

Supporting Information

Trifunctional organometallic frameworks and cages based on all-cis-1,3,5-triethynyl-1,3,5-trisilacyclohexanes

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Experimental Part

General methods

All manipulations were performed under dried argon or nitrogen *Schlenk* techniques. Tetrahydrofuran was dried over potassium, before use, solvents were distilled. Phenylmercuric bromide^[1] and *all-cis*-1,3,5-triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane^[2] (**1**) were prepared along the lines of established protocols. NMR measurements were operated with Bruker Avance III 500, Bruker Avance III 300 and Bruker DRX 500. NMR-spectra were referenced to the residual signal of used protonated solvents (¹H, ¹³C) (⁷Li: LiCl in D₂O; ²⁹Si: TMS; ¹⁹⁹Hg: Hg(NO₃)₂ in D₂O, external standard). FT-IR spectra were collected on a Bruker ALPHA FT-IR-spectrometer. Elemental analyses were performed with CHNS elemental analyser HEKAtech EURO EA (too low values for carbon are due to the known formation of silicon carbide).

Synthesis of {[CH₂Si(Me)(C₂Li)]₃(THF)₃]₂ (**2a**)

1,3,5-Triethynyl-1,3,5-trimethyl-1,3,5-trisilacyclohexane (**1a**, 94 mg, 0.38 mmol) was dissolved in 10 mL tetrahydrofuran. To the resulting a solution of a *n*-BuLi in *n*-hexane (0.71 mL, 1.14 mmol, 1.6 M) was added at -20 °C and the mixture stirred for 30 min. All volatiles were removed and a colourless solid remained. Single crystals suitable for X-ray diffraction of **2a** were obtained by gradual evaporation of THF in an H-tube. Yield: 182 mg (0,19 mmol, 100%). M. p.: 249 °C (decomposition). ¹H NMR (500 MHz, THF-d₈, 298 K): δ [ppm] = 3.62 (m, 12H, THF), 1.77 (m, 12H, THF), 0.00 (d, ²J_{H,H} = 13 Hz, 3H, -SiCH₂Si-), 0.00(s, 9H, -SiCH₃), -0.77 (d, ²J_{H,H} = 13 Hz, 3H, -SiCH₂Si-); ⁷Li{¹H} NMR (117 MHz, THF-d₈, 298 K): δ [ppm] = 0.53 (s); ¹³C{¹H} NMR (126 MHz, THF-d₈, 298 K): δ [ppm] = 171.2 (s, -LiC≡CSi-), 124.0 (s, -LiC≡CSi-), 68.4 (s, THF), 26.5 (s, THF), 6.1 (s, -SiCH₃), 5.5 (s, -SiCH₂Si-); ²⁹Si{¹H} NMR (99 MHz, THF-d₈, 298 K): δ [ppm] = -28.6. FT-IR (KBr): ν [cm⁻¹] = 3282, 3267, 3252, 2954,

2875, 2859, 1986 (C≡C), 1978 (C≡C), 1619, 1615, 1510, 1461, 1413, 1361, 1261, 1248, 1042, 914, 824, 782, 732, 714, 654, 622, 578, 501, 439; elemental analysis calculated (%) for C₂₄H₃₆Li₃O₃Si₃ (477.62): C 60.35, H 7.60; found: C 58.97, H 8.07.

Synthesis of {[CH₂Si(Ph)(C₂Li)]₃(THF)₃]₂ (2b)

To a solution of 1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (**1b**, 52 mg, 0.12 mmol) in tetrahydrofuran (6 mL) a solution of *n*-butyllithium (1.6 M in hexane, 0.23 mL, 0.37 mmol) was added at -20 °C and the mixture was stirred for 30 min. All volatile components were removed at reduced pressure. The product was obtained as a slightly yellowish solid. Single crystals were obtained by slow evaporation of the solvent in an H-tube. The product obtained in this way contains traces of diethyl ether and *n*-hexane. Yield: 49 mg (0.11 mmol, 91%). ¹H NMR (500 MHz, THF-d₈): δ [ppm] = 7.78 – 7.75 (m, 5H, *o*-CH[Ph]), 7.26 – 7.20 (m, 10H, *m*-/*p*-CH[Ph]), 3.62 (m, THF), 1.77 (m, THF), 0.42 (d, ²J_{H,H} = 13.2 Hz, 3H, -Si-CH₂-Si-), 0.06 (d, ²J_{H,H} = 13.2 Hz, 3H, -Si-CH₂-Si-); ⁷Li-NMR (194 Hz, THF-d₈): δ [ppm] = 0.9; ¹³C{¹H}-NMR (126 MHz, THF-d₈): δ [ppm] = 174.8, (-Si-C≡C-Li), 143.5 (*i*-CH[Ph]), 134.5 (*o*-CH[Ph]), 129.0 (*p*-CH[Ph]), 128.2 (*m*-CH[Ph]), 121.9 (-Si-C≡C-Li), 68.4 (THF), 26.6 (THF), 4.4 (-Si-CH₂-Si-). ²⁹Si{¹H}-NMR (99 MHz, THF-d₈): δ [ppm] = -30.0.

Synthesis of {[CH₂Si(Ph)(C₂SiMe₃)]₃(THF)₃]₂ (3b)

To a solution of 1,3,5-triethynyl-1,3,5-triphenyl-1,3,5-trisilacyclohexane (**1b**, 61 mg, 0.14 mmol) in THF (7 mL) a solution of *n*-butyllithium (1.6 M in hexane 0.27 mL, 0.43 mmol) was added at -20 °C and the mixture was stirred for 30 min. Trimethylchlorosilane (0.20 mL, 1.57 mmol) was added at -10 °C and the mixture was stirred overnight. All volatile components were removed at reduced pressure and the residue was extracted with *n*-pentane (30 mL). After removal of the solvent, the product was obtained as a colourless solid. Single crystals were obtained by continuous evaporation of the solvent from a pentane solution. Yield: 79 mg, 0.12 mmol, 86 %. ¹H NMR (500 MHz, C₆D₆): δ [ppm] = 7.47 – 7.43 (m, 6H, *o*-CH[Ph]), 7.12 – 7.02 (m, 9H, *m*-/*p*-CH[Ph]), 1.09 (s, ²J_{H,H} = 14.3 Hz, 3H, -Si-CH₂-Si-) 0.53 (s, ²J_{H,H} = 14.3 Hz, 3H, -Si-CH₂-Si-), 0.26 (s, 27H, -Si(CH₃)₃); ¹³C{¹H}-NMR (126 MHz, C₆D₆): δ [ppm] = 137.3 (*i*-CH[Ph]), 134.2 (*o*-CH[Ph]), 129.6 (*p*-CH[Ph]), 128.4 (*m*-CH[Ph]), 116.5 (-C≡C-Si(CH₃)₃), 113.4 (-CH₂-Si-C≡C-), 0.1 (-Si(CH₃)₃), -0.6 (-Si-CH₂-Si-); ²⁹Si{¹H}-NMR (99 MHz, C₆D₆): δ [ppm] = -19.0 (-Si(CH₃)₃), -24.9 (-CH₂-Si-CH₂-); MS (EI, 70 eV): *m/z* = 648.2 [M]⁺, 633.2 [M-CH₃]⁺, 575.1 [M-SiMe₃]⁺, [SiMe₂Ph]⁺, 73.0 [SiMe₃]⁺; FT-IR (ATR): ν [cm⁻¹] = 3069 (w, ν_{CH}(=CH)), 3049 (w) 3020 (w), 3008 (w), 2960 (m, ν_{CH}(CH₃)), 2898 (w, ν_{CH}(CH₂)), 1948 (w), 1875 (w) 1689 (w), 1487 (w), 1428 (m), 1409 (w), 1355 (w), 1248 (s), 1190 (w), 1110 (s), 1042 (s), 1024 (s), 838 (s), 754 (s), 726 (s), 693 (s), 676 (m), 664 (s), 628 (m), 606 (m), 519

(m), 477 (s), 433 (m), 416 (m). Analysis calcd for $C_{36}H_{48}Si_6$ ($649.28 \text{ g mol}^{-1}$): C 66.59, H 7.49; found 65.71, H 7.73.

Synthesis of $[SiCH_2MeCCHgCCMeCH_2Si]_3$ (**4a**)

To a solution of **2a** (prepared in situ from **1a**, 100 mg, 0.41 mmol / *n*-BuLi, 1.6 M in hexane, 0.77 mL, 1.22 mmol, 30 min) in 20 mL THF phenylmercuric bromide (448 mg, 1.25 mmol) was added. The suspension was refluxed for 15 min until the whole phenylmercuric bromide was dissolved. After stirring for 30 min water was added to remove LiBr. The THF phase was separated, dried over $MgSO_4$ and the solvent was removed in vacuum. To remove the diphenylmercury the solid was washed with 1,4-dioxane and dried in vacuum. Yield: 130 mg (0.12 mmol, 59%). M. p.: 324 °C (decomposition).

1H NMR (500 MHz, THF- d_8 , 298 K): δ [ppm] = 3.62 (m, THF), 1.78 (m, THF), 0.13 (s, 9H, -SiCH₃), 0.03 (d, $^2J_{H,H} = 13.4$ Hz, 3H, -SiCH₂Si-), -0.38 (d, $^2J_{H,H} = 13.4$, 3H, -SiCH₂Si-); $^{13}C\{^1H\}$ NMR (126 MHz, THF- d_8 , 298 K): δ [ppm] = 144.6 (s, -HgC≡CSi-), 111.1 (s, -HgC≡CSi-), 68.4 (s, THF), 26.6 (s, THF), 4.4 (s, -SiCH₃), 2.9 (s, -SiCH₂Si-); $^{29}Si\{^1H\}$ NMR (99 MHz, THF- d_8 , 298 K): δ [ppm] = -22.6 (s); $^{199}Hg\{^1H\}$ NMR (90 MHz, THF- d_8 , 298 K): δ [ppm] = -1016; FT-IR (KBr): ν [cm^{-1}] = 3075, 3059, 3031, 3003, 2949, 2926, 2910, 2896, 2874, 2855, 2110 (C≡C), 2093 (C≡C), 2086 (C≡C), 2076 (C≡C), 1572, 1480, 1440, 1402, 1348, 1248, 1215, 1147, 1052, 1028, 993, 824, 788, 742, 717, 706, 700, 622, 608, 469(*br*); elemental analysis calculated (%) for $C_{28}H_{38}Hg_3O_2Si_6$ with one 1,4-dioxane ($1175.06 \text{ g mol}^{-1}$): C 28.58, H 3.25; found: C 28.18, H 3.36.

Synthesis of $[SiCH_2PhCCHgCCPhCH_2Si]_3$ (**4b**)

To a solution of **2b** (prepared in situ from **1b**, 72 mg, 0.17 mmol / *n*-BuLi, 1.6 M in hexane, 0.32 mL, 0.50 mmol, 30 min) phenyl mercury bromide (180 mg, 0.50 mmol) was added at -10 °C. The mixture was stirred for 30 min. The reaction mixture was stirred at room temperature for 1 h and then heated to reflux for 10 min. After adding distilled water (10 mL) and diethyl ether (8 mL), the organic phase was separated and dried over sodium sulphate. All volatile components were removed under reduced pressure and the residue washed with 1,4-dioxane (2 mL). The product was obtained as a colourless solid. The product contained traces of dichloromethane, 1,4-dioxane and diethyl ether. Yield 49 mg (0.03 mmol, 20 %). 1H -NMR (500 MHz, pyridine- d_5): δ = 8.11 – 8.08 (m, 6H, *o*-CH[Ph]), 7.55 – 7.45 (m, 9H, *m/p*-CH[Ph]), 0.97 (d, $^2J_{H,H} = 13.5$ Hz, 3H, -Si-CH₂-Si-), 0.68 (d, $^2J_{H,H} = 13.5$ Hz, 3H, -Si-CH₂-Si-); 1H -NMR (500 MHz, THF- d_8): δ = 7.78 – 7.68 (m, 6H, *o*-CH[Ph]), 7.33 – 7.26 (m, 11H, *m/p*-CH[Ph]), 0.46 (d, $^2J_{H,H} = 13.5$ Hz, 3H, -Si-CH₂-Si-), 0.38 (d, $^2J_{H,H} = 13.5$ Hz, 3H, -Si-CH₂-

Si-); $^{13}\text{C}\{^1\text{H}\}$ -NMR (126 MHz, pyridine- d_5): $\delta = 147.9$ ($-\text{C}\equiv\text{C}-\text{Hg}$), 141.2 (*i*-CH[Ph]), 134.7 (*o*-CH[Ph]), 130.0 (*p*-CH[Ph]), 128.8 (*m*-CH[Ph]), 109.6 ($-\text{Si}-\text{C}\equiv\text{C}-$), 2.3 ($-\text{Si}-\text{CH}_2-\text{Si}-$); $^{29}\text{Si}\{^1\text{H}\}$ -NMR (99 MHz, pyridine- d_5): $\delta = -25.4$; ^{199}Hg -NMR (54 MHz, THF- d_8): $\delta = -1039.5$; FT-IR (ATR): ν [cm^{-1}] = 3064 (w), 3045 (w), 2962 (m), 2094 (w, $\nu_{\text{CH}}(\text{CH}_2)$), 1426 (w), 1413 (w), 1260 (s), 1089 (s), 1018 (s), 865 (m), 796 (s), 734 (m), 695 (m), 658 (m), 617 (m), 525 (m), 474 (m), 438 (m).

Crystallographic structure determination

Single crystals suitable for X-ray diffraction measurement were suspended in a paratone-N/paraffin oil mixture, mounted on a glass fibre and transferred onto the goniometer of the diffractometer. The structures were solved by Direct Methods and refined by full-matrix least-squares cycles (programs Olex2^[3] SHELXS-97^[4] and SHELXL-97^[4]). **2b · 6 THF** shows a disorder of the THF molecule with ratio 81:19. Equivalent bond lengths of the disordered molecules were restrained to be same; the neighbouring disordered carbon atoms were constrained to have the same anisotropic displacement parameters pair wisely. Further details on the crystallographic measurements can be found in Table 1.

CCDC 1418361, 1418362, 1901920 and 1901921 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystallographic data of **2a**, **2b**, **3b** and **4a**.

	2a · 6 THF	2b · 6 THF	3b	4a · 2 pyridine
Formula	C ₄₈ H ₇₈ Li ₆ O ₆ Si ₆	C ₇₈ H ₉₀ Li ₆ O ₆ Si ₆	C ₃₆ H ₄₈ Si ₆	C ₃₄ H ₄₀ Hg ₃ N ₂ Si ₆
<i>M</i> _r	961.28	1333.67	649.28	1246.99
<i>T</i> [K]	100.0(1)	200.0(1)	100.0(1)	100.0(1)
Crystal size [mm]	0.16×0.12×0.08	0.19 × 0.13 × 0.10	0.29 × 0.22 × 0.14	0.30×0.19×0.18
Crystal system	triclinic	trigonal	monoclinic	orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>R</i> $\bar{3}$	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>
<i>a</i> [Å]	10.2617(8)	12.1176(2)	10.6904(1)	15.5413(6)
<i>b</i> [Å]	11.8325(13)	12.1176(2)	32.0784(2)	17.0430(9)
<i>c</i> [Å]	13.6055(10)	44.8866(8)	12.7259(1)	30.480(12)
α [°]	108.60(1)	90	90	90
β [°]	104.45(1)	90	113.99(1)	90
γ [°]	104.86(1)	120	90	90
<i>V</i> [Å ³]	1410.9(2)	5708.0(2)	3987.0(1)	8073(3)
<i>Z</i>	1	3	4	8
ρ_{calcd} [g·cm ⁻³]	1.131	1.164	1.082	2.052
μ [mm ⁻¹]	0.189	1.406	2.116	11.585
<i>F</i> (000)	516	2124	1392	4656
2 θ range [°]	3.90 to 60.00	5.91 to 143.91	8.09 to 152.45	4.44 to 60.28
Index range	-14 ≤ <i>h</i> ≤ 14 -16 ≤ <i>k</i> ≤ 16 -19 ≤ <i>l</i> ≤ 19	-14 ≤ <i>h</i> ≤ 14 -14 ≤ <i>k</i> ≤ 14 -55 ≤ <i>l</i> ≤ 55	-13 ≤ <i>h</i> ≤ 13 -39 ≤ <i>k</i> ≤ 40 -15 ≤ <i>l</i> ≤ 16	-21 ≤ <i>h</i> ≤ 21 -24 ≤ <i>k</i> ≤ 24 -43 ≤ <i>l</i> ≤ 43
Reflns collected	27424	63931	90276	387982
Unique reflns	8221	4146	8336	11876
reflns with <i>I</i> > 2 σ (<i>I</i>)	6372	3872	8240	11143
<i>R</i> _{int}	0.0420	0.0328	0.0212	0.0851
Data/restr./param	8221 / 0 / 301	4146/21/168	8336/0/572	11876 / 0 / 412
GoF (<i>F</i> ²)	1.040	1.038	1.038	1.184
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0453, 0.1036	0.0366, 0.1039	0.0272, 0.0730	0.0212, 0.0436
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0648, 0.1128	0.0386, 0.1063	0.0274, 0.0732	0.0240, 0.0443
$\Delta\rho_{(\text{max/min})}$ [e·Å ⁻³]	0.65 / -0.36	0.22/-0.19	0.36 / -0.37	1.91 / -1.10
CCDC-no.	1418361	1901920	1901921	1418362

Additional NMR spectra of compounds 2 and 3:

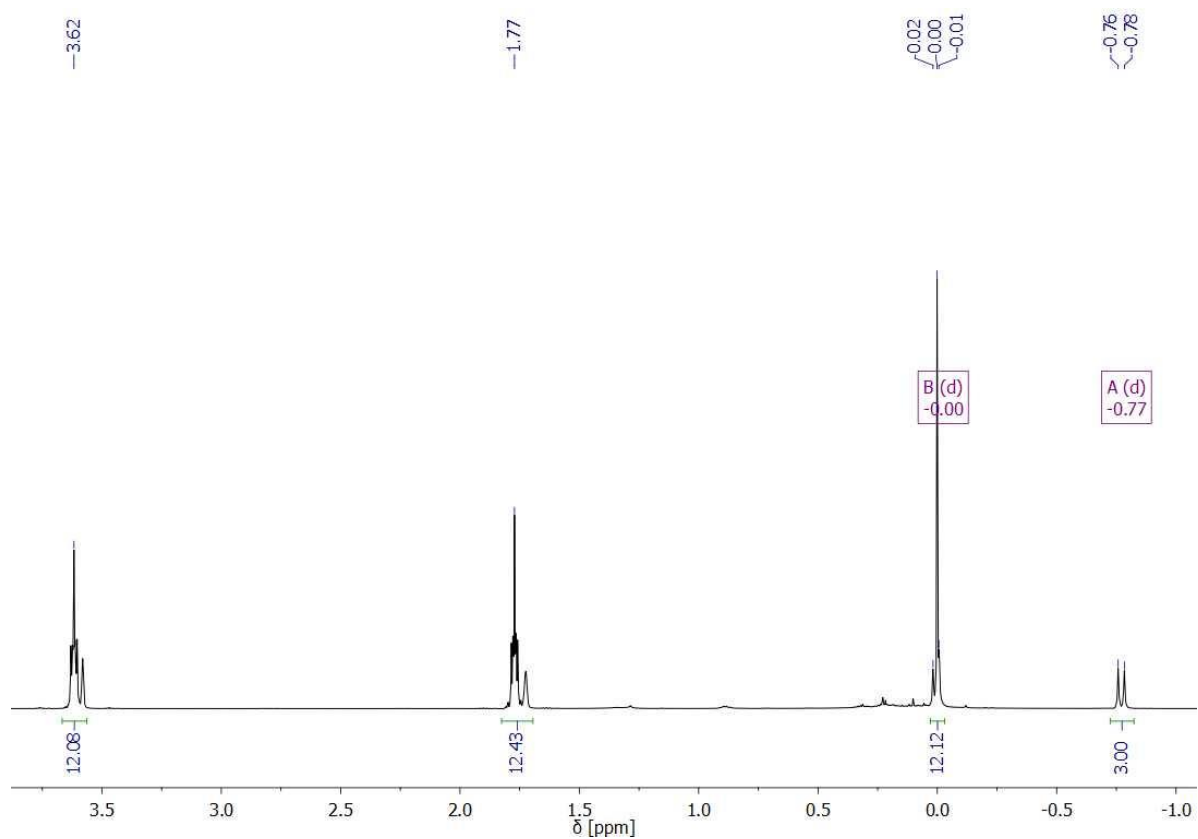


Figure S1. ^1H NMR spectrum of **2a** in $[\text{D}_8]\text{THF}$ at 298 K.

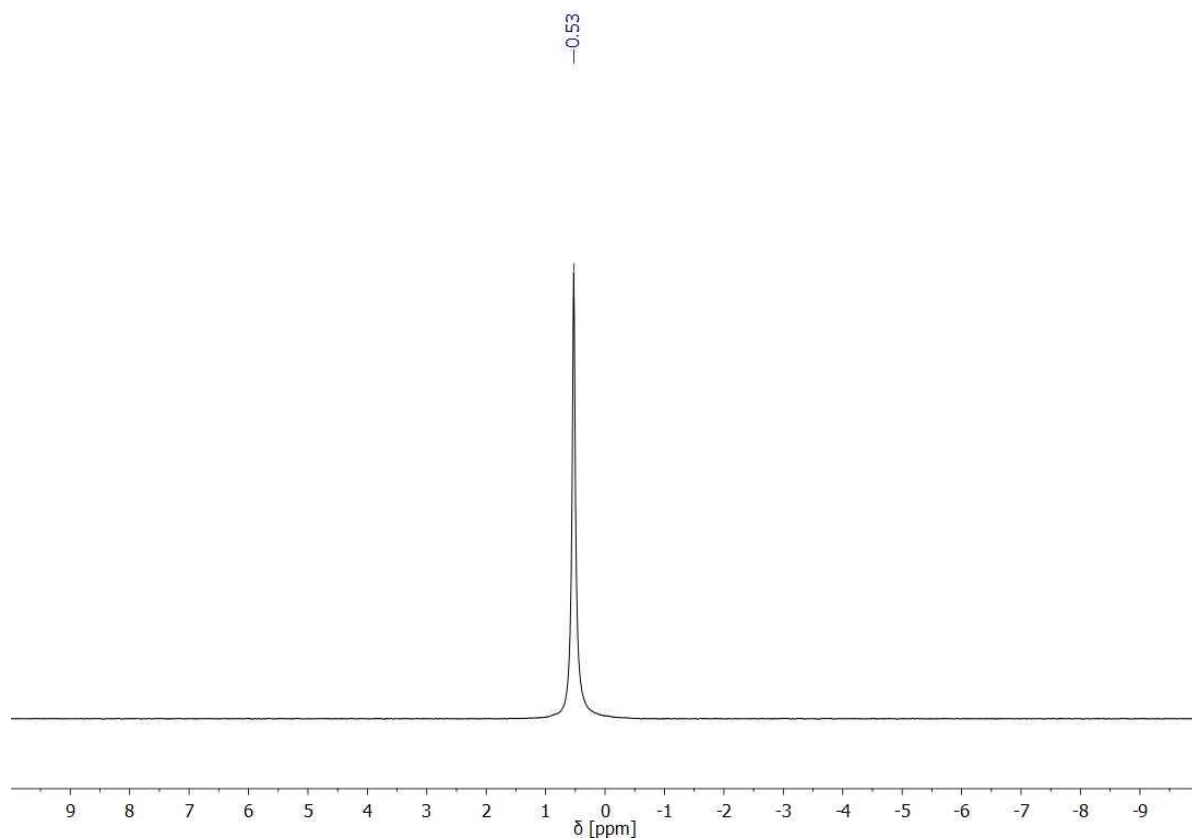


Figure S2. $^7\text{Li} \{^1\text{H}\}$ NMR spectrum of **2a** in $[\text{D}_8]\text{THF}$ at 298 K.

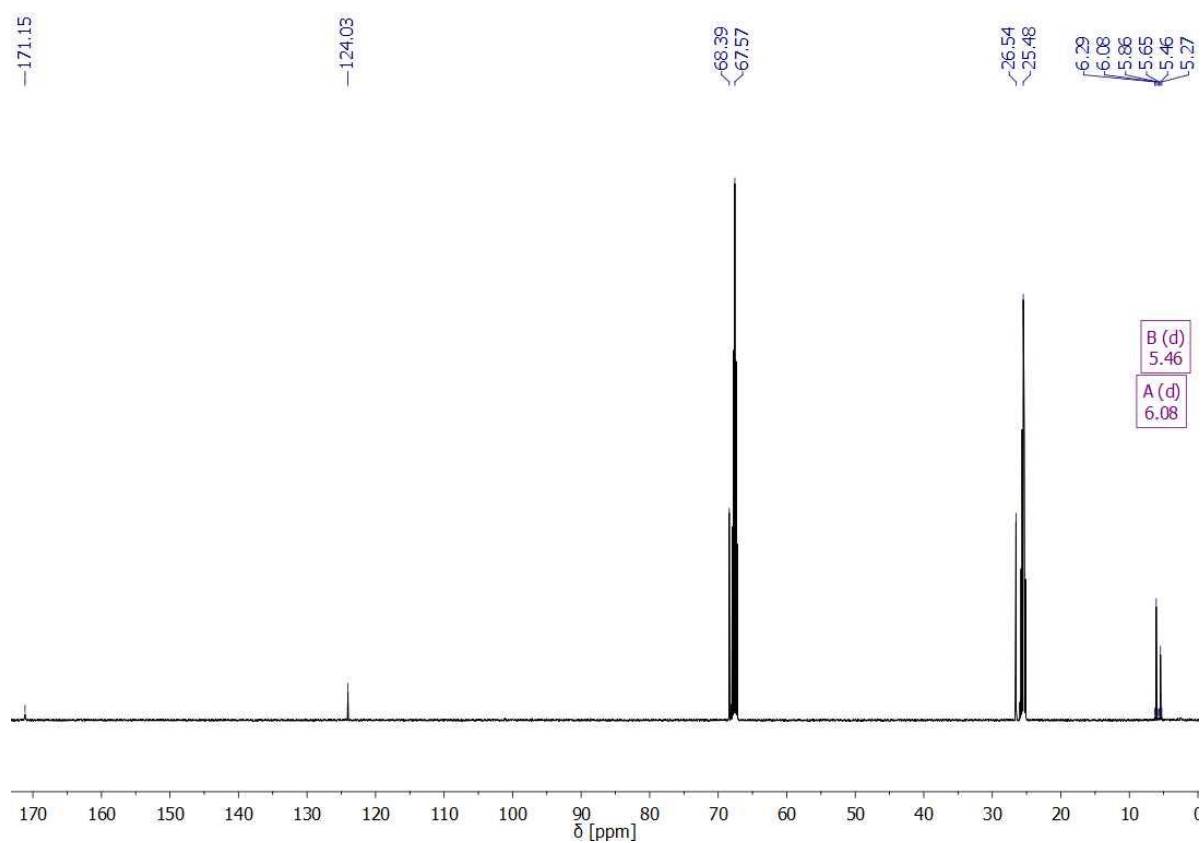


Figure S3. $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2a** in $[\text{D}_8]\text{THF}$ at 298 K.

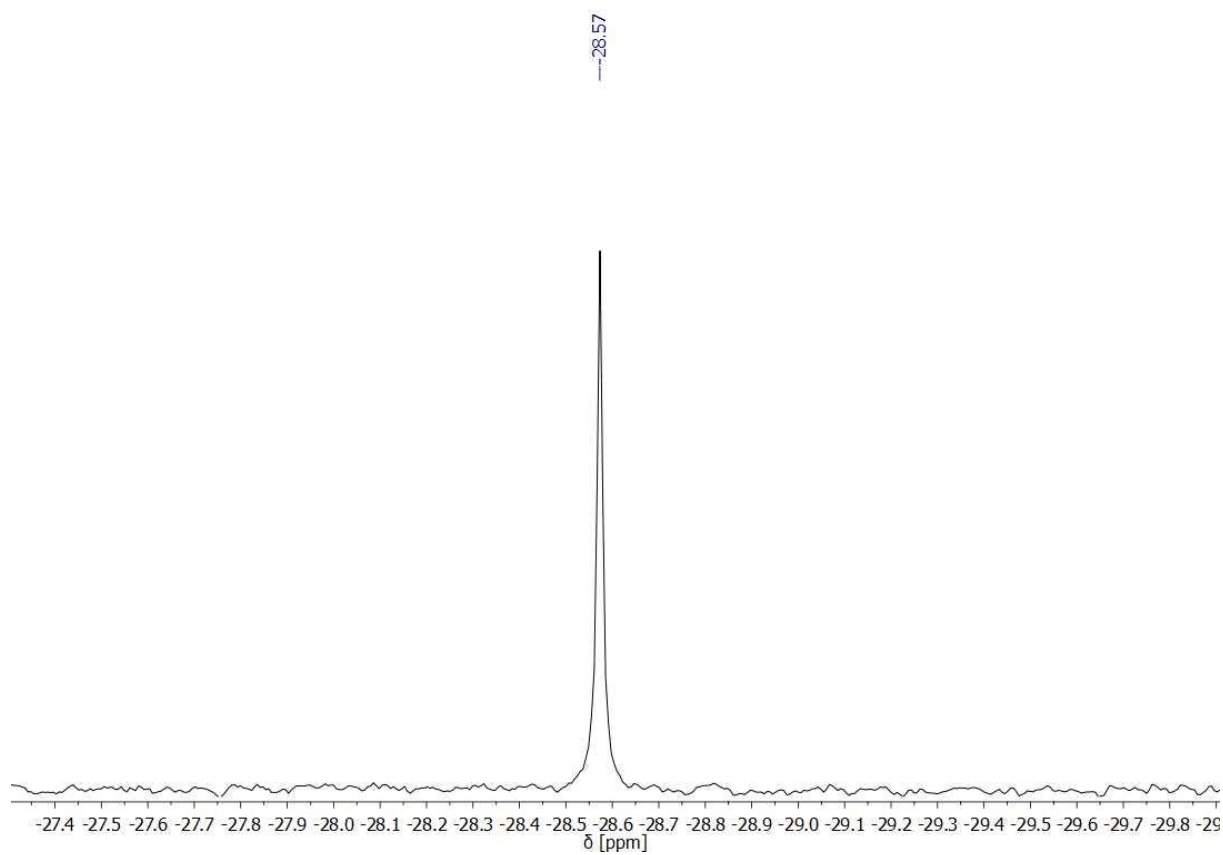


Figure S4. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **2a** in $[\text{D}_8]\text{THF}$ at 298 K.

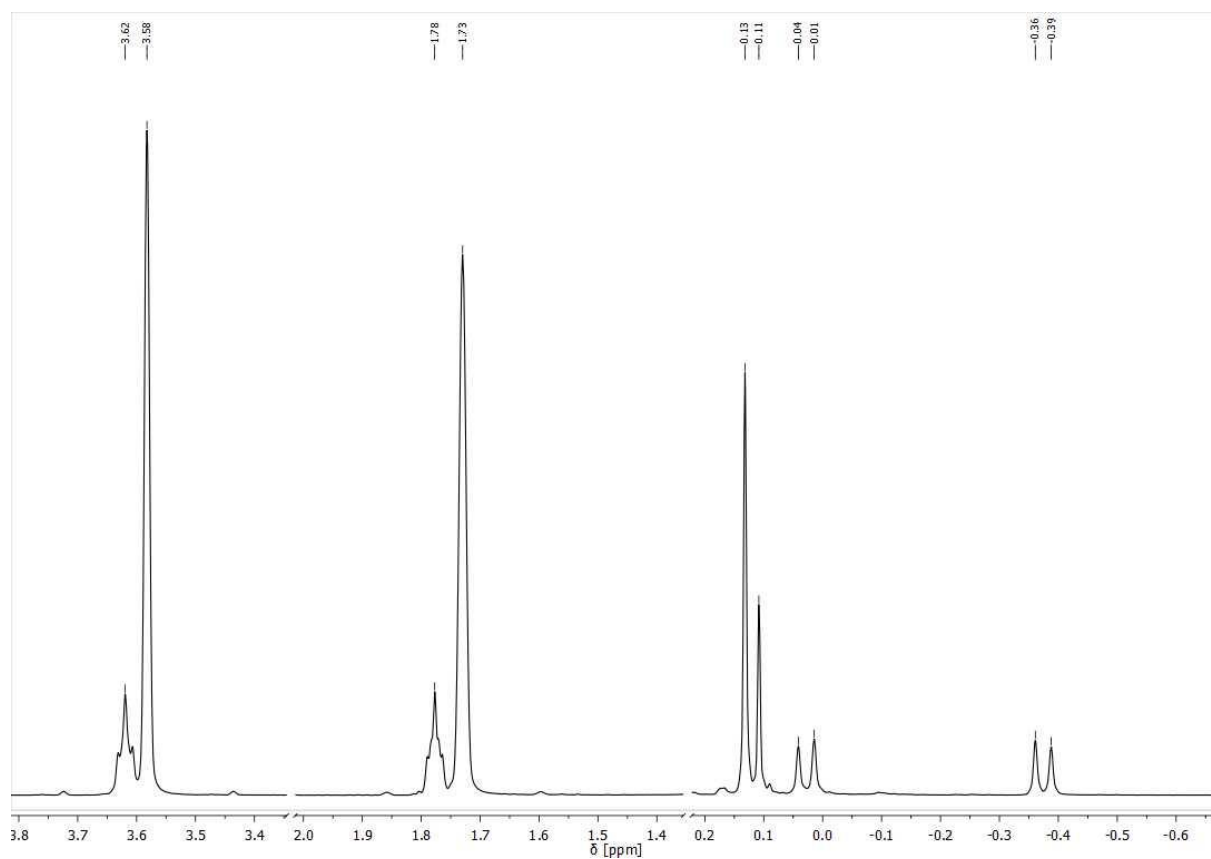


Figure S5. ${}^1\text{H}$ NMR spectrum of **4a** in $[\text{D}_8]\text{THF}$ at 298 K.

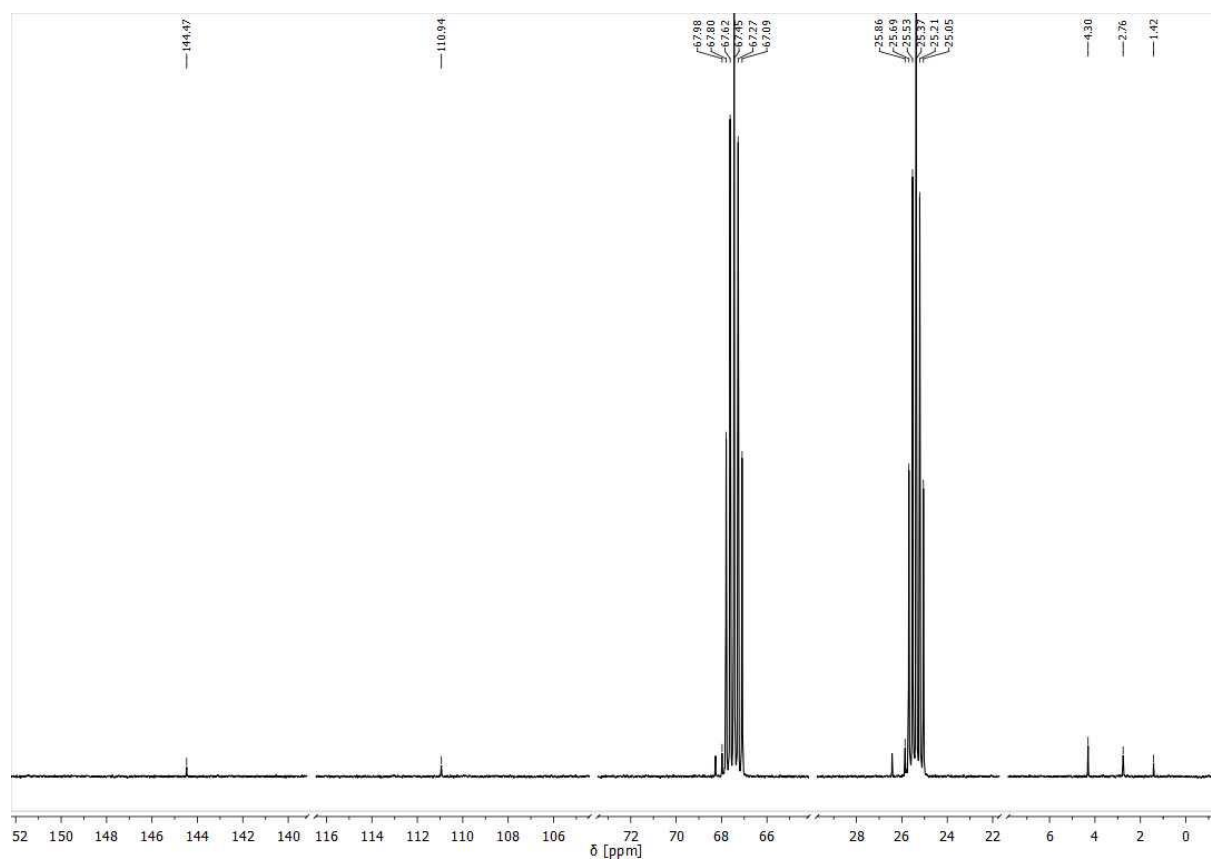


Figure S6. ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR spectrum of **4a** in $[\text{D}_8]\text{THF}$ at 298 K.

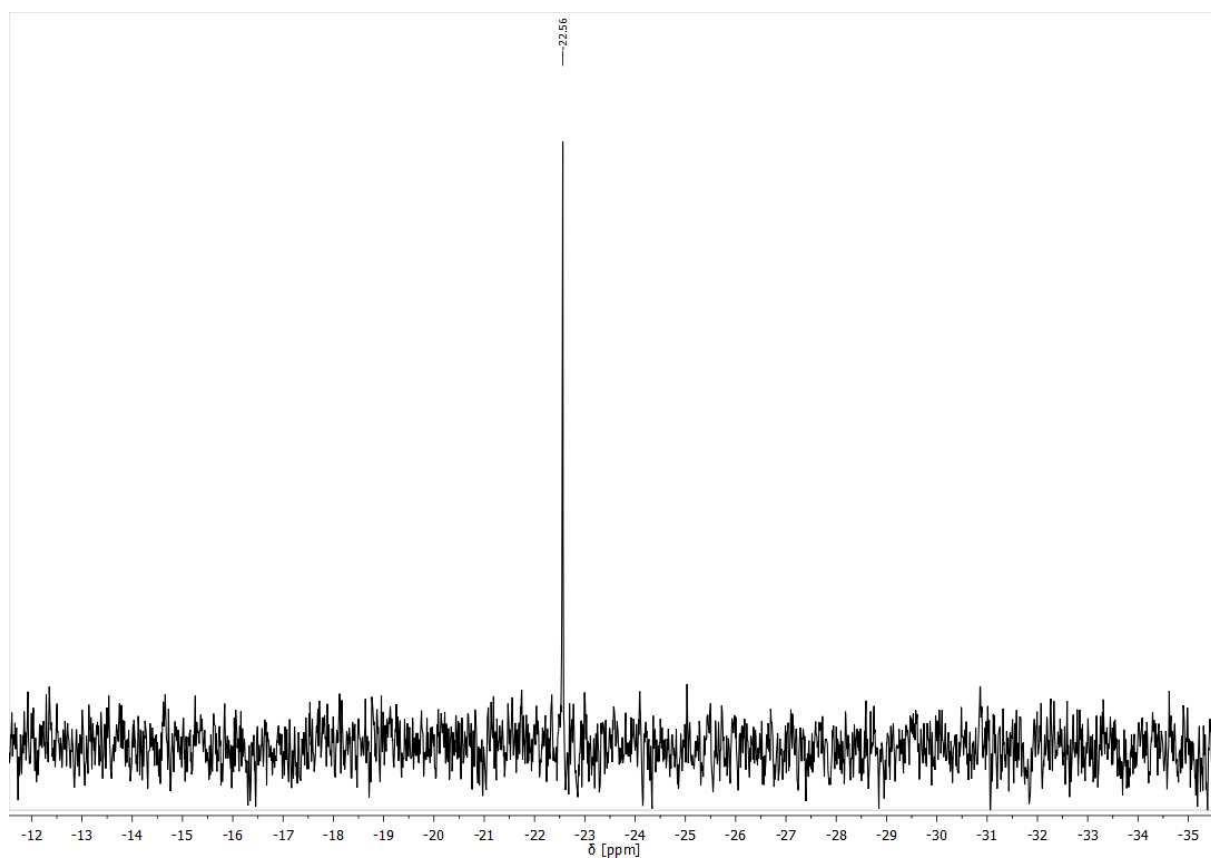


Figure S7. $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of **4a** in $[\text{D}_8]\text{THF}$ at 298 K.

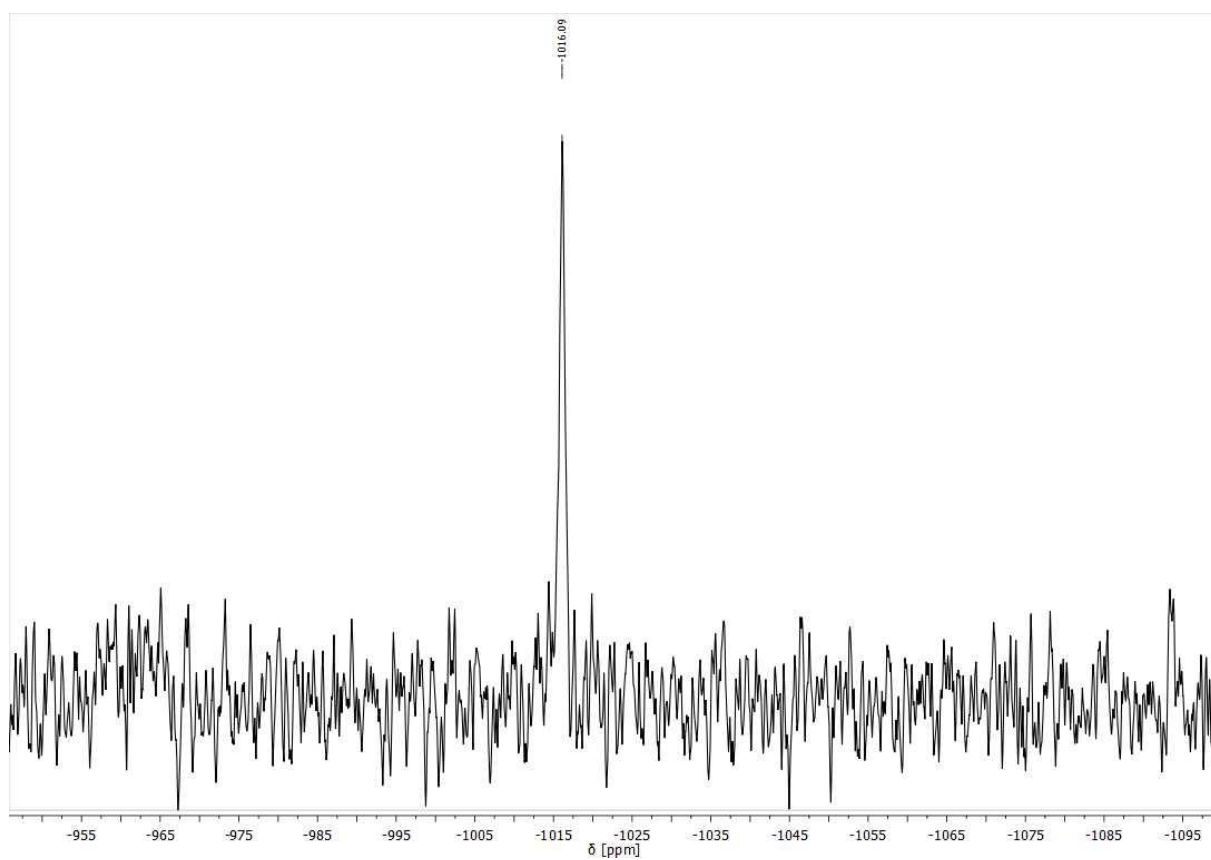


Figure S8. $^{199}\text{Hg}\{^1\text{H}\}$ NMR spectrum of **4a** in $[\text{D}_8]\text{THF}$ at 298 K.

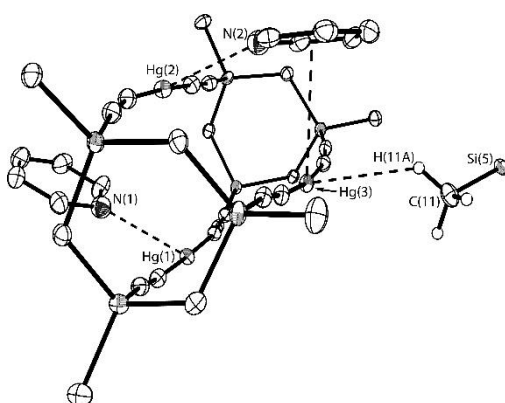


Figure S9. Molecular structure of **4a** with $\pi \cdots \text{Hg}(3)$ interaction. The distance between pyridine plane and Hg(3) is 3.517(2) Å, between Hg(3) and H(11A) with symmetry code $3/2-x, -1/2+y, z$ is 2.842(2) Å.

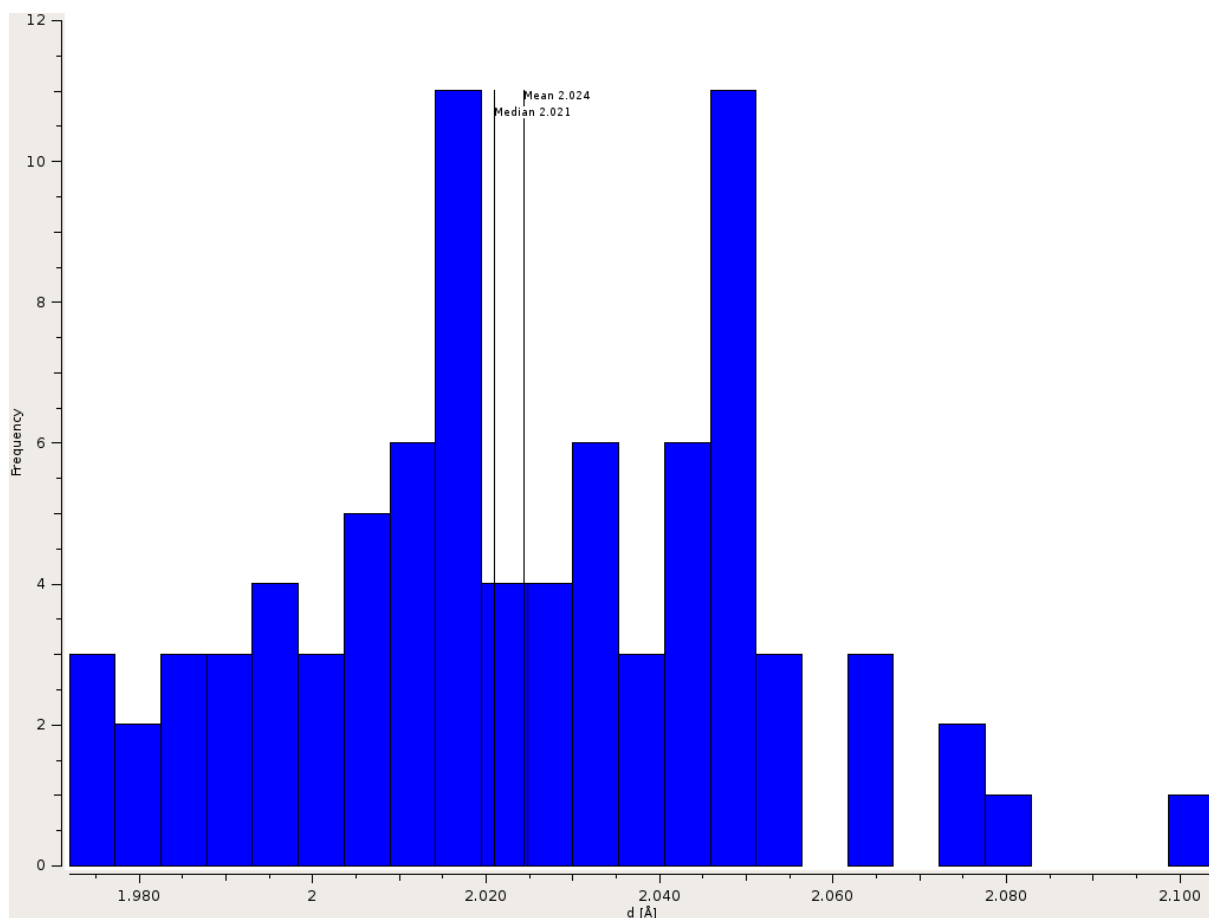


Figure S10. Mercury carbon bond length distribution diagram of Hg-C≡C fragment. Mean: 2.024 Å.

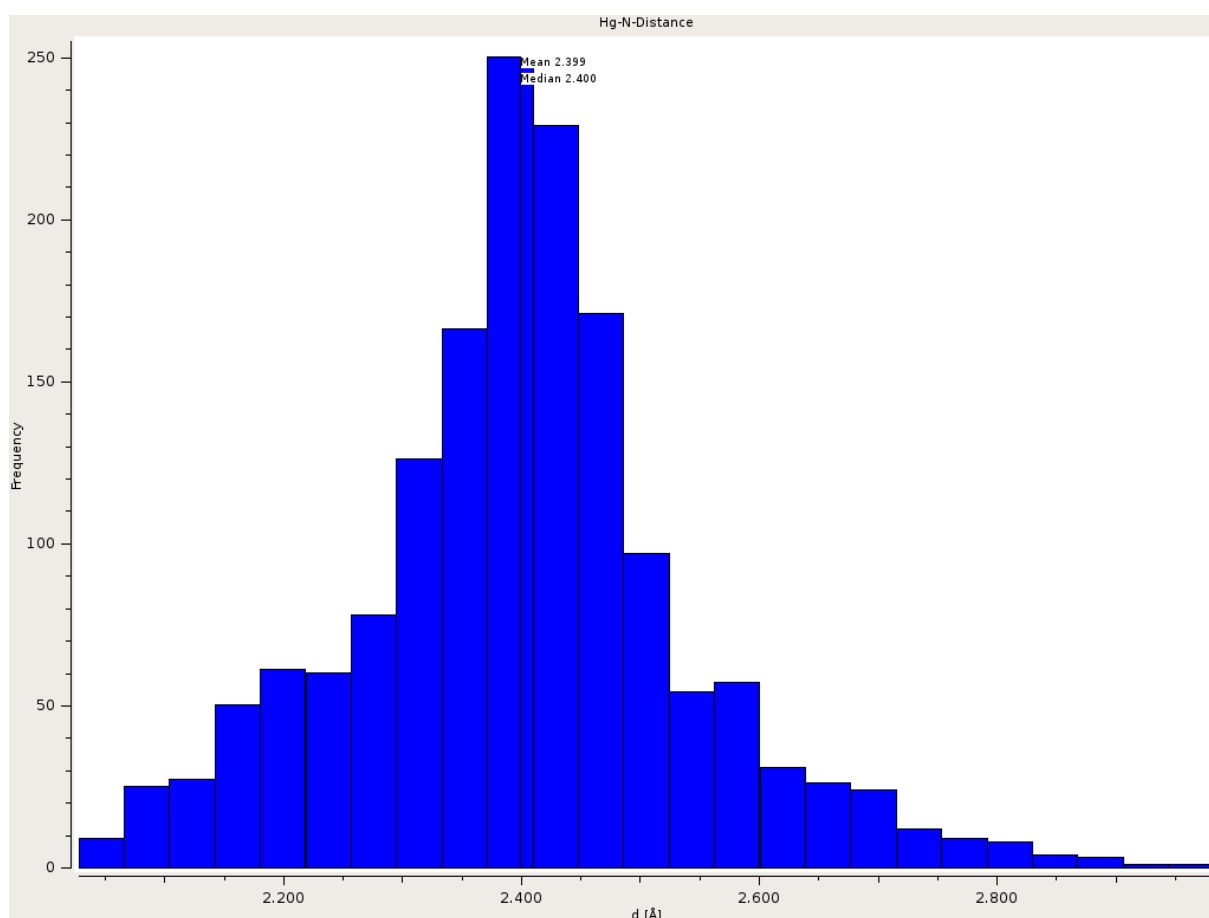


Figure S11. Mercury-nitrogen bond length distribution diagram of Hg–Hg fragment. Mean: 2.944 Å.

References

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