Supporting Information

for

Efficient Molecular Ruthenium Catalysts Containing Anionic Ligands for Water Oxidation

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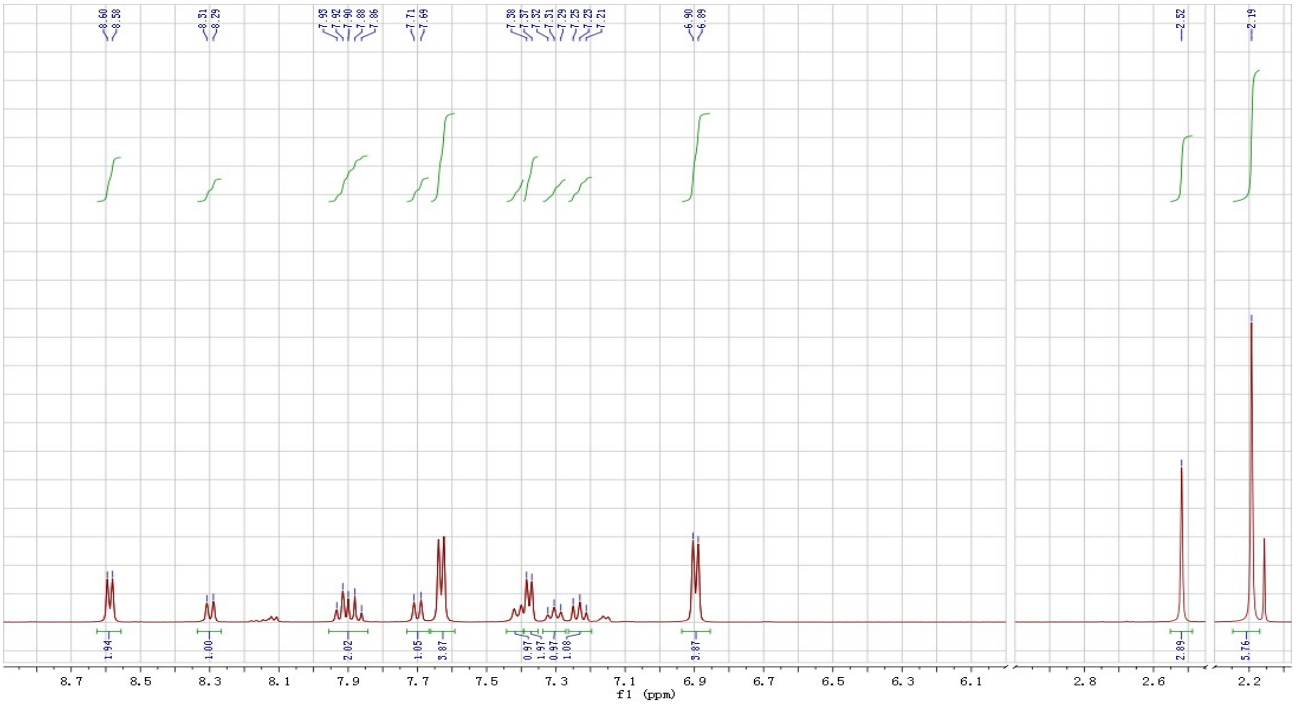

Figure S1. ^{1}H NMR of **1** in d_4-methanol.

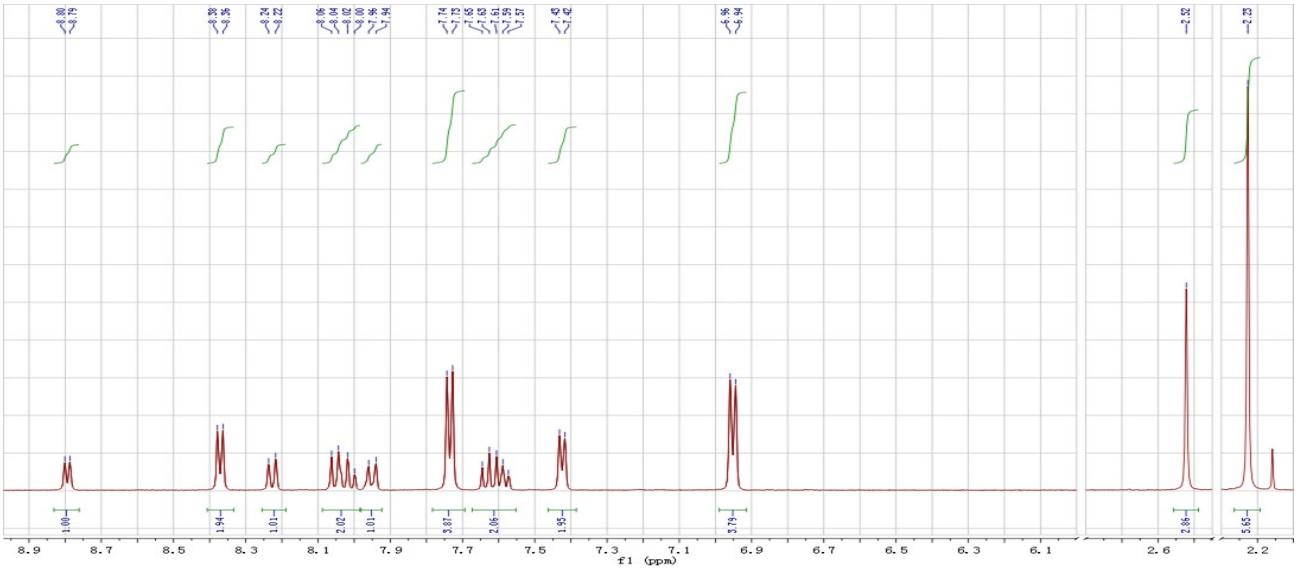

Figure S2. ^{1}H NMR of **2** in d_4-methanol.

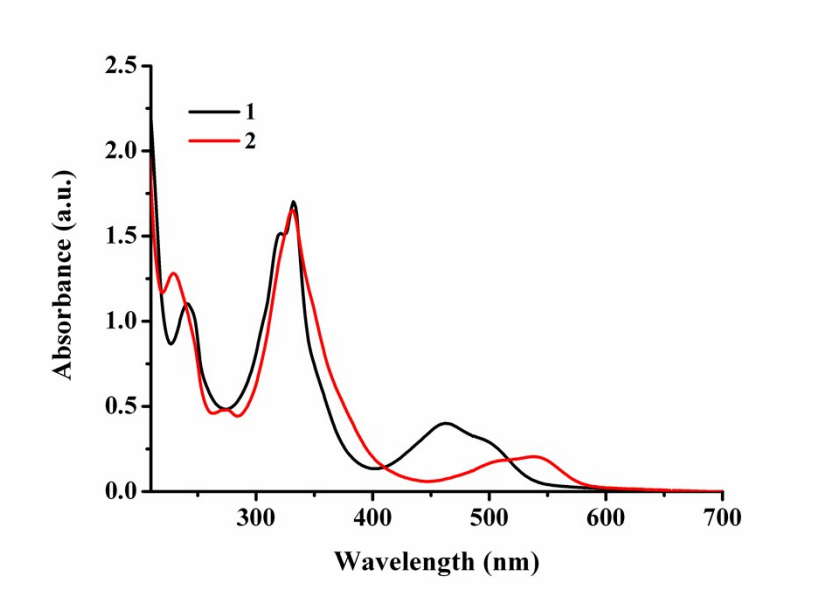

Figure S3. UV−vis absorption spectra of **1** and **2** in CF_3CH_2OH solution.

The UV−vis spectral changes of **1** and **2** upon variation of the pH from 4.28 to 8.03 were recorded in aqueous solutions (Figure S4 and S6). The pKa values for [**1**H] $^+$ and [**2**H]$^+$ were calculated to be 6.43 and 6.67, by nonlinear sigmoidal fits to the absorption changes at 332 and 331 nm respectively, as illustrated in the Figure S5 and S7.

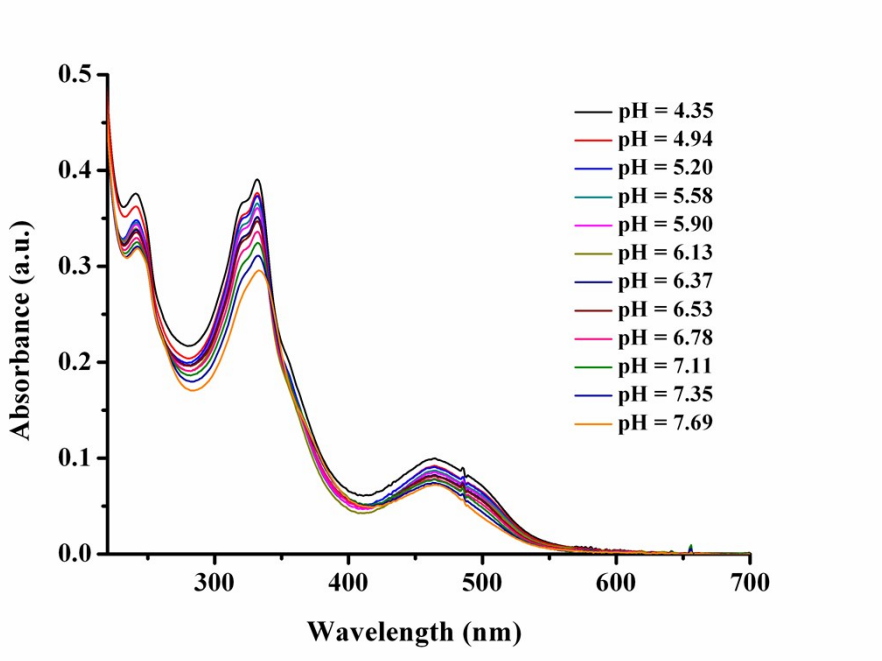

Figure S4. Spectrophotometric titration of **1** in NaH_2PO_4 aqueous solution containing 10% CF_3CH_2OH. The pH value was adjusted by adding triflic acid or 1 M NaOH solution.

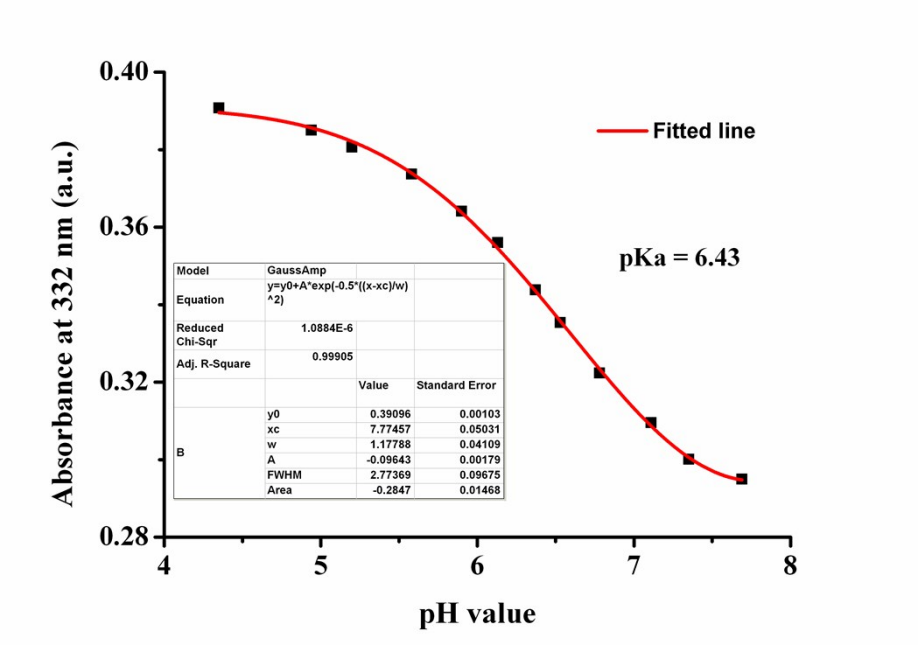

Figure S5. Determination of pKa of **1** by fitting the absorbance at 332 nm.

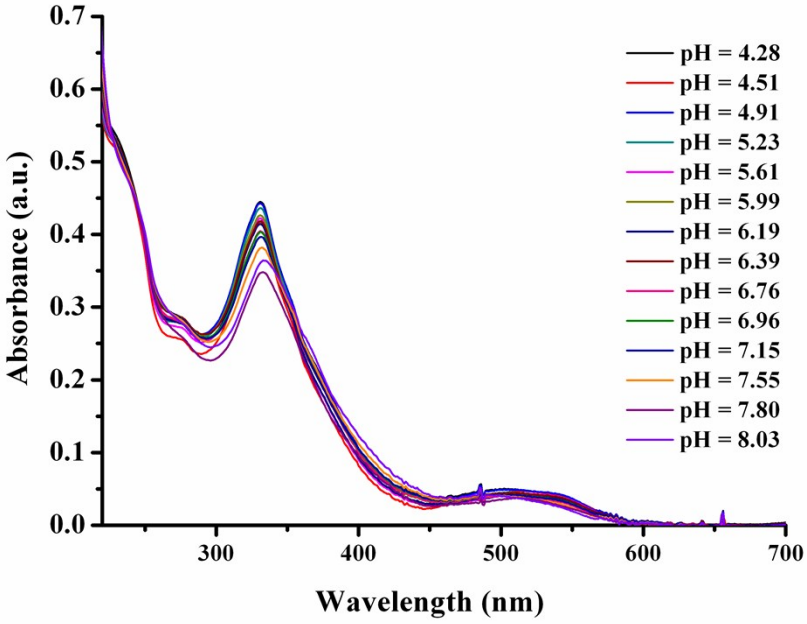

Figure S6. Spectrophotometric titration of **2** in NaH_2PO_4 aqueous solution containing 10% CF_3CH_2OH. The pH value was adjusted by adding triflic acid or 1 M NaOH solution.

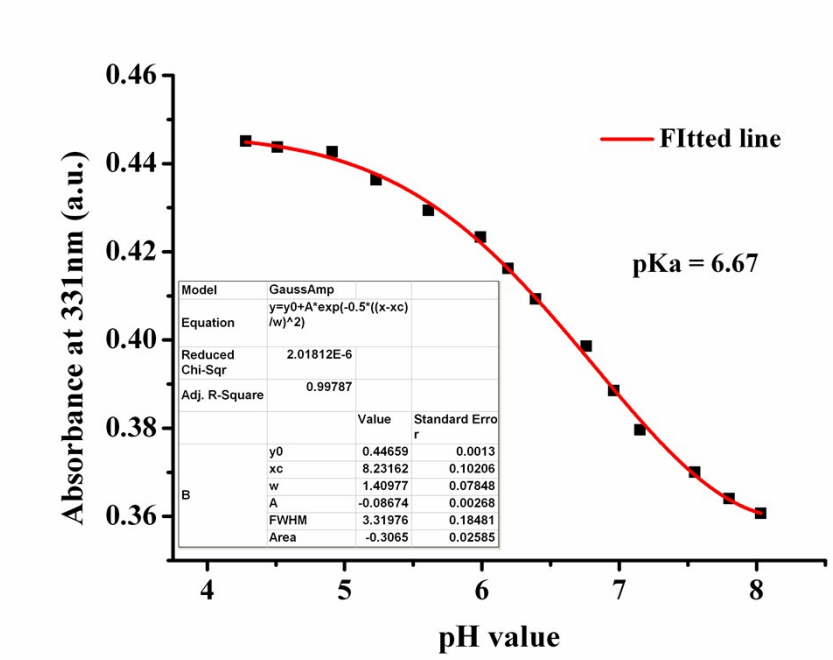

Figure S7. Determination of pKa of **2** by fitting the absorbance at 331 nm.

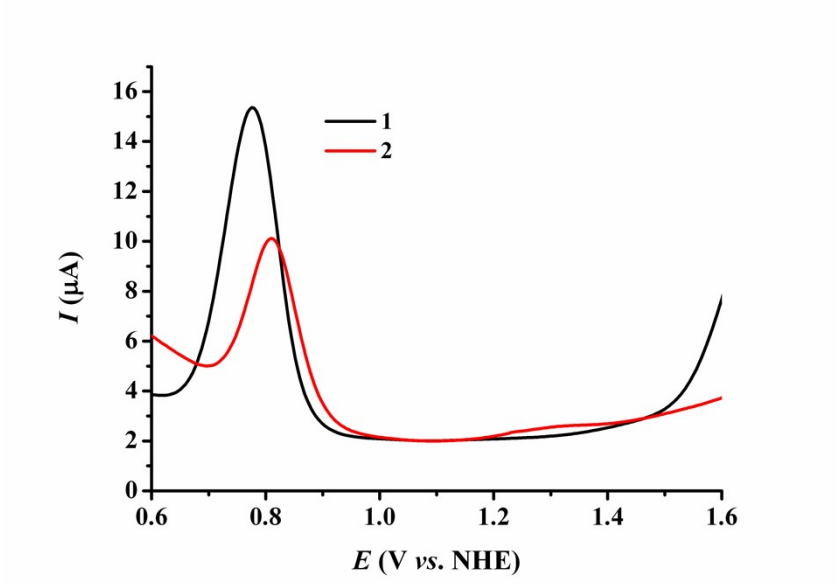

Figure S8. DPV curves of **1** and **2** in CF_3SO_3H (pH 1.0) containing 10% CF_3CH_2OH.

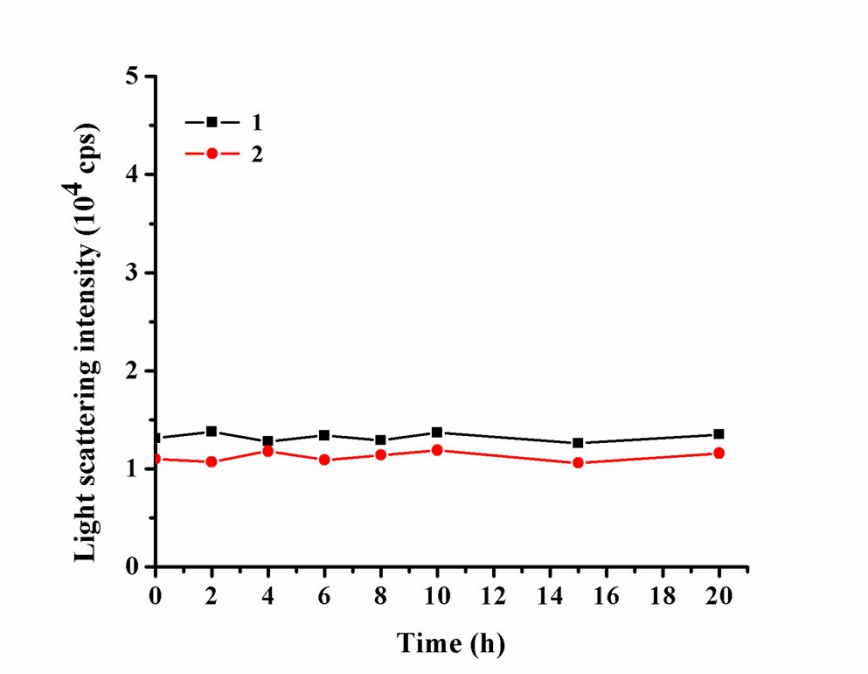

Figure S9. Light scattering intensity as a function of reaction time in an aqueous solution of CF_3SO_3H (pH 1.0) containing Ce^{IV} (0.2 M). black: 10 μM **1**; red: 10 μM **2**.

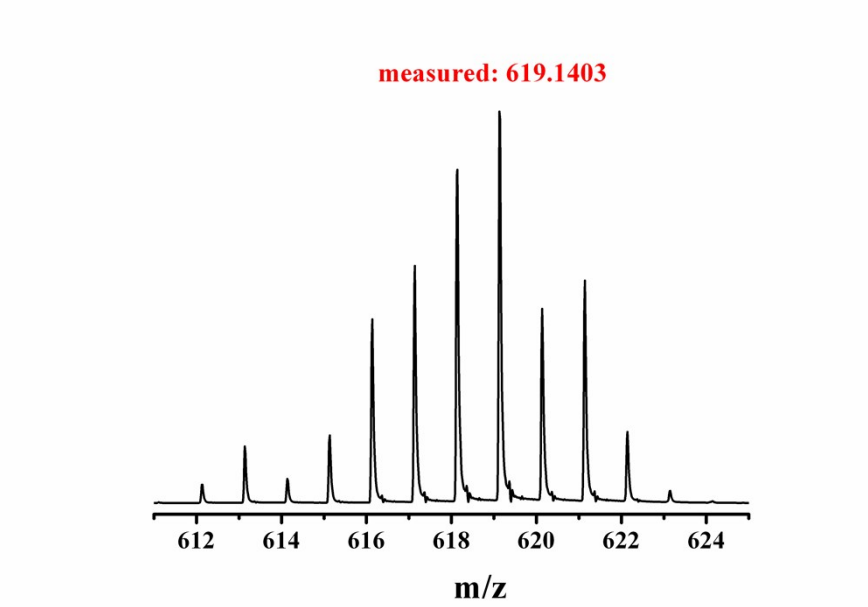

Figure S10. HRMS spectra (positive mode) of $[H(L1)(4\text{-picoline})_3Ru^{II}]^+$ (calculated: 619.1395). Condition: catalyst **1** in CF_3CH_2OH/H_2O (1:9).

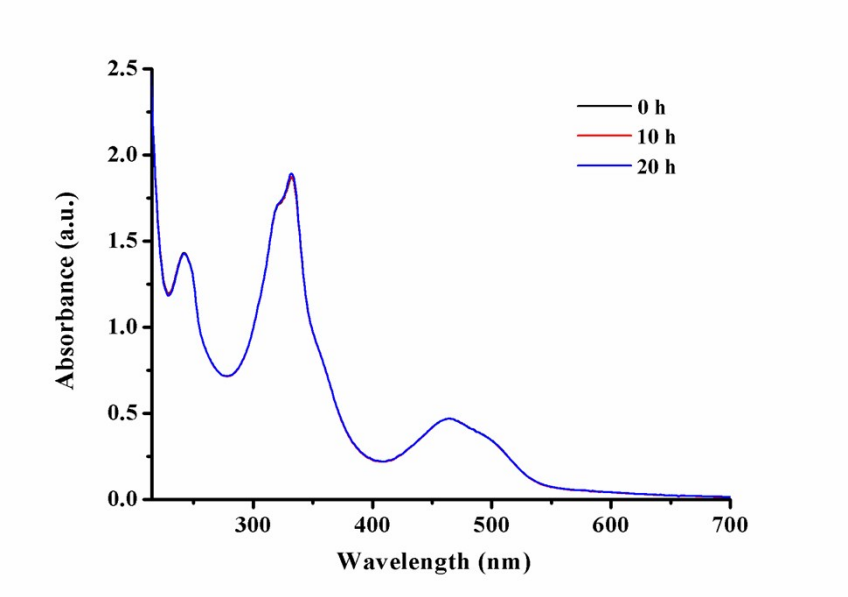

Figure S11. UV-vis absorption spectra of **1** in CF_3SO_3H aqueous solution (pH = 1.0) over a 20 h period.

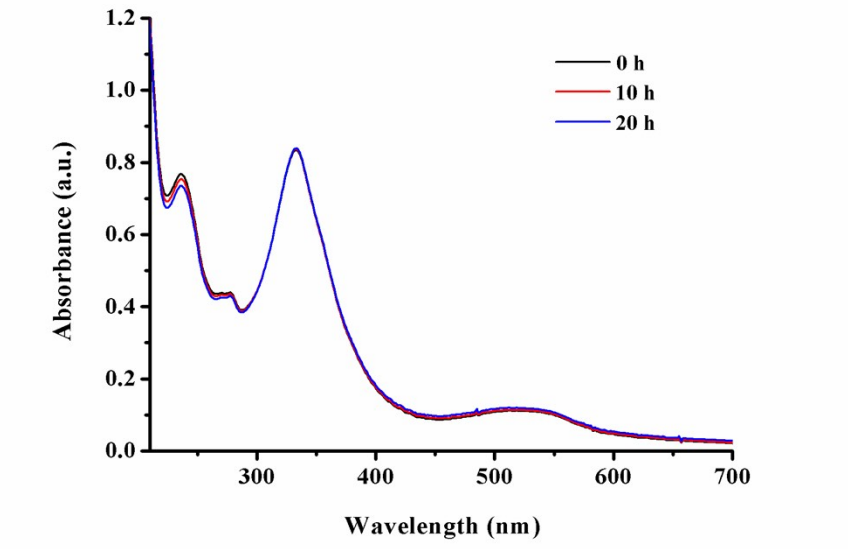

Figure S12. UV-vis absorption spectra of **2** in CF_3SO_3H aqueous solution (pH = 1.0) over a 20 h period.

Table S1. Summary of the Crystal Data for 1

	1
Empirical formula	$C_{31}H_{42}N_6O_9Ru$
Formula weight	743.77
Temperature/K	296(2)
Crystal system	monoclinic
space group	Cc
a/Å	14.819(2)
b/Å	25.424(3)
c/Å	29.317(5)
α/°	90
β/°	99.017(2)
γ/°	90
Volume/Å^3	10909(3)
Z	12
ρ_{calc} g/cm^3	1.359
μ/mm^{-1}	0.488
F(000)	4632.0
Crystal size/mm^3	0.12 × 0.12 × 0.08
Radiation	MoKα (λ = 0.71073)
Theta range for data collection/°	3.204 to 50.054
Index ranges	$-17 \le h \le 16$, $-30 \le k \le 26$, $-34 \le l \le 34$
Reflections collected	23177
Independent reflections	15693 [R_{int} = 0.0572, R_{sigma} = 0.1045]
Data/restraints/parameters	15693/1127/1163
Goodness-of-fit on F^2	0.930
Final R indexes [I>2σ (I)]	R_1 = 0.0592, wR_2 = 0.1316
Final R indexes [all data]	R_1 = 0.1035, wR_2 = 0.1506
Largest diff. peak and hole / e Å^{-3}	0.58/-0.53
Flack parameter	0.34(5)