

Impressive isomerization of 2-cyclohexenol by two Ru(II) complexes, synthesis and characterization of the reaction intermediate.

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Materials and methods

All chemicals were of reagent grade and, unless otherwise stated, were used as received from commercial suppliers. Likewise, all reactions were carried out in a N₂ atmosphere by using standard Schlenk-tube techniques. Water was deoxygenated prior to use and organic solvents have been dried through standard methods. The complexes [RuClCp(PTA)₂] and [RuCp(H₂O-κO)(PTA)₂]CF₃SO₃ were prepared as described in the literature.^{1,2} All NMR spectra were recorded on a Bruker AV500 spectrometer operating at 500.13 MHz (¹H), 202.46 MHz (³¹P) and 125.75 MHz (¹³C). Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (¹H), relative to external 85% H₃PO₄ (³¹P) and the deuterated solvent multiplet (¹³C). Infrared spectra were recorded as KBr disks using a Bruker Vertex 70 FT-IR spectrometer. Elemental analyses (C, H, N, S) were performed on a Fisons Instrument EA1108 elemental analyser. Catalytic reactions have been performed in a carousel system (Radley) with 12 reaction positions. Gas chromatographic measurements were made on a Shimadzu GC-2010-Plus using a Supelco SP-2330 30 m, 0.25 mm, 0.2 μm column and a flame ionization detector.

General procedure for catalytic isomerisation of 2-cyclohexen-1-ol

Catalytic activity of complexes **1** and **2** have been evaluated in water (when required the pH was adjusted by 0.1 M phosphate buffer for pH 7 and 8 while pH = 4.5 was adjusted with a 0.1 M solution of H₃PO₄), MeOH and in biphasic water/cyclohexane 1:1 mixture under air and N₂. In the reaction tube were introduced 2 mL of solvent and 1 mL of a freshly prepared solution of catalyst **1** (10.6 mg, 0.021 mmol) or **2** (14.6 mg, 0.021 mmol) dissolved in 12 mL of water or methanol. Immediately after, the equivalents of 2-cyclohexenol were added and the reaction was brought at the desired temperature and stirred regularly (1000 rpm). At the chosen time the reaction was cooled at room temperature and extracted with CHCl₃ (5 x 1.5 mL for 1 mol% catalyst; 5 x 3 mL for

0.1, 0.02 and 0.01 mol% catalyst). The collected organic layers were passed through a column (5 x 50 mm) packed with 60 mesh silica gel. The conversion of the allylic alcohol into ketone was determined by gas chromatography. The identity of the products was assessed by comparison with commercially available pure samples.

Table S1. Isomerization reactions of 2-cyclohexenol catalyzed by **1** and **2**.

Catalyst	[Ru] mol%	Time	Temperature (°C)	Solvent	Atmosphere	TON	TOF (h ⁻¹)	Yield %
1	1	5 h	70	H ₂ O	N ₂	95	19	95
1	1	5 h	70	H ₂ O	Air	28	5.6	28
1	1	2 h	70	MeOH	N ₂	1	0.5	1
1	1	2 h	70	MeOH	Air	0	0	0
1	0.1	2 h	70	H ₂ O/Cyclohexane	N ₂	70	35	7
1	0.1	2 h	70	H ₂ O/Cyclohexane	Air	60	30	6
1	0.1	2 h	70	H ₂ O	N ₂	30	15	3
1	0.1	2 h	70	H ₂ O	Air	19	9.5	1.9
1	0.01	2 h	70	H ₂ O/Cyclohexane	N ₂	100	50	1
1	0.01	2 h	70	H ₂ O/Cyclohexane	Air	100	50	1
1	0.01	2 h	70	H ₂ O	N ₂	50	25	0.5
1	0.01	2 h	70	H ₂ O	Air	50	25	0.5
2	1	30 min	70	H ₂ O/Cyclohexane	N ₂	>99	198	99
2	1	2 h	70	MeOH	N ₂	97	48.5	97
2	1	2 h	70	MeOH	Air	97	48.5	97
2	1	5 h	70	H ₂ O	N ₂	94	18.8	94
2	1	5 h	70	H ₂ O	Air	78	15.6	78
2	1	30 min	70	H ₂ O/Cyclohexane	Air	71	142	71
2	0.1	3 h	70	H ₂ O/Cyclohexane	N ₂	>999	333	99.9
2	0.1	15 h	70	H ₂ O/Cyclohexane	Air	510	34	51
2	0.1	2 h	70	H ₂ O	N ₂	304	152	30.4
2	0.1	2 h	70	H ₂ O	Air	97	48.5	9.7
2	0.02	15 h	70	H ₂ O/Cyclohexane	N ₂	1550	103.3	31
2	0.01	21 h	70	H ₂ O/Cyclohexane	N ₂	3420 ^a	162.9	34.2
2	0.01	2 h	70	H ₂ O	N ₂	650	325	6.5
2	0.01	2 h	70	H ₂ O	Air	177	88.5	1.77

a) TON after 7 cycles (H₂O/cyclohexane 1:1, 70°C, [Ru] 0.01 mol%, 3 h/cycle). Yields determined by GC.

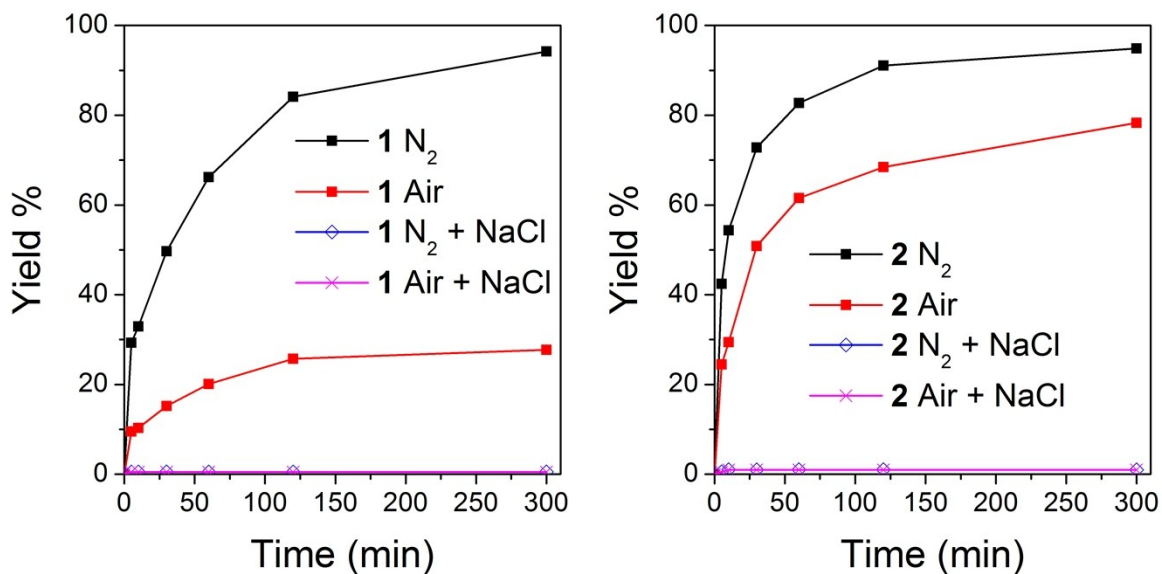


Figure S1. Isomerization of 2-cyclohexenol mediated by **1** and **2** against the addition of 10 eq of NaCl. Conditions: 2 h, 70°C, 1 mol% [Ru], 10 mol% NaCl, H₂O.

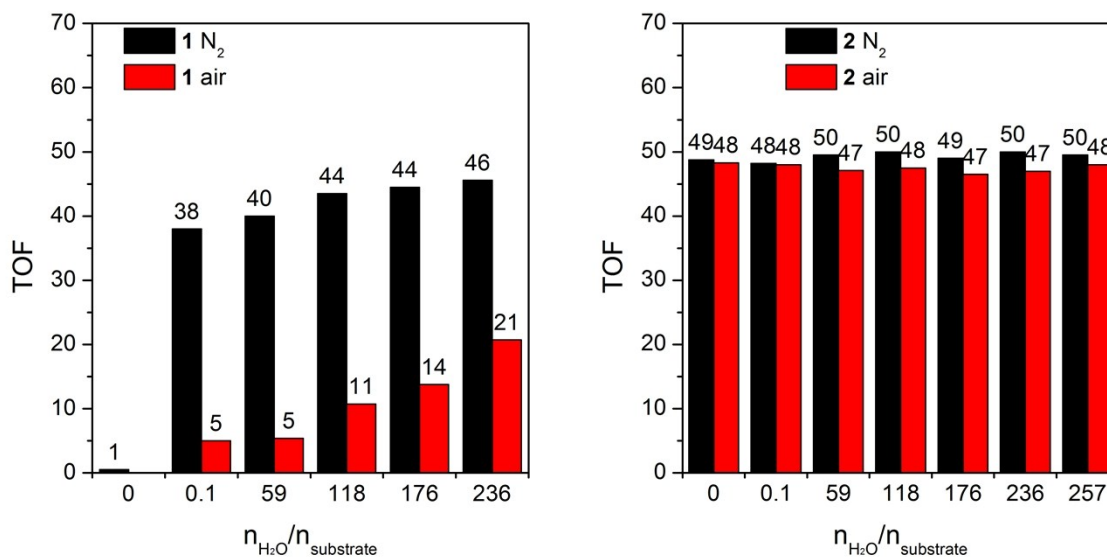


Figure S2. Isomerization of 2-cyclohexenol mediated by **1** and **2** against the presence of water in the reaction media. Conditions: 2 h, 70°C, 1 mol% [Ru], H₂O or MeOH when n_{H₂O}/n_{substrate} = 0.

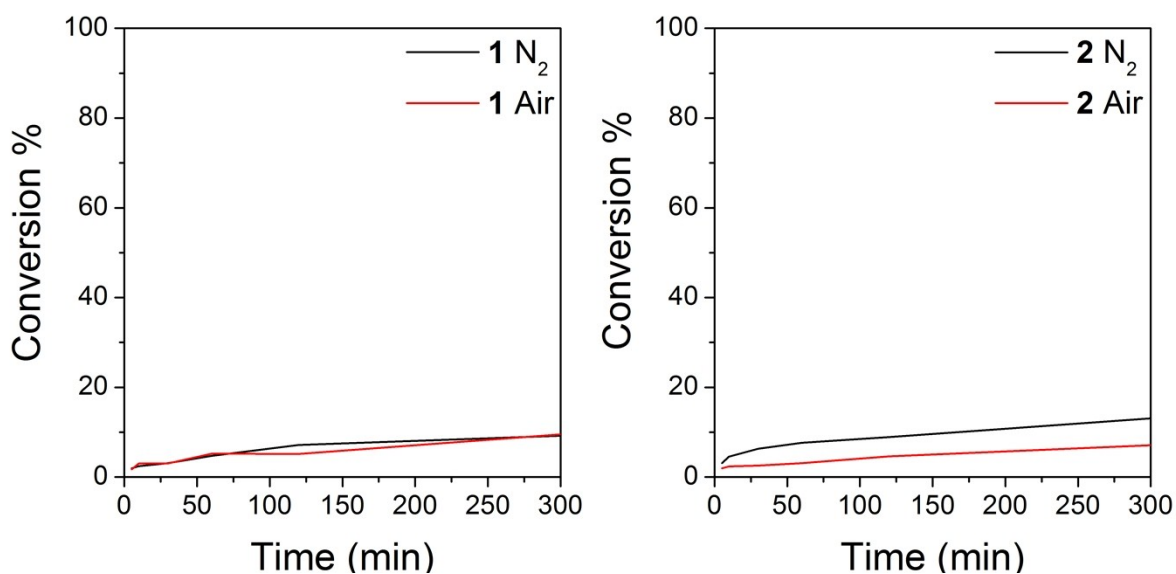


Figure S3. Isomerization of 1-hexen-3-ol mediated by **1** and **2**. Conditions: 70°C, 1 mol% [Ru], water.

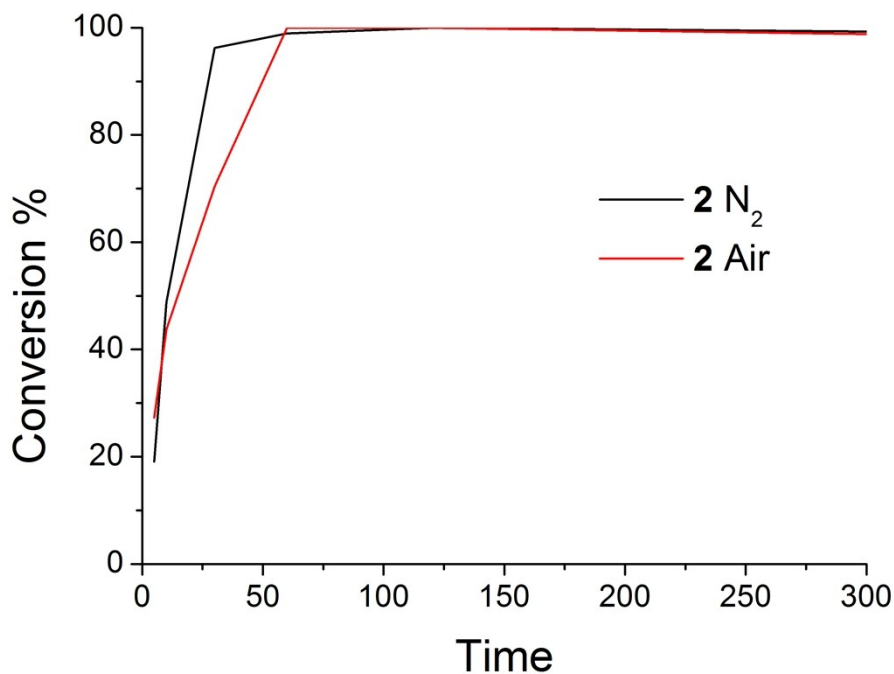


Figure S4. Isomerization of 2-cyclohexenol mediated by **2**. Conditions: 70°C, 1 mol% [Ru], water/cyclohexane 1:1.

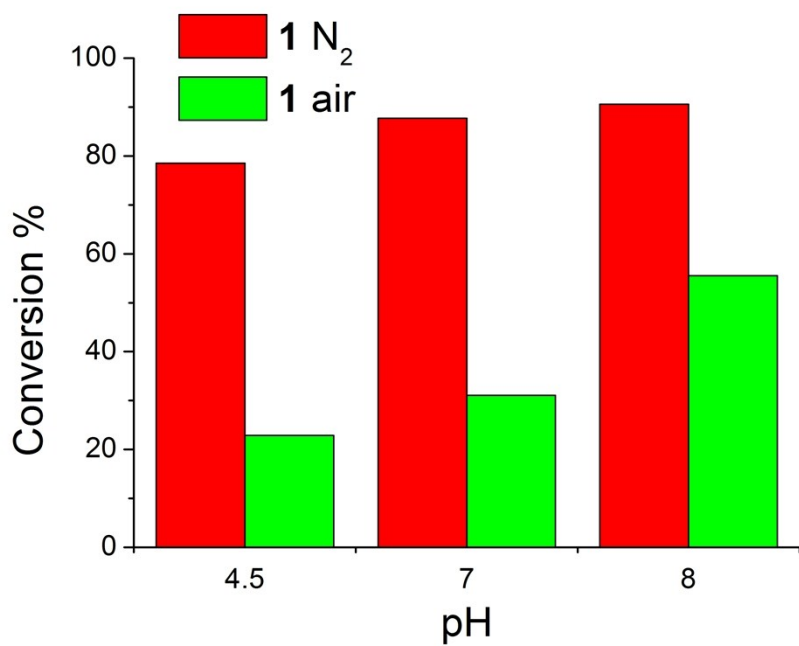


Figure S5. Isomerization of 2-cyclohexenol mediated by **1**. Conditions: 70°C, 1 mol% [Ru], water.

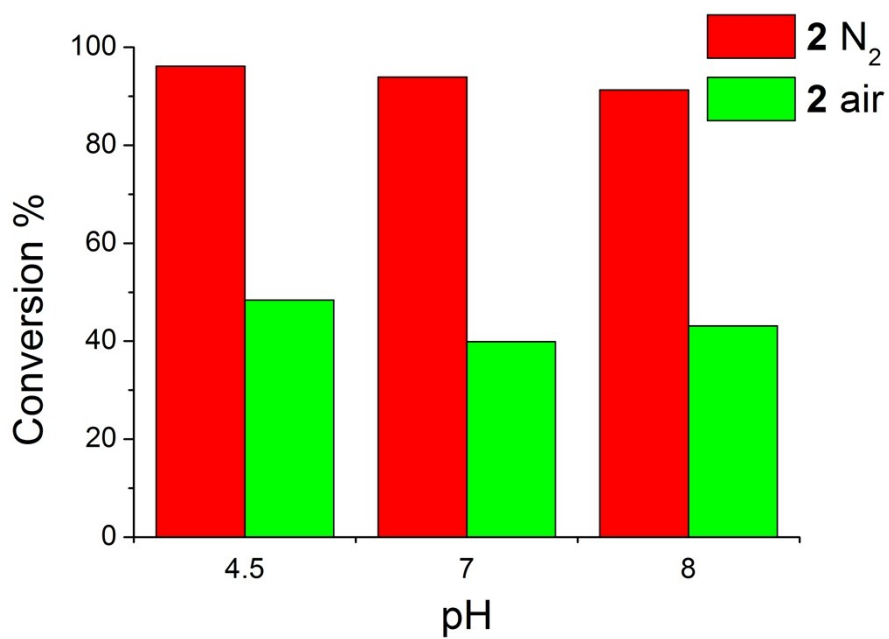


Figure S6. Isomerization of 2-cyclohexenol mediated by **2**. Conditions: 75°C, 1 mol% [Ru], water.

Synthesis of [RuCp(PTA)₂(η²-C₆H₉OH)]CF₃SO₃ (3)

The complex [RuCp(H₂O-κO)(PTA)₂]CF₃SO₃ (20 mg, 0.028 mmol) was dissolved in 1 mL of methanol at 5 °C and 2-cyclohexen-1-ol (14 μL, 1.4 mmol) was added into the solution under stirring. After 4 h a white precipitate formed, which was filtered, washed with Et₂O (3 x 5 mL) and vacuum dried overnight.

Yield = 6.2 mg (31%). C₂₄H₃₉F₃N₆O₄P₂RuS (727.68 g·mol⁻¹); calcd: C 39.61, H 5.40, N 11.55 %; found: C 40.07, H 5.68, N 11.12 %. IR (KBr, cm⁻¹, vs = very strong, s = strong, m = medium, w = weak): 3546 (s), 2943 (m), 2926 (m), 1646 (m), 1447 (m), 1413 (m), 1281 (vs), 1258 (vs), 1244 (vs), 1224 (m), 1156 (s), 1106 (m), 1031 (vs), 1015 (s), 975 (vs), 948 (s), 894 (w), 842 (w), 812 (m), 747 (m), 638 (s), 583 (s), 572 (s), 518 (w), 477 (m), 452 (w), 393 (w). ¹H NMR (500.13 MHz, -20 °C, CD₃OD/D₂O 10:1): δ (ppm) 1.29 (m, 1H, H^{5a}), 1.32 (m, 1H, H^{6b}), 1.68 (m, 1H, H^{5b}), 1.88 (m, 1H, H^{6a}), 2.22 (m, 1H, H^{4a}), 2.68 (m, 1H, H^{4b}), 2.82 (m, 1H, H²), 3.22 (m, 1H, H³), 4.16 (m, 24H, NCH₂P), 4.22 (m, 1H, H¹), 4.791-4.55 (m, 24 H, NCH₂N), 5.26 (s, 5H, Cp). ¹³C{¹H} NMR (125.77 MHz, -20 °C, CD₃OD/D₂O 10:1): δ (ppm) 18.1 (s, CH₂, C⁵), 30.4 (s, CH₂, C⁴), 32.3 (s, CH₂, C⁶), 53.6-54.7 (m, NCH₂P), 56.2 (s, CH, C³), 61.4 (s, CH, C²), 70.9 (m, NCH₂N), 71.2 (s, CH, C¹), 87.2 (s, CH, Cp), 120.2 (q, CF₃, ¹J_{C-F} = 318 Hz). ³¹P{¹H} NMR (202.45 MHz, -20 °C, CD₃OD/D₂O 10:1): δ (ppm): δ -23.24 (d, ²J_{P-P} = 42 Hz, PTA), -21.97 (d, ²J_{P-P} = 42 Hz, PTA).

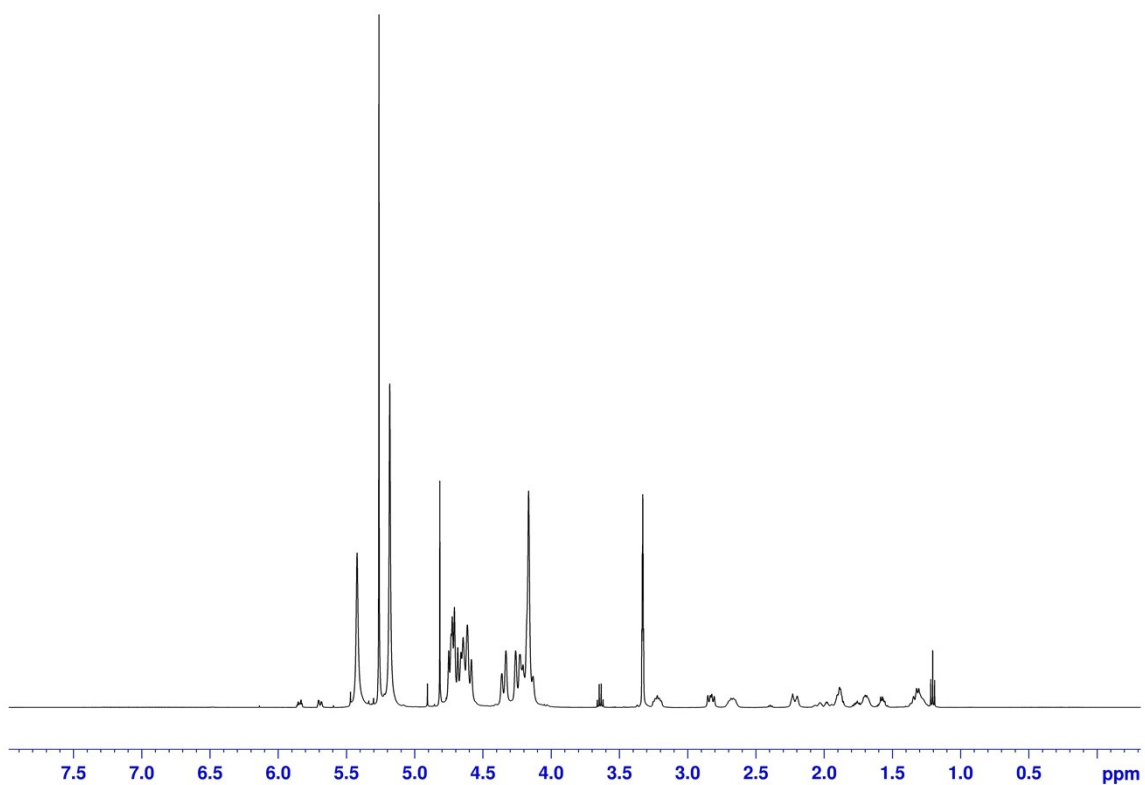


Figure S7. ^1H NMR (-20°C , $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 10:1) spectrum of **3**.

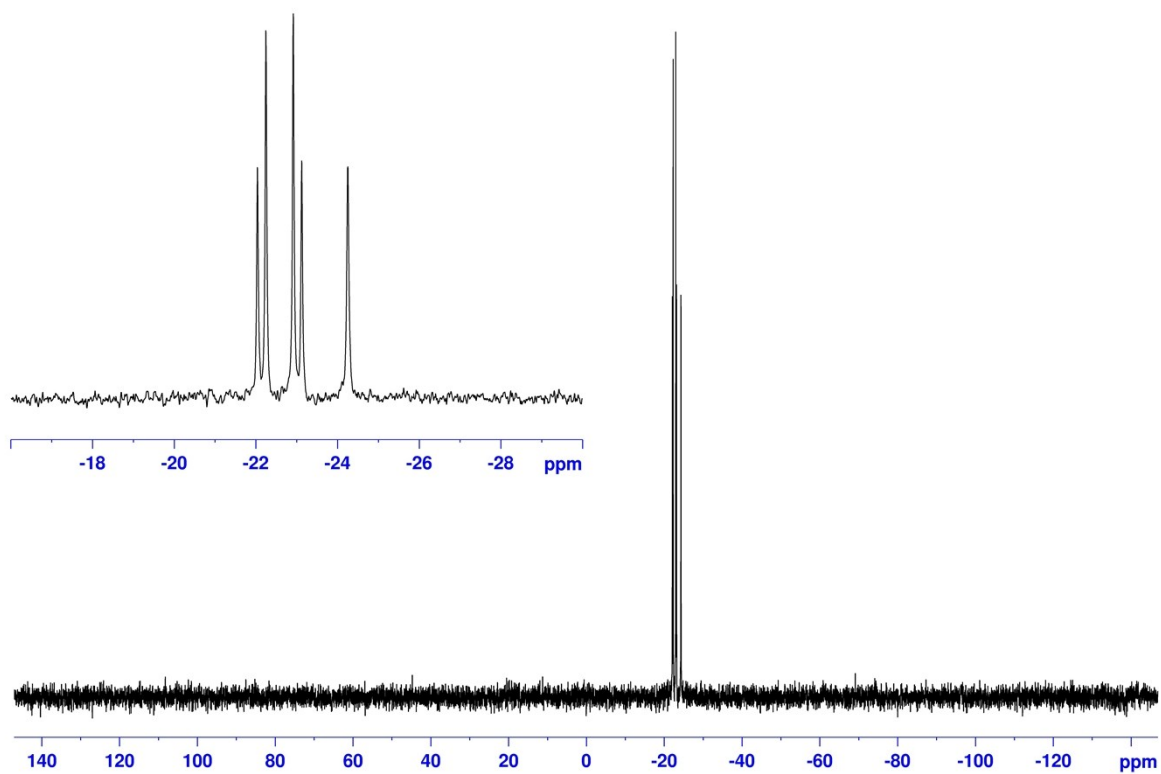


Figure S8. $^{31}\text{P}\{^1\text{H}\}$ NMR (-20°C , $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 10:1) spectrum of **3**.

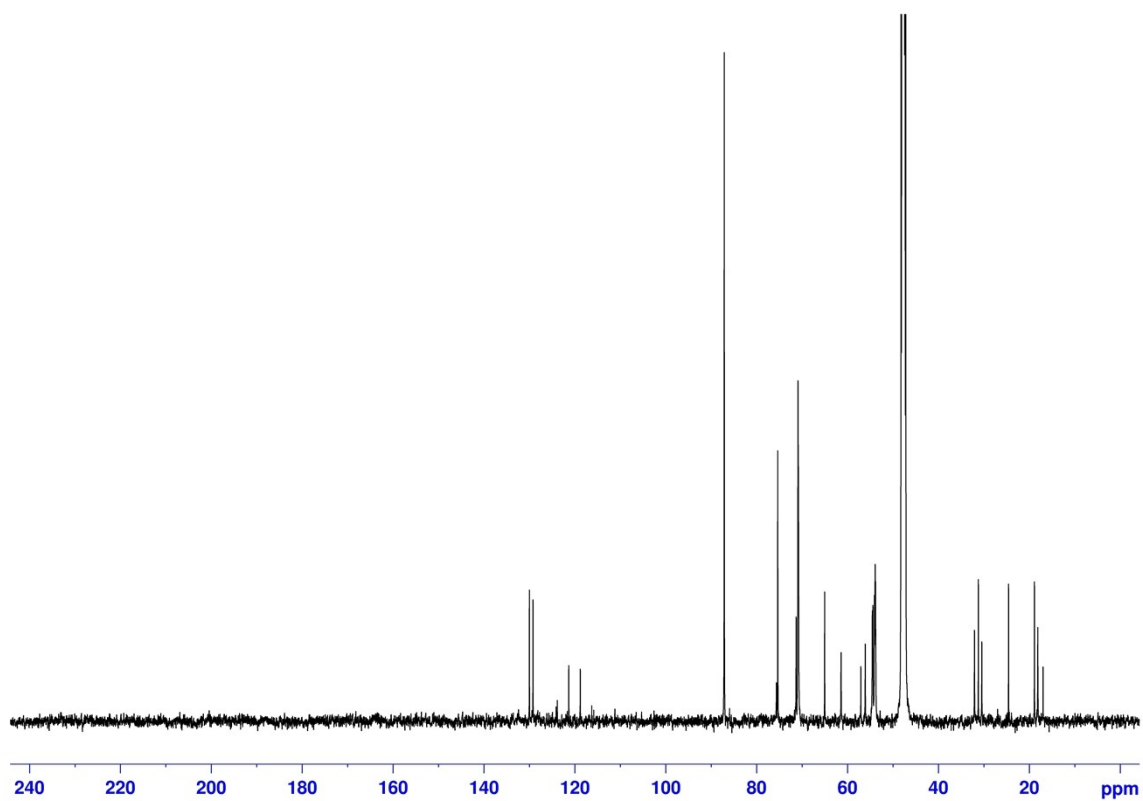


Figure S9. $^{13}\text{C}\{^1\text{H}\}$ NMR (-20°C , $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 10:1) spectrum of **3**.

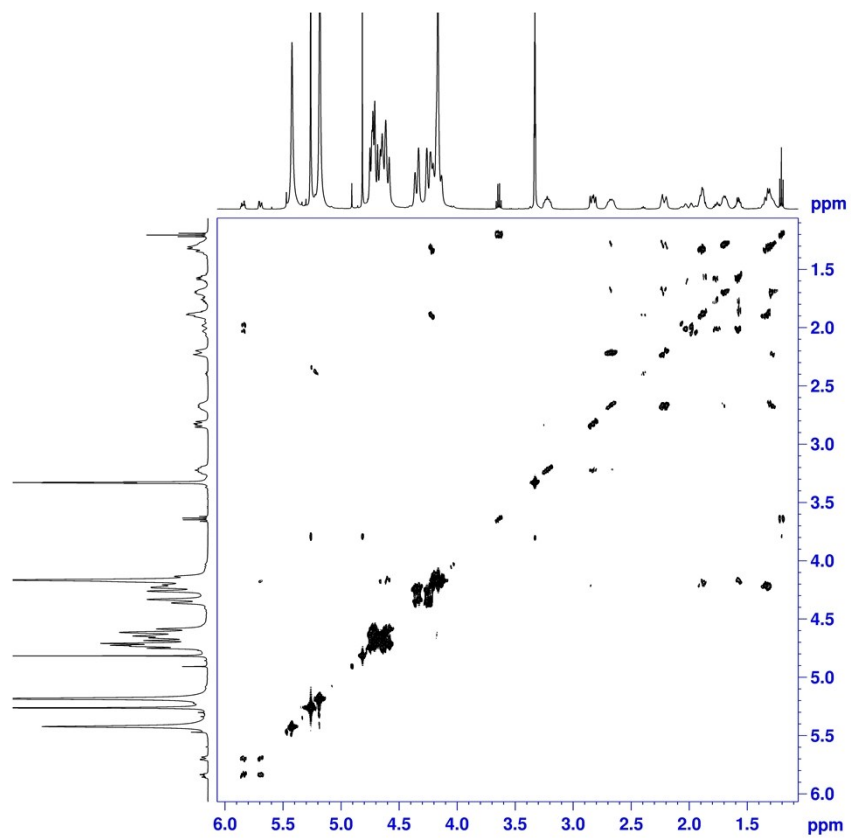


Figure S10. $^1\text{H}-^1\text{H}$ COSY NMR (-20°C , $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 10:1) spectrum of **3**.

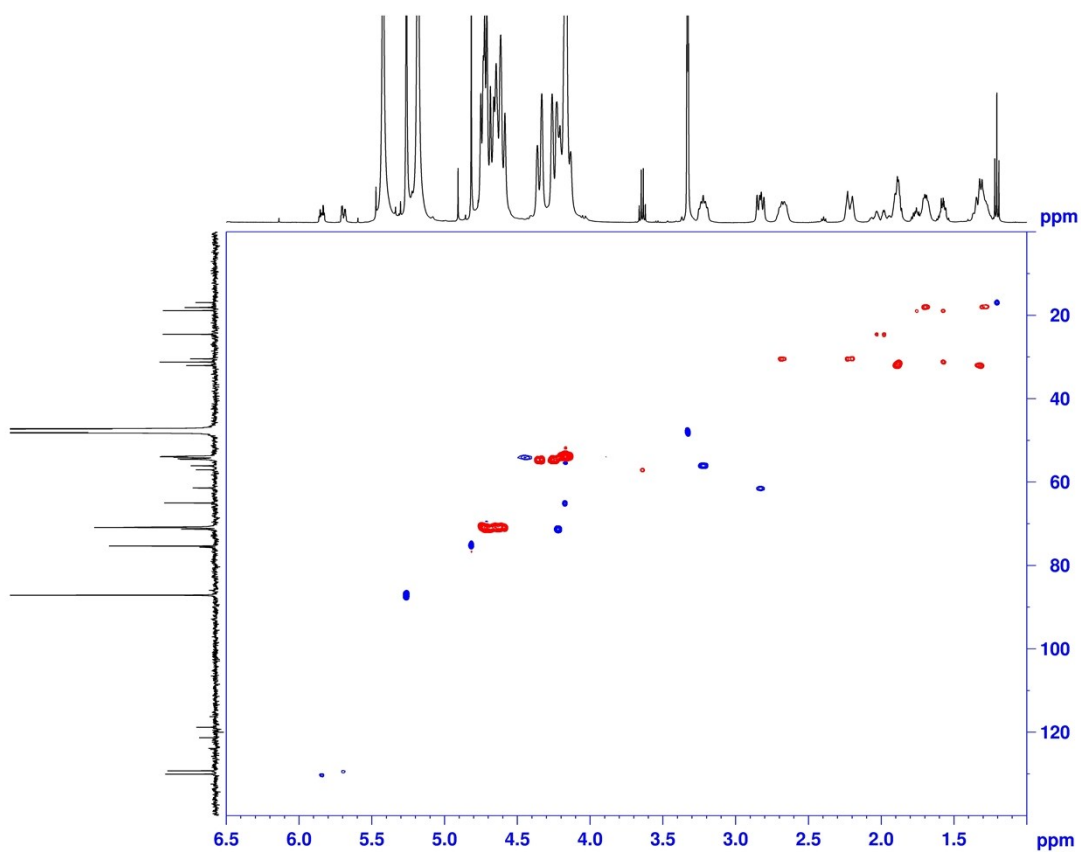


Figure S11. ¹H-¹³C HSQC-DEPT-edited NMR (-20°C, CD₃OD/D₂O 10:1) spectrum of **3**.

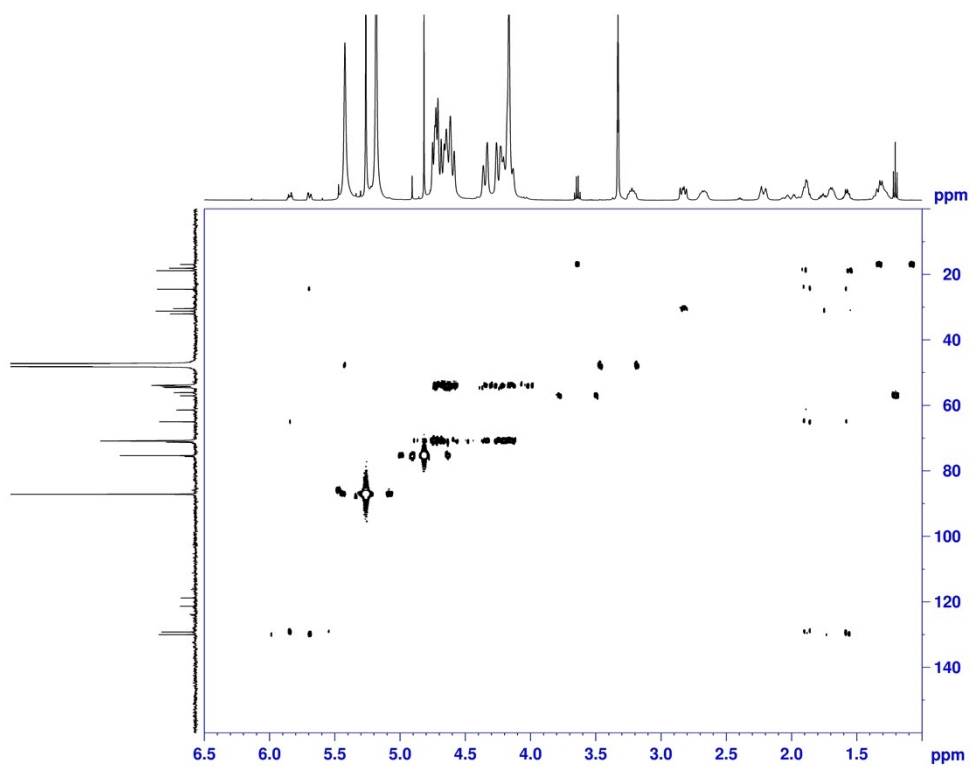


Figure S12. ¹H-¹³C HMBC NMR (-20°C, CD₃OD/D₂O 10:1) spectrum of **3**.

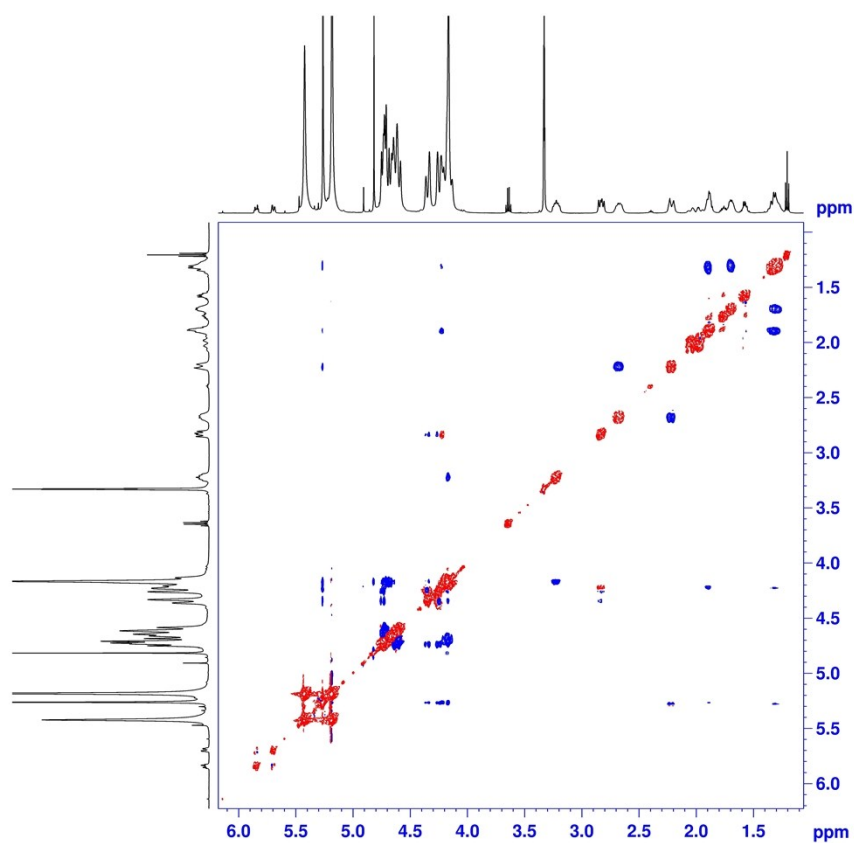


Figure S13. ^1H - ^1H ROESY NMR(-20°C, $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 10:1) spectrum of **3**.

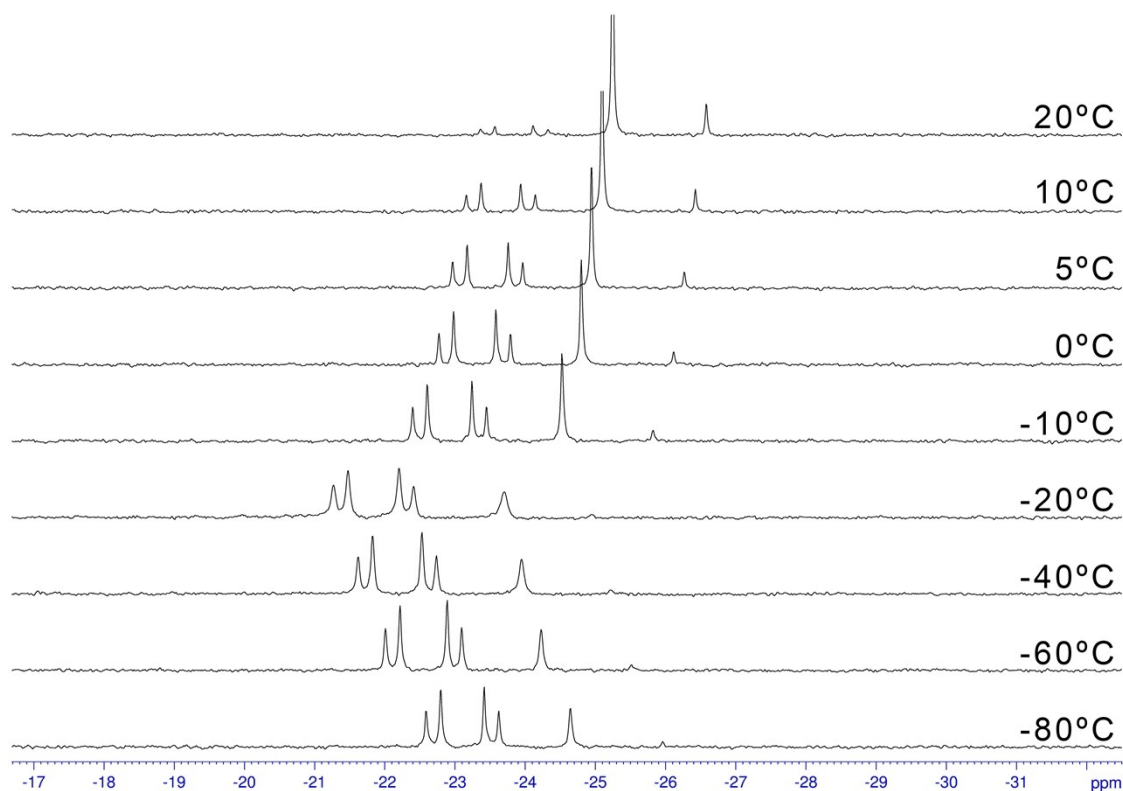


Figure S14. ^1H NMR (-20°C, $\text{CD}_3\text{OD}/\text{D}_2\text{O}$ 10:1) spectra of **3** against temperature.

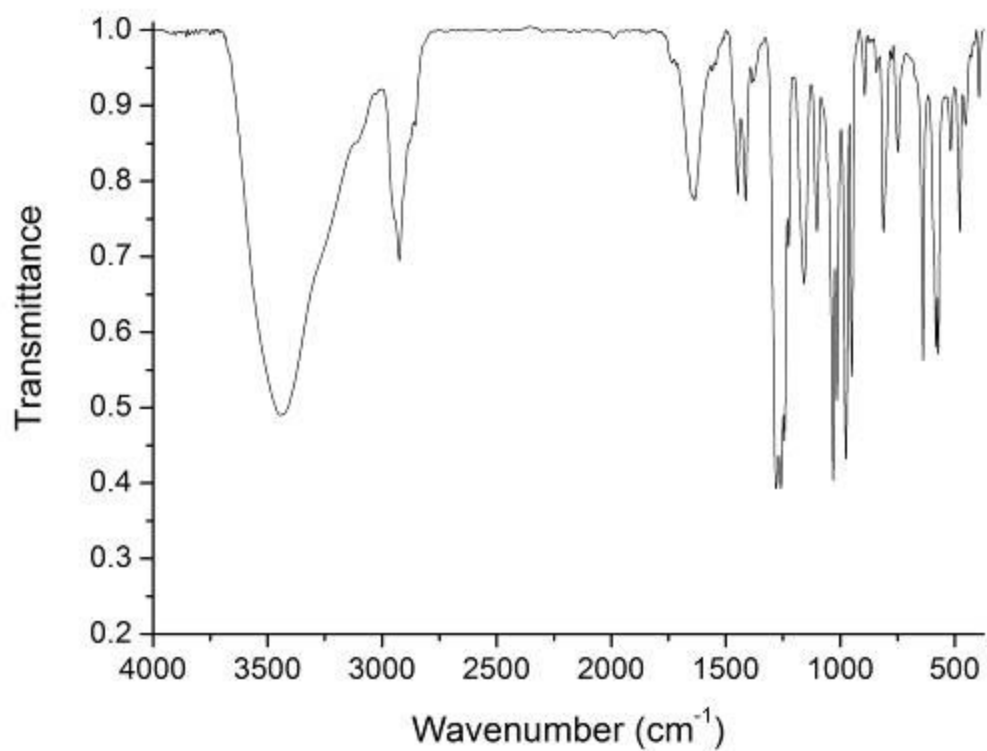


Figure S15. IR (KBr) spectrum of **3**.

References

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