

Supplementary data for article:

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## Supporting information

### Conversion of hydrazides into *N,N'*-diacylhydrazines in the presence of ruthenium(II)-arene complex

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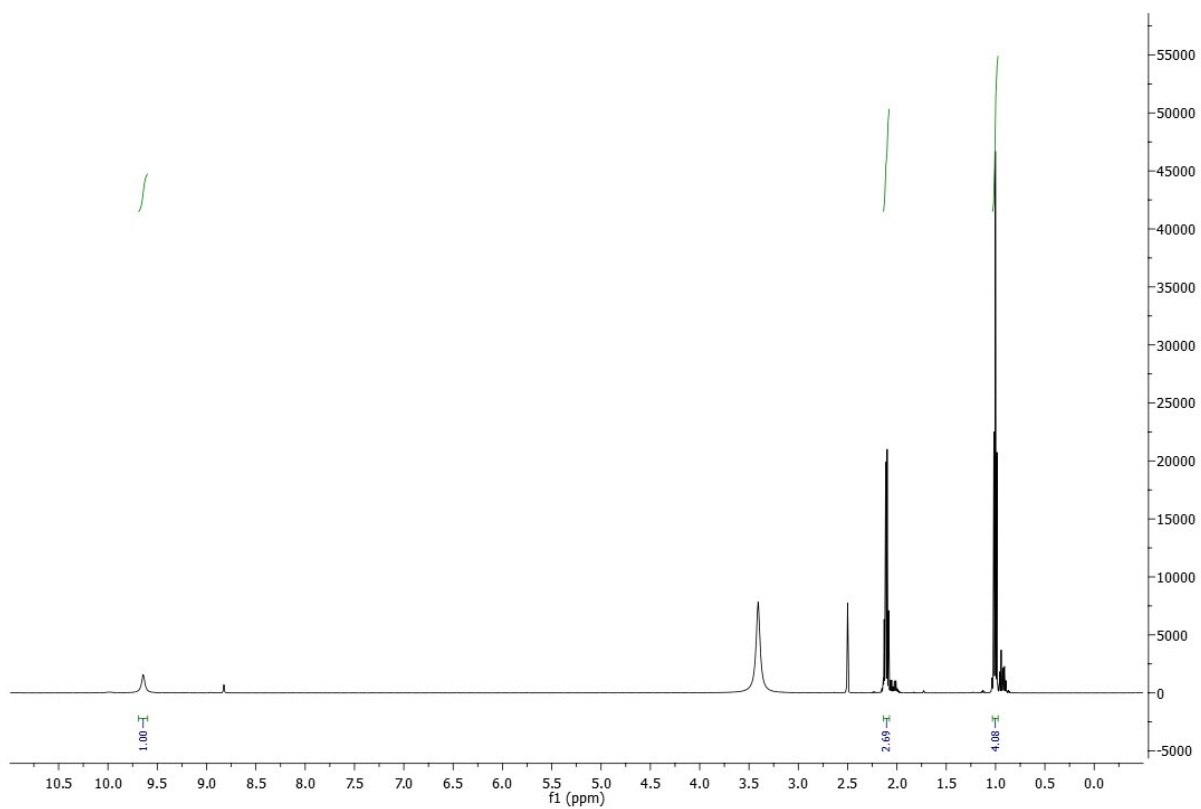
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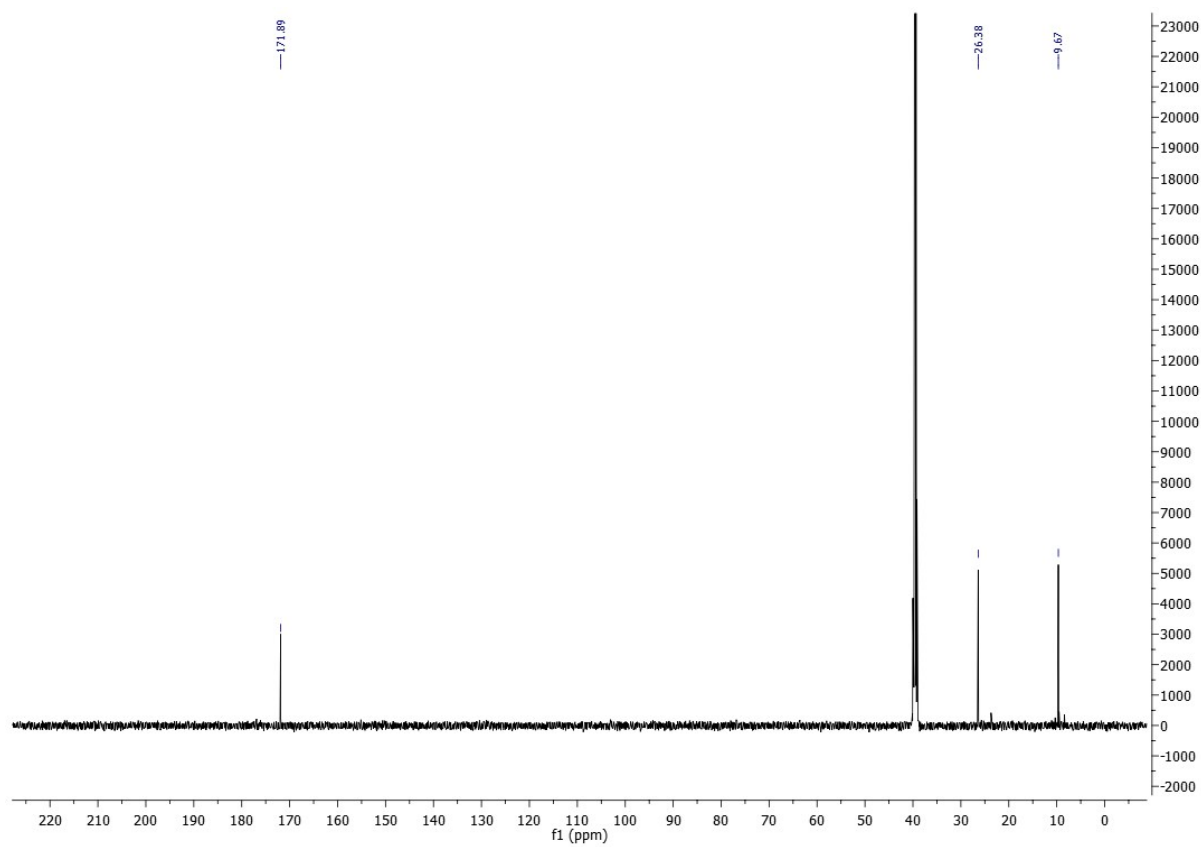
[www.chem.bg.ac.rs/osoblje/36-en.html](http://www.chem.bg.ac.rs/osoblje/36-en.html) Tel: +381 11 3336 742.

## Table of contents

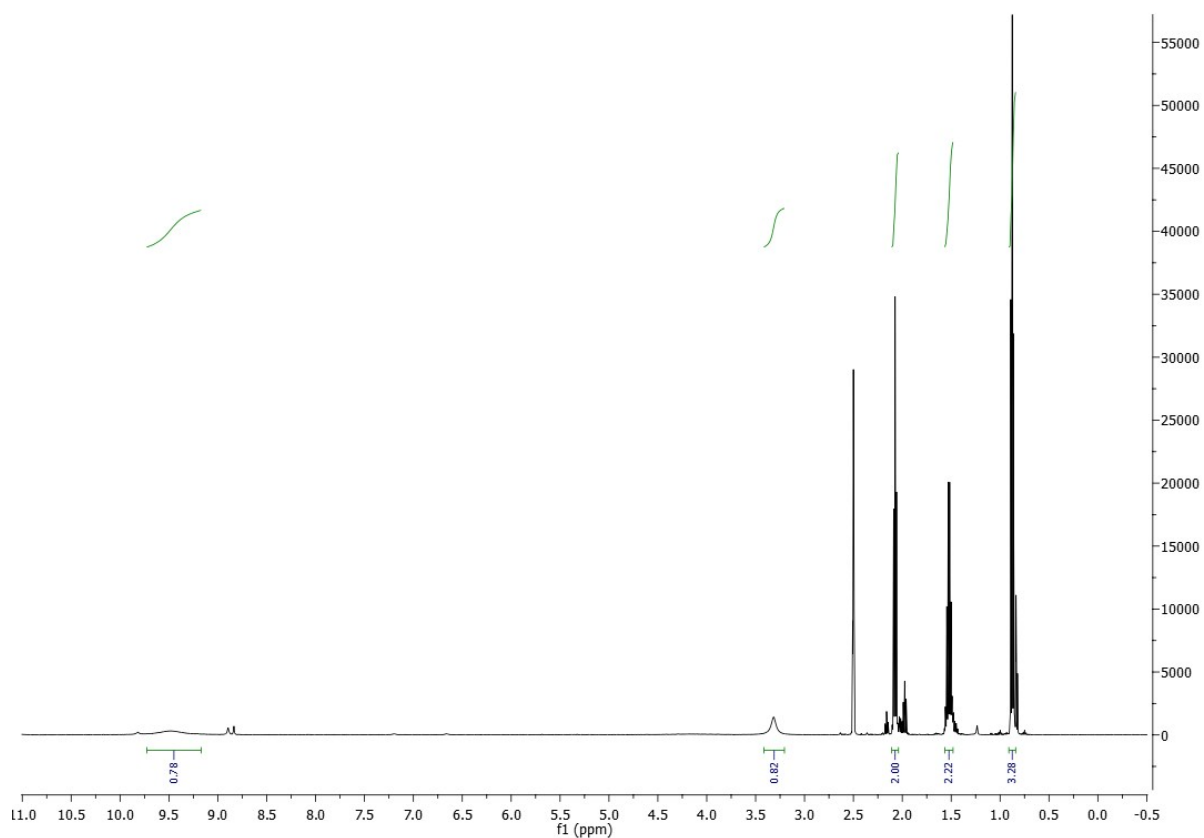
<b>NMR spectra</b> .....	Figure S1-14
<b>X-ray Analysis</b> .....	Figure 1-4; Table 1-10
<b>DFT Calculations</b> .....	Figure S15-S16; Table S1



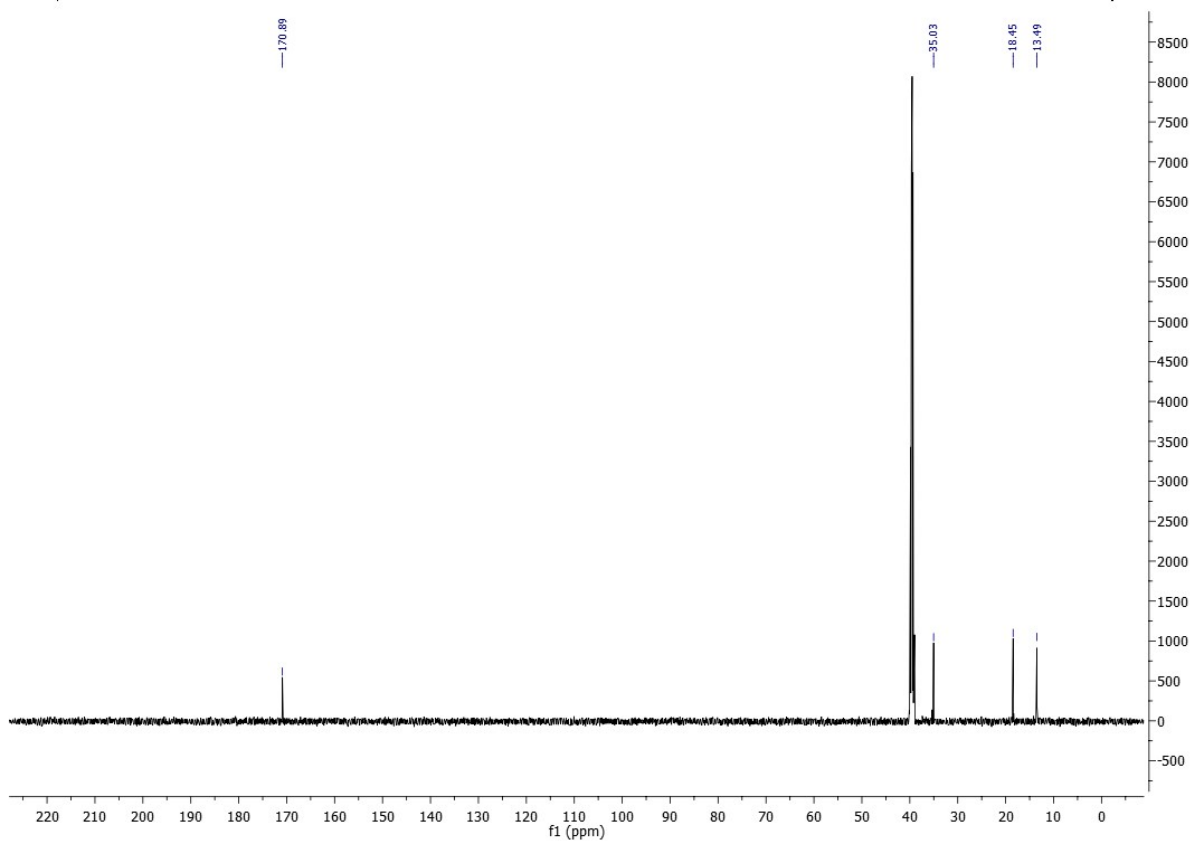
**Figure S1.**  $^1\text{H}$  NMR (500 MHz, DMSO- $d_6$ ) spectrum of  $\text{H}_2\text{L}^2$ .



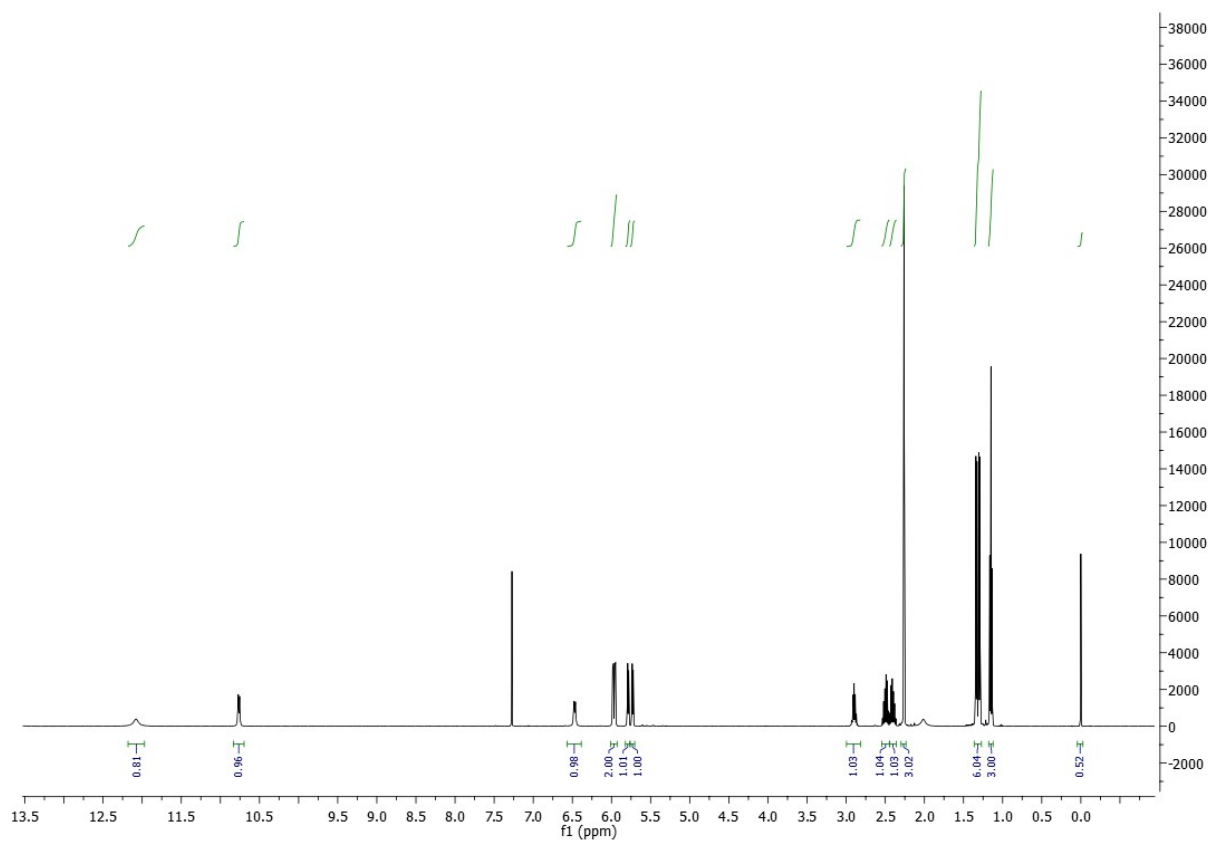
**Figure S2.**  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ) spectrum of  $\text{H}_2\text{L}^2$ .



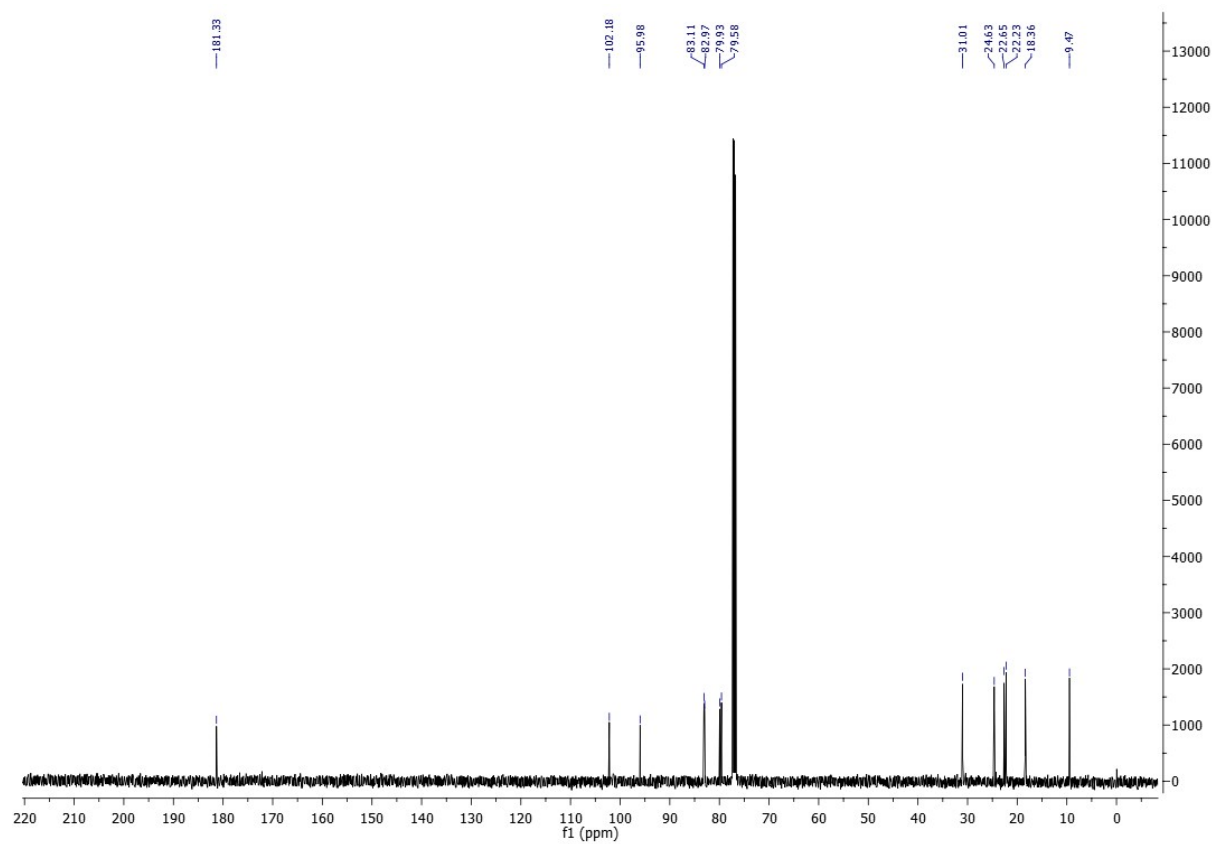
**Figure S3.**  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-d}_6$ ) spectrum of  $\text{H}_2\text{L}^3$



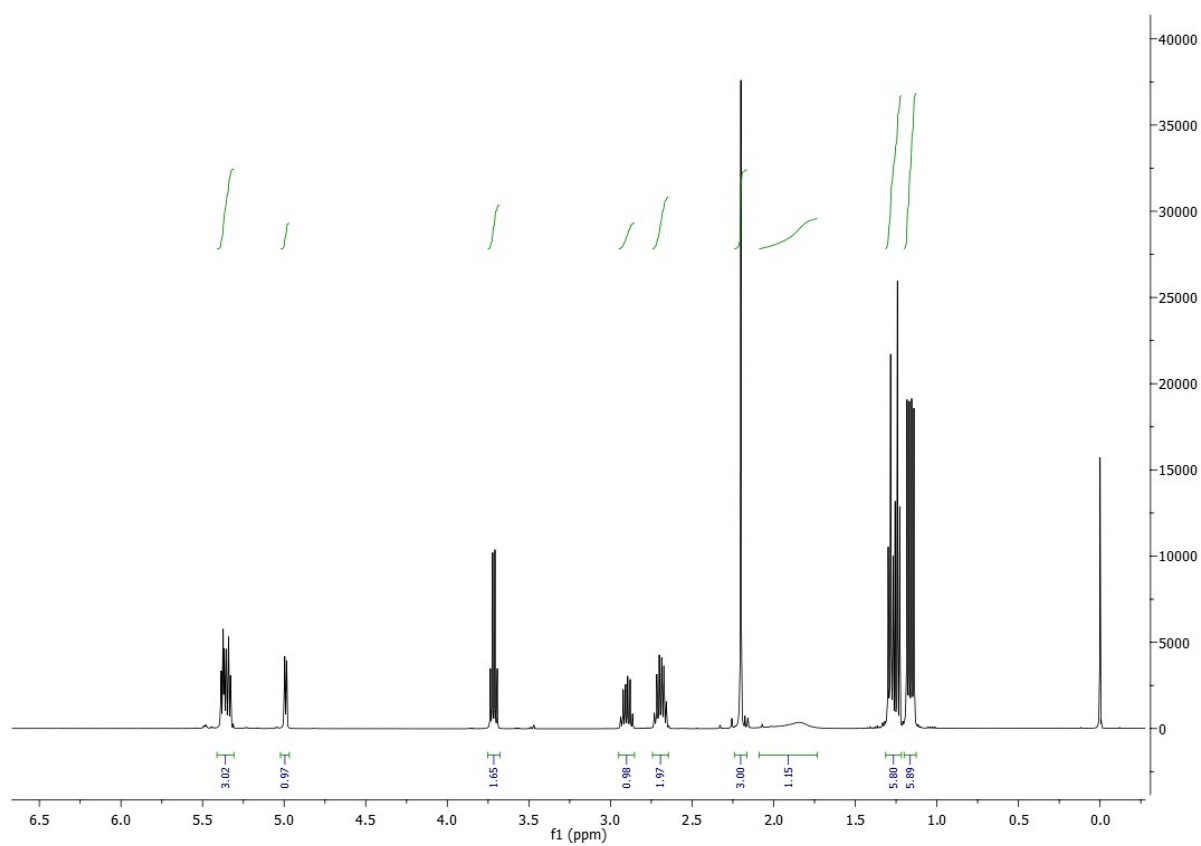
**Figure S4.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ) spectrum of  $\text{H}_2\text{L}^3$



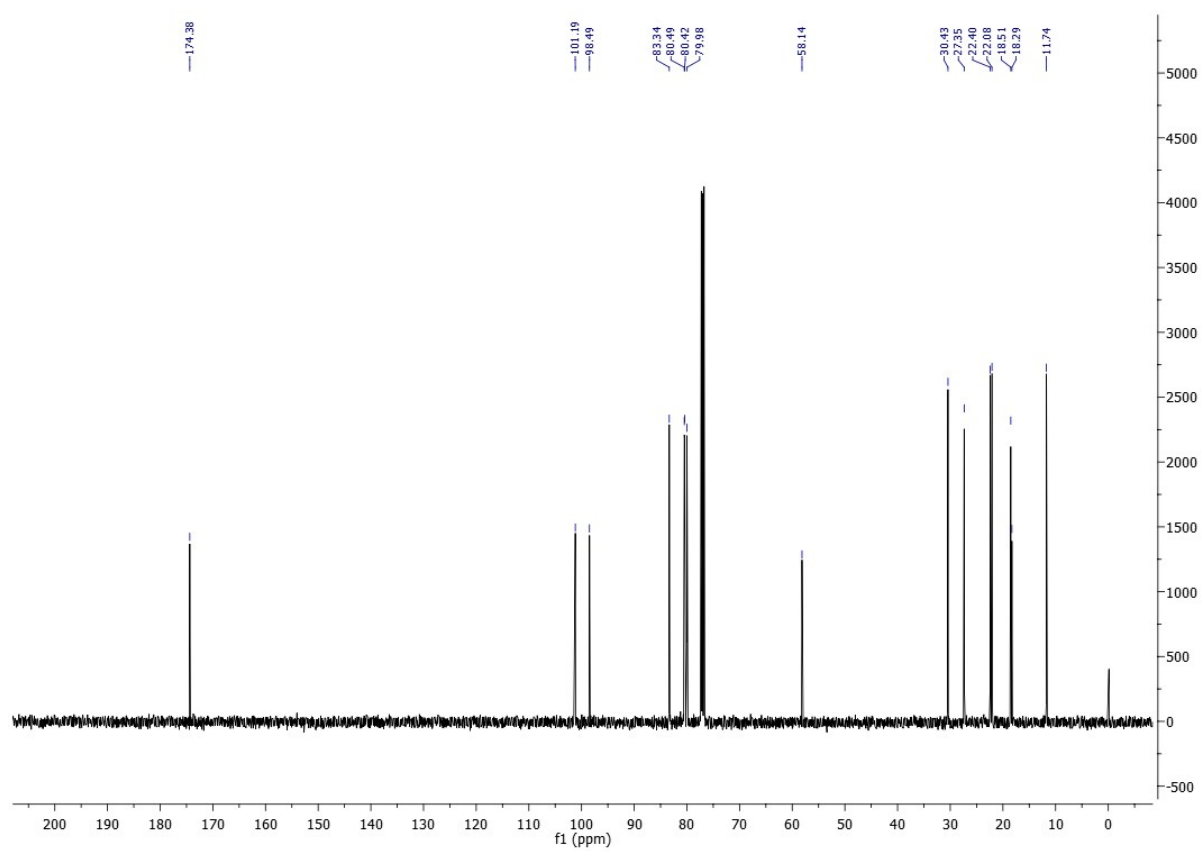
**Figure S5.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **1**



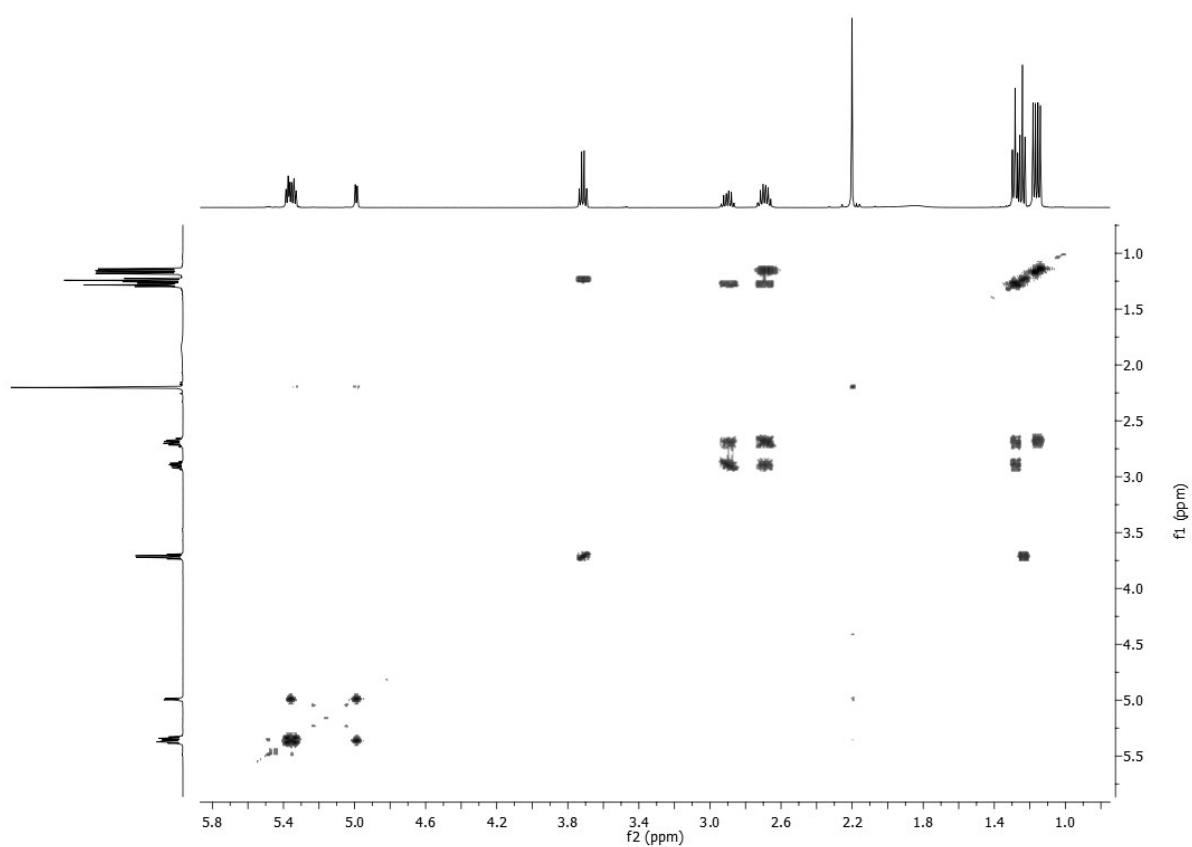
**Figure S6.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **1**



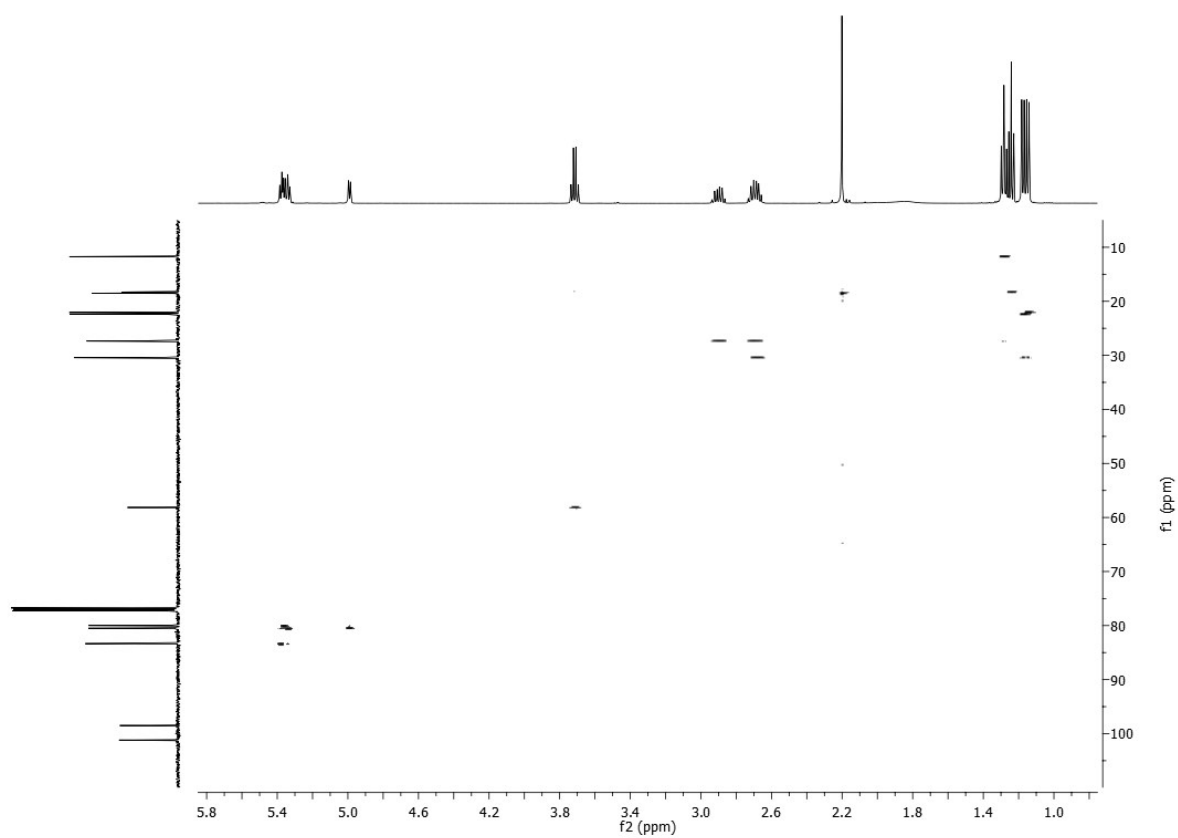
**Figure S7.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **2**



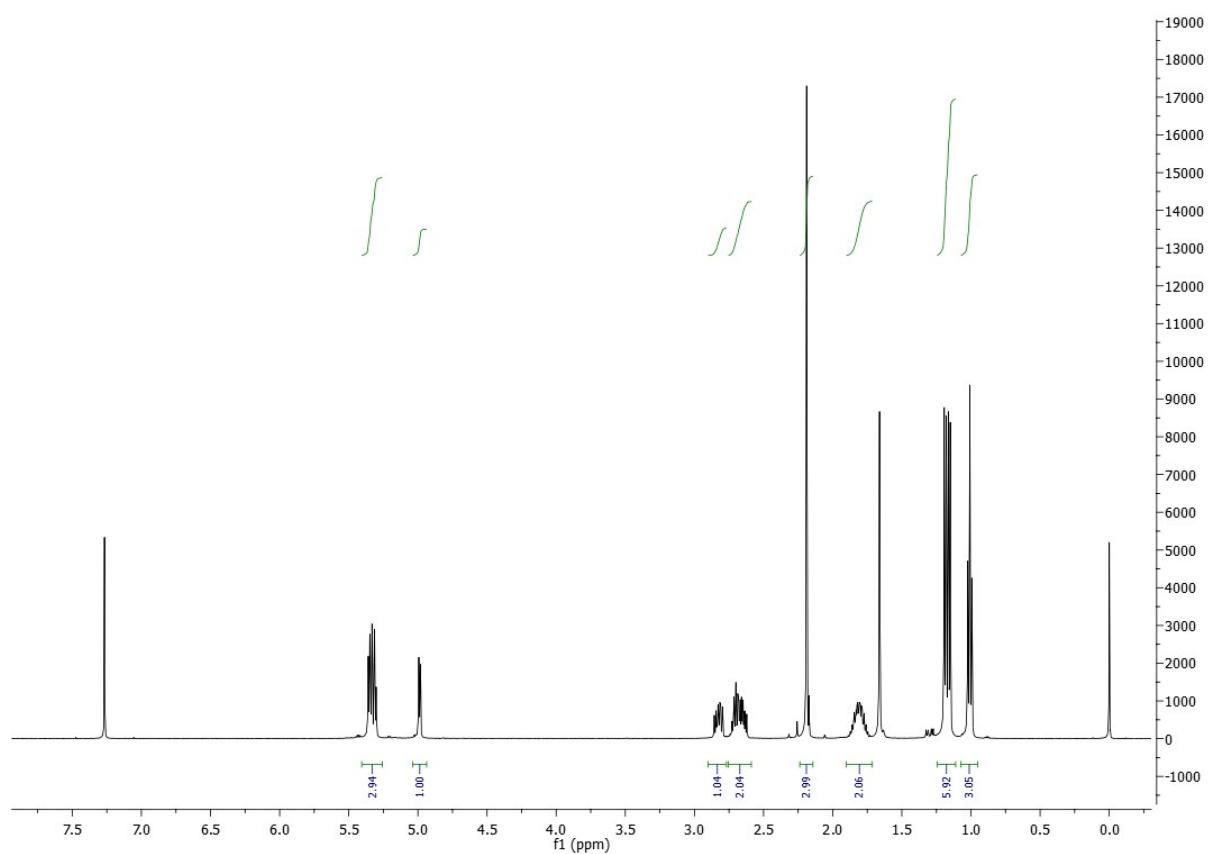
**Figure S8.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **2**



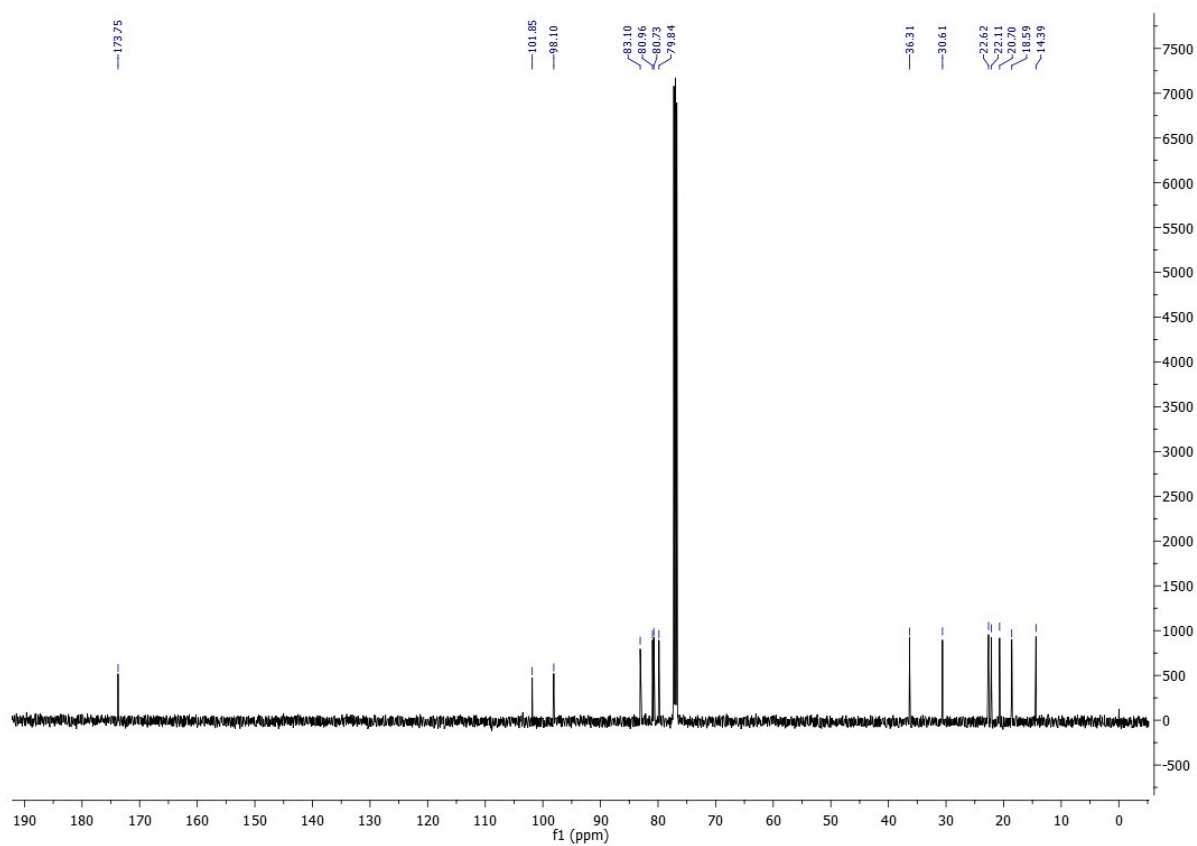
**Figure S9.**  $^1\text{H}$ - $^1\text{H}$  COSY NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **2**



**Figure S10.**  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **2**

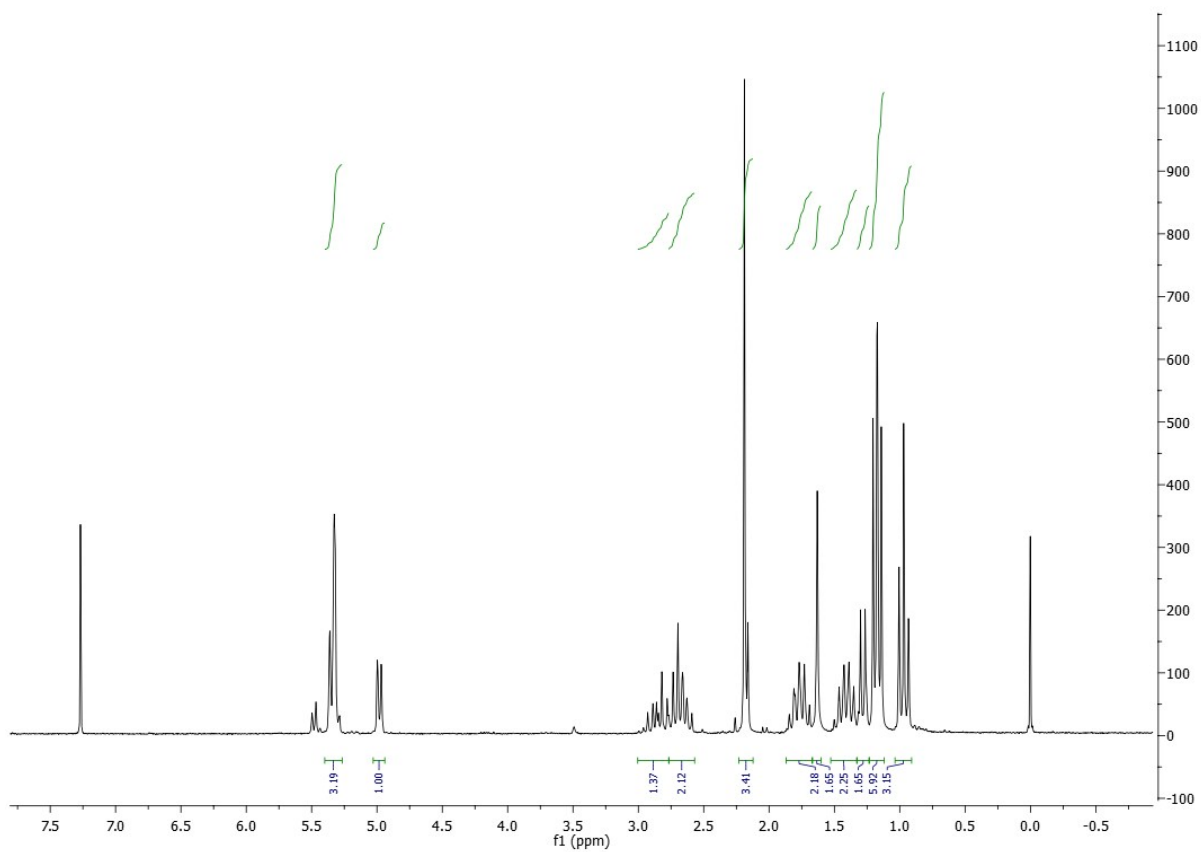


**Figure S11.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **3**

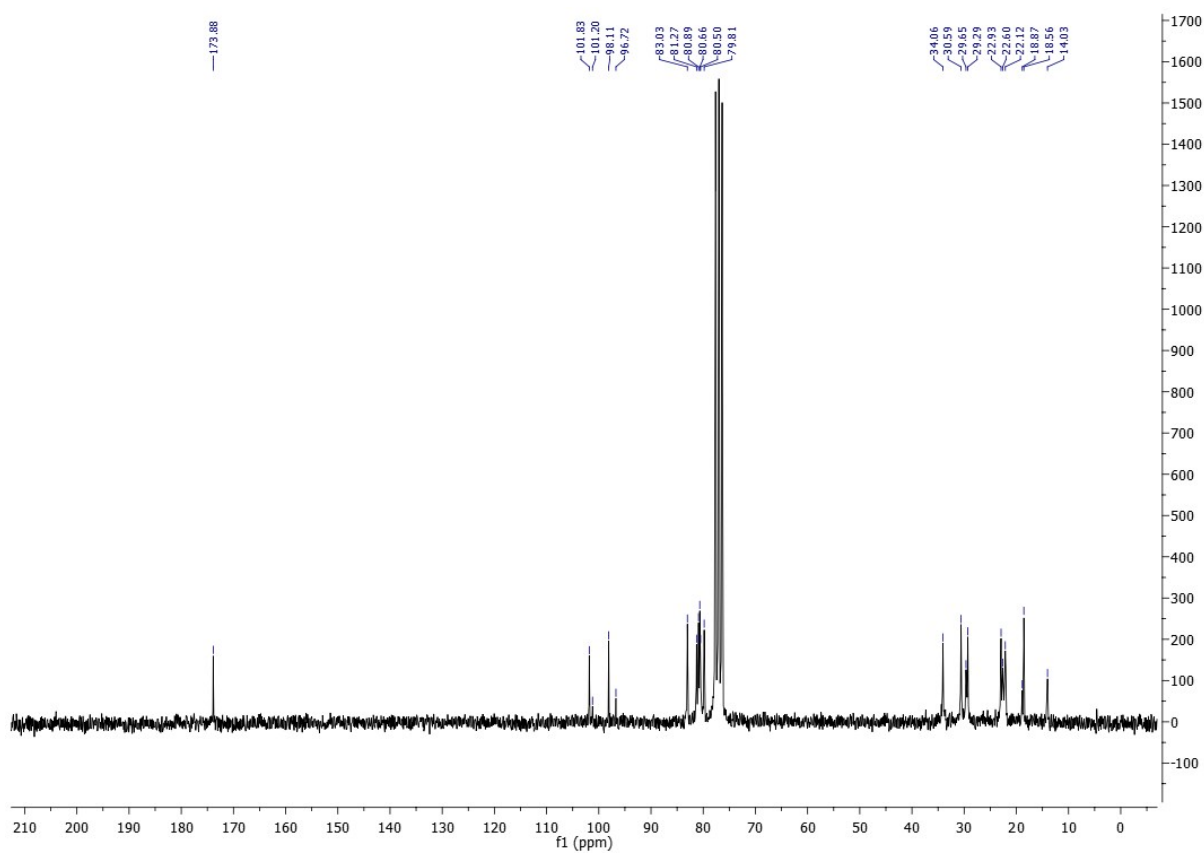


**Figure S12.**  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) spectrum of **3**





**Figure S13.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ ) spectrum of **4**



**Figure S14.**  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ) spectrum of **4**

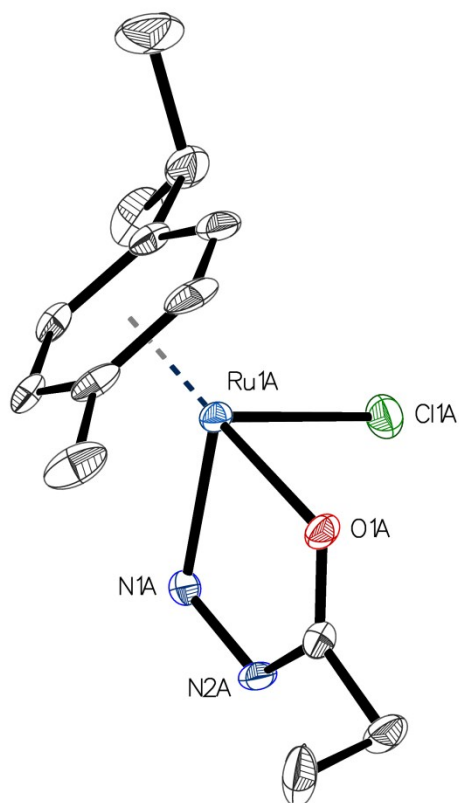
## X-ray Analysis

The X-ray intensity data were measured on Bruker D8 Venture diffractometers equipped with multilayer monochromators, Mo K $\alpha$  INCOATEC micro focus sealed tube and Kryoflex II cooling device. The structures were solved by direct and patterson methods and refined by full-matrix least-squares techniques. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were inserted at calculated positions and refined with a riding model or as rotating groups. The following software was used: Frame integration, *Bruker SAINT software package*<sup>i</sup> using a narrow-frame algorithm, Absorption correction, *SADABS*<sup>ii</sup>, structure solution, *SHELXS-2013*<sup>iii</sup>, refinement, *SHELXL-2013*<sup>iii</sup>, *OLEX2*<sup>iv</sup>, *SHELXLE*<sup>v</sup>, molecular diagrams, *OLEX2*<sup>iv</sup>. Experimental data and CCDC-code can be found in Table 1. Crystal data, data collection parameters, and structure refinement details are given in Tables 2 to 9. Molecular Structure in “Ortep View” is displayed in Figure 1 to 4. A overview about “Metal - Ring Geometry” is given in Table 10.

**Table 1** Experimental parameter and CCDC-Code.

Sample	Machine	Source	Temp.	Detector Distance	Time/Frame	#Frames	Frame width	CCDC
	Bruker		[K]	[mm]	[s]		[°]	
1	D8	Mo	100	40	2.4	1784	0.4	1492601
2	D8	Mo	100	34	8	1630	0.4	1492600
3	D8	Mo	100	35	5.6	1832	0.4	1492602
4	D8	Mo	100	34	15	2626	0.5	1492599

**[RuCl(propionylhydrazine)( $\eta^6$ -p-cymene)]Cl [1] for “New Journal of Chemistry”.**



**Figure 1** Crystal structure of [1], drawn with 50% displacement ellipsoids. Disorder, second moiety of asymmetric unit, counter ion and hydrogens omitted for clarity. The degree of main residue disorder is 31%.

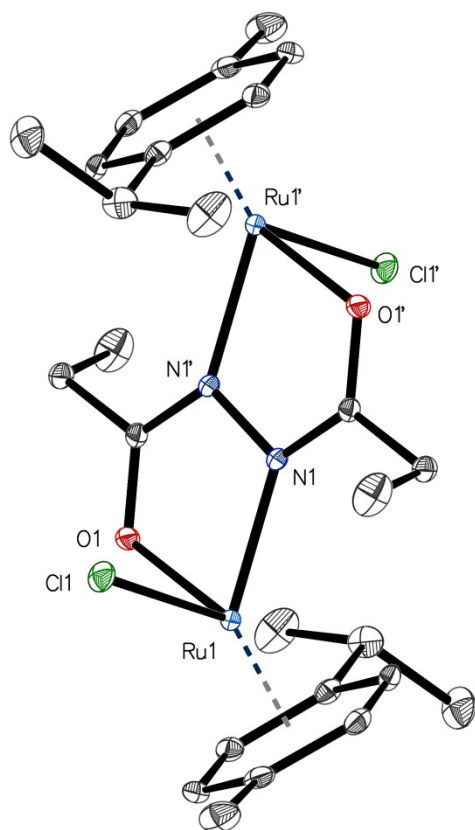
**Table 2** Sample and crystal data of [1].

<b>Chemical formula</b>	C <sub>13</sub> H <sub>22</sub> Cl <sub>2</sub> N <sub>2</sub> ORu	<b>Crystal system</b>	monoclinic	
<b>Formula weight [g/mol]</b>	788.59	<b>Space group</b>	<i>P2<sub>1</sub>/c</i>	
<b>Temperature [K]</b>	100	<b>Z</b>	8	
<b>Measurement method</b>	$\backslash\Phi$ and $\backslash\omega$ scans	<b>Volume [Å<sup>3</sup>]</b>	3308.2(2)	
<b>Radiation (Wavelength [Å])</b>	MoK $\alpha$ ( $\lambda = 0.71073$ )	<b>Unit cell dimensions [Å] and [°]</b>	13.8233(6)	90
<b>Crystal size / [mm<sup>3</sup>]</b>	0.297 × 0.195 × 0.08		20.4127(9)	103.2769(16)
<b>Crystal habit</b>	clear orange block		12.0459(5)	90
<b>Density (calculated) / [g/cm<sup>3</sup>]</b>	1.583	<b>Absorption coefficient / [mm<sup>-1</sup>]</b>	1.265	
<b>Abs. correction Tmin</b>	0.6938	<b>Abs. correction Tmax</b>	0.746	
<b>Abs. correction type</b>	multiscan	<b>F(000) [e<sup>-</sup>]</b>	1600	

**Table 3** Data collection and structure refinement of [1].

<b>Index ranges</b>	$-16 \leq h \leq 16, -24 \leq k \leq 24, -14 \leq l \leq 14$	<b>Theta range for data collection [°]</b>	3.626 to 50.698	
<b>Reflections number</b>	73955	<b>Data / restraints / parameters</b>	6072/36/414	
<b>Refinement method</b>	Least squares	<b>Final R indices</b>	all data	R1 = 0.0353, wR2 = 0.0781
<b>Function minimized</b>	$\Sigma w(F_o^2 - F_c^2)^2$		$I > 2\sigma(I)$	R1 = 0.0298, wR2 = 0.0752
<b>Goodness-of-fit on F<sup>2</sup></b>	1.06	<b>Weighting scheme</b>	$w = 1/[\sigma^2(F_o^2) + (0.0428P)^2 + 0.0437P]$	
<b>Largest diff. peak and hole [e Å<sup>-3</sup>]</b>	0.95/-0.94		where $P = (F_o^2 + 2F_c^2)/3$	

**Ru<sub>2</sub>Cl<sub>2</sub>(N<sup>1</sup>N<sup>2</sup>-dipropionylhydrazine)( $\eta^6$ -p-cymene)<sub>2</sub> [2]** for “New Journal of Chemistry”.



**Figure 2** Grown crystal structure of [2], drawn with 50% displacement ellipsoids. Solvent and hydrogens omitted for clarity. Symmetric atoms are tagged with (') and are equivalent to 2-X,-Y,1-Z.

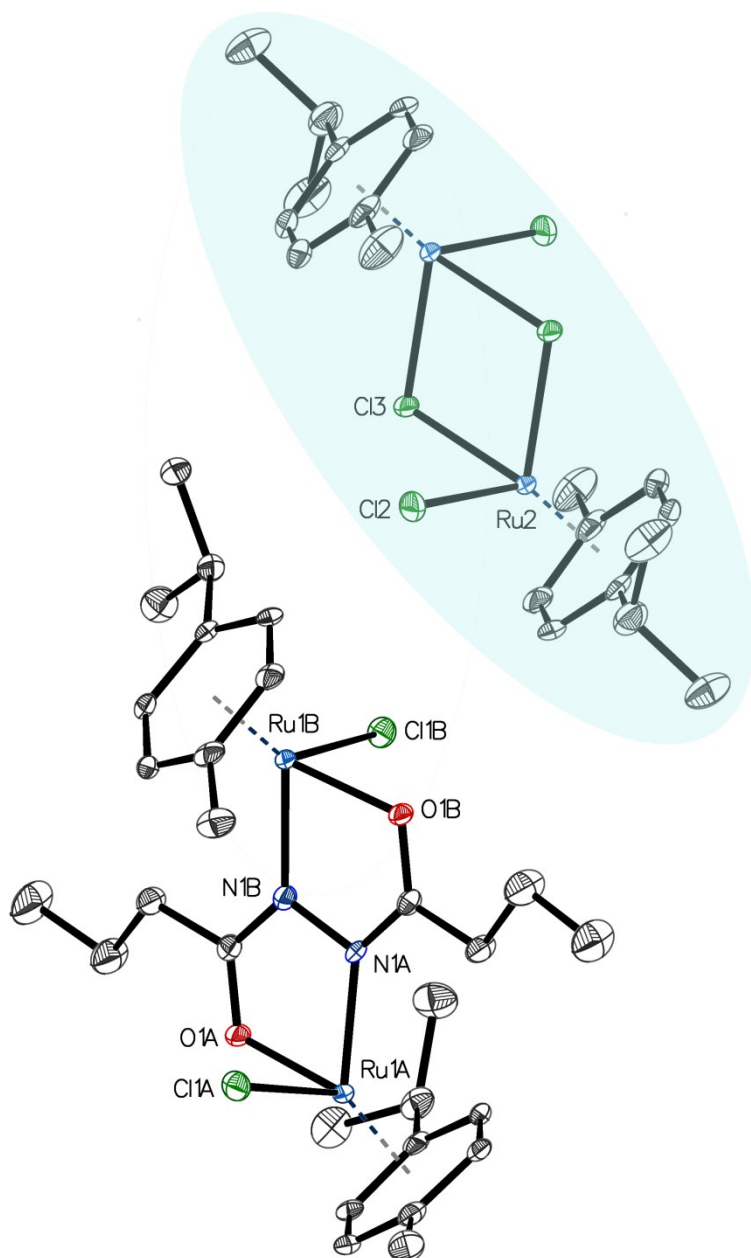
**Table 4** Sample and crystal data of [2].

<b>Chemical formula</b>	C30H50Cl2N2O4Ru2	<b>Crystal system</b>	triclinic	
<b>Formula weight [g/mol]</b>	775.76	<b>Space group</b>	<i>P-1</i>	
<b>Temperature [K]</b>	100	<b>Z</b>	1	
<b>Measurement method</b>	$\backslash\Phi$ and $\backslash\omega$ scans	<b>Volume [Å<sup>3</sup>]</b>	813.93(6)	
<b>Radiation (Wavelength [Å])</b>	MoK $\alpha$ ( $\lambda = 0.71073$ )	<b>Unit cell dimensions [Å] and [°]</b>	9.0536(4)	88.9010(11)
<b>Crystal size / [mm<sup>3</sup>]</b>	0.253 × 0.214 × 0.11		9.0906(4)	88.7726(11)
<b>Crystal habit</b>	clear orange block		9.9218(4)	85.6563(11)
<b>Density (calculated) / [g/cm<sup>3</sup>]</b>	1.583	<b>Absorption coefficient / [mm<sup>-1</sup>]</b>	1.128	
<b>Abs. correction Tmin</b>	0.7056	<b>Abs. correction Tmax</b>	0.746	
<b>Abs. correction type</b>	multiscan	<b>F(000) [e<sup>-</sup>]</b>	398	

**Table 5** Data collection and structure refinement of [2].

<b>Index ranges</b>	-12 ≤ h ≤ 12, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13	<b>Theta range for data collection [°]</b>	4.494 to 60.216	
<b>Reflections number</b>	24472	<b>Data / restraints / parameters</b>	4777/0/187	
<b>Refinement method</b>	Least squares	<b>Final R indices</b>	all data	R1 = 0.0153, wR2 = 0.0390
<b>Function minimized</b>	$\Sigma w(F_o^2 - F_c^2)^2$		I > 2σ(I)	R1 = 0.0149, wR2 = 0.0387
<b>Goodness-of-fit on F<sup>2</sup></b>	1.058	<b>Weighting scheme</b>	w=1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(0.0183P) <sup>2</sup> +0.4424P]	
<b>Largest diff. peak and hole [e Å<sup>-3</sup>]</b>	0.55/-0.75		where P=(F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3	

**Ru<sub>2</sub>Cl<sub>2</sub>(N<sup>1</sup>N<sup>2</sup>-dibutanoylhydrazine)( $\eta^6$ -p-cymene)<sub>2</sub> [3]** for “New Journal of Chemistry”.



**Figure 3** Asymmetric Unit of [3], drawn with 50% displacement ellipsoids. Hydrogen atoms omitted for clarity. Co-crystallized [RuCl<sub>2</sub>( $\eta^6$ -p-cymene)<sub>2</sub>] light blue shaded and grown over center of symmetry °.

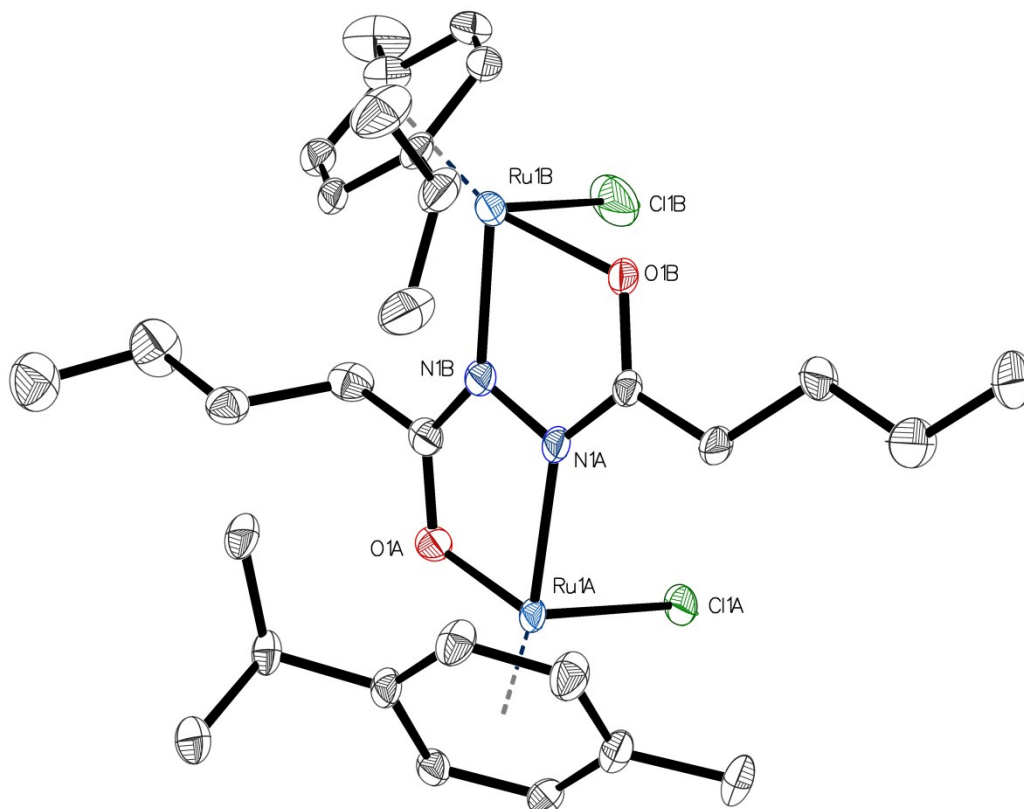
**Table 6** Sample and crystal data of [3].

<b>Chemical formula</b>	C38H56Cl4N2O2Ru3	<b>Crystal system</b>	triclinic	
<b>Formula weight [g/mol]</b>	1017.85	<b>Space group</b>	<i>P-1</i>	
<b>Temperature [K]</b>	100	<b>Z</b>	2	
<b>Measurement method</b>	$\backslash\Phi$ and $\backslash\omega$ scans	<b>Volume [Å<sup>3</sup>]</b>	1983.18(14)	
<b>Radiation (Wavelength [Å])</b>	MoK $\alpha$ ( $\lambda = 0.71073$ )	<b>Unit cell dimensions [Å] and [°]</b>	9.9160(4)	76.1322(15)
<b>Crystal size / [mm<sup>3</sup>]</b>	0.189 × 0.129 × 0.055		12.3781(5)	78.3310(15)
<b>Crystal habit</b>	clear orange block		16.9971(7)	88.3137(16)
<b>Density (calculated) / [g/cm<sup>3</sup>]</b>	1.705	<b>Absorption coefficient / [mm<sup>-1</sup>]</b>	1.433	
<b>Abs. correction Tmin</b>	0.9349	<b>Abs. correction Tmax</b>	1	
<b>Abs. correction type</b>	numerical	<b>F(000) [e<sup>-</sup>]</b>	1028	

**Table 7** Data collection and structure refinement of [3].

<b>Index ranges</b>	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -20 ≤ l ≤ 20	<b>Theta range for data collection [°]</b>	2.52 to 50.7	
<b>Reflections number</b>	49197	<b>Data / restraints / parameters</b>	7252/0/453	
<b>Refinement method</b>	Least squares	<b>Final R indices</b>	all data	R1 = 0.0236, wR2 = 0.0513
<b>Function minimized</b>	$\Sigma w(F_o^2 - F_c^2)^2$		I > 2σ(I)	R1 = 0.0206, wR2 = 0.0498
<b>Goodness-of-fit on F<sup>2</sup></b>	1.057	<b>Weighting scheme</b>	w=1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(0.0253P) <sup>2</sup> +1.7685P]	
<b>Largest diff. peak and hole [e Å<sup>-3</sup>]</b>	1.21/-0.45		where P=(F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3	

**Ru<sub>2</sub>Cl<sub>2</sub>(N<sup>1</sup>N<sup>2</sup>-dipentanoylhydrazine)(η<sup>6</sup>-p-cymene)<sub>2</sub> [4]** for “New Journal of Chemistry”.



**Figure 4** Asymmetric Unit of [4], drawn with 50% displacement ellipsoids. Hydrogen atoms, disorder and free water omitted for clarity. The degree of main residue disorder is 13%.

**Table 8** Sample and crystal data of [4].

<b>Chemical formula</b>	C <sub>30</sub> H <sub>50</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>4</sub> Ru <sub>2</sub>	<b>Crystal system</b>	triclinic	
<b>Formula weight [g/mol]</b>	775.76	<b>Space group</b>	<i>P</i> -1	
<b>Temperature [K]</b>	100	<b>Z</b>	2	
<b>Measurement method</b>	∅ and ∅ scans	<b>Volume [Å<sup>3</sup>]</b>	1658.71(14)	
<b>Radiation (Wavelength [Å])</b>	MoKα (λ = 0.71073)	<b>Unit cell dimensions [Å] and [°]</b>	9.6072(5)	95.264(2)
<b>Crystal size / [mm<sup>3</sup>]</b>	0.164 × 0.164 × 0.067		9.7722(5)	90.7653(18)
<b>Crystal habit</b>	clear orange block		17.7727(8)	93.160(2)
<b>Density (calculated) / [g/cm<sup>3</sup>]</b>	1.553	<b>Absorption coefficient / [mm<sup>-1</sup>]</b>	1.107	
<b>Abs. correction Tmin</b>	0.7093	<b>Abs. correction Tmax</b>	0.746	
<b>Abs. correction type</b>	multiscan	<b>F(000) [e<sup>-</sup>]</b>	796	



**Table 9** Data collection and structure refinement of [4].

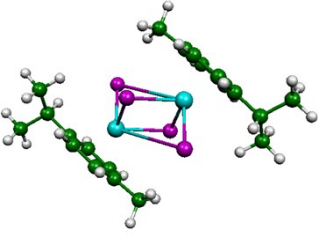
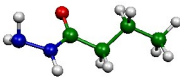
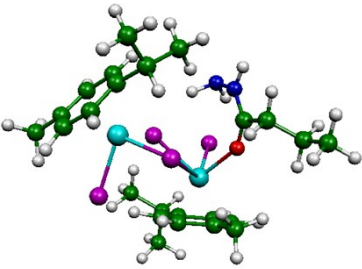
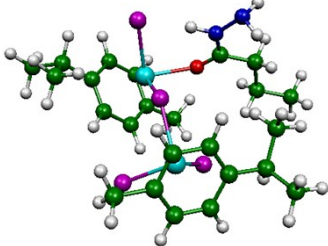
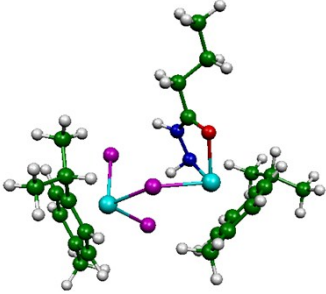
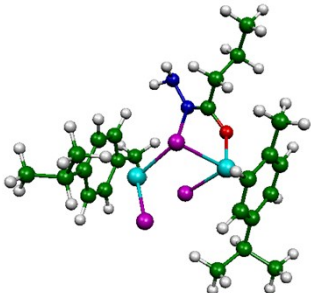
<b>Index ranges</b>	-13 ≤ h ≤ 13, -13 ≤ k ≤ 13, -25 ≤ l ≤ 25	<b>Theta range for data collection [°]</b>	4.592 to 60.19	
<b>Reflections number</b>	92947	<b>Data / restraints / parameters</b>	9735/32/428	
<b>Refinement method</b>	Least squares	<b>Final R indices</b>	all data	R1 = 0.0458, wR2 = 0.0824
<b>Function minimized</b>	$\Sigma w(F_o^2 - F_c^2)^2$		I > 2σ(I)	R1 = 0.0337, wR2 = 0.0747
<b>Goodness-of-fit on F<sup>2</sup></b>	1.063	<b>Weighting scheme</b>	w=1/[σ <sup>2</sup> (F <sub>o</sub> <sup>2</sup> )+(0.0249P) <sup>2</sup> +3.7315P]	
<b>Largest diff. peak and hole [e Å<sup>-3</sup>]</b>	1.90/-2.68		where P=(F <sub>o</sub> <sup>2</sup> +2F <sub>c</sub> <sup>2</sup> )/3	

**Table 10** Metal - Ring Geometry for Compounds 1-4

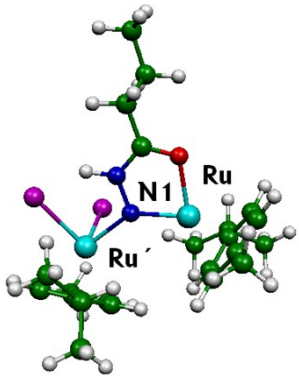
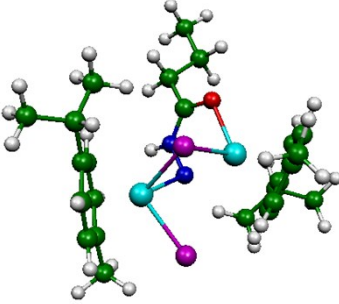
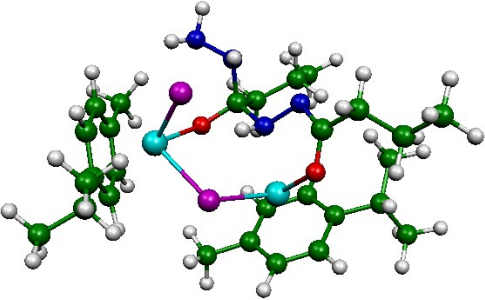
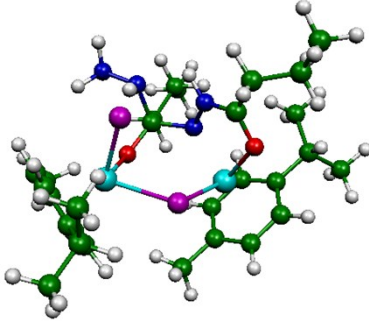
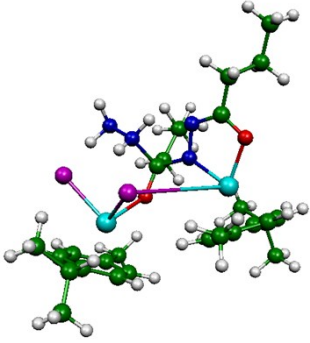
<b>Metal - Ring Geometry</b>				
Compound	Center	Perpendicular Projection of Heavy Atom	Ring Centroid	Ring-Slippage
		[Å]	[Å]	[Å]
<b>1</b>	Ru1A	1.6461(10)	1.6459(4)	0.027
	Ru1B	-	-	-
<b>2</b>	Ru1	1.6610(5)	1.6605(2)	0.041
<b>3</b>	Ru1A	1.6760(9)	1.6759(3)	0.014
	Ru1B	1.6587(9)	1.6580(3)	0.048
<b>4</b>	Ru1A	1.6600(11)	1.6595(3)	0.041
	Ru1B	1.6668(11)	1.6668(3)	0.005
Disordered solutions are, because of constraints and restraints, excluded from detailed analysis				

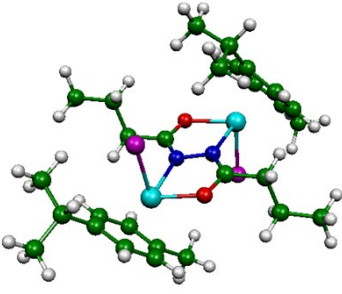
<sup>i</sup> Bruker SAINT V8.32B Copyright © 2005-2016 Bruker AXS<sup>ii</sup> Sheldrick, G. M. (1996). *SHELXS, SHELXL*. University of Göttingen, Germany.<sup>iii</sup> Sheldrick, G.M. (2008). *Acta Cryst. A*64, 112-122.<sup>iv</sup> Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. , *OLEX2*, (2009), *J. Appl. Cryst.* 42, 339-341<sup>v</sup> C. B. Huebschle, G. M. Sheldrick and B. Dittrich, *ShelXle: a Qt graphical user interface for SHELXL*, *J. Appl. Cryst.*, 44, (2011) 1281-1284

## DFT Calculations

	
<b>-11505.489094 (R1)</b>	<b>-342.9131381 (R2)</b>
	
<b>-11848.4142065 (Ia)</b>	<b>-11848.4120083 (Ib)</b>
	
<b>-11387.701511 (IIa)</b>	<b>-11387.6682279 (IIb)</b>

**Figure S15.** The B3LYP optimal structures of studied reactants, intermediates and product. The electronic B3LYP energies are in hartree.

	
<p align="center"><b>-10926.993142 (IIIa)</b></p>	<p align="center"><b>-10926.97686 (IIIb)</b></p>
	
<p align="center"><b>-11269.8755261 (IVa)</b></p>	<p align="center"><b>-11269.8701989 (IVb)</b></p>
	
<p align="center"><b>-11269.8893666 (V)</b></p>	

	
-11158.145344 (P)	

**Figure S15. (continued)** The B3LYP optimal structures of studied reactants, intermediates and product. The electronic B3LYP energies are in hartree.

**Table S1.** The selected gas-phase B3LYP and X-ray bond lengths

<b>Bond</b>	<b>B3LYP</b>	<b>X-ray</b>
C <sub>1</sub> -C <sub>2</sub>	1.528	1.525(3)
C <sub>2</sub> -C <sub>3</sub>	1.540	1.508(3)
C <sub>3</sub> -C <sub>4</sub>	1.507	1.504(3)
C <sub>4</sub> -N <sub>1</sub>	1.315	1.306(3)
N <sub>1</sub> -N <sub>2</sub>	1.408	1.433(2)
N <sub>2</sub> -C <sub>5</sub>	1.315	1.307(3)
C <sub>5</sub> -C <sub>6</sub>	1.507	1.509(3)
C <sub>6</sub> -C <sub>7</sub>	1.540	1.506(3)
C <sub>7</sub> -C <sub>8</sub>	1.528	1.525(3)
C=O	1.282 / 1.283	1.287 / 1.290(2)
Ru-O	2.077 / 2.075	2.095 / 2.069(14)
Ru-Cl	2.439 / 2.439	2.412 / 2.412(5)
C <sub>9</sub> -C <sub>10</sub>	1.417 / 1.425	1.410 / 1.407(3)
C <sub>9</sub> -C <sub>10'</sub>	1.419 / 1.427	1.435 / 1.427(3)
C <sub>10</sub> -C <sub>11</sub>	1.428 / 1.428	1.421 / 1.420(3)
C <sub>10</sub> -C <sub>11'</sub>	1.419 / 1.421	1.403 / 1.402(3)
C <sub>11</sub> -C <sub>12</sub>	1.423 / 1.421	1.412 / 1.409(3)
C <sub>11</sub> -C <sub>12'</sub>	1.432 / 1.428	1.435 / 1.433(3)
C <sub>9</sub> -C <sub>13</sub>	1.502 / 1.503	1.503 / 1.500(3)
C <sub>12</sub> -C <sub>14</sub>	1.527 / 1.519	1.517 / 1.518(3)
C <sub>14</sub> -C <sub>15</sub>	1.538 / 1.532	1.528 / 1.520(3)
C <sub>14</sub> -C <sub>15'</sub>	1.534 / 1.542	1.539 / 1.528(3)

