Supporting Information

pH-sensitive C—ON bond homolysis of alkoxyamines of imidazoline series with multiple ionizable groups as an approach for control of nitroxide mediated polymerization.

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Table 1SI. ^{1}H NMR data of alkoxyamine **4** in D_2O at different pH, δ 200 MHz, ppm.

	pH	Me_2C-O and Me_2C-N, 4*3H, s	Et-CH_2, ABq J_{AB} 14 Hz, J_q 7 Hz	Et-CH_3, t J 7 Hz	NMe_2, 6H s	Py, AA'BB'	Content, %
4A	9.6	1.15, 1,33, 1.41, 1.51	1.67, 2.34	0.88	3.04	7.55, 8.44	75
4B	9.6	0.75, 1.05, 1.41, 1.59	1.86, 2.60	0.89	3.01	7.55, 8.44	25
4A	6.3	1.35 (6H), 1.54, 1,58	1.79, 2.55	1.00	3.34	7.62, 8.50	55
4B	6.3	0.79, 1.08, 1,54, 1.75	2.10, 2.76	0.94	3.27br	7.62, 8.50	45
4A	3.0	1.36, 1.46, 1,58, 1.65	1.89, 2.78	1.06	3.38	8.20, 8.85	60
4B	3.0	1.03, 1.22, 1.65, 1.78	2.30, 2.62	1.04	3.28	8.20, 8.85	40

Table 2SI. Experimental conditions and characteristics of the polymers obtained for the polymerization of styrene at 140 ^oC initiated by alkoxyamine **4** in different forms.

Entry	Initiator	Monomer	M:I	Conditions	Conversion %	PDI	M_n^a 10^{-5} g/mol	$M_{n,th}$ 10^{-5} g/mol
1	4	Sty	1000/1	Pure	74	1.29	0.42	0.76
2	4	Sty	1000/1	1 eq. of CF_3COOH	61	1.35	0.52	0.67
3	4	Sty	1000/1	10 eq. of CF_3COOH	60	1.57	0.7	0.63

^{a} Relative to P-Sty standards.

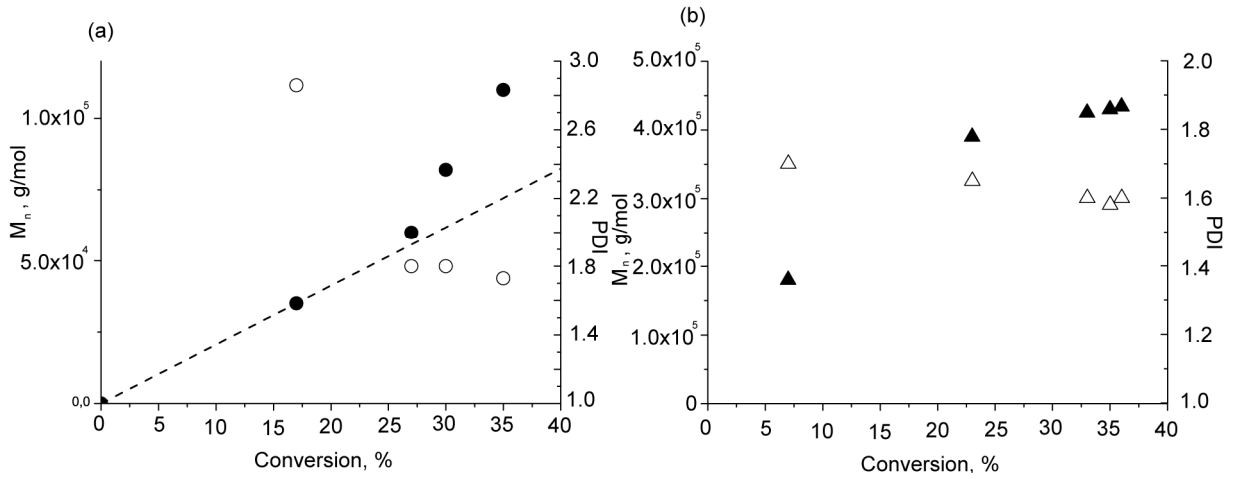

Figure 1 SI. Evolution of molecular weight (●, ▲, left axis) and polydispersity (○, Δ, right axis) during polymerization of (a) 4-vinylbenzenesulfonate initiated by alkoxyamine **5** at pH=6.3 (●,○),the monomer to initiator ratio is 1000/1; (b) 4-vinylbenzenesulfonate initiated by alkoxyamine **5** at pH=2.5 (▲, Δ), monomer to initiator ratio is 1000/1. Temperature of polymerization is 90 °C. Dashed line shows the theoretical M_n.

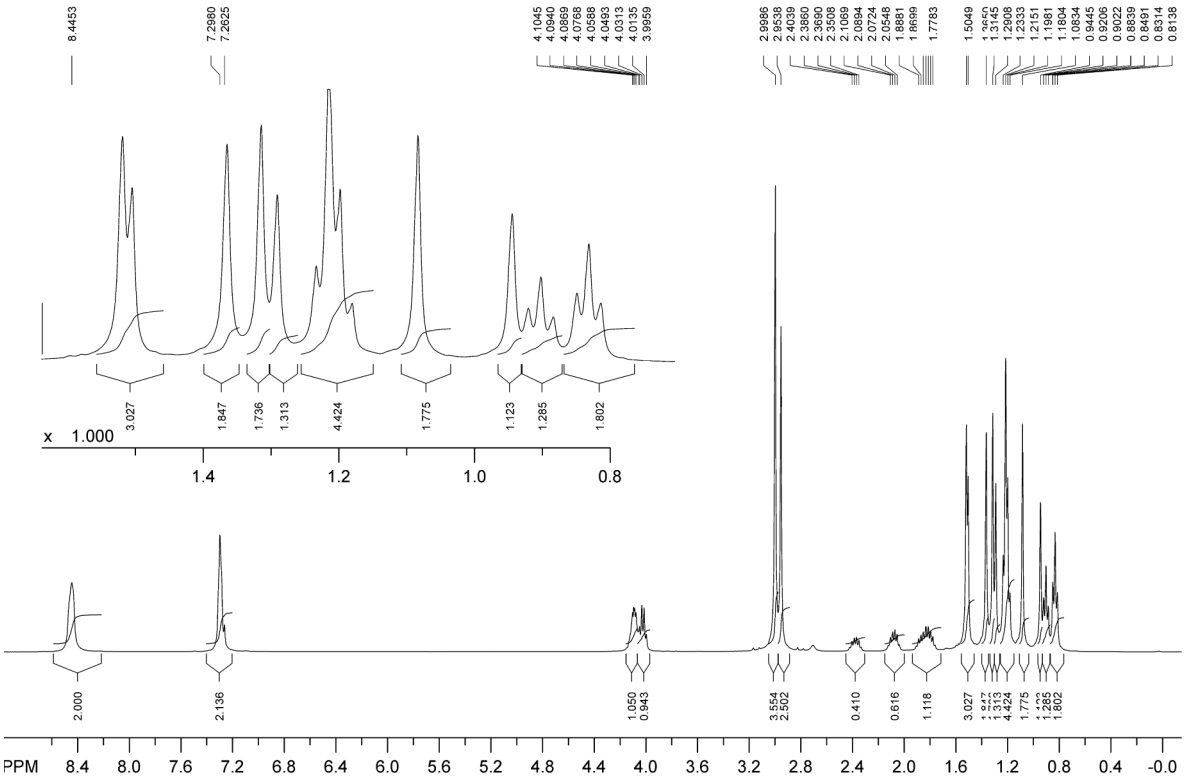

Figure 2 SI. ^{1}H NMR spectrum of alkoxyamine **3** recorded in $CDCl_3$.

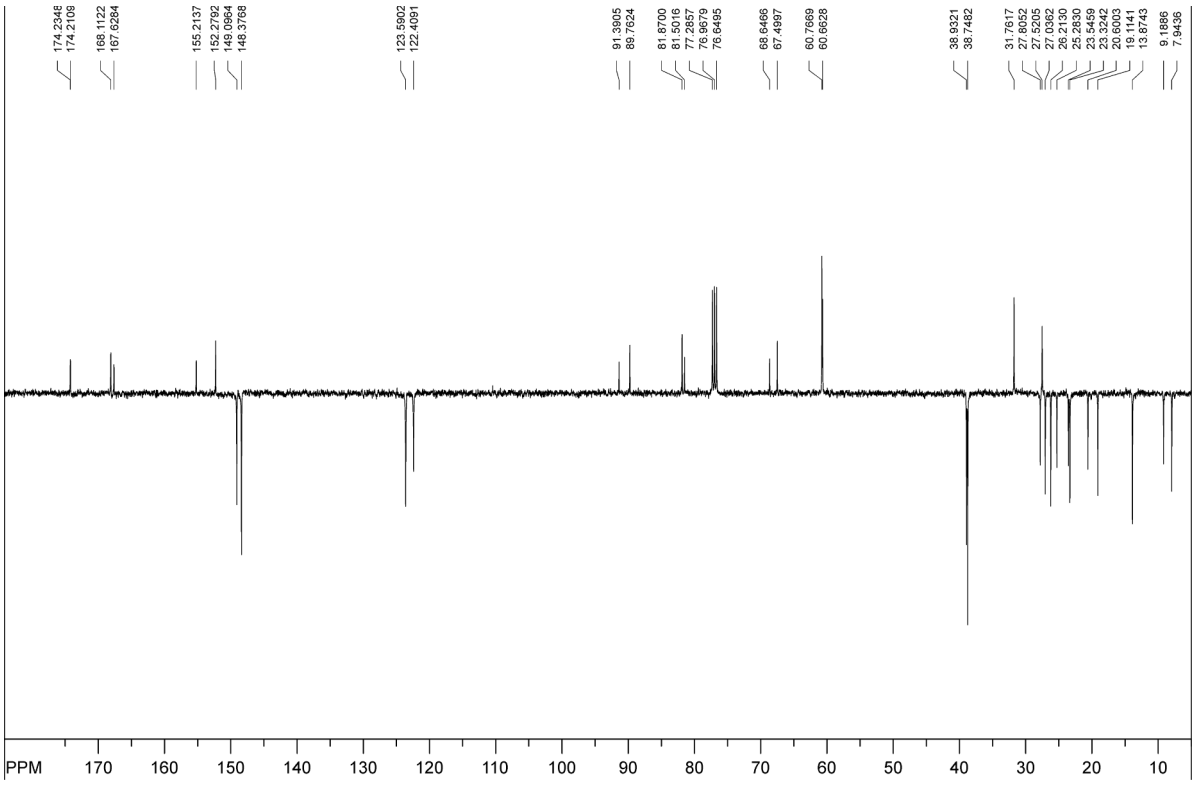

Figure 3 SI. ^{13}C NMR J-mod spectrum of alkoxyamine **3** recorded in $CDCl_3$.

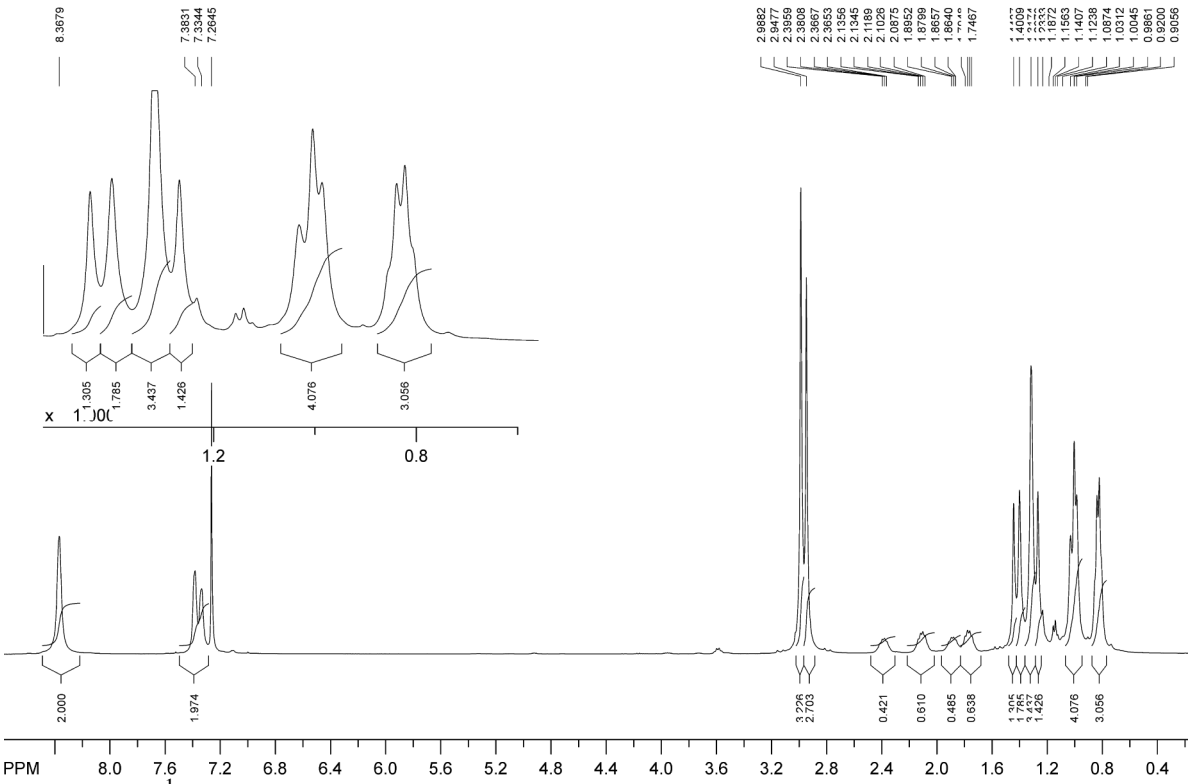

Figure 4 SI. ^{1}H NMR spectrum of alkoxyamine **4** recorded in $CDCl_3$.

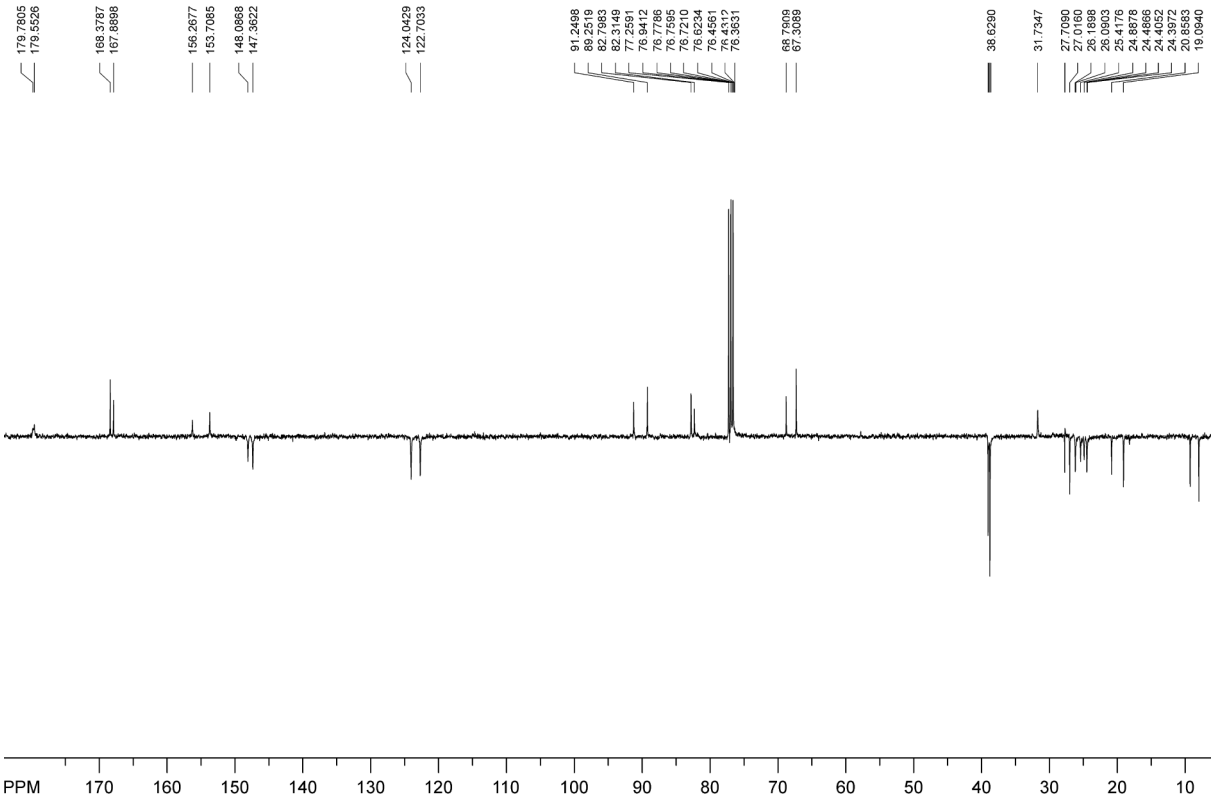

Figure 5 SI. ^{13}C NMR J-mod spectrum of alkoxyamine **4** recorded in $CDCl_3$.

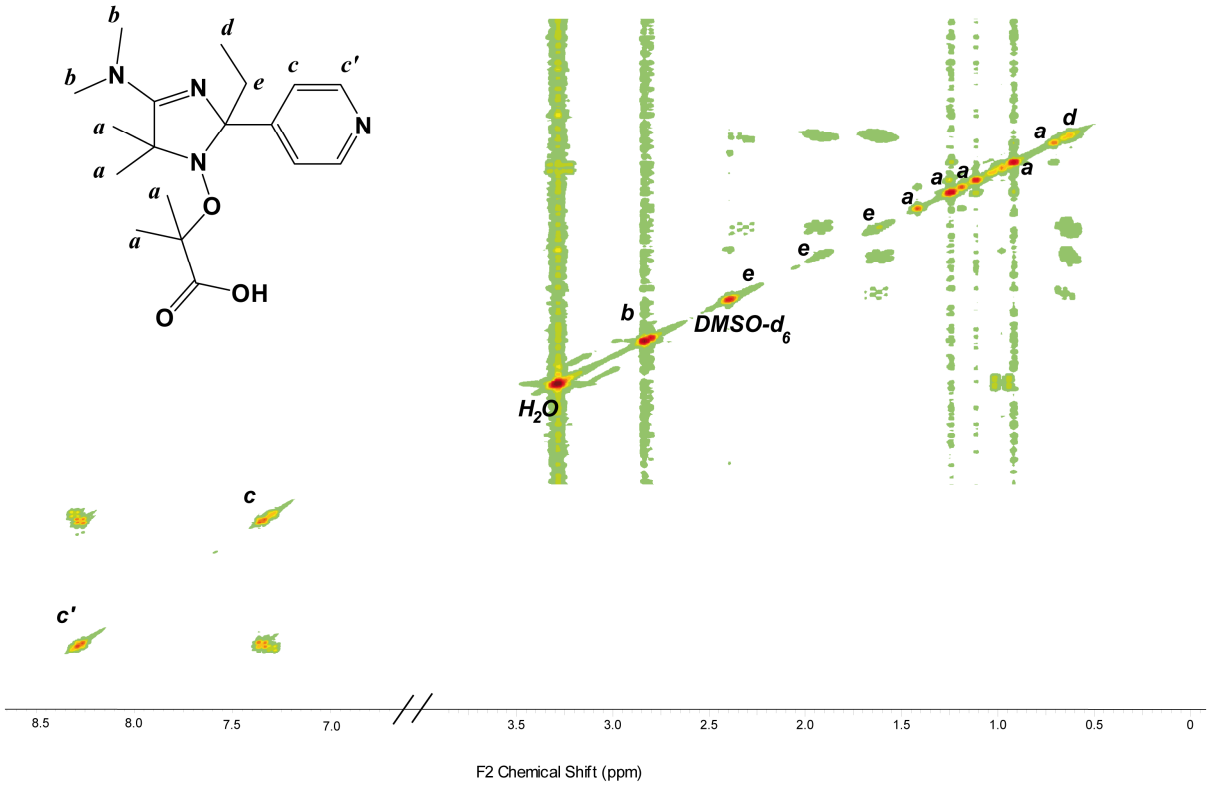

Figure 6 SI. COSY 45 NMR spectrum of alkoxyamine **4** recorded in D_2O.

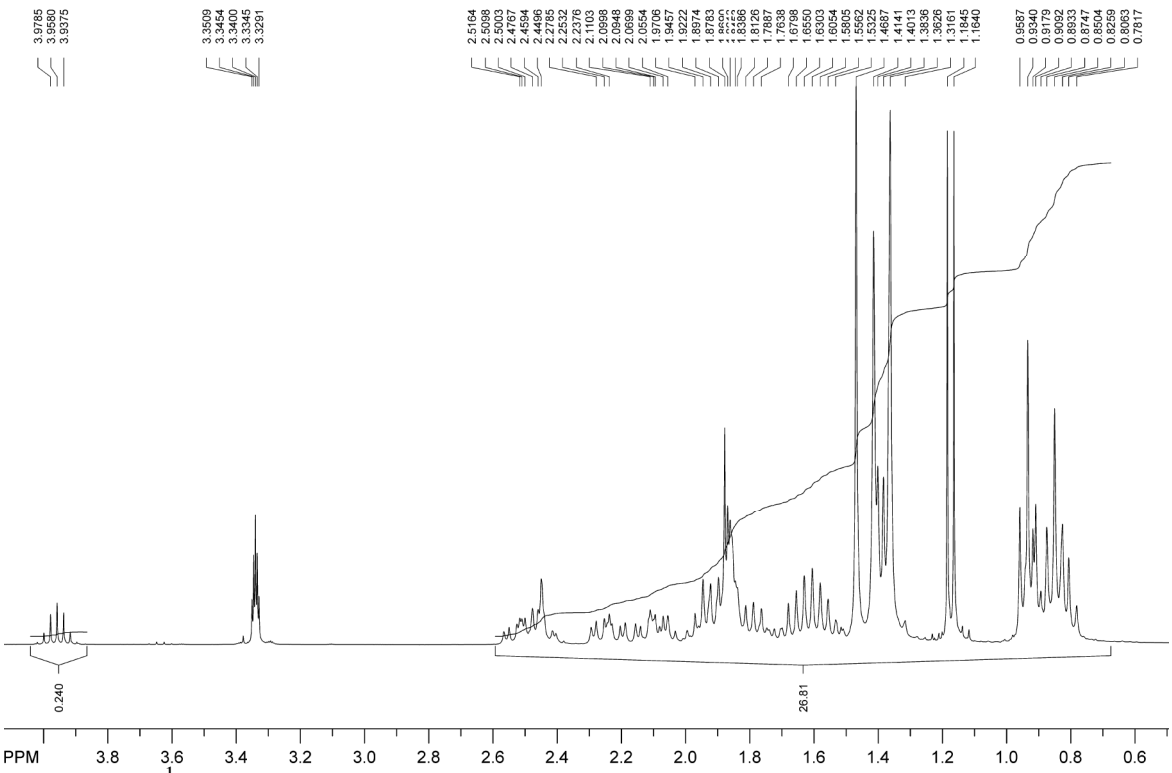

Figure 7 SI. ^{1}H NMR spectrum of alkoxyamine **5** recorded in $CDCl_3/CD_3OD$.

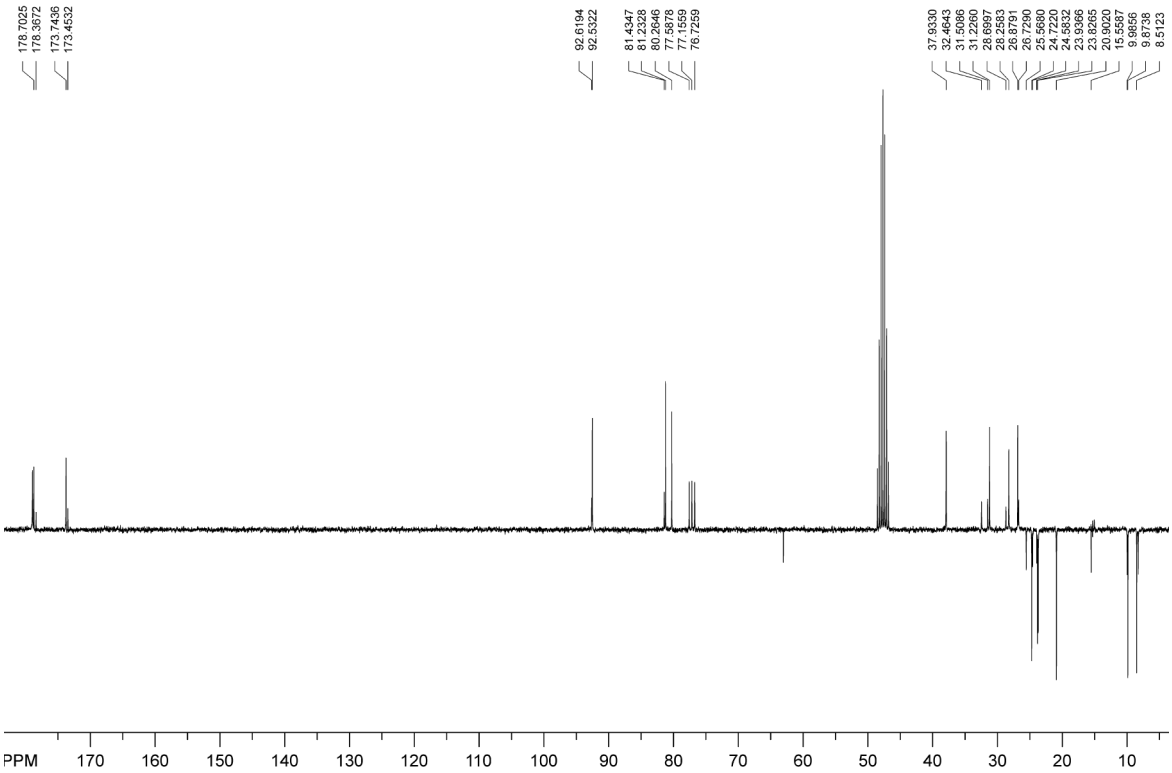

Figure 8 SI. ^{13}C NMR J-mod spectrum of alkoxyamine **5** recorded in $CDCl_3/CD_3OD$.

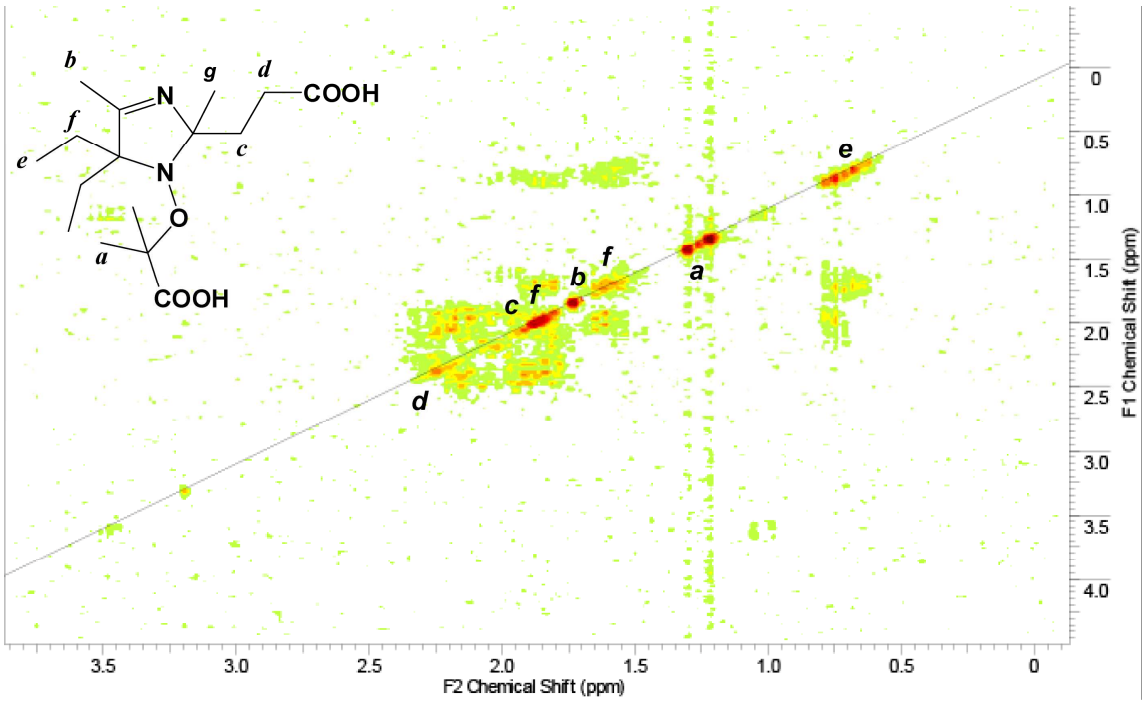

Figure 9 SI. COSY 45 NMR spectrum of alkoxyamine **5** recorded in D_2O.

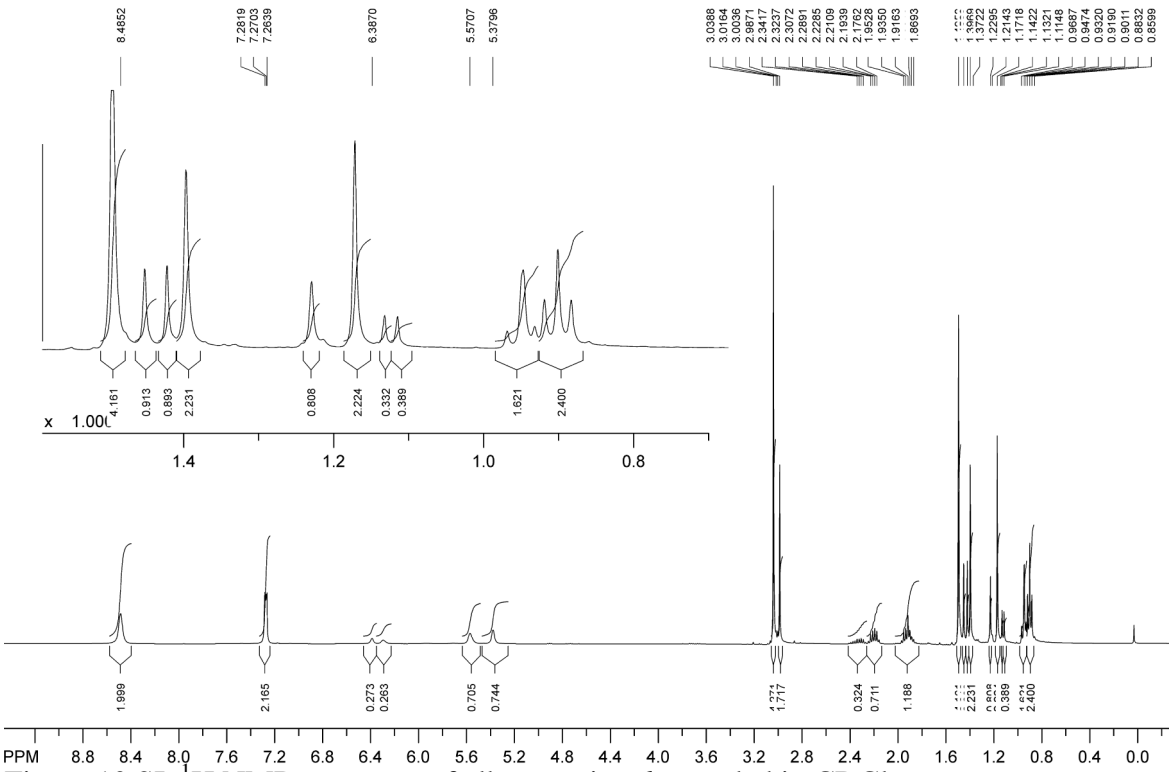

Figure 10 SI. ^{1}H NMR spectrum of alkoxyamine **6** recorded in $CDCl_3$.

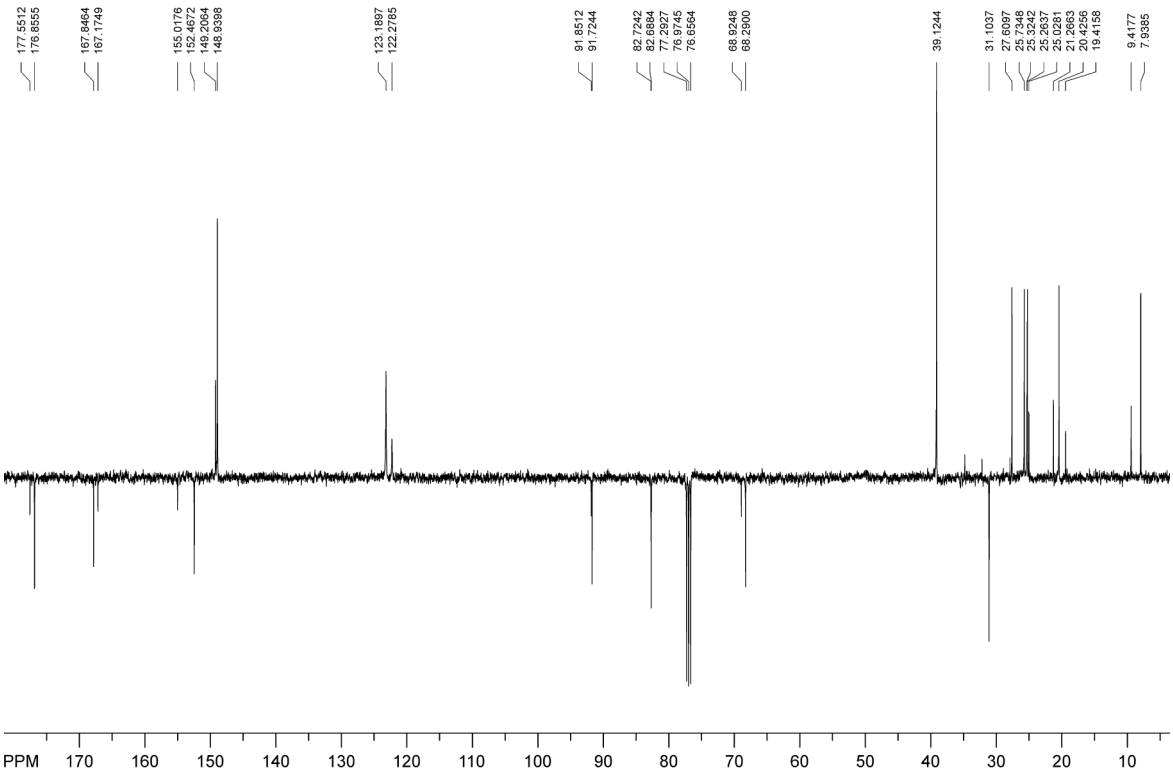

Figure 11 SI. ^{13}C NMR J-mod spectrum of alkoxyamine **6** recorded in $CDCl_3$.

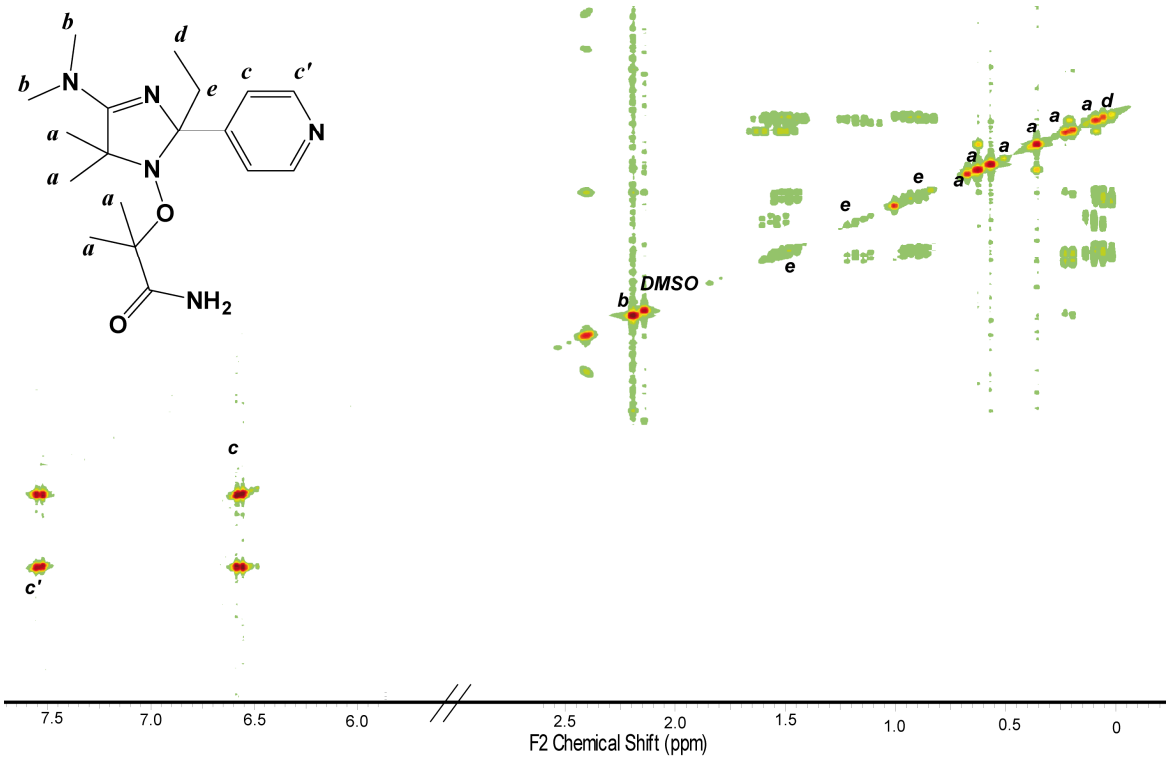

Figure 12 SI. COSY 45 NMR spectrum of alkoxyamine **6** recorded in DMSO-d_6.

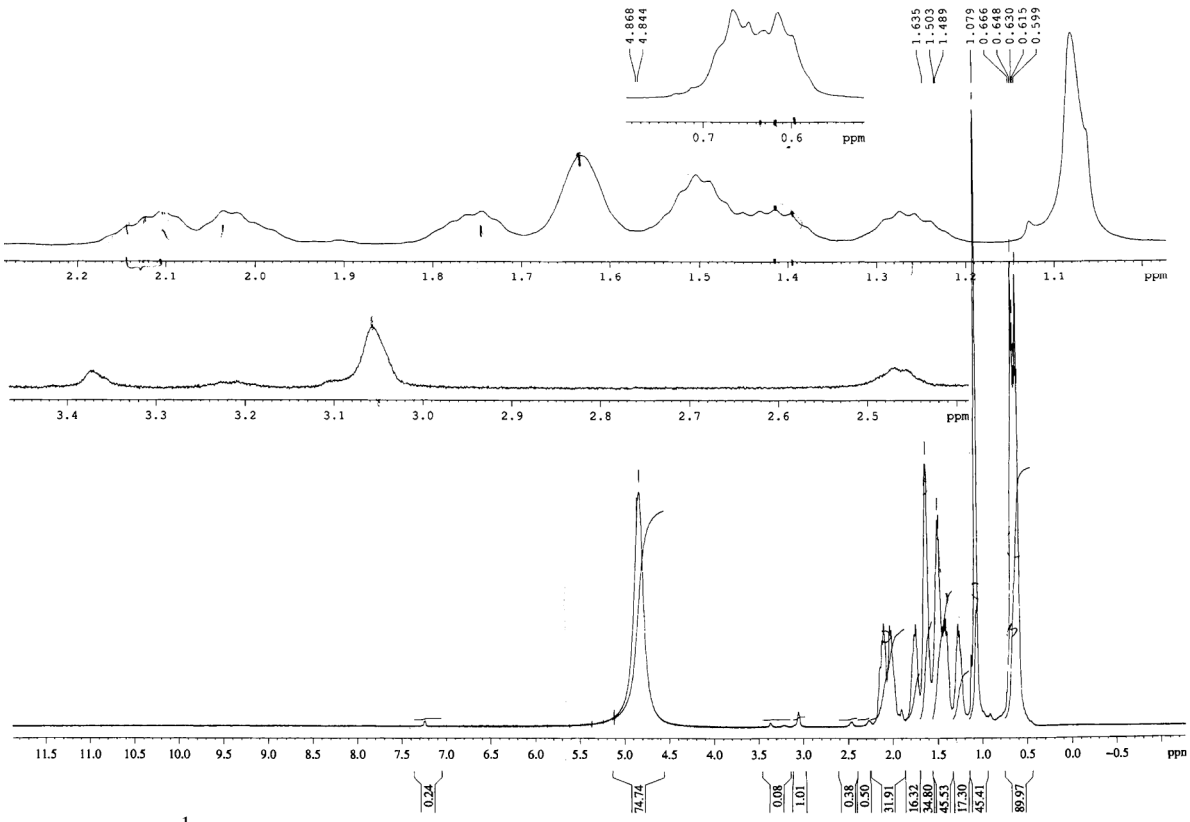

Figure 13 SI. ^{1}H NMR spectrum of hydroxylamine **7** recorded in $CDCl_3$.

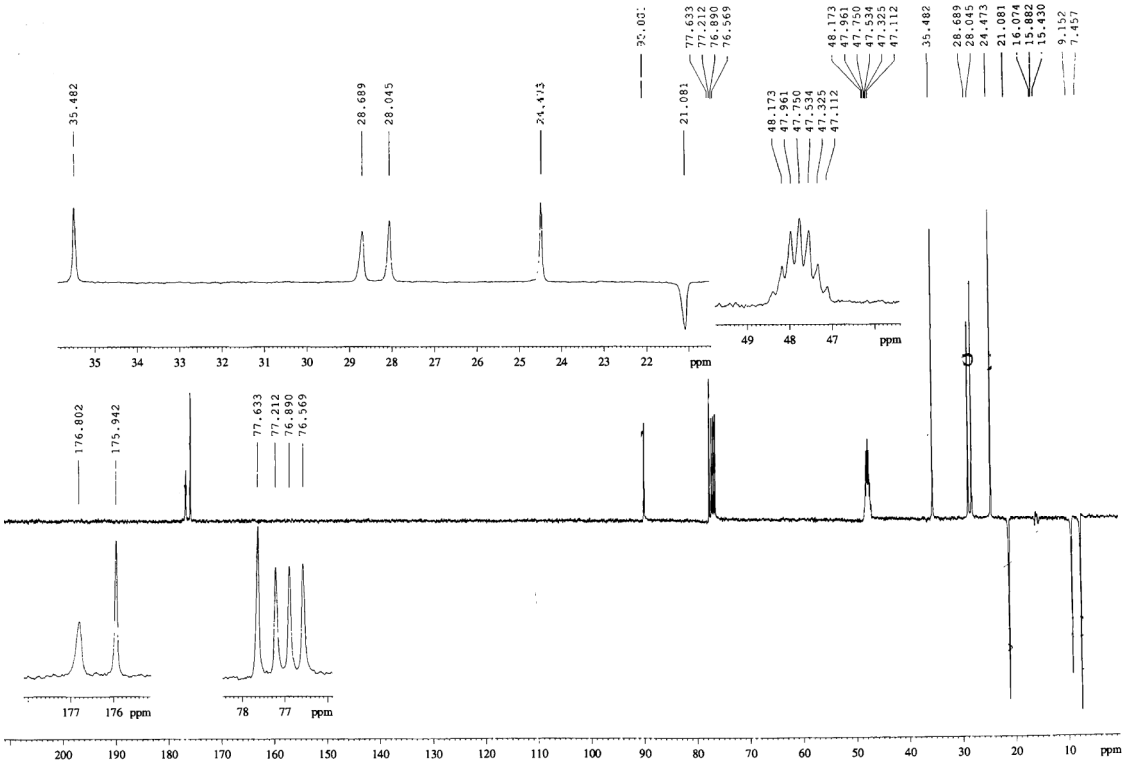

Figure 14 SI. ^{13}C NMR J-mod spectrum of hydroxylamine **7** recorded in $CDCl_3$.

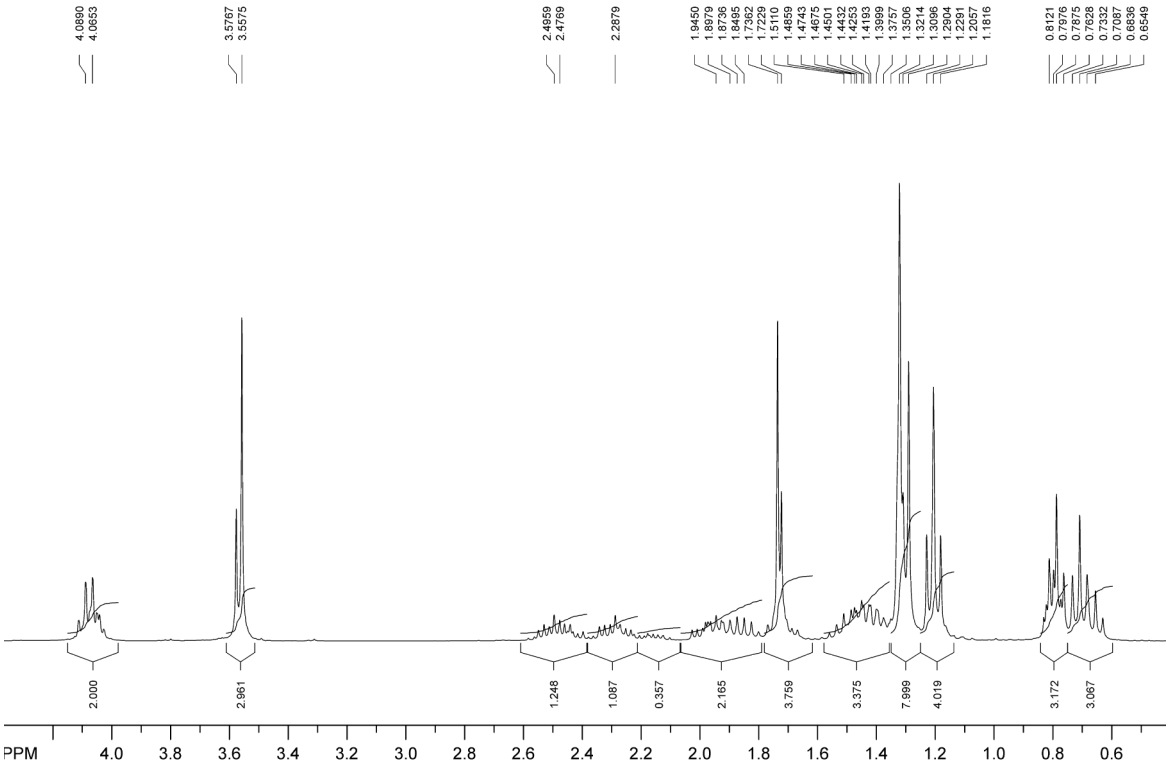

Figure 15 SI. ^{1}H NMR spectrum of alkoxyamine **9** recorded in $CDCl_3$.

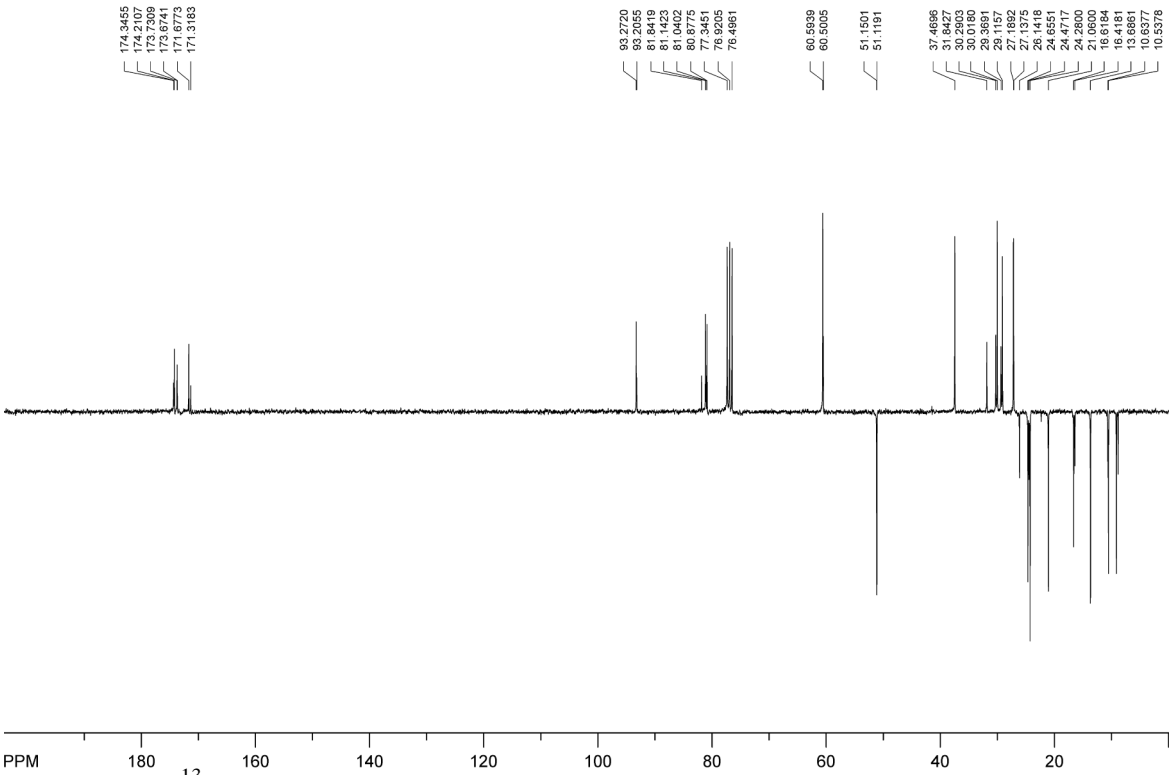

Figure 16 SI. ^{13}C NMR J-mod spectrum of alkoxyamine **9** recorded in $CDCl_3$.