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SYNTHESIS AND PROPERTIES OF 9,9'-SPIROBIFLUORENE-BASED HETEROCYCLES

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Abstract – A series of 9,9'-spirobifluorene-derived *N*-heterocycles were prepared by Frieländer reaction of 2-acetyl-9,9'-spirobifluorene with a series of *ortho*-aminoaldehydes in 74-88% yields. Spectral properties and abilities to form Ru(II) complexes were examined.

The 9,9'-spirobifluorene (**1**) has been attractive due to the characteristic structure since its discovery.¹ After the first examples employed as a motif in the area of molecular recognition were reported by the groups of Prelog,² Diederich,³ and others,⁴ 9,9'-spirobifluorene and related compounds especially oligomers or polymers have been used in a wide range of applications in molecular electronics,⁵ macromolecular chemistry,⁶ light emitting devices,⁷ and others.⁸

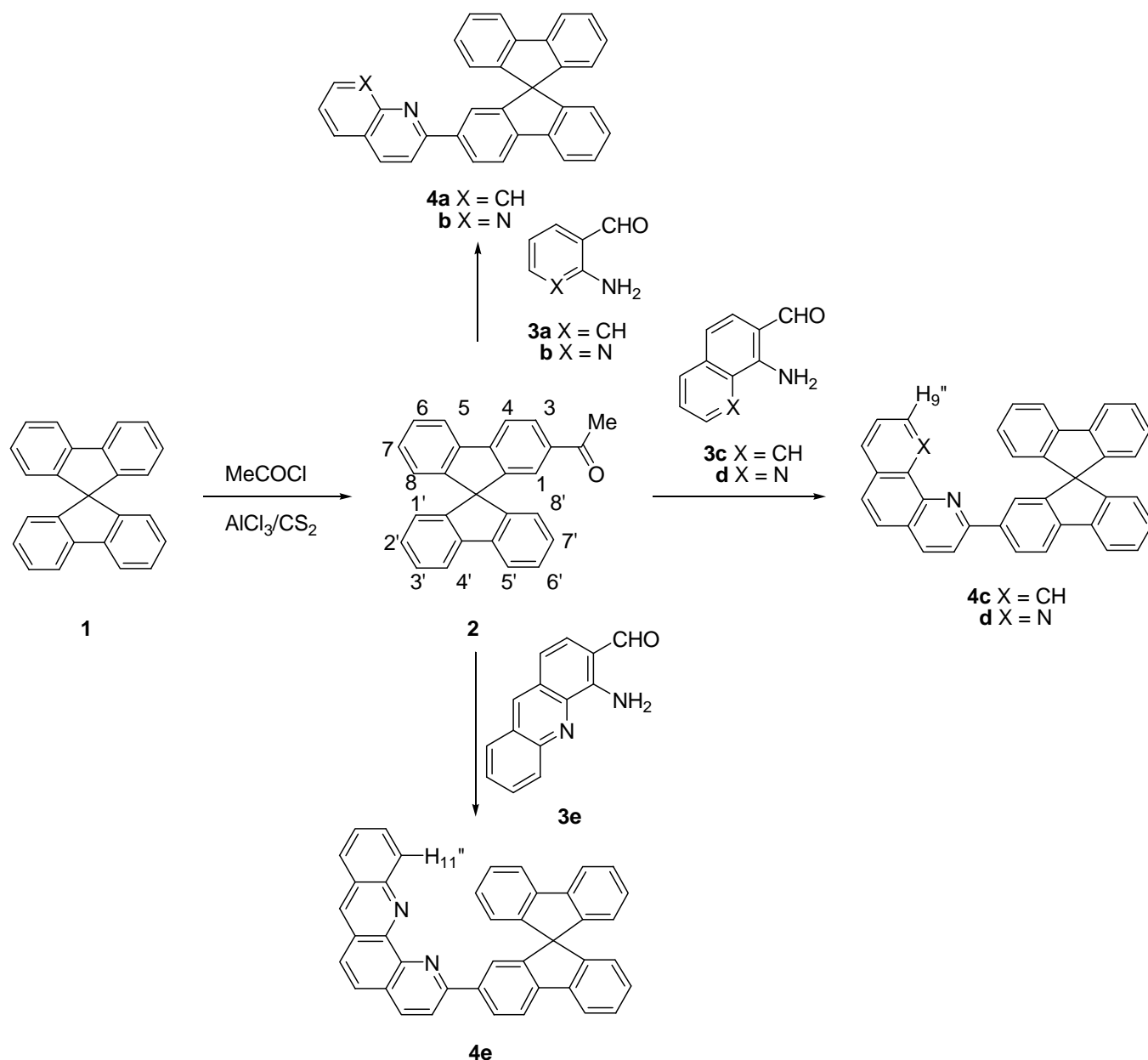
Studies of monomeric 9,9'-spirobifluorenes especially 9,9'-spirobifluorene-derived *N*-heterocycles are very limited. Although a few poly(pyridine-derived-heteroaryl)-9,9'-spirobifluorenes such as 2,2'-di(1,10-phenanthrol-2-yl)-9,9'-spirobifluorene,⁹ 2,2'-di(benzo[*h*]quinol-2-yl)-9,9'-spirobifluorene,¹⁰ and 2,2',7,7'-tetra(benzo[*h*]quinol-2-yl)-9,9'-spirobifluorene,¹⁰ have been reported, 2-(4-phenylquinol-2-yl)-9,9'-spirobifluorene¹¹ is, to the best of our knowledge, the only mono-substituted pyridine-derived heteroaryl-9,9'-spirobifluorene reported so far. In addition, systematic approaches either for the preparation or for the examination of their properties of the systems have not been pursued as yet.

Our interest¹² in the preparation and properties of polydentates as well as their metal complexes spurred to prepare a series of 9,9'-spirobifluorene-derived *N*-heterocycles and to study their properties.

The prerequisite 9,9'-spirobifluorene (**1**) was readily prepared in three steps from relatively cheap 2-bromobiphenyl by a modification of previously reported method.^{1,13} The Grignard reaction of 2-bromobiphenyl with commercially available 9-fluorenone gave 9-(2'-biphenyl)-9-fluorenol, which was subjected to acid-catalyzed cyclization to afford **1** in an overall yield of 52%. The Friedel-Craft acylation of **1** with an equimolar of acetyl chloride afforded 2-acetyl-9,9'-spirobifluorene (**2**)¹⁴ in 11% yield along

with 2,2'-diacetyl-9,9'-spirobifluorene as a major product (51%), which were readily separable by column chromatography and fully characterized.

Synthesis of the 9,9'-spirobifluorene-derived heterocycles was straight-forwards as shown in Scheme 1. The Friedländer condensation of 2-acetyl-9,9'-spirobifluorene (**2**) with a series of *o*-aminoaldehydes (**3**)¹⁵ afforded the corresponding 9,9'-spirobifluorene-derived heteroaromatics (**4**) in 74-88% yields.



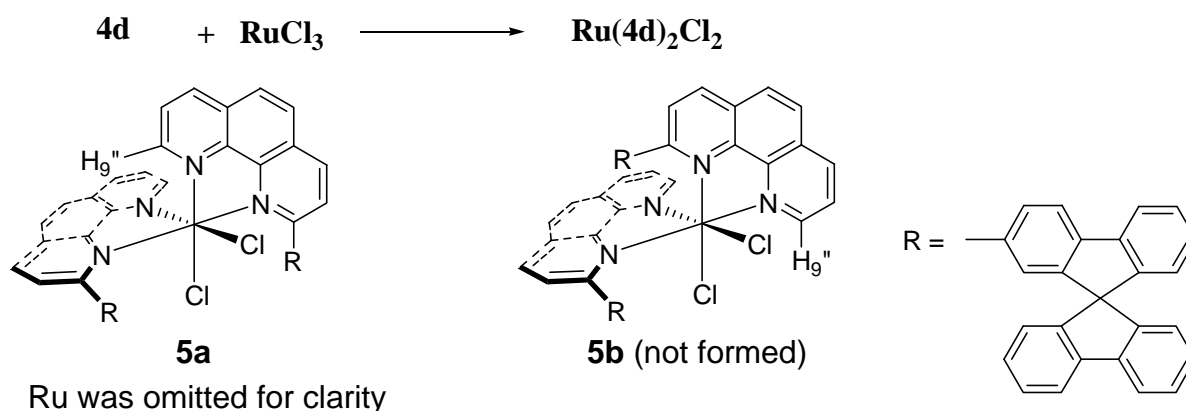
Scheme 1. Synthesis of 9,9'-spirobifluorene-derived heterocycles (**4**)

Some proton resonances of the products were characteristic enough to afford probes for the structure suggested. The protons adjacent to nitrogen such as $\text{H}_{7''}$ of **4b** and $\text{H}_{9''}$ of **4d** are the ones of characteristic chemical shifts (δ 9.02 and 9.15, respectively) with relatively small 3J coupling constant

(4.3 Hz).¹⁶ In addition, the resonances of H1 of 9,9'-spirobifluorene moiety generally appeared in the region of δ 7.47-7.80 with a characteristic *meta*-coupling constant ($^4J = 1.4$ -1.8 Hz). The protons H8, H1' and H8' of the 9,9'-spirobifluorene moiety are the most upfield-shifted ones due to the anisotropic effect of the neighboring two phenyl groups, thus are resonanced in the range of δ 6.80-6.71. Additionally, the protons at the *peri*-position of **4a** and **4e** (H8'' of **4a**, H11'' of **4e**) were resonanced at δ 8.67 and 8.61, respectively, and H10'' of benzo[*h*]quinoline moiety of **4c** was resonanced at δ 9.34 as a doublet of doublet ($^3J = 8.8$ Hz and $^4J = 1.8$ Hz), which experienced anisotropic effect of neighboring pyridine as well as electronic effect of lone pair electrons on N1'' most seriously.

UV absorption spectra of 9,9'-spirobifluorene (**1**) and its derivatives **4** were taken from 95% EtOH (1.6×10^{-5} M) and are summarized in Table 1. Three major absorption maxima originated from the π - π^* transition were observed in the regions of 221-226, 253-274, 296-315, and 330-370 nm. The absorptions in the range of 330-370 nm were not observed in the parent compound 9,9'-spirobifluorene, thus such absorptions were from π - π^* transition of the heterocyclic rings of the system. The absorption maximum is highly dependent on the nature of the heterocycles attached to 9,9'-spirobifluorene. UV spectrum of **4e** showed two characteristic features. Annulation of an additional benzene ring on **4d** not only led bathochromic shift of the absorptions at 233 and 264 nm to 254 and 275 nm, respectively, and increased corresponding intensity, but also increased the absorption intensity for the absorption at 332 nm.

To examine the ability to form metal complexes, a reaction of ligand **4d** with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in refluxing 95% EtOH was pursued to afford $\text{Ru}(\mathbf{4d})_2\text{Cl}_2$ in 83% yield as dark brown solid. The steric congestion around the Ru(II) core induced by the two ligands chelated would not allow approaching of the third ligand for forming tris-complexes.



Although two diastereomers (**5a** and **5b**) were possible in $\text{Ru}(\mathbf{4d})_2\text{Cl}_2$, ^1H NMR of the complex showed only one set of spectrum in $\text{DMSO}-d_6$. The resonance at δ 8.27 with characteristic 3J coupling constant ($^3J = 4.8$ and $^4J = 1.0$ Hz)¹⁶ covered H9'', a sensitive probe for the structure of the complex, which was upfield-shifted by 0.88 ppm compared to that of the parent ligand (**4d**). In complex **5a**, H9'' experiences

the shielding effect of neighboring ligand on the Ru core by lying towards the shielding region to lead 0.88 ppm upfield-shift while H9'' in **5b** lies towards deshielding region of Cl.^{12b,17} It should be noted that reaction of **4e** with RuCl₃·3H₂O afforded a messy mixture of complexes which were not able either to separate nor to characterize. Steric hindrance induced by H11'' of the ligand and/or free rotation through 2,2'-bond would prevent forming not only bis- but also tris-complexes as have been reported for 4'-(pyri-4''-yl)-2,2';6',2''-terpyridine.¹⁸

Table 1. UV absorption spectral data of 9,9'-spirobifluorene-heterocycles

Compound	λ_{\max} (ϵ) (M ⁻¹ cm ⁻¹ , 95% EtOH)				
1	225 (44,400)	239 (25,000)	272 (19,300)	297 (8,300)	308 (12,800)
4a	222 (67,200)	274 (36,500)	296 (24,900)	307 (26,200)	339 (27,500)
4b	224 (53,210)	273 (12,400)	296 (8,200)	307 (8,000)	353 (12,700)
4c	222 (72,900)	245 (sh, 55,100)	295 (sh, 30,800)	308 (37,300)	332 (29,900)
4d	352 (22,200)	368 (21,800)	226 (58,400)	233 (56,600)	264 (29,700)
4e	332 (28,500)	363 (sh, 17,100)	222 (46,100)	254 (47,500)	275 (sh, 28,100)
	369 (sh, 15,400)		309 (21,900)	335 (33,200)	

In conclusion, a series of 9,9'-spirobifluorene-derived *N*-heterocycles were prepared by Frieländer reaction of 2-acetyl-9,9'-spirobifluorene with a series of *ortho*-aminoaldehydes. Studies on photophysical properties of the ligands and their metal complexes are in progress, which will be due in the future.

EXPERIMENTAL

Melting points were determined using a Fischer-Jones melting points apparatus and are not corrected. IR spectra were obtained using a Perkin-Elmer 1330 spectrophotometer. NMR spectra were obtained using a Bruker-250 spectrometer 250 MHz for ¹H NMR and 62.5 MHz for ¹³C NMR and are reported as parts per million (ppm) from tetramethylsilane. The starting 9,9'-spirobifluorene (**1**)^{1,13} and *o*-aminoaldehydes (**3**)¹⁵ were prepared by previously reported methods. Electrospray ionization (ESI) mass spectrometry (MS) experiments were performed on a LCQ advantage-trap mass spectrometer (Thermo Finnigan, San Jose, CA, USA). Elemental analyses were taken on a Hewlett-Packard Model 185B elemental analyzer.

2-Acetyl-9,9'-spirobifluorene (**2**)

A solution of 9,9'-spirobifluorene (5.0 g, 15.8 mmol) in dry CS₂ (30 mL) was slowly added powdered AlCl₃ (9.0 g) in portions (~10 min). To a stirring mixture resulted was added 1.24 g (15.8 mmol) of acetyl chloride in CS₂ (20 mL). After 1 h reflux, the reaction mixture was poured to a mixture of ice (100 g) and 2N HCl (50 mL). The solid formed was collected and chromatographed on silica gel eluting with

benzene:EtOAc (10:1). The early fractions [$R_f = 0.26$ (CH_2Cl_2 :hexane = 4:9)] afforded 0.60 g (11%) of 2-acetyl-9,9'-spirobifluorene (**4**) (CHCl_3 :benzene): mp 225 °C (lit.,¹⁴ mp 225 °C). ^1H NMR (CDCl_3) δ 8.00 (dd, $J = 8.0, 1.6$ Hz, 1H, H3), 7.89 (d, $J = 8.0$ Hz, 1H, H4), 7.87 (d, $J = 8.0$ Hz, 1H, H5), 7.83 (d, $J = 8.0$ Hz, 2H, H4', H5'), 7.39 (td, $J = 7.5, 1.2$ Hz, 1H, H6), 7.35 (td, $J = 7.5, 1.2$ Hz, 2H, H3', H6'), 7.30 (d, $J = 1.8$ Hz, 1H, H1), 7.15 (td, $J = 7.5, 1.2$ Hz, 1H, H7), 7.08 (td, $J = 7.5, 1.2$ Hz, 2H, H2', H7'), 6.73 (d, $J = 7.8$ Hz, 1H, H8), 6.67 (d, $J = 7.5$ Hz, 2H, H1', H8'), 2.43 (s, 3H). The latter fractions [$R_f = 0.07$ (CH_2Cl_2 :hexane = 4:9)] afforded 1.60 g (51%) of 2,2'-diacetyl-9,9'-spirobifluorene.

2-(Quinol-2'-yl)-9,9'-spirobifluorene (4a) (General Procedure)

A mixture of 2-aminobenzaldehyde (133 mg, 1.10 mmol) and 2-acetyl-9,9'-spirobifluorene (358 mg, 1.00 mmol) in absolute EtOH (20 mL) with saturated alcoholic KOH (1 mL) was refluxed for 5h. Upon cooling the reaction mixture the solid formed was collected as a pure product 354 mg (80 %) yellow solid: mp 198 °C. IR (KBr) ν 3056, 1593, 1445, 1429 824 cm^{-1} . ^1H NMR (CDCl_3) δ 8.27 (dd, $J = 7.8, 1.5$ Hz, 1H, H8''), 8.06 (d, $J = 8.0$ Hz, 1H, H4''), 8.04 (d, $J = 8.0$ Hz, 1H, H5''), 7.98 (d, $J = 8.0$ Hz, 1H, H3''), 7.90-7.85 (m, 3H, H1, H3, H7''), 7.69 (d, $J = 7.5$ Hz, 1H, H4), 7.66 (d, $J = 7.0$ Hz, 1H, H5), 7.64 (td, $J = 7.5, 1.5$ Hz, 1H, H6''), 7.44-7.34 (m, 5H, H6, H3', H4', H5', H6'), 7.11 (td, $J = 7.5, 1.3$ Hz, 1H, H7), 7.10 (td, $J = 7.5, 1.3$ Hz, 2H, H2', H7'), 6.77 (dd, $J = 7.5, 1.0$ Hz, 2H, H1' and H8'), 6.72 (dd, $J = 7.5, 1.0$ Hz, 1H, H8). ^{13}C NMR (CDCl_3) δ 157.09, 149.60, 149.21, 148.53, 148.13, 136.47, 129.56, 129.53, 128.18, 127.90, 127.77, 127.71, 127.33, 126.13, 124.21, 124.01, 123.17, 120.42, 120.36, 120.04, 119.14, 66.07. MS (ESI) calcd for $\text{C}_{34}\text{H}_{22}\text{N}$ [$\text{M}+\text{H}^+$]: 444. Found: 444. Anal. Calcd for $\text{C}_{34}\text{H}_{21}\text{N}$: C, 92.07; H, 4.77; N, 3.16. Found: C, 92.07; H, 4.74 N, 3.13.

2-(1'',8''-Naphthrid-2-yl)-9,9'-spirobifluorene (4b)

Yield (88%): mp 142 °C. ^1H NMR (CDCl_3) δ 9.02 (dd, $J = 4.3, 2.0$ Hz, 1H, H7''), 8.36 (dd, $J = 8.3, 1.5$ Hz, 1H, H5''), 8.09 (d, $J = 8.5$ Hz, 1H, H4''), 8.08 (dd, $J = 8.0, 1.2$ Hz, 1H, H3), 7.99 (d, $J = 8.0$ Hz, 1H, H4), 7.91-7.83 (m, 4H), 7.76 (d, $J = 1.0$ Hz, 1H, H1), 7.40-7.33 (m, 4H), 7.11 (td, $J = 7.8, 1.2$ Hz, 1H, H6), 7.08 (td, $J = 7.8, 1.2$ Hz, 2H, H3' and H6'), 6.75 (d, $J = 7.8$ Hz, 2H, H4' and H5'), 6.72 (d, $J = 7.8$ Hz, 1H, H5). ^{13}C NMR (CDCl_3) δ 160.00, 155.88, 153.68, 149.91, 148.30, 144.02, 141.95, 140.84, 138.04, 137.41, 136.65, 128.41, 127.93, 127.83, 127.77, 124.08, 124.04, 123.67, 121.58, 121.54, 120.46, 120.27, 120.17, 119.85, 66.05. MS (ESI) calcd for $\text{C}_{33}\text{H}_{21}\text{N}_2^+$ [$\text{M}+\text{H}^+$]: 573. Found: 573. Anal. Calcd for $\text{C}_{33}\text{H}_{20}\text{N}_2\cdot\text{H}_2\text{O}$ C, 85.69; H, 4.79; N, 6.06. Found: C, 85.73, H, 4.74 N, 6.09.

2-(Benzo[h]quinol-2''-yl)-9,9'-spirobifluorene (4c)

Yield (79%): mp 132 °C. ^1H NMR (CDCl_3) δ 9.34 (dd, $J = 8.8, 1.8$ Hz, 1H, H10''), 8.57 (dd, $J = 8.0, 1.5$ Hz, 1H), 8.04 (dd, $J = 8.0$ Hz, 2H), 7.94-7.85 (m, 4H), 7.71-7.68 (m, 4H), 7.60 (d, $J = 8.5$ Hz, 1H), 7.48 (d, $J = 1.3$ Hz, H1), 7.40 (td, $J = 7.5, 1.0$ Hz, 1H, H6), 7.39 (td, $J = 7.5, 1.0$ Hz, 2H, H3' and H6'), 7.13 (td, $J = 7.5, 1.2$ Hz, 1H, H7), 7.12 (td, $J = 7.5, 1.0$ Hz, 2H, H2' and H7'), 6.81 (d, $J = 8.0$ Hz, 2H, H1' and

H8'), 6.72 (d, $J = 8.0$ Hz, 1H, H8). ^{13}C NMR (CDCl_3) δ 155.37, 149.57, 149.20, 148.59, 146.09, 142.99, 141.85, 141.21, 139.57, 136.24, 133.80, 131.66, 128.13, 128.06, 127.91, 127.84, 127.79 (two C's), 127.30, 126.81, 125.00, 124.63, 124.21, 124.03, 122.78, 120.50, 120.34, 120.05, 119.10, 66.09. MS (ESI) calcd for $\text{C}_{38}\text{H}_{24}\text{N}^+$ [$\text{M}+\text{H}^+$]: 494. Found: 494. Anal. Calcd for $\text{C}_{38}\text{H}_{23}\text{N}$: C, 92.47; H, 4.70; N, 2.84. Found: C, 92.51; H, 4.68; N, 2.87.

2-(1'',10''-phenanthrol-2''-yl)-9,9'-spirobifluorene (4d)

Yield (76%): mp 351 °C. ^1H NMR (CDCl_3) δ 9.15 (dd, $J = 4.3, 1.8$ Hz, 1H, H9''), 8.55 (dd, $J = 8.0, 1.8$ Hz, 1H, H7''), 8.20 (dd, $J = 8.3, 1.8$ Hz, 1H, H3), 8.12 (d, $J = 8.5$ Hz, 1H, H4''), 8.03 (d, $J = 8.0$ Hz, 1H, H4), 7.91 (d, $J = 7.5$ Hz, 1H, H5), 7.86 (d, $J = 7.5$ Hz, 2H, H4' and H5'), 7.81 (d, $J = 8.5$ Hz, 1H, H3''), 7.70 (AB quartet, 2H, H5'' and H6''), 7.59 (dd, $J = 8.0, 4.5$ Hz, 1H, H8'), 7.43 (d, $J = 1.3$ Hz, 1H, H1), 7.38 (td, $J = 7.5, 1.0$ Hz, 1H, H6), 7.36 (td, $J = 7.5, 1.0$ Hz, 2H, H3' and H6'), 7.10 (td, $J = 7.5, 1.0$ Hz, 3H, H7, H2' and H7'), 6.78 (d, $J = 7.5$ Hz, 2H, H1' and H8'), 6.72 (d, $J = 7.5$ Hz, 1H, H8). ^{13}C NMR (CDCl_3) δ 157.66, 150.26, 149.63, 148.91, 148.59 (two C's), 146.24, 145.92, 143.08, 141.85, 141.16, 139.72, 136.51, 136.02, 128.95, 128.79, 128.08, 127.90, 127.73 (two C's), 127.34, 126.28, 126.07, 124.24, 123.93, 123.14, 122.80, 121.08, 120.57, 120.39, 120.00, 66.07. MS (ESI) calcd for $\text{C}_{37}\text{H}_{23}\text{N}_2$ [$\text{M}+\text{H}^+$]: 495. Found: 495. Anal. Calcd for $\text{C}_{37}\text{H}_{22}\text{N}_2$: C, 89.85; H, 4.48; N, 5.66. Found: C, 89.82; H, 4.51; N, 5.63.

2-(Benzo[b]-1,10-phenathrolin-2-yl)-9,9'-spirobifluorene (4e)

Yield (74 %): mp 332 °C. ^1H NMR (CDCl_3) δ 8.71 (s, 1H, H7''), 8.61 (dd, $J = 8.0, 1.5$ Hz, 1H, H11''), 8.55 (d, $J = 8.3$ Hz, 1H, H4''), 8.11 (d, $J = 8.5$ Hz, 1H, H3''), 8.07 (d, $J = 8.0$ Hz, 1H, H5), 8.03 (d, $J = 8.5$ Hz, 1H, H3), 7.94-7.78 (m, 6H), 7.63 (td, $J = 8.0, 1.0$ Hz, 1H, H10''), 7.62 (d, $J = 8.5$ Hz, 1H), 7.48 (d, $J = 1.0$ Hz, 1H, H1), 7.40 (td, $J = 7.5, 1.0$ Hz, 1H, H6), 7.37 (td, $J = 8.0, 1.0$ Hz, 2H, H3' and H6'), 7.10 (td, $J = 7.5, 1.0$ Hz, 3H, H7, H2' and H7'), 6.79 (d, $J = 7.5$ Hz, 2H, H1' and H8'), 6.72 (d, $J = 7.5$ Hz, 1H, H8). ^{13}C NMR (CDCl_3) δ 157.36, 149.67, 149.09, 148.64 (two C's), 148.43, 147.09, 146.63, 143.11, 141.91, 141.25, 139.76, 136.53, 131.16, 129.93, 128.72, 128.02, 127.93, 127.75 (two C's), 127.56, 127.36, 127.08, 126.76, 125.76, 124.28, 123.99, 123.24, 121.43, 120.58, 120.42, 120.03, 66.13. MS (ESI) calcd for $\text{C}_{41}\text{H}_{25}\text{N}_2$ [$\text{M}+\text{H}^+$]: 545. Found: 545. Anal. Calcd for $\text{C}_{41}\text{H}_{24}\text{N}_2$: C, 90.42; H, 4.44; N, 5.14. Found: C, 90.46; H, 4.42; N, 5.12.

Ru(4d)₂Cl₂

A mixture of **4d** (494 mg, 1.0 mmol) and $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (80 mg, 0.31 mmol) in 95% EtOH was refluxed for 8 h. Resulting precipitate was filtered, washed with water and EtOH to give dark red solid: mp > 300 °C. ^1H NMR ($\text{DMSO}-d_6$) δ 8.90 (overlapped d, 4H, $J = 7.5$ Hz), 8.57 (t, 2H, $J = 7.8$ Hz), 8.27 (dd, 2H, $J = 4.8, 1.0$ Hz, H9''), 8.15-7.93 (m, 12H), 7.53 (d, 4H, $J = 7.3$ Hz), 7.42-7.33 (m, 6H), 7.21-7.04 (m, 6H), 6.95-6.91 (d, 4H, $J = 9.3$ Hz), 6.70 (d, 2H, $J = 7.8$ Hz), 6.32 (d, 2H, $J = 7.3$ Hz). Not soluble enough to get ^{13}C NMR spectrum.

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