Supporting Information

Cl^- Anion-responsive luminescent Eu^{3+} complex with chiral tripode: ligand substitution effects on ternary complex stoichiometry and anion sensing selectivity

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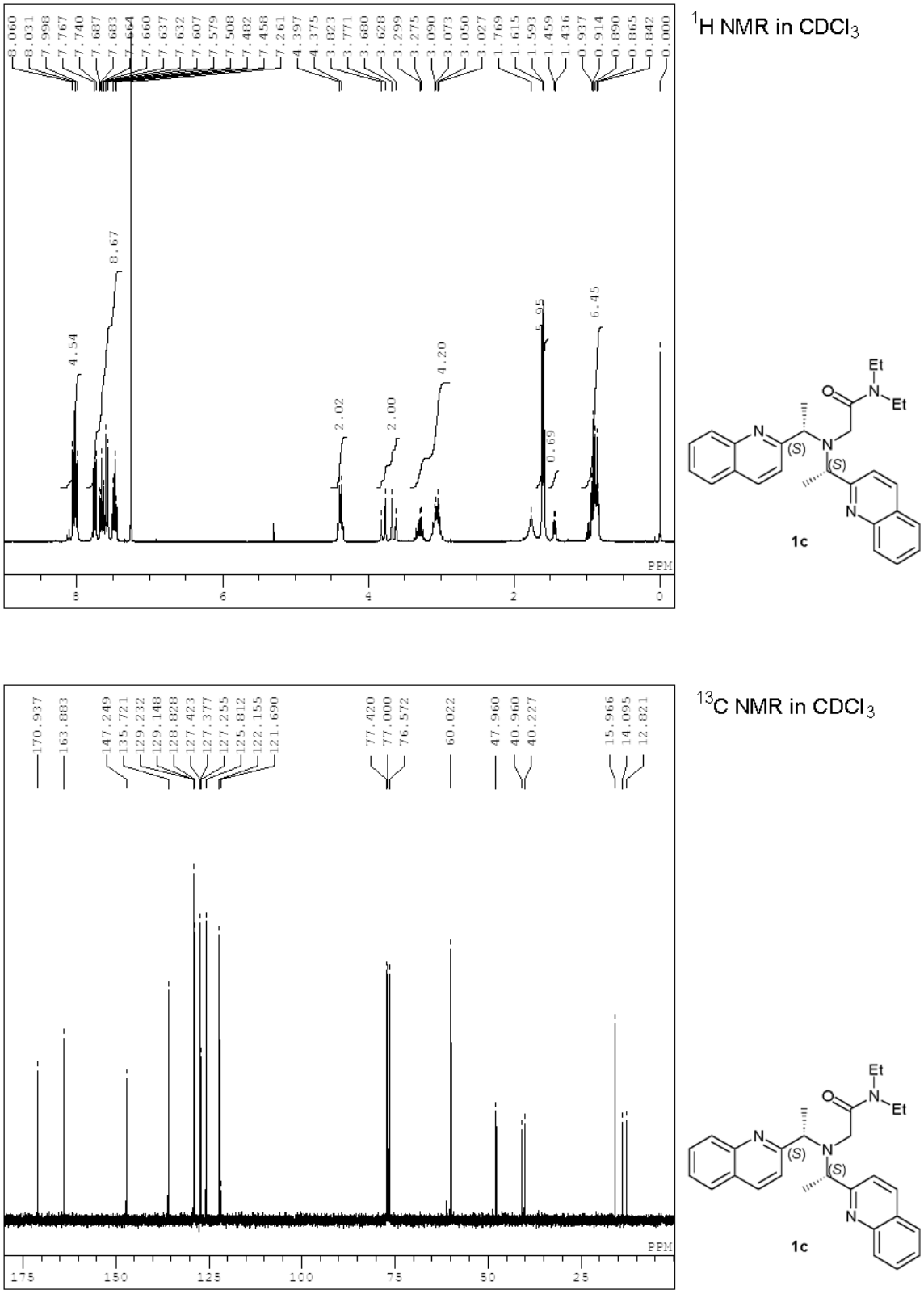
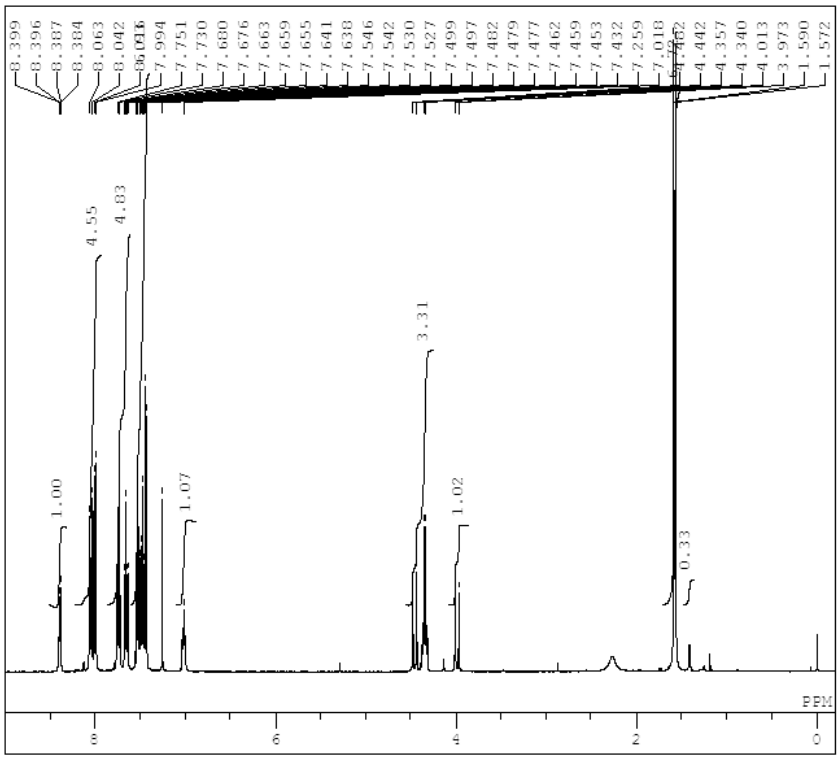


Figure S1. (a) ^{1}H and ^{13}C NMR spectra of tripode **1c**.



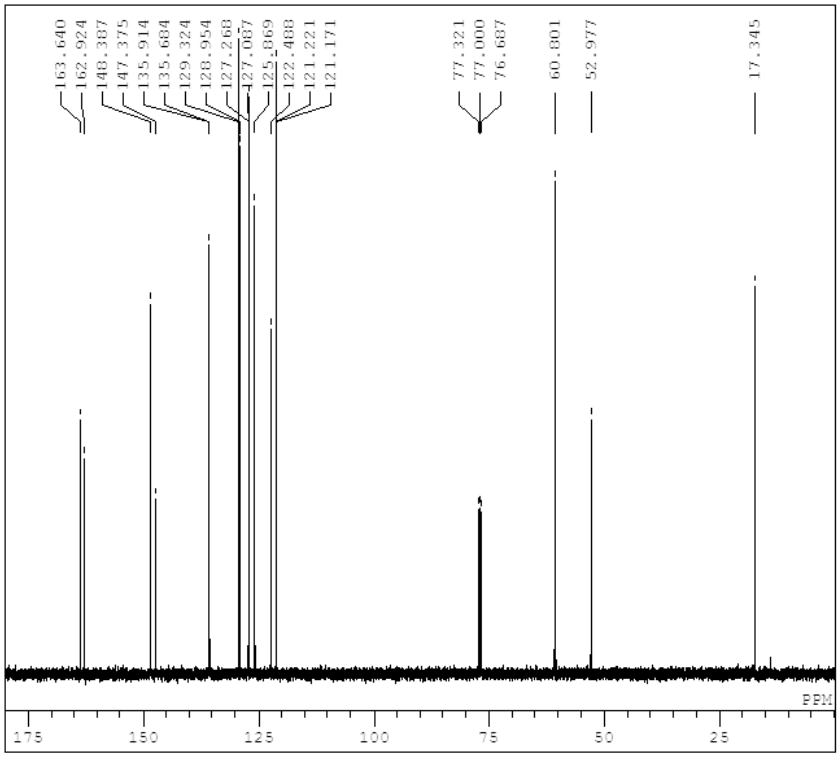


Figure S1. (b) ^{1}H and ^{13}C NMR spectra of tripode **2b**.

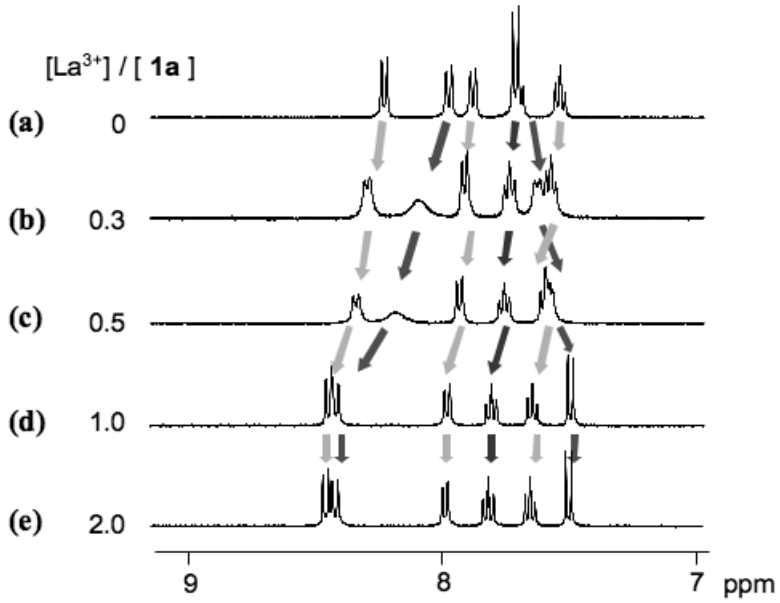


Figure S2. ^{1}H NMR titration of tripode **1a**–$La(NO_3)_3$.
Conditions: Tripode **1a**, 4.0×10^{-4} mol/L: $La(NO_3)_3$; (a) 0 eq.; (b) 0.30 eq., 1.2×10^{-4} mol/L; (c) 0.50 eq., 2.0×10^{-4} mol/L; (d) 1.0 eq., 4.0×10^{-4} mol/L; (e) 2.0 eq., 8.0×10^{-4} mol/L.

Details of Stability Constants Measurements

Ligands. **1a:** (*N,N*-Diethyl-2-{bis[(quinolyn-2-yl)methyl]-amino}ethanamide)
1b: (*(S)-N,N*-Diethyl-2-{bis[(quinolyn-2-yl)methyl]-amino}propanamide)
1c: (*(S,S)-N,N*-Diethyl-bis[1-(quinolyn-2-yl)ethyl]aminoethaneamide)
2a: (Bis(2-quinolylmethyl)(2-pyridylmethyl)amine)
2b: (Bis[1-(2-quinolylmethyl)ethyl](2-pyridylmethyl)amine)

Reagents and Solvent. The reagents and the solvent for measurements were purchased from the companies shown below and used without further purification.

Europium nitrate hexahydrate (99.9%): Nakarai Tesque Inc.
Lanthanum nitrate hexahydrate (99.9%): Nakarai Tesque Inc.
Terbium nitrate hexahydrate (99.9%): Mitsuwa Pure Chem Inc.
Europium chloride hexahydrate (99.9%): Sigma-Ardrich Inc.
Acetonitrile, fluorescence grade (99.8%) Nakarai Tesque Inc.

Titration experiments. UV absorption

Temperature Range. 25℃(±4)

Datum points. 15–18 points

Replicate Measurements. 2 –3 times

Determination of stepwise formation constants. The stepwise formation constants K_1 and K_2 for 1 : 1 and 1 : 2 (lanthanide : ligand) complexes are defined by eqs. (a) and (b):

$M + L = ML$
$ML + L = ML_2$ (M: lanthanide, L: ligand)

$K_1 = [ML] / [M][L]$ ..... (a)
$K_2 = [ML_2] / [ML][L]$ ..... (b)

The total concentration of ligand, L_t, was kept constants during titration experiments and the total concentration of metal ion, M_t, increased. The absorbance was plotted against the molar ratio $X = M_t / L_t$. The absorbance at the region of X (from 0 to 3) was well reproduced by assuming only two complex species (ML_1 and ML_2).

The total concentrations of L_t and M_t are expressed as eqs. (c) and (d):

$M_t = [M] + [ML] + [ML_2]$ .....(c)
$L_t = [L] + [ML] + 2[ML_2]$ ..... (d)

From the eqs. (a) ~ (d), the equilibrium concentrations of free ligand [L] and other species [M], [ML], [ML_2] are obtained by solving the following equations:

$K_1K_2 [L]^3 + (K_1 + K_1K_2L_t + 2K_1K_2L_tx) [L]^2 + (1 – K_1L_t + K_1L_tx) [L] – L_t = 0$
$[M] = L_tx / (1 + K_1[L] + K_1K_2[L]^2)$
$[ML] = K_1[M][L]$
$[ML_2] = K_1K_2[M][L]^2$

When the absorbance was measured in a 1-cm quartz cell, the concentration of all species can be expressed as follow:

$Abs = \varepsilon_{ML}[ML] + \varepsilon_{ML2}[ML_2] + \varepsilon_L[L] + \varepsilon_M[M]$

where ε_y is the molar absorption coefficient (in L mol^{-1} cm^{-1}) of the species y. To fit the titration curve, we treated the following values as variables to be determined: K_1, K_2, ε_{ML} and ε_{ML2}, while ε_L and ε_M were experimentally determined and used as constants for the curve-fitting.

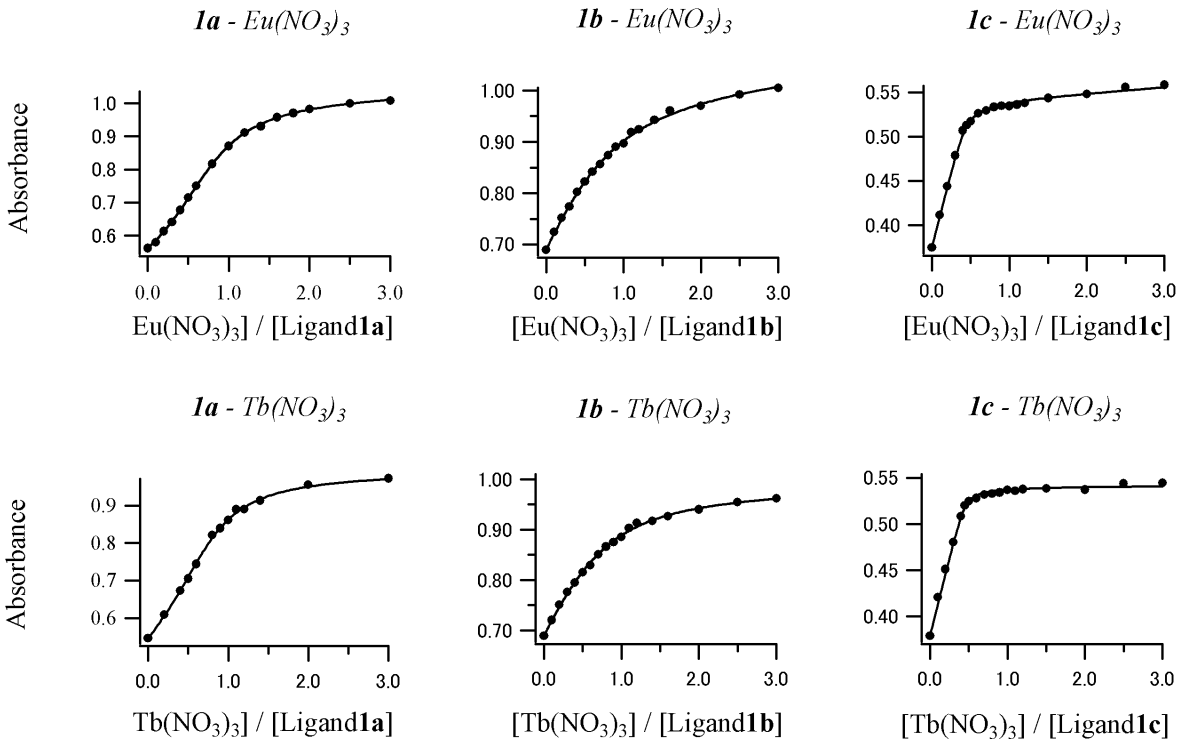


Figure S3. UV titration curves of $Ln(NO_3)_3$ complexes with tripode **1a**–**1c**: solid line, simulation; dots, measurements.
Conditions: Tripode **1a**, 1.0×10^{-4} mol/L; $Ln(NO_3)_3$, $0.10\sim3.0 \times 10^{-4}$ mol/L (0.10~3.0 eq.), plotted at 307 nm: **1b**, 1.4×10^{-4} mol/L; $Ln(NO_3)_3$, $0.14\sim4.2 \times 10^{-4}$ mol/L (0.10~3.0 eq.), plotted at 298 nm: **1c**, 0.80×10^{-4} mol/L; $Ln(NO_3)_3$, $0.080\sim2.4 \times 10^{-4}$ mol/L (0.10~3.0 eq.), plotted at 298 nm.

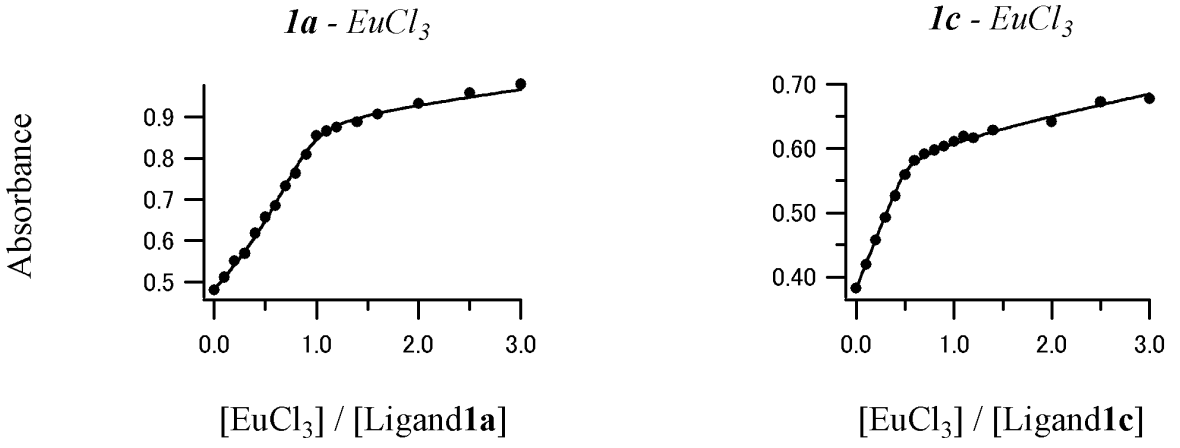
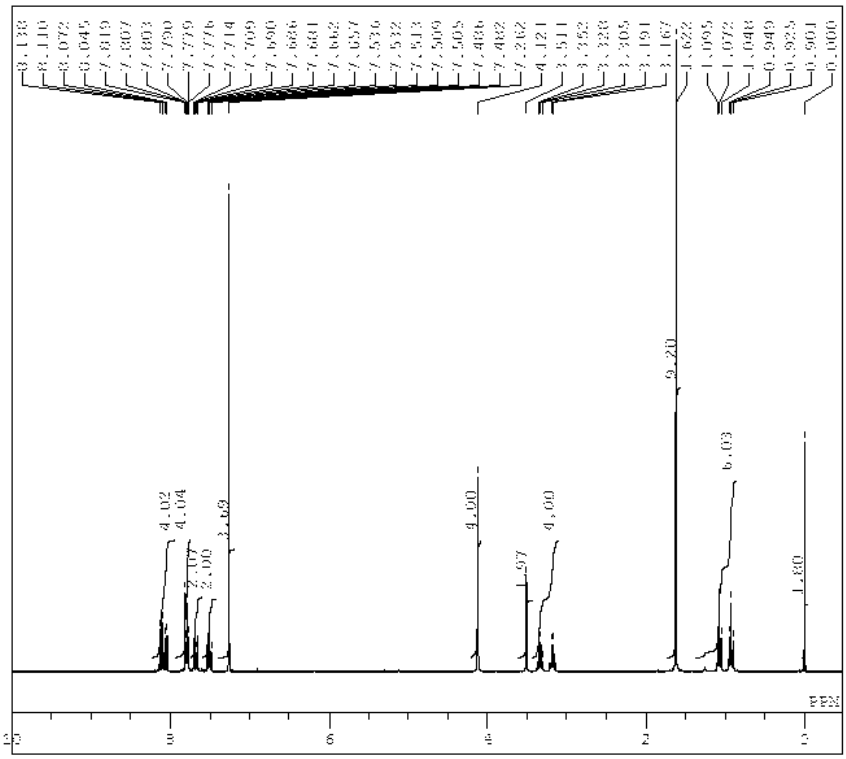


Figure S4. UV titration curves of $EuCl_3$ complexes with tripodes **1a**, **1c**: solid line, simulations; dots, measurements.
Conditions: Tripode **1a**, 1.0×10^{-4} mol/L; $EuCl_3$, $0.10\sim3.0 \times 10^{-4}$ mol/L (0.10~3.0 eq.), plotted at 298nm: **1c**, 0.80×10^{-4} mol/L; $EuCl_3$, $0.080\sim2.4 \times 10^{-4}$ mol/L (0.10~3.0 eq.), plotted at 298nm.



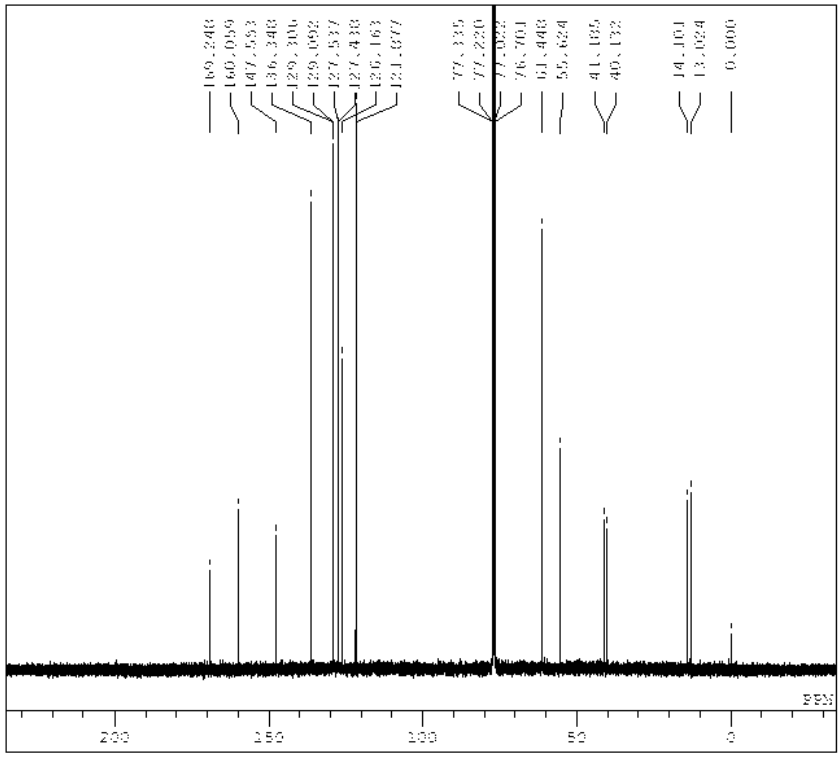
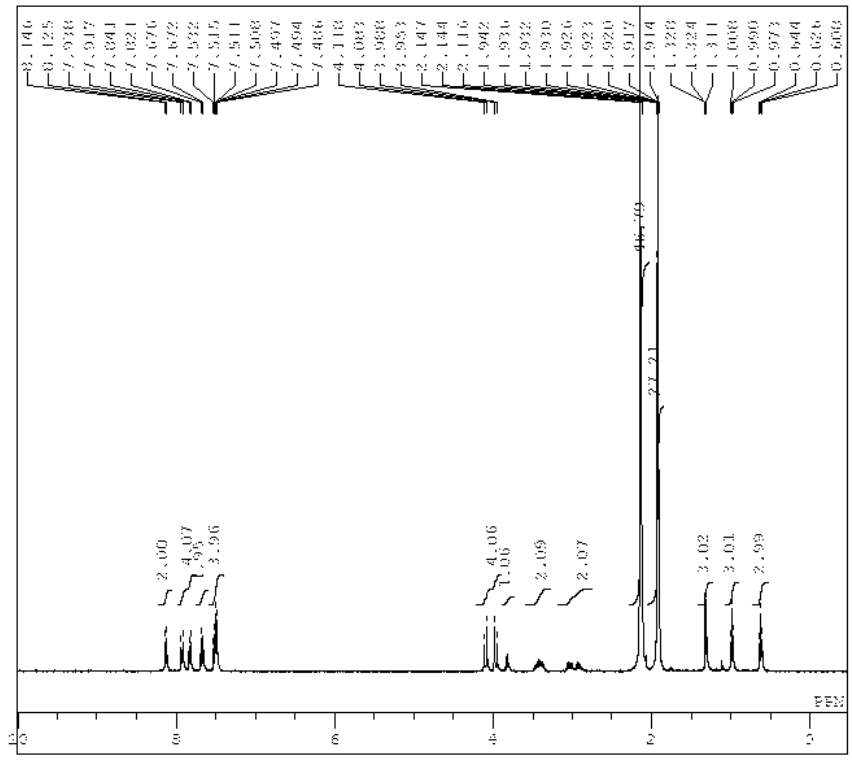


Figure S5. (a) ^{1}H and ^{13}C NMR spectra of tripode **1a**.



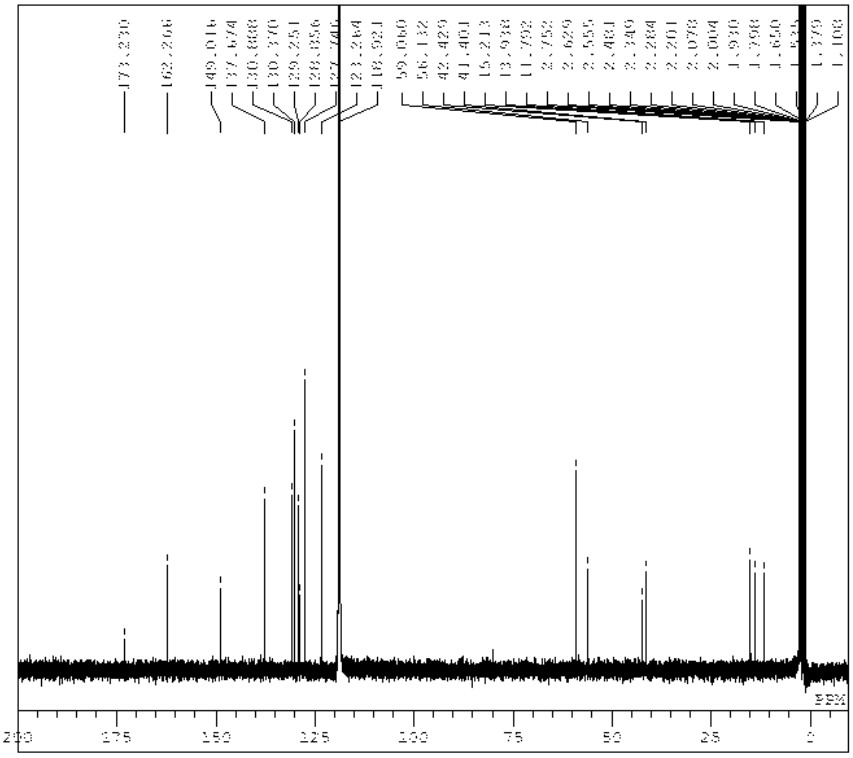


Figure S5. (b) ^{1}H and ^{13}C NMR spectra of tripode **1b**.