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Synthesis, characterization and redox properties of Ar-C=N→Ge←N=C-Ar containing system

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Experimental

^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on Bruker AM300 spectrometer in CD_3OD at ambient temperature using tetramethylsilane as an internal standard. IR spectra were registered in tablets with KBr in the region of 4000–400 cm^{-1} on Bruker ALPHA-T. HRMS spectra with electrospray ionization (ESI) were recorded on a Bruker microTOF II instrument in the mode of positive ions (capillary voltage 4500 V). UV-Vis spectra were recorded with an Agilent 8453 instrument using a 10 mm quartz cell. Cyclic voltammetry was carried out using a PC-piloted digital potentiostat IPC-Pro-MF (Econix). A standard thermostated (T = 25 ± 0.5 °C) 10 ml electrochemical cell was used in a three-electrode configuration. As a working electrode, a GC (1.7 mm) disk was used, polished before each run; a Pt wire was used as an auxiliary electrode. The potentials are referred to the AgCl/KCl sat. electrode separated from the analyte by an electrolytic bridge filled with the same solution. All measurements were carried out under dry argon.

GeO_2 was purchased from "Germanium and Applications Ltd" (DG-B, TY 1774-001-95961127-2010, batch #117). Solvents were purified by standard methods [S1]. Ligand **L** was synthesized with known procedure [S2].

Synthesis of **2**. A mixture of 2-[(2-hydroxybenzylidene)amino]-2-methylpropane-1,3-diol **1** (0.481 g, 2.3 mmol) and GeO_2 (0.121 g, 1.15 mmol) was refluxed in water for 5 h. After cooling the solution, the precipitate was filtered. Additional amounts of the product were isolated from the filtrate after incomplete evaporation of the solvent and filtration. Yield 0.336 g (60%). Single crystals of **2** were obtained by cooling of a saturated MeOH solution.

HRMS (ESI-MS): m/z $[M+H]^+$ 489.1041 (exp.), 489.1081 (calc.); $[M+Na]^+$ 511.0855 (exp.), 511.0900 (calc.); $[M+K]^+$ 527.0597 (exp.), 527.0640 (calc.). IR (KBr): 3417, 3275, 3036, 2814, 1630, 1551, 1475, 1450, 1306, 1214, 1148, 1061, 1031, 896, 823, 755 cm^{-1}. Elemental analysis experimental data are consistent with the calculated ones.

According to the number of signals in ^{1}H NMR (300 MHz, CD_3OD) we can conclude that four conformers are present in the methanol solution of **2**, namely, two major and two minor ones: 8.70 (s, minor CH=N), 8.69 (s, major CH=N), 8.62 (s, major CH=N), 8.60 (s, minor CH=N), 7.48 (m, 1H, arom. CH), 7.39 (m, 1H, arom. CH), 6.83 (m, 1H, arom. CH), 6.76 (m, 1H, arom. CH), 4.04 (m, 0.5H, CH_2), 3.71 (m, 2.5H, CH_2), 3.57 (m, 1H, CH_2), 1.47 and 1.41 (each s, 3H, CH_3). In the ^{13}C NMR (300 MHz, CD_3OD) we can clearly see signals for two major conformers: 2 for CH=N 169.50 and 169.05; 8 for aromatic protons 137.58, 137.38, 136.05, 135.99, 122.11, 122.00, 118.92, 118.62; 4 for CH_2 groups 67.31, 67.23, 67.17, 66.47; 2 for CH_3 groups 19.94, 19.17. To find out whether the temperature affects the ratio of isomers/conformers in solution, the spectrum of compound **2** in DMSO was recorded at 30, 50 and 80 °C. It was shown that the temperature did not affect the conformer ratio, the ratio of integral intensities of CH=N-protons was unchanged. With raising the temperature, the imine and aromatic protons had a weak shift to a high field, while aliphatic protons were slightly shifted downfield. ^{1}H NMR (300 MHz, DMSO-d_6): at 30°C - 8.63 (s, minor CH=N), 8.61 (s, major CH=N), 8.55 (s, major CH=N) total integral 1H; 7.53– 7.47 (m, 1H, arom. CH); 7.37– 7.31 (m, 1H, arom. CH); 6.76-6.71 (m, 1H, arom. CH); 6.61-6.57 (m, 1H, arom. CH); 5.24-5.13 (m, OH); 3.76-3.69 (m, 0.5 H, CH_2); 3.60-3.33 (m, CH_2); 1.32 (s, major) 1.27 (s, minor) 1.26 (s, major) total integral 3H, CH_3. ^{1}H NMR (300 MHz, DMSO-d_6): at 80°C - 8.60 (s, minor CH=N), 8.58 (s, major CH=N), 8.53

(s, major CH=N) total integral 1H; 7.48-7.43 (m, 1H, arom. CH); 7.35-7.28 (m, 1H, arom. CH); 6.75-6.69 (m, 1H, arom. CH); 6.60-6.55 (m, 1H, arom. CH); 4.94-4.88 13 (m, OH); 3.77-3.70 (m, 0.47 H, CH_2); 3.64-3.53 (m, 2.6 H, CH_2); 3.44-3.37 (m, 1 H, CH_2); 1.34 (s, major), 1.30 (s, minor), 1.29 (s, major) total integral 3H, CH_3. ^{13}C NMR (300 MHz, DMSO-d_6) is too complicated to assign: 166.84, 166.72, 166.46, 164.59, 164.50, 135.83, 135.64, 135.00, 134.88, 134.84, 120.81, 120.65, 117.43, 117.34, 116.90, 116.51, 116.42, 66.47, 66.15, 65.77, 65.65, 65.45, 65.33, 65.24, 64.26, 63.92, 63.58, 63.37, 19.91, 19.69, 19.31, 19.25.

All quantum chemical calculations were performed by the ORCA [S3] version 4 [S4] program package using hybrid PBE0 [S5] density functional in triple-zeta basis set with two polarization functions def2-TZVPP [S6] and atom-pairwise dispersion correction with the Becke-Johnson damping scheme (D3BJ) [S7] was included in all calculations. Grid5 integration grids and TightSCF convergence criteria were applied throughout. RI-J and “chain of spheres" COSX approximation [S8] with the def2-TZVPP/J auxiliary basis set [S9] was used to speed up calculations. Full geometry optimization with TightOpt convergence criteria was carried out to find stationary points on the potential energy surfaces. Numerical harmonic frequencies calculations were used to obtain thermodynamic quantities and verify that all stationary point found are local minima. Scalar relativistic all-electron calculations using 0th order regular approximation ZORA [S10,S11] were added to the calculation scheme described above for single-point calculations of frontier orbitals. Chemcraft program version 1.8 (build 562a) [S12] was used to produce visual representations of calculations.

HRMS (ESI-MS) investigations

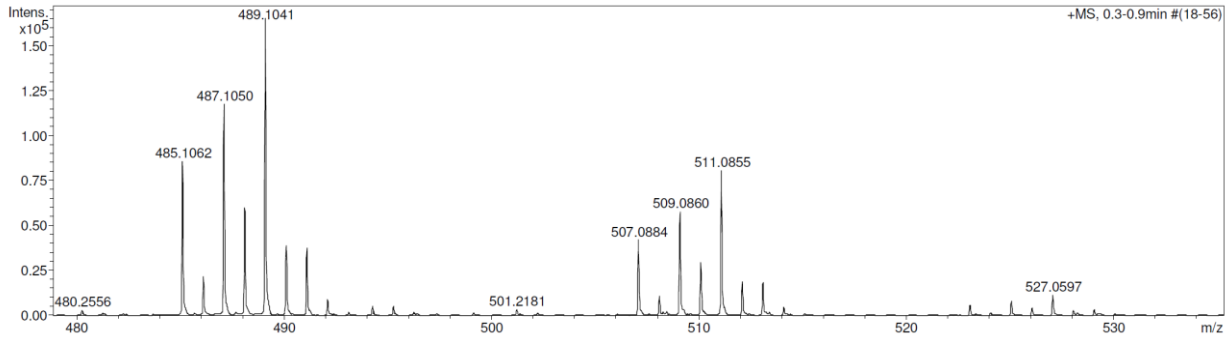

Figure S1 HRMS (ESI-MS) spectrum of **2** (the molecular ion formation upon H^+, Na^+ and K^+-ionization).

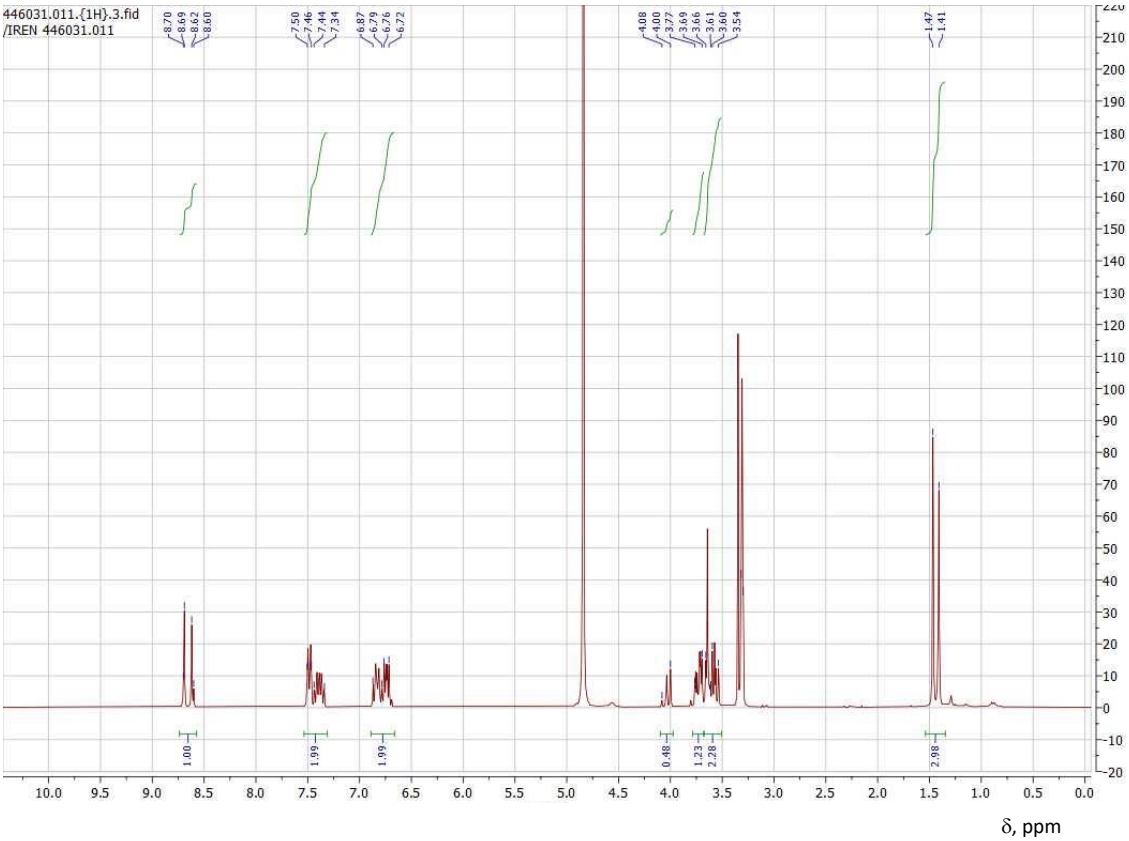

Figure S2. ^{1}H NMR spectrum of **2** in CD_3OD.

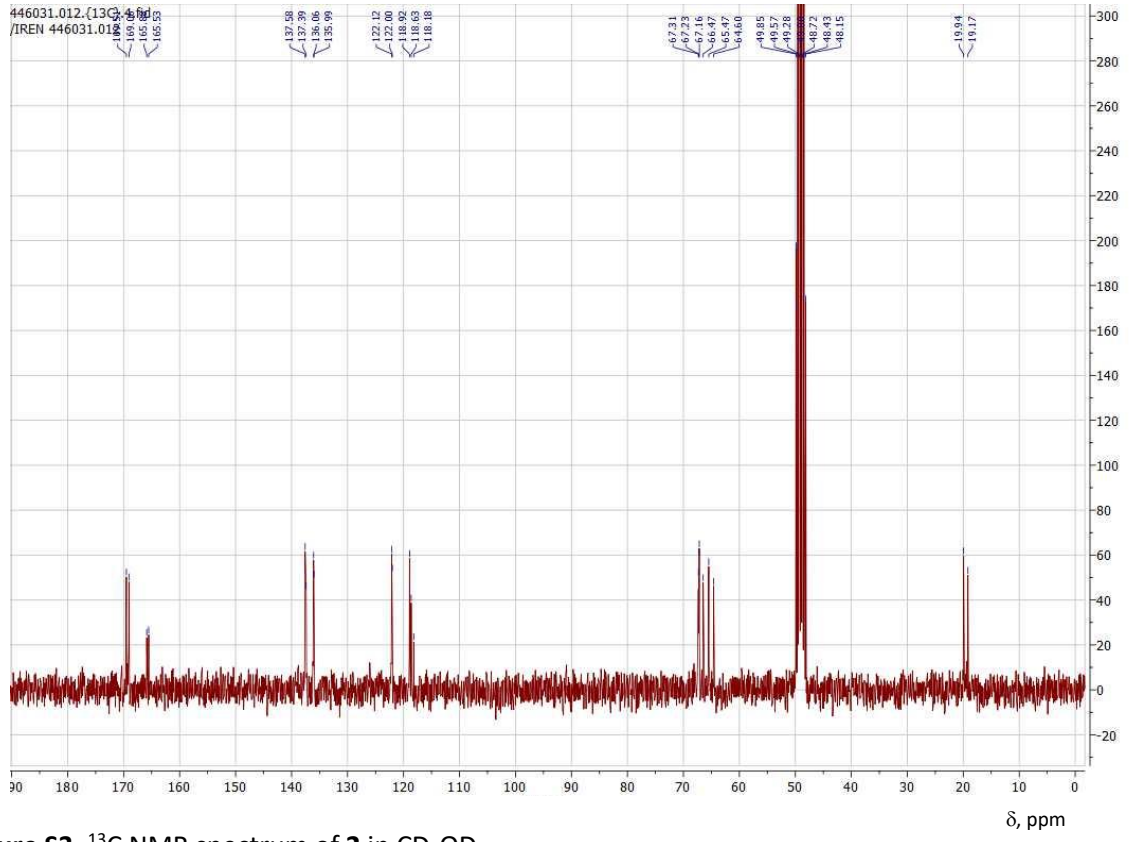

Figure S3. ^{13}C NMR spectrum of **2** in CD_3OD.

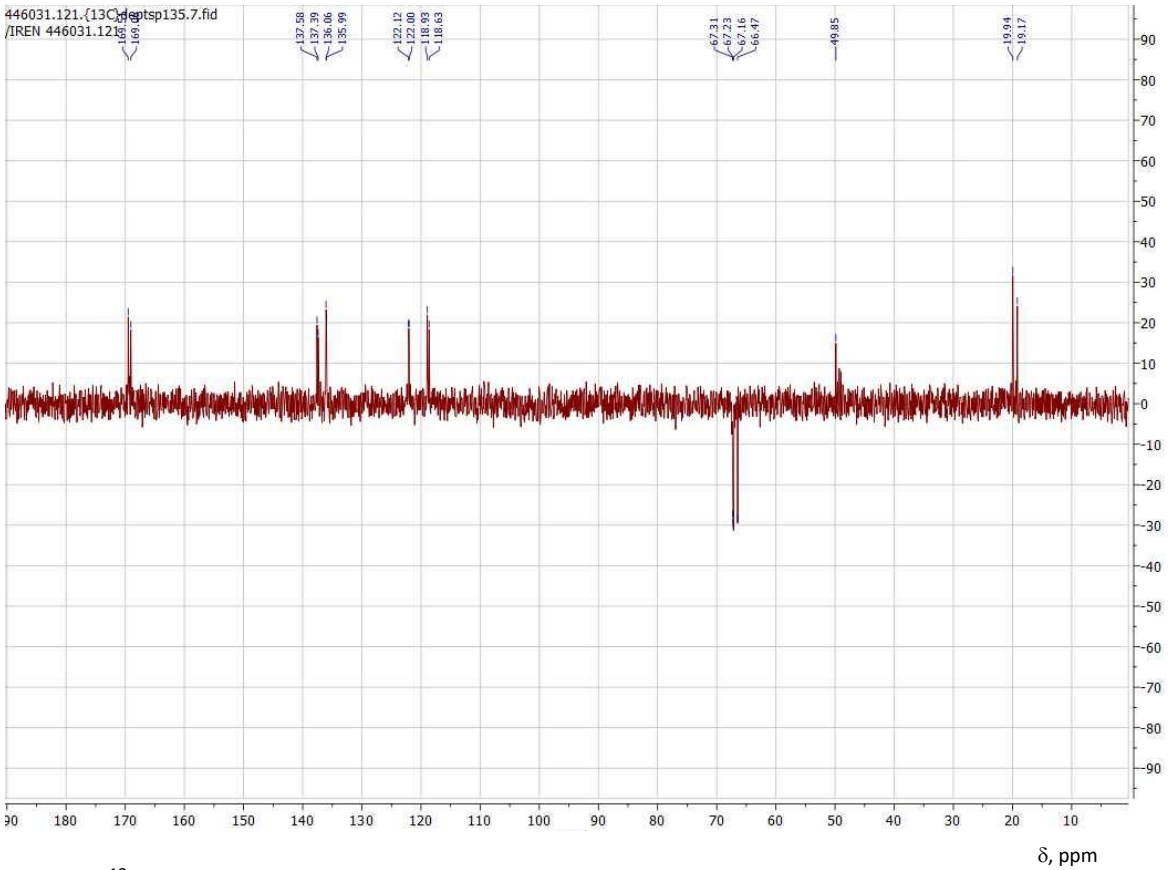

Figure S4. ^{13}C NMR DEPT135 spectrum of **2** in CD_3OD.

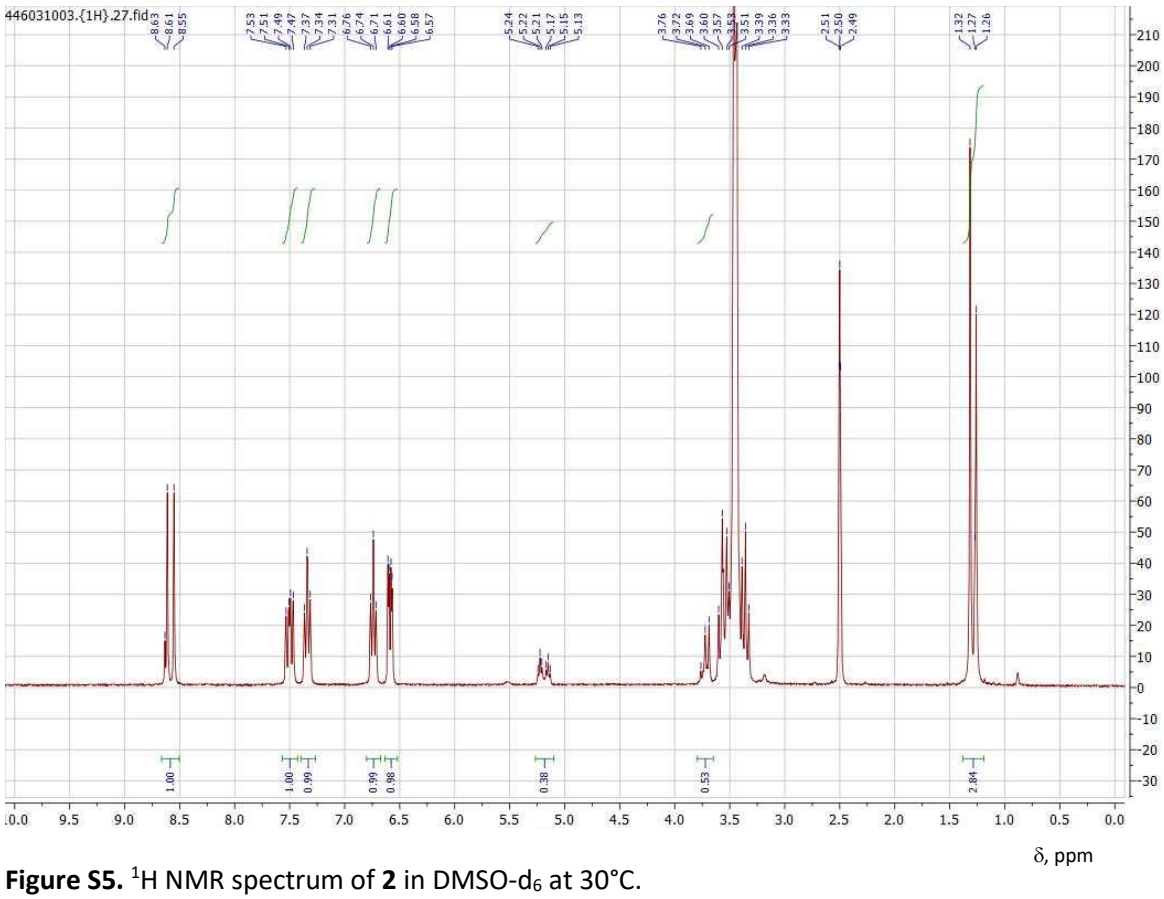

Figure S5. ^{1}H NMR spectrum of **2** in DMSO-d_6 at 30°C.

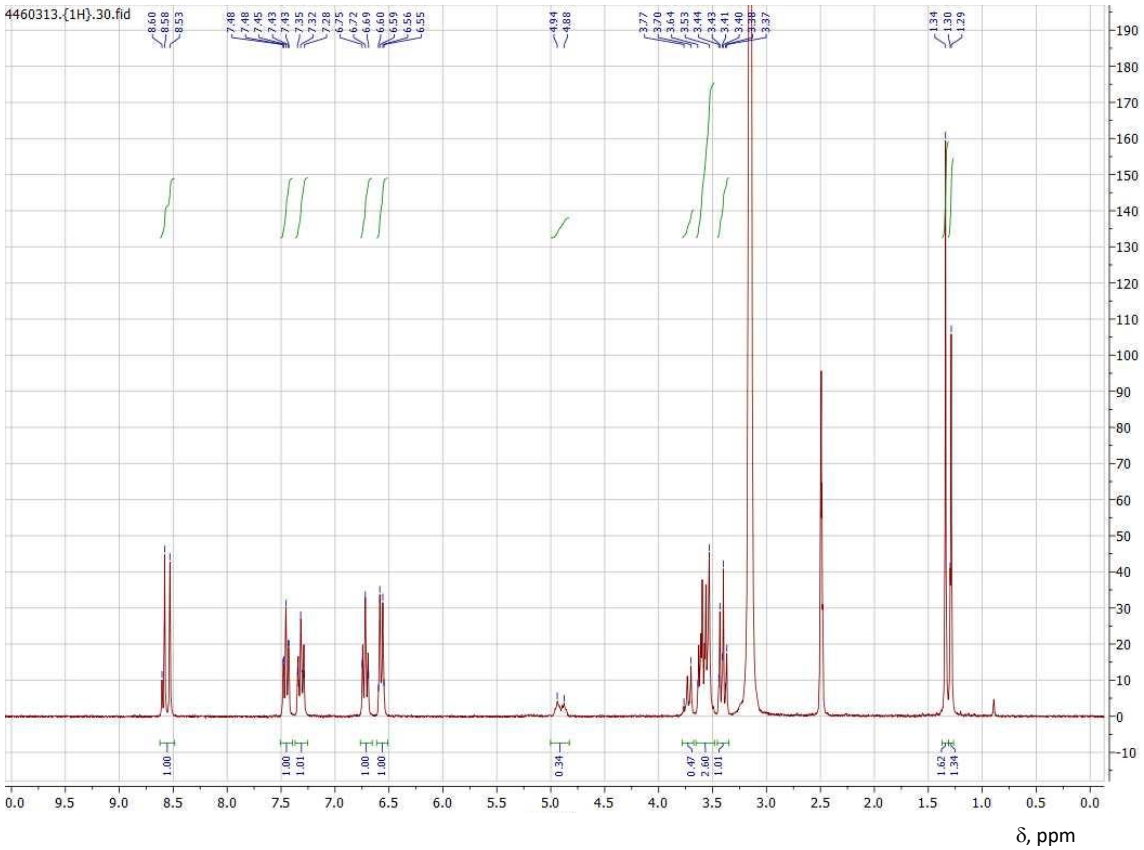

Figure S6. ^{1}H NMR spectrum of **2** in DMSO-d_6 at 80°C.

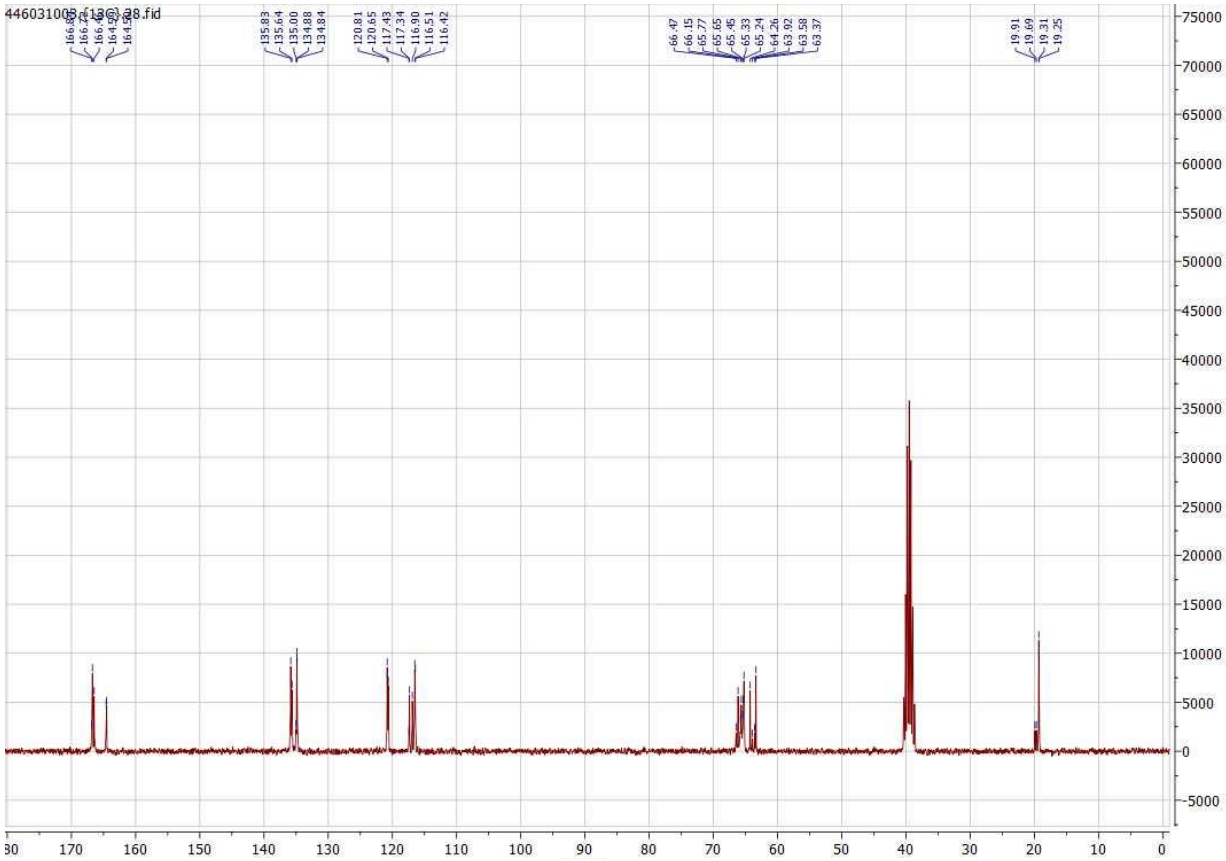

Figure S7. ^{13}C NMR spectrum of **2** in DMSO-d_6 at 30°C.

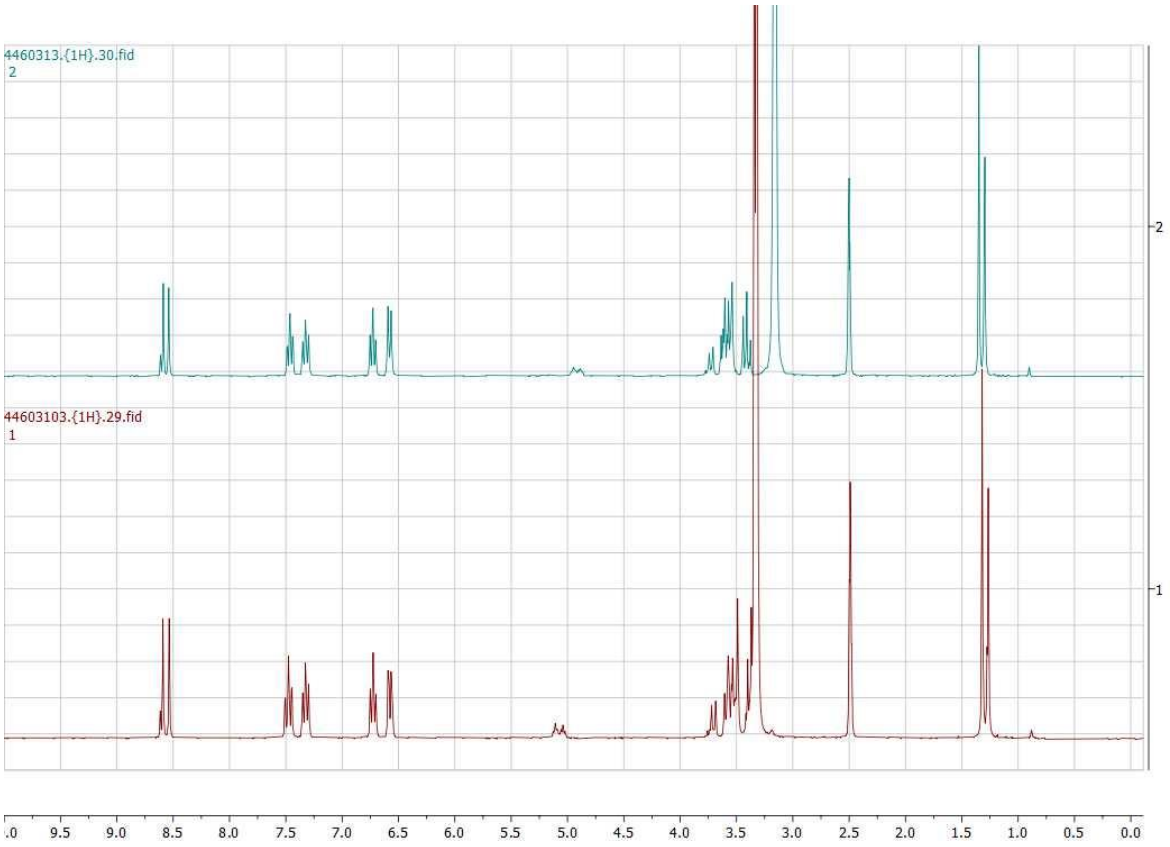

Figure S8. ^{1}H NMR spectrum of **2** in DMSO-d_6 at 30°C (*top*) and 80°C (*bottom*).

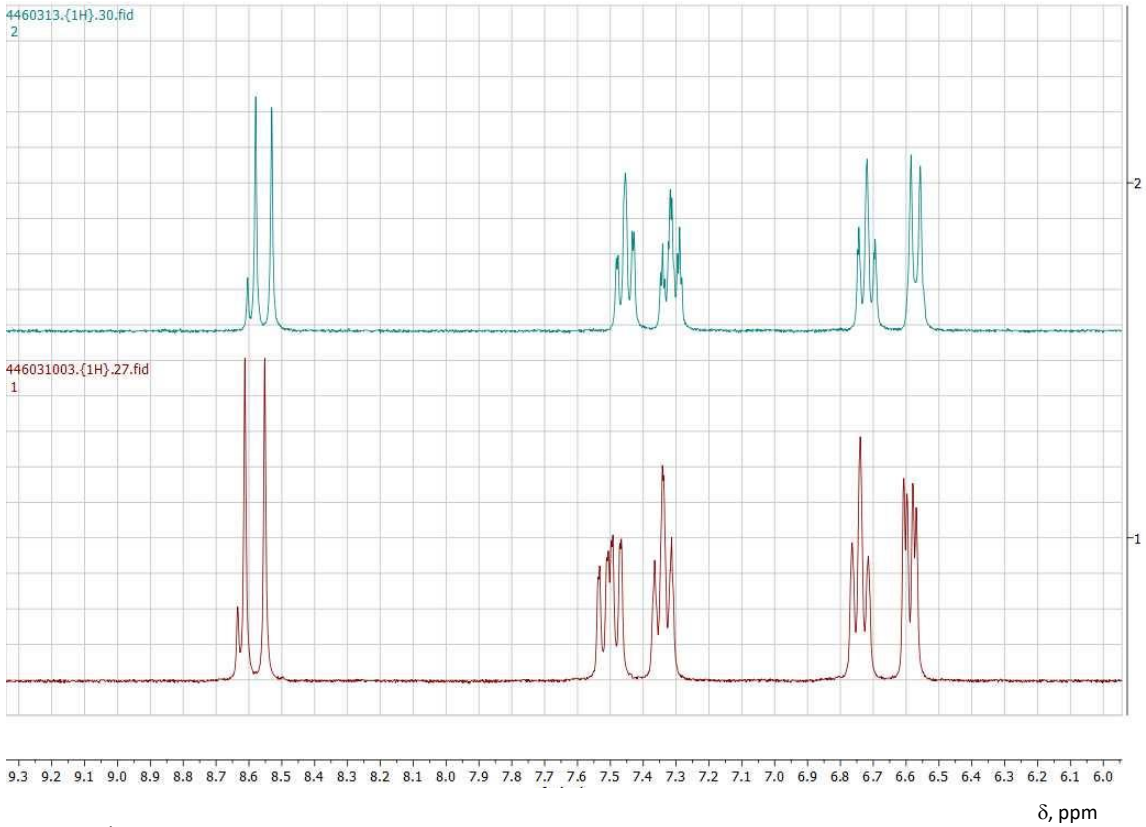

Figure S9. ^{1}H NMR spectrum (low fields) of **2** in DMSO-d_6 at 30°C (*top*) and 80°C (*bottom*).

X-Ray analysis

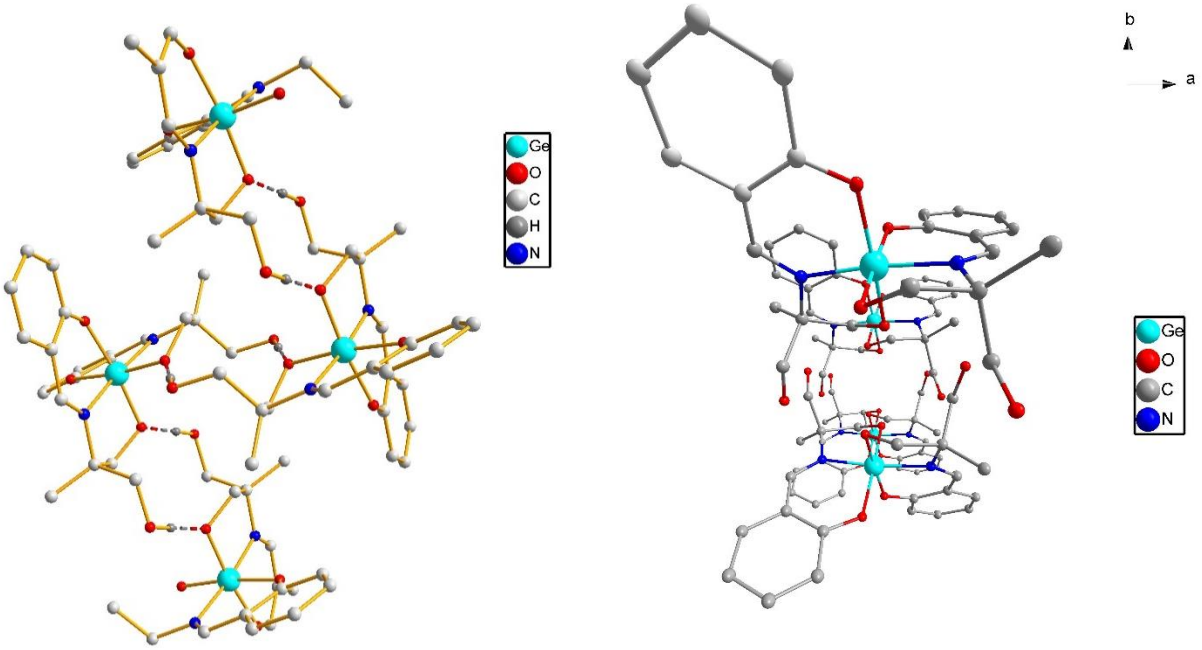

Figure S10. (left) intermolecular hydrogen bonds, (right) packing along axis c. of complex **2**.

Table S1. Experimental and calculated interatomic distances (Å) and angles (°) in **2**.

	experimental	**2**	*calculated* Radical anion of **2**	Cation radical of **2**
Ge1-N1	1.985	1.980	2.070	1.990
Ge1-N1A	1.985	1.980	1.893	1.991
N1-Ge1-N1A	174°	180	179°	179°
Ge1-O1	1.856	1.840	1.862	1.809
Ge1-O3	1.876	1.905	1.866	1.936
Ge1-O1A	1.856	1.840	1.867	1.809
Ge1-O3A	1.876	1.905	1.958	1.938

Quantum chemical calculations

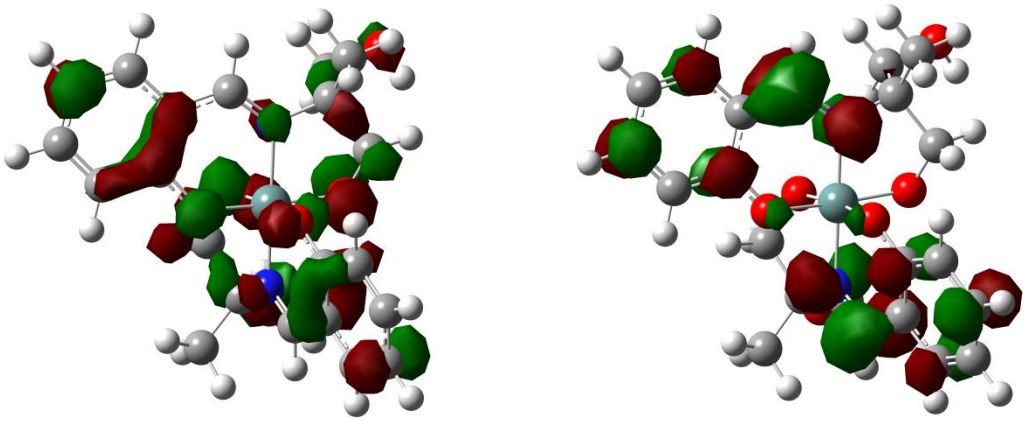

Figure S11. Calculated HOMO and LUMO plots of **2**.

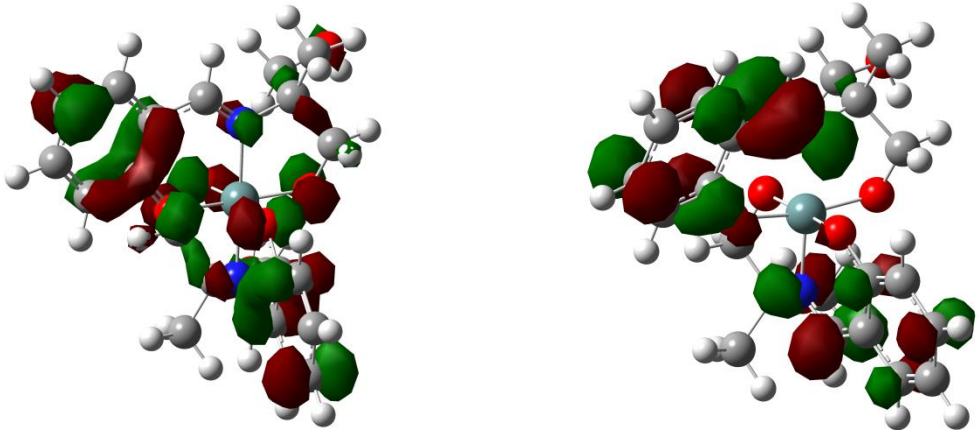

Figure S12. Calculated HOMO plots for cation and anion radicals of **2**.

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