Syntheses and Applications of Symmetrical Dinuclear Half-Sandwich Ruthenium(II)–Dipicolinamide Complexes as Catalysts in the Transfer Hydrogenation of Ketones

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Electronic Supplementary data

1. Synthesis of Phenylene bis(pyridyl-carboxamide) ligands

*1.1.1. Synthesis of (N,N'-(1,2-phenylene)bis(2-pyridyl)carboxamide (**H_2L1**)*

To a solution of pyridine carboxylic acid (0.50 g, 4.06 mmol) in pyridine (10 mL) is added a *o*-phenylenediamine (0.26 g, 2.41 mmol) (0.26 g, 2.41 mmol) and triphenylphosphate (1.00 mL) and refluxed at 110 ^{o}C for 6h to form a while suspension. The reaction mixture was cooled to room temperature, 20 ml of distilled water is added and filtered under vacuum to obtained while crude product. The crude is then washed with dry ethanol (30 mL) and dried in vacuum to obtained white crystalline solid. Yield = 0.66 g (86%). ^{1}H NMR (400 MHz, DMSO) δ_H: 10.71 (s, $2H_{amide}$), 8.65(t, $^{3}J_{HH}$ = 5.6 Hz, $2H_{pyridine}$), 8.19 (d, $^{3}J_{HH}$ = 6.4Hz, $2H_{pyridine}$), 8.06 (d, $^{3}J_{HH}$ = 6.4Hz, $2H_{pyridine}$), 7.79(t, $^{3}J_{HH}$ = 6.4Hz, $2H_{pyridine}$) 7.67(m, $^{3}J_{HH}$ = 6.4Hz, $2H_{benzene}$), 7.32(d, $^{3}J_{HH}$ = 10 Hz, $2H_{benzene}$).^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 163.3, 149.9, 149.0, 138.6, 131.4, 127.5, 126.2, 125.7, 122.9. FT-IR (cm^{-1}): $(\nu_{C=O})_{amidate}$ = 1664; $(\nu_{N-H})_{amidate}$ = 3312. ESI-MS, m/z(%): 341[M+Na^+,100], 659[2M+Na^+, 60].

1.1.2. *Synthesis of N,N'-(4,5-dimethyl-1,2-phenylene)dipicolinamide (**H_2L2**)*

A picolinic acid (0.50 g, 3.62 mmol), 4,5-dimethylbenzene-1,2-diamine (0.26 g, 2.41 mmol), triphenylphosphate (1.10 mL) and in pyridine (10 mL) refluxed at 110 ^{o}C for 6h. white compound was obtained. Yield = 0.63 g (86%). ^{1}H NMR (400 MHz, DMSO) δ: 10.17 (s, $2H_{amide}$), 8.57 (m, $^{3}J_{HH}$ = 5.6 Hz, $2H_{pyridine}$), 8.31 (m, $^{3}J_{HH}$ = 4.8Hz, $2H_{pyridine}$), 7.91 (m, $^{3}J_{HH}$ = 48 Hz, $2H_{pyridine}$) 7.64 (s, $2H_{benzene}$), 7.45(m, $^{3}J_{HH}$ =6.2 Hz, $2H_{pyridine}$), 3.71(s, 3H) 2.34(s, $2C\underline{H}_3$). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ: 162.8, 149.9, 148.2, 137.4, 134.8, 127.8, 126.3, 125.7,122.5, 19.8. FT-IR (cm^{-1}): $(\nu_{N-H})_{amidate}$ = 3325; $(\nu_{C=O})_{amidate}$ = 1663. ESI-MS: m/z (%): 369[M + Na^+, 20], 715[2M + Na^+, 100].

*1.1.3. Synthesis of N,N'-(4-methoxy-1,2-phenylene)dipicolinamide (**H_2L3**)*

A Picolinic acid (0.50 g, 3.62 mmol), 4-methoxybenzene-1,2-diamine (0.26 g, 2.41 mmol), triphenylphosphate (1.10 mL), pyridine (10 mL) and refluxed at 110 ^{o}C for 6 h to give an off-white compound. Yield = 0.74 g (91%). ^{1}H NMR (400 MHz, DMSO), δ: 10.63 (s, 1H$_{amide}$), 10.58 (s, 1H$_{amide}$), 8.69 (d, $^{3}J_{HH}$ = 5.6 Hz, 2H$_{pyridine}$), 8.58 (d, $^{3}J_{HH}$ = 5.6 Hz, 2H$_{pyridine}$), 8.18 (m, $^{3}J_{HH}$ = 6.4Hz, 2H$_{pyridine}$), 8.08 (m, $^{3}J_{HH}$ = 6.4Hz, 2H$_{pyridine}$), 7.68 (m, $^{3}J_{HH}$=6.4 Hz, 4H$_{pyridine}$) 7.64 (m, $^{3}J_{HH}$ = 6.4Hz, 4H$_{pyridine}$), 6.89(d, $^{3}J_{HH}$ =7.2 Hz, 3H$_{benzene}$), 6.83(d, 3J_{HH} =7.2 Hz, H$_{benzene}$),7.36(s, 3H$_{benzene}$), 3.71(s, 3H, OC$\underline{H}_3$). ^{13}C{^{1}H} NMR (101 MHz, DMSO) δ: 163.6, 162.8, 157.7, 150.1, 149.7, 149.6, 148.0, 148.6, 138.7, 138.5, 133.2, 127.6, 127.4, 123.4, 122.8, 111.2, 109.8, 55.8. FT-IR (cm^{-1}): (ν_{N-H}))$_{amidate}$ = 3323; ($\nu_{C=O}$)$_{amidate}$ = 1663. ESI-MS: m/z(%): 371[2M + Na^{+}, 20], 719[2M + Na^{+}, 100].

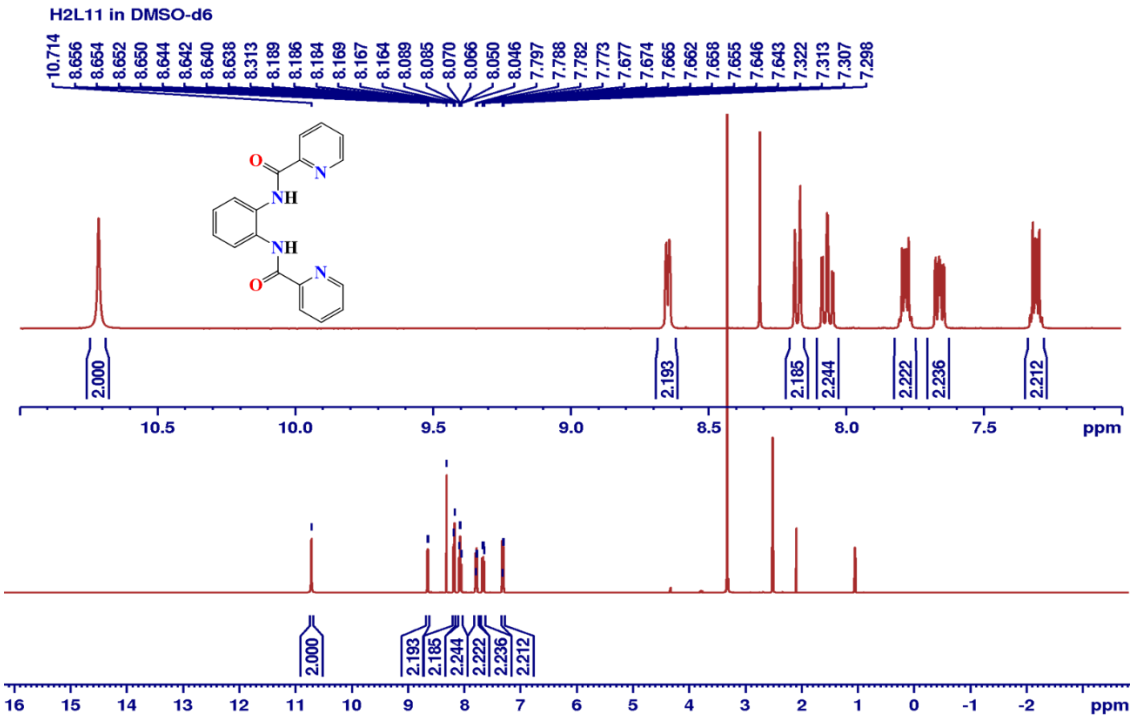


Figure S1. ^{1}H NMR spectrum of *N,N'-(1,2-phenylene)bis(pyridine-2-carboxamide):* **H_2L1** showing N-H signal at 10.74 ppm..

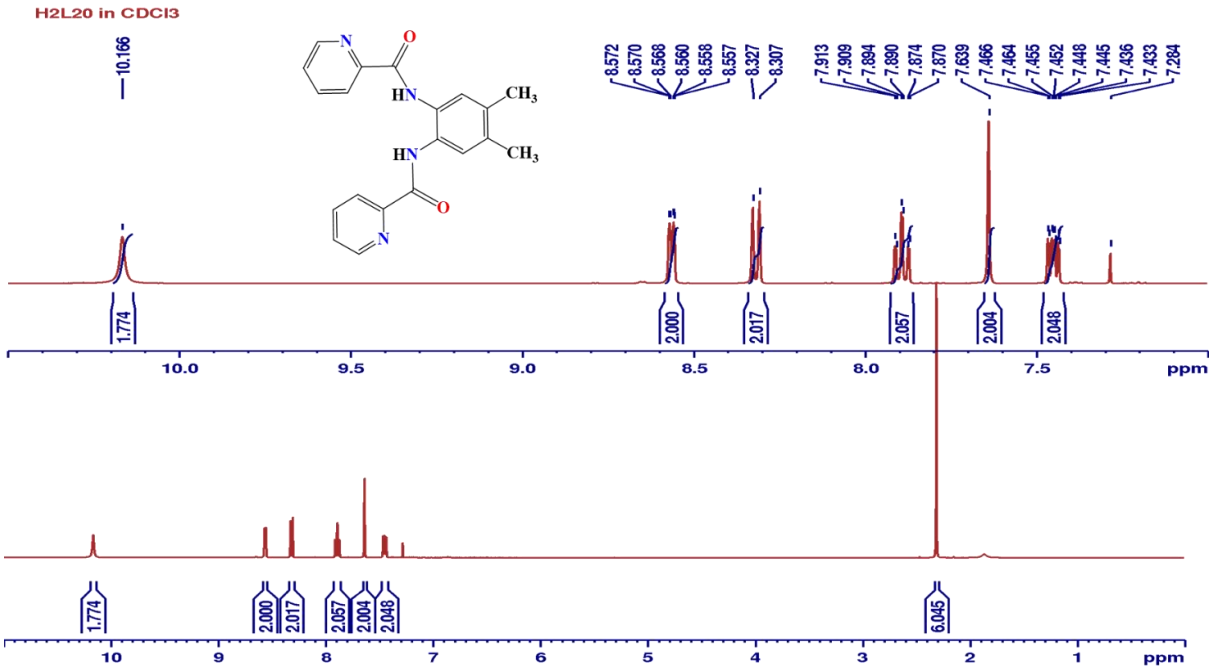


Figure S2. ^{1}H NMR spectrum of *N,N'-(4,5-dimethyl-1,2-phenylene)dipicolinamide:* **H_2L2** showing N-H signal at 10.17 ppm.

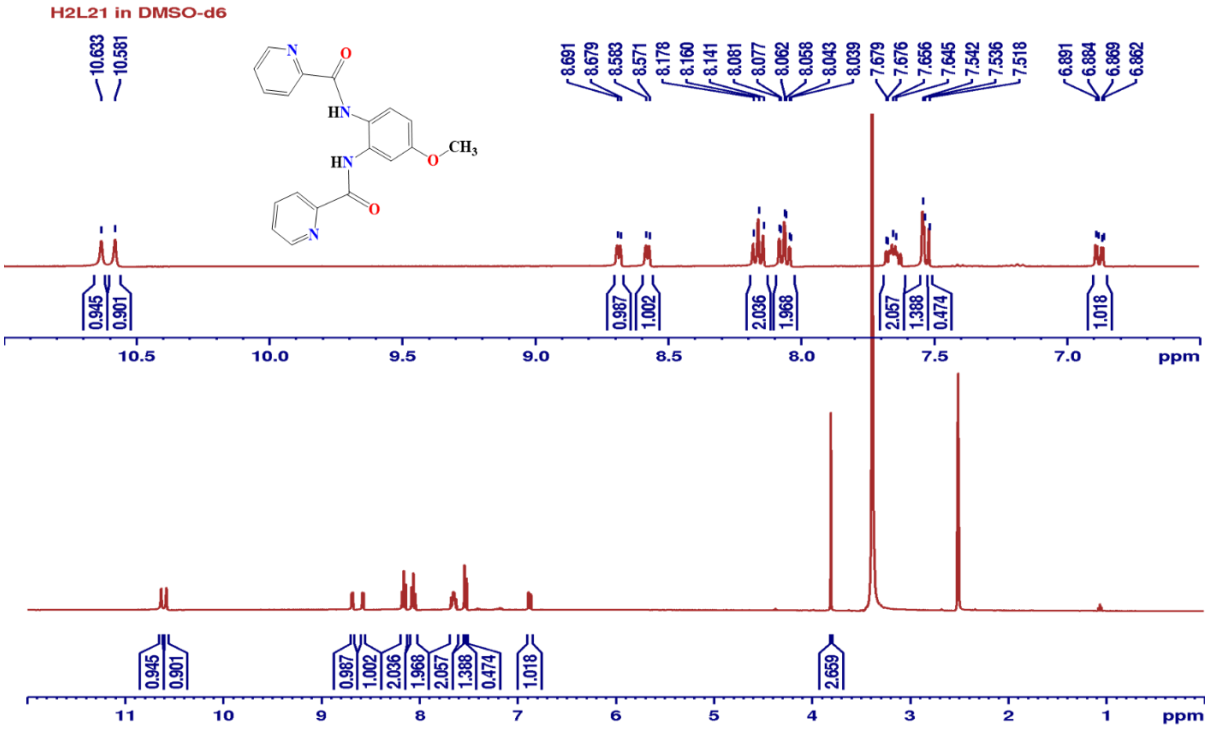


Figure S3. ^{1}H NMR spectrum of *N,N'-(3-methoxy-1,2-phenylene)dipicolinamide:* **H_2L3** showing N-H signal at 10.63 and 10.58 ppm.

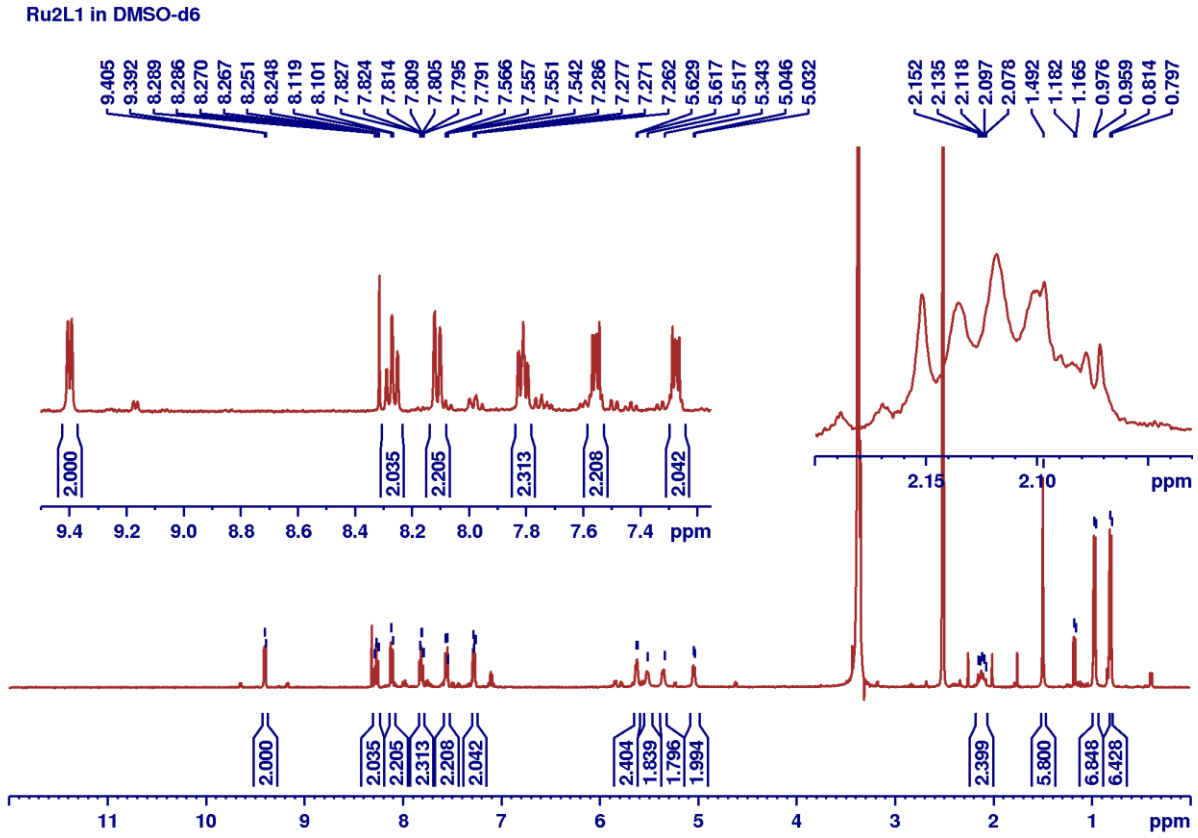


Figure S4. [1]H NMR spectrum of complex **Ru1**.

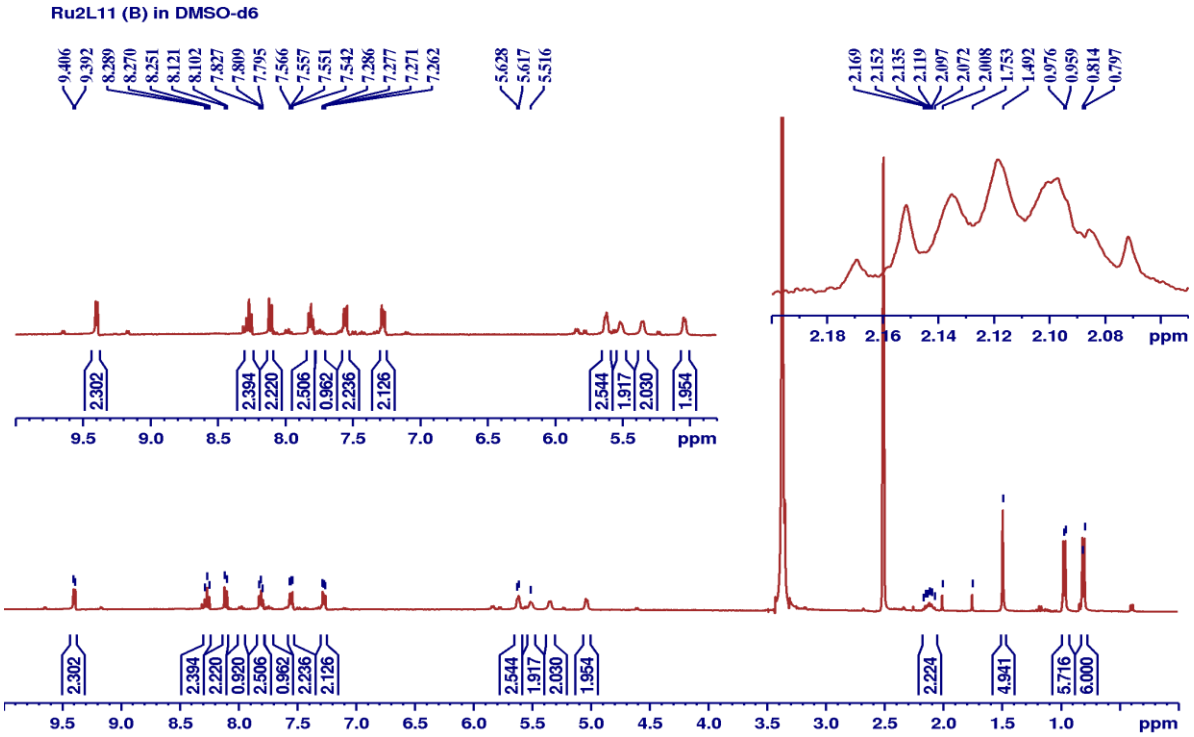


Figure S5. [1]H NMR spectrum of complex **Ru2**.

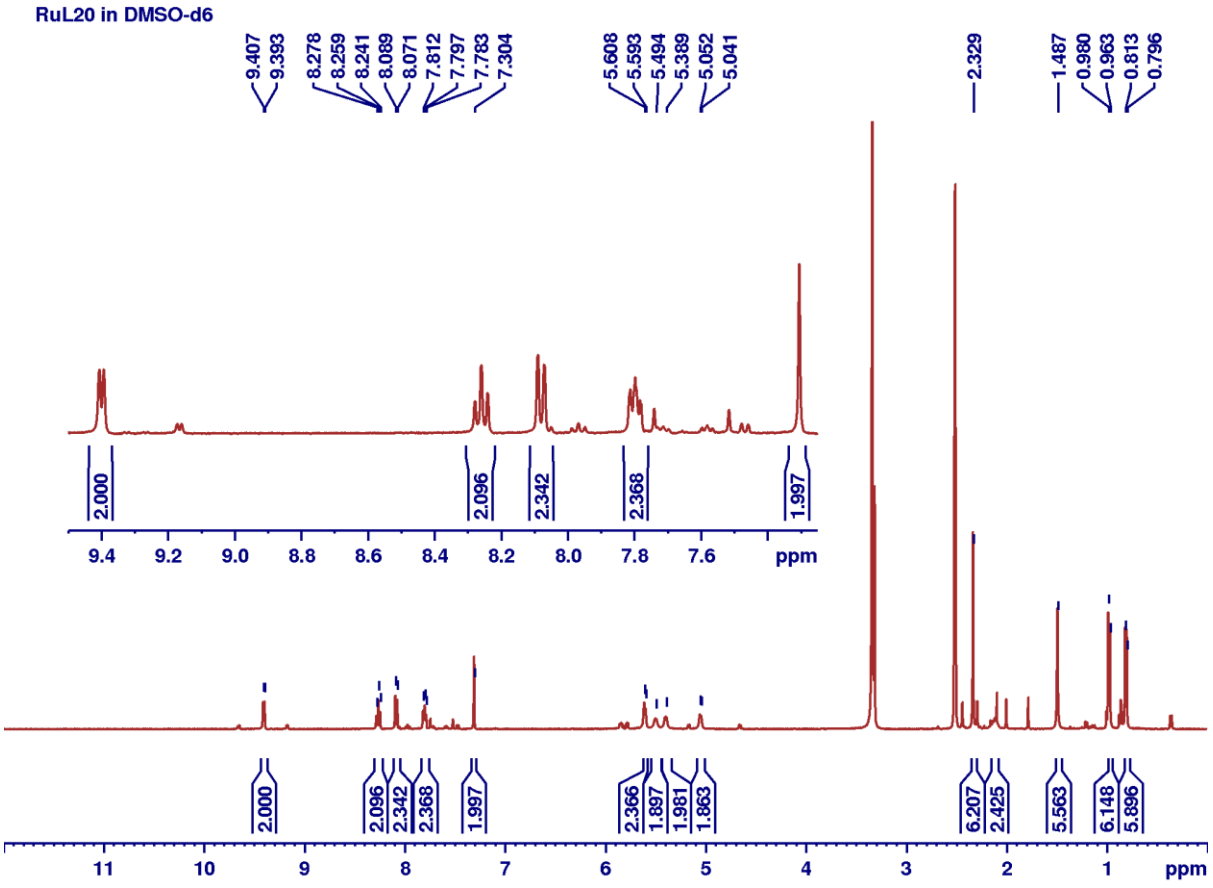


Figure S6. ^{1}H NMR spectrum of complex **Ru3.**

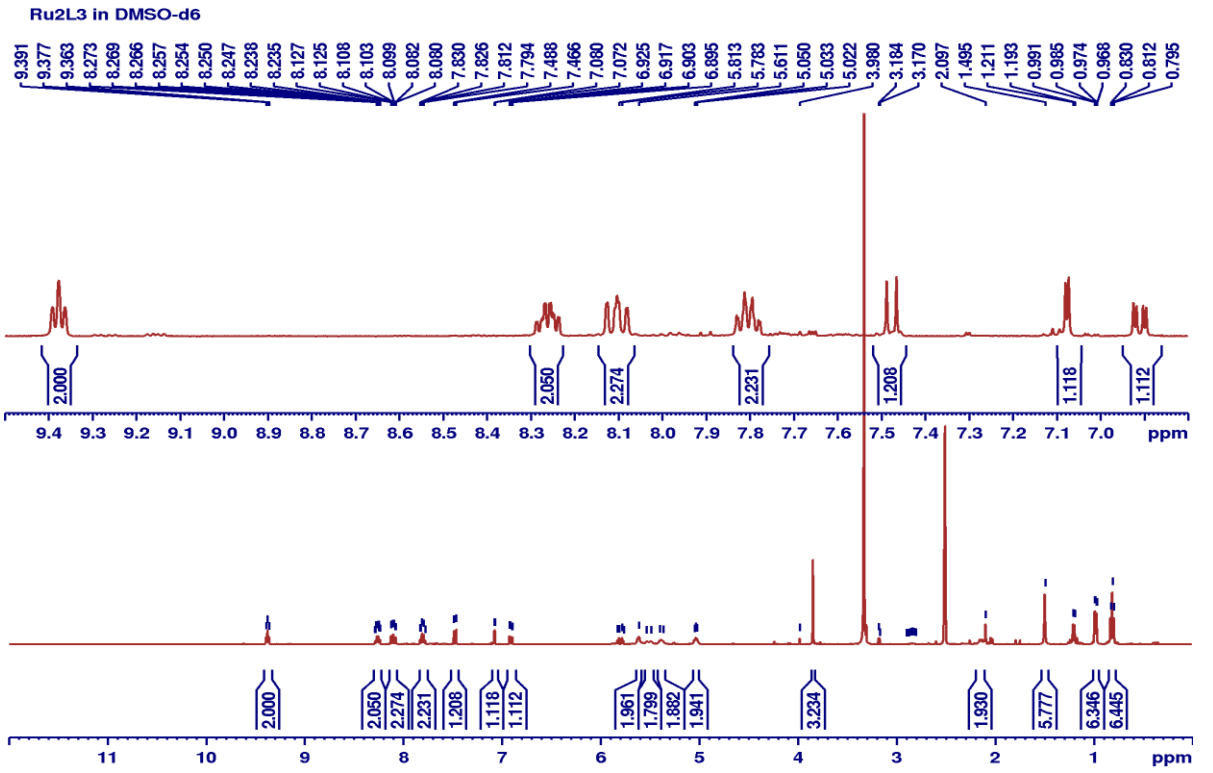


Figure S7. ^{1}H NMR spectrum of complex **Ru4**.

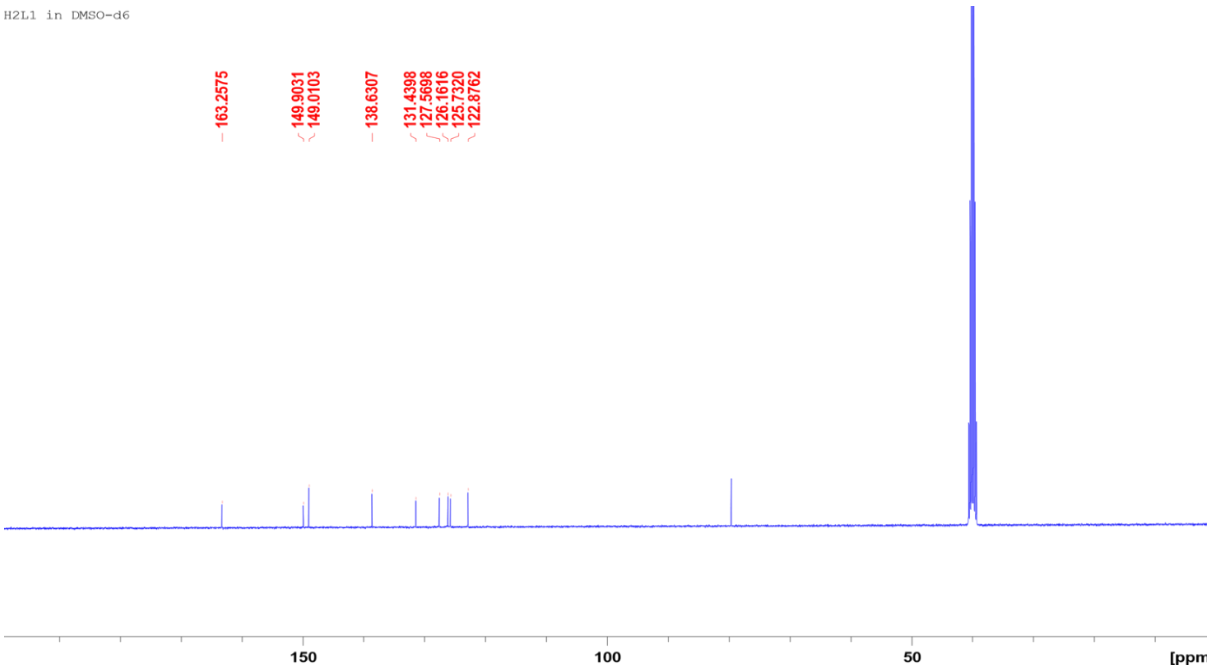


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of *N,N'-(1,2-phenylene)dipicolinamide:* **H_2L1.**

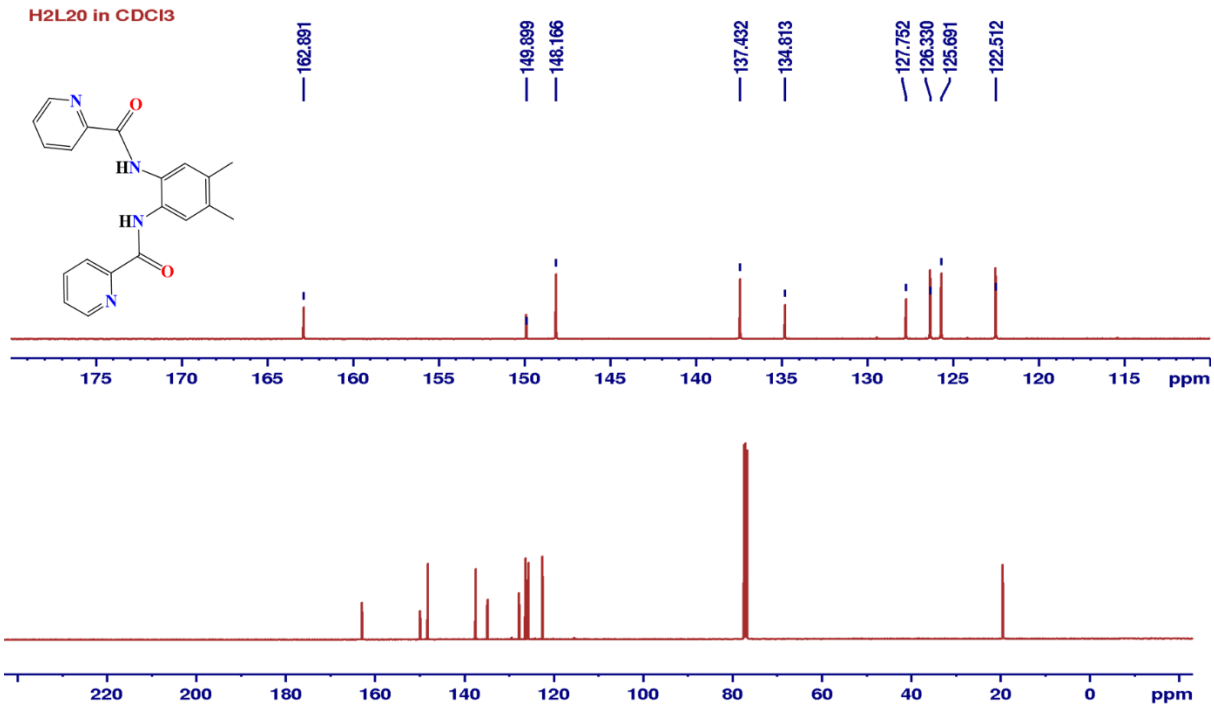


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of *N,N'-(4,5-dimethyl-1,2-phenylene)dipicolinamide:* **H_2L2.**

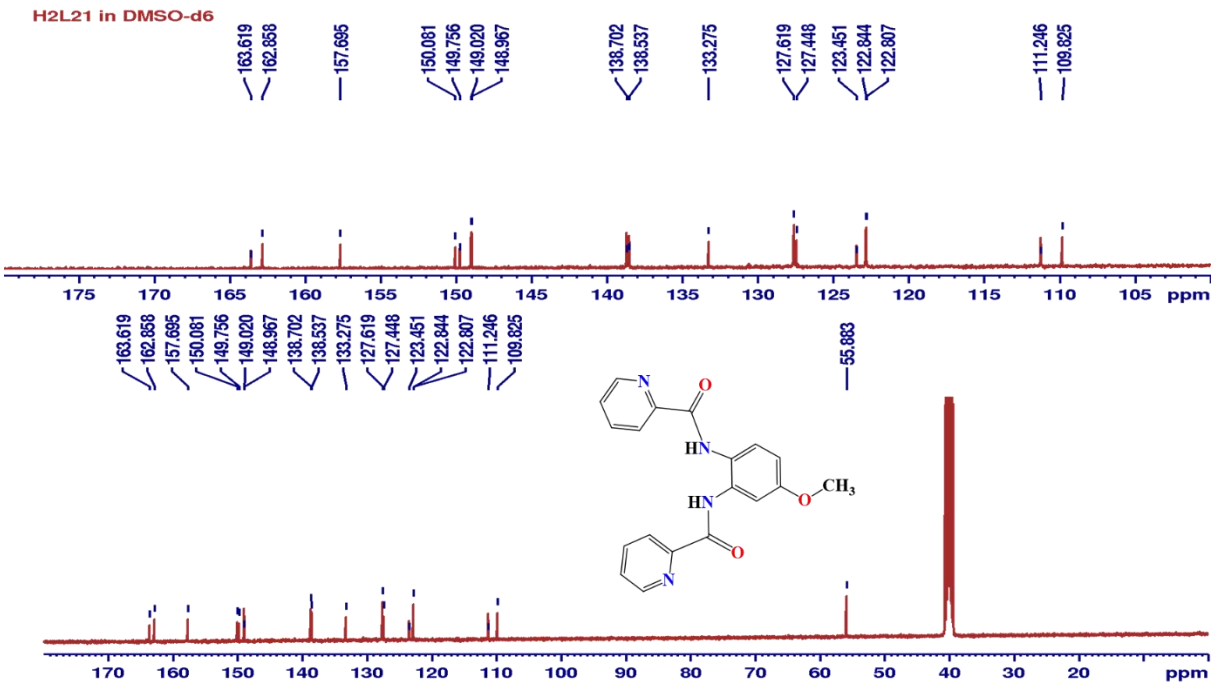


Figure S10. ^{13}C{H} NMR spectrum of *N,N'-(3-methoxy-1,2-phenylene)dipicolinamide:* **H_2L3.**

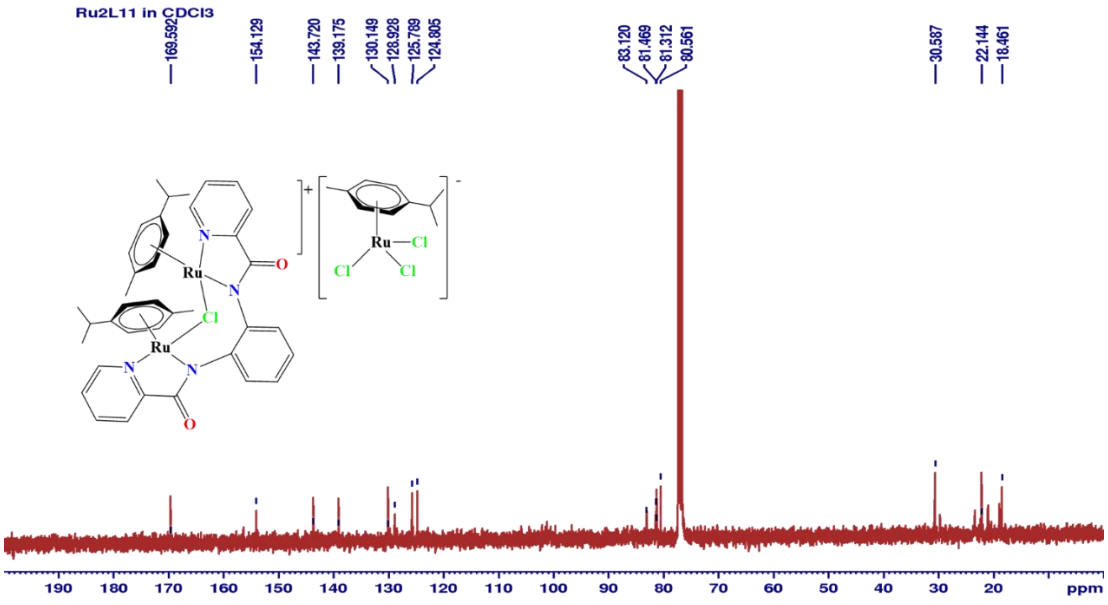


Figure S11. ^{13}C NMR spectrum of complex **Ru1**.

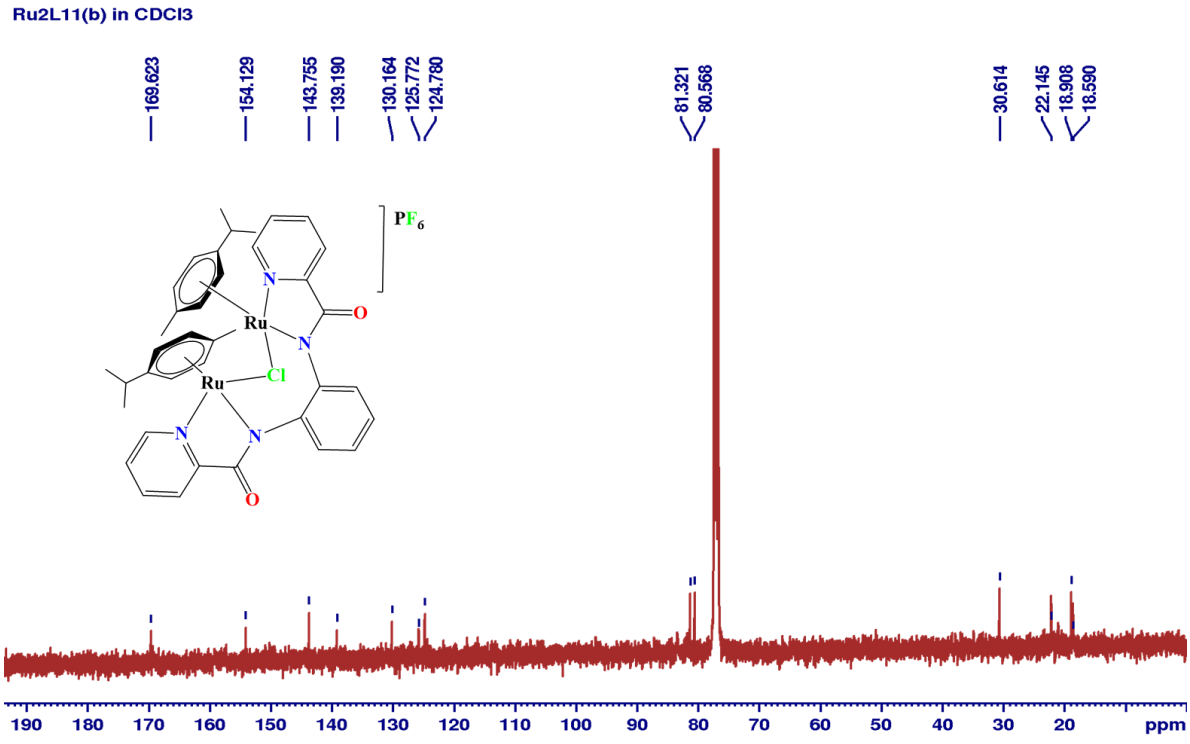


Figure S12. ^{13}C NMR spectrum of complex **Ru2**.

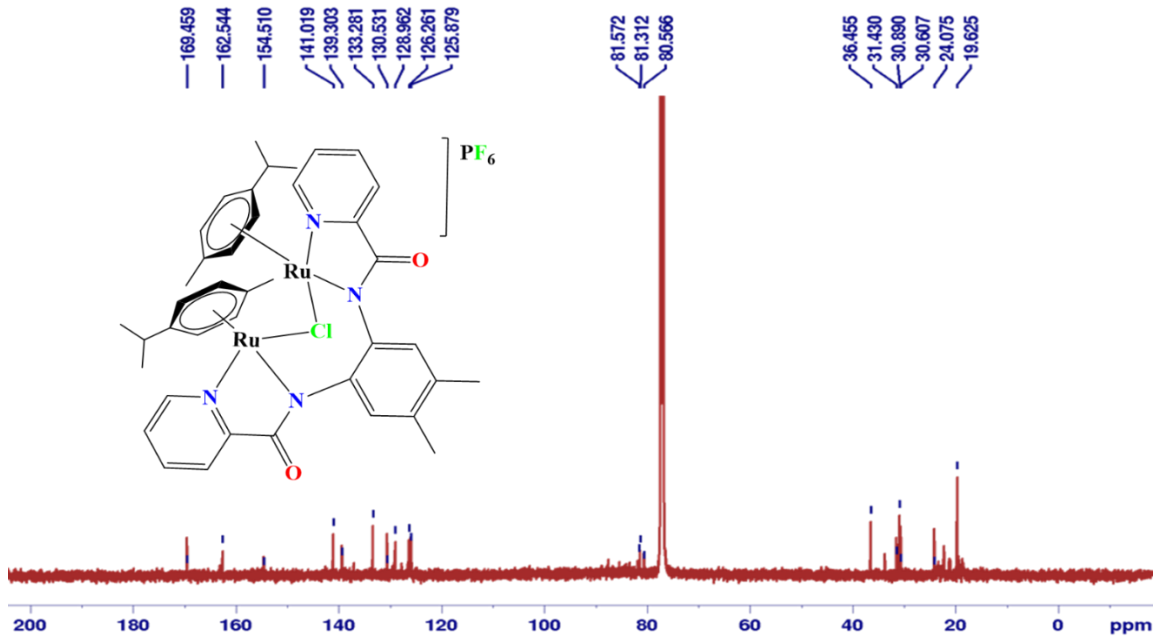


Figure S13. ^{13}C NMR spectrum of complex **Ru3**.

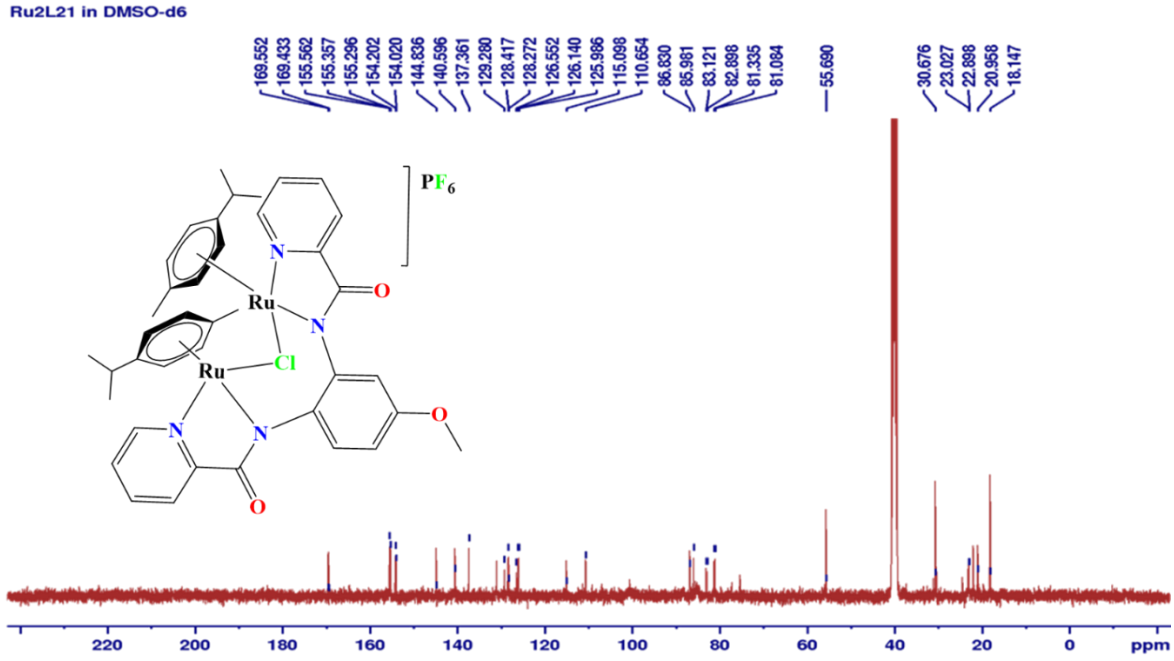


Figure S14. ^{13}C NMR spectrum of complex **Ru4**.

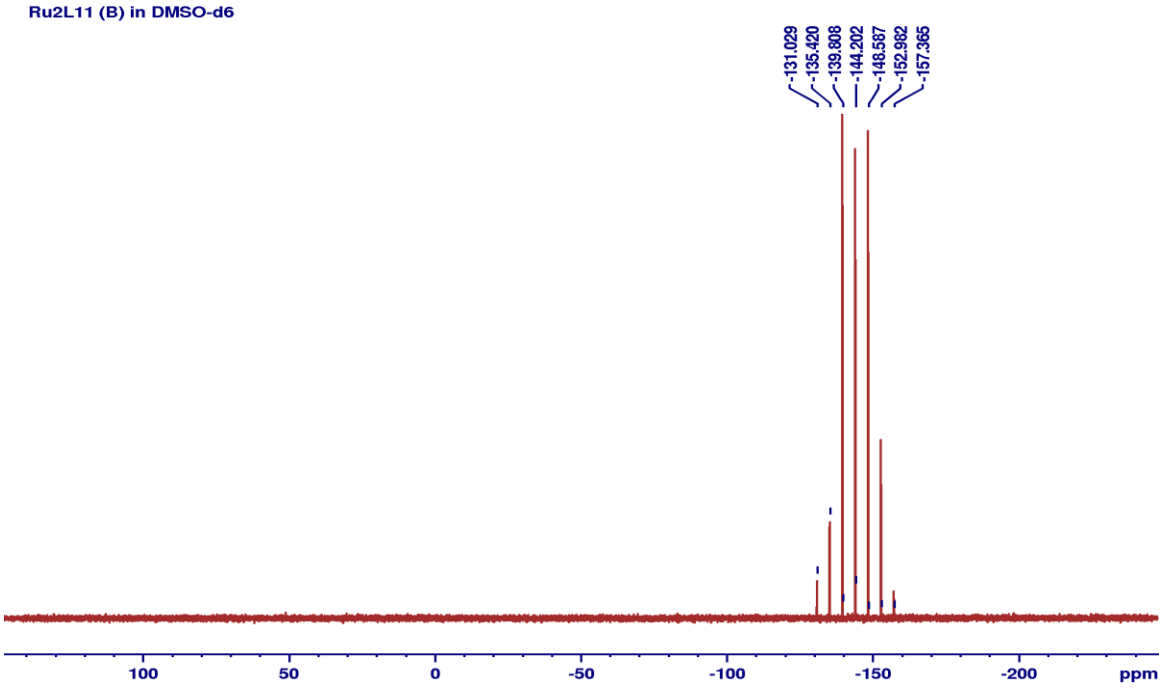


Figure S15. ^{31}P NMR of complex **Ru2** at room temperature.

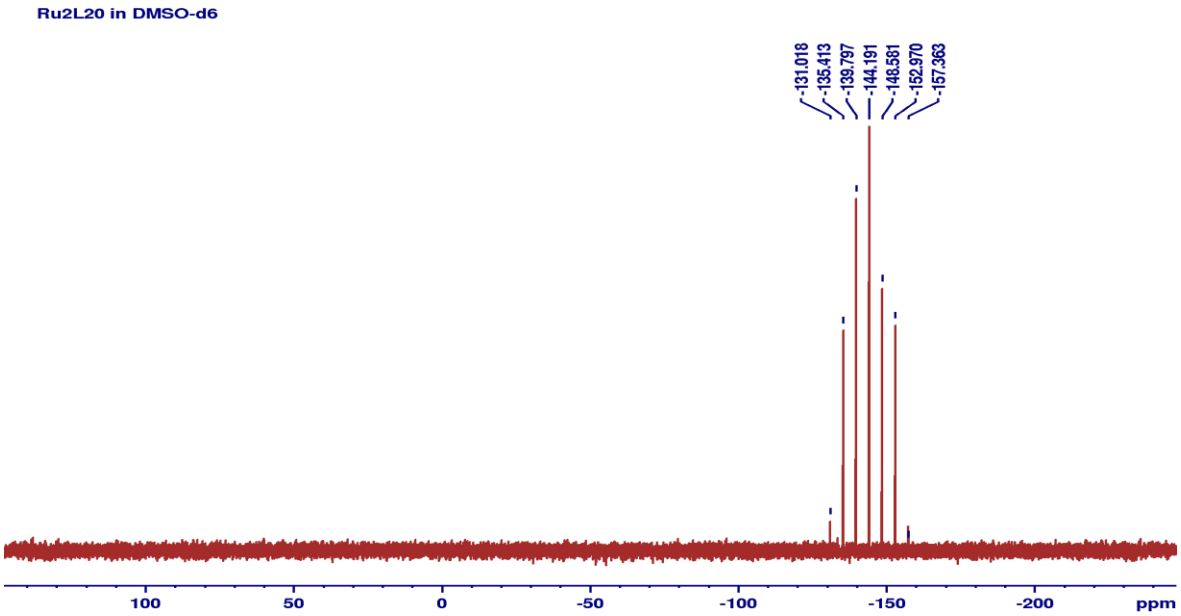


Figure S16. ^{31}P NMR of complex **Ru3** at room temperature.

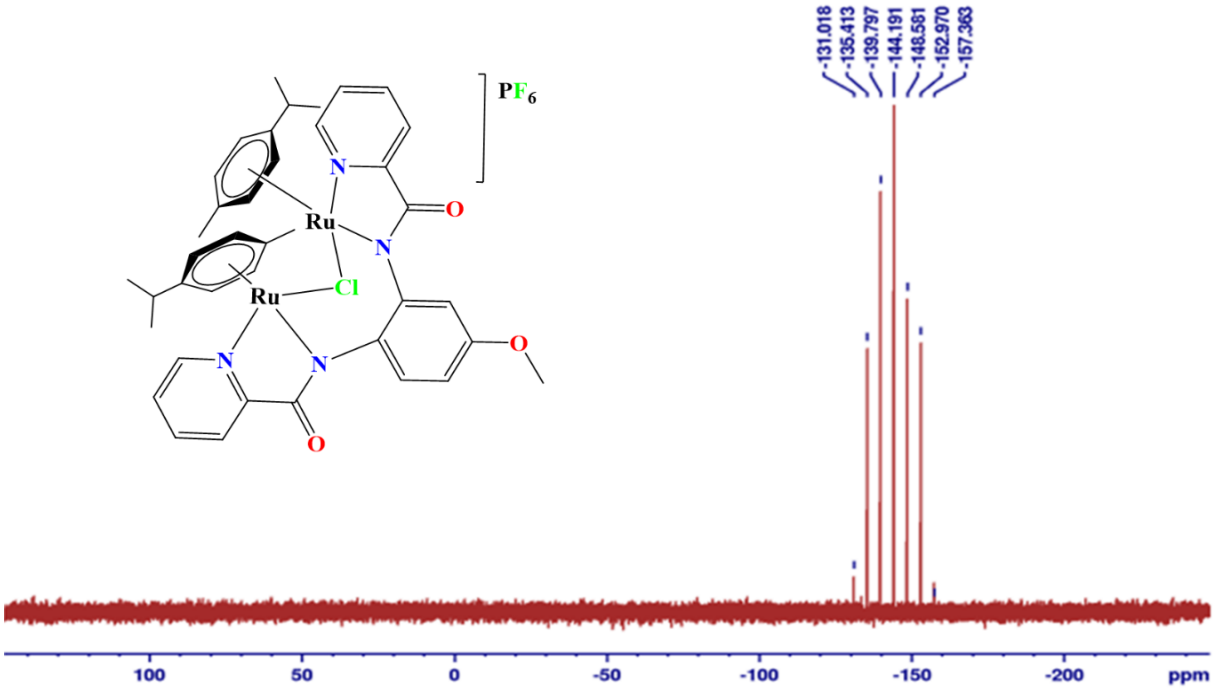


Figure S17. ^{31}P NMR of complex **Ru4** at room temperature.

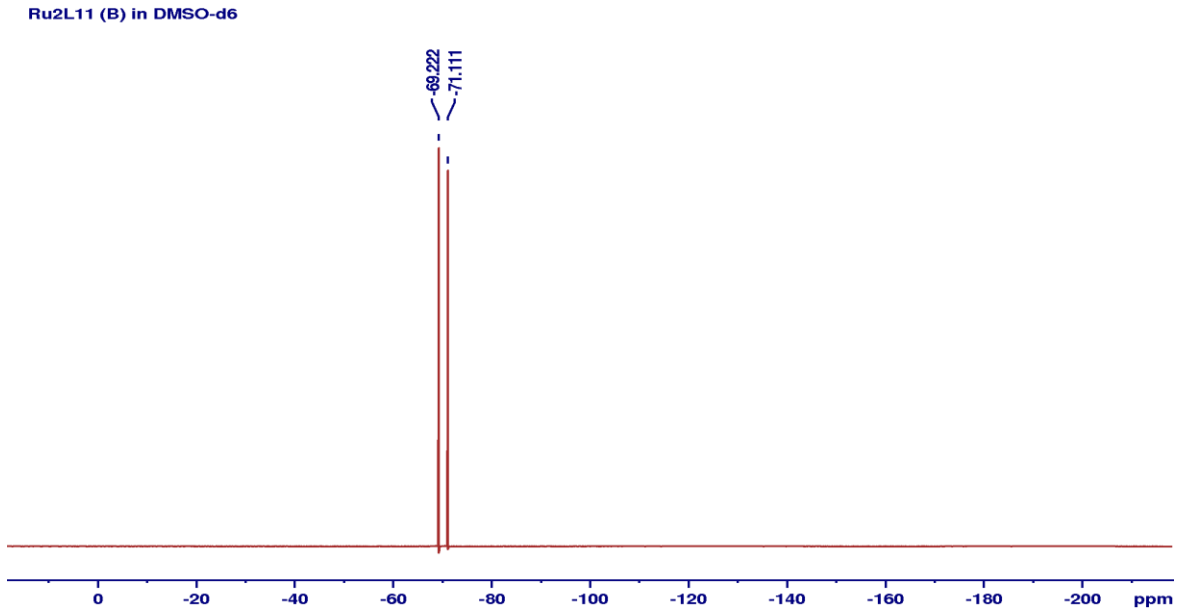


Figure S18. ^{19}F NMR of complex **Ru2** at room temperature.

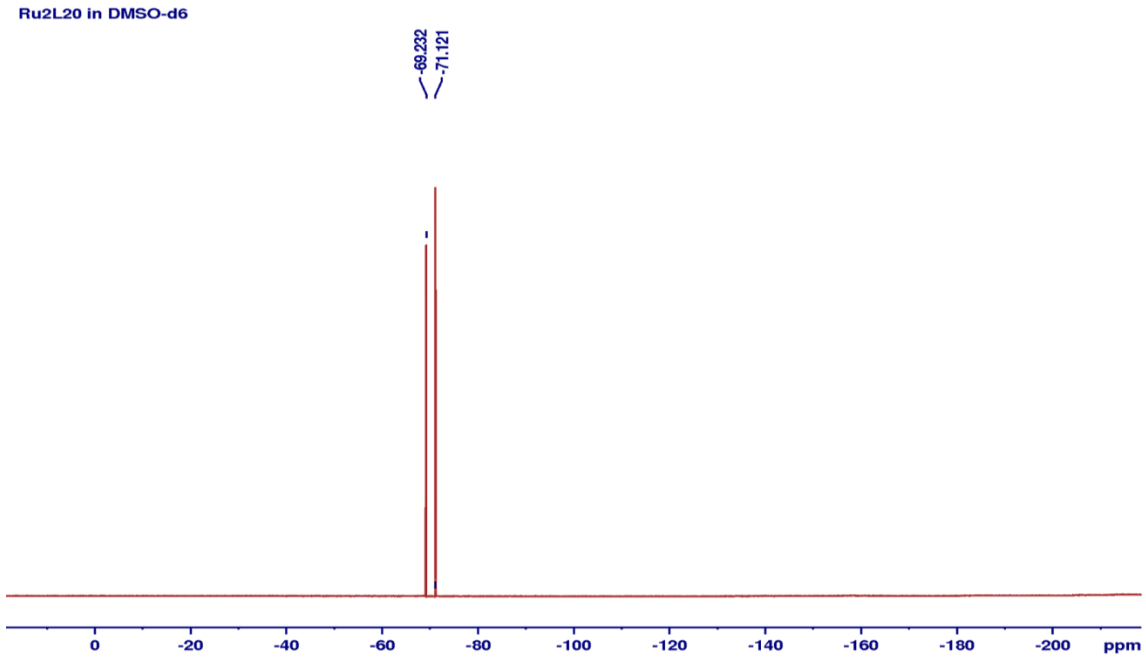


Figure S19. ^{19}F NMR of complex **Ru3** at room temperature.

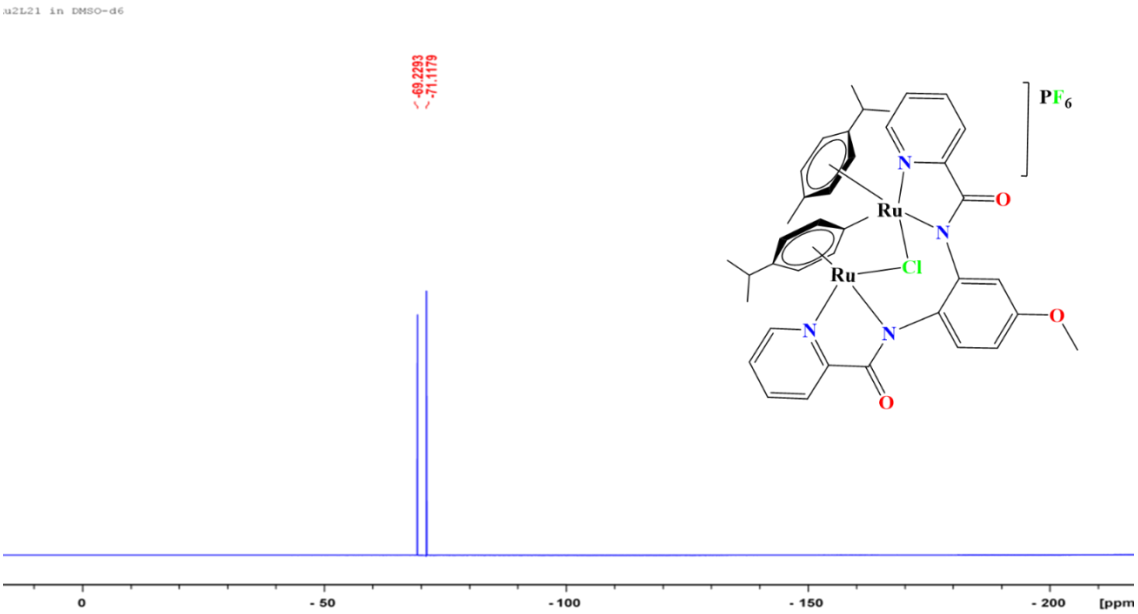


Figure S20. ^{19}F NMR of complex **Ru4** in d_6-DMSO at room temperature.

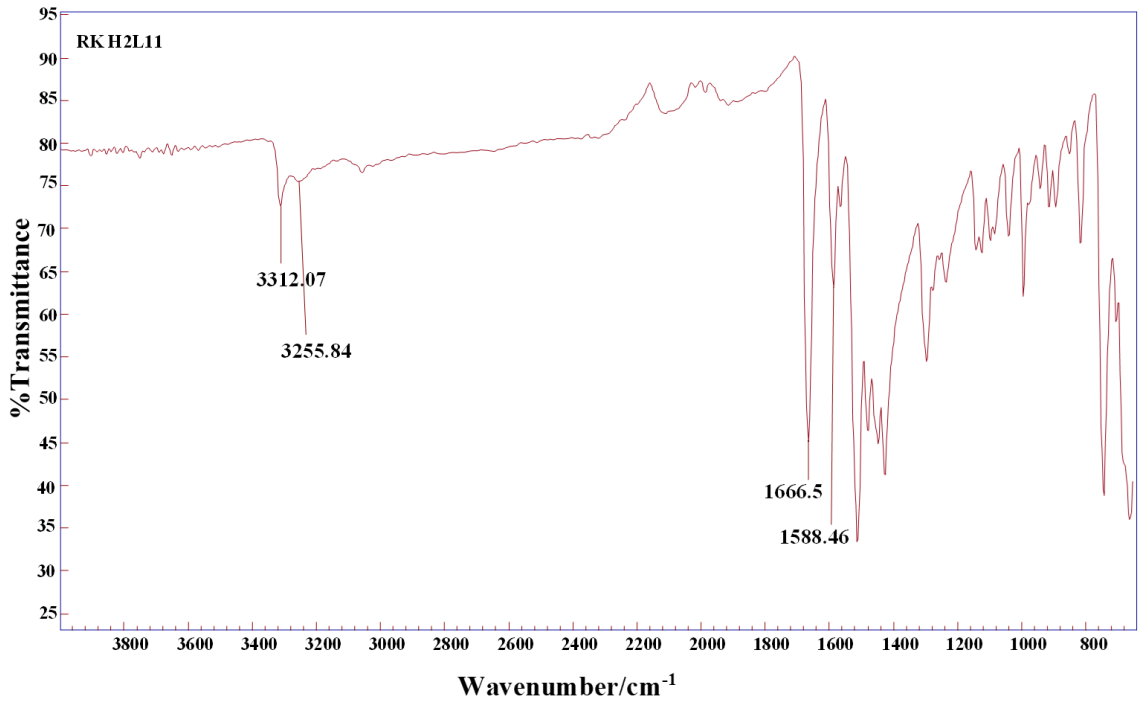


Figure S21. FT-IR of Ligand *N,N'-(1,2-phenylene)dipicolinamide* **H_2L1** showing the carbonyl peak at 1667 cm^{-1}.

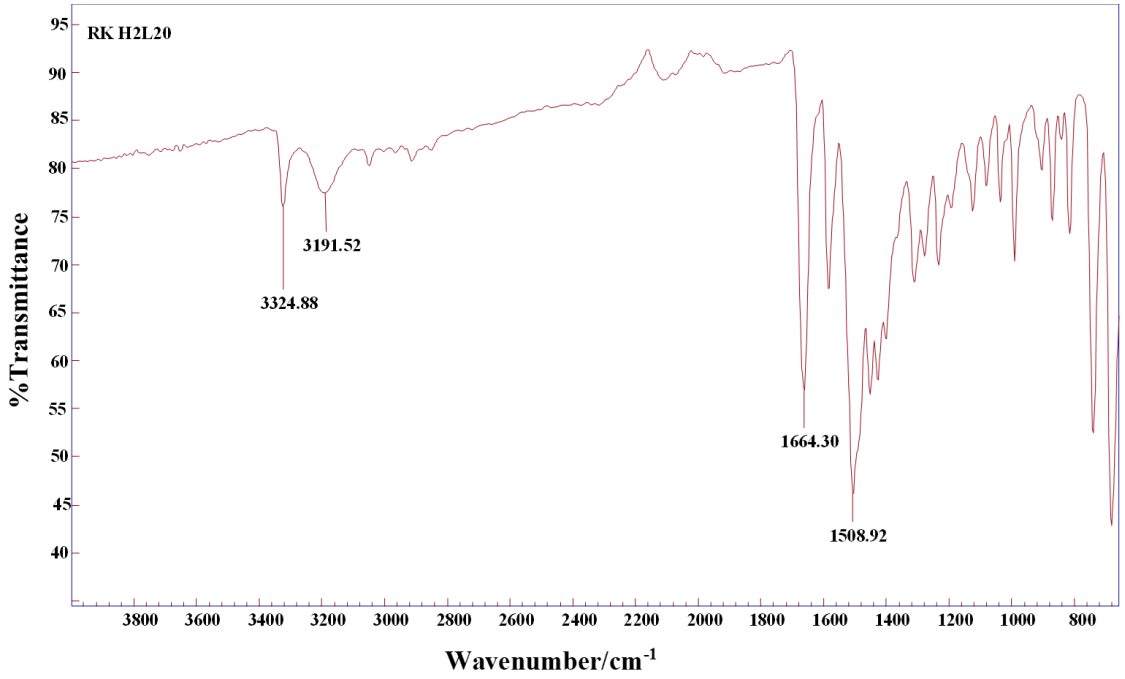


Figure S22. FT-IR of spectrum of *N,N'-(4,5-dimethyl-1,2-phenylene)dipicolinamide:* **H_2L2** showing its carbonyl peak at 1664 cm^{-1}.

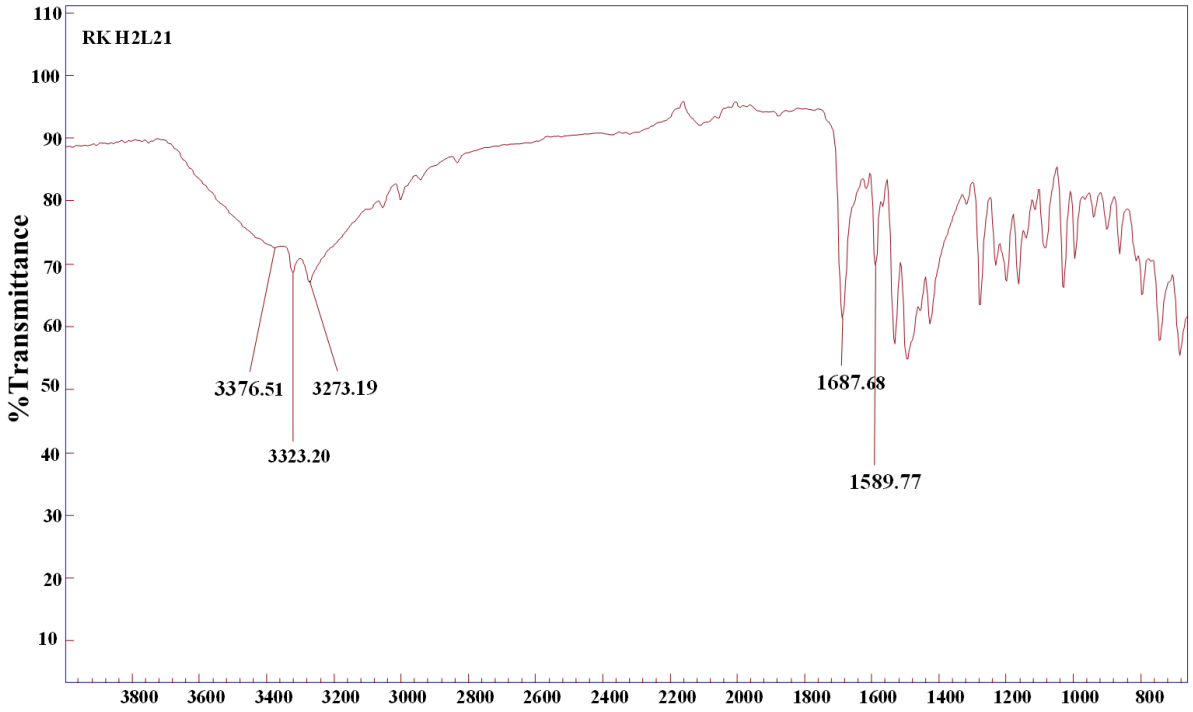


Figure S23. FT-IR of spectrum of *N,N'-(3-methoxy-1,2-phenylene)dipicolinamide*: **H_2L3** showing its carbonyl peak at 1688 cm^{-1}.

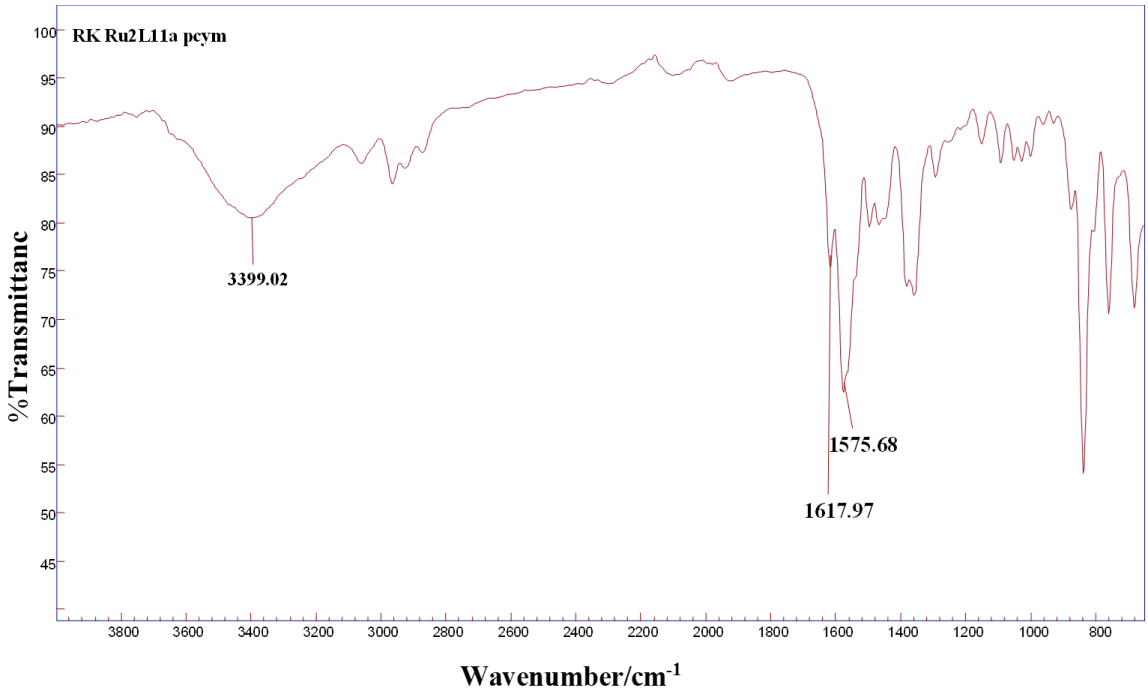


Figure S24. FT-IR of dinuclear complex **Ru1** showing the carbonyl peak at 1618 cm^{-1}.

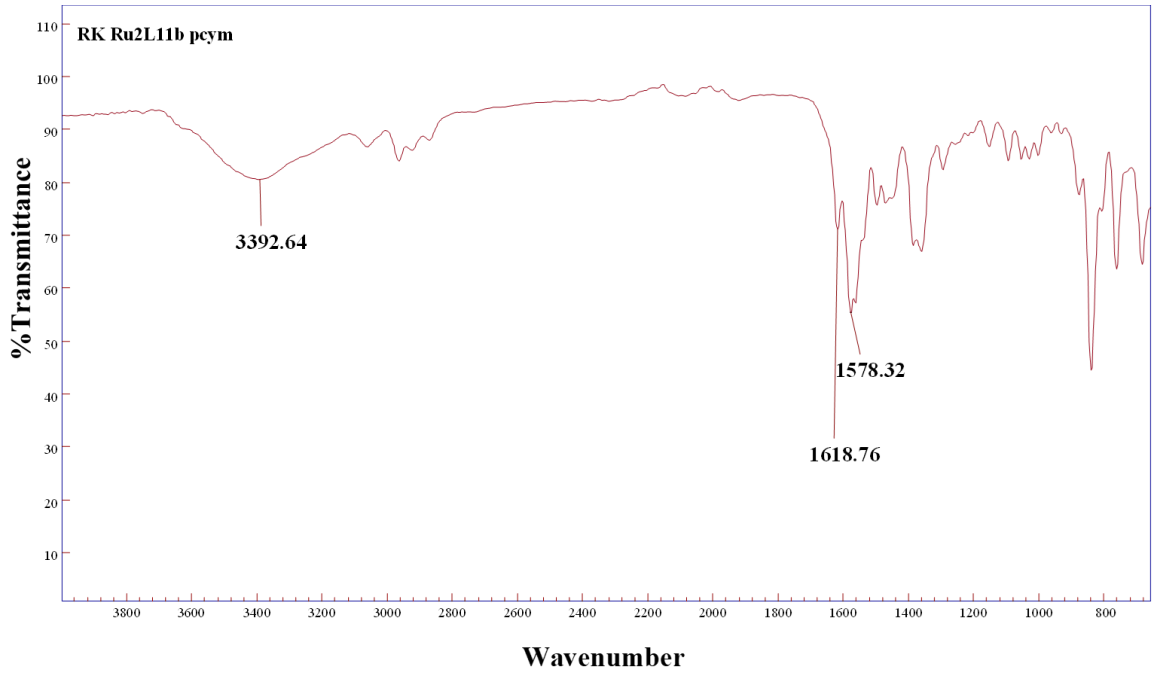


Figure S25. FT-IR of dinuclear complex **Ru2** showing the carbonyl peak at 1619 cm^{-1}.

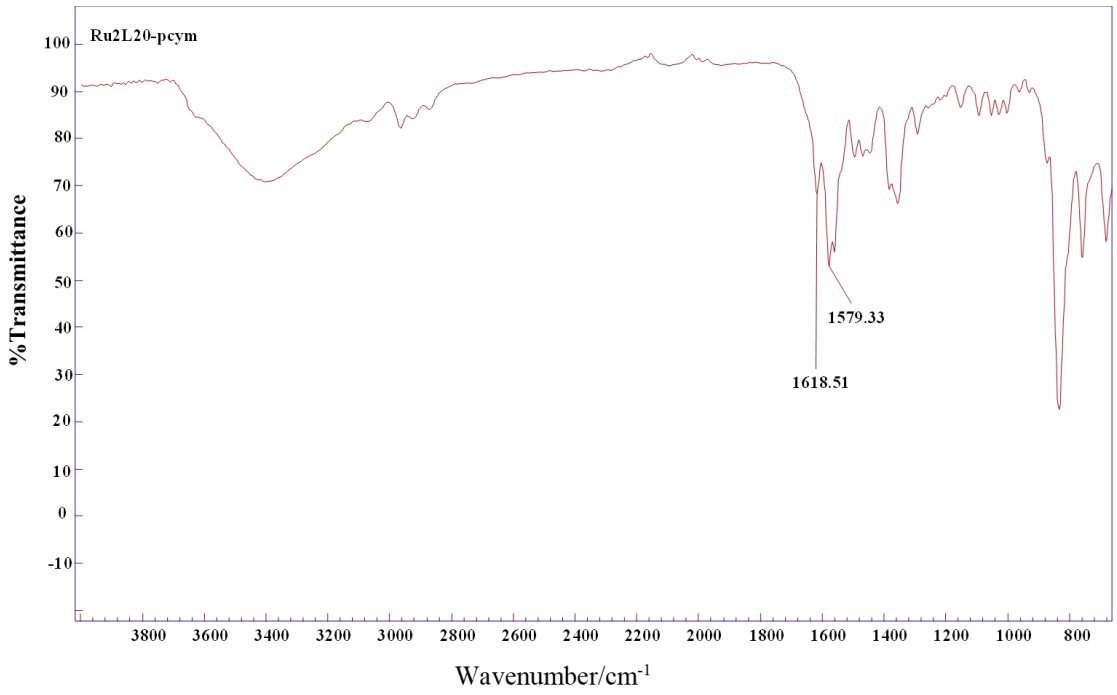


Figure S26. FT-IR of dinuclear complex **Ru3** showing the carbonyl peak at 1619 cm^{-1}.

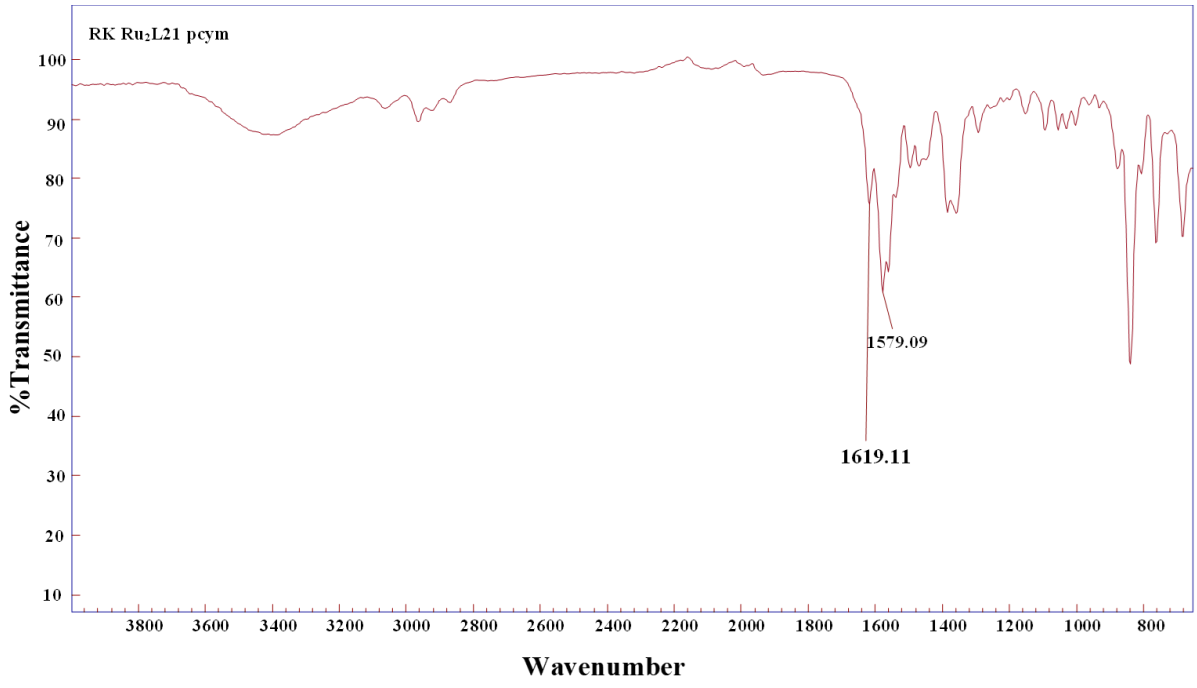


Figure S27. FT-IR of dinuclear complex **Ru4** showing the carbonyl peak at 1619 cm^{-1}.

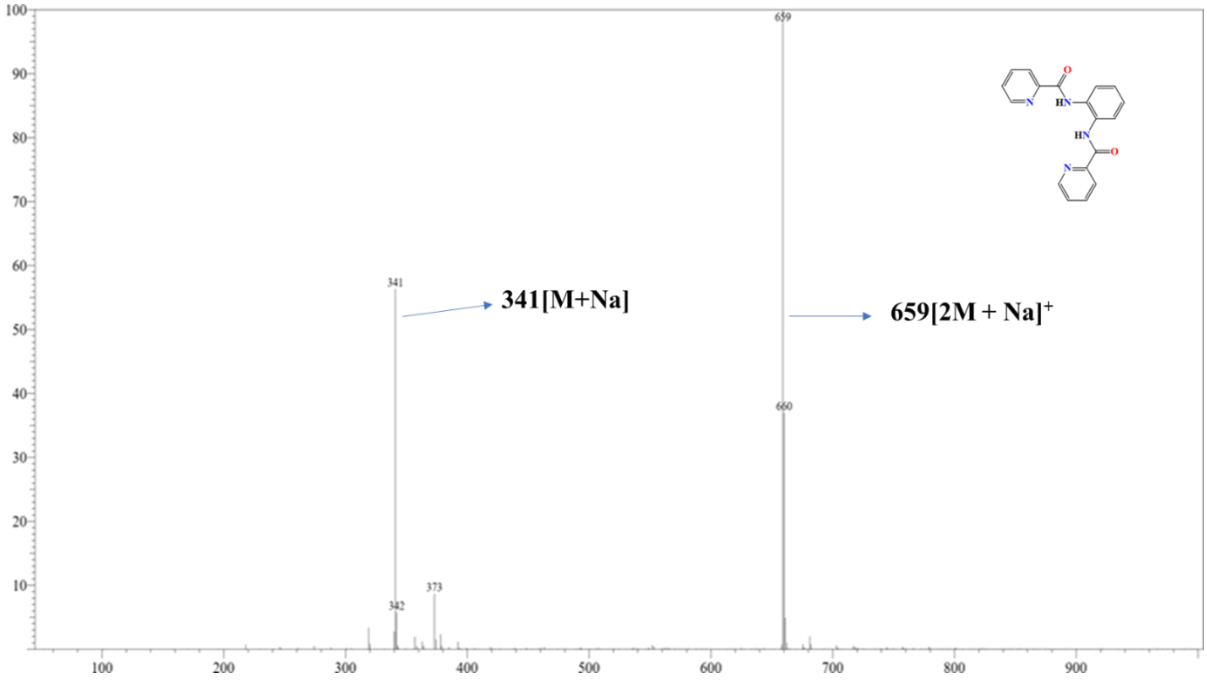


Figure S28. ESI LC-MS (positive mode) of *N,N'-(1,2-phenylene)bis(pyridine-2-carboxamide):* **H_2L1**.

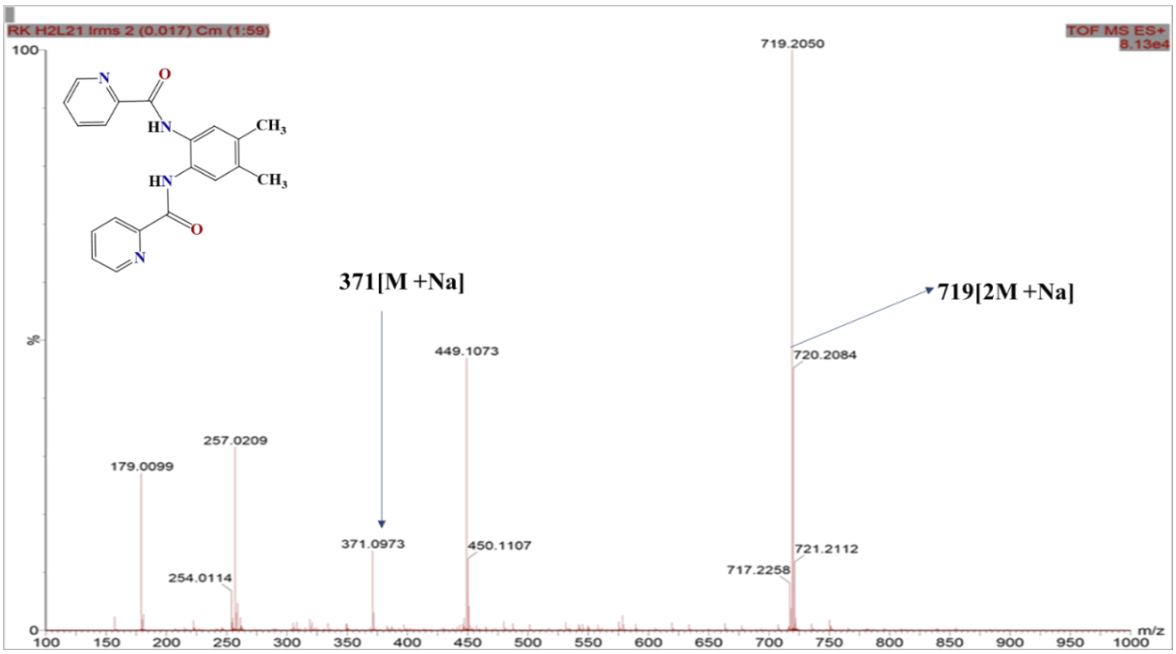


Figure S29. ESI LC-MS (positive mode) of *N,N'-(4,5-dimethyl-1,2-phenylene)dipicolinamide:* **H_2L2**.

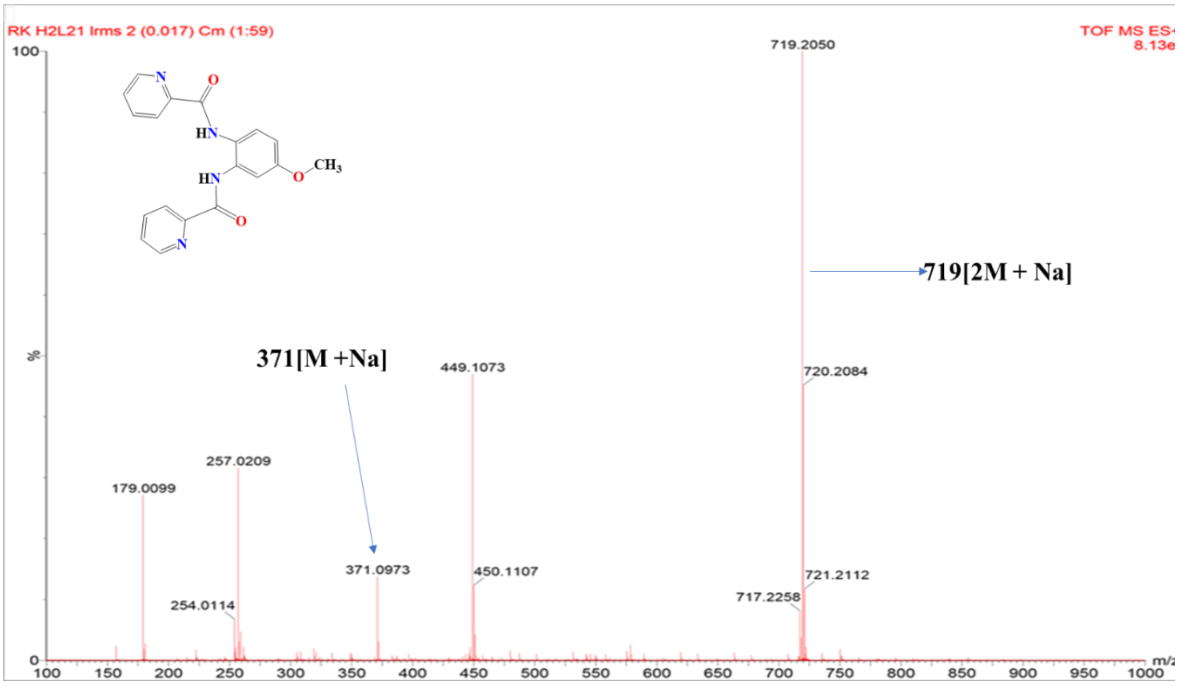


Figure S30. ESI LC-MS (positive mode) of *N,N'-(4 -methoxy-1,2-phenylene)dipicolinamide*: **H_2L3**.

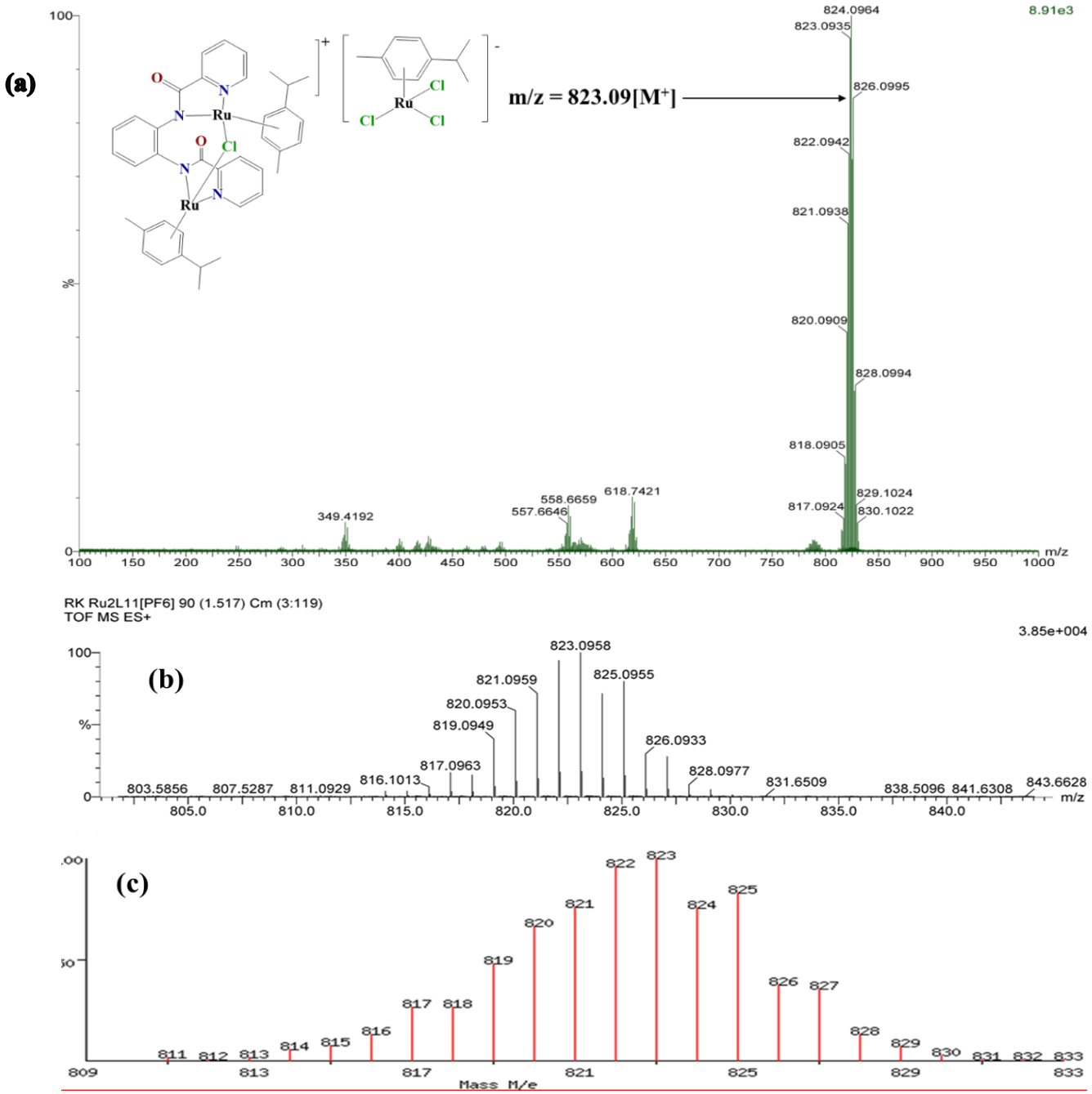


Figure S31. (**a**) ESI -MS (positive mode) of complex **Ru1**, (**b**) HR-MS of complex **Ru1**, (**c**) Theoretical isotopic mass distribution of the complex, **Ru1**.

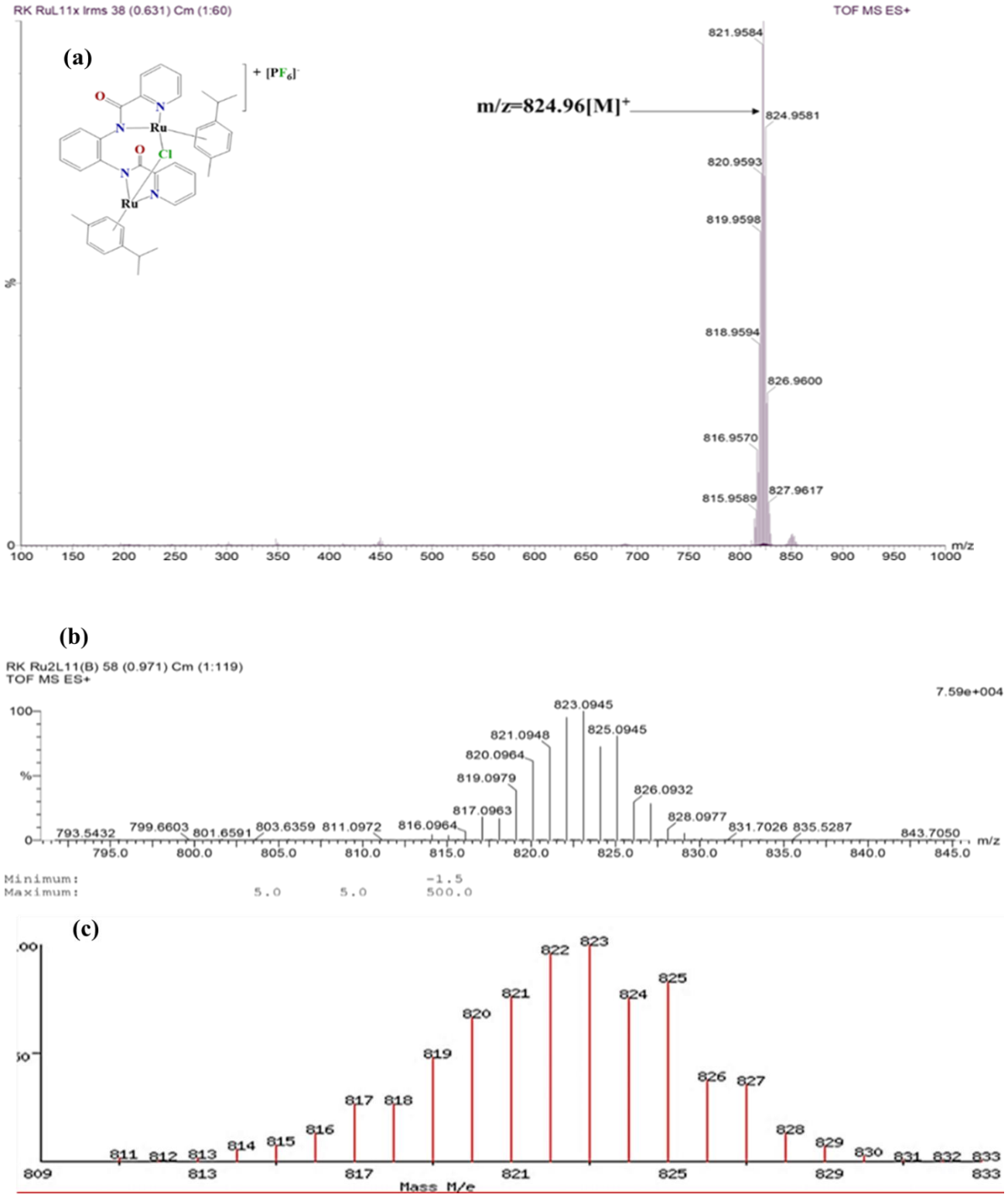


Figure S32. (**a**) ESI MS of complex **Ru2**, (**b**) ESI HR-MS of complex **Ru2**, with the molecular formula, (**c**) Theoretical isotopic mass distribution of the complex, **Ru2**.

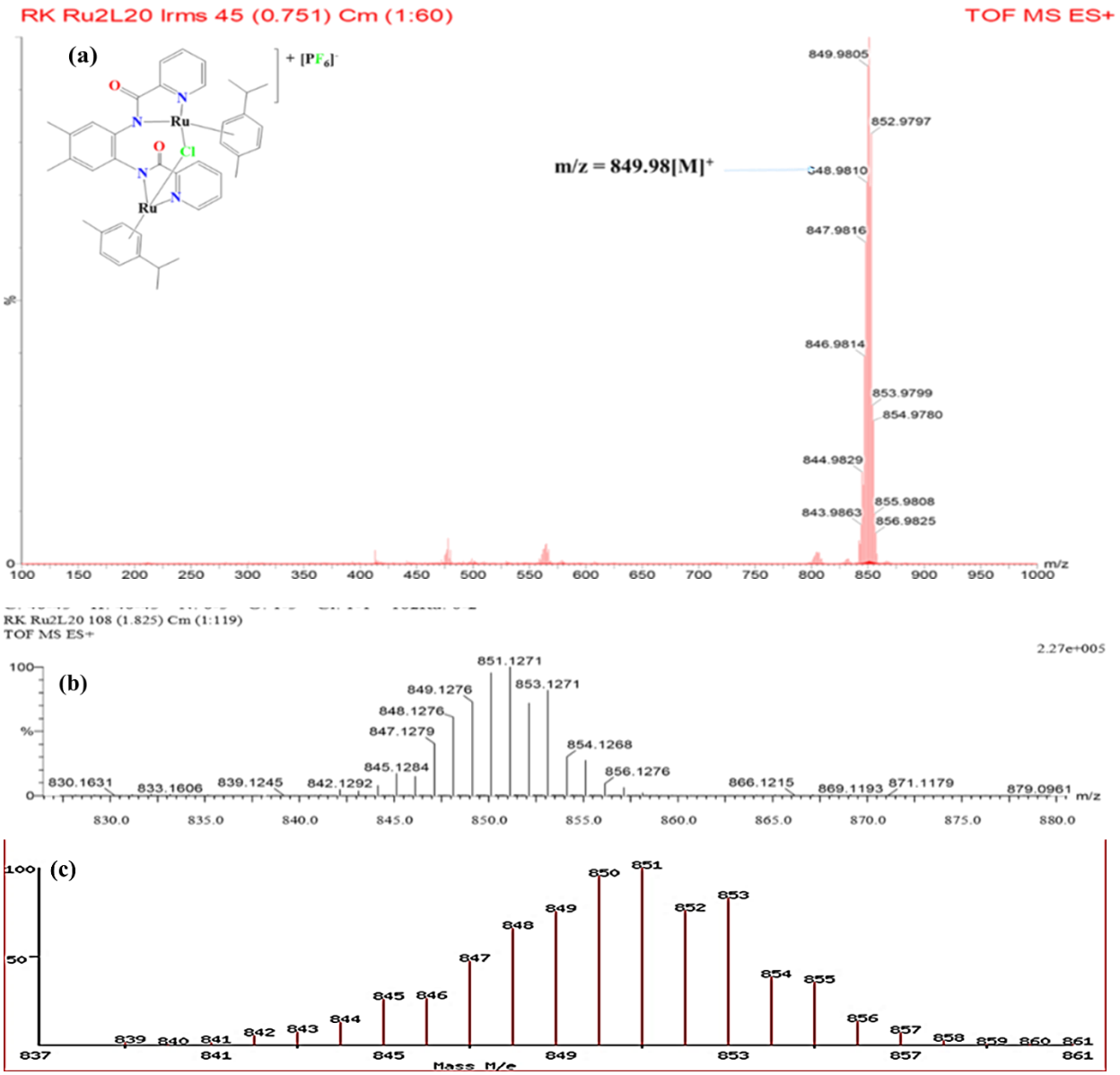


Figure S33. (**a**) ESI-MS (positive mode) of complex **Ru3**, (**b**) ESI HR-MS of complex **Ru3**, (**c**) Theoretical isotopic mass distribution of the complex, **Ru3**.

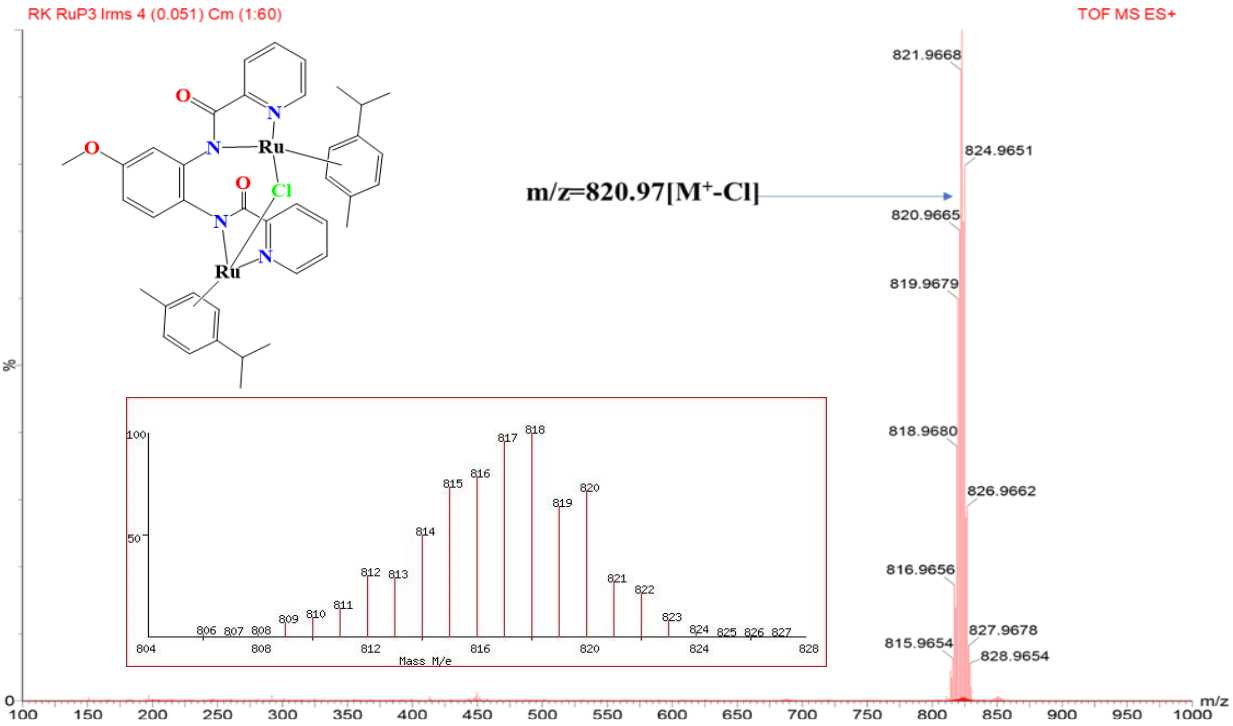


Figure S34. ESI-MS (positive mode) of complex **Ru4**, Theoretical isotopic mass distribution mass spectrometry of **Ru4** (Inset).

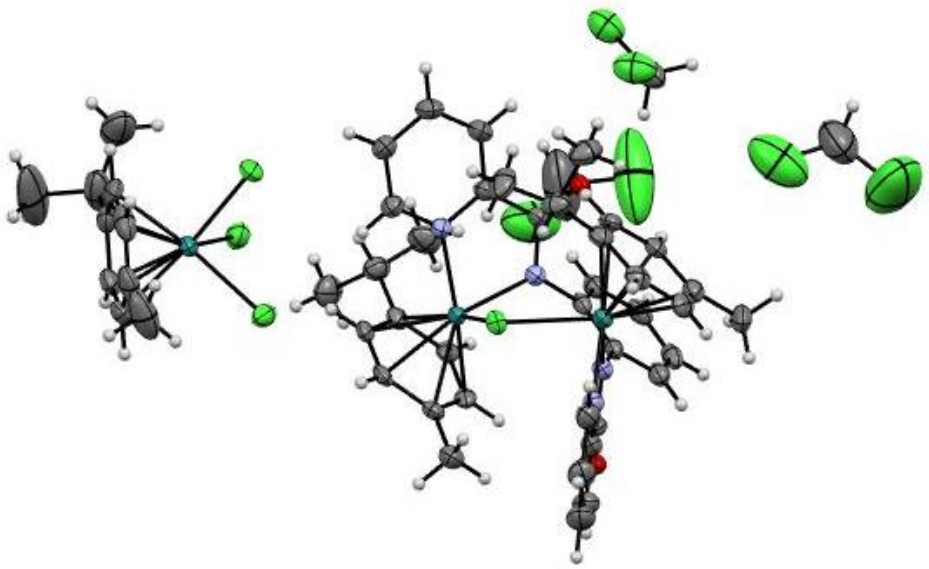


Figure S35. Molecular structure of **Ru1**, with ellipsoids drawn at 50% probability level.

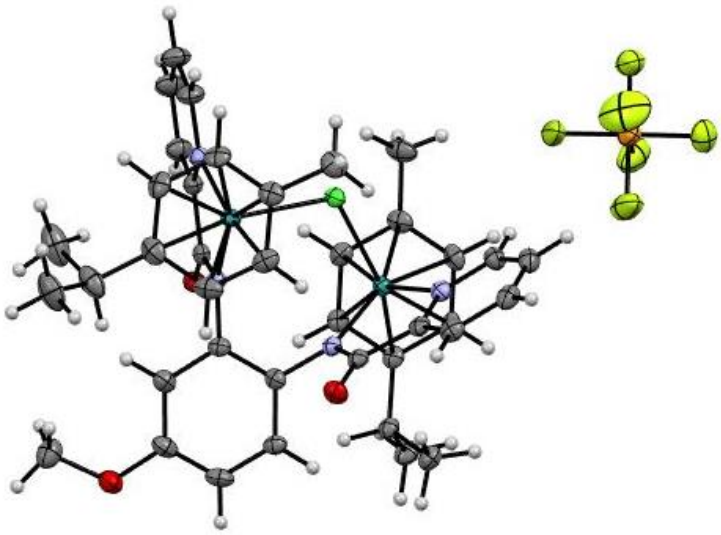


Figure S36. Molecular structure of **Ru4**, with ellipsoids drawn at 50% probability level.

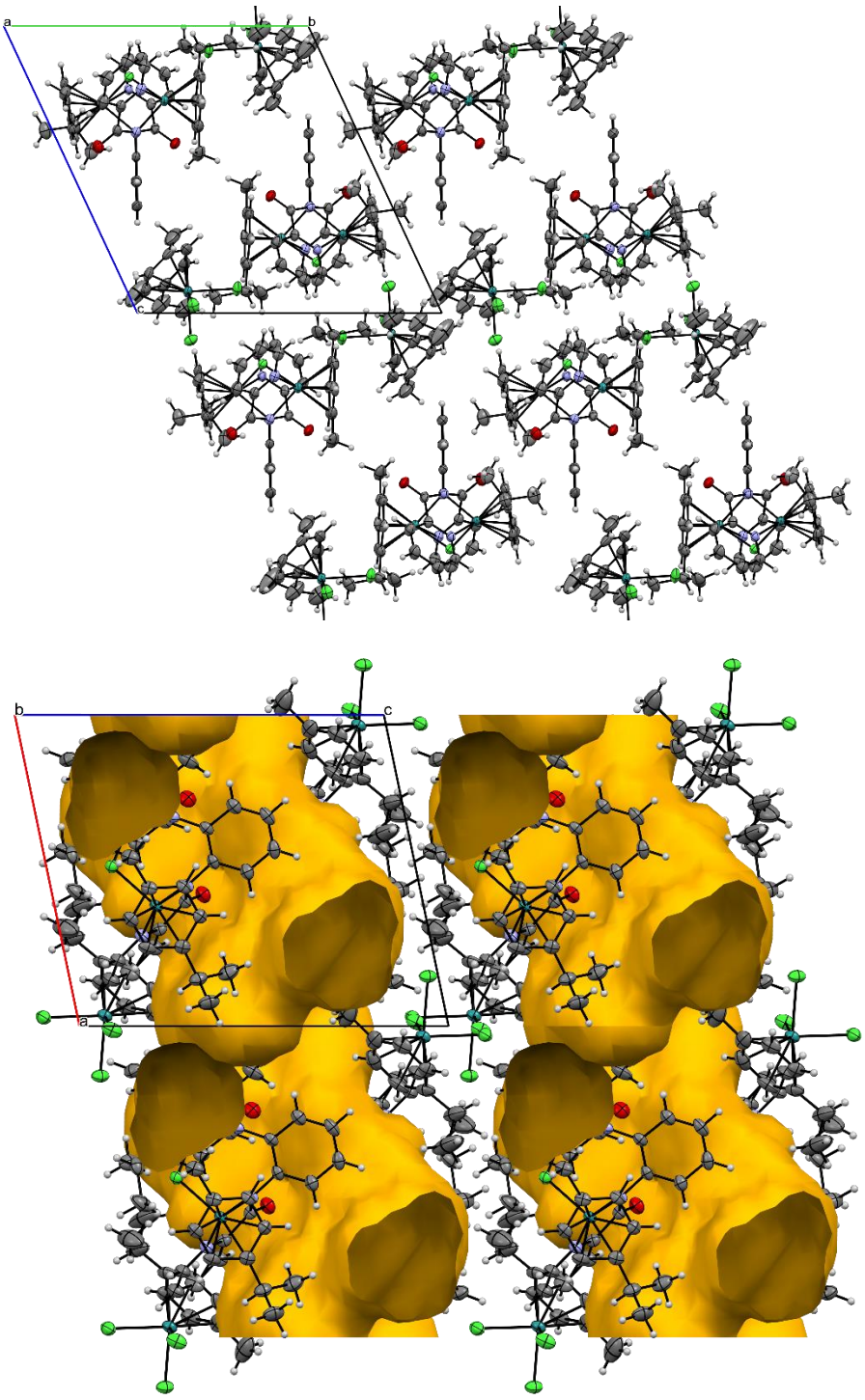


Figure S37. Molecular packing arrangement of **Ru1** viewed along *a*-axis showing two asymmetry units per unit cell (triclinic space group).

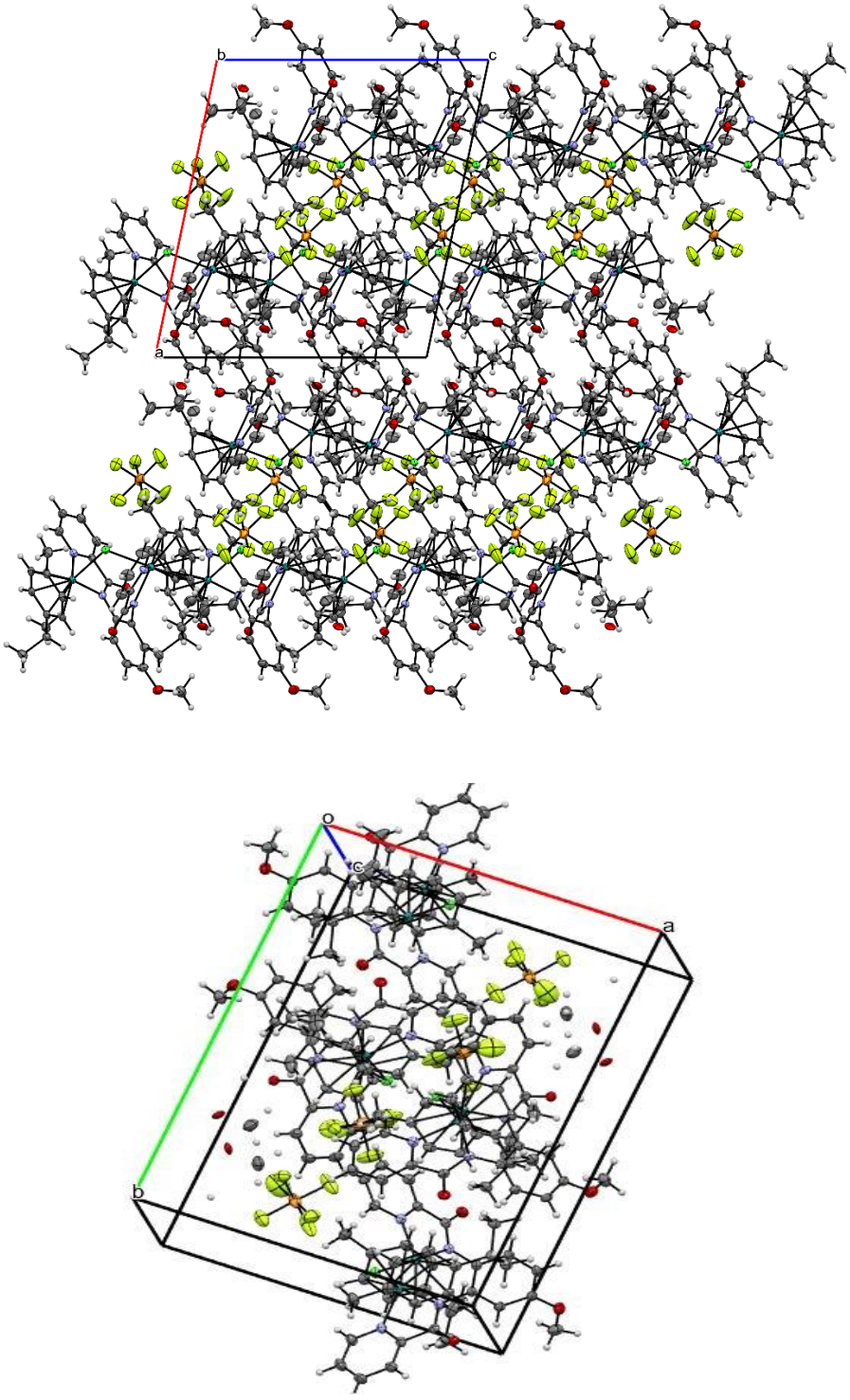


Figure S38. Molecular packing arrangement of **Ru4** viewed along *a*-axis showing four asymmetry units per unit cell (monoclinic space group).

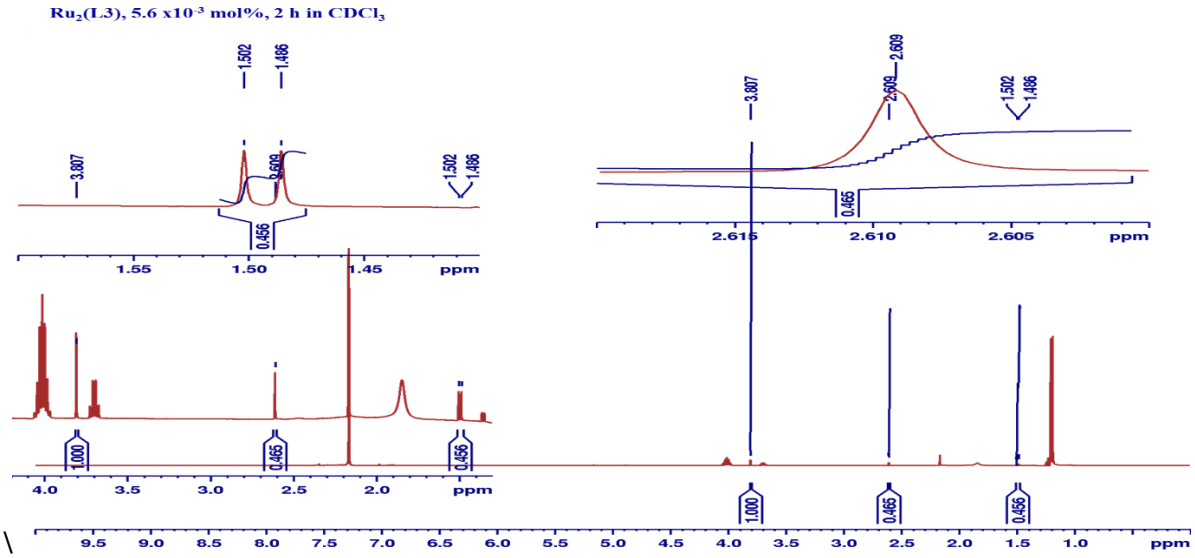


Figure S39. ^{1}H NMR spectrum (400 MHz, *d*-$CDCl_3$) of TH of acetophenone. [**Ru3,** 5.6 x10^{-3} mol%) was used as catalyst]. An aliquot was taken and analysed after 2 h of reaction. The integral values of methyl protons of acetophenone and 1-phenylethanol corresponding to the percentage conversion of 53% and yield of 52% (**Figure 3**).

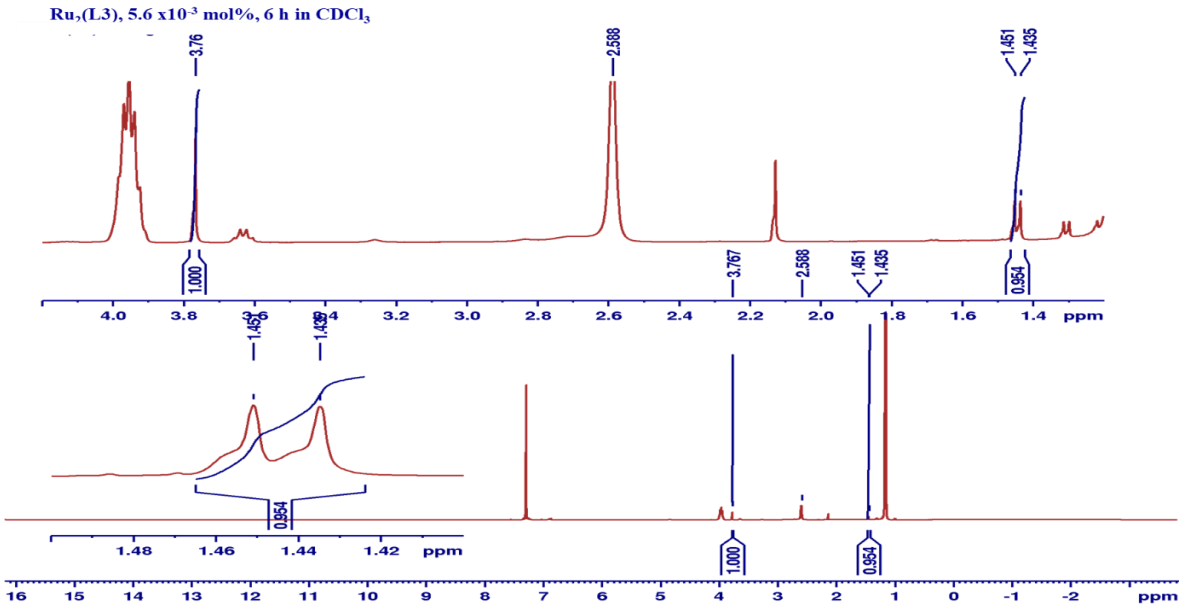


Figure S40. ^{1}H NMR spectrum (400 MHz, *d*-$CDCl_3$) of TH of acetophenone. **Ru1,** 5.00 x10^{-3} mol%) was used as catalyst]. An aliquot was taken and analysed after 6 h of reaction. The integral values of methyl protons of acetophenone and 1-phenylethanol correspond to the percentage conversion of 99% and yield of 98% (**Figure 3, Table 3, entry 2**).

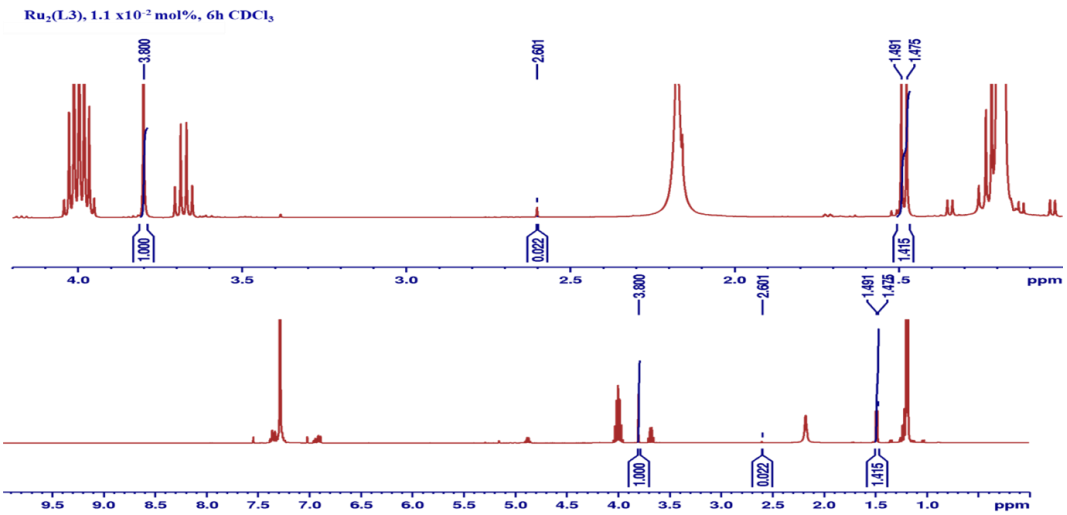


Figure S41. ^{1}H NMR spectrum (400 MHz, *d*-$CDCl_3$) of TH of acetophenone. **Ru1** was used as catalyst]. The aliquot was taken and analysed after 6 h of reaction. The integral values of methyl protons of acetophenone and 1-phenylethanol corresponding to the percentage conversion of 99% and yield of 98% (**Figure 3** and **Table 3**, **entry 2).**

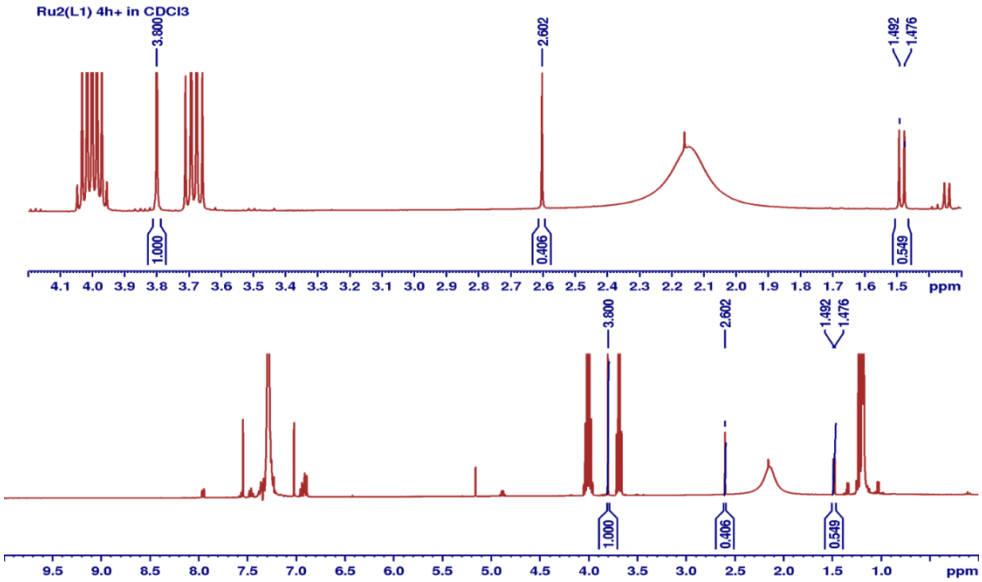


Figure S42. ^{1}H NMR spectrum (400 MHz, *d*-$CDCl_3$) of TH of acetophenone. **Ru2** was used as a catalyst). An aliquot was taken and analysed after 4 h of reaction. The integral values of methyl protons of acetophenone and 1-phenylethanol corresponding to the percentage conversion of 60% and yield of 57% (**Figure 4**).

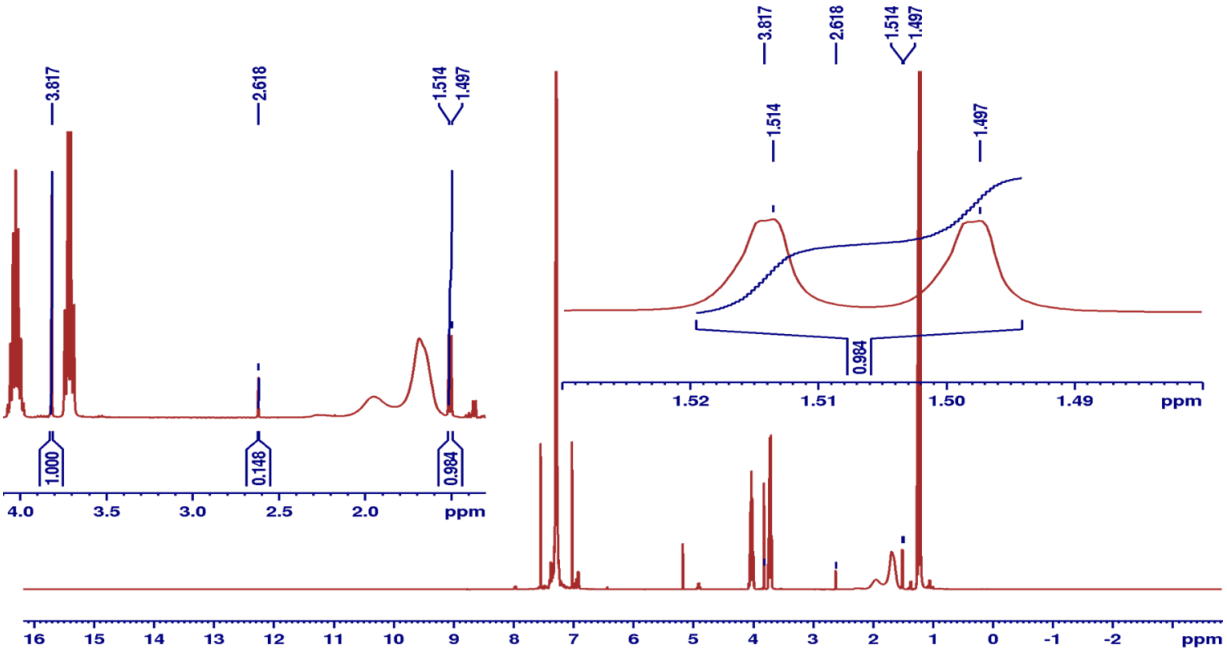


Figure S43. ^{1}H NMR spectrum (400 MHz, *d*-$CDCl_3$) of TH of acetophenone. **Ru2** was used as a catalyst). An aliquot was taken and analysed after 6 h of reaction. The integral values of methyl protons of acetophenone and 1-phenylethanol corresponding to the conversion of 86% and yield of 85% (**Table 2, entry 4**).

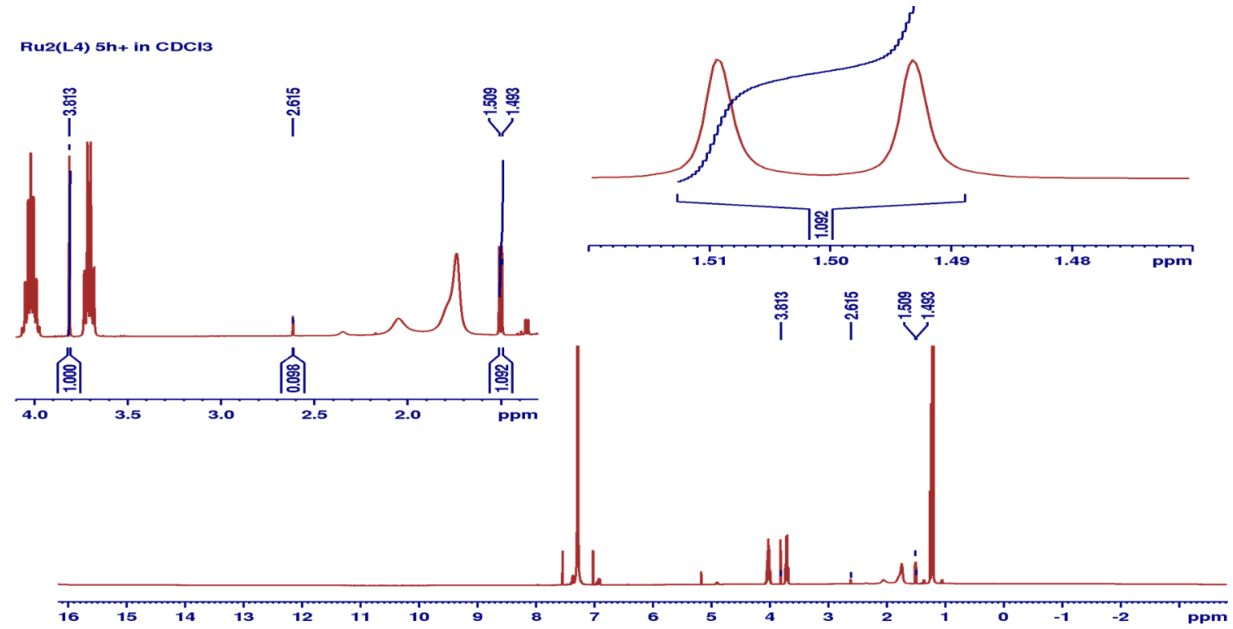


Figure S44. ^{1}H NMR spectrum (400 MHz, *d*-$CDCl_3$) of TH of acetophenone. **Ru4** was used as a catalyst). An aliquot was taken and analysed after 5 h of reaction. The integral values of methyl protons of acetophenone and 1-phenylethanol corresponding to the conversion of 92% and yield of 92% (**Figure 4** and **Table 3, entry 5**).

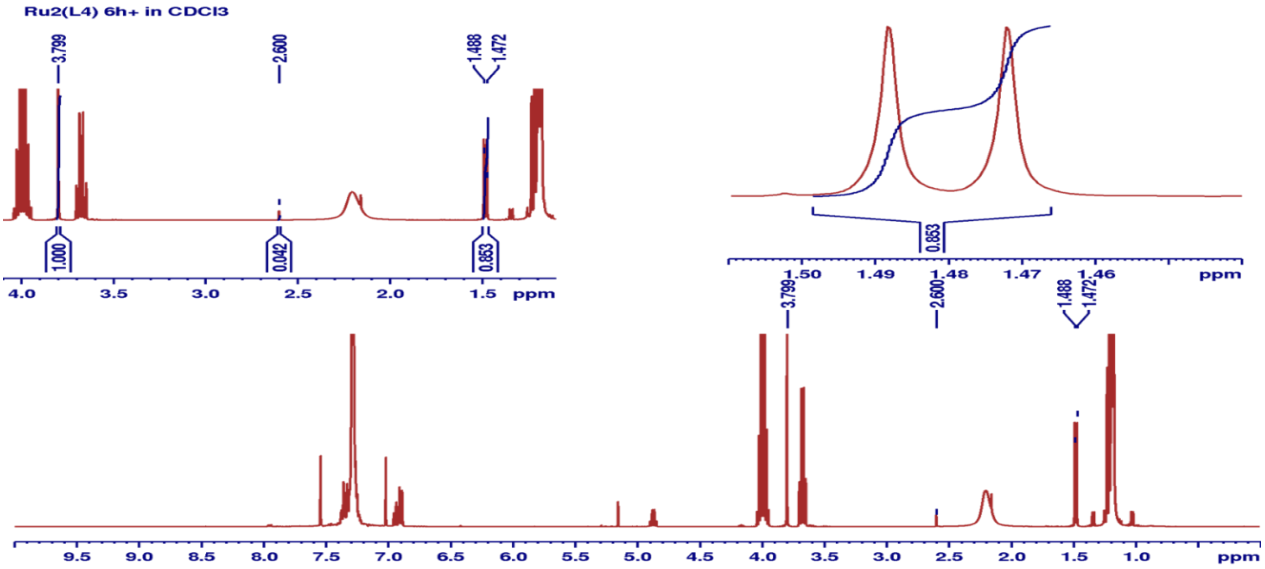


Figure S45. ^{1}H NMR spectrum (400 MHz, *d*-$CDCl_3$) of TH of acetophenone. **Ru3** was used as a catalyst). An aliquot was taken and analysed after 6 h of reaction. The integral values of methyl protons of acetophenone and 1-phenylethanol corresponding to the conversion of 96% and yield of 95% (**Figure 4** and **Table 2, entry 6**).

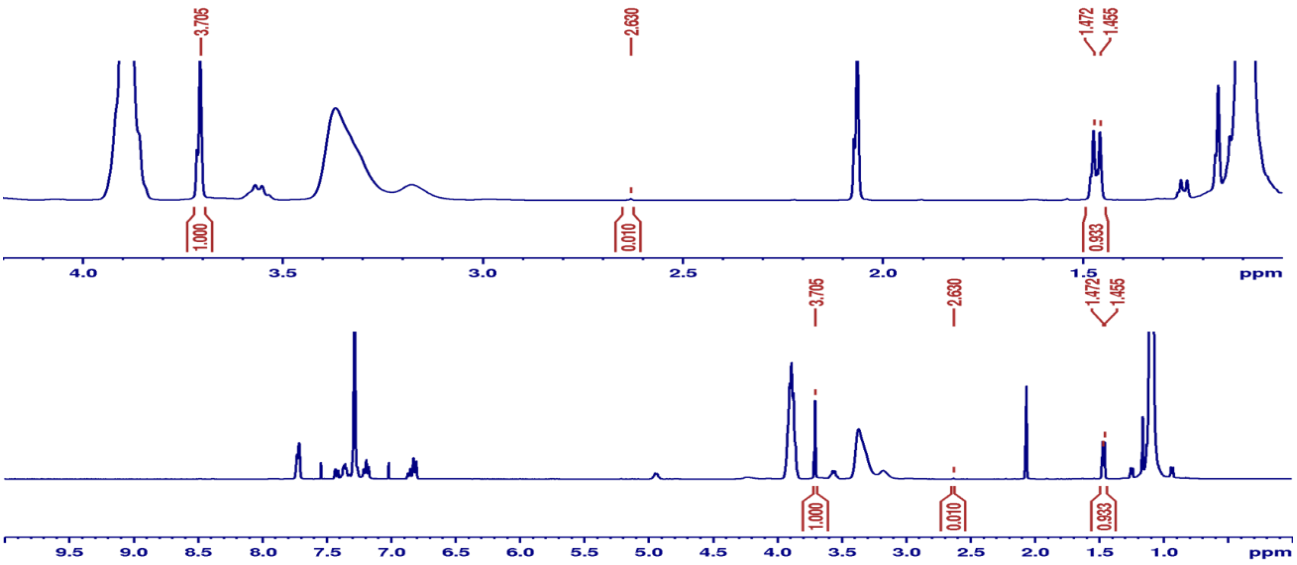


Figure S46. ^{1}H NMR spectrum (400 MHz, *d*-$CDCl_3$) of TH of 2-chloroacetophenone. **Ru2** was used as a catalyst). An aliquot was taken and analysed after 4 h of reaction. The integral values of methyl protons of 2-chloroacetophenone and the product corresponding to the conversion of 99 % and yield of 99% (**Table 4, entry 2**).

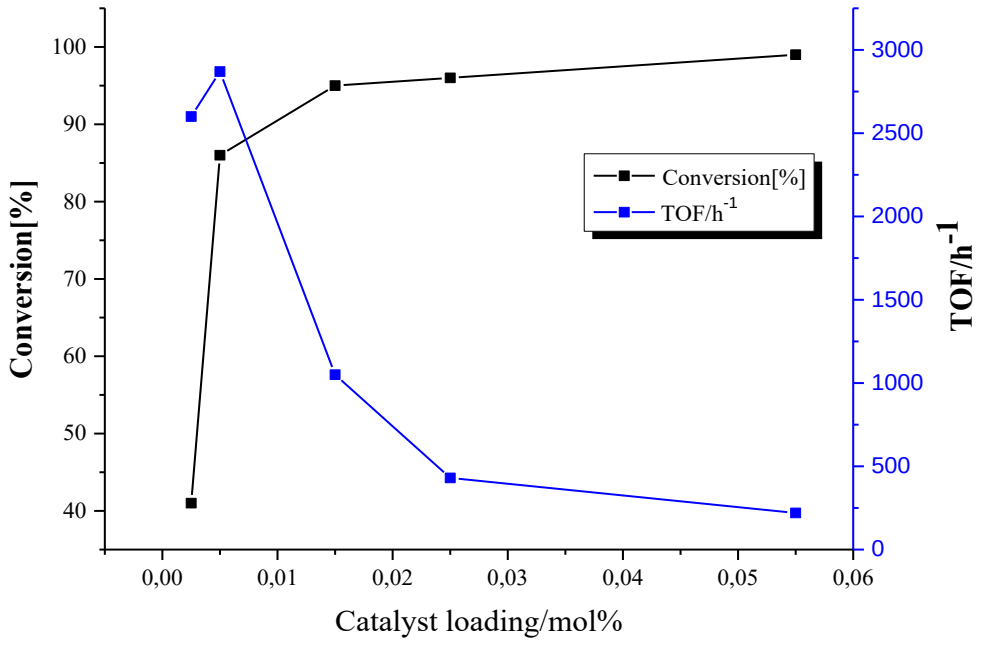
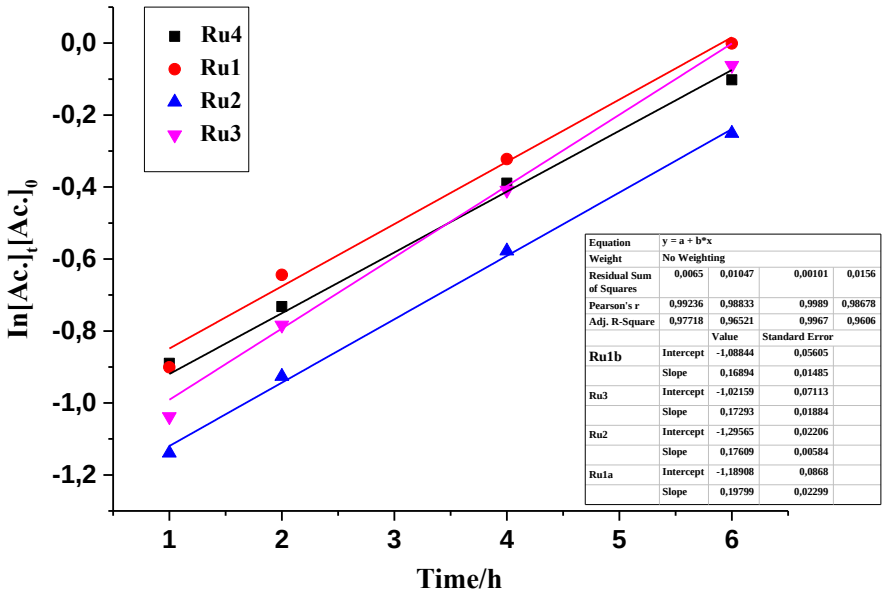


Figure S47. A plot of Conversion, TOF vs catalyst loading used to determine optimised reaction conditions.



Equation	y = a + b*x			
Weight	No Weighting			
Residual Sum of Squares	0,0065	0,01047	0,00101	0,0156
Pearson's r	0,99236	0,98833	0,9989	0,98678
Adj. R-Square	0,97718	0,96521	0,9967	0,9606
		Value	Standard Error	
Ru1b	Intercept	-1,08844	0,05605	
	Slope	0,16894	0,01485	
Ru3	Intercept	-1,02159	0,07113	
	Slope	0,17293	0,01884	
Ru2	Intercept	-1,29565	0,02206	
	Slope	0,17609	0,00584	
Ru1a	Intercept	-1,18908	0,0868	
	Slope	0,19799	0,02299	

Figure S48. The plot of $\ln[Ac.]_t/[Ac.]_0$ vs time for determination of k_{ob} of the catalysts. [Ac.] = concentration of acetophenone, t = time.