Supplementary information

A C_3 Symmetric Nitrate Complex with a Thiophene-Based Tripodal Receptor

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Synthesis

L: To a solution of 2-thiophene aldehyde (4.60 g, 41 mmol) in diethylether (50 mL) was added tris(2-aminoethyl)-amine (2.00 g, 13.7 mmol) in ethanol (50 mL). The mixture was stirred overnight at room temperature, and the solvent was evaporated. After diluting with methanol (100 mL), $NaBH_4$ (2.00 g) was added. The reaction mixture was stirred for another 24 hr. After evaporating the solvent, the residue was partitioned in water/CH_2Cl_2 (50/50 mL). The organic layers were collected and dried with $MgSO_4$ to give an oily product. Yield = 4.38 g (74%). ^{1}H NMR (500 MHz, CD_3Cl, TMS): δ7.106 (m, 3H, Ar), 6.856 (m, 3H, Ar), 6.815 (m, 3H, Ar), 3.873 (s, 6H, ArCH_2), 2.613 (t, *J = 5.8 Hz,* 6H, NCH_2CH_2), 2.497 (t, *J = 5.8 Hz,* 6H, NCH_2CH_2), ^{13}C NMR (125 MHz, CD_3Cl, TMS): δ144.1 (Ar), 126.7 (Ar), 125.0 (Ar), 124.4 (Ar), 54.3 (Ar-CH_2), 48.4 (NCH_2CH_2), 46.9 (NCH_2CH_2), MS (ESI) (*m*/*z*): $[M+1]^+$ calcd for $C_{21}H_{31}N_4S_3^+$, 435.2; found 435.2.

$[H_3\mathbf{L}(NO_3)](NO_3)_2$: The nitrate salt was prepared from the reaction of the free amine (0.20 g, 0.47 mmol) with HNO_3 in ethanol. The white precipitate was obtained after evaporation of the solvent. Crystals suitable for X-ray analysis were grown from slow evaporation of the aqueous solution of the salt. ^{1}H NMR (500 MHz, CD_3Cl, TMS): δ7.590 (m, 3H, Ar), 7.289 (m, 3H, Ar), 7.152 (m, 3H, Ar), 4.482 (s, 6H, Ar-CH_2), 3.143 (t, *J = 6.5 Hz,* 6H, NCH_2CH_2), 2.849 (t, *J = 6.5 Hz,* 6H, NCH_2CH_2), ^{13}C NMR (125 MHz, CD_3Cl, TMS): δ134.12 (Ar), 134.09 (Ar), 131.80 (Ar), 130.82 (Ar), 51.70 (Ar-CH_2), 47.87 (NCH_2CH_2), 46.04 (NCH_2CH_2).

$[H_3\mathbf{L}](TsO)_3$**:** The tosyl salt was prepared from the reaction of the free amine (0.20 g, 0.47 mmol) with *p*-Toluenesulfonic acid (0.27 g, 1.41 mmol) in methanol. The white precipitate was obtained after evaporation of the solvent. ^{1}H NMR (500 MHz, CD_3Cl, TMS): δ8.782 (bs, 6H, NH_2), 7.689 (d, *J = 8 Hz,* 6H, TsAr), 7.133 (d, *J = 5.0 Hz,* 3H, Ar), 7.089 (d, *J = 8 Hz,* 6H, TsAr), 6.949 (bs, 3H, Ar), 6.715 (m, 3H, Ar), 4.334 (s, 6H, Ar-CH_2), 3.493 (s, 6H, NCH_2CH_2), 3.190 (s, 6H, NCH_2CH_2), 3.303 (s, 9H, $TsCH_3$).

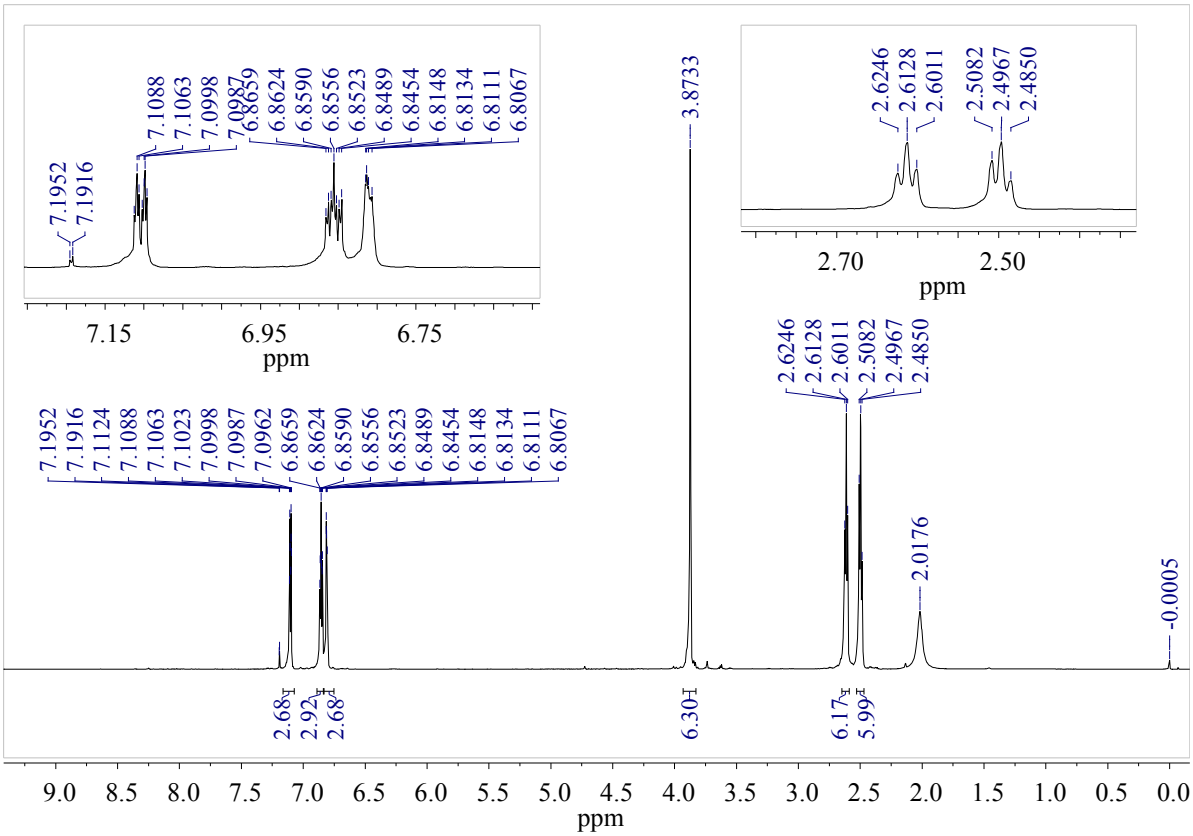

Figure S1. ^{1}H NMR spectra of **L**

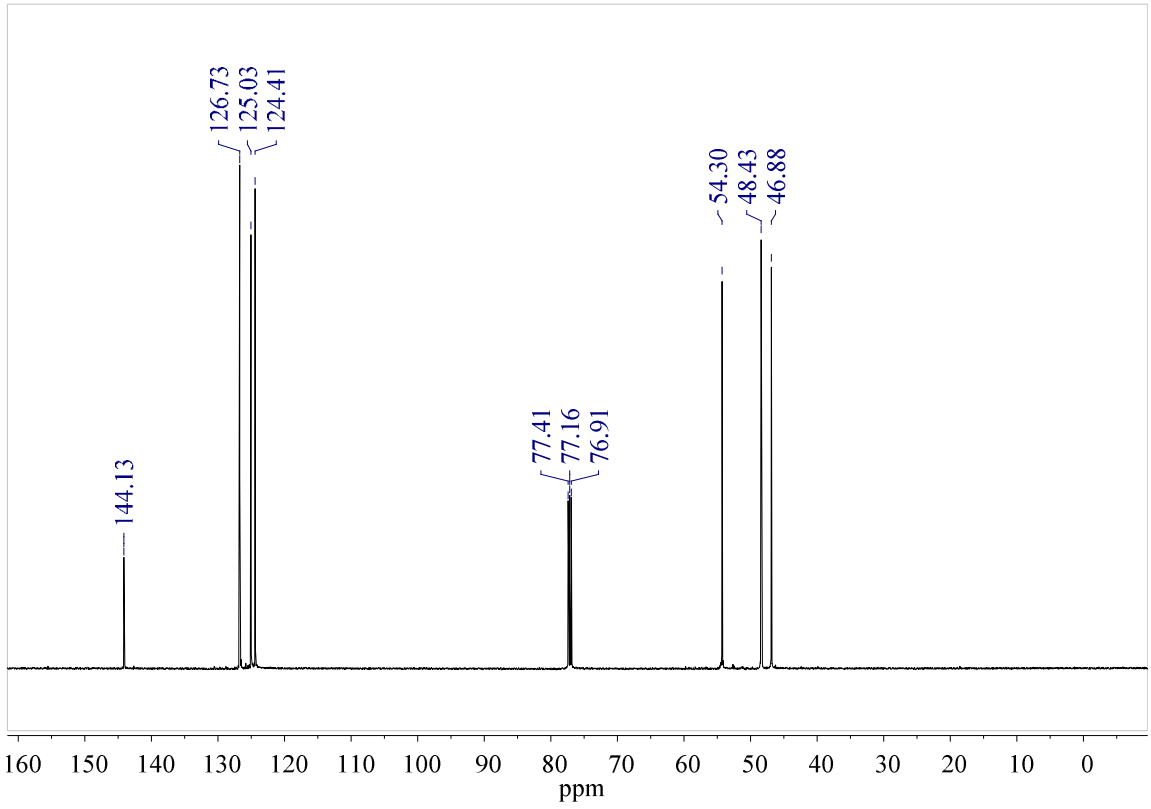

Figure S2.^{13}C NMR spectra of **L**.

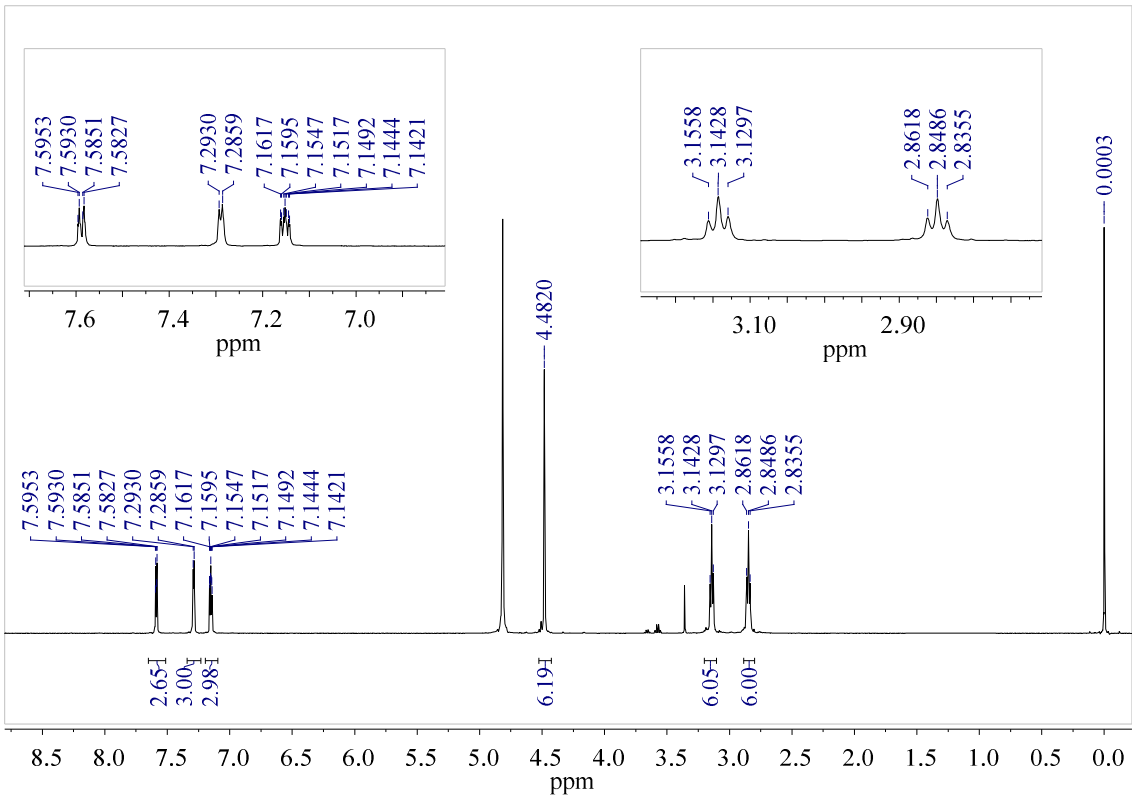

Figure S3. ^{1}H NMR spectra of $[H_3\mathbf{L}(NO_3)](NO_3)_2$.

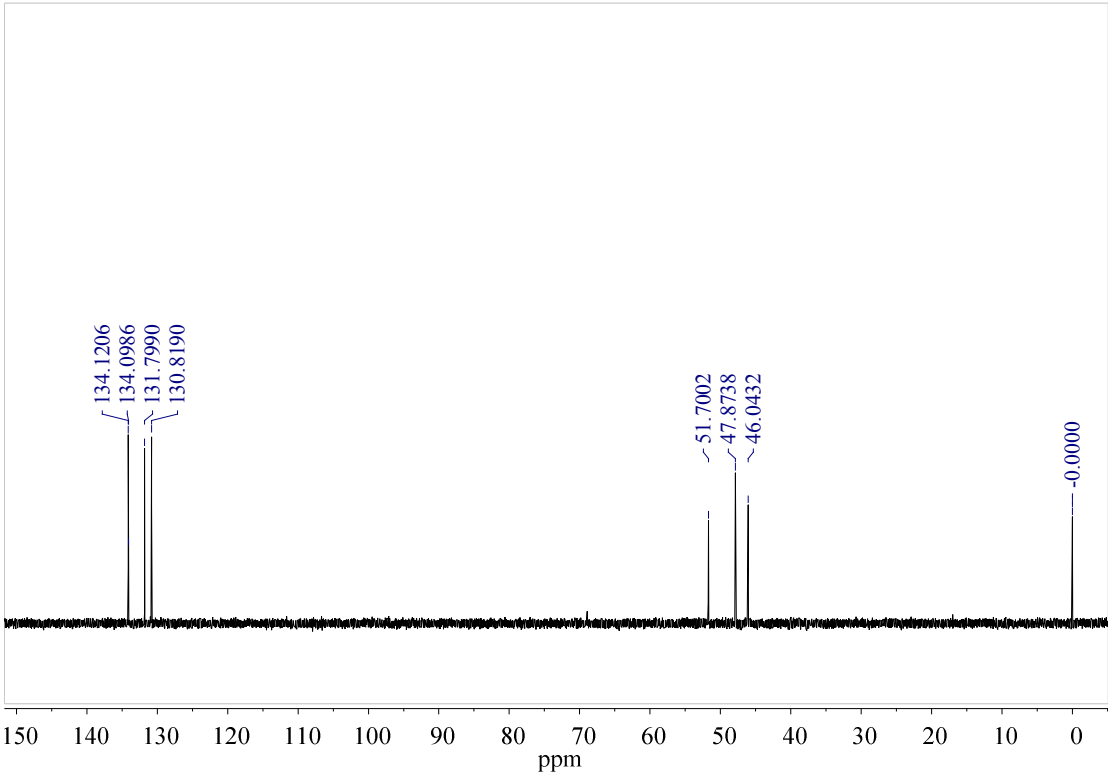

Figure S4.^{13}C NMR spectra of $[H_3\mathbf{L}(NO_3)](NO_3)_2$.

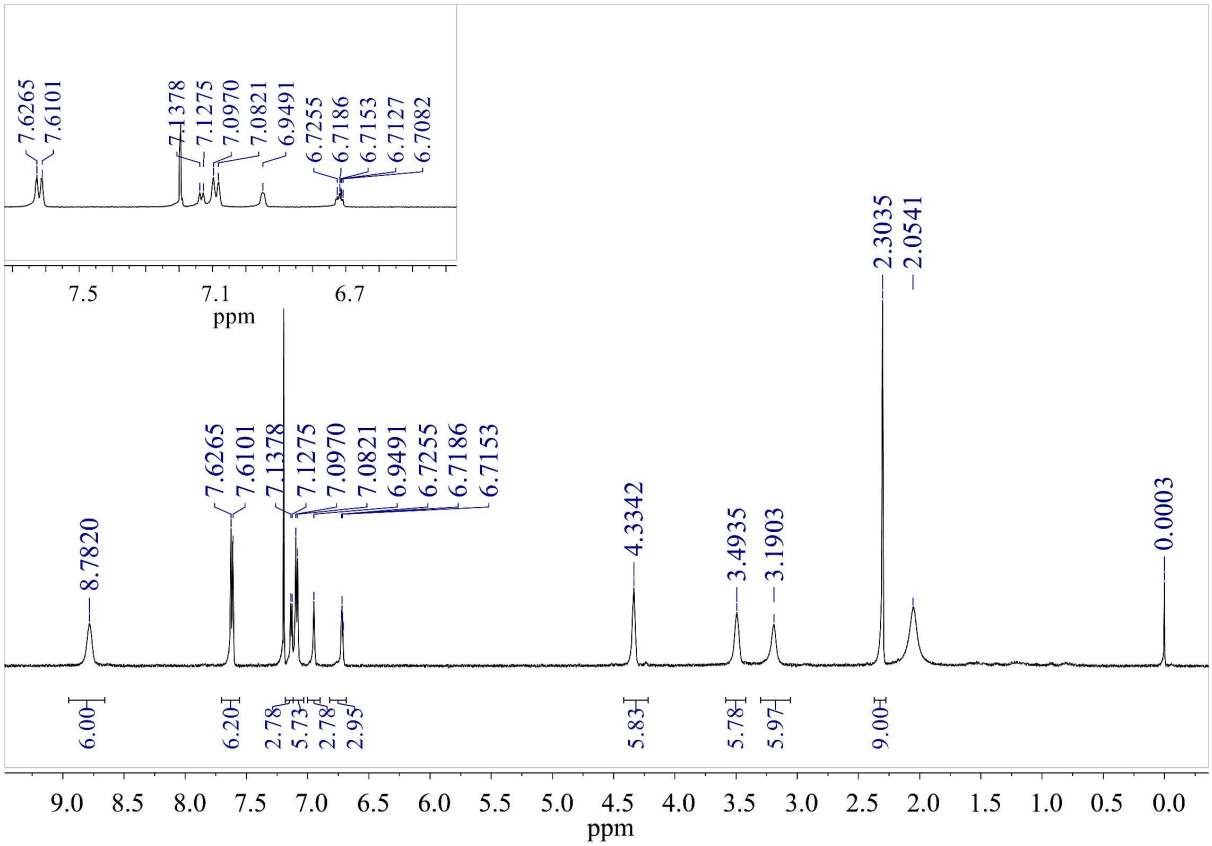

Figure S5. ^{1}**H** NMR spectra of [H_3**L**$(TsO)_3$].

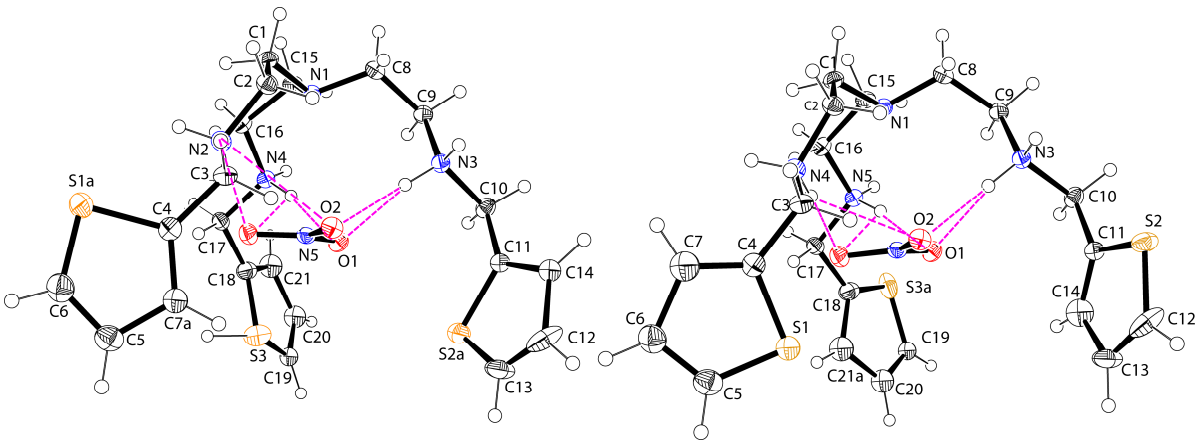

Figure S6. Ortep views of $[H_3\mathbf{L}(NO_3)]^{2+}$ motif showing two positions of thiophene units. In the two positions, all three thiophene units exhibit disorder over two positions related by approximate twofold rotations about C-C bonds linking them to aliphatic groups. The major component (shown left) has populations in the range 0.515(4) - 0.587(5).

Binding Constant (K)**:** Binding constants were obtained by ^{1}H NMR titrations of ligand **L** with tetrabutylammonium salts in $CDCl_3$. All the NMR measurements were carried out using the Varian 500 MHz at room temperature. Initial concentrations were $[\mathbf{L}]_0$ = 2 mM, and $[anion]_0$ = 20 mM. Each titration was performed by 14-16 measurements at room temperature. The association constant *K* was calculated using Sigma Plot software, from the equations: $\Delta\delta = ([A]_0 + [\mathbf{L}]_0 + 1/K - \{([A]_0 + [\mathbf{L}]_0 + 1/K)^2 - 4[\mathbf{L}]_0[A]_0\}^{1/2}) \Delta\delta_{max}/2[\mathbf{L}]_0$ (A = anion). The error limit in *K* was less than 10%.

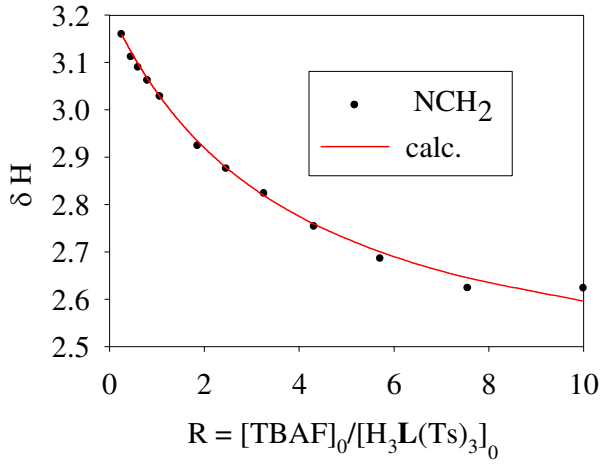

Figure S7. ^{1}H NMR titration curves of $[H_3\mathbf{L}](TsO)_3$ (2mM) with TBAF (20mM) in $CDCl_3$ at 298 K.

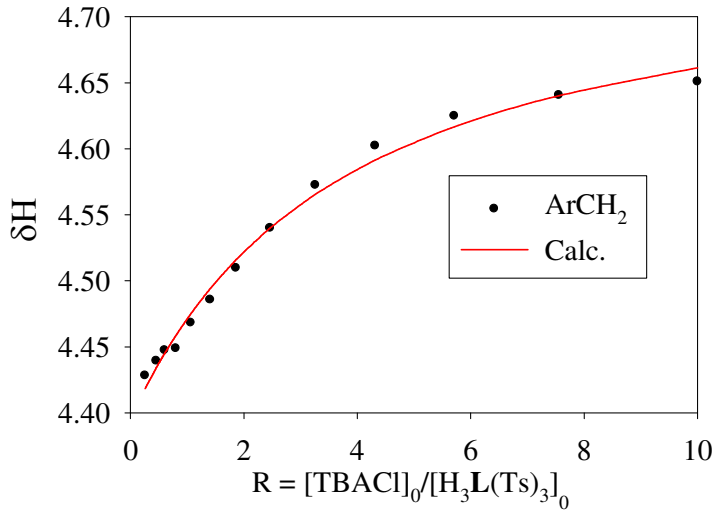

Figure S8. ^{1}H NMR titration curves of $[H_3\mathbf{L}](TsO)_3$ (2mM) with TBACl (20mM) in $CDCl_3$ at 298 K.

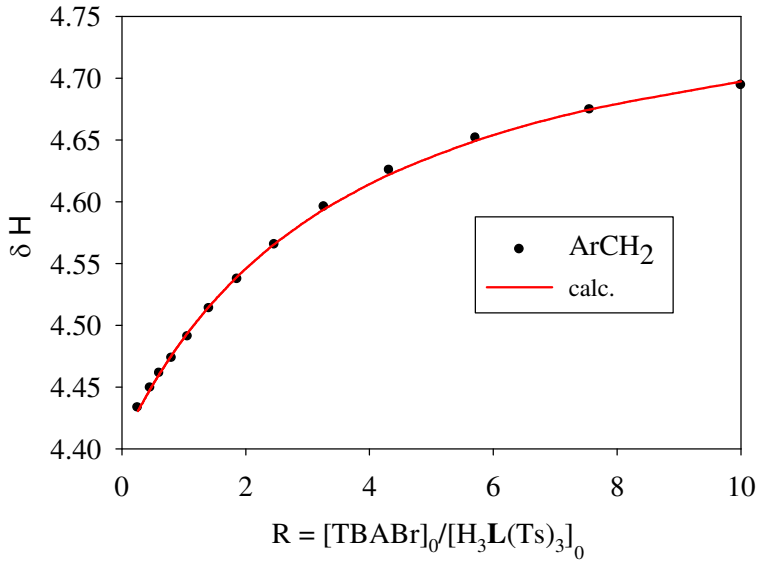

Figure S9. ^{1}H NMR titration curves of $[H_3\mathbf{L}](TsO)_3$ (2mM) with TBABr (20mM) in $CDCl_3$ at 298 K.

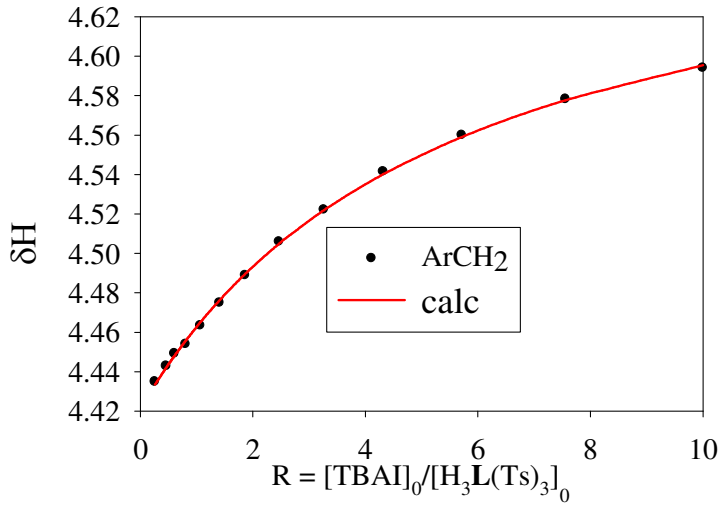

Figure S10. ^{1}H NMR titration curves of $[H_3\mathbf{L}](TsO)_3$ (2mM) with TBAI (20mM) in $CDCl_3$ at 298 K.

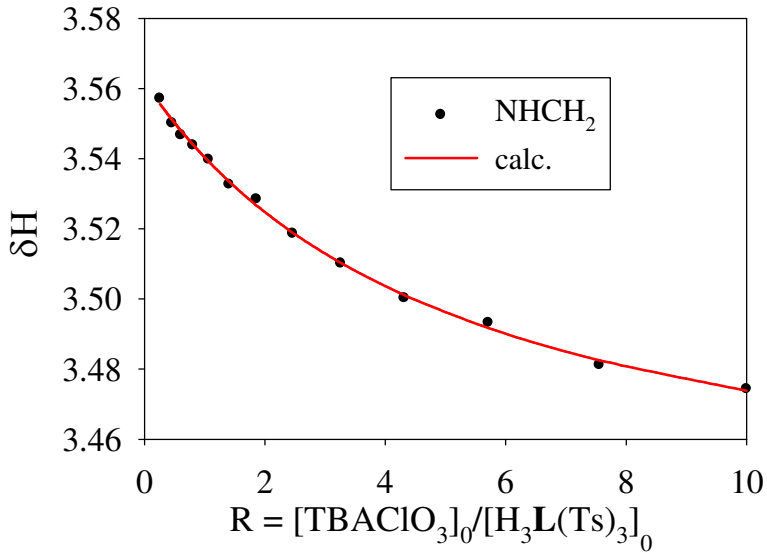

Figure S11. ^{1}H NMR titration curves of $[H_3\mathbf{L}](TsO)_3$ (2mM) with $TBAClO_4$ (20mM) in $CDCl_3$ at 298 K.