






Chromium(VI) oxide-mediated oxidation of polyalkyl-polypyridines to polypyridine-polycarboxylic acids with periodic acid

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Chromium(VI) oxide-mediated oxidation of polyalkyl-polypyridines to polypyridine-polycarboxylic acids with periodic acid

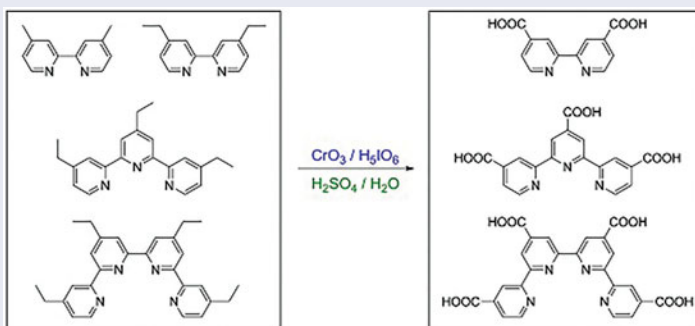
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ABSTRACT

4,4'-Dicarboxy-2,2'-bipyridine was synthesized quantitatively by chromium(VI) oxide-mediated oxidation of 4,4'-dimethyl-2,2'-bipyridine or 4,4'-diethyl-2,2'-bipyridine with periodic acid as the terminal oxidant in sulfuric acid. 5,5'-Dicarboxy-2,2'-bipyridine and 6,6'-dicarboxy-2,2'-bipyridine were also synthesized by the method from the corresponding dimethyl bipyridines in excellent yields. 4,4',4''-Tricarboxy-2,2':6',2''-terpyridine was obtained in 80% yield from 4,4',4''-triethyl-2,2':6',2''-terpyridine, and 4,4',4'',4'''-tetracarboxy-2,2':6',2''':6'',2'''-quaterpyridine was obtained in 72% yield from 4,4',4'',4'''-tetraethyl-2,2':6',2''':6'',2'''-quaterpyridine by the same procedure.

GRAPHICAL ABSTRACT



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KEYWORDS

Bipyridine; chromium (VI) oxide; oxidation; periodic acid; quaterpyridine; terpyridine

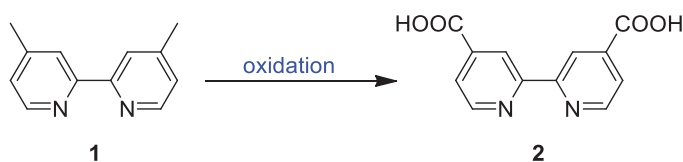
Introduction

Polypyridines such as bipyridines and terpyridines are important class of compounds as the ligand of metal complexes.^[1] Carboxylic acid substituted polypyridines have been used extensively as the key parts of the dyes for dye-sensitized solar cells (DSSCs) over the last two decades.^[2,3] DSSCs are expected as promising alternative to conventional silicon solar cells. Carboxylic acid on polypyridines acts important role as the anchor to

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Scheme 1. Oxidation of 4,4'-Dimethyl-2,2'-bipyridine **1**.

semiconductor (TiO_2) surface. Ruthenium polypyridyl complexes are the first and the most extensively investigated class of dyes for DSSCs. The N3,^[4] ($\text{Ru}(\text{II})(\text{dcbpy})_2(\text{NCS})_2$) (dcbpy = 4,4'-dicarboxy-2,2'-bipyridyl ligand), has been used as the standard dye for the studies of DSSCs at early stage, and then N719,^[5] tetrabutylammonium salt of N3, has been used as the referential dye. Black dye,^[6] a ruthenium complex containing 4,4',4''-tricarboxy-2,2':6',2''-terpyridine as the ligand, is known to show exceeding 11% light-to-electric energy conversion efficiency that is the highest among the ruthenium complex-based DSSCs. Recent papers reported new ruthenium complex dyes having bipyridine, terpyridine, or quaterpyridine ligands possessing tetracarboxylic acid anchor.^[7]

Another recent application of polycarboxy-polypyridines is metal-organic frameworks (MOFs).^[8] MOFs have received much attention because of its nanometer-sized pores that have potential of a wide range of applications such as gas storage and separation, catalysis, sensors, and other technologies.^[9]

In earlier works, 4,4'-dicarboxy-2,2'-bipyridine **2** was synthesized by oxidation of 4,4'-dimethyl-2,2'-bipyridine **1** (Scheme 1) with potassium permanganate.^[10] The yields were moderate and the product contained 4-carboxy-4'-methyl-2,2'-bipyridine as a major impurity. Later, chromium(VI) oxide or potassium dichromate in sulfuric acid was reported as high yield procedures.^[11] Though the yields of 4,4'-dicarboxy-2,2'-bipyridine **2** by the procedures are high (>90%), these methods require stoichiometric amount (>6 equiv.) of chromium reagents. Since the use of large amount of chromium reagents is accompanied by serious potential health risks and associated waste disposal issues, and often causes problems during reaction and work-up, development of oxidizing methods requiring reduced amount of chromium reagent in combination with appropriate stoichiometric oxidant is a subject of interest. Recently, another approach for the oxidation of 4,4'-dimethyl-2,2'-bipyridine **1** using a solvothermal protocol in dilute aqueous nitric acid solutions has been reported.^[12] Although the method is attractive because the procedure is simple and environmentally benign, scale-up is restricted by the size of pressure-resistant reaction vessel.

Here, we report a synthetic procedure of 4,4'-dicarboxy-2,2'-bipyridine **2** and related polycarboxy-polypyridines by chromium(VI) oxide (CrO_3)-mediated oxidations of 4,4'-dimethyl-2,2'-bipyridine **1** and related polyalkyl-polypyridines with periodic acid (H_5IO_6) as the terminal oxidant.

Results and discussion

Previously, we have reported that $\text{CrO}_3/\text{H}_5\text{IO}_6/\text{acetonitrile}$ act as an efficient catalytic system for the oxidation of toluenes to the corresponding benzoic acids,^[13a] and we have adapted the system to the oxidation of **1**. H_5IO_6 has been known as an effective terminal oxidant for chromium-catalyzed oxidation of various substrates.^[13]

Table 1. CrO₃-mediated Oxidation of 4,4'-Dimethyl-2,2'-bipyridine **1** with H₅IO₆ in CH₃CN.^a

Entry	H ₅ IO ₆ (mmol)	CrO ₃ (mmol)	2 (%) ^b	3 (%) ^b
1	7	1	9	3
2	5	2	30	6
3	7	2	36	6
4 ^c	10	2	34	3
5	7	3	35	6

^aReaction at room temperature in CH₃CN + CH₂Cl₂ (30 mL + 3 mL) for 16 h. **1** 1 mmol.

^bIsolated as the mixture of **2** and **3**. The ratios were determined by ¹H-NMR.

^cCH₃CN + CH₂Cl₂ (50 mL + 3 mL).

Table 2. CrO₃-mediated Oxidation of 4,4'-Dimethyl-2,2'-bipyridine **1** with H₅IO₆.^a

Entry	H ₅ IO ₆ (mmol)	CrO ₃ (mmol)	H ₂ SO ₄ /H ₂ O (mL/mL)	Time (h)	2 (%) ^b	3 (%) ^b
1	6	1	20/0	24	97	2
2	6	0.8	20/0	24	83	3
3	6	0.5	20/0	24	50	6
4	6	0.5	20/0	140	48	6
5	5	1	20/0	24	89	1
6	4	1	20/0	24	70	5
7	6	1	10/5	24	99	0
8	6	1	10/10	24	55	8
9	6	1	10/10	140	92	2
10	6	0.5	10/5	24	56	9
11	6	0.5	10/5	72	74	8

^aReaction at room temperature. **1** 1 mmol.

^bIsolated as the mixture of **2** and **3**. The ratios were determined by ¹H-NMR.

At first, CrO₃-mediated oxidation of 4,4'-dimethyl-2,2'-bipyridine **1** in acetonitrile was investigated.^[13a] Because the substrate **1** was hardly soluble in acetonitrile, a small amount of dichloromethane was used as a co-solvent to dissolve the substrate. The results are summarized in Table 1. The use of 7 equiv. H₅IO₆ and 2 equiv. CrO₃ afforded 36% yield of desired product **2** along with 6% 4-carboxy-4'-methyl-2,2'-bipyridine **3**^[14] (entry 3). Unfortunately, the optimization of the reaction in acetonitrile failed.

Next, we examined the reaction in conc. H₂SO₄ (Table 2, entries 1–6). H₂SO₄ is a generally used solvent for oxidations of the alkyl group of alkylbenzenes to carboxy group using CrO₃ as the oxidant.^[15] The influence of the amount of CrO₃ and H₅IO₆ on the oxidation of 4,4'-dimethyl-2,2'-bipyridine **1** was investigated. The reactions were performed by addition of **1** to the stirring solution of H₅IO₆ and CrO₃ in conc. H₂SO₄ at room temperature. The mainly obtained product was 4,4'-dicarboxy-2,2'-bipyridine **2** with a small amount of 4-carboxy-4'-methyl-2,2'-bipyridine **3**. The oxidation of 1 mmol

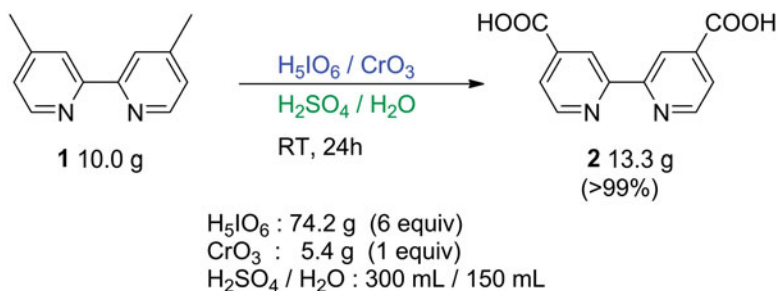
1 with 1 mmol CrO₃ and 6 mmol H₅IO₆ in conc. H₂SO₄ gave **2** in 97% yield with 2% **3** (entry 1). The use of the lower amount of CrO₃ (entries 2 and 3) (0.8 and 0.5 mmol) and the use of the lower amount of H₅IO₆ (entries 5 and 6) (5 and 4 mmol) resulted in lower yields of the product **2**.

The mixture of H₂SO₄ and H₂O has been found to be more effective as the solvent than conc. H₂SO₄ itself. The CrO₃-mediated oxidation of **1** in the mixture of H₂SO₄ and H₂O (10 mL + 5 mL) afforded the dicarboxylic acid **2** quantitatively (entry 7). It is noteworthy that no monocarboxylic acid **3** was detected at all under the conditions of entry 7 by ¹H-NMR. Previously reported procedures using CrO₃ and KMnO₄ as the oxidant require purification process to convert remaining monocarboxylic acid **3** to dicarboxylic acid **2** by refluxing in HNO₃ for a long period^[10d,11b] or esterification-recrystallization-hydrolysis procedure.^[11a] The procedure using CrO₃/H₅IO₆ oxidation system in H₂SO₄/H₂O (2:1) can avoid the troublesome additional treatment. The increasing amount of H₂O (H₂SO₄ + H₂O, 10 mL + 10 mL) retarded the reaction rate, and the yield of the product **2** was 55% along with 8% **3** at 24 h. Prolonged reaction increased the yield of **2** to 92% and decreased the yield of **3** to 2% at 140 h (entries 8 and 9). The reactions in conc. H₂SO₄ and in the mixture of H₂SO₄ and H₂O (10 mL + 5 mL) were compared using 0.5 mmol CrO₃ (entries 3, 4, 10, and 11). The yield of the reaction in conc. H₂SO₄ was 50% at 24 h, and the yield was not increased by prolonged reaction (48% by 140 h reaction). On the other hand, the yield of the reaction in the mixture of H₂SO₄ and H₂O (10 mL + 5 mL) was 56% at 24 h, that was higher than that in conc. H₂SO₄ and prolonged reaction increased the yield of **2** to 74%. These results indicated that the mixture of H₂SO₄ and H₂O (2:1) was a superior solvent than conc. H₂SO₄ for this oxidation.

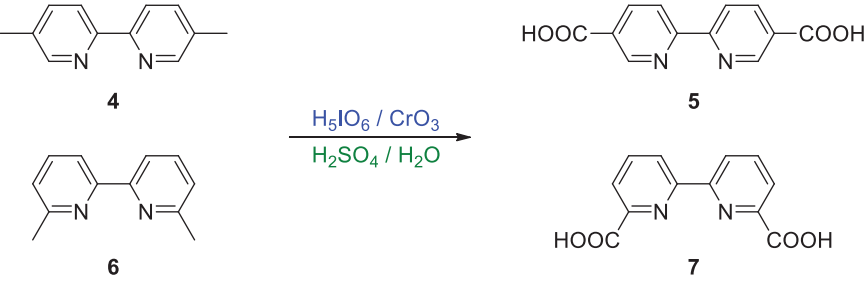
The 10 g scale oxidation of **1** was performed (Scheme 2). The use of 6 equiv. H₅IO₆ and 1 equiv. CrO₃ in the mixture of H₂SO₄ and H₂O (2:1) afforded **2** quantitatively as is the case with 1 mmol scale oxidation. Again, monocarboxylic acid **3** was not observed.

Oxidation of 5,5'-dimethyl-2,2'-bipyridine **4** and 6,6'-dimethyl-2,2'-bipyridine **6** was examined by this oxidation system. The results are summarized in Table 3. 5,5'-Dimethyl-2,2'-bipyridine **4** was oxidized to the corresponding dicarboxylic acid **5** in excellent yield. The oxidations in the mixture of H₂SO₄ and H₂O (2:1) afforded higher yields of dicarboxylic acids **5** than in conc. H₂SO₄, and no monocarboxylic acid^[16,17] was detected (entries 1 and 2).

6,6'-Dimethyl-2,2'-bipyridine **6** required longer reaction time to obtain the corresponding dicarboxylic acid **7** in good yield. The oxidation of **6** at room temperature for 3 days afforded 63% yield of the product **7** (entry 3), and the oxidation over 6 days



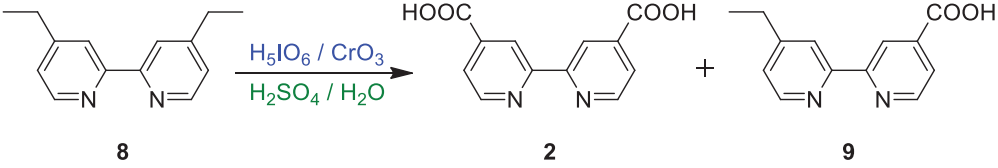
Scheme 2. Large-Scale Synthesis of 4,4'-Dicarboxy-2,2'-bipyridine **2**.

Table 3. CrO₃-mediated Oxidation of 5,5'-Dimethyl-2,2'-bipyridine **4** and 6,6'-Dimethyl-2,2'-bipyridine **6** with H₅IO₆.^a


Entry	Substrate	H ₂ SO ₄ /H ₂ O (mL/mL)	Time (days)	Product	Yield (%) ^b
1	4	20/0	1	5	91 (0.1)
2	4	10/5	1	5	98
3	6	20/0	3	7	62 (0.6)
4	6	20/0	6	7	80 (0.7)
5	6	20/0	10	7	81 (0.1)
6	6	10/5	6	7	95 (0.1)

^aReaction at room temperature. Substrate 1 mmol. Substrate/H₅IO₆/CrO₃ = 1/6/1.

^bIsolated yields. The number in the parentheses are the yield of 5-carboxy-5'-methyl-2,2'-bipyridine^[16,17] (entry 1) or 6-carboxy-6'-methyl-2,2'-bipyridine^[17] (entries 3–6). The ratios were determined by ¹H-NMR.

Table 4. CrO₃-mediated Oxidation of 4,4'-Diethyl-2,2'-bipyridine **8** with H₅IO₆.^a


Entry	H ₅ IO ₆ (mmol)	CrO ₃ (mmol)	H ₂ SO ₄ /H ₂ O (mL/mL)	2 (%) ^b	9 (%) ^c
1	6	1	20/0	21	1
2	6	1	10/5	88	1
3	7	1	10/5	92	<1
4	8	1	10/5	92	<1
5	8	0.5	10/5	54	7
6	8	0.5	10/5	70 ^c	5
7	7	3	10/5	96	0
8	8	2	10/5	94	0
9	0	9	20/0	94	0

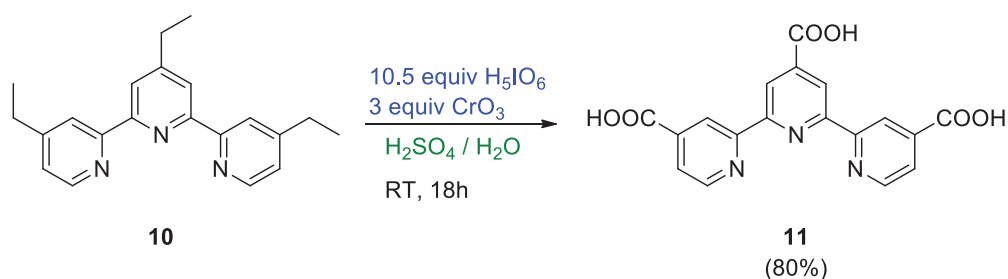
^aReaction at room temperature for 24 h. **8** 1 mmol.

^bIsolated as the mixture of **2** and **9**. The ratios were determined by ¹H-NMR.

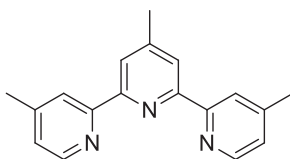
^cAt 72 h.

afforded 81% of the product (entries 4 and 5). Again, the oxidations in the mixture of H₂SO₄ and H₂O (2:1) afforded higher yields of dicarboxylic acids **7** (entry 6). In the oxidation of 6,6'-dimethyl-2,2'-bipyridine **6**, trace amount of monocarboxylic acid^[17] (0.1–0.7%) was detected in every case (entries 3–6).

Oxidation of 4,4'-diethyl-2,2'-bipyridine **8** was studied by this system. The results are summarized in Table 4. The reaction in conc. H₂SO₄ resulted in low yield of dicarboxylic acid **2** only in 21% (entry 1). The same oxidation in the mixture of H₂SO₄ and H₂O (2:1) afforded higher yields of dicarboxylic acids **2** in 88% yield (entry 2). Though the use of 7 equiv. H₅IO₆ increased the yield slightly (entry 3), no more improvement



Scheme 3. Oxidation of 4,4',4''-Triethyl-2,2':6',2''-terpyridine **10**.



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Figure 1. 4,4',4''-Trimethyl-2,2':6',2''-terpyridine **12**.

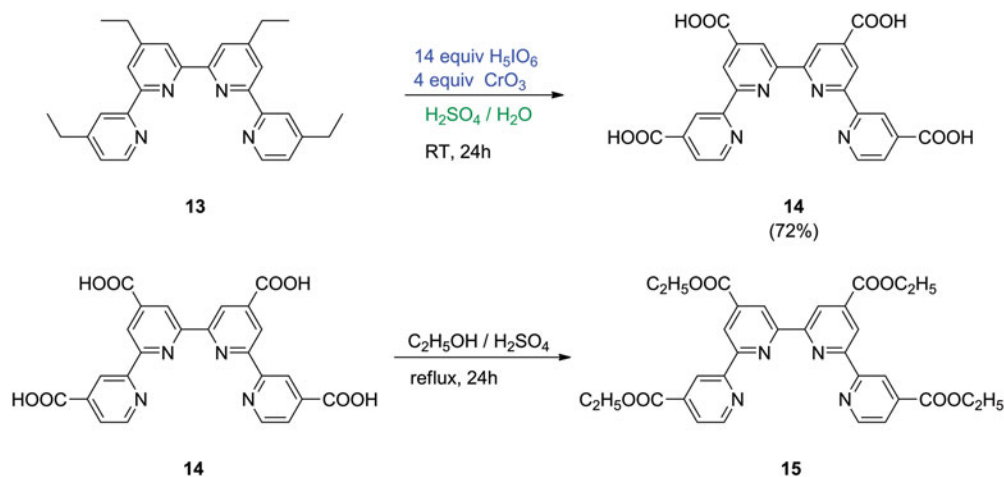
was observed using 8 equiv. H_5IO_6 (entry 4). The use of lower amount of CrO_3 decreased the yield of **2** (entry 5). In this case, longer reaction time increased the yield of product **2** (entry 6). The dicarboxylic acid **2** was obtained in 94–96% yield without any monocarboxylic acid **9** using 2–3 mmol CrO_3 (entries 7 and 8). The stoichiometric CrO_3 oxidation of **8** in conc. H_2SO_4 afforded 94% of **2** (entry 9).

CrO_3 -mediated oxidation of 4,4',4''-triethyl-2,2':6',2''-terpyridine **10** was examined (Scheme 3). The oxidation using 10.5 equiv. H_5IO_6 , 3 equiv. CrO_3 in the mixture of H_2SO_4 and H_2O (2:1) for 18 h afforded corresponding tricarboxy terpyridine **11** in 80% yield. The reported yield of **11** by stoichiometric $\text{K}_2\text{Cr}_2\text{O}_7$ oxidation is 36%.^[6b] The yield of **11** obtained by our method is more than double of the reported yield.

We chose triethylterpyridine **10** as the substrate instead of 4,4',4''-trimethyl-2,2':6',2''-terpyridine **12**, (Figure 1) because triethylterpyridine **10** could be obtained in higher yield (>20%)^[6b] than trimethylterpyridine **12** (2–3%)^[18] by Pd/C-catalyzed coupling reaction of 4-alkylpyridines.^[19] The better yield of **11** may be attributed to the careful control of oxidizing power by increasing water content in solvent sulfuric acid.

Quaterpyridines are another interest for the ligand of ruthenium dyes for DSSCs.^[3,20] CrO_3 -mediated oxidation of 4,4',4'',4'''-tetraethyl-2,2':6',2'':6'',2'''-quaterpyridine **13** was investigated (Scheme 4). The use of 14 equiv. H_5IO_6 , 4 equiv. CrO_3 in the mixture of H_2SO_4 and H_2O (2:1) afforded corresponding tetracarboxy quaterpyridine **14** in 72% yield. The structure of **14** was confirmed by converting to tetraethyl ester **15**. After purification by column chromatography, the structure of **15** was confirmed by its ^1H - and ^{13}C -NMR spectrum.

In summary, $\text{CrO}_3/\text{H}_5\text{IO}_6$ has been found to be an efficient combination for the oxidation of polyalkyl-polypyridines to polycarboxy-polypyridines in the mixture of H_2SO_4 and H_2O (2:1) as the solvent. Dimethylbipyridines and a diethylbipyridine afforded corresponding dicarboxybipyridines in over 90% yields. No monomethyl by-product was detected in suitable reaction conditions. 4,4',4''-Triethyl-2,2':6',2''-terpyridine **10**



Scheme 4. Oxidation of 4,4',4'',4'''-Tetraethyl-2,2':6',2'':6'':2'''-quaterpyridine 13.

afforded corresponding tricarboxyterpyridine **11** in 80% yields, that was double of the yield by stoichiometric chromium oxidation. 4,4',4'',4'''-Tetraethyl-2,2':6',2'':6'':2'''-quaterpyridine **13** was also converted to the corresponding tetracarboxylic acid **14** in good yield. The use of easily accessible commercial reagents, the simple operation, the use of reduced amount of chromium reagent (1/3-1/6 compared to stoichiometric chromium oxidation), and formation of products in good to excellent yields make this method advantageous to existing procedures.

Experimental

10 g scale synthesis of 4,4'-dicarboxy-2,2'-bipyridine 2

H₅IO₆ (74.2 g, 326 mmol) was dissolved in the mixture of conc. H₂SO₄ (300 mL) and H₂O (150 mL) with stirring at room temperature. CrO₃ (5.43 g, 54.3 mmol) was added to the solution and dissolved with stirring (2 h). Powdered 4,4'-dimethyl-2,2'-bipyridine **1** (10.0 g, 54.3 mmol) was added in one portion to the solution. The resulted mixture was stirred vigorously at room temperature for 24 h. The solution was poured slowly into ice-water (2000 mL) with stirring, and the mixture was stirred for 10 min. The white precipitate was collected by filtration and washed well successively with H₂O and methanol. Vacuum drying gave 13.3 g (100%) of 4,4'-dicarboxy-2,2'-bipyridine **2**. ¹H NMR^[21] (400 MHz, D₂O/NaOD(1%), TSP) δ ppm: 7.83 (2H, dd, *J* = 5.0, 1.4 Hz), 8.34 (2H, s), 8.74 (2H, d, *J* = 5.0 Hz); ¹³C NMR (100 MHz, D₂O/NaOD(3%), 40 °C, relative to external dioxane at δ 67.4) δ ppm: 122.0, 124.2, 147.2, 150.7, 156.5, 173.7.

Full experimental detail, copies of ¹H and ¹³C-NMR spectra. This material can be found via the "Supplemental material" section of this article's webpage.

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ORCIDShigekazu Yamazaki  <http://orcid.org/0000-0002-0326-0727>**References**

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