Supporting Information

Mechanism of a Redox Coupling of Seleninic Acid with Thiol

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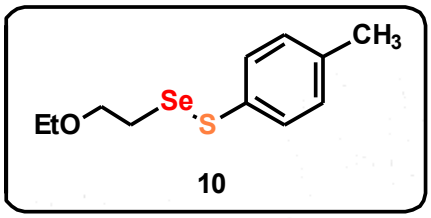
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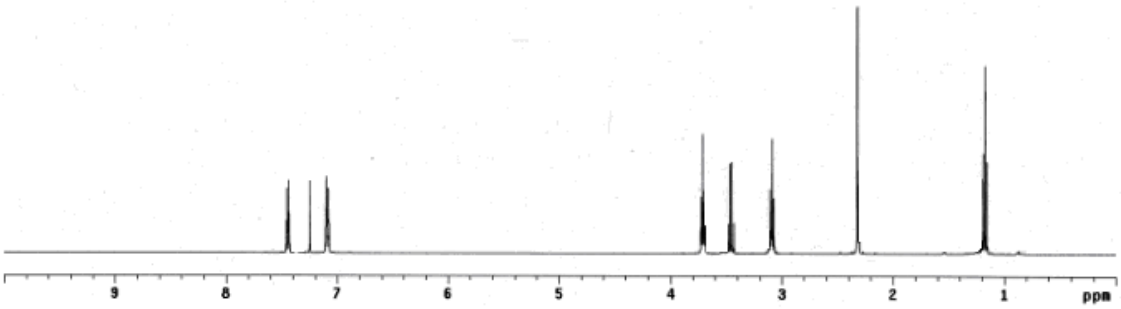
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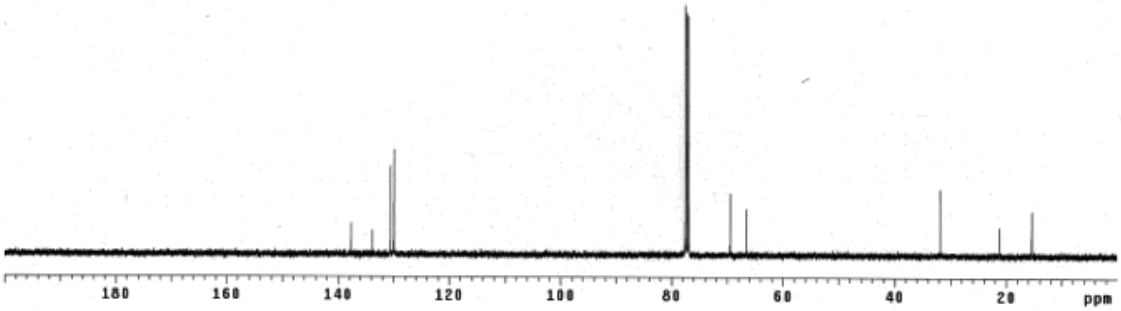
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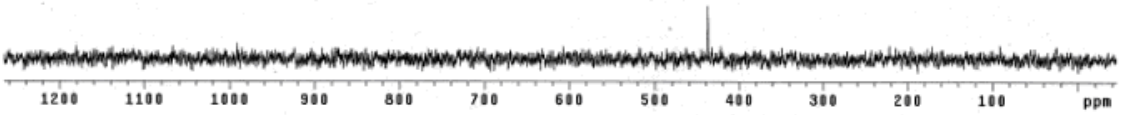
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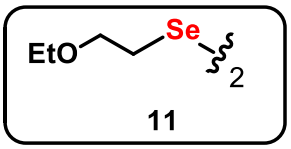
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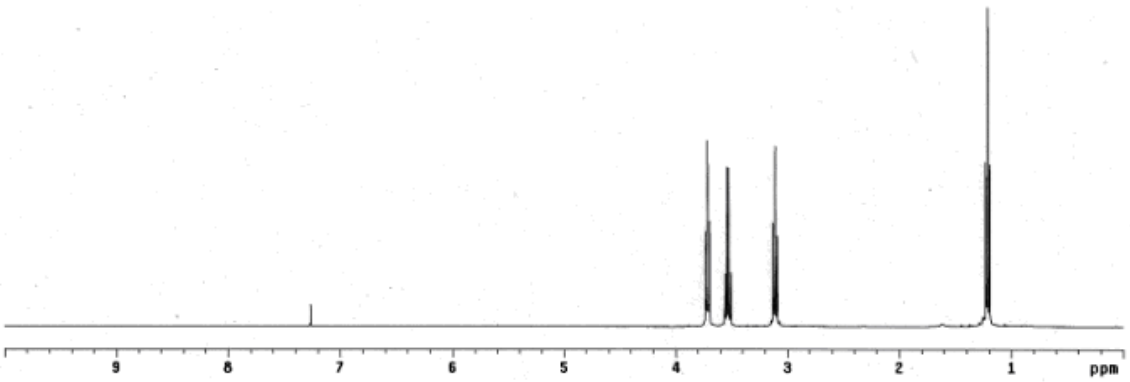
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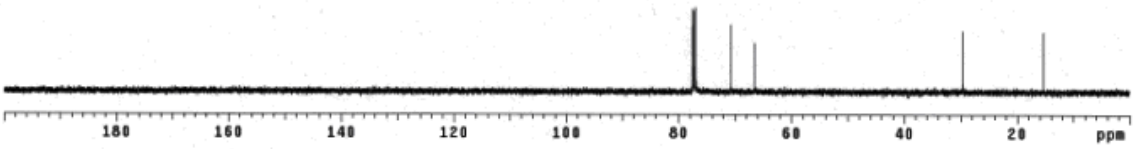
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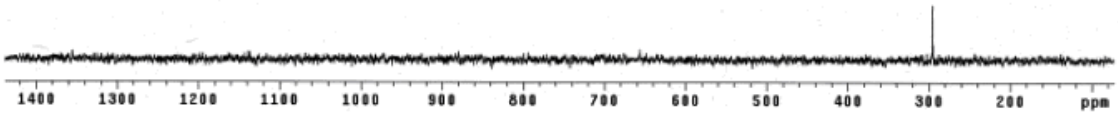
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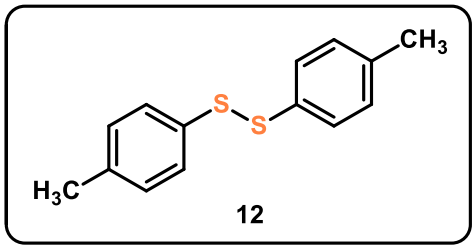

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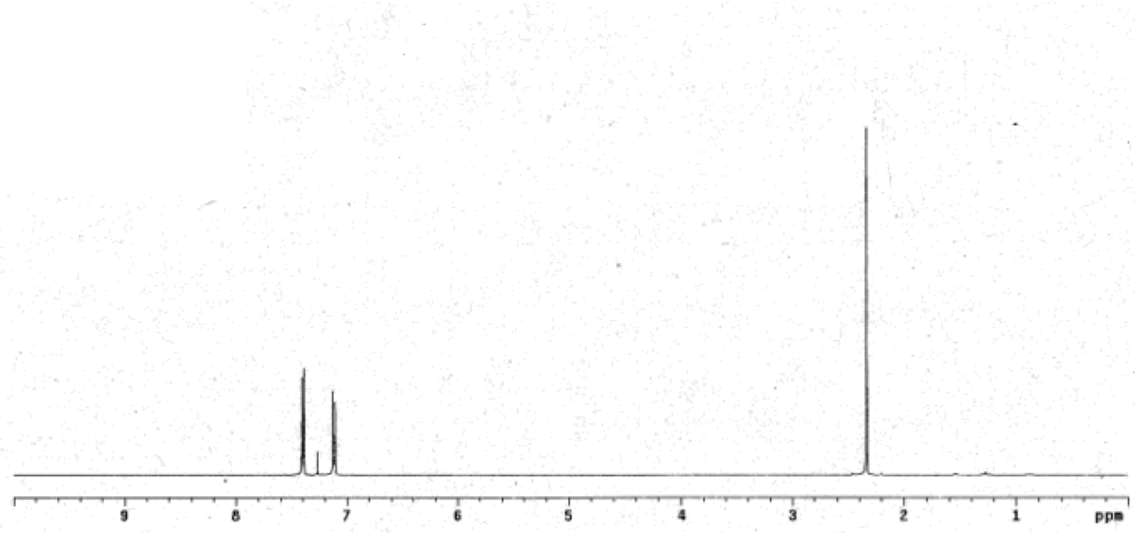

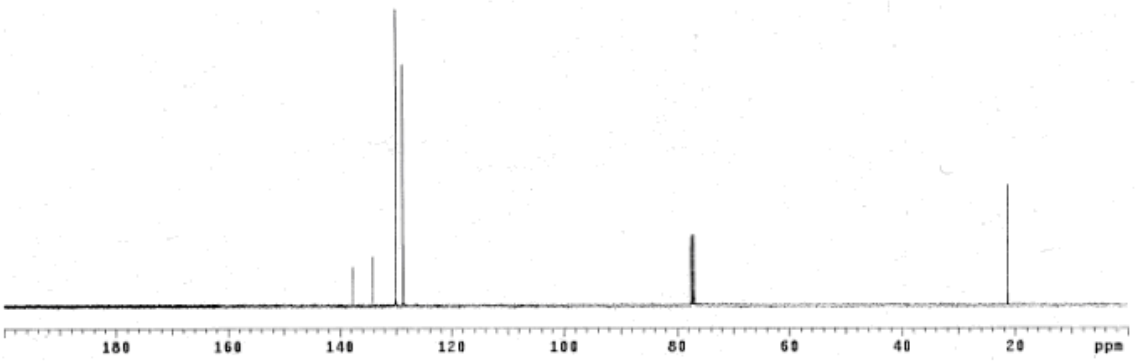

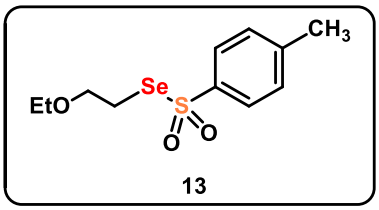
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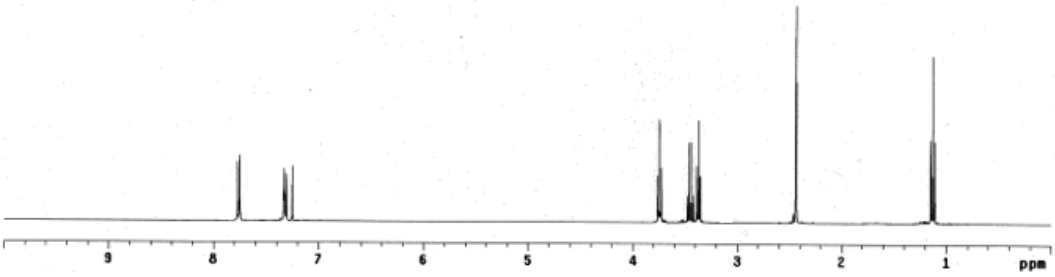
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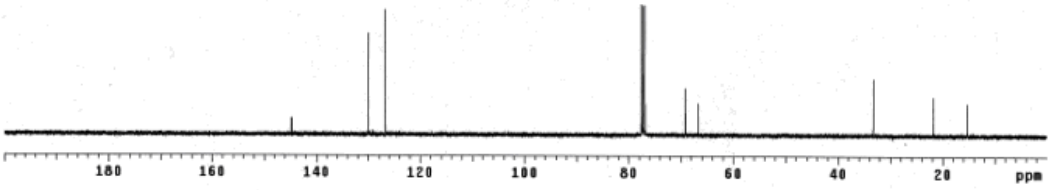
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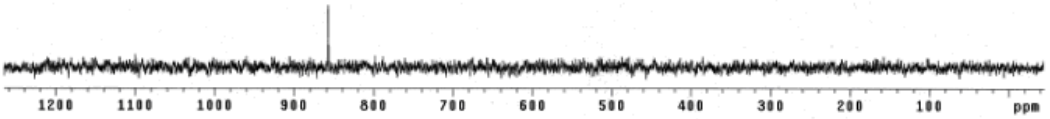
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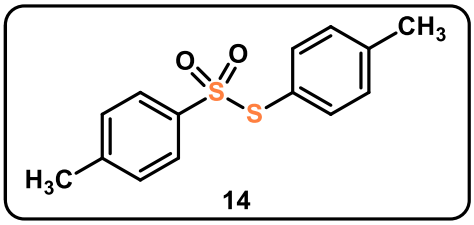

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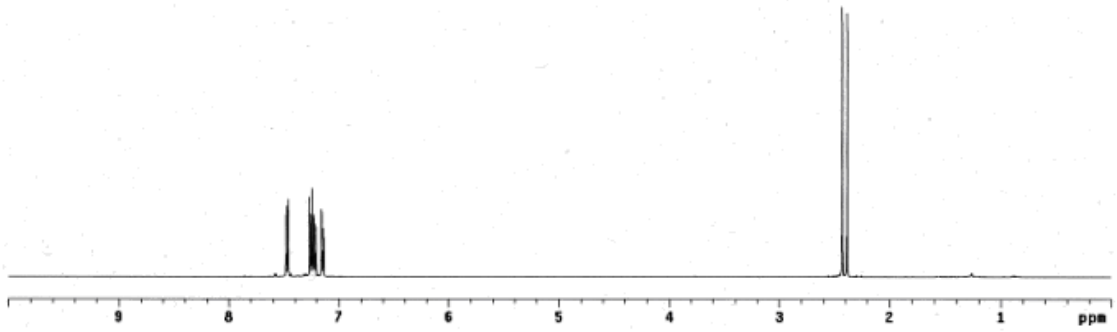
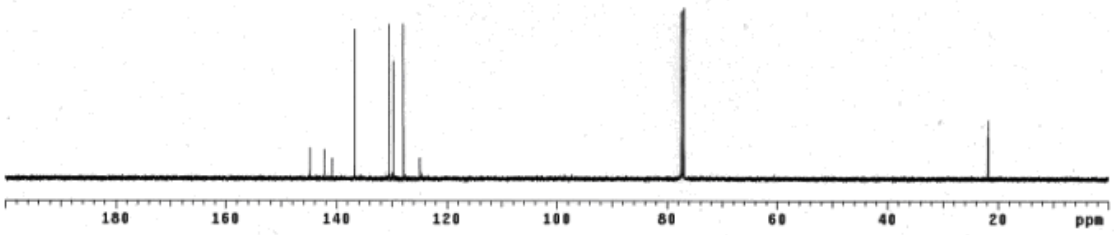
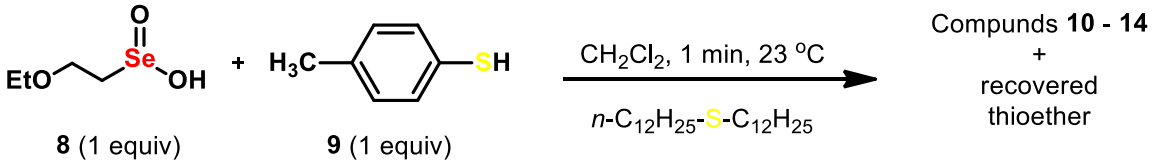


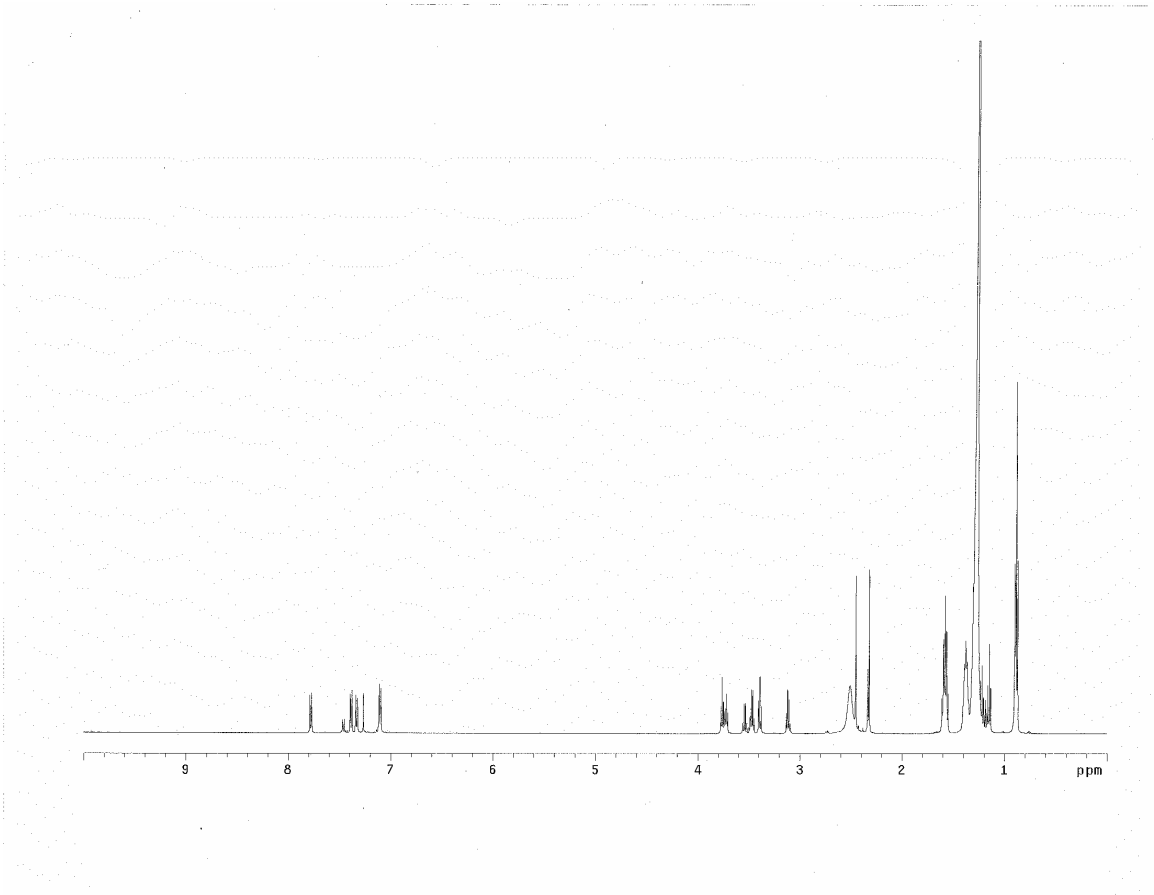


Attempted Trapping of Reactive Intermediates with Reducing Species

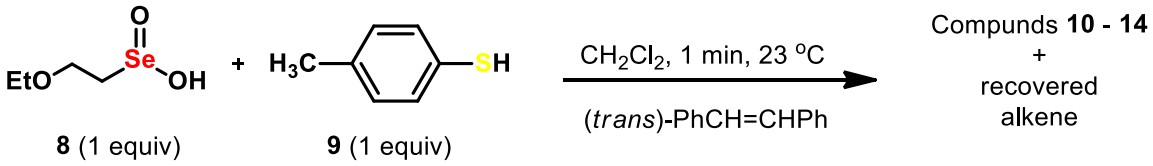
Equimolar condensation of **8** and **9** with addition of didodecyl sulfide: crude ^{1}H NMR spectrum



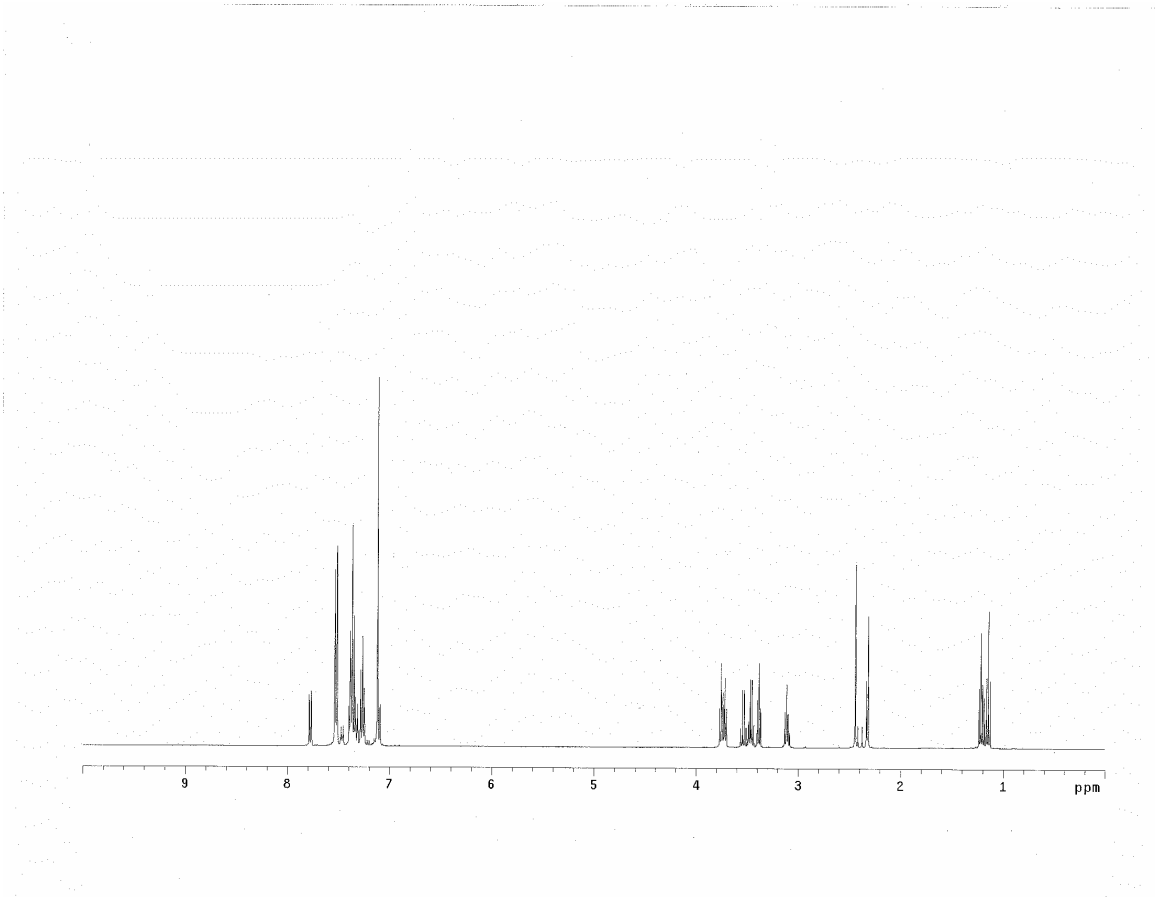
8 (1 equiv) **9** (1 equiv)



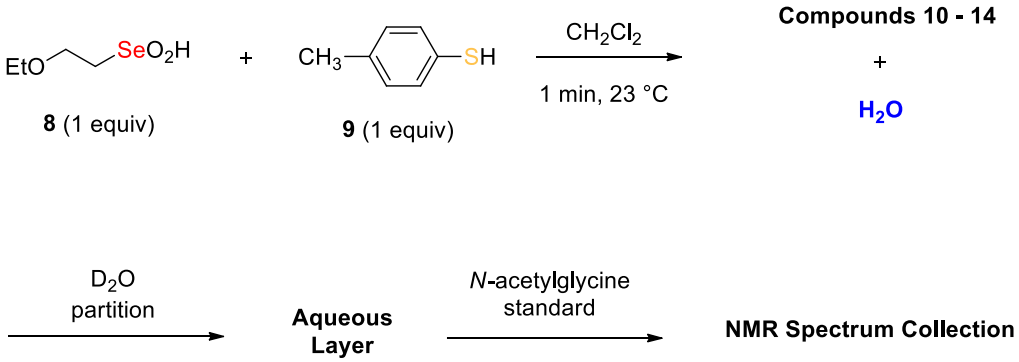
Equimolar condensation of **8** and **9** with addition of trans-stilbene: crude ^{1}H NMR spectrum



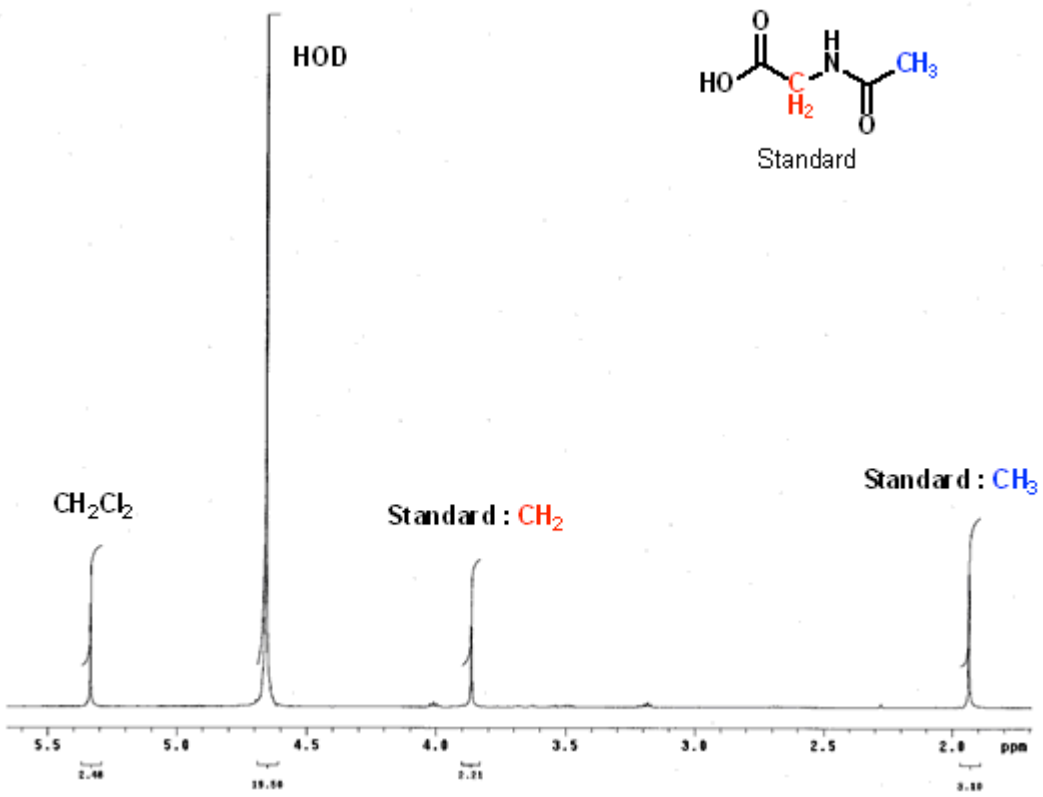
8 (1 equiv) **9** (1 equiv)



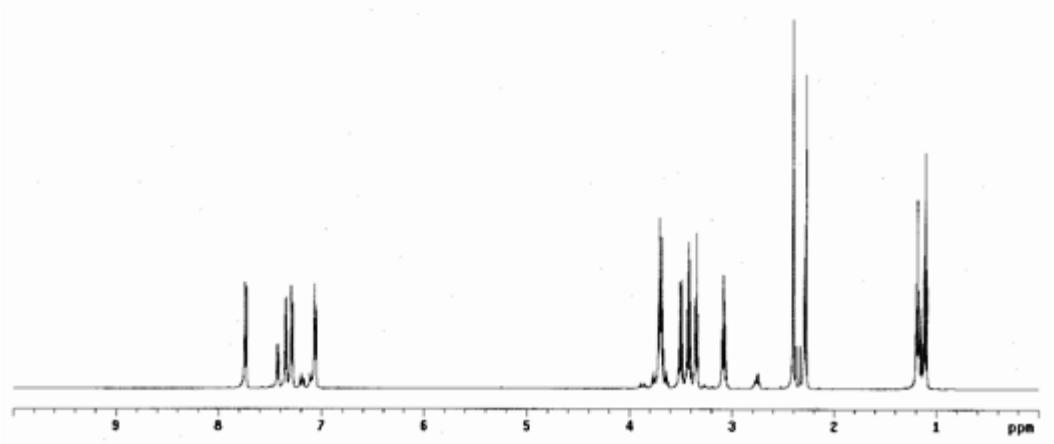
Water of Reaction Quantification

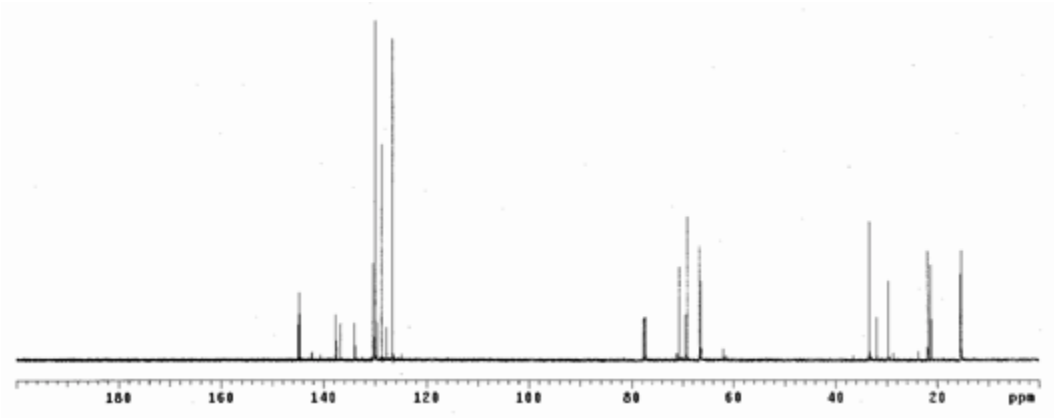


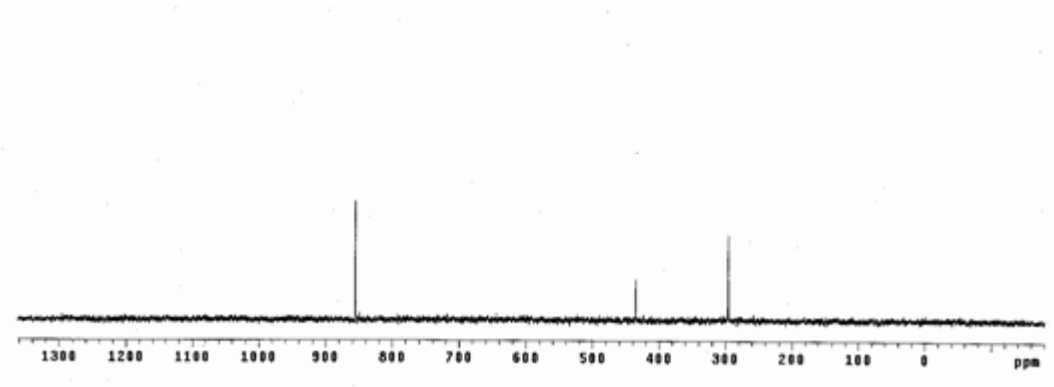
Aqueous layer: crude ^{1}H NMR spectrum



Organic layer: crude ^{1}H, ^{13}C, and ^{77}Se NMR spectra showing compounds **10 – 14**





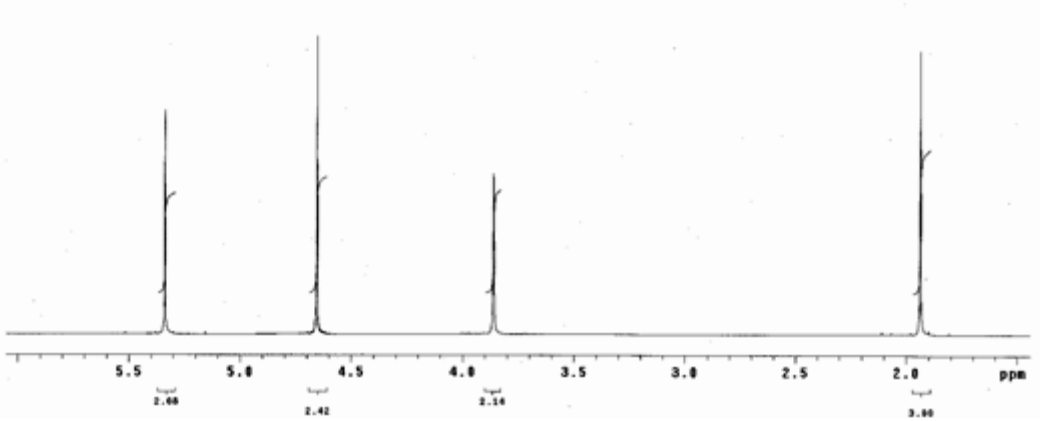


Background:* **dichlroromethane (2 mL)** —D_2O partition (2 mL)→ **Aqueous Layer**

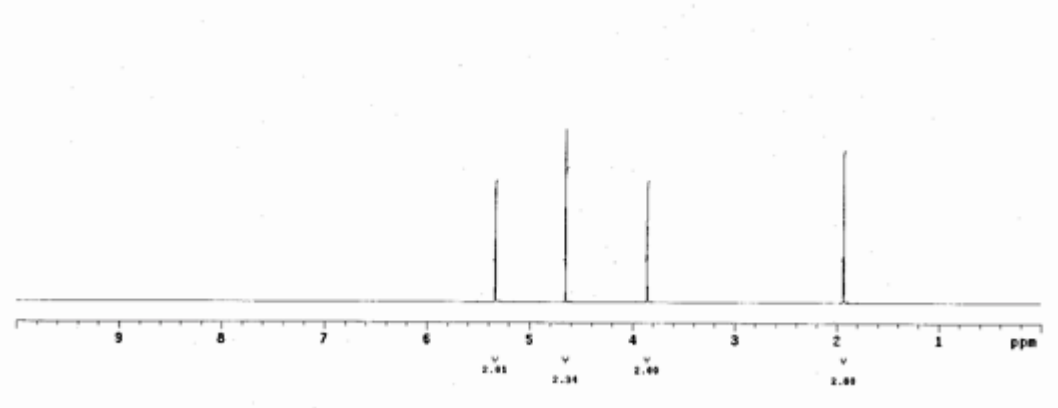
N-acetylglycine standard → **NMR Spectrum Collection**

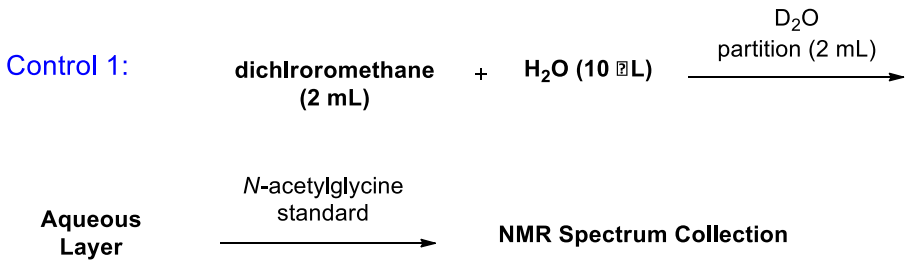
* Background experiment was caried out 2 times

Background 1 ^{1}H NMR spectrum:

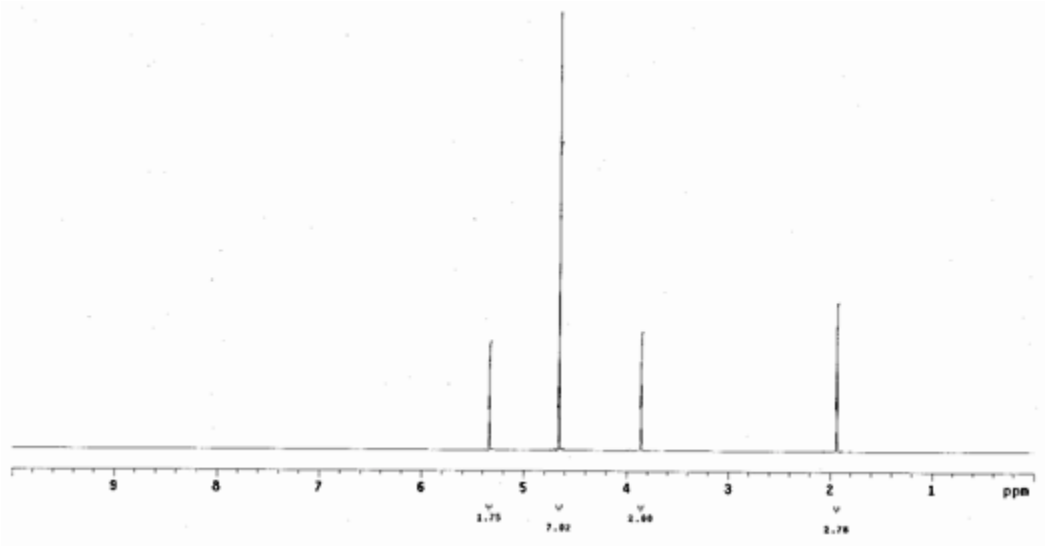


Background 2 ^{1}H NMR spectrum:





Control 1 ^{1}H NMR spectrum:



Control 2:

dichlroromethane (2 mL) + **H_2O (27 μL)** —(D_2O partition (2 mL))→

Aqueous Layer —(*N*-acetylglycine standard)→ **NMR Spectrum Collection**

Control 2 ^1H NMR spectrum:

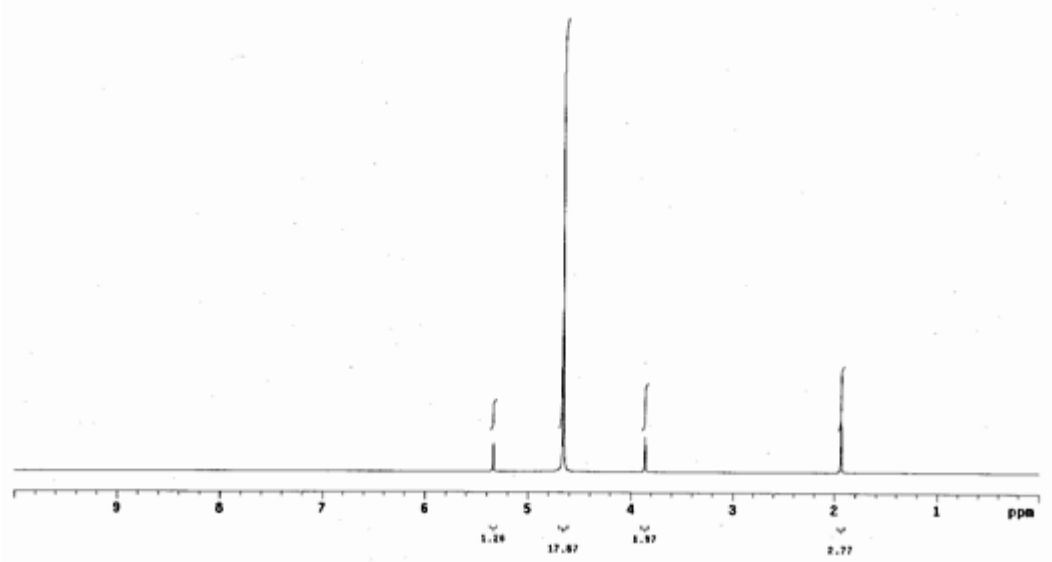


Table 1. Water of reaction from the coupling reaction of *equimolar equivalents* of **8** and **9**

Experiment	N-acetylglycine standard (mmol)	Integration value of HOD	Integration value of *N*-acetylglycine (–CH_2–)	Experimental H_2O (uL)	Experimental H_2O background corrected (uL)	Response factor based on control	Corrected amount of H_2O produced (uL)	Yield of water of reaction
Background #1: no H_2O added	0.0495	2.42	2.14	1.01	--	--	--	--
Background #2: no H_2O added	0.0495	2.34	2.00	1.04	--	--	--	--
Control #1: 10 uL of H_2O added	0.0495	7.02	2.00	3.13	2.12	1.78	--	--
Control #2: 27 uL of H_2O added	0.0495	15.87	1.97	7.18	6.14	1.64	--	--
1.50 mmol of seleninic acid + 1.50 mmol of thiocresol	0.0495	19.50	2.21	7.86	6.85	--	11.2	111%

* Dichloromethane solutions of various experiments were washed with 2.0 mL of D_2O. Only 0.75 mL of D_2O from each solution was used for NMR spectroscopy.

General Methods. All reactions were run in small, capped vials without the specific exclusion of air, moisture, or light. Flash chromatography was performed by using silica gel (E. Merck 230 – 400 mesh) as the stationary phase. Silica gel 60 F_{254} pre-coated plates were used for thin layer chromatography, and visualization was accomplished with UV light (254 nm) and iodine stain. ESI mass spectra were obtained with a Finnigan LCQ_{DUO} LC/MS spectrometer. High resolution mass spectra were obtained with a Waters LC-TOF mass spectrometer (model LCT-XE Premier) using electrospray ionization in positive mode. ^{1}H, ^{13}C, and ^{77}Se NMR spectra were obtained on a Varian UNITY 400 or 500 instrument. Chemical shifts (δ) are reported in parts per million (ppm) and are referenced to the residual solvent peak. Coupling constants (*J*) are reported in hertz (Hz). The usual abbreviations are used to designate multiplicities: s=singlet; d=doublet; t=triplet; q=quartet. NMR solvents were used as received from Aldrich: chloroform-D (99.8% D), deuterium oxide (99.9% D). *N*-Acetylglycine (99%) was used as obtained from Aldrich. All other commercially available reagents were used as received and without any further purification.