Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Rhodium(I) Oxygen Adduct as a Selective Catalyst for One-Pot Sequential Alkyne Dimerization-Hydrothiolation Tandem Reactions

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Contents

S1. Standard Operating Procedures

a. Method

All synthetic manipulations, unless otherwise stated, were performed under an N_2 gas or Ar gas atmosphere using oven or flame dried glassware and standard Schlenk or vacuum line techniques. Air sensitive solids where stored and handled in a PureLab HE glove box. Preparation of NMR and crystallization samples that also require an inert atmosphere were done in the glove box.

b. Materials

Reagent ^{t}BuOCl was prepared according to the method of Mintz and Walling.[i] The precursor compound **3,6-di-*tert*-butyl-1,8-diethynyl-9H-carbazole** and pincer ligand precursor **1b** was prepared as previously reported by us.[ii] **1,3-bis-(2,4,6-trimethylphenyl)triaz-1-ene** was prepared by an adapted procedure, as reported for the synthesis of **1,3-bis-(2,6-di-*iso*-propylphenyl)triaz-1-ene**.[ii] All other reagents were obtained from commercial sources and were used without any further purification.

Unless otherwise stated, only anhydrous solvents were used during experimental procedures. Anhydrous THF and Et_2O were obtained after distillation over sodium and benzophenone under a N_2 gas atmosphere. Anhydrous PhMe and hexane were obtained after distillation over sodium under a N_2 gas atmosphere. Anhydrous CH_2Cl_2 was obtained after distillation over calcium hydride under a N_2 gas atmosphere. Deuterated benzene was dried over sodium and distilled under an Ar gas atmosphere.

c. Characterisation Techniques

Nuclear magnetic resonance (NMR) spectra were obtained using either a Bruker AVANCE-III-300 operating at 300.13 MHz for ^{1}H, 75.47 MHz for ^{13}C, 121.49 MHz for ^{31}P and 282.40 MHz for ^{19}F; or AVANCE-III-400 operating at 400.21 MHz for ^{1}H, 100.64 MHz for ^{13}C, 162.01 MHz for ^{31}P and 376.57 MHz for ^{19}F. ^{1}H Chemical shifts are reported as δ (ppm) values downfield from Me_4Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD_3CN, 1.94ppm; $CDCl_3$, 7.26ppm; C_6D_6, 7.16ppm). ^{13}C chemical shifts are also reported as δ (ppm) values downfield from Me_4Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD_3CN, 1.32 ppm; $CDCl_3$, 77.16 ppm; C_6D_6, 128.06 ppm). Proton coupling constants (*J*) are given in Hz. The spectral coupling patterns are designated as follows: s/S - singlet; d/D - doublet; t/T - triplet; q/Q - quartet; sept-septet; m - multiplet; br - broad signal. Quaternary carbons are designated as $\mathbf{C}_q$.

Chemical shift assignment in the ^{1}H NMR spectra is based on first-order analysis and when required were confirmed by two-dimensional (2D) (^{1}H-^{1}H) homonuclear chemical shift correlation (COSY) experiments. The ^{13}C shifts were obtained from proton-decoupled ^{13}C NMR spectra. Where necessary, the multiplicities of the ^{13}C signals were deduced from proton-decoupled DEPT-135 spectra. The resonances of the proton-bearing carbon atoms were correlated with specific proton resonances using 2D (^{13}C-^{1}H) heteronuclear single-quantum coherence (HSQC) and heteronuclear multiple bond correlations (HMBC) experiments. Standard Bruker pulse programs were used in the experiments.

Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-K_{α} radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on nylon loops then immediately placed in a cold stream of N_2 at 150 K. Structures were solved and refined using Olex2 and SHELXTL. A satisfactory refinement of the crystal structure of **2a** after squeeze methodology was applied in order to eliminate residual electronic density of the solvent that could be refined otherwise [iii-v]

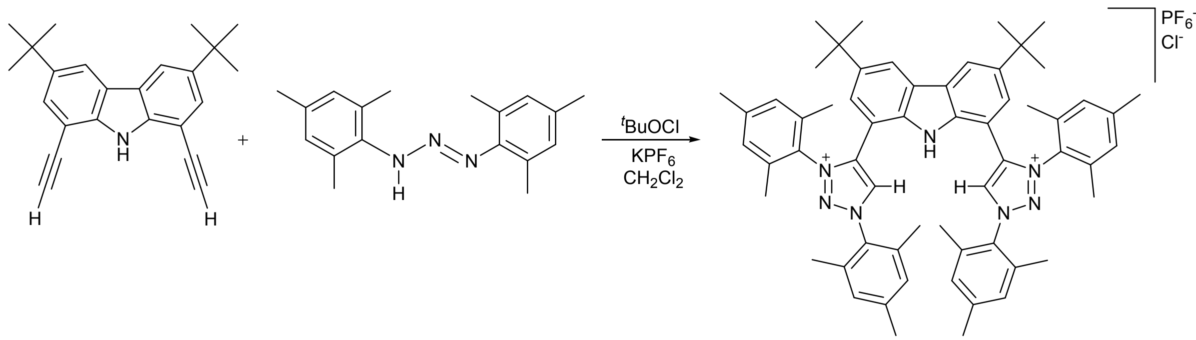
Solution IR spectra (ν(CO)) were recorded on a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer in CH_2Cl_2 as solvent. The range of absorption measured was from 4000-600 cm^{-1}.

Mass spectral analyses were performed on a Waters Synapt G2 HDMS by direct infusion at *5* µL/min with positive electron spray as the ionization technique. The *m/z* values were measured in the range of 400-1500 with acetonitrile as solvent. Prior to analysis, a 5 mM sodium formate solution was used to calibrate the instrument in resolution mode.

Microanalyses (%C, H, N) were performed using a ThermoScientific Flash 2000 elemental analyser. Following extensive drying, analyses of complexes **2** and **3** are outside acceptable limits and are ascribed to the presence of solvent molecules and/or silicon grease. The full ^{1}H and ^{13}C NMR spectra are therefore included in the SI to attest to the purity of the compounds, supported by HRMS, FT-IR and single crystal XRD spectroscopic results.

S2. Synthesis details and characterization

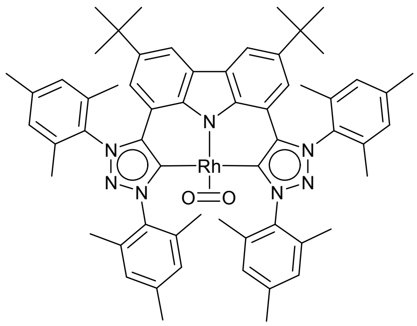
a. Synthesis of 1a



Scheme S1: Synthesis of tridentate CNC pincer ligand precursor **1a**

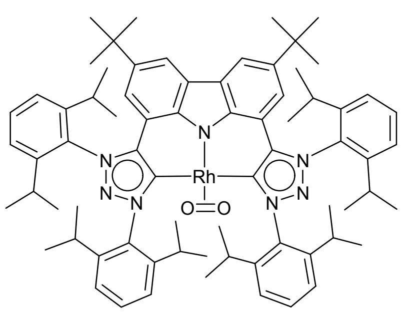
Compound **1a** (Scheme S1) was prepared by a similar method as used for the synthesis of **1b**.[ii] A 500 mL, 3-necked round bottom flask was charged with **3,6-di-*tert*-butyl-1,8-diethynyl-9H-carbazole** (8.00 g, 24.4 mmol), **1,3-bis-(2,4,6-trimethylphenyl)triaz-1-ene** (22.00 g, 78.2 mmol) and potassium hexafluorophosphate (15.24 g, 82.8 mmol). The vessel was purged with N_2(g). The solids were dissolved in dry DCM (250 mL) and the solution was cooled down to -78 °C. To the solution was added *tert*-BuOCl (9.3 mL, 78.2 mmol) in a drop wise manner with subsequent stirring of the solution at -78 °C for two hours. After two hours, the solution was left to slowly warm up to room temperature whilst stirring for 20 hours. The white precipitate was filtered from the brown red solution with subsequent evaporation of the solvent *in vacuo*. Trituration with hexanes followed by Et_2O yielded **1a** as an off-white solid (24.70 g, 23.1 mmol, 95%). Single crystals where obtainable from acetone layered with hexane. For $C_{60}H_{69}N_7ClPF_6$, Anal. Calcd.: C, 67.54; H, 6.51; N, 9.17. Found: C, 67.53; H, 6.56; N, 8.97. ^{1}H NMR (300 MHz, CD_3CN) δ 11.51 (br s, 1H, N$\mathbf{H}_{carb}$), 10.06 (s, 2H, Ar$\mathbf{H}_{\mathbf{Triazolium}}$), 8.42 (d, *J* = 1.8 Hz, 2H, Ar$\mathbf{H}_{carb}$), 7.23 (br s, 4H, Ar$\mathbf{H}_{Mes}$), 7.19 (br s, 4H, Ar$\mathbf{H}_{Mes}$), 7.08 (d, *J* = 1.5 Hz, 2H, Ar$\mathbf{H}_{carb}$), 2.46 (s, 6H, ArC$\mathbf{H_3}$), 2.36 (s, 6H, ArC$\mathbf{H_3}$), 2.26 (s, 12H, ArC$\mathbf{H_3}$), 2.08 (s, 12H, ArC$\mathbf{H_3}$), 1.16 (s, 18H, C(C$\mathbf{H}_3$)$_3$). ^{13}C NMR (75 MHz, CD_3CN) δ 145.3 (Ar$\mathbf{C}_q$), 144.5 (Ar$\mathbf{C}_q$), 144.2 (Ar$\mathbf{C}_q$), 142.3 (Ar$\mathbf{C}_q$), 138.7 (Ar$\mathbf{C}_q$), 136.1 (Ar$\mathbf{C}_q$), 135.9 (Ar$\mathbf{C}_q$), 133.6 (Ar$\mathbf{C}_q$), 132.5 (Ar$\mathbf{C}_q$), 131.3 (Ar**C**H), 130.9 (Ar**C**H), 127.2 (Ar$\mathbf{C}_q$), 125.9 (Ar**C**H), 122.5 (Ar**C**H), 106.9 (Ar$\mathbf{C}_q$), 35.4 (**C**(CH_3)$_3$), 31.5 (C(**C**H_3)$_3$), 21.4 (Ar**C**H_3), 21.2 (Ar**C**H_3), 18.1 (Ar**C**H_3), 18.1 (Ar**C**H_3). ^{19}F NMR (282 MHz, CD_3CN) δ -72.90 (d, *J* = 706.0 Hz, P$\mathbf{F_6}$). ^{31}P NMR (121 MHz, CD_3CN) δ -144.6 (sept, *J* = 706.5 Hz, **P**F_6). HRMS (FIA-ESI): Calculated for $C_{60}H_{69}N_7^{2+}$ $[M]^{2+}$: 443.7802, found: 443.7835.

b. Synthesis of 2a



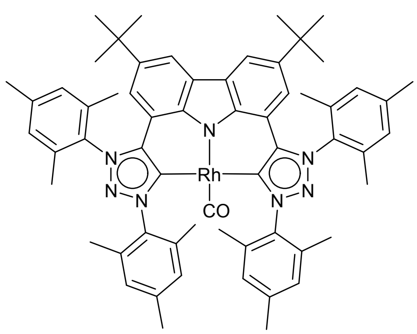
A flame dried Schlenk tube was charged with **1a** (200.0 mg, 1.9 x 10^{-4} mol), $[Rh(C_2H_4)_2Cl]_2$ (58.2 mg, 1.5 x 10^{-4} mol) and $KN[Si(CH_3)_3]_2$ (186.7 mg, 9.4 x 10^{-4} mol). The reaction vessel was evacuated, purged with N_2 (g), and cooled down to -78 °C. The solids were dissolved by addition of THF (20 mL) which was also cooled down to -78 °C. The solution was stirred for one hour at -78 °C. After one hour, the reaction was slowly heated up to RT whilst stirring overnight. The solvent was evaporated *in vacuo* and the product was extracted with hexanes (4 x 15 mL). Hexane was evaporated, *in vacuo*, yielding a brown residue. The residue was re-dissolved in oxygenated dry toluene, and left to settle at RT for 48 hours. After 48 hours, the solvent was evaporated *in vacuo* to obtain **2a** (130.0 mg, 1.3 x 10^{-4}mol, 68 %) as a brown solid. Crystal suitable for X-ray diffraction could not be obtained. For $RhC_{60}H_{66}N_7O_2$, Anal. Calcd.: C, 70.64; H, 6.52; N, 9.61. Found: C, 68.52; H, 6.42; N, 9.01. ^{1}H NMR (300 MHz, C_6D_6) δ 8.55 (d, *J* = 1.8 Hz, 2H, Ar**H**$_{carb}$), 7.55 (d, *J* = 1.8 Hz, 2H, Ar**H**$_{carb}$), 6.78 (s, 4H, Ar**H**$_{Mes}$), 6.71 (s, 4H, Ar**H**$_{Mes}$), 2.43 (s, 12H, ArC**H**$_3$), 2.34 (s, 6H, ArC**H**$_3$), 2.08 (s, 6H, ArC**H**$_3$), 1.77 (s, 12H, ArC**H**$_3$), 1.25 (s, 18H, C(C**H**$_3$)$_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 167.5 (d, *J* = 39.0 Hz, Rh-**C**$_{Carbene}$), 144.4 (Ar**C**$_q$), 141.1 (Ar**C**$_q$), 140.8 (Ar**C**$_q$), 140.4 (Ar**C**$_q$), 138.3 (Ar**C**$_q$), 137.2 (Ar**C**$_q$), 135.7 (Ar**C**$_q$), 135.7 (Ar**C**$_q$), 134.9 (Ar**C**$_q$), 130.0 (Ar**C**H), 127.2 (Ar**C**H), 118.1 (Ar**C**H), 116.4 (Ar**C**H), 113.9 (Ar**C**$_q$), 113.9 (Ar**C**$_q$), 34.7 (**C**(CH$_3$)$_3$), 31.9 (C(**C**H$_3$)$_3$), 21.4 (Ar**C**H$_3$), 21.3 (Ar**C**H$_3$), 21.0 (Ar**C**H$_3$), 21.0 (Ar**C**H$_3$), 18.4 (Ar**C**H$_3$), 18.4 (Ar**C**H$_3$), 17.2 (Ar**C**H$_3$), 17.2 (Ar**C**H$_3$). HRMS (FIA-ESI): Calculated for $C_{60}H_{66}N_7RhO_2^{2+}$ [M + CH_3CN + 2H]$^{2+}$: 531.2377, found: 531.2393.

c. Synthesis of 2b



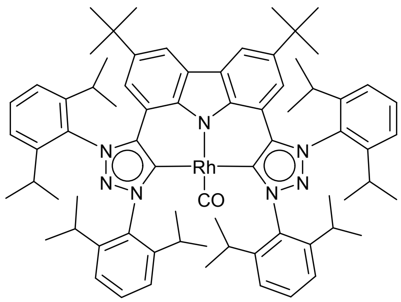
A flame dried Schlenk tube was loaded with **1b**[ii] (200.0 mg, 1.6 x 10^{-4} mol), $[Rh(C_2H_4)_2Cl]_2$ (50.3 mg, 1.3 x 10^{-4} mol) and $KN[Si(CH_3)_3]_2$ (161.3 mg, 8.1 x 10^{-4} mol). The Schlenk tube was evacuated and purged with N_2 (g). The reaction vessel was cooled down to -78 °C, and the solids dissolved by addition of THF (20 mL) which was also cooled down to -78 °C. The solution was stirred for one hour at -78 °C. The reaction, after one hour, was slowly heated up to RT whilst stirring overnight. The solvents were evaporated *in vacuo* and the product was extracted with hexanes (4 x 15 mL). Evaporation of the hexane solvent, *in vacuo*, yielded a brown residue. The residue was re-dissolved in oxygenated dry toluene, and left to settle at RT for 48 hours. After 48 hours, the solvent was evaporated *in vacuo* to obtain **2b** (105.0 mg, 8.8 x 10^{-5} mol, 55%) as a brown solid. Slow evaporation of a toluene solution yielded single crystals suitable for XRD analysis. For $RhC_{72}H_{90}N_7O_2$, Anal. Calcd.: C, 72.77; H, 6.53; N, 8.25. Found: C, 71.65; H, 7.40; N, 7.76. ^{1}H NMR (400 MHz, C_6D_6) δ 8.40 (d, *J* = 2.0 Hz, 2H, Ar**H**$_{carb}$), 7.49 (d, *J* = 2.0 Hz, 2H, Ar**H**$_{carb}$), 7.34 (t, *J* = 7.8 Hz, 2H, Ar**H**$_{Dipp}$), 7.30 (t, *J* = 7.8 Hz, 2H, Ar**H**$_{Dipp}$), 7.16 (d, 4H, Ar**H**$_{Dipp}$ overlaps with C_6D_6), 7.13 (d, *J* = 8.0 Hz, 4H, Ar**H**$_{Dipp}$), 2.98 (sept, *J* = 6.8 Hz, 4H, C**H**(CH_3)$_2$), 2.66 (sept, *J* = 6.8 Hz, 4H, C**H**(CH_3)$_2$), 1.65 (d, *J* = 6.8 Hz, 12H, CH(C**H**$_3$)$_2$), 1.23 (d, *J* = 7.2 Hz, 12H, CH(C**H**$_3$)$_2$), 1.21 (s, 18H, C(C**H**$_3$)$_3$), 1.05 (d, *J* = 6.8 Hz, 12H, CH(C**H**$_3$)$_2$), 0.78 (d, *J* = 6.8 Hz, 12H, CH(C**H**$_3$)$_2$). ^{13}C NMR (100 MHz, C_6D_6) δ 168.4 (d, *J* = 39.2 Hz, Rh-**C**$_{Carbene}$), 146.3 (Ar**C**$_q$), 145.4 (Ar**C**$_q$), 144.4 (Ar**C**$_q$), 141.6 (Ar**C**$_q$), 140.6 (Ar**C**$_q$), 137.5 (Ar**C**$_q$), 135.3 (Ar**C**$_q$), 131.7 (Ar**C**H), 129.1 (Ar**C**H), 125.5 (Ar**C**H), 121.6 (Ar**C**H), 119.6 (Ar**C**H), 116.7 (Ar**C**H), 113.2 (Ar**C**$_q$), 34.6 (**C**(CH_3)$_3$), 32.0 (C(**C**H$_3$)$_3$), 29.6 (**C**H(CH_3)$_2$), 29.1 (**C**H(CH_3)$_2$), 26.0 (CH(**C**H$_3$)$_2$), 24.8 (CH(**C**H$_3$)$_2$), 24.3 (CH(**C**H$_3$)$_2$), 23.2 (CH(**C**H$_3$)$_2$). HRMS (FIA-ESI): Calculated for $C_{72}H_{90}N_7RhO_2^{2+}$ $[M]^{2+}$: 593.8105, found: 593.8127.

d. Synthesis of 3a



To a flame dried Schlenk tube was added **2a** (25.0 mg, 2.5 x 10^{-5} mol). The reaction vessel was purged with N_2 (g). The brown solid was dissolved by adding hexane (5 mL). Carbon monoxide gas was bubbled through the solution for 5 minutes, resulting in a colour change from dark to orange. After filtration, the solvent was removed *in vacuo*, yielding **3a** (8.3 mg, 8.2 x 10^{-6} mol, 33%) as an orange solid. For $RhC_{61}H_{66}N_7O$, Anal. Calcd.: C, 72.10; H, 6.55; N, 9.65. Found: C, 70.37; H, 6.71; N, 9.15. ^{1}H NMR (300 MHz, C_6D_6) δ 8.67 (d, *J* = 1.8 Hz, 2H, Ar**H**$_{carb}$), 7.42 (d, *J* = 1.8 Hz, 2H, Ar**H**$_{carb}$), 6.84 (s, 4H, Ar**H**$_{Mes}$), 6.73 (s, 4H, Ar**H**$_{Mes}$), 2.40 (s, 12H, ArC**H**$_3$), 2.31 (s, 6H, ArC**H**$_3$), 2.09 (s, 6H, ArC**H**$_3$), 1.78 (s, 12H, ArC**H**$_3$), 1.30 (s, 18H, C(C**H**$_3$)$_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 194.9 (d, *J* = 71.6 Hz, Rh-**C**O), 173.4 (d, *J* = 41.1 Hz, Rh-**C**$_{Carbene}$), 144.9 (Ar**C**$_q$), 141.3 (Ar**C**$_q$), 140.6 (Ar**C**$_q$), 139.1 (Ar**C**$_q$), 138.3 (Ar**C**$_q$), 138.0 (Ar**C**$_q$), 136.1 (Ar**C**$_q$), 135.7 (Ar**C**$_q$), 135.6 (Ar**C**$_q$), 129.9 (Ar**C**H), 129.0 (Ar**C**H), 127.1 (Ar**C**$_q$), 117.9 (Ar**C**H), 116.9 (Ar**C**H), 112.7 (Ar**C**$_q$), 34.6 (**C**(CH_3)$_3$), 32.1 (C(**C**H$_3$)$_3$), 21.5 (Ar**C**H$_3$), 21.0 (Ar**C**H$_3$), 18.7 (Ar**C**H$_3$), 17.3 (Ar**C**H$_3$). IR (ν_{CO}, CH_2Cl_2): 1941 cm^{-1}. HRMS (FIA-ESI): Calculated for $C_{60}H_{66}N_7RhCO^+$ $[M]^+$: 1015.4384, found: 1015.4407.

e. Synthesis of 3b



To a Schlenk tube was added **2b** (30.0 mg, 2.5 x 10^{-5} mol), and dissolved by adding CH_2Cl_2 (2 mL) resulting in a brown coloured solution. At room temperature, CO (g) was bubbled through the solution resulting in a colour change from brown to a yellow-brown. The solution was filtered and the solvent removed *in vacuo* yielding **3b** (8.0 mg, 6.8 x 10^{-6} mol, 27%) as a yellow-brown coloured residue. For $RhC_{73}H_{90}N_7O$, Anal. Calcd.: C, 74.02; H, 7.66; N, 8.28. Found: C, 71.87; H, 7.51; N, 7.87. ^{1}H NMR (300 MHz, C_6D_6) δ 8.52 (d, *J* = 1.8 Hz, 2H, Ar**H**$_{carb}$), 7.64 (dd, *J* = 5.7 Hz, 3.3 Hz, 1H, Ar**H**$_{Dipp}$), 7.46 (d, *J* = 1.5 Hz, 2H, Ar**H**$_{carb}$), 7.31 – 7.25 (m, 6H, Ar**H**$_{Dipp}$), 6.93 (dd, *J* = 5.7 Hz, 3.3 Hz, 1H, Ar**H**$_{Dipp}$), 3.04 (sept, *J* = 6.8 Hz, 4H, C**H**(CH_3)$_2$), 2.62 (sept, *J* = 6.8 Hz, 4H, C**H**(CH_3)$_2$), 1.55 (d, *J* = 6.9 Hz, 12H, CH(C**H**$_3$)$_2$), 1.25 (s, 18H, C(C**H**$_3$)$_3$), 1.16 (d, *J* = 6.9 Hz, 12H, CH(C**H**$_3$)$_2$), 1.04 (d, *J* = 6.9 Hz, 12H, CH(C**H**$_3$)$_2$), 0.78 (d, *J* = 6.9 Hz, 12H, CH(C**H**$_3$)$_2$). ^{13}C NMR (75 MHz, C_6D_6) δ 195.4 (d, *J* = 70.2 Hz, Rh-**C**O), 173.4 (d, *J* = 41.6 Hz, Rh-**C**$_{Carbene}$), 146.3 (Ar**C**$_q$), 146.1 (Ar**C**$_q$), 144.4 (Ar**C**$_q$), 142.7 (Ar**C**$_q$), 138.2 (Ar**C**$_q$), 137.6 (Ar**C**$_q$), 135.7 (Ar**C**$_q$), 133.4 (Ar**C**$_q$), 131.5 (Ar**C**H), 130.9 (Ar**C**H), 130.8 (Ar**C**H), 129.1 (Ar**C**H), 127.2 (Ar**C**$_q$), 125.4 (Ar**C**H), 124.1 (Ar**C**H), 119.0 (Ar**C**H), 117.1 (Ar**C**H), 111.8 (Ar**C**$_q$), 34.5 (**C**(CH_3)$_3$), 32.3 (C(**C**H_3)$_3$), 29.3 (**C**H(CH_3)$_2$), 29.1 (**C**H(CH_3)$_2$), 25.6 (CH(**C**H_3)$_2$), 24.8 (CH(**C**H_3)$_2$), 24.2 (CH(**C**H_3)$_2$), 23.1 (CH(**C**H_3)$_2$). IR (ν_{CO}, CH_2Cl_2): 1955 cm^{-1}. HRMS (FIA-ESI): Calculated for $C_{72}H_{90}N_7RhCO^{2+}$ [M + H]$^{2+}$: 592.8204, found: 592.8197.

S3. NMR Spectra of Compounds 2a-b and 3a-b

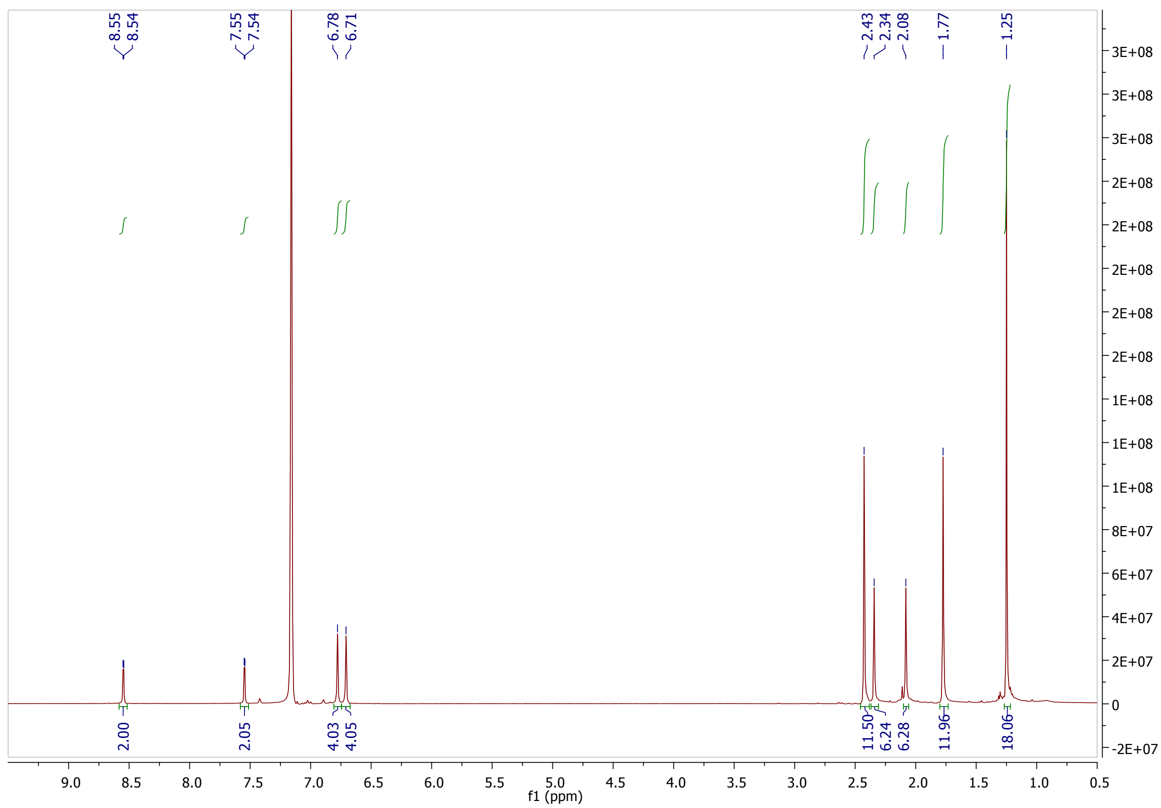


Figure S1. ^{1}H NMR of **2a** in C_6D_6 solvent

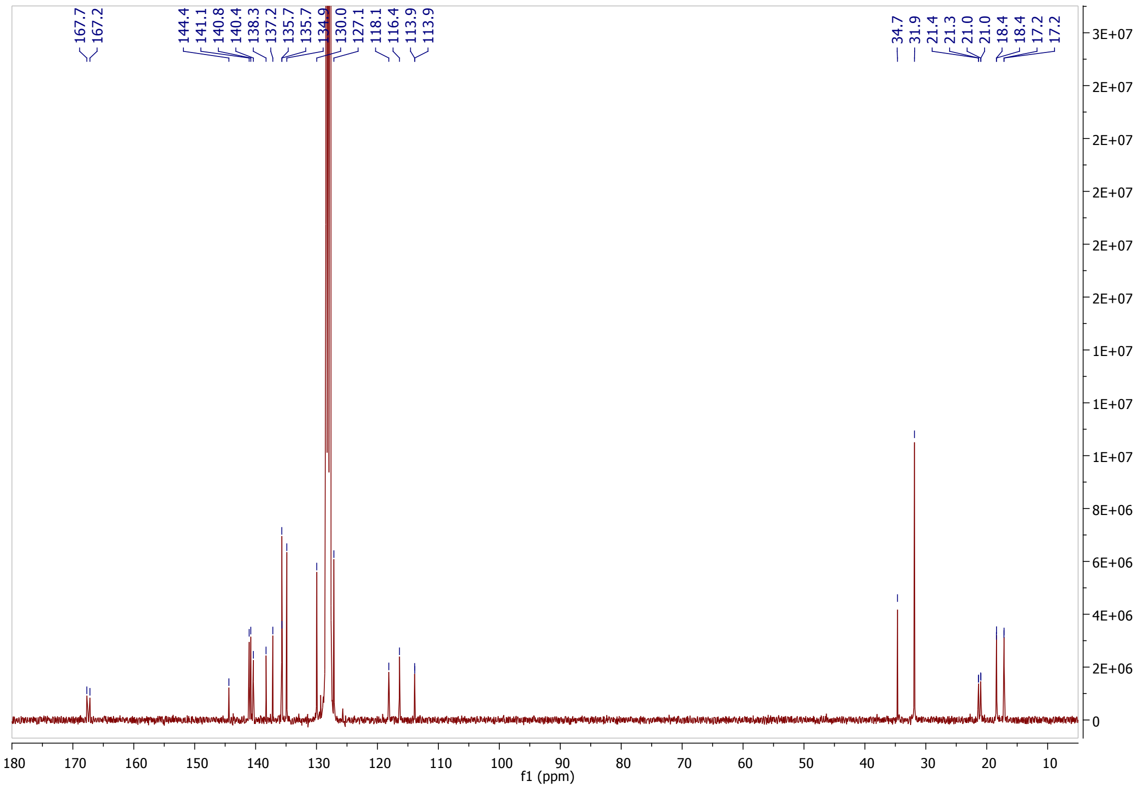


Figure S2. ^{13}C NMR of **2a** in C_6D_6 solvent

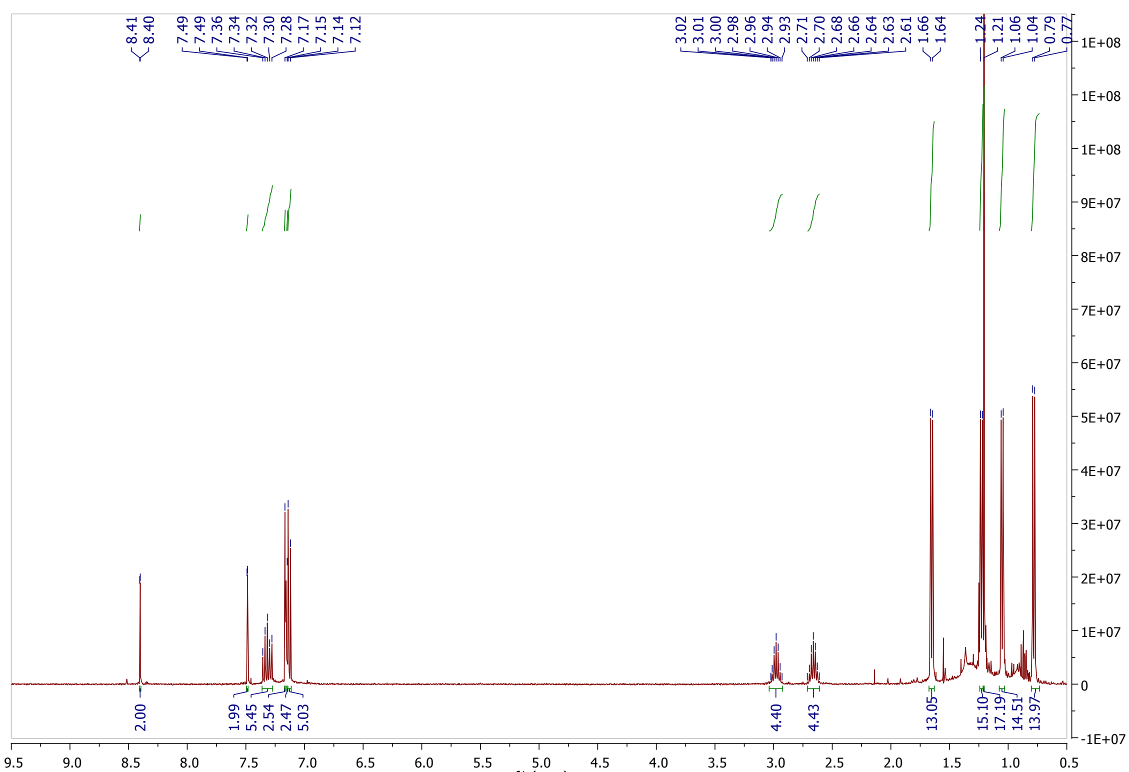


Figure S3. ^{1}H NMR of **2b** in C_6D_6 solvent

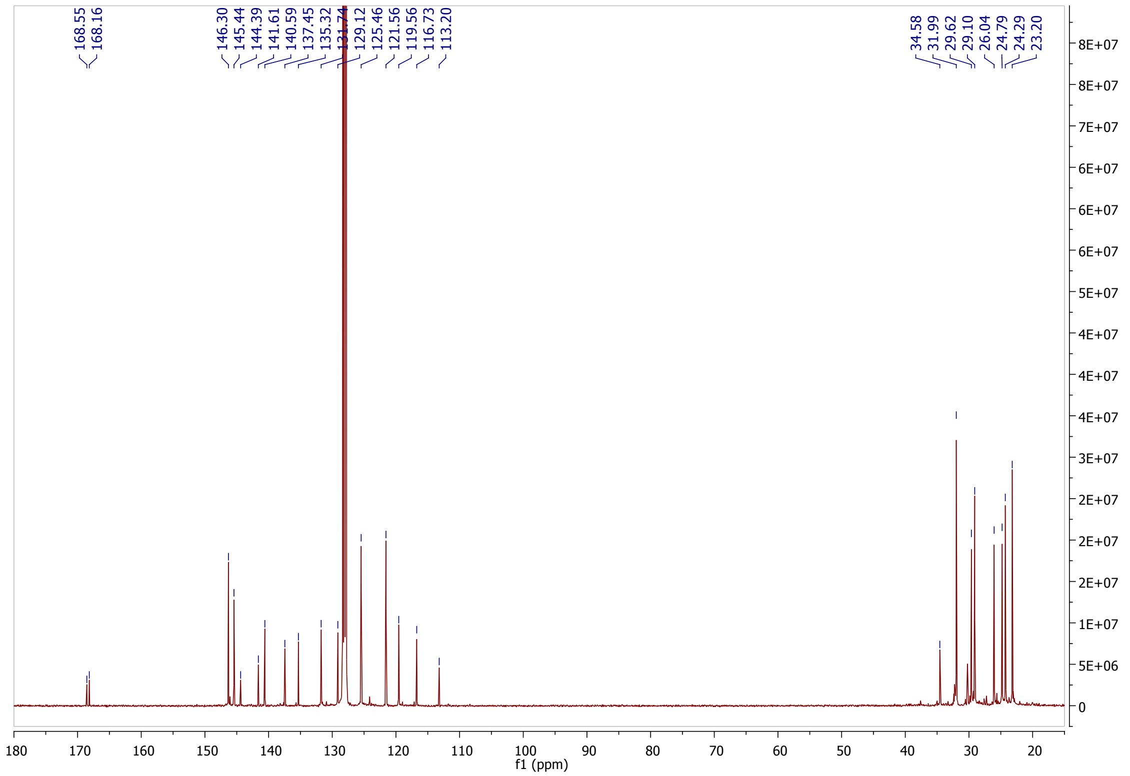


Figure S4. ^{13}C NMR of **2b** in C_6D_6 solvent

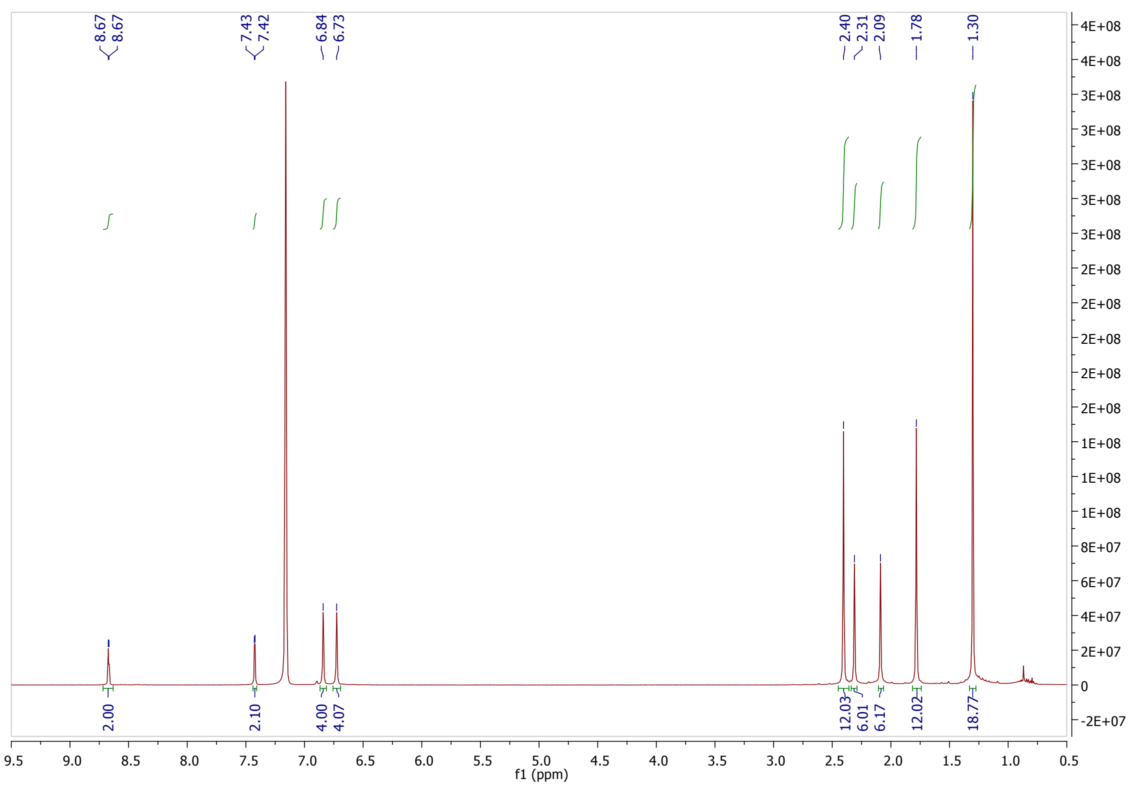


Figure S5. ^1H NMR of **3a** in C_6D_6 solvent

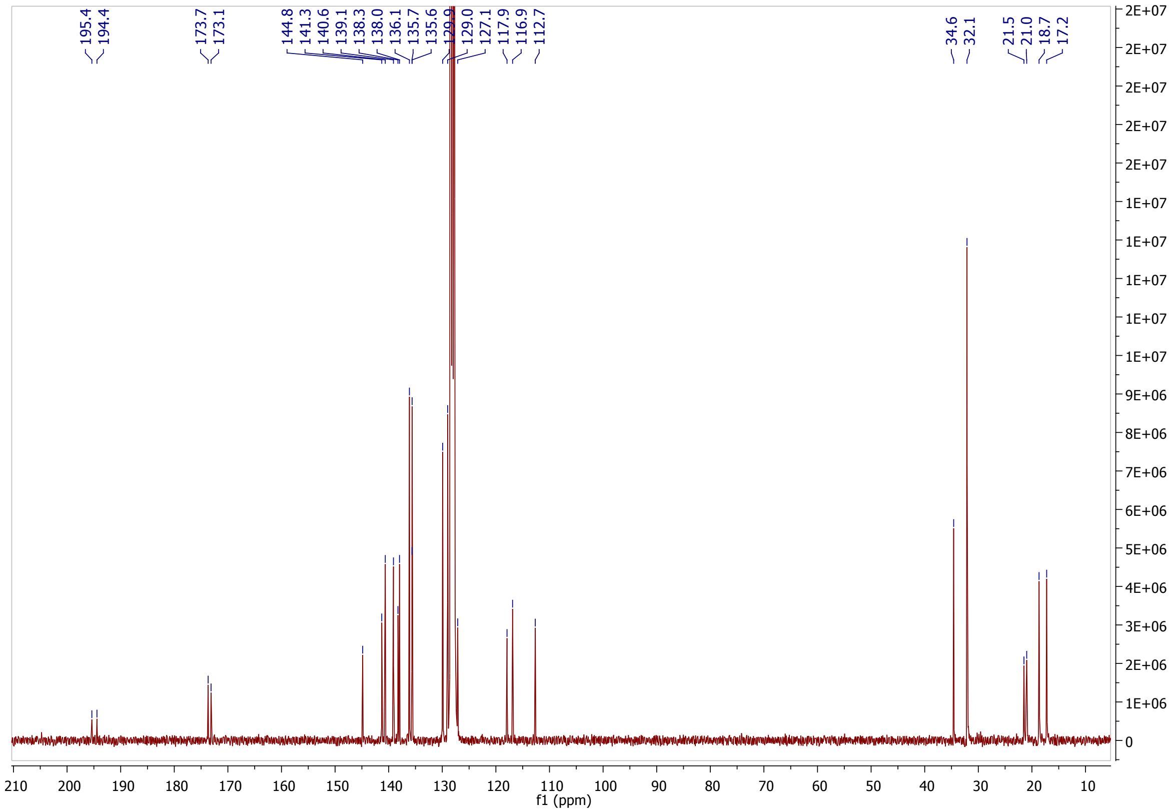


Figure S6. ^{13}C NMR of **3a** in C_6D_6 solvent

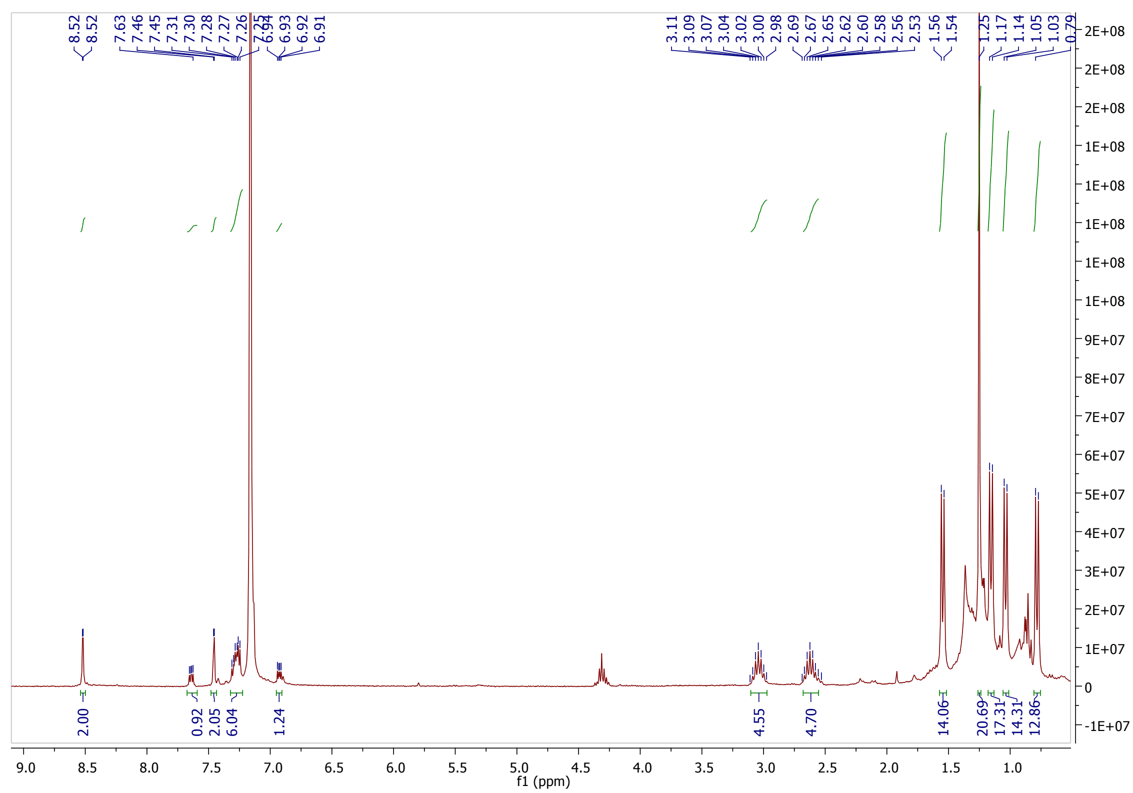


Figure S7. ^{1}H NMR of **3b** in C_6D_6 solvent

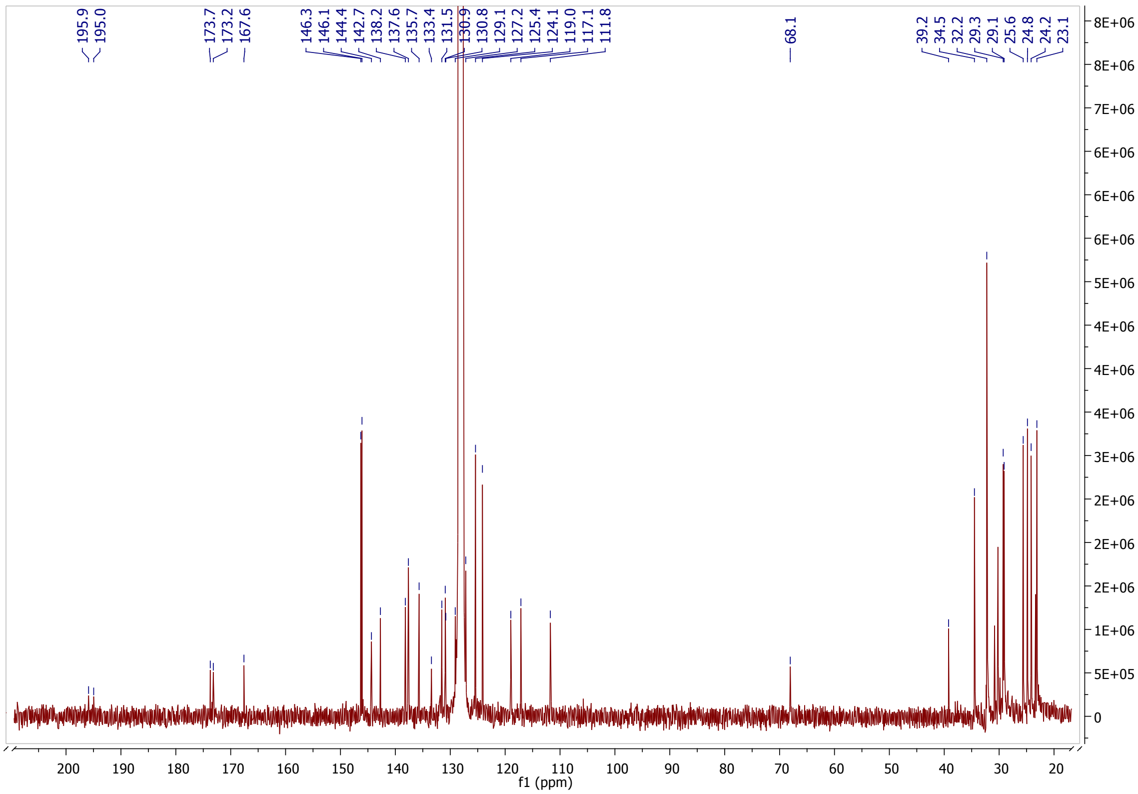


Figure S8. ^{13}C NMR of **3b** in C_6D_6 solvent

S4. Catalytic Dimerization Details

a. Optimisation of Catalytic Dimerization of 1-hexyne to (*gem*)-7-methylene-undec-5-yne

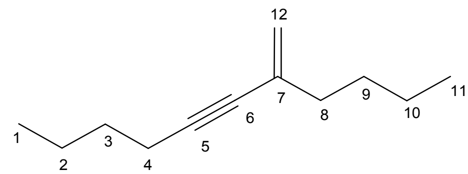
Standard operating procedure for dimerization reactions: a high pressure NMR tube with a J. Young valve was charged with one mol % catalyst **2a** (3.6 mg, 3.5 x 10^{-6} mol) or one mol % catalyst **2b** (4.1 mg, 3.5 x 10^{-6} mol) and 0.25 equivalents of internal standard, 1,4-di-*tert*-butylbenzene (16.6 mg, 8.7 x 10^{-5} mol). Catalytic amount of base was added as indicated in Table S1. To the mixture was added deuterated benzene (0.5 mL). One equivalent of 1-hexyne (40 µL, 3.5 x 10^{-4} mol) was added, and the NMR tube capped. ^{1}H NMR spectroscopy was performed at time 10 min after addition of the alkyne. The reaction mixture was heated up to appropriate temperature and reacted for the duration as indicated (see Table S1). Upon cooling down to room temperature, ^{1}H NMR spectroscopy was performed at the final time. Conversion and calculated yields where determined from NMR analysis based on integration of alkyne and product, referenced to the internal standard. Product identity was confirmed by comparison with previously reported NMR spectra.[vi]

Table S1. 1-hexyne dimerization promoted by **2**.[a]

Entry	Catalyst	Base (mol %)	T (°C)	t (h)	Conversion[b] (%)	Yield[c] (%)	Product distribution		
							Gem-enyne	*E*-enyne	*Z*-enyne
1	**2a**	K_2CO_3 (1)	80	> 1	> 99	99	100	-	-
2	**2a**	K_2CO_3 (1)	40	> 1	6	4	100	-	-
3	**2a**	KO^{t}Bu (1)	80	> 1	> 99	99	100	-	-
4	**2a**	Pyridine (3)	80	> 1	88	88	100	-	-
5	**2b**	K_2CO_3 (1)	80	> 1	0	0	-	-	-
6	**2b**	K_2CO_3 (1)	80	20	9	3	100	-	-
7	**2a**	None	80	> 1	> 99	99	100	-	-

[a]Reaction performed in C_6D_6 (0.5 mL) with internal standard 1,4-di-*tert*-butylbenzene, 1 mol % catalyst (3.5 x 10^{-6} mol) and 3.5 x 10^{-4} mol 1-hexyne.
[b]Conversion as determined through NMR integration based on 1-hexyne referenced to 1,4-di-*tert*-butylbenzene.
[c]Yield as determined from NMR integration based on 1-hexyne.

7-methylene-undec-5-yne



^{1}H NMR (300 MHz, C_6D_6) δ 5.38 (d, *J* = 2.1 Hz, 1H, C=C$\mathbf{H}_2$), 5.09 (m, 1H, C=C$\mathbf{H}_2$), 2.16 (m, 8H, $\mathbf{H}_{4,8}$), 1.59 (tt, *J* = 7.2 Hz, 7.5 Hz, 7.8 Hz, 2H, $\mathbf{H}_9$), 1.43 - 1.23 (m, 6H, $\mathbf{H}_{2,3,10}$ overlaps with -C(C$\mathbf{H}_3$)$_3$ of di-*tert*-butylbenzene), 0.86 and 0.78 (both t, *J* = 7.2 Hz, 6H, $\mathbf{H}_{1,11}$).

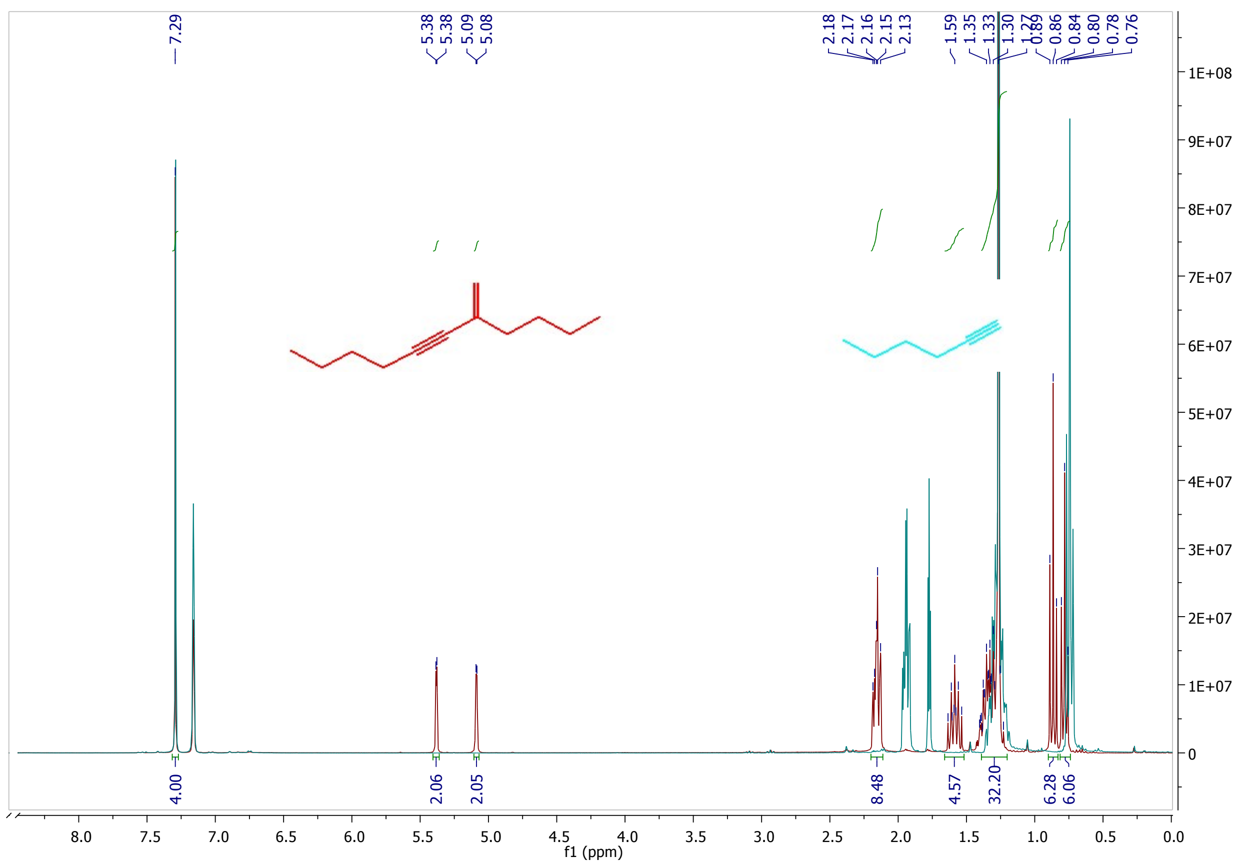


Figure S9. Catalytic dimerization reaction of 1-hexyne (blue) to (gem)-7-methylene-undec-5-yne (red) at time 10 min (blue spectrum) and at time after reaction (red spectrum).

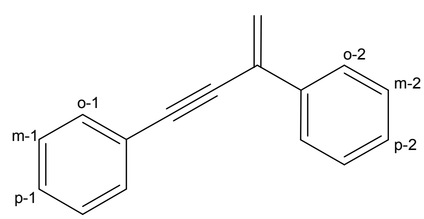
b. Catalytic Dimerization of terminal alkynes to *gem*-enynes catalyzed by 2a

Standard operating procedure for dimerization reactions: a high pressure NMR tube with a J. Young valve was loaded with one mol % catalyst **2a** and 0.25 equivalents of internal standard, 1,4-di-*tert*-butylbenzene. To the mixture was added deuterated benzene (0.5 mL). One equivalent of terminal alkyne was added, and the NMR tube capped. ^{1}H NMR spectroscopy was performed at time 10 min after addition of the alkyne. The reaction mixture was heated up to 80 °C and reacted for the duration as indicated (see Article, Table 1). Upon cooling down to room temperature, ^{1}H NMR spectroscopy was performed at the final time. Conversion and calculated yields where determined from NMR analysis based on integration of alkyne and product, referenced to the internal standard.

Entry 2, Table 1: Dimerization of Phenylacetylene

Experiments were carried out as described above. Amounts of reagents added are as follows: catalyst 1 mol % (3.7 mg, 3.6 x 10^{-6} mol); internal standard 0.25 equivalent (17.3 mg, 9.1 x 10^{-5} mol) and one equivalent phenylacetylene (40 µL, 3.6 x 10^{-4} mol). Product identity was confirmed by comparison with previously reported NMR spectra.[vi]

1,3-diphenylbut-1-yn-3-ene

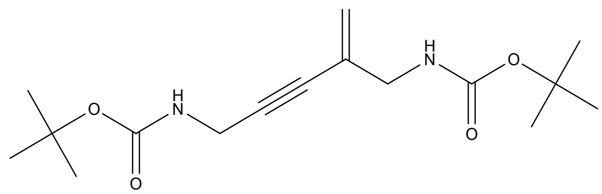


^{1}H NMR (300 MHz, C_6D_6) δ 7.77 - 7.68 (m, 2H, $\mathbf{H}_{o\text{-}1}$), 7.54 - 7.38 (m, 2H, $\mathbf{H}_{o\text{-}2}$, extensive overlap with unreacted phenylacetylene, *E*-enyne, internal standard and residual solvent), 7.09 - 6.87 (m, 6H, $\mathbf{H}_m$ and H_p, extensive overlap with unreacted phenylacetylene, *E*-enyne and internal standard), 5.75 (d, *J* = 0.8 Hz, 1H, C=C$\mathbf{H}_2$), 5.70 (d, *J* = 0.7 Hz, 1H, C=C$\mathbf{H}_2$).

Entry 3, Table 1: Dimerization of *N*-Boc-Propargylamine

Experiments were carried out as described above. Amounts of reagents added are as follows: catalyst 1 mol % (2.6 mg, 2.6 x 10^{-6} mol); internal standard 0.25 equivalent (12.3 mg, 6.4 x 10^{-5} mol) and one equivalent *N*-Boc-propargylamine (40 mg, 2.6 x 10^{-4} mol). Product identity was confirmed by comparison with previously reported NMR spectra.[vii]

N,N-bis(tert-butyloxycarbonyl)-4-methylenepent-2-yne

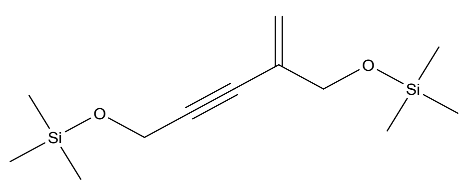


^{1}H NMR (300 MHz, C_6D_6) δ 5.26 (br s, 1H, C=C**H**$_2$), 5.15 (d, *J* = 1 Hz, 1H, C=C**H**$_2$), 4.57 (br s, 2H, CH_2N**H**), 3.82 (d, *J* = 2.8 Hz, 2H, C**H**$_2$NH), 3.66 (d, *J* = 5.3 Hz, 2H, C**H**$_2$NH), 1.42 (s, 9H,-C(C**H**$_3$)$_3$), 1.39 (s, 9H,-C(C**H**$_3$)$_3$).

Entry 4, Table 1: Dimerization of trimethylsilyloxypropyne

Experiments were carried out as described above. Amounts of reagents added are as follows:1 mol % (3.3 mg, 3.3 x 10^{-6} mol); internal standard 0.25 equivalent (15.5 mg, 8.1 x 10^{-5} mol) and one equivalent trimethylsilyloxypropyne (50 µL, 3.3 x 10^{-4} mol). Product identity was confirmed by comparison with previously reported NMR spectra.[viii]

2-trimethylsiloxymethyl-4-trimethylsiloxy-1-penten-3-yne

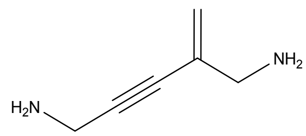


^{1}H NMR (300 MHz, C_6D_6) δ 5.64 (q, *J* = 2.0 Hz, 1H, C=C**H**$_2$), 5.51 (d, *J* = 1.8 Hz, 1H, C=C**H**$_2$), 4.28 (s, 2H, OC**H**$_2$), 4.14 (t, *J* = 1.8 Hz, 2H, OC**H**$_2$), 0.12 (s, 9H, Si(C**H**$_3$)$_3$), 0.06 (s, 9H, Si(C**H**$_3$)$_3$).

Entry 5, Table 1: Dimerization of propargylamine

Experiments were carried out as described above. Amounts of reagents added are as follows: catalyst 1 mol % (4.8 mg, 4.7 x 10^{-6} mol); internal standard 0.25 equivalent (22.3 mg, 1.2 x 10^{-4} mol) and one equivalent propargylamine (30 µL, 4.7 x 10^{-4} mol).

4-methylenepent-2-yne-1,5-diamine

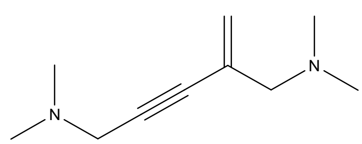


^{1}H NMR (300 MHz, C_6D_6) δ 5.34 (br s, 1H, C=C**H**$_2$), 5.19 (d, *J* = 1.7 Hz, 1H, C=C**H**$_2$), 3.18 (br s, 4H, C**H**$_2$NH$_2$), 0.75 (br s, 4H, CH$_2$N**H**$_2$).

Entry 6, Table 1: Dimerization of *N,N*-dimethylaminopropyne

Experiments were carried out as described above. Amounts of reagents added are as follows: catalyst 1 mol % (3.8 mg, 3.7 x 10^{-6} mol); internal standard 0.25 equivalent (17.7 mg, 9.3 x 10^{-5} mol) and one equivalent *N,N*-dimethylaminopropyne (40 µL, 3.7 x 10^{-4} mol). Product identity was confirmed by comparison with previously reported NMR spectra.[vi]

N,N,N,N-tetramethyl-4-methylenepent-2-yne-1,5-diamine

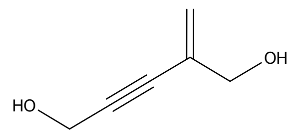


^{1}H NMR (300 MHz, C_6D_6) δ 5.50 (d, *J* = 2.1 Hz, 1H, C=C**H**$_2$), 5.38 (m, 1H, C=C**H**$_2$), 3.24 (s, 2H, C**H**$_2$N(CH$_3$)$_2$), 2.90 (s, 2H, C**H**$_2$N(CH$_3$)$_2$), 2.19 (s, 6H, CH$_2$N(C**H**$_3$)$_2$), 2.12 (s, 6H, CH$_2$N(C**H**$_3$)$_2$).

Entry 7, Table 1: Dimerization of propargyl alcohol

Experiments were carried out as described above. Amounts of reagents added are as follows: catalyst 1 mol % (4.4 mg, 4.3 x 10^{-6} mol); internal standard 0.25 equivalent (20.4 mg, 1.1 x 10^{-4} mol) and one equivalent propargyl alcohol (25 μL, 4.3 x 10^{-4} mol). Product identity was confirmed by comparison with previously reported NMR spectra of similar enyne alcohol-type compounds.[ix]

4-methylenepent-2-yne-1,5-diol

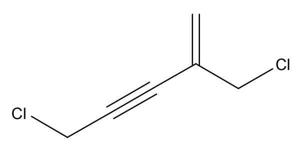


^{1}H NMR (300 MHz, C_6D_6) δ 5.37 (br s, 1H, C=C**H**$_2$), 5.34 (br s, 1H, C=C**H**$_2$), 4.09 (s, 2H, C**H**$_2$OH), 3.96 (s, 2H, C**H**$_2$OH), 2.05 (br s, 2H, CH_2O**H**).

Entry 8, Table 1: Dimerization of propargyl chloride

Experiments were carried out as described above. Amounts of reagents added are as follows: catalyst 1 mol % (2.8 mg, 2.8 x 10^{-6} mol); internal standard 0.25 equivalent (13.2 mg, 6.9 x 10^{-5} mol) and propargyl chloride, 1 equivalent (20 μL, 2.8 x 10^{-4} mol). Product identity was confirmed by comparison with previously reported NMR spectra of similar enyne chloro-type compounds.[x]

1,5-dichloro-4-methylenepent-2-yne



^{1}H NMR (300 MHz, C_6D_6) δ 5.64 (t, *J* = 6.2 Hz, 2H, C=C**H**$_2$), 4.59 (s, 2H, C**H**$_2$Cl), 4.57 (s, 2H, C**H**$_2$Cl).

S5. Catalytic Hydrothiolation Details

a. Optimisation of Catalytic Hydrothiolation of 1-hexyne with thiophenol

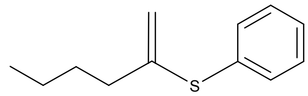
Standard operating procedure for hydrothiolation reactions. A high pressure NMR tube with a J. Young valve was charged with one mol % catalyst **2a** (4.0 mg, 3.9×10^{-6} mol) or one mol % catalyst **2b** (4.7 mg, 3.9×10^{-6} mol) and 0.25 equivalents of internal standard, 1,4-di-*tert*-butylbenzene (18.6 mg, 9.8×10^{-5}). Catalytic amount of base was added as indicated in Table S2. To the mixture was added deuterated benzene (0.5 mL). One equivalent of 1-hexyne (45 µL, 3.9×10^{-4} mol) and one equivalent of thiophenol (40 µL, 3.9×10^{-4} mol) were added, and the NMR tube capped. ^{1}H NMR spectroscopy was performed at time 10 min after addition of the substrates. The reaction mixture was heated up to the appropriate temperature and reacted for the duration as indicated (see Table S2). Upon cooling down to room temperature, ^{1}H NMR spectroscopy was performed at the final time. Conversion and calculated yields were determined from NMR analysis based on the integration of substrates and product, referenced to the internal standard. Product identity was confirmed by comparison with previously reported NMR spectra.[xi]

Table S2.Hydrothiolation of 1-hexyne (1 equivalent) with thiophenol (1 equivalent) promoted by **2**.[a]

Entry	Catalyst	Base (mol %)	T (°C)	t (h)	Conversion (%)[b]	Yield (%)[c]	Product distribution		
							α-vinyl sulfide	β-*E*-vinyl sulfide	β-*Z*-vinyl sulfide
1	**2a**	K_2CO_3 (1)	80	24	77	71	91[d]	6	3
2	**2a**	K_2CO_3 (1)	40	24	14	11	91[d]	5	4
3	**2a**	Pyridine (5)	80	24	74	64	89[d]	8	3
4	**2a**	None	80	24	81	74	91[d]	6	3
5	**2b**	K_2CO_3 (1)	80	24	58	49	92[d]	2	6

[a]Reaction performed in C_6D_6 (0.5 mL) with internal standard 1,4-di-*tert*-butylbenzene, 1 mol % catalyst (3.5×10^{-6} mol) and 3.5×10^{-4} mol 1-hexyne.
[b]Conversion as determined through NMR integration based on 1-hexyne referenced to 1,4-di-*tert*-butylbenzene.
[c]Yield of α-vinyl sulfide as determined from NMR integration based on 1-hexyne.
[d]Plus unidentified products.

2-Phenylthio-1-hexene



^{1}H NMR (300 MHz, C_6D_6) δ 7.44 - 7.40 (m, 2H, Ar**H**), 7.05 - 6.96 (m, 3H, Ar**H** overlaps with unreacted thiophenol), 5.06 (s, 1H, C=C**H**$_2$), 4.97 (s, 1H, C=C**H**$_2$), 2.20 (t, *J* = 7.6 Hz, 2H, C**H**$_2$), 1.50 (tt, *J* = 7.6 Hz, 7.5 Hz, 2H, C**H**$_2$), 1.26 - 1.16 (m, 2H, C**H**$_2$ overlaps with C(CH_3)$_3$ of internal standard), 0.80 (t, *J* = 7.3 Hz, 3H, C**H**$_3$).

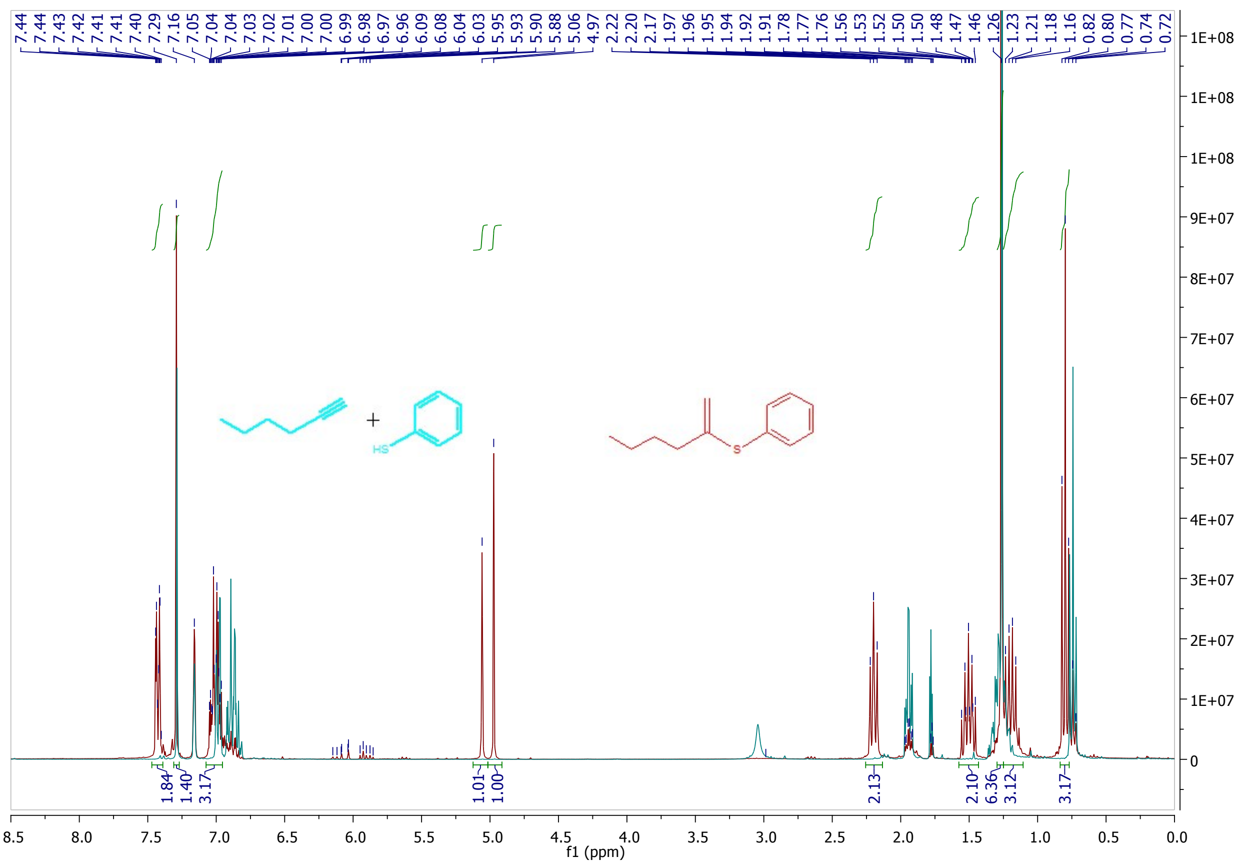


Figure S10. Catalytic hydrothiolation reaction of 1-hexyne (blue) with thiophenol (blue) yielding 2-phenylthio-1-hexene (red) at time 10 min (blue spectrum) and at time after reaction (red spectrum).

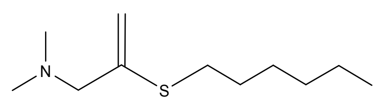
b. Catalytic Hydrothiolation of terminal alkynes with thiols catalyzed by 2a

Standard operating procedure for hydrothiolation reactions: a high pressure NMR tube with a J. Young valve was loaded with one mol % catalyst **2a** and 0.25 equivalents of internal standard, 1,4-di-*tert*-butylbenzene. To the mixture was added deuterated benzene (0.5 mL). One equivalent of terminal alkyne and thiol was added, and the NMR tube capped. ^1H NMR spectroscopy was performed at time 10 min after addition of the substrates. The reaction mixture was heated up to 80 °C and reacted for the duration as indicated (see Article, Table 2). Upon cooling down to room temperature, ^1H NMR spectroscopy was performed at the final time. Conversion and calculated yields where determined from NMR analysis based on integration of alkyne and product, referenced to the internal standard.

Entry 2, Table 2: Hydrothiolation of *N,N*-dimethylaminopropyne with 1-hexanethiol

Experiments were carried out as mentioned. Amounts of reagents added are as follows: 1mol % catalyst **2a** (3.2 mg, 3.2 x 10^{-6} mol); internal standard 0.25 equivalent (15.1 mg, 7.9 x 10^{-5} mol); one equivalent *N*,*N*-dimethylaminopropyne (34.1 µL, 3.2 x 10^{-4} mol) and one equivalent 1-hexanethiol (45 µL, 3.2 x 10^{-4} mol).

N,N-dimethyl-2-hexylthioprop-2-en-1-amine



^1H NMR (300 MHz, C_6D_6) δ 5.24 (t, *J* = 1.0 Hz, 1H, C=C**H**$_2$), 4.78 (s, 1H, C=C**H**$_2$), 3.00 (s, 2H, C**H**$_2$N(CH$_3$)$_2$), 2.56 (t, *J* = 7.3 Hz, 2H, C**H**$_2$), 2.12 (s, 6H, CH$_2$N(C**H**$_3$)$_2$), 1.53 (tt, *J* = 7.5 Hz, 7.2 Hz, 2H, C**H**$_2$), 1.27 - 1.11 (m, 6H, (C**H**$_2$)$_3$ overlaps with C(CH$_3$)$_3$ of internal standard), 0.82 (t, *J* = 0.8 Hz, 3H, C**H**$_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 145.7, 106.3, 66.3, 45.1, 31.8, 31.0, 29.2, 28.7, 22.9, 14.2.

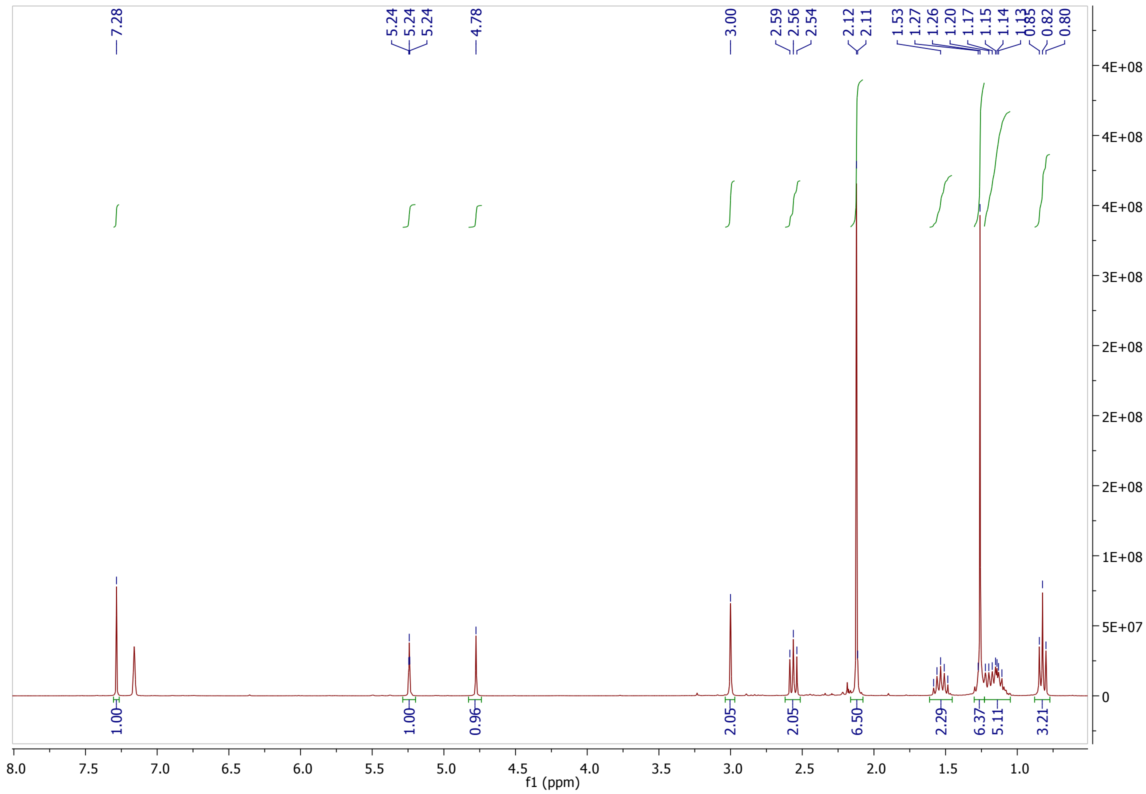


Figure S11. ^{1}H NMR of *N,N*-dimethyl-2-hexylthioprop-2-en-1-amine

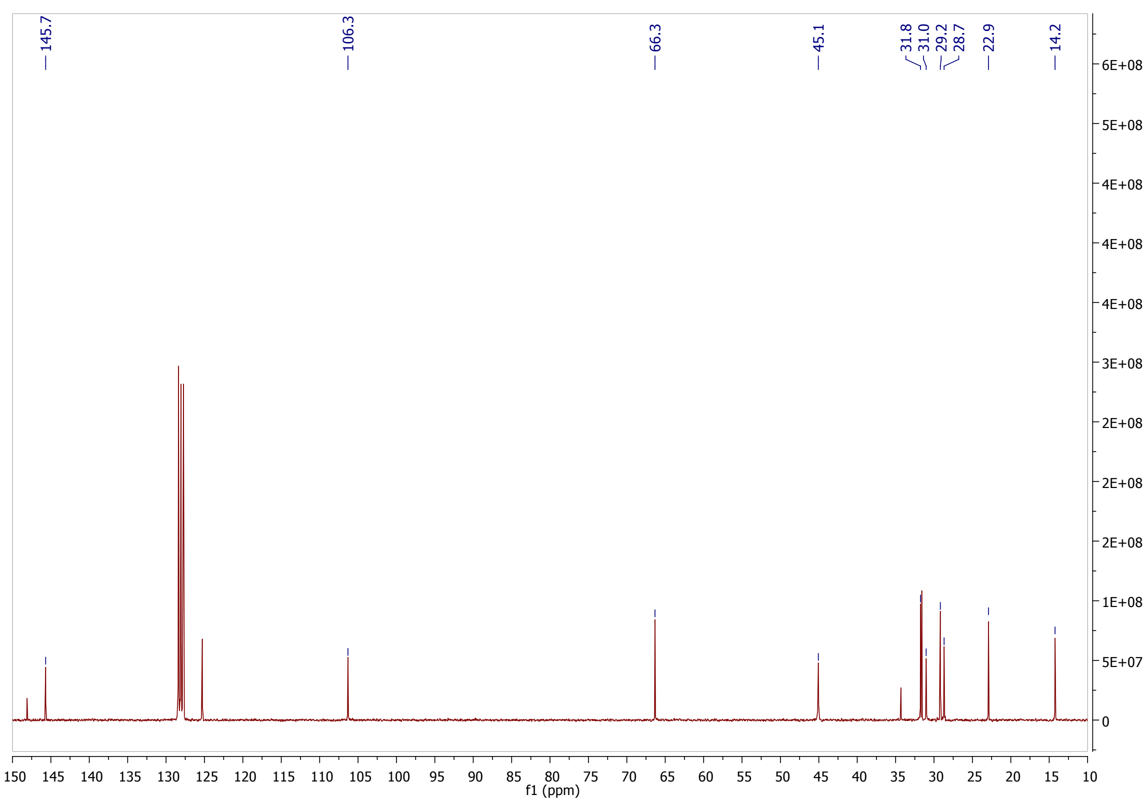
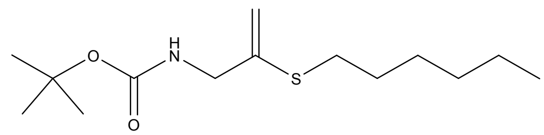


Figure S12. ^{13}C NMR of *N,N*-dimethyl-2-hexylthioprop-2-en-1-amine

Entry 3, Table 2: Hydrothiolation of *N*-Boc-propargylamine with 1-hexanethiol

Experiments were carried out as mentioned. Amounts of reagents added are as follows: 1mol % catalyst **2a** (3.2 mg, 3.2 x 10^{-6} mol); internal standard 0.25 equivalent (15.1 mg, 7.9 x 10^{-5} mol); one equivalent *N*-Boc-propargylamine (49.1 mg, 3.2 x 10^{-4} mol) and one equivalent 1-hexanethiol (45 µL, 3.2 x 10^{-4} mol).

N-tert-butyloxycarbonyl-2-hexylthioprop-2-en-1-amine



^{1}H NMR (300 MHz, C_6D_6) δ 5.14 (s, 1H, C=C**H**$_2$), 4.77 (s, 1H, C=C**H**$_2$), 4.64 (br s, 1H, CH$_2$N**H**), 3.82 (d, *J* = 5.9 Hz, 2H, C**H**$_2$NH), 2.45 (t, *J* = 7.3 Hz, 2H, C**H**$_2$), 1.49 - 1.39 (m, 2H, C**H**$_2$ overlaps with OC(CH$_3$)$_3$), 1.42 (s, 9H, OC(C**H**$_3$)$_3$ overlaps with C**H**$_2$), 1.25 - 1.05 (m, 6H, (C**H**$_2$)$_3$ overlaps with C(CH$_3$)$_3$ of internal standard), 0.82 (t, *J* = 7.0 Hz, 3H, C**H**$_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 155.6, 144.0, 108.0, 79.0, 46.1, 31.7, 31.3, 29.0, 28.7, 28.5, 22.9, 14.2.

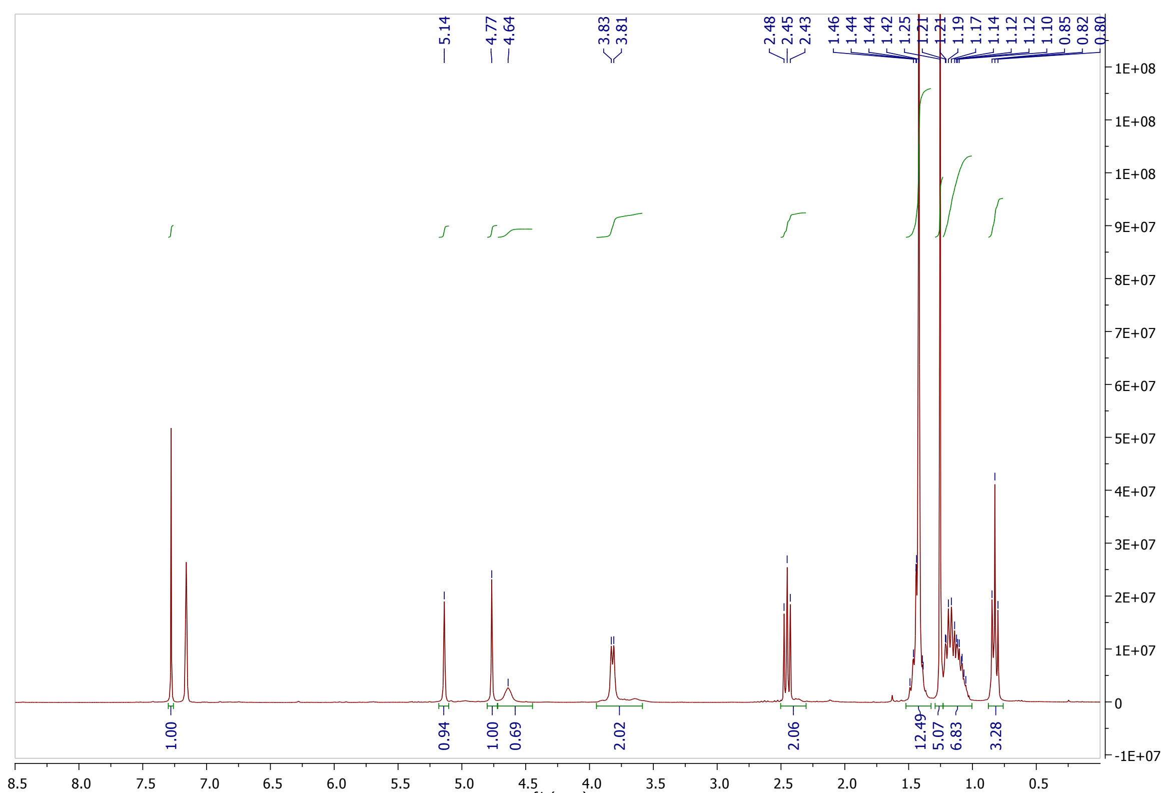


Figure S13. ^{1}H NMR of *N-tert*-butyloxycarbonyl-2-hexylthioprop-2-en-1-amine

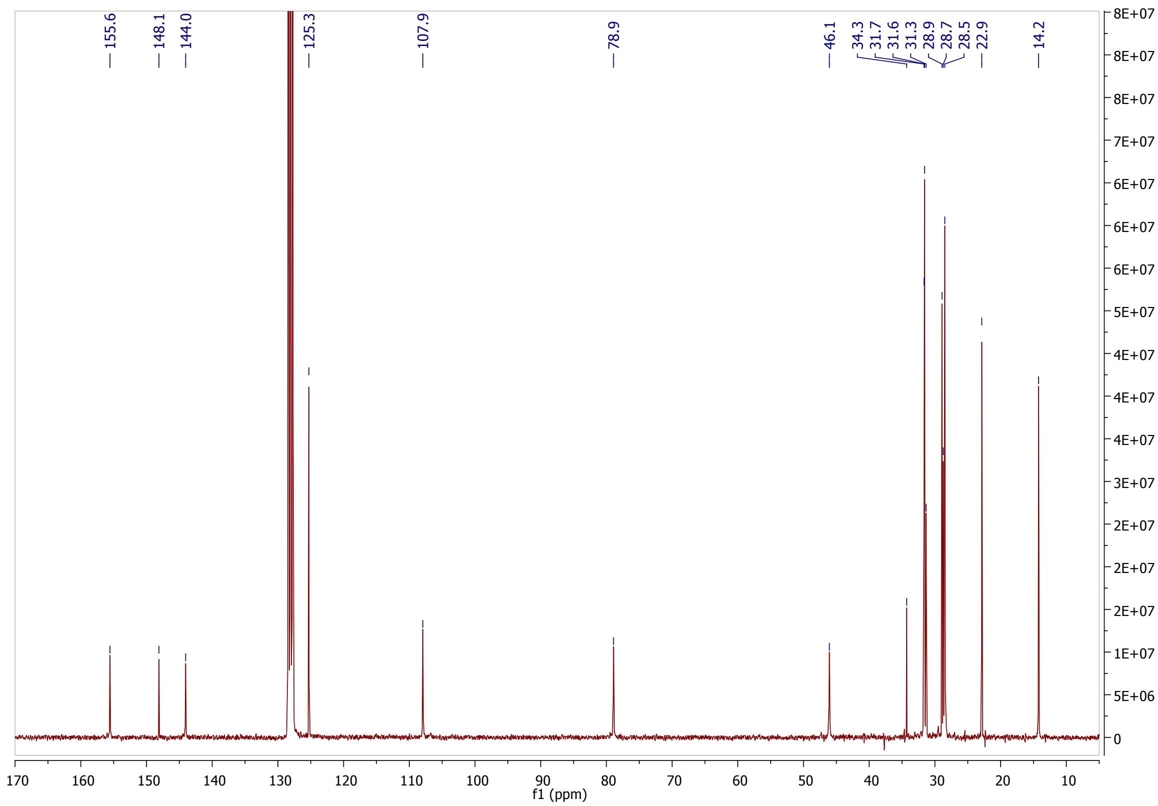
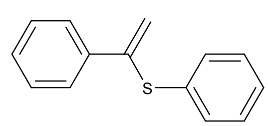


Figure S14. ^{13}C NMR of *N-tert*-butyloxycarbonyl-2-hexylthioprop-2-en-1-amine

Entry 4, Table 2: Hydrothiolation of phenylacetylene with thiophenol

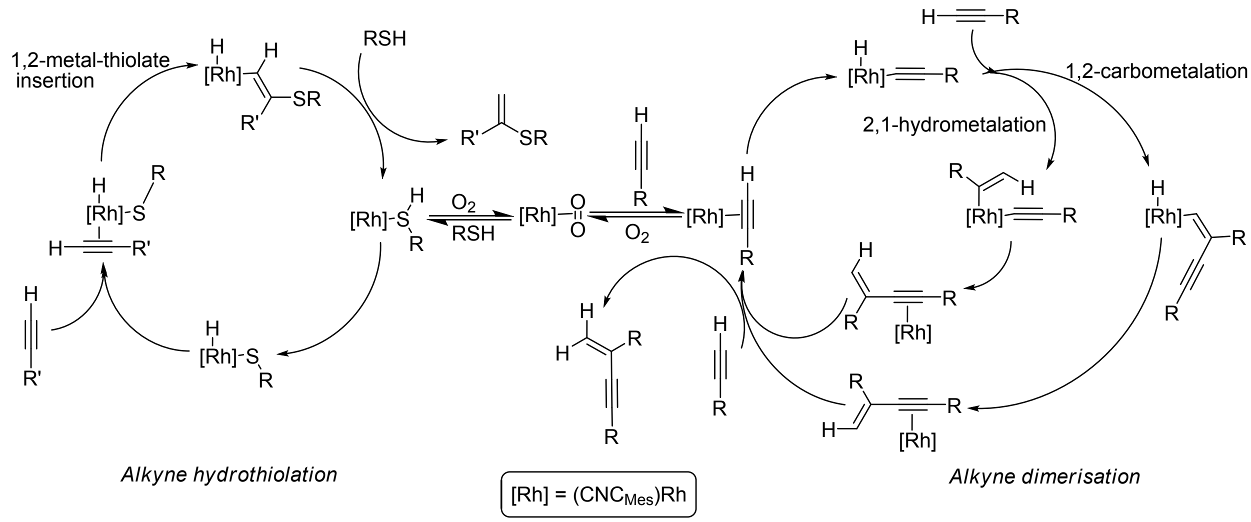
Experiments were carried out as mentioned. Amounts of reagents added are as follows: 1mol % catalyst **2a** (3.5 mg, 3.4 x 10^{-6} mol); internal standard 0.25 equivalent (16.3 mg, 8.5 x 10^{-5} mol); one equivalent phenylacetylene (37.6 µL, 3.4 x 10^{-4} mol) and one equivalent thiophenol (35 µL, 3.4 x 10^{-4} mol). Product identity was confirmed by comparison with previously reported NMR spectra.[xi]

1-Phenyl-1-phenylthioethene



^{1}H NMR (300 MHz, C_6D_6) δ 7.63 - 7.57 (m, 2H, Ar**H** overlaps with *E*- and *Z*-isomers), 7.42 - 7.27 (m, 4H, Ar**H** overlaps with ArH of internal standard and with *E*- and *Z*-isomers), 7.06 - 6.85 (m, 4H, Ar**H** overlaps with *E*- and *Z*-isomers), 5.50 (s, 1H, C=C**H**$_2$), 5.30 (s, 1H, C=C**H**$_2$).

S6. Proposed Reaction Mechanism for Alkyne Dimerisation and Hydrothiolation promoted by 2a



Scheme S2. Proposed mechanistic route of alkyne dimerization and hydrothiolation mediated by **2a**

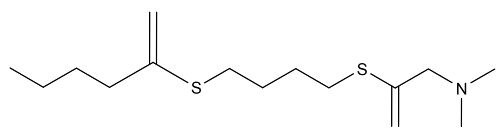
S7. Catalytic Asymmetric bis-Hydrothiolation Details

Standard operating procedure for asymmetric bis-hydrothiolation reactions. A high pressure NMR tube with a J. Young valve was charged with two mol % catalyst **2a** and 0.25 equivalents of internal standard, 1,4-di-*tert*-butylbenzene. To the mixture was added deuterated benzene (0.5 mL). One equivalent of terminal alkyne and one equivalent of the dithiol were added, followed by the NMR tube being capped. ^{1}H NMR spectroscopy was performed at time 10 min after addition of the substrates. The reaction mixture was heated up to 80 °C and reacted for the duration as indicated (see Article, Table 3). ^{1}H NMR spectroscopy confirmed the complete conversion of the substrates to the mono-α-vinyl sulfide product. To the same reaction mixture, in open atmospheric conditions, was added one equivalent of the second terminal alkyne. The NMR tube was capped, a ^{1}H NMR experiment performed, and the tube was subsequently heated up to 80 °C for the duration as indicated in Table 3 (see Article). ^{1}H NMR spectroscopy confirmed the formation of the unsymmetrical bis-α,α'-vinyl sulfide, or unsymmetrical bis-α,β-*E*-vinyl sulfides. Conversion and calculated yields were determined from NMR analysis based on the integration of alkyne and product, referenced to the internal standard.

Entry 1, Table 3: Bis-Hydrothiolation of 1-hexyne and *N*,*N*-dimethylaminopropyne with 1,4-butanedithiol (bis-α,α'-vinyl sulfide)

Experiments were carried out as described above. Amounts of reagents added are as follows: catalyst 2 mol % (6.1 mg, 6.0 x 10^{-6} mol); internal standard 0.25 equivalent (14.2 mg, 7.5 x 10^{-5} mol); 1 equivalent of 1-hexyne (34.3 µL, 3.0 x 10^{-4} mol) and one equivalent of 1,4-butanedithiol (35 µL, 3.0 x 10^{-4} mol). Upon completion of the first hydrothiolation reaction, one equivalent of the second alkyne, *N*,*N*-dimethylaminopropyne (32.1 µL, 3.0 x 10^{-4} mol), was added.

bis-α,α'-vinyl sulfide



^{1}H NMR (300 MHz, C_6D_6) δ 5.20 (d, *J* = 1.3 Hz, 1H, C=C**H**$_2$), 4.99 (d, *J* = 1.4 Hz, 1H, C=C**H**$_2$), 4.72 (s, 1H, C=C**H**$_2$), 4.65 (s, 1H, C=C**H**$_2$), 2.96 (br s, 2H, C**H**$_2$N(CH$_3$)$_2$), 2.48 - 2.41 (m, 4H, (C**H**$_2$)$_2$), 2.20 (tt, *J* = 7.6 Hz, 4.5 Hz, 2H, C**H**$_2$), 2.10 (s, 6H, CH$_2$N(C**H**$_3$)$_2$), 1.58 - 1.46 (m, 6H, (C**H**$_2$)$_3$), 1.31 - 1.18 (m, 2H, C**H**$_2$ overlaps with C(CH$_3$)$_3$ of internal standard), 0.83 (t, *J* = 7.3 Hz, 3H, C**H**$_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 146.4, 145.2, 106.7, 105.2, 66.3, 45.1, 37.8, 31.4, 30.8, 30.4, 28.0, 27.9, 22.4, 14.1.

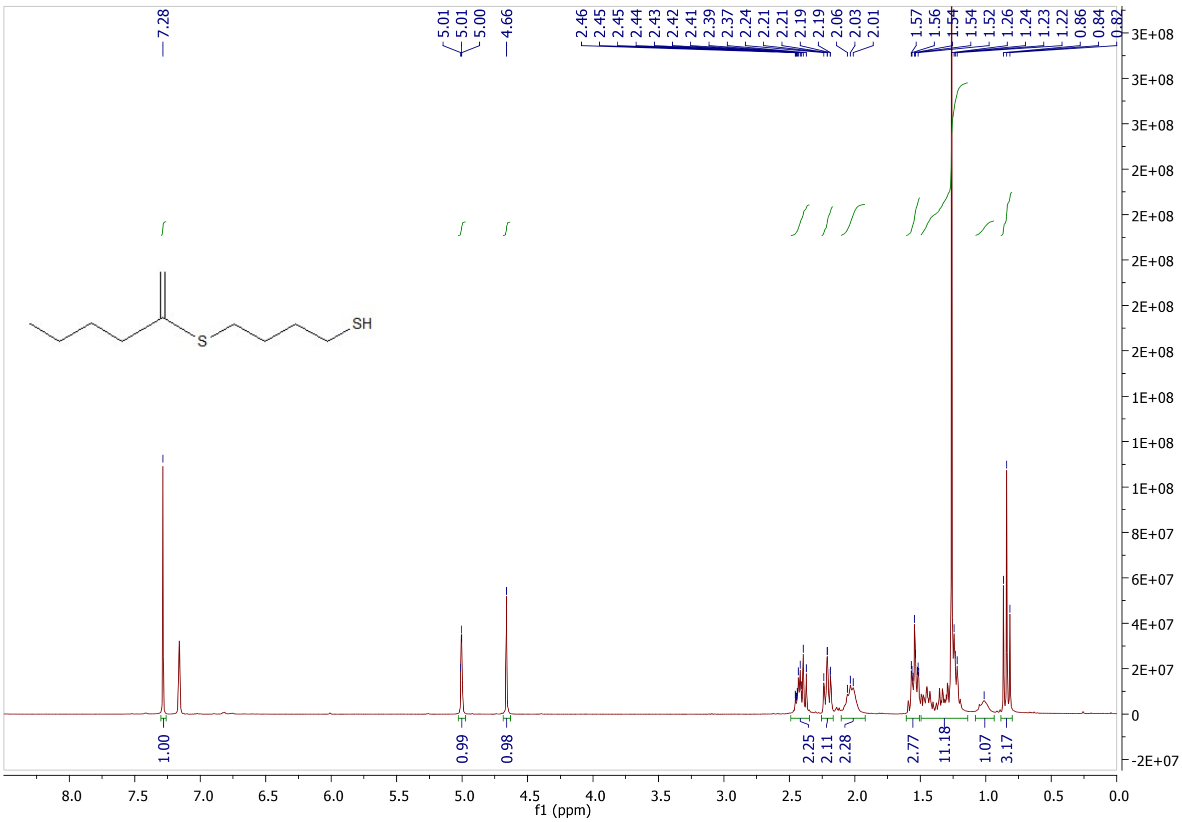


Figure S15. ^{1}H NMR of α-vinyl sulfide intermediate product

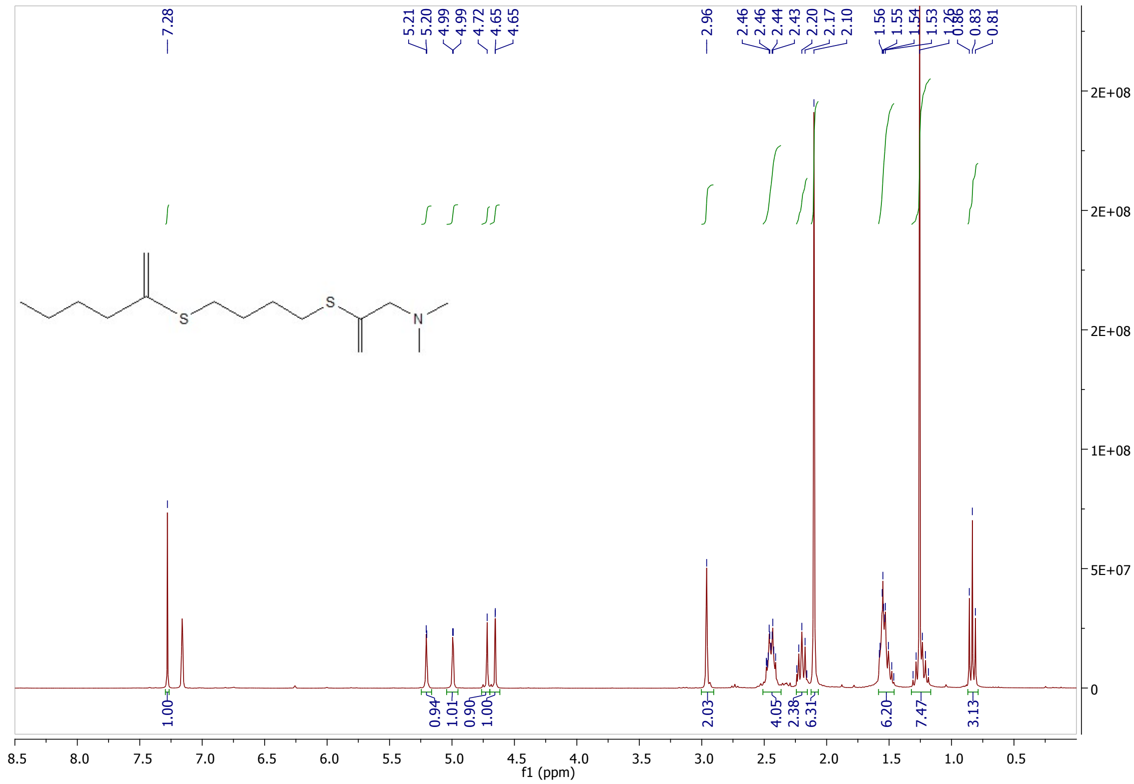


Figure S16. ^{1}H NMR of bis-α,α'-vinyl sulfide

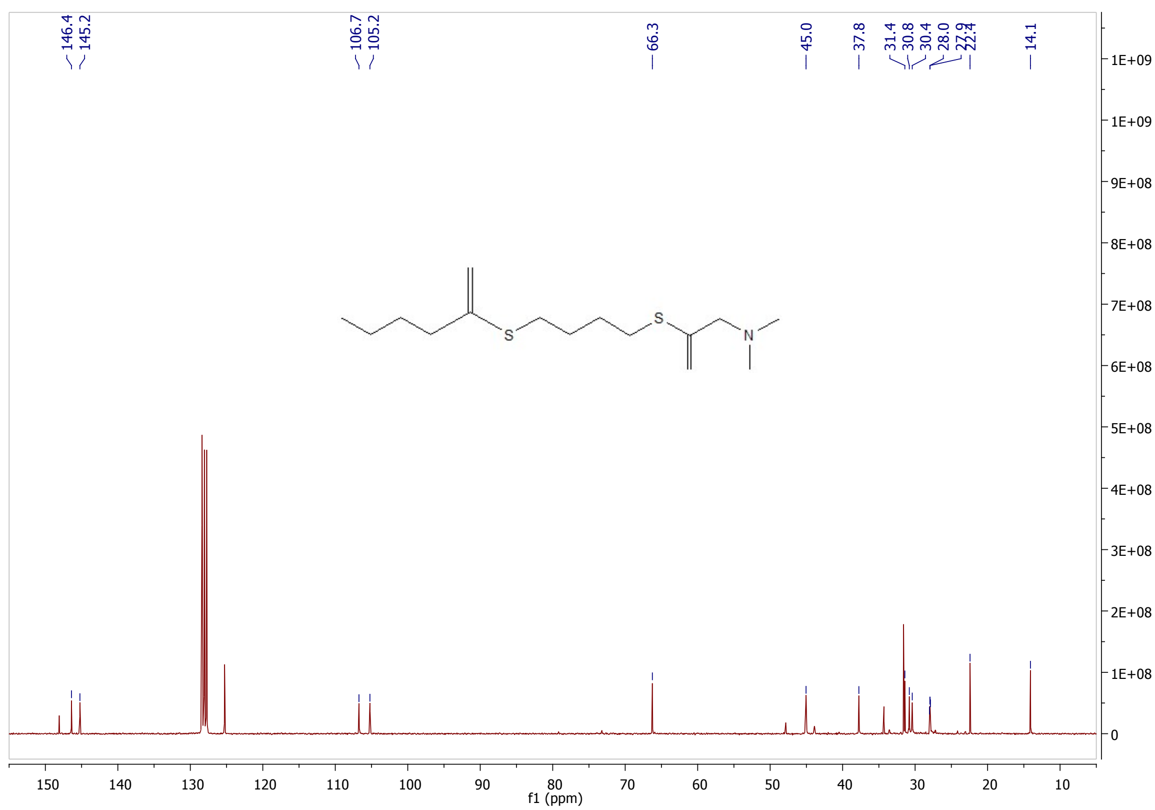


Figure S17. ^{13}C NMR of bis-α,α'-vinyl sulfide

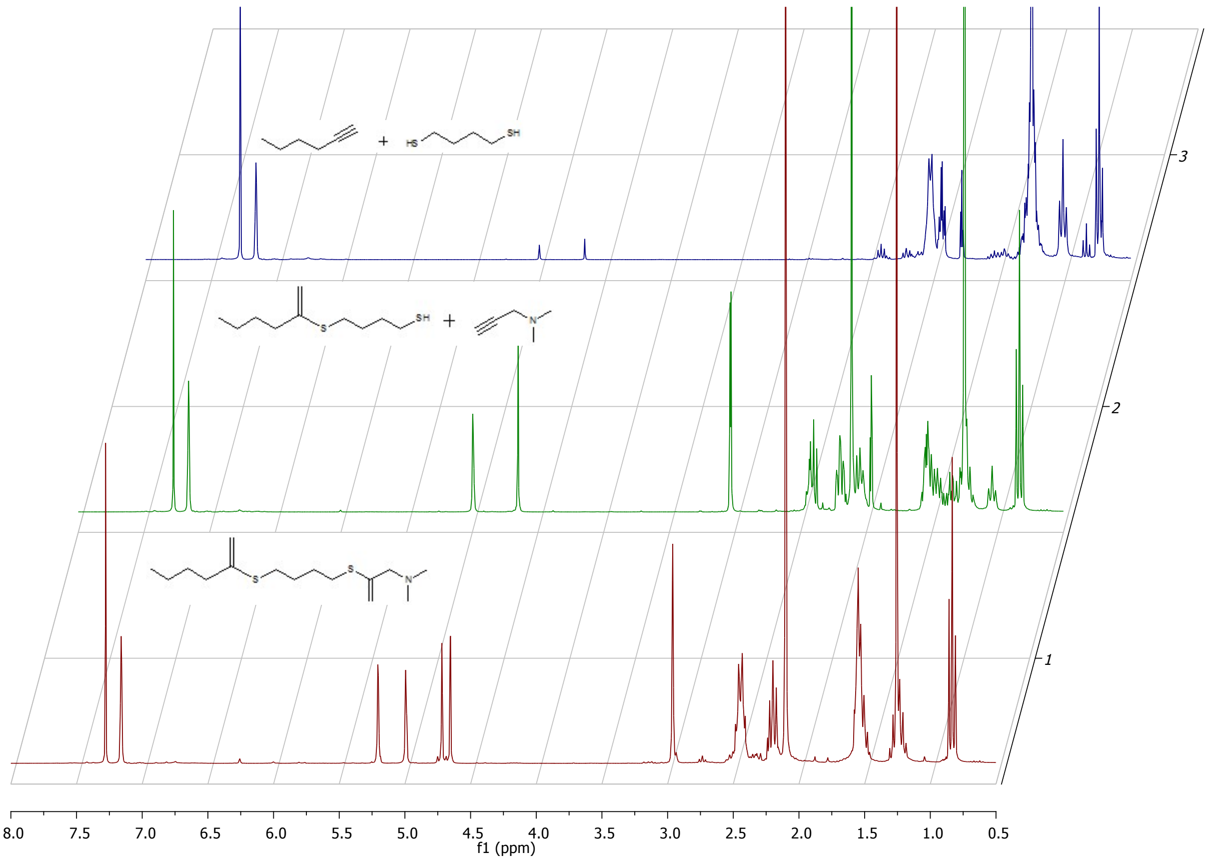
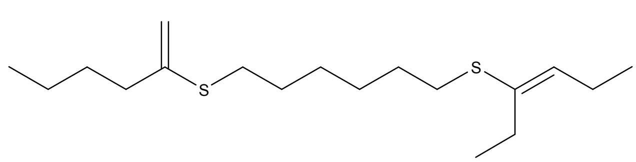


Figure S18. Stacked ^{1}H NMR of asymmetric bis-hydrothiolation reaction at initial time (blue spectrum), intermediate step (green spectrum) and final time (red spectrum)

Entry 2, Table 3: Bis-Hydrothiolation of 1-hexyne and 3-hexyne with 1,6-hexanedithiol (bis-α,β-*E*-vinyl sulfide)

Experiments were carried out as mentioned. Amounts of reagents added are as follows: catalyst 2 mol % (5.3 mg, 5.2 x 10^{-6} mol); internal standard 0.25 equivalent (12.4 mg, 6.5 x 10^{-5} mol); 1 equivalent of 1-hexyne (30.1 µL, 2.6 x 10^{-4} mol) and one equivalent of 1,6-hexanedithiol (40 µL, 2.6 x 10^{-4} mol). Upon completion of the first hydrothiolation reaction, one equivalent of the second alkyne, 3-hexyne (29.7 µL, 2.6 x 10^{-4} mol)), was added.

*Bis-*α,β-*E-vinyl sulfide*



^{1}H NMR (300 MHz, C_6D_6) δ 5.34 (t, *J* = 7.3 Hz, 1H, C=C**H**), 5.02 (d, *J* = 1.1 Hz, 1H, C=C**H**$_2$), 4.70 (s, 1H, C=C**H**$_2$), 2.51 - 2.44 (m, 4H, (C**H**$_2$)$_2$), 2.23 (t, *J* = 7.5 Hz, 2H, C**H**$_2$), 2.21 - 2.13 (m, 2H, C**H**$_2$ overlaps with C**H**$_2$), 1.98 (t, *J* = 7.5 Hz, 2H, C**H**$_2$), 1.61 - 1.50 (m, 2H, C**H**$_2$), 1.50 - 1.40 (m, 4H, (C**H**$_2$)$_2$), 1.33 - 1.12 (m, 6H, (C**H**$_2$)$_3$ overlaps with C(CH_3)$_3$ of internal standard), 1.11 (t, *J* = 7.5 Hz, 3H, C**H**$_3$), 0.90 (t, *J* = 7.5 Hz, 3H, C**H**$_3$), 0.84 (t, *J* = 7.2 Hz, 3H, C**H**$_3$). ^{13}C NMR (75 MHz, C_6D_6) δ 146.8, 136.6, 127.1, 104.9, 37.9, 31.5, 31.4, 31.3, 29.0, 28.9, 28.8, 28.5, 25.4, 22.5, 22.2, 14.8, 14.6, 14.1.

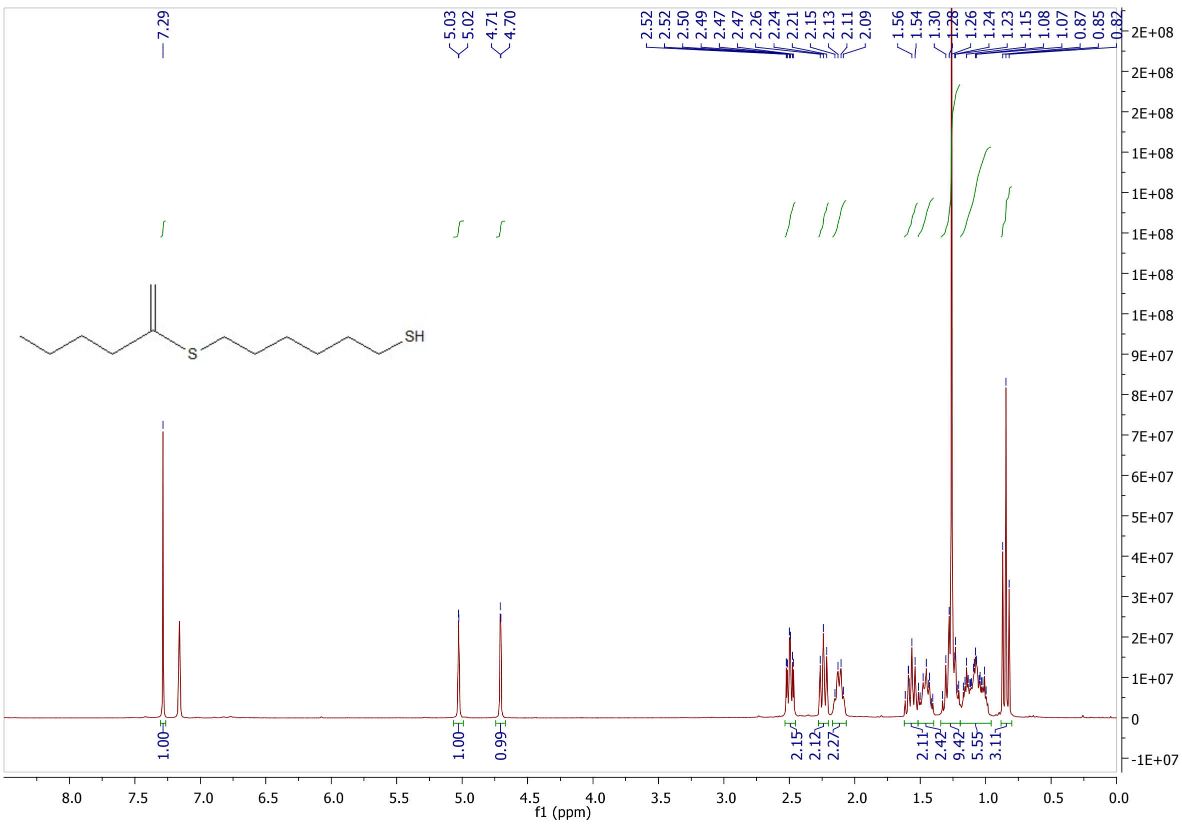


Figure S19. ^{1}H NMR of α-vinyl sulfide intermediate product

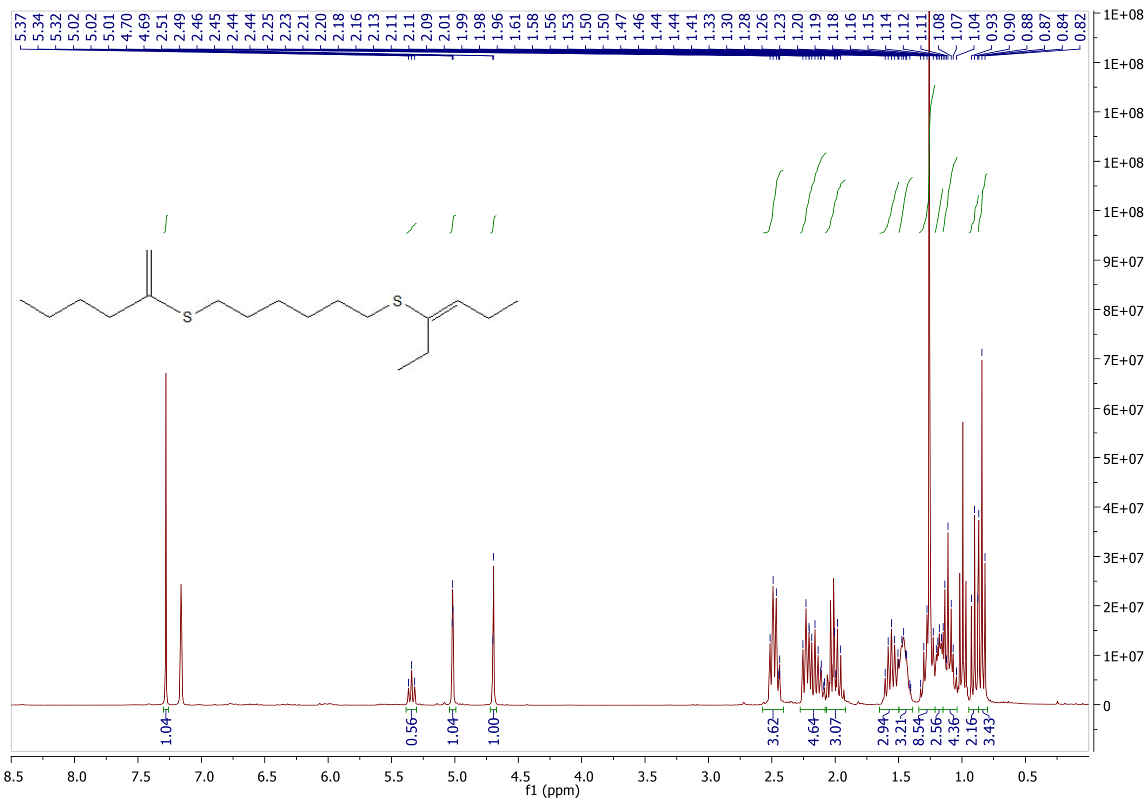


Figure S20. [1]H NMR of bis-α,β-*E*-vinyl sulfide and unreacted intermediate product

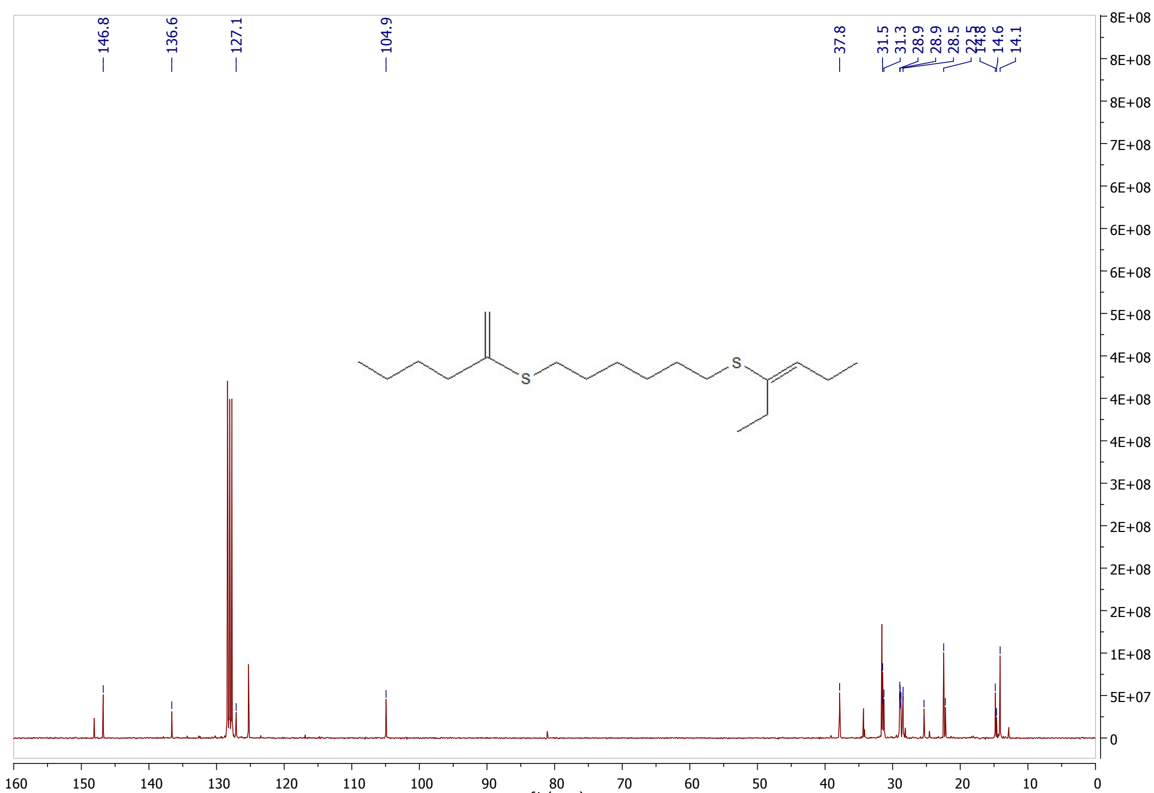


Figure S21. [13]C NMR of bis-α,β-*E*-vinyl sulfide and unreacted intermediate product

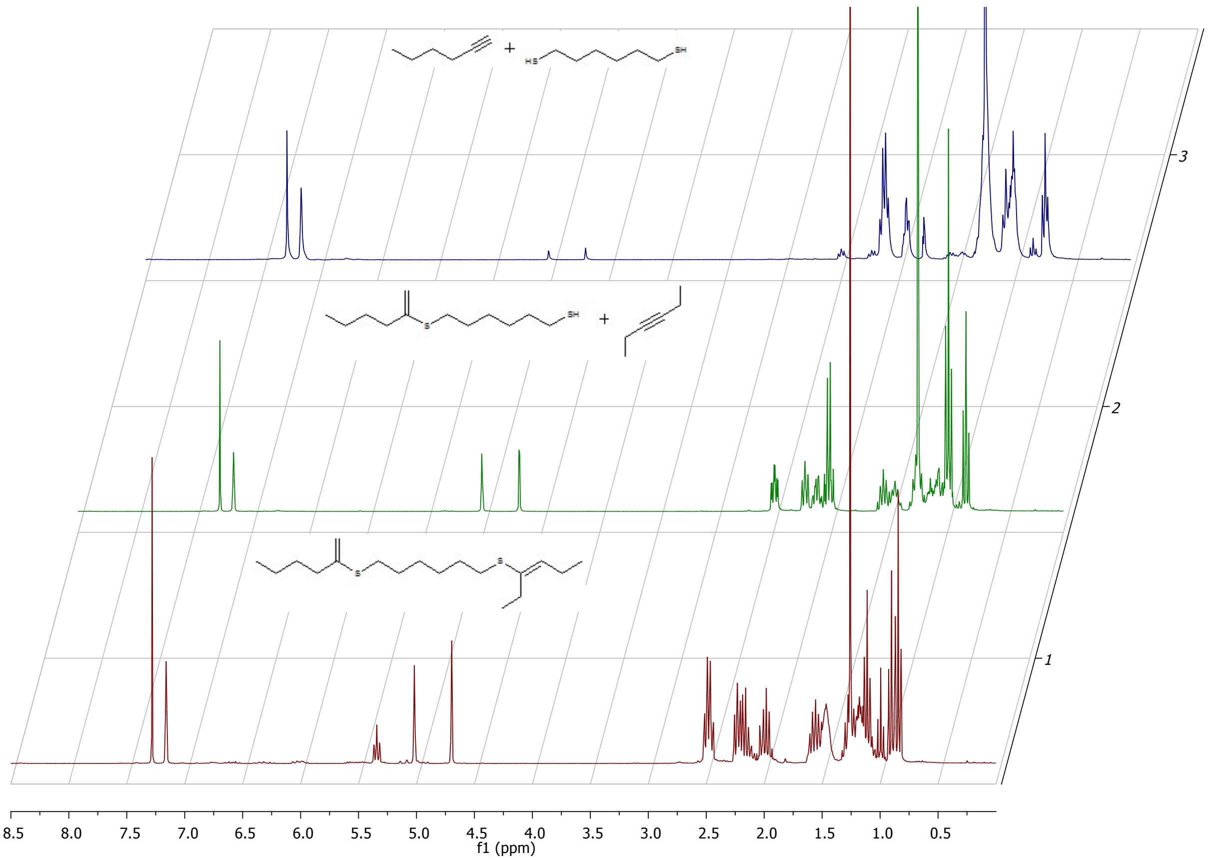


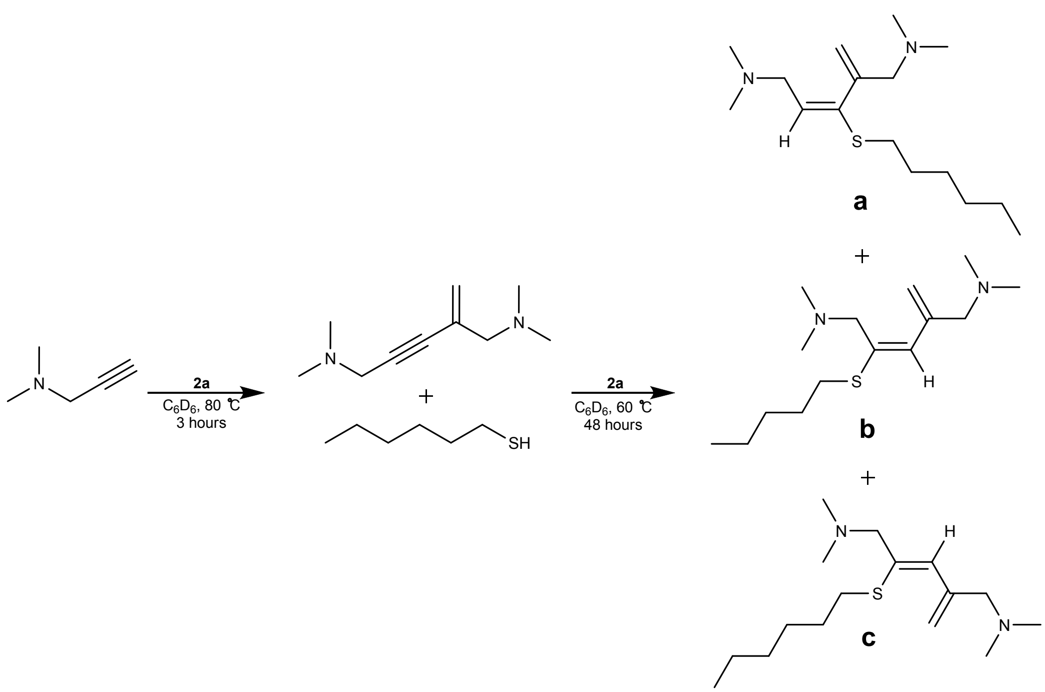
Figure S22. Stacked ^{1}H NMR of asymmetric bis-hydrothiolation reaction at initial time (blue spectrum), intermediate step (green spectrum) and final time (red spectrum)

S8. Sequential bis-hydrothiolation reaction under preparative conditions

The reaction reported in Table 3, Entry 1 was scaled up tenfold. To a Schlenk tube was added 1-hexyne (343 µL, 2.98 x 10^{-3} mol), 1,4-butanedithiol (350 µL, 2.98 x 10^{-3} mol), catalyst **2a** (116 mg, 5.97 x 10^{-5} mol; 2 mol%) and internal standard 1,4-di-tert-butylbenzene (142 mg, 7.46 x 10^{-4} mol, 0.25 equivalent) in 4 mL solvent C_6D_6. The reaction mixture was heated at 80 °C for 14 hours, whereafter the reaction mixture was allowed to cool down to room temperature. The second alkyne substrate, dimethylaminopropyne (321 µL, 2.98 x 10^{-3} mol) was added to the reaction mixture and the reaction vessel heated for an additional 30 hours at 80 °C. After a total reaction time of 44 hours, NMR analysis indicated 64% conversion of the substrates, and a calculated overall yield of the bis-α,α'-vinyl sulfide product of 62%. The reaction mixture was thereafter dry-loaded on an aluminium oxide 90 (neutral, activated) plug, and the product eluted with hexane:EtOAc (3:1). The purified bis-α,α'-vinyl sulfide product was isolated with a yield of 406 mg, 47% overall yield.

S9. Cascade Catalytic Details

A high pressure NMR tube with a J. Young valve was loaded with 3.5 mol % of catalyst **2a** (11.6 mg, 1.1 x 10^{-5} mol) and 0.25 equivalents of internal standard, 1,4-di-*tert*-butylbenzene (15.4 mg, 8.1 x 10^{-5}mol). To the mixture was added deuterated benzene (0.5 mL). One equivalent of *N*,*N*-dimethylaminopropyne (35 µL, 3.3 x 10^{-4} mol) was added to the solution, and the NMR tube was subsequently capped. ^{1}H NMR spectroscopy was performed at time 10 min after addition of the alkyne. The reaction mixture was heated up to 80 °C and left to react for 3 hours. Upon cooling down to room temperature, ^{1}H NMR spectroscopy confirmed complete conversion of *N*,*N*-dimethylaminopropyne to *N¹*,*N¹*,*N⁵*,*N⁵*-tetramethyl-4-methylenepent-2-yne-1,5-diamine. To the same reaction mixture, in open atmospheric conditions, was added 1-hexanethiol (23.1 µL, 1.6 x 10^{-4} mol). The NMR tube was capped, and a ^{1}H NMR experiment performed of the resulting mixture. The reaction mixture was heated up to 60 °C for 48 hours. Upon cooling down to room temperature, a ^{1}H NMR experiment was performed on the resulting mixture. Conversion and calculated yields were determined from NMR analysis based on integration of substrates and product, referenced to the internal standard. Product identity was determined by assignments based on 1D (^{1}H, ^{13}C{^{1}H}, ^{13}C-dept 135) and 2D (COSY, HSQC and HMBC) experiments.



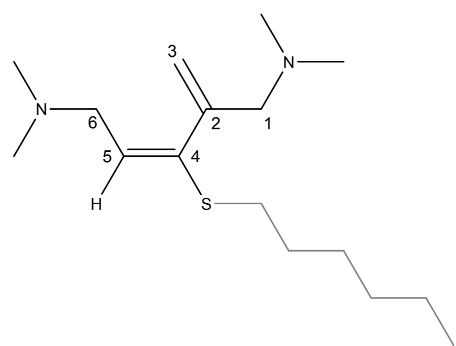
Scheme S3: One-pot alkyne dimerization followed by hydrothiolation of the internal alkyne catalyzed by **2a**

Table S3. Cascade alkyne dimerization/hydrothiolation to form *gem*-ene-vinyl sulfides promoted by **2a**.[a]

Step 1[b]			Step 2[d]					
T (°C)	t (h)	Conversion (%)[c]	T (°C)	t (h)	Conversion (%)[c]	Products	Yield (%)[e]	Product Distribution
80	3	> 99	60	48	82	**a**	29	44
						b	29	43
						c	9	13

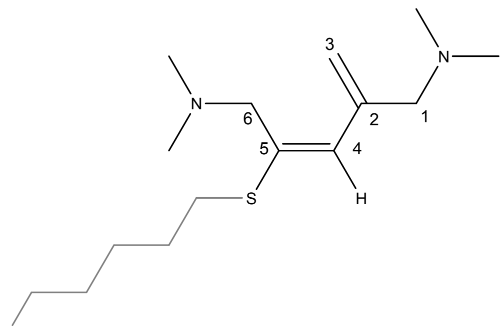
[a]Reaction performed in 0.5 mL C_6D_6 with 1,4-di-*tert*-butylbenzene as internal standard, with catalyst loading 3.5 mol %.
[b]Alkyne homo-dimerization yielding *N,N,N,N*-tetramethyl-4-methylenepent-2-yne-1,5-diamine
[c]Conversion as determined through NMR integration based on substrate and products referenced to 1,4-di-*tert*-butylbenzene.
[d]Hydrothiolation of internal alkyne of enyne formed after step 1, with 1-hexanethiol.
[e]NMR calculated yield.

(a) 1,3-gem-ene-β-E-vinyl-sulfide



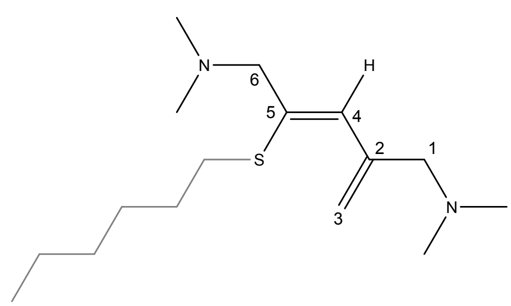
^{1}H NMR (300 MHz, C_6D_6) δ 6.03 (t, *J* = 6.8 Hz, 1H, C5-**H**), 5.44 (dt, *J* = 1.6 Hz, 1.3 Hz, 1H, C3-**H**$_2$), 5.06 (dt, *J* = 1.3 Hz, 1 Hz, 1H, C3-**H**$_2$), 3.10 (t, *J* = 1.3 Hz, 2H, C1-**H**$_2$), 3.03 (d, *J* = 6.8 Hz, 2H, C6-**H**$_2$), 2.18 (s, 6H, C1-N(C**H**$_3$)$_2$), 2.13 (s, 6H, C6-N(C**H**$_3$)$_2$), -S-hexyl moiety (grey scaled) not assigned due to extensive overlap. ^{13}C NMR (100 MHz, C_6D_6) δ 143.8 (C**2**), 138.6 (C**4**), 129.9 (C**5**), 116.9 (C**3**), 63.8 (C**1**), 58.7 (C**6**), $N(CH_3)_2$ not assigned due to extensive carbon overlap.

(b) 1,4-gem-ene-β-E-vinyl-sulfide



^{1}H NMR (300 MHz, C_6D_6) δ 6.03 (s, 1H, C4-**H**), 5.20 (dt, *J* = 1.3 Hz, 1.2 Hz, 1H, C3-$\mathbf{H}_2$), 5.13 (d, *J* = 1.5 Hz, 1H, C3-$\mathbf{H}_2$), 3.35 (d, *J* = 1 Hz, 2H, C6-$\mathbf{H}_2$), 2.86 (br s, 2H, C1-$\mathbf{H}_2$), 2.21 (s, 6H, C6-N(C$\mathbf{H}_3$)$_2$), 2.10 (s, 6H, C1-N(C$\mathbf{H}_3$)$_2$), -S-hexyl moiety (grey scaled) not assigned due to extensive overlap. ^{13}C NMR (100 MHz, C_6D_6) δ 143.6 (C**2**), 140.4 (C**5**), 123.3 (C**4**), 115.9 (C**3**), 67.1 (C**1**), 61.2 (C**6**), N(CH_3)$_2$ not assigned due to extensive carbon overlap.

(c) 1,4-gem-ene-β-Z-vinyl-sulfide



^{1}H NMR (300 MHz, C_6D_6) δ 6.36 (br s, 1H, C4-**H**), 5.12 (d, *J* = 1.3 Hz, 1H, C3-**H**), 5.08 (s, 1H, C3-**H**), 3.23 (s, 2H, C6-**H**), 3.00 (d, *J* = 1.3 Hz, 2H, C1-**H**), 2.16 (s, 6H, C6-N(C$\mathbf{H}_3$)$_2$), 2.14 (s, 6H, C1-N(C$\mathbf{H}_3$)$_2$), -S-hexyl moiety (grey scaled) not assigned due to extensive overlap. ^{13}C NMR (100 MHz, C_6D_6) δ 141.9 (C**2**), 141.7 (C**5**), 128.6 (C**4**), 110.1 (C**3**), 64.1 (C**1**), 57.9 (C**6**), N(CH_3)$_2$ not assigned due to extensive carbon overlap.

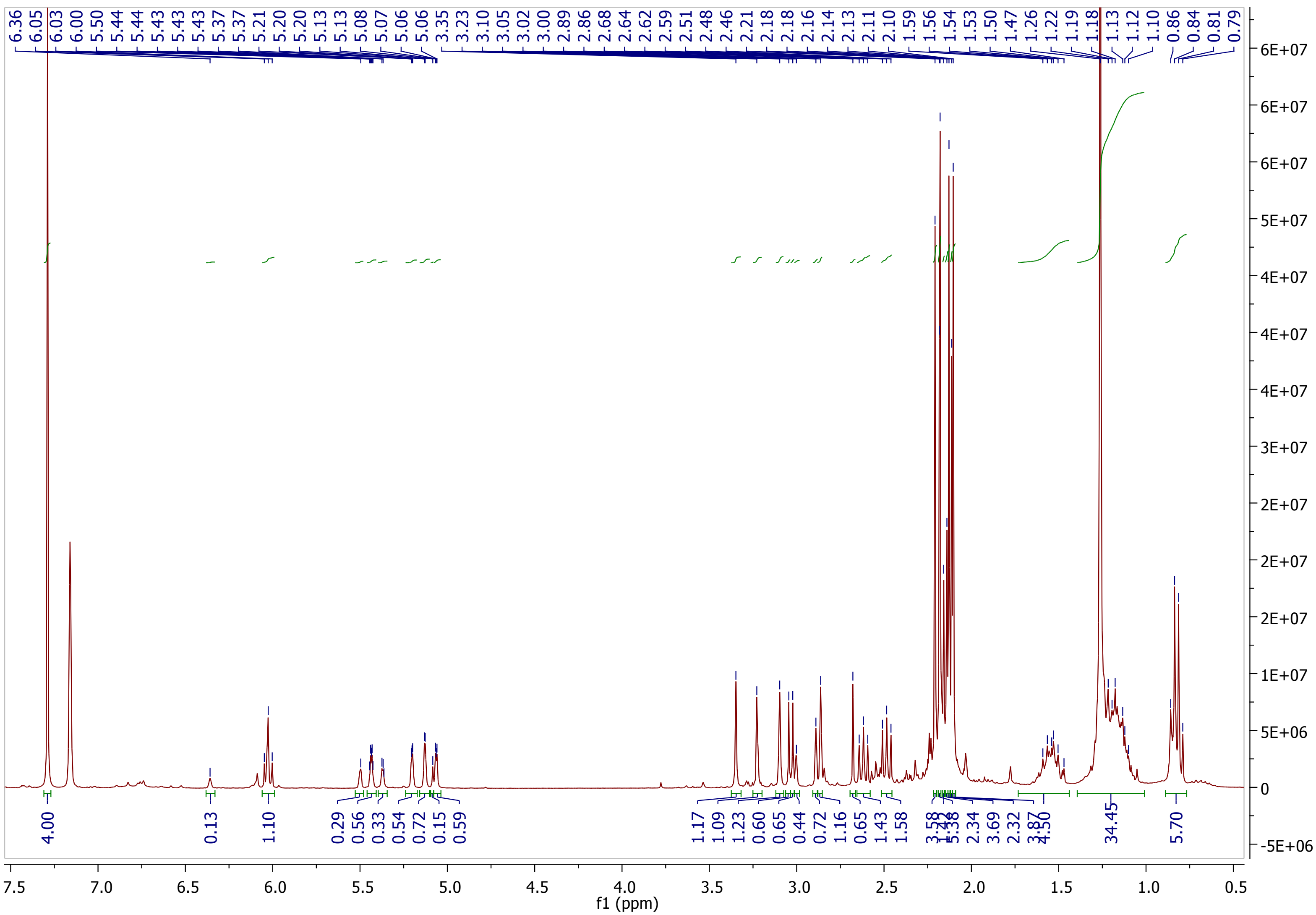


Figure S23. ^{1}H NMR spectrum of products obtained after one-pot catalyzed alkyne dimerization followed by hydrothiolation of the internal alkyne by **2a**

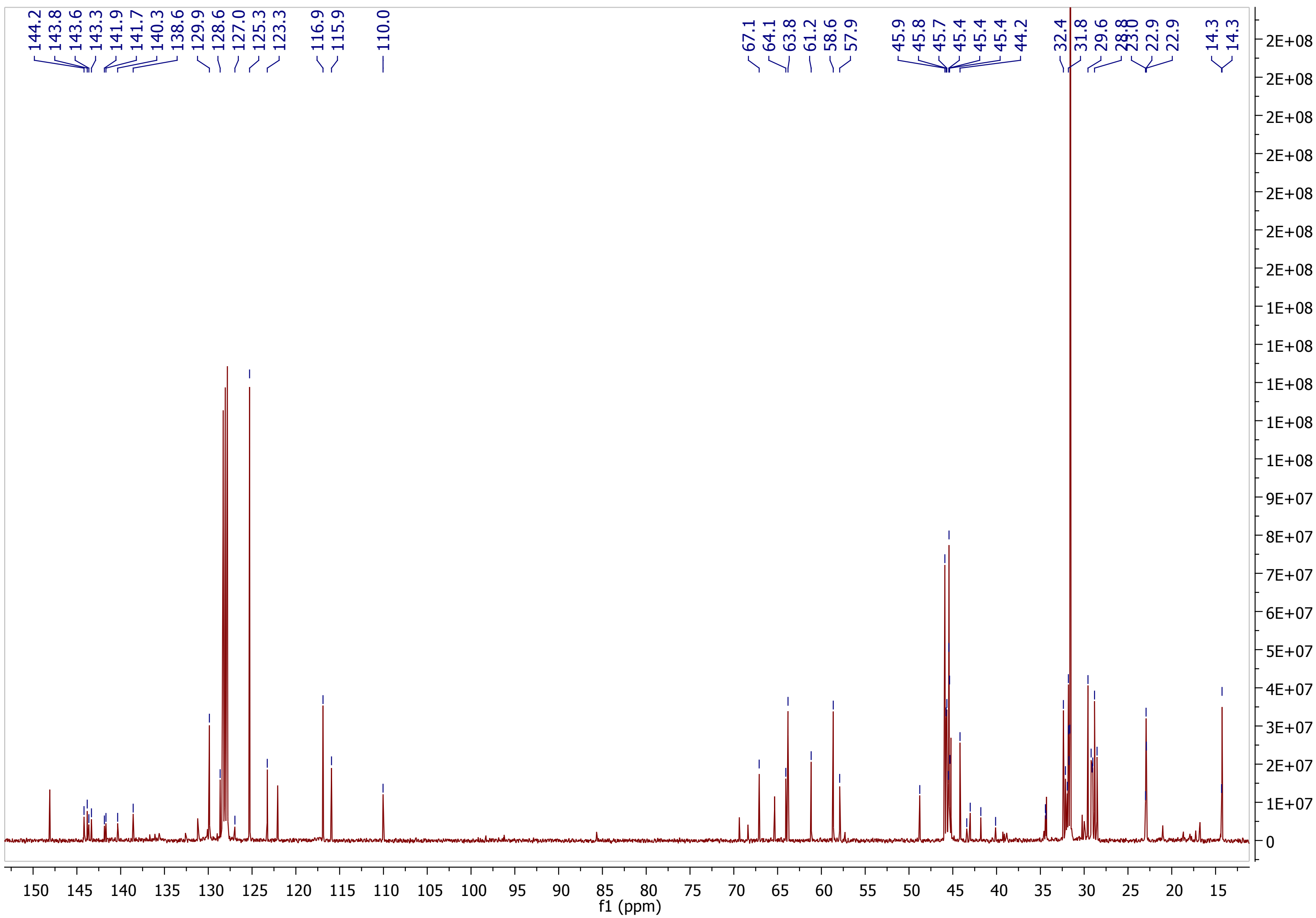


Figure S24. ^{13}C NMR spectrum of products obtained after one-pot catalyzed alkyne dimerization followed by hydrothiolation of the internal alkyne by **2a**

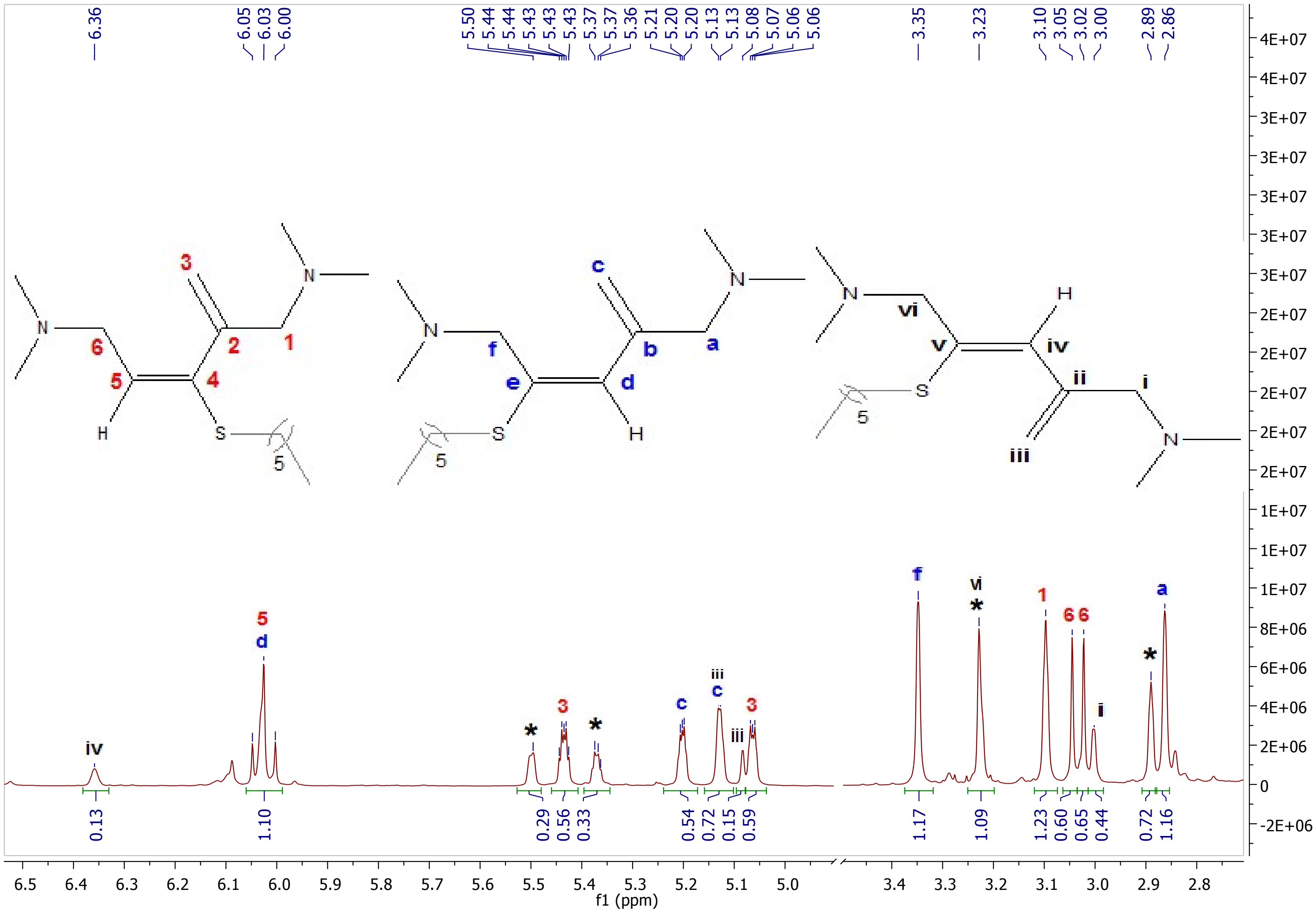


Figure S25. Selected regions of ^{1}H NMR spectrum of products obtained after one-pot catalyzed alkyne dimerization followed by hydrothiolation (* denotes unreacted *gem*-enyne intermediate product)

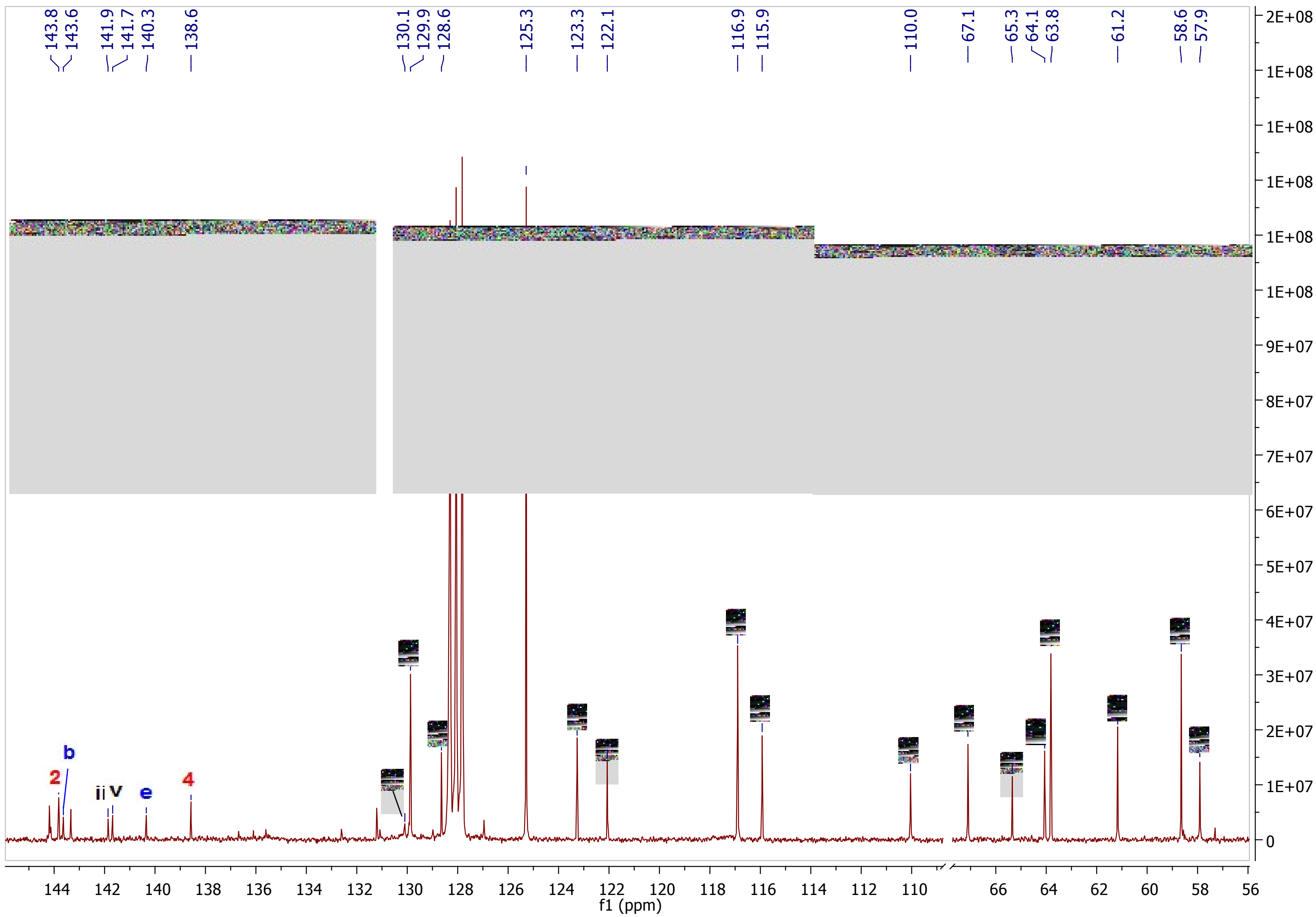


Figure S26. Selected regions of ^{13}C NMR spectrum of products obtained after one-pot catalyzed alkyne dimerization followed by hydrothiolation (* denotes unreacted *gem*-enyne intermediate product)

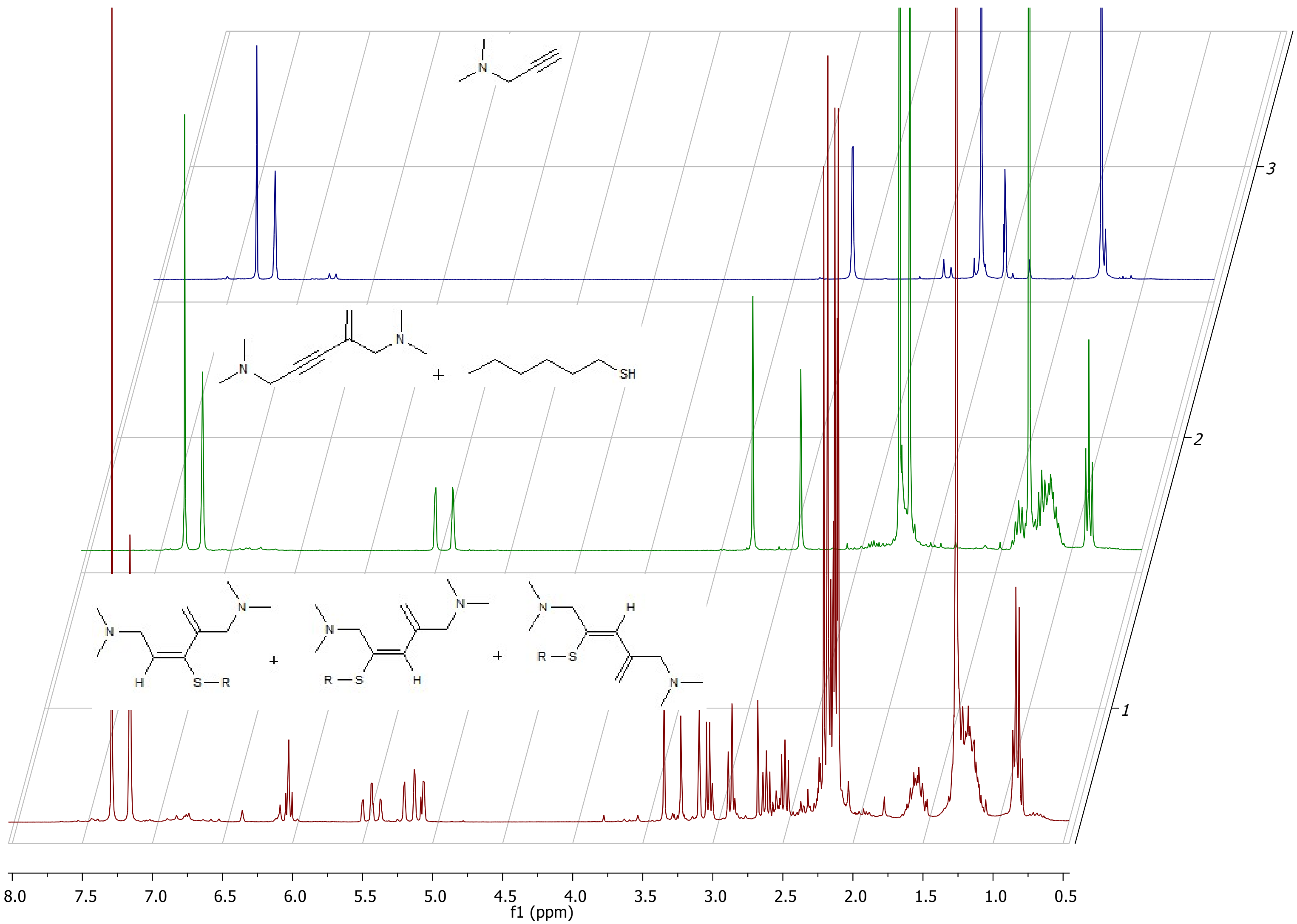


Figure S27. Stacked ^{1}H NMR spectra of one-pot catalyzed alkyne dimerization followed by hydrothiolation at initial time (blue spectrum), intermediate step (green spectrum) and final time (red spectrum)

S10. Tandem Alkyne Dimerization-Hydrothiolation Reaction under Preparative Conditions

The reaction reported in the manuscript Scheme 2 was scaled up tenfold. To a Schlenk tube was added dimethylaminopropyne (350 µL; 3.25 x 10^{-3} mol), catalyst **2a** (116 mg; 1.14 x 10^{-4} mol; 3.5 mol%) and internal standard 1,4-di-tert-butylbenzene (154 mg, 8.13 x 10^{-4} mol, 0.25 equivalent) in 4 mL solvent C_6D_6. The reaction was heated at 80 °C for 5 hours, whereafter it was allowed to cool to room temperature. 1-hexanethiol (231 µL; 1.63 x 10^{-3} mol; 0.5 equivalent) was added to the reaction mixture, and the reaction vessel then heated at 60 °C for an additional 48 hours. NMR analysis revealed 60 % conversion of the substrates, with calculated yields for the different *gem*-ene-vinyl sulfide product isomers as follows: 1,3-*gem*-ene-β-*E*-vinyl sulfide, 28%; 1,4-*gem*-ene-β-*E*-vinyl sulfide, 19%; and 1,4-*gem*-ene-β-*Z*-vinyl sulfide, 9%, with product distribution: 1,3-*gem*-ene-β-*E*-vinyl sulfide: 1,4-*gem*-ene-β-*E*-vinyl sulfide: 1,4-*gem*-ene-β-*Z*-vinyl sulfide = 50 : 34 : 16.

The products were purified by gradient elution with hexane and ethyl actetate after dry loading on an aluminium oxide 90 (neutral, activated) plug to yield all three *gem*-ene-vinyl sulfide products, with an overall crude isolated yield of 180 mg, 6.33 x 10^{-4} mol, 39% yield.

S11. Crystal Structure Details

X-ray structure and crystal data for **1a** and **2b**:

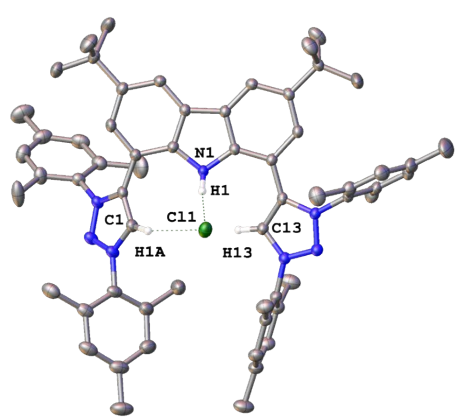


Figure 1: X-ray structure of the salt precursor **1a** with thermal ellipsoids at the 50 %probability level. H atoms except for H1 and H13, and the PF_6 counteranion were omitted for clarity. Selected bond lengths (Å): H1-Cl1 2.203 (5), H1A-Cl1 2.446 (5).

Crystal Data for **1a**: $C_{60}H_{69}N_7ClF_6P$ (*M* =1068.64 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 16.2214(4) Å, *b* = 24.0518(5) Å, *c* = 15.2494(3) Å, *β* = 108.8560(9)°, *V* = 5630.3(2) Å^3, *Z* = 4, *T* = 150.15 K, μ(CuKα) = 1.404 mm^{-1}, *Dcalc* = 1.261 g/cm^3, 198184 reflections measured (5.756° ≤ 2Θ ≤ 144.494°), 11093 unique (R_{int} = 0.0378, R_{sigma} = 0.0120) which were used in all calculations. The final R_1 was 0.0430 (I > 2σ(I)) and wR_2 was 0.1137 (all data).

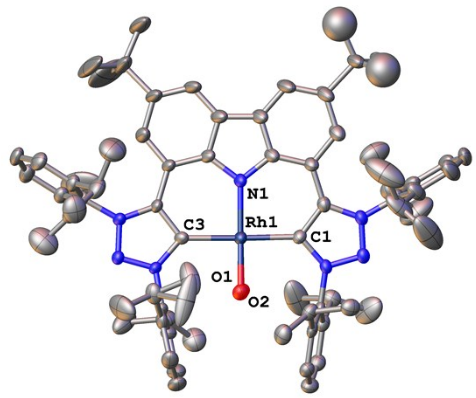


Figure 2: X-ray structure of the salt precursor **2b** with thermal ellipsoids at the 50 %probability level. H atoms were omitted for clarity. Selected bond lengths (Å) and angles (º): Rh1-N1 1.986(3), Rh1-C1 2.035(4), Rh1-C3 2.036(4), Rh1-O1 1.976(3), Rh1-O2 1.980(3), O1-O2 1.389 (7); O1-Rh1-N1 160.91(13), N1-Rh1-C1 89.65 (13), N1-Rh1-C3 89.09 (13), C1-Rh1 C3 178.57(14), O1-Rh1-O2 40.74(11), O1-Rh1-C1 90.21(13).

Crystal Data for **2b**: $C_{72}H_{84}N_7O_2Rh$ (*M* =1182.37 g/mol): triclinic, space group P-1 (no. 2), *a* = 10.8323(5) Å, *b* = 15.4988(8) Å, *c* = 24.8410(13) Å, *α* = 103.4480(14)°, *β* = 97.0590(13)°, *γ* = 107.0370(13)°, *V* = 3795.4(3) Å^3, *Z* = 2, *T* = 150.15 K, μ(MoKα) = 0.267 mm^{-1}, *Dcalc* = 1.035 g/cm^3, 84650 reflections measured (4.428° ≤ 2Θ ≤ 51.56°), 14487 unique (R_{int} = 0.1099, R_{sigma} = 0.0978) which were used in all calculations. The final R_1 was 0.0610 (I > 2σ(I)) and wR_2 was 0.1727 (all data).

S12. References

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