

## Supporting Information

### **Evidence of Entropy-Driven Bistability through $^{15}\text{N}$ NMR Analysis of a Temperature and Solvent Induced, Chiroptical Switching Polycarbodiimide**

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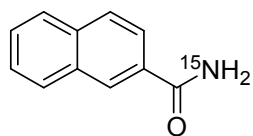
## I. Characterization of Catalysts

Successful synthesis and characterization of (*R*) and (*S*)-BINOL titanium(IV) diisopropoxide (**Cat-1(R)** and **Cat-1(S)**) and were conducted as previously reported.<sup>1</sup>

## II. Synthesis of <sup>15</sup>N-labeled Precursor Compounds

The procedure for the synthesis of the labeled 1-naphthylamine and **Poly-3** was previously reported.<sup>2</sup> The synthesis of the labeled isothiocyanate was carried out using a slightly modified procedure reported by Kai et al.<sup>3</sup> The synthesis the <sup>15</sup>N-octadecylphthalimide and removal of the phthalimide group was performed following the procedure reported by Wood albeit slightly modified.<sup>4</sup> **Poly-4** was synthesized using the original protocol for <sup>15</sup>N-labeling polycarbodiimides reported by DeSousa and Novak involving amidation of an acid chloride with isotopically-enriched ammonium chloride, Hofmann rearrangement to the labeled methyl carbamate, and acidolysis of the carbamate to the amine HCl salt.<sup>5</sup> These reaction procedures, yields, and characterization of compounds can be found below as well as the yields, <sup>1</sup>H NMR data, <sup>13</sup>C NMR data, <sup>15</sup>N NMR data, FTIR data, and MS data of all precursor compounds and final <sup>15</sup>N-enriched polycarbodiimides All J-coupling values are reported in hertz and the FTIR labels are as follows: s= strong intensity, m= moderate intensity, and w= weak intensity. <sup>1</sup>H NMR peak splitting labels are as follows: s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet (greater than quartet), dd= doublet of doublets, td= triplet of doublets, etc.

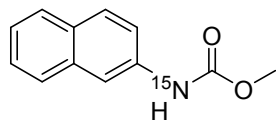
*Synthesis of <sup>15</sup>N-2-naphthamide-*



1.02 g (19.2 mmol, 1.0 eq.) of  $^{15}\text{N}$ -enriched ammonium chloride ( $^{15}\text{NH}_4\text{Cl}$ ) was added to a round bottom flask along with 50 mL of deionized water and a stir bar. The reaction flask was cooled to 0 °C in an ice bath and 80 mL of diethyl ether was added to the unperturbed system. 4.42 g (23.2 mmol, 1.5 eq.) of 2-naphthoyl chloride was then added directly into the ether layer. 6.48 g (116 mmol, 6.0 eq.) of KOH was dissolved in 30 mL of deionized water in a separate beaker and pipetted directly into the bottom of the aqueous layer. Upon addition, the reaction mixture was left unperturbed for 10 minutes followed by mild agitation for 10 minutes. The ice bath was then removed and the mixture was vigorously stirred for an additional 35 minutes. The ether layer was collected in a separate flask and the remaining product was extracted from the aqueous layer with additional diethyl ether (4 x 50 mL). The ether extracts were combined and dried over anhydrous sodium sulfate. The solution was decanted into a clean flask and the solvent was removed via rotatory evaporation. The product was collected and dried under high vacuum without further purification or purified by was recrystallized and filtered.

Yield: 3.10 g (17.9 mmol) of white crystals, 94 %. FTIR (KBr Pellet,  $\text{cm}^{-1}$ ): 3367 ( $^{15}\text{N}$ -H str, s), 3191 ( $^{15}\text{N}$ -H str, s), 3052 (Ar-H, s), 1648 (C=O, s), 1608 ( $^{15}\text{N}$ -H bend, s), 1569 (C=C aryl, m).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 8.51 (Ar-H, s, 1H), 8.20 ( $^{15}\text{N}$ -H,  $J_{^{15}\text{N}-^1\text{H}} = 88.8$  Hz, d, 1H), 7.98 (Ar-H, overlapped, 4H), 7.59 (Ar-H, overlapped, 2H), 7.52 ( $^{15}\text{N}$ -H,  $J_{^{15}\text{N}-^1\text{H}} = 87.6$  Hz).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO-d}_6$ ):  $\delta$  (ppm) 168.0 ( $J_{^{15}\text{N}-^{13}\text{C}} = 16.0$  Hz), 134.2, 132.2, 131.7 ( $J_{^{15}\text{N}-^{13}\text{C}} = 8.3$  Hz), 128.9, 127.9, 127.8, 127.6, 126.7, 124.4.  $^{15}\text{N}$  NMR (40.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 0.482. HRMS-ESI:  $M_{\text{theoretical}} = 195.0547$ ,  $M_{\text{sample}} = 195.0546$ ,  $\Delta M = 0.11$  mmass units (0.64 ppm),  $\text{C}_{11}\text{H}_9^{15}\text{NO}$ .

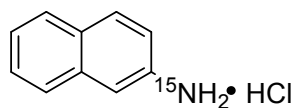
*Hofmann Rearrangement to Methyl  $^{15}\text{N}$ -2-naphthylcarbamate-*



1.19 g (6.90 mmol, 1.0 eq.) of  $^{15}\text{N}$ -2-naphthamide, 1.53 g (8.46 mmol, ~1.2 eq.) for of N-bromosuccinimide (NBS), and 2.10 mL (14.0 mmol, 2.0 eq) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were added to a round bottom flask along with ~300 mL of methanol. The mixture was heated to reflux and allowed to stir for 15 minutes. A second addition of NBS (1.0 eq.) was then added to the boiling mixture slowly and the reflux was continued for an additional 35 minutes. Upon cooling to room temperature, the solvent was removed under reduced pressure. The product was redissolved in ethyl acetate and washed with 6M HCl (2 x 100 mL), 1M NaOH (2 x 100 mL), and Brine solution (1 x 100 mL). The organic layer was then collected and dried over anhydrous sodium sulfate. The solution was decanted into a clean flask and the solvent was again removed under reduced pressure. The product was further purified via column chromatography (3:1 hexanes: ethyl acetate as the mobile phase). The product was collected and dried under high vacuum.

Yield: 0.6112 g (3.02 mmol) off white crystals, 44 %. FTIR (KBr Pellet,  $\text{cm}^{-1}$ ): 3267 (s,  $^{15}\text{N}$ -H str), 3052 (w, Ar-H), 2929 (m,  $-\text{CH}_3$ ), 1699 (s, C=O), 1608 ( $^{15}\text{N}$ -H bend, w), 1579 (m, C=C aryl).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.98 (Ar-H, s, 1H), 7.76 (Ar-H,  $J_{\text{1H-1H}} = 8.4$  Hz, d, 3H), 7.46 (Ar-H,  $J_{\text{1H-1H}} = 7.2$  Hz,  $J_{\text{1H-15N}} = 1.6$  Hz, td, 1H), 7.35 (Ar-H, overlapped, 2H), 6.83 ( $^{15}\text{N}$ -H,  $J_{\text{15N-1H}} = 90.4$  Hz, d, 1H), 3.81 (O- $\text{CH}_3$ , s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 154.4 ( $J_{\text{15N-13C}} = 22.4$  Hz), 135.4 ( $J_{\text{15N-13C}} = 15.9$  Hz), 134.1, 130.4, 129.1, 128.34 128.0, 127.75, 126.7, 125.5, 124.9, 52.6.  $^{15}\text{N}$  NMR (40.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 6.38. HRMS-ESI:  $M_{\text{theoretical}} = 203.0833$ ,  $M_{\text{sample}} = 203.0836$ ,  $\Delta M = -0.29$  mmass units (-1.46 ppm),  $\text{C}_{12}\text{H}_{11}^{15}\text{NO}_2$ .

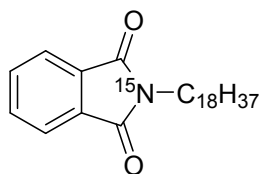
*Deprotection of the Carbamate Functionality with Conc. HCl-*



0.6005 g (2.97 mmol, 1.0 eq.) of methyl  $^{15}\text{N}$ -2-naphthylcarbamate was added to a 250 mL round bottom flask along with ~50 mL of 12M HCl and a stir bar. The mixture was allowed to reflux while stirring for 16 hrs. Upon completion, the mixture was cooled to 0 °C in an ice bath and was neutralized to ~pH = 5 with 1M NaOH solution. The aqueous layer was washed with ethyl acetate (3 x 100 mL) and the solvent from the aqueous layer was removed under reduced pressure. 100 mL of ethanol was added to the flask and the mixture was allowed to stir for 15 min. The remaining solids were filtered off and the filtrate was collected. The solvent was removed and the resulting solid was further dried under high vacuum to afford pure product

Yield: 0.4021 g (2.79 mmol) off orange-brown solid, 94 %. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3386 (s,  $^{15}\text{N}$ -H str), 3311 (s,  $^{15}\text{N}$ -H str), 3068 (m, Ar-H), 3017(w, Ar-H), 1629 (s,  $^{15}\text{N}$ -H bend), 1598 (m, C=C aryl).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.66 (Ar-H,  $J_{\text{1H-1H}} = 8.0$  Hz, q, 2H), 7.59 (Ar-H,  $J_{\text{1H-1H}} = 8.0$  Hz, d, 1H), 7.36 (Ar-H,  $J_{\text{1H-1H}} = 6.8$  Hz, t, 1H), 7.22 (Ar-H,  $J_{\text{1H-1H}} = 7.6$  Hz, t, 1H), 6.95 (Ar-H, overlapped, 2H), 3.86 ( $^{15}\text{NH}_2$ , s, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 144.3 ( $J_{^{15}\text{N}-^{13}\text{C}} = 11.4$  Hz), 135.1, 129.5, 128.2, 127.9, 126.6, 122.7, 118.5, 118.4, 108.8 ( $J_{^{15}\text{N}-^{13}\text{C}} = 2.2$ ).  $^{15}\text{N}$  NMR (40.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -40.31.

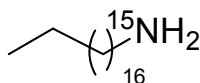
*$^{15}\text{N}$ -Octadecyl phthalimide-*



Yield: 2.00 g (5.01 mmol) white crystalline solid, 90 %. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3110 (w, Ar-H), 3056 (w, Ar-H), 3031 (w, Ar-H), 2915 (s, alkyl-H), 2848 (s, alkyl-H), 1708 (m,

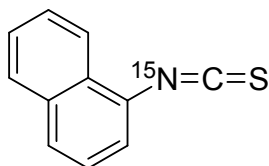
C=O<sub>imide</sub>), 1698 (s, C=O<sub>imide</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 7.84 (Ar-H, *J*<sub>1H-1H</sub> = 4.4 Hz, q, 2H), 7.70 (Ar-H, *J*<sub>1H-1H</sub> = 4.4 Hz, q, 2H), 3.67 (<sup>15</sup>N-CH<sub>2</sub>-, *J*<sub>1H-1H</sub> = 10.4 Hz, t, 2H), 1.68 (<sup>15</sup>N-CH<sub>2</sub>-CH<sub>2</sub>-, m, 2H), 1.27 (-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>15</sub>-CH<sub>3</sub>, m, 30H), 0.88 (-CH<sub>3</sub>, *J*<sub>1H-1H</sub> = 8.8 Hz, t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 168.7 (*J*<sub>15N-13C</sub> = 13.6 Hz), 134.1, 132.5, 132.4, 123.4, 38.3 (*J*<sub>15N-13C</sub> = 8.3 Hz), 32.2, 29.9, 29.8, 29.7, 29.6, 29.4, 28.9, 27.1, 22.9, 14.4. <sup>15</sup>N NMR (40.5 MHz, CDCl<sub>3</sub>): δ (ppm) 67.2.

*Deprotection of Phthalimide Group with Hydrazine-*



Yield: 1.05 g (3.89 mmol) white crystalline solid, 84 %. FTIR (KBr pellet, cm<sup>-1</sup>): 3324 (w, <sup>15</sup>N-H str.), 3251 (w, <sup>15</sup>N-H str.), 3160 (w, <sup>15</sup>N-H), 2917 (s, alkyl-H), 2848 (s, alkyl-H), 1602 (m, <sup>15</sup>N-H bend), 1562 (m, <sup>15</sup>N-H bend). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) 2.67 (<sup>15</sup>N-CH<sub>2</sub>-, *J*<sub>1H-1H</sub> = 6.8 Hz, t, 2H), 1.43 (<sup>15</sup>N-CH<sub>2</sub>-CH<sub>2</sub>-, m, 2H), 1.25 (-CH<sub>2</sub>-CH<sub>2</sub>-(CH<sub>2</sub>)<sub>15</sub>-CH<sub>3</sub>, m, 30H), 1.14 (<sup>15</sup>NH<sub>2</sub>, s, 2H), 0.88 (-CH<sub>3</sub>, *J*<sub>1H-1H</sub> = 8.8 Hz, t, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) 42.5 (*J*<sub>15N-13C</sub> = 3.8 Hz), 34.1, 32.1, 29.9, 29.8, 29.7, 29.6, 27.1, 22.9, 14.3. <sup>15</sup>N NMR (40.5 MHz, CDCl<sub>3</sub>): δ (ppm) -73.1.

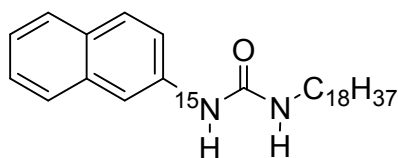
*Synthesis of <sup>15</sup>N-labeled 1-naphthylisothiocyanate-*



Yield: 0.98 g (5.26 mmol) yellow solid, 75 %. FTIR (KBr pellet, cm<sup>-1</sup>): 3058 (w, Ar-H), 2951 (w, Ar-H), 2069 (s, S=C=<sup>15</sup>N), 1508 (m, C=C aryl). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm)

8.12 (Ar-H,  $J_{\text{H-H}} = 8.4$  Hz,  $J_{\text{H-H}} = 0.8$  Hz, dd, 1H), 7.88 (Ar-H,  $J_{\text{H-H}} = 8.0$  Hz, d, 1H), 7.79 (Ar-H, overlapped m, 1H), 7.59 (Ar-H, m, 2H), 7.43 (Ar-H, m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 136.5, 134.2, 129.5, 128.7, 127.9, 127.6, 127.4, 125.6 ( $J_{\text{N-C}} = 3.0$  Hz), 123.7 ( $J_{\text{N-C}} = 2.3$  Hz), 123.0 ( $J_{\text{N-C}} = 1.5$  Hz).  $^{15}\text{N}$  NMR (40.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 65.2.

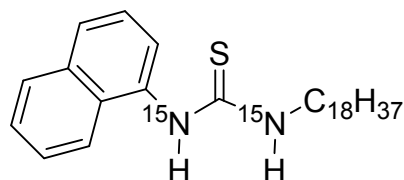
*$^{15}\text{N}$ -2-naphthyl, N-(n-octadecyl)urea-*



Following the outlined procedure for asymmetric ureas/ thioureas: 75 mL of  $\text{CHCl}_3$ , 0.40 g (2.74 mmol, 1.0 eq) of  $^{15}\text{N}$ -2-naphthylamine, and 1.05 mL (3.01 mmol, 1.2 eq.) of *n*-octadecyl isocyanate. Due to insolubility in all conventional NMR solvents (e.g.,  $\text{CDCl}_3$ ,  $\text{CD}_2\text{Cl}_2$ , benzene- $d_6$ , toluene- $d_8$ , THF- $d_8$ , 1,2-dichloroethane- $d_4$ , methanol- $d_4$ , acetone- $d_6$ , DMSO- $d_6$ ), NMR data were collected. The FTIR spectrum was taken in the solid state and HRMS-ESI is reported below.

Yield: 0.88 g (2.01 mmol) white powder, 73 %. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3338 (s, N-H str), 2952 (s, alkyl-H), 2917 (s, alkyl-H), 2848 (m, alkyl-H), 1618 (s, C=O), 1570 (m, C=C aryl). HRMS-ESI:  $M_{\text{theoretical}} = 440.3653$ ,  $M_{\text{sample}} = 440.3662$ ,  $\Delta M = -0.85$  mmass units (-1.94 ppm),  $\text{C}_{29}\text{H}_{46}^{15}\text{NNO}$ .

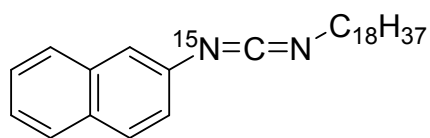
*$^{15}\text{N}$ -(1-naphthyl),  $^{15}\text{N}$ -octadecylthiourea-*



Following the outlined procedure for asymmetric ureas/ thioureas: 0.9729 g (5.22 mmol, 1.0 eq.) of  $^{15}\text{N}$ -labeled 1-naphthyl isothiocyanate and 1.44 g (5.34 mmol, 1.05 eq.) of  $^{15}\text{N}$ -labeled octadecylamine, and 75 mL of DCM

Yield: 2.14g (4.70 mmol) white crystalline powder, 90 %. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3378 (s,  $^{15}\text{N}$ -H str) 3251 (s,  $^{15}\text{N}$ -H str), 3050 (w, Ar-H), 2921 (s, alkyl-H), 2852 (s, alkyl-H), 1523 (s, C=S), 1465 (m,  $^{15}\text{N}$ -H bend).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.01 (Ar-H, m, 1H), 7.92 (Ar-H, m, 2H), 7.65 ( $^{15}\text{N}$ -H, overlapped, 1H), 7.57 (Ar-H, overlapped m, 2H), 7.44 (Ar-H,  $J_{1\text{H}-1\text{H}} = 7.2$  Hz, d, 1H), 5.65 ( $^{15}\text{N}$ -H,  $J_{15\text{N}-1\text{H}} = 87.2$  Hz, d, 1H), 3.56 ( $-\text{CH}_2\text{CH}_2(\text{CH}_2)_{15}\text{CH}_3$ ,  $J_{1\text{H}-1\text{H}} = 6.0$  Hz, q, 2H), 1.44 ( $\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$ , unresolved m, 2H), 1.23 ( $\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_{14}\text{CH}_3$ , m, 30H), 0.88 ( $\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_2\text{CH}_3$ ,  $J_{1\text{H}-1\text{H}} = 6.4$  Hz, t, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 180.7, 134.9, 130.2, 129.3, 128.8, 127.8, 127.4, 126.0 ( $J_{15\text{N}-13\text{C}} = 2.3$  Hz), 125.5, 122.8, 45.8 ( $J_{15\text{N}-13\text{C}} = 11.4$  Hz), 32.2, 29.9, 29.8, 29.7, 29.6, 29.4, 29.2, 26.9, 22.9, 14.4.  $^{15}\text{N}$  NMR (40.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) -2.02, -10.6.

$^{15}\text{N}$ -(2-naphthyl), *N*-octadecylcarbodiimide-

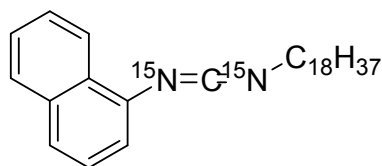


Following the procedure for the synthesis of carbodiimides from ureas/ thioureas: 10 mL of DCM, 1.89 g (4.47 mmol, 1.2 eq.) of dibromotriphenylphosphorane, 1.26 mL (9.11 mmol, 2.5 eq.) of triethylamine, and 1.60 g (3.64 mmol, 1.0 eq.) of  $^{15}\text{N}$ -(2-naphthyl), *N*-octadecylurea.

Yield: 1.09 g (2.59 mmol) of white solid, 71 %. FTIR (KBr thinfilm,  $\text{cm}^{-1}$ ): 3050 (w, Ar-H), 2920 (s, alkyl-H), 2852 (m, alkyl-H), 2130 (s,  $^{15}\text{N}=\text{C}=\text{N}$ ), 1562 (w, C=C<sub>aryl</sub>).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 7.76 (Ar-H, overlapped m, 3H), 7.38 (Ar-H, overlapped m, 3H), 7.24

(Ar-H,  $J_{1H-1H} = 8.4$  Hz,  $J_{1H-1H} = 2.0$  Hz 1H, dt), 3.46 (-**CH**<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>,  $J_{1H-1H} = 6.8$  Hz, 2H, t), 1.72 (-CH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>, 2H, m) 1.44 (-CH<sub>2</sub>CH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>14</sub>CH<sub>3</sub>, 2H, m), 1.25 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(**CH**<sub>2</sub>)<sub>14</sub>CH<sub>3</sub>, 28H, m) 0.88 (-CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>**CH**<sub>3</sub>,  $J = 6.8$  Hz, 3H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 138.4, 136.3, 134.3, 131.1, 129.4, ( $J_{15N-13C} = 1.5$  Hz), 127.9, 127.3, 126.7, 125.3, 123.4 ( $J_{15N-13C} = 3.0$  Hz), 120.5, 47.2, 32.2, 31.7, 30.0, 29.9, 29.8, 29.7, 29.6, 29.4, 27.1, 23.0, 14.4. HRMS-ESI:  $M_{\text{theoretical}} = 422.3548$ ,  $M_{\text{sample}} = 422.3549$ ,  $\Delta M = -0.09$  (-0.22 ppm), C<sub>29</sub>H<sub>44</sub><sup>15</sup>NN.

<sup>15</sup>N-(1-naphthyl), N-octadecylcarbodiimide-



Following the procedure for the synthesis of carbodiimides from ureas/ thioureas: 10 mL of DCM, 1.72 g (4.08 mmol, 1.2 eq.) of dibromotriphenylphosphorane, 1.18 mL (8.51 mmol, 2.5 eq.) of triethylamine, and 1.53 g (3.36 mmol, 1.0 eq.) of <sup>15</sup>N-(1-naphthyl), <sup>15</sup>N-octadecyl thiourea.

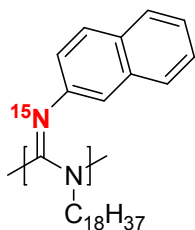
Yield: 0.97 g (2.29 mmol) of pale yellow liquid, 68 %. FTIR (KBr thinfilm, cm<sup>-1</sup>): 3048 (m, Ar-H), 2923 (s, alkyl-H), 2852 (m, alkyl-H), 2379 (s, <sup>15</sup>N=C=N), 1573 (w, C=C<sub>aryl</sub>). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) 8.28 (Ar-H, 1H, m), 7.81 (Ar-H, 1H, m), 7.61 (Ar-H,  $J_{1H-1H} = 8.0$  Hz, 1H, d), 7.50 (Ar-H, 2H, m), 7.40 (Ar-H,  $J_{1H-1H} = 7.2$  Hz, 1H, t), 7.29 (Ar-H, 1H, m), 3.47 (-**CH**<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>,  $J_{1H-1H} = 6.8$  Hz, 2H, t), 1.72 (-CH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>3</sub>, 2H, m) 1.44 (-CH<sub>2</sub>CH<sub>2</sub>**CH**<sub>2</sub>(CH<sub>2</sub>)<sub>14</sub>CH<sub>3</sub>, 2H, m), 1.25 (-CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>(**CH**<sub>2</sub>)<sub>14</sub>CH<sub>3</sub>, 28H, m) 0.88 (-CH<sub>2</sub>CH<sub>2</sub>(CH<sub>2</sub>)<sub>15</sub>**CH**<sub>3</sub>,  $J = 6.8$  Hz, 3H, t). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 137.5, 135.8, 134.6, 129.0, 128.0, 126.6, 126.1, 126.0, 124.7, 123.8, 119.8, 47.2, 32.2, 31.7, 30.0, 29.9, 29.8, 29.7,

29.6, 29.4, 27.1, 23.0, 14.4. HRMS-ESI:  $M_{\text{theoretical}} = 423.3482$ ,  $M_{\text{sample}} = 423.3502$ ,  $\Delta M = -1.98$  (-4.69 ppm),  $C_{29}H_{44}^{15}N_2$ .

### III. The Polymerization of $^{15}N$ -labeled Carbodiimides

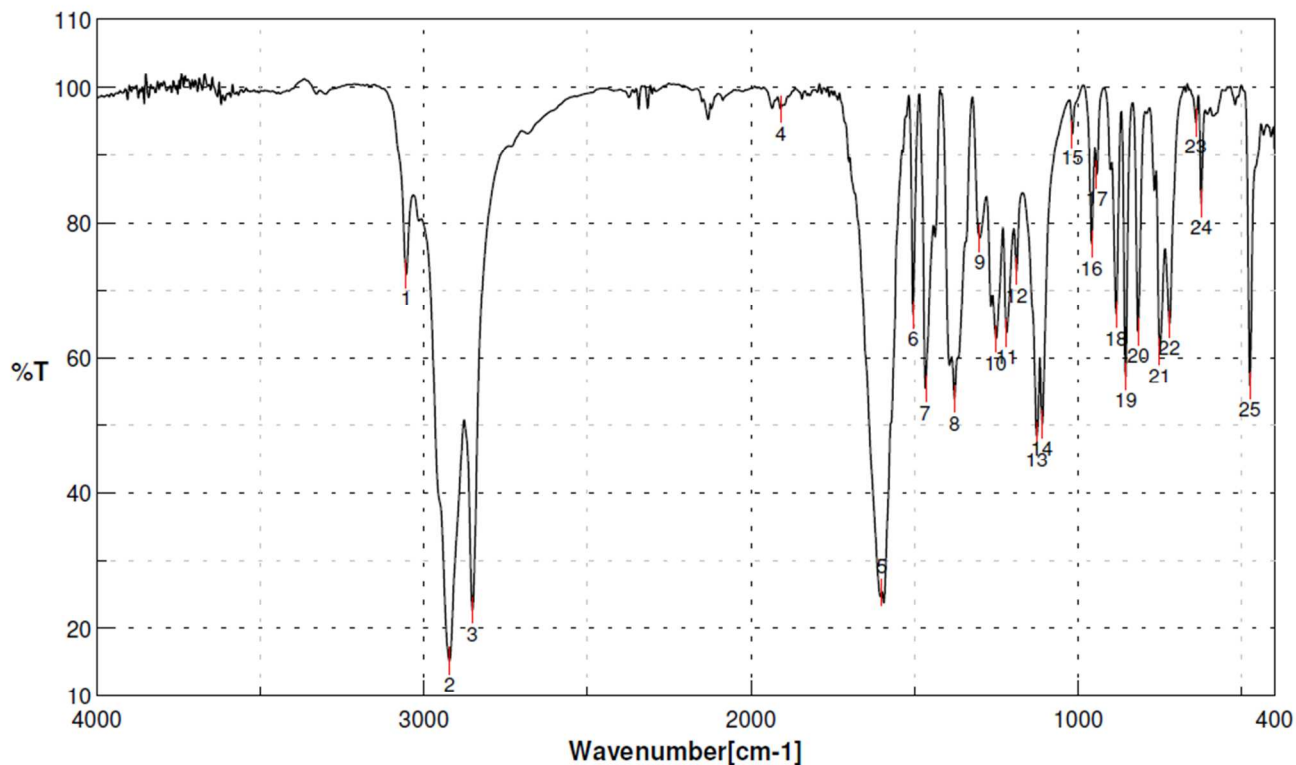
The monomer-to-catalyst ratio, yield,  $^1H$  NMR, IR, and  $^{15}N$  NMR data of each polymer is reported below as well as scans of the IR spectra. The synthesis and characterization of **Poly-3** was previously reported.<sup>2</sup>

*Poly( $^{15}N$ -2-naphthyl-*N*-octadecylcarbodiimide) (Poly-4)-*



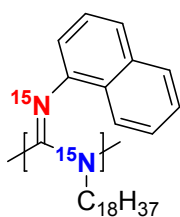
Following the outlined procedure for the polymerization of carbodiimide monomers with titanium(IV) catalysts: 1.08 g (2.56 mmol, 200 eq) of  $^{15}N$ -2-naphthyl-*N*-octadecylcarbodiimide, 5.76 mg (12.8  $\mu\text{mol}$ , 1.0 eq), of **Cat-2R**, 0.40 mL of dry  $CHCl_3$ .

Yield: 0.904 g (2.15 mmol) of orangish-white solid, 84 %. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3054 (m, Ar-H), 2922 (s, alkyl-H), 2852 (s, alkyl-H), 1600 (s,  $^{15}N=C$ ), 1504 (m,  $C=C_{\text{aryl}}$ ).  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 8.01 - 6.92 (Ar-H, broad overlapped), 1.27 (octadecyl-H, broad s), 0.88 ( $-CH_3$ , broad s).  $^{15}N$  NMR (40.5 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 133.6.



No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3054.69	72.3423	2	2921.63	15.1653	3	2852.2	22.6958
4	1909.18	96.8523	5	1600.63	25.4	6	1504.2	66.3504
7	1465.63	55.3878	8	1378.85	53.8403	9	1301.72	77.7586
10	1251.58	62.8196	11	1218.79	63.6852	12	1187.94	72.8859
13	1126.22	48.3964	14	1110.8	50.1234	15	1018.23	93.1258
16	958.448	76.8794	17	943.02	87.0236	18	883.238	66.4209
19	854.311	57.2446	20	815.742	63.7747	21	750.174	60.893
22	721.247	65.0531	23	640.251	94.8303	24	622.895	82.773
25	474.403	55.8184						

*Poly(<sup>15</sup>N-1-naphthyl-<sup>15</sup>N-octadecylcarbodiimide) (Poly-5)-*

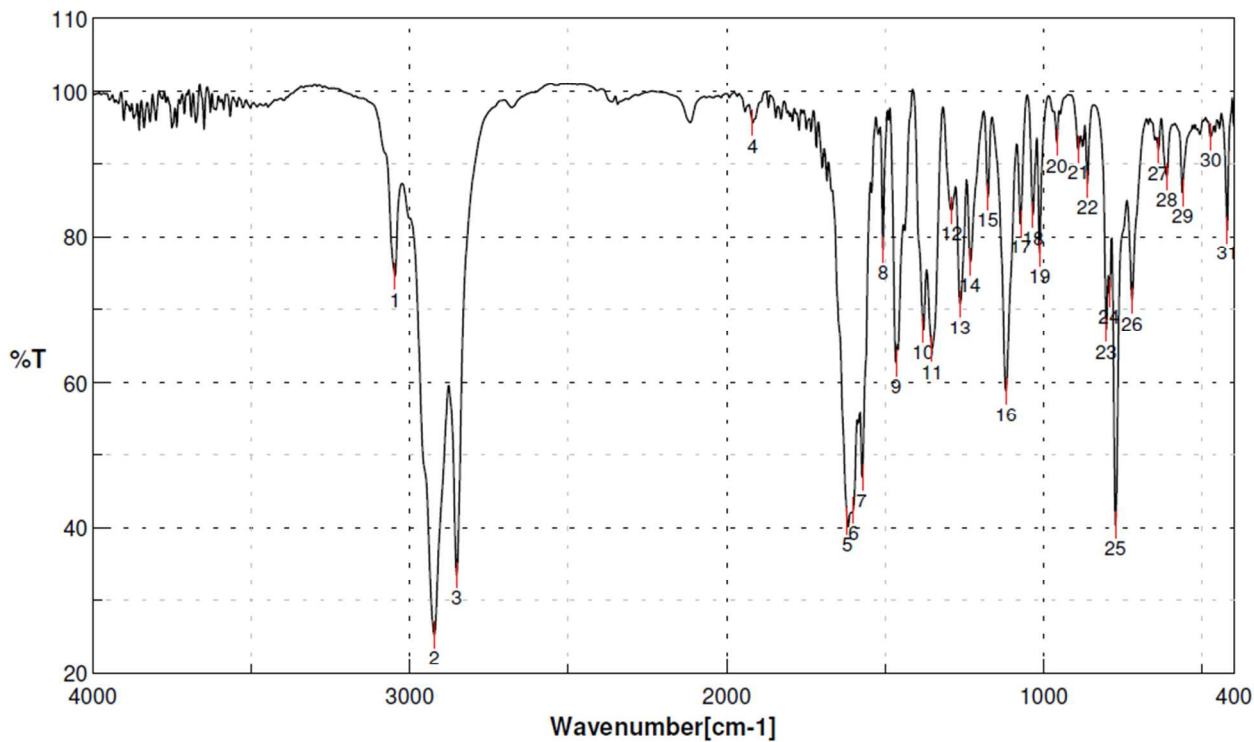


Following the outlined procedure for the polymerization of carbodiimide monomers with titanium(IV) catalysts: 0.944 g (2.24 mmol, 198 eq) of <sup>15</sup>N-1-naphthyl-<sup>15</sup>N-

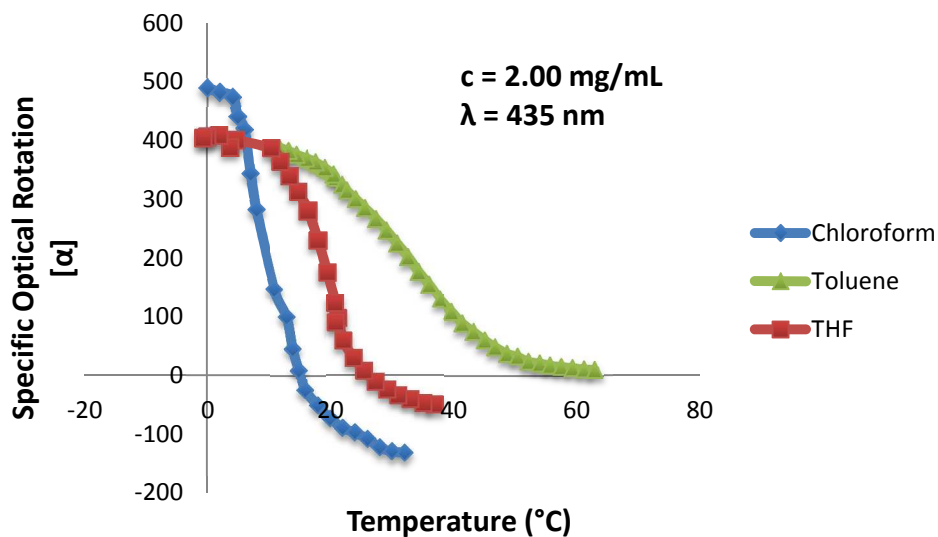
octadecylcarbodiimide, 5.10 mg (11.3  $\mu\text{mol}$ , 1.0 eq), of **Cat-2S**, w/o solvent.

Yield: 0.880 g (2.09 mmol) of orangish-brown solid, 93 %. FTIR (KBr pellet,  $\text{cm}^{-1}$ ): 3046 (m, Ar-H), 2924 (s, alkyl-H), 2852 (s, alkyl-H), 1619 (s,  $^{15}\text{N}=\text{C}$ ), 1601 (s,  $^{15}\text{N}=\text{C}$ ), 1571 (m,  $\text{C}=\text{C}_{\text{aryl}}$ ).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 8.01 - 6.32 (Ar-H, broad overlapped), 1.90 - 1.27 (octadecyl-H, broad s), 0.88 (- $\text{CH}_3$ , broad s).  $^{15}\text{N}$  NMR (40.5 MHz,  $\text{CDCl}_3$ ):  $\delta$  (ppm) 147.7 ( $^{15}\text{N}=\text{C}$ ), 137.8 ( $^{15}\text{N}=\text{C}$ ), 19.9 ( $^{15}\text{N}-\text{C}$ ), 11.5 ( $^{15}\text{N}-\text{C}$ ).

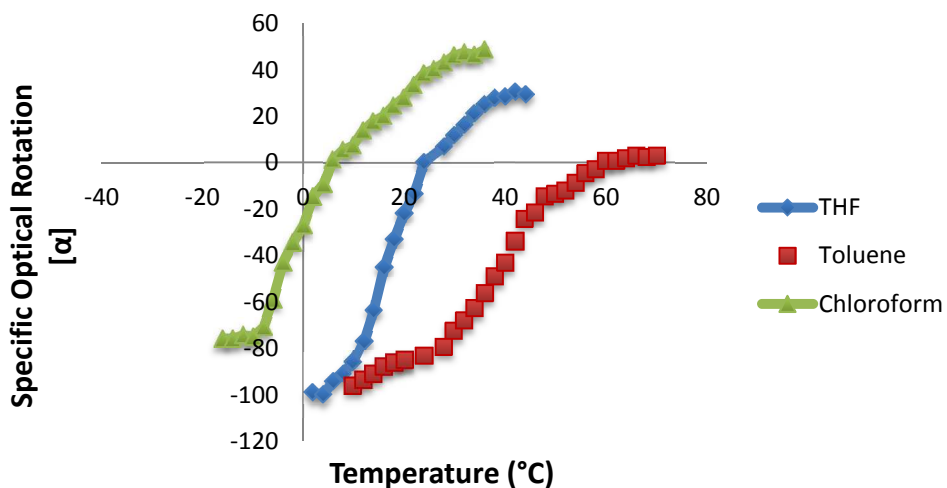
No.	cm-1	%T	No.	cm-1	%T	No.	cm-1	%T
1	3046.98	74.5289	2	2923.56	25.3335	3	2852.2	33.6238
4	1918.82	95.7059	5	1619.91	40.9686	6	1600.63	42.4883
7	1571.7	46.9899	8	1506.13	78.168	9	1465.63	62.6326
10	1380.78	67.2492	11	1351.86	64.6091	12	1290.14	83.6521
13	1263.15	70.7965	14	1232.29	76.4491	15	1176.36	85.5172
16	1118.51	58.8067	17	1072.23	81.818	18	1033.66	83.0662
19	1012.45	77.7033	20	958.448	92.9863	21	890.952	92.0063
22	862.025	87.2934	23	802.242	67.3473	24	792.6	72.2194
25	773.315	40.3542	26	721.247	71.2989	27	638.323	91.9582
28	611.324	88.2695	29	561.184	86.1133	30	472.474	93.7338
31	420.406	80.9864						



#### IV. VT-Polarimetry of Poly-3 and Poly-5-



**Figure S1.** The VT-polarimetry curves of **Poly-3** in chloroform (blue), toluene (green), and THF (red) at 435 nm ( $c = 2.00 \text{ mg/mL}$ ).



**Figure S2.** The VT-polarimetry curves of **Poly-5** in chloroform (green), toluene (red), and THF (blue) at 435 nm ( $c = 2.00 \text{ mg/mL}$ ).

## V. VT-<sup>15</sup>N NMR Scans for Van't Hoff Analysis-

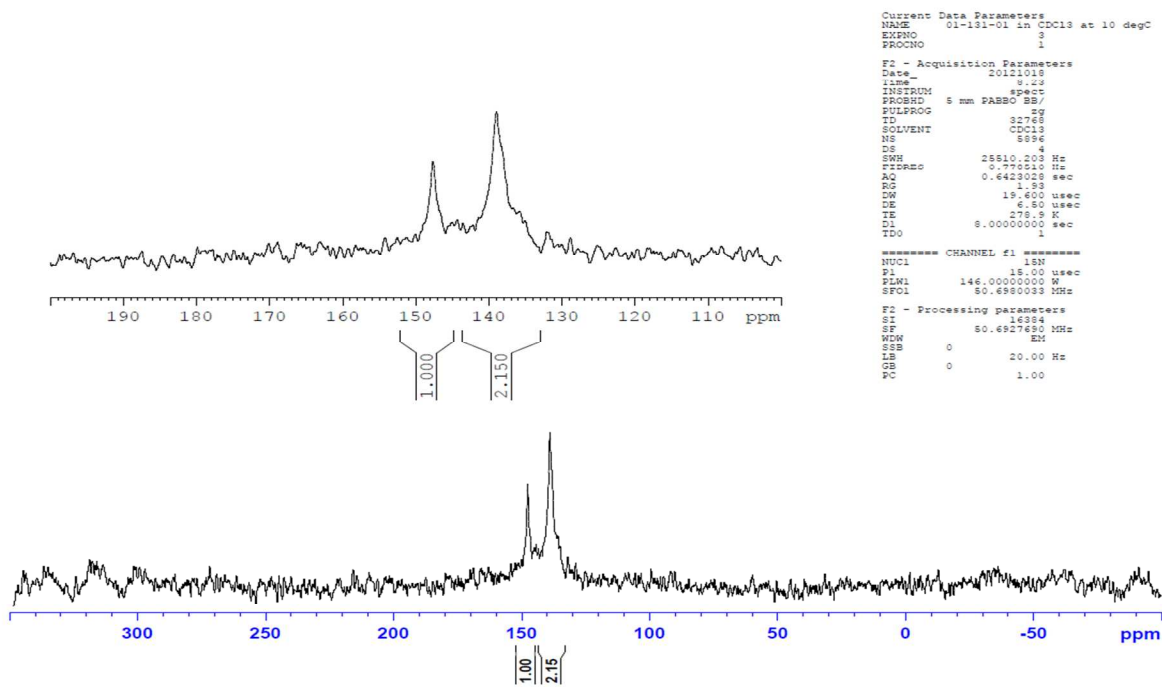


Figure S3. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in CDCl<sub>3</sub> at 10 °C

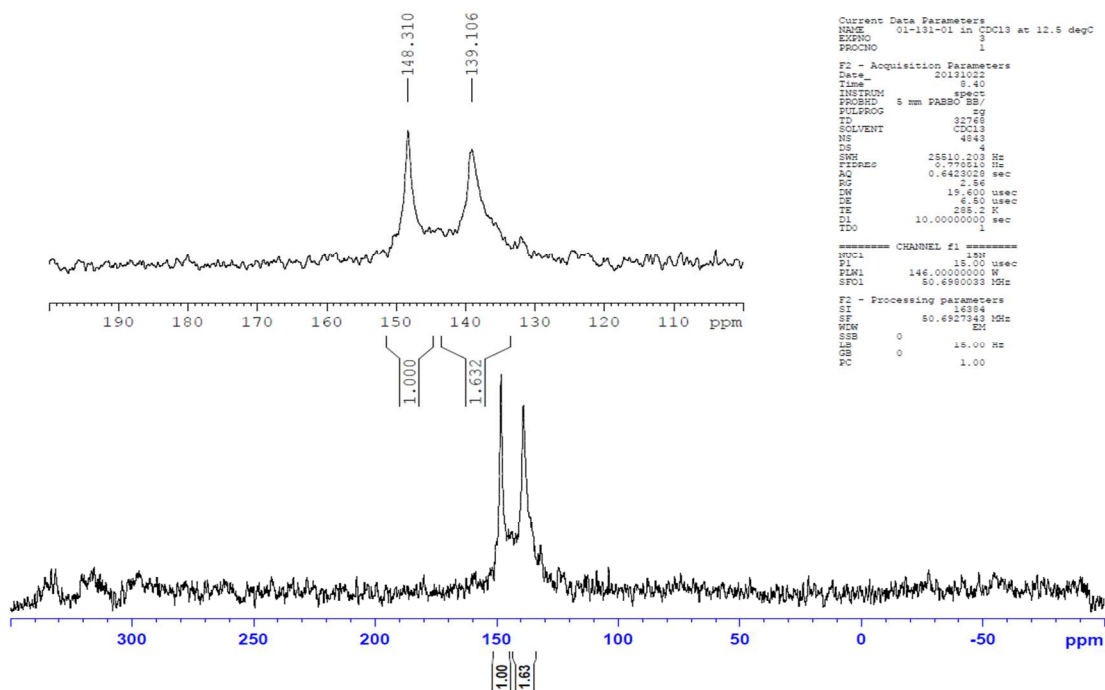


Figure S4. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in CDCl<sub>3</sub> at 12.5 °C

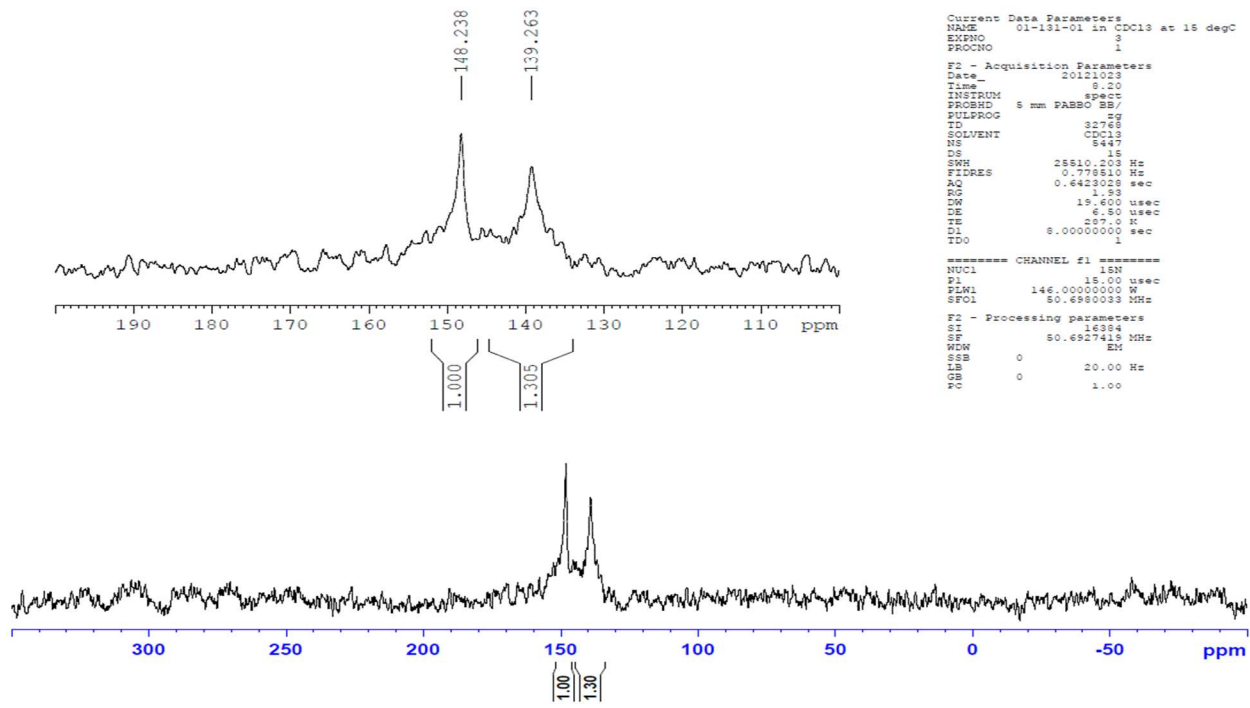


Figure S5. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in CDCl<sub>3</sub> at 15 °C

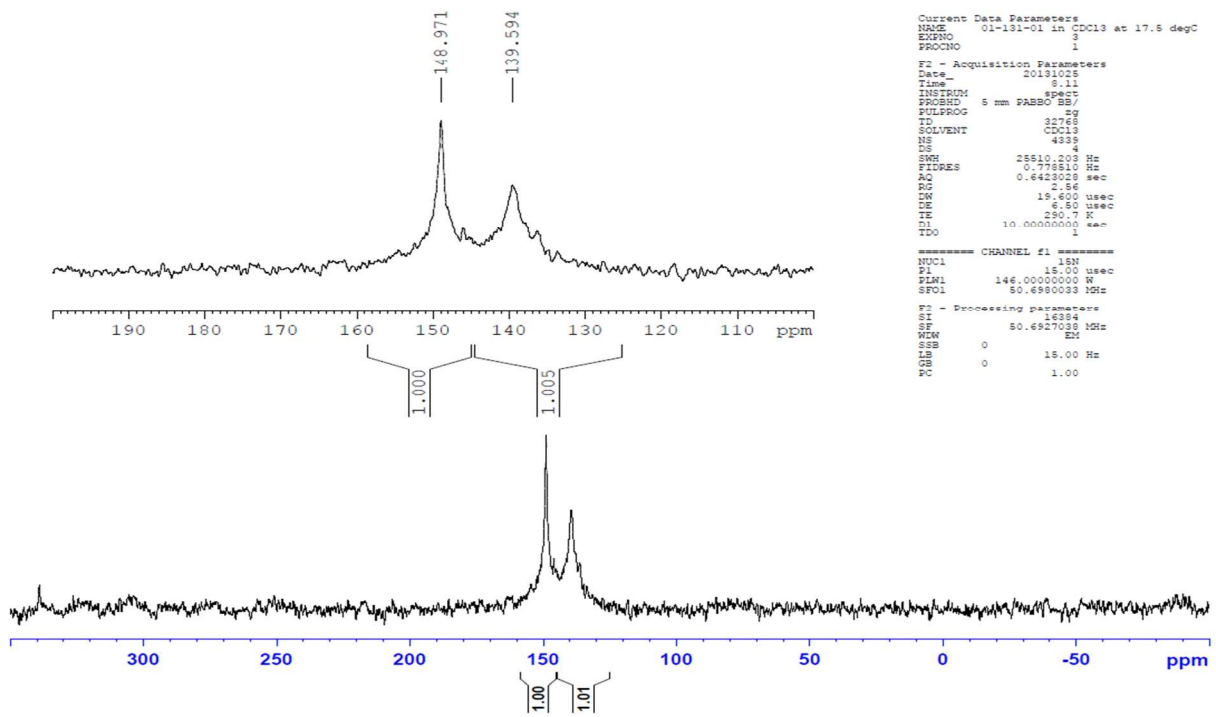


Figure S6. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in CDCl<sub>3</sub> at 17.5 °C

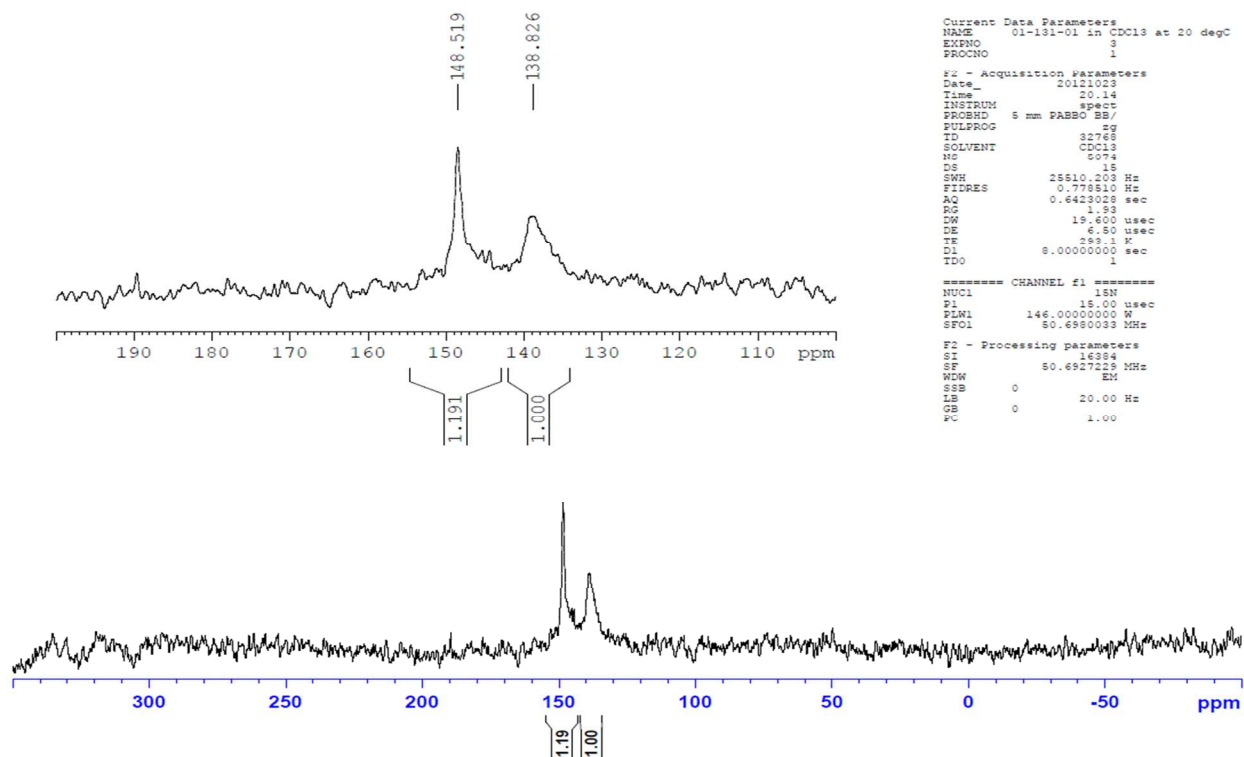


Figure S7. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in CDCl<sub>3</sub> at 20 °C

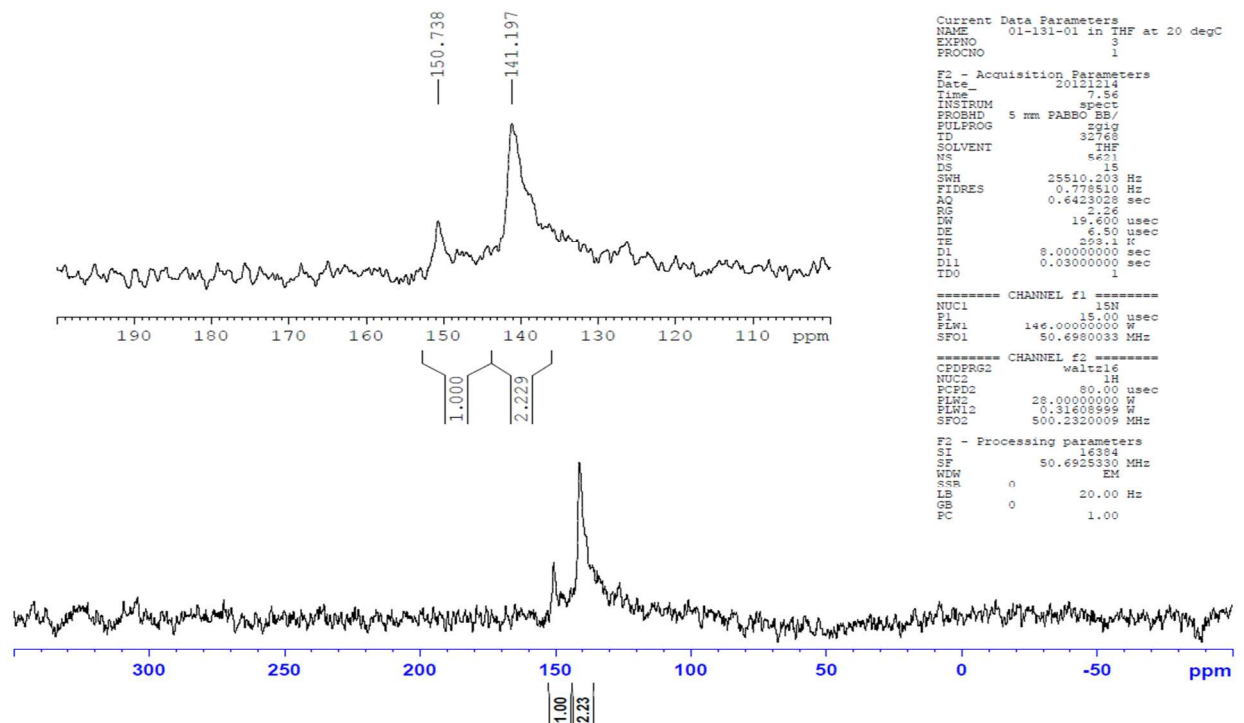


Figure S8. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in THF-*d*<sub>8</sub> at 20 °C

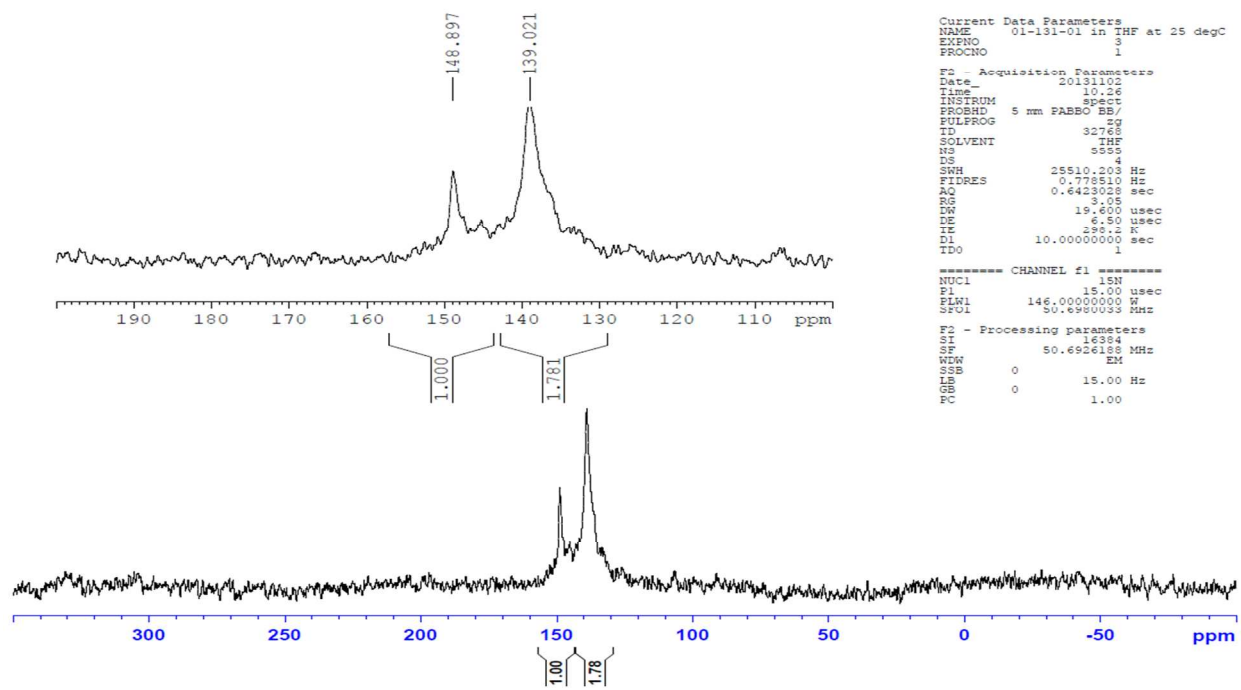


Figure S9. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in THF-*d*<sub>8</sub> at 25 °C

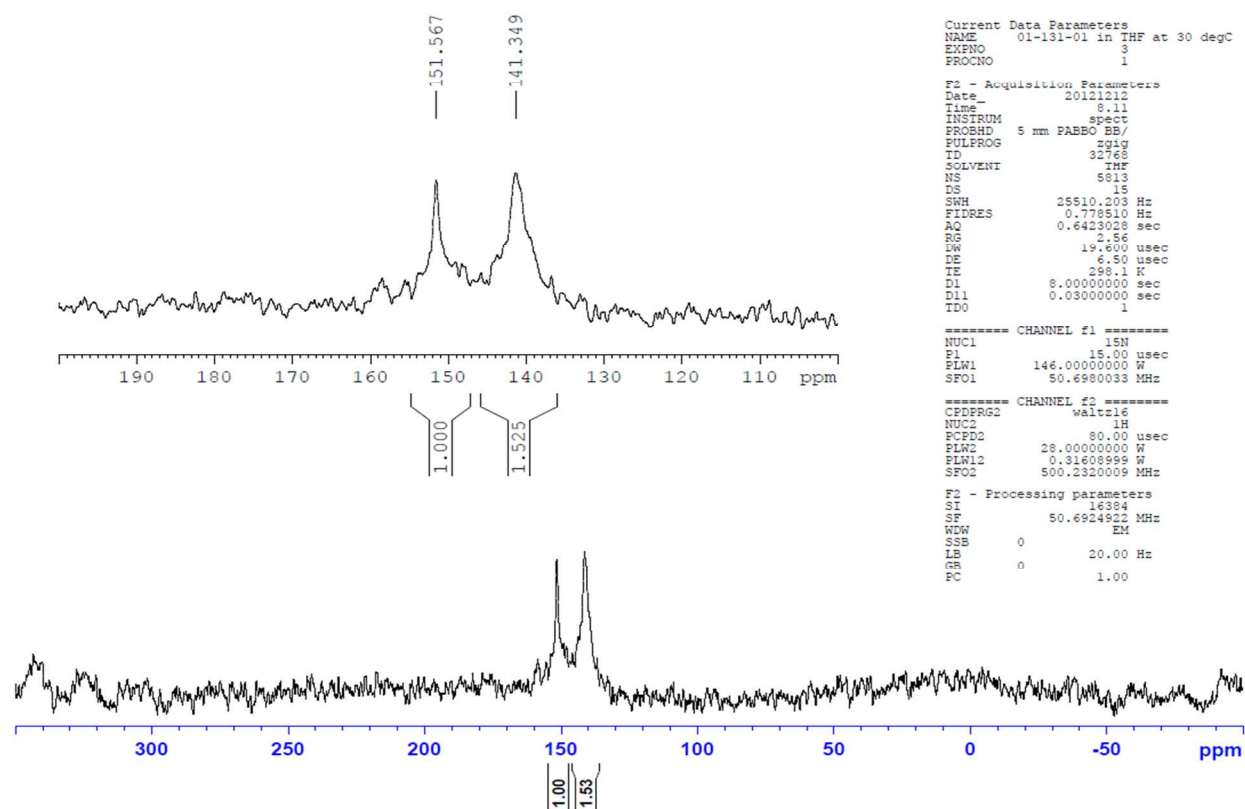


Figure S10. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in THF-*d*<sub>8</sub> at 30 °C

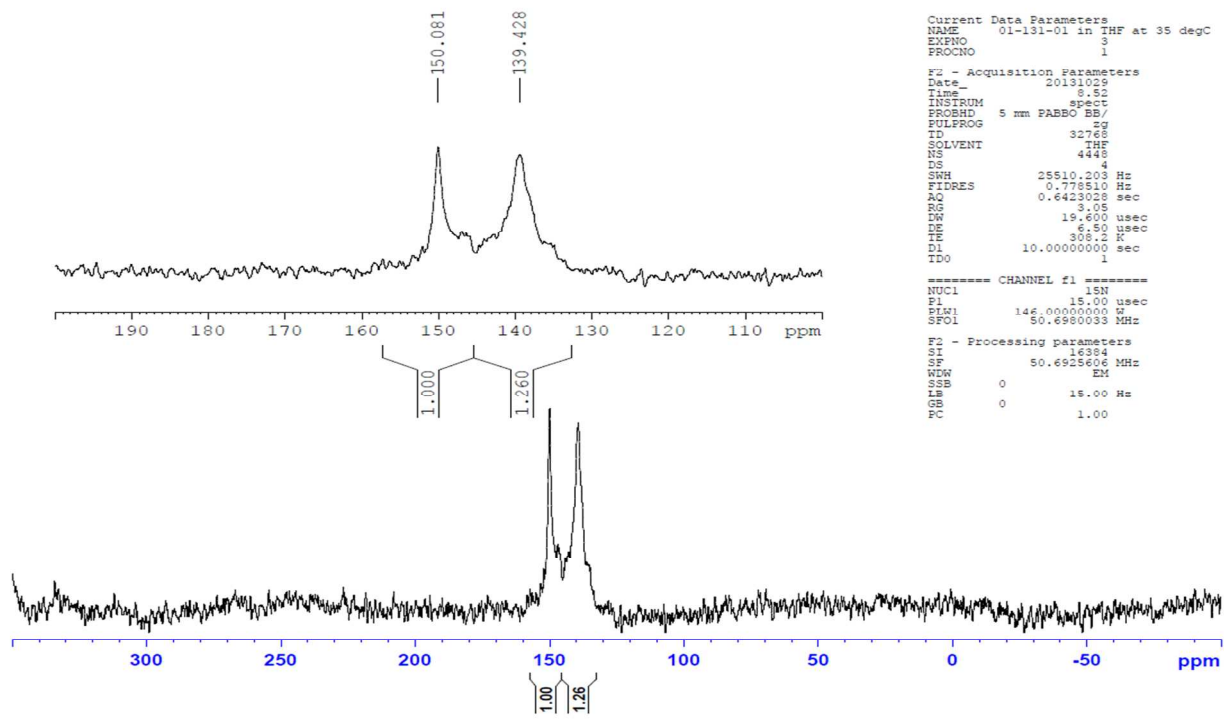


Figure S11. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in THF-*d*<sub>8</sub> at 35 °C

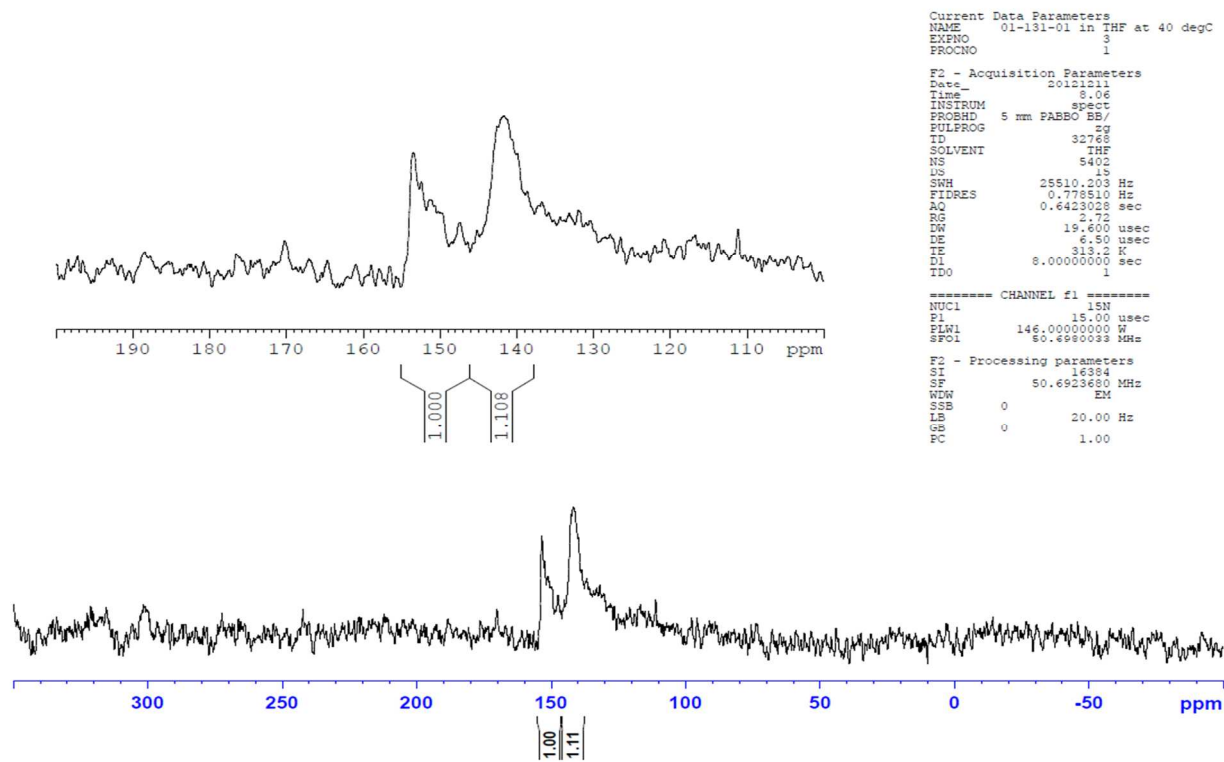


Figure S12. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in THF-*d*<sub>8</sub> at 40 °C

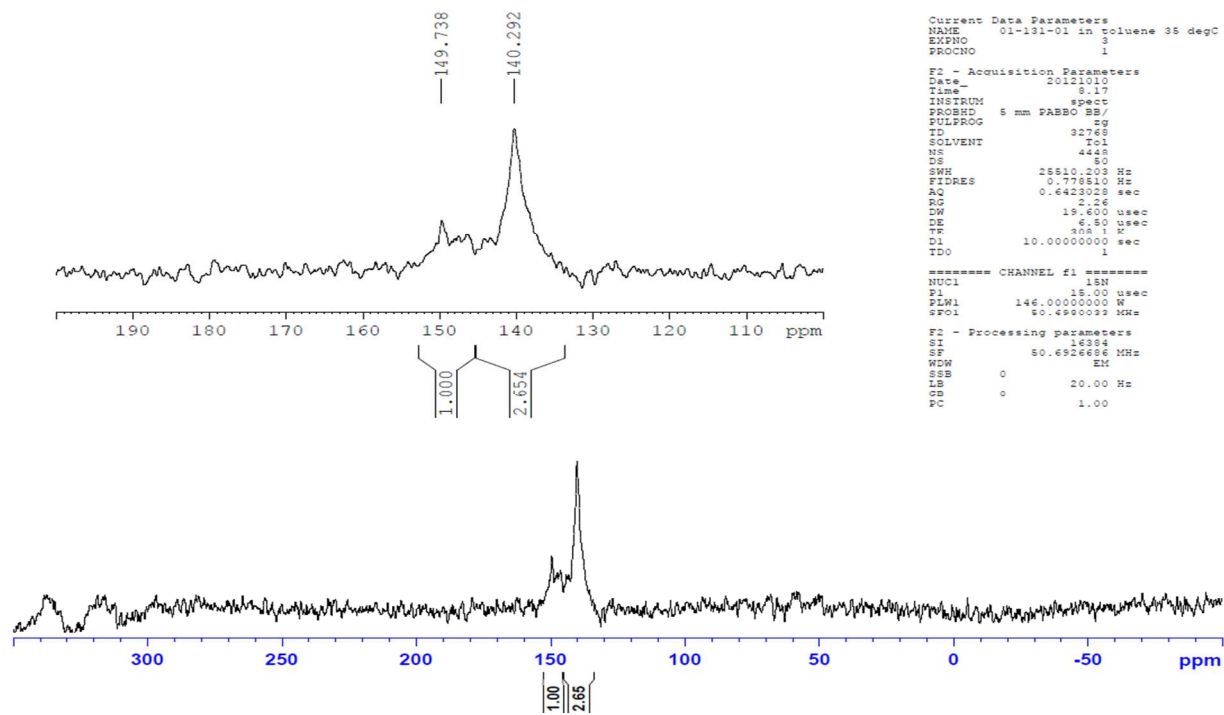


Figure S13. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in toluene-*d*<sub>8</sub> at 35 °C

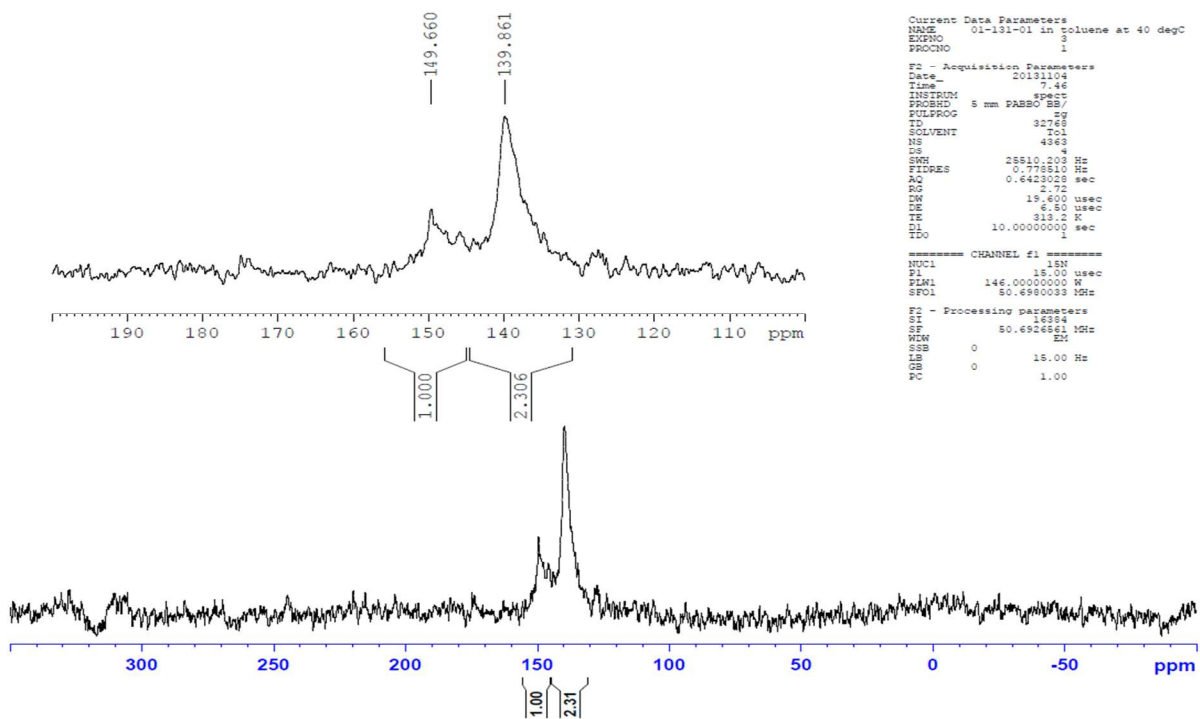


Figure S14. The VT-<sup>15</sup>N NMR spectra of **Poly-3** in toluene-*d*<sub>8</sub> at 40 °C

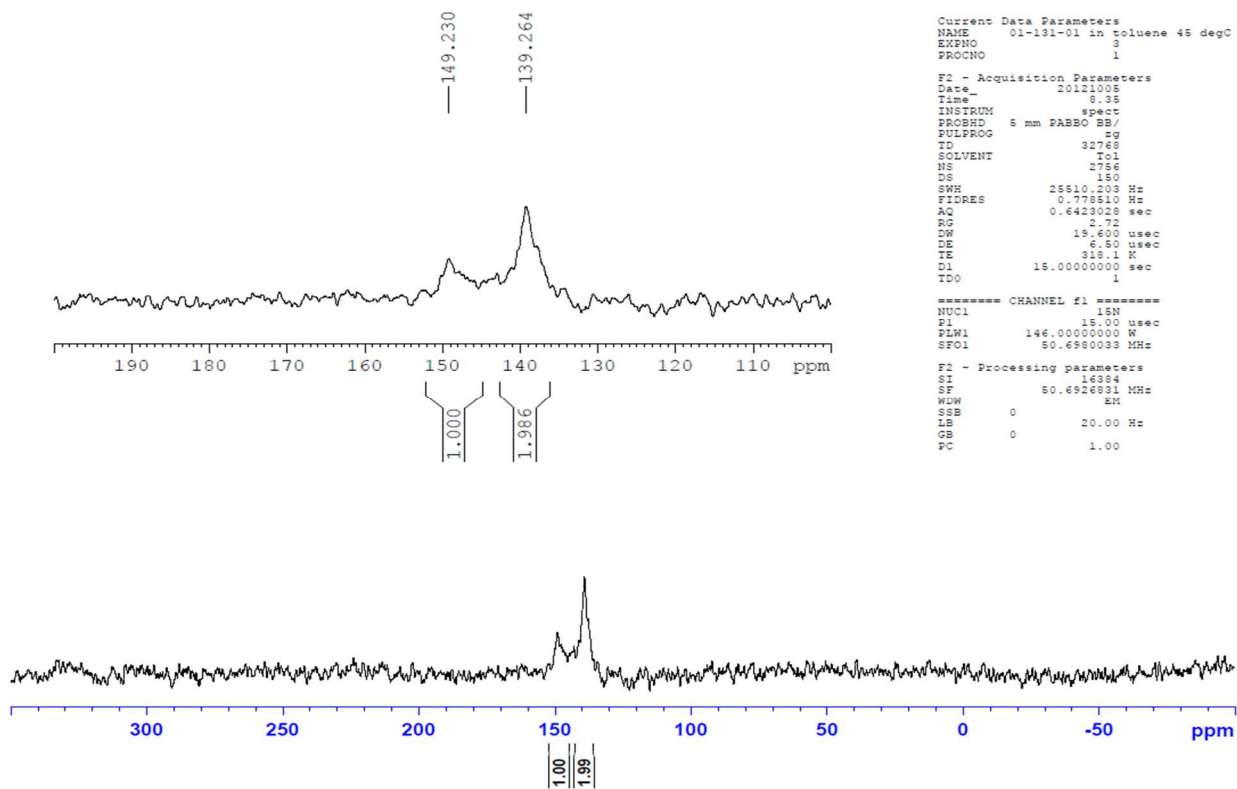


Figure S15. The VT-<sup>15</sup>N NMR spectra of Poly-3 in toluene-*d*<sub>8</sub> at 45 °C

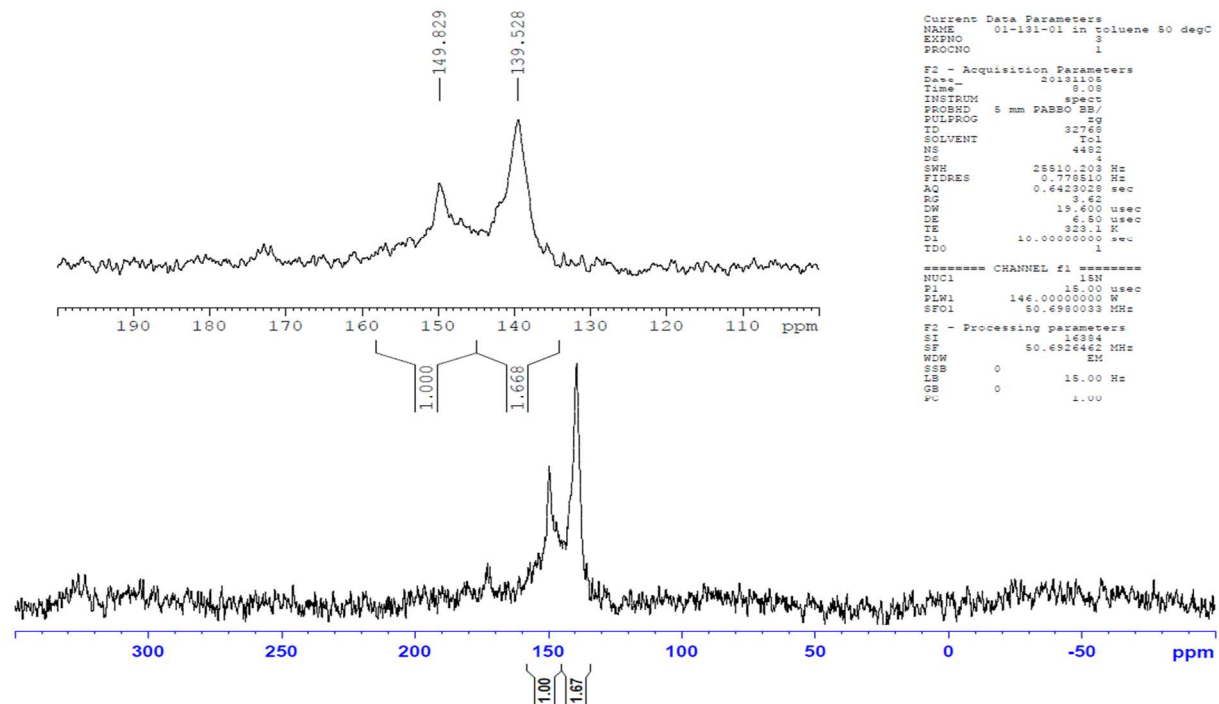


Figure S16. The VT-<sup>15</sup>N NMR spectra of Poly-3 in toluene-*d*<sub>8</sub> at 50 °C

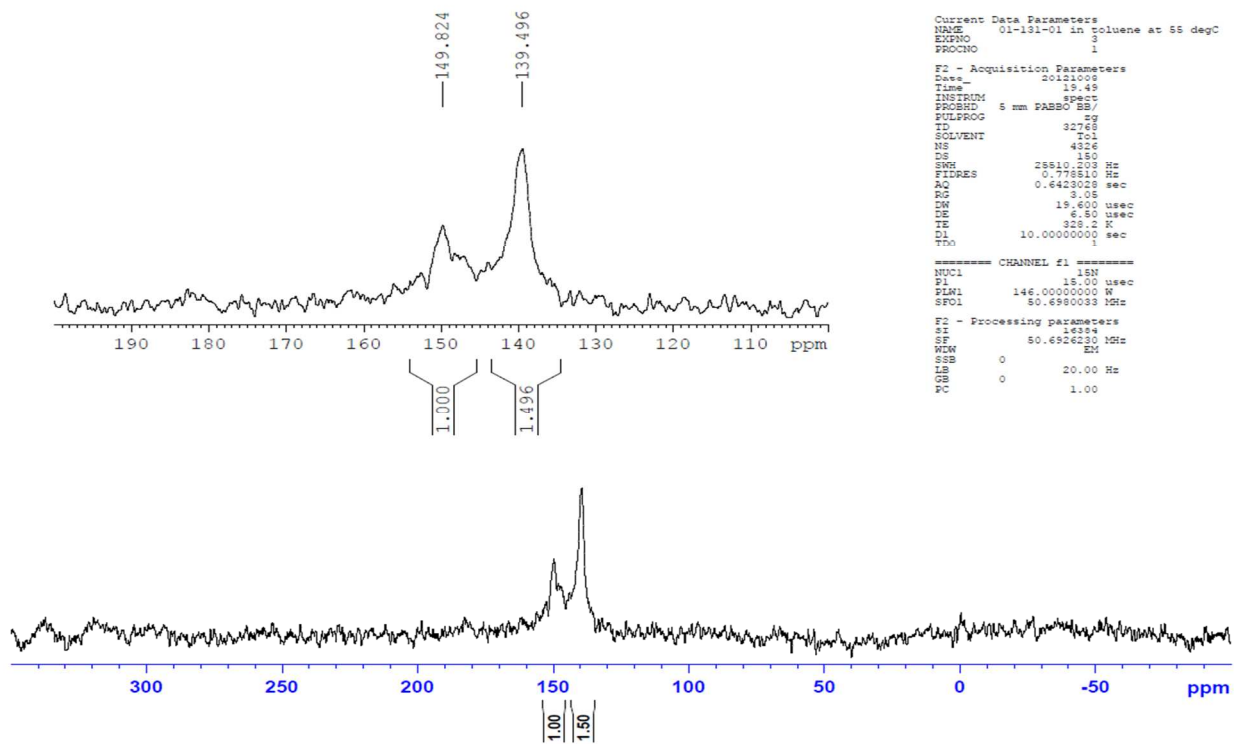


Figure S17. The VT-<sup>15</sup>N NMR spectra of Poly-3 in toluene-*d*<sub>8</sub> at 55 °C

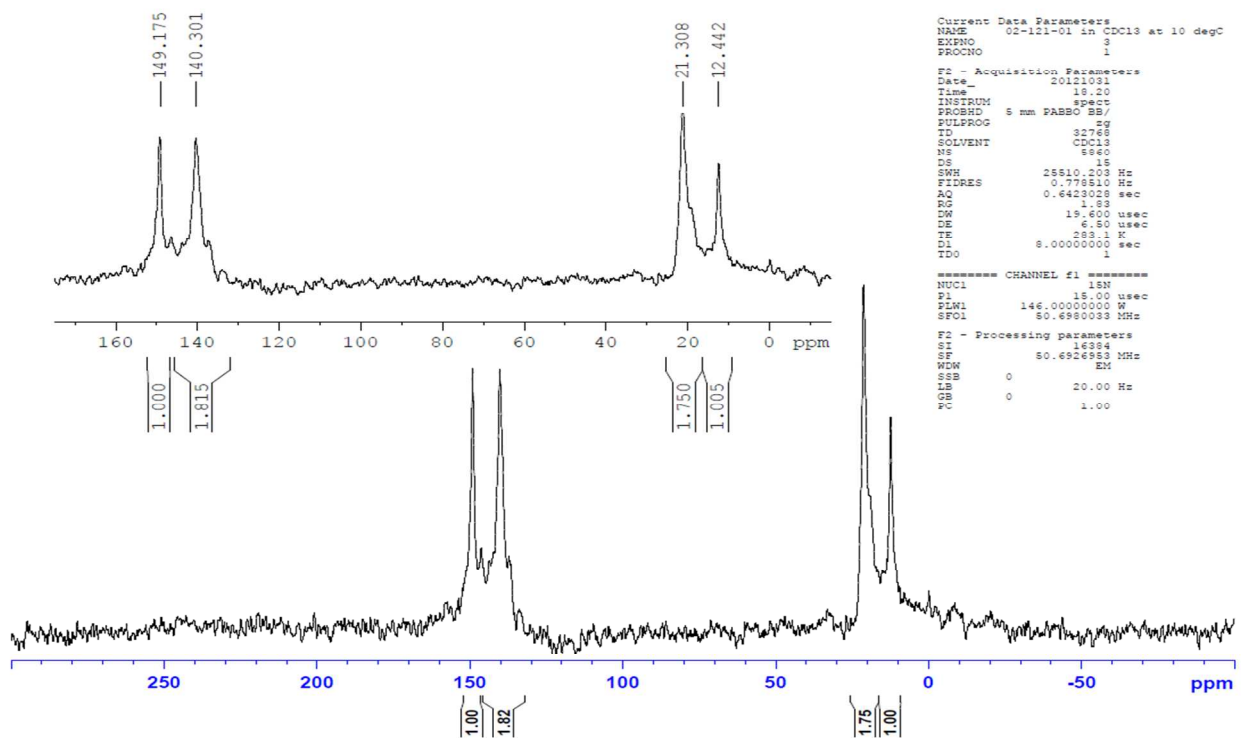


Figure S18. The VT-<sup>15</sup>N NMR spectra of Poly-5 in CDCl<sub>3</sub> at 10 °C

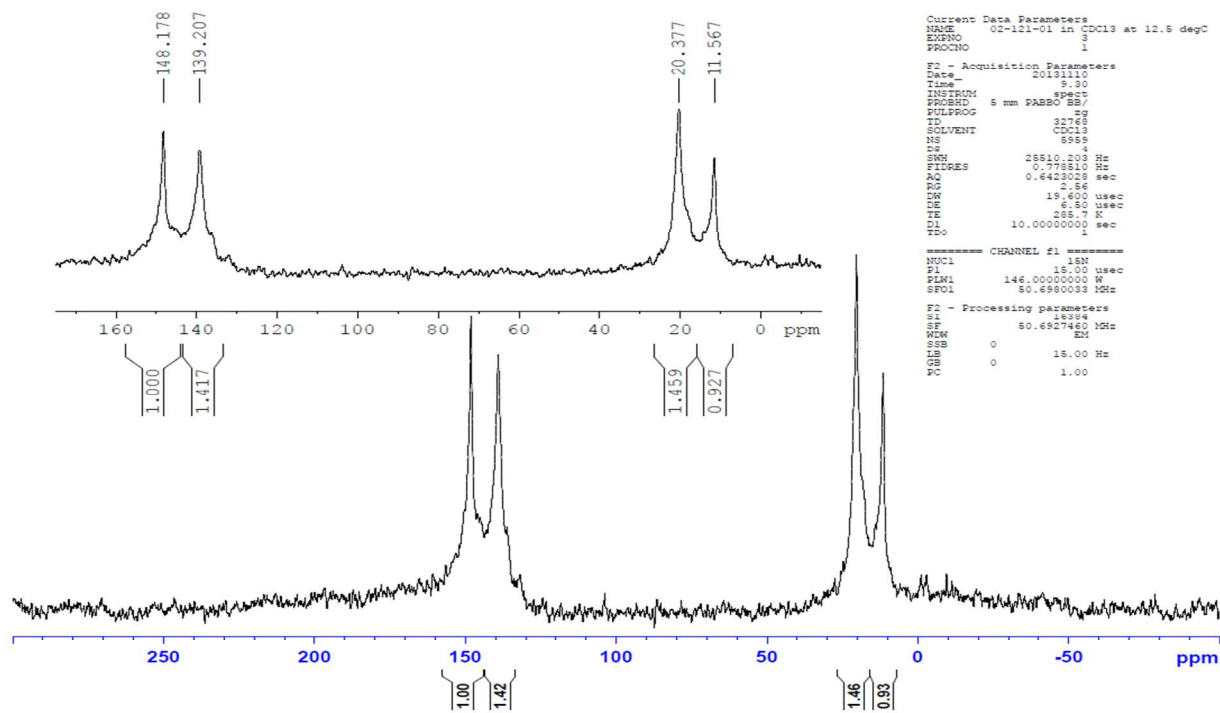


Figure S19. The VT-<sup>15</sup>N NMR spectra of **Poly-5** in CDCl<sub>3</sub> at 12.5 °C

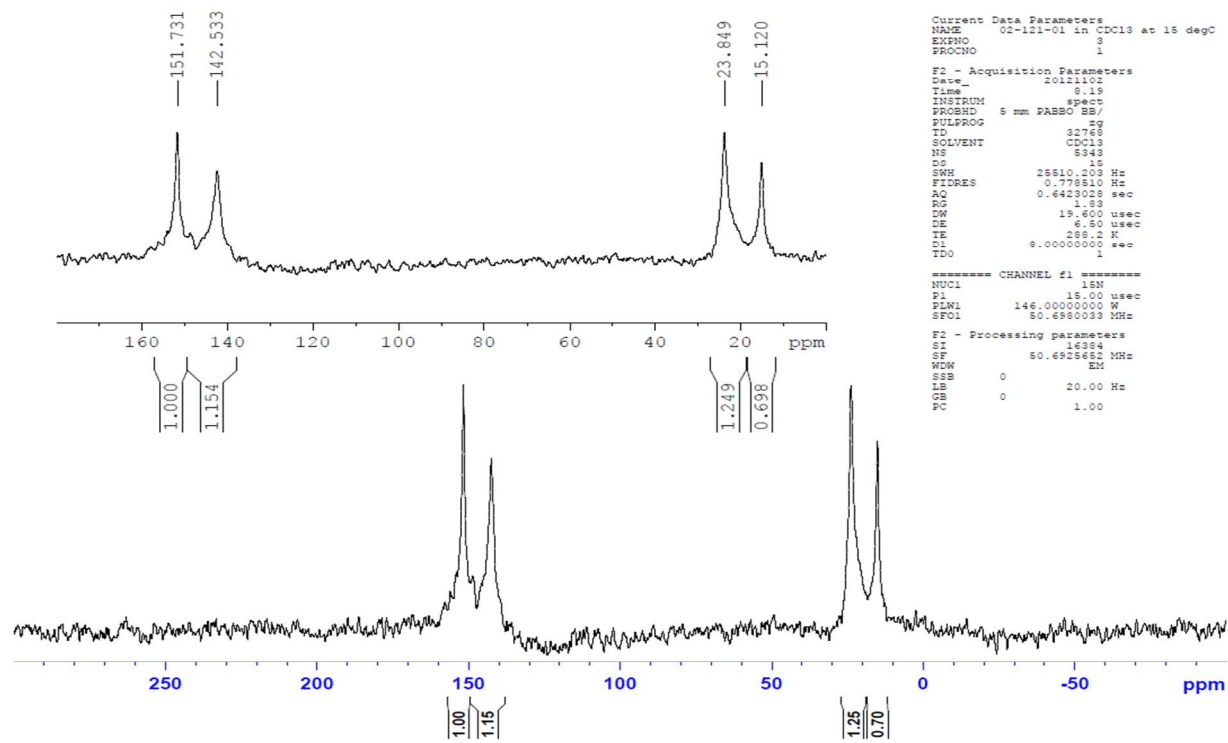


Figure S20. The VT-<sup>15</sup>N NMR spectra of **Poly-5** in CDCl<sub>3</sub> at 15 °C

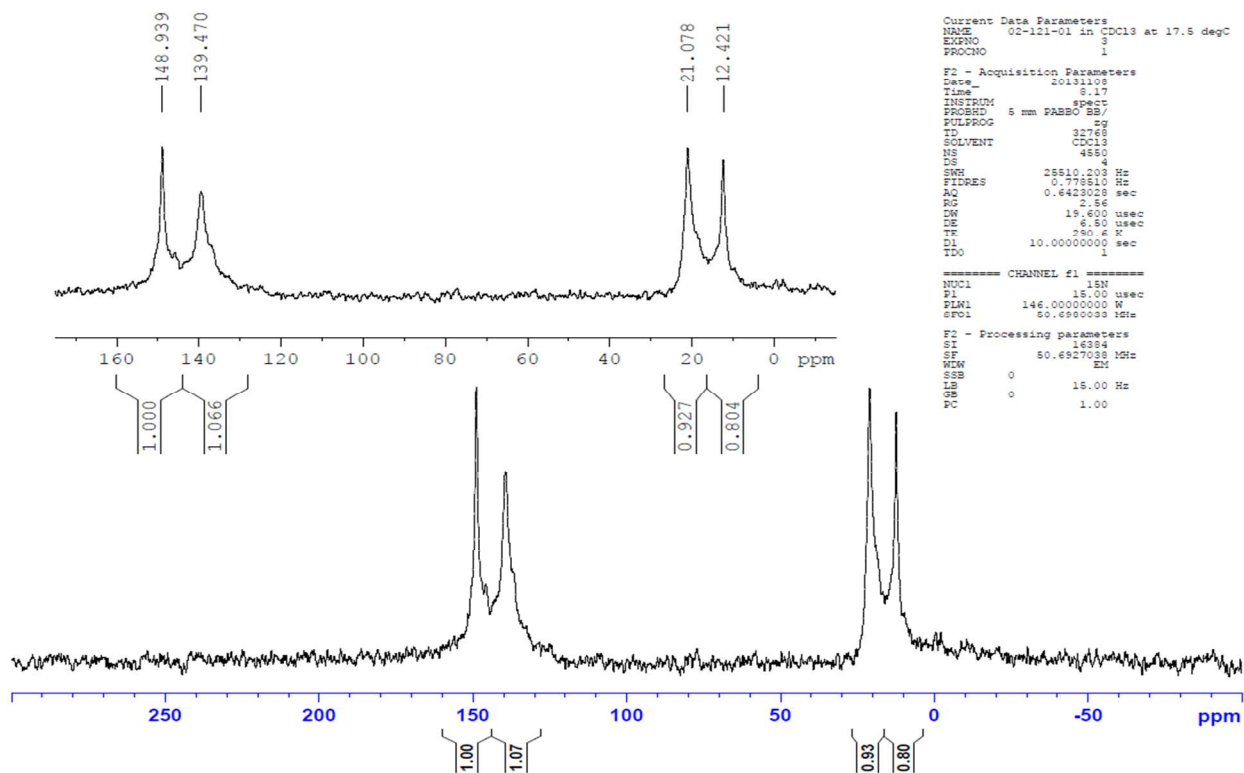


Figure S21. The VT-<sup>15</sup>N NMR spectra of Poly-5 in CDCl<sub>3</sub> at 17.5 °C

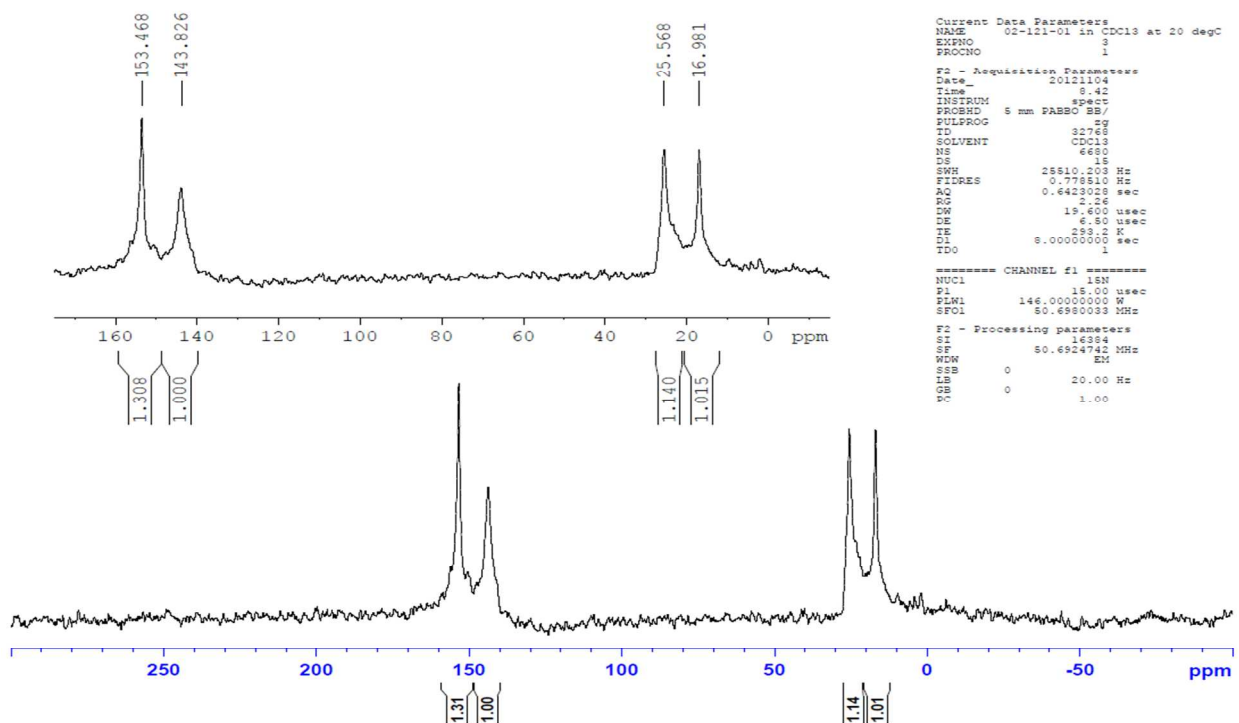


Figure S22. The VT-<sup>15</sup>N NMR spectra of Poly-5 in CDCl<sub>3</sub> at 20 °C

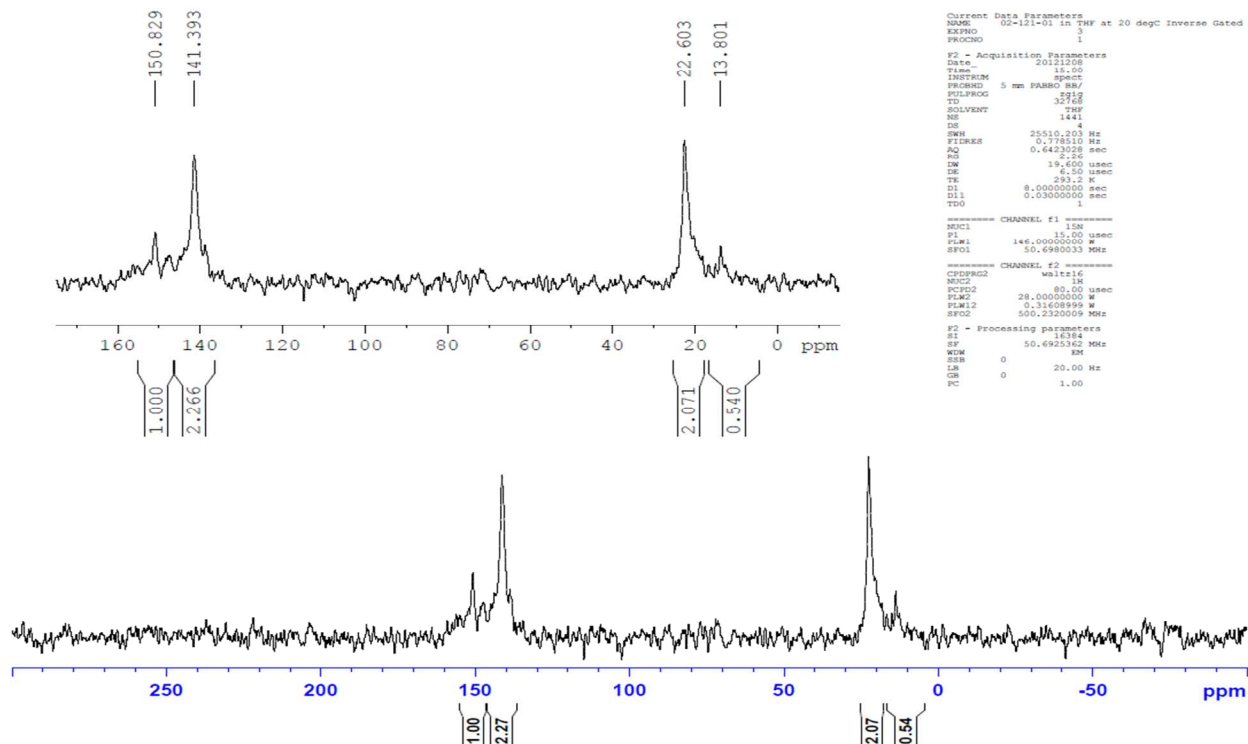


Figure S23. The VT-<sup>15</sup>N NMR spectra of **Poly-5** in THF-*d*<sub>8</sub> at 20 °C

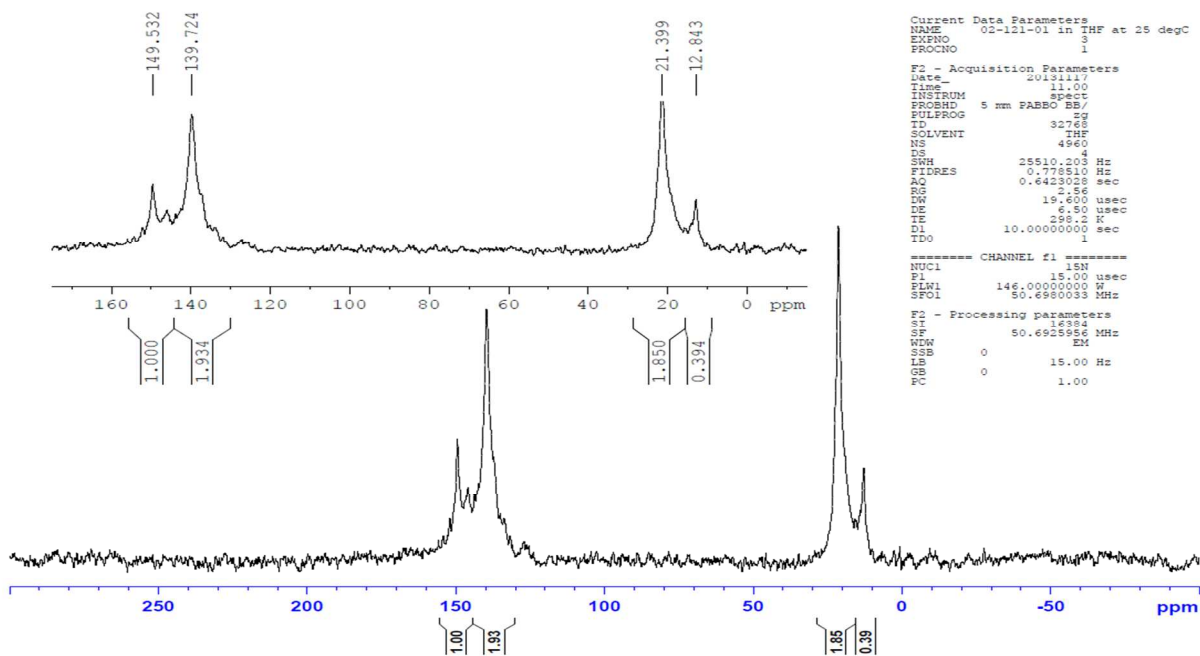


Figure S24. The VT-<sup>15</sup>N NMR spectra of **Poly-5** in THF-*d*<sub>8</sub> at 25 °C

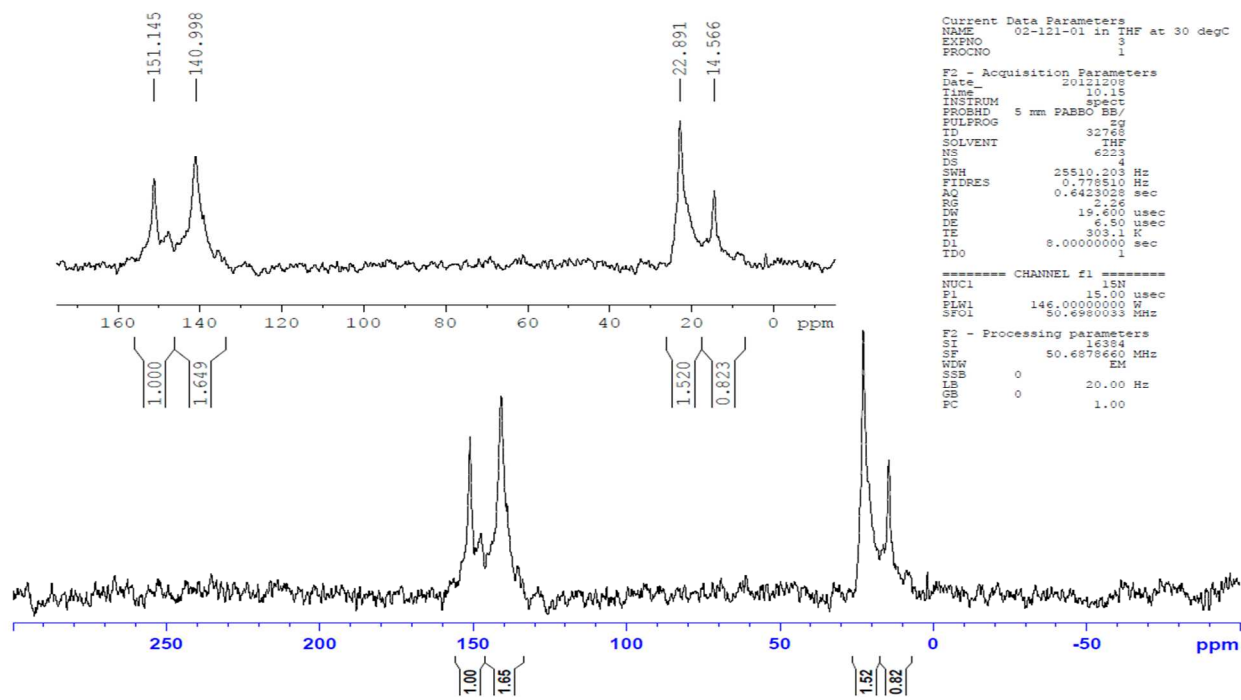


Figure S25. The VT-<sup>15</sup>N NMR spectra of **Poly-5** in THF-*d*<sub>8</sub> at 30 °C

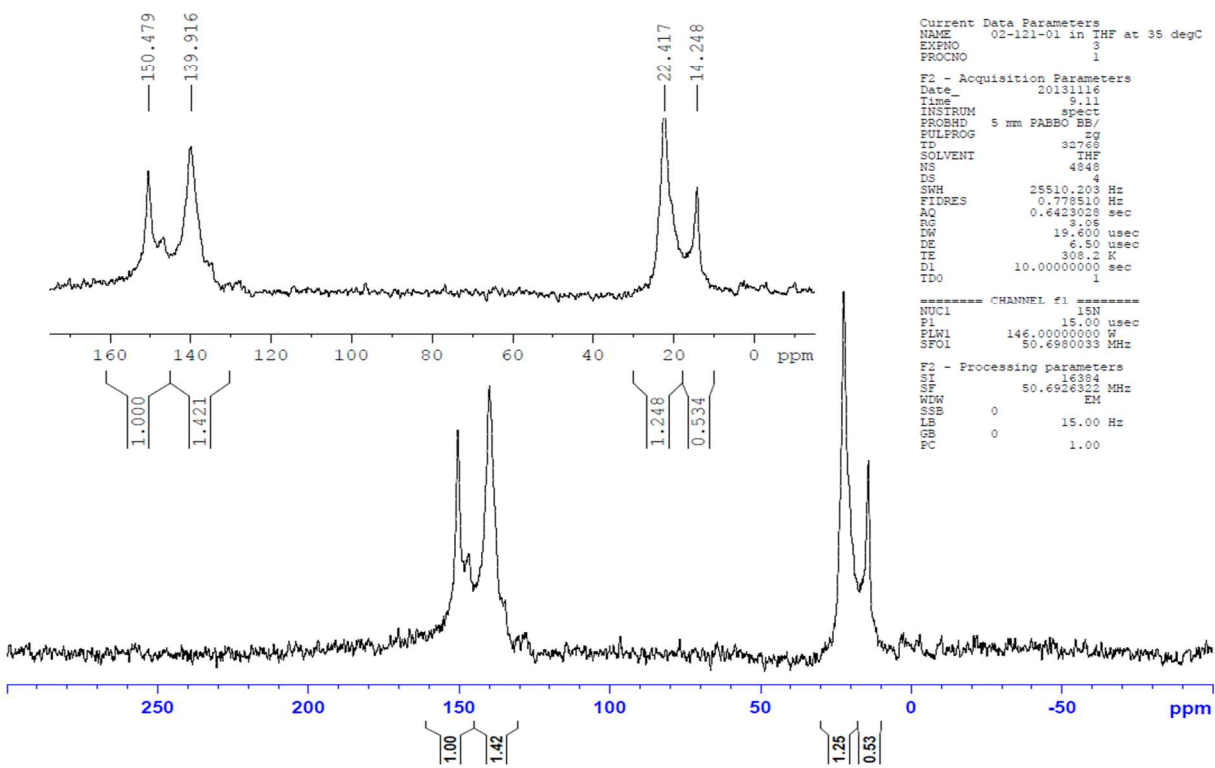


Figure S26. The VT-<sup>15</sup>N NMR spectra of **Poly-5** in THF-*d*<sub>8</sub> at 35 °C

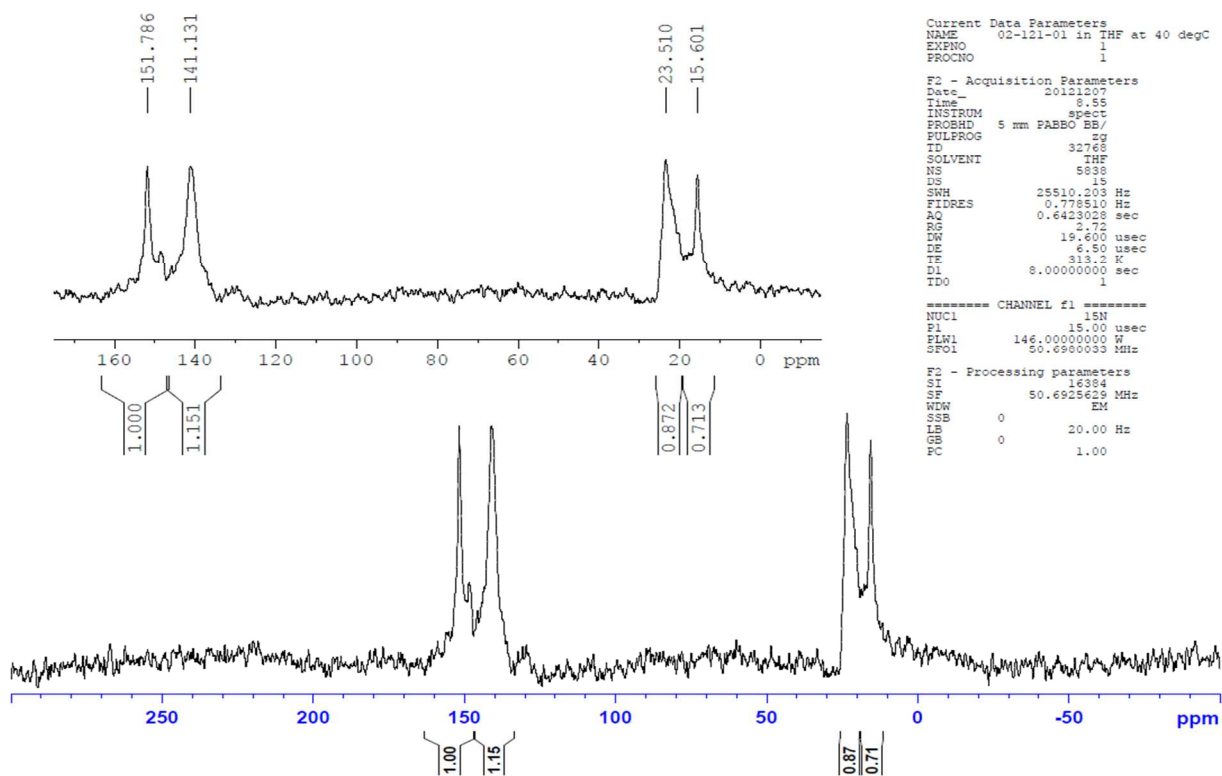


Figure S27. The VT-<sup>15</sup>N NMR spectra of Poly-5 in THF-*d*<sub>8</sub> at 40 °C

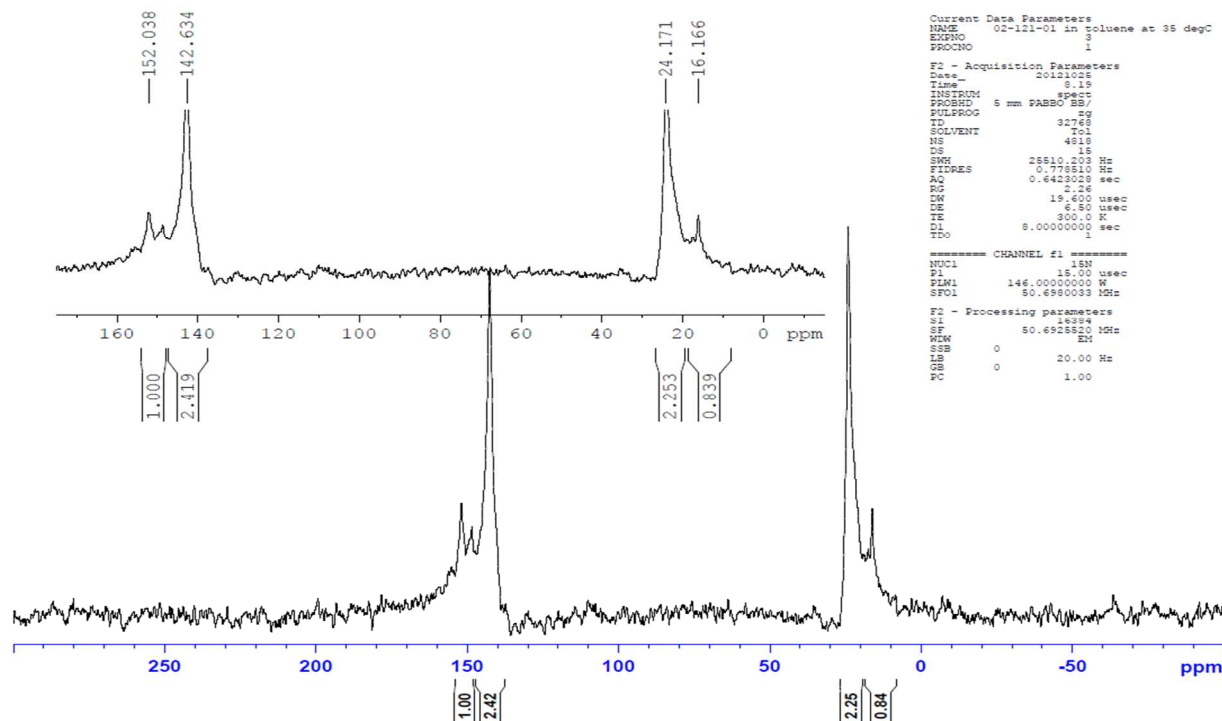


Figure S28. The VT-<sup>15</sup>N NMR spectra of Poly-5 in toluene-*d*<sub>8</sub> at 35 °C

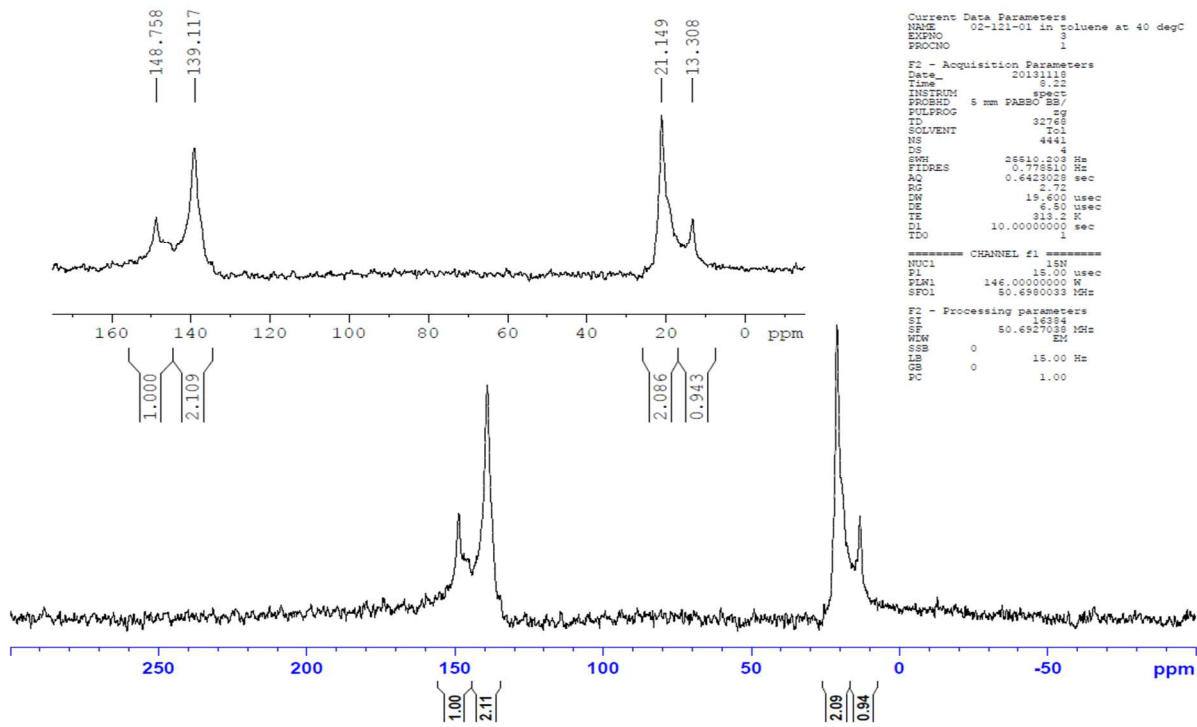


Figure S29. The VT-<sup>15</sup>N NMR spectra of Poly-5 in toluene-*d*<sub>8</sub> at 40 °C

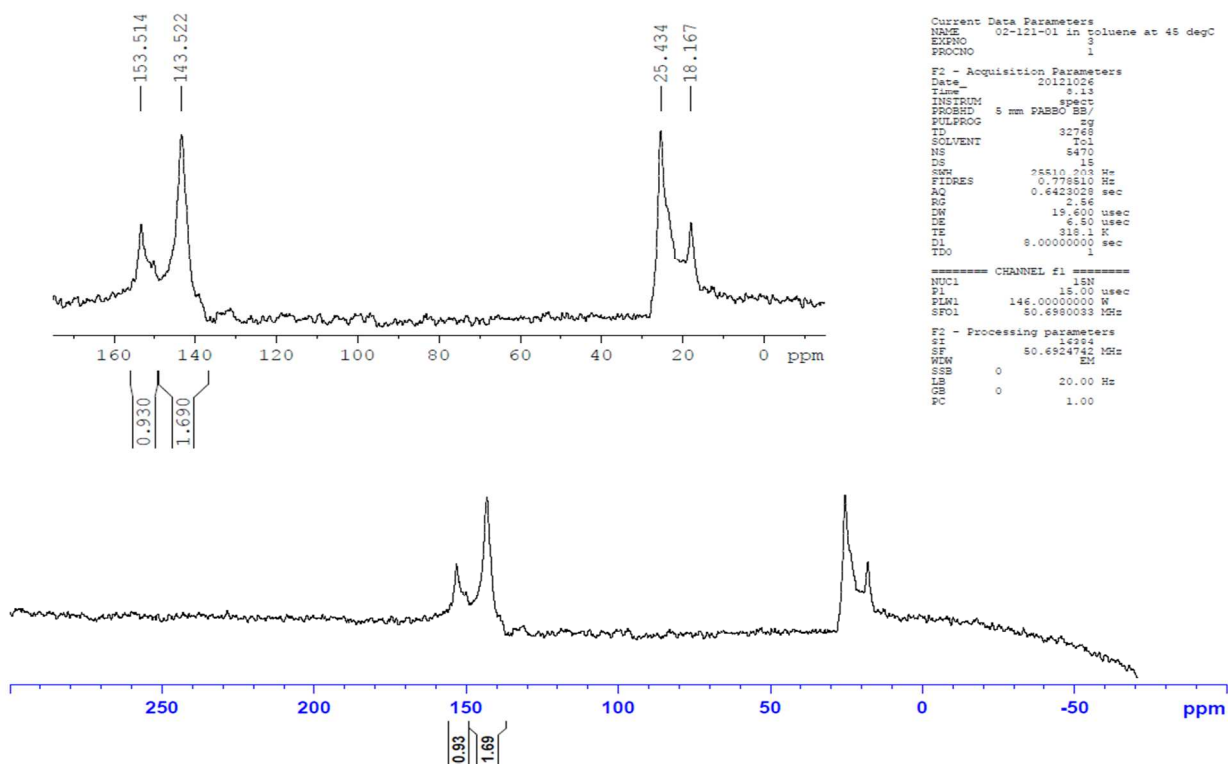


Figure S30. The VT-<sup>15</sup>N NMR spectra of Poly-5 in toluene-*d*<sub>8</sub> at 45 °C

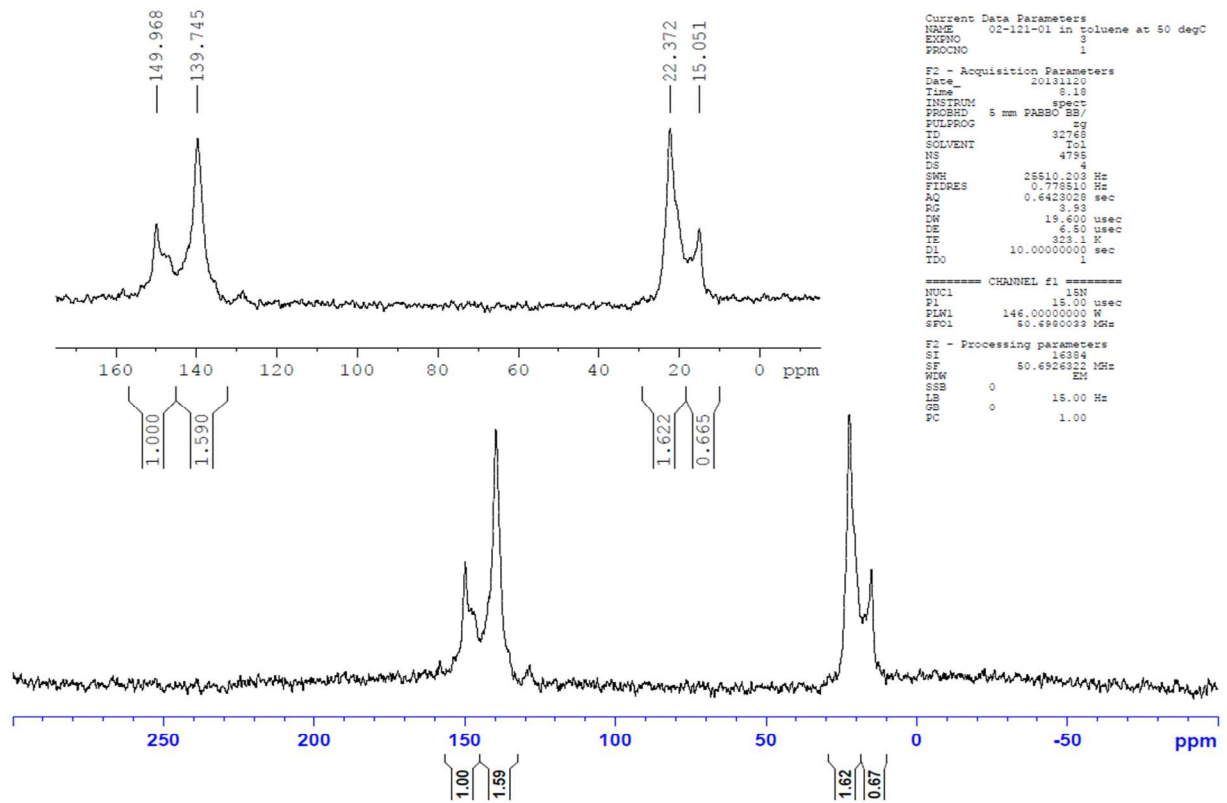


Figure S31. The VT-<sup>15</sup>N NMR spectra of Poly-5 in toluene-*d*<sub>8</sub> at 50 °C

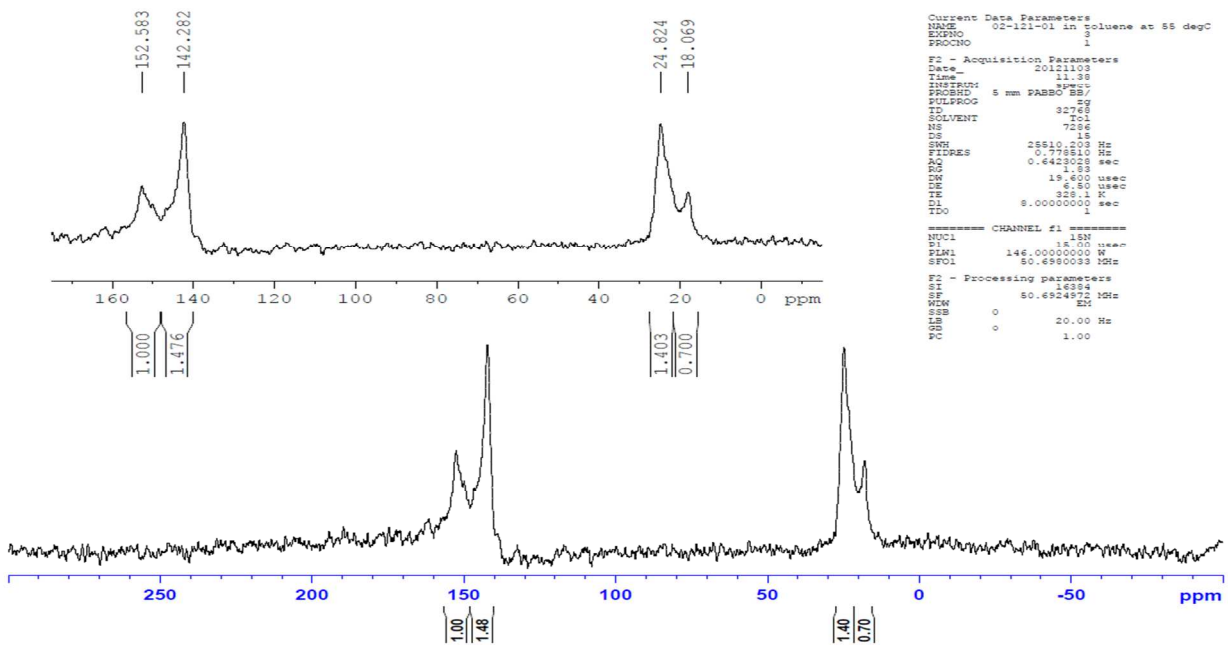
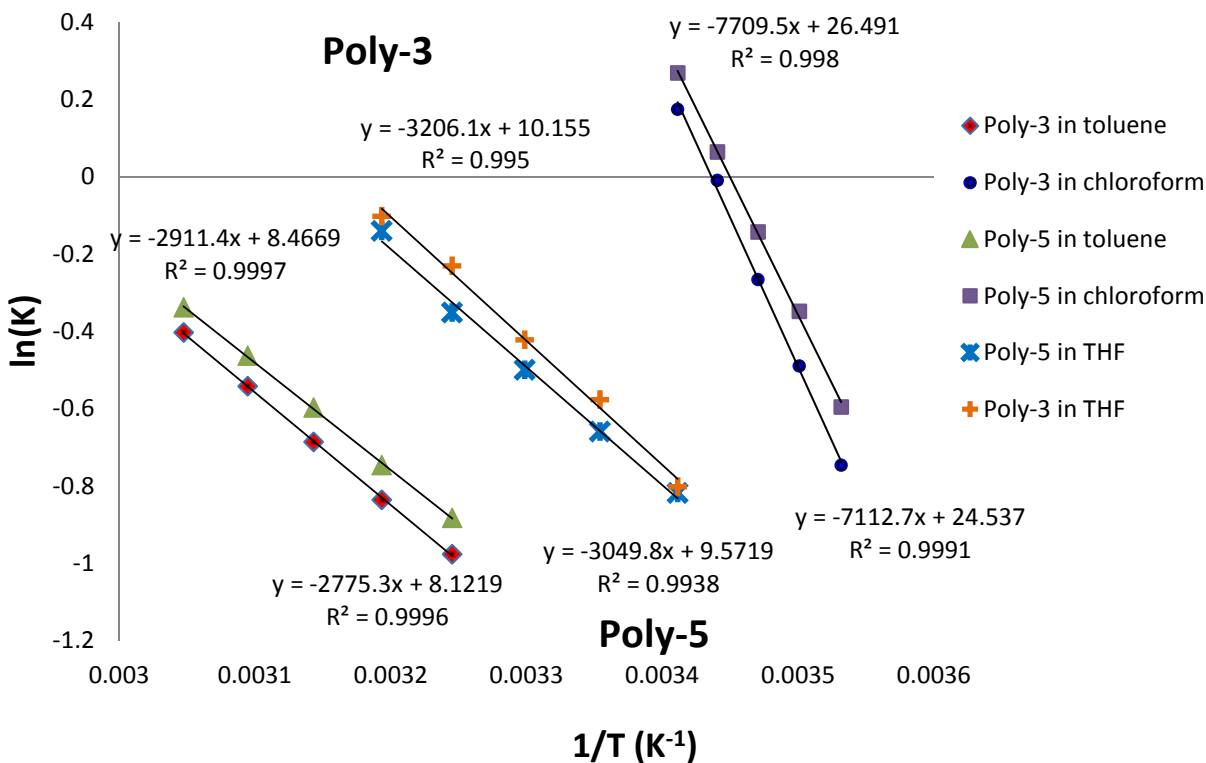


Figure S32. The VT-<sup>15</sup>N NMR spectra of Poly-5 in toluene-*d*<sub>8</sub> at 55 °C



**Figure S33.** Raw van't Hoff data with  $R^2$  values and equations for the trendlines used to calculate enthalpies and entropies of switching

Estimated error values- Maximum Errors associated with each data point were calculated using the errors of integration estimated using the relationship between errors and signal-to-noise in the equation reported by Malz et al.<sup>6</sup> These error values were then extrapolated to the energies values reported in the main text. These errors are believed to be a good estimation of the maximum deviations for each van't Hoff energy value calculated.

## VI. References

- (1) Tian, G.; Lu, Y.; Novak, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4082.
- (2) Reuther, J. F.; D., D. J.; Novak, B. M. *Macromolecules* **2012**, *45*, 7719.
- (3) Kai, H.; Morioka, Y.; Koriyama, Y.; Okamoto, K.; Hasegawa, Y.; Hattori, M.; Koike, K.; Chiba, H.; Shinohara, S.; Iwamoto, Y.; Takahashi, K.; Tanimoto, N. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 6444.
- (4) Wood, G. W. *J. Chem. Soc.* **1953**, 3327.
- (5) DeSousa, J. D.; Novak, B. M. *ACS Macro Lett.* **2012**, *1*, 672.
- (6) Malz, F.; Jancke, H. *J. Pharm. Biomed. Anal.* **2005**, *38*, 813.

