

## New Journal of Chemistry

### Electronic Supplementary Information

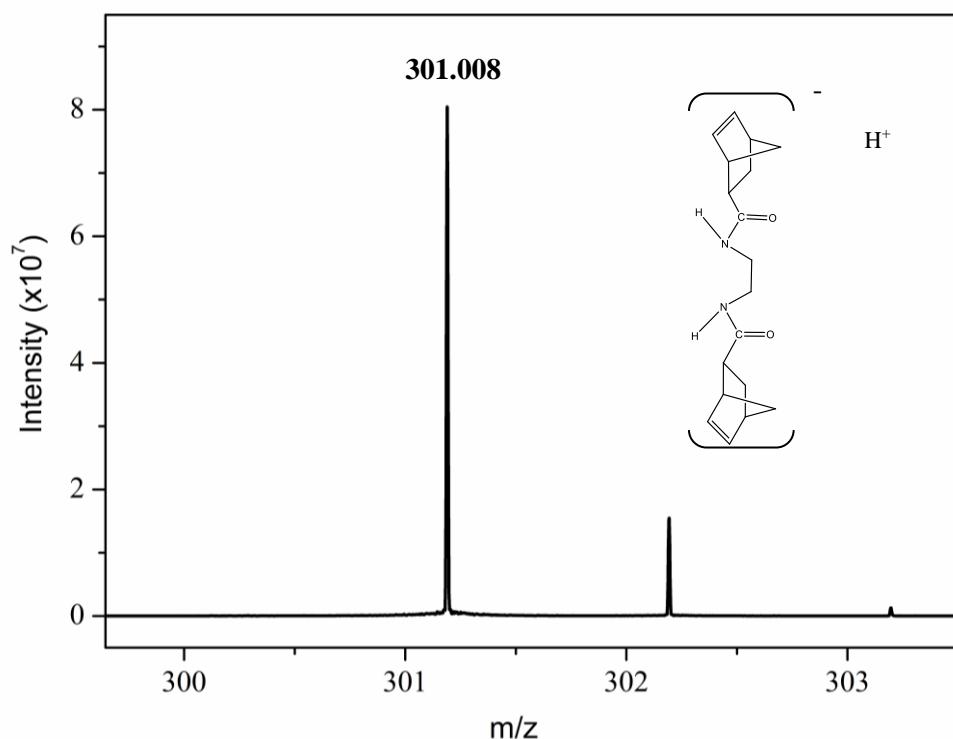
**Development of ruthenium polypyridine metalloc-monomers and characterization**

**of their metallocopolymers obtained by ROMP**

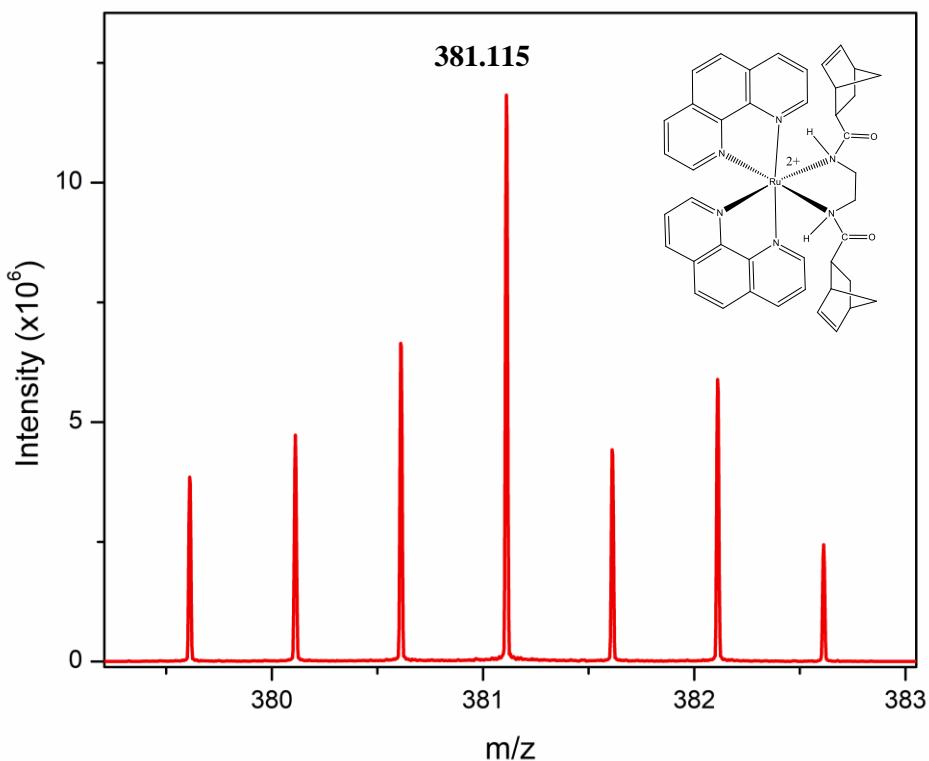
Elizabeth A. Alves,<sup>a</sup> Vinicius K. Tomazett,<sup>a</sup> Daniele M. Martins,<sup>\*a</sup> Benedito S. Lima-Neto<sup>\*a</sup>

<sup>a</sup> São Carlos Institute of Chemistry, University of São Paulo (IQSC-USP), São Carlos, SP 13560-970, Brazil

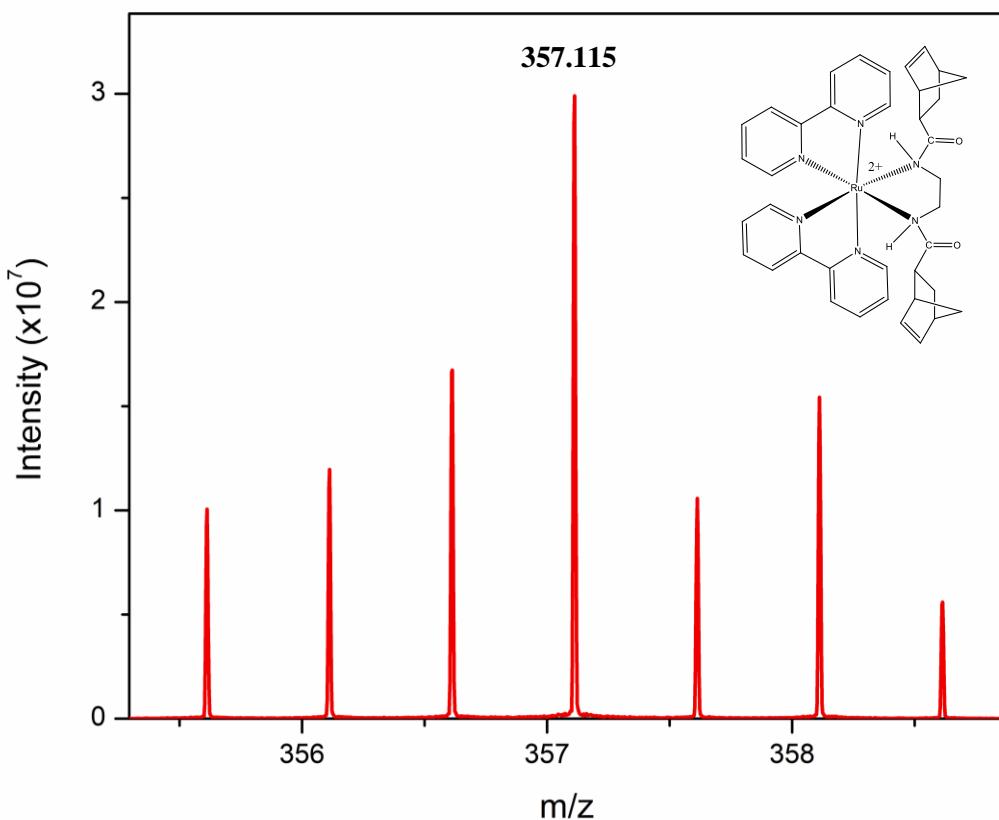
E-mail: martins.mdq@usp.br (DMM); benedito@iqsc.usp.br (BSLN)



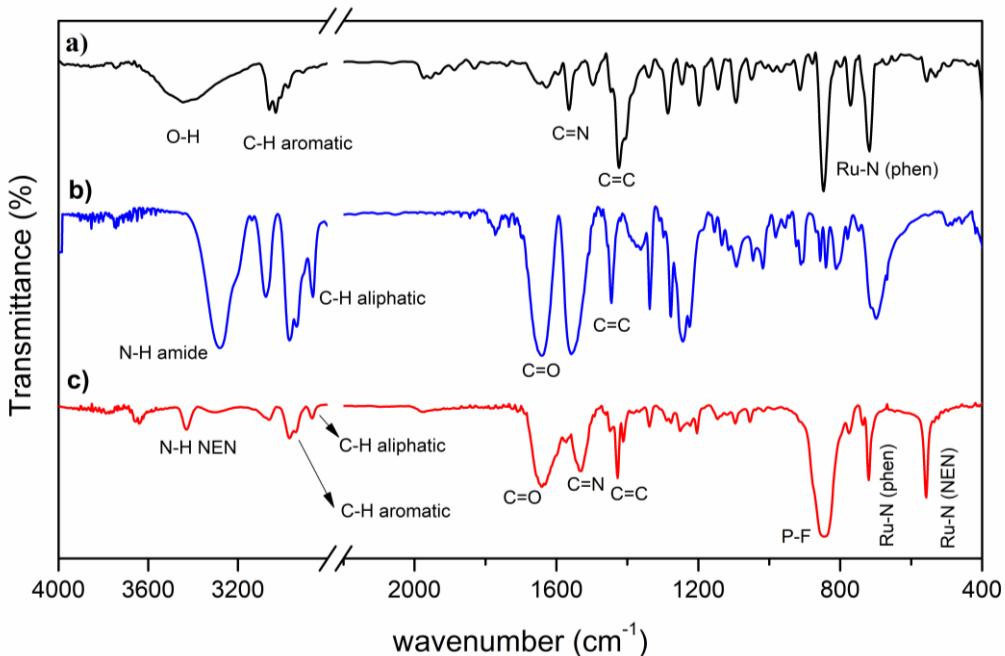
**Figure S1.** Mass spectrum of NEN ligand (**1**). ESI-MS( $m/z$ ): Calc. 300.1877, Found 301.1957 ( $M^-$ ).



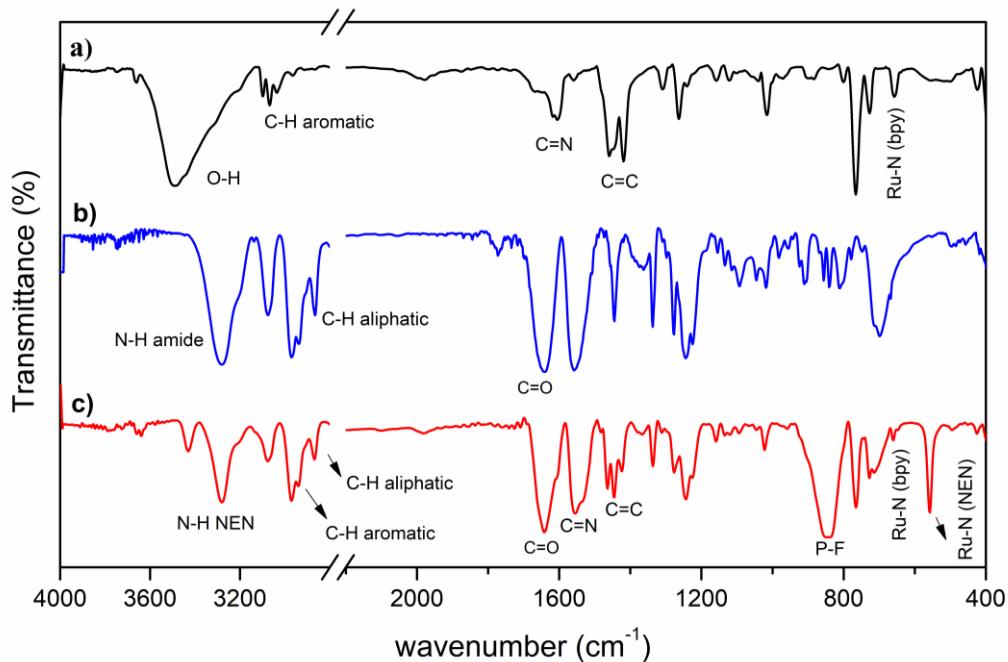
**Figure S2.** Mass spectrum of the complex ion (**3**) ([Ru]phen-NEN) in positive mode. ESI-MS ( $m/z$ ): Calc. 381.1128, Found 381.115 ( $M^+$ ).



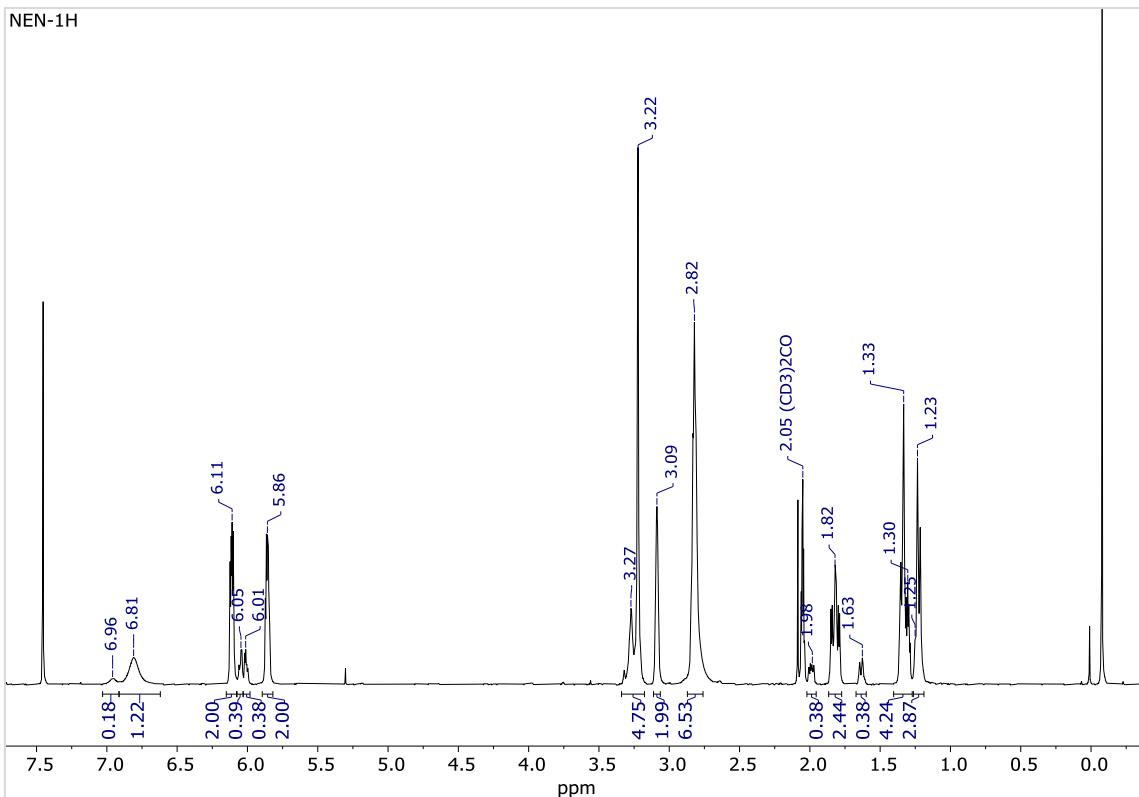
**Figure S3.** Mass spectrum of the complex ion (**5**) ( $[\text{Ru}]\text{bpy}\text{-NEN}$ ), in positive mode. ESI-MS( $m/z$ ): Calc. 357.1128, Found 357.115 ( $\text{M}^+$ ).



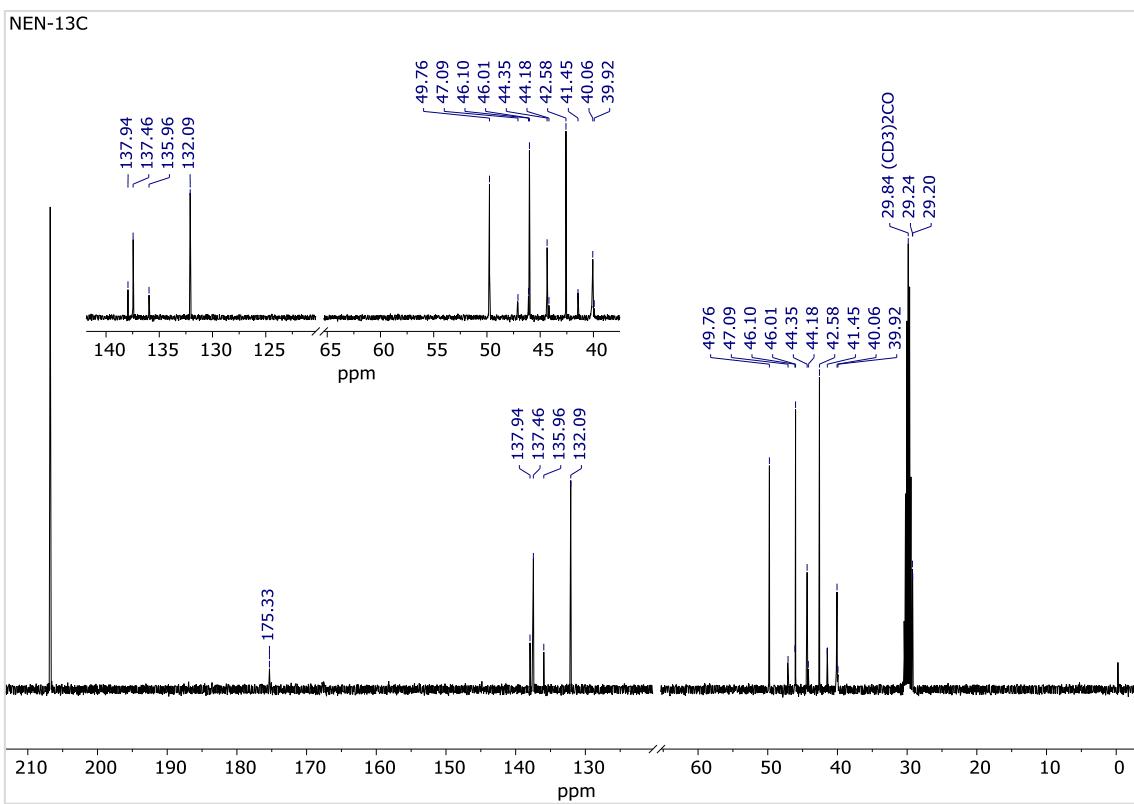
**Figure S4.** Infrared spectra of complexes a)  $[\text{Ru}]\text{phen-Cl}$  (**2**), b) **NEN** (**1**) and c)  $[\text{Ru}]\text{phen-NEN}$  (**3**) in KBr.



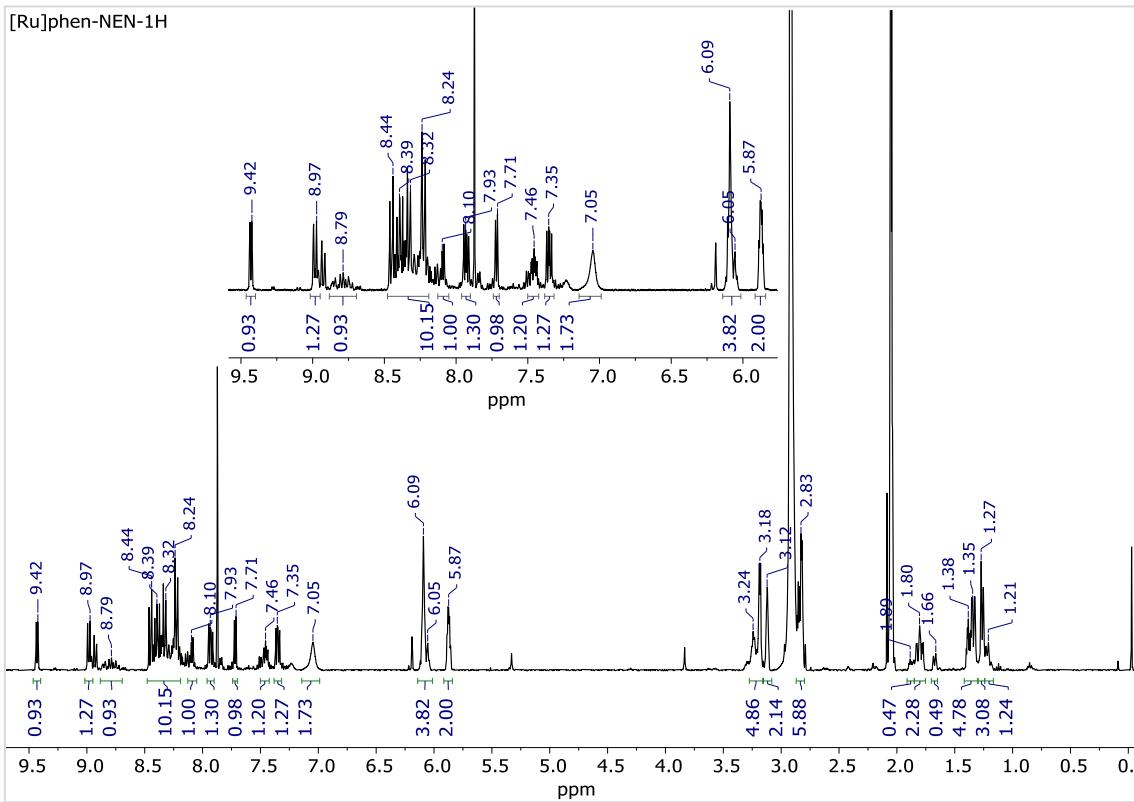
**Figure S5.** Infrared spectra of complexes a)  $[\text{Ru}] \text{bpy-Cl}$  (**4**), b) NEN (**1**) and c)  $[\text{Ru}] \text{bpy-NEN}$  (**5**) in KBr.



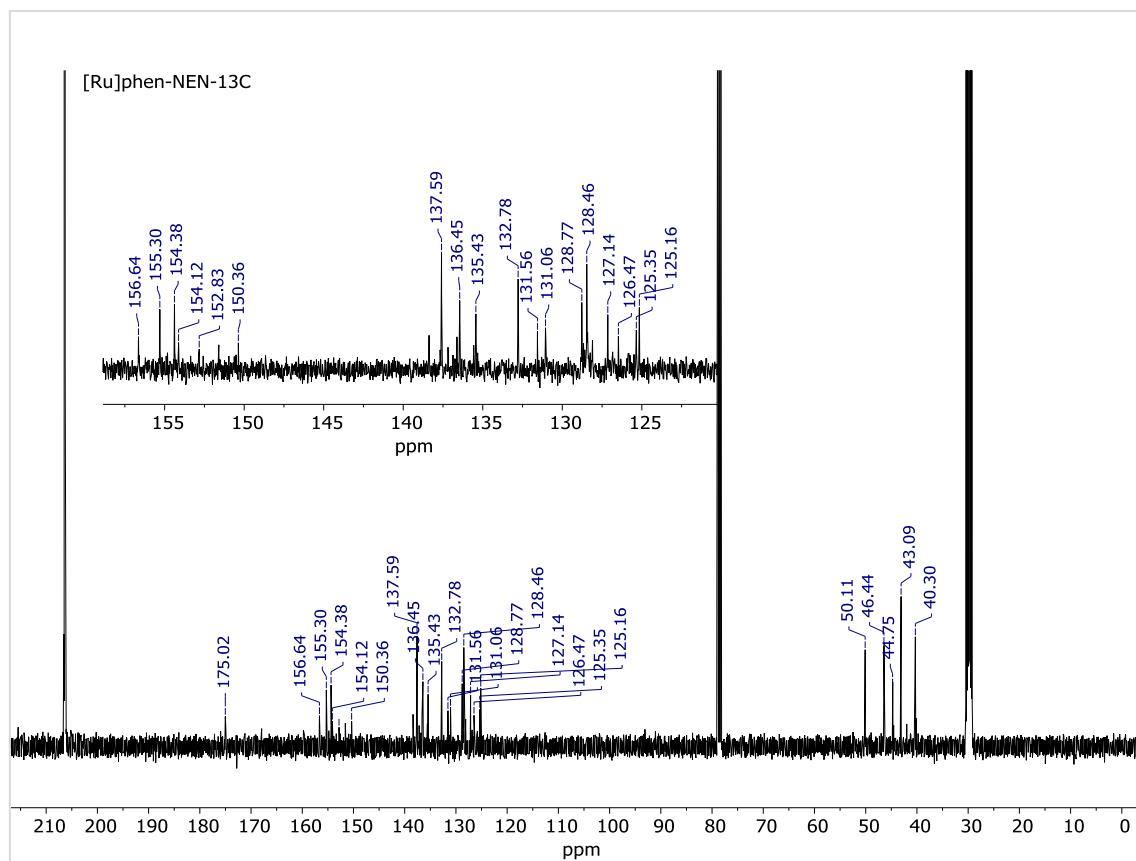
**Figure S6.**  $^1\text{H}$ -NMR (500 MHz) of NEN (**1**) in  $(\text{CD}_3)_2\text{CO}/\text{CDCl}_3$ . The signals corresponding to the *endo*-NEN and *exo*-NEN portions are present at a 4:1 ratio from olefins associated with the mixture of the *endo* and *exo* isomers of 5-norbornene-2-carboxylic acid.



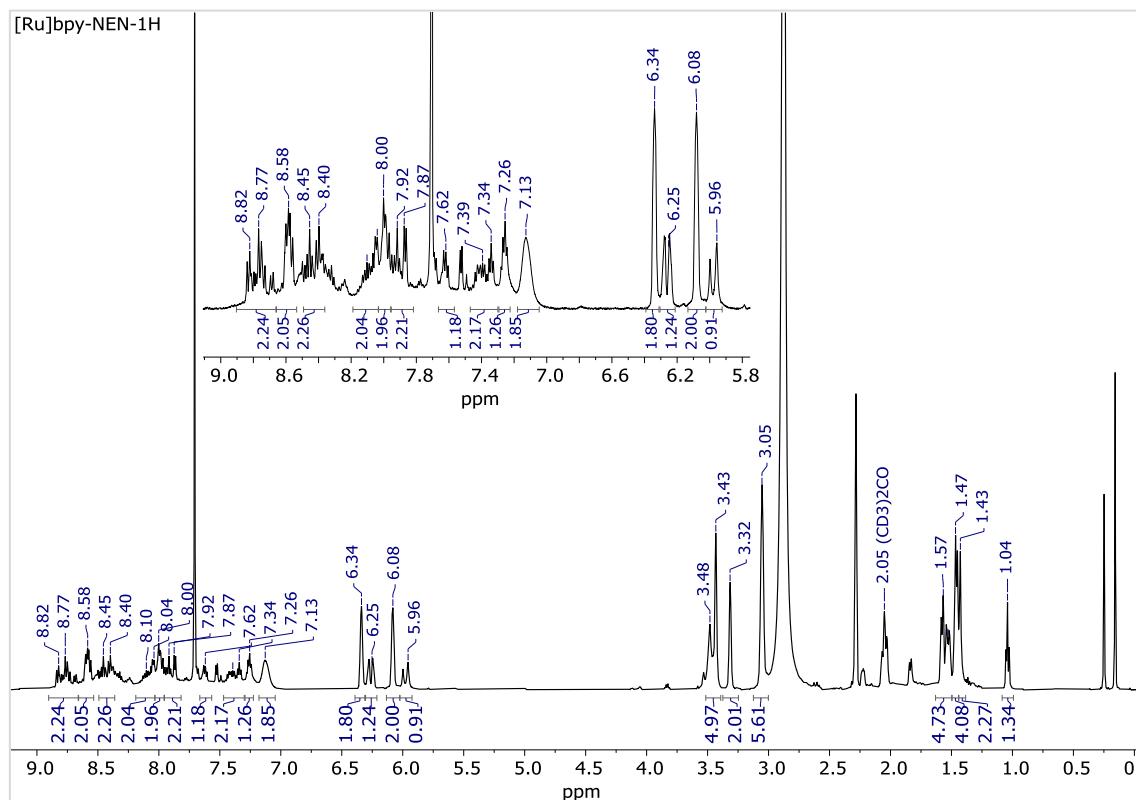
**Figure S7.**  $^{13}\text{C}$ -NMR (500 MHz) of NEN (**1**) in  $(\text{CD}_3)_2\text{CO}/\text{CDCl}_3$ .



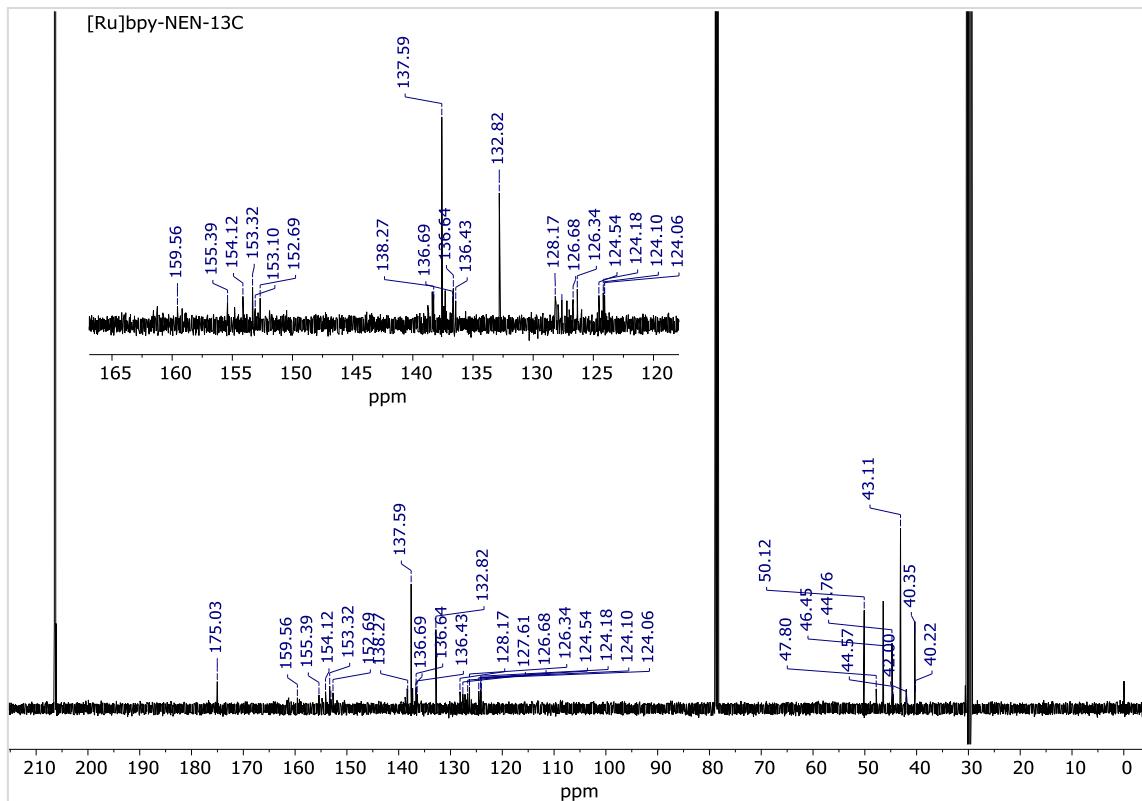
**Figure S8.**  $^1\text{H}$ -NMR (500 MHz) of complex **3** ([Ru]phen-NEN) in  $(\text{CD}_3)_2\text{CO}/\text{CDCl}_3$ .



**Figure S9.** <sup>13</sup>C-NMR (500 MHz) of complex **3** (<sup>[Ru]phen-NEN</sup>) in (CD<sub>3</sub>)<sub>2</sub>CO/CDCl<sub>3</sub>.



**Figure S10.** <sup>1</sup>H-NMR (500 MHz) of complex **5** (<sup>[Ru]bpy-NEN</sup>) in (CD<sub>3</sub>)<sub>2</sub>CO/CDCl<sub>3</sub>.



**Figure S11.**  $^{13}\text{C}$ -NMR (500 MHz) of complex 5 ([Ru]bpy-NEN) in  $(\text{CD}_3)_2\text{CO}/\text{CDCl}_3$ .

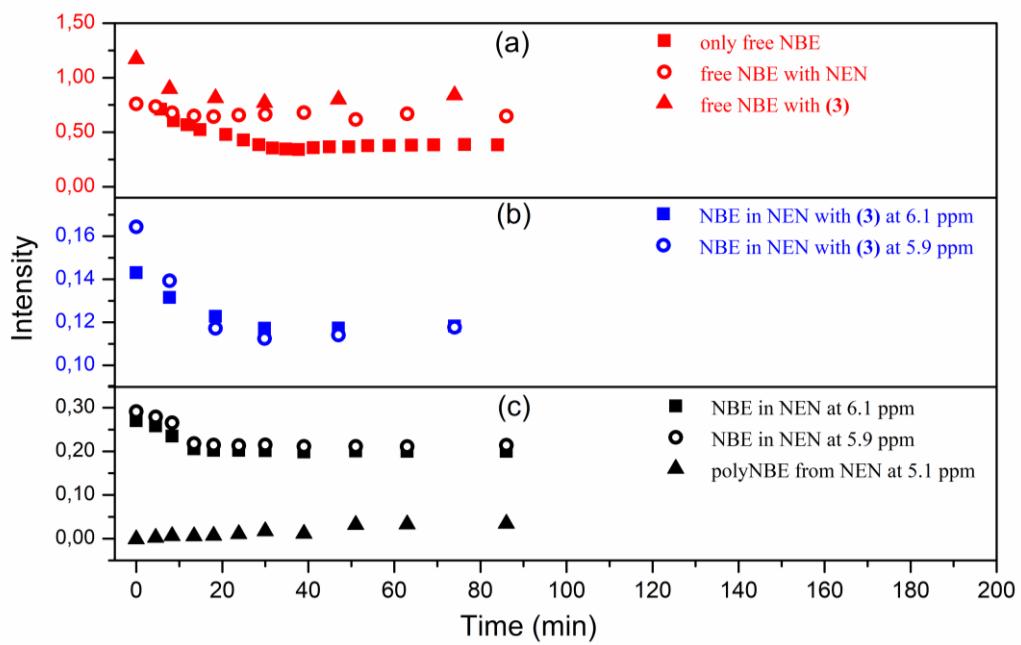
**Table S1.**  $^1\text{H}$  NMR assignments for Figs. S3-S8 obtained in  $(\text{CD}_3)_2\text{CO}/\text{CDCl}_3$  at 25 °C.

	NEN		[Ru]phen-NEN		[Ru]bpy-NEN	
	$^1\text{H}$	$^{13}\text{C}\{^1\text{H}\}$	$^1\text{H}$	$^{13}\text{C}\{^1\text{H}\}$	$^1\text{H}$	$^{13}\text{C}\{^1\text{H}\}$
<b>1</b>	6.11	132.09				
<b>2</b>	3.09	44.35	6.09	132.78	6.34	132.82
<b>3</b>	2.82	49.76	3.12	44.75	3.32	44.76
<b>4</b>	1.82; 1.30	29.24	2.83	50.10	3.05	50.12
<b>5</b>	5.86	137.46	1.80; 1.38		1.43; 1.53	
<b>6</b>	2.82	42.58	5.87	137.59	6.08	137.59
<b>7</b>	1.33; 1.23	46.01	2.83	43.10	3.05	43.11
<b>8</b>		175.33	1.35; 1.27	46.44	1.57; 1.47	46.45
<b>9</b>	6.81			175.02		175.03
<b>10</b>	6.81		7.05		7.13	
<b>11</b>		175.33	7.05		7.13	
<b>12</b>	1.82; 1.30	29.24		175.02		175.03
<b>13</b>	2.82	42.58	1.80; 1.38		1.43 ; 1.53	
<b>14</b>	5.86	137.46	2.83	43.10	3.05	43.11
<b>15</b>	6.11	132.09	5.87	137.59	6.08	137.59
<b>16</b>	2.82	49.76	6.09	132.78	6.34	132.82
<b>17</b>	3.09	44.35	2.83	50.10	3.05	50.12
<b>18</b>	1.33; 1.23	46.01	3.12	44.75	3.32	44.76
<b>19</b>	3.22	40.06	1.35; 1.27	46.44	1.57; 1.47	46.45
			3.18	40.30	3.43	40.35

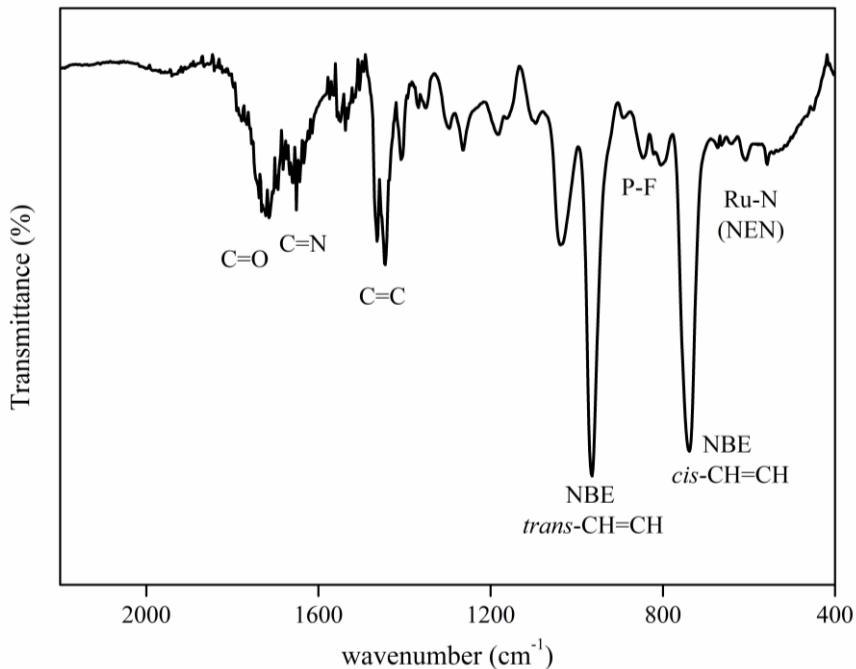
<b>20</b>	3.22	40.06	3.18	40.30	3.43	40.35
<b>21</b>			9.42	155.30	8.82	155.39
<b>22</b>			7.46	135.43	7.39	126.34
<b>23</b>			8.49 - 8.16	128.77	8.58	138.27
<b>24</b>				125.35	8.45	124.06
<b>25</b>			8.49 - 8.16	128.46		159.56
<b>26</b>			8.49 - 8.16	128.46		153.10
<b>27</b>				131.06	7.92	124.18
<b>28</b>			8.49 - 8.16	125.16	8.00	132.69
<b>29</b>			7.93	127.14	7.62	127.61
<b>30</b>			7.71	154.38	8.04	153.32
<b>31</b>				152.63	8.77	154.12
<b>32</b>				156.64	8.10	126.68
<b>33</b>			8.97	155.30	8.58	136.43
<b>34</b>			8.79	135.43	8.40	124.10
<b>35</b>			8.49 - 8.16	128.77		161.23
<b>36</b>				126.47		154.81
<b>37</b>			8.49 - 8.16	128.46	7.34	124.55
<b>38</b>			8.49 - 8.16	128.46	8.00	136.64
<b>39</b>				131.56	7.26	128.17
<b>40</b>			8.49 - 8.16	136.45	7.87	152.69
<b>41</b>			7.35	127.14		
<b>42</b>			8.10	154.38		
<b>43</b>				150.36		
<b>44</b>				154.12		

**a) Syntheses****b) Precipitation****c) Copolymer**

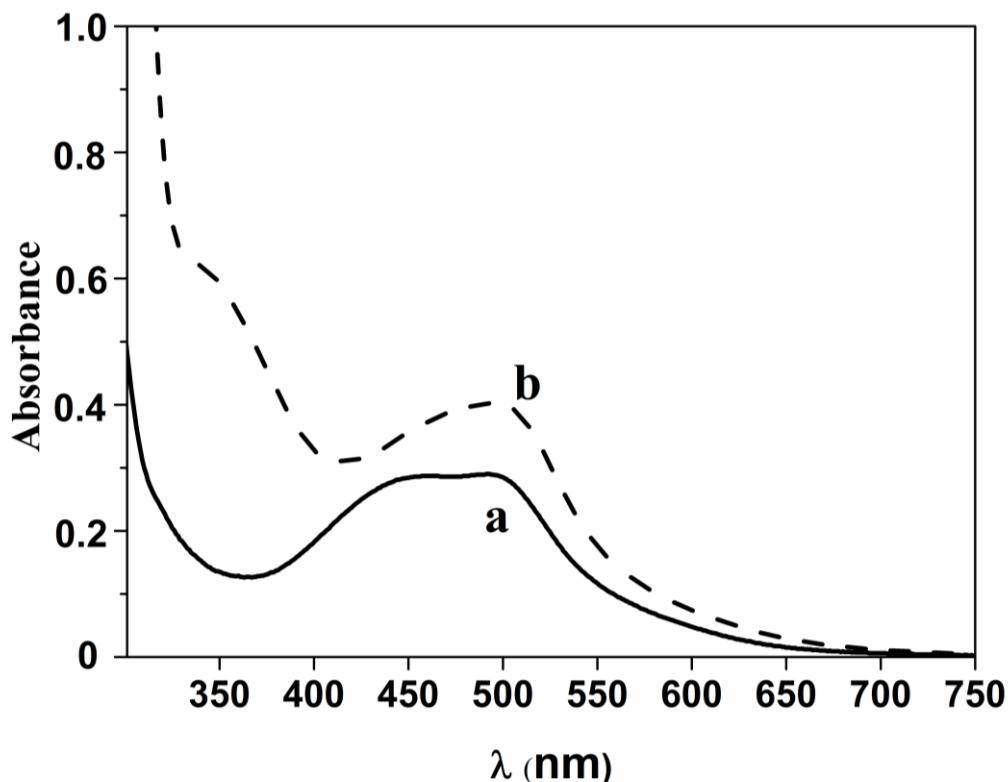
**Figure S12.** Images of **a)** reaction solution during copolymer; **b)** methanol precipitated copolymer; **c)** isolated copolymer.



**Figure S13.** Intensities of signals in the  $^1\text{H}$  NMR spectra from Figure 3, from (a) ROMP of NBE, (b) ROMP of NBE with NEN and (c) ROMP of NBE with **3**.



**Figure S14.** Infrared spectrum of copolymer from ROMP of NBE with complex **3**.



**Figure S15.** UV-Vis spectra of the methanol mother liquor with the chloroform washes from the synthesis of the copolymers from reaction of NBE **a**) with [Ru]phen-NEN (**3**) or **b**) with [Ru]bpy-NEN (**5**) (dashed line).