Electronic Supplementary Material (ESI) for Dalton Transactions.

–Supporting Information for the manuscript entitled–

"Synthesis and Characterisation of Benzotriazole or Benzoxazole Phenoxide Ligands Supported Nb and Ta Metal Complexes and their Application for the Synthesis of Hyperbranched Polyglycerols by Ring-Opening Polymerisation of Glycidol"

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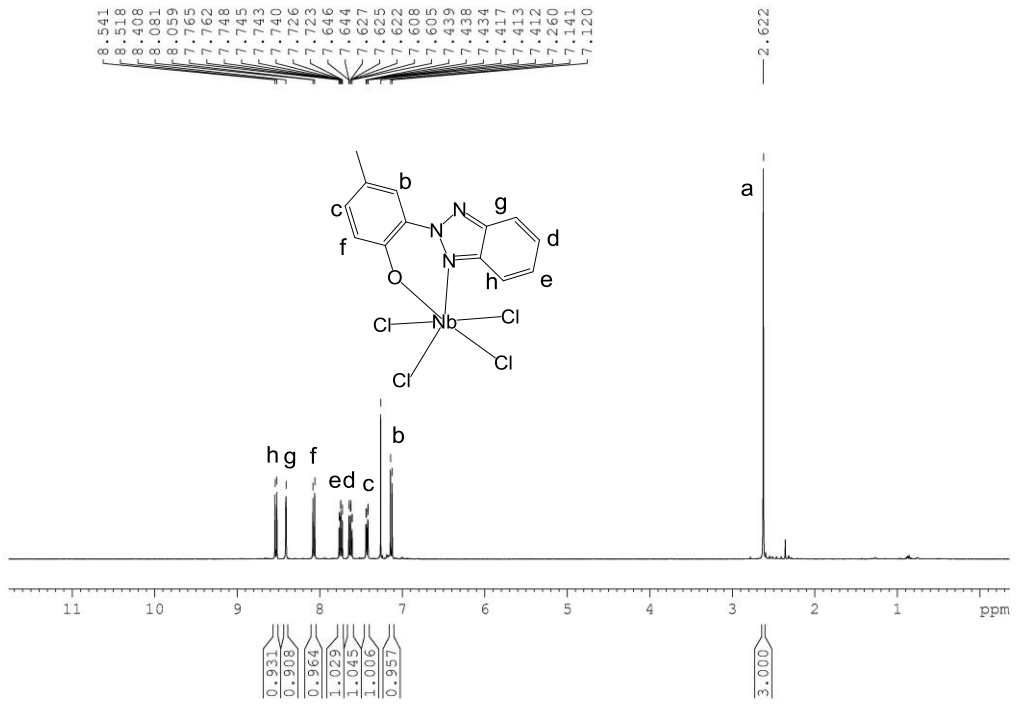

Fig. S1 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **1a**.

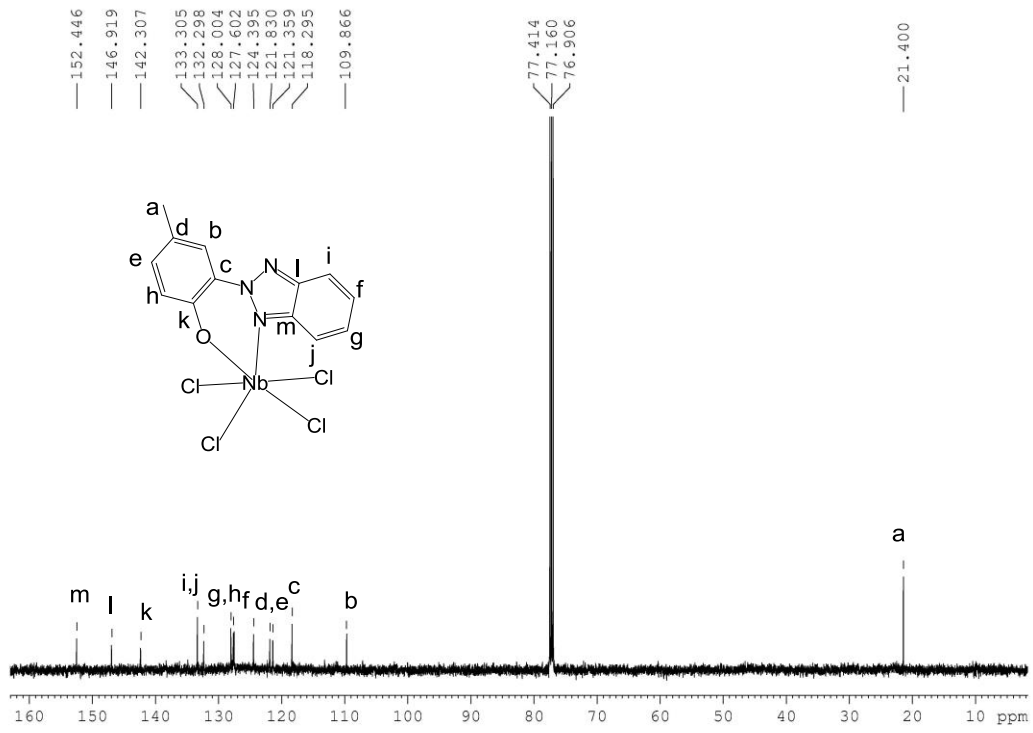

Fig. S2 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **1a**.

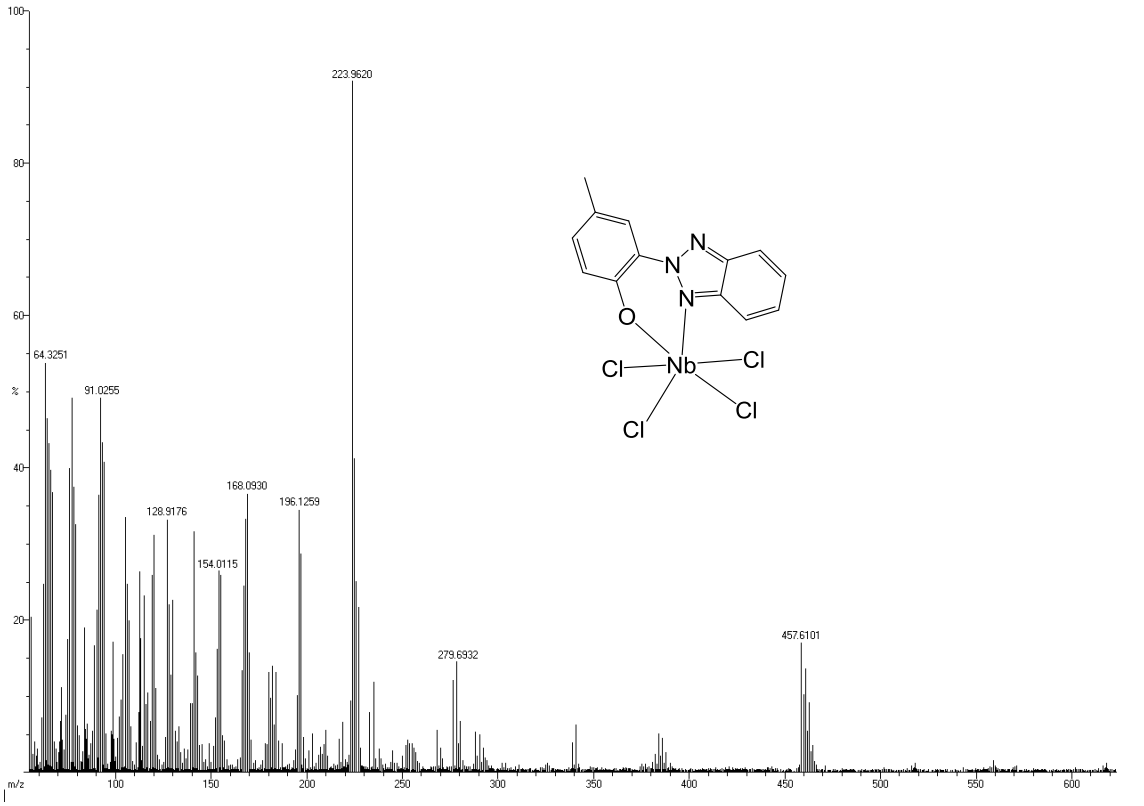

Fig. S3 ESI-Mass Spectrum of compound **1a**.

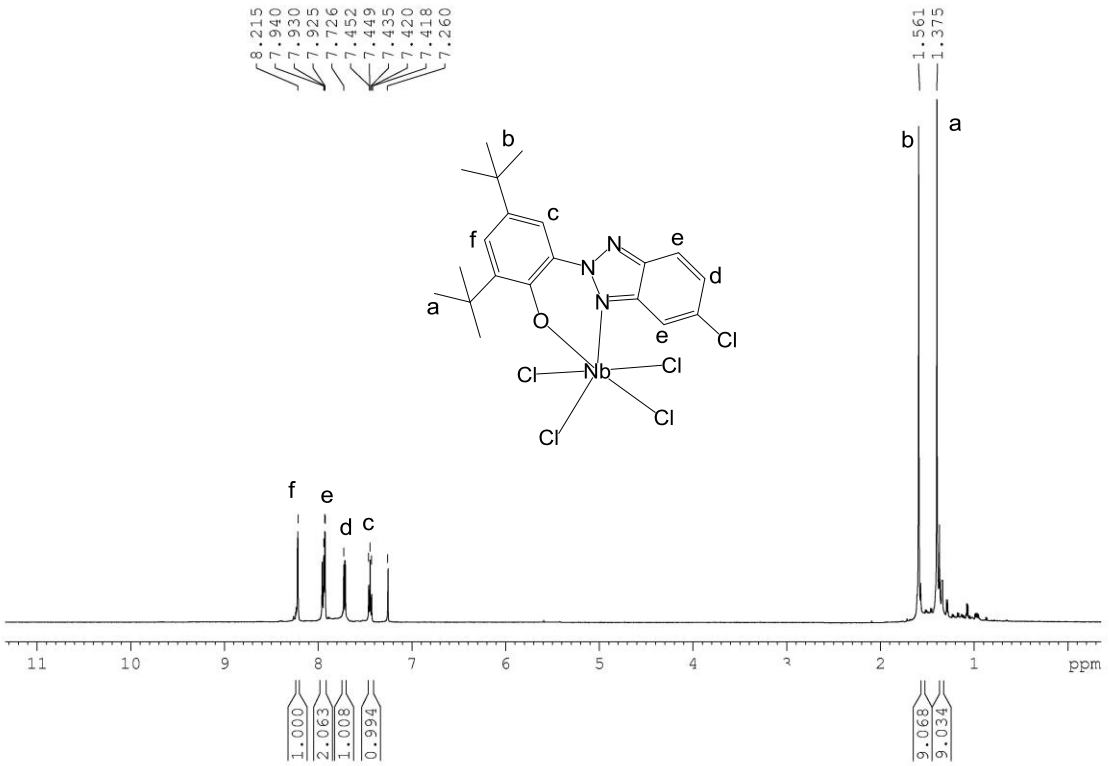

Fig. S4 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.

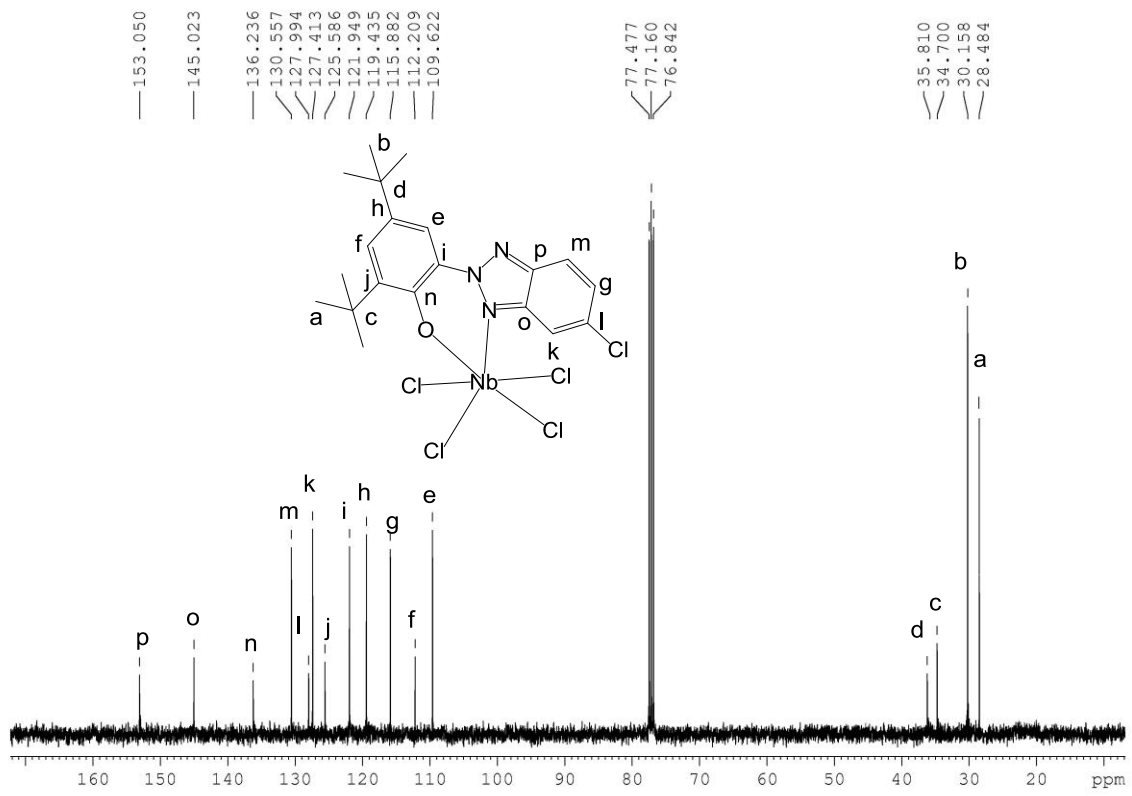

Fig. S5 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2a**.

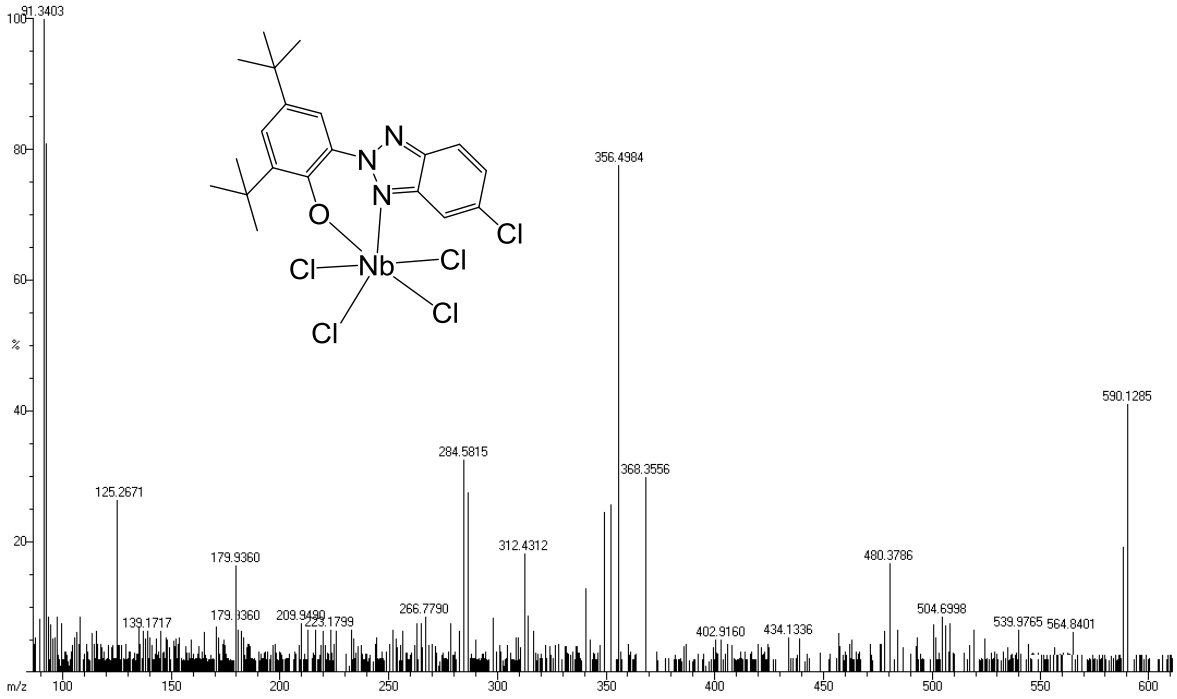

Fig. S6 ESI-Mass Spectrum of compound **2a**.

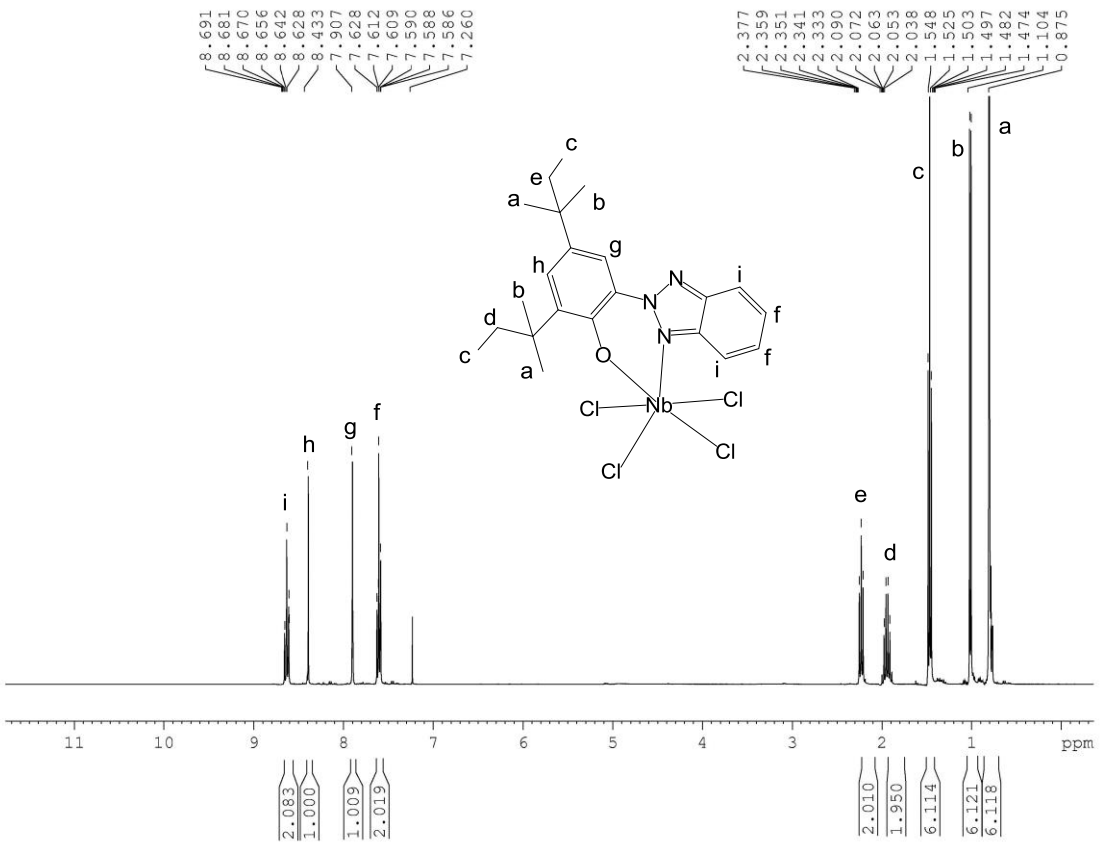

Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3a**.

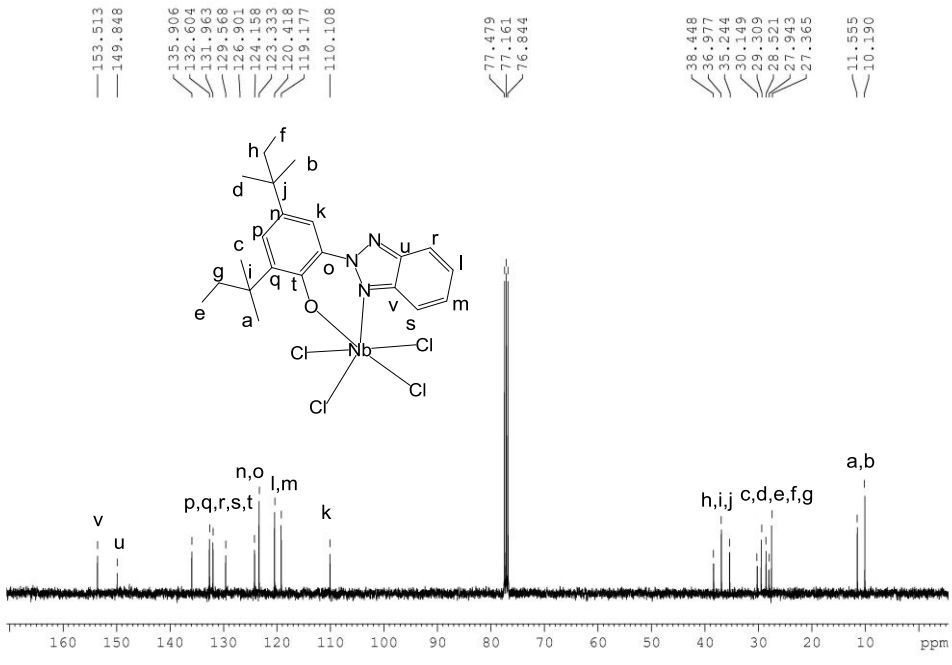

Fig. S8 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3a**.

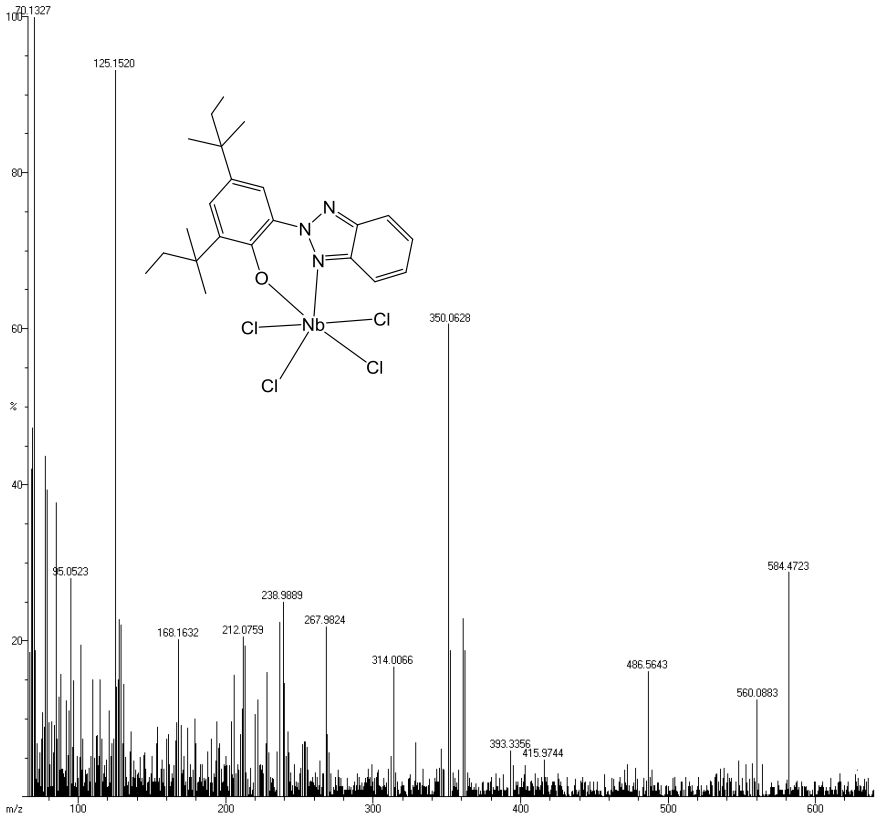

Fig. S9 ESI-Mass Spectrum of compound **3a**.

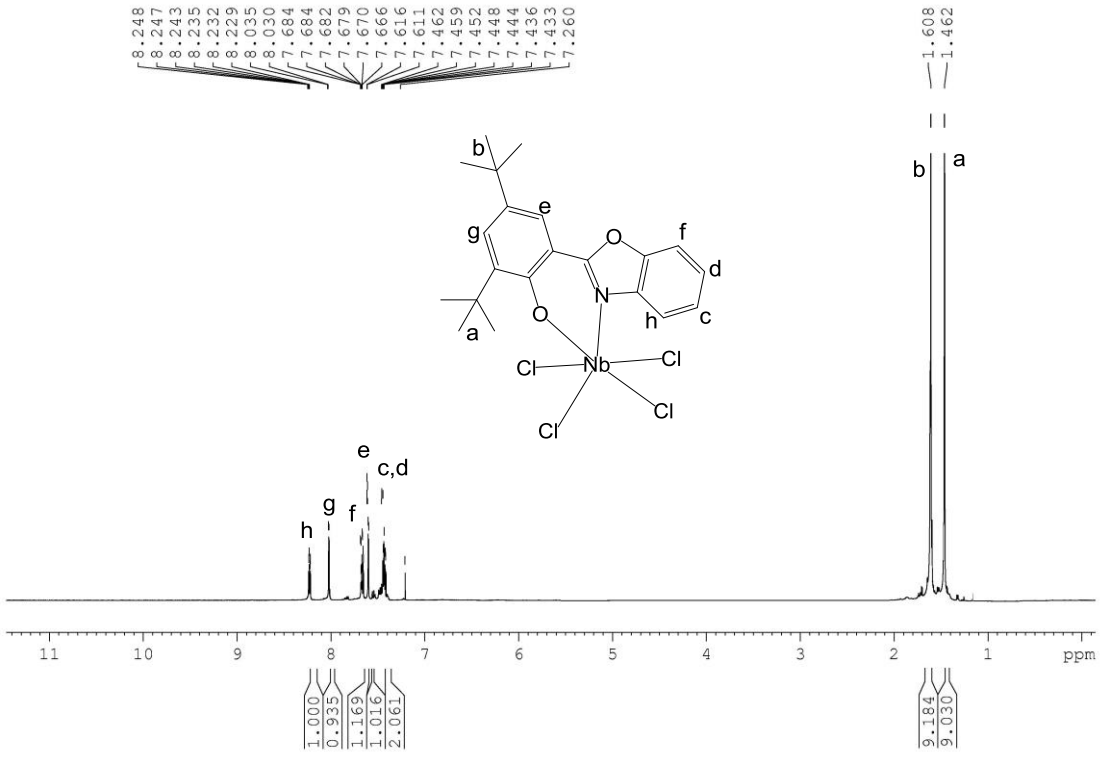

Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4a**.

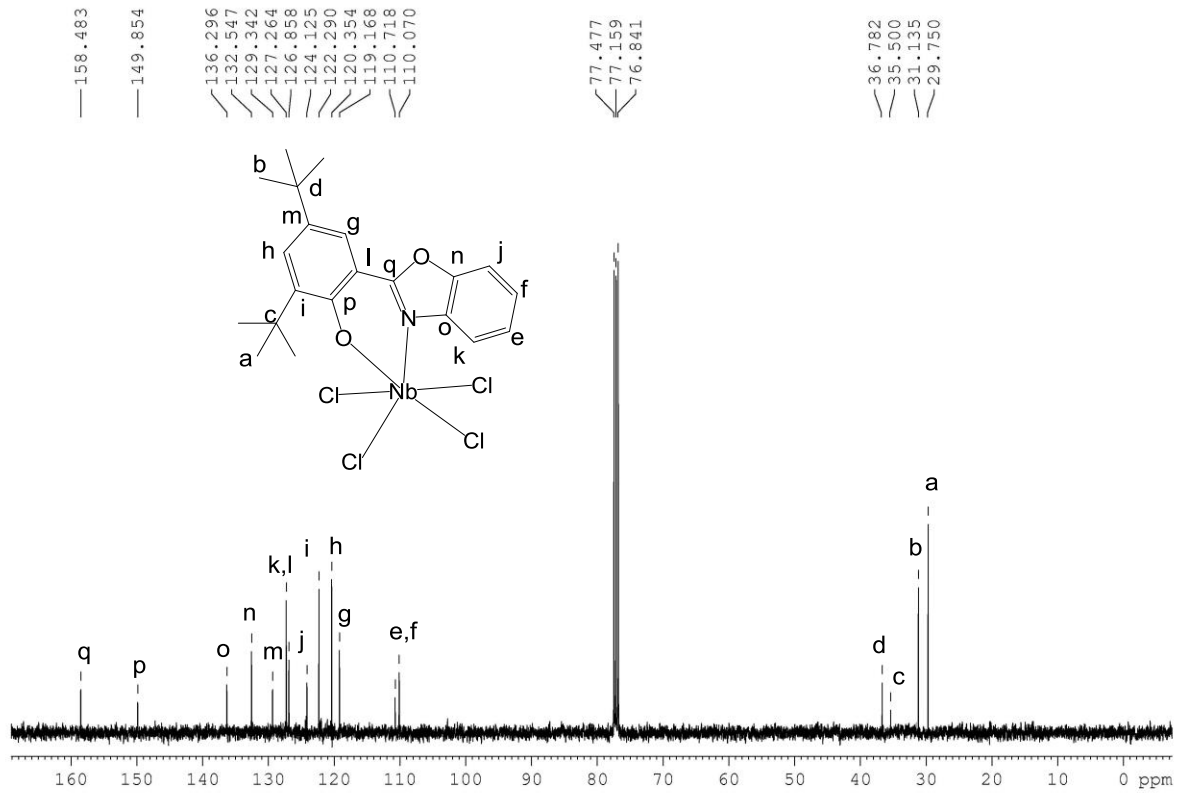

Fig. S11 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4a**.

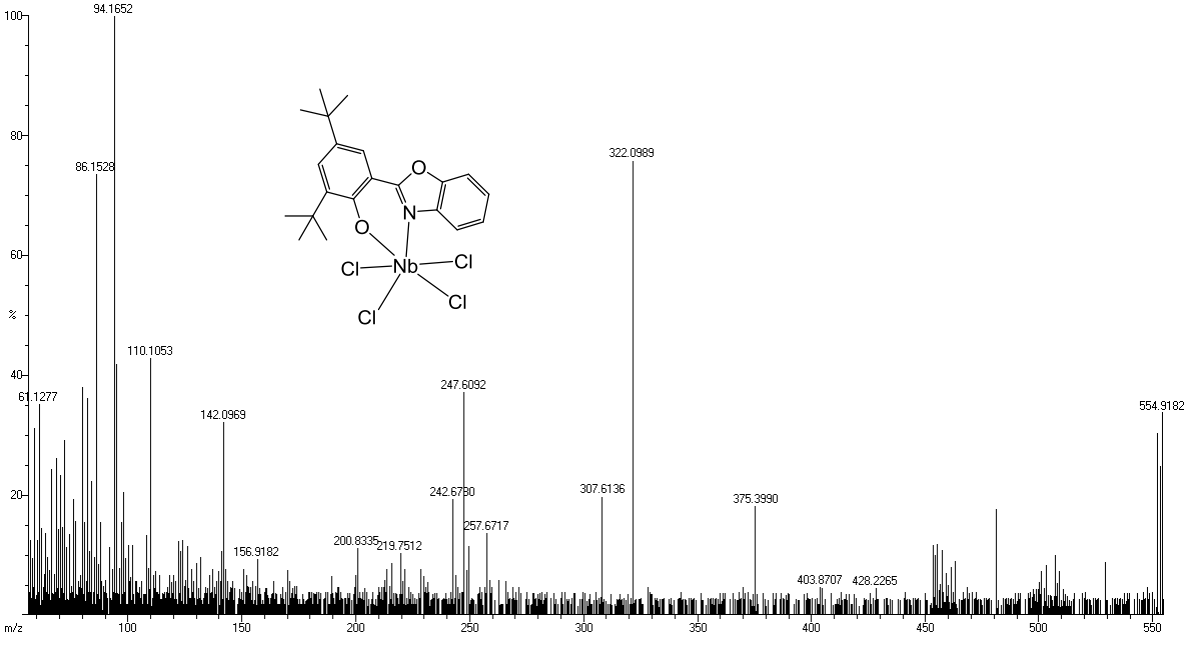

Fig. S12 ESI-Mass Spectrum of compound **4a**.

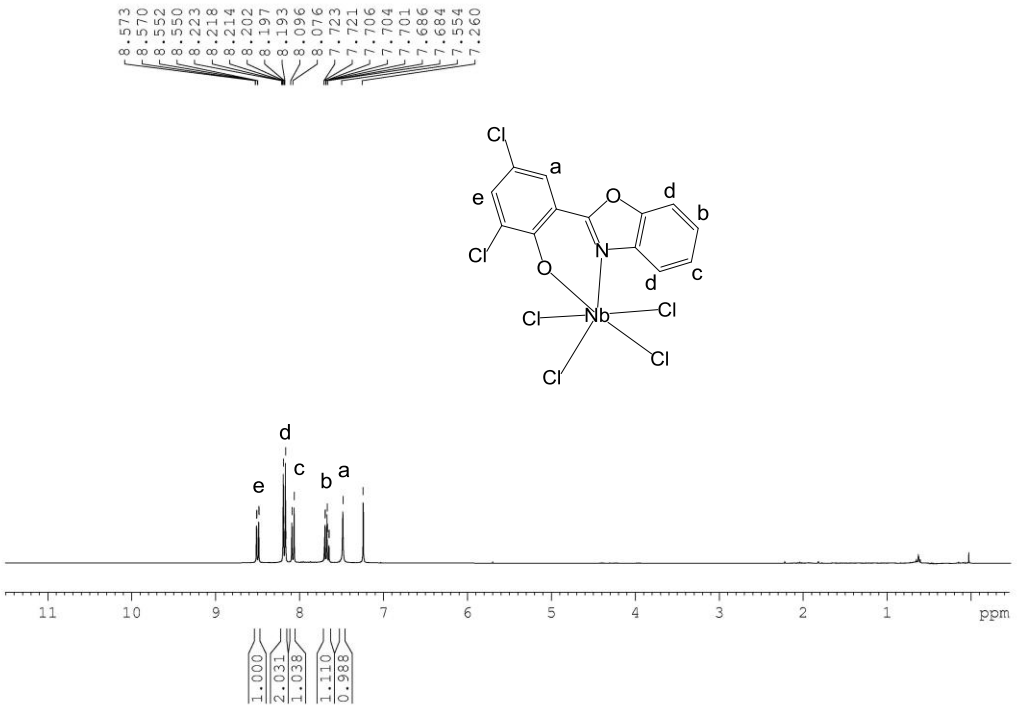

Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5a**.

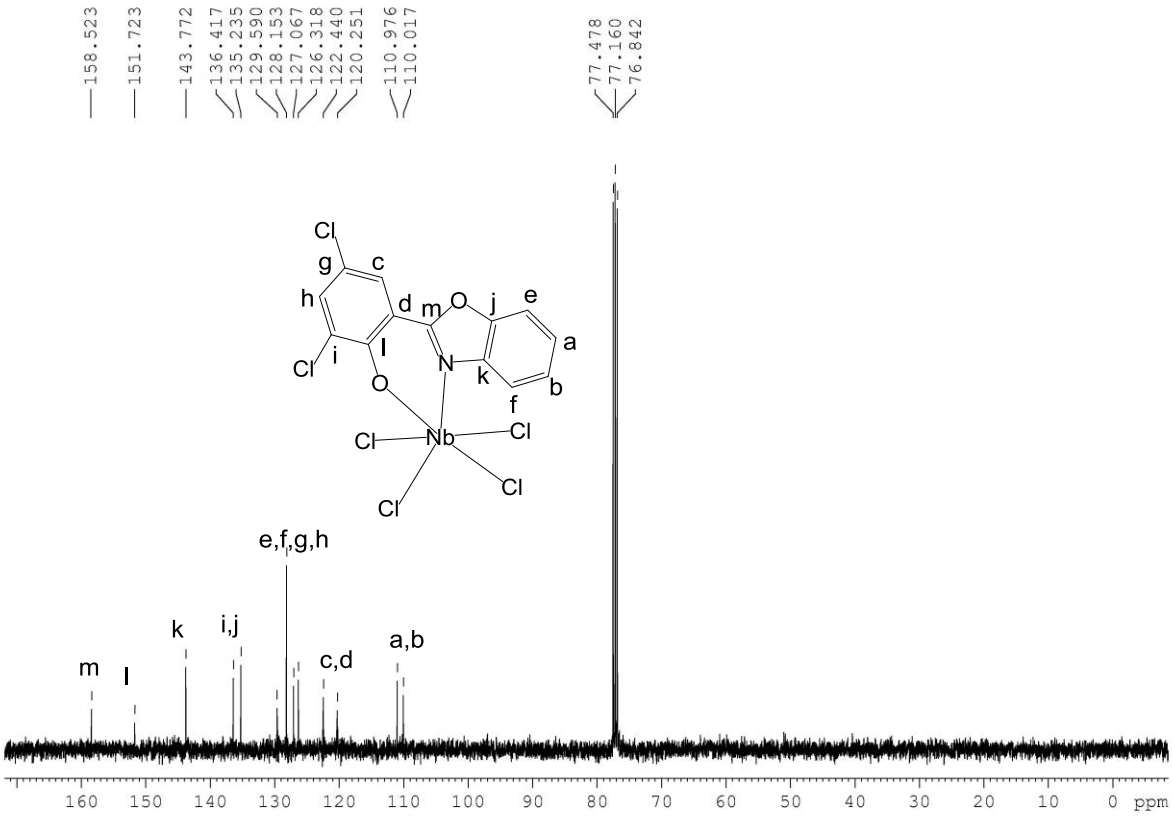

Fig. S14 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5a**.

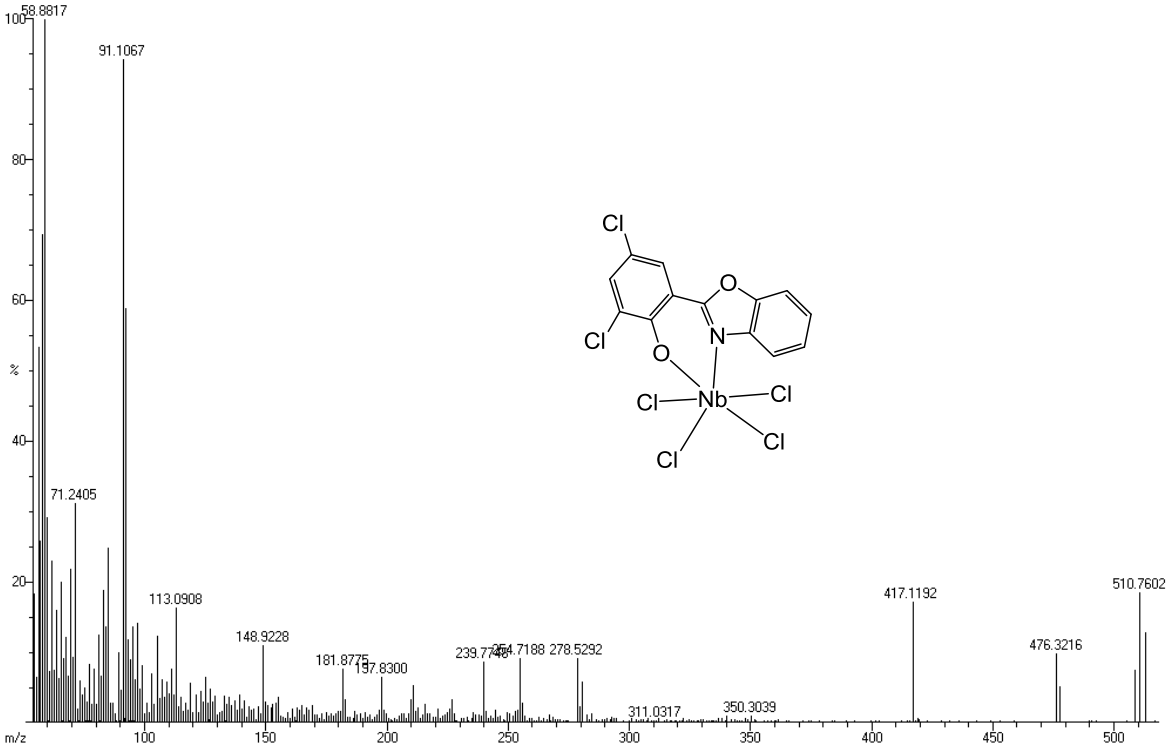

Fig. S15 ESI-Mass Spectrum of compound **5a**.

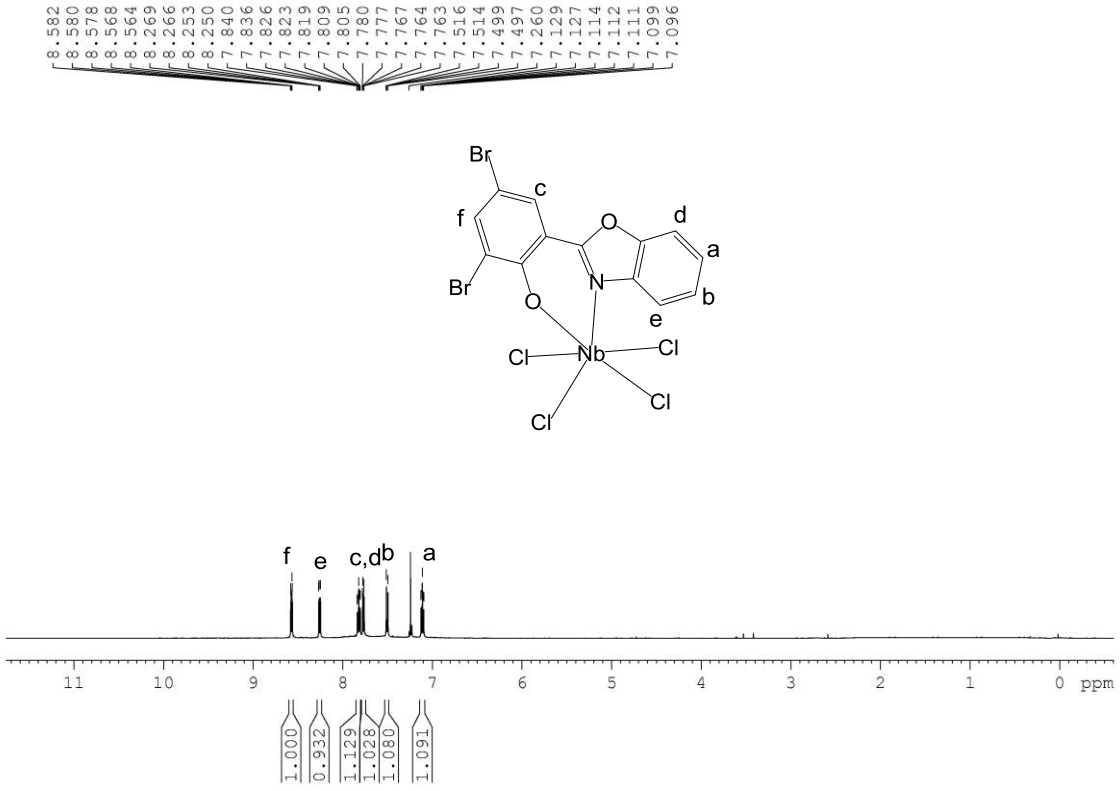

Fig. S16 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **6a**.

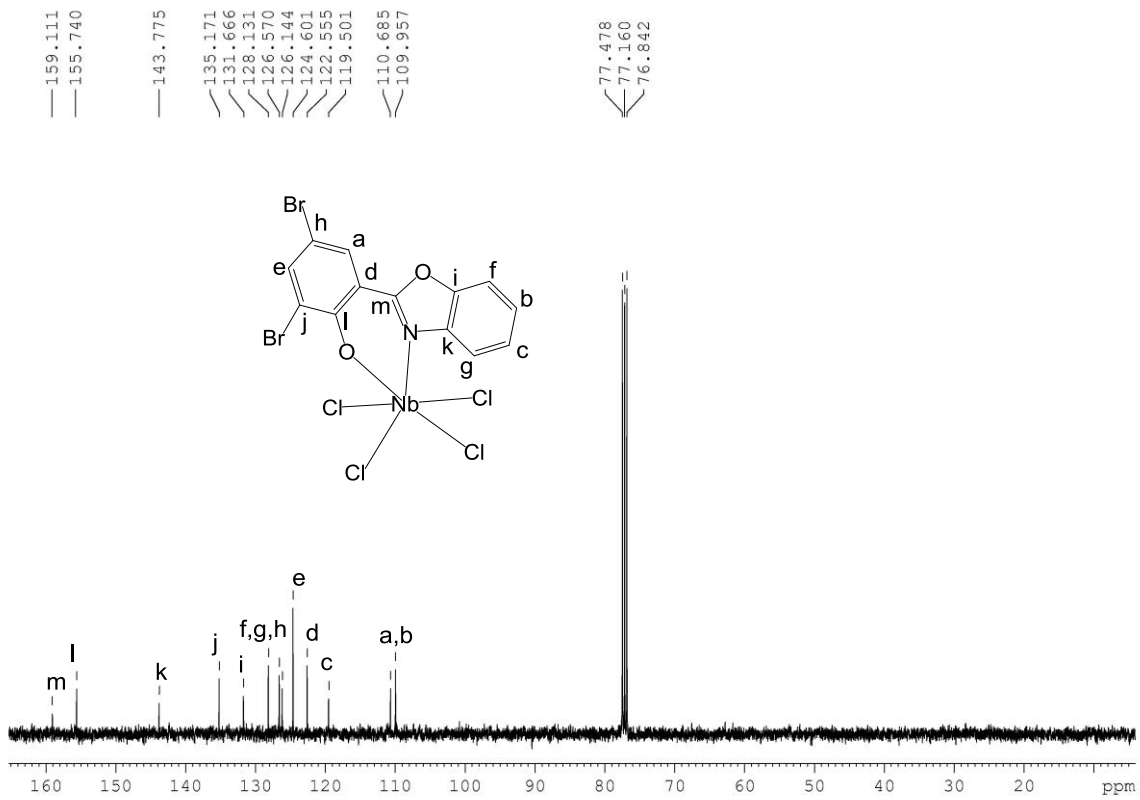

Fig. S17 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **6a**.

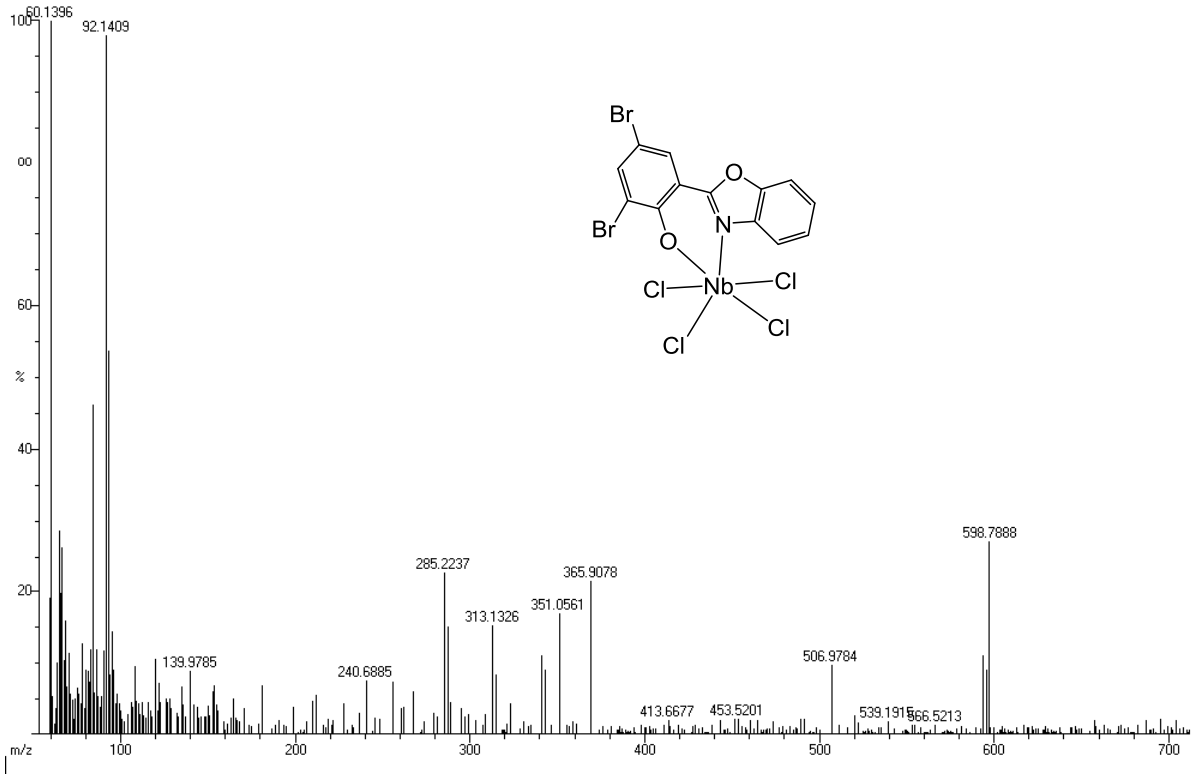

Fig. S18 ESI-Mass Spectrum of compound **6a**.

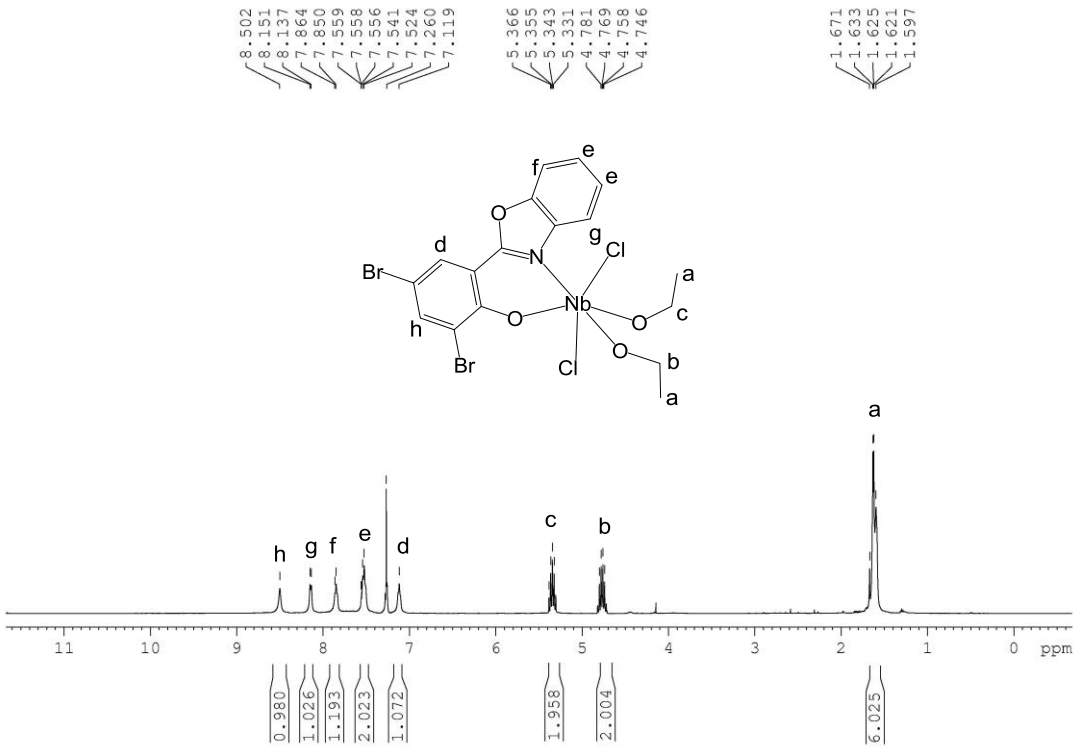

Fig. S19 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **7a**.

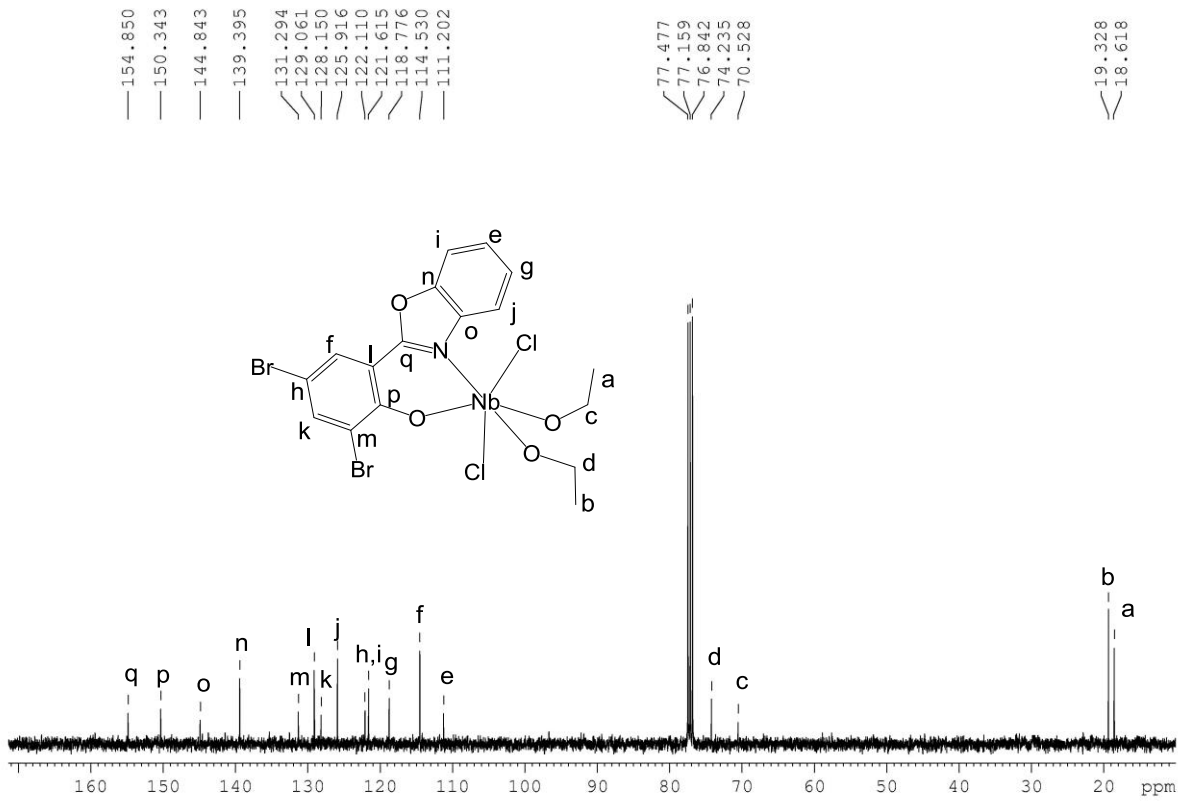

Fig. S20 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **7a**.

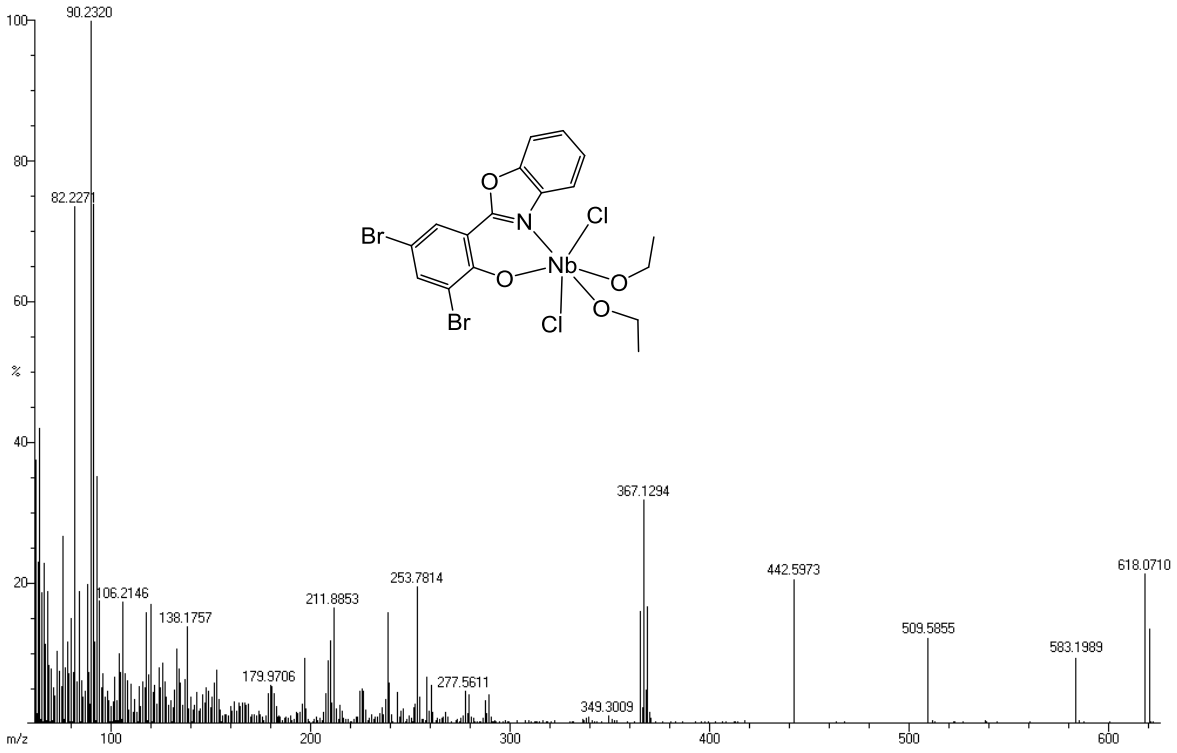

Fig. S21 ESI-Mass Spectrum of compound **7a**.

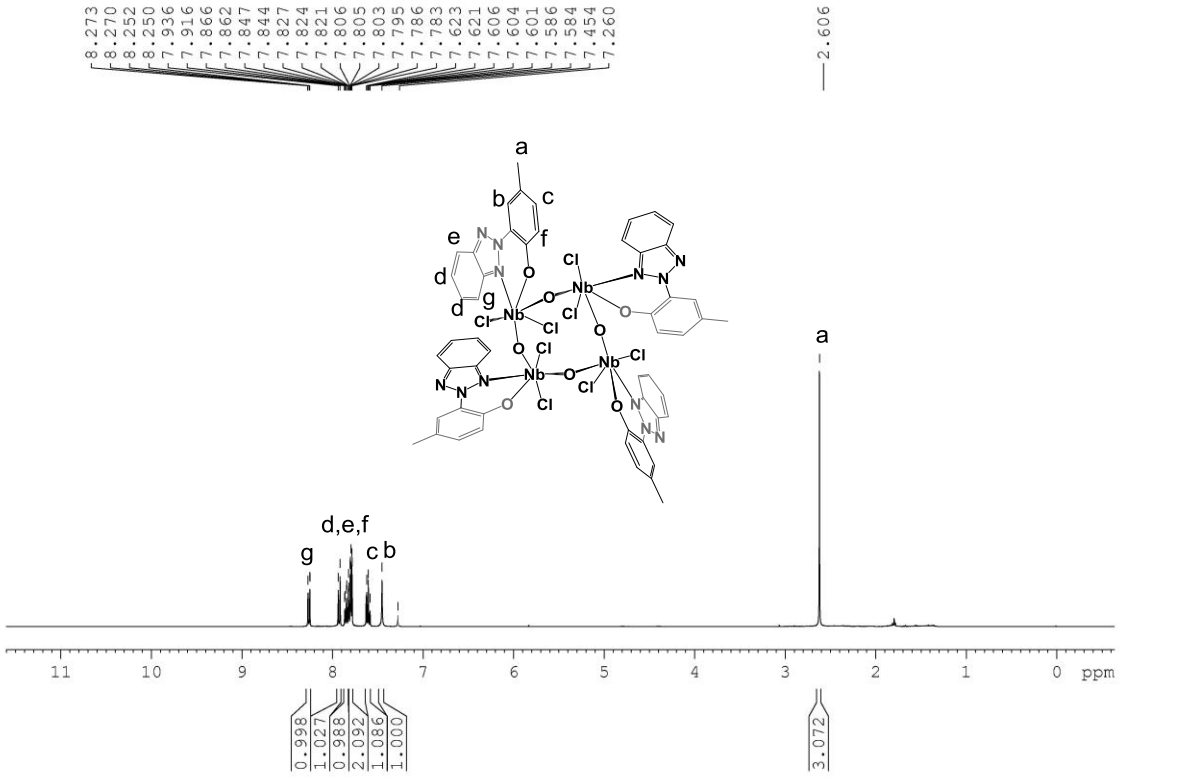

Fig. S22 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **8a**.

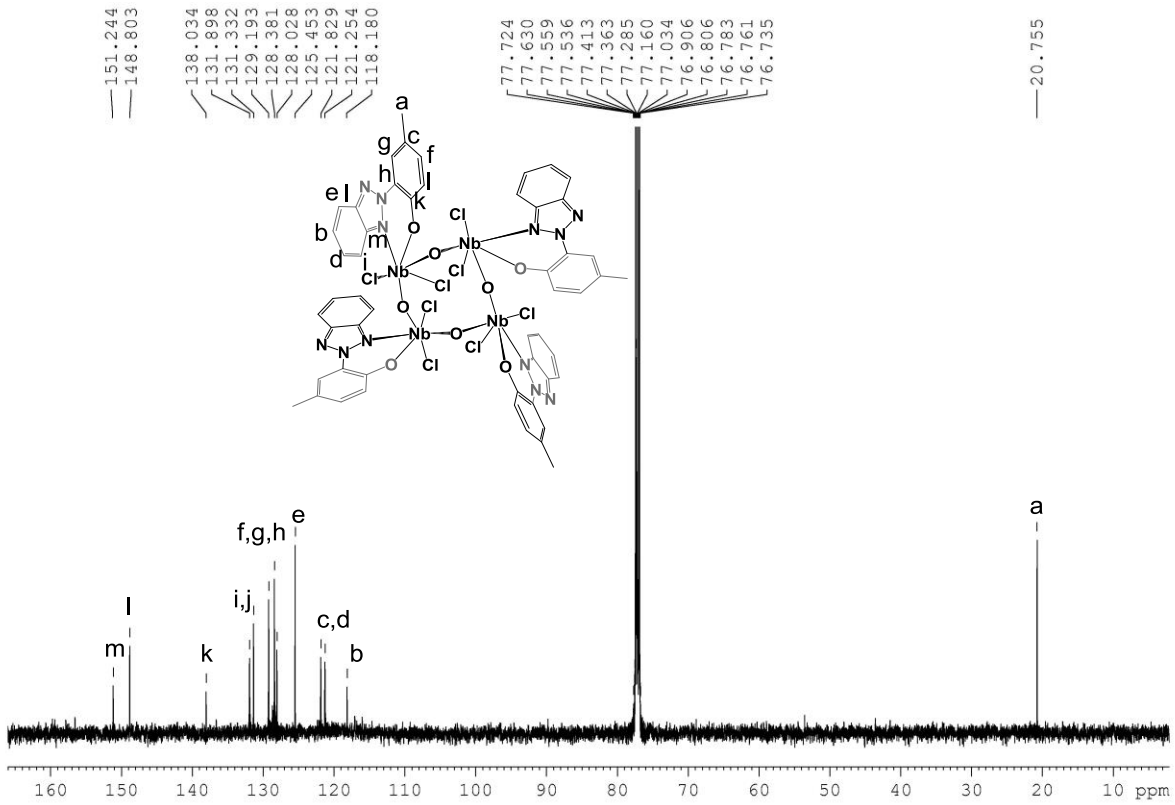

Fig. S23 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **8a**.

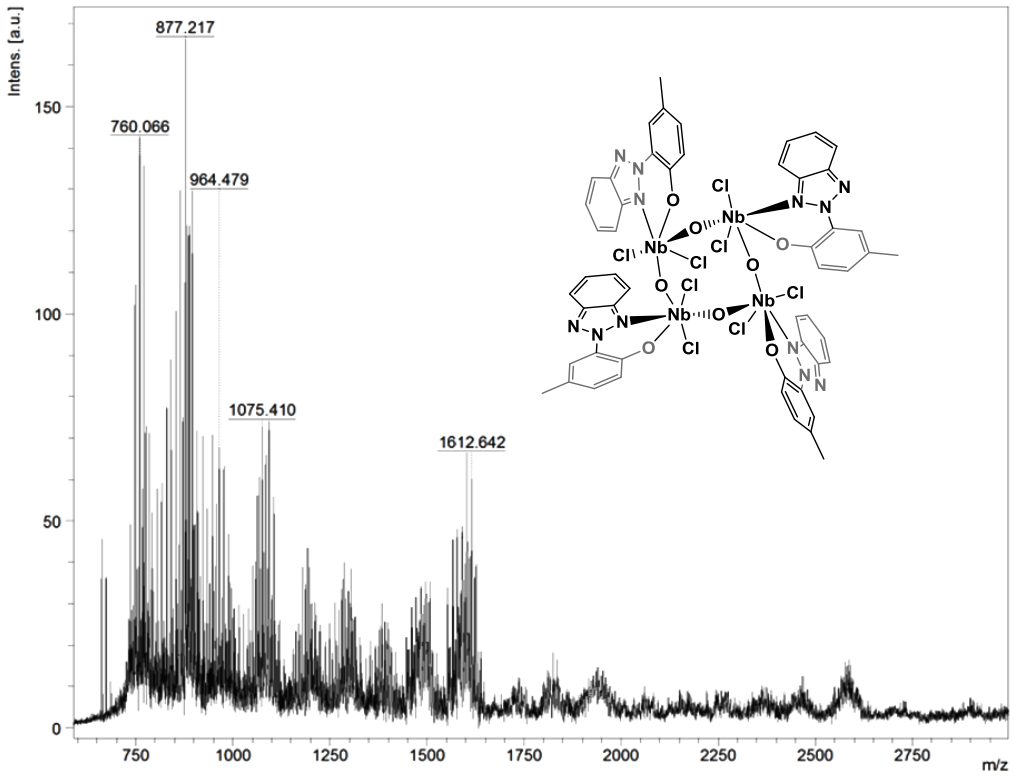

Fig. S24 ESI-Mass Spectrum of compound **8a**.

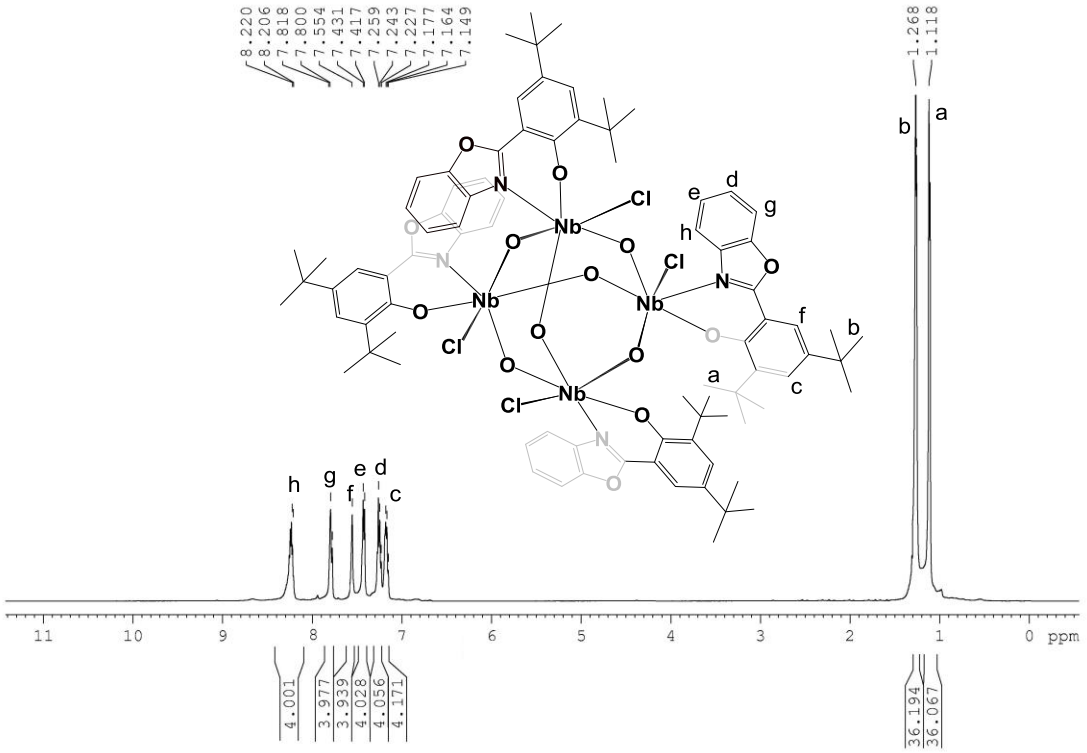

Fig. S25 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **9a**.

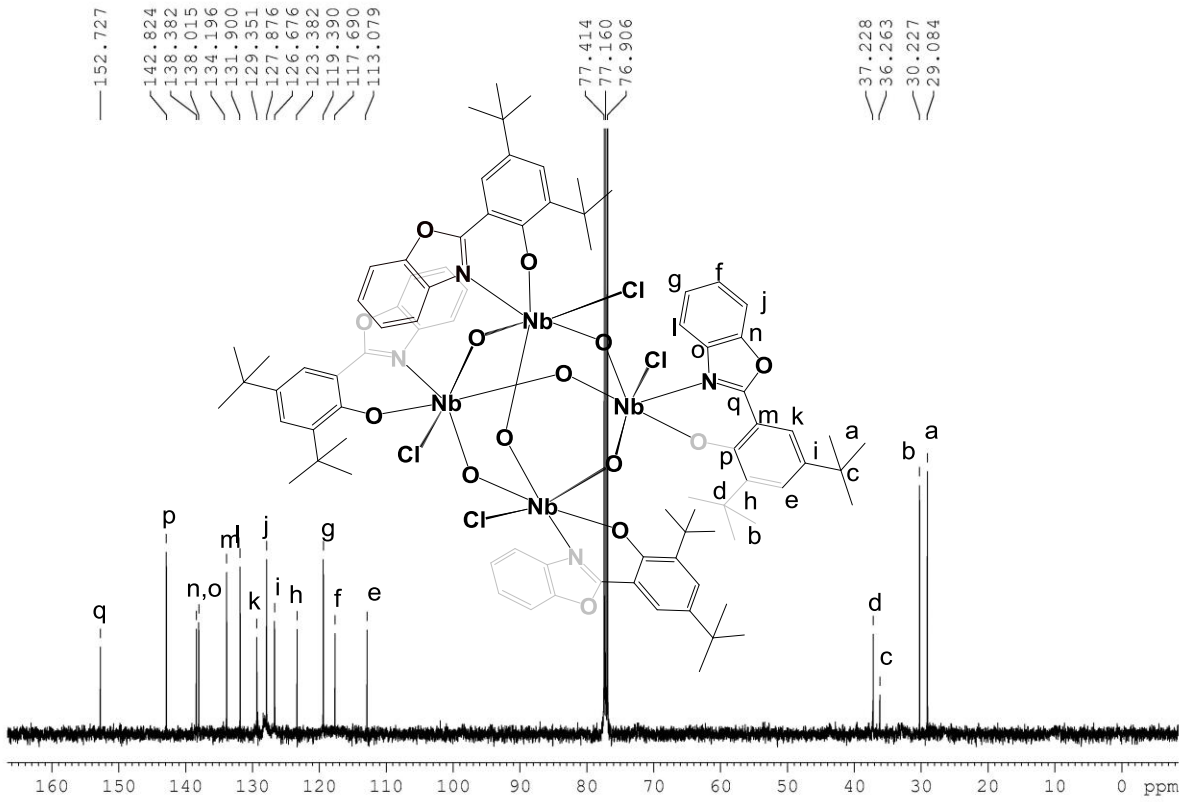

Fig. S26 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **9a**.

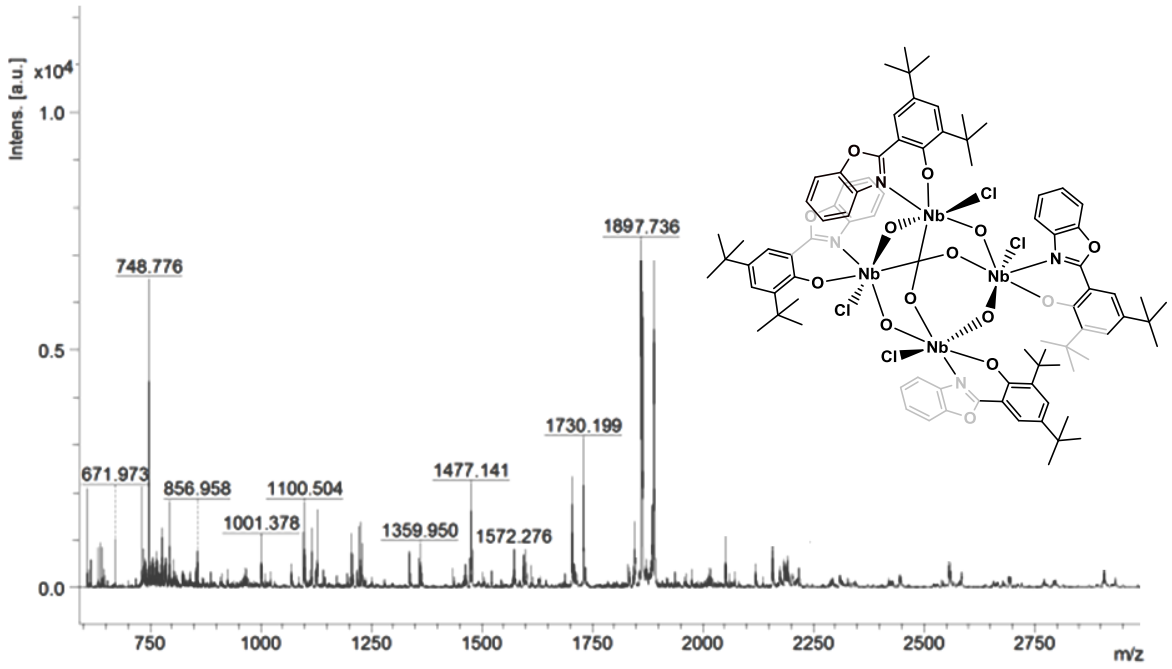

Fig. S27 ESI-Mass Spectrum of compound **9a**.

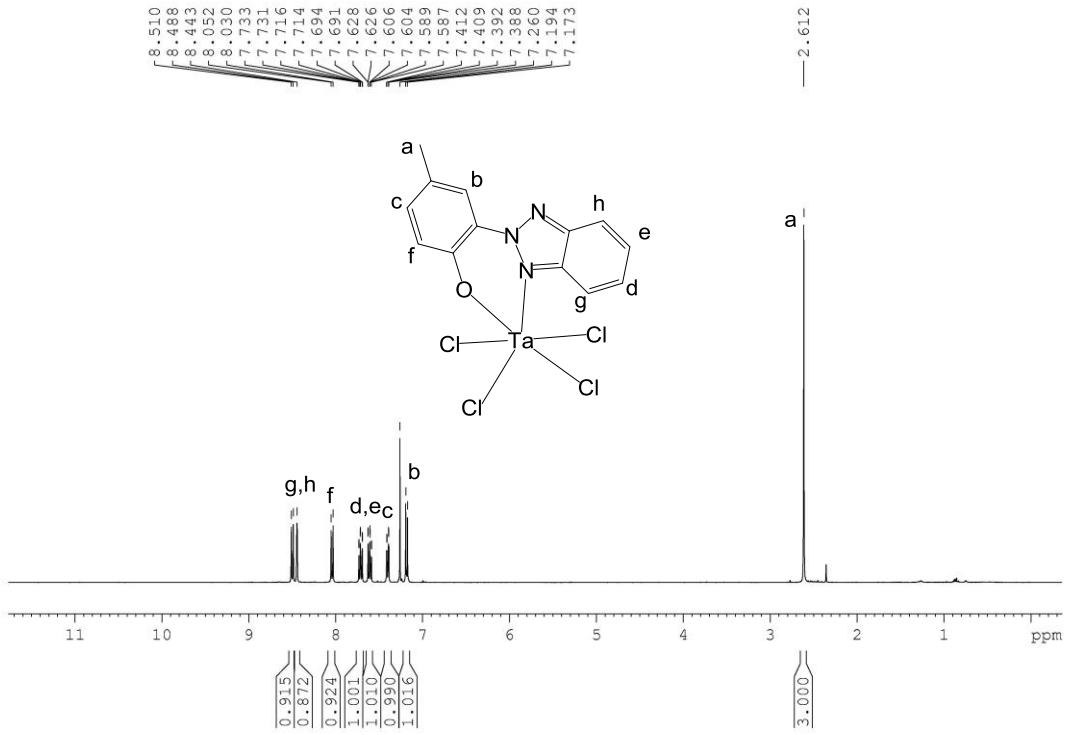

Fig. S28 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **1b**.

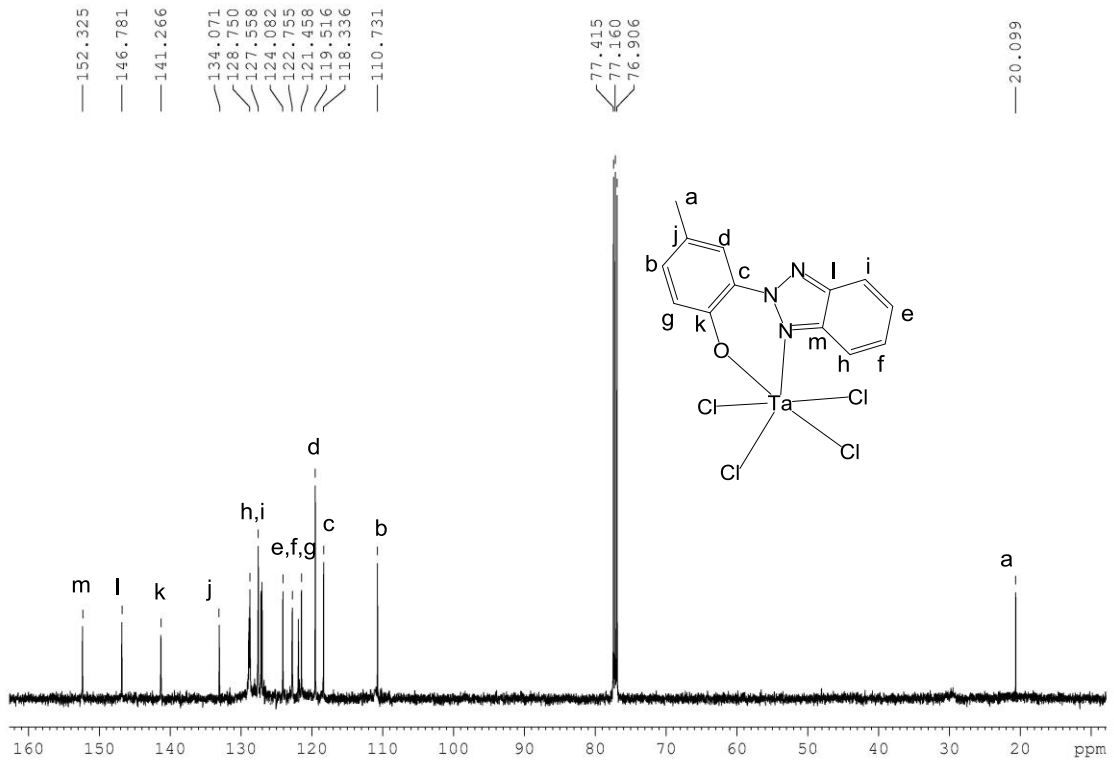

Fig. S29 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **1b**.

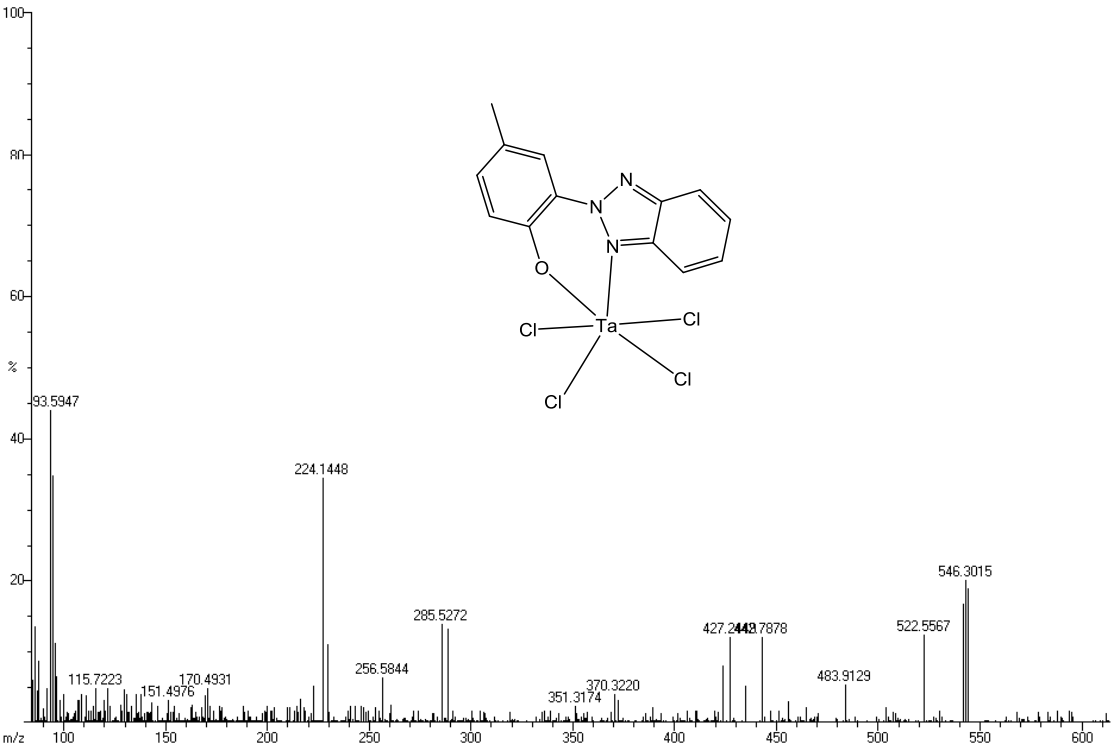

Fig. S30 ESI-Mass Spectrum of compound **1b**.

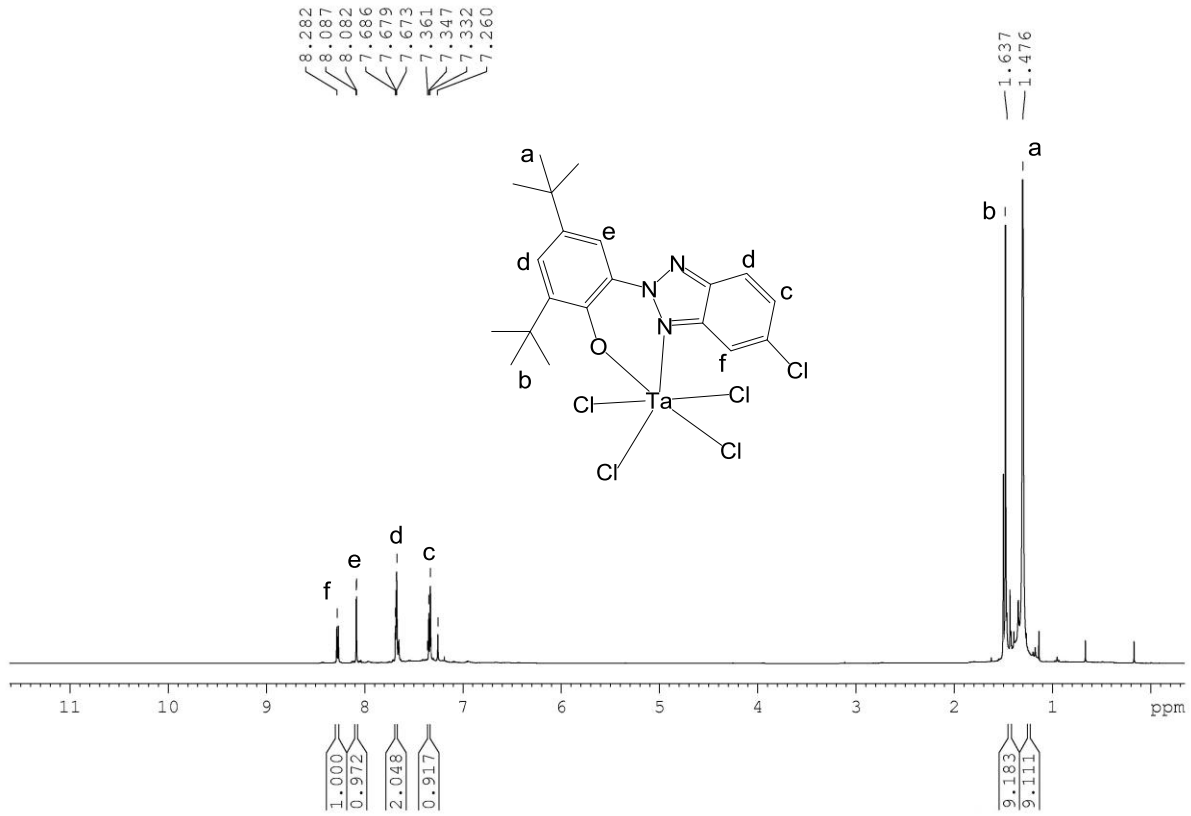

Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **2b**.

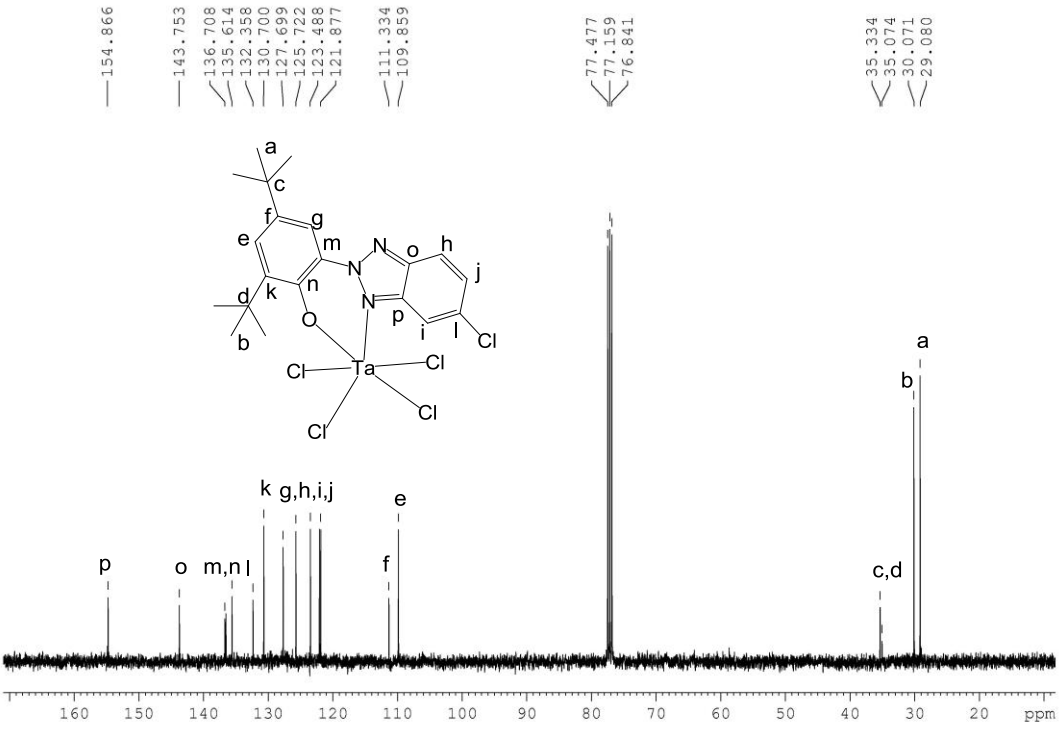

Fig. S32 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **2b**.

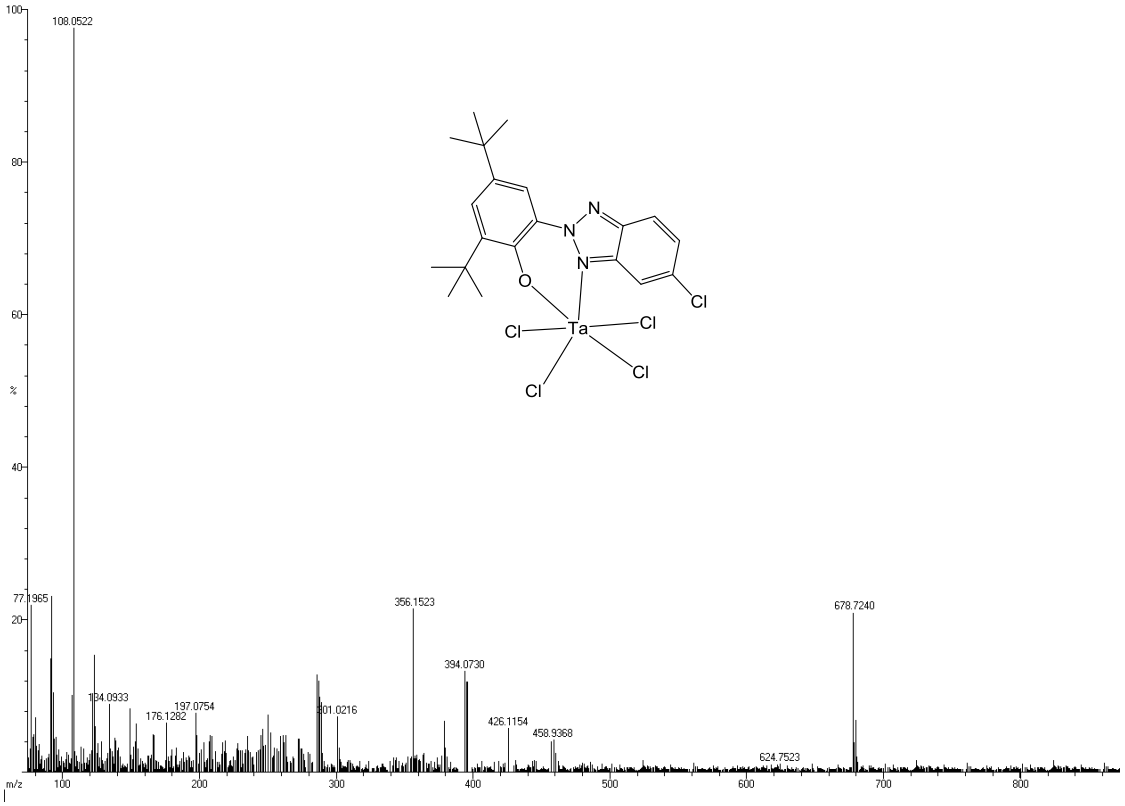

Fig. S33 ESI-Mass Spectrum of compound **2b**.

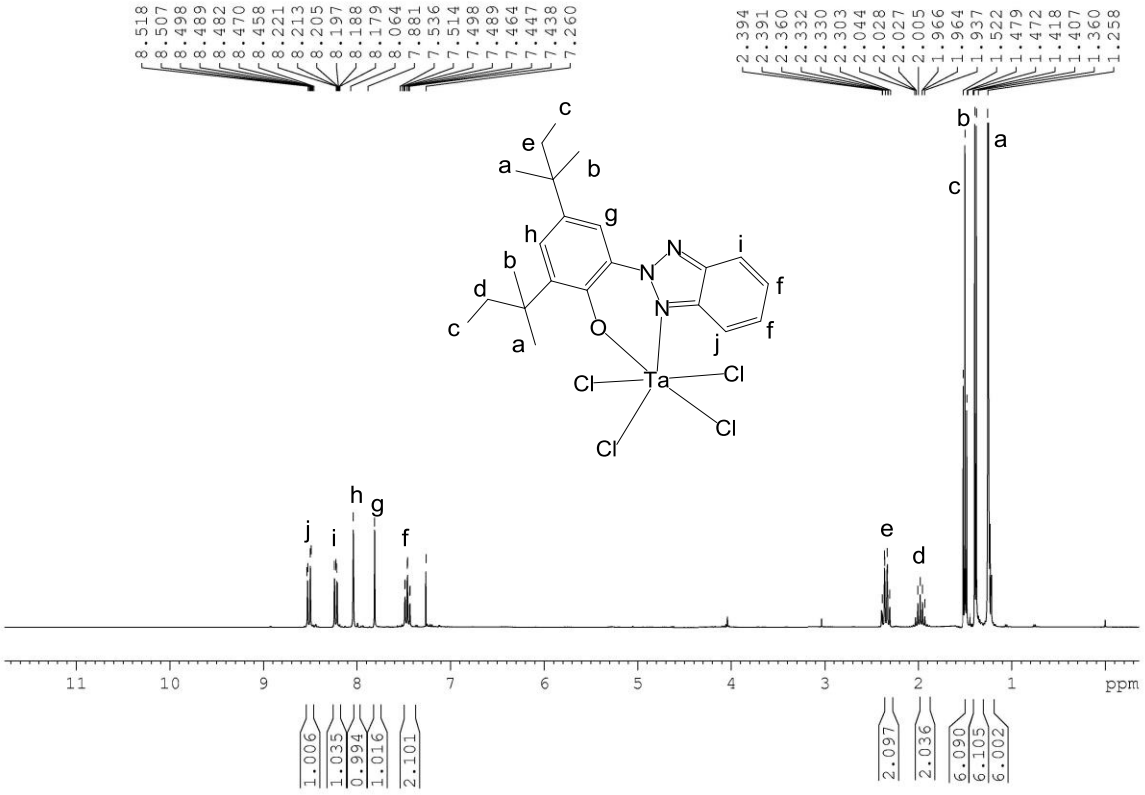

Fig. S34 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **3b**.

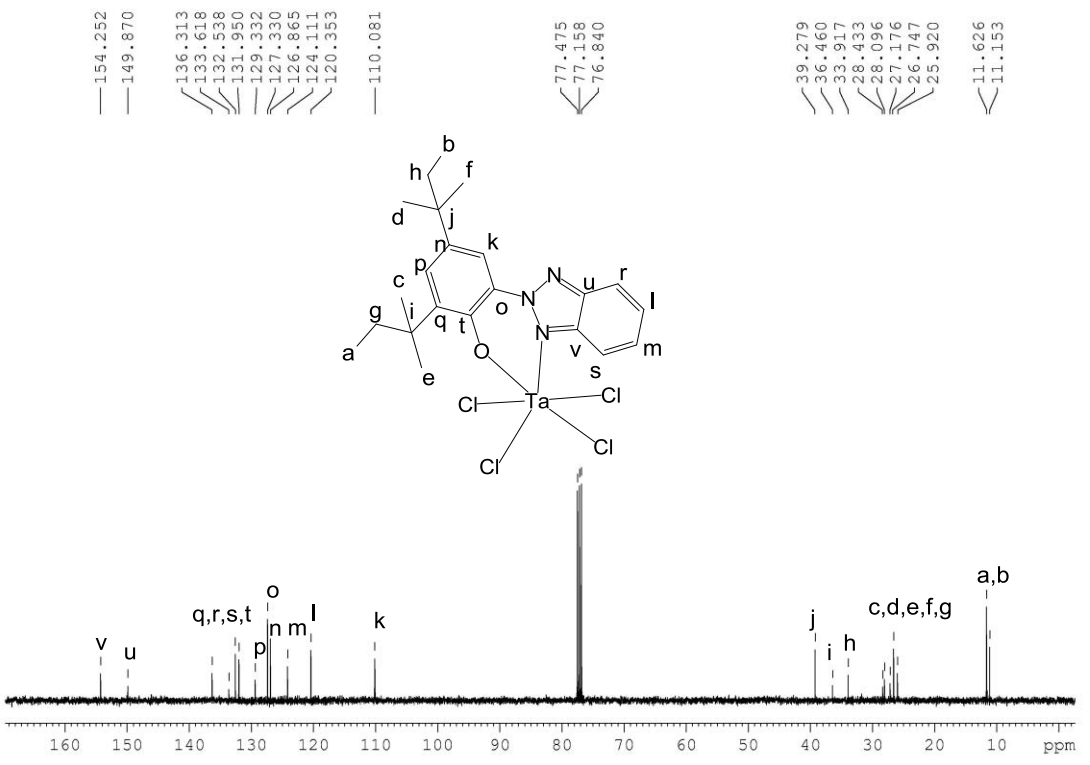

Fig. S35 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **3b**.

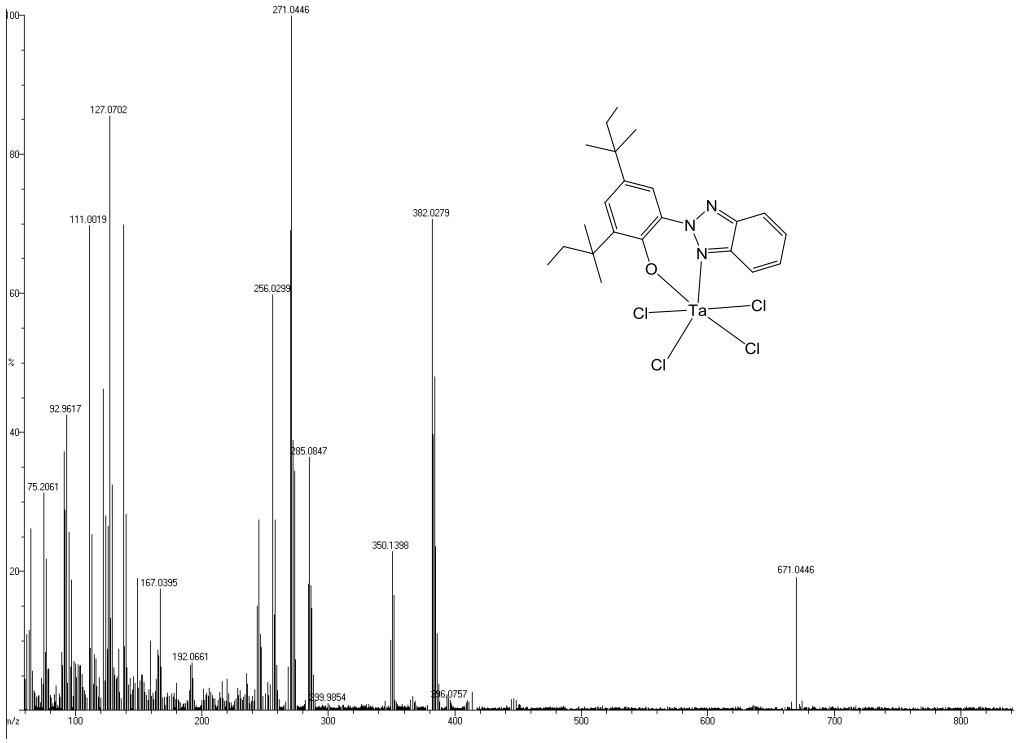

Fig. S36 ESI-Mass Spectrum of compound **3b**.

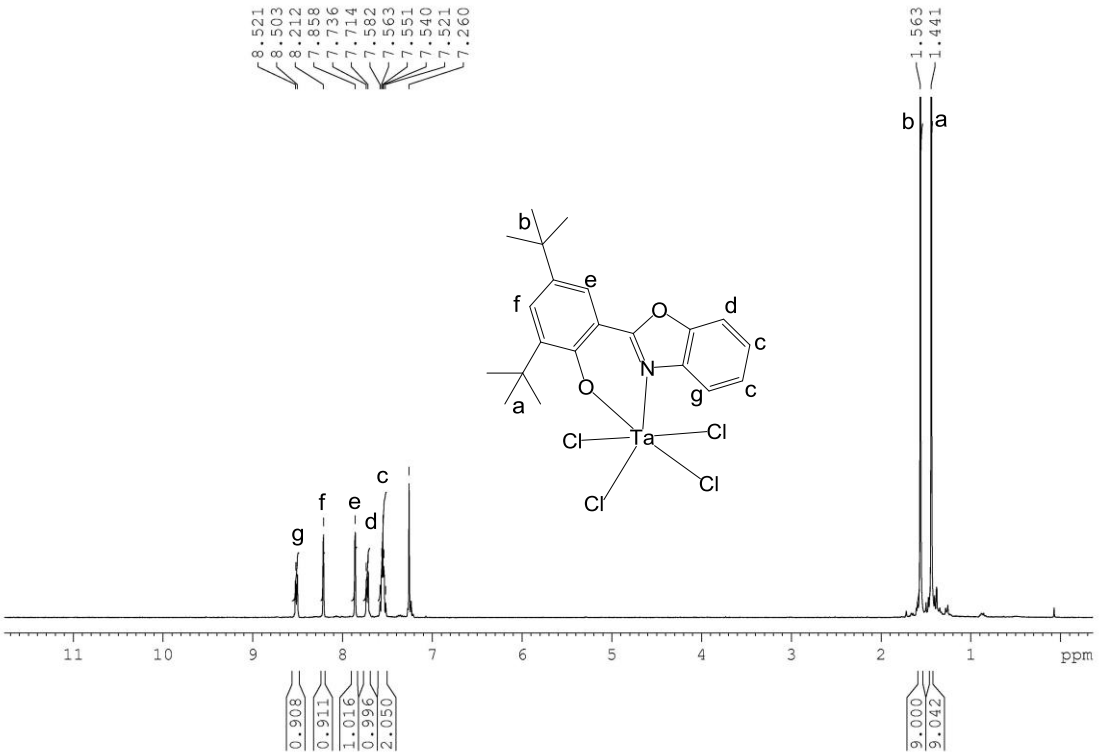

Fig. S37 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **4b**.

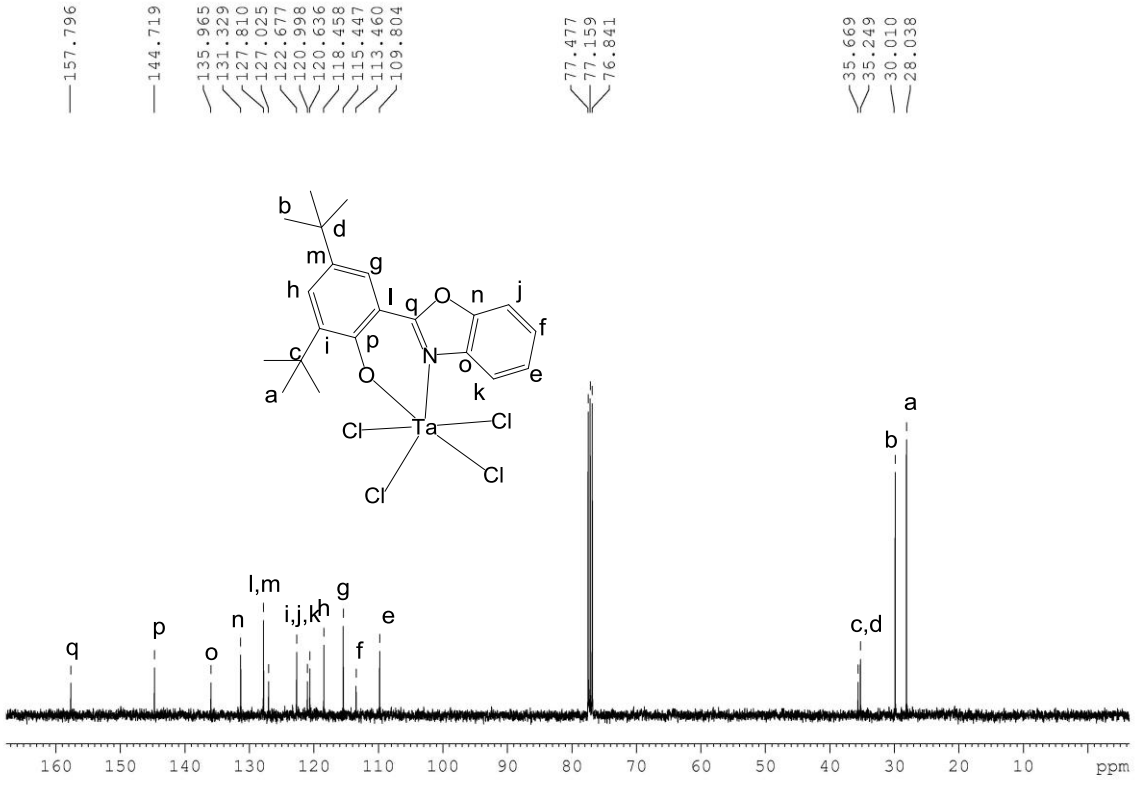

Fig. S38 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **4b**.

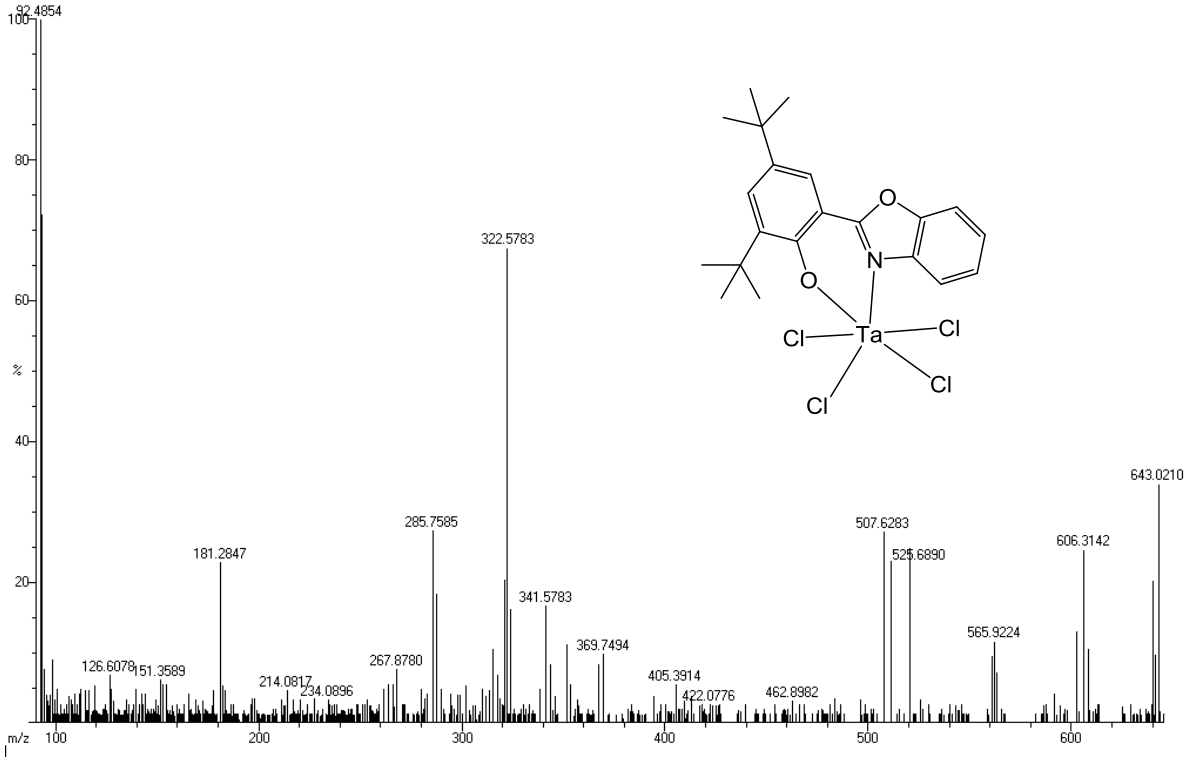

Fig. S39 ESI-Mass Spectrum of compound **4b**.

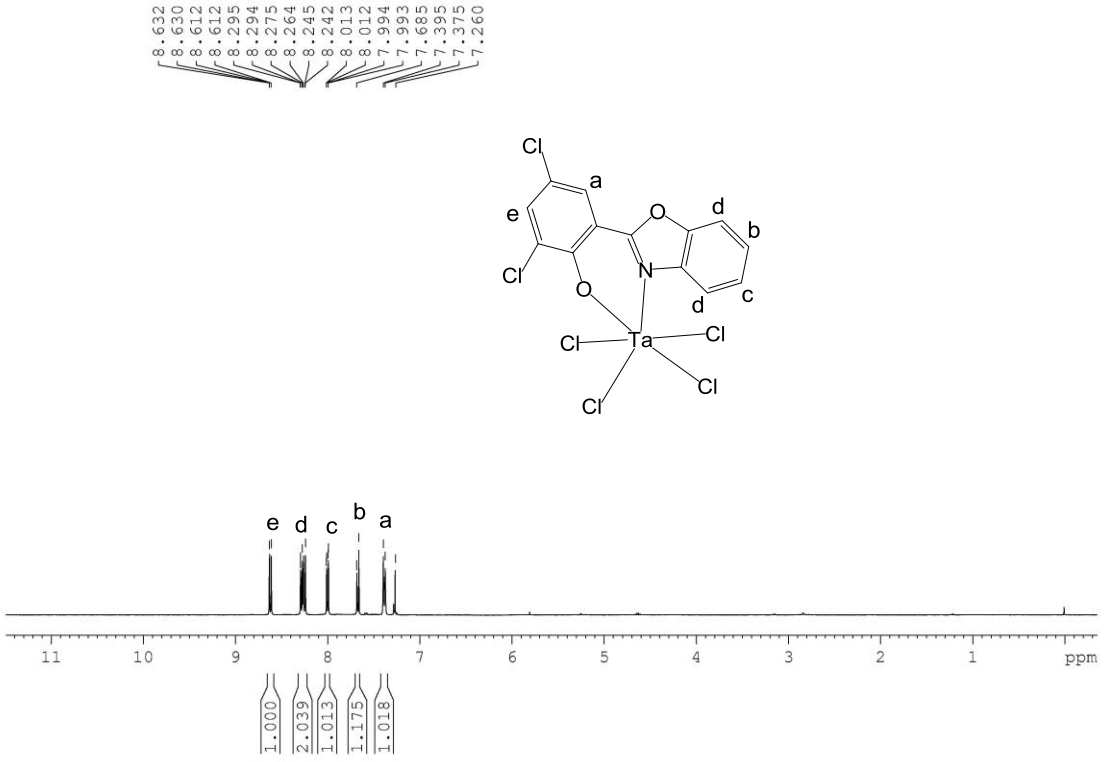

Fig. S40 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **5b**.

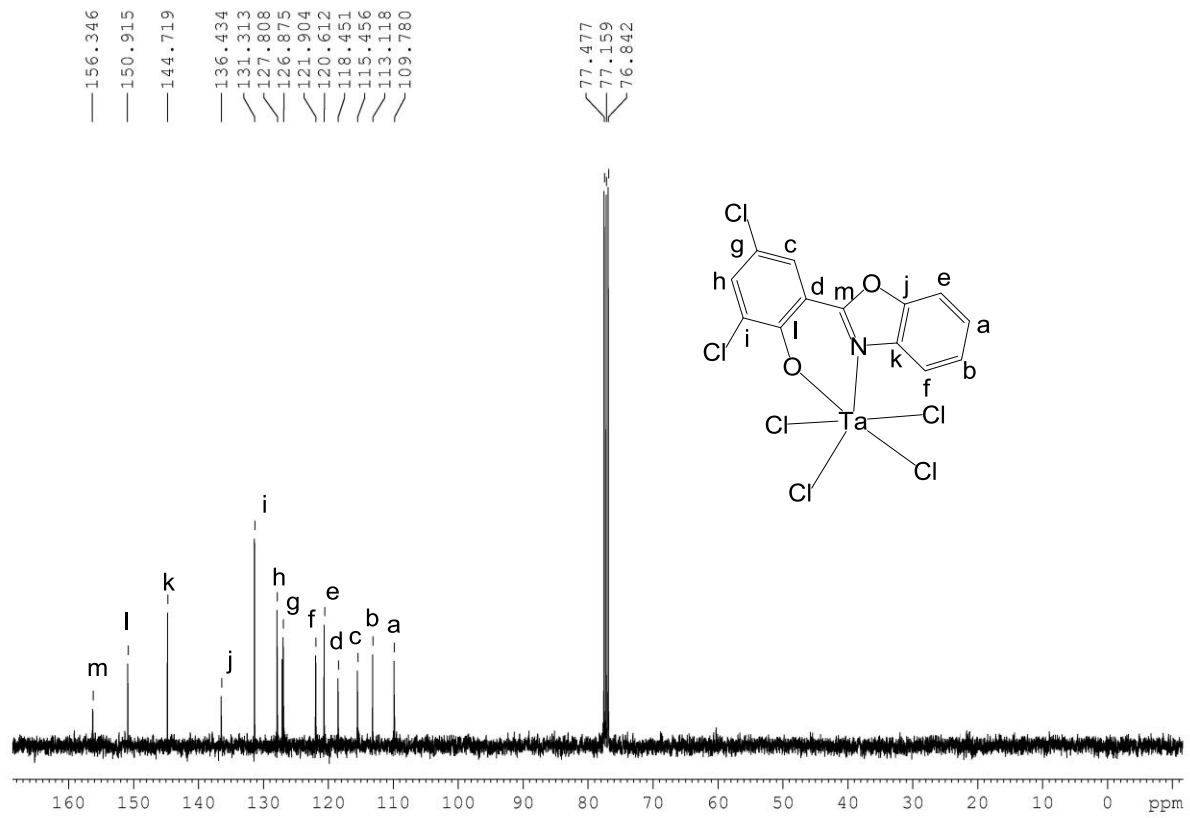

Fig. S41 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **5b**.

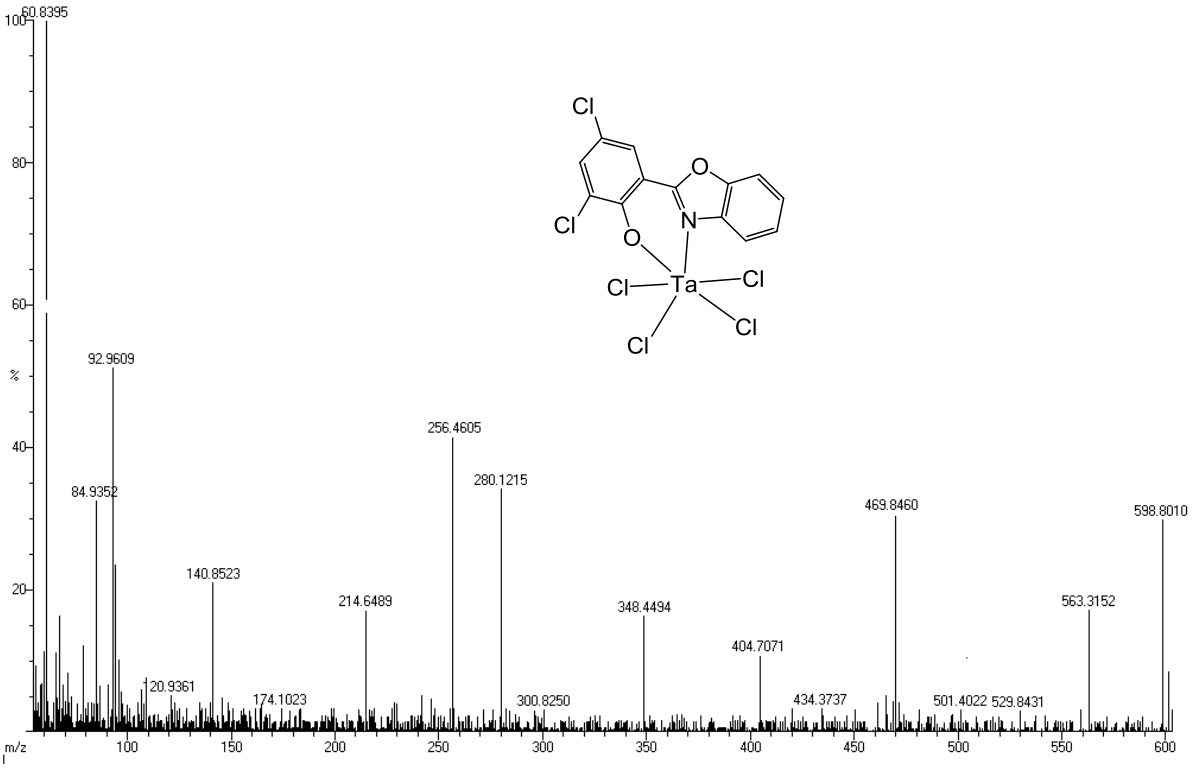

Fig. S42 ESI-Mass Spectrum of compound **5b**.

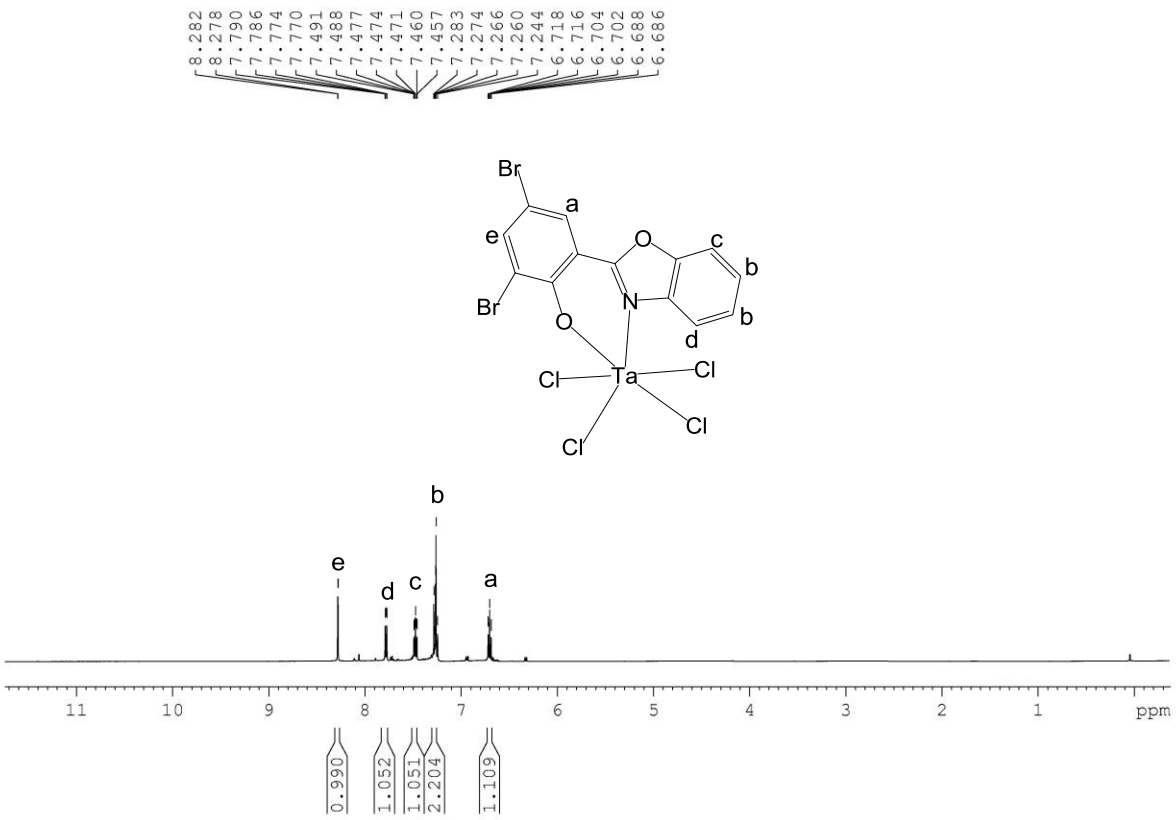

Fig. S43 ^{1}H NMR (400 MHz, $CDCl_3$) of compound **6b**.

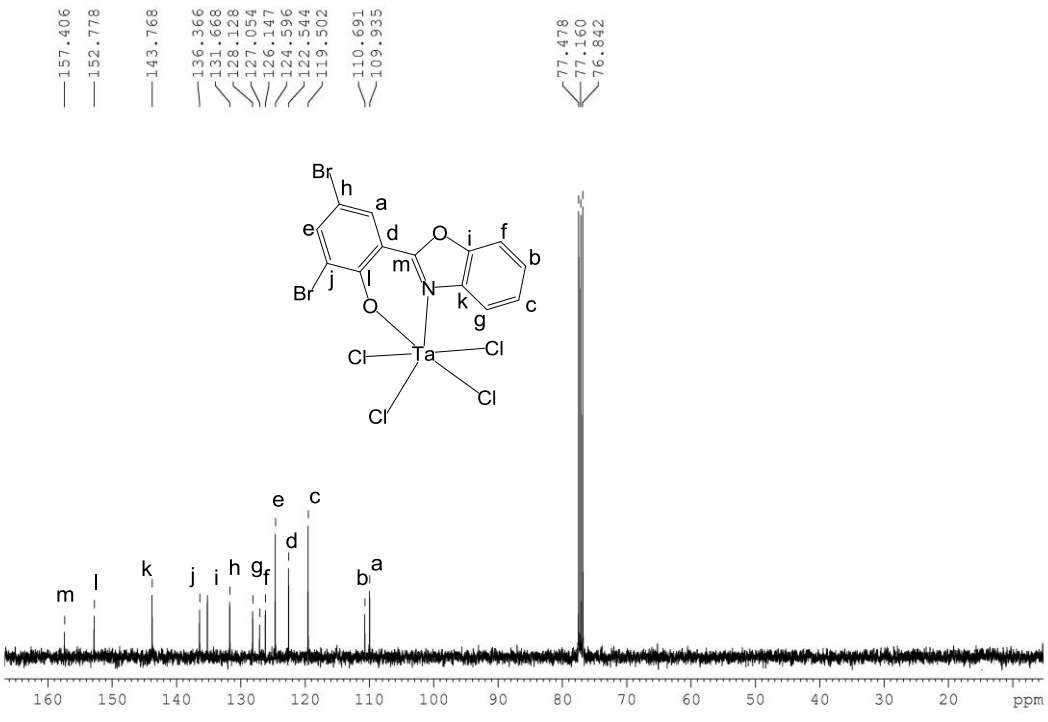

Fig. S44 ^{13}C NMR (100 MHz, $CDCl_3$) of compound **6b**.

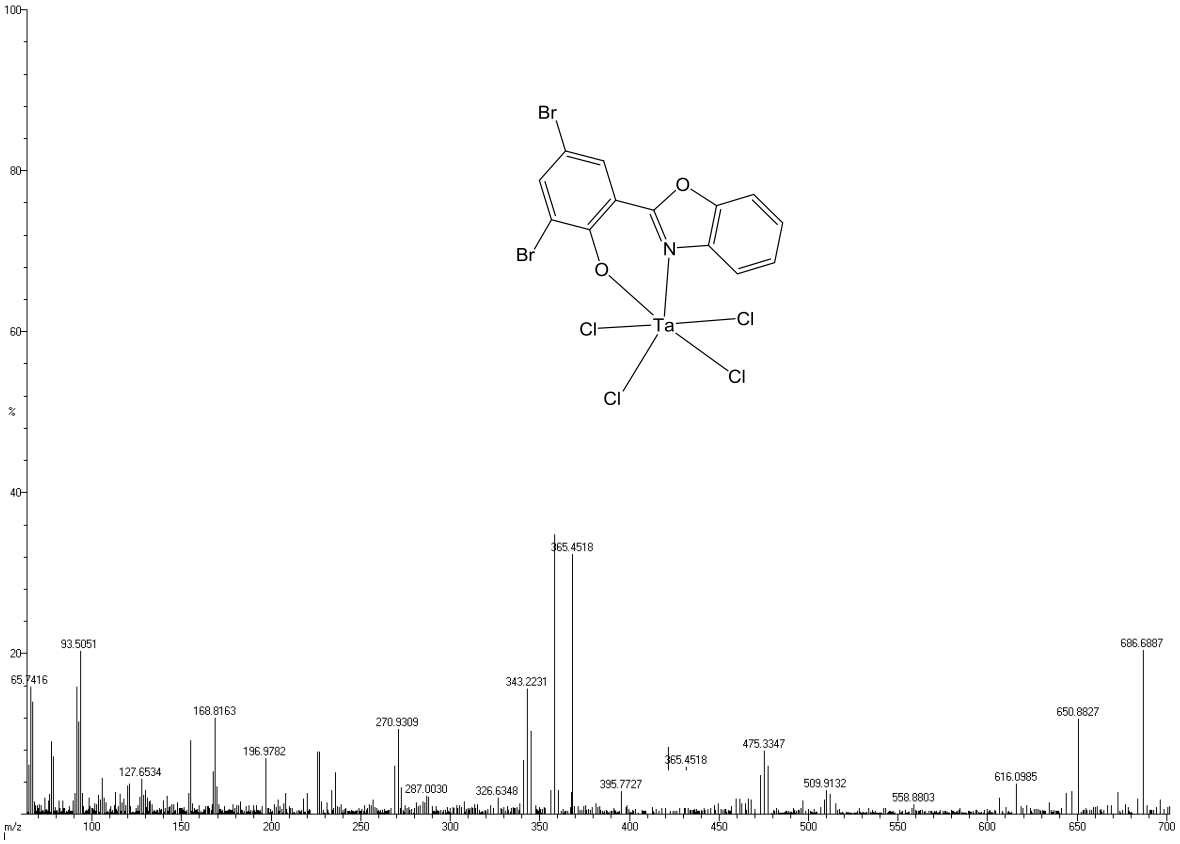

Fig. S45 ESI-Mass Spectrum of compound **6b**.

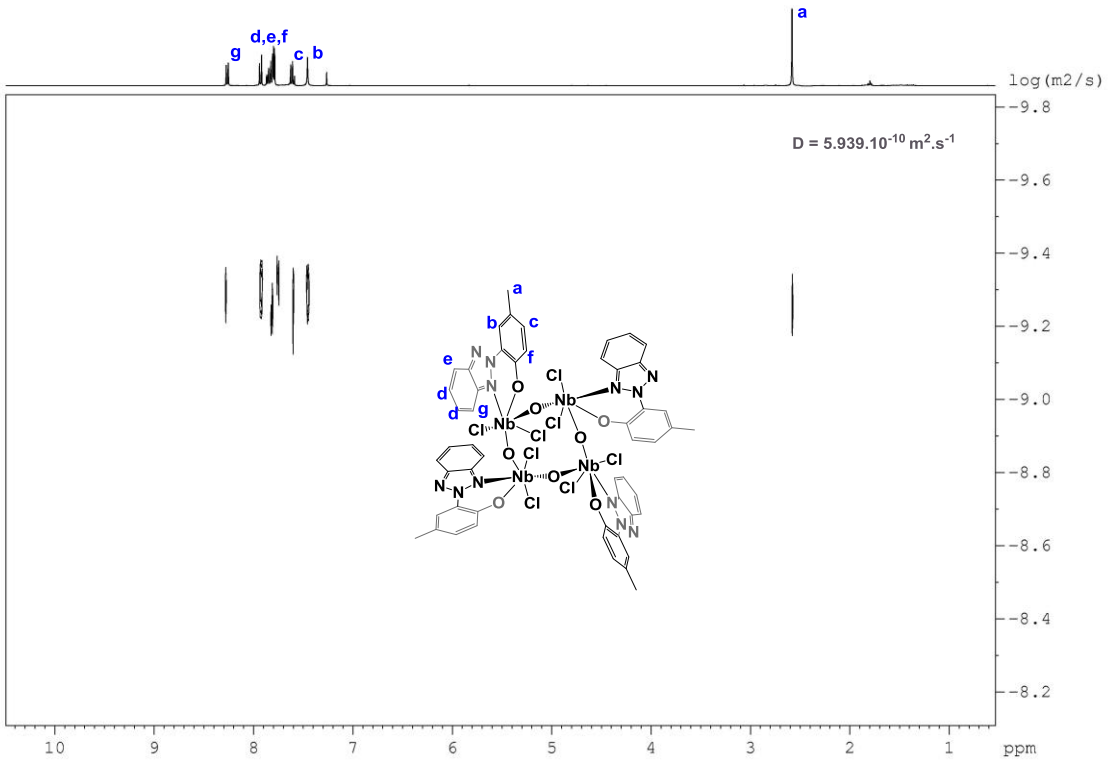

Fig. S46 ^{1}H DOSY NMR (500 MHz, $CDCl_3$) spectrum of **8a**.

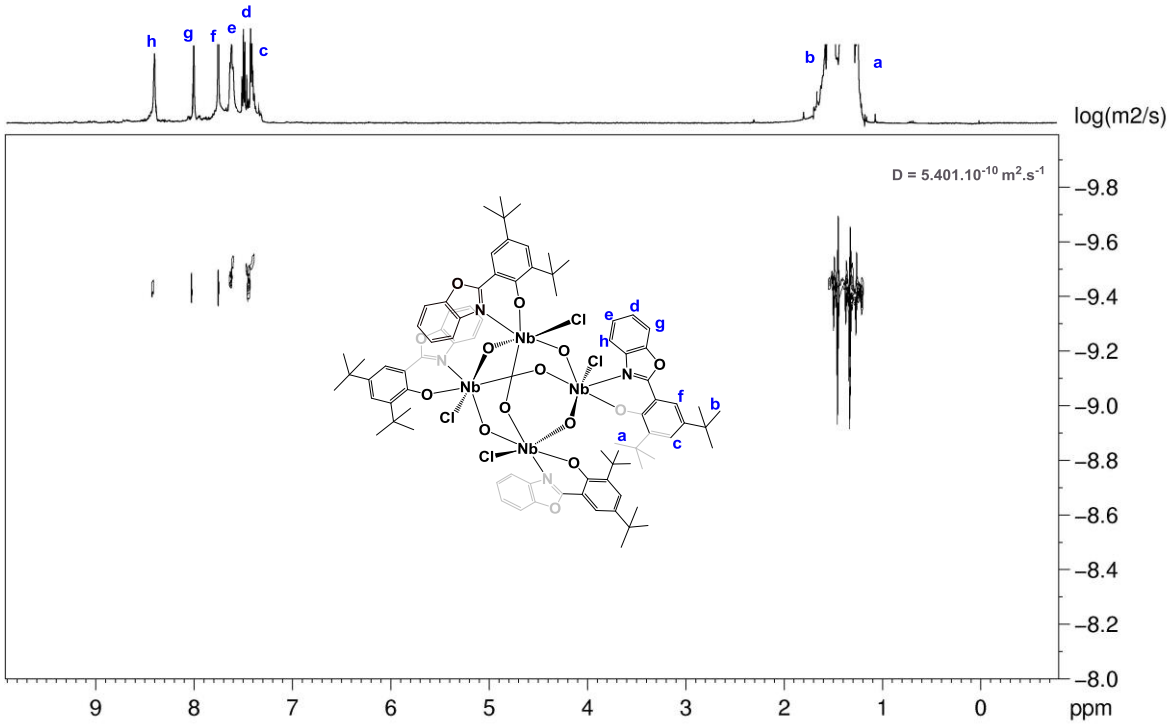

Fig. S47 ^{1}H DOSY NMR (500 MHz, $CDCl_3$) spectrum of **9a**.

General procedure for the calculation of hydrodynamic radius (R_H)

The hydrodynamic radius of **8a** and **9a** was calculated from the average diameter (d_{av}) of d_v (vertical), d_h (horizontal) and d_d (diagonal), obtained from the single crystal XRD structure (taking the measurement between the furthest atoms in each case).[1] The R_H value was then correlated with the value obtained from ^{1}H DOSY NMR spectrum.

$$R_H = d_{av}/2, \text{ where } d_{av} = (d_v + d_h + d_d)/3$$

Although we reported R_H calculated by the above procedure, there is another approach to the calculation. The minimum radius R_{min} can be calculated from the molecular volume determined from www.molinspiration.com by the formula $V_{mol} = (4\pi/3)R_{min}^3$. The maximum distance between the furthest atoms (d max) was obtained from single crystal XRD structure and the maximum radius was determined from d max . The hydrodynamic radius was then calculated from the average of R_{max} and R_{min}.[2] Both the approaches led to almost similar results.

References

1) S. Neogi, Y. Lorenz, M. Engeser, D. Samanta and M. Schmittel, *Inorg. Chem.* 2013, **52**, 6975−6984.

2) L. Azor, C. Bailly, L. Brelot, M. Henry, P. Mobian and S. Dagorne, *Inorg. Chem.*, 2012, **51**, 10876-10883.

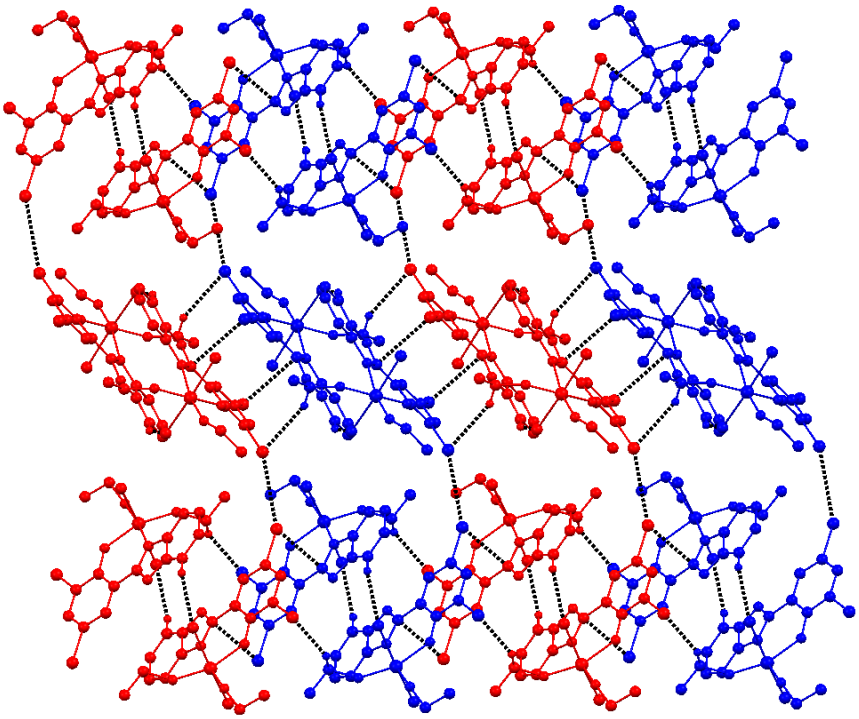

Fig S48. Expanded view of the unit cell of **7a**, the dimer representation with red and blue colours.

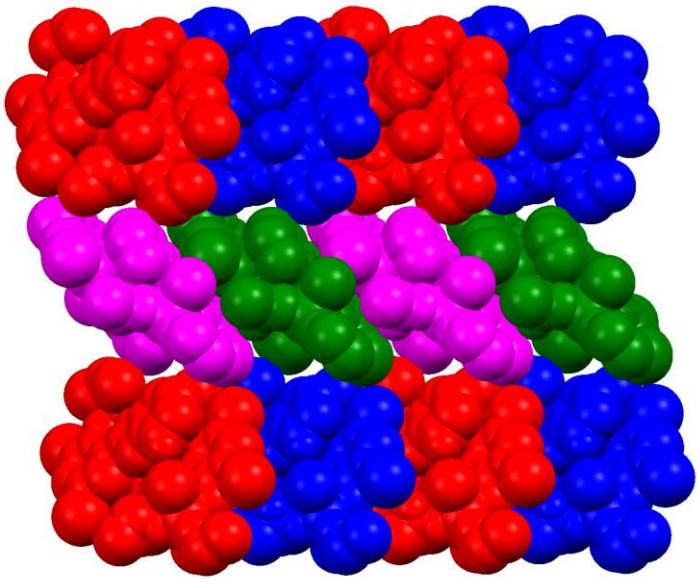

Fig S49. Expanded view of the unit cell of **7a**, showing the same orientation of alternative chains with red and blue colours.

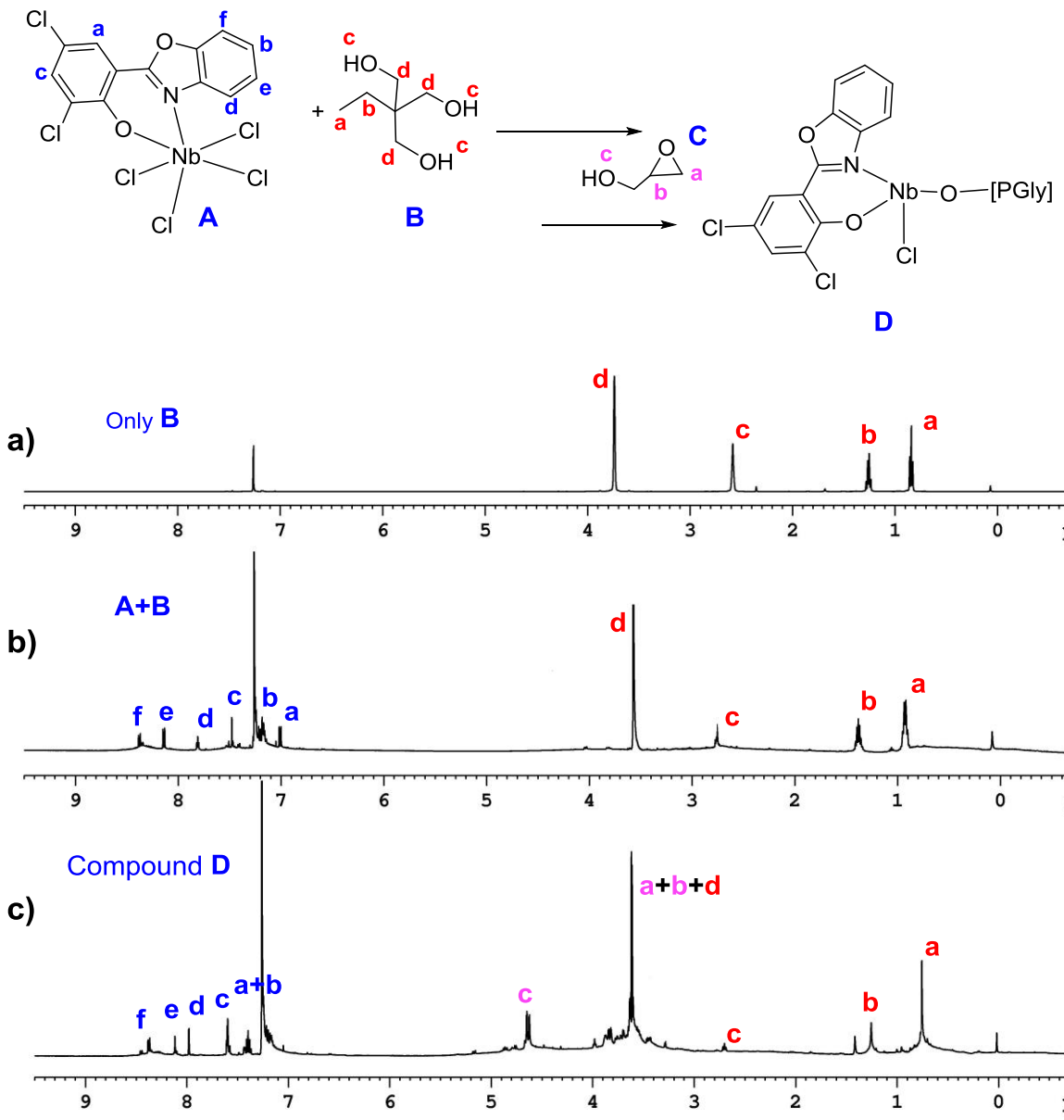

Fig. S50. ^{1}H NMR spectra (400 MHz, $CDCl_3$) of only 1,1,1-Tris(hydroxymethyl)propane (TMP) initiator and TMP reacted complex **5a** in 1:1 molar ratio (a, b) and oligomer species prepared using TMP reacted complex **5a (**1equiv**)** and glycidol (5 equiv) in dry toluene at 95 ^{o}C, 2 h (c).

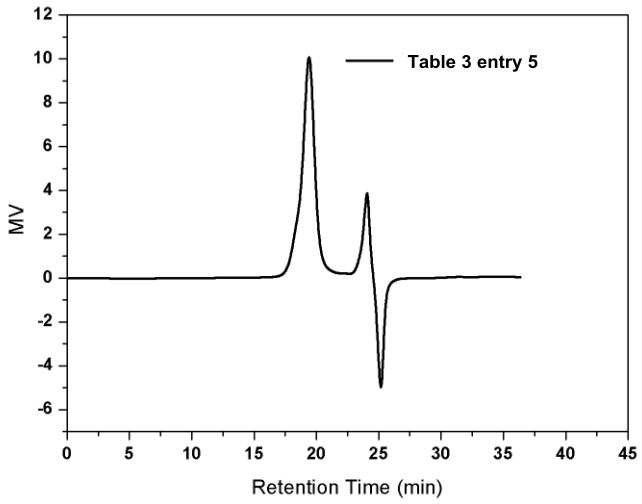

Fig. S51. GPC trace of polyglycerol using complex **5a**.

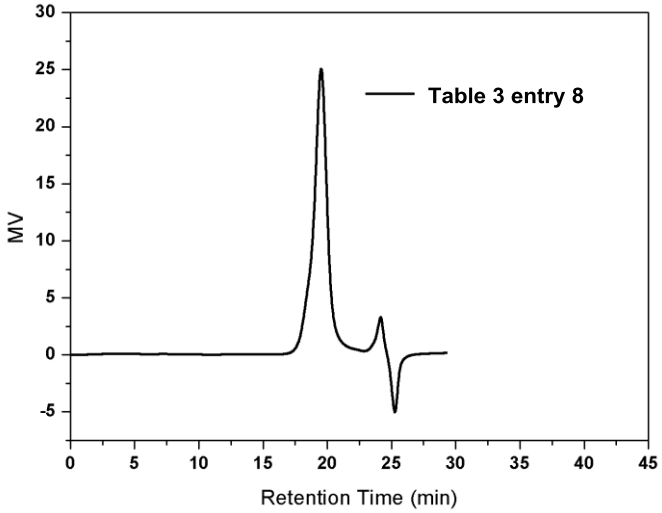

Fig. S52. GPC trace of polyglycerol using complex **6a**.

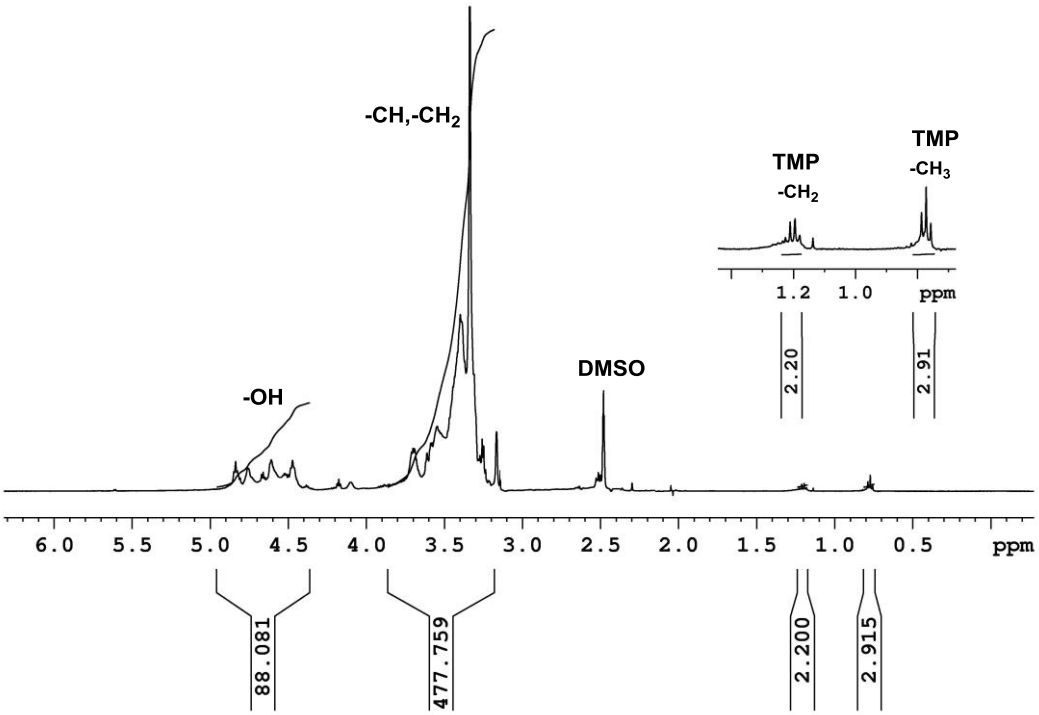

Fig. S53 ^{1}H NMR spectrum (400 MHz, CDCl3) of the polyglycerol obtained using complex **6a** in 100:1:1 molar ratio initiated with 1,1,1-tris(hydroxymethyl)propane (TMP).

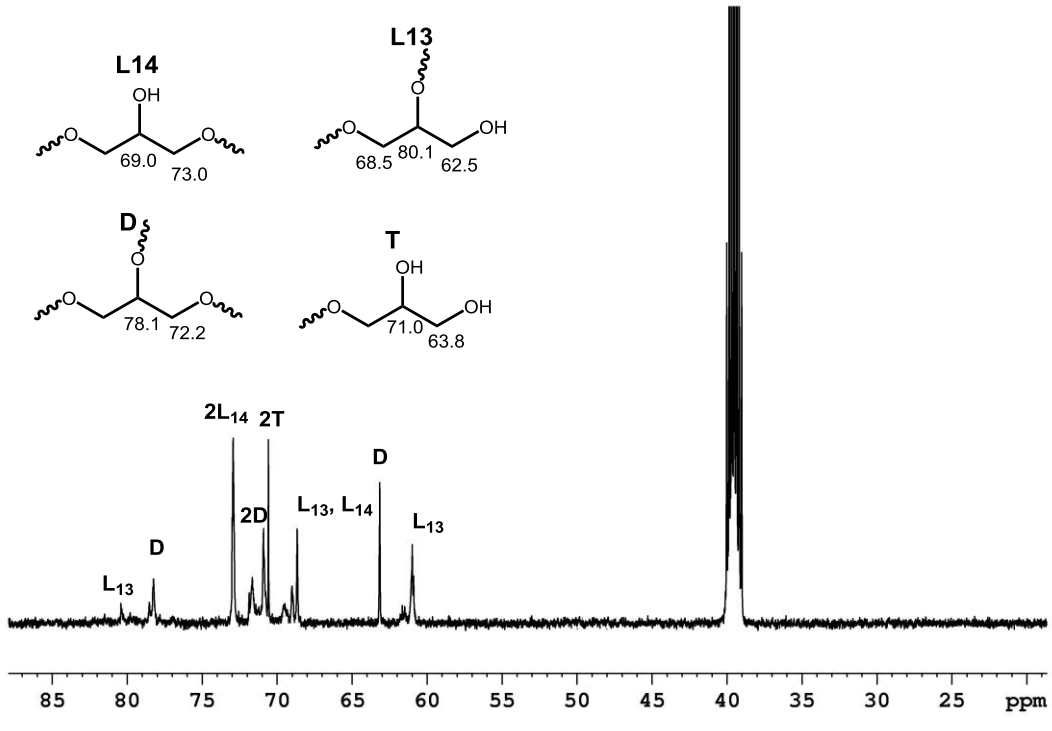

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Fig. S54 IG (Inverse Gated) ^{13}C NMR of hyperbranched polyglycerol synthesized using complex **6a** [L_{13}: Linear 1,3; L_{14}: Linear 1,4; D: Dendritic; T: Terminal].

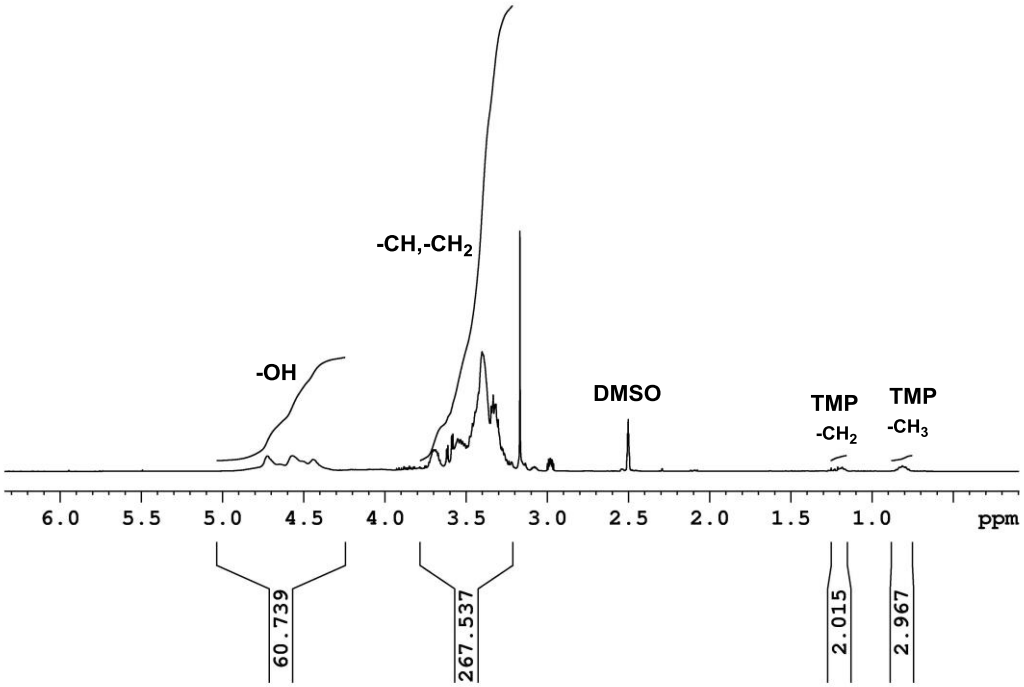

Fig. S55 ^{1}H NMR spectrum (400 MHz, CDCl3) of the polyglycerol obtained using complex **5b** in 100:1:1 molar ratio initiated with 1,1,1-tris(hydroxymethyl)propane (TMP).

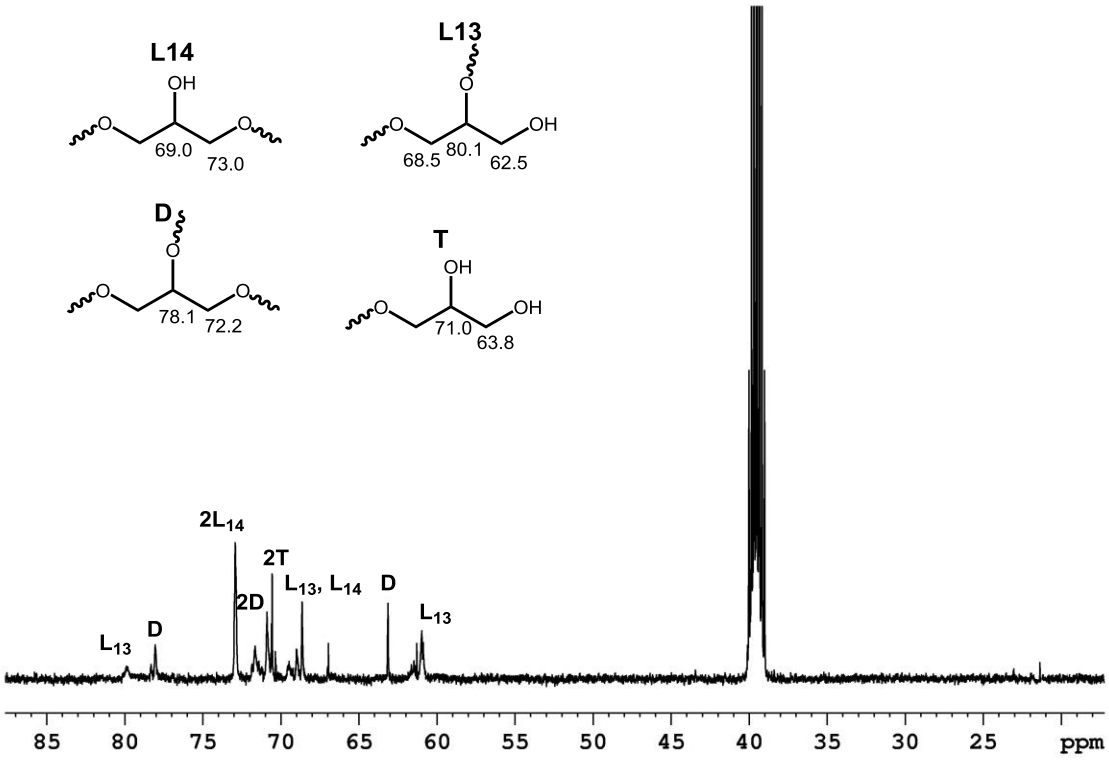

Fig. S56 IG (Inverse Gated) ^{13}C NMR of hyperbranched polyglycerol obtained using complex **5b** in 100:1:1 molar ratio [L_{13}: Linear 1,3; L_{14}: Linear 1,4; D: Dendritic; T: Terminal].

Table S1: Relative integrals of the different repeating units determined by inverse gated (IG) ^{13}C NMR spectroscopy and used for the calculation of the degree of branching.

Entry	Sample	$L_{1,3}$	$L_{1,4}$	D	T	DB
1	HPG polymer using **5a**	0.13	0.30	0.24	0.33	0.53
2	HPG polymer using **6a**	0.15	0.32	0.24	0.29	0.50
3	HPG polymer using **5b**	0.20	0.37	0.23	0.20	0.45
4	HPG polymer using **6b**	0.16	0.37	0.24	0.23	0.48
5	HPG polymer using **2b**	0.20	0.35	0.19	0.26	0.41
6	HPG polymer using **2a**	0.20	0.38	0.22	0.20	0.43

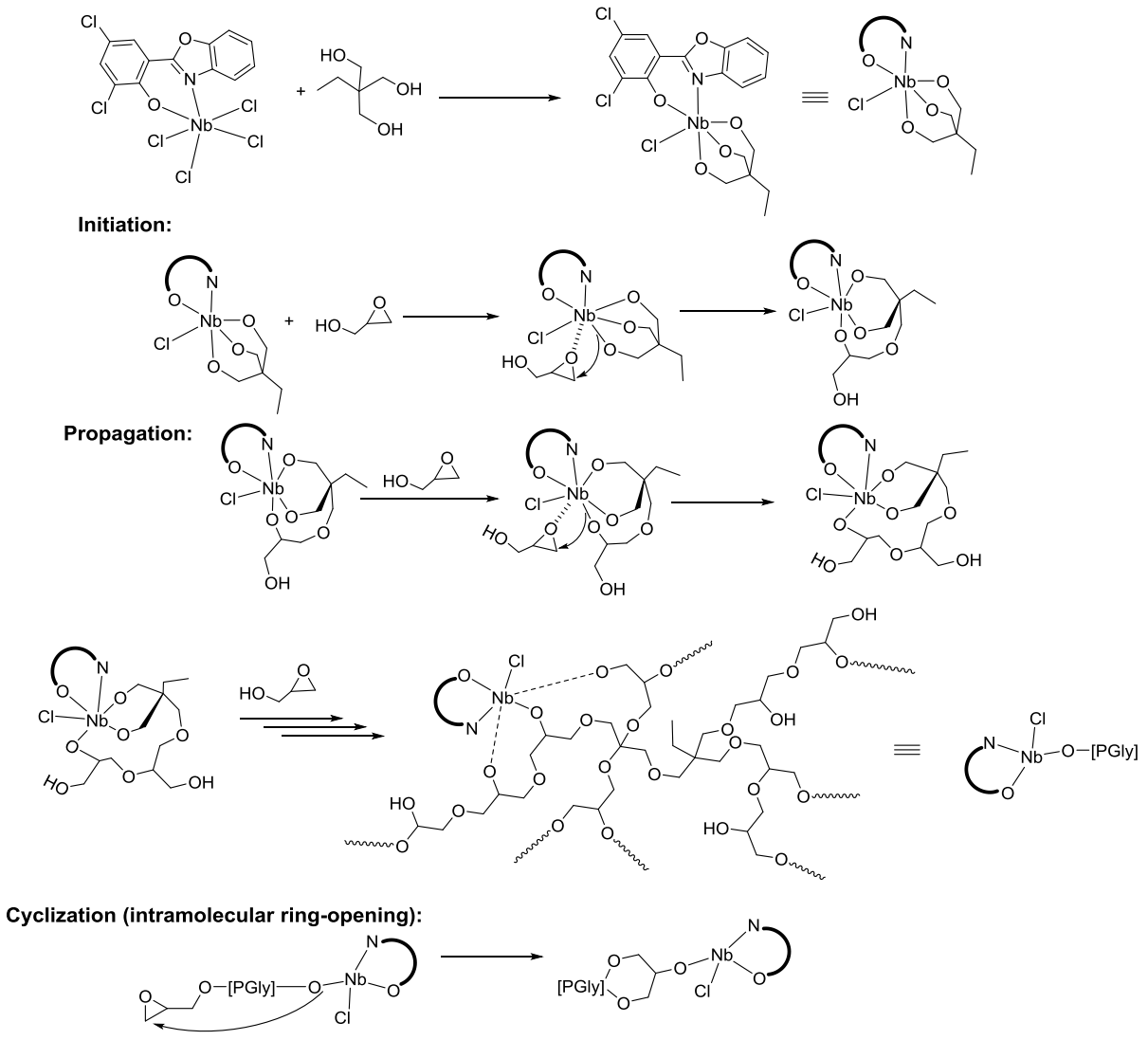

Fig. S57 Proposed mechanism for the initiation, propagation and cyclization reactions for the ROP of glycidol.

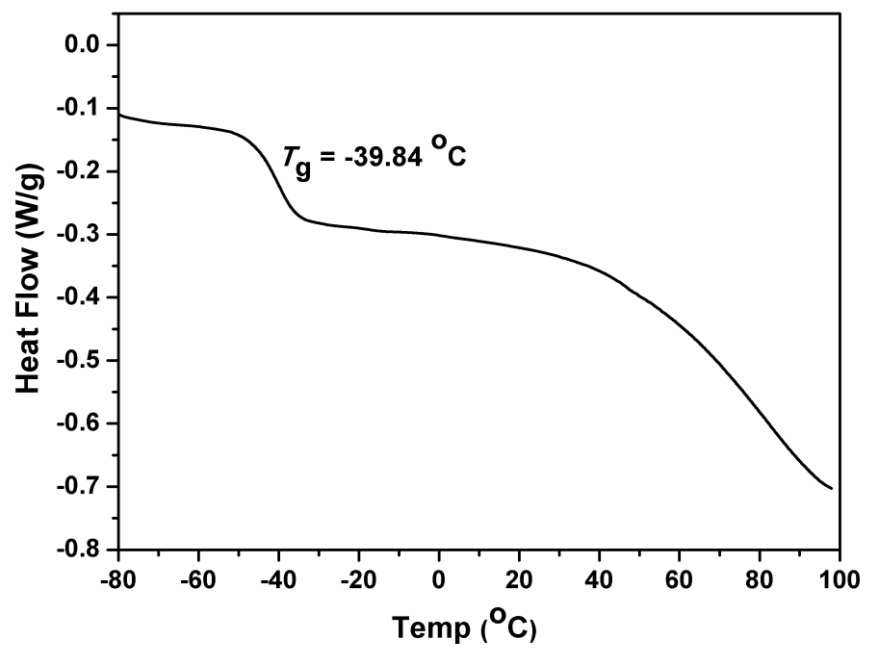

Fig. S58 DSC trace (heating rate: 10 °C/min, 2nd scan) of polyglycerol at 100:1:1 molar ratio (see Table 3, entry 17).

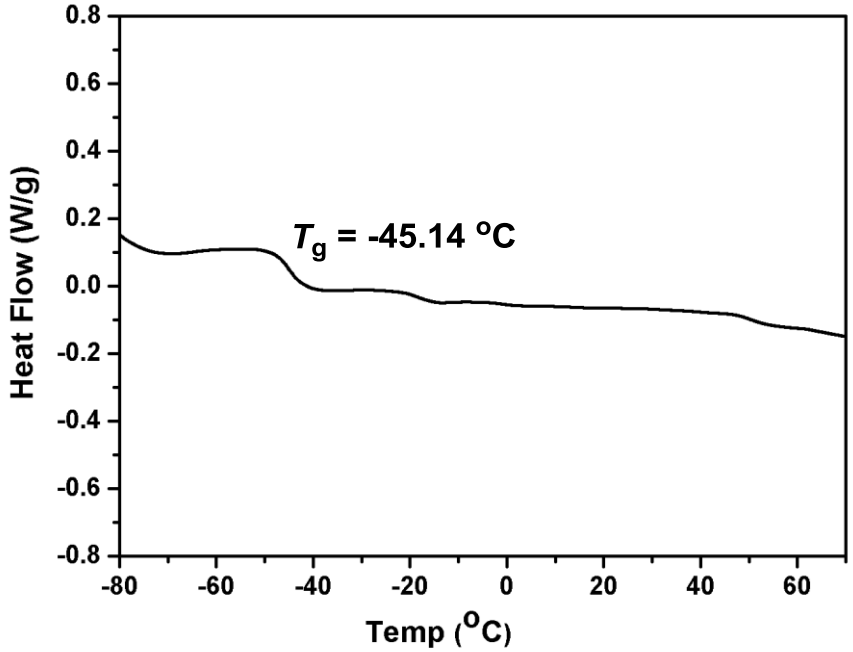

Fig. S59 DSC trace (heating rate: 10 °C/min, 2nd scan) of hyperbranched polyglycerol at 100:1:1 molar ratio (see Table 3, entry 18).