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Alkali metal reduction of 1,3,2-diazagallol-2-ylidene radical derived from acenaphthene-1,2-diimine

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Experimental part.

General information.

Compounds **2**-**4** are sensitive to air and moisture. Therefore all manipulations concerning their preparation and identification were carried out under vacuum using glass ampoules or under argon atmosphere in a Glovebox. Tetrahydrofuran, diethyl ether, dimethoxyethane were dried over sodium/benzophenone, and condensed under vacuum in ampoules just prior to use. THF-d_8 was dried over sodium/benzophenone at ambient temperature and condensed under vacuum into the NMR tubes that contained the sample. The IR-spectra were recorded on a FSM-1201 spectrometer, the ^{1}H NMR – on Bruker Avance NEO 300, Bruker Advance III 400 spectrometers. The ESR spectra were obtained using a Bruker EMX ESR spectrometer (X-band, 9.65 GHz); the signals were referred to the signal of diphenylpicrylhydrazyl (DPPH, g = 2.0037) and simulated with the EasySpin software (version 5.2.28).[S1] Elemental analysis was performed on a Vario EL Cube analyzer. Compound **1** was prepared according to a literature procedure[S2] starting from 0.5 mmol Ar^{BIG}-bian and used *in situ*.

Data collection, initial reflection indexing, refinement of the unit cell parameters and subsequent data integration were carried out with the CrysAlisPro software.[S3] Absorption correction was performed using the SCALE3 ABSPACK scaling algorithm.[S4] All structures were solved by dual-space method[S5] and refined on F_{hkl}^2 using SHELXTL package.[S6,S7] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and were refined using a riding model (U_{iso}(H) = 1.5U_{eq}(C) for CH_3-group and U_{iso}(H) = 1.2U_{eq}(C) for other groups). Solvate molecules of DME and Et_2O were found in crystals of **2**, **3′** and **4** respectively being at common positions in a ratio of 2:1 (**2**) and 1:1 (**3′, 4**) per one molecule of the complexes. The DME molecules, coordinated at the Li atoms in **2** and **3′**, as well as the solvate molecules of DME and Et_2O in **2** and **4**, respectively, are disordered over two positions. In addition, the two Ph- and Me-groups in the big-BIAN ligand of **2** and the K atom in **4** are also observed to be disordered over two positions. EADP, ISOR, SADI and DFIX instructions were used for refinement of disordered fragments.

[(Ar^{BIG}-bian)GaLi(DME)$_3$] (2) × 2 DME. A solution of **1** in 30 mL of THF, prepared *in situ*, was added to lithium metal (0.004 g, 0.58 mmol) and stirring at ambient temperature until a lithium metal is disappeared during 24 h. Then THF was removed by evaporation in vacuum. The residue was dissolved in DME (10 ml) and allowed to stand for 24 h at 25 °C. Brown crystals of **2 × 2 DME** were separated by decantation, washed with cold DME and dried in vacuum. Yield 0.51 g (66 %). Found (%): C, 75.56; H, 7.03; N, 1.63. Calcd. for $C_{98}H_{110}GaLiN_2O_{10}$ (%): C, 75.81; H, 7.14; N 1.80.

^{1}H NMR (400 MHz, THF-d_8, 233 K): δ 7.21-7.16 (m, 10H, Ph), 7.03-6.91 (m, 20H, Ph), 6.83-6.76 (m, 10H, Ph), 6.70 (s, 4H, C_6H_2), 6.59 (s, 4H, C<u>H</u>Ph_2), 6.41 (d, 2H, J = 8.03 napht) 6.29 (pseudo t, 2H, J = 7.28, J = 7.78 napht), 5.47 (d, 2H, J = 6.78, napht), 3.43 (s, 20H, CH_2 DME), 3.28 (s, 30H, CH_3 DME), 2.14 (s, CH_3).

^{13}C NMR (400 MHz, THF-d_8, 233 K): 147.60, 146.99, 144.79, 140.42, 136.94, 136.45, 130.04, 128.28, 127.24, 126.92, 125.64, 125.15, 124.51, 119.46, 114.73, 71.77 (DME), 58.03 (DME), 50.69, 20.92.

IR (Nujol): 1671 w, 1599 s, 1507 s, 1492 s, 1424 s, 1357 s, 1337 s, 1292 m, 1271 s, 1245 m, 1210m, 1189 m, 1177 m, 1156 w, 1120 s, 1108 s, 1079 s, 1029 s, 1001 w, 980 w, 926 s, 867 s, 848 m, 804 m, 797 m, 777 m, 760 s, 744 s, 700 s, 643 w, 622 m, 605 s, 560 m, 536 m, 502 w, 490 w, 479 w cm^{-1}.

[(Ar^{BIG}-bian)GaNa(Et_2O)$_2$(THF)$_2$] (3). A solution of **1** in 30 mL of THF, prepared *in situ*, was added to sodium metal (0.013 g, 0.57 mmol), and stirring at ambient temperature until a sodium metal is disappeared during 24 h. THF was removed by evaporation in vacuum. The residue was dissolved in diethyl ether (30 ml) and allowed to stand for 24 h at 25 °C. Fine crystalline powder of **3** were separated by decantation, washed with cold diethyl ether and dried in vacuum. Yield 0.48 g (76 %). Found (%): C, 78.06; H, 7.16; N, 2.15. Calcd. for $C_{82}H_{90}GaN_2NaO_4$ (%): C, 78.14; H, 7.20; N 2.22. Found: C 78.06; H 7.16; N 2.15.

NMR ^1H (300 MHz, THF-d_8, 298 K): 7.22–7.17 (m, 10H, Ph), 7.06–6.92 (m, 20H, Ph), 6.82–6.71 (m, 10H, Ph, 4H, $C_6\underline{H}_2$), 6.61 (s, 4H, $C\underline{H}Ph_2$), 6.46 (d, 2H, napht, J = 8.08), 6.25 (pst, 2H, napht, J_1 = 6.82, J_2 = 6.82), 5.35 (d, 2H, napht, J = 6.64), 3.59 (s, 8H THF), 3.40(q, 8H, CH_2, Et_2O), 2.17 (s, 6H, $C\underline{H}_3$), 1.74 (s, 8H, THF), 1.13 (t, 12H, CH_3, Et_2O).

^{13}C NMR (100.6 MHz, C_4D_8O, 298 K): 147.72, 147.11, 144.71, 140.71, 136.52, 136.46, 130.15, 129.98, 129.84, 129.53, 129.31, 129.11, 128.23, 128.04, 127.42, 127.21, 126.88, 125.51, 124.0, 119.70, 115.30, 68.03 (THF), 65.40 (Et_2O), 51.23, 25.45, 24.40 (THF), 20.82, 14.79 (Et_2O).

IR (Nujol): 1596 s, 1504 s, 1493 s, 1453 s, 1428 s, 1348 s, 1292 m, 1268 s, 1213 m, 1179 m, 1154 m, 1120 m, 1091m, 1077s, 1045 m, 1031 s, 1001w, 983 w, 926 s, 868 s, 831 w, 808 m, 791 m, 763 s, 746m, 700 s, 676 w, 645 w, 633 w, 622 m, 606 s, 563 m, 556 m, 536 m, 528 w, 502 w, 481 w, 468 w cm^{-1}.

Crystals suitable for X-ray diffraction were obtained by recrystallization from DME: [(Ar^{BIG}-bian)GaNa(DME)$_3$] × DME (**3′**).

[(Ar^{BIG}-bian)K] (4) × Et_2O. A solution of **1** in 30 mL of THF, prepared *in situ*, was added to potassium metal (0.022 g, 0.56 mmol) and stirring at ambient temperature until a potassium metal is disappeared during 24 h. THF was removed by evaporation in vacuum. The residue was dissolved in diethyl ether (10 ml) and allowed to stand for 24 h at 25 °C. The resulting green solution was left for 24 h at 25 °C. Green crystals of compound **4 × Et_2O** were separated by decantation, washed with cold diethyl ether and dried in vacuum. Yield 0.42 g (74 %). Found: C, 86.36; H, 6.10; N, 2.39. Calcd. for $C_{82}H_{70}KN_2O$ (%): C, 86.49; H, 6.20; N, 2.46

EPR spectrum in THF (25 °C) g = 2.0034, $a_i(2\times^{14}N)$ = 0.504 mT.

IR (Nujol): 1597 m, 1578 m, 1516 m, 1492 s, 1410 s, 1347, 1332 m, 1318 m, 1293 w, 1276 w, 1254 m, 1241 m, 1208 m, 1176 s, 1152 m, 1133 w, 1117 m, 1076 m, 1030 m, 1008 m, 980 w, 968 w, 937 w, 915 m, 879 m, 854 m, 845 w, 835 m, 816 m, 800 m, 783 m, 765 m, 740 m, 700 s, 674 w, 642 w, 634 w, 623 w, 604 w, 594 w, 562 m, 547 w, 527 w, 520 w, 496 w, 486 w, 463 w cm^{-1}.

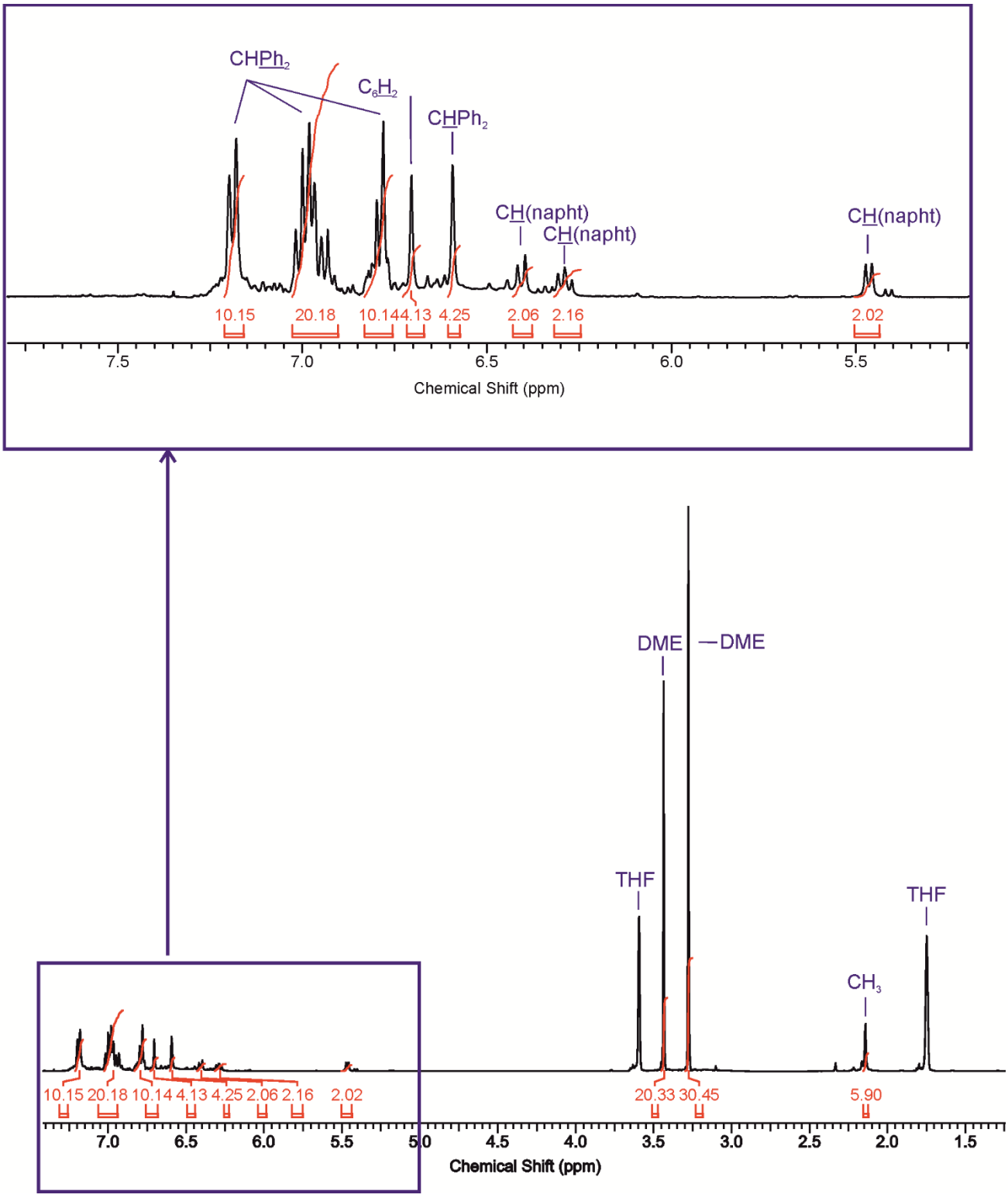

Figure S1. ^{1}H NMR spectrum of complex **2** (400 MHz, C_4D_8O, 233 K).

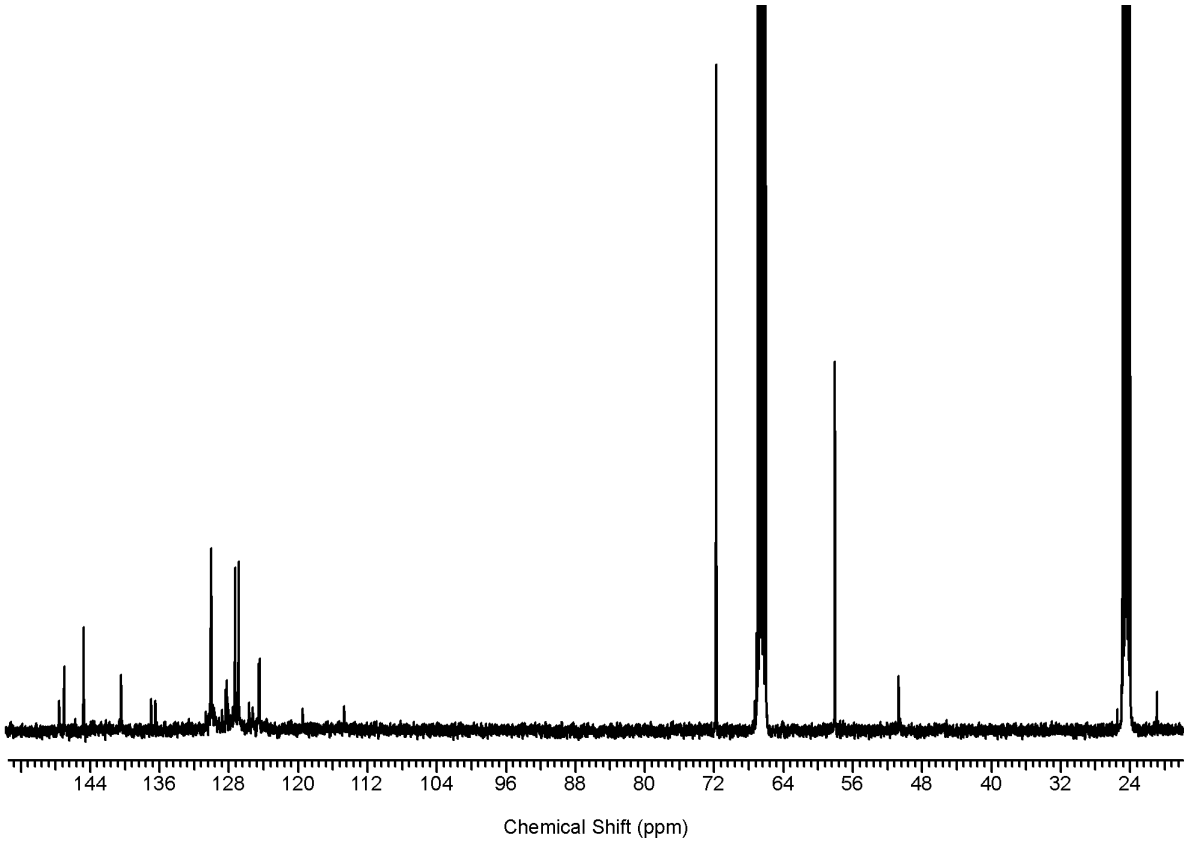

Figure S2. ^{13}C NMR spectrum of complex **2** (400 MHz, THF-d_8, 233 K).

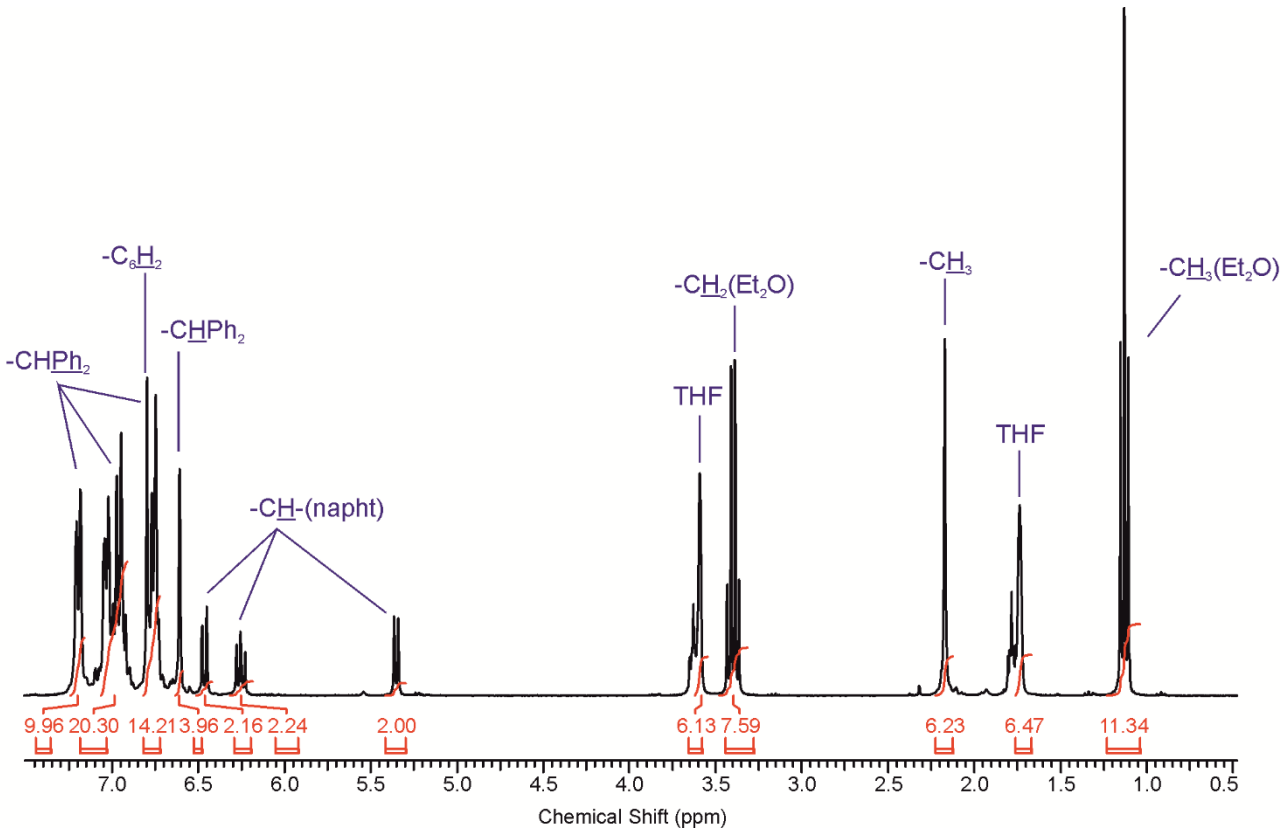

Figure S3. ^{1}H NMR spectrum of complex **3** (300 MHz, THF-d_8, 298 K).

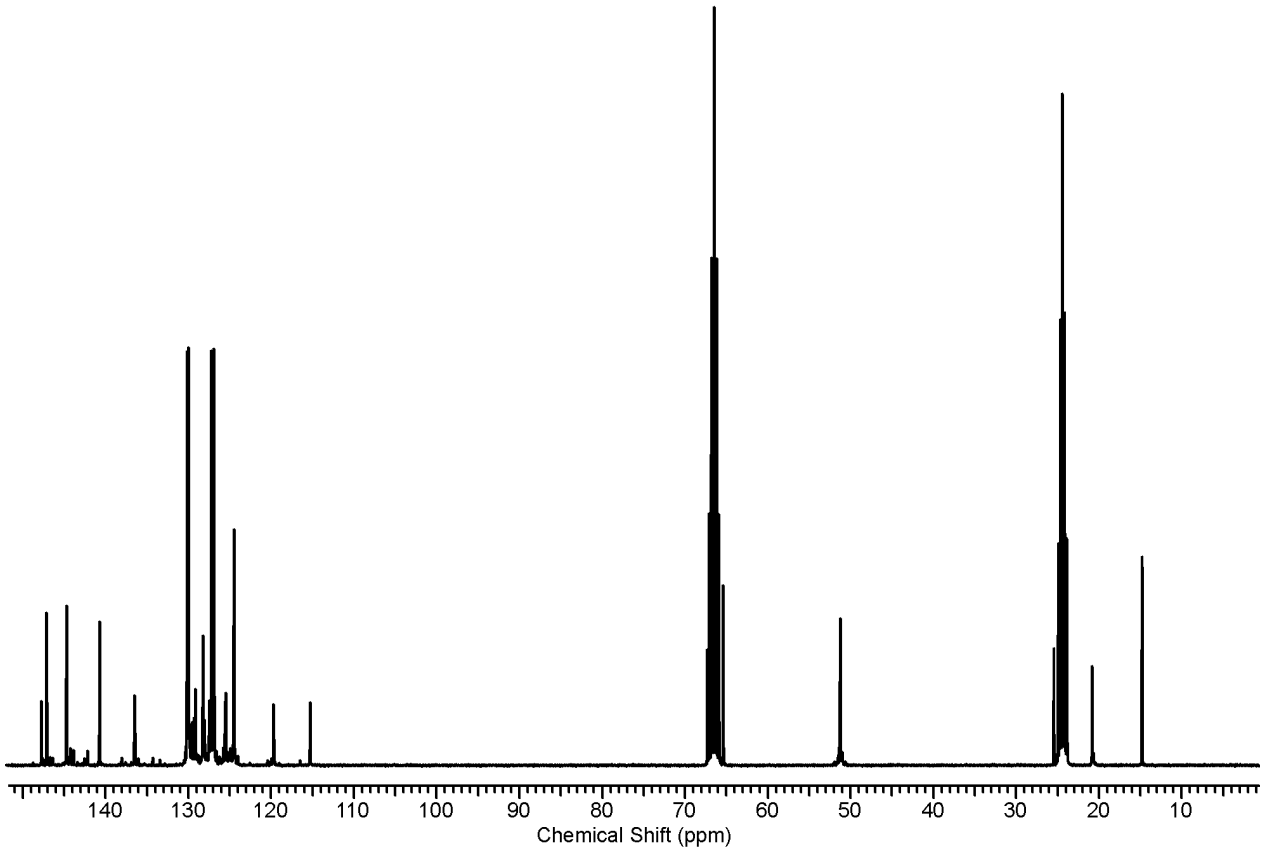

Figure S4. ^{13}C NMR spectrum of complex **3** (300 MHz, THF-d_8, 298 K).

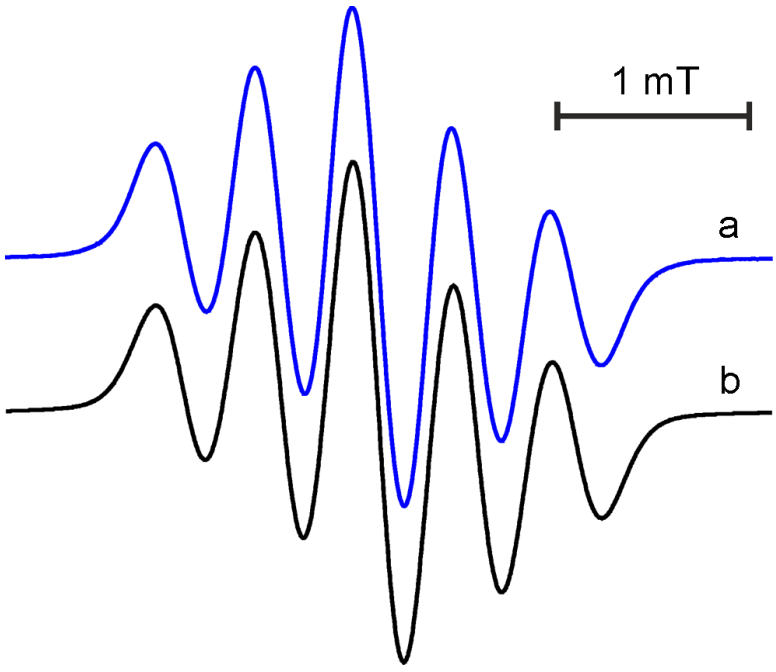

Figure S5. ESR signal of complex **4** (THF, 298 K). (a) experimental; (b) simulated [g = 2.0034, A(^{14}N) = 0.504 (2 N) mT].

References

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