

## **Chapter 3**

**Neutral zinc, lower-order zincate and higher-order zincate derivatives of pyrrole: synthesis and structural characterisation of zinc complexes with one, two, three or four pyrrolyl ligands**

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## Crystallographic data and refinement details for 7-12

**Table S1** Crystallographic data and refinement details for compounds **7-12**.

	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>	<b>12</b>
Empirical formula	C <sub>18</sub> H <sub>34</sub> N <sub>4</sub> Zn	C <sub>14</sub> H <sub>24</sub> N <sub>4</sub> Zn	C <sub>24</sub> H <sub>36</sub> N <sub>3</sub> NaO <sub>3</sub> Zn	C <sub>28</sub> H <sub>48</sub> N <sub>8</sub> Na <sub>2</sub> Zn	C <sub>34</sub> H <sub>62</sub> N <sub>10</sub> Na <sub>2</sub> Zn	C <sub>26</sub> H <sub>54</sub> N <sub>8</sub> Na <sub>2</sub>
Mol. Mass	371.86	313.74	502.92	608.09	722.29	524.75
Crystal system	orthorhombic	orthorhombic	triclinic	tetragonal	monoclinic	monoclinic
Space group	P na2 <sub>1</sub>	P na2 <sub>1</sub>	P-1	P -4n2	P2 <sub>1</sub> /c	P2 <sub>1</sub> /n
<i>a</i> [Å]	15.6099(2)	15.4350(3)	8.3429(2)	12.2787(6)	19.0953(9)	9.3617(5)
<i>b</i> [Å]	9.6563(1)	10.3607(2)	11.0909(3)	12.2787(6)	25.2534(13)	9.6380(4)
<i>c</i> [Å]	27.2685(4)	9.7566(2)	14.1002(3)	11.2091(9)	17.1703(8)	18.0907(8)
∠ [°]	90	90	94.178(2)	90	90	90
∠ [°]	90	90	104.038(2)	90	102.034(5)	100.702(5)
∠ [°]	90	90	95.994(2)	90	90	90
<i>V</i> [Å <sup>3</sup> ]	4110.29(9)	1560.25(5)	1252.28(5)	1689.96(18)	8097.9(7)	1603.90(13)
<i>Z</i>	8	4	2	2	8	2
<i>λ</i> [Å]	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Measured reflections	48155	29629	14316	4944	41267	8124
Unique reflections	10490	4140	6611	1938	17641	3864
<i>R</i> int	0.0214	0.0300	0.0303	0.0440	0.0378	0.0224
Observed rflns [ <i>I</i> > 2σ( <i>I</i> )]	9180	3913	5404	1532	12360	2857

## NMR Analysis

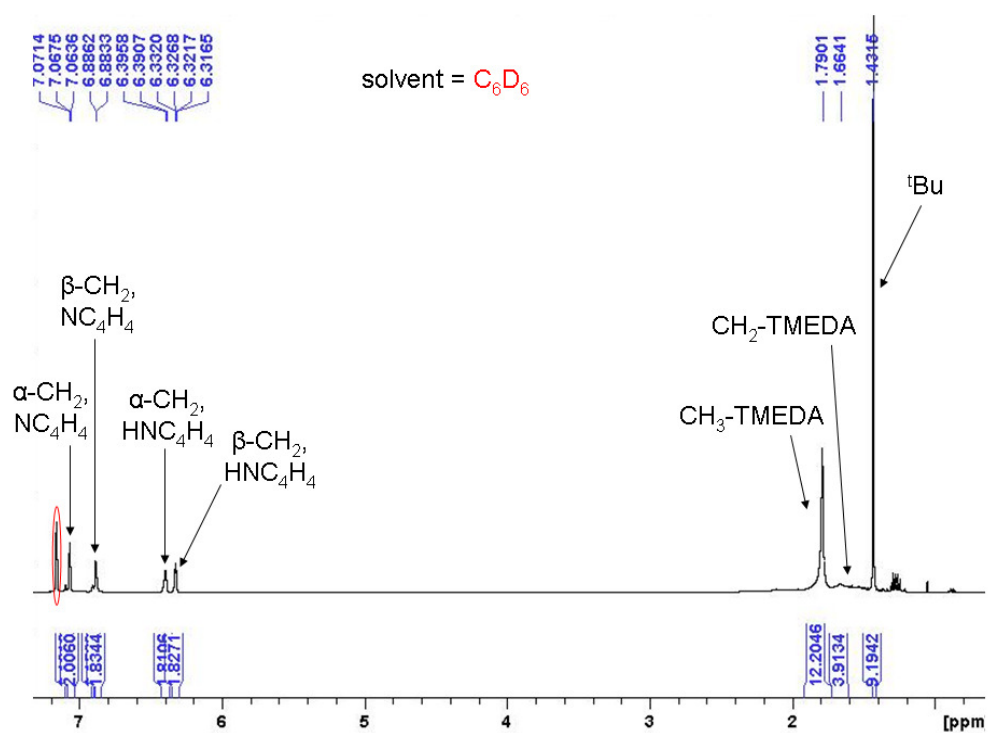


Figure S1  $^1\text{H}$  NMR spectrum of  $[\text{tBuZn}(\text{NC}_4\text{H}_4)(\text{TMEDA})\cdot\text{HNC}_4\text{H}_4]$  (**7**).

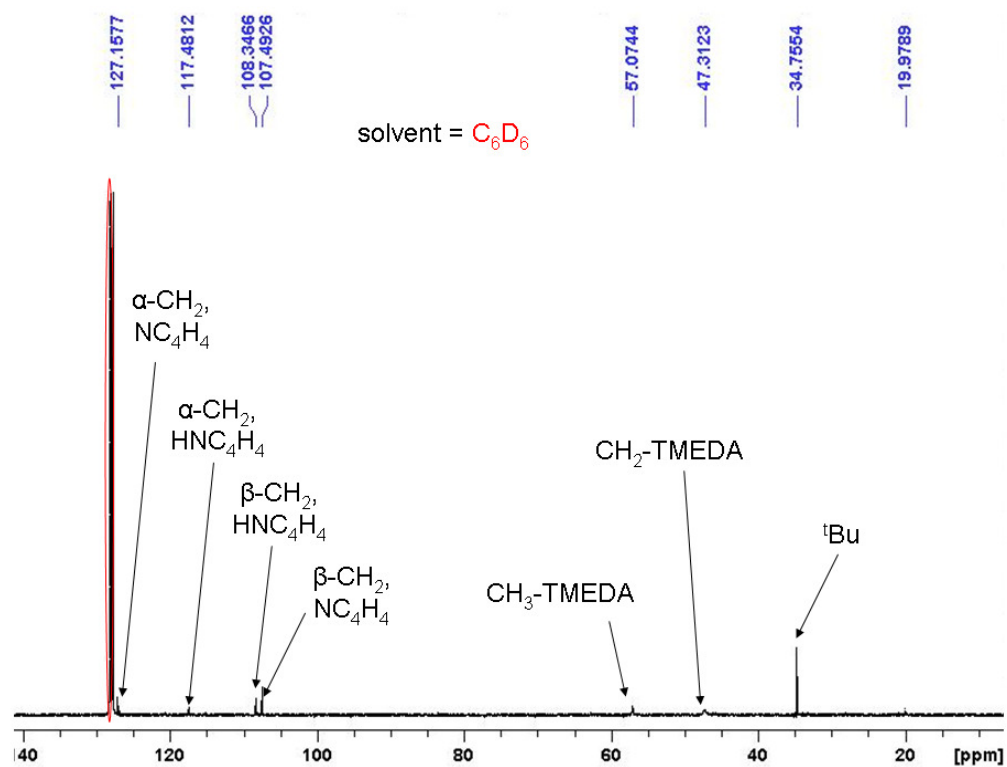
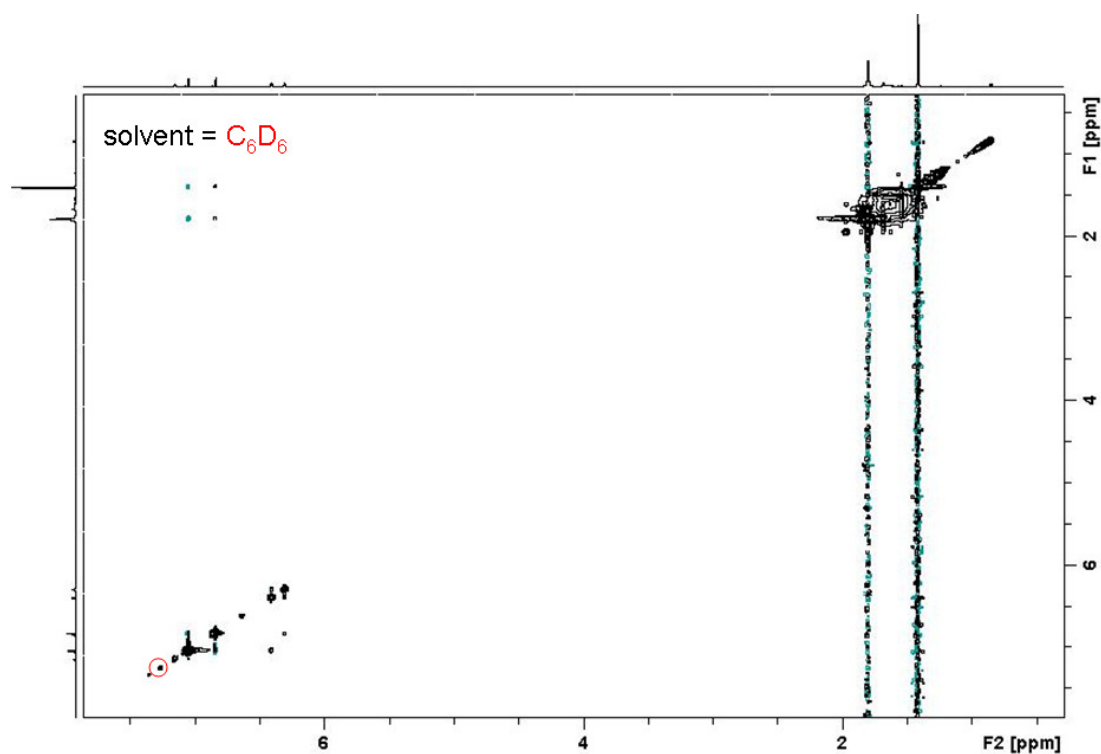
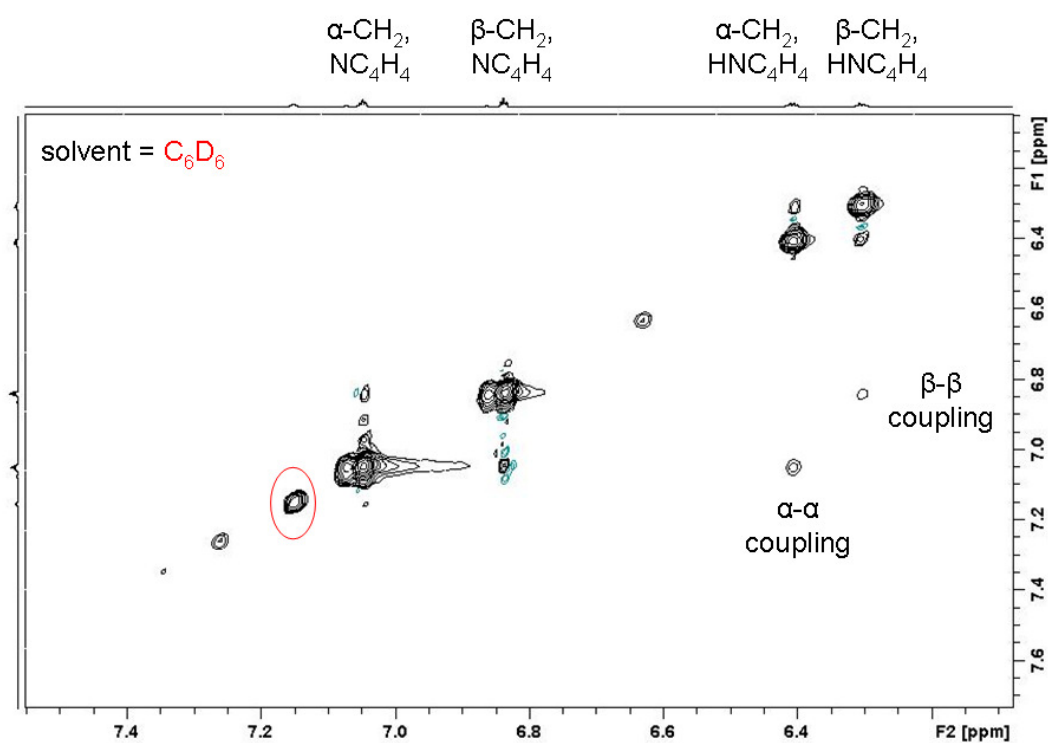


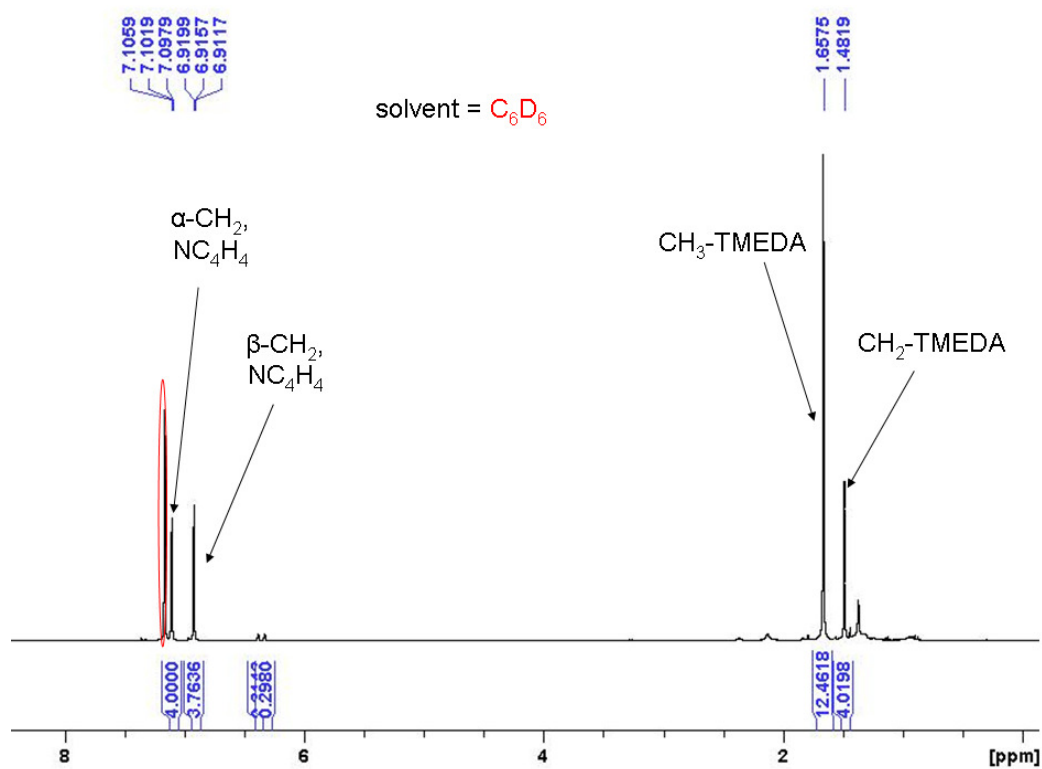
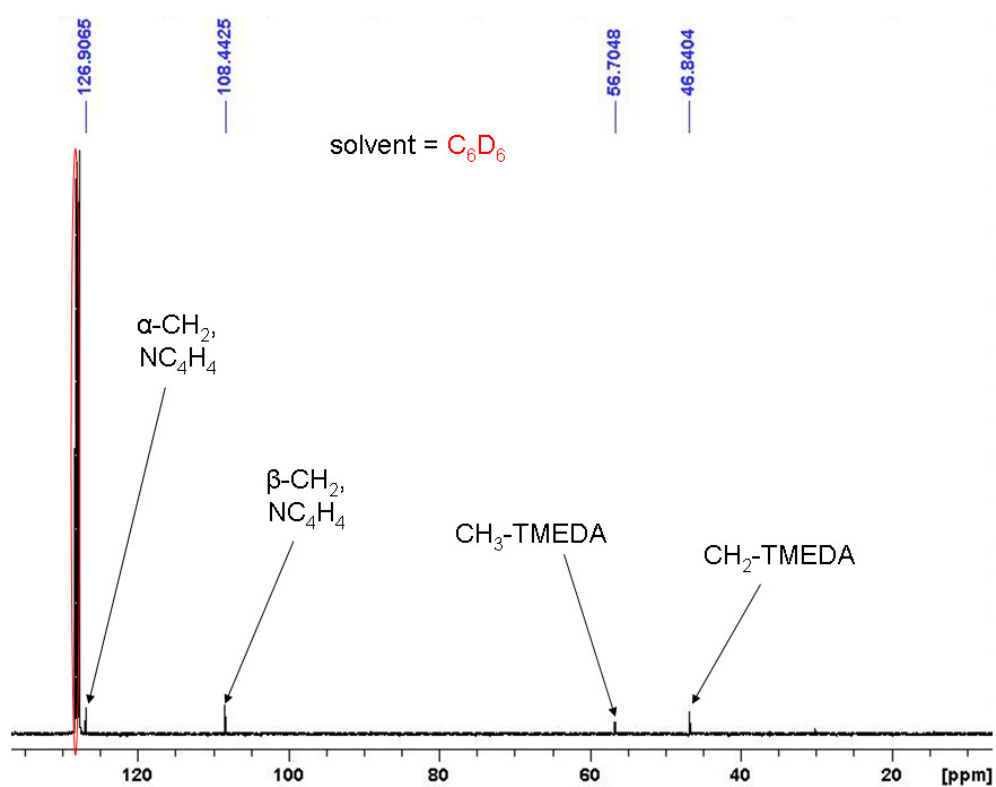
Figure S2  $^{13}\text{C}$  NMR spectrum of  $[\text{tBuZn}(\text{NC}_4\text{H}_4)(\text{TMEDA})\cdot\text{HNC}_4\text{H}_4]$  (**7**).

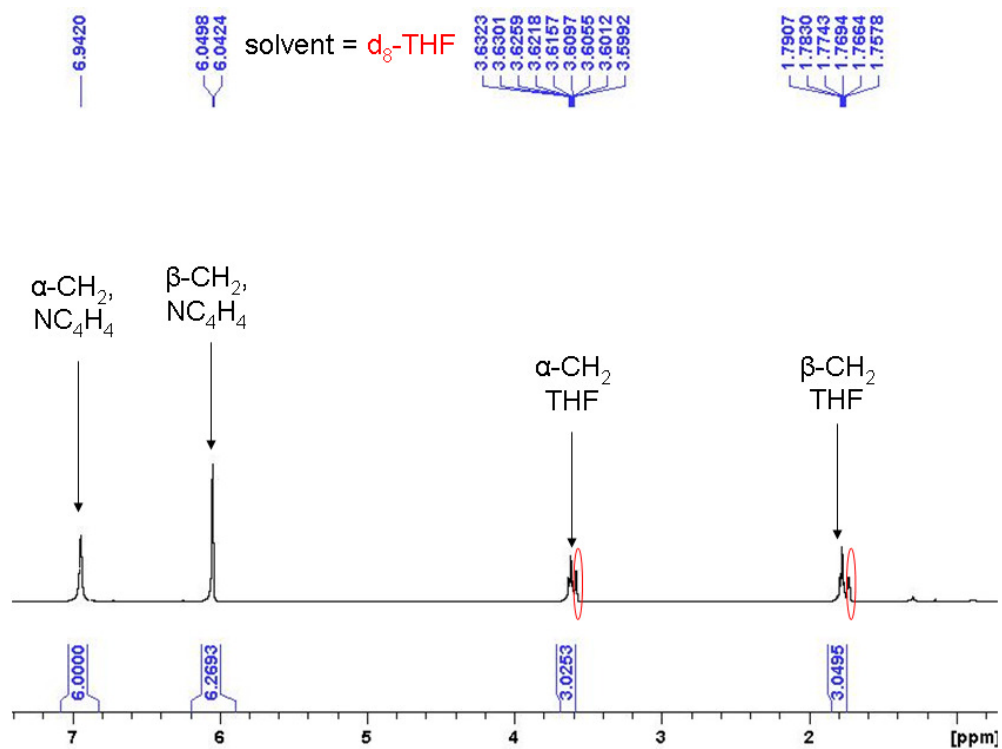


**Figure S3** NOESY NMR spectrum of  $[\text{tBuZn}(\text{NC}_4\text{H}_4)(\text{TMEDA})\cdot\text{HNC}_4\text{H}_4]$  (**7**).

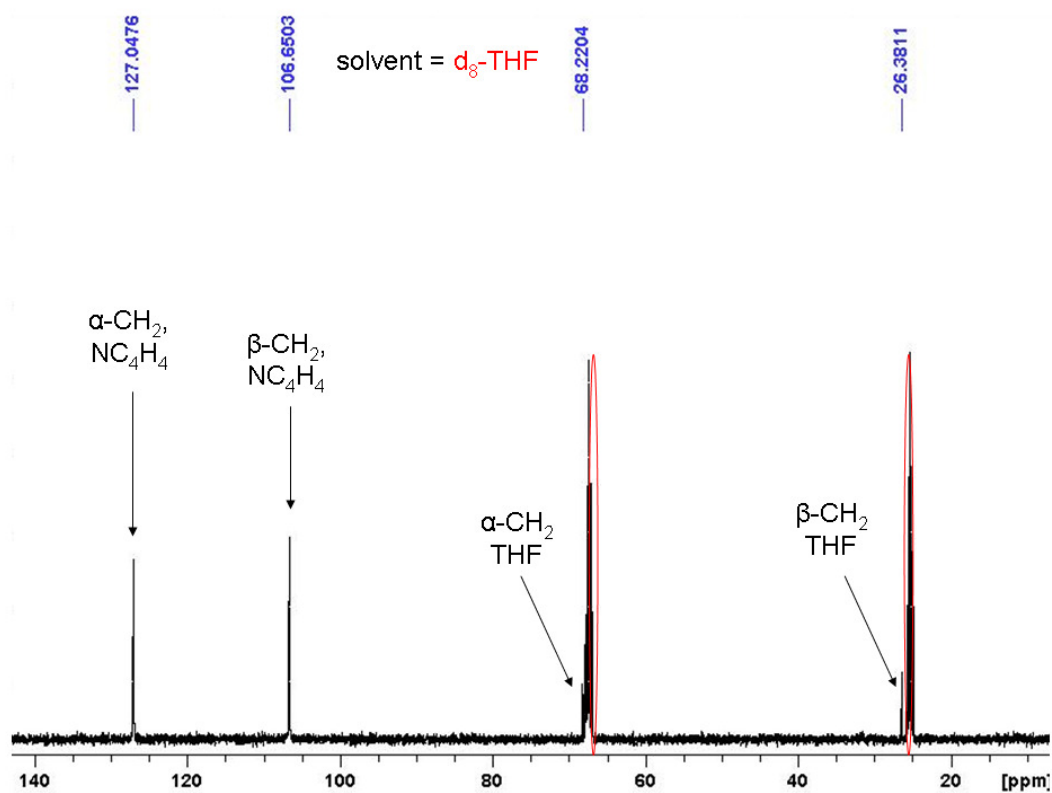


**Figure S4** NOESY NMR spectrum of  $[\text{tBuZn}(\text{NC}_4\text{H}_4)(\text{TMEDA})\cdot\text{HNC}_4\text{H}_4]$  (**7**).

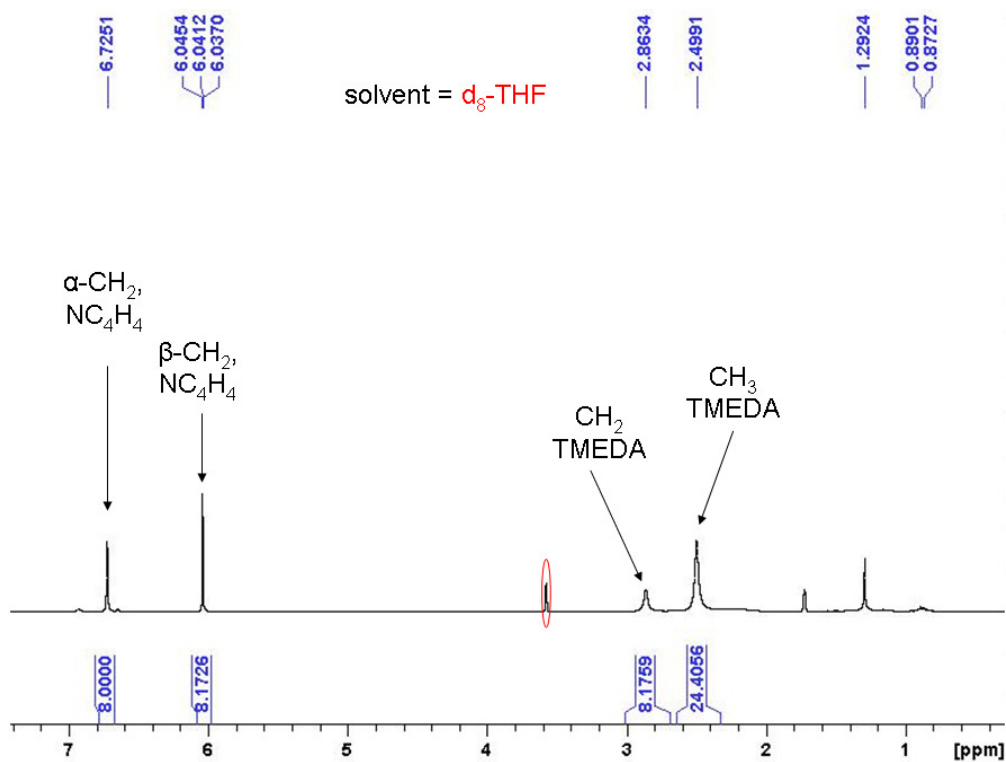
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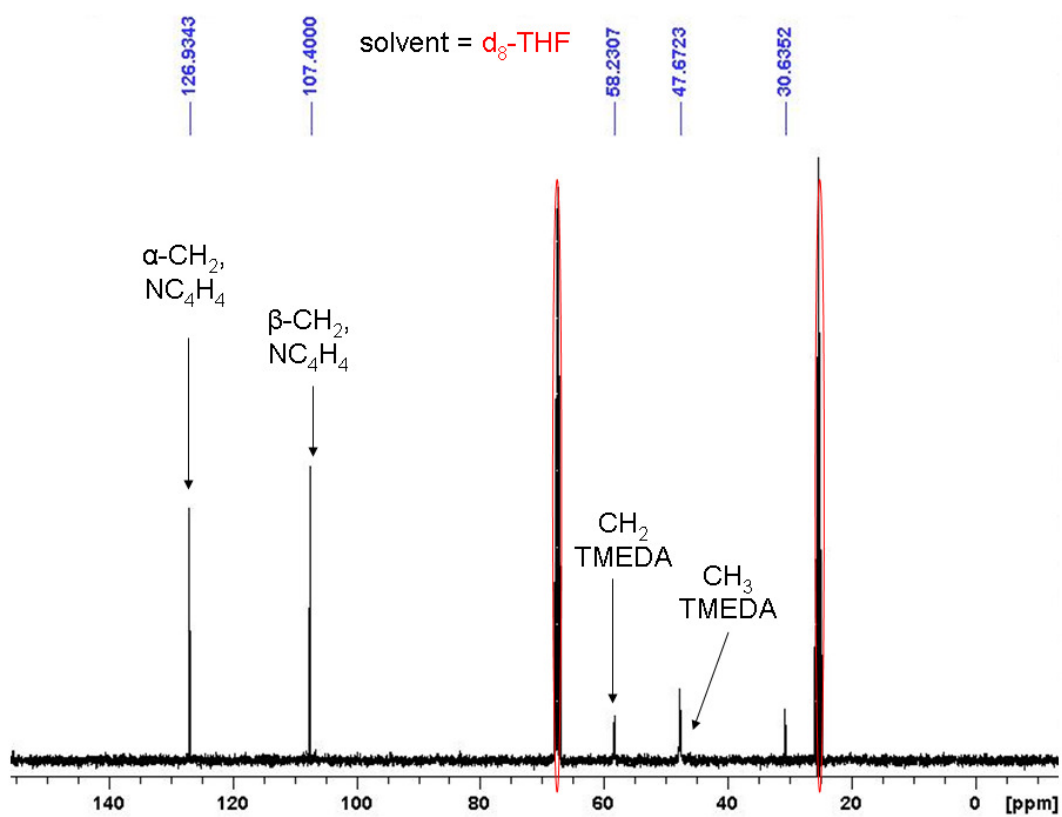
**Figure S7**  $^1\text{H}$  NMR spectrum of  $[\{(\text{THF})_2\cdot\text{NaZn}(\text{THF})(\text{NC}_4\text{H}_4)_3\}_\infty]$  (**9**).



**Figure S8**  $^{13}\text{C}$  NMR spectrum of  $[\{(\text{THF})_2\cdot\text{NaZn}(\text{THF})(\text{NC}_4\text{H}_4)_3\}_\infty]$  (**9**).

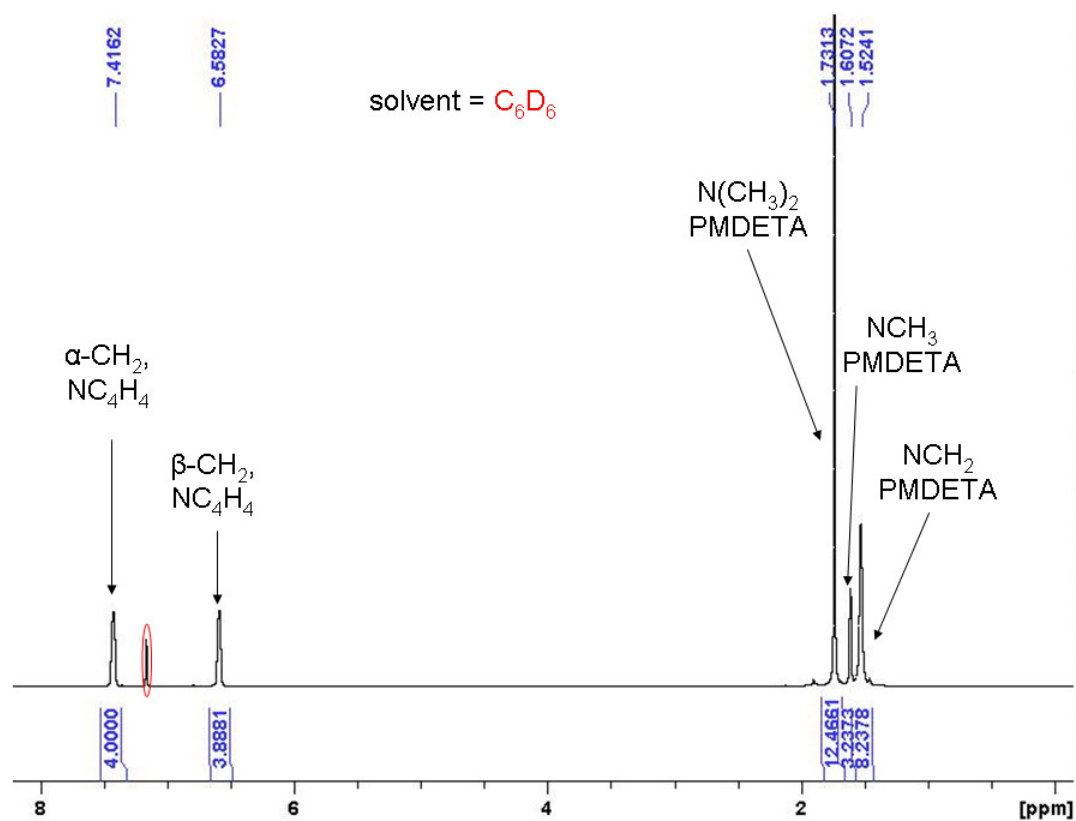


**Figure S9**  $^1\text{H}$  NMR spectrum of  $[(\text{TMEDA})\cdot\text{Na}]_2\text{Zn}(\text{NC}_4\text{H}_4)_4$  (**10**).

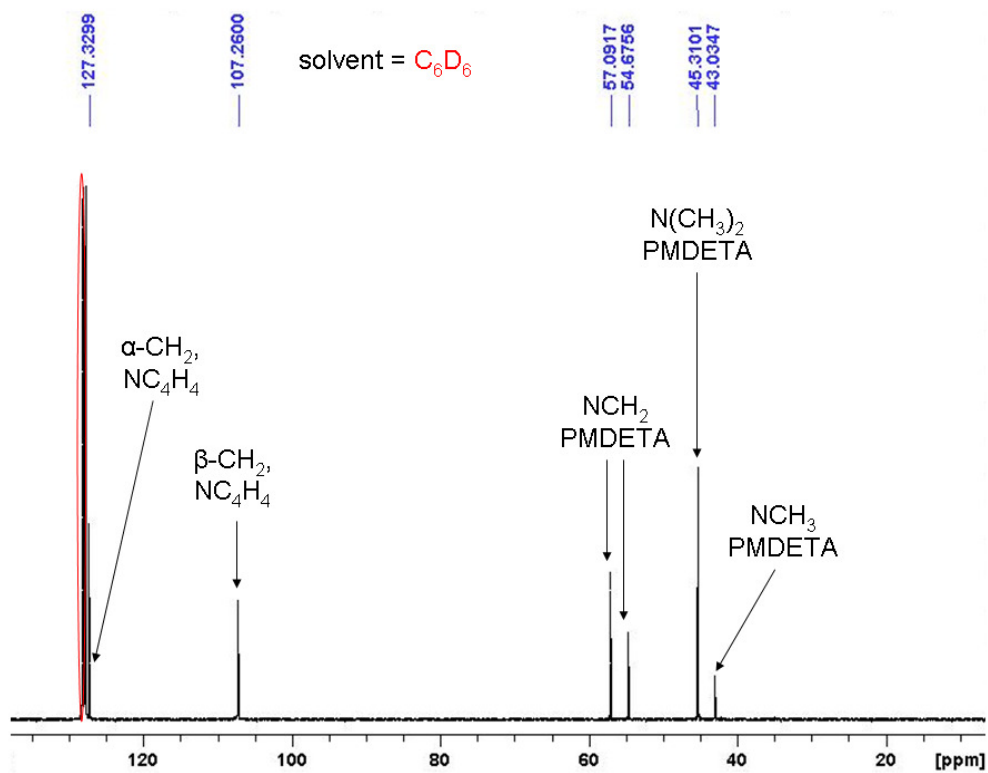


**Figure S10**  $^{13}\text{C}$  NMR spectrum of  $[(\text{TMEDA})\cdot\text{Na}]_2\text{Zn}(\text{NC}_4\text{H}_4)_4$  (**10**).

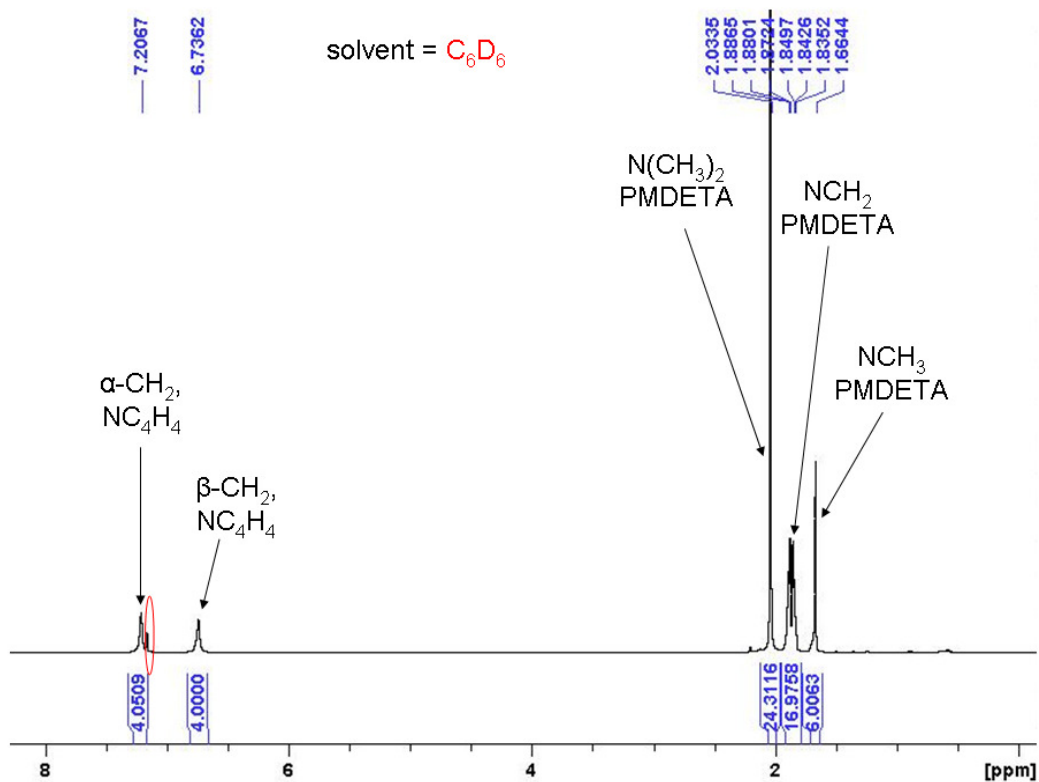




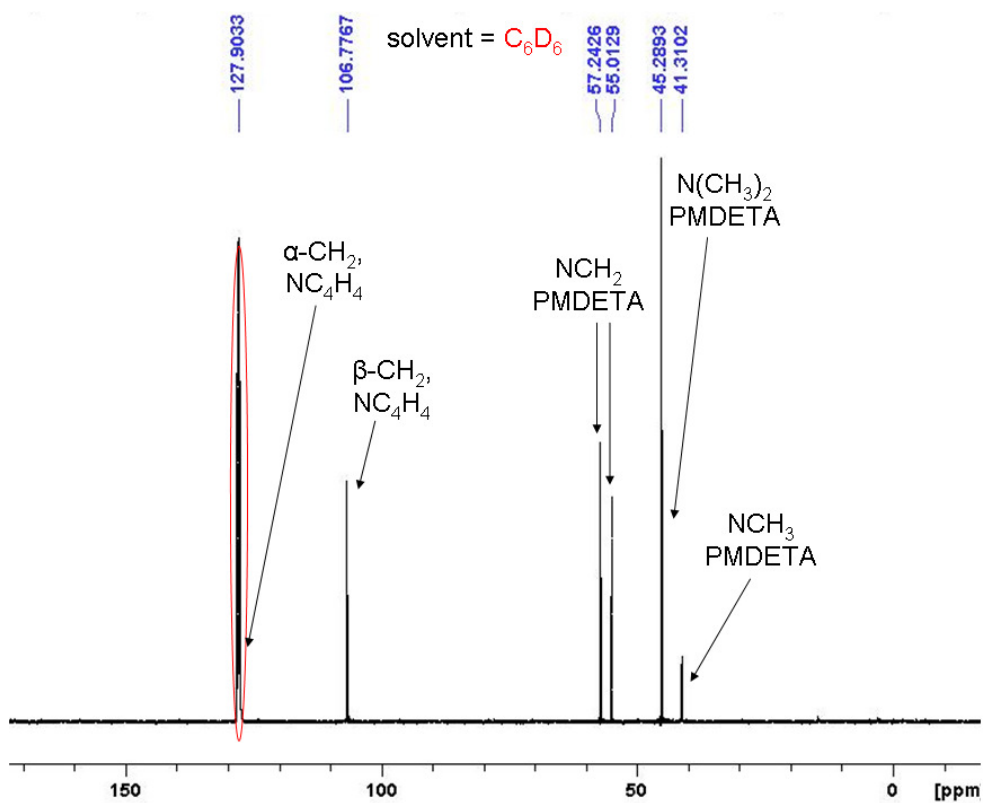
**Figure S11**  $^1\text{H}$  NMR spectrum of  $[\{(\text{PMDETA})\cdot\text{Na}\}_2\text{Zn}(\text{NC}_4\text{H}_4)_4]$  (**11**).



**Figure S12**  $^{13}\text{C}$  NMR spectrum of  $[\{(\text{PMDETA})\cdot\text{Na}\}_2\text{Zn}(\text{NC}_4\text{H}_4)_4]$  (**11**).



**Figure S13**  $^1\text{H}$  NMR spectrum of  $[(\text{PMDTA})\cdot\text{Na}(\text{NC}_4\text{H}_4)]_2$  (**12**).



**Figure S14**  $^{13}\text{C}$  NMR spectrum of  $[(\text{PMDTA})\cdot\text{Na}(\text{NC}_4\text{H}_4)]_2$  (**12**).