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Electronic Supplementary Material

An innovative and efficient route to the synthesis of metal-based glycoconjugates: proof-of-concept and potential applications

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Materials and methods

Materials

(α,β)-D-glucosamine hydrochloride, *N*-acetyl-(α,β)-D-glucosamine, PPh_3, *N*-bromosuccinimide, ethyl isonipecotate, isonipecotamide, isonipecotic acid (TCI), Amberlite IR120 (H^+ form) resin (Merck), methyl-α-D-glucopyranoside, NH_4Cl, (Acros), NaN_3, Pd/C 10%$_w$, CS_2, $ZnCl_2$, $[Zn(OAc)_2]\cdot 2H_2O$, DMF, *N*,*N*-diisopropylethylamine, KI, NaCl, $(Et_4N)Cl\cdot xH_2O$, $(PPh_4)Cl$ (Sigma-Aldrich), $K[AuBr_4]\cdot 2H_2O$, $K_2[PtCl_4]$, $AgNO_3$ (Alfa Aesar), *N*,*N*,*N'*,*N'*-tetramethyl-*O*-(*N*-succinimidyl)uronium tetrafluoroborate (Carbosynth), $[AuCl(PPh_3)]$ (STREM Chemicals), and all deuterated solvents for NMR analysis (Deutero) were of reagent grade or comparable purity and were used as supplied. Anhydrous DMF was obtained by passing the solvent over a column of alumina and stored over 4 Å activated molecular sieves. All other reagents and solvents were used as purchased without any further purification.

Instrumentation

Melting points were recorded on a Stuart SMP10 digital melting point apparatus and are uncorrected.

Thin layer chromatography (TLC) was performed on silica gel Merck 60F$_{254}$ pre-coated aluminum sheets. Spots were visualized by direct UV irradiation at 254 nm or developed by exposure to either *p*-anisaldehyde or potassium permanganate staining solutions as appropriate.

Flash column chromatography was performed on Sigma Aldrich 60 Å silica gel (40-63 µm, 230-400 mesh) as stationary phase using the appropriate eluent.

Elemental analyses (carbon, hydrogen and nitrogen) were performed with a Perkin Elmer 2400 CHNS/O Series II analyzer.

FT-IR spectra of the carbohydrate precursors were recorded from thin films at room temperature on a Perkin Elmer Spectrum 100 FT-IR spectrophotometer equipped with a UATR accessory in the range 4000-650 cm^{-1} (32 scans, resolution 4 cm^{-1}). FT-IR spectra of the metal complexes were recorded from CsI disks at room temperature on a Perkin Elmer Frontier FT-IR/FIR spectrophotometer in the range 4000-600 cm^{-1} (32 scans, resolution 4 cm^{-1}) and in the range 600-200 cm^{-1} (32 scans, resolution 2 cm^{-1}). Data processing was carried out using OMNIC version 5.1 (Nicolet Instrument Corporation).

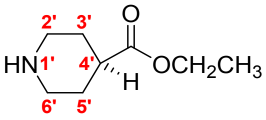
All NMR spectra were acquired in the appropriate deuterated solvent at room temperature on a Jeol 400 MHz spectrometer equipped with *z*-field gradients. ^{1}H and ^{13}C chemical shifts were referenced to TMS at 0.00 ppm *via* internal referencing to the residual peak of the deuterated solvent employed. ^{31}P chemical shifts were referenced to an external standard of 85% H_3PO_4 at 0 ppm. ^{1}H

and $^{13}C\{^{1}H\}$ signals were assigned with the aid of [^{1}H,^{1}H] COSY, ^{13}C DEPT, [^{1}H,^{13}C] HSQC and [^{1}H,^{13}C] HMBC experiments. Data processing was carried out using MestReNova version 12.0 (Mestrelab Research S.L.).

Single crystal X-ray diffraction data were collected using an Oxford Diffraction Xcalibur system at room temperature. The crystal structures were solved using ShelxT[1] and refined by full matrix least-squares using ShelxL,[2] both of which were driven by the Oscail package.[3]

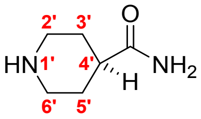
Spectroscopic characterization of the starting isonipecotic and metal reagents

Ethyl isonipecotate



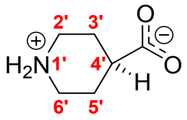
Commercially available. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 1724 (ν, C=O), 1180 (ν, C–OEt), 1044 (ν, O–Et) cm^{-1}. ^{1}H NMR (400 MHz; DMSO-D$_6$; 298 K): δ 4.04 (2 H, q, $OC\boldsymbol{H}_2$), 2.88 (2 H, dt, $C^{2',6'}\boldsymbol{H}_{eq}$), 2.44 (2 H, td, $C^{2',6'}\boldsymbol{H}_{ax}$), 2.36-2.28 (1 H, m, $C^{4'}\boldsymbol{H}$), 1.71-1.67 (2 H, m, $C^{3',5'}\boldsymbol{H}_{eq}$), 1.39 (2 H, qd, $C^{3',5'}\boldsymbol{H}_{ax}$), 1.16 (3 H, t, $C\boldsymbol{H}_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz; DMSO-D$_6$; 298 K): δ 174.6 ($\boldsymbol{C}$=O), 59.6 ($O\boldsymbol{C}H_2$), 45.3 ($\boldsymbol{C}^{2',6'}H_2$), 41.2 ($\boldsymbol{C}^{4'}H$), 29.0 ($\boldsymbol{C}^{3',5'}H_2$), 14.1 ($\boldsymbol{C}H_3$) ppm.

Isonipecotamide



Commercially available. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 3357/3199 ($\nu_{a,s}$, NH$_2$), 1664 (ν, C=O (amide I)), 1627 (δ_{ip}, CNH$_2$ (amide II)) cm^{-1}. ^{1}H NMR (400 MHz; DMSO-D$_6$; 298 K): δ 7.17 (1 H, s, $N\boldsymbol{H}_{cis}$), 6.67 (1 H, s, $N\boldsymbol{H}_{trans}$), 2.89 (2 H, dt, $C^{2',6'}\boldsymbol{H}_{eq}$), 2.39 (2 H, td, $C^{2',6'}\boldsymbol{H}_{ax}$), 2.10 (1 H, tt, $C^{4'}\boldsymbol{H}$), 1.56 (2 H, dd, $C^{3',5'}\boldsymbol{H}_{eq}$), 1.36 (2 H, qd, $C^{3',5'}\boldsymbol{H}_{ax}$) ppm. ^{13}C{^{1}H} NMR (100 MHz; DMSO-D$_6$; 298 K): δ 176.9 ($\boldsymbol{C}$=O), 45.8 ($\boldsymbol{C}^{2',6'}H_2$), 42.5 ($\boldsymbol{C}^{4'}H$), 29.6 ($\boldsymbol{C}^{3',5'}H_2$) ppm.

Isonipecotic acid



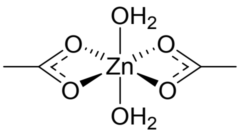
Commercially available. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 2732/2668 ($\nu_{a,s}$, NH$_2^+$), 1643/1602 ($\delta_{a,s}$, NH$_2^+$), 1555 (ν_a, COO$^-$), 1412 (ν_s, COO$^-$) cm^{-1}. ^{1}H NMR (400 MHz; D$_2$O; 298 K): δ 3.37 (2 H, dt, $C^{2',6'}\boldsymbol{H}_{eq}$), 2.98 (2 H, td, $C^{2',6'}\boldsymbol{H}_{ax}$), 2.40 (1 H, tt, $C^{4'}\boldsymbol{H}$), 2.03 (2 H, dd, $C^{3',5'}\boldsymbol{H}_{eq}$), 1.78-1.67 (2 H, m, $C^{3',5'}\boldsymbol{H}_{ax}$) ppm. ^{13}C{^{1}H} NMR (100 MHz; D$_2$O; 298 K): δ 182.2 ($\boldsymbol{C}OO^-$), 43.5 ($\boldsymbol{C}^{2',6'}H_2$), 41.4 ($\boldsymbol{C}^{4'}H$), 25.7 ($\boldsymbol{C}^{3',5'}H_2$) ppm.

Zn^{II}Cl$_2$

$\mathrm{Cl{-}Zn{-}Cl}$

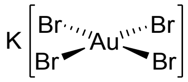
Commercially available. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 503 (ν_a, ClZnCl) cm^{-1}.

$[Zn^{II}(OAc)_2(H_2O)_2]$



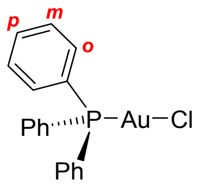
Commercially available. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 3082 (ν, OH), 1620 (δ, HOH), 1556 (ν_a, COO), 1445 (ν_s, COO), 396 (ν_a, H_2O–Zn–OH_2), 281 (ν_a, ZnO_4) cm^{-1}. ^{1}H NMR (400 MHz; D_2O; 298 K): δ 1.85 (6 H, s, $C\boldsymbol{H}_3$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz; D_2O; 298 K): δ 181.7 ($\boldsymbol{C}OO$), 22.5 ($\boldsymbol{C}H_3$) ppm.

$K[Au^{III}Br_4]\cdot 2H_2O$



Commercially available. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 248 (ν_a, $AuBr_4$) cm^{-1}.

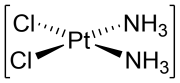
$[Au^{I}Cl(PPh_3)]$



Commercially available. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 1102 ($\nu_{q\ \mathrm{vib}}$, P–Ph_3), 713/693 ($\nu_{r\ \mathrm{vib}}$, P–Ph_3), 547/506/501 ($\delta_{y\ \mathrm{vib}}$, P–Ph_3), 450/439 ($\nu_{t\ \mathrm{vib}}$, P–Ph_3), 330/323 (ν, Au–$^{35/37}$Cl), 276/242 ($\delta_{x\ \mathrm{vib}}$, P–Ph_3 + ν, Au–P) cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$; 298 K): δ 7.56-7.45 (15 H, m, $C\boldsymbol{H}$ Ph) ppm. $^{13}C\{^1H\}$ NMR (100 MHz; $CDCl_3$; 298 K): δ 134.3 (d, *o*-$\boldsymbol{C}H$, $^2J_{C,P}$ = 14.6 Hz), 132.1 (d, *p*-$\boldsymbol{C}H$, $^4J_{C,P}$ = 2.9 Hz), 129.4 (d, *m*-$\boldsymbol{C}H$, $^3J_{C,P}$ = 12.2 Hz), 128.8 (d, $\boldsymbol{C}P$, $^1J_{C,P}$ = 61.6 Hz) ppm. $^{31}P\{^1H\}$ NMR (162 MHz; $CDCl_3$; 298 K): δ 33.8 ($Au\boldsymbol{P}Ph_3$) ppm.

The main IR bands, ^{1}H, ^{13}C and ^{31}P NMR peaks are in agreement with literature data.[4]

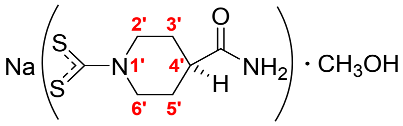
cis-$[Pt^{II}Cl_2(NH_3)_2]$



Cisplatin was prepared according to a literature procedure.[5] FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 3283 (ν_a, NH_3), 3207 (ν_s, NH_3), 1621/1537 (δ_a, NH_3), 1315/1293 (δ_s, NH_3), 785 (ρ, NH_3), 510_{br} ($\nu_{a,s}$, NPtN), 324_{br} ($\nu_{a,s}$, ClPtCl), 252 (δ, NPtN) cm^{-1}. ^{1}H NMR (400 MHz; DMSO-D_6; 298 K): δ 3.95 (6 H, br s, $N\boldsymbol{H}_3$) ppm.

The main IR bands and ^{1}H NMR peak are in agreement with literature data.[6]

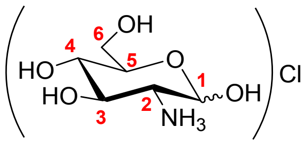
Synthesis and characterization of $Na(SSC\text{-}Inp\text{-}NH_2){\cdot}CH_3OH$



NaOH (340.0 mg, 8.58 mmol) was dissolved in methanol (5 mL) and, subsequently, CS_2 (1.07 mL, 17.76 mmol) was added dropwise under stirring to a methanol solution (5 mL) of isonipecotamide (1.09 g, 8.50 mmol) at 0°C. The mixture was stirred at 0°C for 3 h (pH turned from 10 to 8), treated with further CS_2 (536.0 µL, 8.88 mmol), and stored at 4°C for 16 h (pH further dropped to ~7). The mixture was then treated with diethyl ether (20 mL) at room temperature, leading to the sudden precipitation of a white solid. The precipitate was filtered off, washed with diethyl ether (3×10 mL), and then dried under vacuum over P_2O_5, yielding the title compound as a white solid (1.75 g, 80%). Colorless needle-shaped crystals suitable for X-ray crystallography were obtained upon storing a methanol/diethyl ether solution of the compound at 4°C. M.p. 260-268°C (dec.). Anal. (%) calcd. for $C_8H_{15}N_2NaO_2S_2$ (MM = 258.33 g mol^{-1}): C, 37.20; H, 5.85; N, 10.84; found: C, 37.45; H, 5.77; N, 10.64. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 3390/3198 ($\nu_{a,s}$, NH_2), 1643 (ν, C=O (amide I)), 1626 (δ_{ip}, CNH_2 (amide II)), 1472 (ν, N–CSS), 1004 (ν_a, SCS), 545 (ν_s, SCS) cm^{-1}. ^1H NMR (400 MHz; DMSO-D_6; 298 K): δ 7.25 (1 H, s, $N\boldsymbol{H}_{cis}$), 6.72 (1 H, s, $N\boldsymbol{H}_{trans}$), 5.78 (2 H, dt, $C^{2',6'}\boldsymbol{H}_{eq}$), 4.11 (1 H, q, $O\boldsymbol{H}_{methanol}$), 3.16 (3 H, d, $C\boldsymbol{H}_{3\ methanol}$), 2.83 (2 H, td, $C^{2',6'}\boldsymbol{H}_{ax}$), 2.29 (1 H, tt, $C^{4'}\boldsymbol{H}$), 1.60 (2 H, dd, $C^{3',5'}\boldsymbol{H}_{eq}$), 1.40 (2 H, qd, $C^{3',5'}\boldsymbol{H}_{ax}$) ppm. $^{13}C\{^1H\}$ NMR (100 MHz; DMSO-D_6; 298 K): δ 213.4 (N$\boldsymbol{C}$SS), 176.6 ($\boldsymbol{C}$=O), 48.7 ($\boldsymbol{C}^{2',6'}H_2$), 48.6 ($\boldsymbol{C}H_{3\ methanol}$), 42.0 ($\boldsymbol{C}^{4'}H$), 28.6 ($\boldsymbol{C}^{3',5'}H_2$) ppm.

Synthesis and characterization of the amino-sugar precursors (GlcN1, GlcN2 and GlcN3)

2-Amino-2-deoxy-(α,β)-D-glucose (aka (α,β)-D-glucosamine, GlcN1) hydrochloride



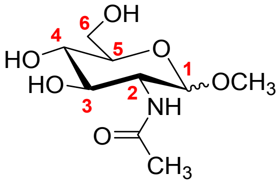
GlcN1

Commercially available. FT-IR (ATR; 298 K): $\tilde{\nu}_{max}$ 3392$_{br}$/3282$_{br}$/3244$_{br}$ (ν, OH), 3093/3035 (ν$_a$, NH_3^+), 2844 (ν$_s$, NH_3^+), 1614/1580/1538 (δ$_{a,s}$, NH_3^+), 1031/1003 (ν, C–OH) cm^{-1}. ^{1}H NMR (400 MHz; DMSO-D$_6$; 298 K): *δ* 8.01 (3 H, br s, N***H***$_3^+$), 7.16 (1 H, d, C^{1}O***H***), 5.67 (1 H, d, C^{3}O***H***), 5.30 (1 H, d, C^{4}O***H***), 5.23 (1 H, br dd, C^1***H***), 4.57 (1 H, br s, C^{6}O***H***), 3.63-3.45 (4 H, m, C^3***H*** + C^5***H*** + C^6***H***$_2$ overlapped), 3.17 (1 H, td, C^4***H***), 2.82 (1 H, dd, C^2***H***, $^3J_{1,2}$ = 3.2 Hz) ppm. ^{13}C{^{1}H} NMR (100 MHz; DMSO-D$_6$; 298 K): *δ* 88.9 (***C***^{1}H), 72.3 (***C***^{5}H), 70.2 (***C***^{4}H), 69.8 (***C***^{3}H), 60.6 (***C***^{6}H$_2$), 54.5 (***C***^{2}H) ppm.

The NMR signals refer to the α anomer and are consistent with literature data,[7] including the $^3J_{1,2}$ value within the 1-4 Hz range.[8] Although the substance is sold as a mixture of α and β anomers, the NMR signals of the latter are hardly detectable and/or overlapped with those of the former. Therefore, the amount of β anomer cannot be quantified based on the ^{1}H NMR spectrum only.

1-*O*-methyl-2-amino-2-deoxy-(α,β)-D-glucopyranoside (GlcN2) acetic acid

1st step. Synthesis of 1-*O*-methyl-2-acetamido-2-deoxy-(α,β)-D-glucopyranoside

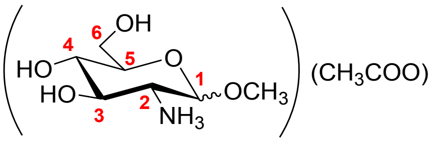


Amberlite IR120 (H$^+$ form) resin (5.2 g) was added to a methanol suspension (70 mL) of *N*-acetyl-(α,β)-D-glucosamine (3.15 g, 14.24 mmol). The mixture was stirred under reflux for 18 h. The mixture was then allowed to cool down to room temperature and the resin was filtered off. The resulting clear solution was evaporated to dryness to give an off-white residue which was washed with diethyl ether and dried under vacuum over P_2O_5, yielding the title compound as a white solid (2.39 g, 72%). FT-IR (ATR; 298 K): $\tilde{\nu}_{max}$ 3350/3293$_{br}$ (ν, OH + NH overlapped), 1646 (ν, C=O (amide I)), 1548 (δ$_{ip}$, CNH (amide II)), 1021 (ν, C–OH + C^1–O–CH$_3$ overlapped) cm^{-1}. ^{1}H NMR (400 MHz; DMSO-D$_6$; 298 K): *δ* 7.76 (1 H, d, N***H*** α), 7.68 (0.3 H, d, N***H*** β), 4.67 (4 H, br s, C^{3}O***H***

+ C^{4}O***H*** + C^{6}O***H*** α and β overlapped), 4.51 (1 H, d, C^1***H*** α, $^3J_{1,2}$ = 3.4 Hz), 4.16 (0.3 H, d, C^1***H*** β, $^3J_{1,2}$ = 8.4 Hz), 3.69-3.40 (~5.2 H, m, C^3***H*** + C^5***H*** + C^6***H***$_2$ α and β overlapped), 3.31 (0.9 H, s, OC***H***$_3$ β), 3.23 (3 H, s, OC***H***$_3$ α), 3.11 (1.3 H, dd, C^4***H*** α and β overlapped), 3.07-3.05 (1.2 H, m, C^2***H***, α and β overlapped), 1.82 (3 H, s, C(O)C***H***$_3$ α), 1.79 (1 H, s, C(O)C***H***$_3$ β) ppm. ^{13}C{^{1}H} NMR (100 MHz; DMSO-D$_6$; 298 K): *δ* 169.5 (***C***=O α), 169.1 (***C***=O β), 101.9 (***C***^{1}H β), 98.0 (***C***^{1}H α), 77.0 (***C***^{3}H β), 74.5 (***C***^{5}H β), 72.7 (***C***^{3}H α), 70.9 (***C***^{5}H α), 70.8 (***C***^{4}H α), 70.6 (***C***^{4}H β), 61.1 (***C***^{6}H$_2$ β), 61.0 (***C***^{6}H$_2$ α), 55.7 (O***C***H$_3$ β), 55.2 (***C***^{2}H β), 54.3 (O***C***H$_3$ α), 53.8 (***C***^{2}H α), 23.2 (C(O)***C***H$_3$ β), 22.7 (C(O)***C***H$_3$ α) ppm.

Experimental data are consistent with those reported in the literature.[9] Solution α:β anomers ratio ≈ 3:1 (based on the ^{1}H NMR spectrum).

2nd step. Synthesis of 1-*O*-methyl-2-amino-2-deoxy-(α,β)-D-glucopyranoside (**GlcN2**) acetic acid



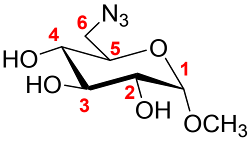
GlcN2

1-*O*-methyl-2-acetamido-2-deoxy-(α,β)-D-glucopyranoside (1.00 g, 4.25 mmol) was dissolved in water (70 mL), and BaO was added batchwise under stirring to give pH 13-14. The mixture was stirred under reflux at 120°C for 6 d, during which small portions of BaO were added over time until the reaction had gone to completion (as monitored by TLC). The mixture was then allowed to cool down to room temperature, filtered to remove insoluble barium salts, treated with dry ice, and filtered again to remove the insoluble BaCO$_3$ formed. The filtered solution (pH 6-7) was evaporated to dryness at low temperature (<30°C), and the resulting viscous residue was dried under vacuum over P$_2$O$_5$, yielding the title compound as a pale yellow syrup (0.78 g, 72%). FT-IR (ATR; 298 K): $\tilde{\nu}_{max}$ 3205$_{br}$ (ν, OH + NH$_3^+$ overlapped), 2844 (ν$_s$, NH$_3^+$), 1628 (δ$_a$, NH$_3^+$), 1546 (ν$_a$, COO$^-$), 1039 (ν, C–OH + C^1–O–CH$_3$ overlapped) cm^{-1}. ^{1}H NMR (400 MHz; DMSO-D$_6$; 298 K): *δ* 4.55 (1 H, d, C^1***H*** α, $^3J_{1,2}$ = 3.5 Hz), 4.07 (3.6 H, br s, C^{3}O***H*** + C^{4}O***H*** + C^{6}O***H*** α and β overlapped), 3.98 (0.3 H, d, C^1***H*** β, $^3J_{1,2}$ = 7.9 Hz), 3.68-3.40 (~2.5 H, m, C^6***H***$_2$ α and β overlapped), 3.38 (0.6 H, s, OC***H***$_3$ β), 3.32-3.28 (1 H, m, C^5***H*** α), 3.26 (3 H, s, OC***H***$_3$ α), 3.22 (1 H, dd, C^3***H*** α), 3.07-3.00 (1.7 H, m, C^4***H*** α + C^3***H*** + C^4***H*** + C^5***H*** β overlapped), 2.45 (1 H, dd, C^2***H*** α), 2.40-2.36 (0.2 H, m, C^2***H*** β), 1.79 (3.2 H, s, C***H***$_3$COO$^-$) ppm. ^{13}C{^{1}H} NMR (100 MHz; DMSO-D$_6$; 298 K): *δ* 174.4 (CH$_3$***C***OO$^-$), 104.5 (***C***^{1}H β), 99.6 (***C***^{1}H α), 77.2 (***C***^{3}H β), 76.1 (***C***^{5}H β), 74.4 (***C***^{3}H α), 73.2 (***C***^{5}H α), 70.4 (***C***^{4}H α), 70.1 (***C***^{4}H β), 61.1 (***C***^{6}H$_2$ β), 61.0 (***C***^{6}H$_2$ α), 57.3 (***C***^{2}H β), 56.1 (O***C***H$_3$ β), 56.0 (***C***^{2}H α), 54.5 (O***C***H$_3$ α), 23.1 (***C***H$_3$COO$^-$) ppm.

Experimental data are consistent with those reported in the literature.[10] Solution α:β anomers ratio ≈ 5:1 (based on the ^{1}H NMR spectrum).

1-*O*-methyl-6-amino-6-deoxy-α-D-glucopyranoside (GlcN3)

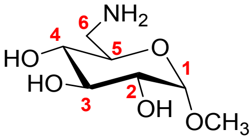
1st step. Synthesis of 1-*O*-methyl-6-azido-6-deoxy-α-D-glucopyranoside



Methyl-α-D-glucopyranoside (4.69 g, 24.18 mmol) and PPh_3 (12.48 g, 47.58 mmol) were transferred into an oven-dry round-bottom flask, dissolved with anhydrous DMF (85 mL), and kept under inert atmosphere by bubbling N_2 into the solution. The mixture was cooled down to 0°C, treated with *N*-bromosuccinimide (8.85 g, 49.72 mmol), and stirred for 20 min at 0°C and for 3 h at 55°C. Methanol (5.2 mL) and NaN_3 (9.46 g, 145.52 mmol) were subsequently added in this order, and the resulting mixture was stirred at 85°C for 4 h. The solvent was evaporated by heating at 75°C with a stream of N_2, and the remaining residue was redissolved in water (90 mL) and treated with dichloromethane (3×90 mL). The aqueous fractions were recovered, filtered and evaporated to dryness. The resulting yellowish residue was purified by column chromatography (eluent: EtOAc/MeOH 9:1; $R_f = 0.53$) and dried under vacuum over P_2O_5, yielding the title compound as a white solid (2.08 g, 39%). FT-IR (ATR; 298 K): $\tilde{\nu}_{max}$ 3356_{br} (ν, OH), 2094 (ν_{oop}, N_3), 1048/1026 (ν, C–OH + C^1–O–CH_3 overlapped) cm^{-1}. ^{1}H NMR (400 MHz; $CDCl_3$; 298 K): δ 4.77 (1 H, d, C^1***H***, $^3J_{1,2}$ = 3.6 Hz), 4.37 (3 H, br s, C^2O***H*** + C^3O***H*** + C^4O***H*** overlapped), 3.74-3.70 (2 H, m, C^3***H*** + C^5***H*** overlapped), 3.57-3.53 (2 H, m, C^2***H*** + C^6***H′*** overlapped), 3.49-3.39 (2 H, m, C^4***H*** + C^6***H″*** overlapped), 3.46 (3 H, s, OC***H***$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz; $CDCl_3$; 298 K): δ 99.5 (***C***^{1}H), 74.2 (***C***^{3}H), 72.0 (***C***^{2}H), 70.9 (***C***^{5}H), 70.8 (***C***^{4}H), 55.9 (O***C***H$_3$), 51.4 (***C***^{6}H$_2$) ppm.

Experimental data are consistent with those reported in the literature and confirm the presence of the α anomer only,[11] including the $^3J_{1,2}$ value within the 1-4 Hz range.[8]

2nd step. Synthesis of 1-*O*-methyl-6-amino-6-deoxy-α-D-glucopyranoside (**GlcN3**)

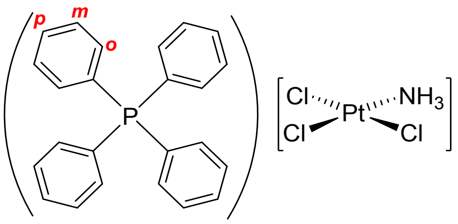


GlcN3

Pd/C 10%$_w$ (0.35 g) was added to a methanol solution (60 mL) of 1-*O*-methyl-6-azido-6-deoxy-α-D-glucopyranoside (2.05 g, 9.35 mmol). The mixture was kept under hydrogen atmosphere by bubbling H_2 into the solution and stirred for 6 h until the reaction had gone to completion (as monitored by TLC). The catalyst was then filtered off on celite and the resulting clear solution was evaporated to dryness. The residue was dried under vacuum over P_2O_5, yielding the title compound as a white solid (1.61 g, 89%). FT-IR (ATR; 298 K): $\tilde{\nu}_{max}$ $3349_{br}/3260_{br}$ (ν, OH + NH_2 overlapped), 1598 (δ, NH_2), 1033/1007 (ν, C–OH + C^1–O–CH_3 overlapped) cm^{-1}. ^1H NMR (400 MHz; DMSO-D_6; 298 K): δ 4.75 (~3 H, br s, $C^2O\boldsymbol{H}$ + $C^3O\boldsymbol{H}$ + $C^4O\boldsymbol{H}$ overlapped), 4.51 (1 H, d, $C^1\boldsymbol{H}$, $^3J_{1,2} = 3.7$ Hz), 3.34 (1 H, dd, $C^3\boldsymbol{H}$), 3.26 (3 H, s, $OC\boldsymbol{H}_3$), 3.24-3.22 (1 H, m, $C^5\boldsymbol{H}$), 3.18 (1 H, dd, $C^2\boldsymbol{H}$), 2.99 (1 H, dd, $C^4\boldsymbol{H}$), 2.83-2.55 (2 H, m, $C^6\boldsymbol{H}_2$). $^{13}C\{^1H\}$ NMR (100 MHz; DMSO-D_6; 298 K): δ 99.7 ($\boldsymbol{C}^1H$), 73.2 ($\boldsymbol{C}^3H$), 72.4 ($\boldsymbol{C}^5H$), 72.1 ($\boldsymbol{C}^4H$), 72.0 ($\boldsymbol{C}^2H$), 54.3 ($O\boldsymbol{C}H_3$), 43.2 ($\boldsymbol{C}^6H_2$) ppm.

Experimental data are consistent with those reported in the literature and confirm the presence of the α anomer only,[12] including the $^3J_{1,2}$ value within the 1-4 Hz range.[8]

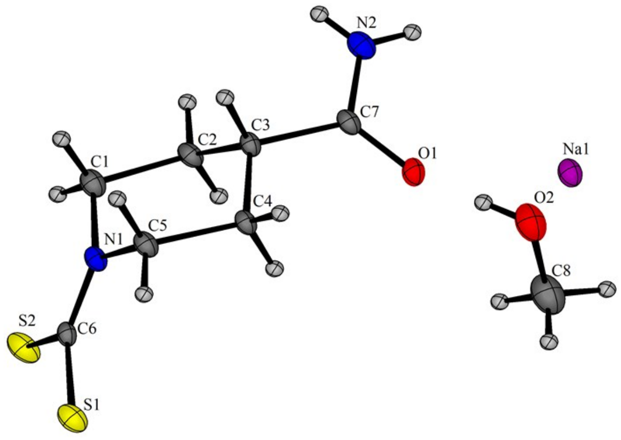
Synthesis and characterization of (PPh$_4$)[Pt^{II}Cl$_3$(NH$_3$)]



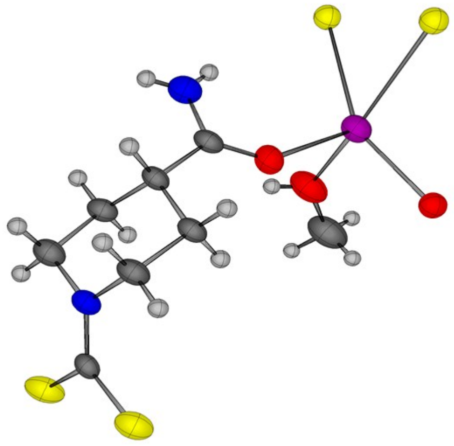
(PPh$_4$)[Pt^{II}Cl$_3$(NH$_3$)] was synthesized according to a literature procedure.[13] (Et$_4$N)Cl·xH$_2$O (220.0 mg, 1.33 mmol) was added under stirring at room temperature to an *N*,*N*-dimethylacetamide (25 mL) solution of cisplatin (338.0 mg, 1.13 mmol) in a two-neck round-bottomed flask. A condenser was connected to the central neck of the flask and the reaction mixture (kept under inert atmosphere by bubbling N$_2$ into the solution) was stirred at 100°C for 6 h, after which the color of the solution turned from yellow to orange and the volume reduced to ~20 mL (***note***: prolonged heating above 105°C results in extensive decomposition of the reaction mixture). The mixture was then cooled down to room temperature and treated with a 1:1 ethyl acetate/*n*-hexane solution (300 mL). The resulting cloudy reaction mixture was stored at -10°C overnight, leading to the formation of a thick orange oil attached to the walls of the flask. The bulk of clear colorless supernatant was discarded, the orange oil dissolved with water (10 mL), and the remaining insoluble residue (*i.e.* unreacted cisplatin) was filtered off and discarded. The resulting clear orange solution was then treated with (PPh$_4$)Cl (475.0 mg, 1.27 mmol), stirred at room temperature for 1 h and stored at 4°C overnight, leading to the formation of a light orange solid. The precipitate was filtered off, washed with cold water (2×10 mL), and then dried under vacuum over P$_2$O$_5$, yielding the title compound as a pale yellow solid (389.0 mg, 52%). Anal. (%) calcd. for C$_{24}$H$_{23}$Cl$_3$NPPt (MM = 657.86 g mol^{-1}): C, 43.82; H, 3.52; N, 2.16; found: C, 44.02; H, 3.48; N, 2.16. FT-IR (CsI disk; 298 K): $\tilde{\nu}_{max}$ 3250 (ν_a, NH$_3$), 3173 (ν_s, NH$_3$), 1638 (δ_a, NH$_3$), 1291 (δ_s, NH$_3$), 1108 ($\nu_{q\ vib}$, P–Ph$_4$), 780 (ρ, NH$_3$), 721 ($\nu_{r\ vib}$, P–Ph$_4$), 527 ($\delta_{y\ vib}$, P–Ph$_4$ + ν, Pt–N overlapped), 456/437 ($\nu_{t\ vib}$, P–Ph$_4$), 337/327 ($\nu_{a,s}$, PtCl$_3$), 260 ($\delta_{x\ vib}$, P–Ph$_4$) cm^{-1}. ^{1}H NMR (400 MHz; DMSO-D$_6$; 298 K): δ 7.97 (4 H, tt, *p*-C***H***), 7.84-7.79 (8 H, m, *m*-C***H***), 7.77-7.71 (8 H, m, *o*-C***H***), 3.97 (3 H, br s, N***H***$_3$) ppm. ^{13}C{^{1}H} NMR (100 MHz; DMSO-D$_6$; 298 K): δ 135.3 (d, *p*-***C***H, $^4J_{C,P}$ = 2.7 Hz), 134.5 (d, *o*-***C***H, $^2J_{C,P}$ = 10.6 Hz), 130.4 (d, *m*-***C***H, $^3J_{C,P}$ = 13.3 Hz), 117.7 (d, ***C***P, $^1J_{C,P}$ = 89.3 Hz) ppm. ^{31}P{^{1}H} NMR (162 MHz; DMSO-D$_6$; 298 K): δ 23.5 (***P***Ph$_4^+$) ppm.

The main IR bands, ^{1}H, ^{13}C and ^{31}P NMR peaks are in agreement with literature data.[13,14]

Crystal structure of $Na(SSC\text{-}Inp\text{-}NH_2)\cdot CH_3OH$ (CCDC 1835869)



Asymmetric unit



Na^+ coordination sphere

Crystal data and structure refinement.

Identification code	and_1	
Empirical formula	C8 H15 N2 Na O2 S2	
Formula weight	258.33	
Temperature	300.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I2/a	
Unit cell dimensions	a = 15.2035(17) Å	α= 90°
	b = 11.0876(11) Å	β= 111.081(13)°
	c = 15.0618(15) Å	γ = 90°
Volume	2369.0(5) $Å^3$	
Z	8	
Density (calculated)	1.449 Mg/m^3	
Absorption coefficient	0.468 mm^{-1}	
F(000)	1088	
Crystal size	0.50 x 0.30 x 0.20 mm^3	
Theta range for data collection	3.675 to 29.001°	
Index ranges	-16<=h<=20, -11<=k<=14, -19<=l<=11	
Reflections collected	5411	
Independent reflections	2706 [R(int) = 0.0280]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.66852	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2706 / 0 / 149	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0500, wR2 = 0.0873	
R indices (all data)	R1 = 0.0840, wR2 = 0.1005	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.378 and -0.236 e.$Å^{-3}$	

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$); U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
S(1)	3590(1)	3956(1)	1502(1)	41(1)
S(2)	3436(1)	5646(1)	2955(1)	44(1)
Na(1)	8130(1)	1459(1)	6119(1)	41(1)
O(1)	6502(1)	1587(2)	5249(1)	41(1)
N(1)	3589(1)	3280(2)	3191(1)	31(1)
O(2)	8238(2)	3563(2)	6408(2)	58(1)
N(2)	5827(2)	1358(3)	6329(2)	44(1)
C(1)	3543(2)	3396(3)	4141(2)	37(1)
C(2)	4486(2)	3079(2)	4902(2)	32(1)
C(3)	4818(2)	1832(2)	4726(2)	27(1)
C(4)	4791(2)	1739(2)	3711(2)	29(1)
C(5)	3819(2)	2048(2)	3010(2)	35(1)
C(6)	3542(2)	4199(2)	2605(2)	29(1)
C(7)	5788(2)	1581(2)	5452(2)	31(1)
C(8)	8689(2)	4524(3)	6166(3)	65(1)

Bond lengths [Å] and angles [°]; symmetry transformations used to generate equivalent atoms: #1 x-1/2,y+1/2,z-1/2 #2 -x+3/2,y,-z+1 #3 x+1/2,y-1/2,z+1/2.

S(1)-C(6)	1.710(2)
S(1)-Na(1)#1	2.8700(14)
S(2)-C(6)	1.715(3)
S(2)-Na(1)#1	2.7845(12)
Na(1)-O(1)#2	2.326(2)
Na(1)-O(1)	2.3514(19)
Na(1)-O(2)	2.368(3)
Na(1)-S(2)#3	2.7845(12)
Na(1)-S(1)#3	2.8700(14)
Na(1)-C(4)#2	3.095(3)
Na(1)-Na(1)#2	3.222(2)
O(1)-C(7)	1.228(3)
O(1)-Na(1)#2	2.326(2)
N(1)-C(6)	1.333(3)
N(1)-C(5)	1.461(3)
N(1)-C(1)	1.463(3)
O(2)-C(8)	1.385(4)
O(2)-H(1O2)	0.79(3)
N(2)-C(7)	1.324(3)
N(2)-H(1N2)	0.82(3)
N(2)-H(2N1)	0.79(3)
C(1)-C(2)	1.520(3)
C(1)-H(1A)	0.9700
C(1)-H(1B)	0.9700
C(2)-C(3)	1.527(3)

C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(7)	1.513(3)
C(3)-C(4)	1.518(3)
C(3)-H(3)	0.9800
C(4)-C(5)	1.515(3)
C(4)-Na(1)#2	3.095(3)
C(4)-H(4A)	0.9700
C(4)-H(4B)	0.9700
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(6)-S(1)-Na(1)#1	87.15(9)
C(6)-S(2)-Na(1)#1	89.85(9)
O(1)#2-Na(1)-O(1)	92.50(7)
O(1)#2-Na(1)-O(2)	94.60(9)
O(1)-Na(1)-O(2)	91.89(9)
O(1)#2-Na(1)-S(2)#3	153.15(6)
O(1)-Na(1)-S(2)#3	109.83(6)
O(2)-Na(1)-S(2)#3	99.22(7)
O(1)#2-Na(1)-S(1)#3	96.76(6)
O(1)-Na(1)-S(1)#3	107.59(6)
O(2)-Na(1)-S(1)#3	156.91(7)
S(2)#3-Na(1)-S(1)#3	62.98(3)
O(1)#2-Na(1)-C(4)#2	60.17(6)
O(1)-Na(1)-C(4)#2	151.57(7)
O(2)-Na(1)-C(4)#2	83.36(8)
S(2)#3-Na(1)-C(4)#2	98.60(5)
S(1)#3-Na(1)-C(4)#2	84.96(6)
O(1)#2-Na(1)-Na(1)#2	46.79(5)
O(1)-Na(1)-Na(1)#2	46.14(5)
O(2)-Na(1)-Na(1)#2	99.70(6)
S(2)#3-Na(1)-Na(1)#2	149.68(5)
S(1)#3-Na(1)-Na(1)#2	102.74(2)
C(4)#2-Na(1)-Na(1)#2	106.94(6)
C(7)-O(1)-Na(1)#2	137.41(15)
C(7)-O(1)-Na(1)	135.04(16)
Na(1)#2-O(1)-Na(1)	87.08(7)
C(6)-N(1)-C(5)	123.3(2)
C(6)-N(1)-C(1)	124.9(2)
C(5)-N(1)-C(1)	111.3(2)
C(8)-O(2)-Na(1)	135.8(2)
C(8)-O(2)-H(1O2)	111(3)
Na(1)-O(2)-H(1O2)	108(3)
C(7)-N(2)-H(1N2)	119(2)
C(7)-N(2)-H(2N1)	121(2)
H(1N2)-N(2)-H(2N1)	120(3)
N(1)-C(1)-C(2)	110.70(19)
N(1)-C(1)-H(1A)	109.5
C(2)-C(1)-H(1A)	109.5
N(1)-C(1)-H(1B)	109.5

C(2)-C(1)-H(1B)	109.5
H(1A)-C(1)-H(1B)	108.1
C(1)-C(2)-C(3)	111.0(2)
C(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2A)	109.4
C(1)-C(2)-H(2B)	109.4
C(3)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
C(7)-C(3)-C(4)	112.45(19)
C(7)-C(3)-C(2)	109.8(2)
C(4)-C(3)-C(2)	110.15(19)
C(7)-C(3)-H(3)	108.1
C(4)-C(3)-H(3)	108.1
C(2)-C(3)-H(3)	108.1
C(5)-C(4)-C(3)	110.72(19)
C(5)-C(4)-Na(1)#2	142.35(16)
C(3)-C(4)-Na(1)#2	105.46(13)
C(5)-C(4)-H(4A)	109.5
C(3)-C(4)-H(4A)	109.5
Na(1)#2-C(4)-H(4A)	46.3
C(5)-C(4)-H(4B)	109.5
C(3)-C(4)-H(4B)	109.5
Na(1)#2-C(4)-H(4B)	66.2
H(4A)-C(4)-H(4B)	108.1
N(1)-C(5)-C(4)	108.7(2)
N(1)-C(5)-H(5A)	110.0
C(4)-C(5)-H(5A)	110.0
N(1)-C(5)-H(5B)	110.0
C(4)-C(5)-H(5B)	110.0
H(5A)-C(5)-H(5B)	108.3
N(1)-C(6)-S(1)	120.84(19)
N(1)-C(6)-S(2)	119.93(18)
S(1)-C(6)-S(2)	119.23(15)
O(1)-C(7)-N(2)	121.6(2)
O(1)-C(7)-C(3)	122.5(2)
N(2)-C(7)-C(3)	115.9(2)
O(2)-C(8)-H(8A)	109.5
O(2)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
O(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5

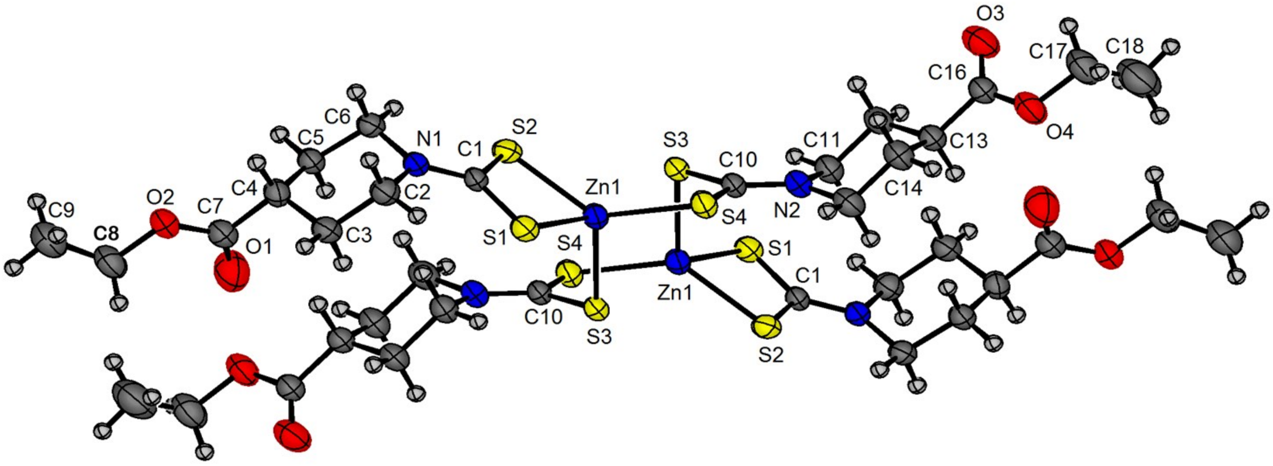
Anisotropic displacement parameters ($Å^2 \times 10^3$); the anisotropic displacement factor exponent takes the form $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
S(1)	49(1)	44(1)	34(1)	-6(1)	20(1)	-1(1)
S(2)	62(1)	34(1)	42(1)	-3(1)	26(1)	3(1)
Na(1)	30(1)	52(1)	38(1)	4(1)	9(1)	1(1)
O(1)	24(1)	58(1)	37(1)	5(1)	7(1)	4(1)
N(1)	28(1)	33(1)	29(1)	-1(1)	6(1)	4(1)
O(2)	53(1)	48(2)	81(2)	5(1)	32(1)	9(1)
N(2)	43(2)	53(2)	32(1)	10(1)	9(1)	0(1)
C(1)	36(1)	42(2)	37(1)	5(1)	18(1)	9(1)
C(2)	36(1)	36(2)	26(1)	2(1)	12(1)	4(1)
C(3)	24(1)	25(1)	32(1)	2(1)	9(1)	-1(1)
C(4)	26(1)	25(1)	31(1)	-3(1)	7(1)	1(1)
C(5)	34(1)	30(2)	33(1)	-7(1)	1(1)	-3(1)
C(6)	18(1)	34(2)	32(1)	-3(1)	7(1)	1(1)
C(7)	32(1)	24(1)	32(1)	-1(1)	6(1)	-1(1)
C(8)	66(2)	51(2)	89(3)	12(2)	41(2)	10(2)

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$).

Atom	x	y	z	U(eq)
H(1A)	3060	2862	4196	48
H(1B)	3374	4216	4236	48
H(2A)	4427	3094	5522	42
H(2B)	4952	3678	4901	42
H(3)	4381	1232	4811	35
H(4A)	5251	2287	3624	37
H(4B)	4956	926	3592	37
H(5A)	3809	1981	2364	46
H(5B)	3357	1492	3083	46
H(8A)	9324	4579	6612	84
H(8B)	8358	5257	6180	84
H(8C)	8696	4401	5538	84
H(1N2)	6340(20)	1280(30)	6760(20)	60(11)
H(2N1)	5360(20)	1360(30)	6452(19)	41(9)
H(1O2)	7780(20)	3780(30)	6480(20)	69(12)

Crystal structure of [Zn^{II}(SSC-Inp-OEt)$_2$] (Zn1) (CCDC 1835870)



Crystal data and structure refinement.

Identification code	ap226	
Empirical formula	C18 H28 N2 O4 S4 Zn	
Formula weight	530.03	
Temperature	299.0(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.4775(7) Å	α= 81.181(6)°
	b = 10.8781(8) Å	β= 72.125(6)°
	c = 12.1158(9) Å	γ = 81.757(6)°
Volume	1168.58(16) Å^3	
Z	2	
Density (calculated)	1.506 Mg/m^3	
Absorption coefficient	1.435 mm^{-1}	
F(000)	552	
Crystal size	0.50 x 0.40 x 0.20 mm^3	
Theta range for data collection	3.558 to 29.223°.	
Index ranges	-12<=h<=11, -14<=k<=14, -16<=l<=15	
Reflections collected	9243	
Independent reflections	5332 [R(int) = 0.0363]	
Completeness to theta = 25.242°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.87706	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5332 / 0 / 264	
Goodness-of-fit on F^2	0.857	
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.0984	
R indices (all data)	R1 = 0.0950, wR2 = 0.1211	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.537 and -0.307 e.Å^{-3}	

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times 10^3$); U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Zn(1)	4512(1)	8404(1)	4975(1)	43(1)
S(3)	6876(1)	9902(1)	4017(1)	40(1)
S(4)	4749(1)	9080(1)	3010(1)	48(1)
S(2)	5812(1)	6867(1)	5966(1)	45(1)
S(1)	2973(1)	6663(1)	5539(1)	46(1)
O(2)	2064(3)	2775(3)	11103(2)	58(1)
N(1)	4212(3)	4938(3)	6859(2)	39(1)
O(4)	8448(3)	12185(3)	-2358(2)	74(1)
N(2)	6448(4)	10888(3)	1965(3)	48(1)
O(3)	10407(4)	11609(4)	-1674(3)	82(1)
O(1)	2001(5)	4837(3)	10855(3)	105(1)
C(1)	4325(4)	6030(3)	6193(3)	37(1)
C(2)	2906(5)	4254(4)	7167(3)	51(1)
C(3)	2092(4)	4269(4)	8460(3)	51(1)
C(4)	3145(5)	3725(4)	9195(3)	49(1)
C(5)	4546(4)	4374(4)	8794(3)	44(1)
C(6)	5291(4)	4388(4)	7489(3)	45(1)
C(7)	2338(5)	3858(4)	10471(4)	56(1)
C(8)	1265(6)	2825(5)	12336(4)	77(2)
C(9)	1177(6)	1509(6)	12897(4)	98(2)
C(10)	6071(4)	10041(3)	2889(3)	40(1)
C(11)	7551(5)	11773(4)	1792(3)	52(1)
C(12)	8698(5)	11712(4)	643(3)	52(1)
C(13)	7979(4)	11955(4)	-351(3)	46(1)
C(14)	6807(5)	11055(4)	-125(3)	59(1)
C(15)	5701(5)	11129(5)	1035(3)	61(1)
C(16)	9105(5)	11895(4)	-1515(3)	50(1)
C(17)	9388(6)	12180(6)	-3552(4)	90(2)
C(18)	9822(6)	13453(7)	-4009(5)	116(3)

Bond lengths [Å] and angles [°]; symmetry transformations used to generate equivalent atoms: #1 -x+1,-y+2,-z+1.

Zn(1)-S(4)	2.3334(11)
Zn(1)-S(2)	2.3357(11)
Zn(1)-S(3)#1	2.3716(10)
Zn(1)-S(1)	2.4426(11)
Zn(1)-S(3)	2.8095(11)
S(3)-C(10)	1.737(4)
S(3)-Zn(1)#1	2.3716(10)
S(4)-C(10)	1.703(4)

S(2)-C(1)	1.716(4)
S(1)-C(1)	1.717(4)
O(2)-C(7)	1.316(5)
O(2)-C(8)	1.458(5)
N(1)-C(1)	1.328(5)
N(1)-C(2)	1.456(5)
N(1)-C(6)	1.466(4)
O(4)-C(16)	1.330(5)
O(4)-C(17)	1.448(5)
N(2)-C(10)	1.327(5)
N(2)-C(11)	1.469(5)
N(2)-C(15)	1.477(5)
O(3)-C(16)	1.191(5)
O(1)-C(7)	1.189(5)
C(2)-C(3)	1.520(5)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.534(5)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(5)	1.505(5)
C(4)-C(7)	1.519(5)
C(4)-H(4)	0.9800
C(5)-C(6)	1.520(5)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(8)-C(9)	1.490(7)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(11)-C(12)	1.484(5)
C(11)-H(11A)	0.9700
C(11)-H(11B)	0.9700
C(12)-C(13)	1.529(5)
C(12)-H(12A)	0.9700
C(12)-H(12B)	0.9700
C(13)-C(16)	1.489(5)
C(13)-C(14)	1.521(5)
C(13)-H(13)	0.9800
C(14)-C(15)	1.479(5)
C(14)-H(14A)	0.9700
C(14)-H(14B)	0.9700
C(15)-H(15A)	0.9700
C(15)-H(15B)	0.9700
C(17)-C(18)	1.476(8)
C(17)-H(17A)	0.9700
C(17)-H(17B)	0.9700
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600

S(4)-Zn(1)-S(2)	134.30(4)
S(4)-Zn(1)-S(3)#1	104.85(4)
S(2)-Zn(1)-S(3)#1	117.89(4)
S(4)-Zn(1)-S(1)	107.13(4)
S(2)-Zn(1)-S(1)	75.79(4)
S(3)#1-Zn(1)-S(1)	107.56(4)
S(4)-Zn(1)-S(3)	69.34(3)
S(2)-Zn(1)-S(3)	95.45(4)
S(3)#1-Zn(1)-S(3)	88.24(3)
S(1)-Zn(1)-S(3)	164.10(4)
C(10)-S(3)-Zn(1)#1	99.89(12)
C(10)-S(3)-Zn(1)	77.67(13)
Zn(1)#1-S(3)-Zn(1)	91.76(3)
C(10)-S(4)-Zn(1)	93.47(13)
C(1)-S(2)-Zn(1)	84.84(13)
C(1)-S(1)-Zn(1)	81.55(13)
C(7)-O(2)-C(8)	116.0(4)
C(1)-N(1)-C(2)	123.3(3)
C(1)-N(1)-C(6)	123.2(3)
C(2)-N(1)-C(6)	113.0(3)
C(16)-O(4)-C(17)	117.5(4)
C(10)-N(2)-C(11)	124.5(3)
C(10)-N(2)-C(15)	123.6(3)
C(11)-N(2)-C(15)	111.7(3)
N(1)-C(1)-S(2)	121.4(3)
N(1)-C(1)-S(1)	121.0(3)
S(2)-C(1)-S(1)	117.6(2)
N(1)-C(2)-C(3)	109.7(3)
N(1)-C(2)-H(2A)	109.7
C(3)-C(2)-H(2A)	109.7
N(1)-C(2)-H(2B)	109.7
C(3)-C(2)-H(2B)	109.7
H(2A)-C(2)-H(2B)	108.2
C(2)-C(3)-C(4)	110.4(3)
C(2)-C(3)-H(3A)	109.6
C(4)-C(3)-H(3A)	109.6
C(2)-C(3)-H(3B)	109.6
C(4)-C(3)-H(3B)	109.6
H(3A)-C(3)-H(3B)	108.1
C(5)-C(4)-C(7)	110.8(3)
C(5)-C(4)-C(3)	110.7(3)
C(7)-C(4)-C(3)	109.0(3)
C(5)-C(4)-H(4)	108.8
C(7)-C(4)-H(4)	108.8
C(3)-C(4)-H(4)	108.8
C(4)-C(5)-C(6)	112.3(3)
C(4)-C(5)-H(5A)	109.1
C(6)-C(5)-H(5A)	109.1
C(4)-C(5)-H(5B)	109.1
C(6)-C(5)-H(5B)	109.1
H(5A)-C(5)-H(5B)	107.9
N(1)-C(6)-C(5)	109.3(3)
N(1)-C(6)-H(6A)	109.8
C(5)-C(6)-H(6A)	109.8

N(1)-C(6)-H(6B)	109.8
C(5)-C(6)-H(6B)	109.8
H(6A)-C(6)-H(6B)	108.3
O(1)-C(7)-O(2)	123.9(4)
O(1)-C(7)-C(4)	123.5(4)
O(2)-C(7)-C(4)	112.7(4)
O(2)-C(8)-C(9)	107.1(4)
O(2)-C(8)-H(8A)	110.3
C(9)-C(8)-H(8A)	110.3
O(2)-C(8)-H(8B)	110.3
C(9)-C(8)-H(8B)	110.3
H(8A)-C(8)-H(8B)	108.6
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
N(2)-C(10)-S(4)	120.5(3)
N(2)-C(10)-S(3)	121.3(3)
S(4)-C(10)-S(3)	118.2(2)
N(2)-C(11)-C(12)	111.1(3)
N(2)-C(11)-H(11A)	109.4
C(12)-C(11)-H(11A)	109.4
N(2)-C(11)-H(11B)	109.4
C(12)-C(11)-H(11B)	109.4
H(11A)-C(11)-H(11B)	108.0
C(11)-C(12)-C(13)	111.0(3)
C(11)-C(12)-H(12A)	109.4
C(13)-C(12)-H(12A)	109.4
C(11)-C(12)-H(12B)	109.4
C(13)-C(12)-H(12B)	109.4
H(12A)-C(12)-H(12B)	108.0
C(16)-C(13)-C(14)	112.5(3)
C(16)-C(13)-C(12)	112.1(3)
C(14)-C(13)-C(12)	109.3(3)
C(16)-C(13)-H(13)	107.6
C(14)-C(13)-H(13)	107.6
C(12)-C(13)-H(13)	107.6
C(15)-C(14)-C(13)	111.6(3)
C(15)-C(14)-H(14A)	109.3
C(13)-C(14)-H(14A)	109.3
C(15)-C(14)-H(14B)	109.3
C(13)-C(14)-H(14B)	109.3
H(14A)-C(14)-H(14B)	108.0
N(2)-C(15)-C(14)	110.6(3)
N(2)-C(15)-H(15A)	109.5
C(14)-C(15)-H(15A)	109.5
N(2)-C(15)-H(15B)	109.5
C(14)-C(15)-H(15B)	109.5
H(15A)-C(15)-H(15B)	108.1
O(3)-C(16)-O(4)	124.5(4)
O(3)-C(16)-C(13)	125.2(4)
O(4)-C(16)-C(13)	110.3(4)

O(4)-C(17)-C(18)	109.0(5)
O(4)-C(17)-H(17A)	109.9
C(18)-C(17)-H(17A)	109.9
O(4)-C(17)-H(17B)	109.9
C(18)-C(17)-H(17B)	109.9
H(17A)-C(17)-H(17B)	108.3
C(17)-C(18)-H(18A)	109.5
C(17)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(17)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5

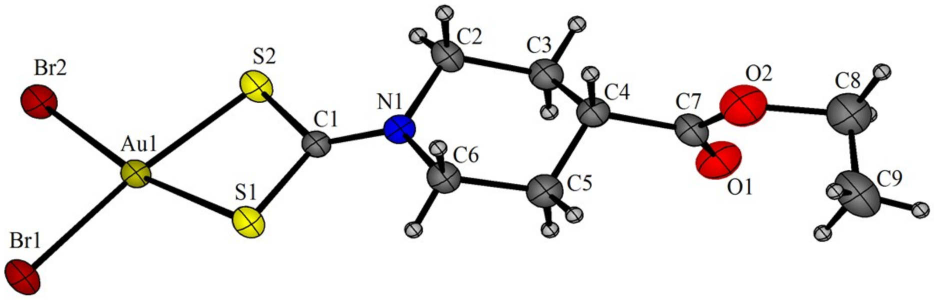
Anisotropic displacement parameters ($Å^2 \times 10^3$); the anisotropic displacement factor exponent takes the form $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Zn(1)	55(1)	36(1)	36(1)	0(1)	-12(1)	-3(1)
S(3)	42(1)	42(1)	34(1)	-4(1)	-10(1)	-1(1)
S(4)	62(1)	46(1)	38(1)	2(1)	-15(1)	-21(1)
S(2)	38(1)	44(1)	52(1)	7(1)	-14(1)	-10(1)
S(1)	50(1)	45(1)	47(1)	4(1)	-24(1)	-10(1)
O(2)	63(2)	63(2)	42(2)	5(2)	-9(1)	-11(2)
N(1)	44(2)	36(2)	38(2)	3(2)	-16(1)	-11(2)
O(4)	63(2)	109(3)	42(2)	4(2)	-15(2)	6(2)
N(2)	53(2)	55(2)	38(2)	4(2)	-12(2)	-25(2)
O(3)	55(2)	126(3)	58(2)	-5(2)	-14(2)	6(2)
O(1)	155(4)	65(2)	72(2)	-20(2)	11(2)	-21(2)
C(1)	42(2)	38(2)	30(2)	-7(2)	-6(2)	-3(2)
C(2)	65(3)	39(2)	55(2)	6(2)	-28(2)	-17(2)
C(3)	50(3)	52(3)	53(2)	0(2)	-15(2)	-22(2)
C(4)	67(3)	39(2)	39(2)	2(2)	-13(2)	-6(2)
C(5)	50(3)	42(2)	42(2)	1(2)	-18(2)	-2(2)
C(6)	43(2)	40(2)	48(2)	3(2)	-15(2)	3(2)
C(7)	57(3)	57(3)	50(3)	-2(2)	-12(2)	-9(2)
C(8)	71(4)	108(5)	42(3)	2(3)	-5(2)	-13(3)
C(9)	87(4)	116(5)	59(3)	30(3)	-3(3)	5(4)
C(10)	43(2)	40(2)	33(2)	-3(2)	-6(2)	-7(2)
C(11)	60(3)	56(3)	43(2)	-3(2)	-11(2)	-19(2)
C(12)	51(3)	65(3)	43(2)	1(2)	-14(2)	-21(2)
C(13)	50(3)	45(2)	44(2)	3(2)	-16(2)	-6(2)
C(14)	63(3)	74(3)	47(2)	10(2)	-24(2)	-32(3)
C(15)	54(3)	83(3)	49(2)	13(2)	-22(2)	-19(3)
C(16)	53(3)	52(3)	44(2)	4(2)	-14(2)	-9(2)
C(17)	76(4)	133(6)	47(3)	-2(3)	-10(3)	11(4)
C(18)	77(4)	205(8)	72(4)	1(5)	-12(3)	-73(5)

Hydrogen coordinates (×10^4) and isotropic displacement parameters (Å^2 ×10^3).

Atom	x	y	z	U(eq)
H(2A)	3210	3397	6994	66
H(2B)	2246	4637	6709	66
H(3A)	1249	3780	8671	66
H(3B)	1717	5121	8619	66
H(4)	3414	2834	9105	64
H(5A)	5238	3953	9211	58
H(5B)	4305	5228	8986	58
H(6A)	6138	4875	7254	59
H(6B)	5649	3542	7302	59
H(8A)	273	3253	12425	100
H(8B)	1792	3271	12695	100
H(9A)	809	1041	12453	127
H(9B)	515	1498	13677	127
H(9C)	2152	1140	12923	127
H(11A)	8030	11580	2409	68
H(11B)	7052	12615	1836	68
H(12A)	9259	10893	625	68
H(12B)	9386	12330	535	68
H(13)	7466	12804	-337	60
H(14A)	6299	11250	-724	77
H(14B)	7290	10208	-173	77
H(15A)	5151	11953	1060	80
H(15B)	4998	10518	1166	80
H(17A)	8854	11918	-4027	117
H(17B)	10271	11597	-3581	117
H(18A)	8972	13991	-4127	151
H(18B)	10594	13426	-4738	151
H(18C)	10182	13768	-3458	151

Crystal structure of [Au^{III}Br$_2$(SSC-Inp-OEt)] (Au1) (CCDC 1835871)



Crystal data and structure refinement.

Identification code	ap228	
Empirical formula	C9 H14 Au Br2 N O2 S2	
Formula weight	589.12	
Temperature	298.0(1) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2$_1$/c	
Unit cell dimensions	a = 8.0665(4) Å	α= 90°
	b = 16.5901(11) Å	β= 102.529(5)°
	c = 11.7403(6) Å	γ = 90°
Volume	1533.72(15) Å^3	
Z	4	
Density (calculated)	2.551 Mg/m^3	
Absorption coefficient	15.064 mm^{-1}	
F(000)	1088	
Crystal size	0.50 x 0.40 x 0.20 mm^3	
Theta range for data collection	3.555 to 25.350°.	
Index ranges	-9<=h<=9, -19<=k<=11, -14<=l<=14	
Reflections collected	6113	
Independent reflections	2814 [R(int) = 0.0306]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.30787	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	2814 / 0 / 155	
Goodness-of-fit on F^2	1.059	
Final R indices [I>2sigma(I)]	R1 = 0.0392, wR2 = 0.0669	
R indices (all data)	R1 = 0.0667, wR2 = 0.0777	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.816 and -0.908 e.Å^{-3}	

Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 ×10^3); U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Atom	x	y	z	U(eq)
Au(1)	500(1)	4354(1)	6612(1)	44(1)
Br(2)	-2432(1)	4179(1)	6791(1)	62(1)
Br(1)	1103(1)	2919(1)	6580(1)	70(1)
S(2)	319(2)	5734(2)	6606(2)	54(1)
S(1)	3162(2)	4790(2)	6459(2)	53(1)
N(1)	3248(7)	6416(5)	6404(5)	46(2)
O(2)	6563(10)	8928(6)	5538(6)	105(3)
O(1)	4665(8)	8544(5)	4017(6)	92(3)
C(1)	2415(9)	5760(5)	6478(6)	40(2)
C(2)	2505(10)	7211(6)	6533(8)	55(2)
C(3)	2984(10)	7814(6)	5703(7)	59(3)
C(4)	4875(10)	7863(6)	5833(7)	52(3)
C(5)	5535(10)	7040(6)	5593(8)	61(3)
C(6)	5087(9)	6387(6)	6395(7)	53(2)
C(7)	5332(12)	8470(6)	5003(9)	59(3)
C(8)	7178(13)	9635(8)	4851(10)	96(4)
C(9)	8509(16)	9195(8)	4466(12)	120(5)

Bond lengths [Å] and angles [°].

Au(1)-S(2)	2.293(3)
Au(1)-S(1)	2.309(2)
Au(1)-Br(1)	2.4322(12)
Au(1)-Br(2)	2.4365(8)
S(2)-C(1)	1.730(7)
S(1)-C(1)	1.720(9)
N(1)-C(1)	1.292(10)
N(1)-C(2)	1.469(10)
N(1)-C(6)	1.486(9)
O(2)-C(7)	1.299(11)
O(2)-C(8)	1.564(13)
O(1)-C(7)	1.172(10)
C(2)-C(3)	1.504(11)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(3)-C(4)	1.501(10)
C(3)-H(3A)	0.9700
C(3)-H(3B)	0.9700
C(4)-C(7)	1.503(12)
C(4)-C(5)	1.514(12)
C(4)-H(4)	0.9800
C(5)-C(6)	1.530(11)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700

C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(8)-C(9)	1.449(14)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600

S(2)-Au(1)-S(1)	75.35(8)
S(2)-Au(1)-Br(1)	171.82(5)
S(1)-Au(1)-Br(1)	96.49(7)
S(2)-Au(1)-Br(2)	93.27(5)
S(1)-Au(1)-Br(2)	168.61(7)
Br(1)-Au(1)-Br(2)	94.90(4)
C(1)-S(2)-Au(1)	87.9(3)
C(1)-S(1)-Au(1)	87.6(3)
C(1)-N(1)-C(2)	121.3(7)
C(1)-N(1)-C(6)	120.5(8)
C(2)-N(1)-C(6)	117.4(7)
C(7)-O(2)-C(8)	118.9(8)
N(1)-C(1)-S(1)	126.8(6)
N(1)-C(1)-S(2)	124.0(7)
S(1)-C(1)-S(2)	109.2(5)
N(1)-C(2)-C(3)	111.2(7)
N(1)-C(2)-H(2A)	109.4
C(3)-C(2)-H(2A)	109.4
N(1)-C(2)-H(2B)	109.4
C(3)-C(2)-H(2B)	109.4
H(2A)-C(2)-H(2B)	108.0
C(4)-C(3)-C(2)	111.6(7)
C(4)-C(3)-H(3A)	109.3
C(2)-C(3)-H(3A)	109.3
C(4)-C(3)-H(3B)	109.3
C(2)-C(3)-H(3B)	109.3
H(3A)-C(3)-H(3B)	108.0
C(3)-C(4)-C(7)	110.9(7)
C(3)-C(4)-C(5)	108.8(7)
C(7)-C(4)-C(5)	109.7(8)
C(3)-C(4)-H(4)	109.1
C(7)-C(4)-H(4)	109.1
C(5)-C(4)-H(4)	109.1
C(4)-C(5)-C(6)	112.6(7)
C(4)-C(5)-H(5A)	109.1
C(6)-C(5)-H(5A)	109.1
C(4)-C(5)-H(5B)	109.1
C(6)-C(5)-H(5B)	109.1
H(5A)-C(5)-H(5B)	107.8
N(1)-C(6)-C(5)	110.5(7)
N(1)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6A)	109.5
N(1)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	108.1

O(1)-C(7)-O(2)	123.7(10)
O(1)-C(7)-C(4)	125.9(9)
O(2)-C(7)-C(4)	110.3(9)
C(9)-C(8)-O(2)	97.1(11)
C(9)-C(8)-H(8A)	112.3
O(2)-C(8)-H(8A)	112.3
C(9)-C(8)-H(8B)	112.3
O(2)-C(8)-H(8B)	112.3
H(8A)-C(8)-H(8B)	109.9
C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5

Anisotropic displacement parameters (Å^2 ×10^3); the anisotropic displacement factor exponent takes the form $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$.

Atom	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Au(1)	42(1)	47(1)	44(1)	4(1)	9(1)	-3(1)
Br(2)	46(1)	68(1)	75(1)	6(1)	19(1)	-9(1)
Br(1)	67(1)	49(1)	89(1)	1(1)	6(1)	2(1)
S(2)	46(1)	50(2)	70(2)	6(1)	24(1)	1(1)
S(1)	42(1)	50(2)	70(2)	4(1)	17(1)	1(1)
N(1)	38(4)	58(6)	45(4)	2(4)	15(3)	-14(4)
O(2)	112(6)	122(8)	75(5)	12(5)	6(4)	-72(6)
O(1)	101(5)	123(8)	46(4)	15(5)	1(4)	-40(5)
C(1)	38(4)	45(6)	37(4)	5(4)	10(3)	5(4)
C(2)	56(5)	47(7)	69(6)	-4(5)	27(5)	4(5)
C(3)	67(6)	62(8)	50(5)	7(5)	18(4)	-4(5)
C(4)	56(5)	59(8)	40(5)	2(5)	6(4)	-21(5)
C(5)	49(5)	78(9)	60(6)	-2(6)	17(4)	-21(5)
C(6)	38(5)	59(7)	66(6)	8(5)	16(4)	3(4)
C(7)	63(6)	55(8)	62(7)	4(6)	18(5)	-18(5)
C(8)	77(7)	111(12)	105(9)	17(9)	33(7)	3(7)
C(9)	121(10)	85(12)	151(13)	5(10)	21(9)	17(8)

Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$).

Atom	x	y	z	U(eq)
H(2A)	2900	7400	7328	72
H(2B)	1278	7164	6383	72
H(3A)	2463	7661	4909	76
H(3B)	2551	8340	5850	76
H(4)	5396	8022	6635	68
H(5A)	6759	7066	5694	80
H(5B)	5061	6894	4788	80
H(6A)	5366	5862	6128	69
H(6B)	5750	6466	7181	69
H(8A)	6297	9819	4204	124
H(8B)	7616	10086	5352	124
H(9A)	9326	9006	5133	157
H(9B)	9058	9544	4009	157
H(9C)	8024	8743	4000	157

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