Electronic Supplementary Information

Alkynyl-functionalised and linked bicyclo[1.1.1]pentanes of group 14

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TOC

1. Experimental Details

1.1 General methods and instrumentation

All manipulations were performed under an argon atmosphere using standard Schlenk techniques. All solvents were freshly distilled under argon from sodium/benzophenone (THF, toluene), $CaSO_4$ (acetone), or CaH_2 (acetonitril, methyliodine) and stored over molecular sieve (3 Å) (acetone, acetonitril, methyliodine) prior to use. C_6D_6 and thf-d_8 were vacuum transferred from potassium/benzophenone into thoroughly dried glassware equipped with Young teflon valves. Air sensitive compounds were stored and weighed in glove boxes (Braun MB150 G-I and Unilab system). Solution NMR spectra were recorded using Bruker Avance instruments operating at ^{1}H Larmor frequencies of 300 or 400 MHz; chemical shifts are given relative to TMS for ^{13}C and ^{1}H. Coupling constants J are given in Hertz as positive values regardless of their real individual signs. The multiplicity of the signals is indicated as s, d, or m for singlets, doublets, or multiplets, respectively. Since we observe in many cases "through cage" couplings, we consider the "back-lobe-to-back-lobe" interaction as "bond", which is also reflected in the superscript numbering for the coupling constants (^nJ). The abbreviation br. is given for broadened signals. Note that Mes-substituted heavy [1.1.1]propellanes and bicyclo[1.1.1]propellanes of group 14 show distinctive resonances in their ^{1}H NMR spectra. Due to the special arrangement of the Mes ligands, three signals for the Me groups (each 18 H) and two resonances for the aromatic protons in *meta* position (each 6 H) of the Mes ligands are usually observed for unsubstituted [1.1.1]propellanes or symmetrically 1,3-disubstituted bicyclo[1.1.1]pentanes. For unsymmetrically 1,3-disubstituted bicyclo[1.1.1]pentanes, however, the number of resonances is doubled and the integrals are bisected according to the non-equivalence of the bridgehead atoms. IR spectra were recorded on a Bruker Alpha FT-IR spectrometer using using the ATR technique (attenuated total reflection) on bulk material, and the data are quoted in wavenumbers (cm^{-1}). The Raman spectra were measured on a Bruker MultiRAM spectrometer with a Ge detector (Laser, 1064 nm, 500 mW). The intensities of the absorption bands are indicated as vs (very strong), s (strong), m (middle), w (weak), vw (very weak), br (broad). UV/Vis spectra were recorded on a Varian Cary 100 Scan in Quartz tubes (d = 1 cm) in a THF solution. Mass spectra and elemental analyses were recorded by the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT).

1.2 Starting materials

Hexakis(2,4,6-trimethylphenyl)trisiladistanna[1.1.1]propellane (**1**)[S1] was prepared according to literature methods. Lithium acetylide ethylendiamine complex (LiC≡CH·en), sodiumacetylide, and lithium hexamethyldisilazide were purchased from ABCR and Sigma-Aldrich and used as received.

1.3 Synthesis of the title compounds

2,2,4,4,5,5-hexakis(2,4,6-trimethylphenyl)-1,3-dimethyl-2,4,5-trisila-1,3-distannabicyclo[1.1.1]pentane (2) (see also Figures S1–S5)

To a stirred solution of **1** (50 mg, 0.048 mmol) in 20 mL THF was added dropwise a 0.032 M solution of methyl lithium in Et_2O (10% excess) at –78°C. Stirring was continued for 20 min. Then methyl iodide was added in excess to obtain the desired compound **2**. The solvent was removed *in vacuo* and the residue was dissolved in 25 mL of toluene and filtered. The filtrate was concentrated to about 7 mL and then layered with 20 mL of acetonitrile to obtain yellow crystals (42 mg, 0.039 mmol, 82 %). Mp. (sealed tube under Ar): > 200°C (decomp.). ^{1}H NMR (300.1 MHz, C_6D_6, ppm): δ = 1.28 ($^2J(^1\text{H},^{119}\text{Sn})$ = 40.3 Hz, $^3J(^1\text{H},^{119}\text{Sn})$ = 11 Hz, Sn–CH_3), 2.10 (s, 18 H, *p*-CH_3), 2.32 (s, 18 H, *o*-CH_3), 2.59 (s, 18 H, *o*-CH_3), 6.29 und 6.66 (s, 12 H, *m*-H). ^{13}C{^{1}H} NMR (75.5 MHz, C_6D_6, ppm): δ = –2.2 (Sn–CH_3), 21.4 (*p*-CH_3), 27.0 (*o*-CH_3), 129.2 and 129.8 (*m*-CH), 133.7 (SiC), 137.8 (*p*-C(CH_3)), 144.4 and 145.7 (*o*-C(CH_3)). ^{29}Si NMR (59.6 MHz, C_6D_6, ppm): δ = –59 ($^1J(^{29}\text{Si},^{119}\text{Sn})$ = 263 Hz). ^{119}Sn{^{1}H} NMR (111.9 MHz, C_6D_6, ppm): δ = –222 ($^1J(^{29}\text{Si},^{119}\text{Sn})$ = 263 Hz, $^1J(^{117}\text{Sn},^{119}\text{Sn})$ = 4877 Hz). UV/Vis (THF, nm): λ_{max} = 290 (ε = 1000 M^{-1} cm^{-1}), 252 (shoulder). IR (ATR, cm^{-1}): ν = 404 (vs), 429 (vs), 464 (m), 492 (s), 549 (vs), 567 (m), 570 (vs), 614 (m), 693 (m), 727 (s), 796 (b), 842 (s), 875 (w), 1012 (vs), 1025 (vs), 1082 (m), 1092 (m), 1260 (m), 1287 (vw), 1365 (vw), 1377 (vw), 1372 (w), 1406 (w), 1434 (w), 1446 (m), 1464 (w), 1494 (vw), 1603 (w), 2853 (vw), 2911 (w), 2962 (w), 3019 (vw). Elemental analysis, found (%): 62.82, H: 6.50; calculated for $C_{56}H_{72}Si_3Sn_2$: C: 63.05, H: 6.80. EI MS (70 eV) *m*/*z* (%): 1065.84 (30).

Synthesis of 3 and 4 *via* sodium acetylide: A suspension sodium acetylide (22% in Xylene, 10% excess) and **1** (50 mg, 0.048 mmol) was stirred in THF at –10°C until the purple colour disappeared; methyl iodide was instantly added. After the solvent was removed, the residue was extracted with toluene, filtered and the solvent was removed under reduced pressure. The NMR spectra showed the formation of a mixture of **3** and **4** (*ca.* 20:80). The solid crude product was dissolved in THF and another crop of sodium acetylide (200% excess) was added to a 10 mL suspension of the previous product mixture. The suspension was stirred for 60 min at –10°C. Addition of an excess of methyl iodide resulted in the formation of **4**. The solvent was removed *in vacuo* and the residue was extracted with toluene. After reducing the volume to about 2 mL, the solution was layered with 25 mL of acetonitrile to obtain yellow crystals of **4** (35 mg, 0.032 mmol, 66% based on **3**). For spectral data, see **3** and **4**.

1-Ethynyl-2,2,4,4,5,5-hexakis(2,4,6-trimethylpheny)-3-methyl-2,4,5-trisila-1,3-distannabicyclo[1.1.1]pentane (3) (see also Figures S6–S11)

Via lithium acetylide ethylenediamine complex: To a stirred solution of **1** (30 mg, 0.029 mmol) in 10 mL THF was added dropwise a 0.05 M (9 mg in 20 mL of THF) solution of $LiC{\equiv}CH{\cdot}en$ in THF at ambient temperature until the solution became colourless. Stirring was continued for 10 min. after which methyl iodide was added in excess. The solvent was evaporated *in vacuo* and the residue was dissolved in 15 mL toluene and filtered. The filtrate was concentrated under vacuum to about 7 mL and afterwards layered with 20 mL acetonitrile to obtain colourless crystals (23 mg, 0.021 mmol, 73 %). Mp. (sealed tube under Ar): >230°C (decomp.). ^{1}H NMR (400.1 MHz, C_6D_6, ppm): δ = 1.29 (s, 3 H, $^{2}J(^{1}H,^{119}Sn)$ = 44 Hz, $^{4}J(^{1}H,^{119}Sn)$ = 16 Hz, Sn–CH_3), 2.08 (s, 18 H, *p*-CH_3), 2.28, 2.48, 2.58, 2.71 (s, each 9 H, *o*-CH_3), 2.38 (s, 1 H, $^{3}J(^{1}H,^{119}Sn)$ = 11Hz, $^{4}J(^{1}H,^{119}Sn)$ = 5Hz, $H_{C\equiv CH}$), 6.28, 6.32, 6.65, 6.68 (s, each 3 H, *m*-H). ^{13}C NMR (100.6 MHz, C_6D_6, ppm): δ = –5.9 (Sn–*C*H_3), 21.4 (*p*-*C*H_3), 25.5, 25.7, 26.9, 27.6 (*o*-*C*H_3), 91.2 (Sn–*C*≡CH), 98.4 (Sn–C≡*C*H), 129.5, 130.1, 132.5, 132.6 (*m*-*C*H), 138.2 (Si*C*), 138.4 (*p*-*C*CH_3) 144.1, 145.1, 145.4, 146.5 (*o*-*C*CH_3). ^{29}Si NMR (59.6 MHz, C_6D_6, ppm): δ = –56 ($^{1}J(^{29}Si,^{119}Sn_{Me})$ = 281 Hz, $^{1}J(^{29}Si,^{119}Sn_{C\equiv CH})$ = 300 Hz). ^{119}Sn{^{1}H} (111.9 MHz, C_6D_6, ppm): δ = –245 ($^{1}J(^{29}Si,^{119}Sn_{C\equiv CH})$ = 281 Hz, $^{1}J(^{117}Sn,^{119}Sn)$ = 7127 Hz, Sn–CH_3), –282 ($^{1}J(^{29}Si,^{119}Sn_{C\equiv CH})$ = 300 Hz, $^{1}J(^{117}Sn,^{119}Sn)$ = 7127 Hz, Sn–C≡CH). IR (ATR, cm^{-1}): ν = 405 (vs), 430 (vs), 464 (w), 502 (w), 549 (s), 566 (w), 615 (s), 658 (w), 727 (m), 749 (w), 843 (m), 959 (m), 1026 (m), 1257 (vw), 1286 (vw), 1365 (vw), 1406 (vw), 1450 (m), 1492 (w), 1602 (w), 2917 (w), 3023 (w), 3277 (vw). UV/Vis (THF, nm): λ_{max} = 288 (ε = 30000 $M^{-1}cm^{-1}$). Elemental analysis, found (%):C: 63.37, H: 6.50; calculated for $C_{57}H_{70}Si_3Sn_2$: C: 63.58, H: 6.55. EI-MS (70 eV) *m/z* (%): 1076 (2).

1-(prop-1-yn)-2,2,4,4,5,5-hexakis(2,4,6-trimethylphenyl)-3-methyl-2,4,5-trisila-1,3-distannabicyclo[1.1.1]pentane (4) (see also Figures S12–S17)

To a stirred solution of **1** (30 mg, 0.029 mmol) in 10 mL THF was added an excess of lithium acetylide ethylenediamine complex (5 mg, 0.05 mmol) at ambient temperature. Stirring was continued for 10 min. Then methyl iodide was added in excess and all volatiles were removed *in vacuo*. The residue was dissolved in 20 mL toluene and filtered. To this solution was added an excess of lithium hexamethyldisilazide (10 mg, 0.06 mmol). The solution was left stirring for 1h and afterwards an excess of methyl iodide was added. The solution was filtered and concentrated to about 8 mL and covered with acetonitrile to obtain slightly yellow crystals (22 mg, 0.020 mmol, 69 %). Mp. (sealed tube under Ar): >200°C (decomp.) ^{1}H NMR (400.1 MHz, C_6D_6, ppm): δ = 1.30 (s, 3 H, $^{2}J(^{1}H,^{119}Sn)$ = 44 Hz, $^{3}J(^{1}H,^{119}Sn)$ = 16 Hz, Sn–CH_3), 1.74 (s, 3 H, $^{4}J(^{1}H,^{119}Sn)$ = 11 Hz, Sn–C≡CMe), 2.08 (s, 18 H, *p*-CH_3), 2.30, 2.50, 2.60, 2.74 (s, each 9 H, *o*-CH_3), 6.28, 6.32, 6.65, 6.68 (s, each 3 H, *m*-H). ^{13}C{^{1}H} NMR (100.6 MHz, C_6D_6, ppm): δ = –6.5 (Sn–CH_3), 5.1 (Sn–C≡C–*C*H_3), 20.7 (*p*-CH_3), 24.8, 24.9, 26.1, 26.9 (*o*-CH_3), 82.5 (Sn–*C*≡C–CH_3), 106.9 (Sn–C≡*C*–CH_3), 128.3, 128.7, 129.0, 129.1 (*m*-*C*H), 132.0 (Si*C*), 137.4 (*p*-*C*CH_3), 143.5, 144.6, 144.7, 145.7 (*o*-*C*CH_3). ^{29}Si NMR (59.6 MHz, C_6D_6, ppm): δ = –57 ($^{1}J(^{29}Si,^{119}Sn_{Me})$ = 281 Hz, $^{1}J(^{29}Si,^{119}Sn_{C\equiv CMe})$ = 308 Hz). ^{119}Sn{^{1}H} NMR (111.9 MHz, C_6D_6, ppm): δ = –241 ($^{1}J(^{29}Si,^{119}Sn_{C\equiv CMe})$ = 281 Hz, $^{1}J(^{117}Sn,^{119}Sn)$ = 6942 Hz, Sn–CH_3), –281 ($^{1}J(^{29}Si,^{119}Sn_{C\equiv CMe})$ = 308 Hz, $^{2}J(^{117}Sn,^{119}Sn)$ = 6942 Hz, Sn–C≡CMe). UV/Vis (THF, nm): λ_{max} = 390 (ε = 1000 M^{-1} cm^{-1}), 252 (shoulder). IR (ATR, cm^{-1}): ν = 404 (vs), 430 (vs), 465 (w), 505 (m), 550 (vs), 567 (w), 596 (vs), 614 (m), 615 (s), 662 (m, 695 (w), 731 (s), 843 (vs), 984 (s), 1025 (s), 1127 (b), 1178 (m), 1233 (s), 1286 (m), 1309 (w), 1366 (w), 1406 (m), 1443 (m), 1494 (m), 1547 (vw), 1603 (w), 2147 (vw), 2726 (vw), 2854 (vw), 2917 (w), 2945 (w), 2966 (w), 3019 (vw). EI-MS (70 eV) *m/z* (%): 1089.41 (45). Elemental analysis, found (%): C: 65.65, H: 6.70; calculated for $C_{58}H_{72}Si_3Sn_2 \cdot C_7H_8$ (as supported by ^{1}H NMR data of the sample and the X-ray crystal structure, see Figure S30): C: 65.99, H: 6.82.

1,2-bis(2,2,4,4,5,5-hexakis(2,4,6-trimethylphenyl)-3-methyl-2,4,5-trisila-1,3-distannabicyclo[1.1.1]pentan)ethyne (5) (see also Figures S18–S25)

To a THF solution (10 mL) of **1** (20 mg, 0.019 mmol) was added dropwise a 0.011 M (10 mg in 10 mL of THF) solution of lithium acetylide ethylenediamine complex in THF at room temperature until the solution turned colourless. After stirring for additional 10 min. a 0.01 M (12.5 µL methyliodine in 20 mL of THF) methyl iodide solution (2 mL) was added. To this mixture was added a slight excess of lithium hexamethyldisilazide (7 mL of a 0.003 M (10 mg in 20 mL) THF solution). After 5 min. of stirring, a 2.5 mM (25 mg, 0.025 mmol in 10 mL of THF) solution of **1** in THF was added dropwise until the colour of the solution turned slightly purple. To this solution was added another 2 mL of the methyl iodide solution. All volatiles were evaporated *in vacuo* and the residue was dissolved in 10 mL toluene and filtered. The filtrate was concentrated to a half and **5** was obtained as colourless crystals at 4°C (25 mg, 0.012 mmol, 65%) Mp. (sealed tube under Ar): >270°C (decomp.) ^{1}H NMR (400.1 MHz, THF-d_8, ppm): δ = 1.16 (s, 6 H, $^{2}J(^{1}\mathrm{H},^{119}\mathrm{Sn})$ = 44 Hz, $^{3}J(^{1}\mathrm{H},^{119}\mathrm{Sn})$ = 14 Hz, Sn–CH_3), 2.11 (s, 18 H, *o*-CH_3), 2.15 (s, 36 H, *p*-CH_3), 2.29, 2.32 (s, each 9 H, *o*-CH_3), 2.35, 2.51, 2.52 (m, 36 H, *o*-CH_3), 6.16, 6.22, 6.69, 6.75, 6.77 (m, 24 H, *m*-CH). ^{13}C NMR (100.6 MHz, THF-d_8, ppm): δ = –5.7 (Sn–CH_3), 21.2, 21.3 (*o*-CH_3), 25.6, 25.8 , 26.0, 26.9, 27.8 (*p*-CH_3), 88.6 (Sn–C≡C–Sn), 129.0, 129.4, 130.0, 130.4 (*m*-CH), 133.1, 133.3(Si*C*) 138.4 (*o*-*C*CH_3), 144.6, 145.6, 145.7, 146.9 (*p*-*C*CH_3). ^{29}Si NMR (59.6 MHz, THF-d_8, ppm): δ = –57 ($^{1}J(^{29}\mathrm{Si},^{119}\mathrm{Sn}_{\mathrm{Me}})$ = 279 Hz, $^{1}J(^{29}\mathrm{Si},^{119}\mathrm{Sn}_{\mathrm{C{\equiv}C}})$ = 305 Hz). ^{119}Sn NMR (79.5 MHz, THF-d_8, ppm): δ = –295 (s, $^{1}J(^{117}\mathrm{Sn},^{119}\mathrm{Sn})$ = 6770 Hz, $^{1}J(^{29}\mathrm{Si},^{119}\mathrm{Sn})$ = 305 Hz, $\mathrm{Sn}_{\mathrm{C{\equiv}C}}$), –296 (s, $^{1}J(^{117}\mathrm{Sn},^{119}\mathrm{Sn})$ = 6760 Hz, $^{1}J(^{29}\mathrm{Si},^{119}\mathrm{Sn})$ = 305 Hz, $\mathrm{Sn}_{\mathrm{C{\equiv}C}}$), –237 ($^{1}J(^{117}\mathrm{Sn},^{119}\mathrm{Sn})$ = 6770 Hz, $^{1}J(^{29}\mathrm{Si},^{119}\mathrm{Sn})$ = 279 Hz, $\mathrm{Sn}_{\mathrm{Me}}$). IR (ATR, cm^{-1}): ν = 404 (vs), 430 (vs), 454 (w), 464 (w), 502 (s), 548 (s), 566 (m), 587 (m), 596 (m), 614 (w), 664 (vw), 693 (m), 727 (m), 842 (s), 876 (vw), 916 (vw), 982 (w), 1028 (m), 1099 (w), 1150 (vw), 1191 (vw), 1236 (w), 1286 (w), 1307 (w), 1364 (w), 1379 (vw), 1406 (m), 1435 (w), 1463 (w), 1494 (vw), 1544 (vw), 1602 (m), 2289 (vw), 2916 (w), 2946 (w), 3020 (vw). Raman (powder, Laser 500 mW, 1064 nm), cm^{-1}): ν =76 (vs), 123 (s), 176 (m), 224 (vw), 287 (vw), 324 (m), 340 (w), 410 (vw), 438 (s), 505 (m), 538 (m), 571 (w), 601 (w), 719 (vw), 785 (vw), 1008 (m), 1052 (m), 1092 (m), 1175 (w), 1263 (vw), 1289 (m), 1376 (w), 1467 (w), 1553 (vw), 1604 (s), 2000 (w), 2043 (m), 2285 (vw), 2329 (vw), 2723 (vw), 2857 (w), 2917 (s), 3022 (w). UV/Vis (THF, nm): $\lambda_{\max}$ = 287 (ε = 150 M^{-1} cm^{-1}), 251 (shoulder). Elemental analysis, found (%): C: 63.23, H: 6.62; calculated for $C_{112}H_{138}Si_6Sn_4$: C: 63.22, H: 6.54. Due to the high molecular mass and non-ionic character of the compound, we were not able to collect EI or ESI mass spectra for **5**.

1.4 Details on the DFT studies

Slightly modified model systems **q2** and **q5** consisting of Ph substituents were used for the calculations, which were performed with the TURBOMOLE program package.[S2] The geometries were optimized in D_3 (**q2**) or C_1 (**q5**) symmetry at the (RI)-BP86[S3] level with the def2-TZVP basis sets.[S4] The coordinates of the minimum structures are compiled at the end of the Supporting Material (Section 5; Cartesian coordinates in bohr units). For molecular orbital plots, see Figure S26.

2. Figures

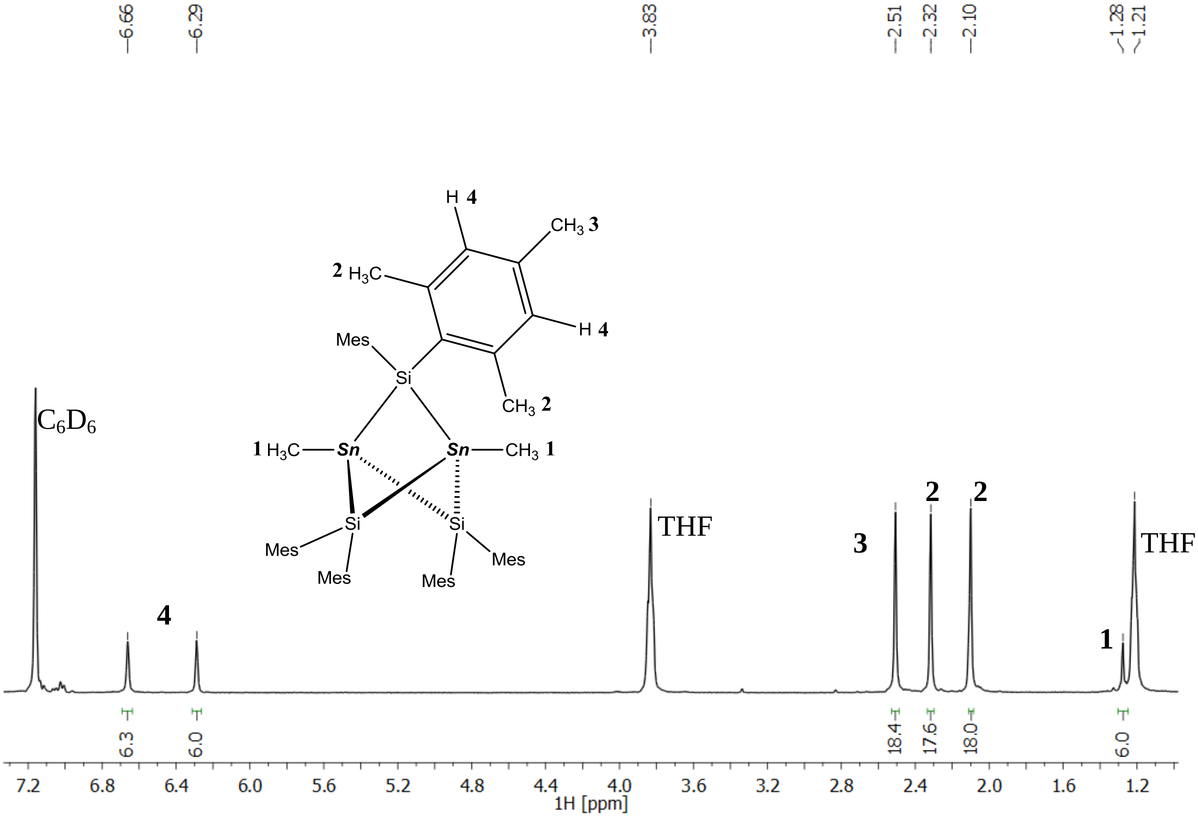


Figure S1 ^{1}H NMR spectrum of **2** (400.1 MHz, C_6D_6); see schematic drawing for numbering.

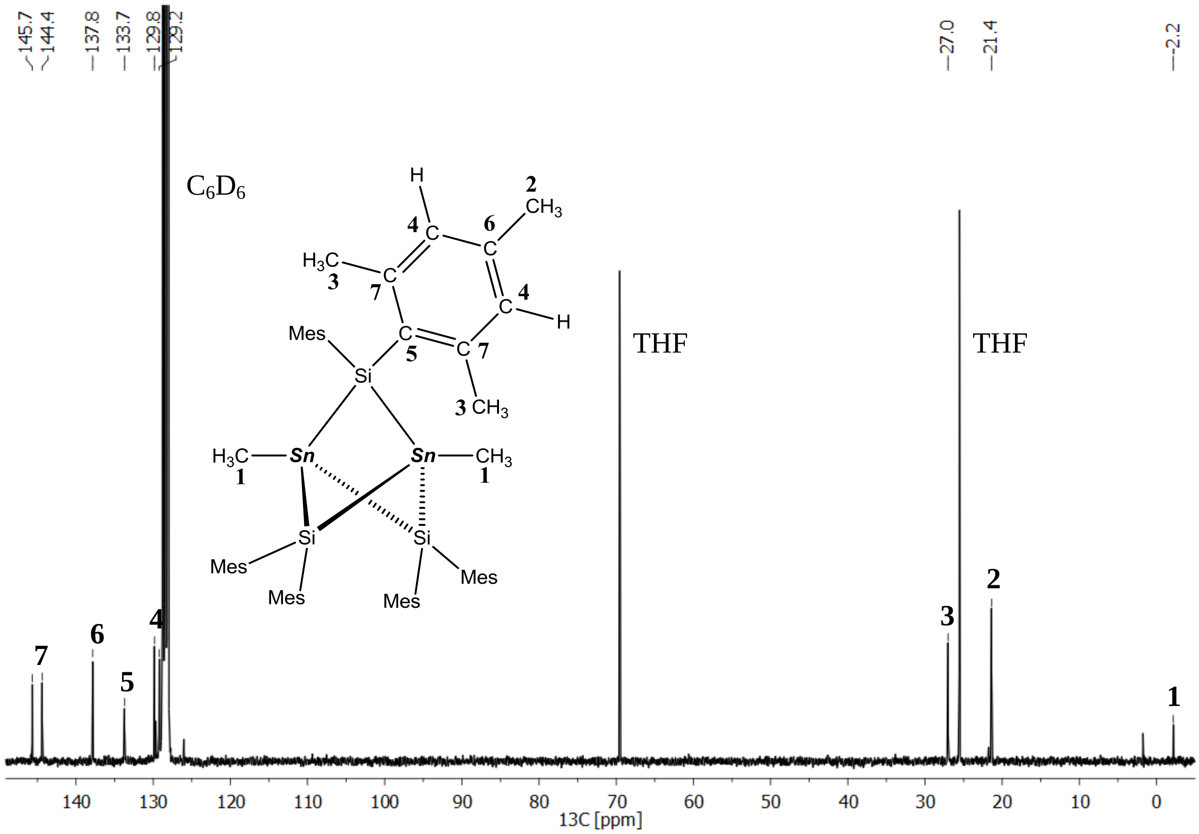


Figure S2 ^{13}C NMR spectrum of **2** (100.6MHz, C_6D_6).

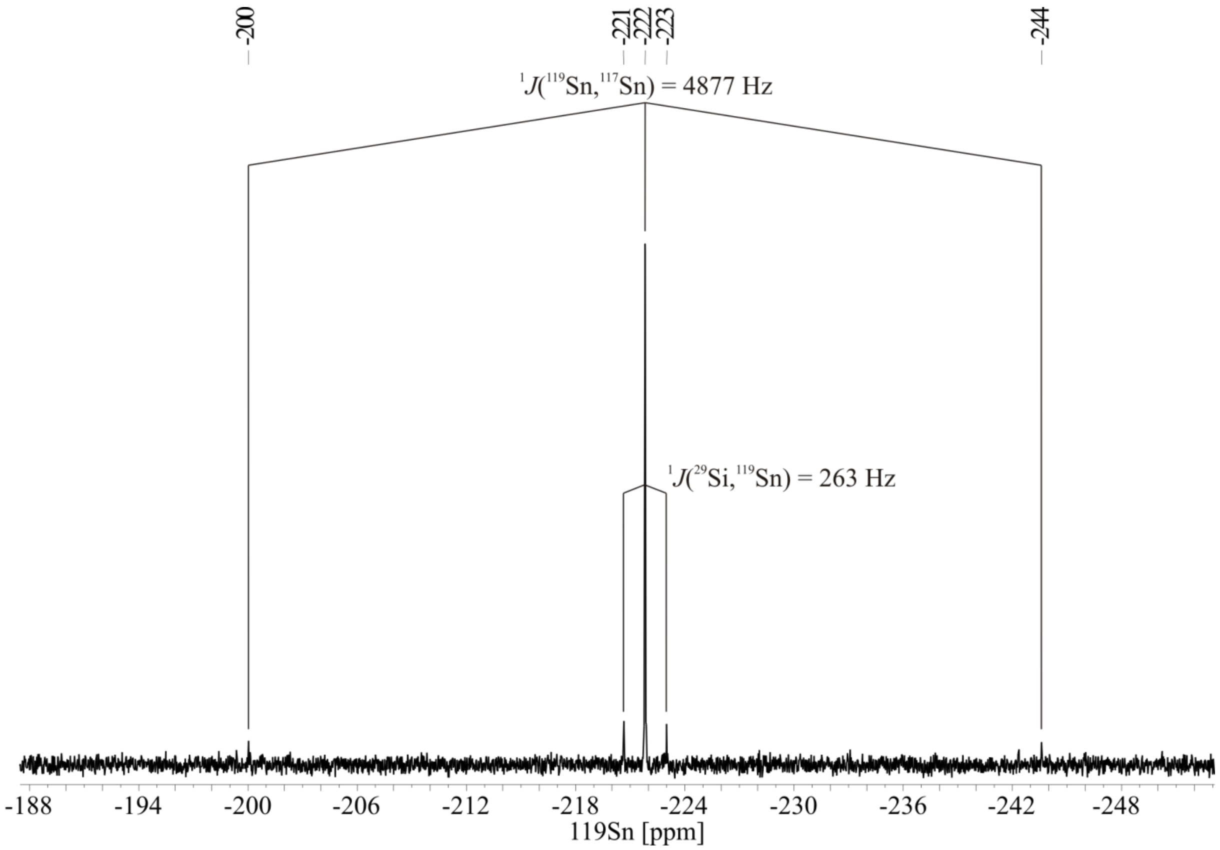


Figure S3 ^{119}Sn{^{1}H} NMR spectrum of **2** (79.5 MHz, C_6D_6).

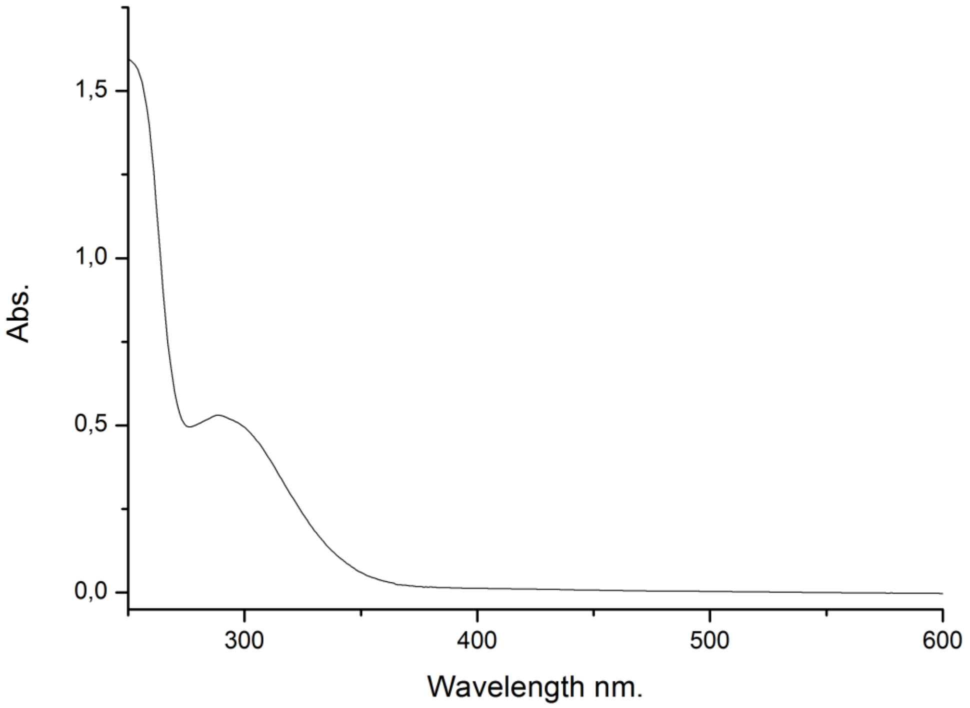


Figure S4 UV/Vis spectrum of **2** in THF.

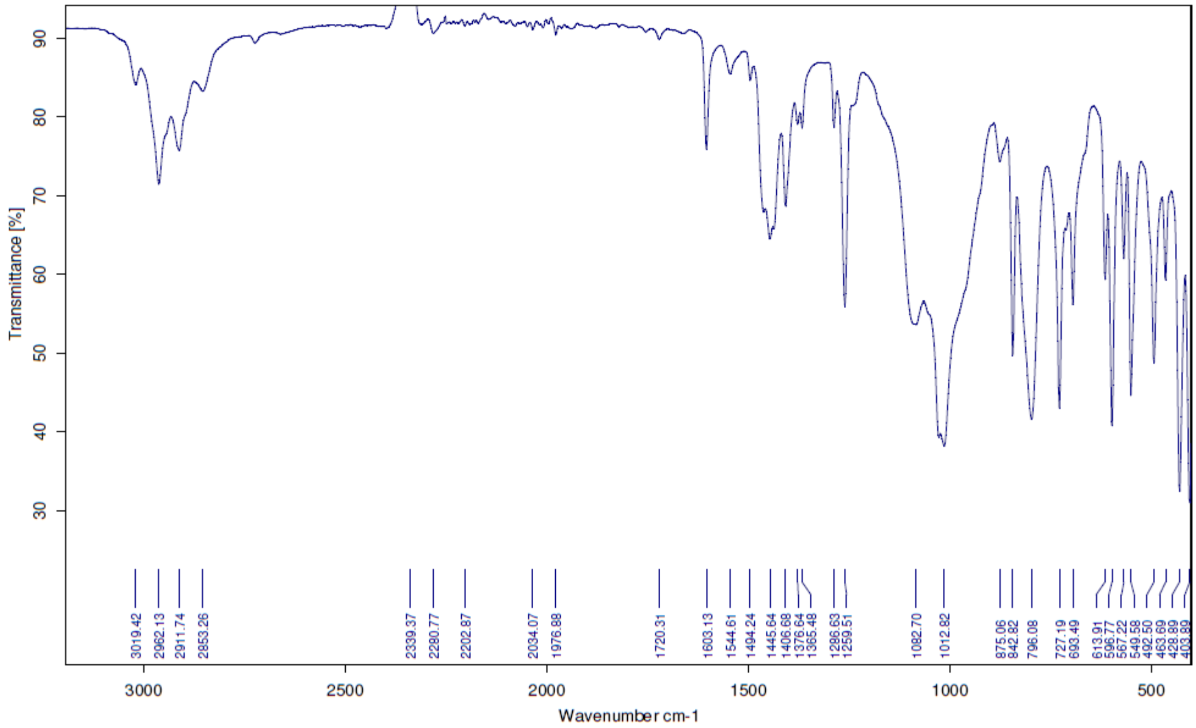


Figure S5 ATR-IR spectrum of **2**.

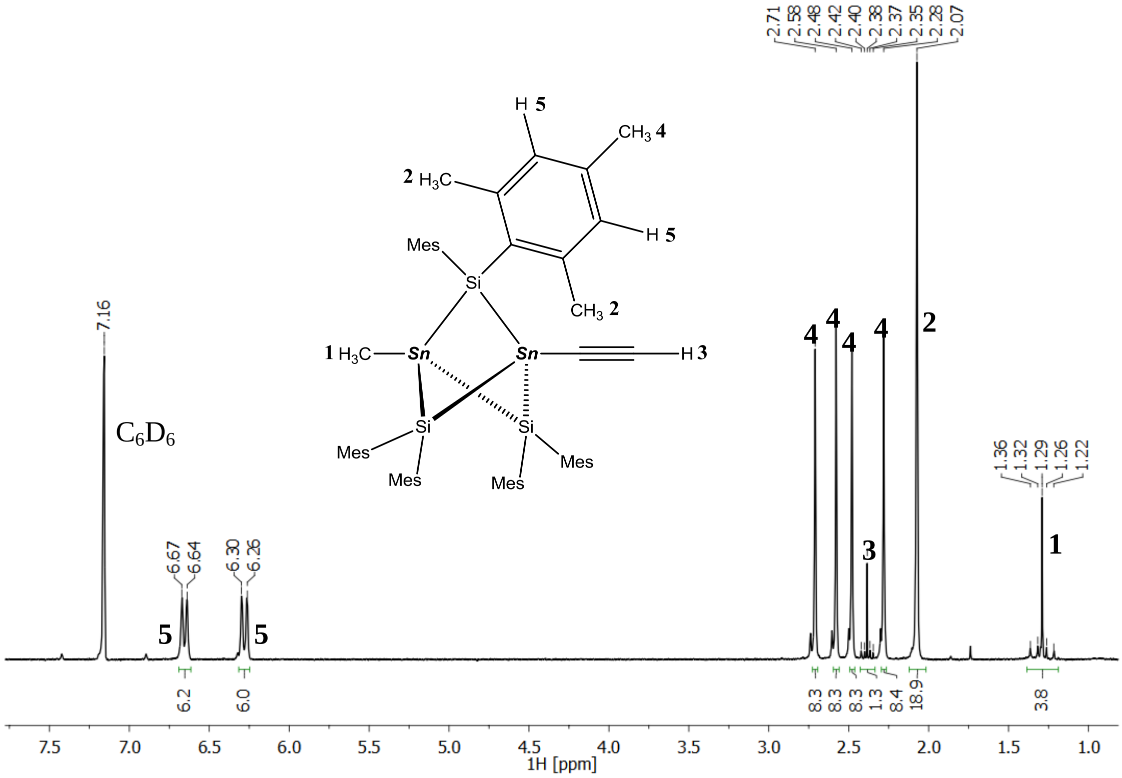


Figure S6 ^{1}H NMR spectrum of **3** (400.1 MHz, C_6D_6); see schematic drawing for numbering.

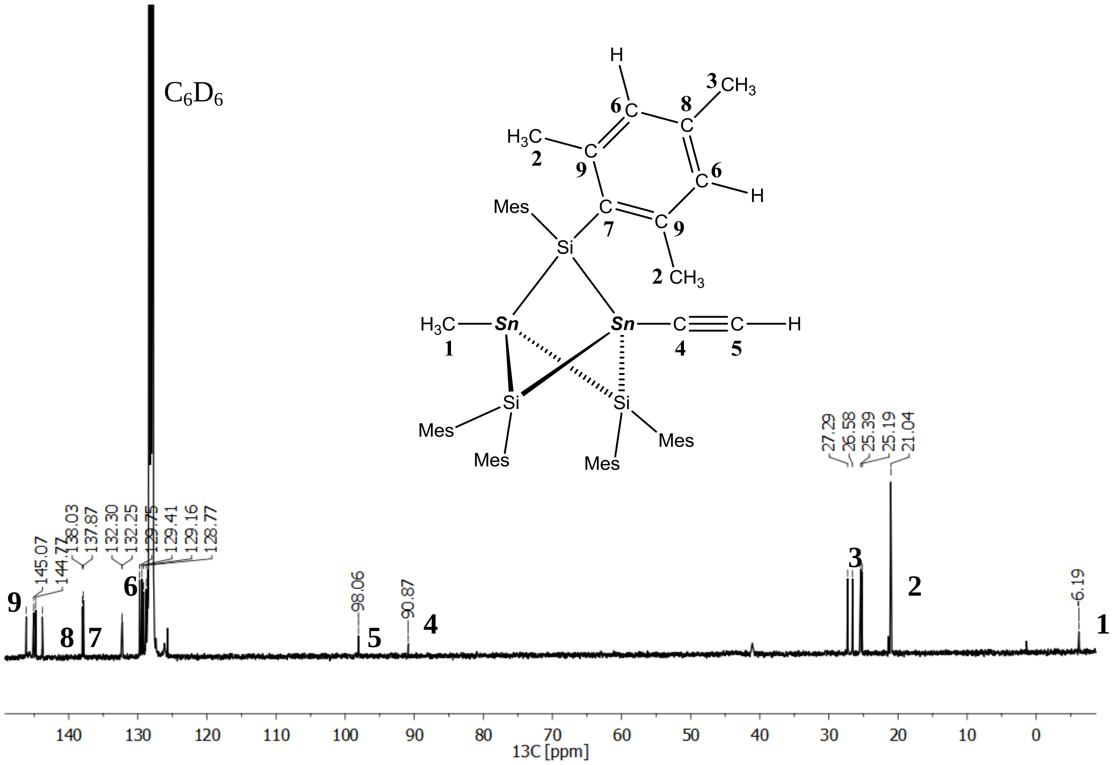


Figure S7 ^{13}C NMR spectrum of **3** (100.6MHz, C_6D_6); see schematic drawing for numbering.

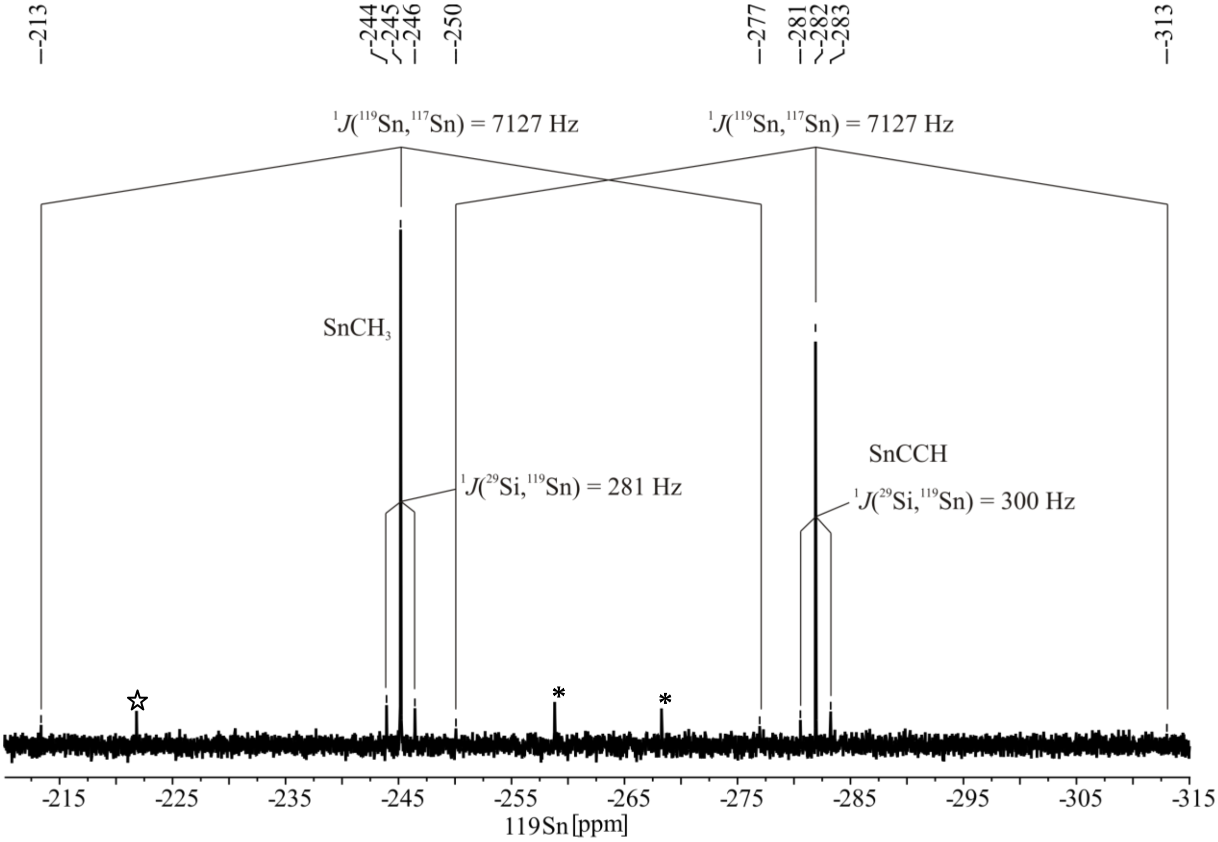


Figure S8 ^{119}Sn{^{1}H} NMR spectrum of **3** (79.5 MHz, C_6D_6). The signals marked with an asterisk are due to ^{1}J(^{119}Sn,^{119}Sn) couplings between the bridgehead tin atoms (expected value = 7455 Hz). The second pair of signals has not been observed due to their very small intensity. For a related spectrum see ref. [S5]. ☆= unknown impurity.

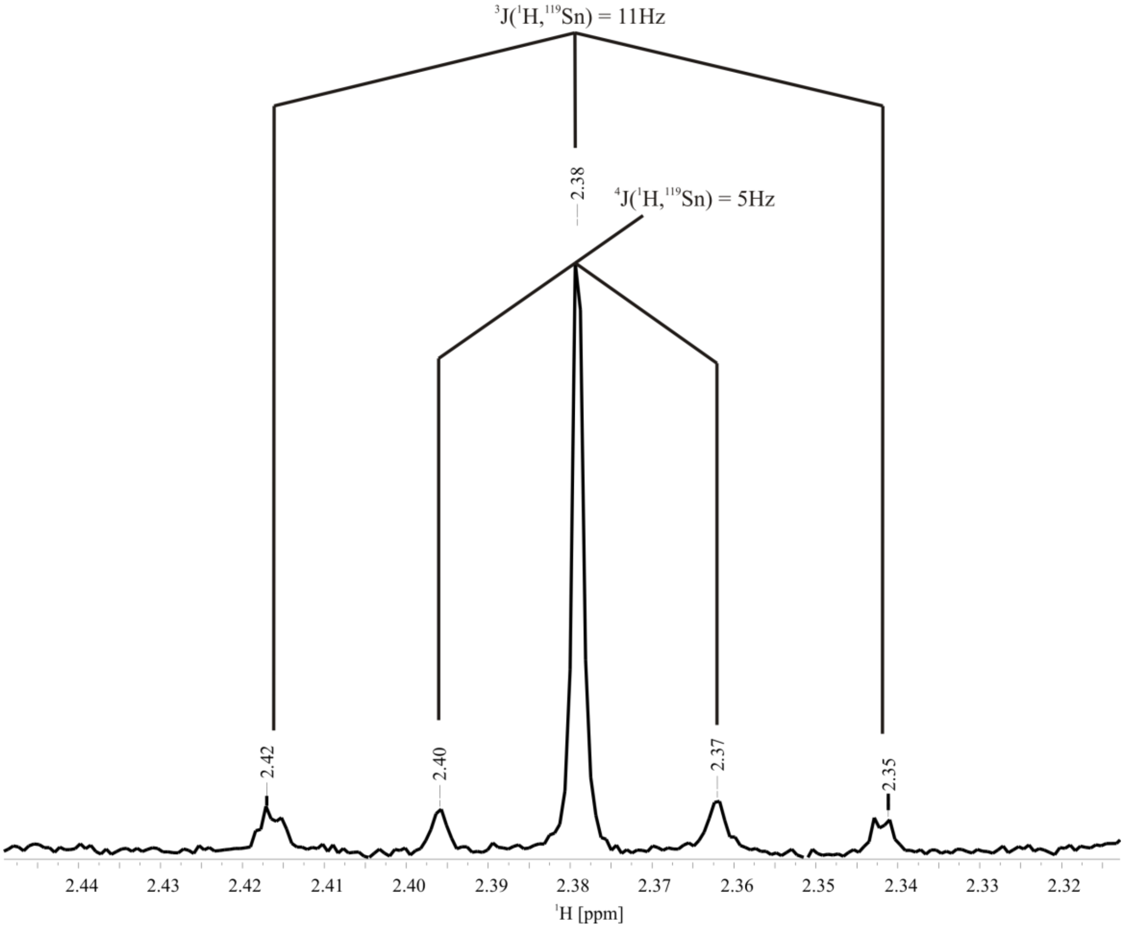


Figure S9 ^{1}H NMR spectrum of **3** in the region of the terminal alkyne proton.

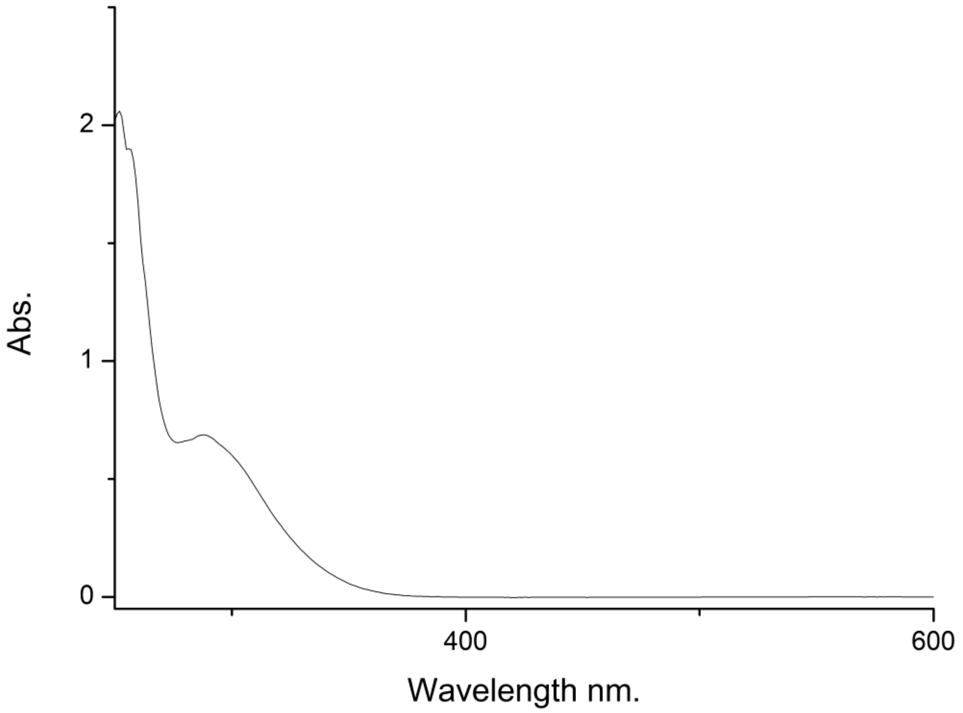


Figure S10 UV/Vis spectrum of **3** in THF.

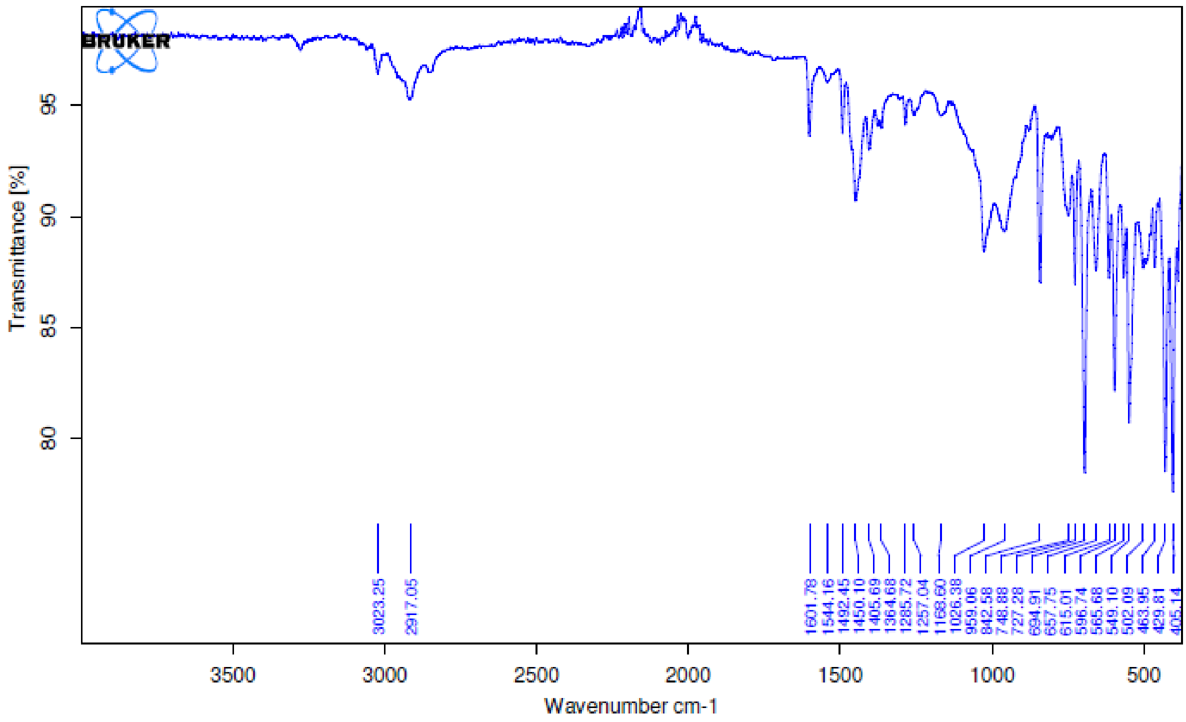


Figure S11 ATR-IR spectrum of **3**.

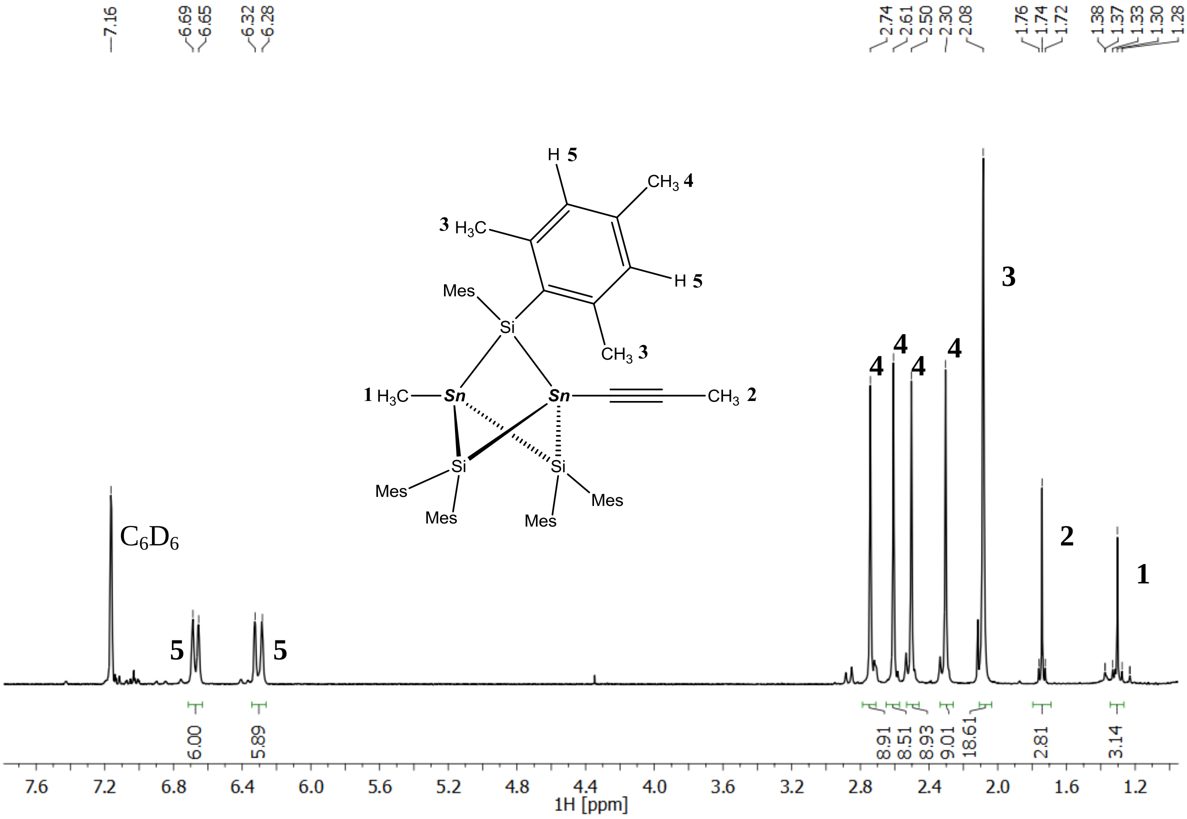


Figure S12 ^{1}H NMR spectrum of **4** (400.1 MHz, C_6D_6); see schematic drawing for numbering.

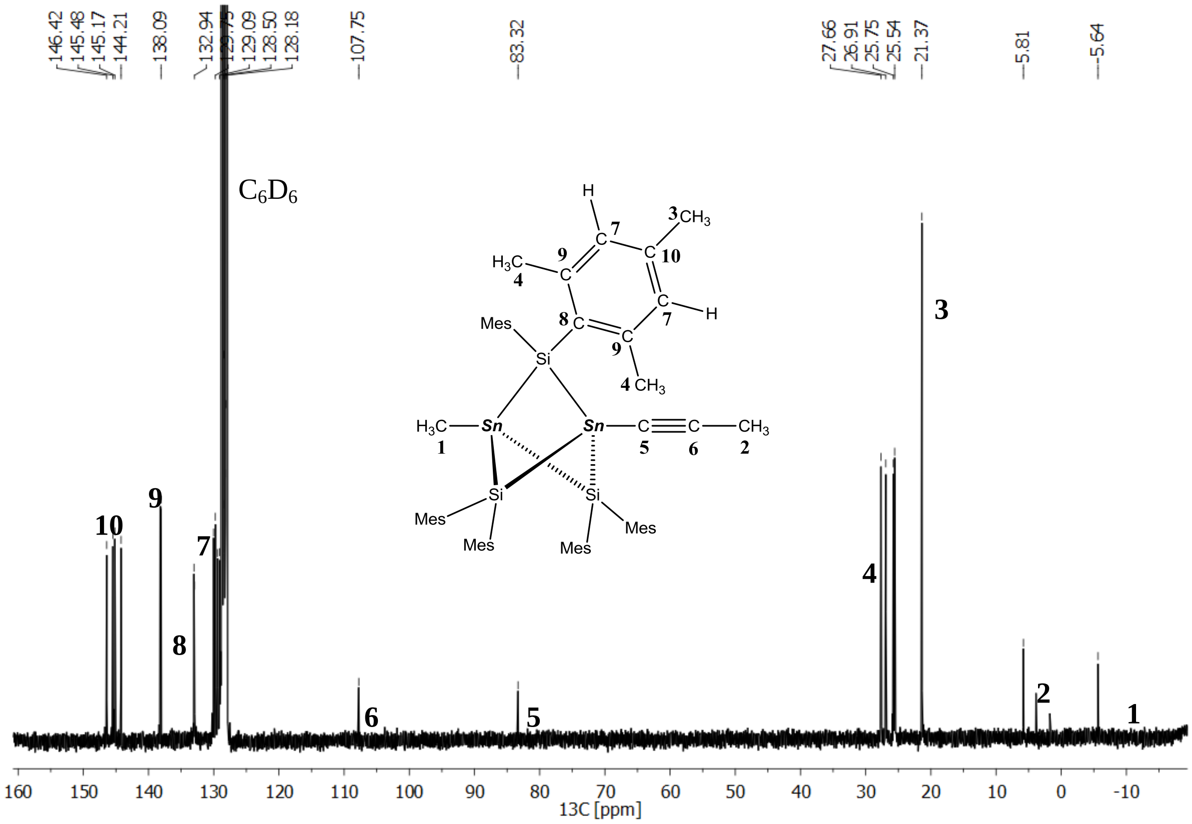


Figure S13 ^{13}C NMR spectrum of **4** (100.6 MHz, C_6D_6); see schematic drawing for numbering.

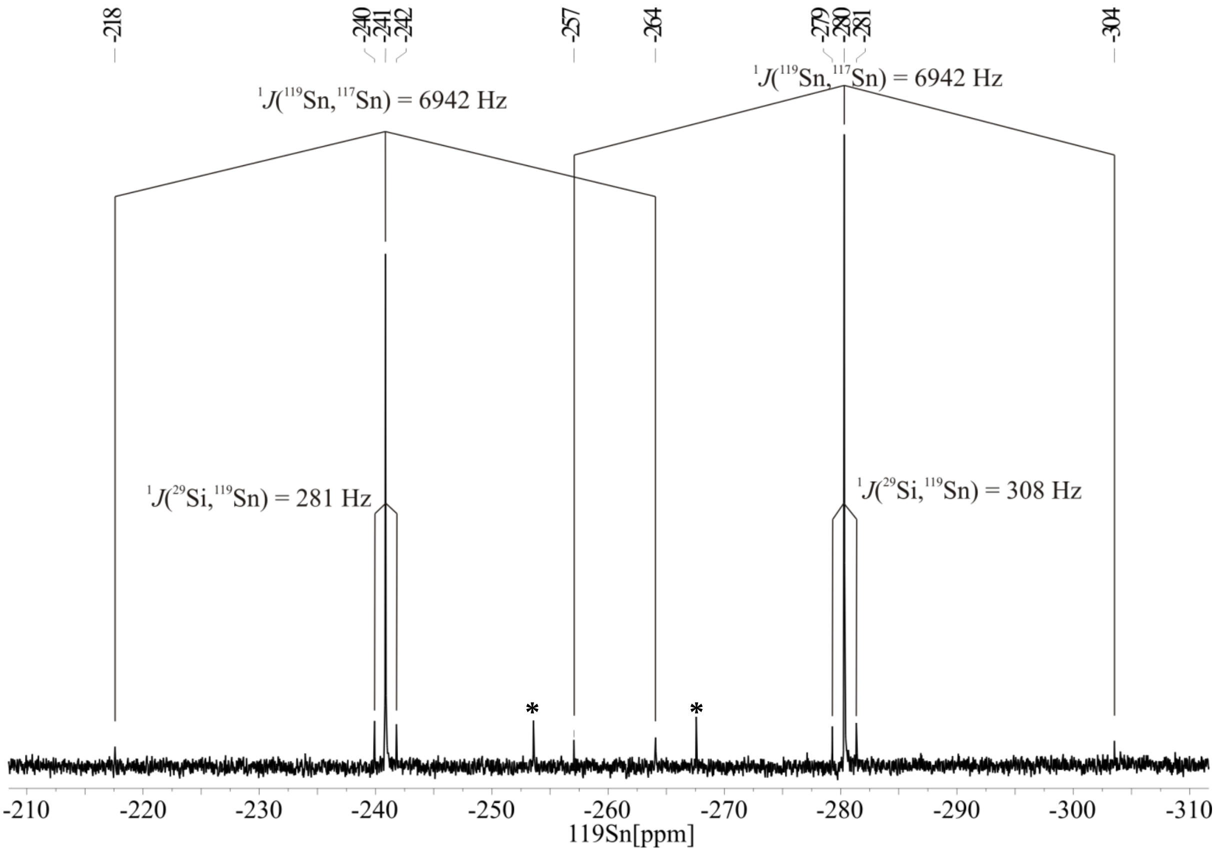


Figure S14 ^{119}Sn{^{1}H} NMR spectrum of **4** (79.5 MHz, C_6D_6). The signals marked with an asterisk are due to $^{1}J(^{119}Sn,^{119}Sn)$ couplings between the bridgehead tin atoms (expected value = 7260 Hz). The second pair of signals has not been observed due to their very small intensity. For a related spectrum see ref. [S5].

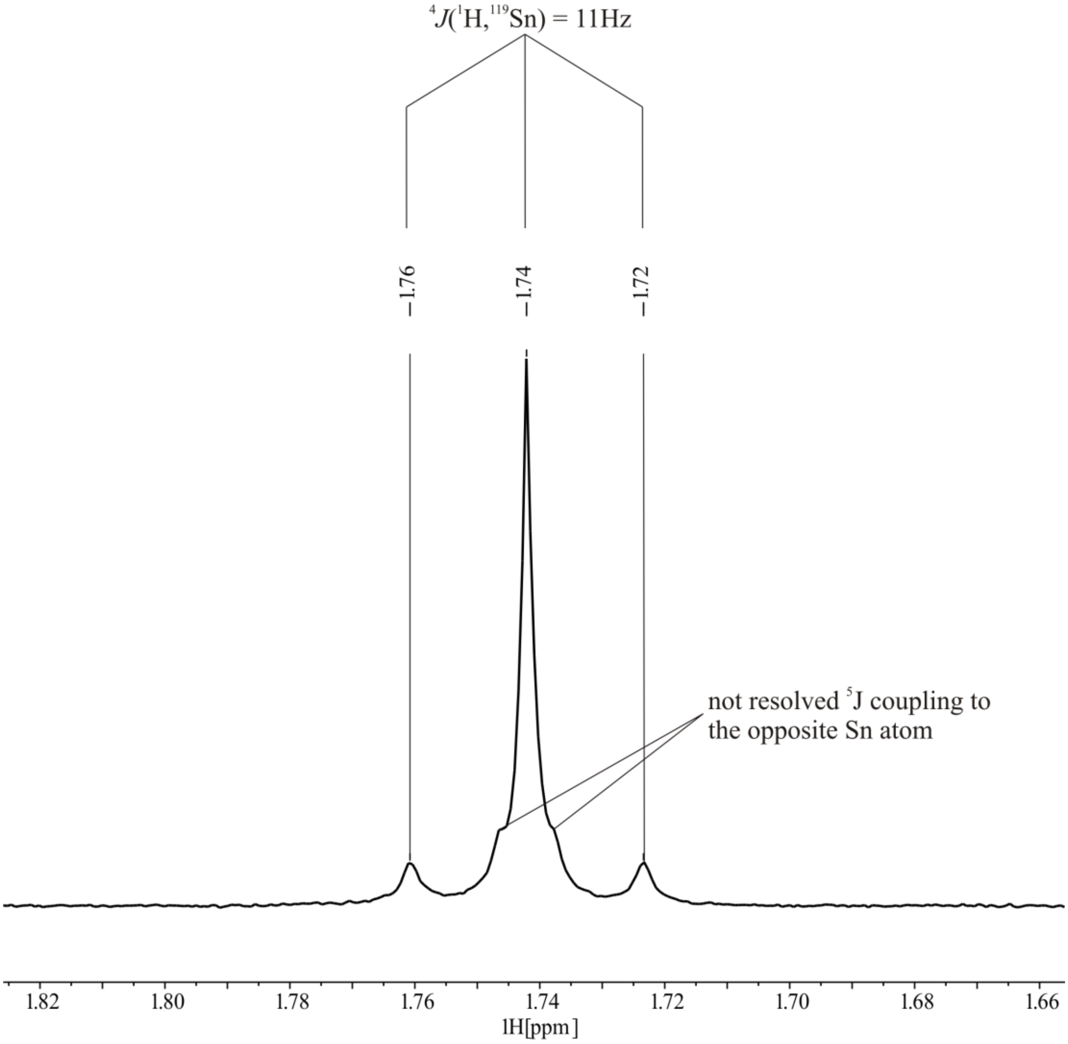


Figure S15 ^{1}H NMR spectrum of **4** in the region of the $C{\equiv}C{-}CH_3$ group.

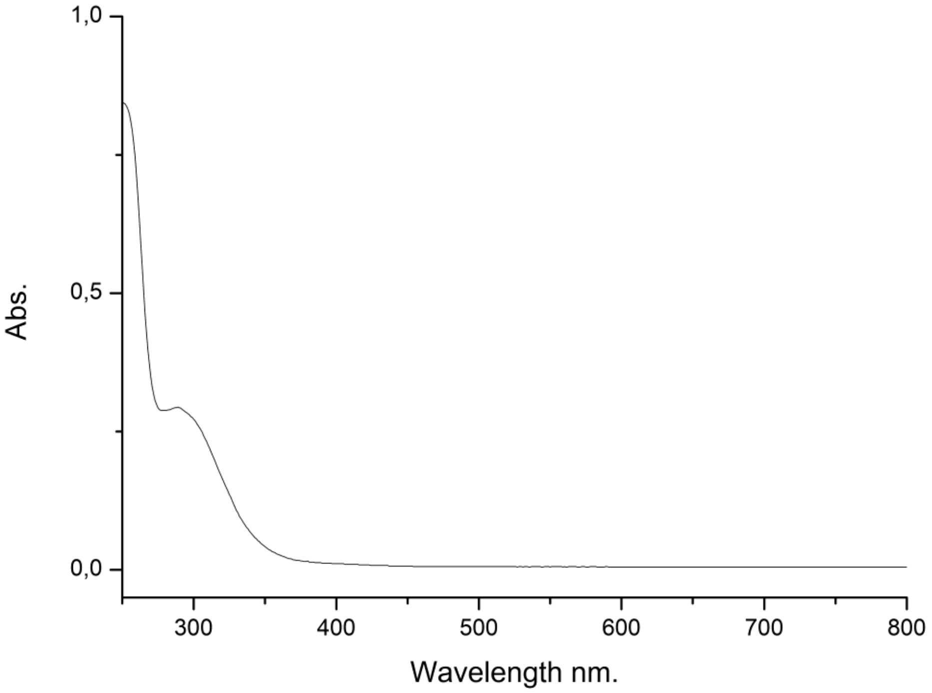


Figure S16 UV/Vis spectrum of **4** in THF.

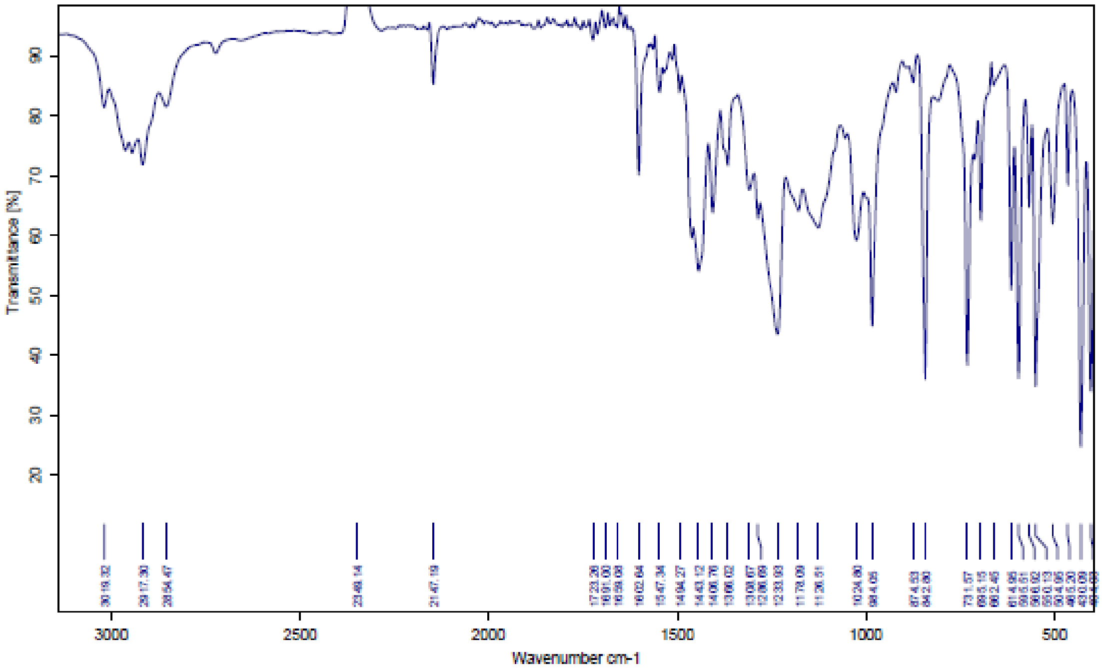


Figure S17 ATR-IR spectrum of **4**.

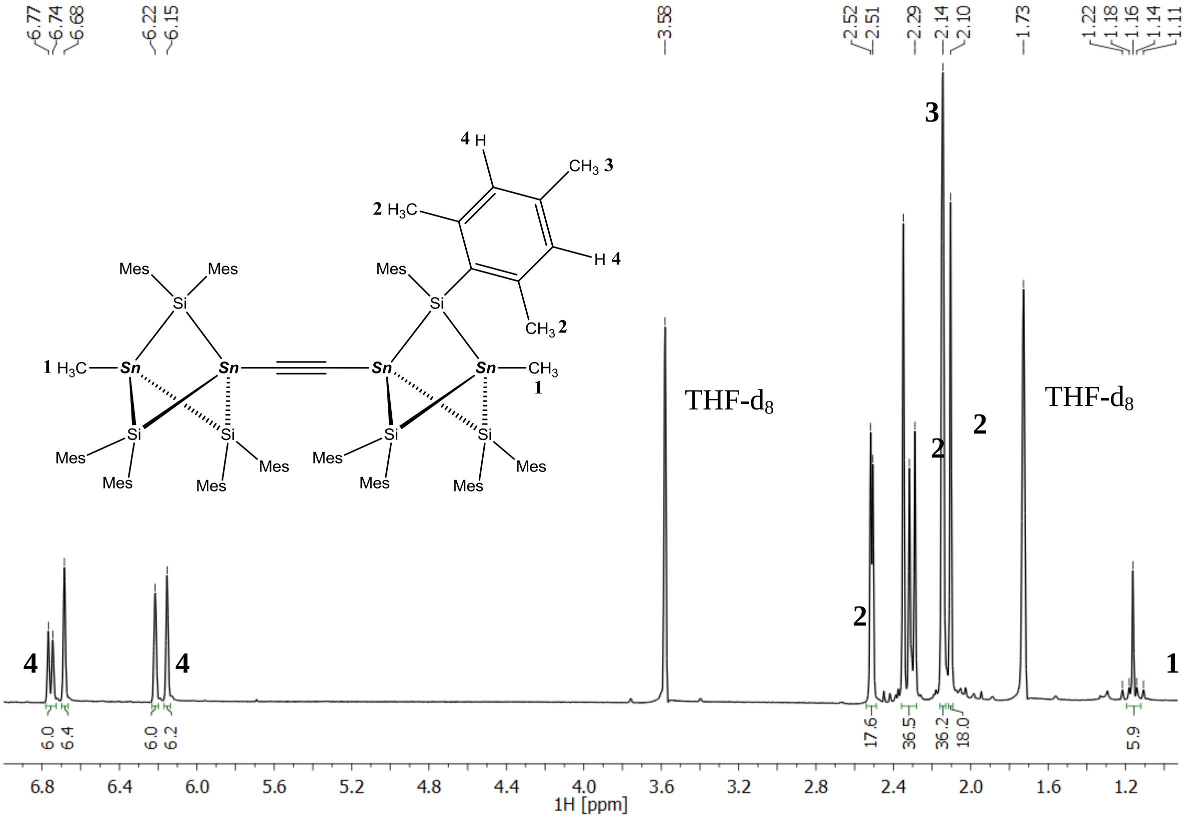


Figure S18 ^{1}H NMR spectrum of **5** (400.1 MHz, THF-d_8); see schematic drawing for numbering.

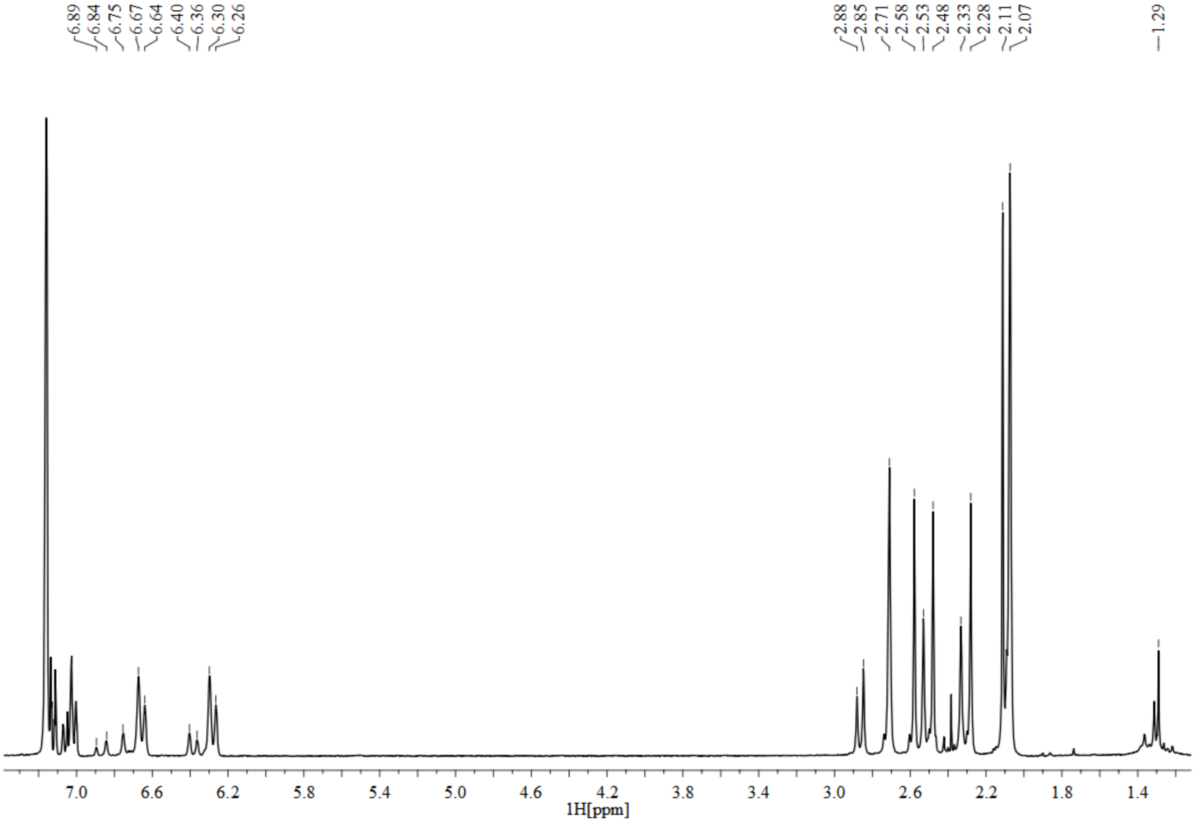


Figure S19 ^{1}H NMR spectrum of **5** in C_6D_6 (300 MHz).

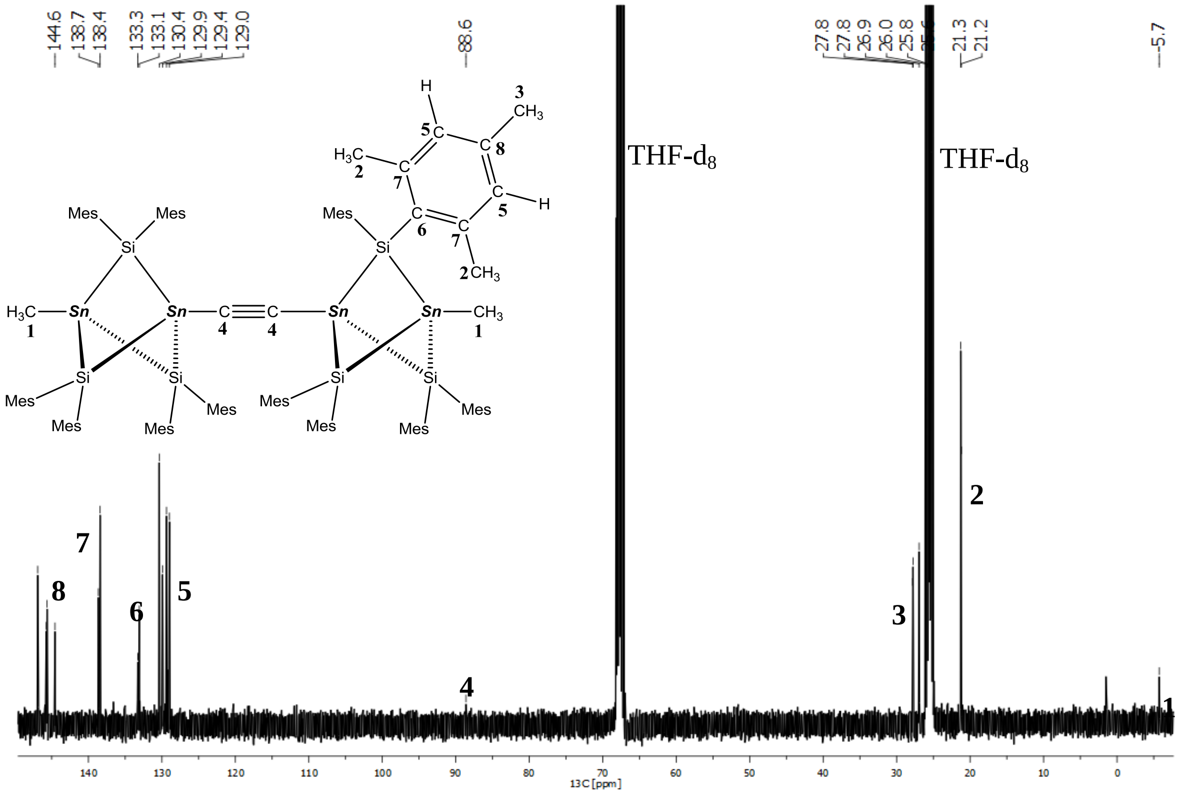


Figure S20 ^{13}C NMR spectrum of **5** (100.6 MHz, THF-d_8); see schematic drawing for numbering.

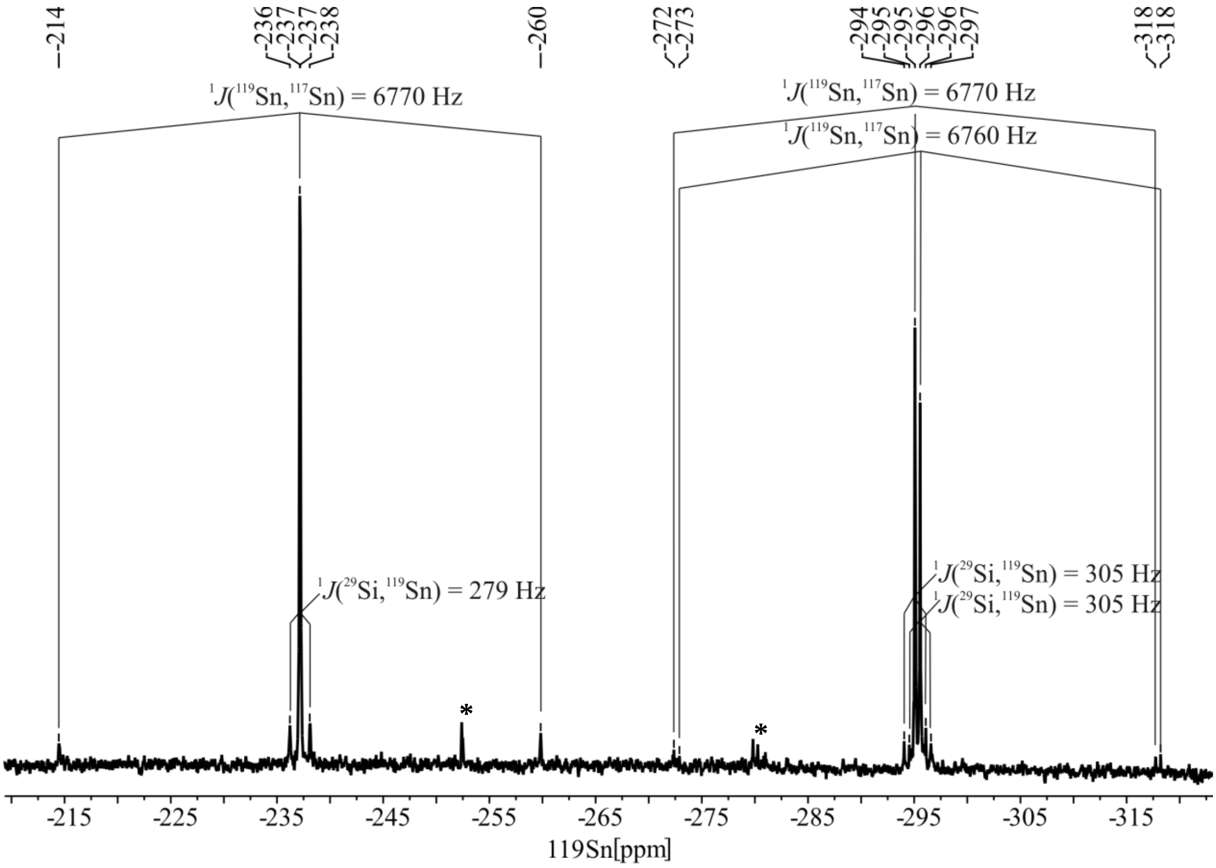


Figure S21 ^{119}Sn{^{1}H} NMR spectrum of **5** (79.5 MHz, THF-d$_8$). The signals marked with an asterisk are due to $^{1}J(^{119}$Sn,^{119}Sn) couplings between the bridgehead tin atoms (two of those on the right hand side; (expected values = 7082 and 7073 Hz). The corresponding satellites have not been observed due to their small intensity.

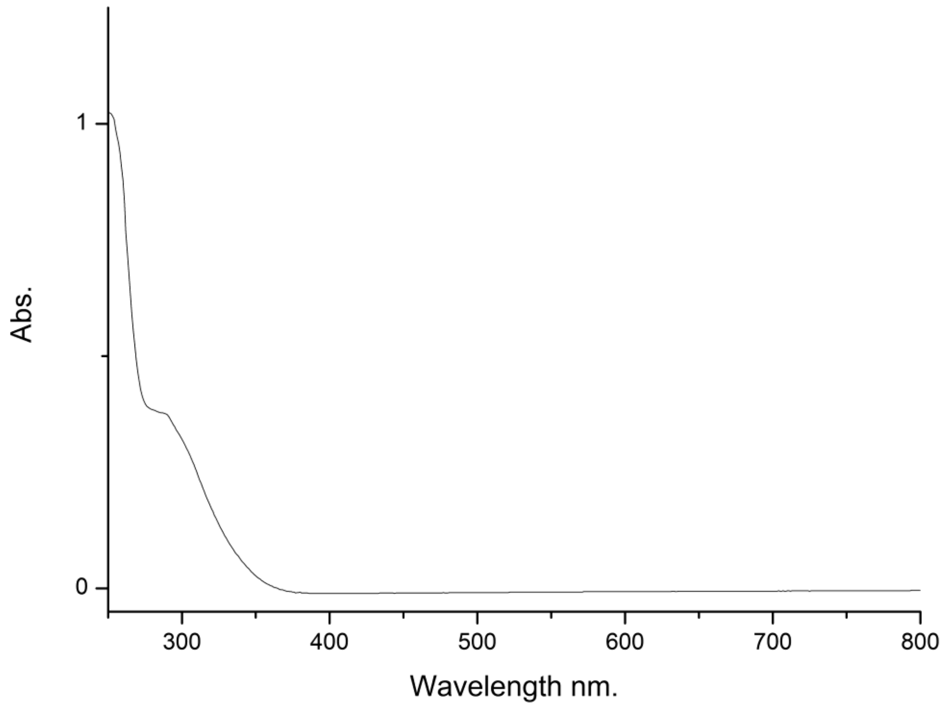


Figure S22 UV/Vis spectrum of **5** in THF.

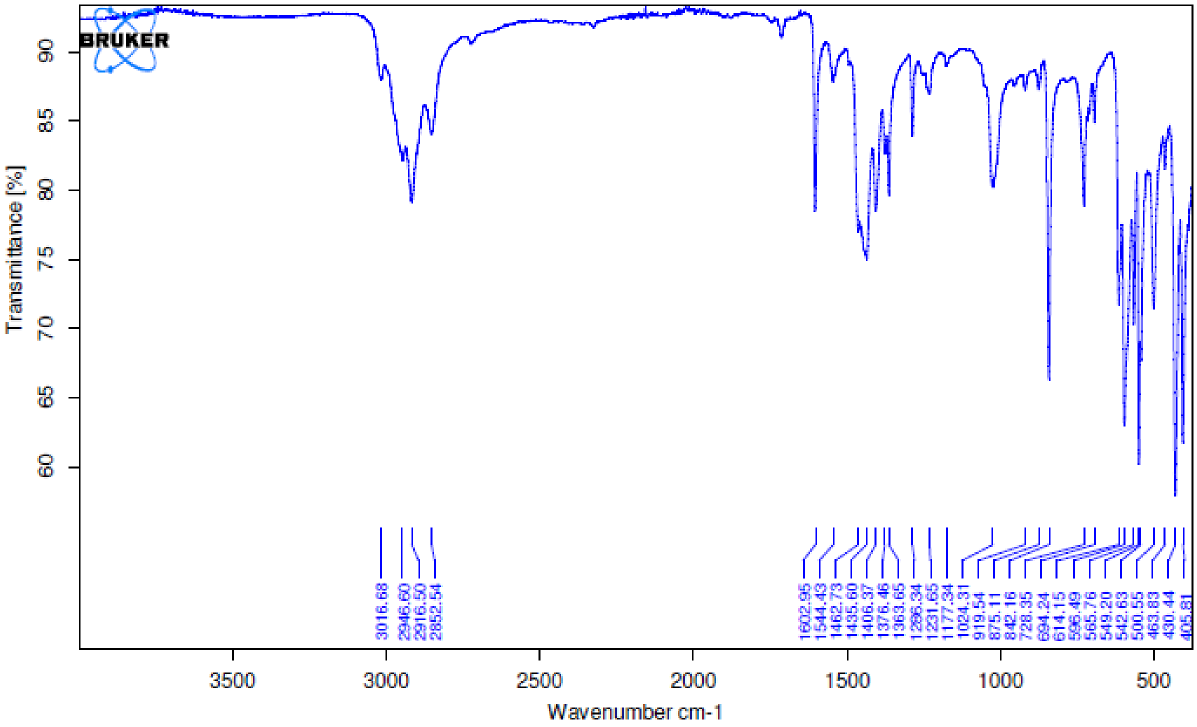


Figure S23 ATR-IR spectrum of **5**.

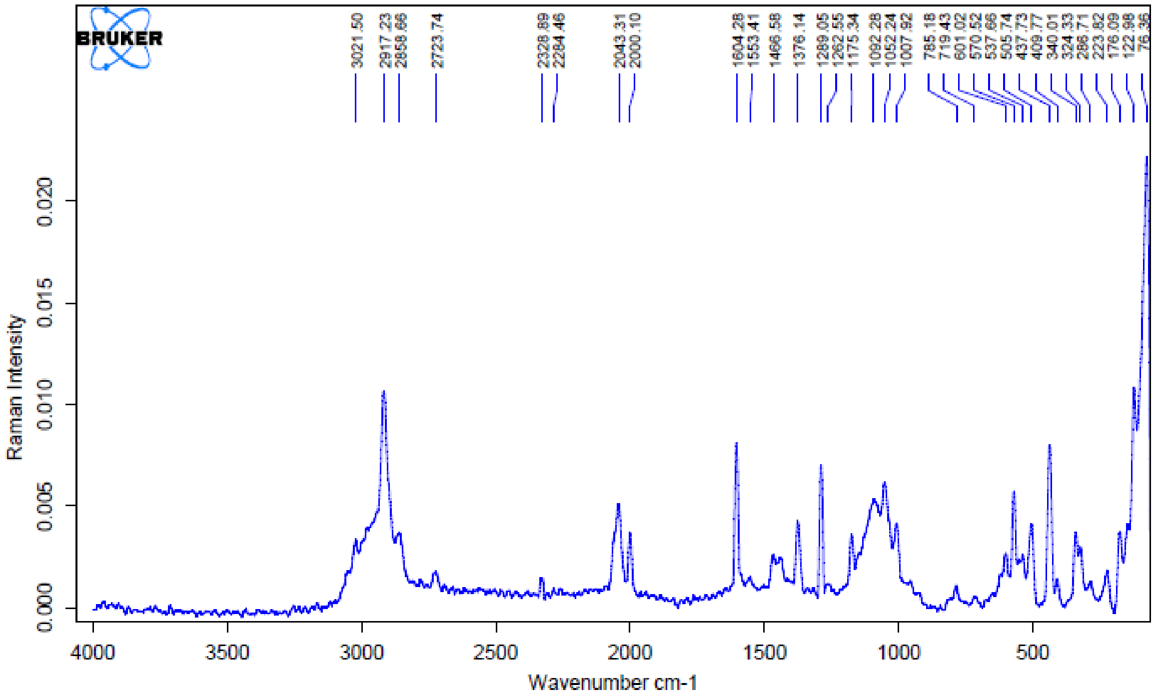


Figure S24 Raman powder spectrum of **5**.

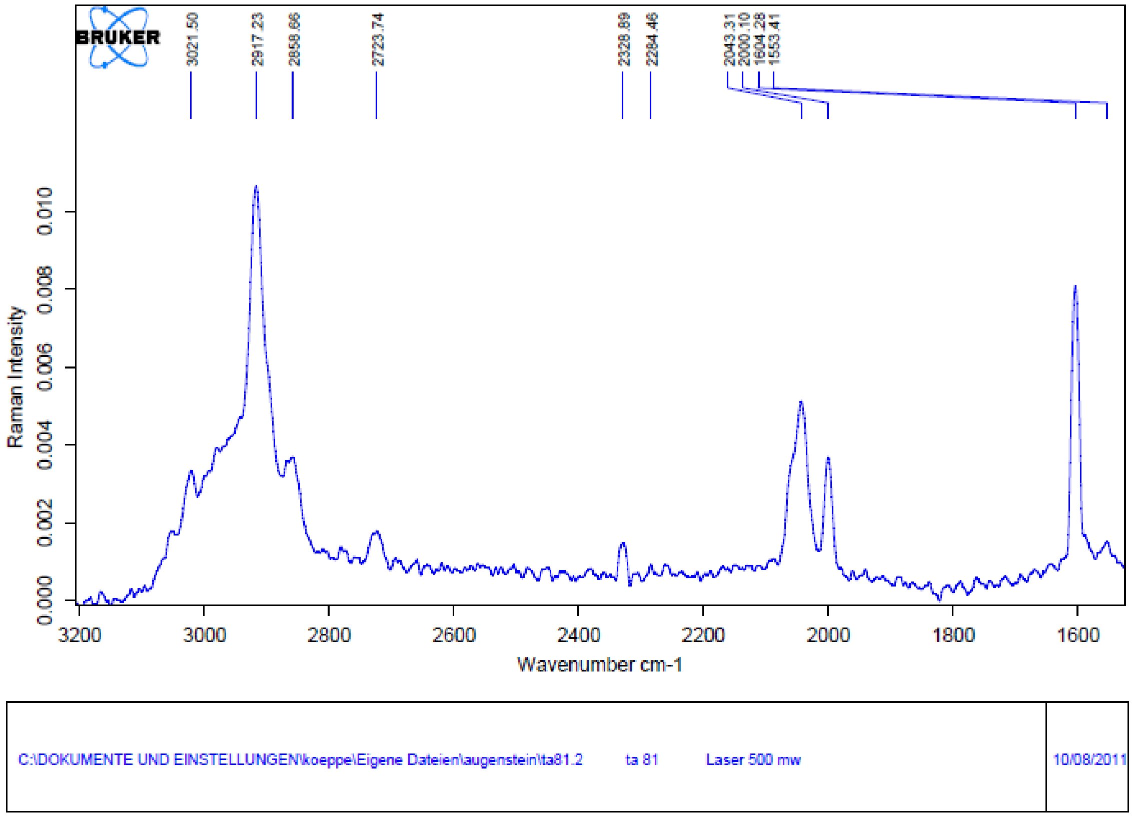


Figure S25 Section of the Raman powder spectrum of **5**.

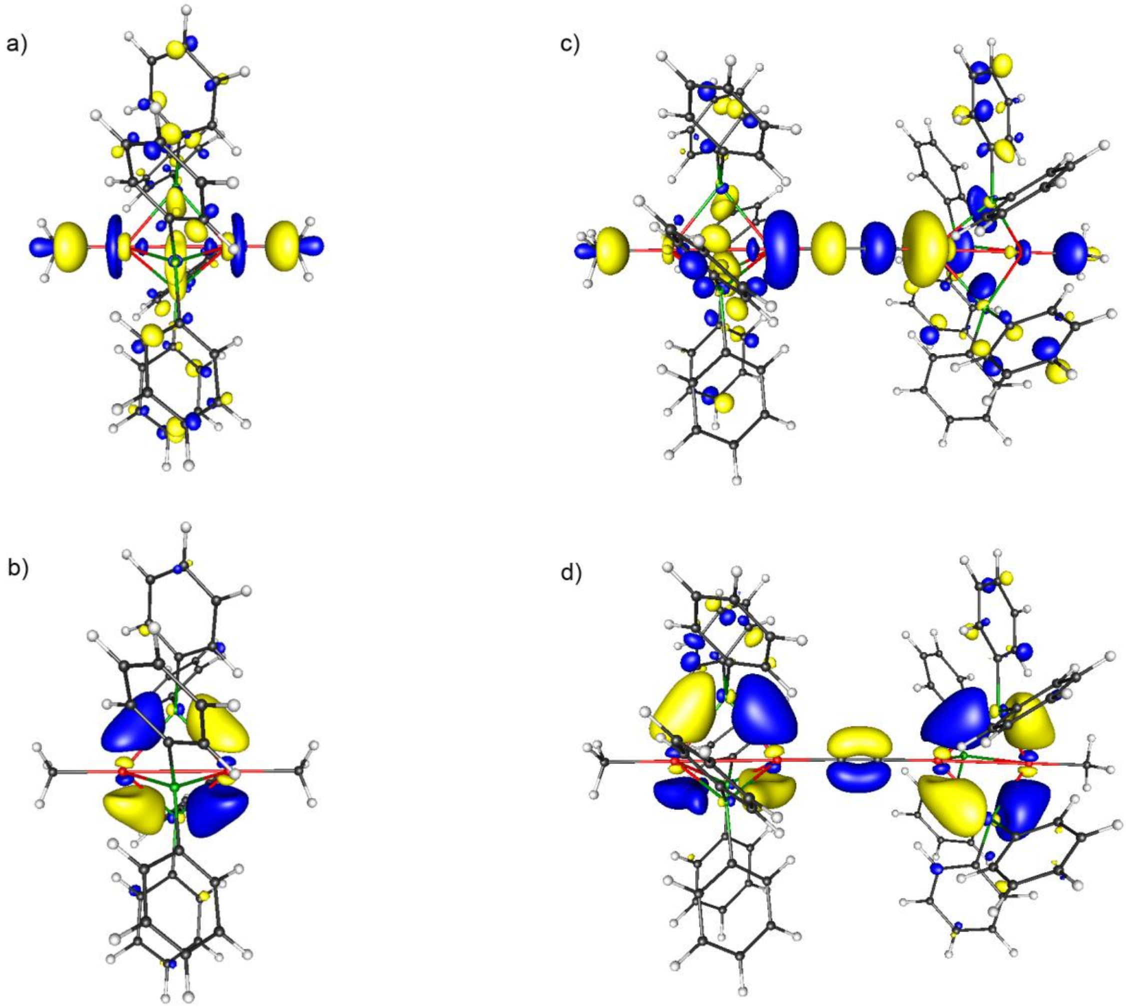


Figure S26 Frontier orbitals of **q2** and **q5**: a) LUMO of **q2**, b) HOMO of **q2** (degenerate set of *e* symmetry, only one is shown), c) LUMO of **q5**, d) HOMO of **q5**. Calculations were performed at the RI-DFT, BP86/def2-TZVP level. Molecular orbital plots were drawn with gOpenMol.

3. Crystal structures and structural parameters

3.1 General conditions

In each case, single crystals were obtained at room temperature from a toluene solution, which was layered with acetonitrile. In order to avoid degradation, the single crystals were mounted on glass fibers using perfluoropolyether oil and cooled rapidly in a stream of cold N_2 using an Oxford Cryosystems Cryostream unit. Diffraction data were measured using a STOE STADI 4 diffractometer with CCD detector and graphite-monochromated $Mo_{K\alpha}$ (0.71073 Å) radiation. All calculations were performed using SHELXTL (ver. 6.12) program suite.[S6] The structures were solved by direct methods and successive interpretation of the difference Fourier maps, followed by full matrix least-squares refinement (against F^2). All non-hydrogen atoms were refined anisotropically (for exceptions, see below). The contribution of the hydrogen atoms, in their calculated positions, was included in the refinement using a riding model. Upon convergence, the final Fourier difference map of the X-ray structures showed no significant peaks. All details of the structure solution and refinements are given in the Supporting Information (CIF data). Furthermore, crystal data collection and processing parameters are given in the Tables S1-S3. A full listing of atomic coordinates, bond lengths and angles and displacement parameters for the structures **3**, **4**, and **5** have been deposited at the Cambridge Crystallographic Data Centre.

The crystal structure of **2** contains several disordered solvent molecules, which could not be refined appropriately, even by measuring different single crystals from different batches. The best refinement ($R1 = 0.0908$, $wR2 = 0.2747$) was reached by placing three (isotropic) six-membered carbon rings (representative for disordered toluene lattice molecules; AFIX 66 restraint in SHELXL) on the disordered positions. Due to this problem, no structural parameters are discussed and no cif-file has been generated for **2**. However, in order to illustrate the connectivity within **2**, the 1,3-dimethyl substituted bicyclo[1.1.1]pentane core structure is shown in Figure S27, relevant unit cell parameters are given in the caption. One molecule of **3** crystallises with three toluene molecules with 50% occupancy each, as indicated by the formula $C_{57}H_{70}Si_3Sn_2 \cdot 1.5\ C_7H_8$ in Table S1. These carbon atoms were not refined anisotropically. Furthermore, the methyl and the ethynyl substituent of **3** were found to be statistically disordered due to a comparable steric demand of both substituents. The two positions were refined against each other by using first a free variable (FVAR) and finally fixed occupation factors of 2 x 50%. Compound **5** crystallises with two acetonitrile and six toluene solvent molecules in the crystal lattice. Four of the latter show occupancies of 100% and 50%, while the third toluene molecule could only be refined as (anisotropic) benzene ring (representative for a disordered toluene molecule; AFIX 66 restraint in SHELXL) with an occupancy of only 25% (formula $C_{112}H_{138}Si_6Sn_4 \cdot 0.5\ C_6H_6 \cdot 3\ C_7H_8 \cdot 2\ C_2H_3N$ in Table S3) Furthermore, the 50% and 25% toluene molecules are located on special crystallographic positions and had to be refined by using appropriate instructions (PART–1 in SHELXL).

3.2 Crystal Data, Data Collection, and Structure Refinement for (2), 3, 4, and 5.

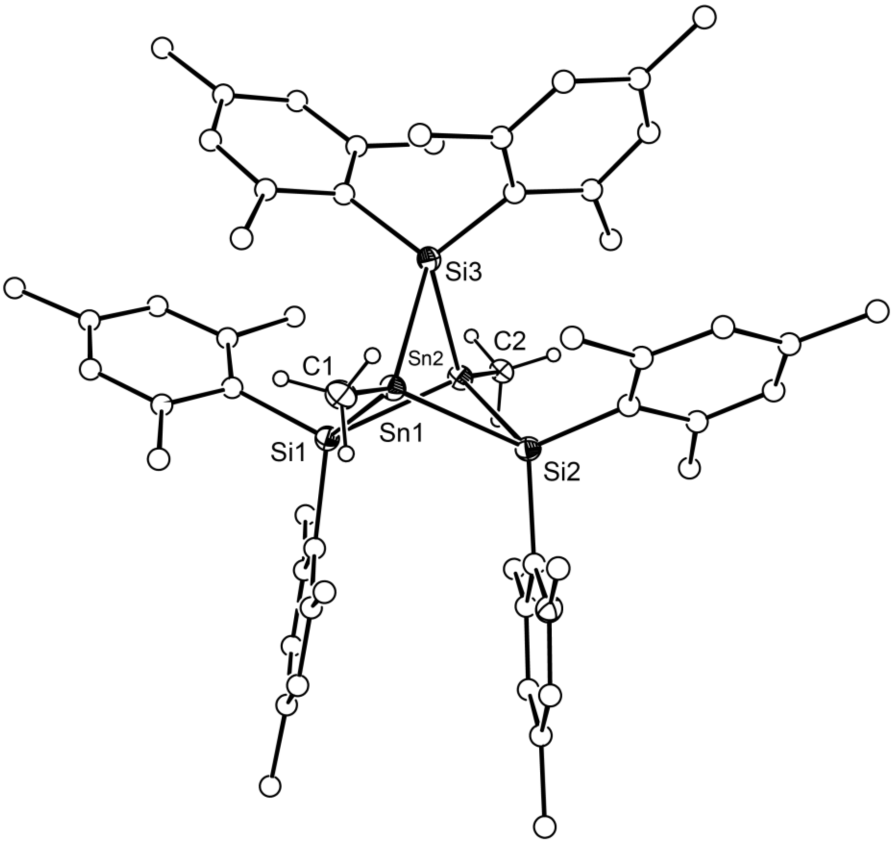


Figure S27 Displacement ellipsoid plot (30% probability) of **2**; hydrogen atoms of the Mes ligands have been omitted and carbon atoms of the Mes substituents have been drawn with arbitrary radii for clarity; selected cell data: monoclinic, $P2_1/c$, a = 1086.8(2) pm, b = 3345.4(7) pm, c = 1978.4(4) pm, β = 99.77(3)°, V = 7089(2) 10^6 pm^3, Z = 4.

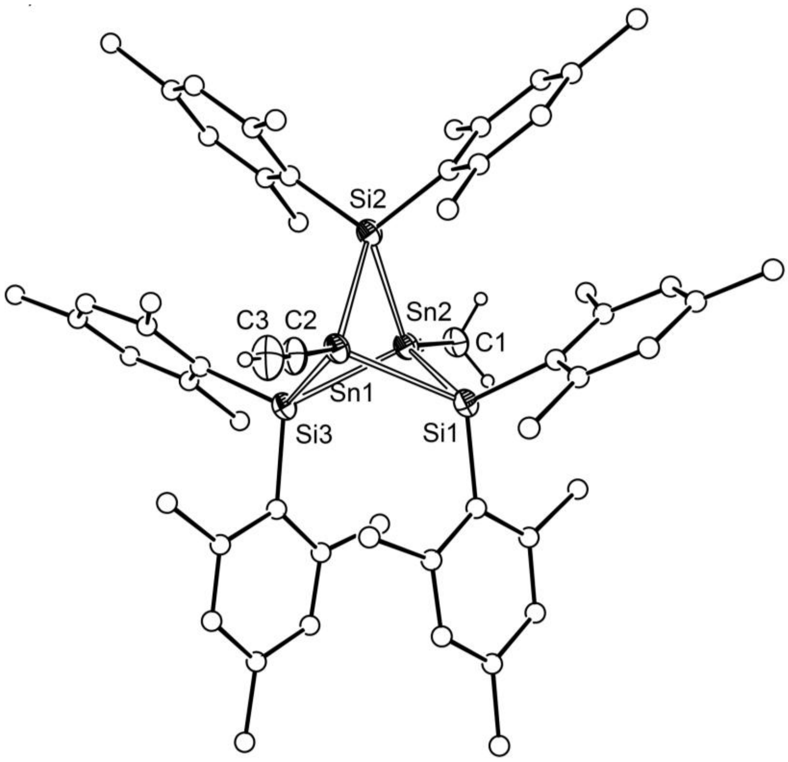


Figure S28 Displacement ellipsoid plot (30% probability) of **3**; hydrogen atoms of the Mes ligands have been omitted and carbon atoms of the Mes substituents have been drawn with arbitrary radii for clarity. Selected bond length (pm) and angles (°): Sn1···Sn2 315.7(1), Sn1–Si1 262.2(2), Sn1–Si2 261.2(2), Sn1–Si3 262.3(1), Sn2–Si1 261.9(2), Sn2–Si2 262.0(2), Sn2–Si3 262.0(2), Si–C 189.8(5)–190.8(5), Sn1−C2 199(1), Sn1−C1' 235(2), Sn2−C2' 200(2), Sn2−C1 235(2), C2−C3 115.6(9), C2'−C3' 108(2); Sn1–Si1–Sn2 74.1(1), Sn1–Si2–Sn2 74.2(1), Sn1–Si3–Sn2 74.1(1), Si1–Sn1–Si2 87.4(1), Si1–Sn1–Si3 87.4(1), Si2–Sn1–Si3 87.5(1), Si1–Sn2–Si2 87.3(1), Si1–Sn2–Si3 87.4(1), Si2–Sn2–Si3 87.5(1), Sn2−C2'−C3' 176.7(20), Sn1−C2−C3 177(2).

Table S1 Crystal data for **3**.

Compound	**3**
Elemental formula	$C_{57}H_{70}Si_3Sn_2 \cdot 1.5\ C_7H_8$
Molar mass	1214.98
Crystallographic system	Triclinic
Space group	P–1
Cell constants	a /pm = 1117.0(2) α /° = 64.00(3) b /pm = 1830.7(4) β /° = 80.10(3) c /pm = 1971.4(4) γ /° = 86.56(3)
V [10^6 pm^3]	3569(1)
Z	2
μ [mm^{-1}]	0.783
Calc. density [g/cm^3]	1.131
Crystal dimensions [mm]	0.30 x 0.30 x 0.20
Measurement temperature [K]	200
$2\theta_{max}$ [°]	50.00
Measured reflexes	30550
Independent reflexes	12505 (R_{int} = 0.0678)
Parameter / Restraints	655 / 82
$R1$	0.0488
$wR2$ (all data)	0.1466
Residual electron density [10^{-6} e/pm^3]	1.355 / –0.670
Diffractometer type	Stoe Stadi4 with CCD detector

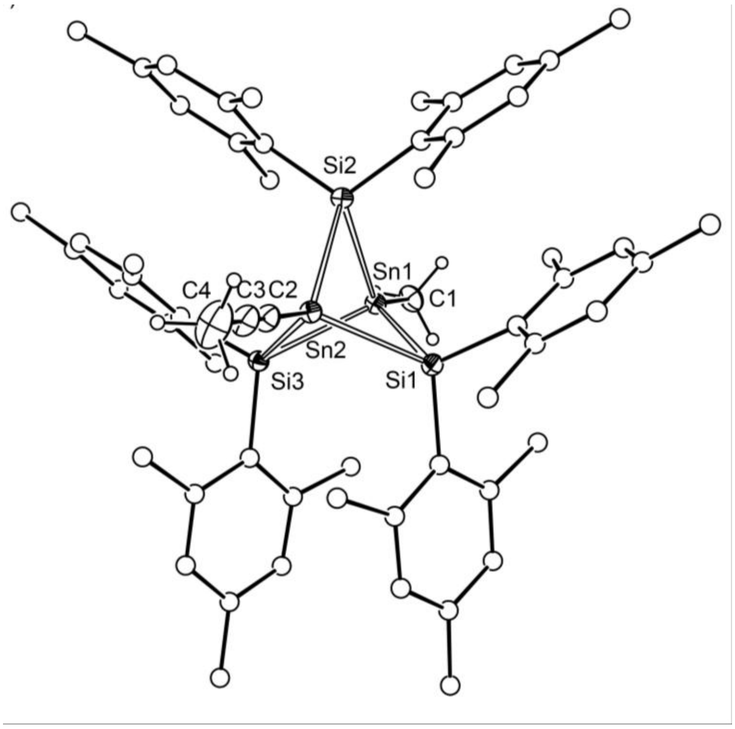


Figure S29 Displacement ellipsoid plot (30% probability) of **4**; hydrogen atoms of the Mes ligands have been omitted and carbon atoms of the Mes substituents have been drawn with arbitrary radii for clarity. Selected bond length (pm) and angles (°): Sn1···Sn2 315.8(1), Sn1–Si1 260.5(1), Sn1–Si2 261.7(1), Sn1–Si3 262.5(1), Sn2–Si1 260.5(1), Sn2–Si2 261.0(1), Sn2–Si3 262.0(1), Si–C 189.0(4)–190.8(4), Sn1−C1 215.1(4), Sn2−C2 210.4(4), C2−C3 113.3(5), C3−C4 151.2(6); Sn1–Si1–Sn2 74.3(1), Sn1–Si2–Sn2 74.4(1), Sn1–Si3–Sn2 74.3(1), Si1–Sn1–Si2 88.4(1), Si1–Sn1–Si3 86.6(1), Si2–Sn1–Si3 87.1(1), Si1–Sn2–Si2 87.7(1), Si1–Sn2–Si3 86.8(1), Si2–Sn2–Si3 86.9(1), Sn1–C2–C3 177.2(4), C2–C3–C4 179.6(6).

Table S2 Crystal data for **4**.

Compound	**4**
Elemental formula	$C_{58}H_{72}Si_3Sn_2 \cdot C_7H_8$
Molar mass	1182.94
Crystallographic system	monoclinic
Space group	$P2_1/c$
Cell constants	a /pm = 1138.4(2) b /pm = 2650.2(5) β /° = 91.70(3) c /pm = 1944.4(4)
V [10^6 pm^3]	5864(2)
Z	4
μ [mm^{-1}]	0.951
Calc. density [g/cm^3]	1.340
Crystal dimensions [mm]	0.20 x 0.10 x 0.10
Measurement temperature [K]	200
$2\theta_{max}$ [°]	50.00
Measured reflexes	40243
Independent reflexes	10267 (R_{int} = 0.0872)
Parameter / Restraints	653 / 0
$R1$	0.0436
$wR2$ (all data)	0.1114
Residual electron density [10^{-6} e/pm^3]	0.875 / –0.834
Diffractometer type	Stoe Stadi4 with CCD detector

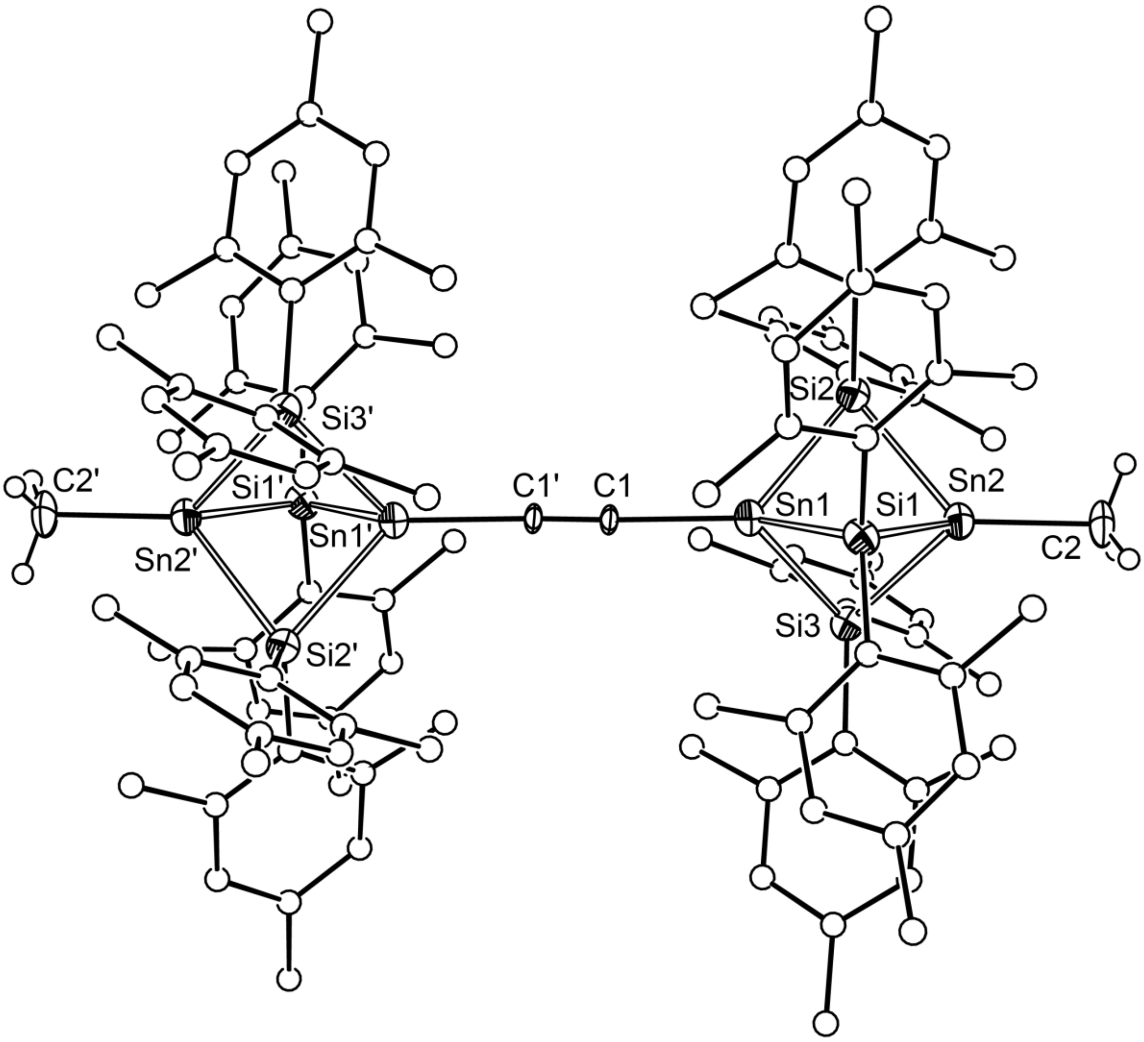


Figure S30 Displacement ellipsoid plot (30% probability) of **5**; hydrogen atoms of the Mes ligands have been omitted and carbon atoms of the Mes substituents have been drawn with arbitrary radii for clarity. Selected bond length (pm) and angles (°): Sn1···Sn2 318.7(2), Sn1–Si1 262.5(2), Sn1–Si2 261.6(2), Sn1–Si3 260.4(2), Sn2–Si1 260.9(2), Sn2–Si2 262.7(2), Sn2–Si3 262.8(2), Si–C 190.0(6)–192.2(6), Sn1–C1 213.8(4), Sn2–C2 217.1(5); Sn1–Si1–Sn2 75.0(1), Sn1–Si2–Sn2 74.9(1), Sn1–Si3–Sn2 75.0(1), Si1–Sn1–Si2 86.5(1), Si1–Sn1–Si3 87.1(1), Si2–Sn1–Si3 86.6(1), Si1–Sn2–Si2 87.7(1), Si1–Sn2–Si3 87.5(1), Si2–Sn2–Si3 85.9(1); atoms denoted with an apostrophe are generated by −x+1, −y+1, −z+1.

Table S3 Crystal data for **5**.

Compound	**5**
Elemental formula	$C_{112}H_{138}Si_6Sn_4 \cdot 0.5\ C_6H_6 \cdot 3\ C_7H_8 \cdot 2\ C_2H_3N$
Molar mass	2525.09
Crystallographic system	triclinic
Space group	P–1
Cell constants	a /pm = 1349.3(3) α /° = 113.74(3) b /pm = 1595.0(3) β /° = 108.71(3) c /pm = 1786.5(4) γ /° = 96.95(3)
V [10^6 pm^3]	3298(1)
Z	1
μ [mm^{-1}]	0.851
Calc. density [g/cm^3]	1.271
Crystal dimensions [mm]	0.15 x 0.15 x 0.10
Measurement temperature [K]	200
$2\theta_{max}$ [°]	50.00
Measured reflexes	22218
Independent reflexes	11460 (R_{int} = 0.0624)
Parameter / Restraints	755 / 123
$R1$	0.0596
$wR2$ (all data)	0.1812
Residual electron density [10^{-6} e/pm^3]	1.942 / –1.175
Diffractometer type	Stoe Stadi 4 with CCD detector

4. References of the ESI

[S1] D. Nied, P. Oña-Burgos, W. Klopper and F. Breher, *Organometallics*, 2011, **30**, 1419.

[S2] (*a*) TURBOMOLE, V6.0, 2009, a development of University of Karlsruhe (TH) and Forschungszentrum Karlsruhe GmbH, 1989–2007, TURBOMOLE GmbH, since 2007, available from http://www.turbomole.com; (*b*) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165; (*c*) O. Treutler and R. Ahlrichs, *J. Chem. Phys.*, 1996, **102**, 346; (*d*) M. Sierka, A. Hogekamp and R. Ahlrichs, *J. Chem. Phys.*, 2003, **118**, 9136; (*e*) R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2004, **6**, 5119.

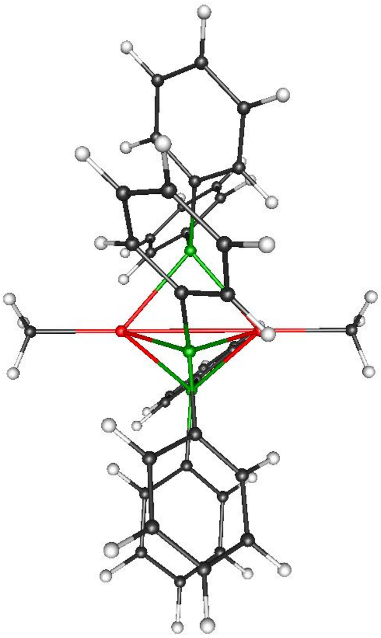
[S3] (*a*) J. C. Slater, *Phys. Rev.*, 1951, **81**, 385; (*b*) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200; (*c*) A. D. Becke, *Phys. Rev. A*, 1998, **38**, 3098; (*d*) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822.

[S4] (*a*) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297; (*b*) F. Weigend, *Phys. Chem. Chem. Phys.*, 2006, **8**, 1057.

[S5] D. Nied, E. Matern, H. Berberich, M. Neumaier and F. Breher, *Organometallics*, 2010, **29**, 6028.

[S6] (*a*) SHELXTL v6.12, Bruker AXS Inst. Inc., Madison, WI, USA, 2000; (*b*) G. M. Sheldrick, *Acta Cryst. Sect. A*, 2008, **64**, 112.

5. Coordinates of the calculated structures



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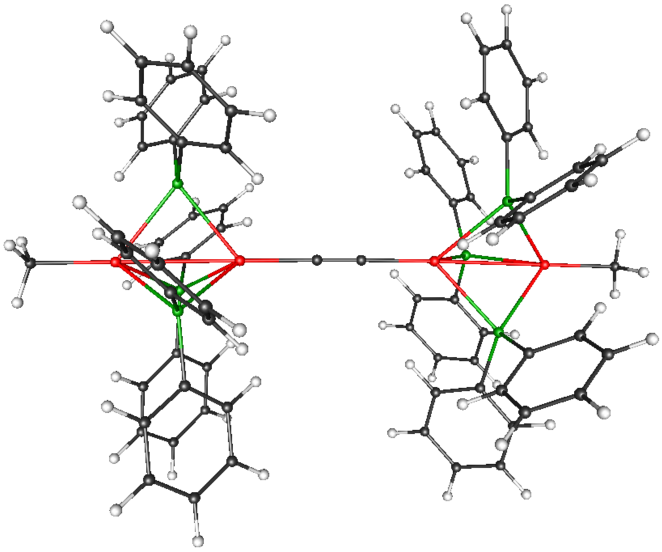

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C	5.2985891	-2.5366213	-3.0324460
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C	4.3154992	-1.5453173	-3.2010957
H	6.0516104	-2.4227878	-2.2494707
C	4.0702174	1.4937924	-3.3197999
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H	-4.2965797	-6.9830414	-2.3217692
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C	-4.2930519	-5.8996323	-2.1908624
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H	6.1064534	3.1855772	-1.2937131
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H	3.0191579	6.7480951	0.2866903
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C	4.4889350	3.6581740	0.0673179
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H	-8.5711535	0.2891879	0.8306254
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H	2.8494059	-3.0429377	3.1656449
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C	-4.8997968	-5.0215309	3.1448377
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H	6.3310504	-0.4884851	3.0778605
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C	-5.5503510	0.6467105	3.8929886
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H	-2.8872177	-1.4038703	4.4541175
C	-3.6754303	-0.6721282	4.6444392
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C	5.2372681	3.3232087	4.7408006
C	5.7465963	-1.2327633	5.0101762
H	3.0787873	-3.2645083	5.6147086
H	5.9899609	3.9727949	5.1915852
C	-5.6920768	1.1814069	5.1759211
H	-6.4833436	1.9051391	5.3774386
C	3.2756023	1.9273582	4.9474180
H	6.5633010	-0.7256230	5.5263240
C	4.8366433	-2.0096817	5.7302527
C	-3.8124624	-0.1386575	5.9272128
C	4.2367574	2.7530164	5.5342191
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H	2.4900155	1.4800820	5.5583998
H	-3.1304609	-0.4508419	6.7203186
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H	-4.9333018	1.2039488	7.2002731
H	4.2054503	2.9556780	6.6060834