

Supporting Information for:

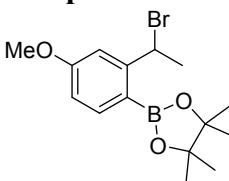
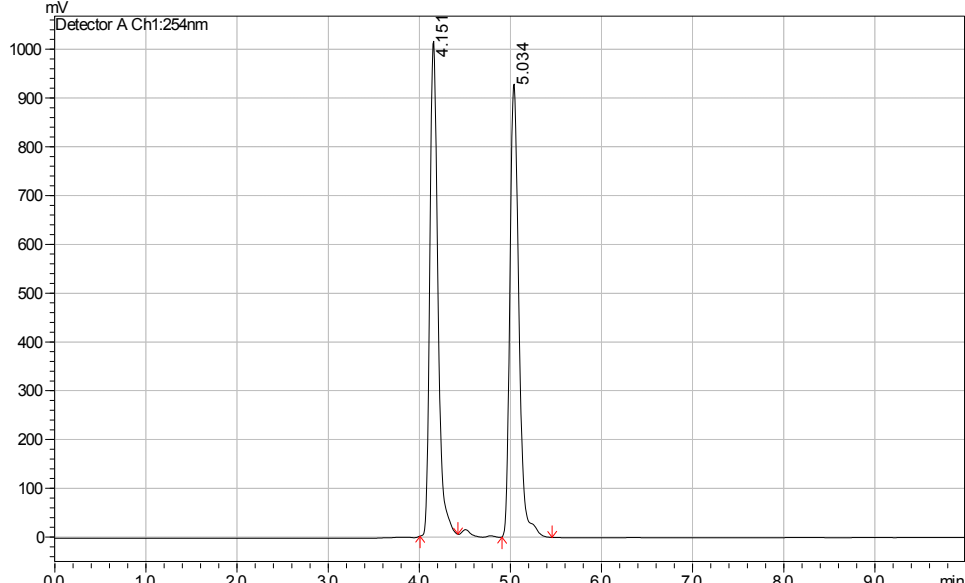
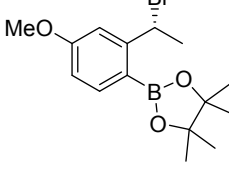
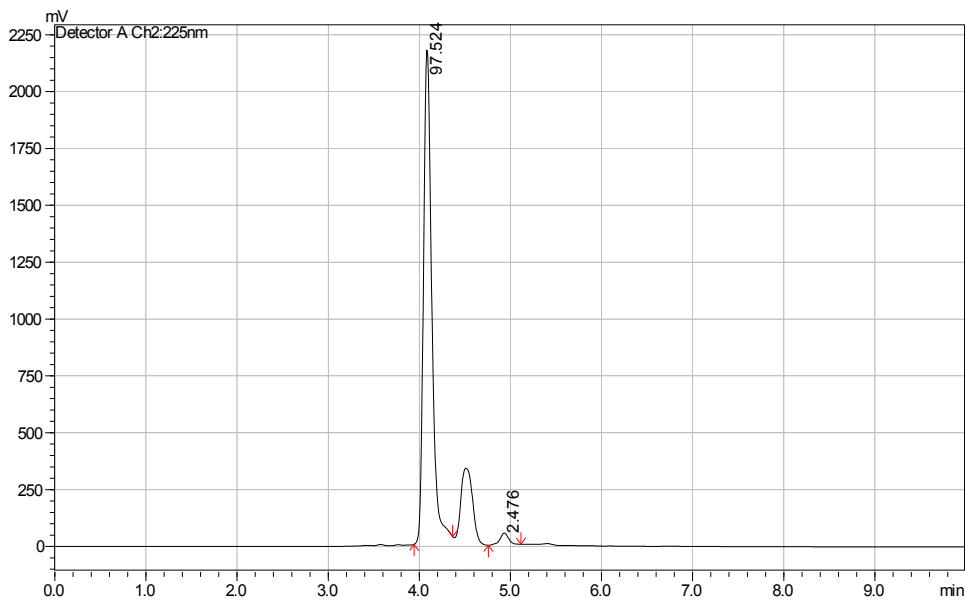
Formal Asymmetric Hydrobromination of Styrenes *via* Copper-Catalyzed 1,3-Halogen Migration

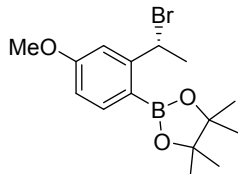
Ryan Van Hoveln, Steven C. Schmid, Maik Tretbar, Carl T. Buttkke, and Jennifer M. Schomaker*

*Department of Chemistry, University of Wisconsin-Madison, 1101 University Avenue
Madison, Wisconsin, 53706-1396*

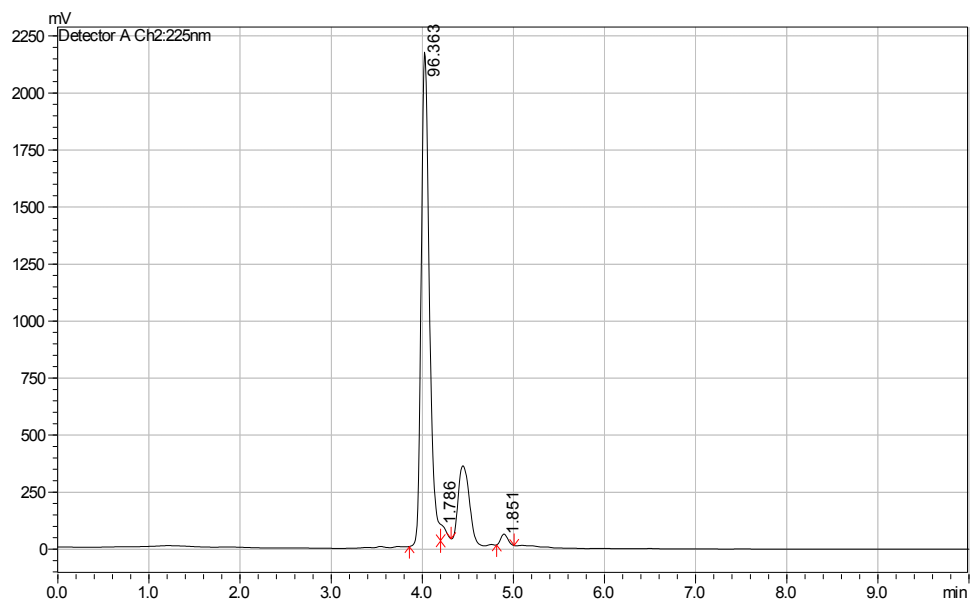
Table of Contents	S1-1
XI. HPLC Chromatograms	S1-2
XII. Selected IR Spectra	S1-20

XIII. HPLC Chromatograms.

Structure	Chromatogram						
<p>Compound 2:</p>  <p>(racemic)</p>	 <p>Detector A Ch1:254nm</p> <table border="1"><thead><tr><th>Retention Time (min)</th><th>Approximate mV</th></tr></thead><tbody><tr><td>4.151</td><td>1000</td></tr><tr><td>5.034</td><td>900</td></tr></tbody></table>	Retention Time (min)	Approximate mV	4.151	1000	5.034	900
Retention Time (min)	Approximate mV						
4.151	1000						
5.034	900						
	 <p>Detector A Ch2:225nm</p> <table border="1"><thead><tr><th>Retention Time (min)</th><th>Approximate mV</th></tr></thead><tbody><tr><td>4.524</td><td>2250</td></tr><tr><td>4.476</td><td>300</td></tr></tbody></table>	Retention Time (min)	Approximate mV	4.524	2250	4.476	300
Retention Time (min)	Approximate mV						
4.524	2250						
4.476	300						

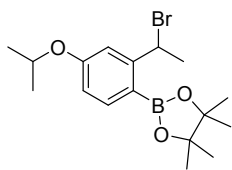


Reintegrated
using Shimadzu
vertical
partitioning
setting

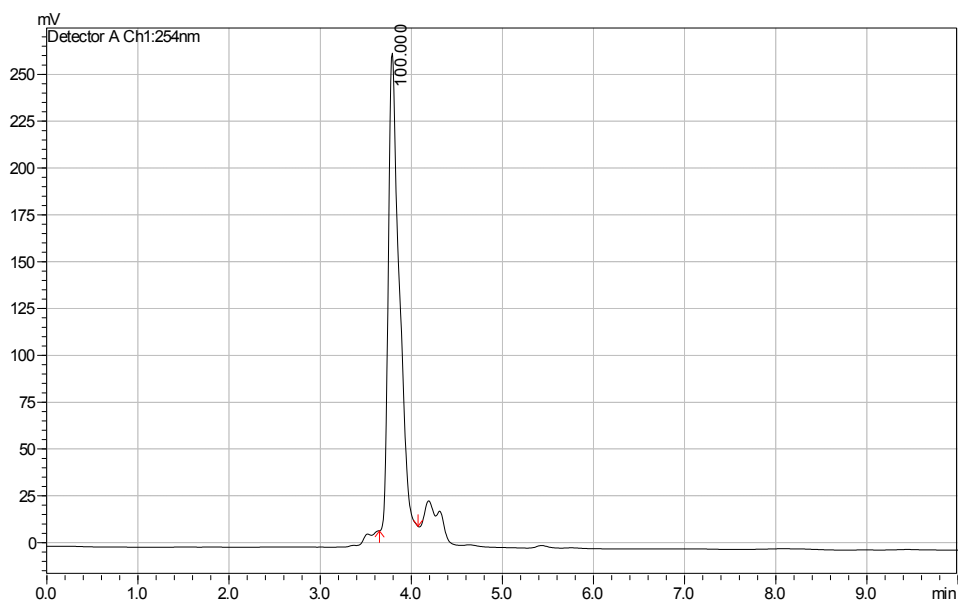
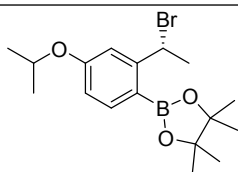
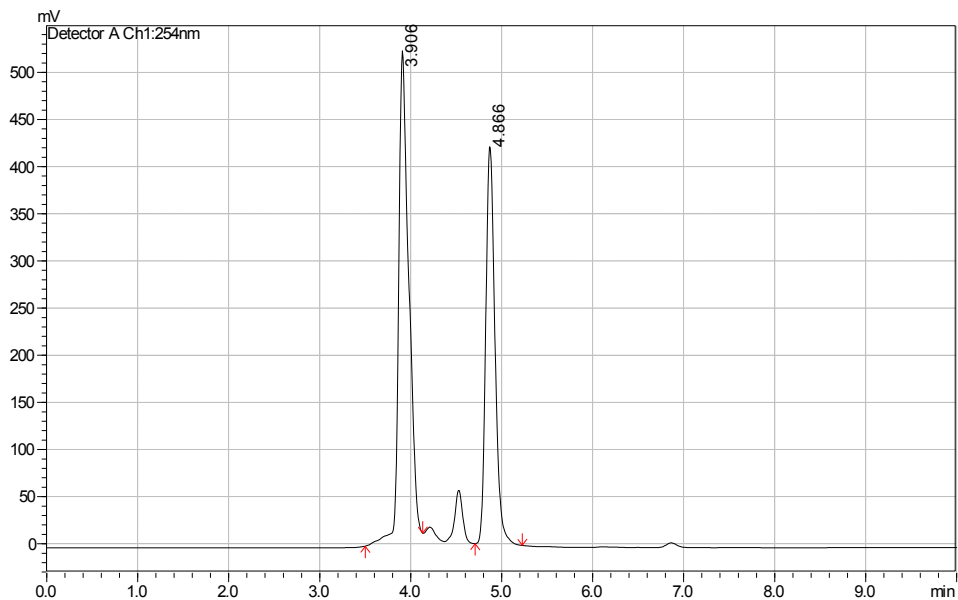


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 1.00% *i*PrOH in hexanes; Detector: UV @ 254 nm

5a:

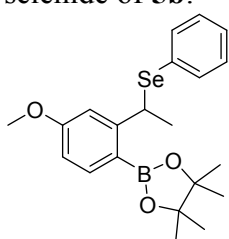


(racemic)

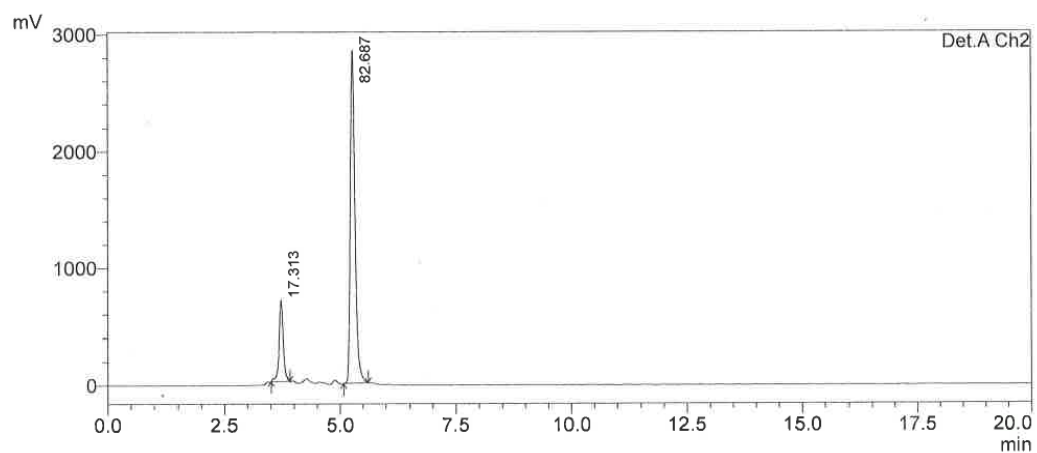
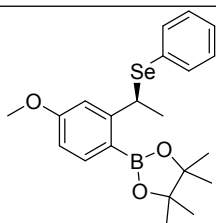
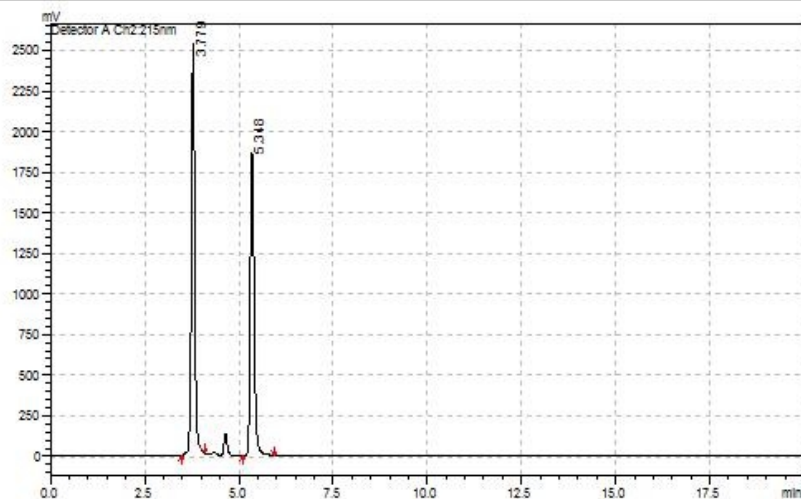


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 0.50% *i*PrOH in hexanes; Detector: UV @ 254 nm

selenide of **5b**:

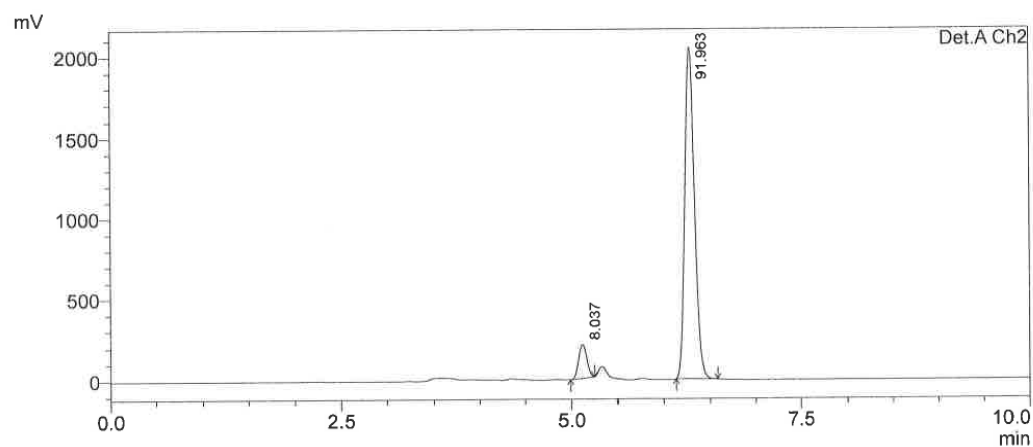
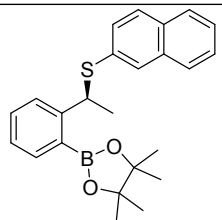
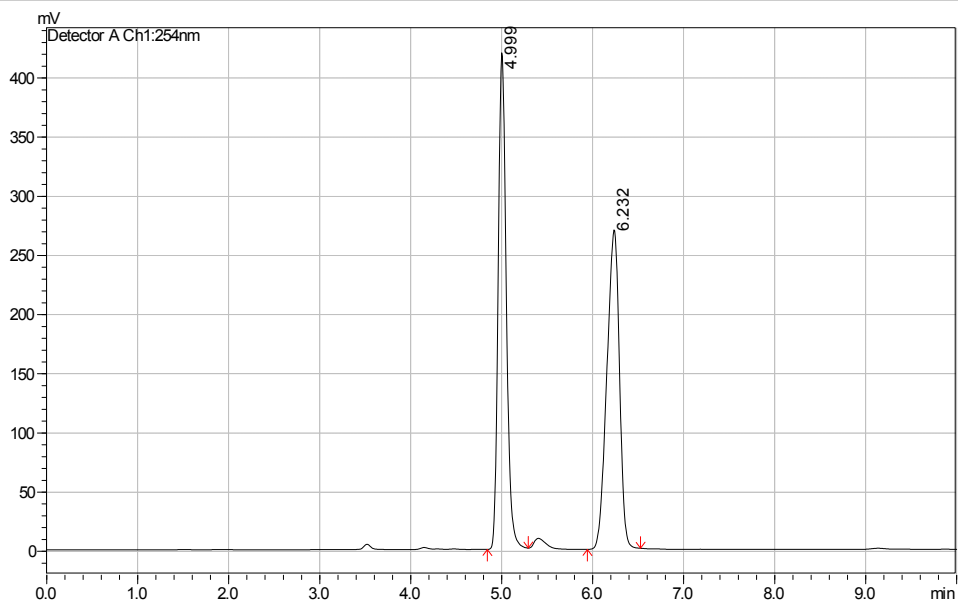
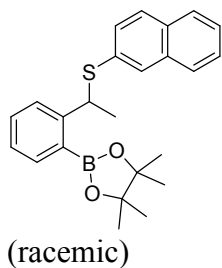


(racemic)



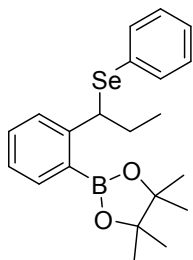
Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 5.00% *i*PrOH in hexanes; Detector: UV @ 215 nm

Thioether of **5c**:

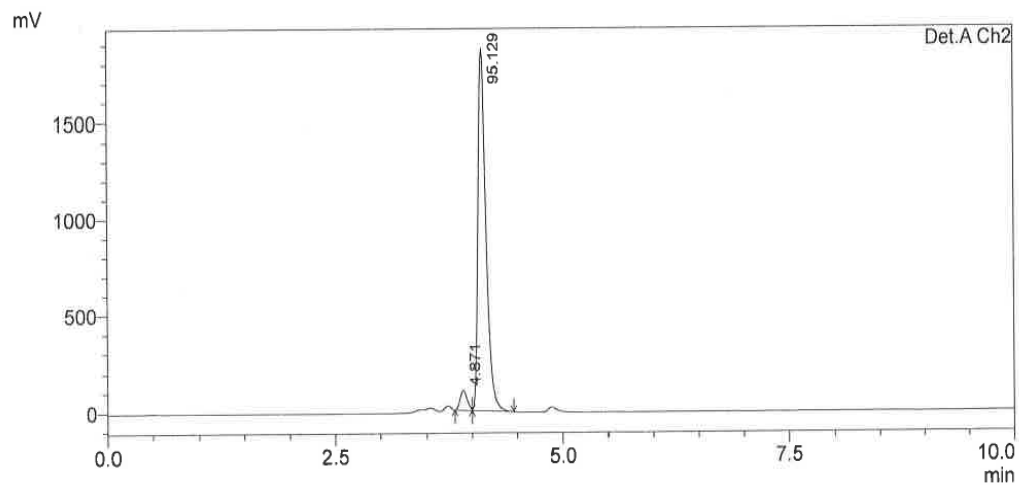
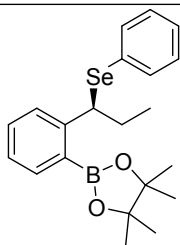
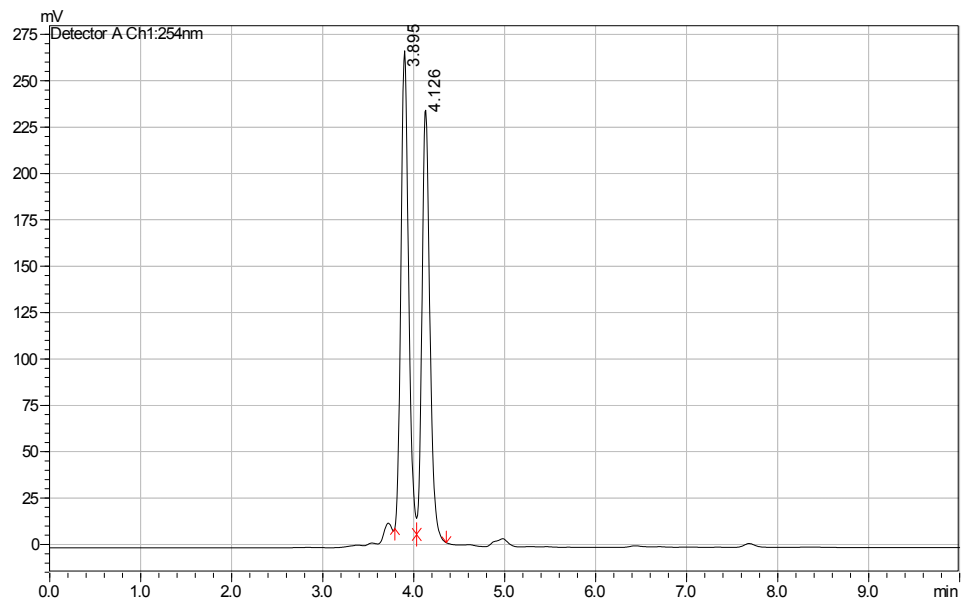


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 1.00% *i*PrOH in hexanes; Detector: UV @ 225 nm and 254 nm

Selenide of **5d**:

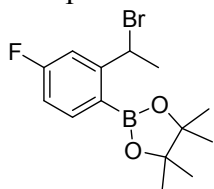


(racemic)

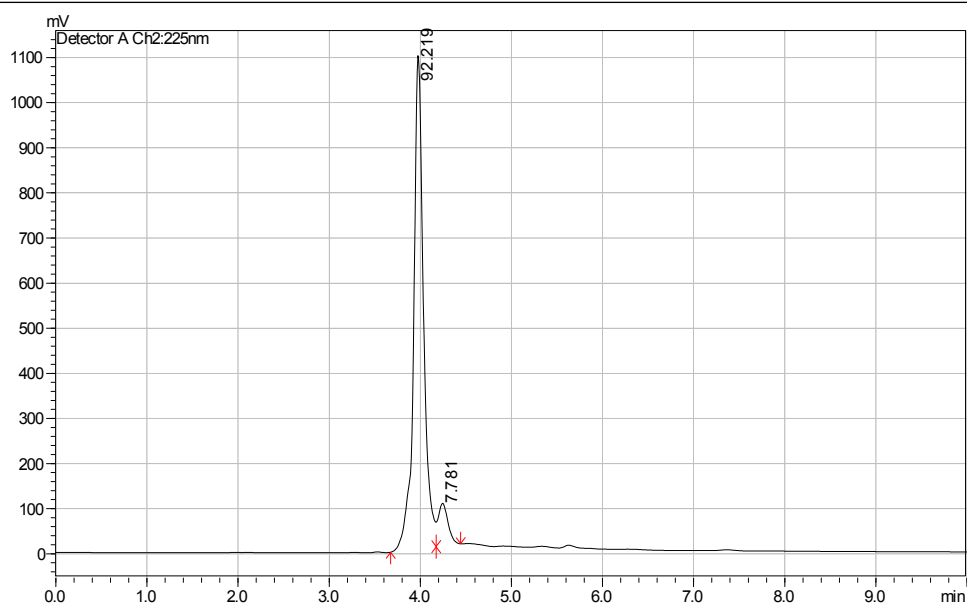
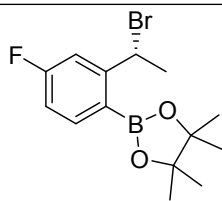
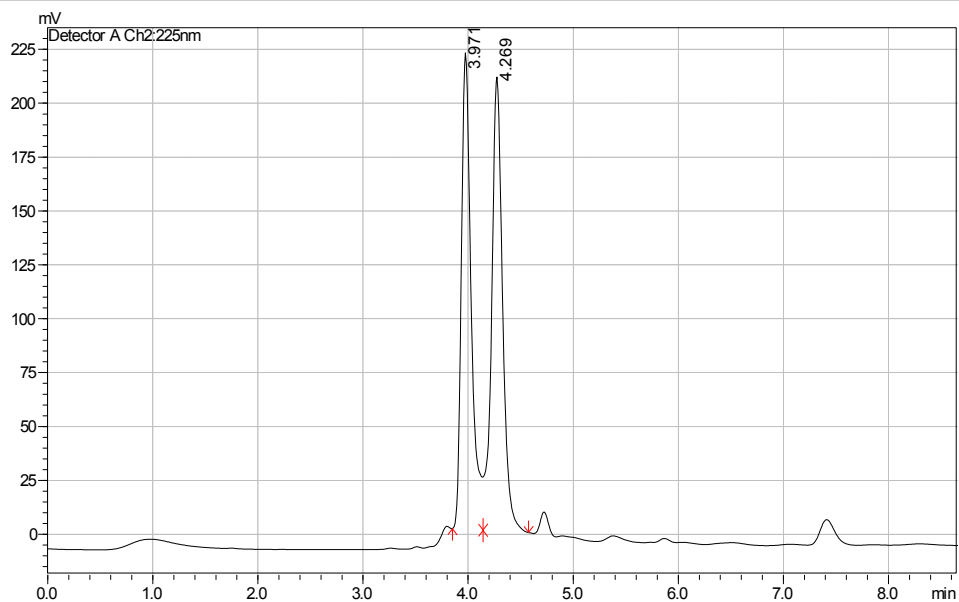


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 0.50% *i*PrOH in hexanes; Detector: UV @ 225 nm

Compound 5e:

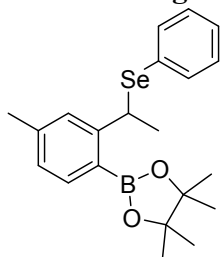


(racemic)

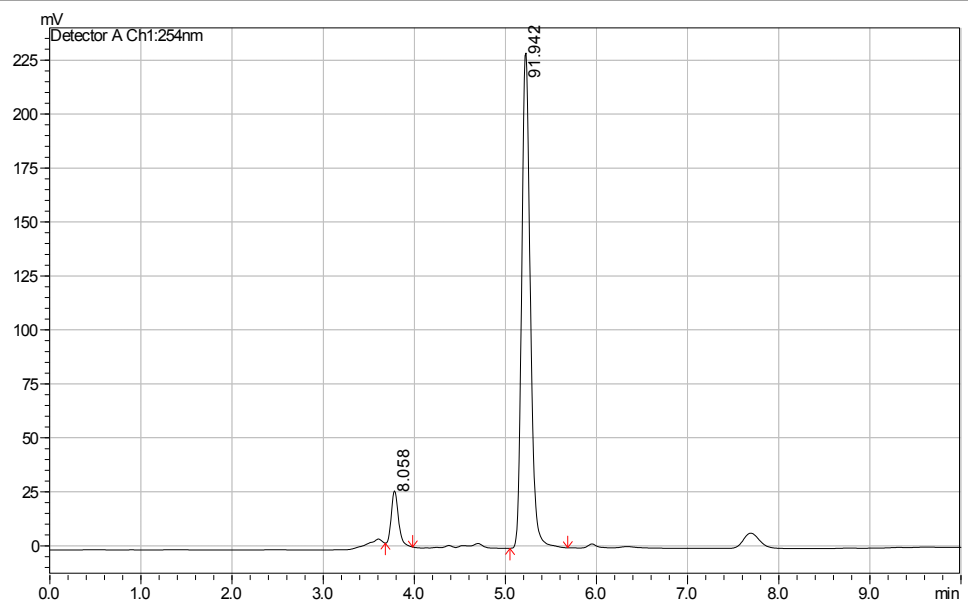
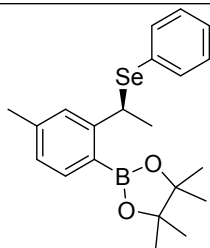
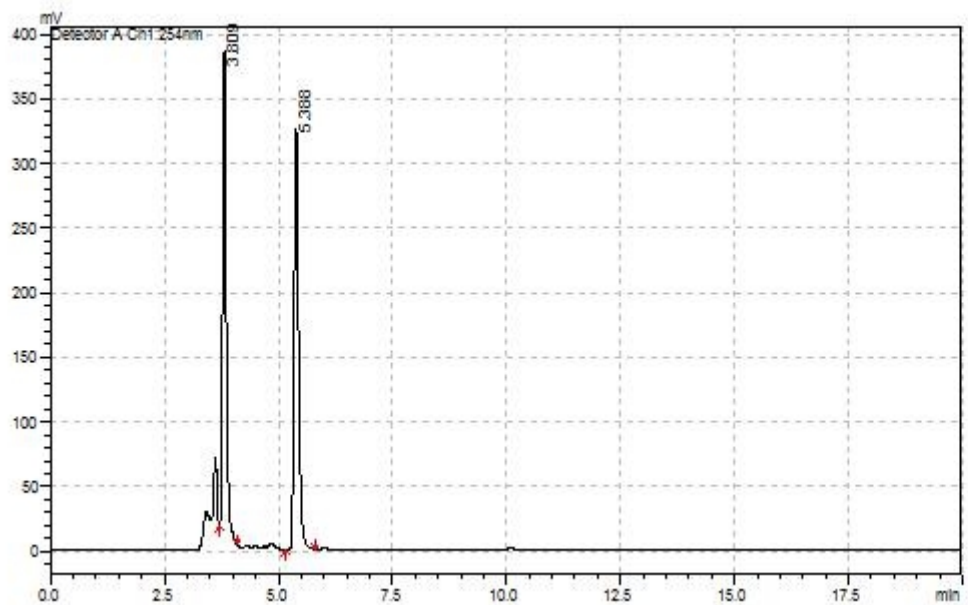


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 0.10% *i*PrOH in hexanes; Detector: UV @ 254 nm

Selenide of **5g**:

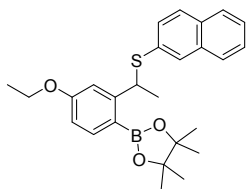


(racemic)

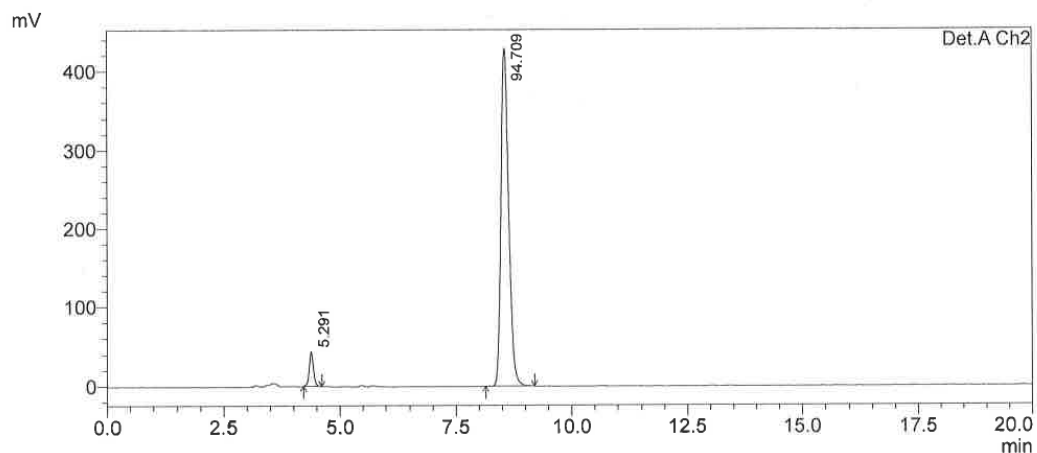
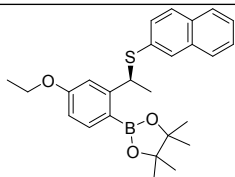
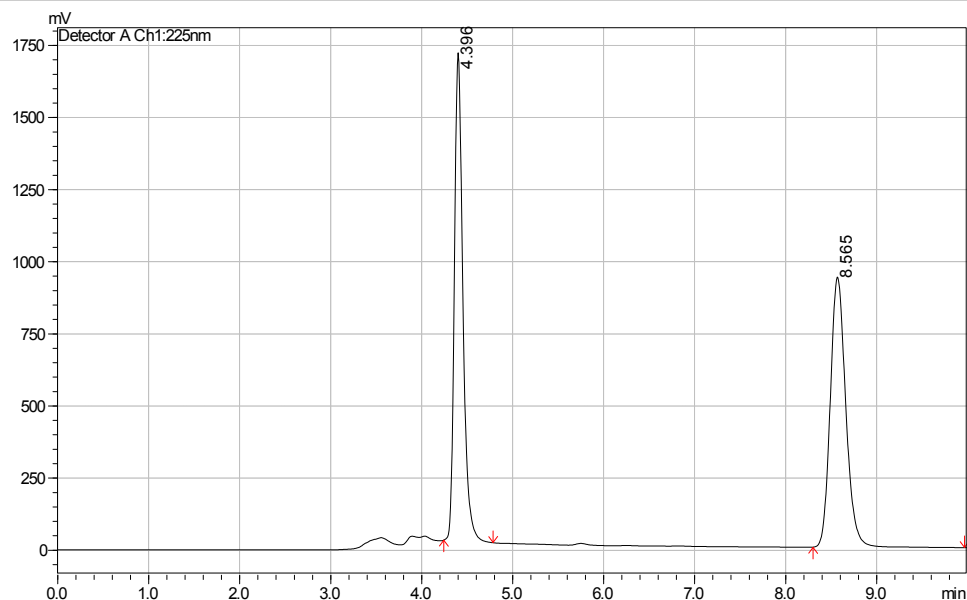


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 5.00% *i*PrOH in hexanes; Detector: UV @ 254 nm

Thioether of **5h**:

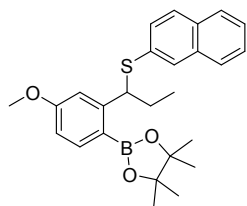


(racemic)

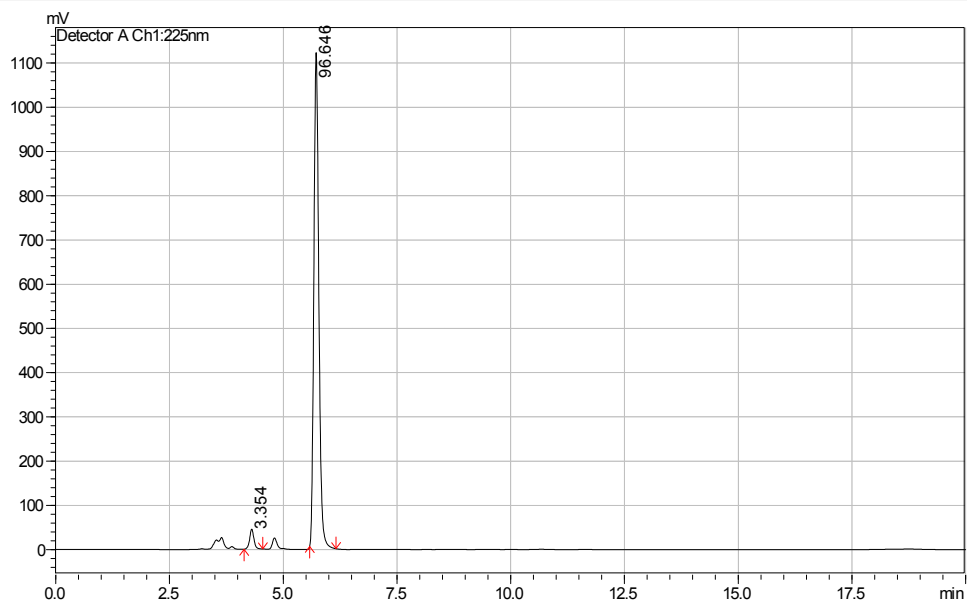
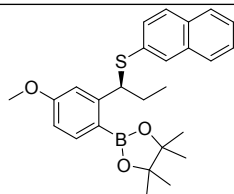
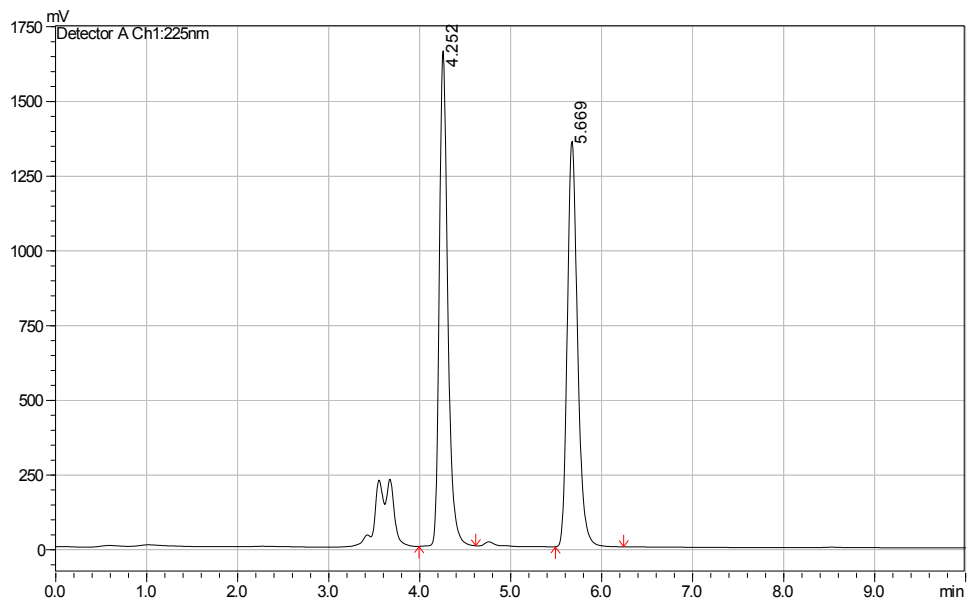


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 5.00% *i*PrOH in hexanes; Detector: UV @ 215 nm and 225 nm

Thioether of **5i**:

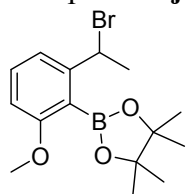


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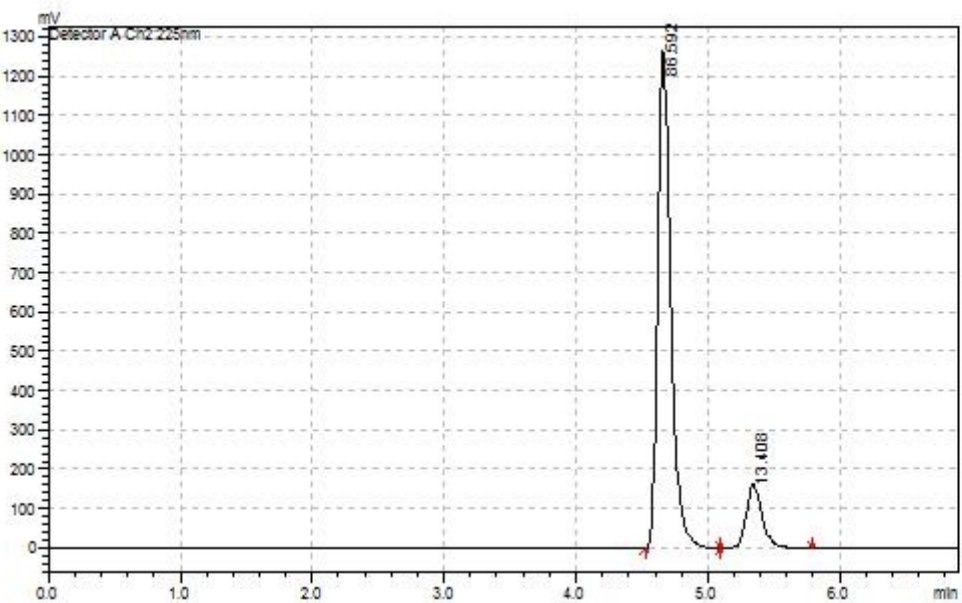
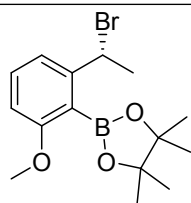
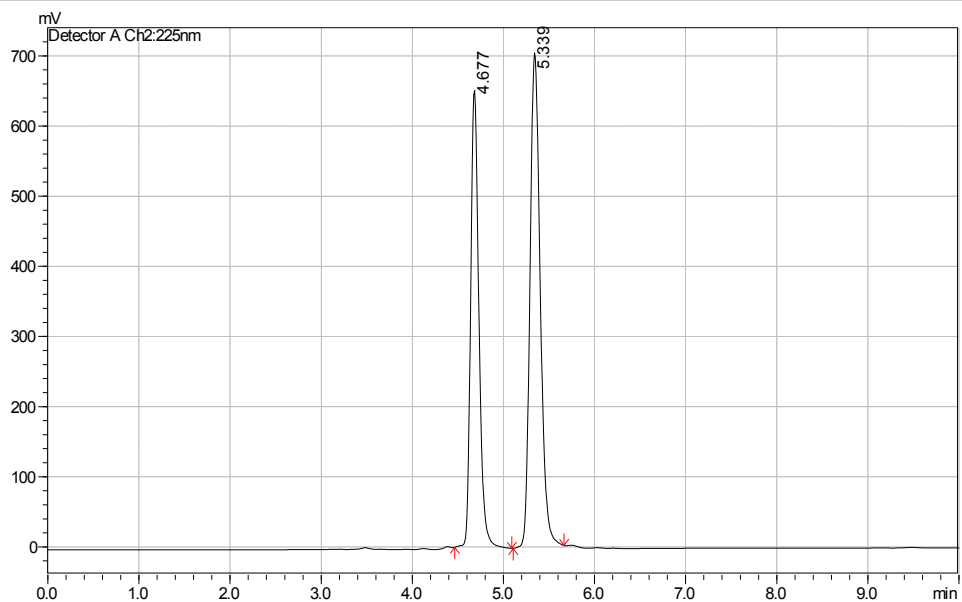


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 5.00% *i*PrOH in hexanes; Detector: UV @ 225 nm

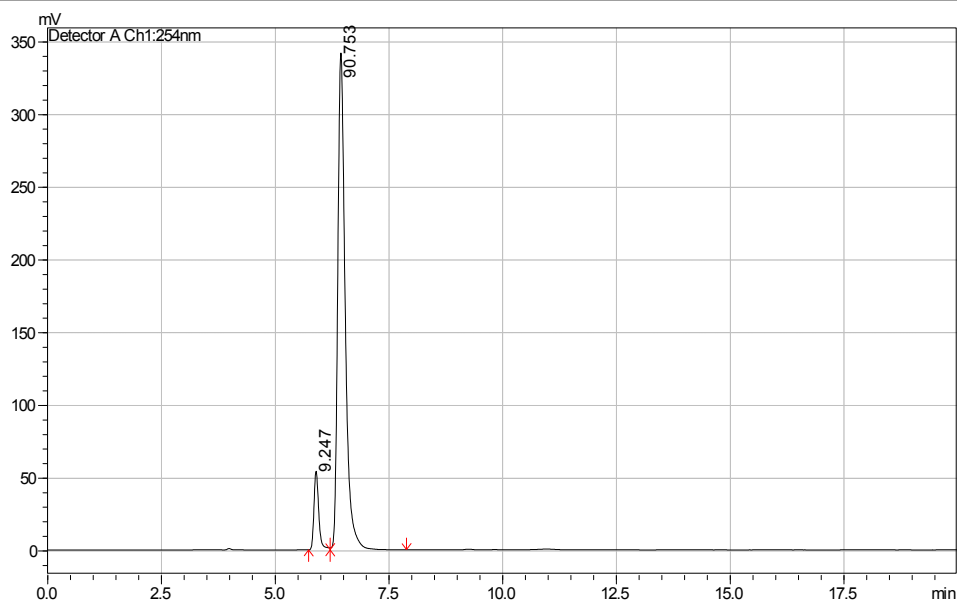
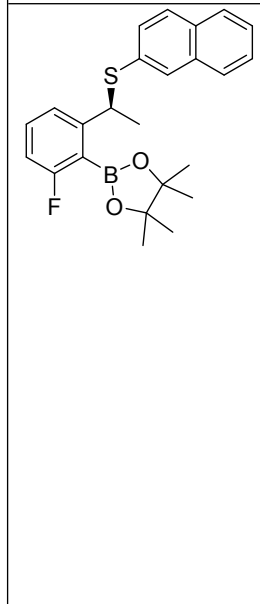
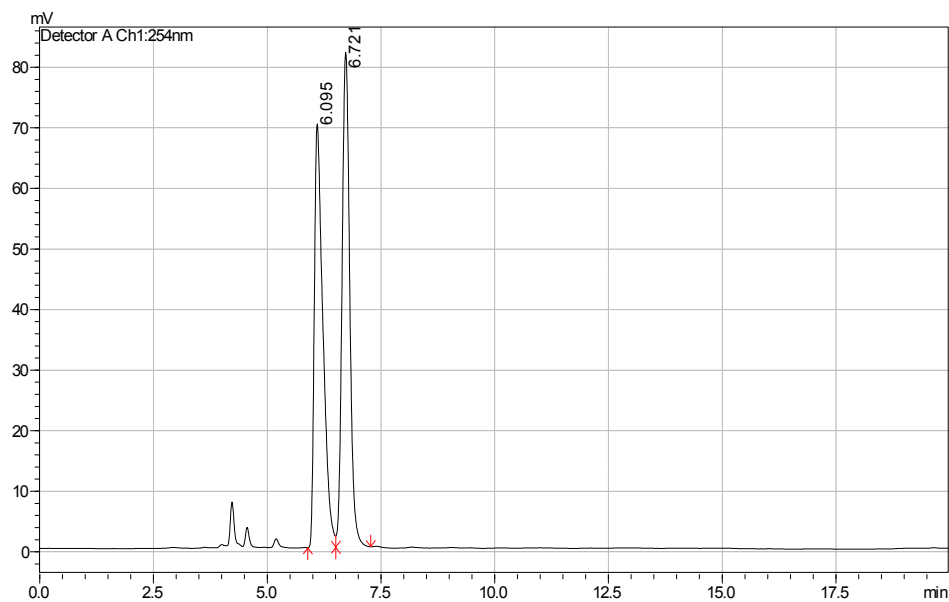
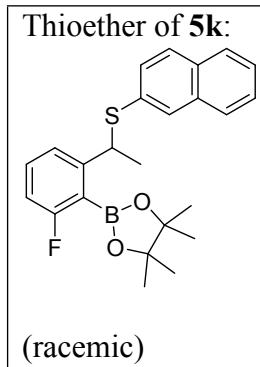
Compound **5j**:



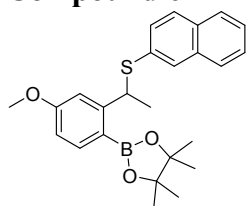
(racemic)



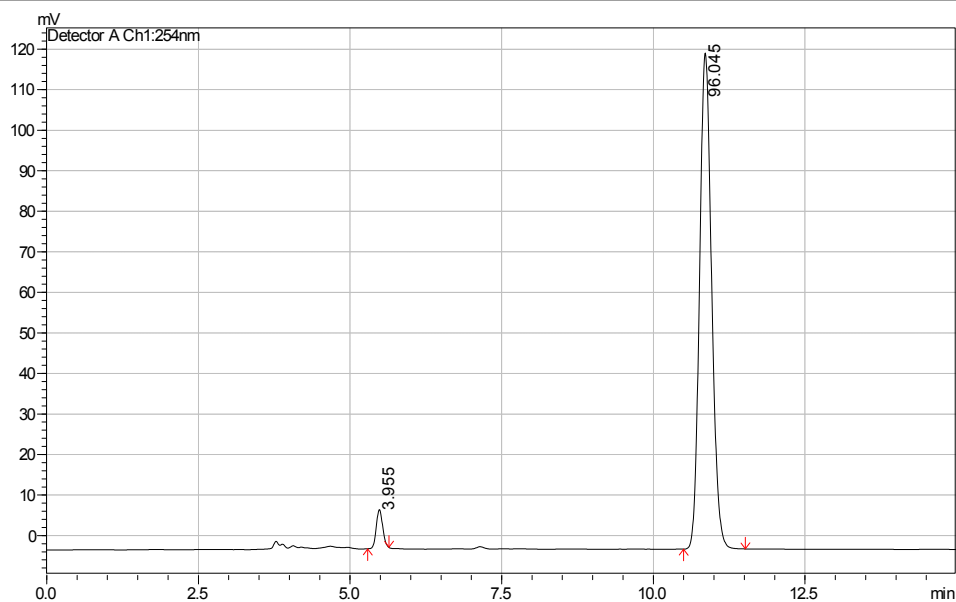
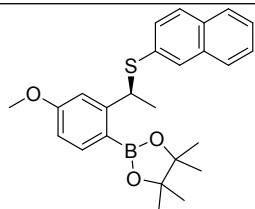
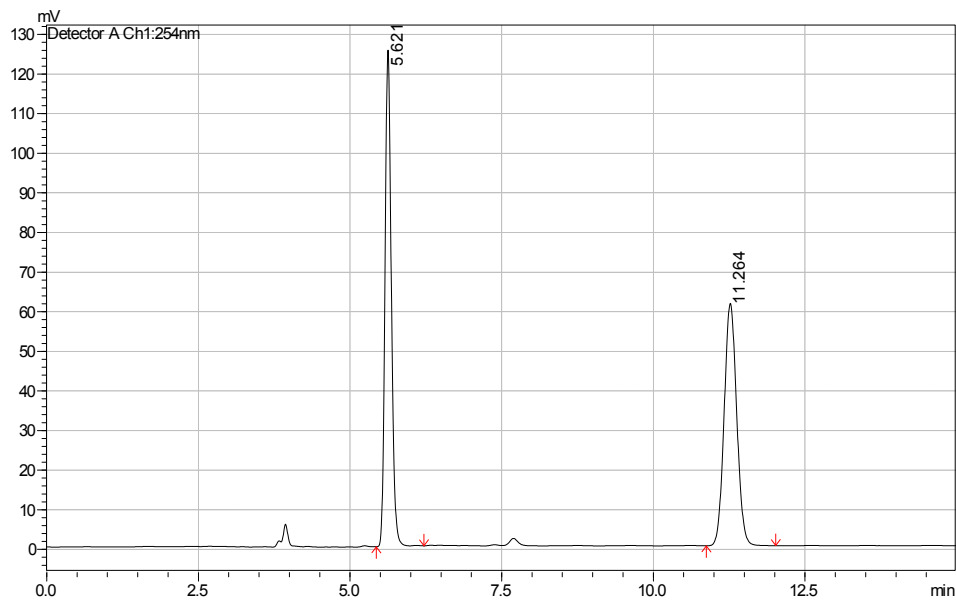
Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 1.00% *i*PrOH in hexanes; Detector: UV @ 225 nm



Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 1.00% *i*PrOH in hexanes; Detector: UV @ 254 nm

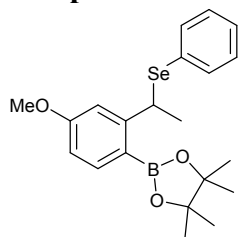
Compound 6

(racemic)

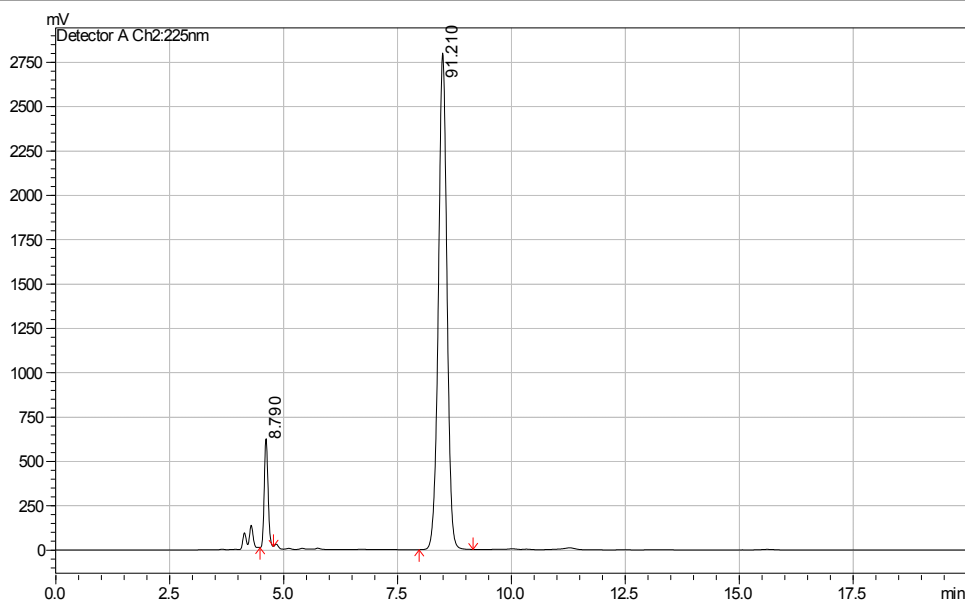
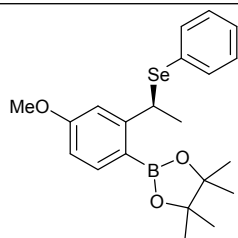
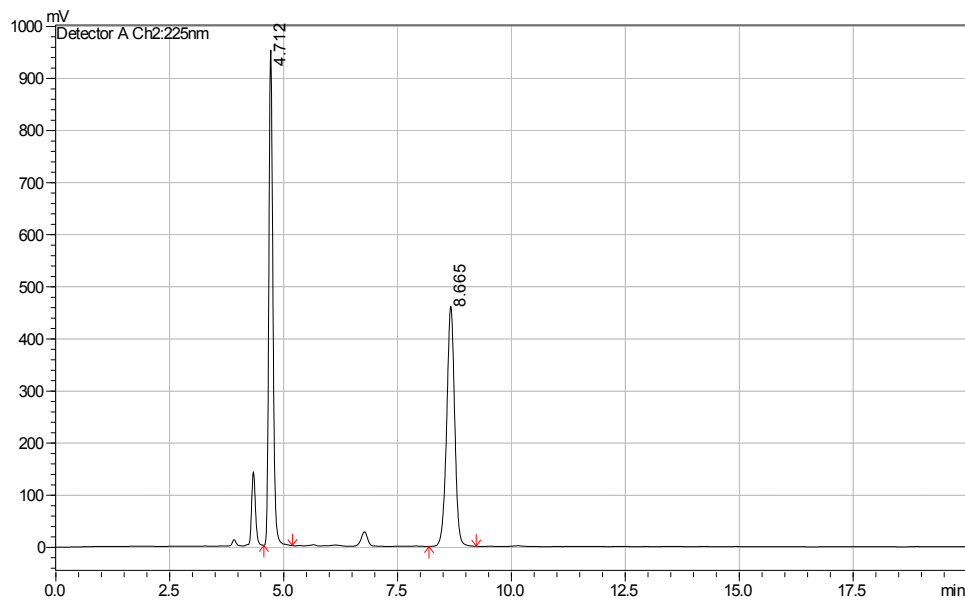


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiracel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 2.00% *i*PrOH in hexanes; Detector: UV @ 254 nm

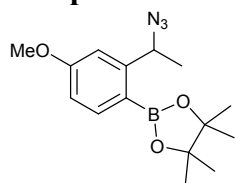
Compound 7



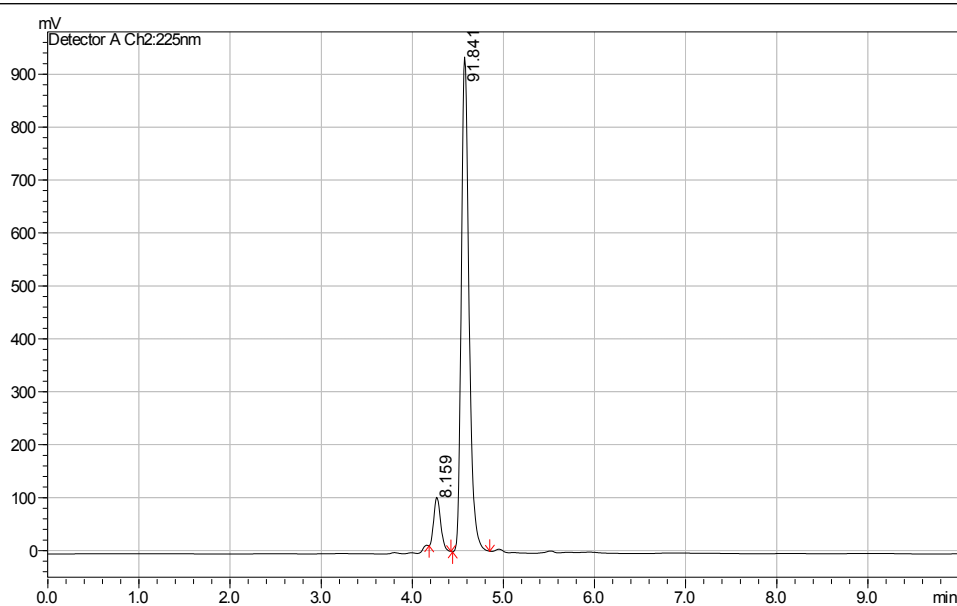
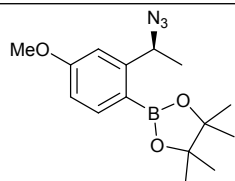
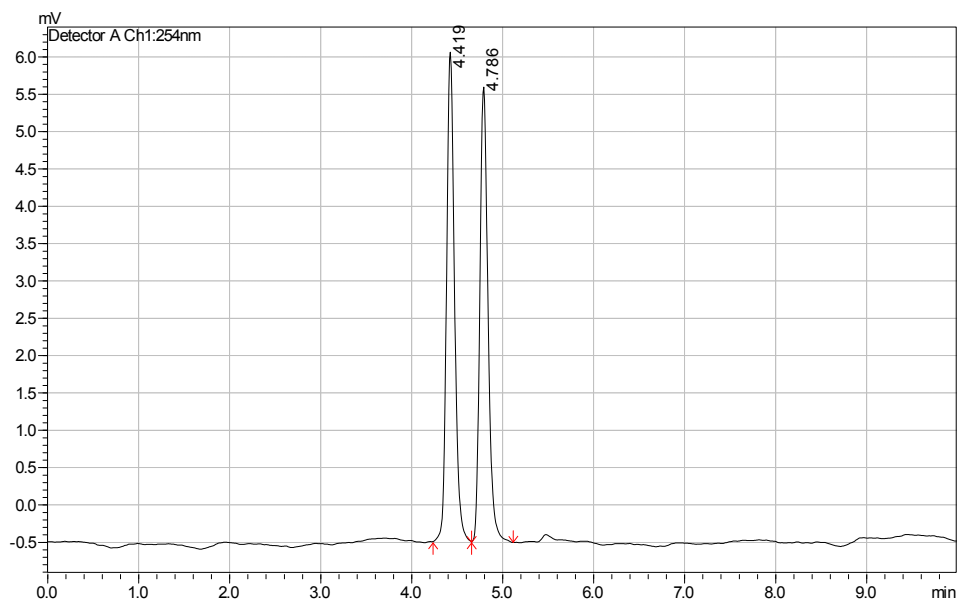
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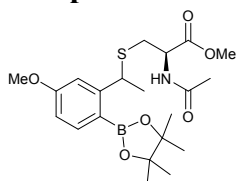
Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 1.00% *i*PrOH in hexanes; Detector: UV @ 254 nm

Compound 8

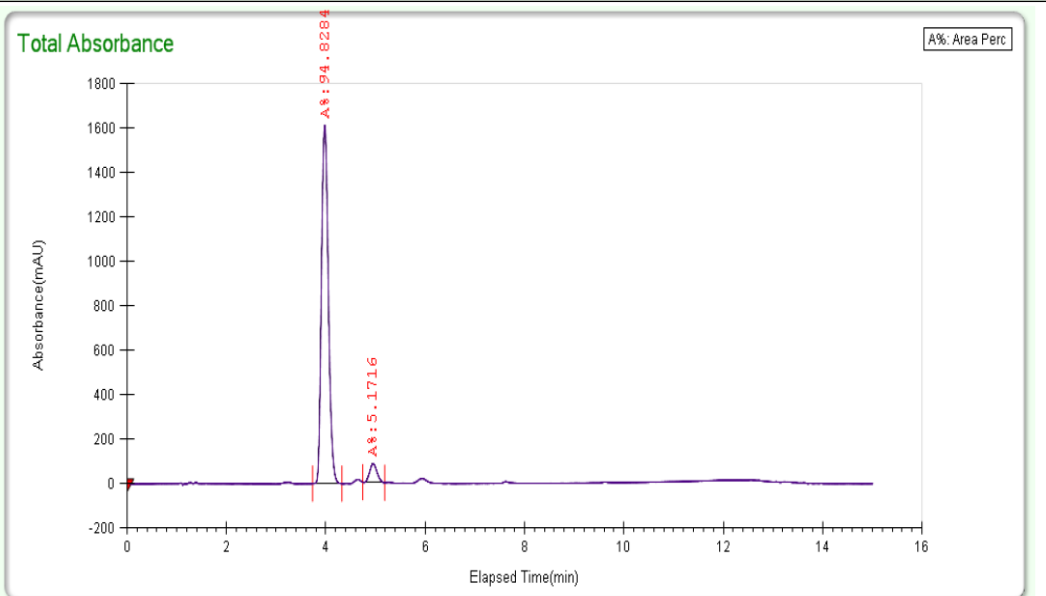
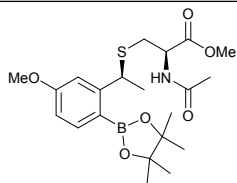
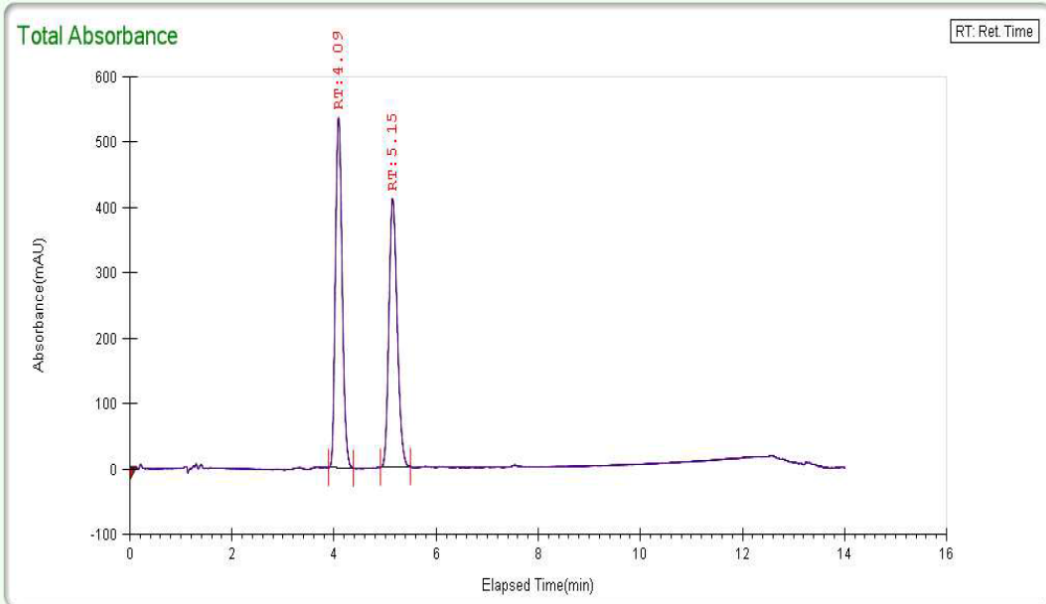
(racemic)



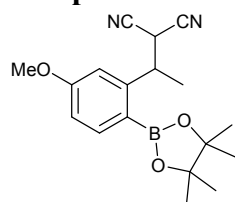
Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 1.00% *i*PrOH in hexanes; Detector: UV @ 254 nm

Compound 9:

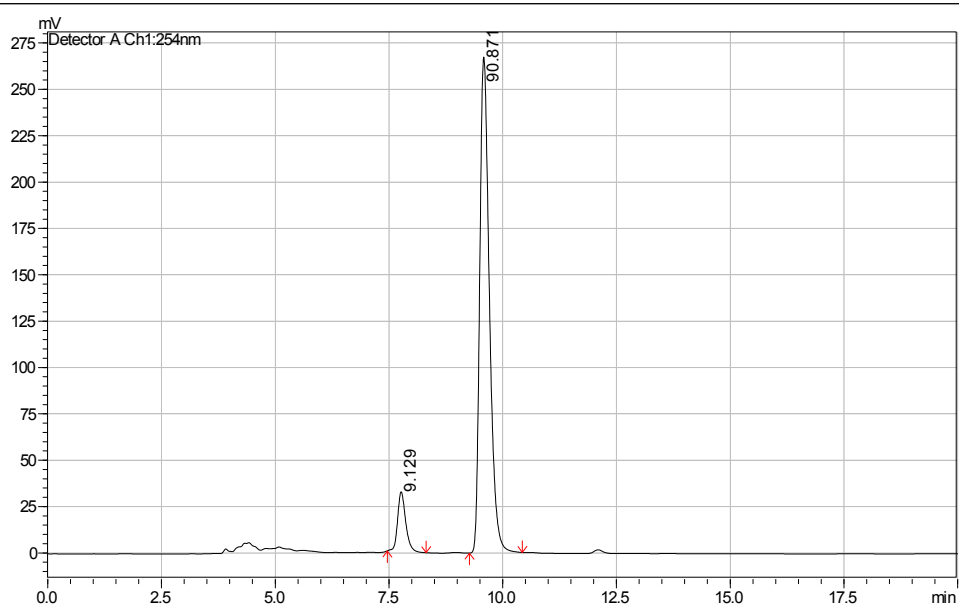
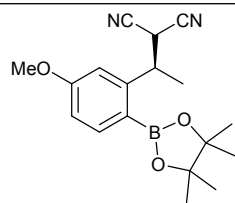
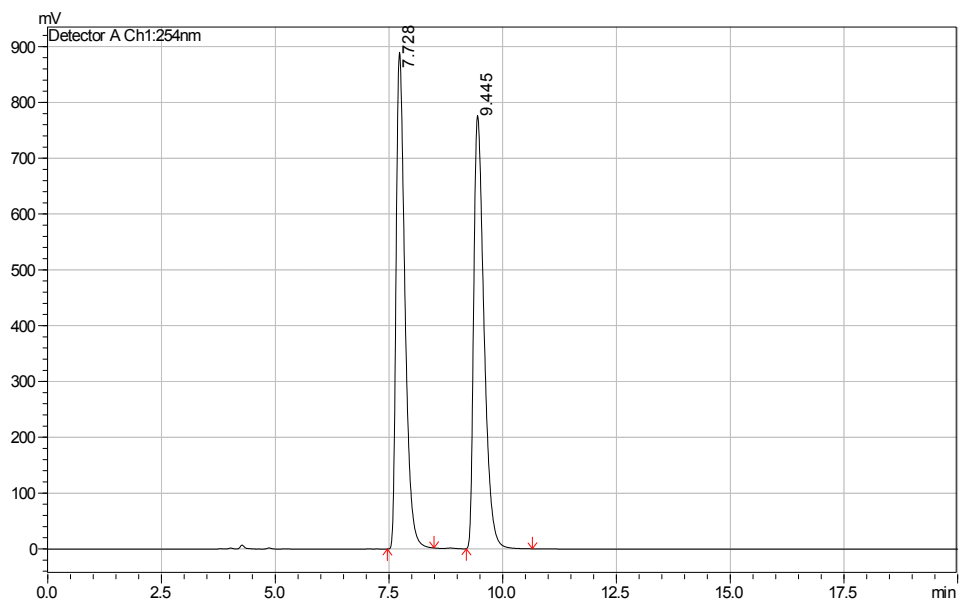
(mixture of diastereomers)



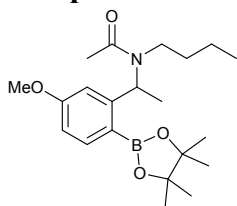
Conditions: Chromatograms were acquired on a Thar SFC equipped with a Chiralcel AD-H column. Flow rate: 3.00 mL/min.; Oven temp: 30.0 °C; Solvent: ramp 5-50% MeOH in CO₂ over 10 min; Detector: UV @ 220-300 nm

Compound 10:

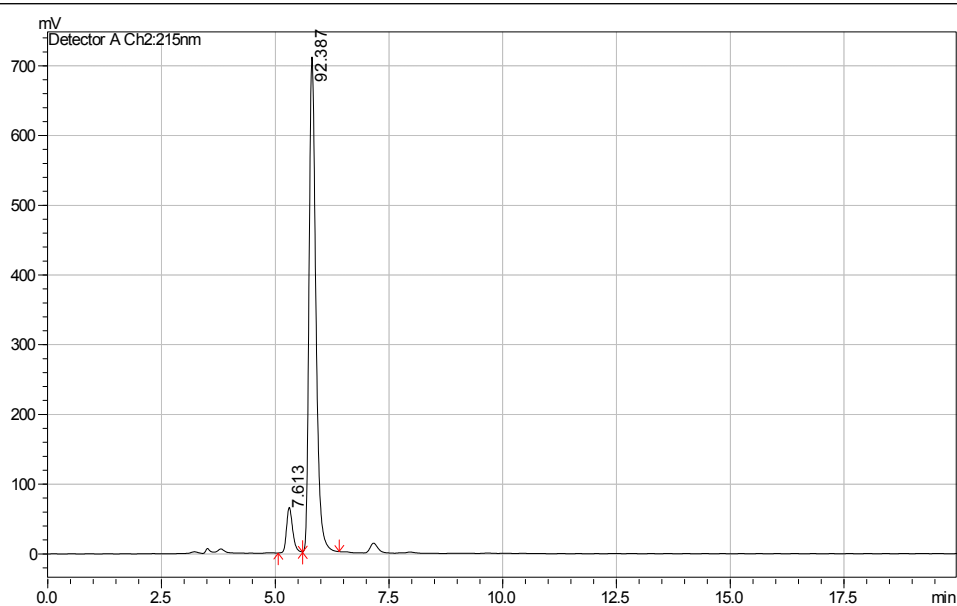
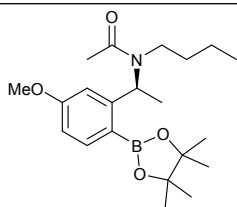
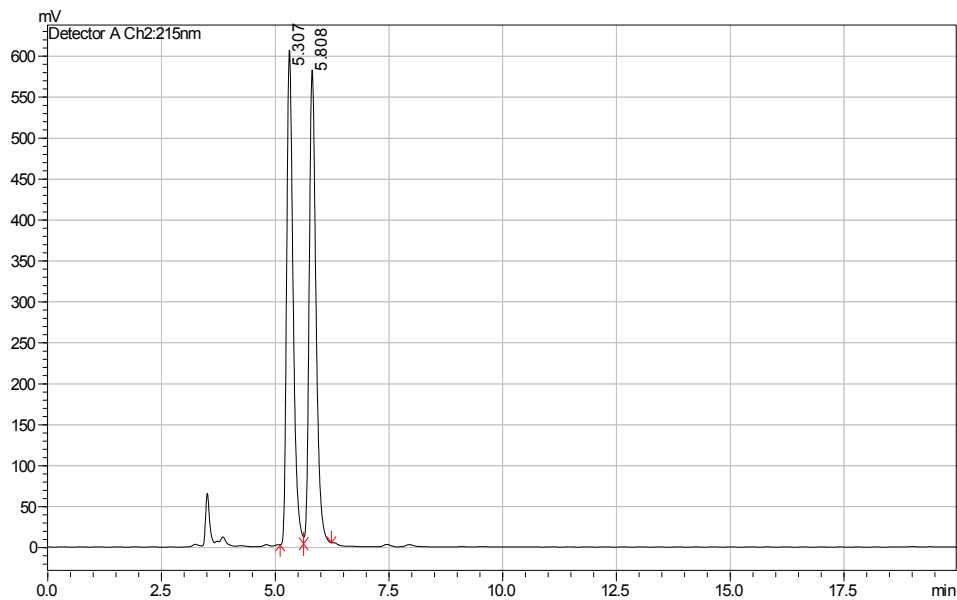
(racemic)



Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 1.00% *i*PrOH in hexanes; Detector: UV @ 254 nm

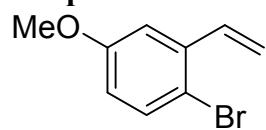
Compound 11:

(racemic)

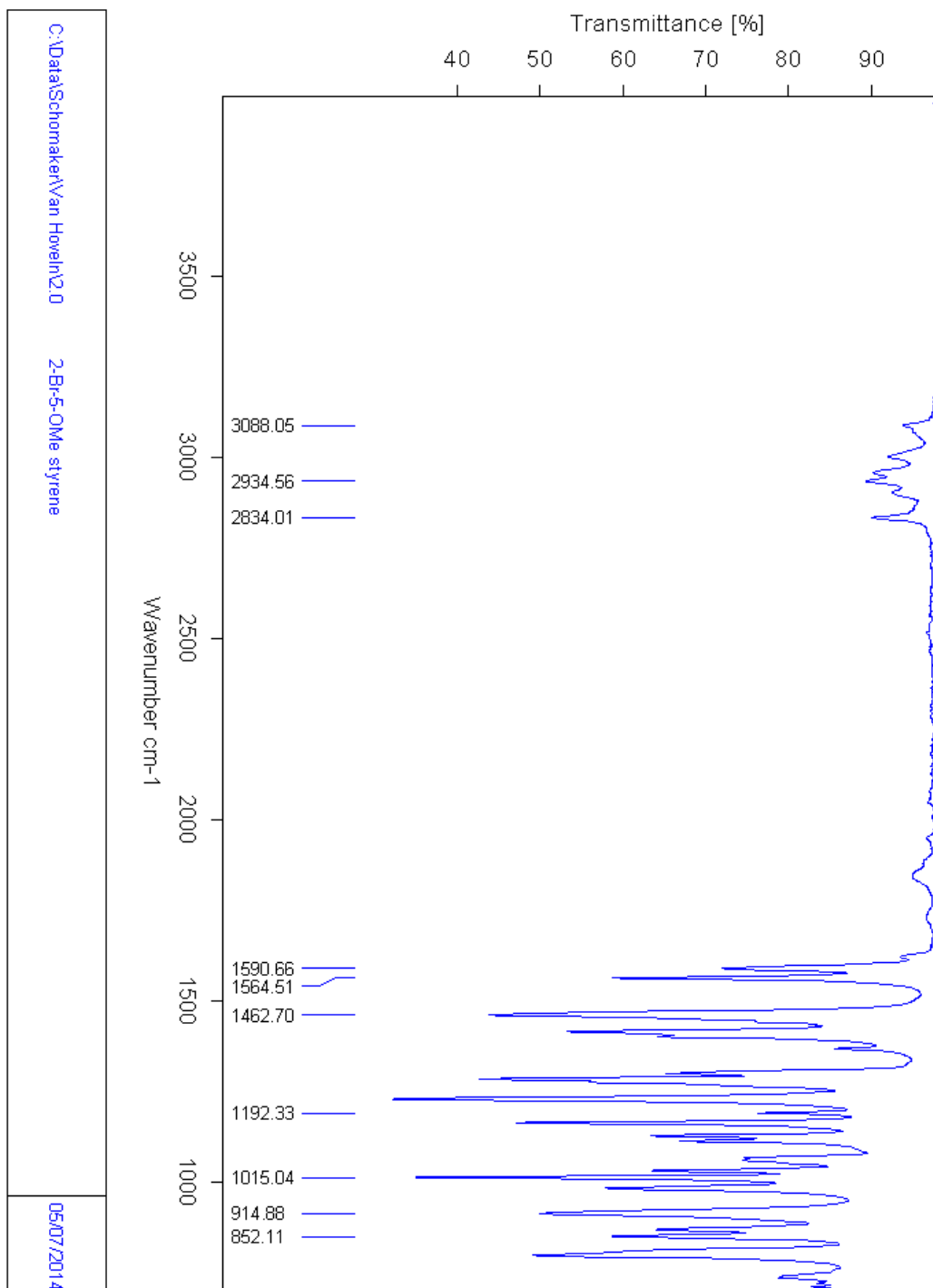


Conditions: Chromatograms were acquired on a Shimadzu Prominence HPLC equipped with a Chiralcel AD-H column. Flow rate: 1.00 mL/min.; Oven temp: 40.0 °C; Solvent: isocratic 5.00% *i*PrOH in hexanes; Detector: UV @ 215 nm

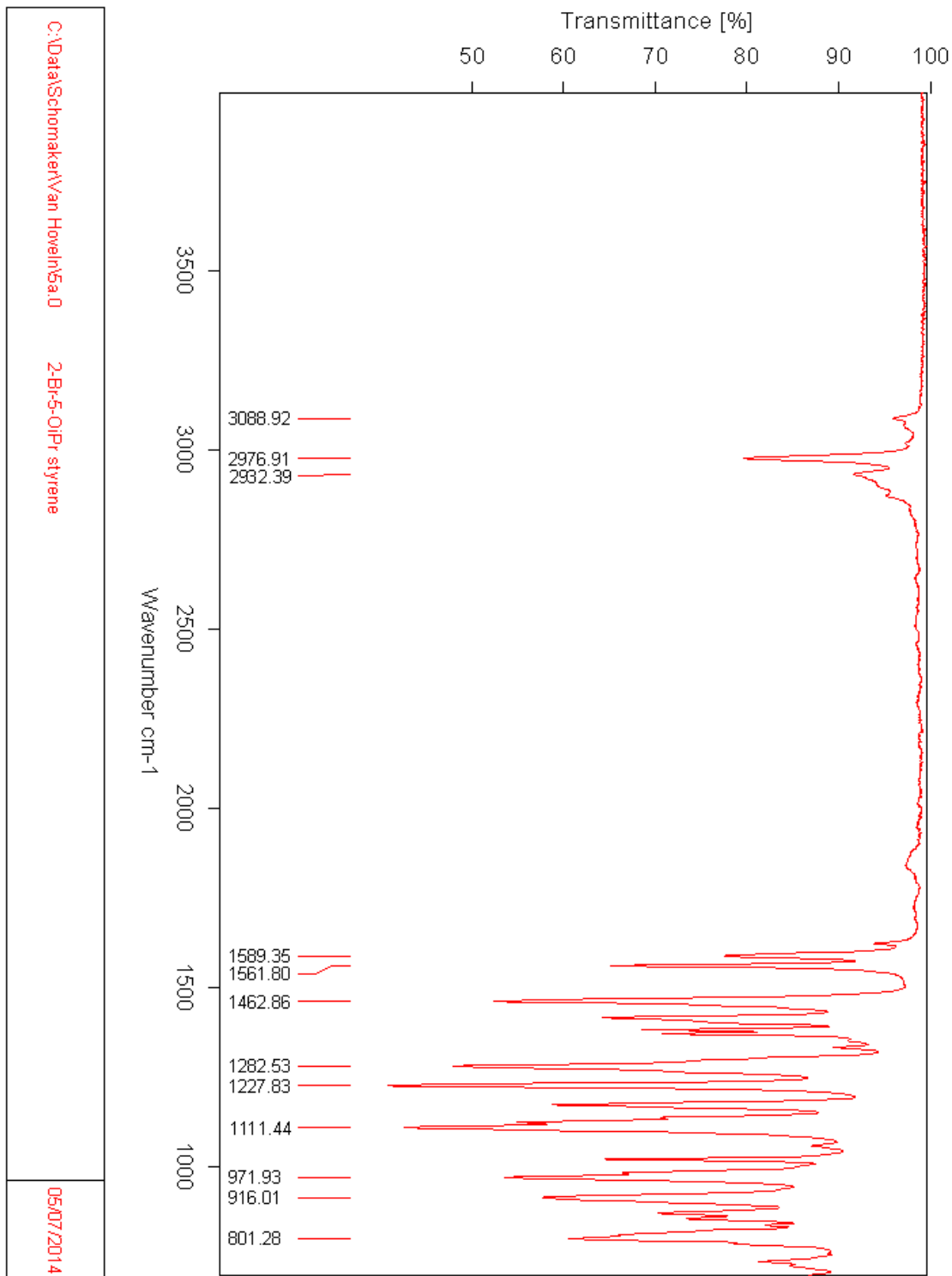
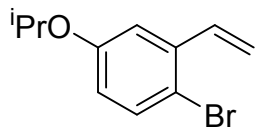
XII. Selected IR Spectra.



Compound 1.



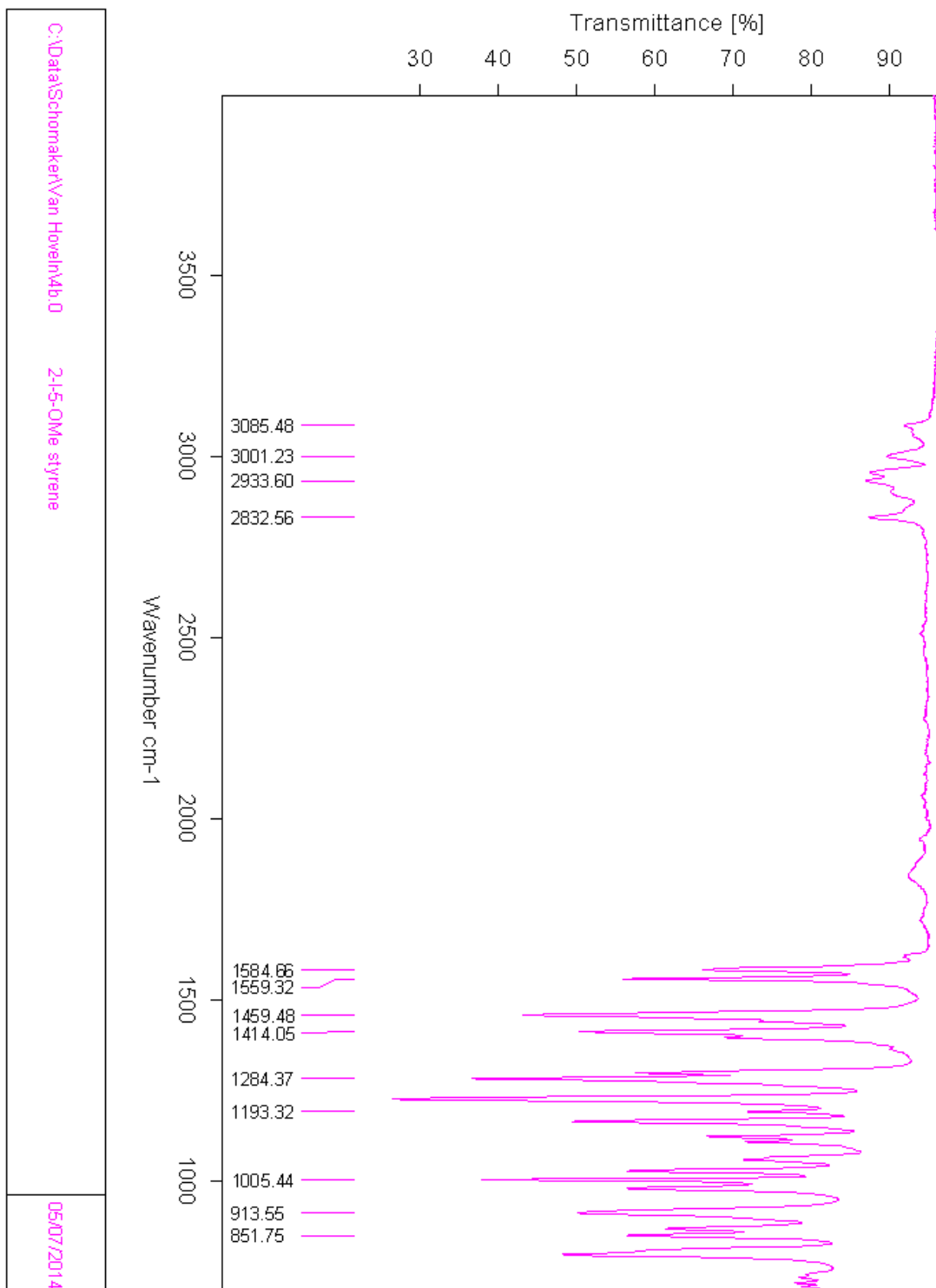
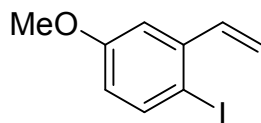
Compound 4a.



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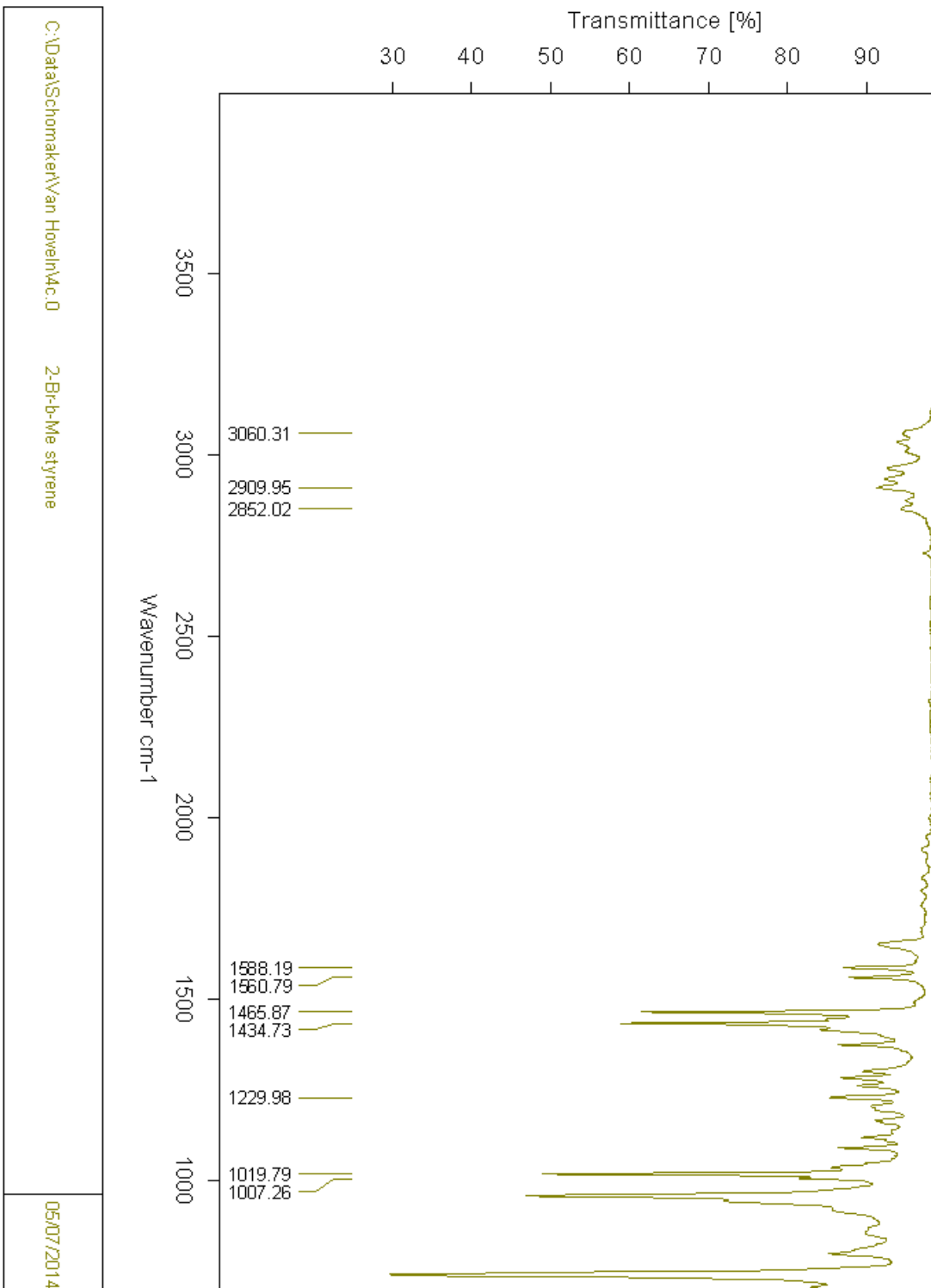
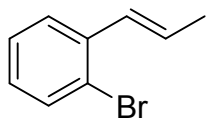
2-Br-5-OiPr-styrene

Compound 4b.

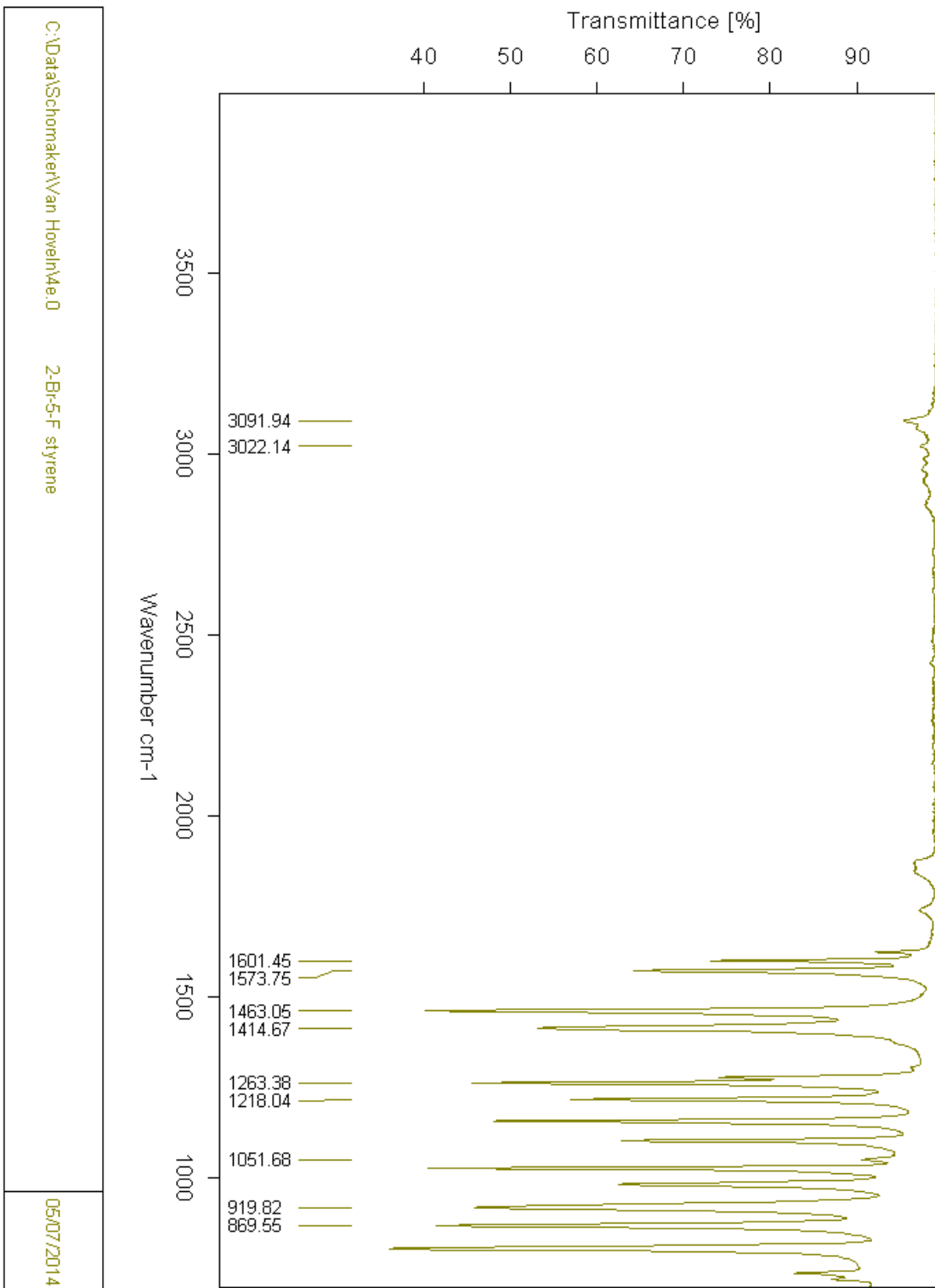
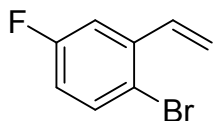


C:\Data\Schomaker\Van Hove\h4b.D 2-I-5-OMe styrene

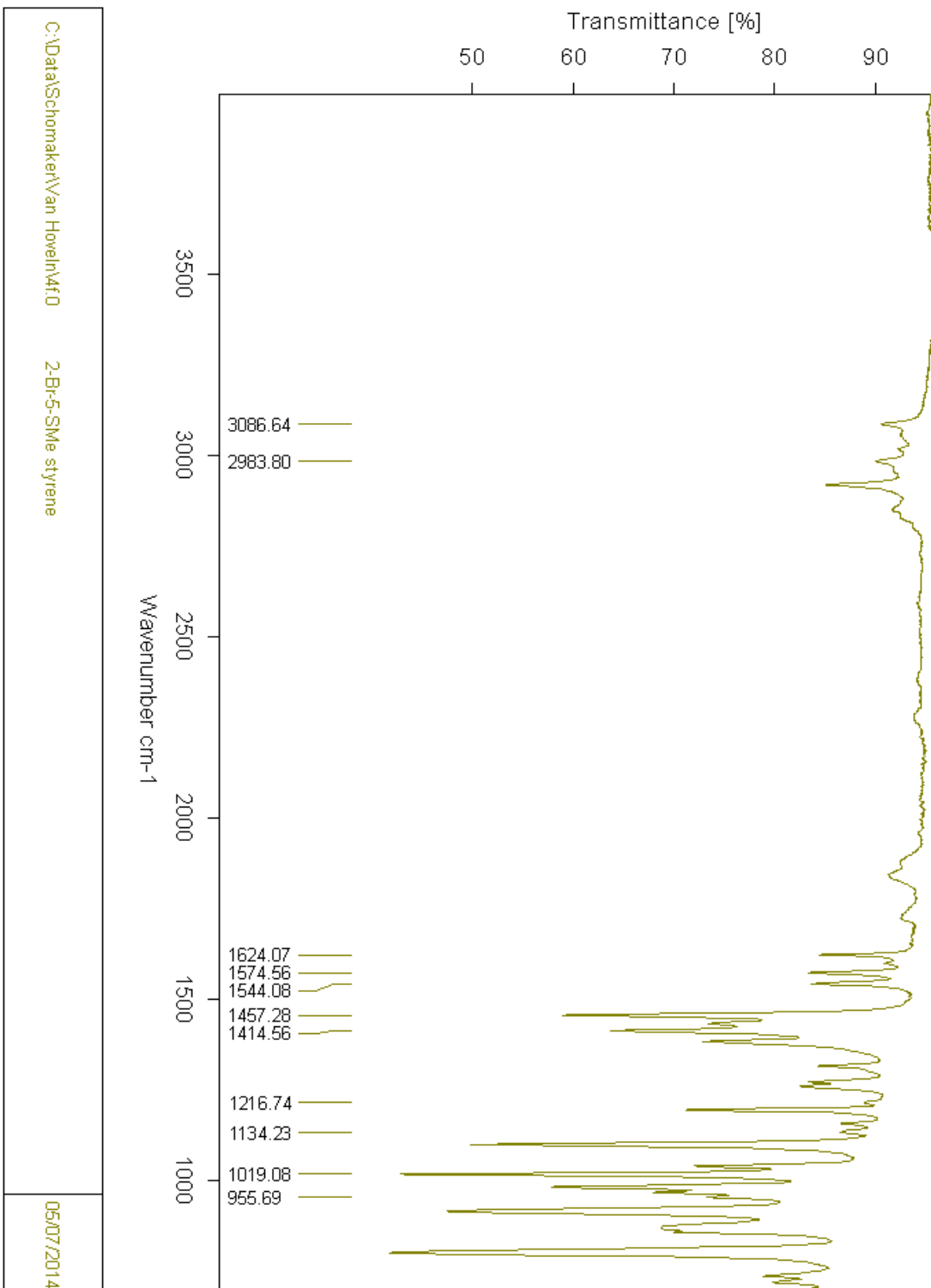
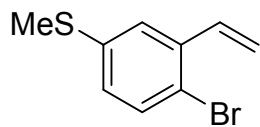
Compound 4d.



Compound 4e.



Compound 4f.

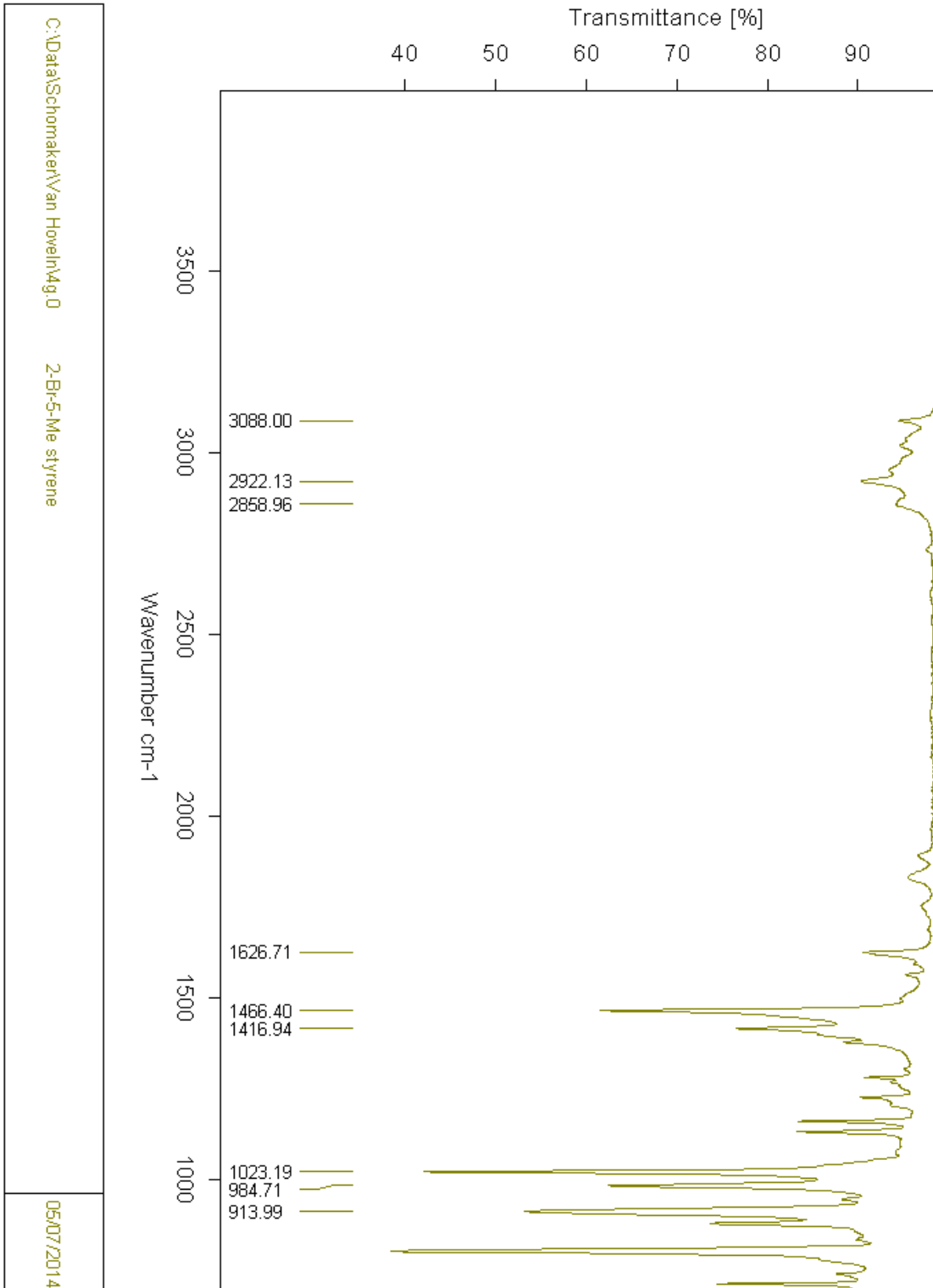
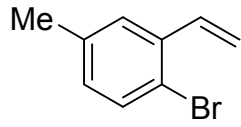


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2-Br-5-Me styrene

05/07/2014

Compound 4g.

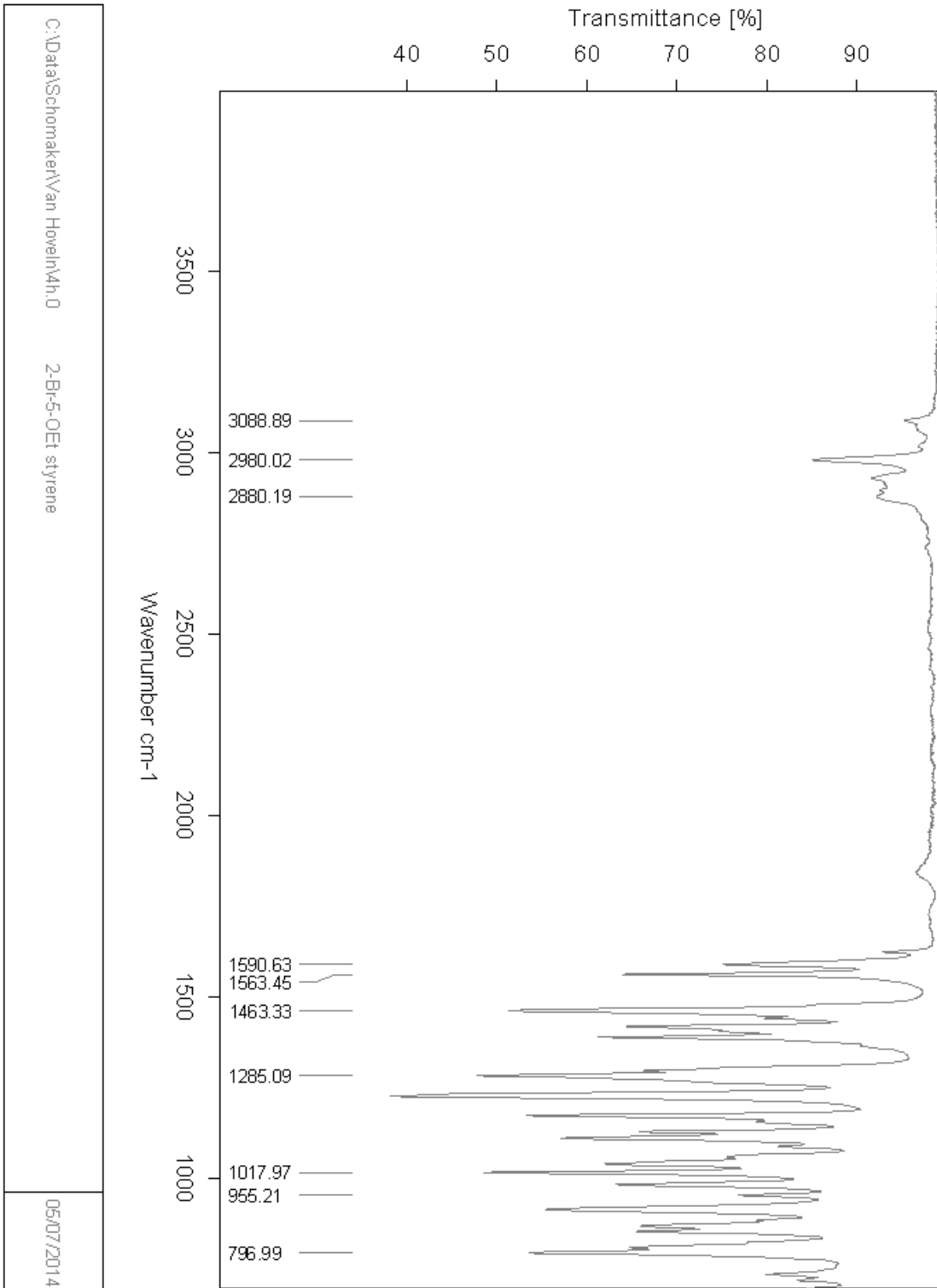
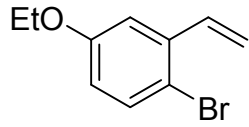


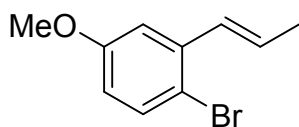
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2-Bromo-5-Methylstyrene

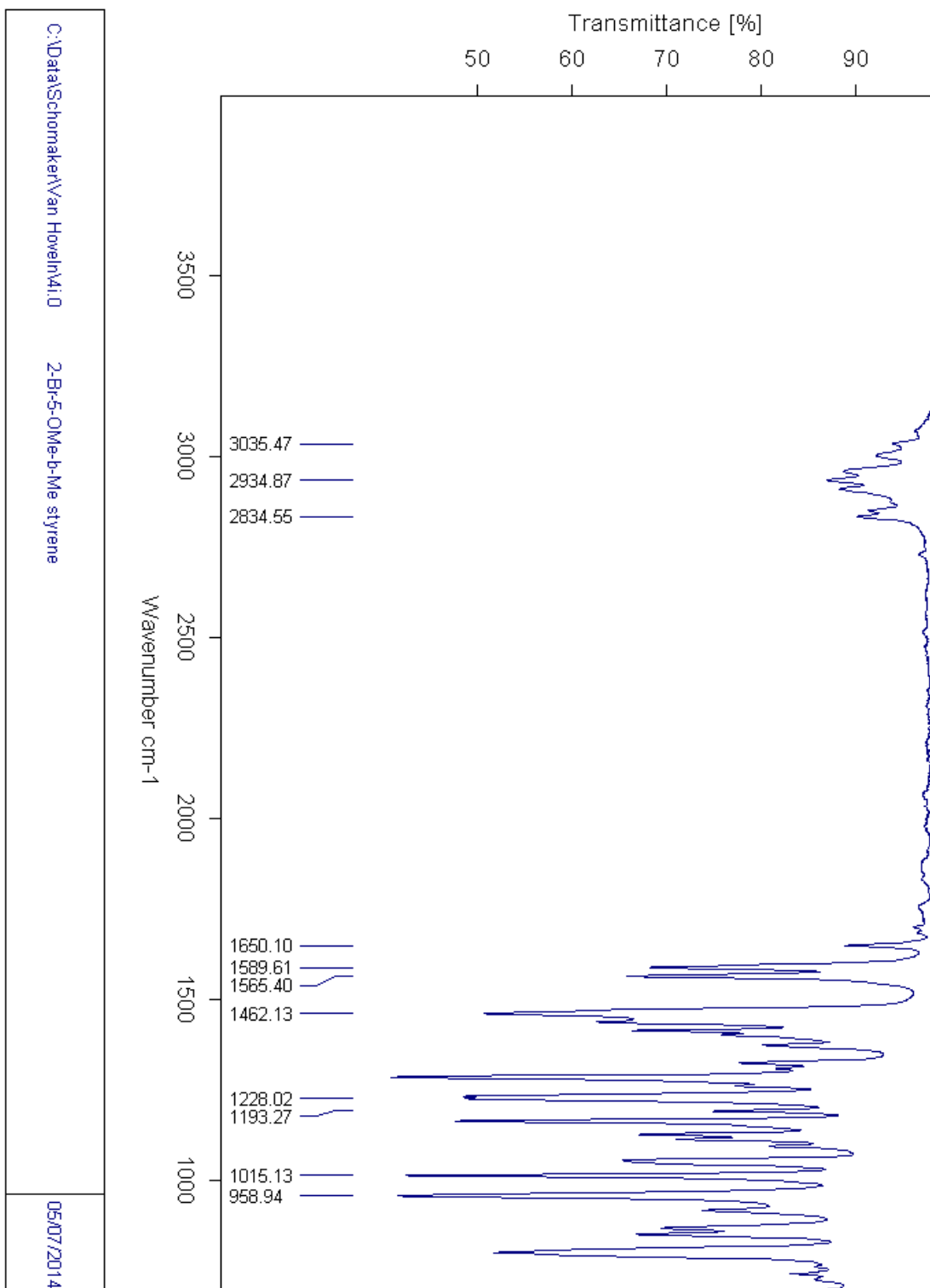
05/07/2014

Compound 4h.

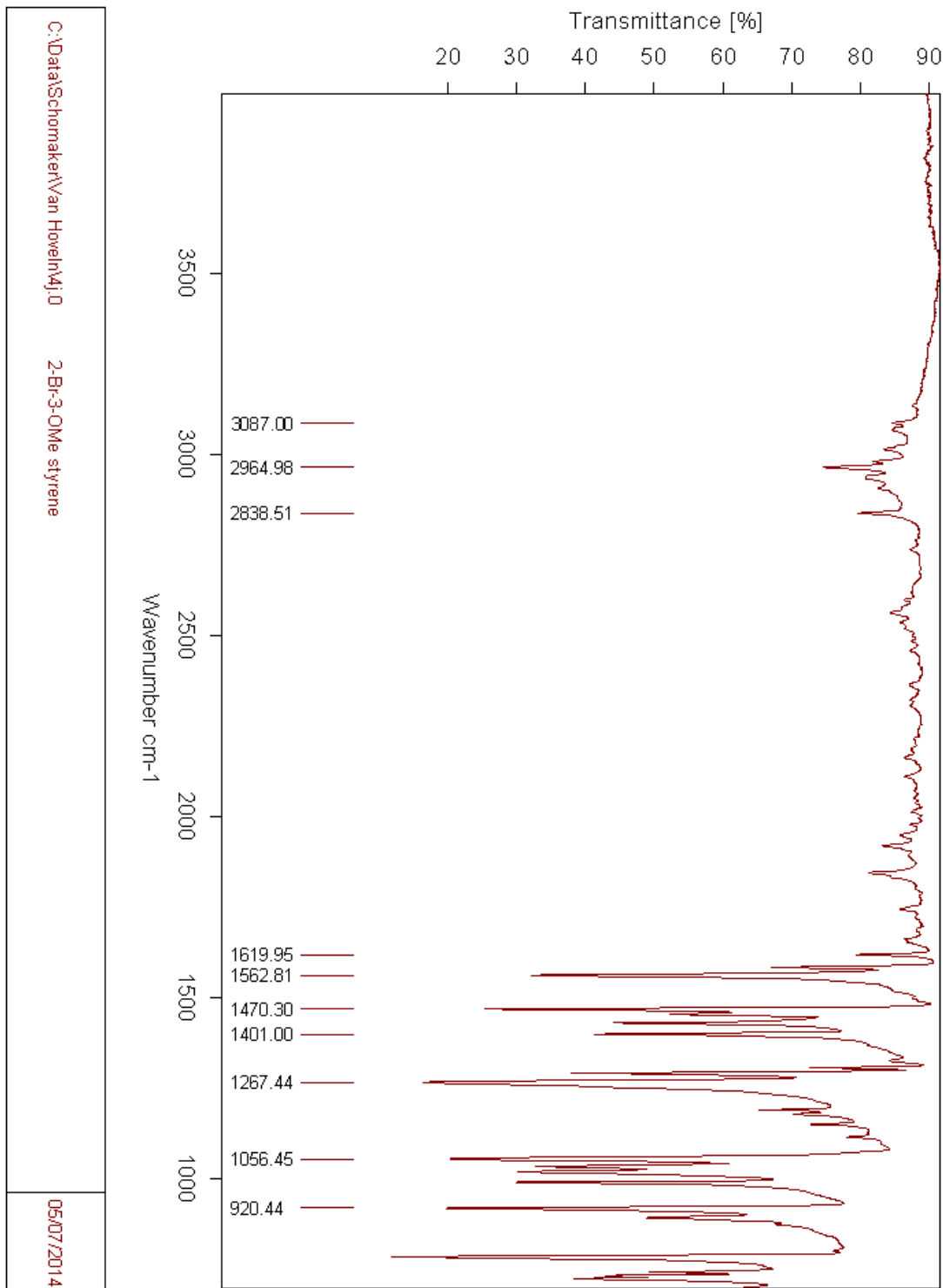
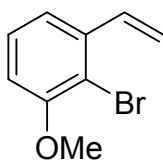




Compound 4i.

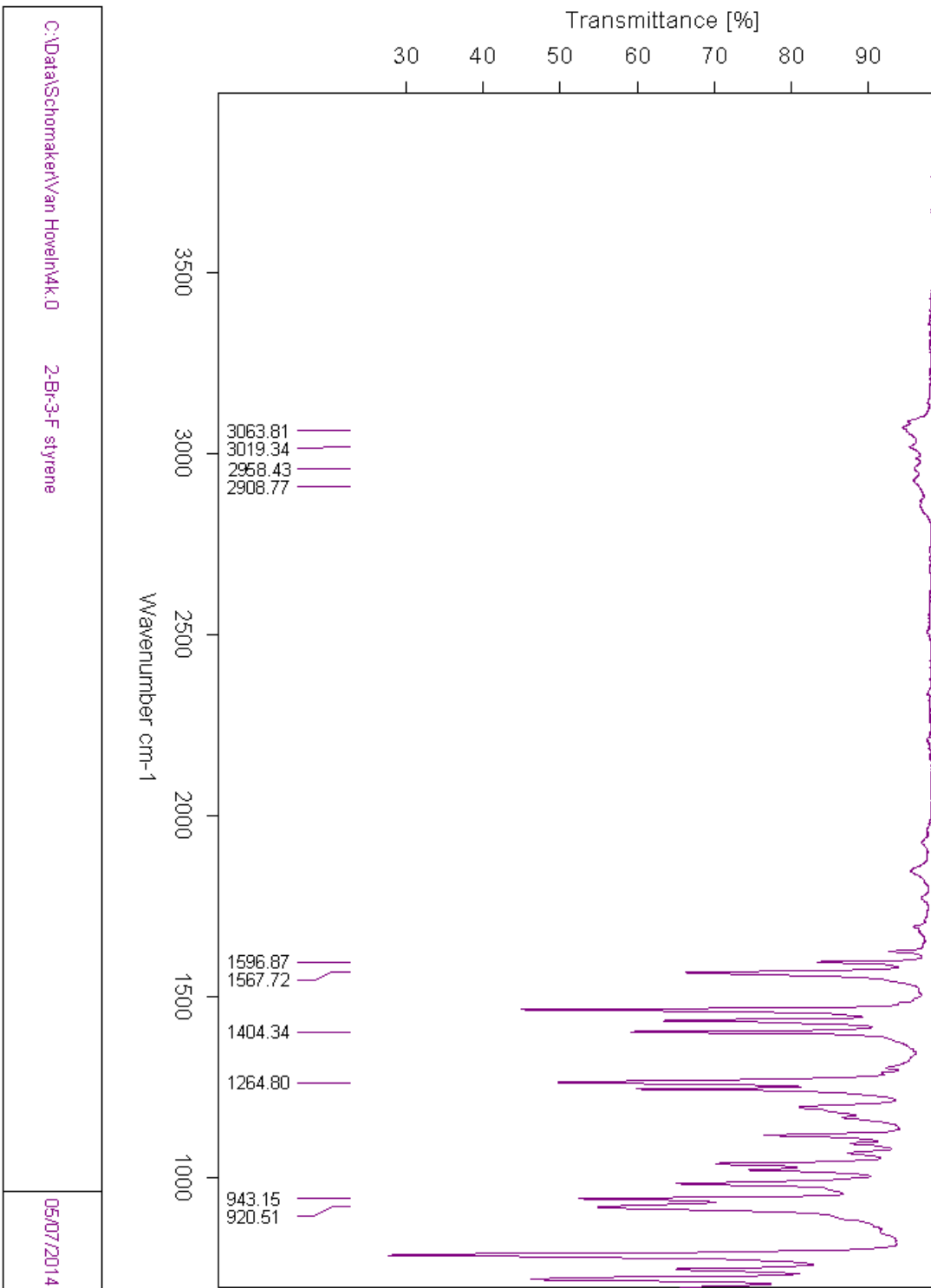
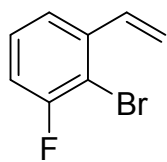


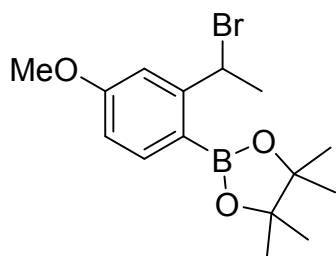
Compound 4j.



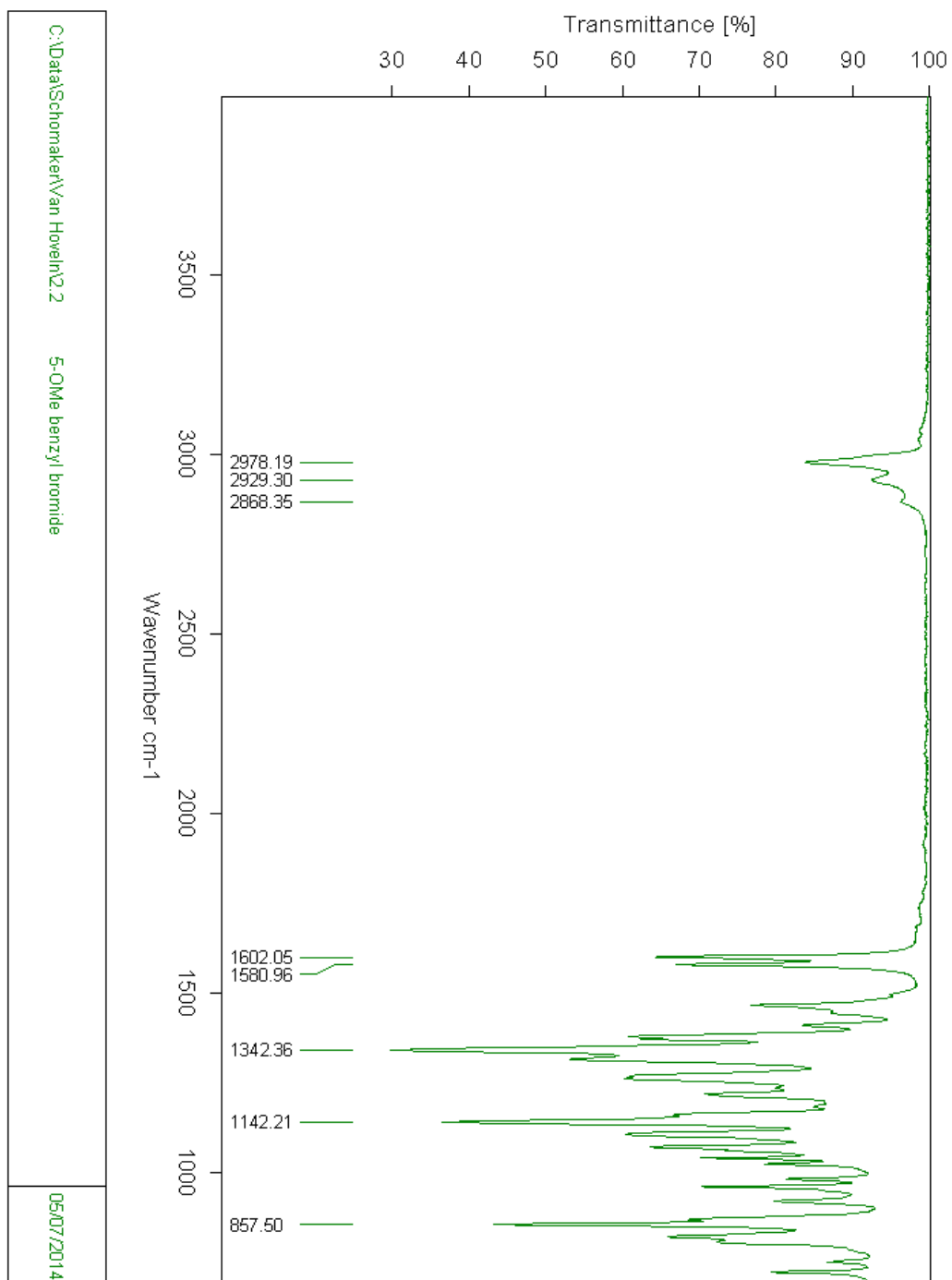
C:\Data\Schomaker\Van Hove\4j.0 2-Br-3-OMe styrene

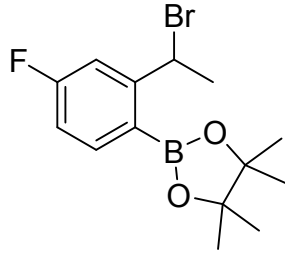
Compound 4k.



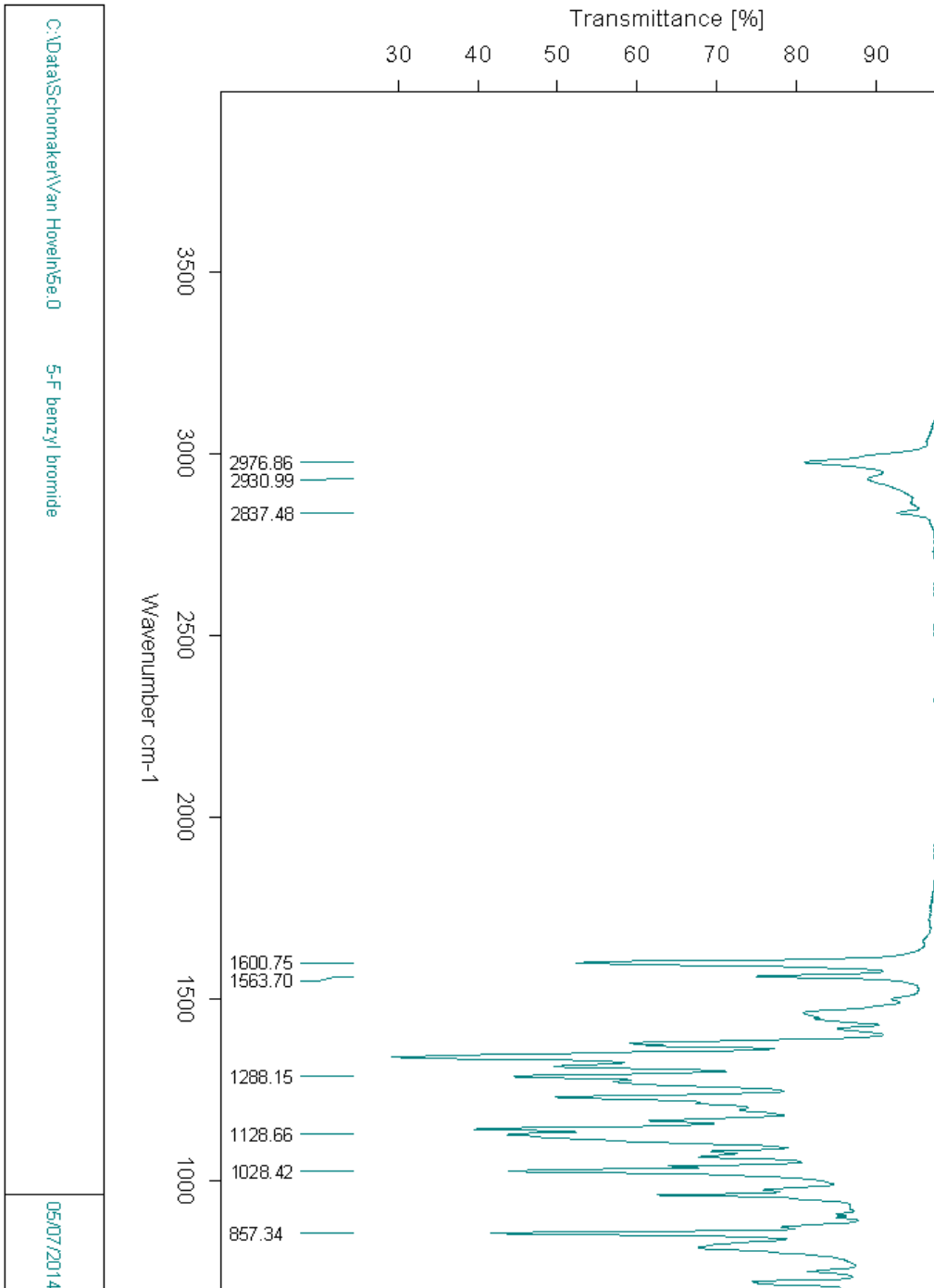


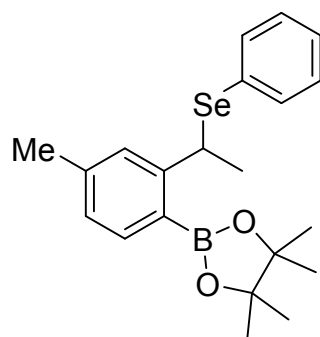
Compound 2.



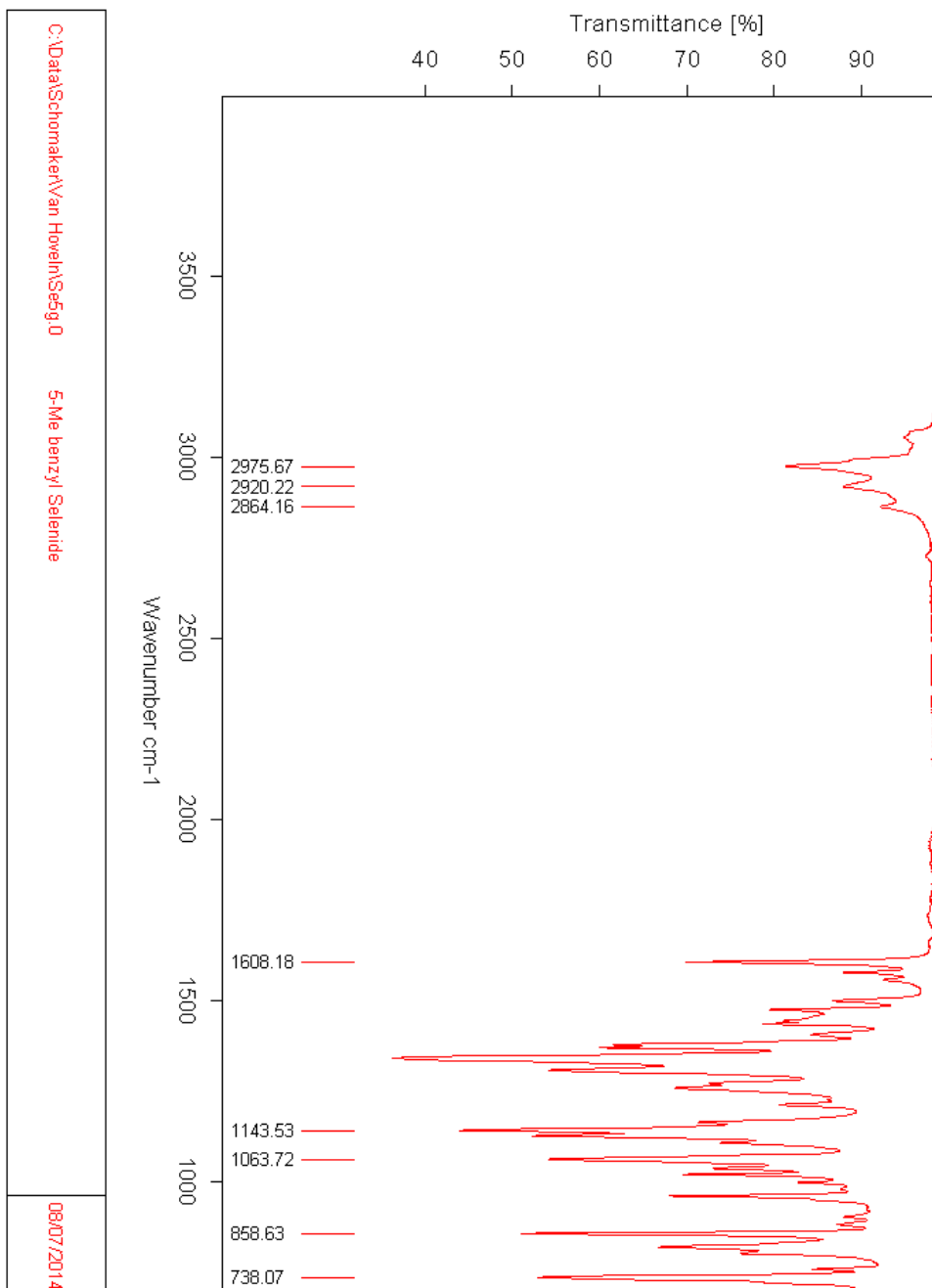


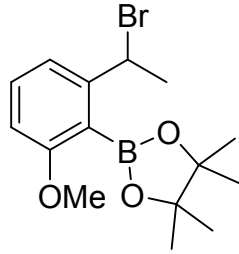
Compound 5e.



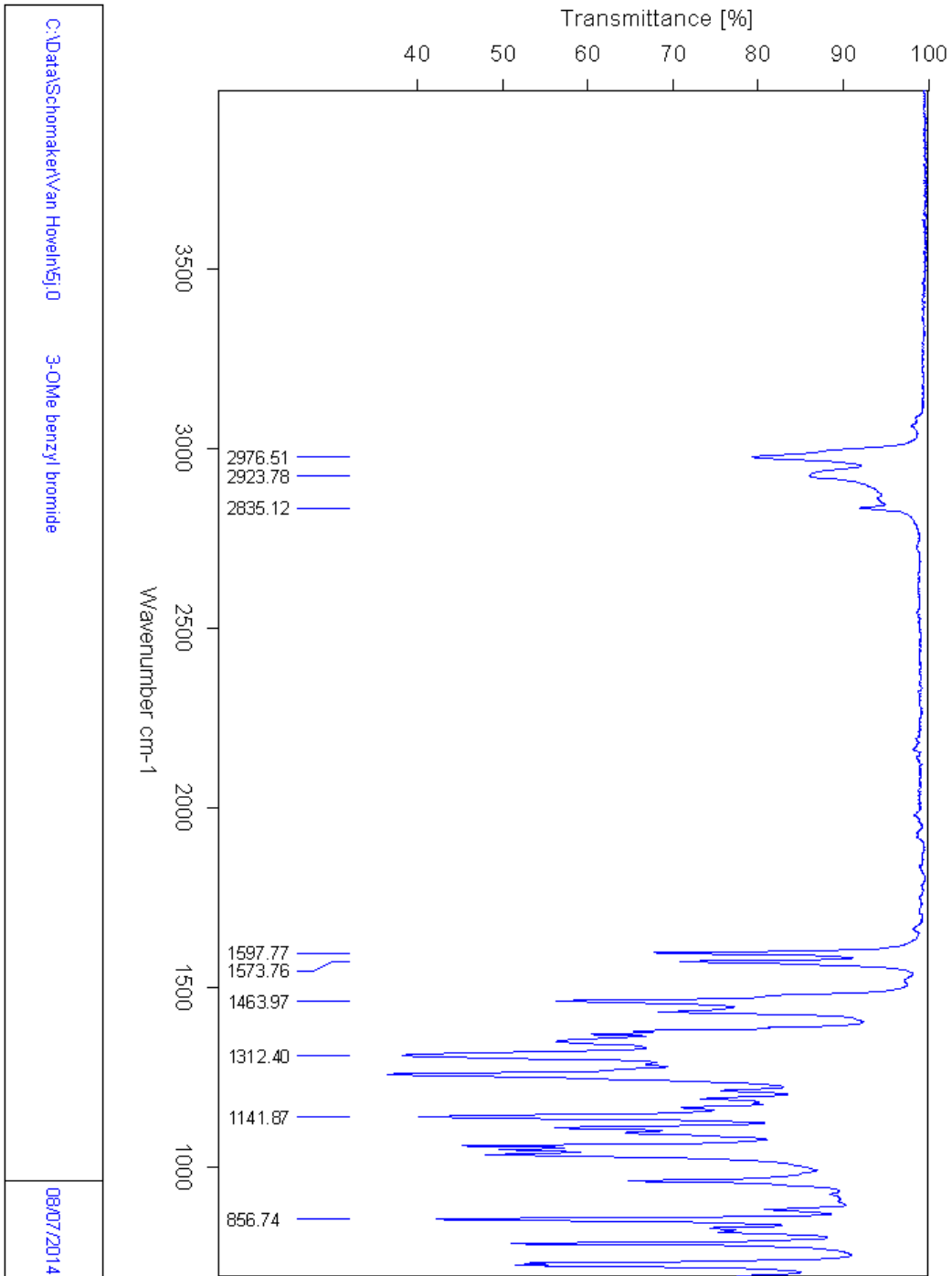


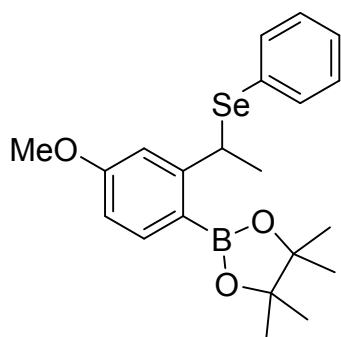
Selenide of Compound 5g.



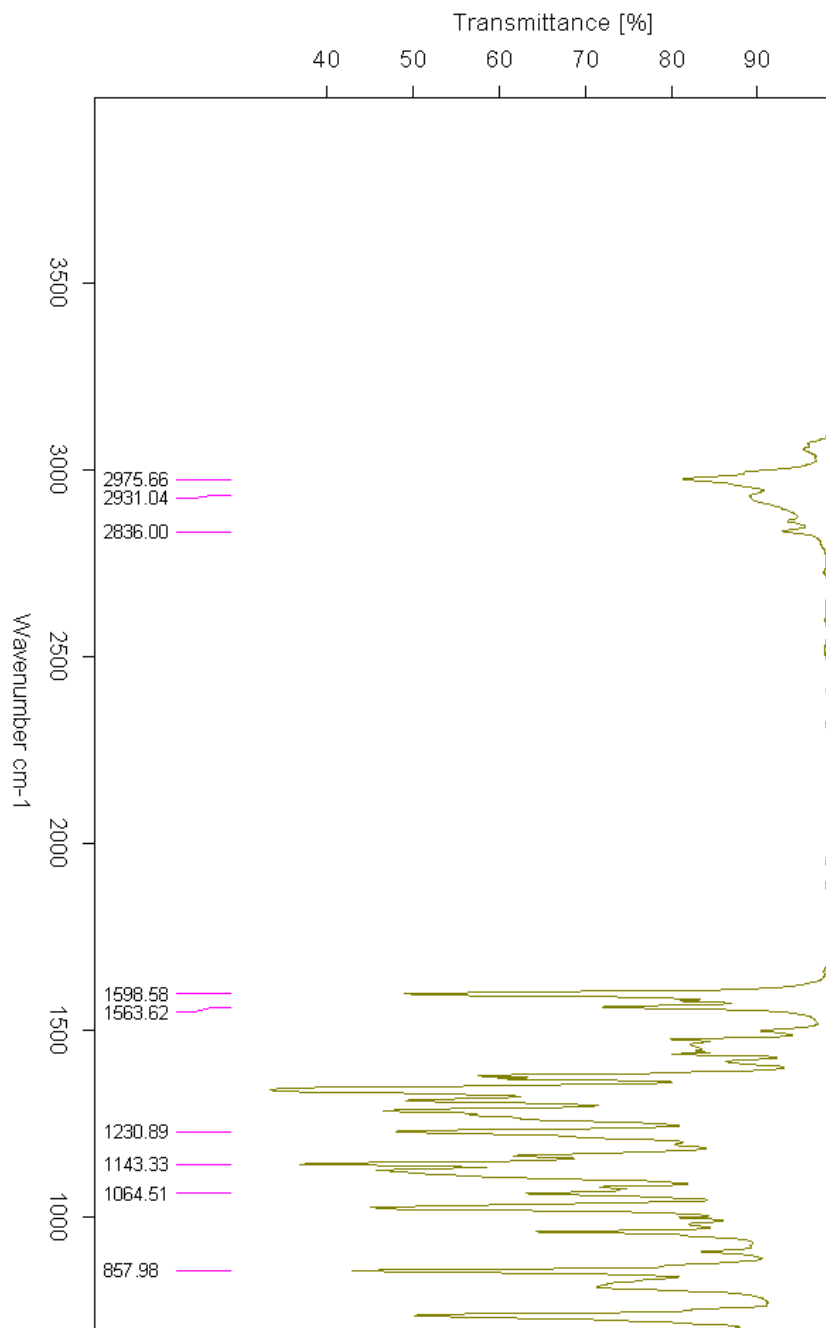


Compound 5j.



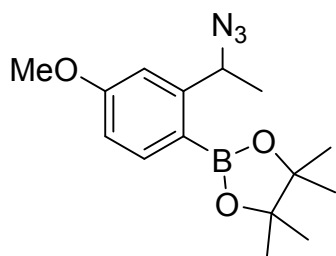


Compound 7.

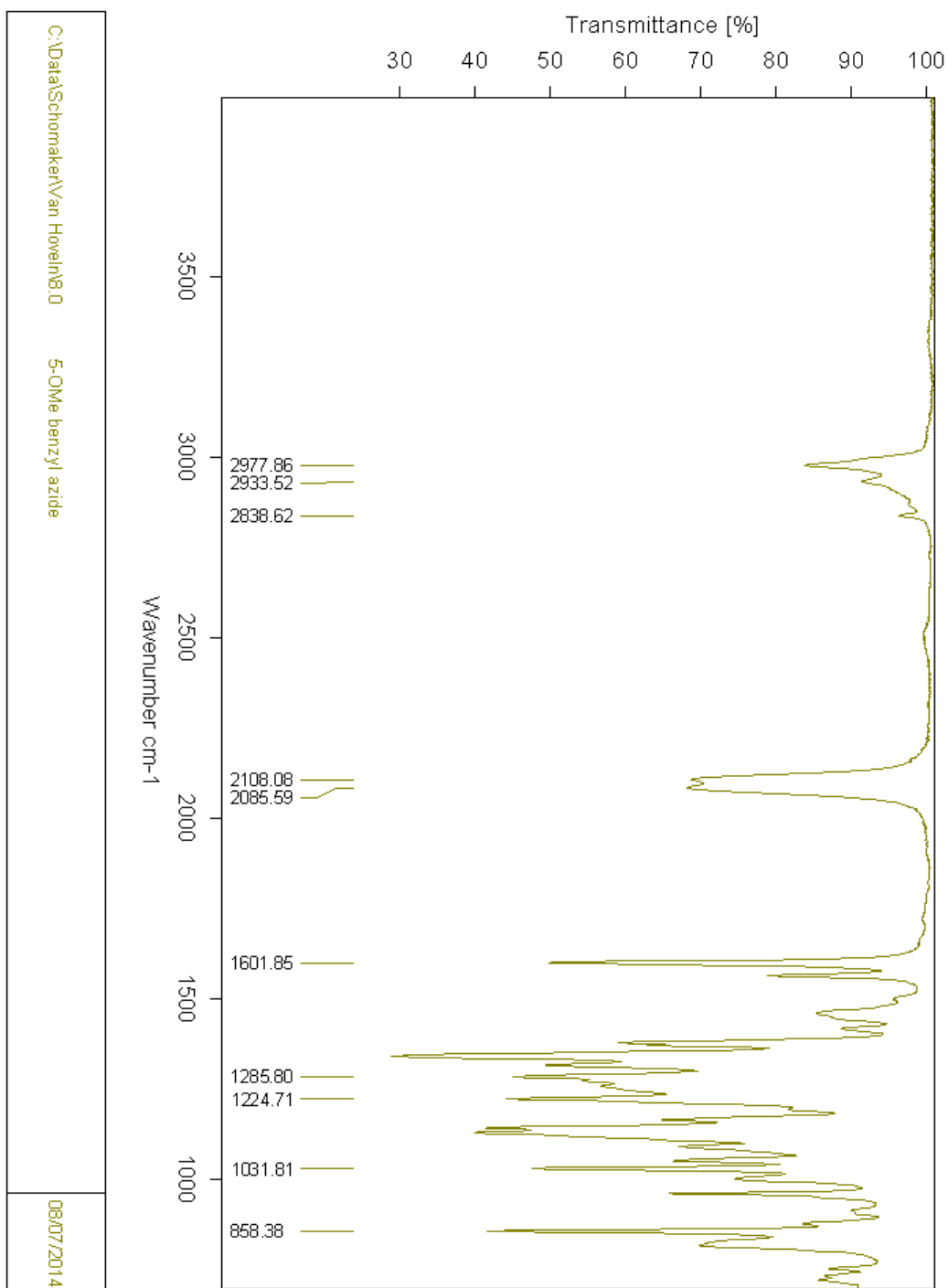


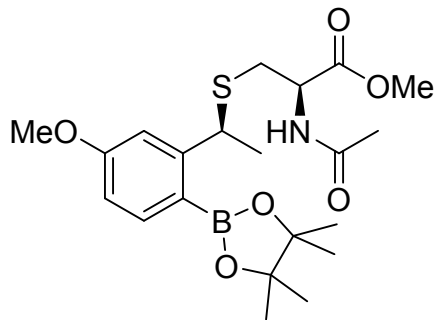
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5-OMe benzyl Selenide

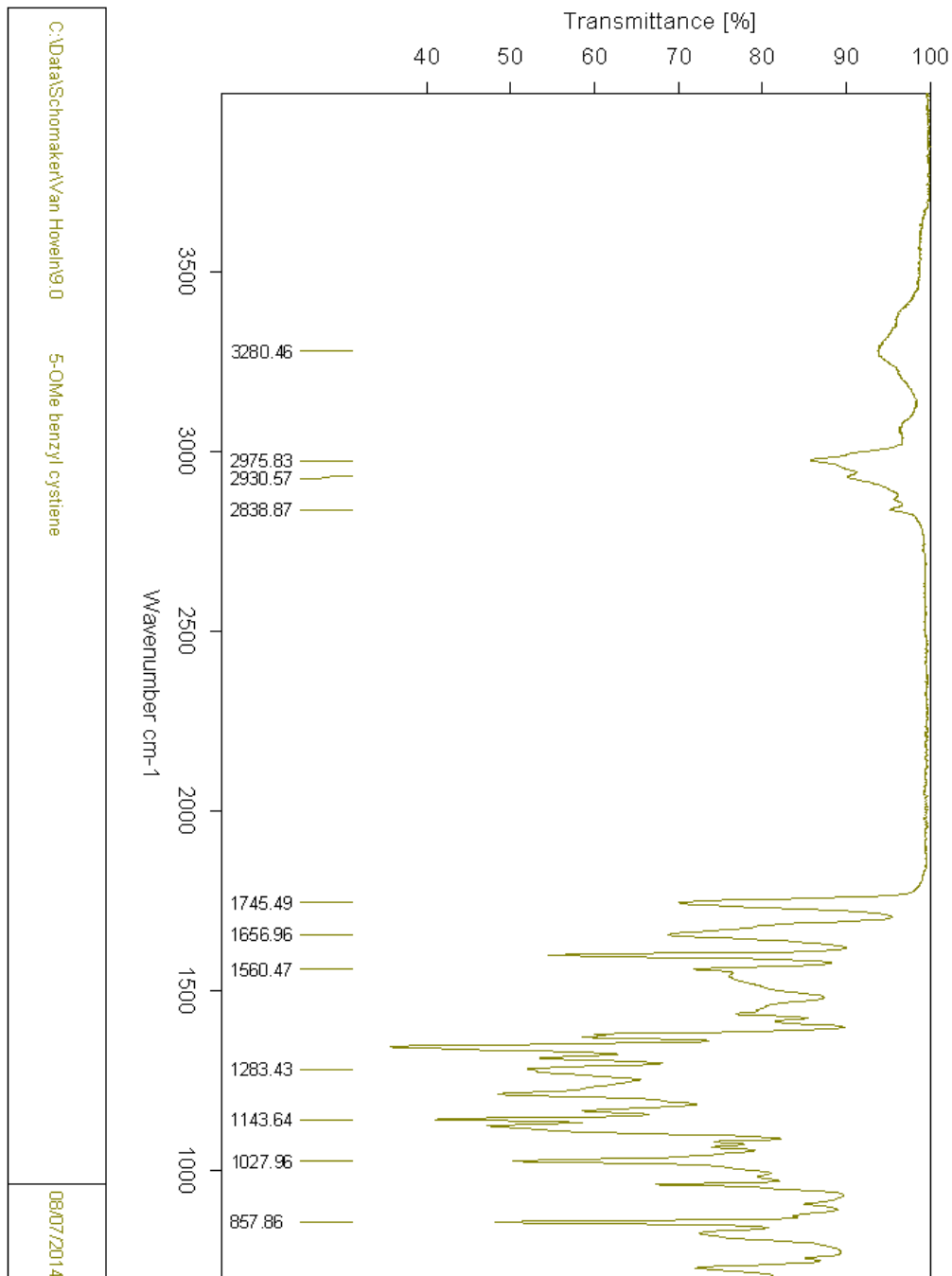


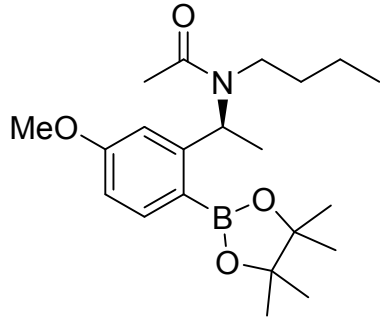
Compound 8.





Compound 9.





Compound 11.

