



## Deprotection of dithioacetals with 30% hydrogen peroxide catalyzed by tantalum(V) chloride–sodium iodide or niobium(V) chloride–sodium iodide

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### ABSTRACT

The reaction of dithioacetals with 30% hydrogen peroxide in the presence of catalytic amounts of tantalum(V) and iodide ion effectively produced carbonyl compounds in high yields. Dithioacetals also can be deprotected using the niobium(V) catalyzed oxidation of iodide ion by hydrogen peroxide under mild conditions.

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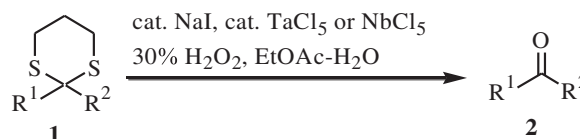
## 1. Introduction

Dithioacetals have been utilized as excellent protecting groups for carbonyl functionalities in organic synthesis due to their stability under both acidic and basic conditions.<sup>1</sup> They are also important synthetic reagents because they can be used as acyl anion equivalents.<sup>2</sup> Although a large number of procedures have been reported on dedithioacetalization,<sup>1,3–5</sup> many of them suffer from drawbacks, such as the use of an excess amount of toxic heavy metals, such as mercury.<sup>4</sup> Recently, hydrogen peroxide mediated deprotections of dithioacetals have been developed by several research groups, because nontoxic water is the sole waste product of these reactions.<sup>5</sup>

We have been working on the development of environmentally benign reactions for organic syntheses using 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>).<sup>6</sup> During the course of these studies, we found that the reaction of dithioacetals with hydrogen peroxide in the presence of catalytic amounts of tantalum(V) chloride (TaCl<sub>5</sub>) and sodium iodide (NaI) produced the corresponding carbonyls in high yields, the results of which were reported as a preliminarily communication.<sup>6b</sup>

This paper further describes the details of the deprotection of dithioacetals using hydrogen peroxide catalyzed by tantalum(V)

and NaI, and also shows that niobium(V) exhibits even greater catalytic activity for this deprotection (Scheme 1).



Scheme 1.

## 2. Tantalum(V) and iodide ion catalyzed deprotection of dithioacetals with 30% hydrogen peroxide

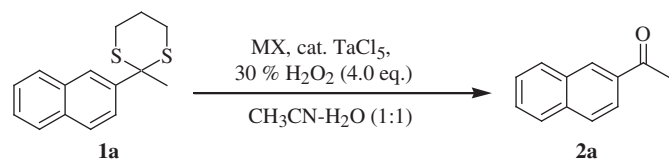
Previously we found that TaCl<sub>5</sub> catalyzed the conversion of the bromide ion (Br<sup>−</sup>) into a bromonium ion (Br<sup>+</sup>) equivalent with H<sub>2</sub>O<sub>2</sub>, and that the reaction is applicable to the electrophilic bromination of organic compounds.<sup>6a</sup> On the other hand, Khan et al. reported that dithioacetals can be deprotected by the vanadium(V) oxide catalyzed oxidation of Br<sup>−</sup> into 'Br<sup>+</sup>' with H<sub>2</sub>O<sub>2</sub>.<sup>5b</sup> The TaCl<sub>5</sub> catalyzed reaction was expected to be an excellent method for the conversion of dithioacetals into the corresponding carbonyl compounds, because the tantalum compounds is nontoxic<sup>7</sup> and hydrogen peroxide produces only water as a waste product after the reaction.

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The dithioacetal (**1a**) prepared from 2-acetonaphthone (**2a**) and 1,3-propanedithiol according to the literature<sup>8</sup> was treated with KBr, catalytic amounts of TaCl<sub>5</sub>, and H<sub>2</sub>O<sub>2</sub> in aqueous acetonitrile at room temperature. Sodium iodide (NaI) was also utilized to examine the effect altering the halogen (Table 1). The desired deprotected product (**2a**) was produced in moderate to high yields (runs 1–4), with the best result obtained when **1a** was reacted with 0.1 equiv of TaCl<sub>5</sub>, 0.1 equiv of NaI, and hydrogen peroxide (run 4). In the absence of TaCl<sub>5</sub>, the reaction did not occur (run 5). The dedithioacetalization also did not occur in the absence of halogen anions (run 6).

**Table 1**

Deprotection of **1a** with 30% hydrogen peroxide in the presence or absence of TaCl<sub>5</sub> and halide ions



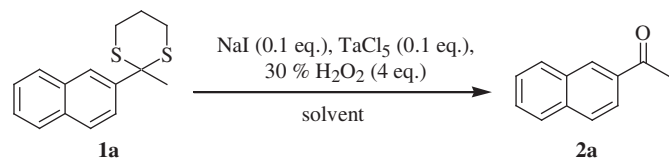
Run	MX (equiv)	Cat. (equiv)	Time (h)	Yield (%)
1	KBr (1.0)	TaCl <sub>5</sub> (0.05)	48	42
2	KBr (1.0)	TaCl <sub>5</sub> (0.1)	19.5	80
3	NaI (1.0)	TaCl <sub>5</sub> (0.05)	25	82
4	<b>NaI (0.1)</b>	<b>TaCl<sub>5</sub> (0.1)</b>	<b>20</b>	<b>93</b>
5	NaI (1.0)	—	90	No reaction
6	—	TaCl <sub>5</sub> (1.0)	20	No reaction

Bold values shows the best result.

The reaction of **1a** with 30% hydrogen peroxide in the presence of 0.1 equiv of TaCl<sub>5</sub> and 0.1 equiv of NaI in various solvents was examined in order to evaluate any solvent effect (Table 2). In a two-phase system using ethyl acetate and water (AcOEt/H<sub>2</sub>O) (run 4), the product (**2a**) was obtained in a high yield with the shortest reaction time.

**Table 2**

Deprotection of **1a** with 30% hydrogen peroxide in the presence of TaCl<sub>5</sub> and NaI in several different solvents



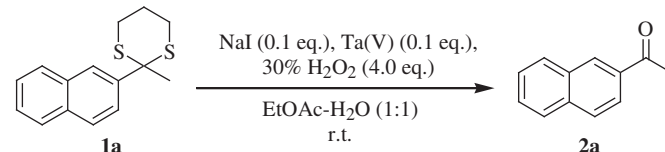
Run	Solvent	Time	Yield (%)
1	CH <sub>3</sub> CN/H <sub>2</sub> O (1:1)	19 h	96
2	CH <sub>3</sub> OH/H <sub>2</sub> O (1:1)	17.5 h	90
3	Acetone/H <sub>2</sub> O (1:1)	3 days	81
4	<b>EtOAc/H<sub>2</sub>O</b>	<b>1 h</b>	<b>95</b>
5	CHCl <sub>3</sub> /H <sub>2</sub> O	9 days	24
6	CH <sub>2</sub> Cl <sub>2</sub> /H <sub>2</sub> O	2 days	74

Bold values shows the best result.

The dithioacetals (**1a**) was treated with 30% hydrogen peroxide, 0.1 equiv of NaI, and 0.1 equiv of several tantalum(V) compounds in AcOEt/H<sub>2</sub>O (1:1, v/v) at room temperature (Table 3). Interestingly, the deprotected compound was obtained in the absence of Ta(V), however, the reaction proceeded very slowly and did not complete in 24 h. Among the tantalum(V) compounds examined, TaCl<sub>5</sub> and tantalum pentaethoxide [Ta(OEt)<sub>5</sub>] exhibited good catalytic activities (runs 1 and 2), whereas tantalum(V) oxide (Ta<sub>2</sub>O<sub>5</sub>) was not effective (run 3).

**Table 3**

Deprotection of **1a** with 30% hydrogen peroxide and NaI in the presence of several Ta(V) compounds



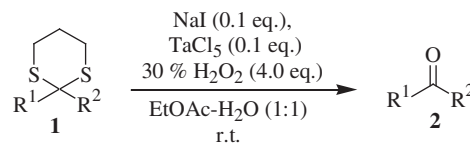
Run	Ta (V)	Time	Yield (%)
<b>1</b>	<b>TaCl<sub>5</sub></b>	<b>1 h</b>	<b>95</b>
2	Ta(OEt) <sub>5</sub>	1.5 h	94
3	Ta <sub>2</sub> O <sub>5</sub>	24 h	21
4	—	24 h	18

Bold values shows the best result.

Based on these results, the deprotection of several dithioacetals (**1**) derived from various ketones with 30% hydrogen peroxide, 0.1 equiv of TaCl<sub>5</sub>, and 0.1 equiv of NaI were further examined in AcOEt/H<sub>2</sub>O (1:1, v/v) at room temperature (Table 4). The corresponding ketones (**2**) were obtained in high yields in most cases. Most of the other functional groups, such as aromatic rings (entries 3–11), the alkene (entry 5), the acetoxy group (entry 7), and the silyloxy group (entry 8), were inert and unaffected under these reaction conditions. The dithioacetal (**1j**) having the tetrahydropyranyl (acetal) group provided the corresponding ketone (**2j**) in 56% yield along with *p*-hydroxyacetophenone (**2g**), which was produced by the further deacetalization of **2g**. Fortunately, the desired compound (**2j**) was quantitatively obtained when a phosphate buffer (pH 7.2) was used as part of the solvent instead of

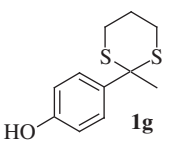
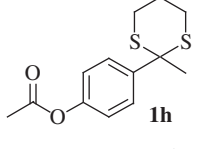
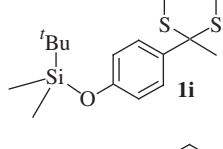
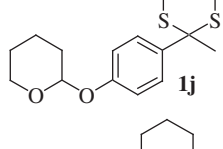
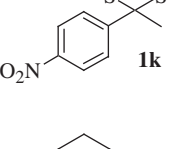
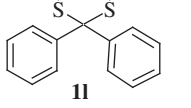
**Table 4**

Deprotection of **1** derived from ketones with 30% hydrogen peroxide catalyzed by TaCl<sub>5</sub> and NaI in ethyl acetate/water



Entry	Starting material	Time (h)	Yield (%)
1	<b>1b</b> (CH <sub>2</sub> ) <sub>8</sub> CH <sub>3</sub>	3.5 h	92
2	<b>1c</b>	5 h	89
3	<b>1d</b>	18 min	quant. <sup>a</sup>
4	<b>1e</b>	2.5 h	91
5	<b>1f</b>	45 min	97

Table 4 (continued)

Entry	Starting material	Time (h)	Yield (%)
6		1 h	quant. <sup>a</sup>
7		1.5 h	94
8		45 min	96
9		30 min 30 min	56 <sup>a</sup> quant. <sup>a,b</sup>
10		24 h	49
11		1.5 h	98 <sup>a</sup>

<sup>a</sup> H<sub>2</sub>O<sub>2</sub> (20 equiv, 30%) was used.

<sup>b</sup> Phosphate buffer (pH=7.2) was used instead of water.

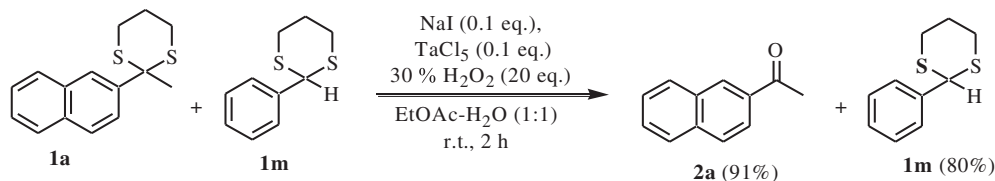
water (entry 9). The dithioacetal (**1k**) bearing an electron poor aromatic ring reacted very slowly to afford the ketone in relatively lower yield (entry 10).

The deprotection of several dithioacetals (**1**) derived from aldehydes was then examined under the same reaction condition (Table 5). The reactions proceeded more slowly than those of dithioacetals derived from ketones.

For an equimolar mixture of **1a** and **1m**, the dithioacetal (**1a**) derived from a ketone chemoselectively reacted to produce **2a** in 91%, and the dithioacetal (**1m**) derived from an aldehyde was recovered (Scheme 2).

### 3. Niobium(V) and iodide ion catalyzed deprotection of dithioacetals with 30% hydrogen peroxide

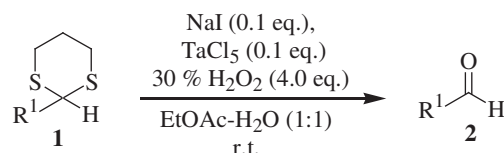
Recently, we found that niobium(V) compounds could be used as catalysts for oxidation of sulfides with 30% hydrogen peroxide, as

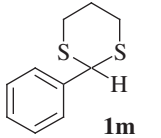
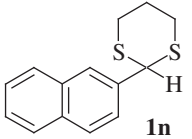
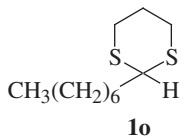
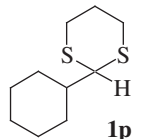


Scheme 2.

Table 5

Deprotection of **1** derived from aldehydes with 30% hydrogen peroxide catalyzed by TaCl<sub>5</sub> and NaI in ethyl acetate/water



Entry	Starting material	Time	Yield (%)
1		92 h	82
2		24 h	quant.
3		68 h	85
4		6 days	81

is the case with tantalum(V) compounds.<sup>6g</sup> Therefore, it was expected that the combination of a niobium(V) salt and sodium iodide could also be used as the catalyst in the hydrogen peroxide mediated deprotection of dithioacetals.

The reaction of **1a** with 0.1 equiv of a niobium(V) compound, 0.1 equiv of sodium iodide, and 4 equiv of 30% hydrogen peroxide was examined in ethyl acetate/water (1:1, v/v) as the solvent at room temperature (Table 6).

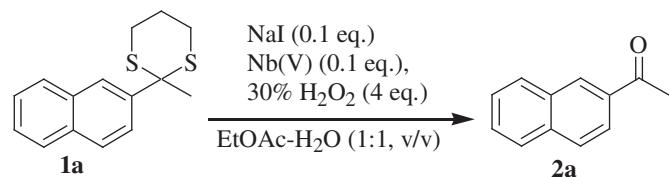
Niobium(V) chloride and niobium(V) ethoxide showed excellent catalytic activity, affording the corresponding ketone (**2a**) almost quantitatively in a relatively short reaction time (runs 1, 3). Conversely, niobium(V) oxide showed no catalytic activity in the deprotection of the dithioacetal with hydrogen peroxide (run 4). In the case of niobium(V) chloride, 0.02 equiv of Nb(V) is sufficient to catalyze the deprotection (run 2).

Several dithioacetals (**1**) were reacted with 4 equiv of 30% hydrogen peroxide in the presence of 0.02 equiv of niobium(V) chloride and 0.1 equiv of sodium iodide in ethyl acetate/water (1:1, v/v) at room temperature (Table 7).

The corresponding carbonyl compounds (**2**) were obtained in high yields in most cases. Similar to the results with tantalum(V) chloride, the aromatic ring (entries 2–9), the double bond (entry 2), the

**Table 6**

Deprotection of **1a** with 30% hydrogen peroxide and NaI in the presence of several Nb(V) compounds



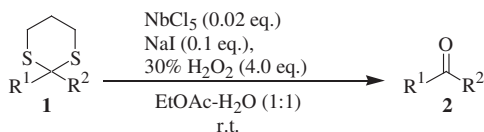
Run	Nb (V)	Time	Yield (%)
1	NbCl <sub>5</sub>	25 min	96
2 <sup>a</sup>	NbCl <sub>5</sub>	45 min	94
3	Nb(OEt) <sub>5</sub>	30 min	98
4	Nb <sub>2</sub> O <sub>5</sub>	24 h	10
5	—	24 h	18

<sup>a</sup> NbCl<sub>5</sub> (0.02 equiv) was used.

acetoxy group (entry 4), and the silyloxy group (entry 5) were inert to the deprotection. In the case of the dithioacetal (**1j**) having the acetal moiety (tetrahydropyranyl), the desired ketone was obtained in 90% yield in ethyl acetate–phosphate buffer (pH 7.2) (entry 6). The

**Table 7**

Deprotection of **1** derived from aldehydes with 30% hydrogen peroxide catalyzed by NbCl<sub>5</sub> and NaI in ethyl acetate/water



Entry	Starting material	Time (h)	Yield (%)
1	<b>1b</b>	3.5 h	91
2	<b>1f</b>	15 min	98
3	<b>1g</b>	10 min	68 <sup>a</sup>
4	<b>1h</b>	45 min	94
5	<b>1i</b>	15 min	95
6	<b>1j</b>	2 h	90 <sup>b</sup>
7	<b>1k</b>	24 h 5 h	53 quant. <sup>c</sup>

**Table 7 (continued)**

Entry	Starting material	Time (h)	Yield (%)
8	<b>1l</b>	24 h	97
9	<b>1n</b>	24 h	quant.

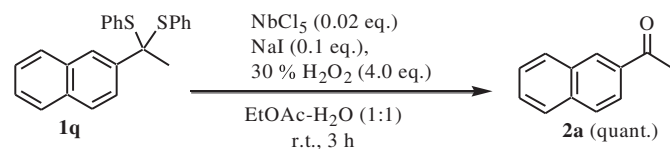
<sup>a</sup> Accompanied with unidentified by-products.

<sup>b</sup> Phosphate buffer (pH=6.8) was used instead of water.

<sup>c</sup> Reaction conditions: 0.1 equiv NbCl<sub>5</sub>, 0.1 equiv NaI, 20.0 equiv 0.30% H<sub>2</sub>O<sub>2</sub>.

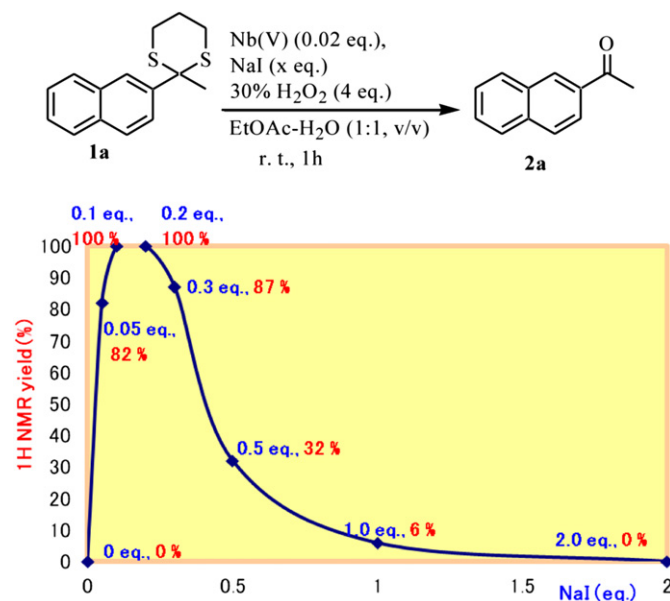
reactivity of the dithioacetal having an aromatic ring with an electron withdrawing functional group (entry 7) was very low, and 0.1 equiv of niobium(V) chloride, 0.1 equiv of sodium iodide, and 20 equiv of 30% hydrogen peroxide were required to produce the desired ketone quantitatively. As with the tantalum(V) chloride catalyzed deprotection, a dithioacetal derived from an aldehyde reacted more slowly than most of the dithioacetals derived from ketones (entry 9).

An acyclic dithioacetal **1q** was also deprotected under the same reaction condition to produce the corresponding ketone **2a** in quantitative yield (Scheme 3).

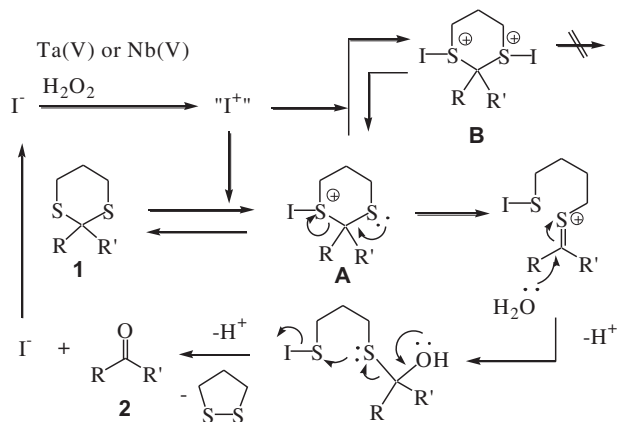
**Scheme 3.**

#### 4. Reaction mechanism

To investigate the catalytic effect of NaI, **1a** was treated with 0.02 equiv of NbCl<sub>5</sub> and 4 equiv of hydrogen peroxide in the presence of varying amount of NaI at room temperature for 1 h (Scheme 4). Interestingly, **2a** was quantitatively obtained for 0.1 and 0.2 equiv of NaI. The reaction did not proceed at all for 0 equiv and 2.0 equiv of NaI existed.

**Scheme 4.** The deprotection in the presence of varying amounts of NaI.

A plausible reaction mechanism is shown in Scheme 5. Tantalum(V) or niobium(V) catalyzed the hydrogen peroxide-mediated oxidation of  $I^-$  to the  $I^+$  equivalent, and the resulting  $I^+$  equivalent then reacts with the dithioacetal to form an iodosulfonium complex (**A**), which is easily hydrolyzed to afford the carbonyl. When excess amounts of  $I^-$  are present, **A** further reacts with the  $I^+$  equivalent to form a bisiodosulfonium complex (**B**), which is inactive toward hydrolysis. This explains why the reaction did not proceed at all in the presence of 2.0 equiv of NaI.



Scheme 5.

## 5. Conclusion

Dithioacetals (**1**) were easily deprotected to form the corresponding carbonyls (**2**) from the reaction of **1** with hydrogen peroxide catalyzed by NaI–TaCl<sub>5</sub> or NaI–NbCl<sub>5</sub>. The combination of NaI–NbCl<sub>5</sub> is more effective catalyst than NaI–TaCl<sub>5</sub>. Most of the other functional groups were inert and unaffected under these reaction conditions.

## 6. Experimental section

### 6.1. General

NMR spectra were acquired using a JEOL JNM-400 spectrometer. All NMR spectra were acquired using CDCl<sub>3</sub> solutions with tetramethylsilane as an internal standard, and coupling constants (*J*) are given in hertz (Hz). Mass spectra (electron impact) were recorded on a Shimadzu GC–MS–QP1100EX spectrometer. Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. Column chromatography was performed on silica gel (Merck Kieselger 60). The dithioacetals (**1**) were prepared according to the literature<sup>8</sup> from the corresponding ketones or aldehydes. The sodium iodide, tantalum(V) compounds, niobium(V) compounds, ketones, and aldehydes were obtained from Wako Pure Chemical Industries, Kanto Kagaku, Nacalai Tesque, Tokyo Kasei Kogyo, or Aldrich, and used without further purification.

### 6.2. General procedure for the deprotection of dithioacetals catalyzed by NaI–TaCl<sub>5</sub>

A mixture of **1** (1.0 mmol), tantalum chloride (35.8 mg, 0.10 mmol), sodium iodide (15.0 mg, 0.10 mmol), and 30% hydrogen peroxide (0.46 ml, 4.0 mmol) in ethyl acetate (6 ml) and water (6 ml) was stirred at room temperature. The reaction was monitored by thin layer chromatography (TLC). After **1** disappeared on TLC, saturated aqueous sodium thiosulfate (4 ml), and saturated aqueous sodium bicarbonate (4 ml) were added to the reaction mixture. The

organic layer was separated and the aqueous phase was extracted with ethyl acetate (25 ml×3). The combined organic phase was washed with brine, dried over anhydrous sodium sulfate, and evaporated. Chromatography on silica gel gave a pure product.

### 6.3. General procedure for the deprotection of dithioacetals catalyzed by NaI–NbCl<sub>5</sub>

A mixture of **1** (1.0 mmol), niobium chloride (5.4 mg, 0.02 mmol), sodium iodide (15.0 mg, 0.10 mmol), and 30% hydrogen peroxide (0.46 ml, 4.0 mmol) in ethyl acetate (6 ml) and water (6 ml) was stirred at room temperature. The reaction was monitored by thin layer chromatography (TLC). After **1** disappeared on TLC, saturated aqueous sodium thiosulfate (4 ml), and saturated aqueous sodium bicarbonate (4 ml) were added to the reaction mixture. The organic layer was separated and the aqueous phase was extracted with ethyl acetate (25 ml×3). The combined organic phase was washed with brine, dried over anhydrous sodium sulfate, and evaporated. Chromatography on silica gel gave a pure product.

**6.3.1. β-Acetonaphthone (2a).** Colorless crystals, mp: 52–54 °C (lit.<sup>9</sup> 52–56 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.73 (3H, s), 7.54–7.62 (2H, m), 7.88 (1H, d, *J*=8.0 Hz), 7.89 (1H, d, *J*=8.6 Hz), 7.97 (1H, d, *J*=8.0 Hz), 8.03 (1H, dd, *J*=1.6, 8.6 Hz). This sample is identical to the commercial reagent (purchased from Kanto Kagaku).

**6.3.2. Undecane-2-one (2b).** Colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.88 (3H, t, *J*=6.8 Hz), 1.20–1.33 (12H, m), 1.55–1.61 (2H, m), 2.13 (3H, s), 2.42 (2H, t, *J*=7.4 Hz). This sample is identical to the commercial reagent (purchased from Nacalai Tesque).

**6.3.3. Cyclododecanone (2c).** Colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.20–1.39 (14H, m), 1.65–1.76 (4H, m), 2.42–2.48 (4H, m). This sample is identical to the commercial reagent (purchased from Tokyo Kasei Kogyo).

**6.3.4. α-Tetralone (2d).** Colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.14 (2H, quintet, *J*=6.3 Hz), 2.65 (2H, t, *J*=6.3 Hz), 2.96 (2H, t, *J*=6.3 Hz), 7.24 (1H, d, *J*=7.4 Hz), 7.30 (1H, t, *J*=7.4 Hz), 7.46 (1H, t, *J*=7.4 Hz), 8.03 (1H, d, *J*=7.4 Hz). This sample is identical to the commercial reagent (purchased from Nacalai Tesque).

**6.3.5. α-Acetonaphthone (2e).** Colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.73 (3H, s), 7.45–7.55 (3H, m), 7.59 (3H, t, *J*=7.2 Hz), 7.86 (1H, d, *J*=8.0 Hz), 7.92 (1H, d, *J*=8.0 Hz), 7.98 (1H, d, *J*=8.0 Hz), 8.74 (1H, d, *J*=8.0 Hz). This sample is identical to the commercial reagent (purchased from Aldrich).

**6.3.6. 4-Phenylbut-3-en-2-one (benzalacetone) (2f).** Brown oil, <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.39 (3H, s), 6.71 (1H, d, *J*=16.4 Hz), 7.26–7.54 (6H, m). This sample is identical to the commercial reagent (purchased from Wako Pure Chemical Industries).

**6.3.7. 4-Acetophenone (2g).** Colorless crystals, mp: 108–112 °C (lit.<sup>9</sup> 107–113 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.56 (3H, s), 5.69 (1H, br s), 6.87 (2H, d, *J*=8.4 Hz), 7.90 (2H, *J*=8.8 Hz). This sample is identical to the commercial reagent (purchased from Wako Pure Chemical Industries).

**6.3.8. 4-Acetoxy acetophenone (2h).** Pale yellow solid, mp: 51–53 °C (lit.<sup>9</sup> 52–55 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 2.33 (3H, s), 2.60 (3H, s), 7.19 (2H, d, *J*=8.6 Hz), 7.99 (2H, d, *J*=8.6 Hz). This sample is identical to the commercial reagent (purchased from Aldrich).

**6.3.9. 4-tert-Butyldimethylsiloxy acetophenone (2i)<sup>10,11</sup>** Brown solid, mp: 33–35 °C (lit.<sup>11</sup> 35 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.23 (6H, s),

0.99 (9H, s), 2.55 (3H, s), 6.86 (2H, d,  $J=8.8$  Hz), 7.87 (2H, d,  $J=8.8$  Hz).

6.3.10. *4-Tetrahydropyran-2-yloxy acetophenone (2j)*<sup>12,13</sup>. Pale yellow solid, mp: 85–87 °C (lit.<sup>13</sup> 84–86 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.86–2.16 (6H, m), 2.55 (3H, s), 3.60–3.63 (2H, m), 5.51 (1H, t,  $J=3.05$  Hz), 7.07–7.09 (2H, m), 7.91–7.93 (2H, m).

6.3.11. *4-Nitroacetophenone (2k)*. Yellow crystals, mp: 75–79 °C (lit.<sup>9</sup> 75–78 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  2.69 (3H, s), 8.12 (2H, d,  $J=8.7$  Hz), 8.32 (2H, d,  $J=8.7$  Hz). This sample is identical to the commercial reagent (purchased from Tokyo Kasei Kogyo).

6.3.12. *Benzophenone (2l)*. Colorless crystals, mp: 47–49 °C (lit.<sup>9</sup> 47–51 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.48–7.59 (6H, m), 7.78–7.83 (4H, m). This sample is identical to the commercial reagent (purchased from Kanto Kagaku).

6.3.13. *Benzaldehyde (2m)*. Colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.49–7.57 (2H, m), 7.60–7.68 (1H, m), 7.88 (2H, m), 10.03 (1H, s). This sample is identical to the commercial reagent (purchased from Nacalai Tesque).

6.3.14. *Naphthalene-2-carbaldehyde (2n)*. Colorless crystals, mp: 59–61 °C (lit.<sup>9</sup> 59–63 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.63 (2H, td,  $J=22.9$ , 6.8 Hz), 7.90–8.03 (4H, m), 8.35 (1H, s), 10.17 (1H, s). This sample is identical to the commercial reagent (purchased from Kanto Kagaku).

6.3.15. *Octanal (2o)*. Colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.87 (3H, t,  $J=5.0$  Hz), 1.26–1.32 (10H, m), 1.61–1.66 (2H, m), 2.42 (2H, dt,  $J=7.4$ , 1.8 Hz), 9.76 (1H, s). This sample is identical to the commercial reagent (purchased from Tokyo Kasei Kogyo).

6.3.16. *Cyclohexanecarbaldehyde (2p)*. Colorless liquid, <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.20–1.43 (5H, m), 1.62–1.68 (1H, m), 1.72–1.79 (2H, m), 1.84–1.93 (2H, m), 2.19–2.29 (1H, m), 9.62 (1H, s). This sample is

identical to the commercial reagent (purchased from Tokyo Kasei Kogyo).

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