CURRICULUM VITAE

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Prof. Masakatsu Shibasaki,
Laboratory of Synthetic Organic Chemistry,
Institute of Microbial Chemistry,
3-14-23, Kamioosaki, Shinagawa-ku,
Tokyo 141-0021, Japan.

Academic qualifications:

April 2011-till date	**JSPS Postdoctoral fellow. Prof. Masakatsu Shibasaki,** Laboratory of synthetic organic chemistry, Institute of Microbial Chemistry, 3-14-23, Kamioosaki, Shinagawa-ku, Tokyo 141-0021, Japan.
August 2005 – March 2011	**Ph. D in Organic Chemistry** Research supervisor: Prof. S. Chandrasekaran Thesis Title " **Synthesis of Novel Chalcogenides using Acyloxyphosphonium Intermediates and Doubly Activated Cyclopropanes**" Department of Organic Chemistry, Indian Institute of Science, Bangalore, Karnataka, India.
July 2003 – May 2005	**Master of Science in Organic Chemistry** First class with distinction **(80%)** Department of Organic Chemistry University of Madras, Chennai, Tamil Nadu, India.
July 2000 - May 2003	**Bachelor of Science in Chemistry** First class with distinction **(83.5%)** Ramakrishna mission Vivekananda College, Chennai, Tamil Nadu, India.

Academic Achievements

- Awarded **JSPS Postdoctoral Research Fellowship,** 2011.
- Awarded **Junior & Senior Research Fellowships** by CSIR for the CSIR-JRF exam conducted in December 2004.
- All India **21st rank** with **99.33** percentile in **GATE (**Graduate Aptitude Test in Engineering) **2005.**
- Received **Prize** for standing **first** in the entire School of Chemical Sciences in M. Sc at University of Madras.
- Received Prof. S. Swaminathan Endowment Lectureship and **Prize** for **outstanding student** in M. Sc Organic Chemistry.
- One among the **top 20%** of the students qualified in CSIR-JRF exam held in December 2004.
- One among the **top eight students** selected for the interview of **Shyama Prasad Mukherjee Fellowships** by CSIR for the CSIR-JRF exam conducted in June 2005.

Skill Set

- Multi-step organic synthesis in *organic chemistry*, as well as carbohydrate chemistry.
- Synthesis and performing air, moisture and light sensitive reactions.
- Well versed with various chemistry related computer packages viz. Chem Draw, PC model, Gauss View, ChemCraft, SciFinder Scholar etc. X-ray packages viz. WinGX, PLATON, Mercury etc.
- Knowledge of Techniques and expertise in handling instruments like UV (Shimadzu and JASCO), IR (Perkin-Elmer1310IR, JASCO FT-IR 8300), NMR (JEOL-300 MHz), and HPLC (Shimadzu and Waters).

Research Interests

- Development of new synthetic methodologies
- Drug design and development
- Catalysis
- Asymmetric synthesis

Publication record:

1. Synthesis of Thioesters from Carboxylic Acids via Acyloxyphosphonium Intermediates with Benzyltriethylammonium Tetrathiomolybdate as the Sulfur Transfer Reagent
   Purushothaman Gopinath, Ravindran Sasitha Vidyarini, and Srinivasan Chandrasekaran
   J. Org. Chem. **2009**, *74* (16), 6291–6294.

2. Synthesis of Thioesters by Simultaneous Activation of Carboxylic Acids and Alcohols Using PPh_3/NBS with Benzyltriethylammonium Tetrathiomolybdate as the Sulfur Transfer Reagent
   Purushothaman Gopinath, Ravindran Sasitha Vidyarini, and Srinivasan Chandrasekaran
   Eur. J. Org. Chem. **2009**, 6043-6047.

3. Synthesis of S-functionalized Thioesters using Thioaroylate ions derived from Carboxylic acids and Tetrathiomolybdate via Acyloxyphosphonium intermediates
   Purushothaman Gopinath, Chanda Debasree, Ravindran Sasitha Vidyarini, and Srinivasan Chandrasekaran
   Tetrahedron **2010**, *66*, 7001-7011.

4. Synthesis of Functionalized Dihydrothiophenes from Doubly Activated Cyclopropanes using Tetrathiomolybdate as the Sulfur Transfer Reagent
   Purushothaman Gopinath, Srinivasan Chandrasekaran
   J. Org. Chem. **2011**, *76*, 700-703.

5. Tetraethylammonium Tetraselenotungstate
   Purushothaman Gopinath & Srinivasan Chandrasekaran in *Encyclopedia of reagents for Organic Synthesis*, Ed:. David Crich, John Wiley & Sons LTD, England.
   2011.

6. Benzyltriethylammonium Tetrathiomolybdate, a Versatile Reagent for the Synthesis of Various Interesting Sulfur Compounds through Doubly Activated Cyclopropane Ring Opening
   Purushothaman Gopinath, Srinivasan Chandrasekaran
   (To be submitted)

7. A Highly Regioselective and Mild Protocol for the Nucleophilic Ring Opening of Doubly Activated Cyclopropanes using Selenolates Generated *in situ*
   Purushothaman Gopinath, R. N. Chandrakala, Srinivasan Chandrasekaran
   (To be submitted)

8. A Facile, Efficient and One Pot Synthesis of Bromo Esters and Bromo Thioesters via Ring Opening-Acylation of Cyclic Ethers and Thiiranes
   Purushothaman Gopinath, Srinivasan Chandrasekaran
   (Manuscript under preparation)

Conference papers and presentation

- Presented a Poster entitled " **Doubly activated cyclopropanes – A versatile tool for the synthesis of 1,3–bifunctionalized compounds**" **in 8th AFMC International Medicinal Chemistry Symposium "Frontier of Medicinal Science",** Tokyo, Japan, 2011.
- Participated in the **119th BASF International Summer Course** and also presented a poster entitled '**Benzyltriethylammonium tetrathiomolybdate [BnEtN$_3$]$_2$ MoS$_4$, a versatile reagent for the synthesis of novel sulfur compounds'** held at Ludwigshafen, **Germany** from 27th July – 6th August 2010.
- Delivered a talk on **'Benzyltriethylammonium tetrathiomolybdate, a versatile reagent for the synthesis various interesting sulfur compounds through doubly activated cyclopropane ring opening'** during **J-NOST Symposium** held at IIT-Kanpur, India in December 2009.
- Presented a Poster entitled **'Benzyltriethylammonium tetrathiomolybdate [BnEtN$_3$]$_2$ MoS$_4$, a versatile reagent for the synthesis of novel sulfur compounds'** in the **'RSC-CRSI Symposium on Chemistry'** held at Pune, India in February 2009.
- '***Current Trends in Organic Synthesis***' November 20-22**, 2008**, organized by the Department of Organic Chemistry, Indian Institute of Science, Bangalore**,** India.
- ***'Tenth RSC-CRSI National Symposium'*** Feb 1–3, **2008**, an International symposium organized by Chemical Research Society of India, Indian Institute of Science, Bangalore, India.

- ***'Chemistry Today and Tomorrow'*** January 4 – 7, **2006**, an International Symposium organized by the Department of Organic Chemistry, Indian Institute of Science, Bangalore, India.
- ***'Indo-Russian Symposium in Organic Chemistry'*** on Nov 7-8, **2005**, Indian Institute of Science, Bangalore

Personal Details

- **Gender** **: Male**
- **Date of Birth** **: 24th Dec 1982**
- **Nationality** **: Indian**
- **Marital status** **: Single**

References

1. Prof. Masakatsu Shibasaki,
   Laboratory of synthetic organic chemistry,
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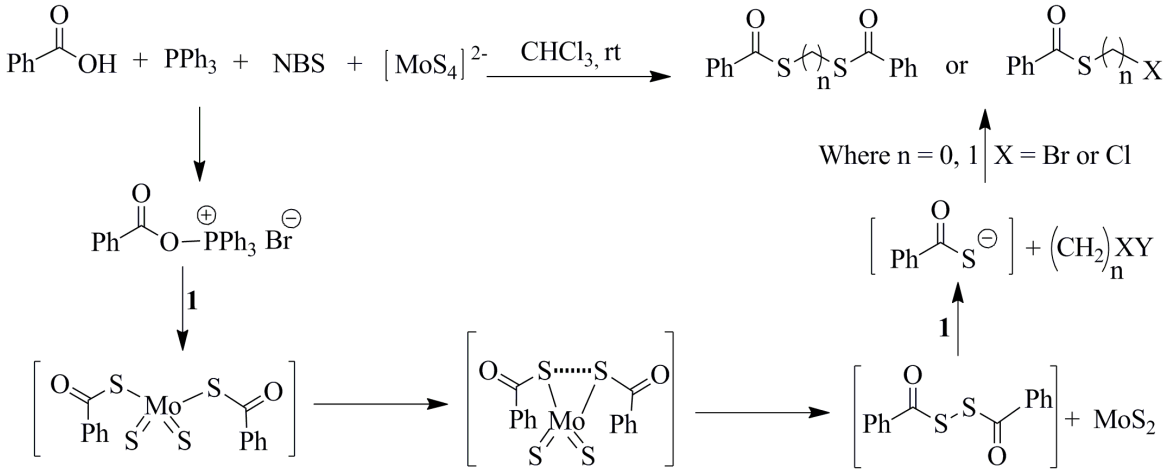
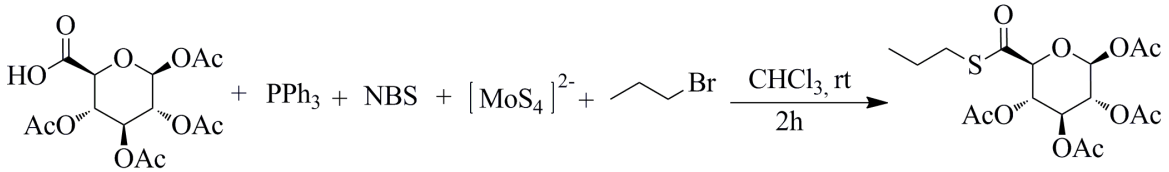
Work Summary

In the first part functionalized thioesters were synthesized from acyloxy phosphonium intermediates (generated from carboxylic acids, PPh_3 & NBS), benzyltriethylammonium tetrathiomolybdate $[BnEt_3N]_2\,MoS_4$, **1** and the corresponding alkyl halides / dihalides.

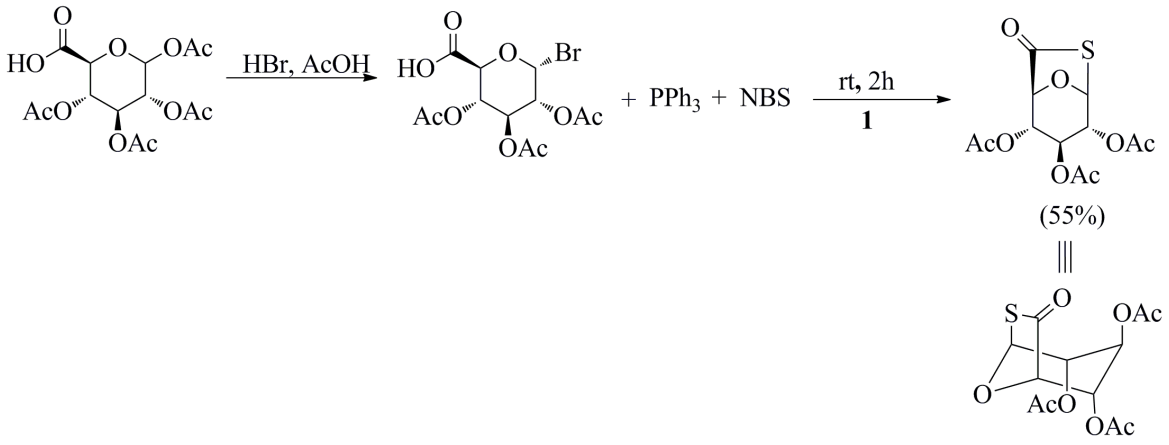


This methodology was then extended to carbohydrate-based thioesters as they are important synthetic intermediates in various transformations and also they could be deprotected later to synthetically more valuable thiols.



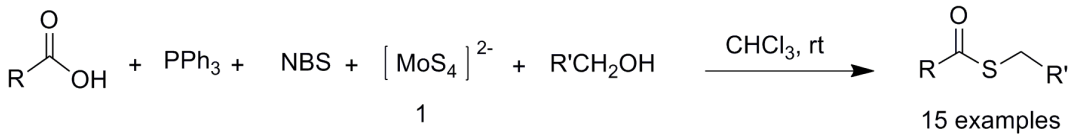
(55%)

An intramolecular version of the reaction was carried out with α-D-bromo-glucopyranuronic acid, PPh_3, NBS and reagent, **1** to give the corresponding bicyclic thiolactone in 55% yield.

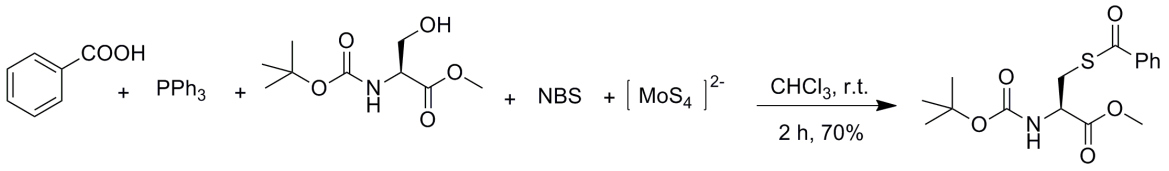


(55%)

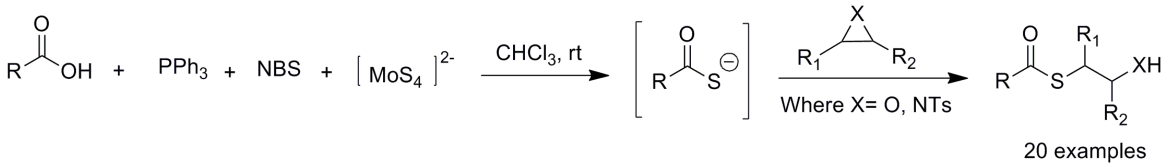
We also then synthesized thioesters from carboxylic acids and alcohols as well. This was achieved by taking excess of PPh_3 and NBS for activating both carboxylic acids and alcohols.



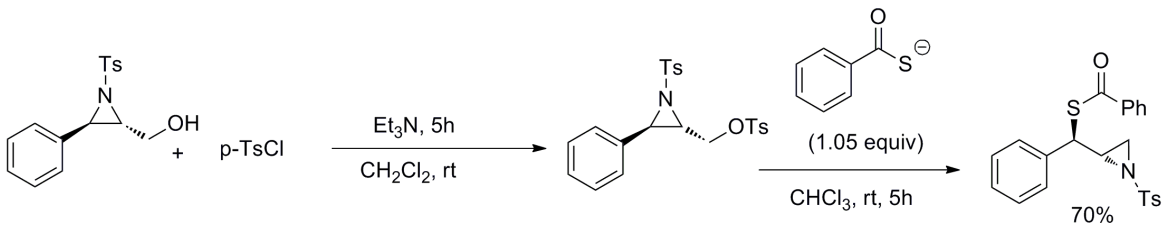
The same methodology was then used for a one-pot conversion of N-Boc serine ester to S-protected cysteine using reagent **1** as the key sulfur transfer reagent**.**

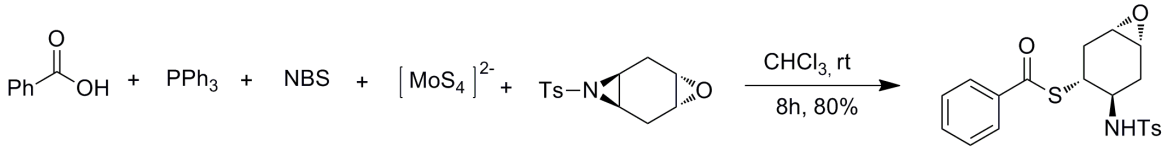


We then demonstrated nucleophilic ring opening of aziridines and epoxides using thioaroylate ions generated from acyloxyphosphonium salts and tetrathiomolybdate, **1**.

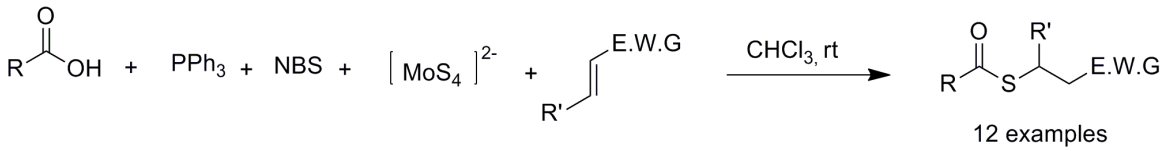


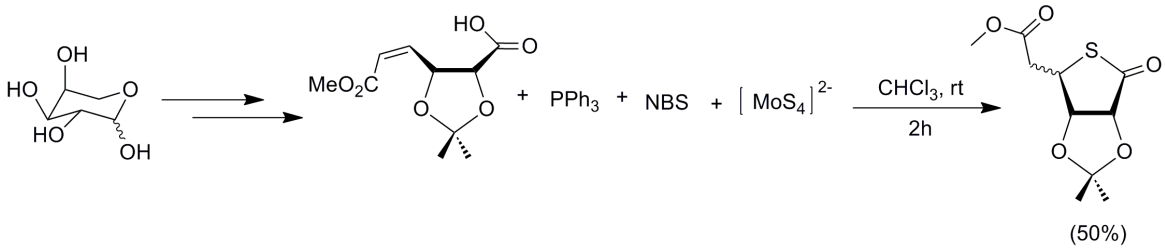
We also extended our methodology to show the chemoselective ring opening of aziridines in the presence of an epoxide and tosylate.



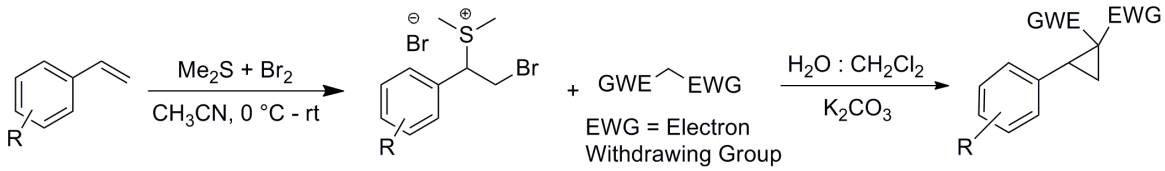


We also showed an easy and alternative protocol for the Michael addition of thioacids to various Michael acceptors.

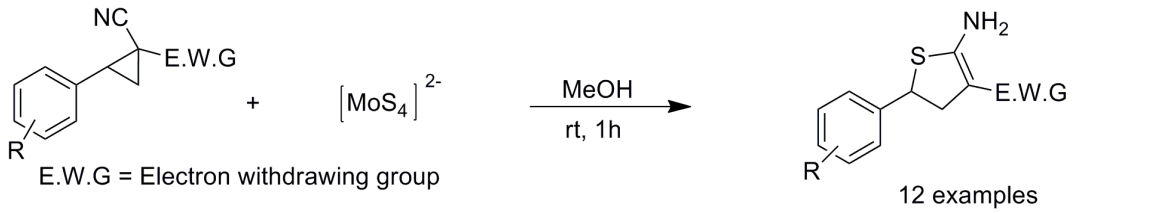




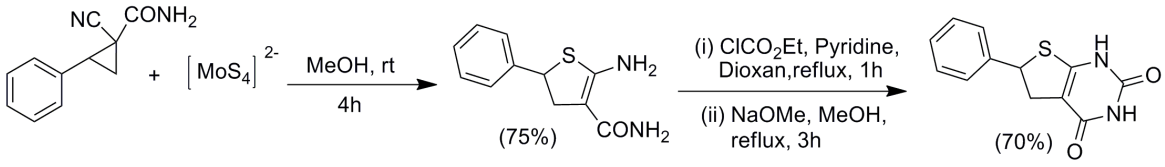
In the second part, we synthesized some interesting sulfur molecules through doubly activated cyclopropane ring opening. At first we synthesized doubly activated cyclopropanes from bromosulfonium bromides.



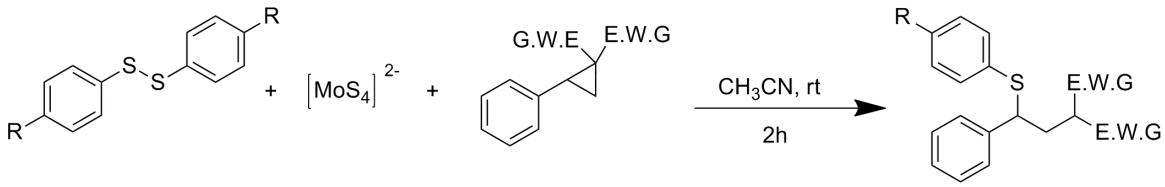
In the next step, we attempted the ring opening of cyano-substituted cyclopropanes with tetrathiomolybdate, **1** to form the corresponding dihydrothiophene derivatives in good to excellent yields.



Additionally, we have used our methodology for the synthesis of HIV-1 reverse transcriptase inhibitor.

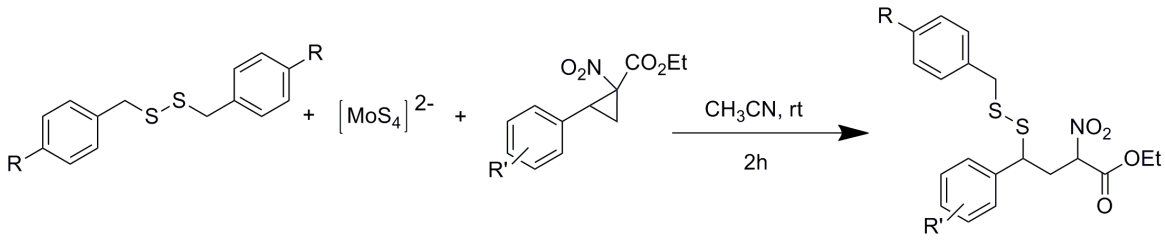


Tetrathiomolybdate is known to mediate reduction of disulfides to thiolates. Diaryl disulfides in the presence of activated cyclopropane derivative and tetrathiomolybdate gave the monosulfides as products, while a similar reaction with dialkyl disulfides gave mixed/unsymmetrical disulfides as the major product.



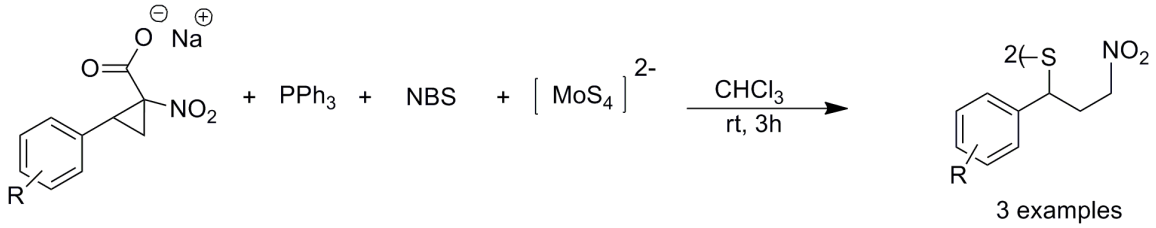
E.W.G = Electron withdrawing group

12 examples



6 examples

A one-pot disulfide formation followed by decarboxylation of nitro-carboxylic acid substituted cyclopropanes was carried out with tetrathiomolybdate in the presence of PPh_3 and NBS.



3 examples