Supporting Information

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

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**S1. Standard Operating Procedures**

**a. Method**

All synthetic manipulations, unless otherwise stated, were performed under an N₂ gas or Ar gas atmosphere using oven or flame dried glassware and standard Schlenk or vacuum line techniques. Air sensitive solids were 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 'BuOCl was prepared according to the method of Mintz and Walling. 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. 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. 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 Et₂O were obtained after distillation over sodium and benzophenone under a N₂ gas atmosphere. Anhydrous PhMe and hexane were obtained after distillation over sodium under a N₂ gas atmosphere. Anhydrous CH₂Cl₂ was obtained after distillation over calcium hydride under a N₂ 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 ¹H, 75.47 MHz for ¹³C, 121.49 MHz for ³¹P and 282.40 MHz for ¹⁹F; or AVANCE-III-400 operating at 400.21 MHz for ¹H, 100.64 MHz for ¹³C, 162.01 MHz for ³¹P and 376.57 MHz for ¹⁹F. ¹H Chemical shifts are reported as δ (ppm) values downfield from Me₄Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD₃CN, 1.94 ppm; CDCl₃, 7.26 ppm; C₆D₆, 7.16 ppm). ¹³C chemical shifts are also reported as δ (ppm) values downfield from Me₄Si and chemical shifts where referenced to residual non-deuterated solvents peaks (CD₃CN, 1.32 ppm; CDCl₃, 77.16 ppm; C₆D₆, 128.06 ppm). Proton coupling constants (J) are given in Hz. The spectral coupling patterns are
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$_\alpha$ radiation ($\lambda = 0.71073$ 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.

Solution IR spectra ($\nu$(CO)) were recorded on a Perkin-Elmer Spectrum RXI FT-IR spectrophotometer in CH$_2$Cl$_2$ 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 $\mu$L/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.\(^5\) 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\(_2\)O 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\(_7\)ClPF\(_6\), 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\(_3\)CN) \(\delta\) 11.51 (br s, 1H, NH\(_{\text{carb}}\)), 10.06 (s, 2H, ArNH\(_{\text{Triazolium}}\)), 8.42 (d, \(J = 1.8\) Hz, 2H, ArH\(_{\text{carb}}\)), 7.23 (br s, 4H, ArH\(_{\text{Mes}}\)), 7.19 (br s, 4H, ArH\(_{\text{Mes}}\)), 7.08 (d, \(J = 1.5\) Hz, 2H, ArH\(_{\text{carb}}\)), 2.46 (s, 6H, ArCH\(_3\)), 2.36 (s, 6H, ArCH\(_3\)), 2.26 (s, 12H, ArCH\(_3\)), 2.08 (s, 12H, ArCH\(_3\)), 1.16 (s, 18H, C(CH\(_3\))\(_3\)). \(^{13}\)C NMR (75 MHz, CD\(_3\)CN) \(\delta\) 145.3 (ArC\(_q\)), 144.5 (ArC\(_q\)), 144.2 (ArC\(_q\)), 142.3 (ArC\(_q\)), 138.7 (ArC\(_q\)), 136.1 (ArC\(_q\)), 135.9 (ArC\(_q\)), 133.6 (ArC\(_q\)), 132.5 (ArC\(_q\)), 131.3 (ArCH), 130.9 (ArCH), 127.2 (ArC\(_q\)), 125.9 (ArCH), 122.5 (ArCH), 106.9 (ArC\(_q\)), 35.4 (C(CH\(_3\))\(_3\)), 31.5 (C(CH\(_3\))\(_3\)), 21.4 (ArCH\(_3\)), 21.2 (ArCH\(_3\)), 18.1 (ArCH\(_3\)), 18.1 (ArCH\(_3\)). \(^{19}\)F NMR (282 MHz, CD\(_3\)CN) \(\delta\) -72.90 (d, \(J = 706.0\) Hz, PF\(_6\)). \(^{31}\)P NMR (121 MHz, CD\(_3\)CN) \(\delta\) -144.6 (sept, \(J = 706.5\) Hz, PF\(_6\)). HRMS (FIA-ESI): Calculated for C\(_{60}\)H\(_{69}\)N\(_7\)\(_2\)\(_6\)[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(C₂H₄)₂Cl]₂ (58.2 mg, 1.5 x 10⁻⁴ mol) and K[Si(CH₃)₃]₂ (186.7 mg, 9.4 x 10⁻⁴ mol). The reaction vessel was evacuated, purged with N₂ (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 RhC₆₀H₆₆N₇O₂, Anal. Calcd.: C, 70.64; H, 6.52; N, 9.61. Found: C, 68.52; H, 6.42; N, 9.01. ¹H NMR (300 MHz, C₆D₆) δ 8.55 (d, J = 1.8 Hz, 2H, ArH-carb), 7.55 (d, J = 1.8 Hz, 2H, ArH-carb), 6.78 (s, 4H, ArHMes), 6.71 (s, 4H, ArHMes), 2.43 (s, 12H, ArCH₃), 2.34 (s, 6H, ArCH₃), 2.08 (s, 6H, ArCH₃), 1.77 (s, 12H, ArCH₃), 1.25 (s, 18H, CH₃(C₆H₃)). ¹³C NMR (75 MHz, C₆D₆) δ 167.5 (d, J = 39.0 Hz, Rh-Carben), 144.4 (ArC), 141.1 (ArC), 140.8 (ArC), 140.4 (ArC), 138.3 (ArC), 137.2 (ArC), 135.7 (ArC), 135.7 (ArC), 134.9 (ArC), 130.0 (ArCH), 127.2 (ArCH), 118.1 (ArCH), 118.4 (ArCH), 116.4 (ArCH), 113.9 (ArC), 113.9 (ArC), 34.7 (C(CH₃)₃), 31.9 (C(CH₃)₃), 21.4 (ArCH₃), 21.3 (ArCH₃), 21.0 (ArCH₃), 21.0 (ArCH₃), 18.4 (ArCH₃), 18.4 (ArCH₃), 17.2 (ArCH₃), 17.2 (ArCH₃). HRMS (FIA-ESI): Calculated for C₆₀H₆₆N₇RhO₂²⁺ [M + CH₃CN + 2H]²⁺: 531.2377, found: 531.2393.

c. Synthesis of 2b

A flame dried Schlenk tube was loaded with 1b (200.0 mg, 1.6 x 10⁻⁴ mol), [Rh(C₂H₄)₂Cl]₂ (50.3 mg, 1.3 x 10⁻⁴ mol) and K[Si(CH₃)₃]₂ (161.3 mg, 8.1 x 10⁻⁴ mol). The Schlenk tube was evacuated and purged with N₂ (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_{2}O_{2}, Anal. Calcd.: C, 72.77; H, 6.53; N, 8.25. Found: C, 71.65; H, 7.40; N, 7.76. 1H NMR (400 MHz, C_{6}D_{6}) δ 8.40 (d, J = 2.0 Hz, 2H, ArH_{carb}), 7.49 (d, J = 2.0 Hz, 2H, ArH_{carb}), 7.34 (t, J = 7.8 Hz, 2H, ArH_{Dipp}), 7.30 (t, J = 7.8 Hz, 2H, ArH_{Dipp}), 7.16 (d, 4H, ArH_{Dipp} overlaps with C_{6}D_{6}), 7.13 (d, J = 8.0 Hz, 4H, ArH_{Dipp}), 2.98 (sept, J = 6.8 Hz, 4H, CH(CH_{3})_{2}), 2.66 (sept, J = 6.8 Hz, 4H, CH(CH_{3})_{2}), 1.65 (d, J = 6.8 Hz, 12H, CH(CH_{3})_{2}), 0.78 (d, J = 6.8 Hz, 4H, CH(CH_{3})_{2}), 7.34 (t, J = 7.2 Hz, 12H, CH(CH_{3})_{2}), 1.23 (d, J = 7.2 Hz, 12H, CH(CH_{3})_{2}), 1.21 (s, 18H, C(CH_{3})_{3}), 1.05 (d, J = 6.8 Hz, 12H, CH(CH_{3})_{2}). 13C NMR (100 MHz, C_{6}D_{6}) δ 168.4 (d, J = 39.2 Hz, Rh-C_{carbene}), 146.3 (ArC_{q}), 145.4 (ArC_{q}), 144.4 (ArC_{q}), 141.6 (ArC_{q}), 140.6 (ArC_{q}), 137.5 (ArC_{q}), 135.3 (ArC_{q}), 131.7 (ArC_{q}), 129.1 (ArC_{q}), 125.5 (ArC_{q}), 121.6 (ArC_{q}), 119.6 (ArC_{q}), 116.7 (ArC_{q}), 113.2 (ArC_{q}), 34.6 (C(CH_{3})_{3}), 32.0 (C(CH_{3})_{3}), 29.6 (CH(CH_{3})_{2}), 29.1 (CH(CH_{3})_{2}), 26.0 (CH(CH_{3})_{2}), 24.8 (CH(CH_{3})_{2}), 24.3 (CH(CH_{3})_{2}), 23.2 (CH(CH_{3})_{2}). HRMS (FIA-ESI): Calculated for C_{72}H_{90}N_{2}RhO_{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_{60}H_{66}N_{2}O_{2}, Anal. Calcd.: C, 72.10; H, 6.55; N, 9.65. Found: C, 70.37; H, 6.71; N, 9.15. 1H NMR (300 MHz, C_{6}D_{6}) δ 8.67 (d, J = 1.8 Hz, 2H, ArH_{carb}), 7.42 (d, J = 1.8 Hz, 2H, ArH_{carb}), 6.84 (s, 4H, ArH_{mes}), 6.73 (s, 4H, ArH_{mes}), 2.40 (s, 12H, ArCH_{3}), 2.31 (s, 6H, ArCH_{3}), 2.09 (s, 6H, ArCH_{3}), 1.78 (s, 12H, ArCH_{3}), 1.30 (s, 18H, C(CH_{3})_{3}). 13C NMR (75 MHz, C_{6}D_{6}) δ 194.9 (d, J = 71.6 Hz, Rh-CO), 173.4 (d, J = 41.1 Hz, Rh-C_{carbene}), 144.9 (ArC_{q}), 141.3 (ArC_{q}), 140.6 (ArC_{q}), 139.1 (ArC_{q}), 138.3 (ArC_{q}), 138.0 (ArC_{q}), 136.1 (ArC_{q}), 135.7 (ArC_{q}), 135.6 (ArC_{q}), 129.9 (ArCH), 129.0 (ArCH), 127.1 (ArC_{q}), 117.9 (ArCH), 116.9 (ArCH), 112.7 (ArC_{q}), 34.6 (C(CH_{3})_{3}), 32.1 (C(CH_{3})_{3}), 21.5 (ArCH), 21.0 (ArCH), 18.7 (ArCH), 17.3 (ArCH). IR (ν_{CO}, CH_{2}Cl_{2}): 1941 cm^{-1}. HRMS (FIA-ESI): Calculated for C_{60}H_{66}N_{2}RhCO^{+} [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\(_2\)Cl\(_2\) (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 \textit{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\(_{7}\)O, 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\(_6\)D\(_6\)) \(\delta\) 8.52 (d, \(J = 1.8\) Hz, 2H, Ar carb), 7.64 (dd, \(J = 5.7\) Hz, 3.3 Hz, 1H, ArDipp), 7.46 (d, \(J = 1.5\) Hz, 2H, Ar carb), 7.31 – 7.25 (m, 6H, ArDipp), 6.93 (dd, \(J = 5.7\) Hz, 3.3 Hz, 1H, ArDipp), 3.04 (sept, \(J = 6.8\) Hz, 4H, CH(CH\(_3\))\(_2\)), 2.62 (sept, \(J = 6.8\) Hz, 4H, CH(CH\(_3\))\(_2\)), 1.55 (d, \(J = 6.9\) Hz, 12H, CH(C(CH\(_3\)))\(_2\)), 1.04 (d, \(J = 6.9\) Hz, 12H, CH(CH\(_3\)))\(_2\)), 0.78 (d, \(J = 6.9\) Hz, 12H, CH(CH\(_3\)))\(_2\)). \(^{13}\)C NMR (75 MHz, C\(_6\)D\(_6\)) \(\delta\) 195.4 (d, \(J = 70.2\) Hz, Rh-CO), 173.4 (d, \(J = 41.6\) Hz, Rh-Carbene), 146.3 (Ar\(_q\)), 146.1 (Ar\(_q\)), 144.4 (Ar\(_q\)), 142.7 (Ar\(_q\)), 138.2 (Ar\(_q\)), 137.6 (Ar\(_q\)), 135.7 (Ar\(_q\)), 133.4 (Ar\(_q\)), 131.5 (Ar\(_CH\)), 130.9 (Ar\(_CH\)), 130.8 (Ar\(_CH\)), 129.1 (Ar\(_CH\)), 127.2 (Ar\(_q\)), 125.4 (Ar\(_CH\)), 124.1 (Ar\(_CH\)), 119.0 (Ar\(_CH\)), 117.1 (Ar\(_CH\)), 111.8 (Ar\(_q\)), 34.5 (C(CH\(_3\)))\(_3\)), 32.3 (C(CH\(_3\)))\(_3\)), 29.3 (CH(CH\(_3\)))\(_2\)), 29.1 (CH(CH\(_3\)))\(_2\)), 25.6 (CH(CH\(_3\)))\(_2\)), 24.8 (CH(CH\(_3\)))\(_2\)), 24.2 (CH(CH\(_3\)))\(_2\)), 23.1 (CH(CH\(_3\)))\(_2\)). IR (\(\nu_{CO}\), CH\(_2\)Cl\(_2\)): 1955 cm\(^{-1}\). HRMS (FIA-ESI): Calculated for C\(_{72}\)H\(_{90}\)N\(_7\)RhCO\(^{2+}\) [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$_6$D$_6$ solvent
Figure S2. $^{13}$C NMR of 2a in $\text{C}_6\text{D}_6$ solvent

Figure S3. $^1$H NMR of 2b in $\text{C}_6\text{D}_6$ solvent
Figure S4. $^{13}$C NMR of 2b in C$_6$D$_6$ solvent

Figure S5. $^1$H NMR of 3a in C$_6$D$_6$ solvent
Figure S6. $^{13}$C NMR of $3a$ in C$_6$D$_6$ solvent

Figure S7. $^1$H NMR of $3b$ in C$_6$D$_6$ solvent
Figure S8. $^{13}$C NMR of 3b in C$_6$D$_6$ 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.\(^a\)

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<th>Entry</th>
<th>Catalyst</th>
<th>Base (mol %)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Conversion(^b) (%)</th>
<th>Yield(^c) (%)</th>
<th>Product distribution</th>
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<td></td>
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<td>E-enyne</td>
<td>Z-enyne</td>
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<td>2a</td>
<td>K(_2)CO(_3) (1)</td>
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<td>&gt; 99</td>
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<td>100</td>
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<tr>
<td>2</td>
<td>2a</td>
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<td>100</td>
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<tr>
<td>3</td>
<td>2a</td>
<td>KO'Bu (1)</td>
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<td>&gt; 1</td>
<td>&gt; 99</td>
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<td>100</td>
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<tr>
<td>4</td>
<td>2a</td>
<td>Pyridine (3)</td>
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<td>&gt; 1</td>
<td>88</td>
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<td>100</td>
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<tr>
<td>5</td>
<td>2b</td>
<td>K(_2)CO(_3) (1)</td>
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<tr>
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<td>&gt; 1</td>
<td>&gt; 99</td>
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\(^a\)Reaction performed in C\(_6\)D\(_6\) (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

$\text{H NMR (300 MHz, C}_6\text{D}_6 \delta 5.38 (d, } J = 2.1 \text{ Hz, 1H, C=CH}_2, 5.09 (m, 1H, C=CH}_2, 2.16 (m, 8H, H}_{4,8}, 1.59 (tt, J = 7.2 \text{ Hz, 7.5 Hz, 7.8 Hz, 2H, H}_9, 1.43 - 1.23 (m, 6H, H}_{2,3,10} \text{ overlaps with } -\text{C(CH}_3)_3 \text{ of di-tert-butylbenzene), 0.86 and 0.78 (both } t, J = 7.2 \text{ Hz, 6H, H}_{1,11}).$

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. ¹H 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, 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 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.⁶

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

1H NMR (300 MHz, C₆D₆) δ 7.77 - 7.68 (m, 2H, H₀-1), 7.54 - 7.38 (m, 2H, H₀-2, extensive overlap with unreacted phenylacetylene, E-enyne, internal standard and residual solvent), 7.09 - 6.87 (m, 6H, Hₘ and Hₚ, extensive overlap with unreacted phenylacetylene, E-enyne and internal standard), 5.75 (d, J = 0.8 Hz, 1H, C=CH₂), 5.70 (d, J = 0.7 Hz, 1H, C=CH₂).
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, \( 2.6 \times 10^{-6} \) mol); internal standard 0.25 equivalent (12.3 mg, \( 6.4 \times 10^{-5} \) mol) and one equivalent \( N \)-Boc-propargylamine (40 mg, \( 2.6 \times 10^{-4} \) mol). Product identity was confirmed by comparison with previously reported NMR spectra.\( ^{vii} \)

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

\[
\begin{align*}
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{N} \\
\text{O} & \quad \text{O}
\end{align*}
\]

\( ^{1} \)H NMR (300 MHz, \( CD_{6} \)) \( \delta \) 5.26 (br s, 1H, \( \text{C}=\text{CH}_{2} \)), 5.15 (d, \( J = 1 \) Hz, 1H, \( \text{C}=\text{CH}_{2} \)), 4.57 (br s, 2H, \( \text{CH}_{2} \text{NH} \)), 3.82 (d, \( J = 2.8 \) Hz, 2H, \( \text{CH}_{2} \text{NH} \)), 3.66 (d, \( J = 5.3 \) Hz, 2H, \( \text{CH}_{2} \text{NH} \)), 1.42 (s, 9H, -\( \text{C(C}_{3} \text{H}_{3})_{3} \)), 1.39 (s, 9H, -\( \text{C(CH}_{3})_{3} \)).

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, \( 3.3 \times 10^{-6} \) mol); internal standard 0.25 equivalent (15.5 mg, \( 8.1 \times 10^{-5} \) mol) and one equivalent trimethylsilyloxypropyne (50 \( \mu \)L, \( 3.3 \times 10^{-4} \) mol). Product identity was confirmed by comparison with previously reported NMR spectra.\( ^{viii} \)

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

\[
\begin{align*}
\text{O} & \quad \text{Si} \\
\text{O} & \quad \text{Si}
\end{align*}
\]

\( ^{1} \)H NMR (300 MHz, \( CD_{6} \)) \( \delta \) 5.64 (q, \( J = 2.0 \) Hz, 1H, \( \text{C}=\text{CH}_{2} \)), 5.51 (d, \( J = 1.8 \) Hz, 1H, \( \text{C}=\text{CH}_{2} \)), 4.28 (s, 2H, \( \text{OCH}_{3} \)), 4.14 (t, \( J = 1.8 \) Hz, 2H, \( \text{OCH}_{3} \)), 0.12 (s, 9H, \( \text{Si(CH}_{3})_{3} \)), 0.06 (s, 9H, \( \text{Si(CH}_{3})_{3} \)).
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

\[\text{H}_2\text{N} = \text{CH} = \text{CH} - \text{NH}_2\]

\(^1\text{H}\) NMR (300 MHz, CD\(_6\)) \(\delta\) 5.34 (br s, 1H, C=CH\(_2\)), 5.19 (d, \(J = 1.7\) Hz, 1H, C=CH\(_2\)), 3.18 (br s, 4H, CH\(_2\)NH\(_2\)), 0.75 (br s, 4H, CH\(_2\)NH\(_3\)).

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

\[\text{N} = \text{CH} = \text{CH} - \text{N} = \text{CH} \text{CH}_2\text{N} = \text{CH}_3\]

\(^1\text{H}\) NMR (300 MHz, CD\(_6\)) \(\delta\) 5.50 (d, \(J = 2.1\) Hz, 1H, C=CH\(_2\)), 5.38 (m, 1H, C=CH\(_2\)), 3.24 (s, 2H, CH\(_2\)N(CH\(_3\))\(_2\)), 2.90 (s, 2H, CH\(_2\)N(CH\(_3\)))\(_2\)), 2.19 (s, 6H, CH\(_2\)N(CH\(_3\)))\(_2\)), 2.12 (s, 6H, CH\(_2\)N(CH\(_3\)))\(_2\)).

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.\textsuperscript{i}x

\textit{4-methylenepent-2-yne-1,5-diol}

\begin{center}
\includegraphics[width=0.5\textwidth]{4_methylenepent_2_yne_1_5_diol}
\end{center}

\textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}) δ 5.37 (br s, 1H, C=CH\textsubscript{2}), 5.34 (br s, 1H, C=CH\textsubscript{2}), 4.09 (s, 2H, CH\textsubscript{2}OH), 3.96 (s, 2H, CH\textsubscript{2}OH), 2.05 (br s, 2H, CH\textsubscript{2}OH).

**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.\textsuperscript{x}

\textit{1,5-dichloro-4-methylenepent-2-yne}

\begin{center}
\includegraphics[width=0.5\textwidth]{1_5_dichloro_4_methylenepent_2_yne}
\end{center}

\textsuperscript{1}H NMR (300 MHz, C\textsubscript{6}D\textsubscript{6}) δ 5.64 (t, J = 6.2 Hz, 2H, C=CH\textsubscript{2}), 4.59 (s, 2H, CH\textsubscript{2}Cl), 4.57 (s, 2H, CH\textsubscript{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, $3.9 \times 10^{-6}$ mol) or one mol % catalyst 2b (4.7 mg, $3.9 \times 10^{-6}$ mol) and 0.25 equivalents of internal standard, 1,4-di-tert-butylbenzene (18.6 mg, $9.8 \times 10^{-5}$). 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, $3.9 \times 10^{-4}$ mol) and one equivalent of thiophenol (40 µL, $3.9 \times 10^{-4}$ 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.\textsuperscript{xi}

Table S2. Hydrothiolation of 1-hexyne (1 equivalent) with thiophenol (1 equivalent) promoted by 2.\textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Base (mol %)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>Conversion (%)\textsuperscript{b}</th>
<th>Yield (%)\textsuperscript{c}</th>
<th>Product distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\alpha$-vinyl sulfide</td>
<td>$\beta$-E-vinyl sulfide</td>
<td>$\beta$-Z-vinyl sulfide</td>
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<tr>
<td>1</td>
<td>2a</td>
<td>$\text{K}_2\text{CO}_3$ (1)</td>
<td>80</td>
<td>24</td>
<td>77</td>
<td>71</td>
<td>91\textsuperscript{d} 6 3</td>
</tr>
<tr>
<td>2</td>
<td>2a</td>
<td>$\text{K}_2\text{CO}_3$ (1)</td>
<td>40</td>
<td>24</td>
<td>14</td>
<td>11</td>
<td>91\textsuperscript{d} 5 4</td>
</tr>
<tr>
<td>3</td>
<td>2a</td>
<td>Pyridine (5)</td>
<td>80</td>
<td>24</td>
<td>74</td>
<td>64</td>
<td>89\textsuperscript{d} 8 3</td>
</tr>
<tr>
<td>4</td>
<td>2a</td>
<td>None</td>
<td>80</td>
<td>24</td>
<td>81</td>
<td>74</td>
<td>91\textsuperscript{d} 6 3</td>
</tr>
<tr>
<td>5</td>
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<td>80</td>
<td>24</td>
<td>58</td>
<td>49</td>
<td>92\textsuperscript{d} 2 6</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Reaction performed in C\textsubscript{6}D\textsubscript{6} (0.5 mL) with internal standard 1,4-di-tert-butylbenzene, 1 mol % catalyst ($3.5 \times 10^{-6}$ mol) and $3.5 \times 10^{-4}$ mol 1-hexyne.

\textsuperscript{b} Conversion as determined through NMR integration based on 1-hexyne referenced to 1,4-di-tert-butylbenzene.

\textsuperscript{c} Yield of $\alpha$-vinyl sulfide as determined from NMR integration based on 1-hexyne.

\textsuperscript{d} Plus unidentified products.
2-Phenylthio-1-hexene

\[
\text{H NMR (300 MHz, C}_6\text{D}_6) \delta \text{ 7.44 - 7.40 (m, 2H, ArH), 7.05 - 6.96 (m, 3H, ArH overlaps with unreacted thiophenol), 5.06 (s, 1H, C=CH}_2\text{), 4.97 (s, 1H, C=CH}_3\text{), 2.20 (t, J = 7.6 Hz, 2H, CH}_2\text{), 1.50 (tt, J = 7.6 Hz, 7.5 Hz, 2H, CH}_2\text{), 1.26 - 1.16 (m, 2H, CH}_2\text{ overlaps with C(CH}_3\text)_3\text{ of internal standard), 0.80 (t, J = 7.3 Hz, 3H, CH}_3\text{).}
\]

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. $^1$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 2). 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 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

$^1$H NMR (300 MHz, C$_6$D$_6$) $\delta$ 5.24 (t, $J = 1.0$ Hz, 1H, C=CH$_2$), 4.78 (s, 1H, C=CH$_2$), 3.00 (s, 2H, CH$_2$N(CH$_3$)$_2$), 2.56 (t, $J = 7.3$ Hz, 2H, CH$_2$), 2.12 (s, 6H, CH$_2$N(CH$_3$)$_2$), 1.53 (tt, $J = 7.5$ Hz, 7.2 Hz, 2H, CH$_2$), 1.27 - 1.11 (m, 6H, (CH$_3$)$_3$ overlaps with C(CH$_3$)$_3$ of internal standard), 0.82 (t, $J = 0.8$ Hz, 3H, CH$_3$). $^{13}$C NMR (75 MHz, C$_6$D$_6$) $\delta$ 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*

![Chemical structure](image)

$^1$H NMR (300 MHz, C$_6$D$_6$) δ 5.14 (s, 1H, C=CH$_2$), 4.77 (s, 1H, C=CH$_2$), 4.64 (br s, 1H, CH$_2$NH), 3.82 (d, $J$ = 5.9 Hz, 2H, CH$_2$NH), 2.45 (t, $J$ = 7.3 Hz, 2H, CH$_2$), 1.49 - 1.39 (m, 2H, CH$_2$ overlaps with OC(CH$_3$)$_3$), 1.42 (s, 9H, OC(CH$_3$)$_3$ overlaps with CH$_2$), 1.25 - 1.05 (m, 6H, (CH$_2$)$_3$ overlaps with C(CH$_3$)$_3$ of internal standard), 0.82 (t, $J$ = 7.0 Hz, 3H, CH$_3$). $^{13}$C NMR (75 MHz, C$_6$D$_6$) 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*
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.\(^{\text{xi}}\)

1-Phenyl-1-phenylthioethene

\[ \text{1H NMR (300 MHz, C}_6\text{D}_6) \delta 7.63 - 7.57 (m, 2H, ArH overlaps with E- and Z-isomers), 7.42 - 7.27 (m, 4H, ArH overlaps with ArH of internal standard and with E- and Z-isomers), 7.06 - 6.85 (m, 4H, ArH overlaps with E- and Z-isomers), 5.50 (s, 1H, C=CH\textsubscript{2}), 5.30 (s, 1H, C=CH\textsubscript{2}). \]
S6. Proposed Reaction Mechanism for Alkyne Dimerisation and Hydrothiolation promoted by 2a

![Reaction Mechanism Diagram]

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*

![bis-α,α'-vinyl sulfide](image)

**H NMR (300 MHz, C₆D₆) δ 5.20 (d, J = 1.3 Hz, 1H, C=CH₂), 4.99 (d, J = 1.4 Hz, 1H, C=CH₂), 4.72 (s, 1H, C=CH₂), 4.65 (s, 1H, C=CH₂), 2.96 (br s, 2H, CH₂N(CH₃)₂), 2.48 - 2.41 (m, 4H, (CH₂)₂), 2.20 (tt, J = 7.6 Hz, 4.5 Hz, 2H, CH₂), 2.10 (s, 6H, CH₂N(CH₃)₂), 1.58 - 1.46 (m, 6H, (CH₂)₂), 1.31 - 1.18 (m, 2H, CH₂ overlaps with C(CH₃)₃ of internal standard), 0.83 (t, J = 7.3 Hz, 3H, CH₃).**

**C NMR (75 MHz, C₆D₆) 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-$\alpha,\alpha'$-vinyl sulfide

Figure S17. $^{13}$C NMR of bis-$\alpha,\alpha'$-vinyl sulfide
**Entry 2, Table 3: Bis-Hydrothiolation of 1-hexyne and 3-hexyne with 1,6-hexanediithiol (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-hexanediithiol (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$_6$D$_6$) $\delta$ 5.34 (t, $J = 7.3$ Hz, 1H, C=CH), 5.02 (d, $J = 1.1$ Hz, 1H, C=CH$_2$), 4.70 (s, 1H, C=CH$_2$), 2.51 - 2.44 (m, 4H, (CH$_2$)$_2$), 2.23 (t, $J = 7.5$ Hz, 2H, CH$_3$), 2.21 - 2.13 (m, 2H, CH$_2$ overlaps with CH$_3$), 1.98 (t, $J = 7.5$ Hz, 2H, CH$_3$), 1.61 - 1.50 (m, 2H, CH$_3$), 1.50 - 1.40 (m, 4H, (CH$_2$)$_2$), 1.33 - 1.12 (m, 6H, (CH$_2$)$_3$ overlaps with C(CH$_3$)$_3$ of internal standard), 1.11 (t, $J = 7.5$ Hz, 3H, CH$_3$), 0.90 (t, $J = 7.5$ Hz, 3H, CH$_3$), 0.84 (t, $J = 7.2$ Hz, 3H, CH$_3$). $^{13}$C NMR (75 MHz, C$_6$D$_6$) $\delta$ 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 ($343 \, \mu$L, $2.98 \times 10^{-3}$ mol), 1,4-butanedithiol ($350 \, \mu$L, $2.98 \times 10^{-3}$ mol), catalyst 2a ($116 \, \text{mg}$, $5.97 \times 10^{-5}$ mol; 2 mol%) and internal standard 1,4-di-tert-butylbenzene ($142 \, \text{mg}$, $7.46 \times 10^{-4}$ mol, 0.25 equivalent) in 4 mL solvent $\text{C}_6\text{D}_6$. 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 ($321 \, \mu$L, $2.98 \times 10^{-3}$ 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-$\alpha,\alpha'$-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-$\alpha,\alpha'$-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 N\(^2\),N\(^1\),N\(^5\),N\(^5\)-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.

<table>
<thead>
<tr>
<th>Step 1b</th>
<th>Step 2d</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>t (h)</td>
</tr>
<tr>
<td>80</td>
<td>3</td>
</tr>
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<td></td>
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<tr>
<td>c</td>
<td>9</td>
</tr>
</tbody>
</table>

aReaction performed in 0.5 mL C₆D₆ with 1,4-di-tert-butylbenzene as internal standard, with catalyst loading 3.5 mol %.
bAlkyne homo-dimerization yielding N,N,N,N-tetramethyl-4-methylenepent-2-yne-1,5-diamine.
cConversion as determined through NMR integration based on substrate and products referenced to 1,4-di-tert-butylbenzene.
dHydrothiolation of internal alkyne of enyne formed after step 1, with 1-hexanethiol.
eNMR calculated yield.

(a) 1,3-gem-ene-β-E-vinyl-sulfide

1H NMR (300 MHz, C₆D₆) δ 6.03 (t, J = 6.8 Hz, 1H, C₅-H), 5.44 (dt, J = 1.6 Hz, 1.3 Hz, 1H, C₃-H₂), 5.06 (dt, J = 1.3 Hz, 1 Hz, 1H, C₃-H₂), 3.10 (t, J = 1.3 Hz, 2H, C₁-H₂), 3.03 (d, J = 6.8 Hz, 2H, C₆-H₂), 2.18 (s, 6H, C₁-N(CH₃)₂), 2.13 (s, 6H, C₆-N(CH₃)₂), -S-hexyl moiety (grey scaled) not assigned due to extensive overlap.

13C NMR (100 MHz, C₆D₆) δ 143.8 (C₂), 138.6 (C₄), 129.9 (C₅), 116.9 (C₃), 63.8 (C₁), 58.7 (C₆), N(CH₃)₂ not assigned due to extensive carbon overlap.
(b) 1,4-gem-ene-β-E-vinyl-sulfide

\[
\begin{align*}
{^1}H \text{ NMR (300 MHz, C}_6D_6) \delta & 6.03 (s, 1H, C4-H), 5.20 (dt, J = 1.3 \text{ Hz}, 1.2 \text{ Hz}, 1H, C3-H_2), 5.13 (d, J = 1.5 \text{ Hz}, 1H, C3-H_2), 3.35 (d, J = 1 \text{ Hz}, 2H, C6-H_2), 2.86 (br s, 2H, C1-H_2), 2.21 (s, 6H, C6-N(CH}_3}_2), 2.10 (s, 6H, C1-N(CH}_3}_2), -S\text{-hexyl moiety (grey scaled) not assigned due to extensive overlap.} \\
{^{13}}C \text{ NMR (100 MHz, C}_6D_6) \delta & 143.6 (C2), 140.4 (C5), 123.3 (C4), 115.9 (C3), 67.1 (C1), 61.2 (C6), N(CH}_3}_2 \text{ not assigned due to extensive carbon overlap.}
\end{align*}
\]

(c) 1,4-gem-ene-β-Z-vinyl-sulfide

\[
\begin{align*}
{^1}H \text{ NMR (300 MHz, C}_6D_6) \delta & 6.36 (br s, 1H, C4-H), 5.12 (d, J = 1.3 \text{ Hz}, 1H, C3-H), 5.08 (s, 1H, C3-H), 3.23 (s, 2H, C6-H), 3.00 (d, J = 1.3 \text{ Hz}, 2H, C1-H), 2.16 (s, 6H, C6-N(CH}_3}_2), 2.14 (s, 6H, C1-N(CH}_3}_2), -S\text{-hexyl moiety (grey scaled) not assigned due to extensive overlap.} \\
{^{13}}C \text{ NMR (100 MHz, C}_6D_6) \delta & 141.9 (C2), 141.7 (C5), 128.6 (C4), 110.1 (C3), 64.1 (C1), 57.9 (C6), N(CH}_3}_2 \text{ not assigned due to extensive carbon overlap.}
\end{align*}
\]
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-eneyne 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 \(\text{C}_6\text{D}_6\). 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 acetate 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-C1 2.203 (5), H1A-C1 2.446 (5).]
Crystal Data for 1a: C_{60}H_{69}N_{7}ClF_{6}P (M =1068.64 g/mol): monoclinic, space group P2_1/c (no. 14), \(a = 16.2214(4) \text{ Å} \), \(b = 24.0518(5) \text{ Å} \), \(c = 15.2494(3) \text{ Å} \), \(\beta = 108.8560(9)^{\circ} \), \(V = 5630.3(2) \text{ Å}^3 \), \(Z = 4 \), \(T = 150.15 \text{ K} \), \(\mu(\text{CuK}^{\alpha}) = 1.404 \text{ mm}^{-1} \), \(D_{\text{calc}} = 1.261 \text{ g/cm}^3 \), 198184 reflections measured (5.756° \(\leq 2\Theta \leq 144.494^{\circ} \)), 11093 unique (\(R_{\text{int}} = 0.0378 \), \(R_{\sigma} = 0.0120 \)) which were used in all calculations. The final \(R_1 \) was 0.0430 (\(I > 2\sigma(I) \)) 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 (°): 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_{7}O_{2}Rh (M =1182.37 g/mol): triclinic, space group P-1 (no. 2), \(a = 10.8323(5) \text{ Å} \), \(b = 15.4988(8) \text{ Å} \), \(c = 24.8410(13) \text{ Å} \), \(\alpha = 103.4480(14)^{\circ} \), \(\beta = 97.0590(13)^{\circ} \), \(\gamma = 107.0370(13)^{\circ} \), \(V = 3795.4(3) \text{ Å}^3 \), \(Z = 2 \), \(T = 150.15 \text{ K} \), \(\mu(\text{MoK}^{\alpha}) = 0.267 \text{ mm}^{-1} \), \(D_{\text{calc}} = 1.035 \text{ g/cm}^3 \), 84650 reflections measured (4.428° \(\leq 2\Theta \leq 51.56^{\circ} \)), 14487 unique (\(R_{\text{int}} = 0.1099 \), \(R_{\sigma} = 0.0978 \)) which were used in all calculations. The final \(R_1 \) was 0.0610 (\(I > 2\sigma(I) \)) and \(wR_2 \) was 0.1727 (all data).

S12. References