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Supporting Information

A Free Silanide from Nucleophilic Substitution at Silicon(II)

Léon Witteman,^[a] Tim Evers,^[a] Martin Lutz,^[b] and Marc-Etienne Moret^{*[a]}

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Experimental section

General

All reactions involving air-sensitive compounds were conducted under an N₂ atmosphere by using standard glovebox or Schlenk techniques. Acetonitrile and n-hexane were dried with an MBRAUN MB SPS-79 system, THF and DCM were distilled from benzophenone/Na or CaH₂, respectively, HMDSO was not pre-dried. All solvents were degassed by bubbling with N₂ for 30 min, and stored over molecular sieves in a glovebox. Deuterated acetonitrile, THF, and DCM were degassed by four freeze-pump-thaw cycles and stored over molecular sieves in a glovebox. Skatole, KH 30w% in mineral oil, 2,6-diisopropylaniline, HSiCl₃, KOtBu (≥97%), FeCl₂, Cu(MeCN)₄PF₆ were purchased from Sigma-Aldrich. Triethyl orthoformate, glyoxal 40w%, TMSCl, paraformaldehyde, 18-crown-6, CuCl were purchased from Acros. All commercially obtained chemicals were used as received, except for 18-crown-6 and CuCl. Drying of 18-crown-6 was done according to literature.¹ From CuCl, copper oxides and hydroxides were removed with hydrochloric acid as described in literature and the resulting solid was azeotropically dried with acetonitrile until $\nu(\text{C}\equiv\text{N})$ in IR disappeared.² All NMR measurements

were performed on a Varian VNMRS400 or Varian MRF400 spectrometer, shifts are reported relative to TMS with the residual solvent signal as internal standard.³ All DOSY spectra were recorded with a gradient pulse duration of 2 ms and a gradient delay of 30 ms. All NMR experiments involving air-sensitive compounds were conducted in J-Young NMR tubes under an N₂ atmosphere. IR spectra were recorded on a Perkin-Elmer Spectrum Two FT-IR spectrometer. ESI-MS measurements were performed on a Waters LCT Premier XE KE317 spectrometer. Elemental analysis was conducted by the Mikroanalytisches Laboratorium Kolbe. The compounds (tmim)₃,⁴ Idipp,⁵⁻⁷ Idipp-SiCl₂,⁸ were prepared according to reported procedures. The Idipp-SiCl₂ contained ~10% unidentified Idipp-containing impurities after purification.

X-ray crystal structure determinations

(tmim)Si⁻ K[18-crown-6]⁺ (1-K[18-c-6])

[C₁₄H₂₇KNO₆][C₂₈H₂₂N₃Si] · CH₃CN, Fw = 814.09, colourless block, 0.36 × 0.32 × 0.31 mm³, monoclinic, C2/m (no. 12), a = 24.8529(8), b = 14.0712(6), c = 12.6649(6) Å, β = 100.339(2) °, V = 4357.1(3) Å³, Z = 4, D_x = 1.241 g/cm³, μ = 0.20 mm⁻¹. 101617 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. The crystal appeared to be broken in two fragments. Consequently, two orientation matrices were used for the integration with the Eval15 software⁹ and the reflection data were stored in the HKLF5 format.¹⁴ A multiscan absorption correction and scaling was performed with TWINABS¹⁰ (correction range 0.69-0.75). 5285 Reflections were unique (R_{int} = 0.025), of which 4759 were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.¹¹ Least-squares refinement was performed with SHELXL-2014¹² against F² of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The crown ether and the non-coordinated acetonitrile were refined with a disorder model. Hydrogen atoms of the cation were located in difference Fourier maps and all other hydrogen atoms were introduced in calculated positions. All hydrogen atoms were refined with a riding model. 383 Parameters were refined with 300 restraints (distances, angles and displacement parameters of the disordered groups). R1/wR2 [I > 2σ(I)]: 0.0319 / 0.0898. R1/wR2 [all refl.]: 0.0358 / 0.0927. S = 1.023. Batch scale factor BASF = 0.3652(13). Residual electron density between -0.24 and 0.38 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.¹³

(tmim)Si-Si[Cl]←ldipp (2)

C₅₅H₅₈ClN₅Si₂ + disordered solvent, Fw = 880.69^[*], orange block, 0.45 × 0.32 × 0.12 mm³, monoclinic, P2₁/c (no. 14), a = 11.2805(5), b = 22.6490(13), c = 22.1298(13) Å, β = 91.097(2) °, V = 5652.9(5) Å³, Z = 4, D_x = 1.035 g/cm³^[*], μ = 0.15 mm⁻¹^[*]. 68885 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.61 Å⁻¹. The crystal appeared to be broken in many fragments. Only the orientation matrix of the major component was used for the integration with the Eval15 software⁹. A multiscan absorption correction and scaling was performed with SADABS¹⁰ (correction range 0.62-0.75). 10538 Reflections were unique (R_{int} = 0.065), of which 6886 were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.¹¹ Least-squares refinement was performed with SHELXL-2014¹² against F² of all reflections. The crystal structure contains large voids (1356 Å³ / unit cell) filled with severely disordered THF solvent molecules. Their contribution to the structure factors was secured by back-Fourier transformation using the SQUEEZE algorithm¹⁵ resulting in 325 electrons / unit cell. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 579 Parameters were refined with no restraints. R1/wR2 [I > 2σ(I)]: 0.0631 / 0.1740. R1/wR2 [all refl.]: 0.0961 / 0.1966. S = 1.036. Residual electron density between -0.42 and 0.49 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.¹³ [*] Derived values do not contain the contribution of the disordered THF solvent molecules.

Dimer of (tmim)SiCuCl⁻ K[18-crown-6]⁺ (3)

[C₁₂H₂₄KO₆]₂[C₅₆H₄₄Cl₂Cu₂N₆Si₂] · 4.5CH₂Cl₂, Fw = 2044.12, colourless block, 0.26 × 0.10 × 0.08 mm³, triclinic, P 1̄ (no. 2), a = 11.3775(4), b = 12.8622(5), c = 19.0019(7) Å, α = 106.992(1), β = 91.818(2), γ = 114.690(2) °, V = 2378.09(15) Å³, Z = 1, D_x = 1.427 g/cm³, μ = 0.93 mm⁻¹. 42675 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.65 Å⁻¹. The X-ray intensities were integrated with the Eval15 software⁹. A multiscan absorption correction and scaling was performed with SADABS¹⁰ (correction range 0.65-0.75). 10915 Reflections were unique (R_{int} = 0.059), of which 6898 were observed [I > 2σ(I)]. The structure was solved with Patterson superposition methods using SHELXT.¹¹ Least-squares refinement was performed with SHELXL-2016¹² against F² of all reflections. Diffuse electron density at the inversion center at 0,1/2,0 was modeled as disordered CH₂Cl₂ with partial occupancy. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 562 Parameters were refined with 45 restraints (distances, angles and displacement parameters of the dichloromethane molecules). R1/wR2 [I > 2σ(I)]: 0.0508 / 0.1138. R1/wR2 [all refl.]: 0.0997 / 0.1321. S = 1.041. Residual electron density between -0.73 and 1.07 e/Å³. Geometry calculations and checking for higher symmetry was performed with the PLATON program.¹³

(tmim)SiFeCl₂⁻ K[18-crown-6]⁺ (4)

[C₂₀H₄₀KO₈][C₃₂H₃₀Cl₂FeN₃O₅Si], Fw = 1075.05, colourless block, 0.36 × 0.16 × 0.08 mm³, triclinic, P 1̄ (no. 2), a = 13.9803(9), b = 20.5521(11), c = 22.1248(11) Å, α = 64.722(3), β = 75.222(2), γ = 76.287(2) °, V = 5498.1(5) Å³, Z = 4, D_x = 1.299 g/cm³, μ = 0.52 mm⁻¹. 98856 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of (sin θ/λ)_{max} = 0.59 Å⁻¹. The X-ray intensities were integrated with the Eval15 software⁹. A multiscan absorption correction and scaling was performed

with SADABS¹⁰ (correction range 0.54-0.75). 19386 Reflections were unique ($R_{\text{int}} = 0.062$), of which 12712 were observed [$I > 2\sigma(I)$]. The structure was solved with Direct Methods using SHELXS-97.¹⁶ Least-squares refinement was performed with SHELXL-2016¹² against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. Two of potassium coordinated THF molecules were refined with a disorder model. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 1323 Parameters were refined with 579 restraints (distances, angles and displacement parameters of the THF molecules). $R1/wR2$ [$I > 2\sigma(I)$]: 0.0635 / 0.1635. $R1/wR2$ [all refl.]: 0.1045 / 0.1903. $S = 1.020$. Residual electron density between -0.55 and $1.69 \text{ e}/\text{\AA}^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.¹³

(tmim)SiCu(NCCH₃)₃ (3a)

$\text{C}_{34}\text{H}_{31}\text{CuN}_6\text{Si} \cdot 3.5\text{CH}_3\text{CN}$, $F_w = 758.96$, colourless block, $0.14 \times 0.13 \times 0.11 \text{ mm}^3$, monoclinic, $I2/m$ (no. 12), $a = 14.3323(7)$, $b = 13.9735(6)$, $c = 20.1085(10) \text{ \AA}$, $\beta = 98.613(2)^\circ$, $V = 3981.8(3) \text{ \AA}^3$, $Z = 4$, $D_x = 1.266 \text{ g/cm}^3$, $\mu = 0.62 \text{ mm}^{-1}$. 43775 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator ($\lambda = 0.71073 \text{ \AA}$) at a temperature of $150(2) \text{ K}$ up to a resolution of $(\sin \theta/\lambda)_{\text{max}} = 0.65 \text{ \AA}^{-1}$. The X-ray intensities were integrated with the Eval15 software⁹. A multiscan absorption correction and scaling was performed with SADABS¹⁰ (correction range 0.69-0.75). 4766 Reflections were unique ($R_{\text{int}} = 0.049$), of which 3684 were observed [$I > 2\sigma(I)$]. The structure was solved with Patterson superposition methods using SHELXT.¹¹ Least-squares refinement was performed with SHELXL-2017¹² against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. The non-coordinated acetonitrile molecules were refined with a disorder model. Hydrogen atoms were introduced in calculated positions and refined with a riding model. 293 Parameters were refined with 99 restraints (distances, angles and displacement parameters of the acetonitrile molecules). $R1/wR2$ [$I > 2\sigma(I)$]: 0.0376 / 0.0869. $R1/wR2$ [all refl.]: 0.0568 / 0.0950. $S = 1.051$. Residual electron density between -0.26 and $0.38 \text{ e}/\text{\AA}^3$. Geometry calculations and checking for higher symmetry was performed with the PLATON program.¹³

Synthesis of (tmim)Na₃

A solution of (tmim)H₃ (4.95 g, 12.3 mmol) in THF (10 mL) was added to pre-washed (hexane 3 x 5 mL & THF 5 mL) NaH (60% in oil, 2.07 g, 52 mmol) under THF (20 mL) over 15 minutes and stirred for 2.75h. The excess NaH was removed by filtration and the orange (green luminescent) filtrate was freed of solvent *in vacuo*, yielding a yellow powder (8.46 g, quantitative). Analysis by ¹H NMR showed only (tmim)Na₃ and THF (~30 w%). A titration with HCl (0.10 M in H₂O) on a sample (100.4 mg) in a mixture of THF (4mL) and water (1 mL) was performed to determine the base content, which was consistent with 68.4 w% (tmim)Na₃. ¹H NMR (400 MHz, Acetonitrile-*d*₃, 25 °C): δ 7.19 (m, 6H, ArH), 6.62 (m, 6H, ArH), 6.25 (s, 1H, R₃CH), 2.41 ppm (s, 9H, CH₃). ¹³C NMR (101 MHz, Acetonitrile-*d*₃, 25 °C): δ = 151.4, 146.0, 132.4, 116.6, 116.2, 115.3, 114.8, 101.8, 37.7 (R₃CH), 10.1 ppm (CH₃).

Reaction of (tmim)Na₃ with Idipp·SiCl₂

A -79°C solution of Idipp·SiCl₂ (57.6 mg, 0.118 mmol) in THF (2 mL) was added to a pre-cooled solution of (tmim)Na₃ (75.0 mg, 27 w% THF, 0.117 mmol) in THF (3 mL). The mixture was stirred at r.t. for 16h. Filtration and removal of the solvent *in vacuo* afforded 116.7 mg of a complex mixture containing at least (tmim)Na₃, Idipp and Idipp·SiCl₂. This mixture was redissolved in THF (4 mL) and stirred for another 16h. Crystals suitable for x-ray crystallography were grown from this solution by vapor diffusion with hexane.

Synthesis of (tmim)K₃

A solution of (tmim)H₃ (2.00 g, 4.96 mmol) in THF (10 mL) was added to pre-washed (hexane 3 x 5 mL) KH (2.36g, 30 w% in oil, 18 mmol) under THF (2 mL) and stirred for 1.75h. The excess KH was removed by filtration and the orange solution, which exhibits green luminescence, was freed of solvent *in vacuo*, yielding a yellow powder (3.08g, 4.76 mmol, 96%). A titration with HCl (0.01 M in H₂O) on a sample (duplo; 11.1 mg & 13.6 mg) in a mixture of THF (4mL) and water (1 mL) was performed to determine the content (tmim)K₃ (81.2 ± 1.5 w%). ¹H NMR (400 MHz, CD₃CN + C₄H₈O 1:1, 25 °C): δ 7.23 (d, ³J_{HH} = 7.8 Hz, 1H, indole-H7), 7.18 (d, ³J_{HH} = 7.9 Hz, 1H, indole-H4), 6.67 (ddd, ³J_{HH} = 8.0 Hz, ³J_{HH} = 6.7 Hz, ⁴J_{HH} = 1.4 Hz, 1H, indole-H5), 6.60 (ddd, ³J_{HH} = 7.8 Hz, ³J_{HH} = 6.7 Hz, ⁴J_{HH} = 1.2 Hz, 1H, indole-H6), 6.17 (s, 1H, R₃CH), 2.24 ppm (s, 3H, CH₃); ¹³C NMR (101 MHz, CD₃CN + C₄H₈O 1:1, 25 °C): δ = 153.2, 146.2, 132.1, 116.5, 116.4, 115.3, 114.2, 101.1, 39.1, 10.0 ppm

Synthesis of (tmim)Si⁻ K[18-crown-6]⁺ (1-K[18-c-6])

A -79 °C solution of Idipp-SiCl₂ (700.6 mg, 90% purity, 1.293 mmol) in THF (15 mL) was added to a pre-cooled yellow suspension with green luminescence of (tmim)K₃ (674.5 mg, 10 w% THF, 1.172 mmol) and 18-crown-6 (310.1 mg, 1.173 mmol) in THF (45 mL) and stirred for 30 min. Upon warming to r.t. over 30 min the suspension became less turbid, less luminescent, and darker orange. From this moment, immediate work-up is necessary to prevent formation of by-products. Following filtration and evaporation the solid was suspended in THF (10 mL) and precipitated and washed with hexane (30 mL + 10 mL). The orange solid was washed with acetonitrile (16 mL in 4 portions) and the remaining white powder was extracted in acetonitrile (120 mL), leaving a small amount of unidentified white residue. Evaporation of the filtrate yielded a white solid (468.9 mg, 0.641 mmol, 55%). Crystals suitable for X-ray crystallography were grown from a concentrated acetonitrile solution at -35 °C. ¹H NMR (400 MHz, CD₃CN, 25 °C): δ 7.71 ('dt', ³J_{HH} = 8.1 Hz, ⁴J_{HH} = 1.0 Hz, ⁵J_{HH} = 1.0 Hz, 3H, indole-H7), 7.30 (ddd, ³J_{HH} = 7.7 Hz, ⁴J_{HH} = 1.3 Hz, ⁵J_{HH} = 0.8 Hz, 3H, indole-H4), 6.95 (ddd, ³J_{HH} = 8.2 Hz, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.3 Hz, 3H, indole-H6), 6.85 (ddd, ³J_{HH} = 7.9 Hz, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.1 Hz, 3H, indole-H5), 5.92 (s, 1H, R₃CH), 3.54 (s, 34H, K[18-crown-6]⁺), 2.40 ppm (s, 9H, CH₃); ¹³C NMR (101 MHz, CD₃CN, 25 °C): δ = 142.2, 141.8, 131.2, 120.5, 118.7, 118.2, 112.1, 104.3, 70.9, 33.8, 8.7 ppm ²⁹Si NMR (79 MHz, C₄H₈O, 25 °C): δ -48.10 ppm; DOSY NMR (400 MHz, CD₃CN, 25 °C): D = 12.5 ((tmim)Si⁻), 14.7 (K[18-crown-6]⁺) × 10⁻¹⁸ m²/s; Elemental analysis calcd (%) for C₄₀H₄₆N₃O₆SiK: C 65.63, H 6.33, N 5.74; found: C 64.90, H 6.19, N 6.41.

Synthesis of (tmim)SiCuCl⁻ K[18-crown-6]⁺ (3)

THF (2 mL) was added to a solid mixture of 1-K[18-c-6] (31.4 mg, 0.0429 mmol) and CuCl (4.3 mg, 0.043 mmol) and stirred for 30 minutes. The resulting grey suspension was filtered, washed with THF (3 × 1 mL) and the grey solid extracted in DCM (5 × 1 mL). Drying *in vacuo* afforded complex **3** as a white powder (31.2 mg, 0.0375 mmol, 87.4%) Crystals suitable for X-ray crystallography were grown by vapor diffusion of Et₂O into a concentrated solution of **3** in DCM at room temperature. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C): δ 7.97 (d, ³J_{HH} = 8.1, 3H, indole-H7), 7.36 (d, ³J_{HH} = 7.7 Hz, 3H, indole-H4), 7.06 ('t', ³J_{HH} = 7.6 Hz, 3H, indole-H6), 6.94 ('t', ³J_{HH} = 7.4 Hz, 3H, indole-H5), 5.92 (s, 1H, R₃CH), 3.31 (s, 26H, K[18-crown-6]⁺), 2.40 (s, 9H, CH₃); ¹³C NMR (101 MHz, CD₂Cl₂, 25 °C) δ = 140.4, 140.0, 131.0, 120.9, 118.6, 112.6, 105.7, 70.3, 33.0, 8.7 ppm; ²⁹Si NMR could not be measured due to large quadrupole moment of the adjacent copper atom (Q_{exp}(⁶³Cu) = -21.1(4) e fm², Q_{exp}(⁶⁵Cu) = -19.5(4) e fm²);¹⁷ DOSY NMR (400 MHz, CD₂Cl₂, 25 °C): D = 9.3 ((tmim)SiCuCl⁻), 9.9 (K[18-crown-6]⁺) × 10⁻¹⁸ m²/s; ESI-MS⁻ C₂₈H₂₂N₃SiCuCl⁻ m/z calc = 526.0568; found = 526.0645.

Generation of (tmim)SiCu(NCCH₃)₃ in solution from **3** (**3a**)

A solid sample (~10 mg, ~12 μmol) of **3** was dissolved in CD₃CN (~0.5 mL). ¹H NMR (400 MHz, CD₃CN, 25 °C): δ 7.95 (d, ³J_{HH} = 8.2 Hz, 3H, indole-*H7*), 7.35 (d, ³J_{HH} = 7.8 Hz, 3H, indole-*H4*), 7.04 (br t, 3H, indole-*H6*), 6.94 (t, ³J_{HH} = 7.4 Hz, 3H, indole-*H5*), 6.00 (s, 1H, R₃CH), 3.54 (s, 27H, K[18-crown-6]⁺), 2.40 (s, 9H, CH₃);

Note: solubility of KCl in CH₃CN in pure acetonitrile and acetonitrile containing 0.15 M 18-crown-6 at 25 °C was reported by Liotta *et al.*¹⁸ Pure: 2.43*10⁻⁴, 0.15 M 18-crown-6: 5.55*10⁻² mol/L == 28 μmol/0.5 mL. That means that ratio K[18-c-6]⁺:18-c-6 = 1:3. Present solution is ~10 mg/0.5 mL == 12 μmol/0.5 mL CD₃CN, which is well within solubility.

Synthesis of (tmim)SiCu(NCCH₃)₃ from Cu(NCCH₃)₄PF₆ (**3a**)

A solution of Cu(NCCH₃)₄PF₆ (15.2 mg, 0.0408 mmol) in CH₃CN (1 mL) was added to a suspension of **1**-K[18-c-6] (30.1 mg, 0.0411 mmol) in CH₃CN (1 mL), and the remaining Cu(NCCH₃)₄PF₆ solution was transferred using CH₃CN (1 mL). The suspension immediately dissolved fully and produced a coarse, white and a fine, brown precipitate within 5 minutes. Agitation and decantation of the liquid provided clean white solid, which was dried *in vacuo* (8.4 mg, 0.0137 mmol, 33%), more crops could be obtained by precipitation from the mother liquor. Crystals suitable for X-ray crystallography were grown by storing a concentrated CH₃CN solution at -35 °C for 16h. ¹H NMR (400 MHz, CD₂Cl₂, 25 °C) δ 7.75 (d, ³J_{HH} = 8.1 Hz, 3H, indole-*H7*), 7.39 (d, ³J_{HH} = 7.7 Hz, 3H, indole-*H4*), 7.06 ('t', ³J_{HH} = 7.5 Hz, 3H, indole-*H6*), 6.97 ('t', ³J_{HH} = 7.4 Hz, 3H, indole-*H5*), 5.93 (s, 1H, R₃CH), 2.41 (s, 9H, CH₃), 2.14 (s, 9H, CH₃CN). ¹H NMR (400 MHz, CD₃CN, 25 °C) δ 7.96 ('dt', ³J_{HH} = 8.2 Hz, ⁴J_{HH} = 0.9 Hz, ⁵J_{HH} = 0.9 Hz, 3H, indole-*H7*), 7.34 ('dt', ³J_{HH} = 7.9 Hz, ⁴J_{HH} = 1.0 Hz, ⁵J_{HH} = 1.0 Hz, 3H, indole-*H4*), 7.04 (ddd, ³J_{HH} = 8.2 Hz, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.3 Hz, 3H, indole-*H6*), 6.93 (ddd, ³J_{HH} = 8.0 Hz, ³J_{HH} = 7.0 Hz, ⁴J_{HH} = 1.1 Hz, 3H, indole-*H5*), 5.97 (s, 1H, R₃CH), 2.39 (s, 9H, CH₃), 1.96 (s, CH₃CN); ¹³C NMR (101 MHz, CD₂Cl₂, 25 °C) δ = 140.2, 139.9, 131.2, 120.5, 118.9, 118.5, 111.7, 106.3, 33.0, 8.7, 2.4 ppm ;DOSY NMR (400 MHz, CD₂Cl₂, 25 °C): D = 9.5 × 10⁻¹⁸ m²/s; No satisfactory elemental analysis could be obtained because of the MeCN solvation.

Synthesis of (tmim)SiFeCl₂⁻ K[18-crown-6]⁺ (**4**)

A suspension of **1**-K[18-c-6] (70.1 mg, 0.0958 mmol) in THF (4 mL) was added to a suspension of FeCl₂ (12.1 mg, 0.0955 mmol) in THF (2 mL). Over 60 min the solution became almost clear yellow. The mixture was filtered, concentrated to 2 mL and Et₂O was added until nucleation was observed. At room temperature, over 30 minutes a microcrystalline solid appeared, after which the solution was stored at -35 °C for 16h, filtration, washing with THF (0.2 mL, -35 °C) and extracting in THF (3 × 0.5 mL) afforded a pale yellow/green solid after removal of the solvent *in vacuo* (48.1 mg, 19w% THF, 0.0499 mmol, 52%). Crystals suitable for X-ray crystallography were grown by vapor diffusion of HMDSO into a THF solution. ¹H NMR (400 MHz, C₄H₈O, 25 °C) δ 26.97 (br s, 3H*, Indole-*H*), 9.96 (br s, 3H*, Indole-*H*), 8.66 (br s, 3H*, Indole-*H*), 6.99 (br s, 3H*, Indole-*H*), 4.36 (br s, 1H*, R₃CH), 4.08 (br s, 26H*, K⁺[18-crown-6]), 3.61 (br s, 10H*, THF), 1.73 (br s, 10H*, THF), 1.33 (br s, 9H*, CH₃). ¹³C NMR (101 MHz, C₄H₈O, 25 °C) δ = 149.0 (Indole-C), 145.2 (Indole-C), 137.6 (Indole-C), 134.5 (Indole-CH), 128.0 (Indole-CH), 126.5, 116.9 (Indole-CH), 76.2 (K⁺[18-crown-6]), 56.8 (R₃CH), 32.1 ppm (CH₃). *integrals obtained by peak deconvolution. No satisfactory elemental analysis could be obtained due to the high reactivity of **4**.

Computational studies

Computational methods

Calculations were performed using Gaussian09, Revision D.01.¹⁹ All the treated structures were optimized using the TPSS functional²⁰ with the TZVP basis set (Mo: SDD incl. ECP), except for the LCpIrCO complexes. The absence of negative eigenvalues was confirmed for all structures. On the optimized geometries, NMR calculations were conducted as single point with the TPSS functional and IGLO-III basis set (Li: def2TZVP; Mo: SDD incl. ECP). In accordance with Gusev et al.²¹, the CEP calculations were performed using the MPW1PW91 functional with the basis sets SDD (associated with ECP) for Ir (and Mo) and 6-311+G(d,p) for all other atoms. Tight geometry optimizations and the ultrafine integration grid (int=ultrafine) were employed for all Ir-complexes. NBO analysis was done with the NBO6 program,²² the amount of *s*-character for **4** was obtained by averaging over α and β spin. The cartesian coordinates of the optimized structures can be obtained as ESI from <http://pubs.acs.org>

NMR (tmim)Si⁻ and related silanides.

The ²⁹Si shifts are reported relative to TMS, calculated using the same method. The method was benchmarked with the known silanides E(Pz)₃Si⁻ (E=Li or Mo(CO)₃)^{23,24} and showed a deviation of ± 2.4 ppm. The calculated $\delta(^{29}\text{Si})$ of (tmim)Si⁻ is very close to the observed one; $\delta(\text{calc}) = -49.3$ ppm, $\delta(\text{obs}) = -48.1$ ppm.

Inclusion of a solvent model in the NMR calculation (SCRF=acetonitrile) showed a slightly better correlation with the measured values for both E(Pz)₃Si⁻ silanides (± 1.3 vs ± 2.4 ppm), but not for the (tmim)Si⁻ silanide ($\Delta\delta = 1.2$ ppm vs -1.5 ppm)

Table S1: Calculated and measured chemical shifts of selected silanides, relative to TMS.

	$\delta\text{Si calc'd}$	$\delta\text{Si obs'd}$	deviation	
LiPz3Si	-37.0	-35.0	2.0	
MoPz3Si ⁻	-36.2	-38.6	-2.4	
(tmim)Si ⁻	-49.3	-48.1	1.2	
LiPz3Si	-36.3	-35.0	1.3	SCRF=MeCN
MoPz3Si ⁻	-37.3	-38.6	-1.3	SCRF=MeCN
(tmim)Si ⁻	-46.6	-48.1	-1.5	SCRF=MeCN

Tolman cone angle

As described by Tolman²⁵ the cone angle can be constructed from the half angles according to the equation $\theta = \frac{2}{3} \sum_{i=1}^3 \frac{\theta_i}{2}$. Using this equation and the measured half angles ($\frac{\theta_i}{2} = 97.3^\circ$) in (tmim)SiNi(CO)₃⁻ the cone angle is 194.6° , which is essentially the same as that of the published²⁶ (o-tol)₃P ($194(6)^\circ$).

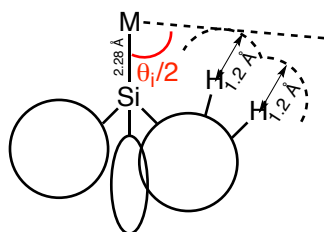


Figure S1: Definition of half angle in (tmim)SiNi(CO)₃⁻

Tolman electronic parameter

The computational analogue of the Tolman electronic parameters (CEP) have been calculated for a series of neutral 2 e⁻ donor ligands (bound atoms: C, P, N, O, Xe) by Gusev et al.²¹ using an LCpIrCO complex, which they argue to be more generally applicable than the Ni(CO)₃ complexes often used in practice. The data of Perrin et al.²⁷ showed that the correlation between CEP and TEP is very good for a total of 68 cationic, neutral, and anionic ligands in LNi(CO)₃, showing the applicability of the method to charged ligands. (tmim)Si⁻ was compared to related silanides and weakly donating NHSi's, selected on PA (σ-donor strength) according to Benedek et al. (shown in Table 2 in the main text).^{28,29}

X-ray crystal structures

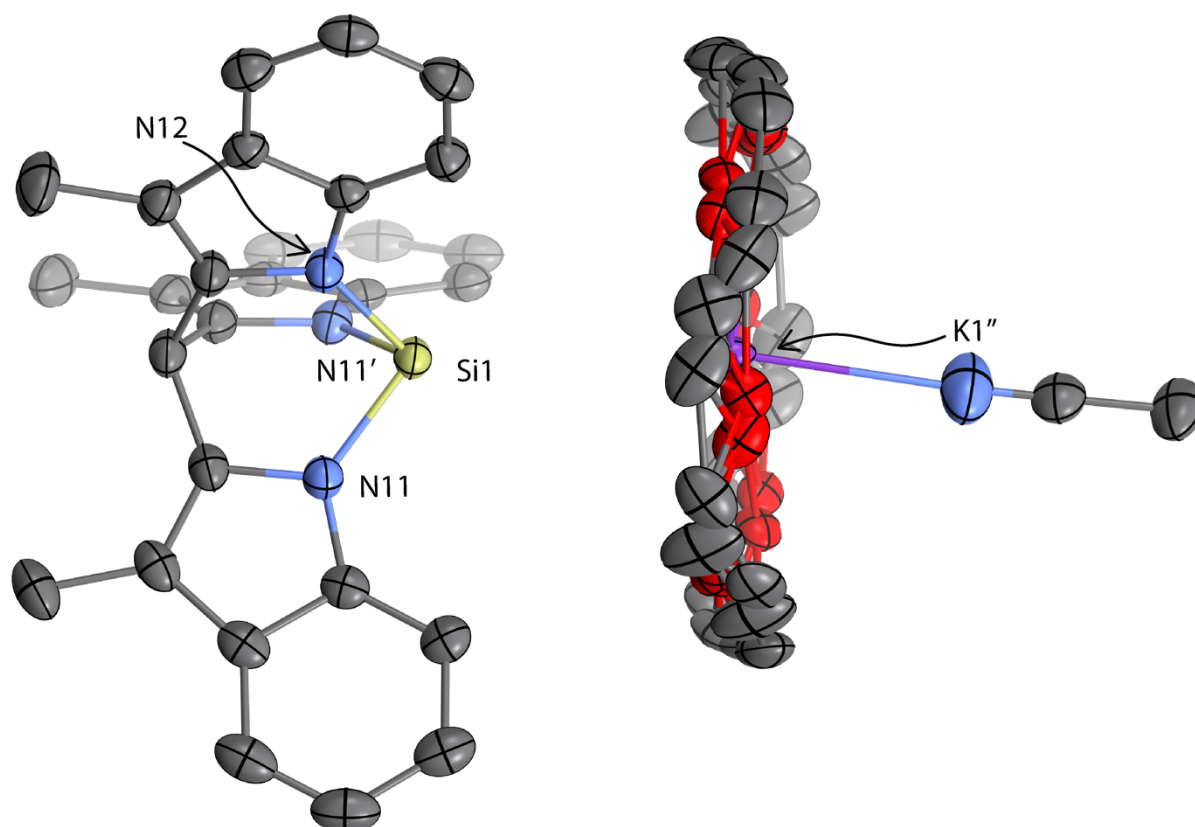


Figure S2: Molecular structure of **1** in the crystal. Ellipsoids are drawn at 50% probability. Hydrogen atoms and co-crystallized non-coordinated acetonitrile omitted for clarity. Symmetry code ' = $x, 1-y, z$; '' = $0.5-x, y+0.5, 1-z$. Selected bond distances (Å) and angles (°): Si1–K1'' 3.8807(6), N11–Si1 1.8421(10), N12–Si1 1.8405(14), N11–Si1–N11' 90.30(6), N11–Si1–N12 91.14(4).

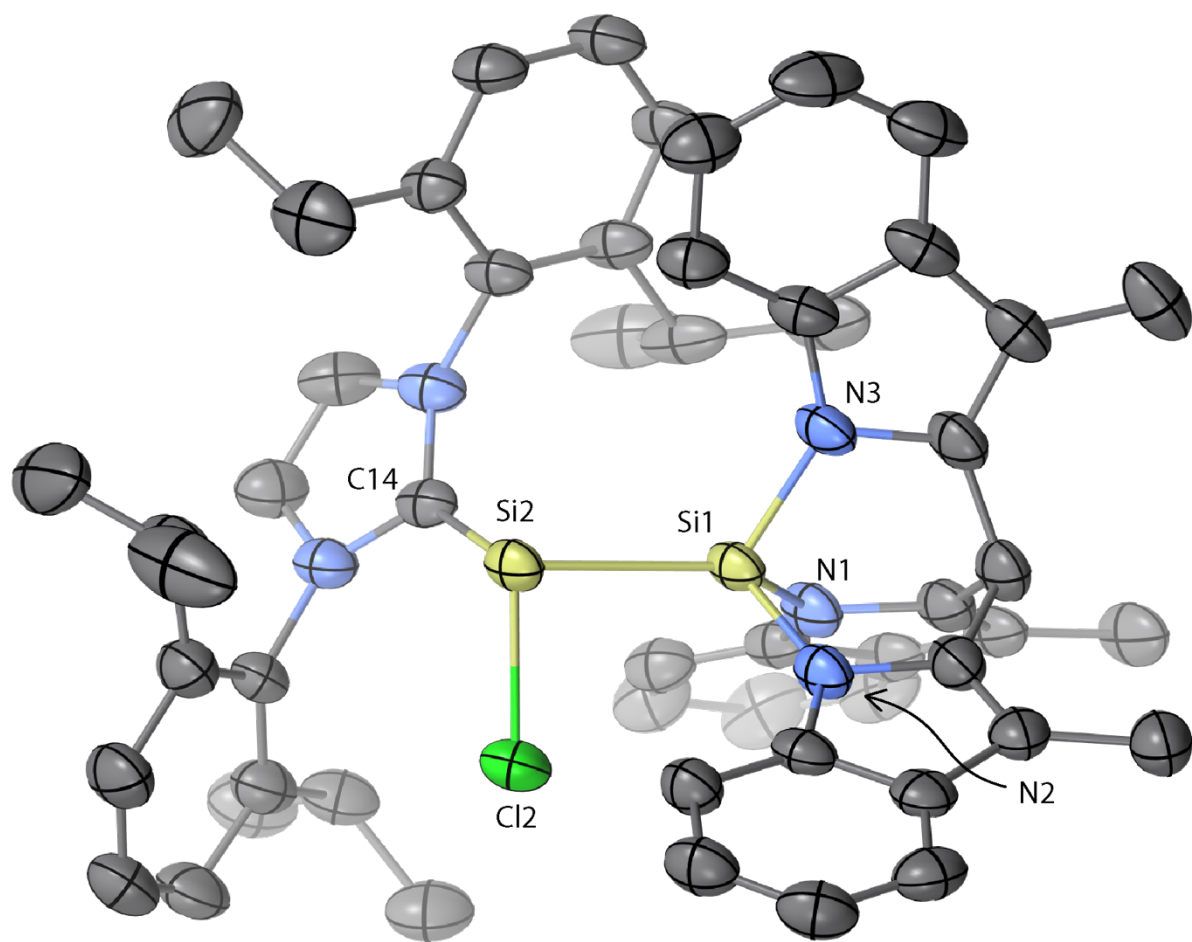


Figure S3: Molecular structure of **2** in the crystal. Severely disordered THF solvent molecules are omitted in the drawing. Selected bond distances (\AA) and angles ($^\circ$): Si1-Si2 2.3732(11), Si2-Cl2 2.1678(11), C14-Si2 1.967(3), N1-Si1 1.769(3), N2-Si1 1.783(3), N3-Si1 1.770(3), N1-Si-N2 96.25(12), N2-Si-N3 95.61(13), N3-Si-N1 99.29(12), Si1-Si2-C14 107.98(9), Si1-Si2-Cl2 86.86(4), Cl2-Si2-C14 97.55(9).

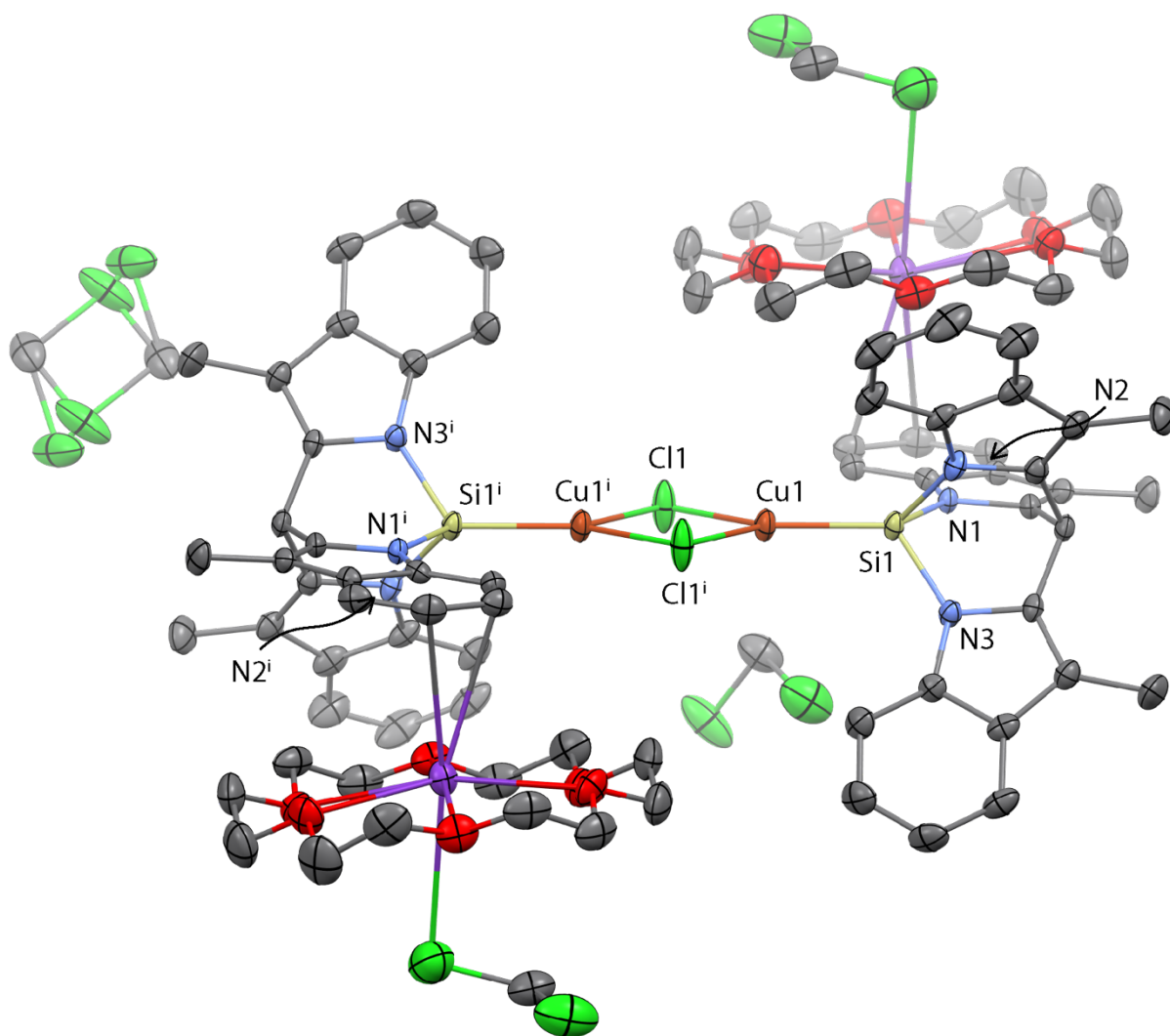


Figure S4: Molecular structure of the dimer of **3** in the crystal. Ellipsoids are drawn at 50% probability. Hydrogen atoms omitted for clarity. Symmetry code $i = -x, -y, -z$. Selected bond distances (Å) and angles (°): Si1–Cu1 2.1905(9), N1–Si1 1.799(2), N2–Si1 1.805(3), N3–Si1 1.798(3), Cu1–Cl1 2.3126(9), Cu1–Cl1 i 2.3155(9), N1–Si1–N2 93.62(11), N2–Si1–N3 93.41(12), N3–Si1–N1 93.74(11), Cl1–Cu1–Cl1 i 94.45(3), Cu1–Cl1–Cu1 i 85.55(3), Si1–Cu1–Cl1 134.78(3), Si1–Cu1–Cl1 i 130.77(3).

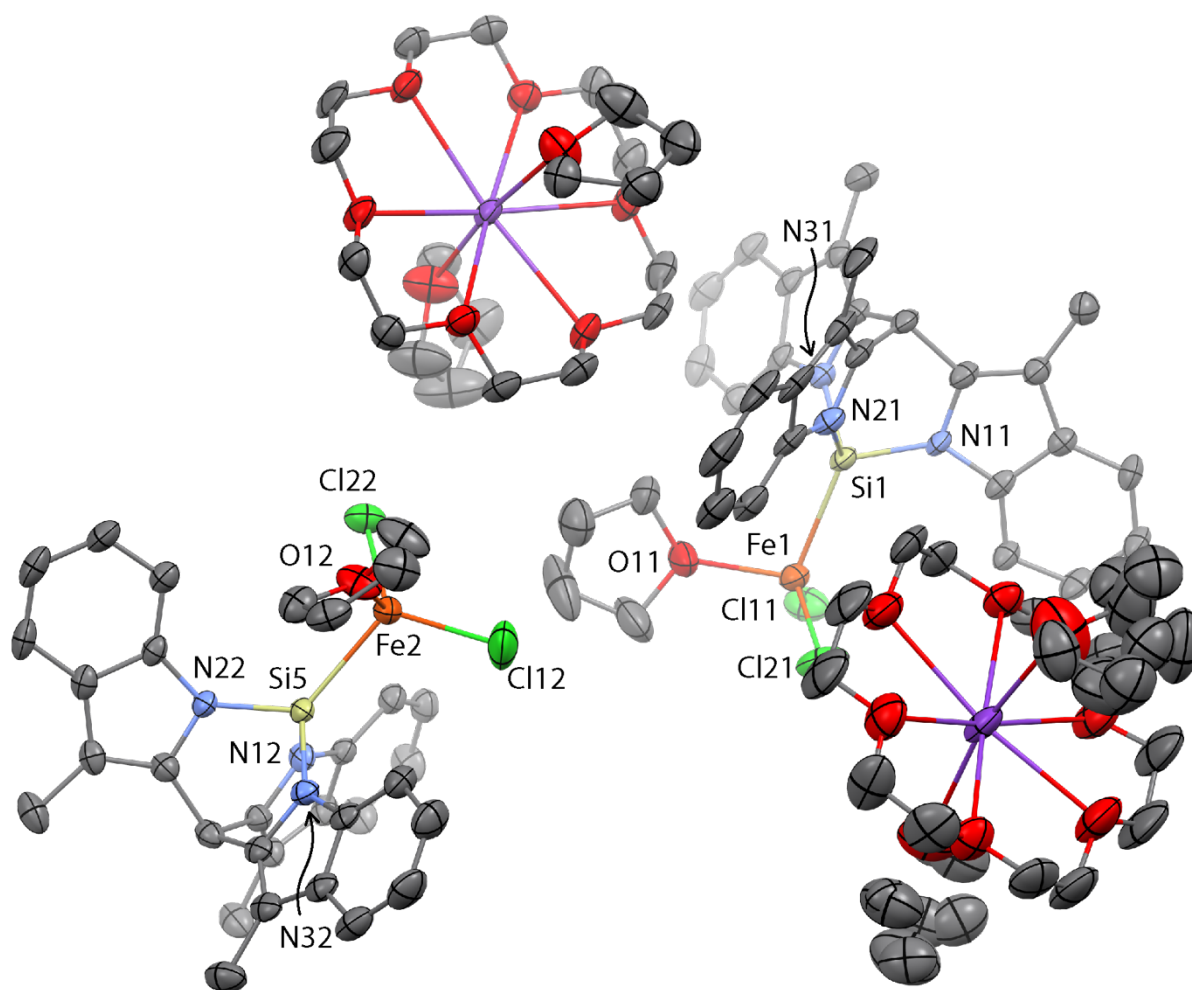


Figure S5: Molecular structure of **4** in the crystal. Ellipsoids are drawn at 50% probability. Two distinct molecules are present in the asymmetric unit. Hydrogen atoms omitted for clarity. Selected bond distances (Å) and angles (°): Unit 1: Si1–Fe1 2.4482(12), Cl11–Fe1 2.2281(13), Cl21–Fe1 2.2427(14), N11–Si1 1.789(3), N21–Si1 1.808(3), N31–Si1 1.806(3), Cl11–Fe1–Cl21 118.00(5), Cl11–Fe1–Si1 114.67(5), Cl21–Fe1–Si1 111.24(5), N11–Si1–N21 94.05(16), N21–Si1–N31 94.55(15), N31–Si1–N11 94.28(15). Unit 2: Si5–Fe2 2.4589(12), Cl12–Fe2 2.2479(15), Cl22–Fe2 2.2325(13), N12–Si5 1.792(3), N22–Si5 1.801(3), N32–Si5 1.810(3), Cl12–Fe2–Cl22 119.01(6), Cl12–Fe2–Si5 114.46(5), Cl22–Fe2–Si5 110.96(5), N12–Si5–N22 92.54(15), N22–Si5–N32 94.49(15), N32–Si5–N12 94.80(15).

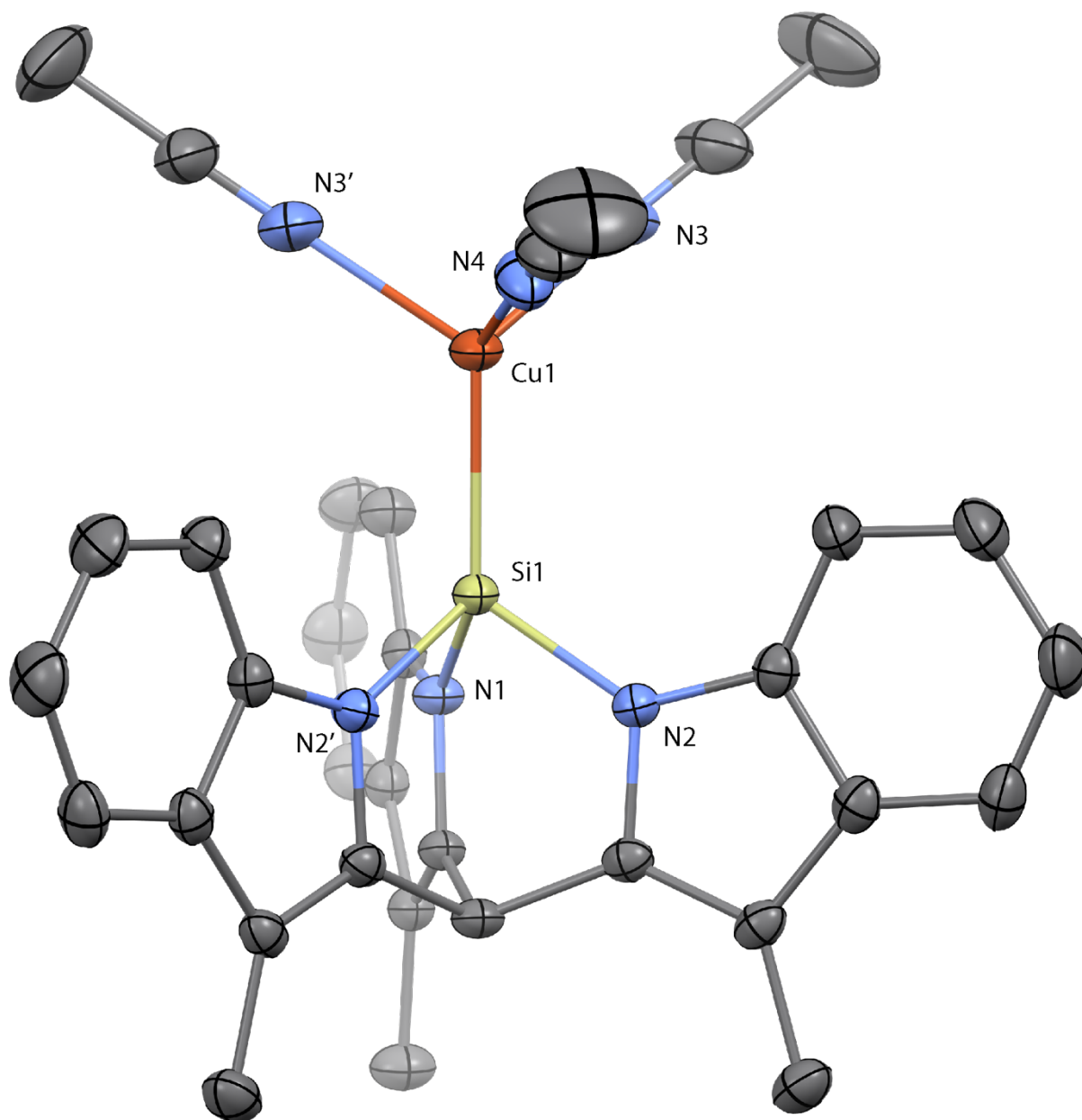


Figure S6: Molecular structure of **3a** in the crystal. Ellipsoids are drawn at 50% probability. Hydrogen atoms and co-crystallized non-coordinated acetonitrile omitted for clarity. Symmetry code $' = x, -y, z$. Selected bond distances (Å) and angles (°): Si1–Cu1 2.2106(7), N1–Si1 1.805(2), N2–Si1 1.8069(15), N1–Si1–N2 93.30(7), N2–Si1–N2' 92.14(10).

Analytical data
Compound 1

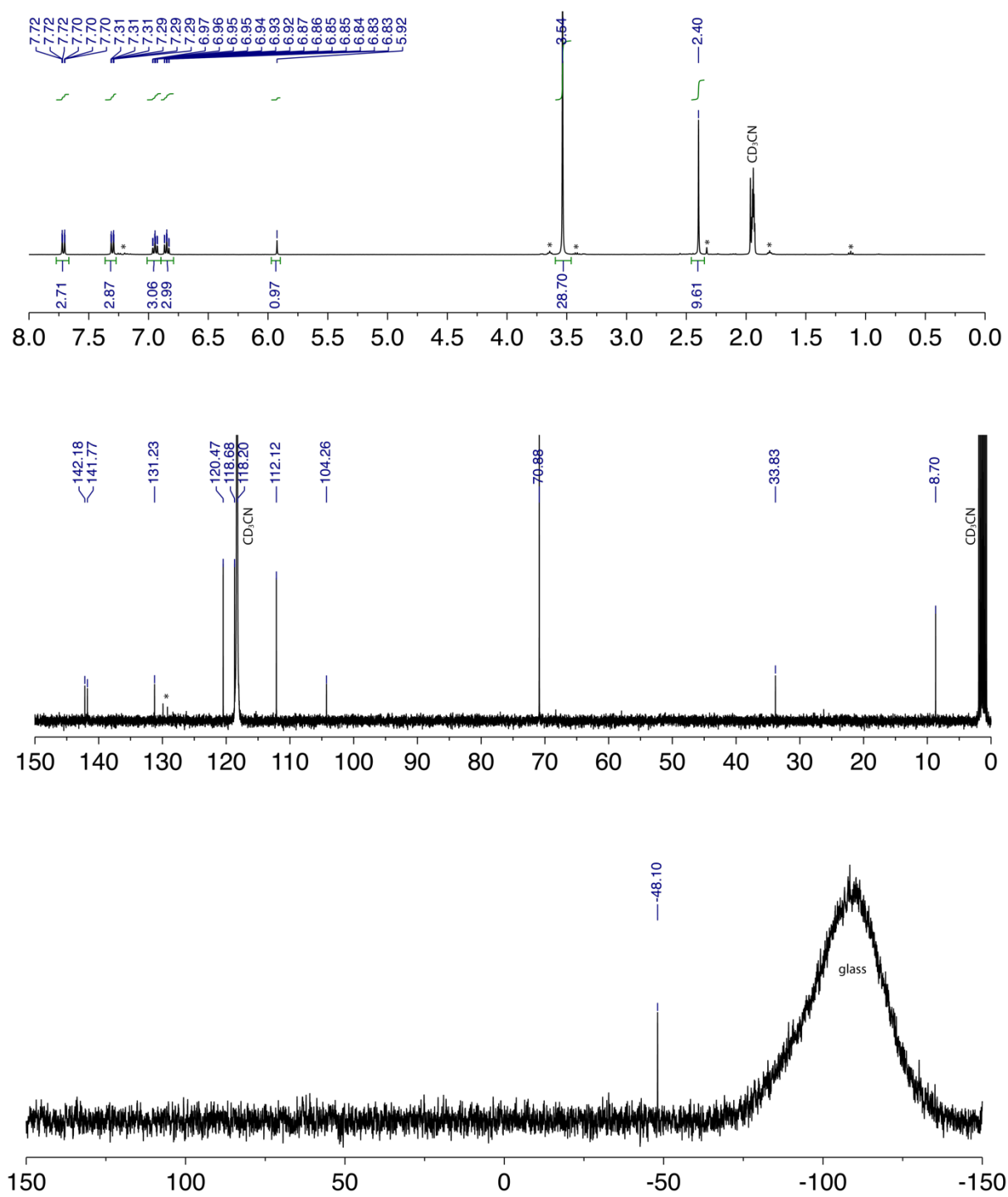


Figure S7: from top to bottom: ^1H (CD_3CN), ^{13}C (CD_3CN), and ^{29}Si (THF-H_8) NMR of compound 1. * denotes solvent traces.

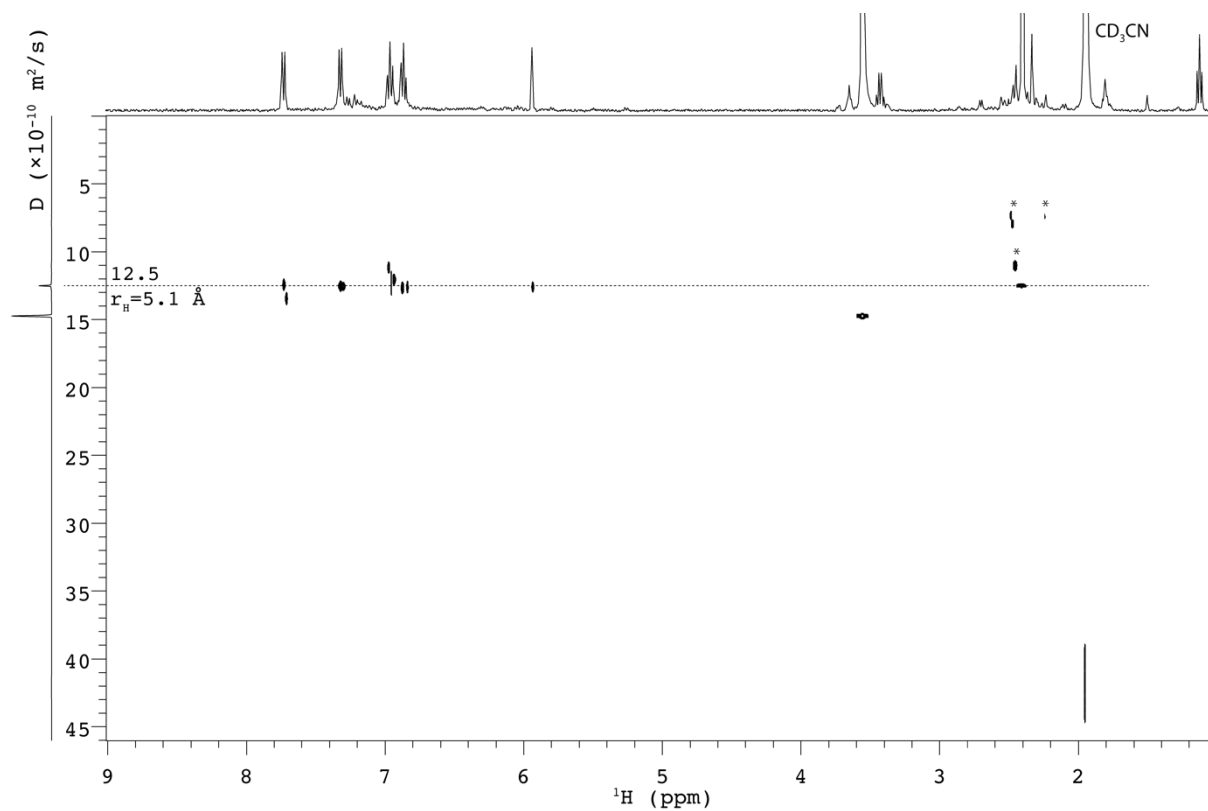


Figure S8: DOSY NMR in CD_3CN of compound **1**. Straight lines are guides to the eye, not fitted. Diffusion constants (D in $10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$): anion = 12.5, cation = 14.8. * denotes unknown impurities.

Compound 3

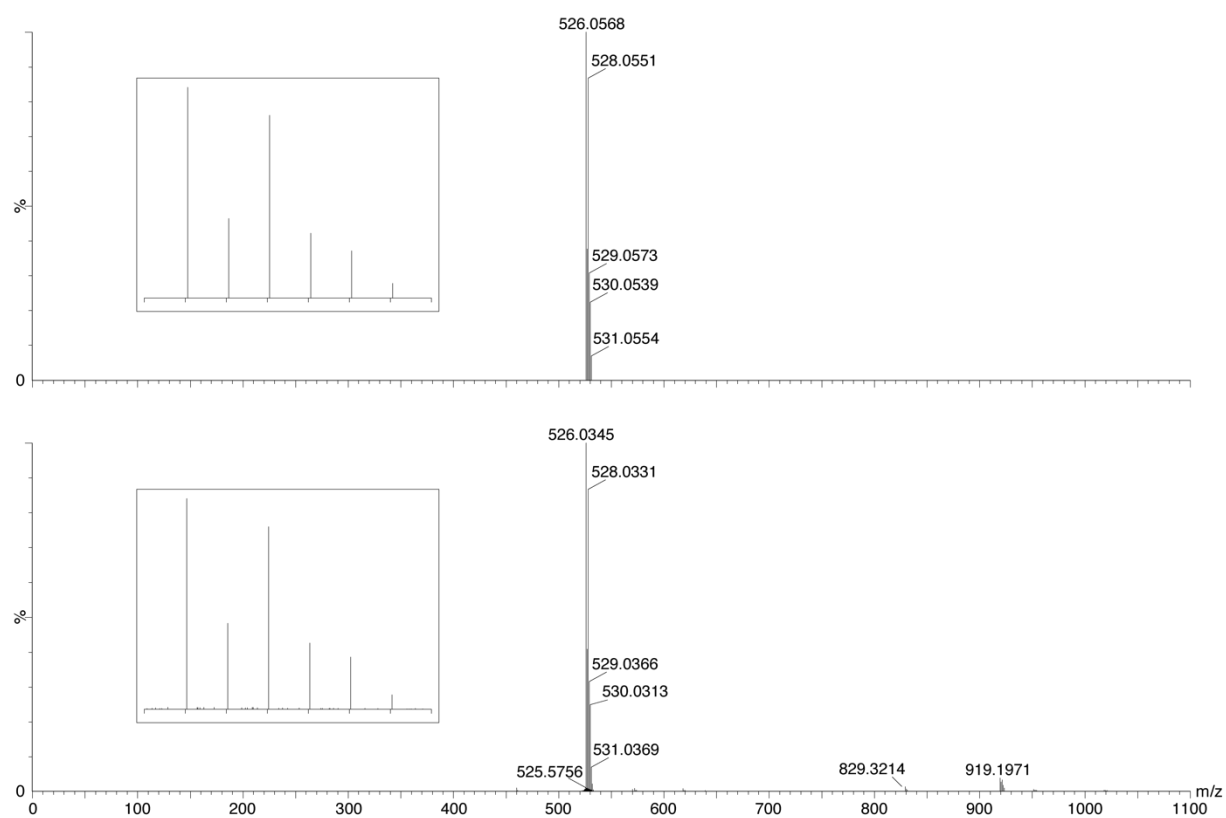


Figure S9: ESI-MS of compound **3** in THF. Top: calculated spectrum for $C_{28}H_{22}N_3SiCuCl$; Bottom: Experimental spectrum.

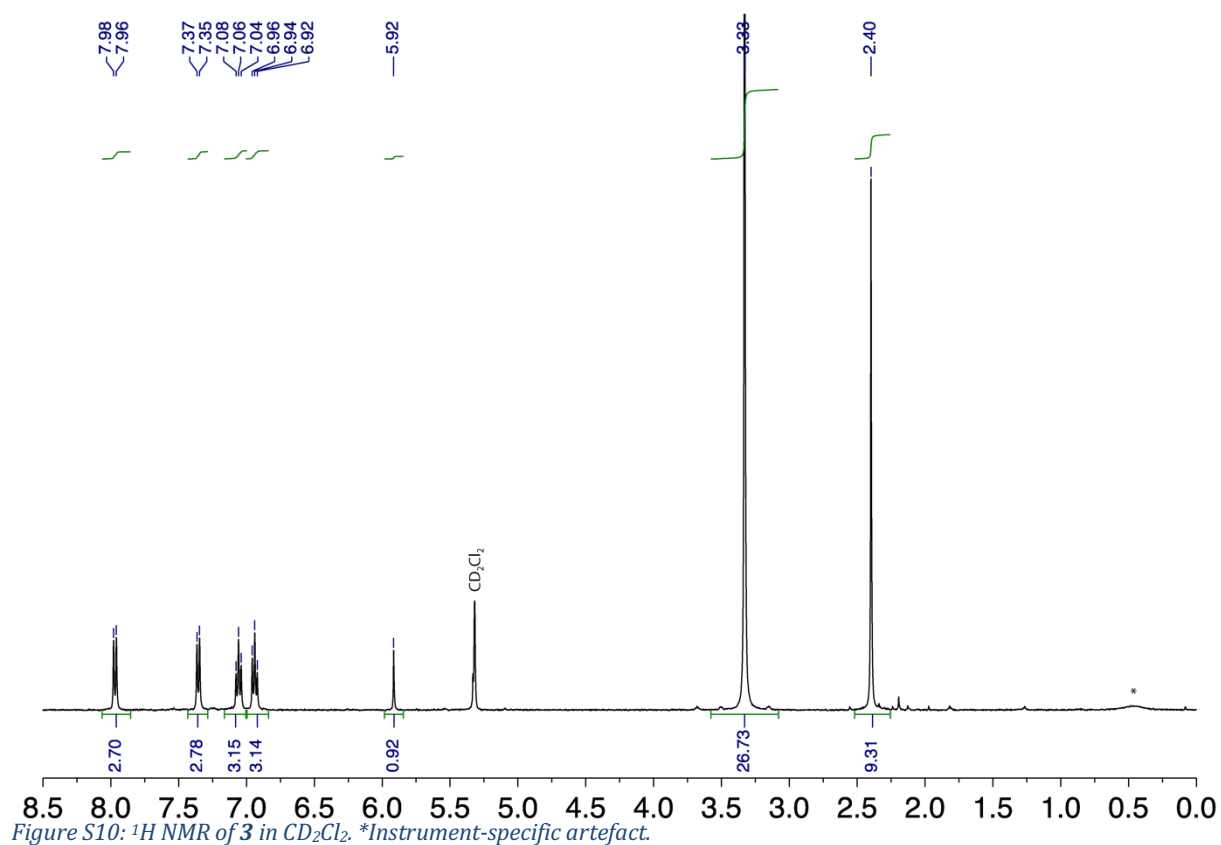


Figure S10: 1H NMR of **3** in CD_2Cl_2 . *Instrument-specific artefact.

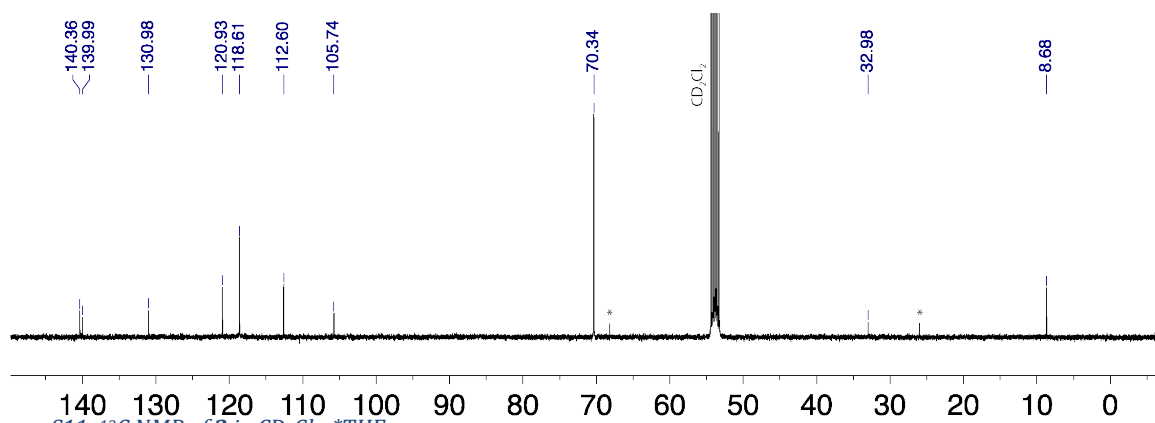


Figure S11: ^{13}C NMR of **3** in CD_2Cl_2 . *THF.

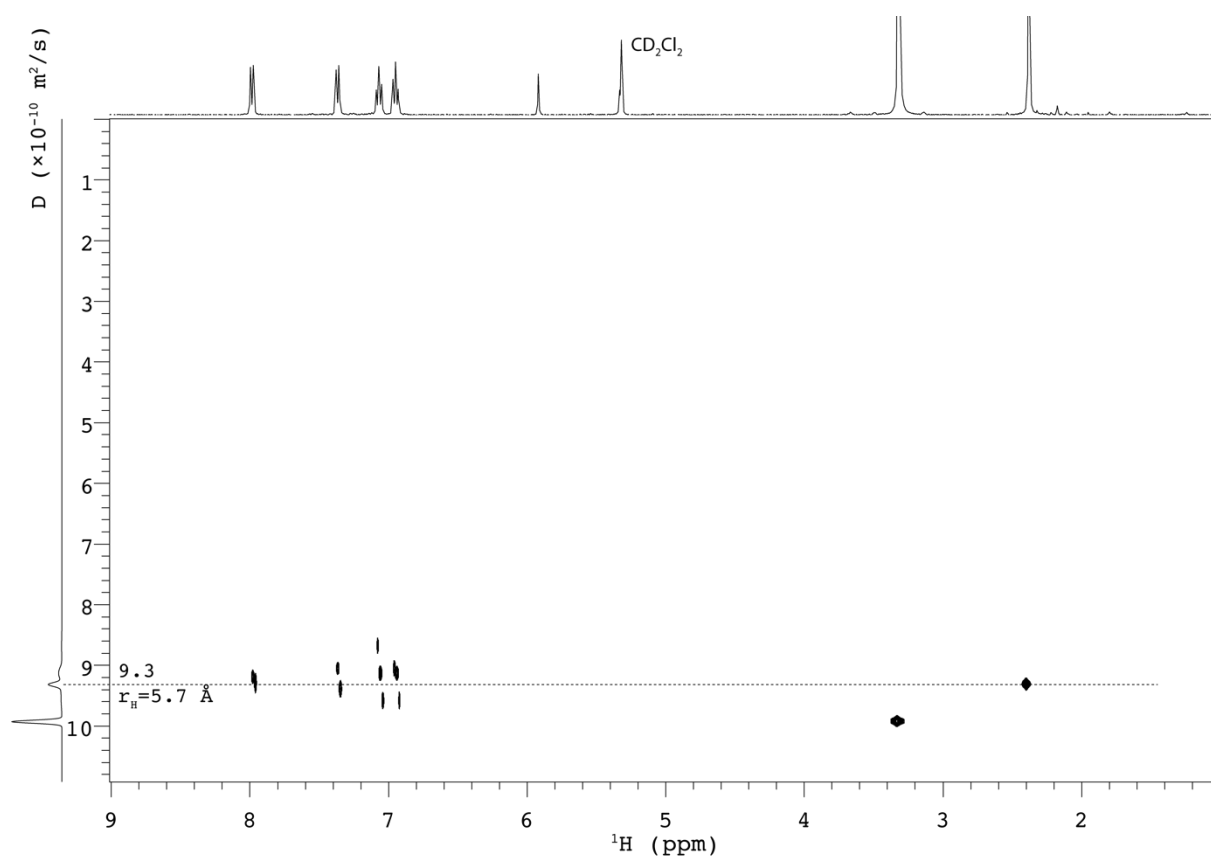


Figure S12: DOSY NMR of **3** in CD_2Cl_2 . Straight lines are guides to the eye, not fitted. Diffusion constants (D in $10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$): anion = 9.3, cation = 9.9.

Compound **3a** from **3**

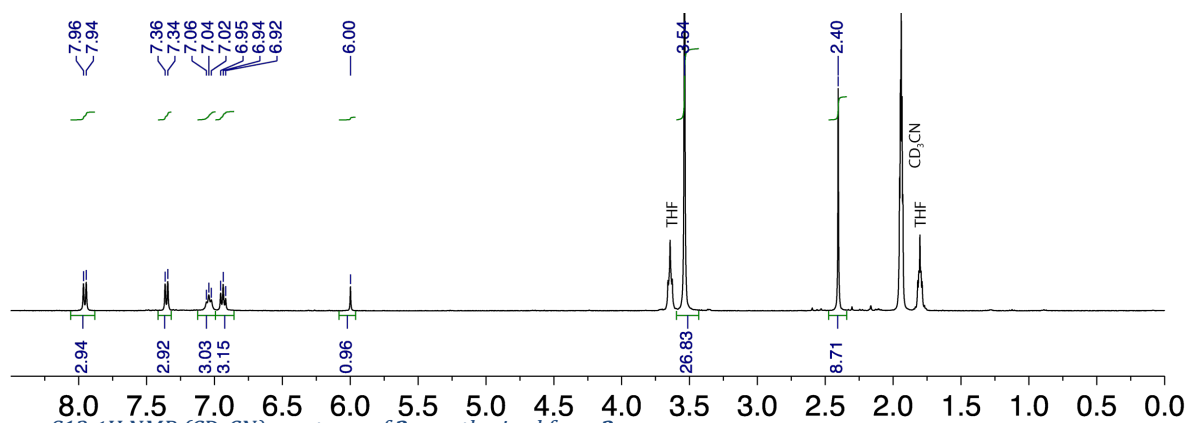


Figure S13: ¹H NMR (CD₃CN) spectrum of **3a** synthesized from **3**.

Compound **3a** from $\text{Cu}(\text{NCCH}_3)_4\text{PF}_6$

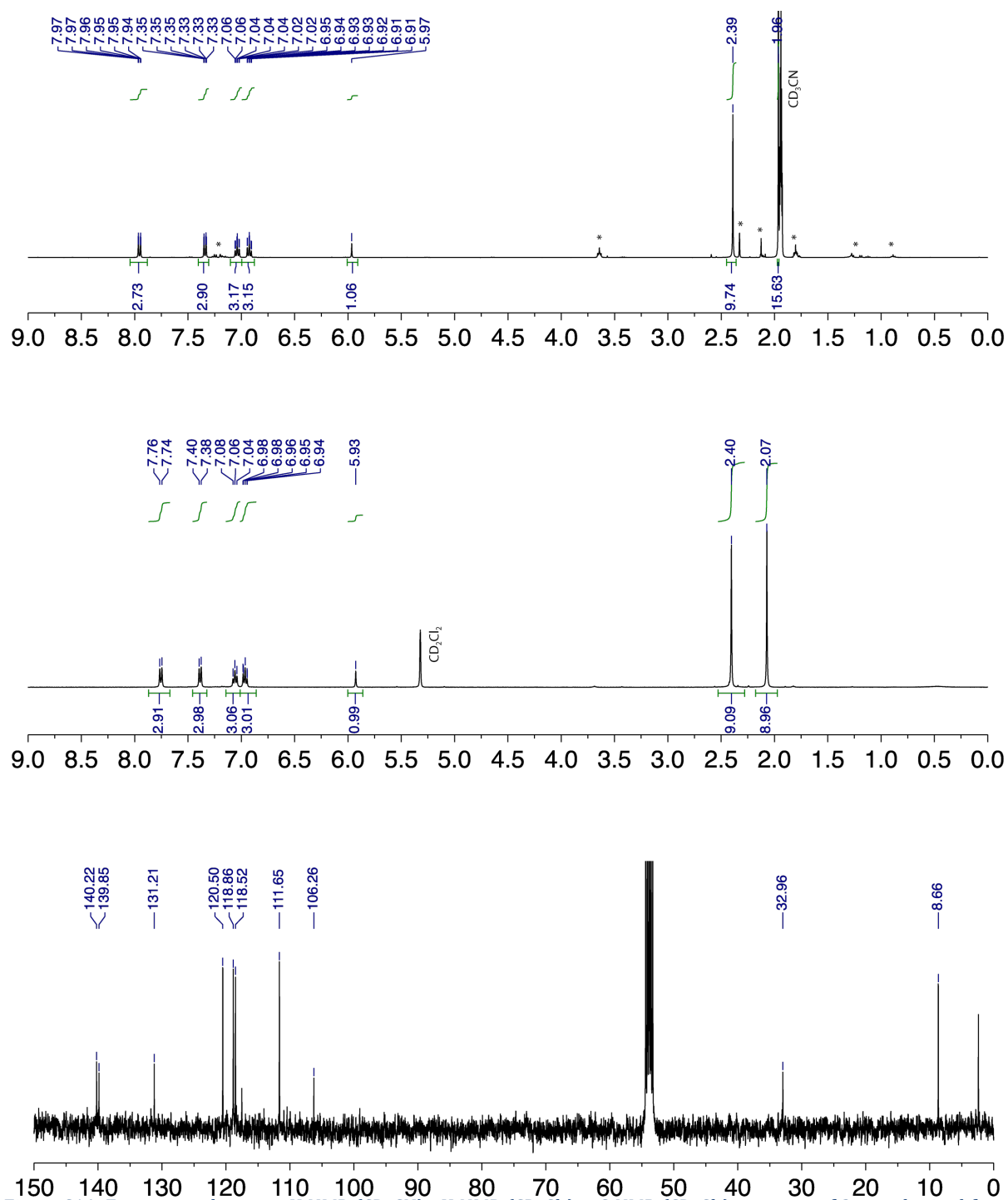


Figure S14: From top to bottom: $^1\text{H NMR}$ (CD_3CN), $^1\text{H NMR}$ (CD_2Cl_2), $^{13}\text{C NMR}$ (CD_2Cl_2) spectrum of **3a** synthesized from $\text{Cu}(\text{NCCH}_3)_4\text{PF}_6$. * denotes solvent traces.

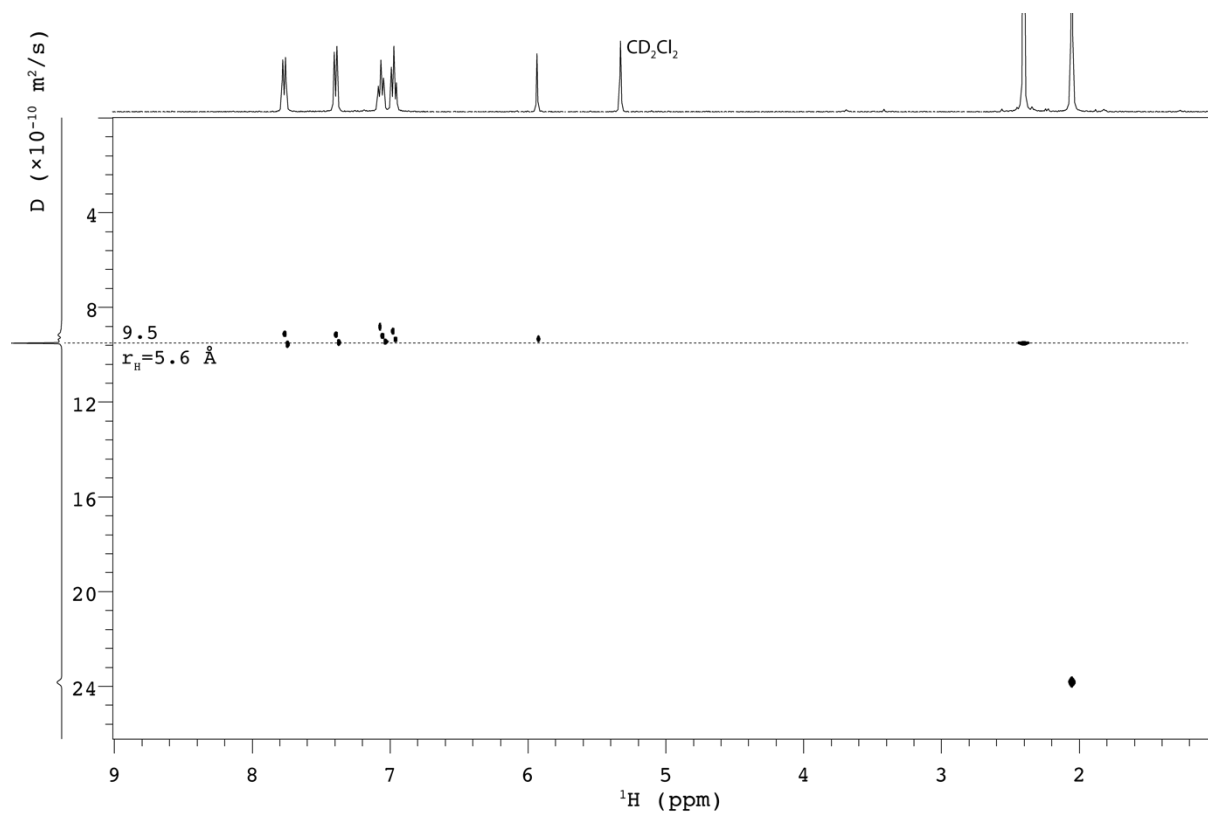


Figure S15: DOSY NMR (CD_2Cl_2) of **3a**. Straight lines are guides to the eye, not fitted. Diffusion constants $D(\text{anion}) = 9.5 \times 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$.

Compound 4

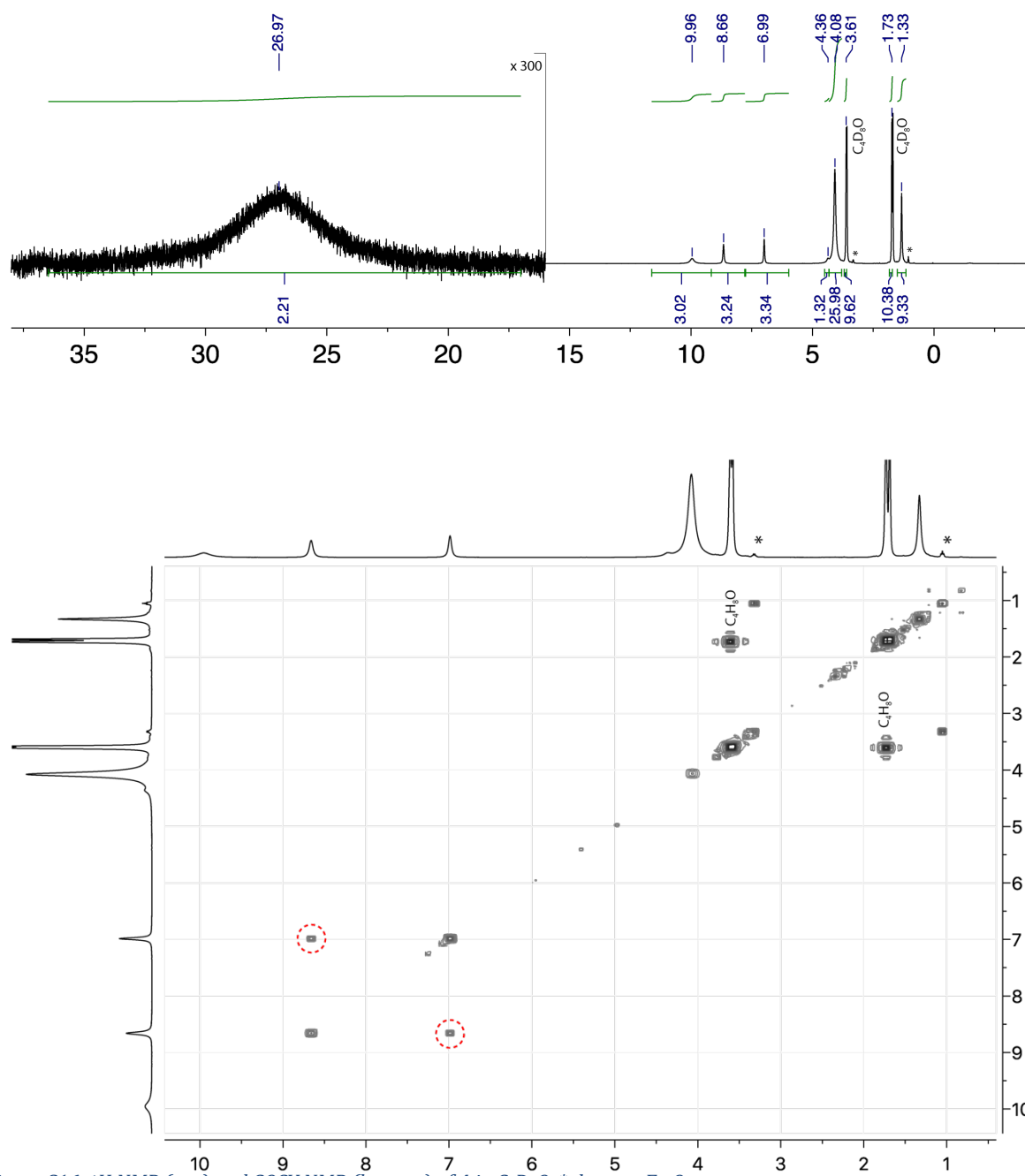


Figure S16: ^1H NMR (top) and COSY NMR (bottom) of 4 in $\text{C}_4\text{D}_8\text{O}$. * denotes Et_2O .

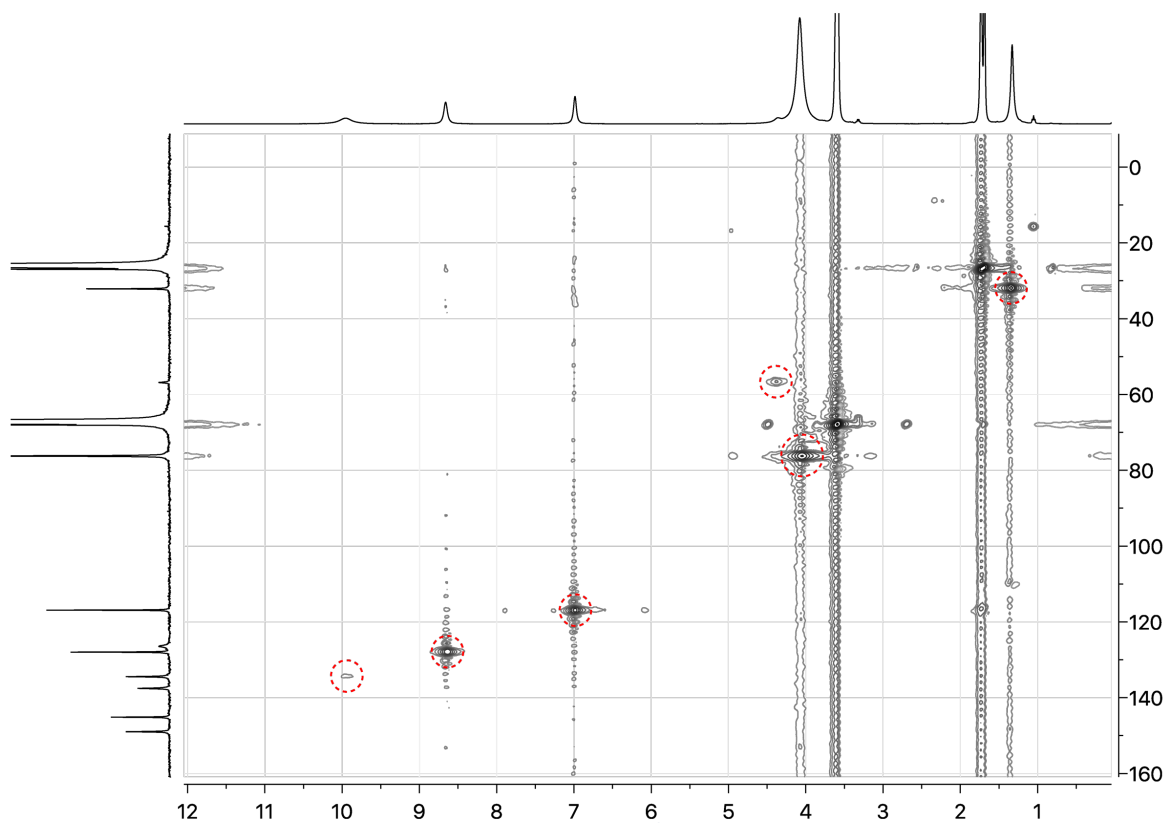
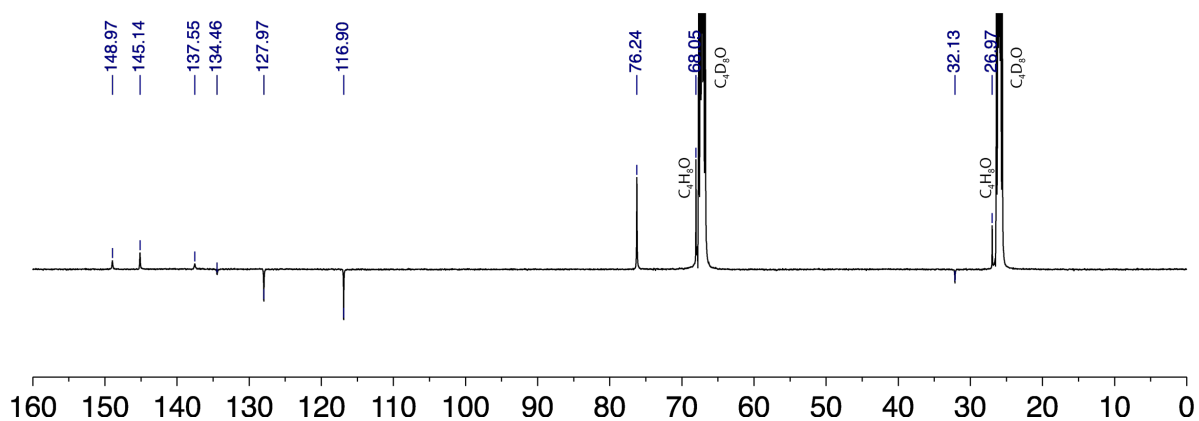
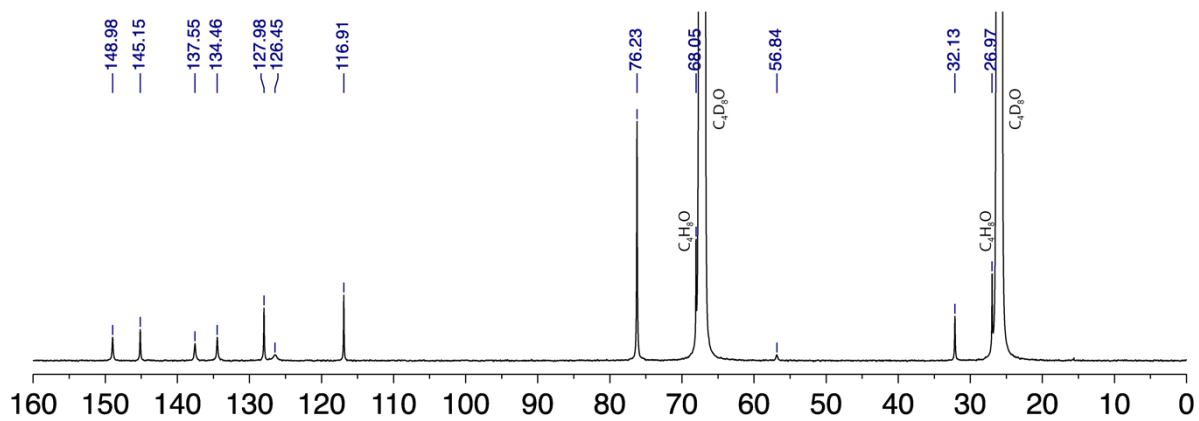


Figure S17: From top to bottom; ^{13}C , ^{13}C apt, and ASAPHMQC NMR of **4** in $\text{C}_4\text{D}_8\text{O}$.

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