Supporting Information

A Dual-Site Catalyst for Mild, Selective Nitrile Reduction

Zhiyao Lu and Travis J. Williams*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, Los Angeles, California, 90089-1661 travisw@usc.edu

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I. General Procedures

All air and water sensitive procedures were carried out either in a Vacuum Atmosphere glove box under nitrogen (0.1-10 ppm O₂ for all manipulations) or using standard Schlenk techniques under nitrogen. Deuterated NMR solvents were purchased from Cambridge Isotopes Laboratories. Acetonitrile- d_3 and acetonitrile were dried over calcium hydride, methanol- d_4 and methanol was dried over sodium. These solvents were distilled prior to use. Methylene chloride and hexanes were obtained from a J. C. Meyer Solvent Dispensing System (SDS) and used without further purification. Deionized water was purchaced from Arrowhead. Dichloro(p-cymene)ruthenium(II) dimer and thallium triflate were purchased from Strem Chemicals. 2-Methyl-6-nitrobenzonitrile, 4bromophenylacetonitrile, 4-(dimethylamino)benzonitrile, and 4-cyanopyridine were purchased from Sigma Aldrich. Cinnamyl nitrile was purchased from Eastman Chemical Company. 4-(Trifluoromethyl)benzonitrile was purchased from Matrix Scientific. 3,4-Dimethoxybenzonitrile and 4-acetyl-benzonitrile were purchased from Alfa Aeser. Potassium bis(pyrazolyl)borate was synthesized and purified by the method used by Hill.¹ ¹H, ¹¹B, ¹³C, ¹⁹F NMR spectra were obtained on Varian 400MR, VNMRS 500, or VNMRS 600 spectrometers with chemical shifts reported in units of ppm. All ¹H chemical shifts are referenced to the residual ¹H solvent (relative to TMS). All ¹¹B chemical shifts are referenced to a BF₃·OEt₂ in diglyme co-axial external standard (0 ppm). All ¹⁹F chemical shifts are referenced to the trichlorofluoromethane standard (0 ppm). All air and water sensitive NMR spectra were acquired using 8" J-Young tubes (Wilmad) with Teflon valve plugs. The J-Young NMR tubes were shaken vigorously for several minutes with chlorotrimethylsilane then dried in vacuo on a Schlenk line prior to use. ESI-HRMS data were acquired on an Agilent LC-TOF (2006). The GC-MS data were acquired on a Thermo Scientific Focus DSQ II GC-MS system.

Safety Notes.

Extreme caution should be used when treating any borohydride reagent with a ruthenium catalyst, because this can result in the release of hydrogen gas and lead to sudden pressurization of a reaction vessel.

Chemical practitioners should be aware that thallium is a toxic metal for which a dose of 15 mg/m³ is "immediately dangerous to life or health". This can be compared with the IDLH doses of lead (100 mg/m³) or organotin compounds (25 mg/m³). See http://www.cdc.gov/niosh/idlh. Always read reagent MSDSs.

II. Synthesis and Structural Data

A. Catalyst Synthesis



 $[\kappa^2-(1-pz)_2BH_2]Ru(cymene)Cl$ 4: A solution of potassium bis(pyrazolyl)borate (1.64 mmol, 305 mg) in 30 mL acetonitrile was added dropwise to a stirred solution of $[Ru(cym)Cl_2]_2$ (0.82 mmol, 500 mg) in 30 mL acetonitrile. During the addition, a color change from dark red to light red was observed. The reaction was stirred at room temperature (~10 °C) for 15 minutes. The solvent was then removed and the residue was dried under vacuum for overnight. This residue was dissolved in a minimal amount of

benzene, and insoluble materials were filtered off. The benzene solution was then saturated with hexane and concentrated under reduced pressure. A red precipitate was collected and identified as **4** in 40% yield (273 mg).

¹H NMR (600 MHz in methylene chloride- d_2 at 25 °C): 7.69 (d, pyrazolyl 2H, J = 2.2 Hz), 7.55 (d, pyrazolyl 2H, J = 2.3 Hz), 6.24 (t, pyrazolyl 2H, J = 2.3 Hz), 5.56 (d, cym aromatic 2H, J = 6.3 Hz), 5.38 (d, cym aromatic 2H, J = 6.3 Hz), 3.8~3.2 (d, BH₂, $J_{BH} = 120$ Hz), 2.90 (septet, cym methine 1H, J = 6.9 Hz), 1.94 (s, cym methyl, 3H), 1.26 (d, sym isopropyl methyls 6H, J = 6.9 Hz).

¹³C NMR (150 MHz in methylene chloride- d_2 at 25 · C): δ = 144.19 (pyrazolyl), 136.73 (pyrazolyl), 105.73 (pyrazolyl), 105.21 (ipso cymene), 99.15 (ipso cymene), 84.95 (cymene aromatic), 83.79 (cymene aromatic), 30.65 (cym methine), 22.1(cym isopropyl methyls), 18.03 (cym methyl).

¹¹B NMR (192 MHz in methylene chloride- d_2 at 50 • C): δ = -7.88 (d, $J_{B,H}$ = 100 Hz)

ESI-HRMS for $C_{16}H_{23}N_4RuCl$: calculated [MH]⁺ 419.0742, found 419.0736.



 $\{[\kappa^3-(1-pz)_2HB(N=CHCH_3)]Ru(cymene)\}^+$ TfO⁻ **3**: A solution of potassium bis(pyrazolyl)borate (1.30 mmol, 244 mg) in 30 mL acetonitrile was added dropwise to a stirred solution of $[Ru(cym)Cl_2]_2$ (0.65 mmol, 400 mg) in 30 mL acetonitrile. During the addition, a color change from dark red to light red was observed. The reaction was stirred at room temperature for 15 minutes. An aliquot of thallium triflate (2.7 mmol, 970 mg) was added to the solution. A white precipitate was observed immediately.

The resulting mixture was stirred for another 15 minutes before it was filtered though celite. The filtrate was decanted, extracted with methylene chloride, concentrated, and dried under vacuum overnight. The residue can be washed with a ^{*i*}PrOH to hexane 4:1 solvent to afford a bright yellow powder which was later identified as **3** (320 mg, 43%). The crude product can also be recrystallized from an ^{*i*}PrOH/hexane solvent system to form crystals for X-ray diffraction analysis.

Alternatively, **3** can be made using the less toxic AgOTf in place of TlOTf. The synthetic procedure is very similar: a solution of potassium bis(pyrazolyl)borate (0.65 mmol, 122 mg) in 10 mL acetonitrile was added dropwise to a stirred solution of $[Ru(cym)Cl_2]_2$ (0.32 mmol, 200 mg) in 10 mL acetonitrile. During the addition, a color change from dark red to light red was observed. The reaction was stirred at room temperature for 15 minutes. An aliquot of silver triflate (1.3 mmol, 353 mg) was added to the solution. A brownish white precipitate was observed immediately. The resulting mixture was stirred for another 15 minutes before it was filtered though celite. The filtrate was decanted, extracted with methylene chloride, concentrated, and dried under vacuum overnight. The residue can be washed with an ^{*i*}PrOH to hexane 4:1 solvent to afford **3** (108 mg, 29%).

¹H NMR (600 MHz in acetonitrile- d_3 at 25 ° C): $\delta = 8.28$ (q, N=CHCH₃ 1H, J = 5.3 Hz), 8.10 (d, pyrazolyl 2H, J = 2.2 Hz), 7.66 (d, pyrazolyl 2H, J = 2.3 Hz), 6.31 (t, pyrazolyl 2H, J = 2.3 Hz), 6.15 (d, cym aromatic 2H, J = 6.4 Hz), 6.02 (d, cym aromatic 2H, J = 6.4 Hz), 3.72 (q, BH, $J_{BH} = 120$ Hz) 2.83 (septet, cym methine 1H, J = 6.9 Hz), 2.34 (d, N=CHCH₃, 3H, J = 5.3 Hz) 2.22 (s, cym methyl, 3H), 1.09 (d, sym isopropyl methyls 6H, J = 6.9 Hz).

¹³C NMR (150 MHz in acetonitrile- d_3 at 25 °C): $\delta = 177.5$ (N=CHCH₃), 142.89 (pyrazolyl), 132.6 (pyrazolyl), 107.6 (pyrazolyl), 105.7 (ipso cymene), 100.0 (ipso cymene), 83.99 (cymene aromatic), 83.6 (cymene aromatic), 30.6 (cym methine), 24.1 (N=CHCH₃), 21.5(cym isopropyl methyls), 17.8 (cym methyl).

¹¹B NMR (192 MHz in acetonitrile- d_3 at 50 • C): $\delta = 1.53$ (d, $J_{B,H} = 120$ Hz)

¹⁹F NMR (562 MHz in acetonitrile- d_3 at 25 • C): δ = -78.96 (s, triflate)

ESI-HRMS for $C_{18}H_{25}N_5Ru$: calculated [M]⁺ 424.1241, found 424.1256.



 $\{[\kappa^3-(1-pz)_3BH]Ru(cymene)\}^+$ PF₆⁻ **6**: Potassium tris(pyrazolyl)borate (0.36 mmol, 92 mg) was added to a stirred methylene chloride solution of $[Ru(cym)Cl_2]_2$ (0.18 mmol, 112 mg). The reaction mixture was stirred at room temperature for an hour with a color change from dark red to orange and eventually to yellow. Then thallium triflate (0.76 mmol, 267 mg) was added and the reaction was stirred overnight. This mixture was filtered through celite,

dried under vacuum overnight, then triturated with Et_2O . The expected product 6 was collected with a 55% overall yield (120 mg).

6 was identified by NMR, and data are consistent with a previously-reported sample.²

B. Ammonia-Borane Dehydrogenation and Water Oxidation

Catalyst 3 has comparable reactivity to 2 in ammonia borane dehydrogenation and water oxidation (Table S1). While 3 is modestly faster initially, 2 generates a somewhat higher extent of dehydrogenation. Further, both 2 and 3 have reactivity in water oxidation. For example, in the presence of aqueous cerium(IV), O₂ could be produced at 70 °C at a rate of 7.2×10^{-4} s⁻¹ (entry 3). The juxtaposition of successful reactions in both oxidative and reductive conditions highlight the unique ability of 3's novel borate scaffold to support both electron rich and poor catalytic transition states.

Figure S1. Time Course Graphs for Ammonia Borane Dehydrogenation and Water Oxidation with Catalyst Precursors 2 and 3.^a



(left) H₂ production from AB with 5.0 mol % [Ru] (2 or 3) under air at 70 °C under optimized conditions in tetraglyme (3) or diglyme (2) solution. (middle) AB consumption by ¹¹B NMR at 70 °C in 2:1 diglyme/benzene solution. Data are fit to exponential decay (first order reaction kinetics with respect to AB). (right) O₂ production from water with 6 μ mol [Ru] (2 or 3) at 70 °C in presence of Ce(IV).

Ammonia Borane Dehydrogenation: In a typical ¹¹B NMR reaction, 7.7 mg AB was combined with ruthenium catalyst (**2** or **3**, 5 mol %) in a J. Young NMR tube while in a glovebox under nitrogen. Diglyme (0.4 mL) and benzene- d_6 (0.2 mL) were added to the tube. Because **3** is not soluble in the diglyme solution, **3** (7.1 mg, 5 mol % to 7.7 mg of AB) and 1.0 equiv. of AB (0.4 mg) was heated at 70 °C for 10-15 minutes until there is no undissolved solid in the tube. Then of AB (7.7 mg) was added to the tube in a glovebox under nitrogen. The sample tube was immediately inserted into a preheated NMR (70 °C) and the kinetic monitoring commenced after quick locking and shimming. Disappearance of AB in the solution was monitored by the relative integration of its characteristic peak in the ¹¹B spectrum (-22 ppm) and the BF₃-OEt₂ standard. All spectra were processed using VNMRJ (v. 2.3). The acquisition involved a 1.67 sec pulse sequence in which 4,096 complex points were recorded, followed by 1 sec relaxation delay. To eliminate B-O peaks from the borosilicate NMR tube and probe, the ¹¹B FIDs were processed with back linear prediction, ca. 5-15 points.

In a typical eudiometry reaction, 7.7 mg AB (0.25 mmol) was combined with catalyst (1, 7.2 mg, 5.0 mol %) in a 2 mL Schlenk tube equipped with a Teflon stir bar while in a glovebox under nitrogen. tetraglyme (0.60 mL) was added to the tube. The side arm of the valve was connected to a piece of Tygon tubing, which was adapted to 20 gauge (0.03") Teflon tubing with a needle. For reactions run under N_2 , a three-way valve was

inserted between the 20 gauge Teflon tubing and the Tygon tubing so that the tubing could be thoroughly purged with N_2 gas after assembling the entire apparatus. In either case, the 20 gauge tubing was threaded through a porous septum that was sized to fit over the open end of a buret that was flame sealed on the other end. The role of the septum is to help keep the tubing inside the buret during the reaction. The buret was filled with water and the septum was attached. The entire apparatus was then inverted into a one-liter cylinder filled with water and clamped onto a metal ring stand. The reactor's valve was opened to release gas from the reactor headspace while heating in a regulated oil bath at 70 °C. The volume of liberated gas was recorded periodically until gas evolution ceased. Liberated hydrogen was quantified by recording its volume displacement in the eudiometer and correcting its volume for water content.

Water Oxidation: In a typical reaction, 6 μ mol ruthenium complex (1 or 3) was suspended in 2 mL deionized water in a 15 mL Schlenk flask connected with a eudiometer. To the solution, 1.1 g ceric ammonium nitrate (2 mmol) was added. The reaction was then heated in a 70 °C oil bath. The reaction was monitored by observing O₂ formation by eudiometry.

No gas evolution was observed in an analogous reaction that was free of ruthenium.

C. Optimization Nitrile Reduction Conditions

General procedures for screening reaction conditions for nitrile reductions: 4trifluoromethyl benzonitrile (0.05 mmol), NaBH₄ (0.1 mmol), NaO^tBu (0.05 mmol), and ruthenium catalyst (5 mol % if used) were dissolved in methanol- d_4 (0.6 mL) in a J.-Young NMR tube in a dry box. Four parallel runs were set up using (1) no ruthenium catalyst (2) **2**, (3) **3**, and (4) **6**, respectively. The tubes were then heated in an oil bath at 70 °C, and ¹H NMR spectra were taken at several time points. The nitrile conversion as a function of time is plotted in Table S2. The reaction involving catalyst **3** reached completion much faster than the others and reached an NMR yield of > 90% upon hydrolysis, whereas other reactions did reach completion after 85 h and had lower NMR yields when they were eventually analyzed following hydrolysis after 245 h. See Table 1 (main text). The integration standard for NMR conversions was residual solvent, *CHD*₂OD, in a sealed J-Young NMR tube. NMR yields were similarly determined after the specified extended reaction time upon addition of water (200 µL) to the tube.

Table S2. Nitrile Reduction Condition Screening.



D. Nitrile Reduction

General procedure for nitrile reduction: Catalyst **3** (0.05 mmol, 28.6 mg) and sodium *tert*-butoxide (1 mmol, 96.1 mg) were dissolved in 15 mL methanol. The solution was heated in an oil bath at 70 °C for about 2 minutes until all the solids was dissolved. Then nitrile substrate (1 mmol), sodium borohydride (4 mmol, 150.4 mg) were added to the solution. The solution was again heated in a 70 °C oil bath and the reaction was monitored by TLC (typically eluting with CH_2Cl_2 :MeOH:Et₃N = 50:1:1). Once the reaction was finished, the methanol solvent was removed under reduced pressure. The residue was extracted with EtOAc (20 mL × 3) from H₂O (20 mL), dried over anhydrous sodium sulfate, and purified by column chromatography (typically eluting with CH_2Cl_2 100 mL, then CH_2Cl_2 :MeOH = 50:1 250 mL, then CH_2Cl_2 :MeOH:Et₃N = 50:1:1 250 mL).



(4-(Trifluoromethyl)phenyl)methanamine **8a**: **7a** was subjucted to the conditions described above. This reaction afforded the product as a white solid (143 mg, 82%).

¹H NMR (400 MHz in acetonitrile- d_3 at 25 ° C): δ = 7.67 (d, 2H, J = 8.0 Hz), 7.57 (d, 2H, J = 8.0 Hz), 4.00 (s, 2H), 2.65 (br, NH₂ 2H).

¹³C NMR (100 MHz in acetonitrile- d_3 at 25 ° C): δ = 143.9, 135.0, 129.7, 124.4, 124.3, 72.2, 45.5.

IR (neat cm⁻¹): 3344, 3096, 1434, 1325, 1166.

GC-MS for C₈H₈F₃N: calculated [M] 175.06, found 175.14.

MeO NH₂ (3,4-Dimethoxyphenyl)methanamine **8b**: **7b** was subjucted to the conditions described above, except more sodium borohydride was used (8 mmol, 300.7 mg). This reaction afforded the product as a white solid (145 mg, 87%).

¹H NMR (600 MHz in methanol- d_4 at 25 • C): δ = 7.01 (d, 1H, J = 2.0 Hz), 6.93 (s, 1H), 6.91 (d, 2H, J = 2.0 Hz), 3.86 (s, 3H), 3.83 (s, 3H). 3.81 (s, 2H).

¹³C NMR (150 MHz in methanol- d_4 at 25 ° C): $\delta = 150.7$, 150.1, 134.1, 121.5, 113.2, 113.0, 56.6, 56.5, 45.9.

IR (neat cm⁻¹): 3370, 3303, 2998, 2835, 1639, 1515, 1264, 1027.

GC-MS for C₉H₁₃NO₂: calculated [M] 167.19, found 167.09.



(2-Methyl-6-nitrophenyl)methanamine **8c**: **7c** was subjucted to the conditions described above. This reaction afforded the product as a white solid (145 mg, 87%).

¹H NMR (600 MHz in acetonitrile- d_3 at 25 • C): δ = 7.00 (t, 1H, J = 7.8 Hz), 6.55 (d, 1H, J = 8.2 Hz), 6.52 (d, 1H, J = 7.8 Hz), 6.34 (br, NH₂, 2H), 4.42 (s, 2H), 2.29 (s, 3H).

¹³C NMR (150 MHz in acetonitrile- d_3 at 25 °C): δ = 171.99, 146.28, 136.07, 130.61, 123.47,120.09, 114.20, 20.38.

IR (neat cm⁻¹): 3471, 3435, 3326, 1641, 1579, 1466, 1391, 1299.

GC-MS for C₈H₁₀N₂O₂: calculated [M] 166.12, found 166.07.



2-(4-Bromophenyl)ethanamine **8d**: **7d** was subjucted to the conditions described above, except more sodium borohydride was used (8 mmol, 300.7 mg in total). This reaction afforded the product as a white solid (170 mg, 85%).

¹H NMR (600 MHz in acetonitrile- d_3 at 25 • C): δ = 7.46 (d, 2H, J = 8.1 Hz), 7.24 (d, 2H, J = 8.1 Hz), 3.14 (t, 2H, J = 8.4 Hz), 3.01 (t, 2H, J = 8.4 Hz), 2.49 (br, NH₂ 2H).

¹³C NMR (150 MHz in acetonitrile- d_3 at 25 · C): δ = 138.8, 132.6, 132.1, 120.9, 41.4, 33.4.

IR (neat cm⁻¹): 3391, 2994, 2900, 1619, 1467, 1378, 1178, 816, 563.

GC-MS for C₈H₁₀BrN: calculated [M] 199.00, found 199.01.



1-(4-(Aminomethyl)phenyl)ethanol **8e**: **7e** was subjucted to the conditions described above. This reaction afforded the product as a white solid (121 mg, 80%).

¹H NMR (600 MHz in methanol- d_4 at 25 • C): δ = 7.47 (d, 2H, J = 8.3 Hz), 7.43 (d, 2H, J = 8.3 Hz), 4.11 (s, 2H), 3.49 (q, 1H, J = 7.0 Hz), 1.44 (d, 2H, J = 6.4 Hz).

¹³C NMR (150 MHz in methanol- d_4 at 25 • C): δ = 149.2, 133.4, 130.2, 127.5, 70.5, 44.3, 25.9.

IR (neat cm⁻¹): 3280, 3220, 2969, 1377, 1081, 1010.

GC-MS for C₉H₁₃NO: calculated [M] 151.10, found 151.17.



4-(aminomethyl)-N,N-dimethylaniline **8f**: **7f** was subjucted to the conditions described above. This reaction afforded the product as a white solid (126 mg, 84%).

¹H NMR (600 MHz in acetonitrile- d_3 at 25 ° C): δ = 7.18 (d, 2H, J = 8.8 Hz), 6.71 (d, 2H, J = 8.8 Hz), 3.65 (s, 2H), 3.31 (br, NH₂ 2H), 2.89 (s, 6H).

¹³C NMR (150 MHz in acetonitrile- d_3 at 25 ° C): δ = 151.2, 130.4, 128.1, 113.6, 52.8, 41.0.

IR (neat cm⁻¹): 3371, 2885, 2801, 1614, 1523, 1349, 1164, 808.

GC-MS for C₉H₁₄N₂: calculated [M] 151.12, found 151.19.



3-Phenylpropan-1-amine **8g**: **7g** was subjucted to the conditions described above. This reaction afforded the product as a white solid (81 mg, 60%).

¹H NMR (600 MHz in acetonitrile- d_3 at 25 • C): δ = 7.29 (t, 2H, *J* = 7.8 Hz), 7.22 (d, 2H, *J* = 7.8 Hz), 7.19 (t, 1H, *J* = 7.6 Hz), 4.16 (br, NH₂ 2H), 2.79 (t, 2H, *J* = 7.6 Hz), 2.66 (t, 2H, *J* = 7.6 Hz), 1.88 (tt, 2H, *J* = 7.6 Hz).

¹³C NMR (150 MHz in acetonitrile- d_3 at 25 ° C): δ = 142.7, 129.5, 129.4, 127.0, 41.03, 33.5, 32.3.

IR (neat cm⁻¹): 3102, 3024, 2927, 1576, 1379.

GC-MS for C₉H₁₃N: calculated [M] 135.10, found 135.15.



Pyridin-4-ylmethanamine **8h**: **7h** was subjucted to the conditions described above, except more sodium borohydride was used (8 mmol, 300.7 mg). This reaction afforded the product as a white solid (70 mg, 65%).

¹H NMR (500 MHz in methanol- d_4 at 25 ° C): δ = 8.61 (s, 2H), 7.52 (d, 2H, J = 4.4 Hz), 4.19 (s, 2H).

¹³C NMR (126 MHz in methanol- d_4 at 25 • C): δ = 151.0, 146.2, 125.0, 123.9, 43.5.

IR (neat cm⁻¹): 3351, 3151, 3030, 2929, 1680, 1602, 1414, 1325, 1030, 638.

GC-MS for C₆H₈N₂: calculated [M] 108.06, found 108.16.

Furan-2-carboxamide **9i**: **7i** was subjucted to the conditions described above. This reaction afforded the product as a white solid (58 mg, 53%). ¹H NMR (600 MHz in acetonitrile- d_3 at 25 ° C): δ = 7.60 (d, 1H, *J* = 1.8 Hz), 7.05 (d, 1H, *J* = 3.5 Hz), 6.56 (dd, 1H, *J* = 1.8, 3.5 Hz), 6.63 (br, NH₂ 1H), 6.02 (br, NH₂ 1H).

¹³C NMR (150 MHz in acetonitrile- d_3 at 25 • C): δ = 160.8, 149.2, 146.1, 115.2, 113.1.

IR (neat cm⁻¹): 3347, 3168, 1661, 1480, 1374, 1227, 1105.

GC-MS for C₅H₅NO₂: calculated [M] 108.06, found 108.16.

 N_{H_2} Thiophene-2-carboxamide **9j**: **7j** was subjucted to the conditions described above. This reaction afforded the product as a white solid (90 mg, 77%).

¹H NMR (600 MHz in acetonitrile- d_3 at 25 • C): $\delta = 7.62$ (dd, 1H, J = 1.2, 5.2 Hz), 7.59 (dd, 1H, J = 1.2, 3.6 Hz), 7.12 (dd, 1H, J = 3.6, 5.2 Hz), 6.72 (br, NH₂ 1H), 6.07 (br, NH₂ 1H).

¹³C NMR (150 MHz in acetonitrile- d_3 at 25 • C): δ = 164.4, 140.4, 132.0, 129.8, 129.0.

IR (neat cm⁻¹): 3363, 3174, 1651, 1607, 1432, 1395, 1243, 1123, 712.

GC-MS for C₅H₅NO₂: calculated [M] 127.01, found 127.05.















F. Graphical Kinetic Data for Reduction of 3

3 (5.7 mg, 10 μ mol), NaBH₄ (1.0 mg, 26 μ mol) and NaO^{*t*}Bu (1.0 mg, 10 μ mol) were dissolved in methanol- d_4 (0.6 mL) in a J.-Young NMR tube. The sample tube was immediately inserted into a NMR (25 °C) and the kinetic monitoring commenced after quick locking and shimming. All spectra were processed using VNMRJ (v. 2.3).

8.2	8.0	7.8	7.6	7.4	7.2	7.0	6.8	6.6	6.4	6.2	6.0	5.8	ppm
Mu			u	5 min		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~)M.	r.s.M.	MnMh	
			tu	15 min						l	M	M.M.	
			L	25 min							M		
			1	35 min									
ll			Lange and the second	45 min								M	

G. Crystal Structure of 3

A clear light yellow prism-like specimen compound **3** were grown by slow evaporation of a saturated DCM/hexane solution at ambient temperature. Diffraction data for $C_{19}H_{25}BF_3N_5O_3RuS$ were collected at 100.1(2) K on a Bruker APEX II CCD system equipped with a TRIUMPH curved-crystal monochromator and a MoK α fine-focus tube ($\lambda = 0.71073$ Å).

A total of 2520 frames were collected. The total exposure time was 7.00 hours. The frames were integrated with the Bruker SAINT software package using a SAINT V8.18C algorithm. The integration of the data using a monoclinic unit cell yielded a total of 112504 reflections to a maximum θ angle of 30.02° (0.71 Å resolution), of which 13663 were independent (average redundancy 8.234, completeness = 99.9%, Rint = 5.29%, Rsig = 3.24%) and 10943 (80.09%) were greater than $2\sigma(F^2)$. The final cell constants of a = 13.1714(7) Å, b = 13.8135(7) Å, c = 25.8235(13) Å, β = 95.3220(10)°, volume = 4678.2(4) Å³, are based upon the refinement of the XYZ-centroids of 9664 reflections above 20 $\sigma(I)$ with 4.667° < 2 θ < 60.82°. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.857. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8149 and 0.8869.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P 1 21/c 1, with Z = 8 for the formula unit, $C_{19}H_{25}BF_3N_5O_3RuS$. The final anisotropic full-matrix least-squares refinement on F^2 with 621 variables converged at R1 = 3.77%, for the observed data and wR2 = 8.83% for all data. The goodness-of-fit was 1.025. The largest peak in the final difference electron density synthesis was 1.763 e⁻/Å³ and the largest hole was -1.356 e⁻/Å³ with an RMS deviation of 0.100 e⁻/Å³. On the basis of the final model, the calculated density was 1.625 g/cm³ and F(000), 2320 e⁻.

Chemical formula	$C_{19}H_{25}BF_3N_5O_3RuS$	
Formula weight	572.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.150 x 0.170 x 0.260 n	nm
Crystal habit	clear light yellow prism	L
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.1714(7) Å	$\alpha = 90^{\circ}$
	b = 13.8135(7) Å	$\beta = 95.3220(10)^{\circ}$
	c = 25.8235(13) Å	$\gamma = 90^{\circ}$
Volume	4678.2(4) Å ³	
Ζ	8	
Density (calculated)	1.625 g/cm^3	
Absorption coefficient	0.814 mm^{-1}	
F(000)	2320	

Table S3	. Samp	le and	Crystal	Data.
1 11010 55	. Sump	ie una	Ciybui	Dutu.

Diffractometer	Bruker APEX II CCD
Radiation source	fine-focus tube, MoKα
Theta range for data collection	1.55 to 30.02°
Index ranges	-18<=h<=18, -19<=k<=19, -36<=l<=36
Reflections collected	112504
Independent reflections	13663 [R(int) = 0.0529]
Coverage of independent reflections	99.9%
Absorption correction	multi-scan
Max. and min. transmission	0.8869 and 0.8149
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL 2012-4 (Sheldrick, 2012)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	13663 / 64 / 621
Goodness-of-fit on F ²	1.025
Δ/σ_{max}	0.002
Final R indices	10943 data; R1 = 0.0377, wR2 = 0.0815 $I>2\sigma(I)$
	all data $R1 = 0.0540$, $wR2 = 0.0883$
Weighting scheme	w=1/[$\sigma^2(F_o^2)$ +(0.0317P) ² +10.5182P] where P=(F_o^2 +2 F_c^2)/3
Largest diff. peak and hole	1.763 and -1.356 eÅ ⁻³
R.M.S. deviation from mean	0.100 eÅ ⁻³

Table S4	Data	Collection	and St	ructure	Refinement
1 1010 57.	Data	Concention	and Di	<i>i</i> ucture	iterinement.

(11)					
	x/a	y/b	z/c	U(eq)	
B1	0.1854(3)	0.7367(2)	0.00982(13)	0.0240(6)	
B2	0.4316(3)	0.2803(2)	0.34351(12)	0.0223(6)	
C1	0.8963(2)	0.9093(2)	0.06870(11)	0.0204(5)	
C2	0.9235(2)	0.8637(2)	0.11792(11)	0.0209(5)	
C3	0.9094(2)	0.7636(2)	0.12476(10)	0.0204(5)	
C4	0.8697(2)	0.70375(19)	0.08197(10)	0.0185(5)	
C5	0.84253(19)	0.7491(2)	0.03382(11)	0.0194(5)	
C6	0.8560(2)	0.8509(2)	0.02732(11)	0.0206(5)	
C7	0.9106(3)	0.0158(2)	0.06094(13)	0.0287(6)	
C8	0.8579(2)	0.5954(2)	0.08845(12)	0.0222(5)	
C9	0.7490(3)	0.5722(3)	0.09945(19)	0.0478(10)	
C10	0.8896(3)	0.5380(2)	0.04245(13)	0.0302(6)	
C11	0.2332(2)	0.5796(2)	0.06902(13)	0.0293(7)	
C12	0.1919(3)	0.5433(2)	0.11199(13)	0.0325(7)	
C13	0.1125(2)	0.6055(2)	0.12096(11)	0.0263(6)	
C14	0.2922(2)	0.8931(2)	0.04330(12)	0.0243(6)	
C15	0.2695(2)	0.9701(2)	0.07421(11)	0.0236(6)	
C16	0.1701(2)	0.95279(19)	0.08700(10)	0.0201(5)	
C17	0.0417(2)	0.7363(2)	0.94172(11)	0.0246(6)	
C18	0.9380(3)	0.7444(2)	0.91471(12)	0.0317(7)	
C19	0.50458(19)	0.53189(19)	0.22649(10)	0.0169(5)	
C20	0.3992(2)	0.51524(19)	0.21696(10)	0.0176(5)	
C21	0.32909(19)	0.55565(19)	0.25003(10)	0.0171(5)	
C22	0.3631(2)	0.61082(18)	0.29371(10)	0.0169(5)	
C23	0.47106(19)	0.62610(18)	0.30435(10)	0.0171(5)	
C24	0.53974(19)	0.58829(18)	0.27133(10)	0.0171(5)	
C25	0.5768(2)	0.4893(2)	0.19101(11)	0.0214(5)	
C26	0.2910(2)	0.6543(2)	0.33002(11)	0.0205(5)	
C27	0.2931(5)	0.7649(3)	0.3250(3)	0.0298(12)	
C28	0.1811(4)	0.6169(5)	0.3205(3)	0.0353(14)	
C29	0.6288(2)	0.2355(2)	0.34209(11)	0.0270(6)	
C30	0.7099(2)	0.2868(2)	0.32654(12)	0.0273(6)	
C31	0.6690(2)	0.3746(2)	0.30746(11)	0.0219(5)	
C32	0.4050(2)	0.3430(2)	0.43944(11)	0.0240(6)	
C33	0.4120(2)	0.4339(2)	0.46110(11)	0.0246(6)	

Table S5. Atomic Coordinates and Equivalent Isotropic Atomic Displacement Parameters $(Å^2)$

	x/a	y/b	z/c	U(eq)
C34	0.4284(2)	0.4965(2)	0.42022(10)	0.0196(5)
C35	0.3037(2)	0.2854(2)	0.26895(11)	0.0220(5)
C36	0.2399(2)	0.3198(2)	0.22198(11)	0.0250(6)
C37	0.4962(9)	0.3716(8)	0.0541(4)	0.0566(13)
C38	0.0587(2)	0.9496(2)	0.26008(13)	0.0308(7)
C27A	0.2595(14)	0.7533(10)	0.3096(7)	0.0298(12)
C28A	0.2031(13)	0.5890(12)	0.3379(8)	0.0353(14)
C37A	0.4893(12)	0.3657(11)	0.0506(5)	0.0566(13)
F1	0.5896(4)	0.3588(4)	0.07657(19)	0.0647(7)
F2	0.5050(4)	0.3551(4)	0.0025(2)	0.0647(7)
F3	0.4727(4)	0.4660(5)	0.0646(2)	0.0647(7)
F4	0.95706(17)	0.94033(19)	0.25681(11)	0.0597(7)
F5	0.0938(2)	0.93638(17)	0.30946(8)	0.0548(6)
F6	0.09323(16)	0.87668(14)	0.23290(8)	0.0386(5)
F1A	0.5758(6)	0.3217(6)	0.0643(3)	0.0647(7)
F2A	0.4609(6)	0.3603(6)	0.9992(3)	0.0647(7)
F3A	0.5074(6)	0.4599(6)	0.0600(3)	0.0647(7)
N1	0.10521(17)	0.67535(16)	0.08485(9)	0.0194(4)
N2	0.18043(18)	0.65950(17)	0.05304(10)	0.0222(5)
N3	0.13513(16)	0.87054(16)	0.06447(8)	0.0166(4)
N4	0.21070(17)	0.83432(17)	0.03749(9)	0.0201(5)
N5	0.06943(19)	0.74925(16)	0.98953(9)	0.0209(5)
N6	0.56812(17)	0.37493(16)	0.31085(8)	0.0175(4)
N7	0.54358(19)	0.28891(16)	0.33232(9)	0.0205(5)
N8	0.43046(17)	0.44591(16)	0.37623(8)	0.0175(4)
N9	0.41644(18)	0.35104(17)	0.38851(9)	0.0210(5)
N10	0.37307(18)	0.33126(16)	0.29631(9)	0.0192(4)
01	0.2965(4)	0.3507(4)	0.06473(19)	0.0394(5)
O2	0.4188(7)	0.3135(6)	0.1365(3)	0.0394(5)
O3	0.3941(4)	0.2041(4)	0.06404(19)	0.0394(5)
O4	0.04689(19)	0.13406(17)	0.26801(9)	0.0365(6)
05	0.05233(16)	0.06396(16)	0.18200(8)	0.0273(4)
O6	0.20423(17)	0.06513(17)	0.24273(11)	0.0395(6)
01A	0.3167(5)	0.3390(5)	0.0462(3)	0.0394(5)
O2A	0.4077(10)	0.3283(8)	0.1340(4)	0.0394(5)
O3A	0.4343(5)	0.2037(5)	0.0713(3)	0.0394(5)

	x/a	y/b	z/c	U(eq)
Ru1	0.001899(15)	0.785475(14)	0.059137(7)	0.01383(5)
Ru2	0.445275(15)	0.469553(14)	0.296638(7)	0.01282(5)
S1	0.3925(9)	0.3048(7)	0.0810(4)	0.0256(4)
S2	0.09480(5)	0.06703(5)	0.23530(3)	0.02158(14)
S1A	0.3934(12)	0.2967(10)	0.0813(5)	0.0256(4)

 $U(\mbox{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

<i>Table S6.</i> Bond Lengths (Å)				
B1-N4	1.548(4)	O5-S2	1.437(2)	
B1-N5	1.578(4)	O1A-S1A	1.419(11)	
B2-N7	1.534(4)	O3A-S1A	1.425(11)	
B2-N10	1.549(4)	B1-N2	1.549(4)	
C1-C6	1.403(4)	B1-H1B	1.11(3)	
C1-C7	1.499(4)	B2-N9	1.545(4)	
C2-C3	1.408(4)	B2-H2B	1.15(3)	
C3-Ru1	2.198(3)	C1-C2	1.434(4)	
C4-C5	1.409(4)	C1-Ru1	2.233(3)	
C4-Ru1	2.201(3)	C2-Ru1	2.197(3)	
C5-Ru1	2.198(3)	C3-C4	1.439(4)	
C6-Ru1	2.211(3)	C4-C8	1.516(4)	
C8-C9	1.522(4)	C5-C6	1.429(4)	
C11-N2	1.349(4)	C8-C10	1.518(4)	
C14-C15	1.380(4)	C11-C12	1.375(5)	
C15-C16	1.400(4)	C12-C13	1.389(5)	
C16-N3	1.339(3)	C13-N1	1.339(3)	
C17-N5	1.267(4)	C14-N4	1.342(3)	
C19-C20	1.406(4)	C17-C18	1.480(4)	
C19-C25	1.501(4)	C19-C24	1.436(4)	
C20-C21	1.429(4)	C19-Ru2	2.213(3)	
C21-Ru2	2.205(2)	C20-Ru2	2.184(2)	
C22-C23	1.438(4)	C21-C22	1.400(4)	
C22-Ru2	2.229(3)	C22-C26	1.519(4)	
C23-Ru2	2.195(3)	C23-C24	1.400(4)	
C24-Ru2	2.195(2)	C26-C28A	1.497(12)	
C26-C27A	1.510(12)	C26-C27	1.534(5)	
C26-C28	1.535(5)	C29-C30	1.373(5)	
C29-N7	1.347(4)	C30-C31	1.398(4)	
C32-C33	1.374(4)	C31-N6	1.339(3)	
C33-C34	1.397(4)	C32-N9	1.342(3)	
C34-N8	1.336(3)	C35-C36	1.488(4)	
C35-N10	1.271(3)	C37-F2	1.365(10)	
C37-F1	1.323(10)	C37-S1	1.838(10)	
C37-F3	1.373(10)	C38-F6	1.331(4)	
C38-F5	1.328(4)	C38-S2	1.824(3)	

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C38-F4	1.340(4)	C37A-F3A	1.341(13)
C37A-F1A	1.311(12)	C37A-S1A	1.822(13)
C37A-F2A	1.346(12)	N1-Ru1	2.107(2)
N1-N2	1.362(3)	N3-Ru1	2.106(2)
N3-N4	1.362(3)	N6-N7	1.363(3)
N5-Ru1	2.138(2)	N8-N9	1.365(3)
N6-Ru2	2.086(2)	N10-Ru2	2.134(2)
N8-Ru2	2.108(2)	O2-S1	1.448(8)
O1-S1	1.443(9)	O4-S2	1.438(2)
O3-S1	1.459(9)	O6-S2	1.437(2)
		O2A-S1A	1.424(11)

N4-B1-N2	106.8(2)	N4-B1-N5	102.6(2)
N2-B1-N5	102.2(2)	N4-B1-H1B	112.1(17)
N2-B1-H1B	112.5(17)	N5-B1-H1B	119.5(17)
N7-B2-N9	106.6(2)	N7-B2-N10	103.5(2)
N9-B2-N10	102.4(2)	N7-B2-H2B	114.5(16)
N9-B2-H2B	111.3(16)	N10-B2-H2B	117.3(16)
C6-C1-C2	117.9(2)	C6-C1-C7	120.4(3)
C2-C1-C7	121.7(3)	C6-C1-Ru1	70.77(16)
C2-C1-Ru1	69.80(15)	C7-C1-Ru1	130.5(2)
C3-C2-C1	121.2(2)	C3-C2-Ru1	71.34(15)
C1-C2-Ru1	72.45(15)	C2-C3-Ru1	71.30(15)
C2-C3-C4	120.7(2)	C5-C4-C8	121.1(2)
C4-C3-Ru1	71.02(15)	C5-C4-Ru1	71.21(15)
C5-C4-C3	117.8(2)	C8-C4-Ru1	128.86(19)
C3-C4-C8	121.1(2)	C4-C5-Ru1	71.44(15)
C3-C4-Ru1	70.80(15)	C1-C6-Ru1	72.42(15)
C4-C5-C6	121.1(2)	C4-C8-C9	109.6(2)
C6-C5-Ru1	71.60(15)	C11-C12-C13	105.6(3)
C1-C6-C5	121.2(2)	N4-C14-C15	108.5(3)
C5-C6-Ru1	70.60(15)	N3-C16-C15	109.5(3)
C4-C8-C10	113.0(2)	C20-C19-C24	118.0(2)
C10-C8-C9	111.6(3)	C24-C19-C25	122.0(2)
N2-C11-C12	108.3(3)	C24-C19-Ru2	70.30(14)
N1-C13-C12	109.6(3)	C19-C20-C21	120.9(2)
C14-C15-C16	105.2(2)	C21-C20-Ru2	71.83(14)
N5-C17-C18	128.2(3)	C22-C21-C20	121.2(2)
C20-C19-C25	120.0(2)	C20-C21-Ru2	70.19(14)
C20-C19-Ru2	70.23(14)	C21-C22-C23	118.1(2)
C25-C19-Ru2	129.72(18)	C23-C22-C26	119.2(2)
C19-C20-Ru2	72.49(14)	C23-C22-Ru2	69.75(14)
C22-C21-Ru2	72.53(14)	C24-C23-C22	120.8(2)
C21-C22-C26	122.8(2)	C22-C23-Ru2	72.31(14)
C21-C22-Ru2	70.67(15)	C23-C24-C19	121.0(2)
C26-C22-Ru2	130.90(18)	C19-C24-Ru2	71.67(14)

Table S7. Bond angles (°).

C24-C23-Ru2	71.37(15)	C28A-C26-C27A	113.7(8)
C23-C24-Ru2	71.42(14)	C27A-C26-C22	108.1(7)
C28A-C26-C22	112.4(7)	C27A-C26-C27	22.3(6)
C28A-C26-C27	129.2(8)	C28A-C26-C28	24.4(7)
C22-C26-C27	109.0(3)	C22-C26-C28	113.7(3)
C27A-C26-C28	91.4(7)	C29-C30-C31	105.4(3)
C27-C26-C28	110.2(3)	N9-C32-C33	108.3(3)
N7-C29-C30	108.6(3)	N8-C34-C33	109.6(2)
N6-C31-C30	109.4(3)	F1-C37-F2	104.3(8)
C32-C33-C34	105.5(2)	F2-C37-F3	113.1(9)
N10-C35-C36	128.1(3)	F2-C37-S1	114.7(8)
F1-C37-F3	104.9(8)	F5-C38-F6	107.3(3)
F1-C37-S1	117.4(8)	F6-C38-F4	106.4(3)
F3-C37-S1	102.3(8)	F6-C38-S2	112.0(2)
F5-C38-F4	107.7(3)	F1A-C37A-F3A	105.4(11)
F5-C38-S2	112.3(2)	F3A-C37A-F2A	105.2(11)
F4-C38-S2	110.7(2)	F3A-C37A-S1A	123.1(12)
F1A-C37A-F2A	113.3(12)	C13-N1-N2	107.1(2)
F1A-C37A-S1A	105.0(11)	N2-N1-Ru1	114.24(16)
F2A-C37A-S1A	105.0(10)	C11-N2-B1	136.8(3)
C13-N1-Ru1	137.9(2)	C16-N3-N4	107.2(2)
C11-N2-N1	109.3(3)	N4-N3-Ru1	113.93(16)
N1-N2-B1	113.9(2)	C14-N4-B1	135.5(3)
C16-N3-Ru1	138.86(19)	C17-N5-B1	119.4(3)
C14-N4-N3	109.6(2)	B1-N5-Ru1	102.25(17)
N3-N4-B1	114.8(2)	C31-N6-Ru2	138.47(19)
C17-N5-Ru1	138.4(2)	C29-N7-N6	109.2(2)
C31-N6-N7	107.3(2)	N6-N7-B2	114.4(2)
N7-N6-Ru2	114.12(17)	C34-N8-Ru2	139.36(19)
C29-N7-B2	136.2(3)	C32-N9-N8	109.7(2)
C34-N8-N9	106.9(2)	N8-N9-B2	113.7(2)
N9-N8-Ru2	113.71(16)	C35-N10-Ru2	138.2(2)
C32-N9-B2	135.9(2)	N3-Ru1-N1	82.67(9)
C35-N10-B2	119.4(2)	N1-Ru1-N5	77.82(9)
B2-N10-Ru2	102.39(16)	N1-Ru1-C2	117.93(10)

N3-Ru1-N5	77.08(9)	N3-Ru1-C3	122.99(9)
N3-Ru1-C2	97.05(9)	N5-Ru1-C3	156.91(9)
N5-Ru1-C2	162.72(9)	N3-Ru1-C5	156.07(9)
N1-Ru1-C3	92.64(10)	N5-Ru1-C5	99.02(10)
C2-Ru1-C3	37.36(10)	C3-Ru1-C5	67.38(10)
N1-Ru1-C5	119.98(9)	N1-Ru1-C4	92.81(9)
C2-Ru1-C5	79.67(10)	C2-Ru1-C4	68.46(10)
N3-Ru1-C4	160.71(9)	C5-Ru1-C4	37.35(10)
N5-Ru1-C4	120.43(9)	N1-Ru1-C6	157.75(10)
C3-Ru1-C4	38.18(10)	C2-Ru1-C6	66.92(10)
N3-Ru1-C6	119.11(9)	C5-Ru1-C6	37.81(10)
N5-Ru1-C6	101.43(10)	N3-Ru1-C1	95.13(9)
C3-Ru1-C6	79.49(10)	N5-Ru1-C1	125.77(9)
C4-Ru1-C6	68.12(10)	C3-Ru1-C1	67.92(10)
N1-Ru1-C1	155.37(10)	C4-Ru1-C1	81.18(10)
C2-Ru1-C1	37.76(10)	N6-Ru2-N8	82.63(9)
C5-Ru1-C1	67.69(10)	N8-Ru2-N10	77.51(9)
C6-Ru1-C1	36.81(10)	N8-Ru2-C20	157.04(9)
N6-Ru2-N10	77.17(9)	N6-Ru2-C24	93.94(9)
N6-Ru2-C20	119.34(9)	N10-Ru2-C24	158.87(9)
N10-Ru2-C20	99.80(9)	N6-Ru2-C23	119.36(9)
N8-Ru2-C24	120.83(9)	N10-Ru2-C23	161.36(9)
C20-Ru2-C24	67.61(10)	C24-Ru2-C23	37.20(9)
N8-Ru2-C23	95.27(9)	N8-Ru2-C21	119.57(9)
C20-Ru2-C23	80.09(10)	C20-Ru2-C21	37.99(9)
N6-Ru2-C21	157.17(9)	C23-Ru2-C21	67.17(10)
N10-Ru2-C21	101.20(9)	N8-Ru2-C19	158.47(9)
C24-Ru2-C21	79.53(9)	C20-Ru2-C19	37.28(9)
N6-Ru2-C19	93.49(9)	C23-Ru2-C19	68.13(10)
N10-Ru2-C19	122.43(9)	N6-Ru2-C22	157.03(9)
C24-Ru2-C19	38.04(9)	N10-Ru2-C22	124.67(9)
C21-Ru2-C19	67.86(9)	C24-Ru2-C22	67.82(9)
N8-Ru2-C22	94.60(9)	C21-Ru2-C22	36.80(9)
C20-Ru2-C22	67.89(10)	O1-S1-O2	112.0(7)
C23-Ru2-C22	37.94(9)	O2-S1-O3	111.6(7)

C19-Ru2-C22 80.72(9) O2-S1-C37 102.4(9) O1 S1 O2 111 5(8) O5 S2 O6 115 00(15)
01 \$1 02 111 5(8) 05 \$2 06 115 00(15)
01-51-05 111.5(8) 05-52-00 115.09(15)
O1-S1-C37 109.3(7) O6-S2-O4 115.02(15)
O3-S1-C37 109.5(7) O6-S2-C38 103.17(15)
O5-S2-O4 115.36(13) O1A-S1A-O2A 120.4(9)
O5-S2-C38 102.64(14) O2A-S1A-O3A 115.5(9)
O4-S2-C38 102.94(15) O2A-S1A-C37A 102.7(12)
O1A-S1A-O3A 121.0(9)
O1A-S1A-C37A 89.3(10)
O3A-S1A-C37A 96.0(10)

III. References

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