3.1 Introduction and applications of B(C$_6$F$_5$)$_3$ catalyst

Tris(pentafluorophenyl)boron [B (C$_6$F$_5$)$_3$] is a Lewis acid catalyst, consists of three pentafluorophenyl groups attached in a paddle-wheel manner to a central boron atom. The BC$_3$ core is planar in structure. It has been described as the ideal Lewis acid because of its versatility and relative inertness of the B-C bonds. However, special properties of B(C$_6$F$_5$)$_3$ have made this a strong boron Lewis acid, an increasingly preferable catalyst in organic and organometallic chemistry. This includes catalytic hydrometallation reactions, alkylations and catalyzed aldol type reactions. The Lewis acidity of B(C$_6$F$_5$)$_3$ is somewhere between that of BF$_3$ and BCl$_3$, as judged by the method of Childs et al.$^1$ This property indicates that the electronegativity of the C$_6$F$_5$ group and a halide are similar. It was found to be a strong Lewis acid that formed adducts with triphenylphosphine and other Lewis bases.

Figure 1: structure of Tris(pentafluorophenyl) borane

Tris(pentafluorophenyl)borane was first prepared and described by Stone, Massey and Park in 1963.$^2$ It can be easily prepared by the addition of Grignard reagent (C$_6$F$_5$MgBr) to BCl$_3$ to give a white solid in good yields (Scheme 1).

\[ 3 \text{C}_6\text{F}_5\text{MgBr} + \text{BCl}_3 \rightarrow (\text{C}_6\text{F}_5)_3\text{B} + 3\text{MgBrCl} \]

Scheme 1
The development of efficient and practically useful Lewis acid catalysts for various organic transformations is of great importance. \( \text{B(C}_6\text{F}_5\text{)}_3 \) was first known for its role as an excellent activator component in homogeneous Ziegler–Natta olefin polymerization catalyst and their related chemistry. A growing number of such examples indicates an increasing application potential of Lewis acid \( \text{B(C}_6\text{F}_5\text{)}_3 \) aside from its established role in olefin polymerization catalysis (Scheme 2).

![Scheme 2](image)

For many years, tris(pentafluorophenyl)borane was known to be synonymous with homogeneous Ziegler-Natta catalyst activation, when recently an increasing number of reactions from the literature enounced the special features of \( \text{B(C}_6\text{F}_5\text{)}_3 \) other than in polymerization catalysis. Its high Lewis acidity combined with steric bulk, its pronounced ability for anion, specially carbanion equivalent abstraction and persistence of the resulting anions have made \( \text{B(C}_6\text{F}_5\text{)}_3 \) as a useful catalyst to induce a variety of specific reactions in organic and organometallic chemistry and to open synthetic pathways to unusually structured new compounds. This interesting new development will be illustrated by a number of selected examples in this perspective.

Yamamoto et. al., have used \( \text{B(C}_6\text{F}_5\text{)}_3 \) for the first time as a catalyst in the Mukaiyama aldol reactions of various silyl enol ethers and ketene silyl acetals with aldehydes or other electrophiles, which proceeds smoothly in presence of 2 mol% of catalyst. These aldol-type reactions do not proceed when triphenylborane is used as catalyst (Scheme 3).

![Scheme 3](image)
Conjugate addition of silyl enol ethers to $\alpha,\beta$-unsaturated ketones proceeds regioselectively in presence of 2 mol% of $\text{B(C}_6\text{F}_5)_3$. The products can be isolated as synthetically valuable silyl enol ethers when the crude product is worked up without exposure to acid (Scheme 4).

\[
\begin{align*}
\text{R}_1\text{R}_2\text{C} &= \text{CH}_2\text{Cl}_2, -78^\circ\text{C}, 12\text{ h,} \\
& 85-94\%
\end{align*}
\]

Scheme 4

$\text{B(C}_6\text{F}_5)_3$ is a highly active catalyst for aldol-type reactions between ketene silyl acetalts and imines because of its stability (comparatively low- N-B bond energy) and affinity towards nitrogen-containing compounds. $^4\text{b, c}$ $\text{N-Benzylimines are useful substrates because }\beta\text{-benzylamino acid esters can be readily debenzylated by hydrogenolysis on palladium/carbon. Catalysis is carried out using a 0.2 mol\% catalyst loading in toluene.}$

In most cases the condensation proceeds smoothly even with aliphatic enolizable imines derived from primary or secondary aliphatic aldehydes. The $\text{syn/anti}$ stereo selectivity of $\text{N-benzylidenebenzylamine}$ is dependent on the geometry of the ketene silyl acetal double bond: (E) and (Z)-ketene silyl acetals gave $\text{anti}$ and $\text{syn}$ products respectively, as the major diastereomers. The use of $\text{N-trialkylsilylimines}$ can be advantageous, since protected $\text{N-substituent}$ can easily cleaved from the $\beta$-[(trialkylsilyl) amino] acid esters produced in the reaction. $\text{Borane Lewis acid is an effective catalyst for the reaction of N-trimethylsilylimines.}$ The reaction of mono or di-substituted ketene silyl acetals with $\text{N-(tri- methylsilyl)benzylideneamine}$ proceeds smoothly to give the corresponding $\beta$-amino acid esters in good yield (Scheme 5).$^4\text{c}$

\[
\begin{align*}
\text{NHBn} & \quad + \\
& \quad \text{B(C}_6\text{F}_5)_3, 0.2 - 10 \text{ mol\%} \\
& \quad \text{toluene, } -78^\circ\text{C}, 13\text{ h,} \\
& \quad 25^\circ\text{C}, 2\text{ h,} \quad 55-99\%
\end{align*}
\]

Scheme 5
B(C₆F₅)₃ was used as a versatile catalyst for several organic transformations and recently explored as a non-conventional Lewis acid catalyst. This catalyst operates *via* hyper co-ordination at the boron center.⁵ Allylation of the formyl group in *o*-anisaldehyde is favored by a >20:1 margin over that in *p*-anisaldehyde, in a competitive situation (Scheme 6).⁶

![Scheme 6](image)

B(C₆F₅)₃ is a highly efficient catalyst in rearrangement of epoxides.⁷ Rearrangement of tri substituted epoxides readily takes place in presence of catalytic amounts of B(C₆F₅)₃, resulting in a highly selective alkyl shift to give the corresponding aldehydes. Exceptional bulkiness of B(C₆F₅)₃ may play a role in ensuring high selectivity of this process (Scheme 7).

![Scheme 7](image)

Lewis acid mediated cleavage of epoxides with various nucleophiles such as alcohols, amines and thiols is an important transformation in organic synthesis. Our group has found B(C₆F₅)₃ to be a highly efficient catalyst for ring opening of epoxides.⁸ Ring opening reaction of epoxides in presence of this catalyst (5 mol%) with various hetero atoms *viz.*, O, N and S generated β- hydroxy ethers, amines and sulfides in high yield. Acid labile protecting groups like TBDMS and THP were
stable under these reaction conditions (Scheme 8). In presence of catalytic amount of B(C$_6$F$_5$)$_3$, optically active styrene oxide and its analogs are directly converted into corresponding acetals such as acetonides or cyclopentylidene acetals to complete optical purity on the treatment with ketones.$^9$

\[
\begin{align*}
R & \quad \text{XH, B(C$_6$F$_5$)$_3$, CH$_2$Cl$_2$, rt} \\
\text{X} & \quad \text{O} & \quad \text{O} & \quad \text{O} & \quad \text{O}
\end{align*}
\]

\[R= \text{alkyl, aryl}\]

\[\text{X} = \text{NHPh, SHPh}\]

**Scheme 8**

B(C$_6$F$_5$)$_3$ was also involved in ring opening reactions of non-activated aziridines. There have been few reports on the ring opening of simple $N$-alkyl aziridines. Ring opening of non-activated aziridines with amine nucleophiles in presence of B(C$_6$F$_5$)$_3$ (10 mol%) in acetonitrile at 65 °C yielded the corresponding trans-diamine (Scheme 9).$^{10}$

\[
\begin{align*}
\text{R$_3$N} & \quad \text{B(C$_6$F$_5$)$_3$, 10 mol%, HX, CH$_3$CN, 65 °C} \\
\text{R$_1$} & \quad \text{NHR$_3$} & \quad \text{R$_2$} & \quad \text{X}
\end{align*}
\]

**Scheme 9**

B(C$_6$F$_5$)$_3$ is an effective catalyst for dehydrogenative silation of primary, secondary, tertiary and phenolic alcohols with variety of silanes (R$_3$SiH, R$_2$SiH$_2$, R$_2$R'SiH). Generally, the reaction occurs at room temperature using 2 mol% of catalyst, clean and high yielding with hydrogen as the only by product (Scheme 10).$^{11}$

\[
\begin{align*}
\text{R-OH} & \quad \text{B(C$_6$F$_5$)$_3$, 2 mol%, R$_3$SiH, toluene} \\
& \quad \text{R-OSiR$_3^1$ + H$_2$}
\end{align*}
\]

\[R= \text{Alkyl/ aryl}\]

\[R^1 = \text{Et, Ph}\]

**Scheme 10**

Carbonyl compounds undergo partial reduction with R$_3$SiH in the presence of B(C$_6$F$_5$)$_3$ as catalyst. In this method one equivalent of the silane reagent was essential
for clean reaction since further reduction of silyl ethers or silyl acetal products was observed when excess of silane used. Exhaustive reduction of aliphatic carbonyl function (aldehyde, acyl chloride, ester and carboxylic acid) to methyl group was achieved using catalytic amount of B(C$_6$F$_5$)$_3$ with stoichiometric amount of Et$_3$SiH (Scheme 11).$^{12a}$

\[
\begin{align*}
\text{R} & = \text{alkyl, } \text{X} = \text{H, Cl, OMe, OH} \\
\text{R-CH}_3 & \xrightarrow{\text{B(C}_6\text{F}_5)_3, 5 \text{ mol\%}} \text{Et}_3\text{SiH, CH}_2\text{Cl}_2
\end{align*}
\]

Scheme 11

Reduction of aromatic carbonyl compounds was achieved even with an excess of Et$_3$SiH. It was found that aromatic carbonyl functions underwent smooth partial reduction with Et$_3$SiH to afford silyl ethers.$^{12b}$ Aromatic $\alpha$- diketones also well participated in this transformation to produce corresponding silyl-protected 1, 2-diols (Scheme 12).$^{12c}$

\[
\begin{align*}
\text{R} & = \text{aryl, } \text{X} = \text{H, Cl, OMe, OH} \\
\text{R-CH}_2\text{OSiEt}_3 & \xrightarrow{\text{B(C}_6\text{F}_5)_3, (5 \text{ mol\%)}} \text{Et}_3\text{SiH, CH}_2\text{Cl}_2
\end{align*}
\]

Scheme 12

Our group has used B(C$_6$F$_5$)$_3$ as an excellent catalyst for activation of polymeric hydride source Polymethylhydrosiloxane (PMHS), a co-product of the silicon industry. A combination of PMHS and catalytic amount of B(C$_6$F$_5$)$_3$ efficiently reduced carbonyl compounds to corresponding methlenes (Scheme 13).$^{13}$ This procedure has advantages such as, selective reduction of ketone in presence of olefins.
and esters. Acid sensitive protecting groups like TBS and THP ethers are unaffected during this transformation.

\[ \text{R} \quad \text{O} \quad \text{R}_1 \quad \xrightarrow{\text{B(C}_6\text{F}_5)_3, \text{PMHS}} \quad \text{R-CH}_2\text{-R}_1 \]

\( \text{R} = \text{alkyl, aryl}, \quad \text{R}_1 = \text{H, alkyl, aryl} \)

**Scheme 13**

B(C\(_6\)F\(_5\))\(_3\) as a catalyst in conjunction with PhMe\(_2\)SiH efficiently hydrosilated benzaldimines and ketimines.\(^{14}\) B(C\(_6\)F\(_5\))\(_3\) abstracts hydride from PhMe\(_2\)SiH in presence of imines and forms silyliminium cation with hydridoborate counterion. The reaction proceeds *via* activation of imine by “PhMe\(_2\)Si\(^{+}\)”, spectral evidences support intermediacy of a silyliminium cation. Reductive coupling of carbonyl compounds with alkoxy silanes using Polymethylhydrosiloxane (PMHS) and catalytic amount of B(C\(_6\)F\(_5\))\(_3\) as the activator of the PMHS produce symmetrical and unsymmetrical ethers (Scheme 14).\(^{15}\)

\[ \text{R}_1 \quad \text{R}_2 \quad \xrightarrow{\text{B(C}_6\text{F}_5)_3, \text{PMHS}} \quad \text{R}_3 \quad \text{R}_4 \]

**Scheme 14**

A reaction between tri-\(O\)-acetyl-D-glucal and sulfonamides was effectively promoted by 0.5 mol% B(C\(_6\)F\(_5\))\(_3\) in acetonitrile at room temperature to produce aza-pseudoglycals *via* Ferrier rearrangement in good yields and preferential anomeric selectivity (Scheme 15).\(^{16}\) Extension of this to \(N\)-substitued sulfonamides (\(N\)-phenyl and \(N\)-benzyl sulfonamides) and carbamates (benzyl carbamate and *tert*-butyl carbamate) furnished corresponding \(N\)-pseudoglycals in moderate yields.
Scheme 15

B(C₆F₅)₃ was used as an efficient catalyst for synthesis of β-keto enol ethers from various β-diketones in presence of 2 mol% of B(C₆F₅)₃ at room temperature under rapid and mild conditions (Scheme 16).¹⁷

Scheme 16

Synthesis of 1,8-dioxo decahydroacridinediones was achieved under mild and solvent free conditions in the presence of catalytic amount of B(C₆F₅)₃ with moderate to excellent yields (scheme 17).¹⁸

Scheme 17

B(C₆F₅)₃ acts as a co-catalyst in metallocene mediated carbometalation of olefins and cyclocarbometalation of diolefins¹⁹ or amino alkenes.²⁰ B(C₆F₅)₃ catalyzes tautomerization reactions and is able to very effectively stabilize otherwise disfavored tautomeric isomers by adduct formation through N–B or O–B bond formation. The reaction between α-naphthol and B(C₆F₅)₃ is a typical example.
Stirring of a suspension of the α-naphthol with borane for 12 h at rt in pentane eventually gave a crystalline product which was shown to be the B(C₆F₅)₃ adduct of the benzoyleclohexadienone tautomer. Several other phenolic derivatives behaved similarly with B(C₆F₅)₃, but some gave equilibrium mixtures (Scheme 18).

A synthetically useful and convenient method for the B(C₆F₅)₃-catalyzed hydrostannylation of alkynes with tributyltin hydride, prepared *in situ* from easily handled and inexpensive chlorostannane and hydrosilane has been developed by Yamamoto *et al.* The hydrostannylation of mono-substituted alkynes proceeds in a regio specific manner affording exclusively the β-hydrostannylation products. The reaction is *trans*-stereo selective and can also be applied to the hydrostannylation of alkenes and allenes (Scheme 19).

\[
\text{R} \equiv \text{R}_1 + \text{Bu}_3\text{SnCl} + \text{Et}_3\text{SiH} \xrightarrow{\text{B(C₆F₅)₃ (10 mol%)}} \text{R} \equiv \text{SnBu₃}
\]

\[
\text{C₆H₄} \equiv + \text{Bu}_3\text{SnCl} + \text{Et}_3\text{SiH} \xrightarrow{\text{B(C₆F₅)₃ (10 mol%)}} \text{C₆H₄} \equiv \text{SnBu₃}
\]

\[\text{Scheme 19}\]

B(C₆F₅)₃ has found to be an efficient catalyst for Friedel-Crafts reactions between activated arenes or heteroarenes and α-amidosulfones in dichloromethane at room temperature. The products undergo further Friedel-Crafts reactions with activated heteroarenes leading to the synthesis of unsymmetrical triarylmethanes (Scheme 20).

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The treatment of the imidazole and thiazole ring with highly Lewis acidic borane B(C₆F₅)₃ forms a B-N adduct, which further treated with a strong base, such as methyllithium or LDA to form a cyclized skeletons via a Coordination/Cyclization Protocol with B(C₆F₅)₃ (Scheme 21). These cyclized imidazolyl and thiazolyl-containing π-conjugated frameworks have several advantages as candidates for n-type semiconductors and exhibits relatively high electron accepting properties.²⁴

1, 3- Dicarboxyl compounds undergo alkylation with various alcohols as alkylating agents in the presence of B(C₆F₅)₃ as a milder acid catalyst in dichloromethane under reflux conditions gave corresponding α-alkylated- β-diketones in good yields.²⁵
Gerhard Erker has used $B(C_6F_5)_3$ catalyst as an alternative reagent for hydroboration reactions. Strongly electrophilic boranes $R-B(C_6F_5)_2$ react readily with a variety of 1-alkynes by means of a 1, 1-carboboration/photochemical isomerization sequence to yield alkenylborane products, which subsequently used as reagent in metal catalyzed cross-coupling reactions in the presence of aryl halide and catalytic amounts of Pd(PPh$_3$)$_4$ in basic medium to produce coupling product in good yields (Scheme 23).  

\[
\begin{align*}
R^1 &= \text{Ph, (CH$_2$)$_2$Ph} \\
(C_6F_5)_2B &\xrightarrow{\text{CH$_2$Cl$_2$, rt, 3h}} (C_6F_5)_2B + ArX \\
&\xrightarrow{\text{Pd (0)}} Ar
\end{align*}
\]

Scheme 23

$B(C_6F_5)_3$ promotes regio and stereo selective cyclizations of unsaturated alkoxy silanes to generate oxasilinanes and oxasilepanes. These products are available directly from alkenols via tandem silylation and hydrosilylation. Addition of $B(C_6F_5)_3$ to a solution of unsaturated alkoxy silane resulted in regioselective formation of oxasilinane with high $3, 5$-trans diastereoselectivity. Oxidative desilylation of these hindered siloxanes was attempted by various oxidation conditions provided corresponding diols with high stereo selectivity (Scheme 24).  

\[
\begin{align*}
\text{Hex} &\xrightarrow{\text{Ph$_2$SiH$_2$, B(C$_6$F$_5$)$_3$}} \text{Hex} \\
\text{[Ox]} &\xrightarrow{} \text{Hex}
\end{align*}
\]

Scheme 24

Tris(pentafluorophenyl) borane was also used as a novel electrolyte additive for silicon (Si) thin film anodes in lithium ion batteries. The introduction of $B(C_6F_5)_3$
catalyst significantly enhances the capacity retention and coulombic efficiency. Specifically, B(C$_6$F$_5$)$_3$ enables the improved properties by forming stable solid-electrolyte interphase (SEI) layers and suppressing surface pulverization.$^{28}$ The addition of 5 mol% boron catalyst enables almost a twofold capacity retention at the 100th cycle and higher coulombic efficiencies.

Dargaville and his co-workers have utilized borane catalyst in silicon chemistry to prepare amphiphilic silicone architectures.$^{29}$ B(C$_6$F$_5$)$_3$-catalyzed condensation of alkoxysilanes and vinyl functionalized hydrosilanes to give silicones and alkane byproducts. The resulting pure silicones were coupled to thiol-terminated PEG oligomers using photogenerated radicals under anaerobic conditions provided thiol-ene coupling products. These products were much useful in cosmetics, paints, coatings and for the stabilization of bubbles in polyurethane foam structures.$^{30}$

\[ \text{Si} \equiv \text{O} \quad \text{Si} \equiv \text{O} \quad \text{Si} \equiv \text{O} \]

\[ + \quad \text{HS} \bigg\{ \text{O} \bigg\} \quad \text{n} \]

\[ \text{B(C}_6\text{F}_5\text{)}_3 \quad \text{DMPA} \]

\[ \text{Si} \equiv \text{O} \quad \text{Si} \equiv \text{O} \quad \text{Si} \equiv \text{O} \]

\[ \text{H} \quad \text{OEt} \quad \text{EtO} \]

\[ \text{O} \quad \text{Si} \equiv \text{O} \quad \text{Si} \equiv \text{O} \]

\[ \text{EtO} \quad \text{Si} \equiv \text{O} \quad \text{Si} \equiv \text{O} \]

\[ \text{Si} \equiv \text{O} \quad \text{Si} \equiv \text{O} \quad \text{Si} \equiv \text{O} \]

\[ \text{DMPA} = 2, 2\text{-dimethoxy-2-phenylacetophenone} \]

**Scheme 25**
3.2 REFERENCES:


Chapter-III, Section A


SYNTHESIS OF TRIARYL AND TRIHETEROARYL METHANES.

3.3 INTRODUCTION:

Friedel-Crafts alkylation of aromatic compounds is one of the most important C-C bond-forming reactions in organic chemistry,\(^1\) which has found significant applications in the synthesis of various biologically active compounds.\(^2\) Acid-catalyzed Friedel–Crafts alkylation of arenes with aromatic aldehydes has been known since 1886.\(^3\) Friedel-Crafts arylation reactions of carbonyl compounds,\(^4\) epoxides\(^5\) and electron-deficient olefins\(^6\) as substrates have been extensively studied. Triaryl- and triheteroarylmethanes have attracted much attention from all fields of chemists from last decade after discovery of triphenylmethyl radical by Gomberg in 1900.\(^7\) Many of these compounds have found widespread applications in synthetic, medicinal and industrial chemistry.\(^8\) The triarylmethyl derivatives are useful as protective groups\(^9\), photochromic agents\(^10\) and dyes.\(^11\) Ring hydroxylated triarylmethanes have been reported to exhibit antitumor and antioxidant activities.\(^12\) Also, bisheteroarylmethanes are of interest to the food industry as natural components of certain food and beverage items as well as flavor agents in coffee.\(^13\) Triarylmethanes and bis-heteroarylarylmethanes have been prepared by using Lewis acid or protic acid-catalyzed Friedel-Crafts arylation reactions of aldehydes with electron-rich arenes and heteroarenes.\(^14\) Triaryl methanes (TRAMs) including triheteroaryl methanes have attracted the attention of chemists because of the interesting properties associated with their derivatives. They have exhibited varied biological activities as antiviral, antitumor, antitubercular, antifungal and anti-inflammatory agents.\(^15\) Many of the important bisindolyl methanes and trisindolyl methanes (BIMs and TIMs) were widely isolated from various terrestrial and marine natural sources. These natural products have novel structures and exhibit a range of important biological activities.\(^16\) A number of methods were reported in the literature for the synthesis of trialkylmethanes with various electron rich arenes, most of which are multistep processes and require harsh reaction conditions with longer reaction timings.\(^14\) Some of the important previous approaches are discussed here.
3.4 PREVIOUS APPROACHES:

Vijay Nair’s approach:

Vijay Nair et al. prepared triaryl and triheteroaryl methanes using electron rich arenes (Indole, 1, 3, 5-trimethoxy benzene, 2-methyl furan etc) with various aromatic aldehydes under the influence of 1 mol% of AuCl₃ in acetonitrile solvent at rt for 12 h with 40-90% yield. An electron-rich arene, 1, 3, 5-trimethoxybenzene additionally required catalytic system of AuCl₃/AgOTf and a slightly elevated temperature (50 °C) to condense effectively with benzaldehyde. However, with a more activated electrophile (4-nitro benzaldehyde), the reaction took place at room temperature to afford the tris aryl adduct in good yield (Scheme 1).

\[
\text{Scheme 1}
\]
Kodomari’s approach:

Kodomari and his group have developed a method for the synthesis of triarylmethanes and 9, 10-diarylanthracenes by Friedel-crafts alkylation of electron rich arenes with aromatic aldehydes in presence of catalytic amount of silicagel supported Zinc bromide (ZnBr₂/SiO₂) and acetyl bromide in benzene medium at room temperature with moderate yields. Polymethylbenzene such as o- and m-xylene and 1, 2, 3-trimethylbenzene required a slightly elevated temperature (50 °C) to condense effectively with benzaldehyde. The ratio of formation of arene:aldehyde is changed from 4:1 to 1:3, disubstituted anthracenes were obtained in good yields. Veratrole (1 equiv) with benzaldehyde (3 equiv) and AcBr (4 equiv) in benzene was carried out in the presence of ZnBr₂/SiO₂ at room temperature for 4 h to give anthracene in 77% yield (scheme 2).

Scheme 2
Silveira’s approach:

Silveira and his co-workers have described a method for the synthesis of bis(indolyl)methanes through a reaction of indoles with various aromatic and aliphatic aldehydes in presence of catalytic amount of CeCl$_3$·7H$_2$O at 75 °C for 3 hours in glycerin, used as recyclable solvent (scheme 3).\textsuperscript{19}

\[
\text{Indole} + \text{Aldehyde} \rightarrow \text{Bis(indolyl)methane}
\]

\textbf{Scheme 3}

**Genovese approach:**

Salvatore Genovese \textit{et al} have prepared various triarylmethanes and triheteroarylmethanes with 2-methyl furan and anisole used as electron rich arenes in presence of Yb(OTf)$_3$ under solvent free conditions at room temperature for 3 hours with 70-90\% (scheme 4).\textsuperscript{20}

\[
\text{Furan} + \text{Aryl} \rightarrow \text{Triarylmethane}
\]

\textbf{Scheme 4}

**Cheng’s approach:**

Jin-Pei Cheng and his co-workers have described a method for the synthesis of bis(indolyl)methanes through the condensation of indole with aldehydes, ketones and
imines in presence of catalytic amount of Dy(OTf)₃ immobilized in ionic liquid at room temperature with 76-95% yield (scheme 5).²¹

Scheme 5
3.5 PRESENT WORK:

To our knowledge, only few reports regarding the synthesis of triaryl and triheteroaryl methanes in the literature was described.\textsuperscript{17-21} Reaction conditions employed in some of these methods involve expensive reagents, harsh conditions and lengthy reaction times. Hence, the development of new methods using mild Lewis acid catalyst in catalytic amounts is of practical importance. In continuation of our interest in Lewis acid catalyzed transformations herein, in the present work, we have described an efficient and mild Lewis acid-catalyzed method for the synthesis of triaryl and tri hetero arylmethanes with various electron rich arenes and variety of aromatic aldehydes in presence of tris(pentafluorophenyl)borane in dichloromethane at room temperature in good yields (Scheme 6).

\[
\text{Ar-CHO} + \text{R} \xrightarrow{\text{B(C6F5)3 (5 mol\%)} \text{CH}_2\text{Cl}_2, \text{rt, 0.5-3 h, 90\%}} \text{Ar} \text{R} \text{R}
\]

\(\text{R= Indole, 2-Me-Furan, 1, 3, 5-trimethoxy benzene}\)

Scheme 6

Initially, our attempts started from the treatment of commercially available 1, 3, 5-trimethoxybenzene (an electron rich arene) with 3, 4, 5-trifluorobenzaldehyde 1 (entry 1, table1) in CH\(_2\)Cl\(_2\) in presence of 5 mol\% tris(pentafluorophenyl) borane at room temperature and observed the formation of corresponding triaryl methane 1a in 82\% yield (scheme 7, entry 1, table 1). This process took 3 h before total conversion was observed by TLC. \(^1\text{H}\) NMR of compound 1a revealed the presence of resonance at 6.10 ppm as a singlet for four aromatic (\(-\text{CH=CH}\)) protons and triphenyl methyl (Ph\(_3\)CH) proton. Two more singlet peaks resonating at 3.79 ppm for 6H and 3.55 ppm for 12H clearly indicated the presence of six aromatic methoxy (OCH\(_3\)) protons. \(^{13}\text{C}\) NMR spectrum of 1a showed a peak at 36.4 ppm for triphenyl methyl (Ph\(_3\)CH) carbon indicated the formation of product. The product was further confirmed by its HRMS spectrum which showed [M+H]\(^+\) peak at 479.1675.
Later we treated 1, 3, 5-trimethoxybenzene with other aldehydes such as \( p \)-hydroxy bromo benzaldehyde 3 (entry 3, table1) and \( o \)-nitro benzaldehyde 4 (entry 4, table1) were also participated in the similar manner and yielded the corresponding
triaryl methane 3a and 4a in 78 and 91% yield respectively. All the products were fully characterized by IR, \(^1\)H NMR and \(^{13}\)C NMR spectroscopy and results are summarized in table 1.

**Table 1.** \(\text{B}(\text{C}_6\text{F}_3)_3\) catalyzed alkylation of 1, 3, 5- trimethoxy benzene with various aldehydes

<table>
<thead>
<tr>
<th>S.No</th>
<th>Aldehyde</th>
<th>Product</th>
<th>Time (h)</th>
<th>Yield(^a) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>\begin{align*} &amp; \text{CHO} \ F &amp; - &amp; F \ F &amp; - &amp; F \ \text{CHO} \end{align*} \quad \begin{align*} &amp; \text{F} \ &amp; - \ &amp; \text{F} \ &amp; - \ &amp; \text{F} \end{align*} \quad \begin{align*} &amp; \text{2, 4, 6 (OMe)}_3 \ &amp; \text{2} \end{align*}</td>
<td>3</td>
<td>82%</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>\begin{align*} &amp; \text{MeO} \ \text{CHO} \end{align*}</td>
<td>\begin{align*} &amp; \text{MeO} \ &amp; - \ &amp; \text{OH} \end{align*}</td>
<td>2.5</td>
<td>89%</td>
</tr>
<tr>
<td>3</td>
<td>\begin{align*} &amp; \text{Br} \ \text{CHO} \end{align*}</td>
<td>\begin{align*} &amp; \text{Br} \ &amp; - \ &amp; \text{NO}_2 \end{align*}</td>
<td>3</td>
<td>78%</td>
</tr>
<tr>
<td>4</td>
<td>\begin{align*} &amp; \text{CHO} \ \text{NO}_2 \end{align*}</td>
<td>\begin{align*} &amp; \text{NO}_2 \ &amp; - \ &amp; \text{OH} \end{align*}</td>
<td>3</td>
<td>91%</td>
</tr>
</tbody>
</table>

\(^a\) isolated yield
Our next focus of interest was to prepare triheteroaryl methanes by the condensation of various aromatic aldehydes with heteroarenes such as indole and 2-methyl-furan. Interestingly, these heteroarenes were actively participated in this transformation with high yields and in less reaction time. \( p \)-Nitrobenzaldehyde 5 was condensed with 2-methyl-furan (entry 1, table 2) in dichloromethane in the presence of (5 mol%) tris (pentafluorophenyl) borane at room temperature for 0.5 h to achieve the corresponding triheteroarylmethane 5a in 85% yield (scheme 9). \(^1\)H NMR of 5a revealed the presence of resonance at 5.37 ppm as a singlet for one proton corresponding to triheteroaryl methane (Ph\(_3\)CH) proton and resonance at 2.25 ppm as singlet for six aromatic methyl (Ar-C\(\text{H}_3\)) protons. \(^{13}\)C NMR spectrum showed a peak at 44.7 ppm for triheteroaryl methyl (Ar\(_3\)CH) carbon which suggested the formation of product 5a. It was further confirmed by its EI-MS spectrum which showed [M+Na]\(^+\) peak at m/z 297.3.

\[
\begin{align*}
\text{NO}_2 & \quad + \quad \text{CHO} \\
\text{B(C}_6\text{F}_5)_3 (5 \text{ mol\%)} & \quad \text{CH}_2\text{Cl}_2, \text{rt, 0.5 h, 85\%)} \\
\rightarrow & \quad \text{NO}_2 \\
& \quad \text{5} \\
& \quad \text{5a}
\end{align*}
\]

\textbf{Scheme 9}

This result encouraged us to explore other aldehydes and to our delight aldehyde 6 (entry 2, table 2) participated in this reaction to form the corresponding triarylmethane 6a with 2-methyl-furan in the presence of 5 mol\% of tris (pentafluorophenyl) borane at room temperature. The reaction proceeded smoothly in 1h and produced corresponding triaryl methane 6a in 92\% yield (scheme 10). \(^1\)H NMR of 6a revealed the presence of resonance at 5.52 ppm for one proton as a singlet corresponding to triheteroaryl methane (Ph\(_3\)CH) proton and resonance at 2.25 ppm as singlet for six aromatic methyl (Ar-C\(\text{H}_3\)) protons. \(^{13}\)C NMR spectrum of 6a showed a peak at 39.8 ppm for triheteroaryl methyl (Ar\(_3\)CH) carbon confirmed the formation of product.
Later another electron rich arene, indole was explored by reaction with 3, 4, 5-trifluoro benzaldehyde 7 (entry 3, table 2) in presence of 5 mol% of borane catalyst in dichloromethane at room temperature. The reaction proceeded smoothly in 30 min and provided the corresponding triheteroarylmethane 7a in 93% yield (scheme 10). $^1$H NMR spectra of compound 7a revealed the presence of resonance at 6.67 ppm as singlet for two protons represents aromatic (CH=CH) protons of indole and resonance at 5.82 ppm as a singlet for one proton corresponding to triheteroaryl methane (Ph$_3$CH) proton which suggested the formation of product 7a. It was further confirmed by its $^{13}$C NMR spectrum which showed a peak at 39.5 ppm for triheteroaryl methyl (Ar$_3$CH) carbon.

Similarly, the reaction between indole and benzaldehyde 8 (entry 3, table 2) has also participated well in this transformation in presence of 5 mol% of tris (pentafluorophenyl) borane in 30 min at room temperature and provided corresponding triheteroaryl methane 8a in 86% yield. The results are summarized in table 2.
In summary, we have demonstrated an efficient and mild lewis acid B(C₆F₅)₃-catalyzed synthesis of triaryl and triheteroaryl methanes by condensation of electron-rich arenes with various aldehydes at room temperature. The simple procedure, mild reaction conditions and high yields of the products makes this methodology attractive for applications in organic synthesis.
3.6 Experimental Section

Experimental procedure:

To a stirred solution of arene (1 mmol) in dichloromethane (10 mL), aromatic aldehyde (0.5 mmol) and 5 mol% of B(C₆F₅)₃ were added at room temperature and the reaction progress was monitored by TLC analysis. After completion of the reaction (0.5 h), solvent was evaporated under vacuum and residue was purified by column chromatography on silica gel using ethyl acetate and hexanes (10:90 to 15:85) as eluent to give triarylmethanes and triheteroarylmethanes in 93% yield.

2, 2'-(3, 4, 5-Trifluorophenyl) methylene) bis (1, 3, 5-trimethoxybenzene) (1a):

Nature of the compound : Yellow solid.
Melting point : 168-170 °C.
¹H NMR (300 MHz, CDCl₃) : δ 6.72-6.59 (m, 2H), 6.10 (s, 5H), 3.79 (s, 6H), 3.55 (s, 12H).
¹³C NMR (75 MHz, CDCl₃) : δ 159.5, 152.0, 151.8, 148.7, 148.6, 142.5, 112.1, 111.5, 111.2, 91.4, 55.8, 55.1, 36.4.
IR (KBr) : ν max 2934, 2838, 1593, 1225, 1124cm⁻¹.
HRMS-ESI (m/z) : calcd for C₂₅H₂₆F₆O₆ [M+H]: 479.1676, found: 479.1675.
2, 2’-((2, 5-Dimethoxyphenyl) methylene) bis (1, 3, 5-trimethoxybenzene) (2a):

![Chemical Structure of 2a](image)

**Nature of the compound**: white solid.

**Melting point**: 172-174 °C

**$^1$H NMR (300 MHz, CDCl$_3$)**: 6.68 (d, $J = 8.7$ Hz, 1H), 6.59 (dd, $J = 2.8$, 8.7 Hz, 1H), 6.52 (d, $J = 2.8$ Hz, 1H), 6.23 (s, 1H), 6.1 (s, 4H), 3.76 (s, 6H), 3.65 (s, 3H), 3.58 (s, 3H), 3.49 (s, 12H).

**$^{13}$C NMR (75 MHz, CDCl$_3$)**: 159.3, 158.6, 153.1, 152.2, 135.6, 116.4, 114.6, 110.6, 108.9, 91.9, 56.6, 56.2, 55.4, 55.0, 32.5.

**IR (KBr)**: $\nu_{\text{max}}$ 2938, 2931, 2832, 1594, 1223, 1122 cm$^{-1}$.

**HRMS-ESI (m/z)**: calcd for C$_{27}$H$_{33}$O$_8$ [M+H]$^+$: 485.217, found: 485.2169.

3-(bis (2, 4, 6-Trimethoxyphenyl) methyl)-4-bromophenol (3a):

![Chemical Structure of 3a](image)
Nature of the compound : White solid.
Melting point : 188-189 °C.
$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.15-7.05 (m, 2H), 6.65 (d, $J = 8.8$ Hz, 1H), 6.13 (s, 1H), 6.10 (s, 4H), 3.77 (s, 6H), 3.57 (s, 12H).
$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 159.6, 159.3, 154.7, 132.8, 129.1, 117.3, 111.4, 91.7, 56.0, 55.1, 34.0.
IR (KBr) : $\nu_{\text{max}}$ 2925, 2843, 1596, 1461, 1117 cm$^{-1}$.

2, 2'-(2-Nitrophenyl) methylene) bis (1, 3, 5-trimethoxybenzene) (4a):

Nature of the compound : Yellow solid.
Melting point : 202-205 °C.
$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.69 (d, $J = 7.7$ Hz, 1H), 7.33 (t, $J = 7.7$ Hz, 1H), 7.26-7.16 (m, 1H), 7.10 (d, $J = 7.7$ Hz, 1H), 6.84 (s, 1H), 6.08 (s, 4H), 3.76 (s, 6H), 3.51 (s, 12 H).
$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 159.5, 159.4, 149.5, 139.9, 131.3, 130.4, 125.1, 123.2, 123.0, 111.9, 91.6, 56.1, 55.0, 33.5.
IR (KBr) : $\nu_{\text{max}}$ 2924, 2849, 1596, 1151, 1119 cm$^{-1}$.
HRMS-ESI (m/z) : calcd for C$_{25}$H$_{28}$NO$_8$ [M+H]$^+$ : 470.1809, found: 470.1806.
5, 5'-((4-Nitrophenyl) methylene) bis (2-methylfuran) (5a):

![Chemical structure of 5a]

Nature of the compound : Yellow solid.
Melting point : 85-88 °C.

\[ ^1H \text{ NMR (200 MHz, CDCl}_3 \text{)} : \delta 8.17 (d, J = 8.7 \text{ Hz, 2H}), 7.38 (d, J = 8.7 \text{ Hz, 2H}), 5.90-5.85 (m, 4H), 5.37 (s, 1H), 2.25 (s, 6H). \]

\[ ^13C \text{ NMR (75 MHz, CDCl}_3 \text{)} : \delta 152.0, 150.0, 147.3, 129.2, 123.7, 108.7, 106.2, 44.7, 13.5. \]

IR (KBr) : \( \nu_{\text{max}} 3115, 2924, 2863, 2358, 1563, 1347, 790 \text{ cm}^{-1}. \)

3-(bis (5-Methylfuran-2-yl) methyl)-4-bromophenol (6a):

![Chemical structure of 6a]

Nature of the compound : White solid.
Melting point : 89-90 °C.

\[ ^1H \text{ NMR (300 MHz, CDCl}_3 \text{)} : \delta 7.24 (dd, J = 2.4, 8.5 \text{ Hz, 1H}), 7.19 (d, J = 8.5 \text{ Hz, 1H}), 6.69 (d, J = 8.5 \text{ Hz, 1H}), 5.93 (dd, J = 3.0, 14.5 \text{ Hz, 4H}), 5.57 (br, 1H), 5.52 (s, 1H), 2.25 (s, 6H). \]
$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 152.7, 152.0, 150.6, 132.4, 131.2, 128.0, 118.2, 112.8, 108.7, 106.2, 77.4, 76.9, 76.5, 39.8, 13.6

IR (KBr) : $\nu_{\text{max}}$ 3503, 2921, 2853, 1487, 1216, 782 cm$^{-1}$.

3, 3'-(3, 4, 5-Trifluorophenyl) methylene) bis (1H-indole) (7a):

Nature of the compound : White solid
Melting point : 92-94 °C
$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.97 (s, 2H), 7.44-7.29 (m, 4H), 7.28-7.13 (m, 2H), 7.11-6.88 (m, 4H), 6.67 (s, 2H), 5.82 (s, 1H)

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 136.6, 126.5, 123.4, 122.2, 119.6, 119.5, 118.1, 112.6, 112.3, 111.2, 39.5.

IR (KBr) : $\nu_{\text{max}}$ 3415, 1627, 1523, 1342, 1093, 750 cm$^{-1}$.

3, 3'-(Phenylmethylene) bis (1H-indole)(8b):

3, 3'-(Phenylmethylene) bis (1H-indole)(8b):
Nature of the compound : White amorphous solid.

Melting point : 87-88 °C

$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.81 (s, 2H), 7.42-7.10 (m, 11H), 6.99 (t, $J = 7.3$ Hz, 2H), 6.59 (s, 2H), 5.87 (s, 1H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 143.9, 136.5, 128.6, 128.1, 126.9, 126.0, 123.5, 121.8, 119.8, 119.6, 119.1, 110.9, 40.1.

IR (KBr) : $\nu_{\text{max}}$ 3412, 2922, 1453, 1122, 744 cm$^{-1}$.

ESI-MS : $m/z$ 321 [M-H]$^+$.
3.7 References:


3.9 INTRODUCTION:

Masking of hydroxyl functionalities early in a synthetic route with different protecting groups is often necessary to successfully perform subsequent multistep synthetic reactions. The selection of suitable protecting group has still got ambiguity in the field of synthetic organic chemistry, because of failures to fulfill many requirements. It must react selectively in good yields and give protected compounds which should be stable for next steps of the projected reactions. So one should consider, in detail, about all the reactants, reagents, reaction conditions and functionalities involved in the proposed synthetic scheme. The ability to easily install the desired protecting group, followed by facile removal at the end of synthesis is important for the selection of specific protecting group. Many protecting groups have been reported till date and more are being developed for this purpose.¹

In continuation of these efforts, we developed a facile method for the protection of alcohols as its trityl ethers. The triphenylmethyl (trityl) group is a most commonly used protecting group for alcohols especially in carbohydrate² and nucleoside chemistry.³ Tritylation of other heterocyclics such as Nitrogen⁴a and Sulfur⁴b is also known in literature. Trityl functionality represents an attractive protecting group, because of its stability towards neutral and basic conditions.⁵ Moreover; it is readily removed under mild acidic conditions⁶ to regenerate the alcohol. The advantage of suitably derivatizedtrityl moieties for the introduction of various functional features on synthetic DNA without affecting the genetic integrity of it becomes more attractive. Furthermore, additional chromophore in trityl group, along with increased lipophilicity helps in purification of intermediate. With these advantages, formation of trityl ethers is not always straightforward. Some procedures require extensive preparation of tritylating reagents and harsh conditions,⁷, ⁸ others require lengthy reaction times.⁹, ¹⁰
3.10 PREVIOUS APPROACHES:

Hanessian’s approach:

Hanessian and Staub have described a method for tritylation of various alcohols using $N$-triphenylmethylpyridiniumtetrafluoroborate (prepared from Trityl chloride and pyridine) in CC1$_4$ under reflux conditions for 3h to give corresponding tritylethers in 88% overall yield (Scheme 1).\(^7\)

![Scheme 1](image)

Noyori’s approach:

Noyori and Murata have described a method for tritylation of trimethylsilylated hydroxyl compounds with trimethyltrityloxysilane and 1 mol% of trimethylsilyltriflate in dichloromethane at 0 °C to achieve corresponding tritylated ethers in 90% yield (Scheme 2).\(^8\) The reaction timings varied from 30 min to 18 h depending upon the hydroxyl moities.

![Scheme 2](image)

Hernandez’s approach:

Hernandez et al.described tritylation of alcohol using 4- dimethylamino-$N$-triphenylmethylpyridinium chloride (which was derived from trityl chloride) in dichloromethane at 25 °C for 16 h to achieve corresponding trityl ethers in 65% yield (Scheme3).\(^9\)
Messager’s approach:

Messager et al. described a method for tritylation of primary and secondary alcohols using trityl chloride and DBU as a base in dichloromethane at room temperature for 2 days which gave corresponding trityl ethers in 90% yield (Scheme 4).  

Reddy’s approach:

Reddy et al. described solid phase tritylation of hydroxyl function of nucleoside bound to controlled pore glass (CPG) using dimethoxytrityl chloride in the presence of 2, 4, 6-collidine in dichloromethane to achieve corresponding trityl ether in 90% yield (Scheme 5).
Lundquist’s approach:

Lundquist and his coworkers have described silver triflate assisted method for trityl protection of alcohols in solution phase in presence of 2, 6-di-tert butylpyridine as a mild base with 70% yield (Scheme 6).\(^{12}\)

\[
\begin{array}{c}
\text{R-} \quad \text{Br} \\
\text{R-} \quad \text{AgOTf} \\
\text{CH}_2\text{Cl}_2, 0 \degree \text{C}, 1 \text{ h, 70%}
\end{array}
\]

Scheme 6

Kusumoto’s approach:

Kusumoto et al. have described a method for tritylation of alcohols using benzyl trityl ether as tritylating agent in presence of DDQ in dichloromethane and 4A° MS at 30-50 °C under anhydrous conditions for 36 h which gave corresponding trityl ethers in 90% yield (Scheme 7).\(^{13}\)
Iranpoor’s approach:

First generation:

Nasser Iranpoor and his co-workers have described a selective method for catalytic conversion of allylic and tertiary benzylic alcohols into their corresponding trityl ethers in presence of CAN (Ceric Ammonium Nitrate) under refluxed conditions for 2 h in both solvolytic and non solvolytic conditions in good yields (Scheme 9).\(^\text{14}\)

\[
\text{Scheme 8}
\]

Second generation:

Iranpoor group have described another method for tritylation of various alcohols to tritylethers in presence of FeCl\(_3\) under reflux conditions which gave poor to moderate yields (Scheme 9).\(^\text{15}\)

\[
\text{Scheme 9}
\]

Sarma’s approach:

Sarma and his group described tritylation of alcohols using \(p\) -methoxybenzyltrityl ether (\(p\)-MBTE) or prenyltrityl ether (PTE) as tritylating agent in presence of DDQ and Mn(OAc)\(_3\) at room temperature gave the protected alcohols in 65-85% yield (Scheme 11).\(^\text{16}\)
Most of these tritylating agents are commercially not available and have to be prepared from trityl chloride. To date, there are very limited examples known in literature describing protection of alcohols as trityl ethers with triphenylmethanol (as tritylating agent) in presence of an acid catalyst.\textsuperscript{14,15} Reaction conditions employed in some of these methods involve strong acidic conditions\textsuperscript{17} (H\textsubscript{2}SO\textsubscript{4}, FeCl\textsubscript{3}, etc.). Furthermore, these catalysts were studied using only a few examples and no systematic study on chemoselectivity has been carried out. Thus, development of a new Lewis acid for chemoselective protection of alcohols as trityl ethers under mild reaction conditions is of interest to synthetic organic chemists.
3.11 PRESENT WORK:

This section describes an efficient and mild acid-catalyzed protection of alcohols as trityl ethers using triphenylmethyl alcohol (trityl alcohol) in presence of tris(pentafluorophenyl) borane (3 mol%) in dichloromethane at room temperature which gave moderate to good yields (Scheme 11).

\[
\begin{array}{c}
\text{OH} \quad + \quad \text{Ph} \quad \text{OH} \\
\text{R} \quad \text{R}_1 \quad \text{Ph} \quad \text{Ph} \quad \text{B(C}_6\text{F}_5)_3 \quad (3 \text{ mol%}) \quad \text{Ph} \quad \text{Ph} \\
\text{CH}_2\text{Cl}_2, \text{rt, 3-8 h} \quad \text{O} \quad \text{OTr} \\
\text{R} = \text{alkyl, aryl; R}_1 = \text{H, alkyl}
\end{array}
\]

Scheme 11

Our attempts started with the treatment of 3-phenyl-1-propanol 1a, a commercially available starting material, with triphenylmethanol in presence of 3 mol \% B(C_6F_5)_3 in dichloromethane at room temperature. Reaction proceeded smoothly in 3 h and afforded the corresponding trityl ether 2a in 92\% isolated yield (Table 1, entry 1, scheme 12). \(^1\)HMR spectrum of 2a showed two multiplets resonating at \(\delta\) 7.5-7.41 for 6H and 7.35-7.06 for 14H which clearly indicated the formation of trityl product. Product was further confirmed by its mass spectrum which showed [M+H]' peak at \(m/z\) 379.5.

\[
\begin{array}{c}
\text{Ph} \quad \text{OH} \\
\text{1a} \quad \text{3 mol % B(C}_6\text{F}_5)_3 \\
\text{CH}_2\text{Cl}_2, \text{rt, 3h, 92 \%} \quad \text{Ph} \quad \text{OTr} \\
\text{2a}
\end{array}
\]

Scheme 12

This result prompted us to look for other alcohols which can participate in trityl ether formation with trityl alcohol in presence of tris(pentafluorophenyl)borane and we found that they participated well in this transformation and results are summarized in table 1. Accordingly, propargyl alcohol 1b (entry 2, Table 1, scheme 13) was used as alcohol component and found the product 2b was formed in 87\% yield. \(^1\)H NMR spectrum of compound 2b revealed peaks that resonates between \(\delta\)
7.55-7.10 as a multiplet for 15H clearly indicated the presence of trityl group and another singlet at δ 3.75 for 2H indicating presence of -CH₂O attached to triple bond of the product. This was further confirmed by its mass spectrum, which showed [M+H]⁺ peak at m/z 299.2.

![Scheme 13](image)

All primary alcohols 1a-1c were participated in tritylation reaction to yield corresponding trityl ethers 2a-2c in quantitative yields (Table1). Secondary benzyl alcohols 1d and 1e reacted slowly at room temperature, however, they reacted under refluxing conditions to provide the corresponding trityl ethers 2d and 2e in 48 and 56% yields, respectively (Scheme 14, entries 4 and 5). Bulkiness of three phenyl rings in trityl group creates steric hinderance and decreases reactivity of secondary alcohols towards tritylation while compared to primary alcohols.

![Scheme 14](image)

Chemoselectivity of this protocol is demonstrated by studying tritylation of a primary alcohol in presence of a secondary alcohol (entries 6 and 8). Scheme 15 clearly demonstrates the chemoselective protection of a primary benzylic alcohol in presence of a phenolic hydroxyl group. Compound 1f reacts smoothly in 4.5 h and to give the corresponding trityl ether 2f as a sole product.
### Table 1  B(C₆F₅)₃ catalyzed tritylation of alcohols

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time (h)</th>
<th>Product</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhCH₃OH</td>
<td>3</td>
<td>PhCOTr</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>CH₂CH₂OH</td>
<td>3.5</td>
<td>CH₂COTr</td>
<td>87</td>
</tr>
<tr>
<td>3</td>
<td>CH₂CH₂OH</td>
<td>4</td>
<td>CH₂COTr</td>
<td>93</td>
</tr>
<tr>
<td>4</td>
<td>PhCH₂OH</td>
<td>8</td>
<td>PhCOTr</td>
<td>48&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>PhCH₂CH=CH₂</td>
<td>8</td>
<td>PhCOTr</td>
<td>56&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>PhCH₃OH</td>
<td>4.5</td>
<td>PhCOTr</td>
<td>88</td>
</tr>
<tr>
<td>7</td>
<td>1g</td>
<td>4</td>
<td>2g</td>
<td>90</td>
</tr>
<tr>
<td>8</td>
<td>1h</td>
<td>4</td>
<td>2h</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>1i</td>
<td>4</td>
<td>2i</td>
<td>94</td>
</tr>
<tr>
<td>10</td>
<td>1j</td>
<td>4</td>
<td>2j</td>
<td>87</td>
</tr>
<tr>
<td>11</td>
<td>1k</td>
<td>3.5</td>
<td>2k</td>
<td>95</td>
</tr>
</tbody>
</table>

<sup>a</sup> Isolated yields after column chromatography.

<sup>b</sup> Yield from the reaction carried out at reflux.
\(^1\)HMR spectrum of 2f showed a broad singlet at \(\delta 5.25\) and its IR spectrum showed a peak at 3465 cm\(^{-1}\) indicating the presence of phenolic OH. Chemoselectivity was confirmed by its \(^1\)H NMR spectrum, which revealed a singlet at \(\delta 4.13\) for two protons (deshielding region) clearly indicating the protection at benzyl alcoholic function and not at phenolic function. Product was further confirmed by its mass spectrum which showed (M+Na\(^{+}\)) peak at \(m/z\) 389.1.

\[
\begin{align*}
\text{OH} & \quad \text{3 mol % B(C}_6\text{F}_3\text{)}_3 \\
\text{CH}_2\text{Cl}_2, 4.5\text{ h, rt} & \quad \rightarrow \\
\text{OH} & \quad \text{2f}
\end{align*}
\]

Scheme 15

Chemoselective tritylation was also performed with other substrates 1g to 1i which were selectively converted to trityl ethers 2g to 2i without effecting acid-labile acetonide, ketal and benzyl protecting groups (Table 1, entries 7-9). Similarly, reaction succeeded with alcohols 1j and 1k, keeping acid-sensitive tert-butylcarbamate (NBoc) protecting group intact (Table 1, entries 10 and 11, scheme 16).

\[
\begin{align*}
\text{N} & \quad \text{Boc} \\
\text{1j} & \quad \text{3 mol% B(C}_6\text{F}_3\text{)}_3 \\
\text{CH}_2\text{Cl}_2, 4\text{ h, rt, 87%} & \quad \rightarrow \\
\text{Boc} & \quad \text{2j}
\end{align*}
\]

Scheme 16

To check compatibility and to confirm the mildness of the reagent system, we studied protection of 1, 3-propanediol mono ether substrates 3a to 3h having a free hydroxyl group at one end and a hydroxyl-protecting group (particularly acid labile protecting groups) at the other end. These substrates underwent tritylation at free hydroxyl group without affecting protecting groups such as silyl (TBS, TBDPS), methoxy methyl (MOM), benzyl (Bn), Tosyl (Ts) and other groups. The results are summarized in Table 2 (entries 1–8).
Table 2  Tritylation of alcohols in the presence of other protecting groups

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Time(h)</th>
<th>Product</th>
<th>Yield(%)a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HO-OTHP</td>
<td>3</td>
<td>TrO-4a</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>HO-OTBDMS</td>
<td>3.5</td>
<td>TrO-4b</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>HO-OTBDPS</td>
<td>4</td>
<td>TrO-4c</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td>HO-OMOM</td>
<td>4</td>
<td>TrO-4d</td>
<td>85</td>
</tr>
<tr>
<td>5</td>
<td>HO-OPMB</td>
<td>4</td>
<td>TrO-4e</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>HO-OBn</td>
<td>3.5</td>
<td>TrO-4f</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>HO-OTr</td>
<td>4</td>
<td>TrO-4g</td>
<td>93</td>
</tr>
<tr>
<td>8</td>
<td>HO-OTS</td>
<td>4</td>
<td>TrO-4h</td>
<td>95</td>
</tr>
</tbody>
</table>

a Isolated yields after column chromatography.

Efficiency of other Lewis acids was also investigated for this transformation using 3-phenylpropanol as a model substrate. Treatment of 3-phenylpropanol with triphenylmethanol in presence of 3 mol% of BF₃.Et₂O led to a complex mixture. Other acid catalysts such as ZnCl₂, AlCl₃, p-TSA, and I₂ also participated in tritylation reaction and gave trityl ethers, results are summarized in Table 3 (entries 1–5). Among these catalysts, B(C₆F₅)₃ was found to be more effective in terms of yield, reaction profile and selectivity (Table 3, entry 6).

Deprotection of the trityl group, which is well known under acidic conditions, was also attempted using the same catalyst [B(C₆F₅)₃] in methanol but without success, even at refluxing temperature.
In conclusion, we have demonstrated an extremely facile and efficient method for protection of alcohols as trityl ethers in presence of 3 mol% of tris(pentafluorophenyl) borane. Using this procedure, primary alcohols were selectively protected as trityl ethers in presence of secondary alcohols under mild reaction conditions. Stability of acid-labile protecting groups is an added advantage of this method. In addition, the protocol offers an opportunity to install a trityl protecting group in presence of base-sensitive functionalities such as esters.
3.12 Experimental Section

Typical experimental procedure:

To a mixture of 3-phenyl-1-propanol 1a (1.0 mmol) and triphenylmethanol (1.5 mmol) in dichloromethane (5 mL), 3 mol% of B(C₆F₅)₃ was added and mixture was allowed to stir for 3h at room temperature. After completion of reaction (monitored by TLC), the mixture was diluted with dichloromethane (5 mL) and washed with water (1 x 5 mL) and then with brine (1 x 5 mL). Organic layer was separated and dried over Na₂SO₄ and evaporated in vacuo. Residue was purified by column chromatography on silica gel using ethyl acetate and hexanes (4:96) as eluent to give corresponding trityl ethers 2a in 92% yield.

SPECTRAL DATA

((3-Phenylpropoxy)-methanetrityl)tribenzene(2a).

Nature of the compound : White solid.
Melting point : 80-82 °C.

¹H NMR (200 MHz, CDCl₃) : δ 7.5-7.41 (m, 6H), 7.35-7.06 (m, 14H), 3.15 (t, J = 5.8 Hz, 2H), 2.77 (t, J = 7.3 Hz, 2H), 2.05-1.89 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) : δ 144.6, 142.3, 128.8, 128.6, 128.4, 127.9, 127.0, 125.8, 86.5, 62.9, 32.7, 31.9.

IR (KBr) : \( \nu_{\text{max}} \) 3018, 1215, 758 cm⁻¹.

Triphenyl (prop-2-ynyloxy) methane (2b).
Nature of the compound : white solid
Melting point : 111-113 °C
$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.55-7.10 (m, 15H), 3.75 (s, 2H), 2.30 (s, 1H).
$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 143.5, 128.7, 128.0, 127.4, 87.5, 80.6, 73.4, 52.9.
IR (KBr) : $v$ 3291, 3058, 1062, 760, 703 cm$^{-1}$.
EIMS (m/z) : 321.1 (M+Na)$^+$. 

((Cyclopropylmethoxy)methanetriyl)tribenzene (2c).

Nature of the compound : White solid.
Melting point : 82-84 °C.
$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.80-7.64 (m, 6H), 7.46-7.27 (m, 9H), 3.07 (d, $J$ = 6.6 Hz, 2H), 1.30-1.09 (m, 1H), 0.66-0.55 (m, 2H), 0.32-0.22 (m, 2H).
$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 144.6, 128.9, 128.1, 127.0, 86.3, 68.4, 11.1, 3.0
IR (KBr) : $v_{\text{max}}$ 1488, 1445, 1216, 1058, 759 cm$^{-1}$.

(1-Phenylethoxy)triphenylmethane (2d).

Nature of the compound : Colorless liquid.
$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.51-7.41 (m, 6H), 7.26-7.01 (m, 14H), 4.65 (q, 1H), 1.14 (d, $J$ = 6.2 Hz, 3H).
\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) : \(\delta 146.5, 145.2, 129.2, 128.0, 127.7, 127.0,
126.2, 125.7, 88.0, 77.6, 77.2, 76.8, 73.0,
26.0,\)

IR (KBr) : \(v_{\text{max}} 2985, 1741, 1242, 1047\) cm\(^{-1}\).

EIMS (m/z) : calcd for C\(_{27}\)H\(_{24}\)ONa: 387.1736; found, 387.1738 (M+Na)+.

((1-Phenyl-but-3-enyloxy) methanetriyl)tribenzene (2e).

Nature of the compound : Pale yellow liquid.

\(^1\)H NMR (300 MHz, CDCl\(_3\)) : \(\delta 7.49\) (d, \(J = 6.7\) Hz, 6H), 7.39-7.10 (m, 15H), 5.45-5.28 (m, 1H), 4.82 (d, \(J = 10.5\) Hz, 1H), 4.65 (d, \(J = 17.3\) Hz, 1H), 4.54 (dd, \(J = 8.3, 3.7\) Hz, 1H), 2.20-2.07 (m, 1H), 1.94-1.83 (m, 1H).

\(^{13}\)C NMR (75 MHz, CDCl\(_3\)) : \(\delta 145.0, 143.7, 134.1, 129.2, 128.1, 127.8,
127.7, 127.1, 126.8, 126.5, 111.2, 88.1,
76.4, 43.0,\)

IR (KBr) : \(v_{\text{max}} 3060, 3029, 1447, 1215, 1044, 916,
759\) cm\(^{-1}\)

EIMS (m/z) : 413.2 (M+Na)+.

3-(Trityloxymethyl) phenol (2f).

Nature of the compound : Pale yellow liquid.
Chapter III, section B

$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.56-7.45 (m, 6H), 7.38-7.1 (m, 10H), 6.95-6.85 (m, 2H), 6.7 (dd, $J$ = 7.0, 2.3 Hz, 1H), 5.25 (brs, 1H), 4.13 (s, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 155.7, 144.2, 141.2, 128.9, 128.1, 128.0, 127.4, 119.3, 114.9, 114.0, 87.2, 65.5, 65.2.

IR (KBr) : $\nu_{\text{max}}$ 3465, 2923, 1445, 1326, 1155, 1008, 761 cm$^{-1}$

EIMS ($m/z$) : 389.10 (M+Na)$^+$. 

(3a$R$, 5$R$, 6$S$, 6a$R$)-6-Methoxy-2, 2-dimethyl-5 (trityloxymethyl)tetrahydrofuro[2, 3-d][1, 3]dioxole (2g).

Nature of the compound : Pale yellow oil.

$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.50-7.41 (m, 6H), 7.34-7.17 (m, 9H), 5.85 (d, $J$ = 3.7 Hz, 1H), 4.54 (d, $J$ = 3.7 Hz, 1H), 4.38-4.29 (m, 1H), 3.79 (d, $J$ = 3.2 Hz, 1H), 3.46-3.21 (m, 2H), 3.33 (s, 3H), 1.52 (s, 3H), 1.32 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 144.1, 129.2, 128.8, 128.0, 127.6, 127.3, 127.1, 111.8, 105.1, 86.9, 84.0, 82.1, 79.4, 61.0, 58.1, 26.9, 26.4.

IR (KBr) : $\nu_{\text{max}}$ 3418, 1636, 1215, 757 cm$^{-1}$.

HRMS-ESI ($m/z$) : calcd for C$_{28}$H$_{30}$O$_5$Na: 469.1990; found, 469.1992. (M+Na)$^+$. 

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1-((3aR, 5R, 6S, 6aR)-6-(benzyloxy)-tetrahydro-2, 2-dimethylfuro [2, 3-d][1, 3]dioxol-5-yl)-2-(trityloxy)ethanol (2h).

Nature of the compound: white crystalline solid.

Melting point: 101-103 °C

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.45-7.38 (m, 6H), 7.33-7.15 (m, 14H), 5.84 (d, $J$ = 3.7 Hz, 1H), 4.54 (AB quartet, 2H), 4.50 (m, 1H), 4.28 (dd, $J$ = 3.0 Hz, 1H), 4.09 (q, 2H), 4.01 (d, $J$ = 3.0 Hz, 1H), 3.42 (dd, $J$ = 4.9 Hz, 1H), 3.22 (dd, $J$ = 3.2 Hz, 1H), 2.42 (brs, 1H), 1.47 (s, 3H), 1.29 (s, 3H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 144.0, 137.4, 128.9, 128.7, 128.2, 128.0, 127.3, 111.8, 105.3, 86.9, 82.6, 82.4, 79.7, 72.5, 68.5, 65.3, 60.6, 26.9, 26.5, 21.2, 14.4

IR (KBr): $\nu_{\text{max}}$ 2933, 1214, 1077, 763 cm$^{-1}$.

EIMS ($m/z$): calcd for C$_{35}$H$_{36}$ONa : 575.2432 (M+Na)$^+$. found: 575.2430

2-(2-(Benzyloxy)ethyl)-2-(2-(trityloxy)ethyl)-1, 3-dioxolane (2i).
Nature of the compound : Pale yellow liquid.

$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.49-7.14 (m, 20H), 4.48 (d, $J = 5.3$ Hz, 2H), 3.85-3.67 (m, 4H), 3.60-3.15 (td, $J = 7.3$, 6.5 Hz, 2H), 3.40 (t, $J = 7.3$ Hz, 2H), 2.71 (q, 2H), 1.96 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 144.5, 138.6, 128.8, 128.7, 128.5, 128.4, 127.9, 127.8, 127.7, 127.6, 127.1, 127.0, 109.6, 87.0, 73.2, 65.3, 64.0, 44.0, 37.9, 37.6

IR (KBr) : $\nu_{\text{max}}$ 2985, 1741, 1374, 1242, 1047, 937 cm$^{-1}$.

EIMS (m/z) : 517.2 (M+Na)$^+$. 

**tert-Butyl-3-(trityloxymethyl)-1H-indole-1-carboxylate(2j).**

Nature of the compound : Pale yellow liquid.

$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.56-7.06 (m, 20H), 4.24 (s, 2H), 1.68 (s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 150.0, 147.0, 144.3, 144.1, 135.7, 129.3, 27.9, 126.5, 124.9, 122.9, 119.8, 118.9, 87.2, 83.8, 58.8, 28.4.

IR (KBr) : $\nu$ 2972, 1731, 1450, 1359, 1152, 1087, 1039, 745 cm$^{-1}$.

EIMS (m/z) : 512.2 (M+Na)$^+$. 

**tert-Butyl (S)-1-(methoxycarbonyl)-2-(trityloxy)ethylcarbamate(2k).**
Nature of the compound : White sticky compound.

$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.5-7.1 (m, 15H), 5.39 (d, $J = 17.6$ Hz, 1H), 3.9 (m, 1H), 3.74 (s, 3H), 3.50 (dd, $J = 7.1$, 14.2 Hz, 1H), 3.37 (dd, $J = 7.1$, 14.2 Hz, 1H), 1.47 (s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 171.5, 155.5, 143.6, 86.7, 80.1, 64.1, 54.2, 52.5, 28.5.

IR (KBr) : $\nu_{\text{max}}$ 3495, 3094, 2958, 1794, 1556, 1210, 1110, 798 cm$^{-1}$.

EIMS ($m/z$) : 484.2 (M+Na)$^+$. 

3-(3-(1, 1-Diphenyl-ethoxy)propoxy)tetrahydro-2H-pyran (4a).

Nature of the compound : Pale yellow liquid.

$^1$H NMR (200 MHz, CDCl$_3$) : $\delta$ 7.45-7.20 (m, 15H), 4.59 (s, 1H), 4.0-3.39 (m, 6H), 1.99-1.64 (m, 8H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 144.6, 128.9, 127.9, 127.0, 98.9, 64.7, 62.3, 60.6, 30.8, 30.6, 25.7, 19.6.

IR (KBr) : $\nu$ 2924, 1447, 1213, 1018, 760 cm$^{-1}$.

ESI ($m/z$) : 425.2.

(3-(Trityloxy)propoxy)(tert-butyl)dimethylsilane (4b).
Nature of the compound: Colorless liquid

\(^1\)H NMR (200 MHz, CDCl_3): \(\delta\) 7.47-7.13 (m, 15H), 3.69 (t, \(J = 6.2\) Hz, 2H), 3.15 (t, \(J = 6.2\) Hz, 2H), 1.88-1.63 (m, 2H), 0.9 (s, 9H), 0.6 (s, 3H), 0.1 (s, 3H).

\(^{13}\)C NMR (75 MHz, CDCl_3): \(\delta\) 144.6, 128.9, 127.9, 127.0, 86.6, 60.5, 59.9, 33.6, 26.1, 18.5, -5.1

IR (KBr): \(v_{\text{max}}\) 3449, 2928, 1636, 1088, 836, 702 cm\(^{-1}\).

ESI (m/z): 455.2 (M+Na)^+.

*(3-(Trityloxy) tert-Butyldiphenylpropoxy)silane* *(4c).*

Nature of the compound: Pale yellow liquid.

\(^1\)H NMR (300 MHz, CDCl_3): \(\delta\) 8.05-7.88 (m, 4H), 7.82-7.50 (m, 21H), 4.19 (t, \(J = 6.6\) Hz, 2H), 3.58 (t, \(J = 6.6\) Hz, 2H), 2.30-2.16 (m, 2H), 1.33 (s, 9H).

\(^{13}\)C NMR (75 MHz, CDCl_3): \(\delta\) 144.6, 135.7, 134.1, 129.6, 128.9, 128.5, 127.97, 127.91, 127.7, 127.0, 86.6, 61.1, 59.6, 33.3, 27.0, 19.3.

IR (KBr): \(v_{\text{max}}\) 2925, 1644, 1218, 1101, 767 cm\(^{-1}\).

HRMS-ESI: calcd for C_{38}H_{40}O_2SiNa : 579.2672, found: 579.2671 (M+Na)^+.

*(3-(Methoxymethoxy)propoxy)triphenylmethane* *(4d).*
Nature of the compound : Pale yellow liquid.

$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.49-7.20 (m, 15H), 4.60 (s, 2H), 3.70 (t, $J = 6.0$ Hz, 2H), 3.31 (s, 3H), 3.20 (t, $J = 6.0$ Hz, 2H), 1.98-1.87 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 144.5, 128.9, 128.1, 127.9, 127.4, 127.0, 96.6, 86.6, 65.3, 60.7, 55.3, 30.6

IR (KBr) : $\nu_{\text{max}}$ 3019, 1215, 1042, 762 cm$^{-1}$.

EIMS (m/z) : calcd for C$_{24}$H$_{26}$O$_3$Na : 385.1778, found: 385.1775 (M+Na)$^+$. 

1-Methoxy-4-((3-(trityloxy)propoxy)methyl) benzene(4e).

Nature of the compound : Pale yellow liquid.

$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.44 (d, $J = 6.7$ Hz, 6H), 7.31-7.11 (m, 11H), 6.83 (d, $J = 8.0$ Hz, 2H), 4.37 (s, 2H), 3.77 (t, $J = 6.7$ Hz, 2H), 3.15 (t, $J = 6.7$ Hz, 2H), 2.04-1.78 (m, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 159.0, 144.3, 129.1, 128.6, 127.6, 127.2, 126.8, 113.6, 86.3, 72.5, 67.2, 60.4, 55.2, 30.4.

IR (KBr) : $\nu_{\text{max}}$ 2987, 2934, 2361, 1216, 1077, 1025, 755, 702 cm$^{-1}$.

EIMS (m/z) : 461.2 (M+Na)$^+$. 

128
3-(Benzyloxy)propoxy)methanetriyl)-tribenzene (4f).

![4f]

Nature of the compound : Pale yellow liquid.

$^1$H NMR (300 MHz, CDCl$_3$) : \(\delta 7.42\text{-}7.36 \text{ (m, 6H), 7.31\text{-}7.14 \text{ (m, 14H), 4.46 \text{ (s, 2H), 3.61 \text{ (t, } J = 6.7 \text{ Hz, 2H), 3.18 \text{ (t, } J = 6.7 \text{ Hz, 2H), 1.94\text{-}1.84 \text{ (m, 2H).}})}\)

$^{13}$C NMR (75 MHz, CDCl$_3$) : \(\delta 144.3, 138.5, 128.6, 128.3, 127.8, 127.6, 126.8, 86.4, 72.8, 67.5, 60.4, 30.4.\)

IR (KBr) : \(v_{\text{max}} 3020, 1215, 758, 670 \text{ cm}^{-1}.\)

EIMS \((m/z)\) : 431.1 (M+Na)$^+$.  

1, 3-bis(Trityloxy)propane (4g).

![4g]

Nature of the compound : White solid.

Melting point : 168-170 °C.

$^1$H NMR (200 MHz, CDCl$_3$) : \(\delta 7.42\text{-}7.28 \text{ (m, 12H), 7.27\text{-}7.10 \text{ (m, 18H), 3.23 \text{ (t, } J = 5.8 \text{ Hz, 4H), 1.98\text{-}1.80 \text{ (m, 2H).}})}\)

$^{13}$C NMR (75 MHz, CDCl$_3$) : \(\delta 144.5, 128.9, 127.9, 126.9, 86.6, 60.6, 30.7.\)

IR (KBr) : \(v_{\text{max}} 2926, 1489, 1446, 1217, 1081, 753 \text{ cm}^{-1}.\)

EIMS \((m/z)\) : 583.2 (M+Na)$^+$.  

129
3-(Trityloxy)-propyl-4-methylbenzene-sulfonate(4h).

Nature of the compound : Pale yellow solid
Melting point : 96-98 °C

$^1$H NMR (200 MHz, CDCl$_3$) : δ 7.75 (d, $J = 8.3$ Hz, 2H), 7.38-7.20 (m, 17H), 4.21 (t, $J = 6.7$ Hz, 2H), 3.12 (t, $J = 6.0$ Hz, 2H), 2.43 (s, 3H), 1.90 (q, $J = 6.7$, 6.0 Hz, 2H).

$^{13}$C NMR (75 MHz, CDCl$_3$) : δ 144.8, 144.1, 133.1, 129.9, 128.7, 127.0, 127.9, 127.1, 86.7, 68.1, 59.3, 29.7, 21.8.

IR (KBr) : $\nu_{\text{max}}$ 3058, 3027, 2957, 1447, 1361, 1178, 1095, 1068, 840, 860, 752, 704, 664 cm$^{-1}$.

EIMS (m/z) : 495.1 (M+Na)$^+$.
3.13 References:

    c) Robertson, J.; Stafford, P.M. Carbohydrates. 2003, 9-68.


LIST OF PUBLICATIONS:


4. Enantioselective synthesis of the C5-C23 segment of biselyngbyaside. S.Chandrasekhar, **G. Rajesh**. (To be communicated).