Supporting information

Catalytic Conversion of Alkynes to α-Vinyl Sulfides Mediated by Carbene-linker-carbene (CXC) Rhodium and Iridium Complexes

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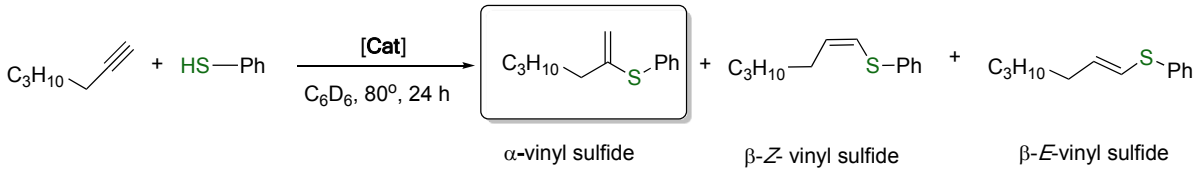
S1. General Methods

All synthetic manipulations, unless otherwise stated, were performed under a N_2 (g) of Ar (g) atmosphere using oven or flame dried glassware and standard Schlenk or vacuum line techniques. Air sensitive solids were stored and handled in an Inert Lab globe box. Preparation of NMR samples that required an inert atmosphere were performed in a glove box. Metal complexes **1a** [Rh(cod)(**COC**)](PF_6), **1b** [Rh(CO)$_2$(**COC**)](PF_6), **2a** [$Rh_2Cl_2(cod)_2$(μ-**COC**)], **2b** [$Rh_2Cl_2(CO)_4$(μ-**COC**)], **3** [Rh(CO)(**C^{H}NC**)] (PF_6), **4a** [$Rh_2(cod)_2$(μ-**CNC**)](PF_6), **4b** [$Rh_2(CO)_4$(μ-**CNC**)](PF_6), **5** [$Rh_2Cl(CO)_3$(μ-**CNC**)], **6a** [Ir(cod)(**COC**)](PF_6), **6b** [Ir(CO)$_2$(**COC**)](PF_6), **7a** [$Ir_2Cl_2(cod)_2$(μ-**CNC**)], **7b** [$Ir_2(CO)_4$(μ-**CNC**)], **8a** [Ir(cod)(H**CNC**)](PF_6) and **8b** [Ir(CO)$_2$(H**CNC**)](PF_6) were synthesized as previously reported.[1] All other reagents were obtained from commercial sources and were used without any further purification. Deuterated benzene was dried over sodium under an Ar (g) atmosphere.

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; or AVANCE-III-500 operating at 500.13 MHz for ^{1}H, 125.31 MHz for ^{13}C, 202.46 MHz for ^{31}P and 470.59 MHz for ^{19}F. ^{1}H Chemical shifts are reported as δ (ppm) values downfield from Me_4Si and chemical shifts were referenced to residual non-deuterated solvent peaks (C_6D_6: 7.160 ppm). Proton coupling constants (*J*) are given in Hz. The spectral coupling patterns are designated as follows: s - singlet; d - doublet; t - triplet; q- quartet; quint – quintet; sept - septet; m - multiplet; dd- doublet of doublets; dt – doublet of triplets; td – triplet of doublets; br - broad signal.

Chemical shift assignment in the ^{1}H NMR spectra is based on first-order analysis experiments. Standard Bruker pulse programs (298 K) were used in all experiments.

S2. Catalytic Studies



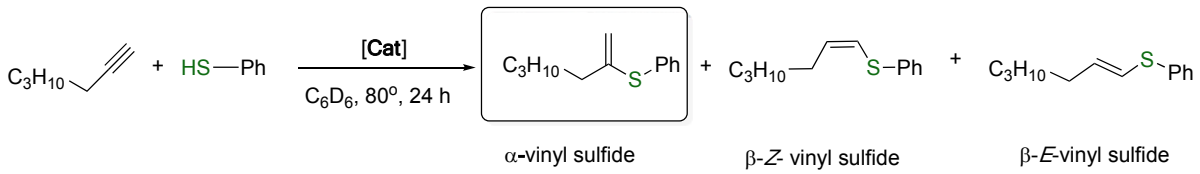
Scheme S1. Schematic representation of the hydrothiolation reaction of 1- hexyne with thiophenol to afford the corresponding α -vinyl sulfide product $C_4H_{12}C(SPh)=CH_2$.

The hydrothiolation of 1-hexyne with thiophenol was performed in duplicate and the average yields and conversion reported. A high pressure NMR tube fitted with a J. Young valve was loaded with 1 mol% catalyst (3.5 x 10^{-6} mol) for monometallic complexes **1a-b**, **3**, **6a-b**, **8a-b** or 0.5 mol% catalyst (1.75 x 10^{-6} mol) for dimetallic complexes **2a-b, 4a-b**, **5**, **7a-b**, substrates (one equiv. of alkyne (3.5 x 10^{-4} mol), one equiv. of the corresponding thiol (3.5 x 10^{-4} mol), and internal standard (0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). The reaction mixture was heated to 80ºC for 24 hours. After this period, ^{1}H NMR spectroscopy of the reaction mixture was performed. Conversion and yields of the α, β-*Z* and β-*E*-vinyl sulfide products were determined by NMR integration based on the alkyne and thiol substrates a t = 0, referenced to the internal standard (1,4-di-*tert*-butylbenzene). Product identity was confirmed by comparison with previously reported NMR data in the literature[2], expect for the reaction products of table 3, entries 2, 8 and 10. ^{1}H NMR data of these new vinyl sulfide products are given in Schemes **S2**, **S8** and **10** and Figures **S3**, **S15** and **S19**.

S2.2 Reaction optimization conditions for catalyst 1a [Rh(cod)(COC)](PF$_6$) and 2a [Rh$_2$Cl$_2$(cod)$_2$ (μ-COC)].

The model reaction performed was the hydrothiolation of 1-hexyne (1 equiv.) with thiophenol (1 equiv.) promoted by either complex **1a** [Rh(cod)(**COC**)](PF$_6$) or complex **2a** [Rh$_2$Cl$_2$(cod)$_2$(μ-**COC**)]. Two conditions that were varied for the optimization: 1) a lower temperature (40°C) and 2) a shorter reaction time (12h).

Table S1: Optimization results of the model hydrothiolation reaction catalyzed by the two top performing catalysts **1a** [Rh(cod)(**COC**)](PF_6) and **2a** [$Rh_2Cl_2(cod)_2$(μ-**COC**)].



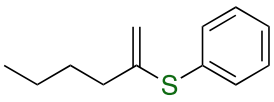
Entry	Catalyst	Cat load (mol%).	Time (h)	Temp (°C)	Conv. (%)	Prod. Distribution (%)		
						α	β-*Z*	β-*E*
1	**1a**	1	24	40	19	88	6	6
2	**2a**	0.5	24	40	15	89	6	6
3	**1a**	1	12	80	68	97	1	1
4	**2a**	0.5	12	80	72	91	6	3
5	**1a**	1	24	80	68	96	2	2
6	**2a**	1	24	80	88	92	3	5
7	**2a**	0.5	24	80	76	96	2	2

Reactions performed in C_6D_6 (0.5 mL) with 1,4-di-*tert*-butylbenzene as internal standard, 1 mol% catalyst (3.5 x 10^{-6} mol) for mononuclear catalyst **1a** [Rh(cod)(**COC**)](PF_6) and 0.5 mol% catalyst (1.75 x 10^{-6} mol) for binuclear catalyst **2a** [$Rh_2Cl_2(cod)_2$(μ-**COC**)]. Conversion and yields of the α, β-*Z* and β-*E*-vinyl sulfide products were determined as the average of duplicate runs as determined from NMR integration based on 1-hexyne and thiophenol ≡─H average referenced to 1,4-di-*tert*-butylbenzene.

S2.3 Catalytic hydrothiolation of 1-hexyne with thiophenol (Table 3, entry 1).

The hydrothiolation of 1-hexyne with thiophenol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst (2.30 mg, 1.75 x 10^{-6} mol) of **2a** [$Rh_2Cl_2(cod)_2$(μ-**COC**)], one equiv. of 1-hexyne (40.21 μL, 3.5 x 10^{-4} mol), one equiv. of the thiophenol (35.94 μL, 3.5 x 10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion: 87%, Yield: 85%, Product distribution (α/β-*Z*/β-*E*: 95/2/2).

Major product: 2-Phenylthio-1-hexene [2]



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.42 (dd, 2H, *J* = 8.4 Hz, *J* = 8.0 Hz, Ph-$\mathbf{H}_{Ortho}$), 7.00 (dd, 3H, *J* = 8.5 Hz, *J* = 7.5 Hz, Ph-$\mathbf{H}_{Meta\&Para}$), 5.06 (s, 1H, C=C$\mathbf{H}_2$), 4.97 (s, 1H, C=C$\mathbf{H}_2$), 2.20 (t, 2H, *J*= 8.0 Hz, H_2C=C(C$\mathbf{H}_2$)), 1.51 (pent, 2H, *J*= 7.5 Hz, H_2C=C(C$\mathbf{H}_2$)^2), 1.20 (hept, 2H, *J*= 7.4 Hz, H_2C=C(C$\mathbf{H}_2$)^3), 0.80 (t, 3H: overlaps with CH_3 from remaining 1-hexyne, *J* = 7.4 Hz, C$\mathbf{H}_3$) X(C$\mathbf{H}_2$)$_n$: where n refers to the position of the CH_2 in the hydrocarbon chain bound to X.

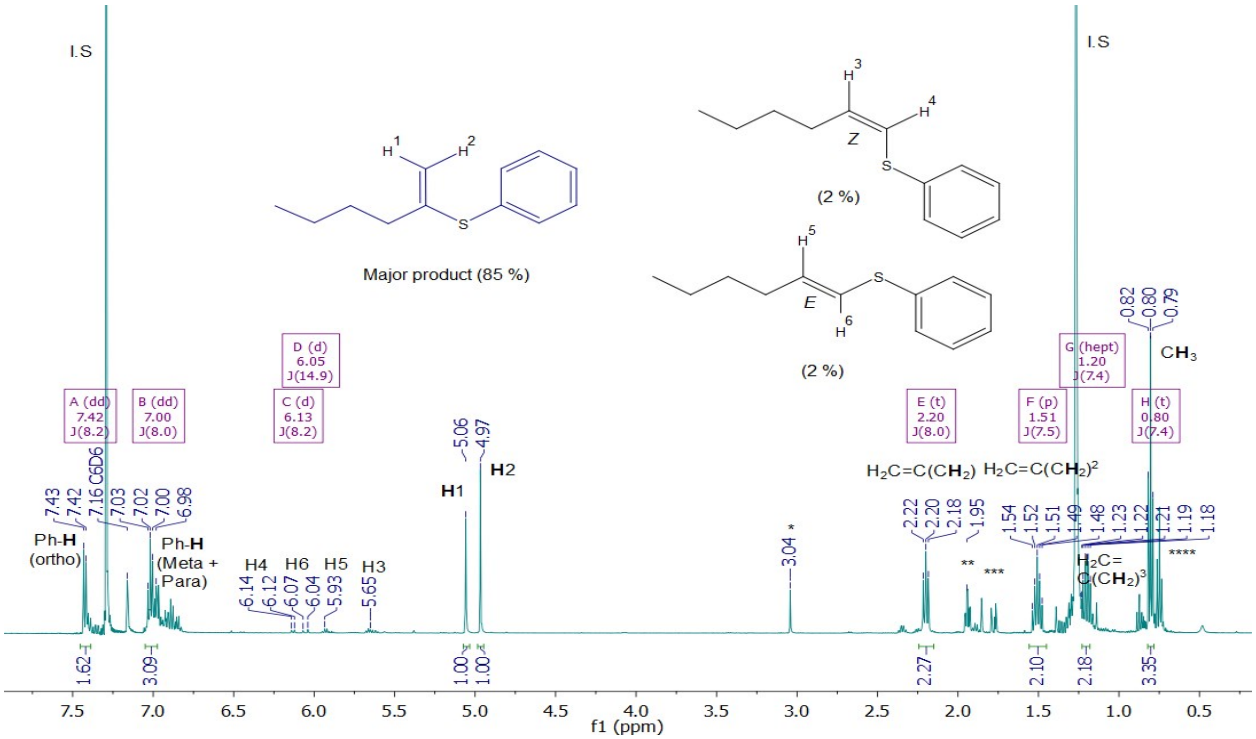


Figure S1: ^{1}H NMR of entry 1 (Table 3) after 24 h. at 80°C in C_6D_6.
Remaining substrates: 1-Hexyne: HC≡CC$\mathbf{H}_2$ **, C$\mathbf{H}$*** and C$\mathbf{H}_3$****; Thiophenol: S$\mathbf{H}$*

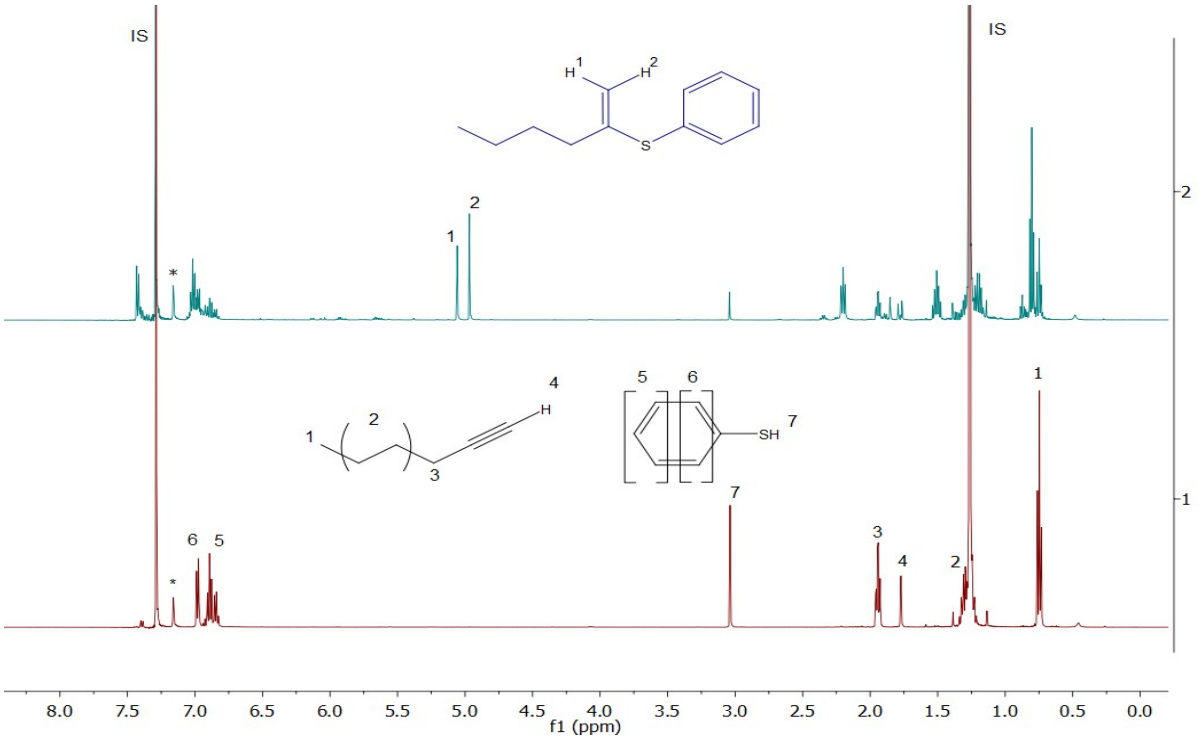
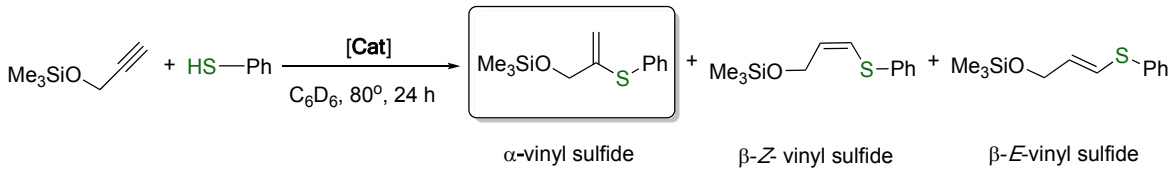


Figure S2: Overlaid ^{1}H NMR spectra of entry 1 (Table 3) in $*C_6D_6$.
Bottom: ^{1}H NMR spectrum of substrates at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

S2.4 Catalytic hydrothiolation of trimethyl(prop-2-yn-1-yloxy)silane with thiophenol (Table 3, entry 2).

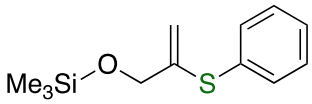


Scheme S2: Schematic representation of the hydrothiolation reaction between trimethyl(prop-2-yn-1-yloxy)silane with thiophenol to afford the corresponding α-vinyl sulfide product $Me_3SiOCH_2C(SPh)=CH_2$.

The hydrothiolation of trimethyl(prop-2-yn-1-yloxy)silane with thiophenol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follow: 0.5 mol% catalyst **2a** $[Rh_2Cl_2(cod)_2(\mu\text{-}\mathbf{COC})]$ (2.30 mg, 1.75 x 10^{-6} mol), one equiv. of 3-TMSO-1-propyne (53.75 µL, 3.5 x10^{-4} mol), one equiv. of thiophenol

(35.94 µL, 3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion: 83%, Yield: 70%, Product distribution (α/β-*Z*/β-*E*: 83/8/8).

Major product: trimethyl((2-(phenylthio)allyl)oxy)silane



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.37 (dd, 2H, *J* = 8.5 Hz, *J* = 8.1 Hz, Ph-**H**$_{Ortho}$), 6.98 (m, 3H, Ph-**H**$_{Meta\&Para}$), 5.73 (s, 1H, C=C**H**$_2$), 5.34 (s, 1H, C=C**H**$_2$), 4.18 (s, 2H, OC**H**$_2$), 0.11 (s, 3H, Si-C**H**$_3$), 0.08 (s, 3H, Si-C**H**$_3$), 0.02 (s, 3H: overlaps with CH_3 from remaining 3-TMSO-1-propyne, Si-C**H**$_3$).

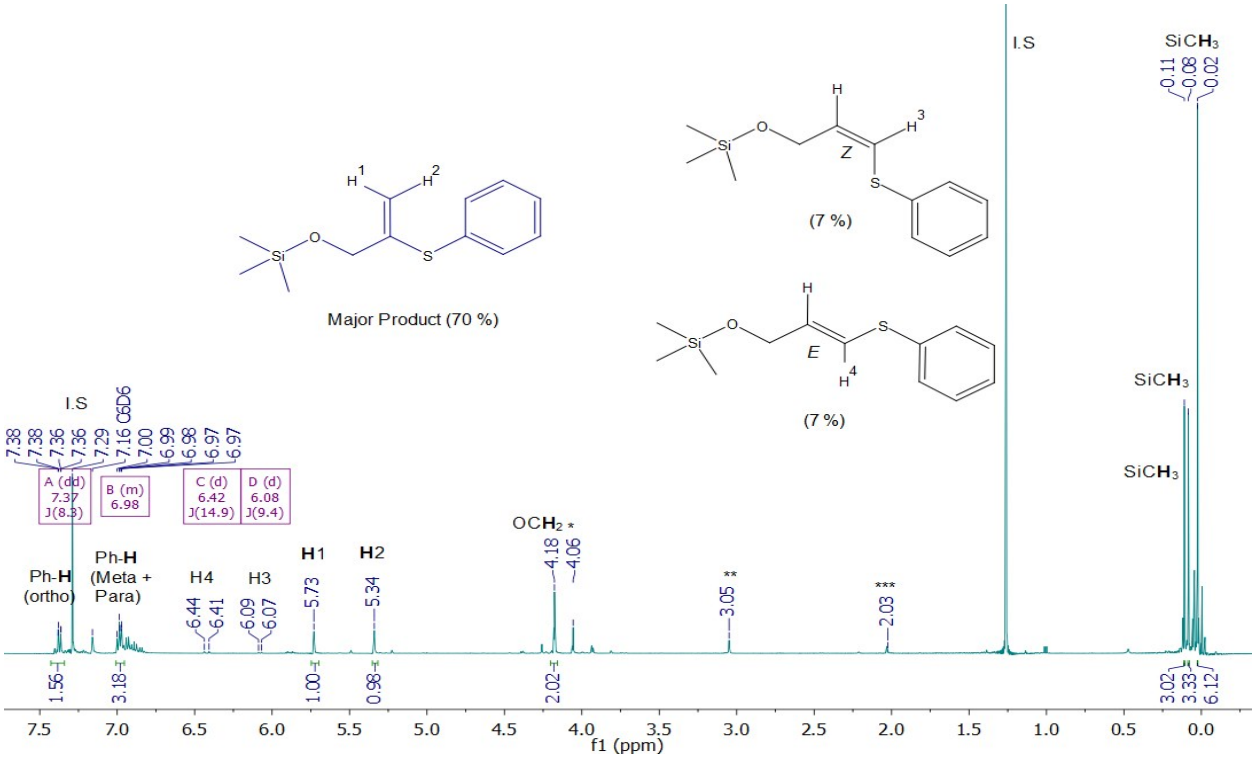


Figure S3: ^{1}H NMR of entry 2 (Table 3) after 24 h. at 80°C in C_6D_6.
Remaining substrates: 3-TMSO-1-propyne: OC**H**$_2$ * and C**H*****; Thiophenol: S**H****

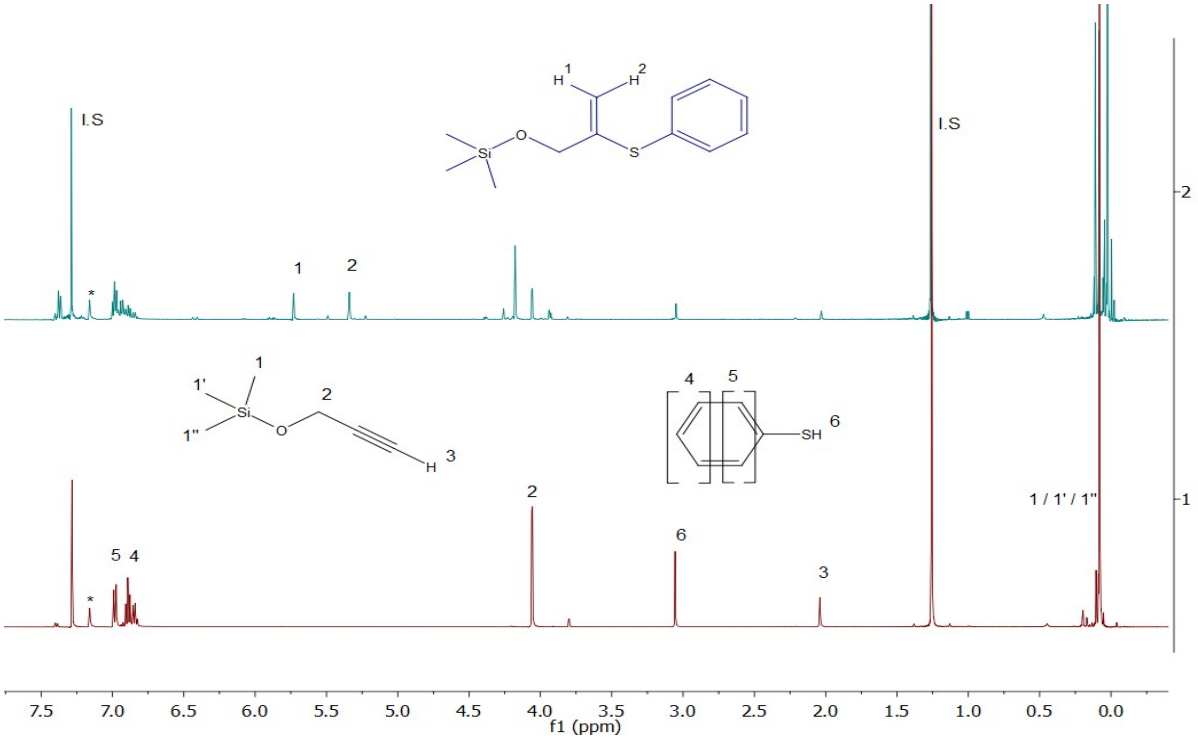
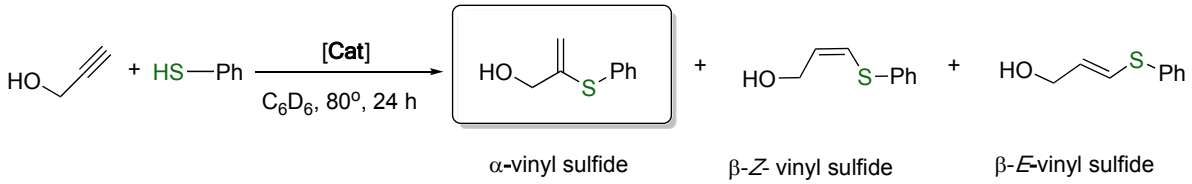


Figure S4: Overlaid ^{1}H NMR spectra of entry 2 (Table 3) in *C_6D_6.
Bottom: ^{1}H NMR spectrum of substrates at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

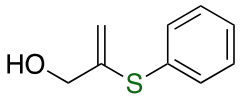
S2.5 Catalytic hydrothiolation of propargyl alcohol with thiophenol (Table 3, entry 3).



Scheme S3: Schematic representation of the hydrothiolation reaction between propargyl alcohol with thiophenol to afford the corresponding α-vinyl sulfide product $HOCH_2C(SPh)=CH_2$.

The hydrothiolation of propargyl alcohol with thiophenol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst **2a** $[Rh_2(cod)_2Cl_2(\mu\text{-}\mathbf{COC})]$ (2.30 mg, 1.75 x 10^{-6} mol), one equiv. of propargyl alcohol (20.37 µL, 3.5 x10^{-4} mol), one equiv. of thiophenol (35.94 µL, 3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion: 93%, Yield: 76%, Product distribution (α/β-*Z*/β-*E*: 90/5/5).

Major Product: 1-(phenylthio)-ethenol [4]



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.34 (dd, 2H, J = 8.3 Hz, J = 8.3 Hz, Ph-**H**$_{Ortho}$), 6.98 (m, 3H, Ph-**H**$_{Meta\&Para}$), 5.50 (s, 1H, C=C**H**$_2$), 5.23 (s, 1H, C=C**H**$_2$), 3.97 (s, 2H, OC**H**$_2$), 2.10 (br s, 1H, O**H**)

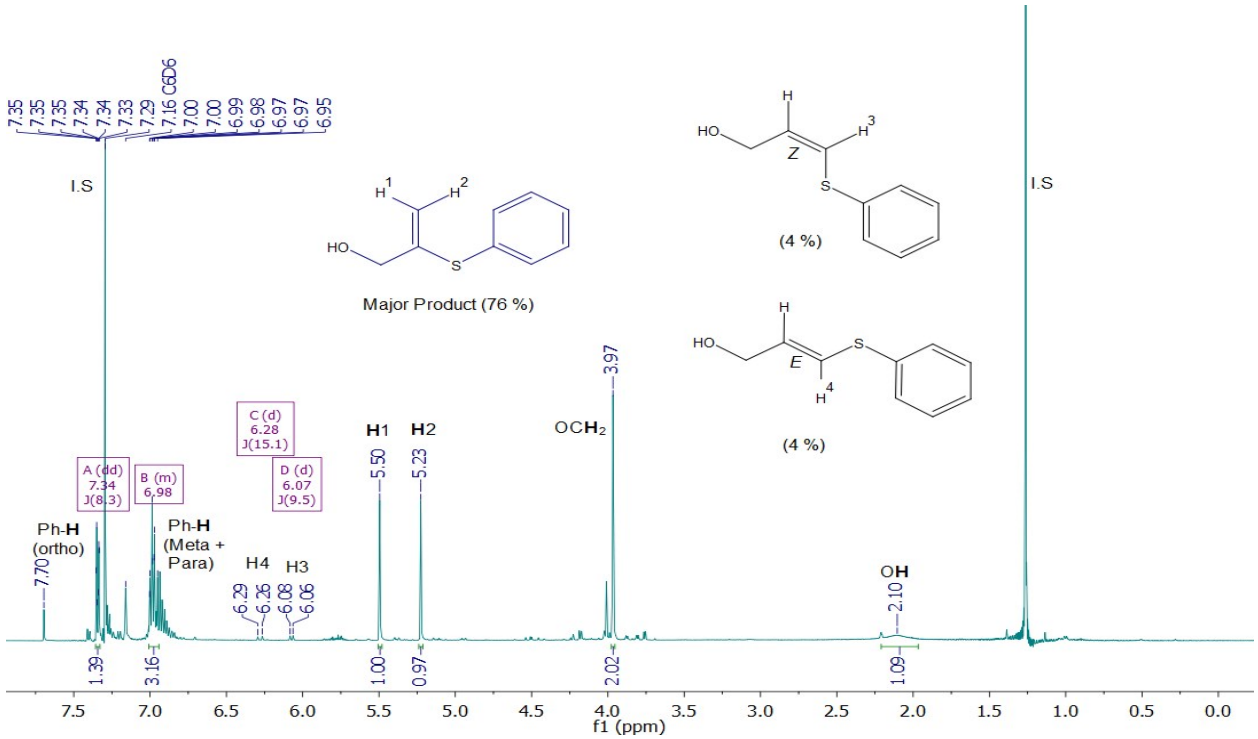


Figure S5: ^{1}H NMR of entry 3 (Table 3) after 24 h. at 80°C in C_6D_6.

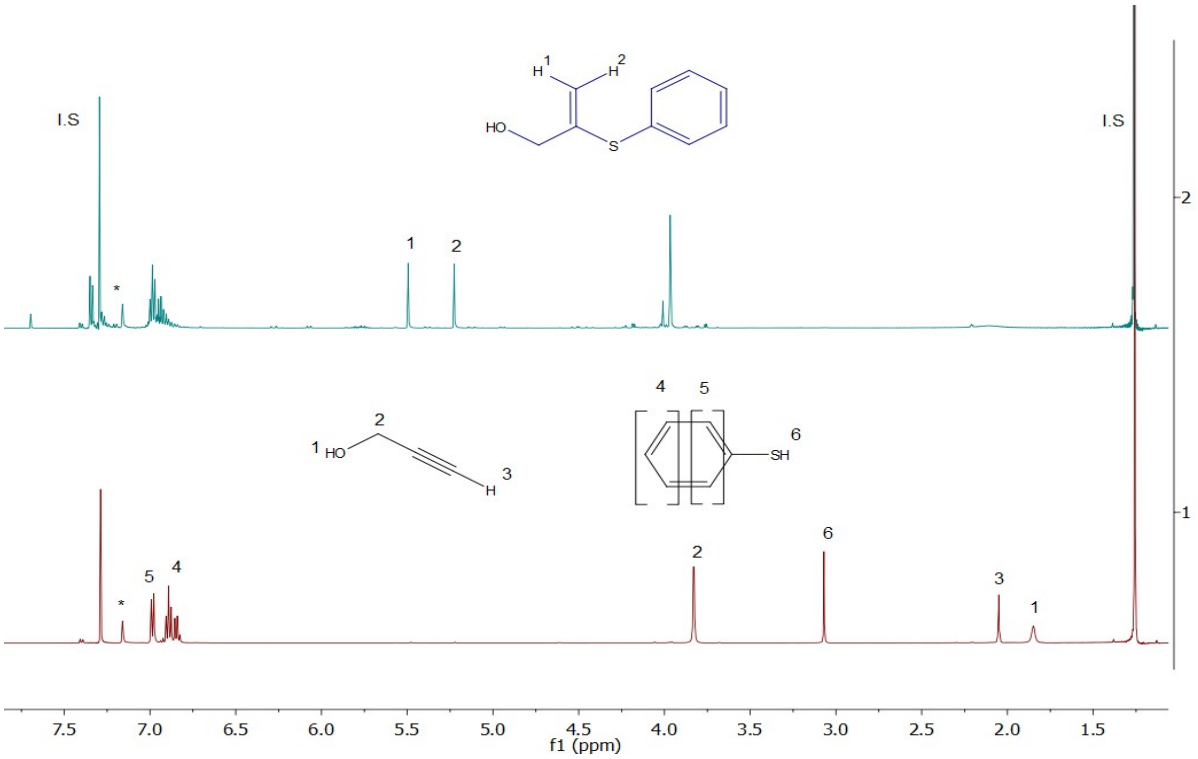
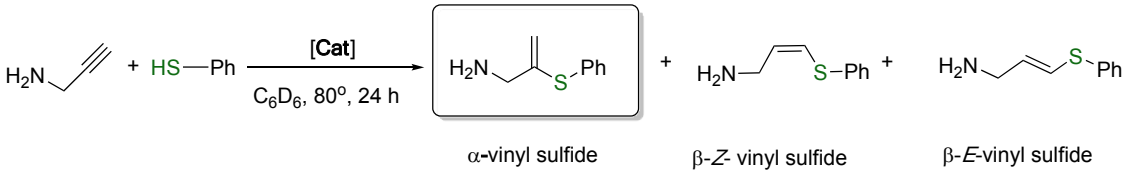


Figure S6: Overlaid ^{1}H NMR spectra of entry 3 (Table 3) in *C_6D_6.
Bottom: ^{1}H NMR spectrum of substrates at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

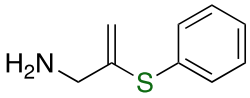
S2.6 Catalytic hydrothiolation of propargylamine with thiophenol (Table 3, entry 4).



Scheme S4: Schematic representation of the hydrothiolation reaction between propargylamine with thiophenol to afford the corresponding α-vinyl sulfide product $NH_2CH_2C(SPh)=CH_2$.

The hydrothiolation of propargylamine with thiophenol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst **2a** $[Rh_2Cl_2(cod)_2(\mu\text{-}\mathbf{COC})]$ (2.30 mg, 1.75 x 10^{-6} mol), one equiv. of propargylamine (22.42 µL, 3.5 x10^{-4} mol), one equiv. of thiophenol (35.94 µL, 3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion: 82%, Yield: 76%, Product distribution (α/β-*Z*/β-*E*: 92/6/1).

Major Product: 2-(phenylthio)prop-2-en-1-amine [3]



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.36 (dd, 2H, *J* = 8.2 Hz, *J* = 8.2 Hz, Ph-**H**$_{Ortho}$), 6.99 (m, 3H, Ph-**H**$_{Meta\&Para}$), 5.25 (s, 1H, C=C**H**$_2$), 5.08 (s, 1H, C=C**H**$_2$), 3.20 (s, 2H, NC**H**$_2$), 1.10 (br s, 2H: overlaps with NH_2 from remaining propargylamine, N**H**$_2$)

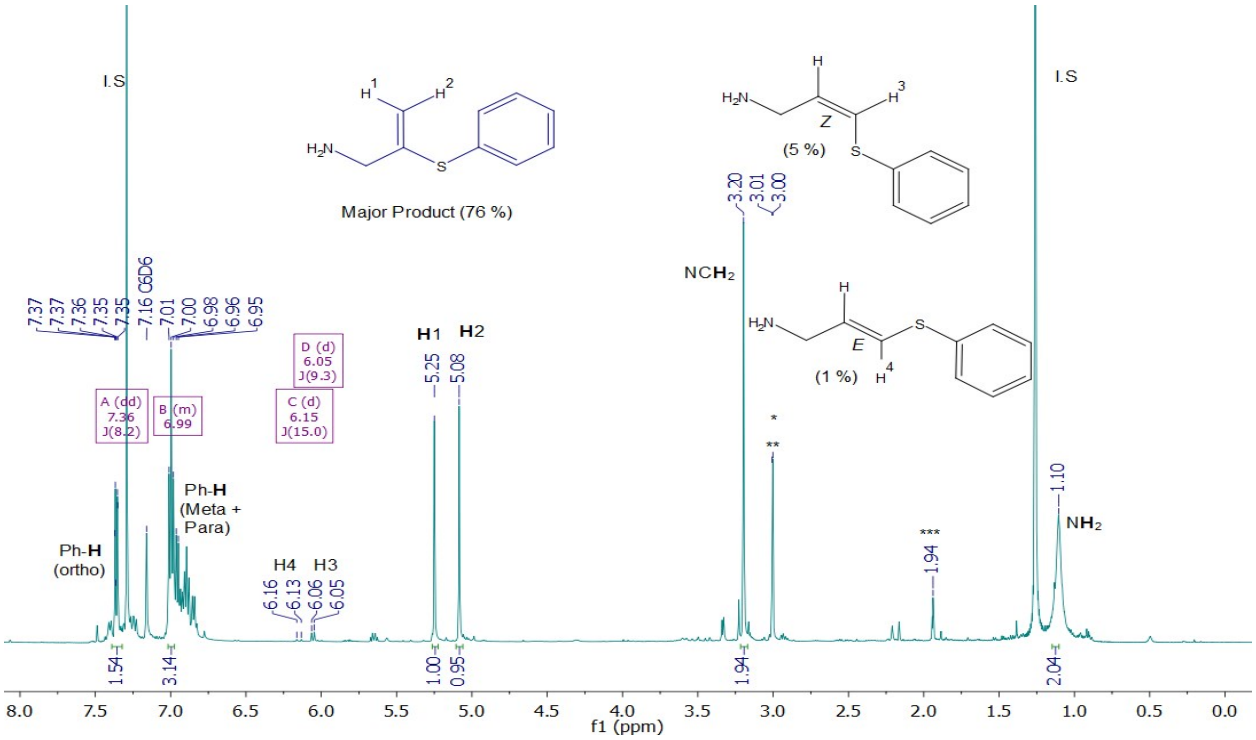


Figure S7: ^{1}H NMR of entry 5 (Table 3) after 24 h. at 80°C in C_6D_6.
Remaining substrates: Propargylamine: NC**H**$_2$ * and C**H*****; Thiophenol: S**H** **

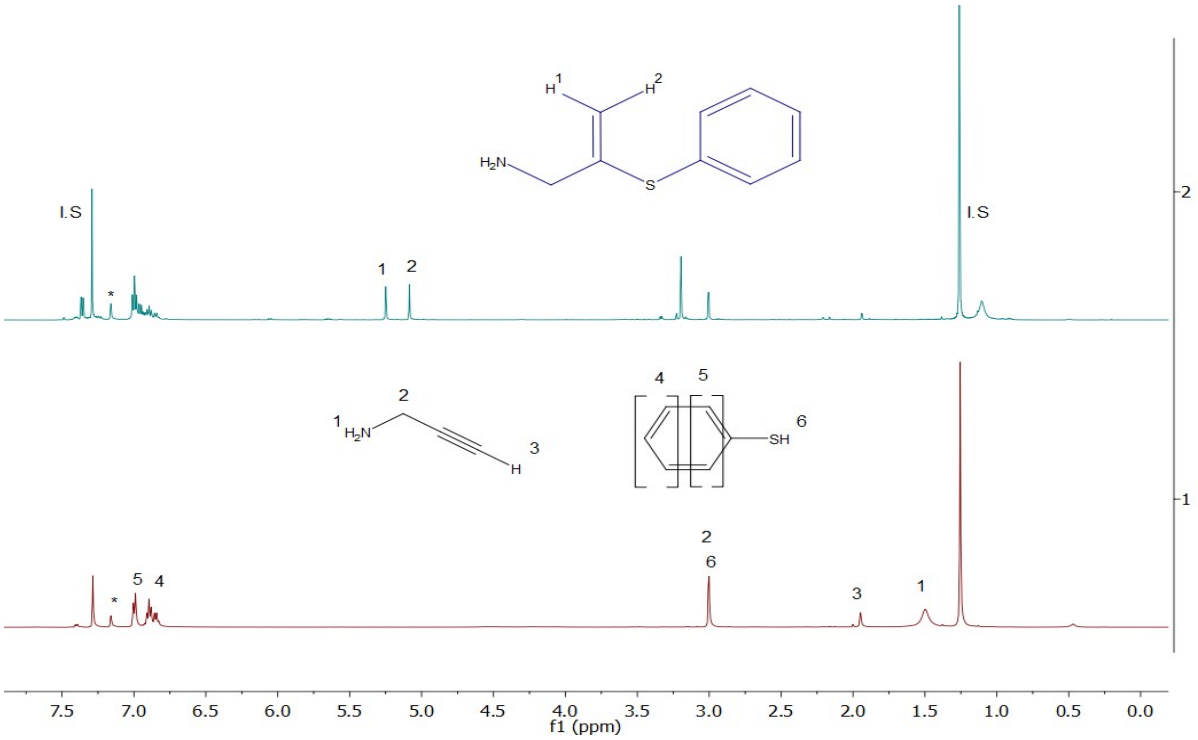
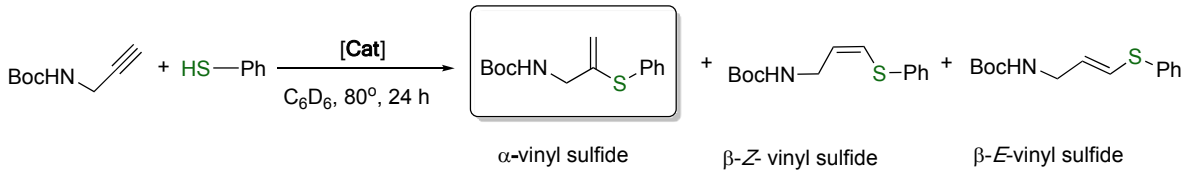


Figure S8: Overlaid ^{1}H NMR spectra of entry 5 (Table 3) in *C_6D_6.
Bottom: ^{1}H NMR spectrum of substrates at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

S2.7 Catalytic hydrothiolation of N-Boc propargylamine with thiophenol (Table 3, entry 5).

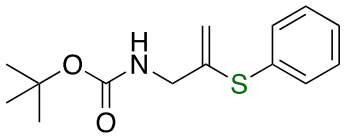


Scheme S5: Schematic representation of the hydrothiolation reaction between N-Boc propargylamine with thiophenol to afford the corresponding α-vinyl sulfide product $BocNHCH_2C(SPh)=CH_2$.

The hydrothiolation of N-Boc propargylamine with thiophenol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst **2a** $[Rh_2Cl_2(cod)_2(\mu\text{-}\mathbf{COC})]$ (2.30 mg, 1.75 x 10^{-6} mol), one equiv. of N-Boc propargylamine (54.28 mg, 3.5 x10^{-4} mol), one equiv. of thiophenol (35.94 µL,

3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion: 90%, Yield: 78%, Product distribution (α/β-*Z*/β-*E*: 94/0/6).

Major Product: *tert*-butyl (2-(phenylthio)allyl)carbamate [3]



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.34 (d, 2H, *J* = 7.5 Hz, Ph-**H**$_{Ortho}$), 7.00 (t, 3H, *J*= 7.3 Hz, Ph-**H**$_{Meta\&Para}$), 5.28 (s, 1H, C=C**H**$_2$), 5.11 (s, 1H, C=C**H**$_2$), 4.61 (br s, 1H, N**H**), 3.74 (d, 2H, *J*= 5.8 Hz, N-C**H**$_2$), 1.40 (s, 9H: overlaps with OC(C**H**$_3$)$_3$ from remaining N-Boc Propargylamine, OC(C**H**$_3$)$_3$).

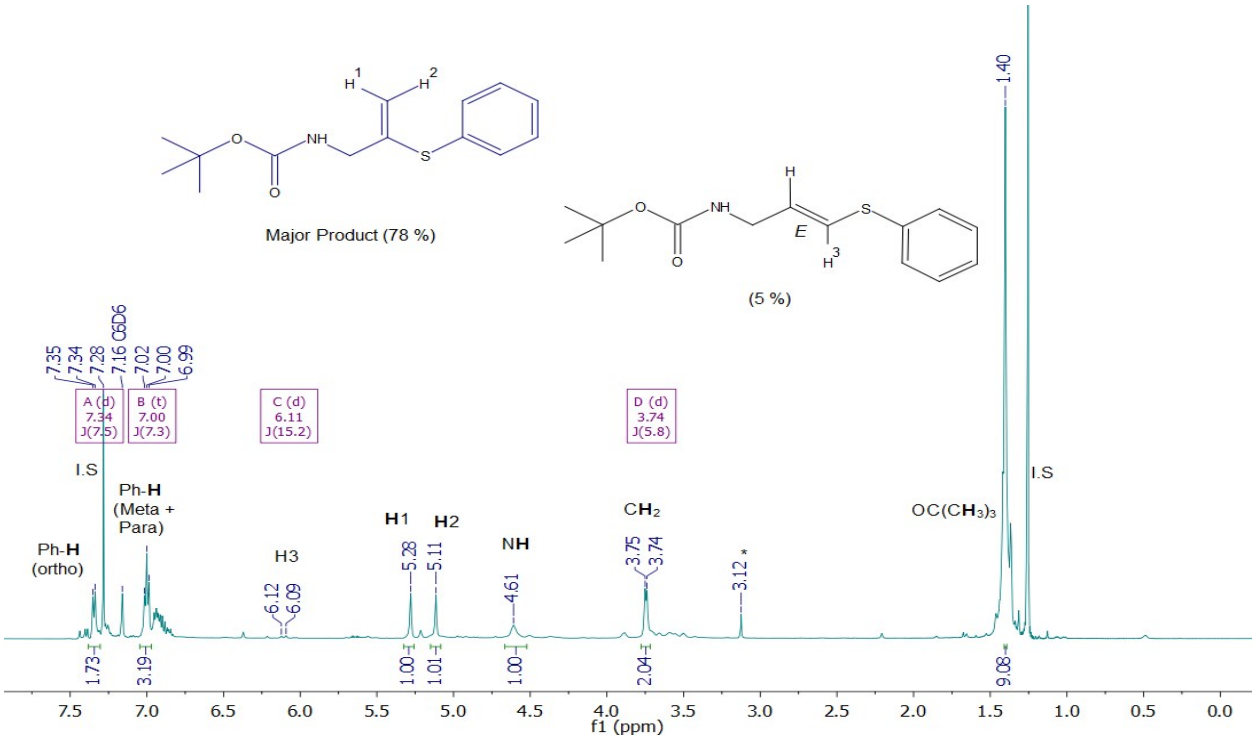


Figure S9: ^{1}H NMR of entry 6 (Table 3) after 24 h. at 80°C in C_6D_6.
Remaining substrates: Thiophenol: S**H** *

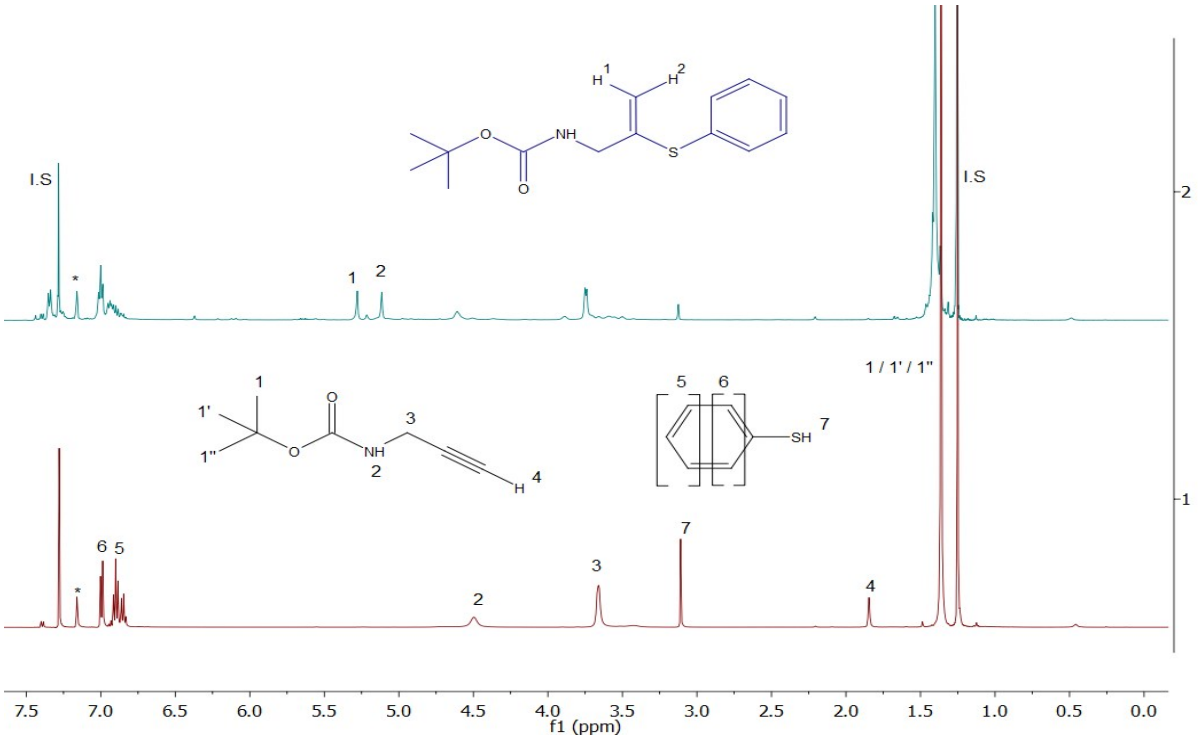
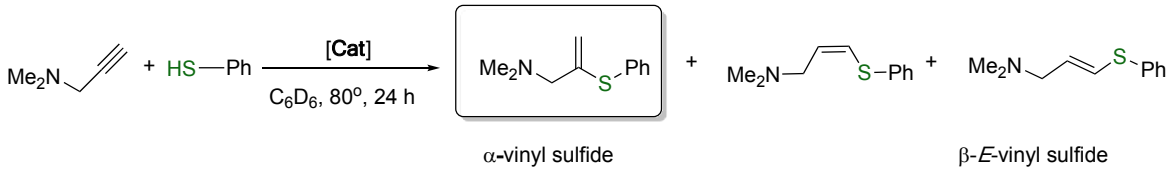


Figure S10: Overlaid ^{1}H NMR spectra of entry 6 (Table 3) in *C_6D_6.
Bottom: ^{1}H NMR spectrum at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

S2.8 Catalytic hydrothiolation of *N*,*N*-dimethylpropargylamine with thiophenol (Table 3, entry 6).

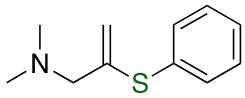


Scheme S6: Schematic representation of the hydrothiolation reaction between *N*,*N*-dimethylpropargylamine with thiophenol to afford the corresponding α-vinyl sulfide product $Me_2NCH_2C(SPh)=CH_2$.

The hydrothiolation of *N*,*N*-dimethylpropargylamine with thiophenol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst **2a** $[Rh_2Cl_2(cod)_2(\mu\text{-}\mathbf{COC})]$ (2.30 mg, 1.75 x 10^{-6} mol), one equiv. of *N*,*N*-dimethylpropargylamine (37.69 µL, 3.5 x10^{-4} mol), one equiv. of

thiophenol (35.94 µL, 3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion 77%, Yield: 60%, Product distribution (α/β-*Z*/β-*E*: >99/0/0).

Major Product: *N*,*N*-dimethyl-2-(phenylthio)-2-propen-1-amine [3,4]



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.48 (dd, 2H, *J* = 8.2 Hz, *J* = 8.2 Hz, Ph-**H**$_{Ortho}$), 6.99 (m, 3H, Ph-**H**$_{Meta\&Para}$), 5.27 (s, 1H, C=C**H**$_2$), 4.89 (s, 1H, C=C**H**$_2$), 2.98 (s, 2H, NC**H**$_2$), 2.09 (s, 6H, N(C**H**$_3$)$_2$).

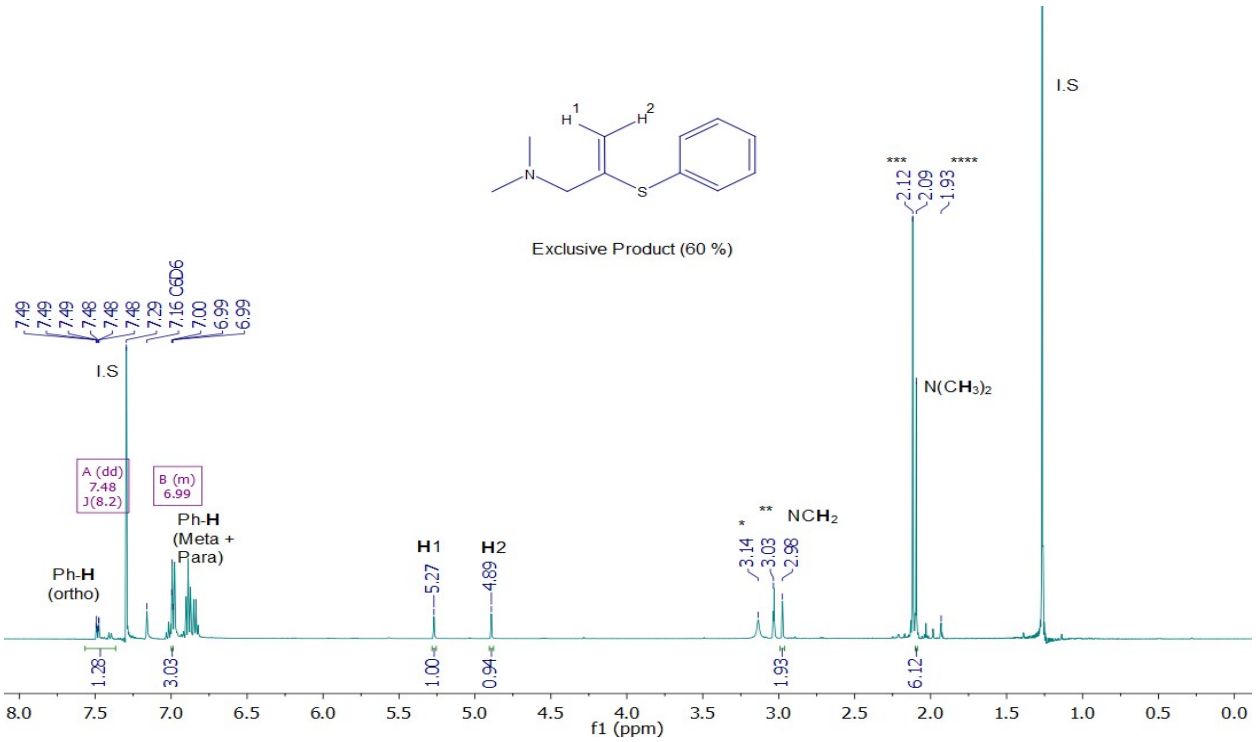


Figure S11: ^{1}H NMR of entry 7 (Table 3) after 24 h. at 80°C in C_6D_6.
Remaining substrates: *N*,*N*-Dimethylpropargylamine: C**H**$_2$**, N(C**H**$_3$)$_2$*** and C**H****; Thiophenol: S**H***

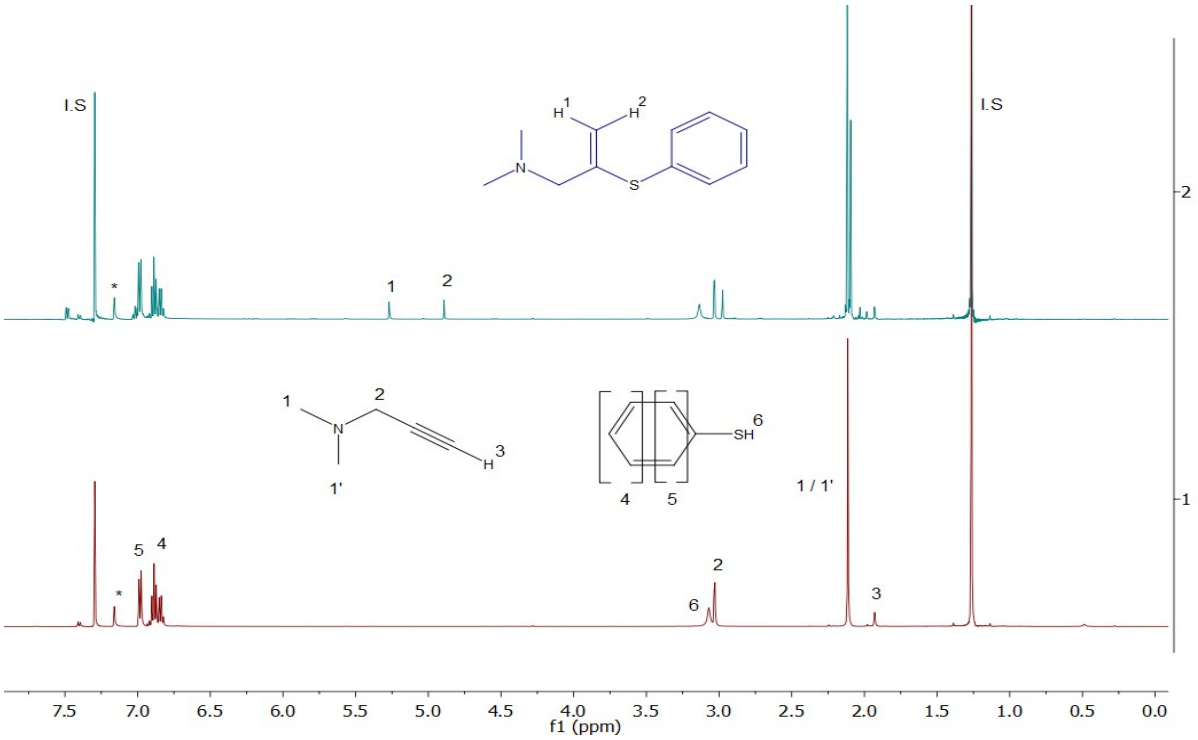
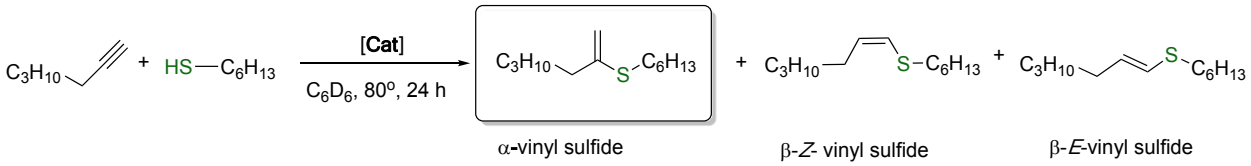


Figure S12: Overlaid ^{1}H NMR spectra of entry 7 (Table 3) in *C_6D_6.
Bottom: ^{1}H NMR spectrum at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

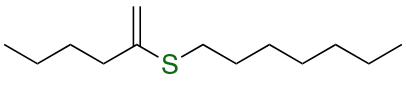
S2.9 Catalytic hydrothiolation of 1-hexyne with 1-hexanethiol (Table 3, entry 7).



Scheme S7: Schematic representation of the hydrothiolation reaction between 1-hexyne with 1-hexanethiol to afford the corresponding α-vinyl sulfide product $C_4H_{12}C(SC_6H_{13})=CH_2$.

The hydrothiolation of 1-hexyne with 1-hexanethiol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst **2a** [$Rh_2Cl_2(cod)_2(\mu$-**COC**)] (2.30 mg, 1.75 x 10^{-6} mol), one equiv. 1-hexyne (40.21 µL, 3.5 x10^{-4} mol), one equiv. of 1-hexanethiol (43.06 µL, 3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion 80%, Yield: 70%, Product distribution (α/β-*Z*/β-*E*: 88/6/6).

Major Product: 2-(heptylthio)-1-hexene



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 5.02 (s, 1H, C=C**H**$_2$), 4.71 (s, 1H, C=C**H**$_2$), 2.54 (t, 2H, *J*= 7.4 Hz, S-C**H**$_2$), 2.24 (t, 2H, *J*= 8.0 Hz, H_2=CC**H**$_2$), 1.54 (tt, 6H, *J* = 7.5 Hz, *J* = 7.5 Hz, *J* = 7.8 Hz, S(C**H**$_2$)$^{2-4}$), 1.34 (m, 2H, S(C**H**$_2$)^5), 0.86 – 0.82 (m, 7H: overlaps with CH_3 of remaining 1-hexanethiol, H_2=C(C**H**$_2$)$^{2-3}$ & S(CH$_2$)$^{1-5}$C**H**$_3$), 0.75 (t, 3H, *J* = 7.2 Hz, overlaps with CH_3 from remaining 1-hexyne, H_2C=C(CH$_2$)$^{1-3}$C**H**$_3$). Note: (X(C**H**$_2$)^n : where n refers to the position of the CH_2 in the hydrocarbon chain bound to X.

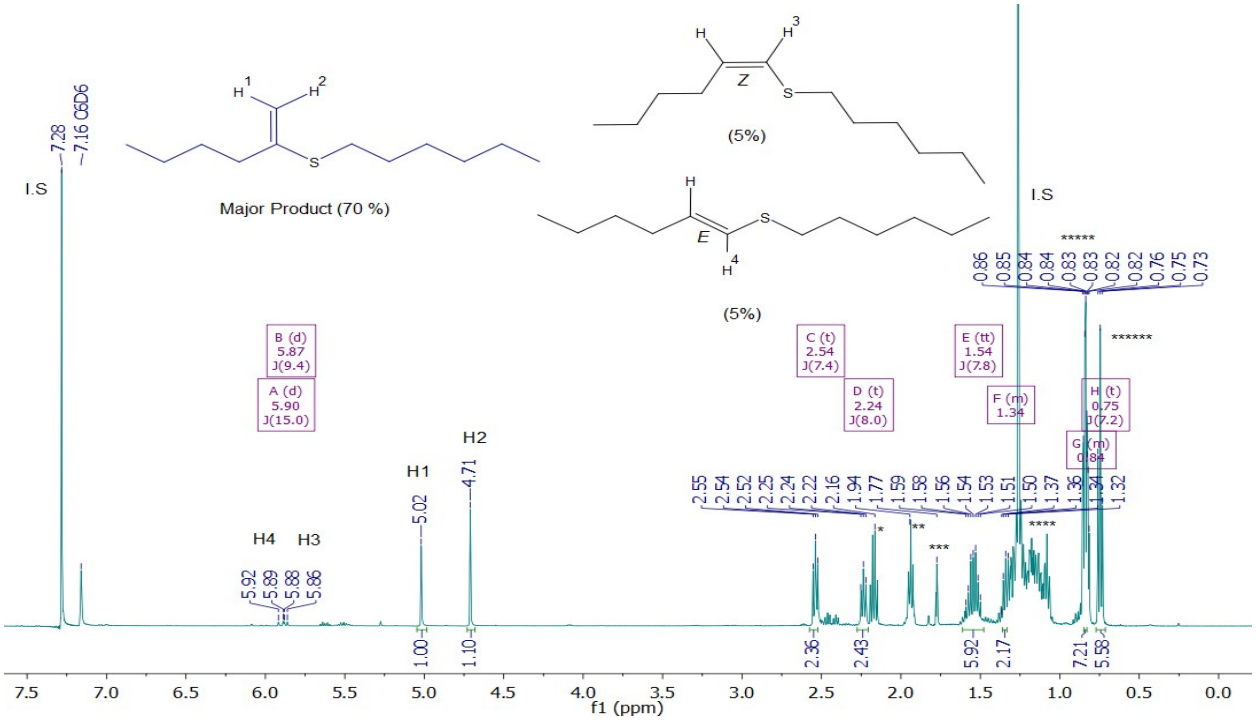


Figure S13: ^{1}H NMR of entry 8 (Table 3) after 24 h. at 80°C in C_6D_6.
Remaining substrates: 1-hexyne: C**H**$_2$ -C≡H **, C**H*****, (C**H**$_2$)$_2$ ****** and C**H**$_3$ ********; 1-hexanethiol: HS-C**H**$_2$*, CH$_3$(C**H**$_2$)$_3$, CH$_3$(CH$_2$)$_3$C**H**$_2$, S**H** ****** and C**H**$_3$ *********

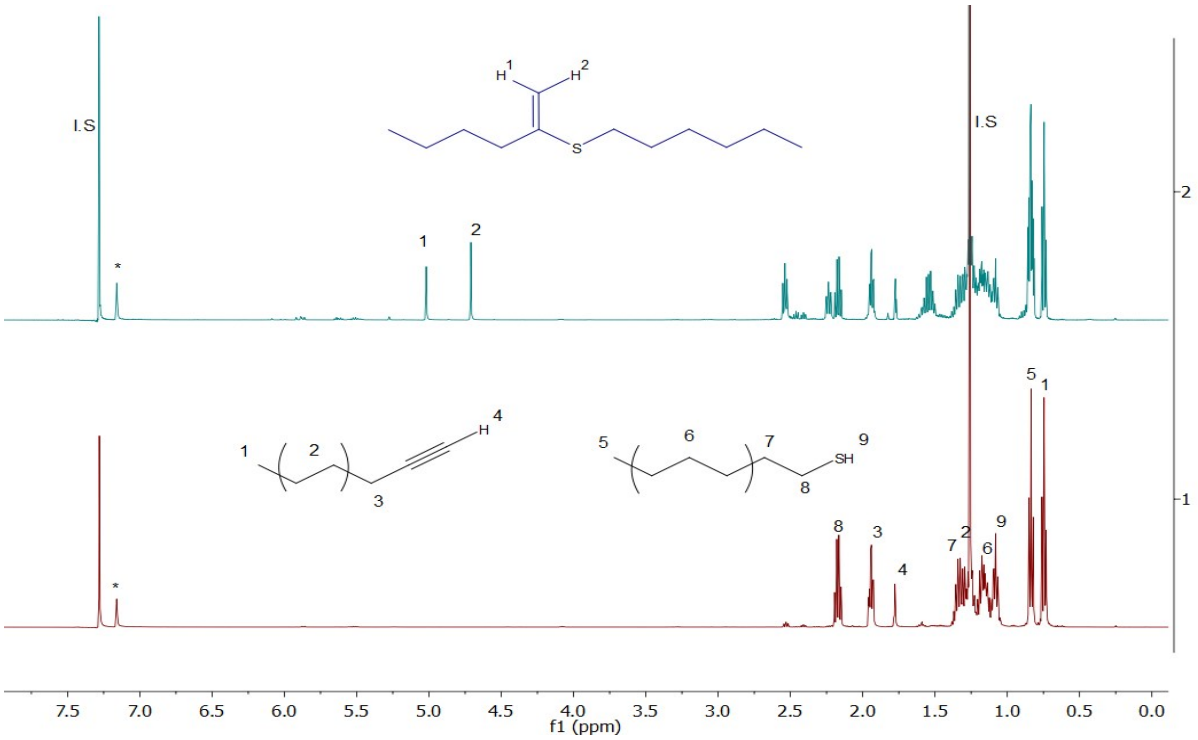
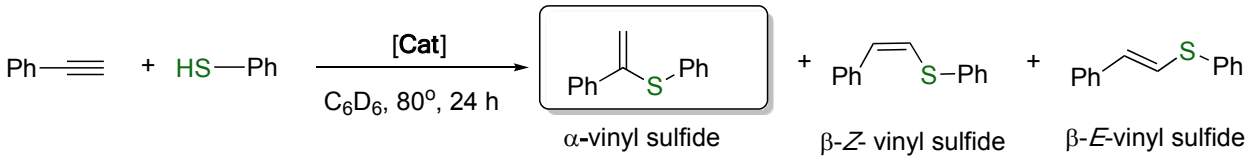


Figure S14: Overlaid ^{1}H NMR spectra of entry 8 (Table 3) in *C_6D_6.
Bottom: ^{1}H NMR spectrum at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

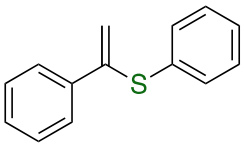
S2.10 Catalytic hydrothiolation of phenylacetylene with thiophenol (Table 3, entry 8).



Scheme S8: Schematic representation of the hydrothiolation reaction between phenylacetylene with thiophenol to afford the corresponding α-vinyl sulfide product PhC(SPh)=CH_2.

The hydrothiolation of phenylacetylene with thiophenol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst **2a** [$Rh_2Cl_2(cod)_2$(μ-**COC**)] (2.30 mg, 1.75 x 10^{-6} mol), one equiv. phenylacetylene (38.44 μL, 3.5 x10^{-4} mol), one equiv. of thiophenol (35.94 μL, 3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion: 79%, Yield: 46%, Product distribution (α/β-*Z*/β-*E*: 47/31/22).

Major Product: Phenyl(1-phenylvinyl)sulfane [2,5-7]



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.62 – 6.84 (m, 10H, overlaps with Ph-H from β-E and β-Z product isomers and remaining phenylacetylene and thiophenol substrates, Ph-**H**), 5.50 (s, 1H, C=C**H**$_2$), 5.30 (s, 1H, C=C**H**$_2$).

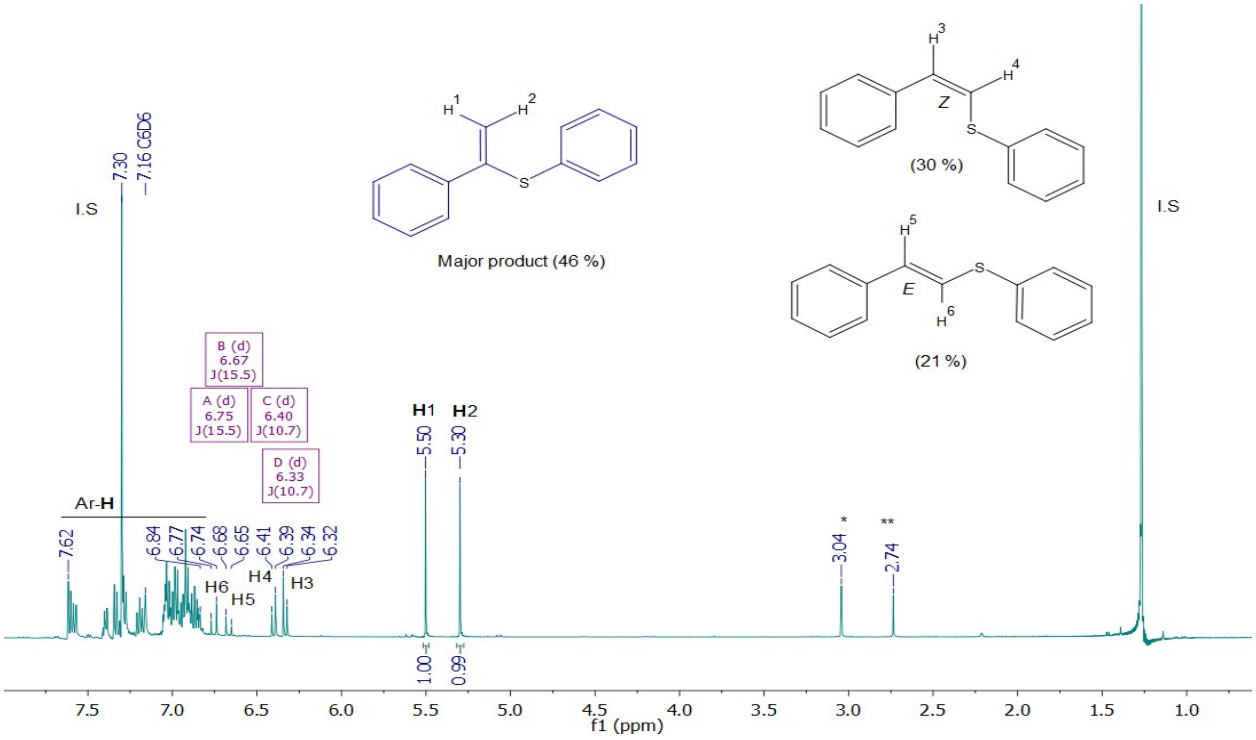


Figure S15: ^{1}H NMR of entry 9 (Table 3) after 24 h. at 80°C in C_6D_6.
Remaining substrates: Phenylacetylene: C**H** **; Thiophenol: S**H***

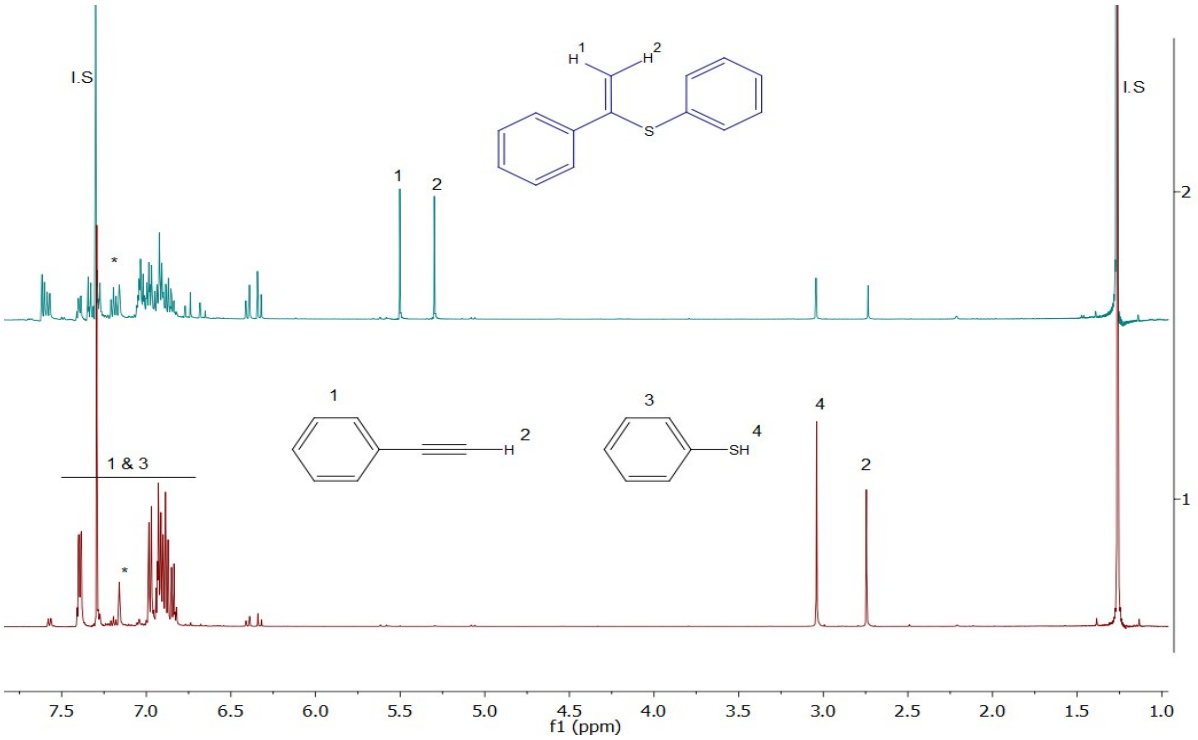
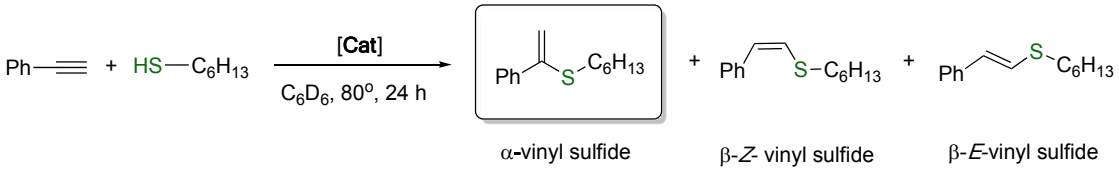


Figure S16: Overlaid ^{1}H NMR spectra of entry 9 (Table 3) in *C_6D_6.
Bottom: ^{1}H NMR spectrum at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

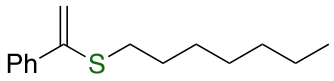
S2.11 Catalytic hydrothiolation of phenylacetylene with 1-hexanethiol (Table 3, entry 19).



Scheme S9: Schematic representation of the hydrothiolation reaction between phenylacetylene with 1-hexanethiol to afford the corresponding α-vinyl sulfide product $PhC(SC_6H_{13})=CH_2$.

The hydrothiolation of phenylacetylene with 1-hexanethiol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst **2a** $[Rh_2Cl_2(cod)_2(\mu\text{-}\mathbf{COC})]$ (2.30 mg, 1.75 x 10^{-6} mol), one equiv. phenylacetylene (38.44 µL, 3.5 x10^{-4} mol), one equiv. of 1-hexanethiol (43.06 µL, 3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion: 69%, Yield: 58%, Product distribution (α/β- *Z*/β-*E*: 51/32/17).

Major Product: [1-(hexylthio)ehenyl]-benzene



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.63 – 6.04 (m, 5H, overlaps with Ph-H from β-E and β-Z product isomers and remaining phenylacetylene substrate, Ph-**H**), 5.40 (s, 1H, C=C**H**$_2$), 5.14 (s, 1H, C=C**H**$_2$), 2.49 (m, 2H, SC**H**$_2$), 2.40 (m, 2H, S(C**H**$_2$)^2), 1.45 (ddt, 6H, *J*= 7.6 Hz, *J*= 7.6 Hz, *J*= 7.6 Hz, S(C**H**$_2$)$^{3-5}$), 0.82 (t, 3H: overlaps with CH_3 of remaining 1-hexanethiol, *J* = 7.2 Hz, C**H**$_3$). Note: X(C**H**$_2$)^n : where n refers to the position of the CH_2 in the hydrocarbon chain bound to X.

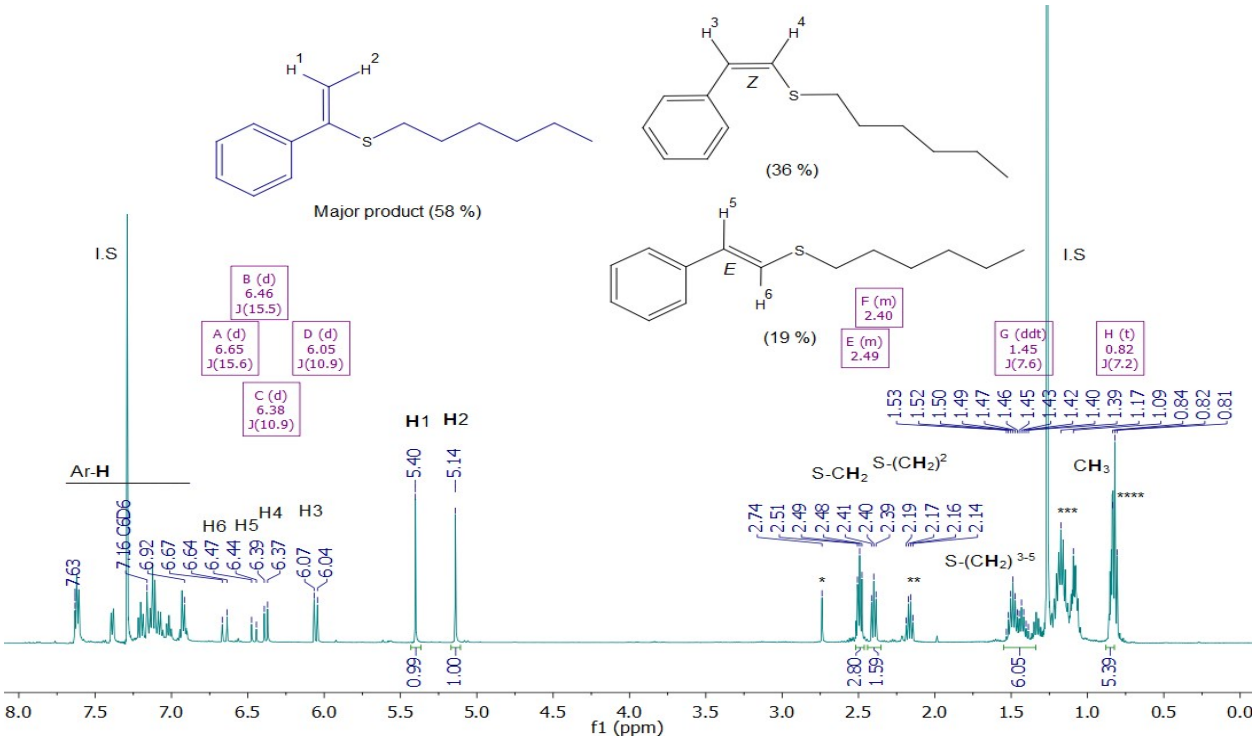


Figure S17: ^{1}H NMR of entry 10 (Table 3) after 24 h. at 80°C in C_6D_6.
Remaining substrates: Phenylacetylene: C**H** *; 1-Hexanethiol: S**H***, HS(C**H**$_2$)**, HS(C**H**$_2$)$^{2-5}$ *** and C**H**$_3$ ****

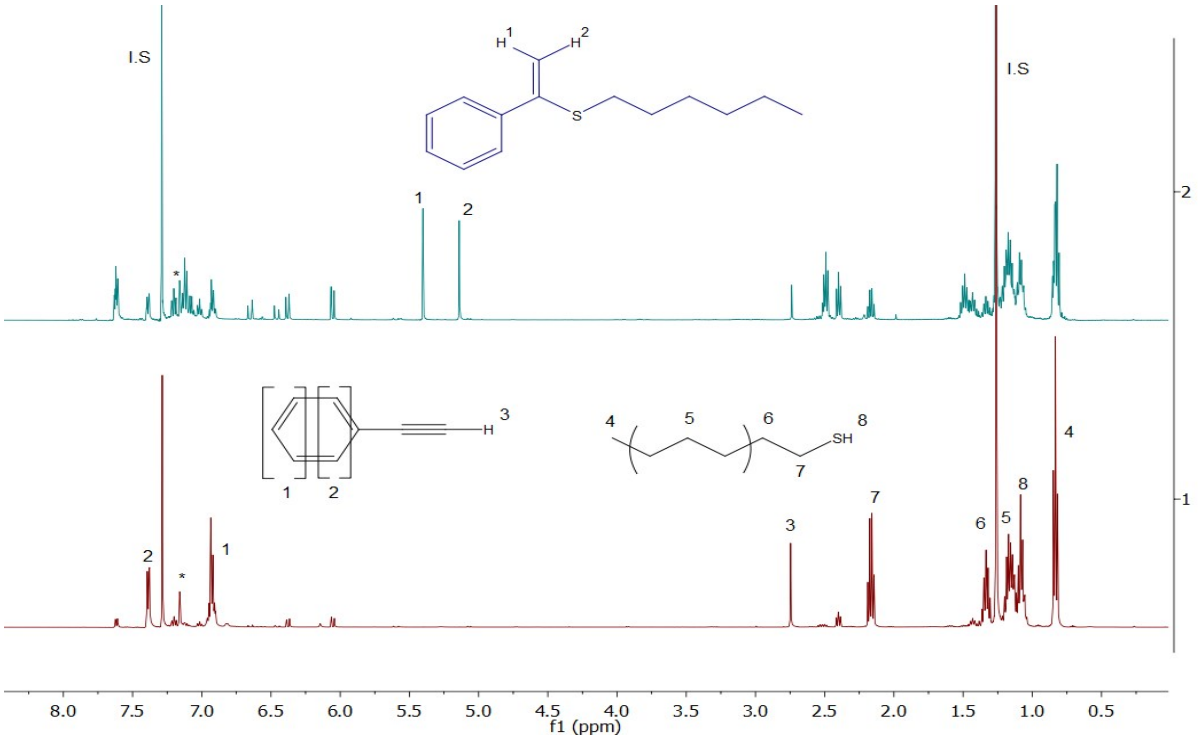
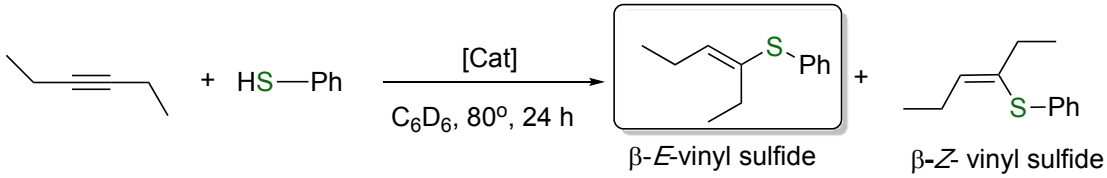


Figure S18: Overlaid ^{1}H NMR spectra of entry 10 (Table 3) in *C_6D_6.
Bottom: ^{1}H NMR spectrum at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

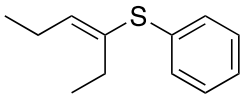
S2.12 Catalytic hydrothiolation of 3-hexyne with thiophenol (Table 3, entry 10).



Scheme S10: Schematic representation of the hydrothiolation reaction between 3-hexyne with thiophenol to afford the corresponding α-vinyl sulfide product $C_2H_5C(SC_2H_5)=CH_2$.

The hydrothiolation of 3-hexyne with thiophenol was performed in duplicate as described in the standard operating procedure. Catalyst, substrate and internal standard loadings were as follows: 0.5 mol% catalyst **2a** [$Rh_2Cl_2(cod)_2$(μ-**COC**)] (2.30 mg, 1.75 x 10^{-6} mol), one equiv. 3-hexyne (39.70 μL, 3.5 x10^{-4} mol), one equiv. of thiophenol (35.94 μL, 3.5 x10^{-4} mol) and 0.25 equiv. of 1,4-di-*tert*-butylbenzene (16.65 mg, 8.75 x 10^{-5} mol). Conversion: 26%, Yield: 11%, Product distribution (α/β-*Z*/β-*E*: -/9/91)

Major Product: [[(1*E*)-1-ethyl-1-buten-1-yl]thio]benzene [8]



^{1}H NMR δ_H (C_6D_6, 500.13 MHz) 7.40 – 6.83 (m, 5H, overlaps with Ph-H of β-Z – vinyl sulfide product and remaining thiophenol, Ph-**H**), 5.86 (t, 1H, *J*= 7.4 Hz, C=C-**H**), 2.12 (q, 2H, *J* = 7. 5 Hz, C**H**$_2$ -CS), 1.90 (pent, 2H *J* = 7.5 Hz, C**H**$_2$-CH^1), 1.03 (t, 3H, *J*= 7.5 Hz, overlaps with $(CH_3)_2$ of remaining 3-hexyne, $SCCH_2C\mathbf{H}_3$), 0.81 (t, 3H, *J*= 7.5 Hz, $H^1CCH_2C\mathbf{H}_3$)

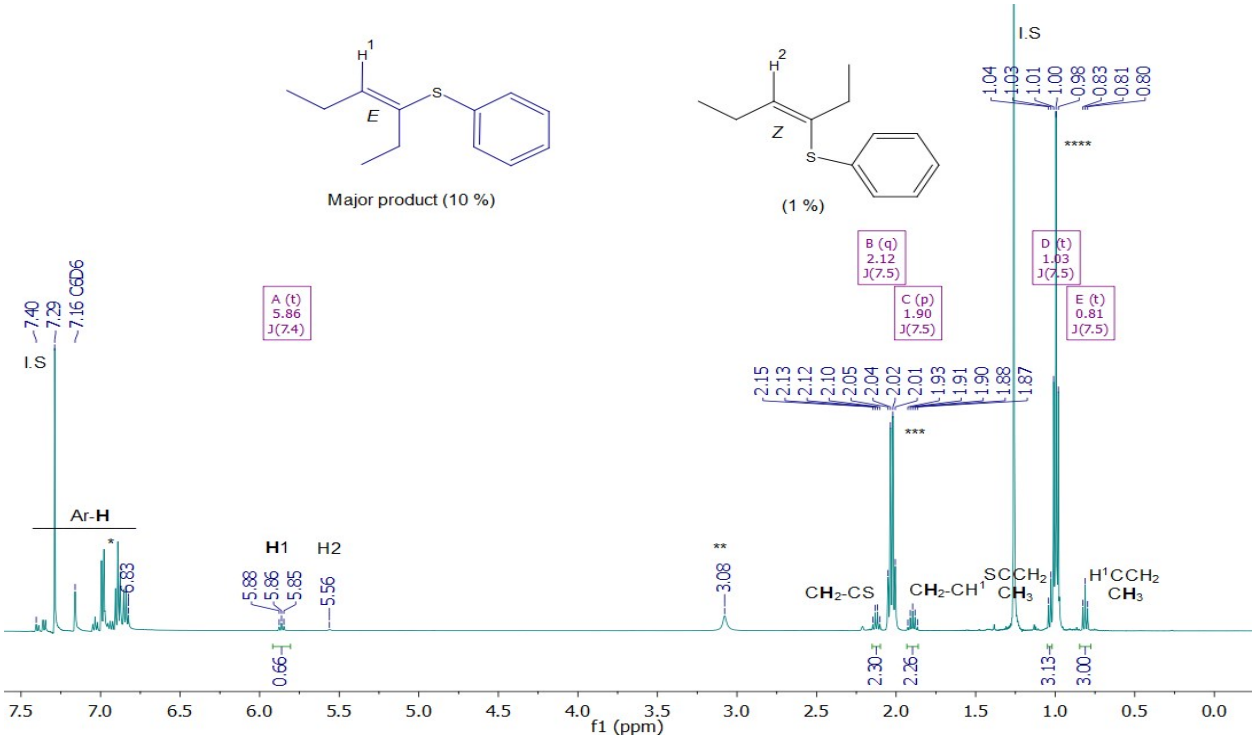


Figure S19: ^{1}H NMR of entry 1 (Table 4) after 24 h. at 80°C in C_6D_6.
Remaining substrates: 3-Hexyne: $(C\mathbf{H}_2)_2$ ***, $(C\mathbf{H}_3)_2$ ****; Thiophenol: Ar-**H***, S**H****,

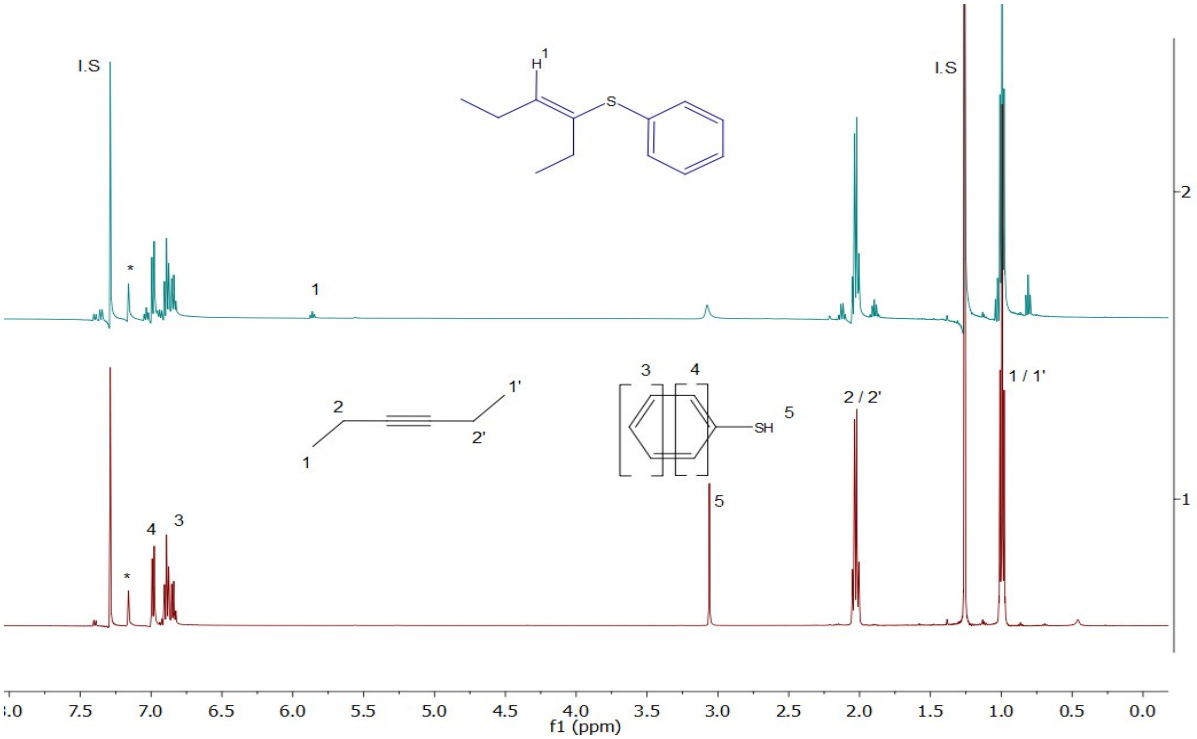


Figure S20: Overlaid ^{1}H NMR spectra of entry 1 (Table 4) in $*C_6D_6$.
Bottom: ^{1}H NMR spectrum at t = 0 h. **Top**: ^{1}H NMR spectrum after 24 h. at 80°C

S3 Computational DFT studies

All the calculations reported in this paper were obtained with the GAUSSIAN 09 suite of programs.[9] Electron correlation was partially taken into account using the B3LYP[10] functional in conjuction with the D3 dispersion correction suggested by Grimme et al.[11] and the double-ζ quality plus polarization functions def2-SVP[12] basis set for all atoms. Solvent effects (solvent = benzene) were taken into account by using the Polarizable Continuum Model (PCM)[13] in the geometry optimizations. This level is denoted PCM(benzene)-B3LYP-D3/def2-SVP. Reactants and products were characterized by frequency calculations,[14] and have positive definite Hessian matrices. Transition structures (TS's) show only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the Intrinsic Reaction Coordinate (IRC) method.[15]

Cartesian coordinates (in Å) and total energies (in a. u., ZPVE included) of all the stationary points discussed in the text. All calculations have been performed at the B3LYP-D3/def2-SVP level.

3: E= -2705.904728

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C	-3.483360000	2.244061000	0.048268000
C	-3.899285000	2.872677000	-1.140288000
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C	3.867035000	4.951197000	0.390922000
H	4.026864000	6.026500000	0.501372000
C	3.732538000	4.400837000	-0.885043000
H	3.785254000	5.053787000	-1.757058000
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C	-1.898425000	3.024773000	3.425595000
H	-2.185555000	1.329527000	2.180437000
H	-4.631047000	0.980241000	2.625380000
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H	-4.652681000	2.439734000	3.640986000
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H	-2.449342000	3.850533000	3.903018000
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C	-3.170446000	-3.236099000	3.391256000
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H	-3.630601000	-1.409672000	2.376740000
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H	-3.827092000	-1.638444000	-2.361041000
H	-6.046951000	-0.589594000	-1.873072000
H	-5.750762000	-0.723495000	-3.627346000
H	-6.854552000	-1.866732000	-2.815564000
H	-3.709579000	-3.928177000	-3.423174000
H	-5.432279000	-3.787067000	-3.855816000
H	-4.262121000	-2.639690000	-4.526671000
C	4.333351000	-2.413870000	2.360878000
C	5.425158000	-1.449465000	2.864416000
C	3.974143000	-3.450437000	3.433344000
H	3.426479000	-1.813167000	2.178748000
H	5.645571000	-0.670225000	2.120512000
H	5.104516000	-0.956038000	3.795265000
H	6.357564000	-1.998971000	3.070594000
H	3.230904000	-4.176290000	3.067526000
H	4.858049000	-4.013575000	3.771601000
H	3.557201000	-2.945173000	4.318353000
C	4.558319000	-2.166068000	-2.749943000
C	3.712351000	-3.041680000	-3.688904000

C	5.843864000	-1.674882000	-3.436320000
H	3.962385000	-1.271934000	-2.513201000
H	2.780244000	-3.370296000	-3.201562000
H	3.444001000	-2.480681000	-4.597922000
H	4.261452000	-3.943431000	-4.003057000
H	6.429671000	-1.029389000	-2.764586000
H	6.483508000	-2.518138000	-3.742130000
H	5.597531000	-1.094440000	-4.339225000
C	3.374495000	2.397217000	-2.436642000
C	2.670194000	3.312533000	-3.446407000
H	3.289402000	4.182195000	-3.717974000
H	2.466364000	2.758309000	-4.376002000
H	1.712853000	3.683529000	-3.048851000
C	3.404644000	1.889205000	2.650023000
C	1.977789000	2.047923000	3.208702000
C	4.467162000	2.156007000	3.725376000
H	3.522532000	0.838684000	2.345392000
H	1.222285000	1.798827000	2.446790000
H	1.826582000	1.387264000	4.078335000
H	1.797803000	3.084694000	3.535912000
H	5.484491000	2.045424000	3.319642000
H	4.376834000	3.167919000	4.150482000
H	4.351085000	1.442639000	4.556548000
C	4.742004000	1.922628000	-2.963236000
H	5.419606000	2.779404000	-3.108796000
H	5.224194000	1.227311000	-2.260133000
H	4.628632000	1.408333000	-3.931239000
H	2.734083000	1.508307000	-2.322476000
C	-4.017850000	2.102336000	-2.450853000
H	-4.245489000	1.054128000	-2.208817000
C	-2.667416000	2.123889000	-3.193363000
H	-1.859775000	1.706015000	-2.572786000
H	-2.728714000	1.536660000	-4.124251000
H	-2.388374000	3.156570000	-3.458119000
C	-5.157167000	2.597952000	-3.350367000
H	-4.959281000	3.605149000	-3.749984000
H	-5.272024000	1.924229000	-4.213977000
H	-6.115385000	2.626205000	-2.808960000

TS1: E= -3335.954951

C	-1.926947000	-0.245853000	-0.115235000
C	-2.078625000	-1.635859000	-0.119669000
C	-0.969650000	-2.616637000	-0.344842000
H	-1.178260000	-3.594177000	0.122407000
C	2.490787000	-1.259477000	-0.330753000
C	2.088910000	0.072905000	-0.251890000
C	-3.695992000	1.537872000	0.144828000
C	-4.141786000	2.127606000	-1.051124000
C	-4.656417000	3.426355000	-0.958916000
H	-5.019306000	3.928888000	-1.856649000
C	-4.686869000	4.098213000	0.262711000
H	-5.071385000	5.119440000	0.308291000
C	-4.213545000	3.488106000	1.424338000
H	-4.236375000	4.038034000	2.365467000

C	-3.713124000	2.179917000	1.395822000
C	-4.015311000	-3.195525000	0.204235000
C	-4.494223000	-3.818074000	-0.962615000
C	-5.033990000	-5.103602000	-0.814536000
H	-5.419528000	-5.628217000	-1.691111000
C	-5.087219000	-5.719371000	0.436512000
H	-5.509695000	-6.722778000	0.528197000
C	-4.613810000	-5.062260000	1.573753000
H	-4.674574000	-5.556431000	2.545383000
C	-4.068483000	-3.774054000	1.487069000
C	3.464530000	2.149580000	0.086610000
C	3.860561000	2.559977000	1.377369000
C	3.898639000	3.940843000	1.610439000
H	4.187386000	4.315771000	2.592335000
C	3.557561000	4.851390000	0.609759000
H	3.579831000	5.922822000	0.822977000
C	3.198498000	4.407370000	-0.661800000
H	2.949461000	5.136551000	-1.432917000
C	3.149348000	3.038873000	-0.956825000
C	4.708759000	-2.430525000	-0.256336000
C	5.204122000	-2.917577000	-1.480680000
C	6.007032000	-4.064363000	-1.421352000
H	6.424905000	-4.480374000	-2.339376000
C	6.287564000	-4.680383000	-0.199341000
H	6.915585000	-5.574236000	-0.177393000
C	5.782724000	-4.162170000	0.993659000
H	6.023741000	-4.652457000	1.939196000
C	4.977180000	-3.014347000	0.995363000
C	-0.129625000	0.639304000	-2.167374000
Rh	0.055754000	0.338527000	-0.263023000
N	-3.213172000	0.179709000	0.083040000
N	-4.107545000	-0.800031000	0.200680000
N	-3.396633000	-1.899575000	0.080050000
N	3.287195000	0.734984000	-0.149810000
N	4.353158000	-0.061474000	-0.180932000
N	3.849749000	-1.273512000	-0.281451000
H	-0.854219000	-2.791689000	-1.427773000
O	-0.444914000	0.899640000	-3.243563000
N	0.266463000	-1.976533000	0.139900000
C	1.549226000	-2.417636000	-0.446580000
H	1.374513000	-2.644927000	-1.511918000
H	1.955091000	-3.331987000	0.019456000
H	0.311367000	-2.040588000	1.157333000
S	0.321187000	2.339101000	1.222824000
C	-0.635677000	3.691580000	0.555859000
C	-0.720732000	4.830586000	1.380649000
C	-1.153453000	3.747736000	-0.744182000
C	-1.282423000	6.011243000	0.892050000
C	-1.721356000	4.930798000	-1.221821000
C	-1.782915000	6.068876000	-0.413307000
H	-0.325217000	4.794348000	2.398668000
H	-1.111661000	2.864021000	-1.376845000
H	-1.332217000	6.890840000	1.539218000
H	-2.124913000	4.956997000	-2.236845000
H	-2.227775000	6.991640000	-0.793069000
H	-0.299856000	0.864678000	1.321701000

C	-4.101674000	1.375391000	-2.376233000
H	-3.351961000	0.573815000	-2.284151000
C	-3.557639000	-3.053063000	2.730044000
H	-3.318764000	-2.015325000	2.454132000
C	-4.440565000	-3.145281000	-2.328570000
H	-4.036629000	-2.129674000	-2.198097000
C	4.447322000	-2.429960000	2.299372000
H	3.851130000	-1.537622000	2.061934000
C	4.946631000	-2.179436000	-2.788402000
H	4.028325000	-1.581587000	-2.665774000
C	-3.279273000	1.454888000	2.664450000
C	2.836887000	2.536277000	-2.360598000
H	2.307504000	1.579775000	-2.258000000
C	4.196024000	1.556784000	2.481808000
H	4.744363000	0.729102000	2.008188000
C	3.512841000	-3.408766000	3.029156000
H	3.114072000	-2.944617000	3.945242000
H	2.659179000	-3.699610000	2.395446000
H	4.039246000	-4.330574000	3.323008000
C	5.598909000	-1.964432000	3.205741000
H	6.243225000	-1.238480000	2.686880000
H	5.200461000	-1.483055000	4.112790000
H	6.228471000	-2.810356000	3.523991000
C	2.926220000	0.966269000	3.125141000
H	3.201335000	0.224833000	3.892484000
H	2.327960000	1.755682000	3.605052000
H	2.280476000	0.468583000	2.387627000
C	5.122396000	2.125390000	3.564096000
H	6.020615000	2.589573000	3.128945000
H	4.614101000	2.879084000	4.186489000
H	5.448240000	1.315882000	4.235559000
C	-2.612747000	2.369558000	3.698740000
H	-2.225002000	1.766035000	4.534536000
H	-1.772141000	2.921643000	3.257002000
H	-3.324904000	3.093391000	4.125682000
H	-2.527612000	0.702950000	2.373975000
C	-2.263879000	-3.696341000	3.259673000
H	-1.464812000	-3.690650000	2.500698000
H	-1.896347000	-3.150024000	4.142707000
H	-2.431912000	-4.743950000	3.556485000
C	-4.633743000	-2.978860000	3.825047000
H	-4.900725000	-3.978233000	4.202696000
H	-4.265946000	-2.389140000	4.679018000
H	-5.549924000	-2.499838000	3.448413000
C	-3.497744000	-3.896585000	-3.283843000
H	-3.419451000	-3.364494000	-4.245002000
H	-2.484757000	-3.990252000	-2.860833000
H	-3.866677000	-4.913599000	-3.492112000
C	-3.654480000	2.255174000	-3.551805000
H	-3.543581000	1.642187000	-4.459677000
H	-4.388464000	3.044528000	-3.777164000
H	-2.684335000	2.732643000	-3.349067000
C	-5.459672000	0.706637000	-2.656666000
H	-5.747006000	0.032919000	-1.835770000
H	-6.251407000	1.465314000	-2.765381000
H	-5.419192000	0.119151000	-3.587890000

C	-5.846690000	-2.990320000	-2.930962000
H	-6.510621000	-2.432984000	-2.253179000
H	-5.794595000	-2.442782000	-3.884942000
H	-6.309012000	-3.969636000	-3.132334000
C	4.715415000	-3.117716000	-3.980288000
H	3.924024000	-3.854158000	-3.768622000
H	4.415313000	-2.535063000	-4.864926000
H	5.629076000	-3.669586000	-4.251420000
C	6.096699000	-1.191342000	-3.062296000
H	5.894076000	-0.603913000	-3.971628000
H	6.227035000	-0.493203000	-2.222079000
H	7.045354000	-1.733248000	-3.205860000
C	4.145806000	2.251644000	-3.121618000
H	3.931104000	1.840815000	-4.121645000
H	4.730574000	3.176700000	-3.250744000
H	4.776271000	1.528319000	-2.582496000
C	1.914682000	3.465709000	-3.157282000
H	1.015958000	3.727359000	-2.579108000
H	2.421567000	4.400263000	-3.445701000
H	1.592610000	2.967815000	-4.084668000
C	-4.477566000	0.706402000	3.280840000
H	-4.161480000	0.131363000	4.165773000
H	-5.253535000	1.421185000	3.598723000
H	-4.935443000	0.010521000	2.562739000

TS1′: E= -3222.714280

C	-1.912184000	-0.157951000	-0.177963000
C	-2.033927000	-1.535778000	-0.406396000
C	-0.891686000	-2.402265000	-0.823244000
H	-1.039995000	-3.458003000	-0.542026000
C	2.553759000	-1.074445000	-0.384626000
C	2.110423000	0.215272000	-0.079730000
C	-3.693168000	1.422652000	0.719224000
C	-4.636124000	2.042093000	-0.126951000
C	-5.148742000	3.276206000	0.294970000
H	-5.873671000	3.799209000	-0.329666000
C	-4.745217000	3.847825000	1.500571000
H	-5.154141000	4.814461000	1.804702000
C	-3.829687000	3.194100000	2.324710000
H	-3.543621000	3.649032000	3.273710000
C	-3.286926000	1.954933000	1.958308000
C	-3.811975000	-3.259045000	0.025655000
C	-4.527339000	-3.722917000	-1.093887000
C	-4.985226000	-5.046716000	-1.044414000
H	-5.542605000	-5.455199000	-1.889310000
C	-4.741837000	-5.849347000	0.071686000
H	-5.108382000	-6.878506000	0.088027000
C	-4.044013000	-5.346721000	1.170781000
H	-3.877006000	-5.984764000	2.041220000
C	-3.562273000	-4.030119000	1.176586000
C	3.461829000	2.270184000	0.456681000
C	3.583346000	2.580780000	1.822063000
C	3.691376000	3.938872000	2.154611000
H	3.778767000	4.233486000	3.201764000

C	3.684337000	4.919771000	1.163591000
H	3.770298000	5.972535000	1.443715000
C	3.560611000	4.571794000	-0.182932000
H	3.545868000	5.357614000	-0.939032000
C	3.435712000	3.232562000	-0.570305000
C	4.810606000	-2.162816000	-0.601355000
C	5.200186000	-2.435713000	-1.924196000
C	6.054636000	-3.531840000	-2.116592000
H	6.388900000	-3.782172000	-3.125566000
C	6.488796000	-4.299596000	-1.036759000
H	7.156172000	-5.147429000	-1.208991000
C	6.085245000	-3.992332000	0.265120000
H	6.447106000	-4.601067000	1.095011000
C	5.230765000	-2.911659000	0.517101000
Rh	0.084604000	0.410706000	-0.134806000
N	-3.165005000	0.138553000	0.319403000
N	-3.981015000	-0.908724000	0.435179000
N	-3.275391000	-1.921625000	-0.011392000
N	3.298135000	0.883723000	0.092393000
N	4.384558000	0.137131000	-0.079713000
N	3.913178000	-1.058370000	-0.368834000
H	-0.748499000	-2.360765000	-1.914567000
N	0.299814000	-1.790328000	-0.185950000
C	1.632067000	-2.212718000	-0.686689000
H	1.560761000	-2.372400000	-1.774311000
H	1.968543000	-3.163574000	-0.239072000
H	0.259705000	-1.972562000	0.818890000
S	0.183943000	2.763218000	0.101048000
C	-1.148059000	3.542601000	-0.796482000
C	-1.828133000	4.622530000	-0.213902000
C	-1.364097000	3.234525000	-2.151666000
C	-2.699393000	5.397630000	-0.984129000
C	-2.225809000	4.021028000	-2.917081000
C	-2.890704000	5.109460000	-2.337872000
H	-1.668851000	4.854973000	0.840389000
H	-0.825537000	2.396733000	-2.598984000
H	-3.229341000	6.233699000	-0.521314000
H	-2.375048000	3.788068000	-3.974451000
H	-3.563082000	5.724567000	-2.940645000
H	-0.355905000	1.505208000	0.987832000
C	-5.155827000	1.368196000	-1.394368000
H	-4.381698000	0.663493000	-1.740467000
C	-2.821331000	-3.475539000	2.388564000
H	-2.567433000	-2.423486000	2.189913000
C	-4.772326000	-2.844652000	-2.314545000
H	-4.542773000	-1.805769000	-2.034927000
C	4.828329000	-2.518262000	1.933910000
H	3.880367000	-1.958294000	1.871157000
C	4.750995000	-1.582899000	-3.104381000
H	4.078493000	-0.796397000	-2.729146000
C	-2.400956000	1.166783000	2.916731000
C	3.283392000	2.822925000	-2.029638000
H	2.678961000	1.902349000	-2.044052000
C	3.535517000	1.503359000	2.899490000
H	3.788687000	0.543001000	2.426986000
C	4.574229000	-3.723474000	2.849457000

H	4.172179000	-3.382813000	3.816256000
H	3.853674000	-4.428240000	2.405175000
H	5.500839000	-4.278504000	3.063542000
C	5.879724000	-1.568540000	2.540162000
H	6.021346000	-0.677108000	1.912031000
H	5.567476000	-1.236458000	3.542731000
H	6.851601000	-2.078867000	2.634863000
C	2.109436000	1.377253000	3.465031000
H	2.062045000	0.578706000	4.223907000
H	1.793155000	2.318393000	3.941914000
H	1.383724000	1.145000000	2.671481000
C	4.565184000	1.726033000	4.015551000
H	5.582125000	1.833606000	3.608071000
H	4.338653000	2.624116000	4.611381000
H	4.562281000	0.868973000	4.707452000
C	-1.474860000	2.047689000	3.763567000
H	-0.778747000	1.417460000	4.338154000
H	-0.878442000	2.722363000	3.130798000
H	-2.034927000	2.657316000	4.490227000
H	-1.751981000	0.512843000	2.316443000
C	-1.501013000	-4.224089000	2.638220000
H	-0.840302000	-4.188110000	1.755961000
H	-0.961573000	-3.778457000	3.489052000
H	-1.677190000	-5.285624000	2.873087000
C	-3.716261000	-3.483223000	3.638931000
H	-3.982952000	-4.509426000	3.937174000
H	-3.193667000	-3.011255000	4.485517000
H	-4.648772000	-2.927152000	3.460035000
C	-3.827810000	-3.236656000	-3.464380000
H	-3.977058000	-2.573930000	-4.331471000
H	-2.771195000	-3.167116000	-3.160976000
H	-4.015051000	-4.272404000	-3.790914000
C	-5.420564000	2.344303000	-2.548033000
H	-5.676264000	1.782734000	-3.460469000
H	-6.270664000	3.010735000	-2.331606000
H	-4.542827000	2.967598000	-2.756612000
C	-6.432586000	0.560096000	-1.084835000
H	-6.261644000	-0.187080000	-0.298480000
H	-7.236734000	1.234967000	-0.749496000
H	-6.783084000	0.038132000	-1.989483000
C	-6.241016000	-2.867361000	-2.763777000
H	-6.915592000	-2.606730000	-1.934616000
H	-6.397689000	-2.139188000	-3.574764000
H	-6.536331000	-3.855911000	-3.149162000
C	3.961120000	-2.409978000	-4.132365000
H	3.093215000	-2.908246000	-3.671194000
H	3.593380000	-1.762734000	-4.944060000
H	4.589372000	-3.191645000	-4.587956000
C	5.949657000	-0.872148000	-3.755439000
H	5.607701000	-0.209368000	-4.565730000
H	6.495582000	-0.260714000	-3.021340000
H	6.656813000	-1.597368000	-4.188439000
C	4.656750000	2.495738000	-2.645392000
H	4.543240000	2.132748000	-3.679739000
H	5.295329000	3.393694000	-2.668057000
H	5.183982000	1.722947000	-2.066588000

C	2.521695000	3.852712000	-2.872836000
H	1.554180000	4.104880000	-2.413222000
H	3.096010000	4.782987000	-3.007971000
H	2.327722000	3.444202000	-3.877212000
C	-3.274629000	0.254669000	3.799988000
H	-2.645980000	-0.372606000	4.452942000
H	-3.940714000	0.854096000	4.441424000
H	-3.905617000	-0.409856000	3.190461000

INT1: E= -3335.984095

C	-2.019558000	-0.086326000	0.007438000
C	-2.271841000	-1.424260000	-0.294783000
C	-1.217369000	-2.386371000	-0.754779000
H	-1.457790000	-3.430987000	-0.495943000
C	2.353819000	-1.369112000	-0.288062000
C	2.029983000	-0.058958000	0.055194000
C	-3.606024000	1.710245000	0.789105000
C	-4.287581000	2.498966000	-0.157769000
C	-4.581724000	3.817973000	0.214326000
H	-5.100268000	4.473553000	-0.486004000
C	-4.212715000	4.307389000	1.466307000
H	-4.443126000	5.342087000	1.731463000
C	-3.554147000	3.489404000	2.384836000
H	-3.279728000	3.894066000	3.359239000
C	-3.234156000	2.163373000	2.069221000
C	-4.290287000	-2.911199000	-0.118601000
C	-4.922889000	-3.240993000	-1.331262000
C	-5.552545000	-4.492080000	-1.392048000
H	-6.057530000	-4.796308000	-2.310942000
C	-5.546865000	-5.352512000	-0.292991000
H	-6.044889000	-6.322467000	-0.363202000
C	-4.918893000	-4.982794000	0.897541000
H	-4.935378000	-5.664920000	1.750210000
C	-4.273751000	-3.744176000	1.016258000
C	3.505588000	1.874409000	0.650717000
C	3.582128000	2.190940000	2.015334000
C	3.777319000	3.541334000	2.337857000
H	3.833155000	3.841131000	3.386256000
C	3.890481000	4.506997000	1.338796000
H	4.039975000	5.554297000	1.612626000
C	3.807371000	4.150804000	-0.009089000
H	3.889159000	4.923393000	-0.774553000
C	3.604578000	2.819045000	-0.387864000
C	4.515361000	-2.637302000	-0.503192000
C	4.910921000	-2.876470000	-1.831157000
C	5.661527000	-4.038498000	-2.064874000
H	5.993991000	-4.268683000	-3.079183000
C	5.996348000	-4.896770000	-1.018455000
H	6.584736000	-5.794616000	-1.222181000
C	5.594731000	-4.617718000	0.290447000
H	5.879231000	-5.298966000	1.093543000
C	4.839200000	-3.475480000	0.583514000
C	0.171344000	0.701935000	-1.962217000
Rh	0.013857000	0.325062000	-0.012907000

N	-3.248489000	0.359476000	0.411336000
N	-4.196105000	-0.574245000	0.399192000
N	-3.586439000	-1.656052000	-0.032557000
N	3.251671000	0.501511000	0.283012000
N	4.272994000	-0.330657000	0.111559000
N	3.710271000	-1.470725000	-0.233638000
H	-1.101525000	-2.333021000	-1.850302000
O	0.377251000	0.873377000	-3.070919000
N	0.043995000	-1.912042000	-0.137756000
C	1.334789000	-2.397840000	-0.683202000
H	1.249670000	-2.451082000	-1.781688000
H	1.593046000	-3.409079000	-0.325655000
H	0.015320000	-2.127582000	0.860117000
S	0.042341000	2.552593000	0.803812000
C	-0.220419000	3.739579000	-0.486062000
C	0.427165000	4.986100000	-0.346322000
C	-1.044531000	3.539814000	-1.608294000
C	0.270287000	5.984696000	-1.307757000
C	-1.165308000	4.530089000	-2.587830000
C	-0.512370000	5.758306000	-2.446157000
H	1.077416000	5.152522000	0.514541000
H	-1.600826000	2.607311000	-1.708411000
H	0.786643000	6.939908000	-1.178724000
H	-1.784941000	4.343266000	-3.468866000
H	-0.613210000	6.530155000	-3.212667000
H	-0.005724000	0.088764000	1.554318000
C	-2.579198000	1.230811000	3.080119000
C	-3.648742000	0.362753000	3.772041000
C	-1.706325000	1.953222000	4.112009000
H	-1.910205000	0.561371000	2.520810000
H	-4.262221000	-0.190205000	3.045219000
H	-3.176310000	-0.368427000	4.448133000
H	-4.328490000	0.989754000	4.371392000
H	-0.979294000	2.613882000	3.618313000
H	-2.308698000	2.551978000	4.814198000
H	-1.148969000	1.215968000	4.710989000
C	-3.598861000	-3.334158000	2.320216000
C	-2.415775000	-4.257426000	2.656458000
C	-4.610721000	-3.268456000	3.475923000
H	-3.193643000	-2.318385000	2.198337000
H	-1.675627000	-4.281698000	1.839740000
H	-1.907266000	-3.912741000	3.570701000
H	-2.749757000	-5.292810000	2.829202000
H	-5.437533000	-2.582081000	3.238689000
H	-5.041013000	-4.259079000	3.692104000
H	-4.119633000	-2.907341000	4.392956000
C	-4.919623000	-2.302988000	-2.531489000
C	-6.342476000	-2.017610000	-3.037478000
C	-4.022921000	-2.849767000	-3.655807000
H	-4.496594000	-1.338892000	-2.211002000
H	-6.980383000	-1.626855000	-2.230955000
H	-6.314199000	-1.268986000	-3.844620000
H	-6.818702000	-2.924041000	-3.443124000
H	-2.990369000	-3.014121000	-3.308364000
H	-4.403312000	-3.812214000	-4.033718000
H	-3.990471000	-2.144368000	-4.501060000

C	4.444584000	-3.114360000	2.011291000
C	5.542790000	-2.251725000	2.663567000
C	4.113238000	-4.336396000	2.878189000
H	3.532001000	-2.496484000	1.963429000
H	5.739356000	-1.342545000	2.077298000
H	5.241600000	-1.947125000	3.678057000
H	6.483302000	-2.820254000	2.740751000
H	3.363857000	-4.986116000	2.398963000
H	5.007064000	-4.945591000	3.084155000
H	3.715248000	-4.009586000	3.851249000
C	4.579714000	-1.921934000	-2.972032000
C	3.726604000	-2.602540000	-4.055645000
C	5.860403000	-1.311707000	-3.566454000
H	3.987765000	-1.087613000	-2.566048000
H	2.799428000	-3.025941000	-3.636955000
H	3.449634000	-1.876978000	-4.836454000
H	4.274951000	-3.424068000	-4.543248000
H	6.452999000	-0.801568000	-2.792684000
H	6.494675000	-2.084797000	-4.028193000
H	5.606598000	-0.575296000	-4.344703000
C	3.550036000	2.400598000	-1.852220000
C	2.825774000	3.408755000	-2.753097000
H	3.388404000	4.350479000	-2.849967000
H	2.713830000	2.990356000	-3.765550000
H	1.825714000	3.648568000	-2.366485000
C	3.421674000	1.142855000	3.109334000
C	2.091920000	1.331055000	3.860117000
C	4.620337000	1.131860000	4.070859000
H	3.388078000	0.151370000	2.632313000
H	1.236237000	1.287794000	3.171918000
H	1.967462000	0.546322000	4.624403000
H	2.059382000	2.306139000	4.371867000
H	5.565623000	0.973080000	3.529619000
H	4.702238000	2.079021000	4.627019000
H	4.509063000	0.323470000	4.811167000
C	4.970141000	2.099872000	-2.366857000
H	5.591705000	3.009179000	-2.336274000
H	5.464400000	1.332224000	-1.752495000
H	4.939295000	1.741939000	-3.408341000
H	2.975715000	1.462990000	-1.909951000
C	-4.744430000	1.939620000	-1.501531000
H	-4.060895000	1.116539000	-1.772435000
C	-6.165271000	1.352766000	-1.384740000
H	-6.216536000	0.564378000	-0.621476000
H	-6.880790000	2.143778000	-1.108236000
H	-6.485579000	0.925735000	-2.348171000
C	-4.687291000	2.964939000	-2.642236000
H	-4.871086000	2.465181000	-3.606277000
H	-5.460319000	3.741378000	-2.529483000
H	-3.712710000	3.467951000	-2.689558000

INT2: E= -3339.380456

C	-2.005582000	-0.070889000	-0.368137000
C	-2.308242000	-1.432284000	-0.293934000

C	-1.282617000	-2.525882000	-0.370989000
H	-1.549186000	-3.390205000	0.259534000
C	2.316464000	-1.457739000	-0.265597000
C	2.006813000	-0.098261000	-0.285227000
C	-3.503270000	1.921149000	-0.052105000
C	-3.402418000	2.730362000	-1.200865000
C	-3.578929000	4.107918000	-1.016333000
H	-3.492566000	4.783554000	-1.866654000
C	-3.858427000	4.633469000	0.244029000
H	-3.976365000	5.712639000	0.365382000
C	-3.988004000	3.796832000	1.351576000
H	-4.213788000	4.233606000	2.324440000
C	-3.811284000	2.412162000	1.234719000
C	-4.431834000	-2.744418000	-0.012300000
C	-4.932802000	-3.304018000	-1.202114000
C	-5.659953000	-4.496090000	-1.078730000
H	-6.073156000	-4.969458000	-1.971883000
C	-5.869819000	-5.080910000	0.171472000
H	-6.442448000	-6.008547000	0.244719000
C	-5.363117000	-4.489043000	1.330267000
H	-5.549582000	-4.955969000	2.299622000
C	-4.626797000	-3.298175000	1.266447000
C	3.330996000	1.864409000	0.536276000
C	3.828337000	2.758806000	-0.424824000
C	3.925928000	4.103945000	-0.048940000
H	4.300118000	4.838520000	-0.763495000
C	3.532999000	4.521945000	1.222388000
H	3.591910000	5.579713000	1.487111000
C	3.051246000	3.604293000	2.154396000
H	2.745363000	3.954607000	3.140635000
C	2.939556000	2.245037000	1.833681000
C	4.384274000	-2.776305000	0.268888000
C	5.098965000	-3.187709000	-0.872657000
C	5.794537000	-4.400394000	-0.778483000
H	6.363671000	-4.762593000	-1.637142000
C	5.771220000	-5.149792000	0.399215000
H	6.317809000	-6.094445000	0.450222000
C	5.066007000	-4.698657000	1.515913000
H	5.072565000	-5.292525000	2.432158000
C	4.356795000	-3.489426000	1.481433000
C	-0.558611000	-0.651021000	-2.998006000
Rh	0.027322000	0.255093000	-0.551073000
N	-3.234687000	0.507181000	-0.188924000
N	-4.235010000	-0.360441000	-0.052638000
N	-3.652862000	-1.538303000	-0.113553000
N	3.161096000	0.475194000	0.172966000
N	4.137316000	-0.393995000	0.430126000
N	3.603945000	-1.569319000	0.163738000
H	-1.184197000	-2.897374000	-1.403473000
C	0.592759000	-0.323825000	-3.228729000
N	0.007200000	-1.901953000	0.018950000
C	1.270637000	-2.510984000	-0.487511000
H	1.135324000	-2.710119000	-1.561802000
H	1.522153000	-3.463383000	0.006114000
H	0.055131000	-1.855847000	1.038637000
S	0.229521000	2.434525000	-1.395645000

C	0.078605000	3.722300000	-0.195477000
C	-0.473270000	3.552871000	1.085249000
C	0.513325000	5.013081000	-0.566380000
C	-0.575198000	4.627398000	1.969577000
C	0.399328000	6.085743000	0.317953000
C	-0.139794000	5.902668000	1.597610000
H	-0.833538000	2.570434000	1.377617000
H	0.953665000	5.167274000	-1.554712000
H	-1.008500000	4.462444000	2.960276000
H	0.747142000	7.075030000	0.007225000
H	-0.221262000	6.743175000	2.291047000
H	0.032751000	0.736549000	0.890663000
H	-1.587724000	-0.954491000	-2.962947000
C	1.929841000	0.082834000	-3.635201000
H	2.085828000	1.141969000	-3.386150000
H	2.701865000	-0.513684000	-3.127912000
H	2.048564000	-0.048530000	-4.722032000
C	5.118819000	-2.367586000	-2.157466000
C	4.352882000	-3.082385000	-3.283541000
C	6.551088000	-2.007185000	-2.582702000
H	4.604279000	-1.415099000	-1.963615000
H	3.310987000	-3.292313000	-2.992495000
H	4.334055000	-2.460341000	-4.192405000
H	4.828033000	-4.042232000	-3.541213000
H	7.081570000	-1.476772000	-1.777404000
H	7.135280000	-2.902893000	-2.846037000
H	6.529928000	-1.351589000	-3.467514000
C	3.609457000	-2.984339000	2.710206000
C	4.555624000	-2.830255000	3.912431000
C	2.409775000	-3.882684000	3.057475000
H	3.217700000	-1.980935000	2.484567000
H	5.394124000	-2.159216000	3.673607000
H	4.013956000	-2.408468000	4.773139000
H	4.972758000	-3.800147000	4.225438000
H	1.697606000	-3.956809000	2.219786000
H	2.734412000	-4.905174000	3.307606000
H	1.869116000	-3.480397000	3.928864000
C	4.288373000	2.273302000	-1.789869000
C	5.800465000	1.982910000	-1.776194000
C	3.893860000	3.223478000	-2.927436000
H	3.781332000	1.317820000	-1.980643000
H	6.054035000	1.249164000	-0.995229000
H	6.127892000	1.577992000	-2.747925000
H	6.374843000	2.902331000	-1.577972000
H	2.815075000	3.441843000	-2.893673000
H	4.442280000	4.177211000	-2.875344000
H	4.130024000	2.768181000	-3.902644000
C	2.488481000	1.220267000	2.868241000
C	1.375189000	1.728464000	3.793225000
C	3.700226000	0.727861000	3.681507000
H	2.075004000	0.355281000	2.325495000
H	0.532920000	2.135243000	3.218140000
H	1.004370000	0.904688000	4.423877000
H	1.734102000	2.518052000	4.471780000
H	4.473916000	0.297273000	3.028814000
H	4.153417000	1.563805000	4.238017000

H	3.394739000	-0.039478000	4.410364000
C	-4.724209000	-2.645619000	-2.561252000
C	-6.063643000	-2.199543000	-3.170512000
C	-3.934868000	-3.553004000	-3.518922000
H	-4.126578000	-1.732965000	-2.415063000
H	-6.601850000	-1.523695000	-2.488663000
H	-5.893540000	-1.665170000	-4.118312000
H	-6.715509000	-3.062420000	-3.380311000
H	-2.958148000	-3.835049000	-3.093251000
H	-4.483551000	-4.481845000	-3.741109000
H	-3.754560000	-3.036139000	-4.474768000
C	-4.103074000	-2.623673000	2.528852000
C	-3.218487000	-3.562295000	3.364433000
C	-5.263762000	-2.048831000	3.358943000
H	-3.473036000	-1.772587000	2.228527000
H	-2.377509000	-3.958074000	2.771582000
H	-2.804159000	-3.023158000	4.231003000
H	-3.787668000	-4.421623000	3.752202000
H	-5.867450000	-1.346512000	2.764400000
H	-5.930003000	-2.850218000	3.716042000
H	-4.876877000	-1.510388000	4.238667000
C	-3.172601000	2.119211000	-2.579307000
C	-2.664809000	3.117039000	-3.624002000
C	-4.448792000	1.413682000	-3.081026000
H	-2.381631000	1.364859000	-2.462868000
H	-1.764806000	3.636992000	-3.266341000
H	-2.401082000	2.580999000	-4.549277000
H	-3.431620000	3.863996000	-3.886185000
H	-4.826664000	0.668182000	-2.366440000
H	-5.255247000	2.145978000	-3.248159000
H	-4.255072000	0.901565000	-4.037889000
C	-3.919865000	1.491721000	2.451449000
C	-4.849768000	2.032748000	3.544660000
C	-2.536072000	1.157891000	3.039945000
H	-4.366871000	0.548580000	2.106285000
H	-5.830676000	2.320138000	3.136480000
H	-5.012189000	1.259123000	4.311422000
H	-4.420744000	2.910420000	4.053801000
H	-1.865713000	0.713551000	2.290357000
H	-2.048387000	2.065589000	3.428564000
H	-2.636659000	0.444926000	3.874525000

INT2-iso: E= -3339.379166

C	-1.990077000	-0.057388000	-0.418205000
C	-2.288958000	-1.421074000	-0.369321000
C	-1.254546000	-2.497504000	-0.508226000
H	-1.527926000	-3.411988000	0.043830000
C	2.330347000	-1.442427000	-0.245748000
C	2.022627000	-0.084282000	-0.306785000
C	-3.447078000	1.916781000	0.144847000
C	-3.422296000	2.802612000	-0.950417000
C	-3.586930000	4.164433000	-0.666210000
H	-3.556207000	4.892943000	-1.475408000

C	-3.782108000	4.607308000	0.640114000
H	-3.892716000	5.675627000	0.838739000
C	-3.831493000	3.699618000	1.696577000
H	-3.988153000	4.071868000	2.708796000
C	-3.662633000	2.326365000	1.479968000
C	-4.351765000	-2.753858000	0.162671000
C	-5.000836000	-3.340880000	-0.938338000
C	-5.698721000	-4.532504000	-0.698683000
H	-6.227301000	-5.020538000	-1.520077000
C	-5.732015000	-5.099678000	0.576264000
H	-6.283393000	-6.028442000	0.740838000
C	-5.072010000	-4.488813000	1.643930000
H	-5.114114000	-4.944101000	2.635535000
C	-4.362567000	-3.293480000	1.463141000
C	3.414075000	1.915904000	0.250866000
C	3.711811000	2.728752000	-0.856778000
C	3.844592000	4.100618000	-0.613225000
H	4.066910000	4.777832000	-1.438417000
C	3.671573000	4.620119000	0.670525000
H	3.757216000	5.696637000	0.833498000
C	3.369023000	3.783892000	1.743345000
H	3.223084000	4.214932000	2.734267000
C	3.227334000	2.402025000	1.557166000
C	4.426630000	-2.746414000	0.200927000
C	4.995732000	-3.264081000	-0.978541000
C	5.702669000	-4.468691000	-0.861999000
H	6.167432000	-4.907357000	-1.747492000
C	5.824582000	-5.111628000	0.370844000
H	6.377634000	-6.051459000	0.438725000
C	5.254270000	-4.560900000	1.519637000
H	5.367396000	-5.074663000	2.476340000
C	4.542650000	-3.354278000	1.464871000
C	-0.444069000	-0.555221000	-3.282258000
Rh	0.038738000	0.271554000	-0.589264000
N	-3.197097000	0.512205000	-0.100822000
N	-4.180814000	-0.364569000	0.099908000
N	-3.607159000	-1.538947000	-0.054238000
N	3.209052000	0.502892000	0.030579000
N	4.199883000	-0.356538000	0.257399000
N	3.645611000	-1.540685000	0.089569000
H	-1.117828000	-2.778333000	-1.564558000
C	0.725481000	-0.288237000	-3.064077000
N	0.011652000	-1.886693000	-0.030047000
C	1.296532000	-2.511310000	-0.441990000
H	1.213683000	-2.774712000	-1.508135000
H	1.527263000	-3.434628000	0.113646000
H	-0.017483000	-1.835257000	0.989895000
S	0.169319000	2.465811000	-1.406749000
C	0.061694000	3.733060000	-0.180436000
C	-0.352024000	3.531118000	1.147052000
C	0.392030000	5.047209000	-0.579469000
C	-0.421395000	4.596364000	2.046315000
C	0.313469000	6.108723000	0.321649000
C	-0.087034000	5.893126000	1.646607000
H	-0.633535000	2.530893000	1.465859000
H	0.721623000	5.228775000	-1.605667000

H	-0.749770000	4.406794000	3.072301000
H	0.578695000	7.115675000	-0.012930000
H	-0.142084000	6.725198000	2.352670000
H	0.042759000	0.733280000	0.859136000
H	1.770121000	-0.043142000	-3.038946000
C	4.877964000	-2.553303000	-2.322424000
C	4.144550000	-3.418010000	-3.361394000
C	6.257894000	-2.103198000	-2.831154000
H	4.278859000	-1.641303000	-2.181091000
H	3.139976000	-3.705924000	-3.011855000
H	4.030310000	-2.865189000	-4.307195000
H	4.699847000	-4.343497000	-3.581357000
H	6.759980000	-1.457331000	-2.095128000
H	6.912522000	-2.966253000	-3.031075000
H	6.152922000	-1.535154000	-3.768847000
C	3.923778000	-2.752741000	2.721452000
C	4.967204000	-2.568608000	3.834768000
C	2.729562000	-3.590580000	3.210180000
H	3.545154000	-1.750254000	2.471822000
H	5.811260000	-1.952941000	3.489883000
H	4.511844000	-2.068585000	4.703495000
H	5.366782000	-3.534747000	4.181038000
H	1.947516000	-3.673660000	2.438454000
H	3.043326000	-4.612588000	3.476155000
H	2.276818000	-3.133205000	4.104370000
C	3.914022000	2.126427000	-2.240384000
C	5.367394000	1.646434000	-2.413810000
C	3.486377000	3.058510000	-3.378904000
H	3.264140000	1.239486000	-2.298189000
H	5.652368000	0.931711000	-1.626964000
H	5.501794000	1.153958000	-3.390687000
H	6.063835000	2.498835000	-2.363281000
H	2.457854000	3.415457000	-3.220382000
H	4.155388000	3.929002000	-3.469515000
H	3.524505000	2.521279000	-4.339943000
C	2.936065000	1.464322000	2.723599000
C	1.955970000	2.048440000	3.749551000
C	4.250659000	1.031809000	3.399720000
H	2.457884000	0.559900000	2.312601000
H	1.033421000	2.398757000	3.266705000
H	1.694497000	1.282262000	4.496864000
H	2.394383000	2.897517000	4.296996000
H	4.928991000	0.545166000	2.683725000
H	4.771810000	1.906414000	3.820984000
H	4.051637000	0.326771000	4.222348000
C	-4.981311000	-2.704203000	-2.321254000
C	-6.362441000	-2.129417000	-2.678427000
C	-4.470103000	-3.676959000	-3.394649000
H	-4.280621000	-1.857741000	-2.295307000
H	-6.693215000	-1.399363000	-1.924003000
H	-6.326757000	-1.621828000	-3.655391000
H	-7.120402000	-2.926924000	-2.736326000
H	-3.481501000	-4.084820000	-3.128101000
H	-5.156369000	-4.527046000	-3.533738000
H	-4.381306000	-3.163017000	-4.364758000
C	-3.657090000	-2.618296000	2.633026000

C	-2.570179000	-3.517865000	3.243688000
C	-4.668343000	-2.153229000	3.694379000
H	-3.150998000	-1.717313000	2.257900000
H	-1.830883000	-3.829204000	2.487786000
H	-2.036432000	-2.981628000	4.044560000
H	-2.998918000	-4.431734000	3.684148000
H	-5.426871000	-1.487269000	3.255961000
H	-5.192047000	-3.008523000	4.149781000
H	-4.154538000	-1.605202000	4.499806000
C	-3.271909000	2.292575000	-2.379360000
C	-2.843044000	3.367324000	-3.382115000
C	-4.563753000	1.596515000	-2.852438000
H	-2.457287000	1.555418000	-2.358291000
H	-1.929012000	3.877001000	-3.045802000
H	-2.629233000	2.899184000	-4.355944000
H	-3.633246000	4.117618000	-3.547465000
H	-4.869891000	0.776150000	-2.186413000
H	-5.397598000	2.315599000	-2.893222000
H	-4.429239000	1.180918000	-3.864518000
C	-3.684151000	1.335744000	2.645075000
C	-4.505225000	1.820205000	3.846750000
C	-2.262573000	0.945260000	3.092250000
H	-4.179479000	0.424225000	2.282753000
H	-5.514007000	2.141838000	3.546147000
H	-4.611605000	1.003339000	4.577187000
H	-4.019172000	2.660494000	4.367587000
H	-1.663462000	0.542802000	2.263281000
H	-1.726973000	1.818486000	3.496767000
H	-2.307636000	0.180427000	3.884564000
C	-1.798558000	-0.889721000	-3.708078000
H	-1.955656000	-0.544116000	-4.741894000
H	-1.974112000	-1.976541000	-3.686536000
H	-2.552618000	-0.406420000	-3.074405000

TS2: E= -3339.238121

C	1.931604000	0.186996000	-0.426779000
C	2.064950000	1.563691000	-0.642475000
C	0.929042000	2.475576000	-0.971627000
H	1.112829000	3.511185000	-0.641733000
C	-2.528110000	1.213025000	-0.410888000
C	-2.098247000	-0.106267000	-0.282229000
C	3.728202000	-1.426997000	0.394115000
C	3.911999000	-2.442392000	-0.565635000
C	4.472178000	-3.644677000	-0.113521000
H	4.624489000	-4.468492000	-0.809122000
C	4.838939000	-3.810842000	1.219689000
H	5.271260000	-4.759175000	1.546870000
C	4.644809000	-2.784909000	2.142479000
H	4.931867000	-2.944351000	3.181685000
C	4.078512000	-1.563825000	1.755785000
C	3.892937000	3.245975000	-0.303380000
C	4.556573000	3.759161000	-1.433372000
C	5.039470000	5.071272000	-1.338282000
H	5.569206000	5.514303000	-2.182913000

C	4.854721000	5.820992000	-0.174408000
H	5.238471000	6.842717000	-0.123500000
C	4.189595000	5.277424000	0.924922000
H	4.060653000	5.877157000	1.828450000
C	3.690323000	3.967610000	0.888536000
C	-3.332103000	-2.122269000	0.564854000
C	-3.700650000	-3.051384000	-0.424393000
C	-3.795754000	-4.390768000	-0.028062000
H	-4.079906000	-5.152619000	-0.754736000
C	-3.508481000	-4.771369000	1.283934000
H	-3.579506000	-5.823687000	1.569590000
C	-3.112241000	-3.825322000	2.228731000
H	-2.873784000	-4.147865000	3.243297000
C	-3.010584000	-2.469346000	1.888199000
C	-4.669760000	2.421898000	0.069297000
C	-5.444160000	2.754978000	-1.056831000
C	-6.210935000	3.925582000	-0.970989000
H	-6.831109000	4.225688000	-1.818234000
C	-6.192878000	4.710951000	0.182340000
H	-6.796368000	5.620705000	0.227132000
C	-5.417007000	4.342149000	1.282971000
H	-5.423681000	4.966274000	2.178802000
C	-4.635098000	3.179202000	1.256610000
C	-0.040932000	-0.327807000	-2.749739000
Rh	-0.105267000	-0.330868000	-0.490486000
N	3.208284000	-0.149161000	-0.041645000
N	4.068775000	0.872996000	-0.015922000
N	3.348689000	1.912091000	-0.369257000
N	-3.218112000	-0.733551000	0.187853000
N	-4.268587000	0.072095000	0.353665000
N	-3.824906000	1.257997000	-0.009959000
H	0.754287000	2.500855000	-2.058838000
C	0.059758000	-1.516035000	-3.180961000
N	-0.258218000	1.865660000	-0.332642000
C	-1.592679000	2.303842000	-0.819978000
H	-1.543914000	2.373185000	-1.918769000
H	-1.887096000	3.293404000	-0.435654000
H	-0.207585000	2.020824000	0.676483000
S	-0.328747000	-2.626090000	-1.020484000
C	0.640198000	-3.748788000	-0.050104000
C	1.105528000	-3.413688000	1.231651000
C	0.817615000	-5.063345000	-0.523747000
C	1.693018000	-4.387143000	2.040129000
C	1.425750000	-6.025787000	0.284942000
C	1.856984000	-5.696120000	1.574769000
H	0.994119000	-2.390263000	1.586591000
H	0.456814000	-5.332073000	-1.519960000
H	2.042120000	-4.113291000	3.038506000
H	1.555969000	-7.043225000	-0.093538000
H	2.327861000	-6.451768000	2.208038000
H	-0.096006000	-0.506072000	1.074689000
H	-0.074577000	0.591832000	-3.339802000
C	0.111562000	-2.641016000	-4.112002000
H	0.944804000	-3.320139000	-3.891055000
H	-0.825831000	-3.216848000	-4.092473000
H	0.252602000	-2.232364000	-5.129980000

C	-5.460755000	1.897793000	-2.316757000
C	-4.869195000	2.657510000	-3.516010000
C	-6.873933000	1.372775000	-2.618082000
H	-4.825161000	1.016406000	-2.144734000
H	-3.839791000	2.994016000	-3.311610000
H	-4.846277000	2.009923000	-4.406715000
H	-5.469081000	3.547747000	-3.764082000
H	-7.277124000	0.806877000	-1.764571000
H	-7.571426000	2.195537000	-2.841787000
H	-6.853109000	0.703458000	-3.492391000
C	-3.787057000	2.776246000	2.458987000
C	-4.624644000	2.696467000	3.745053000
C	-2.584360000	3.720249000	2.638042000
H	-3.389902000	1.766303000	2.277447000
H	-5.474948000	2.009229000	3.622624000
H	-4.006448000	2.329791000	4.579024000
H	-5.019905000	3.682723000	4.034824000
H	-1.951197000	3.754694000	1.737349000
H	-2.915046000	4.750555000	2.845225000
H	-1.955806000	3.391530000	3.481104000
C	-3.970456000	-2.607974000	-1.856890000
C	-5.429249000	-2.143172000	-2.026877000
C	-3.605468000	-3.677092000	-2.894224000
H	-3.314823000	-1.744050000	-2.053170000
H	-5.684319000	-1.342082000	-1.317955000
H	-5.601100000	-1.766685000	-3.048488000
H	-6.123707000	-2.980706000	-1.851512000
H	-2.586069000	-4.054621000	-2.724235000
H	-4.299558000	-4.532144000	-2.867069000
H	-3.656120000	-3.250763000	-3.908563000
C	-2.604507000	-1.417777000	2.913497000
C	-1.500439000	-1.900200000	3.863958000
C	-3.837308000	-0.920197000	3.689510000
H	-2.185155000	-0.562884000	2.360803000
H	-0.646893000	-2.310411000	3.304965000
H	-1.139882000	-1.060271000	4.479000000
H	-1.861713000	-2.677188000	4.556128000
H	-4.597303000	-0.507400000	3.009262000
H	-4.299747000	-1.746727000	4.252865000
H	-3.553904000	-0.135117000	4.408512000
C	4.793843000	2.898156000	-2.666866000
C	6.153990000	2.183352000	-2.552969000
C	4.679714000	3.677245000	-3.983781000
H	4.014627000	2.118665000	-2.684808000
H	6.214032000	1.587704000	-1.630195000
H	6.309003000	1.508814000	-3.409633000
H	6.975144000	2.918048000	-2.539932000
H	3.725948000	4.224056000	-4.051396000
H	5.497477000	4.405271000	-4.102720000
H	4.739219000	2.982999000	-4.836251000
C	2.981563000	3.371078000	2.100406000
C	1.701295000	4.145681000	2.457701000
C	3.932405000	3.273319000	3.305415000
H	2.676616000	2.343386000	1.855003000
H	1.002622000	4.197299000	1.606753000
H	1.179948000	3.657412000	3.296401000

H	1.925326000	5.180470000	2.760975000
H	4.834549000	2.695952000	3.053303000
H	4.252790000	4.270272000	3.646627000
H	3.430454000	2.773953000	4.149163000
C	3.558477000	-2.225548000	-2.034828000
C	3.455426000	-3.529071000	-2.834027000
C	4.563701000	-1.276105000	-2.716292000
H	2.564906000	-1.750541000	-2.060101000
H	2.737959000	-4.227660000	-2.379102000
H	3.127237000	-3.308564000	-3.860942000
H	4.429266000	-4.037398000	-2.915802000
H	4.651275000	-0.311954000	-2.199543000
H	5.568308000	-1.728776000	-2.738370000
H	4.257785000	-1.076576000	-3.756024000
C	3.821998000	-0.454266000	2.775182000
C	4.716406000	-0.534891000	4.018000000
C	2.337079000	-0.407072000	3.181736000
H	4.063706000	0.498545000	2.283863000
H	5.781539000	-0.608059000	3.750034000
H	4.580333000	0.370116000	4.629755000
H	4.462453000	-1.397608000	4.654451000
H	1.672493000	-0.278315000	2.315863000
H	2.042449000	-1.339440000	3.689736000
H	2.156504000	0.427517000	3.879186000

TS2-iso: E= -3339.231284

C	-1.946211000	-0.194734000	-0.077858000
C	-2.067254000	-1.588377000	-0.080623000
C	-0.924917000	-2.549525000	-0.006810000
H	-1.172344000	-3.437565000	0.599509000
C	2.512715000	-1.196954000	0.269906000
C	2.095008000	0.118282000	0.073518000
C	-3.829126000	1.512023000	0.105551000
C	-3.864503000	2.367610000	-1.009382000
C	-4.417844000	3.640384000	-0.816562000
H	-4.450894000	4.348190000	-1.644497000
C	-4.931532000	4.016024000	0.422340000
H	-5.353264000	5.015121000	0.552668000
C	-4.910185000	3.129775000	1.498763000
H	-5.323197000	3.448020000	2.456002000
C	-4.352778000	1.851814000	1.371719000
C	-3.979913000	-3.209541000	-0.173466000
C	-4.140630000	-3.788065000	-1.446499000
C	-4.699589000	-5.072939000	-1.490136000
H	-4.848926000	-5.561393000	-2.455352000
C	-5.074109000	-5.731500000	-0.318076000
H	-5.512570000	-6.730633000	-0.375062000
C	-4.897277000	-5.124615000	0.926719000
H	-5.203312000	-5.653364000	1.831425000
C	-4.338518000	-3.843435000	1.030794000
C	3.451104000	2.226157000	-0.089139000
C	3.782973000	2.686528000	-1.373718000
C	3.916147000	4.072486000	-1.533974000

H	4.179946000	4.481017000	-2.510739000
C	3.694684000	4.939365000	-0.464815000
H	3.792182000	6.017718000	-0.612815000
C	3.332101000	4.445364000	0.789770000
H	3.139995000	5.144684000	1.603913000
C	3.198925000	3.069210000	1.008930000
C	4.741726000	-2.307657000	0.578537000
C	5.222565000	-2.987707000	-0.556658000
C	6.035036000	-4.106066000	-0.324307000
H	6.433860000	-4.666495000	-1.172395000
C	6.347646000	-4.508957000	0.974988000
H	6.985222000	-5.382251000	1.132037000
C	5.859237000	-3.802615000	2.075024000
H	6.122769000	-4.126651000	3.083959000
C	5.039750000	-2.678276000	1.903180000
C	0.190436000	-0.012115000	-2.425564000
Rh	0.094217000	0.327917000	-0.095806000
N	-3.269604000	0.187788000	-0.057141000
N	-4.141072000	-0.820885000	-0.095876000
N	-3.389700000	-1.897302000	-0.102946000
N	3.279198000	0.804717000	0.091488000
N	4.354626000	0.039072000	0.268237000
N	3.867897000	-1.180282000	0.374614000
H	-0.647582000	-2.909328000	-1.008368000
C	-0.110967000	1.146047000	-2.825402000
N	0.215683000	-1.780059000	0.542101000
C	1.570734000	-2.357206000	0.330583000
H	1.571751000	-2.908776000	-0.621613000
H	1.840871000	-3.079701000	1.118417000
H	0.070220000	-1.658009000	1.544703000
S	0.258512000	2.544936000	-0.931434000
C	-0.741102000	3.744306000	-0.089687000
C	-1.306483000	3.510389000	1.173013000
C	-0.843529000	5.028964000	-0.660902000
C	-1.930186000	4.550058000	1.865139000
C	-1.483721000	6.057409000	0.031394000
C	-2.024146000	5.826156000	1.302120000
H	-1.241769000	2.514598000	1.607325000
H	-0.396818000	5.222228000	-1.639613000
H	-2.361128000	4.353284000	2.849834000
H	-1.553735000	7.049779000	-0.421999000
H	-2.522542000	6.633195000	1.844367000
H	0.041255000	0.729084000	1.420615000
H	-0.372128000	1.941514000	-3.504703000
C	4.888433000	-2.547294000	-1.977171000
C	4.022313000	-3.594675000	-2.698196000
C	6.159824000	-2.227372000	-2.779785000
H	4.301948000	-1.617772000	-1.921113000
H	3.103036000	-3.819863000	-2.134560000
H	3.730502000	-3.231909000	-3.696377000
H	4.568390000	-4.542264000	-2.829993000
H	6.767188000	-1.462650000	-2.273926000
H	6.783929000	-3.124032000	-2.919101000
H	5.894025000	-1.847610000	-3.778630000
C	4.518129000	-1.900063000	3.105059000
C	5.673863000	-1.262342000	3.893748000

C	3.633125000	-2.777486000	4.005733000
H	3.889841000	-1.074872000	2.737792000
H	6.279781000	-0.608724000	3.248144000
H	5.280543000	-0.654645000	4.723483000
H	6.338574000	-2.029705000	4.321376000
H	2.791949000	-3.213226000	3.442019000
H	4.204552000	-3.608908000	4.447863000
H	3.218536000	-2.180441000	4.833265000
C	3.984624000	1.727770000	-2.540530000
C	5.476141000	1.390568000	-2.713468000
C	3.371343000	2.247281000	-3.848342000
H	3.453506000	0.792832000	-2.298402000
H	5.892162000	0.950874000	-1.794911000
H	5.621359000	0.673638000	-3.536964000
H	6.052942000	2.299925000	-2.947615000
H	2.316472000	2.524625000	-3.705696000
H	3.911773000	3.125272000	-4.235682000
H	3.421499000	1.466610000	-4.623978000
C	2.813937000	2.497425000	2.367806000
C	1.937492000	3.439622000	3.201116000
C	4.071544000	2.067190000	3.146976000
H	2.208560000	1.597826000	2.177877000
H	1.059457000	3.777728000	2.630645000
H	1.580474000	2.916743000	4.102532000
H	2.493235000	4.327978000	3.541490000
H	4.688123000	1.364023000	2.567722000
H	4.697786000	2.942420000	3.384437000
H	3.794430000	1.579723000	4.095947000
C	-3.748953000	-3.061550000	-2.727802000
C	-4.985278000	-2.756026000	-3.589900000
C	-2.686167000	-3.841944000	-3.519204000
H	-3.303579000	-2.092597000	-2.456398000
H	-5.726991000	-2.171677000	-3.024741000
H	-4.697251000	-2.174319000	-4.479608000
H	-5.472048000	-3.682566000	-3.933626000
H	-1.800456000	-4.060139000	-2.900858000
H	-3.079219000	-4.803658000	-3.885082000
H	-2.357092000	-3.260527000	-4.394669000
C	-4.169100000	-3.165547000	2.384563000
C	-3.420153000	-4.050644000	3.393038000
C	-5.532598000	-2.710122000	2.933094000
H	-3.558481000	-2.260768000	2.240020000
H	-2.443700000	-4.374601000	2.998177000
H	-3.245091000	-3.495315000	4.327958000
H	-3.993713000	-4.954542000	3.651596000
H	-6.040100000	-2.036636000	2.226110000
H	-6.192127000	-3.574362000	3.111584000
H	-5.405788000	-2.175518000	3.887471000
C	-3.392826000	1.892589000	-2.376715000
C	-2.944338000	3.030792000	-3.298169000
C	-4.481131000	1.035277000	-3.052947000
H	-2.516179000	1.249671000	-2.213488000
H	-2.187173000	3.662836000	-2.810794000
H	-2.514503000	2.616685000	-4.223915000
H	-3.786210000	3.673300000	-3.600964000
H	-4.789161000	0.190072000	-2.420215000

H	-5.378835000	1.639781000	-3.261277000
H	-4.113589000	0.629584000	-4.009720000
C	-4.295848000	0.888221000	2.555955000
C	-5.390771000	1.135572000	3.600849000
C	-2.906236000	0.890848000	3.220775000
H	-4.470648000	-0.122230000	2.160220000
H	-6.390832000	1.169941000	3.142324000
H	-5.384425000	0.324373000	4.345020000
H	-5.231887000	2.077720000	4.149052000
H	-2.106705000	0.641066000	2.508989000
H	-2.680366000	1.882265000	3.645159000
H	-2.875221000	0.157382000	4.043248000
C	0.501479000	-1.334571000	-3.047172000
H	-0.339243000	-2.031614000	-2.906149000
H	0.679324000	-1.252530000	-4.131588000
H	1.392996000	-1.795044000	-2.594529000

INT3: E= -3339.258024

C	1.914500000	0.221303000	-0.371673000
C	1.998954000	1.586173000	-0.670869000
C	0.839494000	2.416850000	-1.104303000
H	0.970405000	3.485659000	-0.868238000
C	-2.585594000	1.127750000	-0.470981000
C	-2.119818000	-0.167506000	-0.257027000
C	3.811212000	-1.279862000	0.465596000
C	4.122077000	-2.247096000	-0.512587000
C	4.805266000	-3.389980000	-0.076511000
H	5.062609000	-4.172669000	-0.789119000
C	5.164408000	-3.546461000	1.260624000
H	5.698099000	-4.446501000	1.575291000
C	4.839364000	-2.571610000	2.202018000
H	5.126763000	-2.720103000	3.242991000
C	4.153144000	-1.407911000	1.828717000
C	3.729947000	3.368719000	-0.350612000
C	4.389171000	3.896416000	-1.475512000
C	4.800382000	5.233889000	-1.394441000
H	5.323648000	5.689316000	-2.236618000
C	4.554901000	5.991806000	-0.247509000
H	4.884824000	7.032615000	-0.206882000
C	3.896476000	5.432639000	0.848382000
H	3.718622000	6.039859000	1.738555000
C	3.464912000	4.098966000	0.824233000
C	-3.312059000	-2.170816000	0.670257000
C	-3.692789000	-3.139082000	-0.277332000
C	-3.749394000	-4.466865000	0.164300000
H	-4.040470000	-5.256860000	-0.528946000
C	-3.416916000	-4.798989000	1.479000000
H	-3.460961000	-5.842430000	1.800633000
C	-3.013595000	-3.814943000	2.381523000
H	-2.744503000	-4.098074000	3.400190000
C	-2.948590000	-2.468726000	1.994932000
C	-4.739996000	2.320003000	-0.024310000
C	-5.531783000	2.603182000	-1.151172000
C	-6.307611000	3.769969000	-1.099403000

H	-6.941715000	4.032427000	-1.948866000
C	-6.279723000	4.599012000	0.022687000
H	-6.889145000	5.505752000	0.040778000
C	-5.487295000	4.277732000	1.126768000
H	-5.487615000	4.935945000	1.997959000
C	-4.697259000	3.120122000	1.134421000
C	0.036807000	-0.748916000	-2.528929000
Rh	-0.122505000	-0.349882000	-0.413629000
N	3.202410000	-0.040502000	0.033839000
N	4.018504000	1.020473000	0.021808000
N	3.258833000	2.006334000	-0.394710000
N	-3.226850000	-0.796466000	0.241735000
N	-4.298300000	-0.007460000	0.362551000
N	-3.880676000	1.165251000	-0.068823000
H	0.687175000	2.320398000	-2.191123000
C	0.082575000	-2.085442000	-2.615403000
N	-0.332727000	1.819202000	-0.433516000
C	-1.670079000	2.198699000	-0.960468000
H	-1.615247000	2.178166000	-2.061126000
H	-1.975678000	3.211615000	-0.653220000
H	-0.296828000	2.047728000	0.561736000
S	-0.360065000	-2.640743000	-0.918916000
C	0.821651000	-3.789096000	-0.215273000
C	1.341081000	-3.514582000	1.055779000
C	1.038147000	-5.035815000	-0.819843000
C	2.069462000	-4.498420000	1.727079000
C	1.800496000	-5.999139000	-0.153590000
C	2.307289000	-5.736890000	1.123682000
H	1.165602000	-2.538521000	1.509210000
H	0.599120000	-5.263131000	-1.793119000
H	2.469492000	-4.284585000	2.719770000
H	1.980647000	-6.966871000	-0.628202000
H	2.889408000	-6.498620000	1.647622000
H	-0.131397000	-0.344443000	1.212730000
H	0.151545000	-0.159685000	-3.452886000
C	0.220372000	-3.064919000	-3.737629000
H	1.069844000	-3.748604000	-3.589222000
H	-0.687603000	-3.681338000	-3.850572000
H	0.386767000	-2.518881000	-4.679514000
C	-5.556485000	1.696254000	-2.375104000
C	-4.998481000	2.414550000	-3.615185000
C	-6.966172000	1.137018000	-2.627212000
H	-4.902961000	0.833376000	-2.177417000
H	-3.970441000	2.772978000	-3.443930000
H	-4.981877000	1.731154000	-4.478838000
H	-5.615941000	3.285238000	-3.888438000
H	-7.344573000	0.602414000	-1.742670000
H	-7.681167000	1.938382000	-2.872817000
H	-6.950358000	0.430795000	-3.472128000
C	-3.831918000	2.765393000	2.340097000
C	-4.646099000	2.752203000	3.643337000
C	-2.616803000	3.703162000	2.453363000
H	-3.446749000	1.744488000	2.200312000
H	-5.503969000	2.067441000	3.567858000
H	-4.014918000	2.418124000	4.481344000
H	-5.028422000	3.753587000	3.895887000

H	-1.993537000	3.678290000	1.545419000
H	-2.932391000	4.747593000	2.606285000
H	-1.981728000	3.412706000	3.305281000
C	-4.014066000	-2.748818000	-1.715174000
C	-5.488027000	-2.323595000	-1.857180000
C	-3.657005000	-3.842764000	-2.729247000
H	-3.386988000	-1.875565000	-1.959763000
H	-5.741174000	-1.504337000	-1.169029000
H	-5.696362000	-1.986636000	-2.885631000
H	-6.156602000	-3.170809000	-1.634274000
H	-2.624951000	-4.195921000	-2.584965000
H	-4.330973000	-4.710703000	-2.652293000
H	-3.747617000	-3.450491000	-3.754102000
C	-2.544003000	-1.373863000	2.973951000
C	-1.390460000	-1.790071000	3.895429000
C	-3.768927000	-0.894638000	3.773422000
H	-2.171354000	-0.524376000	2.382711000
H	-0.533582000	-2.159333000	3.312456000
H	-1.050994000	-0.925216000	4.487084000
H	-1.690106000	-2.575147000	4.607812000
H	-4.562627000	-0.530979000	3.103069000
H	-4.186058000	-1.715663000	4.378832000
H	-3.491425000	-0.075204000	4.455596000
C	4.703873000	3.029543000	-2.686957000
C	6.116051000	2.430178000	-2.546283000
C	4.539011000	3.768223000	-4.021720000
H	3.990787000	2.189028000	-2.692831000
H	6.216087000	1.865197000	-1.607583000
H	6.331235000	1.748095000	-3.383716000
H	6.875899000	3.228249000	-2.547188000
H	3.543196000	4.230415000	-4.109828000
H	5.293230000	4.560779000	-4.148490000
H	4.666137000	3.064019000	-4.858484000
C	2.752243000	3.488160000	2.027150000
C	1.423217000	4.203596000	2.325372000
C	3.666152000	3.460056000	3.263558000
H	2.506292000	2.441541000	1.794786000
H	0.757479000	4.211772000	1.446667000
H	0.892879000	3.701380000	3.149937000
H	1.584962000	5.252189000	2.620853000
H	4.602895000	2.922989000	3.051008000
H	3.925683000	4.477539000	3.596045000
H	3.161050000	2.950547000	4.099536000
C	3.770440000	-2.037206000	-1.982901000
C	3.759357000	-3.334704000	-2.799007000
C	4.719790000	-1.017632000	-2.642129000
H	2.749352000	-1.625122000	-2.016143000
H	3.123703000	-4.101394000	-2.333378000
H	3.375114000	-3.132440000	-3.810007000
H	4.772270000	-3.752128000	-2.915932000
H	4.742442000	-0.058859000	-2.109961000
H	5.750863000	-1.406391000	-2.659705000
H	4.411484000	-0.823265000	-3.682038000
C	3.772204000	-0.347046000	2.859592000
C	4.683354000	-0.330183000	4.092853000
C	2.296420000	-0.490091000	3.273943000

H	3.888373000	0.633150000	2.375653000
H	5.747004000	-0.277570000	3.813925000
H	4.449503000	0.548658000	4.713367000
H	4.537512000	-1.220845000	4.724678000
H	1.613187000	-0.408663000	2.416151000
H	2.119843000	-1.466462000	3.754448000
H	2.023842000	0.294668000	3.998989000

INT3-iso: E= -3339.258660

C	-1.907246000	-0.216475000	-0.304575000
C	-1.989885000	-1.597616000	-0.517041000
C	-0.829223000	-2.463143000	-0.870082000
H	-0.959074000	-3.505722000	-0.536596000
C	2.592288000	-1.109419000	-0.375850000
C	2.125442000	0.192804000	-0.207362000
C	-3.829392000	1.354290000	0.305648000
C	-4.065694000	2.235467000	-0.769309000
C	-4.754855000	3.419257000	-0.476217000
H	-4.953400000	4.140334000	-1.268780000
C	-5.198429000	3.688621000	0.817219000
H	-5.737697000	4.616757000	1.020955000
C	-4.950802000	2.792198000	1.856180000
H	-5.304595000	3.030580000	2.859312000
C	-4.254634000	1.597663000	1.628626000
C	-3.747156000	-3.344815000	-0.164716000
C	-4.377184000	-3.934452000	-1.275268000
C	-4.799535000	-5.262808000	-1.127673000
H	-5.301902000	-5.764467000	-1.956286000
C	-4.590359000	-5.953117000	0.067992000
H	-4.927536000	-6.988280000	0.160310000
C	-3.959399000	-5.333493000	1.147643000
H	-3.810748000	-5.888463000	2.076391000
C	-3.519945000	-4.005353000	1.058501000
C	3.350364000	2.243744000	0.569782000
C	3.704445000	3.156965000	-0.440238000
C	3.795863000	4.504275000	-0.070062000
H	4.070525000	5.253110000	-0.813955000
C	3.519969000	4.907174000	1.237907000
H	3.592022000	5.964458000	1.504589000
C	3.135490000	3.976504000	2.203361000
H	2.908210000	4.315824000	3.215298000
C	3.036712000	2.613550000	1.888771000
C	4.774835000	-2.266358000	0.032983000
C	5.531113000	-2.589620000	-1.107772000
C	6.325493000	-3.742455000	-1.031474000
H	6.933259000	-4.034648000	-1.890416000
C	6.350769000	-4.519815000	0.127157000
H	6.975433000	-5.415535000	0.164245000
C	5.591199000	-4.161004000	1.242447000
H	5.631639000	-4.778930000	2.141931000
C	4.782904000	-3.016069000	1.225544000
C	-0.052277000	0.731186000	-2.471738000
Rh	0.121106000	0.365781000	-0.341261000

N	-3.211807000	0.079783000	0.014584000
N	-4.035299000	-0.974470000	0.035663000
N	-3.265257000	-1.990472000	-0.275374000
N	3.247883000	0.849258000	0.217199000
N	4.329023000	0.072751000	0.331333000
N	3.903342000	-1.120966000	-0.027924000
H	-0.681177000	-2.474777000	-1.961278000
C	-0.078211000	2.071865000	-2.532917000
N	0.343322000	-1.806413000	-0.260572000
C	1.674280000	-2.213018000	-0.779437000
H	1.604753000	-2.270437000	-1.877983000
H	1.989507000	-3.201517000	-0.408596000
H	0.321132000	-1.960287000	0.749513000
S	0.346623000	2.653036000	-0.876770000
C	-0.873489000	3.812685000	-0.264039000
C	-1.392276000	3.627461000	1.021825000
C	-1.125359000	4.994018000	-0.974581000
C	-2.158114000	4.640317000	1.603026000
C	-1.917767000	5.987949000	-0.394266000
C	-2.425274000	5.817664000	0.898097000
H	-1.192521000	2.697574000	1.555012000
H	-0.695052000	5.143739000	-1.967672000
H	-2.563924000	4.497080000	2.606297000
H	-2.125416000	6.905638000	-0.949987000
H	-3.034497000	6.601863000	1.353452000
H	0.131274000	0.397916000	1.290682000
H	-0.198301000	2.773936000	-3.368265000
C	5.499486000	-1.740791000	-2.372469000
C	4.895052000	-2.520562000	-3.552168000
C	6.893335000	-1.188456000	-2.712241000
H	4.849942000	-0.872145000	-2.188577000
H	3.881539000	-2.883979000	-3.317599000
H	4.829371000	-1.877564000	-4.444009000
H	5.511649000	-3.395348000	-3.813897000
H	7.306128000	-0.609086000	-1.872493000
H	7.601855000	-1.998103000	-2.949149000
H	6.836508000	-0.525350000	-3.589729000
C	3.954934000	-2.622182000	2.444795000
C	4.832271000	-2.467624000	3.697382000
C	2.805258000	-3.616436000	2.686915000
H	3.502746000	-1.637431000	2.253327000
H	5.637635000	-1.737106000	3.529118000
H	4.225218000	-2.117136000	4.546383000
H	5.293488000	-3.423714000	3.990632000
H	2.148575000	-3.703813000	1.806342000
H	3.190269000	-4.623821000	2.911724000
H	2.186916000	-3.293041000	3.539415000
C	3.961903000	2.690247000	-1.867784000
C	5.437867000	2.294077000	-2.059312000
C	3.517260000	3.710582000	-2.923286000
H	3.348077000	1.789187000	-2.028560000
H	5.743901000	1.521041000	-1.339322000
H	5.606737000	1.904757000	-3.076404000
H	6.093686000	3.167982000	-1.915651000
H	2.476896000	4.027271000	-2.753373000
H	4.156445000	4.607829000	-2.925703000

H	3.580756000	3.263240000	-3.927491000
C	2.641789000	1.578475000	2.934214000
C	1.507670000	2.059119000	3.848999000
C	3.875267000	1.130943000	3.738199000
H	2.249911000	0.700753000	2.399364000
H	0.646918000	2.407188000	3.258260000
H	1.167461000	1.232181000	4.492233000
H	1.826685000	2.878566000	4.512456000
H	4.651203000	0.716902000	3.076205000
H	4.314705000	1.980116000	4.286233000
H	3.600369000	0.357206000	4.472790000
C	-4.648515000	-3.140761000	-2.545563000
C	-6.073462000	-2.557812000	-2.502315000
C	-4.409455000	-3.949604000	-3.827488000
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H	-4.515006000	-3.297376000	-4.708291000
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C	-3.801478000	-3.216440000	3.444145000
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H	-1.033773000	-3.481480000	3.453043000
H	-1.702509000	-5.057609000	2.970584000
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C	-3.643648000	1.881246000	-2.191801000
C	-3.476077000	3.096419000	-3.109171000
C	-4.624404000	0.872210000	-2.819648000
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H	-2.825824000	3.856828000	-2.655591000
H	-3.020618000	2.780711000	-4.060549000
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H	-4.739915000	-0.031372000	-2.207441000
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H	-4.273559000	0.566504000	-3.818766000
C	-3.947208000	0.621866000	2.762679000
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H	-4.780008000	1.668191000	4.505855000
H	-1.769528000	0.616183000	2.415513000
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H	-2.264884000	0.027708000	4.020735000
C	-0.282487000	-0.143319000	-3.666331000
H	-1.207579000	-0.731714000	-3.523715000
H	-0.388545000	0.418272000	-4.613182000
H	0.534081000	-0.875361000	-3.795282000

S4 References

1 L. C. Tolley, I. Strydom, W. J. Louw, M. A. Fernandes, D. I. Bezuidenhout and G. Guisado-Barrios, *ACS Omega,* 2019, **4**, 6360–6374.

2 G. Kleinhans, G. Guisado-Barrios, D. C. Liles, G. Bertrand and D. I. Bezuidenhout, *Chem. Commun.,* 2016, **52**, 3504–3507.

3 I. Strydom, G. Guisado-Barrios, I. Fernández, D. C. Liles, E. Peris and D. I. Bezuidenhout, *Chem. Eur. J.,* 2017, **23**, 1393–1401.

4 A. Ogawa, T. Ikeda, K. Kimura and T. Hirao, *J. Am. Chem. Soc.,* 1999, **121**, 5108–5114.

5 L. Palacios, M. J. Artigas, V. Polo, F. J. Lahoz, R. Castarlenas, J. J. Pérez-Torrente and L. A. Oro, *ACS Catal.* 2013, **3**, 2910–2919.

6 C. Cao, L. R. Fraser and J. A. Love, *J. Am. Chem. Soc.,* 2005, **127**, 17614–17615.

7 N. Velasco, C. Virumbrales, R. Sanz, S. Suárez-Pantiga and M. A. Fernández-Rodríguez, *Org. Lett.,* 2018, **20**, 2848–2852.

8 A. Di Giuseppe, R. Castarlenas, J. J. Pérez-Torrente, M. Crucianelli, V. Polo, R. Sancho, F. J. Lahoz and L. A. Oro, *J. Am. Chem. Soc.,* 2012, **134**, 8171–8183.

9 Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

10 a) A. D. Becke, *J. Chem. Phys.,* 1993, **98**, 5648-5652; b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B* 1998, **37**, 785-789; c) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.* 1980, **58**, 1200-1211.

11 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.,* 2010, **132**, 154104.

12 F. Weigend and R. Alhrichs, *Phys. Chem. Chem. Phys*., 2005, **7**, 3297-3305.

13 a) S. Miertuš, E. Scrocco and J. Tomasi, *Chem. Phys,.* 1981, **55**, 117; b) J. L. Pascual-Ahuir, E. Silla and I. Tuñón, *J. Comp. Chem.,* 1994, **15**, 1127-1138; c) V. Barone and M. Cossi, *J. Phys. Chem. A*, 1998, **102**, 1995-2001.

14 J. W. McIver and A. K. Komornicki, *J. Am. Chem. Soc.,* 1972, **94**, 2625-2633.

15 C. González, H. B. Schlegel, *J. Phys. Chem*. 1990, **94**, 5523-5527.