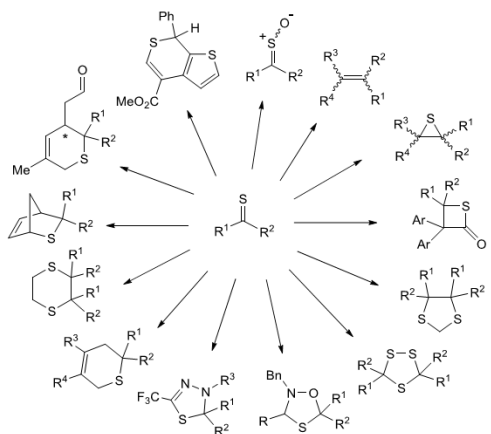


# Aryl, Hetaryl, and Ferrocenyl Thioketones as New Fuels for Heteroatom and Heterocyclic Chemistry; Synthetic and Mechanistic Aspects

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## GRAPHICAL ABSTRACT:



**Abstract:** Methods for the synthesis of hetaryl and ferrocenyl thioketones as well as applications of this class of organic sulfur compounds in the synthesis of both sulfur-containing and sulfur-free organic products are summarized. The most important applications relate to  $[2+2]$ -,  $[3+2]$ -, and  $[4+2]$ -cycloadditions. Aromatic thioketones react with diazomethane at  $-70^\circ\text{C}$ , and the formed 1,3,4-thiadiazolines can be used as convenient precursors of reactive thiocarbonyl *S*-methanides. In contrast, the hetaryl thioketones don't form this type of cycloadducts. Reactions of hetaryl thioketones with thiocarbonyl *S*-methanides are proposed to occur via a stepwise diradical mechanism. Aryl and hetaryl thioketones react as prone heterodienophiles with cyclic and acyclic dienes. The first asymmetric synthesis of dihydrothiopyrans from aryl and hetaryl thioketones was performed using a *L*-proline-derived organocatalyst. Hetaryl thiochalcones are useful heterodienes for the preparation of hetaryl-substituted dihydrothiopyrans also in asymmetric versions of thia-Diels-Alder reactions.

**Keywords** Hetaryl ketones, Hetaryl thioketones, Ferrocenyl derivatives, Ethylene derivatives, Sulfur heterocycles

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### Education

- 1998 Full Professor position at the University of Łódź
- 1998 Professor Title awarded by the President of Republic of Poland,
- 1991 Habilitation in Chemical Sciences, University of Łódź
- 1981 Ph.D , Organic Chemistry with Prof. Romuald Bartnik, University of Łódź
- 1974 Dipl. Chem., University of Łódź, *with highest honors and 'Primus inter Pares' Medal*

### Academic Career

- October 1998 .... to date – Full Professor at the University of Łódź
- March 1981-September 1998 – University Professor at the University of Łódź
- October 1981-February 1991 – Associate Professor (adiunkt) at the Institute of Chemistry
- October 1974-October 1981 – Assistant Professor (asystent/starszy asystent) at the Institute of Chemistry, University of Łódź
- January 1974–October 1974 –Technical Assistant at the Institute of Chemistry University of Łódź

### Research Interest

Organic Chemistry, Heterocyclic Chemistry, Heteroatom Chemistry, Fluoroorganic Chemistry, Diazo Compounds, Coordination Chemistry, Reactive Intermediates, Carbenes Chemistry, Reaction Mechanisms, Catalysis/Organocatalysis and Asymmetric Synthesis

### Awards and Honors

- Gold Medal for the Long-Term Service* - President of the Republic of Poland, May 2015
- Liebig Lecturship - Gesellschaft Deutscher Chemiker* - for outstanding achievements for a foreign organic chemist (2012)
- Polish Chemical Society* – Stanisław Kostanecki Medal for outstanding achievements in organic chemistry (2012)
- Eureka Statue* – for the best research and technological achievements in the City of Łódź (City of Łódź Hall, 2011)
- Polish Ministry of Science and Higher Education* -Team Prize for outstanding research achievements (Team leader: 1999, 2003, 2007, 2012)
- Medal of the Polish Academy of Sciences*-on the occasion of 40<sup>th</sup> Anniversary of Foundation of the Center of Molecular and Macromolecular Studies PAS, Łódź, 2012
- Medal of Brothers Kostanecki High School in Zagórow* – for promotion of chemical sciences in the society (2014)
- Medal of 30<sup>th</sup> Anniversary of Giessen and Łódź Universities Partnership* – Łódź, 2008
- Medal of the Polish Educational Commission* – Ministry of Science and Higher Education, 2006
- Medal 'In Service of Science and the Society'* – University of Łódź, 1999
- Alexander von Humboldt Foundation* – postdoctoral fellowship (1983-1985, 1986-1987, ca. 3 years support)
- The University of Łódź Rector's Team Prize for Research Achievements* (Team leader: 13 times, 1977-2012)
- Copernicus Medal 'Primus inter Pares'* - for the best student of the year (University of Łódź, 1973)

### Community Service

- Chairmanship of the series of annual conferences 'International Mini-Symposia on the Current Problems in Organic Chemistry' (University of Łódź, 2007 – to data)
- Member of the Evaluation Committee of the Polish Science Center (Cracow), (2011 – to date)
- V-ce Chairman of the Lodz Branch, *Societas Humboldtiana Polonorum* (2014 – to date)

V-ce Chairman of the Organizing Committee, *International Symposium on the Organic Chemistry of Sulfur* (ISOCS-27), Jena 2016 (in collaboration with Prof. W. Weigand, Jena)

V-ce Chairman of the Organizing Committee of VIIth International Meeting on Halogen Chemistry (HalChem-7<sup>th</sup>), Częstochowa 2015.

V-ce Chairman of the Organizing Committee, Annual Meeting of the Polish Chemical Society, Częstochowa 2014.

V-ce Chairman of the Organizing Committee, *International Symposium on the Organic Chemistry of Sulfur* (ISOCS-25), Częstochowa 2012.

V-ce Chairman of the Organizing Committee, Annual Meeting of the Polish Chemical Society, Łódź 2009.

V-ce Chairman of the Organizing Committee of the Xth International Conference on the Chemistry of Selenium and Tellurium (ICCST-X), Łódź 2007.

Chairman of 'The Liebig's Colloquium' – Łódź, May 2003

V-ce Chairman of the Organizing Committee of VIIIth International Conference of Heteroatom Chemistry ICHC-7<sup>th</sup>), Łódź 2001

Dean, Faculty of Chemistry (2012 - 2016)

Chair of Department of Organic & Applied Chemistry (2003 – to date)

Chair of Section of Heteroatom Chemistry (2001 – to date)

President of Lodz Branch of the Polish Chemical Society (2010 - 2012)

Member of the Executive Board of the Polish Chemical Society (2000 - 2009)

Associate Dean, Faculty of Mathematics, Physics and Chemistry (1993 – 1996)

### Membership in Editorial Boards

International Advisory Board Member and Guest-Editor *Chemistry of Heterocyclic Compounds* (2016 – to date)

International advisory Board Member, Mini-Reviews in Organic Chemistry (2016 – to date)

International Advisory Board Member, *Egyptian Journal of Chemistry* (2014 – to date)

International Advisory Board Member, *Letters in Organic Chemistry* (2010 – to date)

International Advisory Board Member and Guest-Editor, *Phosphorus, Sulfur, Silicon, and Related Elements* (2004 – to date)

International Advisory Board Member, *Journal of Sulfur Chemistry* (2003 – to date)

Publications

> 300 peer-reviewed publications and 6 patents

> 3800 citations (since 1976), H-index = 32 (Web of Science, November 2016)

**Full list:** <http://www.chemia.uni.lodz.pl/professors/gmloston.html>

### Selected Activities Abroad

1. Alexander von Humboldt Fellow - Institute of Organic Chemistry, University of Munich (Germany), research group of prof. Rolf HUISGEN; 09.1983-06.1985 and continuation between 06.1987 and 09.1988.
2. Alexander von Humboldt 'visiting researcher' Institute of Organic Chemistry, Free University of Berlin (Germany), research group of prof. Hans-Ulrich Reissig (February-May, 2005; October-December 2009)
3. Academic exchange, Lodz-Giessen Partnership, Institute of Organic Chemistry, Justus-Liebig University of Giessen (Germany); research group of prof. Guenther MAIER; 06.1994-07.1994 and subsequently numerous short research stays (last one in December 2014).
4. Visiting scholar - Swiss Government Fellow - Institute of Organic Chemistry, University of Zürich (Switzerland), research group of prof. Heinz HEIMGARTNER; 01.03.-30.05.1995
5. Distinguish visiting scholar - Loker Hydrocarbon Research Institute, University of Southern California (USA), group of Nobel Prize Laureate prof. G. A. Olah; 09.1996-03.1997.

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**List of 10 most relevant publications (2009-2016)**

1. P. R. Schreiner, H. P. Reisenauer, J. Romanski, G. Mloston, A Formal Carbon-Sulfur Triple Bond: H-C≡S-O-H  
*Angew. Chem. Int. Ed.*, **2009**, *48*, 8133-8136.  
*Angew. Chem.*, **2009**, *121*, 8277-8280.
2. P. R. Schreiner, H. P. Reisenauer, J. Romanski, G. Mloston, Oxathiirane.  
*J. Am. Chem. Soc.*, **2010**, *132*, 7240-7241.
3. G. K. Surya Prakash, F. Paknia, T. Mathew., G. Mloston, J. P. Joschek, G. A. Olah, Fluoroanalogs of DDT: BF<sub>3</sub>-H<sub>2</sub>O catalyzed facile synthesis of 1,1,1-trifluoro-2,2-diarylethanes and 1,1-difluoro-2,2-diarylethanes.  
*Org. Lett.* **2011**, *13*, 4128-4131.
4. T. Weisheit, A. Krilitz, H. Görls, G. Mlostoń, W. Imhof, W. Weigand, Reaction of 'non-symmetrical' 1,2,4-trithiolanes with phosphane Pt<sup>0</sup>(η<sup>2</sup>nbe) complexes  
*Chem. Asian J.*, **2012**, *7*, 1383-1393.
5. P. Reisenauer, J. Romański, G. Mlostoń, P. R. Schreiner, The first matrix isolation of the methylsulfinyl radical CH<sub>3</sub>SO.  
*Chem. Commun.*, **2013**, *49*, 9467-9469.
6. M. Jasiński, G. Mlostoń, M. Stolarski, W. Costa, M. Dominguez, H.-U. Reissig, Reactions of cycloaliphatic thioketones and their oxo analogues with lithiated methoxyallene: a new approach to vinylthiiranes.  
*Chem. Asian J.*, **2014**, *9*, 2641-2648.
7. H. P. Reisenauer, J. Romański, G. Mlostoń, P. R. Schreiner, Reactions of methylsulfinyl radical (CH<sub>3</sub>(O)S) with oxygen (<sup>3</sup>O<sub>2</sub>) in solid argon  
*Chem. Commun.*, **2015**, 10022-10025.
8. G. Mlostoń, A. Wróblewska, A. Linden, H. Heimgartner, Studies on the reaction of aryl glyoxals with L-prolinol: Unexpected formation of morpholin-2-one derivatives and stereoselective trifluoromethylation of the bicyclic system.  
*Asian J. Org. Chem*, **2015**, *4*, 770-777.
9. H. Abul-Futouh, L. R. Almazahreh, T. Sakamoto, N. Y T. Stessman, D. L. Lichtenberger, R. S. Glass, H. Görls, M. El-khateeb, P. Schollhammer, G. Mloston, W. Weigand, [FeFe]-hydrogenase h-cluster mimics with unique planar μ-(SCH<sub>2</sub>)<sub>2</sub> ER<sub>2</sub> linkers (E=Ge and Sn).  
*Chem. Eur. J.*, **2016**, *22*, in press; (DOI: 10.1002/chem.201603843).
10. J. Hejmanowska, M. Jasiński, G. Mlostoń, and Ł. Albrecht, Taming of thioketones – the first asymmetric thio-Diels-Alder reaction of thioketones as a convenient entry to optically active dihydro-2*H*-thiopyrans.  
*Eur. J. Org. Chem.*, **2016**, in press (DOI: 10.1002/ejoc.201601307)

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Łódź, Dezember 10<sup>th</sup>, 2016

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*Eureka Statue* – for the best research and technological achievements in the City of Łódź (City of Łódź Hall, 2011)  
*Polish Ministry of Science and Higher Education* -Team Prize for outstanding research achievements (Team leader: 1999, 2003, 2007, 2012)  
*Medal of the Polish Academy of Sciences*-on the occasion of 40<sup>th</sup> Anniversary of Foundation of the Center of Molecular and Macromolecular Studies PAS, Łódź, 2012  
*Medal of Brothers Kostanecki High School in Zagórow* – for promotion of chemical sciences in the society (2014)  
*Medal of 30<sup>th</sup> Anniversary of Giessen and Łódź Universities Partnership* – Łódź, 2008  
*Medal of the Polish Educational Commission* – Ministry of Science and Higher Education, 2006  
*Medal 'In Service of Science and the Society'* – University of Łódź, 1999  
*Alexander von Humboldt Foundation* – postdoctoral fellowship (1983-1985, 1986-1987, ca. 3 years support)  
*The University of Łódź Rector's Team Prize for Research Achievements* (Team leader: 13 times, 1977-2012)  
*Copernicus Medal 'Primus inter Pares'* - for the best student of the year (University of Łódź, 1973)

### **Grants for research projects (2006-2016):**

- 1) **Title:** New, chiral ligands derived from imidazole for enantio- and diastereoselective cyclopropanation and aziridination reactions. Attempted syntheses of new, chiral ionic liquids (# PBZ-KBN-126/T09/2004; 05.2006-05.2009), Ministry of Science and Higher Education of Poland (Project leader)
- 2) **Title:** New trifluoromethylation reactions under exploration of (trifluoromethyl)trimethylsilane (# N204 130 335; 10.2008-10.2011), Ministry of Science and Higher Education of Poland (Project leader)
- 3) **Title:** Exploration of new polyheterocyclic, chiral compounds containing pyrrolidine and imidazole rings in asymmetric synthesis (# 2012/07/N/ST5/01873; 01.2013-07.2016), National Science Center (Cracow, Poland) (Supervisor), (project leader: Aneta Wróblewska, PhD student)
- 4) **Title:** Fluorinated imines as highly reactive components in the new [2+1]- and [3+2]-cycloaddition reactions (# 2014/15/N/ST5/02895; 10.2015-10.2018), National Science Center (Cracow, Poland) (Supervisor), (project leader: Marcin Kowalski, PhD student)
- 5) **Title:** Heteroaromatic thioketones as unique substrates and building blocks for exploration in organic-, materials-, coordination-, and biometalloorganic chemistry (# 2012/06/AST5/00219; 04.2013 – to date), National Science Center (Cracow, Poland) (Project leader)
- 6) **Title:** Development of methods of syntheses of fluorinated heterocycles containing nitrogen, oxygen, sulfur and selenium; from beta-lactams to poliheterocyclic compounds (#2014/13/B/ST5/04004; to date.), National Science Center (Cracow, Poland) (Project leader)