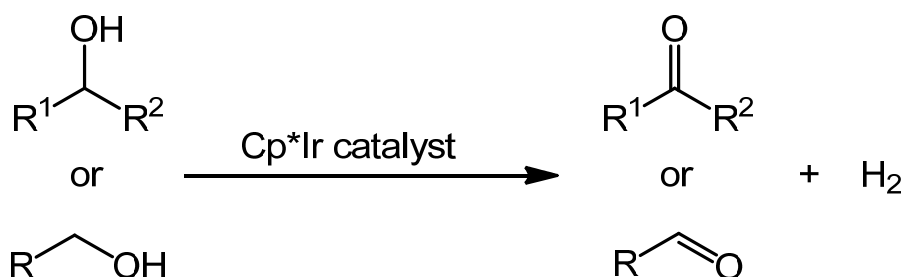


Iridium Catalysts for Oxidation of Alcohols



Kanto Reagents

Oxidation of alcohols is one of the most important reactions in organic syntheses. And the mild and less-toxic reaction systems are required. We Kanto Chemical launched Ir catalysts developed by Emeritus Prof. Ryohei Yamaguchi and Prof. Ken-ichi Fujita of Kyoto University. These Ir catalysts oxidize the primary and secondary alcohols without oxidants, leading to aldehydes and ketones effi-

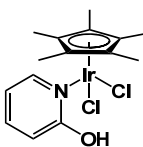
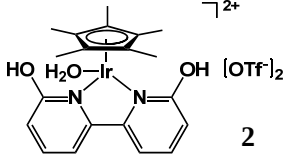
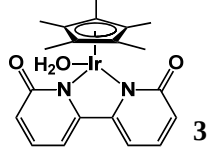


Advantages of this reaction

- No oxidants required
- Cp*Ir Catalyst 2 can be recycled
- Reactions under neutral conditions
- Mild reaction conditions with Cp*Ir Catalyst 3
- High catalytic activities
- Reactions in the air with Cp*Ir Catalyst 2, 3

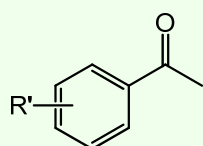
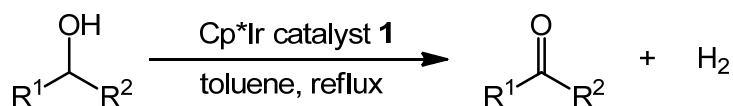


List of products

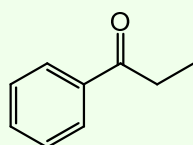
Product	Product number	Package
2-Hydroxy-N-pyridine(pentamethylcyclopentadienyl)iridium(III) dichloride [Dichloro(2-hydroxypyridine)(pentamethylcyclopentadienyl)iridium(III)] FW: 493.45 CAS: 923298-53-7	18017-68	100 mg
 1	18017-65	1 g
Aqua(6,6'-dihydroxy-2,2'-bipyridine)(pentamethylcyclopentadienyl)iridium(III) bis(triflate) FW: 831.78 CAS: 1360870-69-4	01062-68	100 mg
 2	01062-95	500 mg
Aqua(2,2'-bipyridine-6,6'-dionato)(pentamethylcyclopentadienyl)iridium(III) FW: 531.63 CAS: 1436571-06-0	01063-68	100 mg
 3	01063-95	500 mg



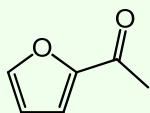
Kanto Kagaku

Preparation of ketones with Cp*Ir Catalyst 1¹⁾

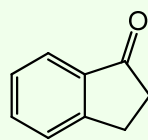
R'	cat. (mol % Ir)	time (h)	yield (%)
H	0.20	20	95
4-Me	0.20	20	82
4-OMe	0.20	20	94
4-Cl	0.20	20	81
4-Br	0.20	50	82
4-NO ₂	0.33	50	86
2-Me	0.20	20	89
3-Me	0.20	20	75



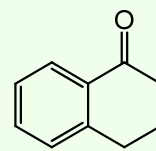
0.20 mol % Ir
92% yield
(20 h)



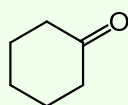
1.0 mol % Ir
76% yield
(50 h)



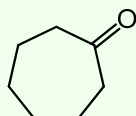
0.20 mol % Ir
97% yield
(20 h)



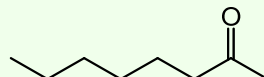
1.0 mol % Ir
86% yield
(50 h)



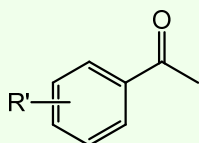
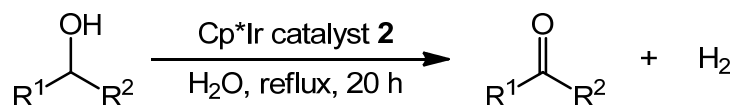
1.0 mol % Ir
85% yield
(50 h)



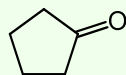
0.20 mol % Ir
92% yield
(20 h)



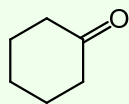
0.33 mol % Ir
93% yield
(50 h)

Preparation of ketones with Cp*Ir Catalyst 2²⁾

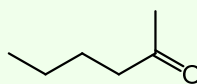
R'	cat. (mol % Ir)	yield (%)
H	1.0	92
4-OMe	1.0	98
2-OMe	1.0	86
4-Cl	1.0	92
4-Br	1.0	92
4-NO ₂	2.0	91



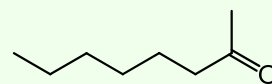
1.0 mol % Ir
86% yield



2.0 mol % Ir
80% yield



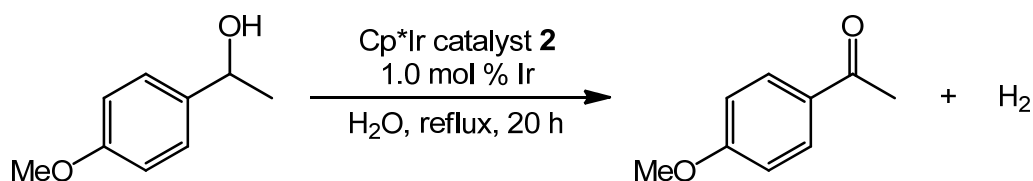
2.5 mol % Ir
82% yield



3.0 mol % Ir
85% yield



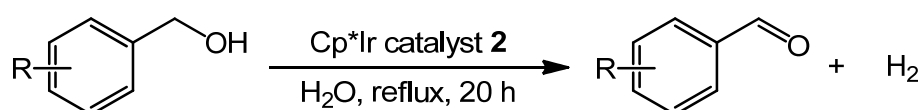
Preparation of ketones with Cp*Ir Catalyst 2 (repeated reactions with the recycled catalyst)²⁾



reuse	1	2	3	4	5	6	7	8
yield (%)	98	97	96	95	95	96	95	94



Preparation of aldehydes with Cp*Ir Catalyst 2²⁾

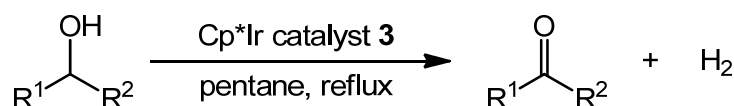


R	cat. (mol % Ir)	yield (%)
H	1.5	92
4-OMe	1.5	93
2-Me	2.5	91
3-Me	1.5	86
4-Me	1.5	94

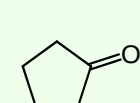
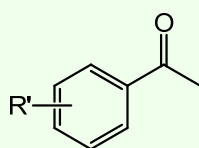
R	cat. (mol % Ir)	yield (%)
4-Cl	2.0	92
4-Br	2.0	93
4-CF ₃	3.0	88
4-CO ₂ Me	3.0	77



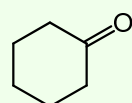
Preparation of ketones with Cp*Ir Catalyst 3³⁾



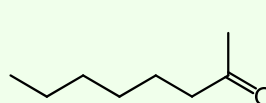
R'	cat. (mol % Ir)	time (h)	yield (%)
H	0.5	5	100
4-OMe	0.5	5	100
2-OMe	1.0	5	92
4-Cl	1.0	5	92
4-Br	1.0	5	90
4-NO ₂	2.0	20	85



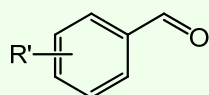
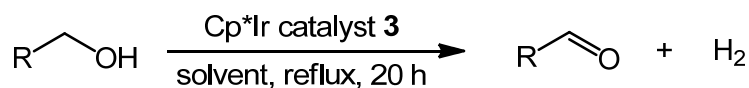
2.0 mol % Ir
93% yield
(20 h)



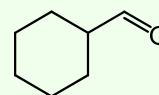
2.0 mol % Ir
82% yield
(20 h)



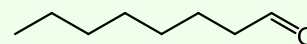
3.0 mol % Ir
80% yield
(20 h)

Preparation of aldehydes with Cp*Ir Catalyst **3**³⁾

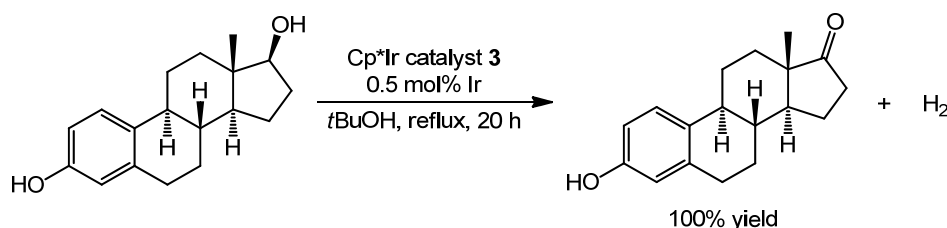
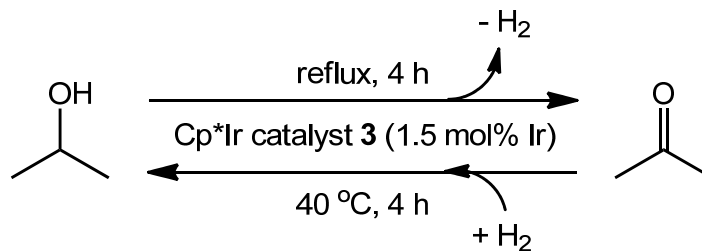
R'	cat. (mol % Ir)	solvent	yield (%)
H	1.5	<i>t</i> BuOH	92
4-OMe	1.5	<i>t</i> BuOH	98
2-Me	2.5	<i>t</i> BuOH	85
3-Me	1.5	<i>t</i> BuOH	91
4-Me	1.5	<i>t</i> BuOH	96
4-Cl	1.5	<i>t</i> BuOH	90
4-Br	1.5	<i>t</i> BuOH	88
4-CF ₃	3.0	heptane	88
4-CO ₂ Me	5.0	<i>t</i> BuOH	80
4-OH	1.0	toluene	79
4-Ph	1.5	<i>t</i> BuOH	93



2.5 mol % Ir
81% yield
(toluene)



5.0 mol % Ir
87% yield
(toluene)

Preparation of estrone with Cp*Ir Catalyst **3**³⁾Application to the hydrogen storage system with Cp*Ir Catalyst **3**³⁾

References

- 1)Fujita, K.; Tanino, N.; Yamaguchi, R. *Org. Lett.* **2007**, 9, 109.
- 2)Kawahara, R.; Fujita, K.; Yamaguchi, R. *J. Am. Chem. Soc.* **2012**, 134, 3643.
- 3)Kawahara, R.; Fujita, K.; Yamaguchi, R. *Angew. Chem. Int. Ed.* **2012**, 51, 12790.



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