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

Supporting Information to

Aerobic Catalysis in Air with Cp*Ir: Influence of Added Ligands and Reaction Conditions on Catalytic Activity and Stability.

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1 General Considerations

All reagents and solvents were used as received unless noted otherwise. $[Cp^*IrCl_2]_2$ was synthesized as previously reported.[1] Stirbars used in catalytic reactions were cleaned with aqua regia for at least 3 h under gentle stirring, rinsed with copious amounts of water, and dried in an oven at 120 °C prior to use. Standard solutions were prepared using volumetric flasks. All reactions were performed with regular laboratory air. All liquid reagents were dispensed by difference using gas-tight Hamilton syringes. Yields are reported as average yields of at least 2 experiments. The reported error is the standard deviation of at least two replicate trials.

GC analyses were performed on an Agilent 7890A Series GC equipped with FID detector, an Agilent HP-5 capillary column (length 30m, diameter 0.32 mm, film thickness 0.25 µm), and a 7693A auto injector module. Yields were calculated by calibrating prepared samples and standard to the response of the instrument. GC-MS investigations were carried out on an Agilent 5975C instrument using a 19091S-433 (HP-5MS; 30 m, 0.25 mm i.d., 0.25 µm df) column. The identities of all oxidation products were verified by comparison of the obtained data with GC and GC-MS data of original samples.

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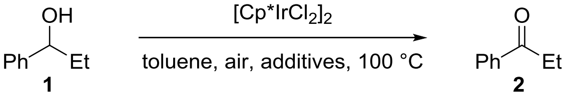
[1] White, C.; Yates, A.; Maitlis, P. M.; Heinekey, D. M., (η^5-Pentamethylcyclopentadienyl)Rhodium and -Iridium Compounds. In *Inorganic Syntheses*, John Wiley & Sons, Inc.: 2007; pp 228-234.

2 Experimental Procedures and Data

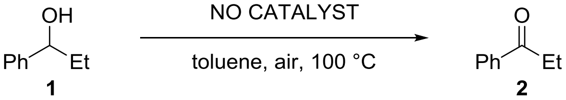
2.1 General Procedure A



To a 20 mL scintillation vial, equipped with a Teflon-coated stirbar, was added 1.6 mg of $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]) and solid additives. Whenever possible, additives were added as standard solutions in toluene. 100 µL (0.20 mmol, 1.0 equiv.) of a standard solution of 1-phenyl-1-propanol (**1**) (2.74 mL, 2.72 g, 20 mmol) in 10 mL toluene was added. The resulting solution was diluted to a total volume of 2.0 mL with toluene.[2]

The vial was sealed with a Teflon-lined cap and heated to 100 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After the reaction time was completed (2 or 24 h) the vial was taken off the heating block and the mixture was allowed to cool to room temperature. 100 µL (80 µmol, 8.6 mg, 0.40 equiv.) of a standard solution of *p*-xylene (1.00 mL, 0.861 g, 8.10 mmol) in 10 mL toluene was added as GC-standard. The solution was diluted to a total volume of 4 mL with toluene or isopropanol. If the solution was cloudy, it was filtered through celite; subsequently, the yield of **2** was determined by calibrated GC analysis.

2.2 Background Reaction



100 µL (0.20 mmol, 1.0 equiv.) of a standard solution of 1-phenyl-1-propanol (**1**) (2.74 mL, 2.72 g, 20 mmol) in 10 mL toluene was diluted to a total volume of 2.0 mL with toluene. The mixture was reacted and analyzed in analogy to general procedure A, providing 0.0% yield and 0.1% yield of **2** after 2 and 24 h, respectively, as determined by GC analysis using *p*-xylene as GC-standard.

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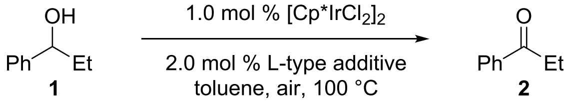
[2] The amount of oxygen in the vial was approximated to be 0.15 mmol (0.77 equiv.) based on the abundance of oxygen in air (20.95%), the remaining volume in the vial (18 mL), and the ideal gas law ($pV = nRT$). If the decomposition of the primary reaction product H_2O_2 into O_2 and H_2O is assumed to be quantitative, only 0.5 equivalent of oxygen are needed for the reaction: alcohol + 0.5 O_2 → ketone + H_2O

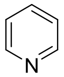
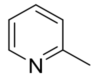
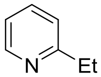
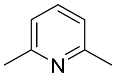
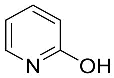
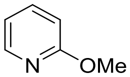
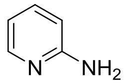
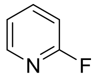
2.3 L-type Additive Effects on $[Cp^*IrCl_2]_2$ Activity

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), additive (2.0 mol %), and **1** (0.20 mmol, 1 equiv.) were reacted in 2.0 mL toluene for 2 or 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 1. GC yields of oxidation product 2 with different L-type additives. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), additive (4.0 µmol, 2.0 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (total volume 2.0 mL), 100 °C, 2 or 24 h.



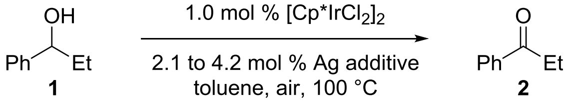
1 **2**

Additive	% GC Yield of **2** (2 h)	% GC Yield of **2** (24 h)
none	10 ± 0	53 ± 2
	9 ± 1	39 ± 1
	3 ± 0	17 ± 0
	34 ± 1	57 ± 0
	6 ± 0	24 ± 0
	10 ± 1	21 ± 1
	8 ± 1	28 ± 1
	9 ± 0	37 ± 1
	5 ± 0	34 ± 1
	8 ± 1	45 ± 1
NEt_3	9 ± 1	21 ± 1
$HNEt_2$	14 ± 0	50 ± 1
HN^iPr_2	14 ± 1	49 ± 2
H_2N^tBu	17 ± 2	52 ± 1

2.4 Ag Additive Effects on $[Cp^*IrCl_2]_2$ Activity

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), Ag additive (2.1 or 4.2 mol %; 4.2 mol % [Ag]), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL toluene for 2 or 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 2. GC yields of oxidation product 2 with different Ag additives. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), Ag additive (2.1 or 4.2 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (total volume 2.0 mL), 100 °C, 2 or 24 h.

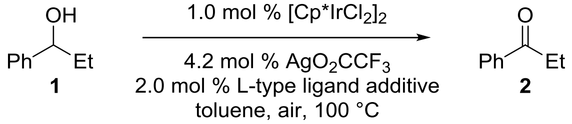


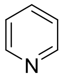
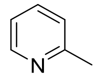
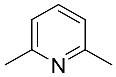
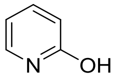
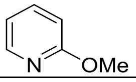
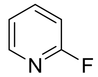
Ag additive (mol %)	% GC Yield of **2** (2 h)	% GC Yield of **2** (24 h)
none	10 ± 0	53 ± 2
AgO_2CCF_3 (4.2 mol %)	34 ± 1	50 ± 0
AgOAc (4.2 mol %)	37 ± 2	53 ± 5
AgOTf (4.2 mol %)	1 ± 1	2 ± 0
$AgBF_4$ (4.2 mol %)	2 ± 0	25 ± 3
$AgPF_6$ (4.2 mol %)	5 ± 0	19 ± 0
$AgNO_3$ (4.2 mol %)	22 ± 2	34 ± 4
Ag_2CO_3 (2.1 mol %)	9 ± 0	41 ± 4
Ag_2SO_4 (2.1 mol %)	9 ± 0	41 ± 5

2.5 Combining L-type Additive and Ag Additive Effects

According to general procedure A, [Cp*IrCl$_2$]$_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), AgO$_2$CCF$_3$ (1.9 mg, 8.4 µmol, 4.2 mol %), L-type additive (2.0 mol%), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL toluene for 2 or 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 3. GC yields of oxidation product 2 with different L-type additives and AgO$_2$CCF$_3$ as Ag Additive. Conditions: [Cp*IrCl$_2$]$_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), additive (4.0 µmol, 2.0 mol %), AgO$_2$CCF$_3$ (1.9 mg, 8.4 µmol, 4.2 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (total volume 2.0 mL), 100 °C, 2 or 24 h.



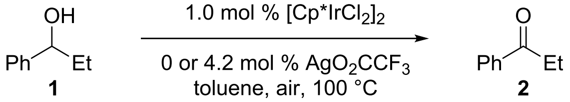
L-type additive	% GC Yield of **2** (2 h)	% GC Yield of **2** (24 h)
none	34 ± 1	50 ± 0
	35 ± 0	49 ± 2
	31 ± 2	60 ± 2
	31 ± 1	39 ± 2
	35 ± 0	52 ± 1
	33 ± 0	48 ± 1
	29 ± 3	45 ± 1
	28 ± 0	45 ± 0
NEt$_3$	24 ± 1	34 ± 0
HNEt$_2$	31 ± 2	50 ± 1
HN^{i}Pr$_2$	24 ± 0	30 ± 1
H$_2$N^{t}Bu	35 ± 1	48 ± 1

2.6 Effects of Oxygen Content and Reaction Time

2.6.1 Higher Oxygen Content

In analogy to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), additives, and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL toluene for 24 h in a 40 mL scintillation vial with a Teflon-lined cap or in a flask equipped with a reflux condenser and a balloon filled with air. The amount of oxygen in the vial was approximated to be 0.32 mmol (1.63 equiv.) based on the abundance of oxygen in air (20.95%), the remaining volume in the vial (38 mL), and the ideal gas law ($pV = nRT$). Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 4. GC yields of oxidation product 2 in larger reaction vial. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), AgO_2CCF_3 (0 to 4.2 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (total volume 2.0 mL), 100 °C, 24 h.

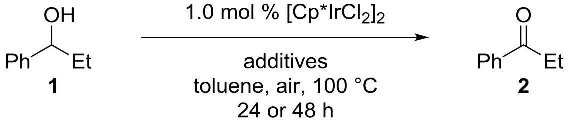


Additives	% GC Yield of **2** (24 h) from reactions with excess air	% GC Yield of **2** (24 h) in 40 mL vials	Comparative % GC Yield of **2** (24 h) in 20 mL vials
none	42 ± 11	53 ± 0	53 ± 2
AgO_2CCF_3 (4.2 mol %)	60 ± 8	57 ± 1	50 ± 0

2.6.2 Longer Reaction Times

In analogy to general procedure A, [Cp*IrCl$_2$]$_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), additives, and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL toluene in a 20 mL scintillation vial for 24 or 48 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 5. GC yields of oxidation product 2 after 24 or 48 h. Conditions: [Cp*IrCl$_2$]$_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), additives, 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (total volume 2.0 mL), 100 °C, 24 or 48 h.

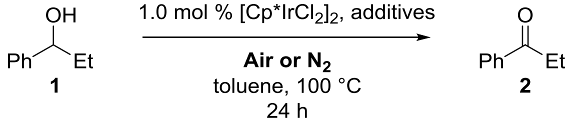


Additives	% GC Yield of **2** (24 h)	% GC Yield of **2** (48 h)
none	53 ± 2	56 ± 7
AgO_2CCF_3 (4.2 mol %)	50 ± 0	39 ± 4

2.6.3 Reactions under N_2 atmosphere

In analogy to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 μmol, 2.0 mol % [Ir]), additives, and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL toluene for 24 h in a 20 mL scintillation vial for 24 h under a N_2 atmosphere. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard. Table 6 contrasts the outcomes of these experiments with the respective experiments in the presence of 18 mL air.

Table 6. Comparison of GC yields of 2 under air and N_2 atmosphere. Conditions: $[Cp^*IrCl_2]_2$ (2.0 μmol, 1.0 mol %; 2.0 mol % [Ir]), additives, 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (2.0 mL), 100 °C, 24 h, air or N_2.

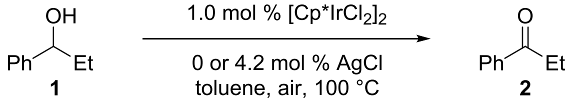


Additives	% GC Yield of **2** (24 h) **with 18 mL air**	% GC Yield of **2** (24 h) **under N_2 atmosphere**
none	53 ± 2	2 ± 1
AgO_2CCF_3 (4.2 mol %)	50 ± 0	12 ± 3

2.7 Effect of AgCl on catalyst stability and activity

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), Ag additive (2.1 or 4.2 mol %), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL toluene for 2 or 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 7. GC yields of oxidation product 2. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), AgCl (0 or 4.2 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (total volume 2.0 mL), 100 °C, 24 h.



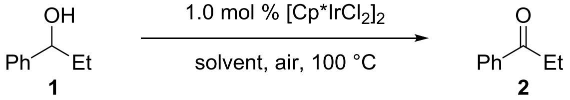
Ag additive	% GC Yield of **2** (24 h)
-	53 ± 2
AgCl (4.2 mol %)	46 ± 1

2.8 Solvent study

2.8.1 Solvents used as received and dried over molecular sieves 4Å

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]) and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL of a solvent (Table 8) for 24 h. All solvents for this study were used as received or were dried over activated molecular sieves (4Å) for at least 24 h before use. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 8. GC yields of oxidation product 2 in different solvents. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), solvent (2.0 mL), 100 °C, 24 h.



Solvent	% GC Yield of **2** (24 h); **Solvents used as received**	% GC Yield of **2** (24 h); **Solvents dried over MS 4Å**
toluene	53 ± 2	28 ± 5
PhCl	12 ± 0	11 ± 1
PhBr	14 ± 0	8 ± 1
$PhCF_3$	31 ± 1	7 ± 1
ortho-$C_6H_4(CH_3)_2$	28 ± 3	28 ± 1
DMF	39 ± 4	29 ± 1
H_2O	18 ± 0	n/a
1900 µL toluene/100 µL CH_2Cl_2	32 ± 3	33 ± 1
1900 µL toluene/100 µL $CHCl_3$	31 ± 1	26 ± 2

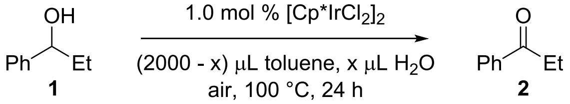
2.8.2 Reaction in dry toluene with 4Å MS added to the reaction mixture

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), pre-activated 4Å molecular sieves (500 mg), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL of toluene for 24 h. Toluene for this study had been dried over activated molecular sieves (4Å) for at least 24 h before use. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard. The reaction afforded 12 ± 1 % of **2** according to calibrated GC analysis.

2.9 Water content study

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]) and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL of a mixture of solvent and water (see Table 9 and Table 10) for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

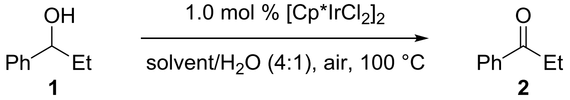
Table 9. GC yields of oxidation product 2 in different toluene/H_2O mixtures. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene/H_2O (total volume 2.0 mL), 100 °C, 24 h.



Toluene [µL]	H_2O [µL]	% GC Yield of **2** (24 h)
2000[a]	0[a]	28 ± 5[a]
1995[a]	5[a]	37 ± 2[a]
1990[a]	10[a]	36 ± 1[a]
1980	20	56 ± 1
1950	50	55 ± 1
1800	200	61 ± 2
1700	300	62 ± 2
1600	400	68 ± 2
1400	600	51 ± 3
1200	800	41 ± 1
1000	1000	32 ± 1

[a] Toluene for these reactions was dried over activated molecular sieves (4Å) for at least 24 h before use.

Table 10. GC yields of oxidation product 2 in solvent/H_2O (4:1) mixtures. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 2.0 mol % [Ir]), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), solvent (1.6 mL), H_2O (0.4 mL), 100 °C, 24 h.

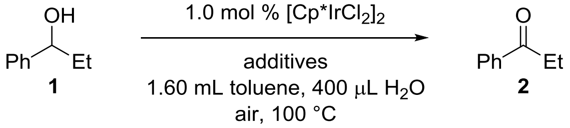


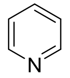
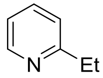
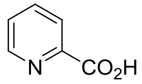
Solvent	% GC Yield of **2** (24 h)
toluene	68 ± 2
PhCl	61 ± 2
$PhCF_3$	55 ± 1
ortho-$C_6H_4(CH_3)_2$	51 ± 1

2.10 L-type additive and Ag additive studies in toluene/H_2O 4:1

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), additives, and **1** (0.20 mmol, 1.0 equiv.) were reacted in a mixture of 1.60 mL toluene and 400 µL water (see Table 11) for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 11. L-type additive and Ag additive studies in toluene/H_2O 4:1. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), additives, 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (1.60 mL), H_2O (400 µL), 100 °C, 24 h.

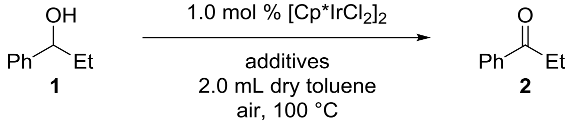


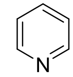
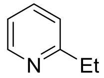
Additives	% GC Yield of **2** (24 h)
none	68 ± 2
AgOAc (4.2mol %)	41 ± 0
AgO_2CCF_3 (4.2 mol %)	44 ± 1
$AgBF_4$ (4.2 mol %)	36 ± 1
Ag_2SO_4 (2.1 mol %)	37 ± 1
Ag_2CO_3 (2.1 mol %)	33 ± 2
 (2.0 mol %)	36 ± 1
 (2.0 mol %)	57 ± 0
 (2.0 mol %)	21 ± 1

2.11 L-type additive and Ag additive in dry toluene

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), additives (see Table 12), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2.0 mL toluene. Toluene for these studies had been dried over activated molecular sieves (4Å) for at least 24 h before use. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 12. L-type additive and Ag additive in dry toluene. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 2.0 mol % [Ir]), additives, 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (2.0 mL), 100 °C, 24 h.

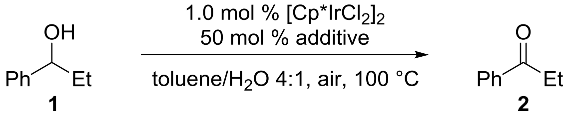


Additives	% GC Yield of **2** (24 h) in dry toluene	Comparative % GC Yield of **2** (24 h) in toluene as received
none	28 ± 5	53 ± 2
AgOAc (4.2 mol %)	53 ± 0	53 ± 5
AgO_2CCF_3 (4.2 mol %)	44 ± 1	50 ± 0
 (2.0 mol %)	15 ± 7	39 ± 1
 (2.0 mol %)	10 ± 1	57 ± 0
NEt_3 (2.0 mol %)	13 ± 1	21 ± 1

2.12 Basic and acidic additives

According to general procedure A, [Cp*IrCl$_2$]$_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), the tested additive (0.10 mmol; 50 mol %; Table 13) and **1** (0.20 mmol, 1.0 equiv.) were reacted in a mixture of 1.6 mL toluene and 0.4 mL H_2O for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 13. GC yields of oxidation product 2 with different acidic and basic additives. Conditions: [Cp*IrCl$_2$]$_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), solvent (2.0 mL), 100 °C, 24 h.



Additive	pK$_a$[a]	% GC Yield of **2** (24 h)
HCl	-3.7[3]	15 ± 0
p-TsOH	-1.9[3]	12 ± 2
F_3CCO_2H	0.52[4]	37 ± 2
AcOH	4.76[3]	48 ± 1
-	-	68 ± 2
NaO_2CCF_3	0.52[4]	56 ± 0
NaOAc	4.76[3]	27 ± 2
Na_2CO_3	10.3[5]	17 ± 2
K_2CO_3	10.3[5]	16 ± 1
NEt_3	10.7[6]	40 ± 2

[a] For basic additives, the pK$_a$ values of the corresponding acids are provided.

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[3] Guthrie, J. P., *Can. J. of Chem.* **1978,** *56*, 2342-2354.

[4] Namazian, M.; Zakery, M.; Noorbala, M. R.; Coote, M. L., *Chem. Phys. Lett.s* **2008,** *451*, 163-168.

[5] Meier, J.; Schwarzenbach, G., *Helv. Chim. Acta* **1957,** *40*, 907-917.

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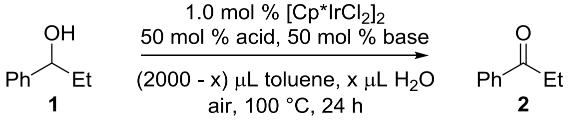
2.13 Buffer Systems

2.13.1 Evaluating AcOH/NaOAc and CF_3CO_2H/NaO_2CCF_3 buffer systems in different toluene/H_2O mixtures

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), the tested acid (0.10 mmol; 50 mol %) and base (0.10 mmol; 50 mol %), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 2 mL of a toluene/H_2O mixture (see Table 14) for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 14. GC yields of oxidation product 2 in different toluene/H_2O mixtures. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), acid (0.10 mmol; 50 mol %), base (0.10 mmol; 50 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene/H_2O (total volume 2.0 mL), 100 °C, 24 h.

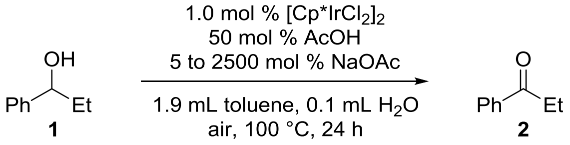


Toluene [µL]/H_2O [µL]	Buffer (0.1 mmol of each acid and base)	% GC Yield of **2** (24 h)
1400/600	AcOH/NaOAc	62 ± 0
1600/400	AcOH/NaOAc	56 ± 3
1900/100	AcOH/NaOAc	61 ± 0
1400/600	CF_3CO_2H/NaO_2CCF_3	54 ± 3
1600/400	CF_3CO_2H/NaO_2CCF_3	50 ± 2
1900/100	CF_3CO_2H/NaO_2CCF_3	30 ± 4

2.13.2 Evaluating AcOH/NaOAc ratio in toluene/H_2O (19:1)

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), NaOAc (5 to 2500 mol %; see Table 15), AcOH (5 to 2500 mol %; see Table 16), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 1.9 mL of a toluene/H_2O mixture for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 15. GC yields of oxidation product 2 with varying NaOAc content in buffer system. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1,0 mol %; 2.0 mol % [Ir]), AcOH (0.10 mmol; 50 mol %), NaOAc (5 to 2500 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), 1.9 mL toluene, 0.1 mL H_2O, 100 °C, 24 h.



NaOAc [mol %]	NaOAc [mg, mmol]	% GC Yield of **2** (24 h)
2500	410 mg, 5.0 mmol	43 ± 3
1250	205 mg, 2.5 mmol	46 ± 1
500	82.0 mg, 1.0 mmol	41 ± 2
250	41.0 mg, 0.50 mmol	42 ± 0
100	16.4 mg, 0.20 mmol	61 ± 0
50	8.2 mg, 0.10 mmol	61 ± 0
25	4.1 mg, 0.050 mmol	59 ± 2
5	0.80 mg, 0.010 mmol	64 ± 4

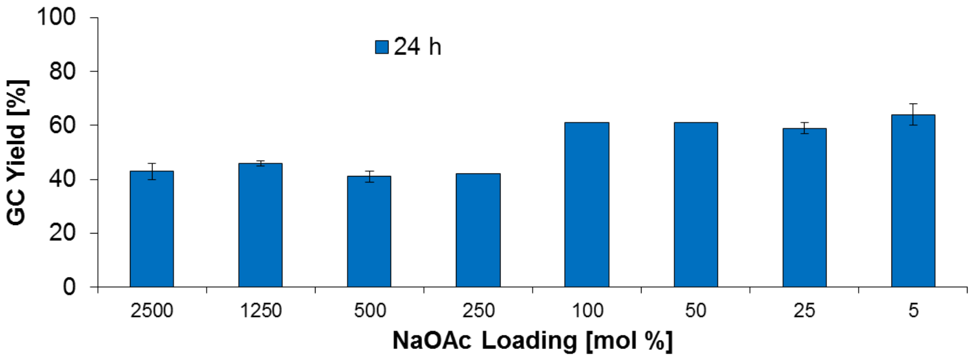
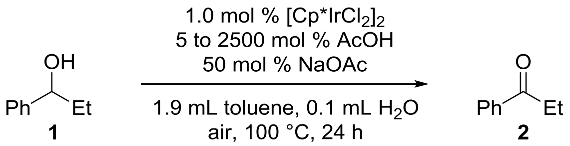


Figure 1. 24 h GC yields of 2 vs. NaOAc content in buffer system. Conditions: see Table 15.

Table 16. GC yields of oxidation product 2 with varying AcOH content in buffer system. Conditions: $[Cp^*IrCl_2]_2$ (2.0 μmol, 1.0 mol %; 2.0 mol % [Ir]), AcOH (5 to 2500 mol %), NaOAc (0.10 mmol; 50 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), 1.9 mL toluene, 0.1 mL H_2O, 100 °C, 24 h.



AcOH [mol %]	AcOH [μL, mmol]	% GC Yield of **2** (24 h)
2500	286 μL, 5.0 mmol	31 ± 0
1250	143 μL, 2.5 mmol	40 ± 0
500	57.2 μL, 1.0 mmol	44 ± 1
250	28.6 μL, 0.50 mmol	60 ± 5
100	11.4 μL, 0.20 mmol	52 ± 2
50	5.7 μL, 0.10 mmol	61 ± 0
25	2.6 μL, 0.050 mmol	41 ± 1
5	0.6 μL, 0.010 mmol	37 ± 2

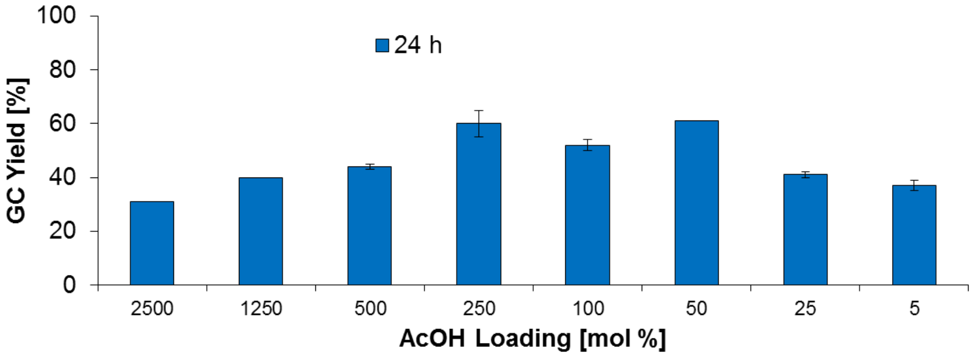
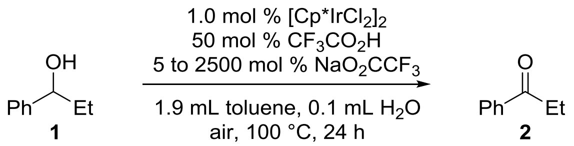


Figure 2. 24 h GC yields of 2 vs. AcOH content in buffer system. Conditions: see Table 16.

2.13.3 Evaluating CF_3CO_2H/NaO_2CCF_3 ratio in toluene/H_2O (9:1)

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), NaO_2CCF_3 (5 to 2500 mol %; see Table 17), CF_3CO_2H (5 to 2500 mol %; see Table 18), and **1** (0.20 mmol, 1.0 equiv.) were reacted in a mixture of 1.9 mL of toluene and 0.10 mL H_2O for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 17. GC yields of oxidation product 2 with varying NaO_2CCF_3 content in buffer system. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), CF_3CO_2H (0.10 mmol; 50 mol %), NaO_2CCF_3 (5 to 2500 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), 1.9 mL toluene, 0.1 mL H_2O, 100 °C, 24 h.



NaO_2CCF_3 [mol %]	NaO_2CCF_3 [mg, mmol]	% GC Yield of **2** (24 h)
2500	680 mg, 5.0 mmol	22 ± 4
1250	340 mg, 2.5 mmol	34 ± 1
500	136 mg, 1.0 mmol	36 ± 1
250	68.0 mg, 0.50 mmol	41 ± 3
100	27.2 mg, 0.20 mmol	32 ± 2
50	13.6 mg, 0.10 mmol	30 ± 4
25	6.8 mg, 0.050 mmol	30 ± 2
5	1.4 mg, 0.010 mmol	27 ± 2

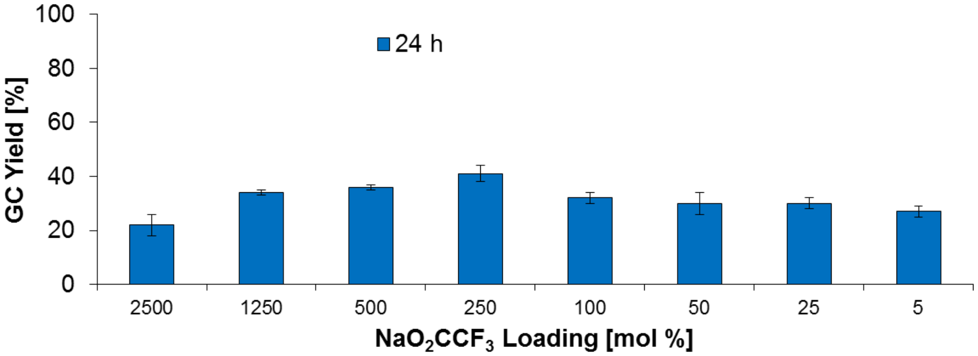
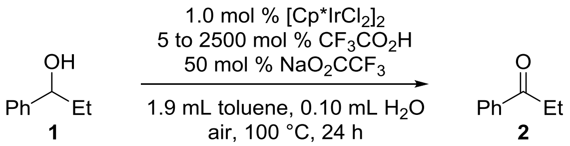


Figure 3. 24 h GC yields of 2 vs. NaO_2CCF_3 content. Conditions: see Table 17.

Table 18. GC yields of oxidation product 2 with varying CF_3CO_2H content in buffer system. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), CF_3CO_2H (5 to 2500 mol %), NaO_2CCF_3 (0.10 mmol; 50 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), 1.9 mL toluene, 0.10 mL H_2O, 100 °C, 24 h.



CF_3CO_2H [mol %]	CF_3CO_2H [µL, mmol]	% GC Yield of **2** (24 h)
2500	383 µL, 5.0 mmol	0 ± 0
1250	191 µL, 2.5 mmol	0 ± 0
500	76.6 µL, 1.0 mmol	5 ± 0
250	38.3 µL, 0.50 mmol	10 ± 2
100	15.3 µL, 0.20 mmol	30 ± 1
50	7.7 µL, 0.10 mmol	30 ± 4
25	3.8 µL, 0.050 mmol	60 ± 2
5	0.8 µL, 0.010 mmol	57 ± 2

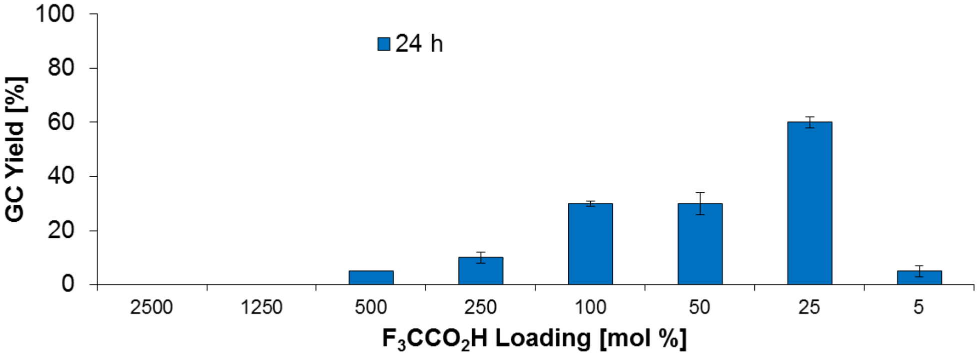
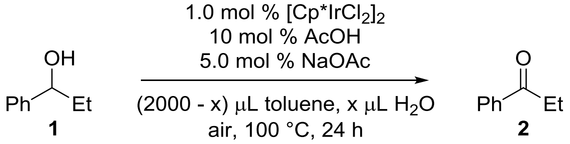


Figure 4. 24 h GC yields of 2 vs. F_3CCO_2H content. Conditions: see Table 18.

2.13.4 Influence of different toluene/H_2O mixtures in presence of NaOAc/AcOH (5 mol % : 10 mol %) buffer

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), NaOAc (5.0 mol %), AcOH (10 mol %), and **1** (0.20 mmol, 1.0 equiv.) were reacted in a toluene/H_2O mixture (2.0 mL total) for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 19. GC yields of oxidation product 2 NaOAc/AcOH 1:2 buffer system in dry toluene. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), NaOAc (5.0 mol %), AcOH (10 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), 2.0 mL toluene/H_2O, 100 °C, 24 h.



toluene [µL]	H_2O [µL]	% GC Yield of **2** (24 h)
2000 (solvent dried over MS 4Å)	0	48 ± 2
1995	5	78 ± 2
1990	10	83 ± 3
1985	15	79 ± 0
1980	20	80 ± 1
1900	100	67 ± 1
1800	200	64 ± 8
1600	400	67 ± 4
1400	600	62 ± 1
1200	800	58 ± 0

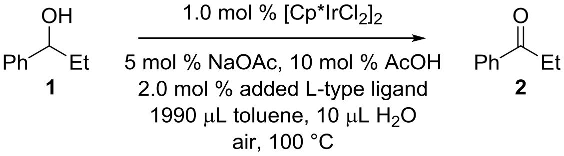
2.13.5 Extended Reaction Times with best Catalyst System

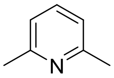
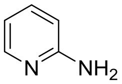
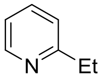
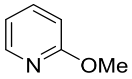
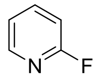
According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), NaOAc (5 mol %), AcOH (10 mol %), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 1990 µL toluene and 10 µL H_2O. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard. After 24 h, a yield of 83 ± 3 was obtained, while elongated reaction times afforded 85 ±2 % (72 h) of **2**, as determined by calibrated GC yield.

2.13.6 L-type Additive Study in NaOAc/AcOH (5 mol % : 10 mol %) buffer with 10 µL H_2O

According to general procedure A, [Cp*IrCl$_2$]$_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), NaOAc (5 mol %), AcOH (10 mol %), additive (2.0 mol %; see Table 20), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 1990 µL toluene and 10 µL H_2O for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 20. L-type additive study in NaOAc/AcOH 1:2 buffer with 10 µL H_2O. Conditions: [Cp*IrCl$_2$]$_2$ (2.0 µmol, 2.0 mol % [Ir]), additive (2.0 mol %), NaOAc (5 mol %), AcOH (10 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (1990 µL), H_2O (10 µL), 100 °C, 24 h.

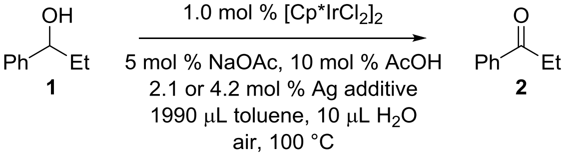


Additive	% GC Yield of **2** (24 h)
none	83 ± 3
	49 ± 4
	63 ± 1
	67 ± 4
	72 ± 7
	72 ± 1
HNEt$_2$	72 ± 1
^{t}BuNH$_2$	61 ± 4
HN^{i}Pr$_2$	57 ± 3
H$_2$NPh	72 ± 2

2.13.7 Ag Additive Study in NaOAc/AcOH (5 mol % : 10 mol %) buffer with 10 µL H_2O

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 2.0 mol % [Ir]), NaOAc (5 mol %), AcOH (10 mol %), Ag additive (2.1 or 4.2 mol %; see Table 21), and **1** (0.20 mmol, 1.0 equiv.) were reacted in 1990 µL toluene and 10 µL H_2O for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 21. Ag additive study in NaOAc/AcOH 1:2 buffer with 10 µL H_2O. Conditions: $[Cp^*IrCl_2]_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), Ag additives (2.1 or 4.2 mol %), NaOAc (5 mol %), AcOH (10 mol %), 1-phenyl-1-propanol (**1**) (0.20 mmol, 1.0 equiv.), toluene (1990 µL), H_2O (10 µL), 100 °C, 24 h.



Ag additive (2.1 or 4.2 mol %)	% GC Yield of **2** (24 h)
none	83 ± 3
AgOTf (4.2 mol %)	41 ± 2
$AgPF_6$ (4.2 mol %)	60 ± 2
Ag_2SO_4 (2.1 mol %)	52 ± 2
$AgNO_3$ (4.2 mol %)	62 ± 1
AgCl (4.2 mol %)	64 ± 0

2.14 Maximizing the TON: Catalysis at 0.1 mol % Catalyst Loading

0.2 mg of $[Cp^*IrCl_2]_2$ (0.16 mg, 0.2 µmol, 0.1 mol %; 0.2 mol % [Ir]), NaOAc (0.8 mg, 10 µmol, 5 mol %), AcOH (1.2 µL, 1.3 mg, 20 µmol, 10 mol %), 1990 µL toluene, 10 µL H_2O, and **1** (0.20 mmol, 1.0 equiv.) were added to a 20 mL scintillation vial, equipped with a Teflon-coated stirbar. The vial was sealed with a Teflon-lined cap and heated to 100 °C on a pre-heated vial plate under vigorous stirring (1500 rpm). After the reaction time was completed (24 or 72 h) the vial was taken off the heating block and the mixture was allowed to cool to room temperature. 100 µL (corresponding to 80 µmol, 8.6 mg, 0.40 equiv. of *p*-xylene) of a standard solution of *p*-xylene (1.00 mL, 0.861 g, 8.10 mmol) in 10 mL toluene were added as internal GC-standard and the yield of **2** was determined by calibrated GC analysis.

Reaction Time	% GC Yield of **2**	TON with respect to $[Cp^*IrCl_2]_2$[7]
24 h	11 ± 3	110
72 h	27 ± 2	270

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[7] The turnover numbers were calculated based on $[Cp^*IrCl_2]_2$ in order to achieve comparability to the TONs calculated by Ison and coworkers in: Jiang, B.; Feng, Y.; Ison, E. A., *J. Am. Chem. Soc.* **2008,** *130* (44), 14462-14464.

2.15 Preparation of $Cp^*Ir(H_2O)_3(OTf)_2$ and Catalysis under Optimized Conditions

2.15.1 Preparation

$Cp^*Ir(H_2O)_3(OTf)_2$ was prepared from $[Cp^*IrCl_2]_2$ (300 mg, 377 µmol, 1.00 equiv.; 2.00 equiv. [Ir]) and AgOTf (387 mg, 1.51 µmol, 4.00 equiv.), according to a literature procedure.[8] After 3 h stirring at room temperature under N_2 in CH_2Cl_2, the yellow suspension was filtered under N_2 through a plug of celite. The yellow filtrate was removed from the glove box and degassed, deionized water (41 µl, 2.3 mmol, 6.0 eq) was added to obtain a precipitate of $Cp^*Ir(H_2O)_3(OTf)_2$. After letting the suspension stand overnight, the supernatant solution was decanted and the precipitate was dried under vacuum. In order to further purify the obtained solid, the yellow powder was redissolved in THF. A suspension was observed, indicating the presence of salt impurities insoluble in THF. Thus, the suspension was filtered through a plug of celite. THF was removed from the filtrate under reduced pressure to obtain $Cp^*Ir(H_2O)_3(OTf)_2$ (165 mg, 243.0 µmol, 32.3 %).

^1H and ^{13}C NMR spectra of the compound were in agreement with the literature values.

2.15.2 Catalysis

According to general procedure A, $Cp^*Ir(H_2O)_3(OTf)_2$ (2.72 mg, 4.0 µmol, 2.0 mol %), NaOAc (5 mol %), AcOH (10 mol %), and **1** (0.20 mmol, 1.0 equiv.) were reacted in a mixture of toluene (1990 µL) and H_2O (10 µL) for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard, resulting in 7 ± 1% yield after 2 h and 19 ± 2% yield of ketone **2** after 24 h, respectively.

2.16 Substrate scope

According to general procedure A, $[Cp^*IrCl_2]_2$ (1.6 mg, 2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), NaOAc (5 mol %), AcOH (10 mol %), and the respective alcohol substrate (0.20 mmol, 1.0 equiv.; see

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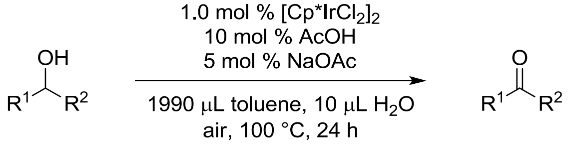
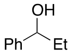
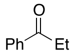
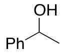
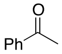
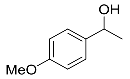
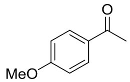
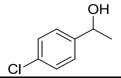
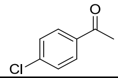
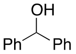
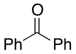
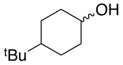
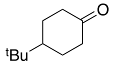
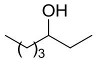
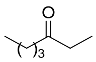
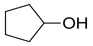
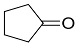
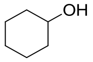
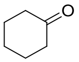
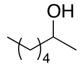
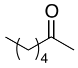
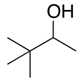
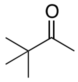
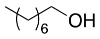
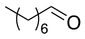
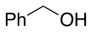
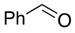
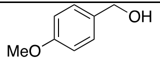
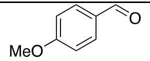
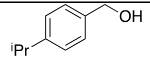
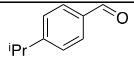
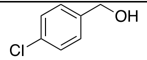
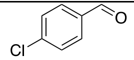
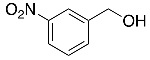
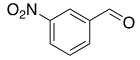
[8] (a) Ogo, S.; Makihara, N.; Watanabe, Y., *Organometallics* **1999,** *18*, 5470-5474; (b) Cayemittes, S.; Poth, T.; Fernandez, M. J.; Lye, P. G.; Becker, M.; Elias, H.; Merbach, A. E., *Inorg. Chem.* **1999,** *38*, 4309-4316.

Table 22) were reacted in a mixture of toluene (1990 μL) and H_2O (10 μL) for 24 h. Workup and analysis were performed as described above in general procedure A, using *p*-xylene as GC-standard.

Table 22. Substrate scope of air oxidation. Conditions: [Cp*IrCl$_2$]$_2$ (2.0 µmol, 1.0 mol %; 2.0 mol % [Ir]), NaOAc (5 mol %), AcOH (10 mol %), alcohol substrate (0.20 mmol, 1.0 equiv.), toluene (1990 µL), H$_2$O (10 µL), 100 °C, 24 h.



Substrate	Product	% GC Yield Product (24 h)	TON (24 h)
		83 ± 3	83
		75 ± 2	75
		83 ± 2	83
		38 ± 1	38
		50 ± 5	50
		53 ± 4	53
		87 ± 1	87
		77 ± 3	77
		59 ± 2	59
		72 ± 2	72
		38 ± 1	38
		3 ± 0	3
		34 ± 4	34
		24 ± 3	24
		23 ± 0	23
		23 ± 1	23
		12 ± 0	12