SUPPORTING INFORMATION

Azobenzene-based ruthenium(II) catalysts for light-controlled hydrogen generation.

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Synthesis, characterization and photoisomerization of new compounds

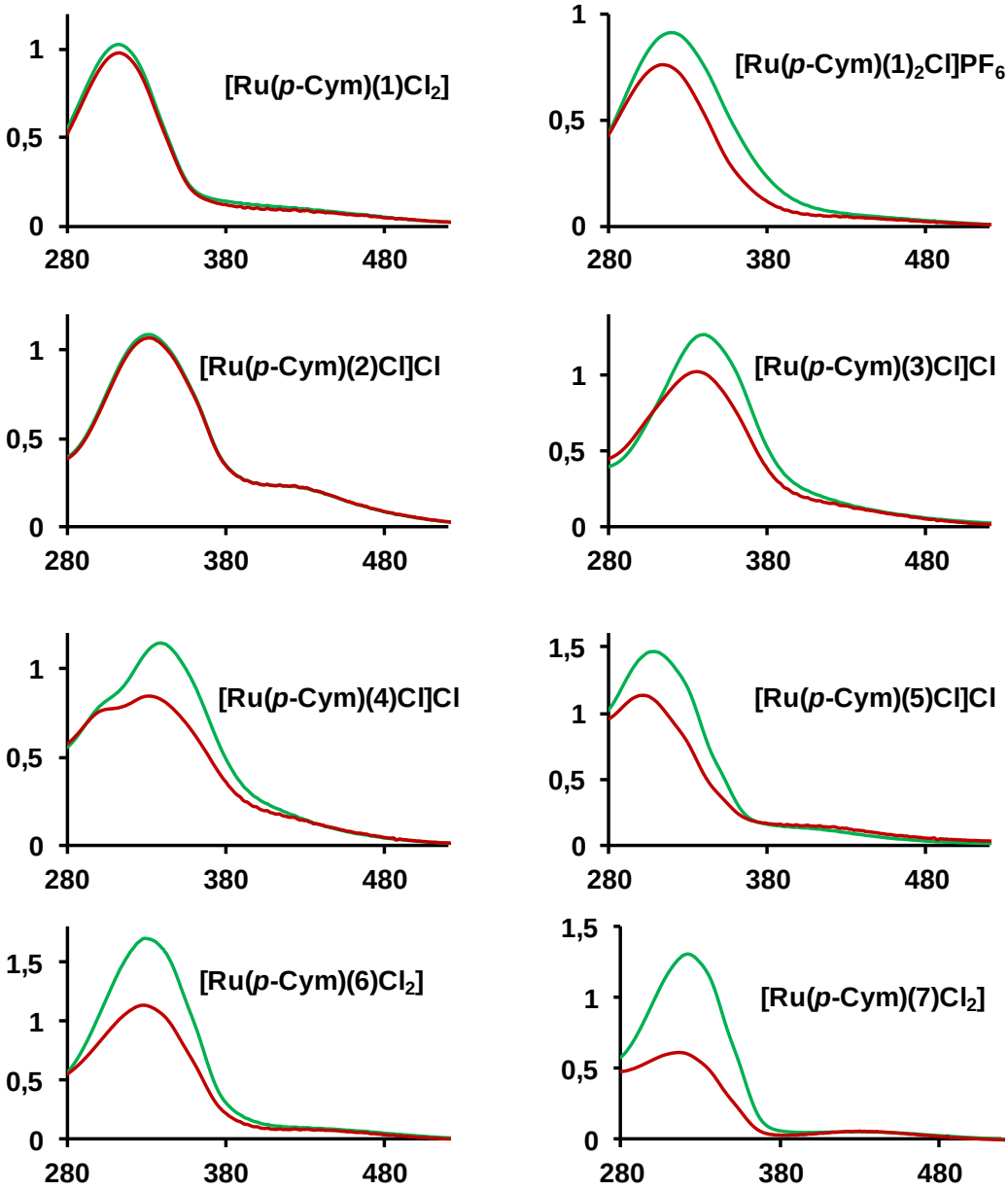

Figure S1. UV-vis spectra (absorbance vs. wavelength (nm)) before (green line) and after (red line) irradiation of azobenzene-containing Ru(II) complexes after 30 min irradiation at $\lambda_{azo\ \pi\rightarrow\pi^*}$ and 30 min irradiation at $\lambda_{optimal}$ (CH_3CN).

Methodology for irradiation:

Due to the heating of the system caused by prolonged irradiation times, the reaction vessel was immersed in a water bath, that was maintained at the desired temperature (±4 °C) by means of a thermostated external cooling jacket. When required the reaction mixture was irradiated during the catalytic process by means of an immersion lamp (125 W, 365 nm), which was also refrigerated by means of an external cooling jacket made of quartz. The reaction vessel used for these reactions was also made of quartz. The experimental setup is presented in Figure S2.

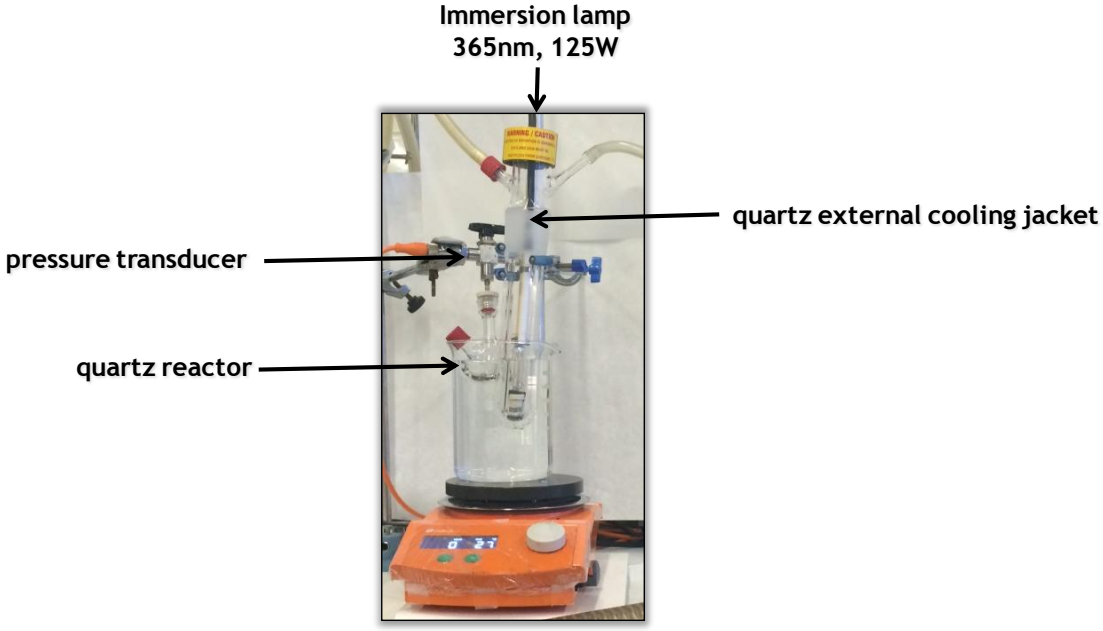

Figure S2. Setup for catalytic experiments under irradiation.

Several experiments before testing azobenzene-containing precatalyts were necessary to analyze the influence of the irradiation on the catalytic process and optimize the reaction conditions. Initially, a blank experiment (without catalyst) was carried out, with continuous irradiation to confirm that light-induced AB cleavage and hydrolysis of the released BH_3 was not competing with the catalyzed process (Figure S3, red-dashed line). The slight slope observed should be attributed an unavoidable temperature increase (~4 °C). To select the temperature at which the thermostatic bath should be fixed to avoid overheating of the system, several experiments were performed with the precatalyst [Ru(*p*-Cym)(**8**)Cl]Cl, which does not contain any azobenzene fragment. The catalytic activity of this precatalyst with the thermostatic bath at different temperatures was compared with the reaction profile obtained at 25 °C (without irradiation) until similar reaction profiles were obtained. In this manner, the ideal temperature of the thermostatic bath was set at 10 °C. By setting the thermostat temperature at 10 °C, the initial temperature measured for irradiated catalysis was 21 °C and it never exceeded the 25 °C, (Figure S3, green (not irradiated) and red (irradiated) lines). For comparative purposes not irradiated reactions were performed at 25 °C (the maximum temperature achieved upon irradiation), to guarantee that any outperformance of the irradiated processes was not a temperature artifact. Consequently, as it can observed in Figure S3, the activity of the precatalyst [Ru(*p*-Cym)(**8**)Cl]Cl (not light-sensitive) was slightly lower when the reaction was irradiated, due to the lower initial temperature. This small difference in profiles will be assumed as the experimental error inherent to the methodology.

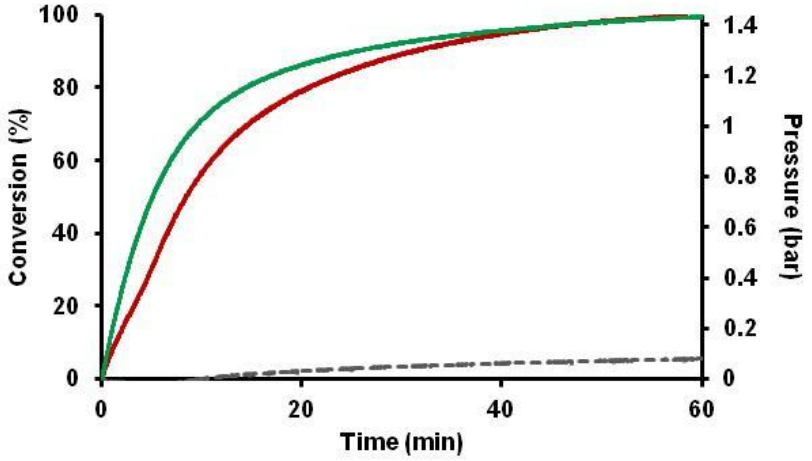

Figure S3. Reaction profiles (conversion/pressure *vs*. time) obtained for the hydrolytic dehydrogenation of AB without precatalyst (grey dashed line, pressure vs time), with [Ru(*p*-Cym)(**8**)Cl]Cl withouth irradiation (green line) and with [Ru(*p*-Cym)(**8**)Cl]Cl under continuous irradiation (red line). Incubation in 0.375 mL of distilled THF, reaction solvent 1.5 mL THF/H_2O = 1/3 (v/v), [cat] = $2.3 \cdot 10^{-3}$ M, [AB]/[cat] = 200

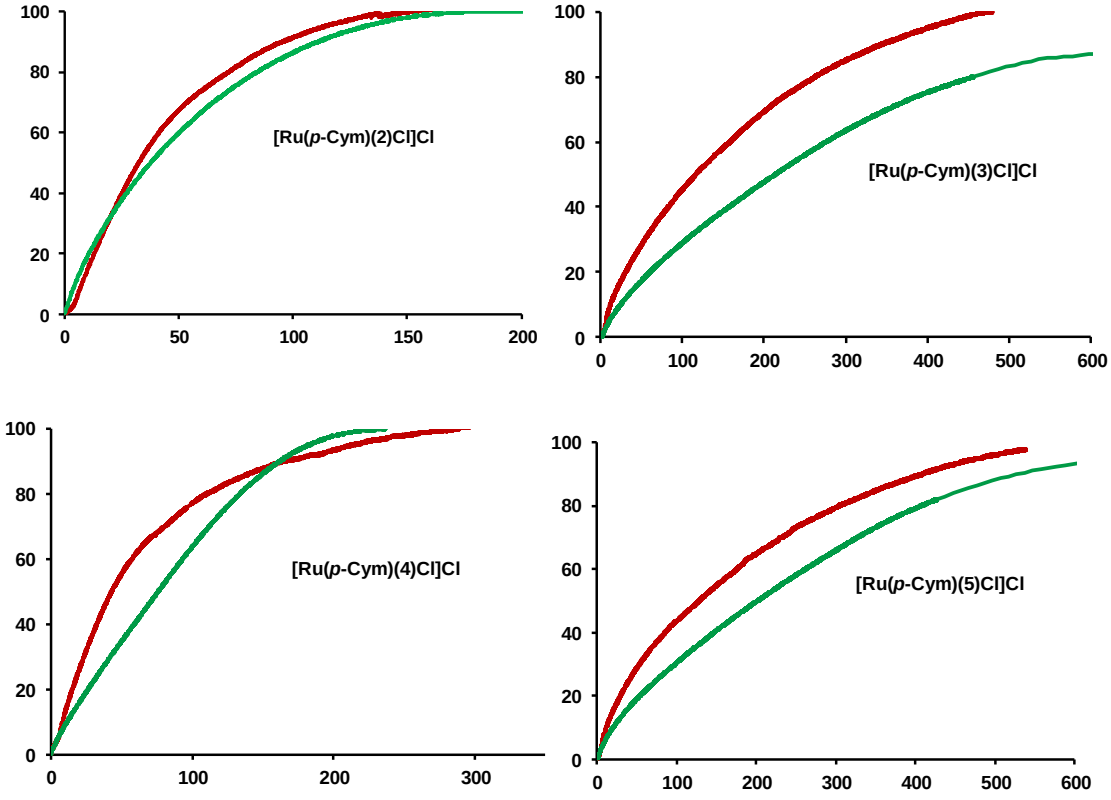

Figure S4. Reaction profiles (conversion *vs*. time) obtained for the hydrolytic dehydrogenation of AB with [Ru(*p*-Cym)(**L**)Cl]Cl (**L** = **2–5**) not irradiated (green line) and under continuous irradiation (red line). Incubation in 0.375 mL of distilled THF, reaction solvent 1.5 mL THF/H_2O = 1/3 (v/v), [cat] = $2.3 \cdot 10^{-3}$ M, [AB]/[cat] = 200.

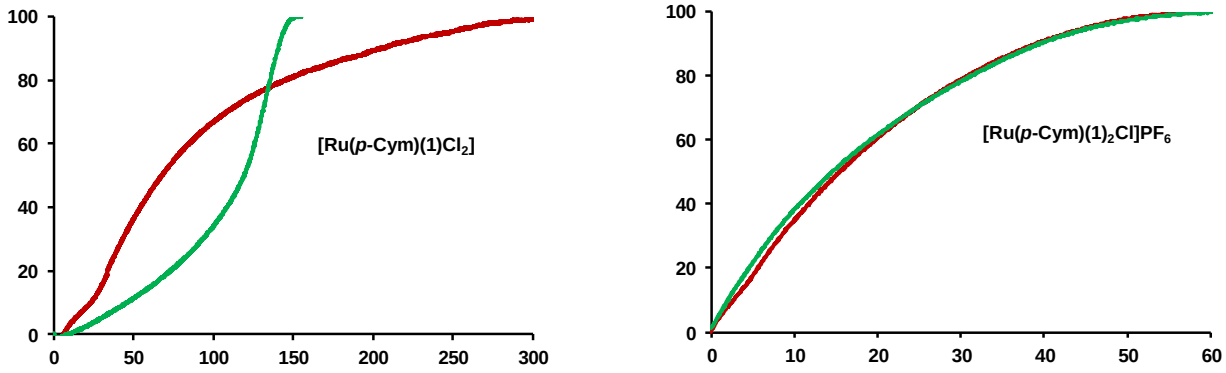

Figure S5. Reaction profiles (conversion *vs*. time) obtained for the hydrolytic dehydrogenation of AB with [Ru(*p*-Cym)(**1**)Cl_2] and [Ru(*p*-Cym)(**1**)$_2$Cl]PF_6 not irradiated (green line) and irradiated (red line). Incubation in 0.375 mL of distilled THF, reaction solvent 1.5 mL THF/H_2O = 1/3 (v/v), [cat] = $2.3 \cdot 10^{-3}$ M, [AB]/[cat] = 200.

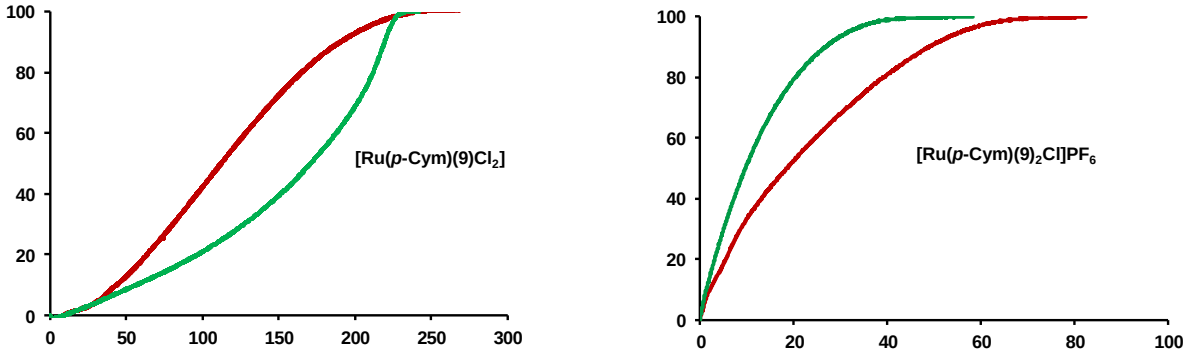

Figure S6. Reaction profiles (conversion *vs*. time) obtained for the hydrolytic dehydrogenation of AB with [Ru(*p*-Cym)(**9**)Cl_2] and [Ru(*p*-Cym)(**9**)$_2$Cl]PF_6 not irradiated (green line) and irradiated (red line). Incubation in 0.375 mL of distilled THF, reaction solvent 1.5 mL THF/H_2O = 1/3 (v/v), [cat] = $2.3 \cdot 10^{-3}$ M, [AB]/[cat] = 200.

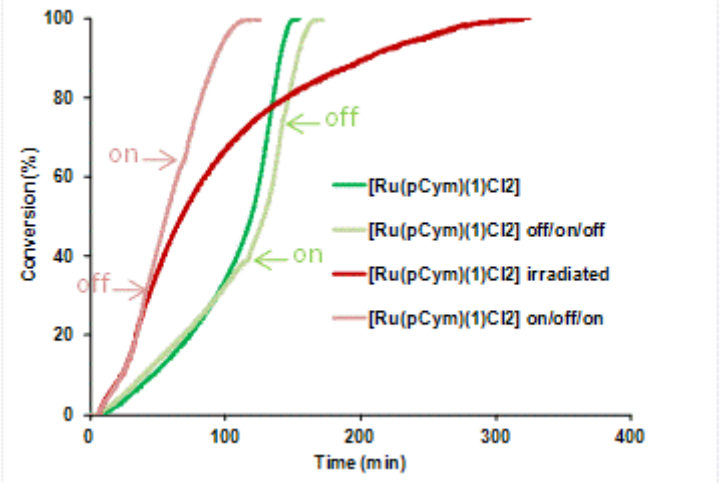

Figure S7. Reaction profiles (conversion *vs*. time) obtained for the hydrolytic dehydrogenation of AB with [Ru(*p*-Cym)(**1**)Cl_2]. Incubation in 0.375 mL of distilled THF, reaction solvent 1.5 mL THF/H_2O = 1/3 (v/v), [cat] = $2.3 \cdot 10^{-3}$ M, [AB]/[cat] = 200.

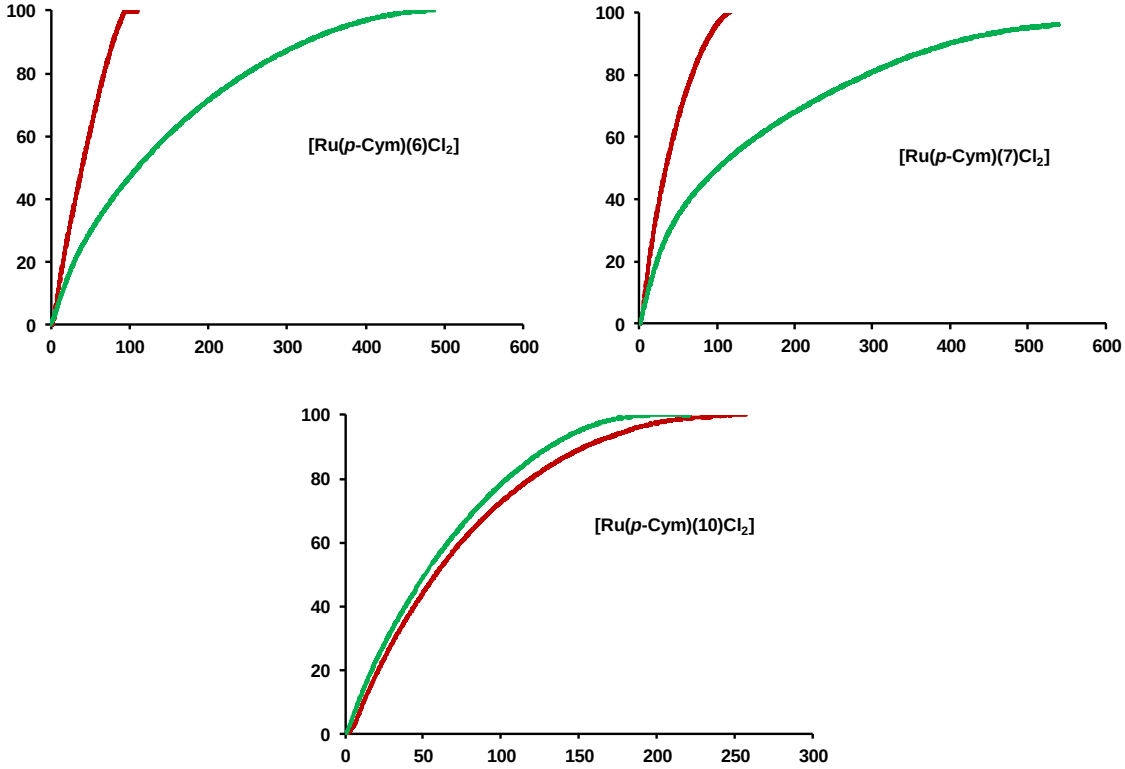

Figure S8. Reaction profiles (conversion *vs*. time) obtained for the hydrolytic dehydrogenation of AB with [Ru(*p*-Cym)(**L**)Cl_2] (**L** = **6, 7** and **10**) not irradiated (green line) and irradiated (red line). Incubation in 0.375 mL of distilled THF, reaction solvent 1.5 mL THF/H_2O = 1/3 (v/v), [cat] = $2.3 \cdot 10^{-3}$ M, [AB]/[cat] = 200.

Ligand 6, tris(*p*-azobenzene)phosphane. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

The starting 4-iodoazobenzene (1.5 g, 4.87 mmol) was azeotropically dried with toluene under a N_2 atmosphere and dissolved in 30 mL of freshly distilled THF. The solution was cooled to -80 °C, *n*-BuLi 1.6 M in hexanes (4.5 mL, 7.3 mmol) were added and it was stirred for 30 min. PCl_3 (142 µL, 1.63 mmol) were added, the reaction temperature was gradually raised up to room temperature and it was stirred overnight. The solvent was evaporated, the residue was washed with EtOH and the product was obtained as an orange solid. Yield 10%.

Elemental Analysis: calculated for ($C_{36}H_{27}N_6P$·EtOH): C, 73.53; H, 5.36; N, 13.54. Found: C, 73.88; H, 4.98; N, 13.85.

Exact Mass: ESI-MS $[C_{36}H_{27}N_6P + H]^+$: calculated: m/z= 575.2113, found: m/z= 575.2123.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.88–7.79 (m, 12H), 7.49–7.38 (m, 15H).

^{13}C APT NMR (75 MHz, $CDCl_3$): δ 152.51 (s, $3C_{quat}$), 152.22 (s, $3C_{quat}$), 139.42 (d, J = 12.7 Hz, $3C_{quat}$), 134.09 (d, J = 20.2 Hz, 6CH), 130.86 (s, 3CH), 128.68 (s, 6CH), 122.54 (s, 6CH), 122.50 (d, J = 6.0 Hz, 6CH).

^{31}P NMR (202.5 MHz, $CDCl_3$): δ -3.69 (s, 1P).

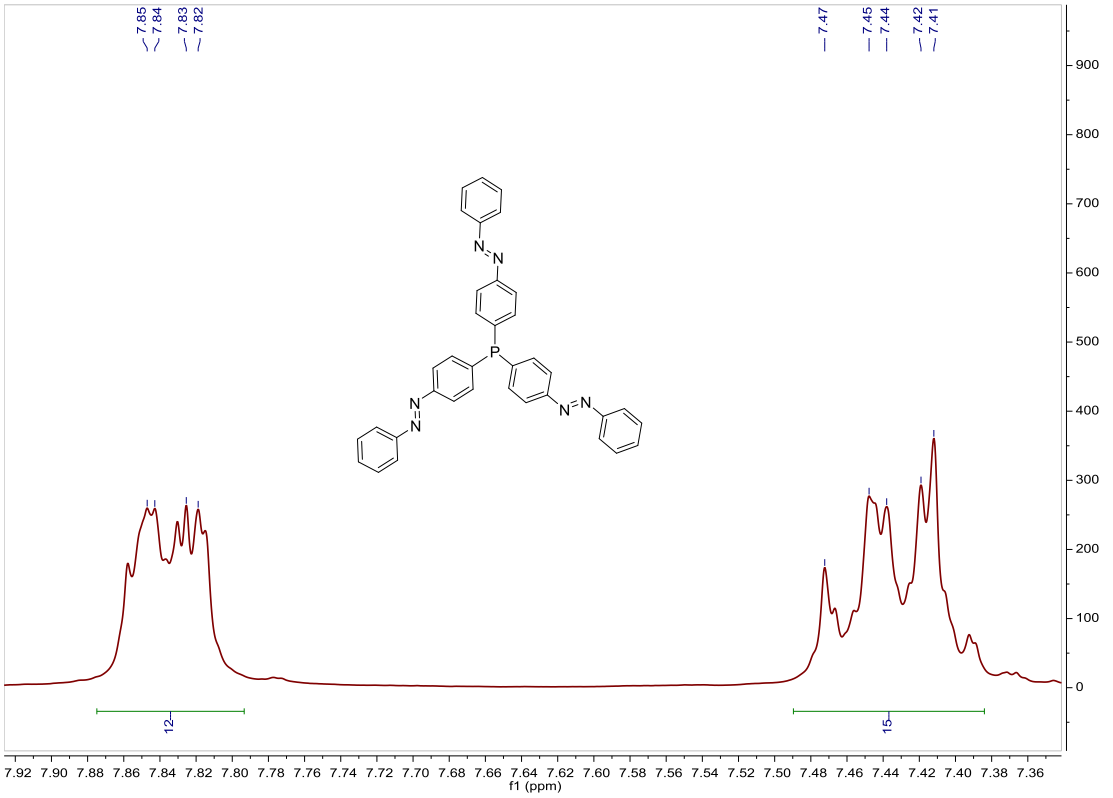

Fig. S9. ^{1}H NMR spectrum of tris(*p*-azobenzene)phosphane **Ligand 6** in $CDCl_3$, 300 MHz.

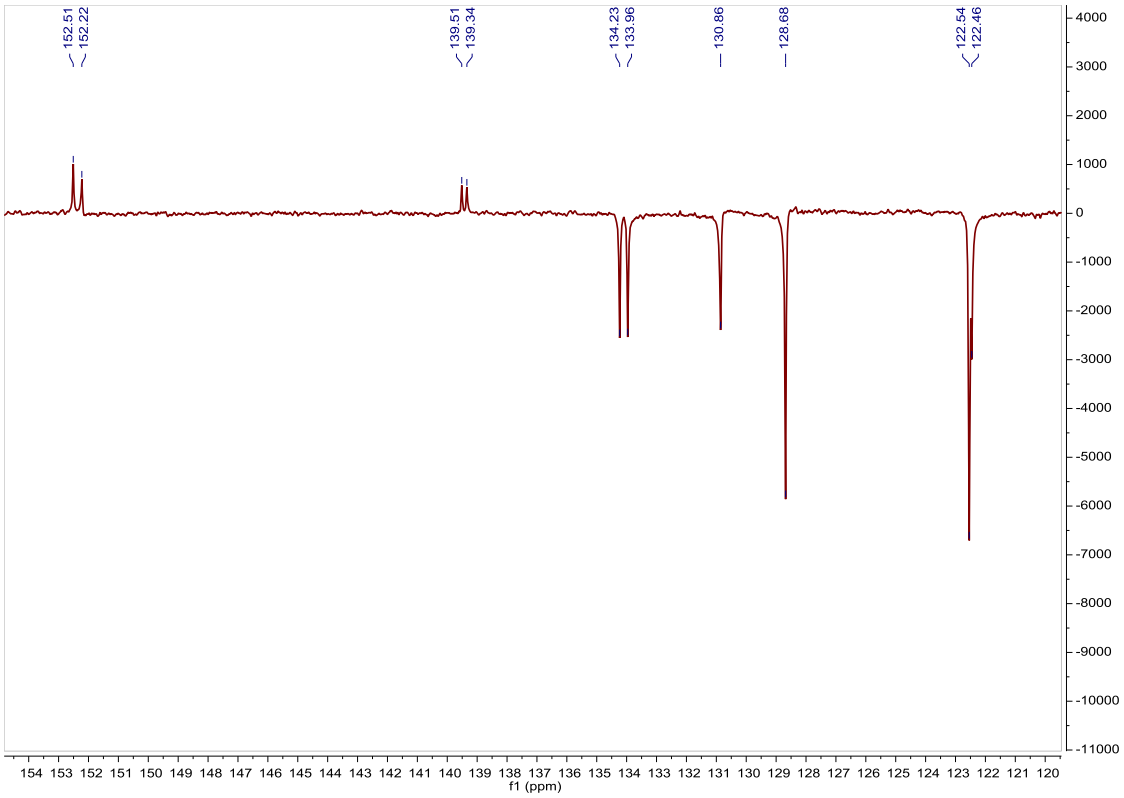

Fig. S10. ^{13}C APT NMR spectrum of tris(*p*-azobenzene)phosphane **Ligand 6** in $CDCl_3$, 75 MHz.

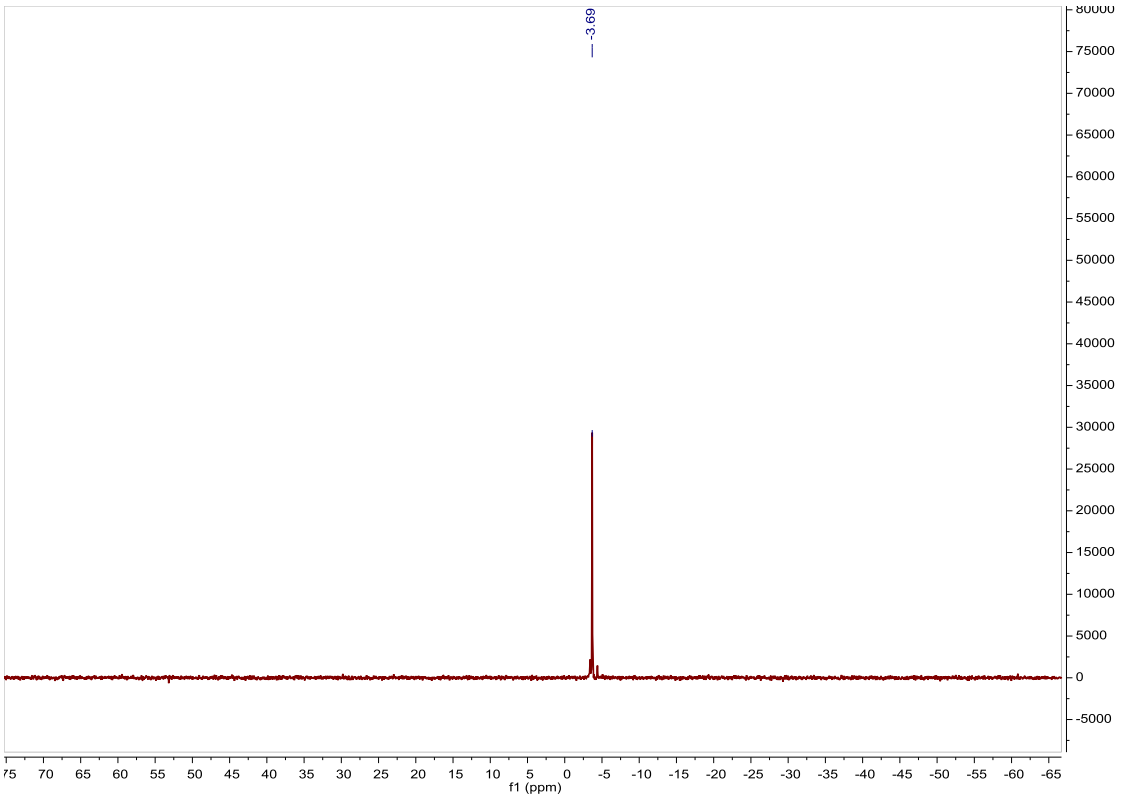

Fig. S11. ^{31}P NMR spectrum of tris(*p*-azobenzene)phosphane **Ligand 6** in $CDCl_3$, 202.5 MHz.

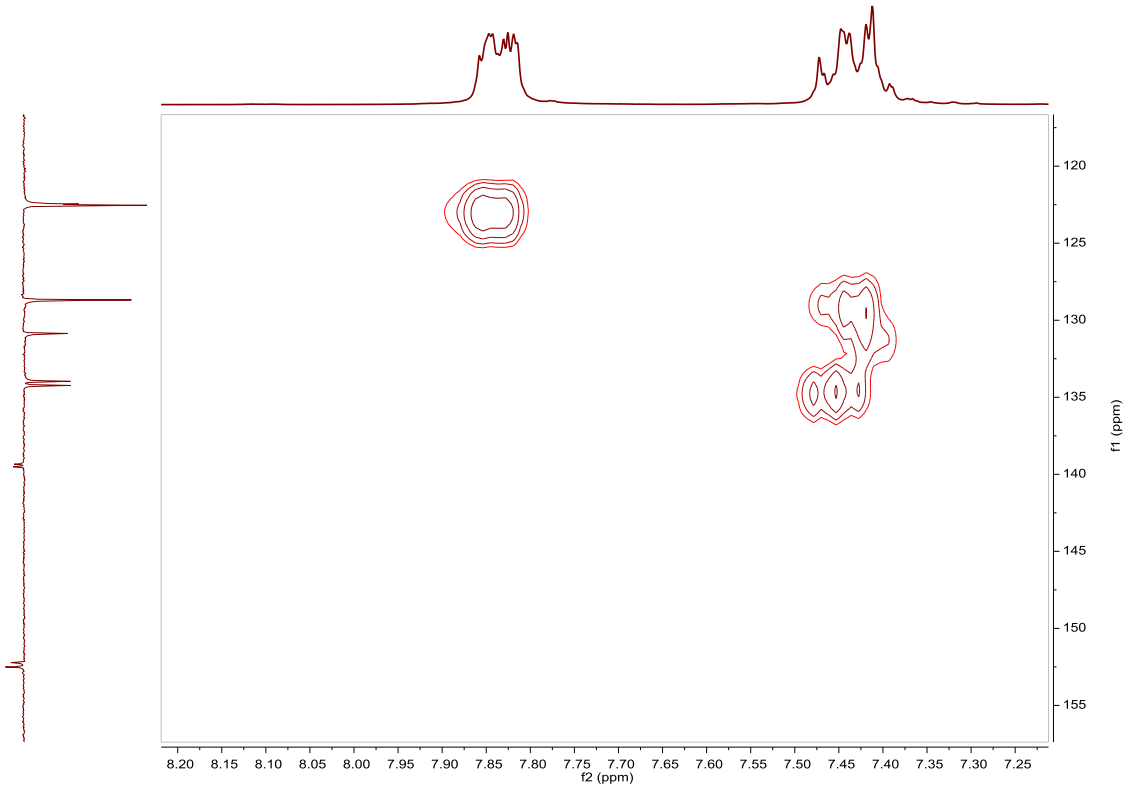

Fig. S12. HSQC NMR spectrum of tris(*p*-azobenzene)phosphane **Ligand 6** in $CDCl_3$.

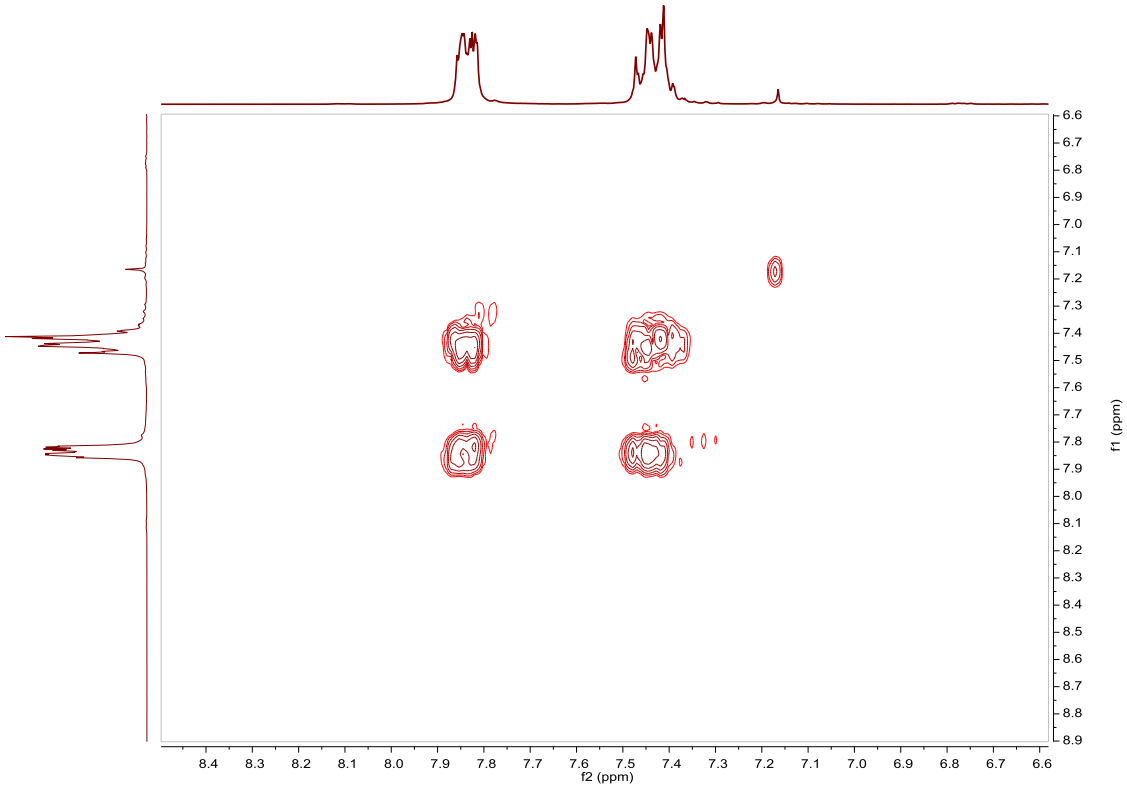

Fig. S13. COSY NMR spectrum of tris(*p*-azobenzene)phosphane **Ligand 6** in $CDCl_3$.

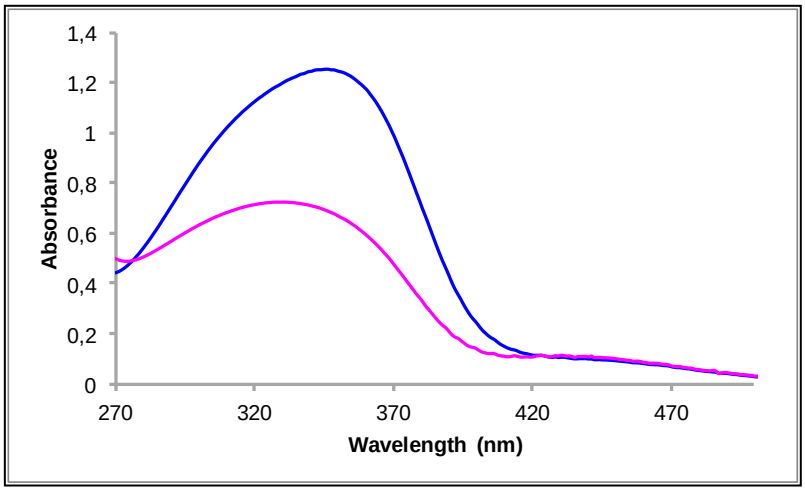

Fig. S14. UV/Vis spectra of tris(*p*-azobenzene)phosphane **Ligand 6** in ACN. Before (blue line) and after (pink line) irradiation at 354nm, $2.72 \cdot 10^{-5}$M.

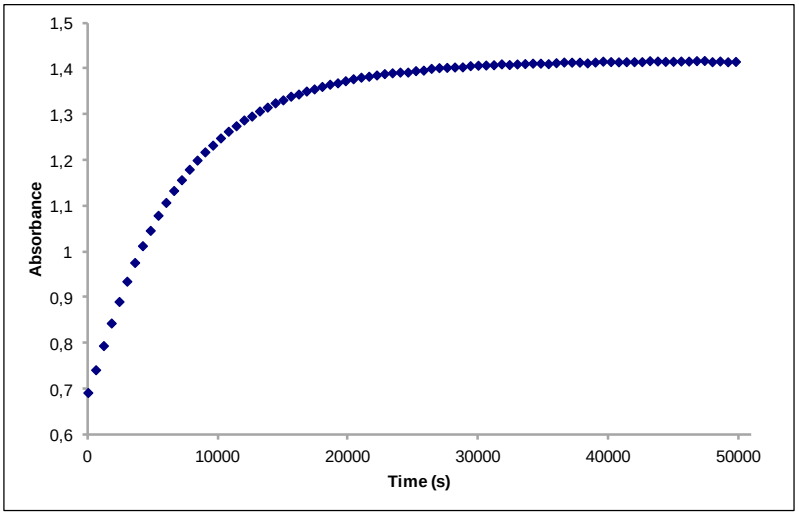

Fig. S15. Cis to trans thermal isomerization kinetics of tris(*p*-azobenzene)phosphane **Ligand 6**. Absorption change of the band 345nm at 338 K in ACN after irradiation at 354 nm. ($2.72 \cdot 10^{-5}$M).

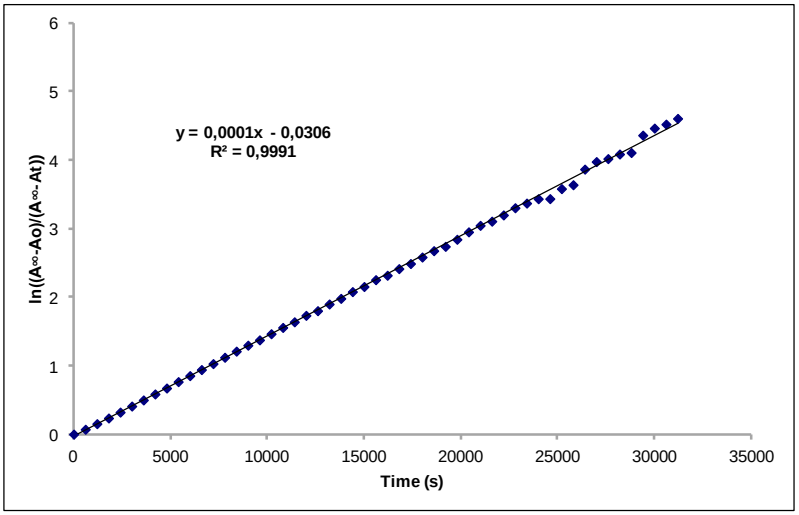

Fig. S16. Cis to trans thermal isomerization kinetics of tris(*p*-azobenzene)phosphane **Ligand 6**. First-order plot. k (s^{-1}) = $1.0 \cdot 10^{-4}$. Half-life (min) = 115.

Compound [Ru(p-Cym)(1)(Cl)$_2$]. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

Under a N_2 atmosphere, Ru_2(p-Cym)$_2Cl_4$ (0.2 g, 0.32 mmol) and (4-phenylazopyridine) (0.117 g, 0.64 mmol) were dissolved in 20 mL of acetone. The reaction mixture was refluxed for 15 h. It was cooled to room temperature, the solvent was evaporated and the product was obtained as an orange solid. Yield 71%.

Elemental Analysis: calculated for ($C_{21}H_{23}Cl_2N_3Ru$): C, 51.54; H, 4.74; N, 8.59. Found: C, 51.51; H, 4.71; N, 8.55.

Exact Mass: ESI-MS $[C_{21}H_{23}ClN_3Ru]^+$ (M-Cl): calculated: m/z= 454.0619, found: m/z= 454.0618.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.26 (d, J = 6.9 Hz, 2H, (azopy)), 8.06–7.96 (m, 2H, (15+19)), 7.75 (d, J = 6.7 Hz, 2H, (azopy)), 7.64–7.55 (m, 3H, (16+17+18)), 5.52 (d, J = 5.7 Hz, 2H, (8)), 5.30 (d, J = 5.8 Hz, 2H, (7)), 3.06 (sep, J = 6.9 Hz, 1H, (11)), 2.17 (s, 3H, (13)), 1.37 (d, J = 6.9 Hz, 6H, (12)).

^{13}C APT NMR (75 MHz, $CDCl_3$): δ 157.12 (C_{quat}, (azopy)), 155.93 (2CH, (azopy)), 151.76 (C_{quat}, (azopy)), 132.78 (CH, (17)), 128.92 (2CH, (16+18)), 123.35 (2CH, (15+19)), 116.50 (2CH, (azopy)), 103.26 (C_{quat}, (p-Cym)), 96.88 (C_{quat}, (p-Cym)), 82.58 (2CH, (8)), 81.88 (2CH, (7)), 30.24 (CH, (11)), 21.86 ($2CH_3$, (12)), 17.83 (CH_3, (13)).

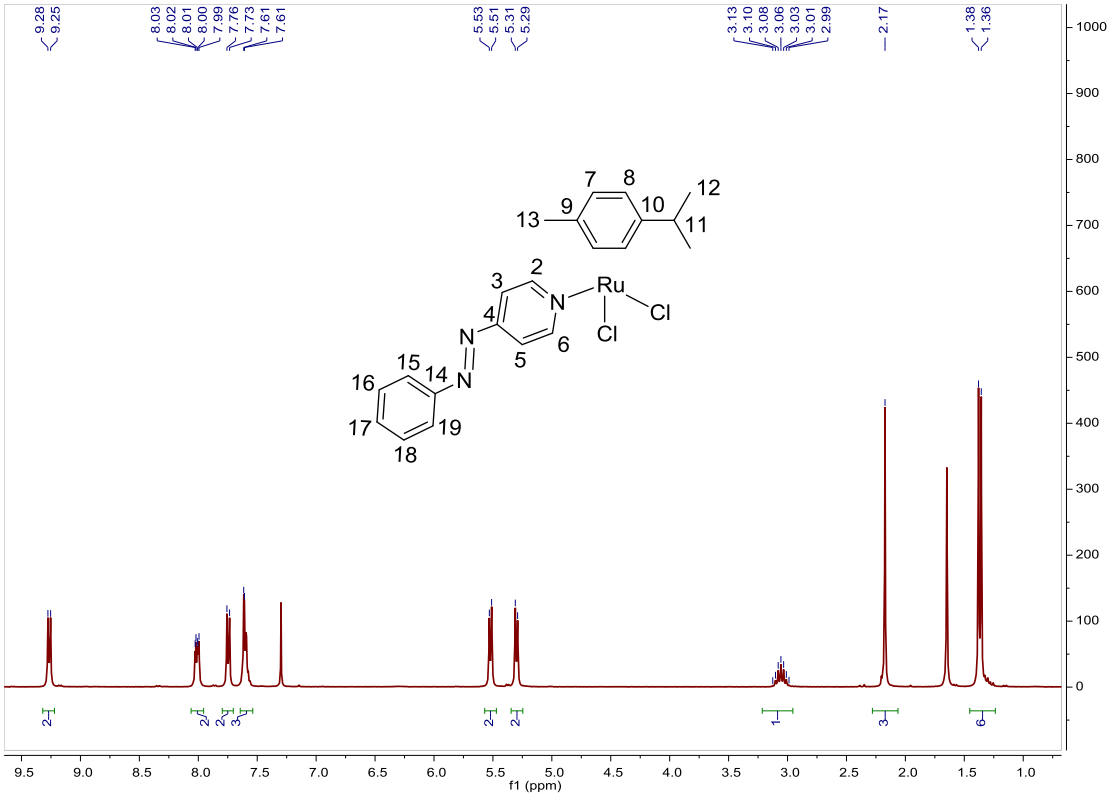

Fig. S17. ^{1}H NMR spectrum of **[Ru(p-Cym)(1)(Cl)$_2$]** in $CDCl_3$, 300 MHz.

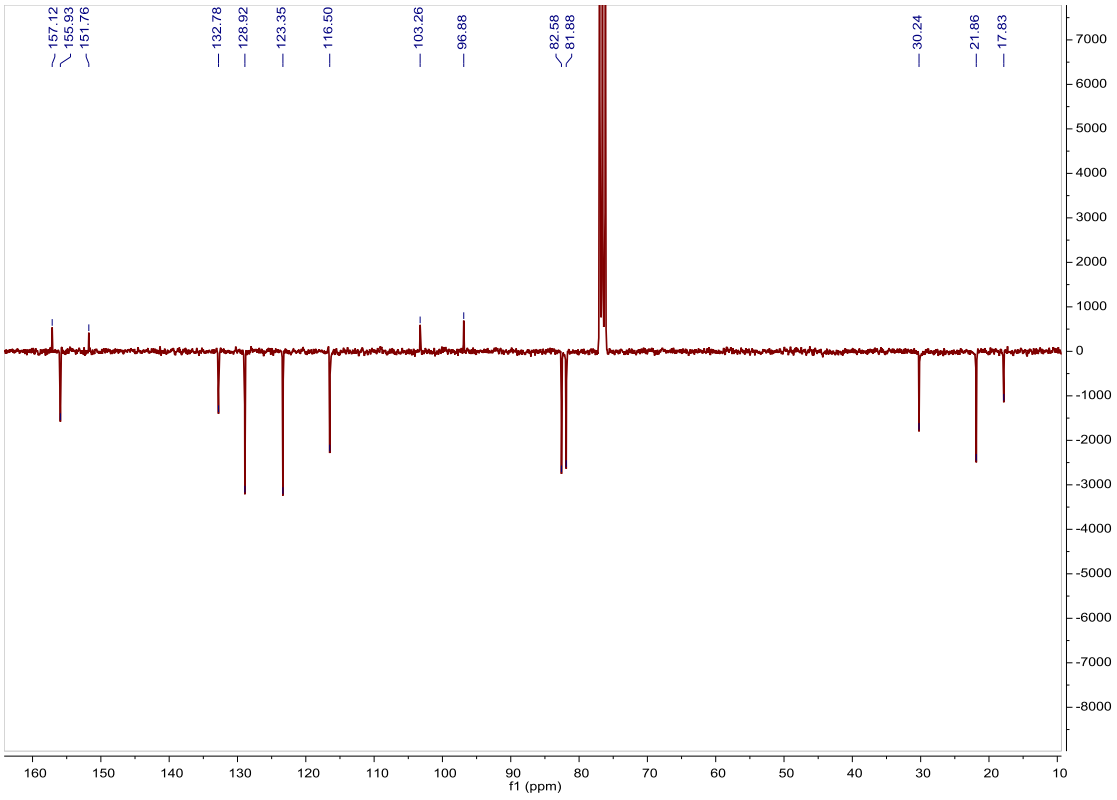

Fig. S18. ^{13}C APT NMR spectrum of **[Ru(p-Cym)(1)(Cl)$_2$]** in $CDCl_3$, 75 MHz.

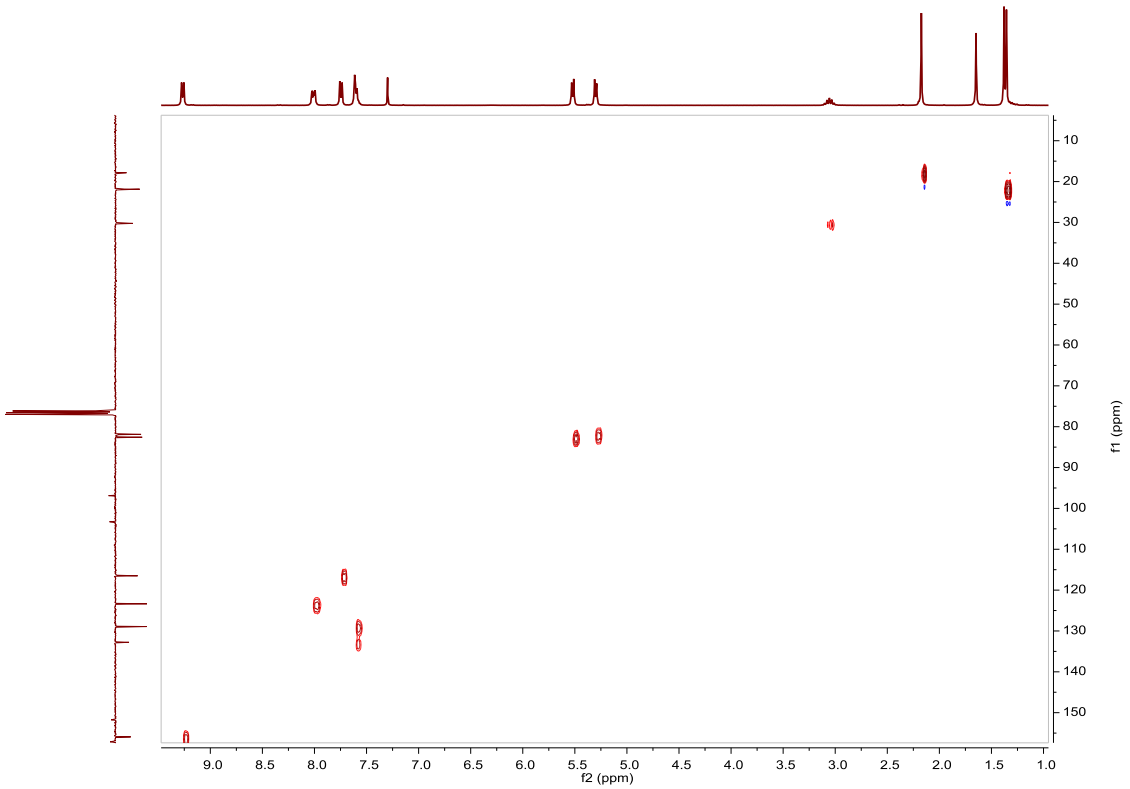

Fig. S19. HSQC NMR spectrum of **[Ru(p-Cym)(1)(Cl)$_2$]** in $CDCl_3$.

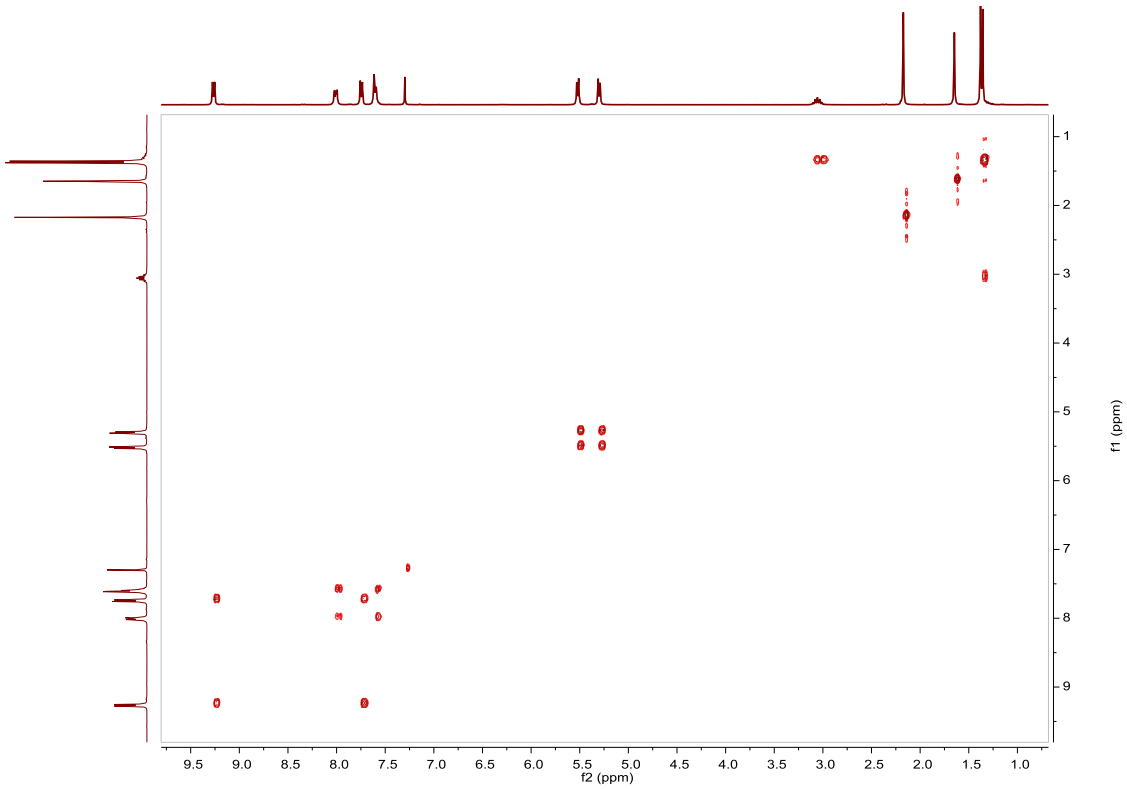

Fig. S20. COSY NMR spectrum of **[Ru(p-Cym)(1)(Cl)$_2$]** in $CDCl_3$.

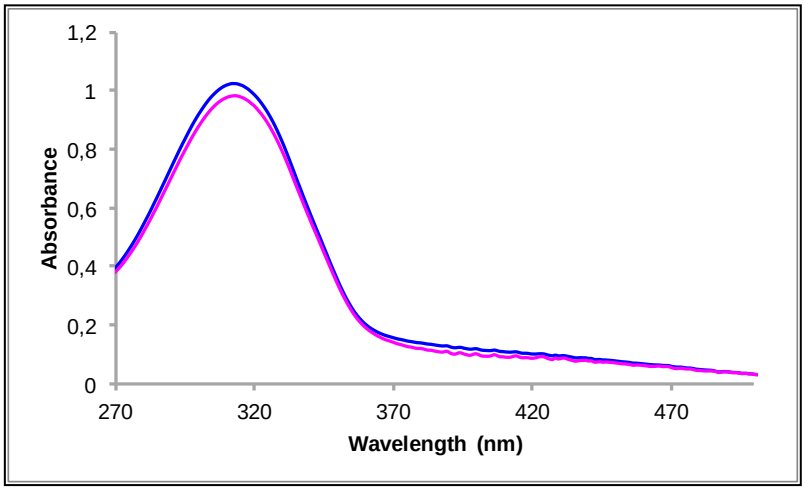

Fig. S21. UV/Vis spectra of **[Ru(p-Cym)(1)(Cl)$_2$]** in ACN. Before (blue line) and after (pink line) irradiation at 311nm, $5.50 \cdot 10^{-5}$M.

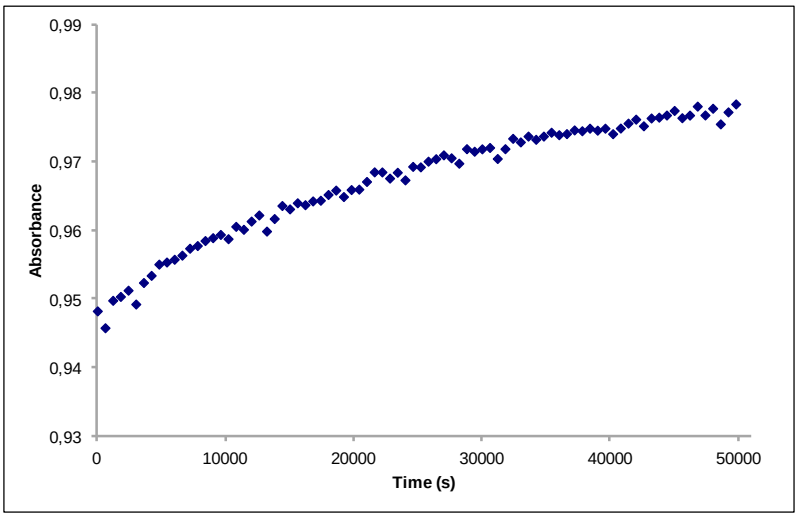

Fig. S22. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(1)(Cl)$_2$]**. Absorption change of the band 312nm at 338 K in ACN after irradiation at 311 nm. ($5.50 \cdot 10^{-5}$M).

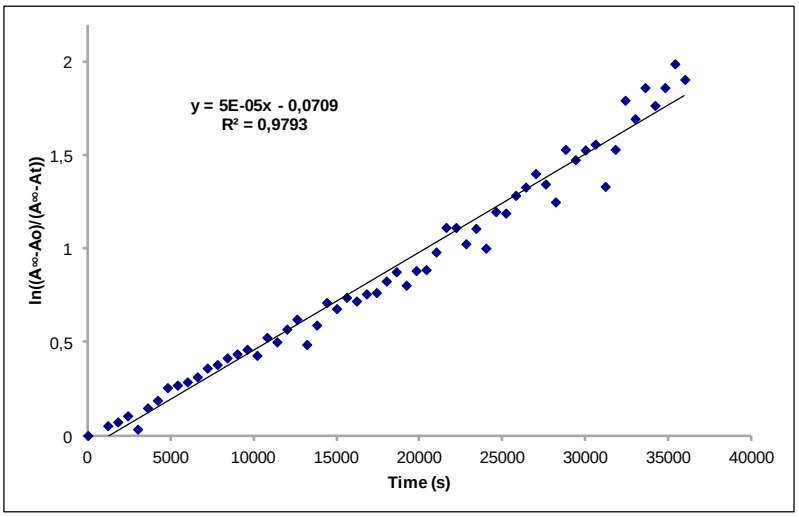

Fig. S23. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(1)(Cl)$_2$]**. First-order plot. k (s^{-1}) = $5.0 \cdot 10^{-5}$. Half-life (min) = 231.

Compound [Ru(p-Cym)(1)$_2$(Cl)]PF$_6$. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

Under a N_2 atmosphere, [Ru(p-Cym)(4-phenylazopyridine)(Cl_2)] (0.319 g, 0.65 mmol) and $AgPF_6$ (0.160 g, 0.63 mmol) were dissolved in 20 mL of acetone and 20 mL of methanol. The mixture was stirred for 1 h, AgCl was removed by filtration and 4-phenylazopyridine (0.119 g, 0.65 mmol) were added. The reaction mixture was stirred for 15 h and the solvent was evaporated. The product was obtained as a red solid after precipitation with acetone/ether. Yield 55%.

Elemental Analysis: calculated for ($C_{32}H_{32}ClN_6RuPF_6$): C, 49.14; H, 4.12; N, 10.75. Found: C, 49.23; H, 4.01; N, 10.59.

Exact Mass: ESI-MS $[C_{21}H_{23}ClN_3Ru]^+$ (M-L-PF_6): calculated: m/z= 454.0619, found: m/z= 454.0618.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.27 (d, J = 6.9 Hz, 4H, (azopy)), 7.97 (dd, J = 1.6 Hz, J = 7.5 Hz, 4H, (15+19)), 7.87 (d, J = 6.9 Hz, 4H, (azopy)), 7.57 (brd, J = 7.3 Hz, 6H, (16+17+18)), 6.03 (d, J = 6.1 Hz, 2H, (8)), 5.78 (d, J = 6.1 Hz, 2H, (7)), 2.67 (sep, J = 6.9 Hz, 1H, (11)), 1.86 (s, 3H, (13)), 1.23 (d, J = 6.9 Hz, 6H, (12)).

^{13}C APT NMR (75 MHz, $CDCl_3$): δ 157.66 (2C_{quat}, (azopy)), 155.29 (4CH, (azopy)), 151.74 (2C_{quat}, (azopy)), 133.09 (2CH, (17)), 128.94 (4CH, (16)), 123.47 (4CH, (15)), 118.22 (4CH, (azopy)), 102.59 (C_{quat}, (p-Cym)), 101.80 (C_{quat}, (p-Cym)), 88.49 (2CH, (8)), 81.77 (2CH, (7)), 30.45 (CH, (11)), 21.84 (2CH_3, (12)), 17.39 (CH_3, (13)).

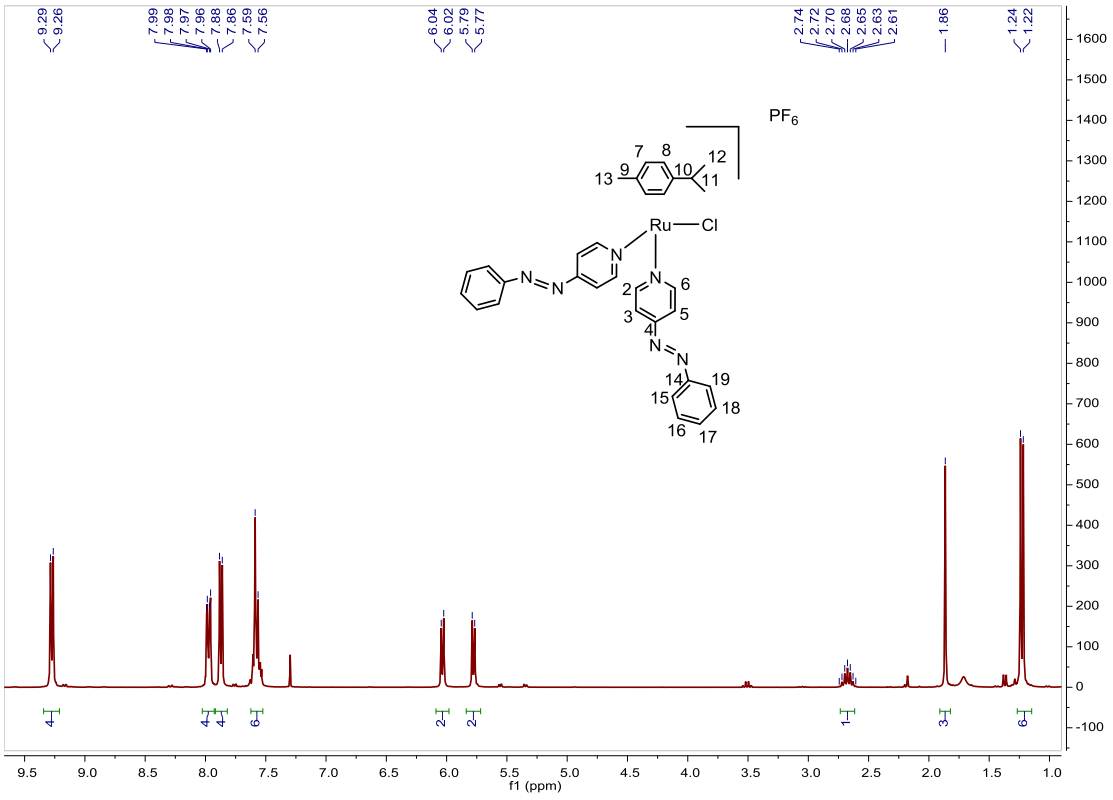

Fig. S24. ^{1}H NMR spectrum of **[Ru(p-Cym)(1)$_2$(Cl)]PF$_6$** in $CDCl_3$, 300 MHz.

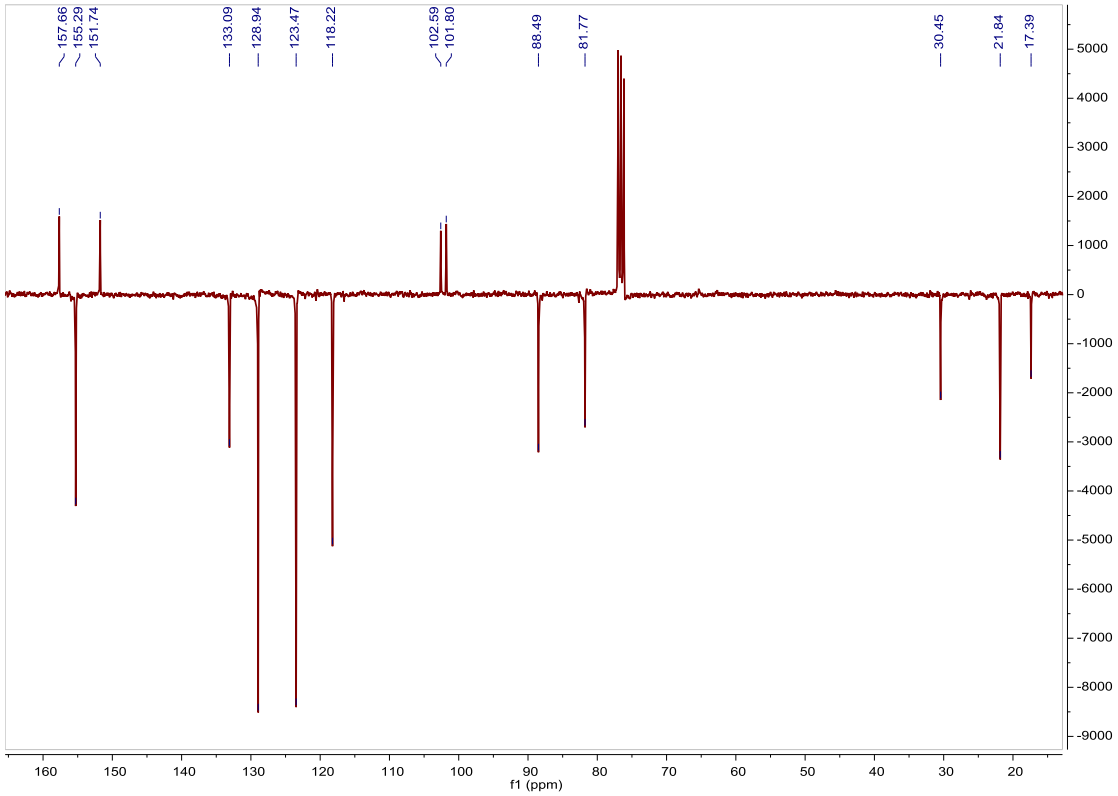

Fig. S25. ^{13}C APT NMR spectrum of **[Ru(p-Cym)(1)$_2$(Cl)]PF$_6$** in $CDCl_3$, 75 MHz.

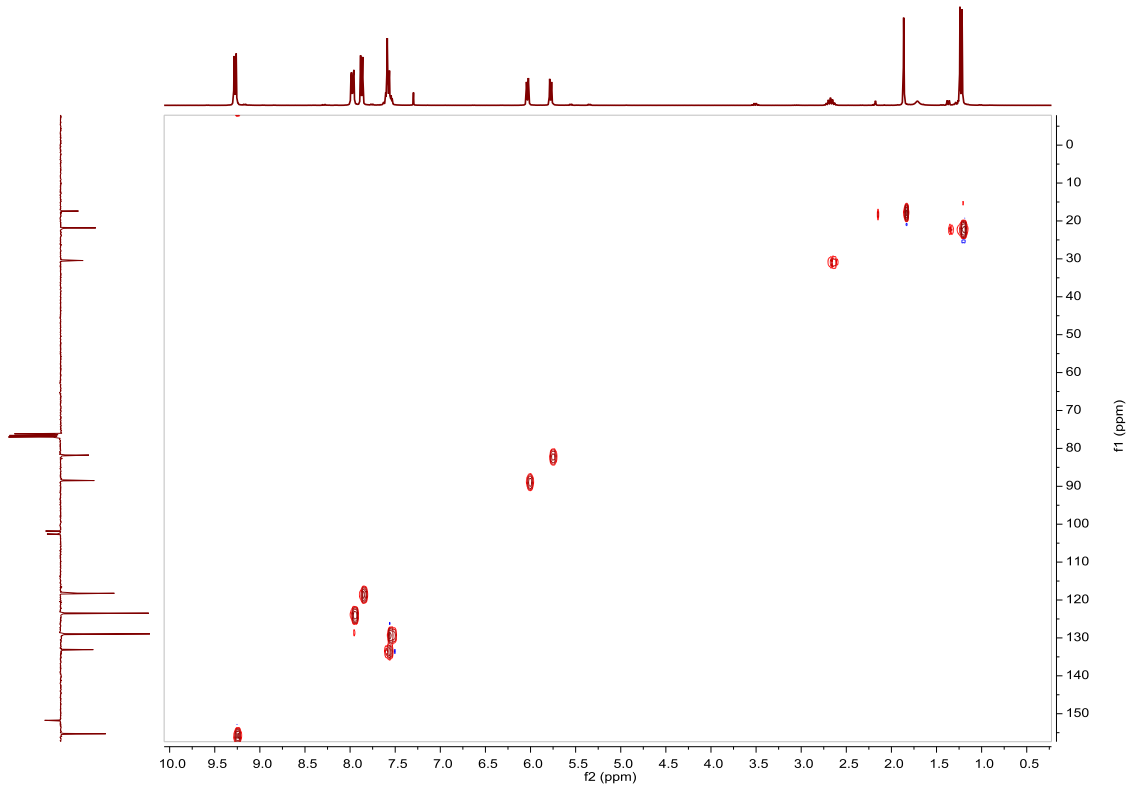

Fig. S26. HSQC NMR spectrum of **[Ru(p-Cym)(1)$_2$(Cl)]PF$_6$** in $CDCl_3$.

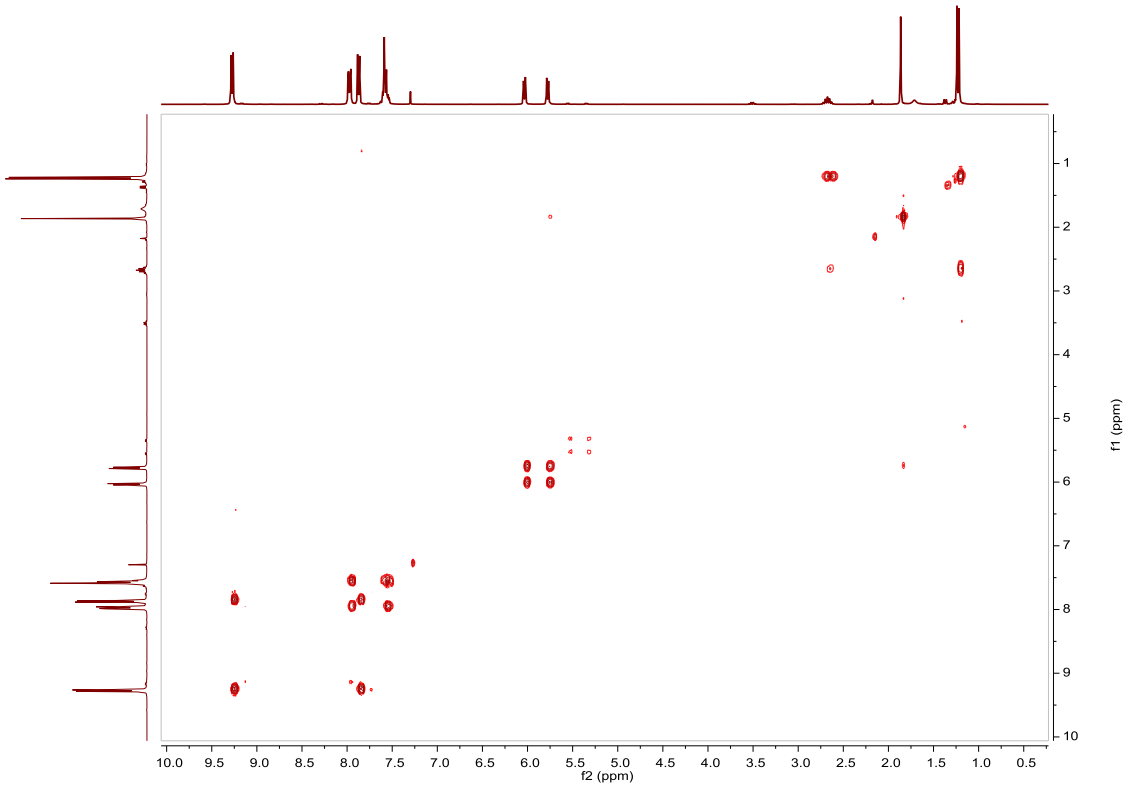

Fig. S27. COSY NMR spectrum of **[Ru(p-Cym)(1)$_2$(Cl)]PF$_6$** in $CDCl_3$.

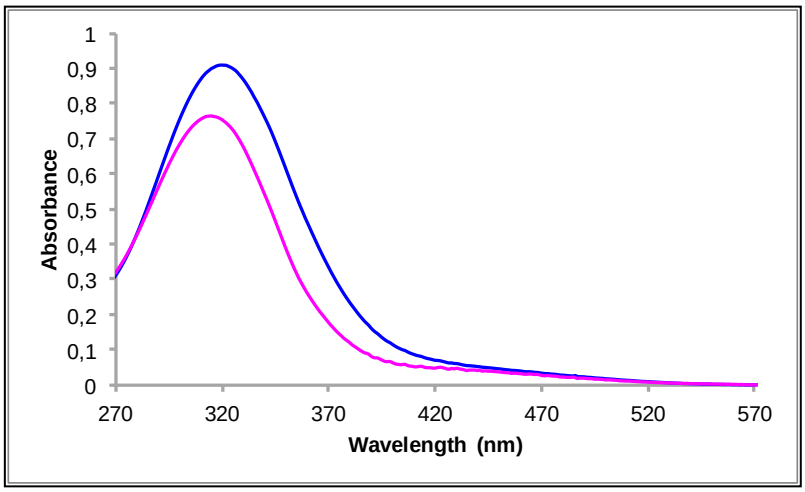

Fig. S28. UV/Vis spectra of **[Ru(p-Cym)(1)$_2$(Cl)]PF$_6$** in ACN. Before (blue line) and after (pink line) irradiation at 347nm, $2.50 \cdot 10^{-5}$M.

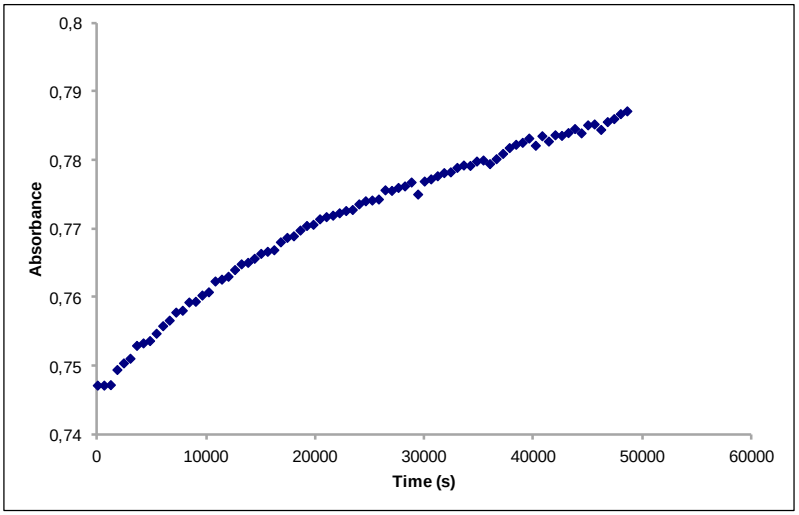

Fig. S29. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(1)$_2$(Cl)]PF$_6$**. Absorption change of the band 320nm at 338 K in ACN after irradiation at 347 nm. (2.50·10^{-5}M).

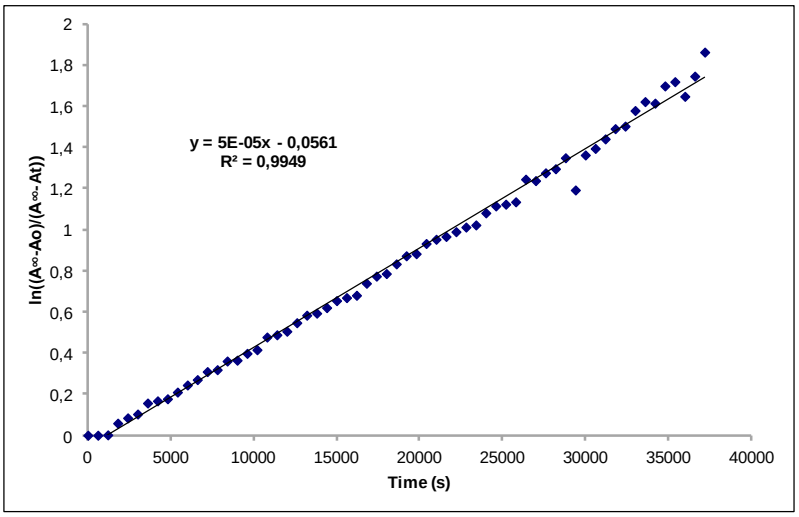

Fig. S30. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(1)$_2$(Cl)]PF$_6$**. First-order plot. k (s^{-1}) = 5.0·10^{-5}. Half-life (min) = 231.

Compound [Ru(p-Cym)(2)(Cl)]Cl. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

Under a N_2 atmosphere, $Ru_2(p\text{-}Cym)_2Cl_4$ (0.1 g, 0.16 mmol) and 2,2'-bis(4-phenylazopyridine) (0.119 g, 0.326 mmol) were dissolved in 10 mL of acetone. The reaction mixture was refluxed for 15 h. It was cooled to room temperature and the solid was filtered. The desired compound was obtained after precipitated with CH_2Cl_2/Et_2O as a dark red solid. Yield 73%.

Elemental Analysis: calculated for ($C_{32}H_{30}Cl_2N_6Ru{\cdot}CH_2Cl_2$): C, 52.46; H, 4.27; N, 11.12. Found: C, 52.33; H, 4.30; N, 11.09.

Exact Mass: ESI-MS $[C_{32}H_{30}ClN_6Ru]^+$: calculated: m/z= 635.1264, found: m/z= 635.1282.

^{1}H NMR (300 MHz, MeOD-*d*$_4$): δ 9.69 (d, J = 6.1 Hz, 2H, (6)), 8.98 (s, 2H, (3)), 8.19–8.04 (m, 6H, (5+15)), 7.77–7.61 (m, 6H, (16+17)), 6.24 (d, J = 6.2 Hz, 2H, (8)), 6.00 (d, J = 6.2 Hz, 2H, (7)), 2.75 (sep, J = 6.8 Hz, 1H, (11)), 2.34 (s, 3H, (13)), 1.13 (d, J = 6.9 Hz, 6H, (12)).

^{13}C APT NMR (75 MHz, MeOD-*d*$_4$): δ 160.37 ($2C_{quat}$, (bipy)), 158.42 (2CH, (6)), 157.91 ($2C_{quat}$, (bipy)), 153.73 ($2C_{quat}$, (bipy)), 135.13 (2CH, (17)), 130.76 (4CH, (16)), 125.16 (4CH, (15)), 120.49 (2CH, (5)), 118.74 (2CH, (3)), 107.02 (C_{quat}, (p-Cym)), 106.04(C_{quat}, (p-Cym)), 88.47 (2CH, (8)), 86.13 (2CH, (7)), 32.34 (CH, (11)), 22.38 ($2CH_3$, (12)), 19.02 (CH_3, (13)).

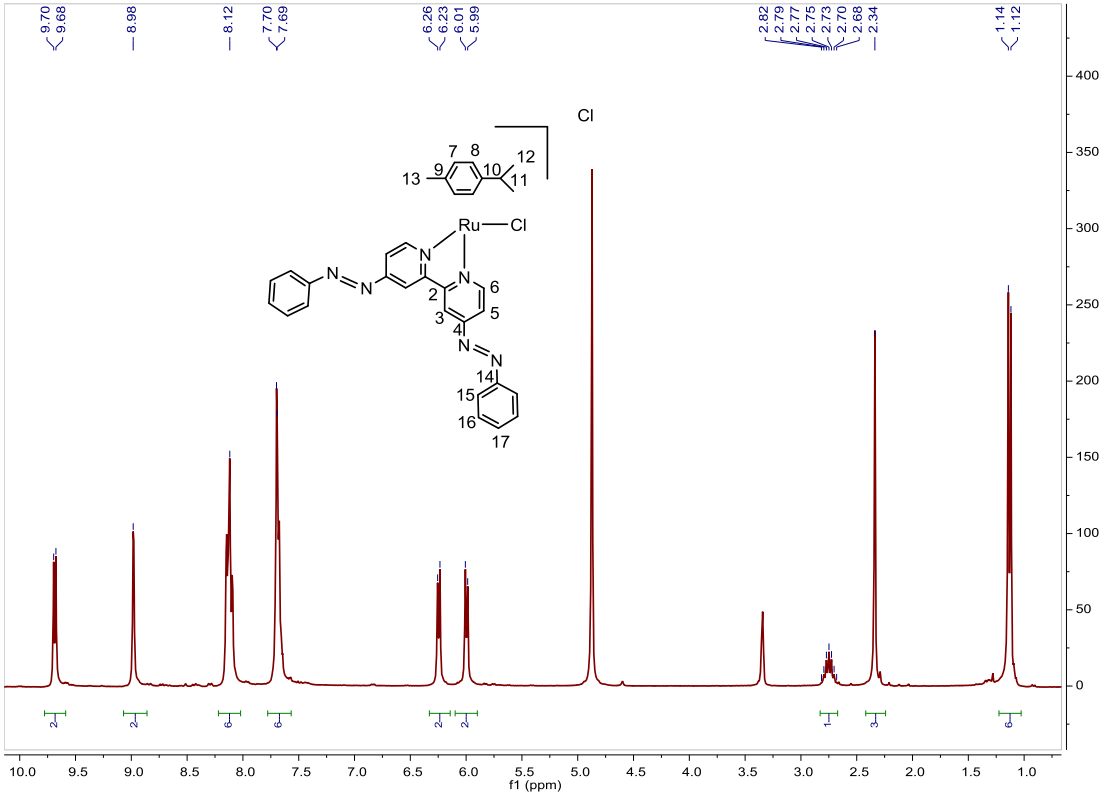

Fig. S31. ^{1}H NMR spectrum of **[Ru(p-Cym)(2)(Cl)]Cl** in MeOD-*d*$_4$, 300 MHz.

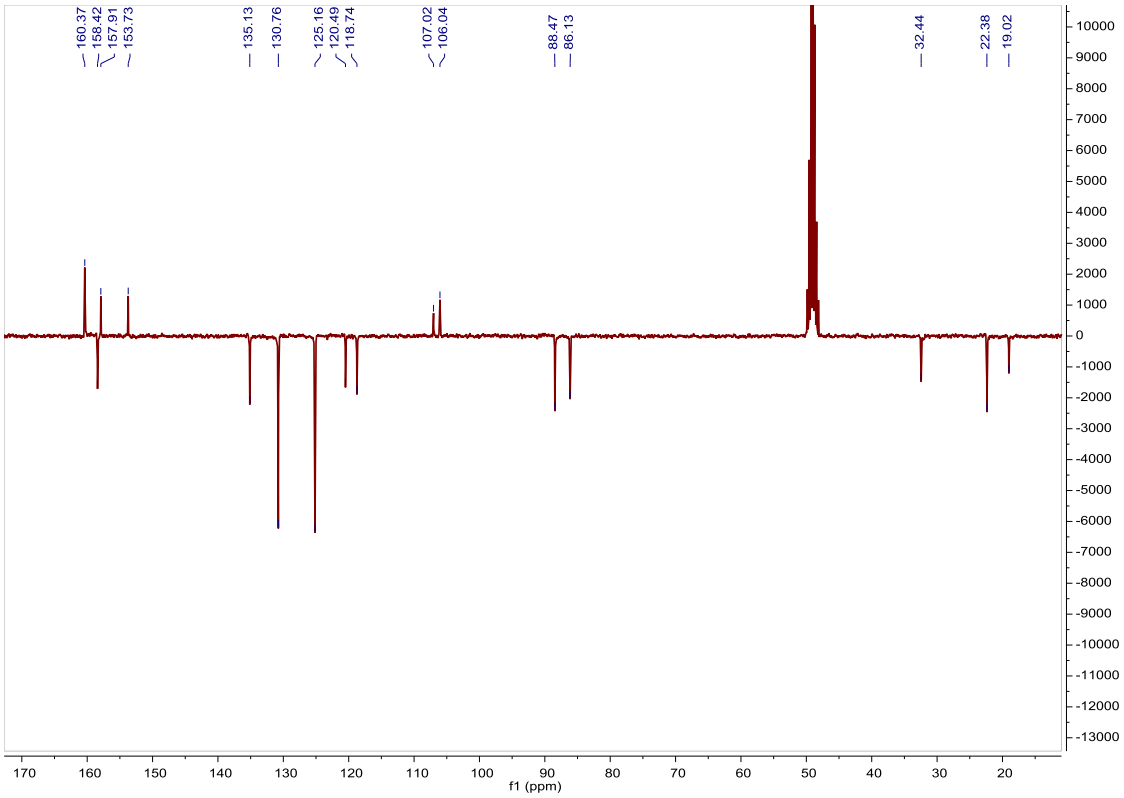

Fig. S32. ^{13}C APT NMR spectrum of **[Ru(p-Cym)(2)(Cl)]Cl** in MeOD-d_4, 75 MHz.

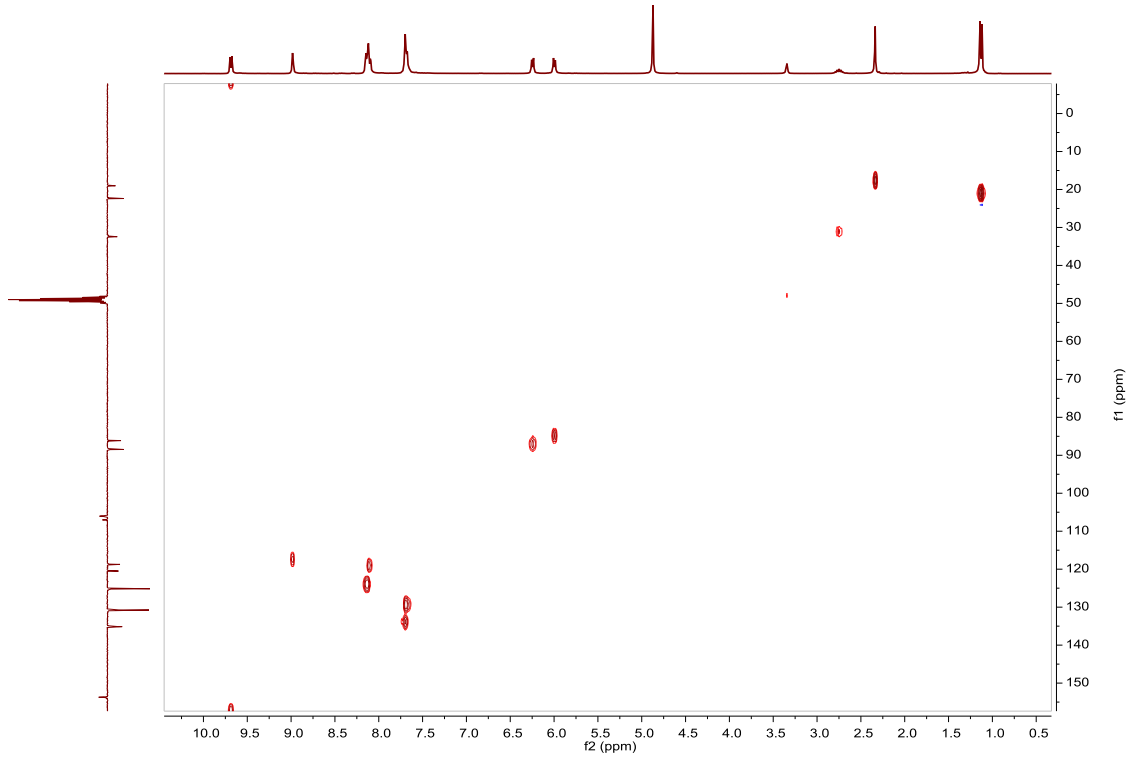

Fig. S33. HSQC NMR spectrum of **[Ru(p-Cym)(2)(Cl)]Cl** in MeOD-d_4.

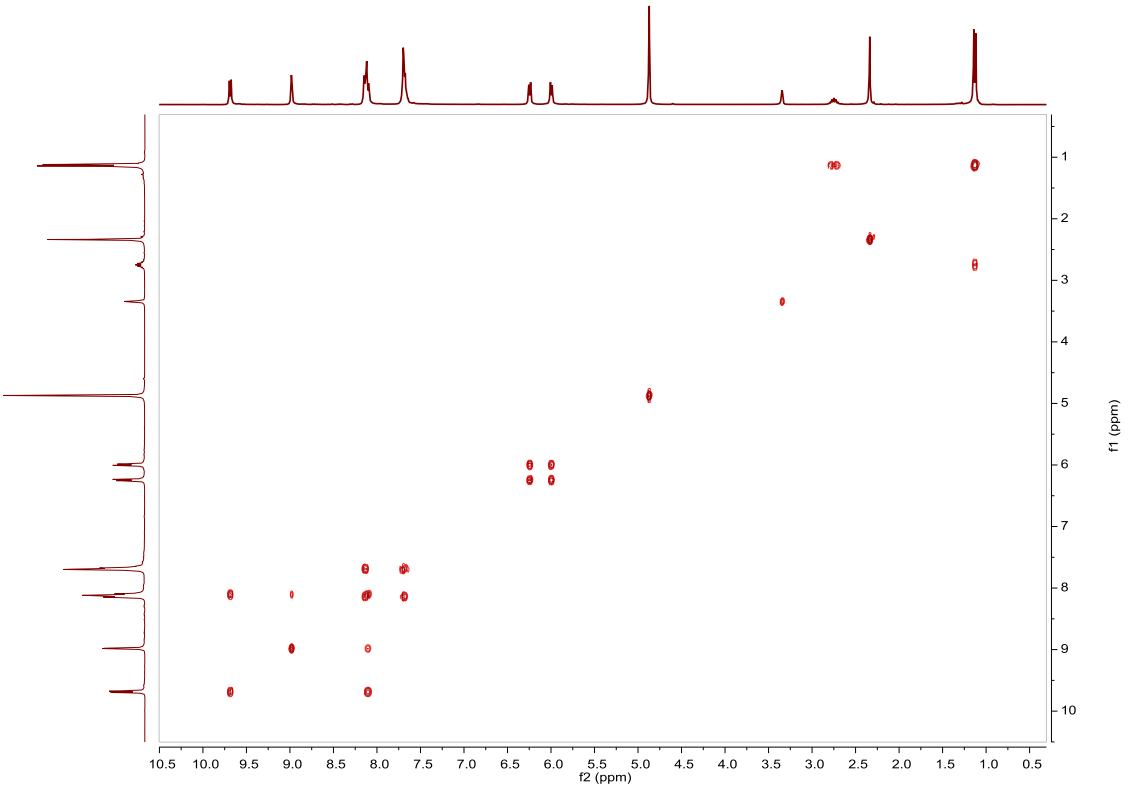

Fig. S34. COSY NMR spectrum of **[Ru(p-Cym)(2)(Cl)]Cl** in MeOD-d_4.

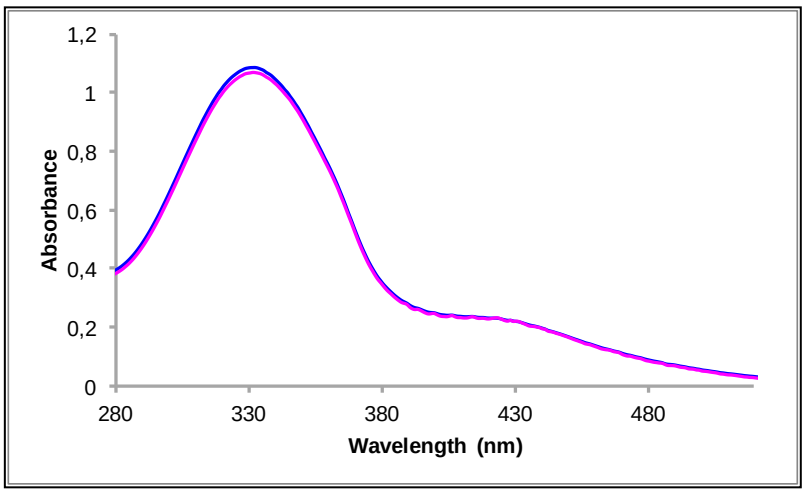

Fig. S35. UV/Vis spectra of **[Ru(p-Cym)(2)(Cl)]Cl** in CH_3CN. Before (blue line) and after (pink line) irradiation at 316nm, $2.62 \cdot 10^{-5}$ M.

Cis to trans thermal isomerization kinetics. Due to the small degree of photoisomerization, it has been not possible to calculate k.

Compound [Ru(p-Cym)(3)(Cl)]Cl. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

Under a N_2 atmosphere, $Ru_2(p\text{-}Cym)_2Cl_4$ (0.100 g, 0.163 mmol) and 4,4'-bis(*p*-azobenzene)-2,2'-bipyridine (0.168 g, 0.326 mmol) were dissolved in 10 mL of acetone. The reaction mixture was refluxed for 15 h. It was cooled to room temperature and the dark red solid was filtered. Yield 70%.

Elemental Analysis: calculated for ($C_{44}H_{38}Cl_2N_6Ru$): C, 64.23; H, 4.66; N, 10.21. Found: C, 63.79; H, 4.70; N, 10.13.

Exact Mass: ESI-MS $[C_{44}H_{38}ClN_6Ru]^+$: calculated: m/z= 787.1890, found: m/z= 787.1917.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.88 (brd, J = 5.5 Hz, 2H, (bipy)), 8.62 (s, 2H, (bipy)), 8.00 (m, 10H, (bipy)), 7.91 (brd, J = 7.9 Hz, 4H, (bipy)), 7.58–7.45 (m, 6H, (bipy)), 6.29 (d, J = 5.6 Hz, 2H, (8)), 6.16 (d, J = 5.4 Hz, 2H, (7)), 2.72 (sep, J = 6.8 Hz, 1H, (11)), 2.28 (s, 3H, (13)), 1.06 (d, J = 6.8 Hz, 6H, (12)).

^{13}C APT NMR (75 MHz, $CDCl_3$): δ 156.48 (2CH, (bipy)), 154.32 ($2C_{quat}$, (bipy)), 153.08 ($2C_{quat}$, (bipy)), 151.98 ($2C_{quat}$, (bipy)), 149.70 ($2C_{quat}$, (bipy)), 136.44 ($2C_{quat}$, (bipy)), 131.20(2CH, (bipy)), 128.70 (4CH, (bipy)), 128.11 (4CH, (bipy)), 125.02 (2CH, (bipy)), 123.35 (4CH, (bipy)), 122.66 (4CH, (bipy)), 120.27 (2CH, (bipy)), 104.46 (C_{quat}, (p-Cym)), 103.47 (C_{quat}, (p-Cym)), 86.87 (2CH, (8)), 84.38 (2CH, (7)), 30.66 (CH, (11)), 21.79 ($2CH_3$, (12)) 18.59 (CH_3, (13)).

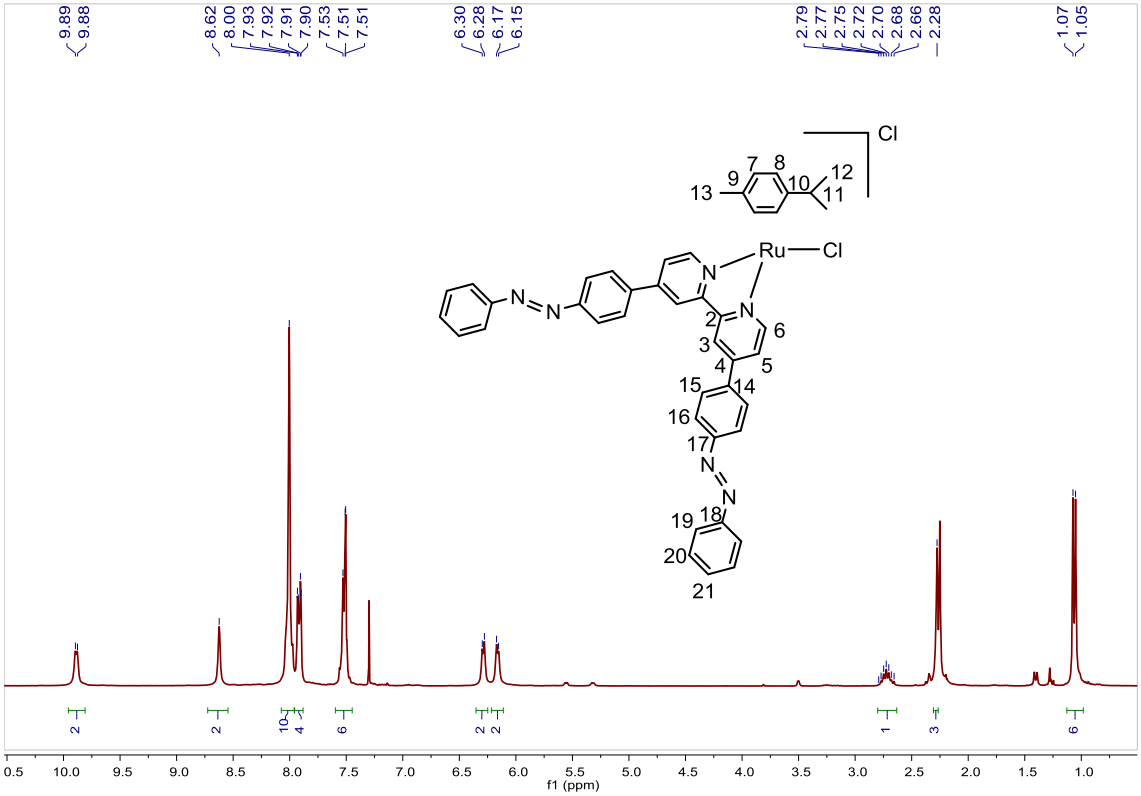

Fig. S36. ^{1}H NMR spectrum of **[Ru(p-Cym)(3)(Cl)]Cl** in $CDCl_3$, 300 MHz.

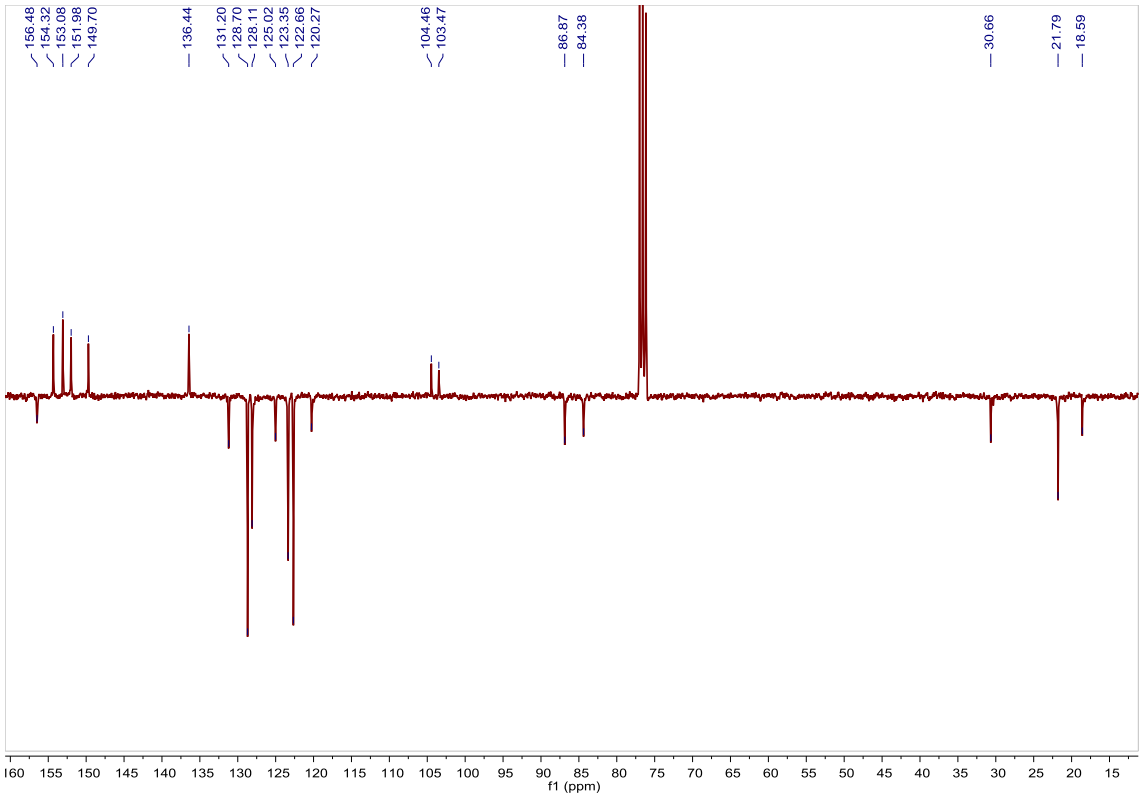

Fig. S37. ^{13}C APT NMR spectrum of **[Ru(p-Cym)(3)(Cl)]Cl** in $CDCl_3$, 75 MHz.

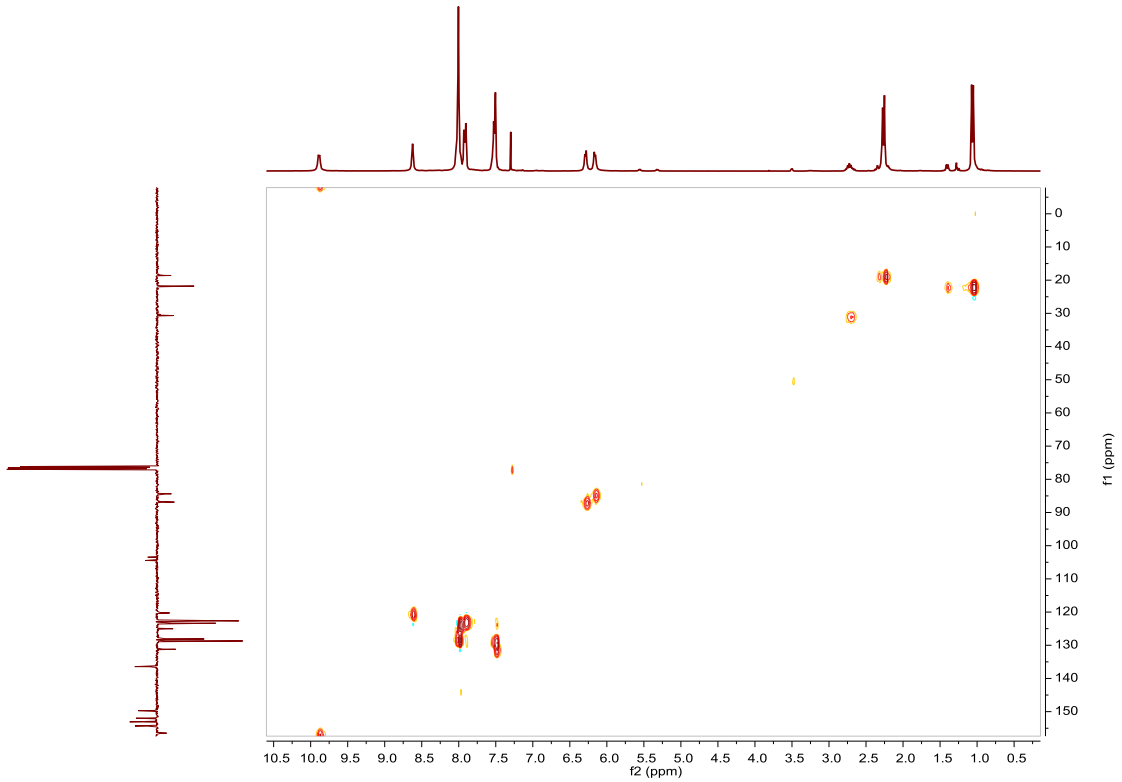

Fig. S38. HSQC spectrum of **[Ru(p-Cym)(3)(Cl)]Cl** in $CDCl_3$.

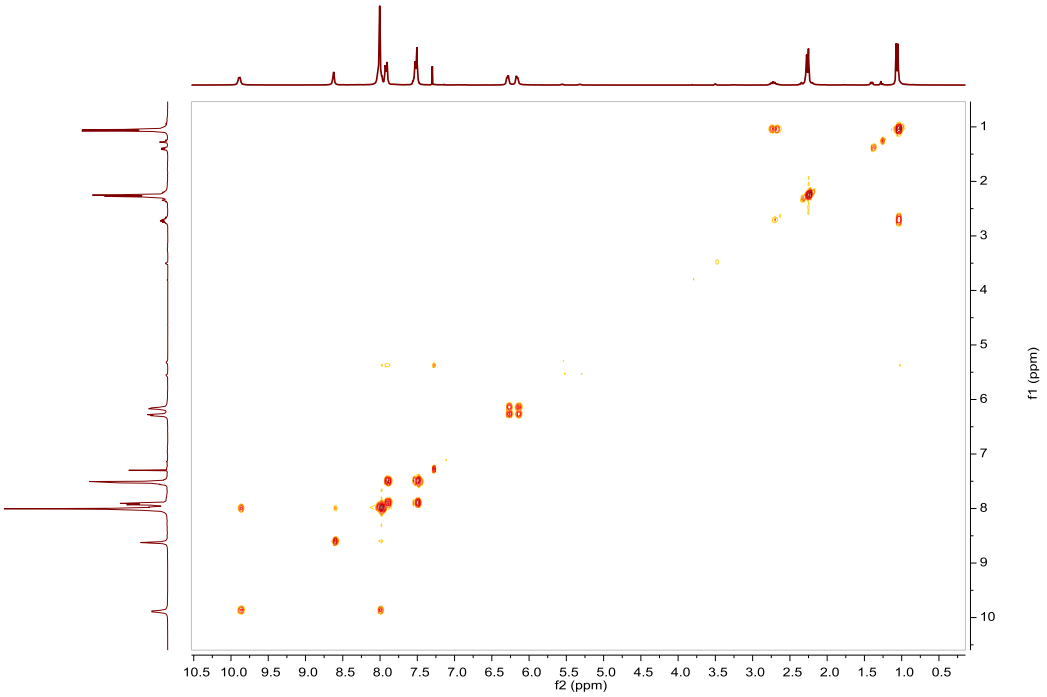

Fig. S39. COSY spectrum of **[Ru(p-Cym)(3)(Cl)]Cl** in $CDCl_3$.

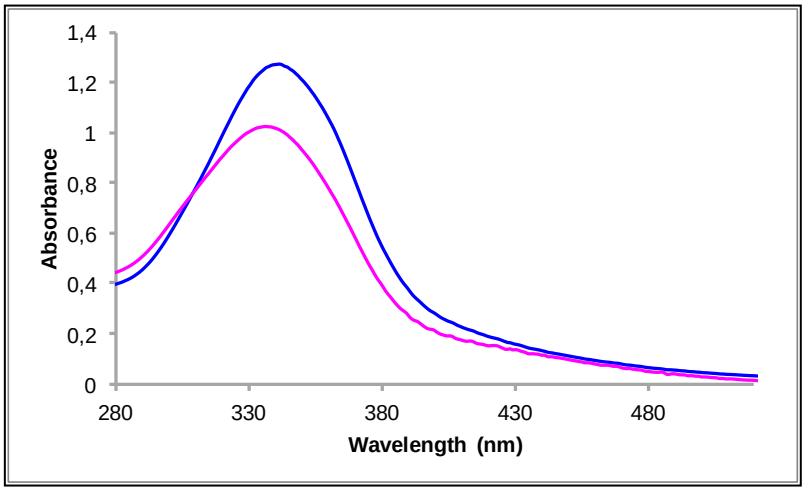

Fig. S40. UV/Vis spectra of **[Ru(p-Cym)(3)(Cl)]Cl** in ACN. Before (blue line) and after (pink line) irradiation at 350nm, $2.54 \cdot 10^{-5}$M.

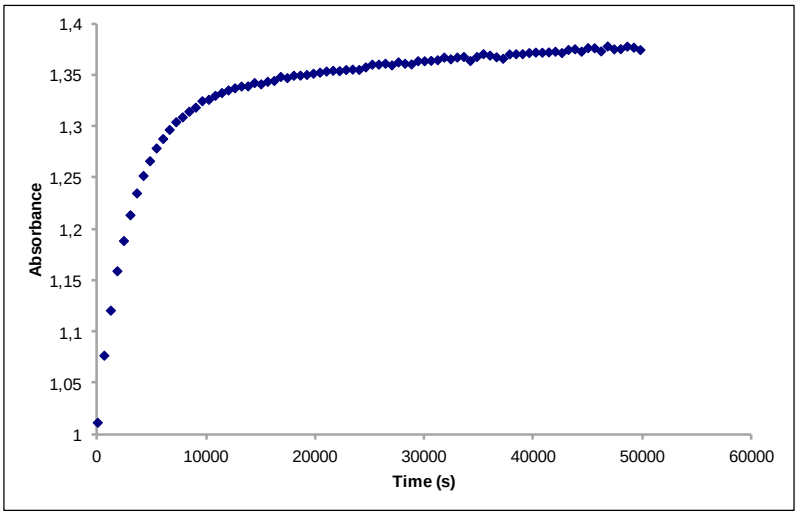

Fig. S41. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(3)(Cl)]Cl**. Absorption change of the band 341nm at 338 K in ACN after irradiation at 350 nm. ($2.54 \cdot 10^{-5}$M).

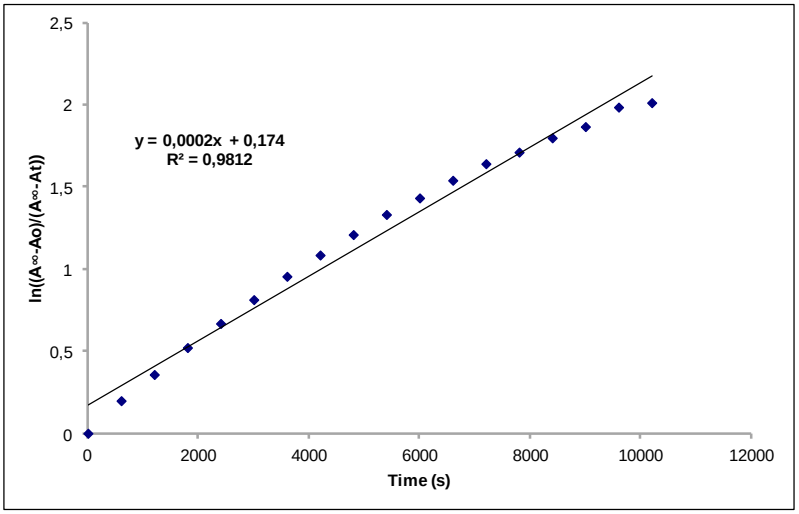

Fig. S42. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(3)(Cl)]Cl**. First-order plot. k (s^{-1}) = $2.0 \cdot 10^{-4}$. Half-life (min) = 58.

Compound [Ru(p-Cym)(4)(Cl)]Cl. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

Under a N_2 atmosphere, $Ru_2(p\text{-}Cym)_2Cl_4$ (0.100 g, 0.163 mmol) and 4-(*p*-azobenzene)-4'-bromo-2,2'-bipyridine (0.135 g, 0.326 mmol) were dissolved in 10 mL of acetone. The reaction mixture was refluxed for 15 h. It was cooled to room temperature and the solid was filtered. The desired compound was obtained after precipitated with CH_2Cl_2/Et_2O as an orange solid Yield 65%.

Elemental Analysis: calculated for ($C_{32}H_{29}BrCl_2N_4Ru{\cdot}CH_2Cl_2$): C, 49.15; H, 3.87; N, 6.95. Found: C, 49.04; H, 3.80; N, 6.77.

Exact Mass: ESI-MS $[C_{32}H_{29}BrClN_4Ru]^+$: calculated: m/z= 685.0308, found: m/z= 685.0334.

^{1}H NMR (300 MHz, MeOD *d_4*): δ 9.39 (d, J = 6.0 Hz, 1H, (bipy)), 9.20 (d, J = 6.1 Hz, 1H, (bipy)), 8.92 (brd, J = 1.8 Hz, 1H, (bipy)), 8.76 (brd, J = 1.5 Hz, 1H, (bipy)), 8.12–7.94 (m, 5H, (bipy)), 7.93–7.80 (m, 3H, (bipy)), 7.52–7.40 (m, 3H, (bipy)), 6.04 (m, 2H, (8+8')), 5.80 (m, 2H, (7+7')), 2.59 (sep, J = 6.9 Hz, 1H, (11)), 2.17 (s, 3H, (13)), 0.99 (d, J = 6.8 Hz, 6H, (12)).

^{13}C APT NMR (75 MHz, MeOD *d_4*): δ 157.24 (C_{quat}, (bipy)), 157.11 (CH, (bipy)), 156.98 (CH, (bipy)), 155.79 (C_{quat}, (bipy)), 155.11 (C_{quat}, (bipy)), 153.96 (C_{quat}, (bipy)), 152.07 (C_{quat}, (bipy)), 138.53 (C_{quat}, (bipy)), 138.05 (C_{quat}, (bipy)), 132.97 (CH, (bipy)), 132.11 (CH, (bipy)), 130.41 (2CH, (bipy)), 129.85 (2CH, (bipy)), 128.83 (CH, (bipy)), 126.43 (CH, (bipy)), 124.77 (2CH, (bipy)), 124.08 (2CH, (bipy)), 122.93 (CH, (bipy)), 106.64 (C_{quat}, (p-Cym)), 105.62 (C_{quat}, (p-Cym)), 88.21 (CH, (8 or 8')), 88.00 (CH, (8 or 8')), 85.87 (CH, (7 or 7')), 85.68 (CH, (7 or 7')), 32.41 (CH, (11)), 22.37 ($2CH_3$, (12)), 18.97 (CH_3, (13)).

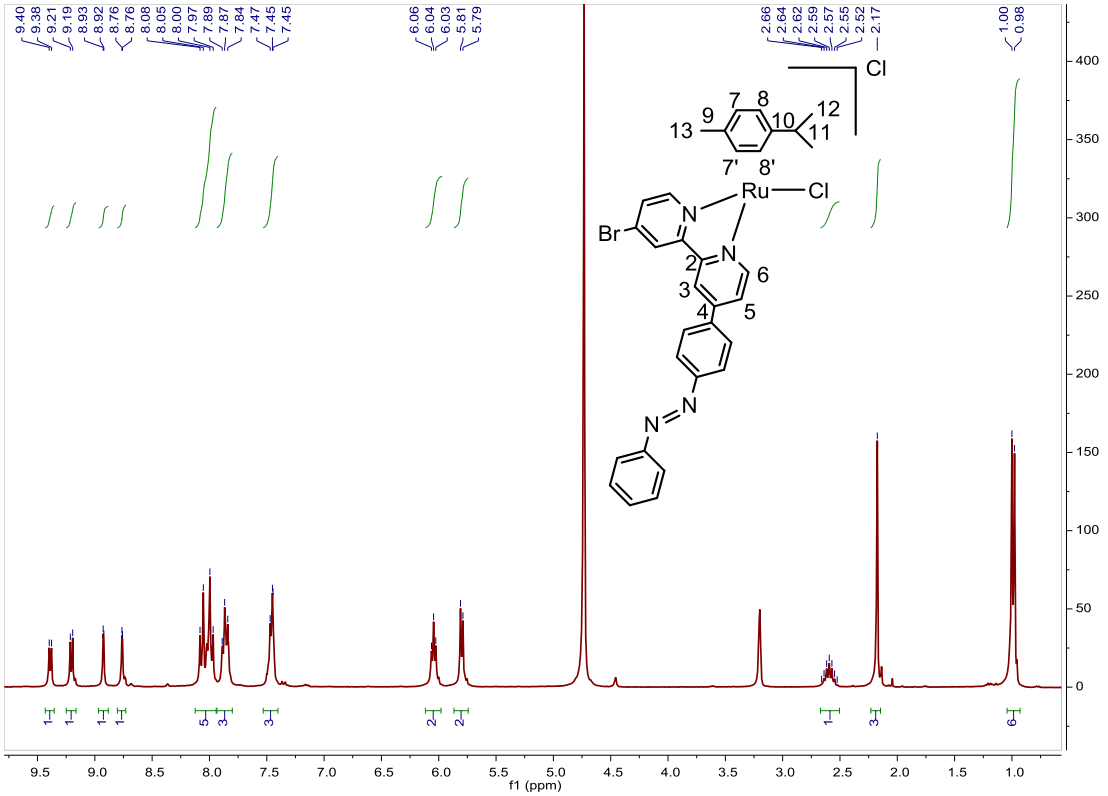

Fig. S43. ^{1}H NMR spectrum of **[Ru(p-Cym)(4)(Cl)]Cl** in MeOD-*d_4*, 300 MHz.

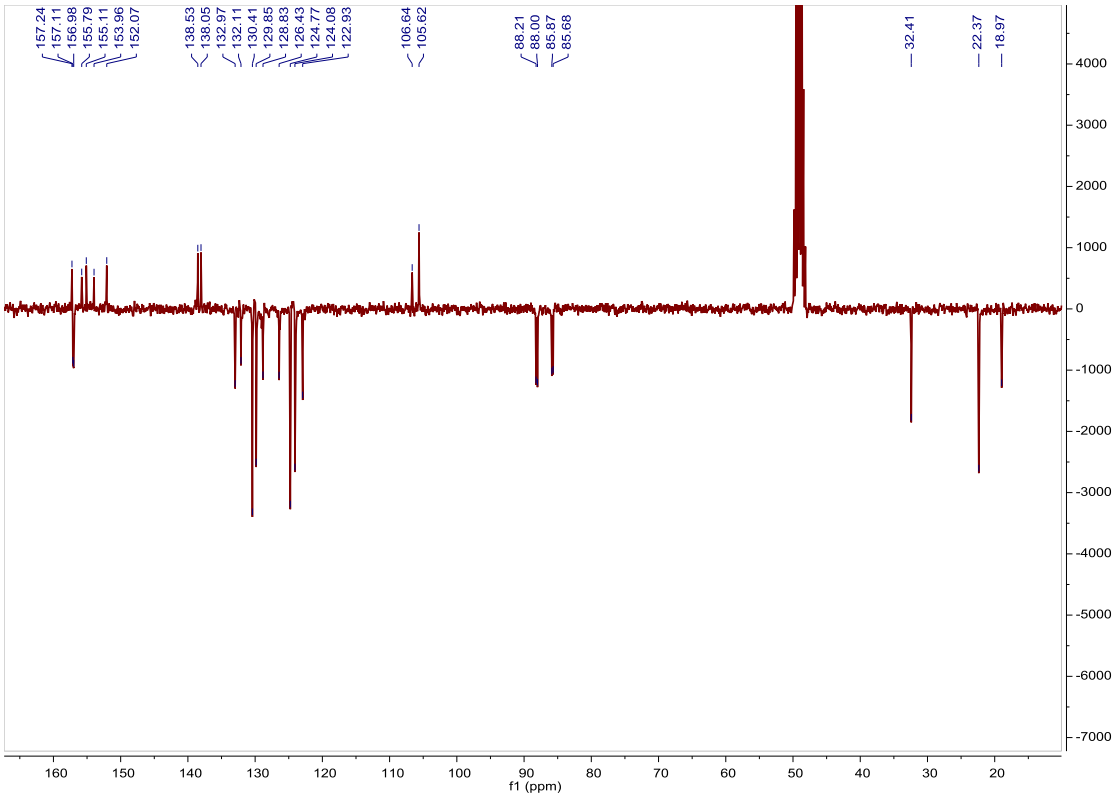

Fig. S44. ^{13}C APT NMR spectrum of **[Ru(p-Cym)(4)(Cl)]Cl** in MeOD-d_4, 75 MHz.

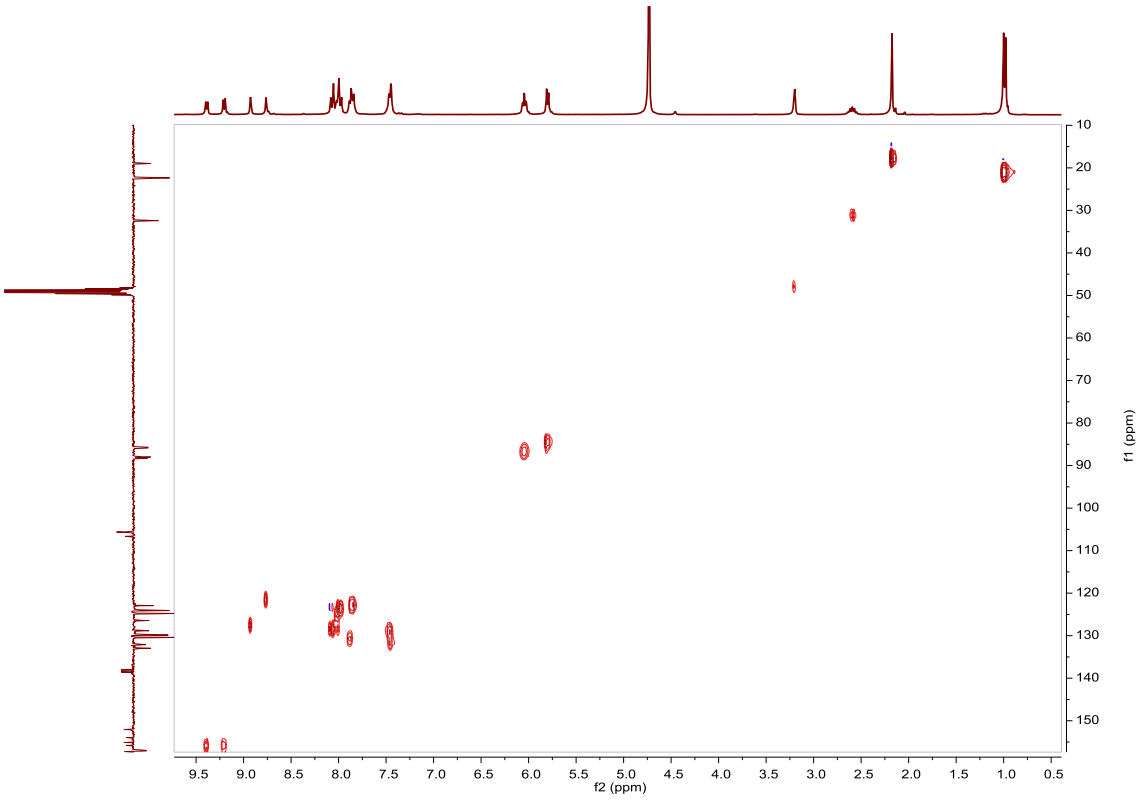

Fig. S45. HSQC NMR spectrum of **[Ru(p-Cym)(4)(Cl)]Cl** in MeOD-d_4.

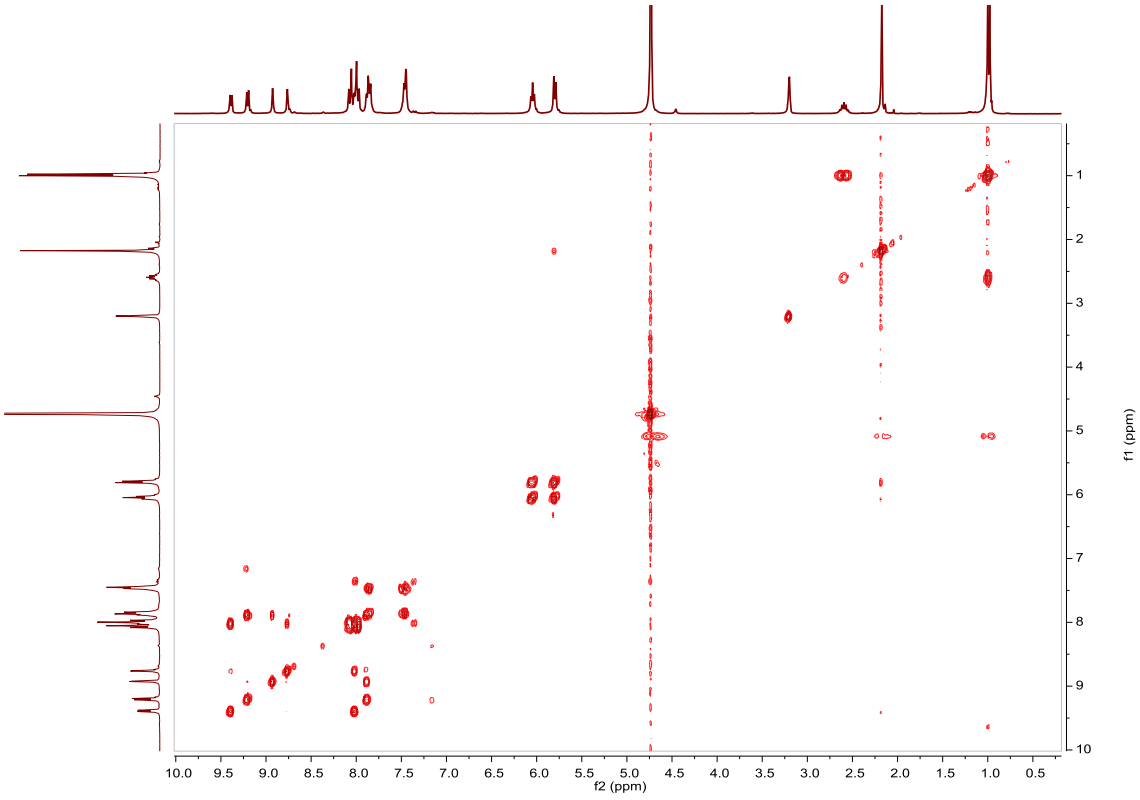

Fig. S46. COSY NMR spectrum of **[Ru(p-Cym)(4)(Cl)]Cl** in MeOD-d_4.

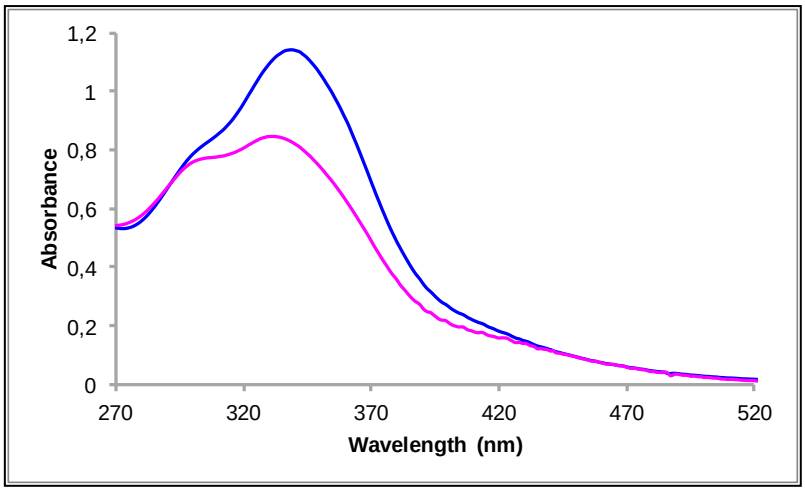

Fig. S47. UV/Vis spectra of **[Ru(p-Cym)(4)(Cl)]Cl** in ACN. Before (blue line) and after (pink line) irradiation at 344nm, $3.09 \cdot 10^{-5}$M.

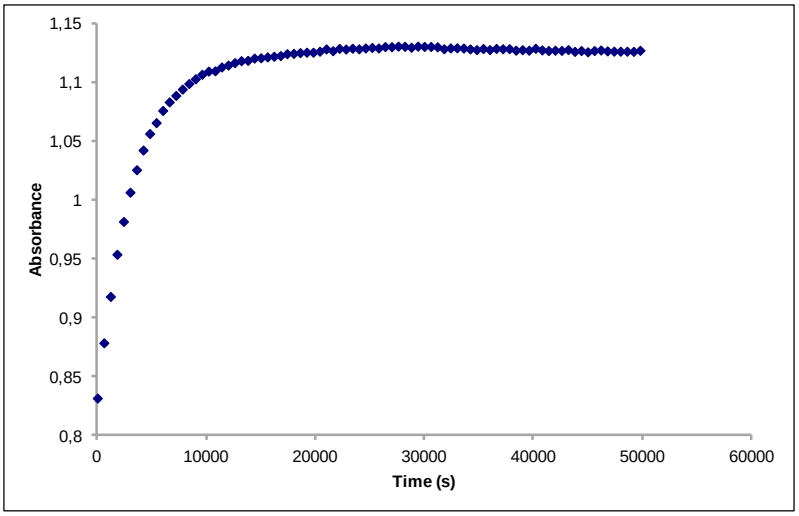

Fig. S48. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(4)(Cl)]Cl**. Absorption change of the band 338nm at 338 K in ACN after irradiation at 344 nm. ($3.09 \cdot 10^{-5}$M).

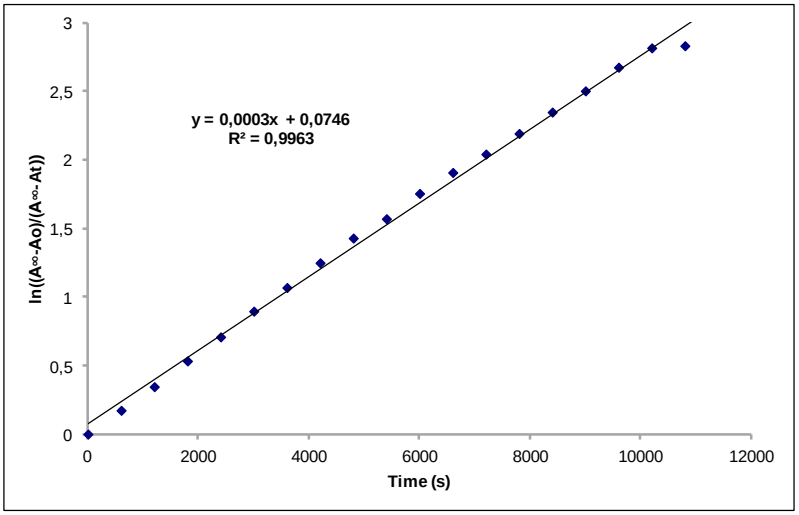

Fig. S49. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(4)(Cl)]Cl**. First-order plot. k (s^{-1}) = $3.0 \cdot 10^{-4}$. Half-life (min) = 38.

Compound [Ru(p-Cym)(5)(Cl)]Cl. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

Under a N_2 atmosphere, $Ru_2(p\text{-}Cym)_2Cl_4$ (0.100 g, 0.163 mmol) and 4,4'-bis(*m*-azobenzene)-2,2'-bipyridine (0.168 g, 0.326 mmol) were dissolved in 10 mL of acetone. The reaction mixture was refluxed for 15 h and ,4-4'-bis(*m*-azobenzene)-2,2'-bipyridine (0.168 g, 0.326 mmol) were added. It was refluxed for another 15 h. It was cooled to room temperature and the solid was filtered. The desired compound was obtained after precipitated with CH_2Cl_2/Et_2O as a brown solid. Yield 54%.

Elemental Analysis: calculated for ($C_{44}H_{38}Cl_2N_6Ru{\cdot}CH_2Cl_2$): C, 59.54; H, 4.44; N, 9.26. Found: C, 58.94; H, 4.43; N, 9.03.

Exact Mass: ESI-MS $[C_{44}H_{38}ClN_6Ru]^+$: calculated: m/z= 787.1890, found: m/z= 787.1920.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.98 (s, 2H, (bipy)), 8.51 (s, 2H, (bipy)), 8.26 (s, 2H, (bipy)), 8.13–7.86 (m, 10H, (bipy)), 7.71 (t, J = 7.2 Hz, 2H, (bipy)), 7.55–7.45 (m, 6H, (bipy)), 6.38 (s, 2H, (7 or 8)), 6.23 (s, 2H, (7 or 8)), 2.79 (m, 1H, (11)), 2.32 (s, 3H, (13)), 1.12 (d, J = 6.4 Hz, 6H, (12)).

^{13}C APT NMR (75 MHz, $CDCl_3$): δ 156.88 (2CH, (bipy)), 154.36 ($2C_{quat}$, (bipy)), 152.64 ($2C_{quat}$, (bipy)), 151.84 ($2C_{quat}$, (bipy)), 150.30 ($2C_{quat}$, (bipy)), 135.76 ($2C_{quat}$, (bipy)), 131.19 (2CH, (bipy)), 130.10 (2CH, (bipy)), 129.50 (2CH, (bipy)), 128.75 (4CH, (bipy)), 125.47 (2CH, (bipy)), 124.69 (2CH, (bipy)), 122.61 (4CH, (bipy)), 121.02 (2CH, (bipy)), 120.24 (2CH, (bipy)), 104.47 (C_{quat}, (p-Cym)), 103.84 (C_{quat}, (p-Cym)), 87.18 (2CH, (7 or 8)), 84.50 (2CH, (7 or 8)), 30.76 (CH, (11)), 21.86 ($2CH_3$, (12)), 18.72 (CH_3, (13)).

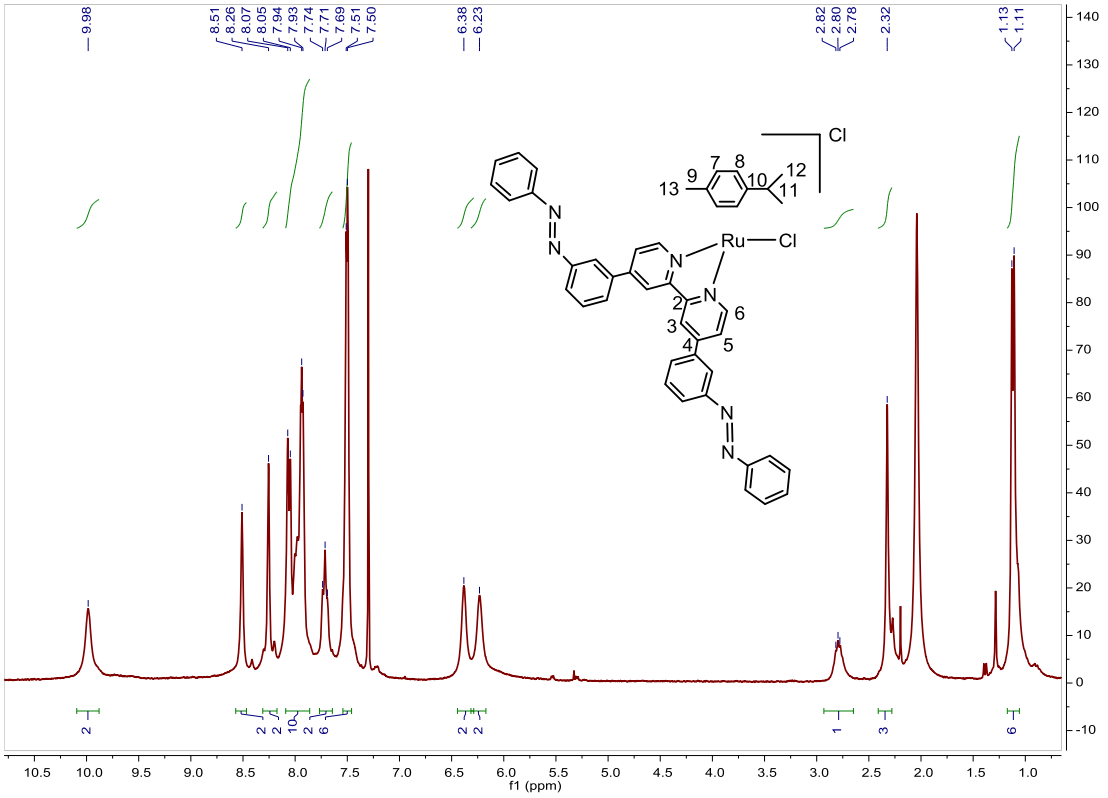

Fig. S50. ^{1}H NMR spectrum of **[Ru(p-Cym)(5)(Cl)]Cl** in $CDCl_3$, 300 MHz.

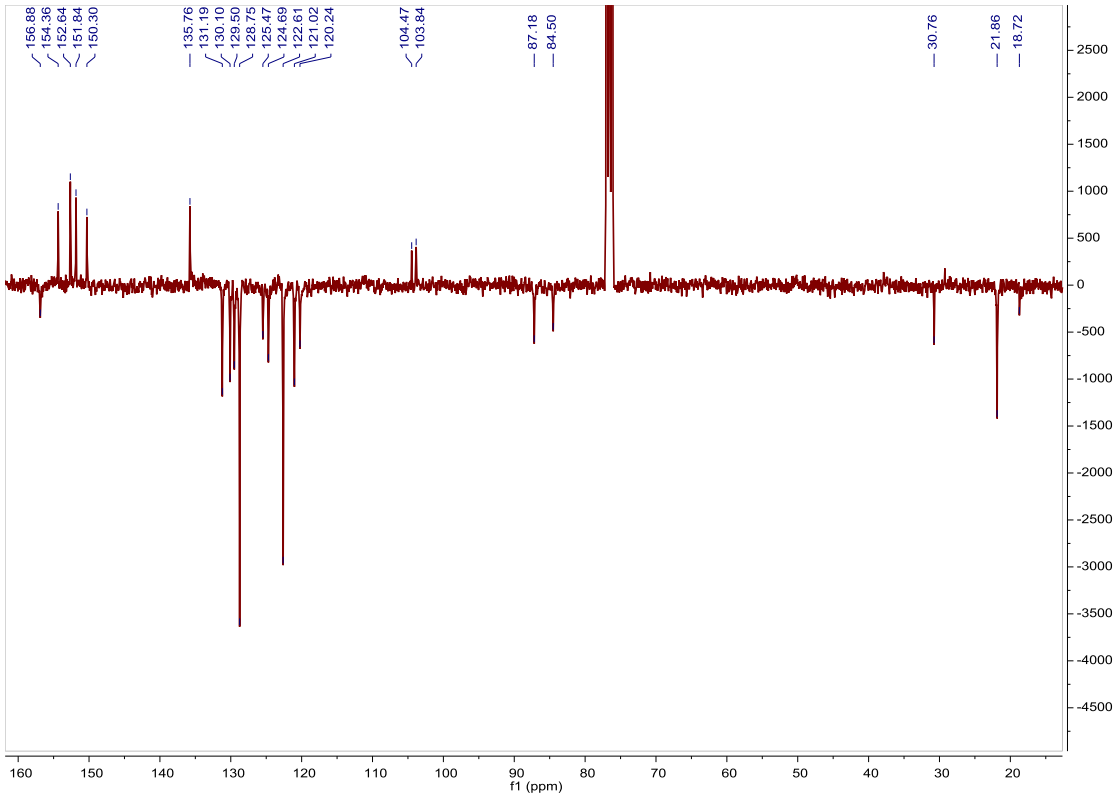

Fig. S51. ^{13}C APT NMR spectrum of **[Ru(p-Cym)(5)(Cl)]Cl** in $CDCl_3$, 75 MHz.

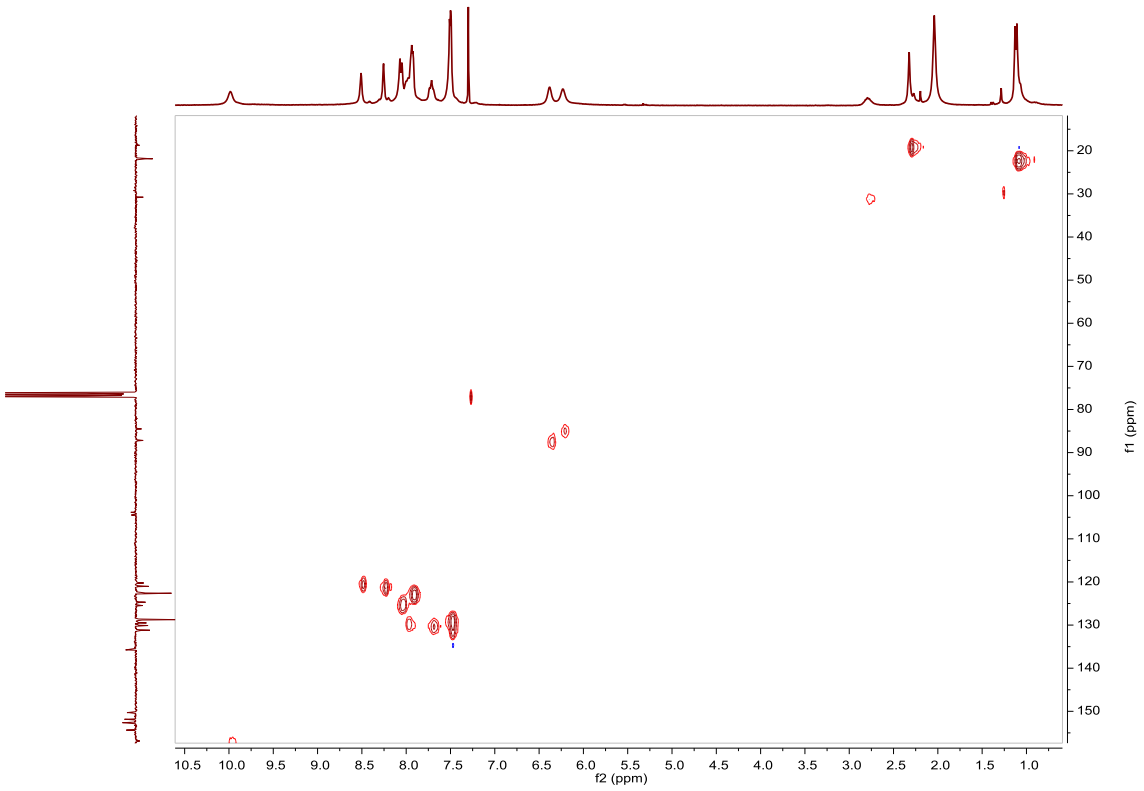

Fig. S52. HSQC NMR spectrum of **[Ru(p-Cym)(5)(Cl)]Cl** in $CDCl_3$.

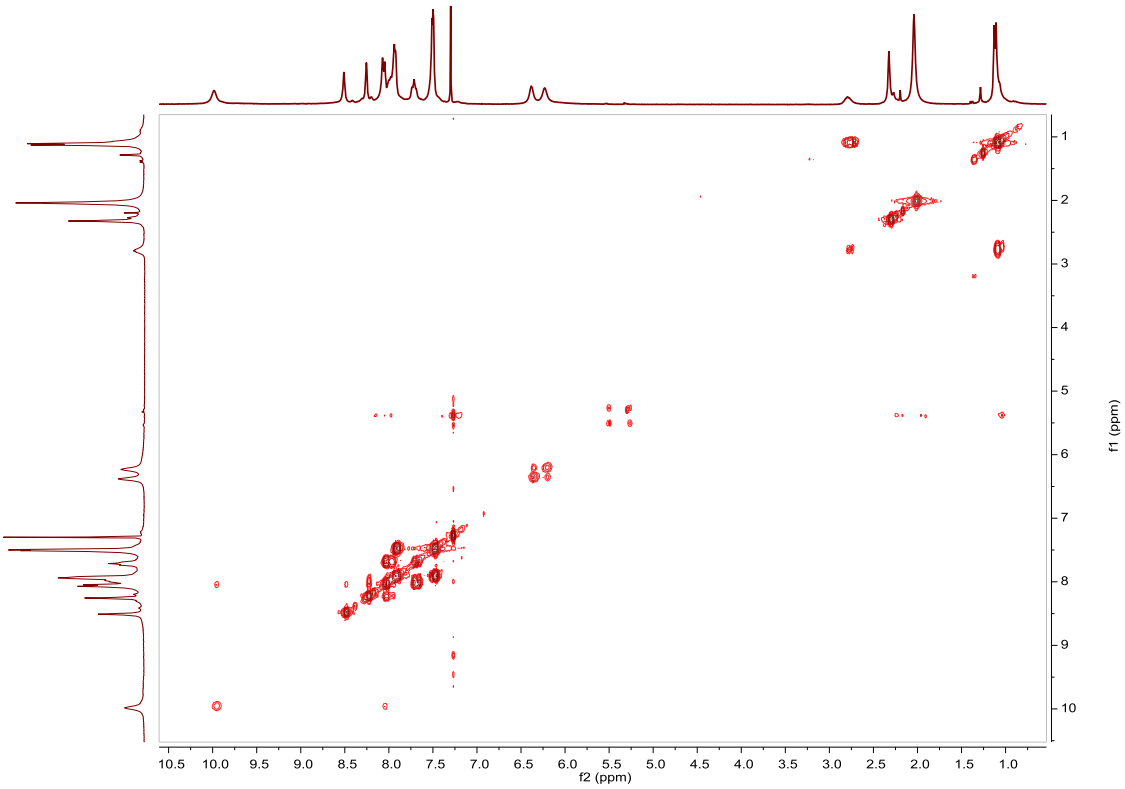

Fig. S53. COSY NMR spectrum of **[Ru(p-Cym)(5)(Cl)]Cl** in $CDCl_3$.

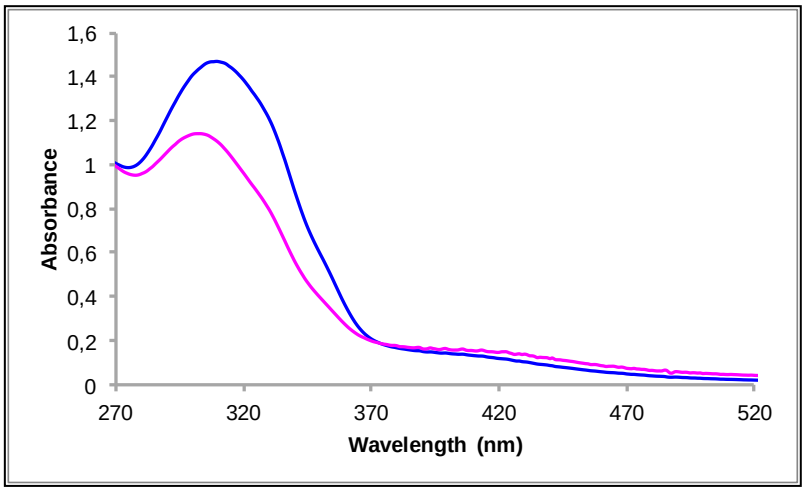

Fig. S54. UV/Vis spectra of **[Ru(p-Cym)(5)(Cl)]Cl** in ACN. Before (blue line) and after (pink line) irradiation at 322nm, $2.61 \cdot 10^{-5}$M.

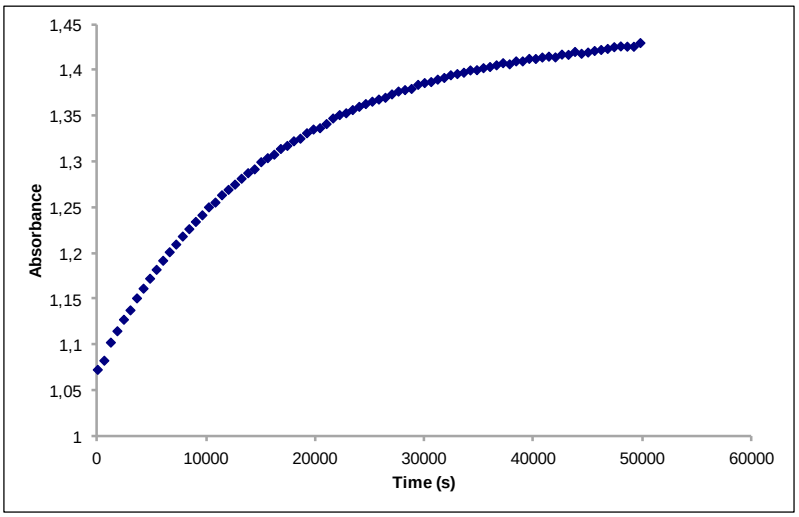

Fig. S55. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(5)(Cl)]Cl**. Absorption change of the band 309nm at 338 K in ACN after irradiation at 322 nm. ($2.61 \cdot 10^{-5}$M).

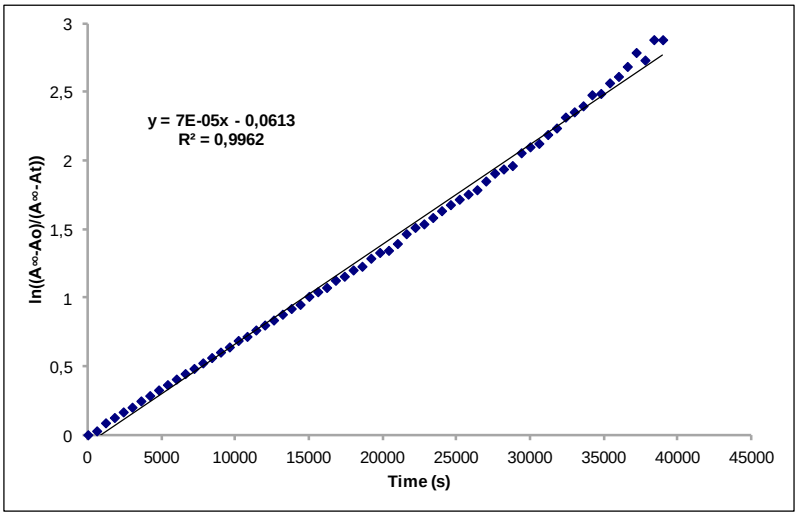

Fig. S56. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(5)(Cl)]Cl**. First-order plot. k (s^{-1}) = $7.0 \cdot 10^{-5}$. Half-life (min) = 165.

Compound [Ru(p-Cym)(6)(Cl)$_2$]. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

Under a N_2 atmosphere, Ru_2(p-Cym)$_2Cl_4$ (0.11 g, 0.17 mmol) and tris(*p*-phenylazobenzene)phosphine (0.2 g, 0.348 mmol) were dissolved in 15 mL of hexane. The reaction mixture was refluxed for 15 h. It was cooled to room temperature and the red solid was filtered. Yield 95%.

Elemental Analysis: calculated for ($C_{46}H_{41}Cl_2N_6PRu$): C, 62.73; H, 4.69; N, 9.54. Found: C, 62.93; H, 4.90; N, 9.36.

Exact Mass: ESI-MS [M-2Cl+H]: calculated: m/z= 811.2252, found: m/z= 811.2229.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.97 (t, J = 8.5 Hz, 6H, (azo)), 7.82 (m, 12H, (azo)), 7.42 (m, 9H, (azo)), 5.21 (d, J = 6.1 Hz, 2H, (8)), 4.98 (d, J = 5.6 Hz, 2H, (7)), 2.83 (sep, J = 6.9 Hz, 1H, (11)), 1.85 (s, 3H, (13)), 1.06 (d, J = 6.9 Hz, 6H, (12)).

^{13}C APT NMR (75 MHz, $CDCl_3$): δ 153.58 (s, 3C_{quat}, (azo)), 152.76 (s, 3C_{quat}, (azo)), 136.22 (d, J = 45 Hz, 3C_{quat}, (azo)), 135.47 (d, J = 9.7 Hz, 6CH, (azo)), 131.78 (s, 3CH (azo)), 129.33 (s, 6CH, (azo)), 123.27 (s, 6CH, (azo)), 122.47 (d, J = 10.5 Hz, 6CH, (azo)), 112.07 (s, C_{quat}, (p-Cym)), 96.65 (s, C_{quat}, (p-Cym)), 89.37 (brd, J = 2.2 Hz, 2CH, (7)), 87.60 (d, J = 5.2 Hz, 2CH, (8)), 30.63 (s, CH, (11)), 22.10 (s, 2CH_3, (12)), 18.13 (s, CH_3, (13)).

^{31}P NMR (202 MHz, $CDCl_3$): δ 25.79 (s, 1P).

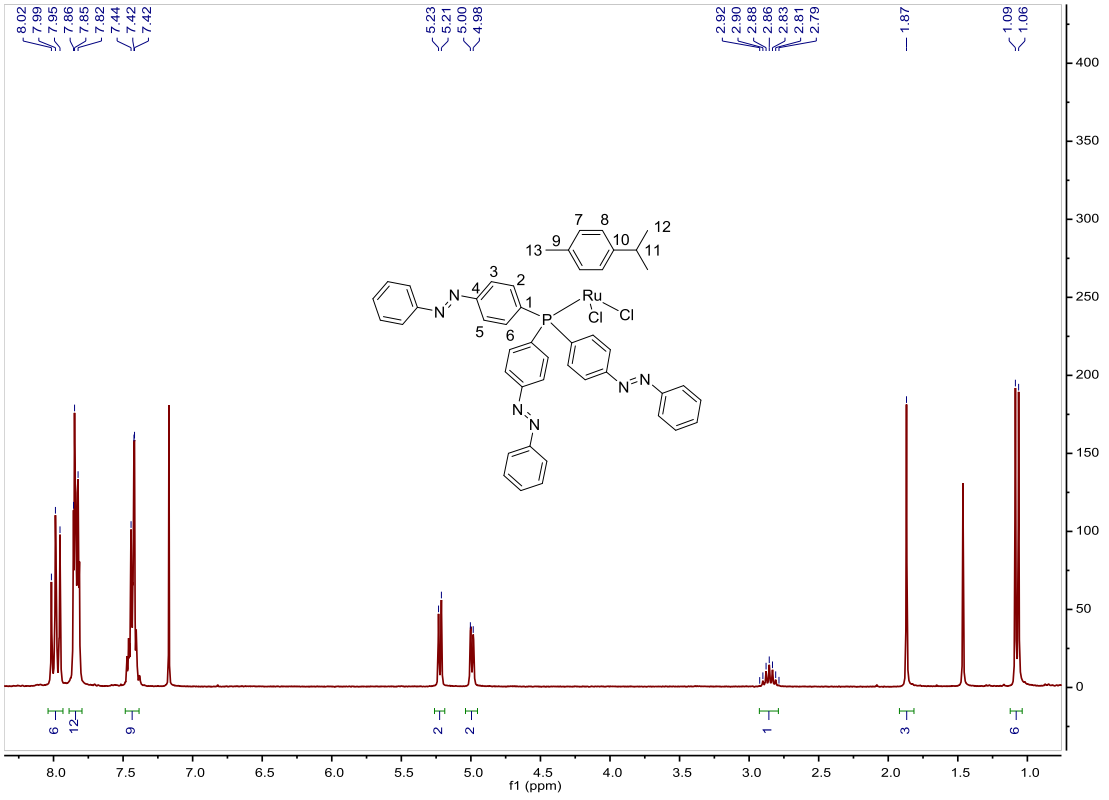

Fig. S57. ^{1}H NMR spectrum of **[Ru(p-Cym)(6)(Cl)$_2$]** in $CDCl_3$, 300 MHz.

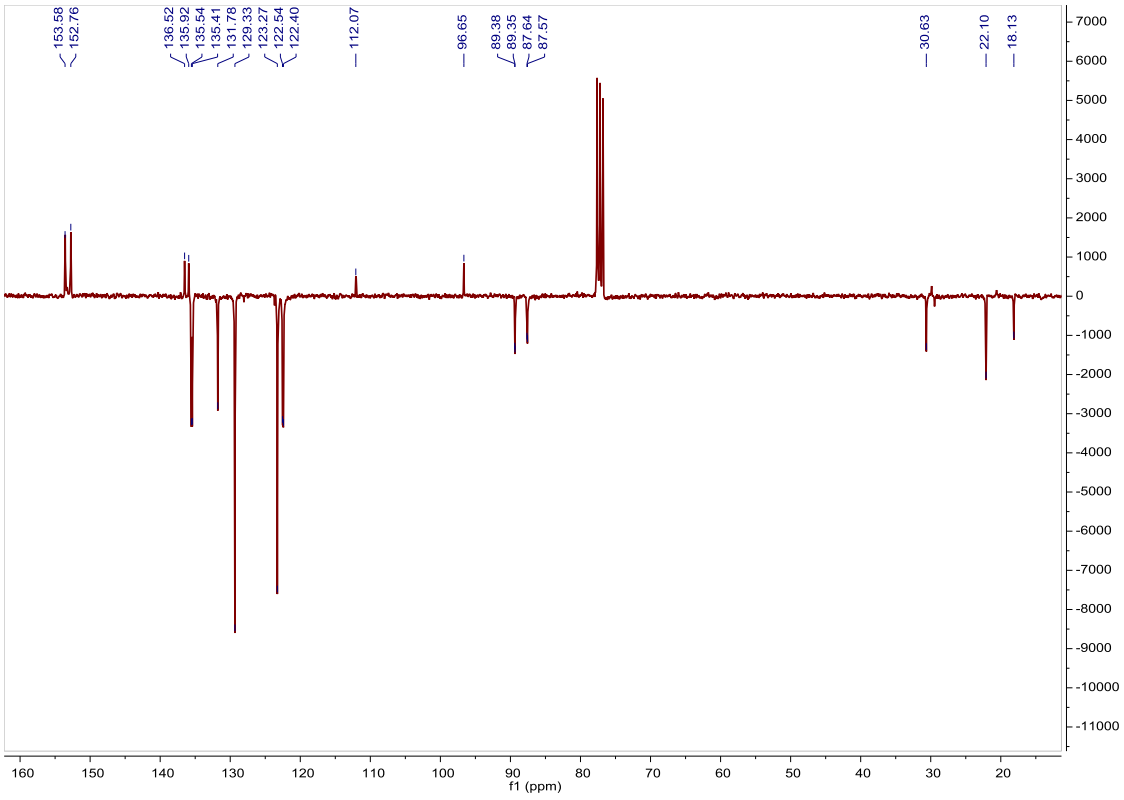

Fig. S58. ^{13}C APT NMR spectrum of **[Ru(p-Cym)(6)(Cl)$_2$]** in $CDCl_3$, 75 MHz.

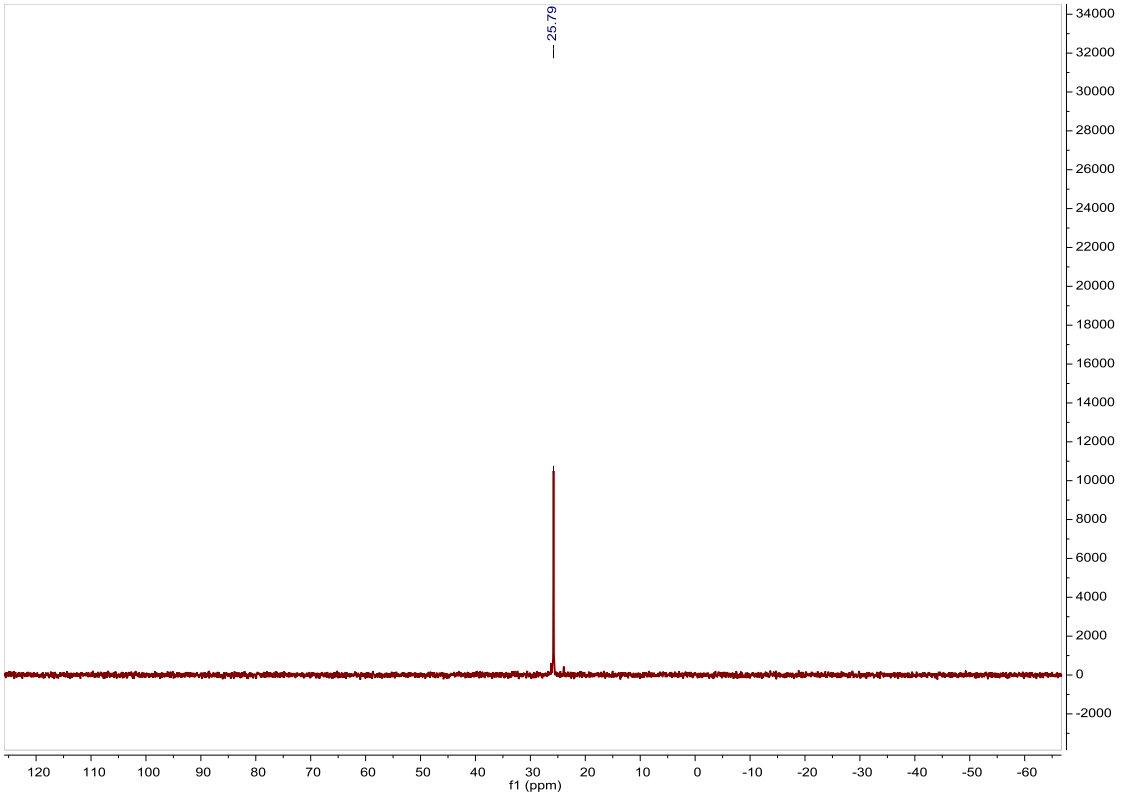

Fig. S59. ^{31}P NMR spectrum of **[Ru(p-Cym)(6)(Cl)$_2$]** in $CDCl_3$, 202 MHz.

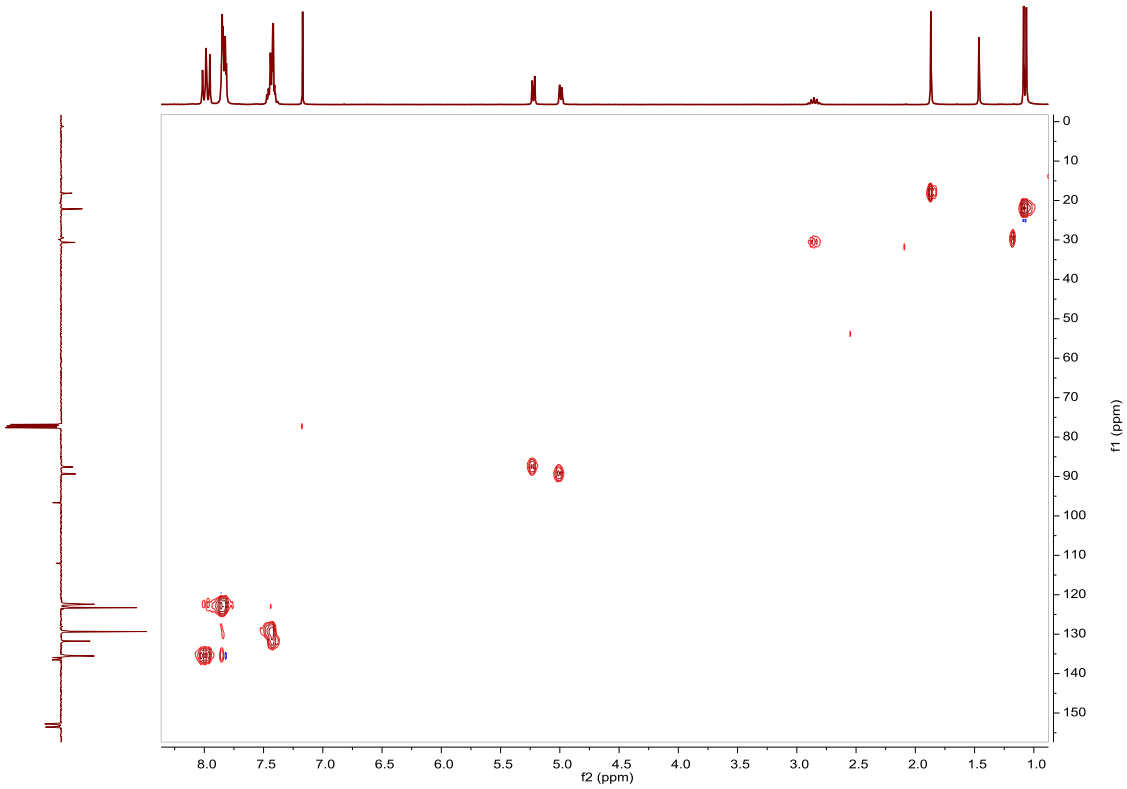

Fig. S60. HSQC NMR spectrum of **[Ru(p-Cym)(6)(Cl)$_2$]** in $CDCl_3$.

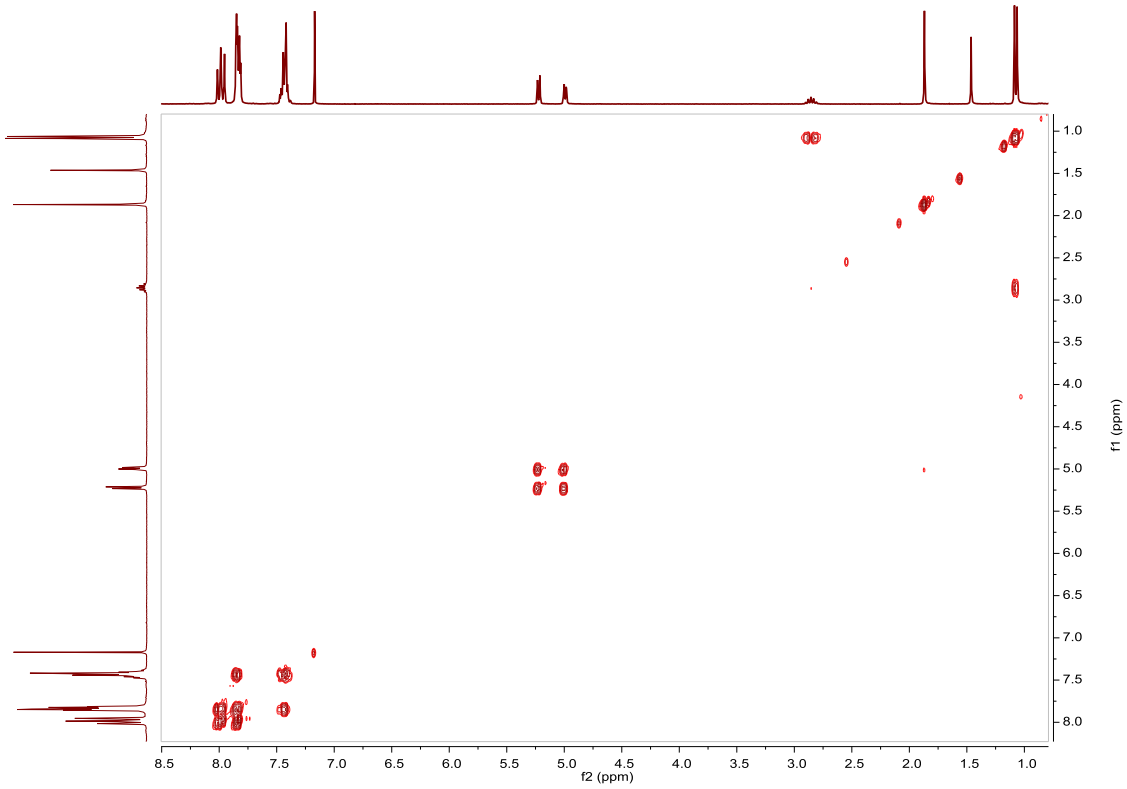

Fig. S61. COSY NMR spectrum of **[Ru(p-Cym)(6)(Cl)$_2$]** in $CDCl_3$.

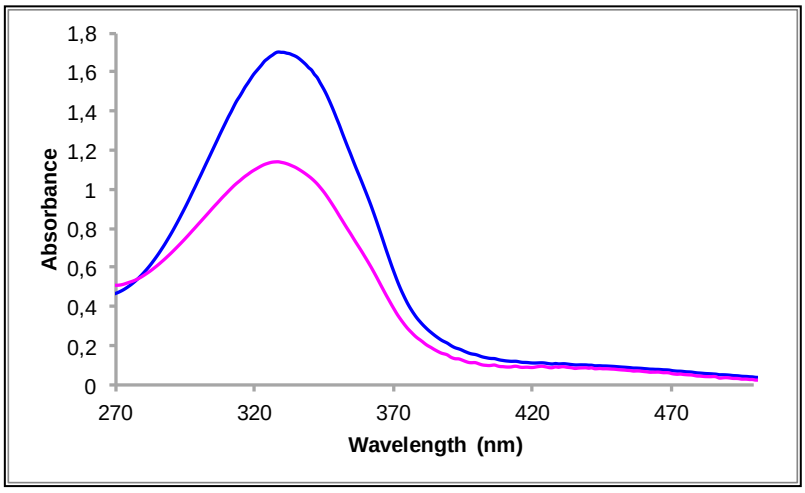

Fig. S62. UV/Vis spectra of **[Ru(p-Cym)(6)(Cl)$_2$]** in ACN. Before (blue line) and after (pink line) irradiation at 334nm, 2.46·10^{-5}M.

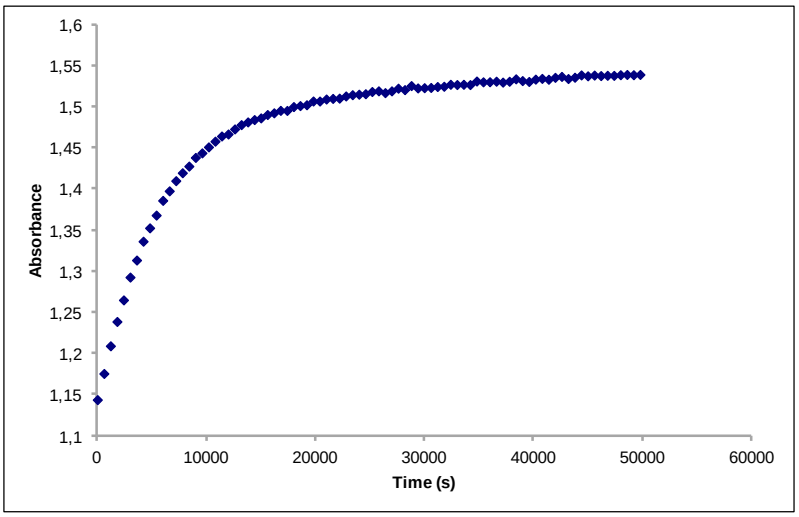

Fig. S63. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(6)(Cl)$_2$]**. Absorption change of the band 328nm at 338 K in ACN after irradiation at 334 nm. (2.46·10^{-5}M).

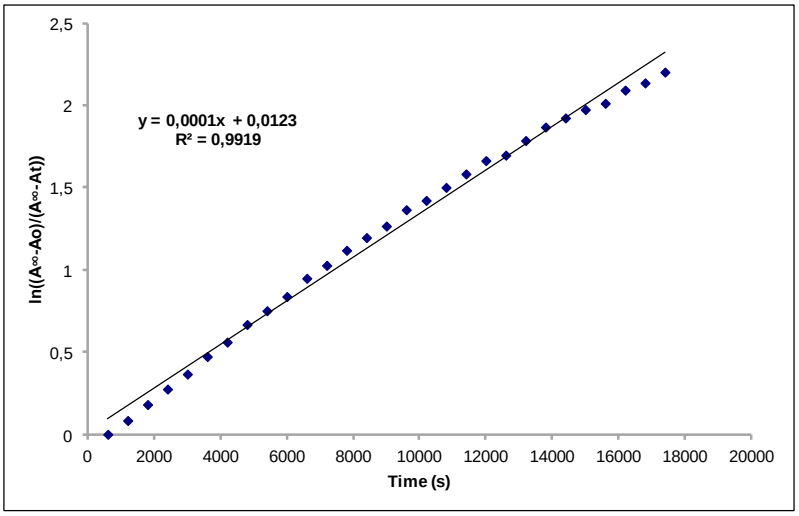

Fig. S64. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(6)(Cl)$_2$]**. First-order plot. k (s^{-1}) = $1.0 \cdot 10^{-4}$. Half-life (min) = 115.

Compound [Ru(p-Cym)(7)(Cl)$_2$]. Synthesis, characterization and photoisomerization studies.

SYNTHESIS

Under a N_2 atmosphere, $Ru_2(p\text{-}Cym)_2Cl_4$ (0.100 g, 0.163 mmol) and tris(*m*-phenylazobenzene)phosphine (0.206 g, 0.359 mmol) were dissolved in 27 mL of hexane. The reaction mixture was refluxed for 15 h. It was cooled to room temperature and the solvent was evaporated. The desired compound was obtained after precipitation with CH_2Cl_2/ether as a red solid. Yield 90%.

Elemental Analysis: calculated for ($C_{46}H_{41}Cl_2N_6PRu$): C, 62.73; H, 4.69; N, 9.54. Found: C, 62.72; H, 4.96; N, 9.28.

Exact Mass: ESI-MS [M-2Cl+H]: calculated: m/z= 811.2252, found: m/z= 811.2248.

^{1}H NMR (300 MHz, $CDCl_3$): δ 8.48 (d, J = 11.0 Hz, 3H, (6)), 8.11 (t, J = 8.7 Hz, 3H, (2)), 7.90 (d, J = 7.0 Hz, 3H, (4)), 7.79 (m, 6H, (15)), 7.48 (ddd, J = 2.5 Hz, J = 7.7 Hz, J = 10.2 Hz, 3H, (3)), 7.38 (m, 9H, (16+17)), 5.27 (d, J = 6.1 Hz, 2H, (8)), 5.09 (d, J = 5.6 Hz, 2H, (7)), 2.81 (sep, J = 6.9 Hz, 1H, (11)), 1.88 (s, 3H, (13)), 1.04 (d, J = 6.9 Hz, 6H, (12)).

^{13}C APT NMR (75 MHz, $CDCl_3$): δ 151.94 (s, C_{quat}), 151.57 (d, J = 9.7 Hz, C_{quat}), 136.70 (d, J = 9.7 Hz, 3CH, (2)), 134.33 (d, J = 45.0 Hz, C_{quat}), 130.89 (s, 3CH, (17)), 128.98 (s, 3CH, (3)), 128.85 (d, J = 4.5 Hz, 3CH, (6)), 128.59 (s, 6CH, (16)), 123.44 (s, 3CH, (4)), 122.57(s, 6CH, (15)), 110.91 (s, C_{quat}), 96.54 (s, C_{quat}), 88.63 (s, 2CH, (7)), 87.07 (d, J = 5.2 Hz, 2CH, (8)), 29.87 (s, CH, (11)), 21.54 (s, $2CH_3$, (12)), 17.42 (s, CH_3, (13)).

^{31}P NMR (202 MHz, $CDCl_3$): δ 28.18 (s, 1P).

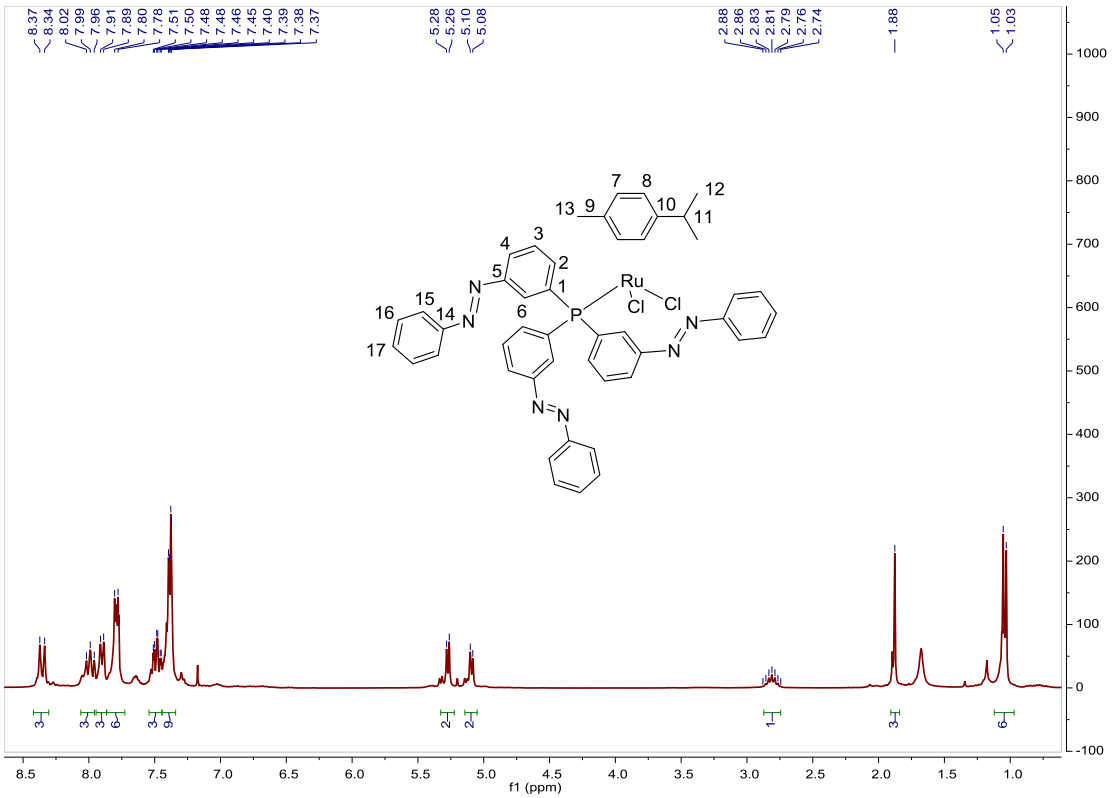

Fig. S65. ^{1}H NMR spectrum of **[Ru(p-Cym)(7)(Cl)$_2$]** in $CDCl_3$, 300 MHz.

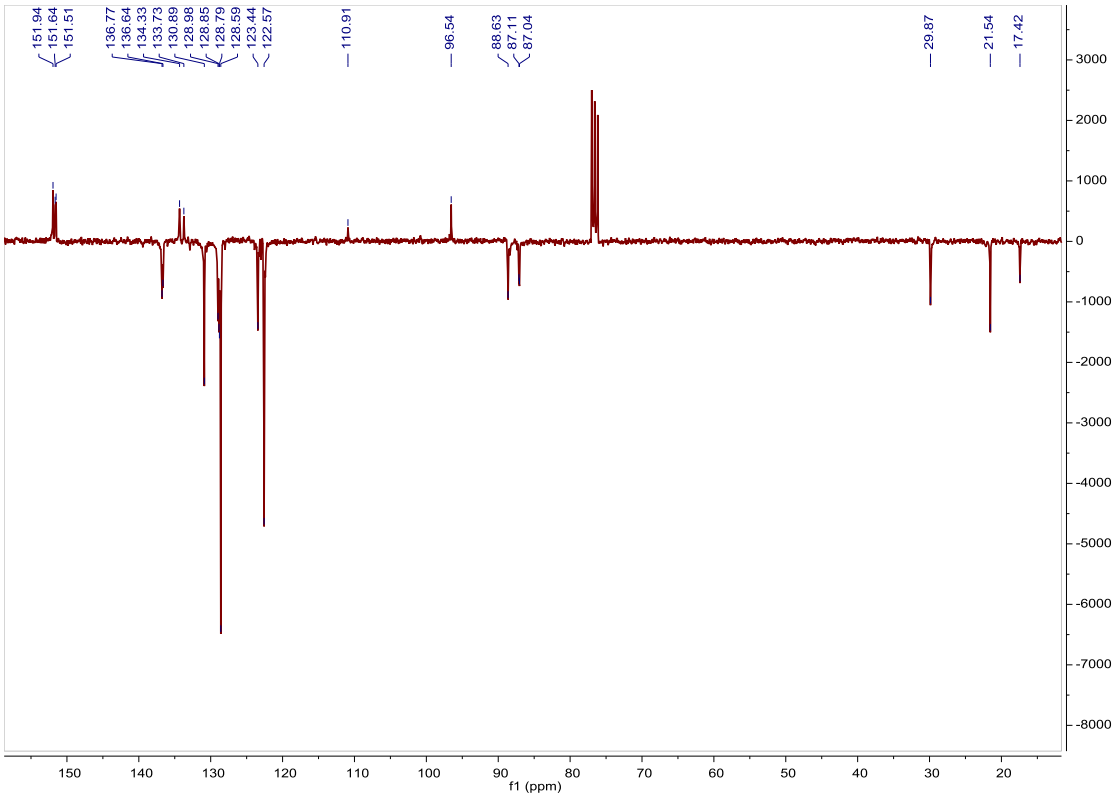

Fig. S66. ^{13}C APT NMR spectrum of **[Ru(p-Cym)(7)(Cl)$_2$]** in $CDCl_3$, 75 MHz.

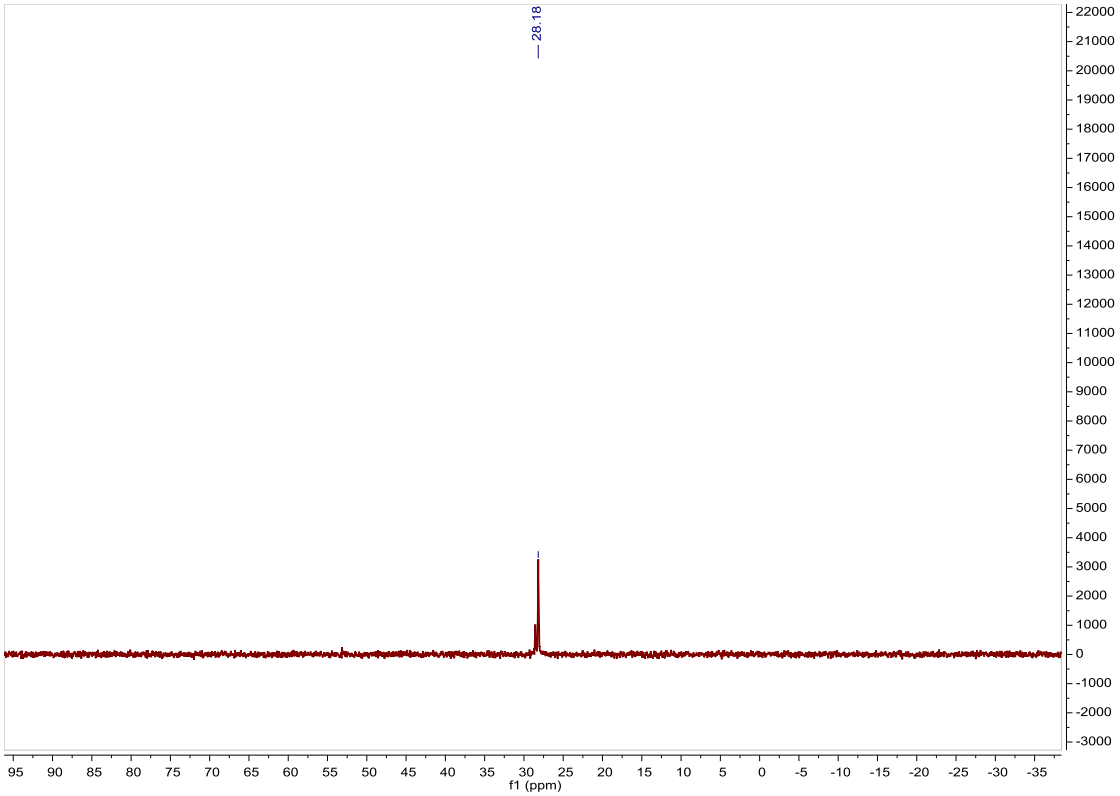

Fig. S67. ^{31}P NMR spectrum of **[Ru(p-Cym)(7)(Cl)$_2$]** in $CDCl_3$, 202 MHz.

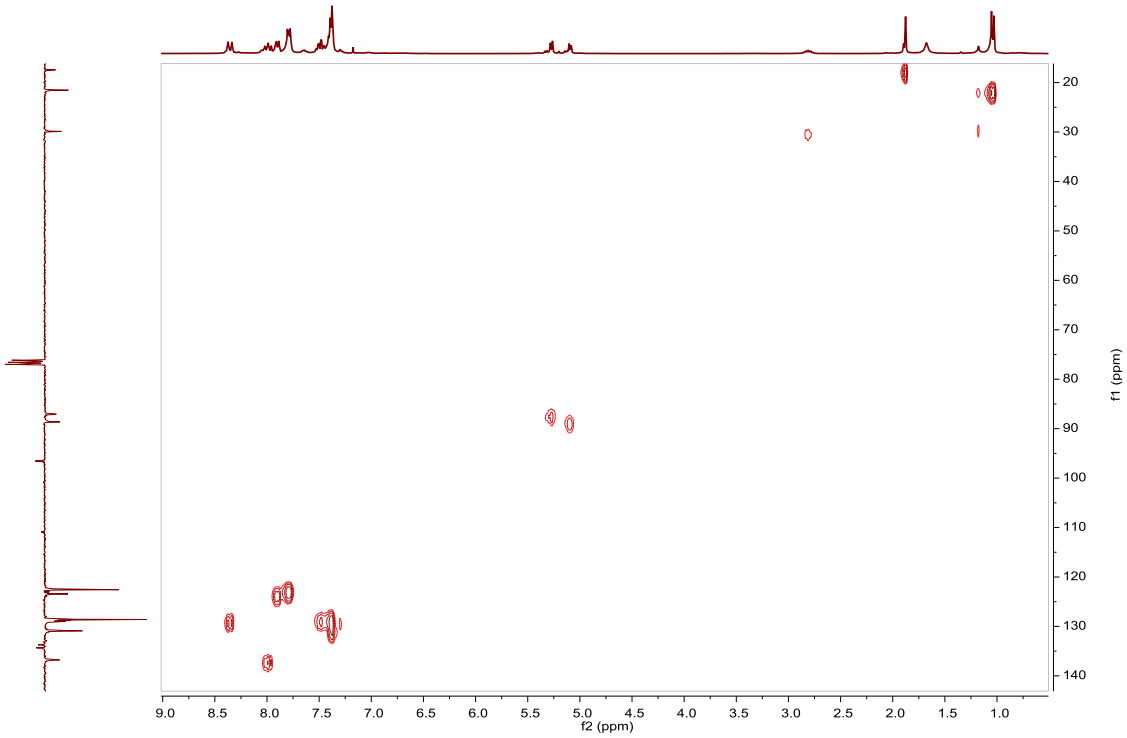

Fig. S68. HSQC NMR spectrum of **[Ru(p-Cym)(7)(Cl)$_2$]** in $CDCl_3$.

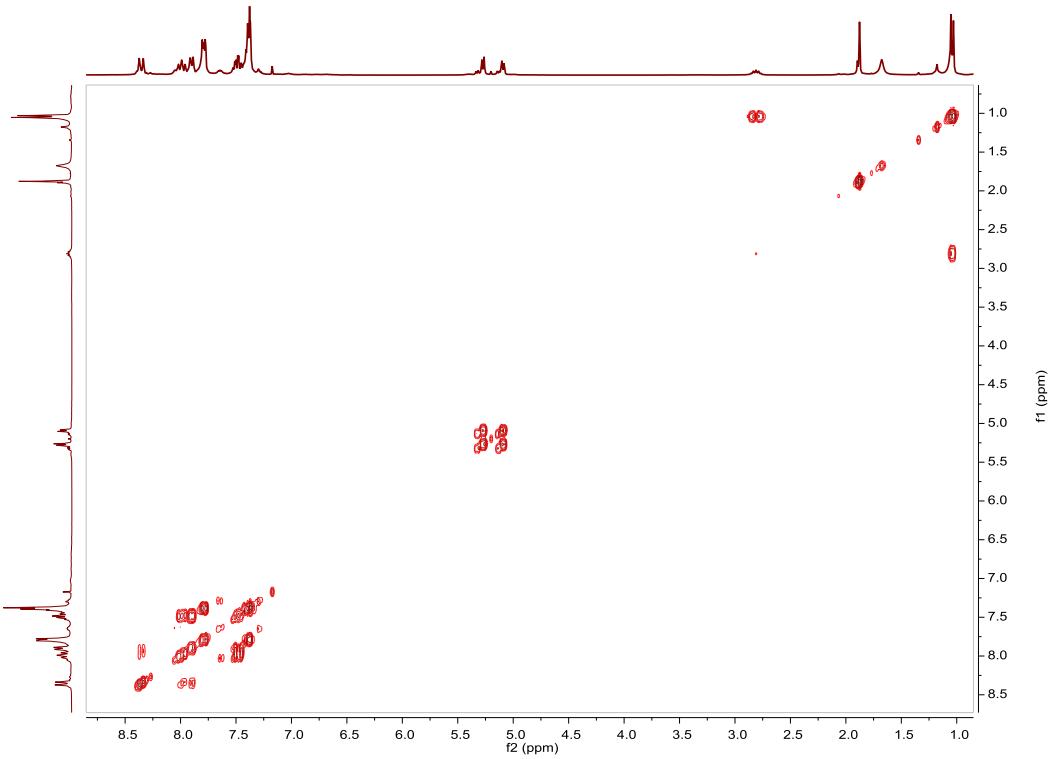

Fig. S69. COSY NMR spectrum of **[Ru(p-Cym)(7)(Cl)$_2$]** in $CDCl_3$.

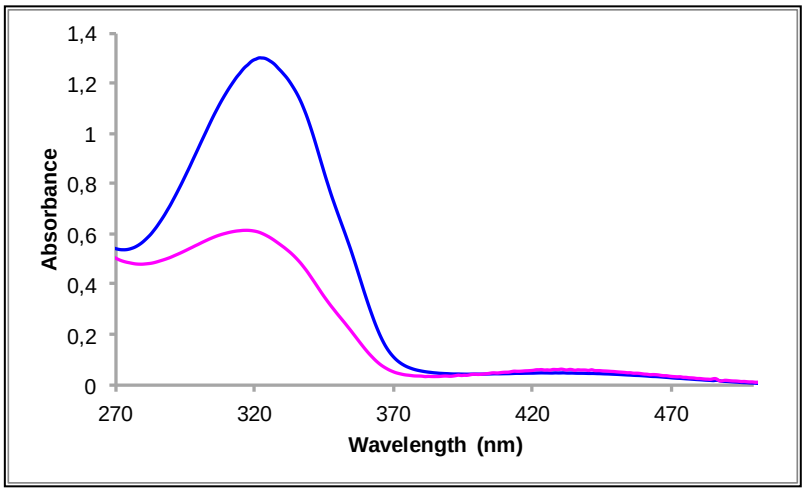

Fig. S70. UV/Vis spectra of **[Ru(p-Cym)(7)(Cl)$_2$]** in ACN. Before (blue line) and after (pink line) irradiation at 324nm, 2.32·10^{-5}M.

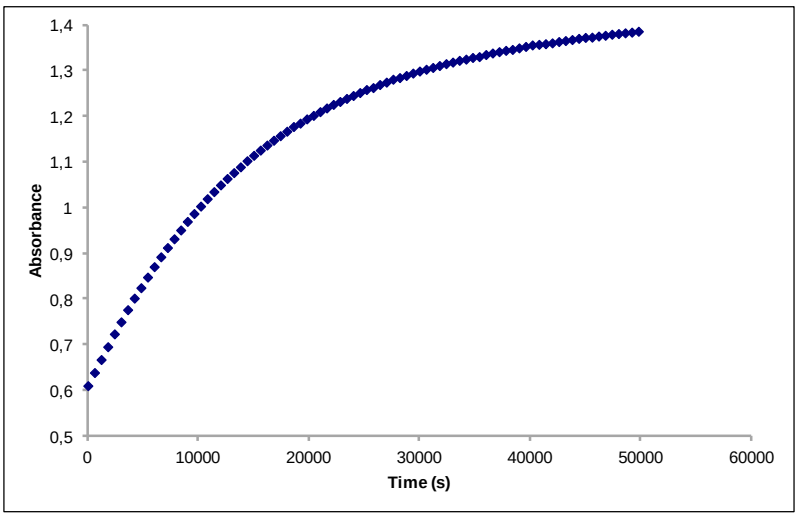

Fig. S71. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(7)(Cl)$_2$]**. Absorption change of the band 321nm at 338 K in ACN after irradiation at 324 nm. (2.32·10^{-5}M).

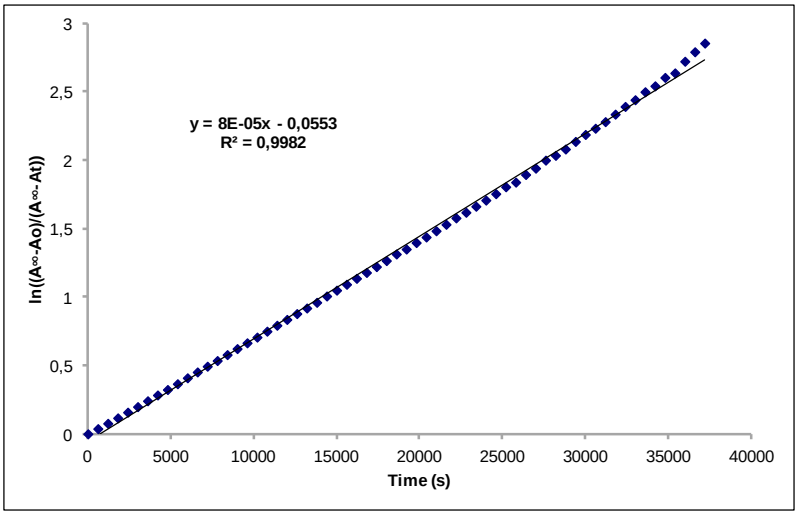

Fig. S72. Cis to trans thermal isomerization kinetics of **[Ru(p-Cym)(7)(Cl)$_2$]**. First-order plot. k (s^{-1}) = $8.0 \cdot 10^{-5}$. Half-life (min) = 144.

Compound [Ru(p-Cym)(9)$_2$(Cl)]PF_6. Synthesis and characterization.

SYNTHESIS

Under a N_2 atmosphere, [Ru(p-Cym)(pyridine)(Cl_2)] (0.218 g, 0.566 mmol) and $AgPF_6$ (0.142 g, 0.566 mmol) were dissolved in 15 mL of acetone and 15 mL of methanol. The mixture was stirred for 1 h, AgCl was removed by filtration and pyridine (0.05 mL, 0.623 mmol) were added. The reaction mixture was stirred for 4 h and the solvent was evaporated. The product was obtained as a yellow solid after precipitation with CH_2Cl_2/ether. Yield 45%.

Elemental Analysis: calculated for ($C_{20}H_{24}ClN_2RuPF_6 \cdot CH_2Cl_2$): C, 38.28; H, 3.98; N, 4.25. Found: C, 38.14; H, 4.00; N, 4.21.

Exact Mass: ESI-MS $[C_{15}H_{19}ClNRu]^+$ (M-L-PF_6): calculated: m/z= 350.0250, found: m/z= 350.0243.

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.09 (brdd, J = 1.6 Hz, J = 6.6 Hz, 4H, (2+6)), 7.87 (tt, J = 1.5 Hz, J = 7.6 Hz, 2H, (4)), 7.54–7.47 (m, 4H, (3+5)), 5.94 (d, J = 6.1 Hz, 2H, (8)), 5.66 (d, J = 6.1 Hz, 2H, (7)), 2.59 (sep, J = 6.9 Hz, 1H, (11)), 1.76 (s, 3H, (13)), 1.19 (d, J = 6.9 Hz, 6H, (12)).

^{13}C NMR (75 MHz, $CDCl_3$): δ 154.14 (4CH, (2+6)), 139.03 (2CH, (4)), 126.23 (4CH, (3+5)), 102.72 (C_{quat}, (p-Cym)), 101.96 (C_{quat}, (p-Cym)), 88.71 (2CH, (8)), 81.97 (2CH, (7)), 30.83 (CH, (11)), 22.25 ($2CH_3$, (12)), 17.68 (CH_3, (13)).

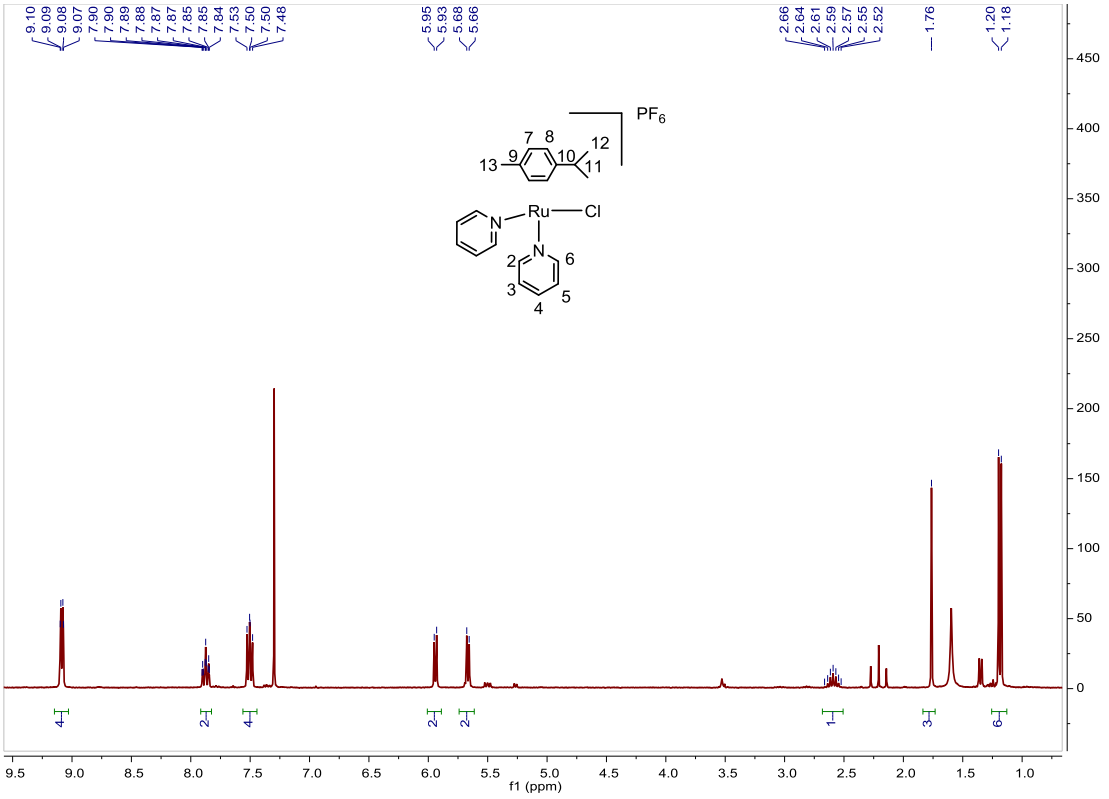

Fig. S73. ^{1}H NMR spectrum of **[Ru(p-Cym)(9)$_2$(Cl)]PF_6** in $CDCl_3$, 300 MHz.

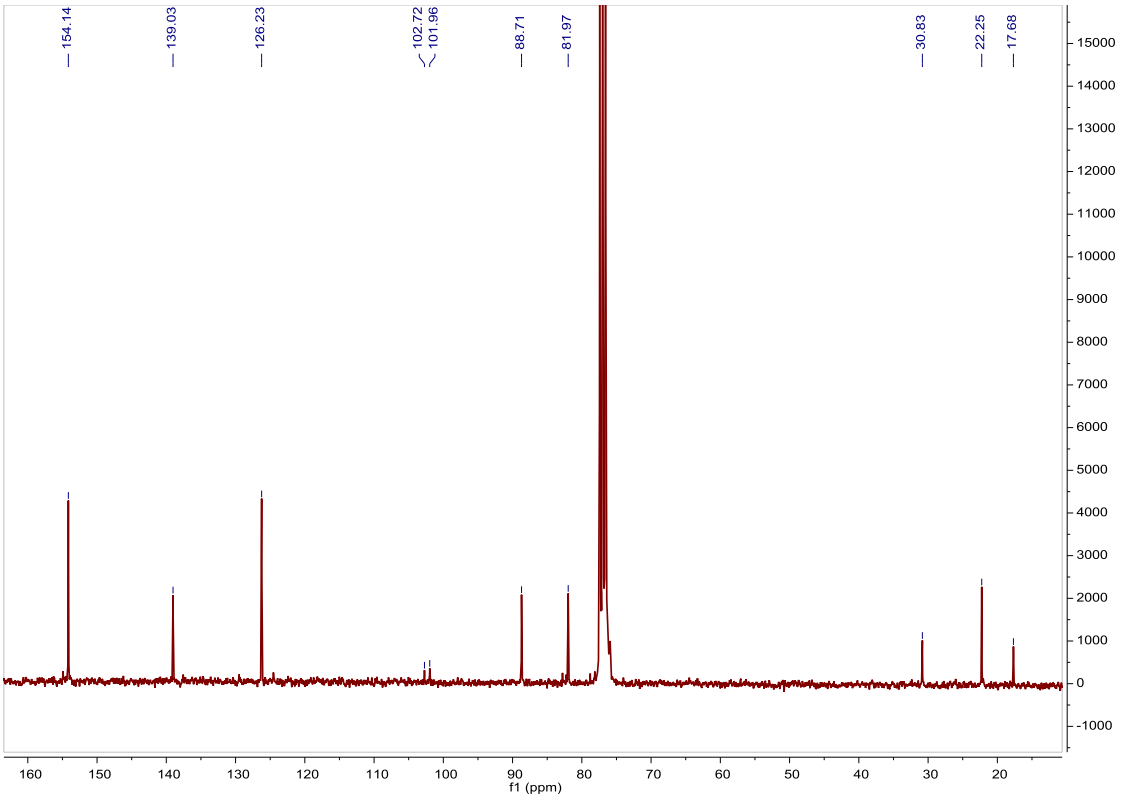

Fig. S74. ^{13}C NMR spectrum of **[Ru(p-Cym)(9)$_2$(Cl)]PF$_6$** in $CDCl_3$, 75 MHz.

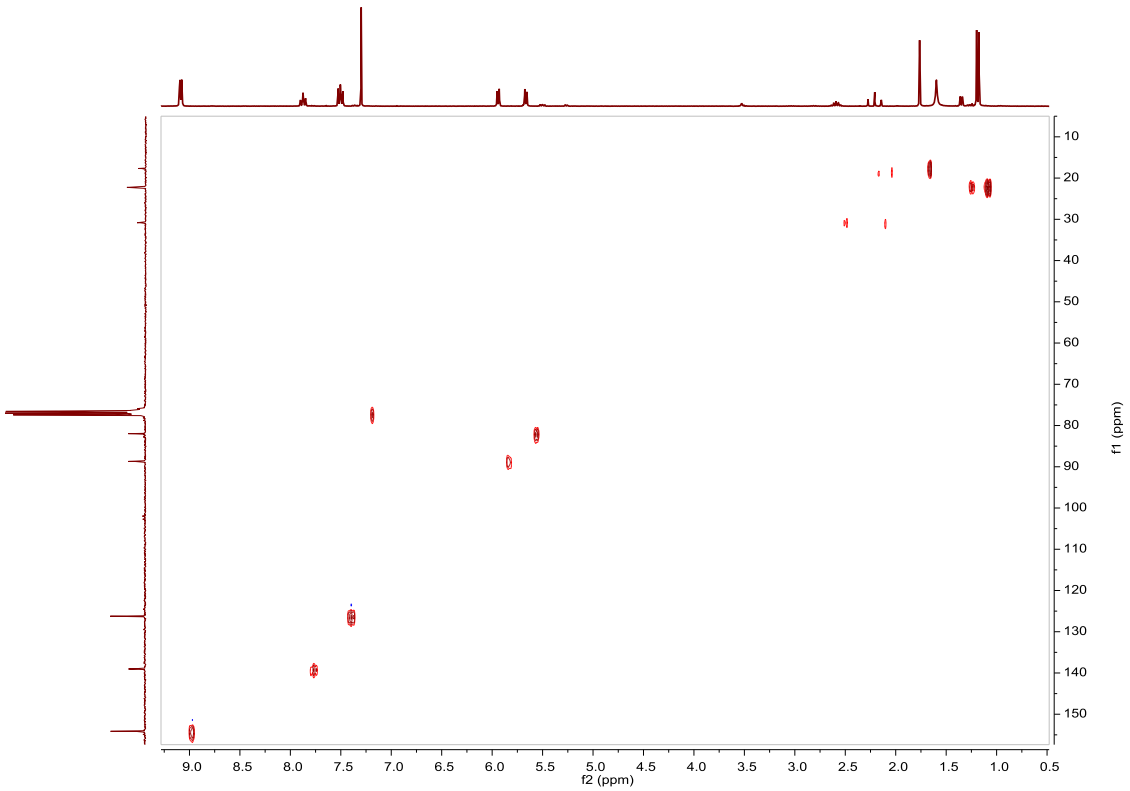

Fig. S75. HSQC NMR spectrum of **[Ru(p-Cym)(9)$_2$(Cl)]PF$_6$** in $CDCl_3$.

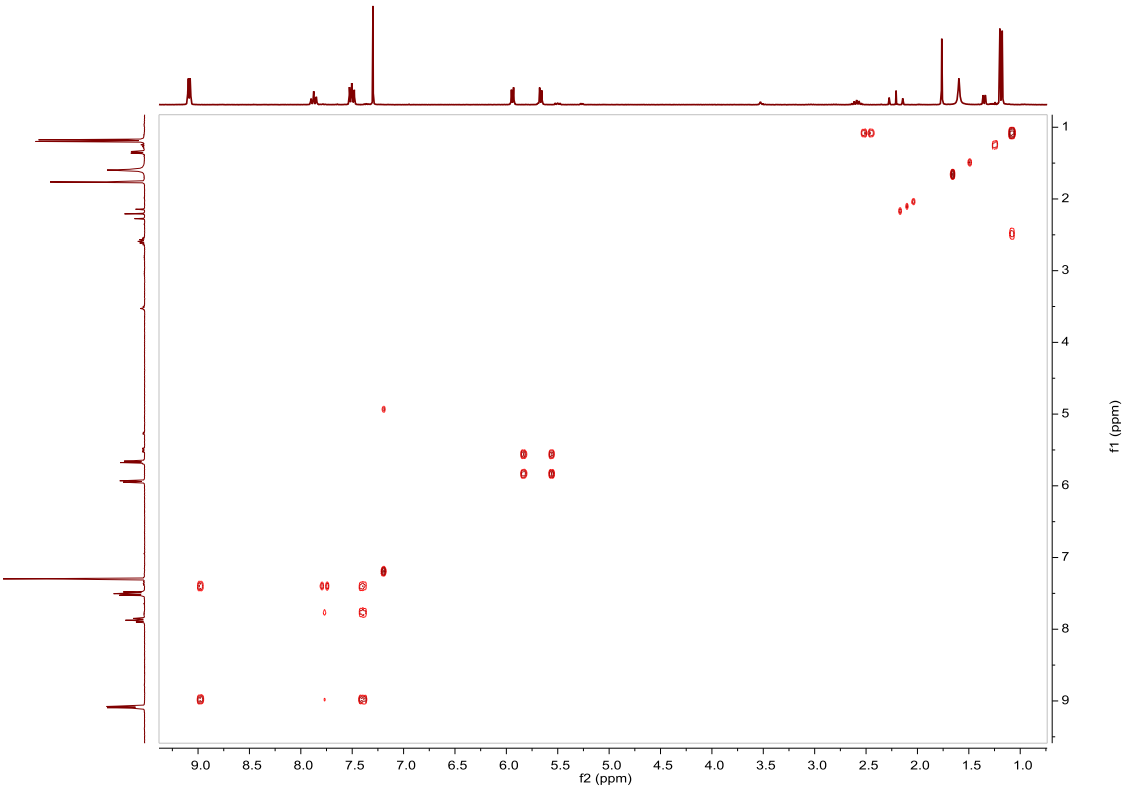

Fig. S76. COSY NMR spectrum of **[Ru(p-Cym)(9)$_2$(Cl)]PF$_6$** in $CDCl_3$.