Supporting Information

Facile Method to Obtain Functionalised η^6-Bound Arenes in Ru(II) and Os(II) Half-Sandwich Complexes

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General Experimental Details

Reagents and solvents

Reagents from commercial sources were used without further purification. $RuCl_3 \cdot 3H_2O$ was acquired from Precious Metals Online and $OsCl_3 \cdot 3H_2O$ from Heralab Technologies S.L. Methanol, dichloromethane, ethyl acetate, diethyl ether and pentane were acquired from VWR International. NMR solvent $CDCl_3$ was obtained from Fisher, while MeOD-d_4 and DMSO-d_6 from VWR international. Iodobenzene, 2-iodoaniline, caesium carbonate, bis(dibenzylideneacetone)palladium(0) ($Pd(dba)_2$), silver hexafluorophosphate and 2,2' bipyridine were acquired from Sigma-Aldrich. 2-Iodobenzyl alcohol and 4-iodobenzyl alcohol were from TCI. 6-Iodoquinoline was from FluoroChem and 2-iodophenylacetonitrile from Alfa Aesar. 8-Iodoquinoline and 8-iodo-coumarin were synthesised following previously reported methodologies.[1] ((4-Iodophenyl)ethynyl)trimethylsilane and 1,8-diazabicyclo[5.4.0]undec-7-ene were purchased in BLD Pharmatech, while 2-azide-1,3-dimethylimidazolinium hexafluorophosphate and nitrosobenzene in TCI.

Instrumentation and methods

Reactions involving heating were performed using heating plates with a thermocouple, while those at room temperature (RT) were carried out at 20-25 ºC. Evaporation of solvents under reduced pressure was carried out using a Büchi rotavapor R-200/210 with a Büchi V-491 heating bath and a Büchi V-800/850 vacuum controller. The rotary evaporator condenser is fitted to Huber Minichiller 280 recirculating cooler filled with ethylene glycol and set to 4 °C. Microwave-assisted reactions were performed in a Biotage Initiator+ microwave reactor, using the program described for individual syntheses in the appropriated microwave vials of different capacity depending on the reaction volume.

Characterization and analysis methods

Nuclear Magnetic Resonance (NMR) spectroscopy

^1H and $^{13}C\{^1H\}$ NMR spectra were acquired in 5 mm NMR tubes using a Bruker DPX 400 MHz spectrometer, by dissolving the compounds in the deuterated solvent at concentrations that vary depending on the analysis to be performed (approx. 1–3 mM). The chemical shifts in NMR were internally referenced to the residual ^1H and ^{13}C signals of the corresponding solvents: $CDCl_3$ (^1H: 7.26 ppm and ^{13}C: 77.16 ppm), MeOD-d_4 (^1H: 3,31 ppm and ^{13}C: 49,00 ppm) and DMSO-d_6 (^1H: 2.50 ppm and ^{13}C: 39.52 ppm). Chemical shifts values (δ) are reported in ppm and coupling constants (*J*) in hertz. The splitting of proton resonances in the reported spectra are defined as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). In ^{13}C APT spectra, methine (CH) and methyl (CH_3) signals are negative, and quaternary (C) and methylene (CH_2) signals are positive. 2D [^1H,^1H] COSY and ^1H-decoupled [^1H,^{13}C] HMQC/HSQC NMR spectra were recorded using standard pulse sequences by Bruker. Data processing was carried out using MestReNova, version 14.0 (Mestrelab Research, S.L.).

Elemental analysis

Elemental analysis (C, H, N) was carried out using a Leco analytical elemental analyser CHNS-932.

Mass spectrometry

Samples were prepared using a solution of 0.1% formic acid in methanol (reagent-grade), as mobile phase. The mass spectra were recorded with a scan range of m/z 150–900 for positive ions, using ion electrospray ionization mass spectra (ESI-MS) on an Advion Expression Compact mass spectrometer.

Single crystal X-ray diffraction

For complexes **13**, **15·PF_6**, **25** and **26**, single suitable crystals were coated with mineral oil, mounted on Mitegen MicroMounts and measured in a Bruker D8 KAPPA APEX II diffractometer with CCD area-detector at 150 K, equipped with graphite-monochromated Mo-Kα radiation source (λ = 0.71073 Å). The substantial redundancy in data allowed empirical absorption corrections (SADABS)[2] to be applied using multiple measurements of symmetry-equivalent reflections. Raw intensity data frames were integrated with the SAINT program, which also applied corrections for Lorentz and polarization effects. The Bruker SHELXTL Software Package was used for space group determination, structure solution, and refinement.[3] The space group determination was based on a check of the Laue symmetry, and systematic absences were confirmed using the structure solution. The structures were solved by direct methods (SHELXL-2014/7),[4] completed with different Fourier syntheses and refined with full-matrix least-squares using SHELXS minimizing $\omega(F_o^2\text{-}Fc^2)^2$. Weighted R factors (Rw) and goodness of fit (S) are based on F^2; conventional R factors (R) are based on F. All non-H atoms were refined with anisotropic displacement parameters. Hydrogen atom positions were geometrically calculated and allowed to ride on their parent carbon or nitrogen atoms with fixed isotropic U. All scattering factors and anomalous dispersion factors are contained in the SHELXTL 6.10 program library.

For complexes **11** and **12**, a suitable crystal was selected and placed on a MiTeGen micromount on an XtaLAB Synergy R, HyPix-Arc 100 diffractometer. The crystal was kept at a steady *T* = 150.00(10) K during data collection. The structure was solved with the ShelXT 2018/2 (Sheldrick, 2018) structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface.[5] The model was refined with version 2018/3 of ShelXL 2018/3 (Sheldrick, 2015) using Least Squares minimisation.

Mercury 3.10.1 was used for visualization and analysis of all crystal structures.

FT-IR Spectroscopy

FT-IR was carried out using a Bruker-ALPHA spectrometer, with platinum ATR single reflection diamond module installed. The samples were measured without the use of any preparation medium.

Synthesis and Characterization

Synthesis of 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid

1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid was prepared according to a literature procedure and the ^{1}H NMR was identical to those previously reported.[6]

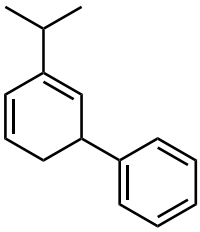
General procedure (I) for the synthesis of the arene precursors (A-H)

The procedure is a simplified version of the one published by Studer et al,[7] with the main difference that we obtain the functionalised products mixing the iodobenzene derivatives directly with 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid, instead of with 5-Isopropyl-1,2-dihydro-1,1'-biphenyl, which implies one less synthesis step.

1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (0.30 mmol) with an iodobenzene derivative (0.33 mmol; 1.1 equiv), Cs_2CO_3 (0.33 mmol;1.1 equiv) and $Pd(dba)_2$ (0.03 mmol; 0.1 equiv) were mixed in toluene (1 mL) inside of a pressure tube. The resulting mixture was bubbled with argon and stirred at 110 °C for 26 h. The reaction crude was extracted with water (10 mL), 1 M HCl (1 mL to pH 1) and CH_2Cl_2 (10 mL). The combined organic extracts were dried over $MgSO_4$, filtered and rota-evaporated to dryness. Purification by silica column chromatography (SiO_2), using an appropriate mobile phase for each type of substrate, afforded the desired coupling product.

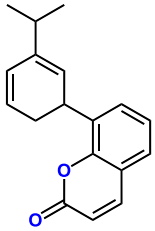
Synthesis of η^6 precursors (A-H)

5-Isopropyl-1,2-dihydro-1,1'-biphenyl (A)



According with general procedure I, the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (50 mg; 0.30 mmol), iodobenzene (67.3 mg; 0.33 mmol; 1.1 equiv), Cs_2CO_3 (107.8 mg; 0.33 mmol; 1.1 equiv) and $Pd(dba)_2$ (17.2 mg; 0.03 mmol; 0.1 equiv) in toluene (1 mL). Purification by flash column chromatography, using pentane as eluent, afforded **A** as a colourless liquid (42.6 mg; 70.6%). The ^{1}H NMR signals agreed with the literature.[7]

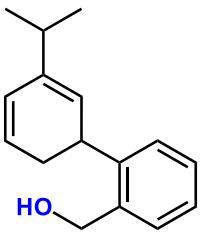
8-(3-Isopropylcyclohexa-2,4-dien-1-yl)coumarin (B)



A modification of the general procedure I was made, the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (691.7 mg; 4.2 mmol), 8-iodo-coumarin (1.6985 g; 6.2 mmol; 1.5 equiv), Cs_2CO_3 (2.033 mg; 6.2 mmol; 1.5 equiv) and $Pd(dba)_2$ (331.5 mg; 0.58 mmol; 0.14 equiv) in toluene (15 mL). Purification by flash column chromatography, using a 9.5:0.5 hexane:ethyl acetate mixture as eluent, afforded **B** as a fluorescent pale-yellow liquid (160 mg; 14.3%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.5 Hz, 1H, *H*-lactone), 7.56 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.34 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.22 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.42 (d, *J* = 9.5 Hz, 1H, *H*-lactone), 5.98 (d, *J* = 9.8 Hz, 1H, *H*-vinylic), 5.81 – 5.75 (m, 1H, *H*-vinylic), 5.46 (d, *J* = 4.3 Hz, 1H, *H*-vinylic), 4.31 (td, *J* = 9.7, 4.3 Hz, 1H, C*H*), 2.70 – 2.62 (m, 1H, C*H*-alkyl), 2.37 (m, *J* = 6.8 Hz, 1H, C*H*-$(CH_3)_2$), 2.31 – 2.24 (m, 1H, C*H*-alkyl), 1.09 (d, *J* = 6.8 Hz, 6H, $(CH_3)_2$). **^{13}C{^{1}H} NMR** NMR (101 MHz, $CDCl_3$) δ 161.06 (s, *C*=O), 151.51 (s, *C*-lactone), 144.15 (s, *C*H-lactone), 143.58 (s, Ar*C*), 133.56 (s, *C*-vinylic), 131.49 (s, Ar*C*H), 126.09 (s, Ar*C*H), 125.92 (s, *C*H-vinylic), 125.69 (s, *C*H-vinylic), 124.27 (s, Ar*C*H), 119.62 (s, *C*H-vinylic), 118.85 (s, *C*-lactone), 116.39 (s, *C*H-lactone), 33.50 (s, *C*H-$(CH_3)_2$), 31.43 (s, *C*H), 30.42 (s, *C*H_2-alkyl), 21.70 (s, $(CH_3)_2$). **MS (ESI)**: m/z calcd for $C_{18}H_{18}O_2Na$ ($[M+Na]^+$) 289.1; found 289.5.

(5'-Isopropyl-1',2'-dihydro-[1,1'-biphenyl]-2-yl)methanol (C)

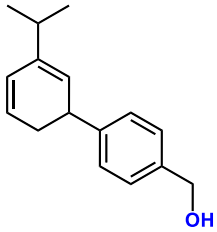


According with general procedure I, the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (50 mg; 0.30 mmol), 2-iodobenzyl alcohol (77.2 mg; 0.33 mmol; 1.1

equiv), Cs_2CO_3 (107.8 mg; 0.33 mmol; 1.1 equiv) and $Pd(dba)_2$ (17.2 mg; 0.03 mmol; 0.1 equiv) in toluene (1 mL). Purification by flash column chromatography, using a 7:3 dichloromethane:hexane mixture as eluent, afforded **C** as a pale-yellow liquid (38.3 mg; 68.5%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.38 (d, *J* = 7.4 Hz, 1H, Ar*H*), 7.29 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.23 (t, *J* = 7.4 Hz, 1H, Ar*H*), 5.98 (d, *J* = 9.8 Hz, 1H, *H*-vinylic), 5.87 – 5.78 (m, 1H, *H*-vinylic), 5.43 (d, *J* = 2.4 Hz, 1H, *H*-vinylic), 4.80 – 4.70 (m, 2H, C*H*$_2$), 4.00 – 3.90 (m, 1H, C*H*), 2.48 (m, 1H, C*H*-alkyl), 2.34 (m, 1H, C*H*-$(CH_3)_2$), 2.30 – 2.18 (m, 1H, C*H*-alkyl), 1.54 (t, *J* = 5.7 Hz, 1H, O*H*), 1.08 (d, *J* = 2.9 Hz, 3H, C*H*$_3$), 1.06 (d, *J* = 2.9 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 144.87 (s, Ar*C*), 142.44 (s, Ar*C*), 130.22 (s, *C*-vinylic), 128.66 (s, Ar*C*H), 128.61 (s, Ar*C*H), 128.48 (s, Ar*C*H), 128.36 (s, Ar*C*H), 126.55 (s, Ar*C*H), 125.91 (s, *C*H-vinylic), 125.74 (s, *C*H-vinylic), 121.85 (s, *C*H-vinylic), 63.36 (s, *C*H_2), 35.87 (s, *C*H), 33.37 (s, *C*H-$(CH_3)_2$), 32.01 (s, *C*H_2-alkyl), 21.71 (s, *C*H_3), 21.63 (s, *C*H_3). **MS (ESI)**: m/z calcd for $C_{16}H_{20}OK$ ($[M+K]^+$) 267.1; found 267.2.

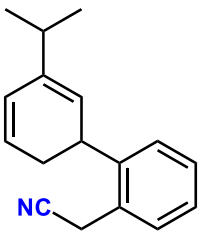
(5'-Isopropyl-1',2'-dihydro-[1,1'-biphenyl]-4-yl)methanol (D)



A modification of the general procedure I was made, the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (50 mg; 0.30 mmol), 4-iodobenzyl alcohol (105.3 mg; 0.45 mmol; 1.5 equiv), Cs_2CO_3 (146.6 mg; 0.45 mmol; 1.5 equiv) and $Pd(dba)_2$ (24.2 mg; 0.042 mmol; 0.14 equiv) in toluene (2 mL). Purification by flash column chromatography, using an 8:2 dichloromethane:hexane mixture as eluent, afforded **D** as a pale-yellow liquid (31.6 mg; 56.5%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 4H, Ar*H*), 5.98 (d, *J* = 9.8 Hz, 1H, *H*-vinylic), 5.82 (m, 1H, *H*-vinylic), 5.48 (d, *J* = 2.7 Hz, 1H, *H*-vinylic), 4.67 (s, 2H, C*H*$_2$), 3.64 – 3.50 (m, 1H, C*H*), 2.54 – 2.41 (m, 1H, C*H*-alkyl), 2.40 – 2.31 (m, 1H, C*H*-$(CH_3)_2$), 2.32 – 2.20 (m, 1H, C*H*-alkyl), 1.57 (s, 1H, O*H*), 1.08 (d, *J* = 1.7 Hz, 3H, C*H*$_3$), 1.06 (d, *J* = 1.7 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 145.89 (s, Ar*C*), 142.46 (s, Ar*C*), 138.91 (s, *C*-vinylic), 128.06 (s, 2C, Ar*C*H), 127.35 (s, 2C, Ar*C*H), 126.10 (s, *C*H-vinylic), 125.72 (s, *C*H-vinylic), 121.54 (s, *C*H-vinylic), 65.44 (s, *C*H_2), 39.94 (s, *C*H), 33.36 (s, *C*H-$(CH_3)_2$), 32.23 (s, *C*H_2-alkyl), 21.68 (d, *J* = 5.6 Hz, $(CH_3)_2$). **MS (ESI)**: m/z calcd for $C_{16}H_{20}OK$ ($[M+K]^+$) 267.1; found 267.2.

2-(5'-Isopropyl-1',2'-dihydro-[1,1'-biphenyl]-2-yl)acetonitrile (E)

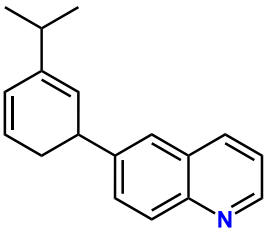


A modification of the general procedure I was made, the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (50 mg; 0.30 mmol), 2-iodophenylacetonitrile (145.8 mg; 0.45 mmol; 1.5 equiv), Cs_2CO_3 (146.6 mg; 0.45 mmol; 1.5 equiv) and $Pd(dba)_2$ (24.2 mg; 0.042 mmol; 0.14 equiv) in toluene (2 mL). Purification by flash column chromatography,

using a 6:4 dichloromethane:hexane mixture as eluent, afforded **E** as a yellow liquid (41.2 mg; 57.8%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 1H, Ar*H*), 7.40 – 7.36 (m, 1H, Ar*H*), 7.27 (m, 1H, Ar*H*), 5.99 (d, *J* = 9.8 Hz, 1H, *H*-vinylic), 5.89 – 5.78 (m, 1H, *H*-vinylic), 5.39 (d, *J* = 2.0 Hz, 1H, *H*-vinylic), 3.78 (d, *J* = 1.4 Hz, 2H, CH_2), 3.74 (m, 1H, C*H*), 2.47 (m, 1H, C*H*-alkyl), 2.35 (m, 1H, C*H*-(CH_3)$_2$), 2.23 (m, 1H, C*H*-alkyl), 1.08 (d, *J* = 2.8 Hz, 6H, (CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 144.20 (s, Ar*C*), 143.17 (s, *C*-vinylic), 129.45 (s, Ar*C*H), 129.04 (s, Ar*C*H), 128.77 (s, Ar*C*H), 127.69 (s, Ar*C*), 127.16 (s, Ar*C*H), 126.05 (s, *C*H-vinylic), 125.64 (s, *C*H-vinylic), 120.61 (s, *C*H-vinylic), 118.21 (s, *C*N), 36.78 (s, *C*H), 33.38 (s, *C*H-(CH_3)$_2$), 31.07 (s, *C*H_2-alkyl), 21.65 (s, *C*H_2), 21.56 (s, (*C*H_3)$_2$). **MS (ESI)**: m/z calcd for $C_{17}H_{19}NK$ $[M+K]^+$ 276.1; found 276.2.

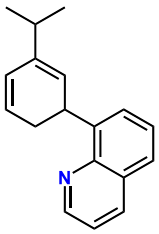
6-(3-Isopropylcyclohexa-2,4-dien-1-yl)quinoline (F)



A modification of the general procedure I was made, the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (452.7 mg; 2.72 mmol), 6-iodoquinoline (1.039 g; 4.07 mmol; 1.5 equiv), Cs_2CO_3 (1.327 mg; 4.07 mmol; 1.5 equiv) and $Pd(dba)_2$ (220 mg; 0.38 mmol; 0.14 equiv) in toluene (10 mL). Purification by flash column chromatography, using a 9:1 hexane:ethyl acetate mixture as eluent, afforded **F** as pale-yellow liquid (411 mg; 60.6 %).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (dd, *J* = 4.3, 1.7 Hz, 1H, Py*H*), 8.15 (dd, *J* = 7.9, 1.6 Hz, 1H, Py*H*), 8.09 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.71 (d, *J* = 8.7 Hz, 1H, Ar*H*), 7.68 (s, 1H, Ar*H*), 7.40 (m, 1H, Py*H*), 6.02 (d, *J* = 9.7 Hz, 1H, *H*-vinylic), 5.85 (m, 1H, *H*-vinylic), 5.56 (d, *J* = 1.2 Hz, 1H, *H*-vinylic), 3.76 (m, 1H, C*H*), 2.57 (m, 1H, C*H*-alkyl), 2.39 (m, 2H, C*H*-alkyl, C*H*-(CH_3)$_2$), 1.11 (dd, *J* = 6.8, 1.3 Hz, 6H, (CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, CDCl3) δ 149.09 (s, Py*C*H), 144.92 (s, Py*C*), 143.06 (s, Py*C*, Ar*C*), 136.88 (s, Py*C*H), 131.05 (s, Ar*C*H), 128.85 (s, Ar*C*H), 128.50 (s, *C*-vinylic), 126.19 (s, Py*C*H), 125.63 (s, *C*H-vinylic), 125.58 (s, *C*H-vinylic), 121.16 (s, Py*C*H), 120.75 (s, Ar*C*H), 40.00 (s, *C*H), 33.45 (s, *C*H-(CH_3)$_2$), 31.96 (s, *C*H_2-alkyl), 21.72 (s, *C*H_3), 21.67 (s, *C*H_3).

8-(3-Isopropylcyclohexa-2,4-dien-1-yl)quinoline (G)

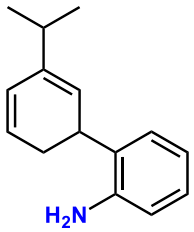


According with general procedure I, the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (50 mg; 0.30 mmol), 8-iodoquinoline (84.2 mg; 0.33 mmol; 1.1 equiv), Cs_2CO_3 (107.8 mg; 0.33 mmol; 1.1 equiv) and $Pd(dba)_2$ (17.2 mg; 0.03 mmol; 0.1 equiv) in toluene (1 mL). Purification by flash column chromatography, using a 9:1 hexane:ethyl acetate mixture as eluent, afforded **G** as a pale-yellow liquid (33.7 mg; 45.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.2, 1.8 Hz, 1H, Py*H*), 8.14 (dd, *J* = 8.2, 1.8 Hz, 1H, Py*H*), 7.74 (dd, *J* = 7.1, 1.3 Hz, 1H, Ar*H*), 7.68 (dd, *J* = 8.1, 1.3 Hz, 1H, Ar*H*), 7.50 (t, *J* = 7.7

Hz, 1H, Ar*H*), 7.39 (dd, *J* = 8.2, 4.2 Hz, 1H, Py*H*), 6.01 (d, *J* = 9.7 Hz, 1H, *H*-vinylic), 5.85 – 5.77 (m, 1H, *H*-vinylic), 5.61 (d, *J* = 2.8 Hz, 1H, *H*-vinylic), 5.05 (m, 1H, C*H*), 2.77 (m, 1H, C*H*-alkyl), 2.45 – 2.38 (m, 1H, C*H*-(CH_3)$_2$), 2.38 – 2.30 (m, 1H, C*H*-alkyl), 1.12 (d, *J* = 6.8 Hz, 6H, (C*H*$_3$)$_2$).**^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 149.44 (s, Py*C*H), 146.24 (s, Py*C*), 144.11 (s, Py*C*), 142.66 (s, Ar*C*), 136.59 (s, Py*C*H), 128.60 (s, *C*-vinylic), 128.01 (s, Ar*C*H), 126.19 (s, Ar*C*H), 125.99 (s, *C*H-vinylic), 125.82 (s, *C*H-vinylic), 121.89 (s, *C*H-vinylic), 120.95 (s, Py*C*H), 33.54 (s, *C*H-(CH_3)$_2$), 32.93 (s, *C*H), 31.41 (s, *C*H_2-alkyl), 21.80 (s, (*C*H_3)$_2$). **MS (ESI)**: m/z calcd for $C_{18}H_{19}NH$ $[M+H]^+$ 250.1; found 250.2.

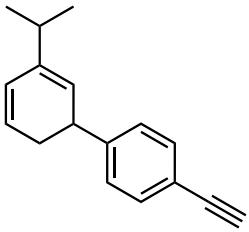
5'-Isopropyl-1',2'-dihydro-[1,1'-biphenyl]-2-amine (H)



According with general procedure I, the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (50 mg; 0.30 mmol), 2-iodoaniline (72.3 mg; 0.33 mmol; 1.1 equiv), Cs_2CO_3 (107.8 mg; 0.33 mmol; 1.1 equiv) and Pd(dba)$_2$ (17.2 mg; 0.03 mmol; 0.1 equiv) in toluene (1 mL). Purification by flash column chromatography, using a 3:2 hexane:dichlorometane mixture as eluent, afforded **H** as a yellow liquid (52.8 mg; 80.6%). The ^{1}H NMR signals agreed with the literature.[7]

Other precursors afforded from those previously synthesised (I-K)

4'-Ethynyl-5-Isopropyl-1,2-dihydro-1,1'-biphenyl (I)

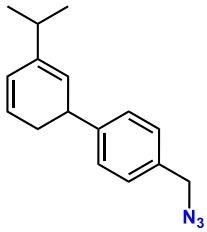


First, precursor ((5'-Isopropyl-1',2'-dihydro-[1,1'-biphenyl]-4-yl)ethynyl)trimethylsilane was synthesised through a modified version of the general procedure I (changing the equivalents), the reagents and amounts used were: 1-Isopropylcyclohexa-2,5-diene-1-carboxylic acid (740 mg; 4.45 mmol), ((4-iodophenyl)ethynyl)trimethylsilane (2.00 g; 6.66 mmol; 1.5 equiv), Cs_2CO_3 (2.17 g; 6.66 mmol; 1.5 equiv) and Pd(dba)$_2$ (358.3 mg; 0.62 mmol; 0.14 equiv) in toluene (16 mL). Purification by flash column chromatography, using hexane as eluent, afforded the desired product as a white solid (249.2 mg; 22.5%). Then, ((5'-Isopropyl-1',2'-dihydro-[1,1'-biphenyl]-4-yl)ethynyl)trimethylsilane (120 mg; 0.41 mmol) was dissolved in $CHCl_3$ (5 mL). To this solution, MeOH (5 mL) and K_2CO_3 (147.3 mg; 1.07 mmol; 2.6 equiv) were added. The mixture was degassed with argon and stirred at RT for 4 h. The white suspension was quenched adding H_2O (8 mL) and the mixture was left to stir for 15 min. The crude was extracted with $CHCl_3$ (5 x 2 mL), dried over $MgSO_4$, filtered out using a syringe filter and rota-evaporated until dryness, affording **I** as a colourless liquid (90 mg; 98.7%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.2 Hz, 2H, Ar*H*), 7.24 (d, *J* = 8.1 Hz, 2H, Ar*H*), 5.97 (d, *J* = 9.8 Hz, 1H, *H*-vinylic), 5.81 (m, 1H, *H*-vinylic), 5.45 (d, *J* = 2.9 Hz, 1H, *H*-vinylic), 3.55 (m, 1H, C*H*), 3.03 (s, 1H, *H*-alkyne), 2.46 (m, 1H, C*H*-alkyl), 2.34 (m, *J* = 6.9 Hz, 1H, C*H*-(CH_3)$_2$), 2.24 (m, 1H, C*H*-alkyl), 1.07 (d, *J* = 6.9 Hz, 6H, (C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 147.22 (s, Ar*C*), 142.76 (s, *C*-vinylic), 132.30 (s, 2C, Ar*C*H), 127.83 (s, 2C, Ar*C*H),

126.12 (s, *C*H-vinylic), 125.64 (s, *C*H-vinylic), 120.94 (s, *C*H-vinylic), 120.00 (s, Ar*C*), 83.95 (s, *C*-alkyne), 76.74 (s, *CH*-alkyne), 40.09 (s, *C*H), 33.38 (s, *C*H-$(CH_3)_2$), 32.01 (s, *C*H_2), 21.69 (s, *C*H_3), 21.64 (s, *C*H_3). **FT-IR**† (liquid, cm^{-1}) 3295 (ν(≡C–H)), 2109 (ν(C≡C)).

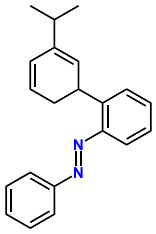
4'-(Azidomethyl)-5-isopropyl-1,2-dihydro-1,1'-biphenyl (J)



To a solution of (5'-Isopropyl-1',2'-dihydro-[1,1'-biphenyl]-4-yl)methanol (**D**; 334.4 mg: 1.46 mmol) in THF (7.3 mL), 2-azide-1,3-dimethylimidazolinium hexafluorophosphate (501 mg; 1.76 mmol; 1.2 equiv) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU; 283.13 µL; 288.8 mg; 1.90 mmol; 1.3 equiv) were added. The mixture was degassed with argon and stirred at RT during 2 h. The reaction was quenched with a saturated aqueous solution of NH_4Cl (8 mL) and extracted with DCM (16 x 2 mL). The combined organic fractions were washed with brine (8 x 2 mL) dried over $MgSO_4$, filtered and rota-evaporated until dryness. The crude was purified through a small SiO_2 column, using a 1:1 dichloromethane:hexane mixture as eluent, yielding **J** as a pale-yellow liquid (248 mg; 67.1%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.1 Hz, 2H, Ar*H*), 7.25 (d, *J* = 8.1 Hz, 2H, Ar*H*), 5.97 (d, *J* = 7.8 Hz, 1H, *H*-vinylic), 5.82 (m, 1H , *H*-vinylic), 5.48 (d, *J* = 4.2 Hz, 1H, *H*-vinylic), 4.31 (s, 2H, C*H*$_2$), 3.57 (m, 1H, C*H*), 2.52 – 2.42 (m, 1H, C*H*-alkyl), 2.35 (m, *J* = 6.8 Hz, 1H, C*H*-$(CH_3)_2$), 2.30 – 2.21 (m, 1H, C*H*-alkyl), 1.07 (d, *J* = 6.8 Hz, 6H, (C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 146.49 (s, Ar*C*), 142.62 (s, *C*-vinylic), 133.39 (s, Ar*C*), 128.45 (s, Ar*C*H), 128.30 (s, Ar*C*H), 126.12 (s, *C*H-vinylic), 125.70 (s, *C*H-vinylic), 121.32 (s, *C*H-vinylic), 54.81 (s, *C*H_2), 39.91 (s, *C*H), 33.38 (s, *C*H-$(CH_3)_2$), 32.14 (s, *C*H_2-alkyl), 21.71 (s, *C*H_3), 21.66 (s, *C*H_3). **MS (ESI)**: m/z calcd for $C_{16}H_{19}N_3COOHH$ $[M+COOH+H]^+$ 299.2; found 299.2. **FT-IR**† (liquid, cm^{-1}) 2091 (ν(N=N=N)).

(E)-1-(5'-Isopropyl-1',2'-dihydro-[1,1'-biphenyl]-2-yl)-2-phenyldiazene (K)



In a 25 mL flask, nitrosobenzene (93.8 mg; 0.876 mmol; 1.2 equiv) was dissolved in acetic acid glacial (6 mL), then **H** (157.3 mg; 0.73 mmol) was added. The mixture was degassed, covered with aluminium foil and heated at 40 ºC overnight. The reaction was quenched with H_2O (24 mL) and extracted with DCM (24 mL). The organic layer was washed with brine (24 x 2 mL), dried over Na_2SO_4, filtered and dried under vacuum. The crude was purified through a small column of SiO_2, eluting first with a 1:1 hexane:dichloromethane mixture, then with dichloromethane and finally with a 9:1 dichloromethane:ethyl acetate mixture, affording the desired product as a brown liquid (69.7 mg; 31.6%).

^{1}H NMR* (400 MHz, $CDCl_3$) δ 7.21 (dt, *J* = 8.6, 7.0 Hz, 4H, Ar*H*), 7.10 – 7.05 (m, 2H, Ar*H*), 7.05 – 6.98 (m, 4H, Ar*H*), 6.94 (t, *J* = 7.3 Hz, 2H, Ar*H*), 6.81 – 6.75 (m, 2H, Ar*H*), 6.73 – 6.64

(m, 4H, Ar*H*), 6.28 (dt, *J* = 6.3, 1.9 Hz, 1H, *H*-vinylic), 5.88 (dt, *J* = 6.2, 1.8 Hz, 1H, *H*-vinylic), 4.92 (m, 1H, *H*-vinylic), 4.75 (dd, *J* = 3.7, 1.9 Hz, 1H, *H*-vinylic), 4.53 (m, 1H, *H*-vinylic), 4.36 (t, *J* = 2.5 Hz, 1H, *H*-vinylic), 3.75 – 3.66 (m, 2H, C*H*), 2.67 (m, 1H, C*H*-alkyl), 2.55 (m, 1H, C*H*-alkyl), 1.99 (m, 1H, C*H*-alkyl), 1.92 (m, *J* = 6.8 Hz, 1H, C*H*-$(CH_3)_2$), 1.84 (m, 1H, C*H*-alkyl), 1.39 (m, *J* = 6.9 Hz, 1H, C*H*-$(CH_3)_2$), 0.75 (t, *J* = 6.6 Hz, 6H, $(CH_3)_2$), 0.35 (dd, *J* = 6.9, 4.5 Hz, 6H, $(CH_3)_2$). **^{13}C{^{1}H} NMR*** (101 MHz, $CDCl_3$) δ 152.14 (s, *C*-azo), 151.74 (s, *C*-azo), 149.48 (s, *C*-vinylic), 146.42 (s, *C*-vinylic), 144.46 (s, *C*-azo), 144.22 (s, *C*-azo), 128.45 (s, Ar*C*H), 128.41 (s, Ar*C*H), 127.84 (s, Ar*C*H), 127.82 (s, Ar*C*H), 127.65 (s, Ar*C*H), 127.56 (s, Ar*C*H), 125.80 (s, Ar*C*), 124.87 (s, Ar*C*), 122.85 (s, Ar*C*H), 122.29 (s, Ar*C*H), 121.70 (s, *C*H-vinylic), 120.13 (s, *C*H-vinylic), 118.88 (s, Ar*C*H), 118.36 (s, Ar*C*H), 117.99 (s, Ar*C*H), 115.97 (s, Ar*C*H), 115.91 (s, Ar*C*H), 73.39 (s, *C*H-vinylic), 69.96 (s, *C*H-vinylic), 63.98 (s, *C*H-vinylic), 57.84 (s, *C*H-vinylic), 35.42 (s, *C*H), 33.50 (s, *C*H), 32.48 (s, *C*H-$(CH_3)_2$), 32.19 (s, *C*H-$(CH_3)_2$), 31.03 (s, *C*H_2-alkyl), 29.54 (s, *C*H_2-alkyl), 20.80 (s, *C*H_3), 19.97 (s, *C*H_3), 19.43 (s, *C*H_3), 19.09 (s, *C*H_3).

MS (ESI): m/z calcd for $C_{21}H_{22}N_2(CH_2CHO)_2H$ $[M+2\ CH_2CHO+H]^+$ 389.2; found 388.9. **FT-IR**† (liquid, cm^{-1}) 1486 (ν(N=N)), 1296 (ν(C–N)).

*The spectrum shows two sets of signals in equal proportions, corresponding to the mixture of *cis*- and *trans*-isomers. For a more specific assignment, see Figure S9.

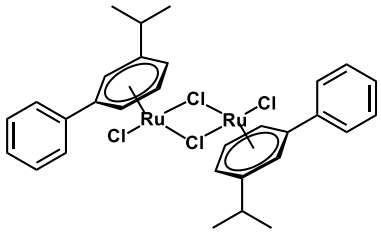
†The bands listed are the most characteristic of each functional group, the rest of the spectrum is shown in Figure S10.

General procedure (II) for the synthesis of the dimers/dichlorido-monomers precursors (1-14)

$MCl_3 \cdot 3H_2O$ (M = Ru or Os) (0.096 mmol) and the arene precursor (**A-H**) (0.288 mmol; 2 or 3 equiv) were mixed in MeOH (0.5 mL) in a 2 mL microwave vial. The reaction mixture was heated at 140 ºC for 5 min (Ru) or 30-60 min (Os) in the microwave reactor. In cases where a little amount of a fine black solid was observed, the resulting crude was filtered out using a syringe filter and the solution volume was reduced under vacuum. The desired product was precipitated and washed with diethyl ether or hexane, then vacuum dried.

Synthesis of dimers/dichlorido-monomers precursors (1-14)

[Ru(η^6-C_6H_4(^{i}Pr)(Ph))(μ-Cl)Cl]$_2$ (1)

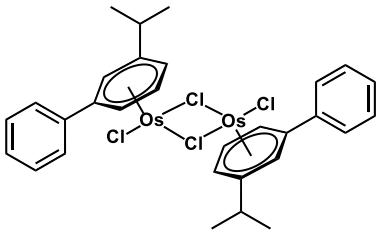


According with general procedure II, the reagents and amounts used were: $RuCl_3 \cdot 3H_2O$ (25.0 mg, 0.096 mmol) and **A** (65.8 mg; 0.288 mmol; 3 equiv) in MeOH (0.5 mL). The crude was filtered out using a syringe filter, and the solvent was removed under vacuum. The resultant solid was redissolved in few drops of dichloromethane and, after the addition of hexane, **1** precipitated as a bright-orange powder, which was washed with more hexane and dried under vacuum (21.6 mg; 62.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 6.4, 2.7 Hz, 2H, Ar*H*), 7.44 – 7.39 (m, 3H, Ar*H*), 5.95 (d, *J* = 2.3 Hz, 2H, η^6*H*), 5.72 (s, 1H, η^6*H*), 5.53 (t, *J* = 2.3 Hz, 1H, η^6*H*), 3.06 (m, *J* = 7.0 Hz, 1H, C*H*-$(CH_3)_2$), 1.31 (d, *J* = 6.9 Hz, 6H, $(CH_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 134.17 (s, Ar*C*), 129.81 (s, Ar*C*H), 129.36 (d, *J* = 2.5 Hz, Ar*C*H), 129.04 (s, *J* = 33.0 Hz, Ar*C*H), 103.13 (d, *J* = 14.3 Hz, η^6*C*), 95.41 (d, *J* = 12.5 Hz, η^6*C*), 83.26 (d, *J* = 4.0 Hz, η^6*C*H), 81.55 (d, *J* = 10.1

Hz, η⁶*C*H), 80.71 (d, *J* = 6.9 Hz, η⁶*C*H), 79.48 (s, η⁶*C*H), 31.12 (d, *J* = 8.4 Hz, *C*H-(CH_3)$_2$), 22.85 (d, *J* = 7.9 Hz, *C*H_3), 21.87 (d, *J* = 9.6 Hz, *C*H_3).

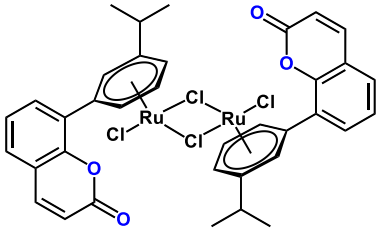
[Os(η⁶-C_6H_4(ⁱPr)(Ph))(μ-Cl)Cl]$_2$ (2)



According with general procedure II, the reagents and amounts used were: $OsCl_3 \cdot 3H_2O$ (42.8 mg, 0.123 mmol) and **A** (72.5 mg; 0.371 mmol; 3 equiv) in MeOH (3 mL). After heating for 30 min, a brown-yellow solution was obtained. The volume of the solution was reduced under vacuum until almost dryness. After the addition of Et_2O, **2** precipitated as a yellow-brown powder, which was washed with more Et_2O and dried under vacuum (30 mg; 58.1%).

¹H NMR (400 MHz, DMSO) δ 7.77 – 7.67 (m, 2H, Ar*H*), 7.51 – 7.42 (m, 3H, Ar*H*), 6.58 (d, *J* = 5.4 Hz, 1H, η⁶*H*), 6.53 (s, 1H, η⁶*H*), 6.40 (t, *J* = 5.4 Hz, 1H, η⁶*H*), 6.24 (d, *J* = 5.4 Hz, 1H, η⁶*H*), 2.94 – 2.81 (m, 1H C*H*-(CH_3)$_2$), 1.32 (d, *J* = 7.0 Hz, 3H, C*H*$_3$), 1.27 (d, *J* = 6.9 Hz, 3H , C*H*$_3$).

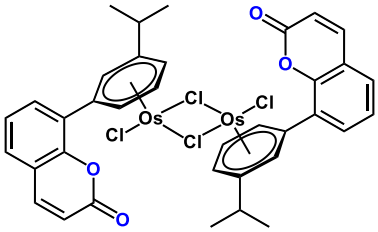
[Ru(η⁶-C_6H_4(ⁱPr)(coumarin))(μ-Cl)Cl]$_2$ (3)



General procedure II was carried out, using the following reagents and amounts: $RuCl_3 \cdot 3H_2O$ (43.8 mg, 0.168 mmol) and **B** (89.6 mg; 0.336 mmol; 2 equiv) in MeOH (1 mL). The crude was filtered out using a syringe filter, and the solution volume was reduced under vacuum until almost dryness. After the addition of diethyl ether, **3** precipitated as an orange powder, which was washed with more Et_2O and dried under vacuum (30.6 mg; 41.0%).

¹H NMR (400 MHz, DMSO) δ 8.13 (d, *J* = 9.6 Hz, 1H, *H*-lactone), 8.09 (dd, *J* = 7.7, 1.6 Hz, 1H, Ar*H*), 7.81 (dd, *J* = 7.7, 1.6 Hz, 1H, Ar*H*), 7.49 (t, *J* = 7.7 Hz, 1H, Ar*H*), 6.54 (d, *J* = 9.6 Hz, 1H, *H*-lactone), 6.34 (s, 1H, η⁶*H*), 6.22 (d, *J* = 5.7 Hz, 1H, η⁶*H*), 6.13 (t, *J* = 5.7 Hz, 1H, η⁶*H*), 6.08 (d, *J* = 5.9 Hz, 1H, η⁶*H*), 2.94 (m, *J* = 6.9 Hz, 1H, C*H*-(CH_3)$_2$), 1.31 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.28 (d, *J* = 6.9 Hz, 3H, C*H*$_3$). **¹³C{¹H} NMR** (101 MHz, DMSO) δ 159.12 (s, *C*=O), 151.90 (s, *C*-lactone), 144.23 (s, *C*H-lactone), 134.36 (s, Ar*C*H), 129.30 (s, Ar*C*H), 124.24 (s, Ar*C*H), 122.68 (s, Ar*C*), 118.88 (s, *C*-lactone), 116.36 (s, *C*H-lactone), 106.09 (s, η⁶*C*), 94.35 (s, η⁶*C*), 92.32 (s, η⁶*C*H), 90.00 (s, η⁶*C*H), 87.03 (s, η⁶*C*H), 81.36 (s, η⁶*C*H), 30.59 (d, *J* = 19.5 Hz, *C*H-(CH_3)$_2$), 22.00 (s, *C*H_3), 21.59 (s, *C*H_3).

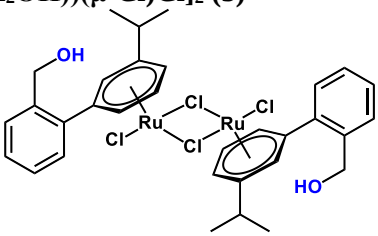
[Os(η^6-C$_6$H$_4$(^{i}Pr)(coumarin))(μ-Cl)Cl]$_2$ (4)



General procedure II was carried out, using the following reagents and amounts: $OsCl_3 \cdot 3H_2O$ (40.0 mg, 0.114 mmol) and **B** (60.0 mg; 0.228 mmol; 2 equiv) in MeOH (1.2 mL). The mixture was heated for 30 min. The crude was filtered out using a syringe filter, and the solution volume was reduced under vacuum until almost dryness. After the addition of diethyl ether, **4** precipitated as a yellow powder, which was washed with more Et_2O and dried under vacuum (40.2 mg; 67.1%).

^{1}H NMR (400 MHz, DMSO) δ 8.11 (d, *J* = 9.6 Hz, 1H, *H*-lactone), 7.91 (dd, *J* = 7.9, 1.6 Hz, 1H, Ar*H*), 7.78 (dd, *J* = 7.8, 1.6 Hz, 1H, Ar*H*), 7.45 (t, *J* = 7.7 Hz, 1H, Ar*H*), 6.52 (m, 1H, *H*-lactone, 2H, η^6*H*), 6.46 (t, *J* = 5.3 Hz, 1H, η^6*H*), 6.38 (d, *J* = 5.4 Hz, 1H, η^6*H*), 2.91 – 2.84 (m, 1H, C*H*-$(CH_3)_2$), 1.28 (t, *J* = 7.6 Hz, 6H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ 159.22 (s, *C*=O), 152.08 (s, *C*-lactone), 144.27 (s, *C*H-lactone), 134.13 (s, Ar*C*H), 129.07 (s, Ar*C*H), 124.28 (s, Ar*C*H), 123.64 (s, Ar*C*), 118.87 (s, *C*-lactone), 116.35 (s, *C*H-lactone), 97.17 (s, η^6*C*), 85.86 (s, η^6*C*H), 85.81 (s, η^6*C*), 82.69 (s, η^6*C*H), 79.01 (s, η^6*C*H), 73.17 (s, η^6*C*H), 30.55 (s, *C*H-$(CH_3)_2$), 22.13 (s, *C*H$_3$), 21.97 (s, *C*H$_3$).

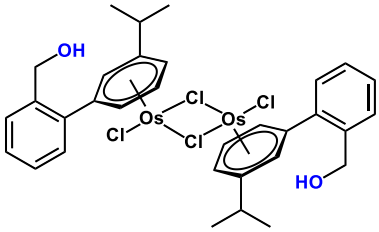
[Ru(η^6-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)-*o*-CH$_2$OH))(μ-Cl)Cl]$_2$ (5)



According with general procedure II, the reagents and amounts used were: $RuCl_3 \cdot 3H_2O$ (26.7 mg, 0.102 mmol) and **C** (70.0 mg; 0.306 mmol; 3 equiv) in MeOH (0.5 mL). The crude was filtered out using a syringe filter, and the solvent was removed under vacuum. The resultant mixture was redissolved in few drops of dichloromethane and, after the addition of hexane, **5** precipitated as an orange powder, which was washed with more hexane and dried under vacuum (34.9 mg; 86.0%).

^{1}H NMR (400 MHz, DMSO) δ 7.89 (d, *J* = 6.5 Hz, 1H, Ar*H*), 7.49 (d, *J* = 6.8 Hz, 1H, Ar*H*), 7.43 (t, *J* = 6.7 Hz, 1H, Ar*H*), 7.38 (t, *J* = 7.4 Hz, 1H, Ar*H*), 6.20 (s, 1H, η^6*H*), 6.04 (m, 2H, η^6*H*), 5.99 (t, *J* = 5.6 Hz, 1H, η^6*H*), 5.26 (t, *J* = 5.2 Hz, 1H, O*H*), 4.48 (m, 2H, CH_2), 2.92 (m, 1H, C*H*-$(CH_3)_2$), 1.26 (dd, *J* = 8.6, 7.1 Hz, 6H, (CH_3)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ 140.80 (s, Ar*C*), 133.74 (s, Ar*C*), 131.54 (s, Ar*C*H), 128.70 (s, Ar*C*H), 128.60 (s, Ar*C*H), 127.25 (s, Ar*C*H), 105.12 (s, η^6*C*), 100.65 (s, η^6*C*), 91.99 (s, η^6*C*H), 89.73 (s, η^6*C*H), 86.21 (s, η^6*C*H), 80.74 (s, η^6*C*H), 60.99 (s, *C*H$_2$), 30.35 (s, *C*H-$(CH_3)_2$), 21.74 (d, *J* = 8.6 Hz, (*C*H$_3$)$_2$).

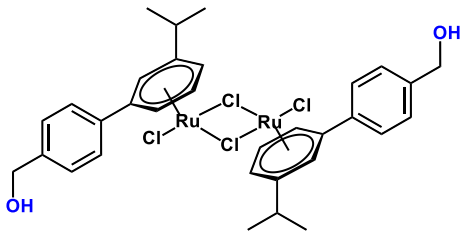
[Os(η^6-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)-*o*-CH$_2$OH))(μ-Cl)Cl]$_2$ (6)



According with general procedure II, the reagents and amounts used were: $OsCl_3 \cdot 3H_2O$ (55 mg, 0.16 mmol) and **C** (108 mg; 0.48 mmol; 3 equiv) in MeOH (1 mL). The mixture was heated for 60 min. The solvent was removed under vacuum. The resultant mixture was redissolved in few drops of dichloromethane and, after the addition of hexane, **6** precipitated as a yellow-green powder, which was washed with more hexane and dried under vacuum (78.6 mg; 84.2%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 2H, Ar*H*), 7.45 (t, *J* = 7.1 Hz, 1H, Ar*H*), 7.35 (d, *J* = 7.4 Hz, 1H, Ar*H*), 6.50 (t, *J* = 5.2 Hz, 1H, η^6*H*), 6.00 (d, *J* = 5.1 Hz, 1H, η^6*H*), 5.93 – 5.87 (m, 2H, η^6*H*), 5.55 – 5.45 (m, 2H, C*H*$_2$), 3.06 – 2.95 (m, 1H, C*H*-(CH$_3$)$_2$), 1.42 – 1.38 (m, 6H, (C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 134.29 (s, Ar*C*), 133.79 (s, Ar*C*), 130.58 (s, Ar*C*H), 129.85 (s, Ar*C*H), 129.81 (s, Ar*C*H), 129.48 (s, Ar*C*H), 103.45 (s, η^6*C*), 85.61(s, η^6*C*), 81.86 (s, η^6*C*H), 72.17 (s, *C*H$_2$), 69.78 (s, η^6*C*H), 68.20 (s, η^6*C*H), 54.57 (s, η^6*C*H), 31.84 (s, *C*H-(CH$_3$)$_2$), 22.21(s, (CH$_3$)$_2$).

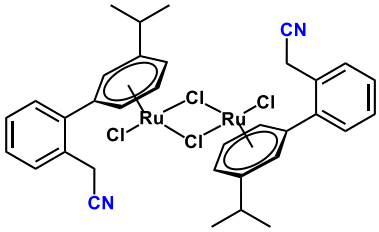
[Ru(η^6-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)-*p*-CH$_2$OH))(μ-Cl)Cl]$_2$ (7)



According with general procedure II, the reagents and amounts used were: $RuCl_3 \cdot 3H_2O$ (25.0 mg, 0.096 mmol) and **D** (65.8 mg; 0.288 mmol; 3 equiv) in MeOH (0.5 mL). The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to obtain **7** as an orange powder (21.0 mg; 55.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H, Ar*H*), 7.41 (d, *J* = 7.8 Hz, 2H, Ar*H*), 5.94 (s, 2H, η^6*H*), 5.70 (d, *J* = 3.6 Hz, 1H, η^6*H*), 5.53 (m, 1H, η^6*H*), 4.71 (s, 2H, C*H*$_2$), 3.11 – 2.97 (m, 1H, C*H*-(CH$_3$)$_2$), 1.52 (s, 1H, O*H*), 1.31 (d, *J* = 6.8 Hz, 6H, (C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 142.70 (s, Ar*C*), 133.35 (s, Ar*C*), 129.58 (d, *J* = 2.9 Hz, Ar*C*H), 127.45 (s, Ar*C*H), 103.50 (s, η^6*C*), 95.50 (s, η^6*C*), 83.44 (d, *J* = 4.3 Hz, η^6*C*H), 81.16 (d, *J* = 13.4 Hz, η^6*C*H), 80.22 (s, η^6*C*H), 79.12 (d, *J* = 4.1 Hz, η^6*C*H), 64.98 (s, *C*H$_2$), 31.18 (s, *C*H-(CH$_3$)$_2$), 22.87 (d, *J* = 5.7 Hz, *C*H$_3$), 21.85 (d, *J* = 7.6 Hz, *C*H$_3$).

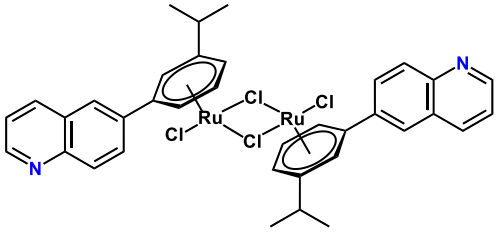
[Ru(η^6-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)CH$_2$CN))(μ-Cl)Cl]$_2$ (8)



According with general procedure II, the reagents and amounts used were: $RuCl_3 \cdot 3H_2O$ (43.0 mg, 0.160 mmol) and **E** (117.0 mg; 0.493 mmol; 3 equiv) in MeOH (0.5 mL). The solution volume was reduced under vacuum until almost dryness and a brown-yellow powder was precipitated after the addition of Et_2O. The solid was washed with Et_2O and cold ethanol, to obtain **8** as a yellow powder (45.7 mg; 70.1%).

^{1}H NMR (400 MHz, DMSO) δ 7.91 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.56 – 7.51 (m, 2H, Ar*H*), 7.35 – 7.25 (m, 1H, Ar*H*), 6.13 (s, 1H, η^6*H*), 6.08 – 6.05 (m, 2H, η^6*H*), 6.01 (d, *J* = 4.9 Hz, 1H, η^6*H*), 4.35 – 4.20 (m, 2H, C*H*$_2$), 2.95 – 2.88 (m, 1H, C*H*-(CH$_3$)$_2$), 1.25 (d, *J* = 9.0 Hz, 6H, (C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ 134.02 (s, Ar*C*), 132.44 (s, Ar*C*H), 130.33 (s, Ar*C*), 129.58 (s, Ar*C*H), 129.01 (s, Ar*C*H), 128.15 (s, Ar*C*H), 118.94 (s, *C*N), 105.76 (s, η^6*C*), 100.38 (s, η^6*C*), 92.03 (s, η^6*C*H), 89.39 (s, η^6*C*H), 85.85 (s, η^6*C*H), 81.66 (s, η^6*C*H), 30.44 (s, *C*H-(CH$_3$)$_2$), 23.81 (s, *C*H$_3$), 21.87 (s, *C*H$_3$), 21.40 (d, *J* = 7.6 Hz, *C*H$_2$).

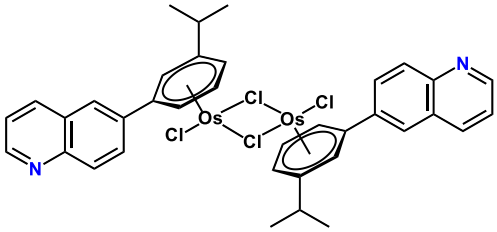
[Ru(η^6-C$_6$H$_4$(^{i}Pr)(quinoline))(μ-Cl)Cl]$_2$ (9)



General procedure II was carried out, using the following reagents and amounts: $RuCl_3 \cdot 3H_2O$ (100 mg, 0.382 mmol) and **F** (190 mg; 0.764 mmol; 2 equiv) in MeOH (4.8 mL). The crude was separated through centrifugation. The precipitate was washed with MeOH and Et_2O. Then, the precipitate was redissolved in acetonitrile and washed several times. The washing waters were collected, and the solvent was removed under vacuum yielding **9** as an orange solid (99.8 mg; 62.3%).

^{1}H NMR (400 MHz, DMSO) δ 9.07 (d, *J* = 4.4 Hz, 1H, Py*H*), 8.65 – 8.58 (m, 2H, Py*H*), 8.28 (d, *J* = 7.7 Hz, 1H, Ar*H*), 8.17 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.74 (dd, *J* = 8.5, 4.5 Hz, 1H, Py*H*), 6.54 (s, 1H, η^6*H*), 6.45 (d, *J* = 5.9 Hz, 1H, η^6*H*), 6.20 (t, *J* = 5.8 Hz, 1H, η^6*H*), 6.00 (d, *J* = 5.7 Hz, 1H, η^6*H*), 3.05 – 2.97 (m, 1H, C*H*-(CH$_3$)$_2$), 1.37 (d, *J* = 7.0 Hz, 3H, *C*H$_3$), 1.31 (d, *J* = 6.8 Hz, 3H, *C*H$_3$). **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ 149.99 (s, Py*C*), 147.70 (s, Py*C*H), 138.90 (s, Py*C*), 131.92 (s, Ar*C*H), 129.74 (s, Ar*C*H), 129.48 (s, Ar*C*H), 128.26 (s, Ar*C*), 126.97 (s, Py*C*H), 126.32 (s, Py*C*H), 109.68 (s, η^6*C*), 98.90 (s, η^6*C*), 87.38 (s, η^6*C*H), 85.85 (s, η^6*C*H), 85.69 (s, η^6*C*H), 84.40 (s, η^6*C*H), 31.28 (s, *C*H-(CH$_3$)$_2$), 24.38 (s, *C*H$_3$), 22.16 (d, *J* = 21.8 Hz, *C*H$_3$).

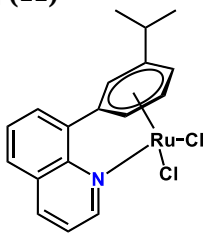
[Os(η^6-C$_6$H$_4$(^{i}Pr)(quinoline))(μ-Cl)Cl]$_2$ (10)



General procedure II was carried out, using the following reagents and amounts: $OsCl_3 \cdot 3H_2O$ (100 mg, 0.285 mmol) and **F** (142 mg; 0.57 mmol; 2 equiv) in MeOH (4 mL). The reaction was heated for 60 min. The crude was separated through centrifugation. The precipitate was washed with MeOH and Et_2O. Then, the precipitate was redissolved in acetonitrile and washed several times. The washing waters were collected, and the solvent was removed under vacuum affording **10** as yellow solid (101.3 mg; 69.9%).

^{1}H NMR (400 MHz, DMSO) δ 9.04 (dd, *J* = 4.5, 1.6 Hz, 1H, Py*H*), 8.57 (d, *J* = 8.5 Hz, 1H, Py*H*), 8.49 (s, 1H, Ar*H*), 8.14 (d, *J* = 1.3 Hz, 2H, Ar*H*), 7.72 (dd, *J* = 8.3, 4.4 Hz, 1H, Py*H*), 6.78 (d, *J* = 5.4 Hz, 1H, η^6*H*), 6.74 (s, 1H, η^6*H*), 6.51 (t, *J* = 5.5 Hz, 1H, η^6*H*), 6.31 (d, *J* = 5.4 Hz, 1H, η^6*H*), 2.96 – 2.88 (m, 1H, C*H*-(CH$_3$)$_2$), 1.36 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.31 (d, *J* = 7.0 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ 151.61 (s, Py*C*), 150.16 (s, Py*C*H), 138.28 (s, Py*C*H), 134.59 (s, Py*C*), 131.73 (s, Ar*C*H), 129.48 (s, Ar*C*H), 128.34 (s, Ar*C*), 127.11 (s, Ar*C*H), 122.78 (s, Py*C*H), 101.07 (s, η^6*C*), 90.74 (s, η^6*C*), 80.51 (s, η^6*C*H), 78.47 (s, η^6*C*H), 77.99 (s, η^6*C*H), 75.77 (s, η^6*C*H), 31.17 (s, *C*H-(CH$_3$)$_2$), 22.38 (s, 2C, (*C*H$_3$)$_2$).

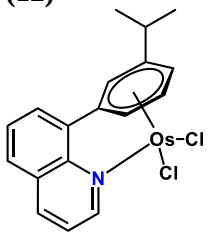
[Ru(η^6:κ^1-C$_6$H$_4$(^{i}Pr)(quinoline))(Cl)$_2$] (11)



According with general procedure II, the reagents and amounts used were: $RuCl_3 \cdot 3H_2O$ (25.0 mg, 0.096 mmol) and **G** (71.8 mg; 0.288 mmol; 3 equiv) in MeOH (0.50 mL). The obtained solid was centrifuged and washed with cold MeOH and then with Et_2O. After drying it under vacuum, **11** was afforded as a bright orange powder (20.2 mg; 51.3%). Orange-brown crystals suitable for X-ray diffraction were yielded by slow evaporation of methanol at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 5.1, 1.5 Hz, 1H, Py*H*), 8.31 (dd, *J* = 8.4, 1.4 Hz, 1H, Py*H*), 7.99 – 7.92 (m, 2H, Ar*H*), 7.73 (dd, *J* = 8.2, 7.1 Hz, 1H, Ar*H*), 7.52 (dd, *J* = 8.4, 5.1 Hz, 1H, Py*H*), 6.12 (t, *J* = 5.7 Hz, 1H, η^6*H*), 5.47 (m, *J* = 5.6 Hz, 2H, η^6*H*), 5.31 (s, 1H, η^6*H*), 3.14 (m, *J* = 6.8 Hz, 1H, C*H*-(CH$_3$)$_2$), 1.44 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.34 (d, *J* = 7.0 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 155.80 (s, Py*C*H), 155.68 (s, Py*C*), 138.15 (s, Py*C*H), 135.56 (s, Py*C*), 129.21 (s, Ar*C*H), 128.86 (s, Ar*C*), 128.77 (s, Ar*C*H), 127.62 (s, Ar*C*H), 124.27 (s, Py*C*H), 116.29 (s, η^6*C*), 103.51 (s, η^6*C*), 93.11 (s, η^6*C*H), 77.37 (s, η^6*C*H), 76.20 (s, η^6*C*H), 69.96 (s, η^6*C*H), 31.76 (s, *C*H-(CH$_3$)$_2$), 22.47 (s, *C*H$_3$), 21.79 (s, *C*H$_3$).

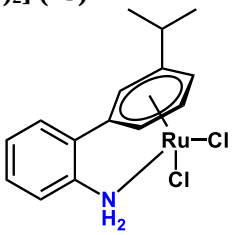
[Os(η^6:κ^1-C$_6$H$_4$(^{i}Pr)(quinoline))(Cl)$_2$] (12)



According with general procedure II, the reagents and amounts used were: $OsCl_3 \cdot 3H_2O$ (45.0 mg, 0.13 mmol) and **G** (96 mg; 0.38 mmol; 3 equiv) in MeOH (0.75 mL). The mixture was heated for 60 min. The obtained solid was centrifuged, washed with cold MeOH and Et_2O. Then, it was redissolved in DCM and filtrated out with a pad of neutral alumina to afford **12** as a yellow powder (25 mg; 38.0%). Yellow crystals suitable for X-ray diffraction were afforded by slow evaporation of methanol at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (dd, *J* = 5.2, 1.4 Hz, 1H, Py*H*), 8.36 (dd, *J* = 8.4, 1.3 Hz, 1H, Py*H*), 8.01 (d, *J* = 7.1 Hz, 1H, Ar*H*), 7.89 (d, *J* = 7.3 Hz, 1H, Ar*H*), 7.73 – 7.65 (m, 1H, Ar*H*), 7.57 (dd, *J* = 8.4, 5.2 Hz, 1H, Py*H*), 6.39 (t, *J* = 5.3 Hz, 1H, η^6*H*), 5.98 (d, *J* = 5.4 Hz, 1H, η^6*H*), 5.83 (d, *J* = 5.1 Hz, 1H, η^6*H*), 5.78 (s, 1H, η^6*H*), 3.00 (m, *J* = 6.9 Hz, 1H, C*H*-(CH_3)$_2$), 1.44 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.36 (d, *J* = 7.0 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 158.81 (s, Py*C*), 155.01 (s, Py*C*H), 138.28(s, Py*C*H), 137.53 (s, Py*C*), 130.57 (s, Ar*C*H), 129.36 (s, Ar*C*), 128.49 (s, Ar*C*H), 128.03 (s, Ar*C*H), 124.52 (s, Py*C*H), 107.81 (s, η^6*C*), 90.91 (s, η^6*C*), 85.48 (s, η^6*C*H), 69.42 (s, η^6*C*H), 68.19 (s, η^6*C*H), 60.62 (s, η^6*C*H), 31.47 (s, *C*H-(CH_3)$_2$), 22.91 (s, *C*H$_3$), 22.05 (s, *C*H$_3$).

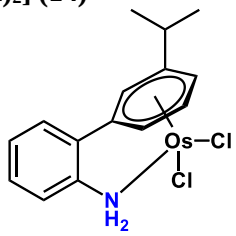
[Ru(η^6:κ^1-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)NH$_2$))(Cl)$_2$] (13)



According with general procedure II, the reagents and amounts used were: $RuCl_3 \cdot 3H_2O$ (26.7 mg, 0.102 mmol) and **H** (65.3 mg; 0.306 mmol; 3 equiv) in MeOH (0.55 mL). The solution volume was reduced under vacuum until almost dryness and a pale-red powder was precipitated after the addition of Et_2O. The solid was washed with Et_2O and DCM, to afford **13** as a yellow powder (31.6 mg; 81.0%). Yellow crystals suitable for X-ray diffraction were afforded by slow evaporation of dichloromethane at room temperature.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.7 Hz, 1H, Ar*H*), 7.50 – 7.44 (m, 1H, Ar*H*), 7.44 – 7.36 (m, 2H, Ar*H*), 5.94 (t, *J* = 5.6 Hz, 1H, η^6*H*), 5.44 (s, 2H, N*H*$_2$), 5.40 (d, *J* = 5.9 Hz, 1H, η^6*H*), 5.25 (d, *J* = 5.4 Hz, 1H, η^6*H*), 5.02 (s, 1H, η^6*H*), 3.03 (m, *J* = 6.9 Hz, 1H, C*H*-(CH_3)$_2$), 1.40 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.32 (d, *J* = 7.0 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 147.97 (s, *C*-NH_2), 136.80 (s, Ar*C*), 130.20 (s, Ar*C*H), 128.04 (s, Ar*C*H), 127.53 (s, Ar*C*H), 127.17 (s, Ar*C*H), 114.59 (s, η^6*C*), 103.03 (s, η^6*C*), 91.72 (s, η^6*C*H), 75.46 (s, η^6*C*H), 74.32 (s, η^6*C*H), 70.26 (s, η^6*C*H), 31.72 (s, *C*H-(CH_3)$_2$), 22.49 (s, *C*H$_3$), 21.63 (s, *C*H$_3$).

[Os(η^6:κ^1-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)NH$_2$))(Cl)$_2$] (14)

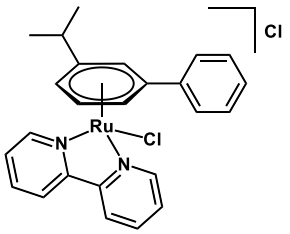


According with general procedure II, the reagents and amounts used were: $OsCl_3 \cdot 3H_2O$ (60 mg, 0.17 mmol) and **H** (110 mg; 0.306 mmol; 3 equiv) in MeOH (0.51 mL). The crude was filtered out using a syringe filter and the solvent was removed under vacuum. The solid was purified through neutral alumina, using as eluent ethyl acetate (EtOAc), then acetonitrile and finally methanol. This last one fraction was dried and then redissolved in EtOAc. Finally, it was filtrated out with a syringe filter (to separate the remaining silica) and dried under vacuum, to afford **14** as a dark red solid (21 mg; 26.0%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 6.2 Hz, 1H, Ar*H*), 7.41 (m, 3H, Ar*H*), 6.28 (t, *J* = 5.2 Hz, 1H, η^6*H*), 5.96 (d, *J* = 5.5 Hz, 1H, η^6*H*), 5.63 (m, 2H, η^6*H*, N*H*), 5.52 (s, 1H, η^6*H*), 2.88 (m, *J* = 7.0 Hz, 1H, C*H*-(CH_3)$_2$), 1.41 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.36 (d, *J* = 7.0 Hz, 3H, C*H*$_3$).

Synthesis of monomers (15-28)

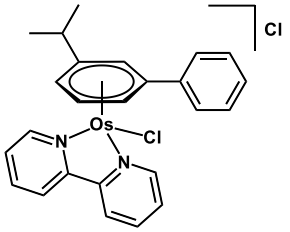
[Ru(η^6-C$_6$H$_4$(^{i}Pr)(Ph))(bpy)Cl]Cl (15)



Complex **1** (15 mg; 0.02 mmol) and 2,2' bipyridine (bpy) (6.2 mg; 0.04 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred at RT for 1 hour. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **15** as a brown-yellow powder (18.2 mg; 86.8%). Orange crystals suitable for X-ray diffraction were afforded in a mixture of **15** and NH_4PF_6 (~5 equiv) in MeOH at -20 °C, affording crystals of **15** with one molecule of PF_6 (**15·PF$_6$**).

^{1}H NMR (400 MHz, DMSO) δ 9.43 (d, *J* = 5.1 Hz, 1H, bpy*H*), 9.06 (d, *J* = 4.9 Hz, 1H, bpy*H*), 8.64 (d, *J* = 7.8 Hz, 1H, bpy*H*), 8.59 (d, *J* = 7.8 Hz, 1H, bpy*H*), 8.29 (t, *J* = 8.0 Hz, 1H, bpy*H*), 8.16 (t, *J* = 7.9 Hz, 1H, bpy*H*), 7.83 – 7.73 (m, 1H, bpy*H*), 7.71 – 7.61 (m, 2H, Ar*H*), 7.51 – 7.47 (m, 1H, bpy*H*), 7.46 (t, *J* = 4.8 Hz, 1H, Ar*H*), 7.39 (t, *J* = 7.4 Hz, 2H, Ar*H*), 6.61 (t, *J* = 6.1 Hz, 1H, η^6*H*), 6.56 (s, 1H, η^6*H*), 6.42 (d, *J* = 6.0 Hz, 1H, η^6*H*), 6.11 (d, *J* = 6.0 Hz, 1H, η^6*H*), 3.03 – 2.90 (m, 1H, C*H*-(CH_3)$_2$), 1.32 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.14 (d, *J* = 6.9 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ 155.64 (s, bpy*C*H), 155.16 (s, bpy*C*H), 154.44 (s, bpy*C*), 154.08 (s, bpy*C*), 139.95 (s, *J* = 24.0 Hz, bpy*C*H), 139.71 (s, bpy*C*H), 132.85 (s, Ar*C*), 130.08 (s, Ar*C*H), 128.79 (s, 2C, Ar*C*H), 128.56 (s, 2C, Ar*C*H), 127.56 (s, bpy*C*H), 127.33 (s, bpy*C*H), 123.82 (s, *J* = 29.8 Hz, bpy*C*H), 123.53 (s, bpy*C*H), 111.57 (s, η^6*C*), 100.22 (s, η^6*C*), 90.23 (s, η^6*C*H), 81.67 (s, 2C, η^6*C*H), 80.94 (s, η^6*C*H), 31.12 (s, *C*H-(CH_3)$_2$), 21.83 (s, *C*H$_3$), 21.40 (s, *C*H$_3$). **MS (ESI)**: m/z calcd for $C_{25}H_{24}ClN_2Ru$ $[M]^+$ 489.1; found 489.0. **Elemental analysis**: Calcd for $C_{25}H_{24}Cl_2N_2Ru \cdot 1.5\ H_2O$ (551.47) C, 54.45; H, 4.93; N 5.08%. Found C, 54.23; H, 5.20; N, 4.95%.

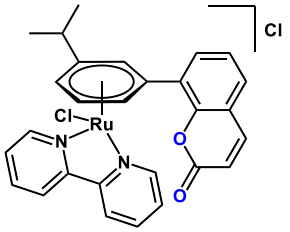
[Os(η^6-C$_6$H$_4$(^{i}Pr)(Ph))(bpy)Cl]Cl (16)



Complex **2** (15 mg; 0.02 mmol) and 2,2' bipyridine (bpy) (6.2 mg; 0.04 mmol; 2 Equiv) were dissolved in MeOH (1 mL) and stirred at RT overnight. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **16** as a brown-yellow powder (18.2 mg; 86.8%).

^{1}H NMR (400 MHz, MeOD) δ 9.19 (d, *J* = 5.7 Hz, 1H, bpy*H*), 8.83 (d, *J* = 5.4 Hz, 1H, bpy*H*), 8.58 (d, *J* = 8.1 Hz, 1H, bpy*H*), 8.53 (d, *J* = 7.9 Hz, 1H, bpy*H*), 8.21 (t, *J* = 7.9 Hz, 1H, bpy*H*), 8.07 (t, *J* = 7.9 Hz, 1H, bpy*H*), 7.67 (t, *J* = 6.7 Hz, 1H, bpy*H*), 7.48 (m, 2H, Ar*H*), 7.42 (m, 1H, Ar*H*), 7.35 (m, 2H, Ar*H*, 1H, bpy*H*), 6.65 (s, 1H, η^6*H*), 6.60 (t, *J* = 5.6 Hz, 1H, η^6*H*), 6.48 (d, *J* = 5.8 Hz, 1H, η^6*H*), 6.26 (d, *J* = 5.8 Hz, 1H, η^6*H*), 3.03 – 2.90 (m, 1H, C*H*-(CH$_3$)$_2$), 1.37 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.33 (d, *J* = 7.0 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 158.60 (s, bpy*C*), 156.73 (s, bpy*C*), 154.96 (s, bpy*C*H), 154.49 (s, bpy*C*H), 139.84 (s, bpy*C*H), 139.59 (s, bpy*C*H), 133.23 (s, Ar*C*), 129.68 (s, Ar*C*H), 128.96 (s, 3C, Ar*C*H), 128.36 (s, 2C, Ar*C*H), 128.00 (s, bpy*C*H), 127.73 (s, bpy*C*H), 123.61 (s, bpy*C*H), 123.22 (s, bpy*C*H), 105.35 (s, η^6*C*), 100.74 (s, η^6*C*), 80.35 (s, η^6*C*H), 75.10 (s, η^6*C*H), 73.57 (s, η^6*C*H), 72.42 (s, η^6*C*H), 31.56 (s, *C*H-(CH$_3$)$_2$), 21.70 (s, *C*H$_3$), 20.64 (s, *C*H$_3$). **MS (ESI)**: m/z calcd for $C_{25}H_{24}ClN_2Os$ $[M]^+$ 579.1; found 579.0.

[Ru(η^6-C$_6$H$_4$(^{i}Pr)(coumarin))(bpy)Cl]Cl (17)

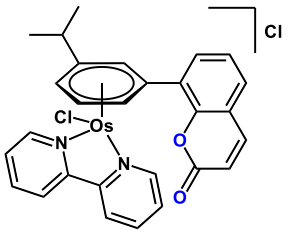


Complex **3** (8.7 mg; 0.01 mmol) and 2,2' bipyridine (bpy) (3.11 mg; 0.02 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred at RT overnight. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **17** as a dark-red powder (10.0 mg; 84.4%).

^{1}H NMR (400 MHz, MeOD) δ 9.54 (d, *J* = 5.6 Hz, 1H, bpy*H*), 8.99 (d, *J* = 5.8 Hz, 1H, bpy*H*), 8.47 (d, *J* = 8.2 Hz, 1H, bpy*H*), 8.38 (d, *J* = 8.0 Hz, 1H, bpy*H*), 8.23 (t, *J* = 7.8 Hz, 1H, bpy*H*), 8.05 – 7.98 (m, 2H, bpy*H*, Ar*H*), 7.89 (d, *J* = 9.6 Hz, 1H, *H*-lactone), 7.76 (m, 2H, bpy*H*, Ar*H*), 7.45 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.32 (t, *J* = 6.7 Hz, 1H, bpy*H*), 6.59 (t, *J* = 6.1 Hz, 1H, η^6*H*), 6.39 (s, 1H, η^6*H*), 6.33 – 6.28 (m, 2H, *H*-lactone, η^6*H*), 6.05 (d, *J* = 6.2 Hz, 1H, η^6*H*), 3.14 (m, *J* = 6.9 Hz, 1H, C*H*-(CH$_3$)$_2$), 1.44 (d, *J* = 6.9 Hz, 3H, *C*H$_3$), 1.37 (d, *J* = 7.0 Hz, 3H, *C*H$_3$). **^{13}C NMR** (101 MHz, MeOD) δ 160.17 (s, *C*=O), 156.95 (s, bpy*C*), 156.80 (s, bpy*C*H), 156.75 (s, bpy*C*), 155.78 (s, bpy*C*H), 152.56 (s, *C*-lactone), 145.42 (s, *C*H-lactone), 140.97 (s, bpy*C*H), 140.77 (s, Ar*C*H), 135.20 (s, bpy*C*H), 132.14 (s, bpy*C*H), 128.73 (s, bpy*C*H), 128.29 (s, Ar*C*H), 126.13 (s, Ar*C*H), 125.30 (s, bpy*C*H), 124.33 (s, bpy*C*H), 120.96 (s, *C*-lactone), 117.27 (s, *C*H-lactone), 115.53 (s, Ar*C*), 109.44 (s, η^6*C*), 98.93 (s, η^6*C*), 92.78 (s, η^6*C*H), 84.32 (s, η^6*C*H), 83.37 (s, η^6*C*H), 83.23

(s, η^6*C*H), 33.17 (s, *C*H-(CH$_3$)$_2$), 22.89 (s, *C*H$_3$), 21.46 (s, *C*H$_3$). **MS (ESI)**: m/z calcd for $C_{28}H_{24}ClN_2O_2Ru$ [M]$^+$ 557.0; found 556.9. **Elemental analysis**: Calcd for $C_{28}H_{24}Cl_2N_2O_2Ru \cdot 3.5\ H_2O$ (655.53) C, 51.30; H, 4.77; N, 4.27%. Found C, 51.36; H, 4.52; N 4.56%.

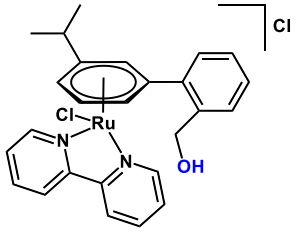
[Os(η^6-C$_6$H$_4$(^{i}Pr)(coumarin))(bpy)Cl]Cl (18)



Complex **4** (15 mg; 0.014 mmol) and 2,2' bipyridine (bpy) (4.5 mg; 0.028 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred at RT overnight. The crude volume was reduced under vacuum until dryness. Then, it was redissolved in dichloromethane, filtered and dried almost completely. A solid was precipitated after the addition of Et$_2$O, which was washed with more Et$_2$O, to afford **18** as a yellow powder (9.0 mg; 47.2%).

^{1}H NMR (400 MHz, MeOD) δ 9.43 (d, *J* = 5.6 Hz, 1H, bpy*H*), 8.92 (d, *J* = 5.7 Hz, 1H, bpy*H*), 8.57 (d, *J* = 8.2 Hz, 1H, bpy*H*), 8.49 (d, *J* = 8.2 Hz, 1H, bpy*H*), 8.22 (t, *J* = 7.9 Hz, 1H, bpy*H*), 8.01 (t, *J* = 7.9 Hz, 1H, bpy*H*), 7.95 (d, *J* = 7.8 Hz, 1H, Ar*H*), 7.87 (d, *J* = 9.5 Hz, 1H, *H*-lactone), 7.73 (m, 2H, bpy*H*, Ar*H*), 7.42 (t, *J* = 7.7 Hz, 1H, Ar*H*), 7.30 (t, *J* = 7.4 Hz, 1H, bpy*H*), 6.73 (t, *J* = 5.7 Hz, 1H, η^6*H*), 6.67 (s, 1H, η^6*H*), 6.51 (d, *J* = 5.6 Hz, 1H, η^6*H*), 6.29 (d, *J* = 9.8 Hz, 1H, *H*-lactone), 6.22 (d, *J* = 5.8 Hz, 1H, η^6*H*), 3.01 (m, 1H, C*H*-(CH$_3$)$_2$), 1.39 (d, *J* = 6.8 Hz, 6H, (*C*H$_3$)$_2$). **^{13}C{^{1}H} NMR (101 MHz, MeOD)** δ 157.61 (s, *C*=O), 157.44 (s, bpy*C*), 156.60 (s, bpy*C*H), 156.49 (s, bpy*C*), 155.54 (s, bpy*C*H), 148.85 (s, *C*-lactone), 145.48 (s, *C*H-lactone), 141.10 (s, bpy*C*H), 140.90 (s, bpy*C*H), 135.67 (s, Ar*C*H), 131.57 (s, bpy*C*H), 129.42 (s, Ar*C*H), 128.88 (s, bpy*C*H), 126.24 (s, Ar*C*H), 125.38 (s, bpy*C*H), 124.49 (s, bpy*C*H), 123.09 (s, *C*-lactone), 117.19 (s, *C*H-lactone), 105.74 (s, Ar*C*), 100.50 (s, η^6*C*), 88.53 (s, η^6*C*), 83.47 (s, η^6*C*H), 77.30 (s, η^6*C*H), 75.25 (s, η^6*C*H), 74.68 (s, η^6*C*H), 32.90 (s, *C*H-(CH$_3$)$_2$), 23.38 (s, *C*H$_3$), 21.55 (s, *C*H$_3$). **MS (ESI)**: m/z calcd for $C_{28}H_{24}ClN_2O_2Os$ [M]$^+$ 647.1; found 647.0. **Elemental analysis**: Calcd for $C_{28}H_{24}Cl_2N_2O_2Os \cdot 3H_2O$ (735.69) C, 45.71; H, 4.11; N, 3.81%. Found C, 45.93; H, 4.06; N 3.72%.

[Ru(η^6-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)-*o*-CH$_2$OH))(bpy)Cl]Cl (19)

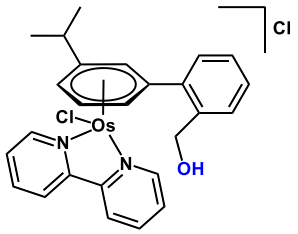


Complex **5** (15 mg; 0.019 mmol) and bpy (5.9 mg; 0.038 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred at RT for 1 h. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et$_2$O, which was washed with more Et$_2$O, to afford **19** as a dark-red bright powder (12.5 mg; 59.3%).

^{1}H NMR (400 MHz, DMSO) δ 9.42 (d, *J* = 5.5 Hz, 1H, bpy*H*), 9.23 (d, *J* = 5.5 Hz, 1H, bpy*H*), 8.68 (m, 2H, bpy*H*), 8.31 (t, *J* = 8.0 Hz, 1H, bpy*H*), 8.24 (t, *J* = 8.0 Hz, 1H, bpy*H*), 7.82 – 7.75 (m, 1H, bpy*H*), 7.64 – 7.59 (m, 1H, bpy*H*), 7.55 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.46 – 7.37 (m, 1H, Ar*H*), 7.17 (m, 2H, Ar*H*), 6.62 (s, 1H, η^6*H*), 6.52 (t, *J* = 6.0 Hz, 1H, η^6*H*), 6.28 (m, 2H, η^6*H*), 5.40 (t, *J* = 5.2 Hz, 1H, O*H*), 4.56 (m, 2H, C*H*$_2$), 2.86 (m, *J* = 6.7 Hz, 1H, C*H*-(CH$_3$)$_2$), 1.21 (d, *J*

= 6.9 Hz, 3H, C*H*$_3$), 1.10 (d, *J* = 6.9 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, DMSO) δ 155.50 (s, 2C, bpy*C*H), 154.50 (s, bpy*C*), 154.24 (s, bpy*C*), 141.55 (s, Ar*C*), 140.12 (s, bpy*C*H), 139.99 (s, bpy*C*H), 132.60 (s, Ar*C*), 129.69 (s, Ar*C*H), 129.20 (s, Ar*C*H), 129.05 (s, Ar*C*H), 127.65 (s, Ar*C*H), 127.57 (s, bpy*C*H), 127.36 (s, bpy*C*H), 124.07 (s, bpy*C*H), 123.95 (s, bpy*C*H), 106.78 (s, η^6*C*), 99.20 (s, η^6*C*), 88.19 (s, η^6*C*H), 86.43 (s, η^6*C*H), 86.12 (s, η^6*C*H), 85.65 (s, η^6*C*H), 60.92 (s, *C*H$_2$), 30.85 (s, *C*H-(CH$_3$)$_2$), 21.78 (d, *J* = 5.8 Hz, (*C*H$_3$)$_2$). **MS (ESI)**: m/z calcd for $C_{26}H_{26}ClN_2ORu$ $[M]^+$ 519.1; found 519.0. **Elemental analysis**: Calcd for $C_{26}H_{26}Cl_2N_2ORu \cdot 1.5H_2O$ (581.48) C, 53.70; H, 5.03; N, 4.82%. Found C, 53.37; H, 4.95; N 5.11%.

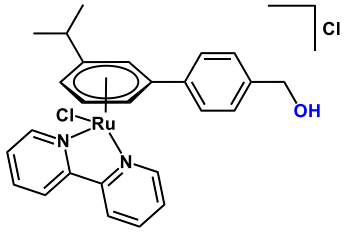
[Os(η^6-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)-*o*-CH$_2$OH))(bpy)Cl]Cl (20)



Complex **6** (12.4 mg; 0.019 mmol) and bpy (3.9 mg; 0.038 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred at RT overnight. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **20** as a yellow-green powder (9.2 mg; 55.0%).

^{1}H NMR (400 MHz, MeOD) δ 9.18 (d, *J* = 5.6 Hz, 1H, bpy*H*), 9.12 (d, *J* = 5.3 Hz, 1H, bpy*H*), 8.63 (m, 2H, bpy*H*), 8.24 (t, *J* = 8.0 Hz, 1H, bpy*H*), 8.18 (t, *J* = 7.7 Hz, 1H, bpy*H*), 7.66 (t, *J* = 6.4, 6.4 Hz, 1H, Ar*H*), 7.60 – 7.50 (m, 2H, bpy*H*, Ar*H*), 7.42 (m, 1H, bpy*H*), 7.19 (m, 2H, Ar*H*), 6.89 (s, 1H, η^6*H*), 6.46 (m, 3H, η^6*H*), 4.71 (m, 2H, C*H*$_2$), 2.81 (m, *J* = 6.8 Hz, 1H, C*H*-(CH$_3$)$_2$), 1.22 (d, *J* = 6.9 Hz, 6H, (C*H*$_3$)$_2$). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 157.26 (s, bpy*C*), 156.89 (s, bpy*C*), 156.36 (s, bpy*C*H), 156.22 (s, bpy*C*H), 142.24 (s, Ar*C*), 141.39 (s, bpy*C*H), 141.30 (s, bpy*C*H), 135.43 (s, Ar*C*), 131.62 (s, Ar*C*H), 131.02 (s, Ar*C*H), 130.65 (s, Ar*C*H), 129.59 (s, bpy*C*H), 129.50 (s, bpy*C*H), 125.32 (s, bpy*C*H), 125.16 (s, bpy*C*H), 99.15 (s, η^6*C*), 90.11 (s, η^6*C*), 84.76 (s, η^6*C*H), 80.16 (s, η^6*C*H), 79.99 (s, η^6*C*H), 76.78 (s, η^6*C*H), 63.15 (s, *C*H$_2$), 32.93 (s, *C*H-(CH$_3$)$_2$), 23.40 (s, *C*H$_3$), 22.09 (s, *C*H$_3$). **MS (ESI)**: m/z calcd for $C_{26}H_{26}ClN_2OOs$ $[M]^+$ 609.1; found 608.9. **Elemental analysis**: Calcd for $C_{26}H_{26}Cl_2N_2OOs \cdot 1.5H_2O$ (670.61) C, 46.57; H, 4.36; N, 4.18%. Found C, 46.81; H, 4.55; N, 3.65%.

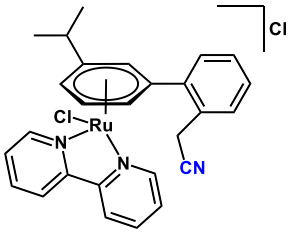
[Ru(η^6-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)-*p*-CH$_2$OH))(bpy)Cl]Cl (21)



Complex **7** (14.1 mg; 0.018 mmol) and bpy (5.6 mg; 0.036 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred at RT for 1 h. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **21** as a red-orange powder (18.1 mg; 93.3%).

^{1}H NMR (400 MHz, MeOD) δ 9.31 (d, *J* = 5.7 Hz, 1H, bpy*H*), 8.91 (d, *J* = 5.7 Hz, 1H, bpy*H*), 8.49 (d, *J* = 7.8 Hz, 1H, bpy*H*), 8.43 (d, *J* = 8.1 Hz, 1H, bpy*H*), 8.22 (td, *J* = 8.0, 1.4 Hz, 1H, bpy*H*), 8.08 (td, *J* = 8.0, 1.4 Hz, 1H, bpy*H*), 7.75 – 7.67 (m, 1H, bpy*H*), 7.59 (d, *J* = 8.3 Hz, 2H, Ar*H*), 7.43 – 7.34 (m, 3H, Ar*H* (2H) and bpy*H* (1H)), 6.45 (t, *J* = 6.1 Hz, 1H, η^6*H*), 6.38 (s, 1H, η^6*H*), 6.27 (d, *J* = 6.0 Hz, 1H, η^6*H*), 6.07 (d, *J* = 6.2 Hz, 1H, η^6*H*), 4.69 – 4.58 (m, 2H, C*H*$_2$), 3.08 (m, *J* = 6.9 Hz, 1H, C*H*-(CH$_3$)$_2$), 1.41 (d, *J* = 6.9 Hz, 3H, C*H*$_3$), 1.33 (d, *J* = 7.0 Hz, 3H, C*H*$_3$). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 156.66 (s, bpy*C*H), 156.52 (s, bpy*C*), 156.20 (s, bpy*C*H), 156.09 (s, bpy*C*), 145.98 (s, Ar*C*), 141.16 (s, bpy*C*H), 140.92 (s, bpy*C*H), 129.64 (s, 2C, Ar*C*H), 128.86 (s, Ar*C*), 128.75 (s, bpy*C*H), 128.61 (s, bpy*C*H), 128.56 (s, 2C, Ar*C*H), 124.94 (s, bpy*C*H), 124.50 (s, bpy*C*H), 115.14 (s, η^6*C*), 102.74 (s, η^6*C*), 91.62 (s, η^6*C*H), 83.30 (s, η^6*C*H), 82.61 (s, η^6*C*H), 81.39 (s, η^6*C*H), 64.35 (s, *C*H$_2$), 33.17 (s, *C*H-(CH$_3$)$_2$), 22.58 (s, *C*H$_3$), 21.98 (s, *C*H$_3$). **MS (ESI)**: m/z calcd for $C_{26}H_{26}ClN_2ORu$ [M]$^+$ 519.1; found 519.0. **Elemental analysis**: Calcd for $C_{26}H_{26}Cl_2N_2ORu \cdot 0.5H_2O$ (563.49) C, 55.42; H, 4.83; N, 4.97%. Found C, 55.5; H, 5.47; N, 4.68%.

[Ru(η^6-C$_6$H$_4$(*i*Pr)((C$_6$H$_4$)CH$_2$CN))(bpy)Cl]Cl (22)

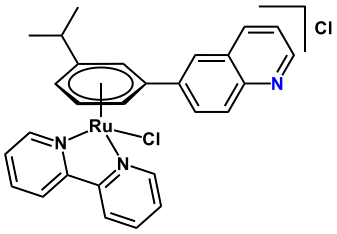


Complex **8** (15.3 mg; 0.019 mmol) and bpy (5.9 mg; 0.036 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred at RT for 1 h. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **22** as a dark-yellow powder (12.5 mg; 59.3%).

^{1}H NMR (400 MHz, MeOD) δ 9.32 (d, *J* = 5.7 Hz, 1H, bpy*H*), 9.27 (d, *J* = 5.7 Hz, 1H, bpy*H*), 8.60 – 8.52 (m, 2H, bpy*H*), 8.30 – 8.24 (m, 1H, bpy*H*), 8.24 – 8.19 (m, 1H, bpy*H*), 7.76 – 7.70 (m, 1H, bpy*H*), 7.66 – 7.62 (m, 1H, bpy*H*), 7.61 (d, *J* = 7.1 Hz, 1H, Ar*H*), 7.54 – 7.49 (m, 1H, Ar*H*), 7.35 – 7.29 (m, 2H, Ar*H*), 6.47 (s, 1H, η^6*H*), 6.39 – 6.34 (m, 2H, η^6*H*), 6.29 (m, 1H, η^6*H*), 4.08 (d, *J* = 1.9 Hz, 2H, C*H*$_2$), 2.89 (m, *J* = 6.9 Hz, 1H, C*H*-(CH$_3$)$_2$), 1.27 (d, *J* = 6.9 Hz, 3H, *C*H$_3$), 1.19 (d, *J* = 6.9 Hz, 3H, *C*H$_3$). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 156.68 (s, 2C, bpy*C*H), 156.52 (s, bpy*C*), 156.49 (s, bpy*C*), 141.66 (s, Ar*C*), 141.50 (s, bpy*C*H), 141.42 (s, bpy*C*H), 131.92 (s, Ar*C*H), 131.52 (s, Ar*C*H), 131.46 (s, Ar*C*H), 130.07 (s, Ar*C*H), 129.14 (s, Ar*C*), 128.97 (s, 2C, bpy*C*H), 125.32 (s, bpy*C*H), 125.22 (s, bpy*C*H), 108.31 (s, η^6*C*), 99.58 (s, η^6*C*), 92.49 (s,

*C*N), 92.43 (s, η^6*C*H), 89.16 (s, η^6*C*H), 89.09 (s, η^6*C*H), 86.21 (s, η^6*C*H), 32.91 (s, *C*H-(CH_3)$_2$), 22.66 (s, *C*H_3), 22.53 (s, *C*H_2), 22.27 (s, *C*H_3). **MS (ESI)**: m/z calcd for $C_{27}H_{25}ClN_3Ru$ $[M]^+$ 528.1; found 528.0. **Elemental analysis**: Calcd for $C_{27}H_{25}Cl_2N_3Ru$ (563.49) C, 57.55; H, 4.47; N, 7.46%. Found C, 57.60; H, 5.04; N, 6.47%.

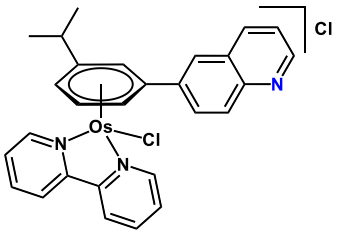
[Ru(η^6-C_6H_4(*i*Pr)(quinoline))(bpy)Cl]Cl (23)



Complex **9** (10.1 mg; 0.012 mmol) and 2,2' bipyridine (bpy) (3.7 mg; 0.024 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred for 1 h. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **23** as a dark-red powder (9.9 mg; 71.7%).

^{1}H NMR (400 MHz, MeOD) δ 9.34 (d, *J* = 5.6 Hz, 1H, bpy*H*), 8.99 (d, *J* = 5.6 Hz, 1H, bpy*H*), 8.95 (d, *J* = 3.4 Hz, 1H, Py*H*), 8.52 (d, *J* = 8.2 Hz, 1H, bpy*H*), 8.45 (m, 3H, bpy*H*, Py*H*, Ar*H*), 8.24 (t, *J* = 7.8 Hz, 1H, bpy*H*), 8.04 (t, *J* = 8.3 Hz, 1H, bpy*H*), 7.98 (d, *J* = 8.9 Hz, 1H, Ar*H*), 7.87 – 7.82 (m, 1H, Ar*H*), 7.72 (t, *J* = 6.6 Hz, 1H, bpy*H*), 7.64 (dd, *J* = 8.3, 4.4 Hz, 1H, Py*H*), 7.30 (t, *J* = 6.5 Hz, 1H, bpy*H*), 6.59 (s, 1H, η^6*H*), 6.55 (t, *J* = 6.1 Hz, 1H, η^6*H*), 6.47 (d, *J* = 5.9 Hz, 1H, η^6*H*), 6.15 (d, *J* = 6.0 Hz, 1H, η^6*H*), 3.14 – 3.07 (m, 1H, C*H*-(CH_3)$_2$), 1.45 (d, *J* = 6.8 Hz, 3H, *C*H_3), 1.33 (d, *J* = 6.9 Hz, 3H, *C*H_3). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 156.74 (s, bpy*C*H), 156.52 (s, bpy*C*), 156.30 (s, bpy*C*H), 156.26 (s, bpy*C*), 156.22 (s, Py*C*), 153.08 (s, Py*C*H), 141.30 (s, bpy*C*H), 141.03 (s, bpy*C*H), 138.88 (s, Py*C*H), 132.96 (s, Py*C*), 131.76 (s, Ar*C*), 130.64 (s, Ar*C*H), 130.36 (s, Ar*C*H), 130.01 (s, Ar*C*H), 128.92 (s, bpy*C*H), 128.62 (s, bpy*C*H), 125.11 (s, bpy*C*H), 124.69 (s, bpy*C*H), 123.75 (s, Py*C*H), 121.97 (s, η^6*C*),101.35 (s, η^6*C*), 91.50 (s, η^6*C*H), 84.13 (s, η^6*C*H), 84.08 (s, η^6*C*H), 82.54 (s, η^6*C*H), 33.21 (s, *C*H-(CH_3)$_2$), 22.55 (s, *C*H_3), 22.05 (s, *C*H_3). **MS (ESI)**: m/z calcd for $C_{28}H_{25}ClN_3Ru$ $[M]^+$ 540.1; found 539.9.

[Os(η^6-C_6H_4(*i*Pr)(quinoline))(bpy)Cl]Cl (24)

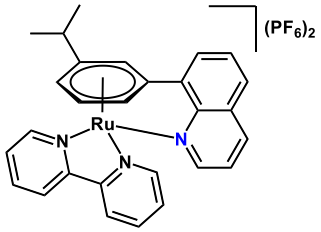


Complex **10** (6.2 mg; 0.006 mmol) and 2,2' bipyridine (bpy) (2.0 mg; 0.012 mmol; 2 equiv) were dissolved in MeOH (1 mL) and stirred at RT overnight. The crude was filtered out using a syringe filter and the solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **24** as a yellow powder (5.2 mg; 64.2%).

^{1}H NMR (400 MHz, MeOD) δ 9.22 (d, *J* = 5.8 Hz, 1H, bpy*H*), 8.96 – 8.87 (m, 2H, bpy*H*, Py*H*), 8.61 (d, *J* = 8.1 Hz, 1H, bpy*H*), 8.55 (d, *J* = 8.1 Hz, 1H, bpy*H*), 8.42 (d, *J* = 8.6 Hz, 1H, Py*H*), 8.33 (s, 1H, Ar*H*), 8.22 (t, *J* = 7.9 Hz, 1H, bpy*H*), 8.03 (t, *J* = 8.0 Hz, 1H, bpy*H*), 7.94 (d, *J* = 8.8 Hz, 1H, Ar*H*), 7.73 (dd, *J* = 9.0, 2.1 Hz, 1H, Ar*H*), 7.68 (t, *J* = 6.7 Hz, 1H, bpy*H*), 7.62 (dd, *J* = 8.4, 4.4 Hz, 1H, Py*H*), 7.28 (t, *J* = 6.5 Hz, 1H, bpy*H*), 6.87 (s, 1H, η^6*H*), 6.69 (m, 2H, η^6*H*), 6.34

(d, *J* = 4.7 Hz, 1H, η^6*H*), 2.98 (m, *J* = 6.7 Hz, 1H, C*H*-(CH_3)$_2$), 1.42 – 1.38 (m, 3H, *C*H_3), 1.31 (d, *J* = 7.0 Hz, 3H, *C*H_3). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 156.88 (s, bpy*C*), 156.43 (s, bpy*C*H), 156.20 (s, bpy*C*), 156.00 (s, bpy*C*H), 154.19 (s, Py*C*), 152.75 (s, Py*C*H), 141.37 (s, bpy*C*H), 141.13 (s, bpy*C*H), 138.78 (s, Py*C*H), 134.04 (s, Py*C*), 133.75 (s, Ar*C*), 130.61 (s, Ar*C*H), 130.27 (s, Ar*C*H), 130.23 (s, Ar*C*H), 129.56 (s, bpy*C*H), 129.20 (s, bpy*C*H), 125.16 (s, bpy*C*H), 124.79 (s, bpy*C*H), 124.15 (s, η^6*C*), 123.62 (s, Py*C*H), 104.94 (s, η^6*C*), 81.67 (s, η^6*C*H), 77.65 (s, η^6*C*H), 75.51 (s, η^6*C*H), 74.73 (s, η^6*C*H), 33.02 (s, *C*H-(CH_3)$_2$), 23.00 (s, *C*H_3), 22.19 (s, *C*H_3). **MS (ESI)**: m/z calcd for $C_{28}H_{25}ClN_3Os$ $[M]^+$ 630.1; found 630.0. **Elemental analysis**: Calcd for $C_{28}H_{25}Cl_2N_3Os \cdot 2.5H_2O$ (709.70) C, 47.39; H, 4.26; N, 5.92%. Found C, 47.39; H, 4.55; N, 5.36%.

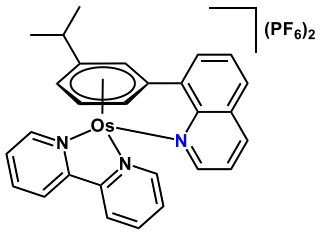
[Ru(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))(bpy)]$(PF_6)_2$ (25)



A suspension of **11** (19.6 mg; 0.047 mmol) in MeOH (2 mL) was mixed with $AgPF_6$ (23.6 mg; 0.0934; 2 equiv) and left stirring for 1 h at RT. After that, AgCl white precipitate was filtered out using a syringe filter and bpy (4 mg; 0.026 mmol; 1 equiv) was added to the remaining solution, which was left to stir for 1 h at RT. After that time, a pale-yellow precipitate was observed. The solvent was reduced until ca. 5% of its original volume, and the solid was centrifuged and washed with dichloromethane, to afford **25** as a pale-yellow powder (15 mg; 63.7%). Yellow crystals suitable for X-ray diffraction were afforded by slow evaporation of methanol at room temperature.

^{1}H NMR (400 MHz, MeOD) δ 9.44 (d, *J* = 5.1 Hz, 1H, bpy*H*), 9.29 (d, *J* = 5.1 Hz, 1H, bpy*H*), 8.80 (d, *J* = 4.6 Hz, 1H, bpy*H*), 8.78 (d, *J* = 4.5 Hz, 1H, bpy*H*), 8.63 (dd, *J* = 8.4, 1.2 Hz, 1H, Py*H*), 8.43 (m, 2H, bpy*H*), 8.38 (dd, *J* = 7.2, 1.1 Hz, 1H, Ar*H*), 8.24 (dd, *J* = 8.3, 1.0 Hz, 1H, Ar*H*), 8.01 (t, *J* = 8.2 Hz, 1H, Ar*H*), 7.85 – 7.79 (m, 1H, bpy*H*), 7.79 – 7.73 (m, 1H, bpy*H*), 7.29 (dd, *J* = 8.4, 5.2 Hz, 1H, Py*H*), 6.77 (t, *J* = 6.1 Hz, 1H, η^6*H*), 6.67 (dd, *J* = 5.2, 1.2 Hz, 1H, Py*H*), 6.49 (s, 1H, η^6*H*), 6.42 (d, *J* = 6.1 Hz, 1H, η^6*H*), 5.75 (d, *J* = 6.1 Hz, 1H, η^6*H*), 3.01 – 2.85 (m, 1H, C*H*-(CH_3)$_2$), 1.41 (d, *J* = 6.9 Hz, 3H, *C*H_3), 0.67 (d, *J* = 6.8 Hz, 3H, *C*H_3). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 157.93 (s, bpy*C*), 157.33 (s, bpy*C*H), 157.11 (s, bpy*C*), 156.50 (s, Py*C*), 156.08 (s, bpy*C*H), 153.23 (s, Py*C*H), 142.92 (s, bpy*C*H), 142.62 (s, bpy*C*H), 142.21 (s, Py*C*H), 135.29 (s, Py*C*), 131.91 (s, Ar*C*H), 131.33 (s, Ar*C*), 131.16 (s, Ar*C*H), 130.28 (s, Ar*C*H), 130.04 (s, bpy*C*H), 129.69 (s, bpy*C*H), 126.79 (s, bpy*C*H), 126.43 (s, bpy*C*H), 125.47 (s, Py*C*H), 121.75 (s, η^6*C*), 117.82 (s, η^6*C*), 100.38 (s, η^6*C*H), 81.97 (s, η^6*C*H), 81.84 (s, η^6*C*H), 74.07 (s, η^6*C*H), 32.32 (s, *C*H-(CH_3)$_2$), 25.05 (s, *C*H_3), 18.25 (s, *C*H_3). **MS (ESI)**: m/z calcd for $C_{28}H_{25}N_3Ru$ $[M]^+$ 505.1; found 505.1. **Elemental analysis**: Calcd for $C_{28}H_{25}F_{12}N_3P_2Ru$ (794.52) C, 42.33; H, 3.17; N, 5.29%. Found C, 42.55; H, 3.43; N, 5.46%.

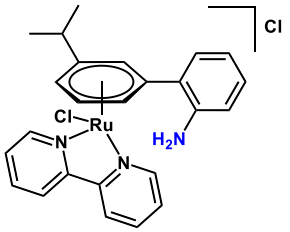
[Os(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))(bpy)]$(PF_6)_2$ (26)



A suspension of **12** (19.4 mg; 0.047 mmol) in MeOH (2 mL) was mixed with $AgPF_6$ (23.6 mg; 0.0934; 2 equiv) and left stirring for 3 h at RT. After that, AgCl white precipitate was filtered out using a syringe filter and bpy (4 mg; 0.026 mmol; 1 equiv) was added to the remaining solution, which was left to stir for overnight at RT. After that time, a pale-yellow precipitate was observed. The solvent was reduced until ca. 5% of its original volume, and the solid was centrifuged and washed with dichloromethane, to afford **26** as a pale-yellow powder (17.3 mg; 41.7%). Yellow crystals suitable for X-ray diffraction were afforded by slow evaporation of methanol at room temperature.

^{1}H NMR (400 MHz, MeOD) δ 9.39 (d, *J* = 5.9 Hz, 1H, bpy*H*), 9.28 (d, *J* = 5.8 Hz, 1H, bpy*H*), 8.87 (d, *J* = 8.2 Hz, 2H, bpy*H*), 8.71 – 8.66 (m, 1H, Py*H*), 8.46 – 8.35 (m, 3H, 2H bpy*H*, 1H Ar*H*), 8.20 (dd, *J* = 8.3, 1.3 Hz, 1H, Ar*H*), 7.98 (dd, *J* = 8.3, 7.2 Hz, 1H, Ar*H*), 7.83 – 7.71 (m, 2H, bpy*H*), 7.30 (dd, *J* = 8.4, 5.3 Hz, 1H, Py*H*), 6.96 (dd, *J* = 5.2, 1.4 Hz, 1H, Py*H*), 6.85 (t, *J* = 5.8 Hz, 1H, η^6*H*), 6.66 (s, 1H, η^6*H*), 6.49 (d, *J* = 5.7 Hz, 1H, η^6*H*), 5.98 (d, *J* = 5.9 Hz, 1H, η^6*H*), 2.83 (m, *J* = 6.8 Hz, 1H, C*H*-$(CH_3)_2$), 1.51 (d, *J* = 6.9 Hz, 3H, *C*H_3), 0.58 (d, *J* = 6.8 Hz, 3H, *C*H_3). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 157.32 (s, bpy*C*), 156.94 (s, bpy*C*H), 156.68 (s, bpy*C*), 155.60 (s, bpy*C*H), 152.44 (s, Py*C*H), 142.98 (s, bpy*C*H), 142.59 (s, bpy*C*H), 142.49 (s, Py*C*H), 135.93 (s, Py*C*), 133.08 (s, Ar*C*H), 131.99 (s, Py*C*), 131.05 (s, Ar*C*H), 130.66 (s, Ar*C*H), 130.58 (s, bpy*C*H), 130.42 (s, bpy*C*H), 126.75 (s, bpy*C*H), 126.42 (s, bpy*C*H), 125.67 (s, Py*C*H), 112.65 (s, η^6*C*), 106.99 (s, η^6*C*), 91.61 (s, η^6*C*H), 73.51 (s, η^6*C*H), 73.43 (s, η^6*C*H), 65.93 (s, η^6*C*H), 31.67 (s, *C*H-$(CH_3)_2$), 25.42 (s, *C*H_3), 18.06 (s, *C*H_3). **MS (ESI)**: m/z calcd for $C_{28}H_{25}N_3Ru$ $[M]^{+2}$ 297.6; found 297.4. **Elemental analysis**: Calcd for $C_{28}H_{25}F_{12}N_3P_2Os\cdot(CH_3CH_2)_2O$ (957.81) C, 40.13; H, 3.68; N, 4.39%. Found C, 39.83; H, 3.54; N, 4.93%.

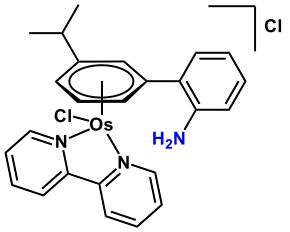
[Ru(η^6-C_6H_4(^{i}Pr)((C_6H_4)NH_2)(bpy)Cl]Cl (27)



Complex **13** (14.1 mg; 0.026 mmol) and bpy (4 mg; 0.026 mmol; 1 equiv) were dissolved in MeOH (2 mL) and stirred at RT for 2 h. The solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O, to afford **27** as a red-purple powder (7.8 mg; 56.0%).

^{1}H NMR (400 MHz, MeOD) δ 9.24 (d, *J* = 5.5 Hz, 1H, bpy*H*), 9.13 (d, *J* = 5.7 Hz, 1H, bpy*H*), 8.52 (d, *J* = 8.3 Hz, 1H, bpy*H*), 8.49 (d, *J* = 8.1 Hz, 1H, bpy*H*), 8.23 (t, *J* = 7.9 Hz, 1H, bpy*H*), 8.17 (t, *J* = 7.9 Hz, 1H, bpy*H*), 7.71 – 7.65 (m, 1H, bpy*H*), 7.55 (t, *J* = 6.7 Hz, 1H, bpy*H*), 7.24 – 7.17 (m, 1H, Ar*H*), 7.04 (d, *J* = 7.8 Hz, 1H, Ar*H*), 6.90 (d, *J* = 8.3 Hz, 1H, Ar*H*), 6.67 – 6.59 (m, 1H, Ar*H*), 6.45 (s, 1H, η^6*H*), 6.30 (d, *J* = 5.3 Hz, 1H, η^6*H*), 6.25 (m, 2H, η^6*H*), 2.93 (m, *J* = 6.8 Hz, 1H, C*H*-$(CH_3)_2$), 1.26 (t, *J* = 6.9 Hz, 6H, $(CH_3)_2$). **^{13}C{^{1}H} NMR** (101 MHz, MeOD) δ 156.63 (s, bpy*C*H), 156.33 (s, bpy*C*H), 156.22 (s, bpy*C*), 156.12 (s, bpy*C*), 141.26 (s, bpy*C*H), 141.10 (s, bpy*C*H), 140.41 (s, Ar*C*), 132.72 (s, Ar*C*), 132.18 (s, Ar*C*H), 132.13 (s, Ar*C*H), 128.75 (s, 2C, bpy*C*H), 125.11 (s, bpy*C*H), 124.76 (s, bpy*C*H), 118.61 (s, Ar*C*H), 117.48 (s, Ar*C*H), 109.66 (s, η^6*C*), 99.17 (s, η^6*C*), 87.58 (s, 2C, η^6*C*H), 86.97 (s, η^6*C*H), 86.94 (s, η^6*C*H), 32.95 (s, *C*H-$(CH_3)_2$), 22.92 (s, *C*H_3), 21.83 (s, *C*H_3). **MS (ESI)**: m/z calcd for $C_{25}H_{25}ClN_3Ru$ $[M]^+$ 504.1; found 504.0. **Elemental analysis**: Calcd for $C_{26}H_{27}Cl_2N_3Ru\cdot0.5H_2O$ (562.50) C, 55.52; H, 5.02; N, 7.47%. Found C, 55.57; H, 5.18; N, 6.52%.

[Os(η^6-C$_6$H$_4$(^{i}Pr)((C$_6$H$_4$)NH$_2$)(bpy)Cl]Cl (28)



Complex **14** (21 mg; 0.044 mmol) and bpy (6.9 mg; 0.044 mmol; 1 equiv) were dissolved in MeOH (2 mL) and stirred at RT for 3 days. The solution volume was reduced under vacuum until almost dryness. Then, a solid was precipitated after the addition of Et_2O, which was washed with more Et_2O. Then, it was redissolved in EtOH and filtrated out with a syringe filter, affording complex **28** as a dark-red powder (7.8 mg; 56.0%).

^{1}H NMR (400 MHz, MeOD) δ 9.12 (d, *J* = 5.7 Hz, 1H, bpy*H*), 9.08 (d, *J* = 5.7 Hz, 1H, bpy*H*), 8.61 (m, 2H, bpy*H*), 8.19 (m, 2H, bpy*H*), 7.64 (t, *J* = 6.9 Hz, 1H, bpy*H*), 7.57 – 7.51 (m, 1H, bpy*H*), 7.17 (t, *J* = 7.6 Hz, 1H, Ar*H*), 6.98 (d, *J* = 7.3 Hz, 1H, Ar*H*), 6.88 (d, *J* = 8.3 Hz, 1H, Ar*H*), 6.69 (s, 1H, η^6*H*), 6.61 (t, *J* = 7.5 Hz, 1H, Ar*H*), 6.50 (m, 2H, η^6*H*), 6.39 (t, *J* = 5.6 Hz, 1H, η^6*H*), 2.85 – 2.74 (m, 1H, C*H*-(CH$_3$)$_2$), 1.25 (d, *J* = 6.9 Hz, 3H, *C*H$_3$), 1.19 (d, *J* = 6.9 Hz, 3H, *C*H$_3$). **MS (ESI)**: m/z calcd for $C_{25}H_{25}ClN_3Os$ $[M]^+$ 594.1; found 593.9.

Crystallographic Analysis

The X-ray crystal structures of complexes **11**, **12**, **13**, **15·PF$_6$**, **25** and **26** have been analysed, and are included in Figure 3 in the main text and Figure S39. Selected bonds and angles are listed in Table S2, and crystallographic data are shown in Table S3.

Non-tether complex **15·PF$_6$** crystallises in the orthorhombic *P* 2_1 2_1 2_1 space group, closed-tethered complexes **11** and **12** in the monoclinic *P* $2_{1/c}$ space group, and complexes **13**, **25** and **26** crystallise in the *P* 1 $2_{1/c}$ 1 space group. All compounds have four molecules per unit cell. The compounds show the expected pseudo-octahedral three-legged piano-stool geometry, present in other similar Ru(II)/Os(II) half-sandwich arene compounds,[8] in which three of the six octahedral positions on the coordination sphere are occupied by the π-bonded η^6-arene ligand, and two others by chlorido ligands (**11**, **12** and **13**) or the bpy bidentate ligand (**15·PF$_6$**, **25** and **26**). The third position is occupied by a chloride atom (**15·PF$_6$**), by a NH_2 nitrogen (pendant from the η^6-arene; **13**), or by a quinoline group (**11**, **12**, **25** and **26**). The latter are the first X-ray structures to be reported for a Ru(II)/Os(II) half-sandwich complex with a tethered quinoline.

In all complexes, the M–$C_{(arene)}$ bond lengths were in a range between 2.088(3)–2.247(3) Å, agreeing with similar reported compounds.[8-9] Also, it was observed that in all closed-tethered complexes, the bond distance M–C6 (the one holding the functionality) was significantly smaller, in comparison with the analogous distance in non-tethered complex **15·PF$_6$** (2.228(8) Å); attributed to the pull caused by the 5-membered tether-ring.

The M–centroid distances were also expected for this kind of Ru(II)/Os(II) compounds. [8-9] Complexes bearing bpy in the XY positions of the structure have the largest M–centroid distance (**15·PF$_6$** (1.697 Å), **25** (1.683 Å) and **26** (1.676 Å)), in contrast with dichlorido monomers (1.646 Å for **13**, and 1.648 Å for **11** and **12**). Ruthenium complex **25** had also a longer M–centroid distance compared to its osmium analogue **26** and its dichlorido precursor **11**.

The bond distance M–N1 (tether-ring forming nitrogen) were similar comparing both ruthenium (**25**, 2.114(3) Å) and osmium (**26,** 2.115(3) Å) analogues, and with their respective dichlorido monomer precursors **11** (2.119(2) Å) and **12** (2.126(3) Å).

Comparing the three dichlorido monomer precursors, **11**, **12** and **13**, the M–Cl distances were significant longer in complex **13**.

The bite angle X–M–Y of bpy complexes **15·PF$_6$** (77.2(3)º), **25** (76.9(1)º) and **26** (76.44(11)º) are considerably smaller than the Cl1–M–Cl2 angle in dichlorido monomers **11** (87.04(2)º), **12** (85.96(3)º) and **13** (89.24(3)º). Comparing metal analogues **11** vs **12** and **25** vs **26**, a significant difference can also be observed; not only for the bite angle, but also in X–M–N1 and Y–M–N1 angles.

The angle formed between the metal and the carbons of the pendant ring C6 and C7 is very similar in closed-tethered complexes **13** (113.2(2)º), **11** (113.3(2)º), **12** (112.9(3)º), **25** (112.0(2)º) and **26** (111.9(2)º). However, in non-tethered complex **15·PF$_6$** (127.4(6)), this angle is considerably larger, evidencing the pull generated by the tether-ring. An analogous trend was observed by comparing the closed- vs open-tethered complexes C7-offset. As expected, all closed-tethered complexes offsets towards the metal are considerably larger (0.455(+) – 0.489(+) Å), in comparison with non-tethered complex **15·PF$_6$** (0.071(+) Å).

The hydrogen bond interactions D–H···A in complex **13**, were also evaluated. The donor (D) was the N1 atom from the pendant NH_2 group, and the acceptors (A) were the chlorido atoms Cl1 and Cl2 of an adjacent molecule (

Table **S4**), as shown in Figure S40 (H1···Cl1, 2.61(3) Å and H2···Cl2, 2.63(3) Å). The angle between D–H···A atoms is 148(3) for N1–H1···Cl1 and 145(3)° for N1–H2···Cl2. These distances and angles suggest that the hydrogen bond interactions are moderated–week, according to Jeffrey's classification.[10]

Deposition numbers 2364343 (**11**), 2365018 (**12**), 2364341 (**13**), 2364342 (**15·PF_6**) 2364344 (**25**) and 2364345 (**26**), contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Supplementary Figures

Figure S1

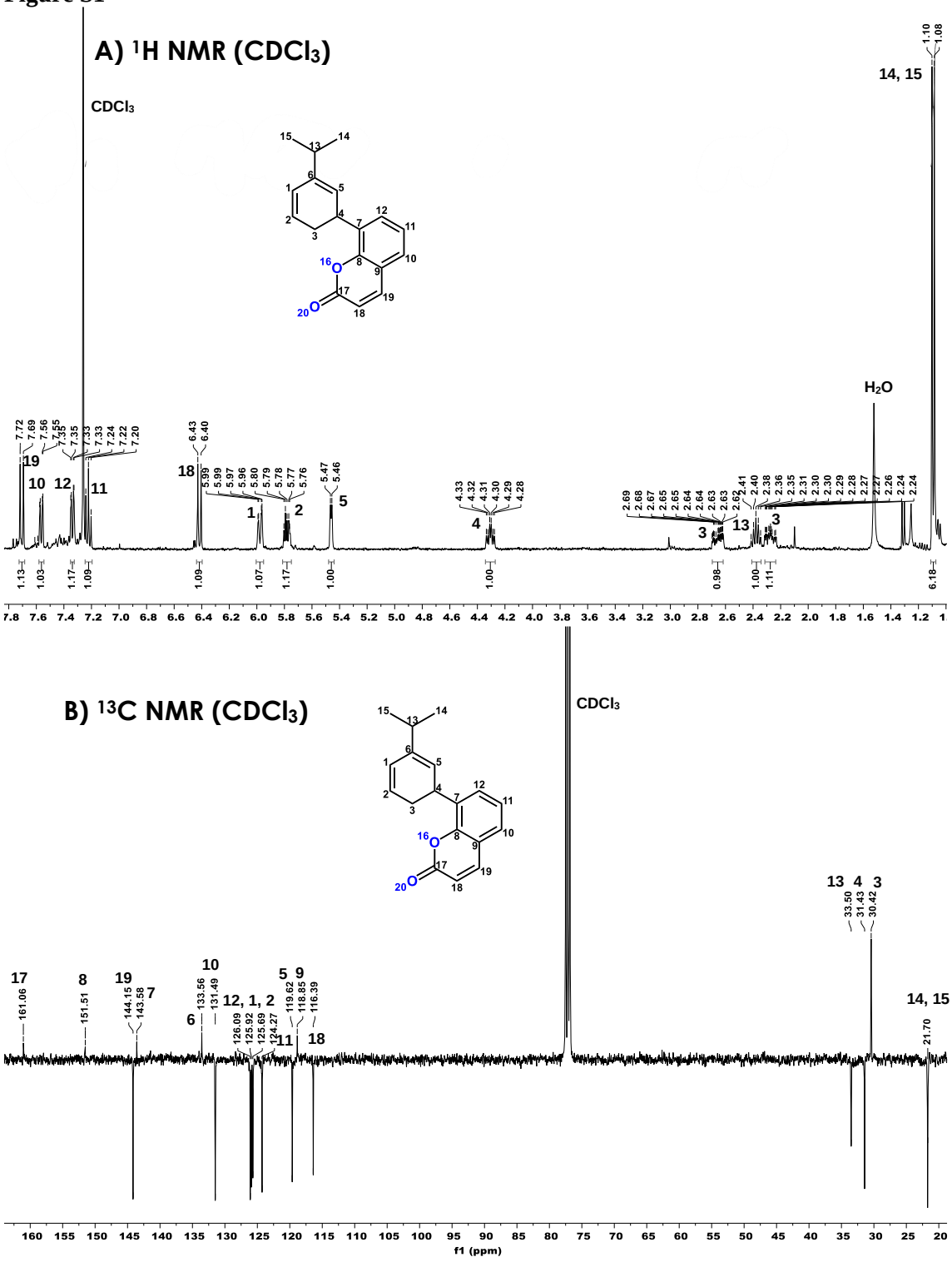


Figure S1. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ APT (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **B**.

Figure S2

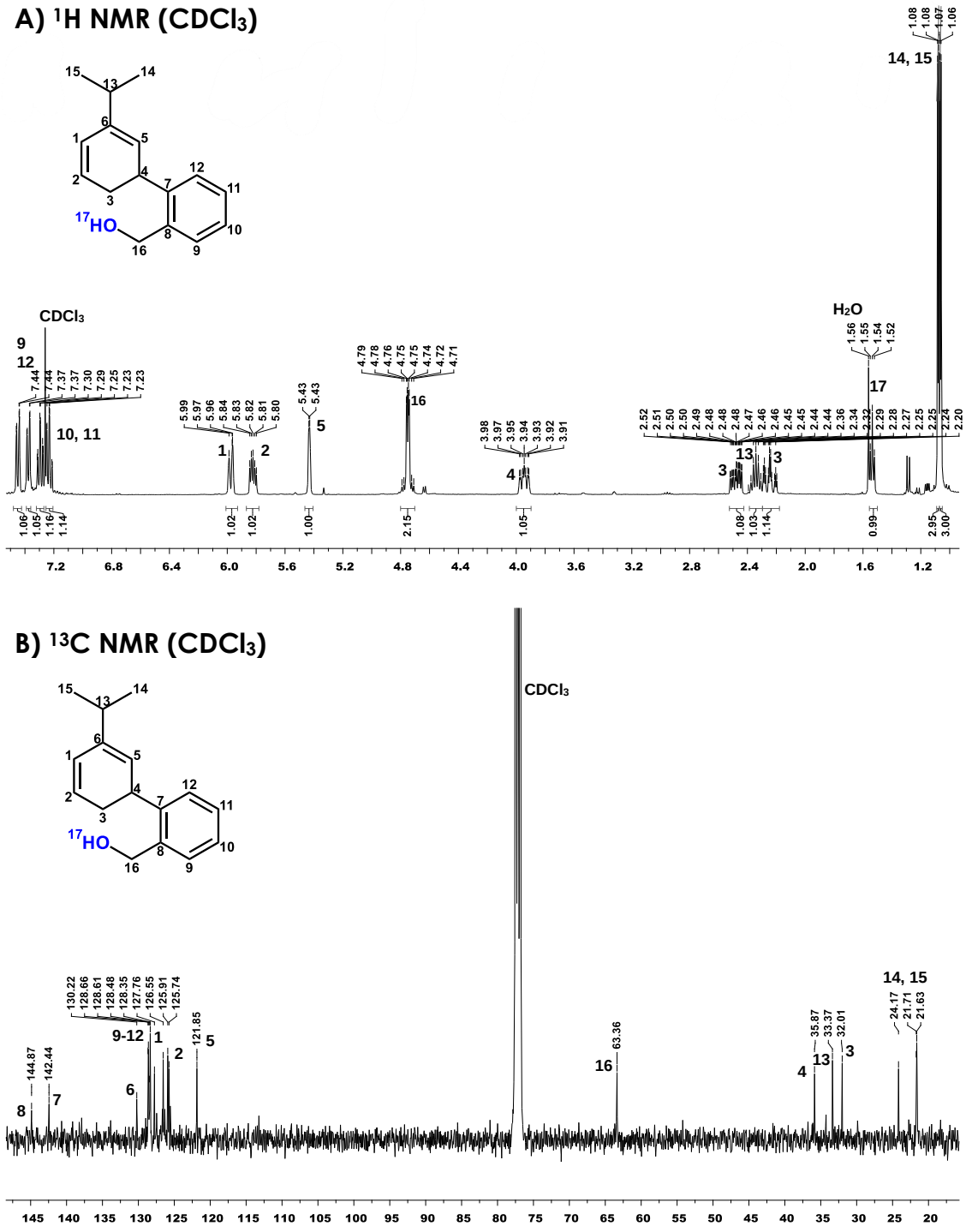


Figure S2. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **C**.

Figure S3

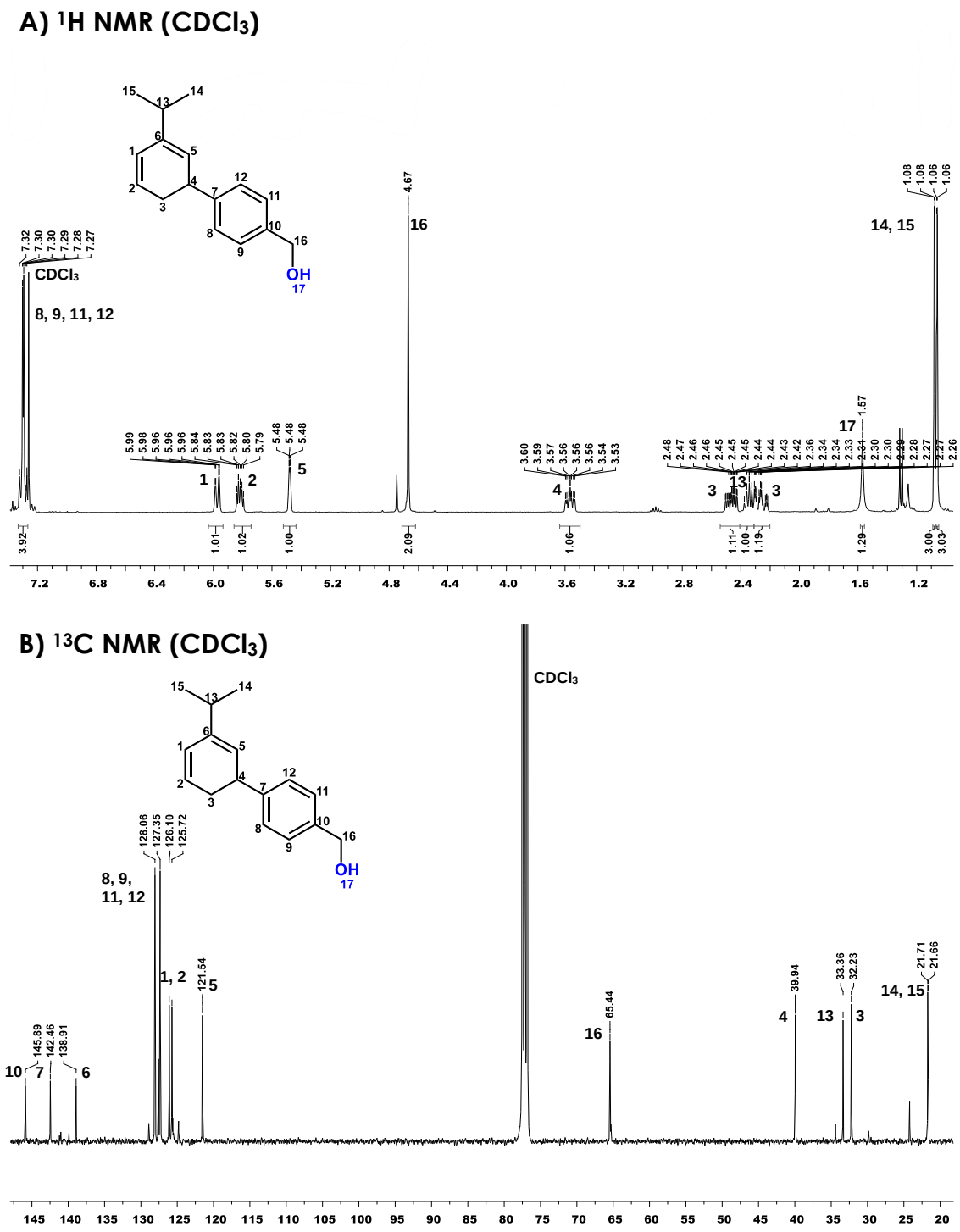


Figure S3. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **D**.

Figure S4

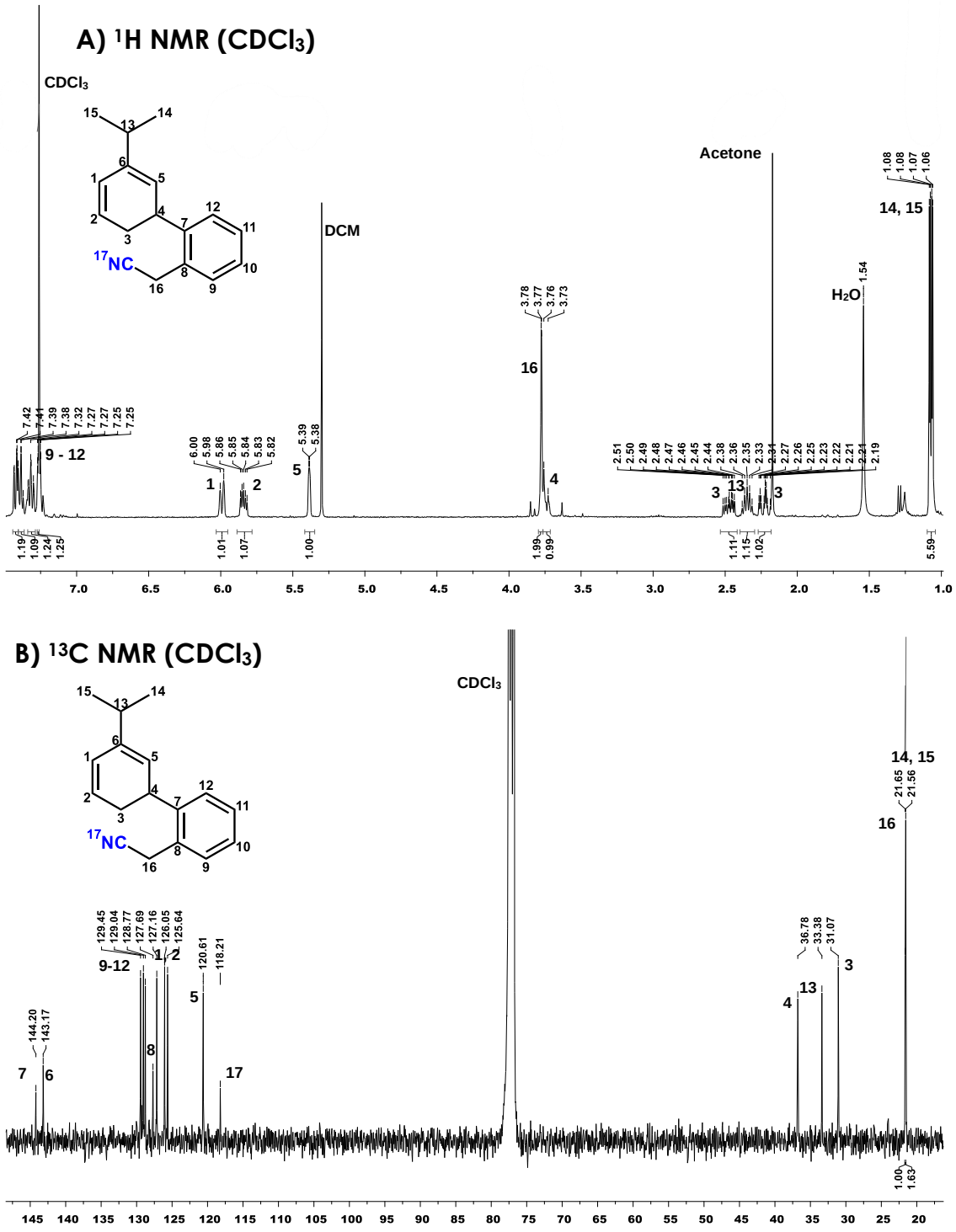


Figure S4. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **E**.

Figure S5

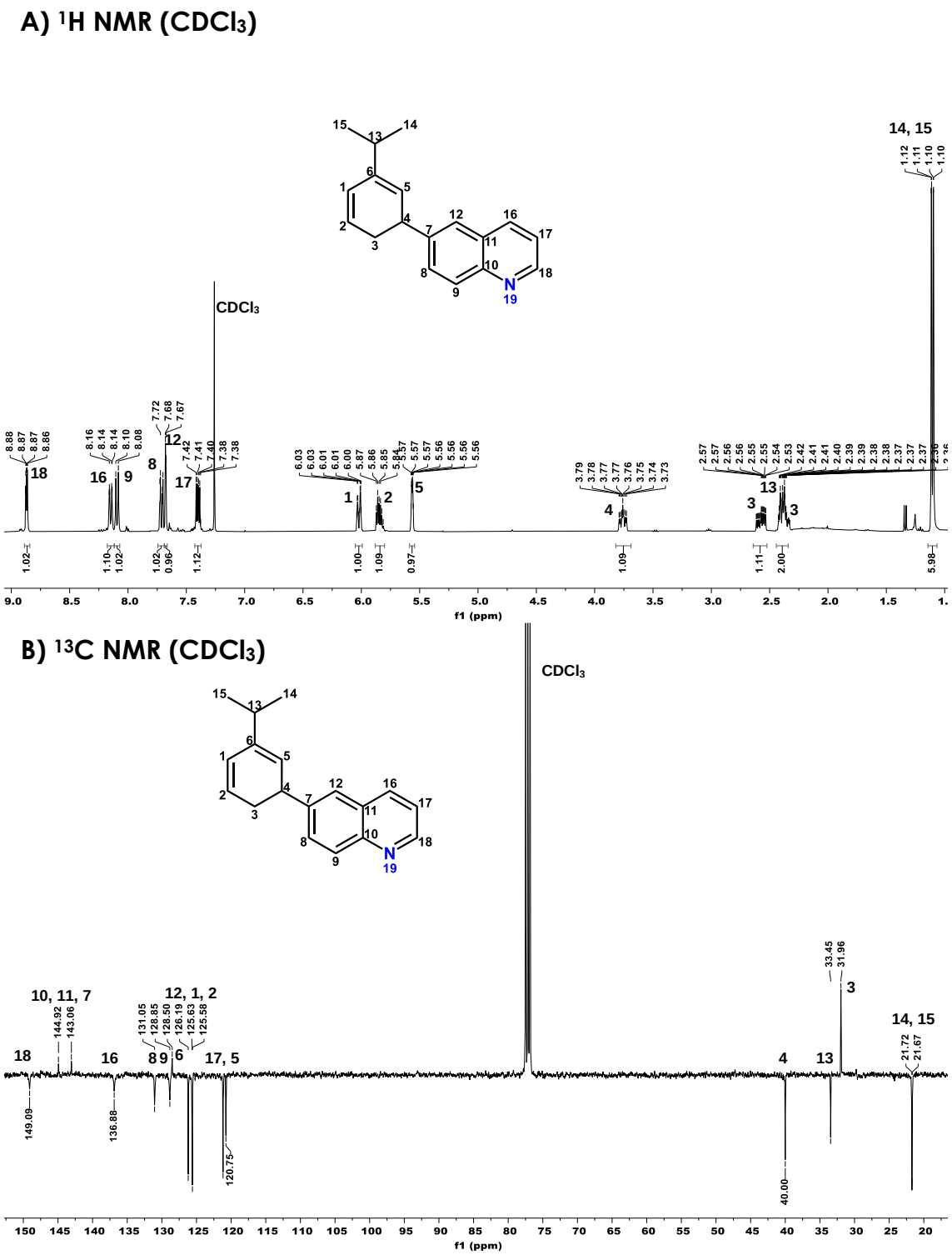


Figure S5. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ APT (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **F**.

Figure S6

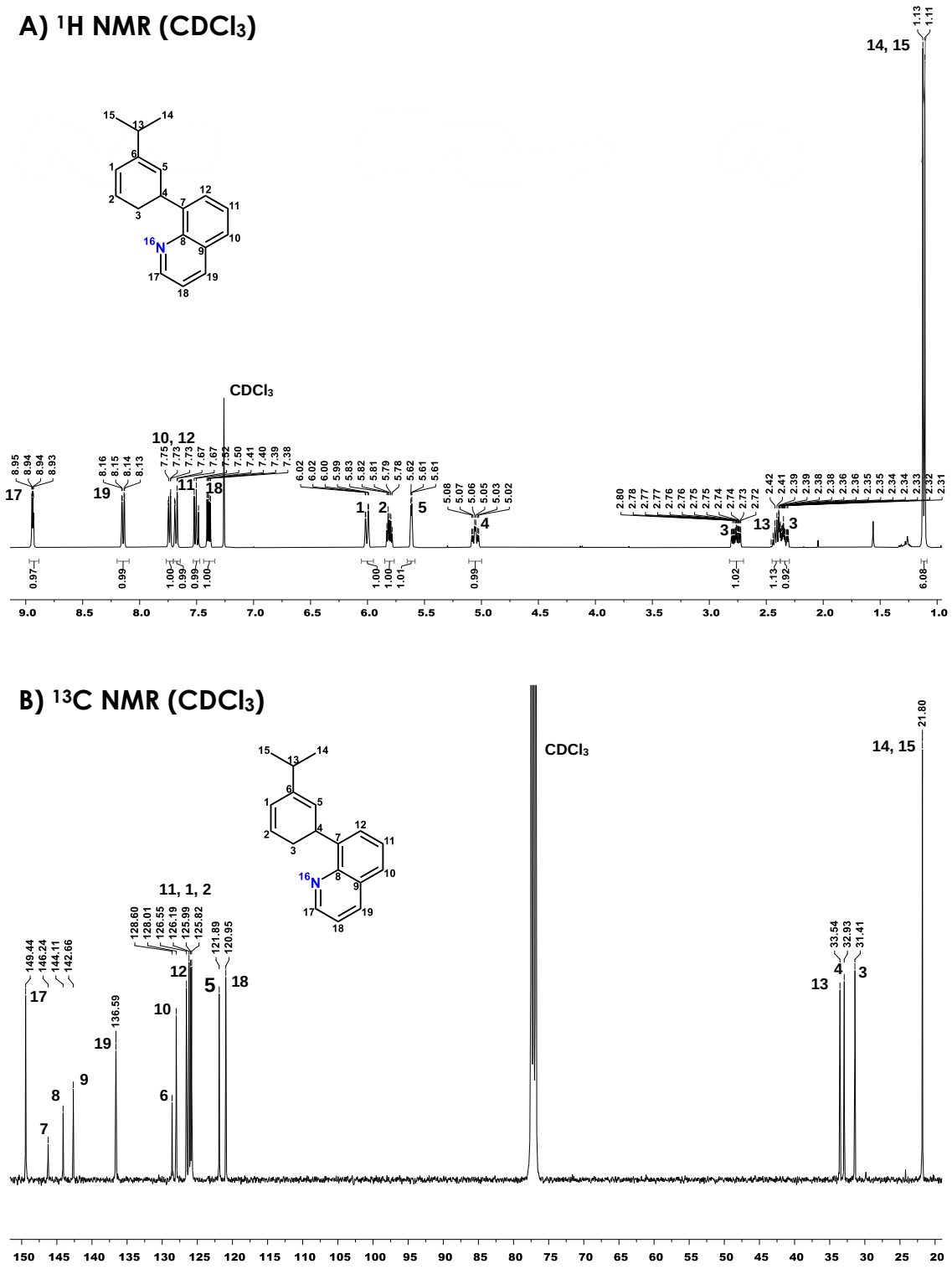


Figure S6. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **G**.

Figure S7

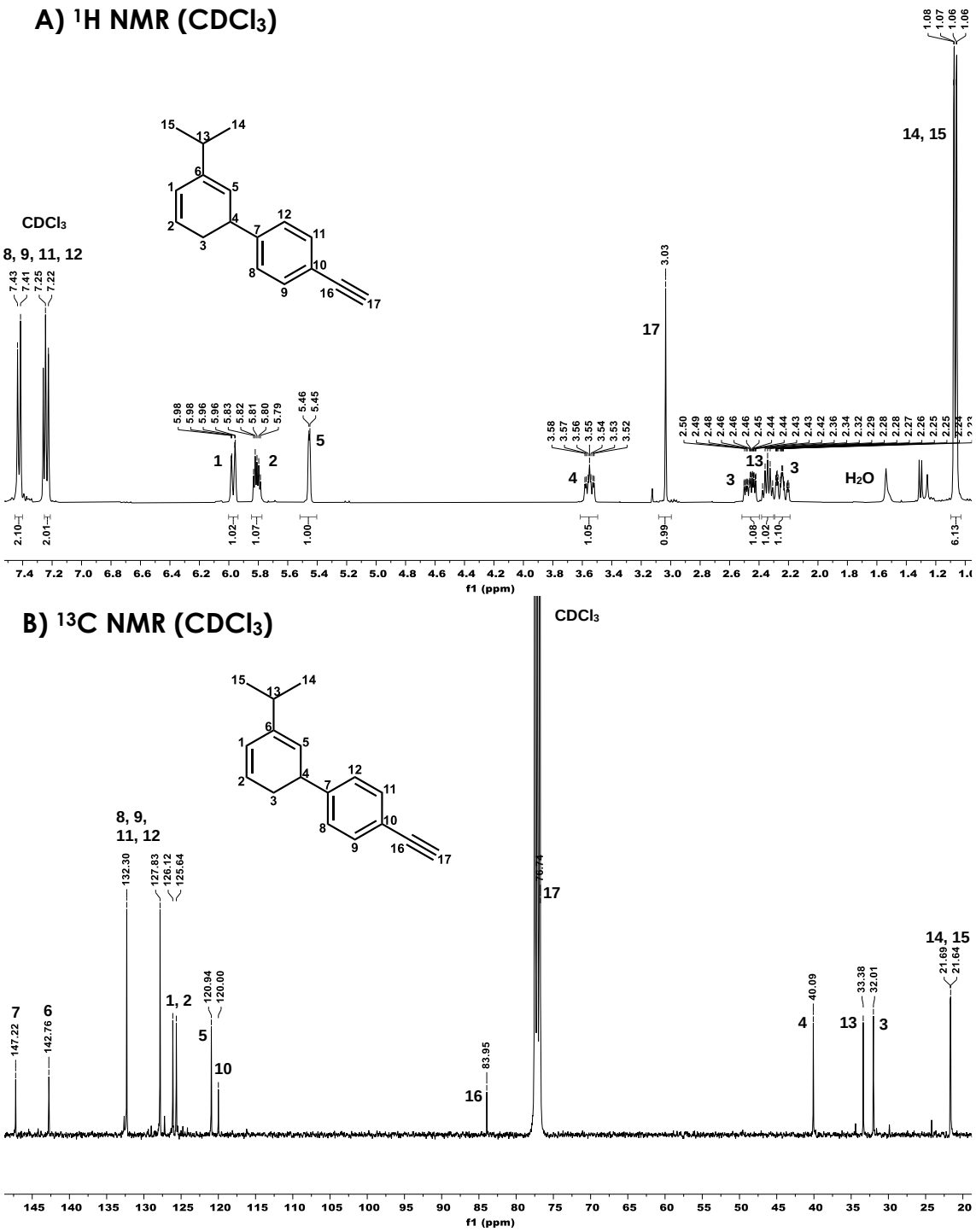


Figure S7. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **I**.

Figure S8

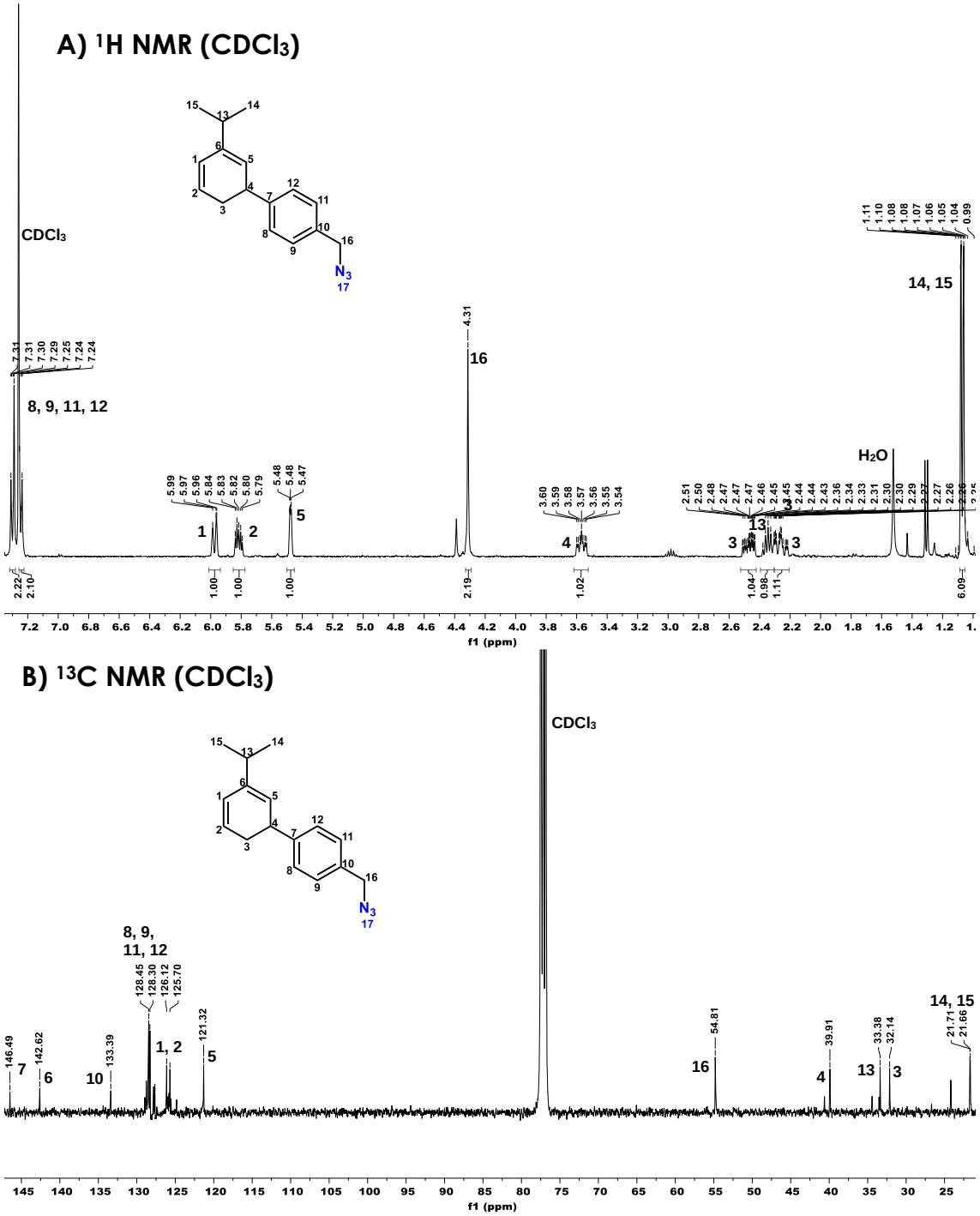


Figure S8. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **J**.

Figure S9

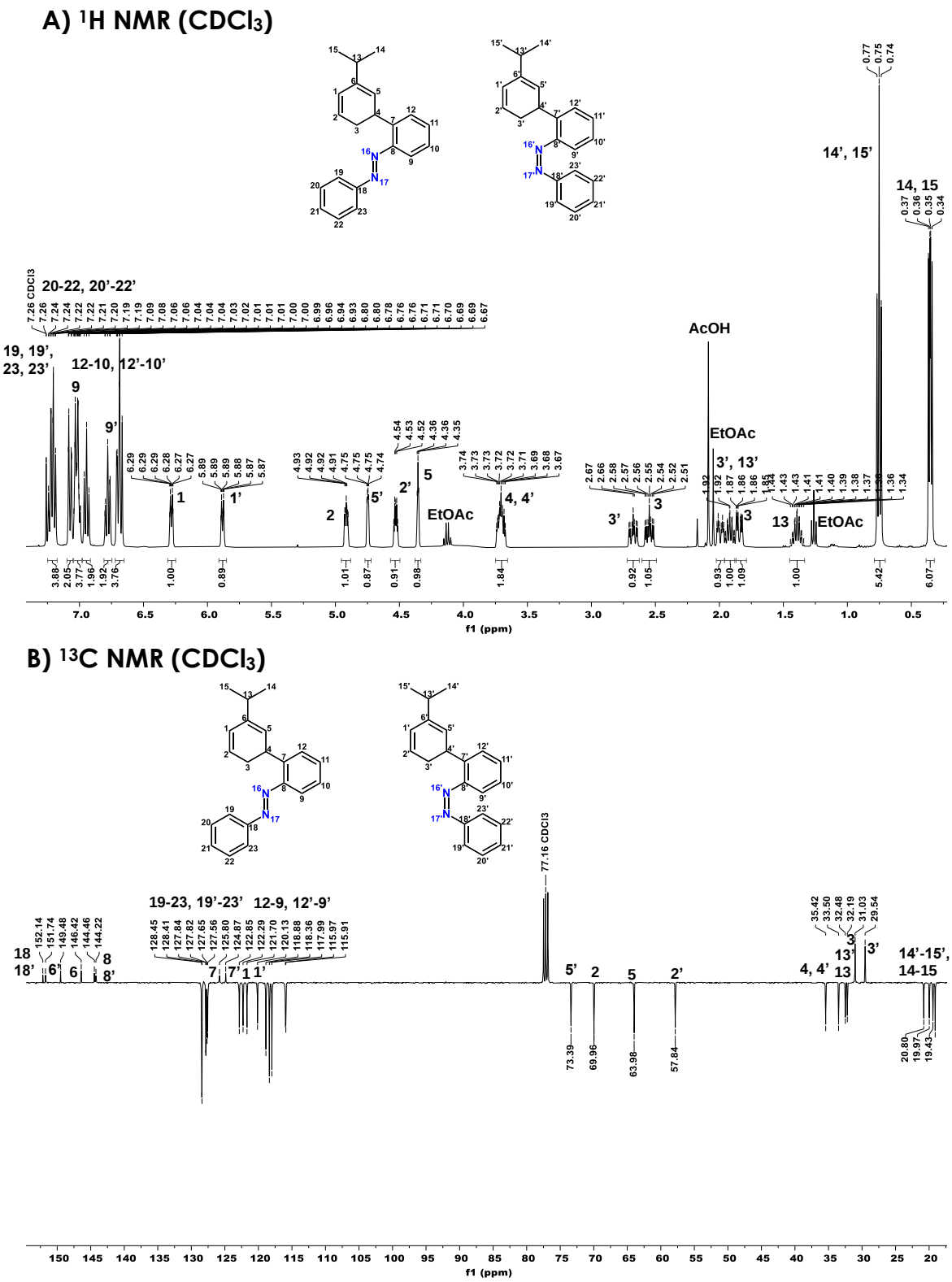


Figure S9. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ APT (101 MHz, $CDCl_3$) (B) NMR spectra of precursor **K**.

Figure S10

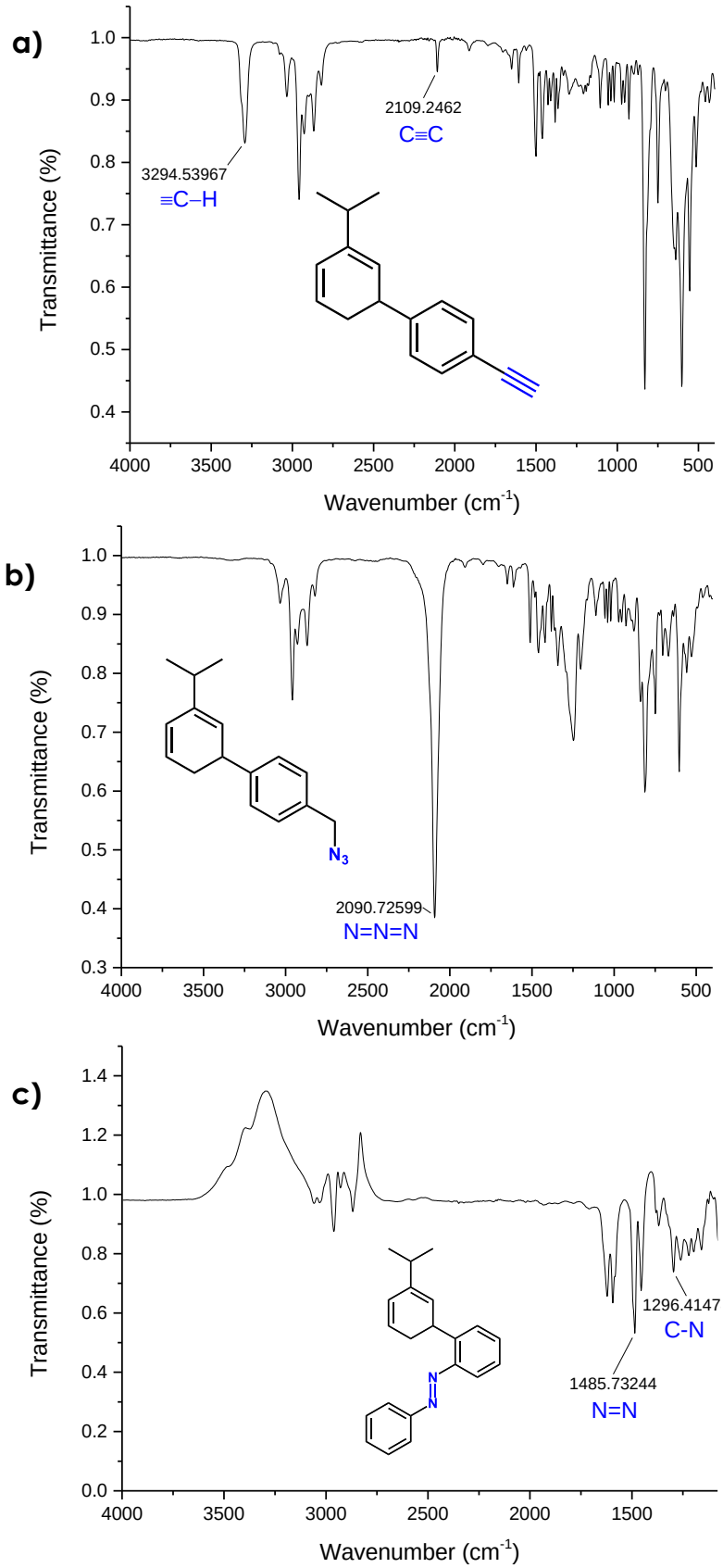


Figure S10. FT-IR spectra of precursors **I** (a), **J** (b) and **K** (c), highlighting the most important band(s) of their distinctive functional group.

Figure S11

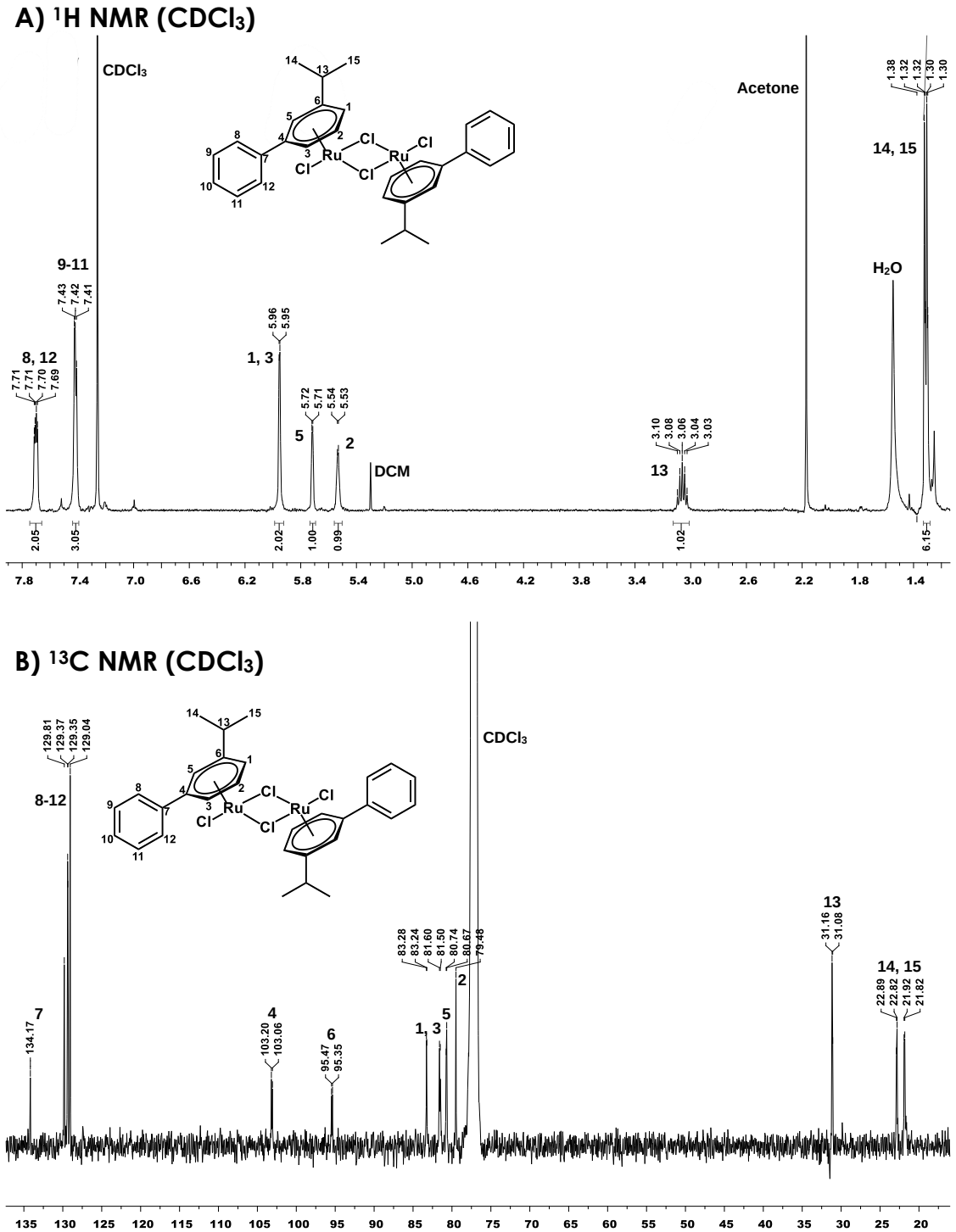


Figure S11. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of dimer **1**.

Figure S12

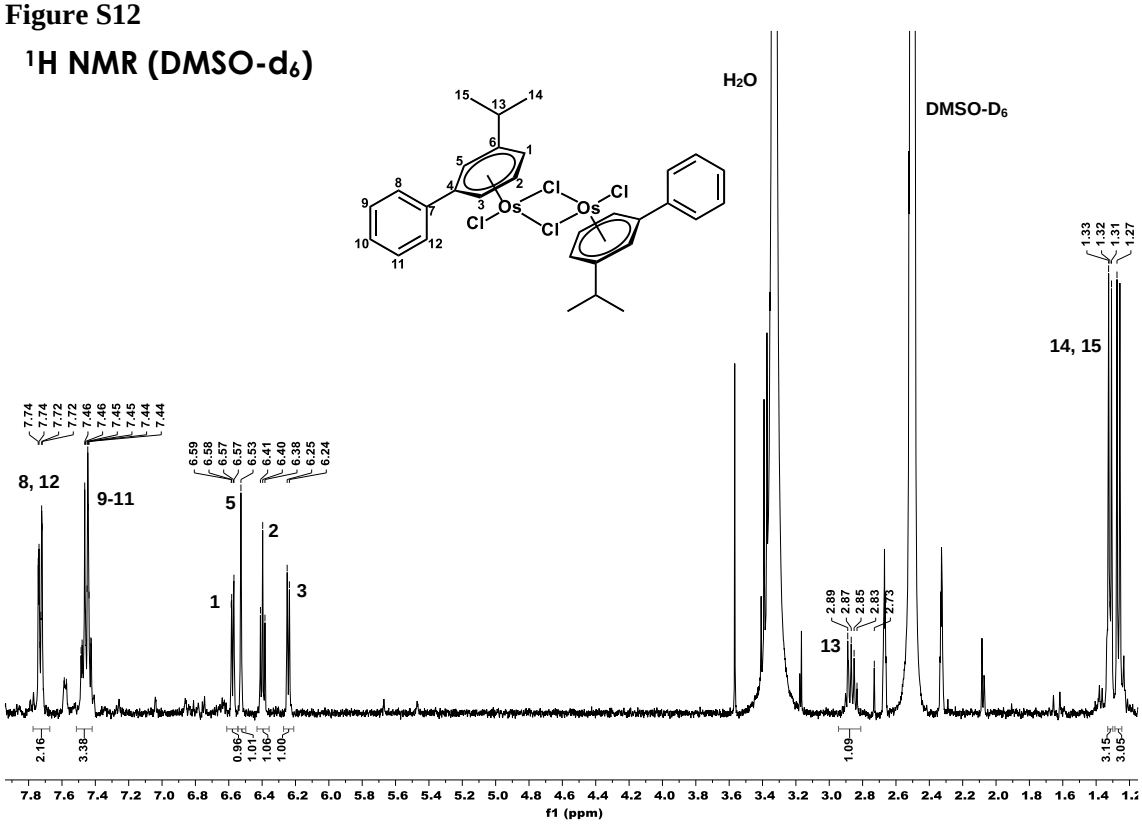


Figure S12. ^{1}H (400 MHz, DMSO-d_6) NMR spectra of dimer **2**.

Figure S13

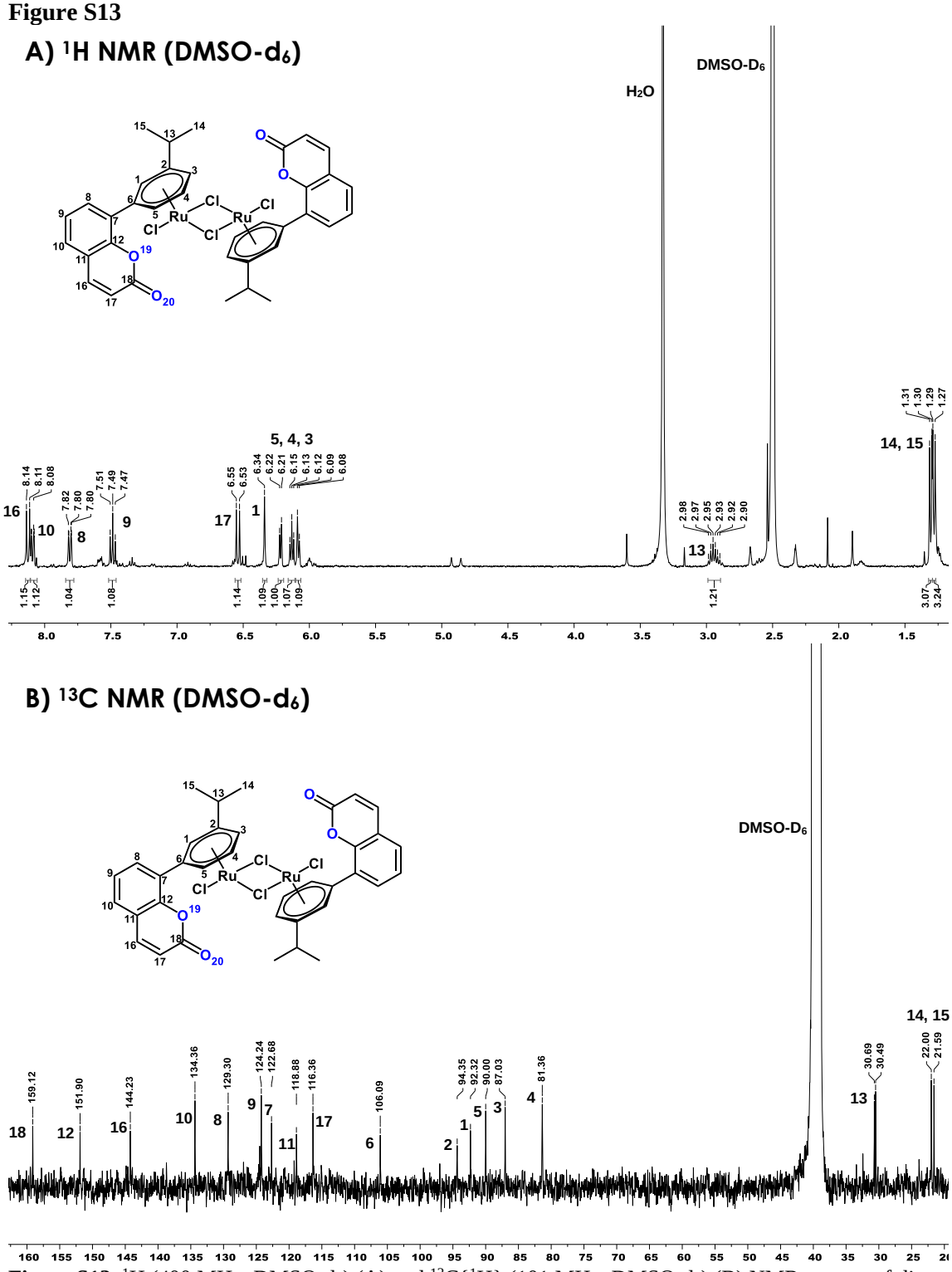


Figure S13. ^{1}H (400 MHz, DMSO-d_6) (A) and $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6) (B) NMR spectra of dimer **3**.

Figure S14

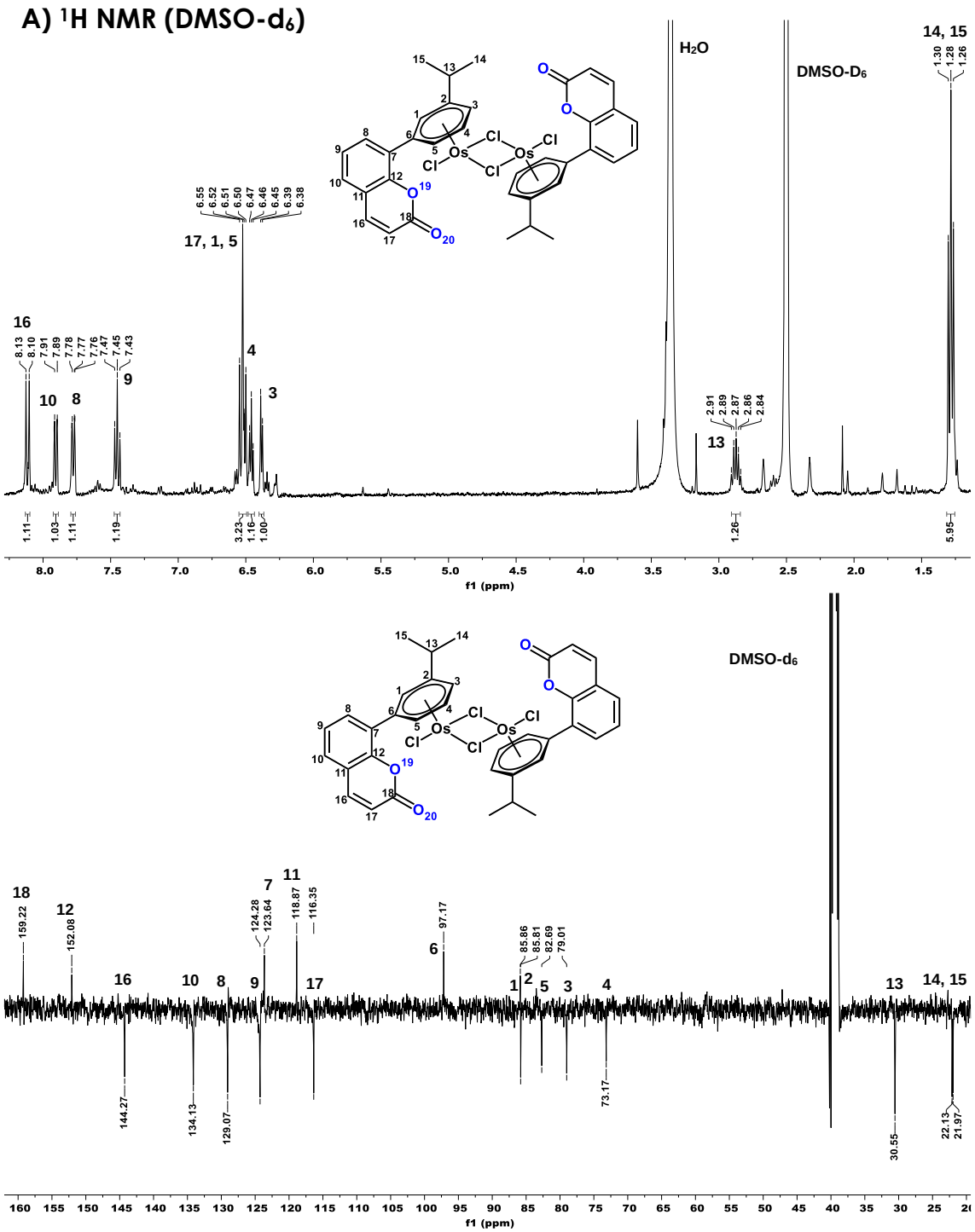


Figure S14. ^{1}H (400 MHz, DMSO-d$_6$) (A) and ^{13}C{^{1}H} APT (101 MHz, DMSO-d$_6$) (B) NMR spectra of dimer **4**.

Figure S15

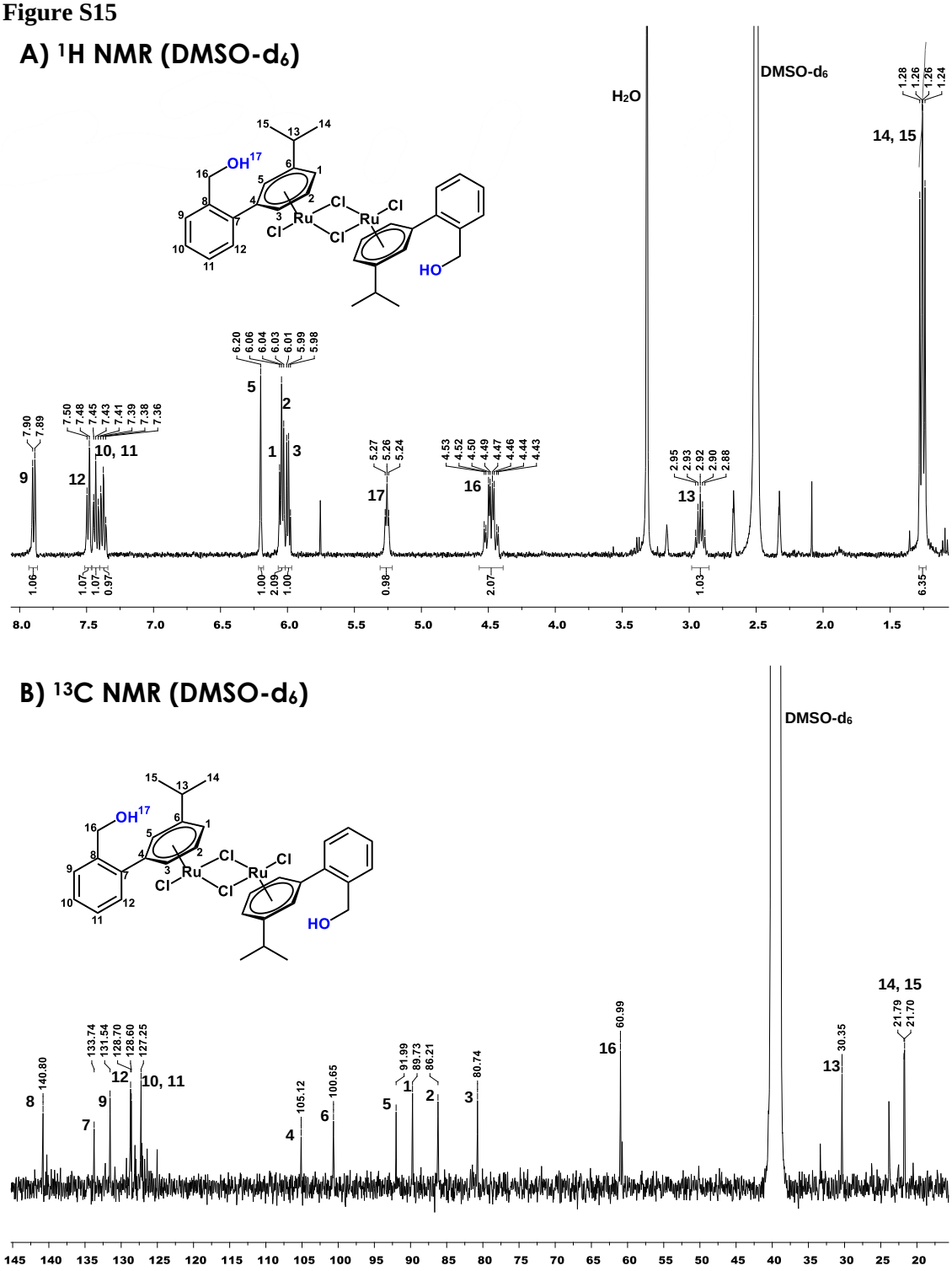


Figure S15. ^{1}H (400 MHz, DMSO-d_6) (A) and $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6) (B) NMR spectra of dimer **5**.

Figure S16

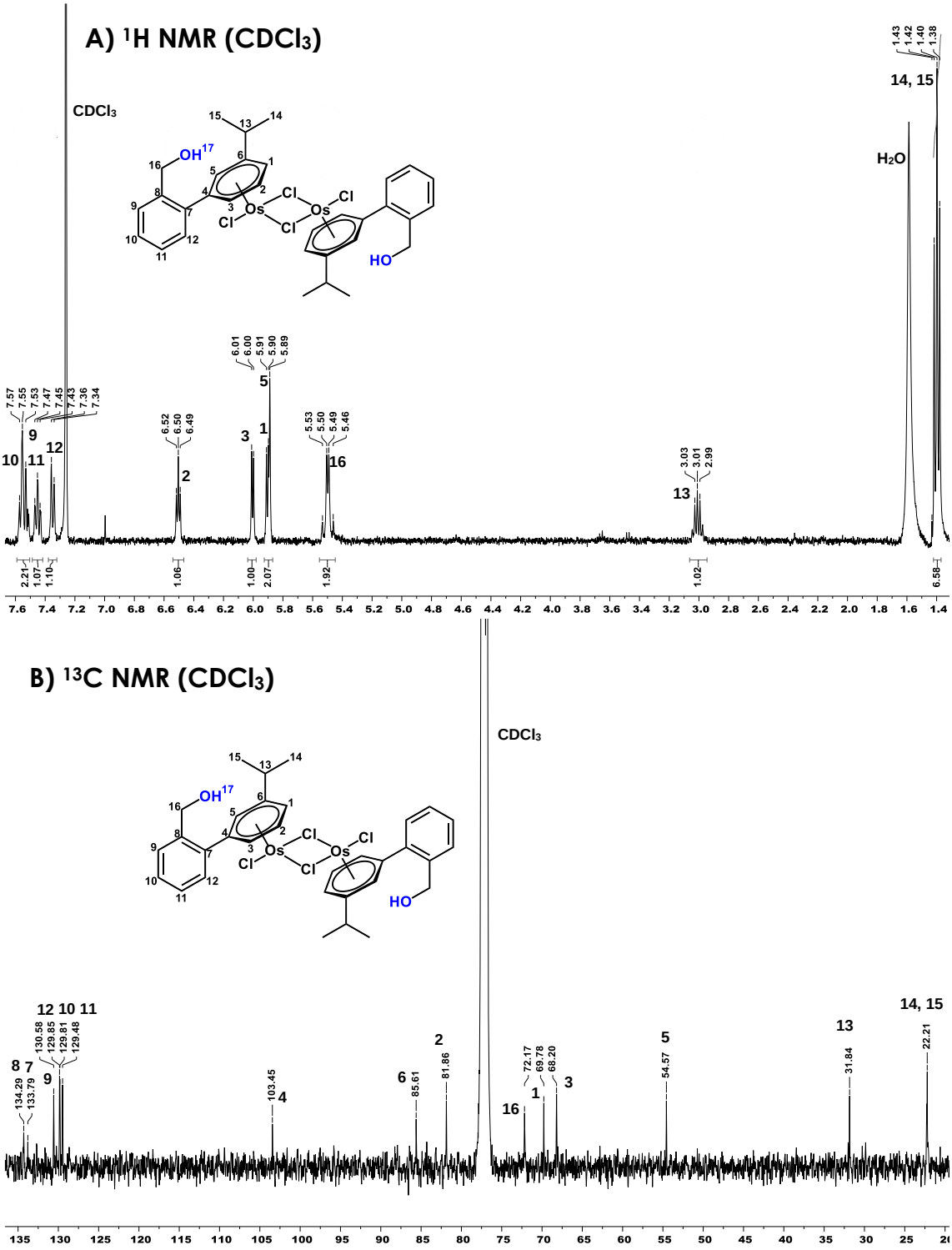


Figure S16. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of dimer **6**.

Figure S17

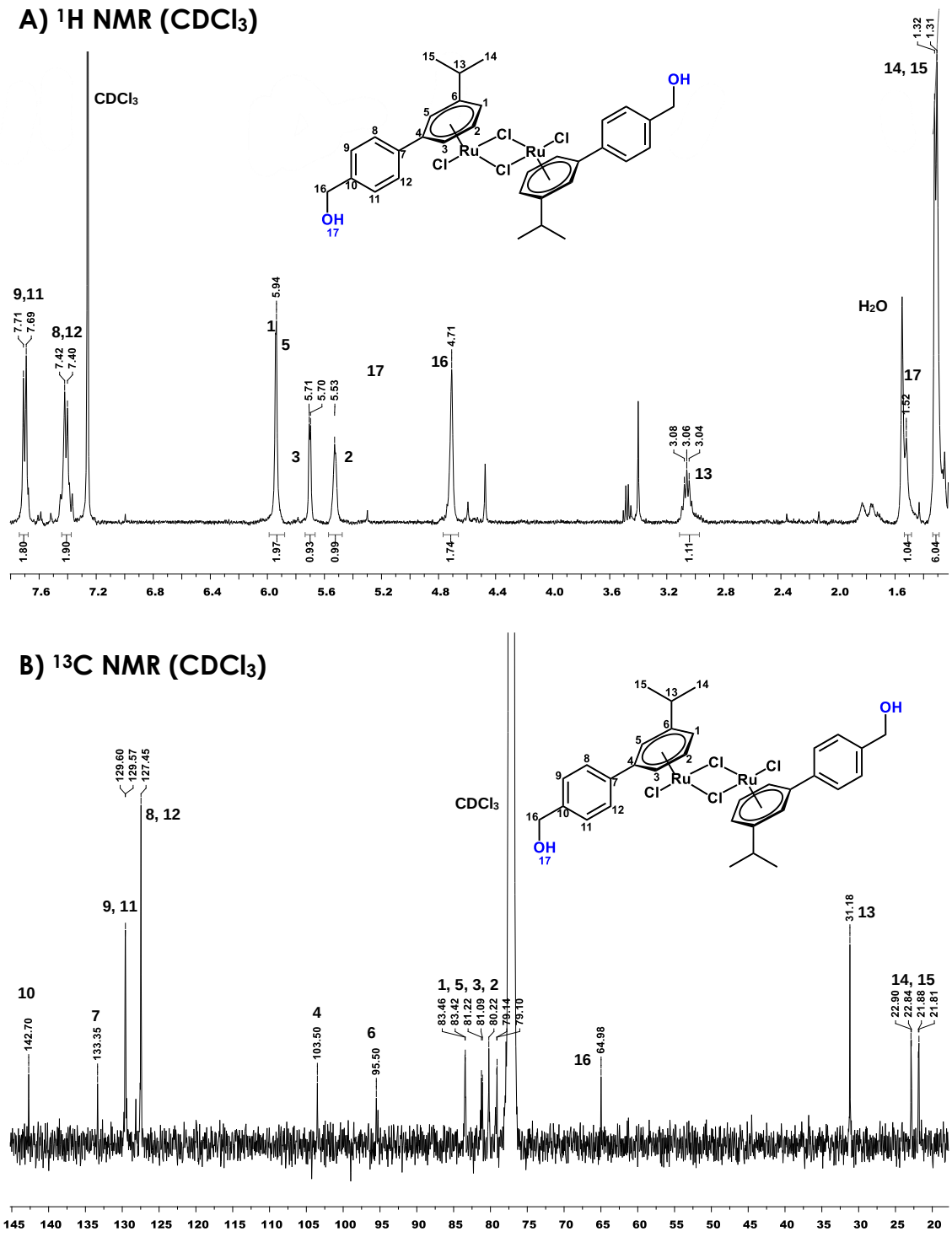


Figure S17. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of dimer **7**.

Figure S18

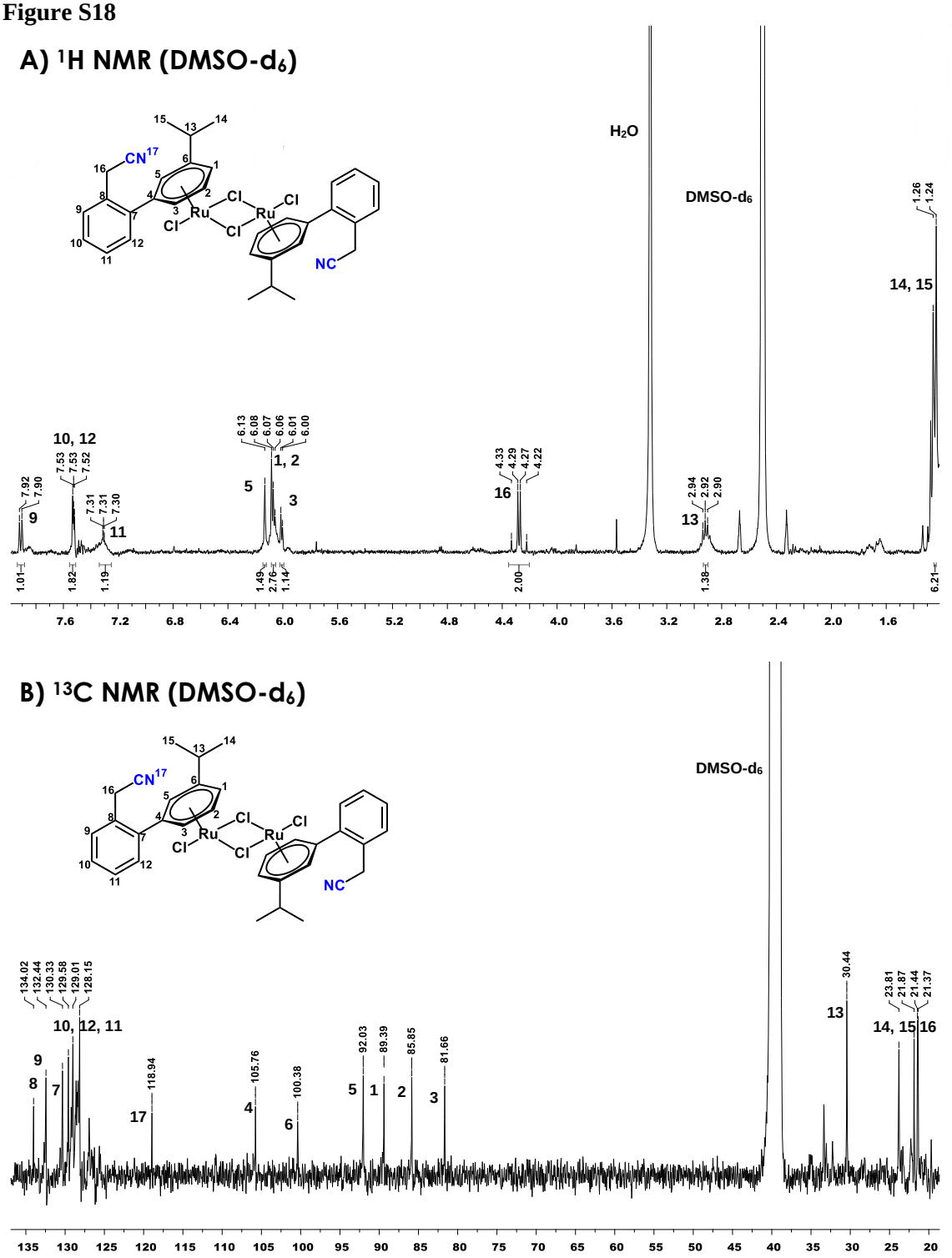


Figure S18. ^{1}H (400 MHz, DMSO-d_6) (A) and $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6) (B) NMR spectra of dimer **8**.

Figure S19

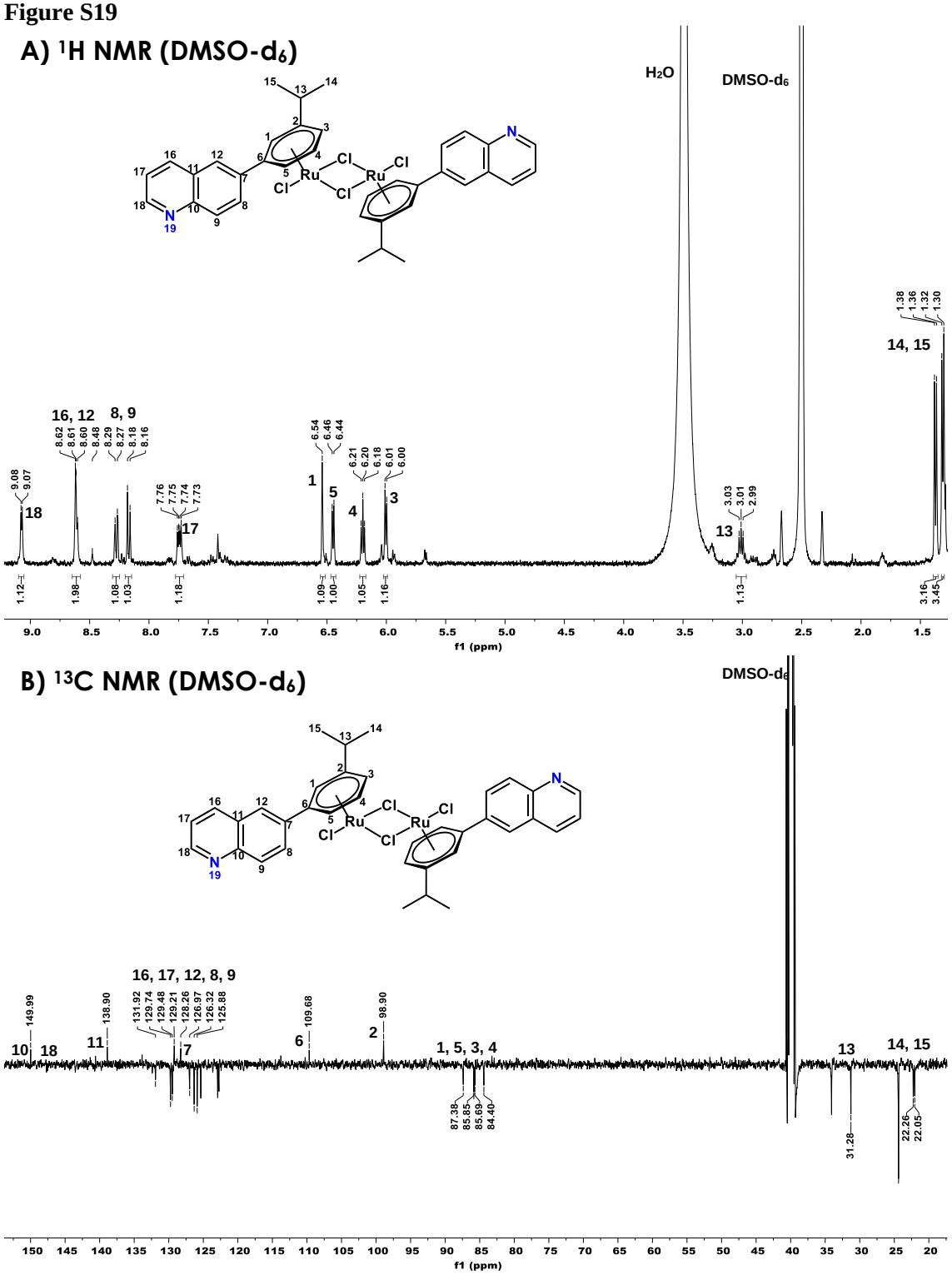


Figure S19. ^{1}H (400 MHz, DMSO-d_6) (A) and $^{13}C\{^{1}H\}$ APT (101 MHz, DMSO-d_6) (B) NMR spectra of dimer **9**.

Figure S20

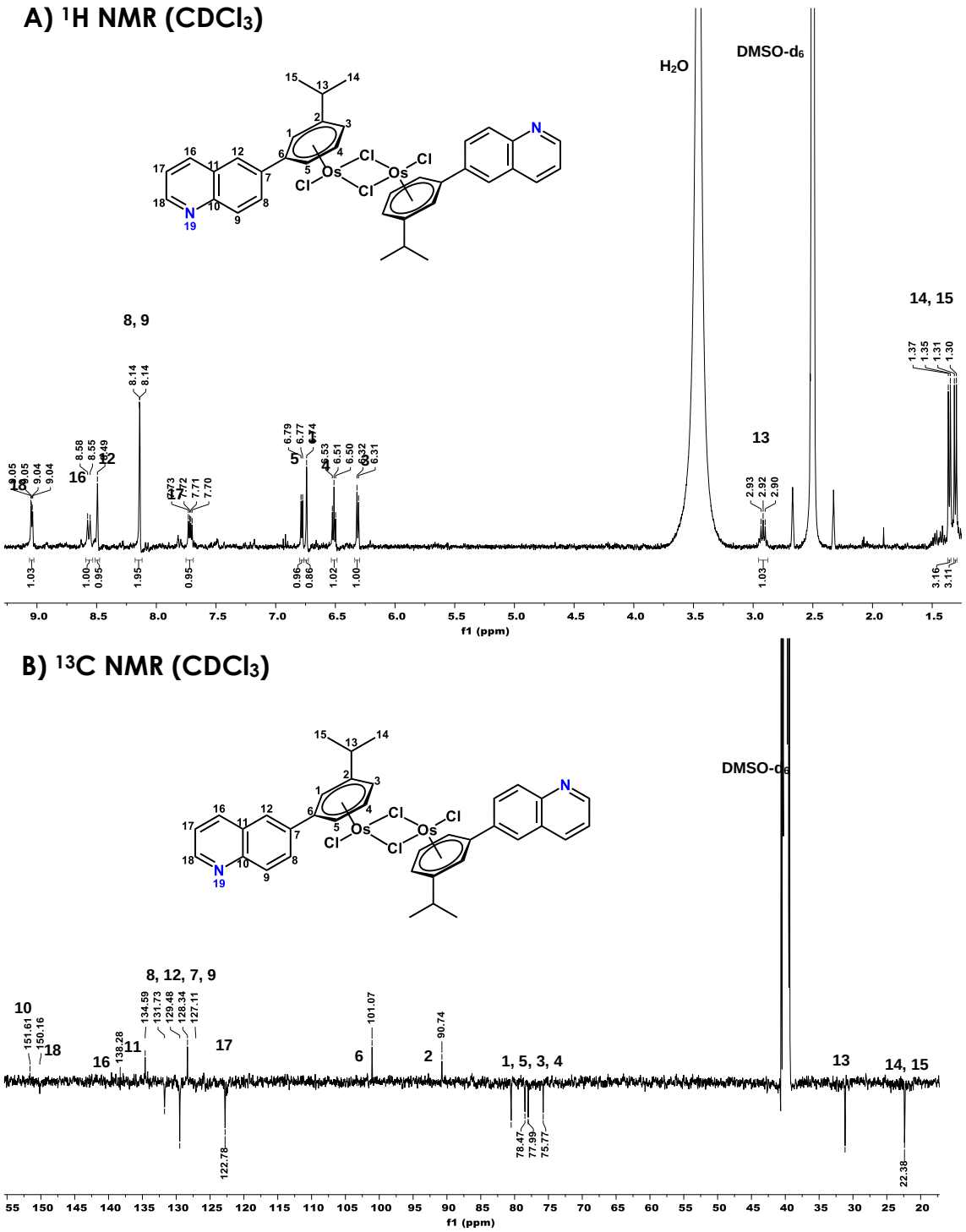


Figure S20. ^{1}H (400 MHz, DMSO-d_6) (A) and $^{13}C\{^{1}H\}$ APT (101 MHz, DMSO-d_6) (B) NMR spectra of dimer **10**.

Figure S21

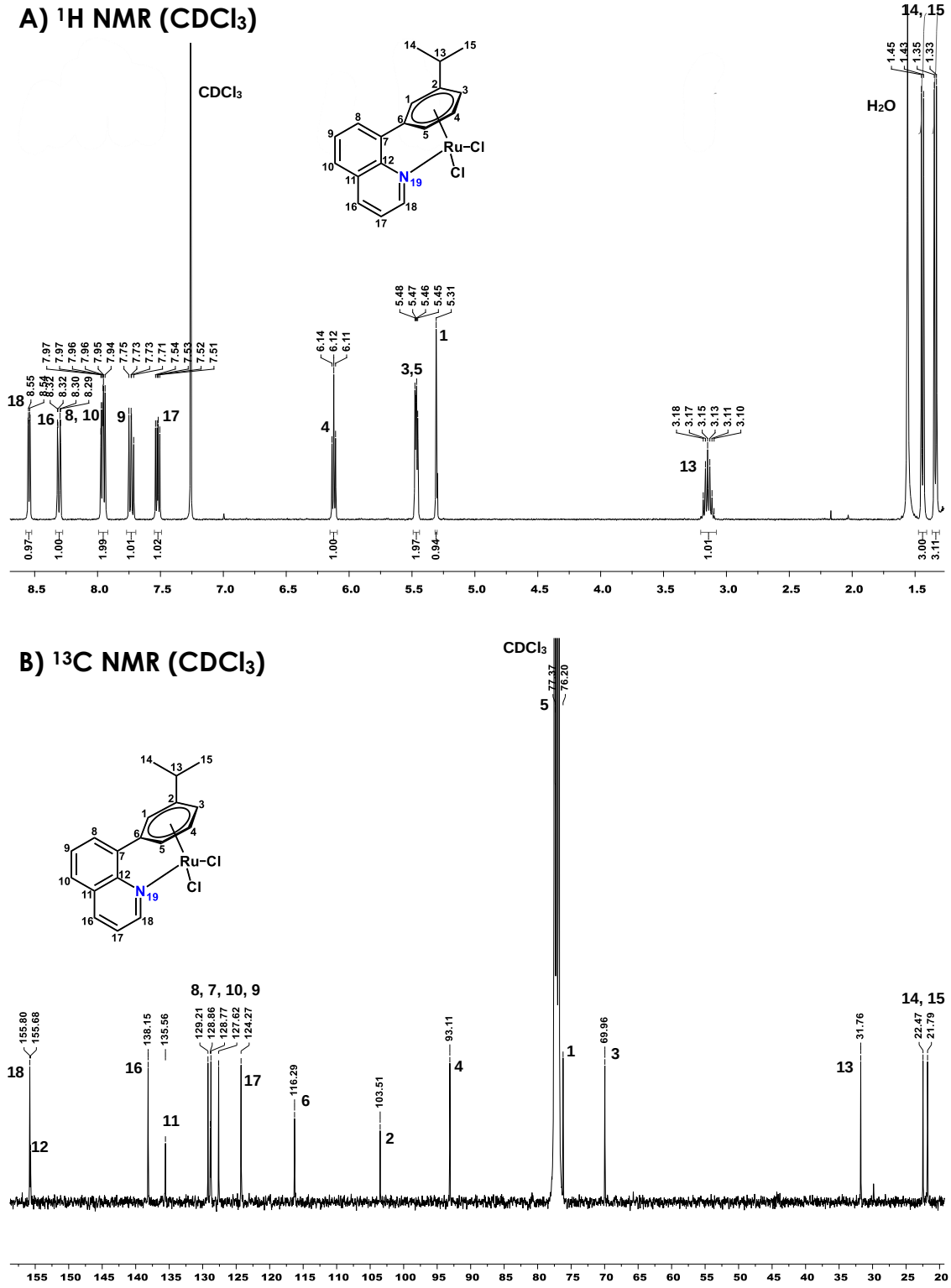


Figure S21. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of dichlorido monomer **11**.

Figure S22

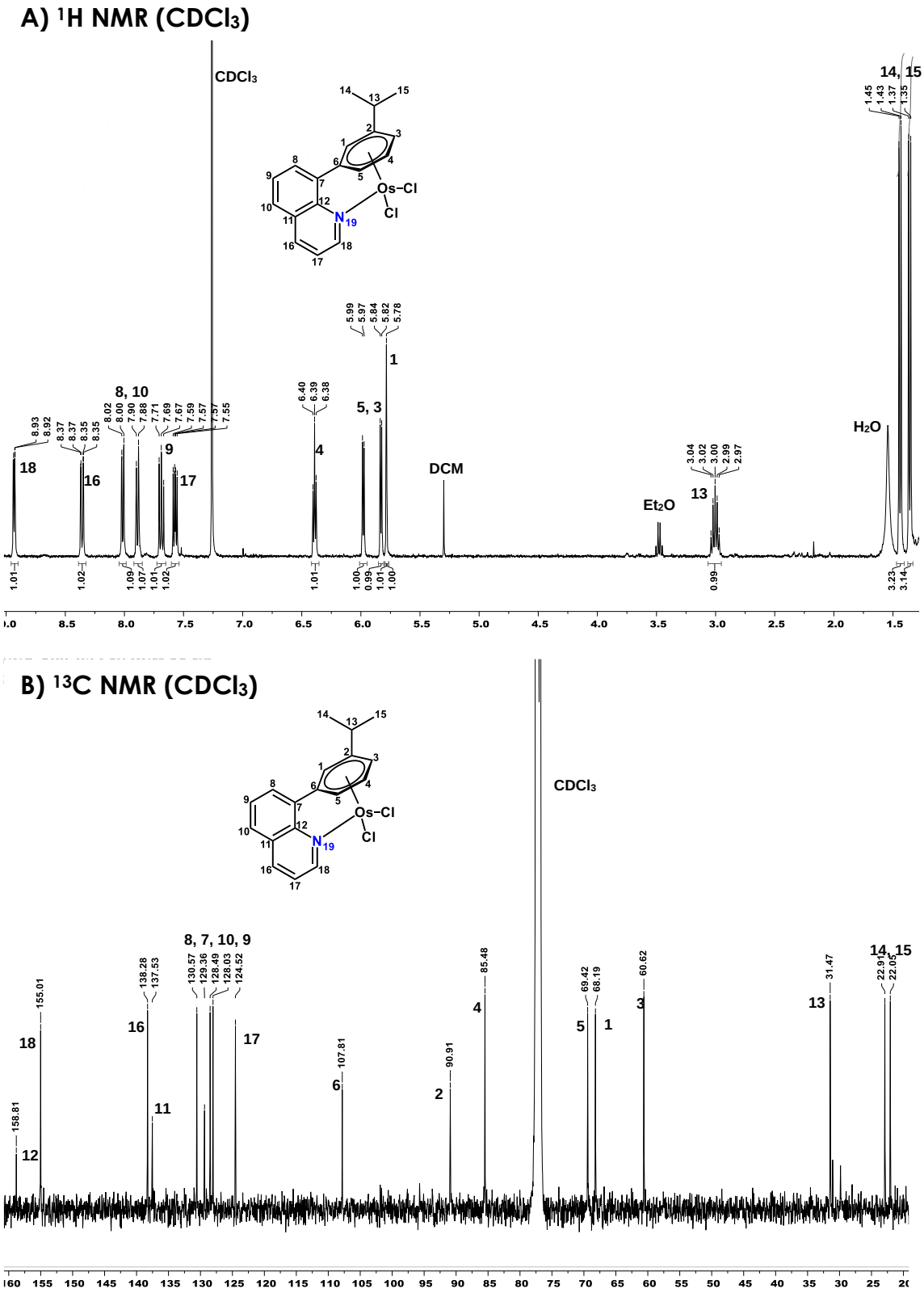


Figure S22. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of dichlorido monomer **12**.

Figure S23

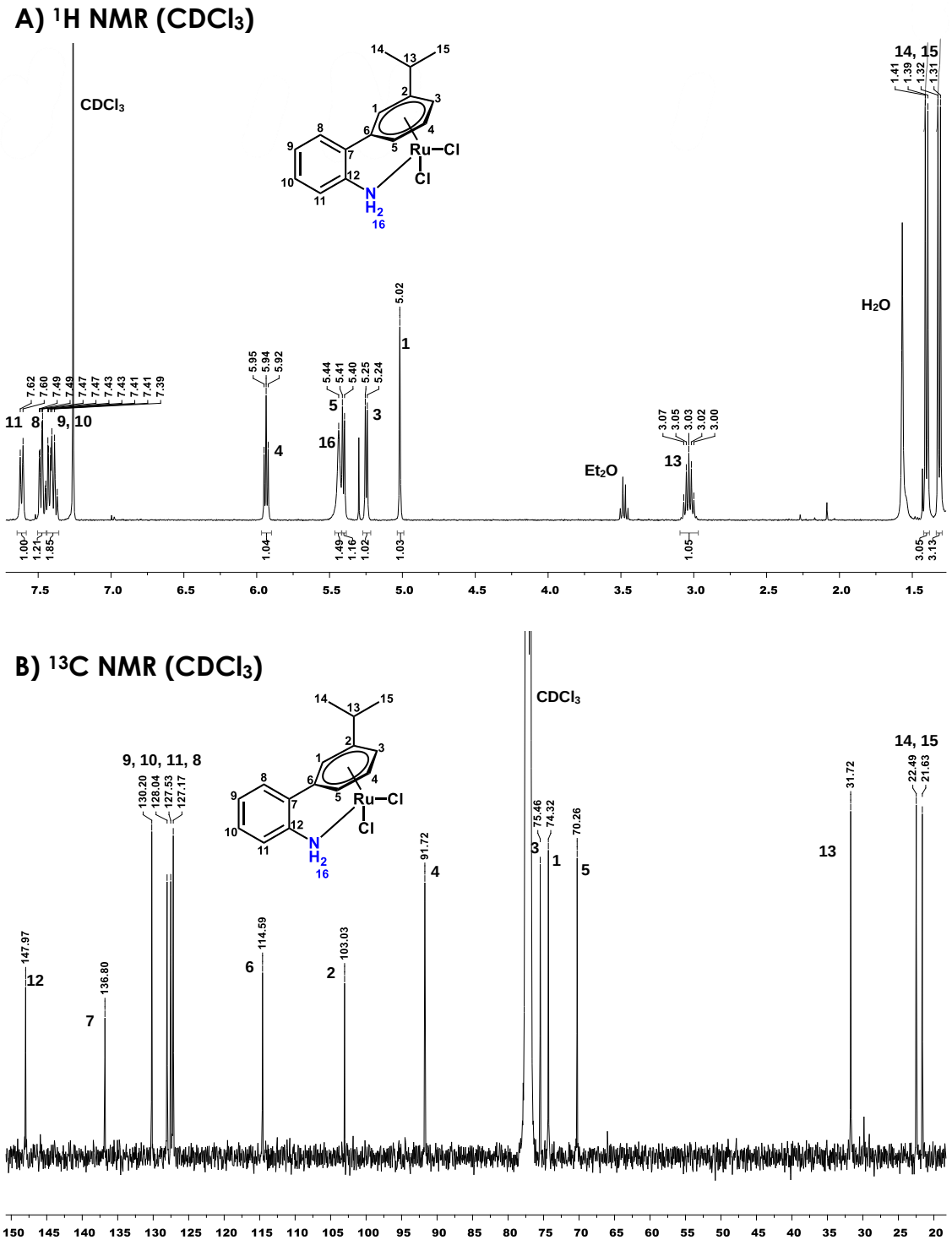


Figure S23. ^{1}H (400 MHz, $CDCl_3$) (A) and $^{13}C\{^{1}H\}$ (101 MHz, $CDCl_3$) (B) NMR spectra of dichlorido monomer **13**.

Figure S24

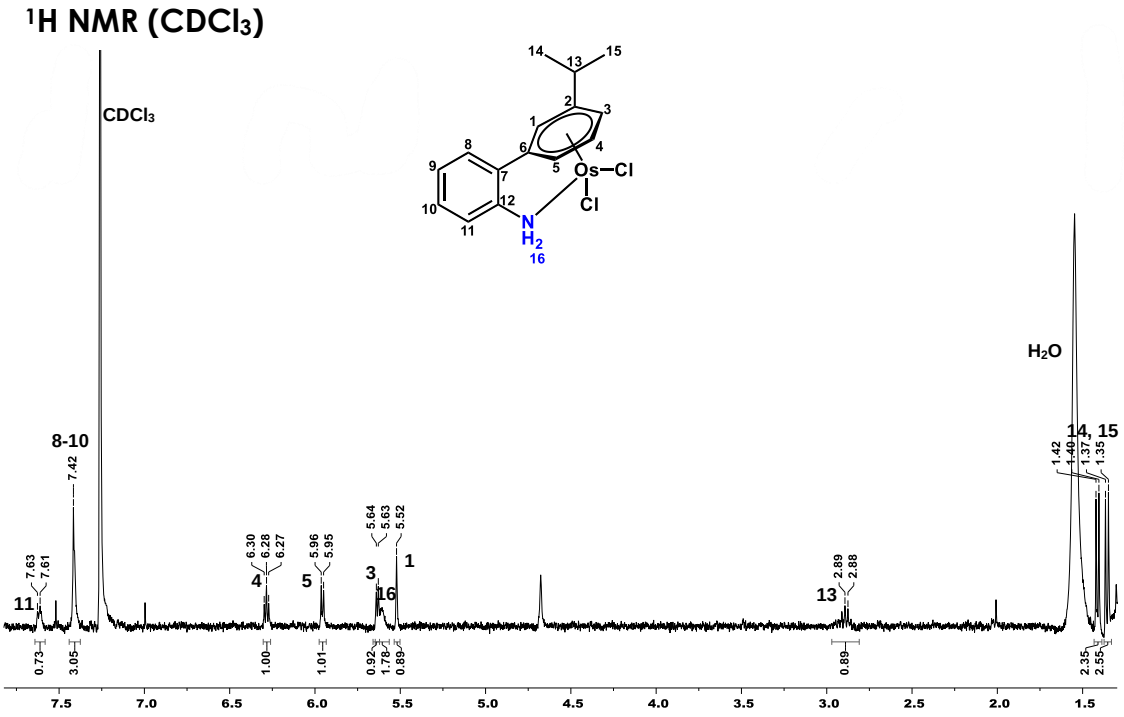


Figure S24. ^{1}H (400 MHz, $CDCl_3$) NMR spectra of dichlorido monomer **14**.

Figure S25

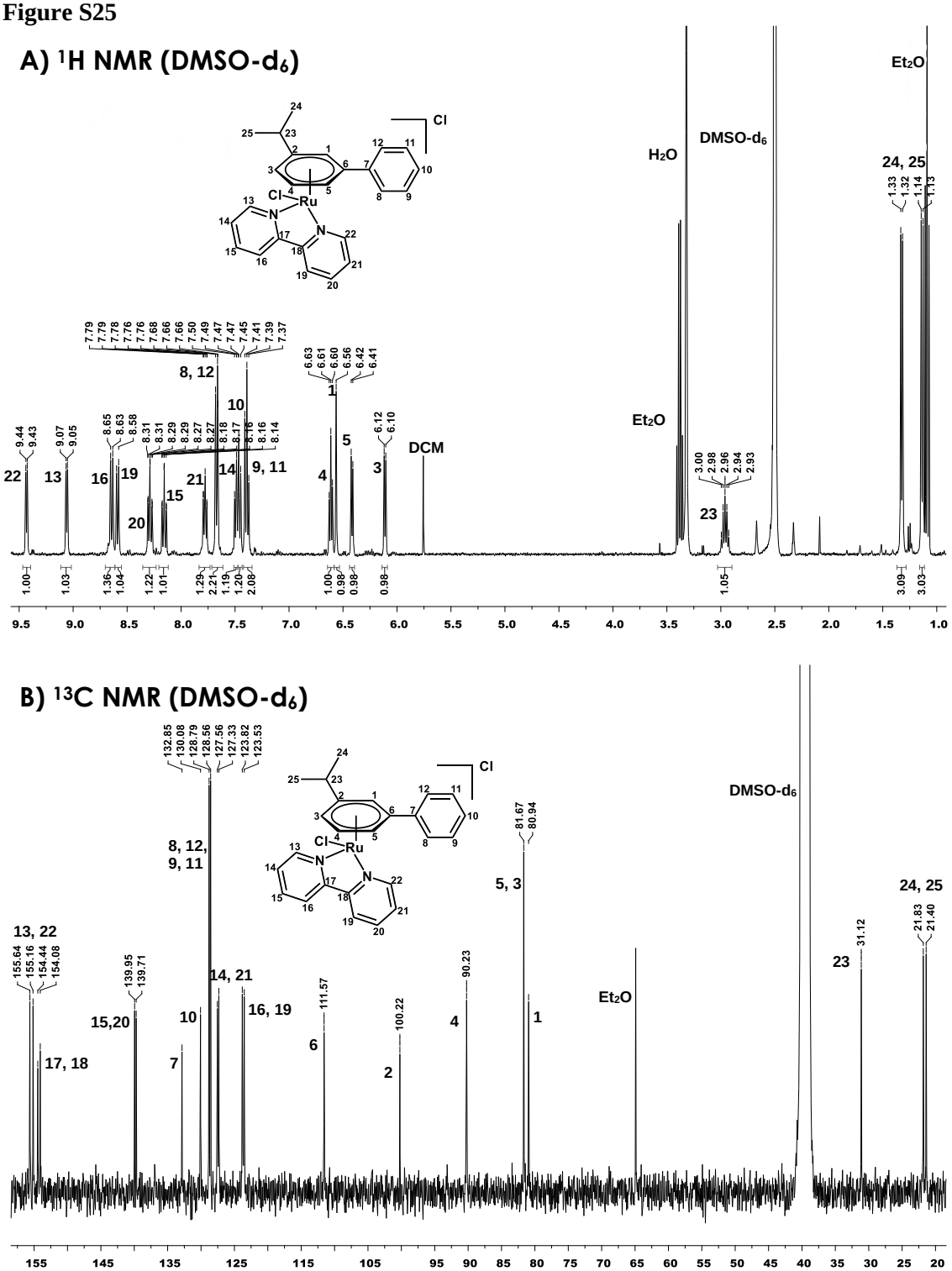


Figure S25. ^{1}H (400 MHz, DMSO-d_6) (A) and $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6) (B) NMR spectra of monomer **15**.

Figure S26

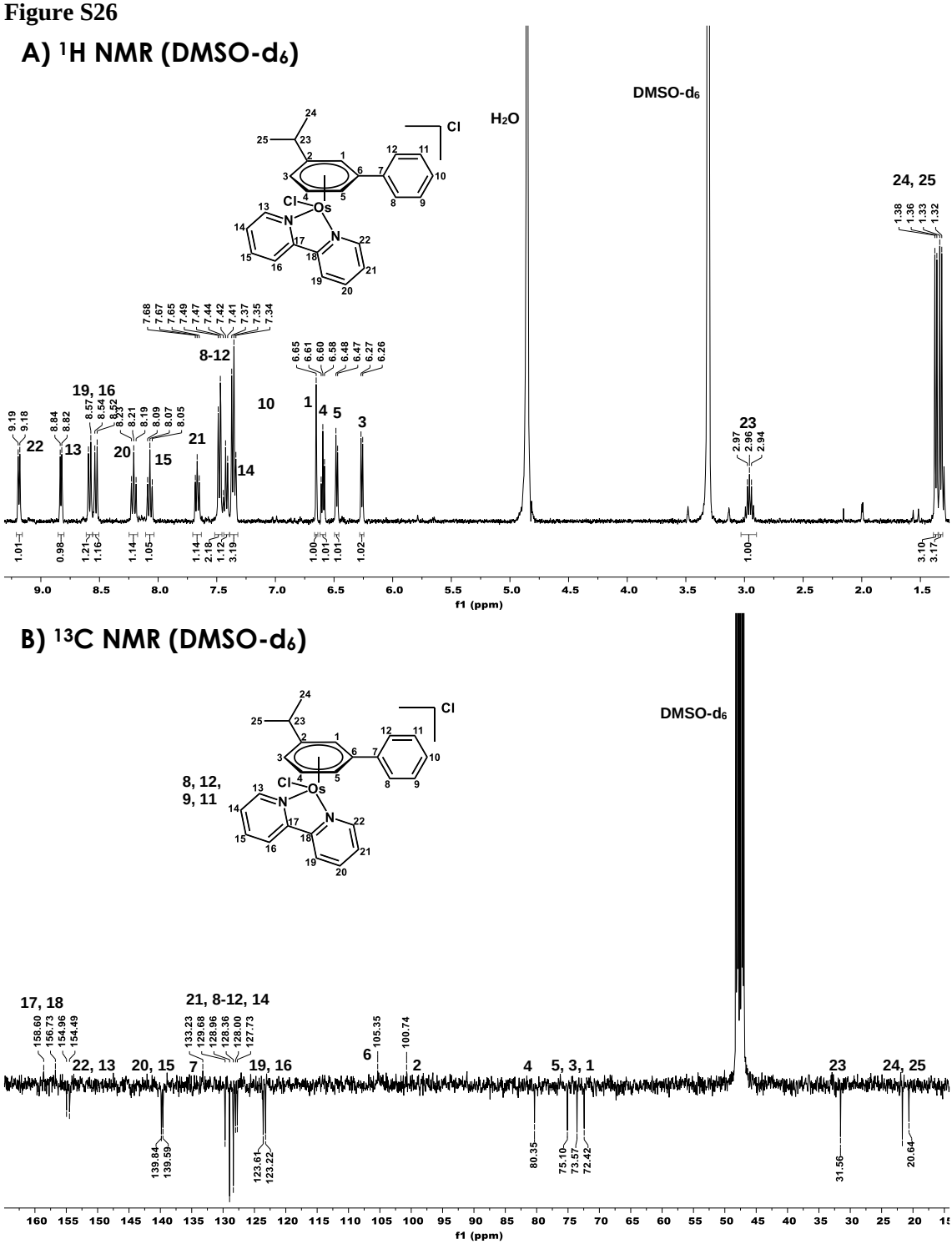


Figure S26. ^{1}H (400 MHz, DMSO-d_6) (A) and $^{13}C\{^{1}H\}$ APT (101 MHz, DMSO-d_6) (B) NMR spectra of monomer **16**.

Figure S27

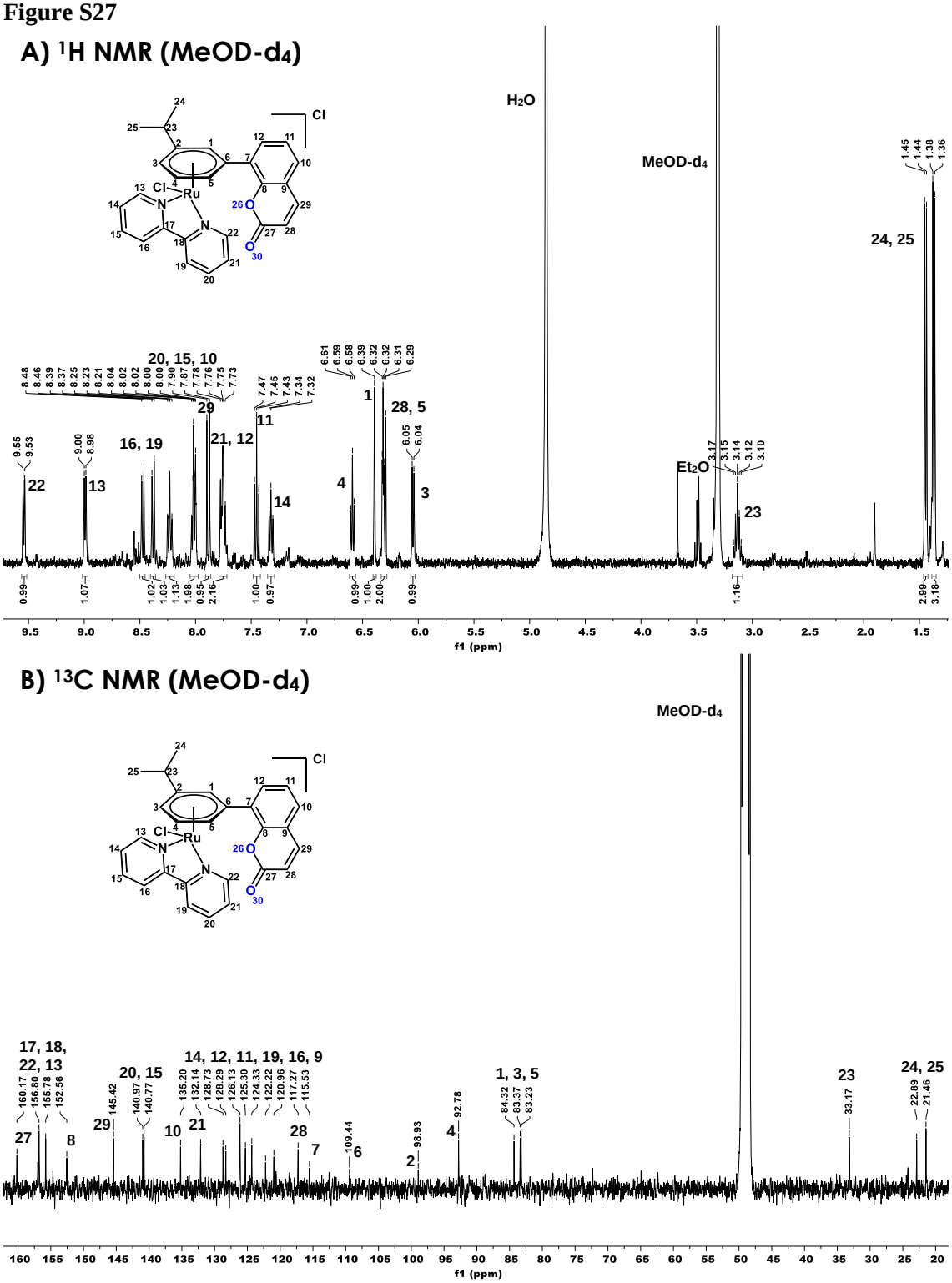


Figure S27. ^{1}H (400 MHz, MeOD-d_4) (A) and $^{13}C\{^{1}H\}$ (101 MHz, MeOD-d_4) (B) NMR spectra of monomer **17**.

Figure S28

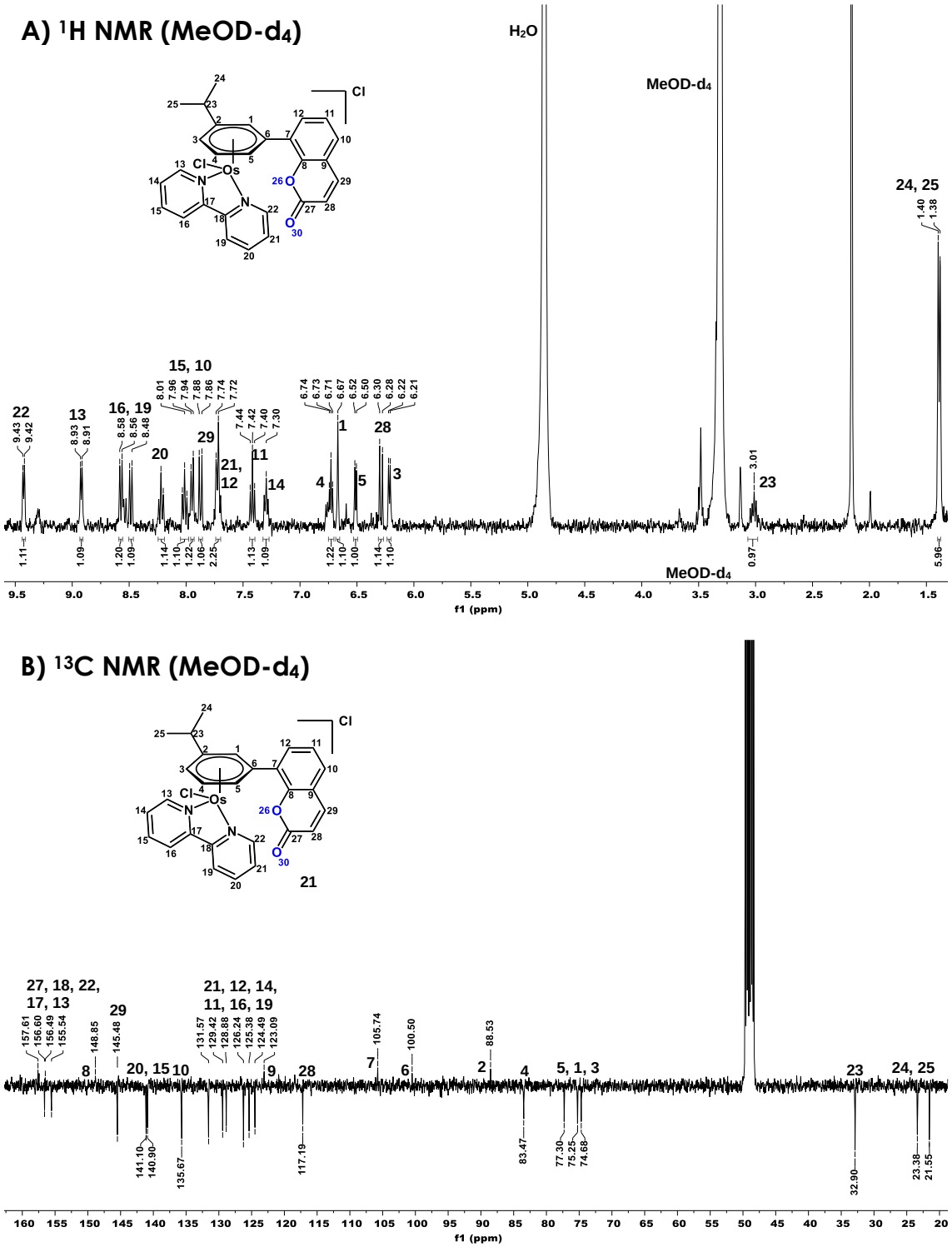


Figure S28. ^{1}H (400 MHz, MeOD-d_4) (A) and $^{13}C\{^{1}H\}$ APT (101 MHz, MeOD-d_4) (B) NMR spectra of monomer **18**.

Figure S29

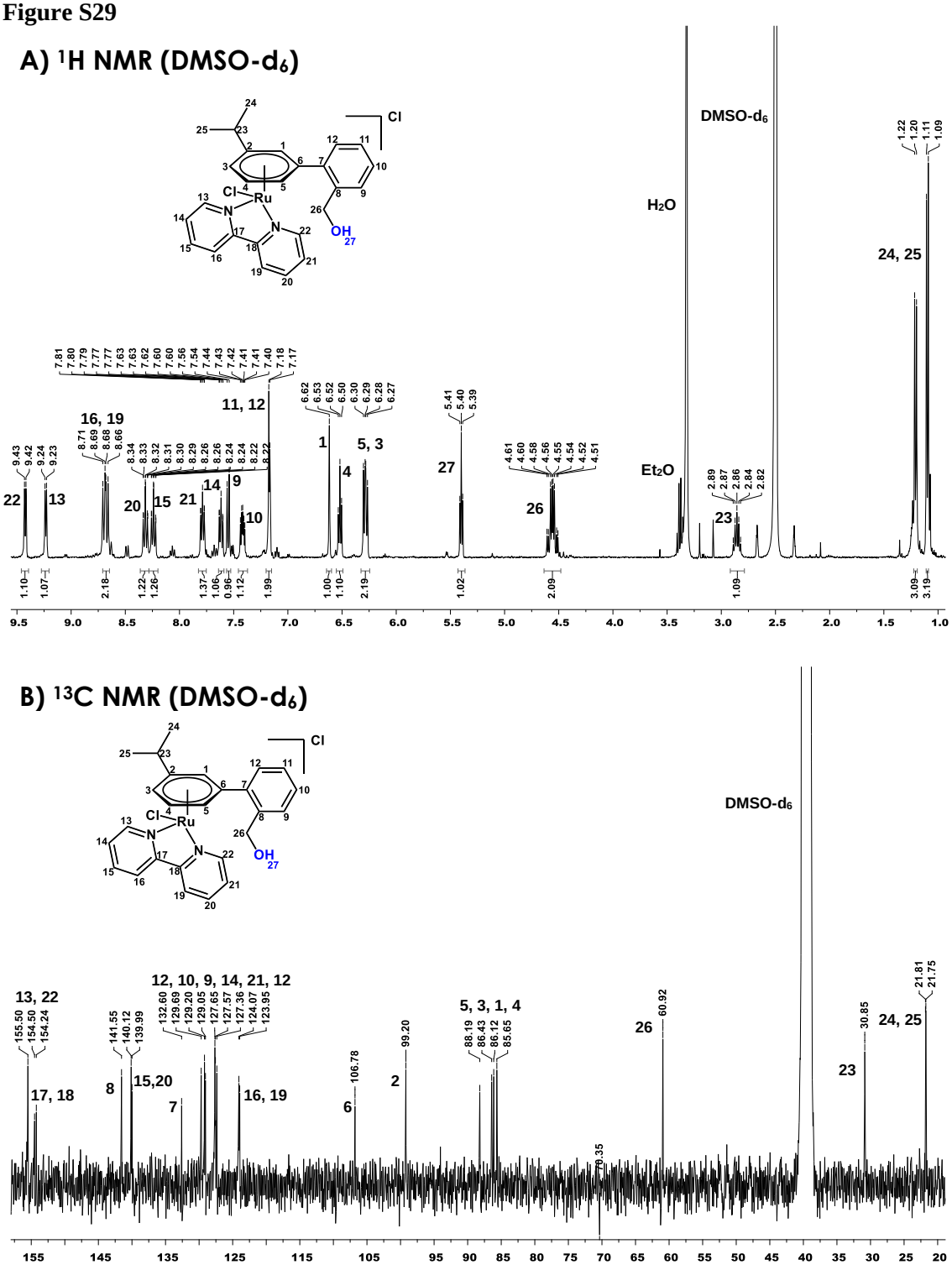


Figure S29. ^{1}H (400 MHz, DMSO-d_6) (A) and $^{13}C\{^{1}H\}$ (101 MHz, DMSO-d_6) (B) NMR spectra of monomer **19**.

Figure S30

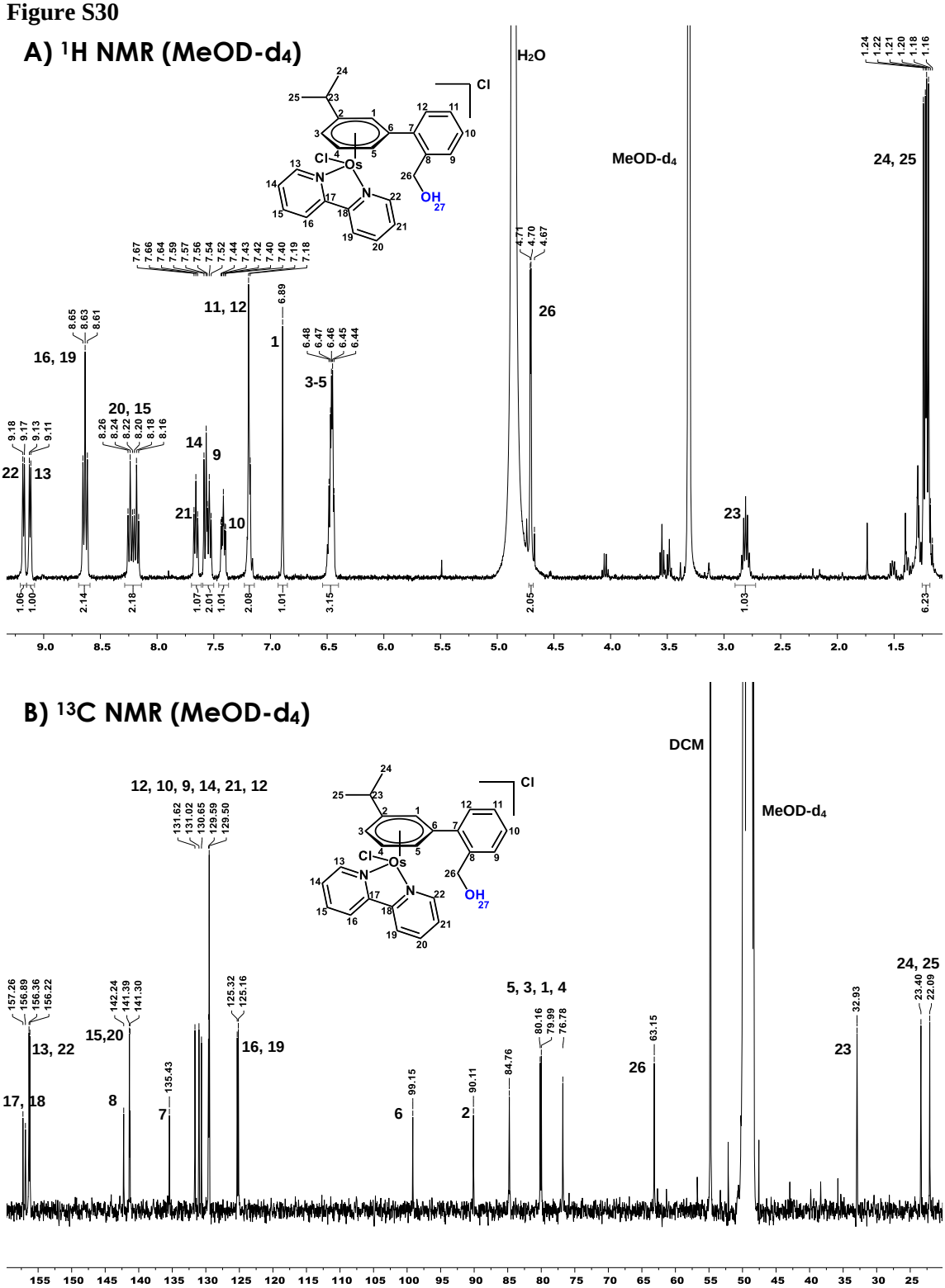


Figure S30. ^{1}H (400 MHz, MeOD-d4) (A) and $^{13}C\{^{1}H\}$ (101 MHz, MeOD-d4) (B) NMR spectra of monomer **20**.

Figure S31

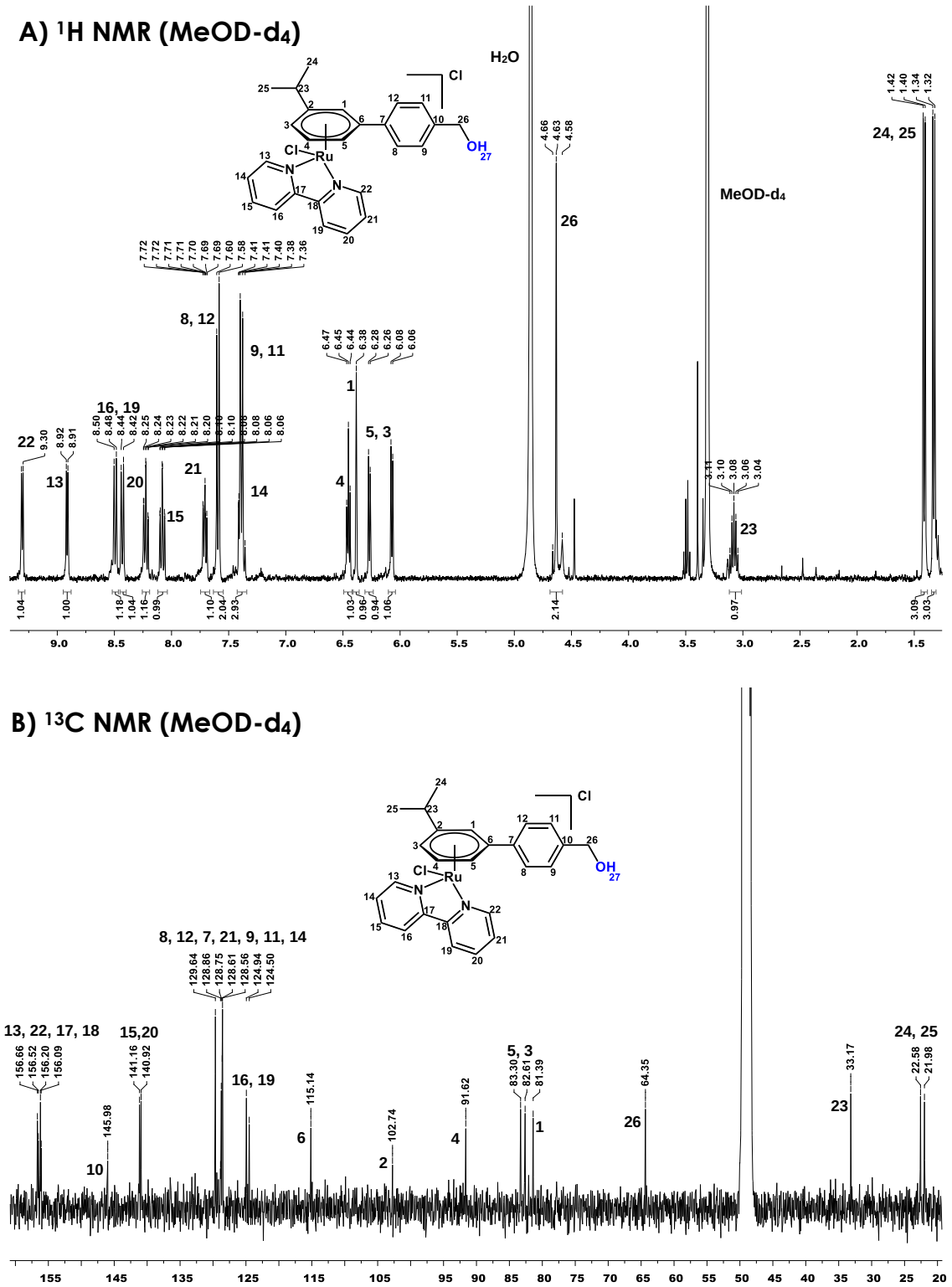


Figure S31. ^{1}H (400 MHz, MeOD-d_4) (A) and $^{13}C\{^{1}H\}$ (101 MHz, MeOD-d_4) (B) NMR spectra of monomer **21**.

Figure S32

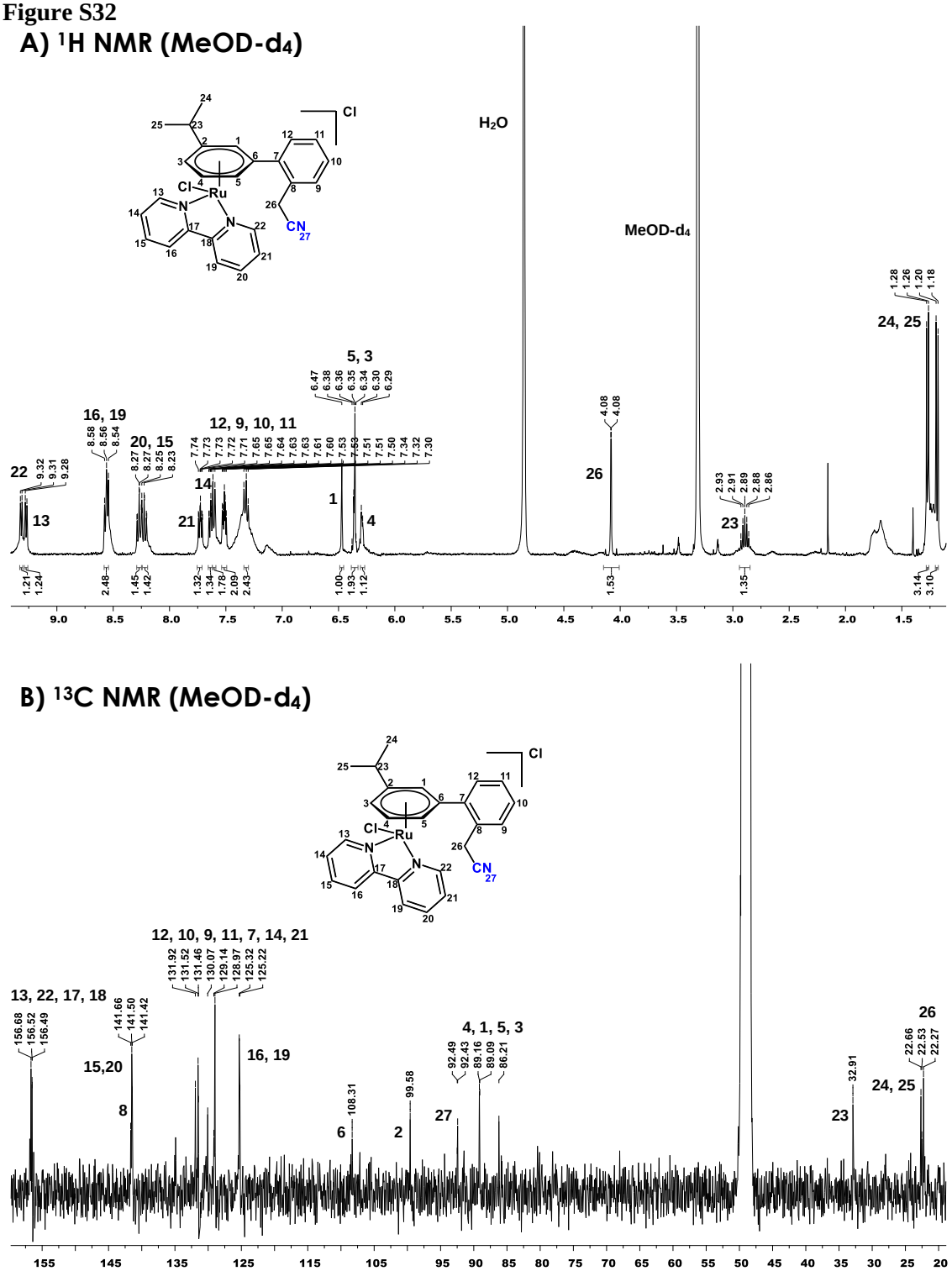


Figure S32. ^{1}H (400 MHz, MeOD-d_4) (A) and $^{13}C\{^{1}H\}$ (101 MHz, MeOD-d_4) (B) NMR spectra of monomer **22**.

Figure S33

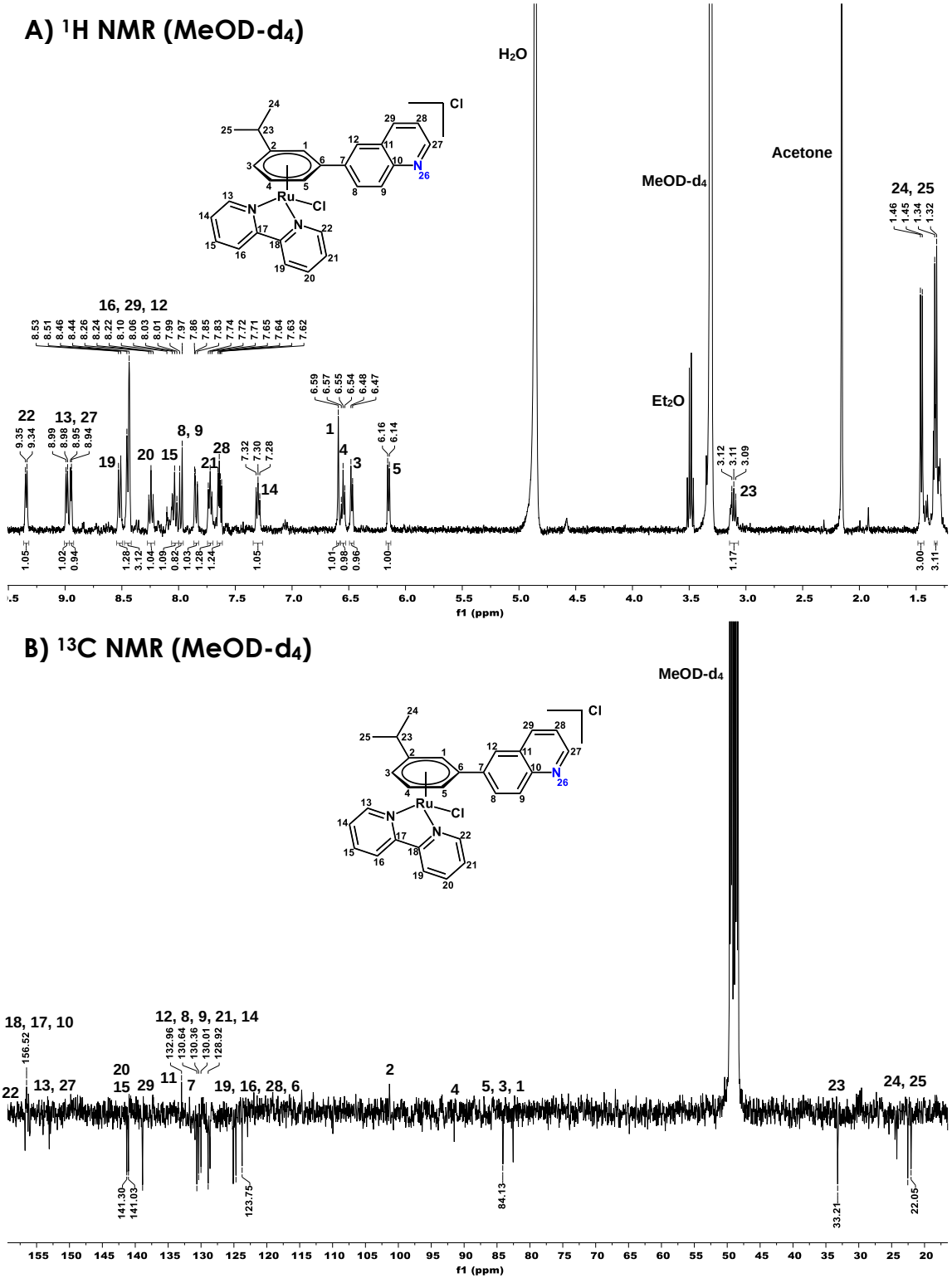


Figure S33. ^{1}H (400 MHz, MeOD-d_4) (A) and $^{13}C\{^{1}H\}$ (101 MHz, MeOD-d_4) (B) NMR spectra of monomer **23**.

Figure S34

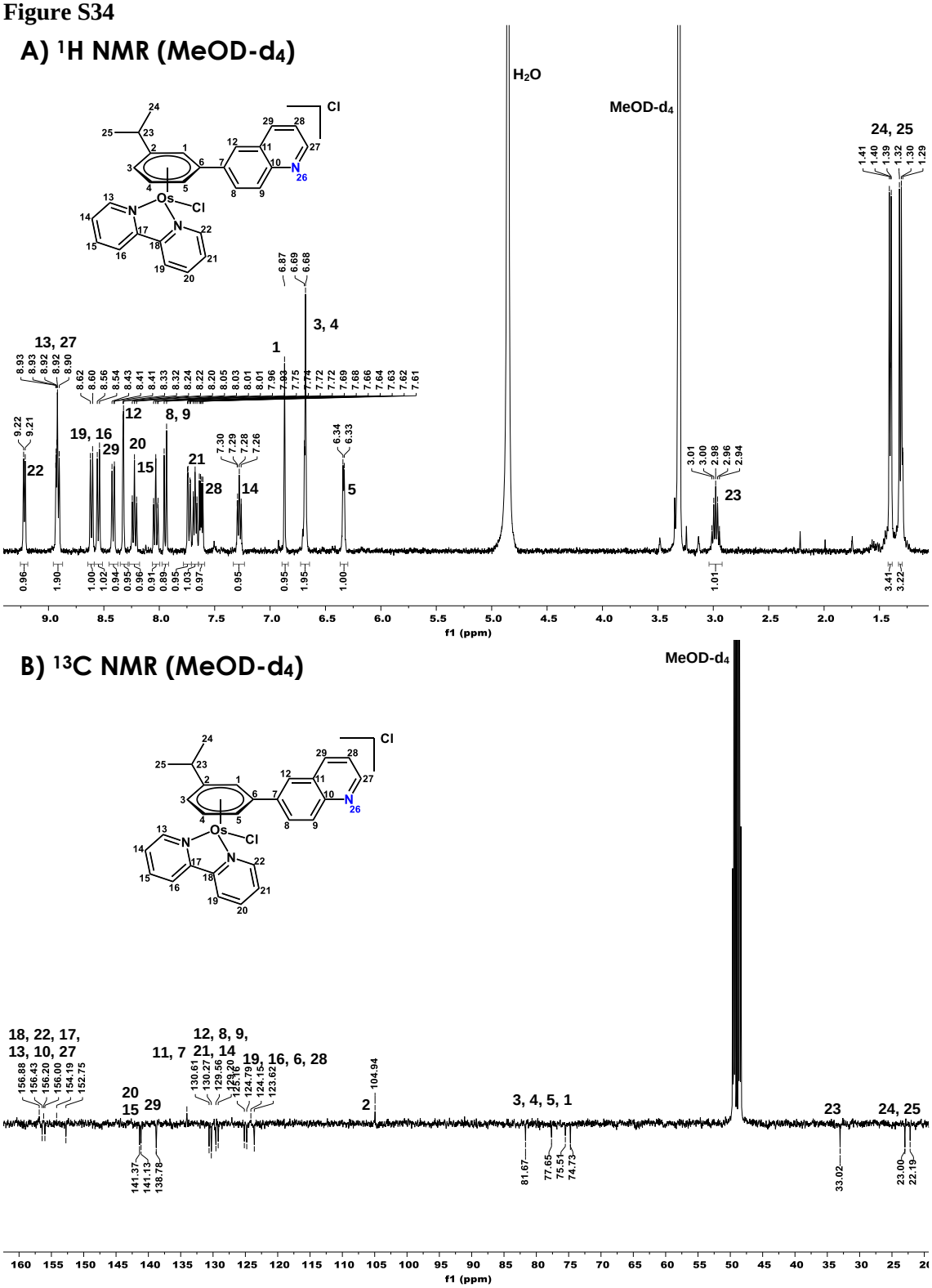


Figure S34. ^{1}H (400 MHz, MeOD-d_4) (A) and $^{13}C\{^{1}H\}$ APT (101 MHz, MeOD-d_4) (B) NMR spectra of monomer **24**.

Figure S35

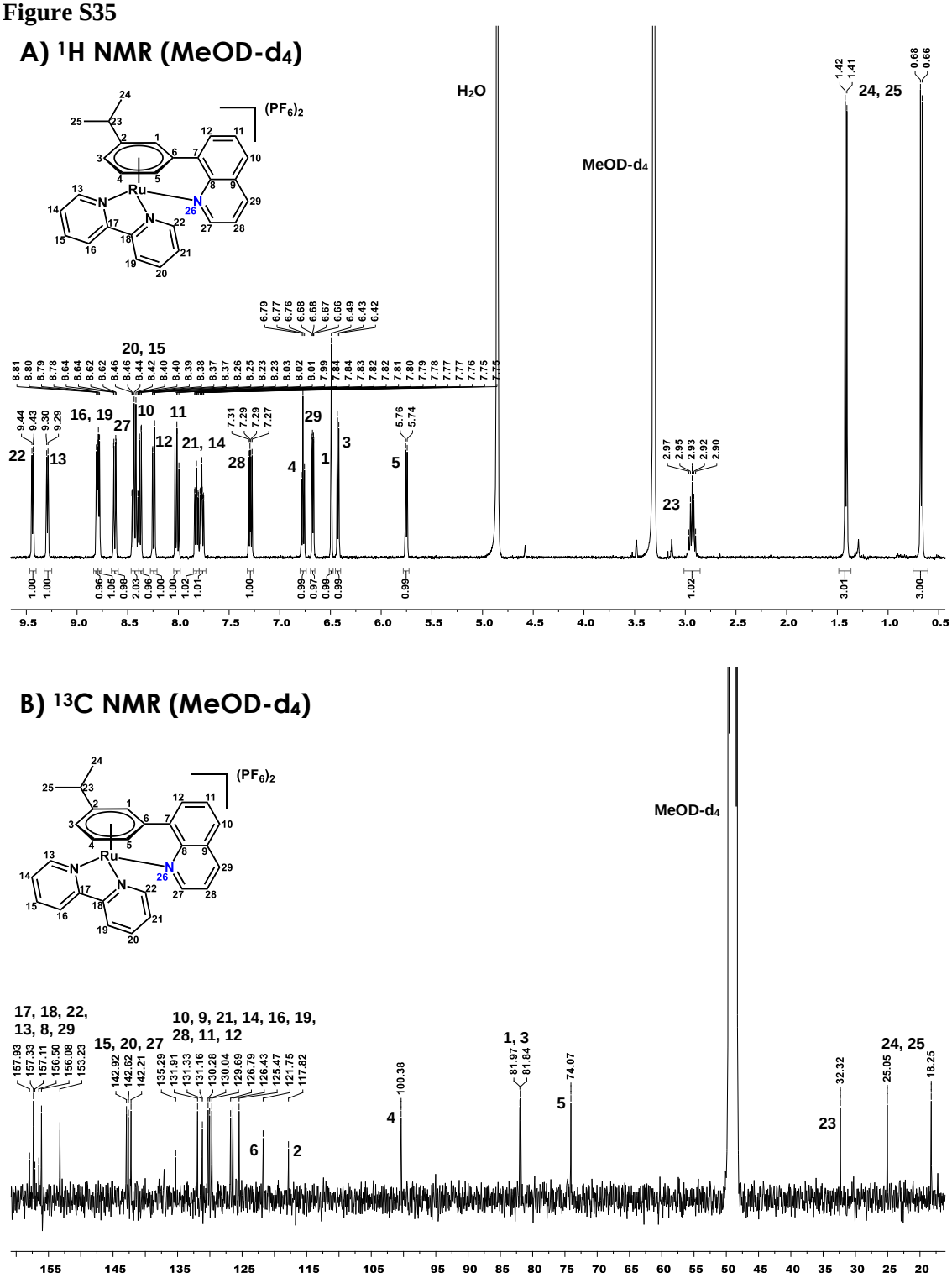


Figure S35. ^{1}H (400 MHz, MeOD-d_4) (A) and $^{13}C\{^{1}H\}$ (101 MHz, MeOD-d_4) (B) NMR spectra of monomer **25**.

Figure S36

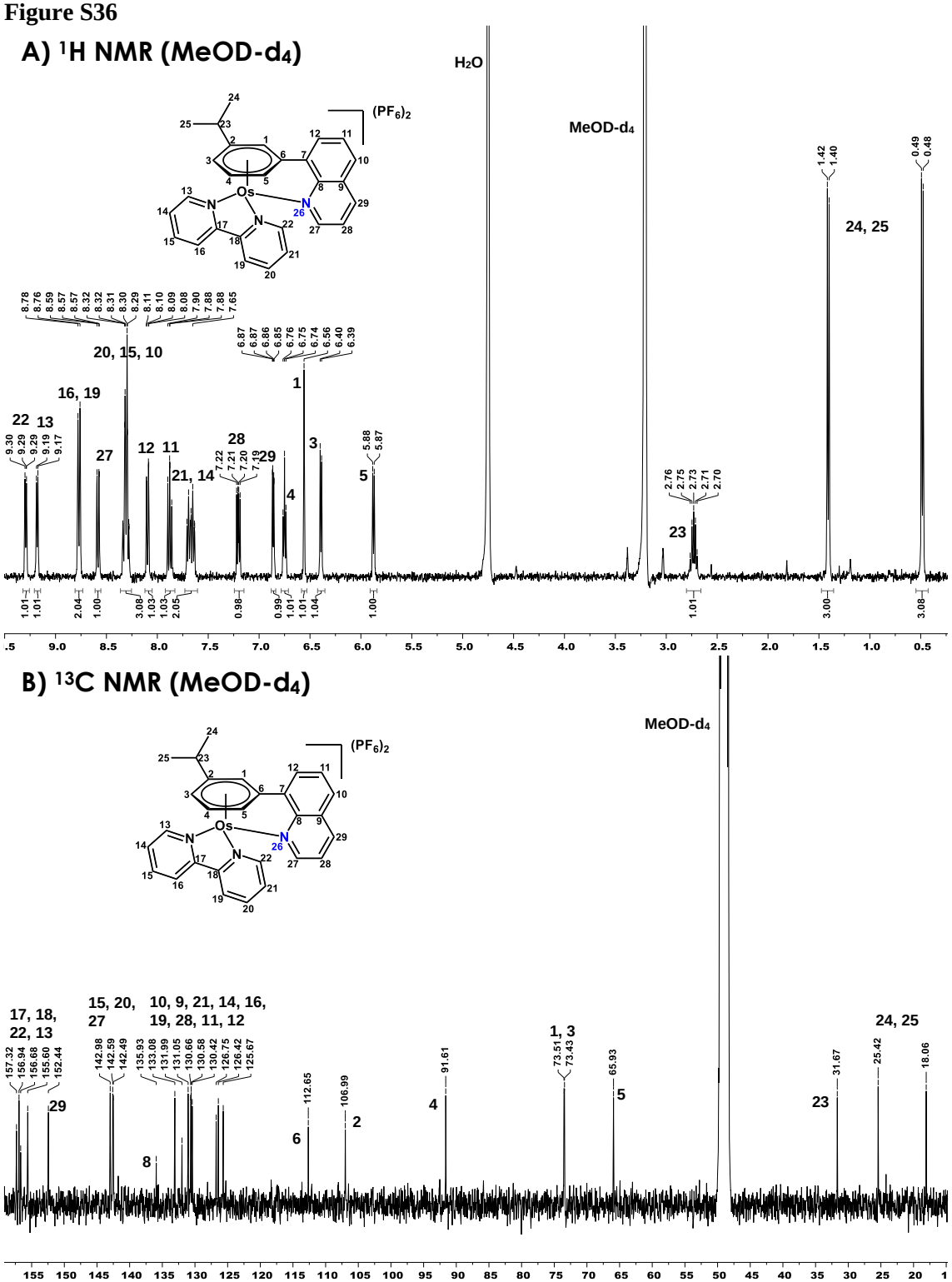


Figure S36. ^{1}H (400 MHz, MeOD-d4) (A) and $^{13}C\{^{1}H\}$ (101 MHz, MeOD-d4) (B) NMR spectra of monomer **26**.

Figure S37

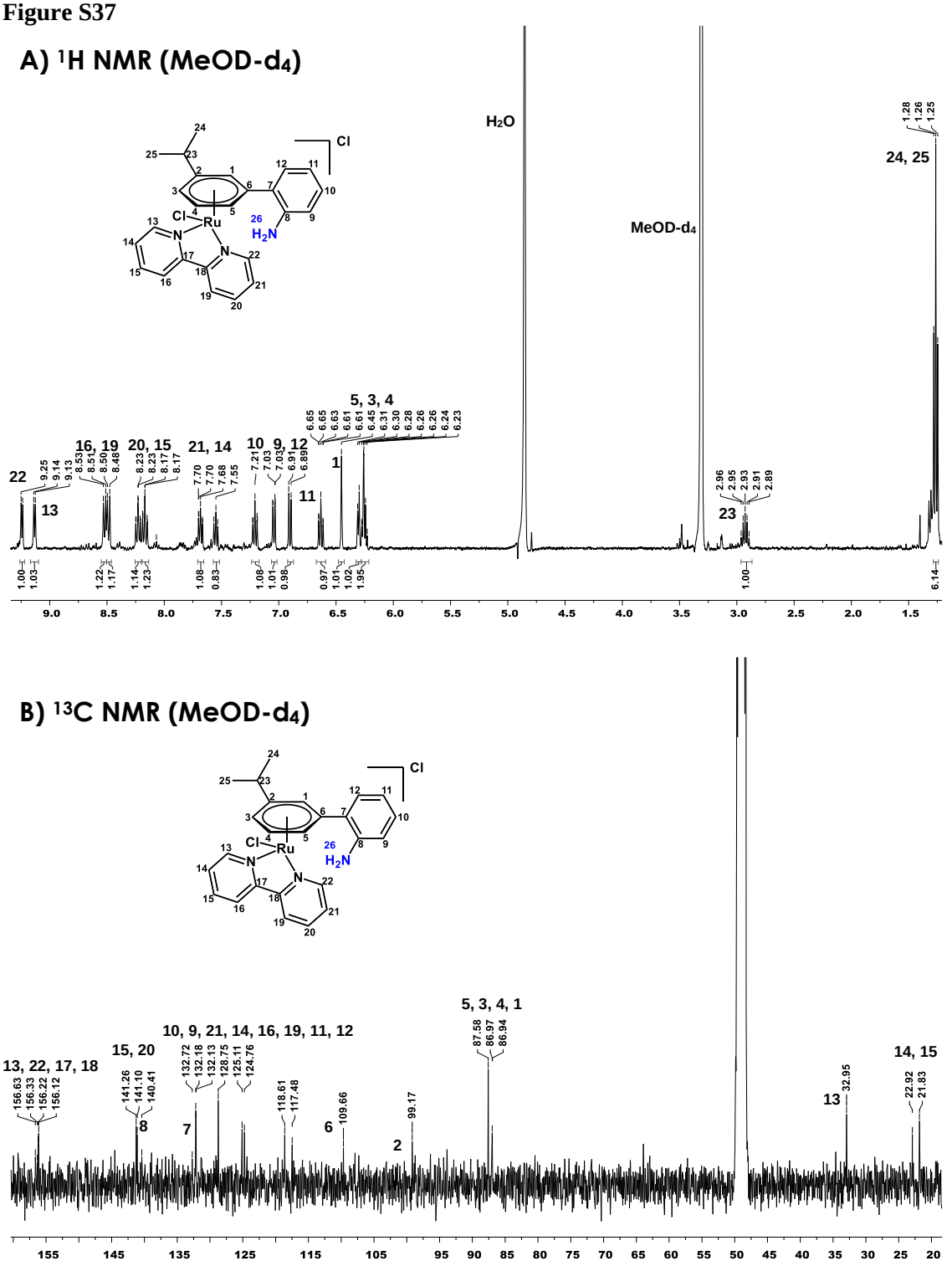


Figure S37. ^{1}H (400 MHz, MeOD-d_4) (A) and $^{13}C\{^{1}H\}$ (101 MHz, MeOD-d_4) (B) NMR spectra of monomer **27**.

Figure S38

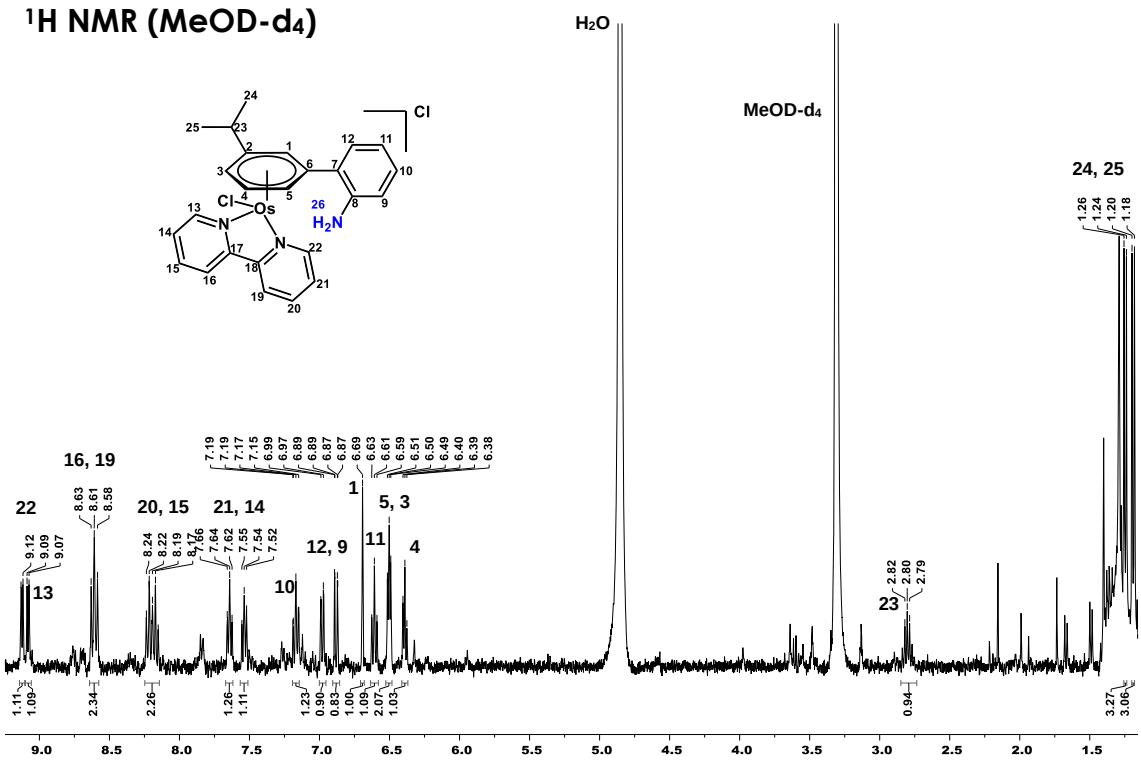


Figure S38. ^{1}H (400 MHz, MeOD-d$_4$) NMR spectra of monomer **28**.

Figure S39

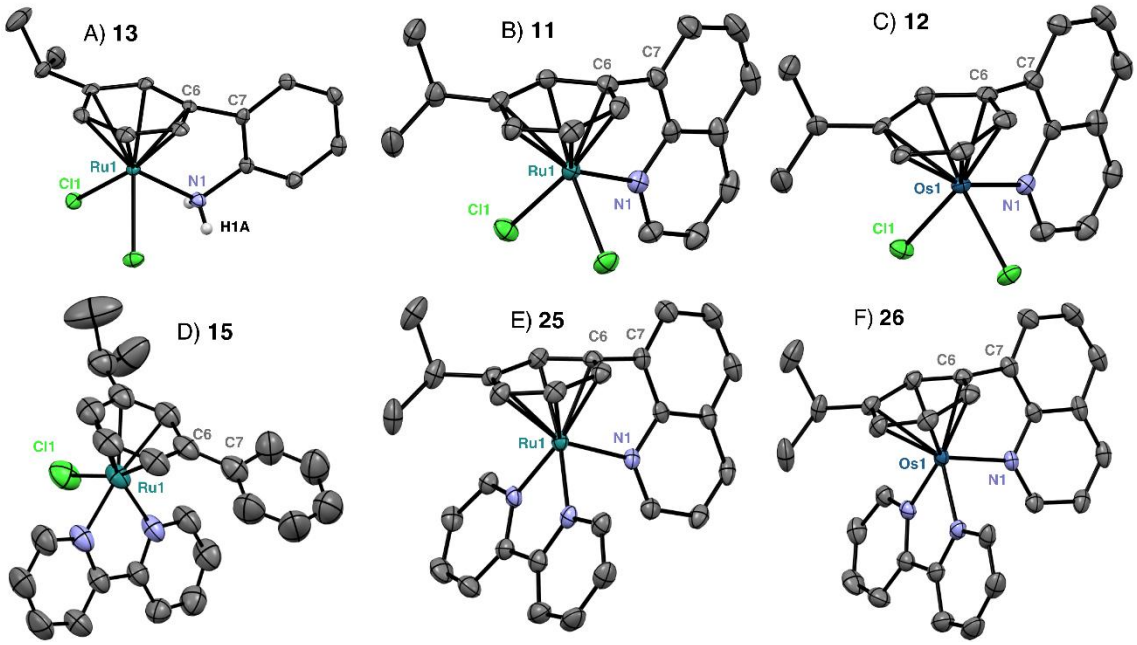


Figure S39. ORTEP diagrams and atom numbering schemes for compounds: A) **13** [Ru(η^6:κ^1-C_6H_4(^{i}Pr)((C_6H_4)NH_2))$(Cl)_2$], B) **11** [Ru(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))$(Cl)_2$], C) **12** [Os(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))$(Cl)_2$], D) **15·PF$_6$** [Ru(η^6-C_6H_4(^{i}Pr)(Ph))(bpy)Cl]PF_6, E) **25** [Ru(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))(bpy)]$(PF_6)_2$ and F) **26** [Os(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))(bpy)]$(PF_6)_2$ (50% probability ellipsoids). The H atoms (except those on the nitrogen pendant from the tether in **13**) and the PF_6^- counterions in **15·PF$_6$**, **25** and **26** have been omitted for clarity.

Figure S40

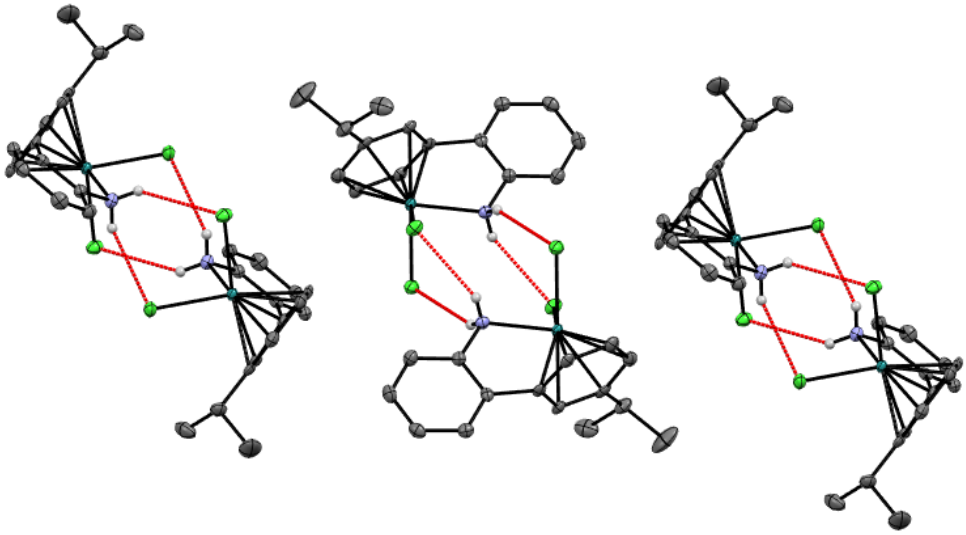


Figure S40. ORTEP diagrams showing directional hydrogen bonding between adjacent molecules (50% probability ellipsoids) in **13**, marked as red dotted lines. D(donor)-to-A(acceptor) distances and angles are in

Table **S**4.

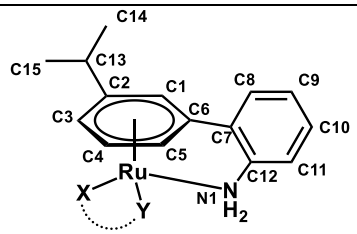
Supplementary Tables

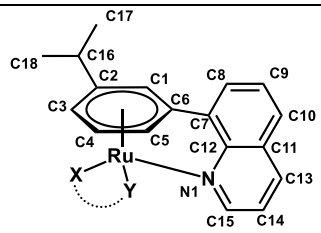
Table S1. Summarised ^{1}H NMR chemical shifts of the bound-arene protons of complexes **1**–**28** reported in this work.

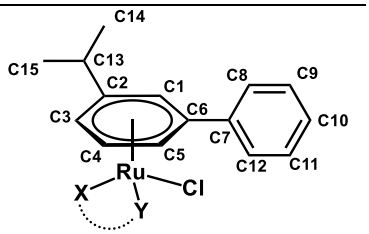
Complex Type	Complex	η^6***H*** δ (ppm)	Solvent
Dimer	**1**	5.95 (d, *J* = 2.3 Hz, 2H), 5.72 (s, 1H), 5.53 (t, *J* = 2.3 Hz, 1H)	$CDCl_3$
	2	6.58 (d, *J* = 5.4 Hz, 1H), 6.53 (s, 1H), 6.40 (t, *J* = 5.4 Hz, 1H), 6.24 (d, *J* = 5.4 Hz, 1H)	DMSO-d_6
	3	6.34 (s, 1H, η^6*H*), 6.22 (d, *J* = 5.7 Hz, 1H, η^6*H*), 6.13 (t, *J* = 5.7 Hz, 1H), 6.08 (d, *J* = 5.9 Hz, 1H)	DMSO-d_6
	4	6.52 (m, 1H, *H*-lactone, 2H, η^6*H*), 6.46 (t, *J* = 5.3 Hz, 1H), 6.38 (d, *J* = 5.4 Hz, 1H)	DMSO-d_6
	5	6.20 (s, 1H), 6.04 (m, 2H), 5.99 (t, *J* = 5.6 Hz, 1H)	DMSO-d_6
	6	6.50 (t, *J* = 5.2 Hz, 1H), 6.00 (d, *J* = 5.1 Hz, 1H), 5.93 – 5.87 (m, 2H)	$CDCl_3$
	7	5.94 (s, 2H), 5.70 (d, *J* = 3.6 Hz, 1H), 5.53 (s, 1H)	$CDCl_3$
	8	6.13 (s, 1H), 6.08 – 6.05 (m, 2H), 6.01 (d, *J* = 4.9 Hz, 1H)	DMSO-d_6
	9	6.54 (s, 1H), 6.45 (d, *J* = 5.9 Hz, 1H), 6.20 (t, *J* = 5.8 Hz, 1H), 6.00 (d, *J* = 5.7 Hz, 1H)	DMSO-d_6
	10	6.78 (d, *J* = 5.4 Hz, 1H), 6.74 (s, 1H), 6.51 (t, *J* = 5.5 Hz, 1H), 6.31 (d, *J* = 5.4 Hz, 1H)	DMSO-d_6
Dichlorido Monomer	**11**	6.12 (t, *J* = 5.7 Hz, 1H), 5.47 (m, *J* = 5.6 Hz, 2H), 5.31 (s, 1H)	$CDCl_3$
	12	6.39 (t, *J* = 5.3 Hz, 1H), 5.98 (d, *J* = 5.4 Hz, 1H), 5.83 (d, *J* = 5.1 Hz, 1H), 5.78 (s, 1H)	$CDCl_3$
	13	5.94 (t, *J* = 5.6 Hz, 1H), 5.40 (d, *J* = 5.9 Hz, 1H), 5.25 (d, *J* = 5.4 Hz, 1H), 5.02 (s, 1H)	$CDCl_3$
	14	6.28 (t, *J* = 5.2 Hz, 1H), 5.96 (d, *J* = 5.5 Hz, 1H), 5.63 (m, 2H, η^6*H*, N*H*), 5.52 (s, 1H)	$CDCl_3$
Open Monomer	**15**	6.61 (t, *J* = 6.1 Hz, 1H), 6.56 (s, 1H), 6.42 (d, *J* = 6.0 Hz, 1H), 6.11 (d, *J* = 6.0 Hz, 1H)	DMSO-d_6
	16	6.65 (s, 1H), 6.60 (t, *J* = 5.6 Hz, 1H), 6.48 (d, *J* = 5.8 Hz, 1H), 6.26 (d, *J* = 5.8 Hz, 1H)	MeOD
	17	6.59 (t, *J* = 6.1 Hz, 1H), 6.39 (s, 1H), 6.33 – 6.28 (m, 2H, *H*-lactone, η^6*H*), 6.05 (d, *J* = 6.2 Hz, 1H)	MeOD
	18	6.73 (t, *J* = 5.7 Hz, 1H), 6.67 (s, 1H), 6.51 (d, *J* = 5.6 Hz, 1H), 6.22 (d, *J* = 5.8 Hz, 1H)	MeOD
	19	6.62 (s, 1H), 6.52 (t, *J* = 6.0 Hz, 1H), 6.28 (m, 2H)	DMSO-d_6
	20	6.89 (s, 1H), 6.46 (m, 3H)	MeOD
	21	6.45 (t, *J* = 6.1 Hz, 1H), 6.38 (s, 1H), 6.27 (d, *J* = 6.0 Hz, 1H), 6.07 (d, *J* = 6.2 Hz, 1H)	MeOD
	22	6.47 (s, 1H), 6.39 – 6.34 (m, 2H), 6.29 (m, 1H)	MeOD
	23	6.59 (s, 1H), 6.55 (t, *J* = 6.1 Hz, 1H), 6.47 (d, *J* = 5.9 Hz, 1H), 6.15 (d, *J* = 6.0 Hz, 1H)	MeOD
	24	6.87 (s, 1H), 6.69 (m, 2H), 6.34 (d, *J* = 4.7 Hz, 1H)	MeOD
	27	6.45 (s, 1H), 6.30 (d, *J* = 5.3 Hz, 1H), 6.25 (m, 2H)	MeOD
	28	6.69 (s, 1H), 6.50 (m, 2H), 6.39 (t, *J* = 5.6 Hz, 1H)	MeOD

Closed Monomer	**25**	6.77 (t, *J* = 6.1 Hz, 1H), 6.49 (s, 1H), 6.42 (d, *J* = 6.1 Hz, 1H), 5.75 (d, *J* = 6.1 Hz, 1H)	MeOD
	26	6.85 (t, *J* = 5.8 Hz, 1H), 6.66 (s, 1H), 6.49 (d, *J* = 5.7 Hz, 1H), 5.98 (d, *J* = 5.9 Hz, 1H)	MeOD

Table S2. Selected bond lengths (Å) and angles (°) for the crystal structures of complexes [Ru(η^6:κ^1-C_6H_4(^{i}Pr)((C_6H_4)NH_2))Cl_2] (**13**), [Ru(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))Cl_2] (**11**), [Os(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))Cl_2] (**12**), [Ru(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))(bpy)]$(PF_6)_2$ (**25**), [Os(η^6:κ^1-C_6H_4(^{i}Pr)(quinoline))(bpy)]$(PF_6)_2$ (**26**) and [Ru(η^6-C_6H_4(^{i}Pr)(Ph))(bpy)Cl]PF_6 (**15·PF$_6$**).







Complex	**13**	**11** and **12**	**25** and **26**	**15·PF$_6$**
X	Cl1	Cl1	N2	N2
Y	Cl2	Cl2	N3	N1[#]
M	-	Ru (**11** and **25**); Os (**12** and **26**)		-

BOND DISTANCES (Å) AND ANGLES (º)	**13**	**11**	**12**	**25**	**26**	**15·PF$_6$**
M-C1 (Å)	2.175(3)	2.178(2)	2.181(4)	2.190(3)	2.196(3)	2.209(8)
M-C2 (Å)	2.219(3)	2.240(2)	2.244(3)	2.247(3)	2.235(3)	2.230(9)
M-C3 (Å)	2.213(3)	2.212(3)	2.212(4)	2.232(3)	2.226(3)	2.213(10)
M-C4(Å)	2.178(3)	2.176(3)	2.175(5)	2.201(3)	2.191(3)	2.192(9)
M-C5 (Å)	2.167(3)	2.158(3)	2.166(4)	2.193(3)	2.202(3)	2.192(9)
M-C6 (Å)	2.088(3)	2.090(3)	2.101(4)	2.122(3)	2.132(3)	2.228(8)
M-centroid (Å)	1.646	1.648	1.648	1.683	1.676	1.697
M-N1 (Å)	2.121(3)	2.119(2)	2.126(3)	2.114(3)	2.115(3)	-
M-X (Å)	2.4092(7)	2.4033(6)	2.406(1)	2.081(3)	2.086(3)	2.086(7)
M-Y (Å)	2.4119(8)	2.4066(7)	2.408(1)	2.077(3)	2.091(3)	2.072(7)
X-M-Y (º)	89.24(3)	87.04(2)	85.96(3)	76.9(1)	76.44(11)	77.2(3)
X-M-N1 (º)	86.18(8)	87.70(6)	86.99(9)	89.3(1)	88.73(11)	-
Y-M-N1 (º)	83.57(8)	86.54(6)	85.95(9)	90.9(1)	90.37(11)	-
M-C6-C7 (º)	113.2(2)	113.3(2)	112.9(3)	112.0(2)	111.9(2)	127.4(6)
C6-centroid-M (º)	85.50	85.52	85.81	86.04	86.68	90.02
Propeller twist (º)	89.45	89.10	88.93	81.71	82.49	14.66
C7 offset[*] (Å)	0.471(+)	0.455(+)	0.475(+)	0.479(+)	0.489(+)	0.071(+)
σ[**] (º)	-2.2(2)	-0.0(2)	-0.2(3)	-6.4(2)	-5.6(2)	-

[*]Offset of C7 with respect to the plane containing the bound arene (carbons C1 and C6); (+) toward metal centre.
[**]Torsion angle of the planes containing N1, M, C6 and C7.
[#]Unlike the rest of the complexes, this N1 belongs to the XY BPY ligand, since **15·PF$_6$** has no tether ring.

Table S3. Crystallographic data of complexes **11**, **12**, **13**, **15·PF$_6$**, **25** and **26**.

	11	**12**	**13**	**15·PF$_6$**	**25**	**26**
Chemical formula	$C_{18}H_{17}Cl_2NRu$	$C_{18}H_{17}Cl_2NOs$	$C_{15}H_{17}Cl_2NRu$	$C_{25}H_{24}ClF_6N_2PRu$	$C_{28}H_{25}F_{12}N_3P_2Ru$	$C_{28}H_{25}F_{12}N_3OsP_2$
Molecular weight (g/mol)	419.30	508.42	383.27	633.95	794.52	883.65
Crystal Description	Clear yellow plate	Clear pale yellow	Clear intense yellow-orange plate	Clear intense yellow prism	Clear yellow-green prism	Clear pale yellow-green prism
Wavelength (Å)	1.54184	1.54184	0.71073	0.71073	0.71073	0.71073
Temperature (K)	150(10)	150.00(10)	150(2)	150(2)	150(2)	150(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\ 2_{1/c}$	$P\ 2_{1/c}$	$P\ 1\ 2_{1/c}\ 1$	$P\ 2_1\ 2_1\ 2_1$	$P\ 1\ 2_{1/c}\ 1$	$P\ 1\ 2_{1/c}\ 1$
a (Å)	10.32170(10)	10.3372(2)	10.0271(5)	11.204(3)	17.5378(9)	17.6681(6)
b (Å)	16.4107(2)	16.3941(3)	9.9616(5)	11.914(4)	8.9998(6)	9.0053(4)
c (Å)	9.69320(10)	9.7316(2)	15.4734(6)	18.984(5)	19.7552(12)	19.7826(6)
α (°)	90	90	90	90	90	90
β (°)	103.1790(10)	102.969(2)	107.260(2)	90	108.763(2)	109.2480(10)
γ (°)	90	90	90	90	90	90
Volume (Å^3)	1598.65(3)	1607.14(6)	1475.98(12)	2534.1(13)	2952.4(3)	2971.60(19)
Z	4	4	4	4	4	4
R$^{(a)}$	0.0978	0.0267	0.0362	0.0711	0.0548	0.0247
Rw$^{(b)}$	0.1147	0.0661	0.0614	0.1195	0.0848	0.0520
GOF$^{(c)}$	1.035	1.067	1.062	1.029	1.022	1.095

[a]Residual factor for all reflections satisfying the resolution limits established (R_factor_all) not only the residual factor for the significantly intense reflections.
[b]Weighted residual factors for all reflections included in the refinement (wR_factor_ref), not only the significantly intense reflections.
[c]The least-squares goodness-of-fit parameter S for all reflections included in the refinement after the final cycle of refinement.

Table S4. Hydrogen bond distances (Å) and angles (°) between the N (donor, D) hydrogen atoms of complex **13** and the chloridos (acceptor, A) from an adjacent molecule.

D–H···A	**D–H**	**A···H**	**D···A**	**∠ D–H···A (°)**
N1–H1···Cl1	0.78(3)	2.61(3)	3.301(3)	148.(3)
N1–H2···Cl2	0.83(3)	2.63(3)	3.344(3)	145.(3)

References

[1] a) M. M. Mogorosi, M. C. Maumela and M. J. Overett (Sasol Technology Pty Ltd), US9533922B2, **2014**; b) J.-H. Son, M. A. Pudenz and J. D. Hoefelmeyer, *Dalton Trans.* **2010**, *39*, 11081.
[2] A. X. S. Bruker, *Bruker AXS Inc., Madison, Wisconsin, USA* **2008**.
[3] A. X. S. Bruker, *Bruker AXS, Madison, WI* **2000**.
[4] a) G. M. Sheldrick, *Acta Crystallogr. Sect. A: Found. Crystallogr.* **2008**, *64*, 112; b) G. M. Sheldrick, *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2015**, *71*, 3.
[5] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339.
[6] H.-C. Tsai, Y.-H. Huang and C.-M. Chou, *Org. Lett.* **2018**, *20*, 1328.
[7] C.-M. Chou, I. Chatterjee and A. Studer, *Angew. Chem. Int. Ed.* **2011**, *50*, 8614.
[8] a) A. M. Pizarro, M. Melchart, A. Habtemariam, L. Salassa, F. P. A. Fabbiani, S. Parsons and P. J. Sadler, *Inorg. Chem.* **2010**, *49*, 3310; b) S. Infante-Tadeo, V. Rodríguez-Fanjul, A. Habtemariam and A. M. Pizarro, *Chem. Sci.* **2021**, *12*, 9287; c) S. Infante-Tadeo, V. Rodriguez-Fanjul, C. C. Vequi-Suplicy and A. M. Pizarro, *Inorg. Chem.* **2022**, *61*, 18970; d) F. Martínez-Peña and A. M. Pizarro, *Chem. Eur. J.* **2017**, *23*, 16231.
[9] F. Martínez-Peña, Reversible Activation Dynamics of Tethered Ruthenium(II) Arene Complexes, Universidad Autónoma de Madrid (Madrid), **2018**
[10] a) G. A. Jeffrey, *An introduction to hydrogen bonding*, Oxford university press, New York, **1997**, p. 228; b) T. Steiner, *Angew. Chem. Int. Ed.* **2002**, *41*, 48.