Electronic Supplementary Material (ESI) for RSC Advances.

SUPPORTING INFORMATION

Ruthenium hydroxycyclopentadienyl *N*-heterocyclic carbene complexes as transfer hydrogenation catalysts

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SUMMARY

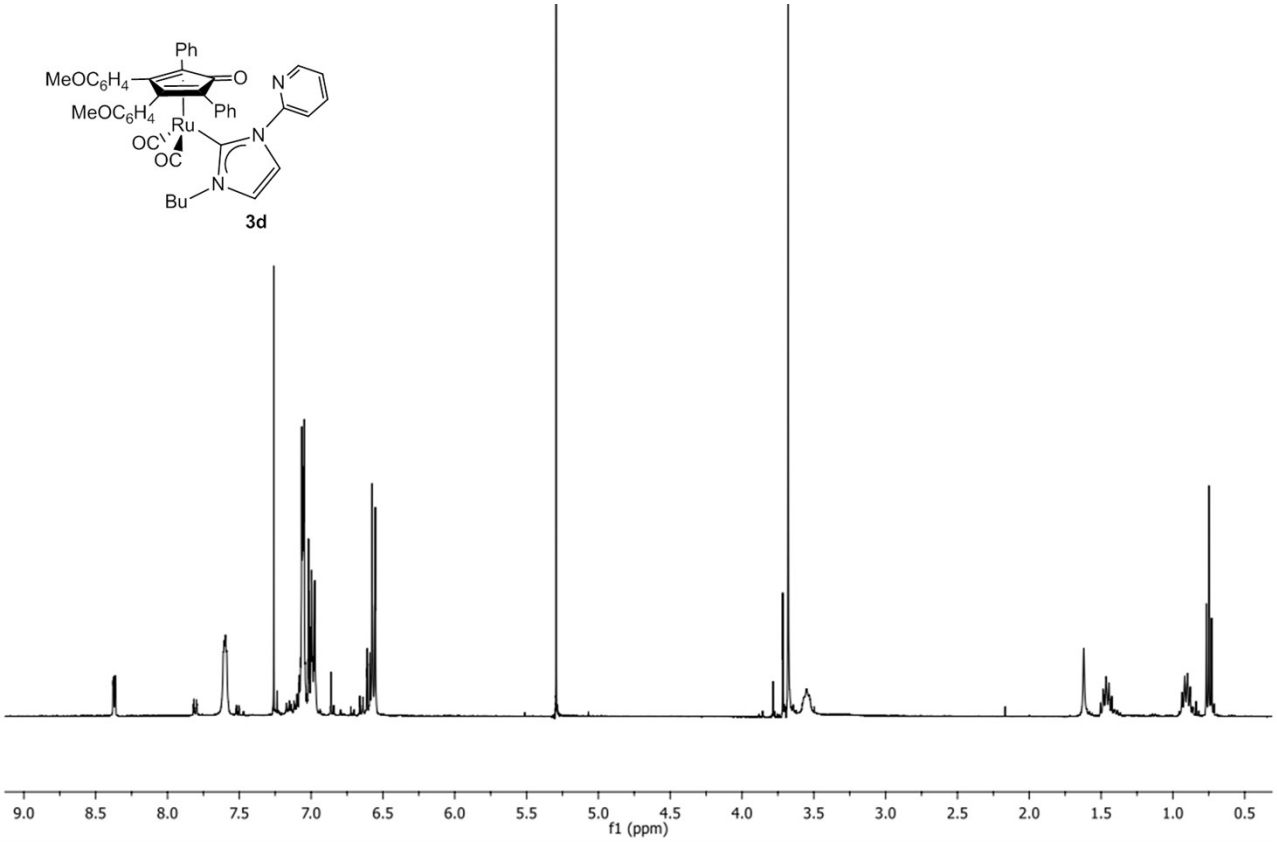


Figure S1. ^{1}H-NMR spectrum of **3d** in $CDCl_3$.

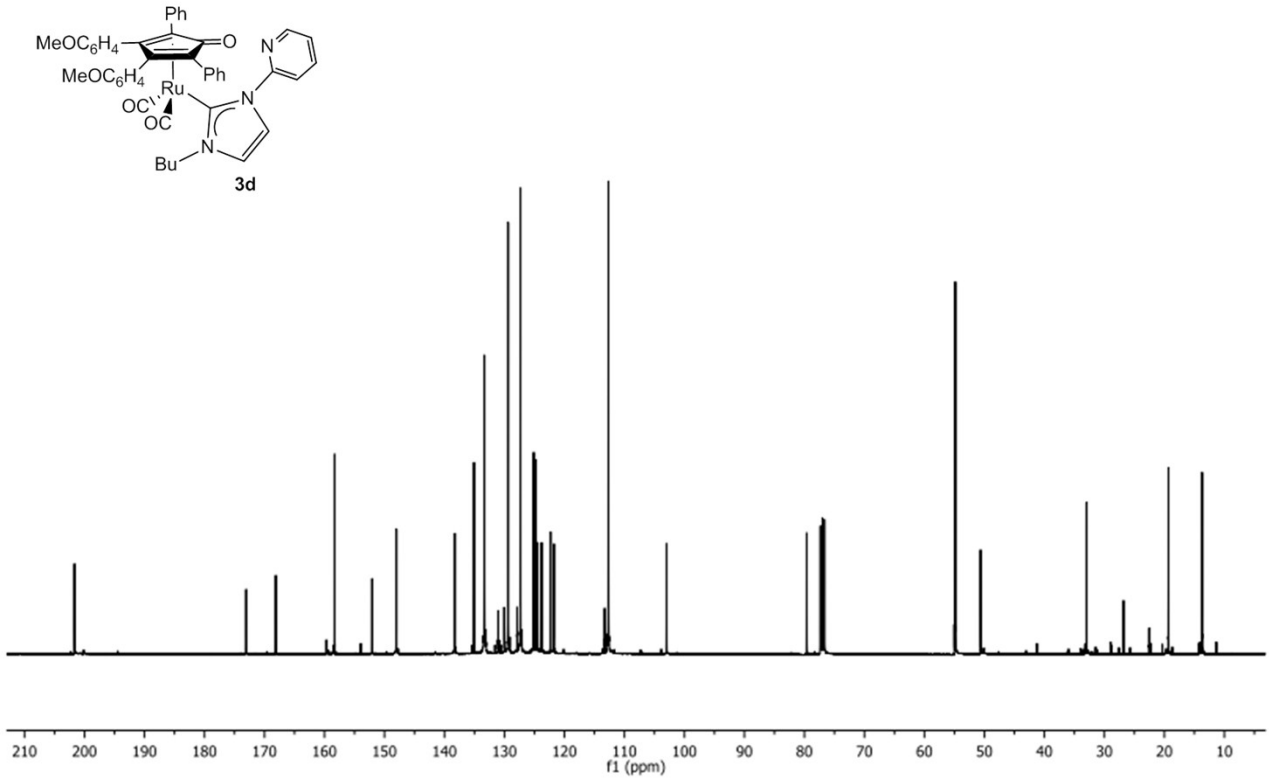


Figure S2. ^{13}C-NMR spectrum of **3d** in $CDCl_3$.

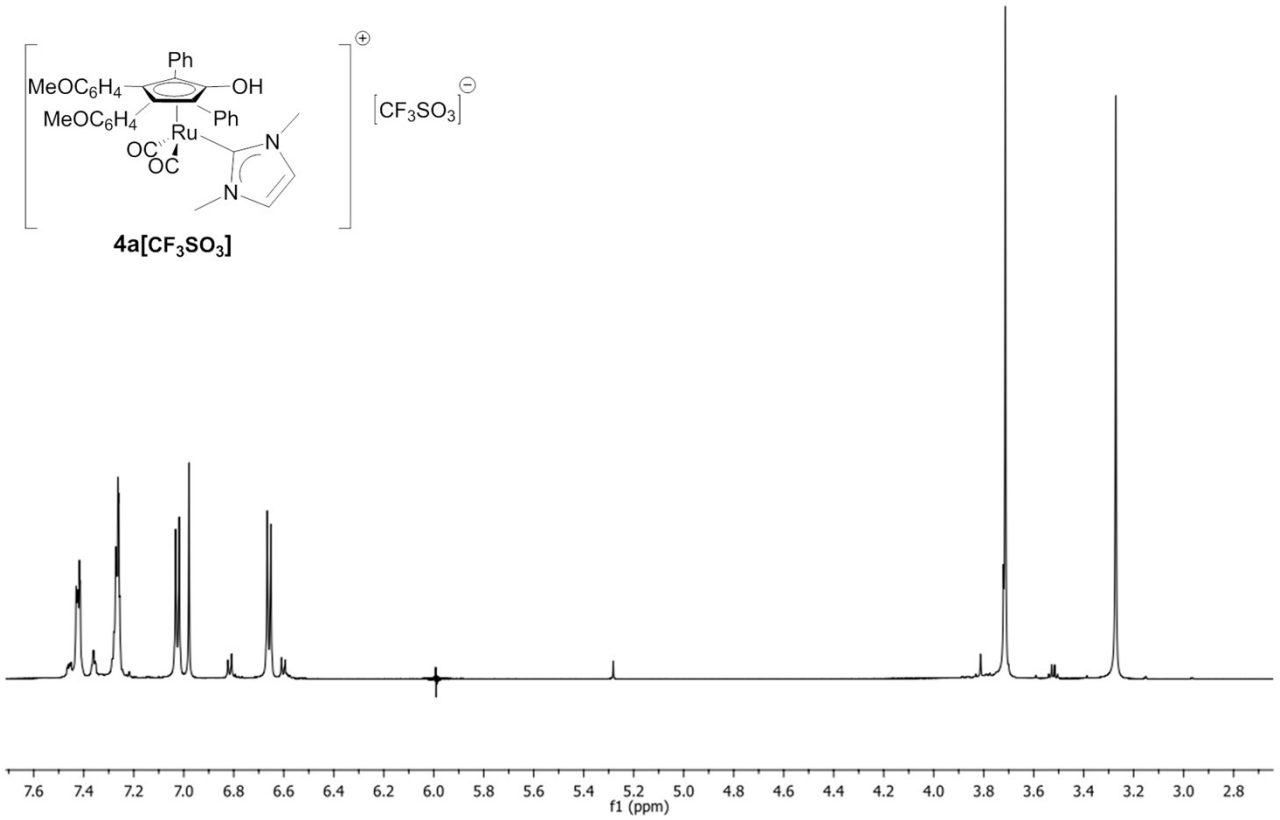


Figure S3. ^{1}H-NMR spectrum of **4a[CF_3SO_3]** in $CDCl_3$.

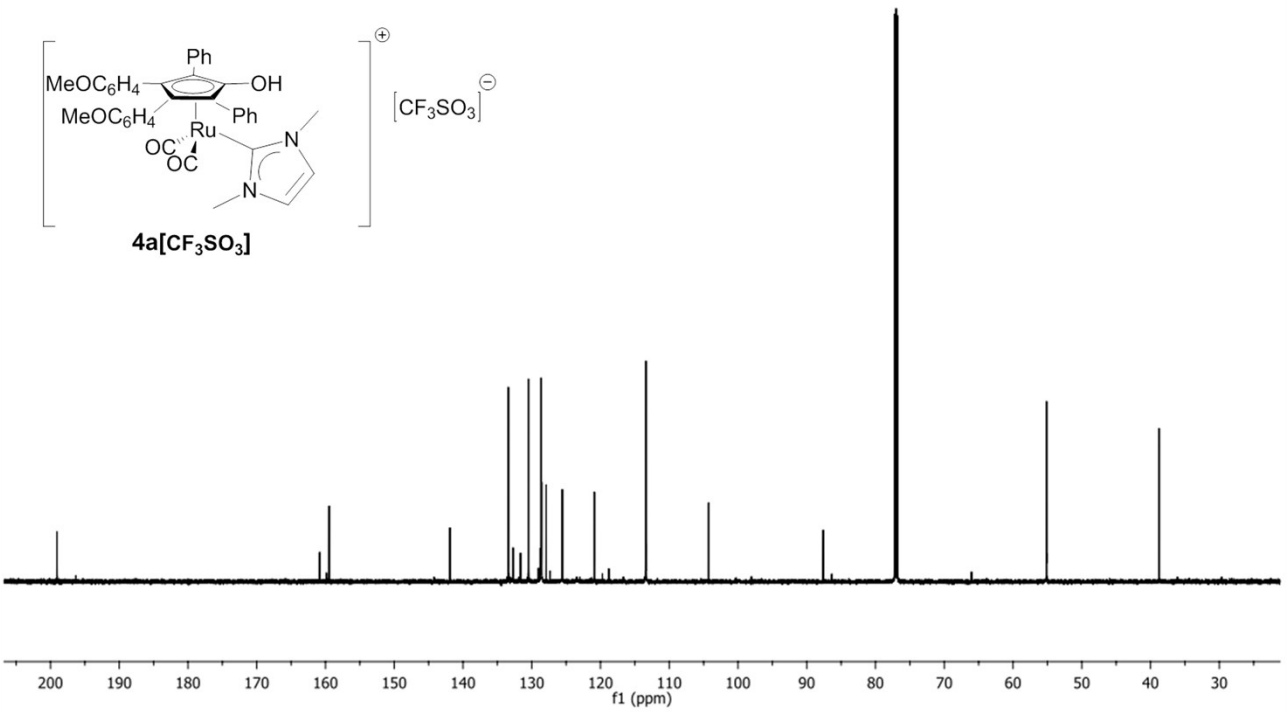


Figure S4. ^{13}C-NMR spectrum of **4a[CF_3SO_3]** in $CDCl_3$.

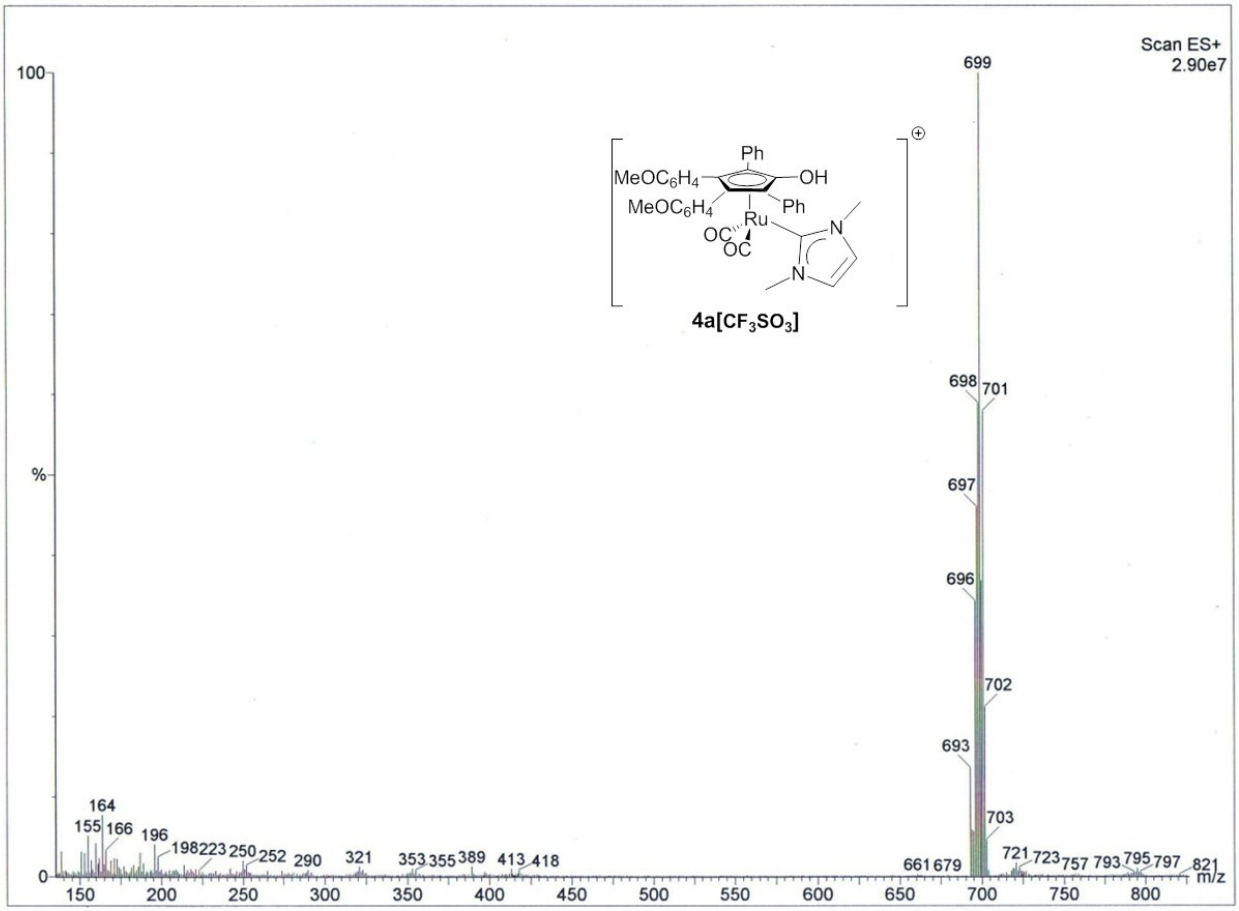


Figure S5. ESI-MS spectrum of **4a[CF_3SO_3]** in $CDCl_3$.

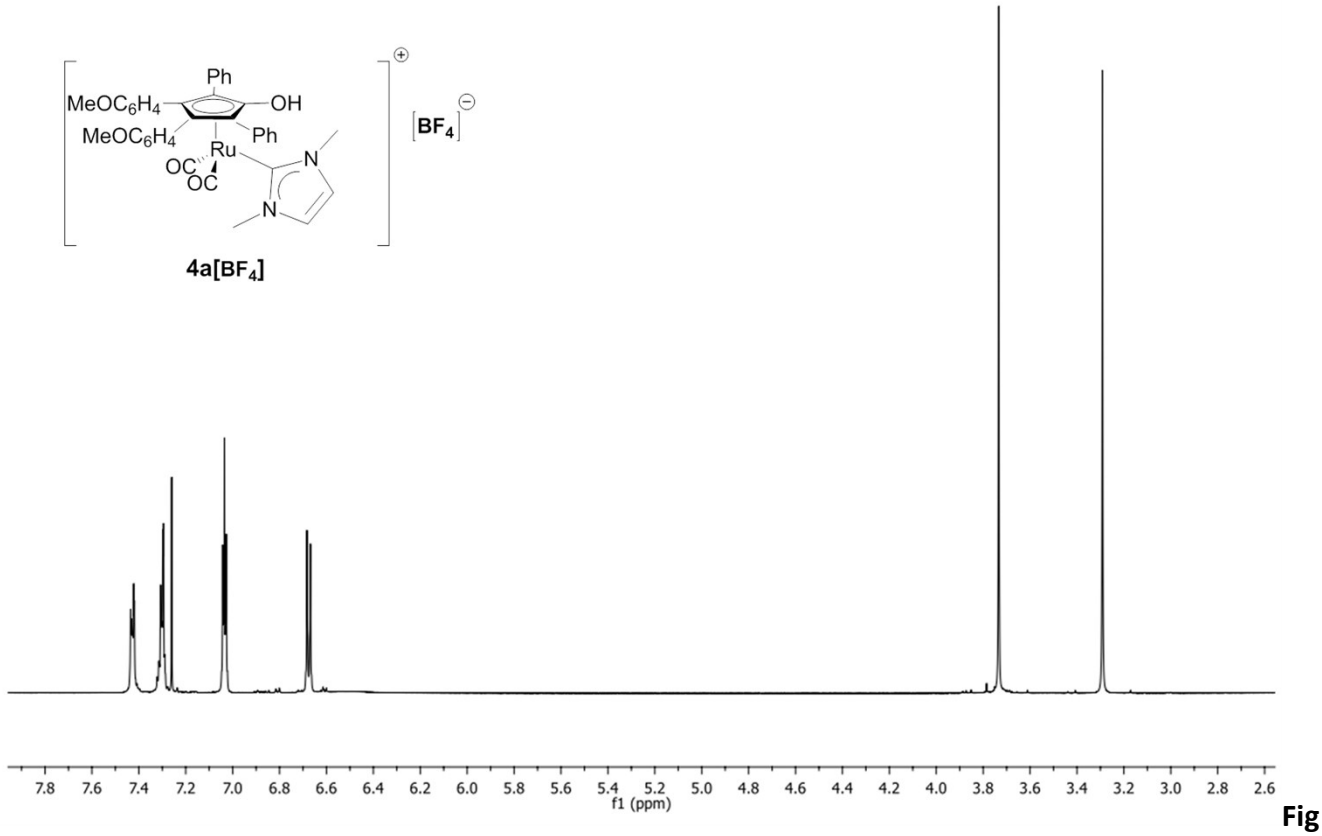


Figure S6. ^{1}H-NMR spectrum of **4a[BF_4]** in $CDCl_3$.

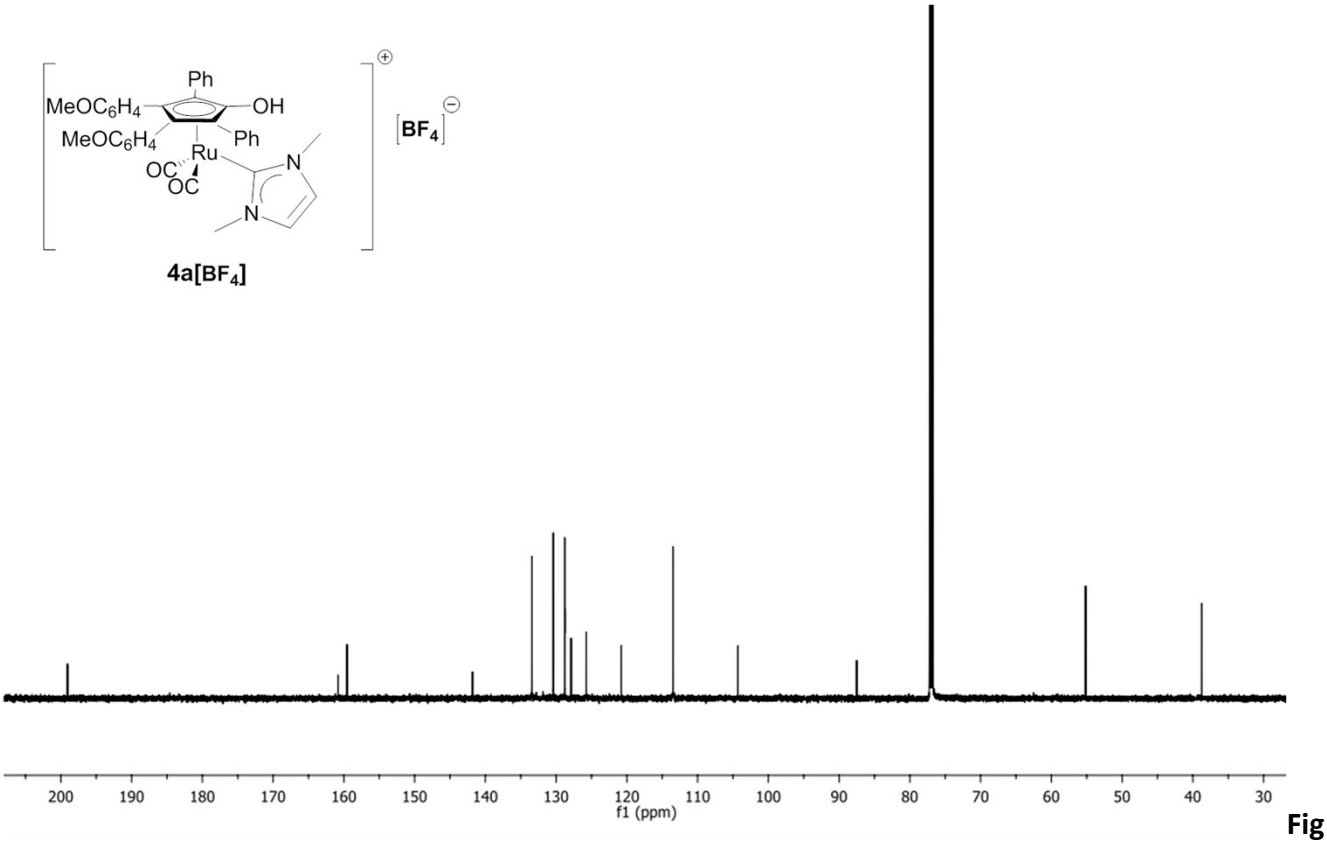


Figure S7. ^{13}C-NMR spectrum of **4a[BF_4]** in $CDCl_3$.

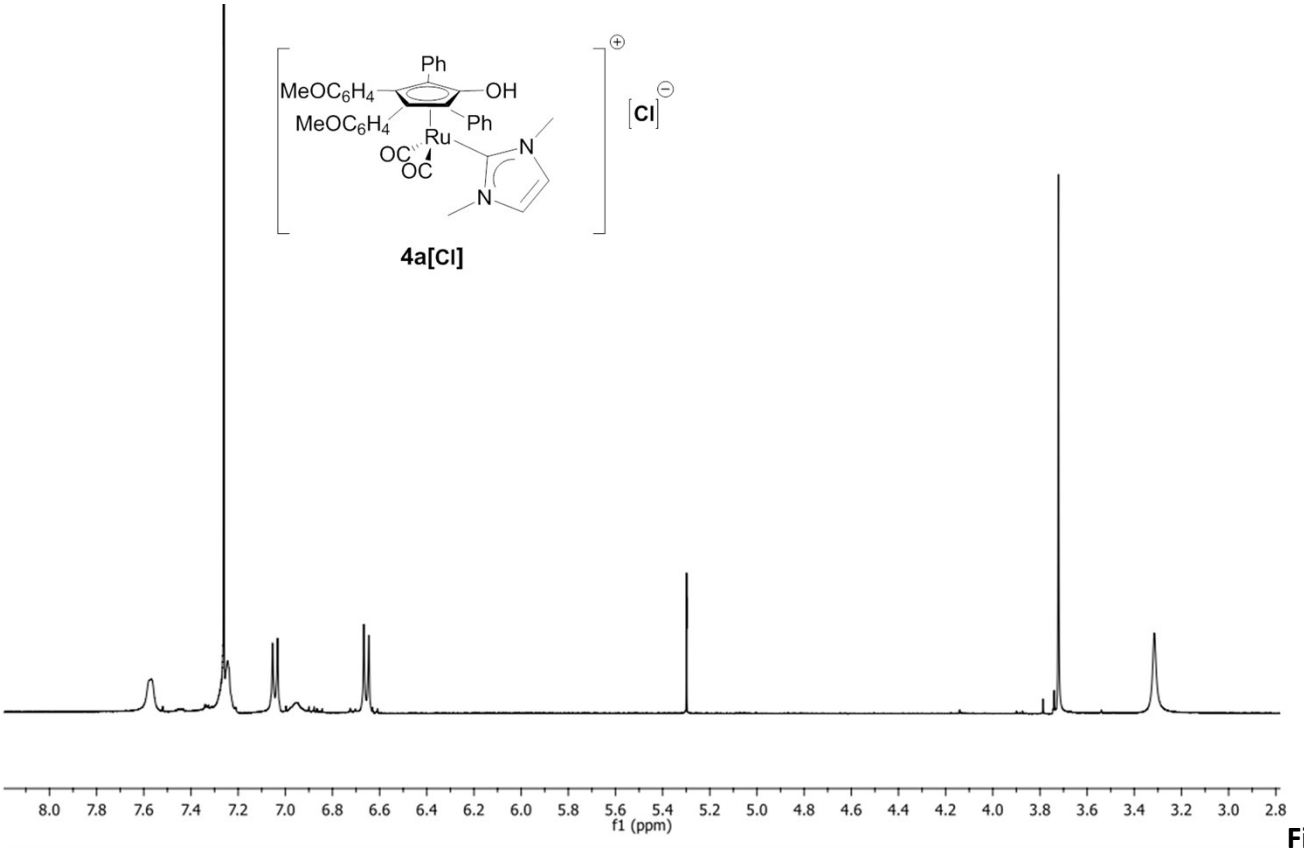


Figure S8. ^{1}H-NMR spectrum of **4a[Cl]** in $CDCl_3$.

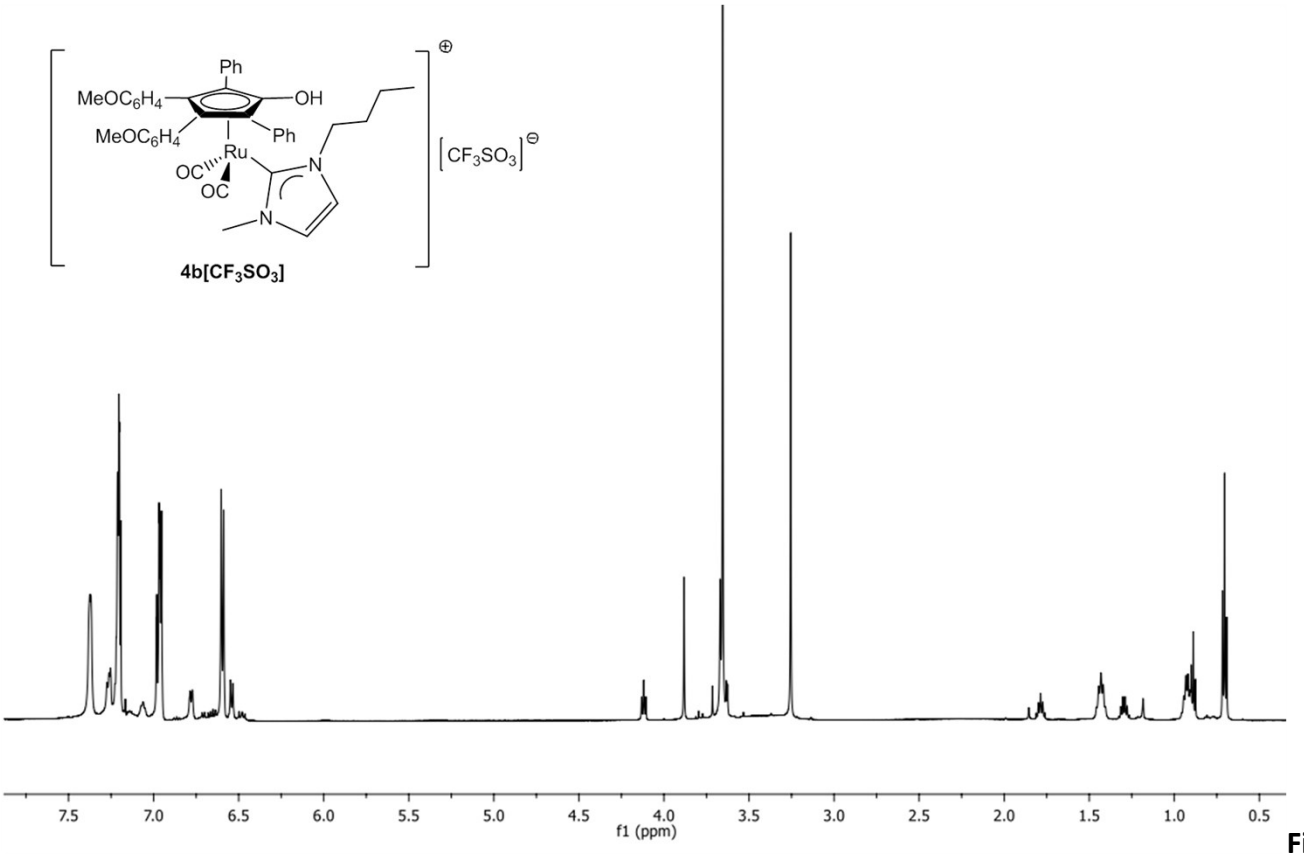


Figure S9. ^{1}H-NMR spectrum of **4b[CF_3SO_3]** in $CDCl_3$.

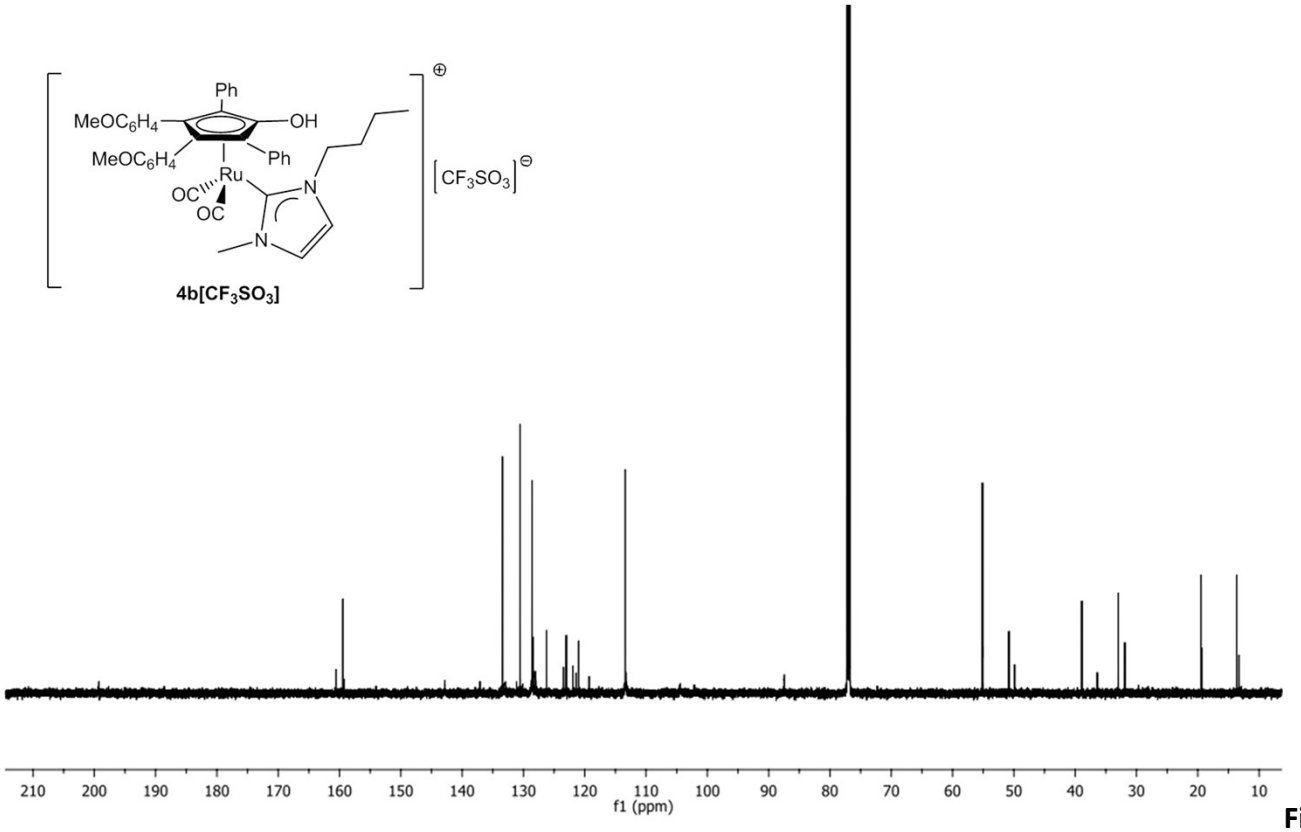


Figure S10. ^{13}C-NMR spectrum of **4b[CF_3SO_3]** in $CDCl_3$.

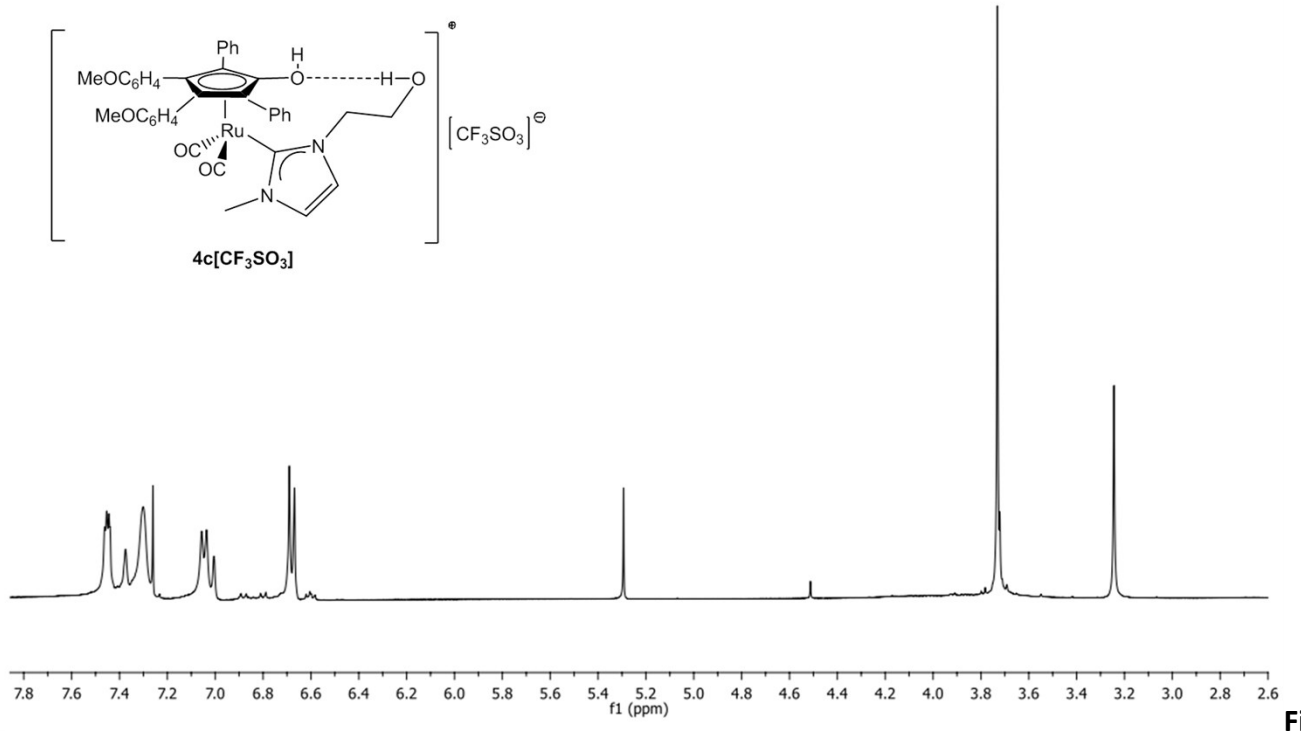


Figure S11. ^{1}H-NMR spectrum of **4c[CF_3SO_3]** in $CDCl_3$.

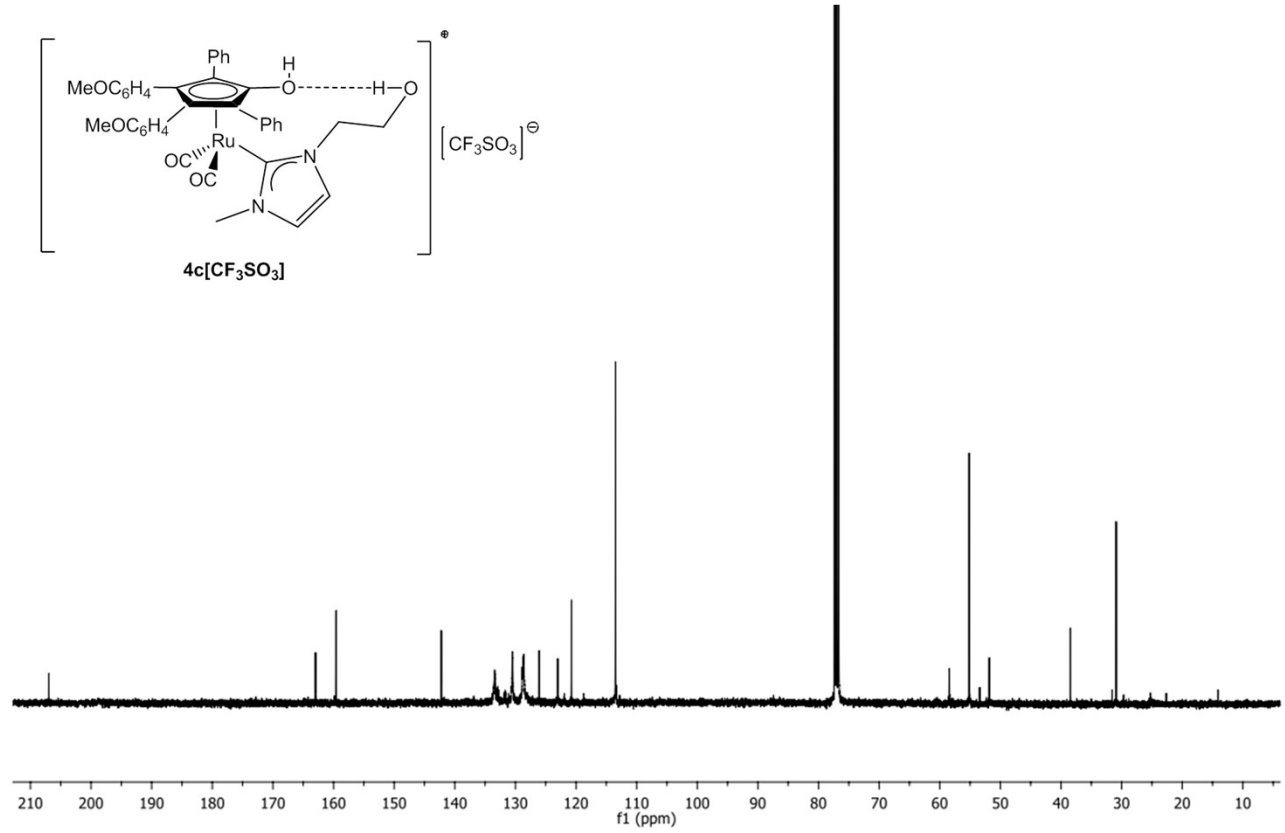


Figure S12. ^{13}C-NMR spectrum of **4c[CF_3SO_3]** in $CDCl_3$.

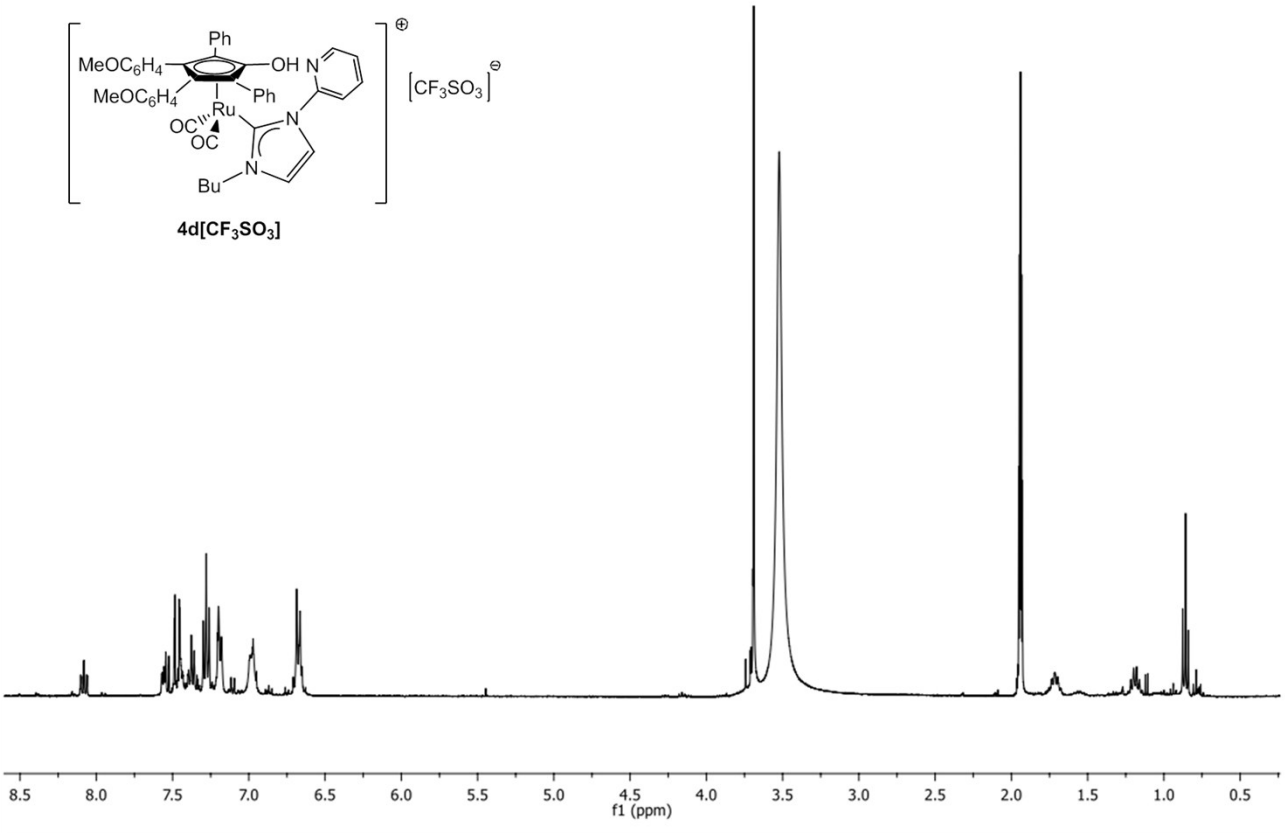


Figure S13. ^{1}H-NMR spectrum of **4d[CF_3SO_3]** in CD_3CN.

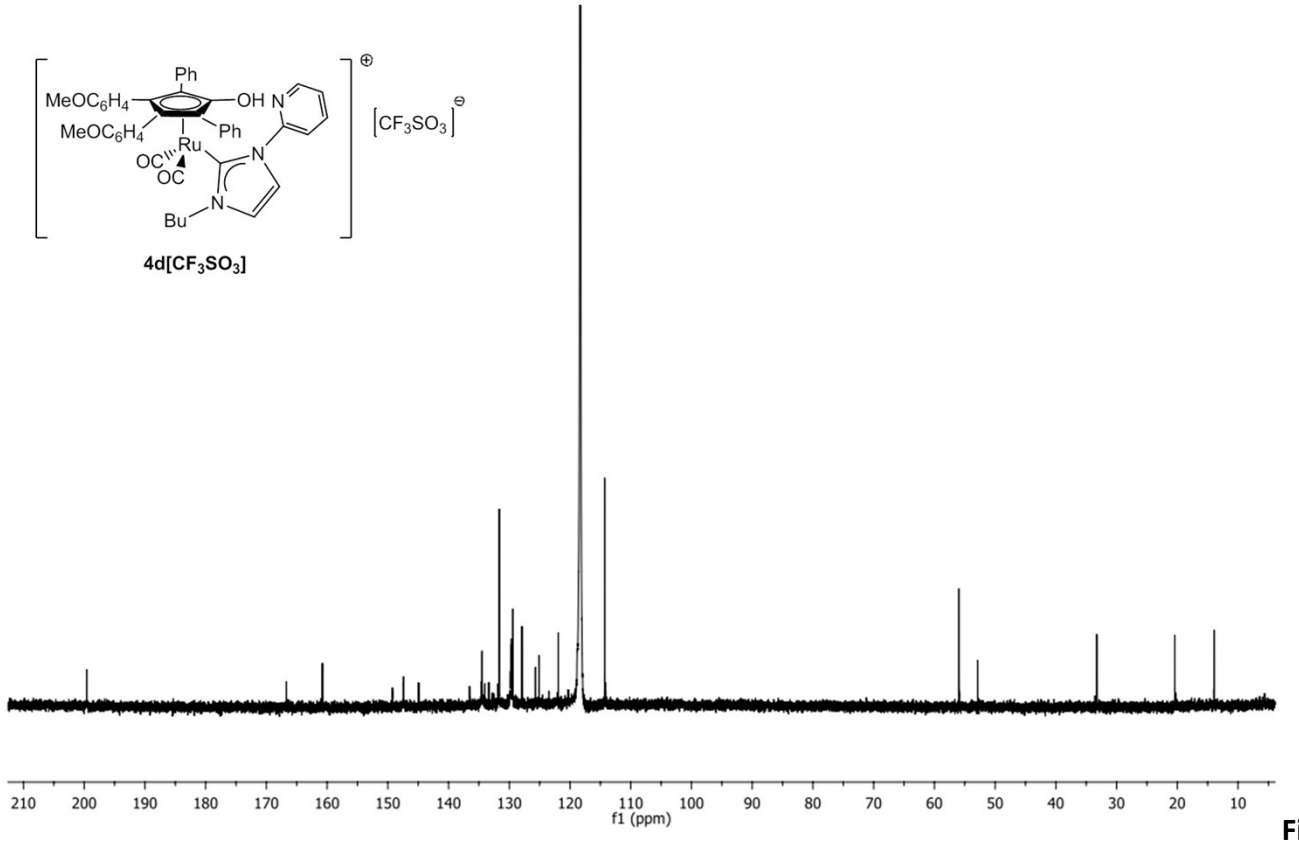


Figure S14. ^{13}C-NMR spectrum of **4d[CF_3SO_3]** in CD_3CN.

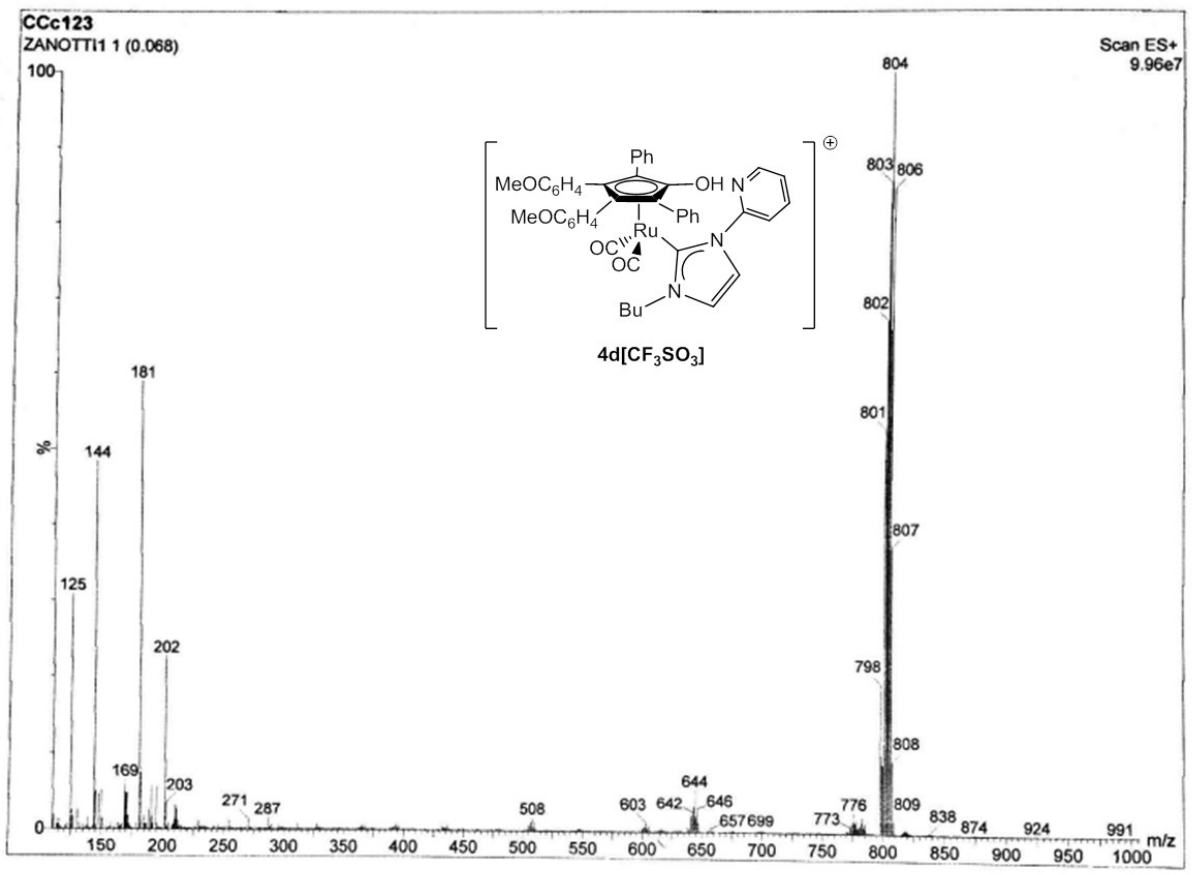


Figure S15. ESI-MS spectrum of **4d[CF_3SO_3]** in CH_3CN.

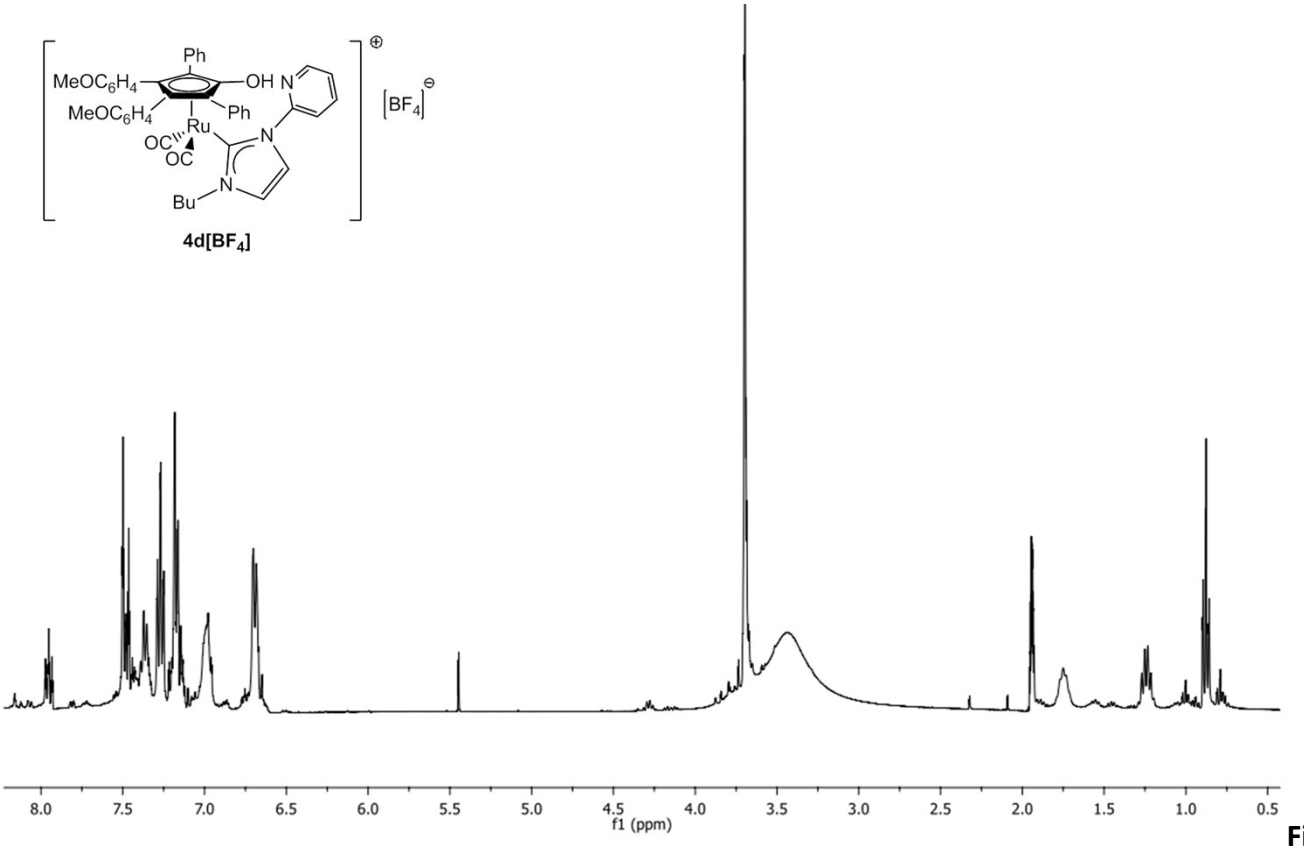


Figure S16. ^{1}H-NMR spectrum of **4d[BF_4]** in CD_3CN.

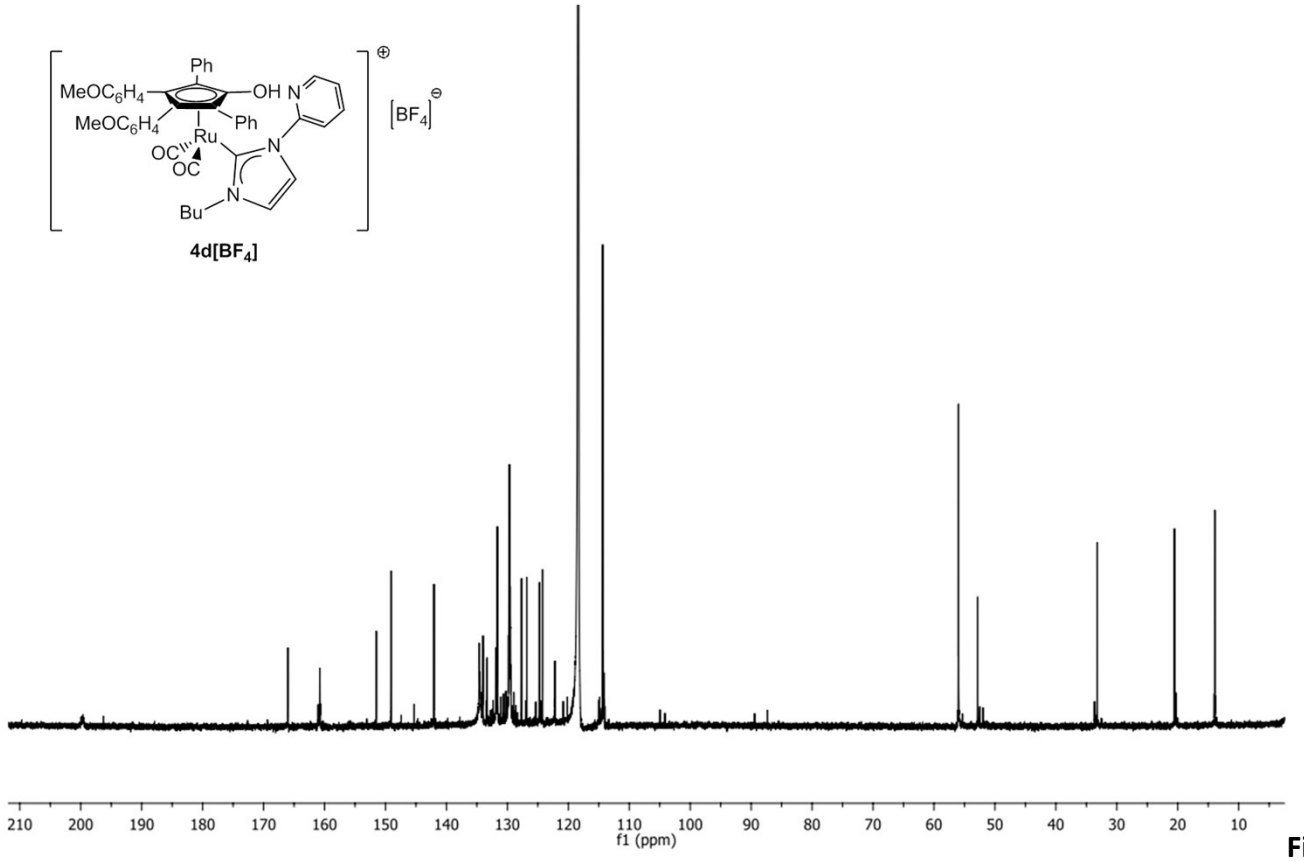


Figure S17. ^{13}C-NMR spectrum of **4d[BF_4]** in CD_3CN.

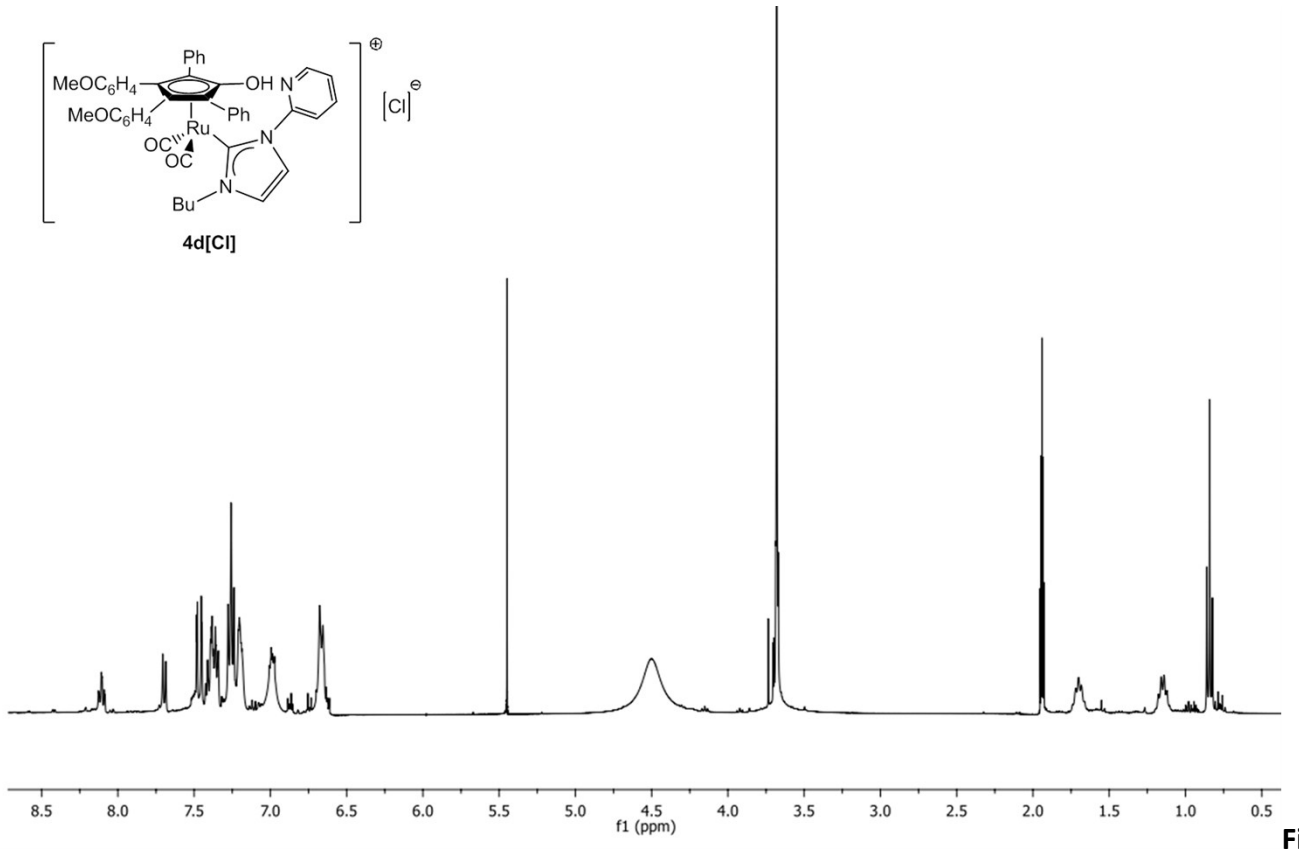


Figure S18. ^{1}H-NMR spectrum of **4d[Cl]** in CD_3CN.

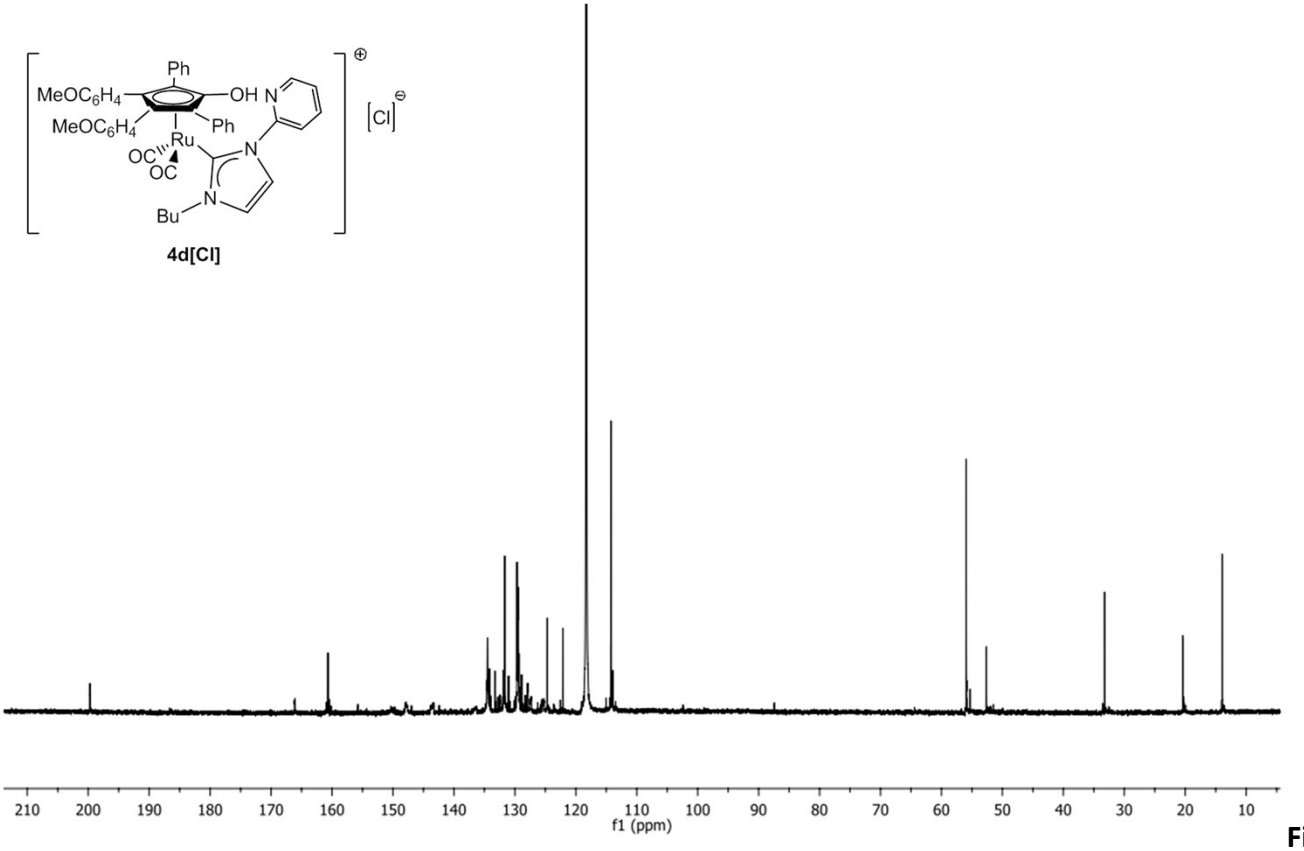


Figure S19. ^{13}C-NMR spectrum of **4d[Cl]** in CD_3CN.

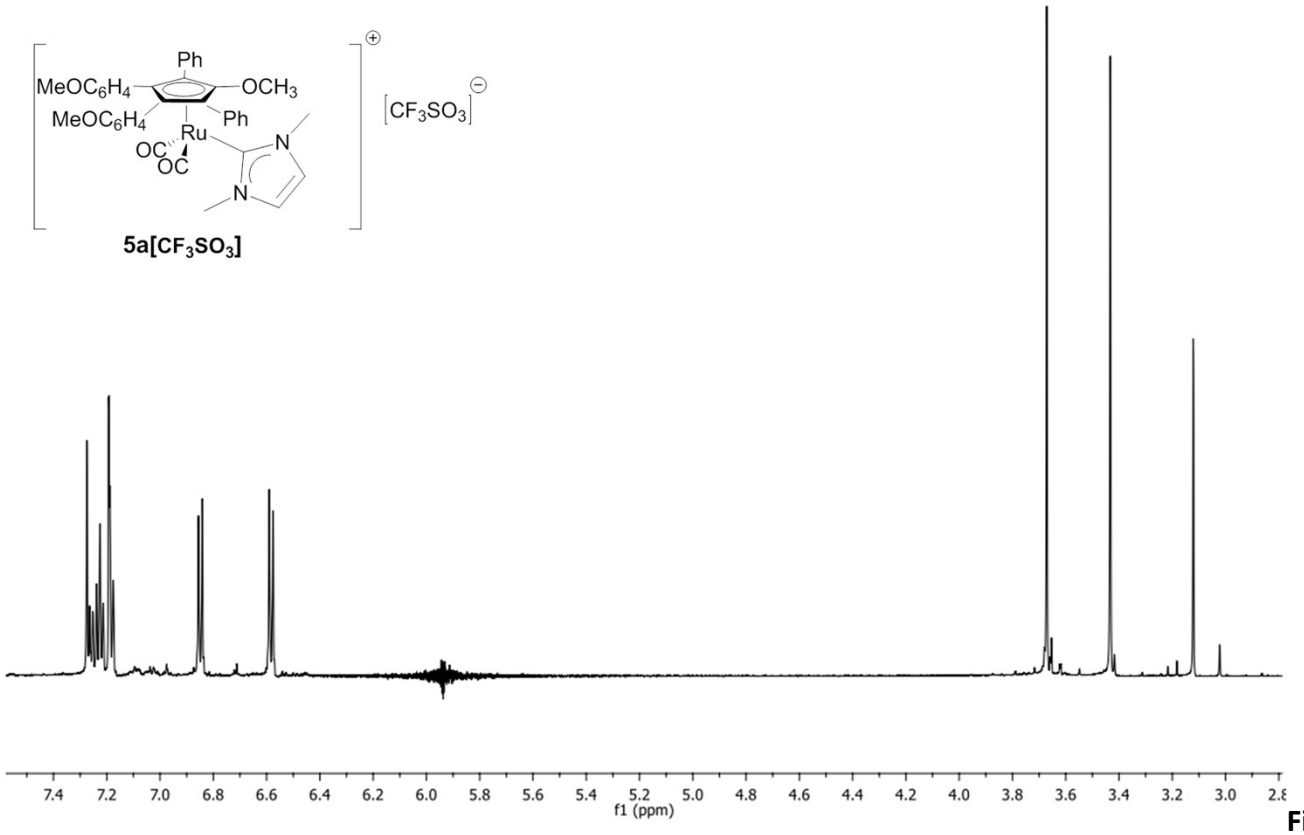


Figure S20. ^{1}H-NMR spectrum of **5a[CF_3SO_3]** in $CDCl_3$.

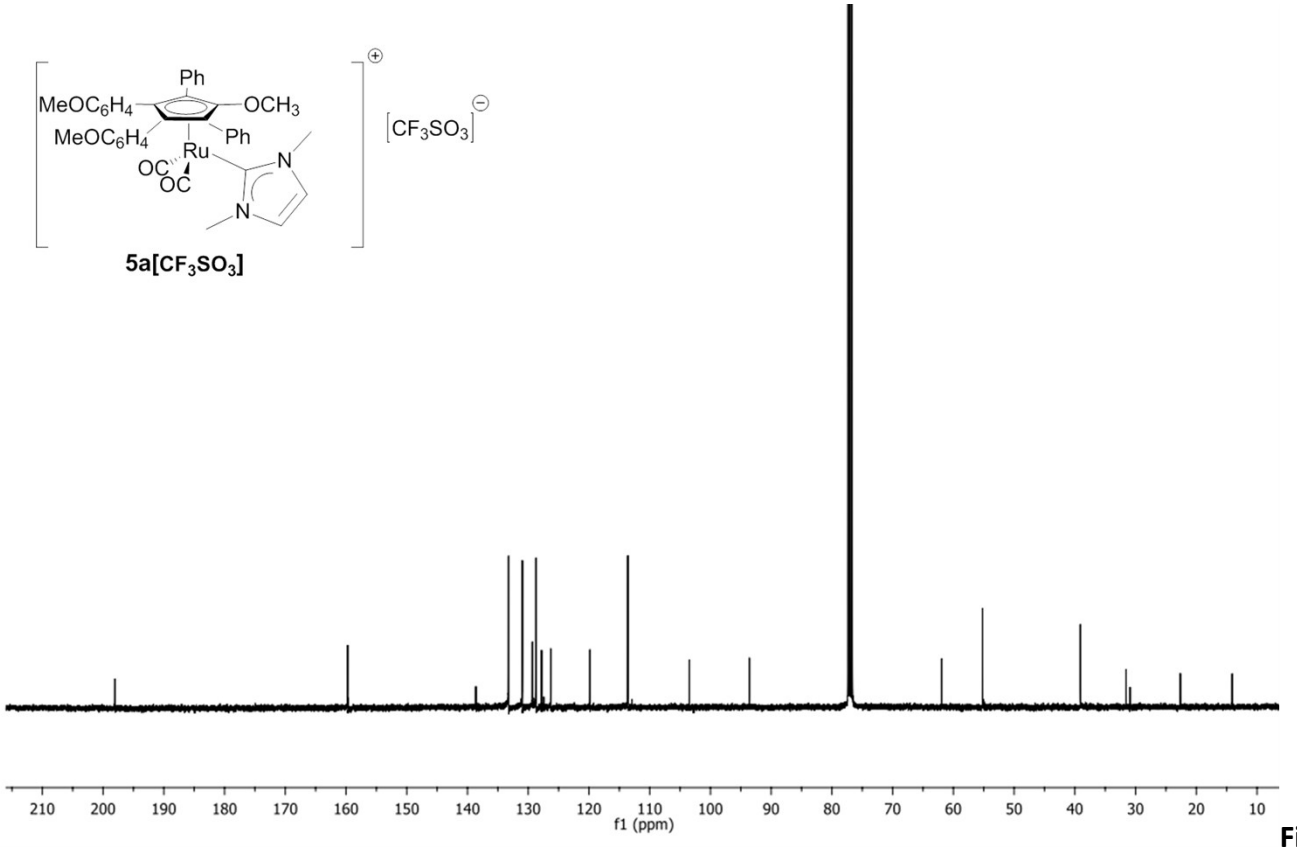


Figure S21. ^{13}C-NMR spectrum of **5a[CF_3SO_3]** in $CDCl_3$.

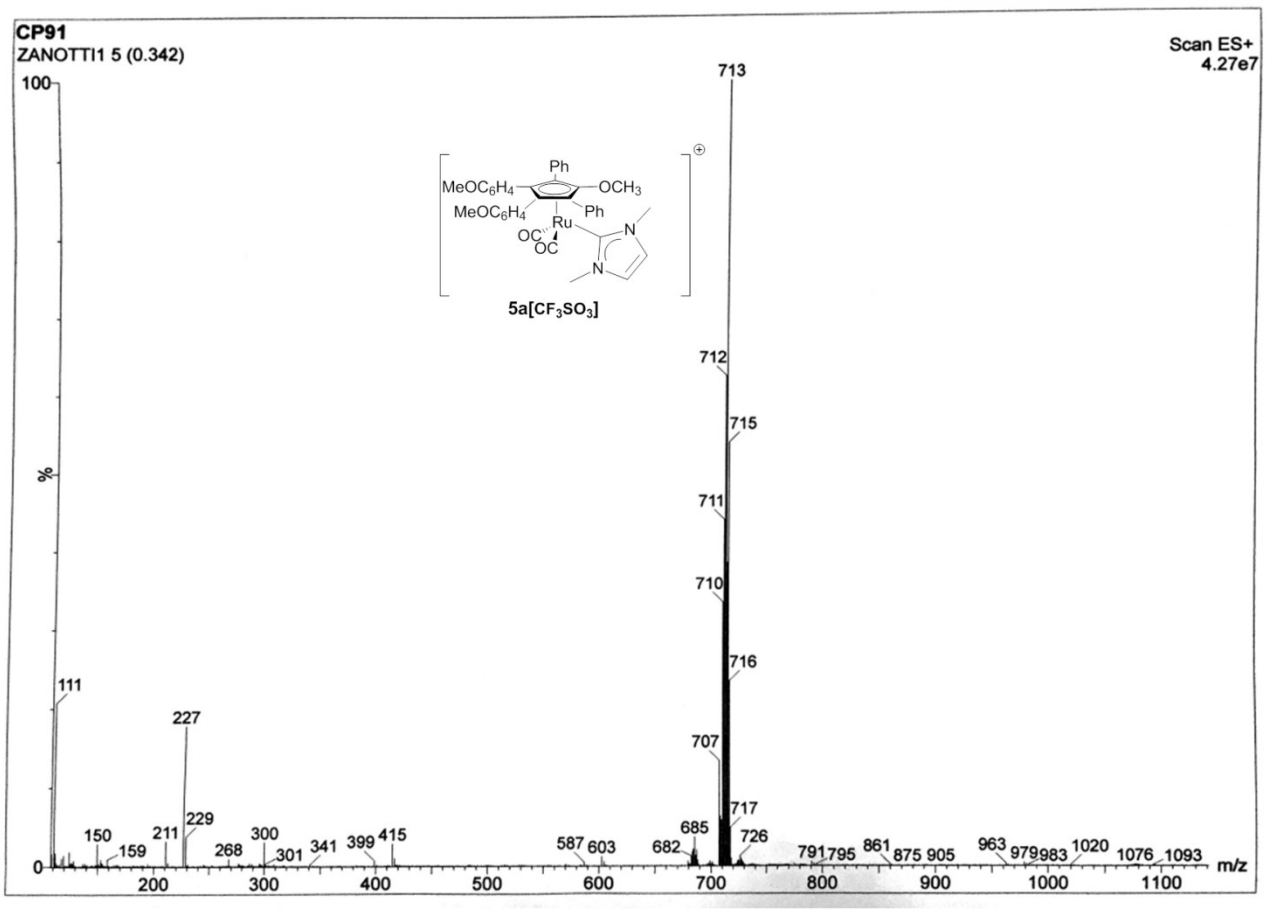


Figure S22. ESI-MS spectrum of **5a[CF_3SO_3]** in CH_3CN.

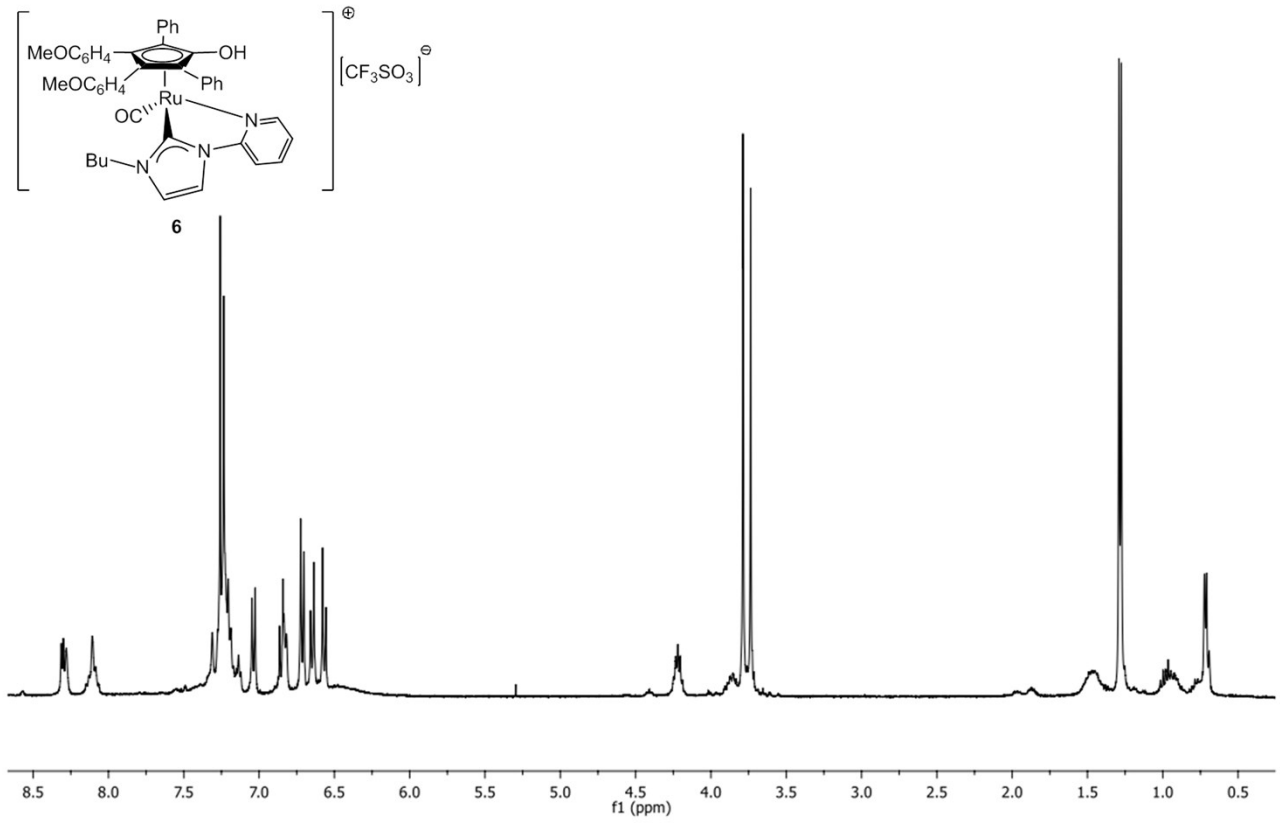


Figure S23. ^{1}H-NMR spectrum of **6** in $CDCl_3$.

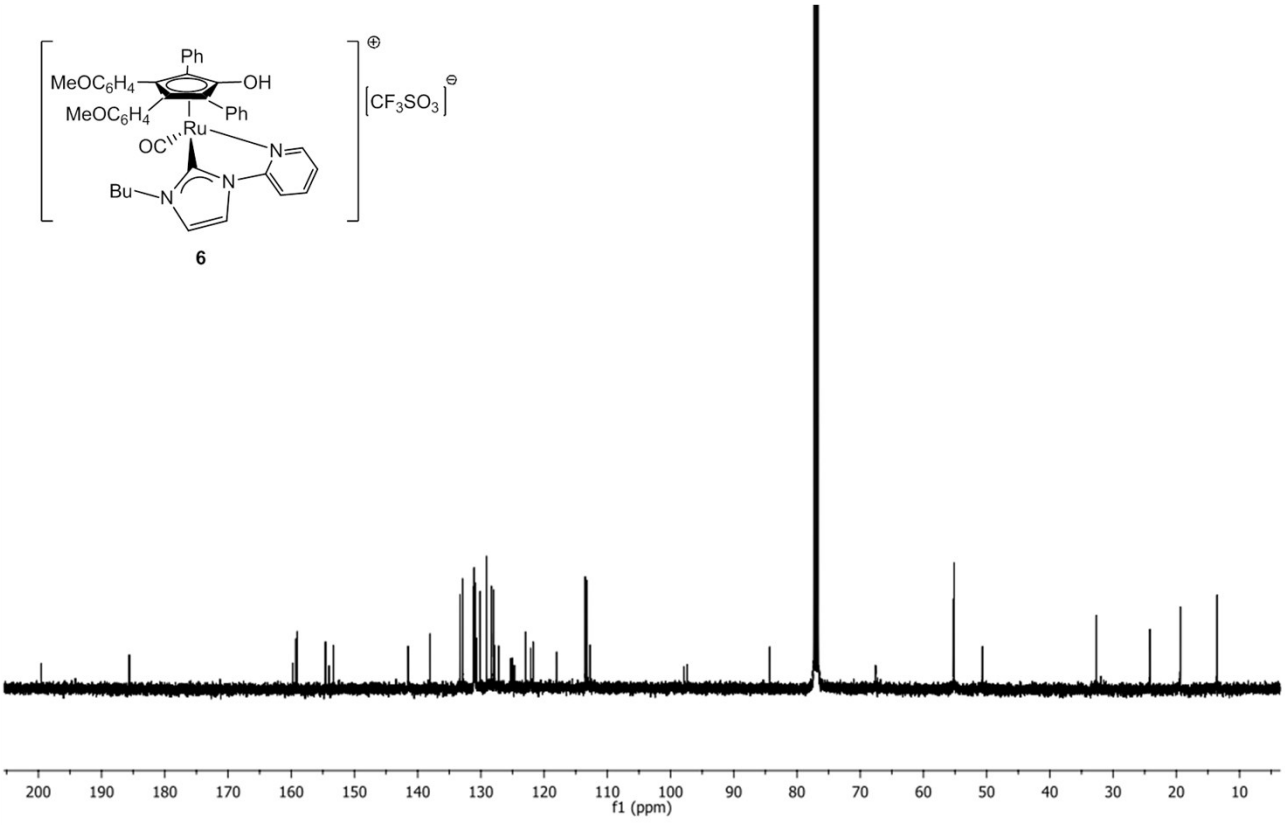


Figure S24. ^{13}C-NMR spectrum of **6** in $CDCl_3$.

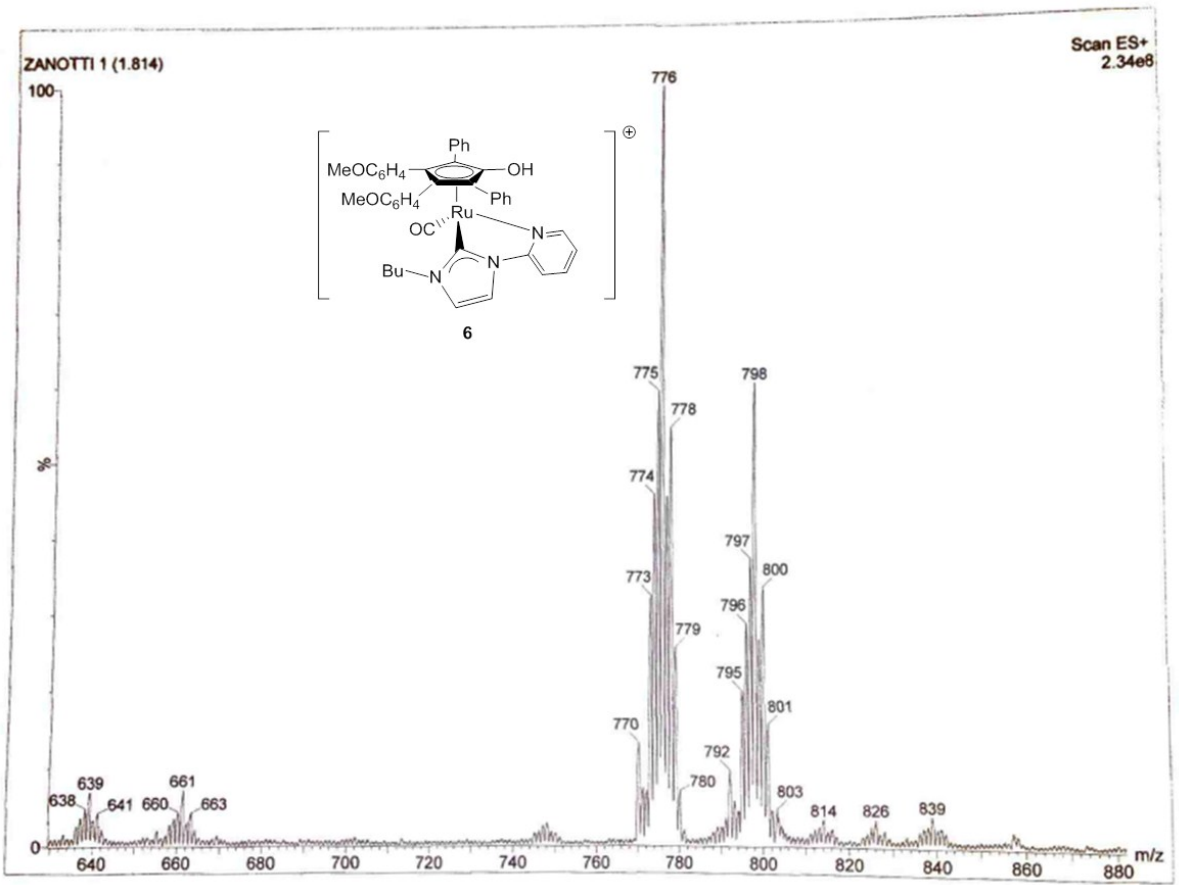


Figure S25. ESI-MS spectrum of **6** in CH_3CN.

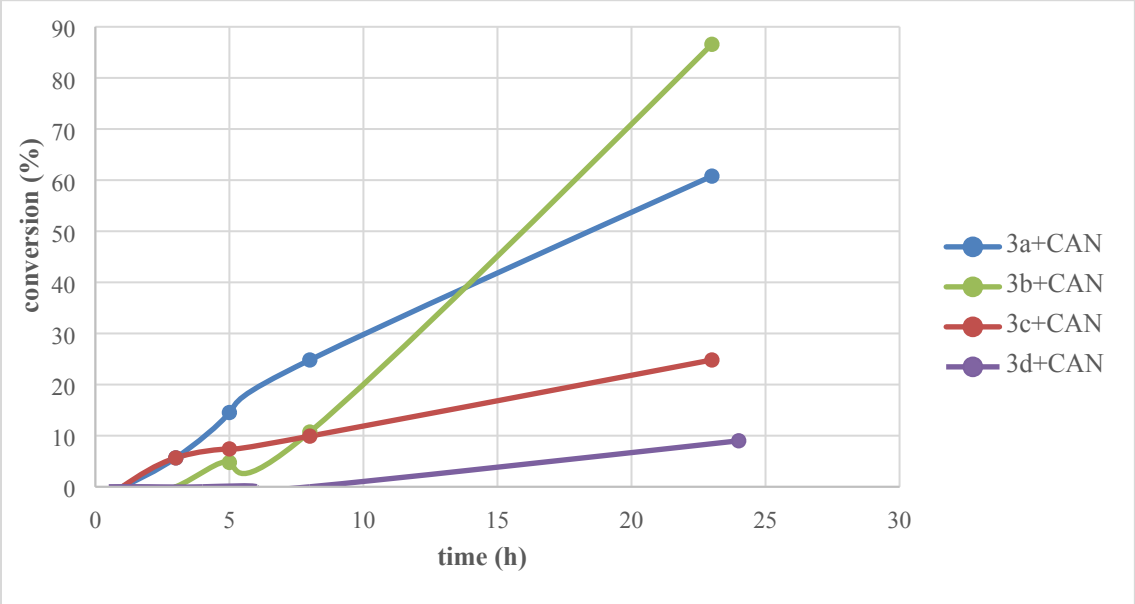
Table S1

Crystal data and experimental details for ***3d·0.5CH_2Cl_2, [4a][CF_3SO_3]·0.5toluene, [4c][CF_3SO_3]·$CHCl_3$*** *and* ***[6d][CF_3SO_3]****.*

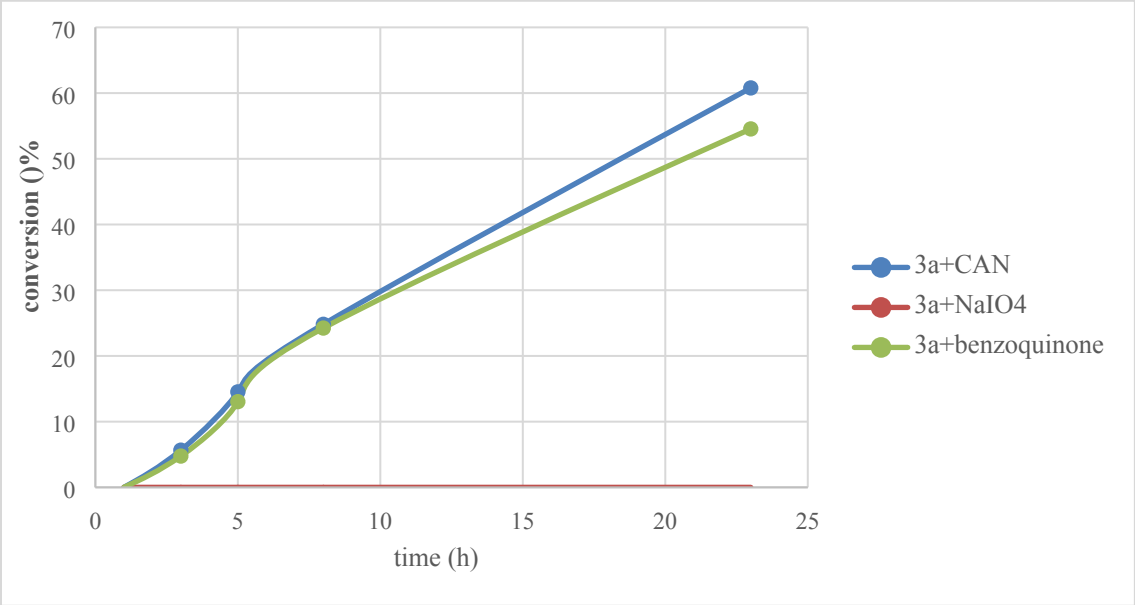
	3d·0.5CH_2Cl_2	**[4a][CF_3SO_3]·0.5toluene**
Formula	$C_{45.5}H_{40}ClN_3O_5Ru$	$C_{42.5}H_{37}F_3N_2O_8RuS$
Fw	845.33	893.87
T, K	293(2)	294(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	$P2_1/n$
a, Å	34.655(3)	24.1374(17)
b, Å	10.7672(8)	14.9455(10)
c, Å	23.2262(18)	24.6819(17)
α, °	90	90
β, °	100.455(8)	114.6170(10)
γ, °	90	90
Cell Volume, $Å^3$	8522.6(12)	8094.6(10)
Z	8	8
D_c, g cm^{-3}	1.318	1.467
μ, mm^{-1}	0.478	0.508
F(000)	3480	3656
Crystal size, mm	0.18×0.16×0.13	0.19×0.16×0.12
θ limits, °	1.78–25.03	1.54–25.03
Reflections collected	53344	76067
Independent reflections	7457 [R_{int}= 0.1264]	14300 [R_{int}= 0.1315]
Data / restraints /parameters	7457 / 363 / 435	14300/ 513 / 1042
Goodness on fit on F^2	1.049	1.004
R_1 (I> 2σ(I))	0.1302	0.0621
wR_2 (all data)	0.3601	0.1331
Largest diff. peak and hole, e $Å^{-3}$	3.643 / –2.129	1.007 / –0.721

	[4c][CF_3SO_3]·$CHCl_3$	**[6d][CF_3SO_3]**
Formula	$C_{41}H_{36}Cl_3F_3N_2O_9RuS$	$C_{45}H_{40}F_3N_3O_7RuS$
Fw	997.20	924.93
T, K	100(2)	100(2)
λ, Å	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	12.0563(6)	12.0040(4)
b, Å	20.5906(11)	35.1188(12)
c, Å	35.1658(19)	10.2256(4)
α, °	90	90
β, °	95.724(3)	95.344(2)
γ, °	90	90
Cell Volume, $Å^3$	8686.3(8)	4292.0(3)
Z	8	4
D_c, g cm^{-3}	1.525	1.431
μ, mm^{-1}	0.662	0.480
F(000)	4048	1896
Crystal size, mm	0.19×0.16×0.12	0.19×0.16×0.12
θ limits, °	1.53–26.00	1.16–28.27
Reflections collected	126772	76597
Independent reflections	17081 [R_{int}= 0.0741]	10513 [R_{int}= 0.0719]
Data / restraints /parameters	17081 / 144 / 1095	10513/ 967 / 644
Goodness on fit on F^2	1.139	1.129
R_1 (I> 2σ(I))	0.0883	0.1087
wR_2 (all data)	0.2451	0.2626
Largest diff. peak and hole, e $Å^{-3}$	2.741 / –1.475	0.862 / –1.227

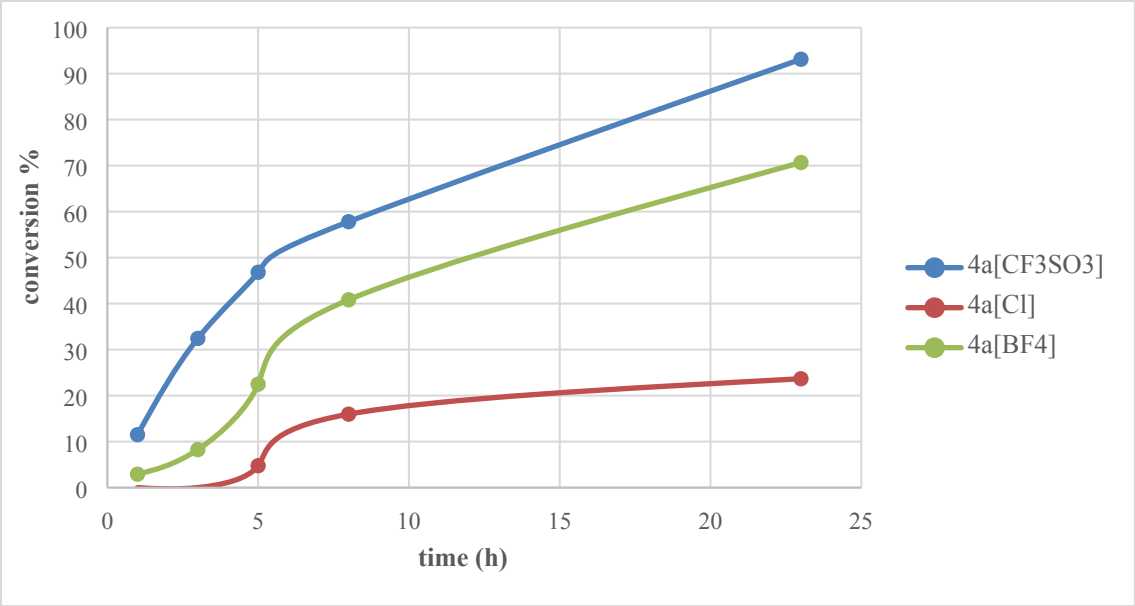
Catalytic time-conversion profiles



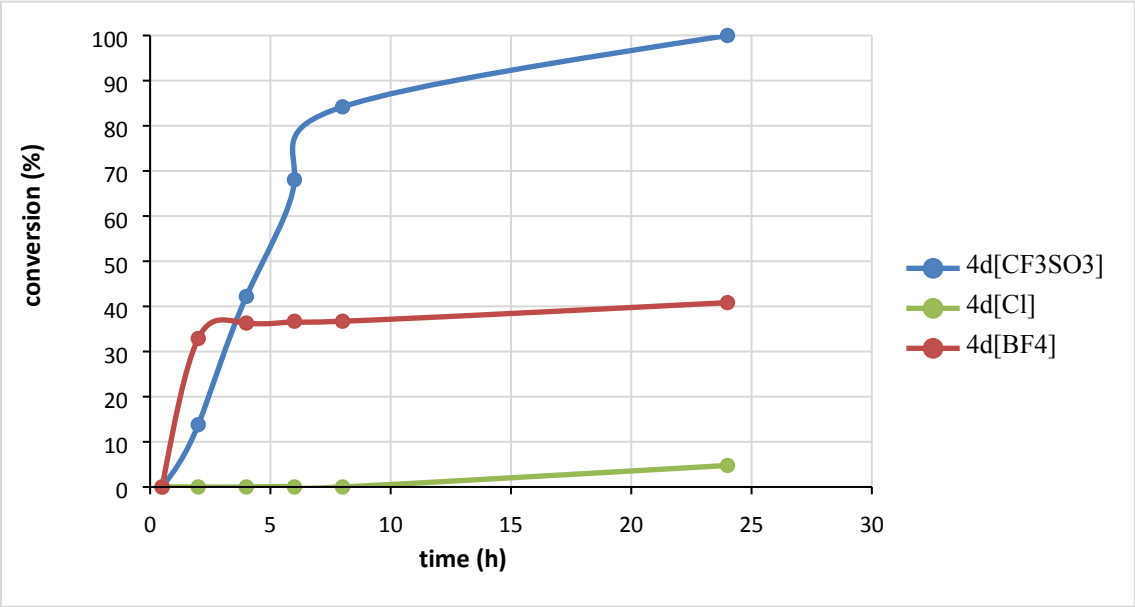
Graphic S1. Comparison of conversion for transfer hydrogenation of 4-fluoroacetophenone with 5mol% of the neutral complexes **3a-d** as pre-catalyst with 1 equivalent (per Ru center) of CAN as additive.



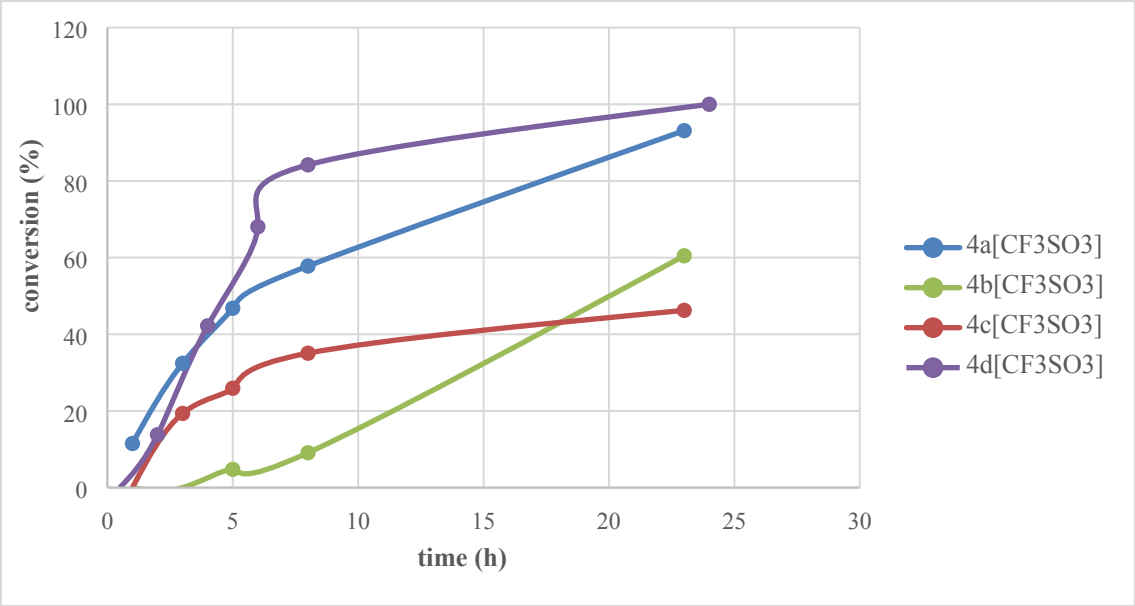
Graphic S2. Comparison of conversion for transfer hydrogenation of 4-fluoroacetophenone with 5mol% of the neutral complexes **3a** as pre-catalyst in the presence of 1 equivalent of different oxidant additives.



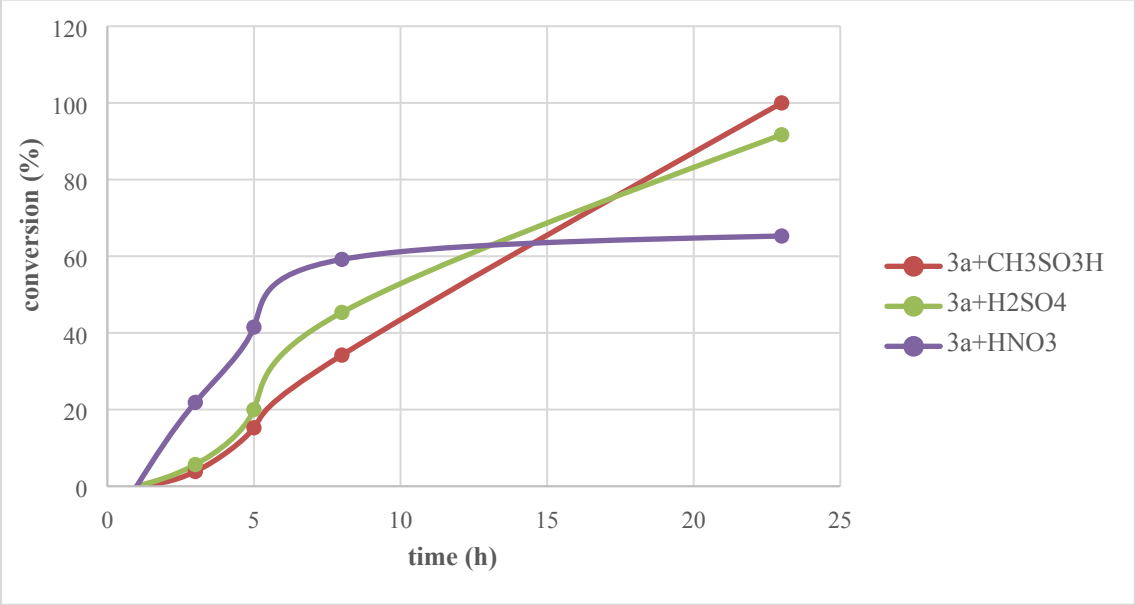
Graphic S3. Comparison of conversion for transfer hydrogenation of 4-fluoroacetophenone with 5mol% of the cationic complexes **4a[CF_3SO_3]**, **4a[Cl]** and **4a[BF_4]** as pre-catalysts.



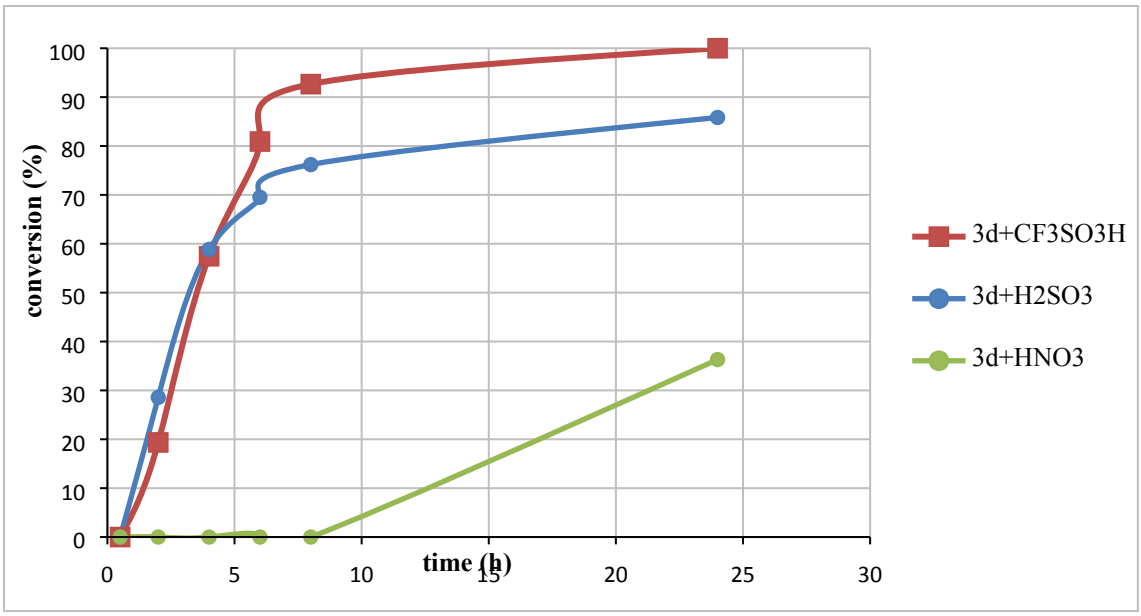
Graphic S4. Comparison of conversion for transfer hydrogenation of 4-fluoroacetophenone with 5mol% of the cationic complexes **4d[CF_3SO_3]**, **4d[Cl]** and **4d[BF_4]** as pre-catalysts.



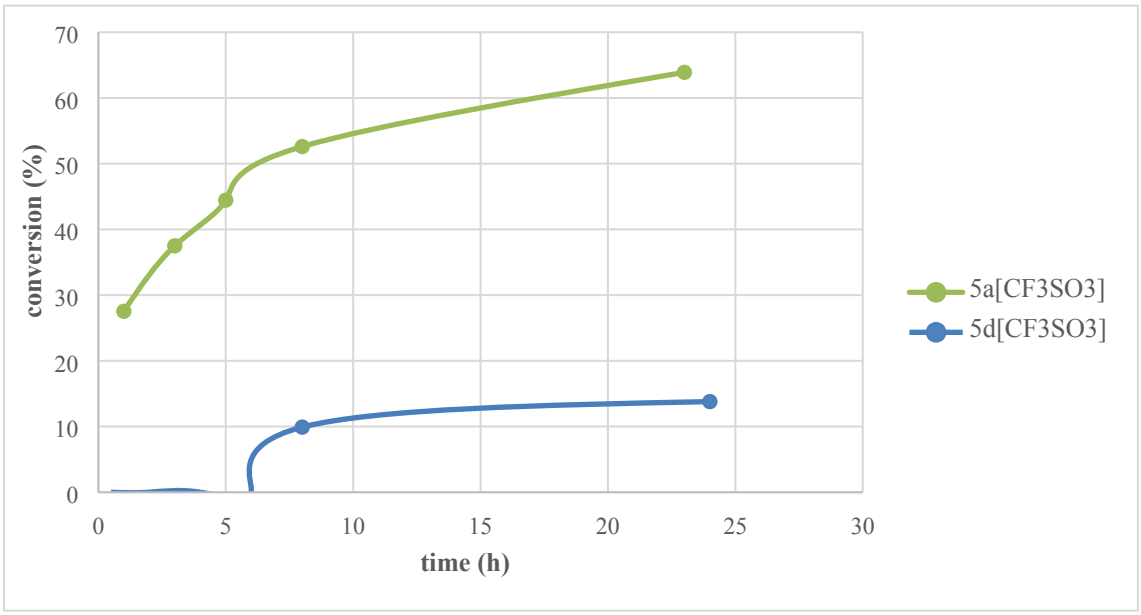
Graphic S5. Comparison of conversion for transfer hydrogenation of 4-fluoroacetophenone with 5mol% of the cationic complexes **4a-d[CF_3SO_3]** as pre-catalysts.



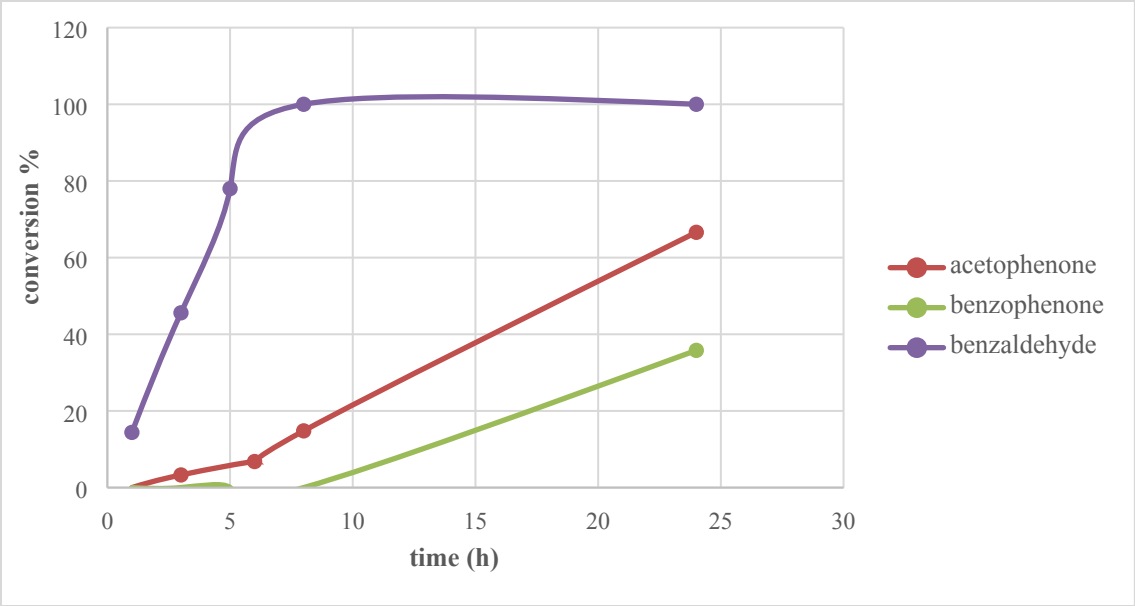
Graphic S6. Comparison of conversion for transfer hydrogenation of 4-fluoroacetophenone with 5mol% of the neutral complex **3a** as pre-catalyst with *in situ* addition of various acids.



Graphic S7. Comparison of conversion for transfer hydrogenation of 4-fluoroacetophenone with 5mol% of the neutral complex **3d** as pre-catalyst with *in situ* addition of various acids.

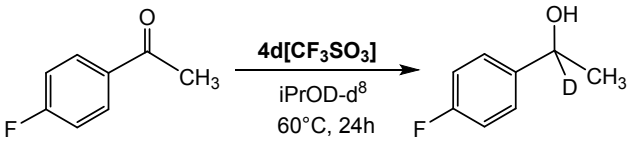


Graphic S8. Comparison of conversion for transfer hydrogenation of 4-fluoroacetophenone with 5mol% of the methylated complexes **5a[CF_3SO_3]** and **5d[CF_3SO_3]** as pre-catalyst.



Graphic S9. Comparison of conversion for transfer hydrogenation of different substrates such as acetophenone benzophenone and benzaldehyde with 5mol% of the cationic complex **4a[CF_3SO_3]** as pre-catalyst.

Labeling experiments in isopropanol-d_8



Complex **4d[CF_3SO_3]** (0.007 g, 7.5 µmol, 5 mol%) was dissolved in 2-propanol d^8 (0.5 mL) in a NMR tube and heated at 60°C for 10 minutes, then the substrate 4-fluoroacetophenone (18 µL, 150 µmol) and the internal standard anisole (10 µL, 150 µmol) were added. The reaction mixture were heated at 60°C for 24h and followed by ^{1}H-NMR spectroscopy at regular intervals. The mixture at the end of the catalysis was further characterized by GC-MS analysis.

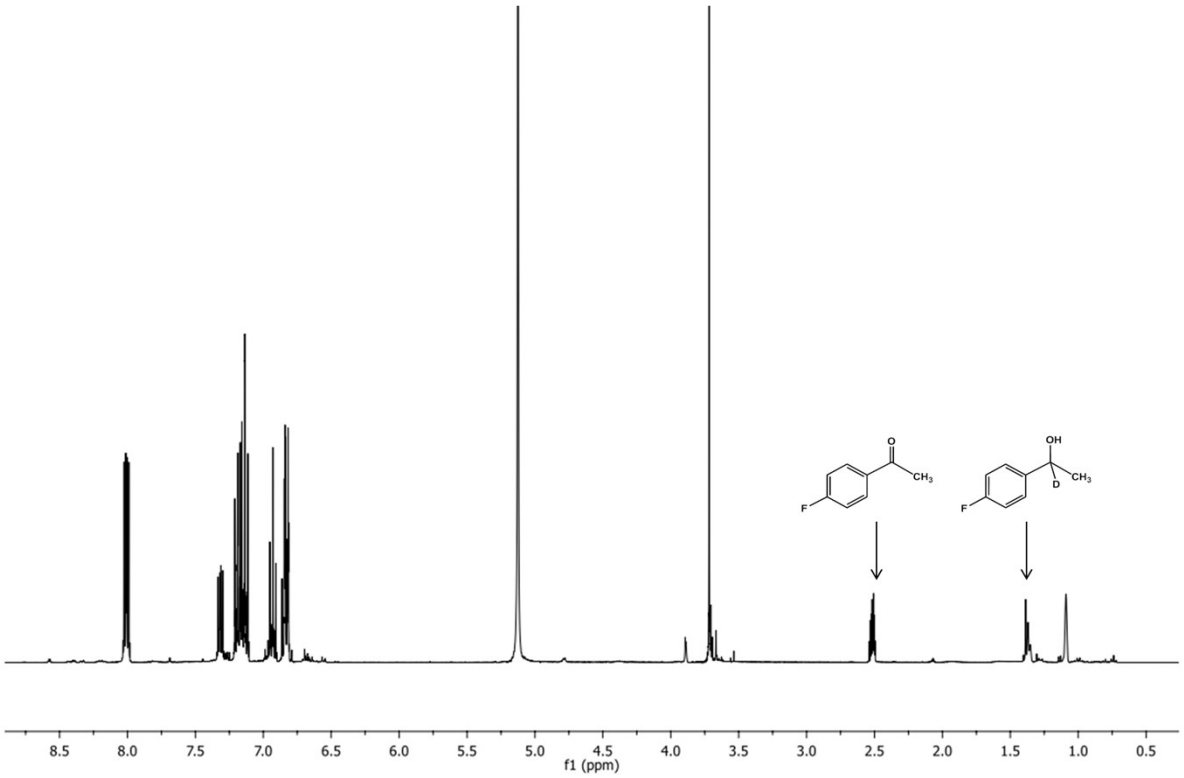


Figure S25. ^{1}H-NMR spectrum in 2-propanol-d^8 after 24h of reaction.

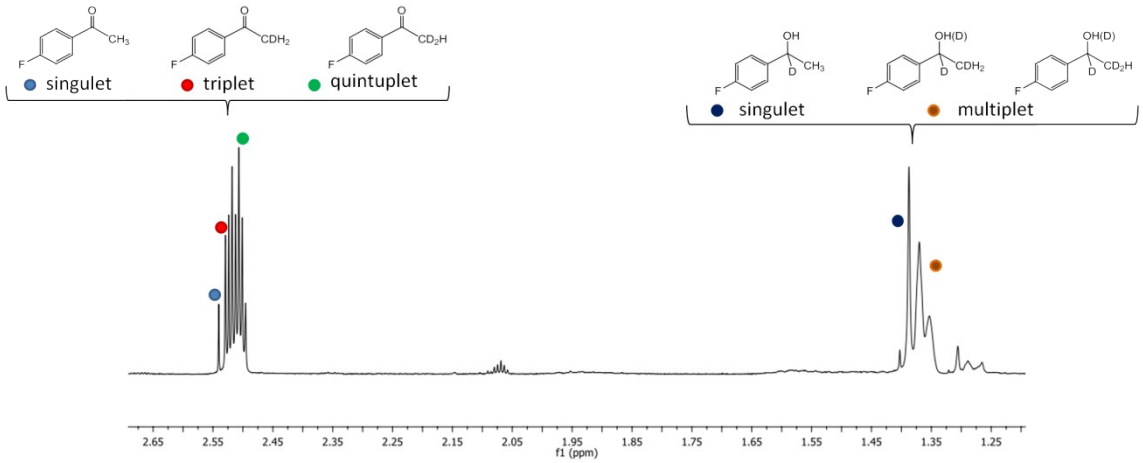


Figure S26. Enlargement of the range 1.25-2.65 ppm of the ^{1}H-NMR spectrum in 2-propanol-d^8 after 24h of reaction.

GC-MS analysis were performed on the instrument Focus-DSQ Thermo.

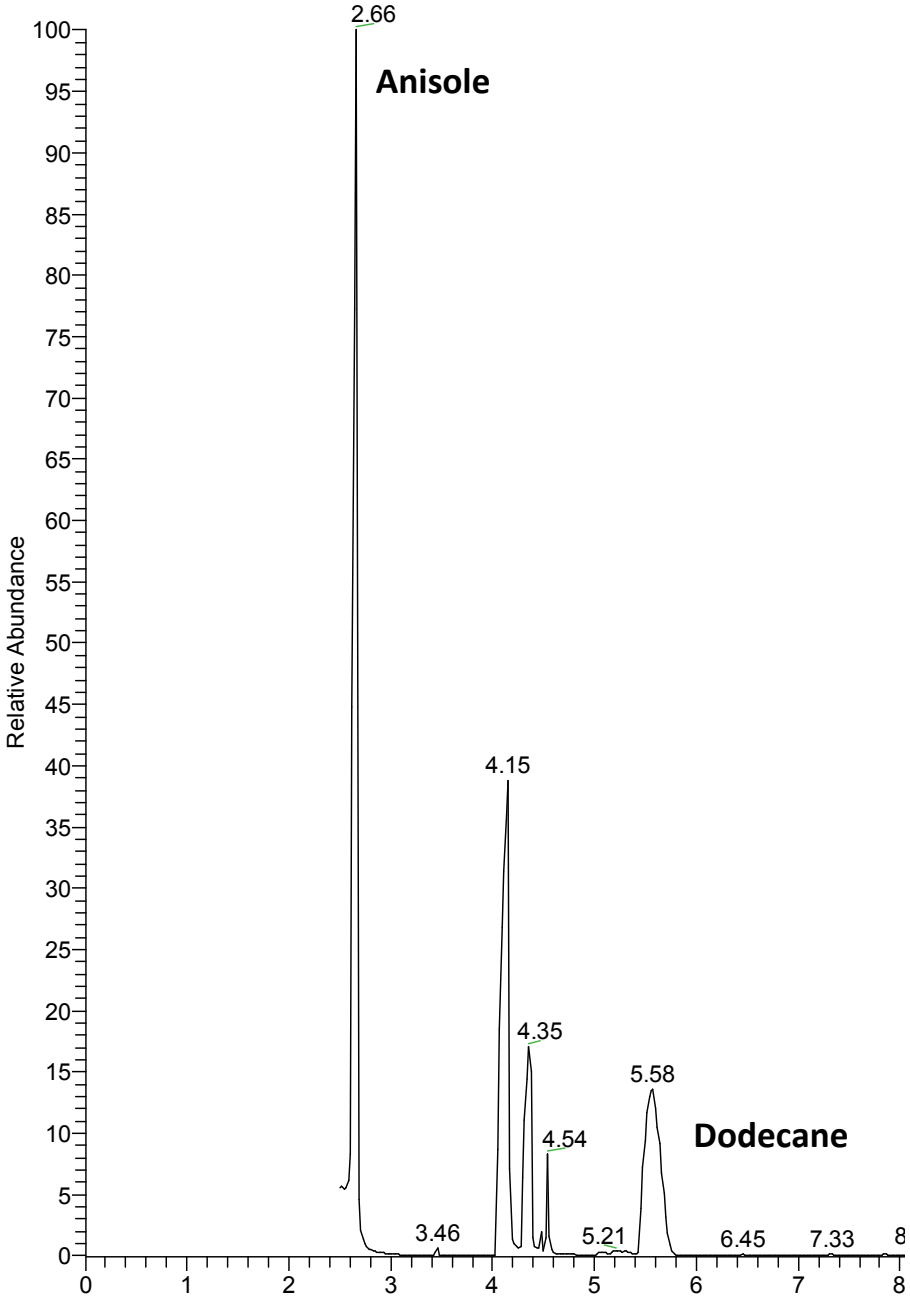


Figure S27. GC-MS spectrum in 2-propanol-d^8 after 24h of reaction.

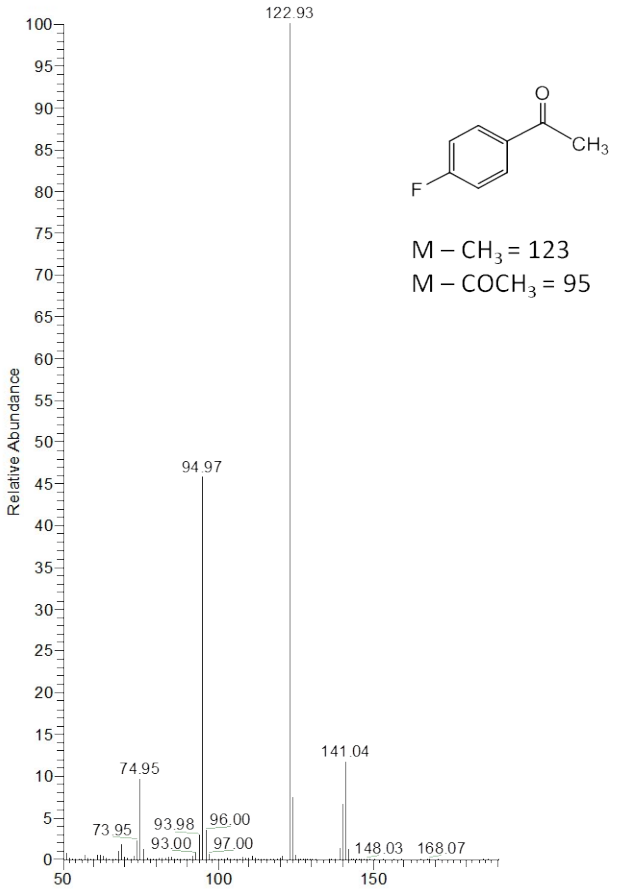


Figure S28. GC-MS spectrum in 2-propanol-d[8] after 24h of reaction. Retention time = 4.15 min.

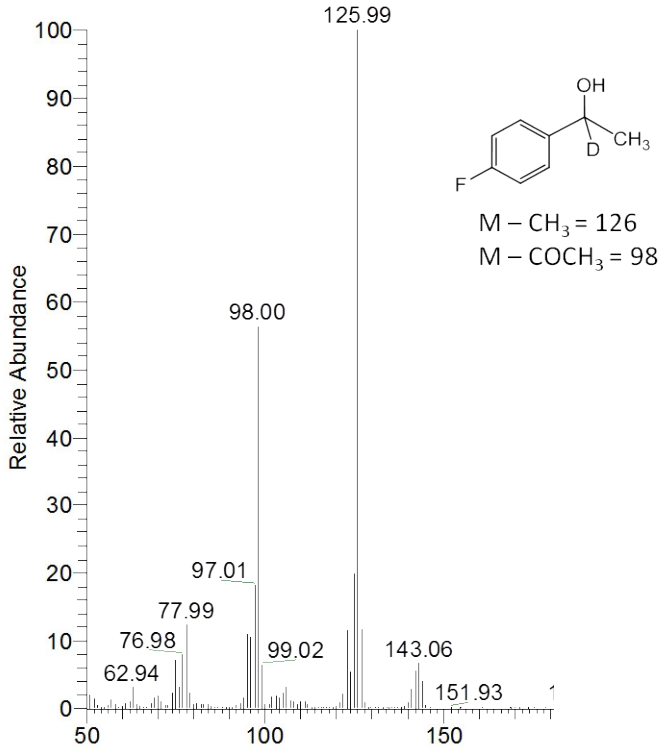


Figure S29. GC-MS spectrum in 2-propanol-d[8] after 24h of reaction. Retention time = 4.35 min.

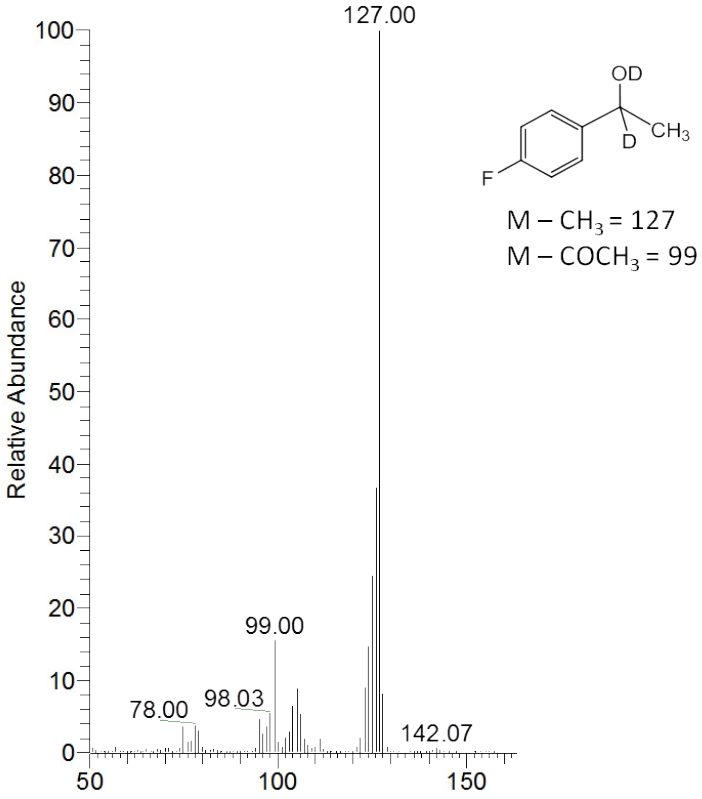


Figure S30. GC-MS spectrum in 2-propanol-d^8 after 24h of reaction. Retention time = 4.54 min.