Acceptoless Dehydrogenative Cyclization of N-Tosylhydrazones and Anilines: Dual Role of B(C₆F₅)₃

Highlighted article by M. M. Guru, S. De, S. Dutta, D. Koley, B. Maji
Dear Readers,

Are you ready for the new decade? SYNFORM certainly is! In the era of research visibility and public outreach, SYNFORM – supported by the Thieme Chemistry journals and social media – has become a powerful tool for reaching increasingly larger audiences with your publications and is entering its third decade in sparkling form and more ambitious than ever! In case you had any doubts, just look at the content of this first issue of 2020: I am really pleased that the decade-opening article comes from India, which is taking giant leaps in chemistry, as apparent from the excellent work presented by Koley and Maji on $\text{B(C}_6\text{F}_5\text{)}_3$-promoted synthesis of triaryl-1,2,4-triazoles. The second article of the decade is Q. Song’s (P. R. of China) elegant stereoconvergent synthesis of ketoximes. The third article is from the lab of an absolute heavy-weight of organic chemistry: Prof. K. Barry Sharpless. In this case, supported by J. Dong (P. R. of China), who co-authored a new chapter of the click-chemistry saga recently published in Nature. Finally, the first Young Career Focus interview of the decade takes us to the Antipodes, where B. C. Hawkins (New Zealand) tells us about his molecular targets in organic synthesis.

You can tell it’s gonna be a good decade!!

Enjoy your reading!!!

Matteo Zanda

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If you have any questions or wish to send feedback, please write to Matteo Zanda at: synform@outlook.com
Acceptorless Dehydrogenative Cyclization of N-Tosylhydrazones and Anilines: Dual Role of B(C₆F₅)₃

Chem. Sci. 2019, 10, 7964–7974

Tris(pentafluorophenyl)borane [B(C₆F₅)₃] acts as a powerful Lewis acid catalyst for numerous organic transformations. In combination with a sterically demanding Lewis base, it forms Frustrated Lewis-acid Pairs (FLPs), which have recently been applied for small-molecule activations and metal-free hydrogenation as well as dehydrogenation reactions. Recently, the group of Professor Debasis Koley and Professor Biplab Maji at the Indian Institute of Science Education and Research (Kolkata, India) described the B(C₆F₅)₃-catalyzed cyclization of N-tosylhydrazones 1 and anilines 2 to form triaryl-1,2,4-triazoles 3 (Scheme 1a), which are essential heterocyclic scaffolds in pharmaceutical, biological, and materials sciences. Professor Maji explained: “The work utilizes a unique dual mode of activation of B(C₆F₅)₃, which initially acts as a Lewis acid to activate 1 thus triggering its cyclization with 2 (Scheme 1b, right).” He continued: “Later, the FLP generated from B(C₆F₅)₃ and 2 acts as a dehydrogenation catalyst to liberate hydrogen from the saturated triazole intermediate 7 without the need of an acceptor. The gain in aromaticity drives the dehydrogenation reaction (Scheme 1b, left). The reaction operates at low loading of catalyst, tolerates several functional groups and can be extended to unsymmetrical 1,2,4-triazoles when utilizing two different N-tosylhydrazones.”

Professor Maji remarked that it is highly challenging to design acceptorless dehydrogenative transformations, even with transition-metal catalysts, whereas metal-free protocols are

![Scheme 1](image-url)
elusive. Using B(C$_6$F$_5$)$_3$ as a catalyst, Dr. M. M. Guru – one of the authors – explored the scope of the synthesis of symmetrical triazoles (Figure 1), where p-toluene sulfonamide (TsNH$_2$) and hydrogen were obtained as byproducts.

“Expansion of the protocol for the synthesis of unsymmetrical 1,2,4-triazoles using two different N-tosylhydrazones was challenging, as the selectivity remained poor after several trials (Scheme 2a),” said Professor Maji. A competitive equilibrium study was performed with two electronically biased N-tosylhydrazones (1a vs 1c) with B(C$_6$F$_5$)$_3$ which afforded the Lewis acid–base adduct 4a whereas 1c remained unreacted (4a:1c = 1:1) (Scheme 2b). Professor Maji remarked: “Thus, we realized that the electronic difference might be a crucial factor for the selectivity of unsymmetrical 1,2,4-triazole formation. Indeed, we solved the issue by utilizing electronically biased N-tosylhydrazones which afforded good to excellent yields of unsymmetrical 1,2,4-triazoles (Scheme 2c).”

He continued: “Moreover, from the Hammett correlation study performed by varying different electronic groups on the aryl ring of 2, we determined a small $\rho = -1.17$, which plausibly indicates a weak resonance interaction involving a positive charge at the N-center of aniline in the rate-determining step (Scheme 2d).”

Professor Koley and co-authors Mr. De and Mr. Dutta performed DFT calculations [B3LYP-D3/TZVP(CPCM)//B3LYP/SVP level of theory] to investigate the detailed reaction mechanism, the specific role of B(C$_6$F$_5$)$_3$, and the rate-limiting-step in the reaction, and finally the product distribution for the unsymmetrical coupling. Professor Koley said: “As per the experimentally observed equilibrium ratio in Scheme 2b, the formation of 4a is computed to be more facile than 4c by ca. 3.0 kcal mol$^{-1}$ (Figure 2).” He continued: “Eventually, the activation barrier for B(C$_6$F$_5$)$_3$ coordination is 3.6 kcal mol$^{-1}$ more favorable for the OMe substituent ($\Delta\Delta$G$_{a}$; Figure 2). What is more interesting is that the overall energy span for the formation of 5 is substantially higher for the Cl than the OMe substituent (42.5 vs. 33.3 kcal mol$^{-1}$), clearly indicating the preference for 1a to undergo B(C$_6$F$_5$)$_3$-assisted intramolecular proton transfer in a facile manner. Therefore, when 5aa couples with another hydrazone unit, the preferred choice will be the chloro-substituted analogue 1c as most of 1a will be available in the adduct form 4a.”

As for the potential applications of the triazole products, the group has recently shown that pyrene-appended triazole-linked dimers could be applied in solution-processable resistive memory devices on a flexible substrate (Chem. Commun. 2019, 55, 4643).

“In summary, we have developed B(C$_6$F$_5$)$_3$-catalyzed single-pot, acceptorless dehydrogenative cyclization of hydrazones with anilines to access both symmetrical and unsymmetrical 1,2,4-triazoles,” said Professor Maji. He concluded: “Mechanistic experiments and DFT calculations suggest that the boron catalyst plays a dual role, initially acting as a Lewis acid to activate the hydrazone for the nucleophilic attack and later forming an FLP with aniline for acceptorless dehydrogenation. This chemoselective and mild reaction protocol could foster further studies and generate further interest in main-group-catalyzed chemical transformations performed without the use of transition-metal catalysts.”

![Figure 1 Selected examples for the synthesis of symmetrical 1,2,4-triazoles.](image-url)
Scheme 2  a) Challenges associated with selective formation of unsymmetrical 1,2,4-triazole.

b) Equilibrium studies with electronically different N-tosylhydrazones.

c) B(C₆F₅)₃-Catalyzed selective formation of unsymmetrical 1,2,4-triazole: selected examples.

d) Hammett analysis by varying aniline.

**Scheme 2**  a) Challenges for the synthesis of unsymmetrical 1,2,4-triazoles. b) Equilibrium studies with electronically different N-tosylhydrazones. c) Selected examples for the synthesis of unsymmetrical 1,2,4-triazoles. d) Hammett analysis.
Figure 2 Overlaid energy profiles for the formation of unsymmetrical triazole 3aca and symmetrical triazole 3aaa up to the formation of 5. Energy values are concerning the starting materials [1a/c + B(C₆F₅)₃]. For green solid line, Ar¹ = p-MeOC₆H₄ and Ar² = p-MeC₆H₄ where for red solid line, Ar¹ = p-ClC₆H₄ and Ar² = p-MeC₆H₄. All the energy values (ΔG°) are in kcal mol⁻¹.
About the authors

Murali Mohan Guru received his Ph.D. from Indian Institute of Technology Guwahati (India) in 2013 under the supervision of Prof. T. Punniyamurthy. Subsequently, he moved to RIKEN (Japan) as a postdoctoral researcher in the lab of Prof. Zhaomin Hou, working there from 2013–2016. He returned to India in 2017 and joined the group of Dr. Biplab Maji in IISER Kolkata (India) as a SERB-NPDF. Currently, he is working on novel organic transformations using main-group borane catalysts.

Sriman De was born in Burdwan, West Bengal, India. He completed his B.Sc. at Burdwan University (India) in 2011. In 2013, he completed his study in chemistry with his M.Sc. degree at Visva-Bharati University (India). In 2014, he started as a Ph.D. student under the supervision of Dr. Debasis Koley at IISER Kolkata (India). His research interests are focused on bimetallic complexes in catalysis using computational methods.

Sayan Dutta received his B.Sc. from Visva-Bharati University (India) in 2011. He obtained his M.Sc. in chemistry from the same university in 2013 before joining Dr. Debasis Koley’s research group at IISER Kolkata (India) in 2014 as a Ph.D. student. His current research focuses on mechanistic investigations of main-group- and transition-metal-mediated chemical transformations and theoretical exploration of the bonding scenario in various donor–acceptor complexes.

Debasis Koley studied chemistry (honors) at Ramakrishna Mission Vidyamandira (India) from 1996 to 1999. In 2001, he completed his M.Sc. in chemistry at Indian Institute of Technology Delhi (India). In 2005, he received his doctoral degree from Heinrich Heine Universität Düsseldorf (Germany), working under the supervision of Professor Walter Thiel at MPI für Kohlenforschung, Mülheim an der Ruhr (Germany). During 2006 to 2008, he was engaged as a postdoctoral researcher at MPI für Biophysikalische Chemie, Göttingen (Germany). Later he moved to IISc Bangalore (India) as a Centenary postdoctoral fellow in the Inorganic and Physical Chemistry Department under the supervision of Professor S. Ramakrishnan. Since 2011, he has been at the Indian Institute of Science Education and Research (IISER) Kolkata (India), currently a professor in the Department of Chemical Sciences. His Computational Chemistry and Molecular Modelling (CCMM) group focuses on structure, bonding and mechanistic interpretations of various chemical systems using state-of-the-art computational techniques.

Biplab Maji was born in Howrah (India) in 1987. He obtained his B.Sc. in chemistry (Honors) from University of Calcutta (India) in 2004 and M.Sc. in chemistry from the Indian Institute of Technology Kanpur (India) in 2009. Subsequently, he joined the group of Prof. Herbert Mayr at the Ludwig Maximilian Universität München (Germany) for his doctoral studies, which he completed in 2012. In 2013, he joined the group of Prof. Hisashi Yamamoto at the Molecular Catalyst Research Center of Chubu University (Japan) as a postdoctoral fellow. In 2015, he moved to the group of Professor Frank Glorius at Westfälische Wilhelms-Universität Münster (Germany) as an Alexander von Humboldt fellow. Since 2016, he has been working as an assistant professor in the Department of Chemical Sciences, IISER Kolkata (India). His research focuses on organic synthesis, catalysis, and mechanistic studies.
Stereochemically pure oximes are ubiquitous structural motifs in drugs, bioactive molecules and food additives. They are also very important starting materials for the Beckmann rearrangement, which has been successfully employed for the industrial production of many valuable fine chemicals. The prototypical ketoxime synthesis involves condensation of ketones with hydroxylamine or tautomerization of C-nitroso species, as well as reduction of nitro compounds. However, the ratio of the resulting E/Z-isomers is under thermodynamic control and depends on the nature of the substrates, which usually causes major problems when it comes to isolating a single geometric isomer, unless the two substituents of the ketoximes are structurally very different (Scheme 1a). “This is why the practical and universal direct stereoselective synthesis of stereochemically pure ketoximes, especially of thermodynamically less stable ones, remains an unsolved challenge in modern chemical transformations,” said Professor Qiuling Song, from the Key Laboratory of Molecule Synthesis and Function Discovery, College of Chemistry, Fuzhou University (P. R. of China).

Stereospecific 1,4-Metallate Shift Enables Stereoconvergent Synthesis of Ketoximes


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**Scheme 1** (a) Typical approaches for ketoxime synthesis. (b) Stereoconvergent synthesis of stereochemically pure ketoximes. (c) Selected examples of the substrate scope.
Professor Song continued: “With these issues in mind, we were interested in developing a mechanistically distinct strategy, independent of the configuration of the starting materials and not involving transition metals, which would represent a general method for the synthesis of single-geometry ketoximes.” Nitrile oxides caught the group’s attention, as ketoximes can be obtained from the reaction of organometallic reagents or aromatic nucleophiles and nitrile oxides. Unfortunately, the authors of this study found that the diversity and stereoselectivity of ketoxime products was highly restricted owing to the instability of nitrile oxides and the strong nucleophilicity of these organometallic reagents.

“We then envisioned that nitrile oxides could attack the electrophilic boron atom of arylboronic acids, resulting in a boron ‘ate’-complex that might lead to stereochemically pure ketoximes via a stereospecific 1,4-metallate shift (Scheme 1b),” said co-author Dr. Kai Yang. Considering the instability of nitrile oxides, they selected oxime chlorides as precursors of nitrile oxide. The resulting protocol enabled Professor Song and co-authors to synthesize diverse stereochemically pure ketoximes, including diaryl ketoximes and thermodynamically less stable aryl alkyl ketoximes.

Control experiments were conducted to evaluate the practicality of the protocol (Scheme 2a), and the team performed comparison experiments to synthesize two different stereospecific ketoximes (Scheme 2b). Next, a gram-scale experiment was carried out by postgraduate student Feng Zhang, and demonstrated the preparative utility of this protocol (Scheme 2c). Meanwhile, the team went on to explore the reactivity of ketoximes as directing group in C–H activation reactions and Beckmann rearrangement (Scheme 2d).

“In summary,” said Professor Song, “we have developed a protocol to directly synthesize stereochemically pure ketoximes from oxime chlorides and arylboronic acids via stereospecific 1,4-metallate rearrangement. This approach shows a broad substrate scope and good functional group tolerance. It also provides a good opportunity for the development of oxime chemistry and demonstrates a promising approach to prepare single-geometry ketoximes that could be used by both the chemistry community and pharmaceutical scientists.”

**Scheme 2** (a) Control experiments. (b) Comparison experiments. (c) Gram-scale synthesis experiment. (d) Selected examples of the synthetic applications.
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<th>Background</th>
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Modular Click Chemistry Libraries for Functional Screens Using a Diazotizing Reagent

*Nature* 2019, 574, 86–91

Click chemistry – a term coined by 2001 Chemistry Nobel Prize Laureate Professor Barry Sharpless, at Scripps Research (USA) – aims to be a quick and modular synthesis concept for finding new molecules with desirable properties. Professor Sharpless had the intention of connecting 2 or 3 modules together in solution, in sequence, within a few hours and submitting the mixture directly to screening. “This original hope seemed absurd until his lab discovered the CuAAC triazole annulation reaction in 2002,” said Professor Dong, who remarked: “This one perfect reaction instantly solved nearly all of our needs for intermolecular ligation. Compared with known combinatorial chemistry strategies based on solid-phase synthesis, this ideal click chemistry plan in solution takes advantage of the near-perfect reactivity of CuAAC and does not involve protecting groups. More importantly, and almost uniquely among combinatorial chemistry strategies, it can make any compound of interest pure on a milligram to gram scale in a day or less, very soon after the biologist has revealed the screening results.”

Professor Dong joined Professor Sharpless’ laboratory in 2009 as a research associate and paid tribute to him, saying: “Barry is more than a mentor for me. His visionary lecture about click chemistry at SIOC in 2004 was really inspiring for me as a young chemist there, while others simply thought that he had lost his mind! I have been fortunate to work closely with him in the last ten years, in Scripps and now at SIOC.”

In the first six years, synthesizing and collecting azides or alkynes had become Professor Dong’s daily work. During that time, he noticed at least three aspects having key importance for the aim of generating such a library:

1. The number of commercially accessible azide and alkyn modules is very low.

2. While collecting terminal alkyn molecules, it became evident that usually those molecules hardly tolerated other functional groups or protecting groups, which were generally difficult and laborious to incorporate. Therefore, the alkyn chemical space was limited for this particular application, especially for low-molecular-weight modules.

3. Although many procedures are known for the synthesis of azides, the synthesis of low-molecular-weight azides was even more complicated than the synthesis of alkynes.

Firstly, there were significant safety concerns regarding their reactions and purifications; secondly, azides are unstable, especially in solution. The so-called “Diazotransfer process” was already well known at that time. However, the two standard reagents used for this procedure (TfN$_3$ and imidazole-1-sulfonyl azide hydrochloride) require metal catalysts, excess azide reagent, and sometimes risky purification steps (as mentioned in this Nature article). An excess of diazotransfer reagents would affect the CuAAC reaction if both reactions were run in sequence in one-pot.

Professor Dong explained: “It has been known for years that the CuAAC reaction is unusually predictable; however, it relies on the power of two highly energetic functional groups nature did not use, which kills the accessibility aspect. The commercial availability of both groups is very low compared to those that medicinal chemists often use. While ready availability of azides/alkynes would be highly desirable, in reality this option is simply too difficult to achieve and too expensive.”

The exciting discovery of this methodology has an interesting origin, partially based on serendipity. In fact, during their experiments, the group wanted to use FSO$_2$N$_3$ for the SuFEx reaction and accidentally discovered the abnormal diazotransfer process. Professor Dong said: “Mistakes are the portals of discovery! We were trying to make FSO$_2$N$_3$ from our imidazolium fluorosulfuryl triflate salt 1, but we knew from our previous publication (Angew. Chem. Int. Ed. 2018, 57, 2605–2610) that the salt would be hydrolyzed very quickly in water. Therefore, three of my students used organic solvents but failed to produce anything. However, our research associate, Genyi Meng, used water and succeeded at the first attempt! So I asked him: “Why did you use water? Didn’t you know the reagent would hydrolyze even without a base?” His answer was, “No, I didn’t know that.” And that is how we found this excellent procedure for making FSO$_2$N$_3$.”

Ever since working with Professor Sharpless at Scripps, Professor Dong had wondered how predictable the ligand-
accelerated CuAAC could be and whether it would be possible to find one SOP to fit every substrate in CuAAC and build a modular synthetic platform. “This discovery inspired me, and we suddenly realized we could have thousands of modules to try this idea now,” remarked Professor Dong. He continued: “But it turned out to be surprisingly harder than we thought! PhD student Tiancheng Ma worked hard on it though and we finally figured out a good set of conditions in plates.”

Concerning the future applications of this new methodology, Professor Dong noted that since its discovery, CuAAC has become the most powerful tool to connect two molecular entities chemically. However, its potential as a powerful synthetic tool to produce new compounds has been overlooked. “With this dramatically improved diazotransfer reaction between primary amines and FSO₂N₃, enormous azide libraries are suddenly a reality,” said Professor Dong. Even more excitingly, Professor Dong considers this reaction to be a powerful leverage of CuAAC or even SuFEx chemistry, not just any new reaction. “It enables a modular synthesis platform based on the most accessible building blocks in medicinal chemistry and on the most predictable connecting method ever known. Just imagine: one could do 1000, even 10000 modifications on a given lead in a predictable fashion without purification, with just one employee in one day or even less!” said Professor Dong.

“In the last two years, we have collaborated with different groups in China and the U.S.; more than a dozen different 1000-mer triazole libraries have been or are going through phenotypic screens aimed at finding useful activity relevant to human diseases,” said Professor Dong. He concluded: “None of the biology results are included in this manuscript. We hope this reaction can help click chemistry towards its goal of speeding up discoveries of useful new molecules, especially much-needed medicines. We are now working on the next version of this azide library: Taijie Guo – a co-author of this study – scaled up our salt to 5 kg and we purchased more than 5000 primary amines. We hope we can hit 4016 pieces soon (LEGO Death Star 75159 had 4016 pieces) and, eventually, a platform with more than 10000 azides.”

Scheme 1
About the authors

Jiajia Dong was born in P. R. of China and received his BA from Xiamen University (P. R. of China) in 2000. Prof. Biao Jiang supervised his 2006 PhD in organic chemistry from Shanghai Institute of Organic Chemistry (SIOC, P. R. of China). He was a senior scientific researcher at Egret Pharma, Shanghai (P. R. of China), before becoming a postdoctoral associate in 2009–2015 with Prof. K. Barry Sharpless' group at The Scripps Research Institute (USA). He is currently a research professor at SIOC. His research interests include the main-group fluoride chemistry and click chemistry.

Nobel Laureate K. Barry Sharpless became W. M. Keck Professor of Chemistry at The Scripps Research Institute and The Skaggs Institute of Chemical Biology (USA) in 1990. Previously a professor at MIT and Stanford (USA), he was educated at Dartmouth College, USA (BA 1963), Stanford (PhD 1968 with E. E. van Tamelen; postdoc 1969 with J. P. Collman), and Harvard, USA (postdoc 1970, K. E. Bloch). He joined the Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, CAS (P. R. of China) as an adjunct professor in 2016.

Genyi Meng obtained his BA and MSc in natural sciences from University of Cambridge (UK) in 2016. From 2016 to 2019, he worked under the supervision of Prof. K. Barry Sharpless at Shanghai Institute of Organic Chemistry (P. R. of China) as a research assistant. In 2019, he started his PhD program at the Scripps Research Institute (USA).

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Tiancheng Ma was born in 1993 in Hefei, P. R. of China. He received his BSc in chemistry in 2015 at Tongji University, Shanghai (P. R. of China). In September 2015, he started his MSc studies at Shanghai Institute of Organic Chemistry (P. R. of China) under the supervision of Prof. Jiajia Dong. In 2017, he transferred to the PhD program.
Interview

SYNFORM What is the focus of your current research activity?

Dr. B. C. Hawkins  Natural products and synthetic derivatives have and will continue to represent a critical source of pharmaceuticals, accounting for almost 50% of clinically used drugs. Despite the first lab-based synthesis of urea occurring almost 200 years ago, and the incredible advances in synthetic methods since then, we are still far from achieving ideality in synthesis. Our research is focused around developing efficient synthetic methods to access bioactive compounds, with a particular focus on natural products. Specifically, current efforts are aimed at utilizing donor–acceptor cyclopropanes as building blocks for the rapid synthesis of medicinally relevant scaffolds and target oriented synthesis. Current synthetic targets in the lab include spiroaspertrione A and spirocalcaridines A and B (Figure 1).

Figure 1  Current synthetic targets in our laboratory

SYNFORM When did you get interested in synthesis?

Dr. B. C. Hawkins  Science in general has always fascinated me; however, my interest in chemistry came in high school and my love of organic synthesis was sparked during my un-
Young Career Focus

SYNFORM What do you think about the modern role and prospects of organic synthesis?

Dr. B. C. Hawkins Organic synthesis will always be a cornerstone in science, a truly enabling discipline that has facilitated the expansion of many disciplines (for example, materials, polymers, supramolecular chemistry, and chemical biology). Both fundamental and translational research are important in a modern society. However, the current trend towards overlooking fundamental research in favor of translational research is short-sighted and ultimately slows progress in organic synthesis and science in general. Serendipity and unexpected results are often the source of game-changing discoveries; by focusing solely on applied research, opportunities to uncover truly unique/unexpected processes could be missed.

SYNFORM Could you tell us more about your group’s areas of research and your aims?

Dr. B. C. Hawkins Our research efforts are relatively broad, encompassing synthetic methodology based around utilizing ring strain to allow entry into medically relevant scaffolds, through to target-oriented syntheses. More recently, we have begun a medicinal chemistry program centered around natural products synthesized in our lab. The end goal of our work is to develop fast and efficient entry into medically relevant chemical entities. These molecules can then be used as biological tools for collaborators to use to probe cellular processes, and consequently increase our understanding of disease processes and ideally help in the rational design of drugs.

SYNFORM What is your most important scientific achievement to date and why?

Dr. B. C. Hawkins Thanks to the hard work of my research group, we have developed several useful synthetic methods to access important compound classes such as oxazinones,1,2 chromones3 and benzannulated spiroketalts.4 However, my group’s synthesis of the marine natural product spiroleuccetadine (Figure 2) is probably the most important achievement of my independent career to date.5,6 This synthesis has enabled access to large quantities of spiroleuccetadine and the subsequent uncovering of unexpected biological activity, which in turn has led us to pursue a medicinal chemistry program focused on establishing a structure–activity relationship and also, with the help of collaborators, efforts have begun to establish the mechanism of action of spiroleuccetadine.

REFERENCES

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- Literature Coverage
  Photoinduced Skeletal Rearrangements Reveal Radical-Mediated Synthesis of Terpenoids

- Literature Coverage
  Unified Prebiotically Plausible Synthesis of Pyrimidine and Purine RNA Ribonucleotides

- Literature Coverage
  Late-Stage Trifluoromethylthiolation of Benzylc C–H Bonds

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