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Titanium tetrachloride catalyzed cyanation of benzylic chlorides with trimethylsilyl cyanide and mechanistic and synthetic studies on substituted tetraphenylethanes

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Titanium Tetrachloride Catalyzed Cyanation of Benzylic Chlorides With Trimethylsilyl Cyanide And Mechanistic And Synthetic Studies On Substituted Tetraphenylethanes

by

Shiming Wo

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Abstract

Titanium Tetrachloride Catalyzed Cyanation of Benzylic Chlorides with Trimethylsilyl Cyanide and Mechanistic and Synthetic Studies on Substituted Tetraphenylethanes

by

Shiming Wo

Advisor: Herman E. Zieger

Six sterically hindered benzylic chlorides have been substituted with cyano groups in excellent yields with trimethylsilyl cyanide and titanium tetrachloride in methylene chloride. Both monochloro substrates such as diphenylmethyl chloride and triphenylmethyl chloride and dichloro substrates such as dichlorodiphenylmethane and sym-tetraphenylethylene dichloride were studied. Because isonitriles are plausible reaction intermediates, the isomerization of trityl isonitrile by titanium tetrachloride and by trityl tetrafluoroborate was studied at 0 °C and -78 °C. Both reagents catalyze conversion to triphenylacetonitrile at 0 °C while only trityl tetrafluoroborate is effective at -78 °C. It was also found that trityl tetrafluoroborate reacts with trimethylsilyl cyanide in the absence of titanium tetrachloride to give triphenylacetonitrile in 96% yield.

A first example of a long-lived substituted tetraphenylethyl cation: 2-cyano-1,1,2,2-tetraphenylethyl cation (**18**) has been synthesized from the reaction of 3-chloro-2,2,3,3-tetraphenylpropanenitrile (**4**) with silver salts as well as with $SbCl_5$. It has been shown that cation **18** is stable at - 75 °C and starts to decompose at a temperature between - 55 °C and - 35 °C. It was also found that cation **18** generated with $AlCl_3$ undergoes reaction intramolecularly to give 9-(cyanodiphenylmethyl)fluorene. The solvolysis of sym-tetraphenylethylene dichloride with CF_3CO_2Ag was studied. In the presence of phenol, the reaction gave a cyclic ortho ester **31**. Similar results were obtained with allyl alcohol and 2-propanol. In the presence of methanol, however, the reaction afforded a sterically hindered ketal, benzopinacolone dimethyl ketal (**39**), which could not be synthesized directly from benzopinacolone. Finally, the reactions of cation **18** and ketal **39** with organosilane reagents and aromatic substrates were carried out and the results are discussed.

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I wish to dedicate this thesis to my wife, Xiaoxin, without whose love and confidence the road to success would have been very difficult.

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INTRODUCTION

I. Cyanation of Tertiary Alkyl Halides With Trimethylsilyl Cyanide.

Cyano groups are synthetically useful because they provide easy access to a host of other functional groups.[1] Besides dehydration of amides or aldoximes,[1] nitriles can be prepared by such procedures as addition of HCN or Et_2AlCN to Michael acceptors,[2] alkylation of deprotonated nitriles[3] or substitution of alkyl halides and tosylates by sodium or potassium cyanide.[1,4] In the last case, the ambident cyanide ions[5] undergo S_N2 reactions preferentially at carbon in accord with the Kornblum rule[6] and the HSAB principle.[7] Unfortunately, the yields are acceptable only for primary and certain secondary alkyl halides. Tertiary derivatives fail because attempted S_N2 reactions at a tertiary carbon atom generally undergo elimination. Switching to S_N1 conditions is of no help, since alkylation then occurs at nitrogen with formation of tertiary amines or amides (Ritter reaction).[8]

Trimethylsilyl cyanide (TMSCN)[9] has been developed into a versatile reagent to introduce cyano groups into organic molecules. It reacts readily with a variety of functional groups such as aldehydes,[10] ketones,[10] acid chlorides,[11] expoxides,[12] isocyanates,[13] sulfenyl chlorides,[14] N-halogen compounds,[15] carbodiimides[16], acetals and ketals.[17] Reetz and his co-workers have shown that tertiary alkyl chlorides react with TMSCN when catalyzed by $SnCl_4$ to provide the cyano compounds in good yields.[18] Based on fifteen tertiary alkyl chlorides which were studied, it was found that open chain tertiary alkyl

chlorides devoid of additional functional groups are readily cyanated. However, compounds containing electron withdrawing groups such as a trichloromethyl moiety or an ester group near the reaction center remain inert, presumably because S_N1 activity is drastically reduced. In the case of a dichloride having two tertiary centers, 2,5-dichloro-2,5-dimethylhexane for example, the corresponding dicyano derivative was not formed to any appreciable extent. It was also found that Lewis acids such as $ZnCl_2$, $ZnBr_2$, ZnI_2, $BiCl_3$, $AlCl_3$, $FeCl_3$ and $TiCl_4$ were either unreactive or caused partial decomposition. In sharp contrast, $SnCl_4$ was found to be effective.

Two alternative mechanisms have been considered in the literature as possible explanations for the formation of nitriles from tertiary alkyl chlorides. In Mechanism 1 the fact that TMSCN is in equilibrium with a small amount of trimethylsilyl isocyanide[19] suggests that the isonitrile could undergo attack by a tertiary carbocation on carbon to form a nitrilium ion intermediate. A similar hypothesis has been invoked to explain the formation of acyl cyanides in the reaction of acid chlorides with trimethylsilyl cyanide.[11c] That nitrilium ion intermediate could break down to give the observed products.

Mechanism 1

i $(CH_3)_3Si-C\equiv N \rightleftharpoons (CH_3)_3Si-\overset{\oplus}{N}\equiv\overset{\ominus}{C}:$

ii $R_3CCl + SnCl_4 \rightleftharpoons R_3C^+SnCl_5^-$

iii $R_3C^+SnCl_5^- + (CH_3)_3Si-\overset{\oplus}{N}\equiv\overset{\ominus}{C}: \rightleftharpoons R_3C-C\equiv\overset{\oplus}{N}-Si(CH_3)_3SnCl_5^-$

iv $R_3C-C\equiv\overset{\oplus}{N}-Si(CH_3)_3SnCl_5^- \longrightarrow R_3C-C\equiv N + (CH_3)_3SiCl + SnCl_4$

In Mechanism 2 the tertiary carbocation intermediate adds to the predominant form of TMSCN at nitrogen forming a nitrilium ion isomeric with that formed in Mechanism 1. This nitrilium ion breaks down to produce the isonitrile of the starting halide. This isonitrile can react with the tertiary carbocation to form a new nitrilium ion. In the final step, dealkylation affords the nitrile. Nitrilium ions are known to be involved as intermediates or stable salts in other processes.[20] Fragmentation to nitrile has been observed in a number of cases, where the more stable carbocation is split off preferentially.[20]

Mechanism 2

i $R_3CCl + SnCl_4 \rightleftharpoons R_3C^+SnCl_5^-$

ii $R_3C^+SnCl_5^- + (CH_3)_3Si-C\equiv N \rightleftharpoons R_3C-\overset{\oplus}{N}\equiv C-Si(CH_3)_3SnCl_5^-$

iii $R_3C-\overset{\oplus}{N}\equiv C-Si(CH_3)_3SnCl_5^- \rightleftharpoons R_3C-\overset{\oplus}{N}\equiv\overset{\ominus}{C}: + (CH_3)_3SiCl + SnCl_4$ (isonitrile)

iv $R_3C^+SnCl_5^- + R_3C-\overset{\oplus}{N}\equiv\overset{\ominus}{C}: \rightleftharpoons R_3C-C\equiv\overset{\oplus}{N}-CR_3SnCl_5^-$

v $R_3C-C\equiv\overset{\oplus}{N}-CR_3SnCl_5^- \rightleftharpoons R_3C-C\equiv N + R_3C^+SnCl_5^-$

It was found that if the cyanation reaction were run in dichloroethane instead of methylene chloride and the reaction was quenched after two or three half-lives, the isonitrile intermediate could be isolated together with the nitrile. This strongly supports Mechanism 2 although it does not exclude Mechanism 1. It should be noted that direct experimental evidence for the isomerization of isonitrile to nitrile (step iv and v) in Mechanism 2 has not been obtained.

Lewis acid catalyzed isomerization of isonitrile to nitrile has been

reported in the literature.[21] It was found that BF_3 and $SnCl_4$ react with tertiary alkyl isonitrile to give the corresponding nitrile as the major product. Lewis acids such as $AlCl_3$ and $TiCl_4$, on the other hand, are reported to form irreversible complexes with alkyl isonitrile and not to induce the isomerization. The striking difference between $SnCl_4$ and $TiCl_4$ as a catalyst in the reaction of alkyl halides with TMSCN can be illustrated in the case of 1-adamantyl chloride. It was reported that 1-adamantyl chloride reacted with TMSCN to give 1-adamantyl nitrile if $SnCl_4$ was used,[22] while another report claims that $TiCl_4$ catalyzed the same reaction to afford 1-adamantyl isonitrile.[23] The different outcomes of these two reactions can be understood if one assumes that both reactions follow mechanism 2 and $SnCl_4$ is capable of isomerizing the isonitrile intermediate to nitrile, while $TiCl_4$ isn't, and therefore isonitrile is isolated.

II. Benzylic Carbocations.

Carbocations are a class of reactive intermediates of fundamental importance in organic chemistry. They are involved as reaction intermediates in numerous substitution, elimination, addition and rearrangement reactions. As such, these intermediates have continued to hold the interest of organic chemists since Hughes and Ingold first formalized the S_N1 concept.[24] A large number of carbocations has been generated and features leading to stability and instability have been the topic of a wide range of studies.

Benzylic carbocations are considered as stable carbocations when compared with alkyl carbocations. The size of the phenyl ring coupled with its ability to delocalize charge by a resonance mechanism, primarily to its ortho and para positions, makes it an extremely efficient group for the stabilization of

a carbocation. Table 1 summarizes the stabilitity and synthesis of some simple benzylic cations.

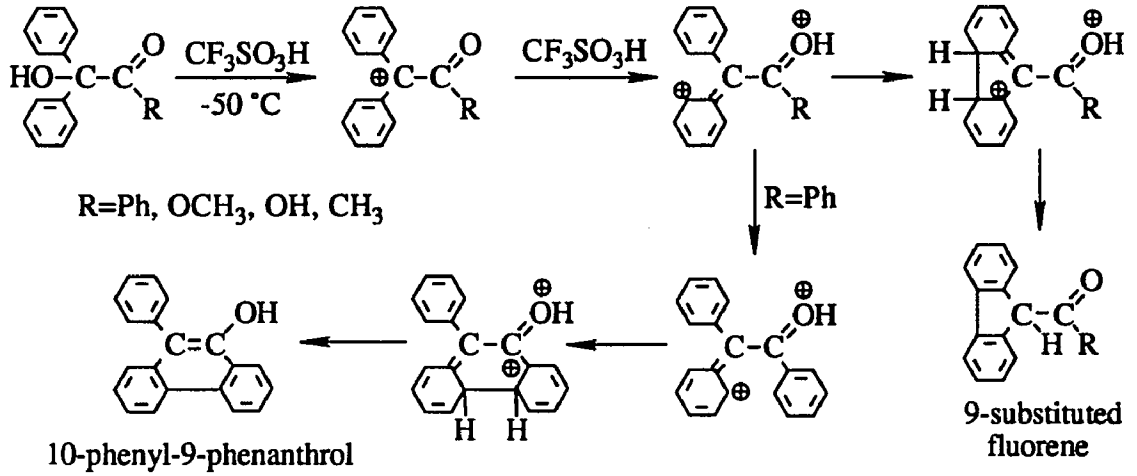
Table 1. Synthesis and Stability of Benzylic Cations

Benzylic Cation	Precursor & Synthesis	Stability
Benzyl	$PhCH_2OH + FSO_3H\text{-}SbF_5$ $PhC(CH_3)OH + FSO_3H\text{-}SbF_5$	Unstable at -60 °C Stable at -60 °C
Diphenylmethyl	$Ph_2CHCl + SbCl_5$	Stable at RT
Triphenylmethyl	$Ph_3CCl + SbCl_5$	Stable at RT
1,1,2,2-tetraphenylethyl	Tetraphenylethylene + $FSO_3H\text{-}SbF_5$	Stable at -60 °C
Pentaphenylethyl	$Ph_3C^+BF_4^-$ + Ph_2C:	Unstable at -60 °C

The benzyl cation has been kinetically established but has not been isolated as a stable intermediate.[25] The pK_{R+} value for the formation of benzyl cation in 50:50 (v:v) trifluoroethanol/water has been measured and was found to be less than -20.[26] Secondary benzyl cations, 1-phenylethyl cation for example, were found to be unstable even in $FSO_3H\text{-}SbF_5$ at -60 °C.[27] However, tertiary benzyl cations such as dimethyl benzyl cation have been generated and characterized.[28]

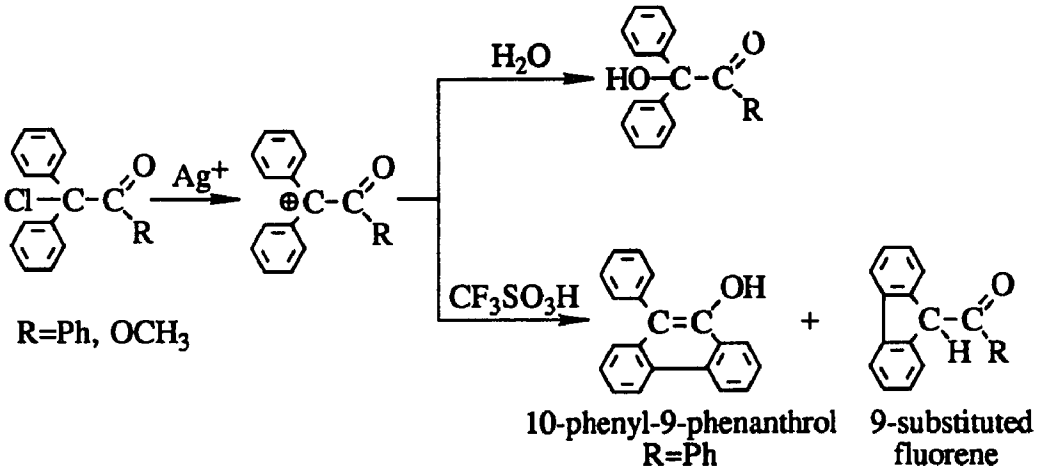
Also, diphenylmethyl cation is a well recognized species in solution and can even be isolated as a stable, although highly reactive, crystalline salt.[29] Diarylmethyl cations have been extensively studied by ultraviolet

spectroscopy[30] and by proton NMR spectroscopy.[27] The pK_{R+} value for benzhydryl cation was determined to be -11.7 in 50:50 (v:v) trifluoroethanol/water,[26] and -13.3 in sulphuric acid.[31] Recently, substituted diphenylmethyl cations have been studied.[32,33] It was found that diphenylmethanol bearing a carbonyl group such as a benzoyl, acetyl, methoxy carbonyl, or carboxyl group gave 9-substituted fluorenes in high yield in the presence of CF_3SO_3H at -50 °C. In the case of the benzoyl substituent, 10-phenyl-9-phenanthrol was formed together with the fluorene (Scheme 1).



Scheme 1

The diphenylmethyl cations substituted with electron withdrawing ketone, ester, or cyano groups were shown to be stable species by silver ion assisted ionization of the corresponding diphenylmethyl chlorides. The reaction of the diphenylmethyl cations bearing ketone and ester groups to give the fluorenes and phenylphenanthrol requires the presence of a strong acid (Scheme 2). It was shown that the formation of fluorenes and 10-phenyl-9-phenanthrol is the result of the intermediacy of carbodications with adjacent carbenium centers.



Scheme 2

The conjugate carbenium centers of the carbodications are significantly stabilized by delocalization of the positive charge over the aromatic rings as shown in Scheme 1. NMR spectroscopic studies demonstrate the existence of such carbodications. The diphenylmethyl, cyanodiphenylmethyl and α-trifluoromethyldiphenylmethyl cations all undergo Friedel-Crafts reactions with benzene to give triphenylmethane, triphenylacetonitrile and α-trifluoromethyltriphenylmethane, respectively.[33,34,35]

The triphenylmethyl cation is stable enough to be isolated as a triphenylmethyl perchlorate at ambient temperature.[36] The x-ray crystal structure of triphenylmethyl cation has been determined. Temperature dependent NMR spectra of trityl cation have also been studied.[37] The pK_{R+} value was measured and found to be -6.65.[38] It is a general phenomenon that benzene and similar aromatic compounds may be readily alkylated with an alkyl halide under Friedel-Crafts conditions. It is however, a curious fact that tetraphenylmethane can not be prepared by such direct alkylation procedures.

Triphenylmethyl chloride fails to alkylate benzene as do similar systems which presumably produce an intermediate triphenylmethyl cation. It was found that the reason that tetraphenylmethane was not obtained is due to the fast dephenylation of tetraphenylmethane to give triphenylmethyl cation under the reaction conditions.[39]

It has been reported that 1,1,2,2-tetraphenylethyl cation can be generated from 1,1,2,2-tetraphenylethanol or tetraphenylethylene in FSO_3H-SbF_5 at -60 °C and has been studied by proton NMR spectroscopy.[27] Tetraarylethylene dications are discrete dications stabilized by delocalization of the substantial positive charge over the adjacent aromatic rings. Tetraphenylethylene dication is one of the most well-known dications and it can be observed by NMR spectroscopy at low temperature, while at elevated temperature this dication yields 9,10-diphenylphenanthrene.[40,41,42,43]

The existence of pentaphenylethyl cation has never been directly proven. The main difficulty appears to be the lack of availability of pentaphenylethane derivatives as precursors to this cation. The only known pentaphenylethyl derivative is the parent hydrocarbon pentaphenylethane which can be prepared from the coupling reaction of triphenylmethylmagnesium bromide with diphenylmethyl bromide.[44a] Attempts to synthesize pentaphenylethyl cation directly from pentaphenylethane with SbF_5 were shown to give tetraphenylethylene.[44b] Pentaphenylethyl carbanion was shown to be stable at -78 °C and upon quenching with MeOD, it gave deuterio pentaphenylethane.[44c] It has been found that the reaction of trityl cation with diphenyldiazomethane gave tetraphenylethylene.[45] The reaction may have involved the pentaphenylethyl cation as an intermediate, which has been confirmed recently

by Olah and his co-workers who repeated the reaction with ^{13}C labeled diphenyldiazomethane and deuterium labeled trityl cation.[46] However, no stable, long-lived pentaphenylethyl cation was observed by NMR under these conditions. A search of the literature reveals that pentaphenylethanol is unknown. Attempt to make it by the reaction of trityl Grignard reagent with benzophenone led to *p*-benzhydryltriphenylmethanol.[47] Treatment of benzopinacolone with phenylmagnesium bromide gave *o*-biphenyl triphenylmethyl ketone by 1,4-addition of the Grignard reagent into the phenyl ring.[48] Halogenation of pentaphenylethane with bromine does not appear to give the bromopentaphenylethane.[49] Instead, bromotriphenylmethane and dibromodiphenylmethane were obtained. Chlorination gave the same results. It is believed that the reaction involved the intermediacy of pentaphenylethyl radical which combines with the bromine radical to give the bromopentaphenylethane. Unfortunately, the bromopentaphenylethane is not stable under the reaction conditions and fragments to trityl radical and bromodiphenylmethyl radical.

Functional groups directly attached to the cationic center of carbocations have important impact on the stability of the carbocations. Substituents such as an alkoxyl group or a halogen atom generally stabilize carbocations.[50] The cyano group is generally considered to be electron withdrawing. This is borne out by σ_p and σ^+ values (0.659, 0.660 respectively) which indicate the cyano group is even more electron withdrawing than the CF_3 group (σ_p=0.569, σ^+=0.54). Despite this fact, a number of cations have been generated which have the cyano group directly attached to the cationic center.[51] Such cations

form, in certain instances, at rates that exceed expectations based on the electron withdrawing properties of the cyano group. Thus stabilities of α-cyano cations generally exceed those of α-trifluoromethyl cations. A number of rate,[51] NMR[35b,c,51e] and computational[52] studies point to mesomeric stabilization of such cations, where charge is further delocalized onto the nitrogen atom of the cyano group. The existence of this mesomeric stabilization depends on the intrinsic demand for stabilization in the specific α-cyano cations.

Pentaphenylethane in its solid state exhibits an abnormal ethane bond length of 1.606 Å along with deformation of several bond angles.[53a] The central ethane bond length in hexaphenylethane has been the subject of many theoretical calculations and it was calculated to be 1.636-1.639 Å.[53b,c,d,e]

STATEMENT OF PROBLEM

For many years organic chemists have tried in vain to synthesized simple derivatives of pentaphenylethane. During the past five years we have reinvestigated earlier attempts incorporating more modern reagents in an effort to prepare such compounds as methoxypentaphenylethane or cyanopentaphenylethane. One idea we had was to prepare the pentaphenylethyl cation and study its reactions with aromatic substrates in an effort to learn whether hexaarylethanes could be obtained by a classical electrophilic aromatic substitution. It also seemed plausible to expect that if the pentaphenylethyl cation could be synthesized, its reaction with vinyltrimethylsilane might produce the vinylpentaphenylethane (3,3,4,4,4-pentaphenyl-1-butene), and then a Diels-Alder cycloaddition could permit construction of a sixth aromatic ring.

A search of the literature showed that early claims of the synthesis of pentaphenylethanol from the addition of phenylmagnesiumiodide to benzopinacolone by Schmidlin and Wohl were spurious.[48a] Mosher and Huber showed that the presumed 'pentaphenylethanol' actually was *o*-biphenyl triphenylmethyl ketone.[48b] Attempts to synthesize pentaphenylethanol from the reaction of trityllithium with benzophenone led to *p*-benzhydryltriphenylmethanol.[47]

This thesis research began with the studies of Grignard reactions on cyclohexyl trityl ketone, dicyclohexyl ketone and tetracyclohexylethanone in an effort to prepare precursors to pentaphenylethanol which possess the proper carbon skeleton such that dehydrogenation could yield the target molecule. Although a number of significant results were obtained and they are described

in the Miscellaneous Reactions, this approach toward the synthesis of pentaphenylethane derivatives was temporarily abandoned since greater progress was being made starting from *sym*-tetraphenylethylene dichloride.

In this plan of attack, the central idea is to study the reaction of substituted tetraphenylethyl cations with aromatic substrates as well as organosilane reagents. A search of the literature showed that substituted tetraphenylethyl cations have not yet been explored. This is probably due to the lack of appropriate cation precursors.

Thus, the first objective was to prepare the cation precursors from the readily available *sym*-tetraphenylethylene dichloride. A second goal was to study the synthesis and the stability of these cations. The third question was whether these cations would react with organosilane reagents such as vinyltrimethylsilane to yield a vinylated product which could be elaborated into a pentaphenylethane derivative by a Diels-Alder cycloaddition followed by a dehydrogenation. Finally, we planned to investigate whether these cations would undergo Friedel-Crafts reactions with aromatic substrates to produce pentaphenylethane derivatives. The result of this study would shed light on the question of whether or not hexaphenylethane could be synthesized from the reaction of pentaphenylethyl cation with aromatic substrates.

In the course of preparing substituted tetraphenylethyl cation precursors from *sym*-tetraphenylethylene dichloride, it became clear that tetraphenylsuccinonitrile is an inordinately stable, easily synthesized substrate. Since it can be formed by the α-coupling of cyanodiphenylmethyl radical, as well as by the route discovered during the work described below, it seemed that a wholly new, third approach toward the synthesis of hexaphenylethane was possible. In brief this plan envisions DIBAL-H reduction of the

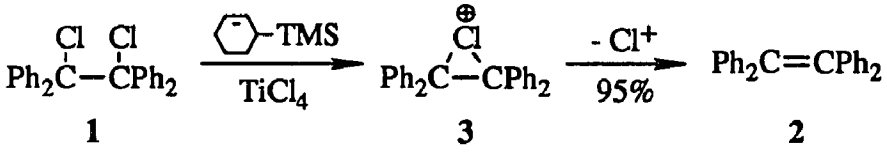
tetraphenylsuccinonitrile to tetraphenylsuccino-dialdehyde followed by Wittig reaction of the dialdehyde with chloromethylenetriphenylphosphorane to give 1,6-dichloro-3,3,4,4-tetraphenyl-1,5-hexadiene. Diels-Alder elaboration of the alkene groups into aryl rings should afford a hexaphenylethane derivative.

RESULTS AND DISCUSSION

I). Cyanation of Benzylic Chlorides With Trimethylsilyl Cyanide in the Presence of Titanium Tetrachloride.

Sym-Tetraphenylethylene dichloride (**1**) is a stable, little studied compound which is easily available in 90% yields by adding chlorine to tetraphenylethylene (**2**).[54] There are several reports in the older literature which describe melting point differences of crystal solvates of **1**,[54] but dichloride **1** has not yet drawn much attention from synthetic organic chemists.

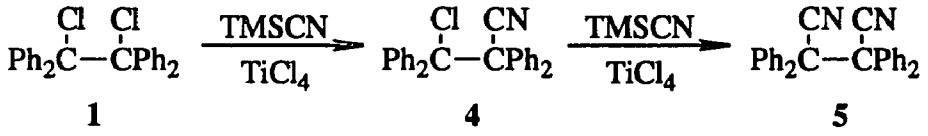
It has been reported that certain simple secondary benzylic halides react with allylsilane to give the allylated derivatives in the presence of Lewis acids.[55] Treatment of dichloride **1** with 3-trimethylsilylcyclohexene in the presence of $TiCl_4$, afforded tetraphenylethylene in 95% yield (Scheme 3).



Scheme 3

This seems to suggest that the intermediate chloronium ion **3** is not stable enough to allow the allylation reaction to take place. It was felt that if one of the chlorine atoms of dichloride **1** could be converted into a cyano group, the formation of tetraphenylethylene could be prevented and then the subsequent reactions with allylsilanes or aromatic substrates could be studied. This calls for the synthesis of 3-chloro-2,2,3,3-tetraphenylpropanenitrile (**4**).

In order to replace one of the chlorine atoms with a cyano group, the reaction of dichloride **1** with TMSCN was studied. It was found that if one adds $TiCl_4$ to a mixture of dichloride **1** and TMSCN in methylene chloride too fast, the reaction gives a mixture of 3-chloro-2,2,3,3-tetraphenylpropanenitrile (**4**), tetraphenylsuccinonitrile (**5**), tetraphenylethylene (**2**) and unreacted dichloride **1**. However, if $TiCl_4$ is added slowly and dropwise, the desired nitrile **4** can be prepared in 93% yield unaccompanied by **2** and **5**. Treatment of nitrile **4** with 1 mol each of TMSCN and $TiCl_4$ gave a 90% yield of succinonitrile **5** after 4.5 h of reaction (Scheme 4). Authentic **5** was prepared from the dimerization of the α-cyanodiphenylmethyl radical generated from the reaction of diphenylacetonitrile with piperidine and t-butyl hydroperoxide in the presence of CuBr in 96% yield according to Kharasch's procedure[56] to confirm the structure (^1H and ^{13}C NMR, mp and undepressed mixed mp).



1 **4** **5**

Scheme 4

That TMSCN substitutes the cyano group for chlorine in tertiary alkyl chlorides was reported by Reetz and his co-workers more than ten years ago.[18] However, the cyanation of benzylic halides by TMSCN does not appear to have been reported in the literature. Inspired by the apparent ease of converting **1** into **4** we sought to establish the generality of the cyanation process by studying a group of benzylic chlorides which are shown in Table 2.

A typical procedure is as follows: to a solution of benzylic chloride (5.0

mmol) and TMSCN in 25 mL of dry CH_2Cl_2 was added $TiCl_4$ (1.0 M in CH_2Cl_2) dropwise with vigorous stirring at 0 °C. After 2 h, the reaction was quenched with 5-10 mL of methanol. The products were purified by flash chromatography or recrystallization. Under these reaction conditions, doubly benzylic chlorides

Table 2. Cyanation of Benzylic Chlorides by TMSCN and $TiCl_4$

Entry	R—Cl [a]	$TiCl_4$ (mmol)	TMSCN (mmol)	R—CN	Yield[b]
1.	Ph_2CHCl	5.5	5.5	Ph_2CHCN	93
2.	Ph_2CCl_2	5.0	5.0	$Ph_2C(Cl)-CN$ [c]	91
		11	11		98
3.[d]	$Ph_2C(Cl)-CN$	5.5	5.5	$Ph_2C(CN)-CN$ [e]	85
4.	Ph_3C-Cl	5.5	5.5	Ph_3C-CN [f]	95
5.	$Ph_2C(Cl)-CPh_2(Cl)$	5.0	5.0	$Ph_2C(Cl)-CPh_2(CN)$	93
6.[g]	$Ph_2C(Cl)-CPh_2(CN)$	5.5	5.5	$Ph_2C(CN)-CPh_2(CN)$ [h]	90
7.	$Ph_2C(Cl)-CPh_2(Cl)$	10	12	$Ph_2C(CN)-CPh_2(CN)$	53

[a] In all entries, 5 mmol of benzylic chlorides was used. [b] The yields are isolated yields. [c] See ref. 57. [d] The reaction was run at 0 °C for 2 h and stirred overnight at room temperature. [e] See ref. 58. [f] See ref. 60. [g] The reaction was run at 0 °C for 2 h and stirred at room temperature for another 2.5 h. [h] See ref. 56.

are substituted by the cyano group with TMSCN and $TiCl_4$ in excellent yields. The most interesting substrate is that of the geminal dichloride, dichlorodiphenylmethane (**6**) (entry #2), which can be monocyanated to afford α-chlorodiphenylacetonitrile (**7**)[57] which in turn can be converted more slowly into diphenylmalononitrile (**8**) (entry #3),[58] a compound not readily available from malonic ester or malononitrile. For entry #3, α-chlorodiphenylacetonitrile (**7**), it seems reasonable to suppose that the electron withdrawing effect of the alpha cyano group reduces the ability of the chlorine to ionize. The result is that the reaction requires higher temperature and a longer reaction time. For entry #6, 3-chloro-2,2,3,3-tetraphenylpropanenitrile (**4**), the cyano group is not directly attached to the reaction center so the deactivation is not as great as in entry #3.

Benzyl chloride did not react and was recovered unchanged after two hours. A reaction that was run at room temperature for 24 hours gave a mixture of polymeric products.

It is worth mentioning that $TiCl_4$ did not cause any decomposition of the starting chlorides, in sharp contrast to the reports for tertiary aliphatic halides.[18] More important, isonitriles are not isolated in all cases in Table 2, which seems to be different from the results obtained in the tertiary alkyl system. The most plausible mechanism (Mechanism 2) for the cyanation reaction of tertiary alkyl halides with TMSCN involved the formation of an isonitrile as a key intermediate which has been isolated when the reaction is catalyzed by $TiCl_4$. Benzylic halides appear to behave differently from the tertiary alkyl halides toward $TiCl_4$, and it is likely that the initially formed benzylic isonitriles may rearrange to nitriles much more readily than alkyl isonitriles.

Table 3. Isomerization of Trityl Isonitrile (9) to Triphenylacetonitrile (10)

$$\underset{\mathbf{9}}{Ph_3C\text{-}N{\equiv}C:} \xrightarrow[CH_2Cl_2,\ 2\ h]{\text{Catalyst}} \underset{\mathbf{10}}{Ph_3C\text{-}C{\equiv}N} + \underset{\mathbf{11}}{Ph_3COH}$$

Catalyst	T °C	10 (Yield %)[a]	11 (Yield %)[a]
$TiCl_4$	0	90	0
$TiCl_4$	-78	0	0
$Ph_3C^+BF_4^-$	0	95	95
$Ph_3C^+BF_4^-$	-78	93	91

[a] Yields are isolated yields.

In order to tell whether the cyanation reaction of benzylic halides with TMSCN and $TiCl_4$ follows the same mechanism (Mechanism 2) as that of the tertiary alkyl halides or an alternative mechanism (Mechanism 1), isomerization of a benzylic isonitrile under the cyanation reaction conditions was then studied (Table 3).

Trityl isonitrile (**9**), is a stable compound obtained by the dehydration of N-tritylformamide.[59] Treatment of isonitrile **9** with $TiCl_4$ at 0 °C for 2.0 h in CH_2Cl_2 gave triphenylacetonitrile (**10**)[60] in 90% yield. Similarly, treatment of **9** with trityl tetrafluoroborate under the cyanation reaction conditions shown in Table 2 again produced nitrile **10** (95%) and triphenylmethanol (**11**) (95%). These experiments show that if the isonitrile **9** is an intermediate, it would have rapidly rearranged to the nitrile under the reaction conditions. The isomerization of **9** to **10** by $TiCl_4$ is not surprising for the benzylic systems shown in Table 2 since the carbocations formed are all doubly or triply benzylic.

When **9** and $TiCl_4$ were combined at -78 °C for 2.0 h in CH_2Cl_2, followed

by quenching with methanol, **9** was recovered unchanged; this showed that $TiCl_4$ cannot isomerize the isonitrile at -78 °C. In contrast when **9** was treated with $Ph_3C^+BF_4^-$ at -78 °C for 2 h and hydrolyzed with water, nitrile **10** (93%) and alcohol **11** (91%) were secured.

Another fact about isonitriles is that they thermally rearrange to nitriles upon heating at 200 °C in unimolecular fashion.[61] It is possible that π-complexation with $TiCl_4$ merely causes this isomerization to occur at a lower temperature.

Trityl tetrafluoroborate (1.0 mmol) in the absence of $TiCl_4$ reacts with TMSCN (1.0 mmol) to give the nitrile **10** (96%) (Scheme 5). This suggests that in the TMSCN reaction of benzylic halides that the function of $TiCl_4$ is primarily that of cation generation.

$$TMS{-}CN + Ph_3C^+BF_4^- \xrightarrow[96\%]{0\ ^\circ C,\ 2\ h} Ph_3C{-}CN + TMS^+BF_4^-$$

Scheme 5

A reaction of TMSCN, Ph_3CCl, $TiCl_4$ in CH_2Cl_2 at -78 °C was carried out in an effort to see if the isonitrile **9** could be isolated at low temperature. Upon treatment with methanol, it gave methyl trityl ether.[62] This seems to suggest that the $Ph_3C^+TiCl_5^-$ does not react with TMSCN at -78 °C.

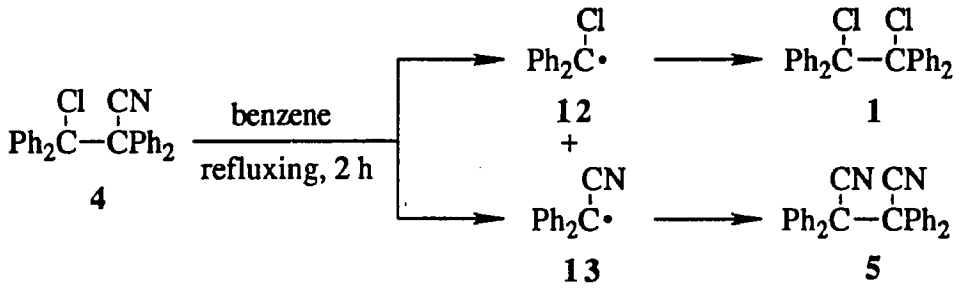
In conclusion, it has been shown that six sterically hindered benzylic chlorides are substituted by the cyano group with TMSCN and $TiCl_4$ in excellent yields. In addition the dichloro substrates **6** and **1** can be mono- or disubstituted as desired in 85-90% yields. Because isonitriles are plausible reaction intermediates, the isomerization of trityl isonitrile by $TiCl_4$ and trityl

tetrafluoroborate was studied at 0 °C and -78 °C. Both reagents catalyze conversion to triphenylacetonitrile at 0 °C while only trityl tetrafluoroborate is effective at - 78 °C. These results can be interpreted in terms of the mechanisms proposed earlier for tertiary alkyl halides, but they do not distinguish whether the carbocation intermediate attacks the isonitrile or nitrile form of TMSCN.

II). Reactions of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) and the Synthesis of 2-Cyano-1,1,2,2-tetraphenylethyl Cation (18).

a). The Stability of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) and Its Reactions With Organometallic Compounds.

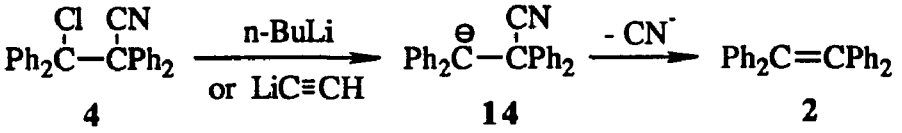
The 3-chloro-2,2,3,3-tetraphenylpropanenitrile (**4**) is a new compound which melts at 140 °C with decomposition. It is stable at room temperature in the air and slowly decomposes in boiling solvents such as methanol, ethanol, acetone, chloroform, carbon tetrachloride and benzene. In boiling benzene, nitrile **4** yielded dichloride **1** and succinonitrile **5** as shown in Scheme 6. These are presumably formed through self-coupling of the chlorodiphenylmethyl radical (**12**) and cyanodiphenylmethyl radical (**13**) respectively, which result from fragmentation of nitrile **4**. Dichloride **1** and succinonitrile **5** both seem to be more stable than nitrile **4**. Refluxing a mixture of **1** and **5** does not give any detectable amount of nitrile **4**.



Scheme 6

Nitrile **4** reacts with n-BuLi or lithium acetylide to give tetraphenylethylene (**2**) (Scheme 7). Presumably, the reaction involved the formation of 2-cyano-1,1,2,2-tetraphenylethyl carbanion (**14**) by a halogen metal exchange mechanism, followed by the elimination of the cyano group as

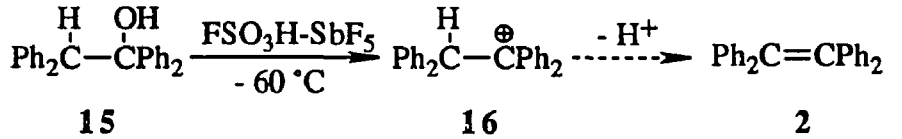
a cyanide ion to give the observed product. A similar dehydrocyanation was proposed by Hauser to explain the formation of olefins from the metallations of certain nitriles which contain β-hydrogen.[63]



Scheme 7

b). The Synthesis of 2-Cyano-1,1,2,2-tetraphenylethyl Cation (18).

Simple benzylic cations such as benzyl, diphenylmethyl and triphenylmethyl cations have been studied by proton and carbon-13 NMR spectroscopy. Pittman reported that tetraphenylethyl cation (**16**) is long-lived and can be generated from 1,1,2,2-tetraphenylethanol (**15**) in FSO_3H-SbF_5 at -60 °C.[27] But the published proton NMR spectrum of the reaction mixture at -60 °C does not permit identification of the benzylic hydrogen and the authors thought its absence was probably due to rapid exchange with the solvent. Since no chemical derivatization was achieved for **16**, one could suggest that the spectrum in the literature is just a spectrum of tetraphenylethylene derived from the decomposition of cation **16**.



Scheme 8

While much effort has been expended on the generation and reactions of substituted diphenylmethyl cations recently,[32,33] similar study of substituted tetraphenylethyl cations does not appear to have been undertaken. It seemed worthwhile to ascertain whether substituted tetraphenylethyl cations could be elaborated into compounds which could ultimately be converted into pentaphenylethyl cation. This seemed logical in the face of our complete inability to make the pentaphenylethyl cation directly from pentaphenylethane.[44b]

Consequently, it became one of the goals of this thesis to prepare cation precursors of the general structure of **A** and **B** as indicated in Figure 1 from 3-chloro-2,2,3,3-tetraphenylpropanenitrile (**4**) and the easily available *sym*-tetraphenylethylene dichloride (**1**).

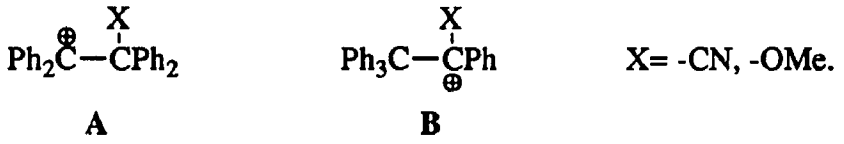
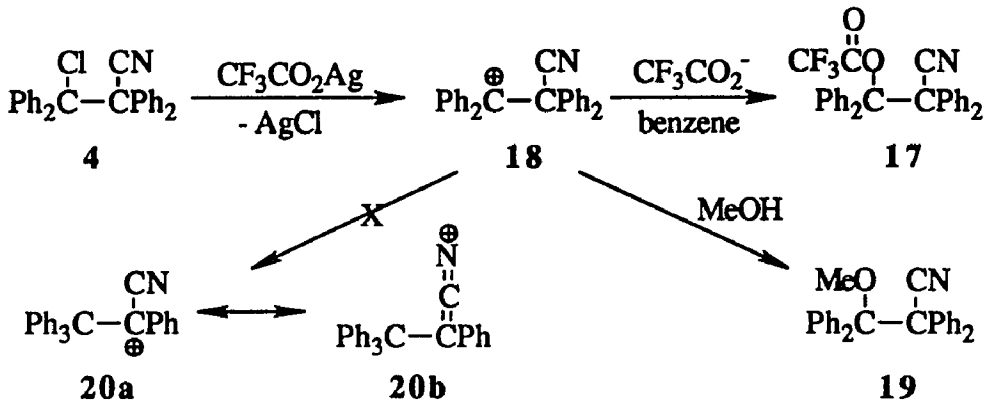


Figure 1. Substituted Tetraphenylethyl Cations

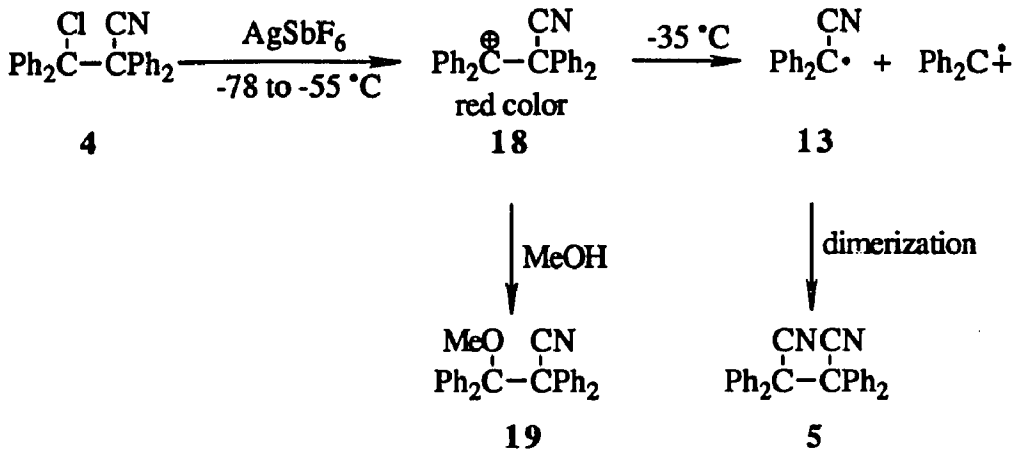
With chloro nitrile **4** in hand, the generation of a cyano substituted tetraphenylethyl cation with silver salts or Lewis acids was expected to be achievable. Upon treatment of nitrile **4** (1.0 mmol) with CF_3CO_2Ag (2.0 mmol) in 20 mL of benzene at 0 °C for 1 h, a 77% yield of 3-trifluoroacetoxy-2,2,3,3-tetraphenylpropanenitrile (**17**) was obtained together with a rapidly formed AgCl precipitate. This suggests the reaction as shown in Scheme 9 may involve the formation of a 2-cyano-1,1,2,2-tetraphenylethyl cation (**18**), which is trapped by trifluoroacetate ion to give the ester derivative **17**. When the same reaction



Scheme 9

was carried out in a CH_2Cl_2 : MeOH solvent system, 3-methoxy-2,2,3,3-tetraphenylpropanenitrile (**19**) was isolated in 98% yield. In both reactions, the possible rearrangement of cation **18** to 1-cyano-1,2,2,2-tetraphenylethyl cation (**20**) by a 1,2-phenyl shift did not occur, which is not so surprising since the electron withdrawing effect of the cyano group in cation **20** is not expected to be completely counter-balanced by the mesomeric contribution. The overall effect of the cyano group should make cation **20** less stable than **18**.[51] It should be pointed out that cation **18** did not undergo a Friedel-Crafts reaction with benzene to give cyanopentaphenylethane under the solvolytic conditions.

In order to study cation **18** under stable ion conditions, $AgSbF_6$ was substituted for CF_3CO_2Ag. Upon treatment of **4** with $AgSbF_6$ in CH_2Cl_2, a red-colored reaction mixture was observed when the temperature was allowed to warm to -55 °C from -78 °C. After 2 h, the reaction was quenched with prechilled (-78 °C) methanol and methoxy nitrile **19** was isolated in 75% yield. This experiment showed that cation **18** can be generated and that it has a reasonable stability at -55 °C for 2 h. If the temperature of a cation **18** solution is warmed to -35 °C, tetraphenylsuccinonitrile (**5**) was generated in 44% yield.



Scheme 10

It seems possible that cation **18** may dissociate at higher temperature into diphenylmethyl radical cation[64] and cyanodiphenylmethyl radical as shown in Scheme 10. The latter dimerizes to give **5**.[56]

The preparation of cation **18** with Lewis acids was also studied. Antimony pentachloride has been successfully employed in the synthesis of diphenylmethyl and triphenylmethyl cations from their corresponding chlorides.[65] A series of reactions of **4** with $SbCl_5$ was carried out in an effort to optimize the reaction conditions for the synthesis of cation **18** and the results are summarized in Table 4. Antimony pentachloride (1.0 M in CH_2Cl_2) was added to a solution of nitrile **4** at the specified temperature. The reaction was quenched with 10 mL of prechilled methanol (-78 °C) followed by the usual aqueous work-up. After concentration, the residue was taken into methanol and the resulting solids (almost white) were dried, weighed and used for NMR spectroscopic analysis. The percent yield of cation **18** was assumed to be equal to the yield of compound **19** which was determined by using a proton integration method, the methoxyl methyl group at 3.22 ppm vs the aromatic protons (from both **4** and **19**) near 7.3 ppm. Reactions run at -75 °C

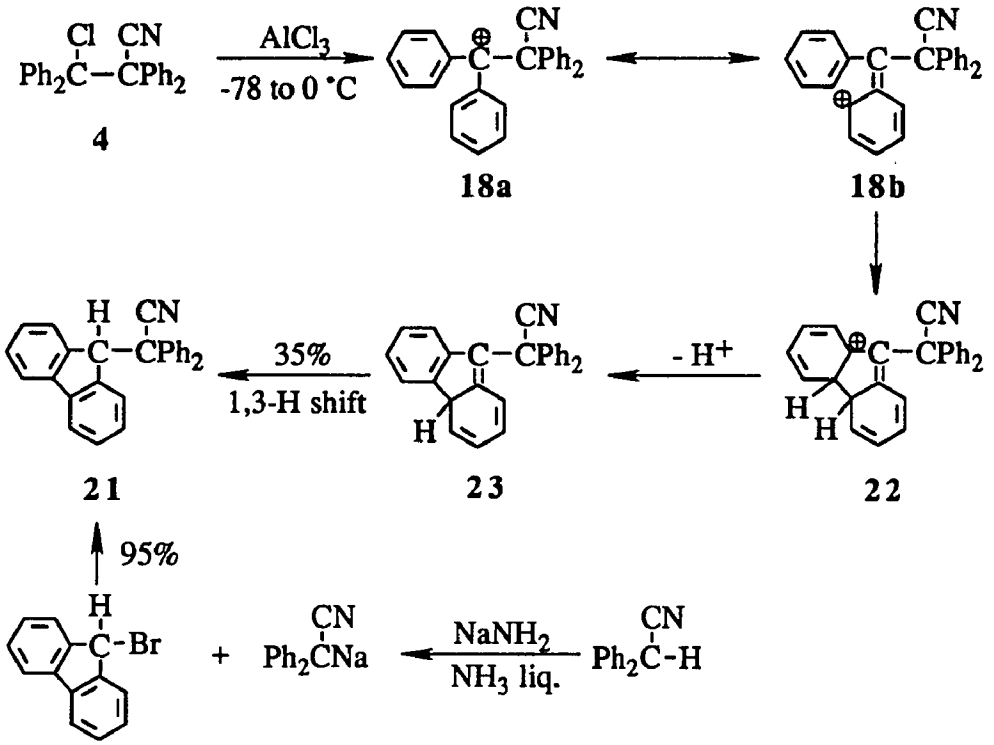
Table 4. The Synthesis of 2-Cyano-1,1,2,2-tetraphenylethyl Cation (18) With $SbCl_5$

Entry	Mole ratio $SbCl_5$: nitrile **4**	T °C	Rect. Time	**19** Yield %	**4** Recovered %
1.	1.5:1	-75	2.5 h	25	68
2.	1.5:1	-75	4.5 h	37	55
3.	1.5:1	-75	6.5 h	45	51
4.	1.5:1	-55	2.5 h	46	46
5.	2.5:1	-75	2.5 h	66	23
6.	2.5:1	-75	4.5 h	93	0

(entry #1, #2 and #3) show small increments of the yield of cation **18** with longer reaction time. Among these, the highest yield of **18** was 46% after 6.5 h of reaction. Although the same result can be achieved in 2.5 h at -55 °C, the reaction was not as clean as at -75 °C as judged by ^{13}C NMR. One possible explanation for the incompletion of the reaction under these reaction conditions would be the complexation of $SbCl_5$ with the cyano group. Therefore, one mole of nitrile **4** may need 2 moles of $SbCl_5$ in order for the conversion to be complete. When the reactions were repeated with 2.5:1 ratio of $SbCl_5$ to nitrile **4**, better results were obtained with respect to the yield of cation **18**. As shown in entry #6, the nitrile **4** has completely disappeared and at least a 93% yield of cation **18** was achieved as judged by the amount of **19**. This strongly suggests that cation **18** is stable at -75 °C for at least 4.5 h. Attempts were made to study

the cation **18** by low temperature ^{13}C NMR but we were unable to obtain a well resolved spectrum. It should be noted that nitrile **4** did not react at all with $SnCl_4$ at - 78 °C and was recovered unchanged.

In contrast to this, when cation **18** was generated with $AlCl_3$ in a mixture of benzene and CH_2Cl_2, 9-(cyanodiphenylmethyl)fluorene (**21**) was obtained in 35% yield (Scheme 11). The structure of **21** was confirmed by comparison with a sample synthesized from 9-bromofluorene and sodiodiphenylacetonitrile in



Scheme 11

liquid NH_3. The formation of the fluorene derivative **21** is probably due to the delocalization of the positive charge into one of the phenyl rings which then attacks one of the ortho positions of the other phenyl ring attached to the same carbon to give a cyclized intermediate **22**. This intermediate can lose a proton followed by a 1,3-hydrogen shift to give the observed product.

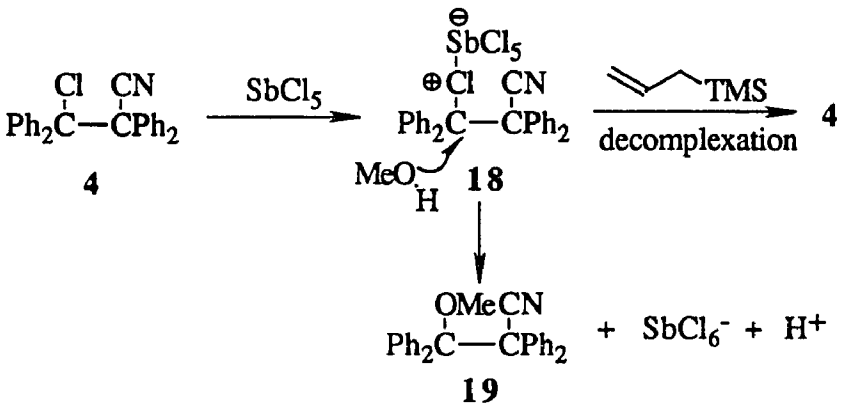
c). The Reactions of 2-Cyano-1,1,2,2-tetraphenylethyl Cation (18) With Organosilane Reagents and Aromatic Substrates.

Having made the cation **18**, its reactions with various organosilane reagents and aromatic substrates were undertaken in order to address the question whether or not a pentaphenylethane derivative could be synthesized by the reaction of a substituted tetraphenylethyl cation with aromatic hydrocarbons. Furthermore, this result may shed light on the question of whether or not one could prepare hexaphenylethane from the reaction of pentaphenylethyl cation with aromatic substrates.

Cation **18** was prepared by the reaction of nitrile **4** with $SbCl_5$ at -75 °C for 4.5 h. Upon treatment of cation **18** with allyltrimethylsilane, the red color disappeared immediately. After quenching with methanol and aqueous work-up, nitrile **4** was isolated accompanied by a small amount of methoxy nitrile **19**. The desired allylated product was not obtained. The recovery of nitrile **4** is not expected and two mechanisms have been considered for the explanation of the formation of nitrile **4**.

In Mechanism 3, it is assumed that cation **18** is not a free cation but a

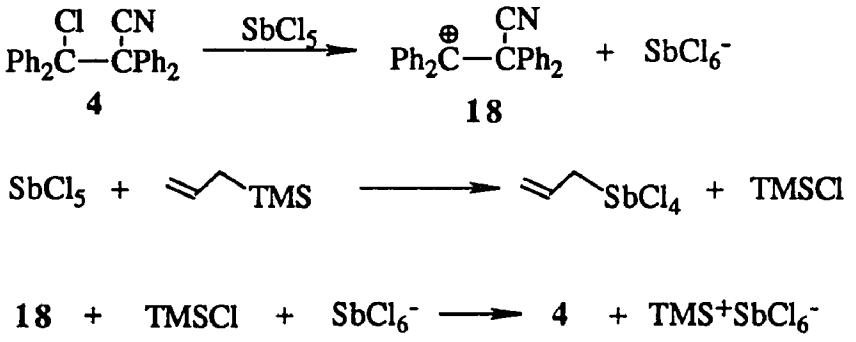
Mechanism 3



complex of nitrile **4** with $SbCl_5$, which might have a red color. This complex may undergo attack by allyltrimethylsilane at Sb with subsequent cleavage of the Sb-Cl bond to release the starting nitrile **4**. The fact that methoxy nitrile **19** was obtained in the previous experiments in Table 4 might be thought to have involved methanol attack of the intermediate complex **18** at the benzylic carbon in a classical manner.

In Mechanism 4, the excess $SbCl_5$ can react with allyltrimethylsilane to give allyltetrachloroantimony and chlorotrimethylsilane. The TMSCl reacts with the free cation **18** to produce the nitrile **4** and $TMS^+SbCl_6^-$.

Mechanism 4



It is important to distinguish between these two mechanisms in order to learn whether **18** is a complex with $SbCl_5$ as shown in Mechanism 3 or a free carbocation as portrayed in Mechanism 4. The excess $SbCl_5$ seems to play an important role only in Mechanism 4. According to Mechanism 4, if the excess $SbCl_5$ could be consumed before the addition of allyltrimethylsilane, the formation of nitrile **4** should be completely stopped.

The above reaction was repeated as follows: the nitrile **4** was treated with 2.5 fold of $SbCl_5$ for 4.5 h at - 75 °C as described in entry #6, Table 4. A

small amount of 2,2-dimethoxypropane was added to the red colored mixture, followed by the addition of allyltrimethylsilane. The reaction was quenched with methanol as before. The purpose of adding 2,2-dimethoxypropane is to consume the excess $SbCl_5$ so that whether or not nitrile **4** is formed will point to which mechanism is operating and the nature of red colored solution **18**. The crude reaction product was analyzed by ^1H and ^{13}C NMR which showed no evidence for existence of nitrile **4**, but suggested the reaction gave a mixture of methoxy nitrile **19** and a small amount of succinonitrile **5**. This result clearly fits in Mechanism 4 and confirmed that the red colored solution **18** from the reaction of nitrile **4** with $SbCl_5$ is a free cation as proposed in Table 4. This result also showed that cation **18** did not react with allyltrimethylsilane to give the allylated product.

The formation of nitrile **4** from cation **18** with TMSCl as proposed in Mechanism 4 was confirmed independently by the treatment of cation **18** with TMSCl, followed by quenching with CH_3OH. The reaction afforded a 83.2% yield of nitrile **4** accompanied with a 15.1% yield of methoxy nitrile **19**.

The reaction of cation **18** with vinyltrimethylsilane was also attempted and it gave a mixture of methoxy nitrile **19** together with succinonitrile **5**. No vinylated product could be detected. Although cation **18** did not seem to react with allyltrimethylsilane and vinyltrimethylsilane, it reacted cleanly with TMSCN to produce a 98.2% yield of succinonitrile **5**.

The reaction of cation **18** with aromatic substrates was investigated. It was found that cation **18** did not react with phenol or anisole to give arylated products at -75 °C and quenching with CH_3OH gave methoxy nitrile **19**. If the reaction temperature was allowed to warm above -55 °C, decomposition of cation **18** occurred and succinonitrile 5 could be isolated. Reaction with furan

was also attempted and it seems that furan reacted with excess $SbCl_5$ to give a complex mixture, one of the products of which was identified as succinonitrile **5**.

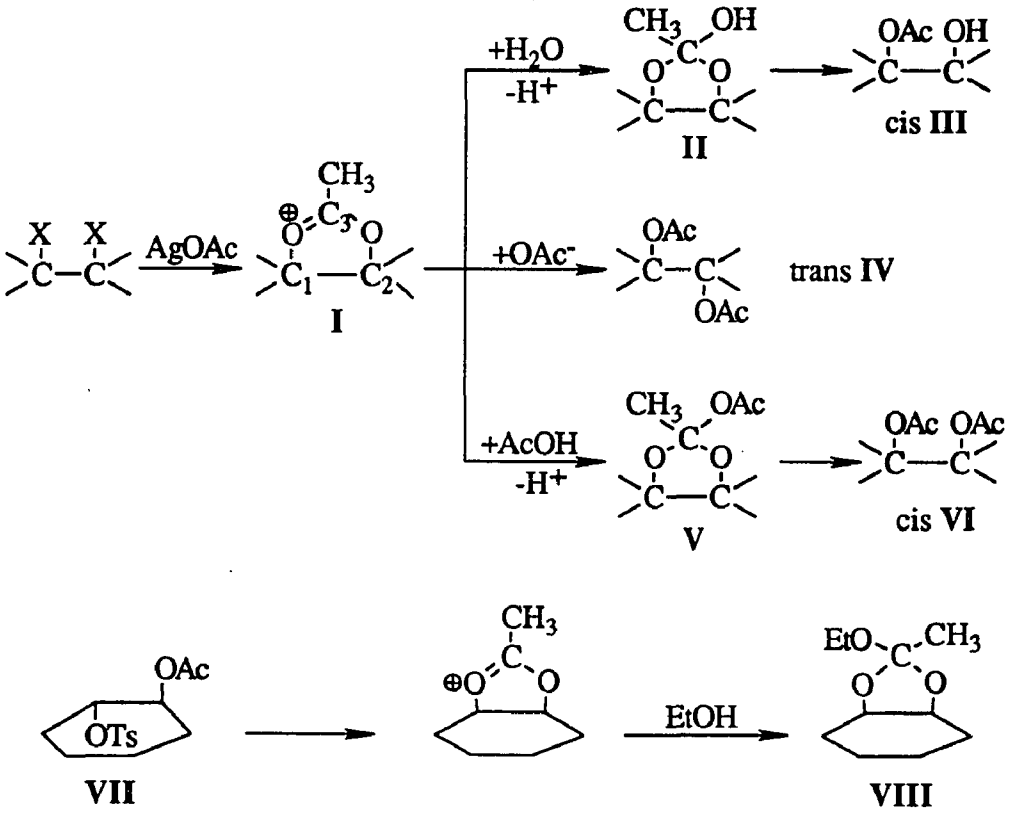
Similarly, cation **18** generated from nitrile **4** with $AgSbF_6$ did not react with allyltrimethylsilane, furan, phenol or anisole.

In conclusion, It has been shown that the first example of a long-lived substituted tetraphenylethyl cation: 2-cyano-1,1,2,2-tetraphenylethyl cation **18** can be generated from **4** with $AgSbF_6$ or $SbCl_5$. It is stable at -75 °C and starts to decompose at a temperature between -55 °C to -35 °C. It is also observed that cation **18** generated with $AlCl_3$ reacted intramolecularly to form fluorene derivative **21**. Cation **18** was found not to undergo aromatic substitution reactions with benzene, anisole, furan or phenol to give a cyanopentaarylethane.

III). The Silver Ion Assisted Reactions of *Sym*-tetraphenylethylene Dichlorides (1) and the Synthesis of Benzopinacolone Dimethyl Ketal (39).

a). Solvolysis Studies on Sym-tetraphenylethylene Dichloride (1).

Inspired by the apparent ease of converting **4** into **19** under solvolytic conditions, the question arises whether dichloride **1** will undergo the same type of reaction with methanol. The reactions of some simple alkyl 1,2-dihalides with AgOAc in acetic acid have been carefully studied by Winstein and his co-workers.[66] It was found that these reactions involved the formation of an intermediate **I** which undergoes secondary reactions as follows:

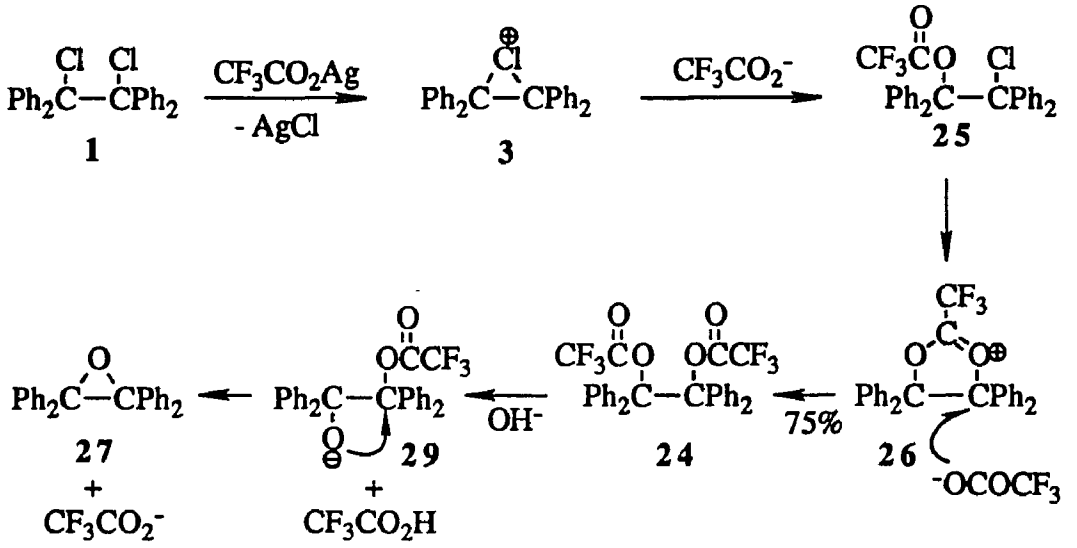


Scheme 12

with water in acetic acid at C-3 carbon to give orthomonoacetate **II** which isomerizes to monoacetate **III**; with acetate ion in acetic acid at C-1 or C-2 carbon to give trans-diacetate **IV**; with acetic acid, in the absence of water or acetate ion, at C-3 carbon to yield orthodiacetate **V** which isomerizes to diacetate **VI**. Interestingly, an ortho ester **VIII** was isolated from the solvolysis reaction of trans-2-acetoxycyclohexyl tosylate **VII** in ethanol.[67] However, it was not reported whether the reaction of dihalides with AgOAc in the presence of ethanol will yield the same ortho ester directly.

It is important to learn if benzylic dichlorides such as dichloride **1** will give similar results in terms of reaction products. Furthermore, it was speculated whether or not dichloride **1** will react with alcohols to produce ortho esters similar to **VIII**.

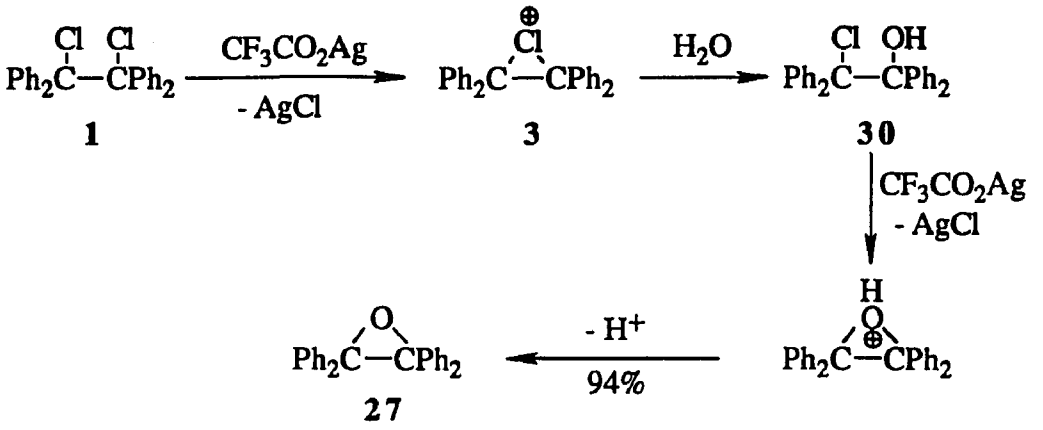
Dichloride **1** reacted with CF_3CO_2Ag in CH_2Cl_2 at 0 °C for 0.5 h to give tetraphenylethylene glycol bistrifluoroacetate (**24**). This reaction appears to involve the formation of a chloronium ion **3** which suffers attack by trifluoroacetate ion to yield a chloro-ester intermediate **25** as outlined in Scheme 13. Ester **25** can react with a second mol of CF_3CO_2Ag to generate cation **26** with neighboring group participation from the trifluoroacetoxyl group. Cation **26** is vulnerable to an S_N2-like reaction with trifluoroacetate ion to give diester **24**. The formation of diester **24** seems to agree with the results obtained in the alkyl system. Diester **24** is quite unstable in the air as expected for such a doubly benzylic ester. Saponification of diester **24** with NaOH in ethanol showed that 2 moles of base was consumed for each mol of **24**. In addition, tetraphenylethylene oxide (**27**)[68] was isolated instead of tetraphenylethane-1,2-diol (**28**)[69]. An explanation for the formation of **27** would involve S_N2 attack by hydroxide on the carbonyl carbon of one of the ester groups followed by



Scheme 13

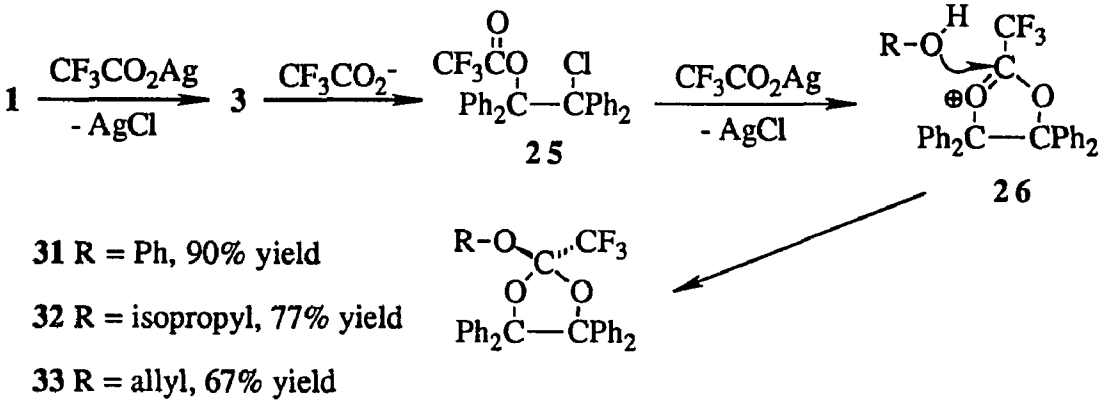
elimination of trifluoroacetic acid to produce the alkoxide intermediate **29** shown in Scheme 13. This alkoxide ion could readily displace the second trifluoroacetate group intramolecularly to give epoxide **27**.

When dichloride **1** was treated with CF_3CO_2Ag in 10 mL of CH_2Cl_2 in the presence of a small amount of H_2O (0.5 mL), the epoxide **27** was obtained in 94% yield. It seems that the first formed chloronium ion **3** undergoes preferential attack by H_2O rather than trifluoroacetate ion. As a result, chlorohydrin **30** may be formed as an intermediate (Scheme 14), prior to removal of the second chlorine atom with a second mol of CF_3CO_2Ag. That this second chlorine atom departure must occur with neighboring group participation from the hydroxyl group is shown by the absence of any rearrangement. Not surprisingly the literature records that epoxide **27** has been prepared by refluxing dichloride **1** in water for 18 h in 62% yield.[68] The formation of epoxide **27** certainly was not expected if dichloride **1** behaved similar to alkyl dihalides.



Scheme 14

An interesting result was found when the reaction of dichloride **1** with CF_3CO_2Ag was carried out in the presence of phenol. More than a 90% yield of an air stable ortho ester derivative **31** was isolated, most likely by Scheme 15. To explain this product, one must assume that intermediate **26** forms upon removal of chloride ion from chloro-ester **25** in the manner shown by Winstein in the alkyl system of Scheme 12. Furthermore, **26** undergoes attack by phenol at the carboxylate carbon of the trifluoroacetoxy moiety rather than at the ethane carbon as was assumed in Scheme 13 for the formation of **24**. If $AgBF_4$ were used instead of CF_3CO_2Ag, the reaction gave tetraphenylethylene (**2**).



31 R = Ph, 90% yield

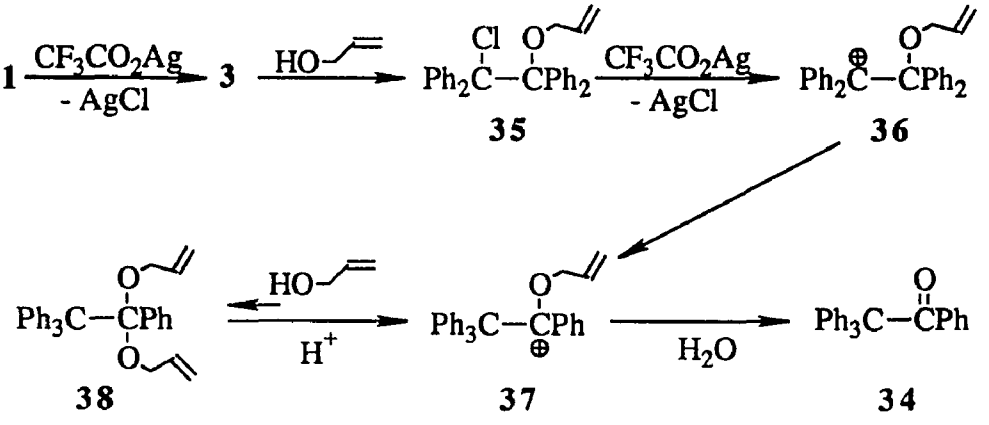
32 R = isopropyl, 77% yield

33 R = allyl, 67% yield

Scheme 15

This seems to suggest that the chloronium ion **3** readily undergoes decomposition in the absence of a good nucleophile.

Similar results were obtained when the reaction was run in the presence of 2-propanol and allyl alcohol. With 2-propanol present, the reaction yielded ortho ester **32** in 77% yield accompanied with a 15% yield of epoxide **27**. The formation of **27** could result from a trace of moisture present in the reaction environment. In the case of allyl alcohol, the reaction afforded ortho ester **33** in 67% yield as well as epoxide **27** and benzopinacolone **34**[70] in 10% and 15% yields respectively. The formation of **34** may suggest the existence of another reaction pathway as outlined in Scheme 16. It is possible that allyl alcohol can



Scheme 16

attack chloronium ion **3** to give an intermediate **35** which upon removal of the second chlorine yielded cation **36**, followed by a 1,2-phenyl shift to produce cation **37**. Cation **37** is in equilibrium with ketal **38** in the acidic reaction media and the equilibrium may lie on the right side due to the steric hindrance of ketal **38**. Upon hydrolysis of cation **37**, the ketone **34** was then produced.

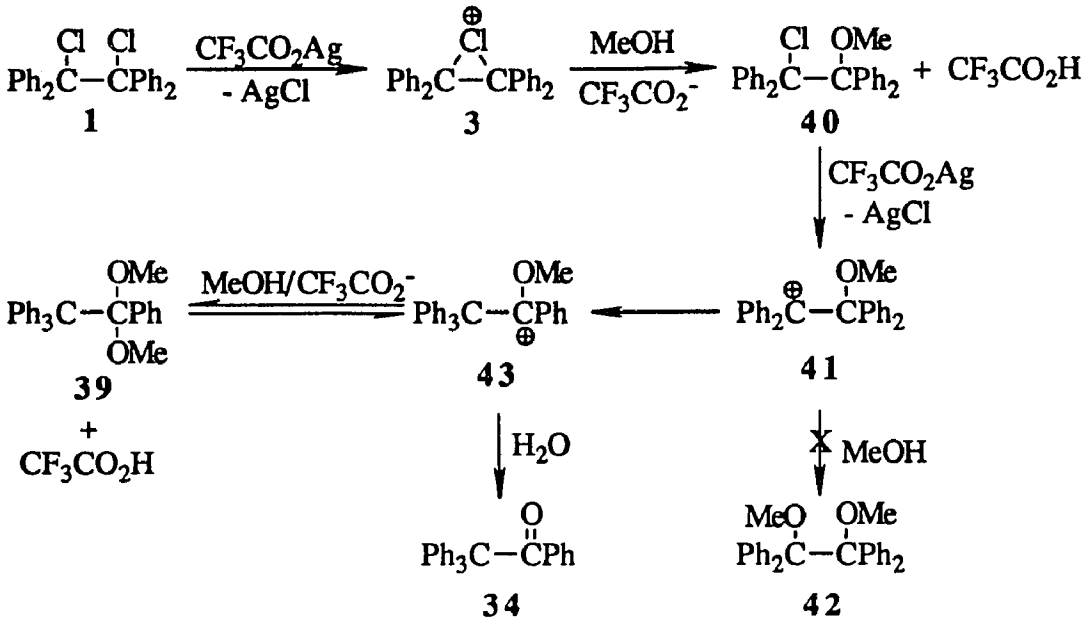
Besides the correct element analyses, the principal evidence for the

structures of ortho esters **31**, **32** and **33** comes from the ^{13}C NMR spectroscopic data for the CF_3 group and the quaternary ortho ester carbon. As Table 5 indicates, the CF_3 group in each case shows a quartet near 120 ppm with a coupling constant (J_{C-F}) in the magnitude of 291 Hz. Furthermore, the quaternary ortho ester carbon also appears as a quartet around 114 ppm with a coupling constant ($^2J_{CCF}$) in the range of 35 - 36 Hz.

Table 5. ^{13}C NMR Spectral Data For Ortho Ester 31, 32 And 33.

Ortho ester	CF_3 Group		Ortho Ester Carbon	
	Chemical Shift (ppm)	Coupling Constant (Hz)	Chemical Shift (ppm)	Coupling Constant (Hz)
31	120.36	291.59	114.72	36.40
32	120.42	291.30	113.60	35.87
33	120.73	291.58	114.02	35.47

When the same reaction was run in the presence of methanol for 2 h, a surprising result was obtained. There was obtained a mixture of 67% benzopinacolone dimethyl ketal (**39**) together with 28% benzopinacolone (**34**). A possible reaction sequence leading to the formation of ketal **39** is outlined in Scheme 17. The reaction probably proceeds via the intermediate **40** instead of **26**, followed by the formation of cation **41**. Since 1,2-dimethoxytetraphenylethane (**42**)[71] was not formed, the rearrangement of **41** to α-methoxy cation **43** by a 1,2- phenyl shift must have happened very rapidly.



Scheme 17

The cation **43** was trapped with methanol to afford ketal **39**. Since two moles of trifluoroacetic acid are formed for each mole of dichloride **1** which reacts, it is possible that ketone **34** was formed via an acid catalyzed hydrolysis reaction[72]. If that were the case, neutralization of the acid with a base such as Na_2CO_3 before the aqueous work-up would increase the yield of ketal **39** and diminish the yield of ketone **34**. This was shown to be true by simply adding anhydrous Na_2CO_3 before the aqueous workup; the yield of ketal **39** is improved to 91% at the expense of ketone **34**. It should be mentioned that the yield of ketal **39** varies with how dry the CF_3CO_2Ag is. The better yields are obtained when the silver salt was dried *in vacuo* overnight before use. The reactions with other silver salts such as Ag_2CO_3 and AgOCN were also studied and the results are summarized in Table 6. The highest yield of ketal **39** was achieved under the reaction conditions where AgOCN was used and the reaction mixture was treated with Na_2CO_3 before aqueous work-up (entry #6). Ketal **39** is a new

compound and all attempts to synthesize it directly from benzopinacolone (**34**) by the reaction of trimethyl orthoformate[73] or by transketalization[74] were unsuccessful.

Table 6. The Synthesis of Benzopinacolone Dimethyl Ketal (39).

Entry	Silver Salt[a]	Ketal **39** (yield %)[b]	Ketone **34** (yield %)[b]
1.	CF_3CO_2Ag	67	28
2.[c]	CF_3CO_2Ag	33	66
3.	CF_3CO_2Ag/Na_2CO_3	91	6
4.	Ag_2CO_3	65	21
5.	AgOCN	80	11
6.	$AgOCN/Na_2CO_3$	92	0

[a] Silver salts are dried overnight *in vacuo* before use unless otherwise specified.
[b] Isolated yields. [c] CF_3CO_2Ag was not dried *in vacuo* over night before use.

There is no simple explanation as to why the reactions of dichloride **1** with CF_3CO_2Ag afforded ortho esters **31**, **32** or **33** when phenol, 2-propanol or allyl alcohol are present but gave epoxide **27** and ketal **39** in the presence of H_2O and methanol. One possible explanaton is that although the trifluoroacetate ion is the strongest nucleophile in the present reactions and it is expected that chloronium ion **3** should undergo attack exclusively by trifluoroacetate ion to give intermediate **26** in all cases, however, H_2O and

methanol are capable of solvating the trifluoroacetate ion through hydrogen bonding. This may reduce the nucleophilic power of the trifluoroacetate ion to a such extend that H_2O or methanol becomes the active nucleophile in attacking the chloronium ion **3** to give **30** or **40** as shown in Scheme 14 and Scheme 17 respectively. While in the cases of phenol and 2-propanol, they may not be able to solvate the trifluoroacetate ion as well as H_2O and methanol so the trifluroacetate ion remains to be the better nucleophile than phenol and 2-propanol and therefore the chloronium ion **3** undergoes attack preferentially by trifluoroacetate ion to yield the intermediate **26**. Allyl alcohol may be a borderline case. it solvates the trifluoroacetate ion to a such degree that both of them compete in the attack of the chloronium **3** to yield two different intermediates **26** and **35** as shown in Scheme 15 and Scheme 16.

b). Single Crystal X-ray Analysis of Ortho Ester 31 and Ketal 39.

Our structural assignments for ortho ester **31** and ketal **39** have been verified by single crystal x-ray analyses. X-ray quality crystals for **31** and **39** were grown from acetone and CH_2Cl_2/MeOH, respectively. All the diffractometer data were collected at room temperature. The crystal data collection and refinement parameter are summarized in Table 7 (for **31**) and Table 8 (for **39**). Views of solid state comformations are given in Figure 2 (for **31**) and Figure 3 (for **39**). Coordinates, bond distances and bond angles are given in Appendix 1 (for **31**) and Appendix 2 (for **39**). The most important bond distance found in ortho ester **31** and ketal **39** was that for the central ethane carbon-carbon bond 1.603(3) Å and 1.591(5)Å respectively.

Table 7. Single Crystal X-Ray Analysis of Ortho Ester 31.

Formula	$C_{34}H_{25}O_3F_3$
FW	538.57
a Å	9.855(1)
b Å	16.744(2)
c Å	16.169(1)
α deg	90
β deg	94.207(4)
γ deg	90
V Å^3	2660.8(4)
Z	4
Space group	$P2_1/n$
temp.	ambient
radiation (graphite monochromator)	Mo Kα (λ = 0.71073)
linear abs coeff., cm^{-1}	0.931
scan mode	Θ/2Θ
2Θ range, deg	0<2Θ<56
unique reflections with $\|F_o\|^2>3\sigma\|F_o\|^2$	2914
Final no. of variables	361
$R^a = \sum[\|F_o\|-\|F_c\|]/\sum\|F_o\|$	0.035
$R_w=[\sum w(\|F_o\|-\|F_c\|)^2/\sum wF_o^2]^{1/2}$	0.038
Std. error in observation of unit wt	1.327

[a] Quantity mimimized ($\sum w(|F_o|-|F_c|)^2$); weight $w = 1/(\sigma^2 + 0.0016\, F_o^2)$

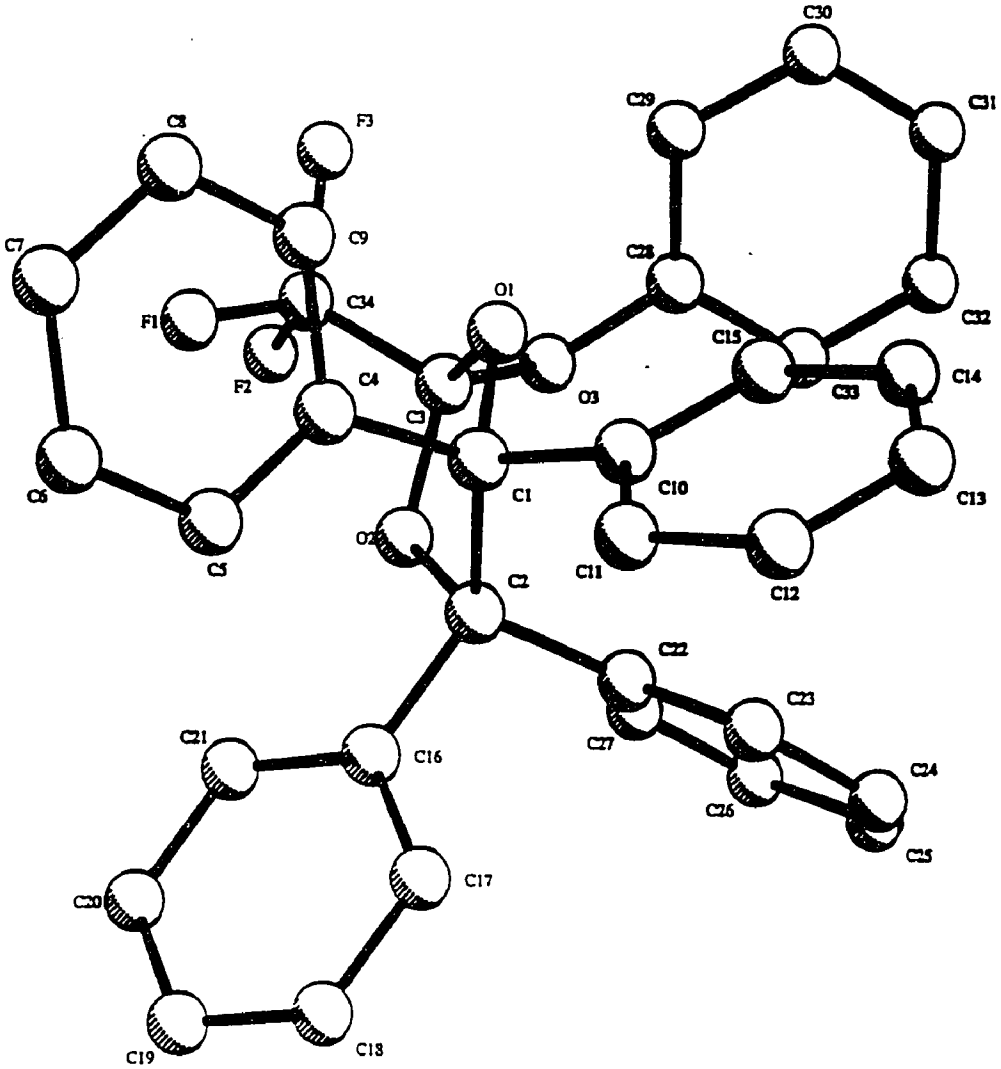


Figure 2. Stereoview of Ortho Ester 31

Table 8. Single Crystal X-Ray Analysis of Dimethyl Ketal 39.

Formula	$C_{28}H_{26}O_2$
FW	394.5
a Å	9.678(2)
b Å	13.117(3)
c Å	8.599(2)
α deg	95.622(13)
β deg	92.101(13)
γ deg	89.556(14)
V Å^3	1085.7(8)
Z	2
Space group	P1bar (#2)
temp.	ambient
radiation (graphite monochromator)	Mo Kα (λ = 0.71073)
linear abs coeff., cm^{-1}	0.692
scan mode	Θ/2Θ
2Θ range, deg	0<2Θ<56
unique reflections with $\|F_o\|^2>4\sigma\|F_o\|^2$	2996
Final no. of variables	271
$R^a=\sum[\|F_o\|-\|F_c\|]/\sum\|F_o\|$	0.079
$R_w=[\sum w(\|F_o\|-\|F_c\|)^2/\sum wF_o^2]^{1/2}$	0.11
Std. error in observation of unit wt	4.51

[a] Quantity mimimized ($\sum w(|F_o|-|F_c|)^2$); weight $w = 1/(\sigma^2 + 0.0016\ F_o^2)$

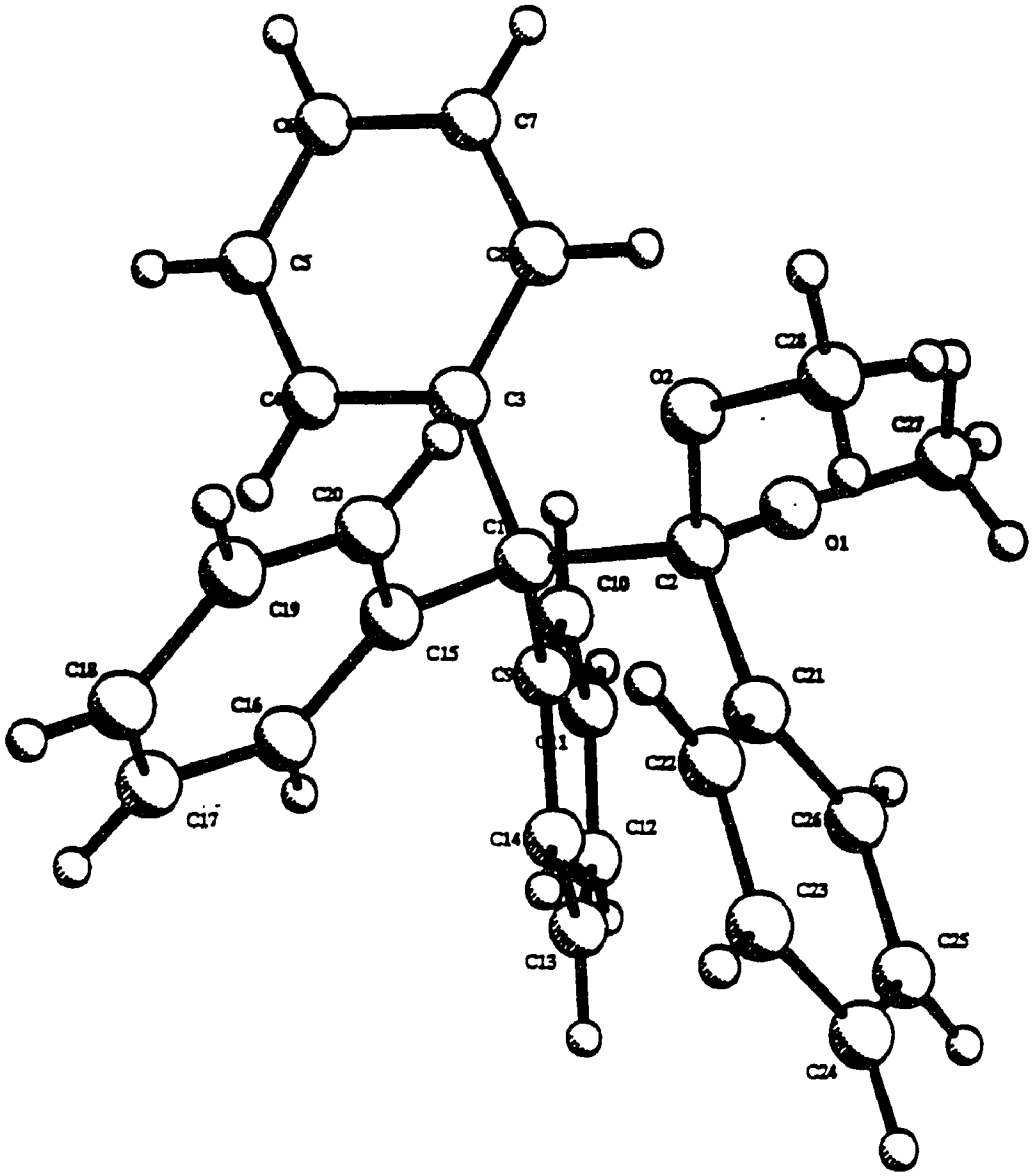


Figure 3. Stereoview of Dimethyl Ketal 39

c). The Reactions of Benzopinacolone Dimethyl ketal (39).

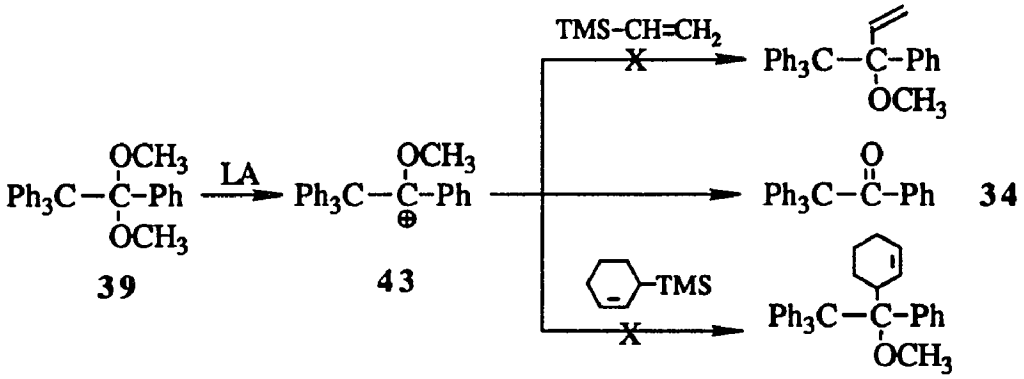
The Lewis acid mediated addition of organosilane reagents to acetals and ketals is a common reaction in organic synthesis that is widely used for the formation of carbon-carbon bonds.[75] The reaction mechanism has recently been reinvestigated by Sammakia and Smith.[76] It was found that, under ordinary conditions of intermolecular additions to acetals, the reaction occurs by an S_N1 mechanism via an oxocarbenium ion intermediate.

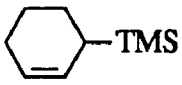
Having synthesized benzopinacolone dimethyl ketal (**39**), we first studied its reaction with vinyltrimethylsilane and 3-trimethylsilylcyclohexene in an effort to replace one of the methoxy groups in ketal **39** with an unsaturated group which could be converted subsequently into a benzene ring. A number of Lewis acids which are commonly used in similar reactions were examined and the results were disappointing; in all the experiments listed in Table 9, benzopinacolone (**34**) was produced rather than the desired products. These results seem to suggest that the cation intermediate **43** undergoes decomposition faster than reaction with the organosilane substrates. Similar to our results, it has been shown that the reaction of 4,4'-dimethoxybenzophenone dimethyl ketal with allyltrimethylsilane in the presence of BF_3 gave only the corresponding ketone while under the same reaction conditions benzophenone dimethyl ketal yielded the allylated product.[77]

The reactions of ketal **39** with aromatic substrates such as furan, phenol or anisole were also attempted and ketone **34** was again obtained as the only product.

In conclusion, ortho esters **31**, **32** and **33** isolated from the reaction of dichloride **1** with CF_3CO_2Ag in the presence of phenol, 2-propanol or allyl alcohol were consistent with the existence of cationic intermediate **26**.

Table 9.[a] The Reactions of Ketal 39 With Vinyltrimethylsilane and 3-Trimethylsilylcyclohexene



Organosilane	Lewis Acid	T °C	Ketone 34 yield %
TMS-CH=CH$_2$	$BF_3(OEt_2)$	0	87
		-78	91
	$TiCl_4$	0	85
		-78	89
	TMSOTf	0	92
		-78	94
	$BF_3(OEt_2)$	0	92
		-78	89
	$TiCl_4$	0	84
		-78	93
	TMSOTf	0	95
		-78	91

[a] A mixture of ketal **39** (1mmol) and the organosilane reagent (1.2 mmol) in 10 mL of CH_2Cl_2 was treated with Lewis acid (1.1 mmol). After 1 h, the reaction was quenched with 5 mL of CH_3OH followed by an aqueous work-up. The product was recrystallized from EtOH.

However, if methanol were present, the reaction took a wholly different pathway and a sterically hindered ketal, benzopinacolone dimethyl ketal (**39**) was obtained.

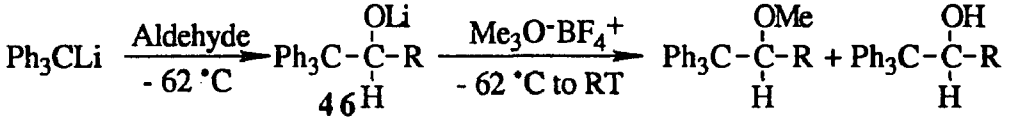
The results obtained from the reaction of ketal **39** with organosilane reagents and aromatic substrates suggested that the reaction intermediate, 1-methoxy-1,2,2,2-tetraphenylethyl cation (**43**) derived from ketal **39** underwent decompostion to give ketone **34** faster than reaction with organosilane reagents and aromatic substrates.

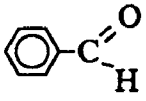
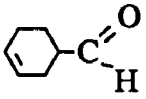
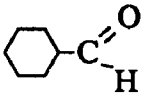
IV). Miscellaneous Reactions.

a). The Synthesis and Reactions of 1-Methoxy-1,2,2,2-tetraphenylethane (47).

The pentaphenylethyl carbanion (**45**) can be synthesized from the metalation of pentaphenylethane (**44**) by n-BuLi-KOtBu at -78 °C and it is stable at this temperature.[78] However, treatment of carbanion **45** with various electrophiles yielded triphenylmethanol and benzophenone derivatives rather than the desired pentaphenylethane derivatives. This led us to the idea of starting with a substituted tetraphenylethane and building the fifth phenyl ring afterwards. The substituent which was chosen is a methoxyl group and 1-methoxy-1,2,2,2-tetraphenylethane (**47**) was then prepared by the addition of Ph_3CLi to benzaldehyde followed by methylation of the alkoxide intermediate **46** with $Me_3O^+BF_4^-$ (Table 10).

Table 10.[a] **Synthesis of Methyl Ether 47, 49 and 51.**



Aldehyde	R	Methyl Ether	Alcohol
		**47**: 57%	**48**: 5%
		**49**: 5%	**50**: 36%
		**51**: 29%	**52**: 6%

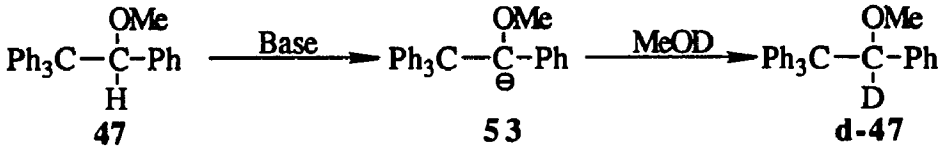
[a] Ph_3CLi was prepared by the treatment of Ph_3CH with n-BuLi at 0 °C for 1 h.

In a like manner 1-(3-cyclohexenyl)-1-methoxy-2,2,2-triphenylethane (**49**) and 1-cyclohexyl-1-methoxy-2,2,2-triphenylethane (**51**) were also obtained. The formation of a small amount of alcohol **48** or **52** is probably due to a trace of moisture introduced during the methylation step. However this can not explain why a significant amount of alcohol **50** was formed. One possible explanation for this unexpected result is as follows: the hydrogen on the carbon bearing the aldehyde group in 1,2,3,6-tetrahydrobenzaldehyde is acidic and it is more accessible than that in cyclohexanecarboxaldehyde; the alkoxide adduct **46** could abstract this hydrogen to yield alcohol **50** before the addition of trimethyloxonium tetrafluoroborate. It should be pointed out that the reason the more expensive trimethyloxonium tetrafluoroborate was used as the methylation agent rather than the relatively cheap CH_3I is that the reaction with CH_3I did not provide any useful amount of the desired methyl ethers.

It was hoped that 1-methoxy-1,2,2,2-tetraphenylethyl carbanion (**53**) would be more stable than the pentaphenylethyl carbanion (**45**) because of the electronegative inductive effect of the oxygen atom. Although it was expected that carbanion **53** would be sterically hindered, it may react with benzyne to afford methoxypentaphenylethane in the manner shown by earlier researchers during the synthesis of tetraphenylmethane.[79]

A series of experiments was carried out in order to select a suitable metalation reagent and optimize the reaction conditions (Table 11). In a typical run, the base was added to a solution of ether **47** in THF and the reaction was quenched with MeOD. After the aqueous work-up, the product was analyzed for the yield of deurated methyl ether **d-47** by using a proton integration method, the benzylic hydrogen singlet at 5.51 ppm vs. the methoxy methyl group's singlet at 3.21 ppm. The yield of carbanion **53** was assumed to be equal to the

Table 11. Metalation of 1-Methoxy-1,2,2,2-tetraphenylethane (47).



47 **53** **d-47**

Entry [a]	Base	Base/**47** mol ratio	T °C	Rect. Time	Color of mixture	Yield of **d-47**%
1	n-BuLi	4.0	-78	2 h	light red	9
2	n-BuLi	4.2	-78	6 h	light red	10
3 [b]	n-BuLi	4.0	rt	18 h	light red to yellow	0
4 [c]	t-BuLi	4.0	-78 to rt	24 h	light red to yellow	0
5	n-BuLi-KOtBu	1.6	-78	2 h	dard red	27
6	n-BuLi-KOtBu	5.0	-78	1 h	dark red	47
7	n-BuLi-KOtBu	4.0	-78	2 h	dark red	66

[a] There were 15 runs and 7 significant runs were selected. [b] For the first 50 min, the mixture was red, and then it turned to yellow. [c] The reaction was run at -78 °C for 2 h and showed a red color. The temperature was then warmed to room temperatue and stirring was continued for another 22 h and the red color vanished.

yield of deurated ether **d-47**.

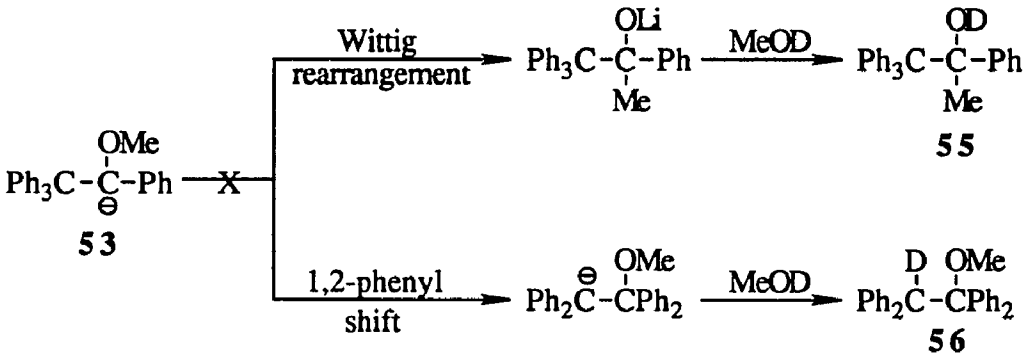
In experiments with n-BuLi at -78 °C (entry #1 and #2), the solution acquired light red colors, which turned out contained less than 10% of the desired carbanion **53**. When the carbanion **53** was generated at room

temperature (entry #3) or at -78 °C then warmed to room temperature (entry #4), the characteristic benzylic anion color vanished and the reaction product is merely the parent methyl ether **47** and no deurated methyl ether **d-47** could be detected. This means that anion **53** is not stable at room temperature.

Potassium t-butoxide activates butyllithium for metalation reactions by modifying the tetra-n-butyllithium aggregate.[80] This mixture is considered as a super base and it cleanly metalates hydrocarbons in the low acidity range of pK_a of 35 to 50. By utilizing this super base for the metalation of methyl ether **47**, a dark red solution was observed for the first time. A 66% yield of anion **53** was secured upon treatment of **47** with 4 equivalent of n-BuLi-KOtBu for 2 h at -78 °C (entry #7).

It is worth mentioning that a variety of α-lithio ethers undergo Wittig rearrangement to give alkoxides, which upon acidification provide alcohols.[81] In all cases shown in Table 11, there was no evidence for products arising from the possible Wittig rearrangement or a 1,2-phenyl shift (Scheme 18).[82]

Unfortunately, attempts to synthesize methoxypentaphenylethane by the reaction of anion **53** with benzyne were unsuccessful. It gave a complex mixture which contained more than seven components. This may be



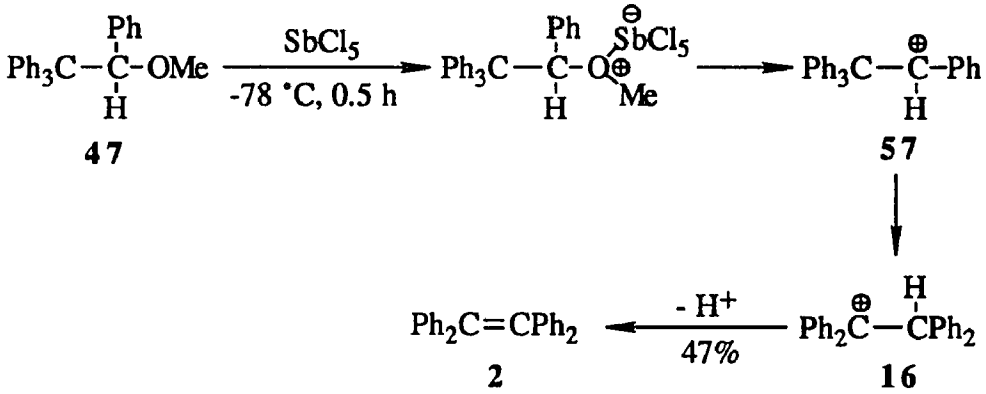
Scheme 18

ascribed to the steric hindrance of anion **53**, the incompletion of the metalation and use of large excess of the base.

Efforts were also made to synthesize 1-methoxy-1,2,2,2-tetraphenylethyl carbocation (**43**) from methyl ether **53** by hydride transfer reactions because it was felt that cation **43** might react with aromatic substrates to provide an analog of methoxypentaphenylethane.

The hydride transfer reaction is a common phenomenon in organic chemistry.[83] Trityl cation is one of the most useful hydride abstracting agents. Treatment of ether **47** with $Ph_3C^+BF_4^-$ did not give the desired cation **43** and ether **47** was recovered unchanged. This suggests that either: (1) trityl cation does not possess sufficient strength to remove the benzylic hydrogen of **47**, or (2) the benzylic hydrogen is too sterically hindered to be abstracted by the bulky trityl cation.

Antimony pentachloride has been successfully used as a hydride abstracting agent in the preparation of trityl, 9,10-dihydroanthracenyl and tropylium cations from their parent hydrocarbons.[65] When **47** was treated with $SbCl_5$ in CS_2 at -78 °C for 0.5 h, tetraphenylethylene (**2**) was isolated (Scheme 19).

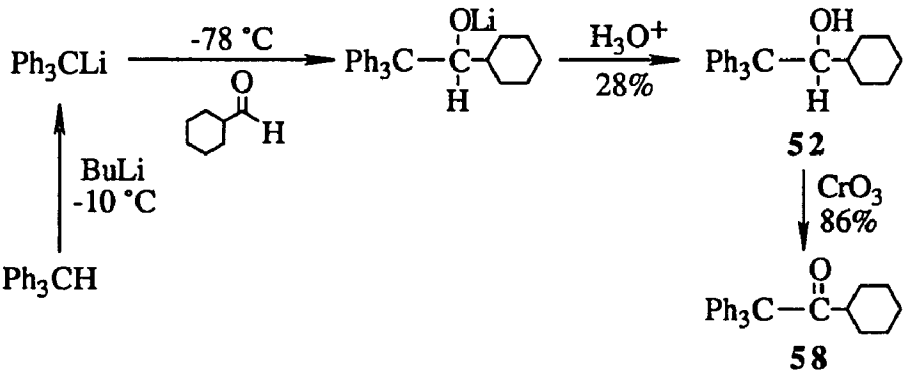


Scheme 19

Evidently, $SbCl_5$ must have coordinated to the methoxy group and as a result the C-O bond cleaved to yield the 1,2,2,2-tetraphenylethyl cation (**57**) which rearranged to the more stable 1,1,2,2-tetraphenylethyl cation (**16**). Cation **16** lost its β-hydrogen to give the observed product.

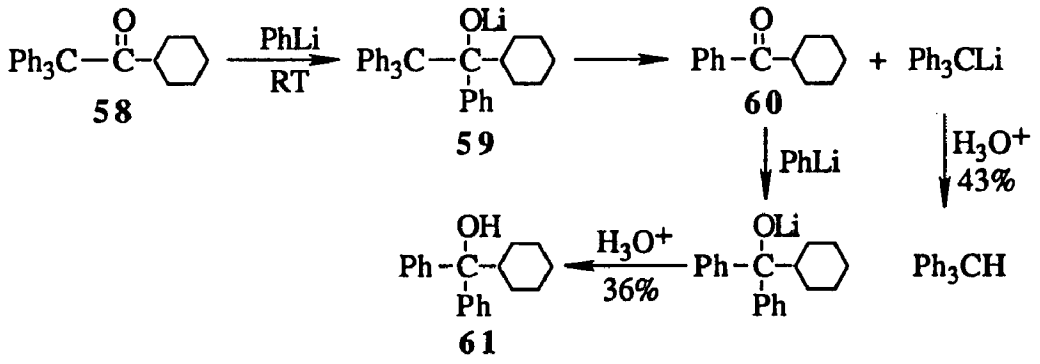
b). The Synthesis and Grignard Reactions of 1-Cyclohexyl-2,2,2-triphenyl-ethanone (58).

A search of the literature reveals that pentaphenylethanol is unknown. The reaction of benzopinacolone (**34**) with phenylmagnesium bromide or phenyllithium gave *o*-biphenyl trityl ketone by 1,4-addition of the Grignard reagent into the phenyl ring.[48] One possible way to circumvent the 1,4-addition problem is to synthesize cyclohexyl trityl ketone (**58**). Simple trityl alkyl ketone have been synthesized readily by CrO_3 oxidation of secondary alcohols obtained from the reaction of tritylllithium with aldehydes.[84] By following this procedure, 1-cyclohexyl-2,2,2-triphenylethanol (**52**) was synthesized in 27.7% yield from tritylllithium and cyclohexanecarboxaldehyde. Upon oxidation with CrO_3, alcohol **52** was smoothly converted to the desired ketone **58** in 86% yield (Scheme 20).



Scheme 20

The reactions of ketone **58** with PhLi and PhMgBr were studied. Upon treatment of **58** with PhLi at room temperature, a mixture of 43% triphenylmethane and 36% cyclohexyldiphenylmethanol (**61**) was obtained. This suggests that PhLi did add to the carbonyl moiety of ketone **58** as desired, but the resulting alkoxide adduct **59** fragmented into trityllithium and cyclohexyl phenyl ketone (**60**) (Scheme 21). In the presence of excess PhLi, ketone **60** was converted into cyclohexyldiphenylmethanol (**61**). Tritylithium, on the other hand, was hydrolyzed to triphenylmethane during aqueous work-up. Reactions run at -78 °C or with PhMgBr resulted in the recovery of the starting ketone **58**.



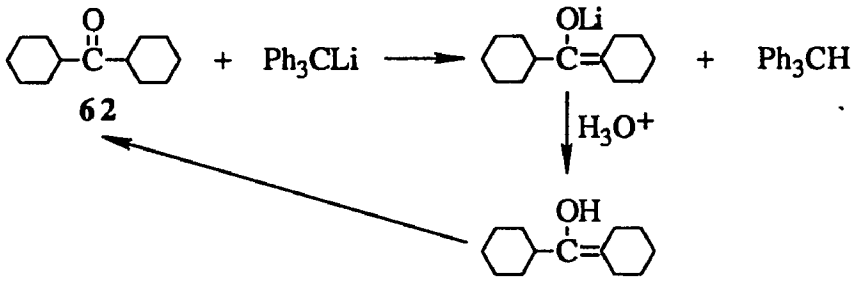
Scheme 21

c). The Reactions of Tritylithium with Dicyclohexyl Ketone (62).

It has been reported in the literature that treatment of benzophenone with tritylithium or tritylmagnesiumbromide does not give pentaphenylethanol but *p*-benzhydryltriphenylmethanol.[47] Presumably this occurs by electrophilic attack by the carbonyl carbon at one of the para positions of the organometallic reagent. Since tritylithium reacted with cyclohexanecarboxaldehyde to yield alcohol **52**, we wondered whether or not tritylithium would react with dicyclohexyl ketone (**62**) to produce 1,1-dicyclohexyl-2,2,2-triphenylethanol

(**63**) or in a manner similar to benzophenone.

It was found that upon adding ketone **62** to tritylllithium, the red color disappeared and ketone **62** and triphenymethane were recovered. This means that ketone **62** was enolized by tritylllithium and the enolate intermediate was converted back to **62** upon hydrolysis work-up as shown in Scheme 22.



Scheme 22

Recently, It has been shown that the 1,2-addition of Grignard reagents to a carbonyl group is significantly enhanced by cerium trichloride with remarkable suppression of side reactions, particularly enolization and conjugated addition.[85] While the activation by oxygen complexation may be the most important driving force for promoting 1,2-addition to carbonyl groups, another factor may be that the strong basicity of the Grignard reagent is moderated by formation of an organocerium reagent such as $RCeCl_2$.

The reactions of ketone **62** with Ph_3CLi were repeated in the presence of $CeCl_3$ and the results are summarized in Table 12. They apparently indicated that the enolization was not overcome by the addition of $CeCl_3$ in this system and the desired tertiary alcohol **63** was not formed. This seems to be ascribed to steric hindrance. The 1,1-dicyclohexyl-1-pentanol isolated in entry #6 (29% yield) probably resulted from the reaction of the unconsumed BuLi with ketone

Table 12.[a] The Reactions of $Ph_3CLi/CeCl_3$ with Dicyclohexyl Ketone (62).

Entry	Ketone **62** (mmol)	$CeCl_3$ (mmol)	Ph_3CLi (mmol)	Temp. (°C)	Trapping Reagent	Products
1	9.0	0	9.0	0	H_3O^+	Ph_3CH, **62**
2	4.0	6.0	6.0	0	H_3O^+	Ph_3CH, **62**, $Ph_3C\text{-}O\text{-}O\text{-}CPh_3$
3	2.0	3.0	3.0	-15	H_3O^+	Ph_3CH, **62**, $Ph_3C\text{-}O\text{-}O\text{-}CPh_3$
4[b]	3.0	4.5	4.5	-78	H_3O^+	Ph_3CH, **62**, $Ph_3C\text{-}O\text{-}O\text{-}CPh_3$
5[c]	4.0	6.0	6.0	-78	CH_3I	Ph_3CCH_3:Ph_3CH:**62** 1:2:2
6[d]	5.0	7.5	7.5	-78	H_3O^+	Bu-C(C_6H_{11})$_2$, Ph_3CH, **62** OH

[a] Ph_3CLi was prepared from the reaction of Ph_3CH with BuLi in THF at 0 °C for 1 h; The Ph_3CLi was added to the suspension of **62** and $CeCl_3$ in THF unless otherwise indicated. [b] In this run, ketone **62** was added to the mixture of Ph_3CLi and $CeCl_3$ in THF. [c] The product's ratio was determined by ^1H NMR. [d] In this run, Ph_3CLi was prepared at -78 °C.

6 2. The ^1H NMR analysis of the products in entry #5 reveals that the mole ratio of Ph_3CCH_3 to Ph_3CH to ketone **6 2** is 1:2:2. This evidently suggests that ketone **6 2** was exclusively enolized by $Ph_3CLi/CeCl_3$. A small amount of trityl peroxide isolated in entry #2, #3 and #4 may be arising from the oxidation of Ph_3CCeCl_2 by oxygen during hydrolysis work-up.

d). The synthesis of Tetracyclohexylethane-1,2-diol (64) and Tetracyclohexylethanone (65).

While pentaphenylethanol remains unknown, pentacyclopropylethanol has been synthesized from the addition of cyclopropyllithium to tetracyclopropylethanone.[86] It is of interest to see if pentacyclohexylethanol could be prepared from the reaction of cyclohexylmagnesium bromide with tetracyclohexylethanone (**65**) because pentacyclohexylethanol should be more sterically hindered than either pentaphenylethanol or pentacyclopropylethanol.

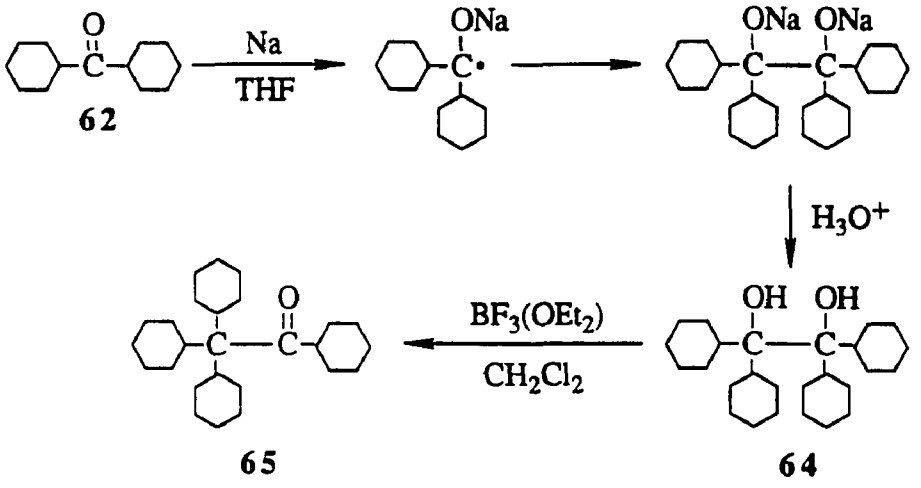
Recently, polycyclohexyl derivatives such as tricyclohexylmethane (**66**) and tetracyclohexylethylene (**67**) have started receiving attention.[87] It was found that in the lowest energy conformation, the cyclohexyl rings in **66** are oriented in a chiral gauche-gauche-anti conformation which showed 5 peaks in ^{13}C NMR at room temperature which implies that three cyclohexyl rings are equivalent and that the rotation of each ring is fast on the NMR time scale. The tetracyclohexylethylene (**67**), on the other hand, was shown to exist in a tongue and groove arrangement and it displays a total of 8 peaks in the aliphatic region which implies that there are two sets of cyclohexyl rings and the rotation of each ring is rapid on the NMR time scale. Earlier, Mislow et al have shown that *sym*-tetracyclohexylethane adopts a gauche conformation both in solution and in the solid state.[88] It displays 7 peaks in the ^{13}C NMR spectrum at room temperature, which suggests that rotation along the central ethane bond is fast and rotation of each ring along the pivot bond connecting to the central ethane carbon is restricted. Interestingly, *sym*-tetracyclohexylethane displays 11 peaks in the ^{13}C NMR spectrum at 193 K. This behavior is called "freezing out".

To our surprise, the synthesis of tetracyclohexylethanone (**65**) and its precursor tetracyclohexylethylene-1,2-diol (**64**) have not been described in the

literature, while their aromatic counterparts benzopinacol and benzopinacolone are well-known compounds. In 1928, a report described the synthesis of diol **64** by the treatment of ethyl oxalate with cyclohexylmagnesium bromide, but the sample described as diol **64** did not give a correct elemental analysis and it was later proven to be 1-hydroxy-1,1,2-tricyclohexylethanone rather than the desired diol **64**.[89]

Recently, low-valent titanium reagents[90] have been utilized in the preparation of 1,2-diols from both aromatic and aliphatic carbonyl compounds and it has been shown that low-valent titanium reagents such as $TiCl_3/K$, $TiCl_4/LiAlH_4$ and $TiCl_3$/Mg-Hg are capable of reducing carbonyl compounds to give a radical anion which then dimerizes to form a 1,2-diol alkoxide; if the 1,2-diol alkoxide intermediate is stable at room temperature, the 1,2-diol could be obtained upon hydrolysis; if the reaction is run under forcing condition, the 1,2-diol intermediate can undergo a deoxygenation reaction to give a olefin. Treatment of dicyclohexyl ketone (**62**) with $TiCl_3/K$ at 0 °C for 8 h, the starting ketone **62** was recovered unchanged. It has been shown that if the reaction was run under forcing condition, it gave tetracyclohexylethylene.[87] Magnesium/I_2 which has been successfully used in the synthesis of benzopinacol[69] from benzophenone did not react with ketone **62**.

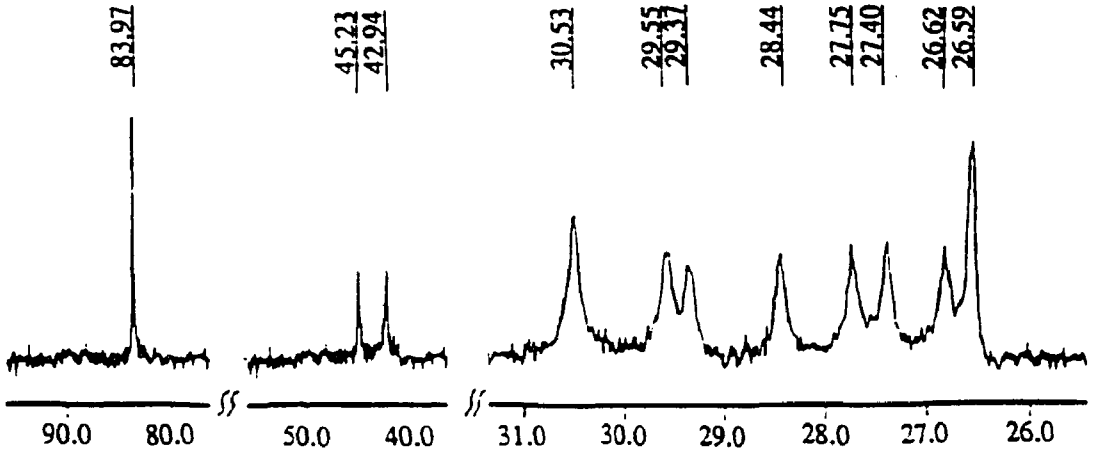
It is well-known that sodium metal reacts with benzophenone to give blue colored benzophenone ketyl radical anion which does not seem to dimerize to give benzopinacol after hydrolysis.[91] However, we found that treatment of dicyclohexyl ketone (**62**) with sodium metal in THF overnight at 0 °C, gave a 50% yield of diol **64** after hydrolysis. The diol **64** undergoes pinacol rearrangement to afford tetracyclohexylethanone (**65**) in 90% yield (Scheme 23).



Scheme 23

It is worth mentioning that ^{13}C NMR of diol **64** recorded at room temperature shows 11 peaks, which implies that the rotation along the central ethane bond as well as the rotation of each cyclohexyl ring along the bond connecting to the central ethane carbons is restricted. This is similar to the 1,1,2,2-tetracyclohexylethane at -193 K, where it showed 11 signals in the ^{13}C NMR spectrum. Besides the steric factor, intramolecular hydrogen bonding seems to play an important role here; it restricts the rotation along the central ethane

Figure 4. ^{13}C NMR Spectrum of Tetracyclohexylethane-1,2-diol



carbon-carbon bond and causes the "freezing out" behavior to occur at room temperature. Since this hydrogen bonding is not expected to completely stop the rotation about the ethane bond, it is therefore causing the broadening of ^{13}C NMR signals. Raising the temperature to 40°C did not change this broadening phenomenon very much.

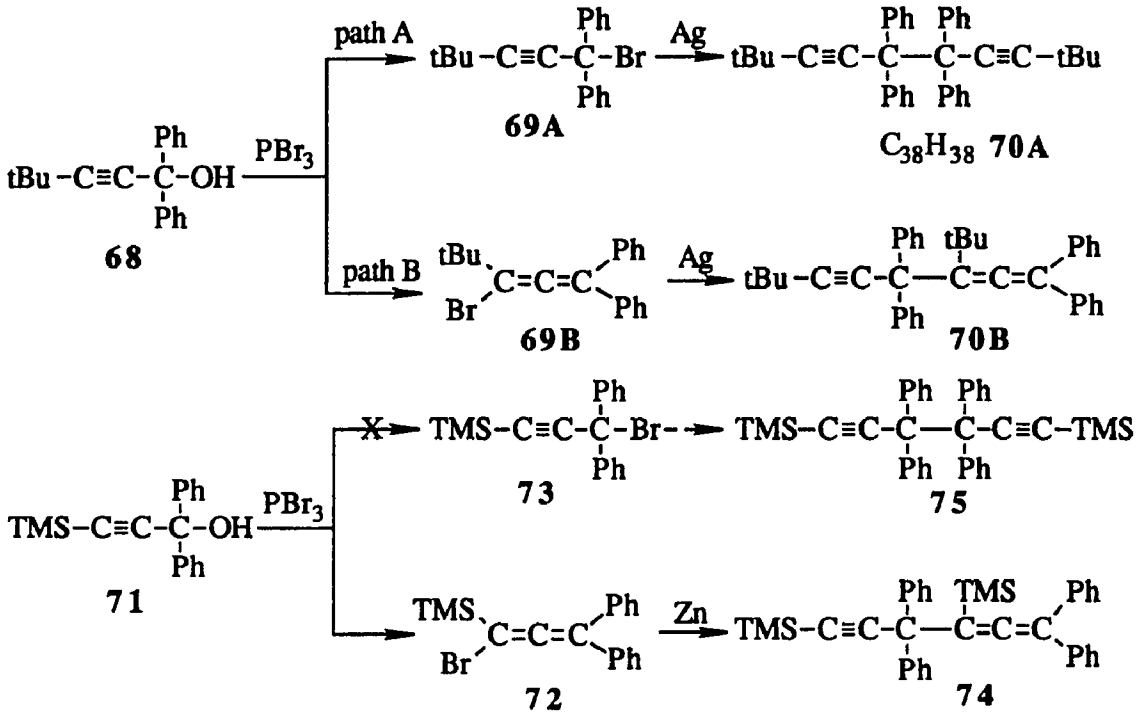
The reactions of ketone **65** with PhMgBr, PhMgBr/$CeCl_3$, PhLi, PhLi/$CeCl_3$ and cyclohexylmagnesiumbromide were carried out under various conditions and ketone **65** was recovered in all cases. These results suggested to us that enolization of ketone **65** by the Grignard reagents was occurring in preference to Grignard addition to the carbonyl group of ketone **65**.

e). The Synthesis of 3-trimethylsilyl-1,1-diphenyl-2-propyn-1-ol (71) and its reaction with PBr_3.

It was reported that upon treatment with PBr_3, alcohol **68** was converted into bromide **69A** which underwent dimerization with silver metal to give a hydrocarbon $C_{38}H_{38}$.[92] This hydrocarbon was described as **70A** although the authors noticed that it was much more stable than would be expected for **70A** toward heat and 40% sodium amalgam.

In an effort to synthesize dimer **75** using the same literature procedure as for the synthesis of **70A**, we prepared the 3-trimethylsilyl-1,1-diphenyl-2-propyn-1-ol (**71**) from the reaction of trimethylsilylethynylmagnesium bromide with benzophenone in 89% yield. In a like manner, 1,1-diphenyl-2-propen-1-ol was synthesized in 89.3% yield. Treatment of alcohol **71** with PBr_3 for 45 min at 0 °C, a 78.4% yield of allene **72** was obtained rather than the desired bromide **73**. Allene **72** reacted with Zn metal to give **74** in 83.6% yield. Based upon this finding, it seems very likely that the real structure for the product obtained from

the reaction of alcohol **68** with PBr_3 is actually allene **69B** and the possible structure for hydrocarbon $C_{38}H_{38}$ is **70B**.

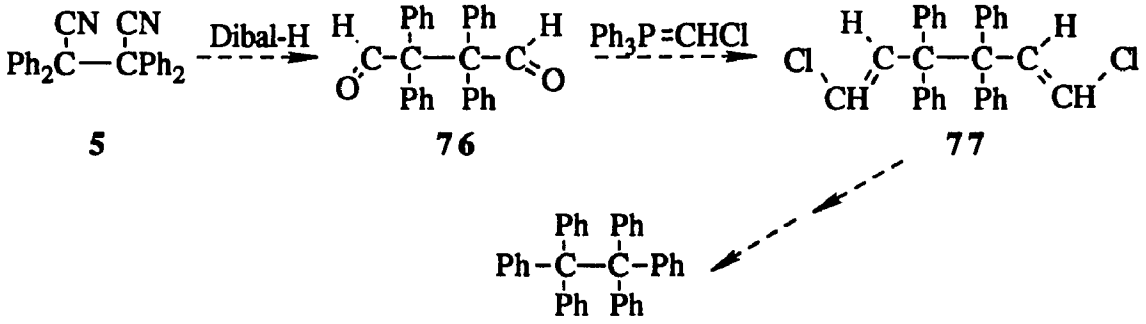


Scheme 24

f). The Reaction of Tetraphenylsuccinonitrile 5 with Dibal-H.

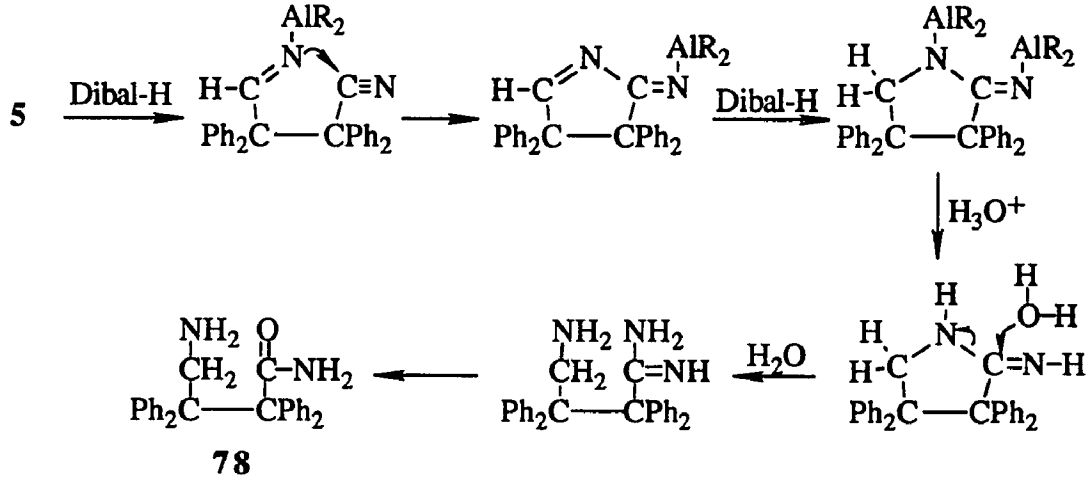
Another approach toward the synthesis of hexaphenylethane is to reduce tetraphenylsuccinonitrile (**5**) to tetraphenylsuccino-dialdehyde (**76**) using DiBAL-H[93] followed by Wittig reaction of the dialdehyde **76** with chloromethylenetriphenylphosphorane to give 1,6-dichloro-3,3,4,4-tetraphenyl-1,5-hexadiene (**77**). Diels-Alder elaboration of the alkene groups into aryl rings may afford a hexaphenylethane derivative (Scheme 25).

A preliminary study of the reaction of succinonitrile **5** with Dibal-H showned that It gave **78** (Scheme 26) rather than the desired dialdehyde **76**.



Scheme 25

The putative structure of the product was determined based on the ^{1}H and ^{13}C NMR spectra, but an elemental analysis of a sample of **78** did not match the calculated data for $C_{28}H_{26}N_2O$. It is possible that the sample was contaminated with inorganic salts such as Al_2O_3. Because we were unable to find a literature citation on the Dibal-H reduction of a vicinal dicycano compound, it is recommended for the future study that the reaction on some model compounds such as succinonitrile should be investigated.

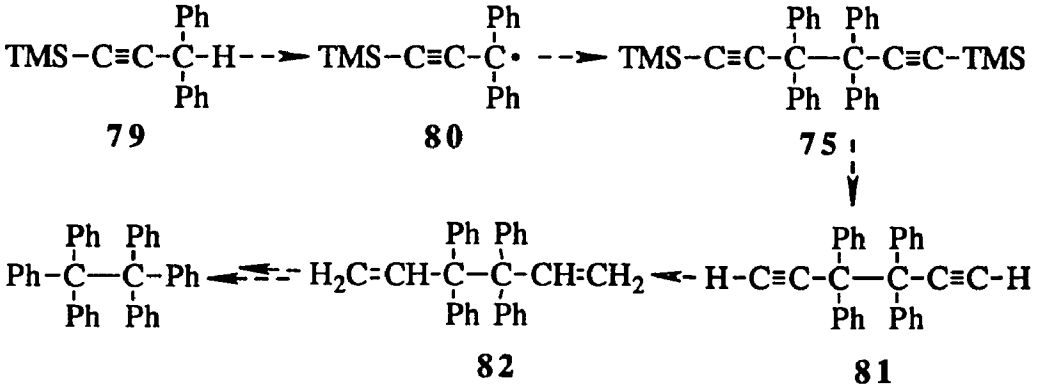


Scheme 26

V). Suggested Extensions for the Synthesis of Polyphenylethane Precursors to Hexaphenylethane.

From this study, it became clear that substituted tetraphenylethyl cations will unlikely undergo intermolecular aromatic substitution reactions to give pentaphenylethane derivatives. Therefore, attempts to synthesize hexaphenylethane from pentaphenylethyl cation with aromatic substrates are not recommended.

However, since succinonitrile **5**[56] forms readily by the alpha coupling of cyanodiphenylmethyl radicals, it occurred to us that 1,1-diphenyl-3-(trimethylsilyl)-2-propynyl radical (**80**) generated from 1-(trimethylsilyl)-3,3-diphenylpropyne (**79**) might couple similarly as shown in Scheme 27 to give **75**. The deprotection of 1-trimethylsilylalkynes with silver nitrate is a known procedure, and has been utilized in the synthesis of 3,3-diphenylpropyne from **79**.[94] Since alkenes undergo Diels-Alder reactions more readily than alkynes, it seems to be necessary to convert hexadiyne **81** to hexadiene **82**. Elaborating the unsaturated centers in **82** into benzene rings could be achieved by means of Diels-Alder reactions. If the synthesis of **82** could be secured, then a model



Scheme 27

precursor of hexaphenylethane will be in hand that possesses six sp^2 hybridized carbons attached to the central ethane carbons. If the thermal stability of **8 2** toward homolysis of the ethane carbon-carbon bond is very low, then it would seem likely that sterically more congested hexaphenylethane should possess a weaker central ethane bond than **8 2**.

EXPERIMENTAL SECTION

Materials and methods:

The following reagents were obtained from Aldrich Chemical Co. unless otherwise indicated and used without additional purification. n-BuLi (2.01 M in hexane), t-BuLi (2.0 M in hexane), lithium acetylide (90% complex with ethylenediamine), phenyllithium (2.0 M in cyclohexane), phenylmagnesium-bromide (1.0 M in THF), lithium aluminum hydride, sodium amide, calcium hydride, potassium tertiary butoxide, copper (I) bromide, phosphorus pentachloride, titanium trichloride, titanium tetrachloride (1.0 M in CH_2Cl_2), tin tetrachloride (1.0 M in CH_2Cl_2), antimony pentachloride, antimony pentachloride (1.0 M in CH_2Cl_2), aluminum trichloride, boron trifluoride etherate, trimethylsilylmethyl trifluoromethanesulfonate (TMSOTf), chlorotrimethylsilane, iodotrimethylsilane, trimethylsilyl cyanide (TMSCN), allyltrimethylsilane, vinyltrimethylsilane, trimethylsilyl acetylene, silver hexafluoroantimonate, silver tetrafluoroborate, trityl tetrafluoroborate (Cationics Inc.), trimethyloxonium tetrafluoroborate, 9-bromofluorene, benzophenone, dicyclohexylmethanol, diphenylacetonitrile, cyclohexene, *p*-toluenesulfonyl chloride (Baker Analyzed Reagent), acetyl chloride (Baker Analyzed Reagent), tertiary butyl hydroperoxide, liquid ammonia (LaRoche Industies Inc.), chlorine gas (Matheson Gas Products Inc.)

Methylene chloride (Baker Analyzed Reagent) was distilled over CaH_2 prior to use. Anhydrous diethyl ether (Fisher Scientific Co.) and tetrahydrofuran (Fisher Scientific Co.) were prepared by distilling the technical grade material from sodium metal and benzophenone. Benzene was shaken with concentrated sulfuric acid and distilled from CaH_2. Dry methanol and ethanol were obtained by distilling over magnesium. Pyridine was distilled over barium oxide before

use. 2-Propanol (Baker Analyzed Reagent) and allyl alcohol (Baker Analyzed reagent) were dried over potassium carbonate and distilled. 2,2-dimethoxypropane and trimethyl orthoformate (Aldrich Chemical Co.) were distilled at atmospheric pressure. Benzyl chloride (Fisher Scientific Co.) and benzhydryl chloride (Aldrich Chemical Co.) were distilled under reduced pressure immediately before use. Benzaldehyde (Fisher Scientific Co.), cyclohexanecarboxaldehyde (Aldrich Chemical Co.) and 1,2,3,6-tetrahydro-benzaldehyde (Aldrich Chemical Co.) were washed with 10% Na_2CO_3 aqueous solution, dried over $MgSO_4$ and distilled under reduced pressure. Cerium trichloride (Aldrich Chemical Co.) was dried *in vacuo* at 135-140 °C for 2 h before use.[85c]

3-Bromocyclohexene was prepared by bromination of cyclohexene with N-bromosuccinimde in 51% yield, bp 69-71 °C at 24 mmHg. 3-Trimethylsilyl-cyclohexene[95] was synthesized from 3-bromocyclohexene, magnesium metal and chlorotrimethylsilane in 32% yield, bp 58-59 °C at 9 mmHg (lit.[95] 45 °C at 5 mmHg). ^1H NMR (benzene d_6) δ: 0.0 (s, 9H), 1.3-2.1 (m, 7H), 5.71 (s, 2H); ^{13}C NMR (benzene d_6) δ: -3.15, 23.02, 24.12, 25.43, 26.37, 125.60, 128.09. IR (neat, cm^{-1}): 3020, 2930, 1640, 1240, 830. Dichlorodiphenylmethane was prepared according to the literature procedure[96] from benzophenone and PCl_5 in 83.8% yield, bp 190-193 °C at 30 mmHg. Chlorotriphenylmethane[97] was synthesized from triphenylmethanol and acetyl chloride in benzene in 92% yield, mp 110-111 °C (lit.[97] mp 111-113 °C). Silver trifluoroacetate[98], silver carbonate[99] and silver cyanate[100] were freshly prepared according to the literature procedures.

Instruments:

NMR spectra were recorded on a Bruker 250 MHz FT NMR spectrometer. Chemical shifts are reported in δ units, parts per million down field from internal tetramethylsilane for proton spectra. For the ^{13}C spectra the middle peaks of the mutiplet due to the deuterated solvents were the references ($CDCl_3$ at 77.01, acetone-d_6 at 29.8 and benzene-d_6 at 128.0)

Infrared spectra were taken using a Perkin-Elmer model 1320 spectrometer and a Perkin-Elmer model 1620 FT-IR. The infrared spectra of the liquids were obtained from the neat liquid between sodium chloride plates. Solid samples were pulverized with KBr using Wig-L-Bug amalgamater and pressed into discs.

X-ray data were obtained using a Enraf Nonius FR 590 CAD 41 diffractometer.

Flash chromatography was performed on silica gel (230-400 mesh) as described by Still.[101] Elemental analyses were done by Desert Analytics, National Chemical Consulting, Inc. and Galbraith Laboratory.

All the melting points were obtained using a Mel-Temp melting point apparatus and were uncorrected.

The Synthesis of Tetraphenylethylene (2)[102]. To a suspension of $TiCl_3$ (97.30 g, 0.63 mol) in 1000 mL of THF was added $LiAlH_4$ (12.38 g, 0.33 mol) in 10 portions with cooling. The resulting black mixture was stirred overnight and then was treated with a solution of benzophenone (57.50 g, 0.32 mol) in 230 mL of THF. The reaction mixture was refluxed for 6 h and 50 mL of EtOH was added, followed by 500 mL of 2N HCL solution. The solid was filtered and washed with water. Upon recrystallization from benzene-EtOH there was obtained 46.8 g of tetraphenylethylene (**2**) in 88.1% yield, mp 220-222 °C (lit.[103] mp 223-224 °C).

^{13}C NMR ($CDCl_3$) δ:126.39, 127.62, 131.31, 140.93, 143.70.

The Synthesis of *Sym*-tetraphenylethylene Dichloride (1). A solution of tetraphenylethylene (40 g, 0.12 mol) in 400 mL of $CHCl_3$ was treated with an excess of Cl_2 gas. After 2.5 h, the yellowish reaction mixture was concentrated and the resulting crude product was recrystallized from CH_2Cl_2-hexane twice to give 45.7 g of dichloride **1** in 94.2% yield, mp 169-171 °C dec. (lit.[54] mp 172 °C with decomposition).

^{13}C NMR ($CDCl_3$) δ:83.23, 125.96, 127.50, 132.75, 143.00.

The Reaction of *Sym*-tetraphenylethylene Dichloride (1) With 3-Trimethylsilylcyclohexene in the Presence of $TiCl_4$. To a solution of dichloride **1** (0.4142 g, 1.03 mmol) and 3-trimethylsilylcyclohexene (0.1715 g, 1.1 mmol) in 15 mL of CH_2Cl_2 was added $TiCl_4$ (1.1 mmol, 1.0 M in CH_2Cl_2) at 0 °C. After 15 min, the reaction mixture was poured into 20 mL of 10% $NaHCO_3$ solution. The product was extracted into CH_2Cl_2 (20 mL). The organic layer was

washed with H_2O, dried over Na_2SO_4 and concentrated. The resulting residue was taken into CH_3OH and tetraphenylethylene (**2**) was precipitated as a white solid (0.3276 g, 95%), mp 220-222 °C.

The Synthesis of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4), (entry #5, Table 2), the general procedure. To a solution of *sym*-tetraphenylethylene dichloride (**1**) (2.02 g, 5.0 mmol) and trimethylsilyl cyanide (0.50 g, 5.0 mmol) in 25 mL of dry CH_2Cl_2 was added $TiCl_4$ (5.0 mL, 1.0 M in CH_2Cl_2) dropwise with stirring at 0 °C. After 2.0 h, the reaction was quenched with 10 mL of CH_3OH and the product was extracted with CH_2Cl_2. The organic layer was washed with water, 10% $NaHCO_3$ solution and water, and then dried over Na_2SO_4. The solvent was removed and the crude product was recrystallized from acetone to afford 1.84 g (93%) of compound **4**, mp 140°C (dec.).

^1H NMR ($CDCl_3$) δ:7.12-7.32 (m);

^{13}C NMR ($CDCl_3$) δ: 61.26, 81.07, 122.33, 126.93, 127.18, 127.91, 128.14, 131.07, 131.63, 138.40, 142.18;

Anal. Calcd for $C_{27}H_{20}NCl$: C, 82.33; H, 5.12; N, 3.56; Cl, 9.00.

Found: C, 82.80; H, 5.21; N. 3.29; Cl, 8.65.

Attempted Cyanation of Benzyl Chloride. Under the above reaction conditions, benzyl chloride (0.6325 g, 5 mmol) did not react with TMSCN (0.55 g, 5.5 mmol) in the presence of $TiCl_4$ (5.5 mmol). After the aqueous work-up, benzyl chloride was recovered in 90% yield by a bulb-to-bulb distillation.

Cyanation of Chlorodiphenylmethane (entry #1, Table 2). Under reaction conditions similar to those for the synthesis of **4**, chlorodiphenylmethane (1.01 g, 5.0 mmol) was cyanated with TMSCN (0.55 g, 5.5 mmol) and $TiCl_4$ (5.5 mmol) to give diphenylacetonitrile (0.89 g, 93% yield), mp 71-72°C. This sample was identical in all respects with a commercially available sample.

^1H NMR ($CDCl_3$) δ:5.12 (s, 1H), 7.25-7.45 (m, 10H);

^{13}C NMR ($CDCl_3$) δ:42.52, 119.61, 127.67, 128.18, 129.14, 135.85.

Cyanation of Dichlorodiphenylmethane (6) (entry #2, Table 2). Under the same reaction conditions as for entry # 5, dichlorodiphenylmethane (**6**) (1.19 g, 5.0 mmol) reacted with TMSCN (0.50 g, 5.0 mmol) and $TiCl_4$ (5.0 mmol) to yield α-chlorodiphenylacetonitrile (**7**) (1.03 g, 91%) as a colorless oil after being purified by flash chromatography (CH_2Cl_2-hexane 1:2). The ^{13}C NMR data in the literature[57] for this compound inadvertently omitted one signal. The complete spectral data are follows:

^1H NMR ($CDCl_3$) δ: 7.36-7.38 (m, 6H), 7.54-7.58 (m, 4H);

^{13}C NMR ($CDCl_3$) δ: 63.34, 118.47, 127.07, 128.84, 129.57, 138.01;

IR (neat, cm^{-1}) 2250, 1490, 1445, 1180, 829, 740, 689.

In another run, when 5.0 mmol of **6** was treated with 11.0 mmol each of TMSCN and $TiCl_4$, a 98% yield of **7** was obtained.

Cyanation of α-Chlorodiphenylacetonitrile (7) (entry #3, Table 2). A solution of α-chlorodiphenylacetonitrile (**7**) (1.14 g, 5.0 mmol) and

TMSCN (0.55 g, 5.5 mmol) in 25 mL of dry CH_2Cl_2 was treated with $TiCl_4$ (5.5 mL, 1.0 M in CH_2Cl_2) at 0 °C. After being stirred for 2.0 h, the reaction mixture was allowed to warm to room temperature and stirring was continued overnight. It was quenched with 5 mL of CH_3OH and extracted with CH_2Cl_2. The organic phase was washed with water, 10% $NaHCO_3$ solution, water and dried over Na_2SO_4. Removal of the solvent and recrystallization of the crude product from CH_3OH-H_2O yielded 0.93 g of diphenylmalononitrile (**8**) (85% yield), mp 83-85 °C (lit.[58] mp 87.5 °C).

^1H NMR ($CDCl_3$) δ: 7.44-7.48 (m, 6H), 7.49-7.54 (m, 4H);

^{13}C NMR ($CDCl_3$) δ: 46.25, 114.73, 126.57, 129.73, 129.97, 133.56.

Cyanation of Chlorotriphenylmethane (entry #4, Table 2). Following the general procedure, 1.39 g (5.0 mmol) of chlorotriphenylmethane and 0.55 g (5.5 mmol) of TMSCN in 25 mL of CH_2Cl_2 were treated with $TiCl_4$ (5.5 mmol). Recrystallization of the crude product from hexane yielded 1.28 g (95%) of triphenylacetonitrile (**10**), mp 127-129 °C (lit.[60] mp 127-128 °C).

^1H NMR ($CDCl_3$) δ:7.21-7.24 (m, 6H), 7.32-7.35 (m, 9H);

^{13}C NMR ($CDCl_3$) δ: 57.40, 123.41, 128.10, 128.62, 128.78, 140.19.

Cyanation of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) (entry #6, Table 2). In a like manner, 1.97 g (5.0 mmol) of **4** and 0.55 g (5.5 mmol) of TMSCN in 35 mL of CH_2Cl_2 were treated with $TiCl_4$ (5.5 mmol). The reaction mixture was stirred at 0 °C for 2.0 h and another 2.5 h at room temperature, followed by methanol quenching. The crude product was recrystallized from acetic acid to afford 1.73 g (90%) of 2,2,3,3-

tetraphenylsuccinonitrile (**5**), mp 219-222 °C (lit.[56] mp 222-224 °C).

^{13}C NMR ($CDCl_3$) δ: 59.20, 121.09, 128.04, 128.54, 130.08, 136.99.

Dicyanation of *Sym*-tetraphenylethylene dichloride (1) (entry #7, Table 2). Under the reaction conditions similar to the synthesis of **4**, dichloride **1** (5 mmol) could be dicyanated with TMSCN (11.2 mmol) and $TiCl_4$ (15 mmol) to give a 54% yield of succinonitrile **5**.

The Synthesis of N-Triphenylmethyl Formamide. A mixture of triphenylmethyl chloride (30.0 g, 0.108 mol) in 55 mL of formamide was heated at 150 °C for 10 min. Upon cooling, the reaction mixture solidified and the crude product was collected by filtration. The solid was washed with water and recrystallized from acetone and there was obtained 25.04 g of N-triphenylmethyl formamide in 81% yield, mp 201-203°C (lit.[104] mp 203 °C).

Preparation of Trityl Isonitrile (9). A modified literature procedure[59] was used to prepare **9**. N-Tritylformamide (10.0 g, 34.8 mmol) in 40 mL of dry pyridine was treated with *p*-toluenesulfonyl chloride (8.25 g). The reaction mixture was stirred at room temperature for 6.0 h, and then cold water was added. After filtration, the solid was washed with water and recrystallized from hexane (or diethyl ether) to afford 4.33 g (46%) of purified **9**, mp 127-130 °C (lit.[59] mp 130-133 °C).

^{1}H NMR ($CDCl_3$) δ: 7.22-7.24 (m, 6H), 7.31-7.43 (m, 9H);

^{13}C NMR ($CDCl_3$) δ: 74.97, 128.08, 128.25, 128.31, 141.64, 157.82.

The Reaction of Trityl Isonitrile (9) With $TiCl_4$ at 0 °C and -78 °C. To a solution of **9** (0.27 g, 1.0 mmol) in 10 mL of CH_2Cl_2 was added $TiCl_4$ (1.0 mL, 1.0 M in CH_2Cl_2) at 0 °C. After 2.0 h, the reaction was quenched with 10 mL of CH_3OH, followed by aqueous work-up. Recrystallization of the crude product from hexane yielded 0.24 g (90%) of triphenylacetonitrile (**10**), mp 127-129 °C.

When the same reaction was run at -78 °C, **9** was recovered in 91% yield.

The Reaction of Trityl Isonitrile (9) With $Ph_3C^+BF_4^-$ at 0 °C and -78 °C. Trityl tetrafluoroborate (0.33 g, 1.0 mmol) was added to a solution of **9** (0.27 g, 1.0 mmol) in 10 mL of CH_2Cl_2 at 0 °C. After stirring for 2 h, the reaction was quenched with 10 mL of cold water. The products were extracted with CH_2Cl_2 and the combined organic layer was dried over Na_2SO_4 and concentrated. The solid residue was subjected to flash chromatography and the following results were obtained:

Triphenylacetonitrile (**10**)	0.26 g, 95% yield	CH_2Cl_2-hexane 3:7
Triphenylmethanol (**11**)	0.25 g, 95% yield	CH_2Cl_2-hexane 7:3

Similarly, when the reaction was carried out at -78 °C, **10** and **11** were isolated in 93% and 91% yields, respectively.

The Reaction of TMSCN With $Ph_3C^+BF_4^-$. $Ph_3C^+BF_4^-$ (0.33 g, 1.0 mmol) was added to a solution of TMSCN (0.099 g, 1.0 mmol) in 10 mL of CH_2Cl_2 at 0 °C. After being stirred for 2 h at the above temperature, the reaction mixture was poured into ice cold H_2O. The product was extracted into CH_2Cl_2 and the organic layer was washed with H_2O, dried (Na_2SO_4) and concentrated.

Recrystallization of the crude product from hexane afforded 0.2572g of **10** in 96% yield.

Cyanation of Chlorotriphenylmethane With TMSCN and $TiCl_4$ at -78 °C. The general cyanation procedure was followed, except that the reaction was run at -78 °C. After quenching the reaction with 20 mL of CH_3OH, followed by aqueous work-up, 1.31 g (96% yield) of methyl trityl ether was obtained (recrystallized from 95% EtOH), mp 79-81 °C (lit.[62] mp 82.6-82.9 °C).

^1H NMR ($CDCl_3$) δ:3.03 (s, 3H), 7.14-7.45 (m, 15H);

^{13}C NMR ($CDCl_3$) δ:51.99, 86.99, 126.85, 127.70, 128.68, 143.93.

Thermal Decomposition of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) in Benzene. A solution of nitrile **4** (0.6167 g, 1.57 mmol) in 20 mL of dry benzene was heated at 80 °C for 2 h. and cooled. the pale yellow reaction mixture was concentrated to a small volume and CH_3OH was added. Upon cooling in an ice bath, 0.4801 g of white solid was formed and filtered. The ^1H NMR and ^{13}C NMR showed that it was a mixture of the starting nitrile **4**, dichloride **1** and succinonitrile **5**.

Thermal Stability Study of a Mixture of *Sym*-tetraphenylethylene Dichloride (1) and Tetraphenylsuccinonitrile (5) in Refluxing Benzene. A solution of dichloride **1** (0.4035 g, 1 mmol) and nitrile **5** (0.384 g, 1 mmol) in 30 mL of dry benzene was heated at 80 °C for 2 h. Benzene was then removed under reduced pressure and a residue was obtained. The ^1H NMR and ^{13}C NMR of which showed it was the starting

materials. No nitrile **4** cross radical coupling product was found.

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With n-BuLi. To a solution of nitrile **4** (0.3935 g, 1.0 mmol) in 20 mL of THF was added n-BuLi (2.0 mL, 2.01 M in THF) at -78 °C. A red color developed immediately and stirring was continued for 2 h. The reaction mixture was poured into ice-cold water, extracted with diethyl ether. The organic layer was washed with water, dried over Na_2SO_4 and concentrated. Recrystallization of the residue from benzene-EtOH yielded 0.3138 g (95% yield) of tetraphenylethylene (**2**), mp 219-222 °C.

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With Lithium Acetylide. Lithium acetylide (0.3680 g, 4 mmol, 90% complex with ethylenediamine) was added to a solution of nitrile **4** (0.4245 g, 1.08 mmol) in 20 mL of THF at room temperature. No reaction was observed (monitored by analytical TLC) after 2 h. DMSO (10 mL) was then added to the above suspension and a red color developed. After 8 h, the reaction mixture was hydrolyzed with water and extracted with CH_2Cl_2. The organic layer was separated, washed with water, dried (Na_2SO_4) and concentrated. The crude product was recrystallized from EtOH and there was obtained 0.3083 g of tetraphenylethylene (**2**) in 86% yield, mp 220-222 °C.

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With CF_3CO_2Ag in Benzene. To a stirring solution of nitrile **4** (0.394 g, 1.0 mmol) in 20 mL of dry benzene was added CF_3CO_2Ag (0.4418 g, 2.0 mmol) in one portion at 0 °C. After 1 h, the reaction mixture was poured into ice cold water and filtered. The solid AgCl was washed with CH_2Cl_2 and the filtrate was

separated. The organic phase was washed with H_2O, dried over Na_2SO_4 and concentrated. The resulting solid was recrystallized from benzene-ligroin (or from acetone-water) and yielded 0.3405 g (77% yield) of 3-trifluoroacetoxy-2,2,3,3-tetraphenylpropanenitrile (**17**) , mp 120-125 °C (dec.). Compound **17** decomposes on prolonged standing in the air.

^{13}C NMR ($CDCl_3$) δ: 63.91, 96.06, 114.47 (q, J_{C-F} = 287.56 Hz), 121.00, 127.31, 127.94, 128.26, 129.22, 130.22, 130.42, 135.57, 136.81, 153.90 (q, $^2J_{CCF}$ = 42.87 Hz);

IR (KBr, cm^{-1}): 2240, 1785, 1220, 1190, 1165, 1140.

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With CF_3CO_2Ag in a Mixture of CH_2Cl_2 and CH_3OH. To a solution of 3-chloro-2,2,3,3-tetraphenylpropanenitrile (**4**) (1.1811 g, 3.0 mmol) in 30 mL of dry CH_2Cl_2 and 15 mL of CH_3OH was added CF_3CO_2Ag (0.991 g, 4.51 mmol) in one portion at 0 °C. After being stirred for 0.5 h, the reaction mixture was poured into ice-cold H_2O and the solid was filtered and washed with CH_2Cl_2. The filtrate was separated and washed with water, dried over Na_2SO_4 and concentrated. The resulting solid was recrystallized from CH_2Cl_2-petroleum ether and yielded 1.1515 g (98%) of 3-methoxy-2,2,3,3-tetraphenylpropanenitrile (**19**), mp 120-140 °C (dec).

^1H NMR ($CDCl_3$) δ: 3.22 (s, 3H), 7.14-7.46 (m, 20H);

^{13}C NMR ($CDCl_3$) δ: 52.46, 62.40, 90.55, 122.73, 126.84, 127.14, 127.46, 127.98, 130.34, 131.24, 138.10, 139.74;

Anal. Calcd for $C_{28}H_{23}NO$: C, 86.34; H, 5.95.

Found: C, 86.30; H, 5.71.

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With $AgSbF_6$ in CH_2Cl_2 at -55 °C. To a solution of **4** (0.3935 g, 1.0 mmol) in 10 mL of dry CH_2Cl_2 was added $AgSbF_6$ (0.5653 g, 1.64 mmol) in one portion at -78 °C. When the temperature was allowed to rise gradually to -55 °C over a 15 min period, the reaction mixture turned red. After 2 h, 10 mL of methanol prechilled to -78 °C was added and the reaction mixture was poured into ice-cold H_2O and filtered. To the filtrate was added 20 mL of CH_2Cl_2 and the organic phase was separated, washed with H_2O, dried (Na_2SO_4) and concentrated. The resulting solid was recrystallized from CH_2Cl_2-petroleum ether and gave 0.2975 g (75% yield) of methoxy nitrile **19**.

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With $AgSbF_6$ in CH_2Cl_2 at -35 °C. To a solution of nitrile **4** (0.3935 g, 1.0 mmol) in 10 mL of dry CH_2Cl_2 was added $AgSbF_6$ (0.4364 g, 1.27 mmol) in one portion at -78 °C. The temperature was allowed to gradually rise to -35 °C over a 20 min period and during that time the reaction mixture turned red. After 1.5 h, 10 mL of methanol prechilled to -78 °C was added and the reaction mixture was poured into ice-cold H_2O and filtered. To the filtrate was added 20 mL of CH_2Cl_2 and the organic phase was separated, washed with H_2O, dried (Na_2SO_4) and concentrated. The resulting residue was diluted with methanol and a pale yellow solid was precipitated. Recrystallization of the crude product from CH_2Cl_2-CH_3OH yielded 0.0862 g (44%) of tetraphenylsuccinonitrile (**5**), mp 219-222 °C (lit.[56] mp 222-224 °C).

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With $SbCl_5$ (Table 4). $SbCl_5$ (1.0 M in CH_2Cl_2) was added to nitrile **4** in

20 mL of CH_2Cl_2 dropwise. The reaction was terminated by adding 10 mL of prechilled (-78 °C) CH_3OH, followed by 20 mL of 10% $NaHCO_3$ aqueous solution. The product was extracted into 20 mL of CH_2Cl_2. The organic layer was separated, washed with H_2O (2x20 mL), dried over Na_2SO_4 and concentrated. The crude product was washed with CH_3OH and solids were collected, dried and subjected to NMR analysis. The ^{13}C NMR showed the solids were a mixture of nitrile **4** and methoxy nitrile **19**. The relative yields of **4** and **19** were determined by a ^1H NMR integration method: the area at 3.22 ppm (from methoxy group of **19**) was arbitrarily set to 30 units and then 200 units of the total area near 7.3 ppm are known from **19** and the rest is from **4**. The following formula was used to calculate the relative yields.

$$\begin{cases} \dfrac{\dfrac{X}{389}}{\dfrac{Y}{393.5}} = \dfrac{200}{A-200} \\ X + Y = W \end{cases}$$

X = the weight of **19**

Y = the weight of **4**

A = the total area near 7.3 ppm

W = the weight of the mixture

Table 4, entry #1: $SbCl_5$ (3.0 mmol) was added, after 2.5 h of reaction time at -75 °C, the reaction was terminated; 0.7260 g of the mixture of **4** and **19** was obtained, total area near 7.3 ppm is 740. **19**, 25% ; **4**, 68%

Table 4, entry #2: $SbCl_5$ (3.0 mmol) was added, after 4.5 h of reaction time at -75 °C, the reaction was terminated; 0.7195 g of the mixture of **4** and **19** was obtained, total area near 7.3 ppm is 596. **19**, 37% ; **4**, 55%

Table 4, entry #3: $SbCl_5$ (3.0 mmol) was added, after 6.5 h of reaction

time at -75 °C, the reaction was terminated; 0.754 g of the mixture of **4** and **1 9** was obtained, total area near 7.3 ppm is 429. **1 9**, 45% ; **4**, 51%

Table 4, entry #4: $SbCl_5$ (3.0 mmol) was added, after 2.5 h of reaction time at -55 °C, the reaction was terminated; 0.7260 g of the mixture of **4** and **1 9** was obtained, total area near 7.3 ppm is 400. **1 9**, 46% ; **4**, 46%

Table 4, entry #5: $SbCl_5$ (5.0 mmol) was added, after 2.5 h of reaction time at -75 °C, the reaction was terminated; 0.6970 g of the mixture of **4** and **1 9** was obtained, total area near 7.3 ppm is 270. **1 9**, 66% ; **4**, 23%

Table 4, entry #6: $SbCl_5$ (5.0 mmol) was added, after 4.5 h of reaction time at -75 °C, the reaction was terminated; 0.7242 g of the mixture of **4** and **1 9** was obtained, total area near 7.3 ppm is 200. **1 9**, 93% ; **4**, 0%

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With $SnCl_4$. $SnCl_4$ (5 mL, 5.0 mmol, 1.0 M in CH_2Cl_2) was added to a solution of nitrile **4** (0.7882 g, 2.0 mmol) in 20 mL of CH_2Cl_2 at -75 °C. After 5 h, the blue colored reaction mixture was quenched with 10 mL of CH_3OH, followed by the usual aqueous work-up. Recrystallization of the crude product from CH_2Cl_2 - hexane afforded 0.75 g of nitrile **4** (95.2% recovery).

The Reaction of 3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4) With $AlCl_3$ in Benzene. To a solution of **4** (0.5772 g, 1.5 mmol) in 25 mL of CH_2Cl_2 and 10 mL of benzene was added dropwise a solution of $AlCl_3$ (0.3986 g, 3.0 mmol) in 10 mL of CH_2Cl_2 at -78 °C. The reaction mixture was allowed to warm to 0 °C and was stirred for 2 h. It was poured into ice-water and

the organic layer was separated, dried over Na_2SO_4 and concentrated. The resulting residue was diluted with 10 mL of methanol and a pale yellow solid was obtained. Recrystallization of the crude product from acetone yielded 0.1858 g (35%) of 9-(cyanodiphenylmethyl)fluorene (**21**), mp 253-255 °C.

^1H NMR ($CDCl_3$) δ: 5.16 (s, 1H), 6.51 (d, 2H, J= 7.74 Hz), 6.98 (t, 2H, J= 7.59 Hz), 7.29-7.58 (m, 12H), 7.71 (d, J= 7.61Hz, 2H);

^{13}C NMR ($CDCl_3$) δ: 53.60, 57.16, 119.86, 120.47, 125.94, 126.72, 127.69, 128.28, 128.35, 128.81, 138.65, 141.96, 142.05;

Anal. Calcd for $C_{27}H_{19}N$: C, 90.72; H, 5.36; N, 3.92.

Found: C, 90.86; H, 5.35; N, 3.96.

The Alternative Synthesis of 9-(Cyanodiphenylmethyl)-fluorene (21). $NaNH_2$ (0.447 g, 11.5 mmol) was dissolved in 30 mL of liquid NH_3 and diphenylacetonitrile (2.45 g, 10 mmol) was added in one portion. The resulting greenish-brown solution was stirred for 15 min and a suspension of 9-bromofluorene (1.94 g, 10 mmol) in 20 mL of ether was added dropwise over a 10 min period. The reaction mixture was stirred for another 0.5 h and liquid NH_3 was allowed to evaporated. The solid was filtered, washed with H_2O (4x40 mL) and recrystallized from acetone to give 3.39 g (95% yield) of **21**, mp 253-255 °C. The ^1H and ^{13}C NMR spectra were identical with those obtained as described above.

The Reaction of 1-Cyano-1,1,2,2-tetraphenylethyl Cation (18) With Allyltrimethylsilane.

Run 1: cation **18** was prepared from nitrile **4** (0.787 g, 2.0 mmol) and $SbCl_5$ (5 mmol) as described in Table 4, entry #6. After 4.5 h, allyltrimethylsilane

(1.1504 g, 10.1 mmol) was added and the red color disappeared. The stirring was continued for another 45 min and 10 mL of CH_3OH was added, followed by 20 mL of 10% $NaHCO_3$ solution. The product was extracted into CH_2Cl_2 and the organic layer was separated, washed with H_2O, dried (Na_2SO_4) and concentrated. The resulting residue was taken into CH_3OH and 0.6628 g of light yellow solid were formed and collected. The ^1H and ^{13}C NMR spectra showed that it contained nitrile **4** (0.6095 g, 77.3%) and methoxy nitrile **19** (0.053 g, 6.8%)

Run 2: Cation **18** was prepared as above, 2,2-dimethoxypropane (0.3388 g, 3.3 mmol) was added, followed by allyltrimethylsilane (1.1504 g, 10.1 mmol). After being stirred for another 2 h at -75 °C, the reaction mixture was treated with 10 mL of CH_3OH, followed by aqueous work-up. Upon adding CH_3OH to the residue, 0.5840 g of pale yellow solid was obtained. ^1H and ^{13}C NMR showed that it contained methoxy nitrile **19** (0.552 g, 70.9%) and succinonitrile **5** (0.032 g, 8.3%).

The Reaction of 1-Cyano-1,1,2,2-tetraphenylethyl Cation (18) With Phenol, Anisole and Furan.

Run 1: Cation **18** was prepared as described in Table 4, entry #6, phenol (1.8388 g, 17.4 mmol) was added and the stirring was continued for another 2 h at -75 °C, and then the temperature was allowed to warm to -40 °C over 1 h period. Upon quenching with CH_3OH, followed by aqueous work-up, it gave 0.3785 g of pale yellow solid. ^1H and ^{13}C NMR analyses showed it was a mixture of methoxy nitrile **19** (0.2476 g, 31.8%) and succinonitrile **5** (0.1282 g, 33.3%).

Run 2: The reaction of cation **18** generated with $SbCl_5$ with anisole (5 mL) gave a result similar to that found in Run 1: methoxy nitrile **19** (0.2036 g, 26.1%) and succinonitrile **5** (0.1342 g, 34.9%)

Run 3: Cation **18** was generated from nitrile **4** (0.787 g, 2.0 mmol) with $AgSbF_6$ (1.2026 g, 3.5 mmol) in 20 mL of CH_2Cl_2 at -55 °C. After 2 h, phenol (1.88 g, 20 mmol) was added and the temperature was slowly warmed to -40 °C over a period of 1 h. Upon quenching with CH_3OH, followed by aqueous work-up, a mixture of methoxy nitrile **19** (0.1564 g, 20.1%) and succinonitrile **5** (0.1471 g, 38.3%) was obtained as judged by ^1H and ^{13}C NMR.

Run 4: Cation **18** was generated with $AgSbF_6$ as above. Anisole (5 mL) was added and temperature was slowly warmed to -40 °C over 1 h period. After quenching with CH_3OH, followed by aqueous work-up, there was obtained a mixture of methoxy nitrile **19** (0.1914 g, 24.9%) and succinonitrile **5** (0.1470 g, 38.3%) as determined by ^1H and ^{13}C NMR.

Run 5: Cation **18** was prepared as in run 3. Furan (5 mL) was added to the red color solution and the temperature was allowed to warm to - 40 °C over 1 h period. Upon treatment with 10 mL of CH_3OH, followed by aqueous work-up, the reaction gave a mixture of methoxy nitrile **19** (0.2001 g, 25.7%) and succinonitrile **5** (0.1458 g, 38%) as suggested by ^1H and ^{13}C NMR.

The Reaction of 1-Cyano-1,1,2,2-tetraphenylethyl Cation (18) With TMSCl. Cation 18 was prepared by the treatment of nitrile **4** (0.787 g, 2.0 mmol) with $SbCl_5$ (5 mmol) at -75 °C for 4.5 h as described in Table 4, entry #6.

TMSCl (0.856 g, 7.9 mmol) was added and stirring was continued for another 0.5 h, followed by quenching with 10 mL of CH_3OH. The product was extracted into CH_2Cl_2, washed with H_2O (3 x 15 mL), dried (Na_2SO_4) , concentrated and diluted with 10 mL of CH_3OH. Upon cooling, light yellow crystals (0.7725 g) were formed, which contained 0.6548 g of nitrile **4** (83.2% yield) and 0.1177 g of methoxy nitrile **19** (15.1% yield) as judged by ^1H and ^{13}C NMR spectra.

The Reaction of 1-Cyano-1,1,2,2-tetraphenylethyl Cation (18) With TMSCN. Cation **18** was prepared as described in Table 4, entry #6. After 4.5 h at -75 °C, TMSCN (0.5208 g, 5.3 mmol) was added and stirring was continued for another 0.5 h, followed by quenching with 10 mL of CH_3OH. After hydrolysis with 20 mL of H_2O, the product was extracted into CH_2Cl_2 (80 mL), separated, washed with H_2O (3 x 15 mL), dried (Na_2SO_4) and concentrated. The resulting residue was recrystallized from CH_2Cl_2-CH_3OH and give 0.7550 g of succinonitrile **5** in 98.2% yield, mp 218-221 °C.

The Reaction of *Sym*-tetraphenylethylene Dichloride (1) With CF_3CO_2Ag in CH_2Cl_2. To a solution of dichloride **1** (1.2108 g, 3.0 mmol) in 30 mL of CH_2Cl_2 was added solid CF_3CO_2Ag (1.6575 g, 7.5 mmol) at 0 °C. After 2.0 h, 40 mL of H_2O was added. The solid was filtered and washed with CH_2Cl_2. The filtrate was separated and the organic layer was washed with H_2O, dried (Na_2SO_4) and concentrated. Recrystallization of the resulting residue from CH_2Cl_2-MeOH afforded 1.2588 g (75% yield) of diester **24** as white crystals, mp 100.5-101 °C dec.

^{13}C NMR ($CDCl_3$) δ: 95.20, 114.38 (q, $J_{C\text{-}F}$ = 286.99 Hz), 127.39, 129.08, 129.66, 133.54, 154.02 (q, $^2J_{CCF}$ = 42.81 Hz).

IR (KBr, cm^{-1}): 1785, 1220, 1150.

The diester **24** is quite unstable as expected for such a doubly benzylic ester. The saponification was carried out as follows: diester **24** (0.5045 g) was refluxed for 45 min in 15.2 mL of 1.37 N ethanolic NaOH solution (prepared by dissolving 8 g of Na in 250 mL of anhydrous ethanol, and after the solution was complete, 25 mL of H_2O was added). The excess alkali was titrated with 20.80 mL of 0.92 N HCl solution and a saponification equivalent of 301 was found. Thus the molecular weight of **24** is equal to 602. The theoretical MW of **24** = 558. The organic solid from the saponification was filtered and recrystallized from benzene : EtOH (1:10) to furnish 0.16 g (51%) of tetraphenylethylene oxide (**27**).

The Reaction of *Sym*-tetraphenylethylene Dichloride (1) With CF_3CO_2Ag in the Presence of H_2O. To a solution of dichloride **1** (0.4035 g, 1.0 mmol) in 10 mL of CH_2Cl_2 and 0.5 mL of H_2O was added solid CF_3CO_2Ag (0.5548 g, 2.5 mmol) at 0 °C. After 0.5 h, 20 mL of 10% $NaHCO_3$ solution was added. The solid was filtered and washed with CH_2Cl_2. The filtrate was separated and the organic layer was washed with H_2O, dried (Na_2SO_4) and concentrated. The resulting residue was recrystallized from benzene-ethanol (1:10) to give 0.3289 g (94%) of epoxide **27**, mp 205-206 °C (lit.[68] mp 204-205 °C).

^{13}C NMR ($CDCl_3$) δ:73.84, 127.03, 127.54, 128.24, 138.66.

The Reaction of *Sym*-tetraphenylethylene Dichloride (1) With CF_3CO_2Ag in the Presence of Phenol. To a solution of dichloride **1** (0.807 g, 2.0 mmol) and phenol (3.7635 g, 40 mmol) in 20 mL of CH_2Cl_2 was

added solid CF_3CO_2Ag (1.1066 g, 5.0 mmol) at 0 °C. After 2.5 h, the reaction was quenched by 40 mL of 10% $NaHCO_3$ solution. The solid was filtered and washed with CH_2Cl_2. The filtrate was separated and the organic layer was washed with H_2O, dried (Na_2SO_4) and concentrated. Recrystallization of the resulting residue from acetone gave 0.9632 g (90% yield) of ortho ester **31** as white crystals, mp 185-189 °C dec.

^{13}C NMR ($CDCl_3$) δ: 97.39, 114.72 (q, $^2J_{CCF}$ = 36.40 Hz), 120.36 (q, J_{C-F} = 291.59 Hz), 120.95, 123.82, 127.12, 127.15, 127.36, 127.41, 128.53, 128.84, 129.31, 140.91, 141.06, 152.79;

IR (KBr, cm^{-1}): 1180, 1115;

Anal. Calcd for $C_{34}H_{25}F_3O_3$: C, 75.83; H, 4.68.

Found: C, 75.59; H, 4.68.

The Reaction of *Sym*-tetraphenylethylene Dichloride (1) With $AgBF_4$ in the Presence of Phenol. To a solution of dichloride **1** (0.8071 g, 2.0 mmol) and phenol (3.9780 g, 42.3 mmol) in 20 mL of CH_2Cl_2 was added solid $AgBF_4$ (1.0605 g, 5.4 mmol) at 0 °C. The blue colored reaction mixture was stirred for 1 h, and was filtered. The solid was washed with CH_2Cl_2 and the filtrate was washed with 10% $NaHCO_3$ solution, H_2O, dried over Na_2SO_4 and concentrated. The resulting residue with diluted with CH_3OH and tetraphenylethylene (**2**) was obtained as a white solid (0.6043 g, 91%).

The Reaction of *Sym*-tetraphenylethylene Dichloride (1) With CF_3CO_2Ag in the Presence of Isopropyl Alcohol. To a solution of dichloride **1** (0.807 g, 2.0 mmol) in 20 mL of CH_2Cl_2 and 5 mL of isopropyl alcohol was added solid CF_3CO_2Ag (1.1050 g, 5.0 mmol) at 0 °C. After 2.5 h,

Na_2CO_3 (1.1635 g, 11 mmol) was added and the reaction mixture filtered. The solid was filtered and washed with CH_2Cl_2. The filtrate was separated and the organic layer was washed with H_2O, dried (Na_2SO_4) and concentrated. The resulting residue was separated by flash chromatography with a mixture of CH_2Cl_2 and petroleum ether (20 : 80, v : v) as a eluent and there was obtained 0.7720 g of ortho ester **32** (76.6% yield), mp 138-140 °C together with 0.1046 g of tetraphenylethylene oxide (**27**) (15.0% yield). For ortho ester **32**:

^1H NMR ($CDCl_3$) δ: 1.03 (d, J = 6.11 Hz, 6 H), 4.25 (septet, J = 6.11 Hz, 1 H), 7.07-7.28 (m, 20 H);

^{13}C NMR ($CDCl_3$) δ: 23.13, 68.91, 94.68, 113.60 (q, $^2J_{CCF}$ = 35.87 Hz), 120.42 (q, $J_{C\text{-}F}$ = 291.30 Hz), 127.27, 127.30, 127.34, 127.45, 128.10, 128.40, 142.18, 142.62;

Anal. Calcd for $C_{31}H_{27}F_3O_3$: C, 73.78; H, 5.40.

Found: C, 73.52; H, 5.42.

The Reaction of *Sym*-tetraphenylethylene Dichloride (1) With CF_3CO_2Ag in the Presence of Allyl Alcohol. To a solution of dichloride 1 (0.807 g, 2.0 mmol) in 20 mL of CH_2Cl_2 and 5 mL of allyl alcohol was added solid CF_3CO_2Ag (1.1108 g, 5.0 mmol) at 0 °C. After 2.5 h, Na_2CO_3 (1.1000 g, 10 mmol) was added and the reaction mixture was filtered from unreacted Na_2CO_3 and AgCl. The solid were filtered and washed with CH_2Cl_2 and the filtrate was separated and the organic layer was washed with H_2O, dried (Na_2SO_4) and concentrated. The resulting residue was separated by flash chromatography and the following results were obtained: ortho ester **33**: 0.6696 g, 66.7% yield, mp 106-108 °C, CH_2Cl_2 : pet. ether (20 : 80); epoxide **27**: 0.0726 g, 10.4% yield, CH_2Cl_2 : pet. ether (20 : 80); benzopinacolone (**34**): 0.1025 g, 14.7%

yield, CH_2Cl_2 : pet. ether (50 : 50), mp 178-179 °C (lit.[70] mp 179-180 °C).

For ortho ester **33**:

^1H NMR ($CDCl_3$) δ: 4.10 (d, J = 4.97 Hz, 2 H), 5.03-5.16 (m, 2 H), 5.59-5.63 (m, 1 H), 7.01-7.27 (m, 20 H);

^{13}C NMR ($CDCl_3$) δ: 66.35, 97.07, 114.02 (q,$^2J_{CCF}$ = 35.47 Hz), 116.69, 120.73 (q, $J_{C\text{-}F}$ = 291.58 Hz), 127.01, 127.10, 127.26, 127.28, 128.64, 129.35, 133.00,142.18, 142.76;

Anal. Calcd for $C_{31}H_{25}F_3O_3$: C, 74.08; H, 5.01.

Found: C, 73.73; H, 5.07.

For ketone **34**: ^{13}C NMR ($CDCl_3$) δ: 71.10, 126.68, 127.62, 127.81, 130.91, 131.06, 131.69, 137.46, 143.20, 198.86.

The Synthesis of Benzopinacolone Dimethyl Ketal (39) (Table 6, entry #1). To a solution of dichloride **1** (0.806 g, 2.0 mmol) in 20 mL of CH_2Cl_2 and 10 mL of CH_3OH was added solid CF_3CO_2Ag (dried overnight) (1.1331 g, 5.13 mmol) in one portion at 0 °C. A white solid precipitated immediately. The reaction mixture was stirred for 2 h and 20 mL of 10% $NaHCO_3$ solution was added. The solid was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was separated, washed with H_2O (2x10 mL), dried (Na_2SO_4) and concentrated. The resulting residue was recrystallized from CH_2Cl_2-EtOH and 0.5238 g (67% yield) of benzopinacolone dimethyl ketal (**39**) was obtained as white crystals, mp 129-130.5 °C. The mother liquor was concentrated and recrystallized from EtOH-H_2O to give 0.1934 g (28% yield) of benzopinacolone (**34**), mp 178-179 °C (lit.[70] mp 179-180 °C).

For ketal **39**: ^1H NMR ($CDCl_3$) δ: 3.41 (s, 6H), 6.77 (d, J = 7.50 Hz, 2H),

7.01-7.25 (m, 18H);

^{13}C NMR ($CDCl_3$) δ: 53.71, 70.03, 110.49, 125.61, 126.35, 126.62, 128.01, 131.05, 132.47, 135.98, 145.18;

IR (KBr, cm^{-1}): 3020, 2920, 1595, 1490, 1440, 1095, 1040, 740, 690;

Anal. Calcd for $C_{28}H_{26}O_2$: C, 85.25; H, 6.64.

Found: C, 85.58; H, 6.65.

Table 6, entry #2. If the CF_3CO_2Ag was not dried overnight before using, the reaction gave a mixture of ketal **39** and ketone **34** which was separated by flash chromatography.

ketal **39**: 0.2622 g, 33% yield, CH_2Cl_2 : hexane (30 : 70)

ketone **34**: 0.4644 g, 66% yield, CH_2Cl_2 : hexane (50 : 50)

Table 6, entry #3. To a solution of dichloride **1** (0.806 g, 2.0 mmol) in 20 mL of CH_2Cl_2 and 10 mL of MeOH was added solid CF_3CO_2Ag (1.1178 g, 5.06 mmol) at 0 °C. After 2 h, anhydrous Na_2CO_3 (1.6218g, 15.3 mmol) was added and the stirring was continued for another 0.5 h. The solid was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was washed with H_2O (2x10 mL), separated, dried (Na_2SO_4) and concentrated. Recrystallization of the resulting residue from CH_2Cl_2-EtOH gave 0.7155 g (91%) of ketal **39**. The mother liquor was concentrated and recrystallized from EtOH-H_2O to give 0.0417 g (6%) of ketone **34**.

Table 6, entry #4. To a solution of dichloride **1** (0.806 g, 2 mmol) in 20 mL of CH_2Cl_2 and 10 mL of CH_3OH was added Ag_2CO_3 (0.5635 g, 2 mmol) at room temperature. After 2 h, the reaction mixture was filtered and the solid was

washed with CH_2Cl_2 (20 mL). The filtrate was washed with 20 mL of 10% $NaHCO_3$ solution, H_2O (2x10 mL), dried (Na_2SO_4) and concentrated. Recrystallization of the residue from CH_2Cl_2-EtOH afforded 0.5111 g of ketal **39** in 65% yield. Concentration of the mother liquor and recrystallization from EtOH-H_2O yield 0.1465 g of ketone **34** in 21% yield.

Table 6, entry #5. Dichloride **1** (0.806 g, 2.0 mmol) in 20 mL of CH_2Cl_2 and 10 mL of CH_3OH was treated with AgOCN (0.9035 g, 6 mmol) at room temperature. After 2 h, 20 mL of 10% $NaHCO_3$ aqueous solution was added and the solid was filtered and washed with CH_2Cl_2 (20 mL). The filtrate was separated, washed with H_2O (2x10 mL), dried (Na_2SO_4) and concentrated. The resulting residue was recrystallized from CH_2Cl_2-EtOH and 0.6319 g of ketal **39** was obtained in 80% yield. The mother liquor was concentrated and recrystallization of the residue from EtOH-H_2O yielded 0.0786 g of ketone **34** in 11% yield.

Table 6, entry #6. The above procedure was followed except in this run, anhydrous Na_2CO_3 (1.1305 g, 10.7 mmol) was added before aqueous work-up. After recrystallization from CH_2Cl_2-EtOH, ketal **39** (0.7265 g) was obtained in 92% yield and no ketone **34** could be detected.

Attempted Synthesis of Benzopinacolone Dimethyl ketal (39) from Benzopinacolone (34).

Run 1: A solution of ketone **34** (4.3500 g, 12.5 mmol) and *p*-toluenesulfonic acid (0.0134 g, 0.078mmol) in 15 mL of CH_3OH and 80 mL of benzene was refluxed for 48 h, during which time a total volume of 50 mL of solvent was distilled by means of a Dean Stark trap and fresh solvents were

introduced to keep the volume constant. The reaction was interrupted by adding 20 mL of 10% $NaHCO_3$ solution. The organic layer was separated, washed with H_2O, dried over Na_2SO_4 and concentrated. The resulting residue was recrystallized from benzene-EtOH and 4.13 g of the starting ketone **34** was recovered in 95% yield.

Run 2: A solution of ketone **34** (3.48 g, 10 mmol) and trimethyl orthoformate (1.455 g, 13.7 mmol), *p*-toluenesulfonic acid (0.1935 g, 1.12 mmol) in 30 mL of CH_3OH and 100 mL of benzene was refluxed for 72 h. The reaction was cooled and Na_2CO_3 1.06 g, 10 mmol) was added. The organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated. Recrystallization of the resulting residue from benzene-EtOH yielded 3.3190 g of ketone **34** in 94.4% yield.

Run 3: Ketone **34** (3.48 g, 10 mmoL), 2,2-dimethoxypropane (2.08 g, 20 mmol) and *p*-toluenesulfonic acid (0.0172 g, 0.1 mmol) in 30 mL of CH_3OH and 100 mL of benzene was refluxed for 36 h. it was then made basic by adding Na_2CO_3 (1.06 g, 10 mmol). The reaction mixture was transferred into a separatory funnel and washed with H_2O, dried over Na_2SO_4 and concentrated. Recrystallization of the residue from benzene-EtOH afforded 3.3215 g of starting ketone **34** in 95.4% yield.

The Reaction of Ketal 39 With Vinyltrimethylsilane in the Presence of Lewis Acids. To a solution of ketal **39** (0.394 g, 1 mmol) and vinyltrimethylsilane (0.12 g, 1.2 mmol) in 10 mL of CH_2Cl_2 was added $BF_3(OEt_2)$ (0.1561 g, 1.1 mmol) at -78 °C. After 1 h, 5 mL of methanol was added and the reaction mixture was poured into 10 mL of 10% $NaHCO_3$

solution. The product was extracted into CH_2Cl_2 and the organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated. Recrystallization of the resulting residue from 95% EtOH afforded 0.3156 g (91% yield) of ketone **34**.

A reaction run at 0 °C yielded ketone **34** in 87% yield.

The results obtained from the reactions with other Lewis acids such as $TiCl_4$ or TMSOTf were summarized in Table 9.

The Reaction of Ketal 39 With 3-trimethylsilylcyclohexene in the Presence of Lewis Acids. To a solution of ketal **39** (0.394 g, 1 mmol) and 3-trimethylsilylcyclohexene (0.1863 g, 1.2 mmol) in 10 mL of CH_2Cl_2 was added TMSOTf (0.2534 g, 1.1 mmol) at -78 °C. After 1 h, 5 mL of methanol was added and the reaction mixture was poured into 10 mL of 10% $NaHCO_3$ solution. The product was extracted into CH_2Cl_2 and the organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated. Recrystallization of the resulting residue from 95% EtOH afforded 0.3181 g (91% yield) of ketone **34**.

A reaction run at 0 °C gave ketone **34** in 95% yield.

The results obtained from the reactions with other Lewis acids such as $BF_3(OEt_2)$ or $TiCl_4$ were summarized in Table 9.

The Reaction of Ketal 39 With Furan in the Presence of $BF_3(OEt_2)$. To a stirred solution of Ketal **39** (0.394 g, 1.0 mmol) in 20 mL of furan was added $BF_3(OEt_2)$ (0.1420 g, 10 mmol) dropwise at -78 °C. After 2 h, the reaction mixture was poured into 20 mL of ice cold 10% $NaHCO_3$ solution and the product was extracted into CH_2Cl_2. The organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated. The crude product was recrystallized from 95% EtOH and 0.3345 g of ketone **34** in 96% yield.

The Reaction of Ketal 39 with Phenol in the presence of TsOH. A mixture of ketal **39** (0.394 g, 1.0 mmol), phenol (1.88 g, 20 mmol) and TsOH (0.0344 g, 0.2 mmol) in 20 mL of benzene was stirred at 0 °C for 3 h. The reaction mixture was poured into 20 mL of 1N NaOH. The organic phase was separated and the combined organic layer was washed with H2O, dried over Na2SO4 and concentrated. The resulting residue was taken into 10 mL of 95% EtOH and upon cooling in an ice bath 0.3224 g of ketone **34** was obtained in 93% yield.

The Synthesis of 1-Methoxy-1,2,2,2-tetraphenylethane (47). To a solution of triphenylmethane (3.6620 g, 15 mmol) in 50 mL of THF was added n-BuLi (15 mmol, 2.01 M in hexane) dropwise at 0 °C. After 1 h, the deep red trityllithium solution was cooled to -62 °C and benzaldehyde was added dropwise until the red color disappeared, followed by the addition of trimethyloxonium tetrafluoroborate (2.3156 g, 15.4 mmol). The reaction mixture was then warmed up to room temperature and poured into ice-cold H_2O. The product was extracted into diethyl ether and the organic layer was washed with H_2O, brine, dried over $MgSO_4$ and concentrated. Chromatography of the resulting residue on silica gel provided 3.0968 g of methyl ether **47** in 57% yield with hexane as eluent, mp 135-137 °C (recrystallized from EtOH).

^{1}H NMR ($CDCl_3$) δ: 3.21 (s, 3 H), 5.52 (s, 1 H), 6.75 (d, J = 7.4 Hz, 2 H), 7.02 (t, J = 7.4 Hz, 2 H), 7.1-7.35 (m, 16 H);

^{13}C NMR ($CDCl_3$) δ: 56.36, 63.92, 86.63, 125.93, 126.91, 127.03, 127.41, 130.31, 130.92, 137.91, 144.49;

Anal. Calcd for $C_{27}H_{24}O$: C, 88.97; H, 6.64.

Found: C, 89.25; H, 6.70.

Upon further eluting the column with 5% ethyl acetate in hexane, there was obtained 0.2665 g of 1,2,2,2-tetraphenylethanol (**48**) in 5% yield, mp 149-151 °C (lit.[105] mp 150-151 °C).

The Synthesis of 1-(3-Cyclohexenyl)-1-methoxy-2,2,2-triphenylethane (49). n-BuLi (15 mmol, 2.01 M in hexane) was added to a solution of triphenylmethane (3.66 g, 15 mmol) in 50 mL of THF at 0 °C. After 1 h, the red colored solution was chilled to -62 °C and 1,2,3,6-tetrahydrobenzaldehyde was added dropwise until the red color disappeared. the reaction mixture was quenched with trimethyloxonium tetrafluoroborate (2.32 g, 15.4 mmol) and the temperature was allowed to warm to room temperature. After hydrolysis with H_2O, the reaction product was extracted into diethyl ether, washed with brine, dried over $MgSO_4$ and concentrated. The resulting residue was separated by flash chromatography. Elution with hexane provided methyl ether **49** (0.2791 g) in 5.1% yield, mp 117-119 °C (recrystallized from EtOH).

^1H NMR ($CDCl_3$) δ: -0.2-0.0 (m, 1 H), 0.78-2.50 (m, 6 H), 3.44-3.47 (s, 3 H), 4.70-4.75 (s, 1 H), 5.2 -5.7 (m, 2 H), 7.11-7.4 (m, 15 H);

^{13}C NMR ($CDCl_3$) δ: 23.05, 25.28, 26.12, 26.74, 32.66, 34.70, 36.61, 60.88, 60.97, 63.39, 85.82, 88.08, 125.34, 125.70, 126.40, 127.37, 127.99, 128.40, 129.87, 129.94, 145.64;

Anal. Calcd for $C_{27}H_{28}O$: C, 88.00; H, 7.66.

Found: C, 87.97; H, 7.72.

Upon further eluting the column with 5% ethyl acetate in hexane, 1.93 g of 1-(3-cyclohexenyl)-2,2,2-triphenylethanol (**50**) was obtained in 36% yield, mp 157-162 °C (recrystallized from ethanol). ^1H NMR ($CDCl_3$) δ: -0.28 to -0.23

7.14-7.42 (m, 15 H); ^{13}C NMR ($CDCl_3$) δ: 22.72, 25.81, 32.96, 35.79, 62.49, 126.12, 126.84, 127.62, 127.97, 129.62, 144.99;

Anal. Calcd for $C_{26}H_{26}O$: C, 88.09; H, 7.39.

Found: C, 88.19; H, 7.34.

The Synthesis of 1-Cyclohexyl-1-methoxy-2,2,2-triphenylethane (51). Tritylllithium was prepared by the reaction of triphenylmethane (3.66 g, 15 mmol) with n-BuLi (15 mmol, 2.01 M in hexane) in 50 mL of THF at 0 °C for 1 h. The cyclohexanecarboxaldehyde was added to tritylllithium solution dropwise at -62 °C until the red color disappeared, and then trimethyloxonium tetrafluoroborate (2,2283 g, 15 mmol) was added. The reaction mixture was allowed to warm to room temperature, followed by hydrolysis with H_2O. The product was extracted into diethyl ether, washed with brine, dried over $MgSO_4$ and concentrated. The crude products were separated by flash chromatography to gave 1.614 g of methyl ether **51** in 29.1% yield (eluting with hexane), mp 118-120 °C (recrystallized from EtOH).

^1H NMR ($CDCl_3$) δ: -0.27 (d, J = 9.71 Hz, 1 H), 0.6-2.2 (m, 10 H), 3.46 (s, 3 H), 4.60 (s, 1 H), 7.10-7.37 (m, 15 H);

^{13}C NMR ($CDCl_3$) δ: 26.50, 26.70, 27.11, 27.80, 36.64, 40.91, 60.92, 63.57, 87.20, 125.62, 127.31, 129.93, 145.77;

Anal. Calcd for $C_{27}H_{30}O$: C, 87.52; H, 8.16.

Found: C, 87.88; H, 8.04.

Further eluting the column with 5% ethyl acetate in hexane provided 0.3073 g of 1-cyclohexane-2,2,2-triphenylethanol (**52**) in 5.75% yield, mp 134-136 °C (recrystallized from EtOH).

1H), 7.0-7.5 (m, 15 H);

^{13}C NMR ($CDCl_3$) δ: 26.17, 26.43, 26.66, 27.16, 34.46, 39.98, 63.21, 77.01, 126.03, 127.64, 129.75, 145.10;

IR (KBr, cm^{-1}) 3480, 2920, 2840, 1490, 1440, 1090, 700.

The Preparation of 1-Methoxy-1,2,2,2-tetraphenylethyl carbanion (53). To a solution of KOtBu (0.59 g, 5.26 mmol) and methyl ether **47** (0.48 g, 1.33 mmol) in 25 mL of THF was added n-BuLi (5.25 mmol, 2.01 M in hexane) at -78 °C. The red colored reaction mixture was stirred for 2 h and was quenched with prechilled (-78 °C) MeOD. After hydrolysis with 1N HCl, the product was extracted into diethyl ether, washed with brine, dried over Na_2SO_4 and concentrated. Recrystallization of the crude product from ethanol gave 0.456 g of a mixture of **d-47** (66%) and the parent methyl ether **47** (34%).

The Reaction of 1-Methoxy-1,2,2,2-tetraphenylethane (47) With $SbCl_5$. Antimony pentachloride (1.4024 g, 4.69 mmol) was added to a solution of **47** (0.7293 g, 2.0 mmol) in 25 mL of CS_2 at -78 °C and a dark red color was observed immediately. After 20 min at that temperature, the reaction was interrupted by the addition of 10 mL of MeOH. After hydrolysis with 10 mL of 10% $NaHCO_3$ solution, the reaction products were extracted into diethyl ether, washed with H_2O, dried (Na_2SO_4) and concentrated. The resulting residue was subjected to flash chromatography with hexane as the eluent. There was obtained 0.3125 g of tetraphenylethylene (**2**) in 46.9% yield and 0.200 g of methyl ether **47** was recovered (27.4%).

The Synthesis of 1-Cyclohexyl-2,2,2-triphenylethanol (52). To

a solution of triphenylmethane (16.11 g, 60.0 mmol) in 160 mL of THF was added n-BuLi (80 mmol, 2.0 M in hexane solution) at -6 °C (ice-NaCl bath). After being stirred for 1 h at -6 °C, the deep red solution was cooled to -78 °C and 8.15g (72.6mmol) of cyclohexanecarboxaldehyde was added dropwise via syringe until the red color disappeared. After the addition was completed, the reaction mixture was poured into 150 mL of saturated NH_4Cl aqueous solution. The aqueous layers were extracted with diethyl ether (4x50 mL). The unified organic phases were washed with 100 mL of water, dried over $MgSO_4$ and concentrated. The resulting yellowish oil was passed through a silica gel (250g, 60A) column; 10.2g (63.1%) of unreacted Ph_3CH was obtained by eluting with pure hexane and 6.50g (27.7% yield) of 1-cyclohexyl-2,2,2-triphenylethanol (**52**), mp 134-136 °C was obtained by 5% ethyl acetate in hexane.

The Synthesis of 1-Cyclohexyl-2,2,2-triphenylethanone (58). A solution of 5.64 g (15.9 mmol) of 1-cyclohexyl-2,2,2-triphenylethanol (**52**) in 100 mL of acetone was cooled down to -15 °C in an ice-methanol bath. A solution of 2.38 g of CrO_3 in 10 mL of water and 2.54 mL of concentrated H_2SO_4 was added dropwise to the reaction flask during 0.5 h with magnetic stirring and the internal temperature remained at -10 °C. After another 20 minutes, no unreacted alcohol **52** could be detected any more by TLC and the precipitate was filtered and washed with 2x50 mL of cold water. After drying over Na_2SO_4, the crude product was recrystallized from ethanol and there was obtained 4.82 g (85.9% yield) of 1-cyclohexyl-2,2,2-triphenylethanone (**58**), mp 141.5-142.5 °C .

^1H NMR ($CDCl_3$) δ: 0.9-1.55 (m,10 H), 2.73 (t, J= 11.26 Hz, 1H), 7.1-7.39 (m,15 H);

^{13}C NMR ($CDCl_3$) δ: 25.67, 25.77, 31.62, 49.18, 74.35, 126.62, 128.00, 130.51, 142.41, 211.66;

IR (KBr, cm^{-1}): 2940, 1700, 1490, 1440;

Anal. Calcd for $C_{26}H_{26}O$: C, 88.09; H, 7.39.
Found: C, 88.45; H, 7.34.

The Reaction of 1-Cyclohexyl-2,2,2-triphenylethanone (58) With PhLi. Phenyllithium (40 mL, 80 mmol, 2 M in cyclohexane) was added to trityl cyclohexyl ketone (0.708 g, 2 mmol) in 25 mL diethyl ether over 10 min at room temperature. After being stirred for 30 min, the reaction mixture was poured into 100 mL of saturated NH_4Cl-ice water. The organic layer was neutralized with 50 mL, 2N HCl. The aqueous layer and washings were extracted by 3x50 mL of diethyl ether. The unified organic layer was washed with 3x50 mL of water, dried over $MgSO_4$ and concentrated. The flash chromatography of the crude products gave the following results:

Triphenylmethane:	0.2183 g,	45%	with hexane
ketone **58**:	0.2842 g,	40%	with 2.5% ethyl acetate in hexane
alcohol **61**:	0.1893 g,	36%,	with 5% ethyl acetate in hexane

The Reaction of 1-Cyclohexyl-2,2,2-triphenylethanone (58) With PhMgBr in the Presence of $CeCl_3$. PhMgBr (2.3 mL, 2.3 mmol, 1.0 M in THF) was added to a suspension of $CeCl_3$ (0.5552 g, 2.25 mmol) in 10 mL of THF at 0 °C and the mixture was well stirred for 1.5 h at the same temperature. Then, cyclohexyl trityl ketone (**58**) (0.3987 g, 1.1 mmol) was added to the mixture. After being stirred for 0.5 h, the reaction mixture was allowed to warm to room temperature and stirring was continued for 64 h, and then it was poured

into 30 mL of ice cold H_2O containing 5 mL of 2 N HCl solution. The product was extracted into diethyl ether, washed with H_2O, dried (Na_2SO_4) and concentrated. Recrystallization of the residue from ethanol afforded 0.3750 g of the starting ketone(**58**) in 94.1% recovery, mp 140-142 °C.

The Synthesis of Dicyclohexyl Ketone (62). To a solution of dicyclohexylmethanol (56.64 g, 0.2885 mol) in 500 mL of acetone was added chromic acid solution (75 mL, 2.7 M chromic acid prepared from 27 g of chromium trioxide, 50 mL of H_2O and 23 mL of concentrated H_2SO_4, and then diluted to 100 mL with H_2O) in 2 mL portions with powerful stirring and the internal temperature remained at 25-45 °C. After completion of the addition, the reaction mixture was stirred for another 10 min, followed by adding 5 mL of 2-propanol. Acetone was removed in the rotary evaporator, and 50 mL of H_2O and 50 mL of diethyl ether were added to the residue, followed by filtration. The organic layer was separated, washed with H_2O, 10% $NaHCO_3$, brine, dried over $MgSO_4$ and concentrated. The crude dicyclohexyl ketone (**62**) was distilled under reduced pressure, bp 71.5-72 °C at 0.085 mmHg. The overall yield was 85.5%.

^1H NMR ($CDCl_3$) δ: 1.69-1.21 (m, 20 H), 2.48 (t, *J*=8.31 Hz, 1 H);

^{13}C NMR ($CDCl_3$) δ: 25.71, 25.87, 28.60, 49.14, 216.70;

IR (neat, cm^{-1}) 2930, 2850, 1695, 1449.

The Reaction of Dicyclohexyl ketone (62) With Trityllithium (Table 12, entry #1). In a 100 mL metallation flask under Argon was dissolved 2.19 g (8.96 mmol) of triphenylmethane in 30 mL of THF at 0 °C and reacted with 4.5 mL of BuLi (9.0 mmol, 2.0 M in hexane) and the resulting red

colored solution was stirred for 75 min. Dicyclohexyl ketone (**62**) (1.74 g, 8.96 mmol) was added dropwise and the mixture decolorized immediately. After 1 h at 0 °C, the reaction mixture was hydrolyzed with 50 mL of 2N HCl and then extracted with diethyl ether. The organic layer was washed with H_2O, dried over $MgSO_4$ and concentrated. The resulting residue was separated by flash chromatography eluting with hexane and there was obtained triphenylmethane (2.09 g, 95.4%) and ketone **62** (1.63 g, 93.7%).

Table 12, entry #2. The dicyclohexylketone (**62**) (0.776 g, 4.0 mmol) was added to a suspension of $CeCl_3$ (1.494 g, 6.0 mmol) in 20 mL of THF. The mixture was stirred at 0 °C for 1 h. In another flask, BuLi (2.95 mL, 5.8 mmol, 2.01 M in hexane) was added to Ph_3CH (1.4657 g, 6.0 mmol) in 15 mL of THF at 0 °C. After the Ph_3CLi was stirred for 1.5 h, it was added to the ketone **62**/$CeCl_3$ over a 10 min period. After being stirred for another 20 min, the reaction mixture was treated with 10% aqueous acetic acid (20 mL). The product was extracted into diethyl ether, the combined extracts were washed with 10% $NaHCO_3$ solution, brine and dried over $MgSO_4$. The ether solution was stored in the refrigerator over night and 0.0291g of Ph_3C-O-O-CPh_3 (1.9% yield) was obtained. The ether was removed under reduced pressure and the resulting residue was separated by flash chromatography. Upon eluting with hexane, triphenylmethane (1.3484 g, 92.0%) and ketone **62** (0.7356 g, 94.8%) were obtained.

Table 12, entry #3. Ketone **62** (0.375 g, 2.0 mmol) was added to a suspension of $CeCl_3$ (0.7443 g, 3.0 mmol) in 14 mL of THF. The mixture was well stirred at -15 °C for 1 h. In another flask, n-BuLi (1.4 mL, 2.8 mmol, 2.01M) was added to Ph_3CH (0.7334 g, 3.0 mmol) in 10 mL THF at 0 °C. After the

Ph_3CLi was stirred for 1 h, it was added to a ketone **62**/$CeCl_3$ suspension with the aid of a dropping funnel over a 10 min period . After being stirred for another 20 min at -15 °C, the reaction mixture was treated with 10% aqueous acetic acid (20 mL). The product was extracted into diethyl ether, the combined extracts were washed with brine, 10% $NaHCO_3$ solution, brine and dried over $MgSO_4$. The ether solution was stored in the refrigerator over night and 0.03 g of Ph_3C-O-O-CPh_3 (3.9% yield) was isolated. The mother liquid was concentrated under reduced pressure and the resulting residue was separated by flash chromatography and triphenylmethane (0.6689 g, 91.2%) and ketone **62** (0.3611 g, 96.3%) were obtained upon eluting with hexane.

Table 12, entry #4. BuLi (1.6 mL,3.2 mmol, 2.01 M in hexane) was added to a solution of Ph_3CH (1.105 g, 4.5 mmol) in 15 mL of THF at 0 °C. After the resulting Ph_3CLi was stirred for 1.5 h, it was added to a suspension of $CeCl_3$ (1.1145 g, 4.5 mmol) in 15 mL of THF which had been stirred for 1 h at 0 °C. After 50 min, the mixture was cooled to -78 °C and a solution of ketone **62** (0.59 g, 3.0 mmol) in 10 mL of THF was added via a dropping funnel over a 10 min period . After being stirred for another 20 min, the reddish reaction mixture was poured into ice cold saturated NH_4Cl solution. The product was extracted into diethyl ether, the combined extracts were washed with H_2O, 10% $NaHCO_3$ solution, brine and dried over $MgSO_4$. The Ph_3C-O-O-CPh_3 (0.0144 g, 1.2%) was obtained as a precipitate from the diethyl ether solution after storing in a refrigerator overnight. The solvent was removed and the resulting residue was subjected to flash chromatography, which furnished triphenylmethane (1.0398 g, 94.1%) and ketone **62** (0.56 g, 95.0%).

Table 12, entry #5. Ketone **62** (0.7705 g, 4 mmol) was added to a

suspension of $CeCl_3$ (1.4801 g, 6 mmol) in 30 mL of THF. The mixture was stirred at 0 °C for 1 h and cooled to -78 °C. In another flask, BuLi (2.95ml, 5.93 mmol, 2.01 M in hexane) was added to Ph_3CH (1.4652 g, 6 mmol) in 30 mL of THF at 0 °C. After 1 h, the Ph_3CLi was added to the ketone **62**/$CeCl_3$ suspension. The resulting reddish reaction mixture was stirred for 30 min then was quenched by 1 mL of CH_3I. The products were extracted into diethyl ether, the combined extracts were washed with H_2O, 10%$NaHCO_3$ solution, brine and dried over $MgSO_4$. The diethyl ether was removed under reduced pressure and the resulting residue was analyzed by ^1H NMR and ^{13}C NMR which showed it was a mixture of the starting ketone **62**, triphenylmethane and 1,1,1-triphenylethane with the mole ratio of 2:2:1.

Table 12, entry #6. Ketone **62** (0.9716 g, 5 mmol) was added to a suspension of $CeCl_3$ (1.854 g, 7.5 mmol) in 35 mL of THF. The mixture was well stirred at room temperature for 1 h and cooled to -78 °C. In another flask, BuLi (4.0 mL, 8.0 mmol, 2.01M) was added to Ph_3CH (1.83 g, 7.5 mmol) in 7.5 mL of THF at -78 °C. After 1 h, it was added to the ketone **62**/$CeCl_3$ suspension and the stirring was continued for 30 min, the reddish reaction mixture was treated with 10% aqueous acetic acid (50 mL). The products were extracted into diethyl ether, the combined extracts were washed with 10% $NaHCO_3$ solution and brine and dried $MgSO_4$. The ether was removed under reduced pressure and the resulting residue was subject to flash chromatography on silica gel, the triphenylmethane (1.7147 g, 93.7%) and ketone **62** were obtained by using pet. ether as eluent. Further eluting the column with diethyl ether 0.3663 g (29.1% yield) of 1,1-dicyclohexyl-1-pentanol was obtained, mp 84-86 °C (recrystallized from EtOH-H_2O).

^{1}H NMR ($CDCl_3$) δ: 0.8-1.0 (m, 3 H), 1.0-1.35 (m, 14 H), 1.35-1.55 (m, 4 H),1.55-1.85 (m, 9 H);

^{13}CNMR ($CDCl_3$) δ: 14.08, 23.79, 26.41, 26.77, 27.05, 27.13, 27.24, 27.52, 34.49, 44.37, 77.13;

IR (KBr, cm^{-1}): 3456, 1400, 1200, 1120.

The Synthesis of Tetracyclohexylethane-1,2-diol (64). Dicyclohexylketone (**62**) (3.88 g, 20 mmol) was added dropwise to freshly cut sodium (1.38 g, 60 mmol) in 20 mL of dry THF. After 16 h, the unreacted sodium was removed and the reaction mixture was poured onto crushed ice and 30 mL of 1N HCl. A white solid was formed and was filtered. The crude sym-tetracyclohexylethane-1,2-diol (**64**) was recrystallized from benzene yielding 1.92 g (50%) white needle-like crystals which melted at 210-220 °C.

^{1}H NMR ($CDCl_3$) δ: 1.0-1.4 (m, 20 H), 1.55-2.1 (m, 24 H), 2.36 (s, 2 H);

^{13}CNMR ($CDCl_3$) δ: 26.59, 26.62, 27.40, 27.75, 28.44, 29.37, 29.55, 30.53, 42.94, 45.23, 83.97;

IR (cm^{-1}): 3397, 2920, 2915, 2845, 1442, 1388, 976;

Anal. Calcd for $C_{26}H_{46}O_2$: C, 79.94; H, 11.87.

Found: C, 80.00; H, 11.66.

The synthesis of Tetracyclohexylethanone (65). To a suspension of tetracyclohexylethane-1,2-diol (**64**) (2.98 g, 7.64 mmol) in 130 mL CH_2Cl_2 at room temperature under argon was added boron trifluoride etherate (1.154 g, 8.13 mmol), and the resulting pinkish mixture was stirred for 4 h at ambient temperature after which it was filtered and the filtrate was washed with 10%

$NaHCO_3$ solution, H_2O, dried over $MgSO_4$ and concentrated. The crude product was recrystallized from acetone and gave 2.57 g (90.4%) of tetracyclohexylethanone (**65**) as white crystals, mp, 149.5-150.5 °C.

^1H NMR ($CDCl_3$) δ: 1.0-1.45 (m, 20 H), 1.55-1.80 (b.d, 20 H), 2.07 (b.s, 3 H), 2.70 (t, 1H);

^{13}C NMR ($CDCl_3$) δ: 26.01, 26.14, 27.09, 29.42, 30.47, 30.62, 42.55, 46.72, 64.67, 211.09;

IR(cm^{-1}): 2926, 2913, 2848, 1681, 1446, 1309, 1142, 999.6, 891;

Anal. Calcd for $C_{26}H_{44}O$: C, 83.81; H, 11.90.

Found: C, 83.93; H, 11.98.

The Reaction of Tetracyclohexylethanone (65) With PhLi in THF (In diethyl ether gave the same results). Phenyllithium (6 mL, 10.8 mmol, 1.8 M in cyclohexane) was added to tetracyclohexylethanone (0.7443 g, 2.0 mmol) in 25 mL of THF. The reaction mixture was first stirred at room temperature for 1 h and then refluxed for 20 h, after which it was poured into 50 mL saturated NH_4Cl aqueous solution and extracted into CH_2Cl_2. The organic layer was washed with water, dried over $MgSO_4$ and concentrated. The resulting residue was dissolved in methanol and ketone **65** (0.6558 g, 89%) was recovered

The Reaction of Tetracyclohexylethanone (65) With PhLi in the Presence of $CeCl_3$. Tetracyclohexylethanone (**65**) (0.744 g, 2 mmol) was added to a suspension of $CeCl_3$ (0.711 g, 3 mmol) in 10mL of THF which was previously stirred at room temperature for 1 h. The mixture was well stirred at room temperature for 1h and cooled to -78°C. Phenyllithium (0.9 mL, 1.62

mmol, 1.8 M in cyclohexane) was added to the above mixture. After 0.5 h, the reaction mixture was treated with 10% aqueous acetic acid (20 mL) and was extracted into diethyl ether. The combined extracts were washed with H_2O and dried over $MgSO_4$. The solvent was evaporated and 0.69 g of ketone **65** was recovered (92%).

The Reaction of Tetracyclohexylethanone (65) With PhMgBr. PhMgBr was prepared from bromobenzene (3.13 g, 20 mmol) and Mg turning (0.5797 g, 24 mmol) in 10 mL of THF. While the PhMgBr was still warm, tetracyclohexylethanone (**65**) (0.7432 g, 2 mmol) in 10 mL of THF was added dropwise. After the addition was completed, the reaction mixture was heated to reflux for 1 h and then was poured into 1N HCl solution. The product was extracted into diethyl ether, washed with H_2O, dried over $MgSO_4$ and concentrated. The resulting residue was taken into CH_3OH and 0.6901 g of ketone **65** was recovered (92%).

The Synthesis of 3-Trimethylsilyl-1,1-diphenyl-2-propyn-1-ol (71). To a solution of EtMgBr (33 mL, 3.0M in diethyl ether) in 20 mL of THF was added trimethylsilyl acetylene (9.73 g, 99 mmol) dropwise at 0 °C. After the reaction was subsided, the ice bath was removed and the stirring was continued for another 20 min. A solution of benzophenone (18.02 g, 100 mmol) in 50 mL of THF was added to the above Grignard reagent over 15 min and then the reaction was refluxed for 1 h. After being cooled in an ice bath, the reaction mixture was poured into 150 mL of ice cold 1N HCl. The product was extracted into diethyl ether and the organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated. The crude product was distilled under reduced pressure to give 24.60 g of 3-Trimethylsilyl-1,1-diphenyl-2-propyn-1-ol (**71**) in

88.8% yield, bp 163-165 °C at 1 mmHg.

^{1}H NMR ($CDCl_3$) δ: 0.27 (s, 9 H), 5.75 (s, 1 H), 7.30-7.65 (m, 10 H);

^{13}C NMR ($CDCl_3$) δ: -0.18, 74.55, 91.83, 107.85, 125.93, 127.54, 128.12, 144.76;

IR(cm^{-1}): 3547, 3452, 2959, 2169, 1450, 1251, 1056, 996, 855, 760, 698;

Anal. Calcd for $C_{18}H_{20}OSi$: C, 77.09; H, 7.19.

Found: C, 77.95; H, 7.25.

Synthesis of 1,1-Diphenyl-2-propen-1-ol. To vinylmagnesium bromide (47 mL, 47 mmol, 1M in THF) was added benzophenone (7.8327 g, 43 mmol) in 50 mL of THF over 20 min at room temperature. After being refluxed for 1 h, the reaction mixture was cooled and poured into 50 mL of 1N HCl. The product was extracted into diethyl ether and the organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated. The crude product was distilled under reduced pressure to give 8.067 g of 1,1-diphenyl-2-propen-1-ol in 89.3% yield, bp 142-144 °C at 0.78 mmHg.

^{1}H NMR ($CDCl_3$) δ: 2.41 (s, 1 H), 5.23-5.30 (m, 2 H), 6.40-6.50 (m, 1 H), 7.21-7.36 (m, 10 H);

^{13}C NMR ($CDCl_3$) δ: 79.35, 113.96, 126.85, 127.17, 128.05, 143.44, 145.68;

IR(cm^{-1}): 3558, 3456, 3059, 3027, 1636, 1599, 1490, 1448, 761, 701.

The Reaction of 3-Trimethylsilyl-1,1-diphenyl-2-propyn-1-ol (71) with PBr_3. PBr_3 (2.850 g, 10.5 mmol) was added to alcohol **71** (7.667 g, 27.4 mmol) in 100 mL of pet. ether. After being stirred for 1 h, the reaction

mixture was diluted with 50 mL of diethyl ether and it was poured into 30 mL of 10% $NaHCO_3$. The organic layer was separated, washed with H_2O, dried over Na_2SO_4 and concentrated. The resulting residue was dissolved in 20 mL of pet. ether. The solution was stored at -15 °C overnight and 0.7372 g of allene **72** in 87.4% yield, mp 52-54 °C.

^1H NMR (acetone-d_6) δ: 0.30 (s, 9 H), 7.38-7.44 (m, 10 H);

^{13}C NMR ($CDCl_3$) δ: -1.57, 89.66, 113.37, 128.00, 128.52, 128.70, 135.07, 204.57;

Anal. Calcd for $C_{18}H_{19}BrSi$: C, 62.97; H, 5.58; Br, 23.27.

Found: C, 63.25; H, 5.67; Br, 22.76.

The Reaction of Allene 72 with Zn in Benzene. To a solution a allene **72** (0.8420 g, 2.45 mmol) in 20 mL of benzene was added Zn metal (0.7332 g, 11.2 mmol) at room temperature. After being stirred for 3 h, the reaction mixture was filtered and the filtrate was concentrated. The resulting residue was recrystallized from 95% EtOH to give 0.5383 g of **74** in 83.6% yield, mp 66-68 °C.

^1H NMR ($CDCl_3$) δ: 0.18 (s, 9 H), 0.34 (s, 9 H), 7.08-7.51 (m, 20 H);

^{13}C NMR ($CDCl_3$) δ: -0.18, 74.55, 91.83, 107.85, 125.93, 127.54, 128.12, 144.76;

The Reduction of Tetraphenylsuccinonitrile (5) with DiBAL-H. DiBAL-H (15 mmol, 1.0 M in hexane) was added to a suspension of succinonitirle **5** (1.92 g, 5 mmol) in 50 mL of CH_2Cl_2 at 0 °C. After 3 h, the temperature was warmed to room temperature and the stirring was continued

solids were collected by filtration. Recrystallization of the crude product from MeOH-H_2O afforded 1.5992 g of the **78** in 78.8% yield, mp 264-266 °C (dec).

^1H NMR (methanol-d_4) δ: 4.91 (s, 2 H), 7.01-7.22 (m, 20 H);

^{13}C NMR ($CDCl_3$, DMSO-d_6) δ: 56.53, 61.00, 69.95, 126.61, 127.53, 127.61, 127.94, 128.64, 131.42, 138.23, 143.40, 173.34;

IR(cm^{-1}, KBr): 3700-2500 (broad), 1680, 1490, 1440, 1190, 1120, 740, 690;

Anal. Calcd for $C_{28}H_{26}N_2O$: C, 82.76; H, 6.40; N, 6.90.

Found: C, 72.10; H, 5.94; N, 5.74.

APPENDIX I

Intramolecular Bond Angles For Ortho Ester 31

atom	atom	atom	angle	atom	atom	atom	angle
C1	O1	C3	110.7(1)	C6	C5	H1	120.52
C2	O2	C3	109.4(1)	C5	C6	C7	121.2(2)
C3	O3	C28	120.8(2)	C5	C6	H2	118.95
O1	C1	C2	99.7(1)	C7	C6	H2	119.88
O1	C1	C4	106.0(1)	C6	C7	C8	118.9(2)
O1	C1	C10	106.8(1)	C6	C7	H3	121.24
C2	C1	C4	119.4(2)	C8	C7	H3	119.88
C2	C1	C10	114.9(1)	C7	C8	C9	120.2(2)
C4	C1	C10	108.5(2)	C7	C8	H4	120.31
O2	C2	C1	99.5(1)	C9	C8	H4	119.45
O2	C2	C16	105.9(1)	C4	C9	C8	121.9(2)
O2	C2	C22	107.4(1)	C4	C9	H5	118.82
C1	C2	C16	117.0(2)	C8	C9	H5	119.32
C1	C2	C22	117.5(2)	C1	C10	C11	119.8(2)
C16	C2	C22	108.1(2)	C1	C10	C15	121.7(2)
O1	C3	O2	108.5(2)	C11	C10	C15	118.5(2)
O1	C3	O3	111.7(2)	C10	C11	C12	120.4(2)
O1	C3	C34	114.3(2)	C10	C11	H6	119.55
O2	C3	O3	111.5(2)	C12	C11	H6	120.00
O2	C3	C34	104.9(2)	C11	C12	C13	120.1(2)
O3	C3	C34	105.9(2)	C11	C12	H7	121.32
C1	C4	C5	127.6(2)	C13	C12	H7	118.57
C1	C4	C5	127.6(2)	C13	C12	H7	118.57
C1	C4	C9	115.2(2)	C12	C13	C14	119.6(2)

atom	atom	atom	angle
C5	C4	C9	117.0(2)
C4	C5	C6	120.8(2)
C4	C5	H1	118.62
C13	C14	H9	120.48
C15	C14	H9	118.95
C10	C15	C14	120.7(2)
C10	C15	H10	119.17
C14	C15	H10	120.15
C2	C16	C17	120.4(2)
C2	C16	C21	121.3(2)
C17	C16	C21	118.3(2)
C16	C17	C18	120.9(2)
C16	C17	H11	119.07
C18	C17	H11	120.02
C17	C18	C19	120.3(2)
C17	C18	H12	119.69
C18	C18	H12	119.97
C18	C19	C20	119.6(2)
C18	C19	H13	120.61
C20	C19	H13	119.82
C19	C20	C21	120.6(2)
C19	C20	H14	120.43
C21	C20	H14	119.01
C16	C21	C20	120.3(2)
C16	C21	H15	119.46

atom	atom	atom	angle
C12	C13	H8	119.33
C14	C13	H8	121.07
C13	C14	C15	120.6(2)
C22	C23	C24	121.2(2)
C22	C23	H16	119.97
C24	C23	H16	118.80
C23	C24	C25	120.5(2)
C23	C24	H17	119.01
C25	C24	H17	120.53
C24	C25	C26	119.5(2)
C24	C25	H18	120.18
C26	C25	H18	120.34
C25	C26	C27	120.1(2)
C25	C26	H19	120.56
C27	C26	H19	119.32
C22	C27	C26	121.7(2)
C22	C27	H20	119.14
C26	C27	H20	119.13
O3	C28	C29	121.9(2)
O3	C28	C33	116.6(2)
C29	C28	C33	121.4(3)
C28	C29	C30	118.7(3)
C28	C29	H21	119.21
C30	C29	H21	122.10
C29	C30	C31	121.2(3)

atom	atom	atom	angle	atom	atom	atom	angle
C20	C21	H15	120.20	C29	C30	H22	119.37
C2	C22	C23	125.2(2)	C31	C30	H22	119.48
C2	C22	C27	117.5(2)	C30	C31	C32	119.6(3)
C23	C22	C27	116.9(2)	C30	C31	H23	120.79
C32	C31	H23	119.63	C31	C32	C33	120.3(3)
C31	C32	H24	119.78	C33	C32	H24	119.91
C28	C33	C32	118.9(3)	C28	C33	H25	121.27
C32	C33	H25	119.86	F1	C34	F2	106.7(2)
F1	C34	F3	107.1(2)	F1	C34	C3	112.1(2)
F2	C34	F3	107.2(2)	F2	C34	C3	111.2(2)
F3	C34	C3	112.2(2)				

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Distance For Ortho Ester 31

atom	atom	distance	atom	atom	distance
F1	C34	1.323(3)	C10	C11	1.388(3)
F2	C34	1.325(3)	C10	C15	1.379(3)
F3	C34	1.321(3)	C11	C12	1.385(3)
O1	C1	1.460(2)	C11	H6	0.979
O1	C3	1.373(2)	C12	C13	1.374(3)
O2	C2	1.450(2)	C12	H7	0.957
O2	C3	1.383(2)	C13	C14	1.370(3)
O3	C3	1.400(2)	C13	H8	0.949
O3	C28	1.403(3)	C14	C15	1.378(3)
C1	C2	1.603(3)	C14	H9	0.983
C1	C4	1.544(3)	C15	H10	0.968
C1	C10	1.520(3)	C16	C17	1.387(3)
C2	C16	1.527(3)	C16	C21	1.378(3)
C2	C22	1.540(3)	C17	C18	1.376(3)
C3	C34	1.529(3)	C17	H11	0.981
C4	C5	1.387(3)	C18	C19	1.365(3)
C4	C9	1.392(3)	C18	H12	0.983
C5	C6	1.382(3)	C19	C20	1.369(3)
C5	H1	0.965	C19	H13	0.969
C6	C7	1.370(3)	C20	C21	1.385(3)
C6	H2	0.978	C20	H14	0.975
C7	C8	1.373(3)	C21	H15	0.981
C7	H3	0.985	C22	C23	1.390(3)
C8	C9	1.376(3)	C22	C27	1.388(3)

atom	atom	distance	atom	atom	distance
C8	H4	0.968	C23	C24	1.383(3)
C9	H5	0.972	C23	H16	0.975
C24	C25	1.367(3)	C24	H17	0.972
C25	C26	1.372(3)	C25	H18	0.960
C26	C27	1.379(3)	C26	H19	0.965
C27	H20	0.972	C28	C29	1.378(3)
C28	C33	1.367(3)	C29	C30	1.375(4)
C29	H21	0.971	C30	C31	1.363(4)
C30	H22	0.967	C31	C32	1.377(4)
C31	H23	0.988	C32	C33	1.387(4)
C32	H24	0.973	C33	H25	0.986

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses

APPENDIX II

Intramolecular Bond Angles For Dimethyl Ketal 39

atom	atom	atom	angle	atom	atom	atom	angle
C2	O1	C27	120.3(3)	C6	C7	C8	120.7(5)
C2	O2	C28	121.4(3)	C6	C7	H4	119.67)
C2	C1	C3	113.1(3)	C8	C7	H4	119.63
C2	C1	C9	106.6(3)	C3	C8	C7	121.7(4)
C2	C1	C15	112.2(3)	C3	C8	H5	119.26
C3	C1	C9	108.3(3)	C7	C8	H5	119.08
C3	C1	C15	103.3(3)	C1	C9	C10	121.0(3)
C9	C1	C15	113.5(3)	C1	C9	C14	121.6(3)
O1	C2	O2	116.6(3)	C10	C9	C14	117.2(4)
O1	C2	C1	102.5(3)	C9	C10	C11	121.4(4)
O1	C2	C21	111.2(3)	C9	C10	H6	119.26
O2	C2	C1	107.0(3)	C11	C10	H6	119.32
O2	C2	C21	112.1(3)	C10	C11	C12	120.4(4)
C1	C2	C21	112.0(3)	C10	C11	H7	119.76
C1	C3	C4	117.3(4)	C12	C11	H7	119.86
C1	C3	C8	125.8(4)	C11	C12	C13	119.9(4)
C4	C3	C8	116.9(4)	C11	C12	H8	120.14
C3	C4	C5	121.5(4)	C13	C12	H8	119.98
C3	C4	H1	119.12	C12	C13	C14	120.2(4)
C5	C4	H1	119.33	C12	C13	H9	119.91
C4	C5	C6	120.1(4)	C14	C13	H9	119.89
C4	C5	H2	119.86	C9	C14	C13	120.9(4)
C6	C5	H2	120.03	C9	C14	H10	119.47
C5	C6	C7	119.0(4)	C13	C14	H10	119.62
C5	C6	H3	120.54	C1	C15	C16	122.6(3)

atom	atom	atom	angle	atom	atom	atom	angle
C7	C6	H3	120.45	C1	C15	C20	119.7(3)
C16	C15	C20	117.3(4)	C23	C24	H18	120.42
C15	C16	C17	121.5(4)	C25	C24	H18	120.31
C15	C16	H11	119.18	C24	C25	C26	120.5(4)
C17	C16	H11	119.29	C24	C25	H19	119.96
C16	C17	C18	119.9(4)	C26	C25	H19	119.59
C16	C17	H12	120.05	C21	C26	C25	121.1(4)
C18	C17	H12	120.08	C21	C26	H20	119.59
C17	C18	C19	119.4(4)	C25	C26	H20	119.35
C17	C18	H13	120.26	O1	C27	H21	109.43
C19	C18	H13	120.38	O1	C27	H22	109.38
C18	C19	C20	121.0(4)	O1	C27	H23	109.48
C18	C19	H14	119.31	H21	C27	H22	109.46
C20	C19	H14	119.65	H21	C27	H23	109.61
C15	C20	C19	120.8(4)	H22	C27	H23	109.48
C15	C20	H15	119.58	O2	C28	H24	109.35
C19	C20	H15	119.62	O2	C28	H25	109.40
C2	C21	C22	121.5(3)	O2	C28	H26	109.35
C2	C21	C26	121.5(4)	H24	C28	H25	109.59
C22	C21	C26	117.0(4)	H24	C28	H26	109.57
C21	C22	C23	121.8(4)	H25	C28	H26	109.57
C21	C22	H16	119.19	C23	C22	H16	119.05
C22	C23	C24	120.3(4)	C22	C23	H17	119.76
C24	C23	H17	119.91	C23	C24	C25	119.3(4)

Angles are in degrees. Estimated standard deviations in the least significant figure are given in parentheses.

Intramolecular Bond Distance For Dimethyl Ketal 39

atom	atom	distance	atom	atom	distance
O1	C2	1.427(4)	C12	C13	1.376(7)
O1	C27	1.393(5)	C12	H8	0.950
O2	C2	1.403(4)	C13	C14	1.384(6)
O2	C28	1.410(6)	C13	H9	0.950
C1	C2	1.591(5)	C14	H10	0.949
C1	C3	1.572(5)	C15	C16	1.377(6)
C1	C9	1.543(5)	C15	C20	1.391(6)
C1	C15	1.568(5)	C16	C17	1.397 (6)
C2	C21	1.523(5)	C16	H11	0.950
C3	C4	1.378(6)	C17	C18	1.371(7)
C4	C5	1.400(6)	C18	C19	1.359(7)
C4	H1	0.949	C18	H13	0.951
C5	C6	1.372(7)	C19	C20	1.387(6)
C5	H2	0.951	C19	H14	0.949
C6	C7	1.366(7)	C20	H15	0.950
C6	H3	0.949	C21	C22	1.388(5)
C7	C8	1.384(6)	C21	C26	1.398(5)
C7	H4	0.948	C22	C23	1.371(6)
C8	H5	0.951	C22	H16	0.951
C9	C10	1.386(5)	C23	C24	1.373(7)
C9	C14	1.398(5)	C23	H17	0.949
C10	c11	1.387(6)	C24	C25	1.379(7)
C10	H6	0.950	C24	H18	0.953
C11	C12	1.354(6)	C25	C26	1.374(6)

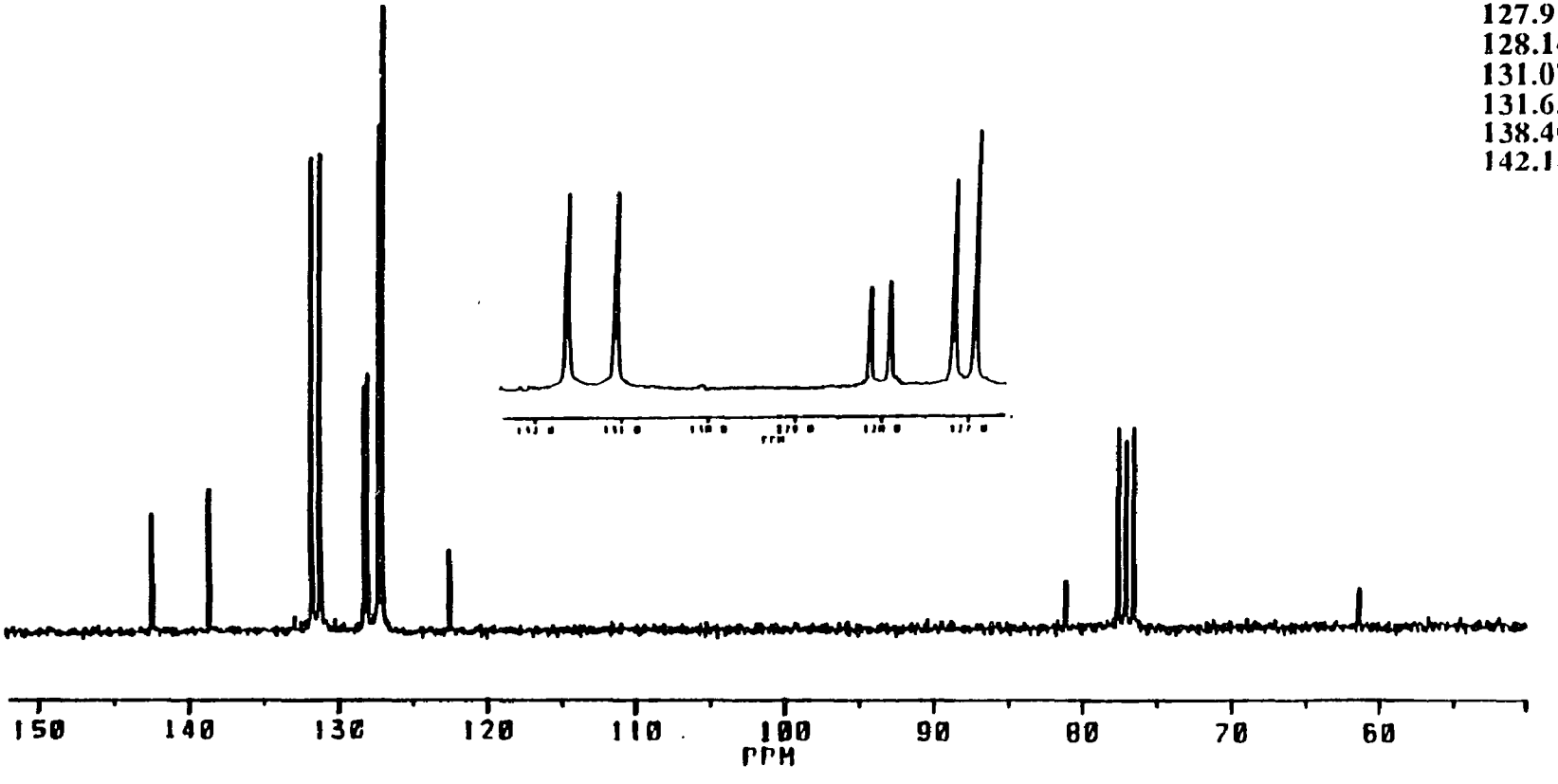
atom	atom	distance	atom	atom	distance
C11	H7	0.950	C25	H19	0.949
C26	H20	0.949	C27	H21	0.949
C27	H22	0.951	C27	H23	0.949
C28	H24	0.949	C28	H25	0.949
C28	H26	0.950			

Distances are in angstroms. Estimated standard deviations in the least significant figure are given in parentheses

APPENDIX III

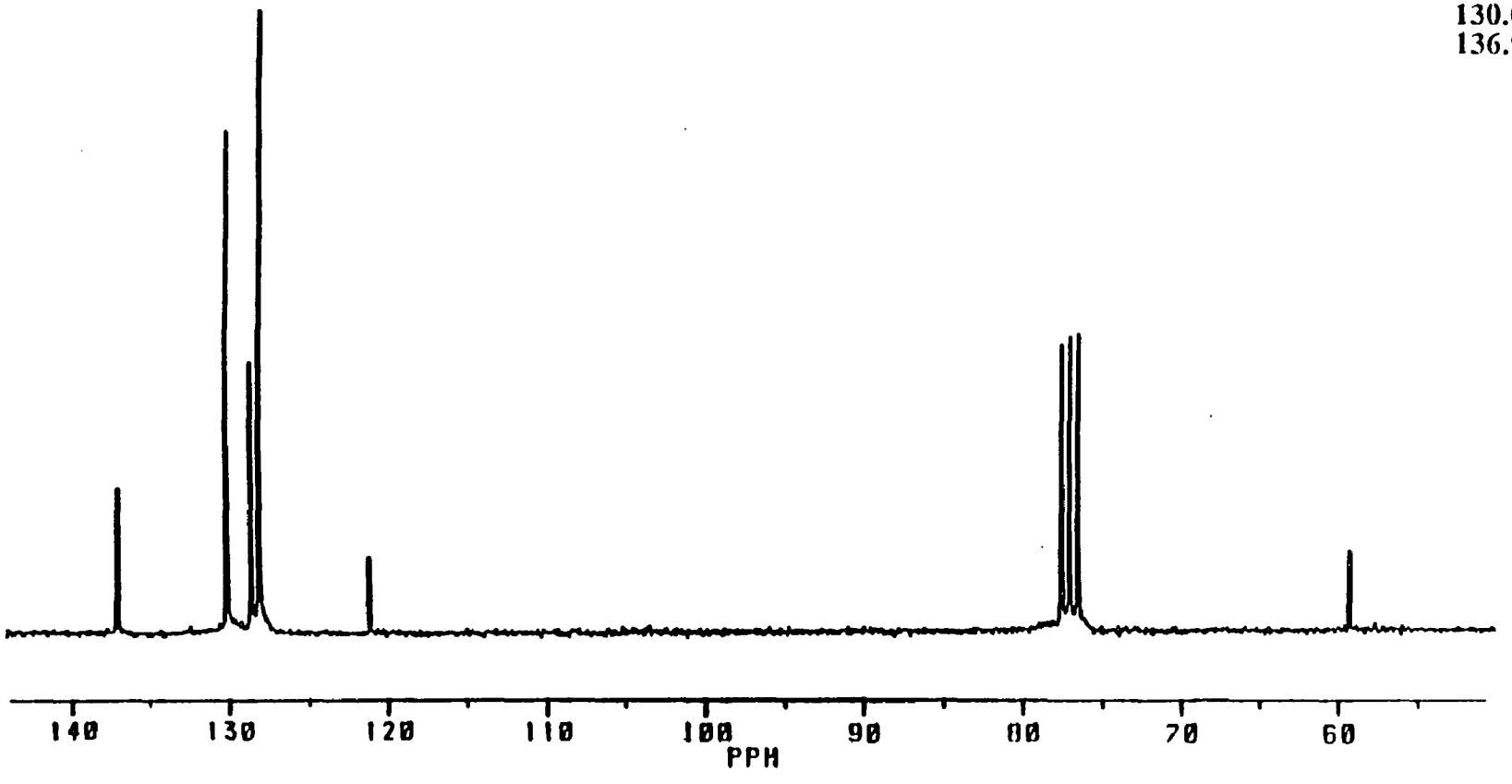
3-Chloro-2,2,3,3-tetraphenylpropanenitrile (4)

Chemical Shift (ppm)
61.26
81.07
122.33
126.93
127.18
127.91
128.14
131.07
131.63
138.40
142.18



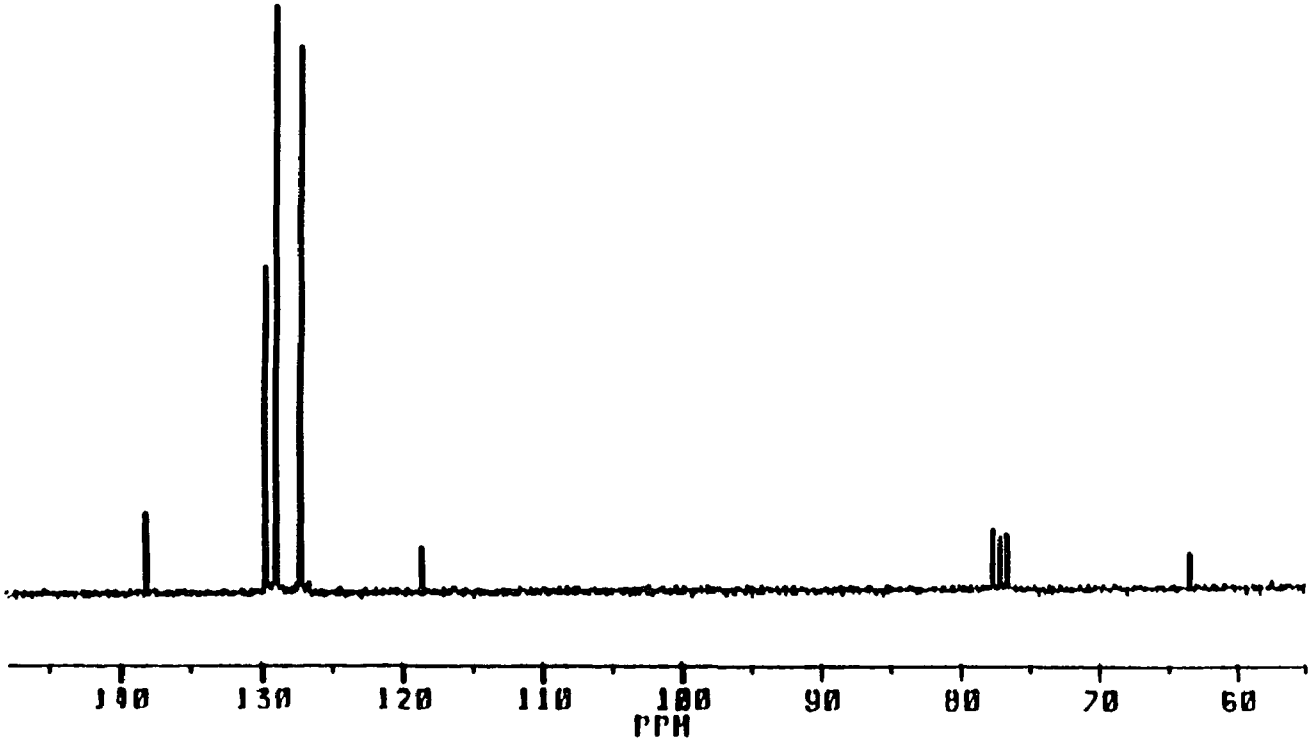
2,2,3,3-Tetraphenylsuccinonitrile (5)

Chemical Shift (ppm)
59.20
121.09
128.04
128.54
130.08
136.99

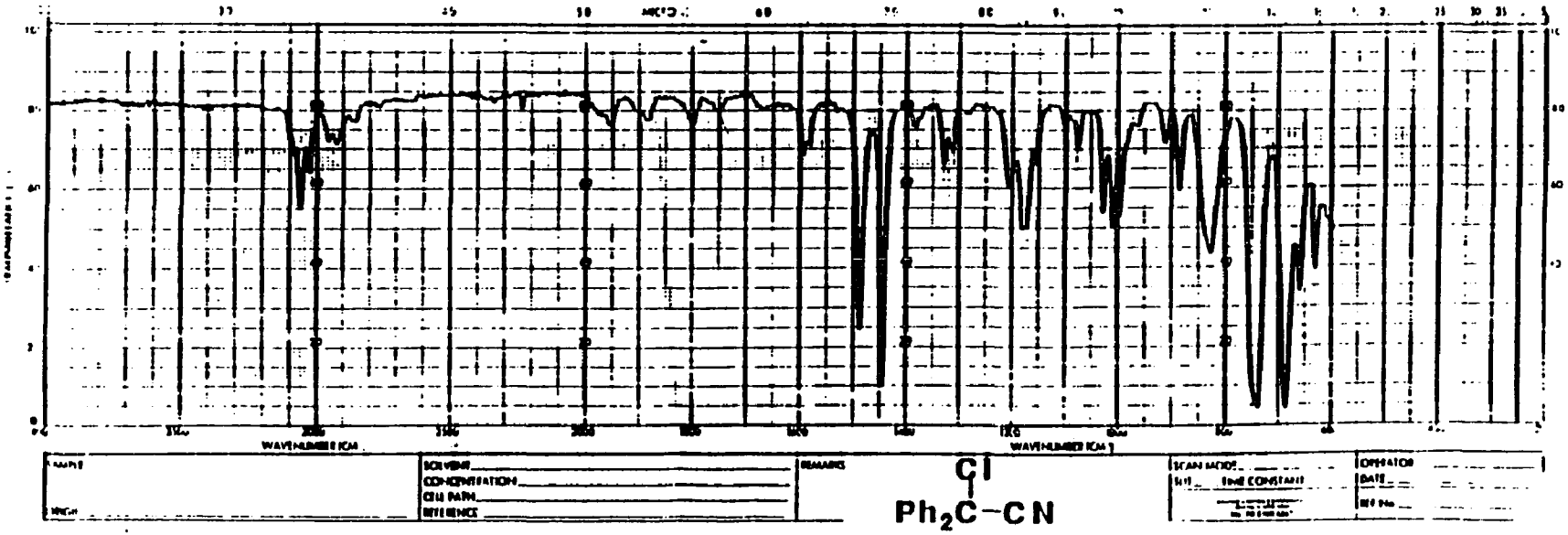


α-Chlorodiphenylacetonitrile (7)

Chemical Shift (ppm)
63.34
118.47
127.07
128.84
129.57
138.01



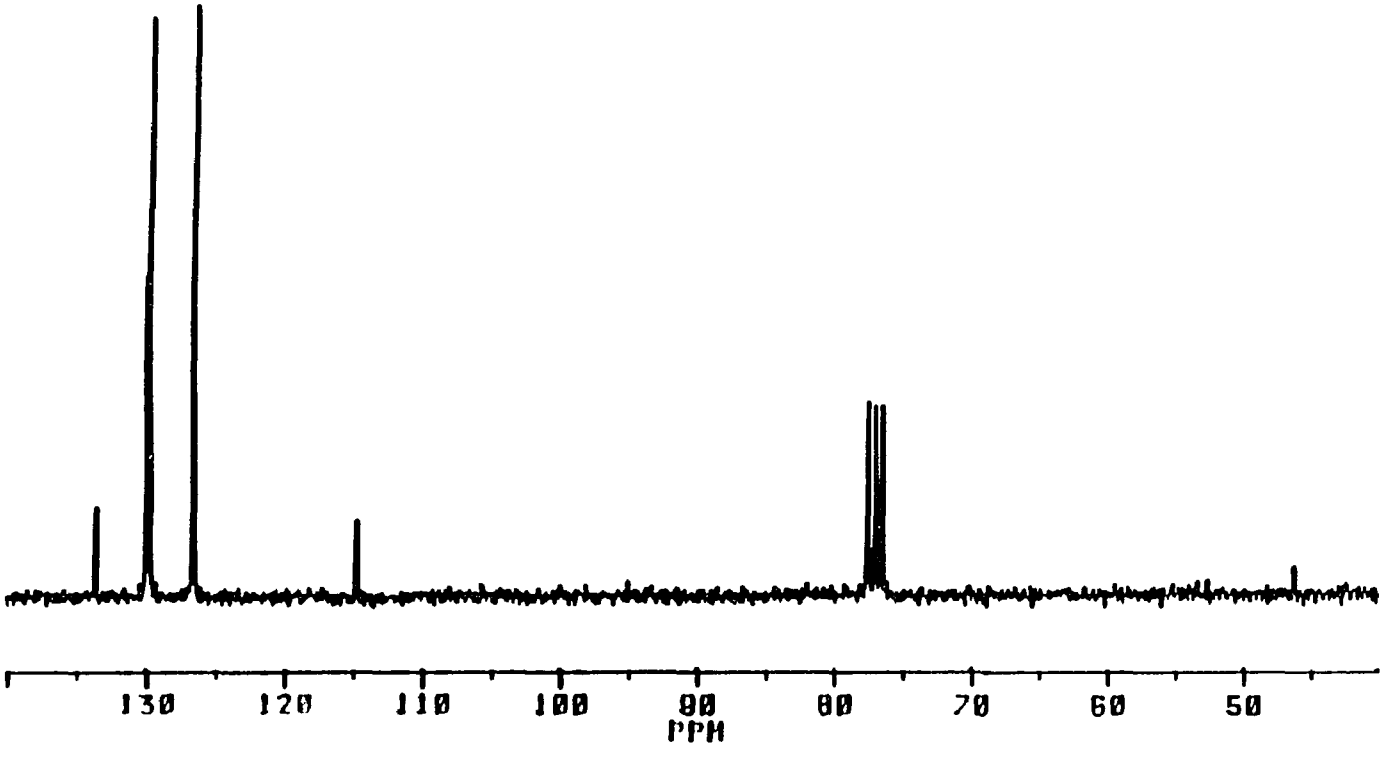
α-Chlorodiphenylacetonitrile



$Ph_2C(Cl)-CN$

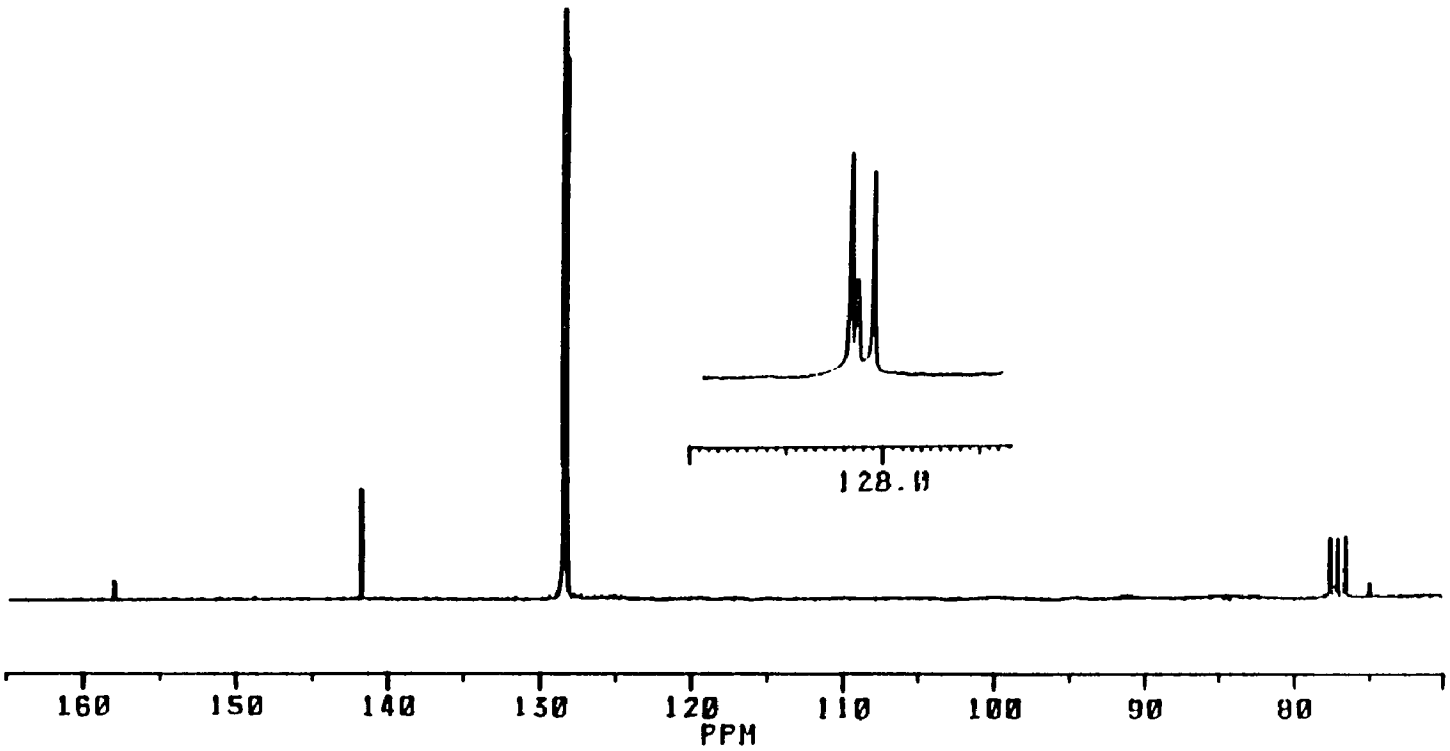
Diphenylmalononitrile (8)

Chemical Shift (ppm)
46.25
114.73
126.57
129.73
129.97
133.56



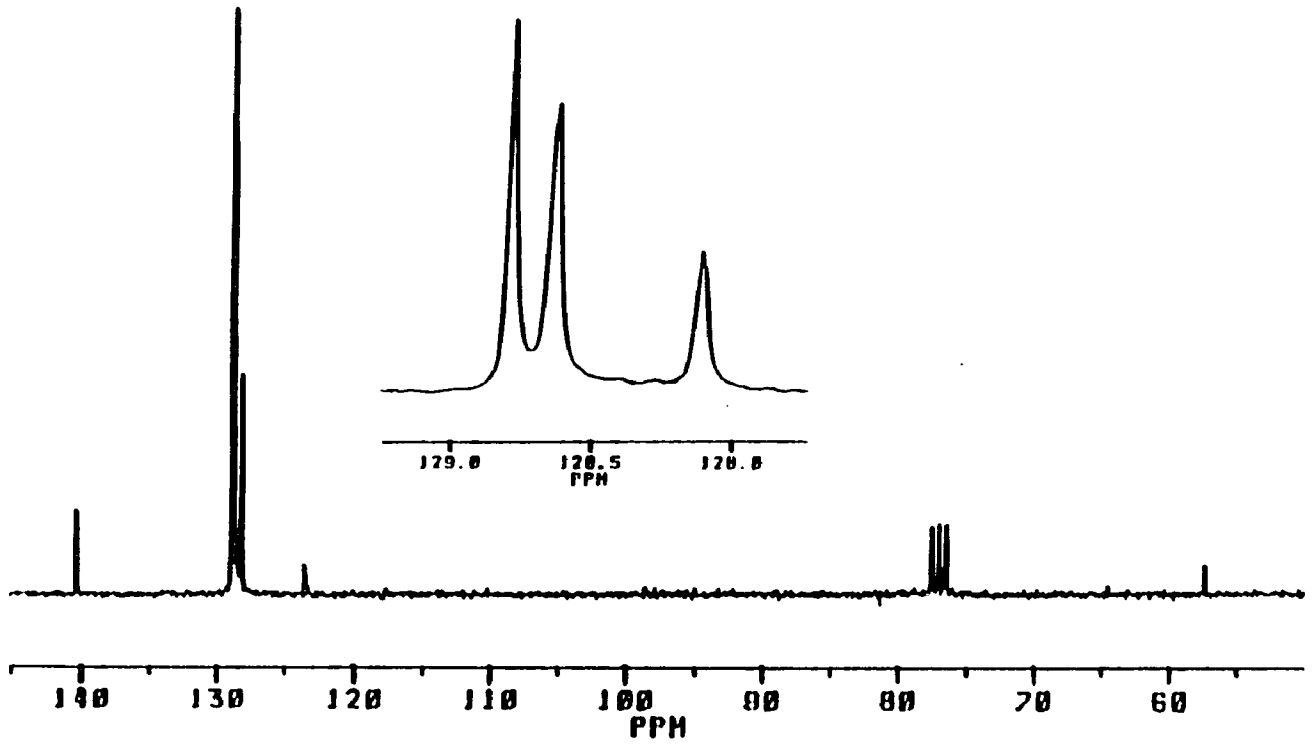
Trityl Isonitrile (9)

Chemical Shift (ppm)
74.97
128.08
128.25
128.31
141.64
157.82



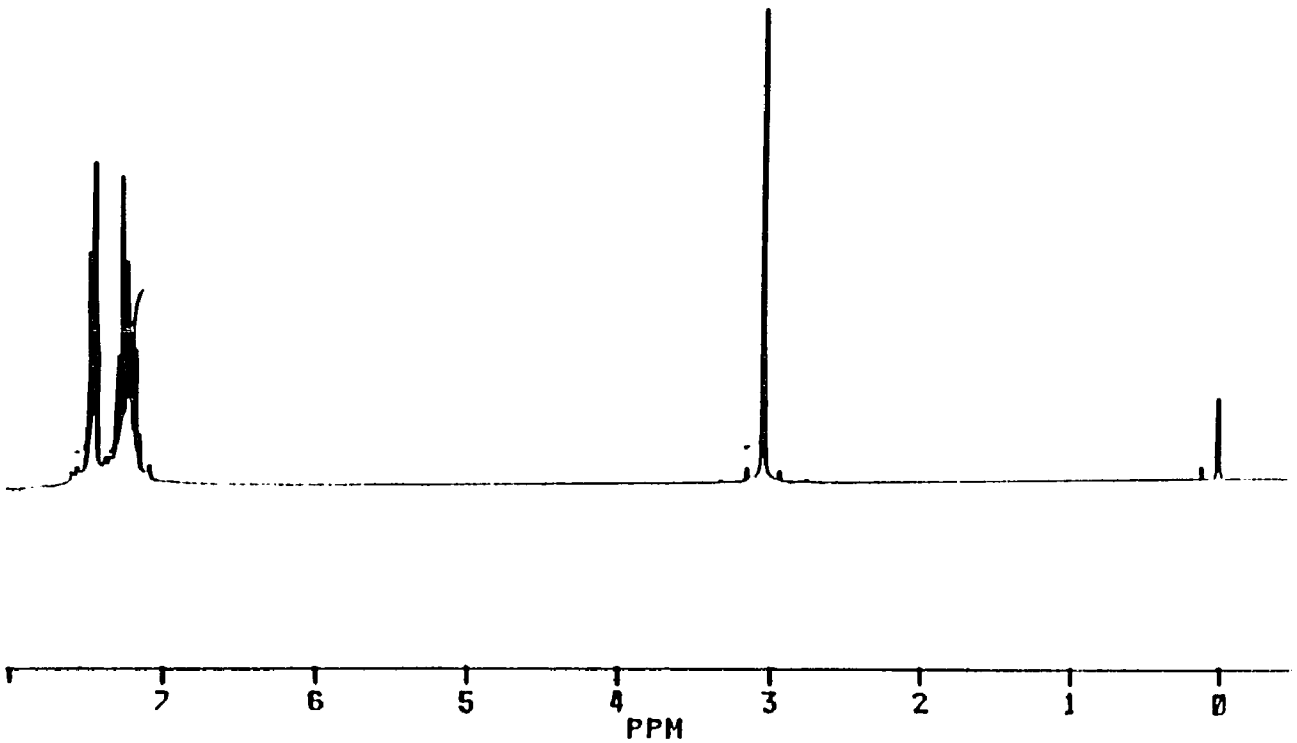
Triphenylacetonitrile (10)

Chemical Shift (ppm)
57.40
123.41
128.10
128.62
128.78
140.19



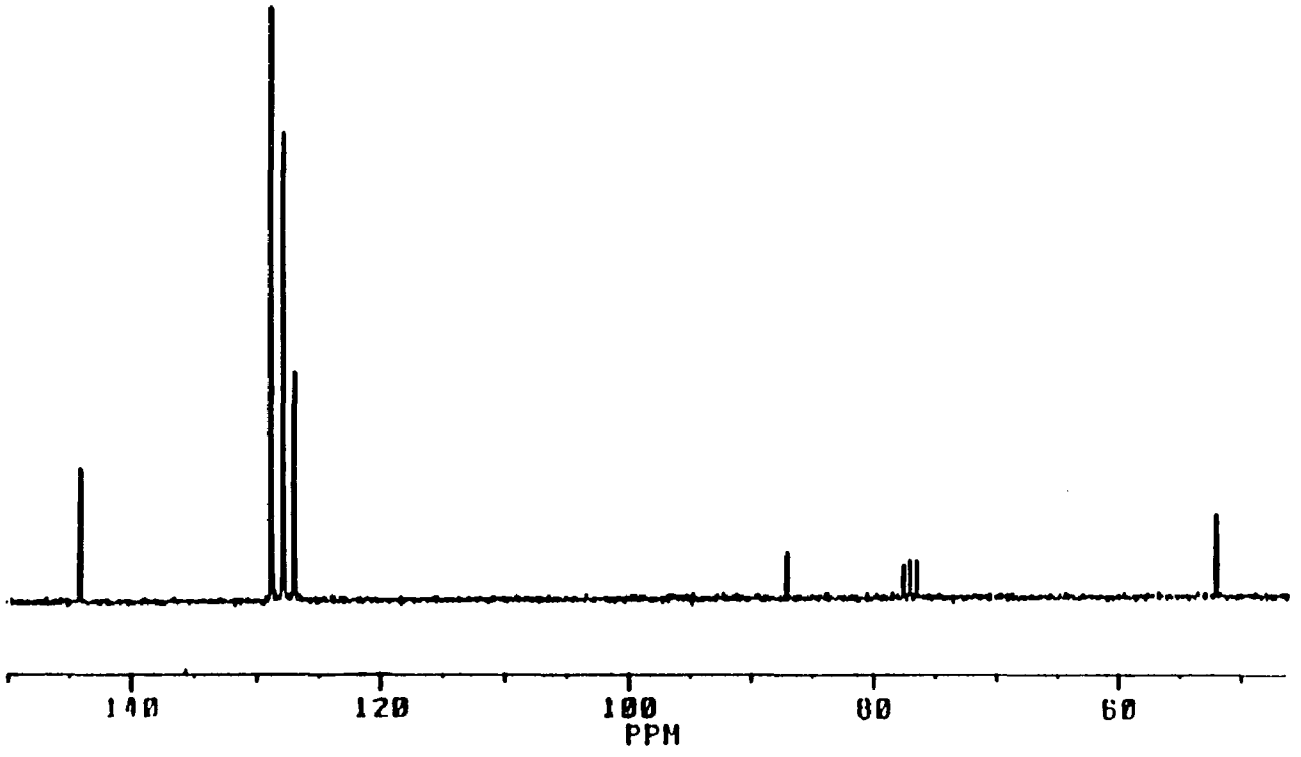
Methyl Trityl Ether

Chemical Shift (ppm)
3.03 (s, 3H)
7.14-7.45(m, 15H)

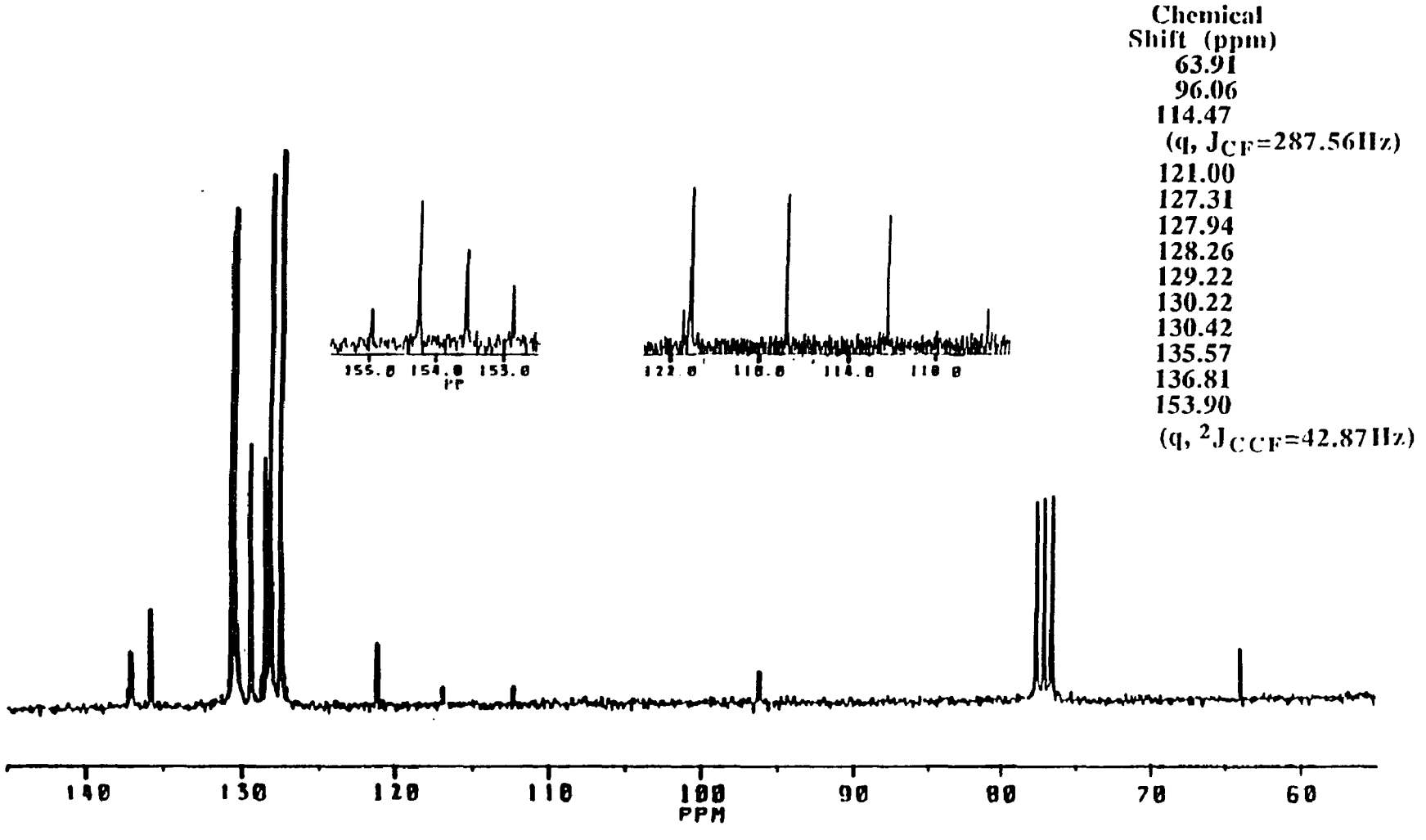


Methyl Trityl Ether

Chemical Shift (ppm)
51.99
86.99
126.85
127.70
128.68
143.93



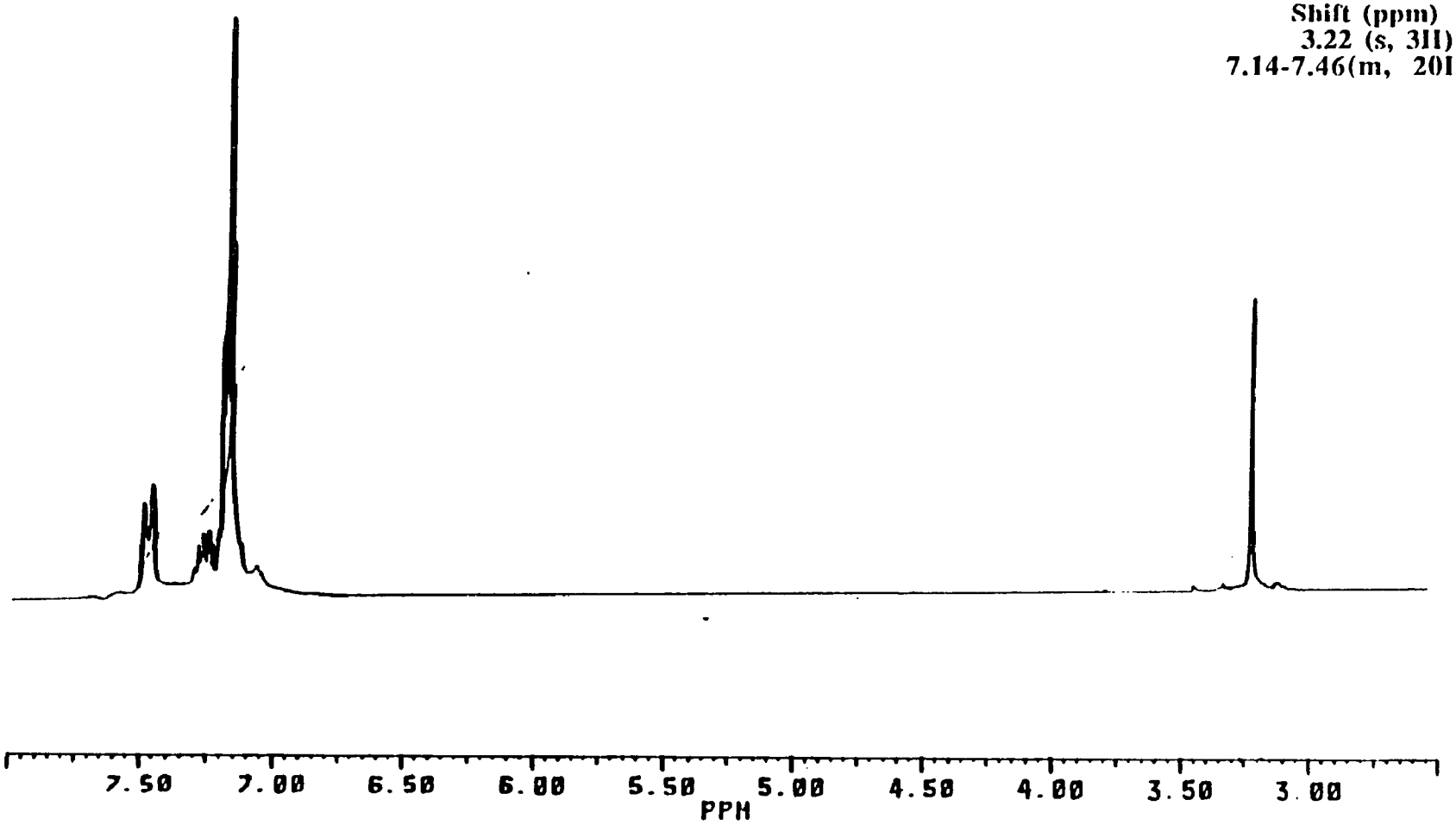
3-Trifluoroacetoxy-2,2,3,3-tetraphenylpropanenitrile (17)



Chemical Shift (ppm)
63.91
96.06
114.47 (q, J_{CF}=287.56Hz)
121.00
127.31
127.94
128.26
129.22
130.22
130.42
135.57
136.81
153.90 (q, $^{2}J_{CCF}$=42.87Hz)

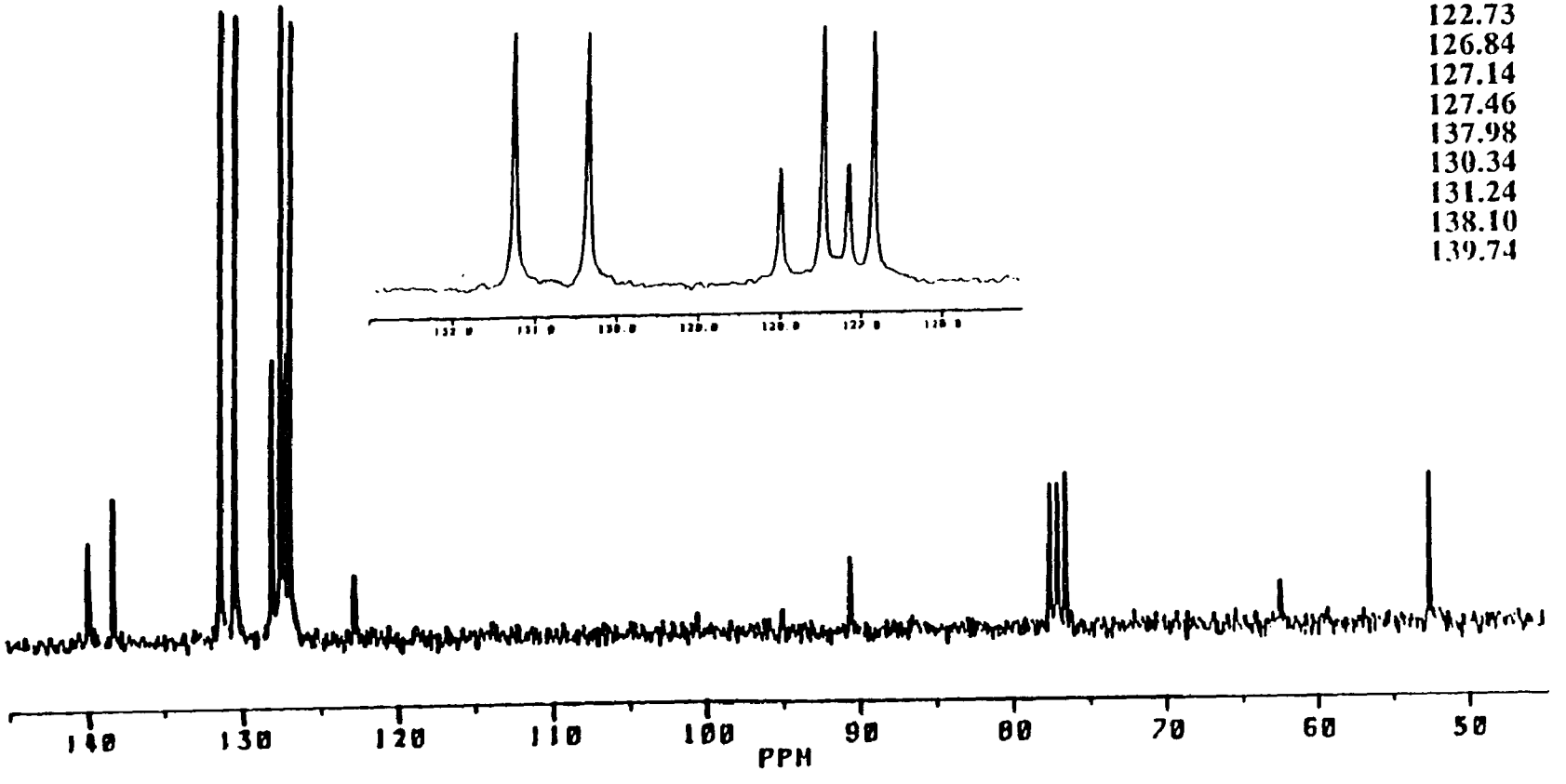
3-Methoxy-2,2,3,3-tetraphenylpropanenitrile (19)

Chemical Shift (ppm)
3.22 (s, 3H)
7.14-7.46(m, 20H)



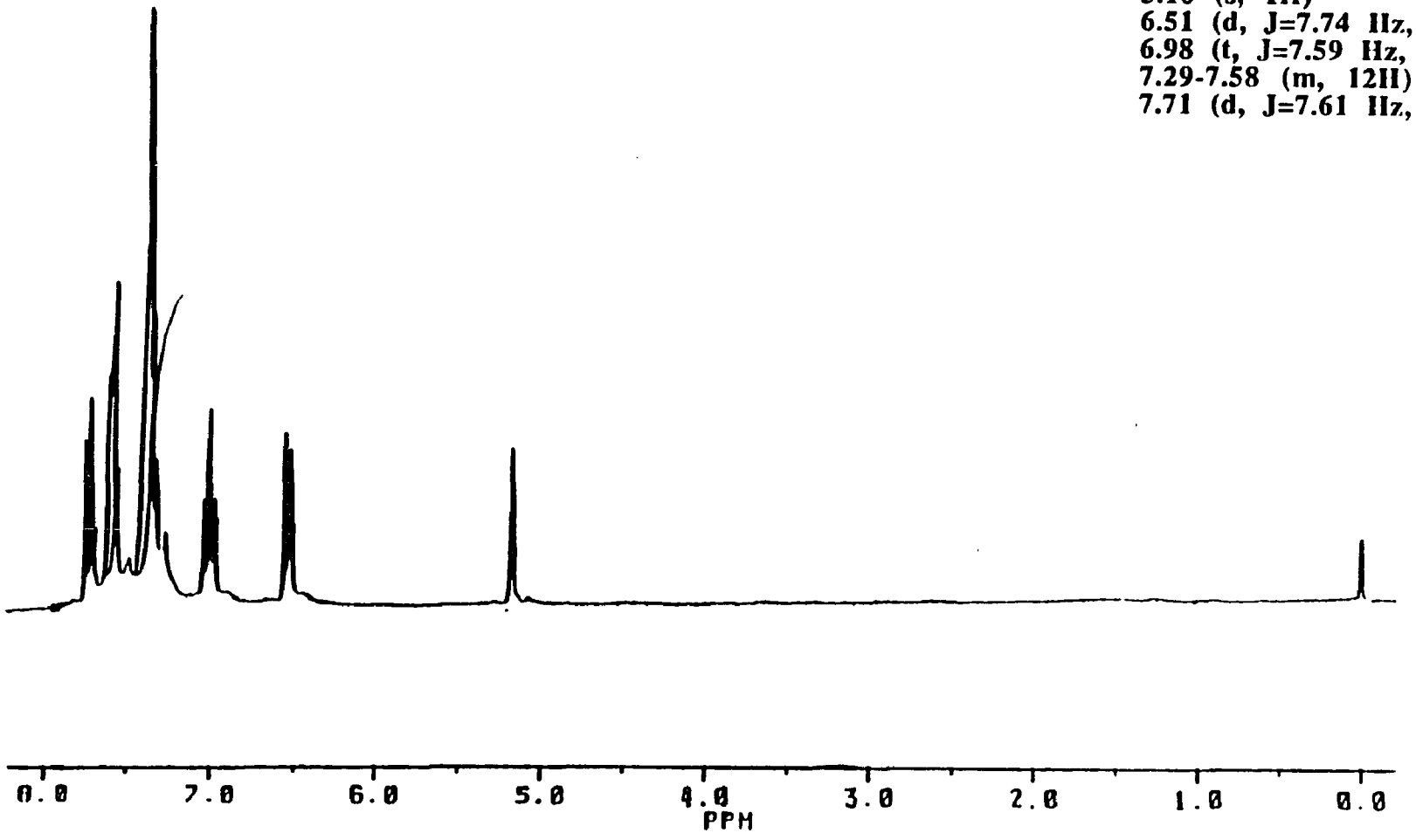
3-Methoxy-2,2,3,3-tetraphenylpropanenitrile (19)

Chemical Shift (ppm)
52.46
62.40
90.55
122.73
126.84
127.14
127.46
137.98
130.34
131.24
138.10
139.74



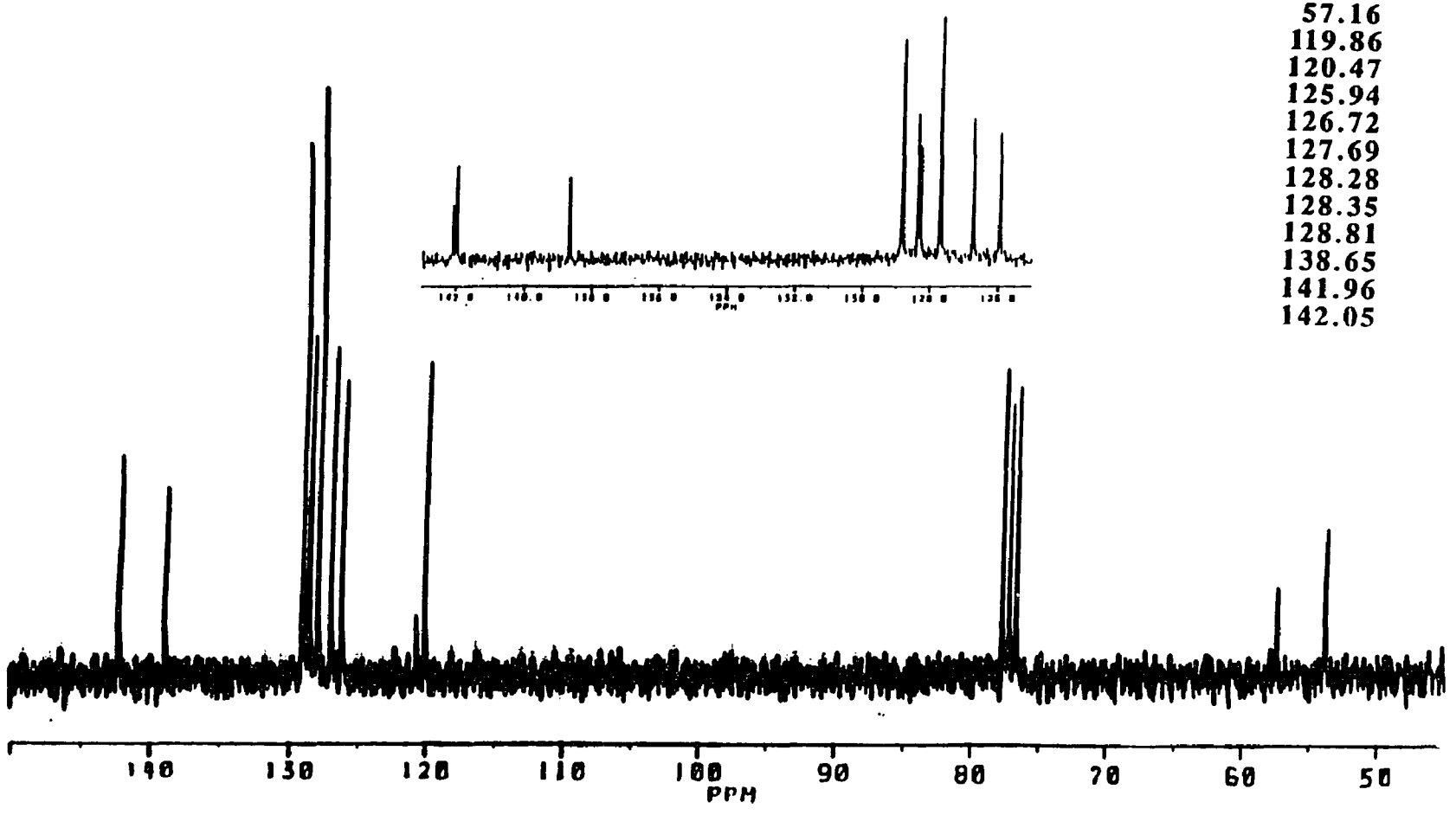
9-(Cyanodiphenylmethyl)fluorene (21)

Chemical Shift (ppm)
5.16 (s, 1H)
6.51 (d, J=7.74 Hz, 2H)
6.98 (t, J=7.59 Hz, 2H)
7.29-7.58 (m, 12H)
7.71 (d, J=7.61 Hz, 2H)

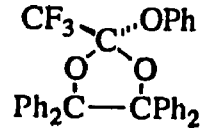


9-(Cyanodiphenylmethyl)fluorene (21)

Chemical Shift (ppm)
53.60
57.16
119.86
120.47
125.94
126.72
127.69
128.28
128.35
128.81
138.65
141.96
142.05

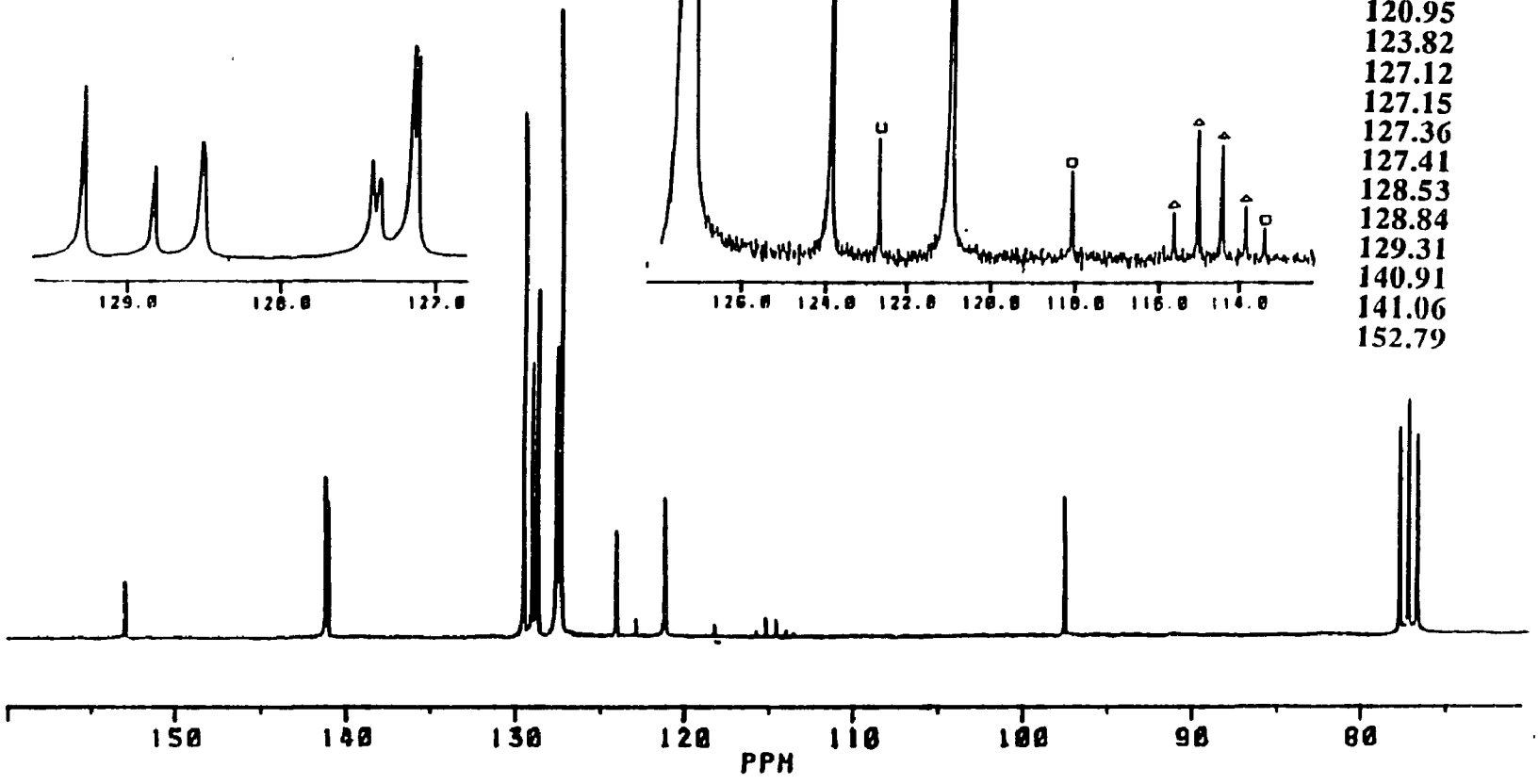


Ortho Ester 31

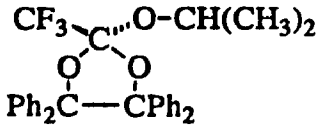


Chemical Shift (ppm)

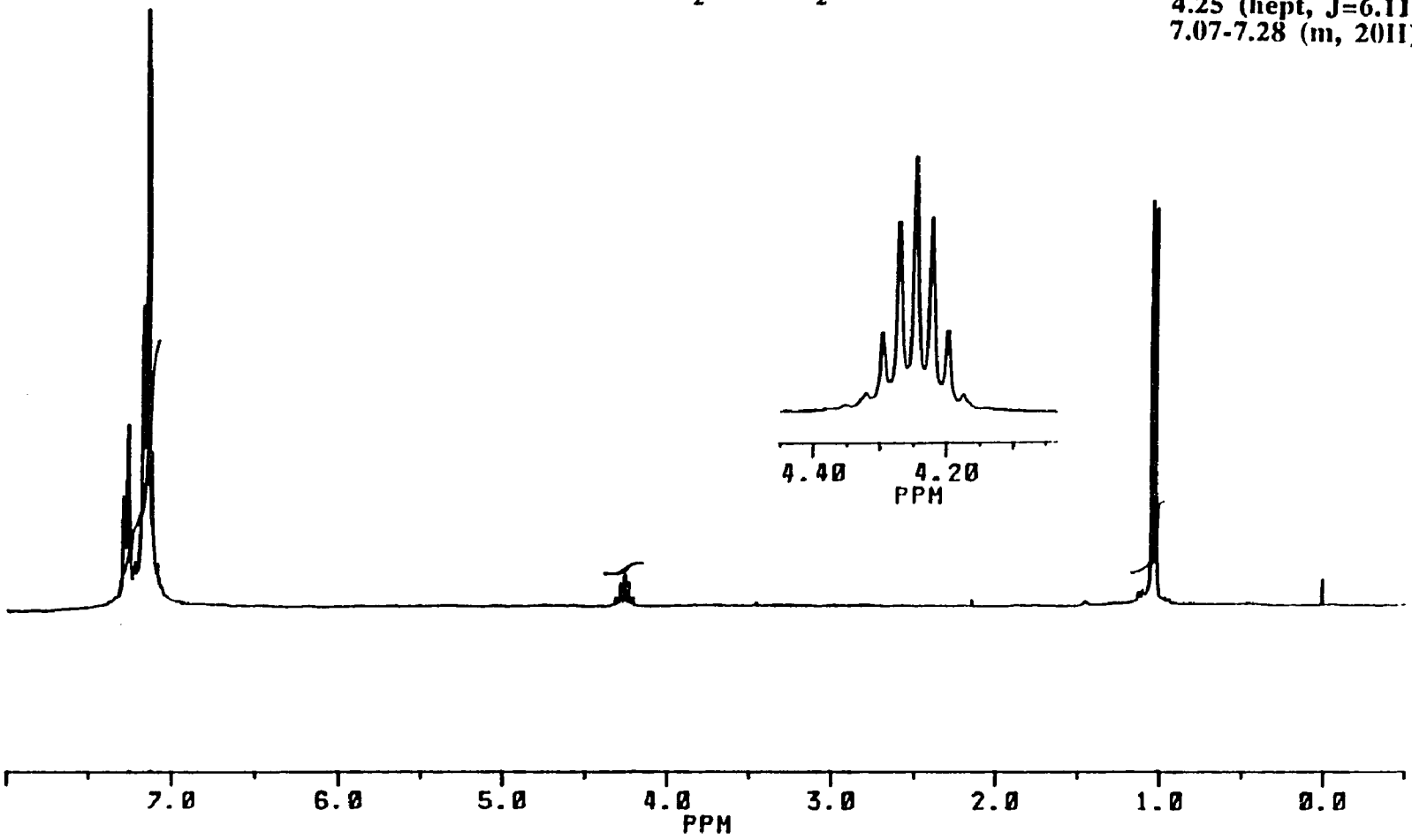
97.39
114.72
(q, $^{2}J_{CCF}$=36.40 Hz)
120.36
(q, J_{CF}=291.59 Hz)
120.95
123.82
127.12
127.15
127.36
127.41
128.53
128.84
129.31
140.91
141.06
152.79



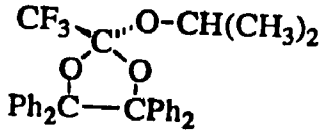
Ortho Ester 32



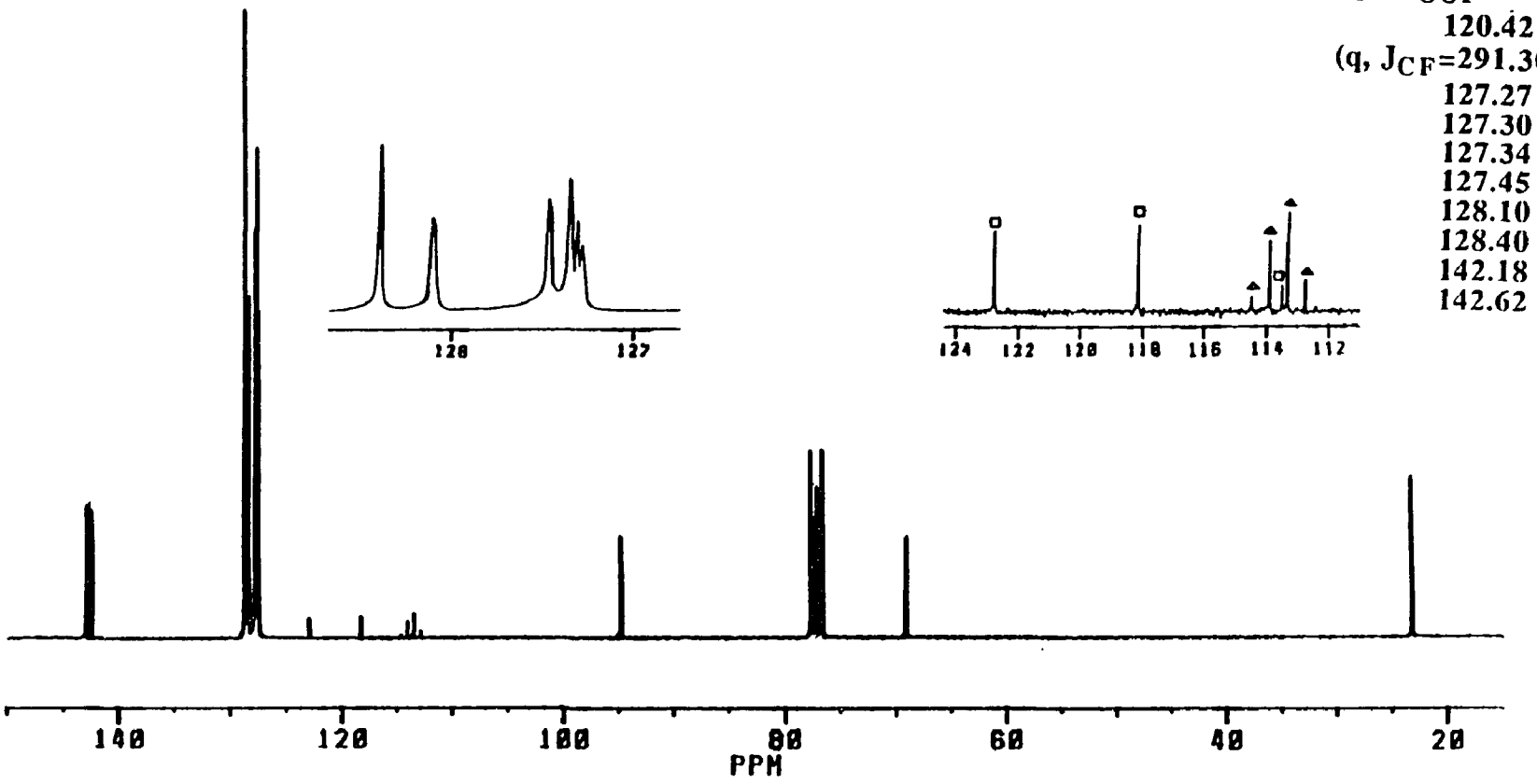
Chemical Shift (ppm)
1.03 (d, J=6.11 Hz, 6H)
4.25 (hept, J=6.11 Hz, 1H)
7.07-7.28 (m, 20H)



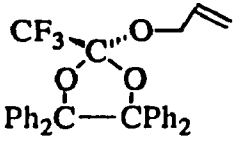
Ortho Ester 32



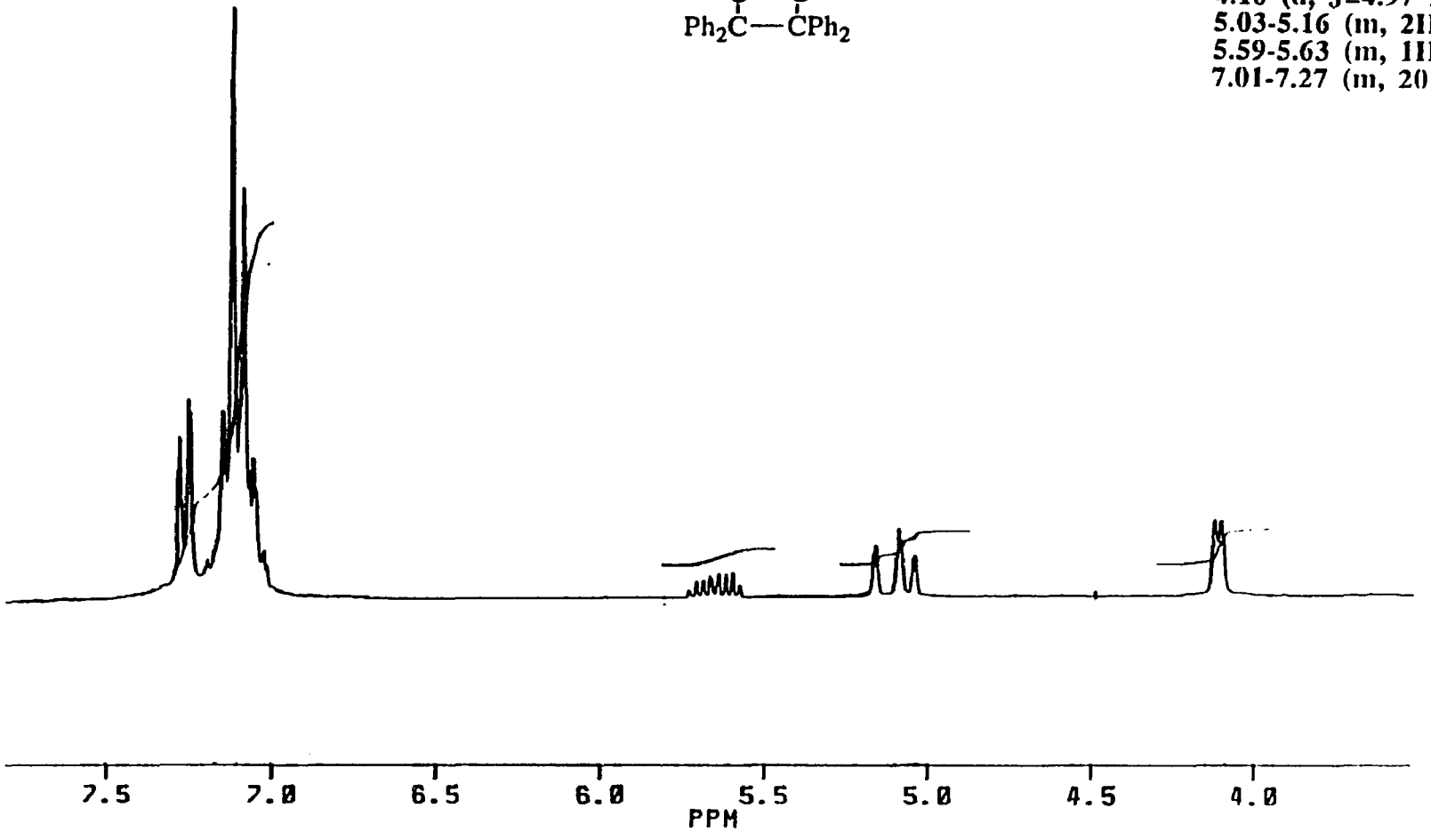
Chemical Shife (ppm)
23.13
68.91
94.68
113.60
(q, $^{2}J_{CCF}$=35.87 Hz)
120.42
(q, J_{CF}=291.30 Hz)
127.27
127.30
127.34
127.45
128.10
128.40
142.18
142.62



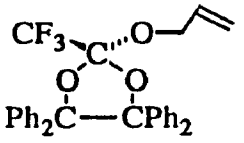
Ortho Ester 33



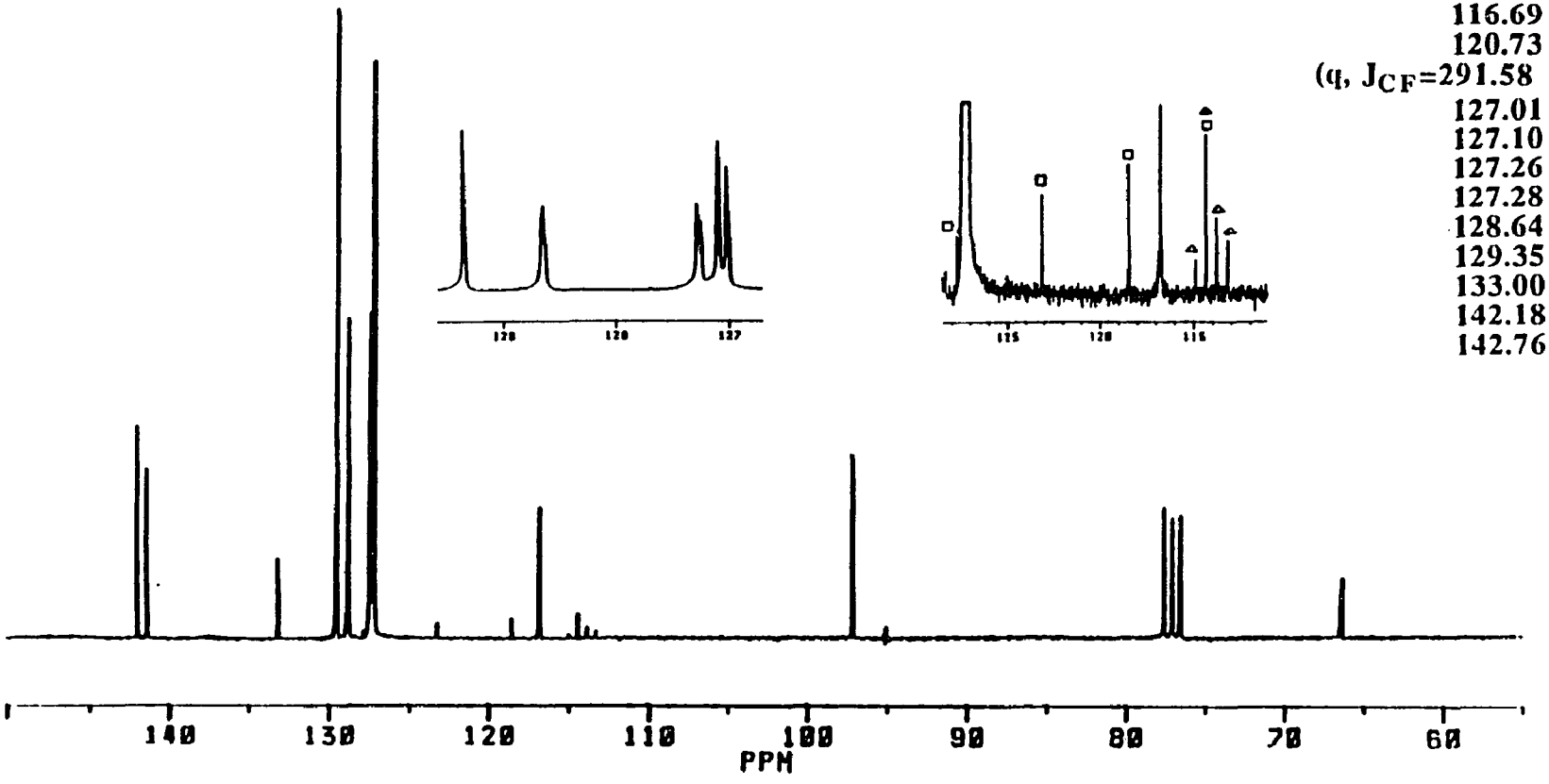
Chemical Shift (ppm)
4.10 (d, J=4.97 Hz, 2H)
5.03-5.16 (m, 2H)
5.59-5.63 (m, 1H)
7.01-7.27 (m, 20H)



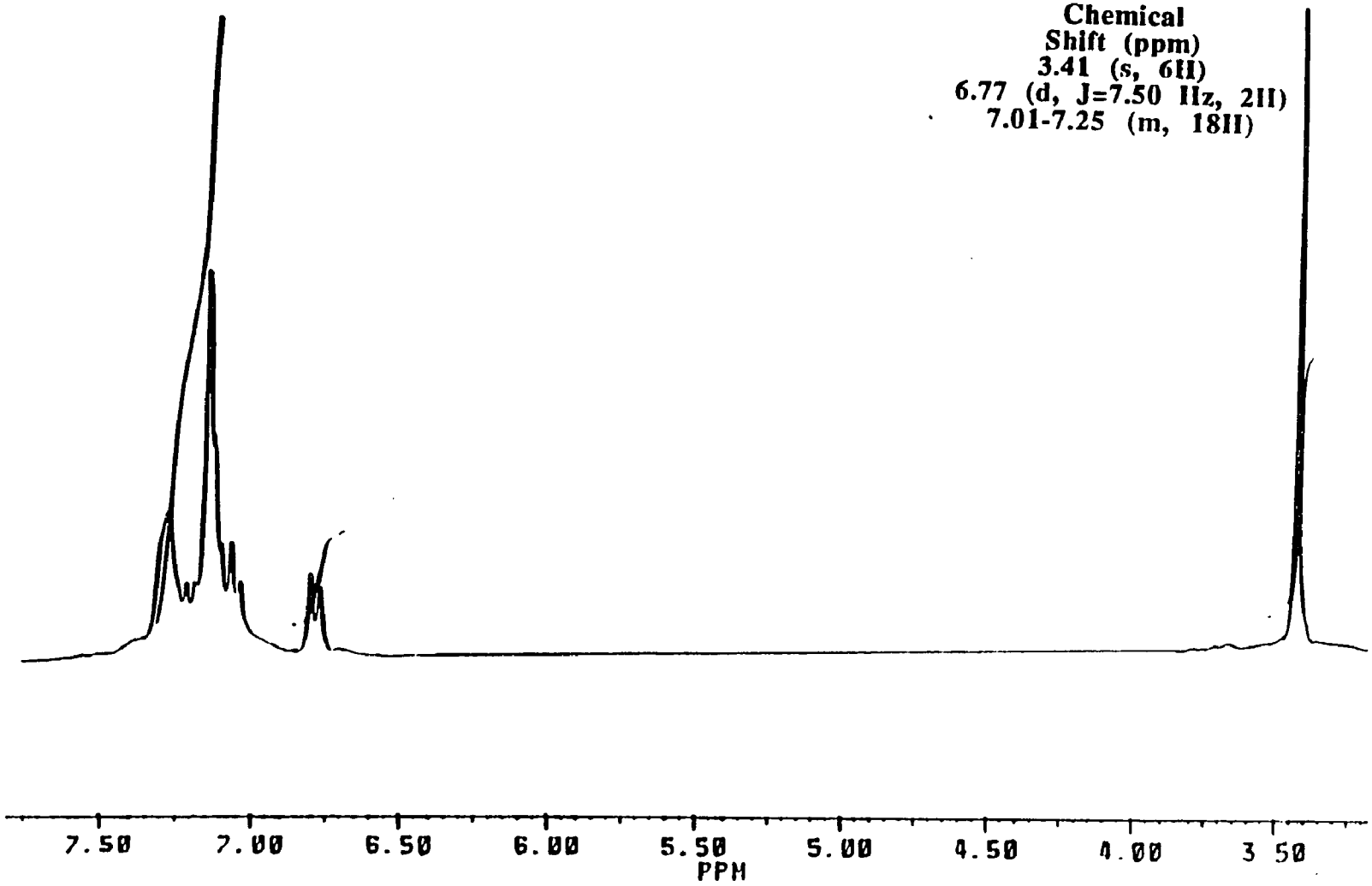
Ortho Ester 33



Chemical Shift (ppm)
66.35
97.07
114.02
(q, $^2J_{CCF}$=35.47 Hz)
116.69
120.73
(q, J_{CF}=291.58 Hz)
127.01
127.10
127.26
127.28
128.64
129.35
133.00
142.18
142.76

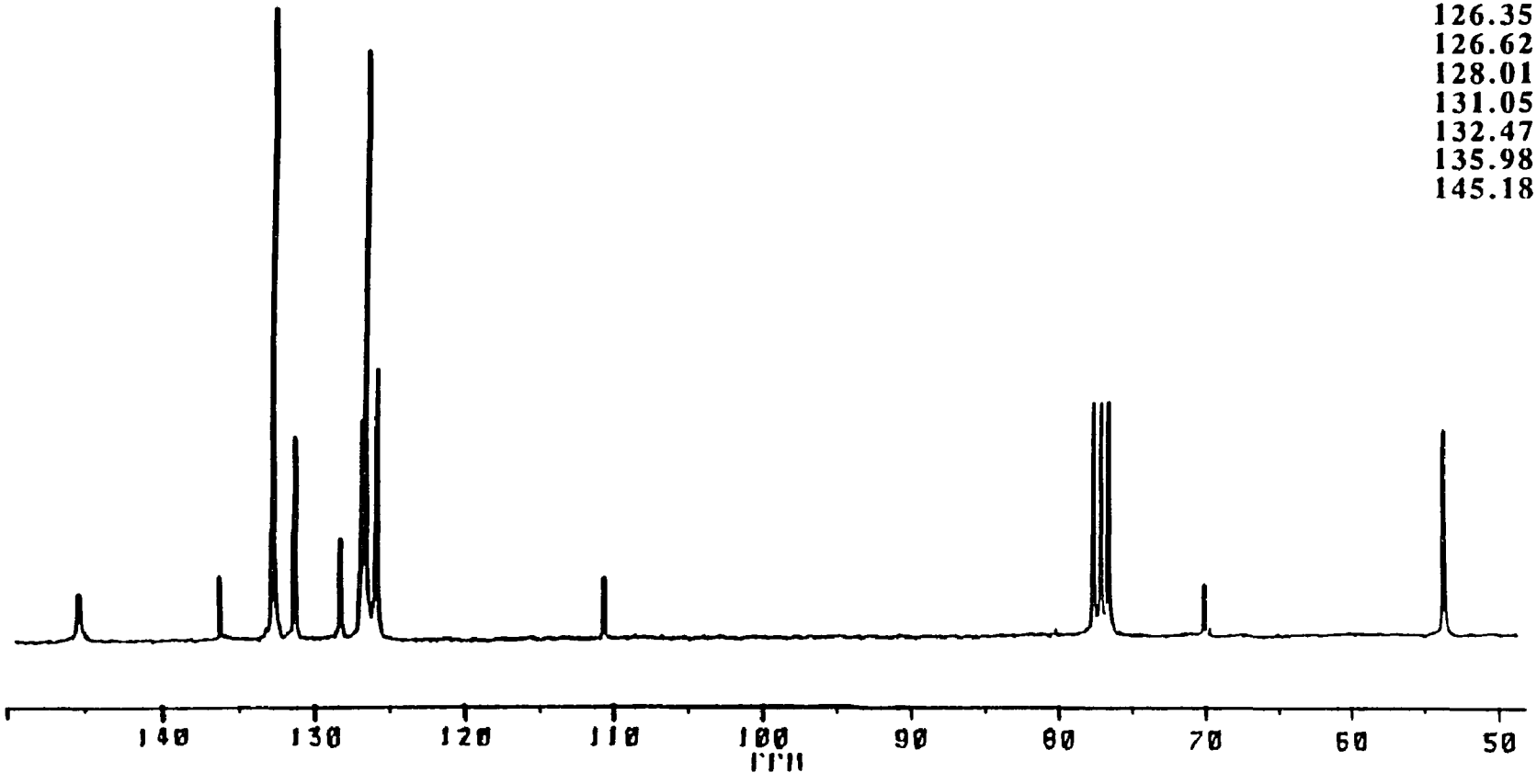


Benzopinacolone Dimethyl Ketal (39)

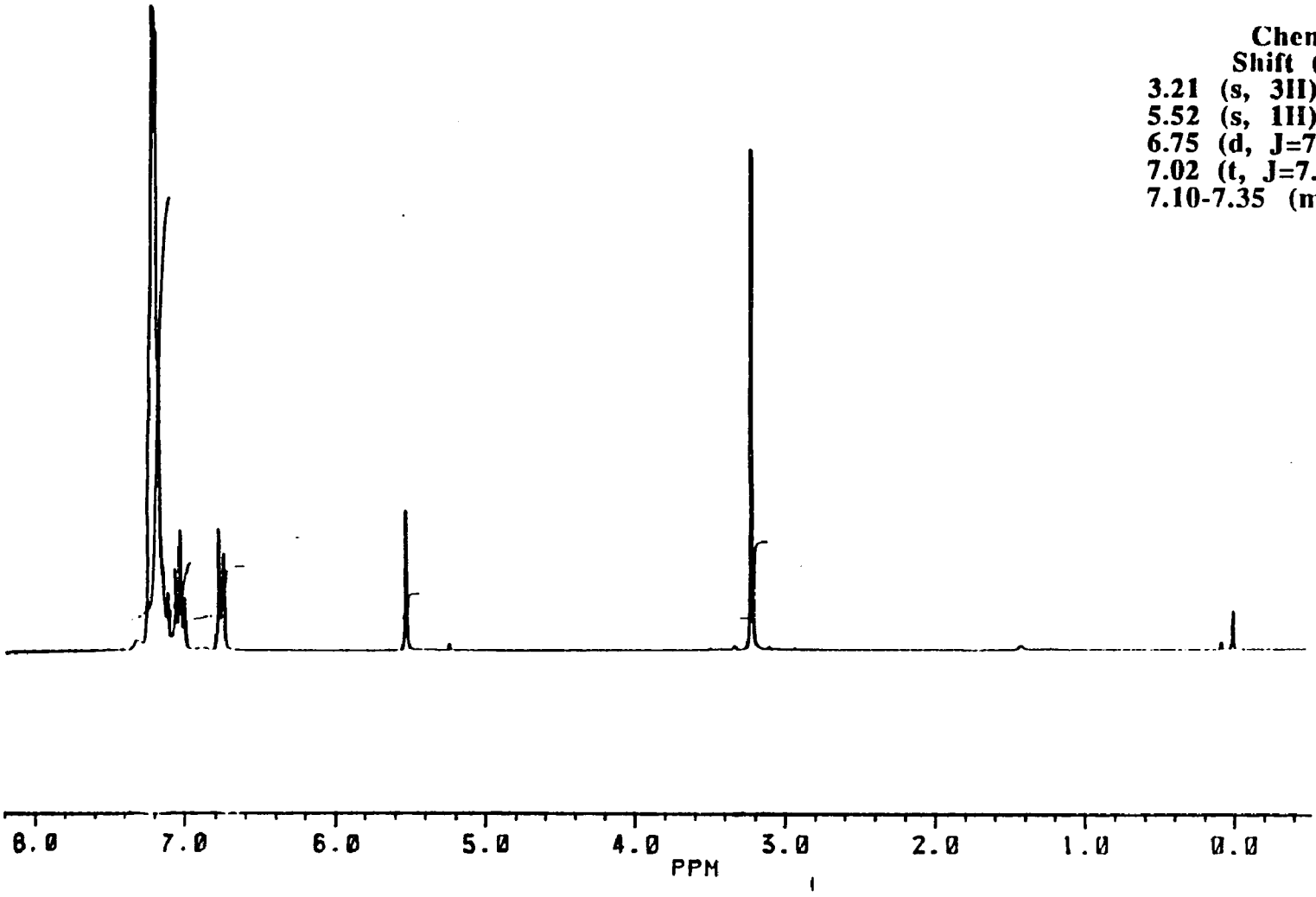


Benzopinacolone Dimethyl Ketal (39)

Chemical Shift (ppm)
53.71
70.03
110.49
125.61
126.35
126.62
128.01
131.05
132.47
135.98
145.18



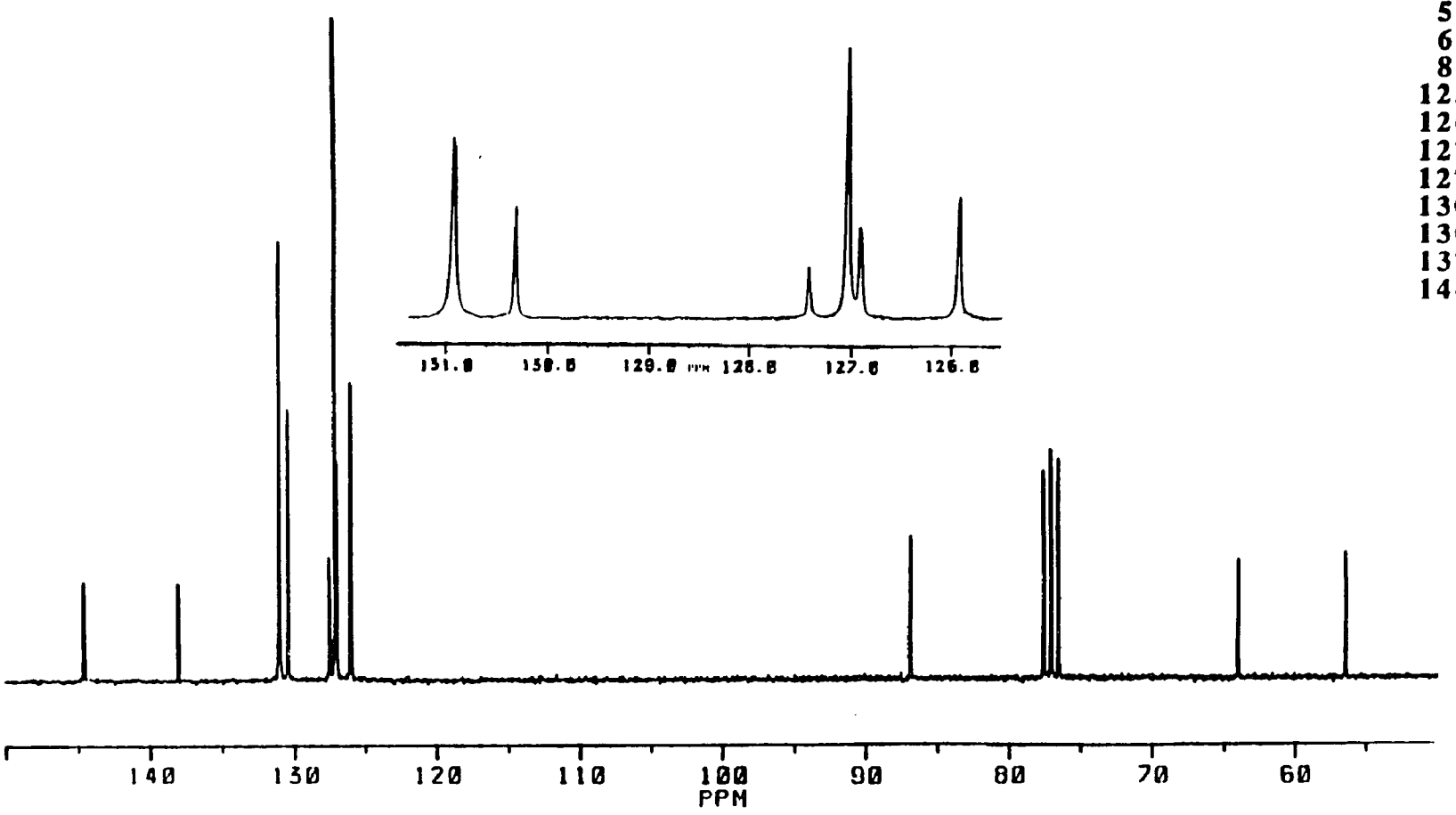
1-Methoxy-1,2,2,2-tetraphenylethane (47)



Chemical Shift (ppm)	
3.21	(s, 3H)
5.52	(s, 1H)
6.75	(d, J=7.40 Hz, 2H)
7.02	(t, J=7.20 Hz, 2H)
7.10-7.35	(m, 16H)

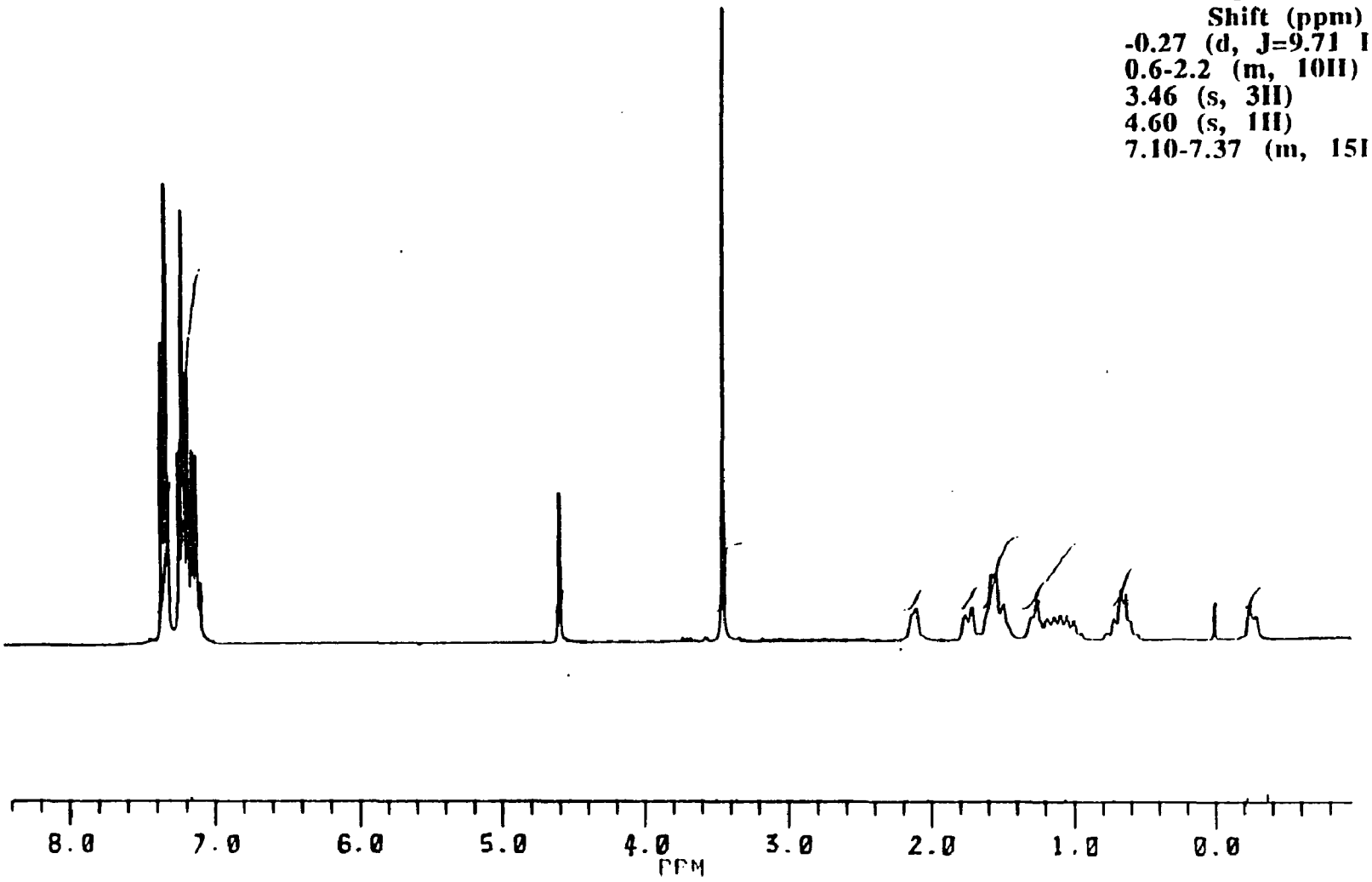
1-Methoxy-1,2,2,2-tetraphenylethane (47)

Chemical Shift (ppm)
56.36
63.92
86.63
125.93
126.91
127.03
127.41
130.31
130.92
137.91
144.49



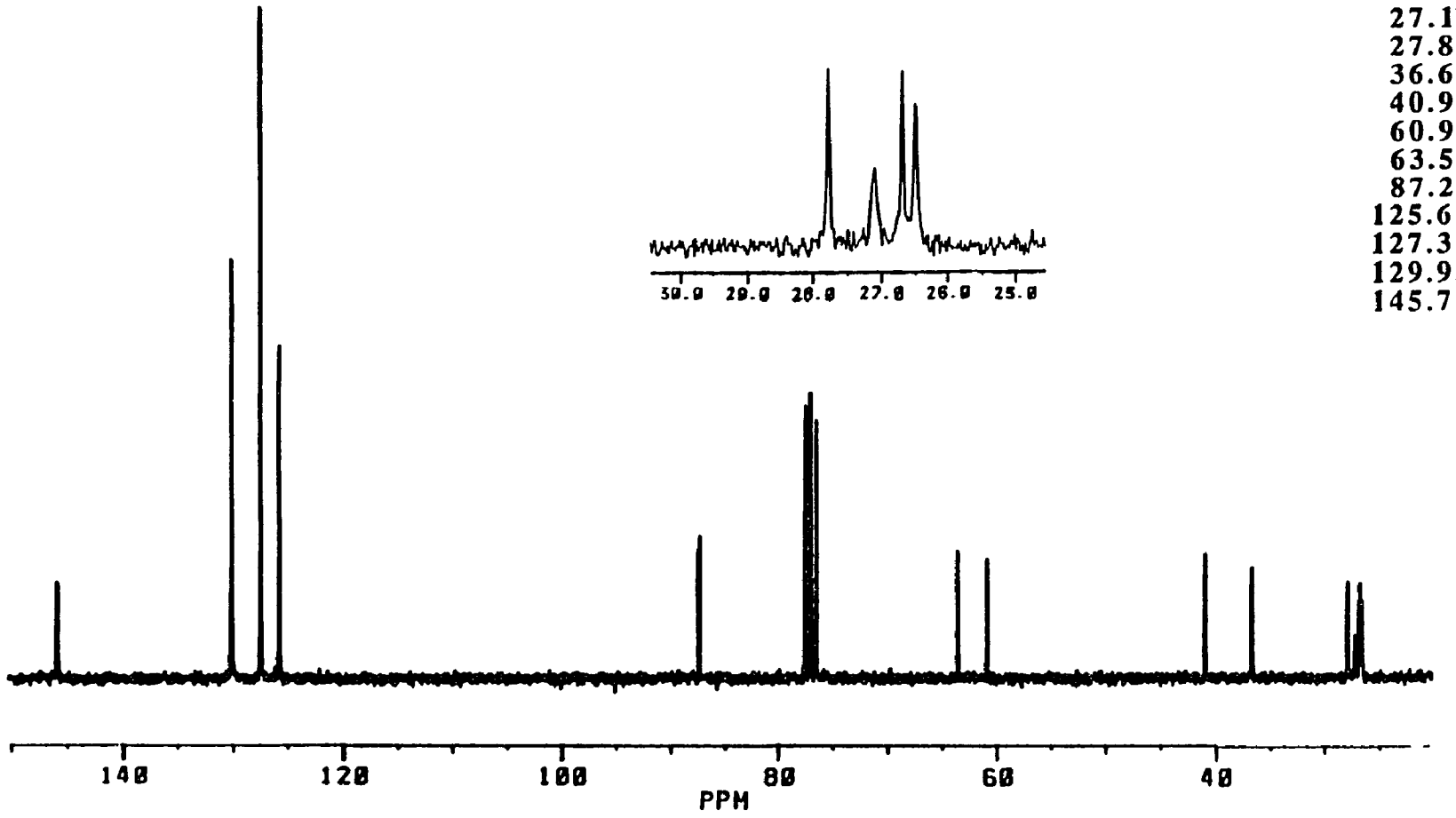
1-Cyclohexyl-1-methoxy-2,2,2-triphenylethane (51)

Chemical Shift (ppm)
-0.27 (d, J=9.71 Hz, 1H)
0.6-2.2 (m, 10H)
3.46 (s, 3H)
4.60 (s, 1H)
7.10-7.37 (m, 15H)

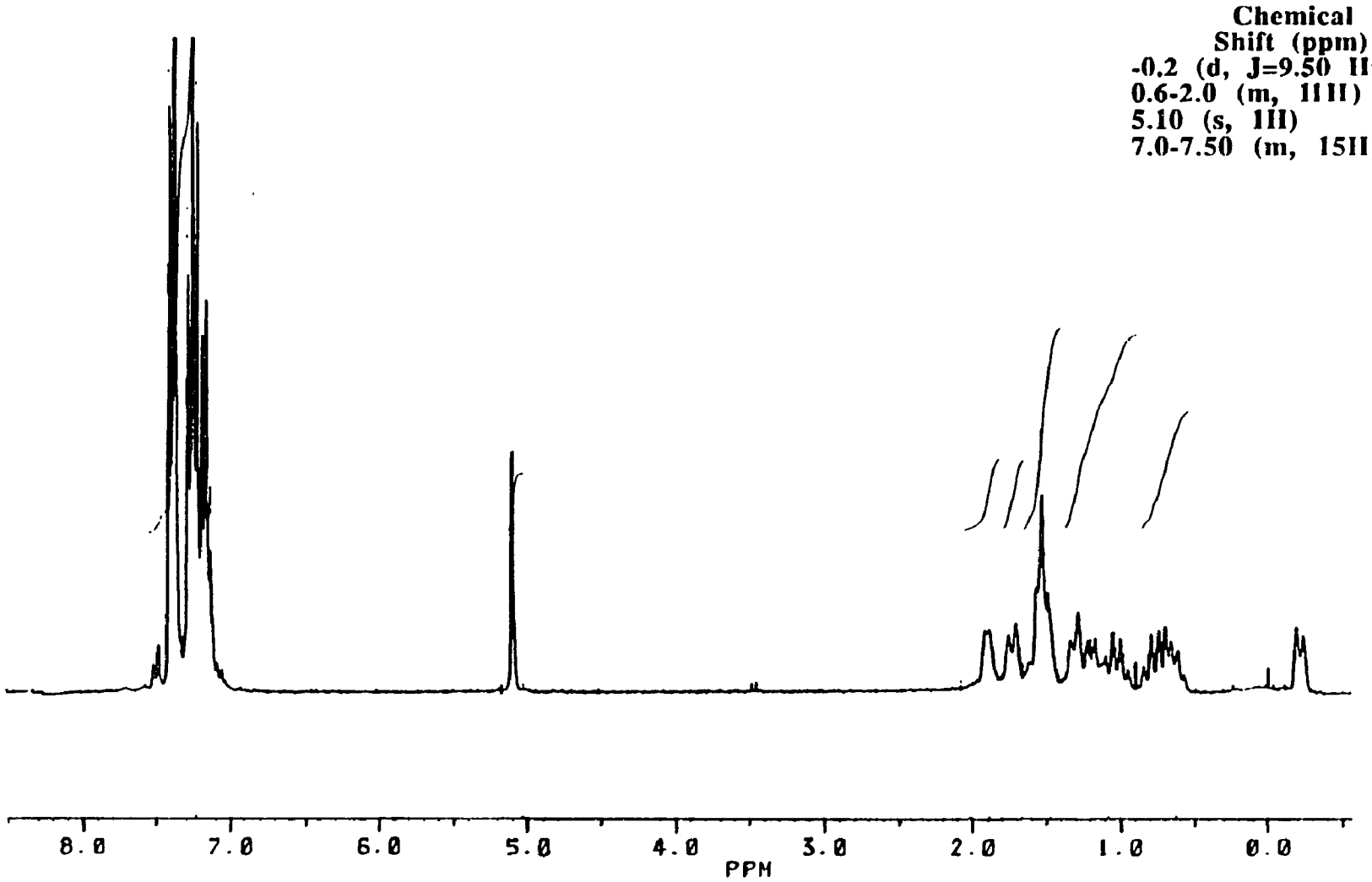


1-Cyclohexyl-1-Methoxy-2,2,2-triphenylethane (51)

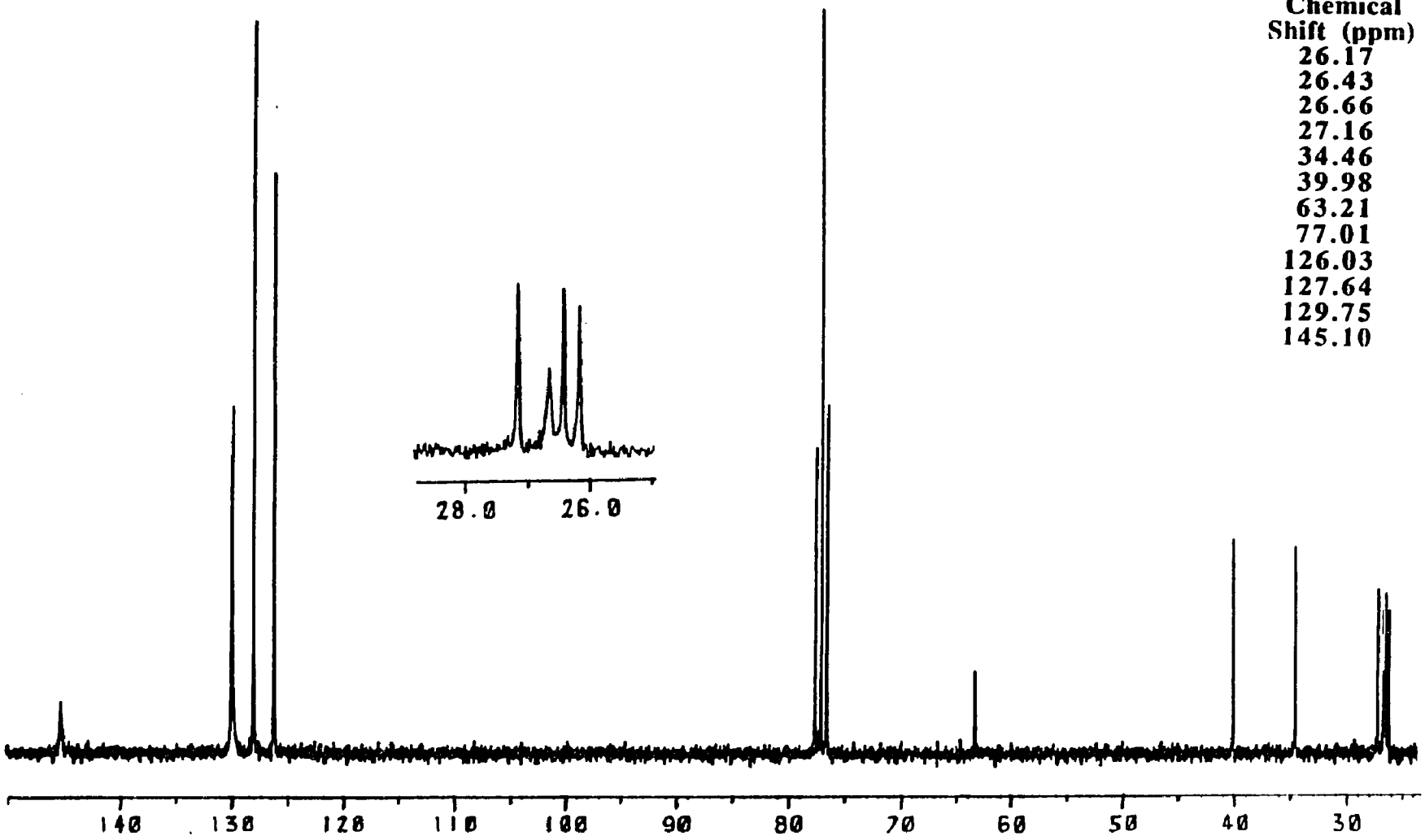
Chemical Shift (ppm)
26.50
26.70
27.11
27.80
36.64
40.91
60.92
63.57
87.20
125.62
127.31
129.93
145.77



1-Cyclohexyl-2,2,2-triphenylethanol (52)



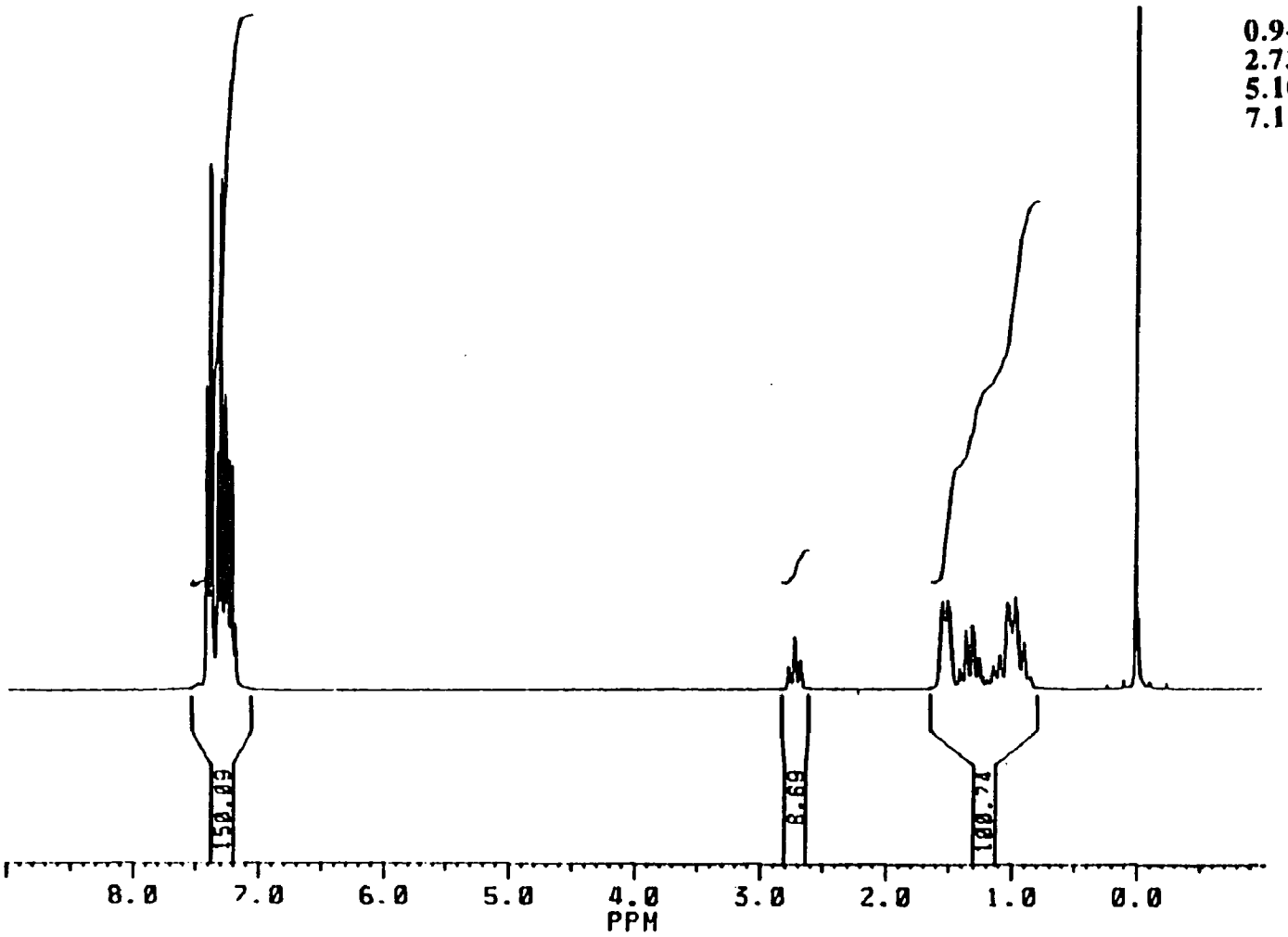
1-Cyclohexyl-2,2,2-triphenylethanol (52)



Chemical Shift (ppm)
26.17
26.43
26.66
27.16
34.46
39.98
63.21
77.01
126.03
127.64
129.75
145.10

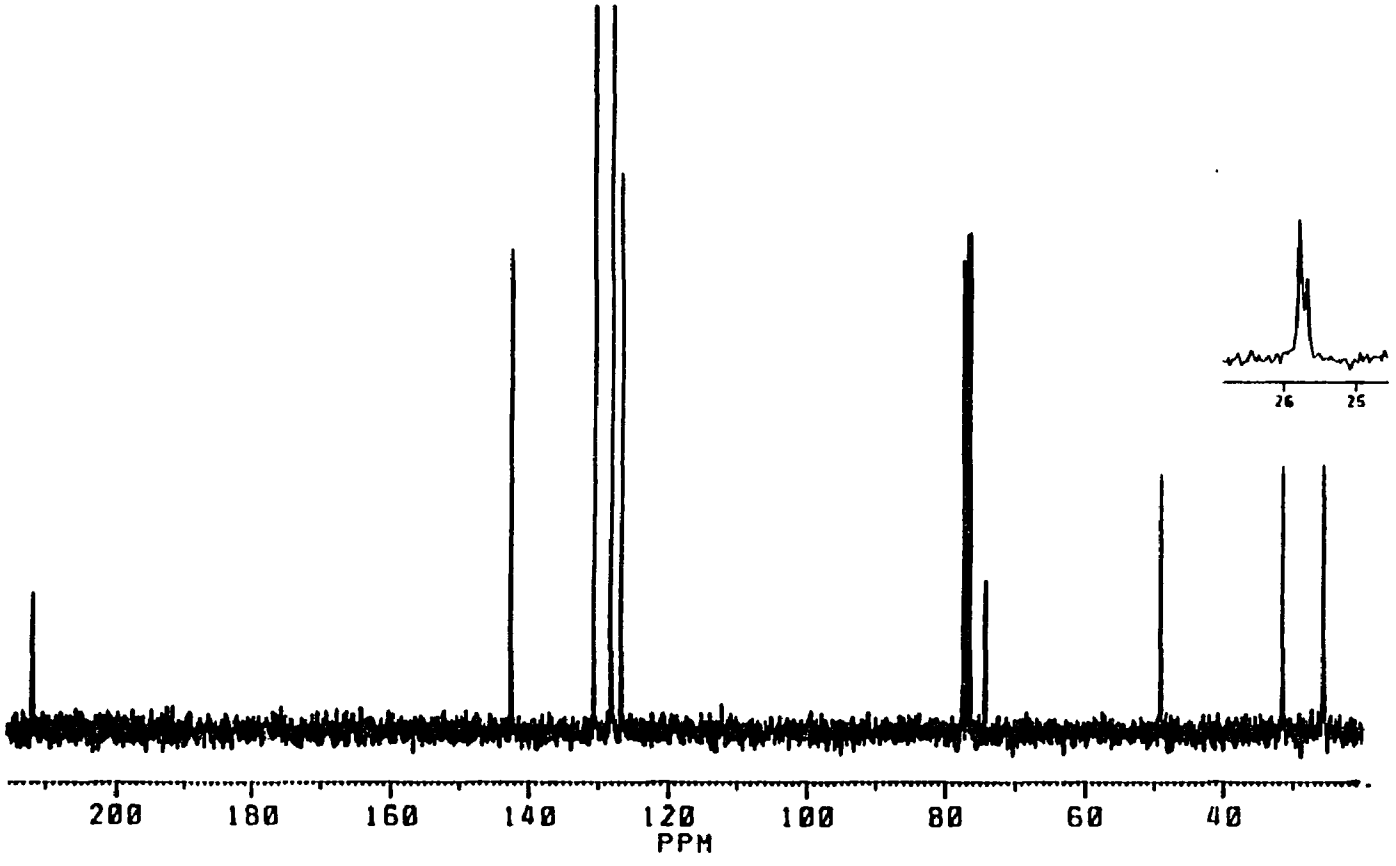
1-Cyclohexyl-2,2,2-triphenylethanone (58)

Chemical Shift (ppm)
0.9-1.55 (m, 10H)
2.73 (t, J=11.26 Hz, 1H)
5.10 (s, 1H)
7.10-7.39 (m, 15H)



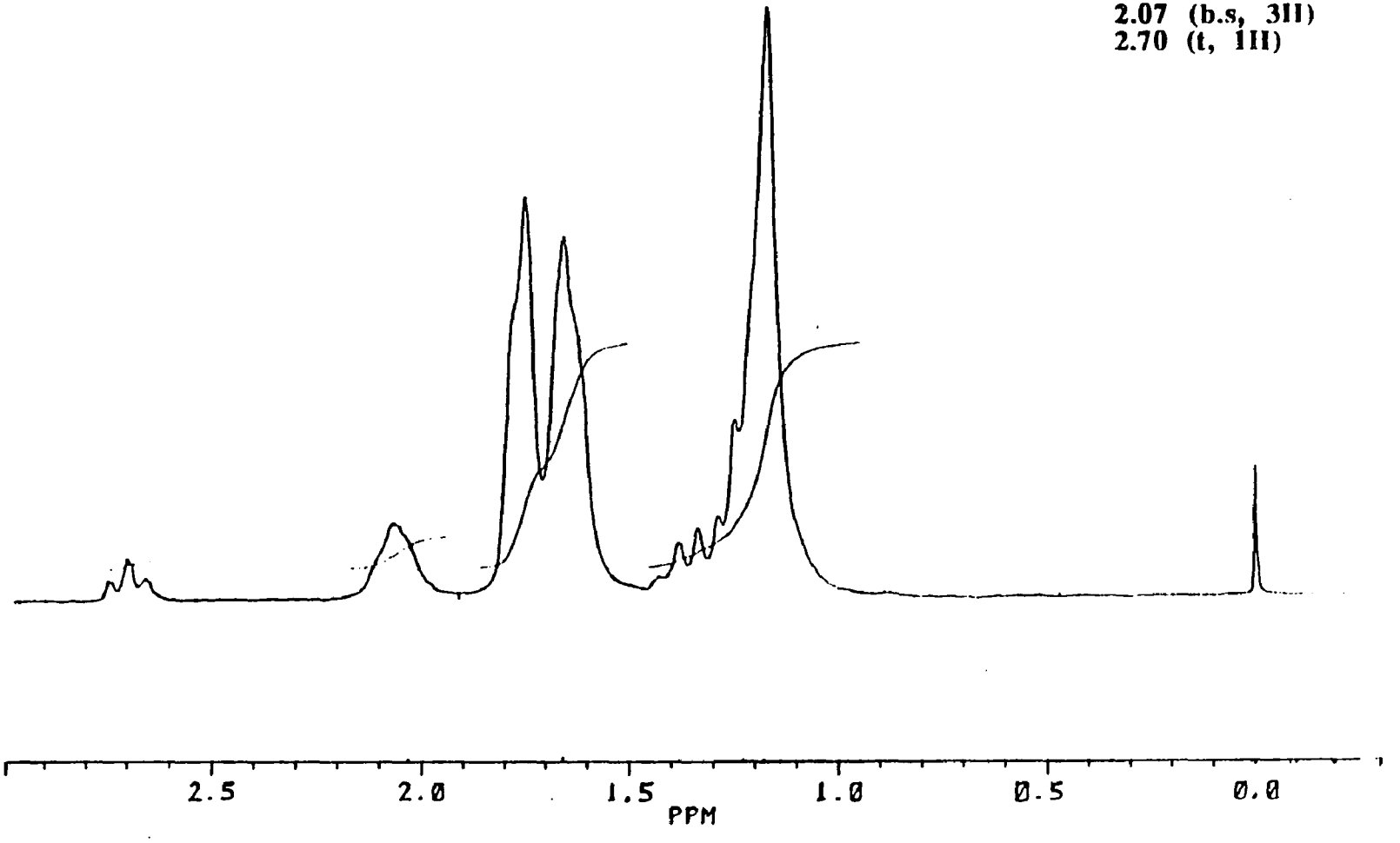
1-Cyclohexyl-2,2,2-triphenylethanone (58)

Chemical Shift (ppm)
25.67
25.77
31.62
49.18
74.35
126.62
128.00
130.51
142.41
211.66



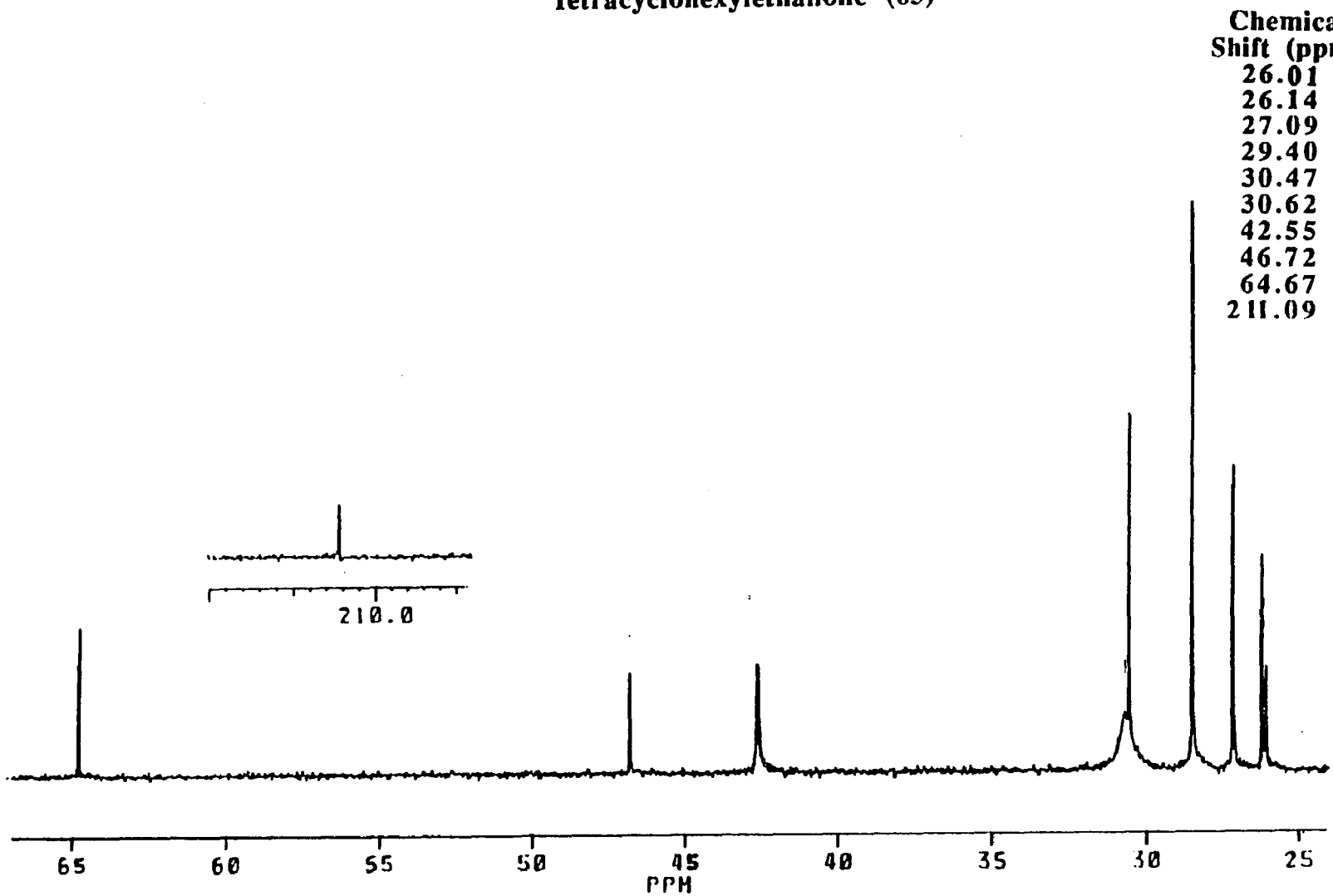
Tetracyclohexylethanone (65)

Chemical Shift (ppm)	
1.00-1.45	(m, 20H)
1.55-1.80	(b.d. 20H)
2.07	(b.s, 3H)
2.70	(t, 1H)



Tetracyclohexylethanone (65)

Chemical Shift (ppm)
26.01
26.14
27.09
29.40
30.47
30.62
42.55
46.72
64.67
211.09



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91. In an efford to synthesize 1,2-dimethoxytetraphenylethane by an alternative method, we treated benzopinacol with NaH and quenched the reaction with iodomethane. Chromatography on silicagel afforded benzhydrol methylether and benzophenone in 44% yields.

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