

Supplementary Information

Azide Alkyne Cycloaddition Facilitated by Hexanuclear Rhenium Chalcogenide Cluster Complexes

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Alternative synthesis of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{py})](\text{BF}_4)_2$. $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5\text{I}]\text{I}$ (500.3 mg, 0.193 mmol) was dissolved in 18 mL CH_2Cl_2 in a Schlenk flask. Separately, 140.2 mg of AgBF_4 (0.720 mmol) was dissolved in 3.4 mL pyridine. The solutions were combined, covered with aluminum foil, and stirred at room temperature for 3 h. The solvent was removed in vacuo. The solid was dissolved in CH_2Cl_2 , filtered through Celite and dripped into Et_2O to afford a crude solid. This solid was purified via column chromatography on a silica gel column eluting with a 1:1 $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ solvent mixture and reduced to dryness. The product was dissolved in minimal CH_2Cl_2 and precipitated in Et_2O to afford the pure product (495.6 mg, 99% yield). ^1H NMR (500 MHz, CDCl_3 , ppm): 9.26 (2H, d, $-\text{NC}_5\text{H}_5$), 7.88 (1H, t, $-\text{NC}_5\text{H}_5$), 7.37 (2H, t, $-\text{NC}_5\text{H}_5$), 2.16 (30H, m, $-\text{CH}_2\text{CH}_3$), 1.09 (45H, m, $-\text{CH}_2\text{CH}_3$). ^{31}P NMR (202.5 MHz, CDCl_3 , ppm): -26.35, -29.33.

Figure S1. 400 MHz ^1H NMR spectrum taken at 24 h of the reaction mixture, in CDCl_3 , containing $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{L1})](\text{BF}_4)$ and BnBr (unreacted BnBr appears at 4.42 ppm).

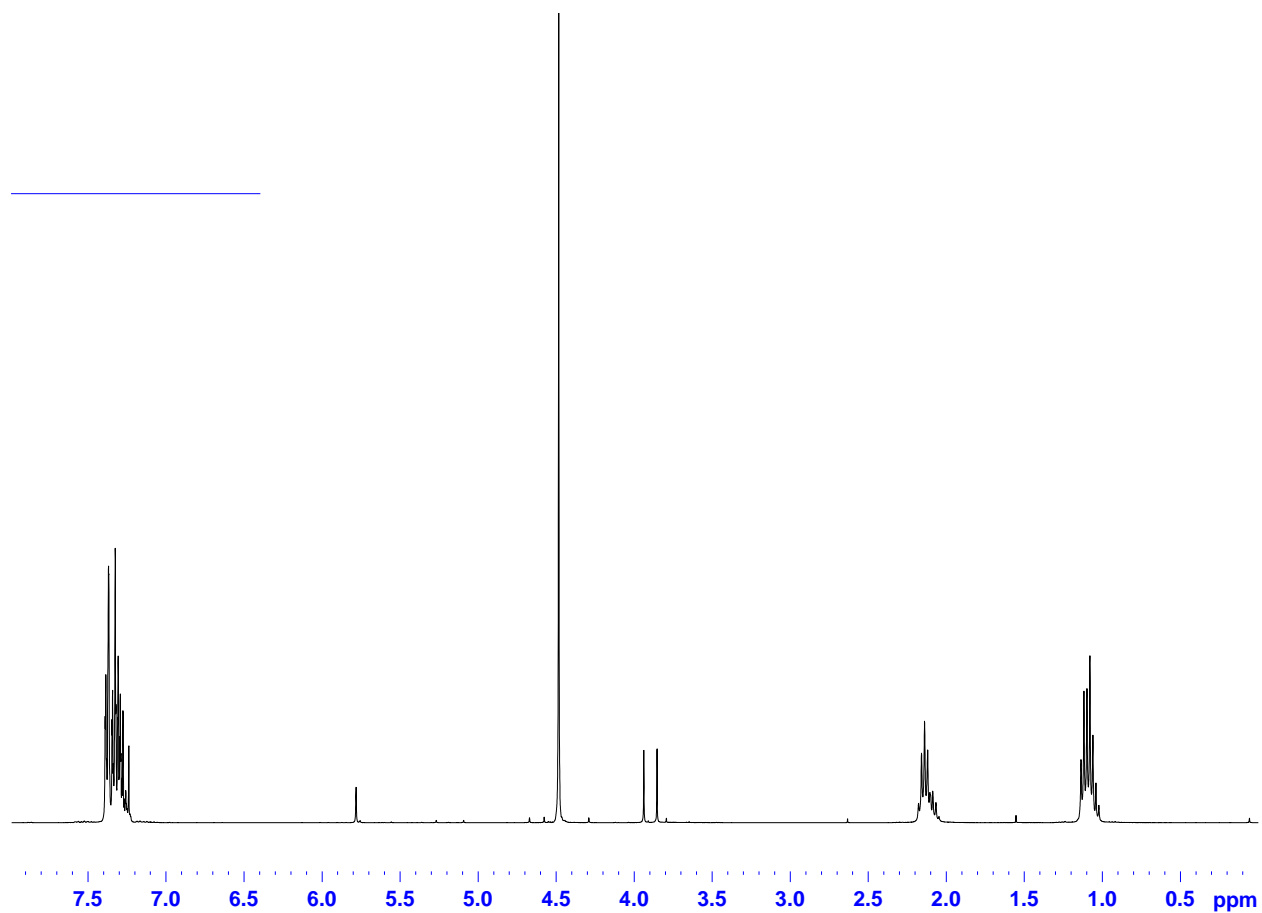


Figure S2. 162 MHz ^{31}P NMR spectra recorded at different time intervals of the reaction mixture, in CDCl_3 , containing $[\text{Re}_6\text{Se}_8(\text{PET}_3)_5(\text{L1})](\text{BF}_4)$ and BnBr .

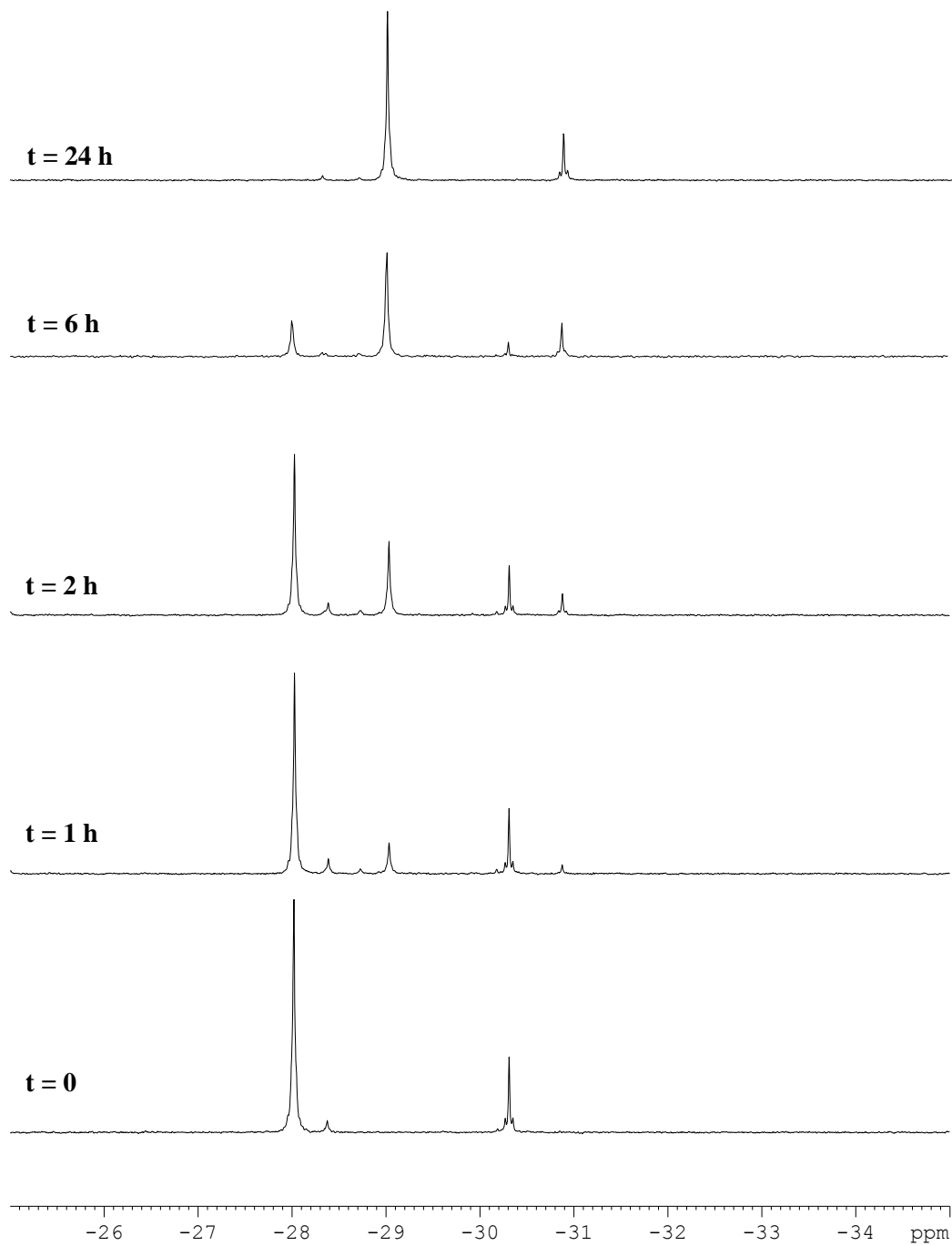


Figure S3. 400 MHz ^1H NMR spectrum taken at 24 h of the reaction mixture containing $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{L1})](\text{BF}_4)$ and MeI in CDCl_3 .

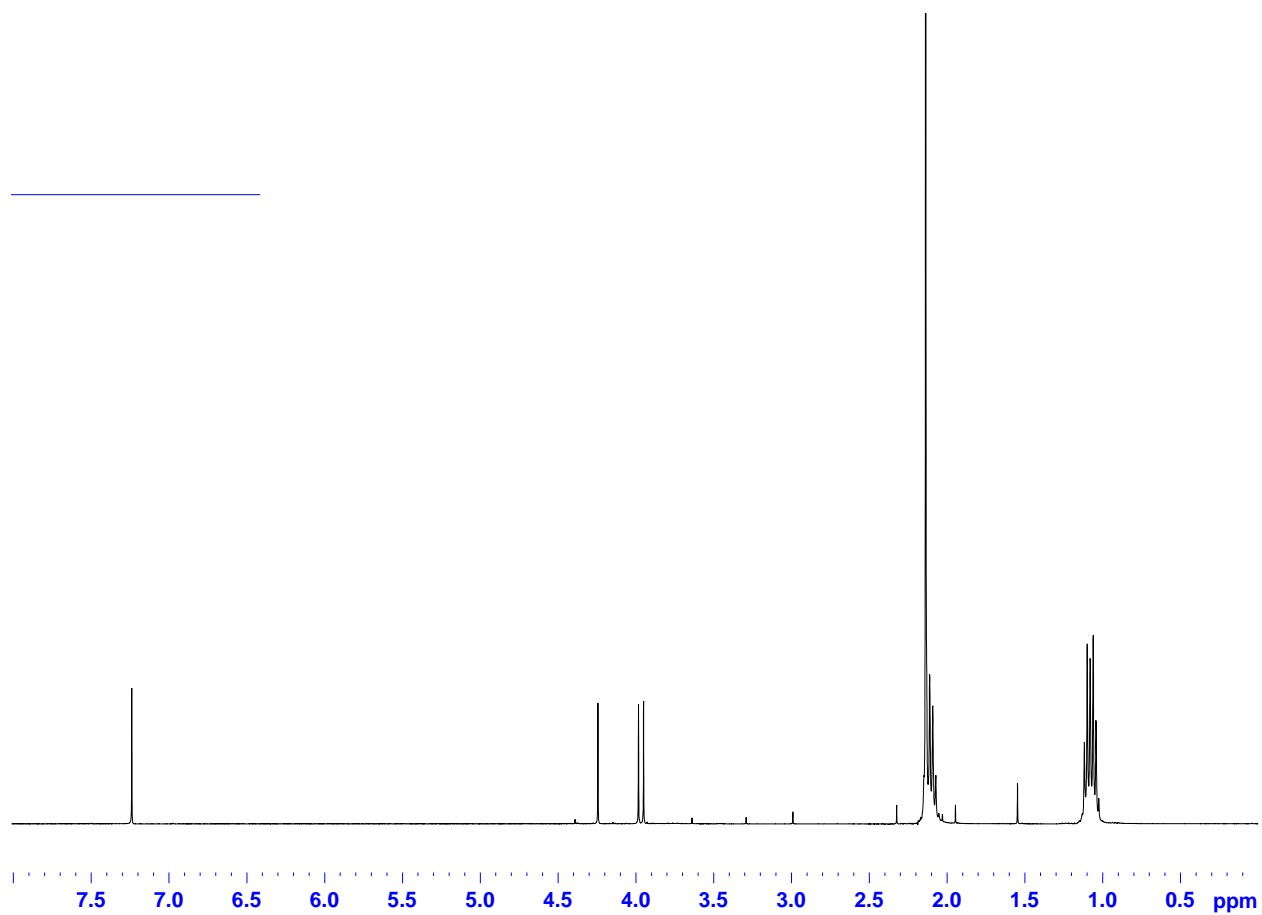


Figure S4. 162 MHz ^{31}P NMR spectra recorded in CDCl_3 at different time intervals of the reaction mixture containing $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{L1})](\text{BF}_4)$ and MeI.

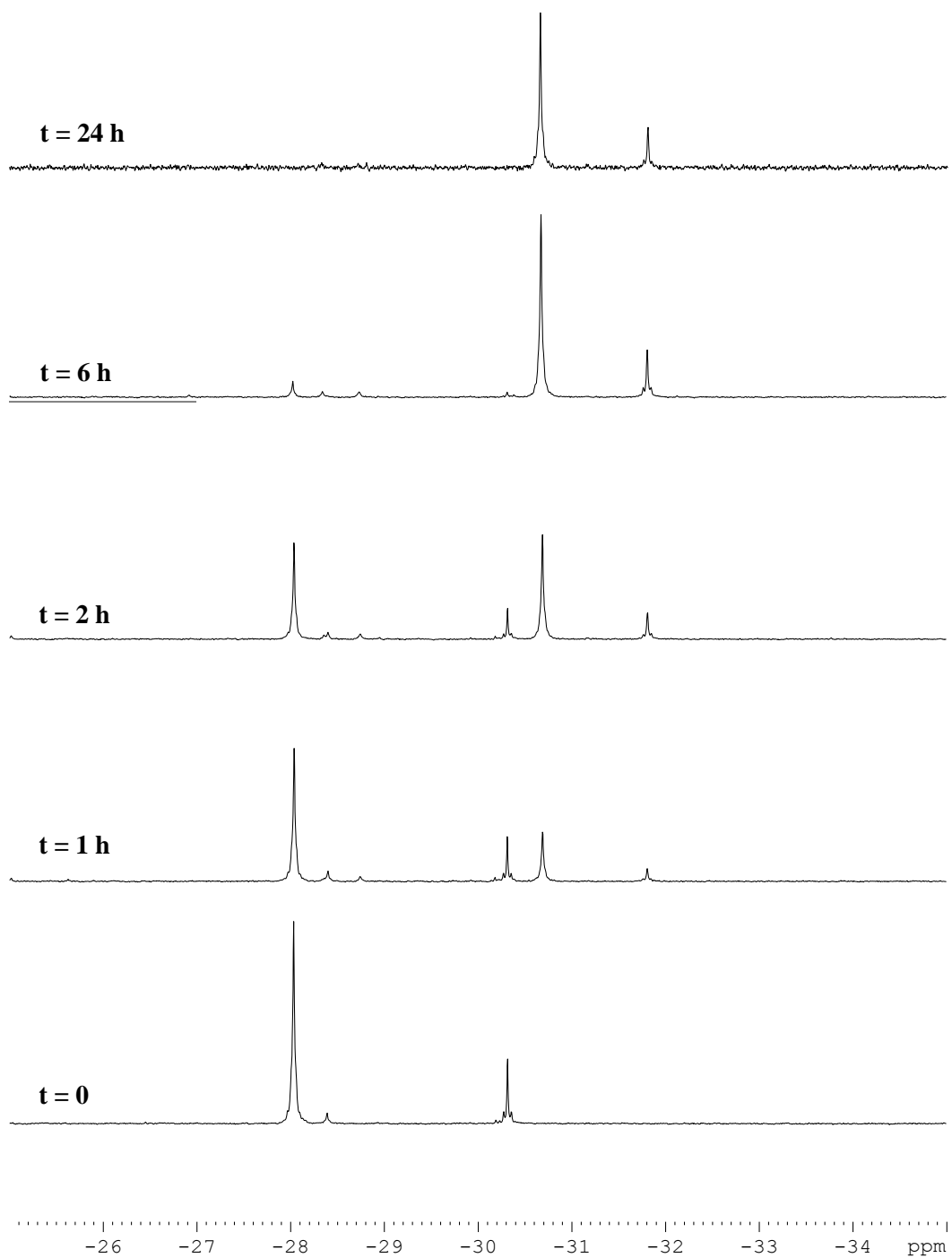


Figure S5. 400 MHz ^1H NMR spectrum (in CDCl_3) of product isolated from the 2 h (100 $^\circ\text{C}$) reaction of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{N}_3)_2]$ and DMAD.

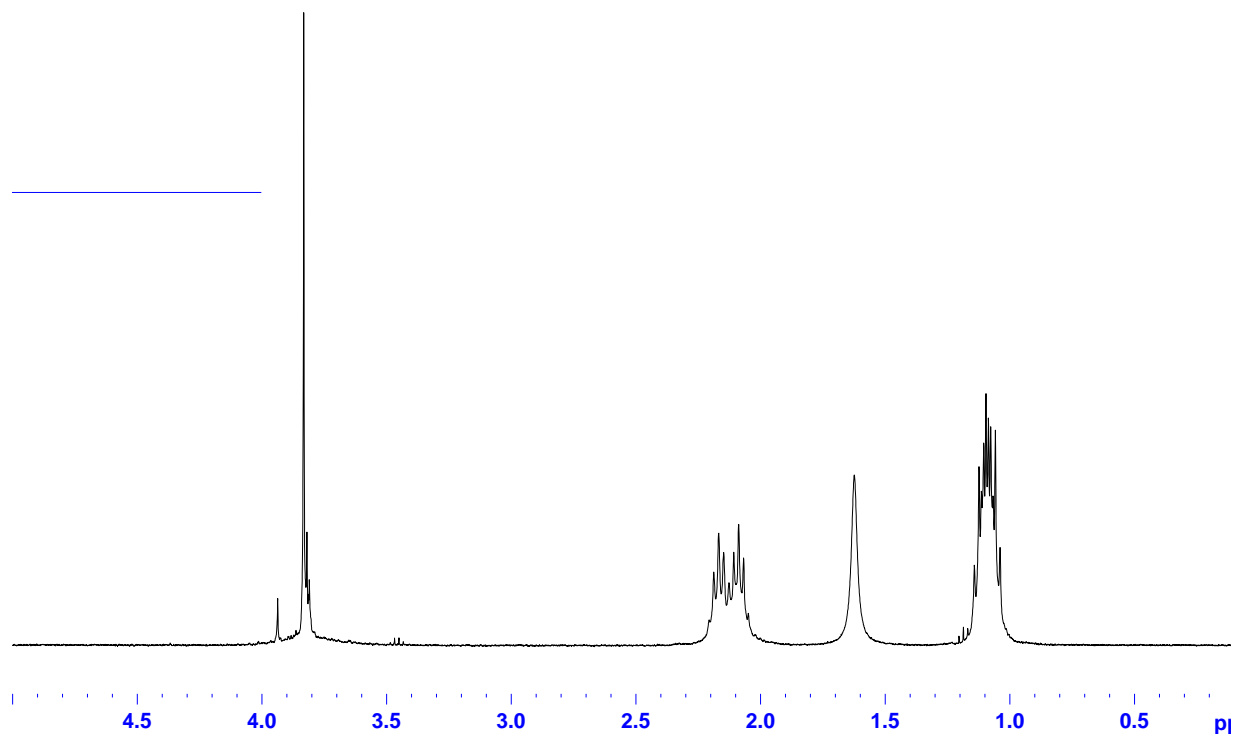


Figure S6. 162 MHz ^{31}P NMR spectrum (in CDCl_3) of product isolated from the 2 h (100 °C) reaction of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_4(\text{N}_3)_2]$ and DMAD.

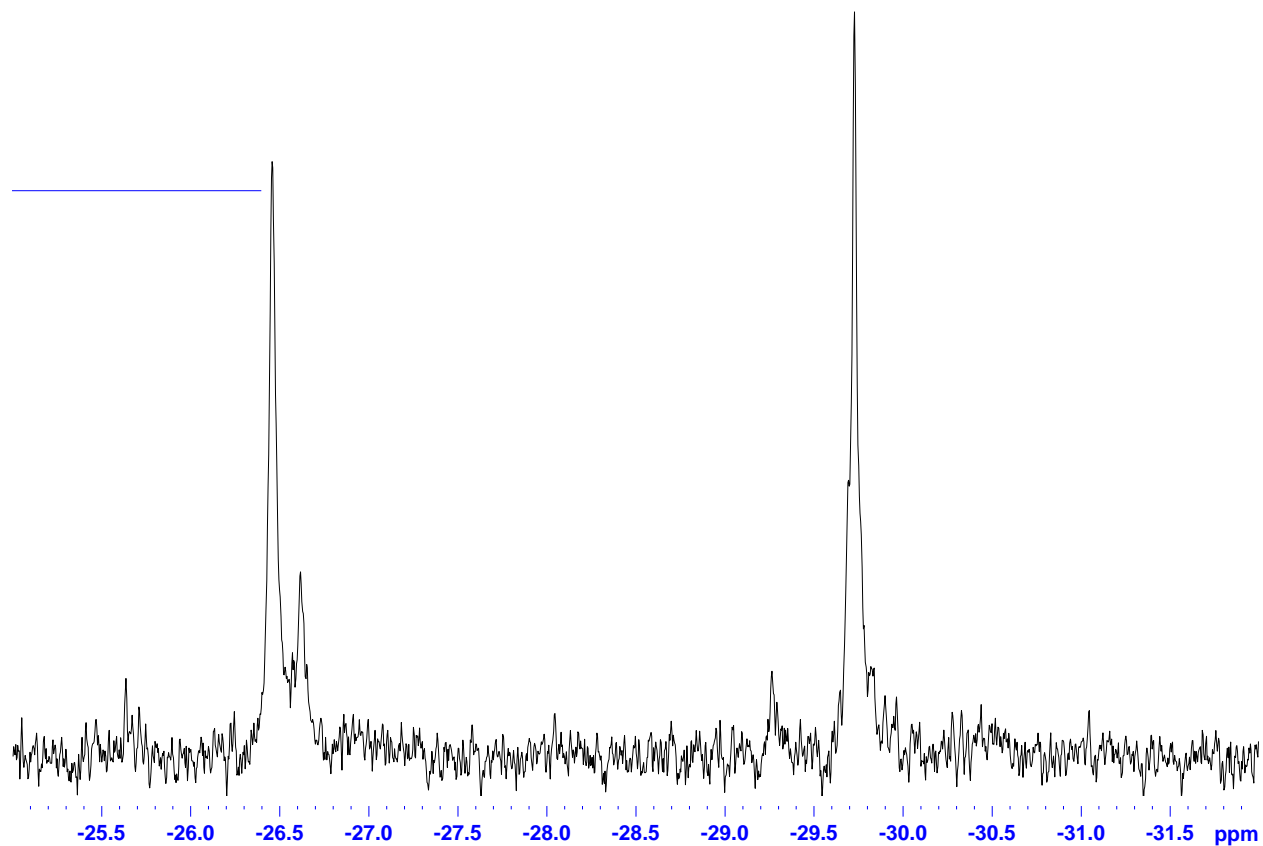


Figure S7. Ge(ATR) IR spectrum of *cis*-[Re₆Se₈(PEt₃)₄(N₃)₂].

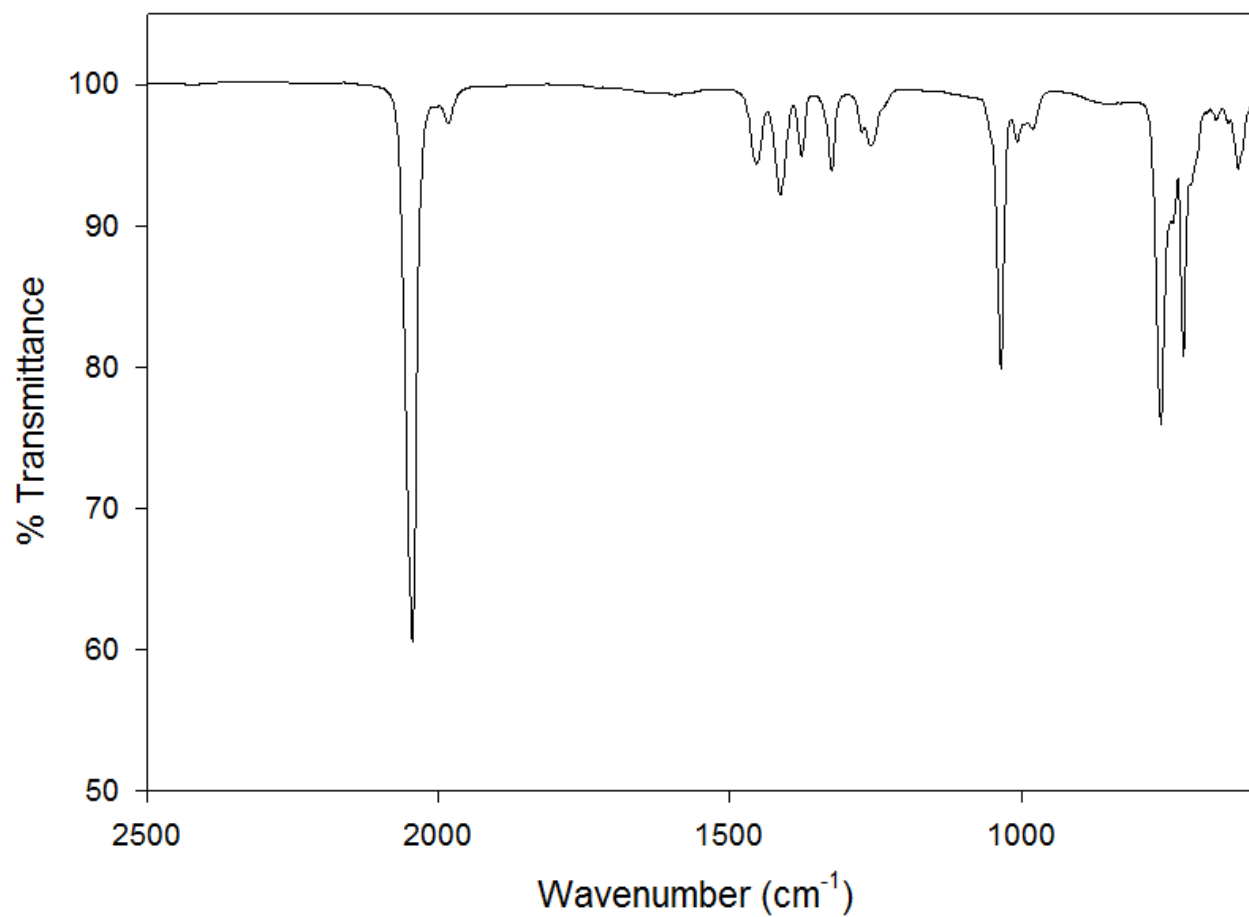


Figure S8. Ge(ATR) IR spectrum of *cis*-[Re₆Se₈(PEt₃)₄(L1)₂].

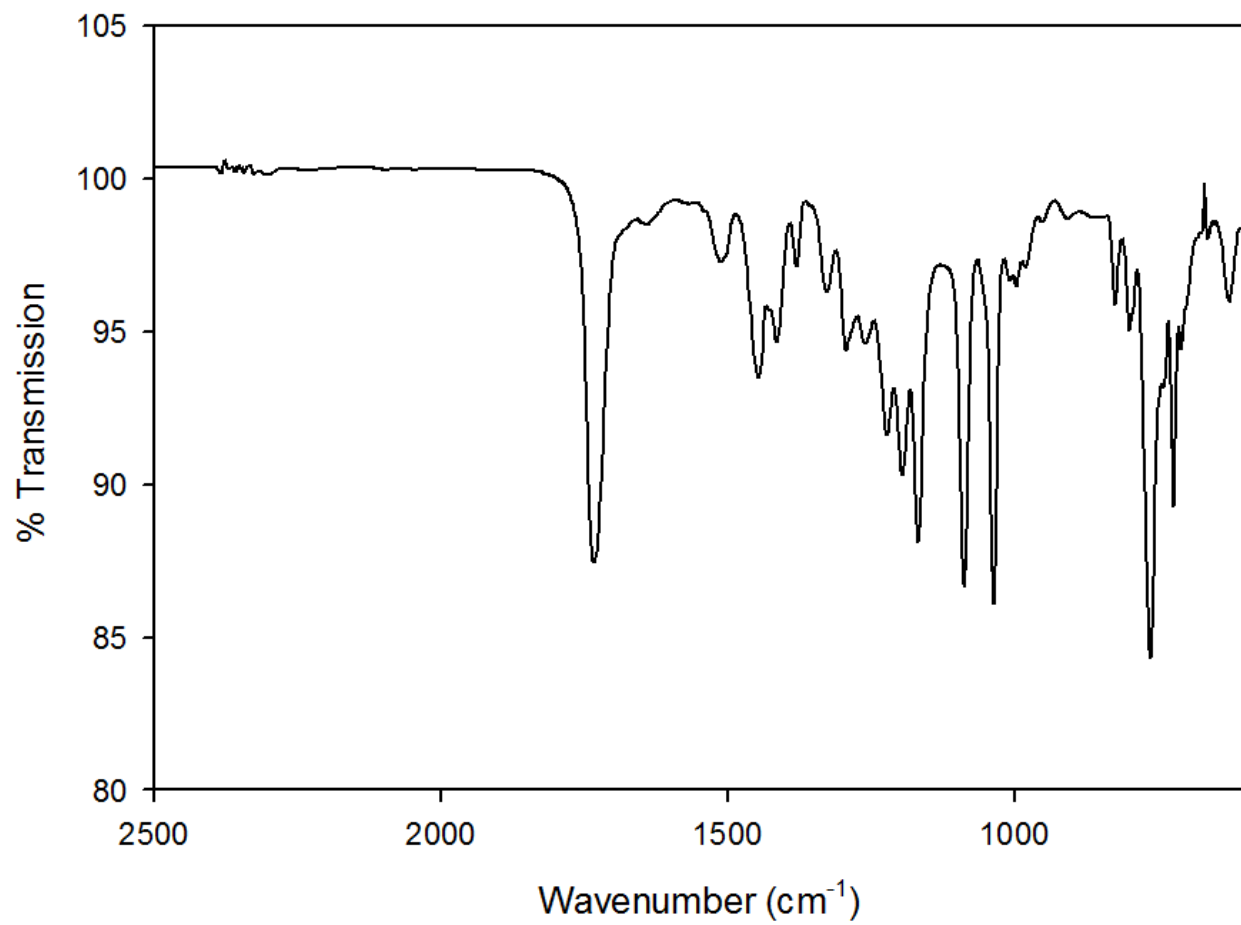


Figure S9. Ge(ATR) IR spectrum of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{N}_3)](\text{BF}_4)$.

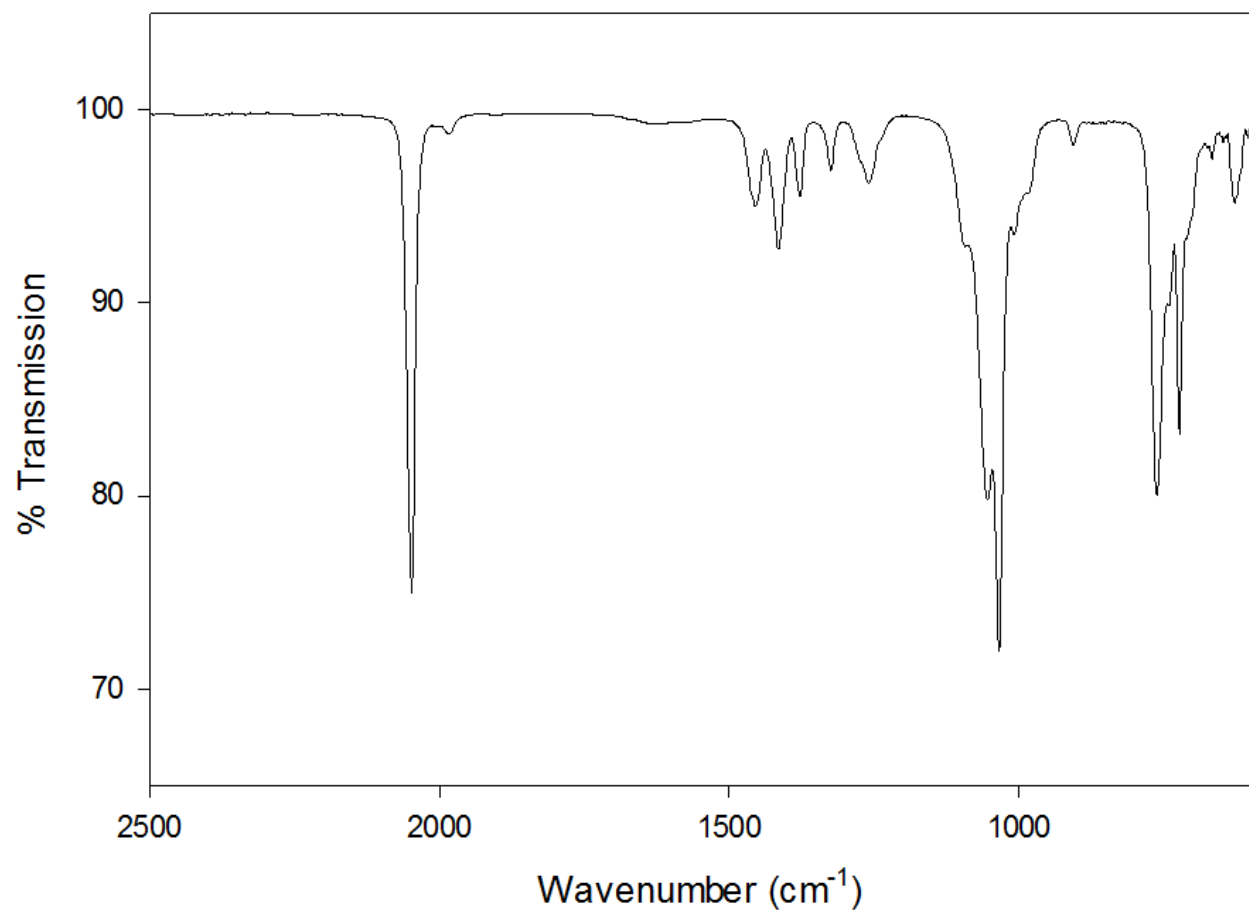


Figure S10. Ge(ATR) IR spectrum of $[\text{Re}_6\text{Se}_8(\text{PEt}_3)_5(\text{L1})](\text{BF}_4)$.

