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Supporting Information

A rigid redox-active-ligand-supported bis(germylene) as a two-centre six-electron donor

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Contents

Methods and materials

All manipulations were performed either under an atmosphere of dry argon or *in vacuo* using standard Schlenk line or glovebox techniques. Deuterated solvents were dried over molecular sieves and degassed by three freeze-pump-thaw cycles prior to use. All other solvents were distilled and degassed from appropriate drying agents. Both deuterated and non-deuterated solvents were stored under argon over activated 4 Å molecular sieves. Solvents and reagents were purchased from Sigma-Aldrich, Alfa Aesar or Fluorochem. Ligand **1**,[1] 5% Na/NaI,[2] $[Cp^{*}Al]_4$,[3] and $Na_2Fe_2(CO)_8$[4] were synthesised using literature procedures.

NMR spectra were acquired either on a Bruker Avance 500 or a Bruker Avance 400 NMR spectrometer. Chemical shifts (δ) are yielded in ppm and internally referenced to the carbon nuclei ($^{13}C\{^{1}H\}$) or residual protons (^{1}H) of the solvent. High-resolution mass spectrometry (HRMS) data were obtained from a Thermo Scientific Exactive Plus spectrometer. Infrared spectra were measured on a Bruker Optics Alpha FT-IR spectrometer in the ATR mode. A baseline correction was applied to the IR spectra. Microanalyses (C, H, N, S) were performed on an Elementar vario MICRO cube elemental analyser. (*Note: both elemental analyses and HRMS were carried out for compounds **2**-**4** but compounds **3** and **4** decomposed too rapidly and only HRMS was possible*.)

Cyclic voltammetry (CV) experiments were performed using a Gamry Instruments Reference 600 potentiostat. A standard three-electrode cell configuration was employed using a platinum disk working electrode, a platinum wire counter electrode, and a silver wire, separated by a *Vycor* tip, serving as the reference electrode. Formal redox potentials are referenced to the ferrocenium/ferrocene ($[Cp_2Fe]^{+/0}$) redox couple by using ferrocene as an internal standard. Tetra-*n*-butylammonium hexafluorophosphate ($[nBu_4N][PF_6]$) was employed as the supporting electrolyte. A scan rate of 250 mV/s and compensation for resistive losses (*iR* drop) were employed for all measurements.

Synthetic procedures

NDI, 1

This compound was synthesised according to a literature report[1] and only the ^{1}H NMR data is recorded for comparison with compound **2.**

^{1}H NMR (400 MHz, C_6D_6) δ: 8.62 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, C*H*, Napth), 7.47 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 2H, C*H*, Napth), 7.18 (m, 2H, C*H*, Dipp) 7.13 (m, 4H, C*H*, Dipp), 2.89 (hept, $^3J_{H\text{-}H}$ = 6.9 Hz, 4H, C*H*Me$_2$), 2.43 (s, 6H, CH_3, imine), 1.18 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH*Me*$_2$), 1.09 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, CH*Me*$_2$).

NDI-Ge$_2$Cl$_2$, 2

Free ligand **1** (106.6 mg, 0.20 mmol), Na/NaCl (5% w/w, 312.6 mg, 0.68 mmol) and 10 mL of solvent (benzene/THF = 1:1, v/v) were mixed. This mixture was sonicated for 2 h to give a dark green solution which was presumed to be NDI-Na$_2$. This solution was added dropwise to the solution of GeCl$_2$-dioxane (115.8 mg, 0.50 mmol) in 5 mL THF. The reaction was stirred overnight then all volatiles were removed under vacuum. The product was extracted with benzene and the volume of the organic phase was reduced to 5 mL for recrystallisation. Compound **2** was obtained as a burgundy solid (60 mg).

Yield: 40%.

1H NMR (400 MHz, C_6D_6) δ: 6.16 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, C*H*, Napth), 5.38 (d, $^3J_{H\text{-}H}$ = 8.7 Hz, 2H, C*H*, Napth). (Low solubility, only the signals for Napth are analysed for comparison with NDI)

^{1}H NMR (400 MHz, THF-d$_8$) δ: 7.29-7.21 (br, 6H, C*H*, Dipp), 7.00 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H, $C^{3,6}$-*H*, Napth), 6.03 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H, $C^{4,5}$-*H*, Napth), 3.31 (br, 2H, C*H*Me$_2$), 2.64 (br, 2H, C*H*Me$_2$), 2.01 (s, 6H, CH_3, imine), 1.23 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 12H, CH*Me*$_2$), 1.15 (br, 12H, CH*Me*$_2$).

^{13}C NMR (101 MHz, THF-d$_8$) δ: 157.8 (s, N*C*N, Napth), 154.5 (s, N=*C*Me), 147.2 (br, one of the C^1, Dipp), 144.4 (br, one of the C^1, Dipp), 139.8 (s, NC*C*, Napth), 136.7 (s, $C^{2,6}$, Dipp), 134.2 (s, $C^{2,7}$, Napth), 130.9 (s, $C^{3,6}$-H, Napth), 128.4 (s, C^4-H, Dipp), 124.8 (br, $C^{3,5}$-H, Dipp), 117.6 (s, $C^{4.5}$-H, Napth), 29.5 (br, *C*HMe$_2$), 28.9 (br, *C*HMe$_2$), 24.6 (s, CH*Me*$_2$), 15.2 (s, N=C*Me*).

HRMS: Calcd for $[C_{36}H_{44}Cl_2Ge_2N_4]^{+\cdot}$ 748.1370, found 748.1345, method FTMS + p ESI.

Elemental analysis for $[C_{36}H_{44}Cl_2Ge_2N_4]$ (M_w = 748.94): calcd. C 57.73, H 5.92, N 7.48%; found C 57.75, H 5.99, N 7.22%.

NDI-Ge_2, 3

The benzene solution (4 mL) of **2** (37.5 mg, 0.05 mmol) was slowly added to the solution of $(Cp^*Al)_4$ (8.0 mg, 0.0125 mmol) in benzene (1 mL) at room temperature. This mixture was stirred for 1 h to give a black solution. The solution volume was reduced to 1 mL for recrystallisation. Compound **3** was obtained as a black solid (9.5 mg). Although the reaction is selective, the process of removing the byproduct Cp^*AlCl_2 by recrystallisation decreases the yield significantly. Prolonged recrystallisation time results in decomposition of NDI-Ge_2.

Yield: 28%.

^{1}H NMR (400 MHz, C_6D_6) δ: 7.60 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H, Napth-*H*), 7.25-7.29 (m, 2H, Dipp-*H*), 7.22-7.18 (m, 4H, Dipp-*H*), 7.05 (d, $^3J_{H\text{-}H}$ = 8.9 Hz, 2H, Napth-*H*), 2.54 (hept, $^3J_{H\text{-}H}$ = 6.8 Hz, 4H, C*H*Me$_2$), 2.28 (s, 6H, N=C*Me*), 1.11 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.04 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 12H, CH*Me*$_2$).

^{13}C NMR (101 MHz, C_6D_6) δ: 148.0 (s, N*C*C, can only be observed in HMBC), 145.7 (s, $C^{2,6}$, Dipp), 138.3 (s, C^1, Dipp), 131.3 (s, $C^{2,7}$, Napth), 127.7 (s, C^4-H, Dipp), 127.6 (s, N*C*Me), 123.6 (s, $C^{3,5}$-H, Dipp), 122.0 (s, $C^{3,6}$-H, Napth), 119.3 (s, $C^{4,5}$-H, Napth), 108.4 (s, NC*C*, Napth), 28.3 (s, *C*HMe$_2$), 26.4 (s, *C*H*Me*$_2$), 23.4 (s, *C*H*Me*$_2$), 13.8 (s, NC*Me*).

HRMS: Calcd for $[C_{36}H_{44}Ge_2N_4]^{+\cdot}$ 678.1993, found 678.1973, method FTMS + p ESI.

Melting point: 140.7 °C (decompose).

NDI-$Ge_2Fe_2(CO)_6$, 4

Compound **2** (22.5 mg, 0.03 mmol), $Na_2Fe_2(CO)_8$ (11.5 mg, 0.03 mmol) and 0.4 mL of C_6D_6 were mixed and heated at 80 °C. This mixture was heated until the ^{1}H NMR shows the total consumption of **2** (approximately 10 h). Recrystallisation from the reaction mixture generated compound **4** as a black powder (19.1 mg).

Alternative route: Compound **3** (13.6 mg, 0.02 mmol), $Fe_2(CO)_9$ (7.3 mg, 0.02 mmol) and 0.3 mL THF-d_8 were mixed and heated at 80 °C. This mixture was heated until the ^{1}H NMR showed the total consumption of **3** (approximately 12 h). In the ^{1}H NMR spectrum, compound **4** was identified as the main product together with other unknown species. The yield was not calculated for this route.

Yield: 67%.

^{1}H NMR (400 MHz, THF-d$_8$) δ: 7.40-7.30 (m, 8H, C^{4,5}-*H*, Napth and Dipp-H), 6.40 (d, $^{3}J_{H\text{-}H}$ = 8.5 Hz, 2H, C^{3,6}-*H*, Napth), 3.15 (hept, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 4H, C*H*Me$_2$), 2.22 (br, 6H, NC*Me*), 1.40 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 12H, CH*Me*$_2$), 1.12 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 12H, CH*Me*$_2$).

^{13}C{^{1}H}, NMR (101 MHz, THF-d$_8$) δ: 217.9 (s, *C*O), 155.0 (s, N*C*Me), 150.8 (s, NC*C, this signal is weak in the ^{13}C NMR spectrum, but obvious in the ^{13}C-HMBC spectrum*), 145.7 (s, *C*^{1}, Dipp), 137.0 (s, *C*^{2,6}, Dipp), 135.9 (s, *C*^{2,7}, Napth), 133.9 (s, NC*C*, Napth), 132.3 (s, *C*^{4,5}-H, Napth), 129.8 (s, *C*^{4}-H, Dipp), 125.6 (s, *C*^{3,5}-H, Dipp), 118.7 (s, *C*^{3,6}-H, Napth), 29.3 (s, *C*HMe$_2$), 25.4 (s, CH*Me*$_2$), 23.7 (s, CH*Me*$_2$), 16.3 (s, NC*Me*).

HRMS: Calcd for [$C_{42}H_{44}Fe_2Ge_2N_4O_6$]$^{+\cdot}$ 958.0407, found 958.0368, method FTMS + p ESI.

IR (ATR, 20 °C) $\tilde{\upsilon}$/cm^{-1}: 2037, 2004, 1956, 1938, 1911.

NMR spectra of isolated compounds

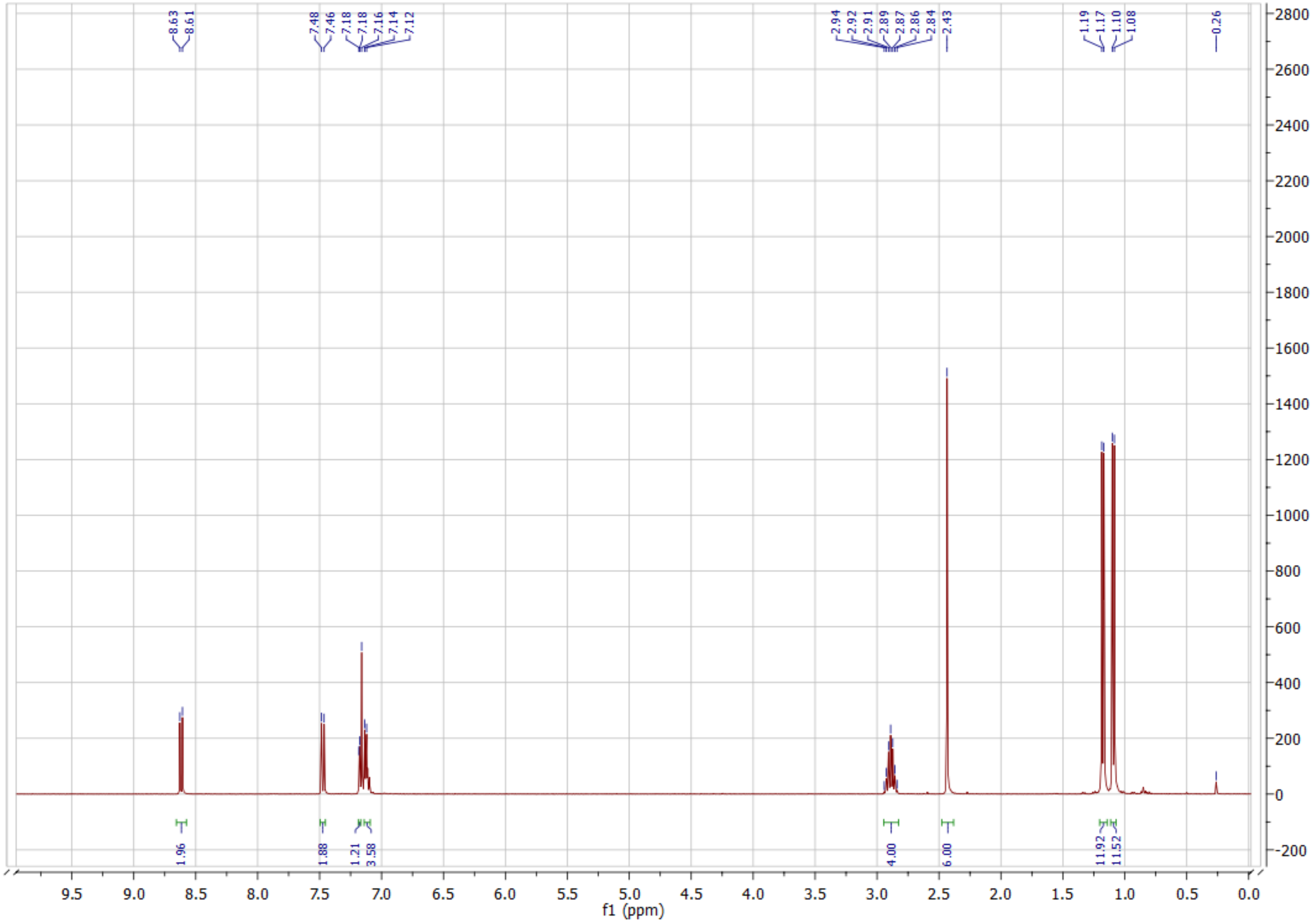


Fig. S1. ^{1}H NMR spectrum of NDI **1** in C_6H_6.

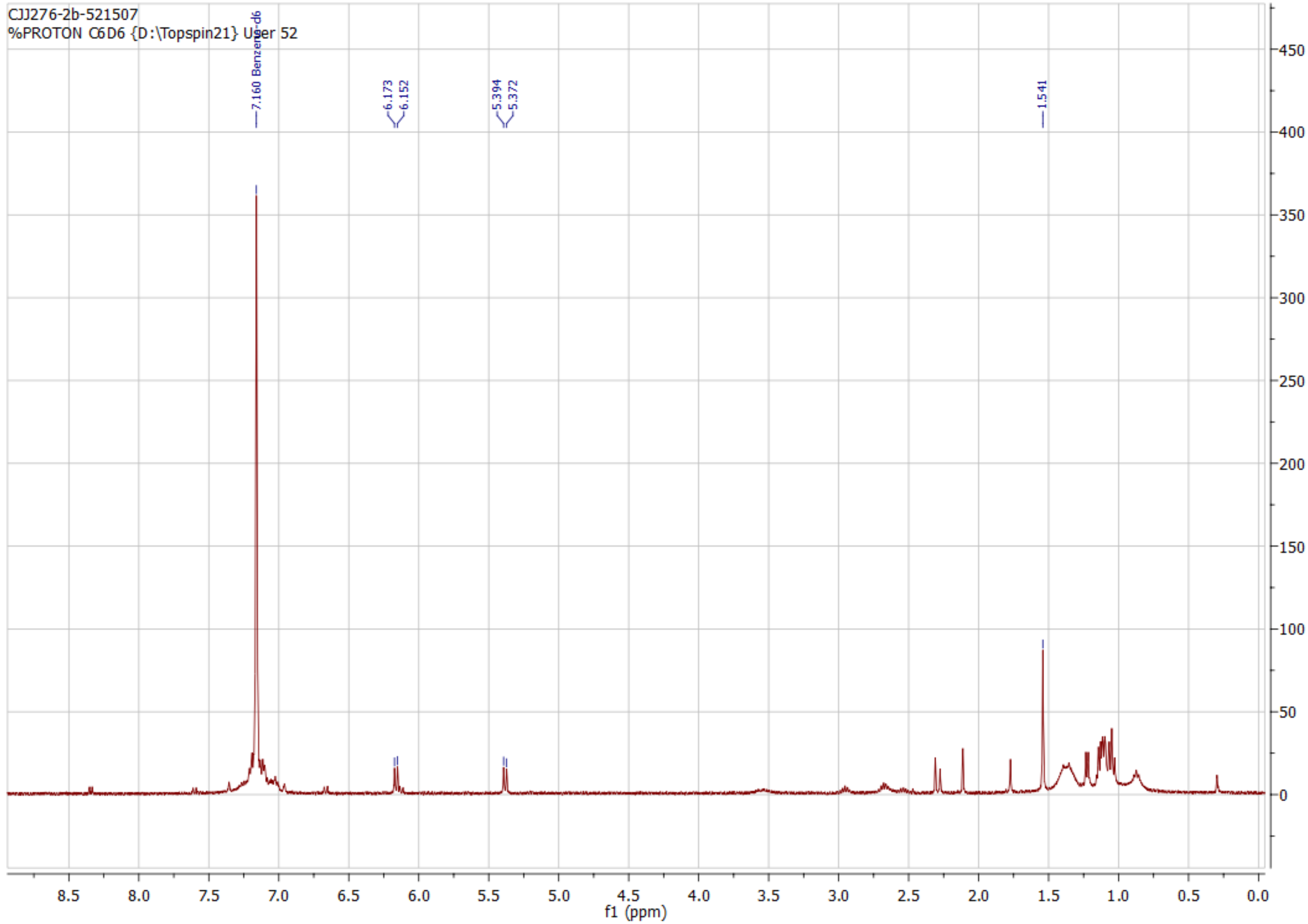


Fig. S2. ^{1}H NMR spectrum of NDI-Ge$_2$Cl$_2$ **2** in C_6H_6. (Low solubility, not pure, only for comparison with **NDI**)

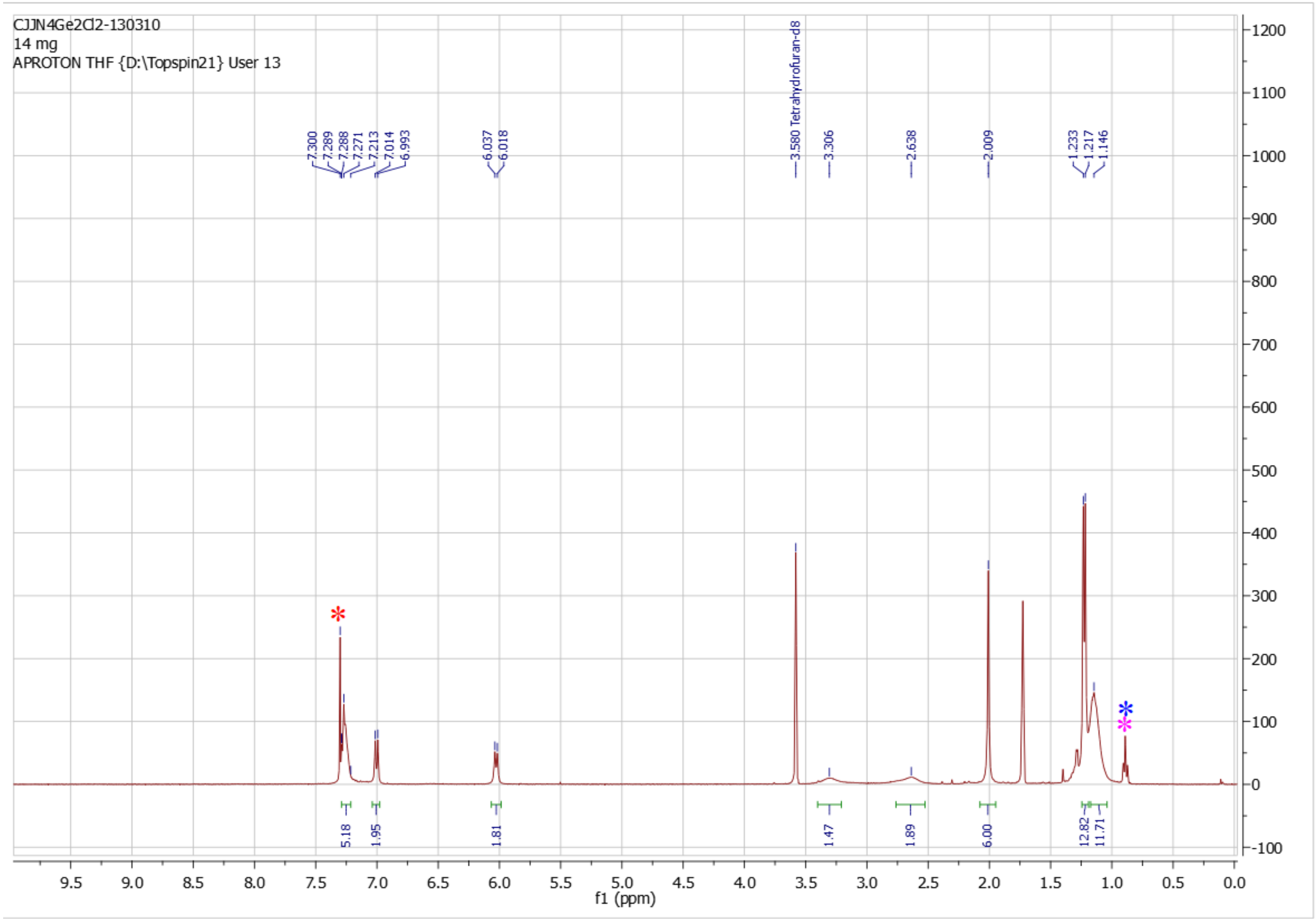


Fig. S3. ^{1}H NMR spectrum of NDI-Ge$_2$Cl$_2$ **2** in THF-d$_8$ (C$_6$H$_6$, hexane, and pentane residue are labeled as red, pink, and blue).

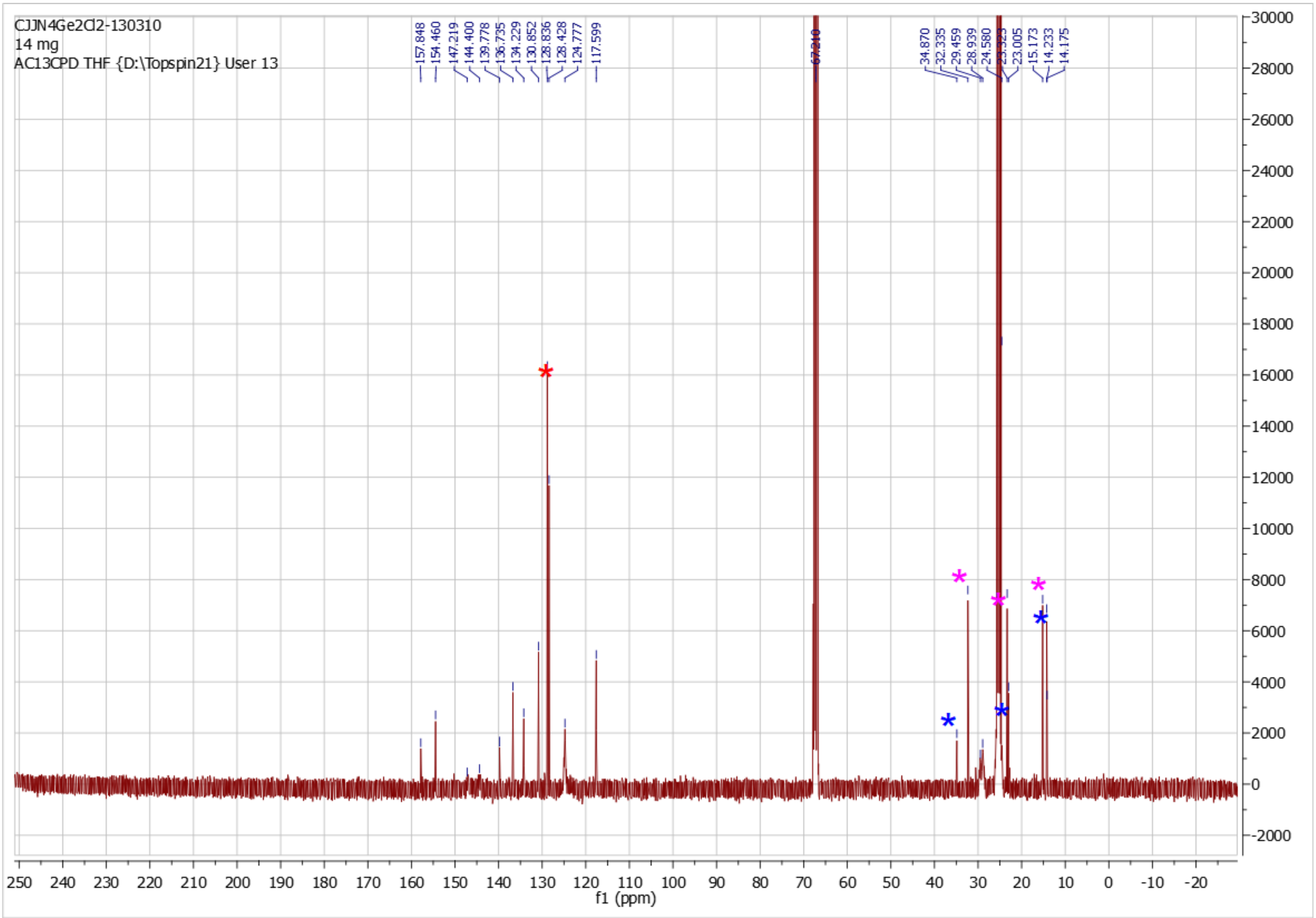


Fig. S4. $^{13}C\{^1H\}$ NMR spectrum of NDI-Ge_2Cl_2 **2** in THF-d_8 (C_6H_6, hexane, and pentane residue are labeled as red, pink, and blue).

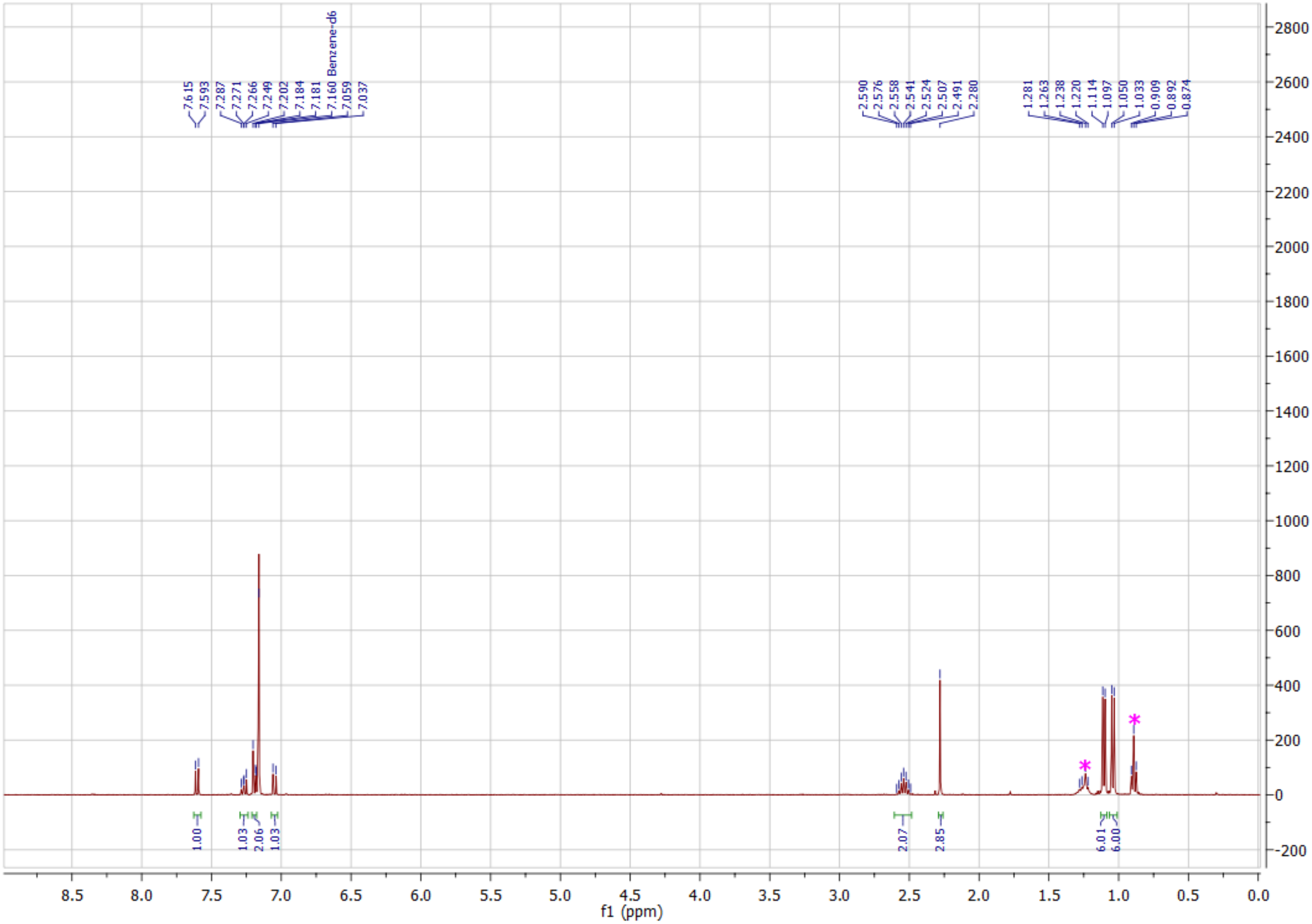


Fig. S5 ^{1}H NMR spectrum of NDI-Ge$_2$ **3** in C_6D_6. (Hexane residue is denoted by pink stars)

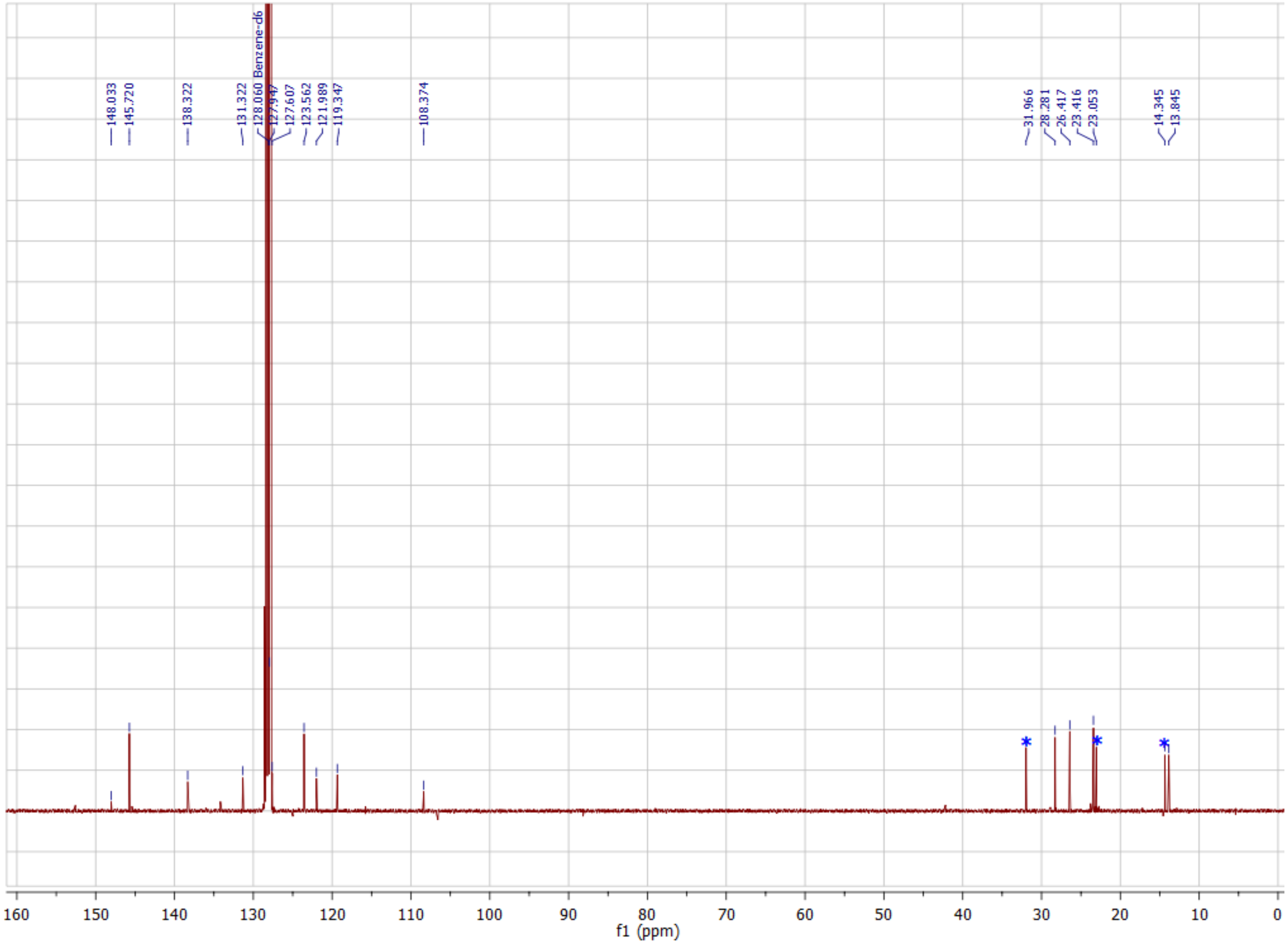


Fig. S6. ^{13}C NMR spectrum of NDI-Ge$_2$ **3** in C_6D_6. (Hexane residue is denoted by blue stars)

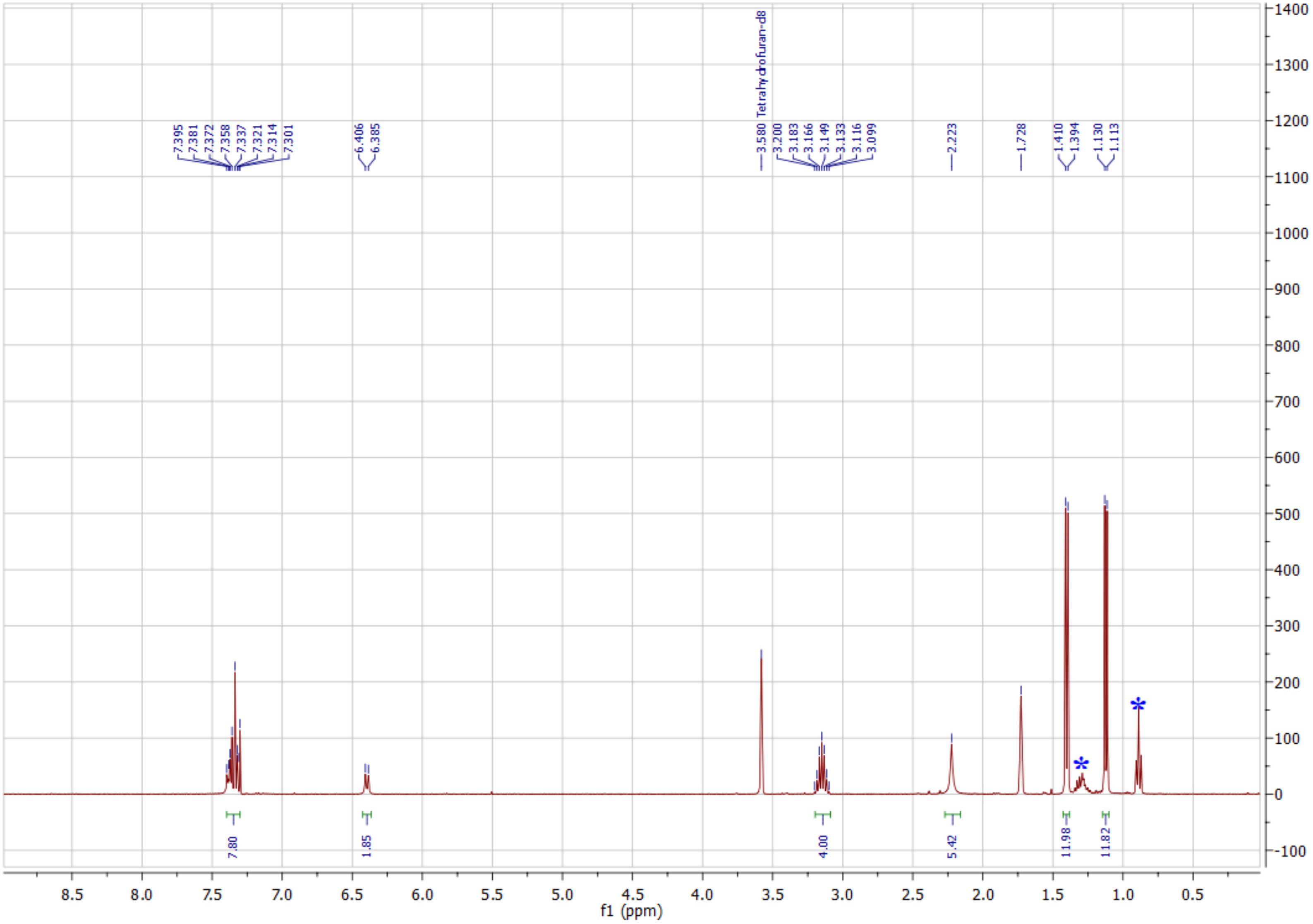


Fig. S7. ^{1}H NMR spectrum of NDI-Ge$_2$Fe$_2$ **4** in THF-d$_8$. (Pentane residue is denoted by blue stars)

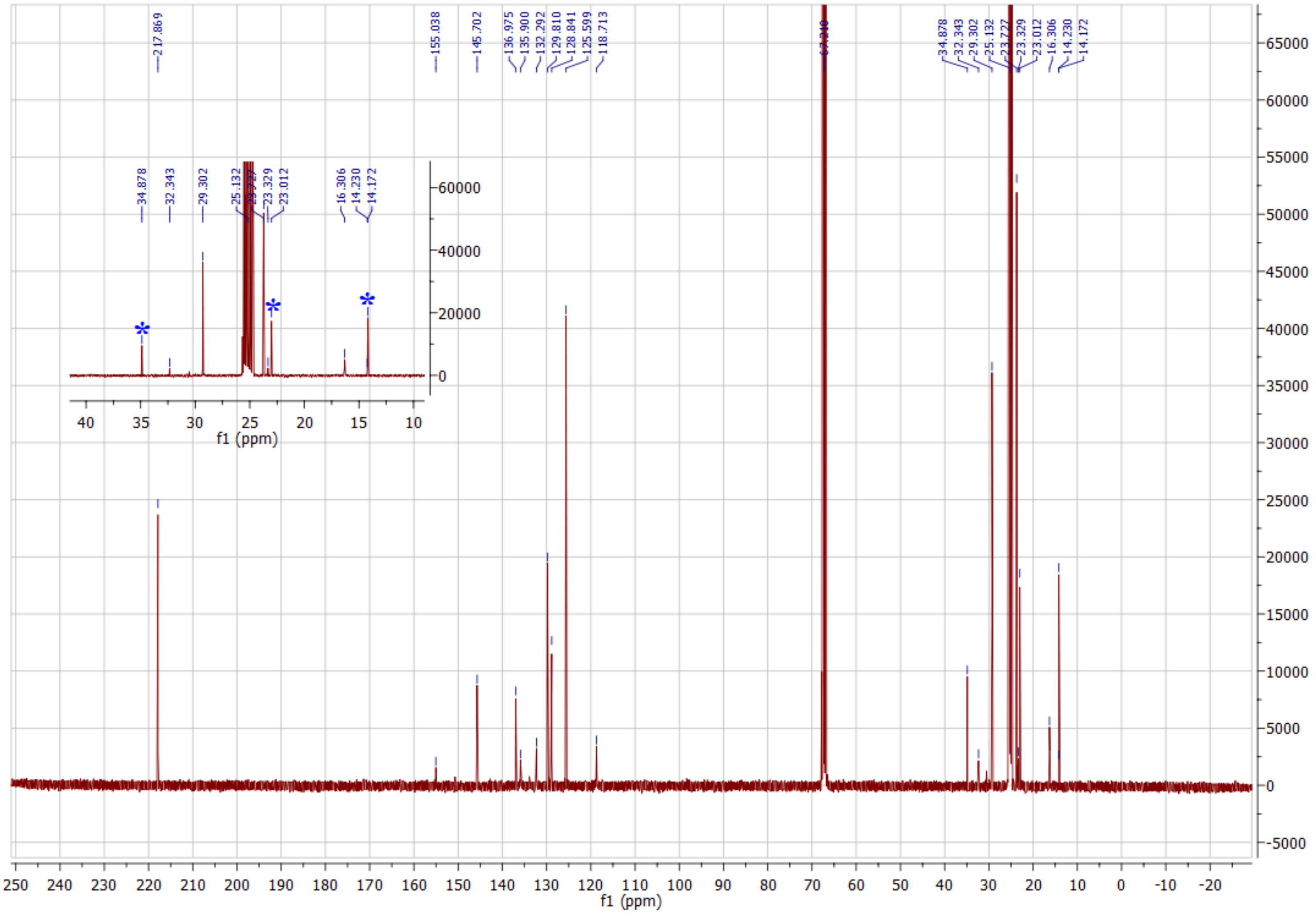


Fig. S8. $^{13}C\{^1H\}$ NMR spectrum of NDI-Ge_2Fe_2 **4** in THF-d_8. (Pentane residue is denoted by blue stars)

IR and CV of compound 4

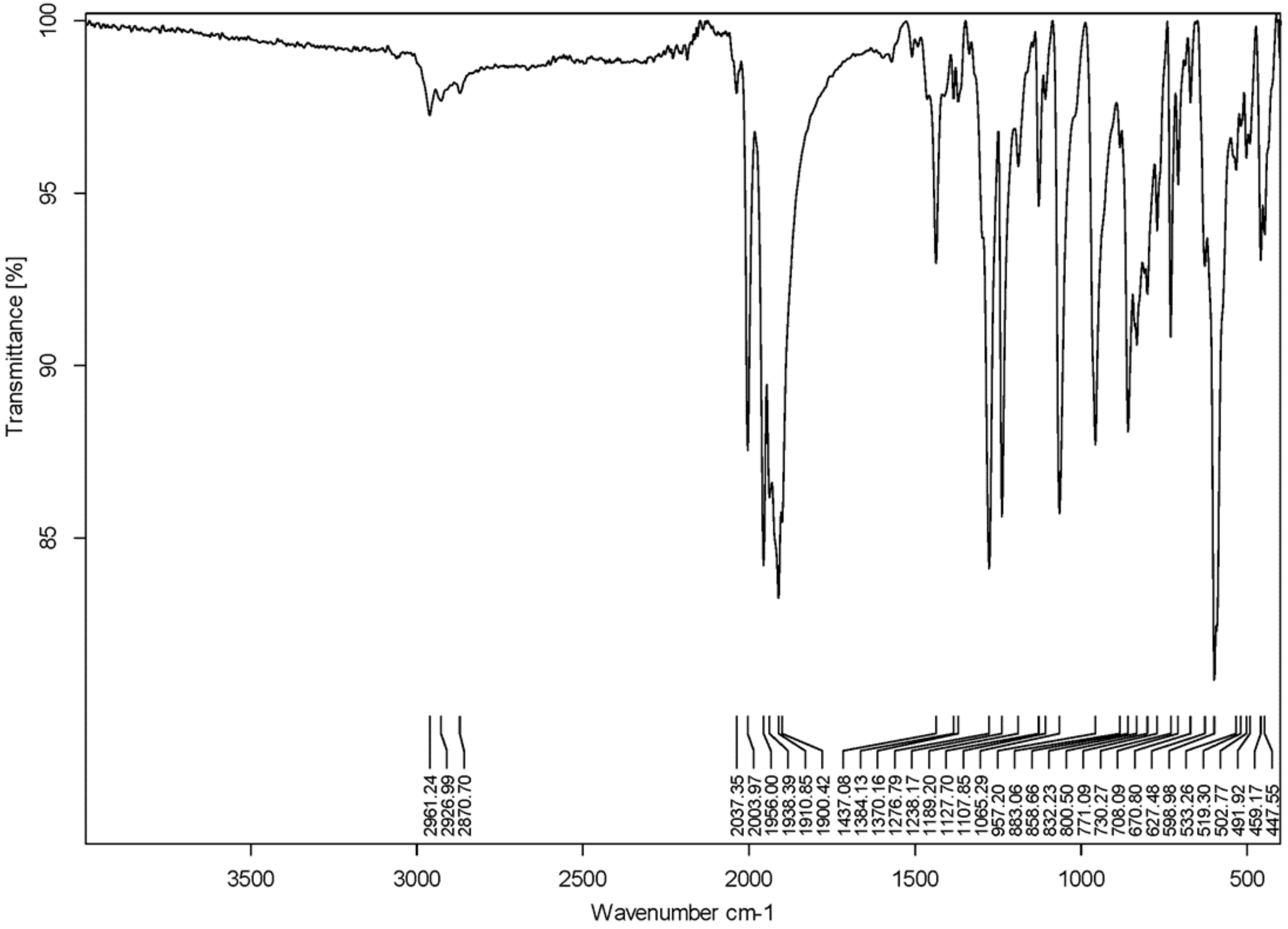


Fig. S9. Solid-state IR spectrum of NDI-Ge_2Fe_2 **4**.

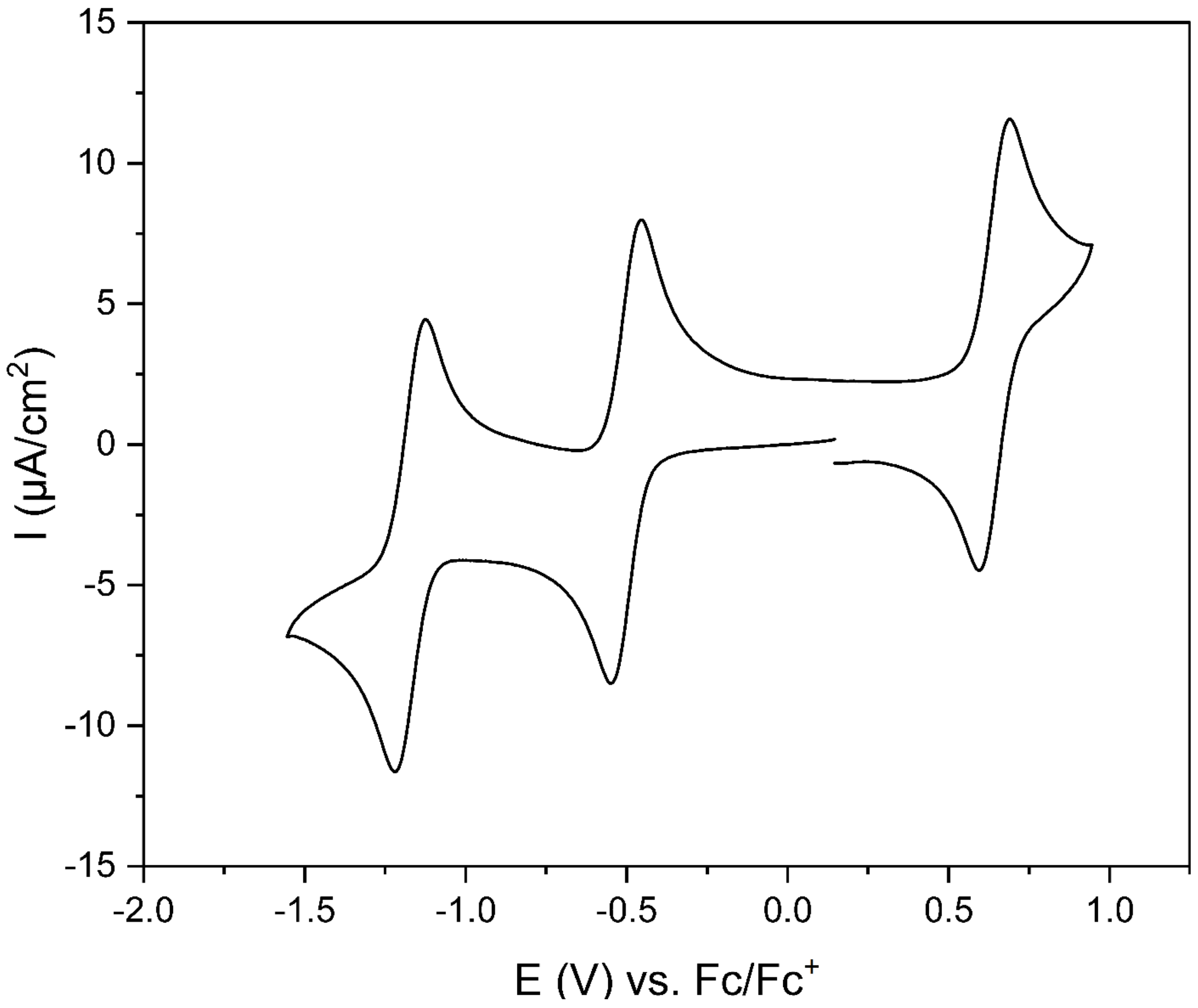


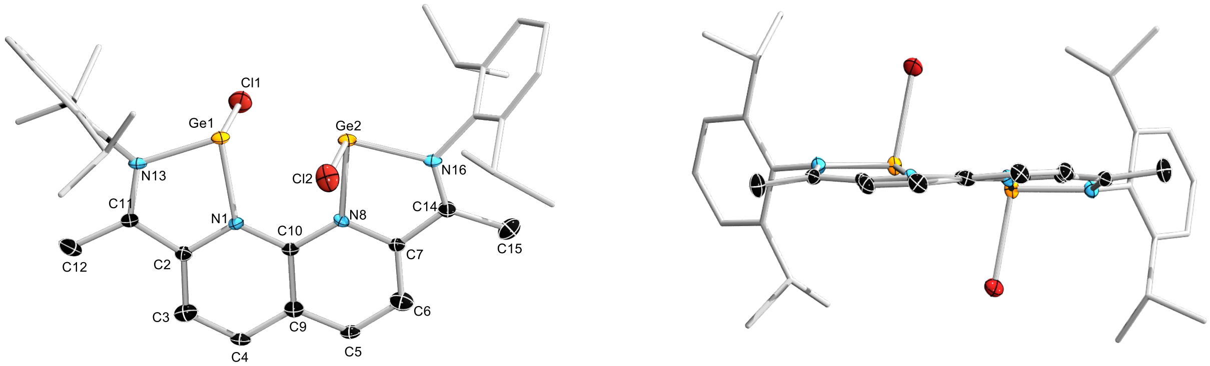
Fig. S10. Cyclic voltammogram of **4** in THF/0.1 M [*n*Bu_4N][PF_6] measured at a scan rate of 250 mVs^{-1}. Formal potentials: $E_{1/2} = -0.51$ V, $E_{1/2} = -1.18$ V and $E_{1/2} = 0.63$ V (relative to Fc/Fc$^+$).

X-ray crystallographic data

The crystal data of **2** were collected on a Bruker D8 Quest diffractometer with a CMOS area detector and multi-layer mirror monochromated $\mathrm{Mo}_{K\alpha}$ radiation. The crystal data of **3** and **4** were collected on a RIGAKU XTALAB SYNERGY-R diffractometer with an HPA area detector and multi-layer mirror monochromated $\mathrm{Cu}_{K\alpha}$ radiation. The structures were solved using the intrinsic phasing method,[5] refined with the ShelXL program[6] and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in structure factor calculations.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-2122989 (**2**), -2122993 (**3**), -2122997 (**4**). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

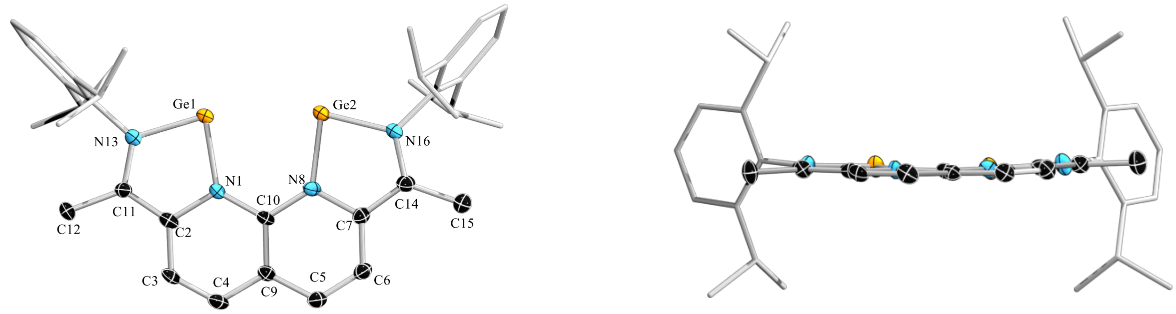
Crystal data for **2**: $C_{42}H_{50}Cl_2Ge_2N_4$, M_r = 826.94, brown block, 0.494 mm × 0.111 mm × 0.08 mm, monoclinic space group *C*2/*c*, *a* = 20.526(6) Å, *b* = 8.661(3) Å, *c* = 22.968(7) Å, ⍰⍰= 90°, ⍰ = 101.352(14)°, ⍰ = 90°, *V* = 003(2) Å^3, *Z* = 4, ⍰$_{calcd}$ = 1.372 g·cm^{-3}, ⍰ = 1.669 mm^{-1}, *F*(000) = 1712, *T* = 100(2) K, R_1 = 0.0236, wR^2 = 0.0566, 3970 independent reflections [2⍰≤52.146°] and 232 parameters.



(a) (b)

Fig. S11. Crystallographically-derived solid-state structure of **2**. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and the hydrogen atoms are omitted for clarity. (a) Front view and (b) side view.

Crystal data for **3**: $C_{36}H_{44}Ge_2N_4$, M_r = 677.93, clear red block, 0.221 mm × 0.089 mm × 0.017 mm, triclinic space group $P\bar{1}$, a = 8.7642(2) Å, b = 13.1954(5) Å, c = 15.0164(5) Å, α = 102.398(3)°, β =95.121(2)°, γ = 97.325(3)°, V = 1670.03(10) Å^3, Z = 2, ρ_{calcd} = 1.348 g·cm^{-3}, μ = 2.436 mm^{-1}, F(000) = 704, T = 100.00(10) K, R_1 = 0.0372, wR^2 = 0.0880, 6311 independent reflections [$2\theta \leqslant 140.15°$] and 389 parameters.



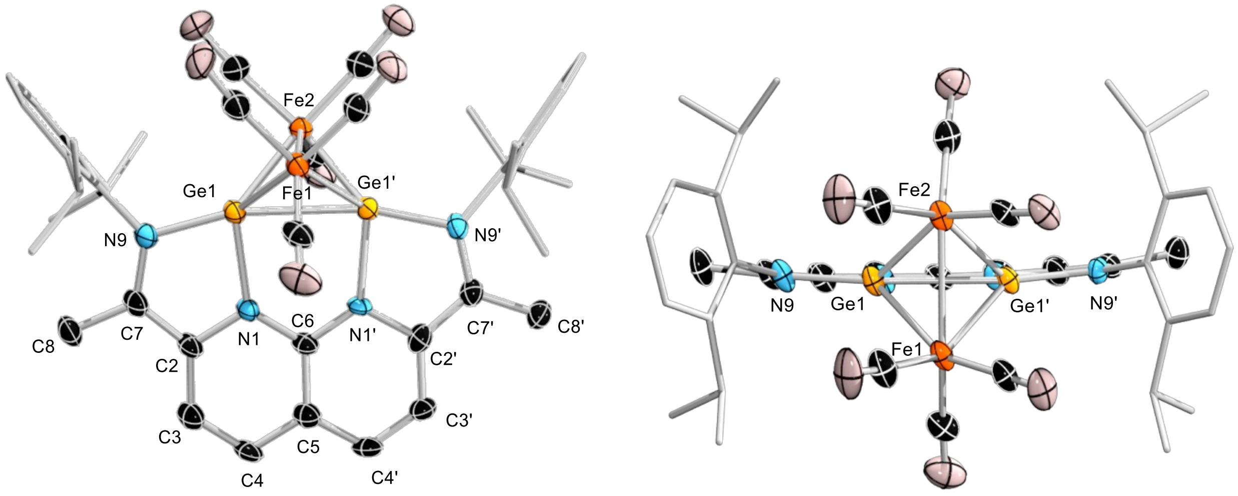
(a)

(b)

Fig. S12. Crystallographically-derived solid-state structure of **3**. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and hydrogen atoms are omitted for clarity.

The crystal data of **4** were collected on a RIGAKU XTALAB SYNERGY-R diffractometer with an HPA area detector and multi-layer mirror monochromated $Cu_{K\alpha}$ radiation.

Crystal data for **4**: $C_{54}H_{56}Fe_2Ge_2N_4O_6$, M_r = 1113.90, clear black plate, 0.350 mm × 0.083 mm × 0.033 mm, space group $P2_1/c$, a = 12.7788(3) Å, b = 21.4273(3) Å, c = 18.6581(3) Å, α = 90°, β = 96.811(2)°, γ = 90°, V = 5072.82(16) Å^3, Z = 4, ρ_{calcd} = 1.459 g·cm^{-3}, μ = 6.291 mm^{-1}, $F(000)$ = 2288, T = 99.99(10) K, R_1 = 0.0682, wR_2 = 0.1288, 9267 independent reflections [$2\theta \leqslant 136.498°$] and 685 parameters.



(a)

(b)

Fig. S13. Crystallographically-derived solid-state structure of **4**. Atomic displacement ellipsoids drawn at 50% probability. Ellipsoids on ligand periphery and hydrogen atoms are omitted for clarity. (a) Front view and (b) side view.

Note: The two benzene solvent molecules showed disorder. The atomic displacement parameters (ADPs) of overlapping atoms from different PARTs (C1, C2, C3, C4, C5, C6 of RESIs 5/15 and 6/16) were restrained using similarity restraint (SIMU) and rigid body restraint (RIGU). Reflection [0 0 3] was affected by beamstop and omitted during refinement using the OMIT keyword.

Computational details

Benchmark studies. Geometry optimisations and Hessian calculations were performed for species **1**-**4** at the density functional theory (DFT) level. All optimised geometries were characterised as minimum energy structures (only positive eigenvalues) by vibrational frequency calculations. All geometry optimisations and vibrational frequencies were performed in Gaussian 16, revision C.01.[7] In order to choose the most appropriate functional, we performed a benchmark study against the available X-ray data of **2**-**4**. We tested six distinct functionals (all using the def2-SVP[8] basis set and the D3[9] dispersion correction whenever suitable): B3LYP,[10] PBE0,[11] BP86,[12] ωb97XD,[13] M06,[14] and M062X.[14] Based on our results (Table S1), except for B3LYP-D3, all other functionals gave root-mean-square deviation (RMSD) average values of less than 0.250, and are therefore suitable for the investigations herein. We therefore chose the M06-D3/def2-SVP level of theory for the DFT computations as it provided the smallest mean absolute errors (MAE) for the Ge–Ge, Ge–Fe, and Fe–Fe bond lengths (Table S2).

Table S1. Benchmark of the DFT functionals against experimental data I: RMSD values. Basis set: def2-SVP.

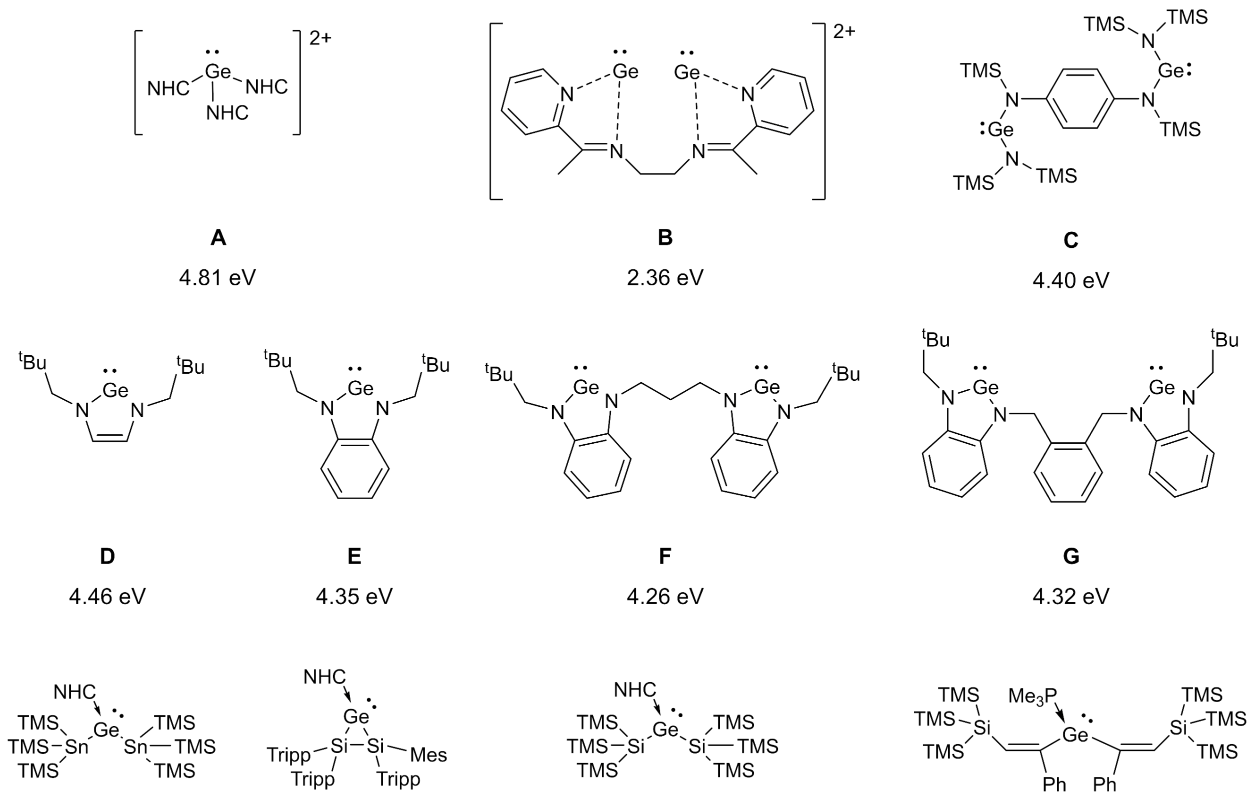
	2	**3**	**4**	Average
B3LYP-D3	0.346	0.250	0.199	0.265
BP86-D3	0.245	0.253	0.238	0.245
M06-D3	0.299	0.264	0.170	0.244
M06-2X-D3	0.248	0.261	0.186	0.232
ωB97XD	0.230	0.250	0.164	0.215
PBE0-D3	0.216	0.251	0.166	0.211

Table S2. Benchmark of the DFT functionals against experimental data II: MAE errors for selected bod lengths. Basis set: def2-SVP.

	Ge–Ge (Å) [error]			Fe–Fe (Å) [error]	Ge–Fe (Å), average [error]	Mean absolute error (MAE)
	2	**3**	**4**	**4**	**4**	-
Exp.	2.894	2.930	2.769	2.734	2.323	-
M06-D3	2.918 [0.024]	2.945 [0.015]	2.762 [-0.007]	2.724 [-0.011]	2.318 [-0.005]	0.012
PBE0-D3	2.846 [-0.048]	2.883 [-0.047]	2.733 [-0.036]	2.705 [-0.030]	2.296 [-0.026]	0.037
BP86-D3	2.925 [-0.021]	2.853 [-0.077]	2.760 [-0.010]	2.767 [0.033]	2.315 [-0.008]	0.030

M062X-D3	2.874 [0.031]	3.000 [0.070]	2.744 [-0.025]	2.720 [-0.015]	2.340 [0.018]	0.032
ωb97XD	2.949 [0.055]	2.994 [0.064]	2.727 [-0.042]	2.718 [-0.017]	2.297 [-0.026]	0.041

Frontier MOs and investigation of open-shell states. The HOMO-LUMO gap obtained for **3** (2.75 eV) was compared to those of selected mono and bis(germylenes). The results, which are shown in Fig. S14, evidence that **3** shows a remarkable small HOMO-LUMO gap, only larger than that of **B**, which was obtained by Majumdar and co-workers using a flexible 2,7-bis(2-pyridyl)-3,6-diazaocta-2,6-diene ligand. Due to their low HOMO-LUMO gap values, we investigated the triplet and open-shell singlet manifolds of both systems for a proper comparison. This was done by performing unrestricted DFT computations and multireference calculations based on the N-electron valence state perturbation theory (NEVPT2)[15] at the complete active space self-consistent field (CASSCF)[16] level with 2 electrons and 2 orbitals in the active space, namely NEVPT2/CASSCF(2,2)/def2-SVP. The results obtained at these levels of calculation ruled out open-shell ground states for both species. Furthermore, **B** was previously described as possessing a triplet biradical ground state,[17] experimentally confirmed by EPR spectroscopy. Our theoretical investigation of **B**, however, could not confirm the proposed triplet ground state, instead finding a closed-shell singlet ground state with a similar singlet-triplet gap to bis(germylene) **3** (see Figs. S14-15). The EPR spectrum of the proposed bis(germylene) triplet biradicaloid dication can instead be attributed to the triplet character of the reduced ligand. Optimisation of the uncharged analogue of the proposed bis(germylene) also shows the structure approaching the geometry of their reported piperazine-stabilised Ge(II) dication intermediate, the ligand being unable to reliably support a Ge dimer in its uncharged state due to its higher flexibility, exhibiting a Ge–Ge distance of 3.95 Å. These investigations highlight the novelty of the bis(germylene) NDI-Ge_2 system **3** obtained in the present work.



A 4.81 eV

B 2.36 eV

C 4.40 eV

D 4.46 eV

E 4.35 eV

F 4.26 eV

G 4.32 eV

H 3.89 eV

I 3.74 eV

J 3.96 eV

K 4.40 eV

Fig. S14. Calculated HOMO-LUMO gaps in eV of selected mono and bis(germylenes) **A**,[18] **B**,[17] **C**,[19] **D**,[20] **E**,[20] **F**,[21] **G**,[21] **H**,[22] **I**,[23] **J**[24] and **K**[24] at the M06-D3/def2-SVP level of theory. For comparison, the HOMO-LUMO gap of **3** at the same level of theory is 2.75 eV.

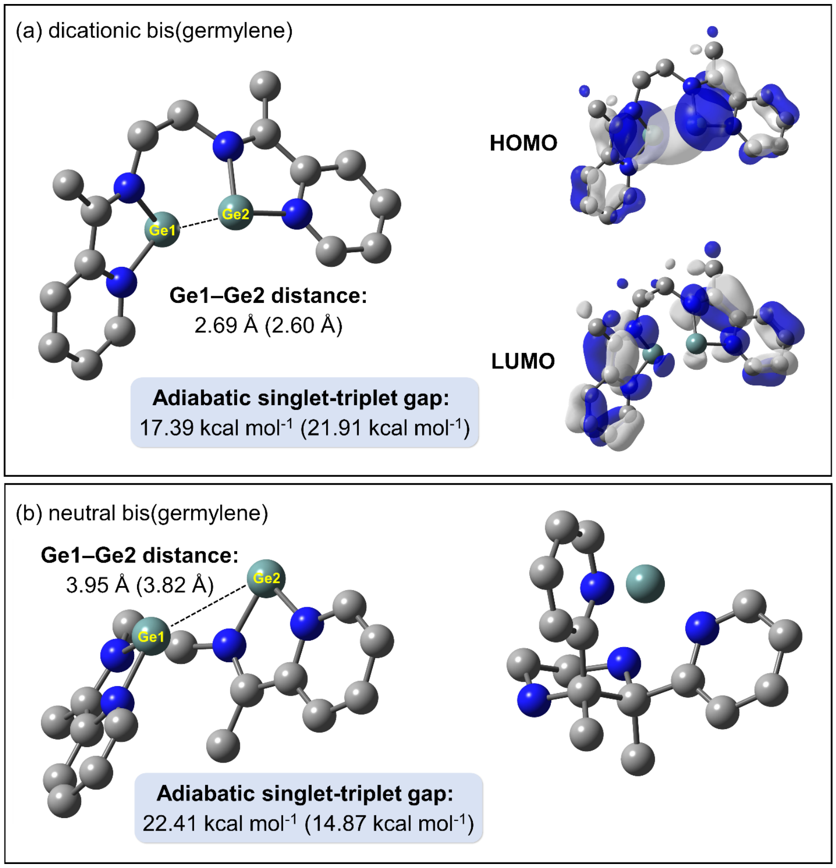


Fig. S15. (a) Optimised structure of dicationic bis(germylene) intermediate proposed by Majumdar and co-workers at the M06-D3/def2-SVP level of theory. Frontier orbitals, Ge–Ge distance and adiabatic singlet-triplet gap are given. (b) Optimised structure of analogous uncharged intermediate at the M06-D3/def2-SVP level of theory, the piperazine-stabilised Ge(II) dication intermediate reported by Majumdar and coworkers is shown for reference. Ge–Ge distance and adiabatic singlet-triplet gap are given. Parentheses indicate the values obtained using B3LYP/6-31G(d,p) in accordance with the level of theory utilised in the work of Majumdar and co-workers.

IBO, NBO, and ELF calculations. Starting from the optimised structures, we performed calculations based on the intrinsic bond orbital (IBO),[25] natural bond orbital (NBO),[26] and electron localisation function (ELF)[27] methods to investigate the bonding situation of the aforementioned molecules. The ELF basin attractors and ELF basin electron density values were obtained through a cubical grid with spacing of 0.20 Bohr in x-, y- and z-direction. Furthermore, the Mayer bond orders (MBOs)[28] were also computed for the Ge–Ge bonds. No clear evidence for a Ge–Ge bond in **3** was indicated by any of these theoretical approaches (Figs. S16-17). The second-order perturbation energies obtained from NBO calculations on **3** reveal the presence of hyperconjugative effects involving each of the Ge lone pairs and two acceptor, in-plane non-

Lewis orbitals of the neighbor Ge atom (Fig. S18). These relatively small but non-negligible bonding effects contribute to the stabilisation of **3** and account for the computed Ge–Ge MBO of 0.26. The same hyperconjugative interactions can also be found in **2**, the higher stabilisation energies correlating with the shorter Ge–Ge distance (Fig. S17c). IBOs were computed with Orca 5.0.1[29] and the IBOview program. The NBO analysis was performed using NBO 7.0.[30] The ELF and MBO calculations were done in Multiwfn 3.8.[31]

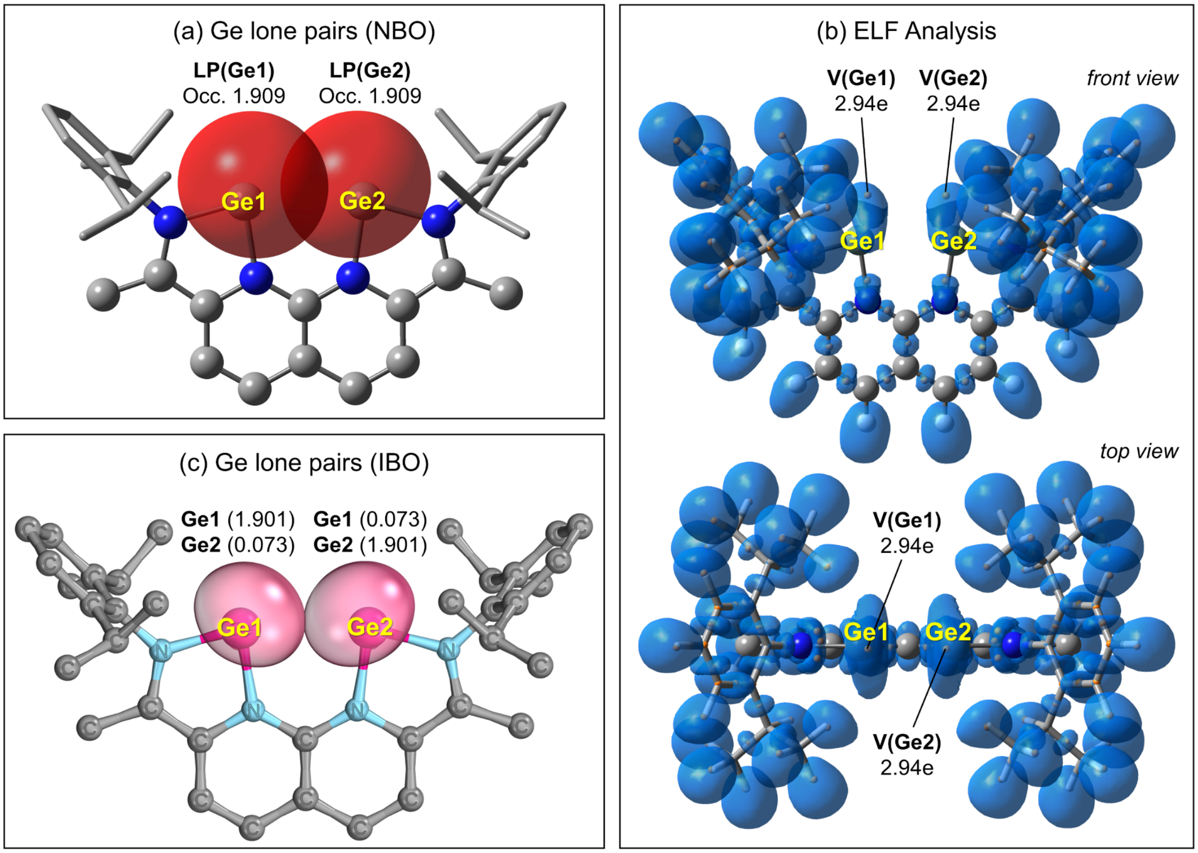


Fig. S14. (a) Selected NBOs of **3** depicting the Ge lone pairs at the M06-D3/def2-SVP level of theory. The occupation numbers of the NBOs are shown in parentheses. (b) Localisation domains (isosurface: 0.8) and the valence ELF attractors of **3** at the M06-D3/def2-SVP level. The ELF basin electron density values for both Ge atoms are 2.94e. (c) Selected IBOs of **3** depicting the Ge lone pairs. The numbers in parentheses indicate the fraction of electrons of the doubly occupied orbital assigned to the individual atoms.

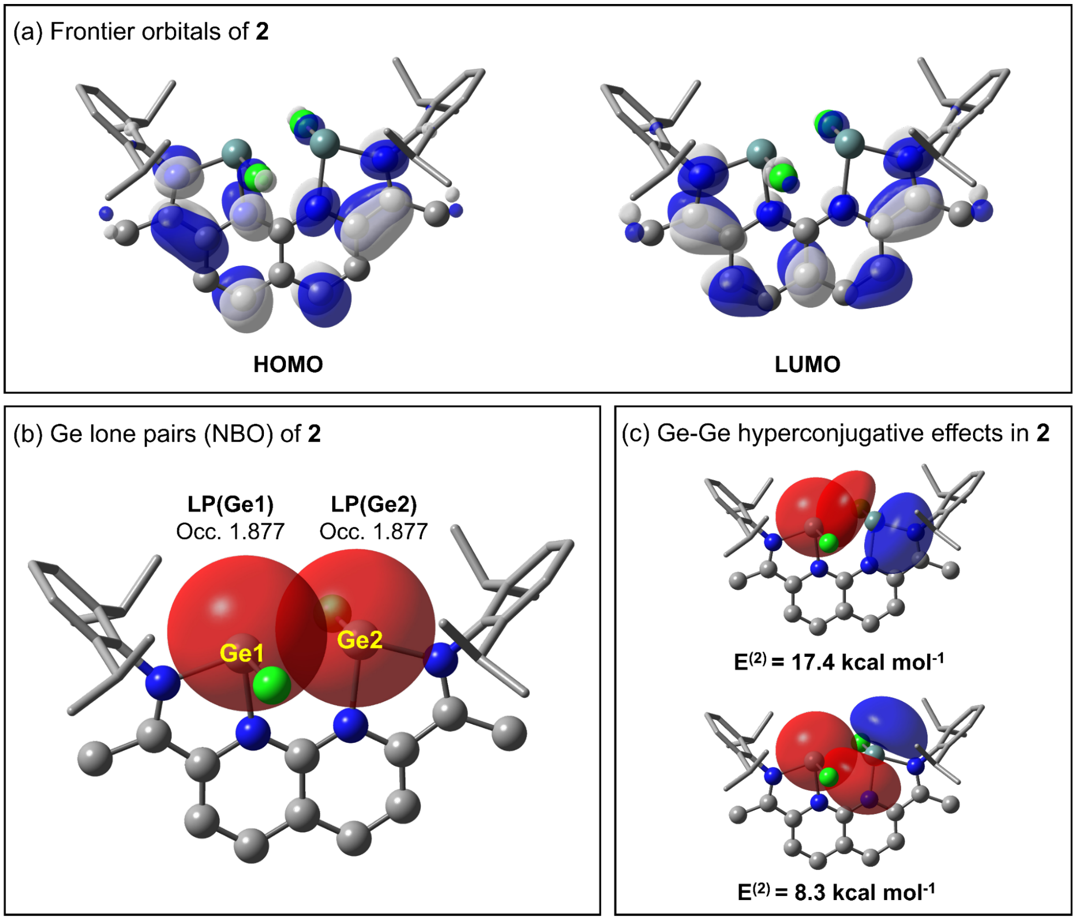
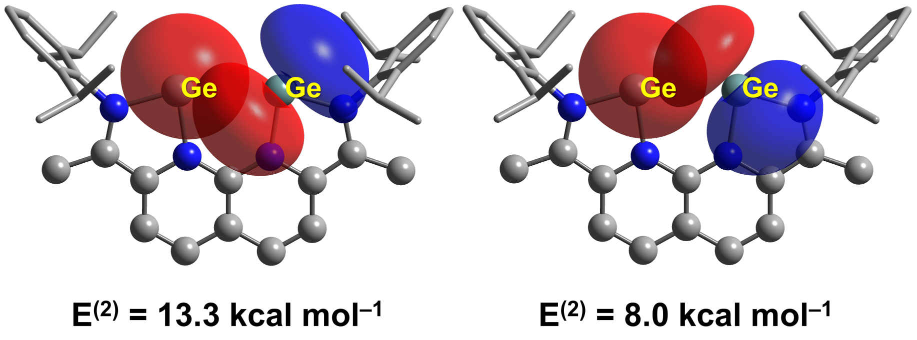


Fig. S17. (a) Frontier orbitals of **2** at the M06-D3/def2-SVP level of theory (Isovalue: 0.03). The occupation numbers of the NBOs are shown in parentheses. (b) Selected NBOs of **2** depicting the Ge lone pairs at the M06-D3/def2-SVP level of theory. The occupation numbers of the NBOs are shown in parentheses. (c) Ge–Ge hyperconjugative effects in **2** as revealed by NBO second-order perturbation energies.



$E^{(2)}$ = 13.3 kcal mol^{-1}

$E^{(2)}$ = 8.0 kcal mol^{-1}

Fig. S15. Ge–Ge hyperconjugative effects in **3** as revealed by NBO second-order perturbation energies.

Aromaticity. We studied the aromaticity of **3** using the anisotropy of the current-induced density (ACID)[32] technique at the M06-D3/def2-SVP level of theory (contour value: 0.02). Inspection of Fig. S19 reveals the presence of strong diatropic, clockwise π-electron ring currents mainly along the two C_2N_2Ge rings, which is characteristic of aromatic systems. Furthermore, the ACID analysis indicates the absence of Ge–Ge π interactions.

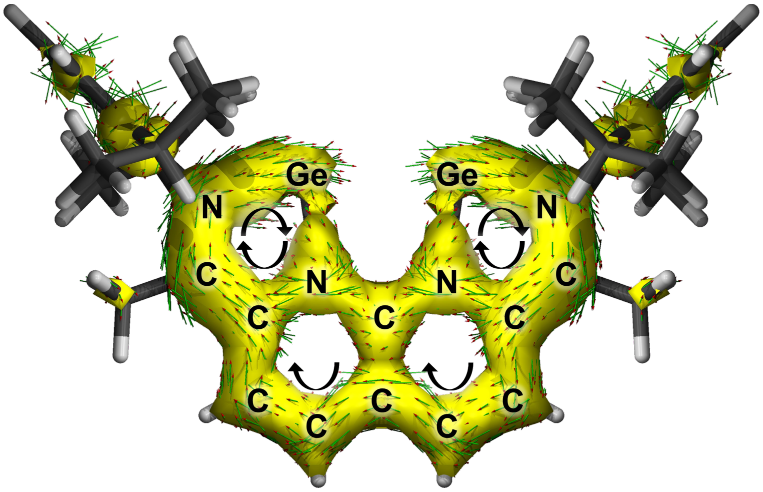


Fig. S16. π-space ACID plot of compound **3** at the M06-D3/def2-SVP level of theory (contour value: 0.02).

We also studied the aromaticity of compound **3** using the nucleus-independent chemical shift (NICS)[33] method (Fig. S20). For comparison, the corresponding plots of the naked NDI ligand are given in Fig. S21. The C_2N_2Ge rings are those where the $NICS_{zz}$ values are the most negative (see the blue curve of Fig. S20), with minimum values of $NICS_{zz}$(min) = –29 ppm at z = ±1.0 Å. In contrast, the $NICS_{zz}$ values of the naphthyridine backbone of **3** (green curve) are less negative than those of the naked NDI system (**3**: $NICS_{zz}$(min) = –13 ppm); NDI: $NICS_{zz}$(min) = –26 ppm). Surprisingly, the $NICS_{zz}$-scan curve of the five-membered central CN_2Ge_2 pseudo-ring (red curve) is also characterised by the presence of minima in the negative NICS region ($NICS_{zz}$(min) = –16 ppm), whose values are even more negative than those of the naphthyridine rings of **3** ($NICS_{zz}$(min) = –13 ppm). We attribute this to an artifact of the method due to the presence of adjacent aromatic rings.[34] All NICS calculations were performed in Gaussian 16, revision C.01.[7]

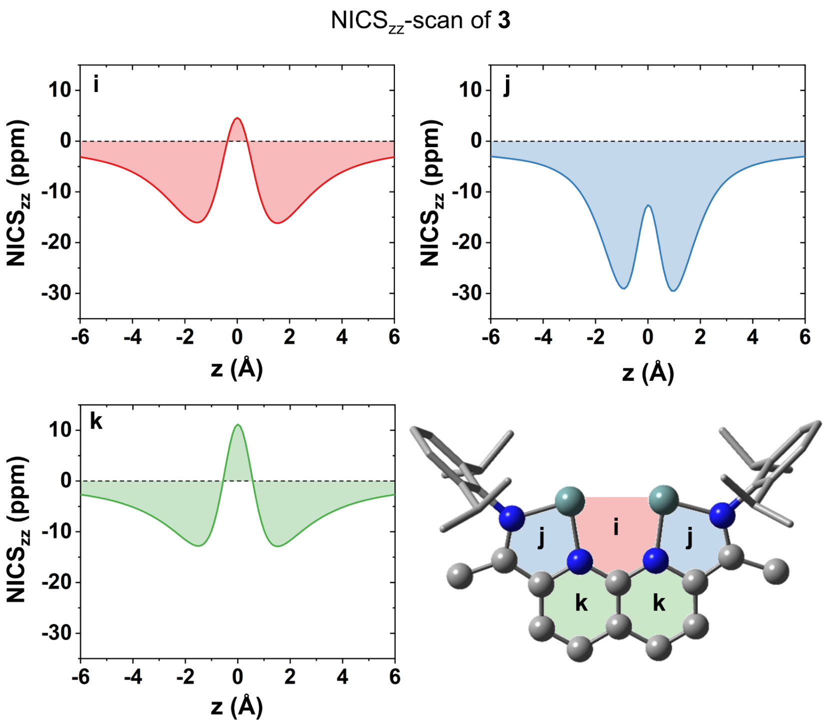


Fig. S20. NICS$_{zz}$-scan curves of the pseudo-ring (i) and distinct rings (j, k) of **3** at the M06-D3/def2-TZVP level.

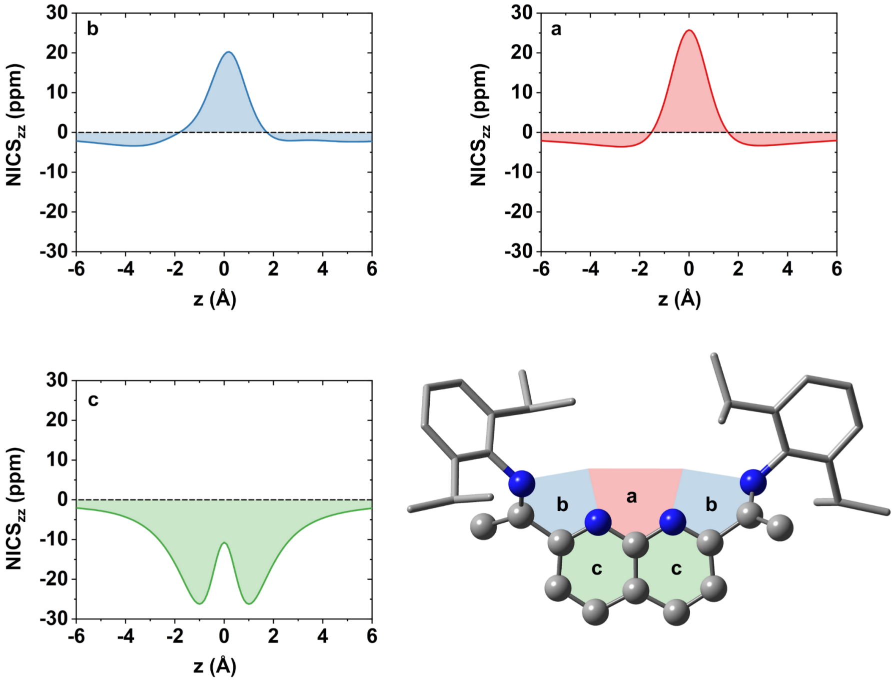


Fig. S21. NICS$_{zz}$-scan curves (M06-D3/def2-TZVP) of the rings of **1**. Additional curves for **1**, but in positions similar to those of the centroid of the additional rings of **3**, are also shown.

EDA-NOCV calculations. We investigated the bonding situation of **4** and the potential role of **3** as a six-electron donor using the energy decomposition analysis based on natural orbitals for chemical valence (EDA-NOCV)[35] method. These calculations were done at the BP86-D3(BJ)[36]/TZ2P level of theory. This functional was chosen for the EDA-NOCV computations due to its previous success in describing similar molecular systems.[37] Scalar relativistic effects were considered for the metals using the zeroth-order regular approximation (ZORA).[38] In the EDA-NOCV approach, the interaction energy (ΔE_{int}) between two fragments (herein the fragments **3** and $Fe_2(CO)_6$ in their singlet states but with corresponding structural conformations corresponding to those found in **4**) is decomposed into physically meaningful contributions, namely electrostatic ($\Delta E_{\mathrm{elstat}}$), Pauli repulsion ($\Delta E_{\mathrm{Pauli}}$), orbital interaction ($\Delta E_{\mathrm{orb}}$), and dispersion ($\Delta E_{\mathrm{disp}}$) energies. In turn, ΔE_{orb} is further decomposed into pairwise NOCV contributions $\Delta E_{\mathrm{orb}(i)}$. The EDA-NOCV calculations were performed using ADF 2019.[39] For illustrating the orbitals participating in the main ΔE_{orb} features of **4**, the MOs of $Fe_2(CO)_6$ are shown in Fig. S22.

Table S3. EDA-NOCV results (BP86-D3(BJ)/TZ2P) of **4** with fragments **3** and $Fe_2(CO)_6$ in their singlet states. Energy terms are given in kcal mol^{-1}. For ΔE_{disp}, $\Delta E_{\mathrm{elstat}}$, and ΔE_{orb}, the values in parentheses show the weight of each contribution with respect to the total attractive interaction. For the pairwise $\Delta E_{\mathrm{orb}(i)}$ terms, the values in parentheses show the weight of each contribution with respect to the total orbital interaction, ΔE_{orb}.

ΔE_{int}	–160.8
$\Delta E_{\mathrm{pauli}}$	562.6
ΔE_{disp}	–38.2 (5.3%)
$\Delta E_{\mathrm{elstat}}$	–362.6 (50.1%)
ΔE_{orb}	–322.7 (44.6%)
$\Delta E_{\mathrm{orb(1)}}$	–165.2 (51.2%)
$\Delta E_{\mathrm{orb(2)}}$	–60.1 (18.6%)
$\Delta E_{\mathrm{orb(3)}}$	–26.7 (8.3%)
$\Delta E_{\mathrm{orb(4)}}$	–19.2 (6.0%)
$\Delta E_{\mathrm{orb(rest)}}$	–51.5 (16.0%)

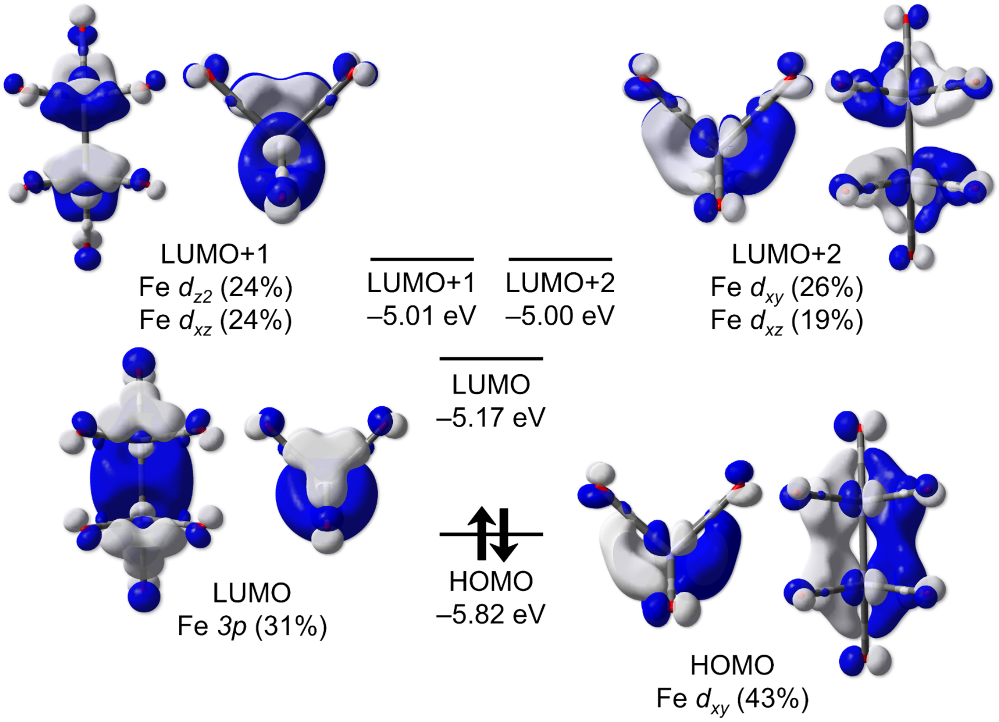


Fig. S22. Frontier Kohn–Sham molecular orbitals of $Fe_2(CO)_6$ and their corresponding orbital energies.

Cartesian coordinates

Coordinates in Ångstrøm, from optimisations at the M06-D3/def2-SVP level of theory.

1

C	3.402350980	1.100110578	-0.681267839
N	3.630866084	0.131977386	0.107199207
C	4.129011009	1.420372221	-1.953991199
H	3.411082103	1.535198668	-2.783880262
H	4.857841087	0.637554501	-2.211439545
H	4.666655342	2.381107789	-1.869982982
N	1.095033112	1.362744131	-0.150638869
N	-3.613305808	0.247645591	0.020439717
C	2.394363568	3.389107933	-0.262285358
H	3.373573269	3.844212523	-0.437840829
N	-1.157003117	1.418541787	0.305414167
C	2.236882170	1.977145783	-0.342465800
C	-0.001510292	2.095540573	0.147968687
C	0.061736876	3.516079696	0.290052993
C	1.306007731	4.152271227	0.071970581
H	1.380221406	5.240278241	0.173372965
C	-1.124560642	4.198965558	0.641620239
H	-1.104420087	5.287363618	0.761937137
C	-2.279104117	3.482027590	0.825830406
H	-3.211638813	3.981343864	1.101541447
C	-2.248603044	2.074055913	0.623330465
C	-4.460276982	1.662905103	1.855556468
H	-3.936903416	1.915412505	2.792332567
H	-5.191401690	0.864636090	2.050992013
H	-5.022198926	2.562859673	1.548977046
C	-3.490360333	1.253176643	0.786450210
C	-4.648195200	-0.686141297	0.125356135
C	-4.434361230	-1.827354829	0.930918832
C	-5.434365438	-2.801447846	0.959885434
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C	-6.603167430	-2.660718295	0.218163668
H	-7.373028833	-3.436691954	0.256678853
C	-6.791717518	-1.530662746	-0.569759741
H	-7.715504993	-1.429169206	-1.146537516
C	-5.824748226	-0.524956687	-0.634203587

C	-5.976182350	0.685722686	-1.532533435
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H	-7.465824191	1.925113372	-2.497906913
H	-8.084010641	1.054020245	-1.070124892
H	-7.810633282	0.191580710	-2.605439783
C	-5.087335258	0.538848376	-2.766692257
H	-5.148440339	1.433029167	-3.409744523
H	-5.410823083	-0.331685636	-3.363672457
H	-4.033376641	0.385977483	-2.486924220
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H	-2.911955910	-1.002887144	2.171877894
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H	-1.023925390	-2.354485008	1.285206487
H	-1.850418379	-1.463257603	-0.010522789
H	-2.149752803	-3.218962605	0.200112738
C	-3.180837172	-3.022068932	2.792442048
H	-2.244615826	-3.006608892	3.373061888
H	-3.283979941	-4.041168977	2.380352483
H	-4.016719490	-2.854618094	3.491677301
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C	5.969438357	-0.605107210	0.126890445
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C	6.438470537	-2.896815715	-0.532648112
H	7.163245667	-3.698621479	-0.700769714
C	5.083246110	-3.124445600	-0.747180157
H	4.749010658	-4.113474052	-1.075425253
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C	2.656441744	-2.333225461	-0.747134626
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C	2.214746791	-1.873390619	-2.134456595
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H	2.430819599	-0.806894576	-2.306090913
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H	5.861072805	1.525215797	0.172547130
C	6.002226497	0.806940249	2.178896224
H	6.270932385	1.784933980	2.612846122
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H	4.918239679	0.658931712	2.306554800
C	7.890682083	1.013395747	0.545168298
H	8.121996307	2.034055214	0.890578147
H	8.218723240	0.927001550	-0.503695677
H	8.507332067	0.325178651	1.148668803

2

Ge	1.450611000	-0.349979000	-0.196555000
Cl	1.273366000	-2.012761000	1.364346000
N	1.175280000	1.114504000	1.229841000
C	0.000201000	1.544896000	1.732061000
C	-0.000035000	2.503507000	2.822413000
C	1.231988000	2.971233000	3.314533000
H	1.229911000	3.697808000	4.131379000
C	2.415064000	2.513146000	2.773604000
H	3.369825000	2.875768000	3.158686000
C	2.396240000	1.578851000	1.741284000
C	3.556422000	1.066773000	1.113345000
C	4.935253000	1.563016000	1.381017000
H	4.982841000	2.310903000	2.180210000
H	5.357846000	2.009543000	0.464682000
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C	5.139738000	-1.452614000	-0.374570000
C	6.101922000	-1.877323000	-1.295325000
H	6.706056000	-2.761808000	-1.066311000
C	6.297147000	-1.205610000	-2.495525000
H	7.051819000	-1.558082000	-3.204603000
C	5.526728000	-0.088366000	-2.797545000
H	5.678825000	0.431023000	-3.749798000
C	4.556500000	0.382049000	-1.909609000
C	4.929788000	-2.230753000	0.907385000
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C	6.206508000	-2.318431000	1.736595000
H	6.011123000	-2.823914000	2.696488000

H	6.626064000	-1.322730000	1.959724000
H	6.991624000	-2.895288000	1.217894000
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H	4.158968000	-4.158415000	1.550234000
H	5.086607000	-4.225736000	0.027755000
H	3.427977000	-3.556493000	0.049330000
C	3.719078000	1.591346000	-2.283337000
H	3.114133000	1.878036000	-1.403270000
C	2.741016000	1.261167000	-3.408179000
H	2.087799000	0.413755000	-3.142320000
H	3.277007000	0.996430000	-4.336264000
H	2.086416000	2.121686000	-3.623466000
C	4.580309000	2.796109000	-2.646993000
H	3.949575000	3.682260000	-2.824888000
H	5.160268000	2.620023000	-3.568930000
H	5.298660000	3.046082000	-1.848325000
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C	-1.232007000	2.930575000	3.349383000
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C	-2.395056000	1.540454000	1.773276000
C	-3.555025000	0.969997000	1.196248000
C	-4.930494000	1.155956000	1.737363000
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H	-5.338702000	0.184288000	2.064297000
H	-5.607589000	1.517873000	0.946424000
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C	-4.372596000	-0.658740000	-0.387851000
C	-5.163840000	-0.208371000	-1.462176000
C	-6.123074000	-1.081718000	-1.982582000
H	-6.749878000	-0.749990000	-2.817359000
C	-6.286348000	-2.362250000	-1.468824000
H	-7.039585000	-3.031621000	-1.894436000
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H	-6.094391000	2.998509000	-2.424852000
H	-6.682538000	2.067933000	-1.023915000
H	-7.055410000	1.526678000	-2.674606000
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H	-3.829959000	-3.263684000	3.292418000
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Ge	-1.452226000	-0.127828000	-0.396445000
Cl	-1.311390000	1.632528000	-1.847910000

3

Ge	-1.472361000	-0.339192000	-0.031164000
C	3.555181000	1.527338000	0.070730000
N	3.299723000	0.188501000	0.013066000
Ge	1.472276000	-0.339414000	-0.026688000
C	4.960607000	2.020153000	0.102127000
H	5.019742000	3.114965000	0.138586000
H	5.523952000	1.681356000	-0.784924000
H	5.504964000	1.624077000	0.977445000
N	1.191800000	1.605398000	0.058693000
N	-3.299782000	0.188495000	0.013366000
C	2.414022000	3.735066000	0.155073000
H	3.368025000	4.265083000	0.180449000
N	-1.191890000	1.605389000	0.059175000
C	2.414910000	2.316853000	0.096060000
C	-0.000039000	2.301392000	0.088333000
C	-0.000039000	3.705547000	0.149324000
C	1.238564000	4.412292000	0.179816000
H	1.213327000	5.504924000	0.225324000
C	-1.238635000	4.412170000	0.182838000

H	-1.213383000	5.504778000	0.228919000
C	-2.414084000	3.734841000	0.160519000
H	-3.368084000	4.264735000	0.188516000
C	-2.414975000	2.316697000	0.099881000
C	-4.960654000	2.019664000	0.110709000
H	-5.019900000	3.114358000	0.150482000
H	-5.503102000	1.620982000	0.986037000
H	-5.525820000	1.683311000	-0.776118000
C	-3.555232000	1.527134000	0.075032000
C	-4.352200000	-0.769947000	-0.026475000
C	-4.844613000	-1.306529000	1.180780000
C	-5.839880000	-2.284952000	1.113129000
H	-6.227857000	-2.721515000	2.039477000
C	-6.341169000	-2.716889000	-0.109041000
H	-7.118086000	-3.486307000	-0.141511000
C	-5.853924000	-2.169040000	-1.289510000
H	-6.253403000	-2.514173000	-2.249011000
C	-4.858839000	-1.188007000	-1.274019000
C	-4.327749000	-0.627874000	-2.577903000
H	-3.726677000	0.267621000	-2.336893000
C	-5.440648000	-0.192874000	-3.524129000
H	-5.019068000	0.309029000	-4.410340000
H	-6.141541000	0.507008000	-3.039871000
H	-6.029337000	-1.051349000	-3.890283000
C	-3.400156000	-1.632800000	-3.255344000
H	-2.987123000	-1.221336000	-4.191436000
H	-3.940951000	-2.562647000	-3.504713000
H	-2.553540000	-1.905141000	-2.602783000
C	-4.293659000	-0.876677000	2.525248000
H	-3.715929000	0.052111000	2.368301000
C	-3.329609000	-1.927943000	3.068430000
H	-2.901628000	-1.611549000	4.034317000
H	-2.493966000	-2.108825000	2.371180000
H	-3.846069000	-2.891112000	3.226373000
C	-5.389385000	-0.569322000	3.538747000
H	-4.954413000	-0.150327000	4.460815000
H	-5.948266000	-1.474964000	3.830555000
H	-6.118631000	0.158746000	3.146707000
C	4.352221000	-0.769803000	-0.027923000
C	4.848118000	-1.304039000	1.178943000

C	5.843429000	-2.282353000	1.110368000
H	6.234069000	-2.717088000	2.036453000
C	6.341437000	-2.716434000	-0.112382000
H	7.118466000	-3.485707000	-0.145598000
C	5.850759000	-2.170903000	-1.292505000
H	6.247644000	-2.517764000	-2.252466000
C	4.855456000	-1.190102000	-1.276092000
C	4.320715000	-0.632593000	-2.579603000
H	3.718976000	0.262463000	-2.338649000
C	5.431045000	-0.197527000	-3.528847000
H	5.006942000	0.302383000	-4.414982000
H	6.020158000	-1.055800000	-3.894803000
H	6.132005000	0.504085000	-3.047211000
C	3.392990000	-1.639678000	-3.253618000
H	2.977270000	-1.229960000	-4.189287000
H	2.548249000	-1.912314000	-2.598780000
H	3.934468000	-2.569100000	-3.503077000
C	4.300649000	-0.871885000	2.524088000
H	3.723331000	0.057168000	2.367150000
C	3.337004000	-1.921652000	3.070900000
H	2.911618000	-1.603697000	4.037421000
H	3.853115000	-2.885016000	3.228807000
H	2.499538000	-2.102825000	2.375922000
C	5.398871000	-0.564151000	3.534763000
H	4.966318000	-0.143214000	4.457080000
H	6.128149000	0.162429000	3.140059000
H	5.957300000	-1.469994000	3.826834000

4

Ge	-1.380830000	0.138857000	-0.277022000
Ge	1.380813000	0.138862000	-0.277074000
Fe	-0.000038000	-1.456296000	-1.246126000
Fe	0.000055000	-0.711358000	1.373717000
C	-0.000012000	-0.946664000	-2.936626000
O	-0.000019000	-0.624210000	-4.044188000
C	-1.299306000	-2.661229000	-1.107477000
O	-2.097892000	-3.484899000	-0.994808000
C	-1.334676000	-1.775555000	1.894150000
O	-2.175630000	-2.486220000	2.233895000
C	-0.000034000	0.612309000	2.530530000

O	-0.000106000	1.482108000	3.291684000
C	1.334857000	-1.775390000	1.894286000
O	2.175850000	-2.485909000	2.234239000
C	1.299077000	-2.661376000	-1.107200000
O	2.097584000	-3.485095000	-0.994332000
N	-1.163944000	2.005755000	-0.860336000
C	0.000022000	2.648323000	-1.077211000
N	1.163990000	2.005710000	-0.860464000
C	2.390893000	2.654009000	-1.025209000
C	2.423273000	3.977599000	-1.467780000
H	3.387010000	4.474068000	-1.604152000
C	1.245590000	4.650648000	-1.721677000
H	1.255272000	5.688542000	-2.064705000
C	0.000033000	4.013620000	-1.521440000
C	-1.245518000	4.650720000	-1.721495000
H	-1.255192000	5.688621000	-2.064504000
C	-2.423199000	3.977729000	-1.467452000
H	-3.386925000	4.474251000	-1.603707000
C	-2.390835000	2.654123000	-1.024917000
C	-3.513235000	1.876917000	-0.678994000
N	-3.251632000	0.621956000	-0.292379000
C	-4.894766000	2.439349000	-0.710897000
H	-5.135333000	2.833757000	-1.711471000
H	-4.993102000	3.277140000	-0.000926000
H	-5.646283000	1.680846000	-0.451492000
C	3.513281000	1.876786000	-0.679276000
N	3.251632000	0.621887000	-0.292502000
C	4.894826000	2.439169000	-0.711235000
H	5.135275000	2.833786000	-1.711754000
H	5.646349000	1.680589000	-0.452069000
H	4.993270000	3.276807000	-0.001099000
C	-4.225381000	-0.245320000	0.296390000
C	-4.783577000	-1.279455000	-0.486568000
C	-5.686428000	-2.143407000	0.135815000
H	-6.131991000	-2.960815000	-0.435842000
C	-6.027256000	-1.988477000	1.475420000
H	-6.733632000	-2.681952000	1.940365000
C	-5.467310000	-0.963789000	2.223722000
H	-5.736216000	-0.855931000	3.279401000
C	-4.549207000	-0.074668000	1.658190000

C	-4.452774000	-1.425573000	-1.961802000
H	-3.364864000	-1.251303000	-2.075347000
C	-5.172547000	-0.374469000	-2.806278000
H	-4.986449000	-0.551534000	-3.878078000
H	-4.842160000	0.651188000	-2.587926000
H	-6.263701000	-0.425026000	-2.641788000
C	-4.762691000	-2.806676000	-2.520209000
H	-4.346060000	-2.901029000	-3.535683000
H	-5.851409000	-2.971807000	-2.603556000
H	-4.333453000	-3.610875000	-1.905652000
C	-3.961994000	1.026740000	2.522296000
H	-3.161176000	1.531333000	1.949559000
C	-3.324537000	0.491863000	3.800865000
H	-2.821011000	1.307452000	4.344691000
H	-2.573213000	-0.284198000	3.593886000
H	-4.077836000	0.056260000	4.478850000
C	-5.022792000	2.068244000	2.874295000
H	-4.578900000	2.898812000	3.447303000
H	-5.815250000	1.621663000	3.499325000
H	-5.513293000	2.490899000	1.983579000
C	4.225378000	-0.245356000	0.296318000
C	4.549297000	-0.074532000	1.658071000
C	5.467380000	-0.963629000	2.223677000
H	5.736341000	-0.855641000	3.279329000
C	6.027228000	-1.988446000	1.475482000
H	6.733595000	-2.681899000	1.940473000
C	5.686325000	-2.143530000	0.135911000
H	6.131834000	-2.961026000	-0.435660000
C	4.783482000	-1.279620000	-0.486538000
C	3.962228000	1.027046000	2.522055000
H	3.161569000	1.531771000	1.949216000
C	5.023218000	2.068357000	2.874050000
H	4.579444000	2.899117000	3.446874000
H	5.513928000	2.490760000	1.983324000
H	5.815498000	1.621698000	3.499246000
C	3.324556000	0.492384000	3.800607000
H	2.821218000	1.308122000	4.344380000
H	4.077702000	0.056597000	4.478645000
H	2.573024000	-0.283479000	3.593615000
C	4.452594000	-1.425903000	-1.961736000

H	3.364692000	-1.251561000	-2.075246000
C	4.762362000	-2.807113000	-2.519959000
H	4.345678000	-2.901578000	-3.535398000
H	4.333074000	-3.611182000	-1.905262000
H	5.851063000	-2.972358000	-2.603326000
C	5.172388000	-0.374969000	-2.806406000
H	4.986241000	-0.552202000	-3.878170000
H	6.263547000	-0.425540000	-2.641956000
H	4.842041000	0.650739000	-2.588221000

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