

**RECENT ADVANCEMENT IN ORGANOCATALYZED
FRIEDEL-CRAFTS REACTION WITH DETAILED
MECHANISTIC INVESTIGATION**

SANJAY SINGH



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

APRIL 2024

© **Indian Institute of Technology Delhi (IITD), New Delhi, 2024**

Recent Advancement in Organocatalyzed Friedel-Crafts Reactions with Detailed Mechanistic Investigation

by

SANJAY SINGH

Department of Chemistry

Submitted

In fulfilment of the requirement of the degree of Doctor of Philosophy



INDIAN INSTITUTE OF TECHNOLOGY DELHI

APRIL 2024

Dedicated

To

My Parents and Teachers

CERTIFICATE

This is to certify that the thesis entitled “*Recent Advancement in Organocatalyzed Friedel-Crafts Reactions with Detailed Mechanistic Investigation*” being submitted by Mr. **Sanjay Singh** to the *Indian Institute of Technology Delhi*, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. Mr. **Sanjay Singh** has worked under my supervision and guidance and has fulfilled all the requirements for the submission of a Ph.D. thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of a Ph.D. degree.

The work embodied in this thesis has not been submitted, in part or full, to another university or institute for the award of any degree or diploma.

Dr. Chinmoy Kumar Hazra

Research Supervisor,

Associate Professor,

Department of Chemistry

Indian Institute of Technology Delhi

Hauz Khas, New Delhi-110016, India.

Acknowledgments

First and foremost, I would like to take this opportunity to thank my research supervisor, **Prof. Chinmoy K. Hazra**, for his constant encouragement, patience, and guidance which has enriched me as a student, a chemist, and as a human being. His vast research experience and skills in organocatalysis and the development of novel synthetic methodologies, have helped me a lot to complete my Ph.D. work. I wish to express my gratitude to him for mentoring me not only in academics but personally also. I would also like to thank him for keeping faith in me, with the responsibilities of the lab. He has set a standard as a perfect teacher, and I see him as a teaching idol in my life.

I would like to extend my gratitude to Mrs. Anwesha Ghosh who treated us like children with her delicious dishes at home on various occasions, especially on Christmas every year, thereby making us feel at home at IIT Delhi.

I would like to thank Prof. Siddharth Pandey, Head, Dept. of Chemistry, and former head of Department Prof. Anil J. Elias and Prof. N. D. Kurur for providing me necessary research facilities. I would like to thank my student research committee (SRC) members, Prof. Nidhi Jain, Prof. Shivajirao L. Gholap, and Prof. Sreedevi Upadhyayula for their time, interest, suggestions, and helpful comments. I would also like to greatly acknowledge Prof. S. Nagendran, coordinator of the X-ray facility, for providing me an opportunity to learn and operate the single crystal X-ray diffractometer. I would like to extend my sincere thanks to all the teachers of this department for their support whenever it was required.

I would like to acknowledge all the teachers I have learned from since my childhood, I would not have reached my present position without their guidance, blessings, and prayers.

I also thank Mr. Manoj, Miss. Poornima, Mr. Ankush, Mr. Kuily, and Miss. Shubhra for recording NMR, HRMS, and IR spectra. I also thank Mr. Virender Sharma, in charge of the central glass-blowing facility for his timely help. I am thankful to all the members of this department who helped me in one way or the other to carry out my work successfully.

I can't find words to express my gratitude to my postdoctoral seniors, Dr. Nagaraju, Dr. Sankalan, Dr. Sharda, Dr. Neha Taneja, and Dr. Bulti for their help and support whenever I required their advice. I thank my fellow lab mates, Pragya, Jabir, Naveen, Aparna, Rahul, Sikandar, Rina, Riya, Rima, and Khyati for creating an atmosphere of brotherhood throughout my Ph.D. work. I want to thank all the project students, Shiv Prashan, Sandeep, Deepak, Swagtam, Suniana, Muskan, Sayantan, Sai, Kanhaiya, and Harshit for their love, affection, and help shown towards me on and off the lab. I am very much grateful to all of them.

Thanks to Parul, Naved, Abu, Abishek, Joshi, Neha Antil, Ketan, Arpit, Pratima, Manjeet, Parveen, Daksh, and Upanshu all my colleagues for providing a great work environment, and for helping and chatting.

I thank all my Ph.D. friends with whom I had spent memorable moments at IIT Delhi. I would like to acknowledge my other friends from school, B.Sc. and M.Sc. for their moral support and motivation, which drives me to give my best.

I wish to convey my utmost respect to my parents, Mr. Khajan Singh and Mrs. Santosh Devi, who sacrificed their best period of their lives and invested in them to nurture my education and well-being. Their love, affection, support, blessings, and prayers for me are priceless. I want to acknowledge my family members Vikram, Suman, Manju, Sonia, Niki, and Armann for their love and moral support.

I acknowledge the University Grants Commission (UGC), Govt. of India, for providing me with a junior and senior research fellowship. I also thank DST, CSIR, and IIT Delhi for financial assistance in my research.

Sanjay Singh

ABSTRACT

The thesis entitled "*Recent Advancement in Organocatalyzed Friedel-Crafts Reactions with Detailed Mechanistic Investigation*" presents the results obtained from the research work carried out on the organocatalysis, development of synthetic methodologies, sustainable catalysis, heterogeneous catalysis in the advancement of typical Friedel-Crafts reactions. Detailed mechanistic investigation to reveal the possible catalytic cycle and synthesis of bioactive molecules and late-stage functionalization of natural products to afford the value-added chemicals. The accompanied research work has been divided into seven chapters.

Chapter 1 The work described in this thesis centers around the summarized introduction of the Friedel-Crafts reaction along with their academic and industrial potential. It also includes recent developments in this area made by the scientific community as well as an outline of the constraints that encouraged our findings and potential significance to circumvent the existing limitations. The overall objective of the research work presented in the thesis is to development of new catalytic synthetic methodologies for the synthesis of polyarylated alkanes and explore deeper to understand the key findings in the mechanistic investigation in typical Friedel-Crafts reactions. We have successfully utilized the developed protocols to synthesize various value-added products viz. diarylmethanes (DAMs) and triarylmethanes (TRAMs). Diarylmethanes (DAMs) and triarylmethanes (TRAMs) precursors have sp^3 hybridized carbon atoms containing two/three aryl groups attached to them. The last couple of decades have witnessed an incredible development in the advancement of catalytic creation of diarylmethanes (DAMs) and triarylmethanes (TRAMs) motifs. The broad-spectrum applications of

DAMs and TRAMs in the area like medicinal chemistry, pharmacology, dyes, and functional materials has urged scientists to invent their efficient synthetic strategies. Due to their extraordinary chemical as well as pharmaceutical properties, triarylmethanes (TRAMs) have gained significant attention in the chemical community. Triarylmethanes (TRAMs) and their derivatives are highly captivating molecules in synthetic organic chemistry because of their structural and physical properties. This chapter describes the scope of the present work carried out and reported in the thesis.

Chapter 2 introduces a mild and robust double hydroarylation strategy for the synthesis of symmetrical /unsymmetrical diaryl- and triarylmethanes in excellent yields using Lambert salt (0.2-1.0 mol%). Despite the anticipated challenges associated with controlling selective product formation, unsymmetrical diaryl- and triarylmethanes products are obtained unprecedentedly. A highly efficient gram scale reaction has also been reported (TON for symmetrical product = 475 and for unsymmetrical product = 390). The synthetic utility of the methodology is demonstrated by the preparation of several unexplored diaryl- and triarylmethanes-based biological relevant molecules, such as arundine, vibrindole A, turbomycin B, and anti-inflammatory agents in one-pot. A facile synthesis of anti-breast cancer agents is also demonstrated. Control experiments, Hammett analysis, HRMS, and GC-MS studies reveal the reaction intermediates and reaction mechanisms.

Chapter 3 describes a mild and efficient synthetic protocol for the synthesis of symmetrical as well as unsymmetrical diarylmethanes (DAMs). Using DMSO as the carbon source and TMSOTf as the Lewis-acid promoter, a series of functionalized symmetrical and unsymmetrical diarylmethanes (DAMs) were synthesized in high yields.

Gratifyingly, DMSO plays a dual role as solvent as well as a carbon source and can also be replaced with its deuterated counterpart DMSO-d₆, enabling the incorporation of the -CD₂ moiety into the diarylmethanes skeleton. The developed approach has been applied to a wide range of substrates having various functional groups and this protocol has also been extended for the synthesis of anti-breast cancer agents, and anticoagulant agents using common feedstock compounds. Further, the postulated mechanism has been explicitly demonstrated based on control experiments.

Chapter 4 describes a green approach to synthesizing unsymmetrical polyarylated alkanes in a one-pot fashion. Generally, unsymmetrical di- and triarylmethanes are synthesized through metal-catalyzed cross-coupling or Friedel-Crafts arylation via multistep harsh reaction conditions using pre-functionalized starting materials. This affects the reaction mass efficiency, and atom economy and produces significant environmental wastes resulting in a high E-factor. As an alternative, herein, using a cheap, commercially available Brønsted acid-catalyst (*p*TSA•H₂O)/HFIP, we describe a one-pot three-component approach for the synthesis of unsymmetrical polyarylated alkanes from renewable feedstock chemicals. Compared to conventional routes, we avoid using any pyrophoric materials, metal catalysts, toxic solvents, and Grignard reagents and report many examples that are difficult to access via reported methods. Calculation of different green metrics (atom economy (95%), atom efficiency (84.5%), reaction mass efficiency (77.1%), and E-factor (1.26 kg/kg of the product with solvent and 0.32 kg/kg of the product without solvent) indicated the greenness of the described protocol. The developed method could also be scaled up and was applied for a short and efficient synthesis of a phenanthrene-based anti-breast cancer agent which reduced the

conventional six-step cross-coupling approach to one-step Friedel-Crafts approach. Also, the method has been applied for the late-stage functionalization of various natural products like Thymol, Menthol, Eugenol, etc., and the used HFIP was recovered highlighting the suitability of the method for industrial applications.

Chapter 5 describes the Friedel-Crafts alkylation of electron-deficient arenes with aldehydes through "catalyst activation" is presented. Strongly electron-withdrawing arenes including arenes with multiple halogen atoms, NO₂, CHO, CO₂R, and CN, groups acted as efficient nucleophiles in this reaction. DFT studies reveal multiple roles of solvent HFIP viz; increasing the Brønsted acidity of the catalyst *p*TSA•H₂O, and stabilization of the transition states through a concerted pathway enabling the challenging reaction. Further, we extended the developed bis arylation protocol to various ketones like 4-nitro acetophenone, 4-phenyl acetophenone, 9-fluorenone, trifluoroacetophenone, etc. Interestingly, the reaction could be extended to a tandem process where the reaction of trifluoromethyl acetophenone with resorcinol resulted in the formation of trifluoromethyl (CF₃) containing tetrasubstituted spiro-xanthene through a tandem Friedel-Crafts reaction cyclization process.

Chapter 6 deals with the development of general and more sustainable heterogeneous catalytic processes for Friedel-Crafts (FC) alkylation reactions is a key objective of interest for the synthesis of pharmaceuticals and commodity chemicals. Sustainable heterogeneous catalysis for the typical FC alkylation of easily accessible carbonyl electrophile and arenes or with two different arene nucleophiles in one-pot is a prime challenge. Herein, we present a resolution to these issues through the design and utilization of a mesoporous silica catalyst that has been functionalized with sulphonic

acid. For the synthesis of sulphonic acid-functionalized mesoporous silica (MSN-SO₃H), thiol-functionalized mesoporous silica was first synthesized by the co-condensation method, followed by oxidation of the thiol functionality to the sulphonic acid group. Sulphonation of mesoporous silica was confirmed by ¹³C CP MAS NMR spectroscopy. Further, the devised heterogeneous catalysis using MSN-SO₃H has been successfully employed in the construction of diverse polyalkanes including various bioactive molecules viz arundine, tatarinoid-C, and late-stage functionalization of natural products like Menthol and Eugenol. Further, we have utilized this sustainable technique to facilitate the formation of unsymmetrical C–S bonds in a one-pot fashion. In addition, the catalyst was successfully recovered and recycled for eight cycles, demonstrating the high sustainability and cost-effectiveness of this protocol for both academic and industrial applications.

Chapter 7 gives the overall conclusions of the entire work carried out in the present study and future outline.

सारांश

शोध-प्रबन्ध का शीर्षक है " *विस्तृत यंत्रवत जांच के साथ कार्बनिक उत्प्रेरक फ्रीडेल-क्राफ्ट्स प्रतिक्रियाओं में नयी प्रगति* " शीर्षक वाली थीसिस विशिष्ट फ्रीडेल-क्राफ्ट्स प्रतिक्रियाओं की प्रगति में ऑर्गेनोकैटलिसिस, सिंथेटिक पद्धतियों के विकास, टिकाऊ उत्प्रेरक, विषम उत्प्रेरक पर किए गए शोध कार्य से प्राप्त परिणाम प्रस्तुत करती है। . संभावित उत्प्रेरक चक्र और बायोएक्टिव अणुओं के संश्लेषण और मूल्यवर्धित रसायनों को वहन करने के लिए प्राकृतिक उत्पादों के देर-चरण क्रियाशीलता को प्रकट करने के लिए विस्तृत यंत्रवत जांच। संलग्न शोध कार्य को सात अध्यायों में विभाजित किया गया है।

अध्याय 1 इस शोध-प्रबन्ध में वर्णित कार्य फ्रीडेल-क्राफ्ट्स प्रतिक्रिया के सारांशित परिचय के साथ-साथ उनकी शैक्षणिक और औद्योगिक क्षमता पर केंद्रित है। इसमें वैज्ञानिक समुदाय द्वारा इस क्षेत्र में किए गए हालिया विकास के साथ-साथ उन बाधाओं की रूपरेखा भी शामिल है जिन्होंने हमारे निष्कर्षों और मौजूदा सीमाओं को पार करने के संभावित महत्व को प्रोत्साहित किया। थीसिस में प्रस्तुत शोध कार्य का समग्र उद्देश्य पॉलीएरिलेटेड अल्केन्स के संश्लेषण के लिए नई उत्प्रेरक सिंथेटिक पद्धतियों का विकास करना और विशिष्ट फ्रीडेल-क्राफ्ट्स प्रतिक्रियाओं में यंत्रवत जांच में प्रमुख निष्कर्षों को समझने के लिए गहराई से पता लगाना है। हमने विभिन्न मूल्य-वर्धित उत्पादों को संश्लेषित करने के लिए विकसित प्रोटोकॉल का सफलतापूर्वक उपयोग किया है। डायरिलमीथेन्स (DAMs) और ट्राईरिलमीथेन्स (TRAMs)। Diarylmethanes (DAMs) और triarylmethanes (TRAMs) अग्रदूतों में sp³ संकरित कार्बन परमाणु होते हैं जिनमें दो/तीन एरिल्स समूह जुड़े होते हैं। पिछले कुछ दशकों में डायरीलमीथेन्स (डीएएम) और ट्राईरिलमीथेन्स (टीआरएएम) रूपांकनों के उत्प्रेरक निर्माण की प्रगति में अविश्वसनीय विकास देखा गया है। औषधीय रसायन विज्ञान, औषध विज्ञान, रंजक और कार्यात्मक सामग्री जैसे क्षेत्र में डीएएम और टीआरएएम के व्यापक स्पेक्ट्रम अनुप्रयोगों ने वैज्ञानिकों को अपनी कुशल सिंथेटिक रणनीतियों का आविष्कार करने के लिए प्रेरित किया है। अपने असाधारण रसायन के साथ-साथ फार्मास्युटिकल गुणों के कारण, ट्राईरिलमीथेन्स (टीआरएएम) ने रासायनिक समुदाय में महत्वपूर्ण ध्यान आकर्षित किया है। ट्राईरिलमीथेन्स (टीआरएएम) और इसके डेरिवेटिव अपने संरचनात्मक और भौतिक गुणों के कारण सिंथेटिक कार्बनिक रसायन

विज्ञान में अत्यधिक आकर्षक अणु हैं। अध्याय थीसिस में किए गए और रिपोर्ट किए गए कार्य के वर्तमान दायरे का वर्णन करता है।

अध्याय 3 में सममित और असममित डायरिलमीथेन (डीएम) के संश्लेषण के लिए एक हल्के और कुशल सिंथेटिक प्रोटोकॉल का वर्णन किया गया था। डीएमएसओ को कार्बन स्रोत के रूप में और टीएमएसओटीएफ को लुईस-एसिड प्रमोटर के रूप में उपयोग करते हुए, उच्च पैदावार में कार्यात्मक सममित और असममित डायरिलमीथेन (डीएम) की एक श्रृंखला को संश्लेषित किया गया था। संतुष्टिदायक बात यह है कि डीएमएसओ विलायक के साथ-साथ कार्बन स्रोत के रूप में दोहरी भूमिका निभाता है और इसे इसके ड्यूटेरेटेड समकक्ष डीएमएसओ-डी6 से भी बदला जा सकता है, जो डायरिलमीथेन्स कंकाल में -सीडी2 अंश को शामिल करने में सक्षम बनाता है। विकसित दृष्टिकोण को विभिन्न कार्यात्मक समूहों वाले सबस्ट्रेट्स की एक विस्तृत श्रृंखला पर लागू किया गया है और इस प्रोटोकॉल को सामान्य फीडस्टॉक यौगिकों का उपयोग करके स्तन कैंसर विरोधी एजेंटों और एंटीकोआगुलेंट एजेंटों के संश्लेषण के लिए भी बढ़ाया गया है। इसके अलावा, नियंत्रण प्रयोगों के आधार पर निर्धारित तंत्र को स्पष्ट रूप से प्रदर्शित किया गया है।

अध्याय 4 में असममित पॉलीएरिलेटेड अल्केन्स तक पहुंचने के लिए एक हरित दृष्टिकोण का वर्णन किया गया है। आम तौर पर, असममित डि- और ट्राइएरिलमीथेन को धातु-उत्प्रेरित क्रॉस-कपलिंग या फ्रीडेल-क्राफ्ट्स एरिलेशन के माध्यम से पूर्व-कार्यात्मक शुरुआती सामग्रियों का उपयोग करके मल्टीस्टेप कठोर प्रतिक्रिया स्थितियों के माध्यम से संश्लेषित किया जाता है। यह प्रतिक्रिया द्रव्यमान दक्षता, परमाणु अर्थव्यवस्था को प्रभावित करता है और महत्वपूर्ण पर्यावरणीय अपशिष्ट पैदा करता है जिसके परिणामस्वरूप उच्च ई-फैक्टर होता है। एक विकल्प के रूप में, यहां, सस्ते, व्यावसायिक रूप से उपलब्ध ब्रोस्टेड एसिड-उत्प्रेरक (पीटीएसए•एच2ओ)/एचएफआईपी का उपयोग करते हुए, हम नवीकरणीय फीडस्टॉक रसायनों से असममित पॉलीरिलेटेड अल्केन्स के संश्लेषण के लिए एक-पॉट तीन-घटक दृष्टिकोण का वर्णन करते हैं। पारंपरिक मार्गों की तुलना में, हम किसी भी पायरोफोरिक सामग्री, धातु उत्प्रेरक, विषाक्त सॉल्वेंट्स और ग्रिगार्ड अभिकर्मकों का उपयोग करने से बचते हैं और कई

उदाहरणों की रिपोर्ट करते हैं जिन्हें रिपोर्ट किए गए तरीकों से एक्सेस करना मुश्किल है। विभिन्न ग्रीन मेट्रिक्स (परमाणु अर्थव्यवस्था (95%), परमाणु दक्षता (84.5%), प्रतिक्रिया द्रव्यमान दक्षता (77.1%), और ई-फैक्टर (विलायक के साथ उत्पाद का 1.26 किग्रा/किग्रा और उत्पाद का 0.32 किग्रा/किग्रा) की गणना विलायक के बिना) ने वर्णित प्रोटोकॉल की हरियाली का संकेत दिया। विकसित विधि को भी बढ़ाया जा सकता है और इसे फेनेथ्रीन-आधारित एंटी-स्टन कैसर एजेंट के संक्षिप्त और कुशल संश्लेषण के लिए लागू किया गया था, जिसने पारंपरिक छह-चरण क्रॉस-कपलिंग दृष्टिकोण को कम कर दिया। एक-चरणीय फ्रिडेल-शिल्प दृष्टिकोण। इसके अलावा, इस विधि को विभिन्न प्राकृतिक उत्पादों जैसे थाइमोल, मेन्थॉल, यूजेनॉल इत्यादि के अंतिम चरण के कार्यान्वयन के लिए लागू किया गया है, और प्रयुक्त एचएफआईपी को औद्योगिक अनुप्रयोगों के लिए विधि की उपयुक्तता पर प्रकाश डालते हुए पुनर्प्राप्त किया गया था।

अध्याय 5 में "उत्प्रेरक सक्रियण" के माध्यम से एल्लिहाइड के साथ इलेक्ट्रॉन-कमी वाले एरेन के फ्रिडेल-क्राफ्ट्स एल्किलेशन का वर्णन प्रस्तुत किया गया है। कई हैलोजन परमाणुओं, NO₂, CHO, CO₂R और CN वाले एरेन्स सहित दृढ़ता से इलेक्ट्रॉन निकालने वाले एरेन्स समूहों ने इस प्रतिक्रिया में कुशल न्यूक्लियोफाइल के रूप में कार्य किया। डीएफटी अध्ययन से विलायक एचएफआईपी की कई भूमिकाओं का पता चलता है; उत्प्रेरक पीटीएसए•एच₂ओ की ब्रॉस्टेड अम्लता को बढ़ाना, और चुनौतीपूर्ण प्रतिक्रिया को सक्षम करने वाले एक ठोस मार्ग के माध्यम से संक्रमण राज्यों को स्थिर करना। इसके अलावा, हमने विकसित बाइसेरिलेशन प्रोटोकॉल को विभिन्न कीटोन्स जैसे 4-नाइट्रोएसेटोफेनोन, 4-फेनिलएसिटोफेनोन, 9-फ्लोरेनोन, ट्राइफ्लूरोएसेटोफेनोन आदि तक विस्तारित किया। दिलचस्प बात यह है कि प्रतिक्रिया को एक अग्रानुक्रम प्रक्रिया तक बढ़ाया जा सकता है जहां रेसोरिसिनॉल के साथ ट्राइफ्लोरोमिथाइल एसिटोफेनोन की प्रतिक्रिया के परिणामस्वरूप बनता है। ट्राइफ्लोरोमिथाइल (CF₃) जिसमें टेंडेम फ्रीडेल-क्राफ्ट्स प्रतिक्रिया चक्रीकरण प्रक्रिया के माध्यम से टेट्राप्रतिस्थापित स्पाइरो-ज़ैन्थीन होता है।

अध्याय 6 फ़िडेल-क्राफ्ट्स (एफसी) एल्किलेशन प्रतिक्रियाओं के लिए सामान्य और अधिक टिकाऊ विषम उत्प्रेरक प्रक्रियाओं के विकास से संबंधित है, जो फार्मास्यूटिकल्स और कमोडिटी रसायनों के संश्लेषण के लिए रुचि का एक प्रमुख उद्देश्य है। आसानी से सुलभ कार्बोनिल इलेक्ट्रोफाइल और एरेन्स के विशिष्ट एफसी एल्किलेशन के लिए या एक-पॉट में दो अलग-अलग एरेन न्यूक्लियोफाइल के लिए सतत विषम कटैलिसीस एक प्रमुख चुनौती है। इसमें, हम मेसोपोरस सिलिका उत्प्रेरक के डिजाइन और उपयोग के माध्यम से इन मुद्दों का समाधान प्रस्तुत करते हैं जिसे सल्फोनिक एसिड के साथ क्रियाशील किया गया है। सल्फोनिक एसिड-फंक्शनलाइज्ड मेसोपोरस सिलिका (एमएसएन-एसओ₃एच) के संश्लेषण के लिए, थियोल-फंक्शनलाइज्ड मेसोपोरस सिलिका को पहले सह-संक्षेपण विधि द्वारा संश्लेषित किया गया था, इसके बाद थियोल कार्यक्षमता को सल्फोनिक एसिड समूह में ऑक्सीकरण किया गया था। 13सी सीपी एमएस एनएमआर स्पेक्ट्रोस्कोपी द्वारा मेसोपोरस सिलिका के सल्फोनेशन की पुष्टि की गई। इसके अलावा, एमएसएन-एसओ₃एच का उपयोग करके तैयार किए गए विषम कटैलिसीस को विभिन्न बायोएक्टिव अणुओं जैसे अरुंडाइन, टैटारिनोइड-सी, और मेन्थॉल और यूजेनॉल जैसे प्राकृतिक उत्पादों के देर-चरण क्रियाशीलता सहित विविध पॉलीएल्केन के निर्माण में सफलतापूर्वक नियोजित किया गया है। इसके अलावा, हमने वन-पॉट फैशन में असममित सी-एस बांड के गठन की सुविधा के लिए इस टिकाऊ तकनीक का उपयोग किया है। इसके अलावा, उत्प्रेरक को सफलतापूर्वक पुनर्प्राप्त किया गया और आठ चक्रों के लिए पुनर्नवीनीकरण किया गया, जो अकादमिक और औद्योगिक दोनों अनुप्रयोगों के लिए इस प्रोटोकॉल की उच्च स्थिरता और लागत-प्रभावशीलता को प्रदर्शित करता है।

अध्याय 7 वर्तमान अध्ययन और भविष्य की रूपरेखा में किए गए संपूर्ण कार्य का समग्र निष्कर्ष देता है।

TABLE OF CONTENTS

			Page
CERTIFICATE			I
ACKNOWLEDGEMENTS			II
ABSTRACT			V
TABLE OF CONTENTS			XIV
ABBREVIATIONS			XX
CHAPTER	1	Introduction	1
	1.1	Friedel-Crafts (FC) Reaction	1
	1.2	History & Background	2
	1.3	Alcohols as Alkylating Agent	4
	1.4	Aldehyde and Ketones as Alkylating Agents	20
	1.5	Alkyl Fluorides as Alkylating Agents	26
	1.6	Epoxide as Alkylating Agents	35
	1.7	Cyclopropanes as Alkylating Agents	40
	1.8	References	42
CHAPTER	2	Development of transition-metal-free Lewis acid-initiated double arylation of aldehyde: A facile approach towards the total synthesis of anti-breast cancer agent	59
	2.1	Introduction	59
	2.2	Results and Discussion	61

2.2.1	Optimization Studies	61	
2.3	Substrate Scope for the Synthesis of Symmetrical Products	62	
2.4	Substrate Scope for the Synthesis of Unsymmetrical Products	66	
2.5	Control Experiments & Mechanistic Studies	70	
2.6	Gram-Scale Synthesis of Triarylmethanes	74	
2.7	Applications	76	
2.8	Conclusion	78	
2.9	Experimental Section	79	
2.9.1	General Procedure for the Synthesis of Symmetrical Diarylmethanes/Triarylmethanes (GP1)	79	
2.9.2	General Procedure for the Synthesis of Unsymmetrical Diarylmethanes/Triarylmethanes (GP2)	79	
2.9.3	General Procedure for FC Arylation of Alcohols (GP3)	80	
2.10	Analytical Data of Synthesized Molecules	80	
2.11	Hammett Analysis	100	
2.12	Copies of Spectral Data	102	
2.13	References	124	
CHAPTER	3	Lewis-acid promoted typical Friedel-Crafts	128

		reactions using DMSO as a carbon source	
	3.1	Introduction	128
	3.2	Results and Discussion	130
	3.3	Substrate Scope of the Reaction	132
	3.4	Mechanistic Investigation	135
	3.5	Conclusion	138
	3.6	Experimental Section	139
	3.6.1	General Experimental Procedure for the Synthesis of Symmetrical Diarylmethanes	139
	3.6.2	General Experimental Procedure for the Synthesis of Unsymmetrical Diarylmethanes	139
	3.7	Analytical Data of Synthesized Molecules	140
	3.8	Copies of Spectral Data	149
	3.9	Crystal Data	175
	3.10	References	176
CHAPTER	4	Hydrogen bonding network enabled Brønsted acid catalyzed Friedel-Crafts reactions: A green approach to access unsymmetrical diaryl- and triarylmethanes	179
	4.1	Introduction	179

	4.2	Results and Discussion	181
	4.3	Mechanistic Studies	186
	4.4	Recycle and Reusability of HFIP Solvent in Gram-Scale Synthesis	192
	4.5	Conclusion	193
	4.6	Experimental Section	194
	4.6.1	General Procedure for Synthesis of Unsymmetrical Diarylmethanes/Triarylmethanes (GP1)	194
	4.6.2	General Procedure for Intra and Inter-Molecular Friedel-Crafts Reaction (GP2)	194
	4.7	Analytical Data of the Synthesized Molecules	195
	4.8	Copies of Spectra Data	207
	4.9	Crystal Data	234
	4.10	Calculation of Green Metrics	235
	4.11	References	239
CHAPTER	5	Cooperative Friedel-Crafts alkylation of electron-deficient arenes via catalyst activation with hexafluoroisopropanol	241
	5.1	Introduction	241
	5.2	Results and Discussion	243
	5.3	Substrate Scope of the Reaction	244
	5.4	Mechanistic Investigation and Computational	248

		Studies	
	5.5	Conclusions	252
	5.6	Experimental Section	253
	5.6.1	General Procedure for the Synthesis of Diarylmethanes/Triarylmethanes with Electron Deficient Arenes (GP1)	253
	5.6.2	General Procedure for the Synthesis of Diarylmethanes/Triarylmethanes for Challenging Substrates (GP2)	253
	5.7	Analytical Data of Synthesized Molecules	254
	5.8	Copies of Spectral Data	266
	5.9	Crystal Data	299
	5.10	References	300
CHAPTER	6	Sustainable sulphonic acid functionalized tubular shape mesoporous silica as a heterogeneous catalyst for selective unsymmetrical Friedel-Crafts alkylation in one- pot	302
	6.1	Introduction	302
	6.2	Results and Discussion	305
	6.2.1	Optimization Studies	310
	6.3	Substrate Scope of the Reaction	311

	6.4	Applications	318
	6.5	Plausible Mechanism of the Reaction	322
	6.6	Conclusion	323
	6.7	Analytical Data of Synthesized Molecules	324
	6.8	Experimental Section	340
	6.8.1	Synthesis of Thiol-Functionalized Mesoporous Silica Nanoparticles	340
	6.8.2	Synthesis of Sulphonated Mesoporous Silica Nanoparticles	340
	6.8.3	General Procedure for the Synthesis of Symmetrical Diarylmethanes/Triarylmethanes	340
	6.8.4	General Procedure for Unsymmetrical Friedel- Crafts Arylation	341
	6.8.5	General Procedure for the Friedel-Crafts Cyclization Reactions	341
	6.9	Crystal Data	342
	6.10	Copies of Spectral Data	343
	6.11	References	349
CHAPTER	7	Conclusion and Future Outline	352
RESUME			355

LIST OF FIGURES

			Page
CHAPTER	1		
Figure	1.1	Various active drug molecules, natural products, and dye precursors containing di- or tri-arylmethanes motif	5
Figure	1.2	(A) and (B) Reactivity of “classical”; (C) “frustrated” Lewis pairs	24
Figure	1.3	(A) "Classical" Lewis acid-base adduct; (B) “frustrated” Lewis pairs	25
CHAPTER	2		
Figure	2.1.	Si–H bond activation by using trityl salt (1)	61
Figure	2.2	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4a	103
Figure	2.3	^1H , ^{19}F and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4b	104
Figure	2.4	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4e	106
Figure	2.5	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4f	107
Figure	2.6	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4n	108
Figure	2.7	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	109

		4o	
Figure	2.8	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	110
		4z	
Figure	2.9	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	111
		4zb	
Figure	2.10	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	112
		6a	
Figure	2.11	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	113
		6g	
Figure	2.12	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	114
		6q	
Figure	2.13	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	115
		6s	
Figure	2.14	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	116
		6t	
Figure	2.15	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	117
		6x	
Figure	2.16	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	118
		6zi	
Figure	2.17	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	119
		9a	
Figure	2.18	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	120
		9c	

Figure	2.19	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 10c	121
Figure	2.20	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 11c	122
Figure	2.21	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 11d	123
CHAPTER 3			
Figure	3.1	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2a	150
Figure	3.2.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2b	151
Figure	3.3	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2d	152
Figure	3.4.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2g	153
Figure	3.5.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2j	154
Figure	3.6	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2m	155
Figure	3.7.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2n	156
Figure	3.8.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	157

		2r	
Figure	3.9	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	158
		2t	
Figure	3.10.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	159
		2u	
Figure	3.11.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	160
		4a	
Figure	3.12.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	161
		4d	
Figure	3.13	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	162
		4e	
Figure	3.14	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	163
		4f	
Figure	3.15	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	164
		4g	
Figure	3.16	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	165
		4j	
Figure	3.17	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	166
		4m	
Figure	3.18	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	167
		4n	
Figure	3.19	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound	168
		4o	

Figure	3.20	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4p	169
Figure	3.21	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4q	170
Figure	3.22	^1H , ^{13}P , and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 5a	171 172
Figure	3.23	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 5b	173
Figure	3.24	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 5c	174
CHAPTER	4		
Figure	4.1	Some representative biologically active molecules	179
Figure	4.2	pKa comparison of pTSA•H ₂ O in two different fluoroalcohol solvents HFIP and TFE using mesityl oxide as the probe through ^{13}C -NMR.	187
Figure	4.3	^{13}C -NMR of pure mesityl oxide	188
Figure	4.4	Real time NMR studies showing the activation of the pTSA•H ₂ O with HFIP.	189
Figure	4.5	Recyclability and reusability of the HFIP solvent in Gram-scale reaction	192
Figure	4.6	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 1	208

Figure	4.7	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2	209
Figure	4.8	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 3	210
Figure	4.9	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4	211
Figure	4.10	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 5	212
Figure	4.11	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 6	213
Figure	4.12	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 11	214
Figure	4.13	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 12	215
Figure	4.14	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 14	216
Figure	4.15	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 16	217
Figure	4.16	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 18	218
Figure	4.17	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 19	219
Figure	4.18	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 23	220
Figure	4.19	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 24	221
Figure	4.20	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 26	222

Figure	4.21	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 28	223
Figure	4.22	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 37	224
Figure	4.23	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 38	225
Figure	4.24	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 40	226
Figure	4.25	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 41	227
Figure	4.26	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 44	228
Figure	4.27	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 45	229
Figure	4.28	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 47	230
Figure	4.29	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 48	231
Figure	4.30	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 49	232
Figure	4.31	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 51	233

CHAPTER 5

Figure	5.1.	Previous reports and the current work.	242
Figure	5.2	DFT calculated Gibbs free energy profile diagram for concerted FC reaction mechanism with cooperative effect of HFIP solvent	250
Figure	5.3	DFT calculations showing the effect of hydrogen bonding network of explicit HFIP solvent on the reaction mechanism	251
Figure	5.4	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 1	267
Figure	5.5.	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 2	269
Figure	5.6	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 3	270
Figure	5.7	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 4	271
Figure	5.8	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 5	272
Figure	5.9	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 7	273
Figure	5.10	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 8.	274
Figure	5.11	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 9	275
Figure	5.12	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 10	276
Figure	5.13	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 12	277
Figure	5.14	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 15	278

Figure	5.15	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 16	279
Figure	5.16	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 19	280
Figure	5.17	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 20	281
Figure	5.18	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in DMSO) spectra of compound 21	282
Figure	5.19	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 23	283
Figure	5.20	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 26	284
Figure	5.21	^1H , ^{19}F , and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 30	285
Figure	5.22	^1H ^{19}F , and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 31	287
Figure	5.23	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 32	288
Figure	5.24	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 33	289

Figure	5.25	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 34	290
Figure	5.26	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 35	291
Figure	5.27	^1H ^{19}F , and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 36	292
Figure	5.28	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 38	294
Figure	5.29	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 40	295
Figure	5.30	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 42	296
Figure	5.31	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 43	297
Figure	5.32	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl_3) spectra of compound 46	298

CHAPTER 6

Figure	6.1	Scheme representing synthesis of sulphonic acid functionalized mesoporous silica particles	307
Figure	6.2	^{13}C CP MAS NMR spectrum of modified mesoporous silica MSN-SH and MSN-SO ₃ H. (b) ^{29}Si single pulse NMR spectra of MSN-SH and MSN-SO ₃ H.	309
Figure	6.3	Recycling and reusability of MSN-SO ₃ H catalyst up to eight cycles	321
Figure	6.4	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl ₃) spectra of compound 3a	344
Figure	6.5	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl ₃) spectra of compound 3c	345
Figure	6.6	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl ₃) spectra of compound 3f	346
Figure	6.7	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl ₃) spectra of compound 3g	347
Figure	6.8	^1H and $^{13}\text{C}\{^1\text{H}\}$ - NMR (in CDCl ₃) spectra of compound 3m	348

LIST OF TABLES

CHAPTER			Page
CHAPTER	2		
Table	2.1	Optimization of the double arylation reaction for the synthesis of triarylmethane (TRAM).	63
CHAPTER	3		
Table	3.1	Initial Optimization for the reaction of 1j	131
CHAPTER	4		
Table	4.1.	Reaction conditions	182
Table	4.2	Comparison of various green metrics of the previous methods with the current work	189
CHAPTER	5		
Table	5.1.	Reaction conditions.	244
CHAPTER	6		
Table	6.1	Reaction conditions	311

List of Abbreviations Used

<i>i</i> Pr	Isopropyl
<i>t</i> Bu	<i>tert</i> -Butyl
FC	Friedel-Crafts
TEOS	Tetraethyl orthosilicate
MPTES	3-Mercaptopropyltriethoxysilane
CP MAS	Cross-polarization magic angle spinning
TGA	Thermogravimetric analysis
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TMB	1,3,5-Trimethoxy benzene
2,6-DMP	2,6-Dimethylphenol
Me	Methyl
Et	Ethyl
Ph	Phenyl
MP	Melting point
RT	Room Temperature
h	Hour(s)
min	Minutes
THF	Tetrahydrofuran
UV	Ultraviolet Spectroscopy
TLC	Thin Layer Chromatography
HFIP	Hexafluoroisopropanol

EtOAc	Ethylacetate
NMR	Nuclear Magnetic Resonance Spectroscopy
HRMS	High-Resolution Mass Spectroscopy
NOESY	Nuclear Overhauser Effect Spectroscopy
BHT	Butylated hydroxytoluene
TEMPO	(2, 2, 6, 6-Tetramethyl piperidine-1-yl)oxyl
TMEDA	Tetramethylethylenediamine
DG	Directing Group
DMSO	Dimethyl sulfoxide
SCXRD	Single crystal X-ray diffraction
DCM	Dichloromethane
DMF	<i>N, N</i> -dimethyl formamide
Aq.	Aqueous
TON	Turn Over Number
DCE	1, 2-Dichloroethane
DDQ	2, 3-Dichloro-5,6-dicyanobenzoquinone
TBHP	<i>tert</i> -Butyl hydroperoxide
GC-MS	Gas Chromatography-Mass Spectrometry
TRAMs	Triarylmethanes
DAMs	Diarylmethanes