

Article

Recyclable Polymer-Supported Terpyridine–Palladium Complex for the Tandem Aminocarbonylation of Aryl Iodides to Primary Amides in Water Using NaN_3 as Ammonia Equivalent

Toshimasa Suzuka *, Hiromu Sueyoshi and Kazuhito Ogihara

Department of Chemistry, Biology and Marine Science, University of the Ryukyus, Nishihara, Okinawa 903-0213, Japan; k168373@eve.u-ryukyu.ac.jp (H.S.); kogihara@sci.u-ryukyu.ac.jp (K.O.)

* Correspondence: suzuka@sci.u-ryukyu.ac.jp; Tel.: +81-98-893-8531

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Abstract: Primary aromatic amides are valuable compounds, which are generally prepared via Beckmann rearrangement of oximes and the hydration of nitriles in organic solvents. We investigated the environmentally friendly catalytic aminocarbonylation in water. Thus, a novel heterogeneous transition-metal catalyst, a polymer-supported terpyridine–palladium(II) complex, was prepared and found to promote azidocarbonylation of aryl iodides with NaN_3 and to reduce the generated benzoyl azides in water under CO gas to yield primary aryl amides with high to excellent yield in a one-pot reaction. The catalyst was recovered and reused several times with no loss of catalytic activity.

Keywords: aminocarbonylation; azidocarbonylation; palladium; terpyridine; water; sodium azide; carbon monoxide; Staudinger reaction

1. Introduction

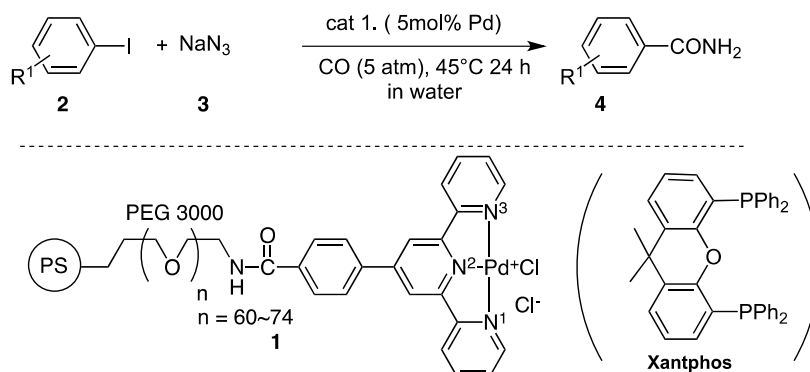
Primary amides are valuable compounds that are present in several natural products, are important structural motifs in pharmacologically active molecules [1], and are useful in engineering materials such as conductive polymers [2,3]. Although general procedures have been established for their preparation [4–8], e.g., the Beckmann rearrangement of oximes and the hydration of nitriles, there is continuing demand for the development of catalytic, new, improved, effective, and environmentally friendly methodologies for the synthesis of primary amides. Recently, we developed the aminocarbonylation of aryl iodides to form primary amides in water using MeONH_2 and a polymer-supported terpyridine–palladium(II) complex as an environmentally friendly synthesis; however, the reported reaction did not yield a high conversion efficiency [9].

Conversely, palladium-catalyzed carbonylation reactions of aromatic halides in the presence of several nucleophiles have undergone rapid development since the pioneering work of Heck and co-workers in 1974 [10]. With regard to the Heck carbonylation reaction, aminocarbonylation reactions have also been developed as an alternative to the preparation of secondary or tertiary amides, as described in [11]. In 2010, Beller and co-workers developed the palladium-catalyzed synthesis of primary amides using carbon monoxide and ammonia [12,13]. This reaction used gaseous ammonia and $\text{Pd}(\text{OAc})_2/\text{dppf}$ or $\text{Pd}(\text{OAc})_2/n\text{BuP}(1\text{-Adamantyl})_2$ as the catalytic system. The toxicity of gaseous ammonia is the same as that of carbon monoxide at a threshold limit values of 50 ppm. Therefore, hexamethyldisilazane [14], formamide [15], titanium-nitrogen complexes, ammonium carbamate [16], and methoxyamine [17] have been researched as effective ammonia equivalents for the palladium-catalyzed aminocarbonylation reaction in an organic solvent.

From the viewpoint of green chemistry, three principal drawbacks of the reported protocol exist despite consideration of the environmental impact and cost of the reported reaction: (1) the expensive palladium catalyst needs to be disposed of after being used a few times; (2) the products might become contaminated; (3) the organic solvent is both expensive and toxic.

On the contrary, we recently developed an amphiphilic polystyrene–poly(ethylene glycol) (PS–PEG) resin-supported terpyridine–palladium complex as a phosphine-free catalyst and found it to be effective for metal-catalyzed reactions in water under heterogeneous and aerobic conditions with high recyclability [18–21]. As an extension of that study, we investigated the catalytic use of the PS–PEG–terpyridine–palladium(II) complex for the azidocarbonylation of aryl halides using sodium azide as an ammonium equivalent and subsequently performed reduction with polymethylhydrosiloxane (PMHS) to produce primary amides in water. Although sodium azide is highly toxic, it is easy to handle because it is not gaseous, and it has advantage that it can be handled stably in water. There is only one reported example of a Pd/Xantphos catalyzed azidocarbonylation reaction in tetrahydrofuran (THF)-producing benzoyl azide products, and this was not performed with the aim of synthesizing primary amines [22].

In this report, complexes of the type $[(R_3P)_2Pd(Ph)N_3]$ have been reported not to undergo CO insertion into a Pd–Ph bond under identical reaction conditions due to conversion to $[(R_3P)_2Pd(Ph)NCO] + N_2$ [23]; these problems could be overcome using Xantphos, which has wide bite angles [24]. We herein report the results of this investigation and demonstrate that the complex effectively catalyzes the aminocarbonylation of various aryl iodides with carbon monoxide in water using a terpyridine ligand having a wide bite angle, N^1 –Pd– N^3 (Scheme 1). This catalyst system presents three benefits: (1) it produces neither organic-solvent waste nor metal-contaminated waste; (2) it is unaffected by oxygen and moisture; (3) it enables the aminocarbonylation reaction to meet green chemical requirements.



Scheme 1. Aminocarbonylation in water using polymeric catalyst **1**. PS, polystyrene; PEG, poly(ethylene glycol).

2. Results

2.1. Coupling Conditions

Upon screening the reaction conditions for the aminocarbonylation in water with the polymeric palladium **1**, we found that the reaction efficiency was greatly enhanced by simple reaction conditions. Firstly, we examined the aminocarbonylation in water according to the reported procedures [22]. Thus, the aminocarbonylations of iodobenzene (**2a**) and NaN_3 (**3**) were carried out in water with PMHS as reducing agent for the generated benzoyl azide in the presence of the polymeric catalyst **1** (5 mol % to Pd) at 50 °C for 8 h under 5 atm of CO gas. The reaction mixture was filtered, and the recovered resin beads were rinsed with a small portion of water and extracted with EtOAc to yield benzamide (**4a**) in only 13% yield (Entry 1, Table 1).

Table 1. Aminocarbonylation of phenyl iodides with NaN₃ using polymeric catalyst **1** in water ^a.

c1ccccc1I (**2a**) + NaN₃ (**3**) $\xrightarrow[\text{NaN}_3, \text{CO (5 atm), additive, temp., 24 h in water}]{\text{PS-PEG-terpyridine-Pd } \mathbf{1} \text{ (5 mol\%)}}$ c1ccccc1C(=O)N (**4a**)

Entry	NaN ₃ (equiv.)	Base (equiv.)	PMHS (equiv.)	Temp. (°C)	Time (h)	Yield of 4a (%)
1	2.0	none	7.5	50	8	13
2	2.0	K ₂ CO ₃	7.5	50	8	9.1
3	2.0	Cs ₂ CO ₃	7.5	50	8	17
4	2.0	Et ₃ N	7.5	50	8	3.0
5	2.0	Cs ₂ CO ₃	7.5	50	24	18
6	2.0	none	7.5	50	24	31
7	1.0	none	7.5	50	24	24
8	3.0	none	7.5	50	24	48
9	4.0	none	7.5	50	24	50
10	5.0	none	7.5	50	24	46
11	4.0	none	6.0	50	24	48
12	4.0	none	4.5	50	24	43
13	4.0	none	3.0	50	24	50
14	4.0	none	0.2	50	24	48
15	4.0	none	0.1	50	24	51
16	4.0	none	none	50	24	53
17	4.0	none	none	45	24	70
18	4.0	none	none	40	24	66

^a All reactions were performed with **2a** (0.4 mmol), NaN₃, polymethylhydrosiloxane (PMHS), and polymeric catalyst **1** (5 mol %) in H₂O (3.0 mL) under a CO atmosphere. Yields were determined by gas chromatography based on *n*-dodecane as an internal standard.

The scope of suitable bases for the aminocarbonylation in water using catalyst **1** was examined. The potassium carbonate, cesium carbonate, and Et₃N produced 9.1%, 17%, and 3.0% yields, respectively (Entries 2–4, Table 1). Next, we tested prolonged reaction times using Cs₂CO₃, but the yield did not improve as expected (Entry 5, Table 1). In contrast, tripling the time gave a high yield when no base was used (Entry 6, Table 1). The amounts of NaN₃ and PMHS were investigated for the aminocarbonylation in water. Thus, the reaction was carried out with 1.0–5.0 equivalents of NaN₃ to produce benzamide (**4a**) in 24%, 48%, 50%, and 46% yields, respectively (Entries 7–10, Table 1). It was surprising to find that, even though PMHS was reduced, the yield remained almost unchanged for this aminocarbonylation, which produced **4a** with 43%–53% yields, where the reaction is a one-pot combination of azidocarbonylation and a reduction of generated benzoyl azide with PMHS (Entries 11–16, Table 1). Finally, the highest yield (70%) was obtained when the reaction was performed under simple reaction conditions with 4 equivalents of NaN₃ in the presence of 5 mol % of catalyst **1** in water at 45 °C for 24 h under 5 atm of CO gas.

2.2. Substrate Tolerance

With the optimal conditions in hand, we examined polymer-supported terpyridine–palladium-catalyzed aminocarbonylation of several iodoarenes, and the results are summarized in Table 2. The reaction of **2a** with sodium azide (**3**) provided the intended benzamide (**4a**) in a 70% yield (Entry 1, Table 2), and the reactions with iodobenzene having methyl groups at the *ortho*-, *meta*-, and *para*-positions on the benzene ring also afforded 4-methylbenzamide (**4b**), 3-methylbenzamide (**4c**), and 2-methylbenzamide (**4d**) in 64%, 59%, and 26% yields, respectively (Entries 2–4, Table 2).

Table 2. Aminocarbonylation of aryl iodides with NaN₃ using polymeric catalyst **1** in water ^a.

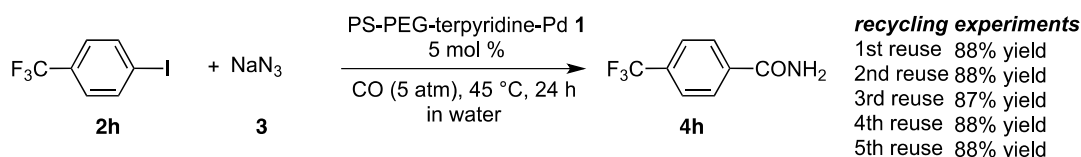
		PS-PEG-terpyridine-Pd 1 5 mol%	
Ar-I		+ NaN ₃	
		CO (5 atm), 45 °C, 24 h in water	
		Ar-CONH ₂	
Entry	2	4	Yield (%) ^a
1	C ₆ H ₅ -I: 2a	C ₆ H ₅ -CONH ₂ : 4a	70
2	<i>p</i> -MeC ₆ H ₄ -I: 2b	<i>p</i> -MeC ₆ H ₄ -CONH ₂ : 4b	64
3	<i>m</i> -MeC ₆ H ₄ -I: 2c	<i>m</i> -MeC ₆ H ₄ -CONH ₂ : 4c	59
4	<i>o</i> -MeC ₆ H ₄ -I: 2d	<i>o</i> -MeC ₆ H ₄ -CONH ₂ : 4d	26
5	1-iodonaphthalene: 2e	1-naphthamide: 4e	4.2
6	<i>o</i> -NO ₂ C ₆ H ₄ -I: 2f	<i>o</i> -NO ₂ C ₆ H ₄ -CONH ₂ : 4f	62 ^b
7	<i>p</i> -MeOC ₆ H ₄ -I: 2g	<i>p</i> -MeOC ₆ H ₄ -CONH ₂ : 4g	41
8	<i>p</i> -CF ₃ C ₆ H ₄ -I: 2h	<i>p</i> -CF ₃ C ₆ H ₄ -CONH ₂ : 4h	90
9	<i>p</i> -NO ₂ C ₆ H ₄ -I: 2i	<i>p</i> -NO ₂ C ₆ H ₄ -CONH ₂ : 4i	84 ^b
10	<i>p</i> -FC ₆ H ₄ -I: 2j	<i>p</i> -FC ₆ H ₄ -CONH ₂ : 4j	82
11	<i>p</i> -ClC ₆ H ₄ -I: 2k	<i>p</i> -ClC ₆ H ₄ -CONH ₂ : 4k	81 ^b
12	<i>p</i> -BrC ₆ H ₄ -I: 2l	<i>p</i> -BrC ₆ H ₄ -CONH ₂ : 4l	65

^a All reactions were performed with **2** (0.4 mmol), NaN₃ (1.6 mmol), and polymeric catalyst **1** (5 mol %) in H₂O (3.0 mL) under 5 atm of CO gas. Yields were determined by gas chromatography based on *n*-dodecane as an internal standard; ^b isolated yield.

The different reaction outcome for 2-substituted iodoarenes **2d–f** is hardly surprising because benzoyl azides bearing an *ortho* substituent are 50–200 times more reactive toward the Curtius rearrangement than their *meta* and *para* isomers [25]. Thus, the reaction of 1-iodonaphthalene (**2e**) occurred under similar reaction conditions to afford the 1-naphthamide (**4e**) in a 4.2% yield. iodobenzene derivatives **2g–l** bearing electron-donating and electron-withdrawing substituents at their *para*-positions produced 4-methoxybenzamide (**4g**), 4-trifluoromethylbenzamide (**4h**), 4-nitrobenzamide (**4i**), 4-fluorobenzamide (**4j**), 4-chlorobenzamide (**4k**), and 4-bromobenzamide (**4l**) in 41%, 90%, 84%, 82%, 81%, and 65% yields, respectively (Entries 7–12, Table 2). A substrate having an electron-withdrawing substituent tended to produce a high yield.

2.3. Recycling Experiments

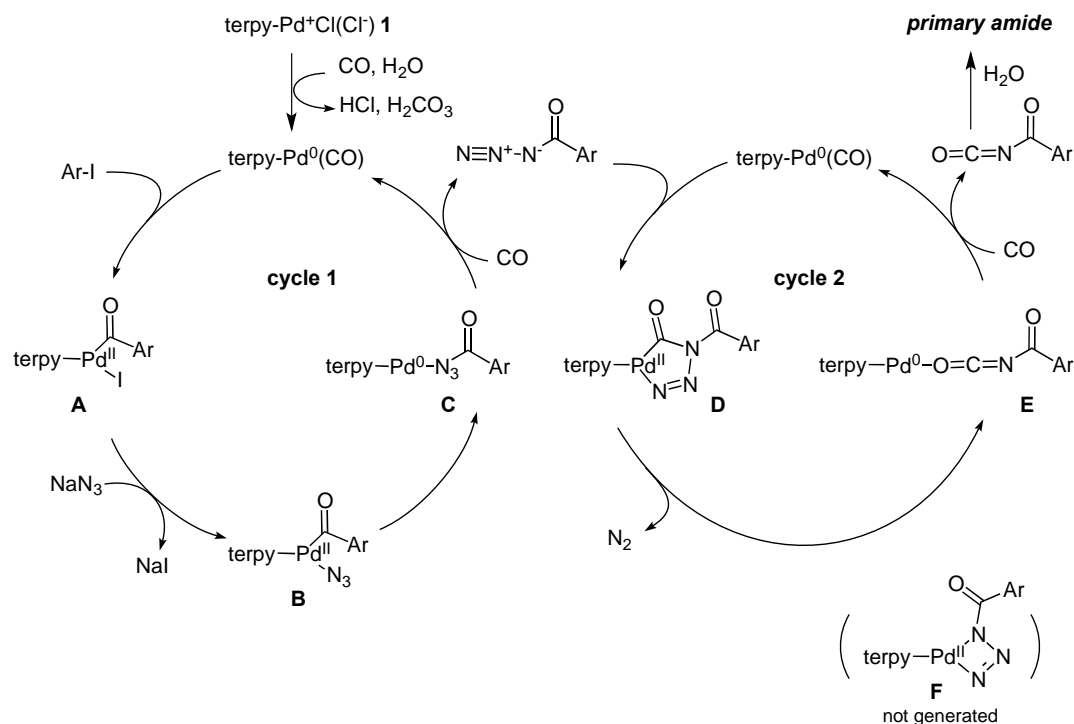
The recyclability of catalyst **1** was examined for the aminocarbonylation of 4-iodobenzotrifluoride (**2h**) with NaN₃ (**3**) (Scheme 2). After the first reaction, which produced 4-(trifluoromethyl)benzamide (**4h**) in a 90% yield, the catalyst was recovered by simple filtration, washed with H₂O, dried under vacuum, and reused five times under similar reaction conditions to afford **4h** in 88%, 88%, 87%, 88%, and 88% yields. After the recycling experiments, inductively coupled plasma-atomic emission spectrometry (ICP–AES) analysis showed that the concentration of Pd leached into the aqueous solution was <3 ppm.

**Scheme 2.** Recycling experiments.

3. Discussion

Reaction Mechanism

To clarify the reaction mechanism, we examined the reduction of benzoyl azide (**5**) with polymeric catalyst **1** (100 mol % Pd) because we postulate that one possible reaction intermediate is the palladacycle (**D** in Scheme 3). The treatment of **5** with a stoichiometric amount of polymeric Pd^{II} catalyst **1** without CO gas did not produce **4a** even when the PS-PEG-terpyridine-Pd⁰(dba) complex was used, but the reaction in the presence of CO gas with a PS-PEG-terpyridine-Pd⁰ complex or a PS-PEG-terpyridine-Pd^{II} complex produced **4a** in 95% and 56% yields, respectively (Table 3).



Scheme 3. Proposed reaction mechanism of aminocarbonylation in water.

Table 3. Stoichiometric reaction.

<p>5</p>	PS-PEG-terpyridine-Pd (1) 1.0 equivalent CO, 45 °C, 24 h in water	<p>4a</p>	(1)
Catalyst	CO (atm)	Yield (%)	
PS-PEG-terpyridine-Pd(dba) (1')	5	95	
PS-PEG-terpyridine-Pd(dba) (1')	none	0	
PS-PEG-terpyridine-Pd ⁺ Cl(Cl ⁻) (1)	5	56	
PS-PEG-terpyridine-Pd ⁺ Cl(Cl ⁻) (1)	none	0	

These results suggest that a palladacycle intermediate **D** derived from terpy-Pd(CO) as a real active species with benzoyl azide is one of the possible reaction intermediates [26,27]; however, if the reaction did not require the use of CO gas, a palladacycle **F** is also a candidate for a possible reaction intermediate derived from a PS-PEG-terpyridine-Pd⁰ and benzoyl azide. Based on the present results and reported work [28], we propose a possible reaction pathway for the PS-PEG-terpyridine-Pd catalyzed the aminocarbonylation reaction in water in Scheme 3.

Initially, the oxidative addition of Ar-I to terpy-Pd⁰(CO) yielded the terpy-Pd^{II}(CO)(Ar)(I), which was quickly converted to **A** via facile CO insertion as shown in cycle 1 of Scheme 3. Transformation of **A** to **B** takes place via ligand exchange followed by reductive elimination, which produces complex **C**. The reaction of **C** with CO gas afforded terpy-Pd⁰(CO) and the azidocarbonylation product (ArCON₃), which is used in the catalytic Staudinger reaction shown in cycle 2 of Scheme 3 [29]. Thus, the oxidative addition of ArCON₃ to terpy-Pd⁰(CO) yields the palladacycle **D** followed by the reductive elimination of **D** to form **E**, which is transformed to the primary amide in water under CO gas.

4. Materials and Methods

4.1. General Methods

All manipulations were conducted under aerobic conditions. Water was deionized with a Millipore Milli-Q Gradient A10 system (Millipore, Bedford, MA, USA). NMR spectra were recorded on a Bruker AVANCE spectrometer (400 MHz for ¹H and 100 MHz for ¹³C, Bruker, Karlsruhe, Germany); ¹H and ¹³C spectra were recorded in dimethyl sulfoxide-d₆ (DMSO-d₆) at 25 °C. Chemical shifts of ¹³C are given relative to CDCl₃ and DMSO-d₆ as internal standards (δ 39.7 ppm). Mass spectra were measured on a JEOL JMS-T100GCv MS detector (GC-MS, JEOL, Tokyo, Japan) and a JEOL JMS-T100LP MS detector (LC-MS, JEOL); the base peak is denoted as “bp.” GC and IR analyses were performed on a Shimadzu GC-2014 instrument (Shimadzu, Kyoto, Japan) and a Jasco FTIR-410 detector (JASCO, Tokyo, Japan), respectively. ICP-AES spectra were measured on a Shimadzu ICPE-9000 instrument (Shimadzu). The high-pressure reaction was performed in an EYELA HIP-7506 autoclave (EYELA, Tokyo, Japan).

4.2. Materials

The PS-PEG-supported terpyridine-palladium complex (PS-PEG-terpyridine-Pd; **1**) was prepared from a PS-PEG amino-resin (TentaGel S NH₂, average diameter 90 μm, 1% divinylbenzene cross-linked, loading value of amino residue 0.31 mmol/g; purchased from Rapp Polymere, Tuebingen, Germany), a polymeric terpyridine ligand, and (C₆H₅CN)₂PdCl₂ in accordance with previously reported procedures [8]. The loading level of Pd in polymeric catalyst **1** was 0.26 mmol/g.

4.3. Aminocarbonylation

The general procedure for obtaining aminocarbonylation products **4a–l** is as described here for **4a**. Iodobenzene (**2a**; 81 mg, 0.40 mmol) was added to a polymeric catalyst mixture (**1**; 77 mg, 0.020 mmol) and NaN₃ (**3**; 104 mg, 1.60 mmol) in H₂O (3.0 mL). The reaction mixture was stirred at 45 °C for 24 h under CO gas (5.0 atm) and filtered. The recovered resin beads were rinsed with H₂O and extracted thrice with EtOAc (6 mL). The EtOAc layer was separated, and the aqueous layer was extracted with EtOAc (3 mL). The combined EtOAc extracts were washed with brine (2 mL) and dried over MgSO₄; *n*-dodecane (20 mg) was then added. The GC sample was transferred from the organic layer to a GC vial. The yield of benzamide (**4a**) determined by GC analysis was 70% with *n*-dodecane as an internal standard.

The compounds and Chemical Abstracts Service (CAS) registry numbers are as follows: benzamide (**4a**), 4-methylbenzamide (**4b**), 3-methylbenzamide (**4c**), 2-methylbenzamide (**4d**), 1-naphthamide (**4e**), 2-nitrobenzamide (**4f**), 4-methoxybenzamide (**4g**), 4-trifluoromethylbenzamide (**4h**), 4-nitrobenzamide (**4i**), 4-fluorobenzamide (**4j**), 4-chlorobenzamide (**4k**), and 4-bromobenzamide (**4l**); 55-21-0, 619-55-6, 618-47-3, 527-85-5, 2243-81-4, 610-15-1, 3424-93-9, 1891-90-3, 619-8-7, 824-75-9, 619-56-7, and 698-67-9, respectively.

5. Conclusions

We developed a novel polymer-supported terpyridine-palladium complex that efficiently catalyzes the tandem aminocarbonylation of aryl halides with NaN₃ in water under CO gas to afford

the corresponding primary amides with up to 90% yield via a catalytic azidocarbonylation reaction and catalytic reduction of azide to amine. To the best of our knowledge, this is the first example of a one-pot aminocarbonylation reaction with NaN_3 and CO in the presence of the same catalyst via catalytic azidocarbonylation and the Staudinger reaction. The catalyst can be recovered and reused several times with no loss of catalytic activity.

In addition, we studied and described the mechanistic details, which included clarifying why the reaction requires CO gas in catalytic cycle 2 of Scheme 3. We are continuing to investigate the scope of aminocarbonylation with other nucleophiles and possible applications of the catalyst to other organic transformations.

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Author Contributions: Toshimasa Suzuka designed and performed the research and experiments and performed data analysis and manuscript writing and revision. Hiromu Sueyoshi performed the experiments and analyzed the data. Kazuhito Ogihara advised us for this research.

Conflicts of Interest: The authors declare no conflict of interest.

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Sample Availability: Samples are not available from the authors.



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