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Supporting Information

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X ray single crystal structure determination: The single crystals were picked under inert atmosphere and placed in immersion oil before mounting. The single crystal XRD data were collected on a Bruker AXS kappa apex2 CCD diffractometer, with graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation at 200 K. The data was integrated using SAINT PLUS and absorption correction was done using multi-scan absorption correction method (SADABS). The structure was solved by direct method (SHELXS-97) and refined using SHELXL-2018/3 program. All non-hydrogen-atoms were refined anisotropically.

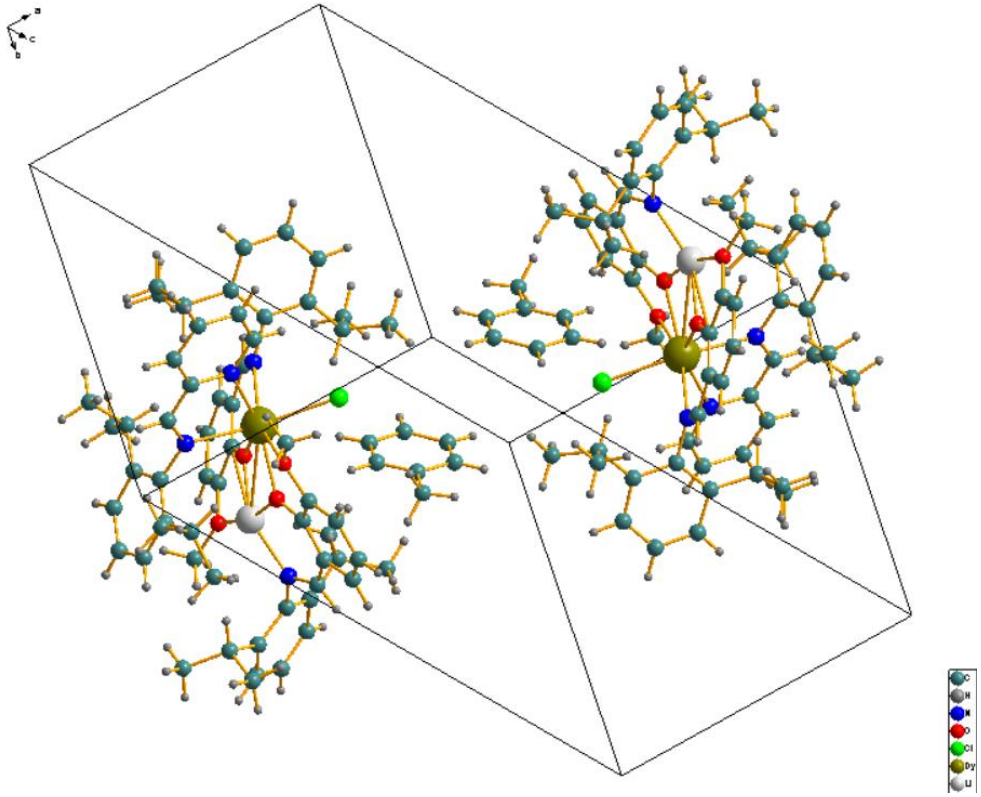


Figure S1. Unit cell packing diagram of complex **1**.

Table S1. Crystal data and structure refinement of complex [Li(I)Dy(III)(L^1)($L^{NN\bullet-}$)(Cl)]·tol (**1**).

Complex	**1**
CCDC Number	2110115
Empirical formula	$C_{65}H_{78}ClDyLiN_4O_4$
Formula weight (g/mol)	1184.20
Temperature (K)	200(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\,\bar{1}$
a (Å)	11.0735 (6)
b (Å)	12.6738 (7)
c (Å)	22.4854 (12)
α (°)	84.436 (2)
β (°)	86.690 (2)
γ (°)	83.969 (2)
V (Å^3)	3119.8 (3)
Z	2
Density (Mg/m^3)	1.261
μ (mm^{-1})	1.29
F(000)	1252
Crystal size (mm^3)	0.150 x 0.100 x 0.100
Theta range (°)	3.049 to 25.122
Index ranges	-13<=h<=13, -15<=k<=15, -26<=l<=26
Reflections collected	93742
Independent reflections	11083 [*R*(int) = 0.0878]
Completeness to theta = 25.000°	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7465 and 0.5366
Refinement method	Full-matrix least-squares on F^2

Data / restraints / parameters	11083 / 85/ 685
Goodness-of-fit on F^2	1.198
Final *R* indices [*I*>2sigma(*I*)]	*R*1 = 0.060, *wR*2 = 0.126
R indices (all data)	*R*1 = 0.063, *wR*2 = 0.125
Extinction coefficient	n/a
Largest diff. peak and hole	0.95, -1.78 e.Å^{-3}

Table S2. Selected bond distances (Å) and bond angles (º) of complex [Li(I)Dy(III)(L^1)($L^{NN\bullet-}$)(Cl)]·tol (**1**).

N4-Dy01	2.387 (5)	O2-Dy01-O3	68.86 (13)
N5-Dy01	2.435 (5)	O2-Dy01-N4	86.77 (16)
N6-Dy01	2.589 (5)	O3-Dy01-N4	89.89 (18)
O2-Dy01	2.240 (3)	O2-Dy01-N5	142.43 (16)
N4-Dy01	2.387 (5)	O3-Dy01-N5	135.48 (16)
O3-Dy01	2.276 (4)	N4-Dy01-N5	68.51 (19)
O4-Dy01	2.671 (4)	O2-Dy01-Cl1	119.65 (11)
Cl1-Dy01	2.5814 (16)	O3-Dy01-Cl1	95.92 (11)
O2-Dy01-O4	130.28 (13)	N4-Dy01-Cl1	153.28 (13)
O3-Dy01-O4	62.04 (13)	N5-Dy01-Cl1	89.61 (14)
N4-Dy01-O4	85.83 (16)	O2-Dy01-N6	72.01 (14)
N5-Dy01-O4	77.42 (15)	O3—Dy01-N6	136.45 (13)
Cl1-Dy01-O4	74.15 (10)	N4-Dy01-N6	106.38 (17)
N6-Dy01-O4	156.06 (14)	N5-Dy01-N6	87.83 (16)
O2-Dy01-Li1	35.7 (2)	Cl1-Dy01-N6	87.15 (10)

Synthesis:

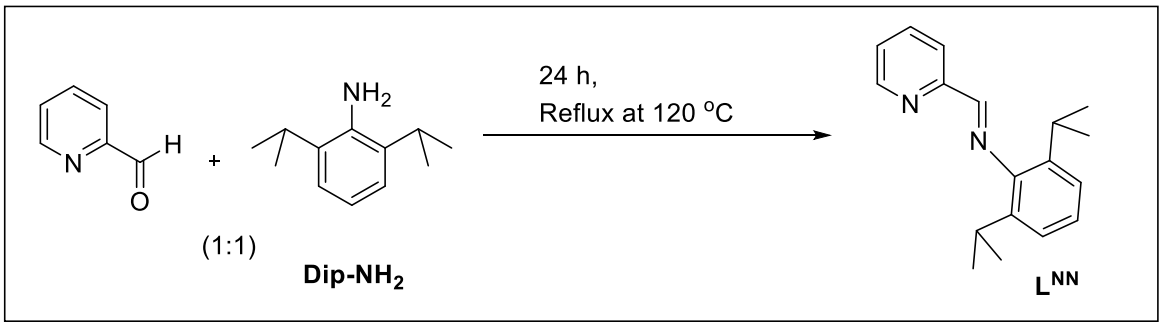
Materials and General Procedure: All the starting materials were purchased from commercially available sources and modified as per the need. Unless otherwise stated, all the reactions were carried out under an inert (argon) atmosphere inside the Mbrown glovebox that was maintained oxygen and moisture level below 0.1 ppm. The α-iminopyridine Ligand (L^{NN}) and other ligands (HL^1) were synthesized as per previous reports and lithium diisopropylamide (LDA) was used to obtain LiL^1.[1-3] The solvents (toluene and THF) were dried by stirring them with NaK alloy for several days and collect under vacuum. $CDCl_3$ was distilled with CaH_2 under argon atmosphere. Anhydrous $DyCl_3$ was purchased from Sigma Aldrich as white powders stored inside sealed ampules.

Synthetic procedures

Synthesis of complex 1: A mixture of $DyCl_3$, iminopyridine ligand (**L^{NN}**) and lithiated salt of co-ligand (**Li-L^1**) was taken in 3:3:4 molar ratio in a Schlenk flask containing 15 mL of dry THF and stirring was started in the glovebox (Scheme 1). After 10 min of stirring, 0.4 mmol of K metal was added to the reaction mixture. The subsequent stirring produced a dark green colour reaction mixture which was stirred for 10 hours. Then, the reaction mixture was dried under a vacuum by removing THF solvent. After that 20 mL of dry toluene, which is a less polar solvent than THF, was added to the reaction mixture and the solution was further stirred for 10 min and the soltion was filtered. The green filtrate was concentrated under vacuum and was kept in the freeze inside glovebox at -40 °C temperature. The block shape green crystals suitable for single-crystal XRD were formed in a week. The yield was calculated to be 46 % based on $DyCl_3$. Anal (%). calcd for complex **1** ($C_{65}H_{78}ClDyLiN_4O_4$): C, 65.92; H, 6.64; N, 4.73 Found: C, 65.86; H, 6.25; N, 4.66. UV-vis bands at 365 and 690 nm.

Preparation of ligands:

Preparation of (E)-N-(2,6-diisopropylphenyl)-1-(pyridin-2-yl)methanimine (L^{NN}) :



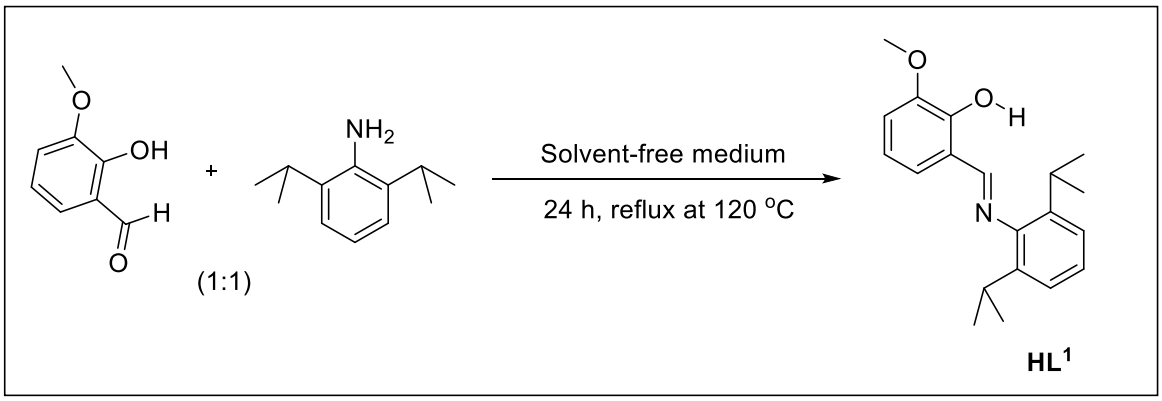
The N-substituted pyridine product was synthesized by the condensation of 2-pyridinecarboxaldehyde (0.95 mL, 10 mmol) and 2,6-diisopropylaniline (1.88 mL, 10 mmol). The two reactants were mixed in a 250 mL Schlenk flask at 120 °C for 24 h under constant stirring. After the reaction, the flask was subjected to vacuum and inert gas purging multiple times to remove water formed during the reaction to obtain a bright fluorescent solid. It was recrystallized from *n*-hexane. Yield: 85%. M.P.: 66 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 298K, ppm): δ = 8.74 (d, *J* = 4.8 Hz, 1H), 8.32 (s, 1H), 8.28 (d, *J* = 7.9 Hz, 1H), 7.85 (td, *J* = 7.7, 1.8 Hz, 1H), 7.42 (ddd, *J* = 7.5, 4.8, 1.2 Hz, 1H), 7.18 (d, *J* = 6.9 Hz, 2H), 7.13 (dd, *J* = 8.7, 6.4 Hz, 1H), 3.04 – 2.90 (m, *J* = 6.9 Hz, 2H), 1.28 (d, *J* = 6.8 Hz, 1H), 1.18 (d, *J* = 6.9 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$, ppm) δ= 163.02, 162.96, 154.39, 149.74, 149.71, 148.40, 137.27, 136.83, 136.74, 125.44, 125.26, 124.49, 124.41, 123.16, 123.11, 123.04, 123.00, 121.38, 27.97, 23.58, 23.38, 23.12.

MS (ESI pos.): ($M+H^+$): 267.18 *m*/*z*.

Preparation of (E)-2-(((2,6-diisopropylphenyl)imino)methyl)-6-methoxyphenol (HL^1):



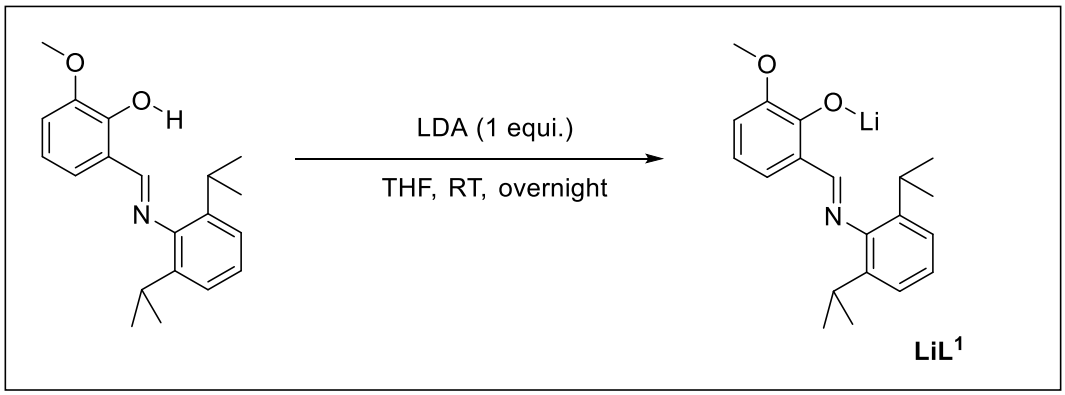
A mixture of o-vanillin (1.25 mL, 10 mmol) and 2,6-diisopropylamine (1.88 mL, 10 mmol) was stirred at refluxing temperature for 24 hours. After the reaction, water was removed through continuous vacuuming and multiple purging with inert gas. It was stored inside the glove box under argon atmosphere. Light yellow color. Yield: 95%; M.P.: 132 °C.

^{1}H NMR (500 MHz, $CDCl_3$, 298K, ppm) δ= 13.54 (d, J = 2.1 Hz, 1H), 8.32 (d, J = 1.8 Hz, 1H), 7.21 – 7.18 (m, 2H), 7.04 (dd, J = 7.9, 1.6 Hz, 1H), 6.99 (dt, J = 7.8, 1.5 Hz, 1H), 6.92 (t, J = 7.9 Hz, 1H), 3.97 (s, 3H), 3.29 – 2.69 (m, 2H), 1.18 (dd, J = 6.9, 1.8 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_{3,\ ppm}$) δ= 166.76, 166.70, 151.37, 148.53, 145.94, 138.78, 125.65, 123.73, 123.52, 123.37, 123.21, 118.72, 118.58, 118.49, 114.70, 114.51, 56.46, 55.79, 28.14, 23.89, 23.62, 23.42, 23.15.

MS (ESI pos.): ($M+H^+$): 312.19 *m*/*z*.

Preparation of lithium (E)-2-(((2,6-diisopropylphenyl)imino)methyl)-6-methoxyphenolate:



The mixture of HL (2.0 g, 6.42 mmol) and LDA (0.686 g, 6.42 mmol) was stirred in 25 ml of distilled THF. After an overnight reaction, THF was removed using a vacuum, and hexane was added. Further sonication assisted in obtaining a white precipitate, which was subsequently filtered and dried. This solid residue was further washed with *n*-hexane and dried under vacuum. Yield: 96%. M.P.: 246 ^{o}C.

^{1}H NMR (500 MHz, $CDCl_3$, 298K) δ ppm 7.93 (d, J = 18.1 Hz, 1H), 7.03 (s, 1H), 6.68 (d, J = 7.9 Hz, 1H), 6.40 – 6.18 (m, 1H), 6.14 (t, J = 7.8 Hz, 1H), 5.99 (d, J = 7.6 Hz, 1H), 3.06 (tt, J = 10.1, 5.4 Hz, 2H), 2.78 (d, J = 14.9 Hz, 1H), 2.64 (s, 3H), 0.95 (d, J = 49.1 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$) δ ppm 167.54, 160.95, 151.90, 150.36, 139.47, 127.95, 124.55, 123.10, 123.02, 120.88, 111.73, 110.91, 110.63, 54.22, 27.92, 27.66, 14.04

MS (ESI pos.): ($M+H^+$): 318.19 *m*/*z*.

NMR spectra

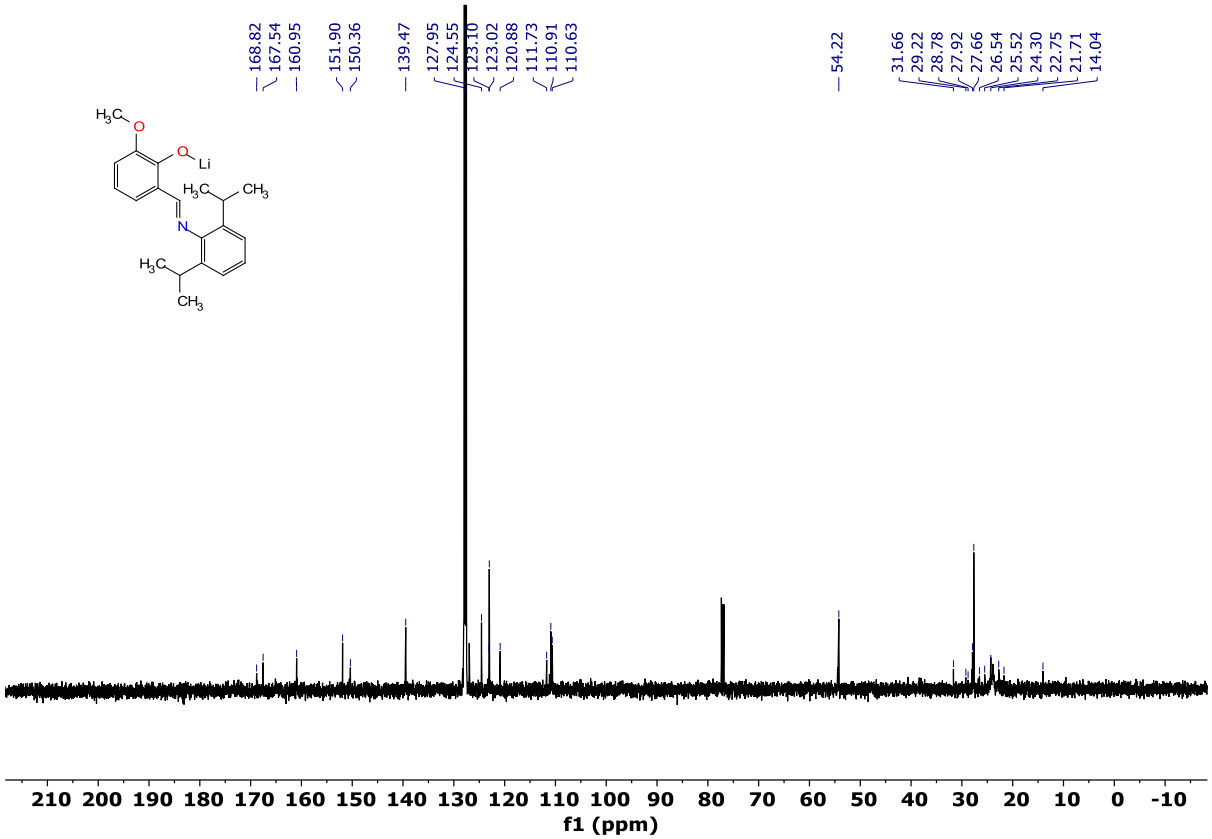


Figure S2. ^{1}H NMR spectrum of Li**L**^{1} in $CDCl_3$ at 298 K (500 MHz).

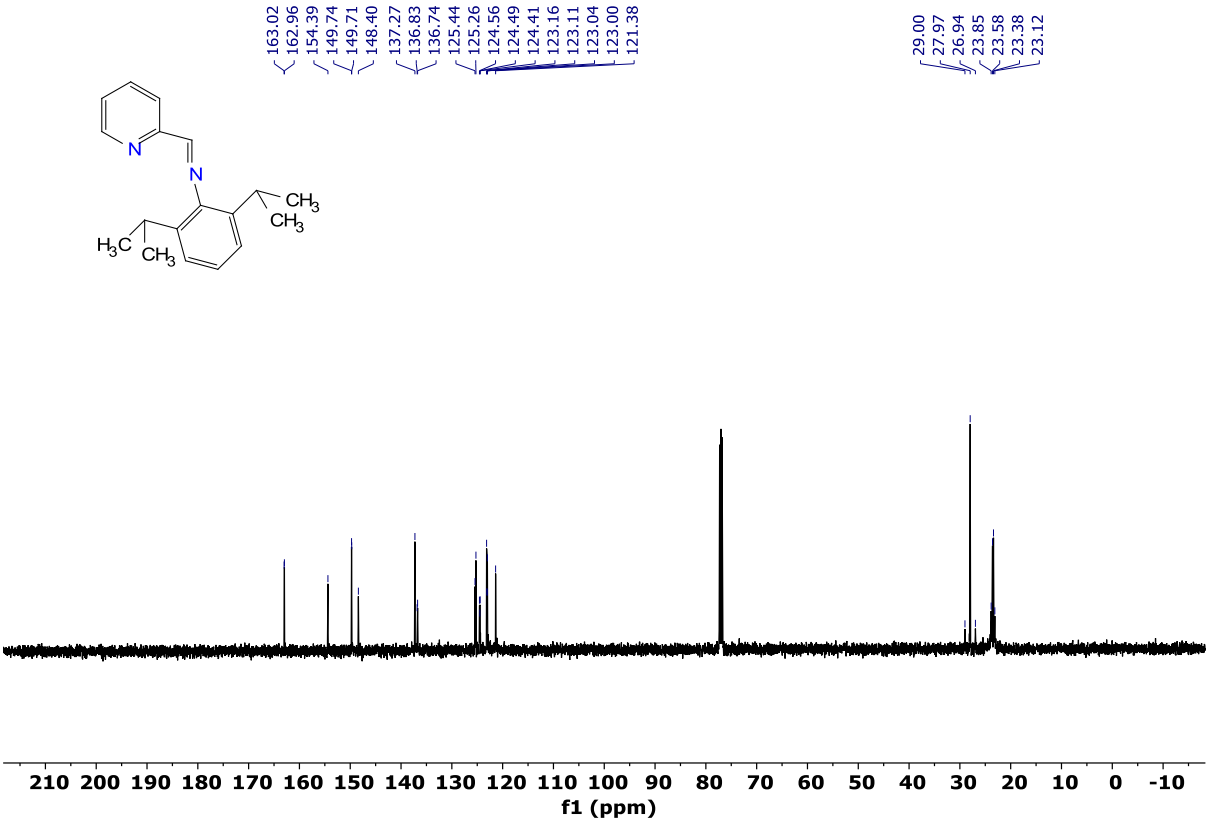


Figure S3. ^{13}C NMR spectrum of $\mathbf{L^{NN}}$ in $CDCl_3$ at 298 K (101 MHz).

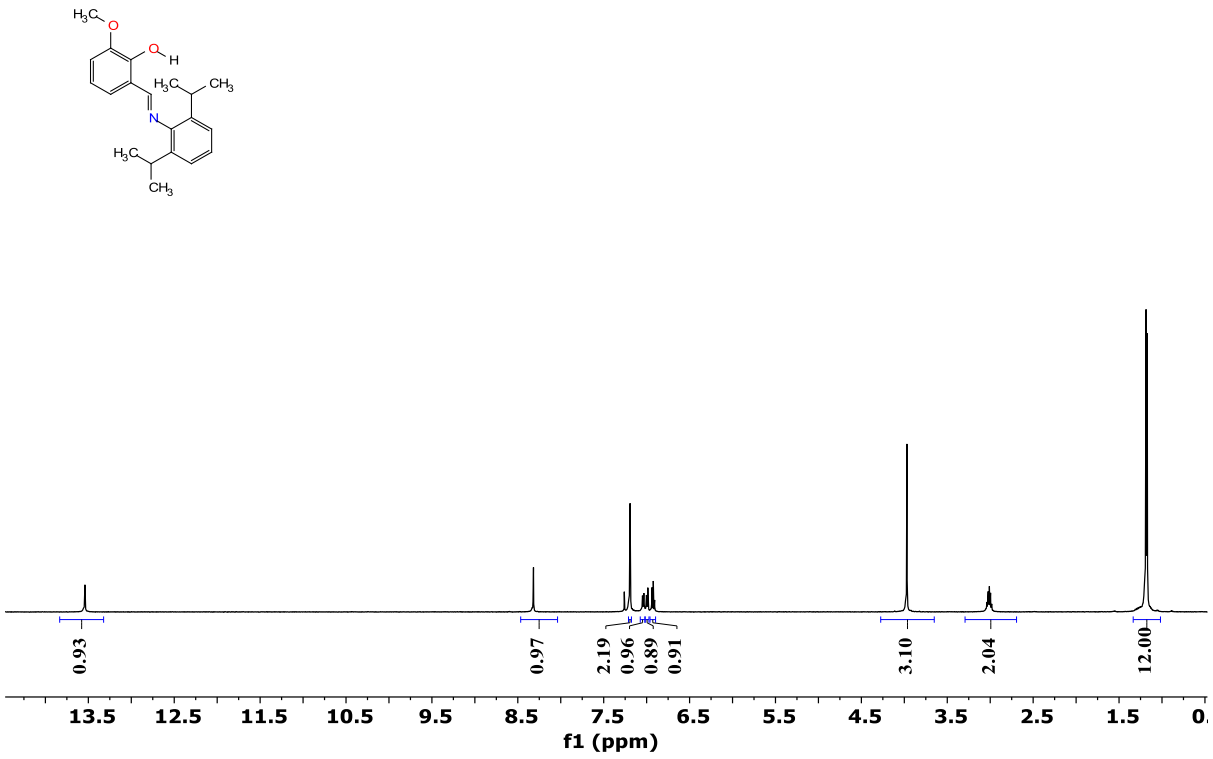


Figure S4. ^{1}H NMR spectrum of **HL^{1}** in $CDCl_3$ at 298 K (500 MHz).

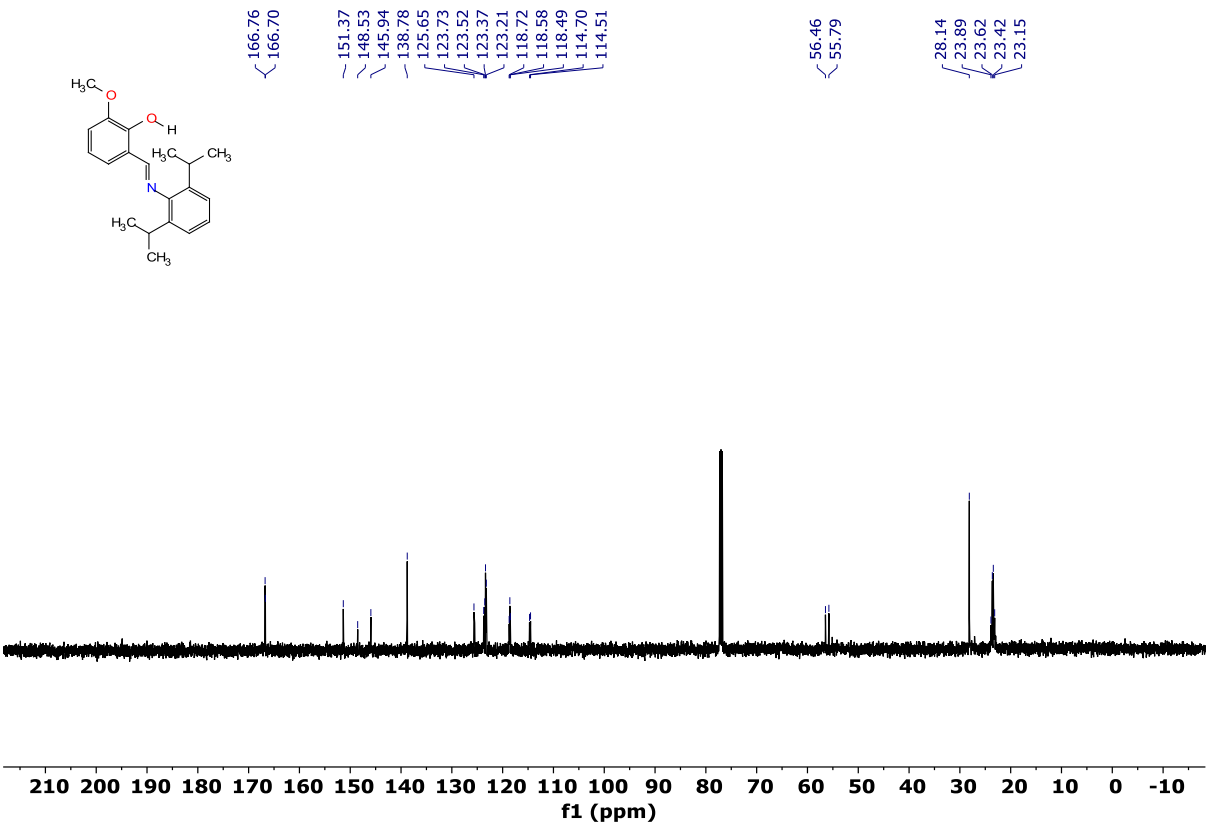


Figure S5. ^{13}C NMR spectrum of **HL^{1}** in $CDCl_3$ at 298 K (101 MHz).

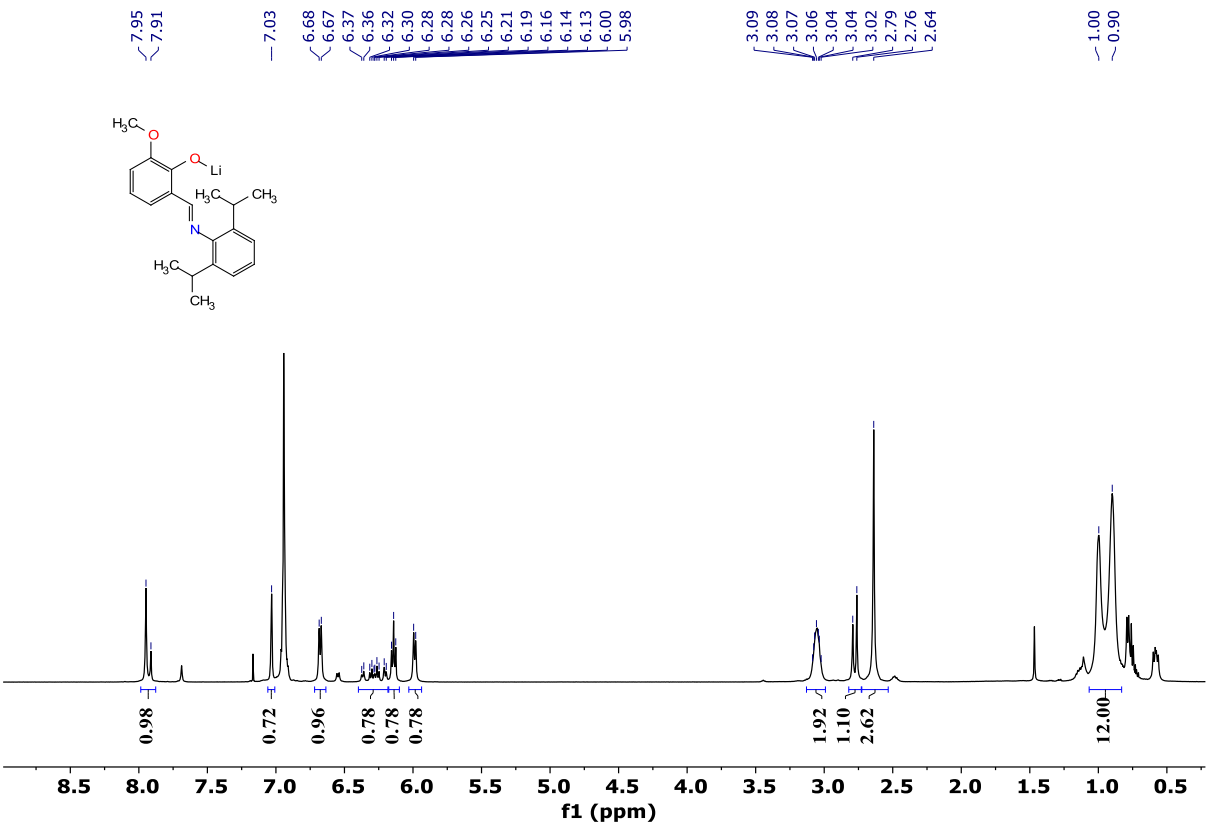


Figure S6. ^{1}H NMR spectrum of **LiL^{1}** in $CDCl_3$ at 298 K (500MHz). The doubling of the resonance may be due to the rotational isomers of **LiL^{1}**.

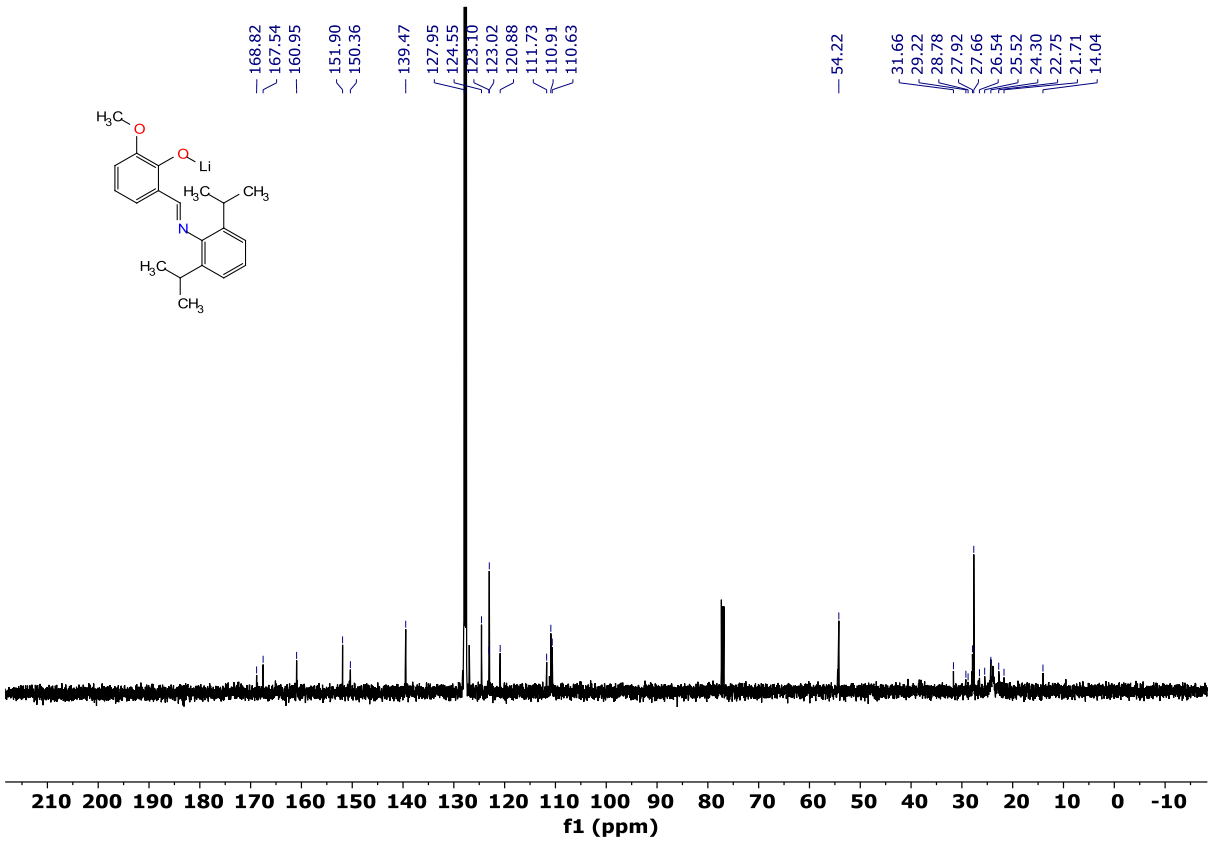


Figure S7. ^{13}C NMR spectrum of **LiL^{1}** in $CDCl_3$ at 298 K (101 MHz).

Magnetic measurements:

DC and AC susceptibility data were performed on a Quantum Design MPMS-XL SQUID magnetometer. DC data was obtained upon cooling from 300 K to 2 K in applied field of 1000 Oe. AC susceptibility data was collected upon scanning the frequencies of alternating field of 3.5 Oe. Magnetization measurements were performed on a Quantum Design MPMS3 VSM SQUID magnetometer equipped with a 7 T magnet. M(H) curves were collected with a stable field at each point. The samples were grounded and fixed in a gelatine capsule using small amounts of eicosane to avoid any movement of the sample. The data obtained were corrected for diamagnetic contributions of the eicosane, the gelatin capsule and the sample holder. Diamagnetic corrections for the sample were estimated using Pascal's constants. The real and imaginary components of the ac susceptibility were modelled using the following Debye modelled equations.

$$\chi'(\omega) = \chi_s + \frac{(\chi_T - \chi_S)[1 + \omega\tau^{1-\alpha}\sin(\alpha\pi/2)]}{1 + 2(\omega\tau)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau)^{2(1-\alpha)}}$$

$$\chi''(\omega) = (\chi_T - \chi_s)\frac{(\omega\tau)^{1-\alpha}\cos(\alpha\pi/2)}{1 + 2(\omega\tau)^{1-\alpha}\sin(\alpha\pi/2) + (\omega\tau)^{2(1-\alpha)}}$$

Table S3. Fitting parameters for [Li(I)Dy(III)(L^1)($L^{NN\bullet-}$)(Cl)].tol (**1**). (H_{DC} = 0 Oe)

***T*/K**	***τ***	***α***	***R2***
2	0.00133	0.61671	0.99997
2.2	0.00114	0.60985	0.99997
2.4	0.00105	0.5981	0.99997
2.6	8.90553E-4	0.58626	0.99997
2.8	7.50337E-4	0.58509	0.99996
3	6.63938E-4	0.58283	0.99998
3.2	5.96523E-4	0.58001	0.99996
3.4	5.30787E-4	0.57702	0.99997
3.6	4.88044E-4	0.57482	0.99997
3.8	4.1319E-4	0.57804	0.99998
4	3.8561E-4	0.57547	0.99995
4.4	3.4767E-4	0.56449	0.99995
4.8	3.16886E-4	0.55834	0.99996
5.2	2.60449E-4	0.56535	0.99996
5.6	2.34558E-4	0.55851	0.99995
6	2.12568E-4	0.55374	0.99994
6.4	1.54587E-4	0.56141	0.99997
6.8	1.37289E-4	0.5631	0.99991

Table S4. SHAPE analysis of the complex **1**

Structure	HP-7	HPY-7	PBPP-7	COC-7	**CTPR-7**	JPBPY-7	JETPY-7
	34.217	21.136	4.370	4.503	**3.625**	7.988	17.278

EPR Measurements: The room temperature EPR sample of complex [Li(I)Dy(III)(L^1)($L^{NN\bullet-}$)(Cl)]·tol (**1**) was prepared by preparing a light green diluted solution in toluene which was placed in a quartz capillary tube and measured at SAIF, IIT Madras, Chennai.

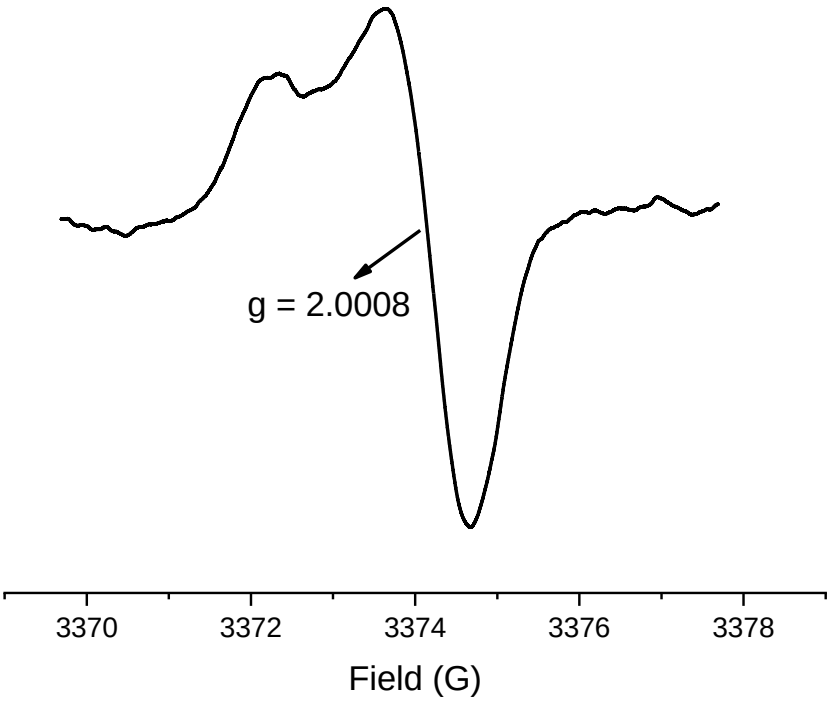


Figure S8. X band EPR spectrum of **Dy-radical** in toluene solution at 298 K showing anisotropic EPR signal. g = 2.0008, centre of field 3374.11 G.

CV Measurements:

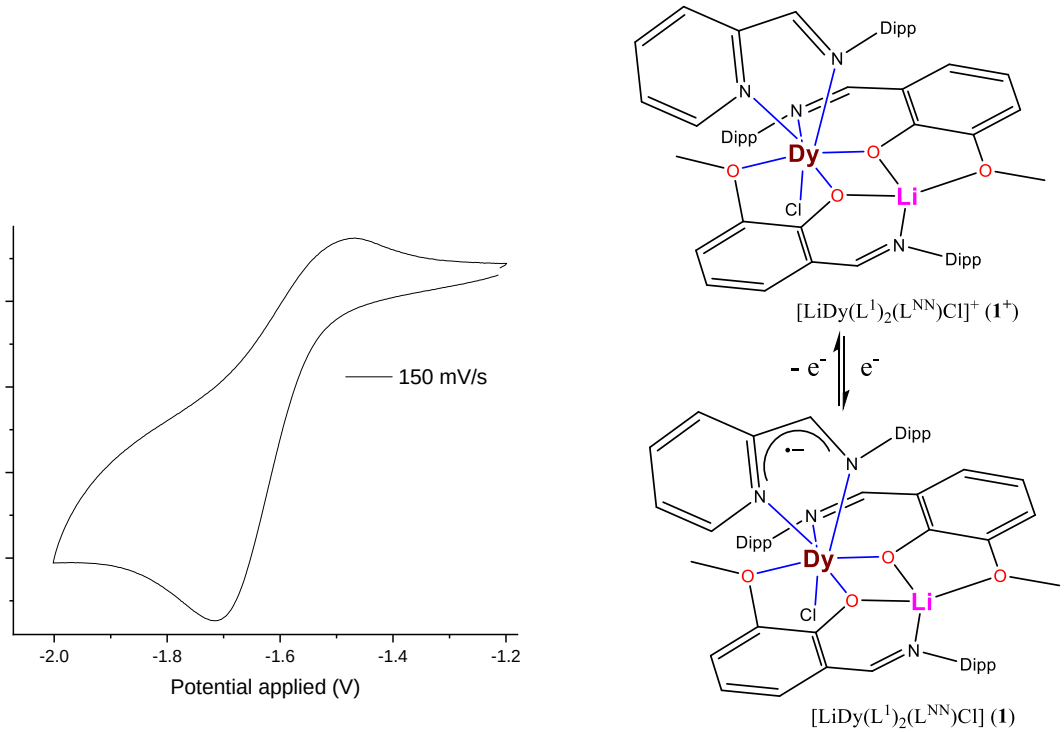


Figure S9. (Top) Packing diagram of complex **1** and (bottom) Cyclic voltammetry (V-$V_{Cp2Fe/Cp2Fe+}$) of complex **1** in THF in the presence of 0.1 N of nBu$_4^+$PF$_6^-$. Complex **1** show one electron oxidative above -1.60 V leading to the loss of radical electron in quasi-reversible manner.

References

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