Supporting Information

	$\tau_{QTM}(s)$	$C(s^{-1}K^{-n})$	n	$\tau_0\ (s)$	U_{eff}
1 (H_{dc} = 0) model 1	$10^{-3.8(2)}$	$10^{-4(6)}$	7(5)		
1 (H_{dc} = 0) model 2	$10^{-3.8(2)}$			$10^{-7(2)}$	100(70)
A (H_{dc} = 0)	-	-	-	2.8×10^{-6}	97.6±1.7K
B (H_{dc} = 0)	-	-	-	1.4×10^{-6}	37.9±1.1K
C (H_{dc} = 0)	-	-	-	4.0×10^{-7}	48.7±0.7K
D (H_{dc} = 0)	0.00282(2)	0.022(2)	2.86(2)	$2.6(5)\times10^{-12}$	546(6) cm^{-1}
D (H_{dc} = 1400 Oe)	-	0.00021(3)	4.08(5)	$4(5)\times10^{-13}$	609(44) cm^{-1}
F (H_{dc} = 0)	-	2.0×10^{-9}	7.8	4×10^{-13}	1285K
G (H_{dc} = 0)	0.0142	0.009	3.17	2.0×10^{-8}	312 cm^{-1}
G (H_{dc} = 1600 Oe)	-	0.0005	3.85	2.0×10^{-8}	314 cm^{-1}
H (H_{dc} = 0)	0.0493	1.85×10^{-3}	3.38	2.75×10^{-8}	475K
H (H_{dc} = 1000 Oe)	-	1.50×10^{-4}	3.86	1.785×10^{-8}	490K

Table S1. Best fit parameters for multiple relaxation pathways for complexes **1** and **A-H.**

Table S2: Relaxation fitting parameters of **1** at 2K to 16.5K from Least-Squares fitting of χ(f) data under zero dc field.

Temperature (K)	$\chi_s\ (emu\ mol^{-1}$	$\chi_t\ (emu\ mol^{-1})$	α	$\tau(s)$
2.00127	1.43609	11.41136	0.37189	2.91902E-4
2.50113	1.42031	9.38413	0.37886	2.32768E-4
3.00084	1.45342	7.86441	0.36974	1.95388E-4
3.50072	1.40731	6.85095	0.37572	1.76012E-4
4.00057	1.40949	5.98606	0.36444	1.60143E-4
4.50053	1.38253	5.37533	0.36204	1.53811E-4
5.00046	1.33697	4.8102	0.35634	1.42162E-4
5.50041	1.33577	4.41949	0.34488	1.43486E-4
6.00036	1.2662	4.06718	0.35045	1.37415E-4
6.50034	1.25938	3.74654	0.33212	1.36164E-4
7.00029	1.20249	3.53844	0.3437	1.38033E-4
7.50029	1.11731	3.33681	0.36425	1.32151E-4
8.00024	1.14514	3.07228	0.31819	1.29224E-4
8.50025	1.11995	2.88162	0.30362	1.26782E-4
9.00022	1.0724	2.76374	0.31286	1.27957E-4
9.50021	1.01683	2.63519	0.32314	1.22347E-4
10.00019	1.01743	2.46313	0.2835	1.1529E-4
10.50019	0.97651	2.41276	0.29944	1.1816E-4
11.00017	0.90776	2.31112	0.31913	1.0553E-4
11.50016	0.93482	2.17009	0.25425	9.9548E-5
12.00015	0.91307	2.06692	0.23066	8.94179E-5
12.50016	0.83779	2.01673	0.27015	7.77901E-5
12.9995	0.86744	1.90183	0.19376	7.08144E-5
13.49935	0.77246	1.88111	0.26051	5.88811E-5
13.99931	0.77784	1.79807	0.2184	5.16871E-5
14.49941	0.76031	1.73304	0.20126	4.38158E-5
14.99942	0.76345	1.6428	0.14798	3.67888E-5
15.49923	0.70219	1.61256	0.18376	2.94319E-5
15.99939	0.74493	1.52338	0.09332	2.60563E-5
16.49925	0.56641	1.52675	0.22517	1.65104E-5

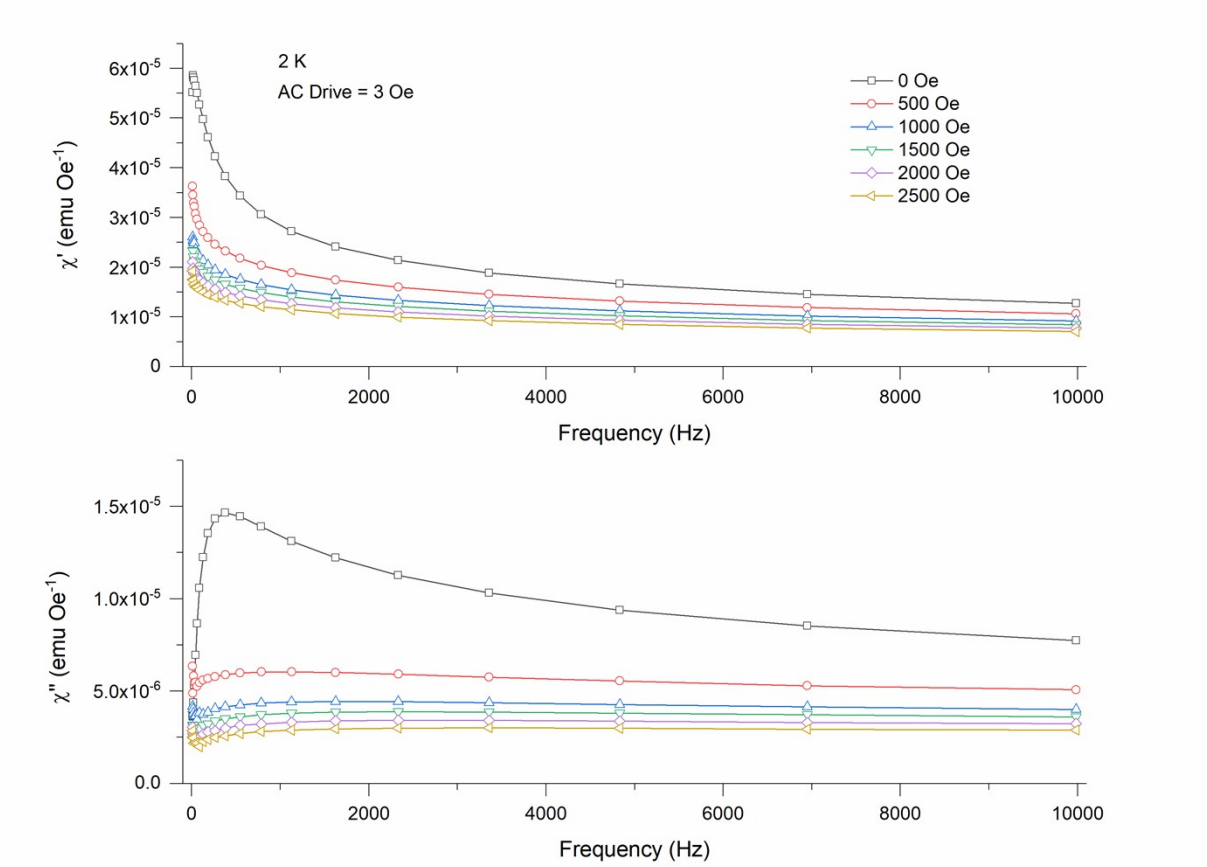


Figure S1. AC susceptibility for complex **1** at 2 K with the dc field varying from 0 to 2500 Oe with ΔH = 500 Oe.

Magnetometry: Single crystals of complex **1** were washed with n-hexane, and 11.77 mg of a powdered sample of **1** was filled into a gelatine capsule (QDS-AGC2 from Quantum Design) and embedded within ~50 mg Icosane under Ar atmosphere. The tablet was attached to a sample holder straw (GDS-AGC2 from Quantum Design) with polyimide tape. The sample was transferred in an Ar-filled container to the measuring device and quickly moved into the sample tube filled with He gas (≈10 Torr) during operation. Magnetic characterizations were performed with a physical property measurement system (PPMS DynaCool) from Quantum Design. The magnetic field and temperature scans have been performed with the vibrating sample magnetometry (VSM) option and the ac susceptibility measurements with the ACMSII option. The sample was cooled to 2 K at a constant magnetic field of 1000 Oe for the magnetic moment vs. temperature measurements. The magnetic moment was measured during heating from 2 K to 50 K in temperature settle mode and from 50 K to 200 K in temperature sweep mode with 1 K/min, both with a 1 K temperature step size. The signal averaging time was 10 seconds per measuring point. The magnetic susceptibility of the temperature scan has been corrected for $-0.027\ \mathrm{cm^3\,mol^{-1}}$ diamagnetic contribution from the Icosane and doubly occupied

orbitals. The magnetic moment vs. field scans has been done at 2, 3, 4, 6, 10, 15, and 20 K from 0 to 70 kOe ($\mu_0 H$ = 7 Tesla) with a uniform field step size of ΔH = 1000 Oe. The signal averaging time was 10 seconds per measuring point. For ac susceptibility characterization, a series of measurements at 2 K were performed with the dc field varying from 0 to 2500 Oe with ΔH = 500 Oe (Figure S1). At each field, the ac excitation frequency was scanned from 10 Hz to 10 kHz with a 20-step logarithmic resolution, a 3 Oe ac excitation field, and an averaging time of 10 seconds per measuring point. The measurement at 0 Oe showed the strongest χ'' signal, and the following ac temperature scans were consequently performed at 0 Oe dc field. Ac temperature scans have been performed from 2 K to 30 K with ΔT = 0.5 K from 2 to 20 K and ΔT = 2 K from 20 to 30 K. For each temperature, the ac excitation frequency was scanned from 10 Hz to 10 kHz with a 35 step logarithmic resolution, a 3 Oe ac excitation field and an averaging time of 10 seconds per measuring point. The experimental ac magnetic data sets were fitted using the CC-Fit2 program[1] that uses a (generalized) Debye model to extract magnetic relaxation times with associated uncertainties.

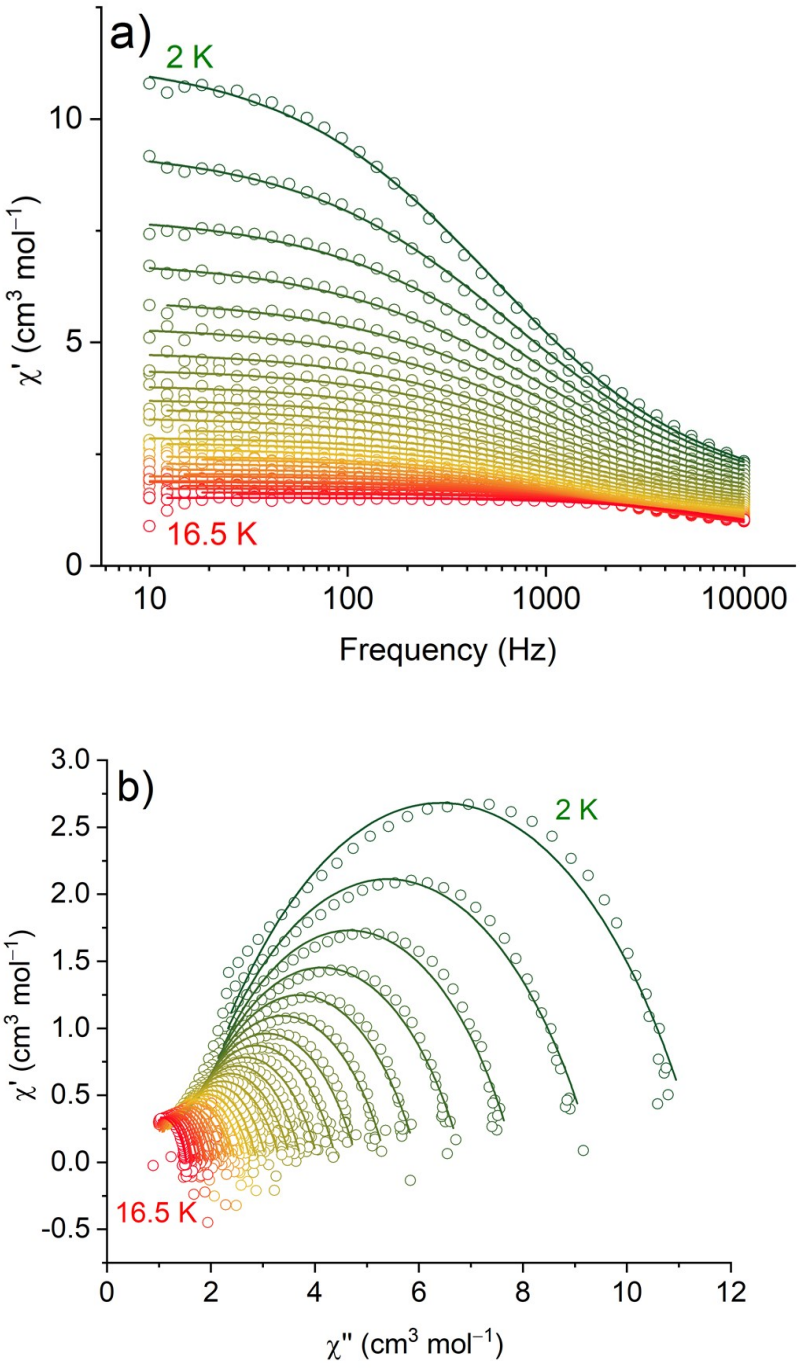


Figure S2. a) In-phase χ′ vs. ac excitation frequency for **1** under zero applied dc field from 2 to 16.5 K (a), Cole-Cole plots as χ′ vs. χ″ (b). Solid lines represent fits to the data, as described in the main text.

Synthesis: The ligand Cp^{Ar3} involves multiple-step synthesis, which is not sensitive to air and moisture.[2] Synthesis of the Dy-complex is highly sensitive to air and humidity. THF/toluene was pre-purified by following standard purification protocols using the Schlenk line with the

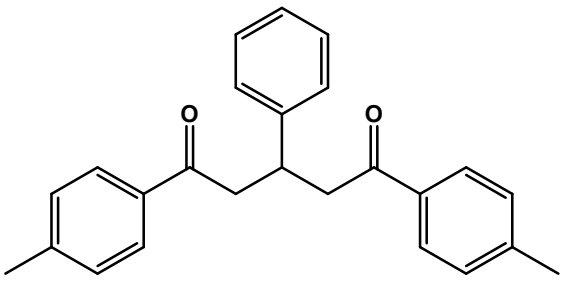
flow of high-purity argon gas. H_2O/O_2 will be killed with NaK under argon flow. All the synthesis will be carried out in the Schlenk line or inside the glove box workstation filled with argon gas (H_2O/O_2 < 0.1 ppm).

The rectangular-shaped yellow crystals of $[(Cp^{Ar3})_4Dy^{III}_2Cl_4K_2]\cdot 3(C_7H_8)$ (**1**), which were separated by filtration, utilized for magnetic and CV measurements.[2]

Cyclic voltammetry (CV) measurements: THF has been distilled three times with NaK alloy under argon flow. The redox properties of the Dy-complex (12 mg) were studied by CV measurements (Figure 5) containing 0.1 M tetrabutylammonium hexafluorophosphate in THF (8 mL) employing silver as a reference electrode, glassy carbon as a working electrode, and platinum as the counter electrode.

2. General Methods and Materials. 4-methylbenzaldehyde, 4-methylacetophenone, acetic acid, potassium and anhydrous $DyCl_3$ were purchased from commercial sources and used as received. Nuclear magnetic resonance (NMR) spectra for newly synthesized compounds were recorded on the Bruker 400 MHz NMR spectrometer. Electron spray ionization mass (ESI-MS) spectra were recorded with an Agilent 6545A Q-TOF mass spectrometer. The syntheses of complexes **2** were carried out under argon atmosphere using standard Schlenk line technique. All solvents (Toluene) were dried by refluxing over Na/K alloy for 8-12 h under argon atmosphere followed by distillation. Further, the dried and oxygen free solvent was stirred for 12 h over 4 Å molecular sieves and distilled under vacuum and stored over molecular sieves (with oxygen and moisture content < 10 ppm). Deuterated solvents, e.g., $CDCl_3$ were purchased from Sigma-Aldrich and further purified by stirring over CaH_2 for two days, followed by reflux for 4 h and distillation under vacuum.

S2. Ligand synthesis 4,4'-(4-phenylcyclopenta-1,3-diene-1,2-diyl)bis(methylbenzene) [Me_2Cp-H (a1)].



Synthesis of 3-phenyl-1,5-di-p-tolylpentane-1,5-dione (1a): The compound **a1** was synthesised at ambient condition. Along with the NaOH pellets (10.55 g, 263.84 mmol), 4-methylacetophenone (18.58 g, 138.51 mmol), and benzaldehyde (7 g, 65.96 mmol) were mixed together in a mortar of 1:2 molar ratio and grounded until the liquid reactants solidified into a red colour. The resulting red solid mass was dissolved in a (1:1:2) v/v solution of ethyl acetate and water, then poured into a 500 mL separating funnel. To eliminate the unreacted NaOH, ethyl acetate layer was removed and repeatedly washed with brine solution and water. Then the ethyl acetate layer was allowed to pass through an anhydrous sodium sulphate to get it dried. The unreacted starting materials (benzaldehyde and 4-methyl acetophenone) were removed from the resulting crude solid by stirring it for 30 min with the excess of hexane (200 mL), then followed by filtering through a Büchner funnel and washed with hexane. The resulting pure 3-phenyl-1,5-di-p-tolylpentane-1,5-dione (**a1**) is a white solid, which was dried for 24 h at 65 °C in a temperature-controlled hot air oven. The yield obtained was 19.42 g (83%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 7.84 (d, 4H, J = 8.0 Hz, ArH), 7.27-7.26 (m, 4H, ArH), 7.24-7.14 (m, 5H, ArH), 4.08-4.01 (m, 1H, methine), 3.45 (dd, 2H, J = 8.0 Hz, 16 Hz, $–CH_2$), 3.31 (dd, 2H, J = 8.0 Hz, 16Hz, $–CH_2$), 2.39 (s, 6H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 198.30, 143.98, 143.87, 134.46, 129.28, 128.60, 128.30, 127.49, 126.64, 44.87, 37.35, 21.66.

FT-IR (cm^{-1}): 1678, 1604, 1418, 1344, 1268, 1230 1203, 1178, 993, 811, 776, 763, 749, 693.

HRMS (ESI-TOF) m/z calculated for $[M+H]^+$: 357.1776 found: 357.1866.

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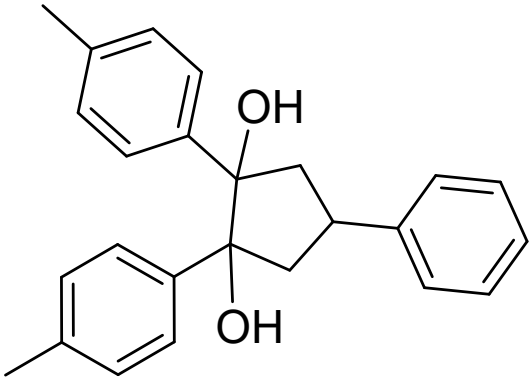


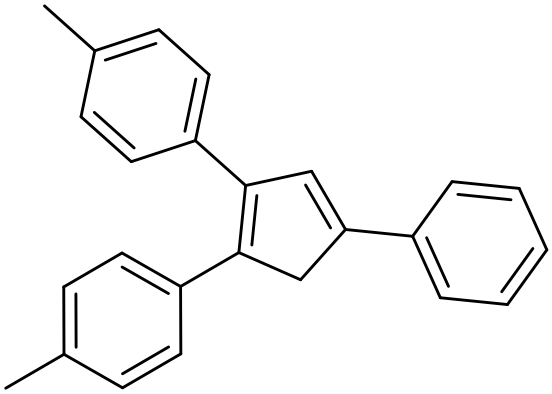
Synthesis of 4-phenyl-1,2-di-p-tolylcyclopentane-1,2-diol (a2): 200 mL of glacial acetic acid was added to the reaction mixture, followed by stirring and refluxing at 90-100 °C for 4 h with the compound **a1** (18.68 gm, 52.47 mmol) and Zn-dust (17.155 g, 262.35 mmol) in a 500 mL round bottom flask. The unreacted Zn-dust was filtered out while the reaction was completed, based on TLC. The yellow solid was produced by adding the filtrate that was produced drop by drop into the crushed ice while vigorous stirring. The excess of acetic acid was then removed from the solid by filtering it and then multiple washes with distilled water. By dissolving the yellow solid in ethyl acetate, the excess of water was removed at this step, allowing the organic layer to be separated from the water using a separating funnel. The resulting crude product 4-phenyl-1,2-di-p-tolylcyclopentane-1,2-diol (**a2**) was further refined by washing multiple times with hexane after ethyl acetate was removed using a rotary evaporator. The final white solid of **a2** was dried for 24 hours at 65 °C in a temperature-controlled hot air oven. The yield was **a2** is 7.4 g (40%).

^{1}H NMR (400 MHz, $CDCl_3$, 298 K) δ ppm: 7.39 (d, 4H, J = 8.0 Hz, ArH), 6.94 (d, 4H, J = 8.0 Hz, ArH), 6.85-6.79 (m, 5H, ArH), 4.10-4.01 (m, 1H, methine), 3.40 (s, 2H, hydroxyl), 2.76 (dd, 2H, J = 12 Hz & 16 Hz, $–CH_2$), 2.57 (dd, 2H, J = 8 Hz, 16 Hz, $–CH_2$), 2.19 (s, 6H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 144.36, 140.22, 136.28, 128.50, 127.99, 127.05, 126.19, 126.10, 85.42, 45.44, 38.22, 20.90.

FT-IR (cm^{-1}): 3110, 1501, 1414, 1324, 1268, 1243, 1235, 1229, 1201, 1168, 991, 881,811, 779, 768, 742, 672.

HRMS (ESI-TOF) m/z calculated for $[M+H]^+$: 359.2011; found: 359.1654.



Synthesis of 4,4'-(4-phenylcyclopenta-1,3-diene-1,2-diyl)bis(methylbenzene): The 60 mL of ethanol were used to dissolve the compound **a2** (11.25 g, 31.38 mmol), and 6 mL of conc. hydrochloric acid (30%) was added dropwise while the mixture was vigorously stirring on the stirrer. The conversion of **a2** into an equivalent yellow solid was noticed after a vigorous stirring and refluxing of the reaction mixture. The resulting yellow solid 4,4'-(4-phenylcyclopenta-1,3-diene-1,2-diyl)bis(methylbenzene) (**a3**) was filtered and dried in a temperature-controlled hot air oven at 65 °C for 24 h after the reaction had finished, to be determined by TLC. In addition, **a3** was purified using column chromatography with the eluents of 2% hexane/EtOAc. The final product yield was calculated as 7.0 gm (70%).

^{1}H NMR (400 MHz, $CDCl_3$, 289 K) δ ppm: 7.55 (d, 2H, J = 8.0 Hz, ArH), 7.35-7.28 (m, 4H, ArH), 7.23-7.18 (m, 3H, ArH), 7.13 (d, 2H, J = 8.0 Hz, ArH), 7.02 (t, 3H, J = 8.00 Hz, ArH), 3.89 (s, 2H, Cp-CH_2), 2.35 (s, 3H, Ar–CH_3), 2.30 (s, 3H, Ar–CH_3).

^{13}C NMR (100 MHz, $CDCl_3$, 298 K) δ ppm: 144.45, 141.31, 138.88, 136.75, 136.17, 135.86, 134.29, 134.13, 132.02, 129.16, 128.96, 128.65, 128.24, 127.60, 126.77, 124.84, 44.90, 21.27, 21.18.

FT-IR (cm^{-1}): 1592, 1512, 1495, 1441, 1404, 1365, 1199, 1180, 1111, 1030, 1016, 906, 823, 906, 813, 746, 689.

HRMS (ESI-TOF) m/z calculated for $[M+H]^+$: 322.1722; found: 322.1542.

S3. Synthesis of $[(Me_2Cp)_4Dy^{III}_2Cl_4K_2]\cdot 3.5\ (C_7H_8)$ (1): The one-pot synthetic strategy was effective. To the mixture of anhydrous $DyCl_3$ (1 mmol, 268 mg), Me_2Cp-H (**a3**) (2 mmol, 644 mg), and potassium (2 mmol, 80 mg) in a 50 mL oven-dried Schlenk flask, added 10 mL of

freshly distilled dry toluene at 0 °C under Ar atmosphere. The reaction mixture was stirred at room temperature for 10 min, followed by 48 h of refluxing at 110 °C. Once the temperature of the reaction mixture attained room temperature, the yellow turbid mixture was filtered-off to obtain a yellow clear filtrate. Finally, the resultant clear filtrate was concentrated to the 3 mL and stored at room temperature for three days to obtain a light yellow coloured block shaped crystals of $[(Me_2Cp)_4Dy^{III}_2Cl_4K_2]\cdot 3(C_7H_8)$ (**1**) in 71% yield. The suitable single crystal of **1** was picked up from the mother liquor for single crystal X- ray diffraction studies.

S4. Structure determination of complex **1**.

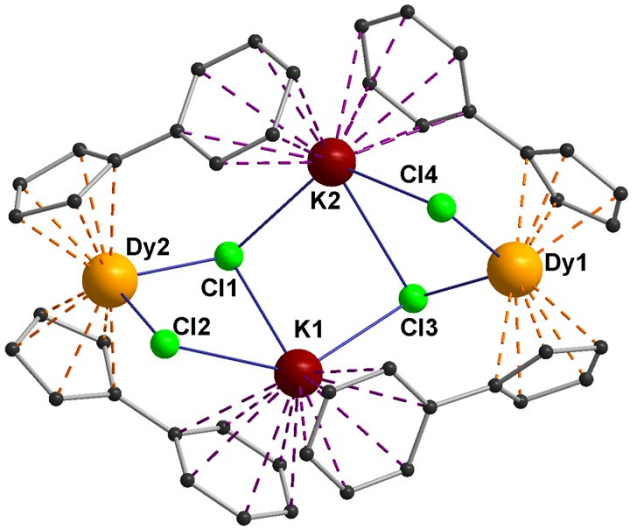
A suitable single crystal of **1** was selected and mounted on a **Bruker APEX-II CCD** diffractometer. The crystal was kept at 200-220 K during data collection. Using Wingx[3], the structure was solved with the SHELXT[4] structure solution program using intrinsic phasing and refined with the SHELXL[5-8] refinement package using least squares minimization. CCDC reference numbers: **2006659** contains the supplementarycrystallographic data for compound **1**, respectively.[2]

Table S3. Crystal refinement data for compounds **1**.[2]

complex	**1**
Empirical formula	$C_{121}H_{108}Cl_4Dy_2K_2$
Molecular weight	2107.07
Crystal size [mm^3]	0.10 × 0.08 × 0.06
Crystal system	Triclinic
Space group	*P*-1
a[Å]	15.0406(5)
b[Å]	18.9527(6)
c [Å]	21.4668(8)
α[°]	65.2020(10)
β[°]	78.557(2)
γ[°]	67.6990(10)°
V[$Å^3$]	5134.0(3)
Z	2
Temperature [K]	200(2)

Table S4. Selected bond lengths and bond angles for complex **1**.

Type of bond	**bond length (Å)/angle (°)**
Dy1-Cl1	2.590
Dy1-Cl2	2.618
Dy2-Cl3	2.591
Dy2-Cl4	2.599
K1-Cl1	3.181
K1-Cl2	3.057
K1-Cl4	3.147
K2-Cl3	3.098
K2-Cl4	3.466
K2-Cl2	3.031
Cp_{cen1}–Dy1	2.391
Cp_{cen2}–Dy1	2.396
Cp_{cen1}–Dy2	2.423
Cp_{cen2}–Dy2	2.415
Cp_{cen1}-Dy1-Cp_{cen2}	129.75°
Cp_{cen1}-Dy2-Cp_{cen2}	130.80°
Ar_{cen1}-K1-Ar_{cen2}	114.09°
Ar_{cen1}-K2-Ar_{cen2}	116.77°



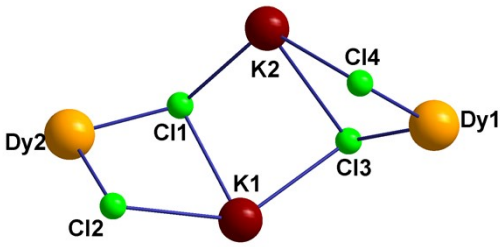
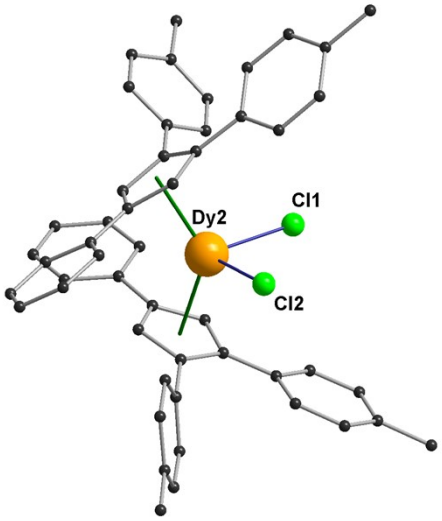


Figure S3. Non-planar $Dy_2K_2Cl_4$ core along with chelating aromatic units of complex **1** (left). Ladder-type assembly of $K_2Cl_4Dy_2$ core constructed by K_2Cl_2 unit together with two μ-Cl^- ions and two Dy^{III} ions (right).



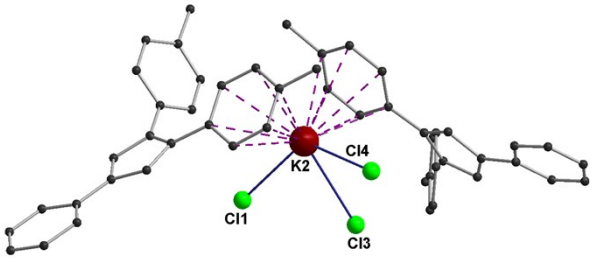
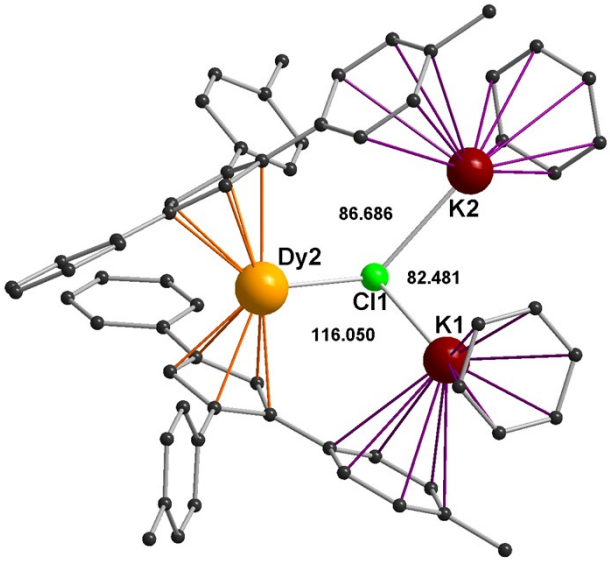


Figure S4. Mononucler fragment, Dy^{III} ion sandwiched between the π-electron clouds of two independent Cp rings and further coordinated by two chloride ions (left). The hydrogen atoms are omitted for the clarity. Bonding scenario in K-sandwich constructed by the π-electronic cloud of two 4- methyl phenyl moieties shared by two individual Cp units (right).



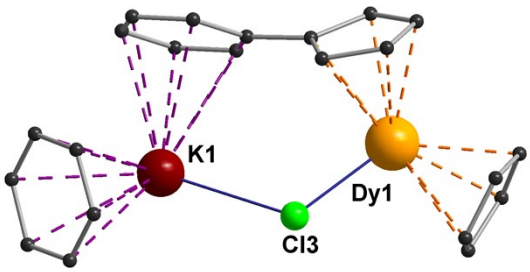


Figure S5. Bridging modes of μ_3-chloride (left) and μ-chloride (right) ions in the molecular structure **1**.

S5. Spectral data of compounds a1, a2 and a3.

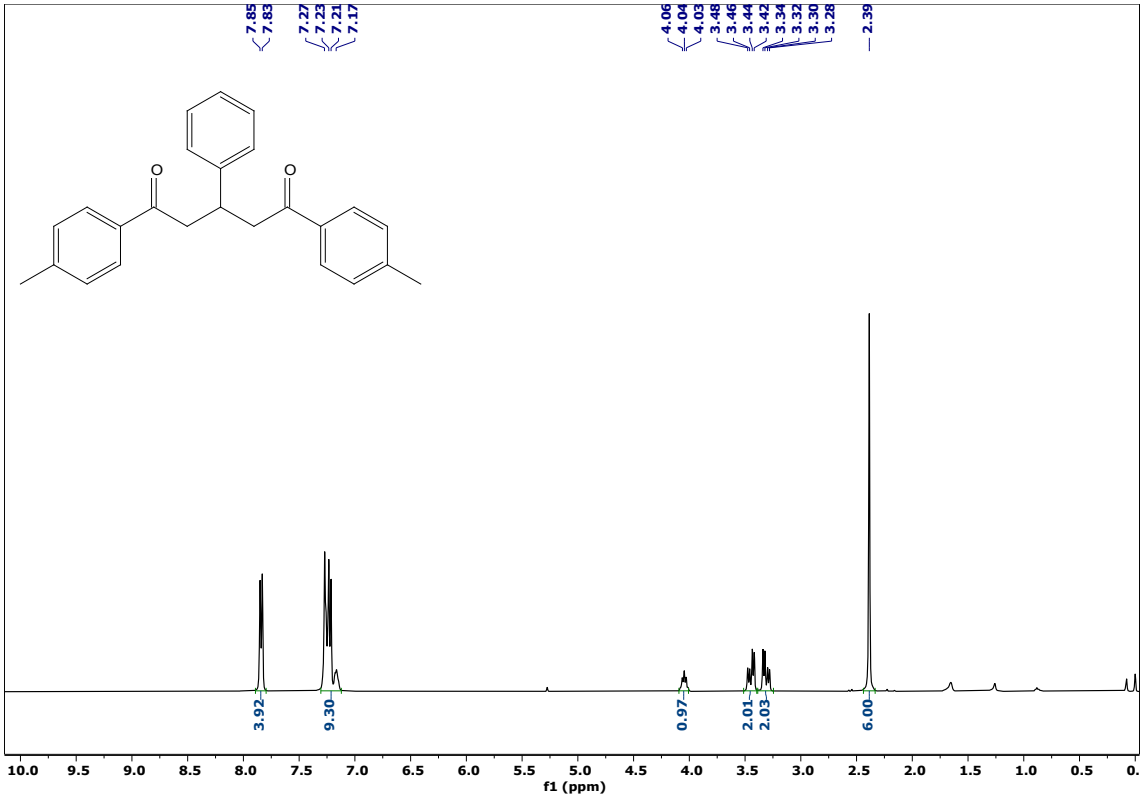


Figure S6. ^{1}H NMR Spectrum of compound **a1** in $CDCl_3$ at 298 K.

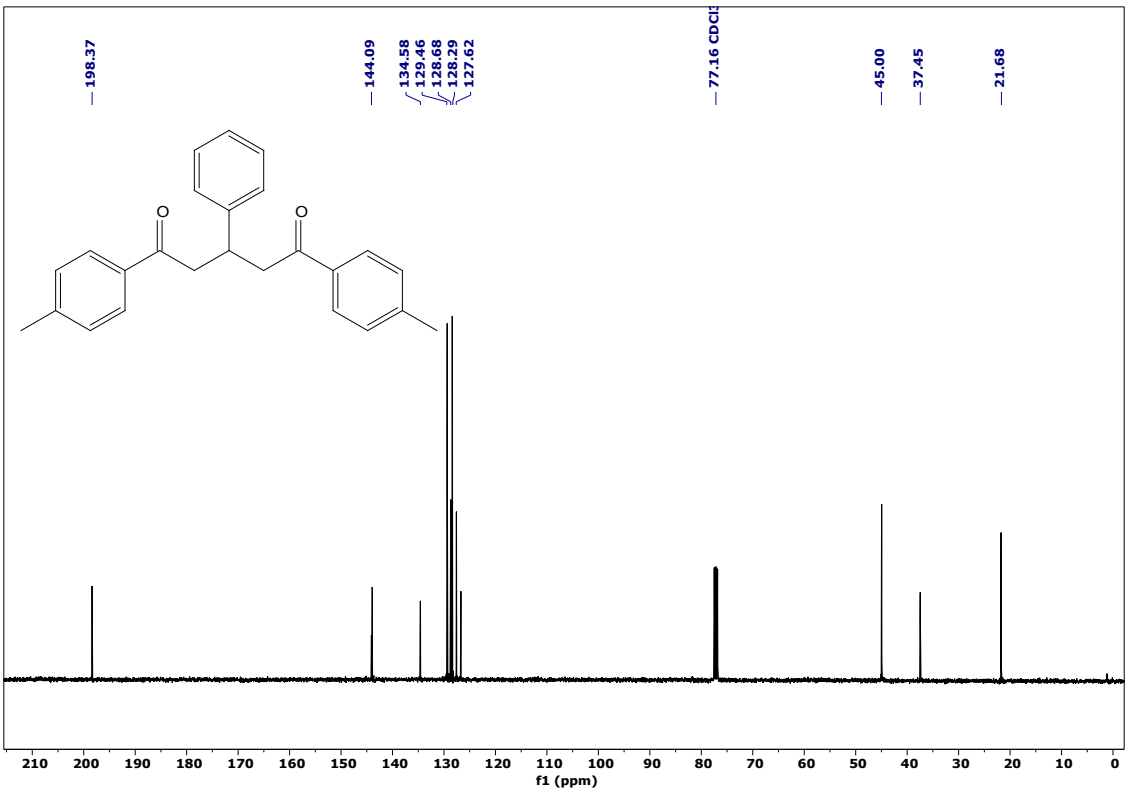


Figure S7. ^{13}C NMR Spectrum of compound **a1** in $CDCl_3$ at 298 K.

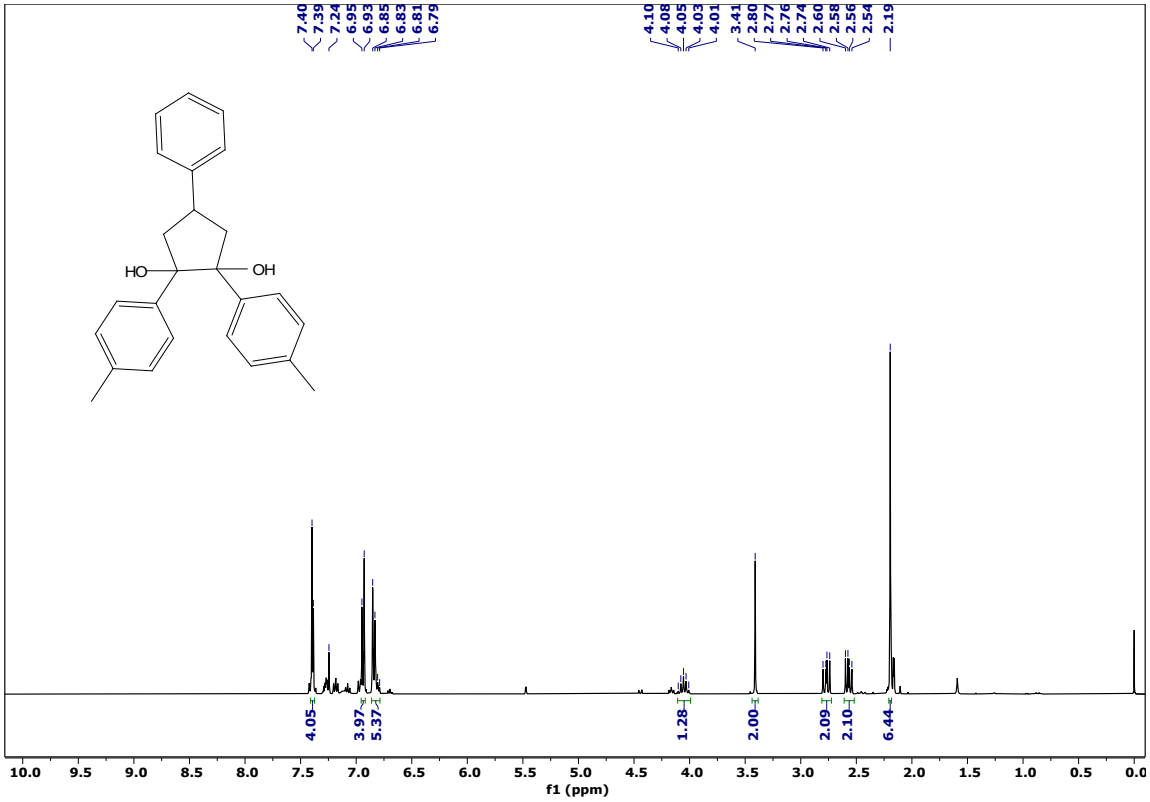


Figure S8. ^{1}H NMR spectrum of compound **a2** in $CDCl_3$ at 298 K.

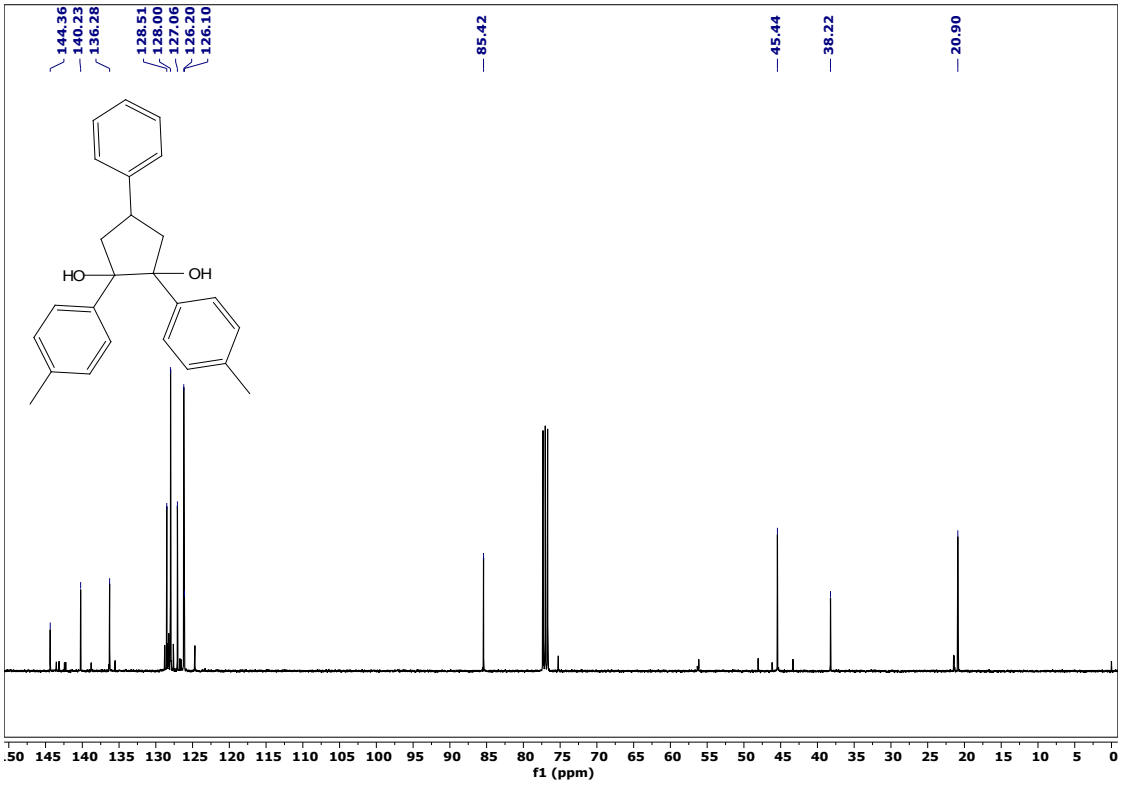


Figure S9. ^{13}C NMR spectrum of compound **a2** in $CDCl_3$ at 298 K.

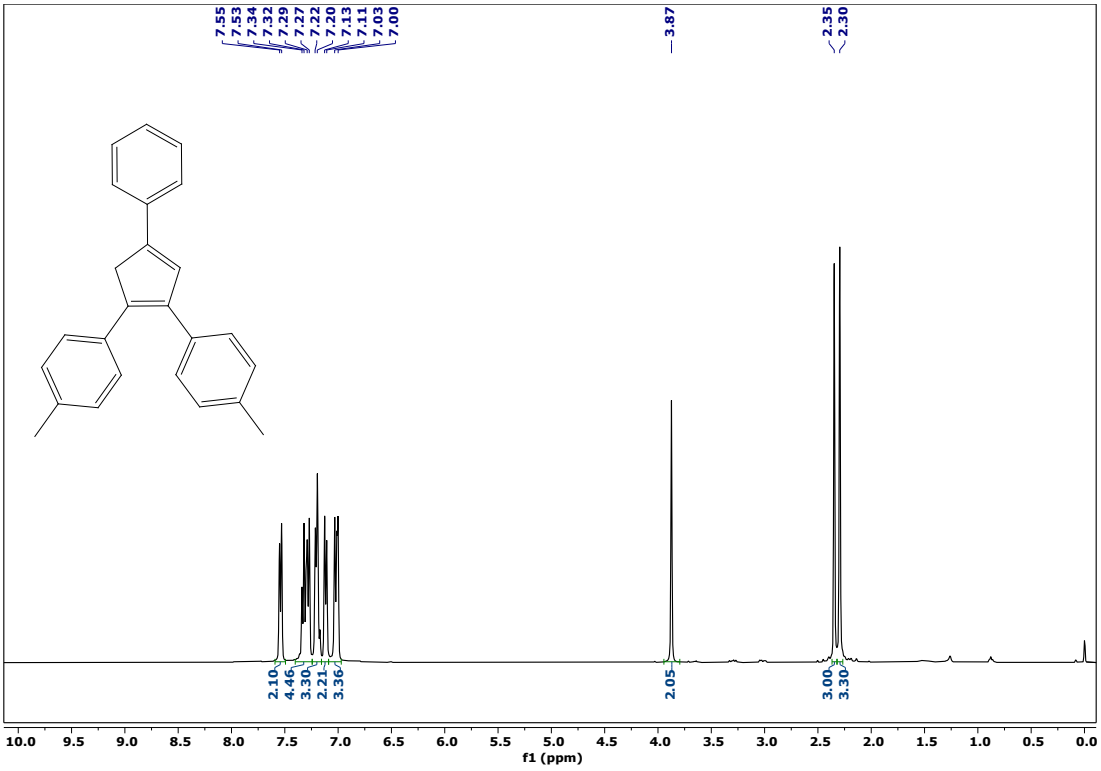


Figure S10. ^{1}H NMR spectrum of compound **a3** in $CDCl_3$ at 298 K.

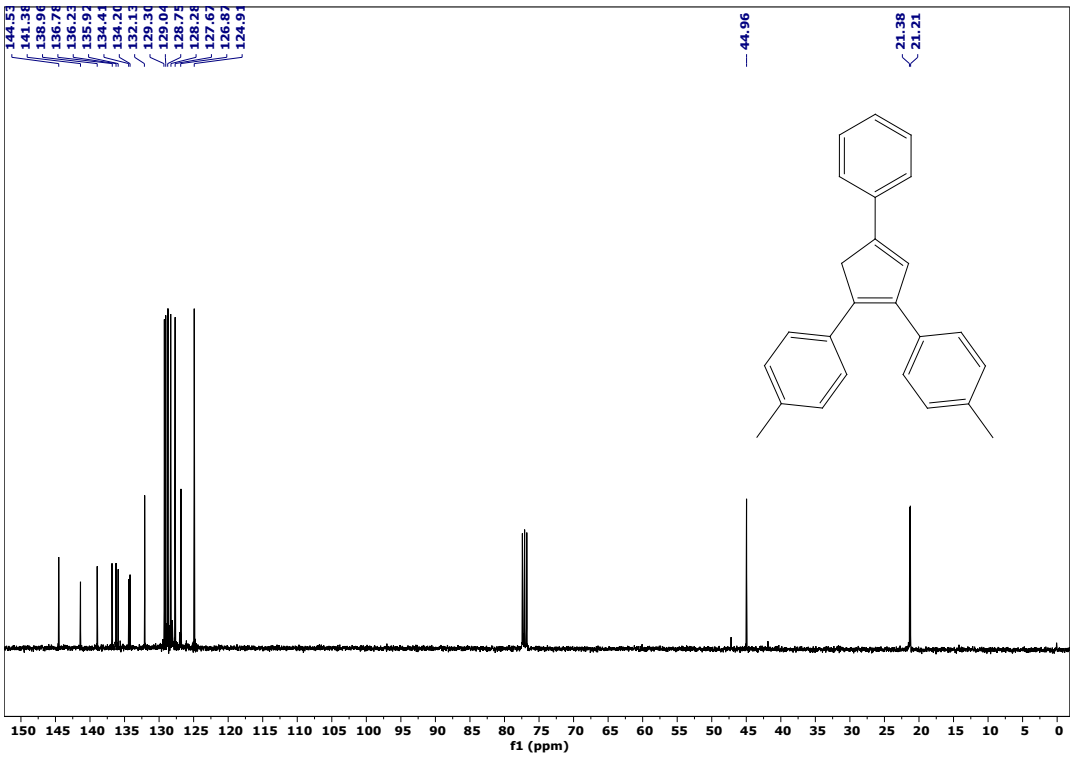


Figure S11. ^{13}C NMR spectrum of compound **a3** in $CDCl_3$ at 298 K.

6 References:

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