Electronic Supplementary Material (ESI) for RSC Advances.

Acid-induced formation of hydrogen-bonded double helix based on chiral polyphenyl-bridged bis(2,2'-bipyridine) ligands

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Supporting information

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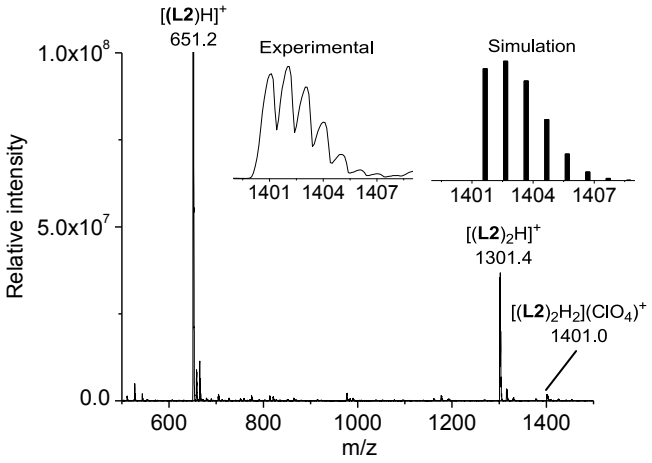
ESI-MS spectra of L2–4 with addition of $HClO_4$



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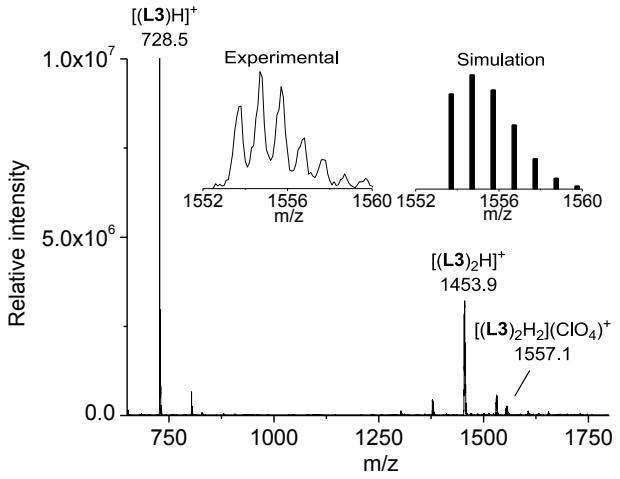

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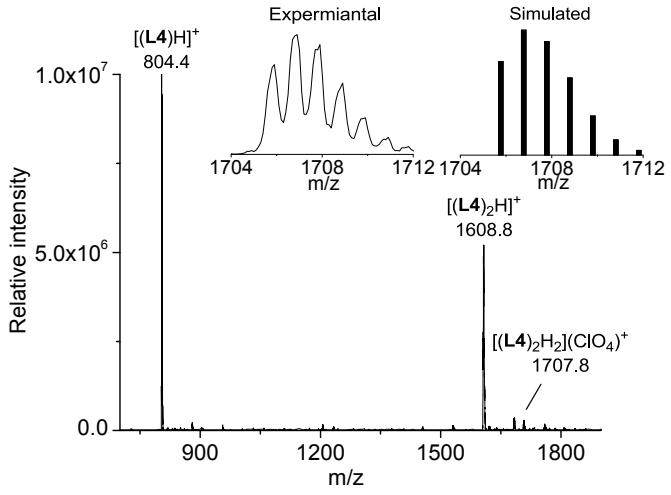


(c)

Figure S1 ESI-MS spectrum of a CH_2Cl_2 solution of **L2–4** with addition of $HClO_4$, inset shows the isotopic distribution of $[(\mathbf{L})_2H_2](ClO_4)^+$ (**L** = **L2–4**)

CD spectra of titration experiments of L2–4 with $HClO_4$

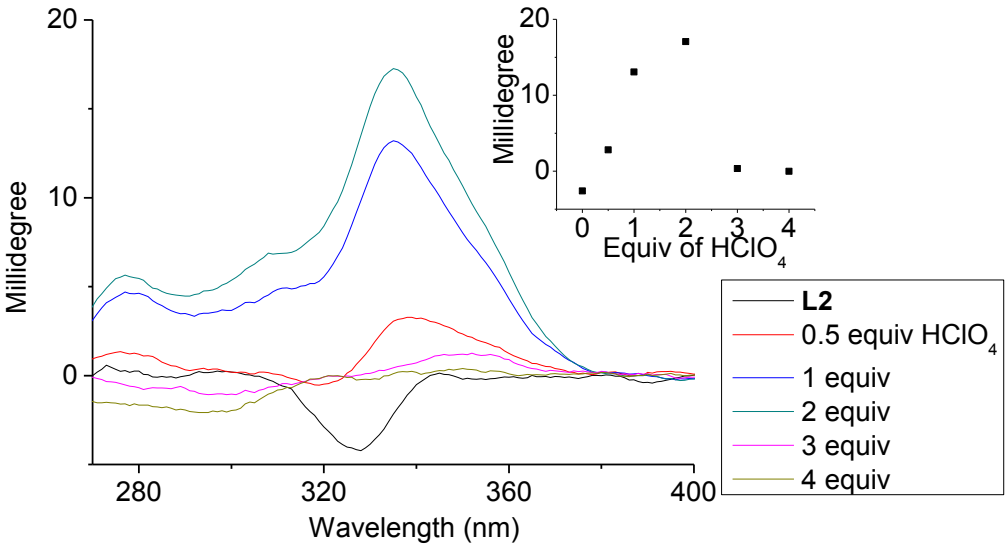


Figure S2 CD spectrum of **L2** in CH_2Cl_2 (3×10^{-4} M) with addition of $HClO_4$ (0 to 4 equiv). The inset shows the change in absorption at 334 nm.

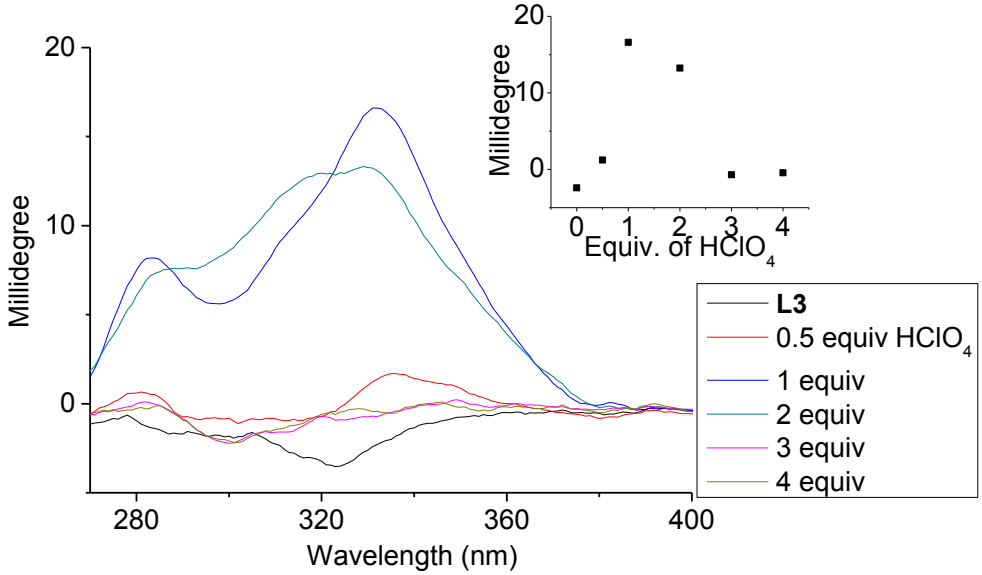


Figure S3. CD spectrum of **L3** in CH_2Cl_2 (3×10^{-4} M) with addition of $HClO_4$ (0 to 4 equiv). The inset shows the change in absorption at 331 nm.

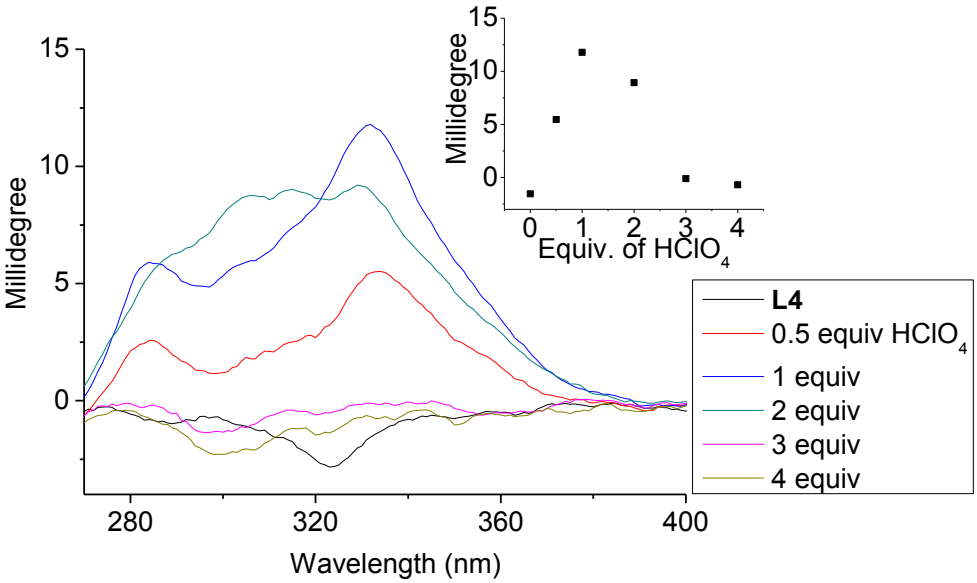


Figure S4 CD spectrum of **L4** in CH_2Cl_2 (3×10^{-4} M) with addition of $HClO_4$ (0 to 4 equiv). The inset shows the change in absorption at 332 nm.

Line-shape analysis on the VT ^{1}H NMR experiments

Analysis of the linewidth of the signals at temperature below coalescence give the exchange rate, k, by using equation (1).[1,2]

$$W_{obs} = W_0 + W_e \text{……..(1)}$$

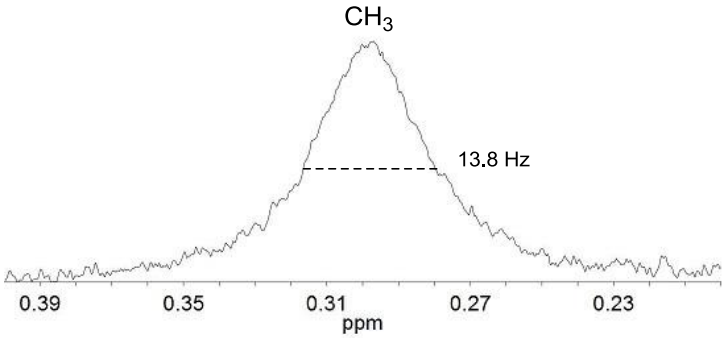
Where W_{obs} is the half height width observed of the broadened signal, W_o is the half height width when there is not exchange, which W_{obs} and W_o are measured experimentally (figure S5–7), and W_e is the composition of half height width come from the exchange which $W_e = k/\pi$

For **L2**, $k_{L2} = (13.8-4)\pi = 31\ s^{-1}$ at −20°C
For **L3**, $k_{L3} = (8.4-3.6)\pi = 15\ s^{-1}$ at −20°C
For **L4**, $k_{L4} = (6.6-2.7)\pi = 12.3\ s^{-1}$ at −10°C

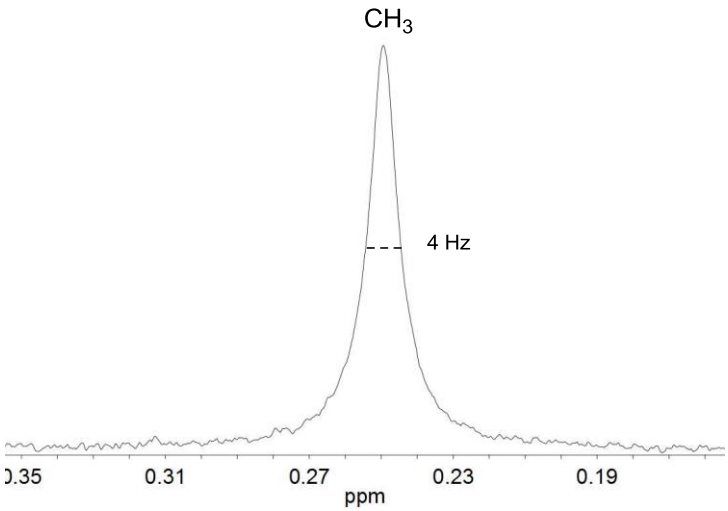
With the exchange rate, the free energy of activation was calculated by using the equation (2)[3]

$$\Delta G^{++} = aT[10.319 + \log(T/k)],\ a = 4.575*10^{-3}\ \text{kcalmol}^{-1} \quad (2)$$

For **L2**, $\Delta G^{++} = 13.0\ \text{kcalmol}^{-1}$
For **L3**, $\Delta G^{++} = 13.4\ \text{kcalmol}^{-1}$
For **L4**, $\Delta G^{++} = 14.0\ \text{kcalmol}^{-1}$

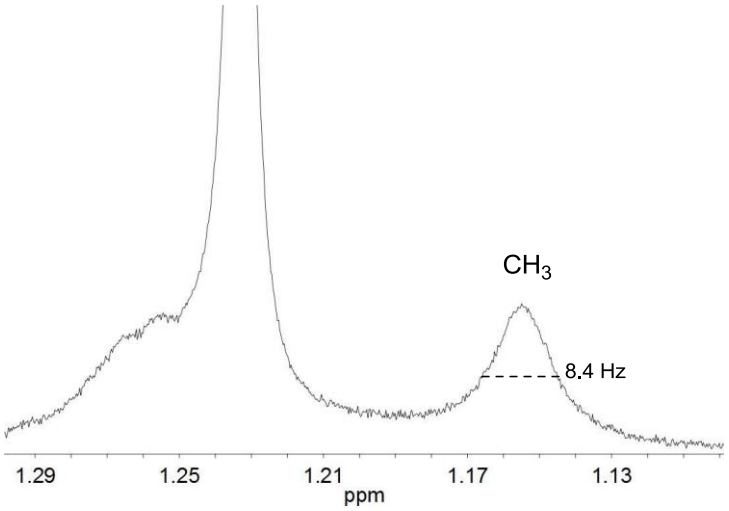


(a)

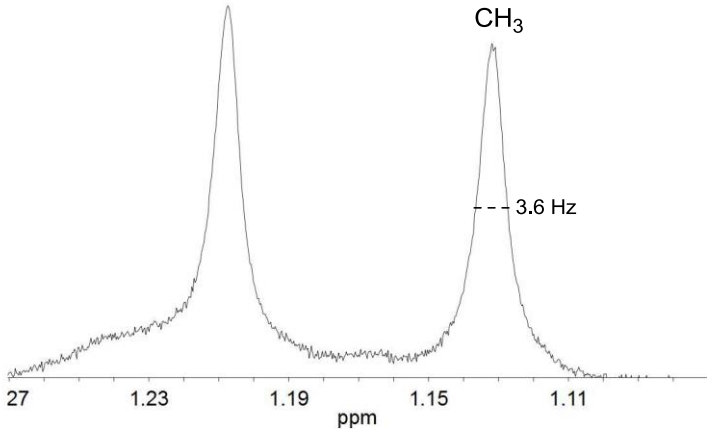


(b)

Figure S5 ^{1}H NMR spectra for **L2** (3×10^{-4} M) in CD_2Cl_2 with addition of 2.0 equiv. of $HClO_4$ which shows the signal of the methyl group (CH_3) on the chiral substituent. The spectrum obtained at (a) −20 °C, (b) −60 °C.

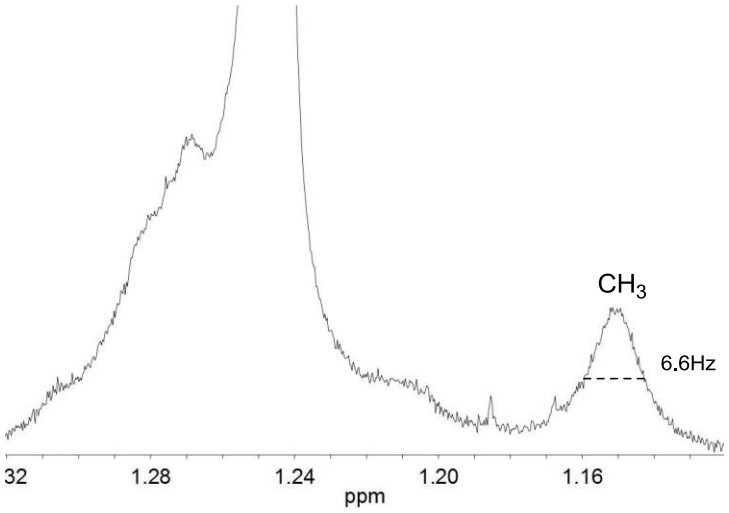


(a)

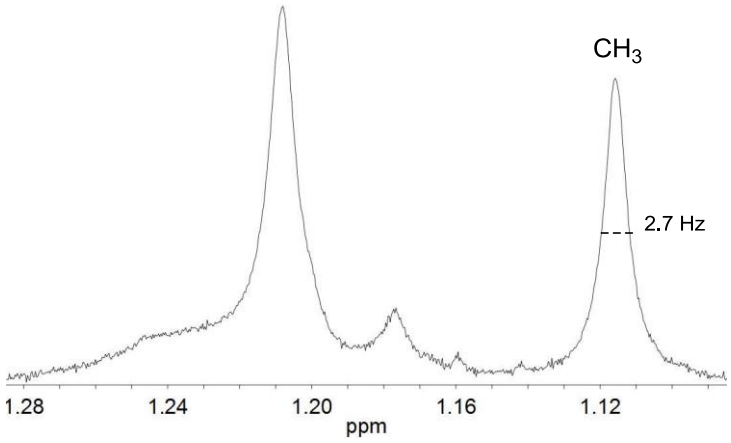


(b)

Figure S6 ^{1}H NMR spectra for **L3** (3×10^{-4} M) in CD_2Cl_2 with addition of 2.0 equiv. of $HClO_4$ which shows the signal of the methyl group (CH_3) on the chiral substituent. The spectrum obtained at (a) −20 °C, (b) −40 °C.



(a)



(b)

Figure S7 ^{1}H NMR spectra for **L4** (3×10^{-4} M) in CD_2Cl_2 with addition of 1.0 equiv. of $HClO_4$ which shows the signal of the methyl group (CH_3) on the chiral substituent. The spectrum obtained at (a) −10 °C, (b) −40 °C.

NMR characterization on intermediates and L1–4

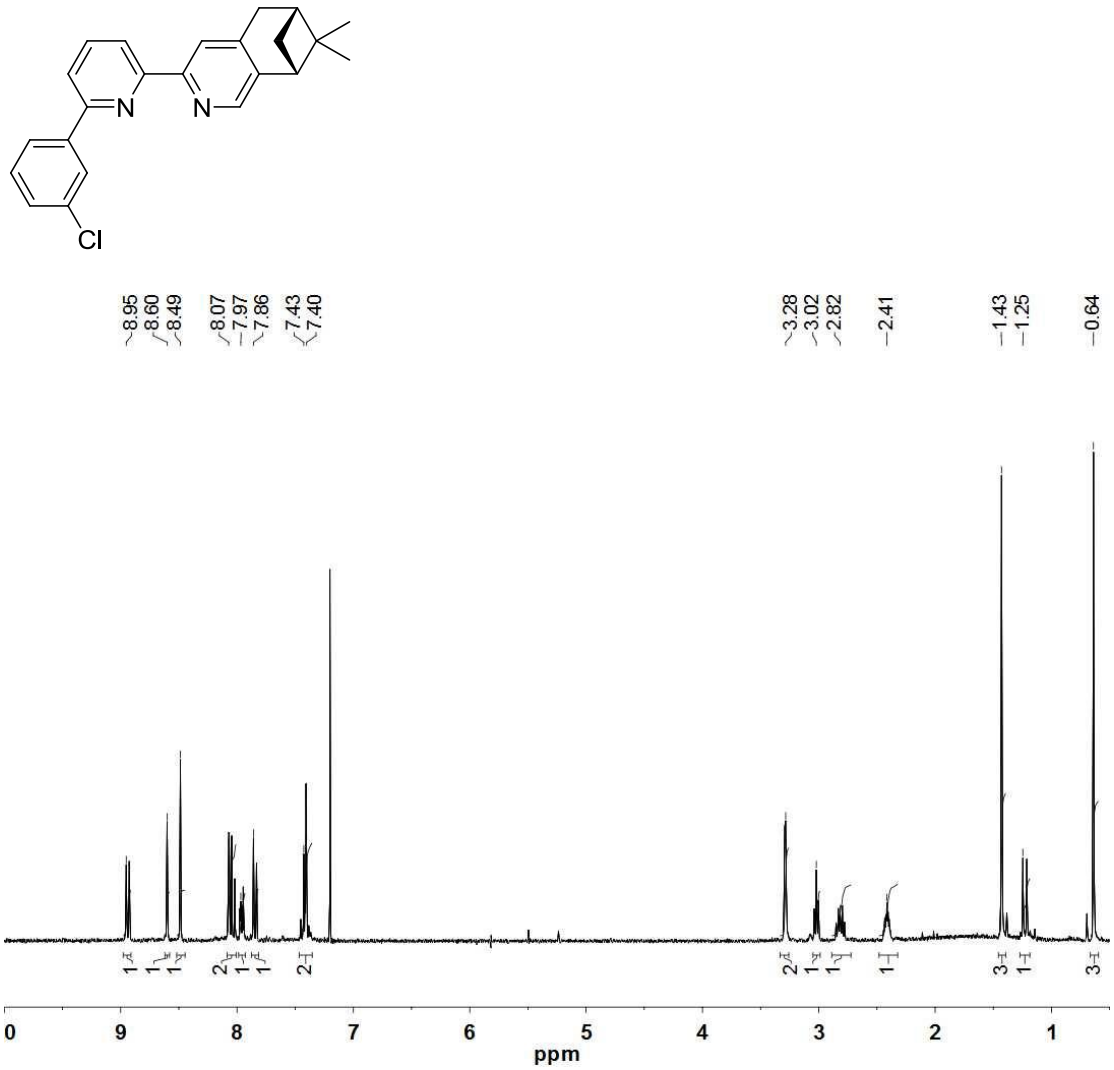


Figure S8 ^{1}H NMR (300 MHz, $CDCl_3$) of intermediate 2

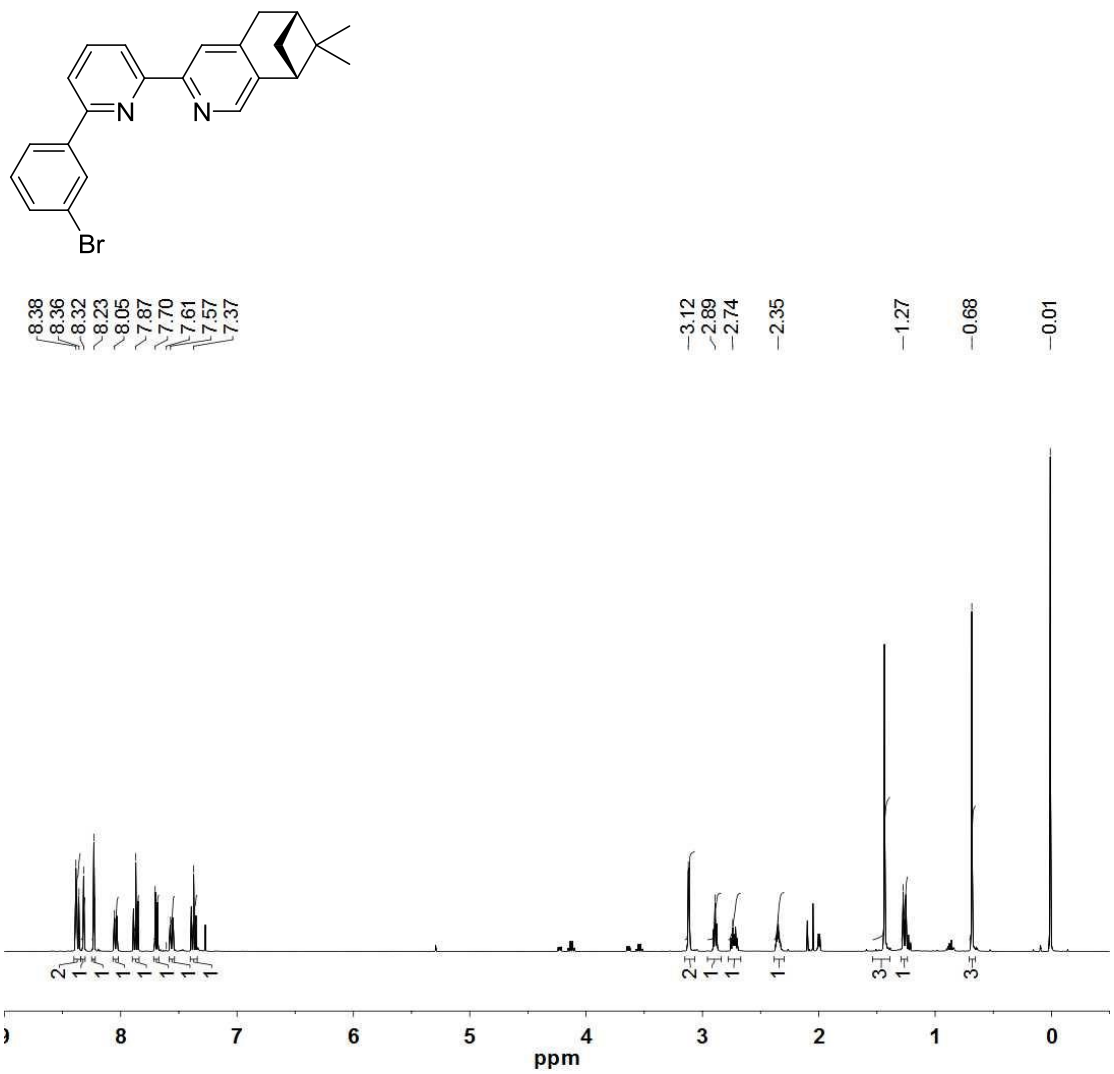


Figure S9 ^{1}H NMR (300 MHz, $CDCl_3$) of intermediate 3

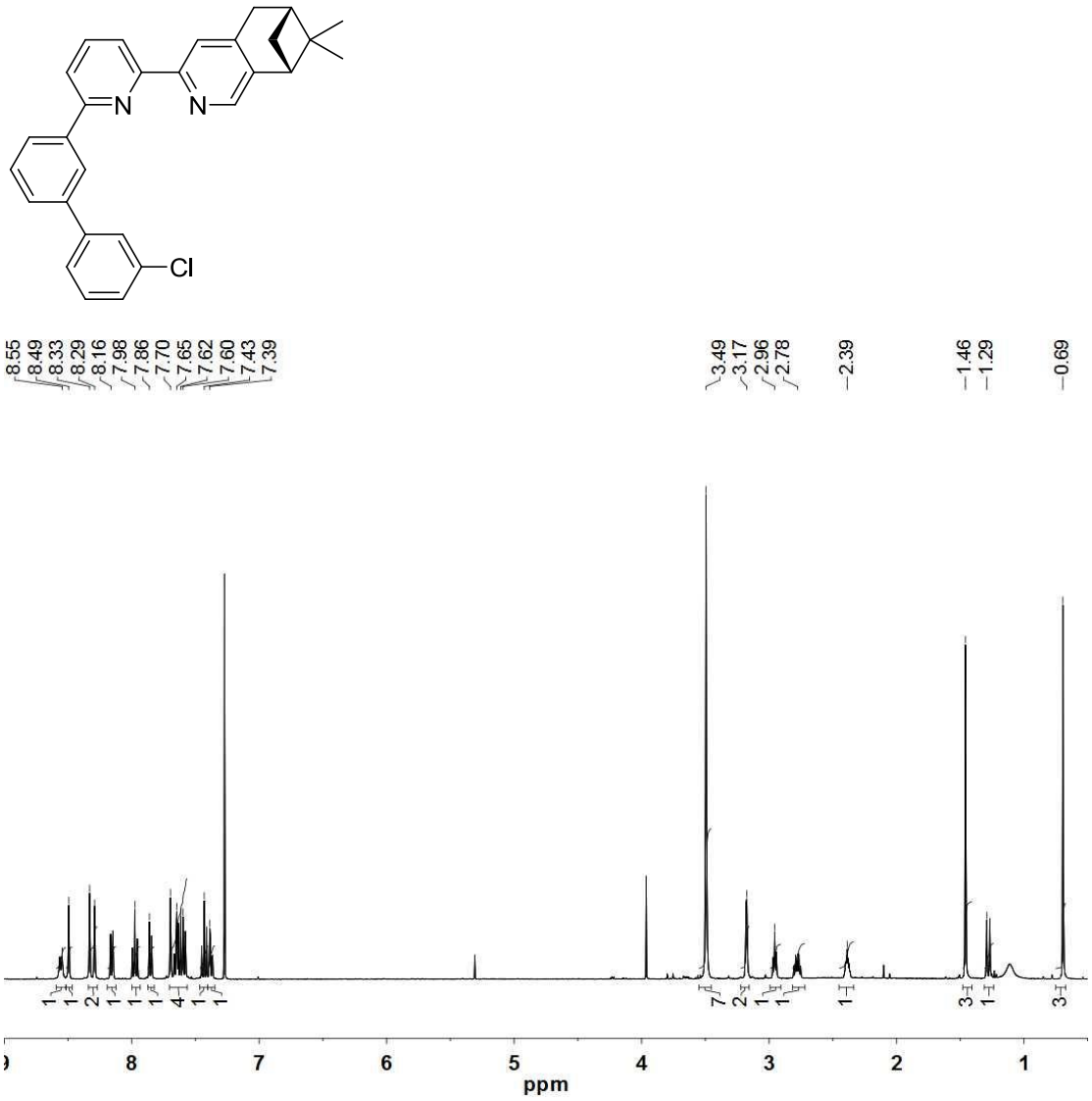


Figure S10 ^{1}H NMR (400 MHz, $CDCl_3$)of intermediate 4

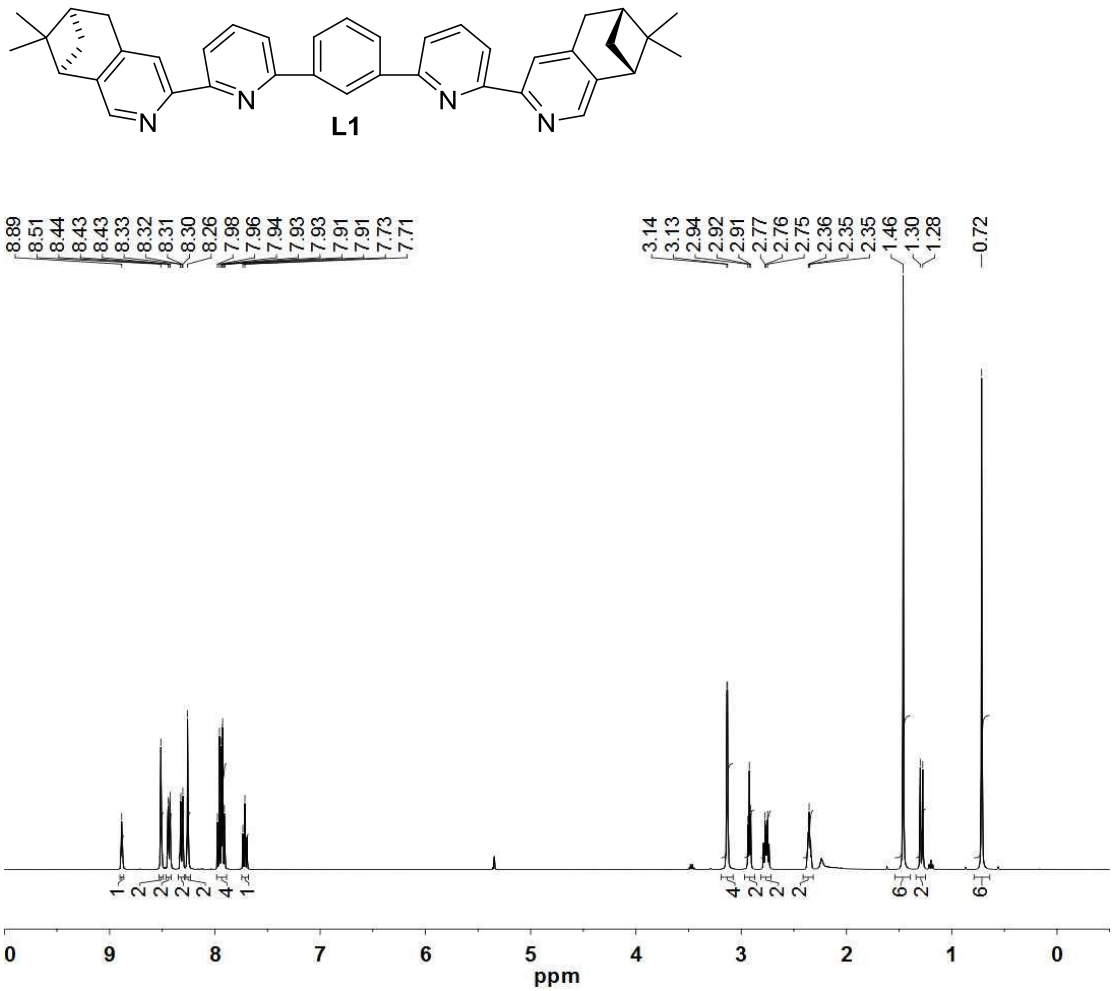


Figure S11 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **L1**

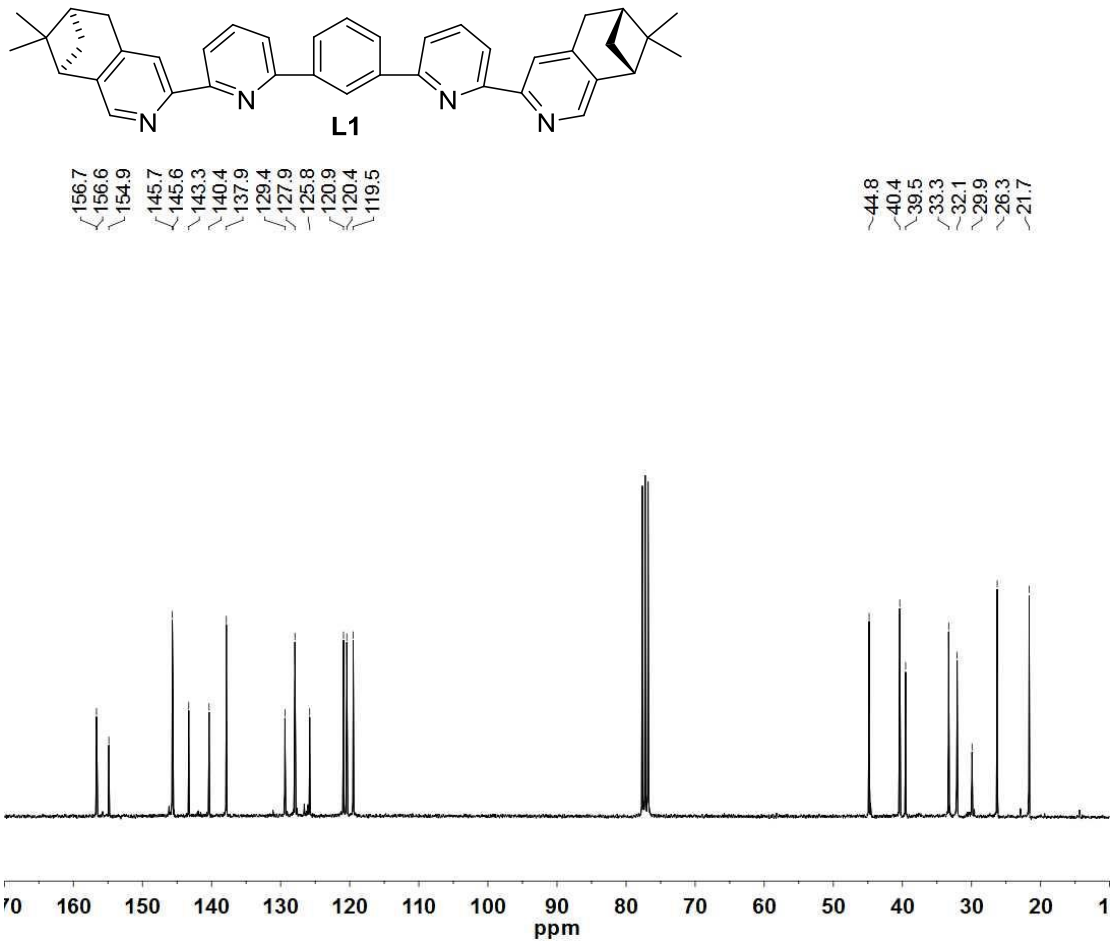


Figure S12 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **L1**

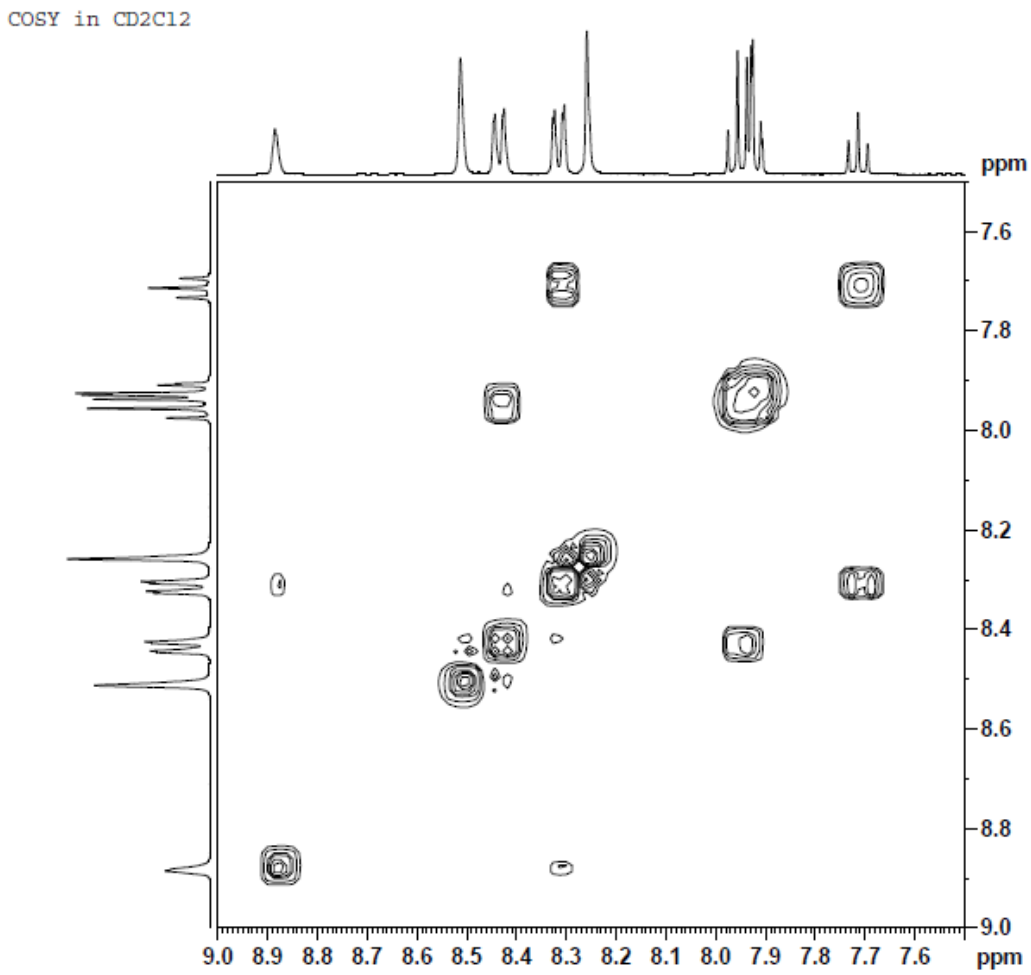


Figure S13 gCOSY spectrum of **L1** in aromatic region 9 to 7 ppm.

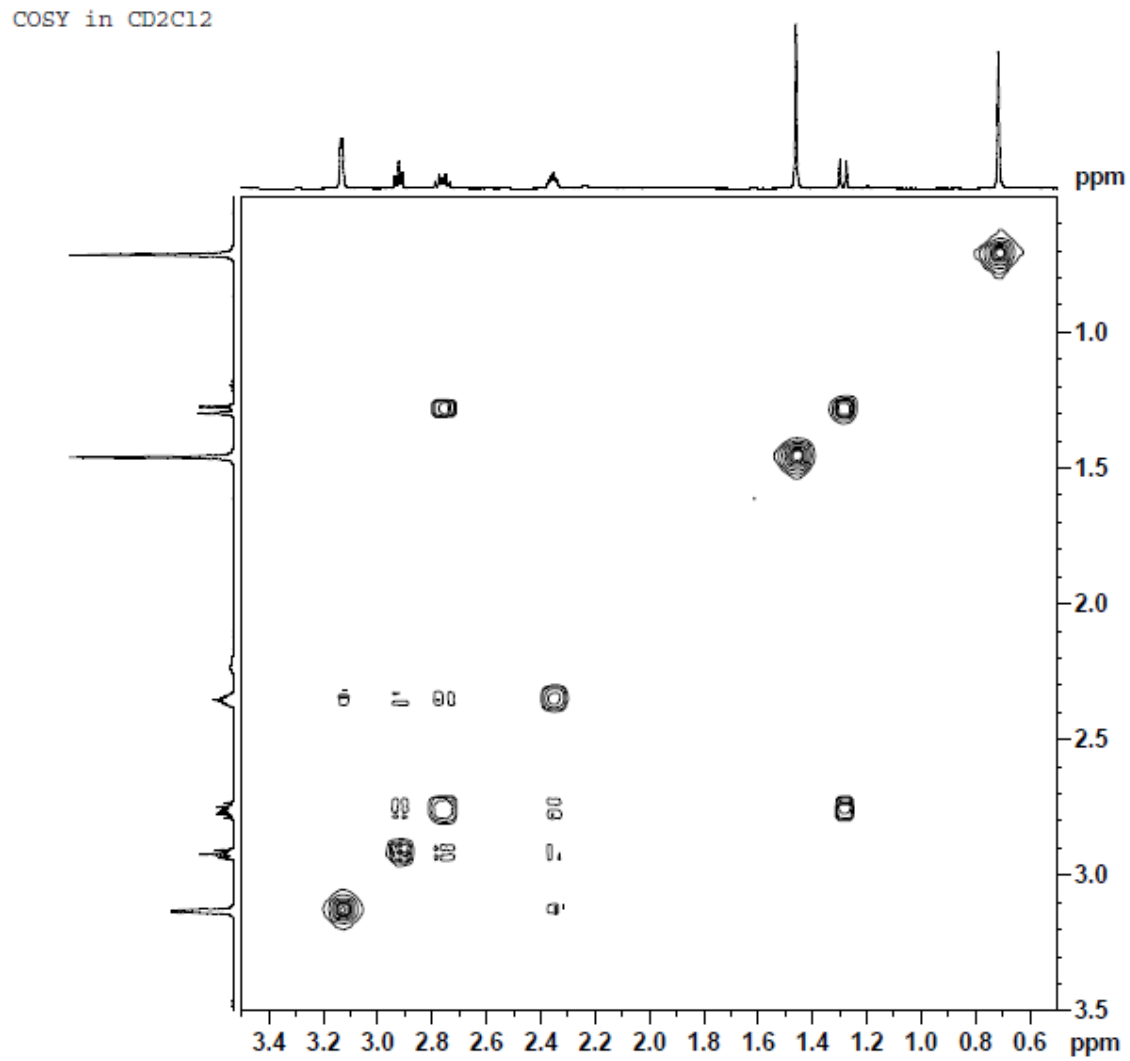


Figure S14 gCOSY spectrum of **L1** in aliphatic region 4 to 0 ppm.

CD2Cl2

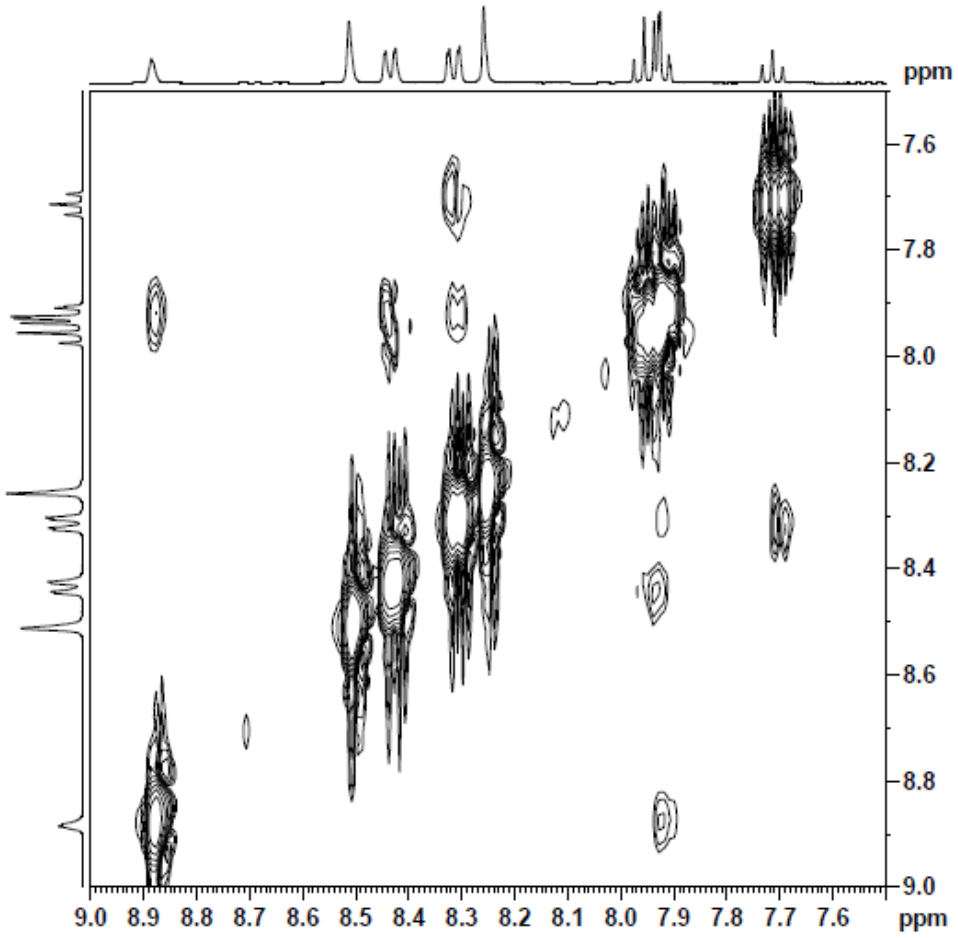


Figure S15 NOESY spectrum of **L1** in aromatic region 9 to 7 ppm.

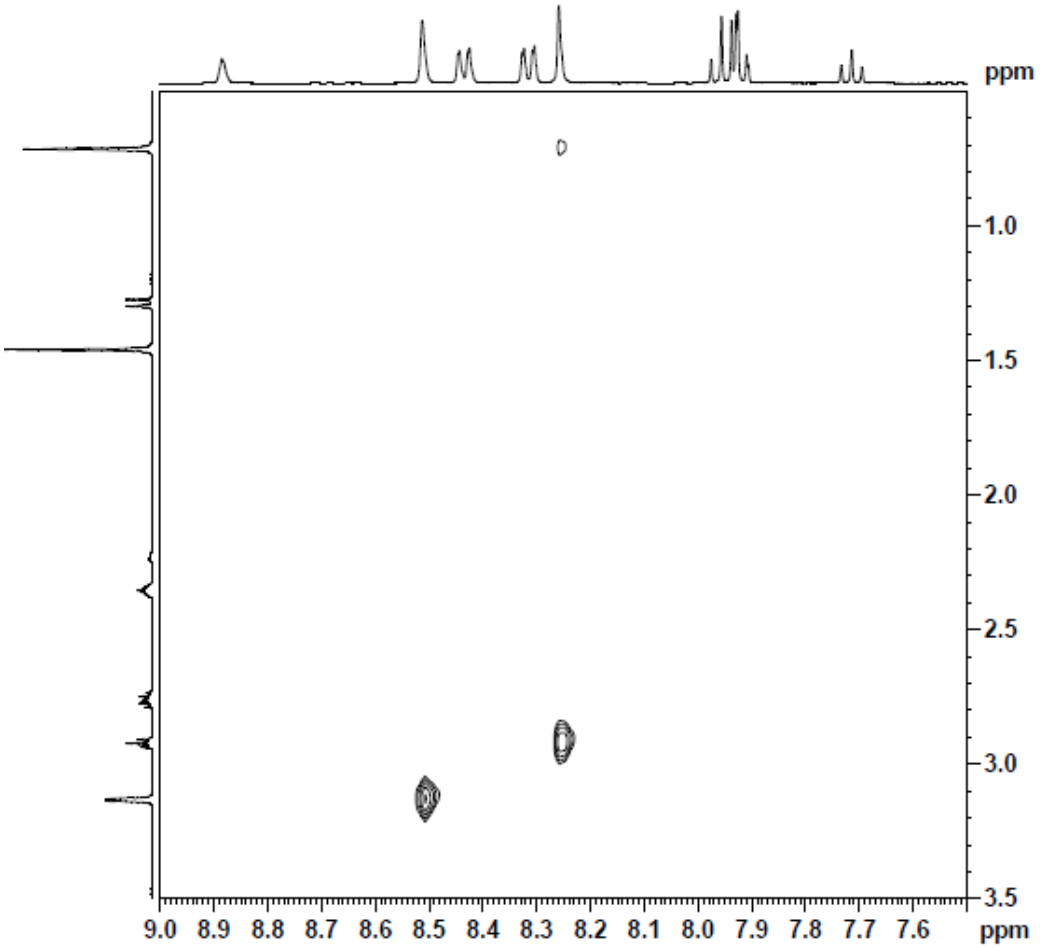


Figure S16 NOESY spectrum of **L1** showing the correlation signals between the protons at aromatic and aliphatic region.

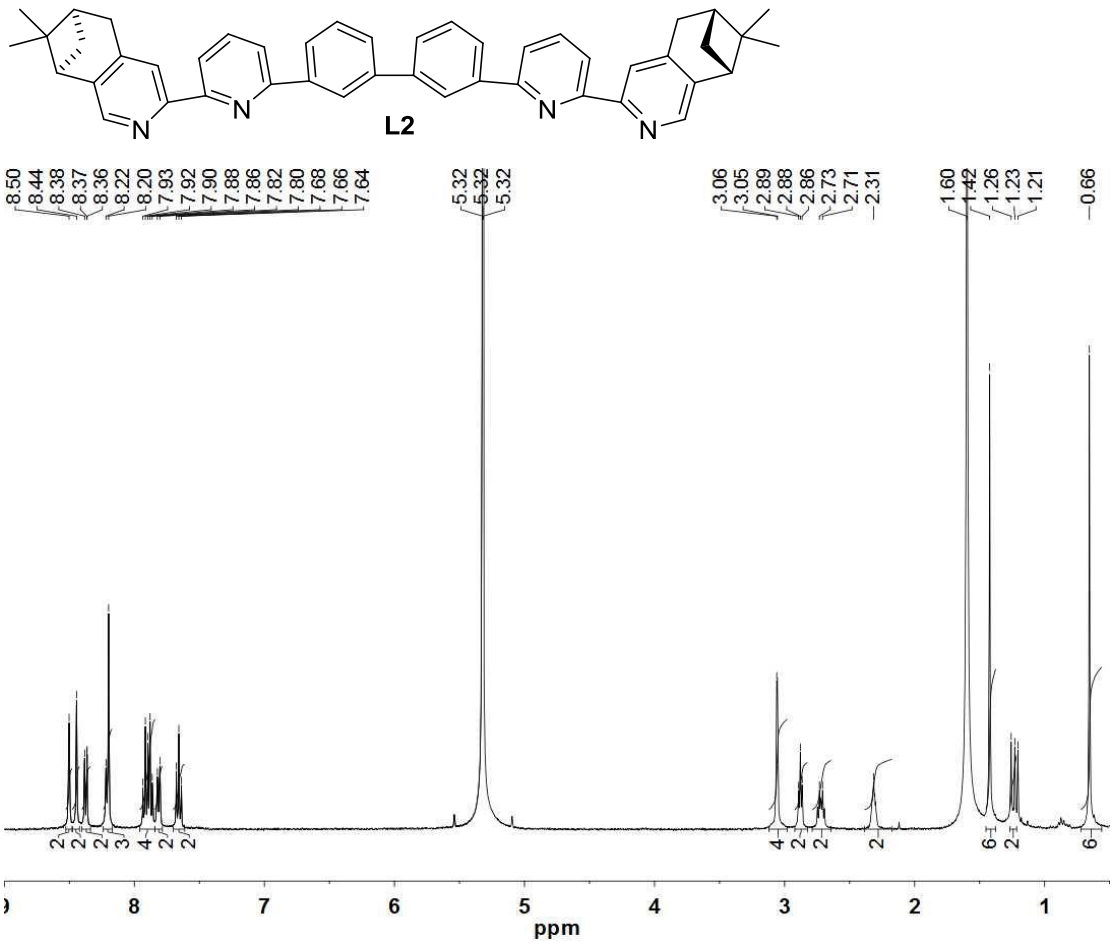


Figure S17 ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz) of **L2**

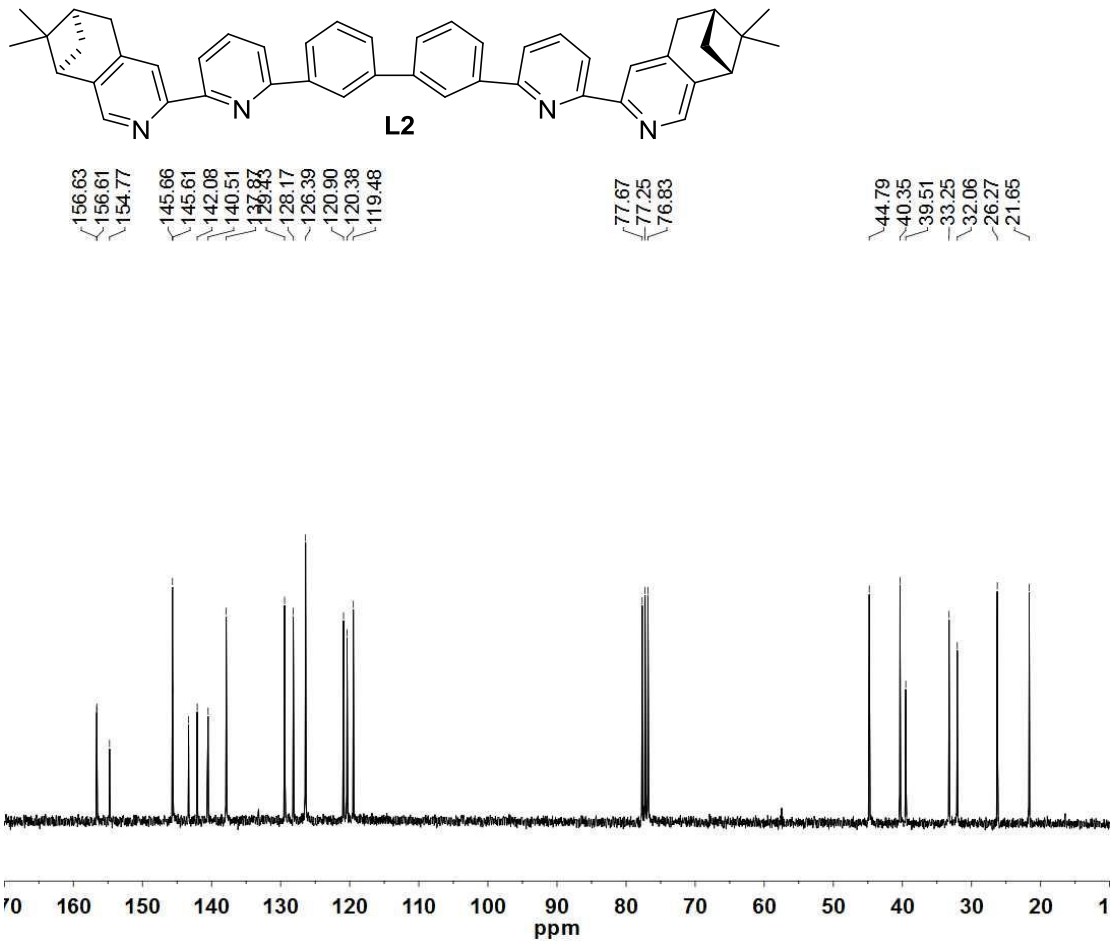


Figure S18 ^{13}C NMR spectrum (CD_2Cl_2, 400 MHz) of **L2**

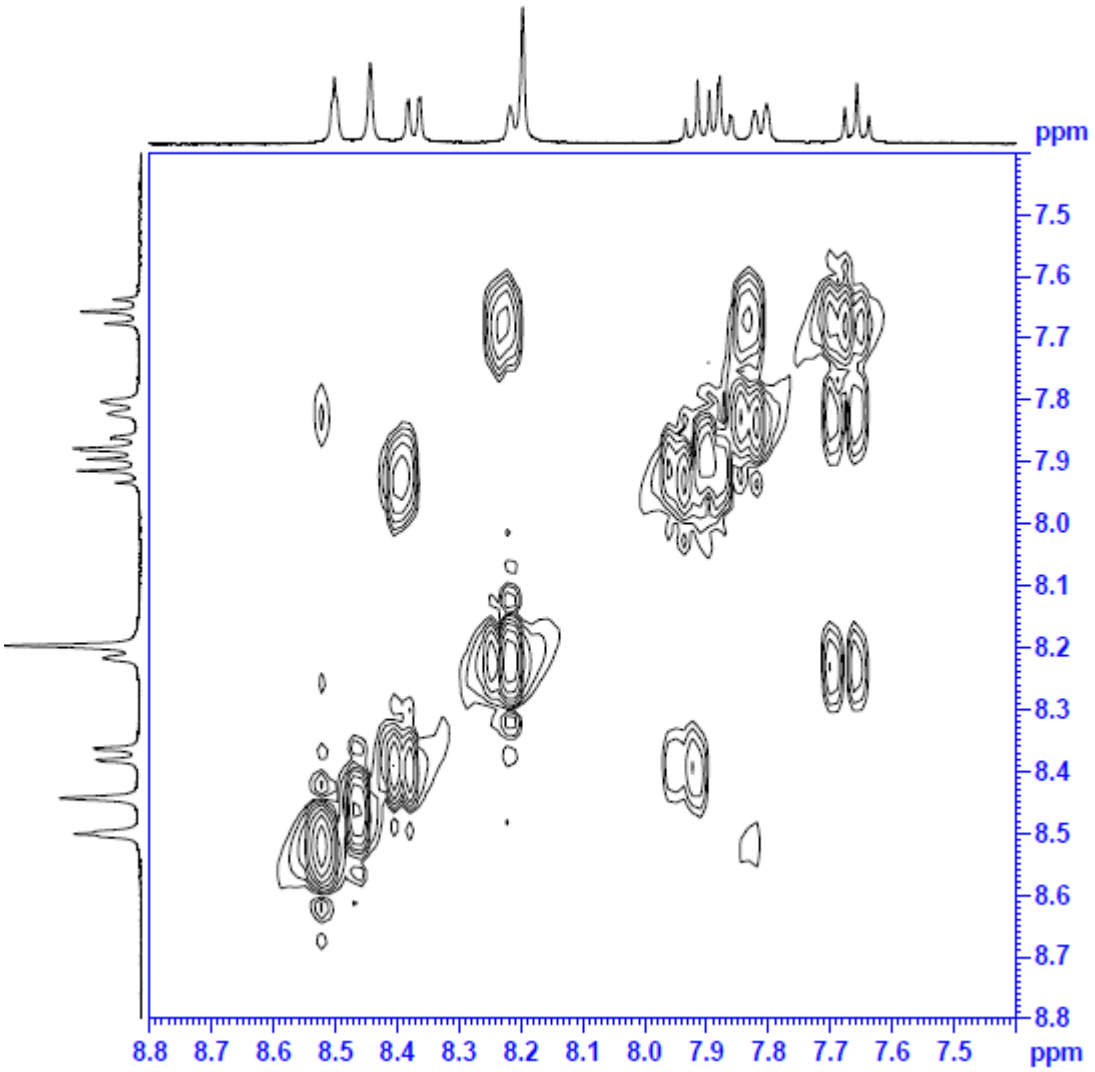


Figure S19 gCOSY spectrum of **L2** in aromatic region 9 to 7 ppm.

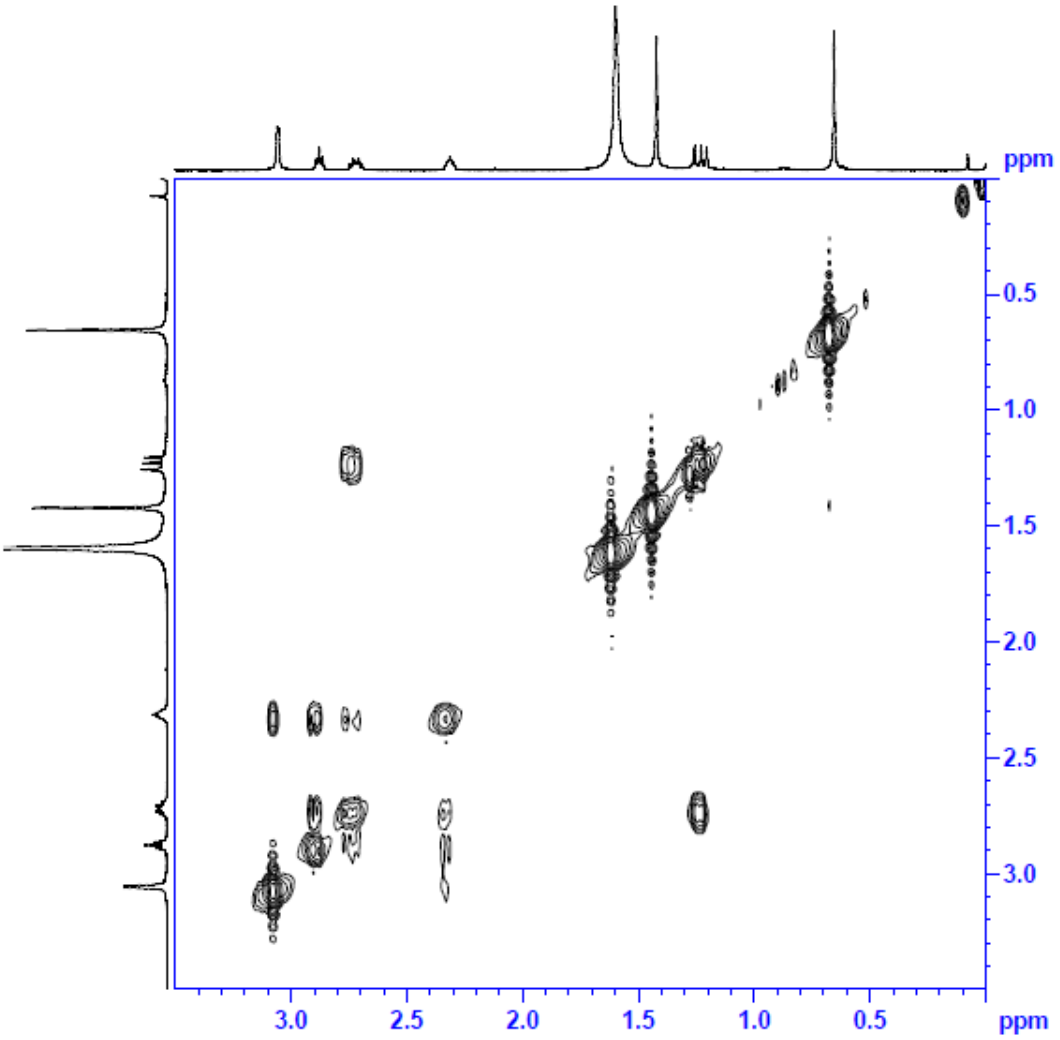


Figure S20 gCOSY spectrum of **L2** in aliphatic region 4 to 0 ppm.

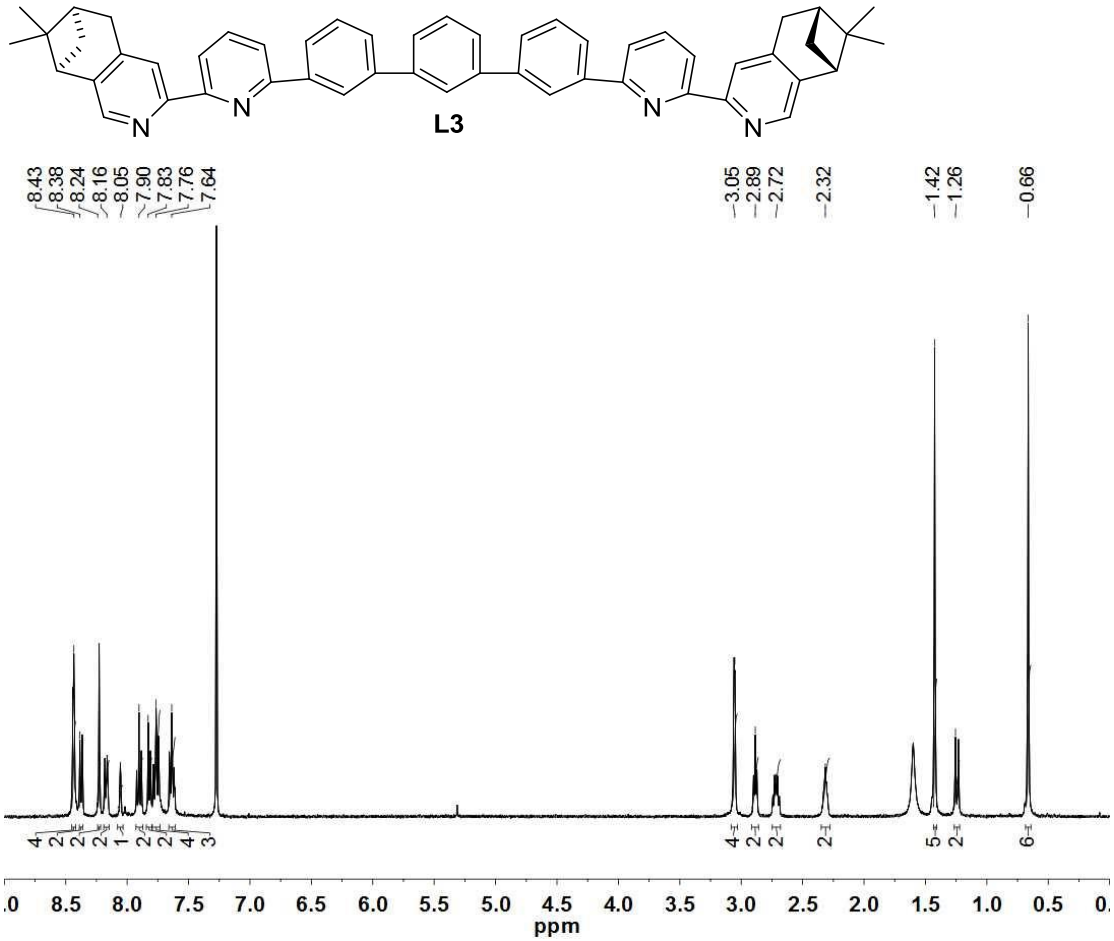


Figure S21 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **L3**

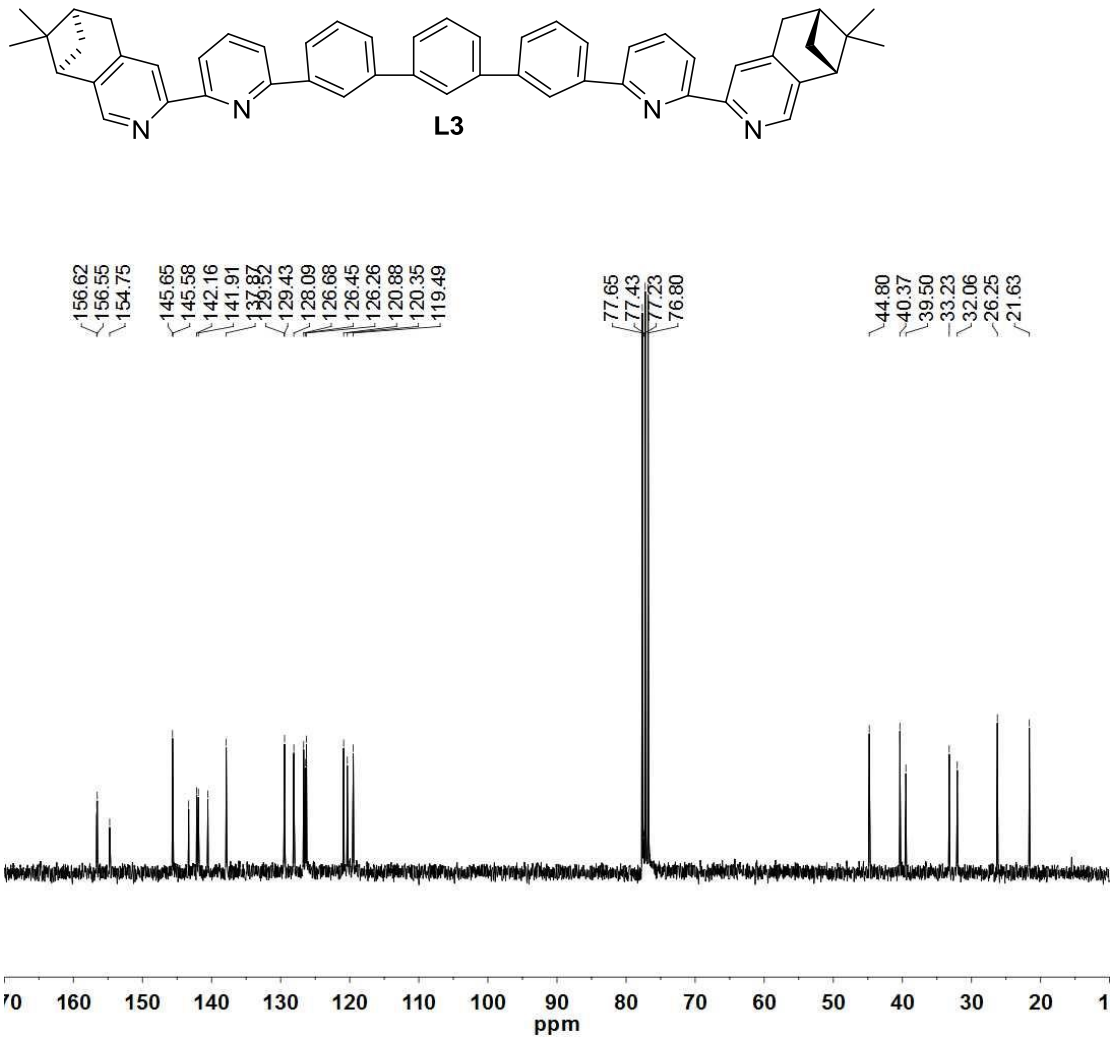


Figure S22 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **L3**

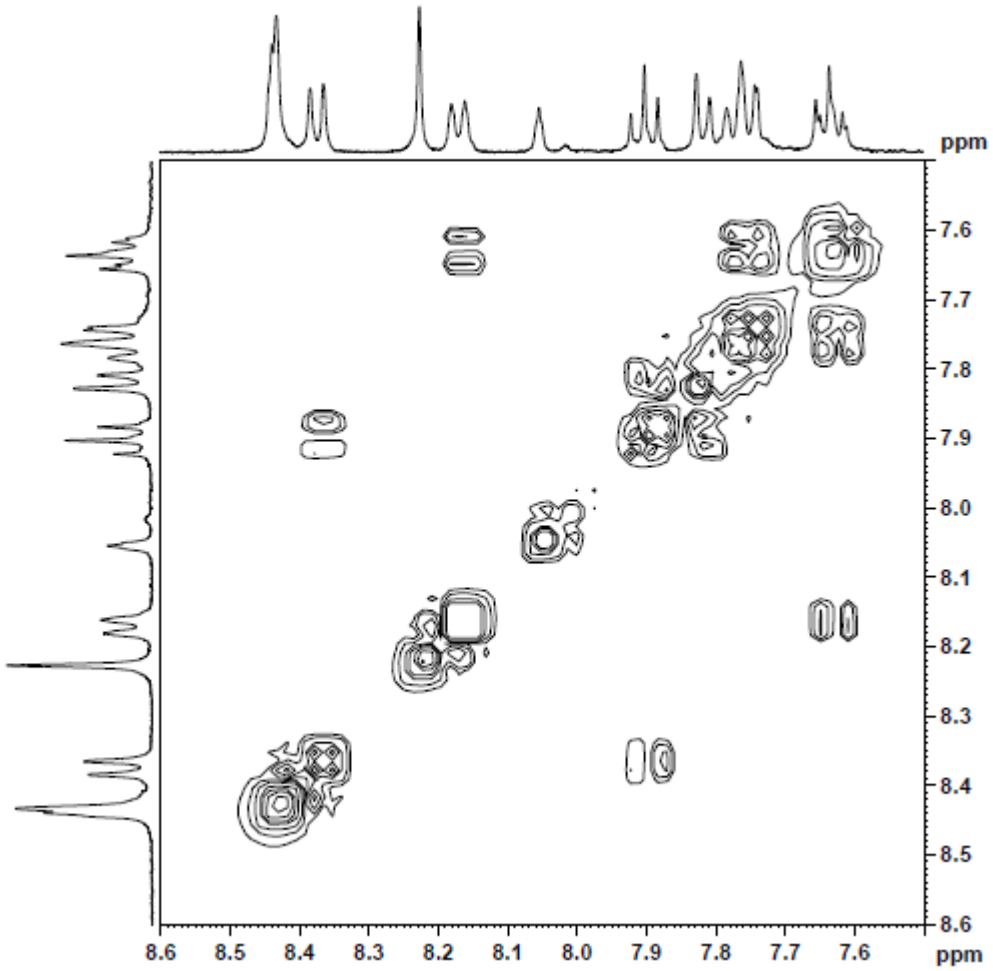


Figure S23 The aromatic region of gCOSY spectrum ($CDCl_3$, 400 MHz) of **L3**

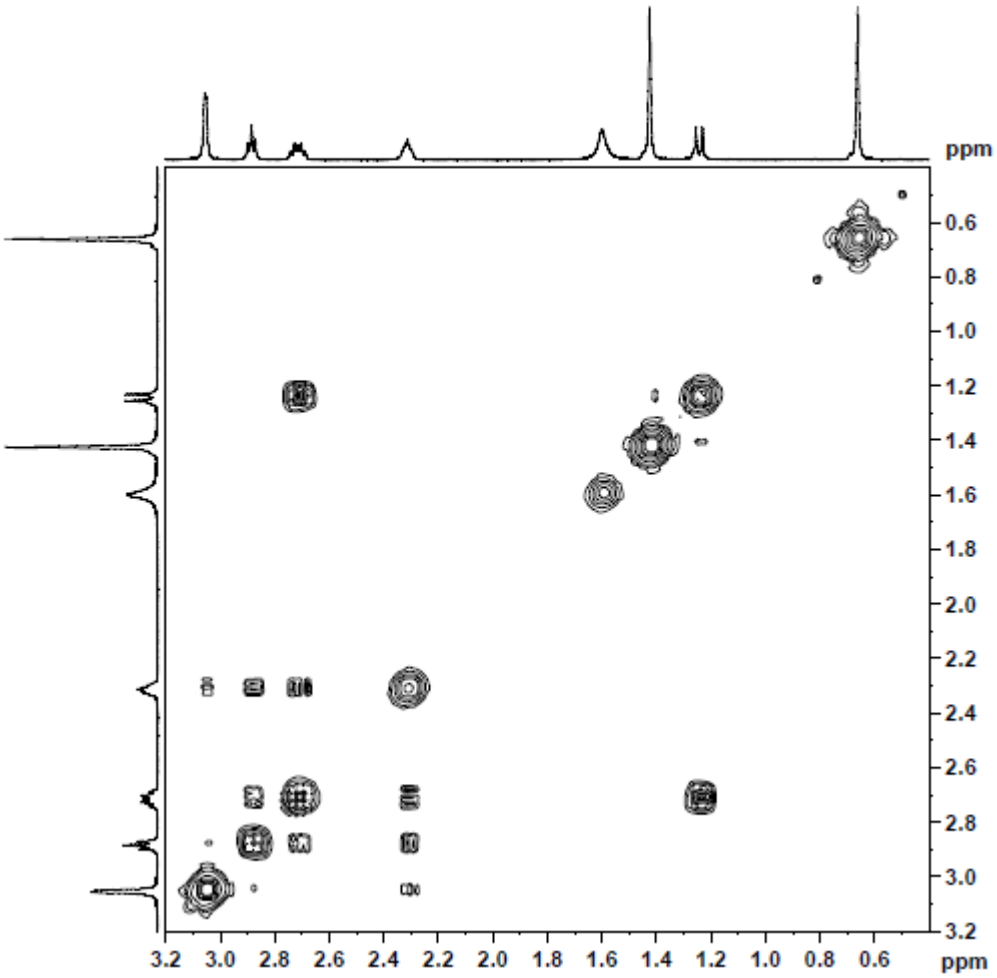


Figure S24 The aliphatic region of gCOSY spectrum ($CDCl_3$, 400 MHz) of **L3**

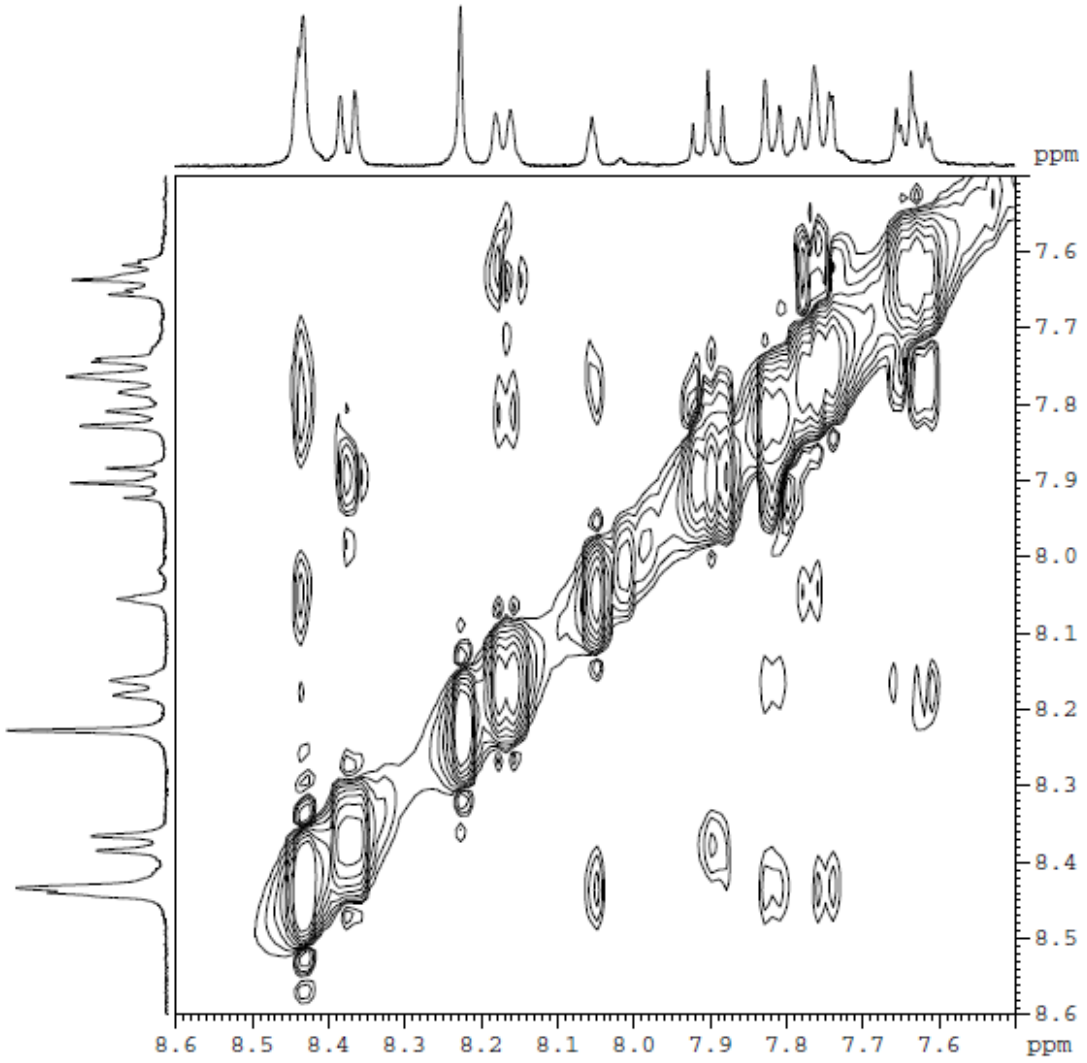


Figure S25 The aromatic region of NOESY spectrum ($CDCl_3$, 400 MHz) of **L3**

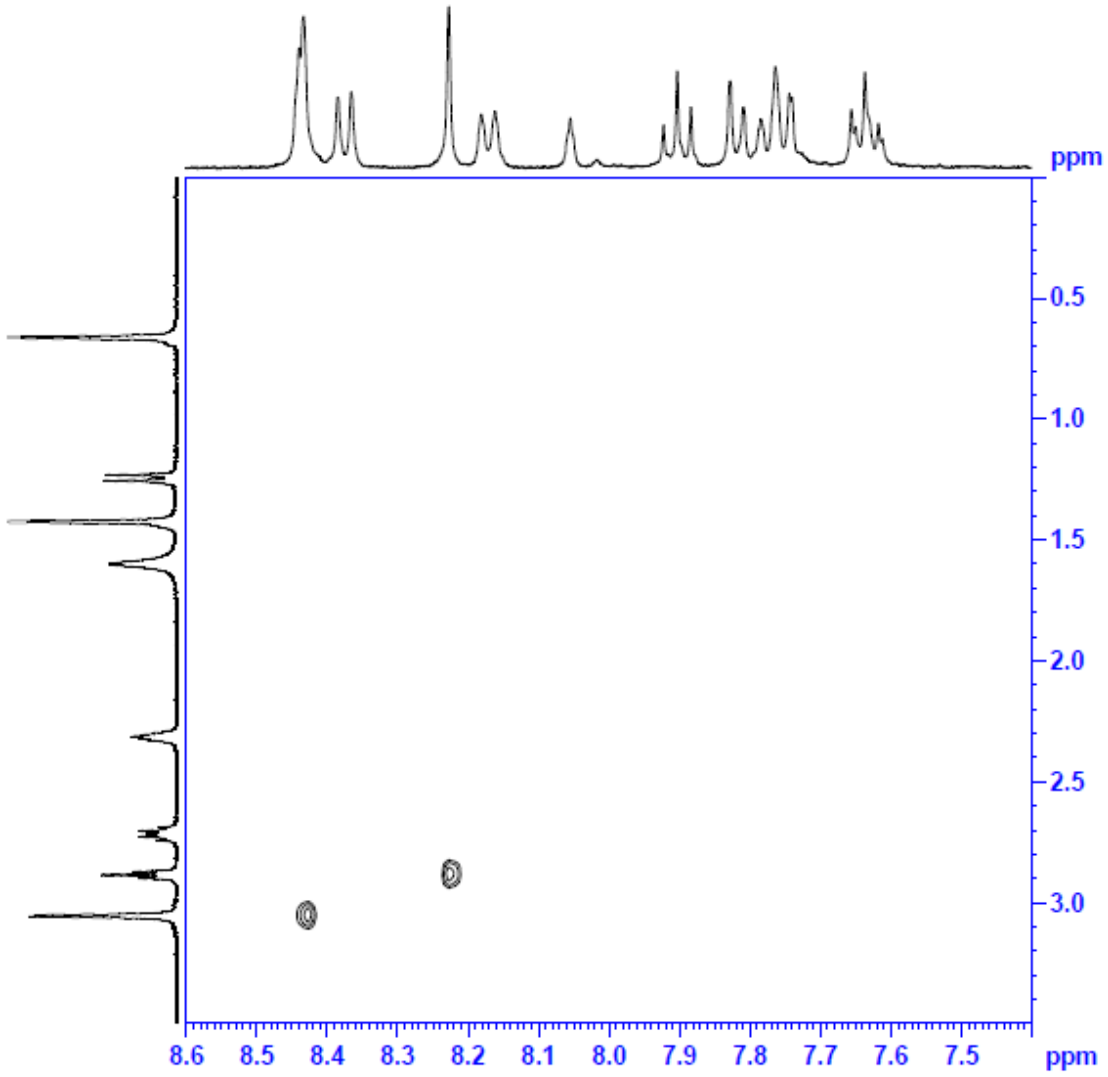
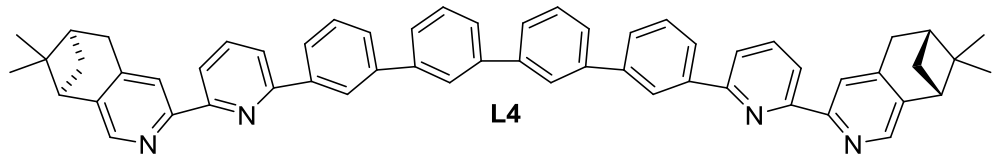


Figure S26 NOESY spectrum ($CDCl_3$, 400 MHz) of **L3** showing the correlation signals between the proton at the aromatic and aliphatic region.



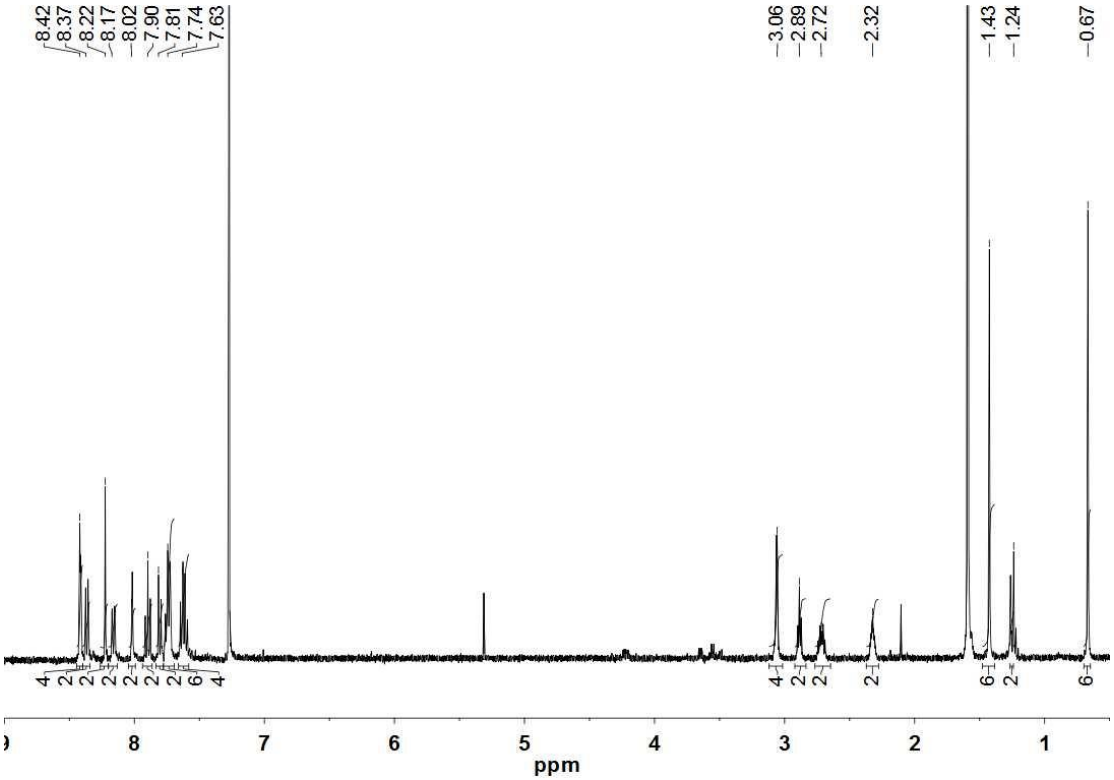


Figure S27 ^{1}H NMR spectrum ($CDCl_3$, 400 MHz) of **L4**

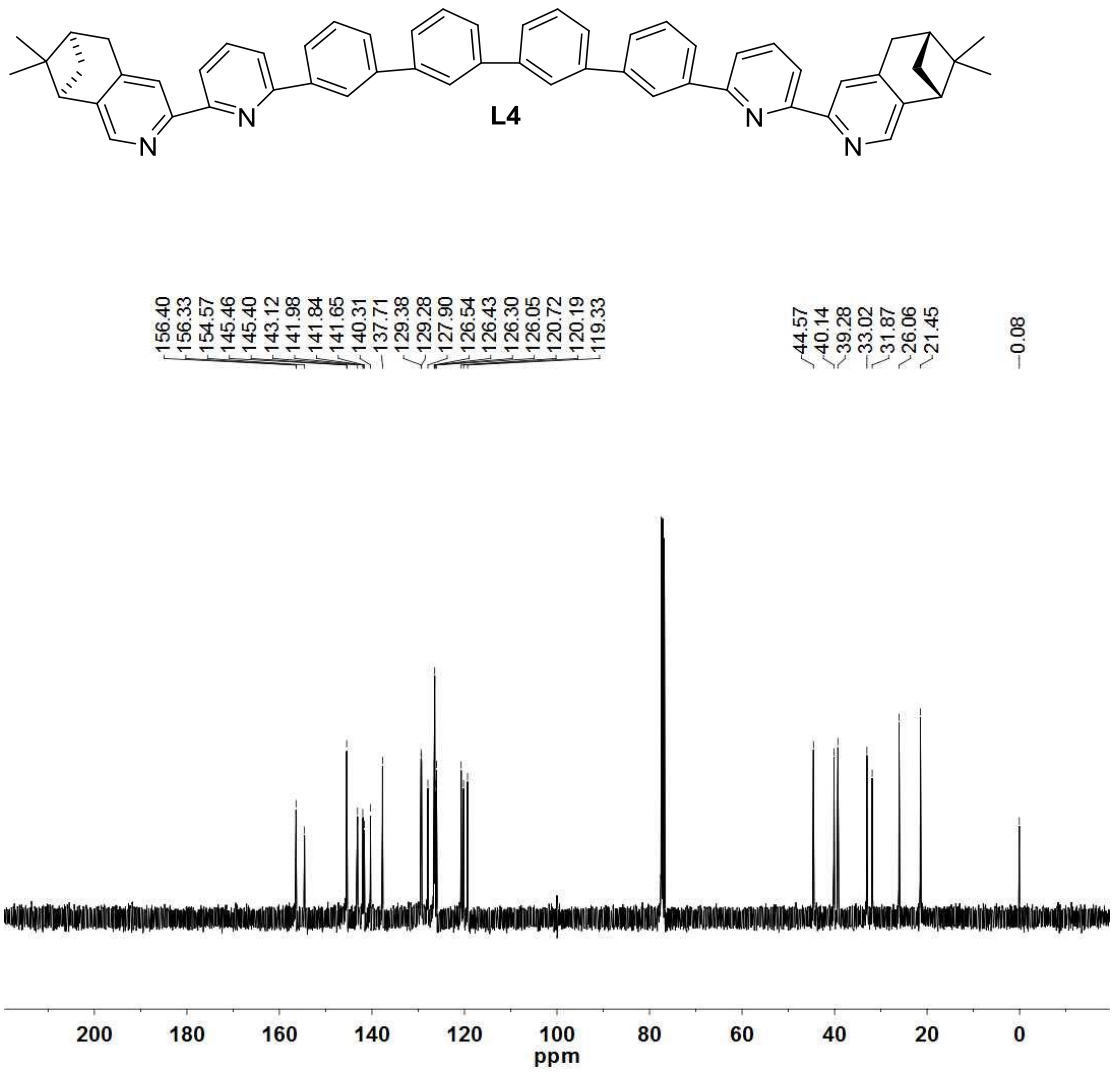


Figure S28 ^{13}C NMR spectrum ($CDCl_3$, 400 MHz) of **L4**

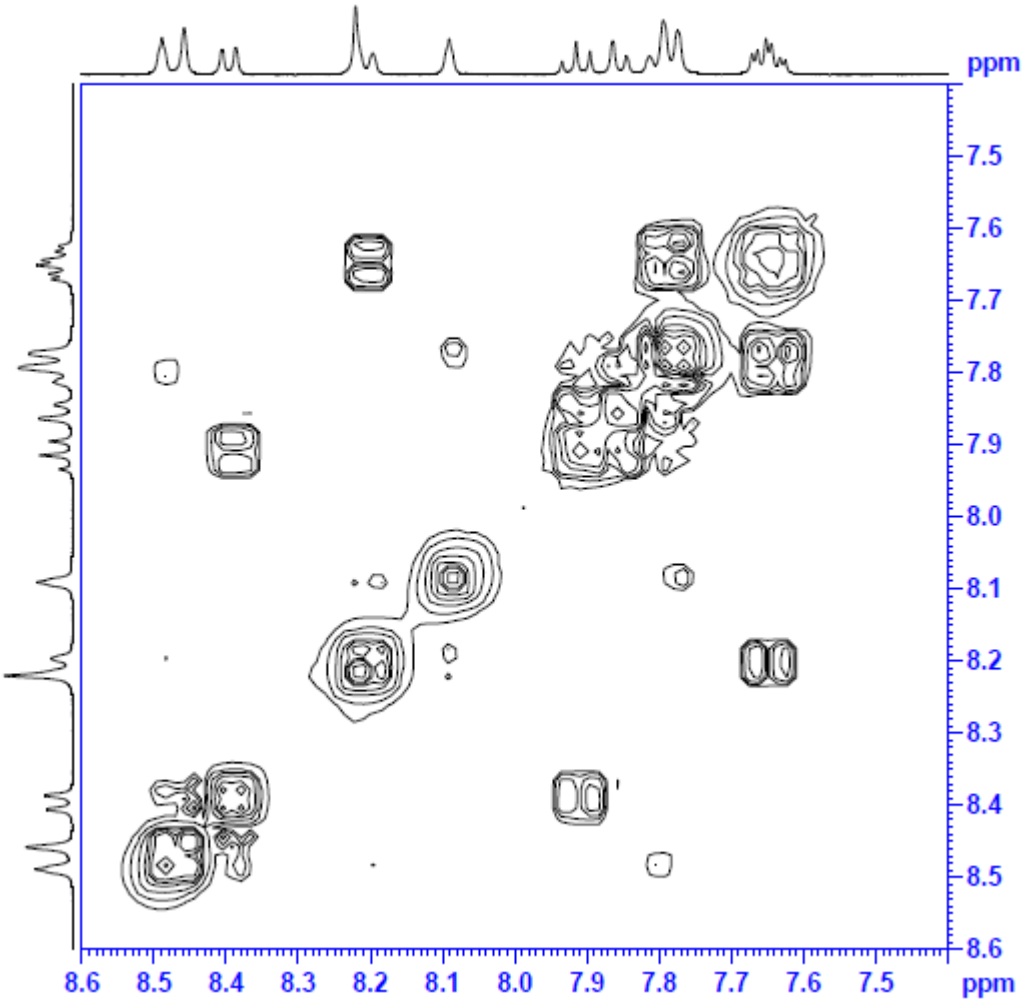


Figure S29 gCOSY spectrum (CD_2Cl_2, 400 MHz) of **L4** showing the aromatic region

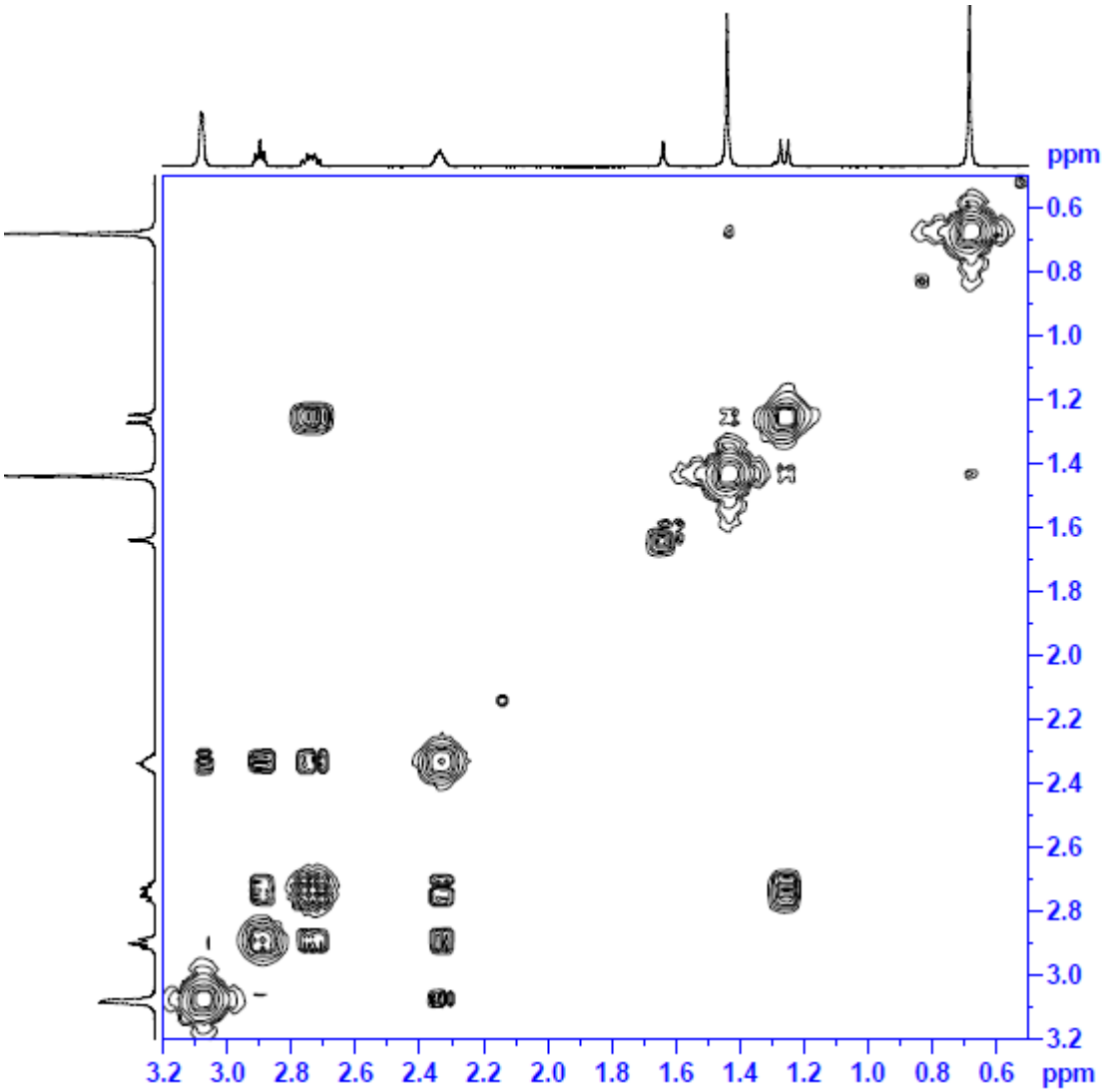


Figure S30 gCOSY spectrum (CD_2Cl_2, 400 MHz) of **L4** showing the aliphatic region

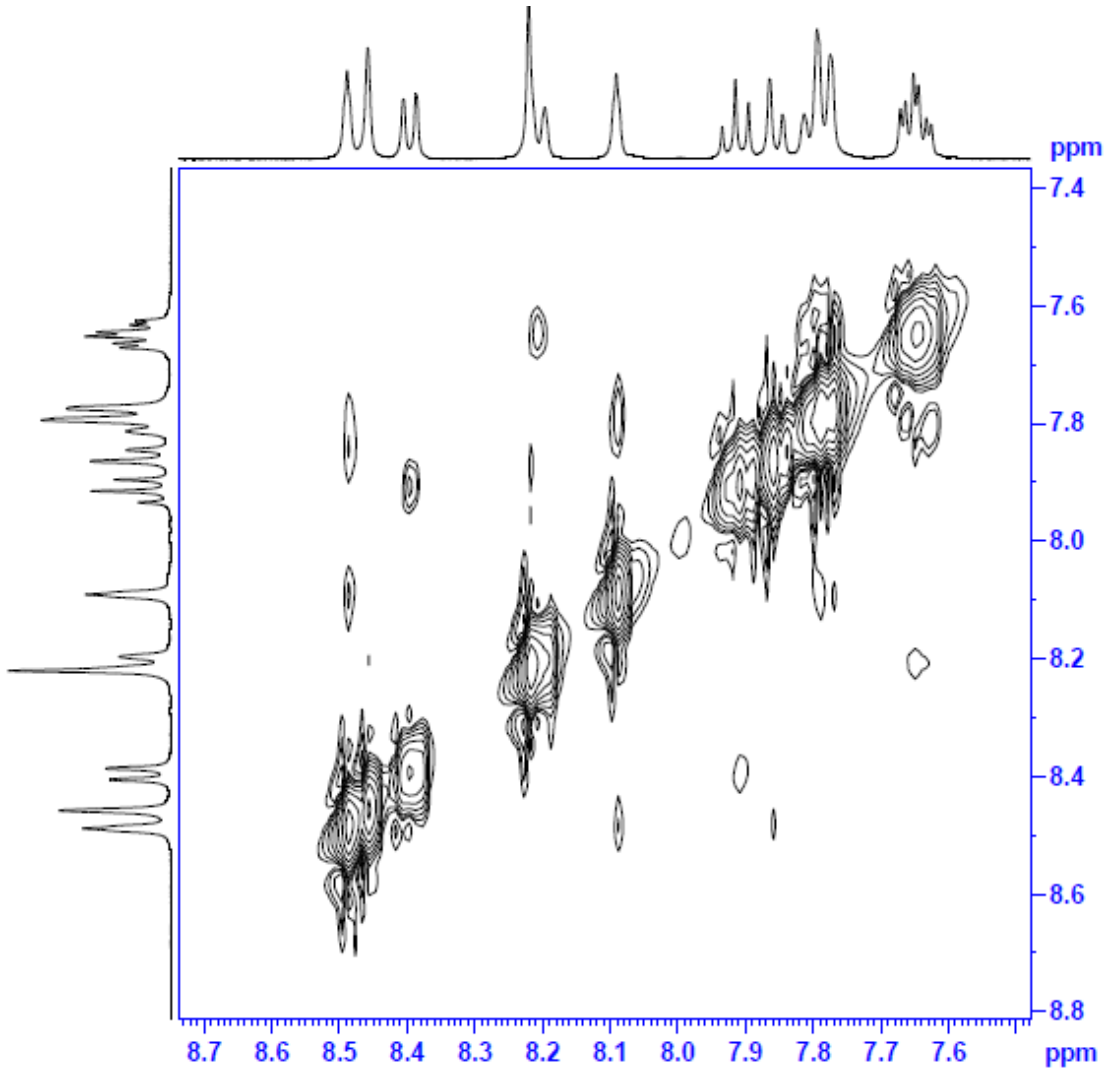


Figure S31 NOESY spectrum (CD_2Cl_2, 400 MHz) of **L4** showing the aromatic region

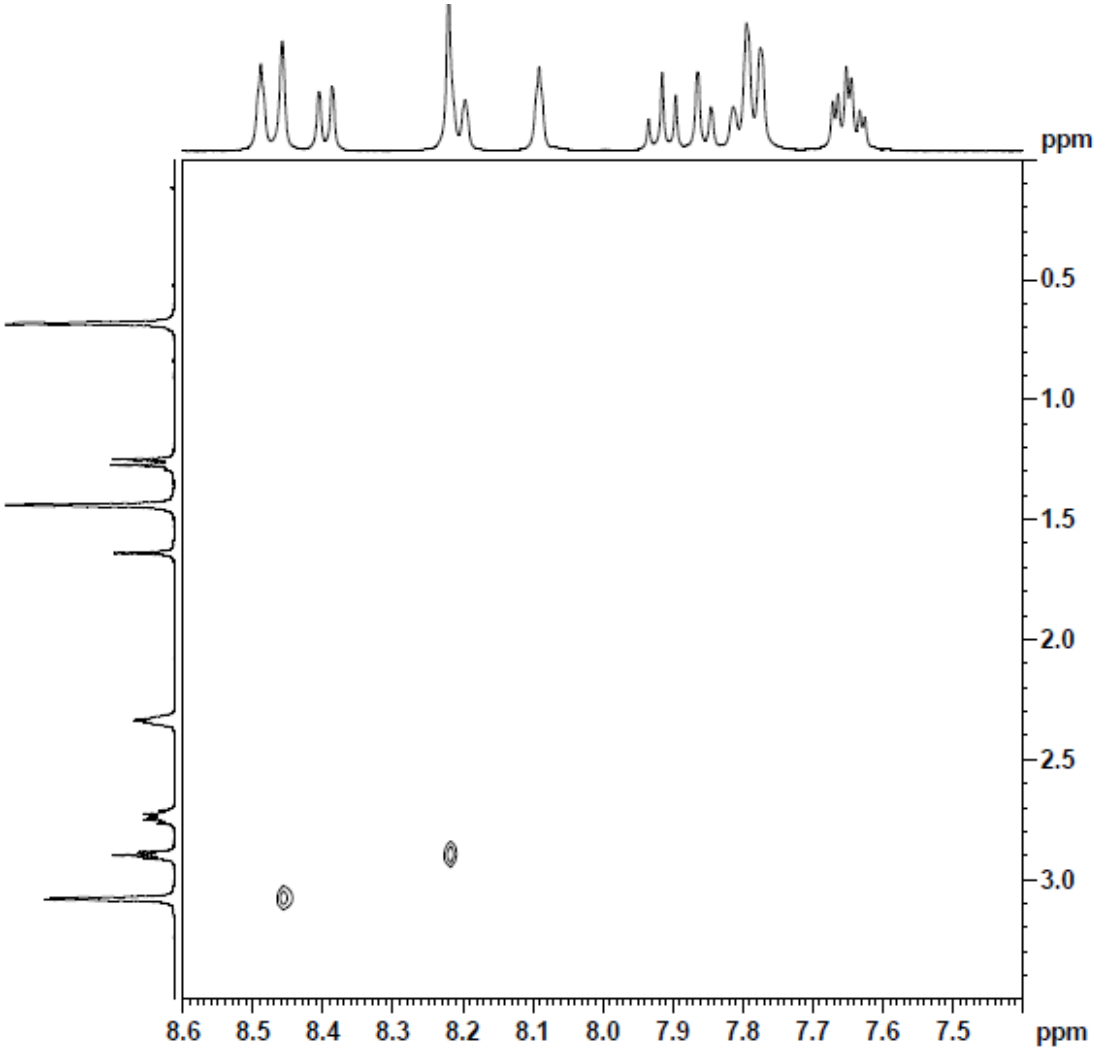


Figure S32 NOESY spectrum ($CDCl_3$, 400 MHz) of **L4** showing the correlation signals between the proton at the aromatic and aliphatic region.

Tables containing selected bond lengths and angles of models obtained in DFT calculations and the results of Atom in molecules (AIM) analysis

D–H···A	H···A/Å	D–H···A/°
N89–H184···N195	1.890	158.00
C130–H20···Cl 191	2.874	129.15
C24–H25···Cl 193	2.801	112.62
C28–H29···Cl 193	2.838	157.31
C28–H29···Cl 194	2.726	119.56
C124–H125···Cl 194	2.805	151.17
C128–H129···Cl 194	2.827	128.67

Table S1 Hydrogen bonding parameters of the model of $[(\mathbf{L2})_2H_2](FeCl_4)_2$ obtained by theoretical calculation at M06-2X/6-31G(d)/LANL2DZ level.

D–H···A	H···A/Å	ρ of BCP	$\nabla^2\rho$ of BCP
N89–H184···N195	1.890	0.035	0.1
C130–H20···Cl 191	2.874	0.008	0.03
C24–H25···Cl 193	2.801	0.009	0.03
C28–H29···Cl 193	2.838	0.007	0.03
C28–H29···Cl 194	2.726	0.010	0.04
C124–H125···Cl 194	2.805	0.007	0.03
C128–H129···Cl 194	2.827	0.008	0.03

Table S2 Results obtained by Atoms in Molecules (AIM) analysis of $[(\mathbf{L2})_2H_2](FeCl_4)_2$. [4,5]

D–H···A	H···A/Å	D–H···A/°
N89–H185···N184	1.940	153.66
C28–H29···O189	2.589	118.0
C124–H125···O189	2.339	154.85
C128–H129···O189	2.344	133.81
C24–H25···O190	2.314	146.80
C28–H29···O190	2.204	172.27
C24–H25···O191	2.423	145.67
C130–H131···O191	2.478	107.31

Table S3 Hydrogen bonding parameters of the model of $[(\mathbf{L2})_2H_2](ClO_4)_2$ obtained by theoretical calculation at M06-2X/6-31G(d)/LANL2DZ level.

D–H···A	H···A/Å	ρ of BCP	$\nabla^2\rho$ of BCP
N89–H185···N184	1.940	0.031	0.09
C28–H29···O189	2.589	0.09	0.03
C124–H125···O189	2.339	0.010	0.04
C128–H129···O189	2.344	0.013	0.05
C28–H25···O190	2.314	0.014	0.05
C24–H29···O190	2.204	0.017	0.05
C24–H25···O191	2.423	0.011	0.04
C130–H131···O191	2.478	0.10	0.04

Table S4 Results obtained by Atoms in Molecules (AIM) analysis of $[(\mathbf{L2})_2H_2](ClO_4)_2$.[4,5]

D–H···A	H···A/Å	D–H···A/°
N4–H205···N5	3.019	153.53
C81–H83···Cl 213	2.688	162.92
C146–H147···Cl 213	2.997	115.34
C152–H153···Cl 213	2.712	150.53
C78–H79···Cl 193	3.001	144.47
C82–H83···Cl 193	2.931	111.86
C76–H77···Cl 216	3.151	115.46
C78–H79···Cl 216	2.741	131.30
C154–H155···Cl 216	3.019	108.30

Table S5 Hydrogen bonding parameters of the model of $[(\mathbf{L3})_2H_2](FeCl_4)_2$ obtained by theoretical calculation at M06-2X/6-31G(d)/LANL2DZ level.

D–H···A	H···A/Å	ρ of BCP	$\nabla^2\rho$ of BCP
N4–H205···N5	3.019	0.032	0.09
C81–H83···Cl 213	2.688	0.010	0.04
C146–H147···Cl 213	2.997	0.006	0.02
C152–H153···Cl 213	2.712	0.009	0.03
C78–H79···Cl 193	3.001	0.006	0.02
C82–H83···Cl 193	2.931	0.009	0.03
C76–H77···Cl 216	3.151	0.004	0.02
C78–H79···Cl 216	2.741	0.009	0.03
C154–H155···Cl 216	3.019	0.006	0.02

Table S6 Results obtained by Atoms in Molecules (AIM) analysis of $[(\mathbf{L3})_2H_2](FeCl_4)_2$. [4,5]

D–H···A	H···A/Å	D–H···A/°
N4–H205···N5	1.974	152.00
C78–H79···O 214	2.192	173.98
C82–H83···O 214	2.145	166.70
C152–H153···O 215	2.427	127.31
C154–H155···O 215	2.787	113.32
C82–H83···O 216	2.393	127.10
C146–H147···O 216	2.529	112.95
C152–H153···O 216	2.315	142.77

Table S7 Hydrogen bonding parameters of the model of $[(\mathbf{L3})_2H_2](ClO_4)_2$ obtained by theoretical calculation at M06-2X/6-31G(d)/LANL2DZ level.

D–H···A	H···A/Å	ρ of BCP	$\nabla^2\rho$ of BCP
N4–H205···N5	1.974	0.029	0.08
C78–H79···O 214	2.192	0.015	0.05
C82–H83···O 214	2.145	0.019	0.06
C152–H153···O 215	2.427	0.012	0.04
C154–H155···O 215	2.787	0.006	0.02
C82–H83···O 216	2.393	0.012	0.04
C146–H147···O 216	2.529	0.009	0.03
C152–H153···O 216	2.315	0.014	0.05

Table S8 Results obtained by Atoms in Molecules (AIM) analysis of $[(\mathbf{L3})_2H_2](ClO_4)_2$. [4,5]

D–H···A	H···A/Å	D–H···A/°
N117–H216···N1	2.07	136.38
C42–H43···Cl 230	2.92	117.67
C185–H186···Cl 230	3.00	120.65
C40–H41···Cl 231	2.88	118.54
C191–H192···Cl 231	2.82	133.84
C187–H188···Cl 232	2.79	152.51
C191–H192···Cl 232	2.69	137.20

Table S9 Hydrogen bonding parameters of the model of $[(\mathbf{L4})_2H_2](FeCl_4)_2$ obtained by theoretical calculation at M06-2X/6-31G(d)/LANL2DZ level.

D–H···A	H···A/Å	D–H···A/°
N4–H103···N114	2.084	137.13
C74–H75···O233	2.161	174.70
C78–H79···O233	2.108	177.15
C155–H156···O 234	2.350	153.65
C78–H79···O 235	2.455	119.70
C153–H154···O 235	2.331	123.35

Table S10 Hydrogen bonding parameters of the model of $[(\mathbf{L4})_2H_2](ClO_4)_2$ obtained by theoretical calculation at M06-2X/6-31G(d)/LANL2DZ level.

D–H···A	H···A/Å	ρ of BCP	$\nabla^2\rho$ of BCP
N4–H103···N114	2.084	0.024	0.07
C74–H75···O233	2.161	0.017	0.06
C78–H79···O233	2.108	0.020	0.06
C155–H156···O 234	2.350	0.012	0.04
C78–H79···O 235	2.455	0.011	0.04
C153–H154···O 235	2.331	0.013	0.05

Table S11 Results obtained by Atoms in Molecules (AIM) analysis of $[(\mathbf{L4})_2H_2](ClO_4)_2$.[4,5]

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