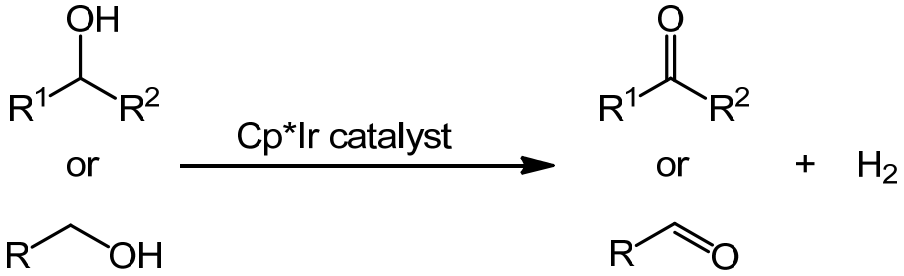
Iridium Catalysts for Oxidation of Alcohols

Kanto Reagents

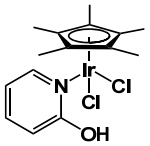
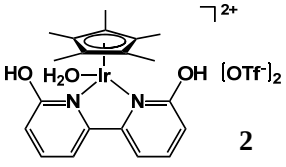
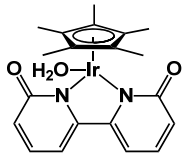
Oxidation of alcohols is one of the most important reactions in organic syntheses. And the mild and less-toxic reaction systems are required. We Kanto Chemical launched Ir catalysts developed by Emeritus Prof. Ryohei Yamaguchi and Prof. Ken-ichi Fujita of Kyoto University. These Ir catalysts oxidize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



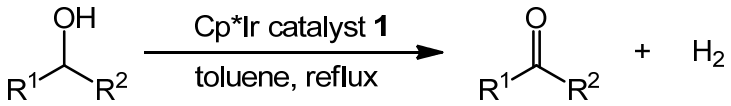
Advantages of this reaction

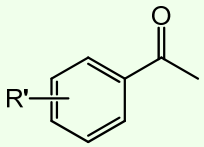
- ●No oxidants required
- ●Reactions under neutral conditions
- ●High catalytic activities
- ●Cp*Ir Catalyst **2** can be recycled
- ●Mild reaction conditions with Cp*Ir Catalyst **3**
- ●Reactions in the air with Cp*Ir Catalyst **2**, **3**

List of products

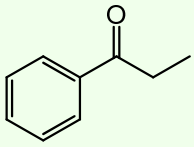
Product	Product number	Package
2-Hydroxy-*N*-pyridine(pentamethylcyclopentadienyl)iridium(Ⅲ) dichloride [Dichloro(2-hydroxypyridine)(pentamethylcyclopentadienyl) iridium(III)] **FW：493.45　CAS：923298-53-7**  **1**	**18017-68**	**100 mg**
	18017-65	**1 g**
Aqua(6,6'-dihydroxy-2,2'-bipyridine)(pentamethylcyclopentadienyl)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

Preparation of ketones with Cp*Ir Catalyst **1**[1)]

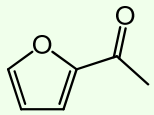




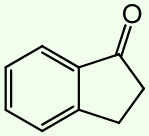
R'	cat. (mol % Ir)	time (h)	yield (%)
H	0.20	20	95
4-Me	0.20	20	82
4-OMe	0.20	20	94
4-Cl	0.20	20	81
4-Br	0.20	50	82
4-NO_2	0.33	50	86
2-Me	0.20	20	89
3-Me	0.20	20	75



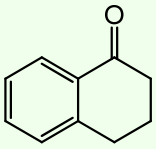
0.20 mol % Ir
92% yield
(20 h)



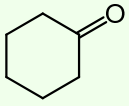
1.0 mol % Ir
76% yield
(50 h)



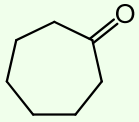
0.20 mol % Ir
97% yield
(20 h)



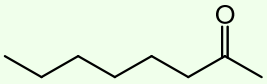
1.0 mol % Ir
86% yield
(50 h)



1.0 mol % Ir
85% yield
(50 h)

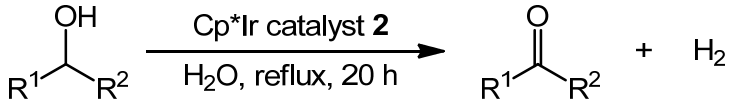


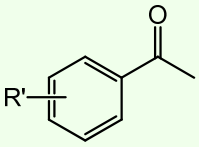
0.20 mol % Ir
92% yield
(20 h)



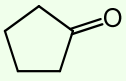
0.33 mol % Ir
93% yield
(50 h)

Preparation of ketones with Cp*Ir Catalyst **2**[2)]

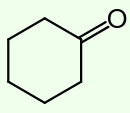




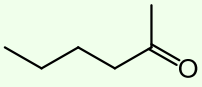
R'	cat. (mol % Ir)	yield (%)
H	1.0	92
4-OMe	1.0	98
2-OMe	1.0	86
4-Cl	1.0	92
4-Br	1.0	92
4-NO_2	2.0	91



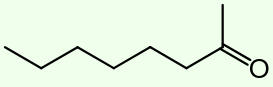
1.0 mol % Ir
86% yield



2.0 mol % Ir
80% yield

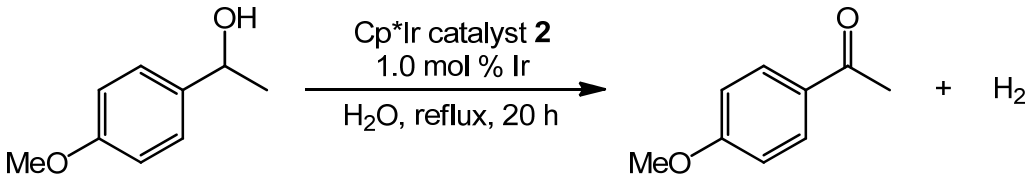


2.5 mol % Ir
82% yield



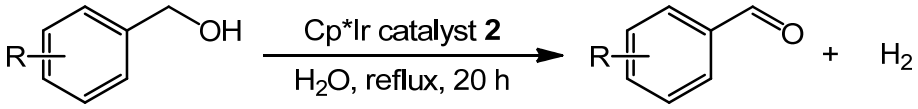
3.0 mol % Ir
85% yield

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

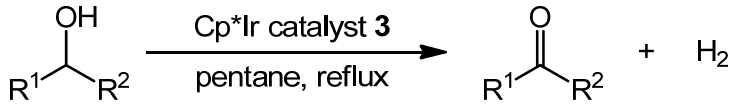
Preparation of aldehydes with Cp*Ir Catalyst **2**[2)]

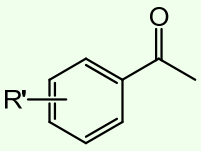


R	cat. (mol % Ir)	yield (%)
H	1.5	92
4-OMe	1.5	93
2-Me	2.5	91
3-Me	1.5	86
4-Me	1.5	94

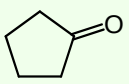
R	cat. (mol % Ir)	yield (%)
4-Cl	2.0	92
4-Br	2.0	93
4-CF_3	3.0	88
4-CO_2Me	3.0	77

Preparation of ketones with Cp*Ir Catalyst **3**[3)]

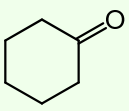




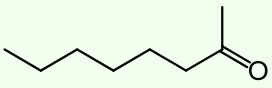
R'	cat. (mol % Ir)	time (h)	yield (%)
H	0.5	5	100
4-OMe	0.5	5	100
2-OMe	1.0	5	92
4-Cl	1.0	5	92
4-Br	1.0	5	90
4-NO_2	2.0	20	85



2.0 mol % Ir
93% yield
(20 h)

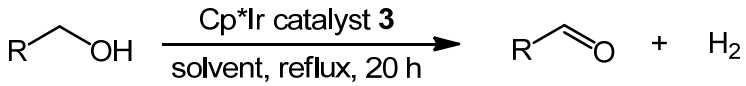


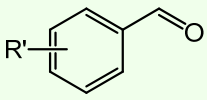
2.0 mol % Ir
82% yield
(20 h)



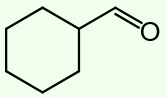
3.0 mol % Ir
80% yield
(20 h)

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

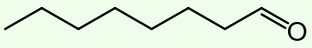




R'	cat. (mol % Ir)	solvent	yield (%)
H	1.5	*t*BuOH	92
4-OMe	1.5	*t*BuOH	98
2-Me	2.5	*t*BuOH	85
3-Me	1.5	*t*BuOH	91
4-Me	1.5	*t*BuOH	96
4-Cl	1.5	*t*BuOH	90
4-Br	1.5	*t*BuOH	88
4-CF_3	3.0	heptane	88
4-CO_2Me	5.0	*t*BuOH	80
4-OH	1.0	toluene	79
4-Ph	1.5	*t*BuOH	93

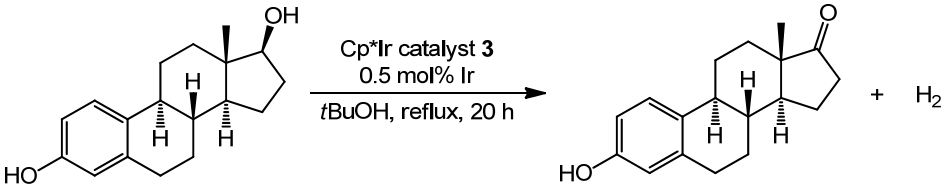


2.5 mol % Ir
81% yield
(toluene)



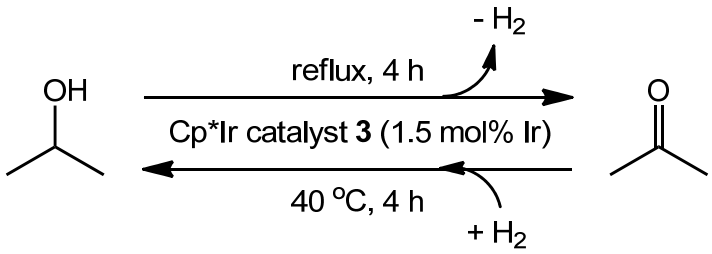
5.0 mol % Ir
87% yield
(toluene)

Preparation of estrone with Cp*Ir Catalyst **3**[3)]



100% yield

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.

KANTO CHEMICAL CO., INC.
REAGENT DIVISION
East Muromachi Mitsui BLDG, 2-1, Nihonbashi Muromachi 2-chome,
Chuo-ku, Tokyo, 103-0022 JAPAN
Telephone +813-6214-1092
Telefax +813-3241-1053
http://www.kanto.co.jp E-mail;kanto-61@gms.kanto.co.jp