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Synthesis and Characterization of 5-Cyano-6-methyl-2,2′-bipyridine Metal-Complex Dyes

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ABSTRACT

New 1:1 5-cyano-6-methyl-2,2′-bipyridine–metal (Co, Ni, Cu, and Zn) complex dyes have been synthesized in good yields. The metals do not significantly affect the wavelength of maximum absorption of the complexes; substituents at the 4-position showed remarkable bathochromic shifts in the following order: $CH{=}CHC_6H_4NMe_2(p) > C_6H_4NMe_2(p) > C_6H_5$, *ferrocenyl.*

1 INTRODUCTION

Pyridine derivatives are important intermediates in the synthesis of dyes, agrochemicals, and pharmaceuticals, etc. Whereas 2,2′-bipyridine and *o*-phenanthroline are known to form metal complexes, and can be used as indicators for metal ions, few derivatives of 2,2′-bipyridine have been synthesized. We have previously reported the synthesis of some 4,6-disubstituted 3-cyano-6-methylpyridines,[1–3] and we now report the synthesis and characterization of 4-substituted 5-cyano-6-methyl-2,2′-pyridine metal-complex dyes.

2 RESULTS AND DISCUSSION

Scheme 1 shows the synthetic path to the 5-cyano-6-methyl-2,2′-bipyridine metal-complex dyes **2**–**M**. 1-(2-Pyridyl)-2-propen-1-ones **1**, prepared by an

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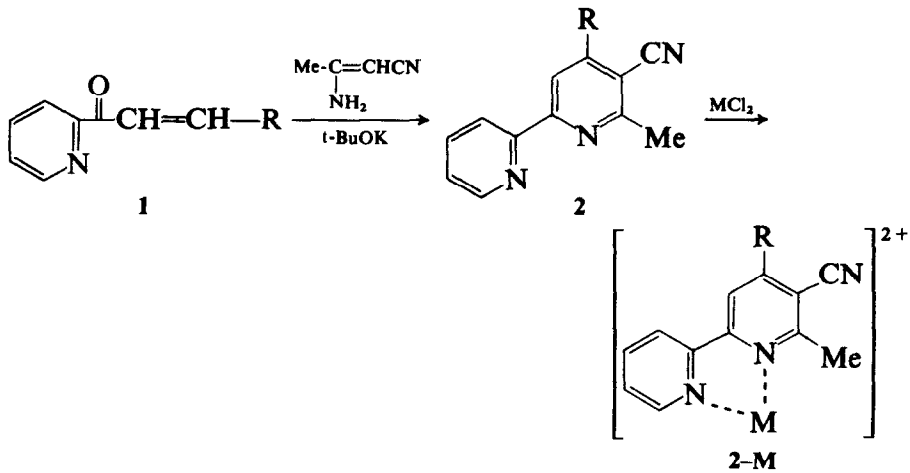

R = C_6H_5, $C_6H_4(NMe_2)$, CH=CH—$C_6H_4(NMe_2)$, Ferrocenyl
M = Co, Ni, Cu, Zn

Scheme 1

aldol condensation of 2-acetylpyridine with aldehydes, were treated with β-aminocrotononitrile in the presence of potassium *t*-butoxide to give 5-cyano-6-methyl-2,2′-bipyridines **2**. A Michael addition of the imino isomer of β-aminocrotononitrile to **1**, followed by intramolecular cyclization, dehydration, and dehydrogenation, gives **2**.[1-3] The complex dyes **2–M** were obtained by treating **2** with metal chlorides.

Figure 1 shows the change in the absorption spectra of **2c** resultant from the addition of Cu^{2+} ($CuCl_2 \cdot 2H_2O$). As a larger amount of Cu^{2+} is added, the absorbance at 417 nm decreases, whereas that at 490 nm increases. This result suggests that **2c** reacts smoothly with Cu^{2+} to form the **2c–Cu** complex. Similar results were obtained in the reaction of **2** with Co^{2+} ($CoCl_2 \cdot 6H_2O$), Ni^{2+} ($NiCl_2 \cdot 6H_2O$), and Zn^{2+} ($ZnCl_2$). No reaction of **2c** was observed with $Cu(Ac)_2$ and $CuSO_4 \cdot 5H_2O$.

Figure 2 shows the plots of absorbance at 490 nm against the molecular fraction of **2c**. The maximum of *c.* 0·50 mol fraction of **2c** indicated that the complex consisted of **2c** and Cu in the ratio of 1:1. The same results were obtained in the reactions of **2** with Co^{2+}, Ni^{2+}, and Zn^{2+}. Bipyridine and *o*-phenanthroline are known to form metal complexes in the ligand:metal ratio of 3:1. The steric effect of the methyl group at the 6-position of **2** may influence the **2**:metal ratio to give the 1:1 adducts **2–M**.

Table 1 summarizes the syntheses of **1**, **2**, and **2–M**. The products were obtained in moderate-to-good yields.

Figure 3 shows the fast-atom-bombardment (FAB) mass spectrum of the **2c–Cu** complex. The ion peak (M^+–2Cl) of **2c–Cu** was observed at m/z 403,

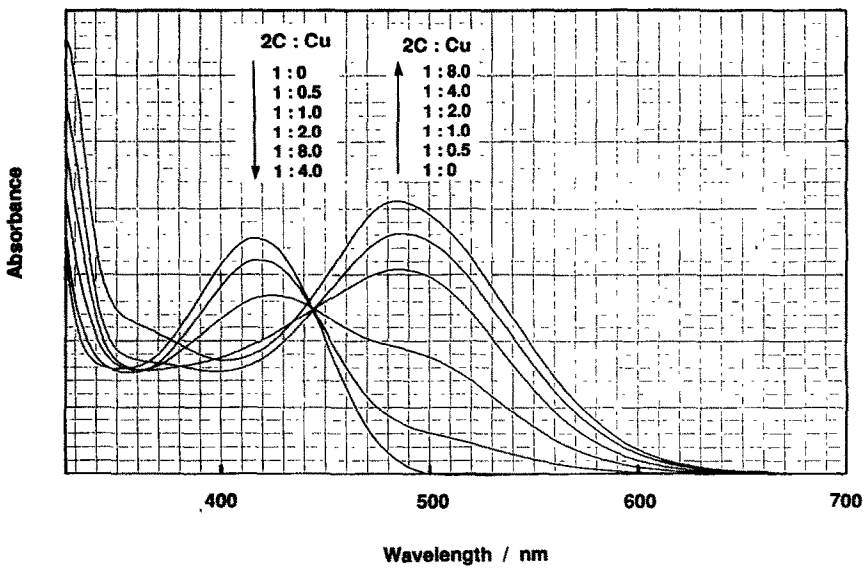

Fig. 1. Change of UV spectra of **2c** by the addition of Cu^{2+}. To an acetone solution of **2c** was added an acetone solution of $CuCl_2 \cdot 2H_2O$ at room temperature.

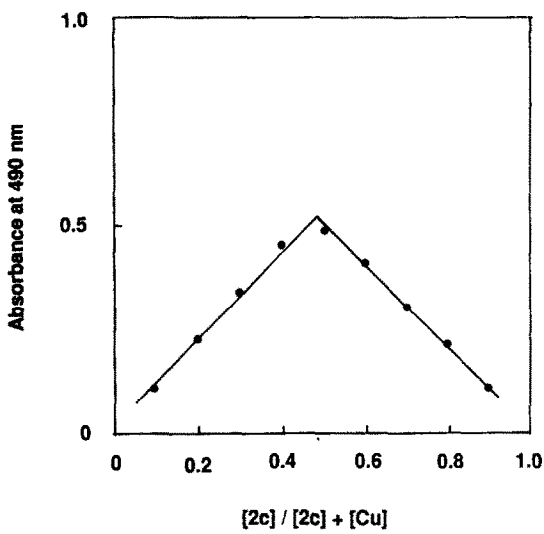

Fig. 2. Continuous-variation plots for **2c**–Cu complex in acetone. To an acetone solution of **2c** was added an acetone solution of $CuCl_2 \cdot 2H_2O$ at room temperature.

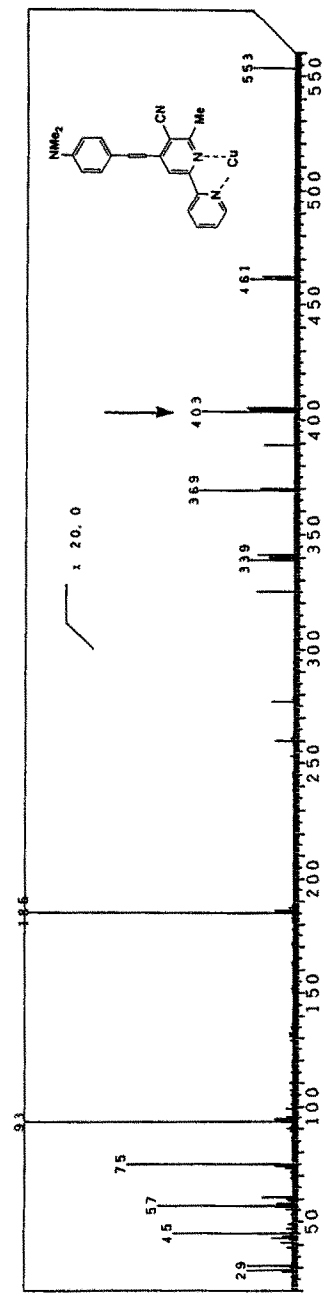

Fig. 3. FAB mass spectrum of **2c**–Cu.

TABLE 1
Syntheses of 1-(2-Pyridyl)-2-propen-1-ones (**1**), 5-Cyano-2-methyl-2,2'-bi-pyridines (**2**), and their Metal-Complex Dyes (**2–M**)

Run	*Compd*	*R*	*Yield*[a] (%)		
			1	***2***	***2–M***
1	a	C_6H_5	93	39	85 ($CoCl_2$)
2					96 ($NiCl_2$)
3					78 ($CuCl_2$)
4					84 ($ZnCl_2$)
5	b	$4\text{-}Me_2NC_6H_4$	76	70	91 ($CoCl_2$)
6					91 ($NiCl_2$)
7					90 ($CuCl_2$)
8					87 ($ZnCl_2$)
9	c	$4\text{-}Me_2NC_6H_4CH{=}CH$	95	42	83 ($CoCl_2$)
10					71 ($NiCl_2$)
11					79 ($CuCl_2$)
12					91 ($ZnCl_2$)
13	d	Ferrocenyl	88	59	95 ($CoCl_2$)
14					94 ($NiCl_2$)
15					99 ($CuCl_2$)
16					73 ($ZnCl_2$)

[a] Isolated yield.

accompanied by ion peaks of the glycerol matrix (m/z = 93, 185, 277, 369, 461, and 553). Measurement of FAB mass spectra of **2–Co** and **2–Zn** were unsuccessful.

Table 2 summarizes the absorption spectra of **2**, **2–M**, and the differences of the absorption maxima wavelength ($\Delta\lambda$) between **2** and **2–M**. The complex dyes **2–M** showed bathochromic shifts compared with the corresponding metal free 2,2'-bipyridines **2**. The absorption maxima of **2–M**, which show very large absorption coefficients ($\varepsilon = 10\,500$–$28\,500$), can be attributed to π–π^* transitions within the molecule. The longest-wavelength absorption maxima, having small extinction coefficients ($\varepsilon = 1300$–2600), of **2d–M** are due to a ferrocenyl group at the 4-position. The co-ordinate metals do not significantly affect the λ_{max} of **2–M**. For example, λ_{max} values of **2c–Co**, **2c–Ni**, **2c–Cu**, and **2c–Zn** were observed at 514, 483, 510, and 494 nm, respectively. This result indicates that the electron density of the nitrogen atom at the 2-position of **2–M** is hardly affected by the nature of the co-ordinate metal. However, substituents at the 4-position drastically affected the λ_{max} of **2–M**. For example, long wavelength bathochromic shifts of **2–Cu** were observed in the following order of the substituents at the

TABLE 2
Absorption Spectra of 5-Cyano-6-methyl-2,2′-bipyridines (**2**) and their Metal-Complex Dyes (**2–M**)[a]

Run	*Compd*	*R*	***2***		***2–M***			$\Delta\lambda$
			λ_{max} (*nm*)	ε	*Metal*	λ_{max} (*nm*)	ε	
1	2a	C_6H_5	304	20900	Co	314	14500	10
2					Ni	320	21600	16
3					Cu	317	19700	13
4					Zn	316	22100	12
5	2b	4-$Me_2NC_6H_4$	381	13600	Co	461	10500	80
6					Ni	437	11600	56
7					Cu	462	13100	81
8					Zn	456	13000	75
9	2c	4-$Me_2NC_6H_4CH{=}CH$	420	20900	Co	514	15900	94
10					Ni	483	13000	63
11					Cu	510	28500	90
12					Zn	494	11600	74
13	2d	Ferrocenyl	301	20900	Co	318	21000	17
			484	1300		542	2000	58
14					Ni	332	17000	31
						570	2300	86
15					Cu	320	18000	19
						575	1800	91
16					Zn	317	23700	16
						565	2600	81

[a] Measured in dichloromethane.

4-position, $CH{=}CHC_6H_4NMe_2(p)$ (510 nm) > $C_6H_4NMe_2(p)$ (465 nm) > C_6H_5 (317 nm), ferrocenyl (317, 565 nm). Similar trends were observed in the cases of **2–Co**, **2–Ni**, and **2–Zn**.

3 EXPERIMENTAL

3.1 General

NMR and mass spectra were recorded on JEOL JNM-270 GX and Shimadzu 9020-DF mass spectrometers, respectively. IR and UV spectra were obtained with Perkin Elmer FT-IR 1640 and Hitachi 330 spectrophotometers, respectively. Melting points were measured with a Yanagimoto micro-melting-point apparatus and were uncorrected.

3.2 Synthesis of 1-(2-pyridyl)-2-propen-1-ones 1 (general procedure)

To an ethanol solution (20 ml) of 2-acetylpyridine (2·4 g, 0·02 mol) and the appropriate aldehyde (0·02 mol), was added 20% aqueous sodium hydroxide solution (6 ml), and the mixture was stirred at room temperature overnight. The resultant precipitate was filtered and recrystallized from ethanol. Physical and spectral data of the 1-(2-pyridyl)-2-propen-1-ones **1** are shown below.

3-Phenyl-1-(2-pyridyl)-2-propen-1-one (**1a**): m.p. 72·5–73·5°C (lit[4] m.p. 75°C); ^{1}H NMR ($CDCl_3$) δ 7·41–7·43 (m, 3H), 7·48 (dd, J = 7·3 and 4·7 Hz, 1H), 7·71–7·75 (m, 2H), 7·88 (dd, J = 8·8 and 7·3 Hz, 1H), 7·94 (d, J = 15·9 Hz, 1H), 8·19 (d, J = 8·8 Hz, 1H), 8·31 (d, J = 15·9 Hz, 1H), and 8·74 (d, J = 4·7 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 209 (M^+ 100).

3-[4-(Dimethylamino)phenyl]-1-(2-pyridyl)-2-propen-1-one (**1b**): m.p. 138·0–139·5°C; ^{1}H NMR ($CDCl_3$) δ 3·03 (s, 6H), 6·68 (d, J = 9·0 Hz, 2H), 7·64 (d, J = 9·0 Hz, 2H), and 7·43–8·80 (m, 6H); EIMS (70 eV) m/z (rel intensity) 252 (M^+, 100); HRMS m/z 252·1267. Calc. for $C_{16}H_{16}N_2O$: 252·1262; anal. found: C, 76·03; H, 6·35; N, 11·00%. Calc. for $C_{16}H_{16}N_2O$: C, 76·17; H, 6·39; N, 11·10%.

5-[4-(Dimethylamino)phenyl]-1-(2-pyridyl)-2,4-pentadiene-1-one (**1c**): m.p. 155·5–156·0°C; ^{1}H NMR ($CDCl_3$) δ 3·02 (s, 6H), 6·70 (d, J = 8·5 Hz, 2H), 6·92–7·04 (m, 2H), 7·41 (d, J = 8·5 Hz, 2H), 7·44–7·47 (m, 1H), 7·65–7·75 (m, 2H), 7·85 (ddd, J = 8·0, 7·6, and 4·8 Hz, 1H), 8·15 (d, J = 8·0 Hz, 1H), and 8·71 (d, J = 4·8 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 278 (M^+, 90) and 172 (100); HRMS m/z 278·1413. Calc. for $C_{18}H_{18}N_2O$: 278·1418; anal. found: C, 77·68; H, 6·47; N, 10·15%. Calc. for $C_{18}H_{18}N_2O$: C, 77·67; H, 6·52; N, 10·06%.

3-Ferrocenyl-1-(2-pyridyl)-2-propen-1-one (**1d**): m.p. 151·5–152·5°C (lit[5] m.p. 158°C); ^{1}H NMR ($CDCl_3$) δ 4·17 (s, 5H), 4·49 (d, J = 1·3 Hz, 2H), 4·17 (d, J = 1·3 Hz, 2H), 7·46 (t, 1H), 7·81–7·94 (m, 3H), 8·18 (d, J = 7·7 Hz, 1H), and 8·73 (d, J = 3·9 Hz, 1H); EIMS (70 eV) m/z (rel intensity) 317 (M^+, 100).

3.3 Synthesis of 5-cyano-6-methyl-2,2'-bipyridines 2 (general procedure)

To an acetonitrile solution (50 ml) of β-aminocrotonitrile (1·2 mmol) and potassium t-butoxide (0·6 g) was added 1-(2-pyridyl)-2-propen-1-one **1** (0·1 mmol). The mixture was stirred at room temperature for 6 h. After the reaction, the product was extracted with ether (100 ml × 3) and dried over sodium sulfate. After evaporation of the solvent, the product was recrystallized from ethanol. Physical and spectral data of 5-cyano-6-methyl-2,2'-bipyridines **2** are shown below.

5-Cyano-6-methyl-4-phenyl-2,2'-bipyridine (**2a**): m.p. 175·5–179·5°C; ^{1}H NMR ($CDCl_3$) δ 2·93 (s, 3H), 7·37 (dd, J = 6·8 and 5·1 Hz, 1H), 7·52–7·56 (m,

3H), 7·67–7·70 (m, 2H), 7·87 (ddd, $J = 7·9$, 6·8 and 1·6 Hz, 1H), 8·45 (s, 1H), 8·53 (d, $J = 7·9$ Hz, 1H), and 8·70 (dd, $J = 5·1$ and 1·6 Hz, 1H); IR (KBr) 2215 cm^{-1}; EIMS (70 eV) m/z (rel intensity) 271 (M^+, 100); HRMS m/z 271·1122. Calc. for $C_{18}H_{13}N_3$ 271·1109; anal. found: C, 79·88; H, 4·71; N, 15·28%. Calc. for $C_{18}H_{13}N_3$: C, 79·68; H, 4·83; N, 15·49%.

5-Cyano-4-[4-(dimethylamino)phenyl]-6-methyl-2,2′-bipyridine (**2b**): m.p. 264·0–265·0°C; ^1H NMR ($CDCl_3$) δ 2·90 (s, 3H), 3·05 (s, 6H), 6·82 (d, $J = 8·5$ Hz, 2H), 7·35 (ddd, $J = 6·7$, 4·2, and 1·8 Hz, 1H), 7·68 (d, $J = 8·5$ Hz, 2H), 7·85 (ddd, $J = 8·0$, 6·7, and 1·8 Hz, 1H), 8·40 (s, 1H), 8·50 (dd, $J = 8·0$ and 1·8 Hz, 1H), and 8·71 (dd, $J = 4·2$ and 1·8 Hz, 1H); IR (KBr) 2219 cm^{-1}; EIMS (70 eV) m/z (rel intensity) 314 (M^+, 100); HRMS m/z 314·1533. Calc. for $C_{20}H_{18}N_4$: 314·1530; anal. found: C, 76·71; H, 5·68; N, 17·81%. Calc. for $C_{20}H_{18}N_4$: C, 76·41; H, 5·77; N, 17·82%.

5-Cyano-4-[4-(dimethylamino)styryl]-6-methyl-2,2′-bipyridine (**2c**): m.p. 267·0–269·5°C; ^1H NMR ($CDCl_3$) δ 2·84 (s, 3H), 3·05 (s, 6H), 6·72 (d, $J = 8·8$ Hz, 2H), 7·21 (d, $J = 15·9$ Hz, 1H), 7·31 (dd, $J = 7·3$ and 4·9 Hz, 1H), 7·55 (d, $J = 8·8$ Hz, 2H), 7·65 (d, $J = 15·9$ Hz, 1H), 7·86 (ddd, $J = 7·8$, 7·3, and 1·8 Hz, 1H), 8·50 (d, $J = 7·8$ Hz, 1H), 8·60 (s, 1H), and 8·74 (dd, $J = 4·9$ and 1·8 Hz, 1H); IR (KBr) 2222 cm^{-1}; EIMS (70 eV) m/z (rel intensity) 340 (M^+, 91) and 325 (100); HRMS m/z 340·1660. Calc. for $C_{22}H_{20}N_4$: 340·1687; anal. found: C, 77·34; H, 5·82; N, 16·06%. Calc. for $C_{22}H_{20}N_4$: C, 77·62; H, 5·92; N, 16·46%.

5-Cyano-4-ferrocenyl-6-methyl-2,2′-bipyridine (**2d**): m.p. 199·0–200·5°C; ^1H NMR ($CDCl_3$) δ 2·87 (s, 3H), 4·19 (s, 5H), 4·55 (s, 2H), 5·19 (s, 2H), 7·36 (dd, $J = 7·6$ and 4·6 Hz, 1H), 7·85 (dd, $J = 8·0$ and 7·6 Hz, 1H), 8·44 (s, 1H), 8·49 (d, $J = 8·0$ Hz, 1H), and 8·73 (d, $J = 4·6$ Hz, 1H); IR (KBr) 2223 cm^{-1}; EIMS (70 eV) m/z (rel intensity) 379 (M^+, 100); HRMS m/z 379·0765. Calc. for $C_{22}H_{17}N_3Fe$: 379·0771; anal. found: C, 69·58; H, 4·43; N, 11·11%. Calc. for $C_{22}H_{17}N_3Fe$: C, 69·68; H, 4·52; N, 11·08%.

3.4 Synthesis of 5-cyano-6-methyl-2,2′-bipyridine metal complex dyes (*2–M*) (general procedure)

To an acetone solution (200 ml) of 5-cyano-6-methyl-2,2′-bipyridine **2** (0·2 mmol) was added an acetone solution (20 ml) of a metal chloride (0·2 mmol, $CoCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $NiCl_2 \cdot 6H_2O$, and $ZnCl_2$). The mixture was stirred at room temperature for 1 h. After evaporation of the solvent, the resulting precipitate was washed with acetone and dried *in vacuo*. Melting points of all **2–M** were over 300°C. The spectral data of **2–M** are shown below.

5-Cyano-6-methyl-4-phenyl-2,2′-bipyridine–cobalt(II) chloride (**2a–Co**): IR (KBr) 2226 cm^{-1}.

5-Cyano-6-methyl-4-phenyl-2,2′-bipyridine–nickel(II) chloride (**2a–Ni**): IR (KBr) 2226 cm^{-1}; FABMS m/z 329 (M^+–2Cl).

5-Cyano-6-methyl-4-phenyl-2,2′-bipyridine–copper(II) chloride (**2a–Cu**): IR (KBr) 2226 cm^{-1}; FABMS m/z 334 (M^+–2Cl).

5-Cyano-6-methyl-4-phenyl-2,2′-bipyridine–zinc(II) chloride (**2a–Zn**): IR (KBr) 2226 cm^{-1}.

5-Cyano-4-[4-(dimethylamino)phenyl]-6-methyl-2,2′-bipyridine–cobalt(II) chloride (**2b–Co**): IR (KBr) 2222 cm^{-1}.

5-Cyano-4-[4-(dimethylamino)phenyl]-6-methyl-2,2′-bipyridine–nickel(II) chloride (**2b–Ni**): IR (KBr) 2222 cm^{-1}; FABMS m/z 372 (M^+–2Cl).

5-Cyano-4-[4-(dimethylamino)phenyl]-6-methyl-2,2′-bipyridine–copper(II) chloride (**2b–Cu**): IR (KBr) 2222 cm^{-1}; FABMS m/z 377 (M^+–2Cl).

5-Cyano-4-[4-(dimethylamino)phenyl]-6-methyl-2,2′-bipyridine–zinc(II) chloride (**2b–Zn**): IR (KBr) 2226 cm^{-1}.

5-Cyano-4-[4-(dimethylamino)styryl]-6-methyl-2,2′-bipyridine–cobalt(II) chloride (**2c–Co**): IR (KBr) 2222 cm^{-1}.

5-Cyano-4-[4-dimethylamino)styryl]-6-methyl-2,2′-bipyridine–nickel(II) chloride (**2c–Ni**): IR (KBr) 2211 cm^{-1}; FABMS m/z 398 (M^+–2Cl).

5-Cyano-4-[4-(dimethylamino)styryl]-6-methyl-2,2′-bipyridine–copper(II) chloride (**2c–Cu**): IR (KBr) 2222 cm^{-1}; FABMS m/z 403 (M^+–2Cl).

5-Cyano-4-[4-(dimethylamino)styryl]-6-methyl-2,2′-bipyridine–zinc(II) chloride (**2c–Zn**): IR (KBr) 2222 cm^{-1}.

5-Cyano-4-ferrocenyl-6-methyl-2,2′-bipyridine–cobalt(II) chloride (**2d–Co**): IR (KBr) 2226 cm^{-1}.

5-Cyano-4-ferrocenyl-6-methyl-2,2′-bipyridine–nickel(II) chloride (**2d–Ni**): IR (KBr) 2238 cm^{-1}; FABMS m/z 437 (M^+–2Cl).

5-Cyano-4-ferrocenyl-6-methyl-2,2′-bipyridine–copper(II) chloride (**2d–Cu**): IR (KBr) 2225 cm^{-1}; FABMS m/z 442 (M^+–2Cl).

5-Cyano-4-ferrocenyl-6-methyl-2,2′-bipyridine–zinc(II) chloride (**2d–Zn**): IR (KBr) 2238 cm^{-1}.

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