Supporting Information

for

Preparation, structure and redox properties of novel ruthenium(II) hexachloromacrobicyclic complexes and the first polyaromatic-terminated diaminoclathrochelate derivative, its physisorption on carbon materials and electrocatalytic activity in the hydrogen evolution reaction $2H^+/H_2$

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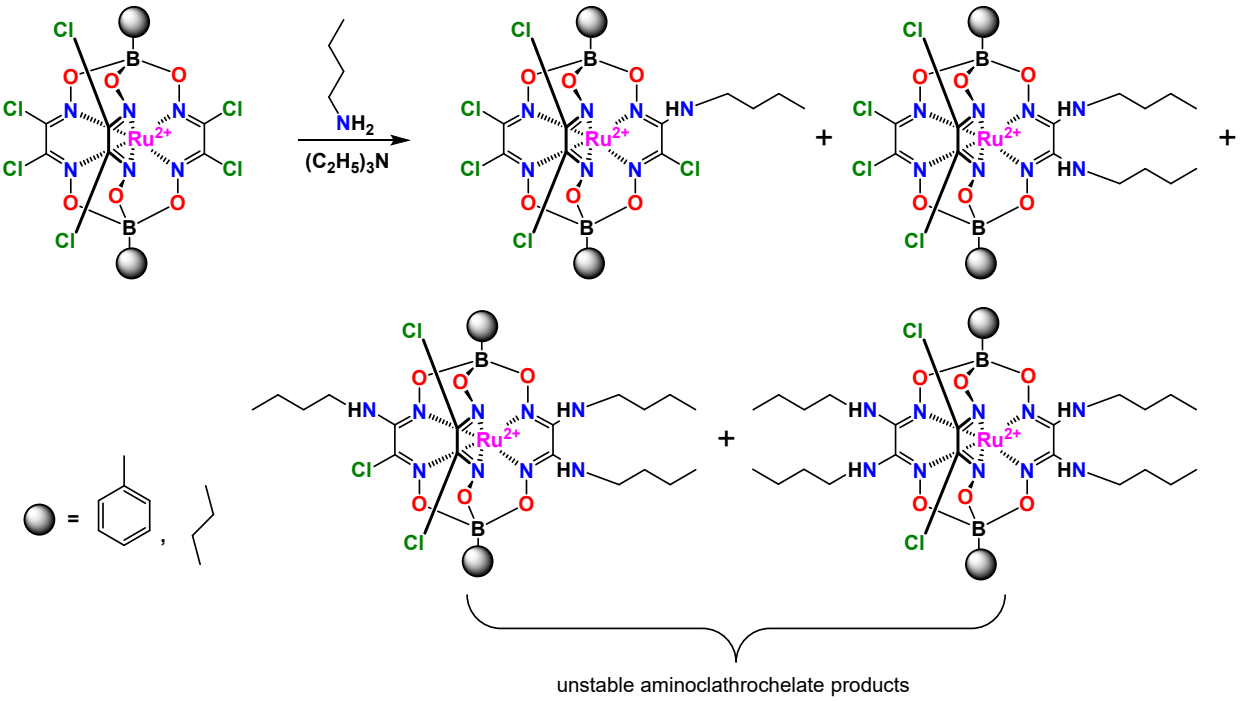

Scheme S1. Attempted stepwise nucleophilic substitution of the obtained ruthenium(II) hexachloroclathrochelates with *n*-butylamine as a model aliphatic unhindered *N*-nucleophile.

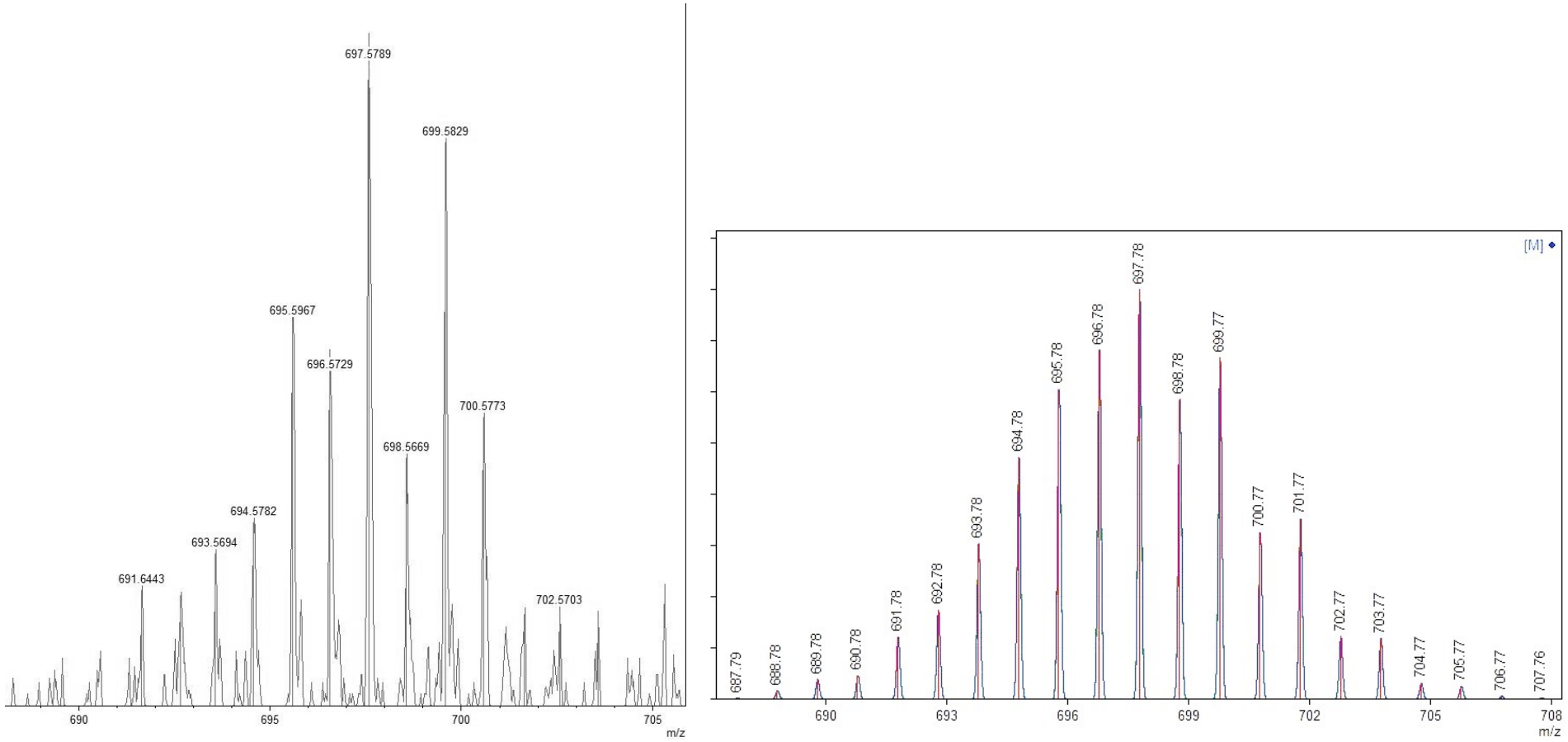

Figure S1. Fragment (left) of MALDI-TOF mass spectrum of the clathrochelate ruthenium(II) $Ru(Cl_2Gm)_3(B4\text{-}C_6H_4CH_3)(BF)$ in its negative range and the theoretically calculated isotopic distribution in the corresponding molecular ion (right).

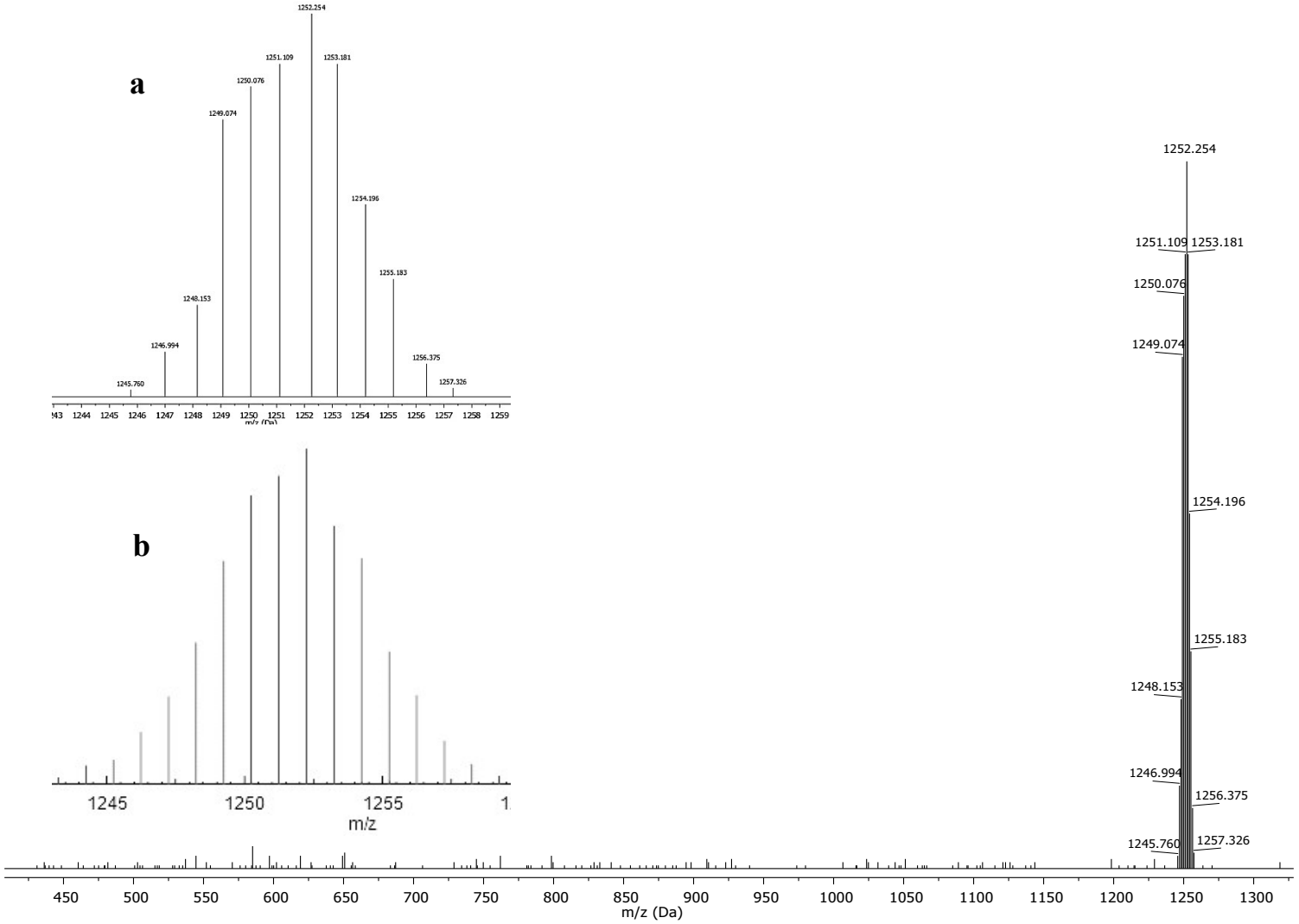

Figure S2. MALDI-TOF mass spectrum of the clathrochelate ruthenium(II) $Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}tert\text{-}C_4H_9C_6H_4)_2$ in its positive range. Inserts: its fragment (**a**) and the theoretically calculated isotopic distribution in the corresponding molecular ion (**b**).

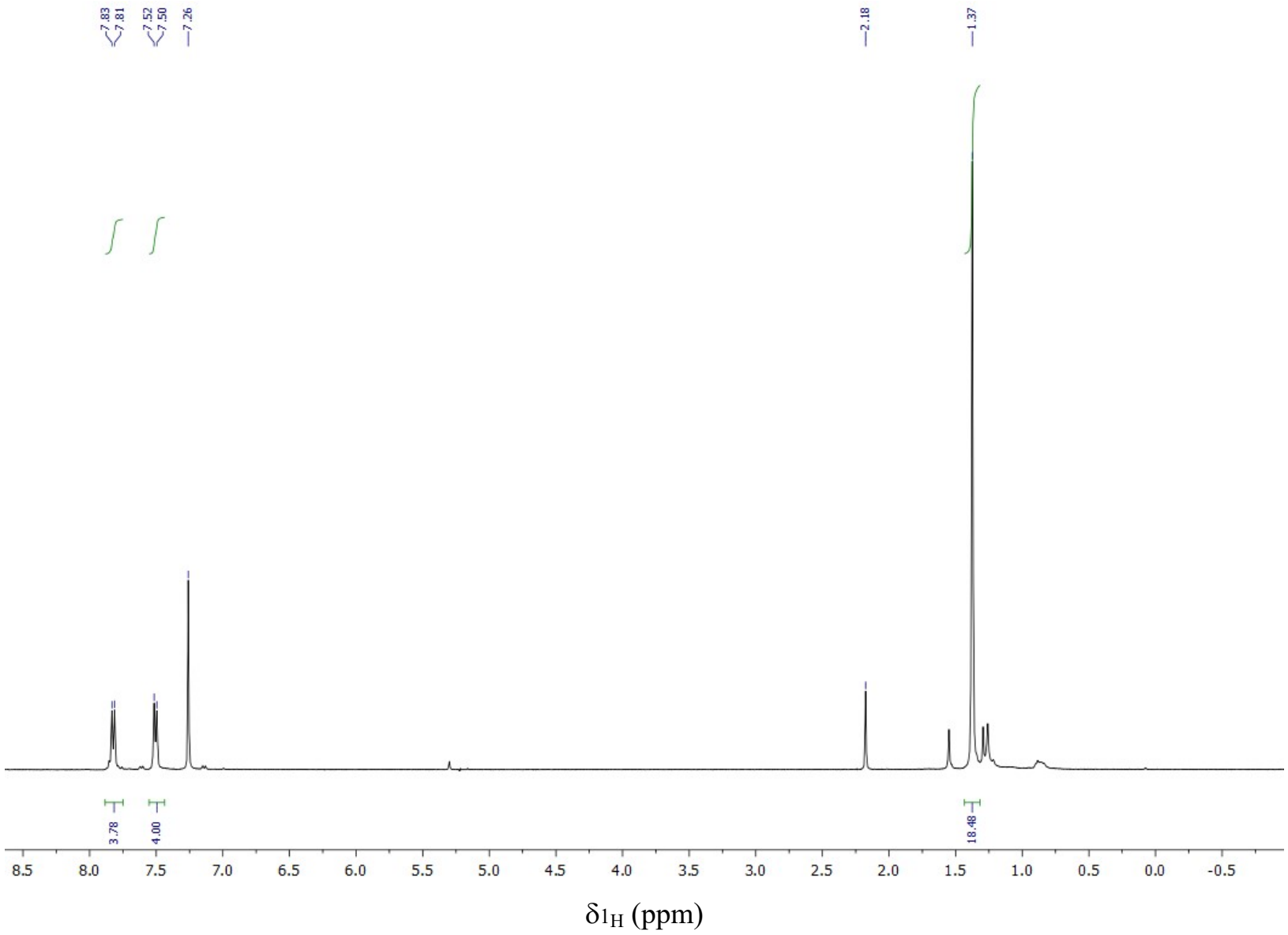

Figure S3. ^{1}H NMR spectrum of the clathrochelate complex $Ru(Cl_2Gm)_3(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$ in $CDCl_3$.

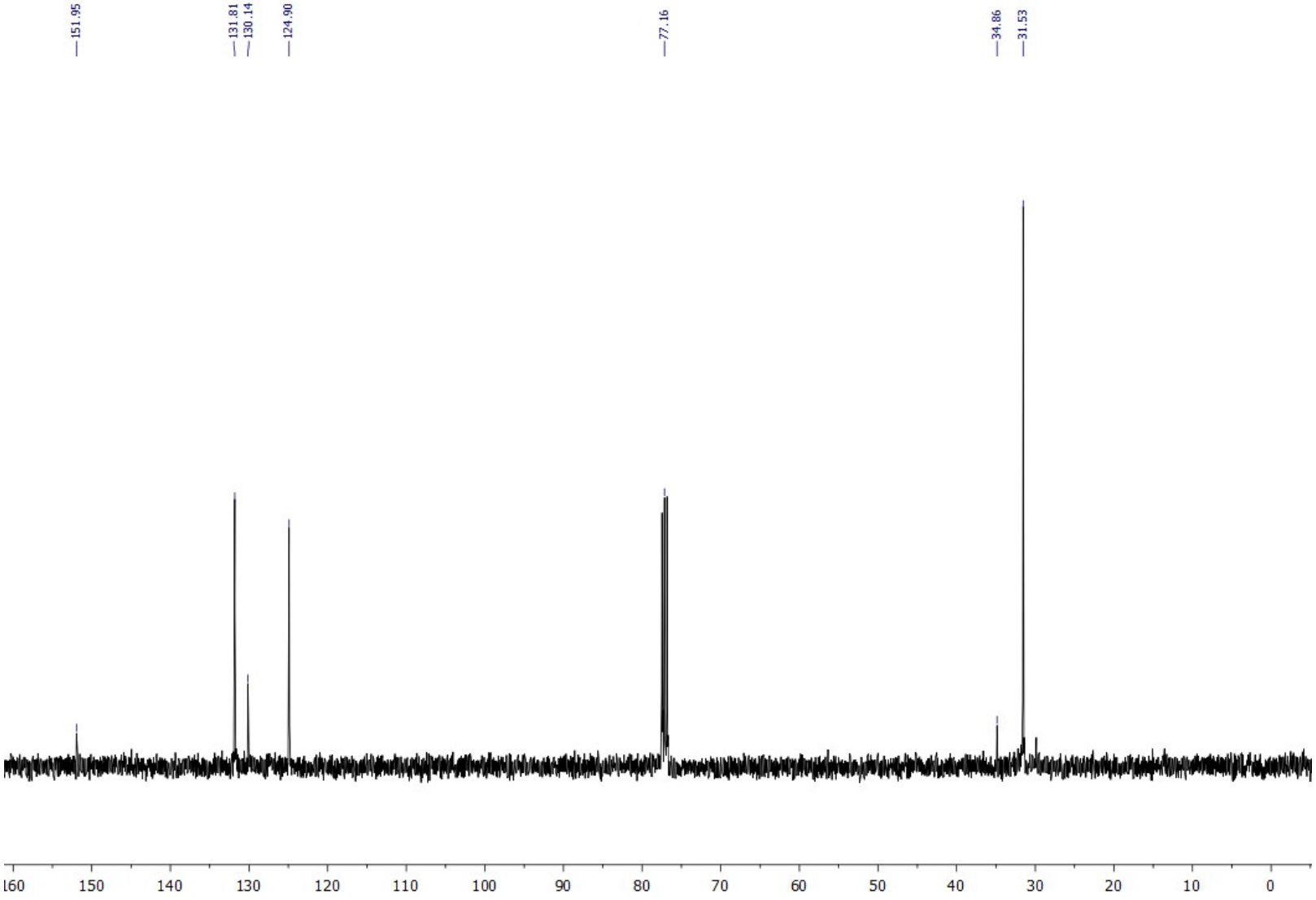

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of the clathrochelate complex $Ru(Cl_2Gm)_3(B4\text{-}(\textit{tert}\text{-}C_4H_9C_6H_4))_2$ in $CDCl_3$.

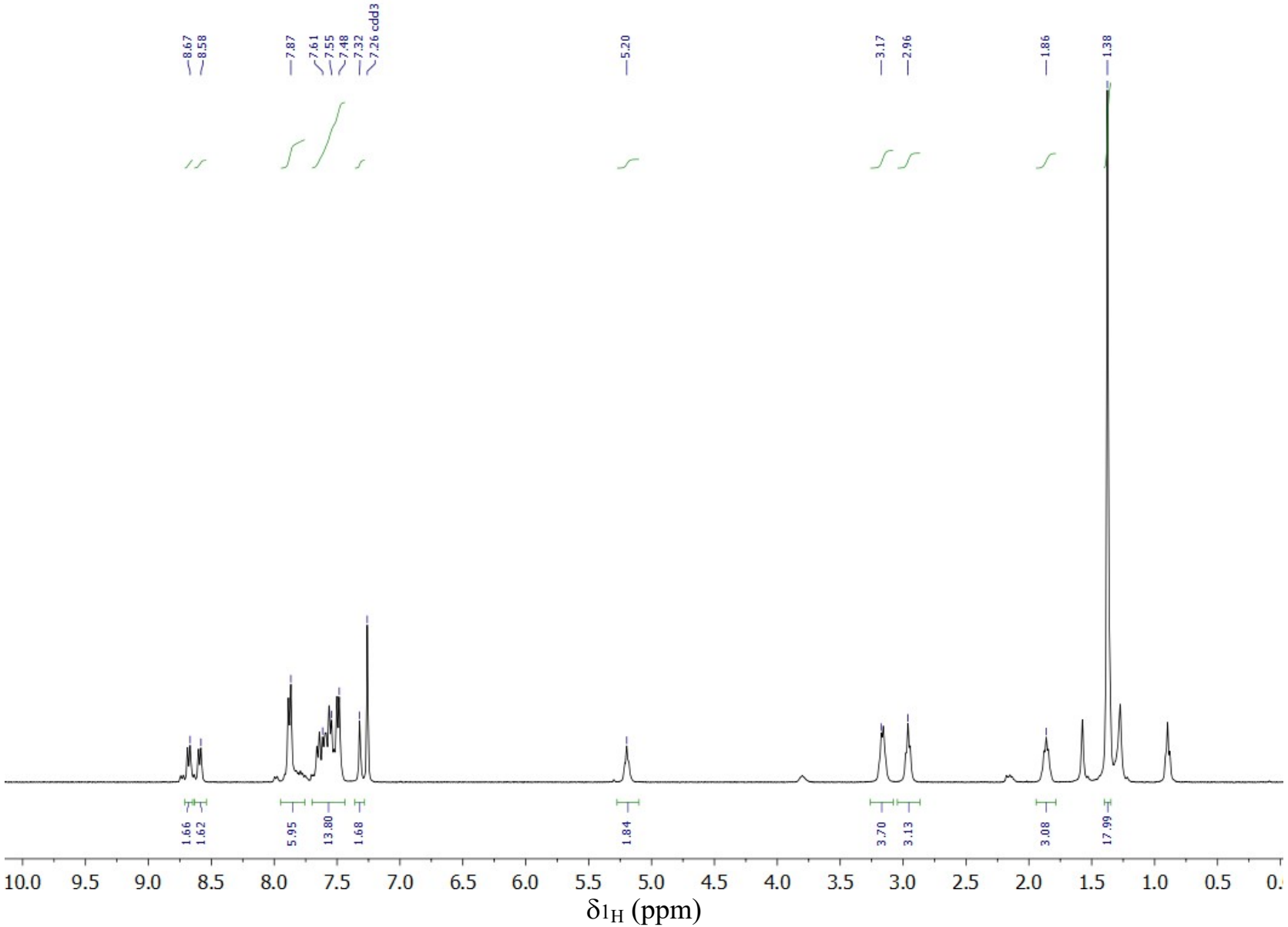

Figure S5. ^{1}H NMR spectrum of the clathrochelate complex $Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$ in $CDCl_3$.

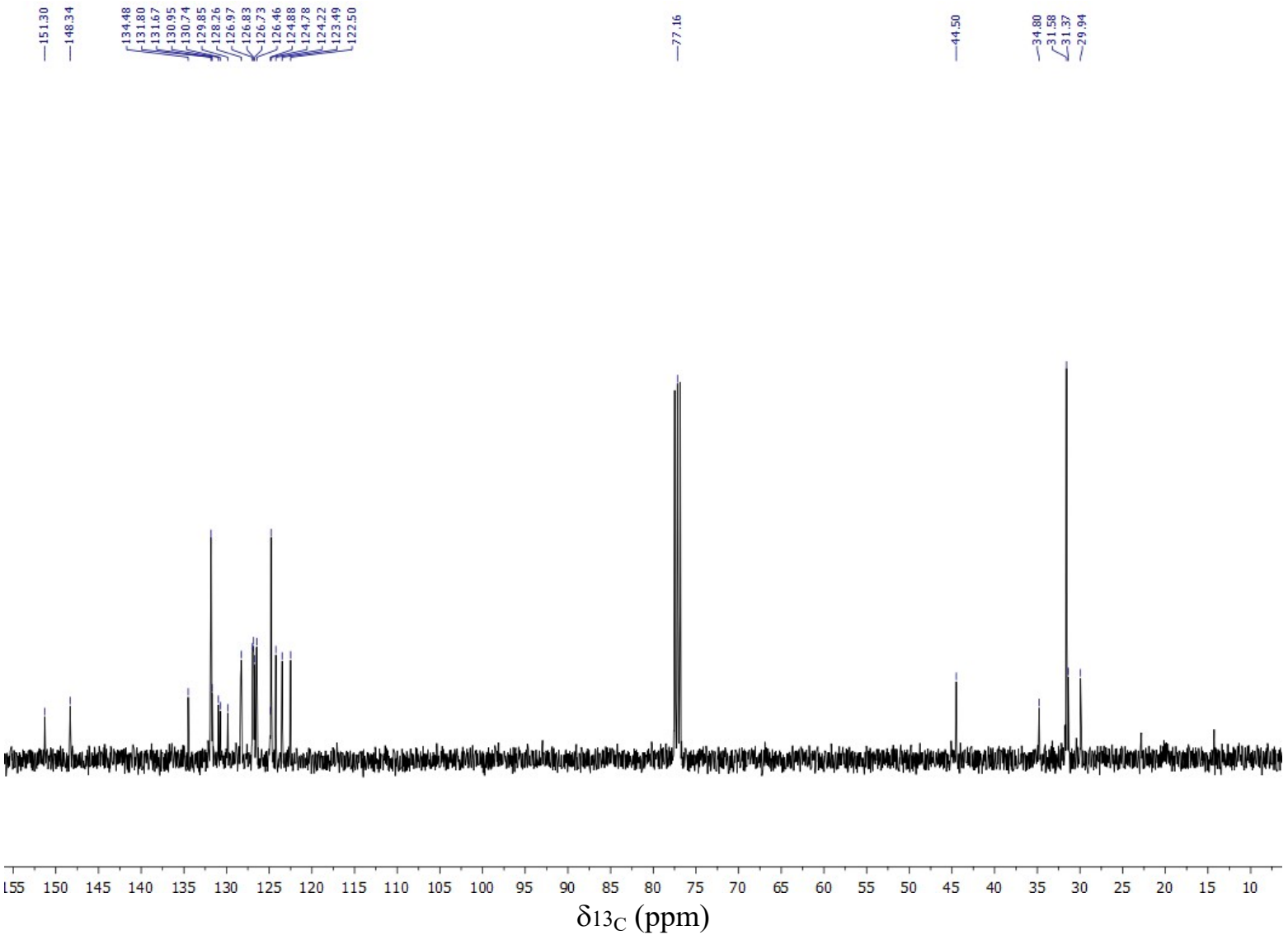

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of the clathrochelate complex $Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}(\textit{tert}\text{-}C_4H_9C_6H_4))_2$ in $CDCl_3$.

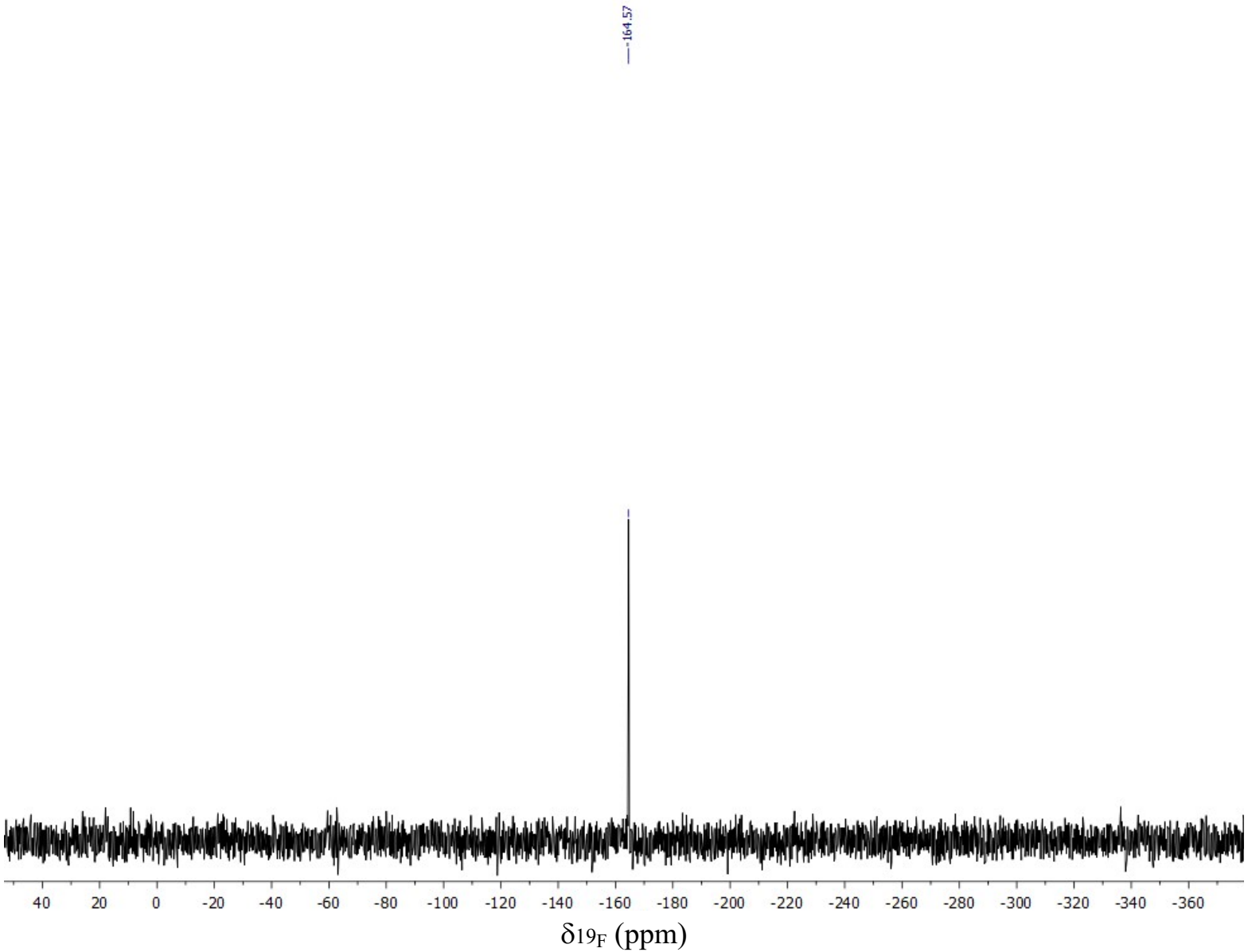

Figure S7. ^{19}F NMR spectrum of the clathrochelate complex $Ru(Cl_2Gm)_3(B4\text{-}C_6H_4CH_3)(BF)$ in $CDCl_3$.

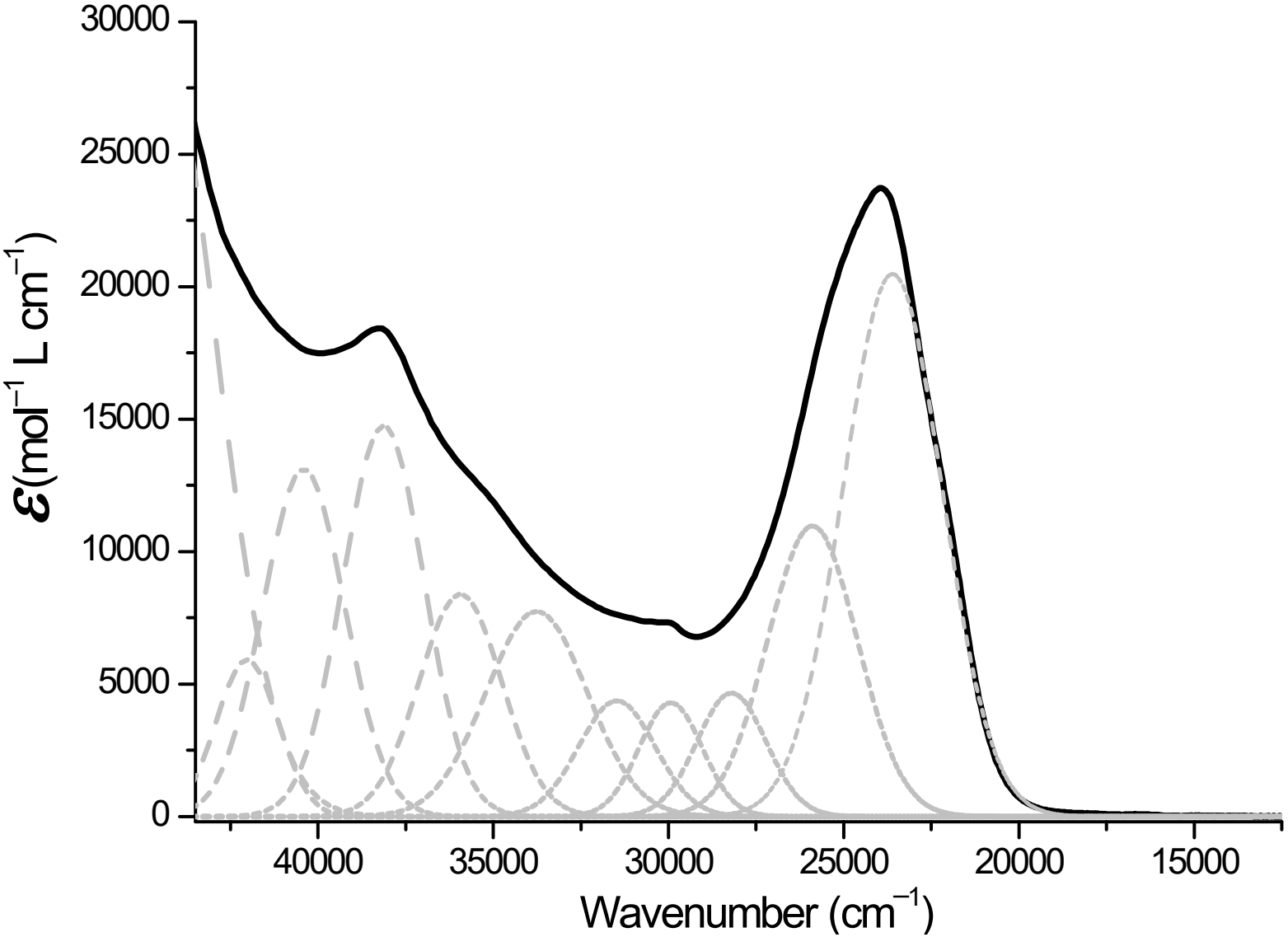

Figure S8. Solution UV-vis spectrum of the clathrochelate $Ru(Cl_2Gm)_3(B4\text{-}C_6H_4CH_3)(BF)$ in CH_2Cl_2 (shown in black line) and its deconvolution into the Gaussian components (shown in grey dotted lines).

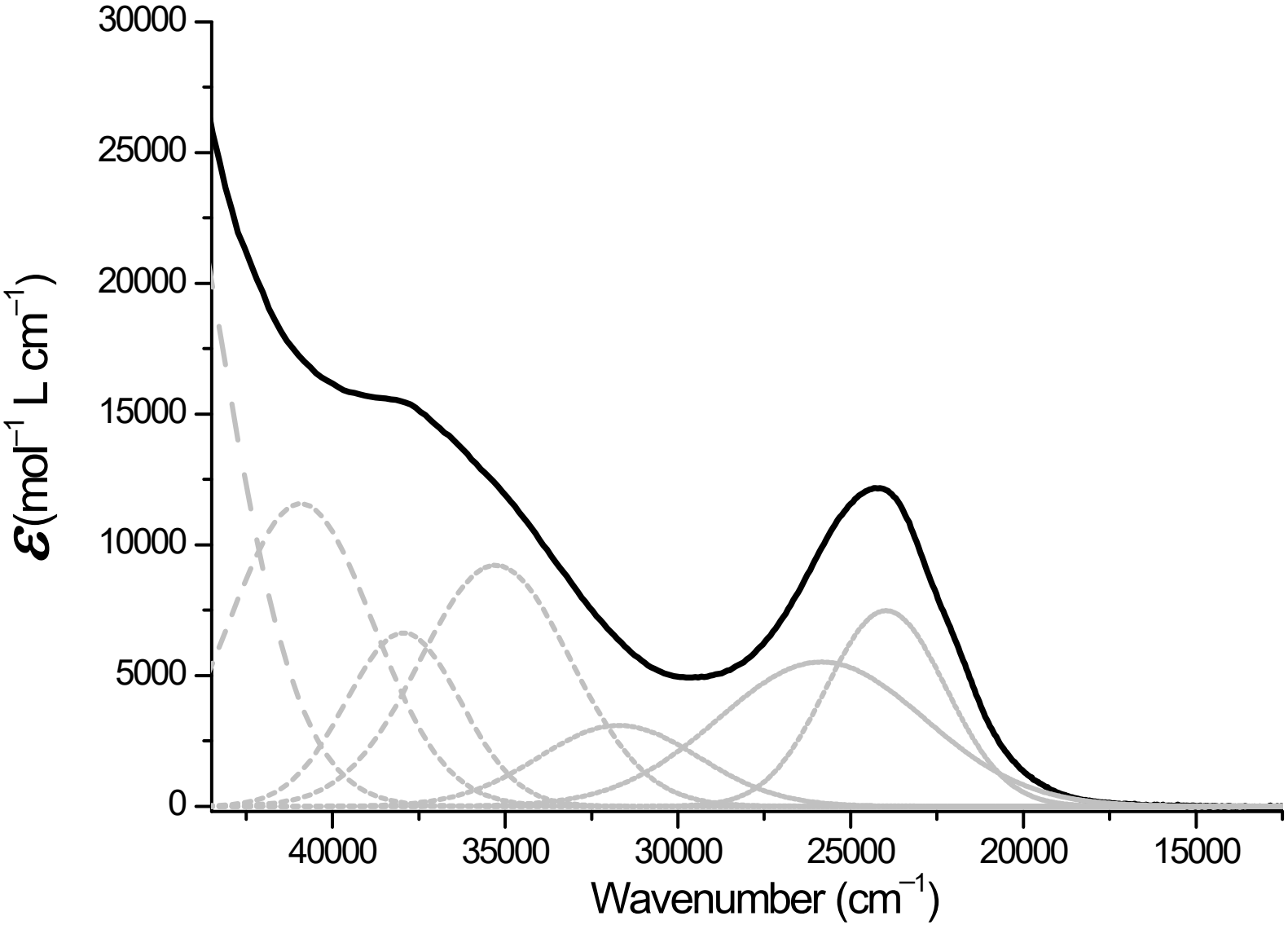

Figure S9. Solution UV-vis spectrum of the clathrochelate $Ru(Cl_2Gm)_3(B4\text{-}C_6H_4CH_3)_2$ in CH_2Cl_2 (shown in black line) and its deconvolution into the Gaussian components (shown in grey dotted lines).

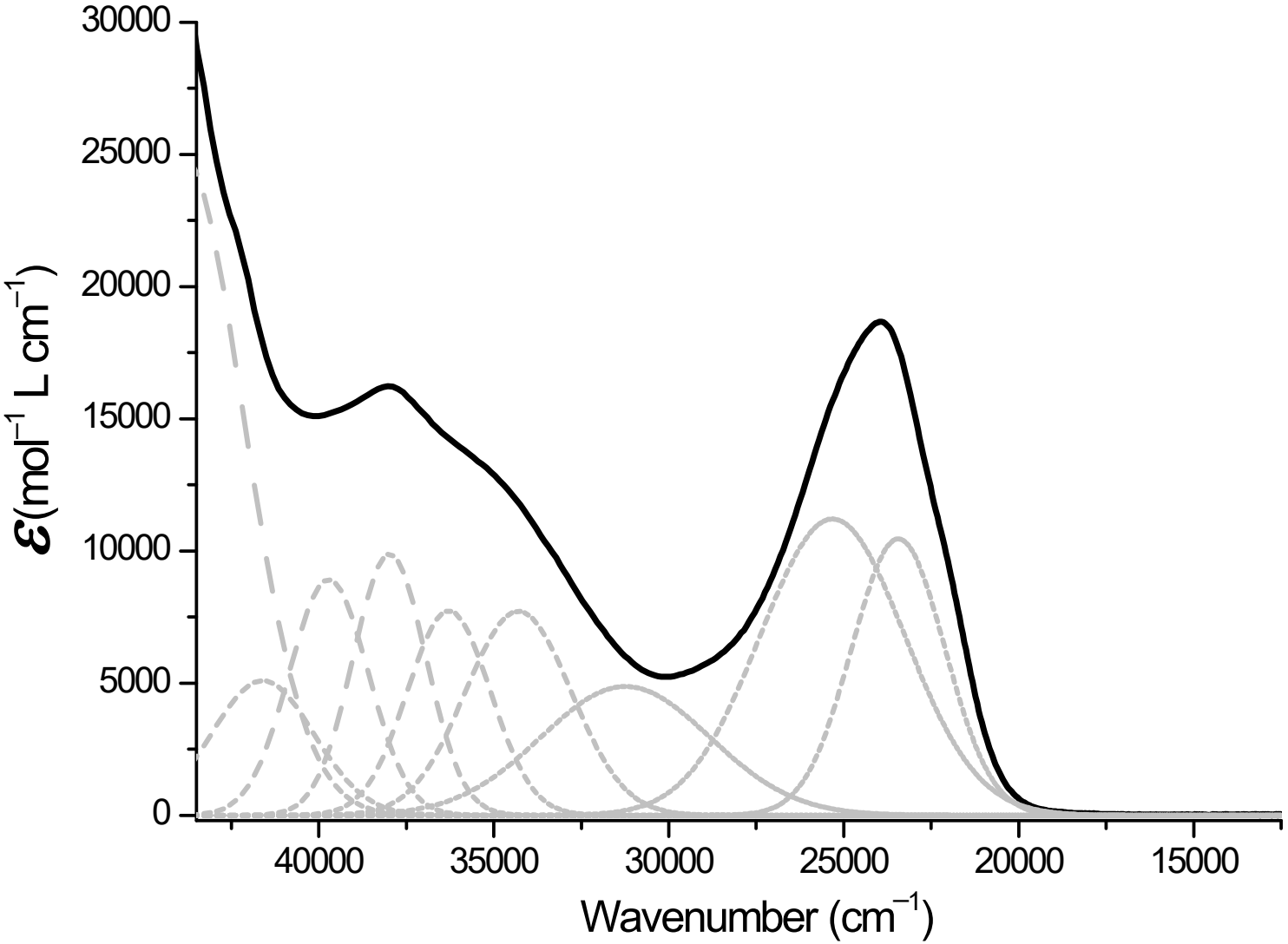

Figure S10. Solution UV-vis spectrum of the clathrochelate $Ru(Cl_2Gm)_3(B4\text{-}(\textit{tert}\text{-}C_4H_9C_6H_4))_2$ in CH_2Cl_2 (shown in black line) and its deconvolution into the Gaussian components (shown in grey dotted lines).

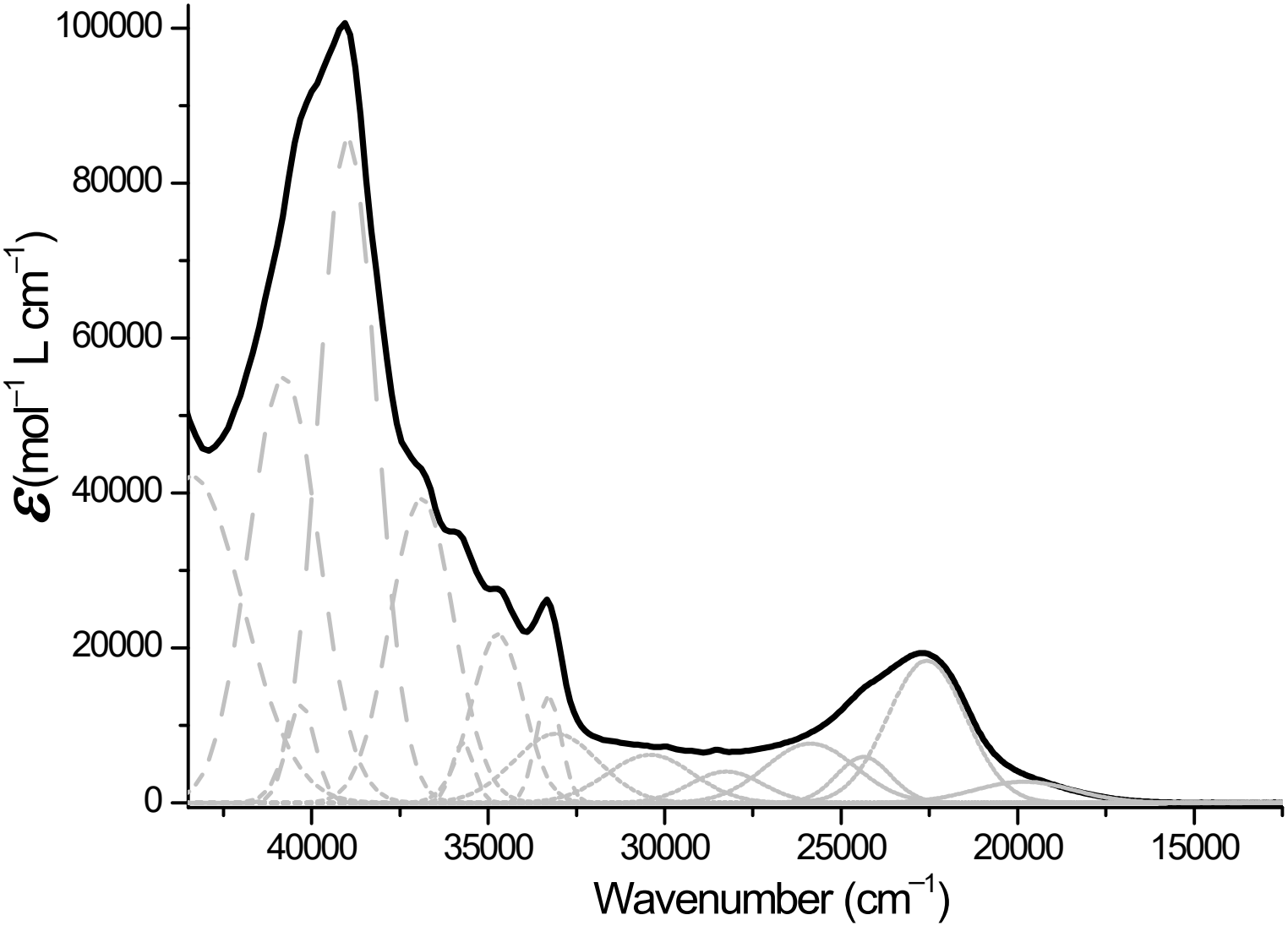

Figure S11. Solution UV-vis spectrum of the clathrochelate $Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$ in CH_2Cl_2 (shown in black line) and its deconvolution into the Gaussian components (shown in grey dotted lines).

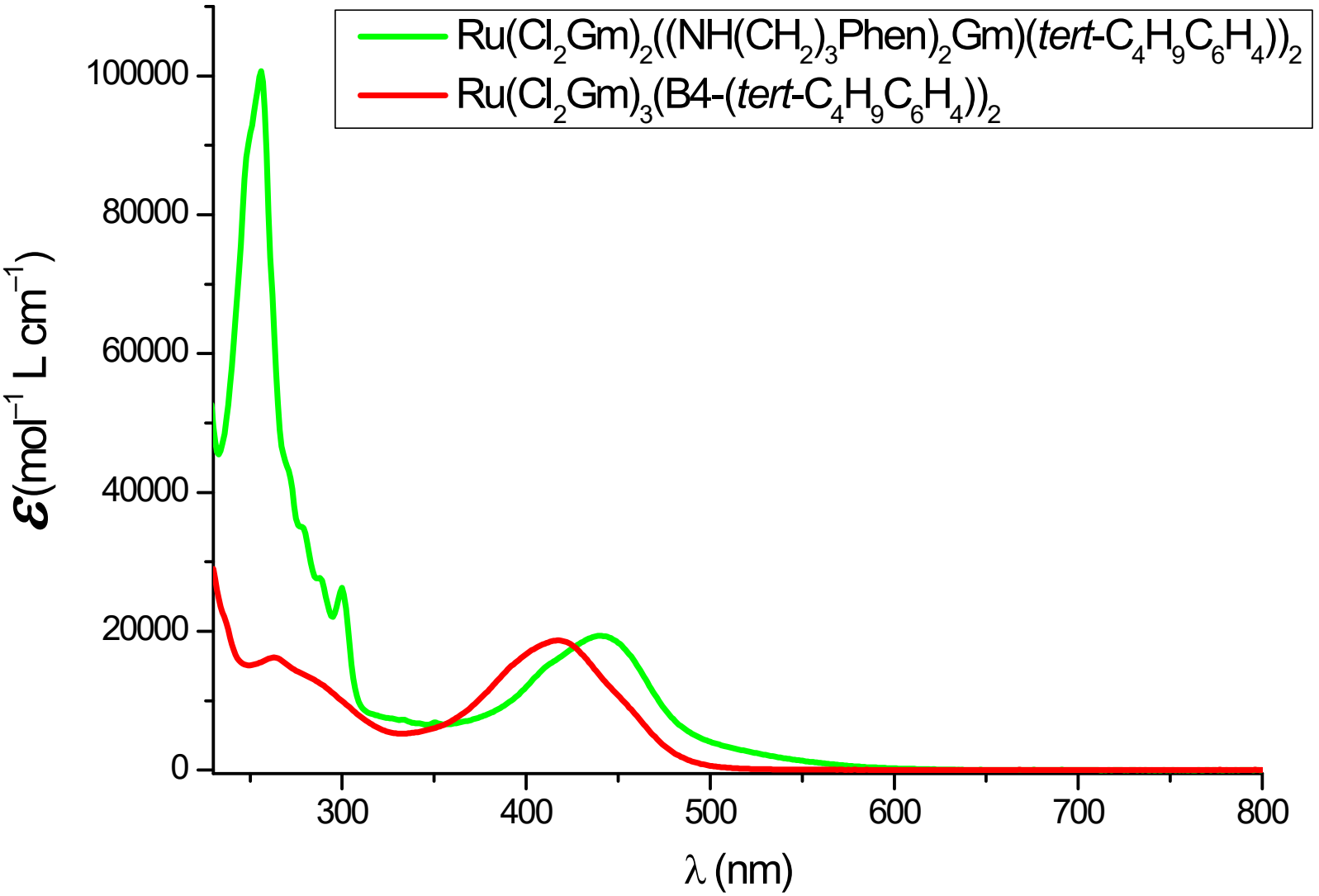

Figure S12. The dichloromethane solution UV-vis spectra of the diphenanthtrenyl-terminated ruthenium(II) diaminoclathrochelate and its precursor.

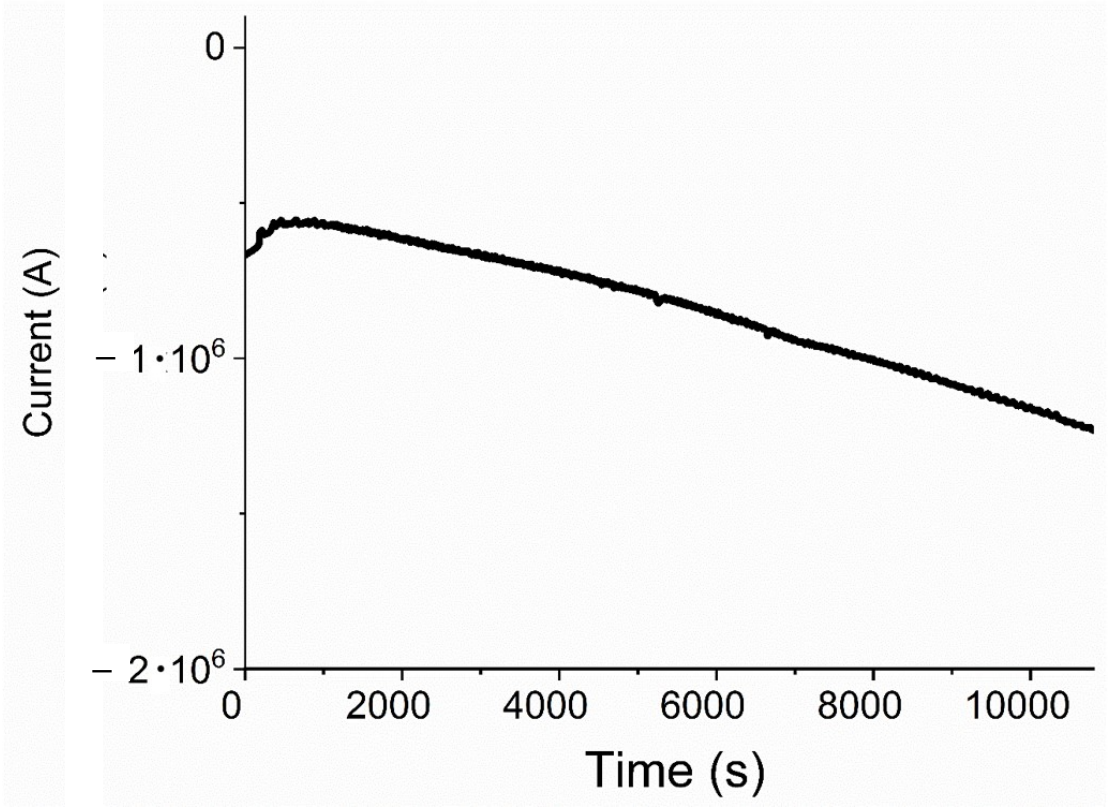

Figure S13. Bulk electrolysis profile at the potential of –1.4V (*vs.* Fc^+/Fc) for the dichloromethane solution of $Ru(Cl_2Gm)_3(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$ in the presence of 20 equiv. of $(DMFH^+)(OTf^-)$), as a source of H^+ ions. Porous carbon was used as a working electrode. Electrolysis was performed in a three-electrode divided cell equipped with platinum auxiliary and $Ag/AgBF_4$ reference electrodes.

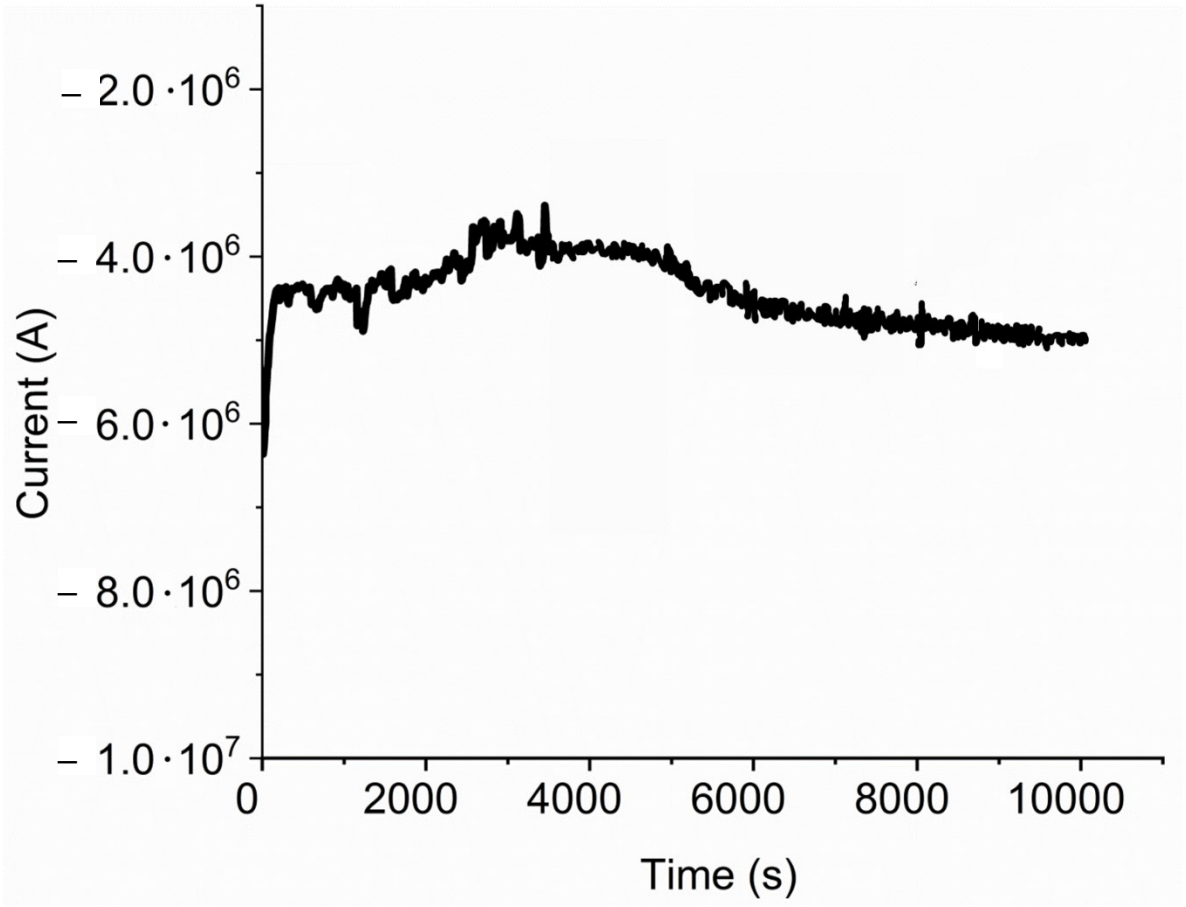

Figure S14. Bulk electrolysis profile at the potential of –1.3V (*vs.* Fc^+/Fc) for the dichloromethane solution of $Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$ in the presence of 20 equiv. of $(DMFH^+)(OTf^-)$), as a source of H^+ ions. Porous carbon was used as a working electrode. Electrolysis was performed in a three-electrode divided cell equipped with platinum auxiliary and $Ag/AgBF_4$ reference electrodes.

Calculation of TONs

Values of TON for the prepared novel ruthenium(II) clathrochelates were calculated using the bulk potential-controlled electrolysis data for their solutions. These experiments were performed at room temperature under intensive stirring in dry N_2 atmosphere with a Ellins P-45X potentiostat using a three-electrode divided cell. It was equipped with platinum auxiliary and $Ag/AgBF_4$ reference electrodes, while the porous carbon was used as a working electrode. This cell contained 0.011mmol of the clathrochelate $Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$ or 0.012mmol of its hexachloromacrobicyclic precursor $Ru(Cl_2Gm)_3(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$, 0.24mmol of $(DMFH^+)(OTf^-)$ as a source of H^+ ions, 0.2M solution of $((n\text{-}C_4H_9)_4N)(BF_4)$ as a supporting electrolyte, and 20mL of dichloromethane. The chamber of a given counter electrode contained 0.1mmol of ferrocene, 0.2M solution of $((n\text{-}C_4H_9)_4N)(BF_4)$, and 1mL of dichloromethane. Total amounts of electrons involved in the redox reaction $2H^+/H_2$ were found to be of 47.3 and of 11.8C, respectively, after 3-hours electrolysis at the potential from –1.3 to –1.4V (*vs.* Fc^+/Fc). These amounts are equal to 0.490 and to 0.122mmol, respectively. Producing of each molecule of H_2 requires two electrons. Therefore, the number of thus produced moles of H_2 corresponds to a half of the equivalents of used electrons (0.245 and 0.061mmol, respectively). 0.012mmols of the complex $Ru(Cl_2Gm)_3(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$ were applied in the corresponding experiment and, therefore, the value of TON for it was calculated to be approximately 20.4 (0.245 mmol per 0.012 mmol). 0.011mmols of the clathrochelate $Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$ were applied and the value of TON for it was calculated to be approximately 5.5 (0.061 mmol per 0.011 mmol).

Table S1. Crystallographic data and refinement parameters for the obtained novel ruthenium(II) clathrochelates

Parameter	$Ru(Cl_2Gm)_3(B4\text{-}C_6H_4CH_3)(BF)\cdot 2CH_3CN$	$Ru(Cl_2Gm)_3(B4\text{-}tert\text{-}C_4H_9C_6H_4)_2$	$Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}tert\text{-}C_4H_9C_6H_4)_2\cdot 1.5C_6H_6$
Empirical formula	$C_{17}H_{13}B_2Cl_6FN_8O_6Ru$	$C_{26}H_{26}B_2Cl_6N_6O_6Ru$	$C_{69}H_{67}B_2Cl_4N_8O_6Ru$
Fw	779.74	853.92	1368.79
Crystal system, space group	Monoclinic, *P2₁/n*	Monoclinic, *C2/c*	Triclinic, *P-1*
a (Å)	10.3997(3)	24.1380(14)	8.1700(16)
b (Å)	10.6405(3)	8.3359(5)	19.690(4)
c (Å)	25.1400(7)	15.9911(9)	22.190(4)
α (°)	90	90	113.28(3)
β (°)	100.306(1)	100.174(2)	99.85(3)
γ (°)	90	90	94.30(3)
V (Å^3)	2737.06(13)	3167.0(3)	3190.4(13)
Z	4	4	2
μ (cm^{-1})	1.217	1.055	0.547
D_{calc} (g cm^{-3})	1.892	1.791	1.425
No. of meas., indep. and obsvd. [$I > 2\sigma(I)$] reflections	58903, 14831, 12706	19003, 4842, 3718	43568, 16984, 13173
R_{int}	0.032	0.051	0.042
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.031, 0.072, 1.01	0.041, 0.124, 1.02	0.066, 0.168, 0.99
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.84, -0.87	1.38, -1.20	3.57, -1.47

Table S2. Deconvoluted solution UV-vis spectra (ν, cm^{-1}, $\varepsilon \times 10^{-3}$, $mol^{-1} \cdot l \cdot cm^{-1}$) of the obtained clathrochelates in dichloromethane

Compound	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}	ν_{14}	ν_{15}
$Ru(Cl_2Gm)_3(B4\text{-}C_6H_4CH_3)_2$	40920 (12)	37950 (6.6)	35280 (9.2)	31710 (3.1)	25840 (5.5)	23970 (7.5)									
$Ru(Cl_2Gm)_3(B4\text{-}tert\text{-}C_4H_9C_6H_4)_2$	41610 (5.1)	39720 (8.9)	37980 (10)	36290 (7.7)	34300 (7.7)	31240 (4.9)	25320 (11)	23440 (10)							
$Ru(Cl_2Gm)_3(B4\text{-}C_6H_4CH_3)(BF)$	42030 (5.9)	40400 (13)	38130 (15)	35940 (8.4)	33760 (7.7)	31470 (4.4)	29940 (4.3)	28200 (4.7)	25890 (11)	23610 (20)					
$Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}tert\text{-}C_4H_9C_6H_4)_2$	43410 (42)	40790 (55)	40300 (13)	38980 (86)	36880 (39)	35720 (7.7)	34730 (22)	33290 (14)	33080 (8.9)	30420 (6.2)	28250 (4.0)	25870 (7.7)	24370 (5.9)	22570 (18)	19820 (2.7)

Table S3. Voltammetric characteristics (V, *versus* the Fc/Fc^+ redox couple) of the novel *tert*-butylphenylboron-capped ruthenium(II) clathrochelates

Complex	CV		DPV	
	E^{red}	E^{ox}	E^{red}	E^{ox}
$Ru(Cl_2Gm)_3(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$	–1.40	[a]n/d	–1.22	[a]n/d
$Ru(Cl_2Gm)_2((NH(CH_2)_3Phen)_2Gm)(B4\text{-}(tert\text{-}C_4H_9C_6H_4))_2$	–1.56	1.25	–1.45	1.17

[a]n/d: not determined