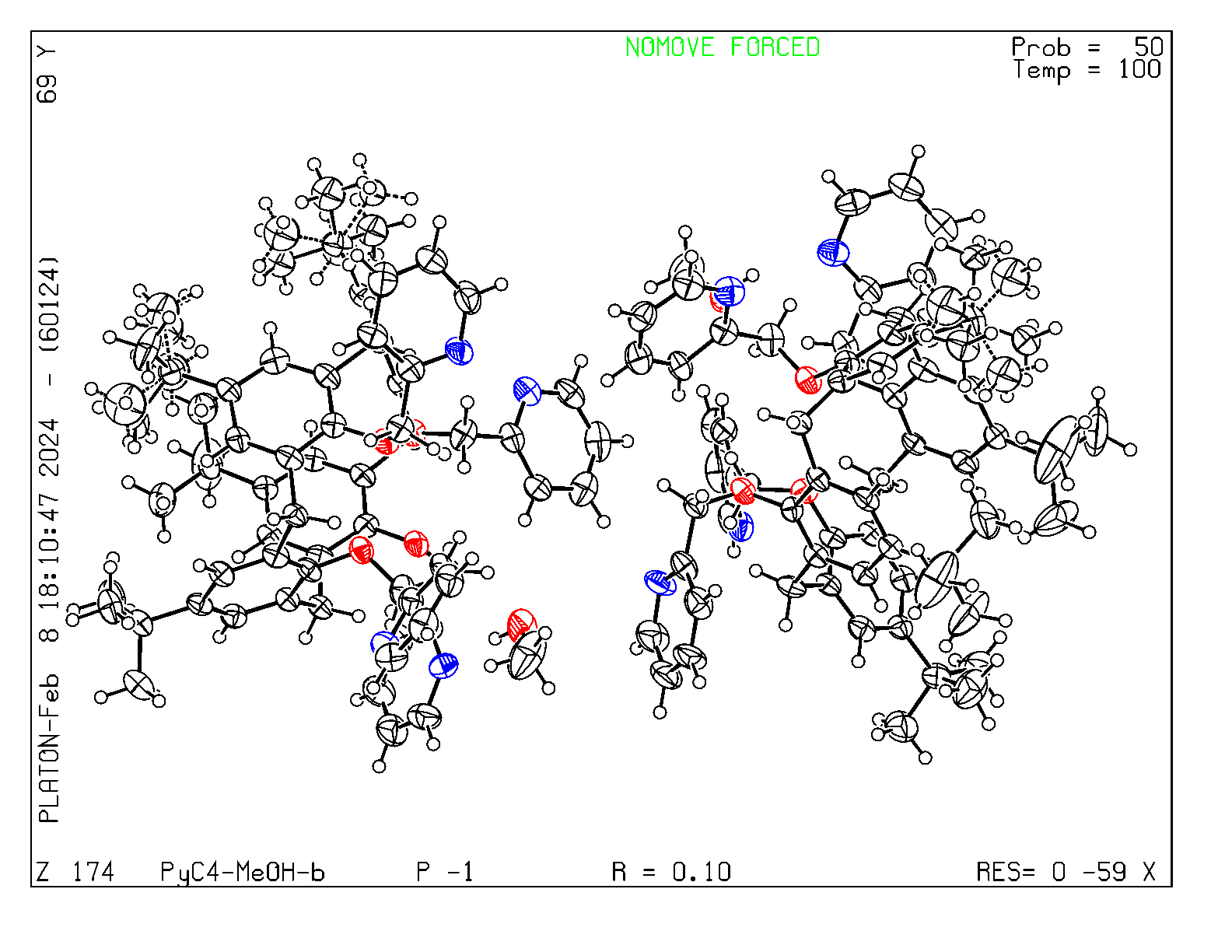


Figure S3. ORTEP drawing of the asymmetric unit for the **PyC4-MeOH-β** crystal form.

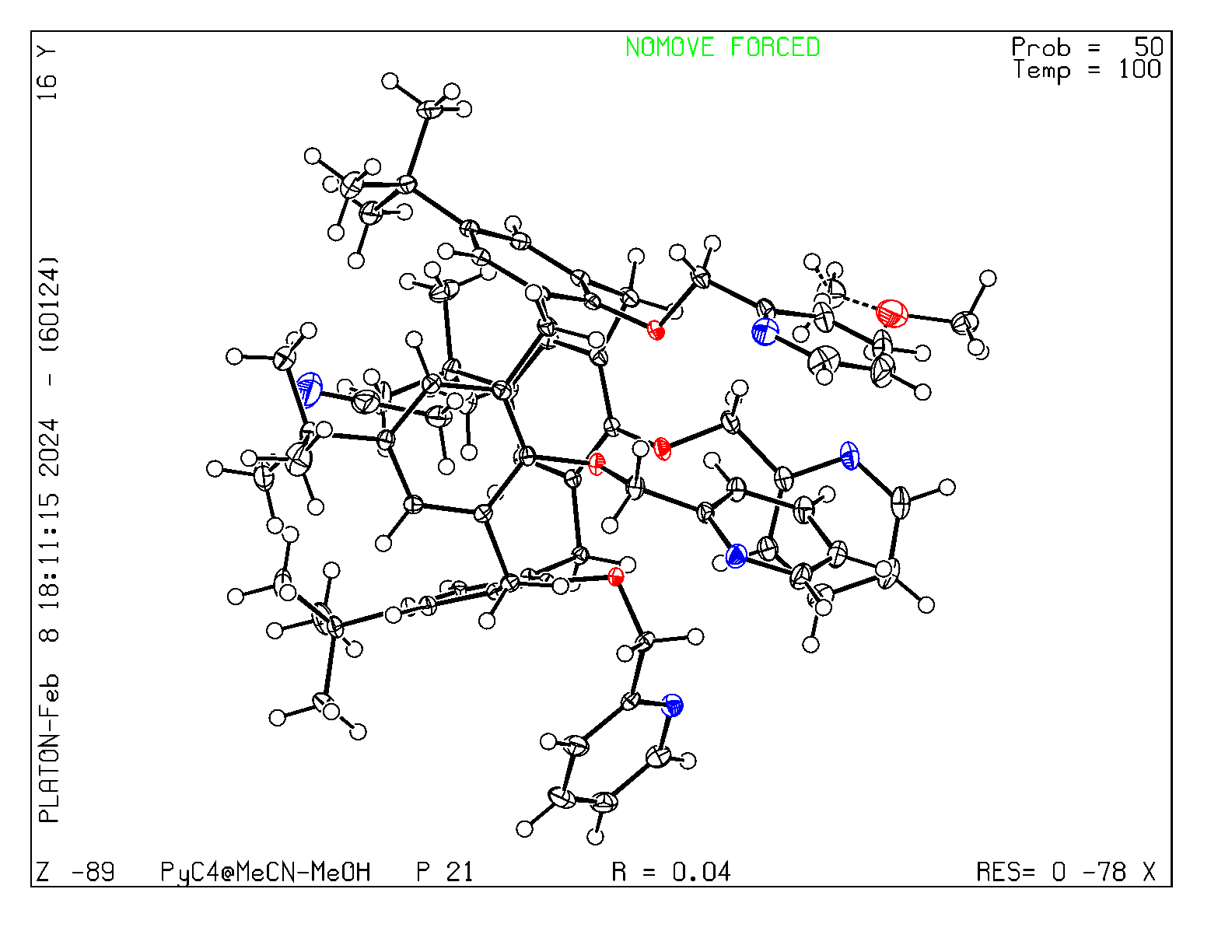


Figure S4. ORTEP drawing of the asymmetric unit for the **PyC4⸦MeCN-MeOH** crystal form.

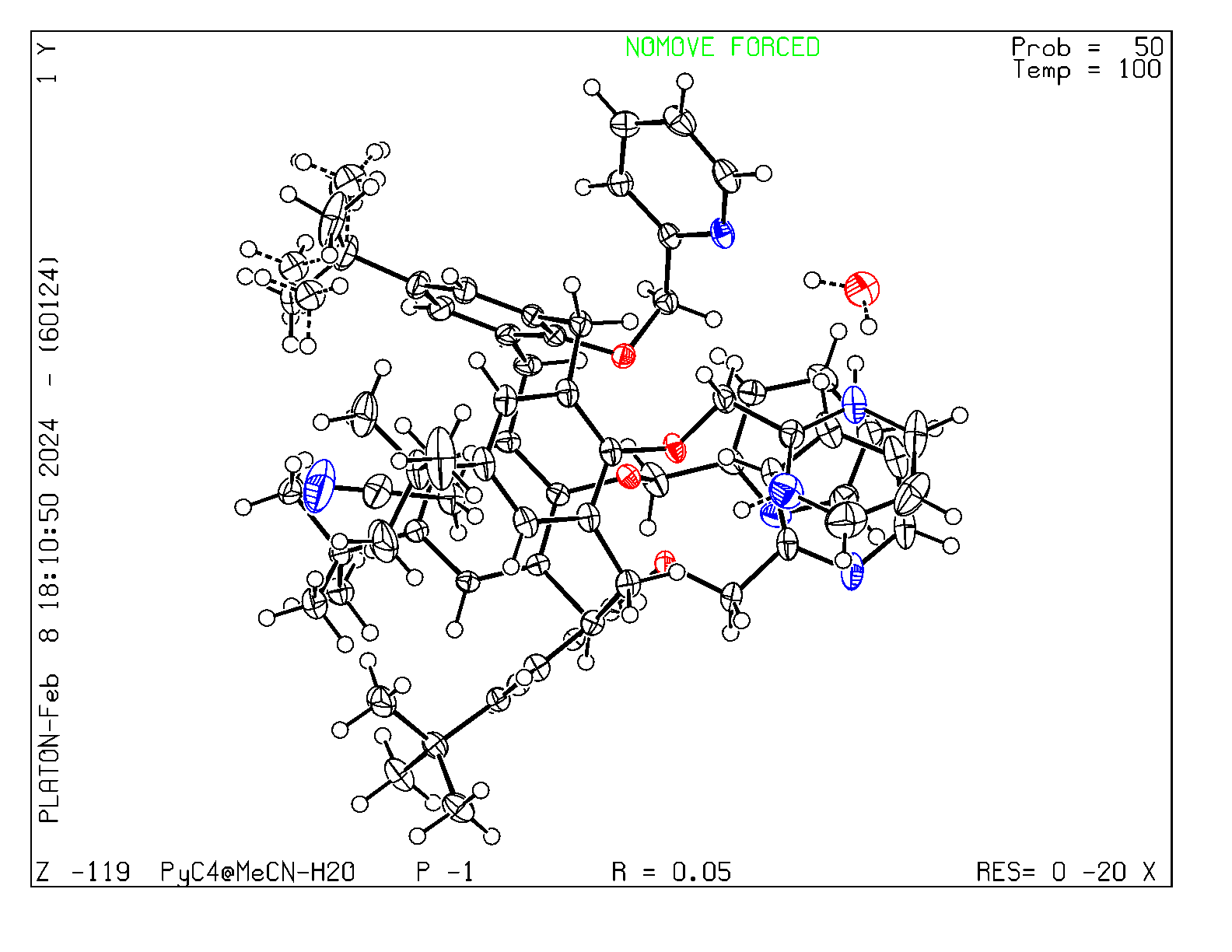


Figure S5. ORTEP drawing of the asymmetric unit for the **PyC4⸦MeCN-H2O** crystal form.

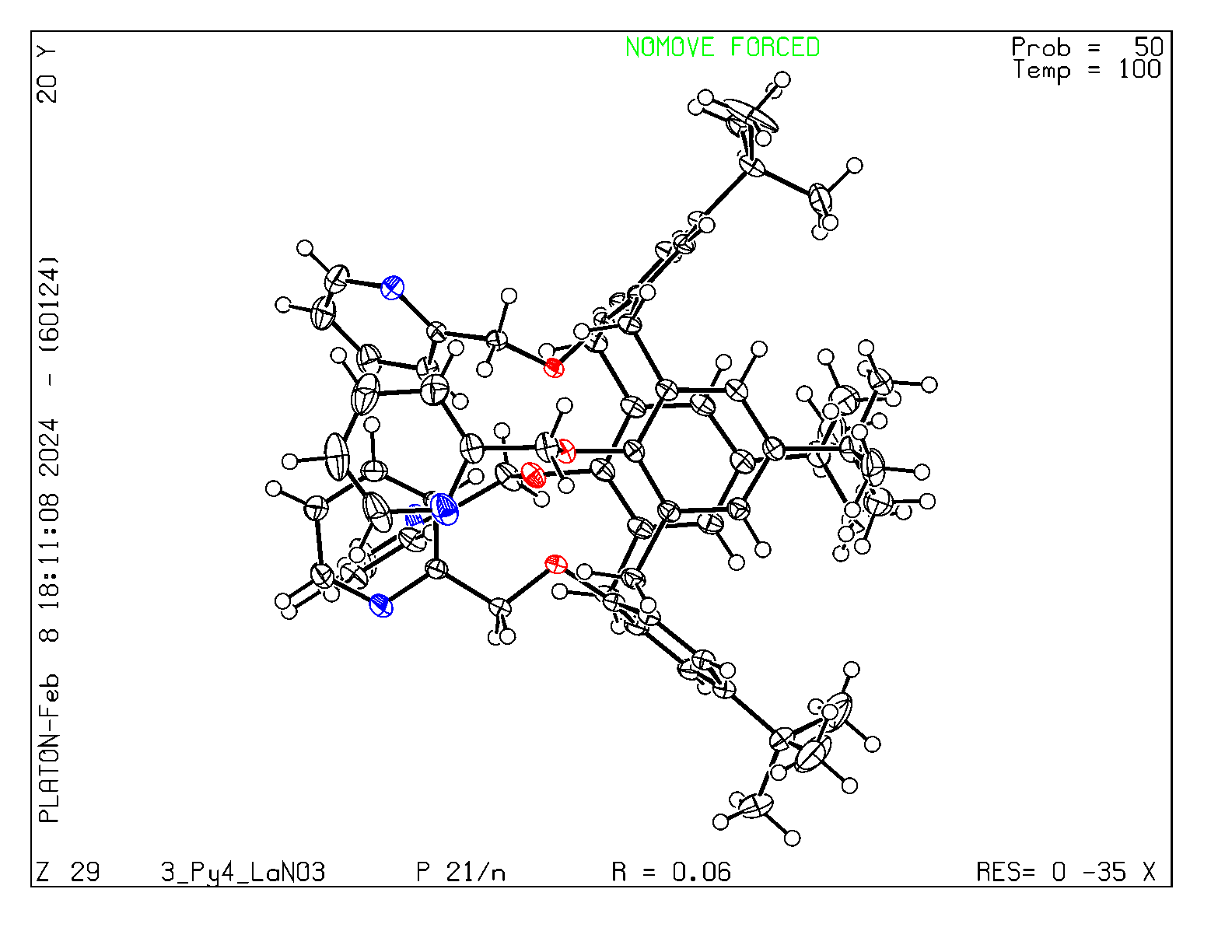


Figure S6. ORTEP drawing of the asymmetric unit for the **PyC4** crystal form.

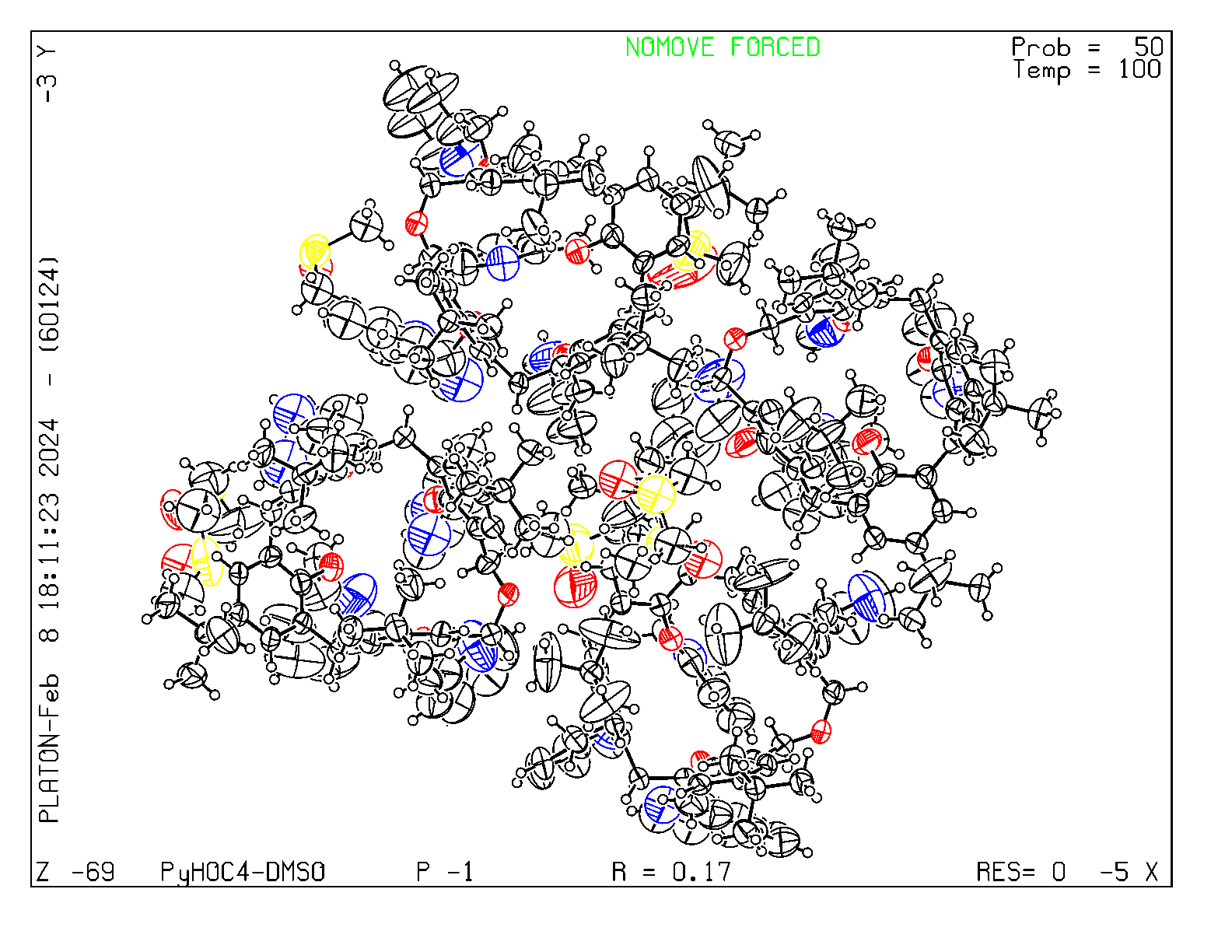


Figure S7. ORTEP drawing of the asymmetric unit for the **PyHOC4-DMSO** crystal form.

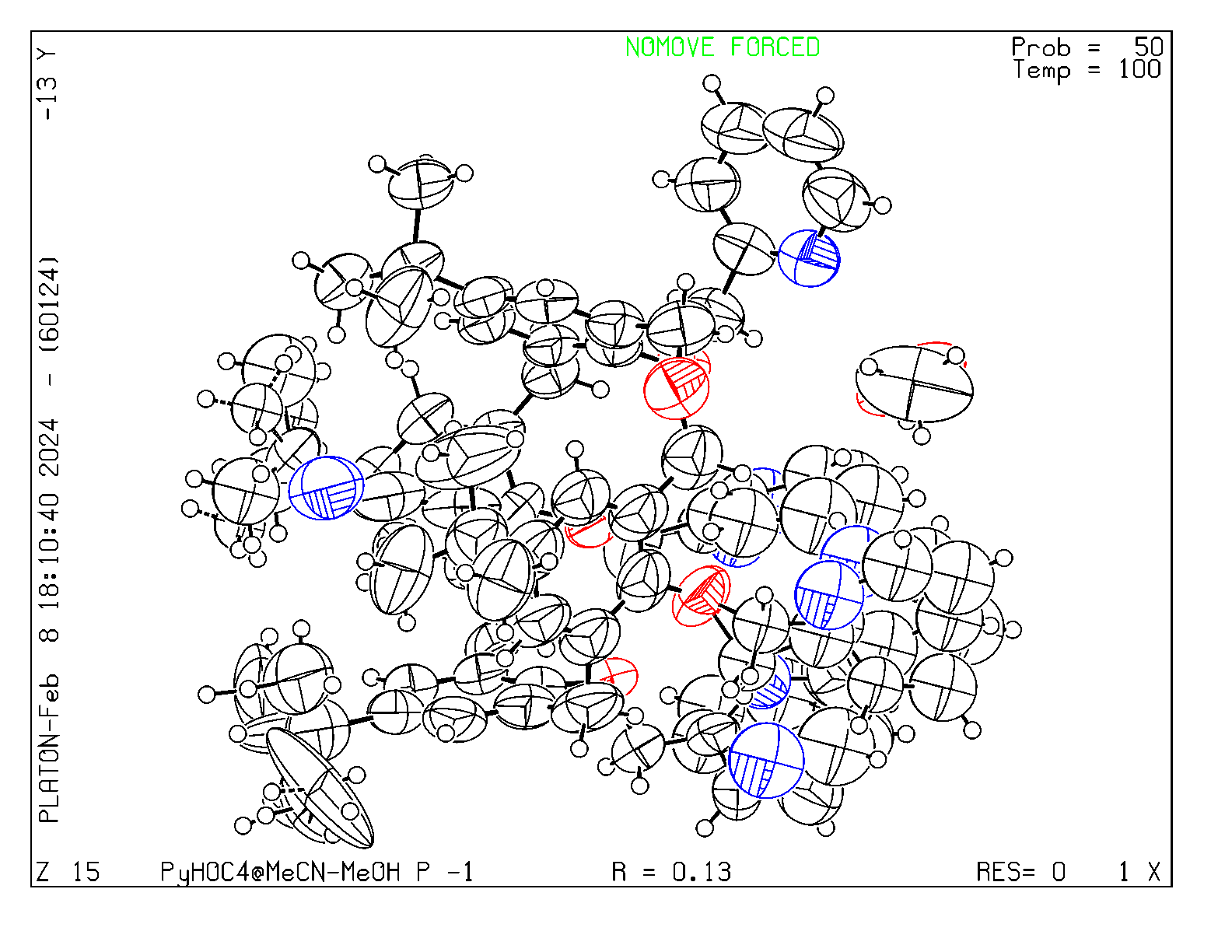


Figure S8. ORTEP drawing of the asymmetric unit for the **PyHOC4⸦MeCN-MeOH** crystal form.

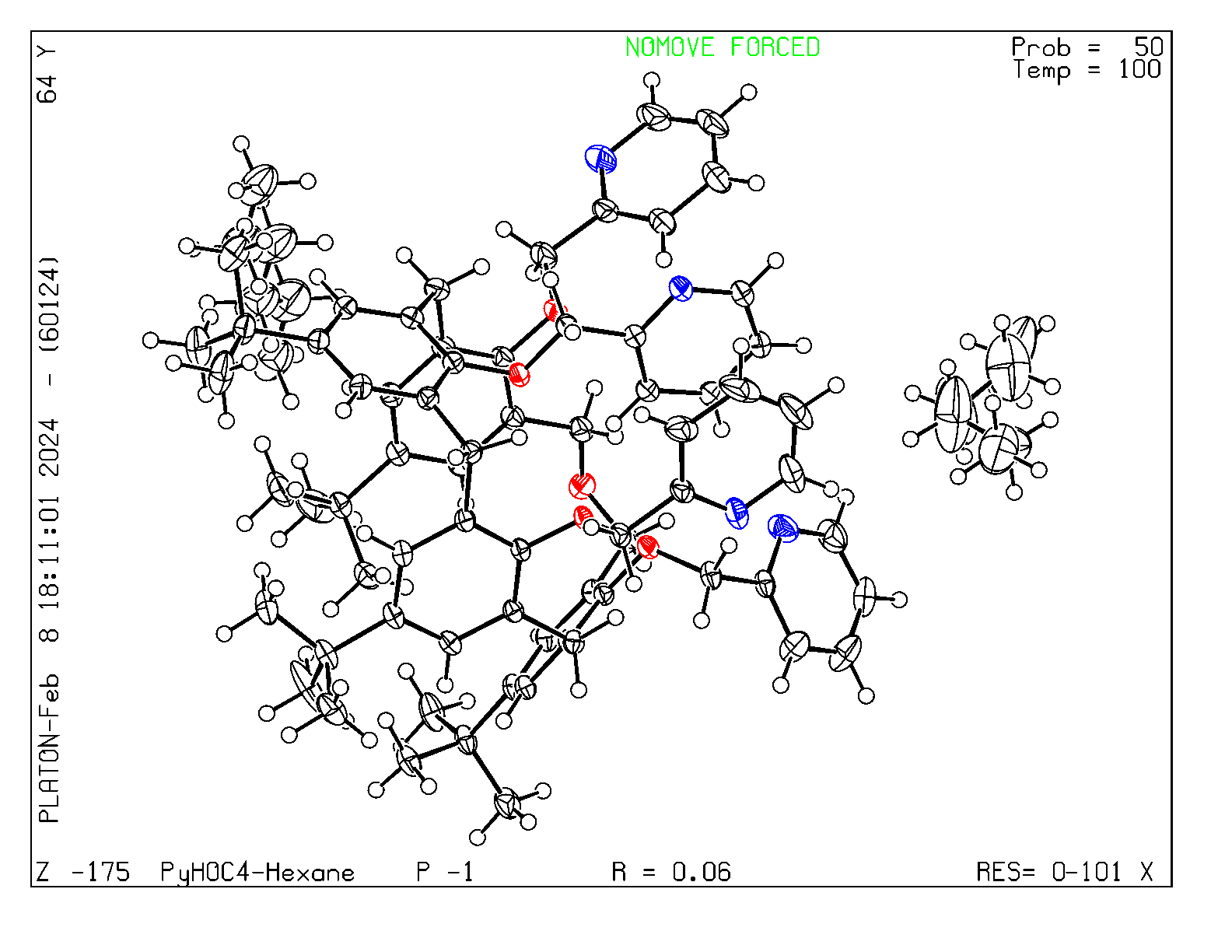


Figure S9. ORTEP drawing of the asymmetric unit for the **PyHOC4-Hexane** crystal form.

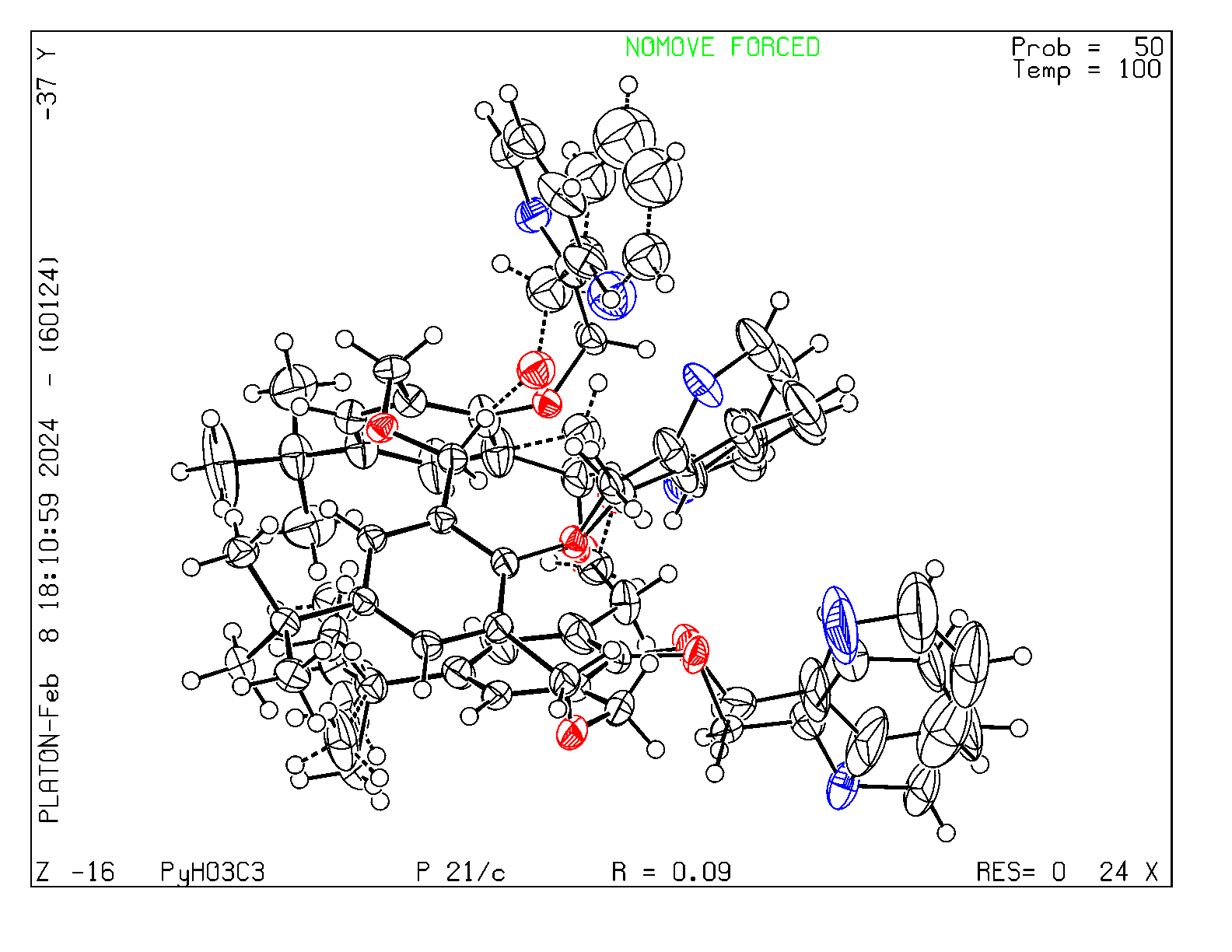


Figure S10. ORTEP drawing of the asymmetric unit for the **PyHO3C3** crystal form.

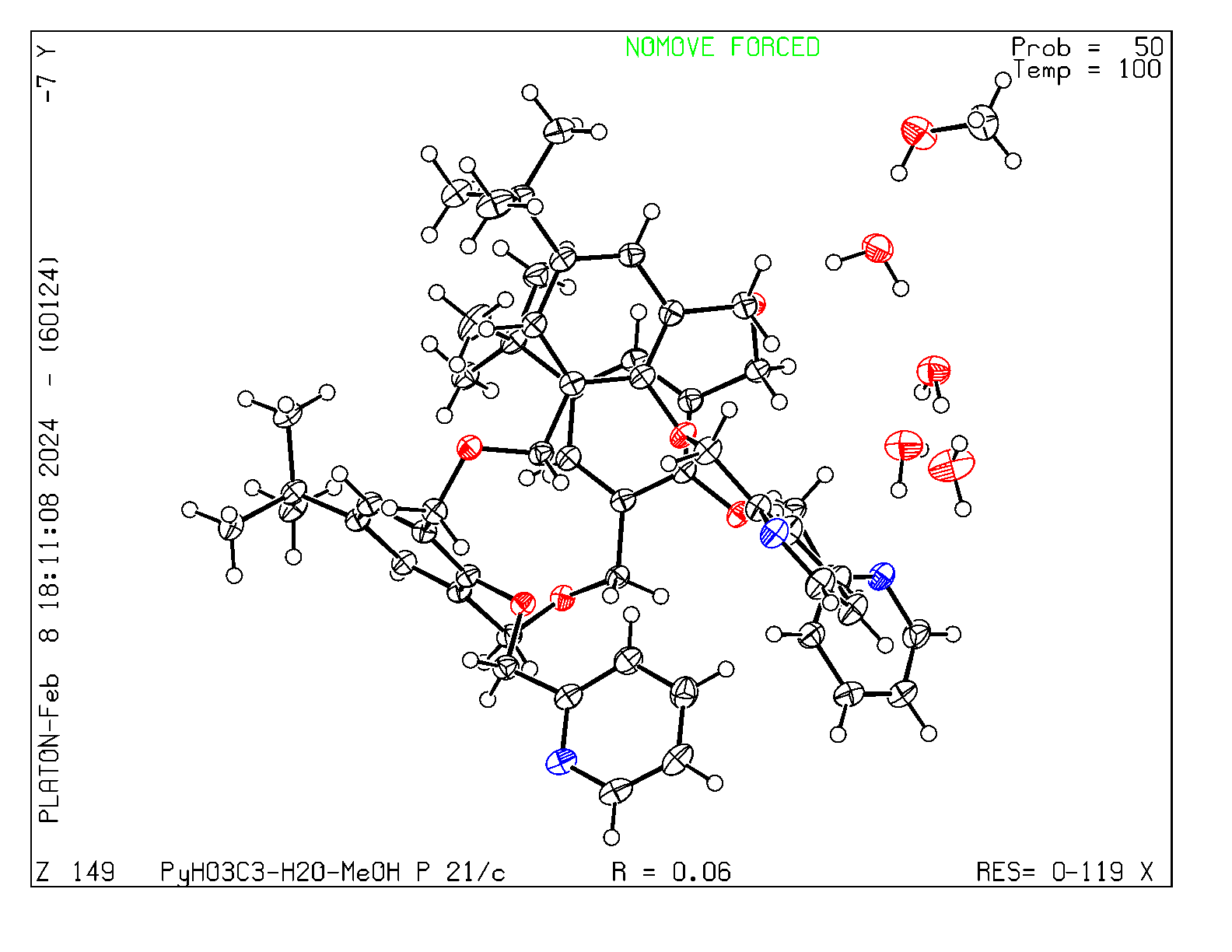


Figure S11. ORTEP drawing of the asymmetric unit for the **PyHO3C3-H2O-MeOH** crystal form.