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SUPPLEMENTARY MATERIAL

Synthesis and Characterisation of Helicate and Mesocate Forms of a Double-Stranded Diruthenium(II) Complex of a Di(terpyridine) Ligand

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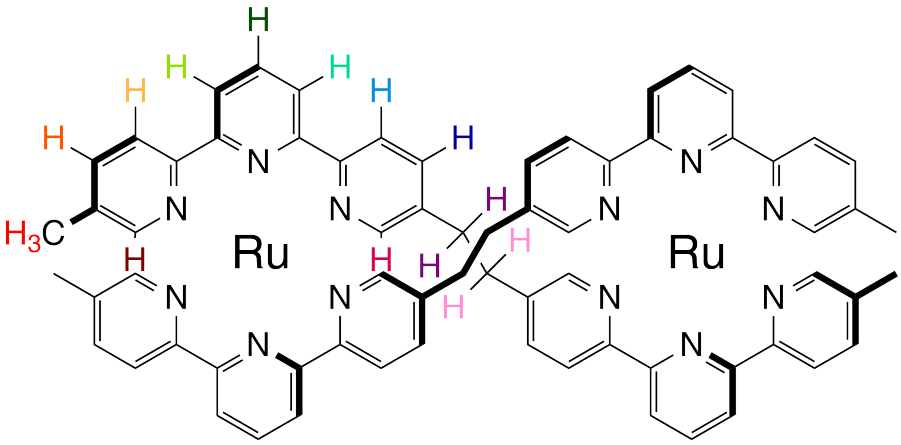
NMR Data

Table S1. Assigned ^{1}H NMR peaks for the diruthenium(II) mesocate (**2**), and helicate (**3**) complexes (ND = not defined). (*Note structure below shows 3D representation of helicate)*



^{1}H NMR – Mesocate **2**				
Assigned	Shift (ppm)	#H	Multiplicity	J (Hz)
H	8.65	4	d	8.14
H	8.58	4	d	8.11
H, H	8.35	8	m	3.94, 3.94, 8.11
H	8.28	4	d	8.25
H	8.00	4	dd	1.50, 8.40
H	7.67	4	dd	0.64, 8.24
H	7.19	4	d	1.46
H	6.67	4	d	0.65
CH_2	2.90	4	m	ND
CH_2	2.50	4	m	ND
CH_3	2.00	12	s	-

^{1}H NMR – Helicate **3**				
Assigned	Shift (ppm)	#H	Multiplicity	J (Hz)
H	8.83	4	d	8.08
H	8.71	4	d	8.11
H	8.50	4	t	8.13, 8.13
H	8.38	4	d	8.29
H	8.34	4	d	8.24
H	7.74	4	d	7.30
H	7.40	4	d	10.36
H	7.15	4	s	
H	6.38	4	s	
CH_2, CH_2	2.63	8	s	
CH_3	2.03	12	s	

Crude Reaction Mixture

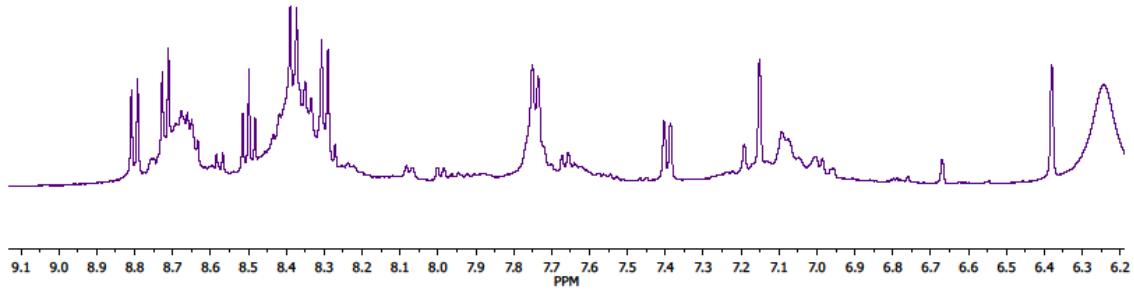


Figure S1: Partial ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) showing the aromatic region of the crude reaction mixture from initial oven heating experiments at 200 °C. Helicate, **3**, is the major product, with mesocate, **2**, as the minor product. Broad peaks corresponding to polymeric material can be clearly seen.

Mesocate, 2

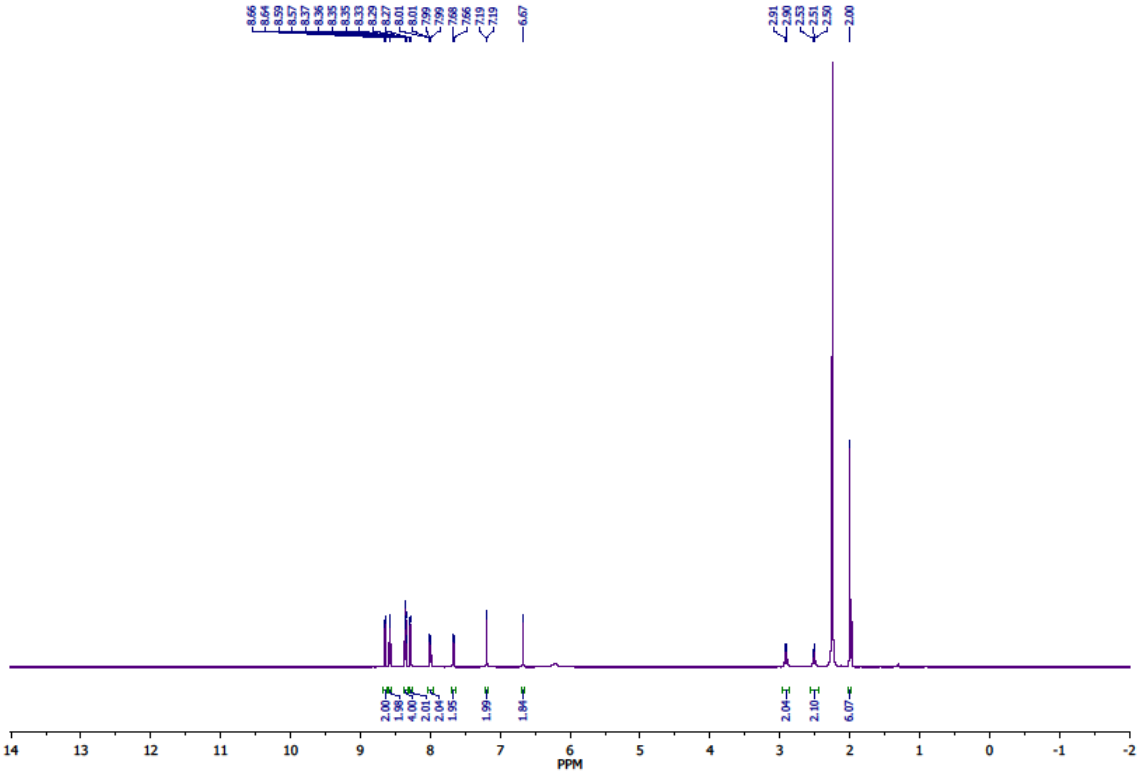


Figure S2: Full ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of the mesocate, **2**.

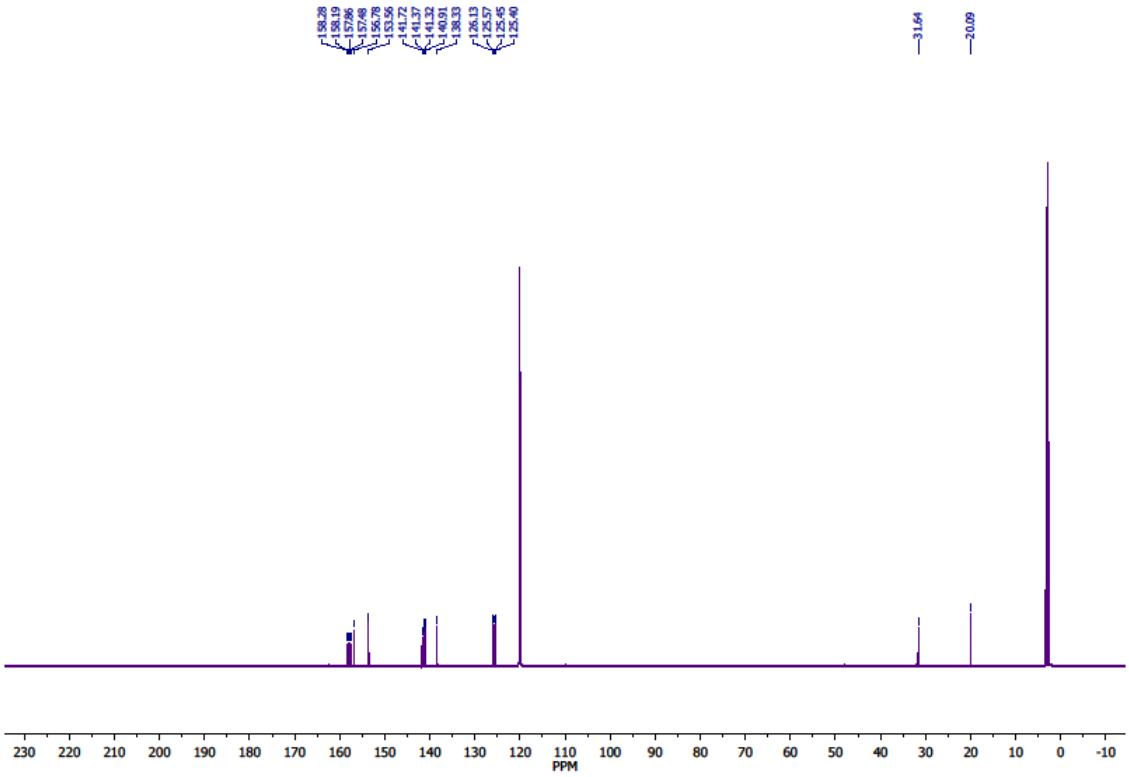


Figure S3: Full ^{13}C NMR spectrum (126 MHz, CD_3CN, 298 K) of the mesocate, **2**.

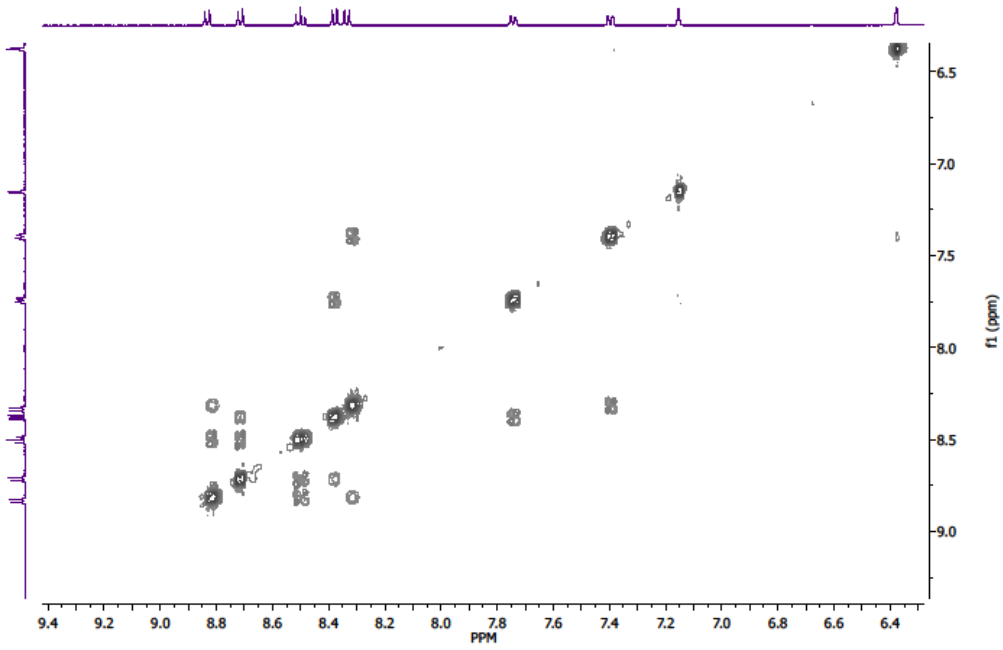


Figure S4: Partial ^{1}H-^{1}H ROESY NMR spectrum showing [1] mesocate, **2**.

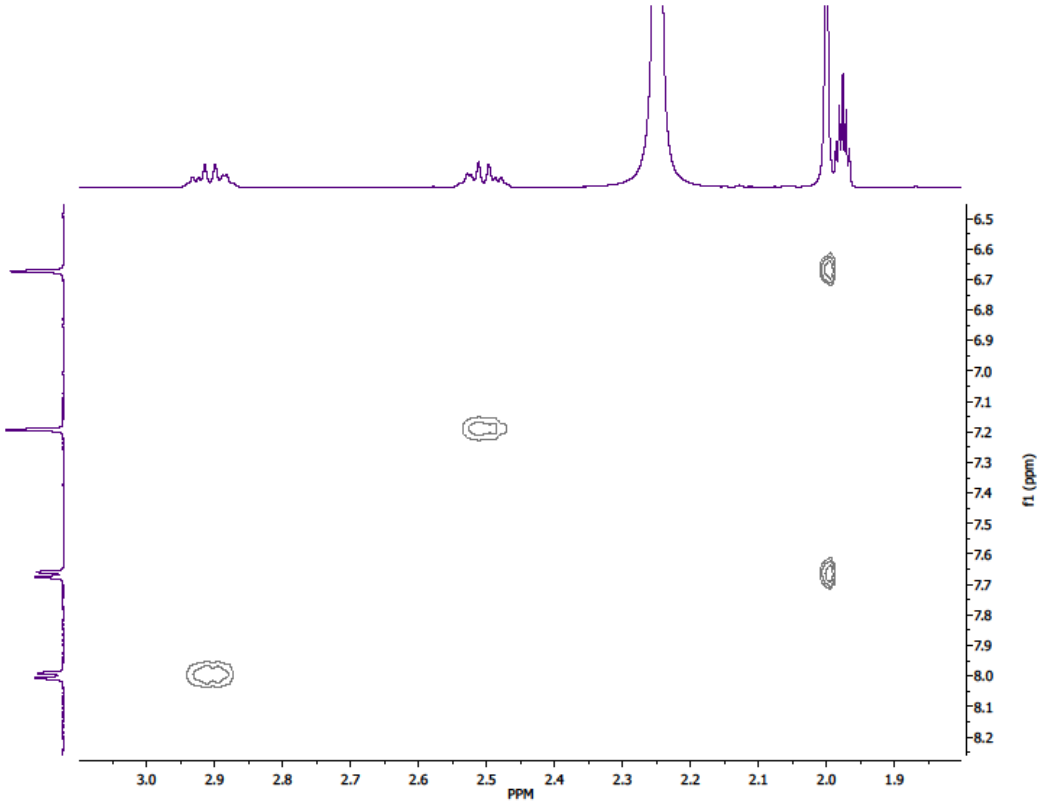


Figure S5: Partial ^{1}H-^{1}H ROESY NMR spectrum showing [1] mesocate, **2**.

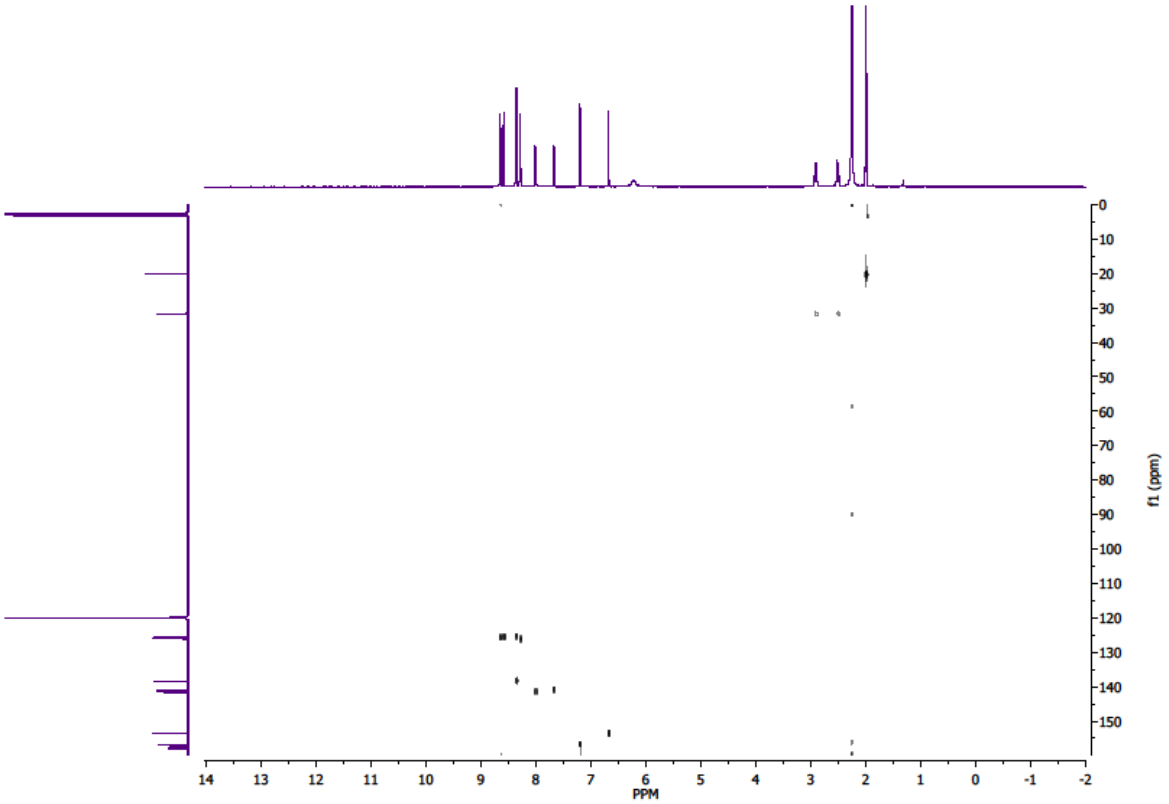


Figure S6: Full ^{1}H-^{13}C HSQC NMR spectrum mesocate, **2**.

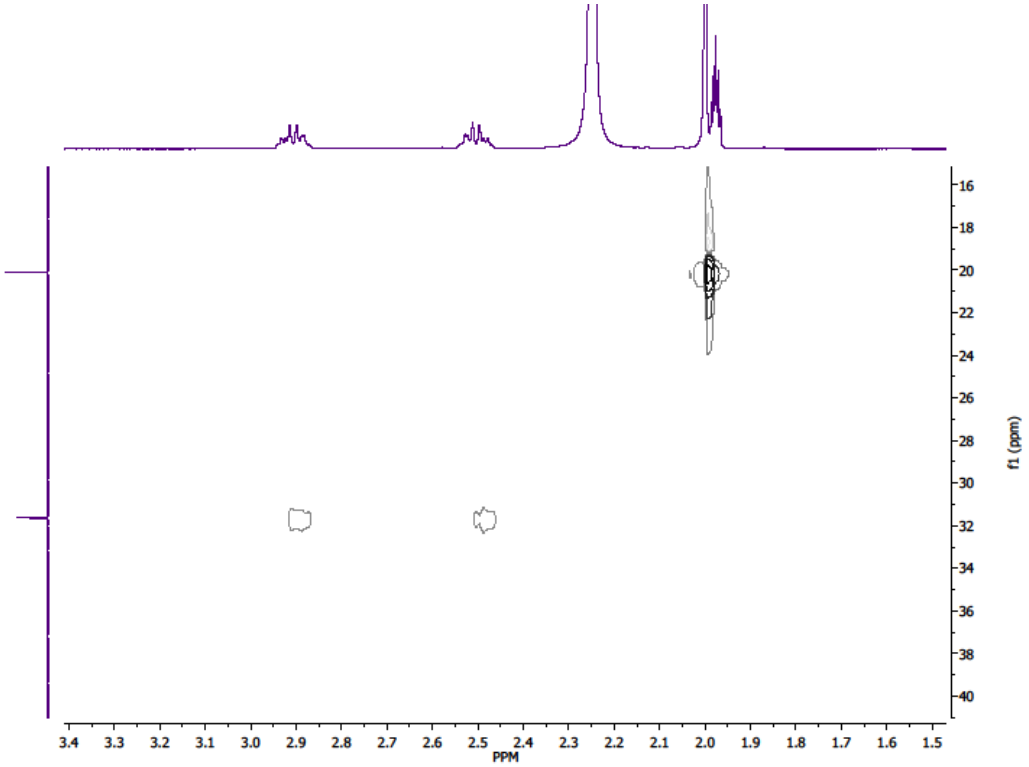
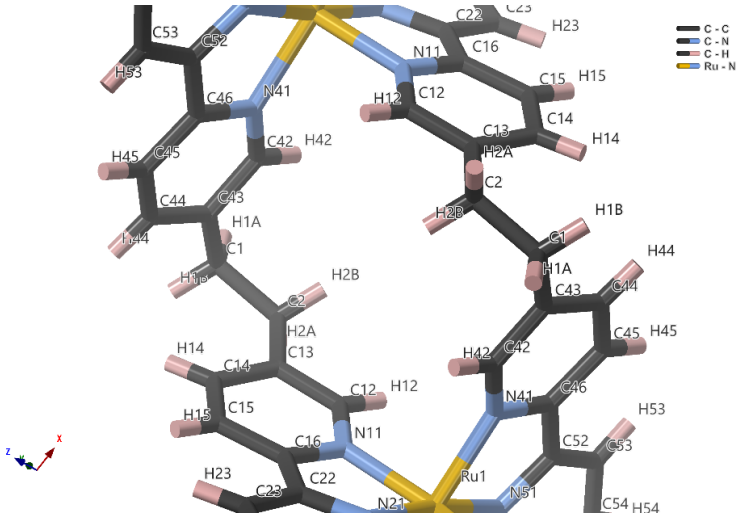


Figure S7: Partial ^{1}H-^{13}C HSQC NMR spectrum showing mesocate, **2**.

Assignment of -CH_2CH_2- bridge



	Distance between atoms (Å)				Chemical Shift	
	H42	**H44**	**H12**	**H14**		
H1A	2.557	3.391	4.674	3.577	**H1A/B**	2.93 ppm
H1B	3.543	2.354	4.561	2.26	**H2A/B**	2.50 ppm
H2A	3.853	4.359	2.858	3.165	**H42/12**	7.19 ppm
H2B	2.614	4.297	2.537	3.524	**H44/14**	8.00 ppm

Figure S8: Assignment of -CH_2CH_2- bridge hydrogens of the mesocate, **2** using interatomic distances from crystal structure.

Helicate, 3

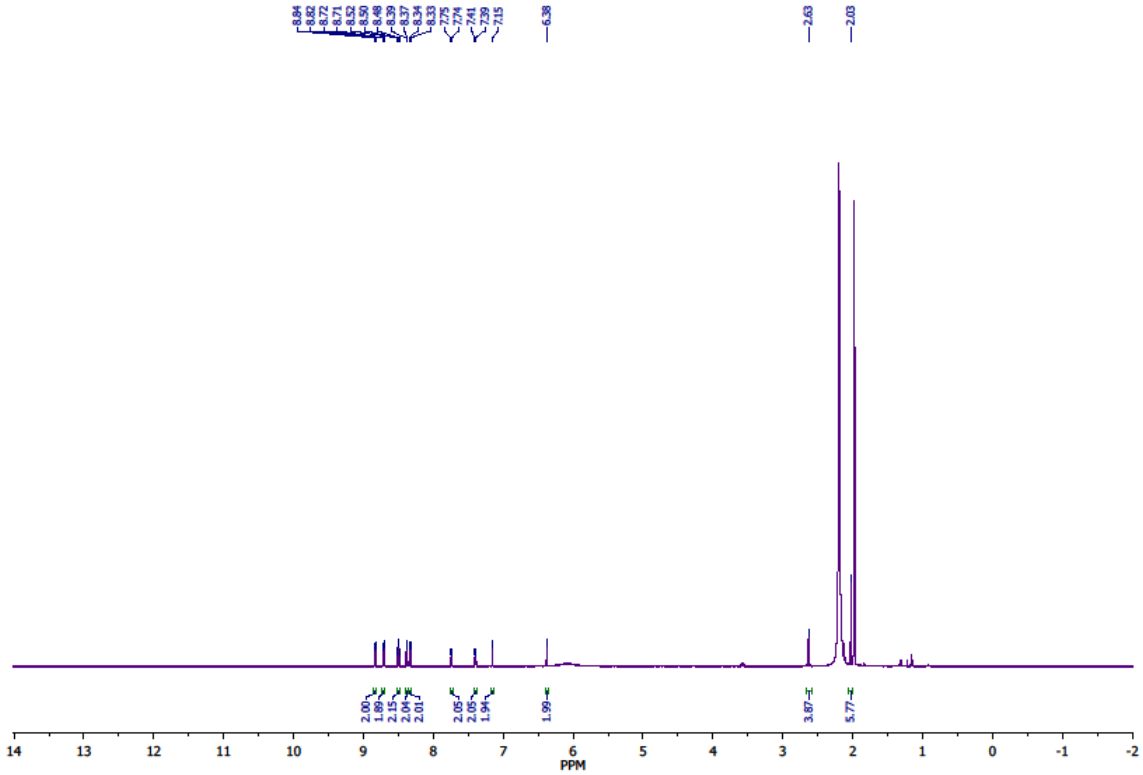


Figure S9: Full ^{1}H NMR spectrum (500 MHz, CD_3CN, 298 K) of the helicate, **3**.

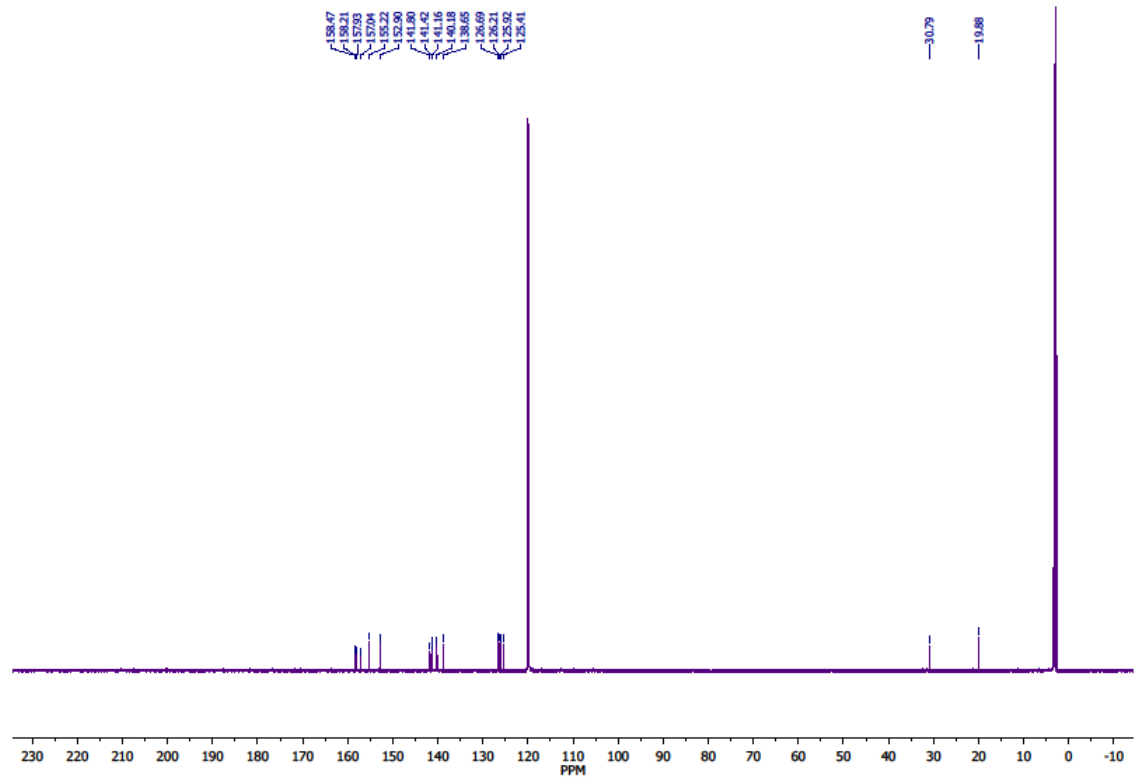


Figure S10: Full ^{13}C NMR spectrum (126 MHz, CD_3CN, 298 K) of the helicate, **3**.

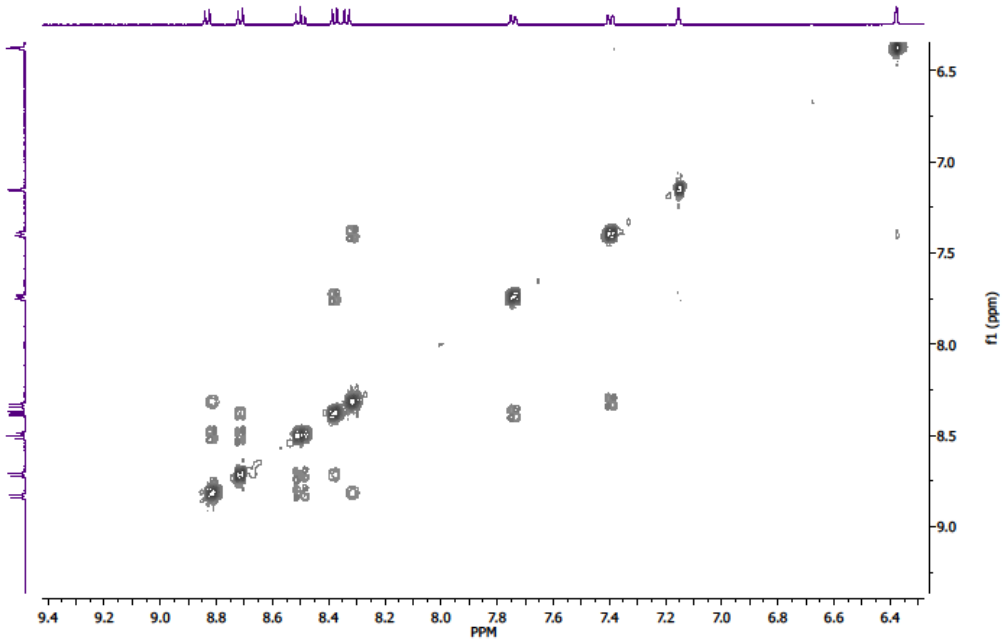


Figure S11: Partial ^{1}H-^{1}H ROESY NMR spectrum showing ^{1}cate, **3**.

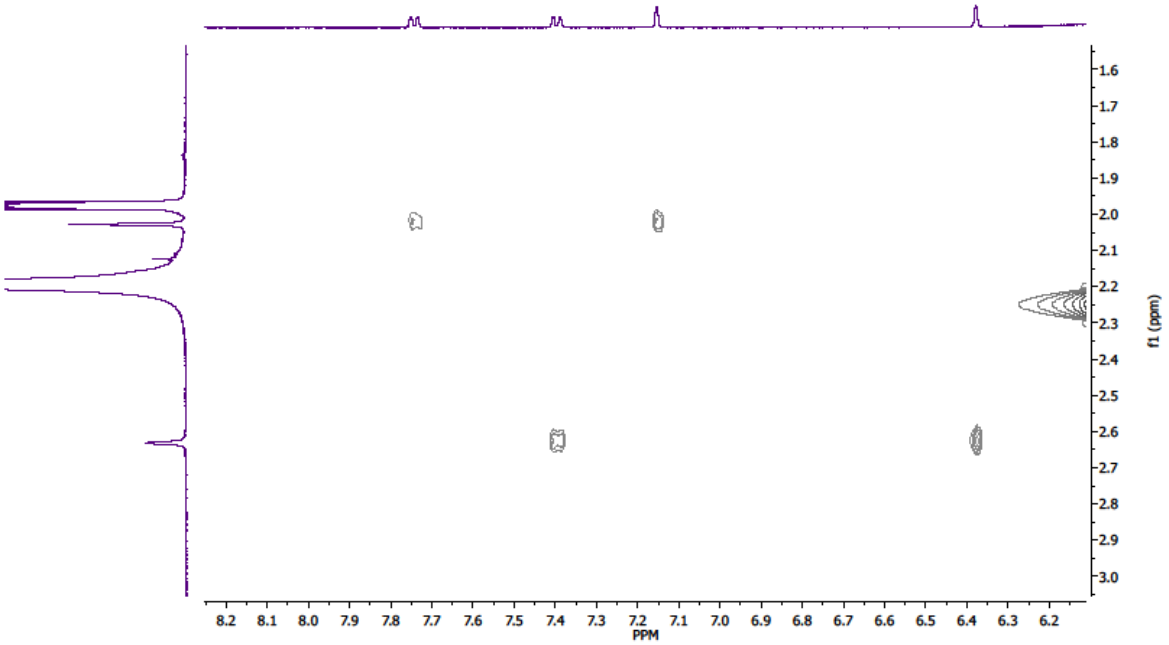


Figure S12: Partial ^{1}H-^{1}H ROESY NMR spectrum showing ^{1} helicate, **3**.

X-ray Crystallography

Mesocate, 2

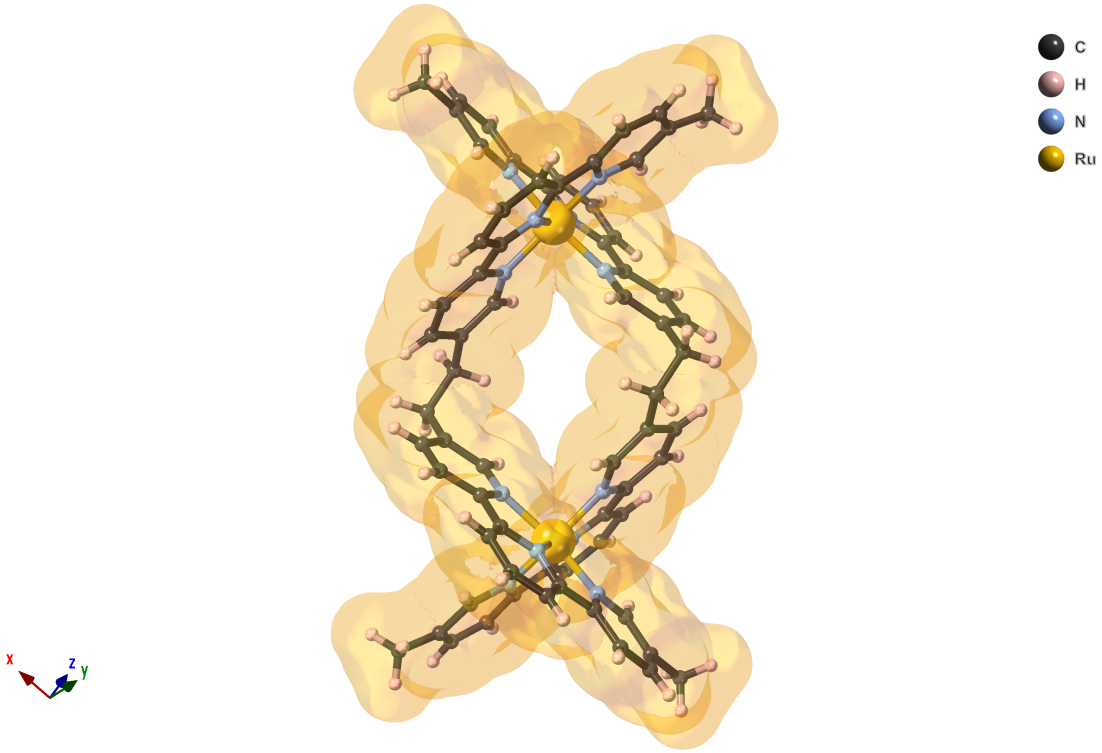


Figure S13: Crystal structure of the diruthenium mesocate, **2**, including van der Waals surface, illustrating accessible central cavity.

Packing

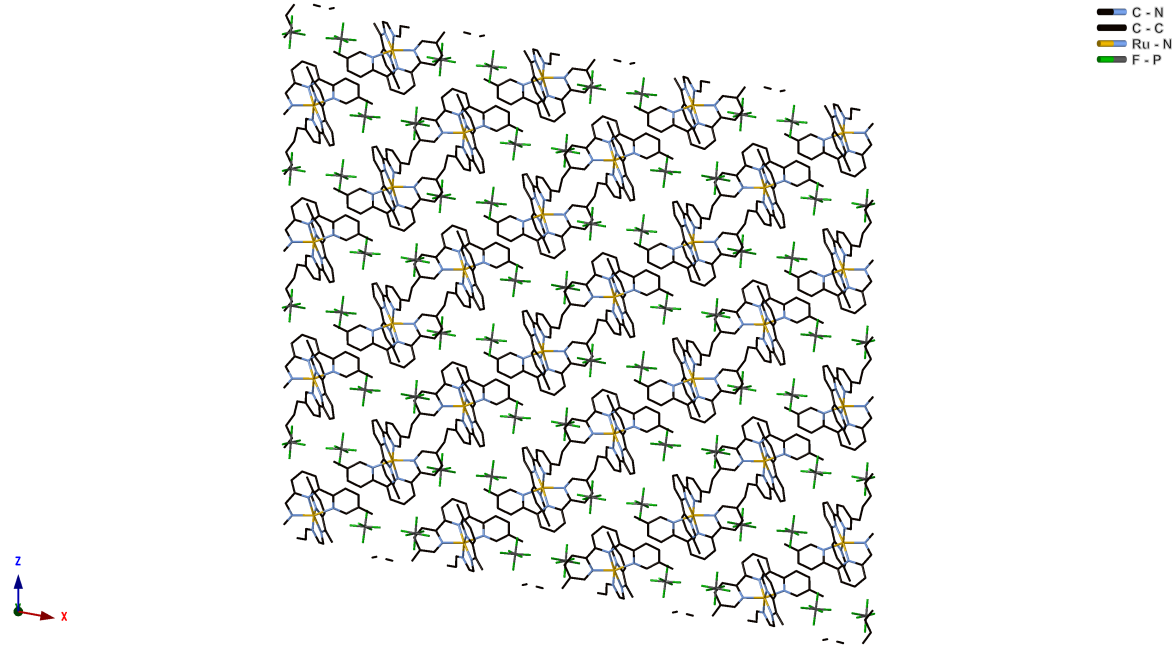


Figure S14: Crystal structure of the diruthenium mesocate, **2**, viewed down *b*-axis, showing integrated cation-anion entities.

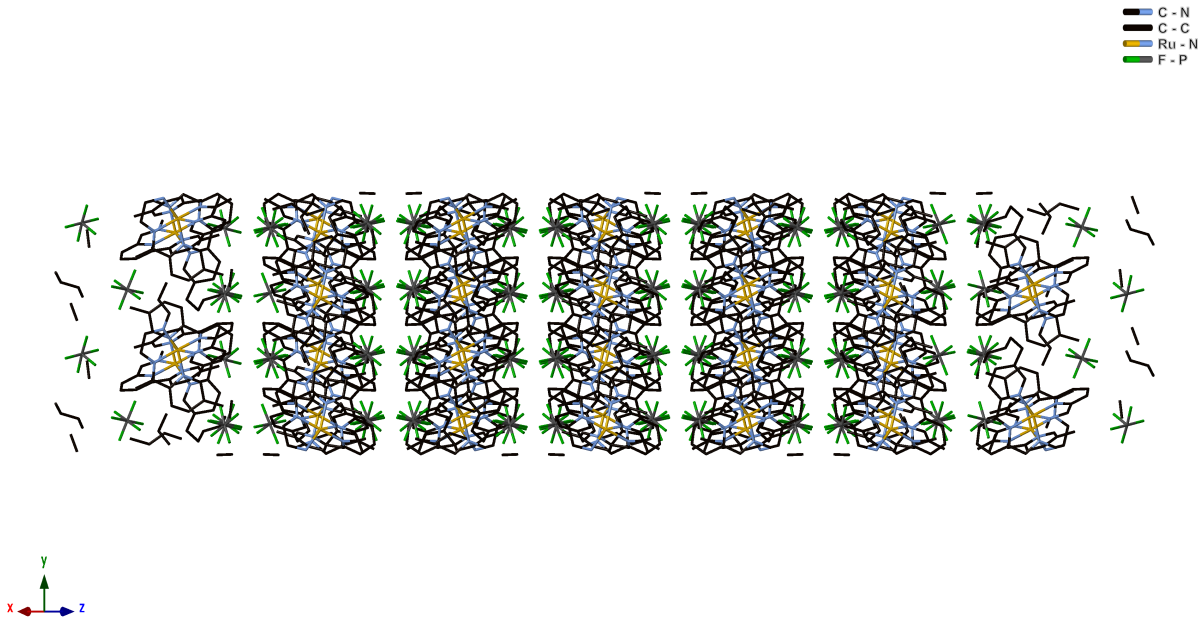


Figure S15: Crystal structure of the diruthenium mesocate, **2**, viewed in the 1 0 1 plane, showing mesocate columns.

Helicate, 3

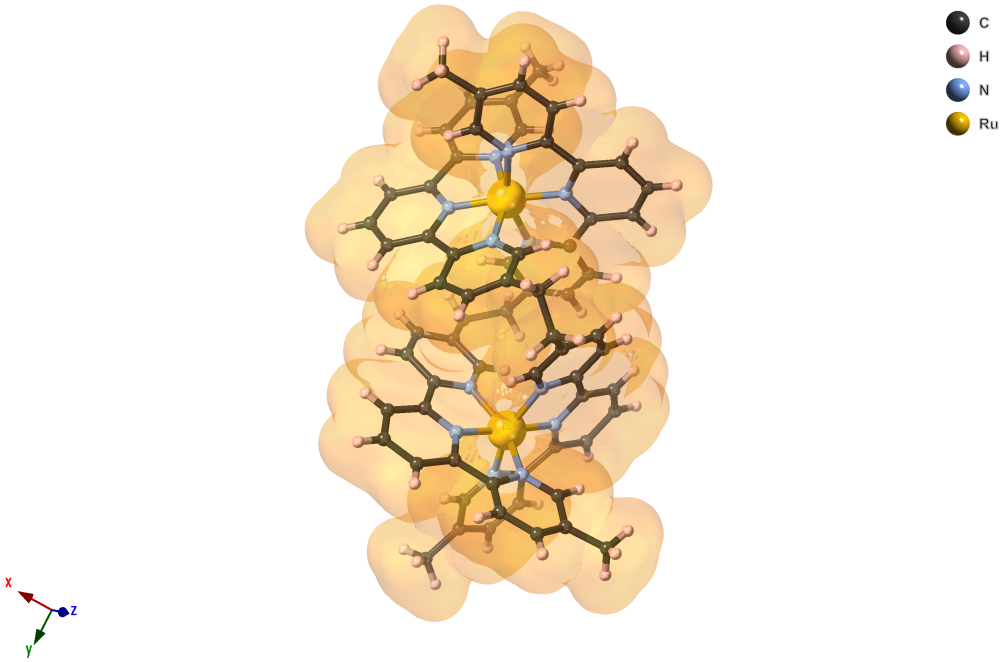


Figure S16: Crystal structure of the diruthenium helicate, **3**, including van der Waals surface, illustrating inaccessible central cavity.

Packing

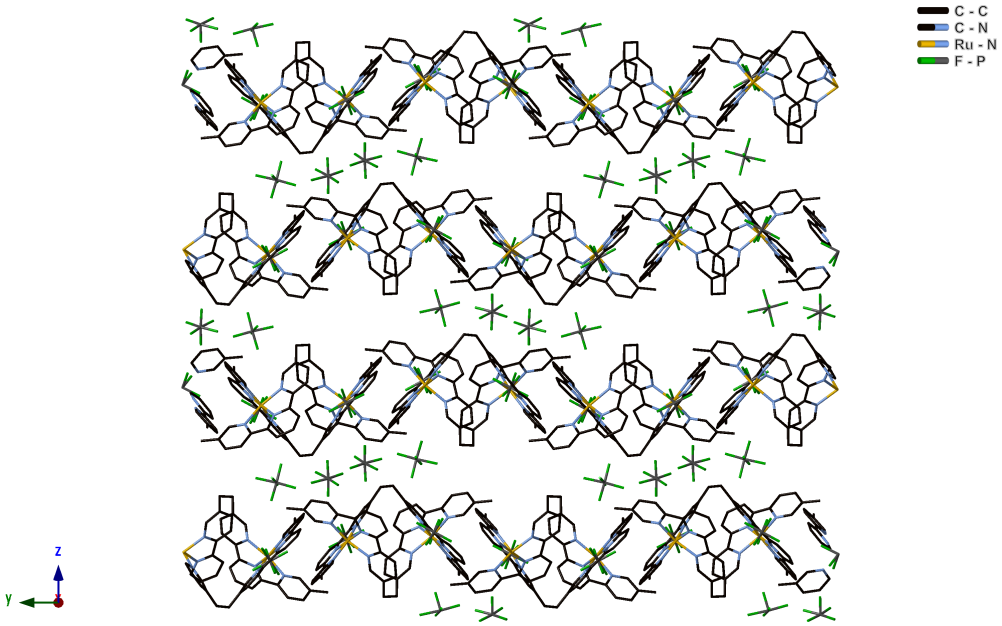


Figure S17: Crystal structure of the diruthenium helicate, **3**, viewed down *a*-axis, showing alternating cation/anion layers.

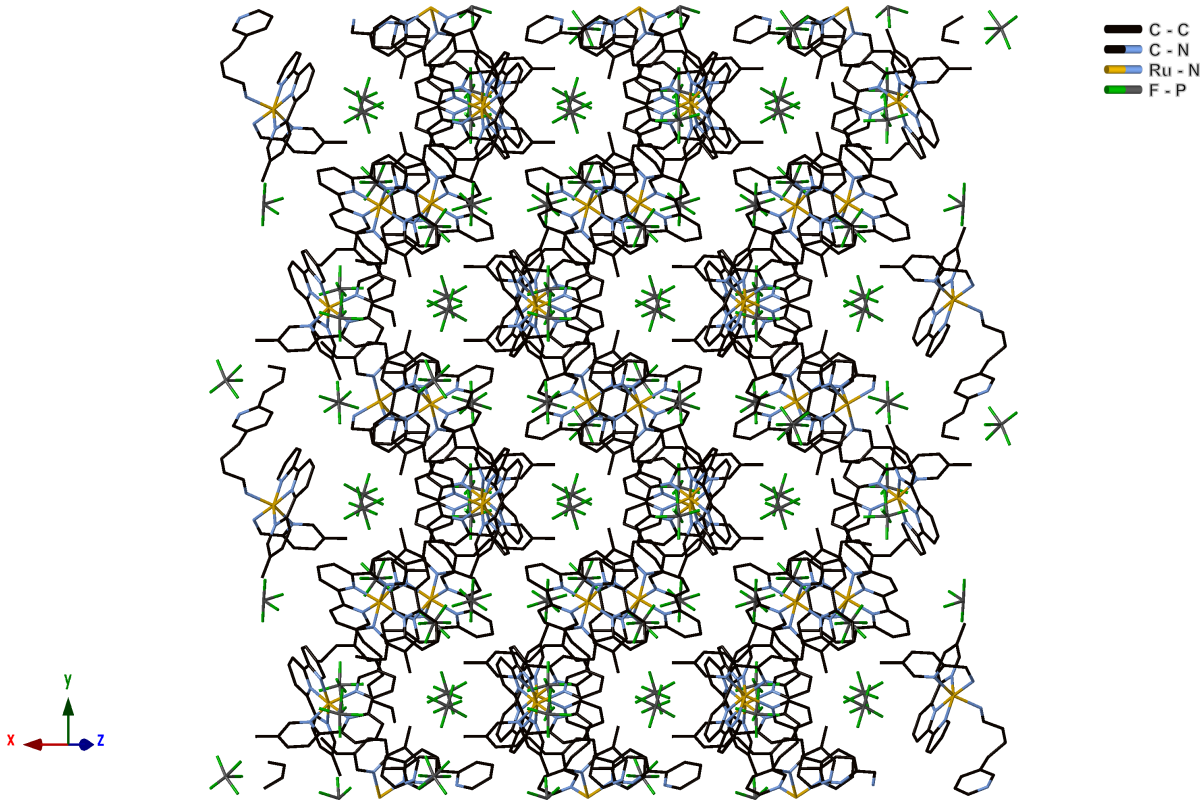


Figure S18: Crystal structure of the diruthenium helicate, **3**, viewed in the *ab* plane, with a "loose" herringbone arrangement incorporating anions.

HR-ESMS Spectra

Mesocate (2)

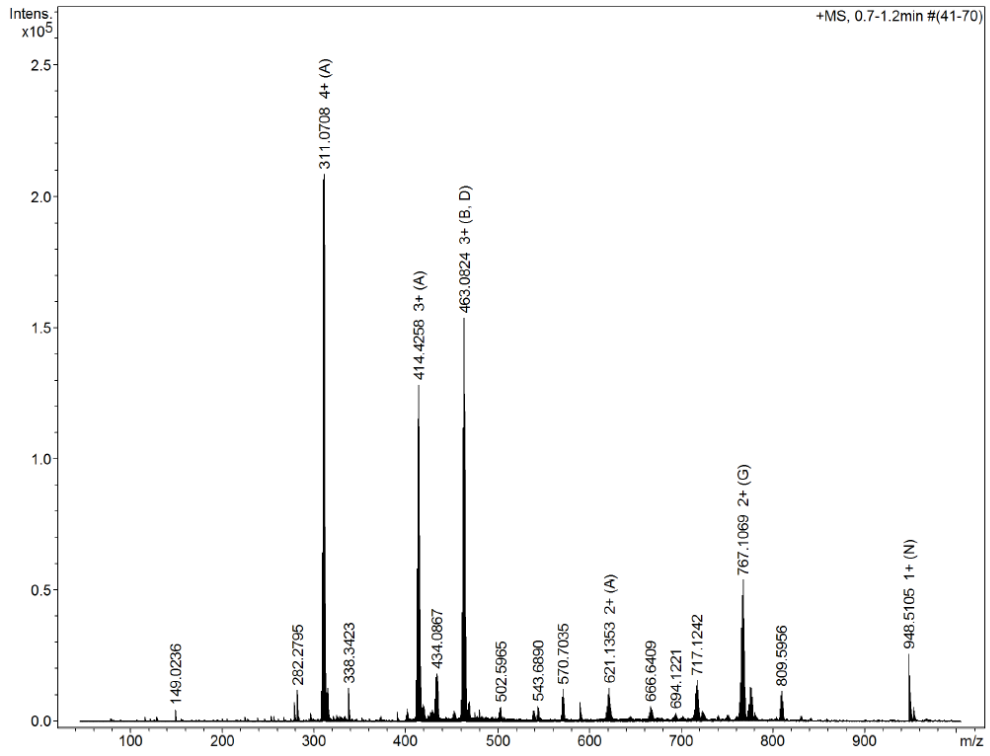


Figure S19: Full HR-ESI MS spectrum (CH_3CN) of the mesocate, **2**.

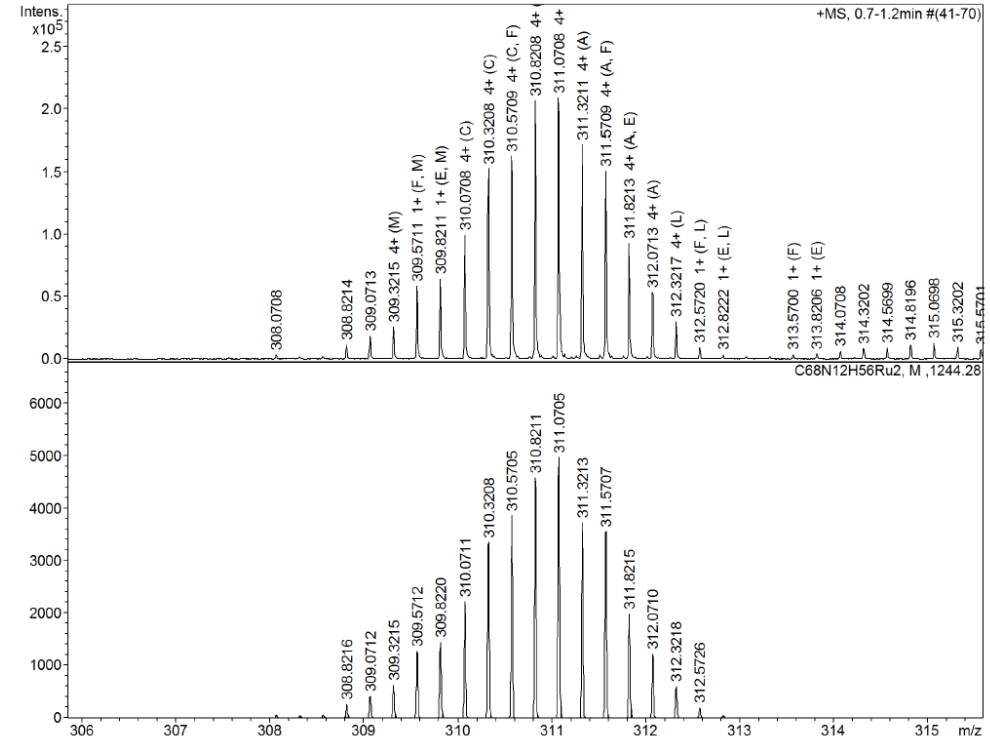


Figure S20: Partial HR-ESI MS (CH_3CN) and calculated isotopic patten of mesocate **2**, peak at *m/z* 311.0708 due to $[\mathbf{2} - 4(PF_6^-)]^{4+}$.

Helicate (3)

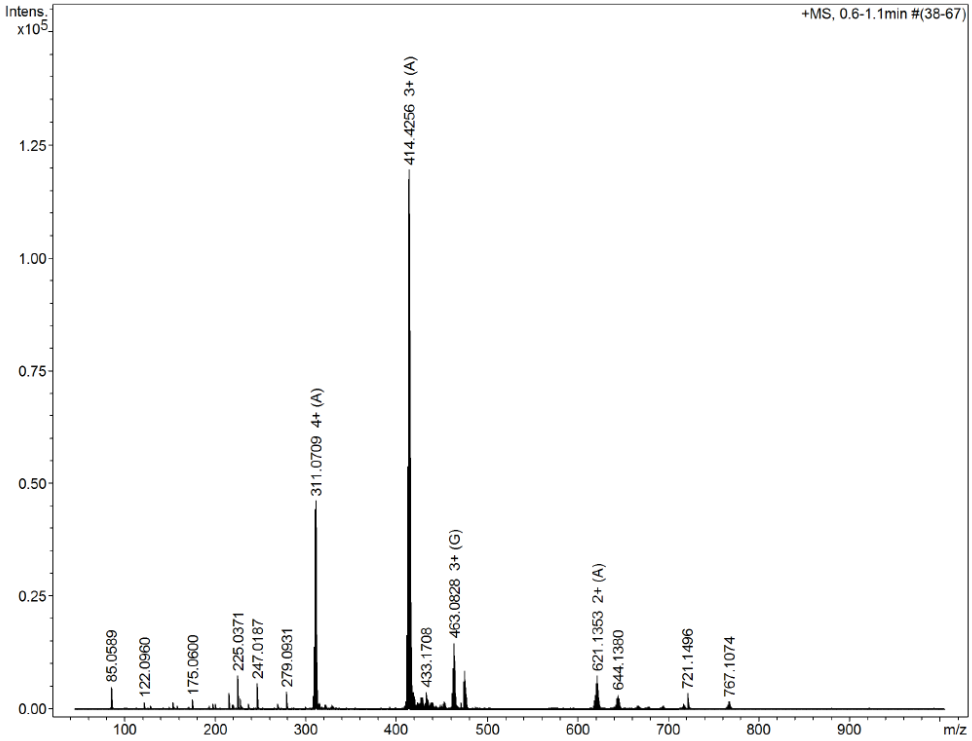


Figure S21: Full HR-ESI MS spectrum (CH_3CN) of the helicate, **3**.

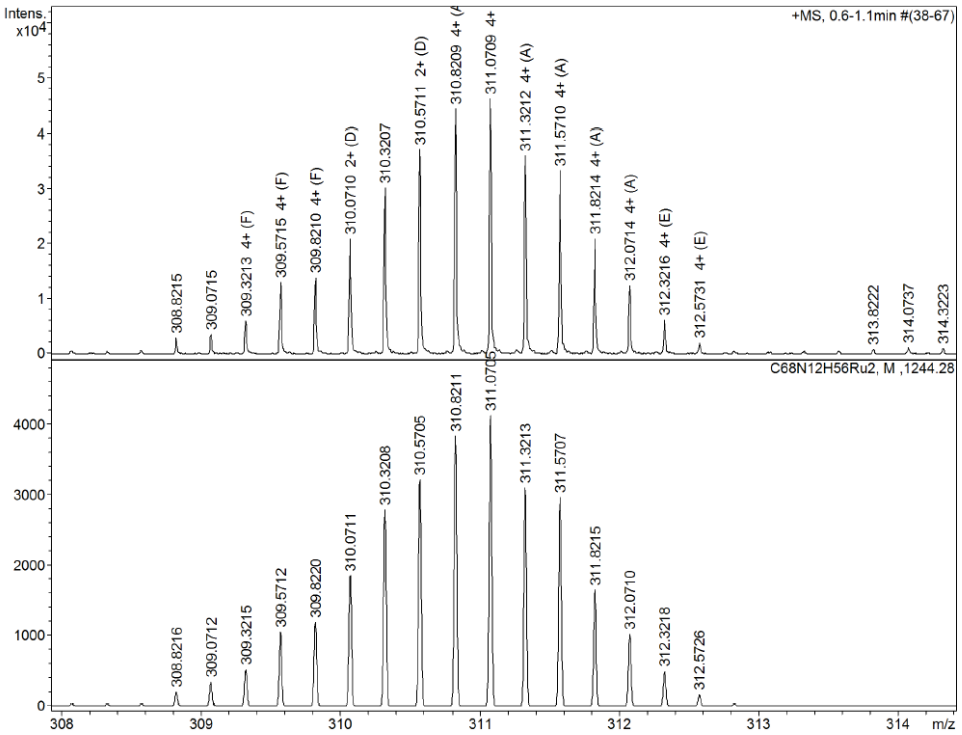


Figure S22: Partial HR-ESI MS (CH_3CN) and calculated isotopic pattern of helicate **3**, peak at *m/z* 311.0708 due to $[\mathbf{3} - 4(PF_6^-)]^{4+}$.

UV-Vis Spectra

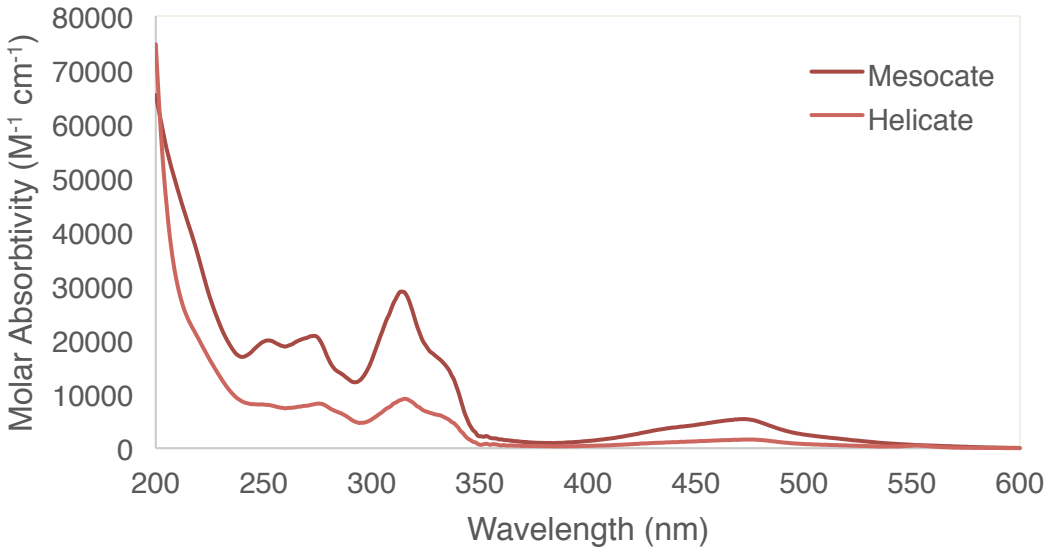


Figure S23: Absorbance spectra of diruthenium mesocate, **2**, and helicate, **3**.