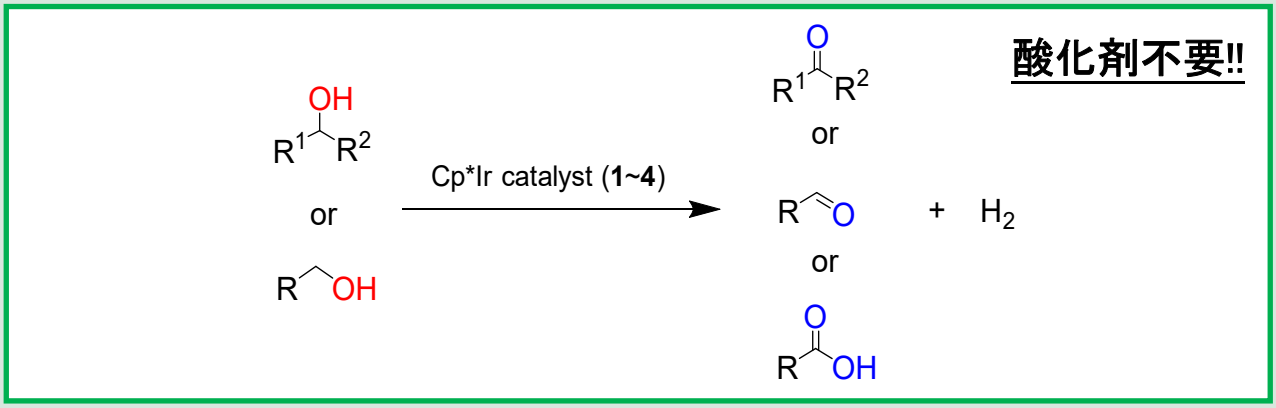
酸化反応用Ir触媒 ver.2

For oxidation of alcohols

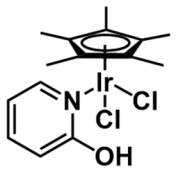
アルコールの酸化反応

– アルデヒド、ケトン、カルボン酸 –

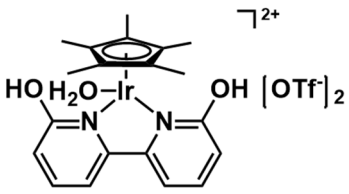


アルコールの酸化反応は有機合成化学において最も重要な反応の1つであり、穏和で毒性の少ない反応系が求められております。弊社では京都大学 山口良平名誉教授、藤田健一教授らによって開発されました、酸化反応用Ir触媒を販売しております。これらは、酸化剤を使用せずに**第一級、第二級アルコールを酸化**し、対応する**アルデヒド**、**ケトン**化合物へ高効率に分子変換します。この度、新製品として**カルボン酸**へ分子変換できる触媒を新たに追加販売いたしました。貴社の製品開発における合成ツールの1つとしてご活用ください。

特長



1



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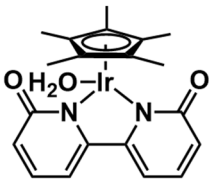

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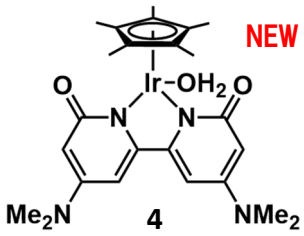


4

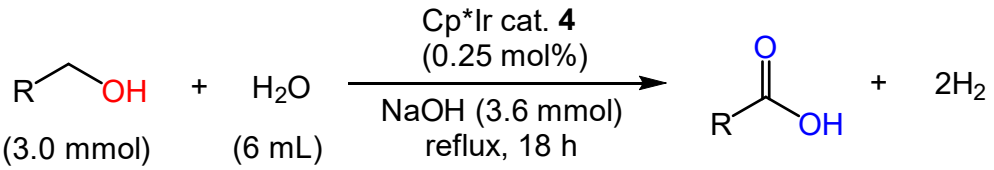
Cp*Ir cat. 1	ケトン合成用、中性条件下でも反応進行、安価
Cp*Ir cat. 2	ケトン、アルデヒド合成用 中性条件、空気雰囲気下で反応可能 触媒の再利用可能(触媒が水溶性)
Cp*Ir cat. 3	ケトン、アルデヒド合成用 中性条件、空気雰囲気下で反応可能 Cp*Ir cat. 1、2と比べ高活性(約100倍)
NEW Cp*Ir cat. 4	カルボン酸合成用、塩基性、水系条件

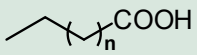
関東化学株式会社

Synthesis of carboxylic acids

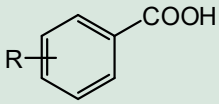
Cp*Ir catalyst 4[1)]

NEW ■ 第一級アルコールから塩基性条件（約0.6M水酸化ナトリウム溶液）でカルボン酸を得られます。





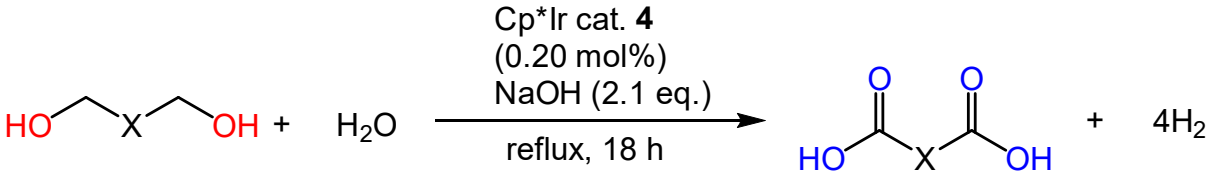
n	yield (%)
0	96
1	71
5	83



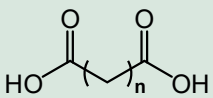
R	yield (%)
4-Me	94
4-OMe	96
4-CF_3	98
4-F	94
4-Cl	100

Cp*Ir catalyst 4[2)]

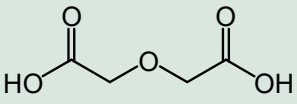
NEW ■ ジオール水溶液から高収率でジカルボン酸へと変換されます。



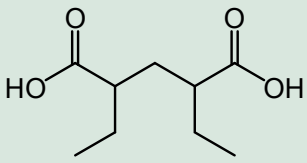
X = alkyl, aryl, amine



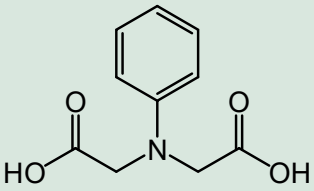
n	yield (%)
3	98
4	97
5	97
6	97



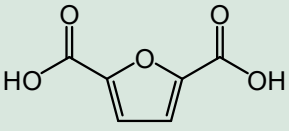
90% yield



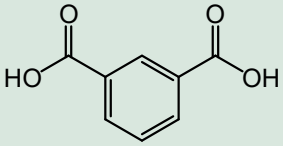
94% yield



93% yield



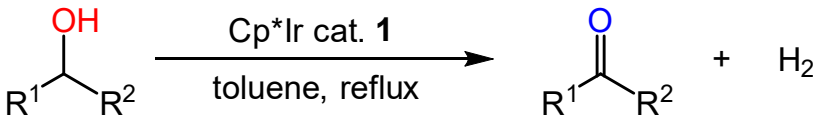
88% yield

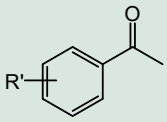


97% yield

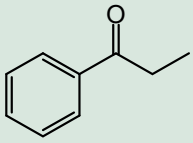
Synthesis of ketones

Cp*Ir catalyst 1[3)]

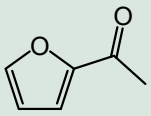




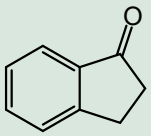
R'	cat. (mol%)	time (h)	yield (%)
H	0.20	20	95
4-Me	0.20	20	82
4-OMe	0.20	20	94
4-Cl	0.20	20	81
4-Br	0.20	50	82
4-NO_2	0.33	50	86
2-Me	0.20	20	89
3-Me	0.20	20	75



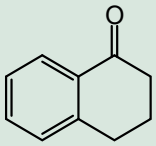
0.20 mol%
92% yield
(20 h)



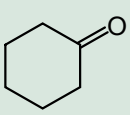
1.0 mol%
76% yield
(50 h)



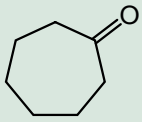
0.20 mol%
97% yield
(20 h)



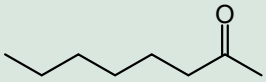
1.0 mol%
86% yield
(50 h)



1.0 mol%
85% yield
(50 h)



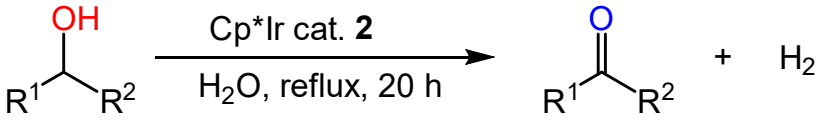
0.20 mol%
92% yield
(20 h)

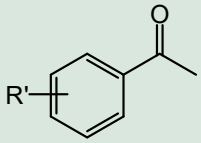


0.33 mol%
93% yield
(50 h)

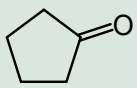
Cp*Ir catalyst 2[4)]

■ 水溶液中で反応が進行いたします。

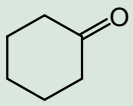




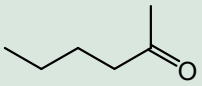
R'	cat. (mol%)	yield (%)
H	1.0	92
4-OMe	1.0	98
2-OMe	1.0	86
4-Cl	1.0	92
4-Br	1.0	92
4-NO_2	2.0	91



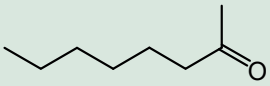
1.0 mol%
86% yield



2.0 mol%
80% yield



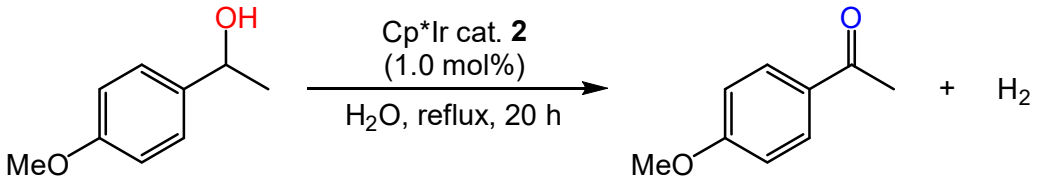
2.5 mol%
82% yield



3.0 mol%
85% yield

Cp*Ir catalyst 2　※繰り返し反応[4)]

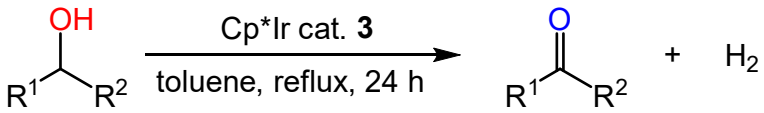
■ 触媒が水溶性のため水層に担持、有機溶媒で洗浄することにより反応を複数回行うことが可能です。

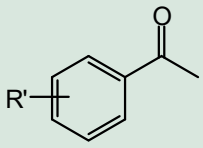


reuse	1	2	3	4	5	6	7	8
yield (%)	98	97	96	95	95	96	95	94

Cp*Ir catalyst 3[5),6)]

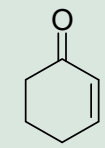
■ 低触媒量でケトンへの分子変換が可能です。



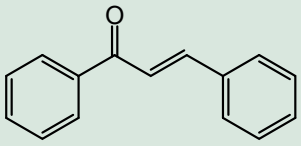


R'	cat. (mol%)	yield (%)
H	0.01	>99
4-OMe	0.01	97
2-Br	1.0	97
3-Br	0.05	83
4-Br	0.01	>99

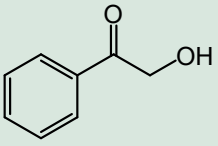
R'	cat. (mol%)	yield (%)
2-F	0.01	84
4-F	0.01	99
4-NO_2	0.01	78
4-NH_2	1.0	>99
3-OH	0.01	97



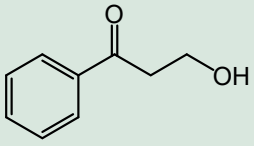
0.01 mol%
97% yield
(3 h)



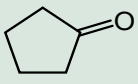
0.1 mol%
95% yield
(MEK 1 h)



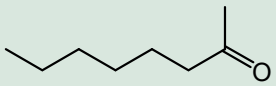
1.0 mol%
81% yield
(acetone, 24 h)



1.0 mol%
96% yield



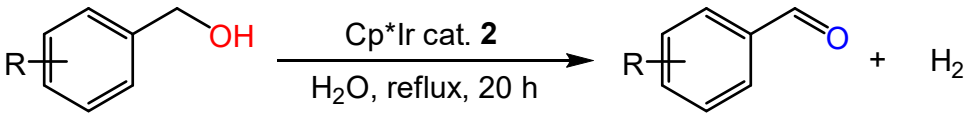
0.01 mol%
>99% yield



3.0 mol%
80% yield
(pentane, 20 h)

Synthesis of aldehydes

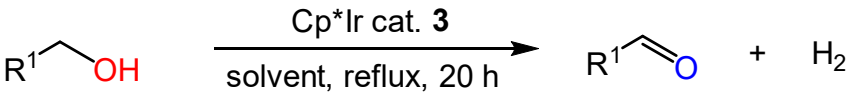
Cp*Ir catalyst 2[4)]

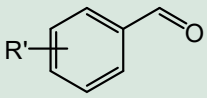


R	cat. (mol%)	yield (%)
H	1.5	92
4-OMe	1.5	93
2-Me	2.5	91
3-Me	1.5	86
4-Me	1.5	94

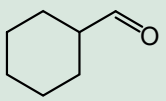
R	cat. (mol%)	yield (%)
4-Cl	2.0	92
4-Br	2.0	93
4-CF_3	3.0	88
4-CO_2Me	3.0	77

Cp*Ir catalyst 3[5)]

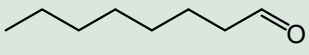




R'	cat. (mol%)	solvent	yield (%)
H	1.5	*t*BuOH	92
4-OMe	1.5	*t*BuOH	98
2-Me	2.5	*t*BuOH	85
3-Me	1.5	*t*BuOH	91
4-Me	1.5	*t*BuOH	96
4-Cl	1.5	*t*BuOH	90
4-Br	1.5	*t*BuOH	88
4-CF_3	3.0	heptane	88
4-CO_2Me	5.0	*t*BuOH	80
4-OH	1.0	toluene	79
4-Ph	1.5	*t*BuOH	93

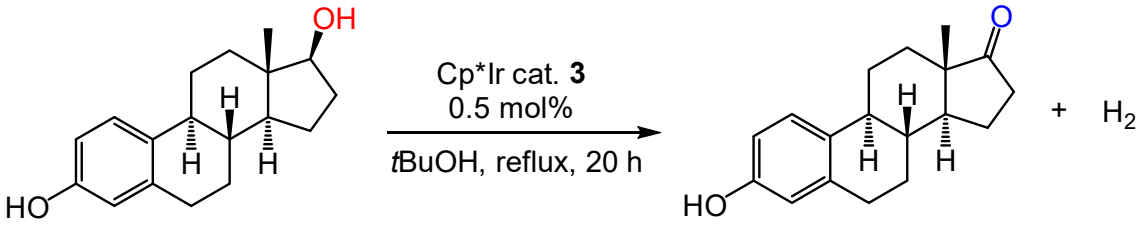


2.5 mol%
81% yield
(toluene)



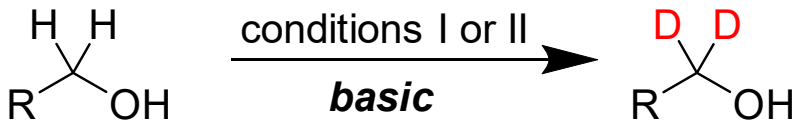
5.0 mol%
87% yield
(toluene)

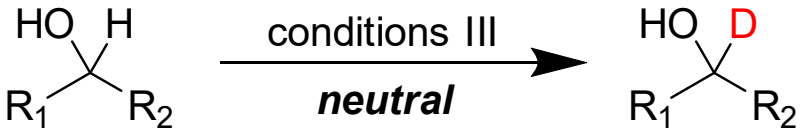
エストロンの合成（Cp*Ir catalyst 3）[5)]



100% yield

NEW アルコール類のα位重水素化（Cp*Ir catalyst 3）[7]



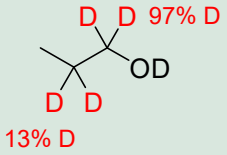


Conditions I:
Cp*Ir cat. **3** (1 mol%), NaOD (3 mol%)
2-propanol (10 mol%)
D_2O (0.5 M), 80 ℃

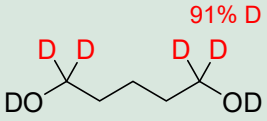
Conditions II:
Cp*Ir cat. **3** (1 mol%), NaOD (3 mol%)
2-propanol (10 mol%)
D_2O/CD_3OD (1:1) (0.5 M), 80 ℃

Conditions III:
Cp*Ir cat. **3** (1 mol%)
2-propanol (10 mol%)
D_2O/CD_3OD (1:1) (0.5 M), 80 ℃

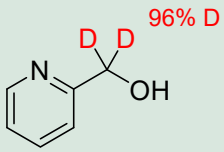
Primary alcohols



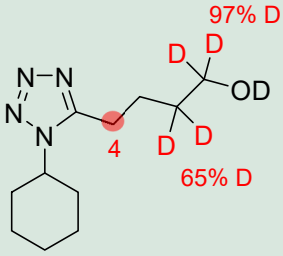
cond. I, 7 h, 95% yield



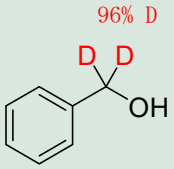
cond. I, 1 d, >99% yield



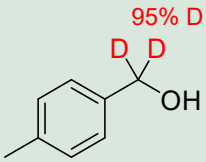
cond. I, 5 h, 81% yield



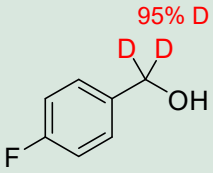
cond. II, 2 d, 91% yield[a]



cond. II, 7 h, 91% yield

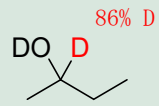


cond. II, 7 h, 92% yield

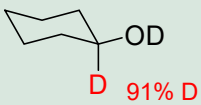


cond. II, 7 h, quant.

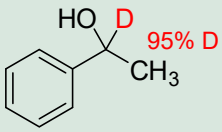
Secondary alcohols



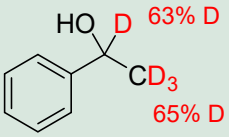
cond. III, 5 d,
94% yield in CD_3OD



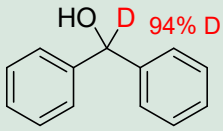
cond. III, 2 d,
>99% yield in CD_3OD



cond. III, 21 h,
84% yield
neutral (run1)

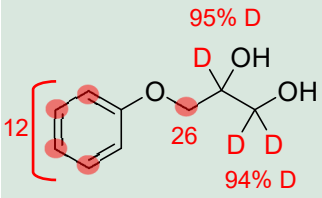


cond. II, 21 h,
79% yield
weakly basic (run2)

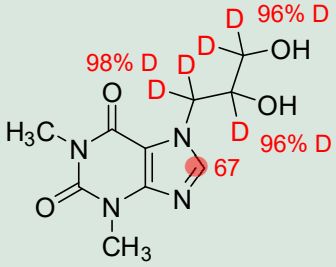


cond. III, 2 d,
98% yield in CD_3OD

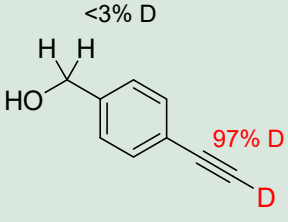
Pharmaceuticals and Alkyne deuteration



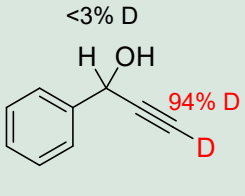
Guaifenesin-d_4
cond. I, 1 d, 75% yield[b]



Diprophyline-d_6
cond. I, 1 d, 37% yield[c]



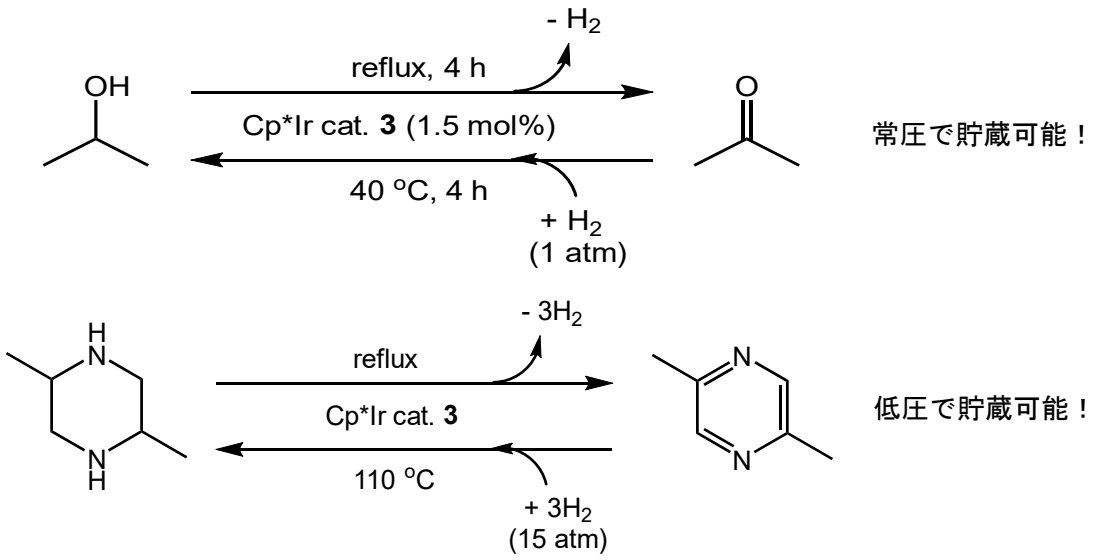
cond. III, 3 h,
90% yield



cond. III, 1 d,
89% yield

[a]Cp*Ir cat. **3** (5 mol%), NaOD (15 mol%), 0.1 M, 100 ℃. [b]Cp*Ir cat. **3** (5 mol%), NaOD (15 mol%), 100 ℃.
[c]Low isolated yield due to high hydrophilicity.

水素貯蔵システムへの応用（Cp*Ir catalyst 3）[8)]



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4) R. Kawahara, K. Fujita, R. Yamaguchi, *J. Am. Chem. Soc*. **134**(8), 3643-3646 (2012).

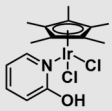
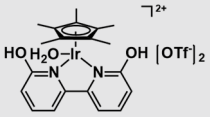
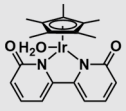
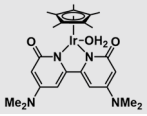
5) R. Kawahara, K. Fujita, R. Yamaguchi, *Angew. Chem. Int. Ed*. **51**(51), 12790-12794 (2012).

6) 日本プロセス化学会　2014 サマーシンポジウム　2P-43.

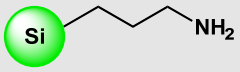
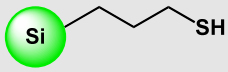
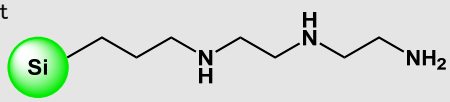
7) M. Itoga, M. Yamanishi, T. Udagawa A. Kobayashi, K. Maekawa, Y. Takemoto, H. Naka, *Chem.Sci.* **13**(30), 8744-8751 (2022).

8) 藤田健一, 有機合成化学協会誌, **77**(2), 112-119 (2019).

製品リスト

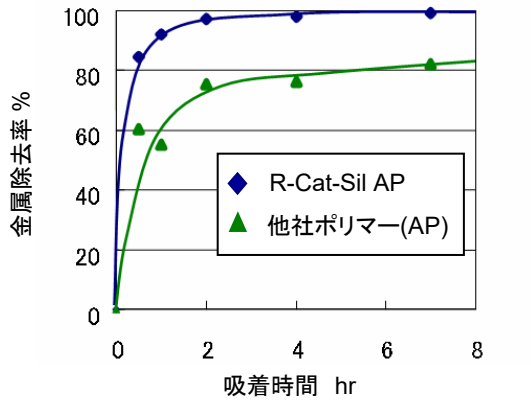
製品名	製品番号	包装	価格（¥）
2-ヒドロキシ-N-ピリジン（ペンタメチルシクロペンタジエニル）イリジウム（Ⅲ）ジクロリド 略称　：　Cp*Ir Catalyst **1** CAS RN®：　923298-53-7 	18017-68 18017-65	100 mg 1 g	7,000 29,500
アクア（6,6'-ジヒドロキシ-2,2'-ビピリジン）（ペンタメチルシクロペンタジエニル）イリジウム（Ⅲ）ビス（トリフラート） 略称　：　Cp*Ir Catalyst **2** CAS RN®：　1360870-69-4 	01062-68 01062-95	100 mg 500 mg	11,500 31,500
アクア（2,2'-ビピリジン-6,6'-ジオナト）（ペンタメチルシクロペンタジエニル）イリジウム（Ⅲ） 略称　：　Cp*Ir Catalyst **3** CAS RN®：　1436571-06-0 	01063-68 01063-95	100 mg 500 mg	12,500 40,000
アクア[4,4'-ビス（ジメチルアミノ）-2,2'-ビピリジン-6,6'-ジオナト]（ペンタメチルシクロペンタジエニル）イリジウム（Ⅲ） 略称　：　Cp*Ir Catalyst **4** CAS RN®：　2228980-42-3　NEW 	01159-65	500 mg	53,000

関連製品（金属スカベンジャー）

製品名	製品番号	包装	価格（￥）
R-Cat-Sil AP Metals removed ： Pd, Ru, Rh, Co, Cu, Fe, Ni Loading ： 2.0 mmol/g 	36044-55	5 g	6,500
	36044-35	25 g	16,500
	36044-25	100 g	48,000
R-Cat-Sil MP Metals removed ： Pd, Ru, Rh, Cu, Pt, Pb, Ag, Hg Loading ： 1.2 mmol/g 	36045-55	5 g	6,500
	36045-35	25 g	16,500
	36045-25	100 g	48,000
R-Cat-Sil TA Metals removed ： Pd, Rh, Co, Cu, Fe, Zu, Pt Loading ： 1.0 mmol/g 	36046-55	5 g	8,000
	36046-35	25 g	18,500
	36046-25	100 g	55,000

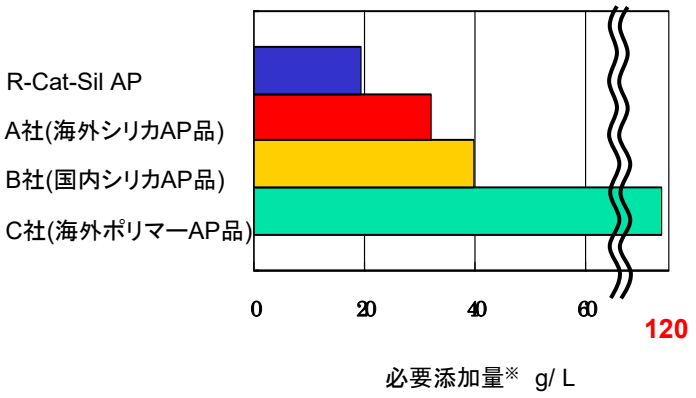
※参考データ　粒子径 ： 50 μm、比表面積 ： 730 m^2/ g

金属吸着速度の比較



Scavenger 添加量：15 g/ L
金属溶液：1000 ppm Pd ($Pd(OAc)_2$ in CH_2Cl_2)

必要添加量の比較



※ Freundlich式より算出したPd濃度を1000 ppmから
0.1 ppmまで 低減する際の必要添加量 ($Pd(OAc)_2$ in CH_2Cl_2)

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