Supporting Information

Dirhodium(II)-Catalyzed Formal [3+2+1] - Annulation of Azomethine Imines with Two Molecules of a Diazo Ketone

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**General:** Reactions were performed in oven-dried (140 °C) glassware under an atmosphere of dry N₂. Dichloromethane (DCM) was passed through a solvent column prior to use and was kept over 3 Å molecular sieves. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F254 plates. The developed chromatogram was analyzed by a UV lamp (254 nm). Liquid chromatography was performed using flash chromatography of the indicated system on silica gel (230-400 mesh). ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a 400 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (J) are given in Hertz. The peak information is described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were performed on a TOF-CS mass spectrometer using CsI as the standard. UV absorption measurements were performed on a UV-Vis spectrometer. A glass cell (1 cm path length) with screw top was used. Lewis acids and dirhodium tetraacetate were purchased and used as received. Other dirhodium catalysts¹ and diazo ketone 4² were synthesized according to literature procedures. Azomethine imines 1 were synthesized according to the literature reference.³
General Procedure for the Synthesis of Azomethine Imines 1.³

Methyl acrylate was added dropwise (2.0 mL, 22.5 mmol) to a solution of hydrazine monohydrate (1.0 mL, 20.5 mmol) in ethanol (20.0 mL). After stirring at 78 °C overnight, the solvent was evaporated, and the residue was dissolved in methanol (5.0 mL). Then aldehyde (30.0 mmol) was added. After stirring overnight at room temperature, the solvent was evaporated; and the residue was directly purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 10:1 to 5:1) to give the pure azomethine imine derivatives 1 in moderate to high yield and ¹H NMR spectra of the products were identical to previously reported data.³

General Procedure for the Synthesis of Diazo Ketone 4.²

Synthesis of 6,6-Dimethylidihydro-2H-pyran-2,4(3H)-dione:²a To an oven-dried flask containing a magnetic stirring bar, NaH (3.2 g, 60% in mineral oil, 80.0 mmol) in anhydrous THF (200.0 mL), was added methyl acetoacetate (9.28 g, 80 mmol) dropwise at 0 °C. After 10 min of stirring, BuLi (50 mL, 1.6M, 80 mmol) was added dropwise, and the orange solution was stirred at 0 °C for 10 min. Dry acetone (7.5 mL, 82 mmol) was added at one time, and the mixture was stirred for 10 min at 0 °C. Aqueous NaOH (80 mL, 2.5M) was then added, and the mixture was stirred at room temperature overnight. The reaction mixture was acidified with aqueous HCl (~120 mL, 2.5M) and then extracted with ether (200 mL X 3). The organic layer was washed with saturated NaCl (200 mL X 2) and dried with anhydrous NaSO₄. After filtration, the solvent was evaporated under reduced pressure. The residue was dissolved in a minimum of DCM, and the product was precipitated with pentane as a brownish solid (3.8–4.5 g, 34%–40% yield). ¹H NMR (400 MHz, CDCl₃):² δ (ppm) 3.44 (s, 2H), 2.71 (s, 2H), 1.52 (s, 6H).
**Synthesis of Diazo Ketone 4:**

To a 100-mL round-bottomed flask containing a magnetic stirring bar, 6,6-dimethylidihydro-2H-pyran-2,4(3H)-dione (1.42 g, 10 mmol), p-acetamidobenzenesulfonyl azide (p-ABSA, 2.48 g, 12 mmol) and acetonitrile (50 mL) were added slowly at 0 °C, followed by triethylamine (3.5 mL). The reaction mixture was warmed to room temperature after 2 hours (pale yellow solid formed during this time) and stirred overnight under this condition. The solid was filtered and washed with ether (20 mL X 2), and the solvent was evaporated under reduced pressure. The reaction mixture was purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 90:10 to 80:20) to give pure diazo ketone 4 (1.5 g, 89% yield). $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 5.70 (bs, 1H), 5.18 (bs, 1H), 2.11 (d, $J$ = 8.0 Hz, 3H), 1.80 (d, $J$ = 8.0 Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): 185.61, 153.84, 121.69, 56.32, 27.46, 20.58.

**General Procedure for the Formal [3+2+1]-Annulation.**

To an oven-dried flask containing a magnetic stirring bar, azomethine imine 1 (0.3 mmol), 4 Å molecular sieves (100 mg) and Rh$_2$(4S-MPPIM)$_4$ (2.0 mol%) in DCM (2.0 mL), was added diazo ketone 4 (1.2 mmol) in DCM (1.0 mL) over 1-h period via a syringe pump at room temperature. The reaction mixture was stirred for 2 days under these conditions then purified by column chromatography on silica gel (eluent: hexanes:EtOAc = 90:10 to 70:30) to give the pure bicyclic pyrazolidinone derivatives 5 in moderate to high yield.

![Image](6-(1-Hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)-5-phenyltetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5a). 90% yield. $^1$H NMR (400 MHz, CDCl$_3$): δ (ppm) 7.39-7.26 (comp, 5H), 5.74 (s, 1H), 5.51 (d, $J$ = 8.7 Hz, 1H), 5.39 (d, $J$ = 8.7 Hz, 1H), 4.72 (s, 1H), 3.56-3.48 (m, 1H), 3.29-3.24 (m, 1H), 2.06 (s, 3H), 1.99 (s, 3H), 1.82 (s, 3H), 1.80 (s, 3H), 1.77-1.74 (m, 1H), 1.00-0.91 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): 187.1, 183.5, 169.6, 157.6, 139.7, 136.8, 129.4, 129.2, 129.1, 119.7, 118.4, 107.7, 64.8, 53.6, 46.8, 30.2, 28.8, 26.1, 21.6, 19.2; HRMS (ESI) calculated for C$_{22}$H$_{27}$N$_2$O$_3$ [M+H]$^+$: 367.2017; found: 367.2032.
5-(4-Chlorophenyl)-6-(1-hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5b). 85% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.40 (d, \(J = 8.4\) Hz, 2H), 7.21 (d, \(J = 8.4\) Hz, 2H), 5.69 (s, 1H), 5.50 (d, \(J = 8.7\) Hz, 1H), 5.40 (d, \(J = 8.7\) Hz, 1H), 4.71 (s, 1H), 3.60-3.51 (m, 1H), 3.25-3.20 (m, 1H), 2.09 (d, \(J = 1.0\) Hz, 3H), 1.99 (d, \(J = 1.0\) Hz, 3H), 1.90-1.83 (comp, 7H), 1.16-1.03 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): 187.0, 183.6, 169.4, 158.2, 140.0, 135.6, 135.3, 130.6, 129.5, 119.5, 118.1, 107.4, 64.2, 53.7, 46.7, 30.2, 28.9, 26.1, 21.7, 19.3; HRMS (ESI) calculated for C\(_{22}\)H\(_{26}\)ClN\(_2\)O\(_3\) [M+H] \(^+\): 401.1627; found: 401.1631. The pure product was recrystallized in DCM, EtOAc and hexanes, and the generated single-crystal was suitable for the X-ray analysis, see S-25.

5-(4-Bromophenyl)-6-(1-hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5c). 89% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.55 (d, \(J = 8.4\) Hz, 2H), 7.15 (d, \(J = 8.4\) Hz, 2H), 5.69 (s, 1H), 5.51 (d, \(J = 8.7\) Hz, 1H), 5.40 (d, \(J = 8.7\) Hz, 1H), 4.70 (s, 1H), 3.60-3.52 (m, 1H), 3.26-3.20 (m, 1H), 2.10 (d, \(J = 1.0\) Hz, 3H), 2.00 (d, \(J = 1.0\) Hz, 3H), 1.90-1.83 (comp, 7H), 1.17-1.07 (m, 1H); \(^13\)C NMR (100 MHz, CDCl\(_3\)): 186.9, 183.6, 169.4, 158.2, 140.0, 136.1, 132.4, 130.9, 123.4, 119.4, 118.0, 107.4, 64.2, 53.7, 46.7, 30.2, 28.9, 26.1, 21.7, 19.2; HRMS (ESI) calculated for C\(_{22}\)H\(_{26}\)BrN\(_2\)O\(_3\) [M+H] \(^+\): 445.1122; found: 445.1159.
6-(1-Hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)-5-(4-methoxyphenyl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5e). 61% yield. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta \) (ppm)  7.17 (d, \(J = 8.5 \) Hz, 2H), 6.94 (d, \(J = 8.5 \) Hz, 2H), 5.76 (s, 1H), 5.51 (d, \(J = 8.7 \) Hz, 1H), 5.40 (d, \(J = 8.7 \) Hz, 1H), 4.68 (s, 1H), 3.83 (s, 3H), 3.54-3.48 (m, 1H), 3.28-3.25 (m, 1H), 2.09 (d, \(J = 1.0 \) Hz, 3H), 2.00 (d, \(J = 1.0 \) Hz, 3H), 1.85-1.80 (comp, 7H), 1.10-1.01 (m, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): 187.2, 183.2, 169.7, 160.3, 157.5, 139.7, 130.5, 128.5, 119.7, 118.4, 114.6, 108.0, 64.3, 55.5, 53.4, 46.8, 30.3, 28.8, 26.1, 21.6, 19.2; HRMS (ESI) calculated for C\(_{23}\)H\(_{29}\)N\(_2\)O\(_4\) [M+H] \(^+\): 397.2122; found: 397.2131.
6-(1-Hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)-5-(4-nitrophenyl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5f). 57% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.29 (d, J = 8.7 Hz, 2H), 7.49 (d, J = 8.7 Hz, 2H), 5.64 (s, 1H), 5.53 (d, J = 8.7 Hz, 1H), 5.39 (d, J = 8.7 Hz, 1H), 4.86 (s, 1H), 3.66-3.58 (m, 1H), 3.27-3.21 (m, 1H), 2.09 (d, J = 1.0 Hz, 3H), 2.01 (d, J = 1.0 Hz, 3H), 1.95-1.88 (m, 1H), 1.85 (d, J = 1.0 Hz, 3H), 1.83 (d, J = 1.0 Hz, 3H), 1.16-1.06 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 186.6, 184.0, 169.1, 159.0, 148.4, 144.9, 140.3, 130.2, 124.2, 119.2, 117.6, 106.8, 64.1, 54.0, 46.6, 30.2, 29.0, 26.1, 21.8, 19.3; HRMS (ESI) calculated for C₂₂H₂₆N₃O₅ [M+H]⁺: 412.1867; found: 412.1889.

5-(2-Chlorophenyl)-6-(1-hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5g). 83% yield. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.49 (dd, J = 7.7, 1.6 Hz, 1H), 7.35-7.26 (comp, 2H), 7.10 (dd, J = 7.7, 1.6 Hz, 1H), 5.79 (s, 1H), 5.51 (d, J = 8.7 Hz, 1H), 5.54 (s, 1H), 5.40-5.37 (m, 1H), 3.55-3.46 (m, 1H), 3.42-3.36 (m, 1H), 2.09 (d, J = 1.0 Hz, 3H), 2.00 (d, J = 1.0 Hz, 3H), 1.93-1.86 (m, 1H), 1.84 (d, J = 1.0 Hz, 3H), 1.83 (d, J = 1.0 Hz, 3H), 1.22-1.13 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): 187.4, 183.0, 169.8, 158.3, 139.9, 135.0, 134.1, 130.9, 130.3, 130.2, 127.9, 119.4, 118.2, 107.6, 59.0, 53.6, 46.2, 30.6, 28.8, 26.1, 21.6, 19.3; HRMS (ESI) calculated for C₂₂H₂₆ClN₂O₃ [M+H]⁺: 401.1627; found: 401.1649.
5-(3-Chlorophenyl)-6-(1-hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5h). 80% yield. \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 7.41-7.12 (comp, 4H), 5.70 (s, 1H), 5.52 (d, \(J = 8.7\) Hz, 1H), 5.40-5.37 (m, 1H), 4.70 (s, 1H), 3.61-3.52 (m, 1H), 3.29-3.23 (m, 1H), 2.09 (d, \(J = 1.0\) Hz, 3H), 1.99 (d, \(J = 1.0\) Hz, 3H), 1.94-1.84 (m, 1H), 1.86 (d, \(J = 1.0\) Hz, 3H), 1.83 (d, \(J = 1.0\) Hz, 3H), 1.19-1.09 (m, 1H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)): 187.0, 183.6, 169.4, 158.2, 140.0, 135.6, 135.3, 130.6, 129.5, 119.5, 118.1, 107.4, 64.2, 53.7, 46.7, 30.2, 28.9, 26.1, 21.7, 19.3; HRMS (ESI) calculated for C\(_{22}\)H\(_{26}\)ClN\(_2\)O\(_3\) [M+H]\(^+\): 401.1627; found: 401.1650.

6-(1-Hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)-5-(naphthalen-1-yl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5i). 73% yield. \(^1^H\) NMR (400 MHz, CDCl\(_3\)): \(\delta\) (ppm) 8.41 (d, \(J = 8.6\) Hz, 1H), 7.97 (d, \(J = 8.2\) Hz, 1H), 7.91 (d, \(J = 8.2\) Hz, 1H), 7.72-7.68 (m, 1H), 7.59 (t, \(J = 7.5\) Hz, 1H), 7.54-7.44 (m, 1H), 7.28-7.26 (m, 1H), 5.90 (s, 1H), 5.66 (s, 1H), 5.61 (d, \(J = 8.7\) Hz, 1H), 5.46-5.43 (m, 1H), 3.43-3.34 (m, 1H), 3.17-3.11 (m, 1H), 2.03 (d, \(J = 1.0\) Hz, 3H), 2.01 (d, \(J = 1.0\) Hz, 3H), 1.85 (d, \(J = 1.0\) Hz, 3H), 1.68-1.61 (m, 1H), 1.54 (s, 3H); \(^1^C\) NMR (100 MHz, CDCl\(_3\)): 188.3, 182.0, 169.8, 157.5, 139.8, 134.1, 132.5, 132.4, 129.9, 129.6, 127.9, 127.4, 126.1, 126.0, 121.5, 119.6, 118.7, 108.4, 57.4, 53.3, 47.0, 30.4, 28.5, 26.1, 21.4, 19.3; HRMS (ESI) calculated for C\(_{26}\)H\(_{29}\)N\(_2\)O\(_3\) [M+H]\(^+\): 417.2173; found: 417.2138.
5-(Furan-2-yl)-6-(1-hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5j). 64% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 7.52-7.51 (m, 1H), 6.42-6.41 (m, 1H), 6.22 (d, $J$ = 3.3 Hz, 1H), 5.72 (s, 1H), 5.44 (d, $J$ = 8.7 Hz, 1H), 5.41-5.34 (m, 1H), 4.85 (s, 1H), 3.60-3.46 (comp, 2H), 2.13 (d, $J$ = 1.0 Hz, 3H), 2.04-1.98 (m, 1H), 1.96 (d, $J$ = 1.0 Hz, 3H), 1.87 (d, $J$ = 1.0 Hz, 3H), 1.81 (d, $J$ = 1.0 Hz, 3H), 1.35-1.25 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$): 187.3, 183.6, 169.8, 158.2, 151.5, 143.6, 139.7, 119.4, 117.8, 112.0, 111.8, 105.9, 57.8, 53.1, 47.5, 29.6, 28.9, 26.1, 21.7, 19.2; HRMS (ESI) calculated for C$_{20}$H$_{25}$N$_2$O$_4$ [M+H]$^+$: 357.1809; found: 357.1802.

5-Cyclohexyl-6-(1-hydroxy-3-methylbut-2-en-1-ylidene)-8-(2-methylprop-1-en-1-yl)tetrahydro-1H-pyrazolo[1,2-a]pyridazine-1,7(8H)-dione (5k). 61% yield. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) 6.24-6.23 (m, 1H), 4.99-4.97 (m, 1H), 4.94 (d, $J$ = 8.2 Hz, 1H), 3.87 (dd, $J$ =6.0, 3.5 Hz, 1H), 3.67 (dd, $J$ =6.0, 1.5 Hz, 1H), 3.56 (m, 1H), 2.96-2.53 (comp, 3H), 2.16 (d, $J$ = 1.0 Hz, 3H), 1.93 (d, $J$ = 1.0 Hz, 3H), 1.80-1.64 (comp, 10H), 1.49-0.71 (comp, 7H); $^{13}$C NMR (100 MHz, CDCl$_3$): 197.8, 189.6, 171.8, 159.5, 140.6, 121.8, 118.1, 67.6, 66.2, 64.8, 49.5, 39.4, 31.7, 29.5, 28.1, 26.65, 26.61, 26.2, 25.7, 21.6, 19.1; HRMS (ESI) calculated for C$_{22}$H$_{33}$N$_2$O$_3$ [M+H]$^+$: 373.2486; found: 373.2488.
General Procedure for UV-Vis Titration of 1a with Rh$_2$(5R-MEPY)$_4$:

**Catalyst Preprocess:** Rh$_2$(5R-MEPY)$_4$(CH$_3$CN)$_2$ was synthesized according to reported method.$^{1d}$ The removal of axial acetonitriles on dirhodium compounds was performed by heating the dirhodium compounds at 130 °C under high vacuum (0.05-0.10 Torr) for 4 h. The complete removal of axial ligands was verified by $^1$H NMR analysis with evidence for the absence of the methyl absorption of acetonitrile. The dirhodium compound that was free of axial ligand (sensitive to oxygen) was stored and weighted in a glovebox under argon.

**General Method:** Rh$_2$(5R-MEPY)$_4$ (15.0 mg, 0.0193 mmol) with no axial acetonitrile was weighed into a 10.00 mL volumetric flask inside a glovebox under argon. Dichloromethane (DCM) was added into the volumetric flask to the 10.00 mL mark to prepare the stock solution (1.93 X 10$^{-3}$ M) of Rh$_2$(5R-MEPY)$_4$ in the glovebox. A DCM solution of 1a (2.00 X 10$^{-1}$ M) was prepared in a similar way. A 3.00 mL portion of the Rh$_2$(5R-MEPY)$_4$ solution was transferred to the cell using a 3.00 mL pipet. The cell was sealed inside the glovebox with the screw top containing a septum. Prior to addition of ligand solution the UV-Vis (400 nm-800 nm) spectrum of Rh$_2$(5R-MEPY)$_4$ was recorded. A 5.0 μL of ligand solution was added to the cell using a 10.0 μL syringe. The cell was inverted twice to ensure thorough mixing before the UV-Vis spectrum was recorded at 20 °C. Fifteen additional aliquots (5.0 μL each) were sequentially added to the cell over 30 min, and the total change in volume was less than 3%. The UV-vis spectrum was recorded after the addition of each aliquot. Association constants were calculated by the method previously developed.$^4$

**Titration curve of Rh$_2$(5R-MEPY)$_4$ with 1a:** $K_{eq1}$ was calculated at 550 nm, 560 nm and 570 nm three different wavelengths and the average $K_{eq1}$ was determined to 57±8.
Similar titration curve was obtained with Rh$_2$(esp)$_2$ catalyst by following the above procedures and the association constant ($K_{eq1}$) of Rh$_2$(esp)$_2$ with 1a was determined in the same way.$^4$

**Titration curve of Rh$_2$(esp)$_2$ with 1a:** $K_{eq1}$ was calculated at 600nm, 610 nm and 615 nm three different wavelengths and the average $K_{eq1}$ was determined to 489±9 M$^{-1}$.
References:


A colorless prism-like specimen of $\text{C}_{11}\text{H}_{12.50}\text{Cl}_{0.50}\text{NO}_{1.50}$ of approximate dimensions $0.16 \text{ mm} \times 0.22 \text{ mm} \times 0.38 \text{ mm}$ was used for the X-ray crystallographic analysis. The X-ray intensity data were measured. Data collection temperature was 150 °K.

The total exposure time was 20.20 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 31473 reflections to a maximum $\theta$ angle of 30.00° (0.71 Å resolution), of which 6039 were independent (average redundancy 5.212, completeness = 100.0%, $R_{int} = 2.10\%$, $R_{sig} = 1.51\%$) and 5174 (85.68%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 23.604(3) \text{ Å}$, $b = 16.7235(18) \text{ Å}$, $c = 10.4891(11) \text{ Å}$, $\beta = 93.9007(17)^\circ$, $V = 4130.9(8) \text{ Å}^3$, are based upon the refinement of the XYZ-centroids of 9901 reflections above $20 \sigma(I)$ with $4.812^\circ < 2\theta < 60.09^\circ$. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.9245 and 0.9672.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group C 1 2/c 1, with $Z = 16$ for the formula unit, $\text{C}_{11}\text{H}_{12.50}\text{Cl}_{0.50}\text{NO}_{1.50}$. The final anisotropic full-matrix least-squares refinement on $F^2$ with 358 variables converged at $R_1 = 3.70\%$, for the observed data and $wR_2 = 7.37\%$ for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.352 e/Å$^3$ and the largest hole was -0.361 e/Å$^3$ with an RMS deviation of 0.040 e/Å$^3$. On the basis of the final model, the calculated density was 1.289 g/cm$^3$ and $F(000)$, 1696 e$^-$.