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Shapiro and Bamford-Stevens reactions – revisited

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Dedicated to Professor Józef Drabowicz on the occasion of his 75th Birthday

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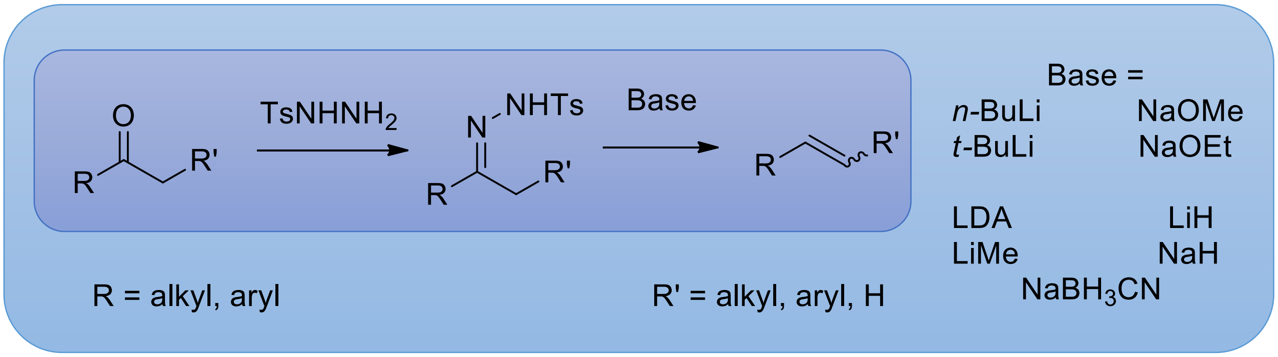
Abstract

The Shapiro as well as the Bamford-Stevens reactions are very convenient methods for preparing numerous olefinic compounds from ketones and aldehydes *via* sulfonylhydrazones. These reactions allow preparation not only of simple molecules with a double bond but also larger, complex systems that could have biological activity. Therefore, the synthetical aspects of above-mentioned reactions are of broad interest to organic chemists. This mini review describes the application of Shapiro as well as Bamford-Stevens reactions in the preparation of olefinic compounds.



Keywords: Shapiro reaction, Bamford-Stevens reaction, tosyl hydrazones, organometallic reagents

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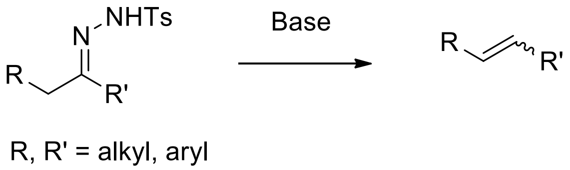
1. Introduction

The Shapiro and Bamford-Stevens reactions are excellent synthetical tools which allow the instalment of a double bond into a molecule without adding an additional carbon atom. In recent years, different modifications have been made in this synthetic area, and numerous compounds have been prepared by application of this methodology.

The contribution of 2020 by Mukund Ghavre[1] summarizes the recent developments on Shapiro and Bamford-Stevens reaction, however some important references need be added in order to bring the topic up to date. For this reason we have decided to "revisit" this research area. To facilitate our approach we have not repeated, except for a few examples, the papers listed by Ghavre,[1] but have focused our attention on new contributions.

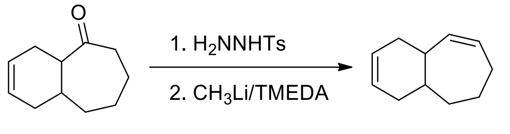
The Bamford-Stevens reaction was first reported in 1952[2], while in 1967 Shapiro presented the variant of the original procedure[3]. Generally, the reaction leads to the formation of an alkene when the tosyl hydrazone of an aldehyde or ketone is treated with a strong base. Mechanistically it is a simple elimination reaction followed by a 1,2-hydrogen shift or a protonation in the last step of the reaction.



The Bamford-Stevens reaction and the Shapiro reaction have very similar mechanistic pathways. There is a broad spectrum of bases that canbe used, that are important to the course of the reaction. The Bamford-Stevens reaction generally yields highly substituted olefins (thermodynamic products), while the Shapiro reaction yields less substituted olefins because kinetic products were being formed preferentially. In the original reaction developed by Bamford and Stevens strong bases such as NaOMe, NaH, LiH, $NaNH_2$, etc. were used, while in the Shapiro reaction the bases used are alkyllithiums and Grignard reagents.

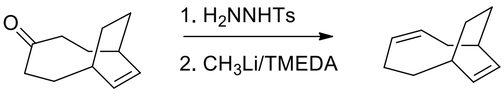
2. Shapiro and Bamford-Stevens reactions- achievements in recent years

In 2014 Baldwin *et al.* reported the preparation of bicyclo[5.4.0]undeca-2,9-diene **2**, employing the Shapiro modification of the Bamford-Stevens reaction, from the bicyclo[5.4.0]undec-9-en-2-one **1**. The reaction was carried out in the presence of *p*-toluenesulfonyl hydrazide, CH_3Li and TMEDA as a base and gave **2** in 52% yield.[4]



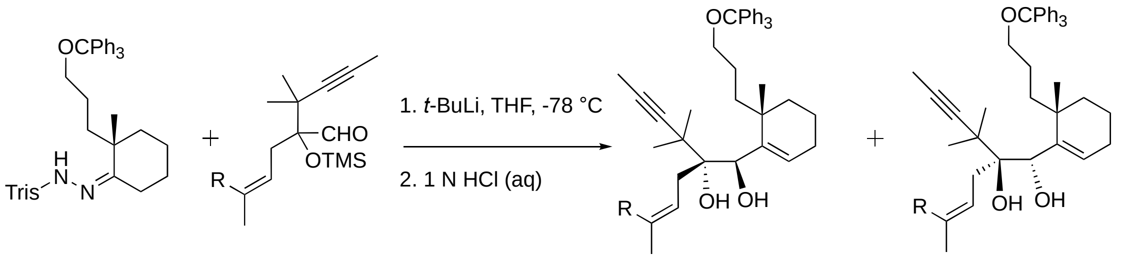
1 **2**

Additionally, using similar reaction conditions, the synthesis of bicyclo[5.2.2]undeca-3,8-diene **4** was achieved.



3 **4**

In the same year, Letort *et al*. published a diastereoselective Shapiro reaction between trisyl hydrazone **5** and aldehydes **6a, 6b** using *t*-BuLi as a base. After acidic hydrolysis of the trimethylsilyl ether, the *trans* diols **7a** and **8a** were obtained in 43% and 40% yields, respectively and the products **7b** and **8b** in 76% combined yield.[5]

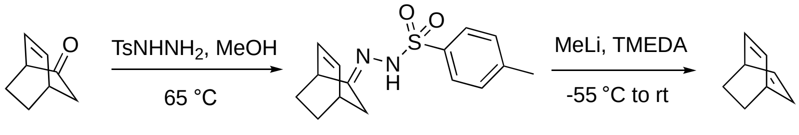


5 **6a, 6b** **7a, 7b** **8a, 8b**

(a) R = H (b) R = CH_3

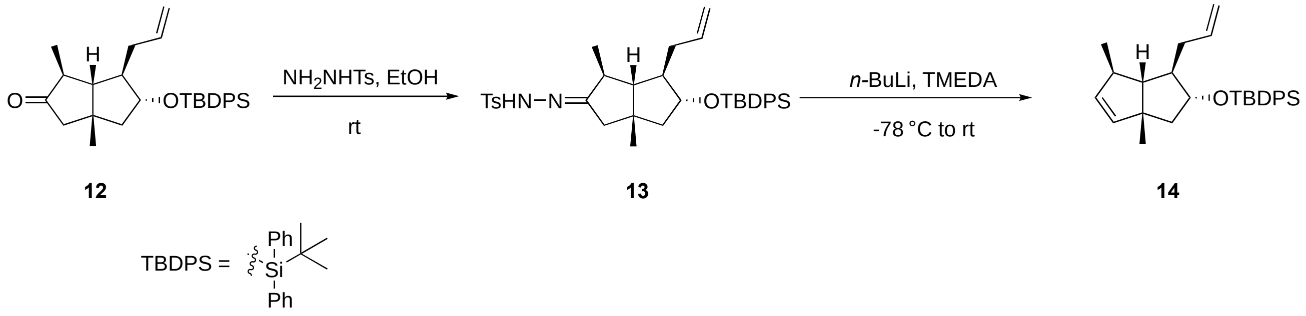
Tris = 2,4,6-triisopropylbenzenesulfonyl

In 2014 the entry presented by Olbrich *et al*.[6] involved the generation of hydrazone **10** from the ketone **9** and further reaction with methyllithium in TMEDA solution. The last step allowed the formation of dihydrobarrelene (**11**) in 71% yield, without further purification.

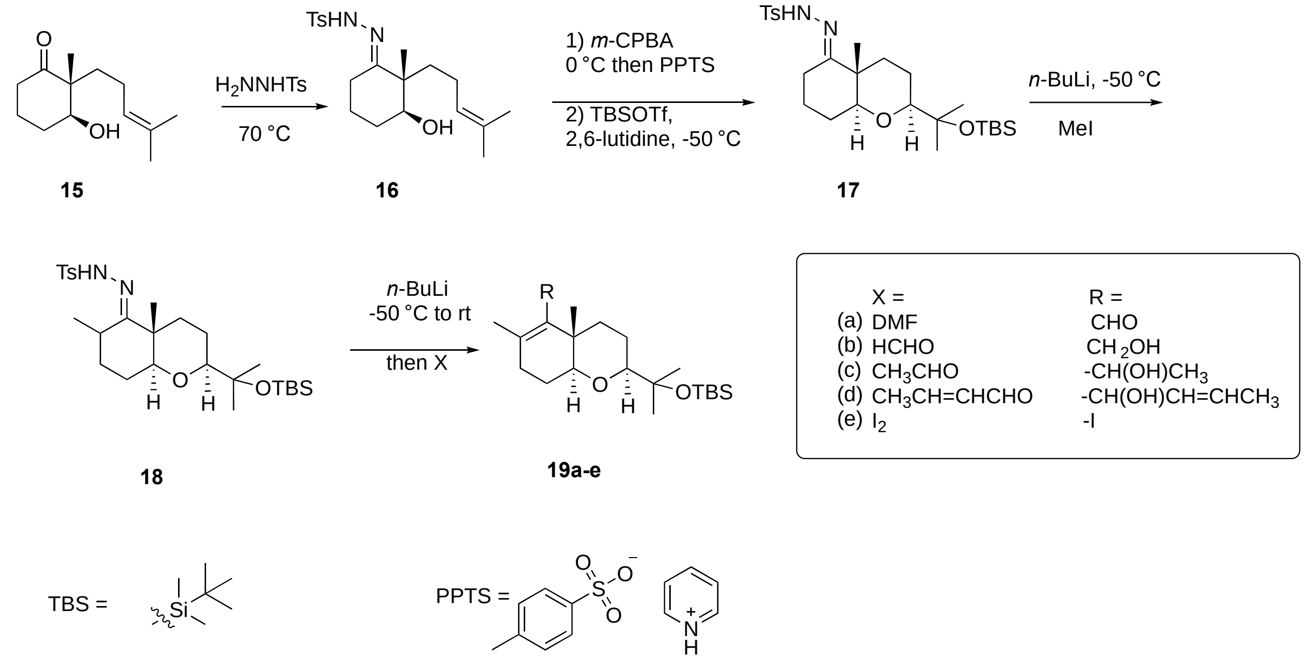


9 **10** **11**

Also in 2014, Lutz *et al*. described the conversion of starting ketone **12** to hydrazone **13** and its subsequent functionalization to alkene derivative **14** in 85% yield, as a yellowish oil. The last step, which involved the Shapiro reaction, was reported to form the product with the less substituted double bond. Compound **14** was found to display antiproliferative activity against L-929 cells.[7]

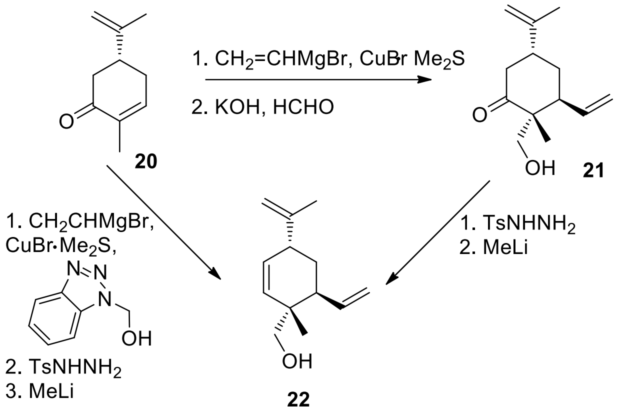


Sharpe and Johnson published in 2015 a report using five different tosyl hydrazone derivatives in a typical Shapiro reaction. The starting ketone **15** was transformed into tosyl hydrazone **16** in 97% yield. Oxidation of **16** with *m*-CPBA caused ring closure and allowed formation of a pyran, *via* initial stereoselective epoxidation in the presence of a tosyl hydrazone group. The next step involved protection of the alcohol by a TBS group that gave the silyl ether tosyl hydrazone **17**, in 77% yield. Methylation of **17** with MeI in the presence of *n*-BuLi proceeded to give product **18** in 95% yield. The last step, a Shapiro reaction, followed by treatment with either DMF, different aldehydes **X(b-d)**, or iodine, produced aldehyde **19a**, alcohols **19b-d** or iodide **19e** in moderate (43%) to very good (67%) yields.[8]

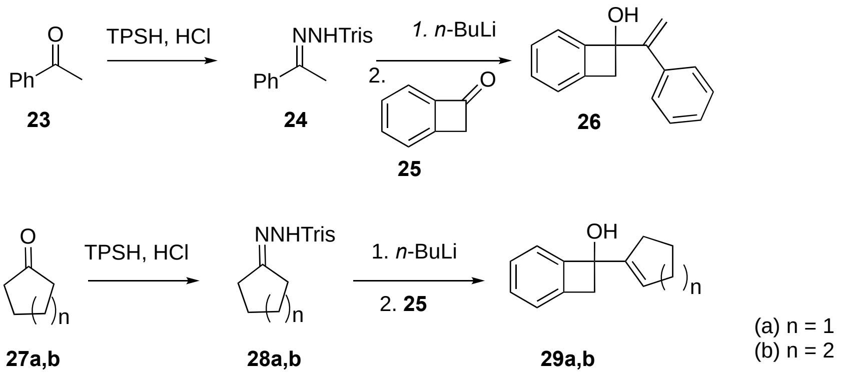


	X =	R =
(a)	DMF	CHO
(b)	HCHO	CH_2OH
(c)	CH_3CHO	$-CH(OH)CH_3$
(d)	$CH_3CH{=}CHCHO$	$-CH(OH)CH{=}CHCH_3$
(e)	I_2	-I

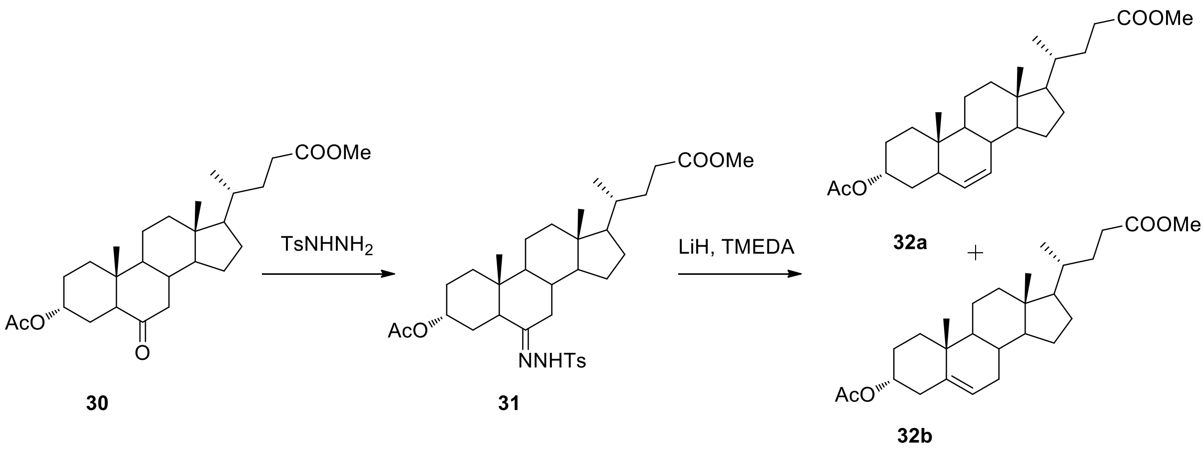
Shi *et al*. studied the formation of the substituted cyclohexene **22** employing Shapiro reaction methodology. The starting ketone **21** was converted into the tosyl hydrazone and subsequent reaction with methyllithium led to the formation of the desired cyclic alkene **22**, in 81% yield.[9] Compound **20** (-)-carvone was also converted to **22** in 55% yield, in a three-step synthetic transformation.



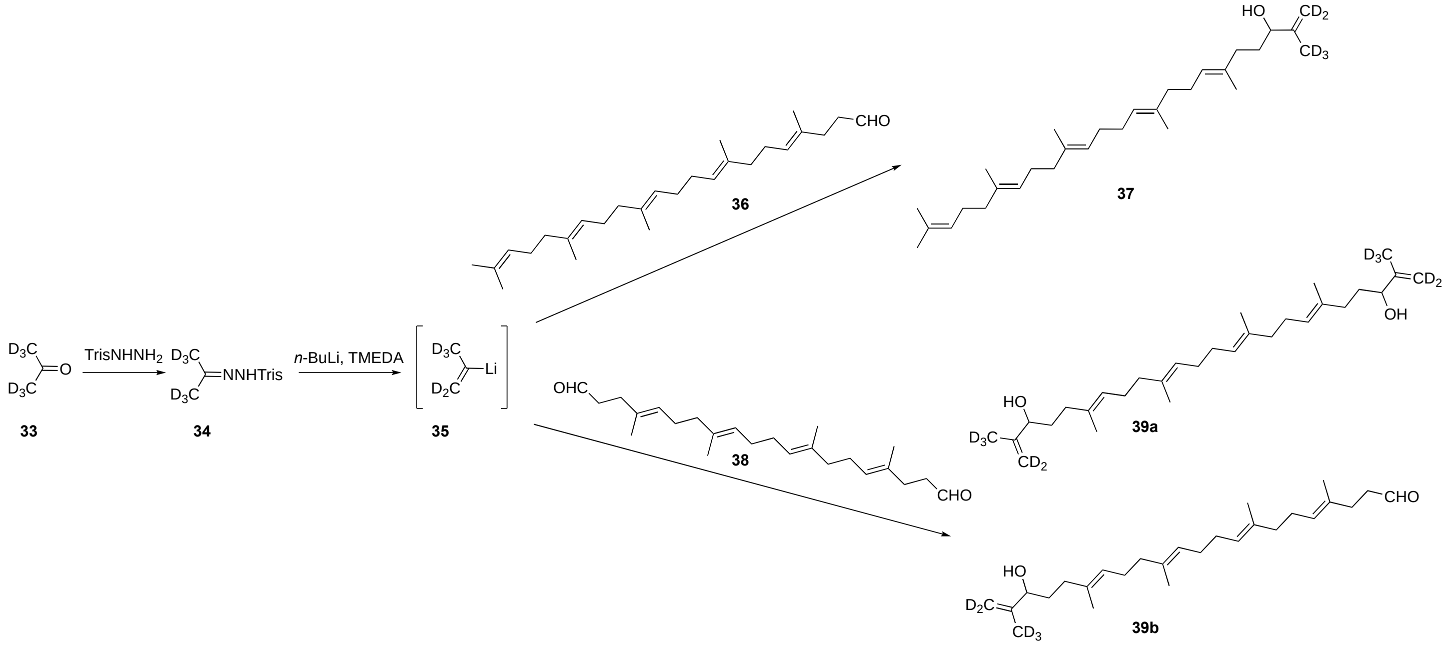
In 2015 Fu *et al*. reported the preparation of enol derivatives employing the Shapiro reaction. Acetophenone (**23**) as well as cyclopentanone (**27a**) and cyclohexanone (**27b**) reacted with 2,4,6-triisopropylbenzenesulfonyl hydrazide (TPSH) and formed trisyl hydrazone derivatives **24**, **28a** and **28b** in 63, 68 and 68% yields, respectively. Further treatment with *n*-BuLi in the presence of bicyclo[4.2.0]octa-1,3,5-trien-7-one (**25**) produced alcohols **26**, **29a** and **29b** in 70, 47 and 50% yields, respectively. All obtained alcohols were unstable. [10]



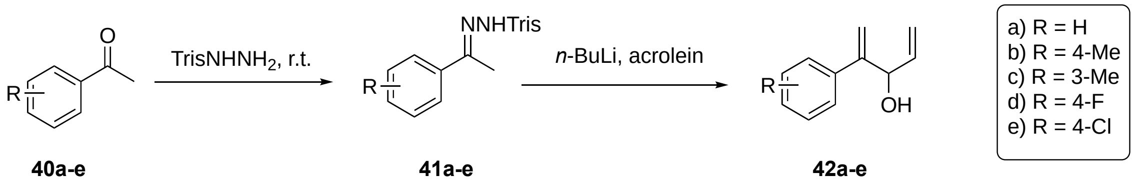
Jiang and Dou described the synthesis of olefins **32a** and **32b**. The starting ketone was converted into hydrazone derivative **31**, in 95% yield. Treatment of **31** with LiH provided a mixture of olefins **32a** and **32b** in 75% yield and in a ratio 15:1. This was the first example of employing lithium hydride as a base in a Shapiro reaction. Using sodium hydride, noticeably lower yields of products (37% yield) were observed.[11]



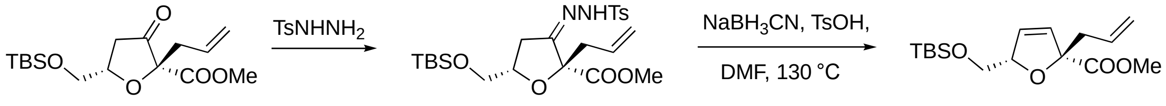
In 2016 Buchy *et al*. investigated the Shapiro reaction with the use of the deuterated isopropylidene end-group. Firstly, the two-step modification yielded (prop-1-en-2-yl-*d*5)lithium (**35**) from trisylhydrazone **34** upon treatment with the *n*-butyllithium and TMEDA. Trisyl hydrazone **34** was synthesized from deuterated acetone (**33**) and trisyl hydrazine. Condensation of vinyllithium intermediate **35** with squalen-aldehyde **36** formed allylic alcohol **37**, in 59% yield. After efficient application of the isopropylidene terminal group, this method was applied to modify a functionalized compound on both ends. Reaction of vinyllithium **35** and dialdehyde **38** a mixture of two derivatives was obtained, diol **39a** and allylic alcohol **39b** in 20% and 15% yields, respectively.[12]



Teramoto *et al.* studied the Shapiro reaction by using five different acetophenone derivatives **40a-e** and TPSH. The first step led to the formation of hydrazones **41a-e** in yields ranging from 67 to 81%. Subsequent treatment with *n*-butyllithium in the presence of acrolein, proceeded to afford a series of allylic alcohols **42a-e**, in 82 to 97% yields.[13]

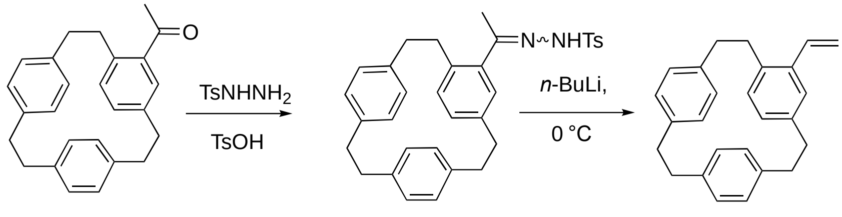


The synthesis of dihydrofuran derivative **45** has been achieved by the Yakura group. The tosyl hydrazone **44** was synthesized in 96% yield from the reaction of ketone **43** with tosyl hydrazide. Treatment of **44** with sodium cyanoborohydride and *p*-toluenesulfonic acid in DMF led to the formation of desired unsaturated compound **45** in 40% yield. The last step was postulated to proceed through the Bamford−Stevens reaction.[14] This method was also reported in another publication of the Yakura group.[15]



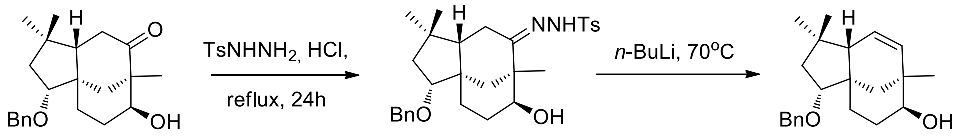
43 **44** **45**

Lehne, Ernst and Hopf investigated the synthesis of aromatic hydrocarbons carrying a vinyl substituent. The synthesis of vinyl[2.2.2]paracyclophane (**48**) featured a conversion of the ketone group of compound **47** to a tosyl hydrazone group in compound **47**. The latter was obtained in 79% yield as a mixture of diastereoisomers (ratio 2:1) while further treatment with the *n*-BuLi led to target molecule **48**, in 38% yield. Aromatic hydrocarbons are interesting intermediates, mostly as dienes for Diels–Alder reactions or for polymerization reactions.[16]



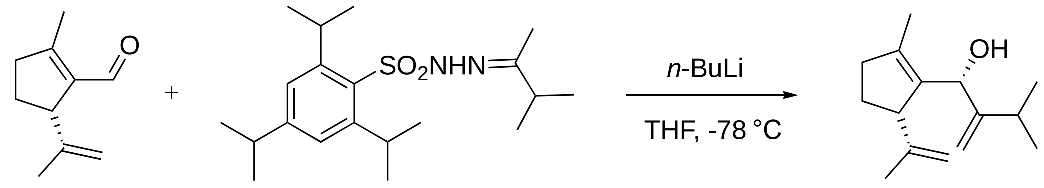
46 **47** **48**

In 2017, Yang *et al.* reported the preparation of clovan-2,9-dione employing the Shapiro reaction as a key, middle step. The synthetic route involved the conversion of the carbonyl group of **49** into a tosyl hydrazone in compound **50** by refluxing with $TsNHNH_2$. The Shapiro reaction of compound **50** with *n*-butyllithium provided cyclic alkene **51**, in 52% yield. [17]



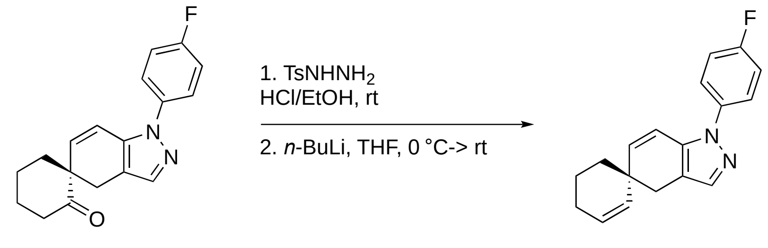
49 **50** **51**

Wang *et al.* synthesized (-)-englerin in 20 steps that included the Shapiro reaction as the one of key steps. Mixing *n*-BuLi and hydrazone **53** at -78 °C and further addition of the α,β-unsaturated aldehyde **52** at 40 °C allowed the formation of alcohol **54**, in 88% yield, as the main diastereoisomer. [18]



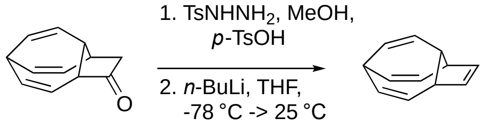
52 **53** **54**

Badarau *et al.* reported the preparation of six-membered spiro olefin **56** by applying the Shapiro reaction. The tosyl hydrazide was mixed with ketone **55** and subsequent treatment with *n*-butyllithium at low temperature furnished the target alkene, but in only 34% yield. [19]



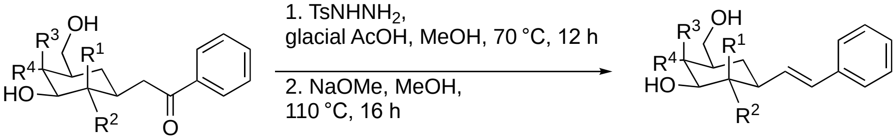
55 **56**

Erden and Gleason reported a synthesis of a hydrocarbon **58** using the Shapiro-Heath reaction. Ketone **57** was converted to the tosyl hydrazone derivative which was subsequently subjected to reaction with two equivalents of *n*-butyllithium at low temperature. The hydrocarbon-**58** that was isolated amounting to an overall yield of 68%.[20]



57 **58**

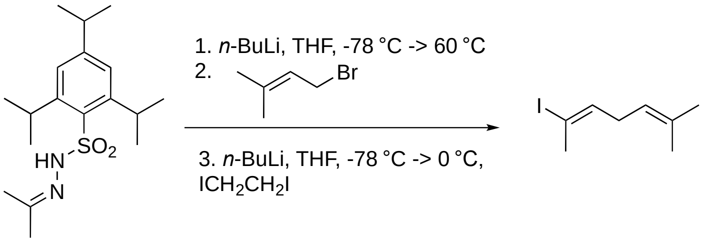
In 2019 Singh *et al.* reported an efficient preparation of 1-phenyl-2-(β-d-glycopyranosyl)ethenes **60a-c** employing the Bamford-Stevens methodology. Ketones **59a-c** were subjected to reaction with *p*-toluenesulfonyl hydrazide and acetic acid as a catalyst. The hydrazones obtained were used in the second step involving NaOMe in MeOH which produced the basic conditions. The styrene C-glycosides **60a-c** were formed selectively as *trans* products in 89%, 89% and 84% yields, respectively. Formation of the *(E)*-ethenes was confirmed by NMR spectroscopy (coupling constants of double bond protons $^3J_{HH}$=16 Hz). [21]



59a-c **60a-c**

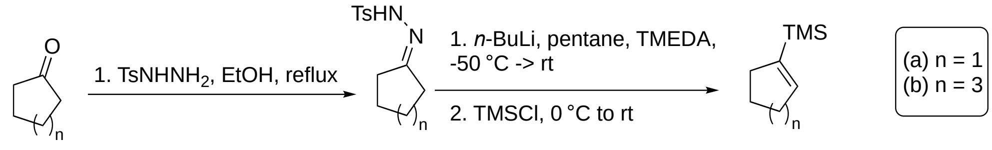
	R^1	R^2	R^3	R^4
(a)	H	OH	H	OH
(b)	H	OH	OH	H
(c)	OH	H	H	OH

A multi-step synthesis of myrsinoic acid F, which is an anti-inflammatory agent, was reported by Mikusek *et al.* The Shapiro reaction was involved as a key step to obtain an alkenyl iodide that is required to complete the synthesis of the target molecule. Therefore, 2,4,6-triisopropylbenzenesulfonyl hydrazone (**61**) reacted with *n*-butyllithium at -78 °C, then prenyl bromide was added to the reaction mixture. In continuation, another equivalent of *n*-BuLi was added and reaction mixture was allowed to warm up. Subsequently, the reaction mixture was cooled to -78 °C again and the solution was treated with 1,2-diiodoethane. This procedure led to a 91% yield of the iodo-olefin **62**. [22]



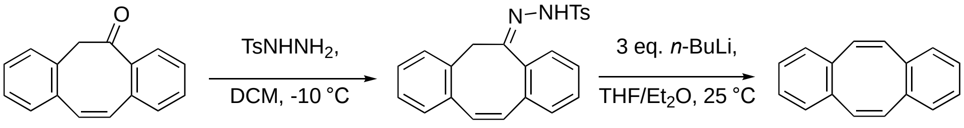
61 **62**

Zimdars *et al.* prepared functionalized acylsilanes using the Shapiro reaction as a middle step. Ketone **63b** was converted into tosyl hydrazone **64b** in 90% yield. Compound **64a** was commercially available. Further treatment of compounds **64a,b** with *n*-BuLi in the presence of TMEDA and TMSCl led to the formation vinylsilanes **65a-b**, in 48 and 66% yield, respectively. [23]



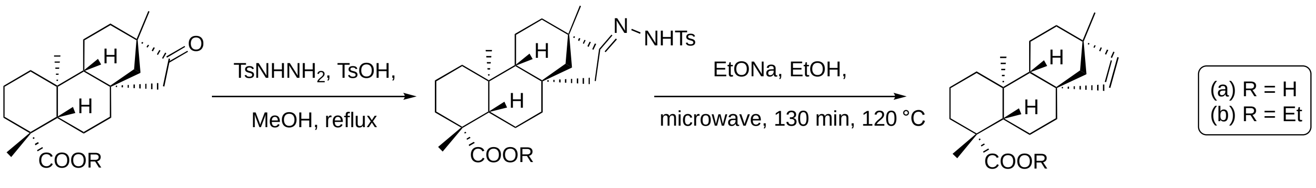
63b **64a-b** **65a-b**

Maier *et al.* investigated the transfer hydrogenation protocol for imines, olefins as well as *N*-heteroarenes using cobalt complexes. Thus, a structurally challenging, polycyclic olefin was synthesized according to the Shapiro reaction protocol. The starting ketone **66** was mixed with tosyl hydrazide in dichloromethane leading to the formation of hydrazone **67**, in 52% yield. The second step was undertaken without further purification. Compound **67** reacted with *n*-BuLi in THF and tricyclic olefin **68** was produced, in 49% yield. [24]



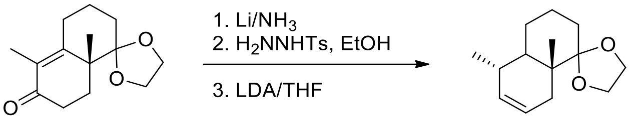
66 **67** **68**

Murillo *et al.* published a synthesis of natural isomeric *ent*-beyerene diterpenes which showed antileishmanial activity and were considered as potential drugs for skin leishmaniasis chemotherapy. The synthesis started from natural stevioside which was hydrolyzed to isosteviol (**69a**), esterified to **69b** and then transformed into tosyl hydrazone **70b**, in 90% yield. Subsequent subjection to the Bamford-Stevens basic reaction conditions under microwave radiation, caused the conversion of hydrazone **70b** into ethyl beyerenoate (**71b**), in 95% yield. Further reduction of the ester group of **71b** to a hydroxymethyl group with $LiAlH_4$ led to the formation of the desired beyerenol.[25]



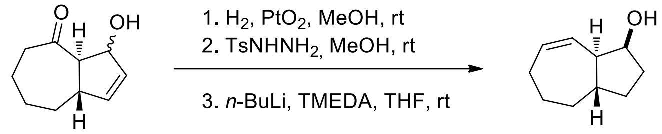
69a-b **70a-b** **71a-b**

A report by Pinkerton *et al.* described the preparation of the *seco*-limonoid BDC ring system containing limonoids. The synthetic route involved the Shapiro reaction as a key internal step. Ketone **72** reacted with Li and NH_3, then was mixed with tosyl hydrazide to obtain the hydrazone derivative. Finally, reaction of the latter with lithium *N*,*N*-diisopropylamide in anhydrous THF afforded the cyclohexene **73**, in 76% yield. [26]



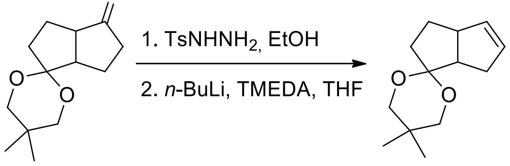
72 **73**

In 2020 Fumito *et al.* reported the multi-step synthesis of perhydroazulenes. The Shapiro reaction was used to convert the unsaturated β-hydroxy ketone **74** into cyclic alkene **75**. Compound **74** found to be unstable, therefore, on formation it was subjected to subsequent reactions. Firstly, the olefin group was hydrogenated in the presence of hydrogen and PtO_2 as catalyst. Further treatment with tosyl hydrazide led to the corresponding tosyl hydrazone, which was reacted with TMEDA and *n*-BuLi to give diastereomerically pure product **75**, in 44% yield. [27]



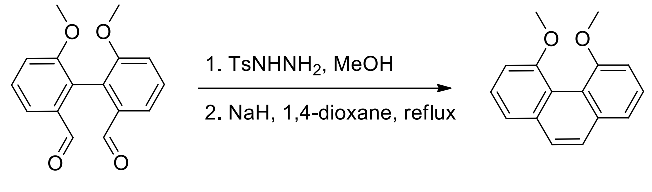
74 **75**

Laschat *et al.* presented the synthesis of functionalized hydropentalenes which play an important role as ligands for asymmetric catalysis and as building blocks for natural products. The Shapiro reaction was employed as a middle step in the synthetic path. Thus, the ketone functionality, in the acetal-protected ketone **76** was removed by reaction with tosyl hydrazide to afford an intermediate tosyl hydrazone which was further treated with *n*-BuLi in the presence of TMEDA, to produce cyclic alkene **77**, in 82% yield.[28]



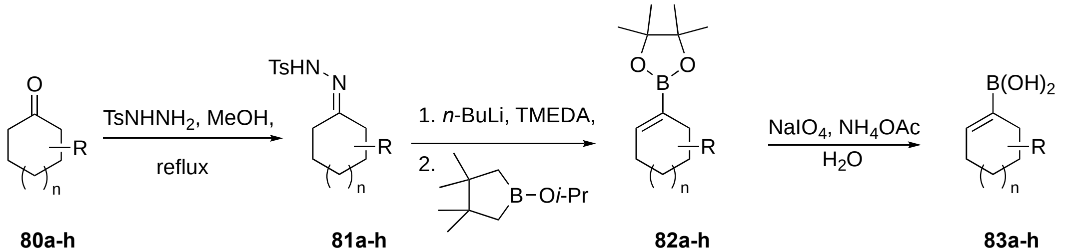
76 **77**

Wilkinson *et al*. presented the synthesis of 4,5-dimethoxyphenanthrene (**79**) via the Bamford-Stevens reaction. Firstly, dialdehyde **78** was converted into the corresponding bistosyl hydrazone by the reaction with tosyl hydrazide and subsequently~~,~~ using sodium hydride, transformed into the desired cyclic alkene **79**, but in only 18% yield.[29]



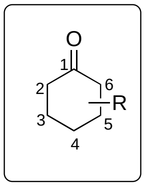
78 **79**

Bi *et al.* published a strategy to prepare tetrahydrocarbazol-1-ones and indolo[2,3-*a*]carbazoles with, among others, arylhydrazines. This work presents an efficient one-pot synthetic route for the functionalization of alkenylboronic acids. The cyclic alkenylboronic acids **82** were obtained from the ketones **80** in the reaction with tosyl hydrazide and subsequently, with TMEDA, *n*-butyllithium and then 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. The last step involved treating compounds **82** with NaIO$_4$ to afford final products **83**, in good yields.[30]

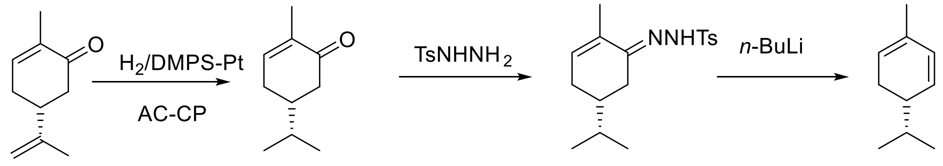


80a-h **81a-h** **82a-h** **83a-h**

	n =	R =		n =	R =
(a)	1	H	e)	1	4-*t*-Bu
(b)	2	H	f)	1	4-Ph
(c)	3	H	g)	1	5-Me
(d)	1	4-Me$_2$	h)	1	6-Me

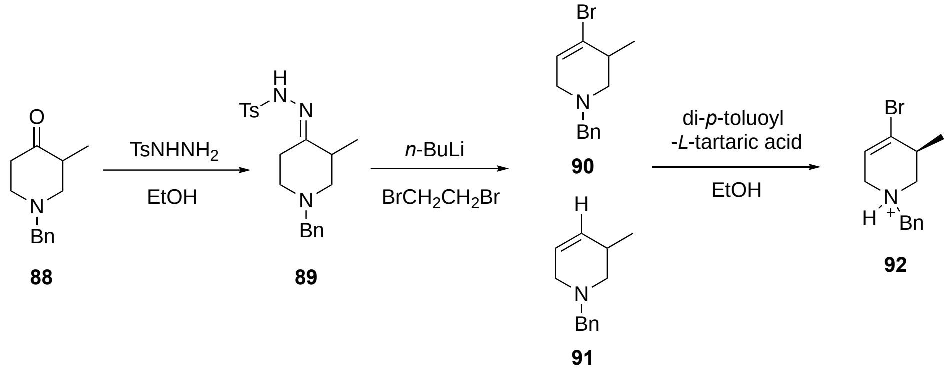


Kobayashi's group synthesized (*S*)-α-phellandrene, an important terpene product, through a three-step sequence, involving the Shapiro reaction under conditions of continuous flow, for the first time. The procedure consists of platinum-catalyzed hydrogenation, subsequent formation of hydrazone and finally the application of the Shapiro reaction. The first step was the selective hydrogenation of alkene **84** in the presence of dimethylpolysilane Pt catalyst (DMPS-Pt) supported on activated carbon and calcium phosphate (AC-CP). Next the α,β-unsaturated ketone group of **85** was reacted with tosyl hydrazide in the presence of sulfonic acid resin and the obtained tosyl hydrazone **86** was subjected to the Shapiro reaction yielding the desired product **87**, in 88% yield and 96% purity.[31]

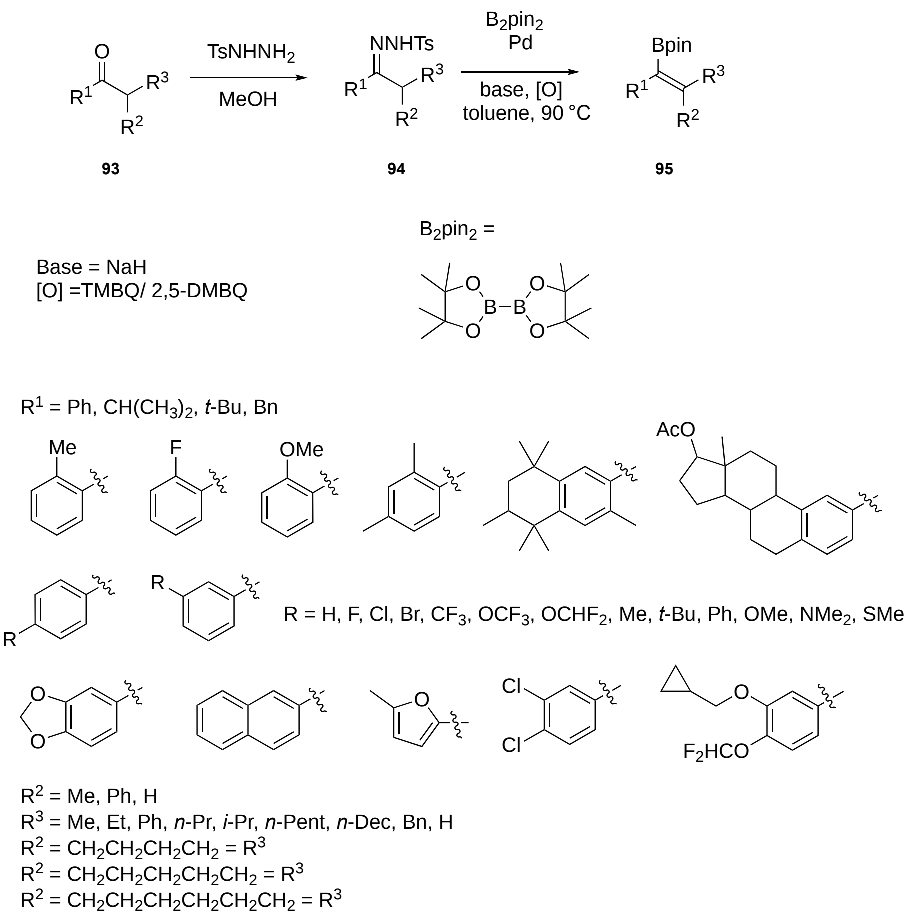


84 **85** **86** **87**

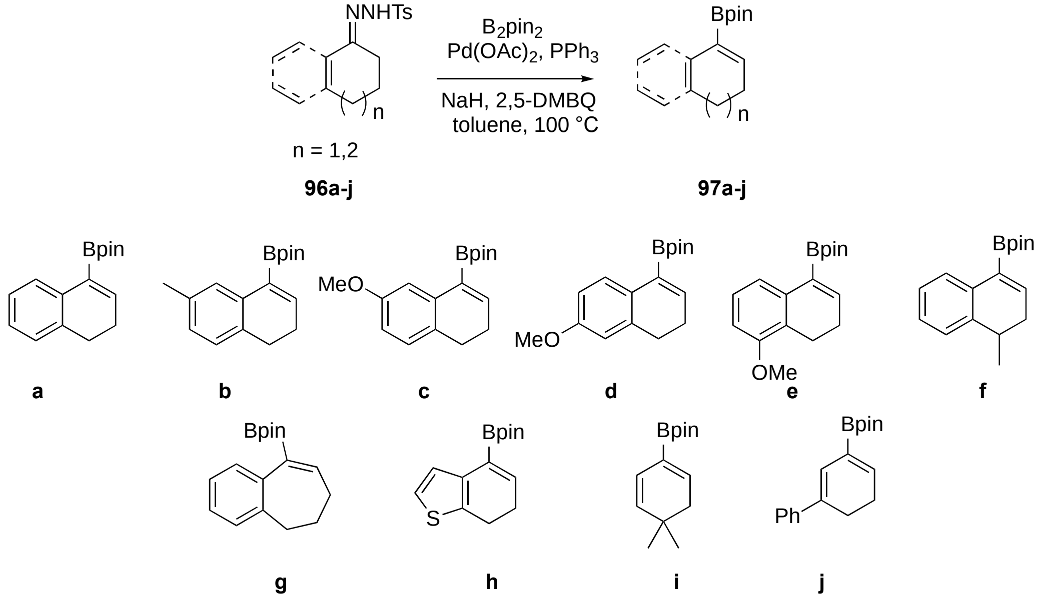
At the end of 2021, Lombardo *et al.* reported an enantiopure kilogram synthesis of (*S*)-1-benzyl-4-bromo-3-methyl-1,2,3,6-tetrahydropyridine (**92**) which is an important precursor to other piperidines, used as intermediates in drug synthesis. Ketone **88** reacted with tosyl hydrazide to yield tosyl hydrazone **89**, in 87% yield. Subsequent Shapiro reaction gave bromoalkene **90** and olefin **91** as a byproduct which was removed by chromatographic separation. Final addition of di-*p*-toluoyl-*L*-tartaric acid provided salt **92**, in 95% yield. [32]



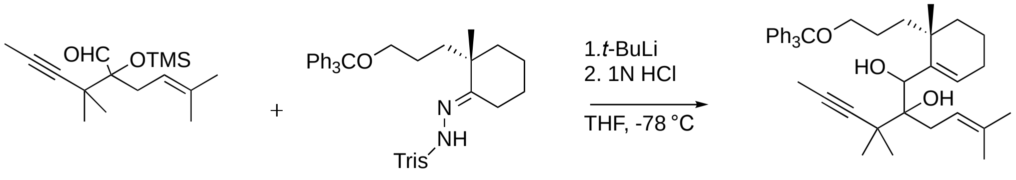
Wang *et al.* [33] investigated the synthesis of di-, tri- as well as tetra-substituted alkenylboronates due to the catalytic oxidative borylation reaction of tosyl hydrazones **94** from ketones **93**. A highly efficient and practical method was presented for the synthesis of 83 alkenyl derivatives **95**.



Furthermore, Wang's group using the same strategy synthesized the cyclic alkenylboronates which cannot be prepared by alkene hydroboration. The final products were obtained from the corresponding cyclic *N*-tosyl hydrazones **96a-j** in moderate (33% for **97j**) to good yields (88% for **97g**).

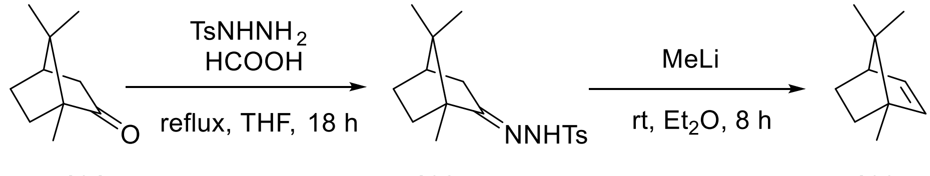


At the beginning of 2022, Prunet *et al*. presented two synthetic routes towards Taxol synthesis involving a relay ring-closing metathesis reaction. A Shapiro reaction was used as a middle step to obtain the diol **100** via the reaction of trisyl hydrazone **99** with aldehyde **98**, in the presence of *t*-BuLi.[34]



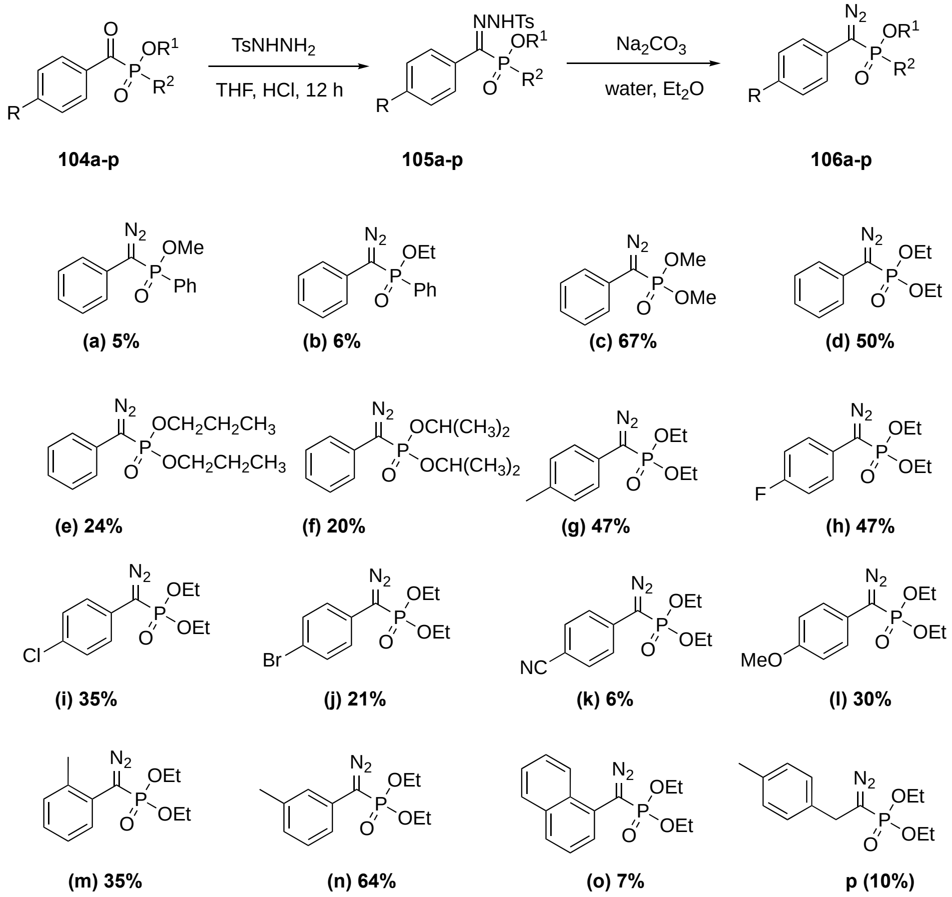
98 **99** **100**

In 2022, Sukowski and co-workers reported a new catalytic system which was based on Pd/norbornene as well as S,O-ligand for the arylation of aryl esters. Norbornene **103** was prepared by Bamford-Stevens reaction using camphor **101** as a starting material and reacted it with tosyl hydrazide. In the second step, the desired product was obtained in 27% yield after reaction with MeLi.[35]



101 **102** **103**

Xu *et al.* presented the visible-light-inducted annulation of phosphoryl diazomethylarenes and pyridinium 1,4-zwitterionic thiolates leading to the dicarboxylate derivatives. The diazophosphinates and diazophosphonates were synthesized from tosyl hydrazones **105a-p** which reacted with sodium carbonate to yield the final products **106a-p** in rather moderate yields. [36]



3. Conclusions

Instalment of a C=C double bond in complex systems is sometimes quite challenging. Shapiro and Bamford-Stevens reactions are widely used in synthetic organic chemistry as a very useful tool for the introduction of the double bond into often complex systems. Herein, in this short review we have presented the usefulness and practical applications of Shapiro and Bamford-Stevens reactions in synthetic organic chemistry.

4. Acknowledgements

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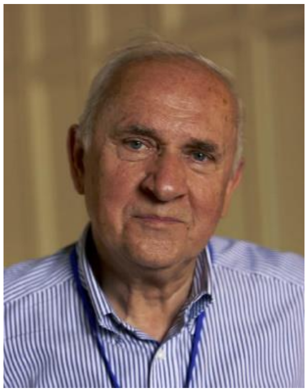
MSc. Katarzyna Salamon-Krokosz was born in 1994 in Poland. She pursued a B.Sc. degree in general chemistry at Adam Mickiewicz University from 2013 to 2016. In 2016, she undertook graduate studies in material chemistry and performed her Master's thesis focusing on the organometallic chemistry. Currently she is working as a third-year Ph.D. student under the supervision of Prof. Henryk Koroniak. Her research focuses on the synthesis of monofluorovinyl amino acid derivatives with potential biological activity.

Dr. Katarzyna Koroniak-Szejn is currently working as an Assistant Professor at Adam Mickiewicz University in Poznań. She finished her studies and graduated with her Master Thesis in 2005 at the Faculty of Chemistry of Adam Mickiewicz University in Poznań. Then, in 2008, she defended her PhD in Germany at the Westfälische Wilhelms-Universität w Münster under the supervision of Professor Günter'a Haufe. Next two years (2009 - 2011) she spent as post-doc at the Karlsruhe Institute of Technology in the group of Professor Stefan Bräse. After her return to home University she continues the research work dealing mainly with the synthesis of fluorinated organic compounds with potential biological activity, derivatives of carbohydrates and amino acids.



Henryk Koroniak is a Professor at Adam Mickiewicz University, Poznań, Poland. He is a Head of Department of Synthesis and Structure of Organic Compounds. His research activity includes: synthesis and structural studies of fluorine containing organic molecules, biologically active fluorochemicals, molecular modelling, and mostly fluorine influence on reactivity and structure of organic compounds. He served as a Dean of Faculty of Chemistry, Adam Mickiewicz University, He was also involved is several activities related to his academic career such as Member of Polish State Committee for Scientific Research; Member of Editorial Board of Journal of Fluorine Chemistry; Editor of "On the borderline between chemistry and biology" (39 volumes up to 2019), Member of Council of The Foundation for Polish Science (FNP), Member of Fluorine Division, American Chemical Society.