

Supplementary Information

A Highly Luminescent Octanuclear Gold(I) Carbide Cluster

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Experimental Section

General Considerations

All manipulations of air-sensitive materials were performed under the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual manifold Schlenk line, interfaced to a high vacuum (10^{-3} torr) line, or in an argon-filled MBraun glove box. Elemental analyses were carried out with an Elementar vario Micro Cube. Hydrocarbon solvents were dried by using an MBraun solvent purification system (SPS-800), degassed and stored under vacuo. Tetrahydrofuran was distilled under nitrogen from potassium benzophenoneketyl before storage over 4 Å molecular sieves. IR spectra were obtained on a Bruker Tensor 37 FTIR spectrometer equipped with a room temperature DLaTGS detector and a diamond ATR (attenuated total reflection) unit; for the mid infrared region a KBr beamsplitter was used. Raman spectra were obtained on a Bruker MultiRam spectrometer. [AuCl(tht)] was prepared according to literature procedure.¹

Synthesis

Synthesis of $[\{\text{Me}_3\text{SiC}\equiv\text{CC}(\text{NDipp})_2\}\text{Li}(\text{thf})_3]$ (**1**)

0.42 mL of trimethylsilylacetylene (288 mg, 2.21 mmol, 1.00 eq.) was dissolved in 30 mL thf and cooled to -78°C . 1.35 mL of a 2.5 molar *n*-buthyllithium solution in *n*-hexane (216 mg, 3.38 mmol, 1.05 eq.) was added slowly. The reaction mixture was stirred for 15 minutes. 1.17 g of bis(2,6-diisopropylphenyl)carbodiimide (3.21 mmol, 1.00 eq.) were dissolved in 20 mL thf and added quickly with a syringe through a septum. The reaction mixture was stirred for 30 min at -78°C and for an additional hour after warming up to ambient temperature. The mixture was concentrated to approximately 10 mL and stored at -30°C overnight. The resulting colourless crystalline product was separated from the mother liquor by decantation and subsequently dried under vacuum for 1 h. Crystalline yield: 1.69 g (84 %).

^1H NMR (300 MHz, C_6D_6): $\delta = -0.22$ (s, 9 H, SiCH_3), 1.28 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12 H, iPr-CH_3), 1.37 (m, 12 H, thf-CH_2), 1.51 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12 H, iPr-CH_3), 3.55 (m, 12 H, thf-OCH_2), 3.74 (hept, $^3J_{\text{HH}} = 6.9$ Hz, 4 H, iPr-CH), 7.12 (m, 2 H, Ar-H), 7.24 (m, 4 H, Ar-H) ppm. – $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): $\delta = -0.53$ (SiCH_3), 24.5 (iPr-CH_3), 25.3 (iPr-CH_3), 25.7 (thf-CH_2), 28.3 (iPr-CH), 68.2 (thf-O), 97.6 ($\text{N}_2\text{CC}\equiv\text{C}$), 99.8 ($\text{N}_2\text{CC}\equiv\text{C}$), 122.4 (4- Ar-CH), 122.8 (3,5- Ar-CH), 143.2 (2,6- Ar-C), 149.3 (1- Ar-C), 156.1 (N_2C) ppm. – ^7Li NMR (117 MHz, C_6D_6): $\delta = 1.67$ ppm. – IR (ATR): $\tilde{\nu} = 2960$ (s), 2867 (w), 2161 (m), 1615 (vs), 1586 (m), 1507 (w), 1457 (m), 1441 (m), 1380 (m), 1360 (m), 1321 (m), 1252 (m), 1208 (s), 1187 (w), 1099 (w), 1059 (w), 1043 (vw), 951 (w), 935 (w), 870 (vs), 845 (vs), 829 (s), 805 (w), 795 (m), 777 (w), 760 (m), 750 (vs), 700 (w), 633 (w), 597 (m), 555 (m), 506 (s), 441 (s) cm^{-1} . Raman (solid state): $\tilde{\nu} = 3051$ (w), 2962 (vs), 2934 (vs), 2897 (vs), 2866 (vs), 2140 (vs), 1590 (s), 1510 (m), 1443 (s), 1369 (m), 1313 (m), 1243 (m), 1106 (w), 1044 (m), 914 (w), 887 (m), 692 (w), 633 (m), 446 (w), 279 (m), 181 (m), 75 (vs) cm^{-1} . – HR-ESI-MS (thf): m/z (%) = 461.33 (calc. = 461.33) ($[\text{M-Li}(\text{C}_4\text{H}_8\text{O})_3+2\text{H}^+]^+$, 100). Elemental analysis calcd. (%) for $[\text{C}_{42}\text{H}_{67}\text{LiN}_2\text{O}_3\text{Si}]$ (683.03): C 73.86, H 9.89, N 4.10; found C 73.80, H 9.78, N 4.09.

Synthesis of $[\{\text{Me}_3\text{SiC}\equiv\text{CC}(\text{NDipp})_2\}_2\text{Au}_2]$ (**2**)

644 mg of compound **1** (0.94 mmol, 2.00 eq) and 302 mg chloro(tetrahydrothiophene)gold(I) (0.94 mmol, 2.00 eq.) were dissolved in 25 mL thf and stirred at ambient temperature overnight. The solvent was evaporated under vacuum and the solid residue was extracted with 35 mL dichloromethane and filtered. The solvent was evaporated and the remaining off white solid was dried under vacuum. Yield: 554 mg (89 %). Single crystals suitable for X-Ray structure determination were grown by slow evaporation of thf within 3 days.

^1H NMR (300 MHz, thf- d_8): δ = -0.41 (s, 18 H, SiCH_3), 1.26 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 24 H, iPr-CH_3), 1.32 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 24 H, iPr-CH_3), 3.68 (hept, $^3J_{\text{HH}}$ = 6.9 Hz, 8 H, iPr-CH), 7.00 (s, 12 H, Ar-H) ppm. – $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = -1.1 (SiCH_3), 24.87 (iPr-CH_3), 24.93 (iPr-CH_3), 28.6 (iPr-CH), 97.3 ($\text{N}_2\text{CC}\equiv\text{C}$), 109.0 ($\text{N}_2\text{CC}\equiv\text{C}$), 124.0 (3,5- Ar-CH), 126.9 (4- Ar-CH), 144.4 (2,6- Ar-C), 145.6 (1- Ar-C), 160.0 (N_2C) ppm. – IR (ATR): $\tilde{\nu}$ = 2959 (w), 2927 (vw), 2867 (vw), 1503 (vs), 1464 (w), 1445 (w), 1376 (w), 1360 (w), 1322 (w), 1249 (m), 1215 (vw), 1103 (vw), 1058 (vw), 969 (w), 913 (w), 845 (s), 798 (w), 782 (w), 760 (w), 751 (m), 723 (vw), 717 (vw), 695 (w), 637 (w), 512 (vw), 429 (w) cm^{-1} . – Raman (solid state): $\tilde{\nu}$ = 3063 (vw), 2961 (w), 2900 (s), 2167 (vs), 1591 (m), 1445 (w), 1375 (m), 1269 (w), 1181 (vw), 1047 (vw), 888 (vw), 720 (vw), 639 (vw), 605 (vw), 536 (vw), 448 (vw) cm^{-1} . – HR-ESI-MS: m/z (%) = 1312.67 (calc. = 1312.57) ($[\text{M}]^+$, 2.6). **Elemental analysis** calcd. (%) for $[\text{C}_{60}\text{H}_{86}\text{Au}_2\text{N}_4\text{Si}_2]$ (1313.48): C 54.87, H 6.60, N 4.27; found C 55.01, H 6.58, N 4.42.

Synthesis of $[\text{Au}_8\{\mu_3-(\eta^1:\eta^2\text{-C}\equiv\text{C})\}_2(\text{Me}_3\text{SiC}\equiv\text{CC}(\text{NDipp})_2)_4(\text{tth})_2]$ (**3**)

Method A: 260 mg of **2** (0.20 mmol, 2.00 eq.), 21 mg lithium trimethylsilylacetylide (0.20 mmol, 2.00 eq.) and 127 mg chloro(tetrahydrothiophene)gold(I) (0.40 mmol, 4.00 eq.) were dissolved in 15 mL thf and the mixture was stirred for 72 h at ambient temperature. The solvent was evaporated and the residue extracted with 15 mL dichloromethane was filtrated. The product was crystallized by slow evaporation of the solvent. The obtained colorless block shaped crystals were washed with cold dichloromethane after decantation of the residual mother liquor. The product was isolated after drying under vacuum. Crystalline yield: 126 mg (35 %).

Method B: 300 mg **1** (0.44 mmol, 4.00 eq.), 23 mg lithium trimethylsilylacetylide (0.22 mmol, 2.00 eq.) and 282 mg chloro(tetrahydrothiophene)gold(I) (0.88 mmol, 8.00 eq.) were dissolved in 20 mL thf and the mixture was stirred for 72 h at ambient temperature. The workup was similar to method A. Crystalline yield: 150 mg (38 %).

^1H NMR (300 MHz, 333 K, C_6D_6): δ = -0.36 (s, 18 H, SiCH_3), -0.28 (s, 18 H, SiCH_3), 0.67 (d, $^3J_{\text{HH}}$ = 6.9 Hz, 12 H, iPr-CH_3), 1.24 (d, 6.9 Hz, 12 H, iPr-CH_3), 1.42 (m, 48 H, iPr-CH_3), 1.57 (m, 24 H, iPr-CH_3), 1.70 (m, 8 H, SCH_2CH_2), 3.31 (m, 8 H, SCH_2), 3.77 (m, 16 H, iPr-CH), 6.87 (m, 6 H, Ar-H), 7.09 (m, 4 H, Ar-H), 7.18 (m, 14 H, Ar-H) ppm. – $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ = -1.2 (SiCH_3), -1.0 (SiCH_3), 23.3 (iPr-CH_3), 23.8 (iPr-CH_3), 24.7 (iPr-CH_3), 25.3 (iPr-CH_3), 27.8 (iPr-CH), 28.0 (iPr-CH), 28.1 (iPr-CH), 30.6 (SCH_2CH_2), 41.4 (SCH_2CH_2), 96.7 ($\text{N}_2\text{CC}\equiv\text{C}$), 97.8 ($\text{N}_2\text{CC}\equiv\text{C}$), 107.3 ($\text{N}_2\text{CC}\equiv\text{C}$), 110.0 ($\text{N}_2\text{CC}\equiv\text{C}$), 123.0, 123.9, 126.0, 126.3, 126.7, 127.6, 143.7 (Ar-C), 144.0 (Ar-C), 144.1 (Ar-C), 144.49 (Ar-C), 144.52 (Ar-C), 145.8 (Ar-C), 154.2 (N_2C) 155.3 (N_2C) ppm. – IR (ATR): $\tilde{\nu}$ = 2958 (m), 2866 (w), 2163 (vw), 1906 (vw), 1509 (vs), 1460 (w), 1441 (w), 1400 (w), 1382 (m), 1360 (w), 1322 (m), 1250 (m), 1213 (w), 1179 (w), 1101 (w), 1056 (w), 978 (w), 909 (w), 843 (vs), 798 (m), 782 (m), 755 (m), 722 (w), 696 (w), 638 (m), 513 (w), 430 (m) cm^{-1} . – Raman (solid state): $\tilde{\nu}$ = 3062 (vw), 2959 (m), 2933 (m), 2900 (s), 2865 (w), 2163 (vs), 1910 (vs), 1591 (s), 1451 (m), 1401 (s), 1385 (m), 1261 (m), 1180 (w), 1162 (w), 1180 (w), 1162 (vw), 1108 (vw), 1046 (vw), 887 (vw), 719 (vw), 640 (vw), 604 (w), 540 (vw), 454 (vw) cm^{-1} . – HR-ESI-MS (thf): m/z (%) =

3677.067 (calc. = 3677.05) ($[M+K]^+$, 29.33); 3551.073 (calc. = 3551.06) ($[M-C_4H_8S+H]^+$, 100); 3463.04 (calc. = 3463.02) ($[M-(C_4H_8S)_2+H]^+$, 50.58)]. **Elemental analysis** calcd. (%) for $[C_{132}H_{188}Au_8N_8S_2Si_4]$ (3639.20): C 43.57, H 5.21, N 3.08, S 1.76; found C 43.83, H 5.08, N 3.06, S 1.75.

Synthesis of lithium trimethylsilylacetylide, $Me_3SiC\equiv CLi$

1.36 mL of trimethylsilylacetylene (0.943 mg, 9.60 mmol, 1.00 eq.) were solved in 20 mL of diethylether and cooled to $-78\text{ }^{\circ}\text{C}$. 4.03 mL of a 2.5 molar *n*-butyllithium solution in *n*-hexane (615 mg, 9.60 mmol, 1.00 eq.) was added slowly. The reaction mixture was stirred for 15 min at $-78\text{ }^{\circ}\text{C}$ and afterwards allowed to warm to ambient temperature. The solvent was evaporated and the resulting white solid was dried under vacuum for 1 h. The product was isolated as a white powder. Yield: 990 mg (99 %).

^1H NMR (300 MHz, THF- d_8): $\delta = -0.03$ (s, $SiCH_3$) ppm. – $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, THF- d_8): $\delta = 1.9$ ($SiCH_3$), 118.3 (CSi), 167.2 (CLi) ppm. – ^7Li NMR (117 MHz, THF- d_8): $\delta = 0.08$ ppm. **IR** (ATR): $\tilde{\nu} = 2960$ (vw), 2900 (vw), 1983 (vw), 1408 (vw), 1263 (w), 1246 (m), 834 (vs), 757 (s), 695 (w), 653 (vs), 568 (s), cm^{-1} .

NMR Spectra

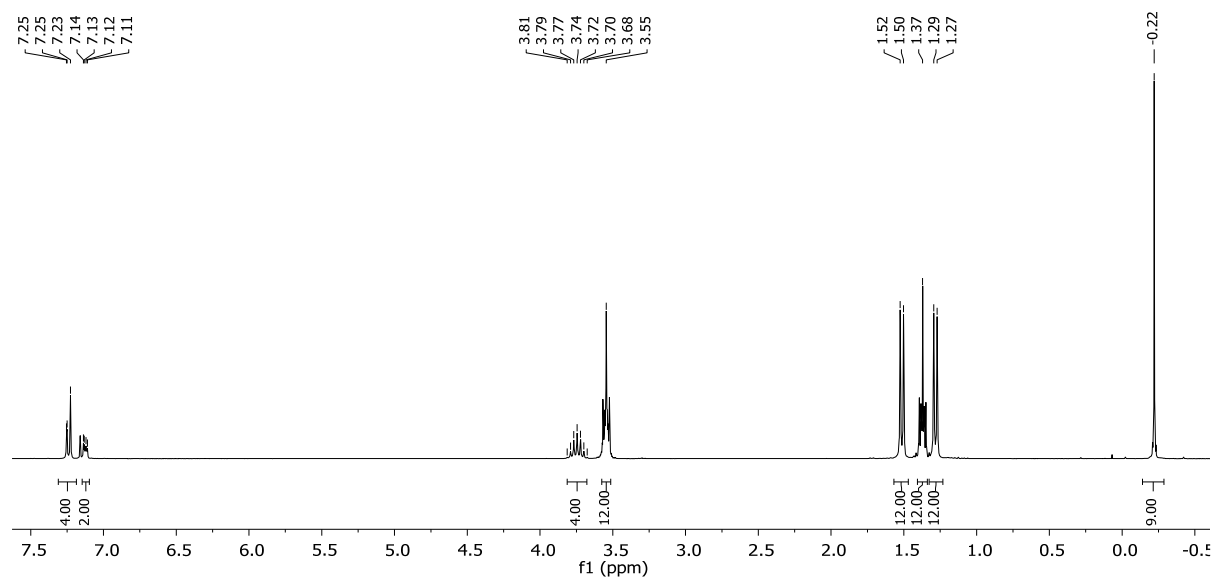


Figure S1 ¹H NMR spectrum of compound **1** in C₆D₆ at 25 °C.

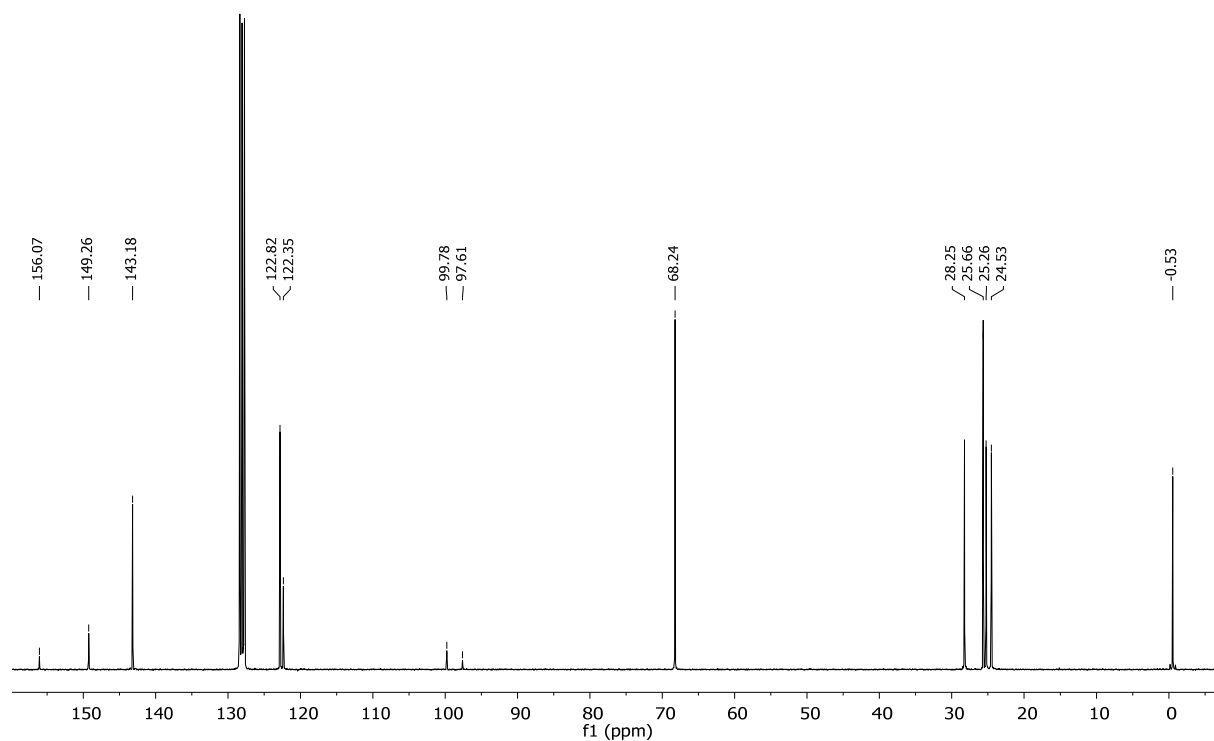


Figure S2 ¹³C{¹H} NMR spectrum of compound **1** in C₆D₆ at 25 °C.

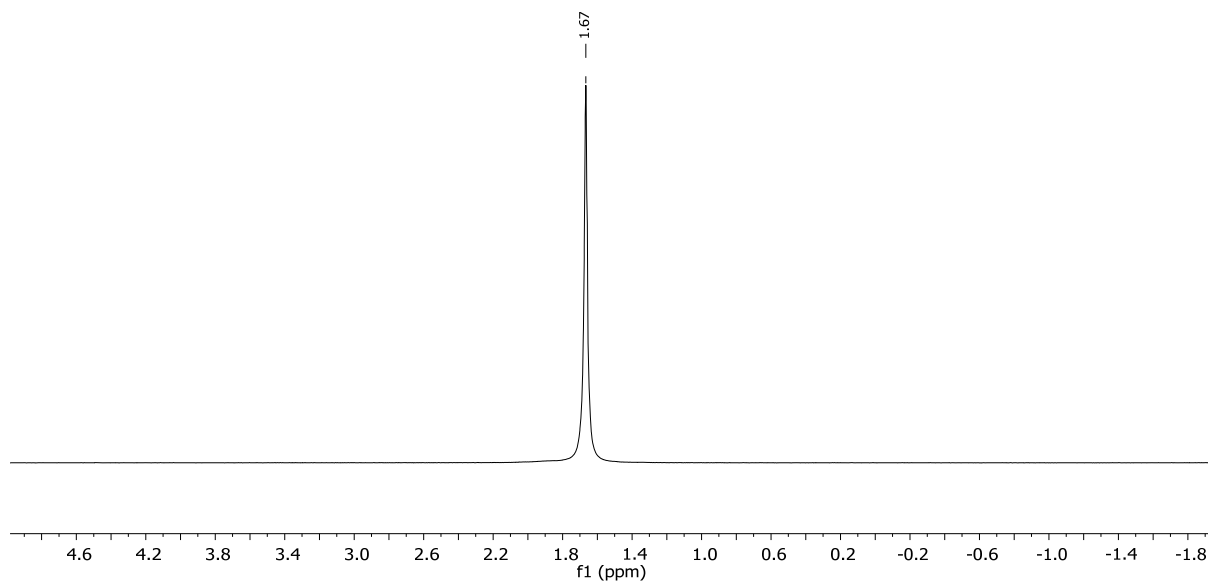


Figure S3 ^7Li NMR spectrum of compound **1** in C_6D_6 at 25 °C.

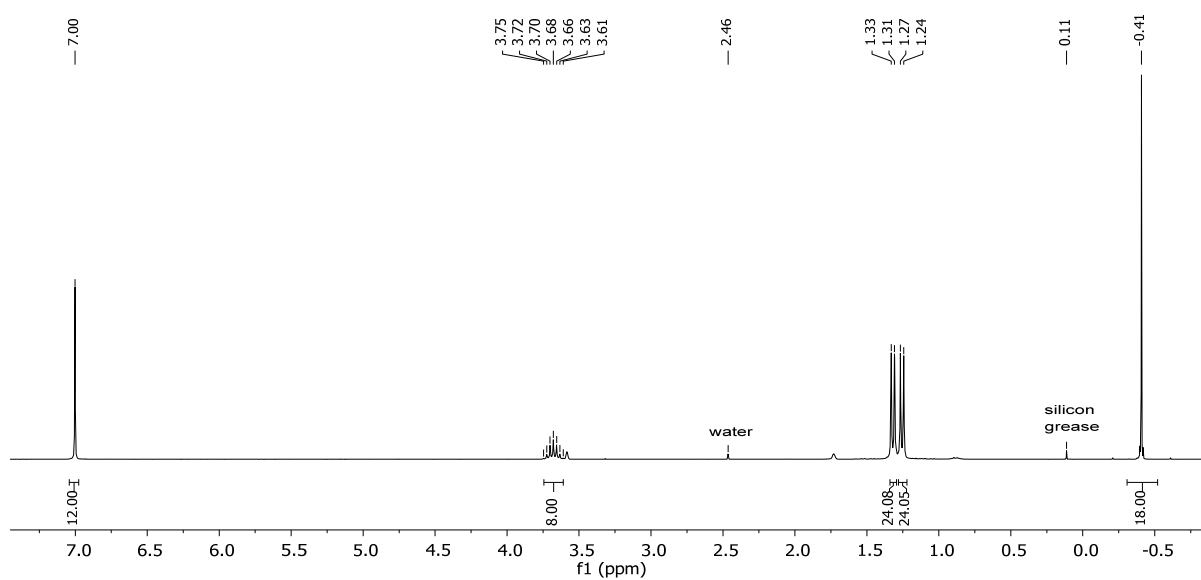


Figure S4 ^1H NMR spectrum of compound **2** in thf-d_8 at 25 °C.

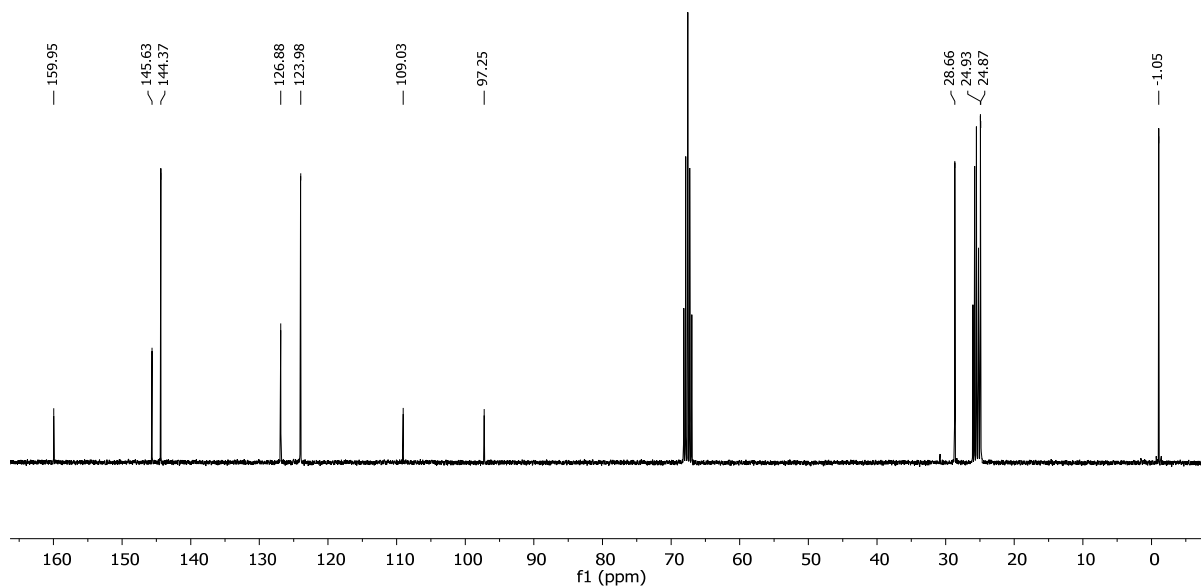


Figure S5 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound **2** in thf-d_8 at 25 °C.

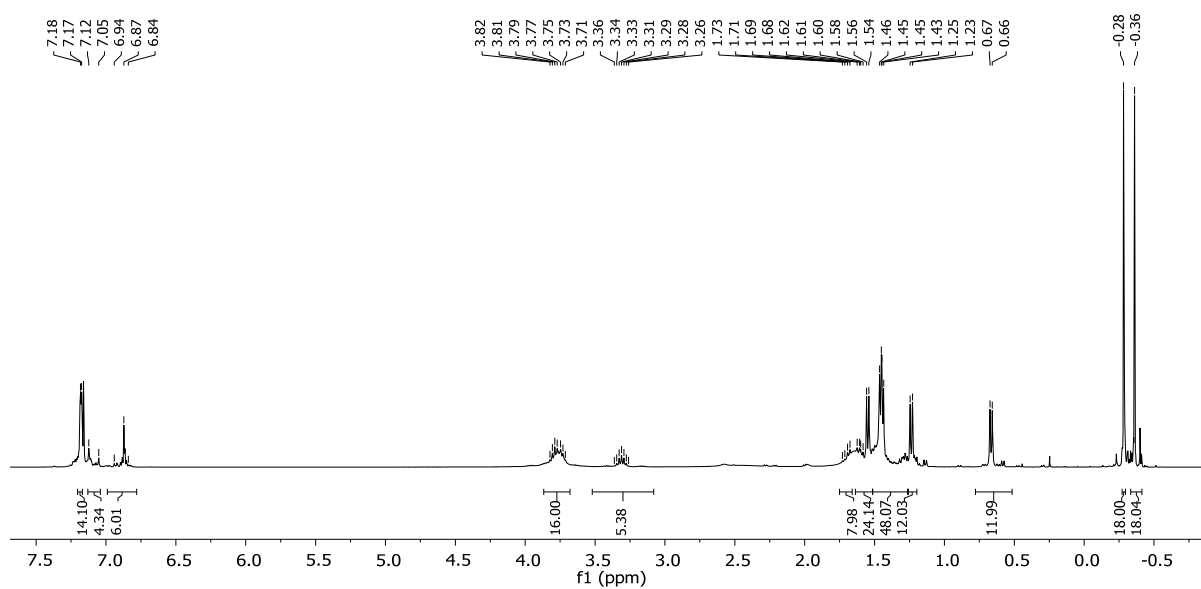


Figure S6 ^1H NMR of compound **3** in C_6D_6 at 60 °C.

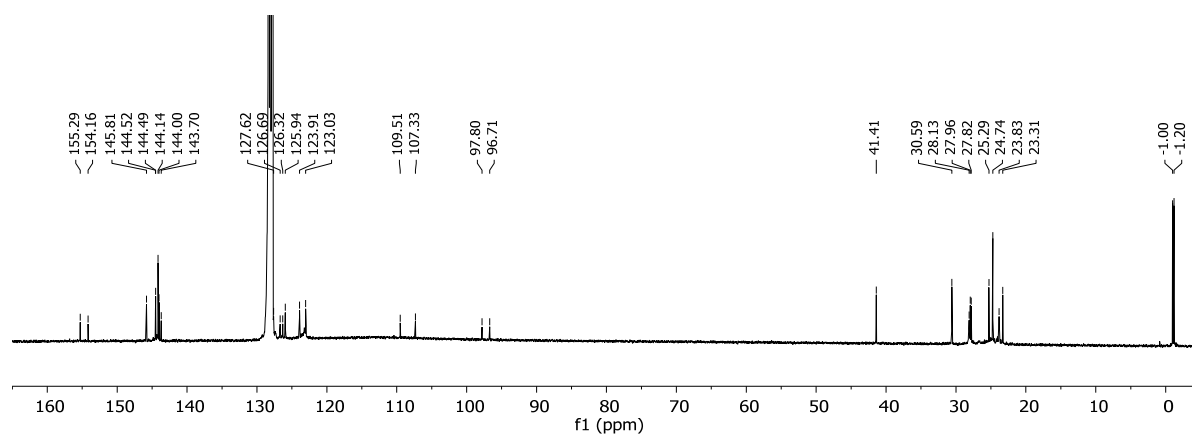


Figure S7 $^{13}\text{C}\{^1\text{H}\}$ NMR of compound **3** in C_6D_6 at 25 °C with 32959 scans.

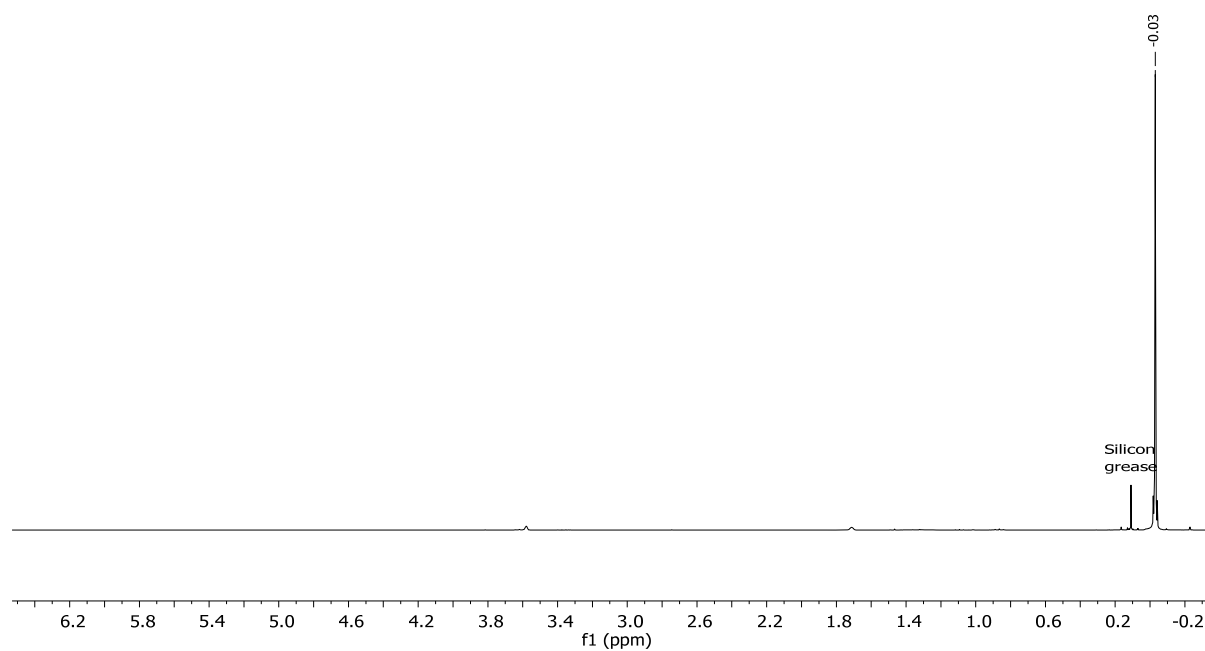


Figure S8 ^1H NMR spectrum of $\text{Me}_3\text{SiC}\equiv\text{CCl}$ in thf-d_8 at 25 °C.

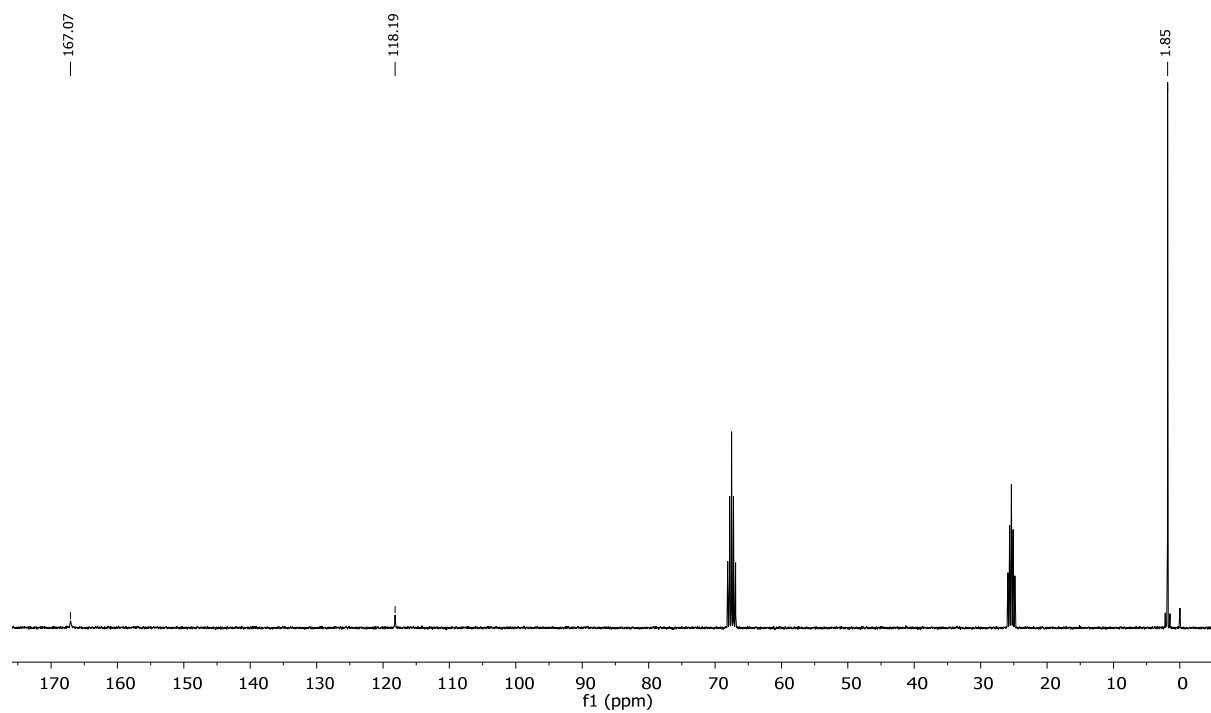


Figure S9 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of $\text{Me}_3\text{SiC}\equiv\text{CLi}$ in thf-d_8 at 25 °C.

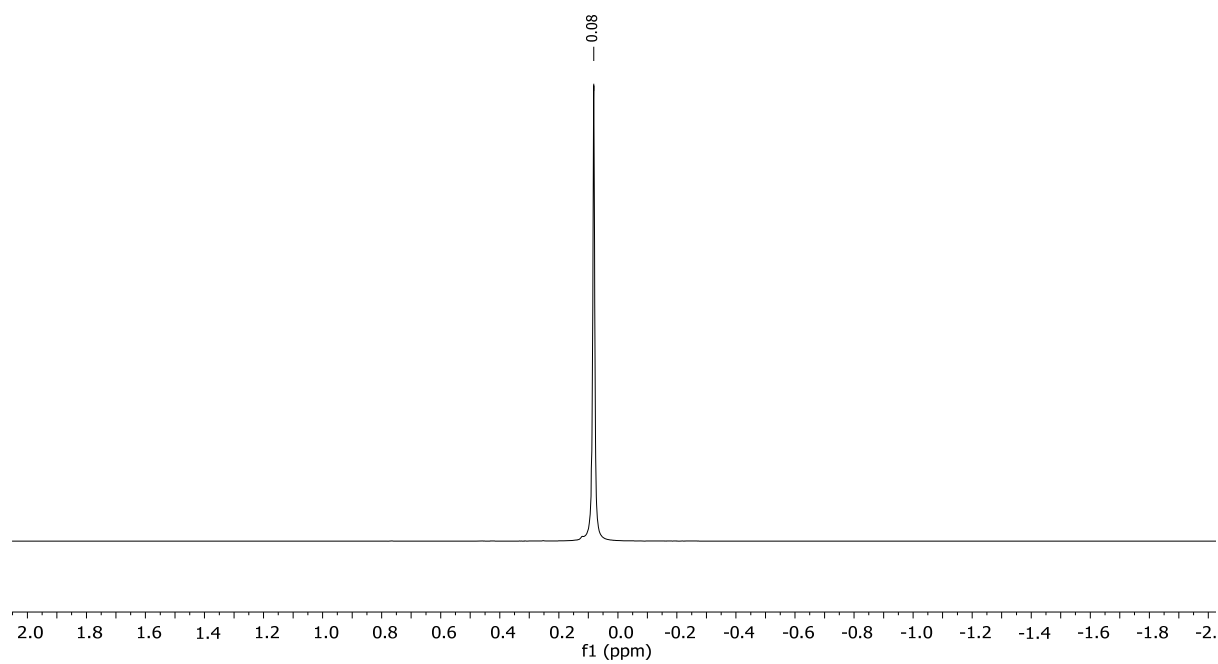


Figure S10 ^7Li NMR spectrum of $\text{Me}_3\text{SiC}\equiv\text{CLi}$ in thf-d_8 at 25 °C.

IR Spectra

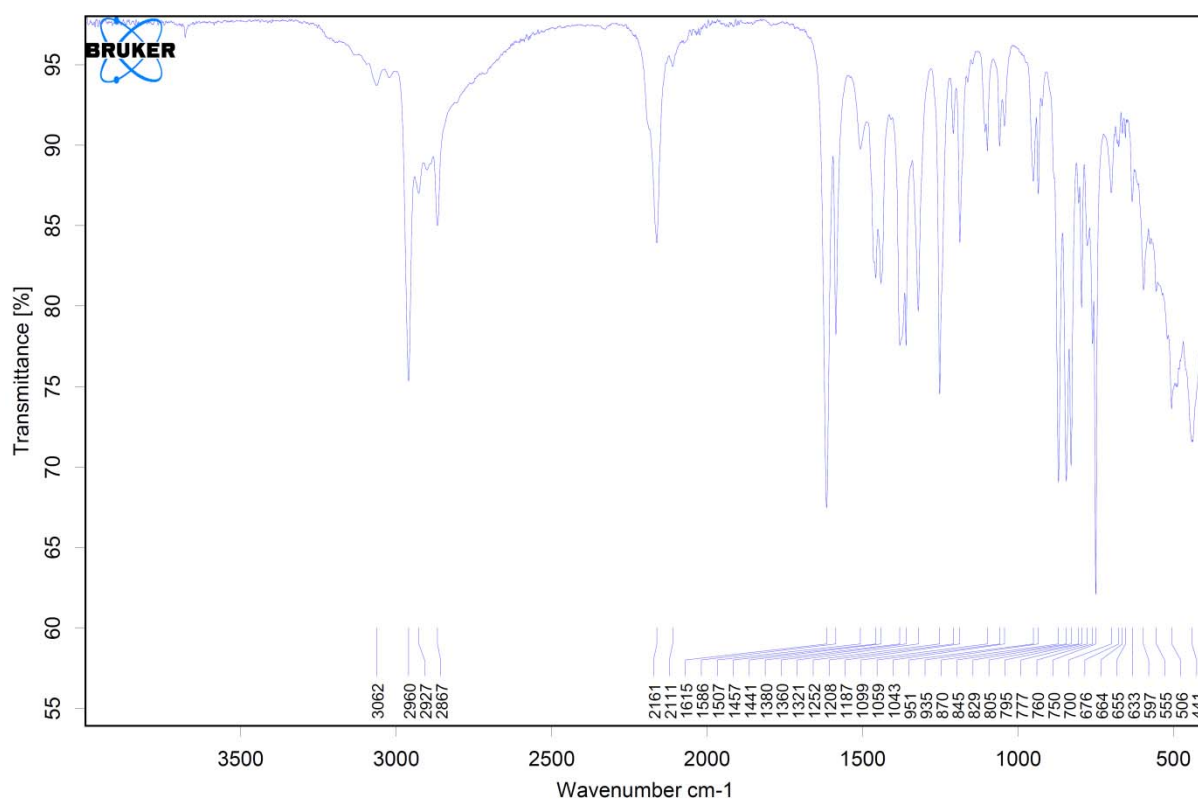


Figure S11 IR spectrum of compound 1.

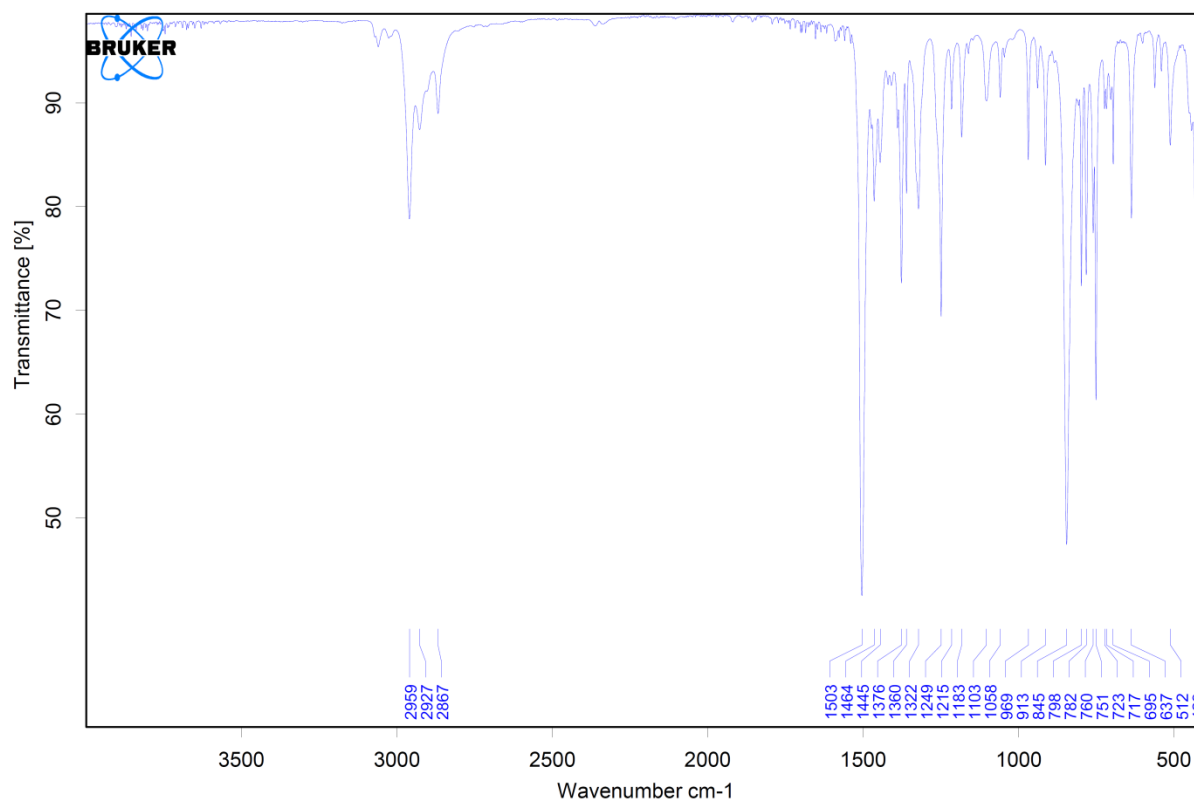


Figure S12 IR spectrum of compound 2.

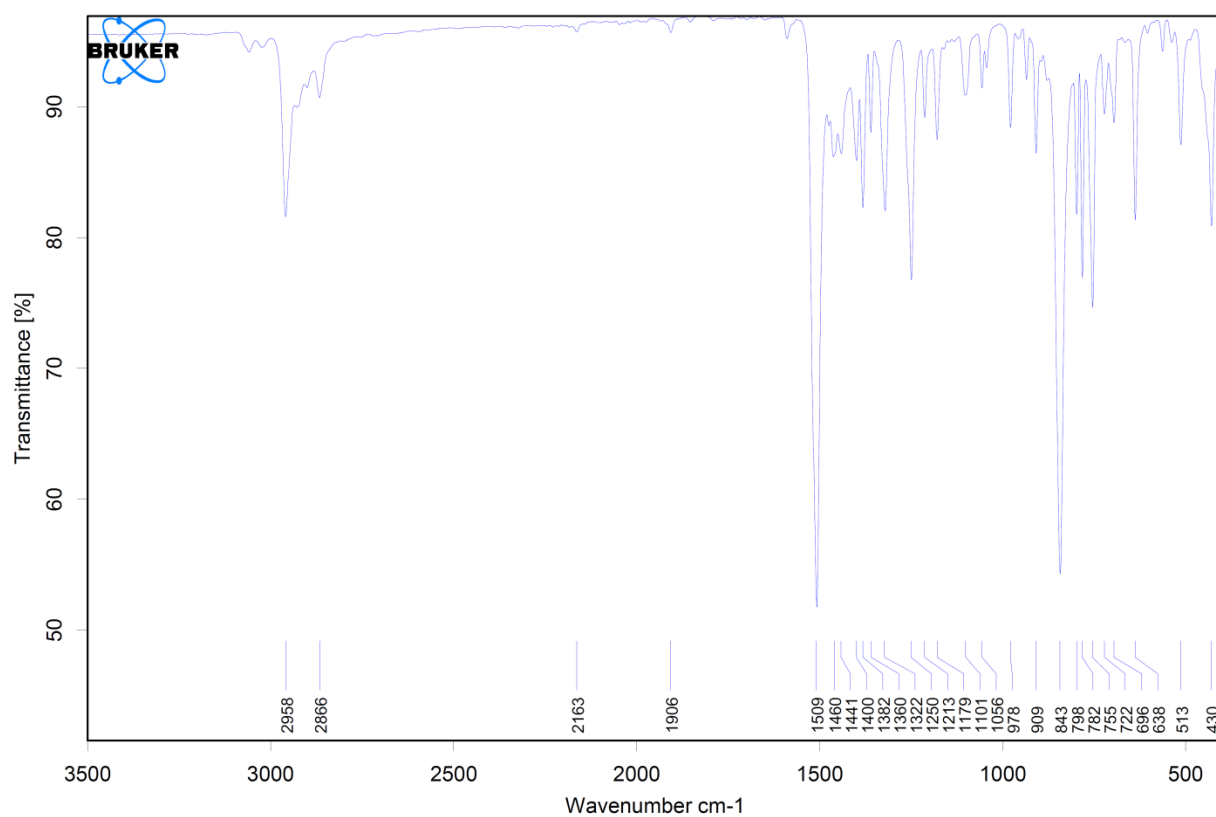


Figure S13 IR spectrum of compound **3**.

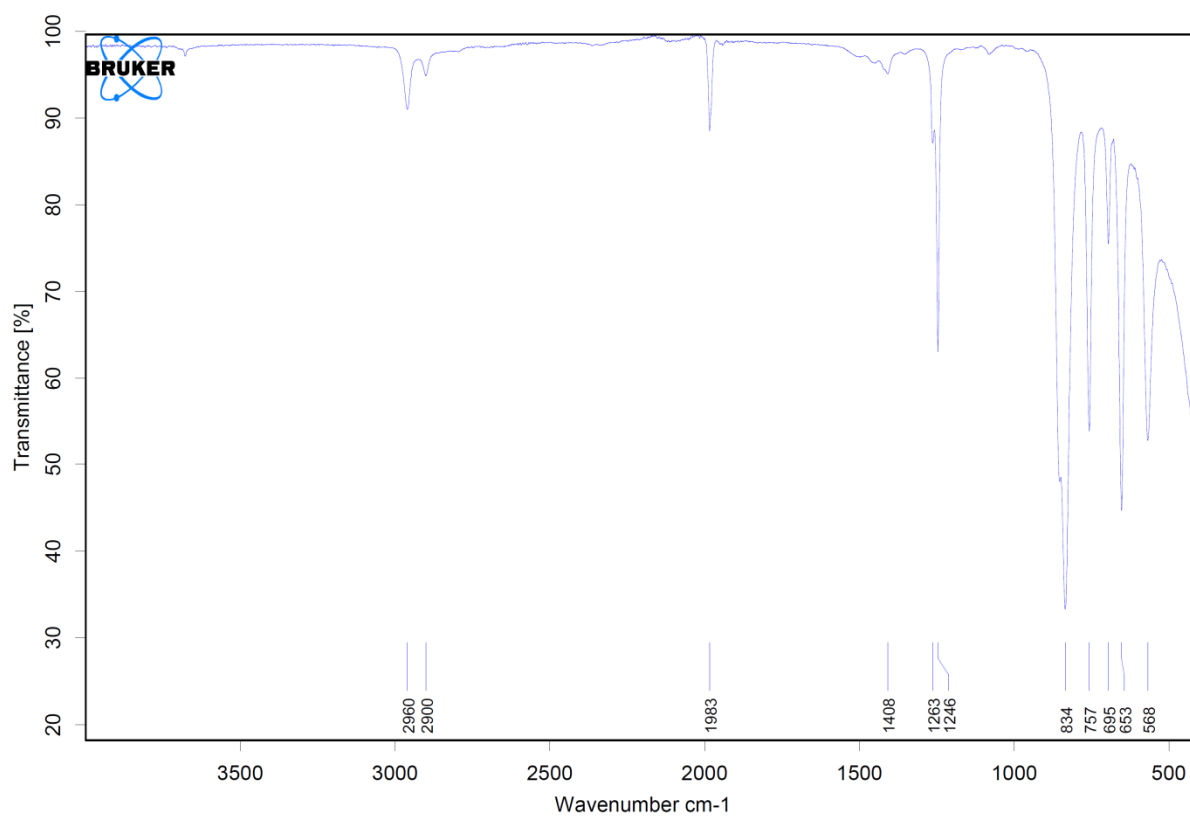


Figure S14 IR spectrum of Me₃SiC≡CCLi.

Raman Measurements

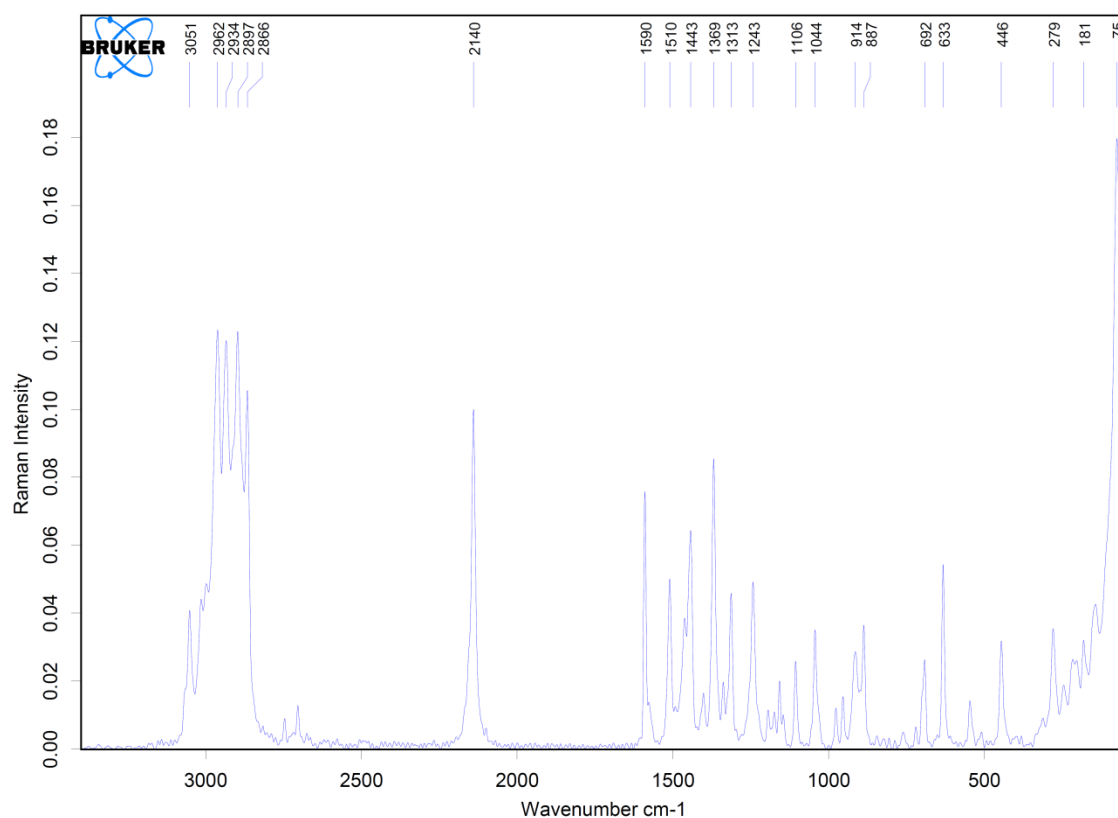


Figure S15 Raman spectrum of compound **1**. $\nu(\text{C}\equiv\text{C}) = 2140 \text{ cm}^{-1}$.

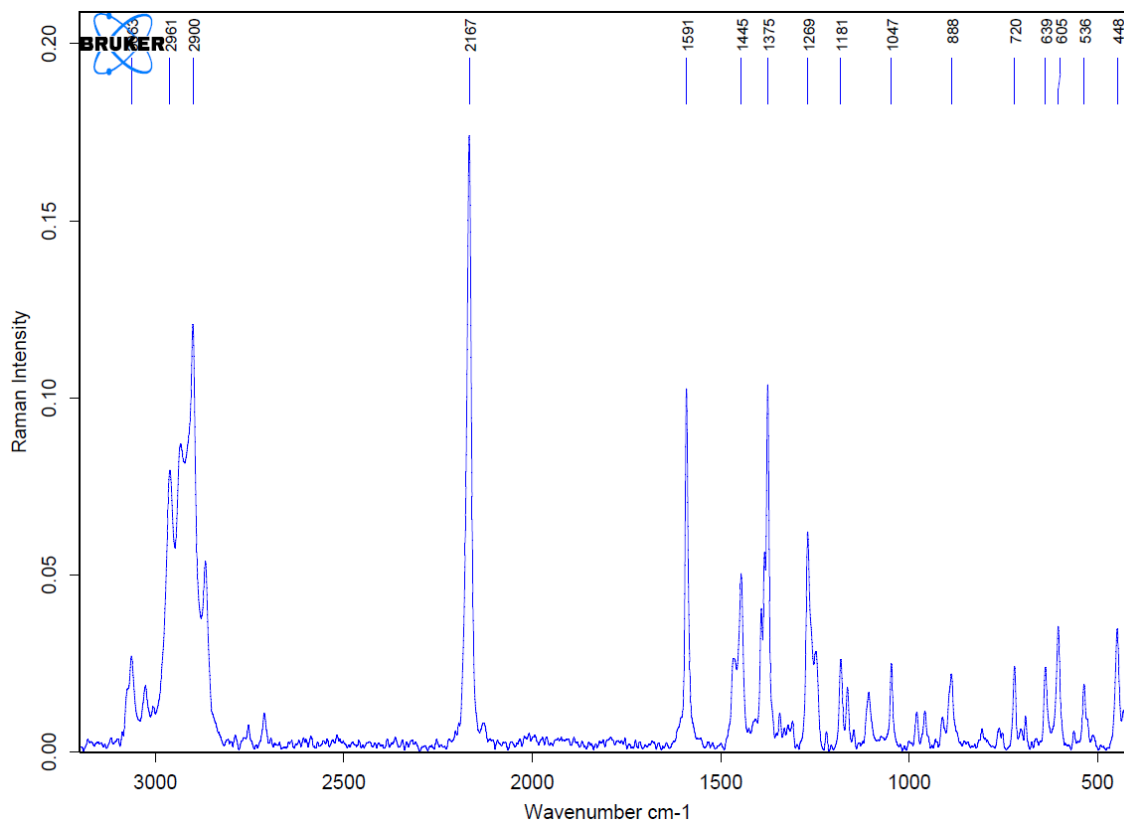


Figure S16 Raman spectrum of compound **2**. $\nu(\text{C}\equiv\text{C}) = 2167 \text{ cm}^{-1}$.

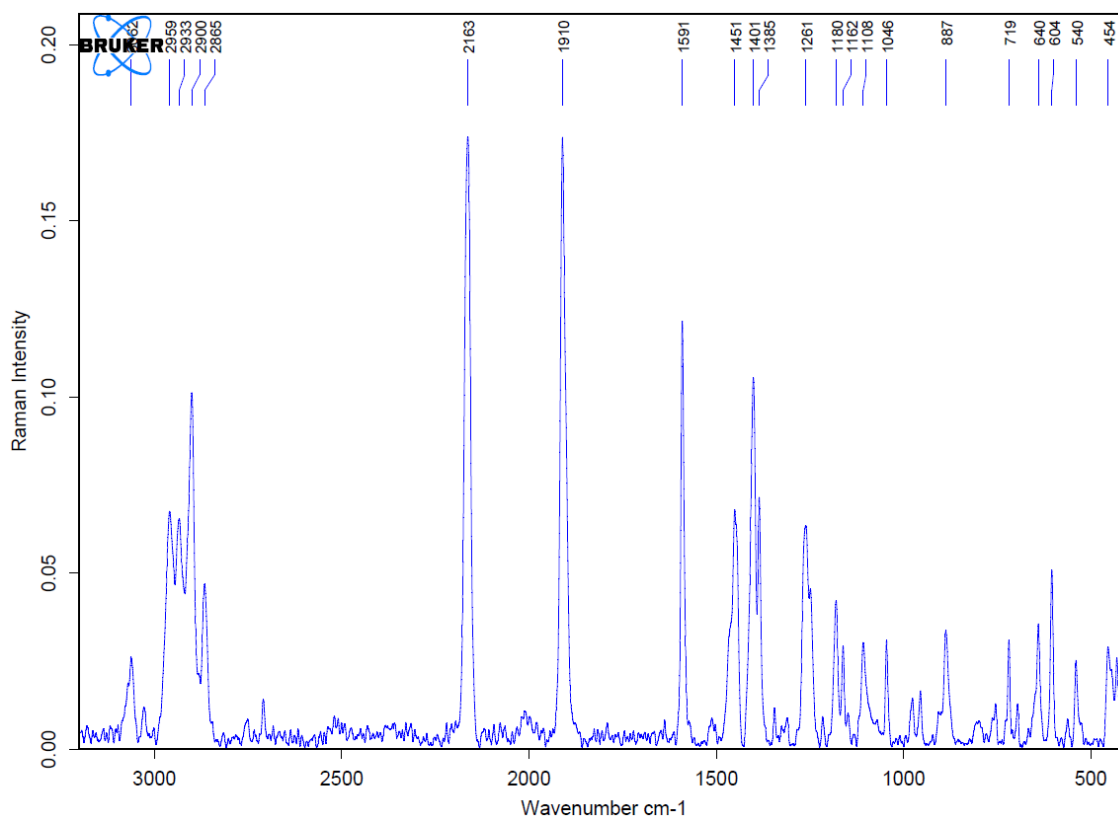


Figure S17 Raman spectrum of compound **3**. $\nu(\text{C}\equiv\text{C}) = 2163 \text{ cm}^{-1}$; $\nu(\mu_3-(\eta^1:\eta^2\text{-C}\equiv\text{C})) = 1910 \text{ cm}^{-1}$.

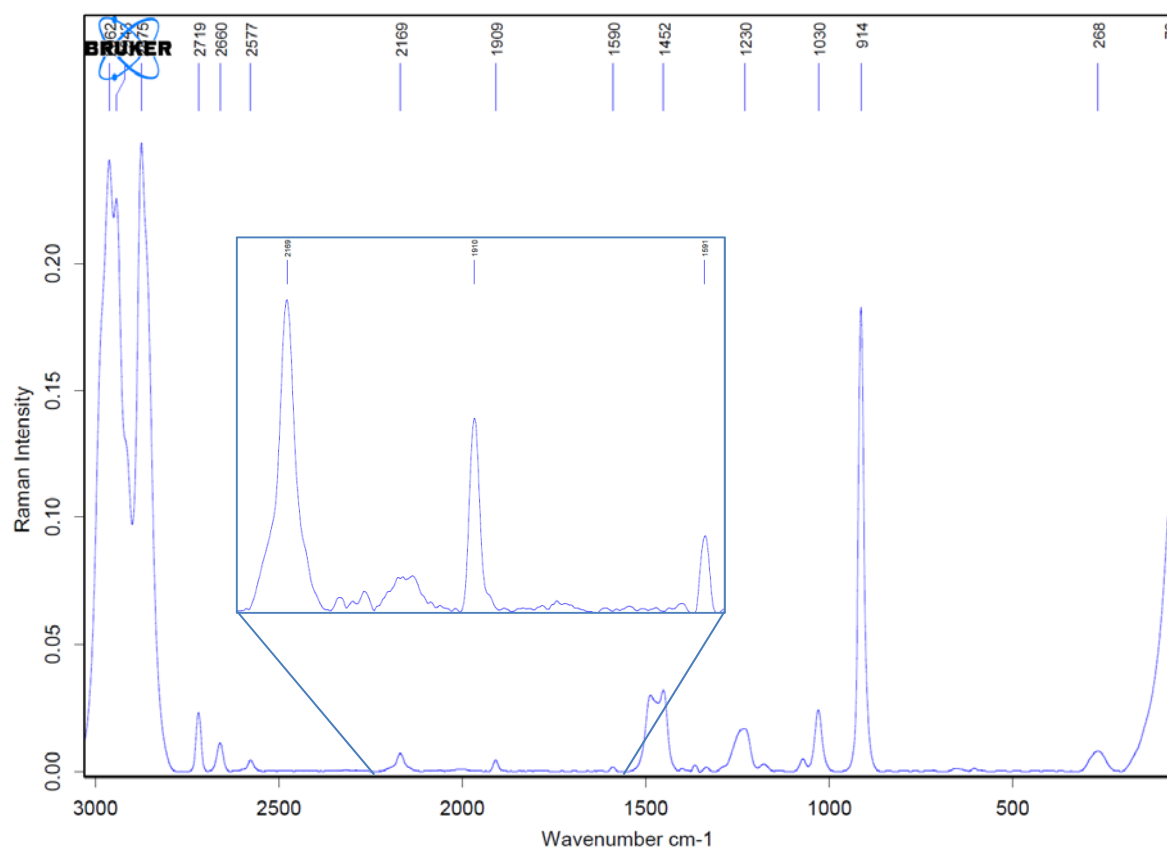


Figure S18 Raman spectrum of compound **3** in thf. $\nu(\text{C}\equiv\text{C}) = 2163 \text{ cm}^{-1}$; $\nu(\mu_3-(\eta^1:\eta^2\text{-C}\equiv\text{C})) = 1910 \text{ cm}^{-1}$. The inset shows the alkyne vibrations in detail.

Mass Spectra

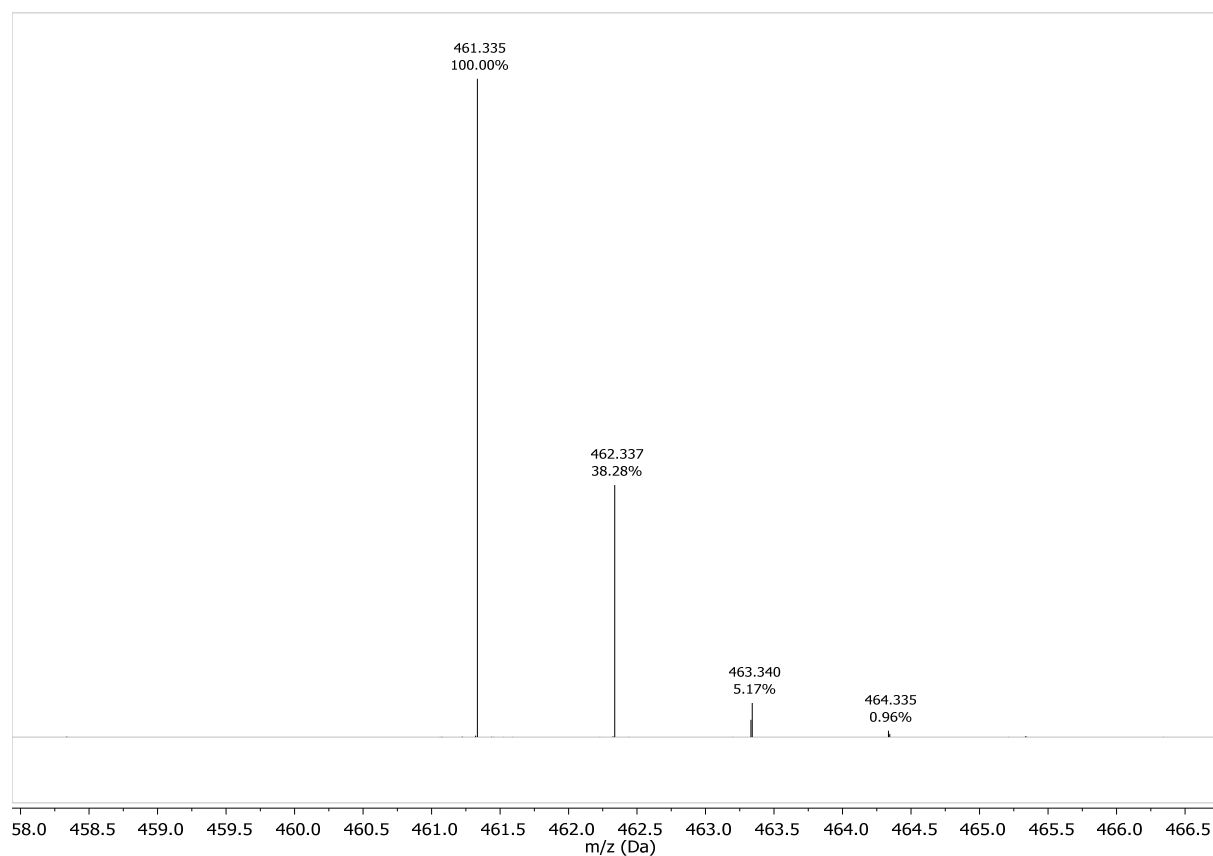


Figure S19 Isotope pattern of the main peak of compound **1**. HR-ESI-MS measurement in thf.

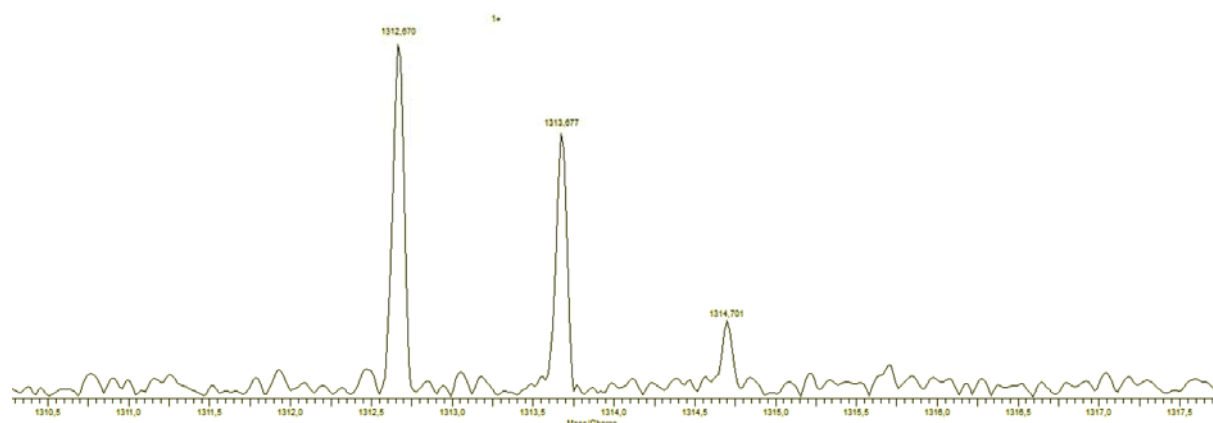


Figure S20 Isotope pattern of the molecule peak of compound **2**. HR-ESI-MS measurement in thf.

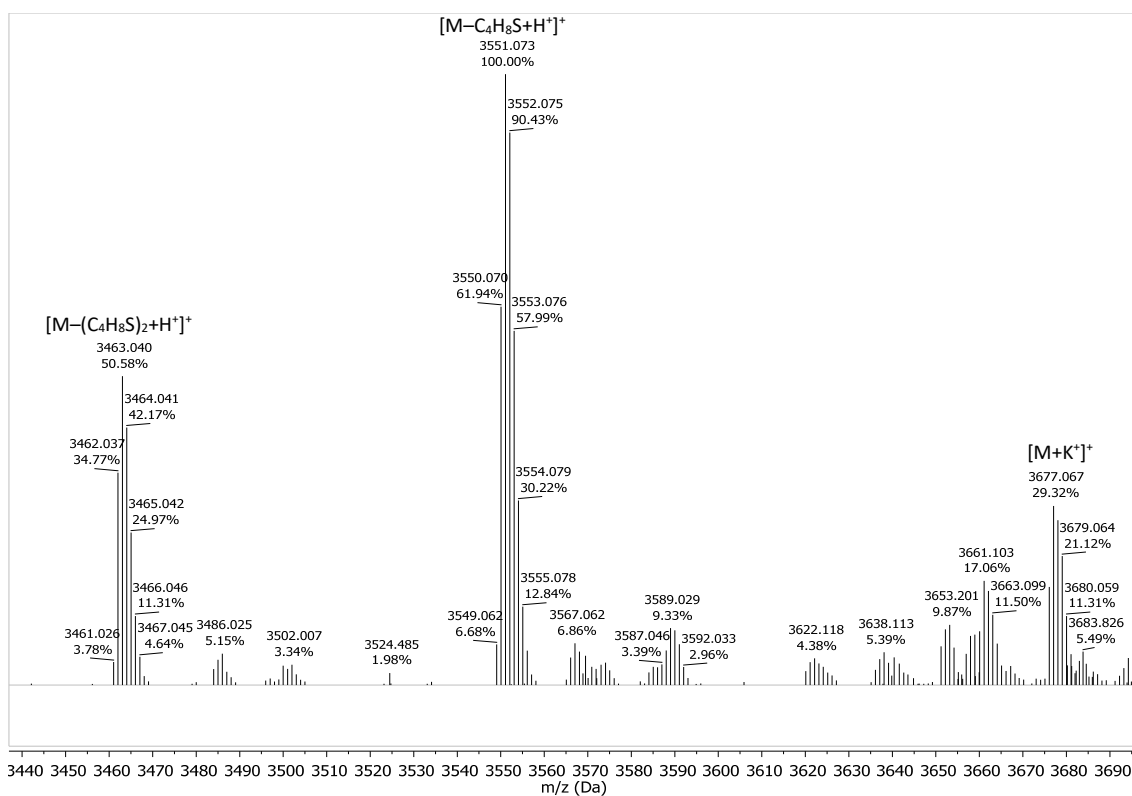


Figure S21 Mass spectrum of compound **3** HR-ESI-MS measurement in thf.

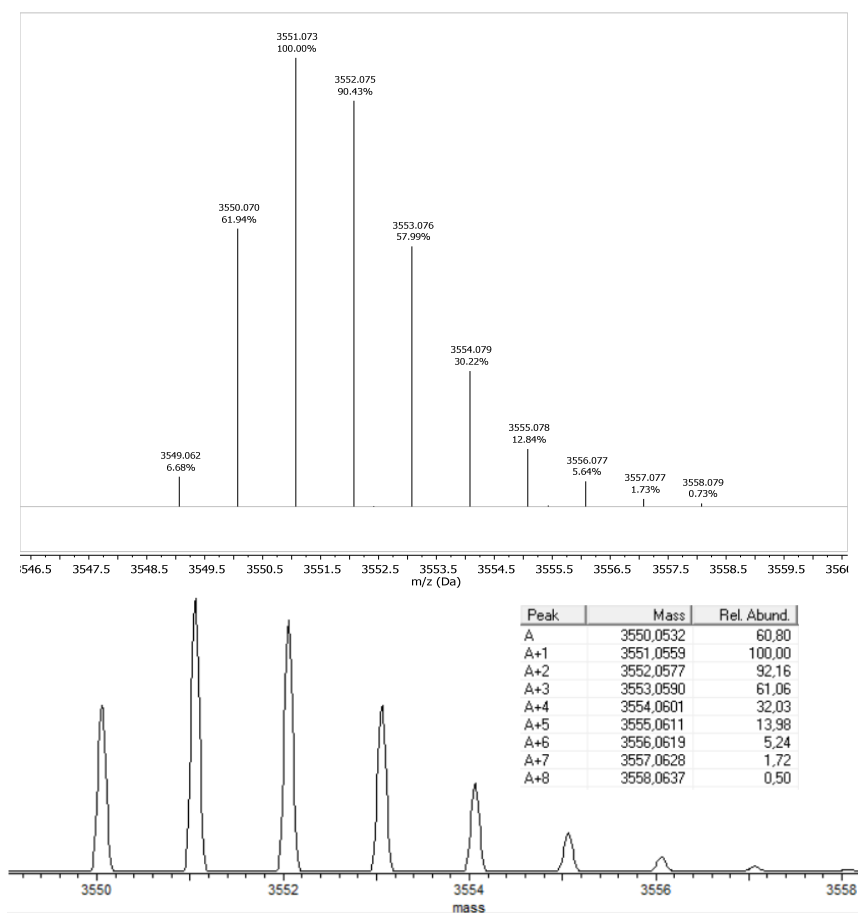


Figure S22 Isotope pattern of the main peak $[M-C_4H_8S+H]^+$ of compound **3** (top), calculated pattern (bottom).

UV/Vis Spectra

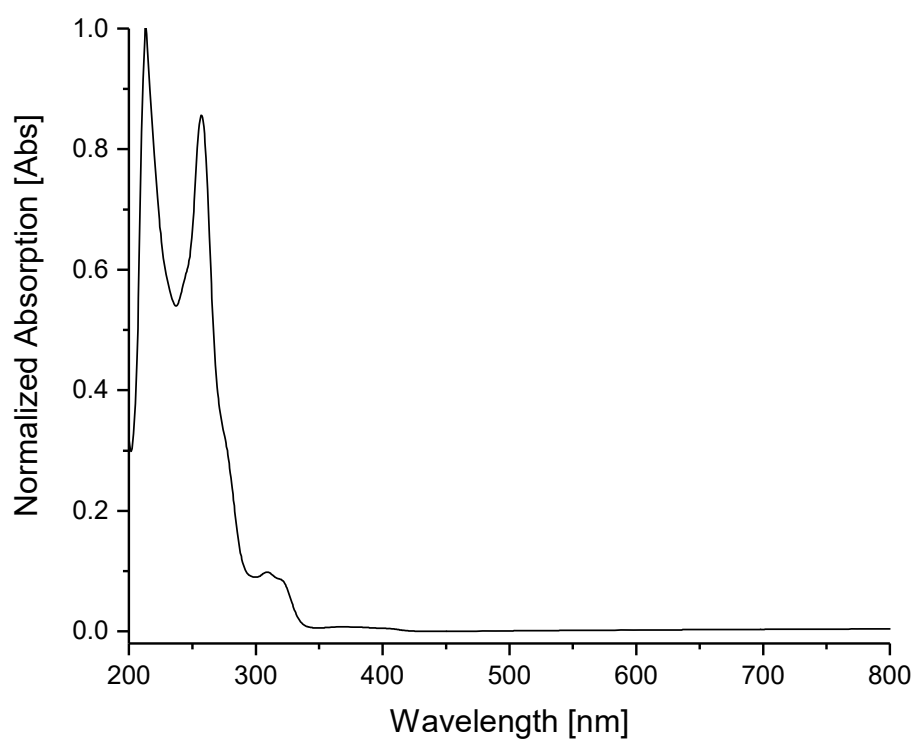


Figure S23 UV/Vis spectrum of compound **2** in thf with maxima at $\lambda_1 = 213$ nm, $\lambda_2([5d\sigma \rightarrow 6p\sigma^*]) = 257$ nm, and $\lambda_3 309$ nm.^[2]

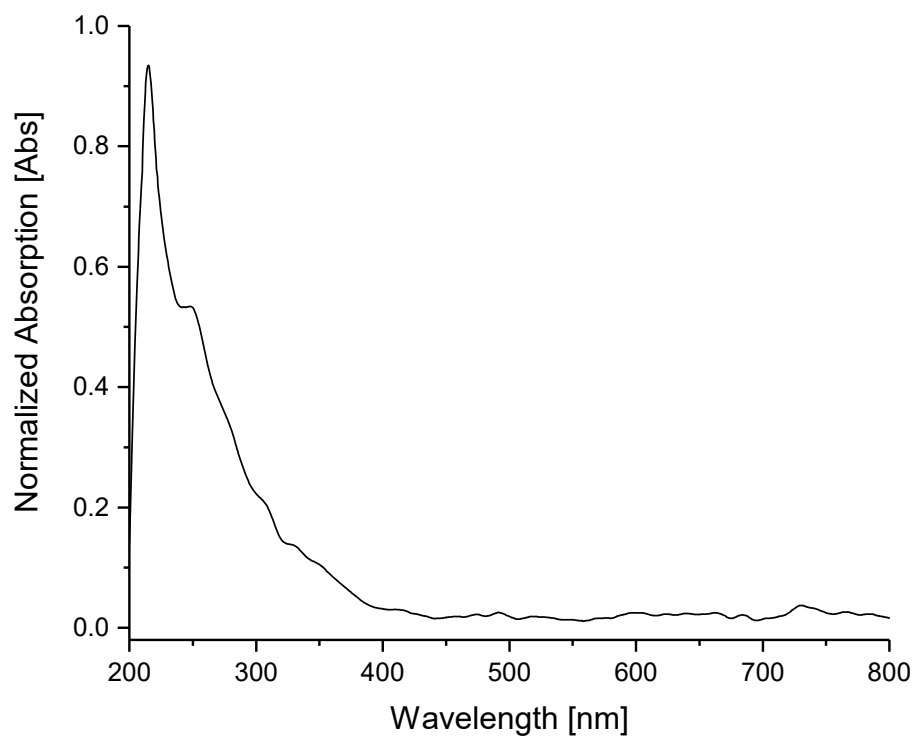


Figure S24 UV/Vis spectrum of compound **3** in thf with maxima at $\lambda_1 = 215$ nm and $\lambda_2([5d\sigma \rightarrow 6p\sigma^*]) = 249$ nm.^[2]

Fluorescence and Quantum Yield Determination

Excitation and emission spectra were recorded using a HORIBA Jobin Yvon Fluorolog 3 photoluminescence spectrometer equipped with a continuous 450 W xenon lamp, double monochromators for excitation and emission beams, an integrating sphere (Ulbricht sphere), and a photomultiplier tube (PMT) as the detector. Excitation and emission spectra were corrected using standard corrections, including the spectral intensity distribution of the lamp, the reflection behavior of the Ulbricht sphere, and the sensitivity of the detector. The determination of the absolute quantum yield was performed as suggested by Friend and co-workers.³ All samples were investigated as solids as well as in solution in thf in spectroscopically pure quartz cuvettes in the front-face mode. For comparison, spectra measured in *n*-heptane solution are shown. First of all, the diffuse reflection of the samples was measured under excitation conditions. Thereafter, the emission was determined at this excitation wavelength. Integration over the reflected and emitted photons by use of the Ulbricht sphere results in the absolute quantum yield.

Phosphorescence Examination

When closing the shutter of the excitation source, however, not any remaining emission is visible for compounds **2** (Figure S25) and **3**. The period for closing the shutter is about 100 ms. If the decay is significantly below 100 ms, certain emission would nevertheless be visible, which is not the case. Therefore, the decay can be considered $\ll 10$ ms, and thus, phosphorescence can be excluded.

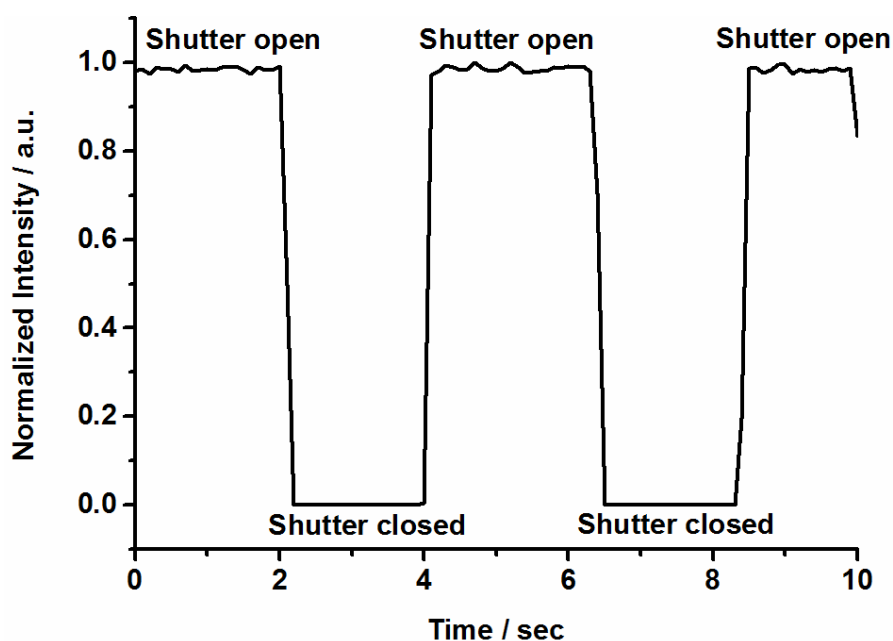


Figure S25 Examination of the luminescence life-time of compound **2**.

Examination of the Solvent dependency of the Luminescence

Additionally, we measured the excitation and emission spectrum of compound **2** in *n*-heptane (Figure S26). Since the spectrum does not show a significant difference to the spectrum in THF we assume that the luminescence is independent from the solvent. For compound **3** we measured a different emission spectrum in *n*-heptane (Figure S27). Herein the double emission band, which is observed in the solid state, is existent as well. Furthermore we observed a brought emission that is shifted even in the IR region. Therefore we assume that the luminescence of **3** is solvent dependent.

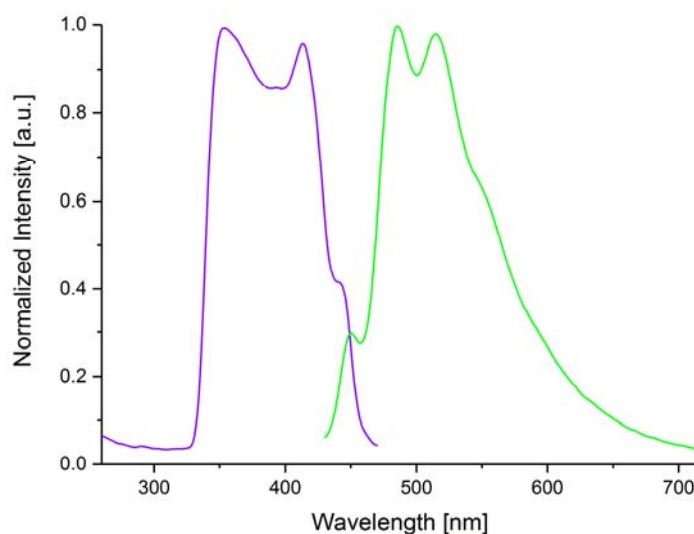


Figure S26 Excitation and emission spectra of compound **2** in *n*-heptane with maxima (nm) at λ_{exc} 353 and 414, λ_{em} 485 and 515.

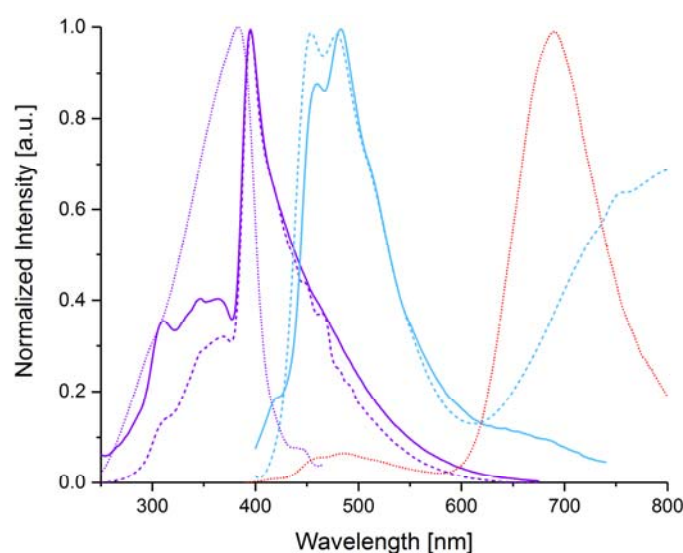


Figure S27 Emission spectra of compound **3** in the solid state (solid line) in thf (dotted line) and in *n*-heptane (dashed line) with maxima (nm) at λ_{ex} (heptane) 395; λ_{em} (heptane): 454, 479, and >800.

X-ray Crystallographic Studies of 1-3. A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fiber. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or STOE StadiVari diffractometer.

Using Olex2,⁴ the structures were solved using SHELXS⁵ and refined with the ShelXL⁶ refinement package using Least Squares minimization. The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F^2 . Carbon-bound hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. For the structure of **3**, two molecules of disordered dichloromethane, and for the structure of compound **2**, two molecules of disordered thf could not be modeled satisfactorily and were therefore removed from the electron density map by using OLEX2 solvent mask.⁴ Furthermore, one trimethylsilyl group in the asymmetric unit of **3** and the trimethylsilyl group of **2** were disordered over two positions, and were therefore refined as two TMS units (occupancy 50:50) using ISOR restraints.

Positional parameters, hydrogen atom parameters, thermal parameters, bond lengths and angles have been deposited as supporting information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. 1552980-1552982. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +(44)1223-336-033; email: deposit@ccdc.cam.ac.uk).

Table S1: Crystal data and structure refinement

Compound	1	2	3·(CH₂Cl₂)₂
Chemical formula	C ₄₂ H ₆₇ LiN ₂ O ₃ Si	C ₆₀ H ₈₆ Au ₂ N ₄ Si ₂	C ₁₃₄ H ₁₉₂ Au ₈ Cl ₄ N ₈ S ₂ Si ₄
Formula Mass	683.00	1313.45	3808.96
Crystal system	orthorhombic	triclinic	monoclinic
Space group	<i>Pna</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	18.886(4)	10.483(2)	16.4652(3)
<i>b</i> /Å	11.516(2)	14.626(3)	18.7339(3)
<i>c</i> /Å	18.802(4)	14.711(3)	25.4701(5)
α /°		62.81(3)	
β /°		71.94(3)	98.247(2)
γ /°		79.18(3)	
Unit cell volume/Å ³	4089.3(14)	1904.6(9)	7775.2(2)
Temperature/K	103	200	110
No. of formula units per unit cell, Z	4	1	2
Radiation type	Mo K α	Mo K α	Mo K α
Absorption coefficient, μ /mm ⁻¹	0.095	3.909	7.687
No. of reflections measured	22735	15651	37690
No. of independent reflections	7848	7403	15225
<i>R</i> _{int}	0.1034	0.0834	0.0428
Final <i>R</i> ₁ values (<i>I</i> > 2 σ (<i>I</i>))	0.0481	0.0319	0.0355
Final <i>wR</i> (<i>F</i> ²) values (<i>I</i> > 2 σ (<i>I</i>))	0.0844	0.0655	0.0668
Final <i>R</i> ₁ values (all data)	0.0779	0.0429	0.0547
Final <i>wR</i> (<i>F</i> ²) values (all data)	0.0935	0.0668	0.0697
Goodness of fit on <i>F</i> ²	0.981	0.819	0.883

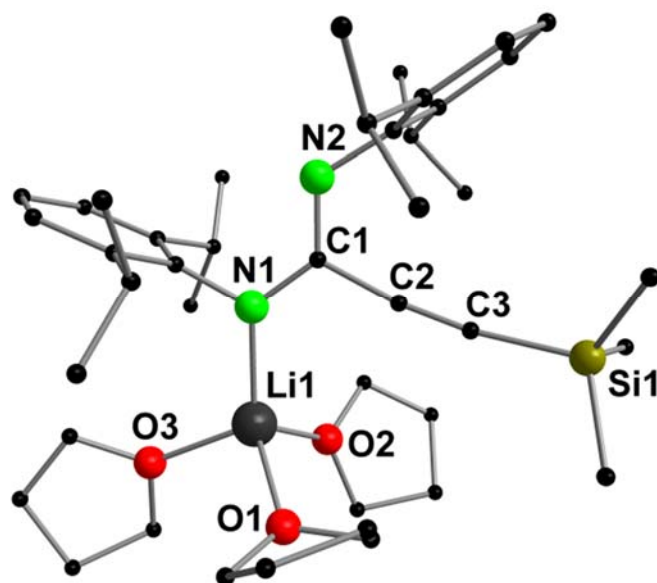


Figure S28 Molecular structure of compound **1** in the solid state. Hydrogen atoms are omitted for clarity. Selected bond- lengths (Å) and angles (°): Li1-N1 2.009(6), Li1-O1 2.012(7), Li1-O2 1.983(6), Li-O3 1.991(6), N1-C1 1.339(5), N2-C1 1.312(4), C2-C3 1.206(5); N1-C1-N2 125.8(3).

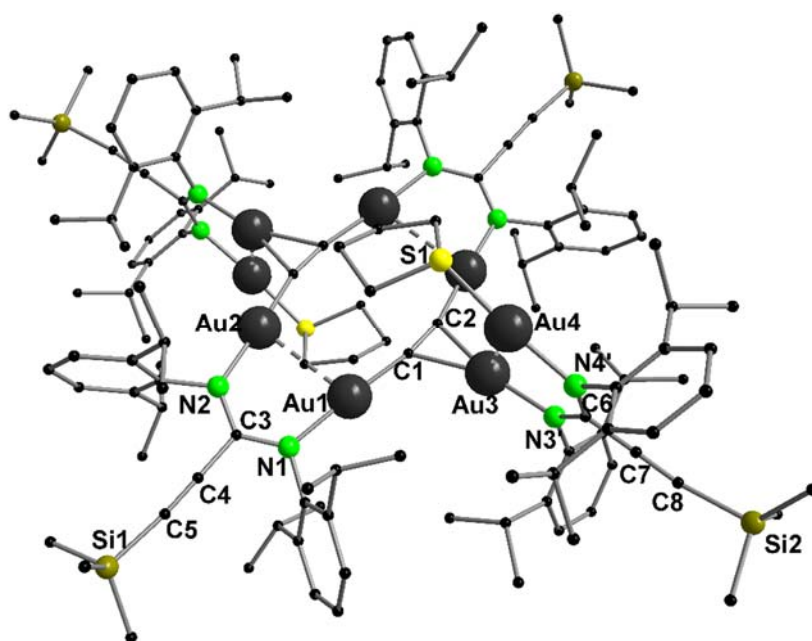


Figure S29 Molecular structure of compound **3** in the solid state. Hydrogen atoms as well as solvent molecules are omitted for clarity. Selected bond- lengths (Å) and angles (°): Au1-Au2 2.9928(3), Au3-Au4 2.9824(4), Au1-C1 1.938(6), Au2-C2 1.966(7), Au3-C1 2.197(6), Au3-C2 2.179(7), Au3-(C≡C) 2.095, Au4-S1 2.2586(2), Au1-N1 2.049(5), Au2-N2 2.055(5), Au3-N3 2.032(5), Au4-N4 2.038(5), C1-C2 1.264(9), C4-C5 1.200(9), C7-C8 1.195(9); Au1-C1-C2 166.4(5), Au2-C2-C1 167.4(6), Au1-C1-Au3 121.0(3), Au2-C2-Au3 118.5(3), N1-Au1-C1 177.3(2), N2-Au2-C2 176.5(2), N3-Au3-C1 159.6(2), N3-Au3-C2 161.7(2), N4-Au4-S1 170.70(2). N1-C3-N2 123.6(6), N3-C6-N4 125.2(6).

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