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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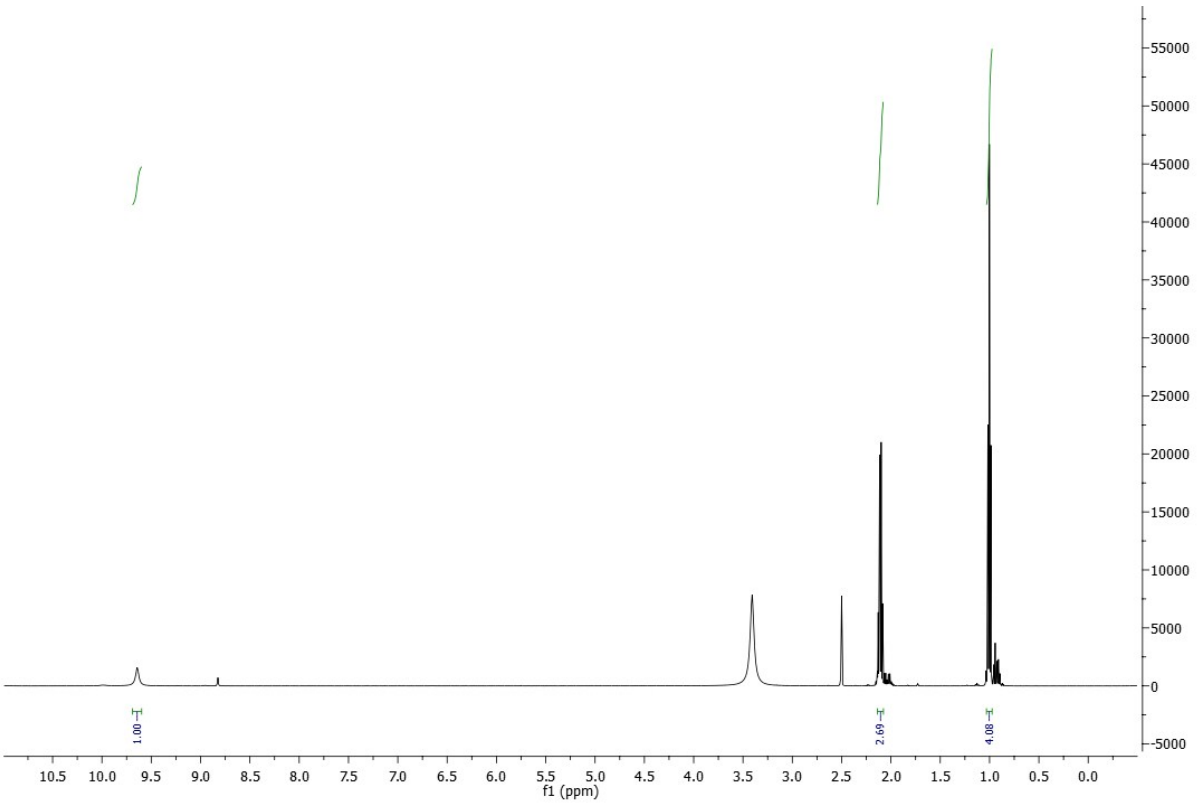


Figure S1. ^{1}H NMR (500 MHz, DMSO-d6) spectrum of $\mathbf{H_2L^2}$.

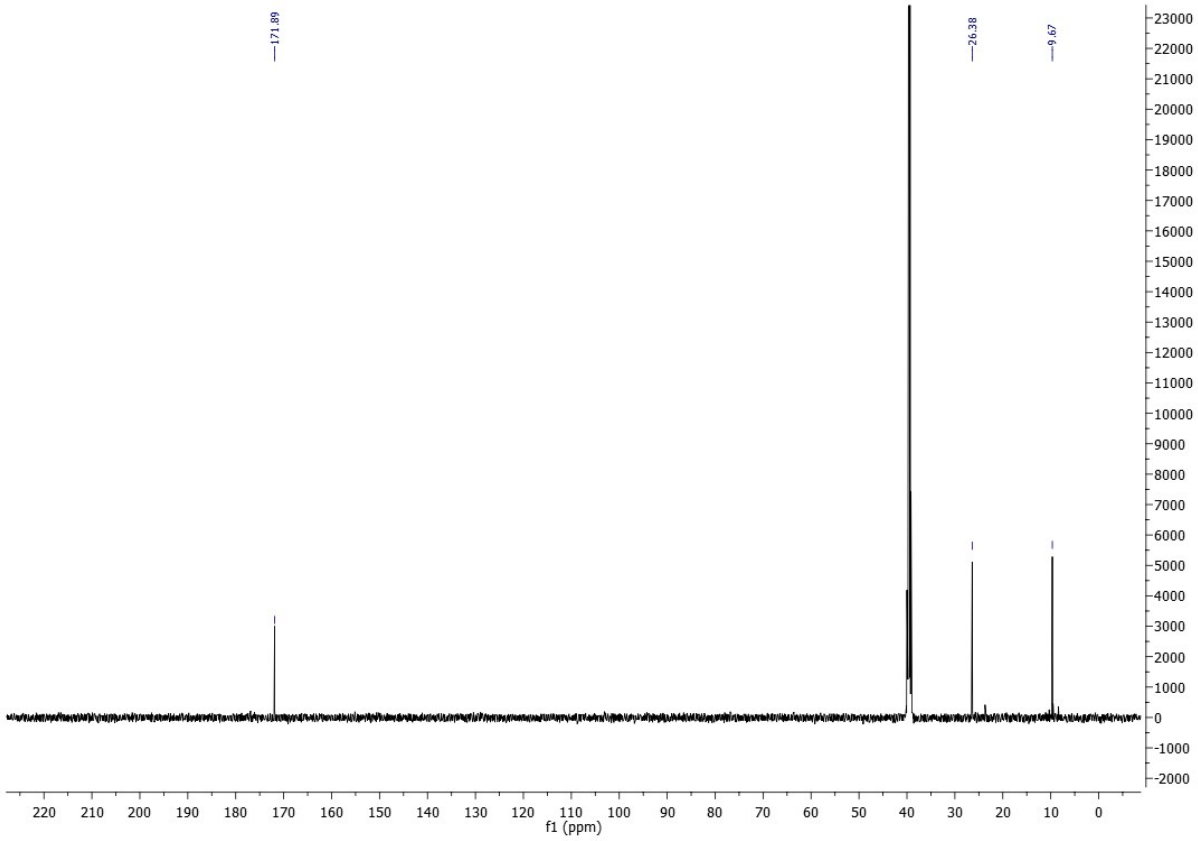


Figure S2. ^{13}C NMR (100 MHz, DMSO-d6) spectrum of $\mathbf{H_2L^2}$

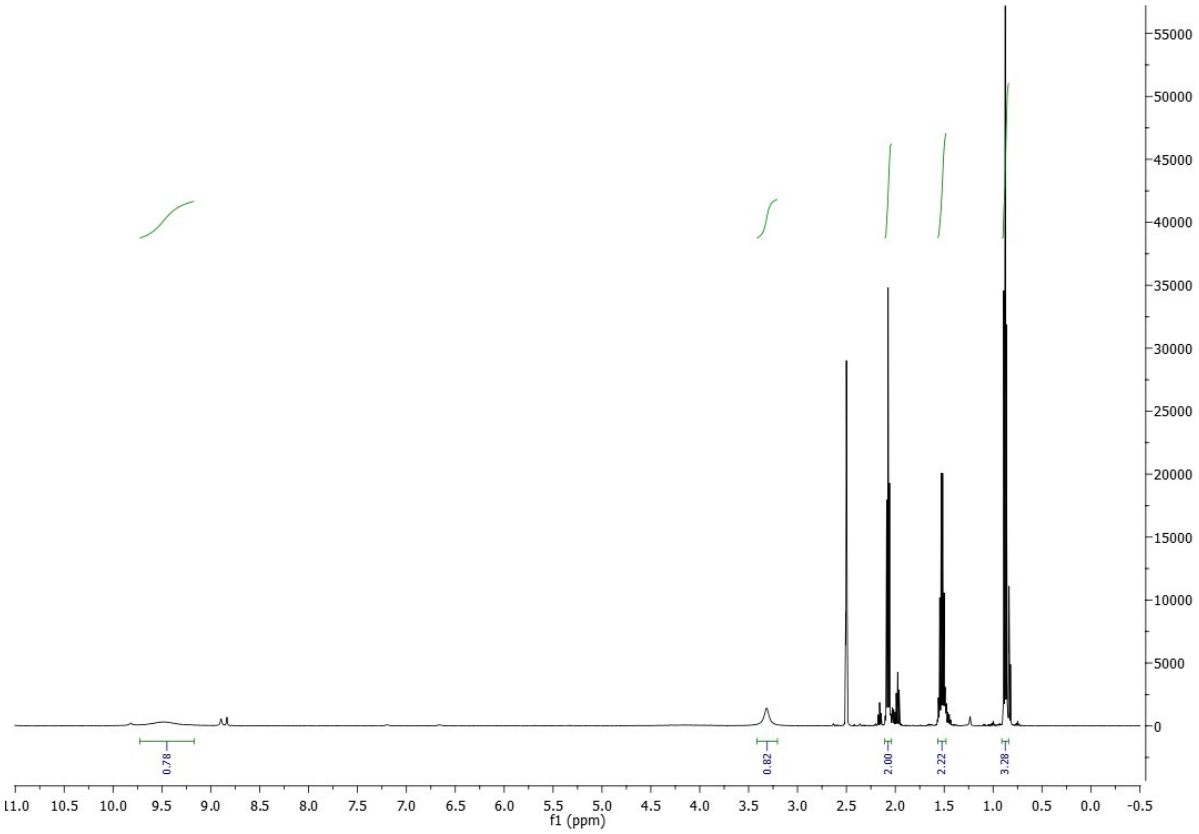


Figure S3. ^{1}H NMR (500 MHz, DMSO-d6) spectrum of $\mathbf{H_2L^3}$

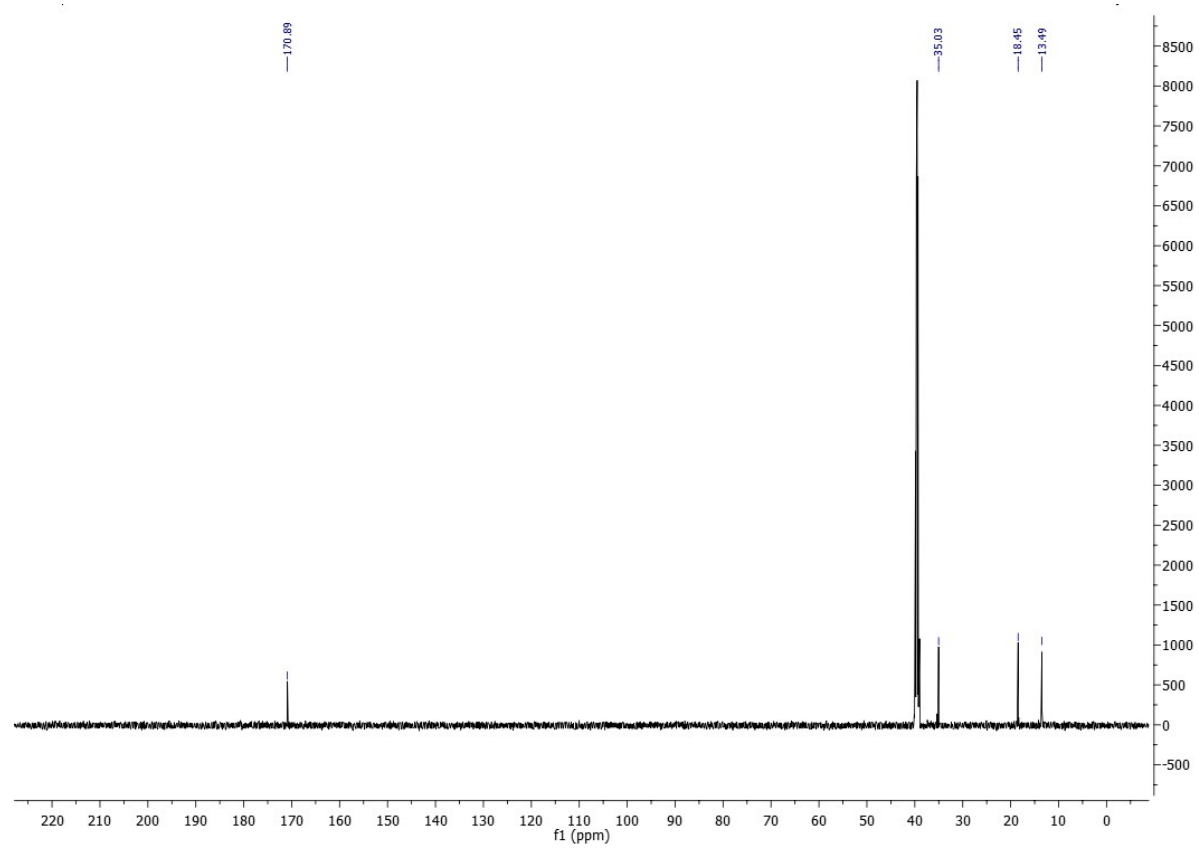


Figure S4. ^{13}C NMR (100 MHz, DMSO-d6) spectrum of $\mathbf{H_2L^3}$

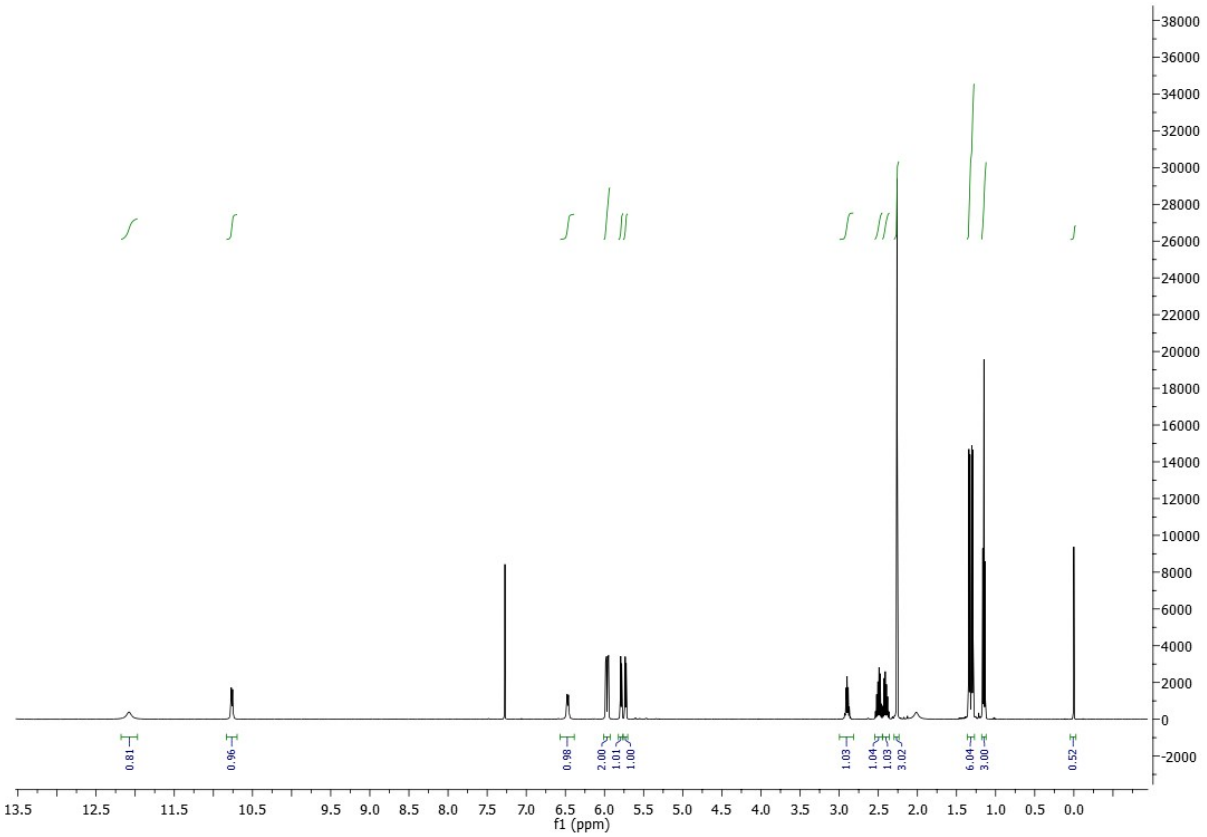


Figure S5. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **1**

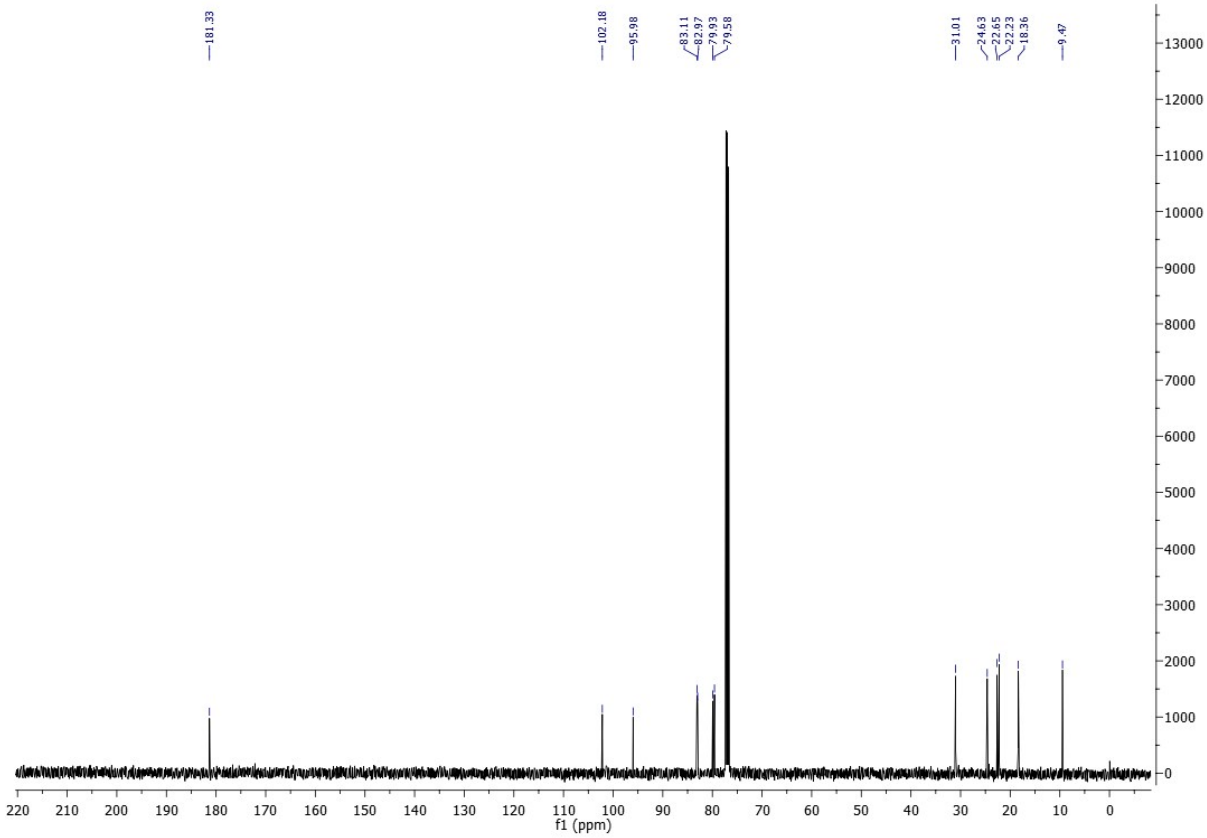


Figure S6. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1**

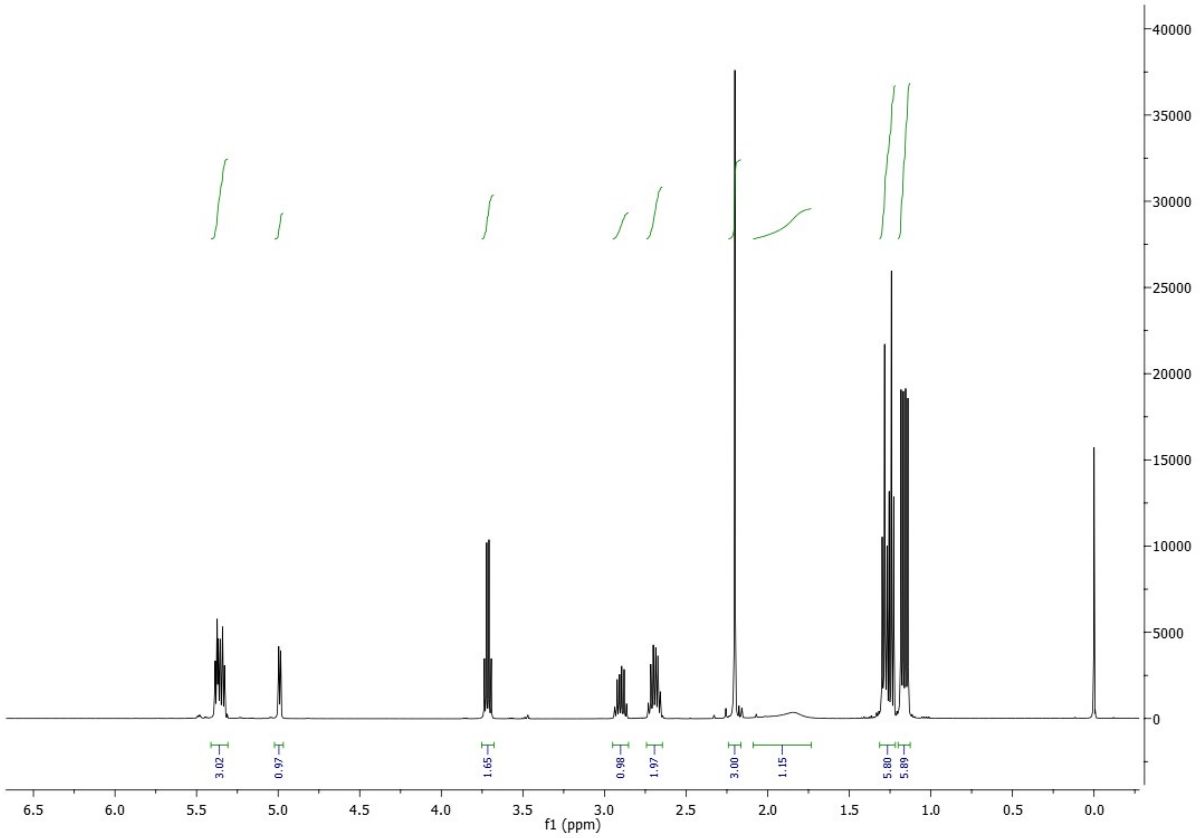


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **2**

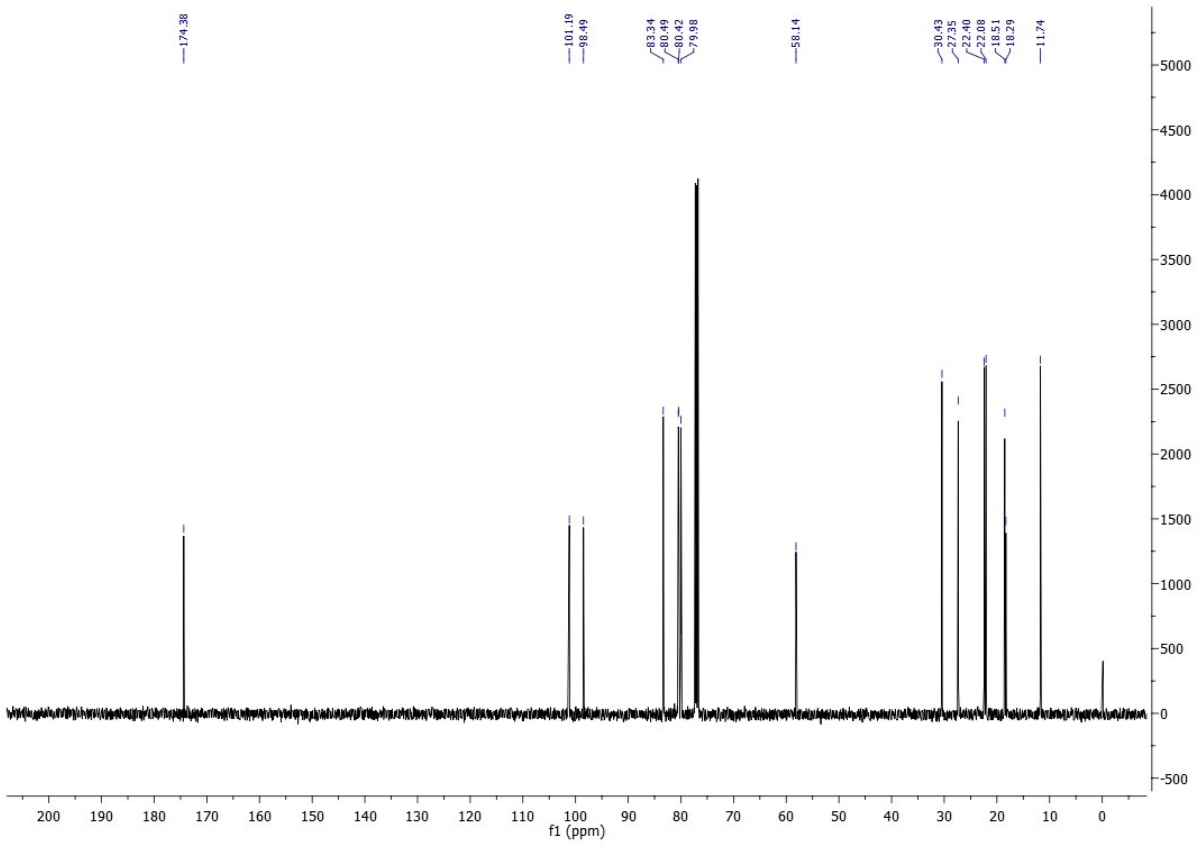


Figure S8. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2**

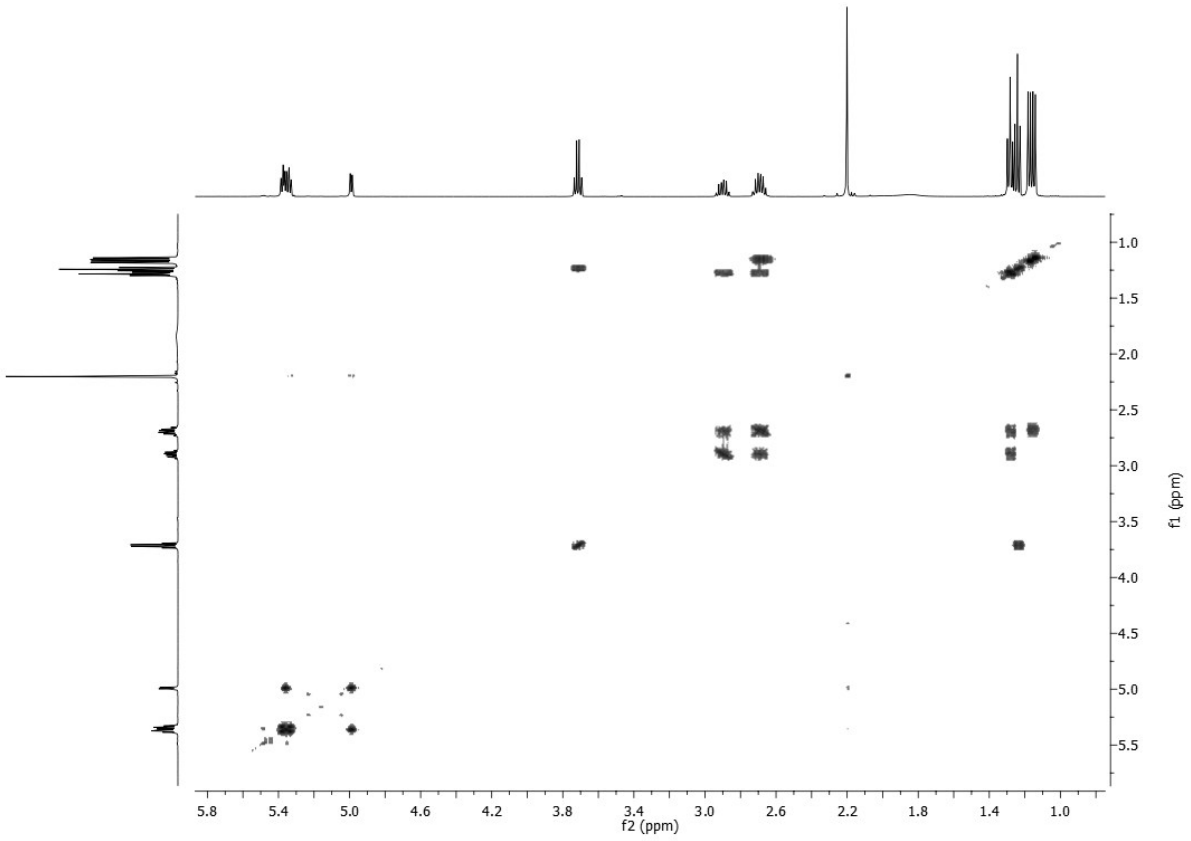


Figure S9. ^{1}H-^{1}H COSY NMR (500 MHz, $CDCl_3$) spectrum of **2**

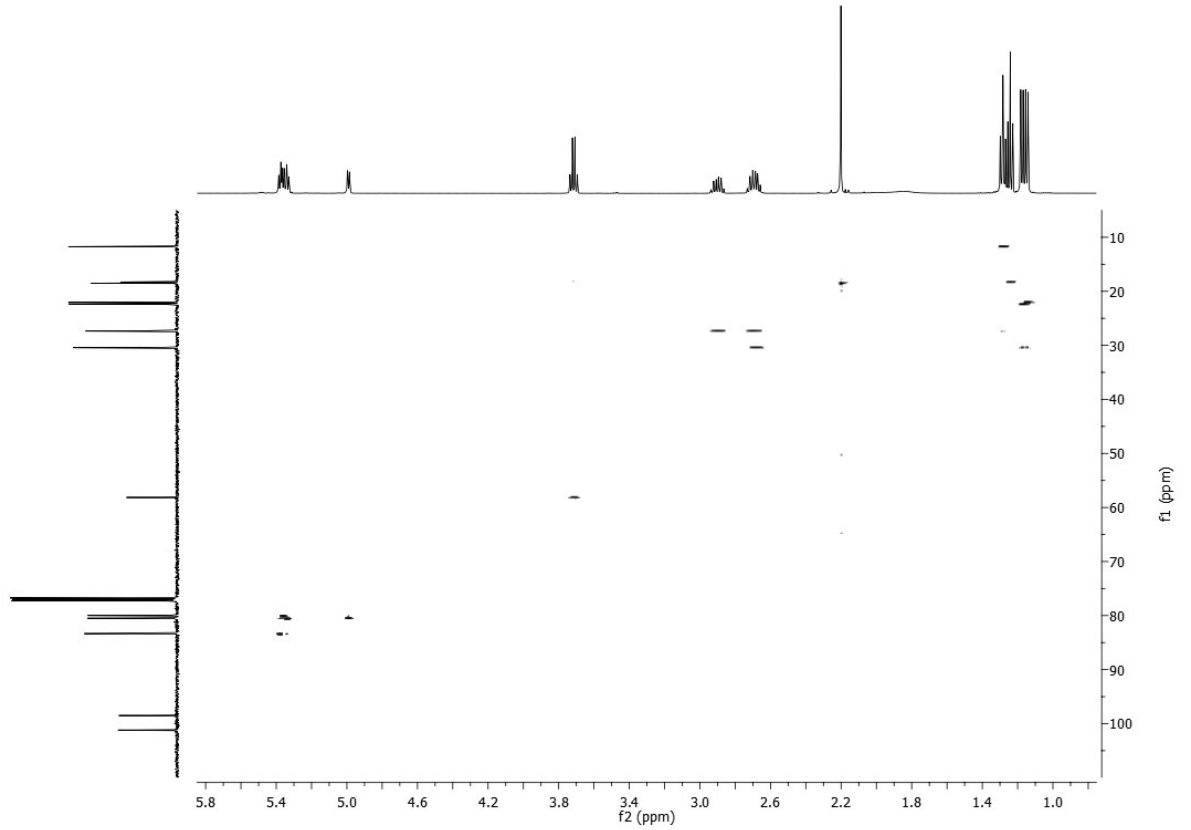


Figure S10. ^{1}H-^{13}C HSQC NMR (500 MHz, $CDCl_3$) spectrum of **2**

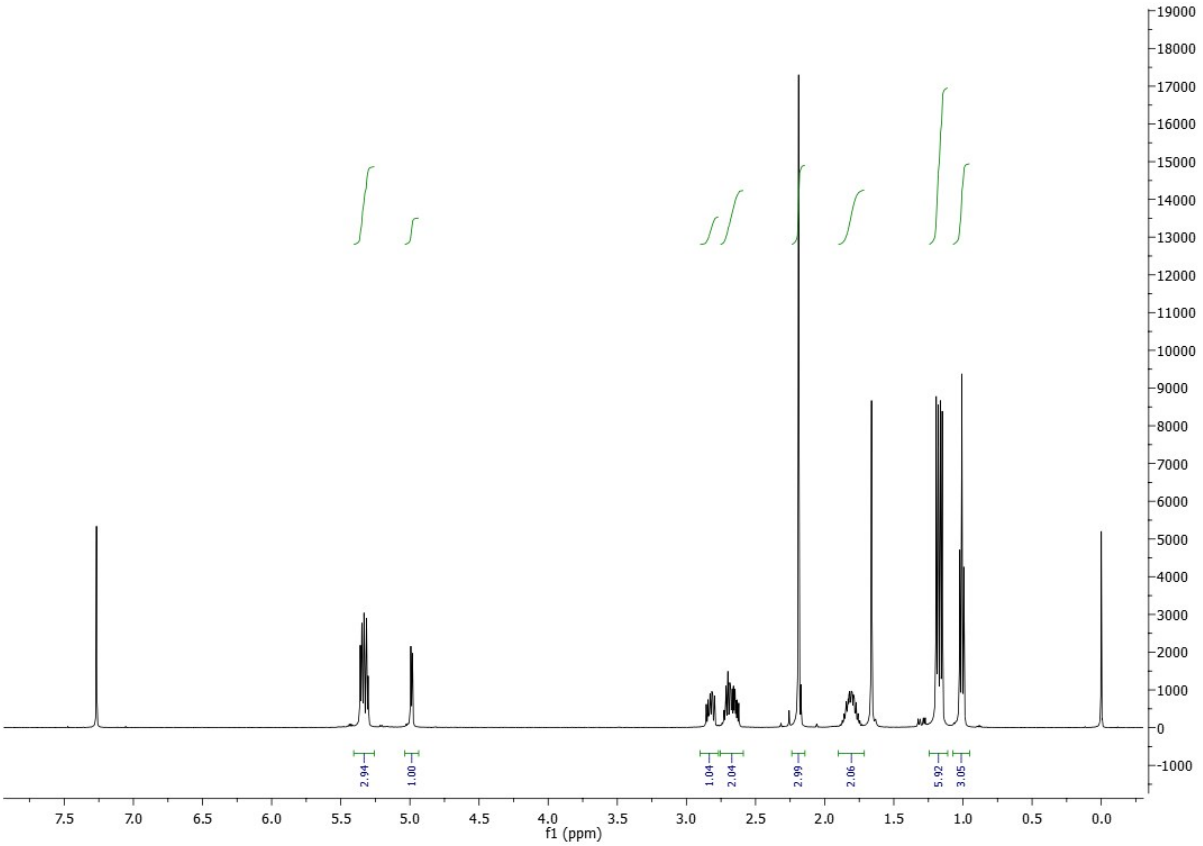


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **3**

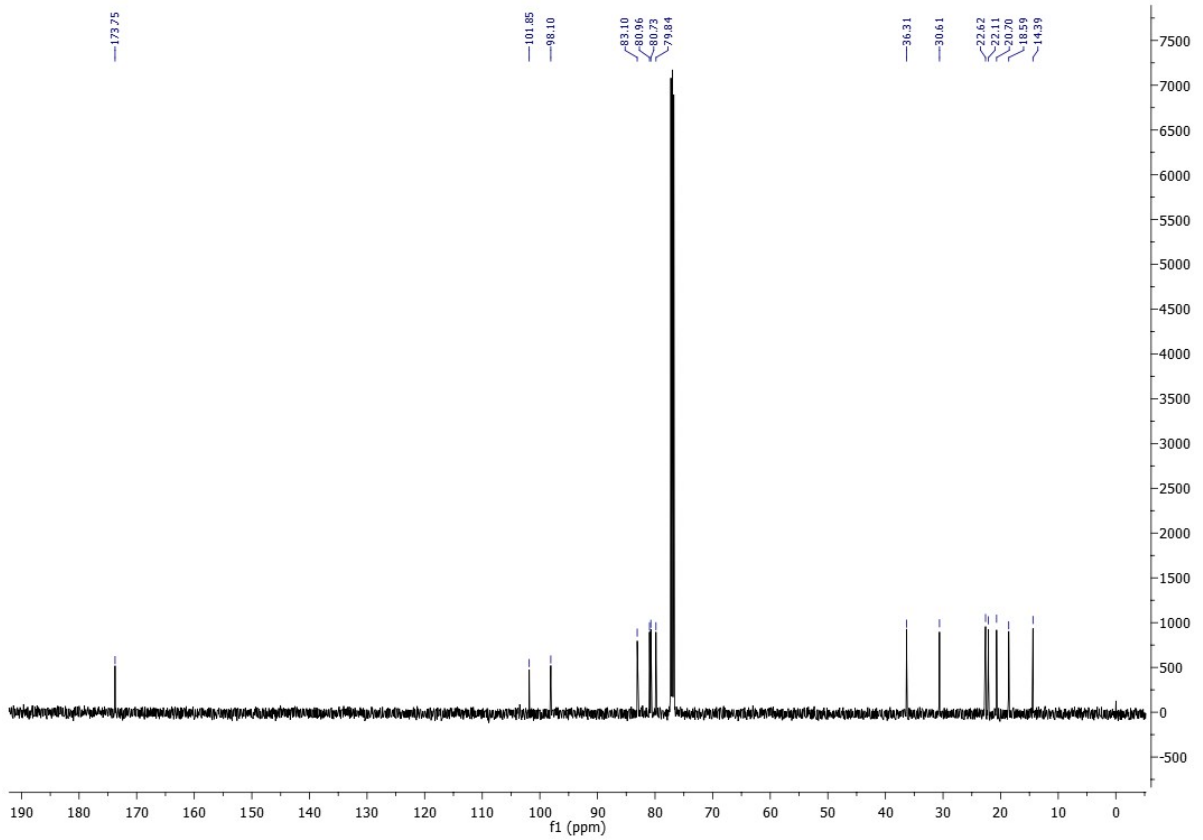


Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **3**

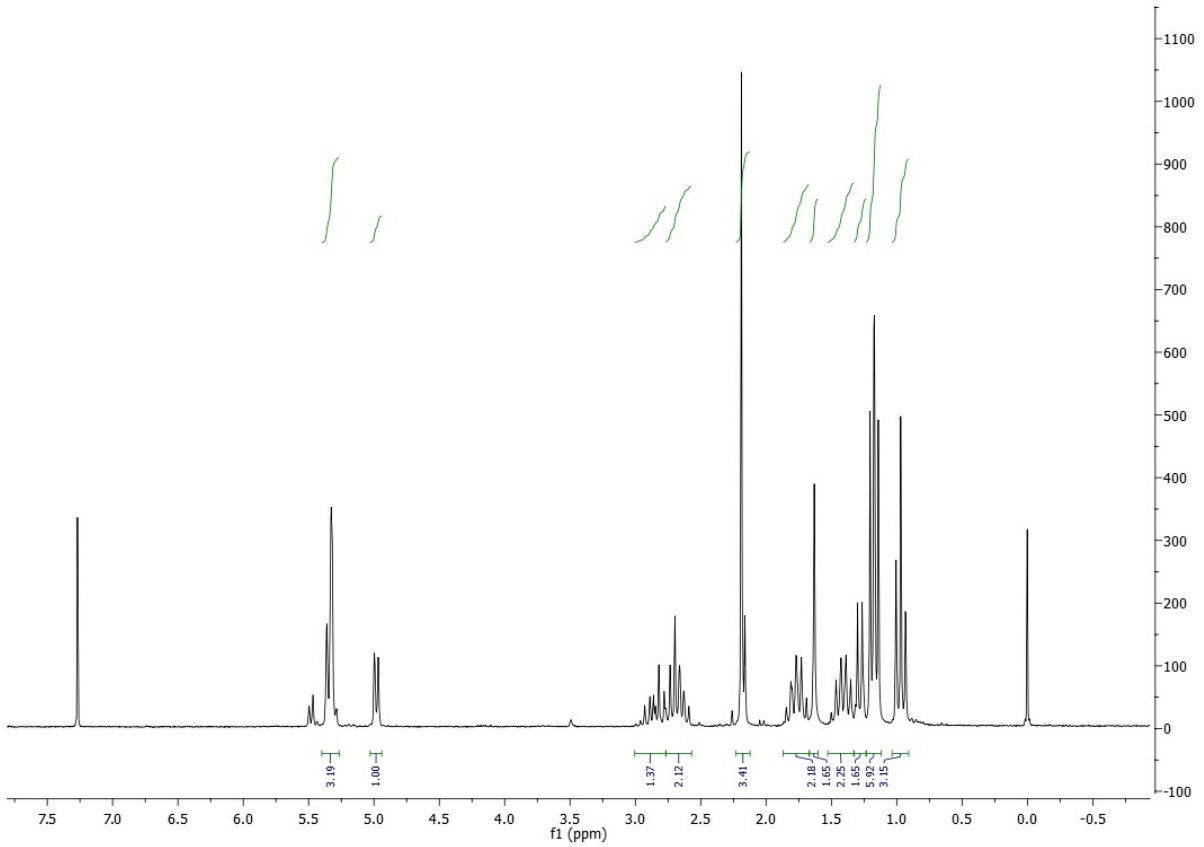


Figure S13. ^{1}H NMR (500 MHz, $CDCl_3$) spectrum of **4**

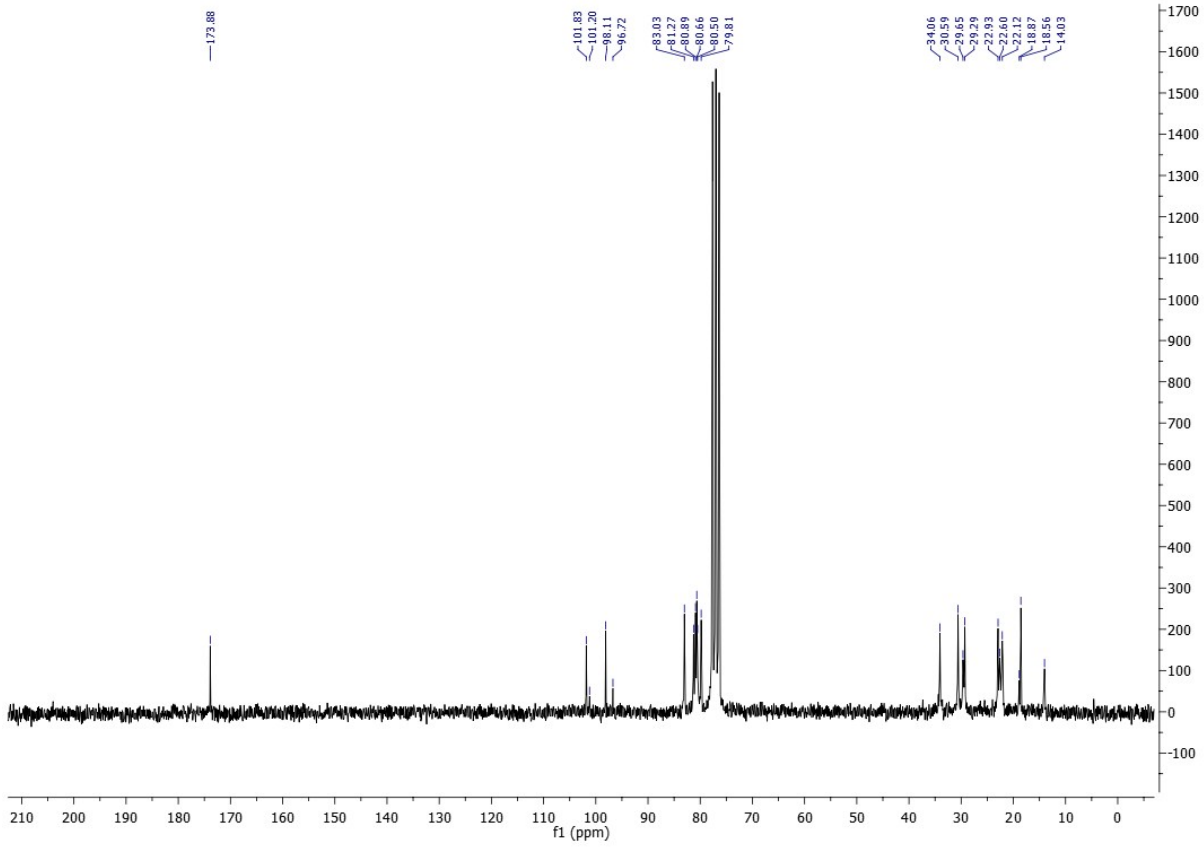


Figure S14. ^{13}C NMR (50 MHz, $CDCl_3$) spectrum of **4**

X-ray Analysis

The X-ray intensity data were measured on Bruker D8 Venture diffractometers equipped with multilayer monochromators, Mo K/a 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*[i] using a narrow-frame algorithm, Absorption correction, *SADABS*[ii] , structure solution, *SHELXS-2013*[iii], refinement, *SHELXL-2013*[iii], *OLEX2*[iv], *SHELXLE*[v], molecular diagrams, *OLEX2*[iv]. 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)(η^6-p-cymene)]Cl [1] for "New Journal of Chemistry".

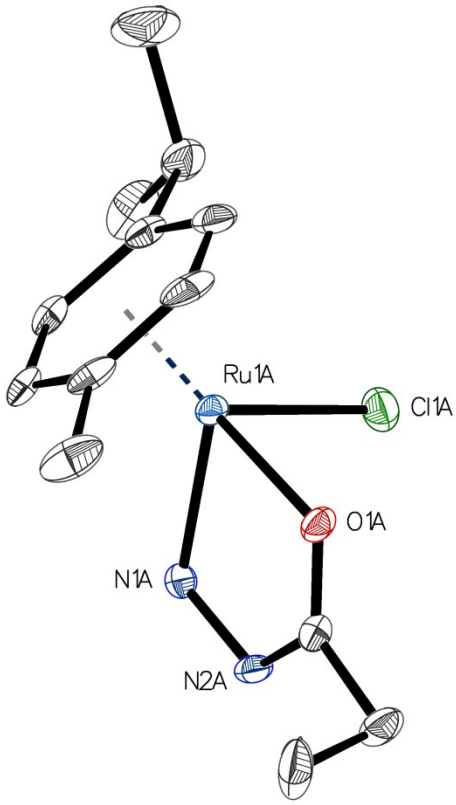


Figure 1 Crystal structure of [**1**], drawn with 50% displacement ellipsoids. Disorder, second moiety of asymmetric unit, counter ion and hydrogens omitted for clarity. The degree of main residue disorder is 31%.

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

Chemical formula	C13H22Cl2N2ORu	**Crystal system**	monoclinic	
Formula weight [g/mol]	788.59	**Space group**	*P21/c*	
Temperature [K]	100	**Z**	8	
Measurement method	\Φ and \ω scans	**Volume [Å^3]**	3308.2(2)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	13.8233(6)	90
Crystal size / [mm^3]	0.297 × 0.195 × 0.08		20.4127(9)	103.2769(16)
Crystal habit	clear orange block		12.0459(5)	90
Density (calculated) / [g/cm^3]	1.583	**Absorption coefficient / [mm^{-1}]**	1.265	
Abs. correction Tmin	0.6938	**Abs. correction Tmax**	0.746	
Abs. correction type	multiscan	**F(000) [e$^-$]**	1600	

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

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

$Ru_2Cl_2(N^1N^2\text{-dipropionylhydrazine})(\eta^6\text{-p-cymene})_2$ [2] for "New Journal of Chemistry".

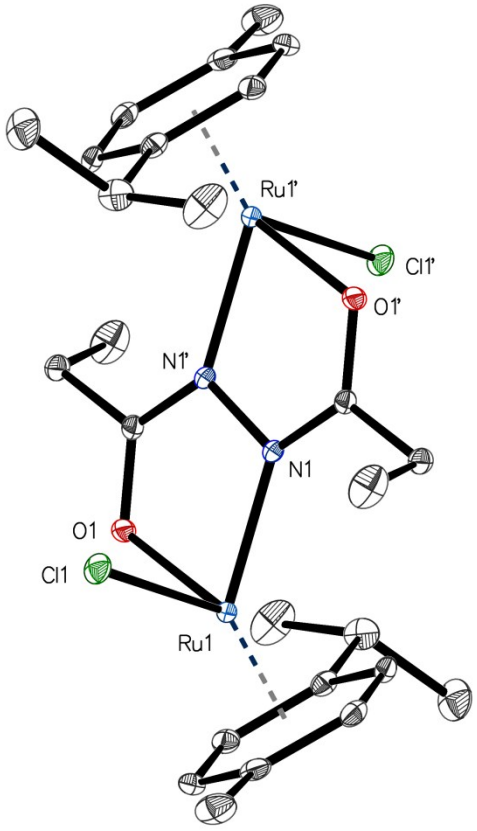


Figure 2 Grown crystal structure of [**2**], drawn with 50% displacement ellipsoids. Solvent and hydrogens omitted for clarity. Symmetric atoms are tagged with (') and are equivalent to 2-X,-Y,1-Z.

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

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

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

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

Ru_2Cl_2(N^1N^2-dibutanoylhydrazine)(η^6-p-cymene)$_2$ [3] for "New Journal of Chemistry".

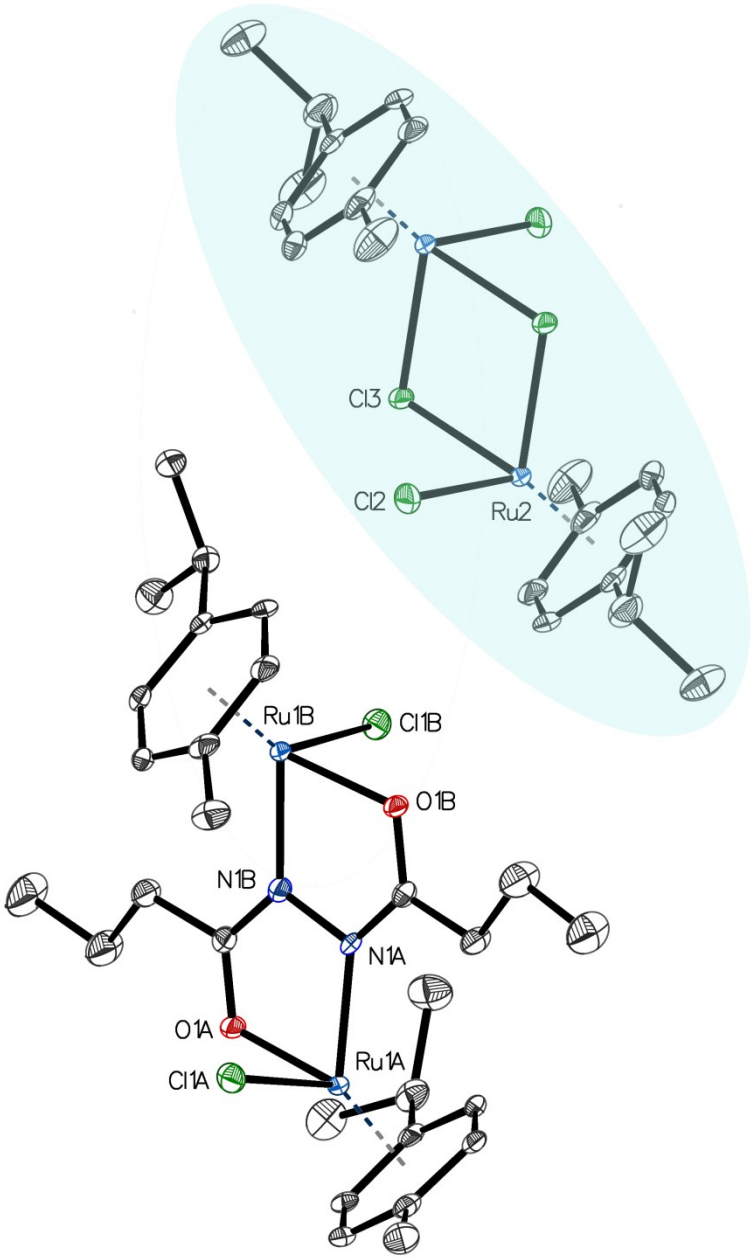


Figure 3 Asymmetric Unit of [**3**], drawn with 50% displacement ellipsoids. Hydrogen atoms omitted for clarity. Co crystalized [$RuCl_2$(η^6-*p*-cymene)]$_2$ light blue shaded and grown over center of symmetry °.

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

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

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

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

$Ru_2Cl_2(N^1N^2$-dipentanoylhydrazine)$(\eta^6$-p-cymene$)_2$ [4] for "New Journal of Chemistry".

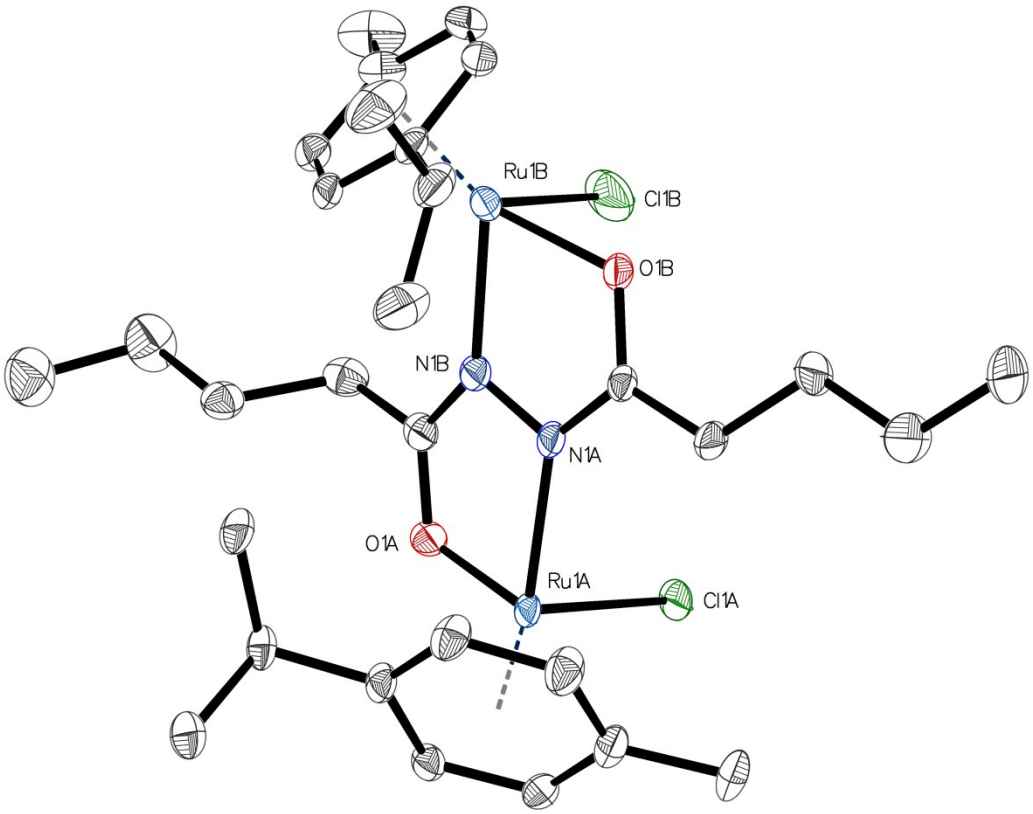


Figure 4 Asymmetric Unit of [**4**], drawn with 50% displacement ellipsoids. Hydrogen atoms, disorder and free water omitted for clarity. The degree of main residue disorder is 13%.

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

Chemical formula	C30H50Cl2N2O4Ru2	**Crystal system**	triclinic	
Formula weight [g/mol]	775.76	**Space group**	*P-1*	
Temperature [K]	100	**Z**	2	
Measurement method	\Φ and \ω scans	**Volume [Å^3]**	1658.71(14)	
Radiation (Wavelength [Å])	MoKα (λ = 0.71073)	**Unit cell dimensions [Å] and [°]**	9.6072(5)	95.264(2)
Crystal size / [mm^3]	0.164 × 0.164 × 0.067		9.7722(5)	90.7653(18)
Crystal habit	clear orange block		17.7727(8)	93.160(2)
Density (calculated) / [g/cm^3]	1.553	**Absorption coefficient / [mm^{-1}]**	1.107	
Abs. correction Tmin	0.7093	**Abs. correction Tmax**	0.746	
Abs. correction type	multiscan	**F(000) [e$^-$]**	796	

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

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

Table 10 Metal - Ring Geometry for Compounds 1-4

Metal - Ring Geometry				
Compound	Center	Perpendicular Projection of Heavy Atom	Ring Centroid	Ring-Slippage
		[Å]	[Å]	[Å]
1	Ru1A	1.6461(10)	1.6459(4)	0.027
	Ru1B	-	-	-
2	Ru1	1.6610(5)	1.6605(2)	0.041
3	Ru1A	1.6760(9)	1.6759(3)	0.014
	Ru1B	1.6587(9)	1.6580(3)	0.048
4	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				

[i] Bruker SAINT V8.32B Copyright © 2005-2016 Bruker AXS

[ii] Sheldrick, G. M. (1996). *SHELXS, SHELXL.* University of Göttingen, Germany.

[iii] Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

[iv] Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. , OLEX2, (2009), J. Appl. Cryst. 42, 339-341

[v] 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

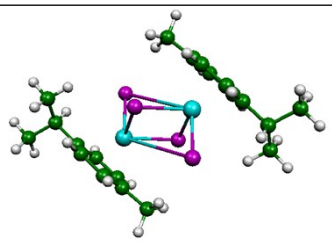
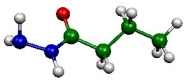
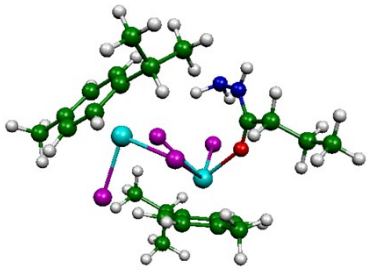
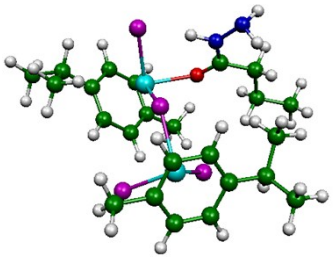
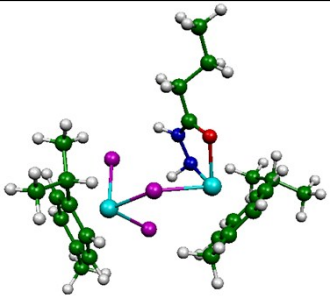
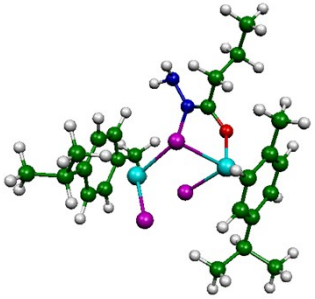
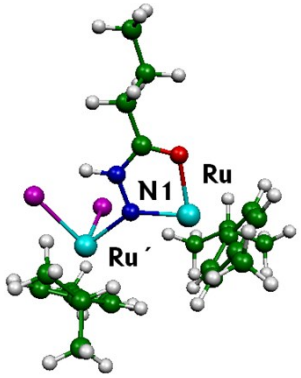
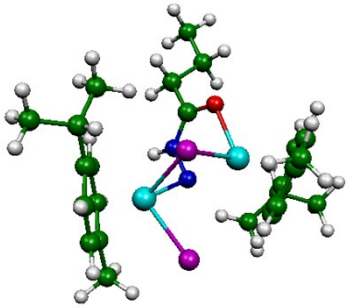
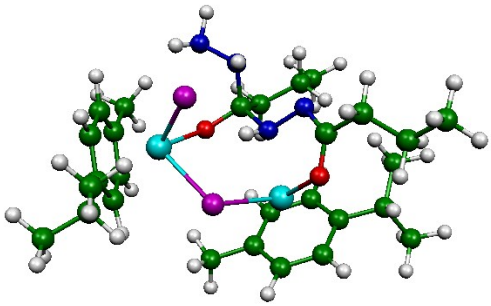
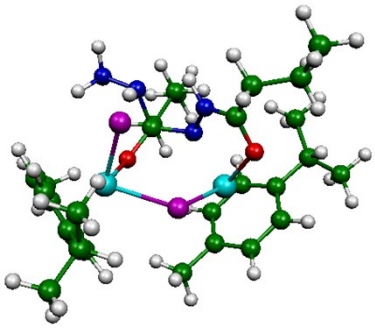
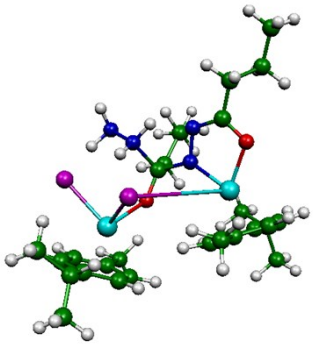
	
–11505.4890094 (R1)	**–342.9131381 (R2)**
	
–11848.4142065 (Ia)	**–11848.4120083 (Ib)**
	
–11387.701511 (IIa)	**–11387.6682279 (IIb)**

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

	
–10926.993142 (IIIa)	**-10926.97686 (IIIb)**
	
–11269.8755261 (IVa)	**–11269.8701989 (IVb)**
	
–11269.8893666 (V)	

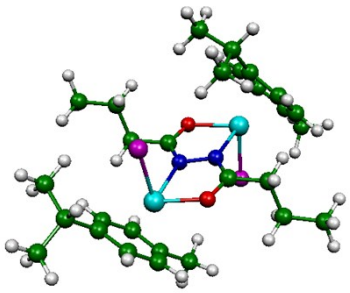
	
–11158.145344 (P)	

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

Bond	B3LYP	X-ray
C_1–C_2	1.528	1.525(3)
C_2–C_3	1.540	1.508(3)
C_3–C_4	1.507	1.504(3)
C_4–N_1	1.315	1.306(3)
N_1–N_2	1.408	1.433(2)
N_2–C_5	1.315	1.307(3)
C_5–C_6	1.507	1.509(3)
C_6–C_7	1.540	1.506(3)
C_7–C_8	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_9–C_{10}	1.417 / 1.425	1.410 / 1.407(3)
C_9–$C_{10'}$	1.419 / 1.427	1.435 /1.427(3)
C_{10}–C_{11}	1.428 / 1.428	1.421 / 1.420(3)
$C_{10'}$–$C_{11'}$	1.419 / 1.421	1.403 / 1.402(3)
C_{11}–C_{12}	1.423 / 1.421	1.412 / 1.409(3)
$C_{11'}$–C_{12}	1.432 / 1.428	1.435 / 1.433(3)
C_9–C_{13}	1.502 / 1.503	1.503 / 1.500(3)
C_{12}–C_{14}	1.527 / 1.519	1.517 / 1.518(3)
C_{14}–C_{15}	1.538 / 1.532	1.528 / 1.520(3)
C_{14}–$C_{15'}$	1.534 / 1.542	1.539 / 1.528(3)

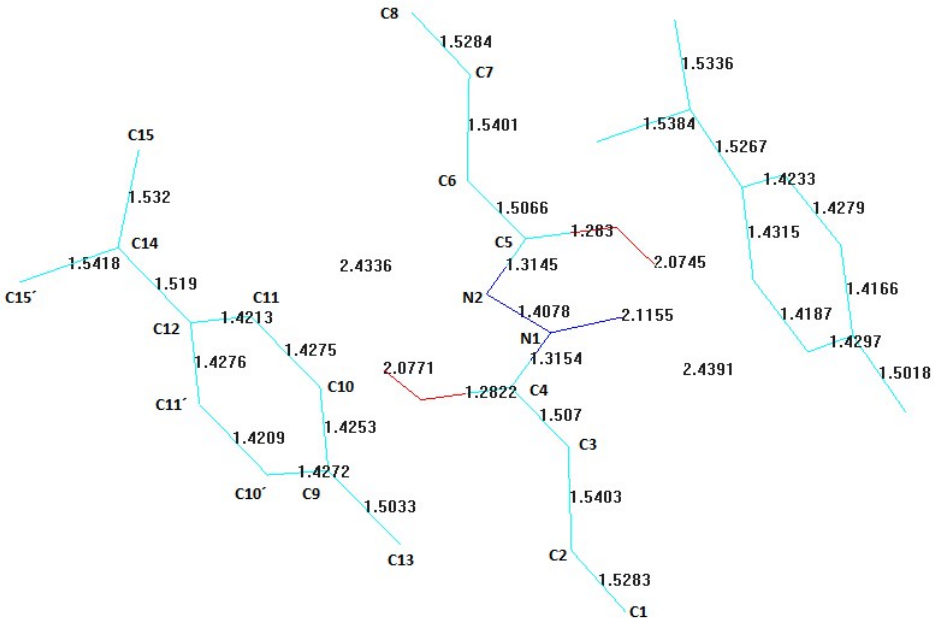


Figure S16. The selected B3LYP bond lengths in angstroms and atom labeling