Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Mechanistic Insight into Ruthenium-Catalysed *Meta*-Sulfonation of 2-Phenylpyridine

Patricia Marcé, Andrew J. Paterson, Mary F. Mahon, Christopher G. Frost*

Department of Chemistry, University of Bath, Bath BA2 7AY, U.K.

Supporting information

General Considerations

All chemicals used were reagent grade and used as supplied unless otherwise specified. HPLC grade acetonitrile (CH_3CN), and diethyl ether were dried using a solvent purification system (PS-400-7®). ^1H and ^{13}C NMR spectra were recorded on Bruker, AV 300, AV 400 or AV 500 spectrometers in CD_3CN as solvent. Chemical shifts (δ) were referenced internally to residual protic solvent signal for CD_3CN (1.94 ppm ^1H (q), 1.39 ppm ^{13}C (sep)). 2D correlation spectra (gCOSY, gHSQC and gHMBC) were recorded to fully characterise the non-reported ruthenium complexes. Multiplicities are presented as: singlet (s), broad singlet (br s), doublet (d), apparent doublet (app d), doublet of doublets (dd), doublet of doublet of doublets (ddd), triplet (t), triplet of doublets (td), doublet doublet doublet of doublets (dddd), triplet of triplets (tt), quartet (q), quintet (quint.), and multiplet (m). Coupling constants (J) were expressed in Hertz (Hz).

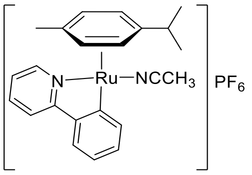
ESI MS were run on an Agilent® 1200 Series LC/MSD. Elemental analysis (C, H, N, S) was run in London Metropolitan University. Analytical thin layer chromatography (TLC) was performed on Merck® silica gel 60 F254 glass or aluminium plates. Organic Compounds were visualized by UV (254 nm) irradiation. Flash column chromatography was carried out using forced flow or by gravity of the indicated solvent on Fluka® silica gel 60 (230-400 mesh) or on Acros® neutral aluminium oxide (50-200 μm, 60 Å).

All complexes were synthesised using standard Schlenck techniques under nitrogen atmosphere. The precursor catalyst $[RuCl_2(p\text{-cymene})]_2$ was purchased from Strem Chemicals and used without further purification. [RuCl(PhPy)(*p*-cymene)],[1] D^5-2-phenylpyridine[2] and D^3-2-phenylpyridine[3] were prepared according literature methods.

CCDC 1479685 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

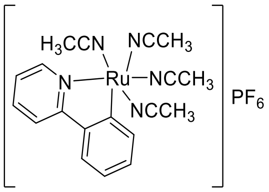
1. Synthesis of Ru Complexes

1.1. Preparation of [Ru(PhPy)(*p*-cymene)(CH_3CN)]PF_6 (4)



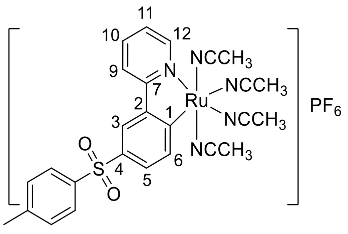
Dixneuf and Jutand method[1c] was used for the synthesis of **4** with modifications. **3** (0.5 g, 1.2 mmol) was dissolved in CH_3CN (12 mL) and $AgPF_6$ (0.44 g, 1.7 mmol) was added. The reaction mixture was stirred for 30 min at room temperature. An aliquot from the reaction mixture was taken and diluted into CD_3CN and analysed by ^1H NMR showing the complete consumption of the starting material. The reaction mixture was filtered over oven-dried neutral alumina and eluted with anhydrous CH_3CN under nitrogen. The solvent was removed under vacuum and the solution poured into petroleum ether. After filtration and drying, **4** was obtained as green solid (0.66 g, 98%). Spectroscopic data was in good agreement with those previously reported.[1c]

1.2. Preparation of [Ru(PhPy)(CH_3CN)$_4$]PF_6 (5)



Dixneuf and Jutand method[1c] was used for the synthesis of **5** with modifications. **4** (0.5 g, 0.87 mmol) was dissolved in CH_3CN (5.4 mL). The reaction mixture was stirred for 2 days at 70 °C. An aliquot from the reaction mixture was taken and diluted into CD_3CN and analysed by ^1H NMR showing the complete consumption of the starting material. The reaction mixture was purified by flash chromatography over oven-dried neutral alumina and eluted with anhydrous CH_3CN under nitrogen. The solution was concentrated under vacuum and the solution poured into petroleum ether. After filtration and drying, **5** was obtained as yellow-green solid (0.37 g, 75%). Spectroscopic data was in good agreement with those previously reported.[1c]

1.3. Preparation of [Ru(TsPhPy)(CH_3CN)$_4$]PF_6 (7)



A dried Schlenck tube under argon was charged with molecular sieves 4 Å, complex **5** (0.1 g, 0.18 mmol) and dry CH_3CN (1.8 mL). Then, *p*-toluenesulfonyl chloride (TsCl) (67 mg, 0.35 mmol) and oven-dried K_2CO_3 (61 mg, 0.44 mmol) were added. After stirring the reaction mixture for 15 h at 120 °C, the reaction crude was purified through oven-dried neutral alumina (Al_2O_3) and eluted with CH_3CN. The solution was concentrated under reduced pressure and precipitated with diethyl ether. After filtration and drying, complex **7** was obtained as green solid (66 mg, 52%). Crystals of **7** were grown by vapour diffusion using $CH_3CN–Et_2O$.

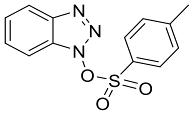
^{1}H NMR (500 MHz, CD_3CN) δ 8.92 (d, *J* = 5.5 Hz, 1H, H12), 8.22 (d, *J* = 8.0 Hz, 1H, H6), 8.14 (d, *J* = 1.8 Hz, 1H, H3), 8.04 (d, *J* = 8.1 Hz, 1H, H9), 7.88 (d, *J* = 8.3 Hz, 2H, Ts), 7.81 (td, *J* = 8.0, 1.5 Hz, 1H, H10), 7.49 (dd, *J* = 8.0, 1.9 Hz, 1H, H5), 7.37 (d, *J* = 8.2 Hz, 2H, Ts), 7.25 (t, *J* = 6.5 Hz, 1H, H11), 2.50 (s, 3H, CH_3CN), 2.38 (s, 3H, Ts), 2.14 (s, 16H, CH_3CN), 1.97 (s, 5H, CH_3CN), 1.96 (s, 3H, CH_3CN).

^{13}C NMR (126 MHz, CD_3CN) δ 201.76 (C1), 167.73 (C7), 153.96 (C12), 149.45 (C2), 145.40 (Ts), 141.64 (Ts), 140.55 (C6), 137.92 (C10), 135.27 (C4), 131.35 (Ts), 128.44 (Ts), 125.52 (C5), 123.74 (C11), 121.56 (C3), 120.02 (C9), 118.69 (s), 21.89 (Ts), 4.75 (CH_3CN), 4.50 (CH_3CN).

HRMS-ESI Calcd for $C_{24}H_{23}N_4O_2RuS$: 533.0585 $[M-CH_3CN]^+$. Found 533.0573.

Anal. Calcd for $C_{26}H_{26}F_6N_5O_2PRuS$: C, 43.46; H, 3.65; N, 9.75; Found: C, 43.35; H, 3.75; N, 9.67.

1.4. Preparation of 1H-benzo[*d*][1,2,3]triazol-1-yl 4-methylbenzenesulfonate (8)[4]



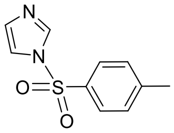
Synthesis of **8** was carried out using the reported method.[4] To a solution of 1-hydroxybenzotriazole hydrate (0.99 g, 7.4 mmol) in dry dichloromethane (30 mL), imidazole (0.51 g, 7.6 mmol) was added. The mixture was cooled to 0 °C under N_2 and a solution of TsCl (recrystallized) (1.43 g, 7.5 mmol) in dichloromethane (4 mL) was added dropwise over a 10 min period. The reaction mixture was warmed to rt and stirred for a further 3 h. The reaction mixture was diluted with dichloromethane (30 mL) and filtered in a sintered funnel over $MgSO_4$ under N_2. The solvent was removed *in vacuo* and the resulting colourless residue was recrystallized from dry dichloromethane/hexane. The product was filtered to recover the pure final compound as a white crystalline solid (1.46 g, 69%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 – 7.99 (m, 1H, Ar), 7.81 – 7.75 (m, 2H, Ar), 7.65 (dt, *J* = 8.3, 1.0 Hz, 1H, Ar), 7.62 – 7.55 (m, 1H, Ar), 7.47 – 7.38 (m, 3H, Ar), 2.50 (s, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.6 (q), 139.8 (q), 134.6 (q), 131.2, 129.8, 129.2 (2 x ArCH), 128.9 (q), 125.9 (2 x ArCH), 114.6, 112.5, 21.4 (CH_3).

HRMS-ESI calculated for $C_{13}H_{11}N_3O_3SNa$: 312.0419 $[M+Na]^+$. Found: 312.0399.

1.5. Preparation of 1-tosyl-1*H*-imidazole (9)[5]



Synthesis of **9** was carried out with some modifications of the reported method.[5] A solution of imidazole (1.38 g, 20.3 mmol) in dry dichloromethane (10 mL) was stirred at 0 °C for 1.5 h under N_2. In a separate flask, a solution of TsCl (recrystallysed) (1.74 g, 9.1 mmol) in dry dichloromethane (10 mL) was stirred at rt for 1.5 h under N_2. The *p*-toluenesulfonyl solution was added dropwise to the imidazole solution for 30 min at 0 °C. The reaction mixture was allowed to reach rt and stirred for a further 17 h. The resulting mixture was filtered through a pad of silica and washed with hexane (20 mL) followed by a mixture of EtOAc:hexane (1:1) (300 mL). The filtrate was concentrate *in vacuo* and the oil residue was dissolved in the minimum amount of EtOAc (1.5 mL) and crashed out with hexane (125 mL) to afford the pure compound as a white solid (1.39 g, 68%).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.01 (s, 1H, NC*H*N), 7.85 – 7.79 (m, 2H, Ar), 7.35 (d, *J* = 8.1 Hz, 1H, Ar), 7.29 (t, *J* = 1.4 Hz, 1H, SO_2NC*H*), 7.08 (s, 1H, Ar), 2.44 (s, 3H, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$) δ 146.5 (q), 136.8, 135.1 (q), 131.6, 130.6, 127.5, 128.9 (q), 125.9, 114.6, 112.5, 21.4 (CH_3).

HRMS-ESI calculated for $C_{10}H_{11}N_2O_2S$: 223.0541 $[M+H]^+$. Found: 223.0535.

2. Study of the Ru(II) complexes involved in the *meta*-sulfonation reaction

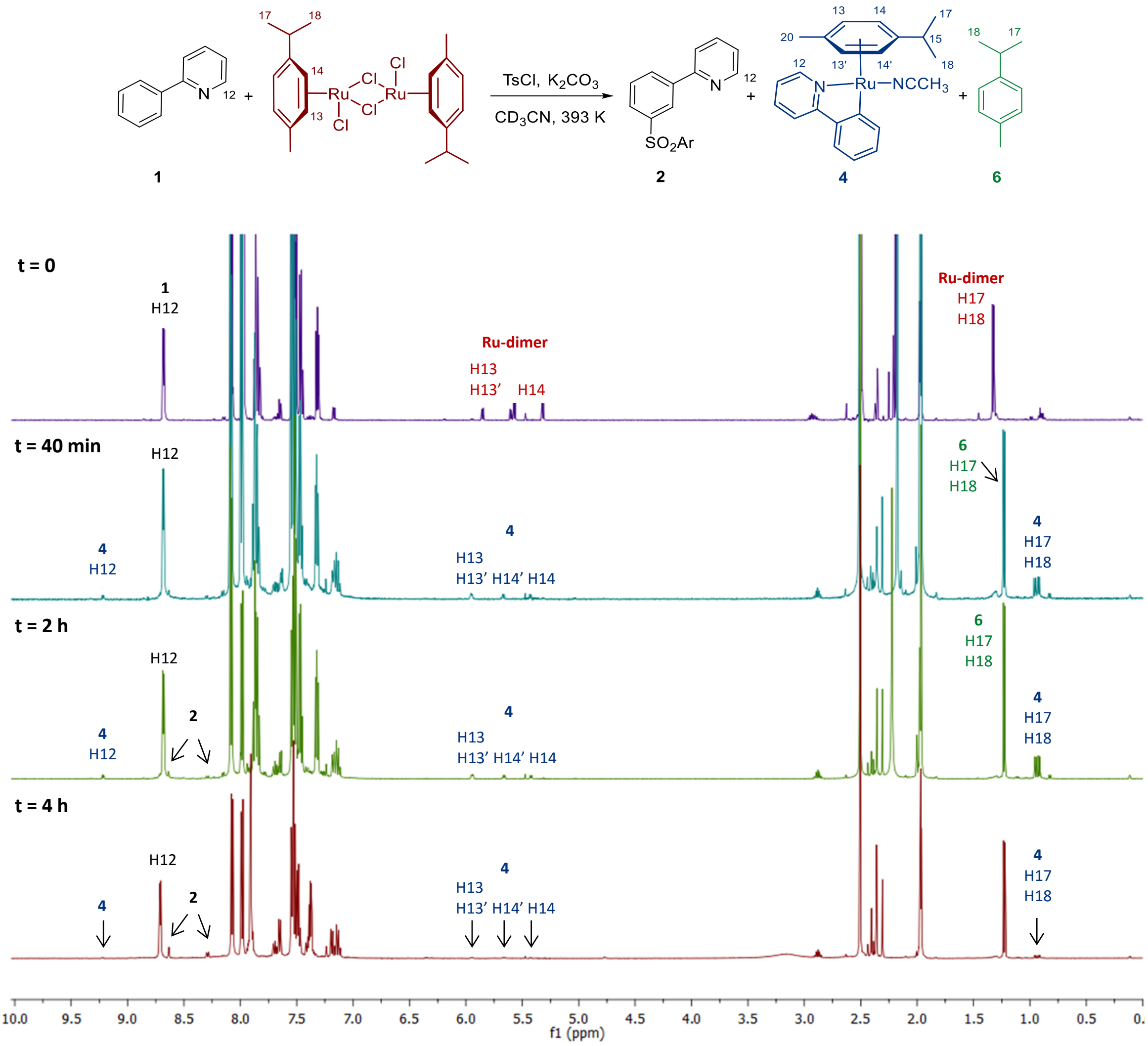
2.1. Catalytic reactions

To a nitrogen-purged ampule, $[RuCl_2(p\text{-cymene})]_2$ (21 mg, 5 mol%), [RuCl(PhPy)(*p*-cymene)] (30 mg, 10 mol%) or $[Ru(PhPy)(p\text{-cymene})(CH_3CN)]PF_6$ (40 mg, 10 mol%) was dissolved in dry CH_3CN (4 mL). Then, phenylpyridine (0.1 mL, 0.70 mmol), K_2CO_3 (0.193 g, 1.4 mmol) and TsCl (0.4 g, 2.1 mmol) were added and the reaction mixture was heated at 120 °C in an oil bath for 15 h. The reaction crude was filtered over celite using EtOAc as eluent and the resulting mixture was purified by flash chromatography (from 20% EtOAc:hexane to 40% EtOAc) affording **2** as yellowish solid (0.11 g, 50%).

2.2. Study of the catalyst behaviour during the *meta*-sulfonation of 2-phenypyridine

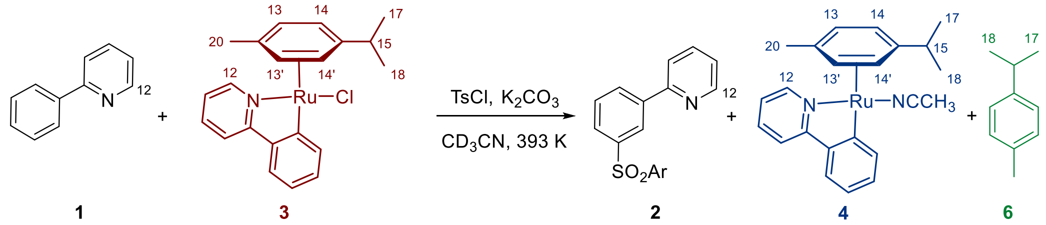
Following the reaction conditions detailed above, the reaction using $[RuCl_2(p\text{-cymene})]_2$, [RuCl(PhPy)(*p*-cymene)] and $[Ru(PhPy)(p\text{-cymene})(CH_3CN)]PF_6$ were prepared in CD_3CN and they were followed by ^{1}H-NMR taking samples at different times.

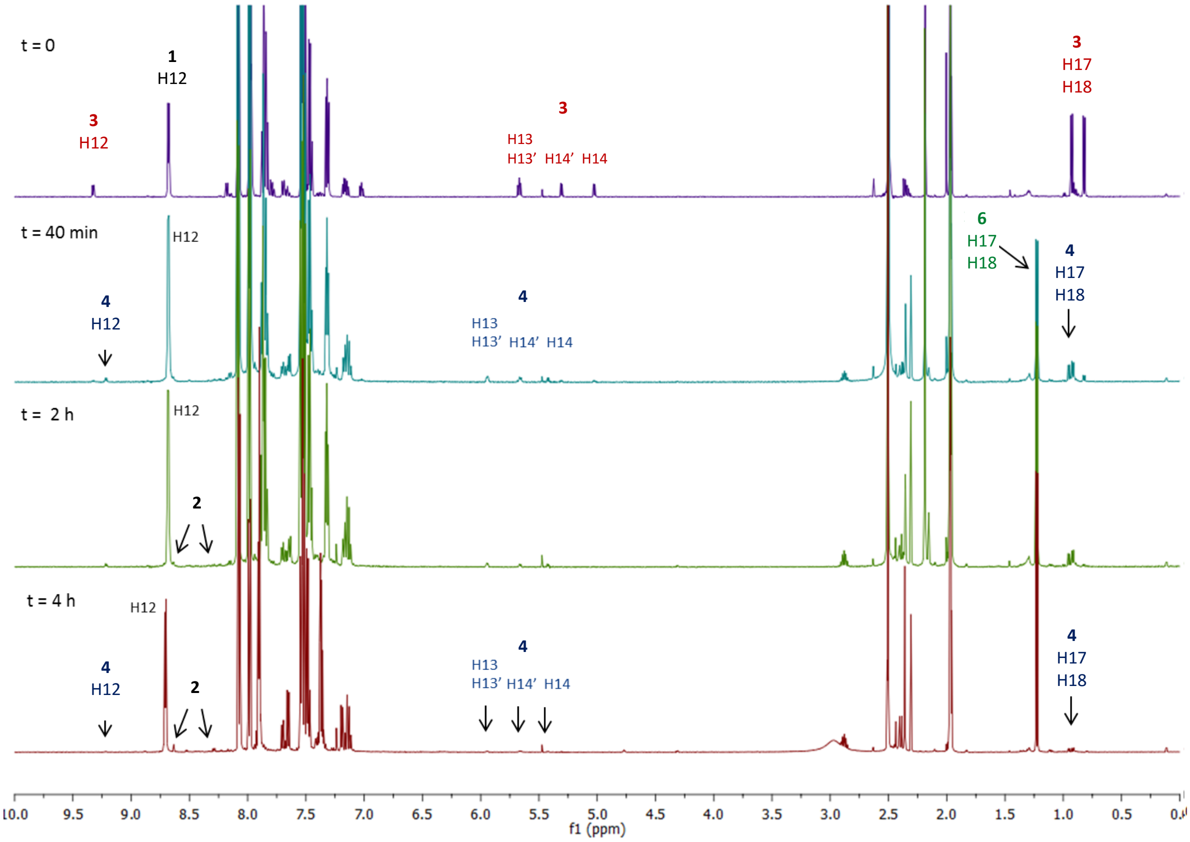
Figure S1. ^{1}H NMR *meta*-sulfonation of phenylphyridine using [RuCl$_2$(*p*-cymene)]$_2$



^{1}H NMR (500 MHz, CD$_3$CN) recorded at 298K

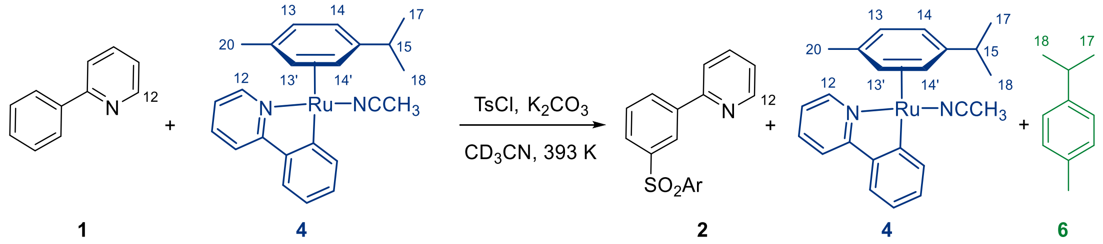
Figure S2. ^{1}H NMR *meta*-sulfonation of phenylphyridine using [[RuCl(PhPy)(*p*-cymene)]

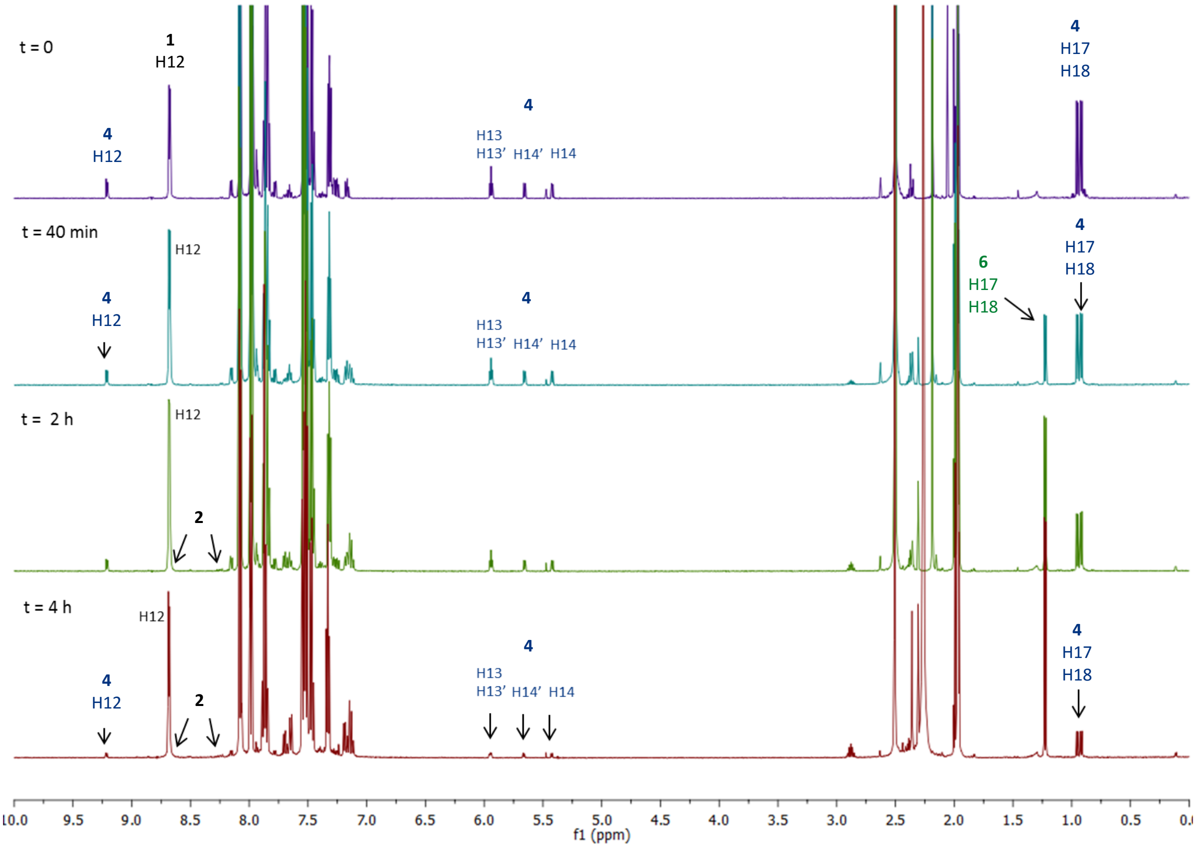




^{1}H NMR (500 MHz, CD$_3$CN) recorded at 298K

Figure S3. ^1H NMR *meta*-sulfonation of phenylphyridine using [Ru(PhPy)(*p*-cymene)(CH_3CN)]PF_6



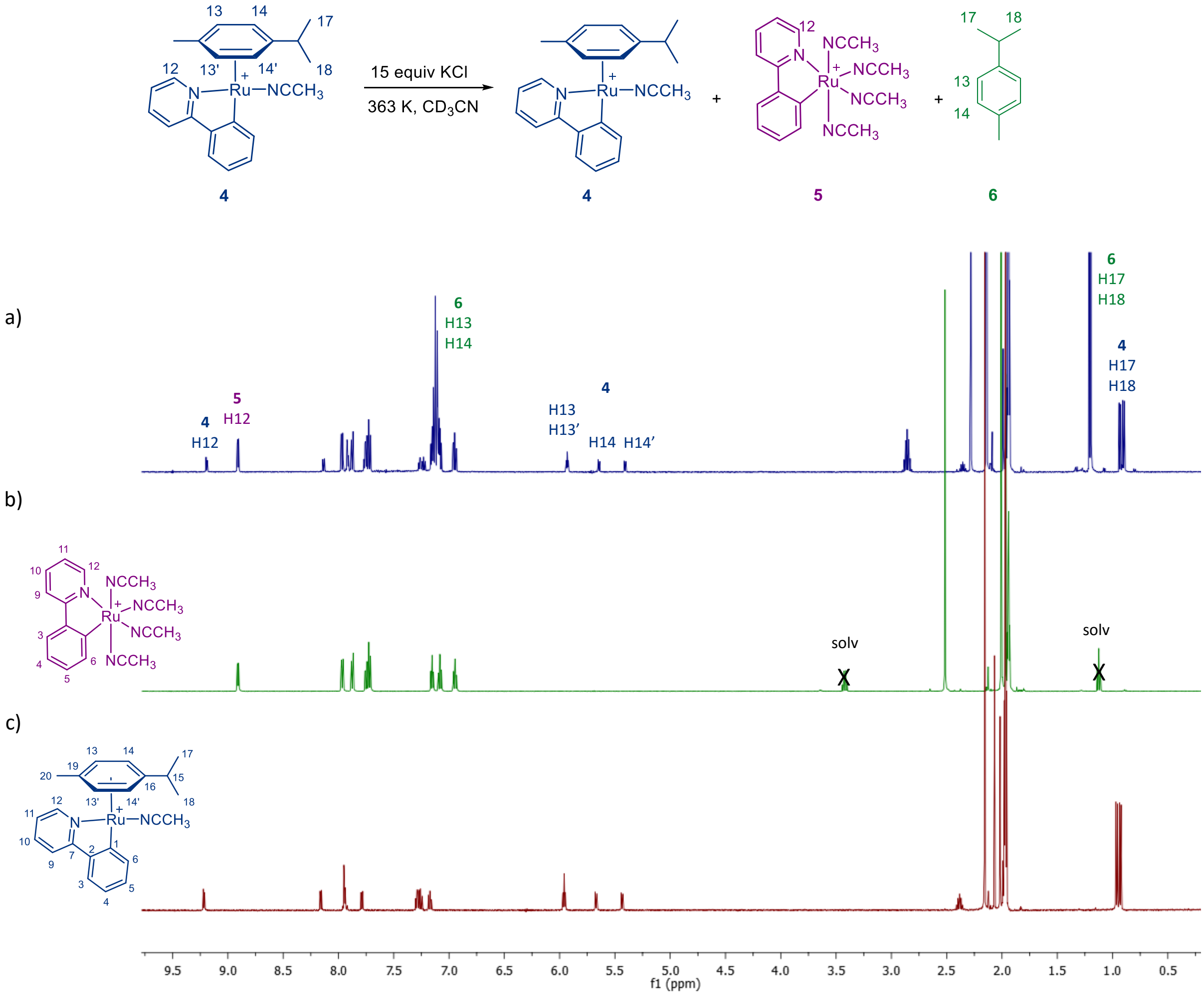


^1H NMR (500 MHz, CD_3CN) recorded at 298K

2.4. Reaction of [Ru(PhPy)(*p*-cymene)(CH_3CN)]PF_6 with KCl

In a flame-dried NMR tube with a young cap, [Ru(PhPy)(*p*-cymene)(CH_3CN)]PF_6 (10 mg, 0.017 mmol) was dissolved in CD_3CN (0.5 mL) and KCl (20 mg, 0.27 mmol) was added. The NMR sample was heated for 15 h at 363 K.

Figure S4. Reaction of [RuPhPy(*p*-cymene)]PF_6 with KCl



^{1}H NMR (500 MHz, CD_3CN) recorded at 298K

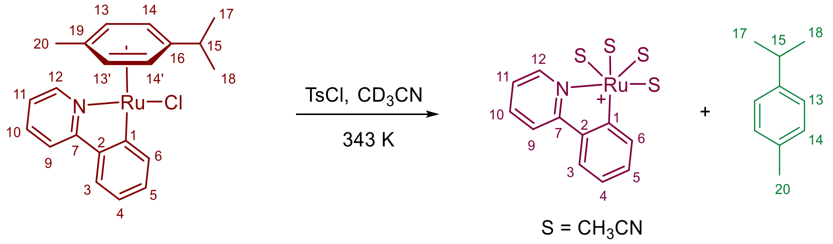
a) ^{1}H-NMR of the reaction mixture after heating **4** at 363 K; b) ^{1}H-NMR of **5** for comparison; c) ^{1}H-NMR of **4** for comparison.

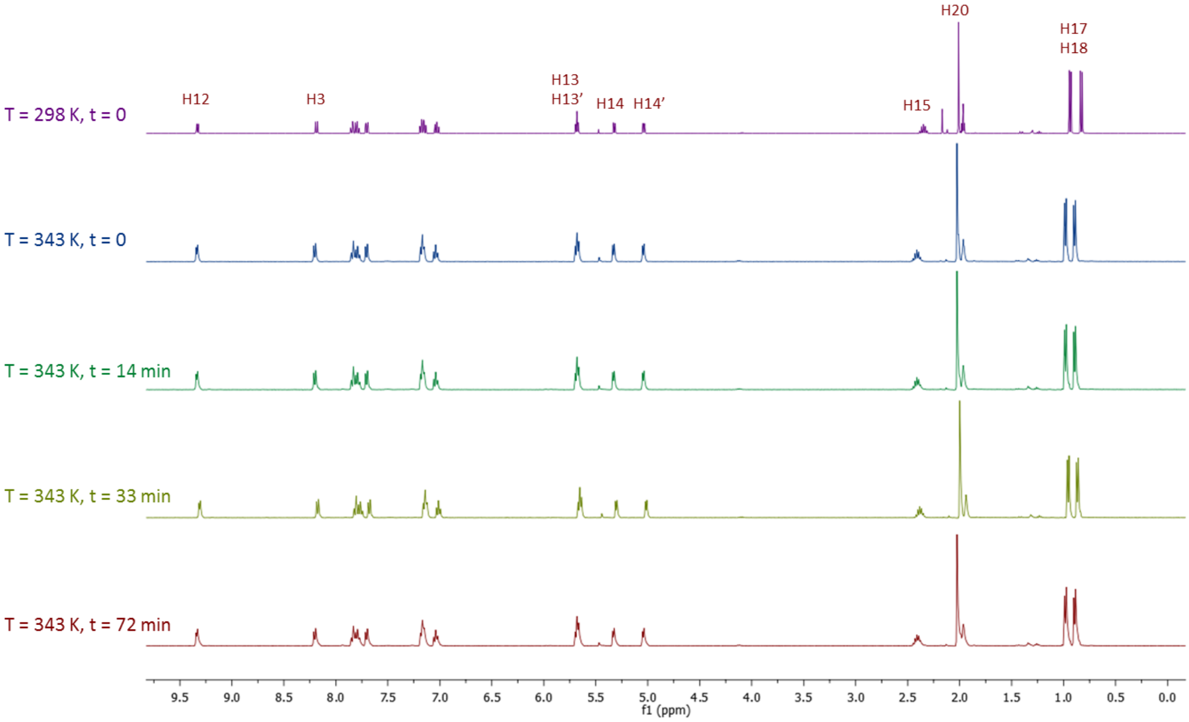
2.5. Study of the stability of [RuCl(PhPy)(*p*-cymene)] in the presence of TsCl

In a flame-dried NMR tube with a young cap, [RuCl(PhPy)(*p*-cymene)] (34 mg, 0.08 mmol) was dissolved in CD_3CN. The sample was placed in the NMR spectrometer which was previously heated at 343 K. ^{1}H-NMR were recorded overtime at this temperature. After 1 h TsCl (23 mg, 0.12 mmol) was added and heated at the same temperature in the NMR spectrometer recording several ^{1}H spectra overtime.

Figure S5. Stability of [RuCl(PhPy)(*p*-cymene)] in the presence of TsCl

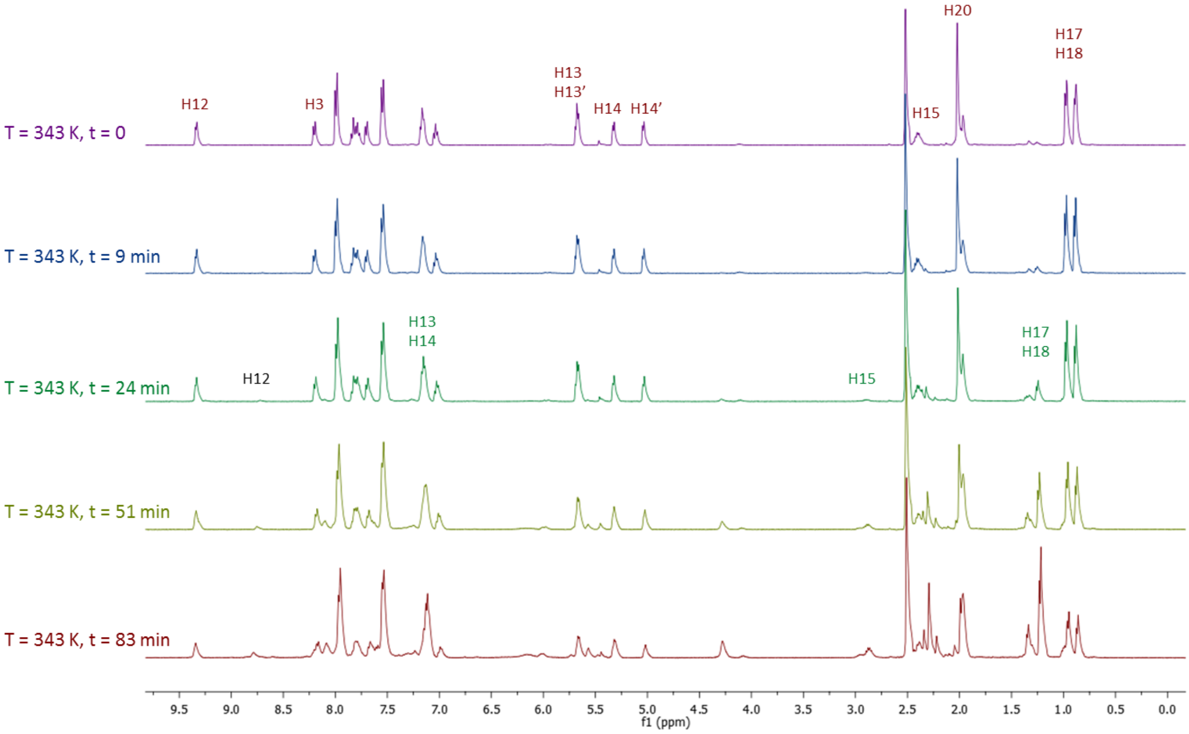
a) [RuCl(PhPy)(*p*-cymene)] in CD_3CN heated at 343 K





^{1}H NMR (400 MHz, CD_3CN) recorded at 298K and 343 K

b) [RuCl(PhPy)(*p*-cymene)] in CD_3CN heated at 343 K in the presence of TsCl



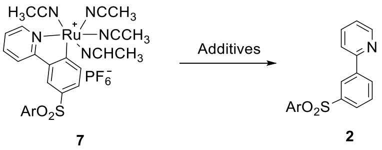
^1H NMR (400 MHz, CD_3CN) recorded at 343 K

3. Study of the protodemetallation step

3.1. Protodemetallation of 7

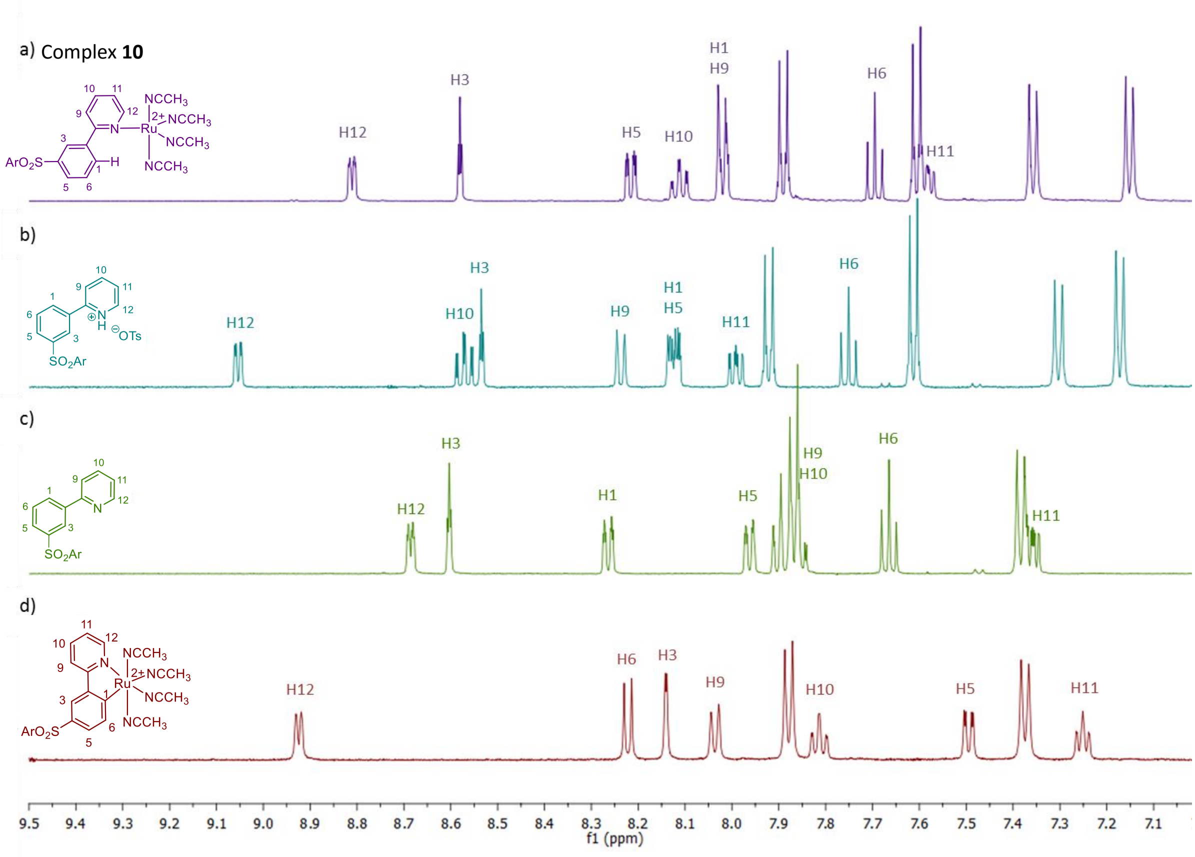
In a flame dried NMR tube with a young cap $[Ru(TsPhPy)(CH_3CN)_4]PF_6$ (7 mg, 0.01 mmol) was dissolved in CD_3CN (0.5 mL) and $KHCO_3$ (9.7 mg, 0.1 mmol), $MesCO_2H$ (1.6 mg, 0.01 mmol) and K_2CO_3 (2.7 mg, 0.02 mmol), $MesCO_2H$ (2.4 mg, 0.015 mmol), $MesCO_2H$ (16 mg, 0.1 mmol), *p*-toluenesulfonic acid (*p*-TSA) (18 mg, 0.094 mmol) or a mixture of PhPy (1.4 mL, 0.01 mmol) and K_2CO_3 (2.7 mg, 0.02 mmol) were added depending on the experiment. The sample was heated for 15 h at 373 K in an oil bath.

Table S1. Protodemetallation conditions of **7**



Entry	**Proton source**	**2** (%)
1	10 equiv $KHCO_3$	--
2	1 equiv $MesCO_2H$ 2 equiv K_2CO_3	--
3	1.5 equiv $MesCO_2H$	--
4	10 equiv $MesCO_2H$	--
5	1 equiv PhPy 2 equiv K_2CO_3	--
6	1.5 equiv *p*-TSA	Complex **10**
7	4.5 equiv TsCl 2 equiv K_2CO_3	23%
8	10 equiv PhPy 2 equiv K_2CO_3	26%

Figure S6. Formation of complex **10**

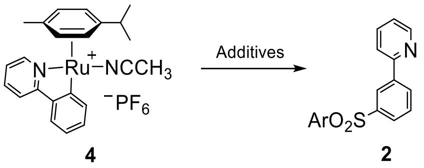


a) ^{1}H-NMR for the compound obtained by treatment of **7** with *p*-TSA and assigned to complex **10**; b) ^{1}H-NMR of the tosylated phenylpyridine salt in CD_3CN by its treatment with 1.5 equivalents of *p*-TSA; c) ^{1}H-NMR of **2** for comparison; d) ^{1}H-NMR of **7** for comparison.

3.2. Protodemetallation of 4

In a flame dried NMR tube with a young cap $[Ru(PhPy)(p\text{-cymene})(CH_3CN)]PF_6$ (7 mg, 0.01 mmol) was dissolved in CD_3CN (0.5 mL) and K_2CO_3 (8 mg, 0.06 mmol), $KHCO_3$ (12 mg, 0.12 mmol) or a mixture of PhPy (2.2 μL, 0.015 mmol) and K_2CO_3 (8 mg, 0.06 mmol) and PhPy (5.7 μL, 0.04 mmol) and K_2CO_3 (8 mg, 0.06 mmol) were added depending on the experiment. The sample was heated for 15 h at 393 K in an oil bath (Table S1).

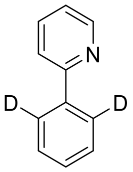
Table S2. Protodemetallation conditions for **4**



Entry	Proton source	**2** (%)
1	1.5 equiv TsCl 5 equiv K_2CO_3	14
2	1.5 equiv TsCl 10 equiv $KHCO_3$	11
3	1.5 equiv TsCl 5 equiv K_2CO_3 1.5 equiv PhPy	33
4	1.5 equiv TsCl 5 equiv K_2CO_3 3.5 equiv PhPy	46

4. Experiments with isotopically labelled compounds

4.1. Synthesis of 2-(2,6-dideuterophenyl)pyridine

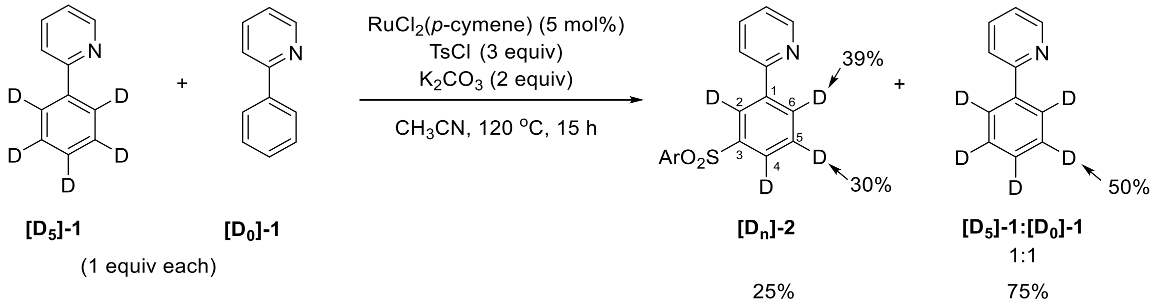


A suspension of $[RuCl_2(p\text{-cymene})]_2$ (76.5 mg, 0.124 mmol), AcOD (0.1 mL, 1.74 mmol), K_2CO_3 (1.38 g, 10 mmol) and **1** (0.71 mL, 4.97 mmol) in degassed D_2O (20 mL) was stirred under N_2 for 20 h at 100 °C. EtOAc (50 mL) and H_2O (50 mL) were added to the reaction mixture at ambient temperature. The separated aqueous phase was extracted with EtOAc (2 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over $MgSO_4$ and concentrated in vacuo. The remaining residue was purified by column chromatography on silica gel (hexane:EtOAc 5:1) and Kugelrohr-distillation to yield **[D$_2$]-1** (56 mg, 72%) as a colourless oil.

4.2. General procedure for the competitive experiments

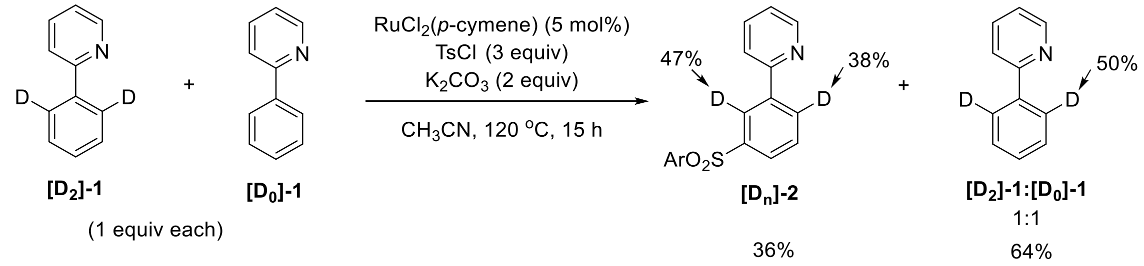
To a nitrogen-purged ampule, $[RuCl_2(p\text{-cymene})]_2$ (11 mg, 5 mol%) was dissolved in dry CD_3CN (4 mL). Then, phenylpyridine (50 μL, 0.35 mmol), **[D$_5$]-1** (56 mg, 0.35 mmol), **[D$_2$]-1** (51 mg, 0.35 mmol) or **[D$_3$]-1** (55 mg, 0.35 mmol) along with K_2CO_3 (97 mg, 0.7 mmol) and TsCl (0.2 g, 1 mmol) were added. The reaction mixture was heated at 120 °C in an oil bath. The reaction mixture was filtered through a pad of celite and the crude was purified by flash chromatography on silica gel (from 20% EtOAc:hexane to 40% EtOAc).

4.2.1. Intramolecular competition experiment between 2-(2,3,4,5,6-pentadeuterophenyl)pyridine and phenylpyridine



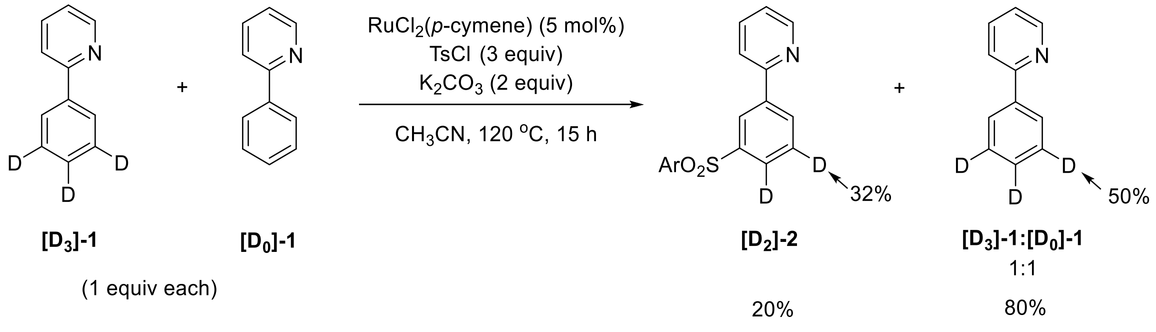
Following the general procedure described above, a mixture of **[D$_n$]-2** (^{1}H NMR ratio H2/H6:D2/D6 1.6:1 and H5:D5 2.3:1, 54 mg, 25%) and a mixture of the re-isolated **[D$_0$]-1** and **[D$_5$]-1** (^{1}H NMR ratio 1:1, 83 mg, 75%) was obtained.

4.2.2. Intramolecular competition experiment between 2-(2,6-dideuterophenyl)pyridine and phenylpyridine



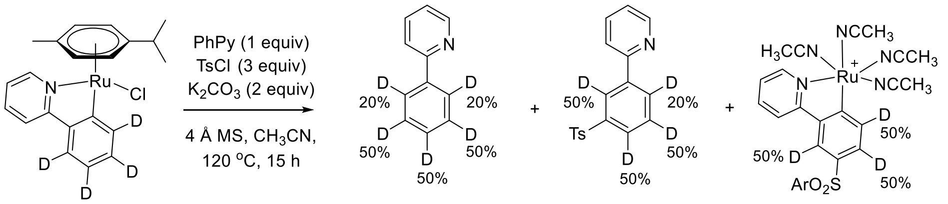
Following the general procedure described above, a mixture of **[D$_n$]-2** (^{1}H NMR ratio H6:D6 1.6:1 and H2/D2 1.1:1, 78 mg, 36%) and a mixture of the re-isolated **[D$_0$]-1** and **[D$_2$]-1** (^{1}H NMR ratio 1:1, 67 mg, 64%) was obtained.

4.2.3. Intramolecular competition experiment between 2-(3,4,5-trideuterophenyl)pyridine and phenylpyridine



Following the general procedure described above, a mixture of **[D$_n$]-2** (^{1}H NMR ratio H5:D5 2.1:1, 43 mg, 20%) and a mixture of the re-isolated **[D$_0$]-1** and **[D$_5$]-1** (^{1}H NMR ratio 1:1, 87 mg, 80%) was obtained.

4.2. Single turnover experiment



[D$_4$]-4

[D$_n$]-1
51%

[D$_n$]-2
13%

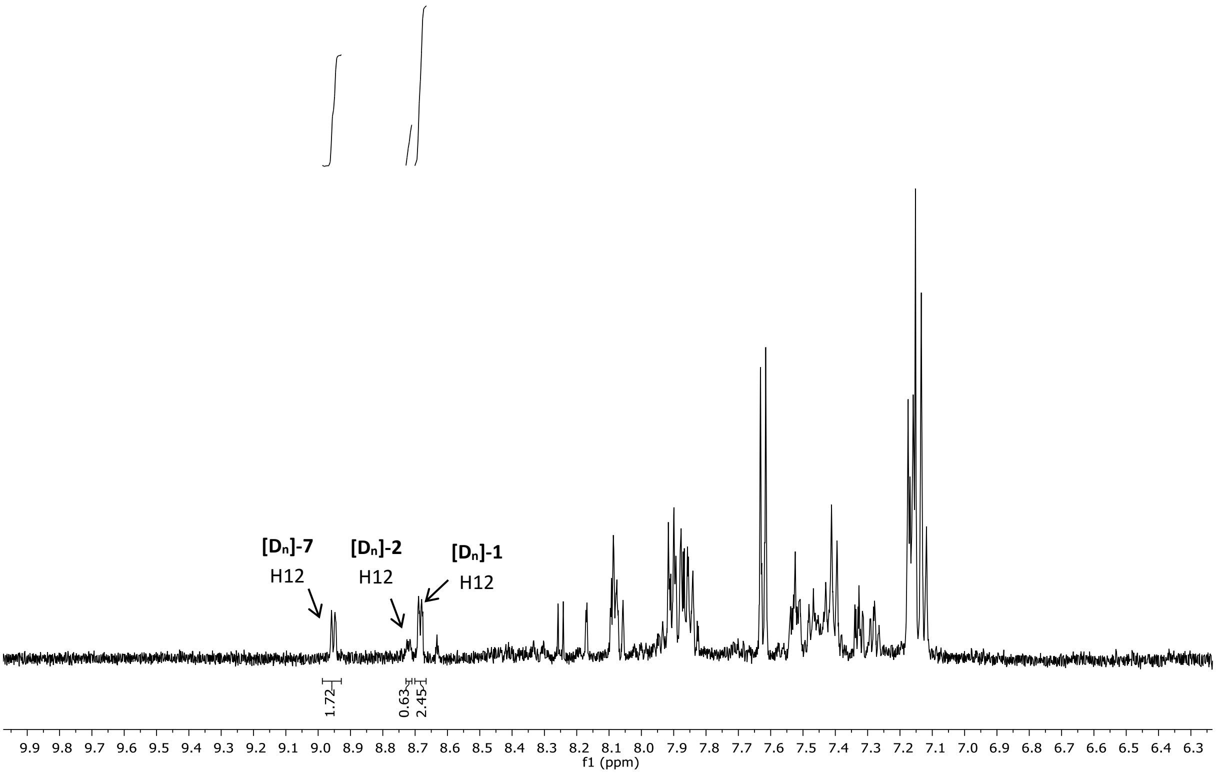
[D$_n$]-7
36%

2-Phenyl pyridine was purified by distillation and dried using 4 Å molecular sieves before use. Tosyl chloride was purified by recrystalisation and thoroughly dried before use.

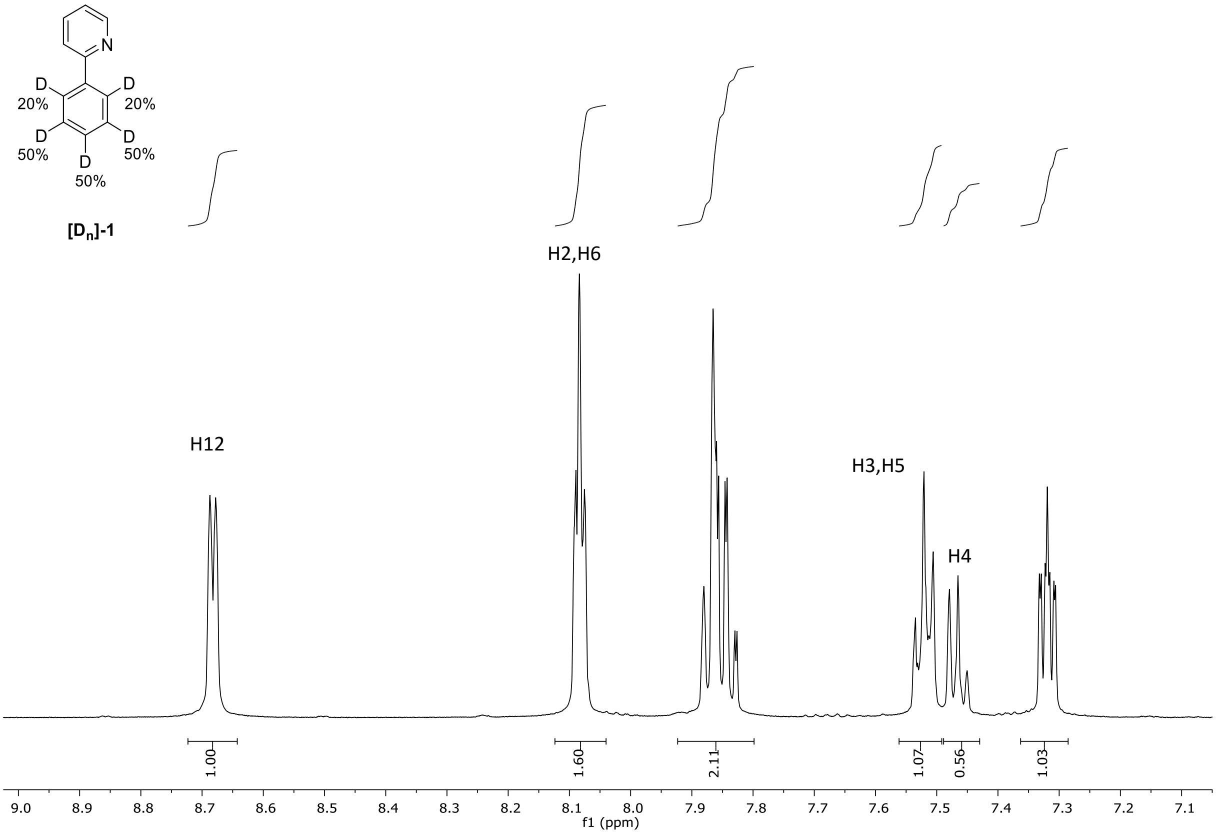
To a flame dried ampule purged with argon, K$_2$CO$_3$ (69 mg, 0.5 mmol) and activated molecular sieves 4 Å (100 mg) were added. Ruthenium complex **[D$_4$]-5** (107 mg, 0.15 mmol), 2-phenyl pyridine (35 μL, 0.25 mmol), tosyl chloride (143 mg, 0.75 mmol) and dry CH$_3$CN (2.5 mL) were then added and the reaction mixture was heated at 120 °C for 15 h.

Analysis of the crude reaction mixture by ^{1}H-NMR was used to calculate reaction composition with respect to total pyridine content. The reaction mixture was purified through oven-dried neutral alumina (Al$_2$O$_3$) and eluted with CH$_3$CN to separate the Ru complex **[D$_n$]-7** and a mixture of **[D$_n$]-1** and **[D$_n$]-2**. The fraction corresponding to the mixture of **[D$_n$]-1** and **[D$_n$]-2** was re-purified by flash chromatography over silica. Deuterium incorporation was calculated by ^{1}H-NMR.

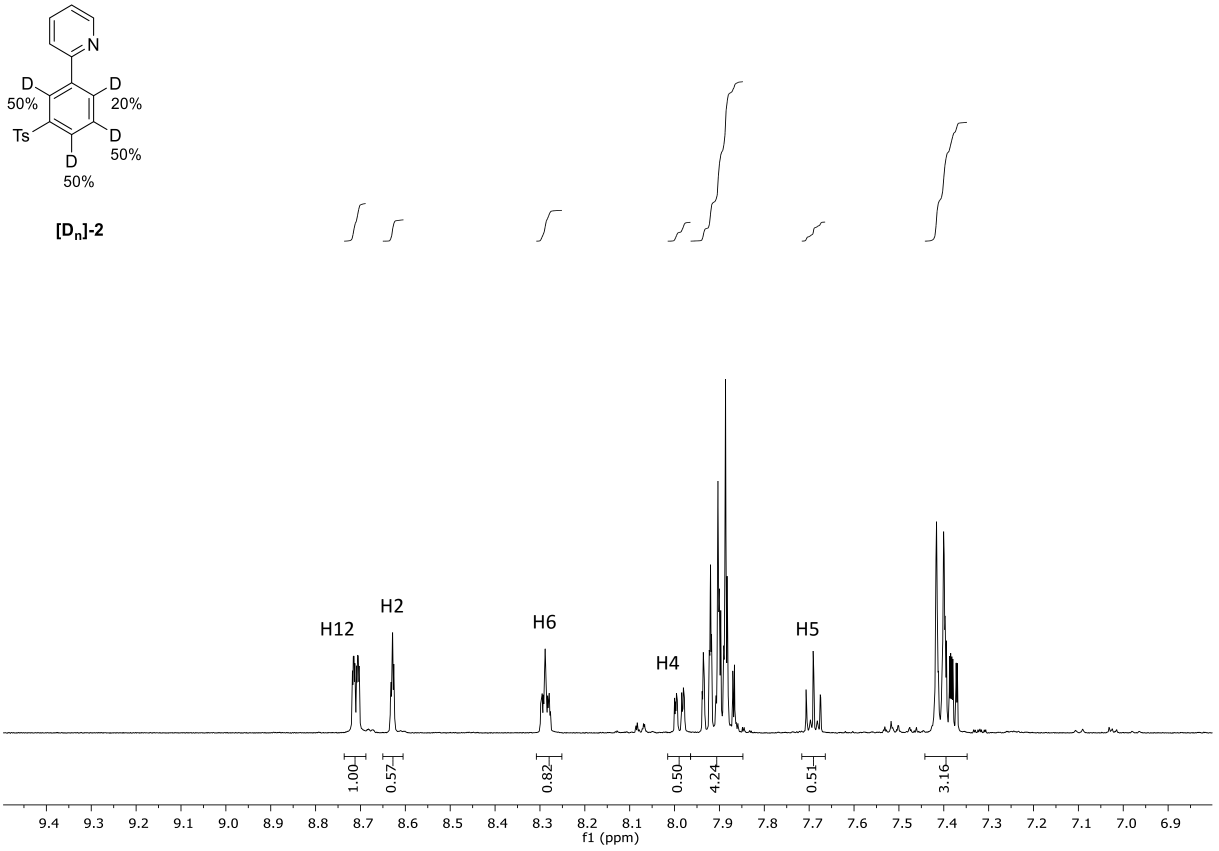
Ratios of [D$_n$]-1, [D$_n$]-2 and [D$_n$]-7



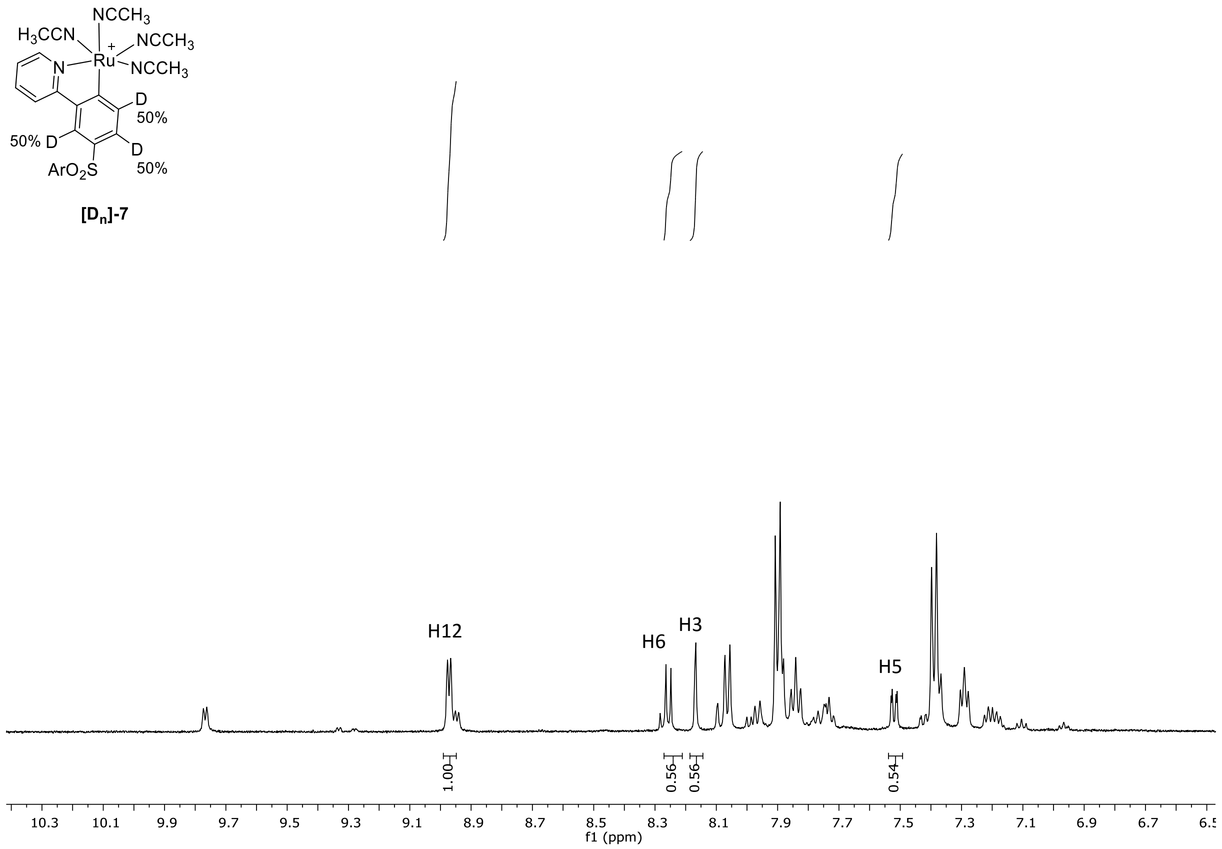
Deuterium Incorporation



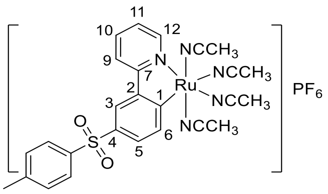
[D$_n$]-1

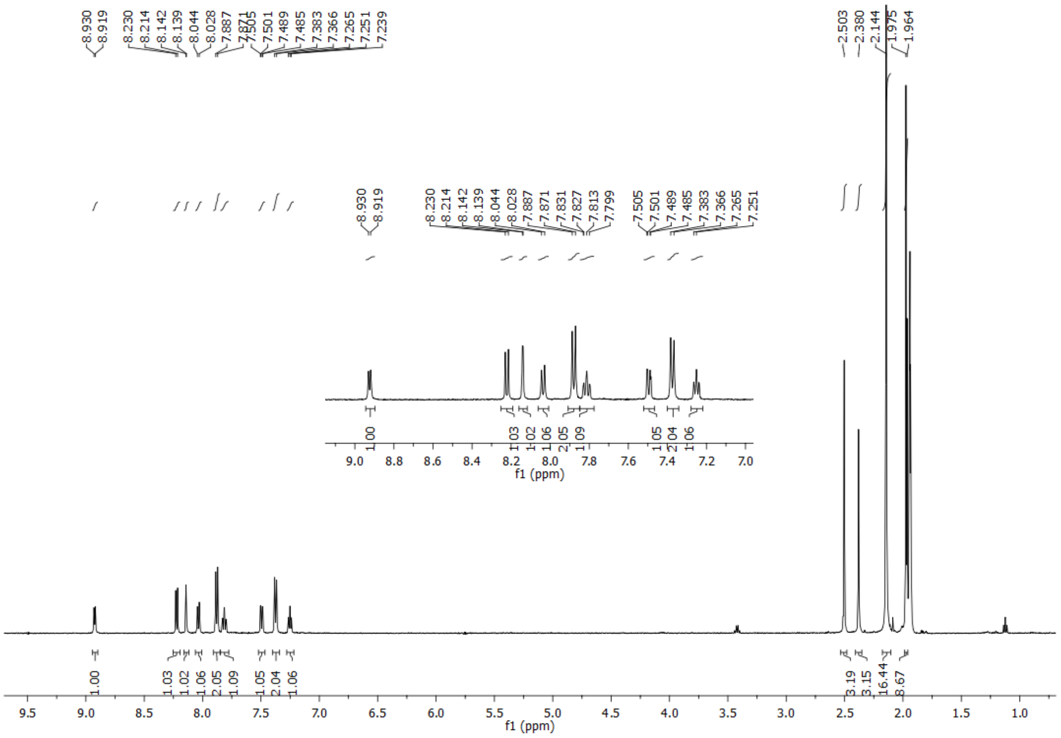


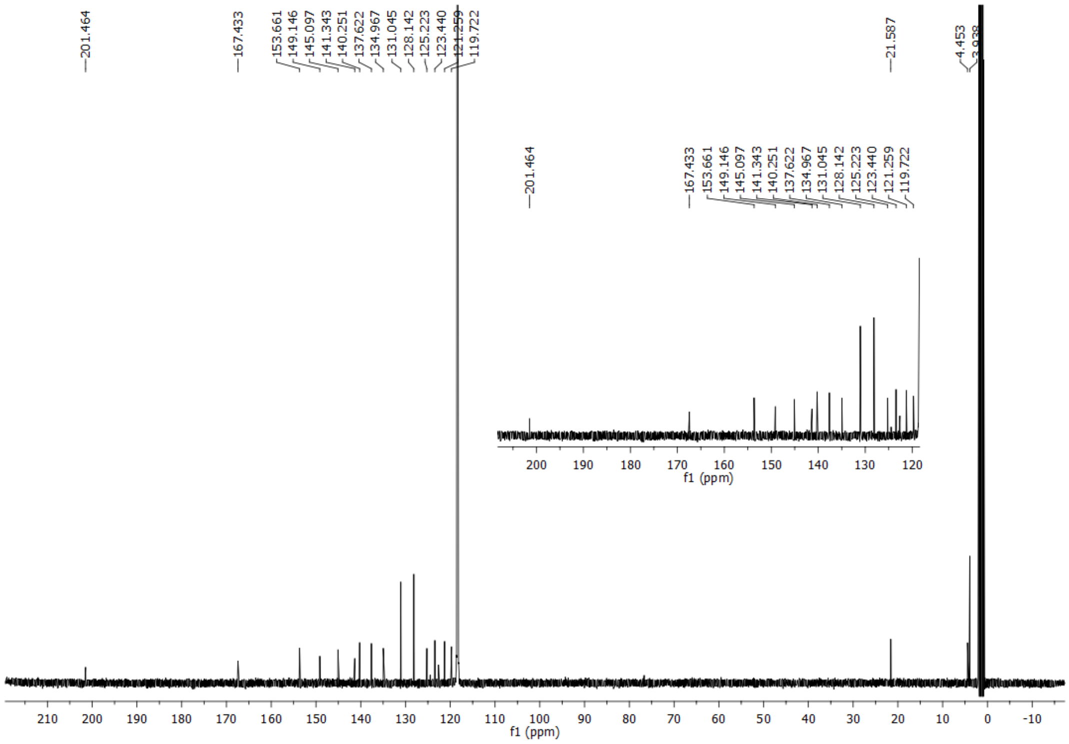
[D$_n$]-2


NCCH3
H3CCN
NCCH3
N
+
Ru
NCCH3
D
50%
50% D
D
ArO2S
50%
[Dn]-7
H12
H6
H3
H5
1.00
0.56
0.56
0.54
10.3
10.1
9.9
9.7
9.5
9.3
9.1
8.9
8.7
8.5
8.3
8.1
7.9
7.7
7.5
7.3
7.1
6.9
6.7
6.5
f1 (ppm)

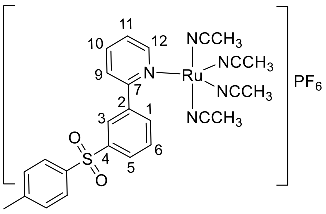
5. ^{1}H-NMR and ^{13}C-NMR spectroscopic data



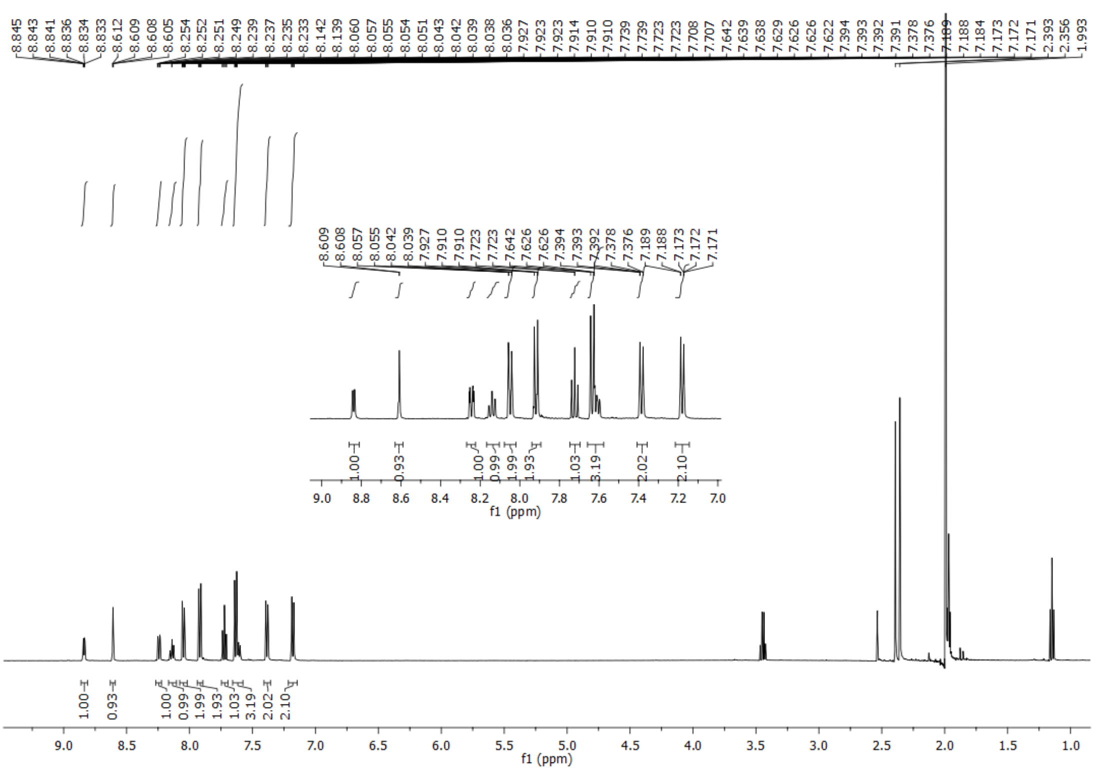




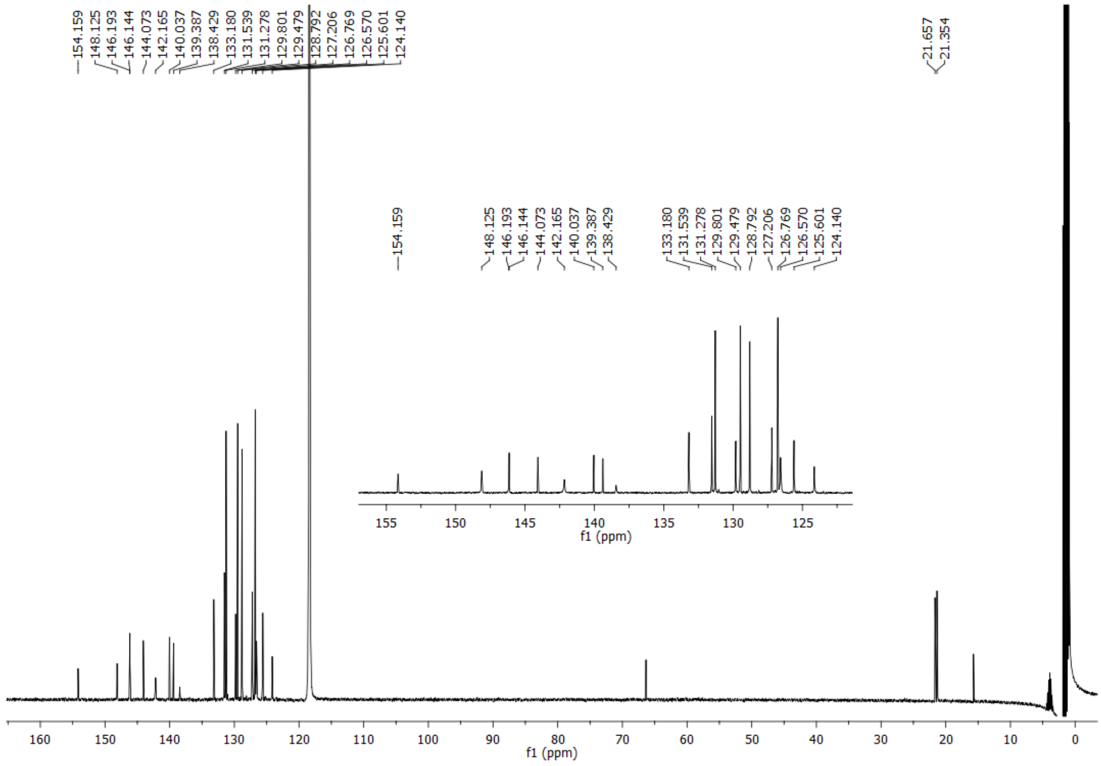
201.464
167.433
153.661
149.146
145.097
141.343
140.251
137.622
134.967
131.045
128.142
125.223
123.440
121.259
119.722
21.587
4.453
3.938
200
190
180
170
160
150
140
130
120
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

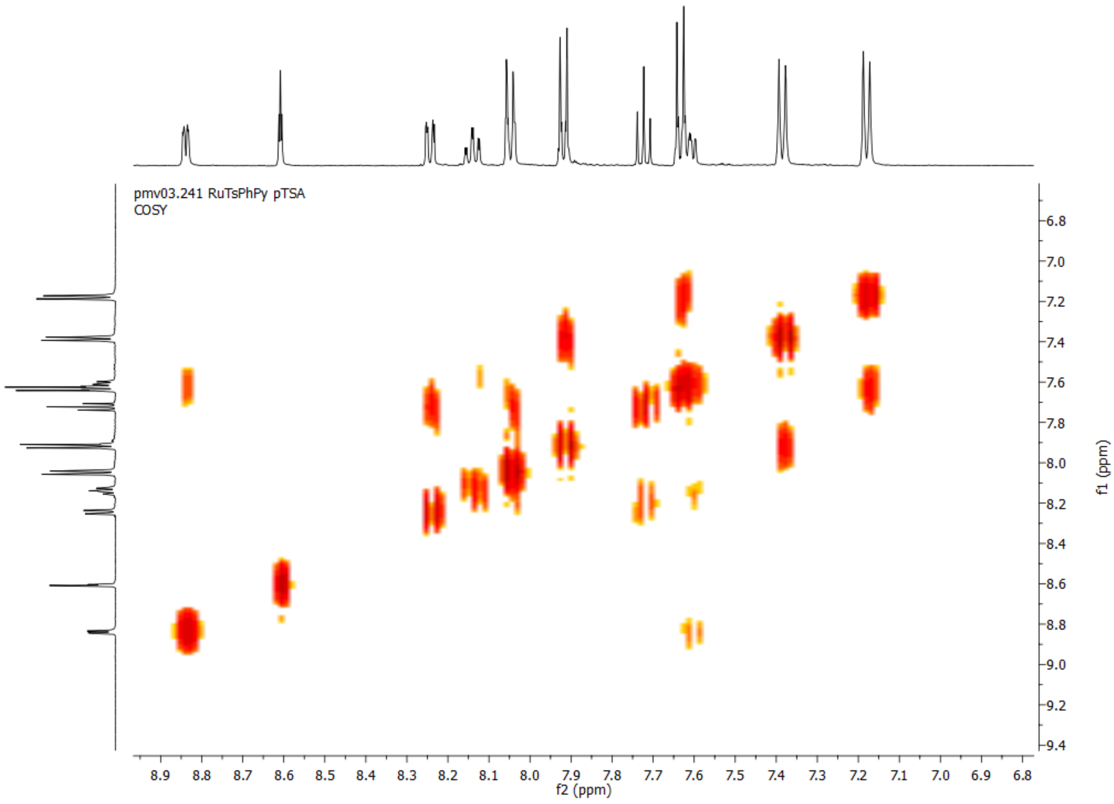


11
10
12
9
N
Ru
NCCH3
NCCH3
NCCH3
NCCH3
PF6
2
7
3
1
6
4
5
O
S
O



8.845
8.843
8.841
8.836
8.834
8.833
8.612
8.609
8.608
8.605
8.254
8.252
8.251
8.249
8.239
8.237
8.235
8.233
8.142
8.139
8.060
8.057
8.055
8.054
8.051
8.043
8.042
8.039
8.038
8.036
7.927
7.923
7.923
7.914
7.910
7.910
7.739
7.739
7.723
7.723
7.708
7.707
7.642
7.639
7.638
7.629
7.626
7.626
7.622
7.394
7.393
7.392
7.391
7.378
7.376
7.189
7.188
7.184
7.173
7.172
7.171
2.393
2.356
1.993
8.609
8.608
8.057
8.055
8.042
8.039
7.927
7.910
7.910
7.723
7.723
7.642
7.626
7.394
7.393
7.392
7.378
7.376
7.189
7.188
7.173
7.172
7.171
1.00
0.93
1.00
0.99
1.99
1.93
1.03
3.19
2.02
2.10
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
1.00
0.93
1.00
0.99
1.99
1.93
1.03
3.19
2.02
2.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)


154.159
148.125
146.193
146.144
144.073
142.165
140.037
139.387
138.429
133.180
131.539
131.278
129.801
129.479
128.792
127.206
126.769
126.570
125.601
124.140
21.657
21.354
155
150
145
140
135
130
125
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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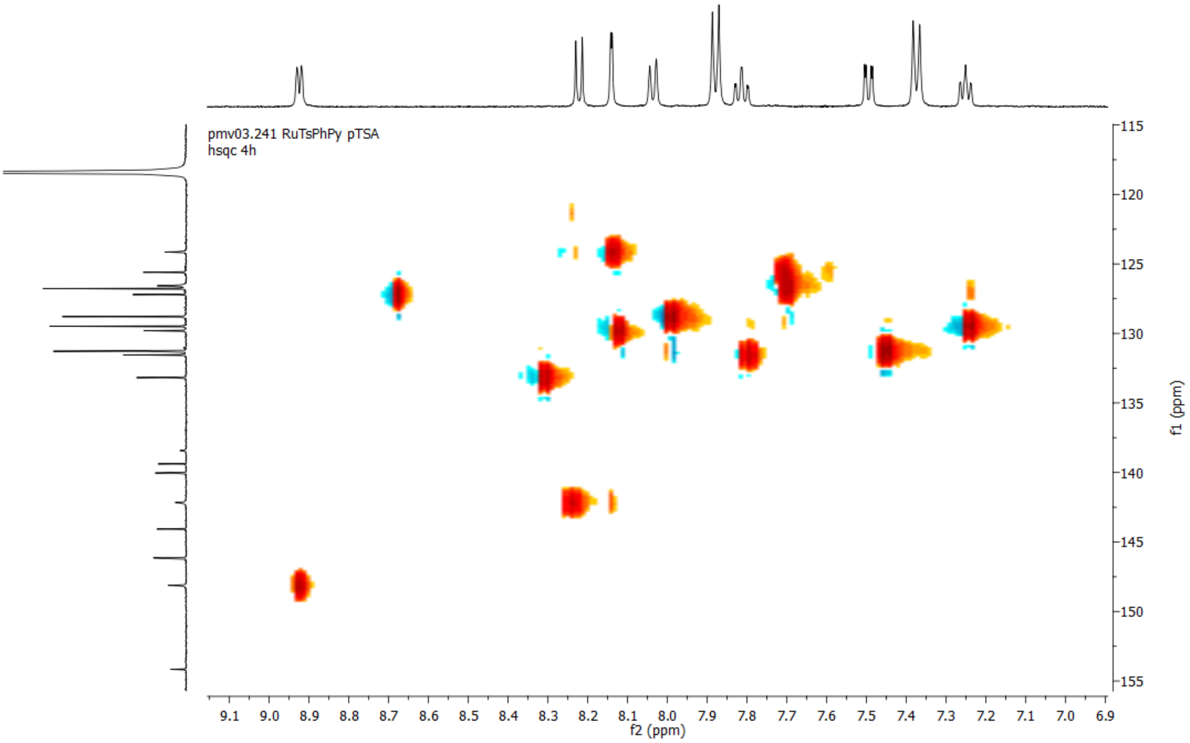
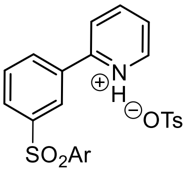
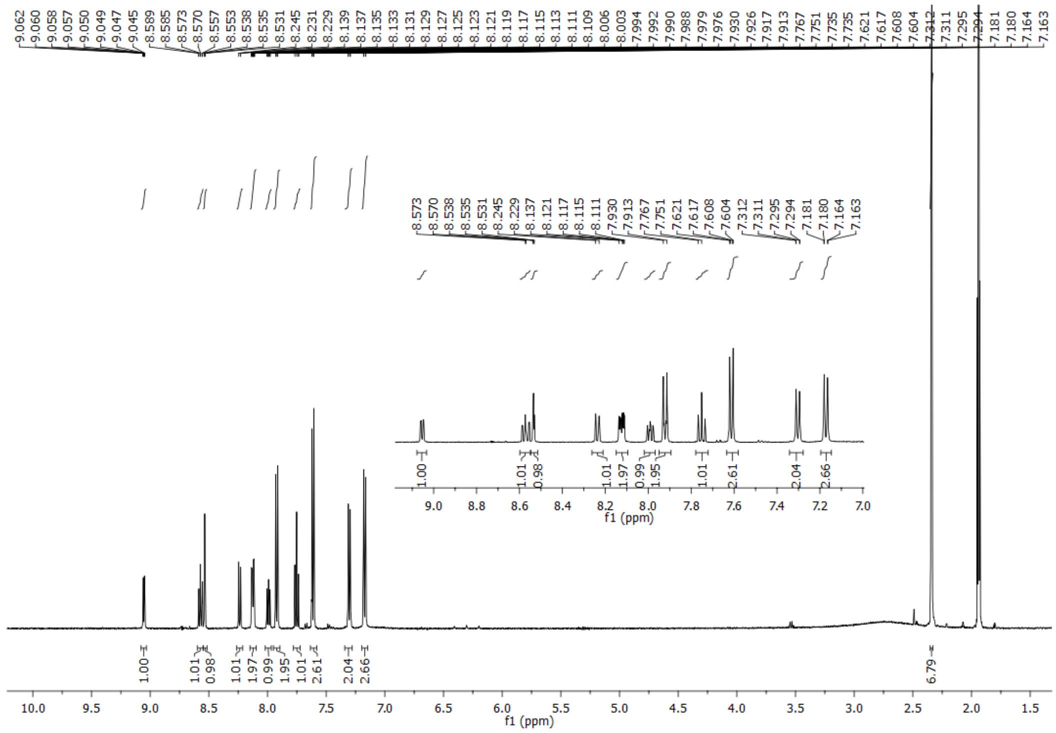
COSY
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
f2 (ppm)
6.8
7.0
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.4
f1 (ppm)


pmv03.241 RuTsPhPy pTSA
hsqc 4h
115
120
125
130
135
140
145
150
155
f1 (ppm)
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
f2 (ppm)


N
H
⊕
⊖OTs
SO2Ar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9.057
9.050
9.049
9.047
9.045
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8.585
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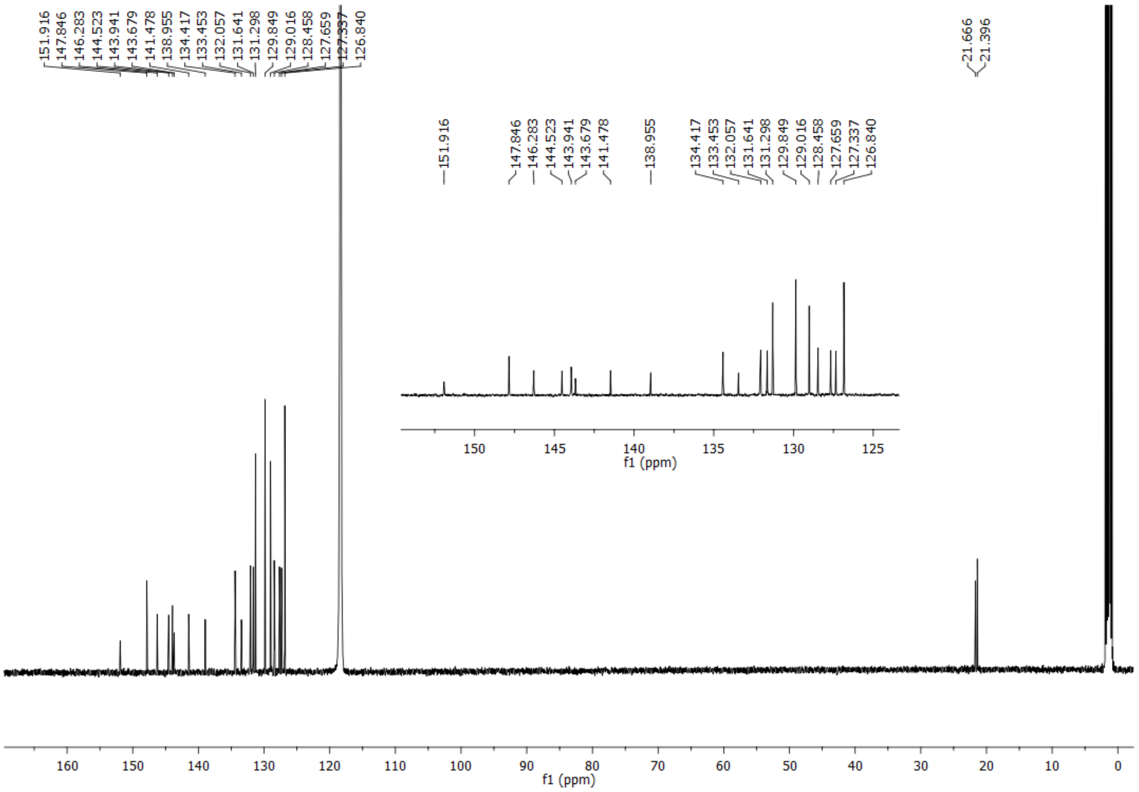
8.557
8.553
8.538
8.535
8.531
8.245
8.231
8.229
8.139
8.137
8.135
8.133
8.131
8.129
8.127
8.125
8.123
8.121
8.119
8.117
8.115
8.113
8.111
8.109
8.006
8.003
7.994
7.992
7.990
7.988
7.979
7.976
7.930
7.926
7.917
7.913
7.767
7.751
7.735
7.735
7.621
7.617
7.608
7.604
7.312
7.311
7.295
7.294
7.181
7.180
7.164
7.163
8.573
8.570
8.538
8.535
8.531
8.245
8.229
8.137
8.121
8.117
8.115
8.111
7.930
7.913
7.767
7.751
7.621
7.617
7.608
7.604
7.312
7.311
7.295
7.294
7.181
7.180
7.164
7.163
1.00
1.01
0.98
1.01
1.97
0.99
1.95
1.01
2.61
2.04
2.66
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)
1.00
1.01
0.98
1.01
1.97
0.99
1.95
1.01
2.61
2.04
2.66
6.79
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
f1 (ppm)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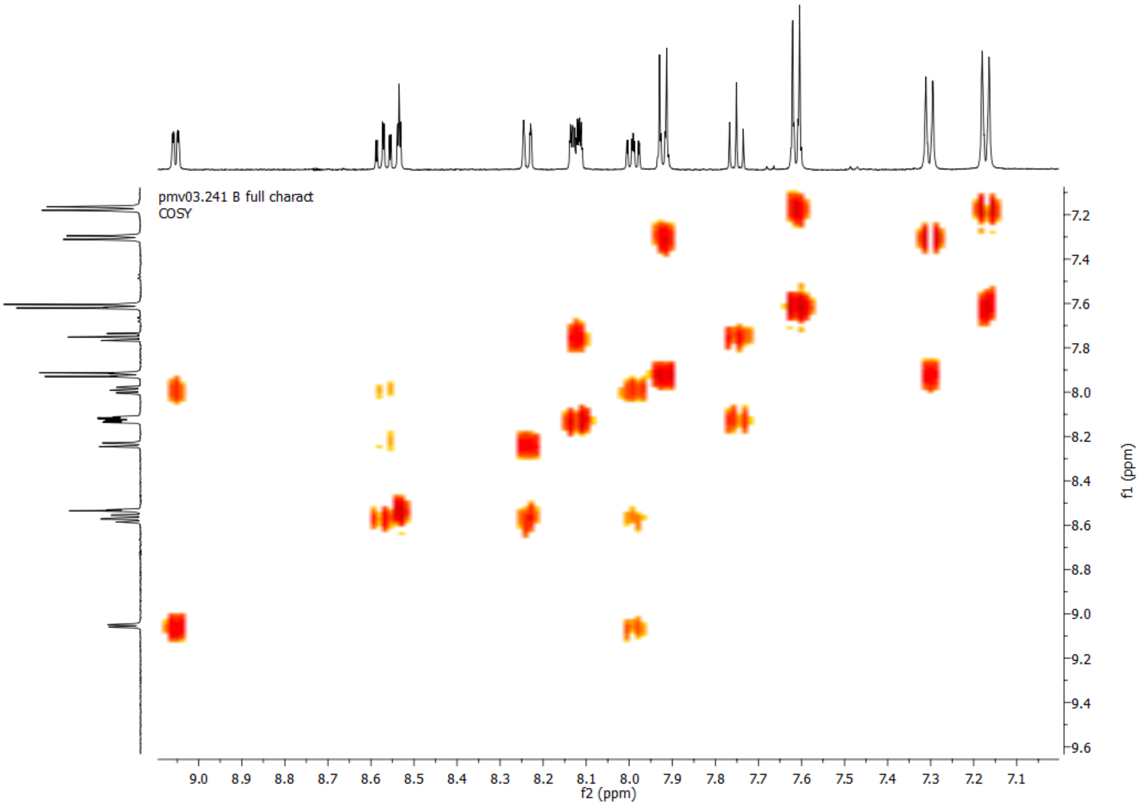
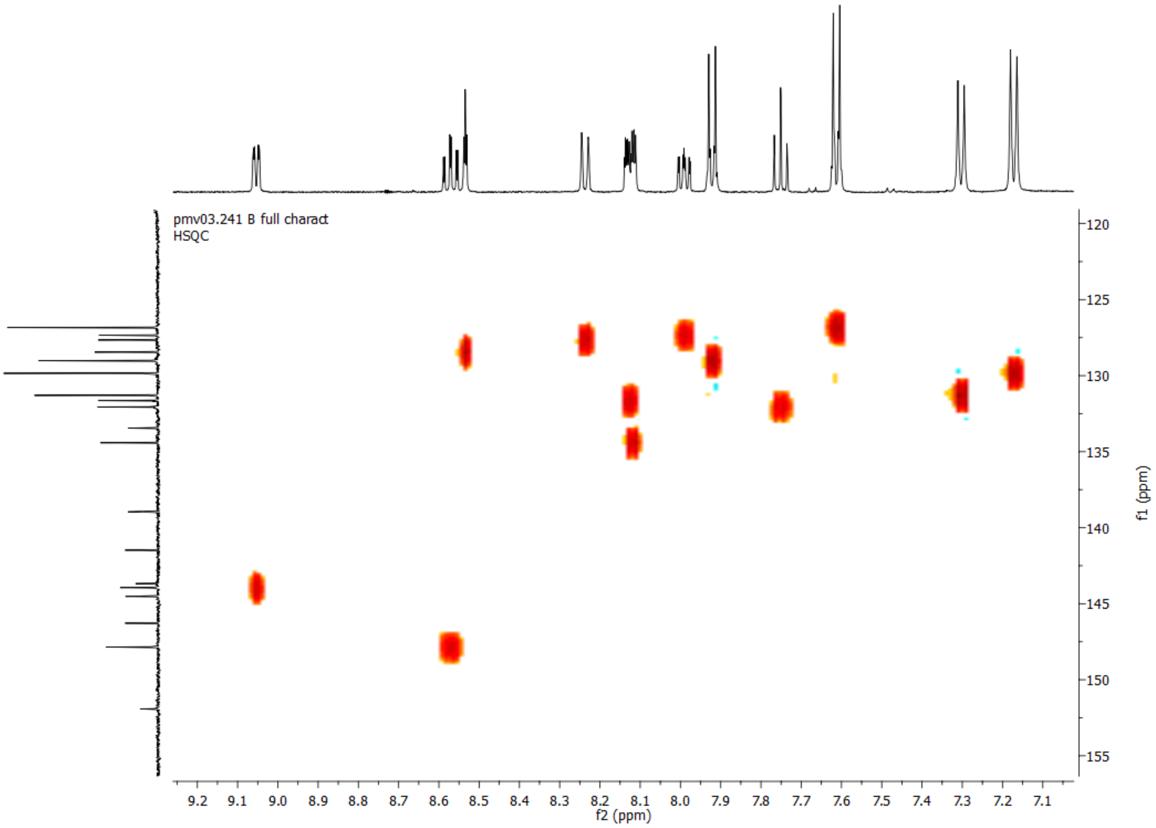
146.283
144.523
143.941
143.679
141.478
138.955
134.417
133.453
132.057
131.641
131.298
129.849
129.016
128.458
127.659
127.337
126.840
21.666
21.396
151.916
147.846
146.283
144.523
143.941
143.679
141.478
138.955
134.417
133.453
132.057
131.641
131.298
129.849
129.016
128.458
127.659
127.337
126.840
150
145
140
135
130
125
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


pmv03.241 B full charact
COSY
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f2 (ppm)
7.2
7.4
7.6
7.8
8.0
8.2
8.4
8.6
8.8
9.0
9.2
9.4
9.6
f1 (ppm)


pmv03.241 B full charact
HSQC
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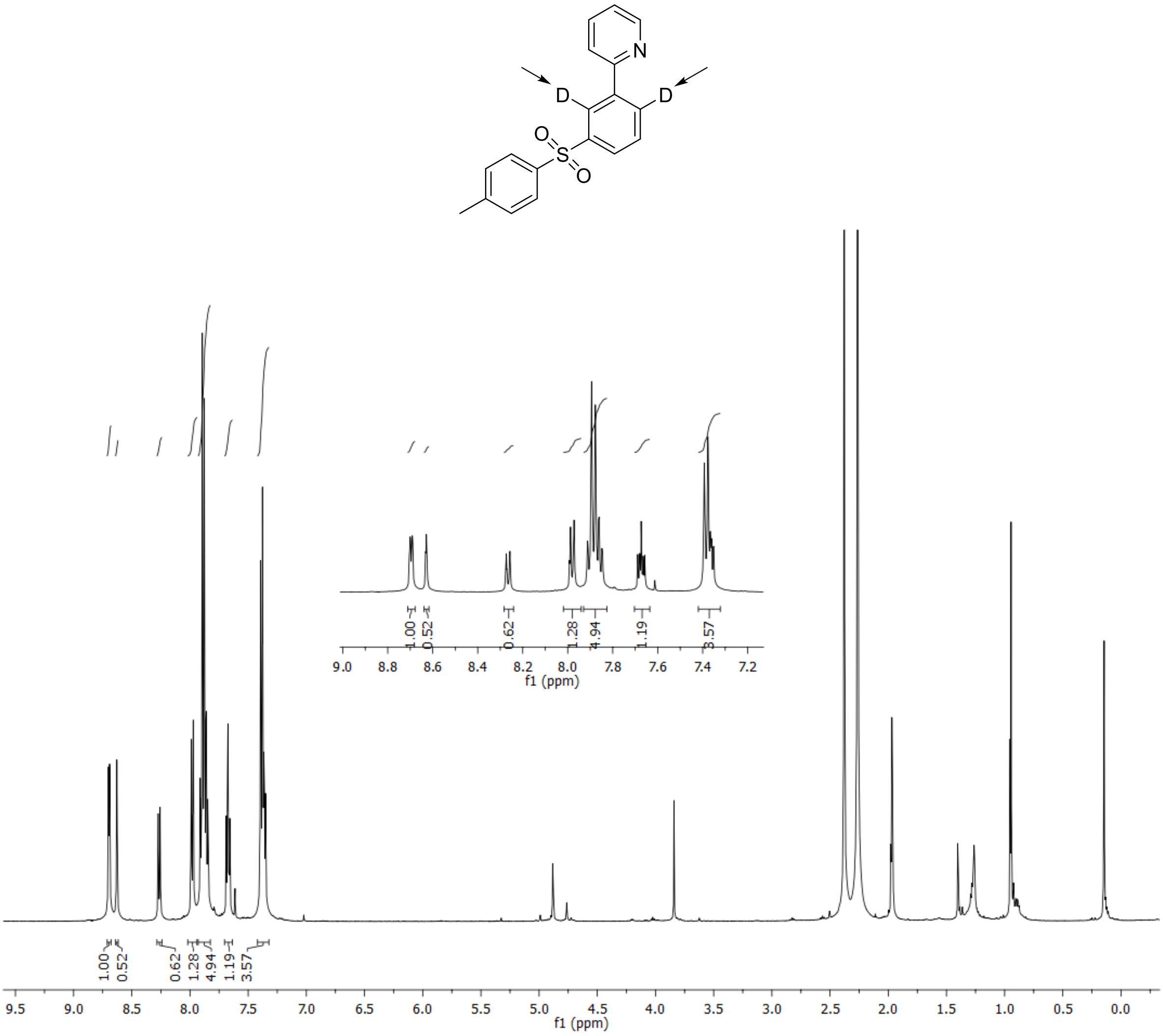
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f2 (ppm)
120
125
130
135
140
145
150
155
f1 (ppm)


N
D
D
O
S
O
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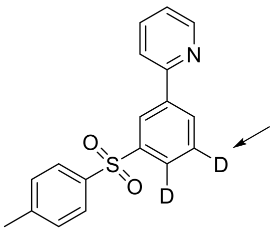
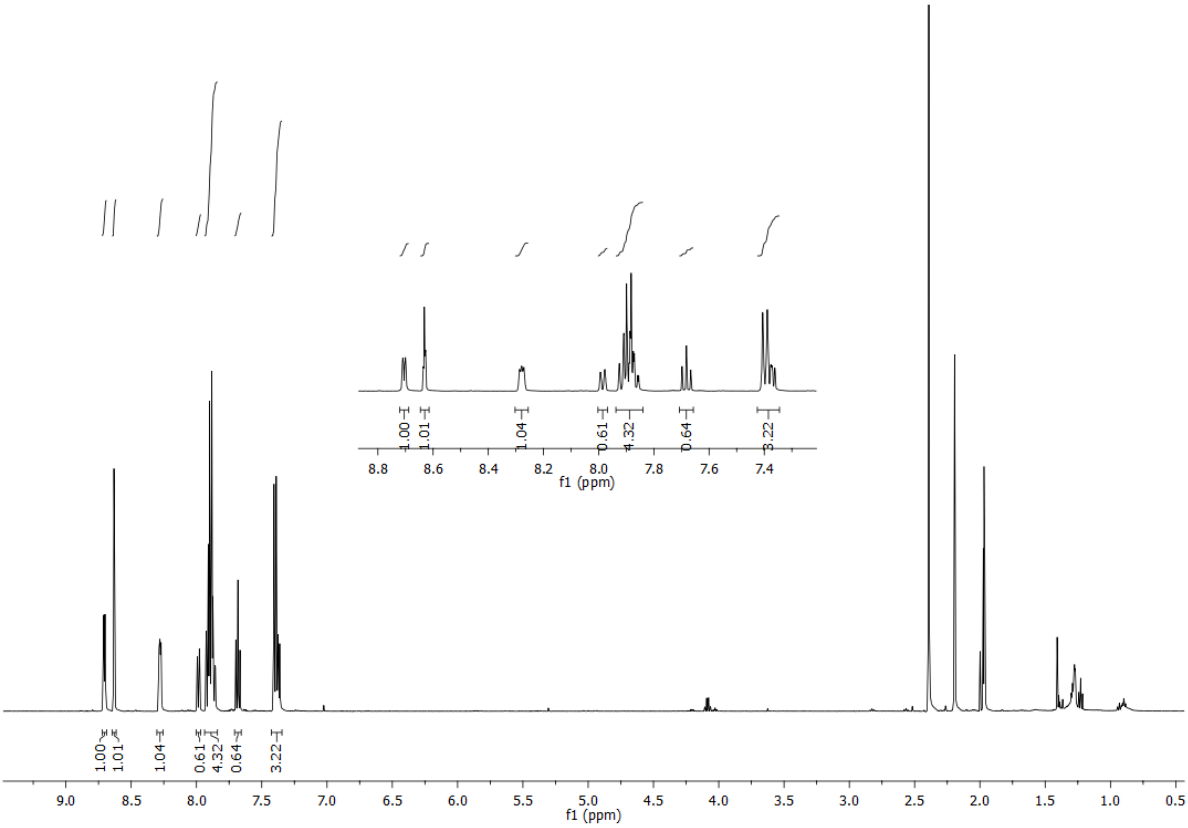
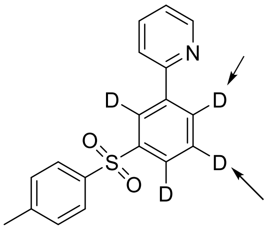
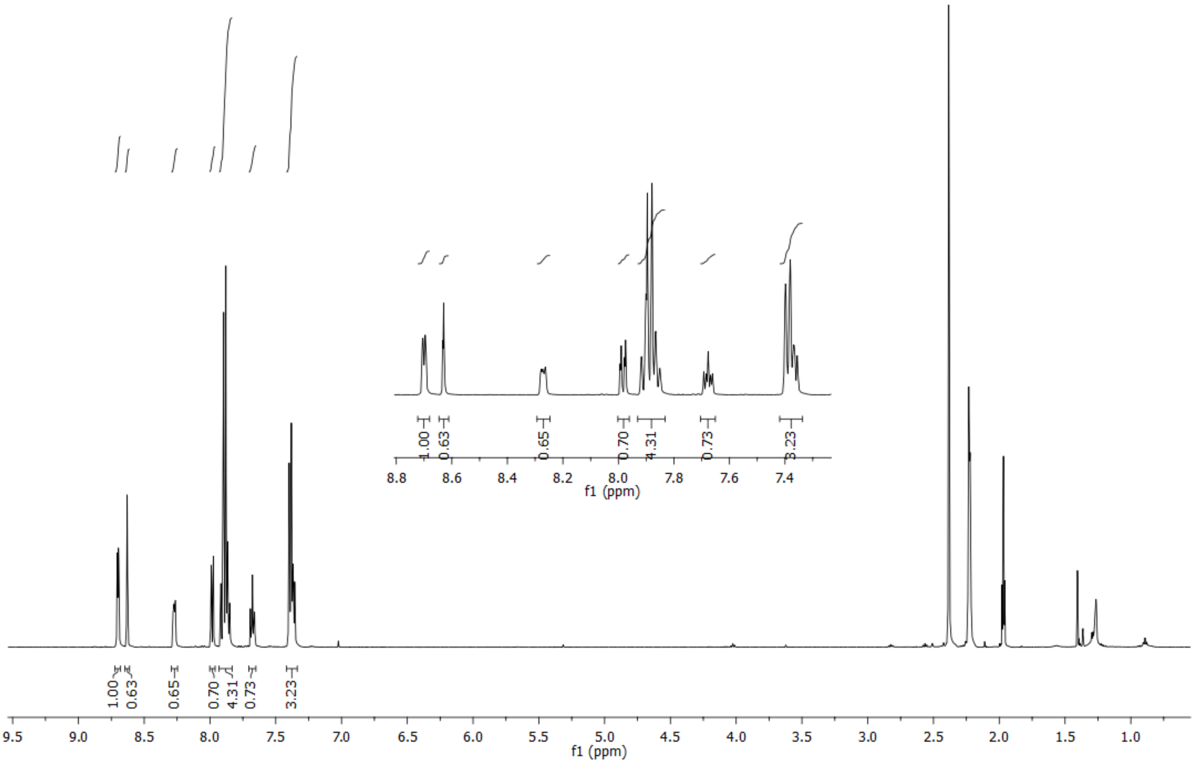
0.52
0.62
1.28
4.94
1.19
3.57
9.0 8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2
f1 (ppm)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


N
O
S
O
D
D


1.00
1.01
1.04
0.61
4.32
0.64
3.22
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
f1 (ppm)
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


N
D
D
D
D
O
S
O


1.00
0.63
0.65
0.70
4.31
0.73
3.23
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)
1.00
0.63
0.65
0.70
4.31
0.73
3.23
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
f1 (ppm)

6. X-Ray structure and data for complex 7

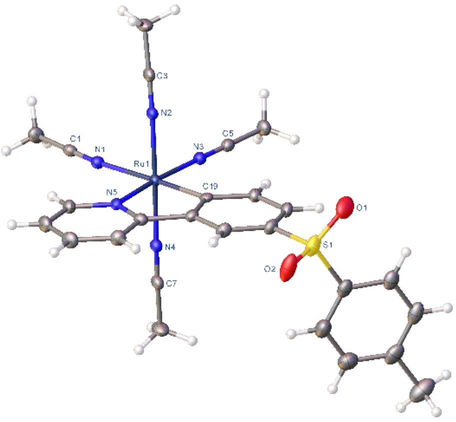


Table 1 Crystal data and structure refinement for 7.

Identification code	1479685
Empirical formula	$C_{30}H_{36}F_6N_5O_3PRuS$
Formula weight	792.74
Temperature/K	150.15
Crystal system	triclinic
Space group	P-1
a/Å	8.2870(1)
b/Å	8.4860(1)
c/Å	25.3050(5)
α/°	95.062(1)
β/°	92.854(1)
γ/°	97.449(1)
Volume/Å^3	1754.25(5)
Z	2
ρ_{calc}g/cm^3	1.501
μ/mm^{-1}	0.622
F(000)	808.0
Crystal size/mm^3	0.3 × 0.25 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.162 to 55.304
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-32 \leq l \leq 33$
Reflections collected	29703
Independent reflections	7976 [R_{int} = 0.0668, R_{sigma} = 0.0727]
Data/restraints/parameters	7976/69/467
Goodness-of-fit on F^2	1.035
Final R indexes [I>=2σ (I)]	R_1 = 0.0439, wR_2 = 0.0819
Final R indexes [all data]	R_1 = 0.0667, wR_2 = 0.0883
Largest diff. peak/hole / e Å^{-3}	0.71/-0.54

Notes:

Asymmetric unit contains one molecule of solvent (Et_2O) in addition to one salt molecule. F3-F6 were found to be disordered in a 65:35 ratio over 2 sites. P-F distance similarity restraints were imposed in the anion. ADPs pertaining to 35% occupancy fluorines were also restrained to assist convergence.

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times 10^3$) for k13cgf2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	**U(eq)**
Ru1	-34.1(2)	1435.0(3)	1710.3(2)	22.21(7)
S1	2410.3(10)	5114.0(11)	4060.0(3)	47.4(2)
P1	3428.0(9)	7141.2(9)	657.2(3)	33.08(18)
F1	4467(3)	8838(3)	641.7(12)	91.5(9)
F2	2413(3)	5445(2)	669.9(12)	87.0(8)
F3	2674(10)	7360(6)	102(2)	99.1(18)
F4	4798(6)	6275(5)	382(3)	77.8(19)
F5	4339(11)	6884(10)	1205(2)	134(3)
F6	2111(7)	8020(5)	918(4)	105(3)
F3A	4070(20)	6620(20)	134(5)	149(6)
F4A	4936(10)	6726(13)	941(6)	94(4)
F5A	2694(19)	7580(20)	1183(5)	149(6)
F6A	1824(10)	7618(13)	387(6)	87(3)
O1	3120(3)	6745(3)	4013.1(10)	62.1(7)
O2	1079(3)	4818(4)	4399.3(9)	67.5(8)
O3	8504(3)	7465(3)	3022.7(10)	60.9(7)
N1	-1074(3)	126(3)	977.1(9)	27.2(5)
N2	-664(2)	3403(3)	1404.1(8)	25.1(5)
N3	2126(3)	1854(3)	1368.2(8)	26.5(5)
N4	595(2)	-576(3)	1977.9(9)	25.8(5)
N5	-2087(2)	1163(2)	2135.2(8)	24.3(5)
C1	-1508(3)	-498(3)	566.0(11)	28.5(6)
C2	-2012(4)	-1284(4)	40.2(11)	40.3(7)
C3	-994(3)	4435(3)	1180.3(11)	30.4(6)
C4	-1435(4)	5742(4)	891.3(14)	45.4(8)
C5	3368(3)	2207(3)	1204.7(10)	28.1(6)
C6	4958(3)	2694(4)	1002.2(12)	37.4(7)
C7	976(3)	-1707(3)	2126.7(12)	31.3(6)
C8	1527(4)	-3146(4)	2306.0(15)	48.2(8)
C9	-3535(3)	328(3)	1951.8(11)	30.9(6)
C10	-4871(3)	155(4)	2258.6(13)	39.6(7)
C11	-4706(3)	842(4)	2779.5(13)	40.6(7)
C12	-3233(3)	1689(4)	2974.2(12)	36.1(7)
C13	-1927(3)	1852(3)	2645.7(10)	26.9(6)
C14	-290(3)	2700(3)	2805.5(10)	27.0(6)
C15	164(3)	3458(3)	3311.1(11)	33.9(6)
C16	1764(3)	4166(4)	3423.5(11)	34.5(7)
C17	2908(3)	4111(3)	3044.0(11)	33.1(6)
C18	2457(3)	3359(3)	2544.3(11)	28.4(6)
C19	844(3)	2631(3)	2403.9(10)	24.2(5)
C20	4020(4)	4070(4)	4260.1(11)	41.6(8)
C21	5596(4)	4856(4)	4325.9(11)	44.5(8)
C22	6854(4)	4025(5)	4472.0(12)	51.8(9)
C23	6560(4)	2409(5)	4544.8(12)	54.9(10)
C24	4974(5)	1648(5)	4471.7(15)	64(1)

C25	3697(4)	2474(5)	4331.7(14)	57.5(10)
C26	7945(5)	1531(6)	4714.5(16)	78.8(13)
C27	6776(4)	5928(5)	2338.7(15)	59.5(10)
C28	7010(4)	6527(5)	2912.8(16)	61(1)
C29	8795(5)	8042(5)	3561.1(17)	74.4(12)
C30	10375(5)	9138(5)	3630.6(19)	82.4(14)

Table 3 Anisotropic Displacement Parameters ($\text{Å}^2\times10^3$) for 7. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ru1	19.45(11)	20.65(12)	26.67(12)	4.85(8)	0.40(8)	1.88(7)
S1	37.8(4)	65.4(6)	36.3(4)	-11.9(4)	-6.2(3)	11.9(4)
P1	30.6(4)	30.3(4)	38.7(4)	3.1(3)	6.7(3)	4.1(3)
F1	59.8(14)	39.4(13)	171(3)	11.9(15)	6.1(15)	-8.4(10)
F2	52.1(13)	43.2(13)	171(3)	34.9(15)	29.5(14)	0(1)
F3	154(6)	81(3)	62(3)	11(2)	-37(3)	29(4)
F4	60(3)	45(2)	138(6)	18(3)	47(3)	21.4(19)
F5	193(9)	151(6)	53(3)	17(3)	-38(4)	12(6)
F6	77(4)	56(3)	187(8)	-20(4)	83(4)	15(2)
F3A	168(12)	189(12)	74(7)	-55(7)	74(8)	-22(9)
F4A	40(4)	91(6)	155(11)	51(8)	-43(6)	16(4)
F5A	153(11)	231(14)	67(6)	-39(7)	53(6)	57(9)
F6A	55(5)	71(6)	134(9)	59(6)	-44(5)	-17(4)
O1	68.9(16)	46.0(15)	65.4(16)	-18.4(12)	-19.9(13)	10.8(12)
O2	36.4(13)	123(2)	38.7(13)	-18.7(14)	0.5(10)	12.8(14)
O3	54.4(15)	59.9(17)	64.9(17)	-0.9(13)	5.2(12)	-1.0(12)
N1	27.4(12)	25.6(13)	29.0(13)	5.2(10)	1.6(9)	3.1(9)
N2	20.1(11)	24.2(12)	30.7(12)	5.3(10)	0.7(9)	0.4(9)
N3	24.4(12)	25.1(12)	30.2(12)	5.6(10)	-0.1(9)	2.4(9)
N4	21.4(11)	24.2(13)	31.6(12)	3.9(10)	2.4(9)	1.9(9)
N5	20.0(11)	23.6(12)	29.9(12)	6.7(10)	-0.8(9)	3.7(9)
C1	28.7(14)	25.2(15)	33.1(16)	9.3(13)	6.7(12)	3.3(11)
C2	49.9(19)	38.9(18)	29.1(15)	0.3(14)	-0.2(13)	-2.5(14)
C3	19.3(13)	29.3(16)	42.2(16)	7.7(13)	0.9(11)	-1.1(11)
C4	36.8(17)	35.4(18)	67(2)	24.9(17)	-2.8(15)	6.2(13)
C5	28.9(15)	25.7(15)	29.8(14)	3.7(12)	-2.1(11)	5.0(11)
C6	25.5(14)	40.6(18)	46.3(18)	10.4(15)	4.2(12)	-0.1(12)
C7	22.4(13)	26.6(16)	44.9(17)	7.8(13)	2.4(12)	-0.1(11)
C8	40.0(18)	30.6(18)	77(2)	19.9(17)	0.1(16)	8.9(14)
C9	24.2(14)	30.3(16)	37.8(16)	6.8(13)	-1.9(11)	1.4(11)
C10	21.3(14)	43.4(19)	54(2)	12.7(16)	2.7(13)	0.1(12)
C11	28.5(15)	48(2)	47.4(19)	12.1(16)	13.2(13)	5.9(13)
C12	33.8(16)	40.5(18)	35.3(16)	4.2(14)	6.4(12)	7.6(13)
C13	26.6(14)	25.5(15)	30.3(14)	6.6(12)	4.8(11)	6.1(11)
C14	27.6(14)	26.5(15)	28.1(14)	5.5(12)	-2.0(11)	7.4(11)
C15	33.8(15)	39.9(17)	29.3(15)	3.7(13)	1.6(12)	10.2(12)
C16	35.2(16)	37.8(17)	29.4(15)	-0.8(13)	-8.2(12)	7.3(13)

C17	24.3(14)	33.6(17)	40.4(16)	4.0(13)	-6.1(12)	2.7(11)
C18	25.9(14)	26.0(15)	32.5(15)	1.5(12)	-1.9(11)	2.9(11)
C19	25.3(13)	20.4(14)	28.6(13)	8.5(11)	-2.1(10)	7.1(10)
C20	36.4(17)	60(2)	26.5(15)	0.5(15)	-3.8(12)	5.1(15)
C21	39.1(17)	63(2)	28.9(16)	-3.4(15)	0.4(13)	4.8(15)
C22	34.2(17)	86(3)	33.0(17)	-7.3(18)	0.9(13)	8.0(17)
C23	52(2)	85(3)	29.6(17)	1.1(18)	-3.2(15)	20(2)
C24	69(3)	67(3)	57(2)	20(2)	-7.1(19)	7(2)
C25	43(2)	75(3)	53(2)	18(2)	-8.6(16)	-2.6(18)
C26	79(3)	107(4)	57(2)	-3(2)	-7(2)	49(3)
C27	49(2)	60(2)	65(2)	-2(2)	6.2(18)	-4.3(17)
C28	47(2)	59(3)	74(3)	-1(2)	19.6(19)	-2.0(18)
C29	84(3)	67(3)	69(3)	-7(2)	-3(2)	11(2)
C30	93(3)	53(3)	95(3)	3(2)	-29(3)	6(2)

Table 4 Bond Lengths for 7.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Ru1	N1	2.156(2)	N5	C9	1.351(3)
Ru1	N2	2.019(2)	N5	C13	1.363(3)
Ru1	N3	2.031(2)	C1	C2	1.451(4)
Ru1	N4	2.010(2)	C3	C4	1.456(4)
Ru1	N5	2.056(2)	C5	C6	1.460(4)
Ru1	C19	2.002(3)	C7	C8	1.459(4)
S1	O1	1.450(3)	C9	C10	1.383(4)
S1	O2	1.442(2)	C10	C11	1.386(4)
S1	C16	1.761(3)	C11	C12	1.379(4)
S1	C20	1.772(3)	C12	C13	1.397(4)
P1	F1	1.584(2)	C13	C14	1.471(4)
P1	F2	1.574(2)	C14	C15	1.391(4)
P1	F3	1.544(4)	C14	C19	1.421(4)
P1	F4	1.588(4)	C15	C16	1.388(4)
P1	F5	1.592(5)	C16	C17	1.385(4)
P1	F6	1.543(4)	C17	C18	1.376(4)
P1	F3A	1.501(8)	C18	C19	1.412(4)
P1	F4A	1.507(6)	C20	C21	1.382(4)
P1	F5A	1.527(8)	C20	C25	1.376(5)
P1	F6A	1.579(6)	C21	C22	1.386(4)
O3	C28	1.383(4)	C22	C23	1.392(5)
O3	C29	1.405(5)	C23	C24	1.383(5)
N1	C1	1.144(3)	C23	C26	1.512(5)
N2	C3	1.139(3)	C24	C25	1.391(5)
N3	C5	1.142(3)	C27	C28	1.491(5)
N4	C7	1.137(3)	C29	C30	1.498(6)

Table 5 Bond Angles for 7.

Atom	Atom	Atom	Angle/˚
N2	Ru1	N1	86.57(8)
N2	Ru1	N3	87.70(8)
N2	Ru1	N5	92.62(8)
N3	Ru1	N1	89.12(8)
N3	Ru1	N5	173.28(9)
N4	Ru1	N1	90.80(8)
N4	Ru1	N2	177.12(9)
N4	Ru1	N3	91.09(8)
N4	Ru1	N5	88.89(8)
N5	Ru1	N1	97.60(8)
C19	Ru1	N1	177.68(9)
C19	Ru1	N2	93.56(9)
C19	Ru1	N3	93.20(9)
C19	Ru1	N4	89.11(9)
C19	Ru1	N5	80.08(9)
O1	S1	C16	109.40(15)
O1	S1	C20	107.01(16)
O2	S1	O1	119.24(16)
O2	S1	C16	107.48(14)
O2	S1	C20	109.41(15)
C16	S1	C20	103.14(14)
F1	P1	F4	91.50(19)
F1	P1	F5	91.6(3)
F2	P1	F1	179.31(14)
F2	P1	F4	87.82(19)
F2	P1	F5	88.3(3)
F2	P1	F6A	85.5(3)
F3	P1	F1	87.2(3)
F3	P1	F2	92.8(3)
F3	P1	F4	89.5(3)
F3	P1	F5	175.2(4)
F4	P1	F5	85.9(3)
F6	P1	F1	87.2(2)
F6	P1	F2	93.4(2)
F6	P1	F3	89.9(4)
F6	P1	F4	178.6(3)
F6	P1	F5	94.7(4)
F3A	P1	F1	88.9(6)
F3A	P1	F2	90.5(6)
F3A	P1	F4A	89.7(8)
F3A	P1	F5A	176.3(8)
F3A	P1	F6A	93.2(8)
F4A	P1	F1	84.6(4)
F4A	P1	F2	95.0(4)
F4A	P1	F5A	91.7(7)
F4A	P1	F6A	177.1(8)
F5A	P1	F1	94.6(6)
F5A	P1	F2	85.9(6)
F5A	P1	F6A	85.5(7)
F6A	P1	F1	95.0(3)
C28	O3	C29	113.3(3)
C1	N1	Ru1	173.7(2)
C3	N2	Ru1	172.8(2)
C5	N3	Ru1	174.1(2)
C7	N4	Ru1	178.9(2)
C9	N5	Ru1	125.11(18)
C9	N5	C13	118.7(2)
C13	N5	Ru1	116.15(16)
N1	C1	C2	178.4(3)
N2	C3	C4	179.3(3)
N3	C5	C6	178.7(3)
N4	C7	C8	177.6(3)
N5	C9	C10	122.8(3)
C9	C10	C11	118.6(3)
C12	C11	C10	119.4(3)
C11	C12	C13	119.9(3)
N5	C13	C12	120.7(2)
N5	C13	C14	114.0(2)
C12	C13	C14	125.3(3)
C15	C14	C13	124.0(2)
C15	C14	C19	121.6(2)
C19	C14	C13	114.3(2)
C16	C15	C14	119.0(2)
C15	C16	S1	120.8(2)
C17	C16	S1	118.1(2)
C17	C16	C15	121.1(3)
C18	C17	C16	119.8(2)
C17	C18	C19	121.8(2)
C14	C19	Ru1	115.46(18)
C18	C19	Ru1	127.80(19)
C18	C19	C14	116.7(2)
C21	C20	S1	119.6(3)
C25	C20	S1	119.7(2)
C25	C20	C21	120.7(3)
C20	C21	C22	119.3(3)
C21	C22	C23	121.1(3)
C22	C23	C26	120.3(4)
C24	C23	C22	118.4(3)
C24	C23	C26	121.3(4)
C23	C24	C25	121.0(4)
C20	C25	C24	119.5(3)
O3	C28	C27	111.0(3)
O3	C29	C30	109.1(4)

Table 6 Torsion Angles for 7.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Ru1	N5	C9	C10	178.6(2)	C13	C14	C15	C16	177.3(2)
Ru1	N5	C13	C12	-177.71(19)	C13	C14	C19	Ru1	1.0(3)
Ru1	N5	C13	C14	0.6(3)	C13	C14	C19	C18	-177.0(2)
S1	C16	C17	C18	179.0(2)	C14	C15	C16	S1	-179.0(2)
S1	C20	C21	C22	-178.7(2)	C14	C15	C16	C17	-0.8(4)
S1	C20	C25	C24	177.9(3)	C15	C14	C19	Ru1	178.4(2)
O1	S1	C16	C15	-124.5(2)	C15	C14	C19	C18	0.4(4)
O1	S1	C16	C17	57.2(3)	C15	C16	C17	C18	0.7(4)
O1	S1	C20	C21	-1.5(3)	C16	S1	C20	C21	113.8(3)
O1	S1	C20	C25	-179.4(3)	C16	S1	C20	C25	-64.1(3)
O2	S1	C16	C15	6.3(3)	C16	C17	C18	C19	-0.1(4)
O2	S1	C16	C17	-172.0(2)	C17	C18	C19	Ru1	-178.1(2)
O2	S1	C20	C21	-132.0(2)	C17	C18	C19	C14	-0.4(4)
O2	S1	C20	C25	50.1(3)	C19	C14	C15	C16	0.2(4)
N5	C9	C10	C11	-1.2(4)	C20	S1	C16	C15	121.9(2)
N5	C13	C14	C15	-178.4(2)	C20	S1	C16	C17	-56.4(3)
N5	C13	C14	C19	-1.0(3)	C20	C21	C22	C23	1.1(5)
C9	N5	C13	C12	0.4(4)	C21	C20	C25	C24	0.0(5)
C9	N5	C13	C14	178.8(2)	C21	C22	C23	C24	-0.5(5)
C9	C10	C11	C12	0.7(4)	C21	C22	C23	C26	-178.8(3)
C10	C11	C12	C13	0.3(4)	C22	C23	C24	C25	-0.4(5)
C11	C12	C13	N5	-0.9(4)	C23	C24	C25	C20	0.6(6)
C11	C12	C13	C14	-179.1(3)	C25	C20	C21	C22	-0.8(5)
C12	C13	C14	C15	-0.1(4)	C26	C23	C24	C25	178.0(3)
C12	C13	C14	C19	177.2(2)	C28	O3	C29	C30	-175.7(3)
C13	N5	C9	C10	0.6(4)	C29	O3	C28	C27	-179.2(3)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 7.

Atom	*x*	*y*	*z*	U(eq)
H2A	-2268	-488	-198	60
H2B	-2982	-2065	62	60
H2C	-1128	-1830	-98	60
H4A	-1771	5342	522	68
H4B	-493	6573	899	68
H4C	-2338	6191	1058	68
H6A	4868	3536	765	56
H6B	5328	1774	805	56
H6C	5746	3098	1300	56
H8A	1811	-3820	1999	72
H8B	653	-3736	2486	72
H8C	2487	-2849	2554	72
H9	-3642	-160	1597	37

H10	-5879	-423	2115	48
H11	-5601	731	3000	49
H12	-3105	2160	3331	43
H15	-610	3491	3575	41
H17	4002	4590	3128	40
H18	3251	3331	2287	34
H21	5813	5955	4271	53
H22	7936	4567	4523	62
H24	4753	543	4518	77
H25	2612	1941	4286	69
H26A	8080	1624	5103	118
H26B	8954	1997	4570	118
H26C	7698	402	4580	118
H27A	6867	6836	2123	89
H27B	5694	5305	2268	89
H27C	7613	5251	2248	89
H28A	6128	7161	3009	73
H28B	6945	5610	3131	73
H29A	8848	7139	3781	89
H29B	7895	8624	3678	89
H30A	11264	8549	3522	124
H30B	10577	9557	4005	124
H30C	10317	10026	3411	124

Table 8 Atomic Occupancy for 7.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
F3	0.65	F4	0.65	F5	0.65
F6	0.65	F3A	0.35	F4A	0.35
F5A	0.35	F6A	0.35		

Experimental

Single crystals of $C_{30}H_{36}F_6N_5O_3PRuS$ **7**. A suitable crystal was selected and **[]** on a **95mm CCD camera on \k-goniostat** diffractometer. The crystal was kept at 150.15 K during data collection. Using Olex2 [1], the structure was solved with the olex2.solve [2] structure solution program using Charge Flipping and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Bourhis, L.J., Dolomanov, O.V., Gildea, R.J., Howard, J.A.K., Puschmann, H. (2015). Acta Cryst. A71, 59-75.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of 7

Crystal Data for $C_{30}H_{36}F_6N_5O_3PRuS$ (M =792.74 g/mol): triclinic, space group P-1 (no. 2), a = 8.28700(10) Å, b = 8.48600(10) Å, c = 25.3050(5) Å, α = 95.0620(10)°, β = 92.8540(10)°, γ = 97.4490(10)°, V = 1754.25(5) Å^3, Z = 2, T = 150.15 K, μ(MoKα) = 0.622 mm^{-1}, $Dcalc$ = 1.501 g/cm^3, 29703 reflections measured (7.162° ≤ 2Θ ≤ 55.304°), 7976 unique (R_{int} = 0.0668, R_{sigma} = 0.0727) which were used in all calculations. The final R_1 was 0.0439 (I > 2σ(I)) and wR_2 was 0.0883 (all data).

Refinement model description

Number of restraints - 69, number of constraints - unknown.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups
 At 1.5 times of:
  All C(H,H,H) groups
2. Restrained distances
 P1-F1 ≈ P1-F2 ≈ P1-F3A ≈ P1-F4A ≈ P1-F5A ≈ P1-F6A ≈
P1-F3 ≈ P1-F4 ≈ P1-F5 ~
 P1-F6
 with sigma of 0.02
3. Uiso/Uaniso restraints and constraints
Uanis(F3A) ≈ Ueq, Uanis(F4A) ≈ Ueq, Uanis(F5A) ≈ Ueq, Uanis(F6A)
≈ Ueq: with sigma of 0.01 and sigma for terminal atoms of 0.02
4. Others
 Fixed Sof: F3(0.65) F4(0.65) F5(0.65) F6(0.65) F3A(0.35) F4A(0.35) F5A(0.35)
 F6A(0.35)
5.a Secondary CH2 refined with riding coordinates:
 C28(H28A,H28B), C29(H29A,H29B)
5.b Aromatic/amide H refined with riding coordinates:
 C9(H9), C10(H10), C11(H11), C12(H12), C15(H15), C17(H17), C18(H18), C21(H21),
 C22(H22), C24(H24), C25(H25)
5.c Idealised Me refined as rotating group:
 C2(H2A,H2B,H2C), C4(H4A,H4B,H4C), C6(H6A,H6B,H6C), C8(H8A,H8B,H8C), C26(H26A,
 H26B,H26C), C27(H27A,H27B,H27C), C30(H30A,H30B,H30C)
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