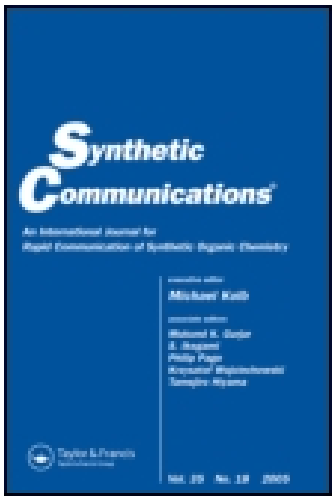

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AN EFFICIENT SYNTHESIS OF ω-(2,2′-BIPYRIDYL)ALKYL ALCOHOLS AND THEIR ACRYLATES

Katsuya Maeyama [a] , Chieri Okumura [a] & Noriyuki Yonezawa [b]

[a] Department of Organic and Polymer Materials Chemistry , Tokyo University of Agriculture and Technology , Koganei, Tokyo, 184-8588, Japan

[b] Department of Organic and Polymer Materials Chemistry , Tokyo University of Agriculture and Technology , Koganei, Tokyo, 184-8588, Japan

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AN EFFICIENT SYNTHESIS OF ω-(2,2′-BIPYRIDYL)ALKYL ALCOHOLS AND THEIR ACRYLATES

Katsuya Maeyama, Chieri Okumura, and Noriyuki Yonezawa*

Department of Organic and Polymer Materials Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo, 184-8588, Japan

ABSTRACT

ω-(2,2′-Bipyridyl)alkyl alcohols were synthesized by treatment of methyl-2,2′-bipyridine with LDA at −78°C followed by the addition of ω-bromoalkyl THP ether and hydrolysis of the resulting THP ether. Furthermore, ω-2,2′-bipyridylalkyl acrylates were obtained by the reaction of the corresponding ω-(2,2′-bipyridyl)alkyl alcohols with acryloyl chloride in good yields.

Key Words: ω-(2,2′-Bipyridyl)alkyl alcohol; ω-(2,2′-Bipyridyl)alkyl acrylate; Carbon–carbon bond formation using alkylation

2,2′-Bipyridine is one of the most widely used ligands for preparation of transition metal complexes through efficient coordinating nature to metals. Though a number of molecules containing plural 2,2′-bipyridines

*Corresponding author. E-mail: yonezawa@cc.tuat.ac.jp

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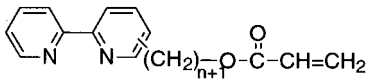


1

Formulae 1. Structures of ω-(2,2′-bipyridyl)alkyl acrylates.

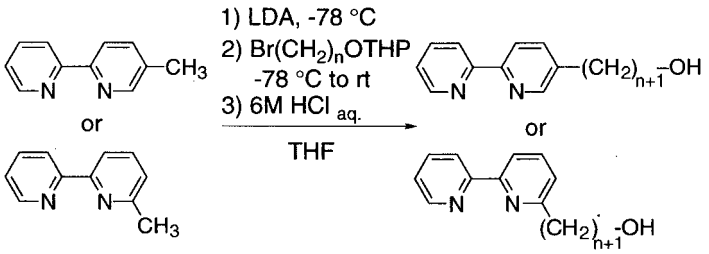
have been reported, there are a few reports on polymers containing 2,2′-bipyridine units in the side chains.[1] To our knowledge, the structures of the reported polymers have been substantially limited to the following cases: polymers where 2,2′-bipyridinyl units are connected with the main chains without any tethers, through methylene tethers, or through other rigid tethers.[2,3] We expected that more flexible circumstance around 2,2′-bipyridyl unit would reveal anomalous functionality. With this expectation, we planned the synthesis of ω-bipyridylalkyl acrylates **1**, in which the acrylate unit is linked to the bipyridyl moiety through *alkylene tethers* (Formulae 1).

For the synthesis of target molecules **1**, the construction of carbon–carbon bond structure between bipyridyl ring and a hydroxyalkyl group is crucial. In this paper, we would like to describe the efficient syntheses of ω-bipyridylalkyl alcohols and their acrylates.

First, we attempted to synthesize target molecule **1** according to Wittig type conversion of 5-(2,2′-bipyridine)carbaldehyde by the action of ω-hydroxyalkylenetriphenylphosphorane derivatives and reduction of the produced olefin. However, the desired carbon–carbon bond formation was not achieved. When the phosphorane prepared from THP-protected ω-hydroxyalkyl halide was subjected to this reaction, no desired compound was obtained. Next, we examined nucleophilic substitution reaction of THP-protected ω-hydroxyalkyl halide with 2,2′-bipyridylmethyl anion.

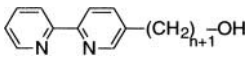
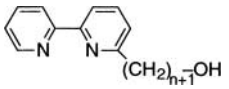
5-Methyl-2,2′-bipyridine was treated with LDA in THF at −78°C followed by addition of 2-bromoethyl THP ether.[4,5] After consumption of the starting material was confirmed, the reaction mixture was quenched with water, followed by chromatographic separation on a short column of alumina. The obtained mixture was treated with aqueous 6 M HCl to hydrolyze the THP ether, yielding the corresponding alcohol (**2a**) in a moderate yield.

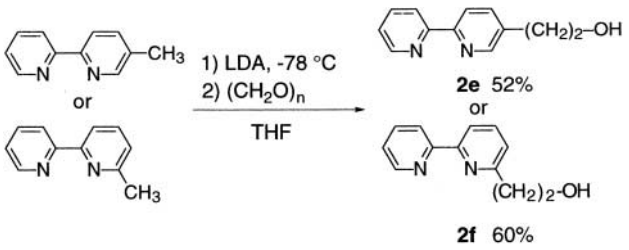
This method is applicable for the preparation of the related ω-bipyridylalkyl alcohols where ω-hydroxyalkyl group is substituted on the different position of the bipyridyl ring and/or the tether has the different length. We synthesized various ω-bipyridylalkyl alcohol homologue and isomers **(2b–d)** (Sch. 1, Table 1). The synthesis of four ω-bipyridylalkyl alcohols



Scheme 1. Synthesis of 3-bipyridylpropanol and 4-bipyridylbutanol.

Table 1. Synthesis of ω-Bipyridylalkyl Alcohols **2**

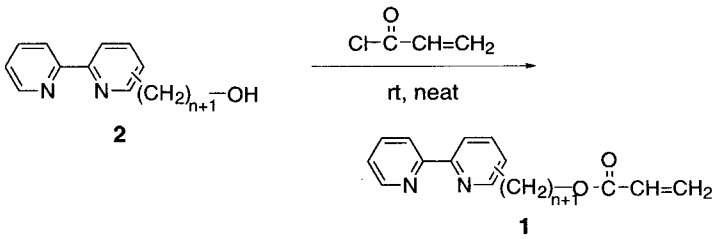
Alcohols **2**	$n+1$	Yield/%
	3 (**2a**)	74
	4 (**2b**)	49
	3 (**2c**)	70
	4 (**2d**)	53



Scheme 2. Synthesis of 2-bipyridylethanol.

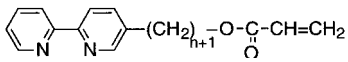
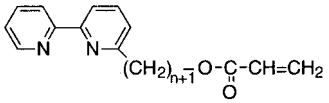
(2a–d) was undertaken by the connection of 5- or 6-methyl-2,2′-bipyridine and 2-bromoethyl or 3-bromopropyl THP ether.

According to Ziessel's method,[6] alcohol **2e** and **2f**, whose alkyl chain are $-CH_2CH_2-$, were also synthesized (Sch. 2). Methylbipyridines were allowed to react with LDA at $-78^{\circ}C$ followed by treatment of paraformaldehyde. The corresponding alcohols were obtained in rather low yields. It is probably due to the lack of solubility of paraformaldehyde. Utilization of trioxane in place of paraformaldehyde had no effect to raise up the yield.



Scheme 3. Synthesis of ω-bipyridylalkyl acrylates **1**.

Table 2. Synthesis of ω-Bipyridylalkyl Acrylates **1**

Acrylates **1**	$n+1$	Yield/%
	2	61
	3	98
	4	90
	2	82
	3	100
	4	88

As a series of ω-bipyridylalkyl alcohols (**2**) were obtained, we examined the synthesis of the target molecules (**1**) from ω-bipyridylalkyl alcohols **2**.

Conversion of ω-bipyridylalkyl alcohols **2** to ω-bipyridylalkyl acrylates **1** was successfully achieved by treatment of ω-bipyridylalkyl alcohols **2** with acrylolyl chloride without solvent. The desired six acrylates were obtained as viscous liquids in good yields (Sch. 3). The results are summarized in Table 2.

In conclusion, we established the synthetic method of ω-bipyridylalkyl acrylates.

In the near future, we will report the polymerization of these molecules and the functionality of the polymers.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-A500 (^{1}H; 500 MHz, ^{13}C; 125 MHz) spectrometer using Me_4Si (^{1}H, δ 0.00) and $CDCl_3$ (^{13}C, δ 77.0) as internal standards. IR spectra were recorded

on a JEOL FTIR-5300 spectrometer. 5-Methyl-2,2′-bipyridine[7] and 6-methyl-2,2′-bipyridine[8] were prepared according to the literatures. 2-(2-Bromoethoxy)-3,4,5,6-tetrahydro-2*H*-pyran or 2-(3-bromopropoxy)-3,4,5,6-tetrahydro-2*H*-pyran was prepared by the reaction of ω-bromoalkyl alcohol and 3,4-dihydro-2*H*-pyran (DHP) in the presence of TsOH in CH_2Cl_2. Diisopropylamine was distilled from CaH_2 before use. Acryloyl chloride was purchased from Aldrich Co. Ltd. and used without further purification. Chromatographic separations were carried out on Wako alumina (activated, about 300 mesh).

5-(3-Hydroxypropyl)-2,2′-bipyridine (2a): To a THF solution (10 mL) of diisopropylamine (3.6 g, 36 mmol) was added a hexane solution of *n*-BuLi (20 mL, 30 mmol, 1.6 M) dropwise at −78°C and the reaction mixture was stirred for 1 h. To this mixture was added a THF solution of 5-methyl-2,2′-bipyridine (5.1 g, 30 mmol) and the resulting mixture was stirred for 3 h. Then, a THF solution of 2-(2-bromoethoxy)-3,4,5,6-tetrahydro-2*H*-pyran (6.3 g, 30 mmol) was added dropwise into the reaction mixture. After the mixture was stirred for 5 h at −78°C, the reaction mixture was quenched by addition of water (10 mL). The organic materials were extracted with chloroform (10 mL × 3) and the combined extracts were dried over Na_2SO_4. After removal of solvents, the residue was purified by a short column of alumina with chloroform as an eluent. The obtained compounds were treated with aqueous 6 M HCl. The mixture was stirred overnight at r.t. The organic materials were extracted with chloroform (10 mL × 3) and the combined extracts were dried over Na_2SO_4. After removal of solvents, the residue was purified by alumina column chromatography with chloroform to give 5-(3-hydroxypropyl)-2,2′-bipyridine (**2a**) (3.1 g, 2.2 mmol, 74%).

IR (neat) 3356, 3007, 2939, 1591, 1462, 1059, 752, 650 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.77 (2H, tt, $J = 8.0$, 6.4 Hz), 2.63 (2H, t, $J = 8.0$ Hz), 3.54 (2H, t, $J = 6.4$ Hz), 7.17 (1H, ddd, $J = 8.0$, 4.8, 1.2 Hz), 7.51 (1H, dd, $J = 8.0$, 2.0 Hz), 7.68 (1H, dt, $J = 8.0$, 2.0 Hz), 8.16 (1H, d, $J = 8.0$ Hz), 8.22 (1H, dd, $J = 8.0$, 1.2 Hz), 8.38 (1H, d, $J = 2.0$ Hz), 8.54 (1H, dd, $J = 4.8$, 1.2 Hz) ppm; ^{13}C NMR δ ($CDCl_3$) 28.8, 33.5, 61.1, 120.7, 120.8, 123.4, 136.8, 136.9, 137.5, 148.9, 149.1, 153.6, 155.9 ppm; Anal. Calcd. for $C_{13}H_{14}N_2O$; C, 72.88; H, 6.59; N, 13.07. Found: C, 73.21; H, 6.74; N, 12.83%.

Compounds **2b–d** were synthesized according to the method for the synthesis of compound **2a** described above.

5-(4-Hydroxybutyl)-2,2′-bipyridine (2b): IR (neat) 3364, 2937, 1589, 1460, 1066, 752 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.60 (2H, quint, $J = 7.5$ Hz), 1.72 (2H, quint, $J = 7.5$ Hz), 2.67 (2H, t, $J = 7.5$ Hz), 2.89 (1H, s), 3.64 (2H, t, $J = 7.5$ Hz), 7.27–7.29 (1H, m), 7.62 (1H, dd, $J = 8.5$, 2 Hz), 7.80 (1H, dt, $J = 8.0$, 1.5 Hz), 8.28 (1H, d, $J = 8.5$ Hz), 8.34 (1H, dd, $J = 8.0$,

1.0 Hz), 8.49 (1H, d, $J = 2$ Hz), 8.65 (1H, dt, $J = 4.5$, 1 Hz) ppm; ^{13}C NMR δ ($CDCl_3$) 27.2, 32.0, 32.4, 62.1, 120.7, 120.8, 123.4, 136.8, 136.9, 137.8, 148.9, 149.1, 153.7, 156.0 ppm; Anal. Calcd. for $C_{14}H_{16}N_2O$; C, 73.66; H, 7.06; N, 12.27. Found: C, 73.35; H, 7.08; N, 12.03%.

6-(3-Hydroxypropyl)-2,2′-bipyridine (2c): IR (neat) 3362, 3061, 2935, 1581, 1458, 1049, 775, 621 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 2.08 (2H, quint, $J = 6.5$ Hz), 3.06 (2H, t, $J = 6.5$ Hz), 3.77 (2H, t, $J = 6.5$ Hz), 7.21 (1H, d, $J = 7.5$ Hz), 7.29–7.32 (1H, m), 7.76 (1H, t, $J = 8.0$ Hz), 7.83 (1H, dt, $J = 7.5$, 1.5 Hz), 8.23 (1H, d, $J = 8.0$ Hz), 8.33 (1H, dd, $J = 8.0$, 1.0 Hz), 8.68–8.69 (1H, m) ppm; ^{13}C NMR δ ($CDCl_3$) 31.2, 35.2, 62.3, 118.8, 121.1, 123.2, 123.7, 137.1, 137.7, 149.2, 155.4, 156.0, 160.8 ppm; Anal. Calcd. for $C_{13}H_{14}N_2O$; C, 72.88; H, 6.59; N, 13.07. Found: C, 71.49; H, 6.07; N, 14.13%.

6-(4-Hydroxybutyl)-2,2′-bipyridine (2d): IR (neat) 3373, 3061, 2937, 1581, 1458, 1060, 777 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.69 (2H, quint, $J = 7.5$ Hz), 1.77 (1H, brs), 1.92 (2H, tt, $J = 7.5$, 6.5 Hz), 2.93 (2H, t, $J = 7.5$ Hz), 3.71 (2H, dt, $J = 6.5$, 1.5 Hz), 7.18 (1H, d, $J = 7.5$ Hz), 7.29–7.31 (1H, m), 7.73 (1H, dt, $J = 8.0$, 1.0 Hz), 7.81 (1H, tt, $J = 7.5$, 1.5 Hz), 8.19 (1H, d, $J = 8.0$ Hz), 8.41 (1H, dd, $J = 8.0$, 1.0 Hz), 8.67–8.68 (1H, m) ppm; ^{13}C NMR δ ($CDCl_3$) 25.7, 32.0, 37.6, 62.6, 118.5, 121.2, 122.9, 123.5, 136.9, 137.2, 149.1, 155.4, 156.4, 161.4 ppm; Anal. Calcd. for $C_{14}H_{16}N_2O$; C, 73.33; H, 7.06; N, 12.27. Found: C, 73.39; H, 6.79; N, 11.98%.

5-(2-Hydroxyethyl)-2,2′-bipyridine (2e): Compound **2e** was synthesized referred to Ziessel's method.[6]

To a THF solution (10 mL) of diisopropylamine (0.53 g, 5.3 mmol) was added a hexane solution of *n*-BuLi (3.1 mL, 5.0 mmol, 1.6 M) dropwise at −78°C and the reaction mixture was stirred for 1 h. A THF solution (4 mL) of 5-methyl-2,2′-bipyridine (0.85 g, 5.0 mmol) was added and stirred for 3 h. Next, a THF suspension of paraformaldehyde (0.18 g, 6.0 mmol) was dropped into the reaction mixture. After the mixture was stirred for 5 h at −78°C, it was quenched by the addition of water (10 mL). The organic materials were extracted with chloroform (10 mL × 3) and the combined extracts were dried over Na_2SO_4. After removal of solvents, the residue was purified by alumina column chromatography with chloroform as an eluent to give 5-(2-hydroxyethyl)-2,2′-bipyridine (**2e**) (0.54 g, 2.6 mmol, 52%).

IR (neat) 3348, 3055, 2939, 1581, 1462, 1051, 750, 650 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 2.91 (2H, t, $J = 6.5$ Hz), 3.90 (2H, dt, $J = 6.5$, 1.5 Hz), 7.28–7.31 (1H, m), 7.68 (1H, d, $J = 8.0$ Hz), 7.81 (1H, tt, $J = 7.5$, 1.5 Hz), 8.30 (1H, d, $J = 8.0$ Hz), 8.34 (1H, dd, $J = 8.0$, 1.5 Hz), 8.52 (1H, s), 8.65–8.67 (1H, m) ppm; ^{13}C NMR δ ($CDCl_3$) 27.2, 32.0, 32.4, 62.1, 120.7, 120.8, 123.4, 136.8, 136.9, 137.8, 148.9, 149.1, 153.7, 156.0 ppm; Anal. Calcd. for $C_{12}H_{12}N_2O$; C, 71.97; H, 6.04; N, 13.99. Found: C, 71.94; H, 6.07; N, 14.13%.

2-(2,2′-Bipyridin-5-yl)ethyl acrylate (1a): Acryloyl chloride (0.21 mL, 7.1 mmol) was added to 5-(2-hydroxyethyl)-2,2′-bipyridine (**2a**) (0.96 g, 4.7 mmol) neatly. The reaction mixture was stirred overnight at r.t. The reaction was quenched by the addition of water and neutralized with aqueous 6 M NaOH. The organic materials were extracted with chloroform (10 mL × 3) and the combined extracts were dried over Na_2SO_4. After removal of solvents, the residue was purified by alumina column chromatography with chloroform as an eluent to give 2-(2,2′-bipyridin-5-yl)ethyl acrylate (**1a**) (1.1 g, 2.9 mmol, 61%).

IR (neat) 3061, 1726, 1581, 1460, 1429, 773 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.94 (2H, t, $J = 6.5$ Hz), 4.32 (2H, t, $J = 6.5$ Hz), 5.78 (1H, d, $J = 10.5$ Hz), 6.06 (1H, dd, $J = 17.5$, 10.5 Hz), 6.35 (1H, d, $J = 17.5$ Hz), 7.24 (1H, t, $J = 7.5$ Hz), 7.65 (1H, d, $J = 8.0$ Hz), 7.75 (1H, t, $J = 7.5$ Hz), 8.31 (1H, d, $J = 7.5$ Hz), 8.33 (1H, d, $J = 7.5$ Hz), 8.52 (1H, s), 8.62 (1H, d, $J = 4.5$ Hz) ppm; ^{13}C NMR δ ($CDCl_3$) 32.0, 64.1, 120.7, 120.8, 123.5, 128.0, 130.9, 133.4, 136.8, 137.2, 149.0, 149.5, 154.6, 155.9, 165.8 ppm; Anal. Calcd. for $C_{15}H_{14}N_2O_2$; C, 70.85; H, 5.55; N, 11.02. Found: C, 70.87; H, 5.67; N, 11.03%.

Acrylates **1b–f** were also synthesized according to above method.

3-(2,2′-Bipyridin-5-yl)propyl acrylate (1b): IR (neat) 3051, 1724, 1589, 1460, 1057, 750 cm^{-1}; ^1H NMR δ ($CDCl_3$) 2.05 (2H, tt, $J = 7.5$, 6.5 Hz), 2.77 (2H, t, $J = 7.5$ Hz), 4.21 (2H, t, $J = 6.5$ Hz), 5.83 (1H, dd, $J = 10.5$, 1.5 Hz), 6.14 (1H, dd, $J = 17.0$, 10.5 Hz), 6.41 (1H, dd, $J = 17.5$, 1.5 Hz), 7.26–7.29 (1H, m), 7.64 (1H, dd, $J = 8.5$, 1.5 Hz), 7.79 (1H, dd, $J = 8.0$, 1.5 Hz), 8.33 (1H, d, $J = 8.0$ Hz), 8.37 (1H, dd, $J = 8.5$, 1.5 Hz), 8.53 (1H, s), 8.66–8.67 (1H, m) ppm; ^{13}C NMR δ ($CDCl_3$) 29.0, 29.6, 63.3, 120.6, 120.6, 123.3, 128.1, 130.6, 136.5, 136.6, 136.7, 148.9, 149.1, 154.0, 155.9, 165.9 ppm; Anal. Calcd. for $C_{16}H_{16}N_2O_2$; C, 71.62; H, 5.97; N, 10.44. Found: C, 71.93; H, 5.77; N, 10.33%.

4-(2,2′-Bipyridin-5-yl)butyl acrylate (1c): IR (neat) 3005, 2943, 1722, 1273, 1195, 810 cm^{-1}; ^1H NMR δ ($CDCl_3$) 1.74–1.85 (4H, m), 2.73 (2H, t, $J = 7.0$ Hz), 4.20 (2H, t, $J = 6.0$ Hz), 5.83 (1H, dd, $J = 10.5$, 1.5 Hz), 6.12 (1H, dd, $J = 17.0$, 10.5 Hz), 6.40 (1H, dd, $J = 17.0$, 1.5 Hz), 7.30 (1H, ddd, $J = 7.5$, 5.0, 1.0 Hz), 7.65 (1H, dd, $J = 8.0$, 2.0 Hz), 7.81 (1H, dt, $J = 7.5$, 2.0 Hz), 8.32 (1H, d, $J = 8.0$ Hz), 8.37 (1H, dt, $J = 7.5$, 1.0 Hz), 8.52 (1H, d, $J = 2.0$ Hz), 8.67 (1H, ddd, $J = 5.0$, 2.0, 1.0 Hz) ppm; ^{13}C NMR δ ($CDCl_3$) 27.4, 28.1, 32.3, 64.1, 120.8, 120.8, 123.4, 128.4, 130.7, 136.8, 136.9, 137.4, 149.1, 149.2, 154.1, 156.1, 166.2 ppm; Anal. Calcd. for $C_{17}H_{18}N_2O_2$; C, 72.32; H, 6.43; N, 9.92. Found: C, 72.10; H, 6.43; N, 9.95%.

2-(2,2′-Bipyridin-6-yl)ethyl acrylate (1d): IR (neat) 3061, 2961, 1724, 1581, 1273, 1188, 810 cm^{-1}; ^1H NMR δ ($CDCl_3$) 3.24 (2H, t, $J = 7.0$ Hz), 4.67 (2H, t, $J = 7.0$ Hz), 5.79 (1H, tt, $J = 10.5$, 1.5 Hz), 6.10 (1H, ddd, $J = 17.5$, 10.5, 1.5 Hz), 6.37 (1H, dt, $J = 17.5$, 1.5 Hz), 7.21 (1H, d, $J = 8.0$ Hz),

7.29–7.32 (1H, m), 7.74 (1H, dt, $J = 8.0$, 2.0 Hz), 7.81 (1H, dt, $J = 8.0$, 1.5 Hz), 8.26 (1H, d, $J = 8.0$ Hz), 8.45 (1H, dd, $J = 8.0$, 1.0 Hz), 8.66–8.68 (1H, m) ppm; ^{13}C NMR δ ($CDCl_3$) 37.2, 63.7, 118.8, 121.2, 123.4, 123.6, 128.4, 130.7, 136.8, 137.2, 149.0 155.7, 156.2, 157.3, 166.2 ppm; Anal. Calcd. for $C_{15}H_{14}N_2O_2$; C, 70.85; H, 5.55; N, 11.02. Found: C, 70.67; H, 5.65; N, 10.87%.

3-(2,2′-Bipyridin-6-yl)propyl acrylate (1e): IR (neat) 3061, 2959, 1726, 1579, 1273, 1194, 810 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 2.25 (2H, quint, $J = 7.0$ Hz), 2.97 (2H, t, $J = 7.0$ Hz), 4.29 (2H, t, $J = 7.0$ Hz), 5.82 (1H, dt, $J = 10.5$, 1.5 Hz), 6.13 (1H, dq, $J = 17.0$, 10.5 Hz), 6.40 (1H, dt, $J = 17.5$, 1.5 Hz), 7.17 (1H, d, $J = 8.0$ Hz), 7.27–7.31 (1H, m), 7.73 (1H, dt, $J = 8.0$, 2.0 Hz), 7.81 (1H, dt, $J = 8.0$, 1.5 Hz), 8.22 (1H, d, $J = 8.0$ Hz), 8.44 (1H, dd, $J = 8.0$, 1.0 Hz), 8.66–8.68 (1H, m) ppm; ^{13}C NMR δ ($CDCl_3$) 28.2, 34.5, 64.1, 118.5, 121.2, 122.8, 123.6, 128.5, 130.6, 136.9, 137.2, 149.0, 155.6, 158.4, 160.2, 166.3 ppm; Anal. Calcd. for $C_{16}H_{16}N_2O_2$; C, 71.62; H, 5.97; N, 10.44. Found: C, 71.32; H, 6.11; N, 10.14%.

4-(2,2′-Bipyridin-5-yl)butyl acrylate (1f): IR (neat) 2951, 1724, 1579, 1273, 1195, 989, 810 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 1.77–1.85 (2H, m), 1.90–1.96 (2H, m), 2.92 (2H, t, $J = 7.0$ Hz), 4.23 (2H, t, $J = 6.5$ Hz), 5.81 (1H, dd, $J = 10.5$, 1.5 Hz), 6.12 (1H, dd, $J = 17.0$, 10.5 Hz), 6.40 (1H, dd, $J = 17.0$, 1.5 Hz), 7.17 (1H, d, $J = 7.5$ Hz), 7.26–7.31 (1H, m), 7.72 (1H, t, $J = 7.5$ Hz), 7.81 (1H, dt, $J = 8.0$, 2.0 Hz), 8.21 (1H, d, $J = 7.5$ Hz), 8.44 (1H, dt, $J = 8.0$, 1.0 Hz), 8.67–8.68 (1H, m) ppm; ^{13}C NMR δ ($CDCl_3$) 25.8, 28.2, 37.6, 64.4, 118.4, 121.2, 122.7, 123.5, 128.6, 130.6, 136.8, 137.1, 149.0, 155.5, 156.6, 161.0, 166.3 ppm; Anal. Calcd. for $C_{17}H_{18}N_2O_2$; C, 72.32; H, 6.43; N, 9.92. Found: C, 72.10; H, 6.45; N, 9.69%.

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REFERENCES

1. Kaes, C.; Katz, A.; Hosseini, M.W. Chem. Rev. **2000**, *100*, 3553.
2. Lewis, A.L.; Miller, J.D. J. Mater. Chem. **1993**, *3*, 897.
3. (a) Pitt, C.G.; Bao, Y.; Seltzman, H.H. J. Polym. Sci. Polym. Lett. **1986**, *24*, 13; (b) Cars, R.J.; Neckers, D.C. Inorg. Chem. **1978**, *17*, 2345.

4. As the example for alkylation of 2,2′-bipyridylmethyl anion derivative, see: Albrecht, M.; Riether, C. Chem. Ber. **1996**, *129*, 829.
5. As the example for alkylations of 5,5′-dimethyl-2,2′-bipyridine employing ethylene oxide or $I(CH_2)_3OTHP$, see: Lindner, E.; Veigel, R.; Ortner, K.; Nachtigal, C.; Steimann, M. Eur. J. Inorg. Chem. **2000**, *5*, 959.
6. Ziessel et al. reported the synthesis of alcohol **2f**. See: Ziessel, R.; Toupet, L.; Chardon-Noblat, S.; Deronizer, A.; Matt, D. J. Chem. Soc., Dalton Trans. **1997**, 3777.
7. (a) Polin, J.; Schmohel, E.; Balzani, V. Synthesis **1998**, 321; (b) Huang, T.L. J. Can. Chem. Soc. **1981**, *59*, 1689; (c) Kröhnke, F. Angew. Chem. **1953**, *59*, 605.
8. Kauffmann, T.; König, J.; Waltermann, A. Chem. Ber. **1976**, *109*, 3864.

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