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Aerobic dehydrogenation of amines to nitriles catalyzed by triazolylidene ruthenium complexes with O_2 as terminal oxidant

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1. NMR spectra of all new complexes

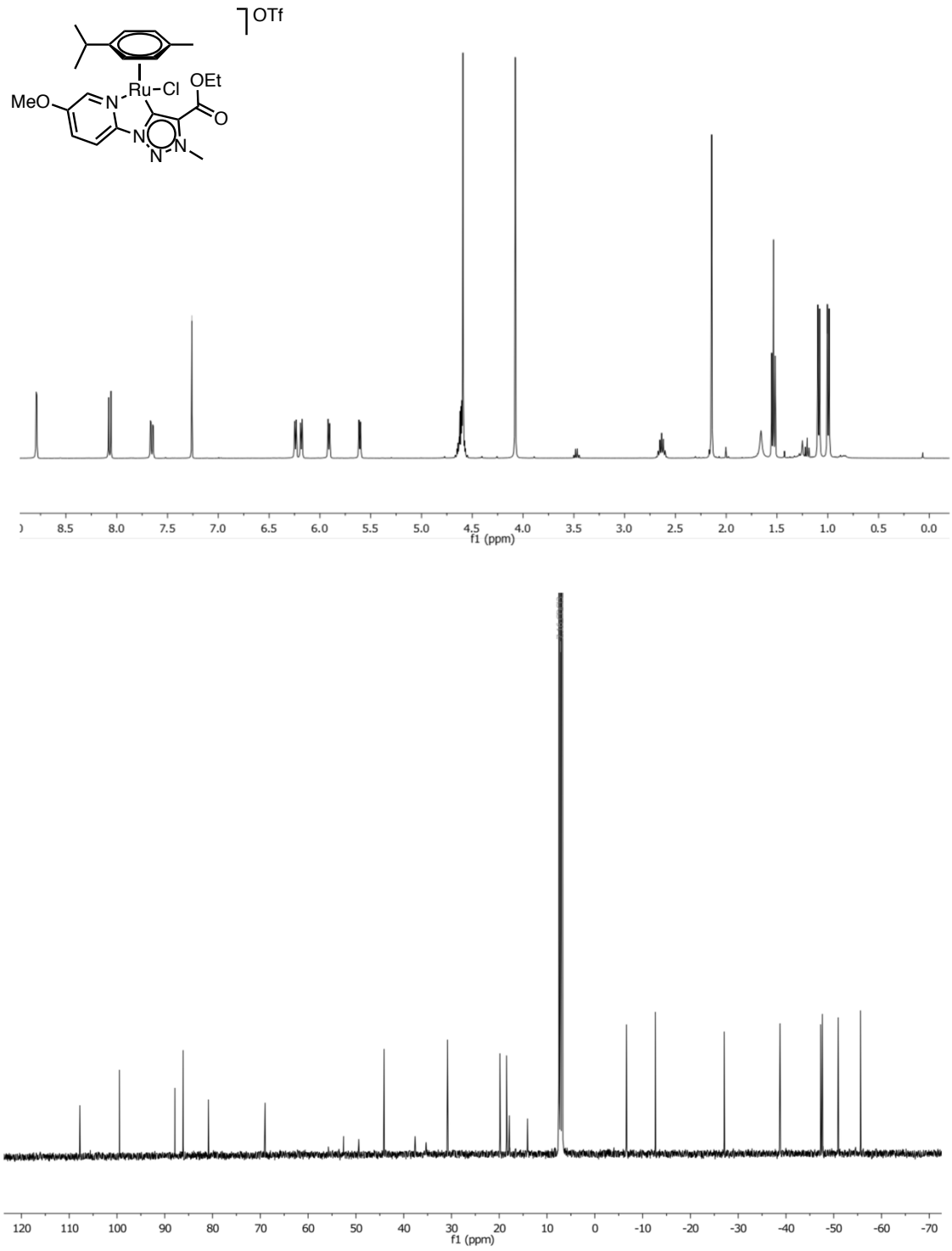


Figure S1. ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR (bottom) spectra of **4b** ($CDCl_3$, 298 K).

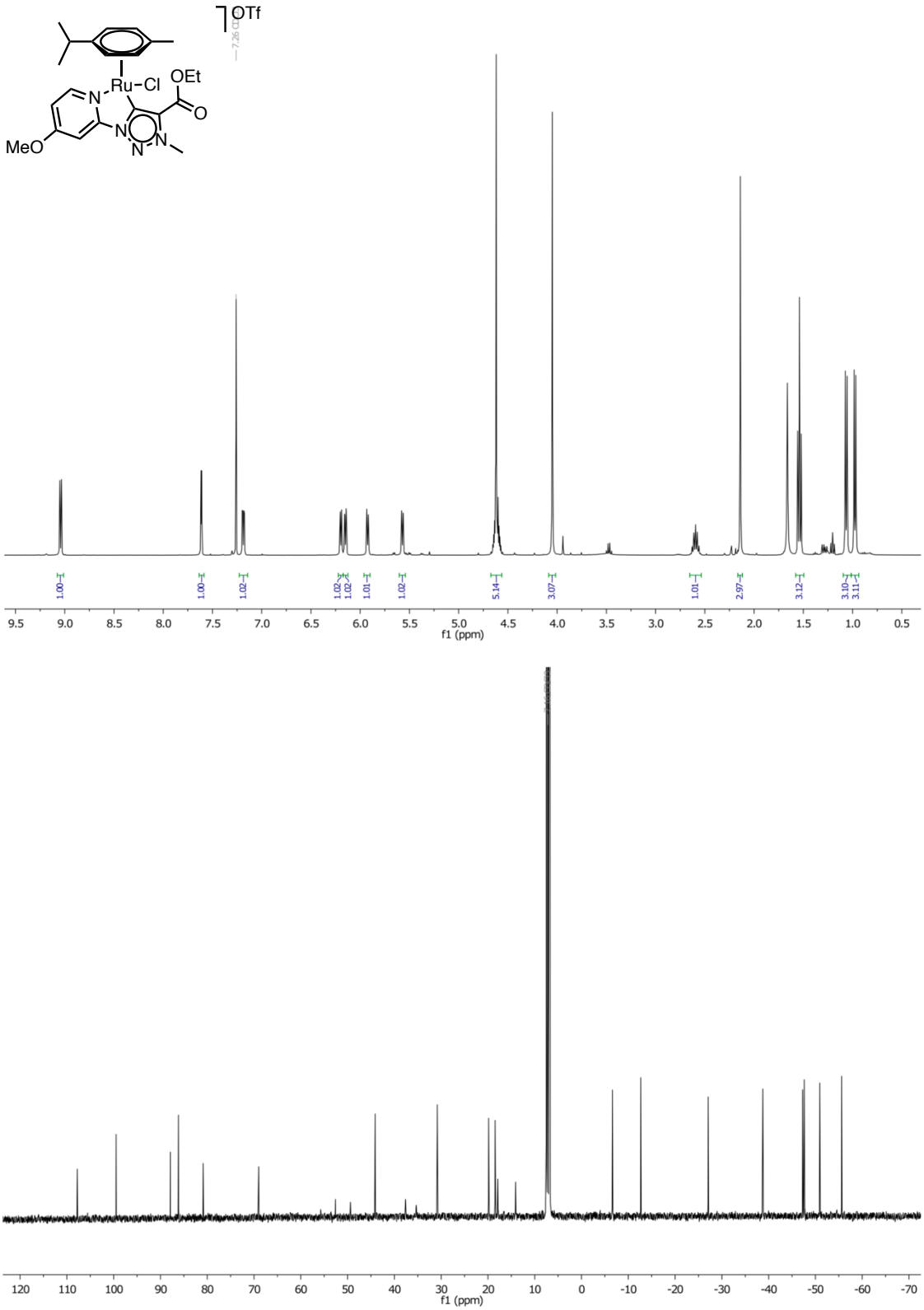


Figure S2. ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR (bottom) spectra of **4c** ($CDCl_3$, 298 K).

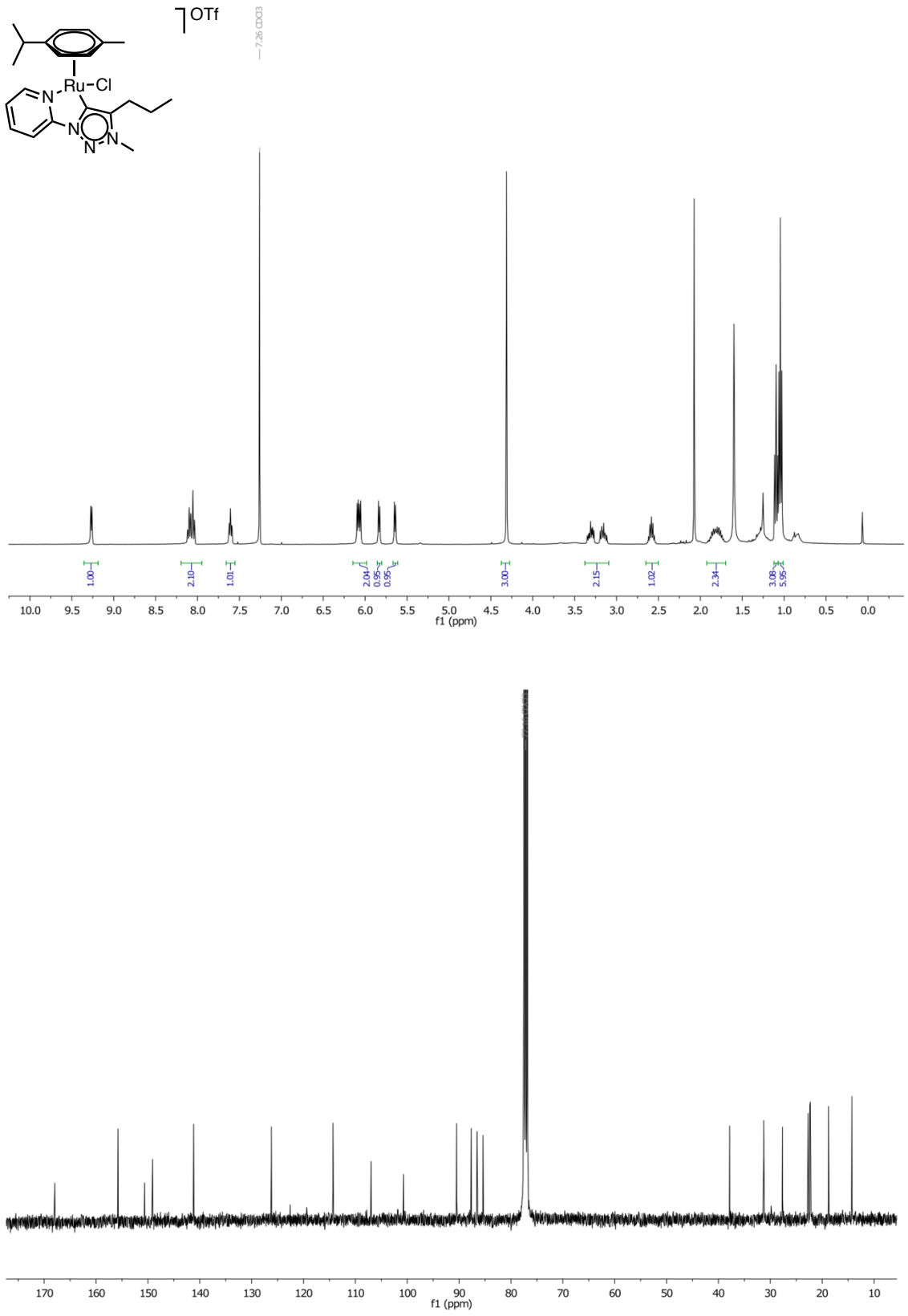


Figure S3. ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR (bottom) spectra of **5** ($CDCl_3$, 298 K).

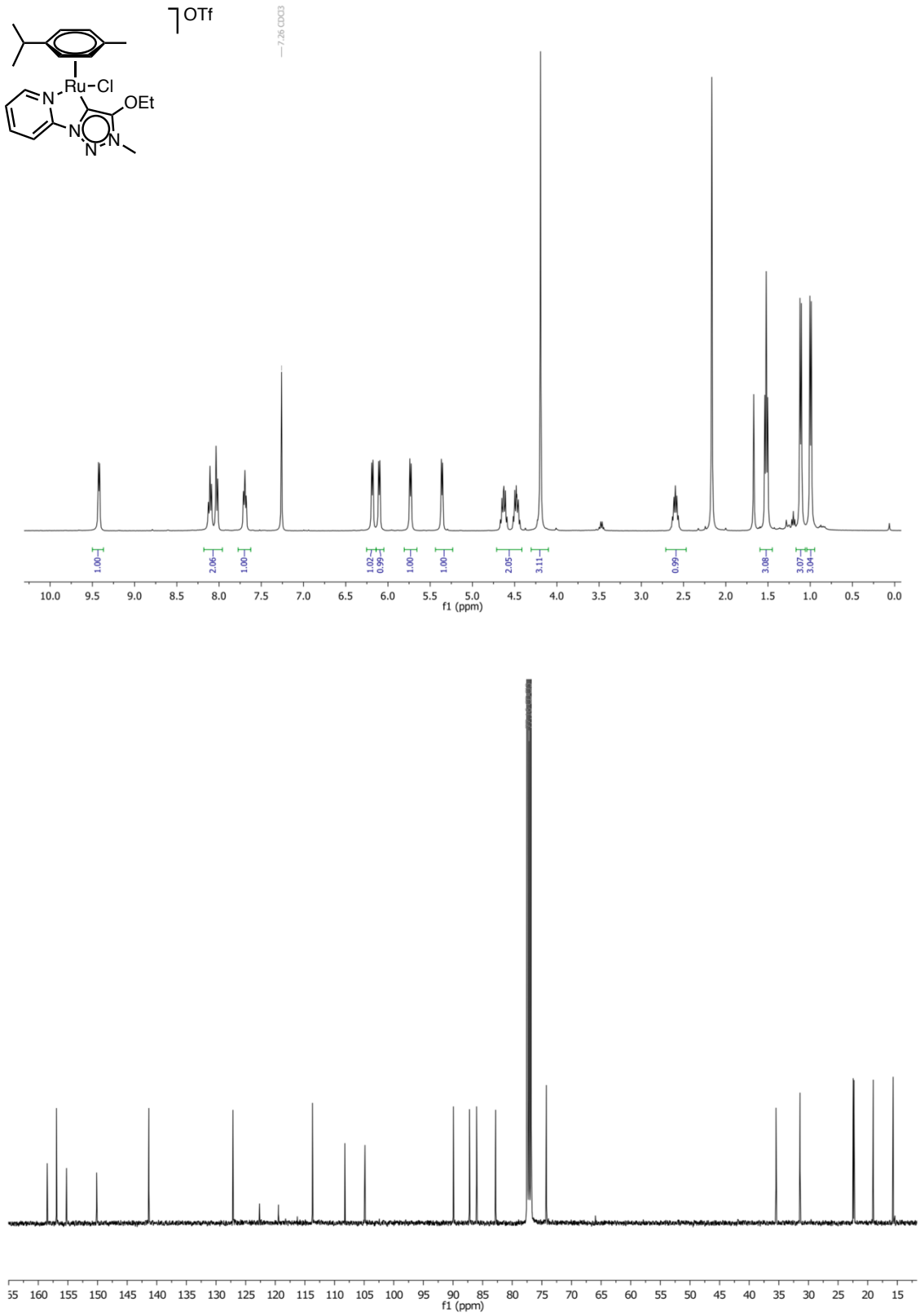


Figure S4. ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR (bottom) spectra of **6a** ($CDCl_3$, 298 K).

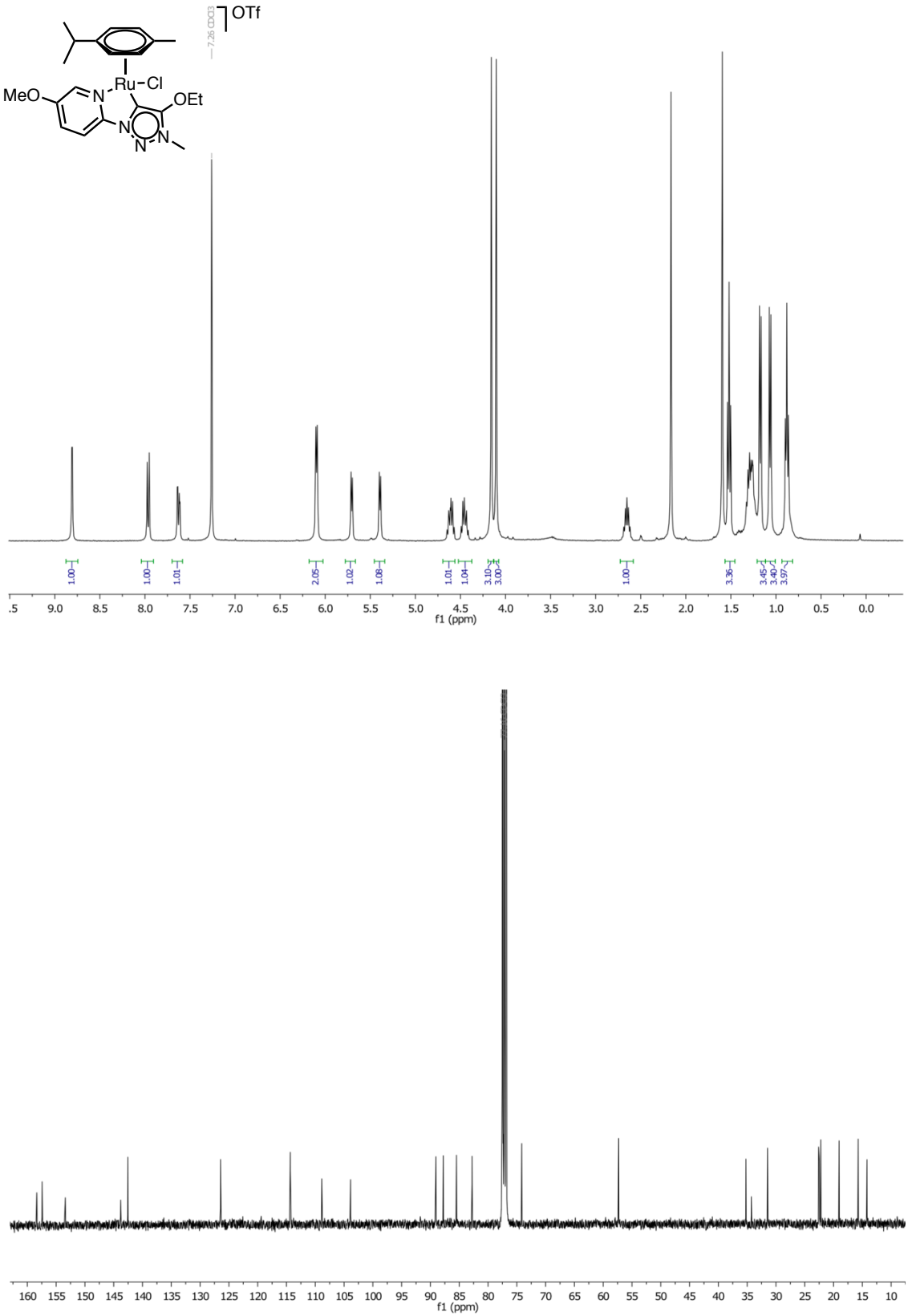


Figure S5. ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR (bottom) spectra of **6b** ($CDCl_3$, 298 K).

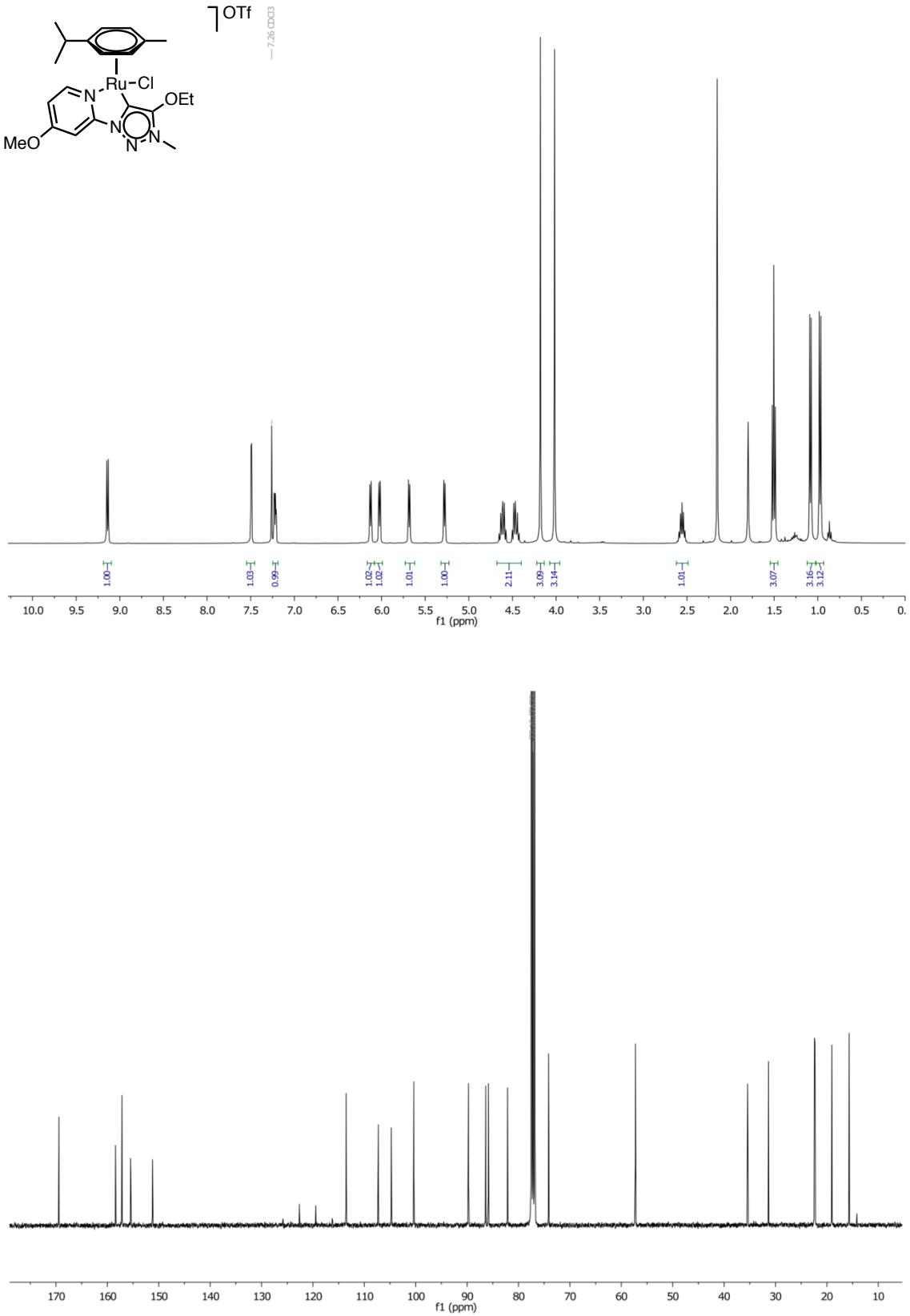
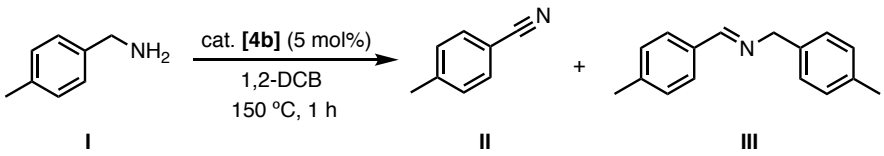


Figure S6. ^{1}H (top) and $^{13}C\{^{1}H\}$ NMR (bottom) spectra of **6c** ($CDCl_3$, 298 K).

2. Catalytic details

Table S1. Variation of conditions for 4-methylbenzylamine oxidation with complex **4b**.[a]



I II III

entry	gas	nitrile (%)	imine (%)	conditions
1	Argon	10	16	open system (flask w condenser), dry solvent
2	N_2	1	2	closed system (Schlenk w minimal headspace)
3	Air	29	49	open system, reagent-grade solvent
4	Air	23	45	closed system, dry solvent
5	H_2	24	55	First 1 h under air (entry 4), then H_2 balloon for 1 h
6	Air	20	35	Air balloon on condenser
7	O_2	89	6	closed system, dry solvent, balloon of O_2

[a] general conditions: 4-methylbenzylamine (0.2 mmol), complex **4b** (0.01 mmol, 5 mol%), 1,2-dichlorobenzene (2 mL), 150 °C.

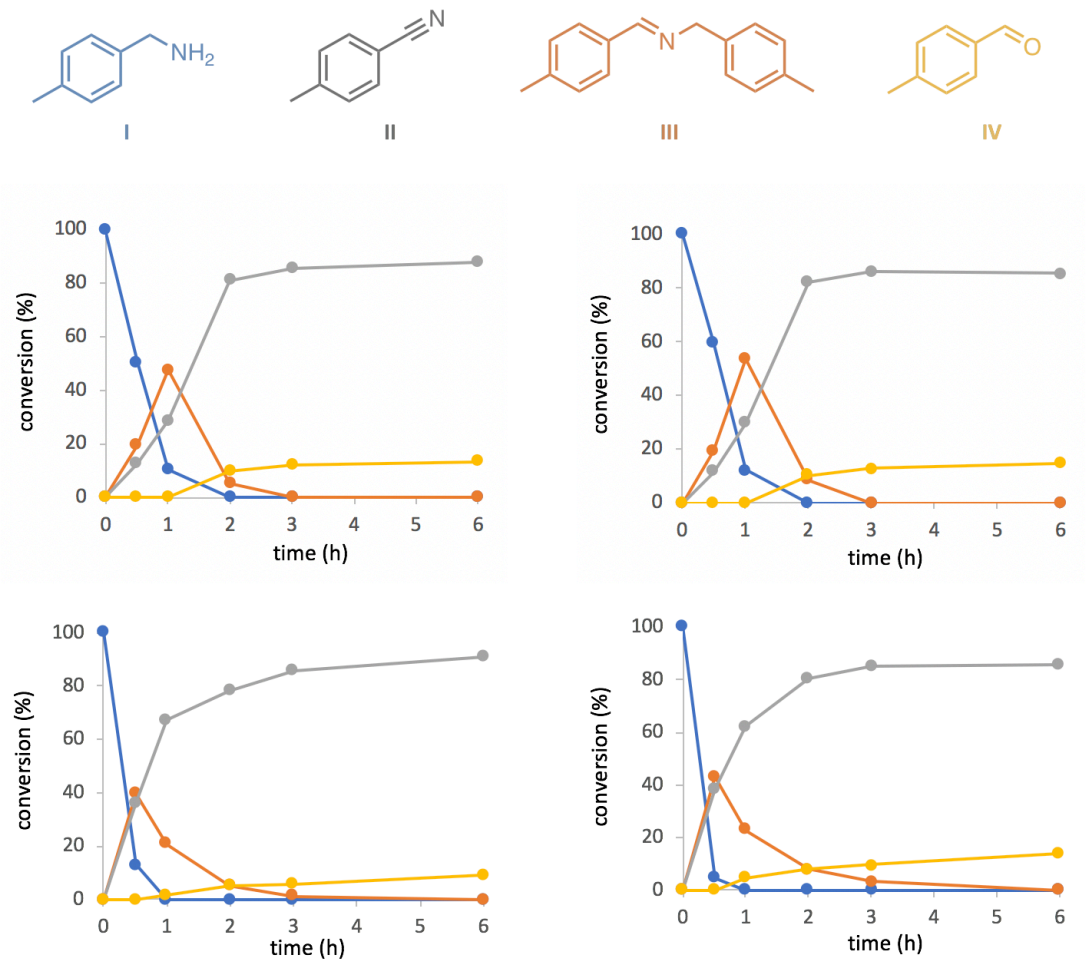


Figure S7. Catalytic profile for the oxidation of 4-methylbenzylamine using complex **4a** (left top panel), **4c** (right top panel), **5** (left bottom panel) and **6a** (right bottom panel) under aerobic reaction conditions (*cf.* entry 3, Table S1). General conditions: 4-methylbenzylamine (0.2 mmol), [Ru] (0.01 mmol, 5 mol%), 1,2-dichlorobenzene (2 mL), 150 °C. For comparison with complex **4b**, see Fig. 2. Conversions were determined by ^{1}H NMR integration (1,3,5-trimethoxybenzene as internal standard) and are averaged over 2 runs.

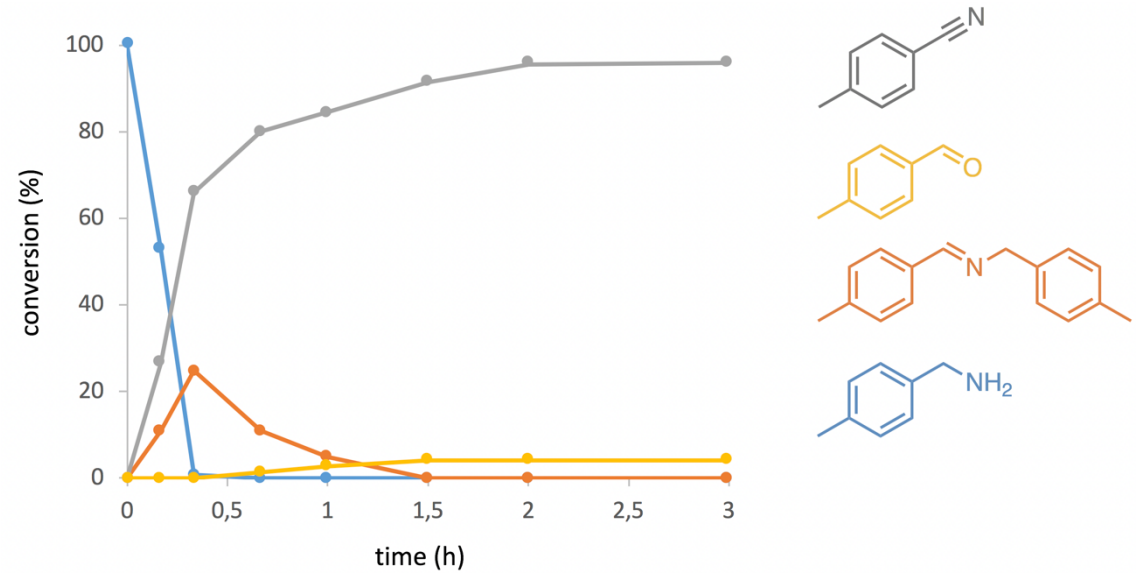


Figure S8. Time-dependent profile for the catalytic oxidation of 4-methylbenzylamine with complex **5** under molecular oxygen conditions. General conditions: 4-methylbenzylamine (0.2 mmol), [Ru] (0.01 mmol, 5 mol%), 1,2-dichlorobenzene (2 mL), 150 °C. Conversions were determined by ^{1}H NMR integration (1,3,5-trimethoxybenzene as internal standard) and are averaged over 2 runs.

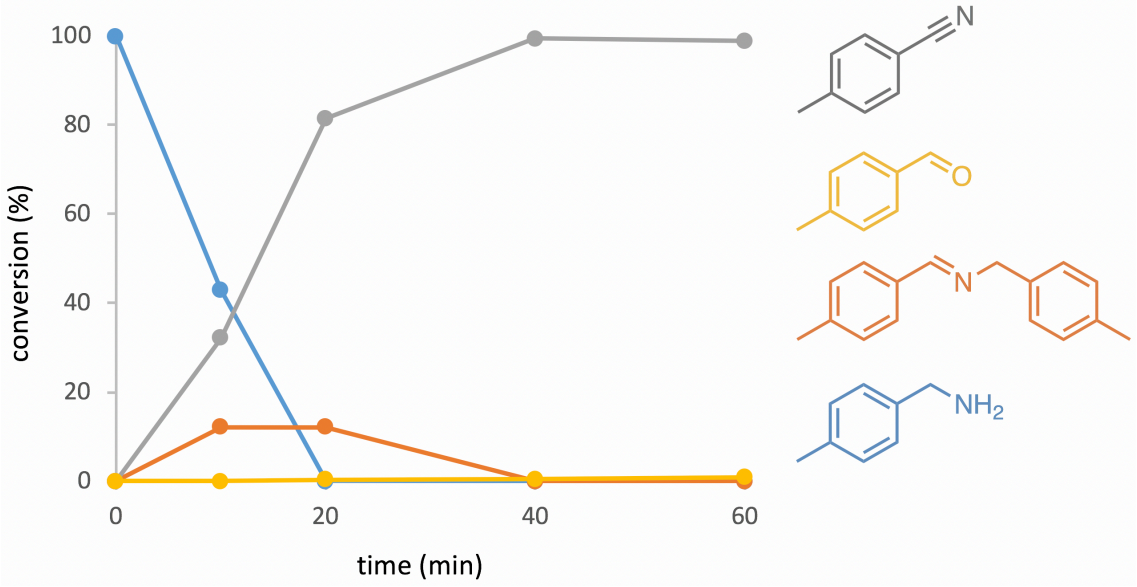


Figure S9. Time-dependent profile for the catalytic oxidation of 4-methylbenzylamine with complex **5** under ammonia gas (6 mL) and molecular oxygen conditions. General conditions: 4-methylbenzylamine (0.2 mmol), [Ru] (0.01 mmol, 5 mol%), 1,2-dichlorobenzene (2 mL), 150 °C. Conversions were determined by ^{1}H NMR integration (1,3,5-trimethoxybenzene as internal standard) and are averaged over 2 runs.

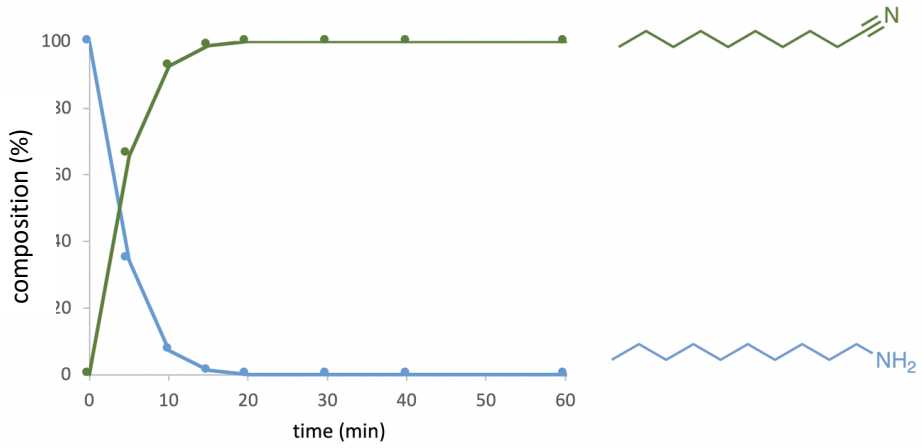


Figure S10. Time-dependent profile for the highly selective catalytic oxidation of decylamine with complex **7** under molecular oxygen and 6 mL ammonia atmosphere. General conditions: decylamine substrate (0.2 mmol), [Ru] (0.01 mmol, 5 mol%), 1,2-dichlorobenzene (2 mL), 150 °C. Conversions were determined by ^{1}H NMR integration (1,3,5-trimethoxybenzene as internal standard) and are averaged over 2 runs.

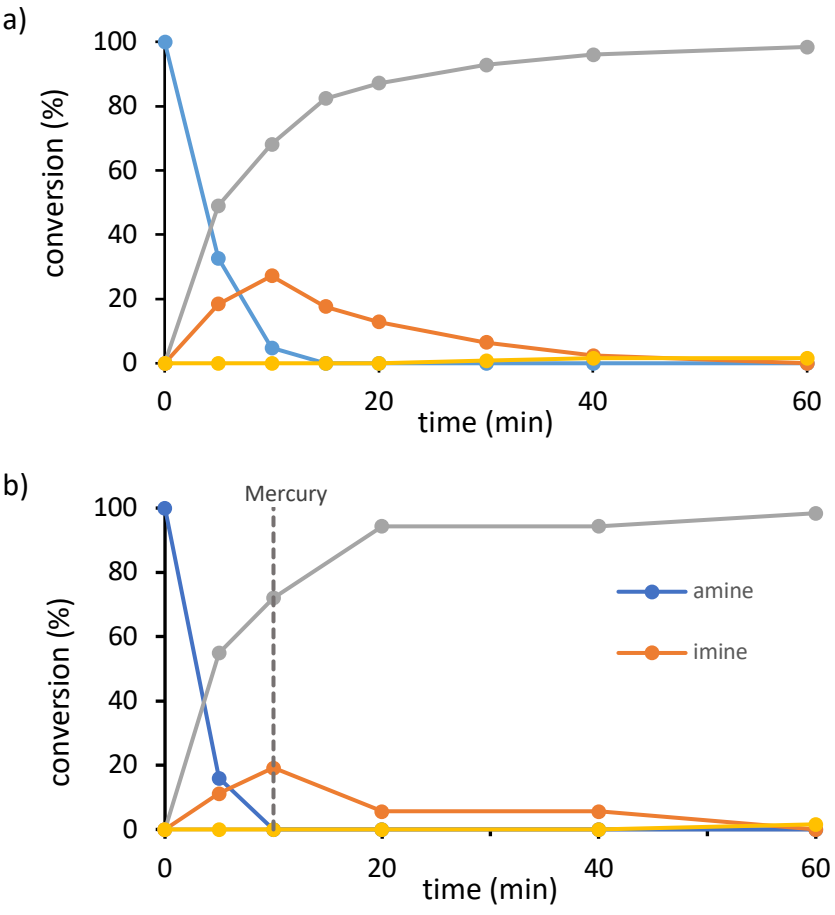


Figure S11. Time-dependent conversion profile for the catalytic oxidation of 4-methylbenzylamine with complex **7** under ammonia gas (6 mL) and molecular oxygen, a) in the absence, and b) in the presence of elemental mercury. General conditions: 4-methylbenzylamine (0.2 mmol), [Ru] (0.01 mmol, 5 mol%), 1,2-dichlorobenzene (2 mL), 150 °C. For b) Hg (9 g, 45 mmol, 4,500 equiv) was added immediately after taking the 10 min sample.

3. Crystallographic details

Table S2. Crystal data and structure refinement for complex **4b**.

Identification No.	1958588
Empirical formula	$C_{23}H_{28}ClF_3N_4O_6RuS$
Formula weight	687.48
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P–1
Unit cell dimensions	a = 9.7705(2) Å
	b = 10.1541(3) Å
	c = 16.0919(5) Å
Volume	1369.33(8) $Å^3$
Z	2
Density (calculated)	1.667 Mg m^{-3}
Absorption coefficient	0.814 mm^{-1}
F(000)	698
Crystal size	0.436 x 0.228 x 0.075 mm^3
Theta range for data collection	2.294 to 28.196°.
Index ranges	–12<=h<=12, –13<=k<=13, –20<=l<=21
Reflections collected	21468
Independent reflections	6208 [R(int) = 0.0244]
Completeness to theta = 25.242°	100 %
Absorption correction	Gaussian
Max. and min. transmission	0.942 and 0.801
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6208 / 0 / 371
Goodness-of-fit on F^2	0.963
Final R indices [I>2sigma(I)]	R1 = 0.026, wR2 = 0.0626
R indices (all data)	R1 = 0.0292, wR2 = 0.0649
Largest diff. peak and hole	0.54 and –0.541 e $Å^{-3}$

Table S3. Crystal data and structure refinement for complex **4c**.

Identification No.	1958592
Empirical formula	$C_{23}H_{28}ClF_3N_4O_6RuS$
Formula weight	687.07
Temperature	173(10) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1$
Unit cell dimensions	a = 12.45753(10) Å
	b = 28.13655(18) Å
	c = 7.85029(6) Å
Volume	2730.25(3) $Å^3$
Z	4
Density (calculated)	1.659 Mg m^{-3}
Absorption coefficient	0.815 mm^{-1}
F(000)	1384.0
Crystal size	0.283 x 0.174 x 0.035 mm^3
Theta range for data collection	3.294 to 56.246°
Index ranges	–16<=h<=16, –36<=k<=37, –10<=l<=10
Reflections collected	58568
Independent reflections	12395 [R(int) = 0.0421]
Completeness to theta	100 %
Absorption correction	Gaussian
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12395 / 139 / 752
Goodness-of-fit on F^2	1.041
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0791
R indices (all data)	R1 = 0.0363, wR2 = 0.0812
Largest diff. peak and hole	0.94 and –0.51 e $Å^{-3}$

Table S4. Crystal data and structure refinement for complex **6a**.

Identification No.	1958633
Empirical formula	$C_{42}H_{52}ClF_6N_8O_9Ru_2S_2$
Formula weight	1264.07
Temperature	173(10) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P–1
Unit cell dimensions	a = 13.3854(4) Å
	b = 14.8258(5) Å
	c = 16.1157(12) Å
Volume	2599.4(2) $Å^3$
Z	2
Density (calculated)	1.615 Mg m^{-3}
Absorption coefficient	0.844 mm^{-1}
F(000)	1280.0
Crystal size	0.2 x 0.1 x 0.02 mm^3
Theta range for data collection	3.34 to 56.38°
Index ranges	–17<=h<=17, –19<=k<=19, –21<=l<=21
Reflections collected	14470
Independent reflections	14470 [R(int) = ?]
Completeness to theta	100 %
Absorption correction	Gaussian
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14470 / 28 / 633
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0706, wR2 = 0.1834
R indices (all data)	R1 = 0.1048, wR2 = 0.1956
Largest diff. peak and hole	2.33 and –1.34 e $Å^{-3}$

Table S5. Crystal data and structure refinement for complex **7**.

Identification No.	1958593
Empirical formula	$C_{21}H_{26}F_6N_8O_6RuS_2$
Formula weight	765.69
Temperature	173(10) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P–1
Unit cell dimensions	a = 11.23950(10) Å
	b = 12.47830(10) Å
	c = 12.55360(10) Å
Volume	1541.05(3) $Å^3$
Z	2
Density (calculated)	1.650 Mg m^{-3}
Absorption coefficient	6.170 mm^{-1}
F(000)	772.0
Crystal size	0.147 x 0.12 x 0.058 mm^3
Theta range for data collection	7.536 to 153.918°
Index ranges	–14<=h<=10, –15<=k<=15, –15<=l<=15
Reflections collected	29678
Independent reflections	6368 [R(int) = 0.0266]
Completeness to theta	100 %
Absorption correction	Gaussian
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6368 / 316 / 440
Goodness-of-fit on F^2	1.070
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1363
R indices (all data)	R1 = 0.0478, wR2 = 0.1370
Largest diff. peak and hole	1.33 and –1.09 e $Å^{-3}$