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The study of reactive intermediates: p-Quinodimethanes and 3-methylene-1,4-pentadiene

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The study of reactive intermediates: *p*-Quinodimethanes and 3-methylene-1,4-pentadiene.

by

Steven Paul Lorimor

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

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2000

Graduate College
Iowa State University

This is to certify that the Doctoral dissertation of

Steven Paul Lorimor

has met the thesis requirements of Iowa State University

Signature was redacted for privacy.

Major Professor

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For the Major Program

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For the Graduate College

I dedicate this dissertation to my wife, Jeanette, and my son, Nicholas. Their continual love, sacrificial support, and constant encouragement made this work possible and meaningful. I thank them for all that they have done.

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LIST OF ABBREVIATIONS AND EXPLANATIONS

Ac	acetyl
acac	acetylacetonate
Bn	benzyl
bp	boiling point
br	broad (spectral)
Bu	butyl
°C	degrees Celsius
calcd	calculated
CI	chemical ionization (in mass spectrometry)
COSY	correlation spectroscopy
δ	chemical shift in parts per million downfield from tetramethylsilane
d	day(s); doublet (spectral)
DEPT	distortionless enhancement by polarization transfer
DMSO	dimethyl sulfoxide
EI	electron impact (in mass spectrometry)
ESR	electron spin resonance
Et	ethyl
FID	flame ionization detection
FVP	flash vacuum pyrolysis
g	gram(s)
GC	gas chromatography
h	hour(s)
HETCOR	heteronuclear chemical shift correlation
HMPA	hexamethylphosphoric triamide
HOMO	highest occupied molecular orbital
Hz	hertz
IPA	isopropyl alcohol
IR	infrared
J	coupling constant (in NMR)

L	liter(s)
LDA	lithium diisopropylamide
LUMO	lowest unoccupied molecular orbital
μ	micro
m	multiplet (spectral), meter(s), milli
M	moles per liter
Me	methyl
MHz	megahertz
min	minute(s)
mM	millimoles per liter
mol	mole(s)
mp	melting point
MS	mass spectrometry
m/z	mass to charge ratio (in mass spectrometry)
NMR	nuclear magnetic resonance
PCC	pyridinium chlorochromate
Ph	phenyl
ppm	parts per million (in NMR)
q	quartet (spectral)
s	singlet (NMR); second(s)
t	triplet (spectra)
TBAF	tetrabutylammonium fluoride
THF	tetrahydrofuran
TLC	thin layer chromatography
TMS	trimethylsilyl, tetramethylsilane

GENERAL INTRODUCTION

For many years, the Trahanovsky research group has been involved with the investigation of reactive species. The goal of this research has been to characterize and explore the chemistry of these reactive molecules. A considerable amount of work has been done investigating *o*-quinodimethanes and *p*-quinodimethanes (*p*-QDM's) derived from benzene, furan, and thiophene. These compounds have been of general interest to organic chemists from a theoretic standpoint and for their application in synthetic chemistry. The five chapters of this dissertation cover work involving regioselectivity of the Diels-Alder reaction of 3-methylene-1,4-pentadiene, characterization of simple *p*-QDM's by NMR spectroscopy, analysis of oligomerization of simple *p*-QDM's, and attempts at characterization of *p*-diphenoquinodimethane by ^{1}H NMR spectroscopy.

Chapter one describes the preparation of a cross-conjugated triene, 3-methylene-1,4-pentadiene, by flash vacuum pyrolysis (FVP) and it characterization by ^{1}H and ^{13}C NMR spectroscopy. It also describes the Diels-Alder reaction of triene and methyl acrylate. Chapter two is a literature review covering stability, formation by pyrolylic and non-pyrolylic methods, and spectroscopy of simple *p*-QDM's. Chapter three describes the preparation and characterization by NMR spectroscopy of three *p*-QDM's. The chapter also describes the analysis of the *p*-QDM's oligomerization products. Chapter four describes the preparation and characterization of four reactive *p*-QDM's by ^{1}H NMR spectroscopy. Rate constants were determined for their decomposition. Chapter five discusses the attempted observation of *p*-diphenoquinodimethane, a biphenyl-based *p*-QDM, by ^{1}H NMR spectroscopy. Evidence of the *p*-QDM's formation was found in the products, both from its reaction with oxygen and its oligomerization.

Dissertation Organization

This dissertation is composed of five separate papers. Chapters 1, 3, 4 and 5 are written in the style suitable for publication in the professional journals published by the American Chemical Society. Each paper has its own numbering system, detailed experimental section, reference section and appendix. A general conclusion follows the last paper of this dissertation.

CHAPTER 1. REGIOSELECTIVITY OF DIELS-ALDER REACTION OF 3-METHYLENE-1,4-PENTADIENE, THE SIMPLEST CROSS-CONJUGATED TRIENE

A paper accepted by Journal of Organic Chemistry

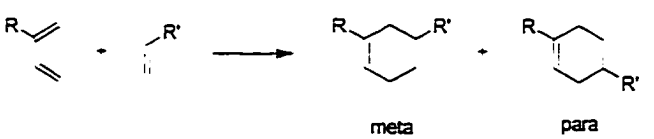
Walter S. Trahanovsky and Steven P. Lorimor

Abstract

The smallest possible cross-conjugated polyene, 3-methylene-1,4-pentadiene (**1**), was prepared by flash vacuum pyrolysis (FVP). Analysis of the ^{13}C NMR spectrum of triene **1** was clarified with the use of HETCOR NMR spectroscopy. The Diels-Alder reaction of triene **1** and methyl acrylate produces methyl 4-vinyl-3-cyclohexenecarboxylate (**5**), the '*para*' 1:1 adduct, and methyl 3-vinyl-3-cyclohexenecarboxylate (**6**), the '*meta*' 1:1 adduct. COSY and HETCOR NMR spectroscopy was used to determine that the yields of the '*para*' 1:1 adduct **5** and the '*meta*' 1:1 adduct **6** are 79% and 6%, respectively.

Introduction

The Diels-Alder reaction of a 2-substitued butadiene and an electron-deficient dienophile can occur to yield two regioisomers, the '*meta*' and the '*para*'. With electron-rich substituents on the butadiene, the favored product is the '*para*' isomer. The ratio of the '*para*' to the '*meta*' isomer can vary from nearly 1: 1 to the point where only the '*para*' product is observed.[1]

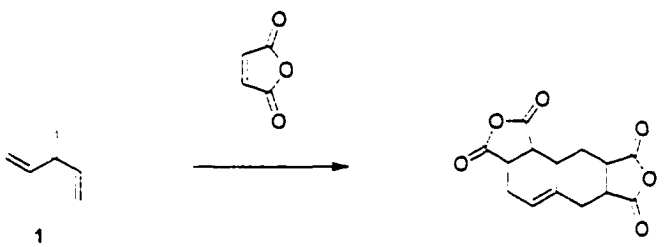


3-Methylene-1,4-pentadiene (**1**)[2,3] is the smallest possible member of the family of

1

cross-conjugated polyenes. These polyenes have been called "dendralenes".[4] Our research group has developed a convenient preparative route to triene 1 and has found that 1 dimerizes at a moderate rate to 1,4,4-trivinylcyclohexene, a [4+2] dimer.[5,6] It was proposed that this dimerization proceeds by a two-step mechanism involving a resonance-stabilized diradical intermediate.[5,6]

The Diels-Alder reaction of triene 1 with symmetric dienophiles has received modest attention. Blomquist and Verdol in 1955 reported the first Diels-Alder reaction of triene 1, the reaction of 1 with maleic anhydride to form the 2:1 adduct, $\Delta^{1(9)}$-octalin-3,4,6,7-tetra-carboxylic anhydride.[2] Later that same year Bailey and Economy reported, in addition to the same 2:1 adduct with maleic anhydride, 2:1 adducts with *p*-benzoquinone, naphthaquinone,



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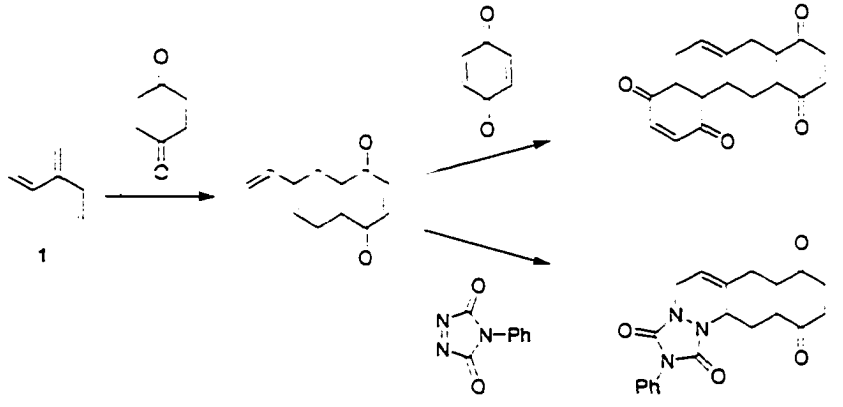
and $\Delta^{2,8a(10a)}$decahydroanthracene-1,4-dione.[3] These earliest examples were studied under conditions that yield only 2:1 adducts.

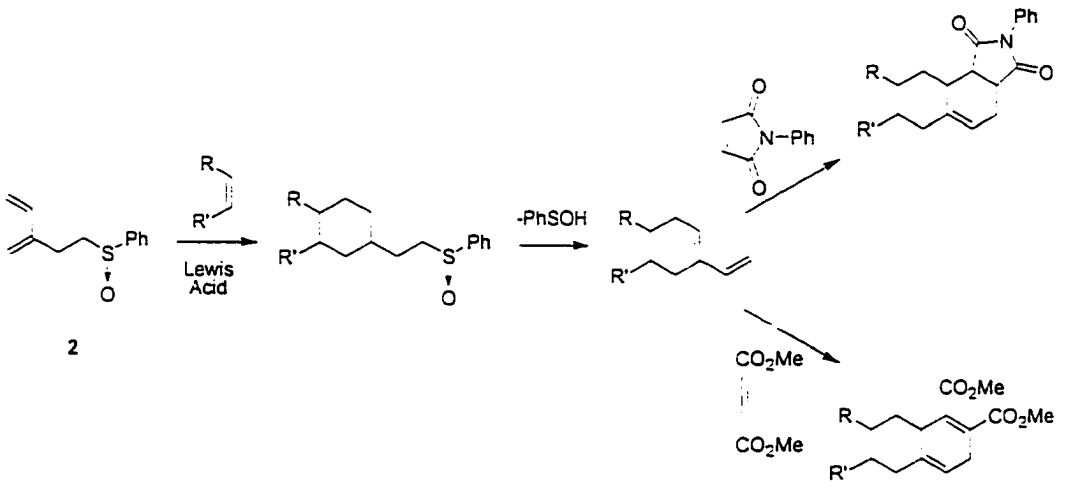
Cadogan and coworkers have found that triene 1 reacts with certain dienophiles to produce 1:1 adducts that still have a diene unit which is available to react with a different second dienophile to produce a mixed adduct.[7] When a single equivalent of *p*-benzoquinone is added to triene 1, a 1:1 adduct is formed which can in turn react with a second equivalent

of *p*-benzoquinone or an equivalent of *N*-phenyl-1,2,4-azoline-3,5-dione to form a mixed adduct. Generally, dienophiles tetracyanoethylene (TCNE) and dimethyl

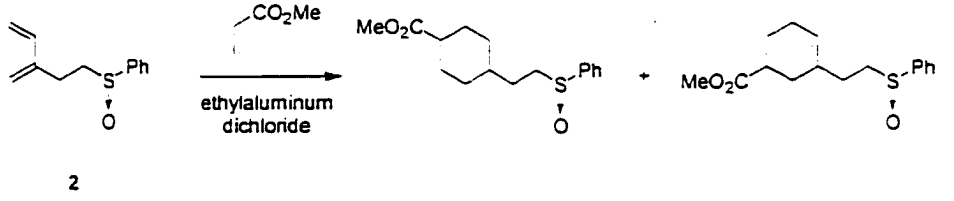


acetylenedicarboxylate (DMAD) add to triene **1** to form only 1:1 adducts but under extreme conditions, a second equivalent of DMAD will add to form the 2:1 adduct.

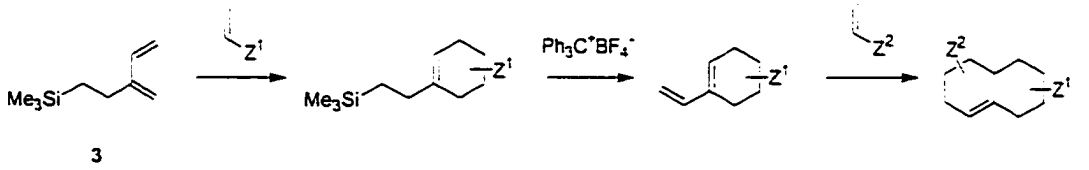
Several researchers, seeking a less reactive synthetic equivalent of triene **1**, have produced 3-methylene-5-phenylsulfinyl-1-pentene (**2**)[8] and 2-trimethylsilylethyl-1,3-butadiene (**3**).[9] In general, the synthetic equivalent is allowed to react with a dienophile to produce a 1:1 adduct which is then converted to a conjugated diene that can react with a second dienophile. Specifically, diene **2** is allowed to react with a dienophile in the presence of a Lewis acid to produce a 1:1 adduct. Benzenesulfinic acid is thermally eliminated from this adduct to form a diene which can react with a second dienophile such as either dimethyl acetylenedicarboxylate or *N*-phenylmaleimide.



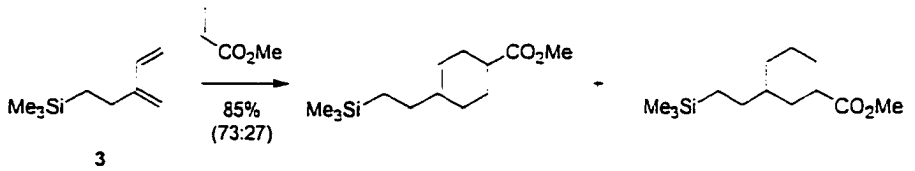
Overall yields are 70-80% and unsymmetrical olefins such as 3-buten-2-one, methyl acrylate, and acrolein gave only limited regioselectivity with para to meta ratios of 70:30, 69:31, and 70:30, respectively.[8]



For the other synthetic equivalent of triene 1, 2-trimethyl-silylethyl-1,3-butadiene (3), after the addition of the first dienophile, the second diene is generated by treating the 1:1 adduct with $Ph_3C^+BF_4^-$. Unsymmetrical dienophiles, such as methyl acrylate and



3-buten-2-one, have only limited regioselectivity in either the first or second Diels-Alder reaction.

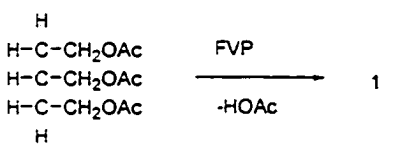


3

In order to determine the regioselectivity of the first Diels-Alder reaction of triene 1, we have studied its reaction with methyl acrylate. The results of this study are reported herein.

Results

1,5-Diacetoxy-3-(acetoxymethyl)pentane (4) was prepared from triethyl tricarballate by the procedure of Bailey and Economy.[3] Flash vacuum pyrolysis (FVP) of triacetate 4 yields triene 1 with side products of acetic acid, acetic anhydride, and benzene. The amount



4

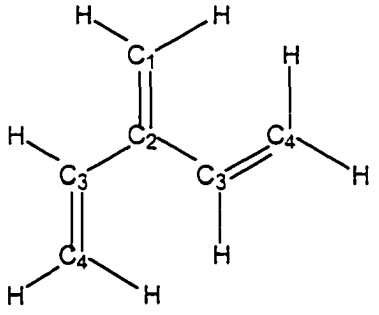
of triacetate 4 that was pyrolyzed varied from 0.5 to 5.0 g. The yields ranged from 95% for the smaller amounts to 65% for the larger amounts. The acetic acid and acetic anhydride were removed by extraction with aqueous base.

Our research group's previously reported[5,6] ^{13}C NMR spectrum assignments for triene 1 were in error. The peak at δ166.14 is now reassigned to acetic anhydride, an impurity. The two up-field signals were overlapping to give the appearance of a single peak at δ115.77. To confirm the ^{13}C peak assignments of triene 1, a HETCOR spectrum in benzene-d_6 was acquired. The results appear in Table 1. Our present ^{13}C NMR data are consistent with the other reported data.[7,10] Cadogan's ^{13}C NMR data[7] show only three peaks but the signal of the quaternary carbon will be absent in the DEPT spectrum. Our present ^{13}C NMR spectrum

Table 1. NMR Data for Triene 1.

Carbon atom[a]	$^{1}H,\delta$	$^{13}C,\delta$
1	5.03	115.64
2		145.08
3	6.36	136.16
4	5.32	115.70
	4.98	

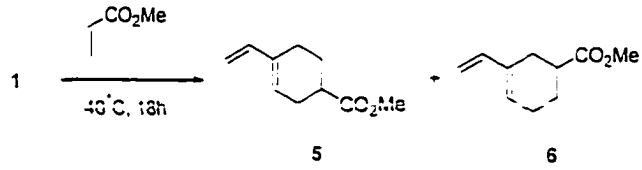
[a] The carbon atom label of triene **1** are as follows:



agrees most closely to the data of Hopf,[10] although the relative assignments of the two up-field signals are reversed. Solvent and temperature changes could explain this reversal of assignments.

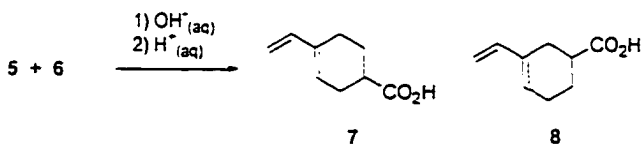
Under mild conditions, 40°C in CCl_4, methyl acrylate and **1** react to yield methyl 4-vinyl-3-cyclohexenecarboxylate (**5**), the '*para*' 1:1 adduct, and methyl 3-vinyl-3-cyclohexenecarboxylate (**6**), the '*meta*' 1:1 adduct, with small amounts of 2:1 adducts (*ca.* 2%) and dimer (ca. 6%). The '*para*' to '*meta*' regioselectivity of the addition was in a ratio of 93:7 as determined by GC analysis of the reaction products with biphenyl as an internal standard to be use later to in determining the yield. A mixture of the two

regioisomers could be isolated from the 2:1 adducts and dimer by column chromatography but attempts to isolate the individual two isomers by column chromatography failed. A ^{1}H NMR, ^{13}C NMR, and mass spectra were obtained of the mixture of esters **5** and **6**.



5 6

The mixture of esters **5** and **6** was converted to the corresponding acids **7** and **8** by basic hydrolysis. Acid **7** was isolated from the mixture of acids by selective recrystallization from acetic acid/water and was further purified by vacuum sublimation. ^{1}H, ^{13}C, HETCOR, and COSY NMR spectra of acid **7** were obtained. The results appear in Table 2. Assignment of acid **7** as the '*para*' 1:1 adduct was confirmed by the analysis of the COSY spectrum. The hydrogen on carbon three is coupled to the hydrogen on carbon two. The hydrogen on carbon two is also coupled to the hydrogen on carbon one. The chemical shift of carbon one is shifted down field because it is α to the carboxylic acid.



7 8

Acid **7** was treated with methanol to yield ester **5**. A GC correction factor for the ester relative to biphenyl was determined. With this GC correction factor and the GC analysis of the crude reaction mixture, the yield of **5** and **6** was determined to be 79% and 6%, respectively. A ^{1}H NMR spectrum of ester **5** was obtained to verify the regio assignments made to the esters **5** and **6**.

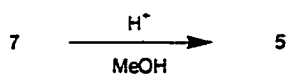
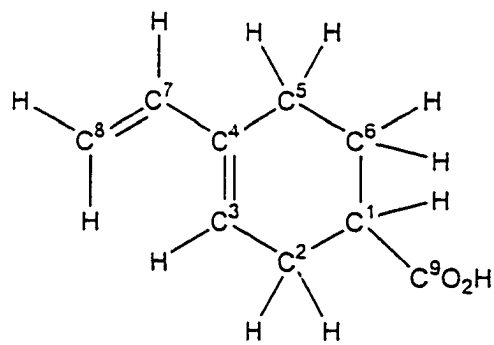


Table 2. NMR Data for 4-Vinyl-3-cyclohexenecarboxylic Acid (7).

Carbon atom[a]	$^{1}H,\delta$	$^{13}C,\delta$
1	2.59	39.14
2	2.4	27.79
	2.4	
3	5.72	127.04
4		135.69
5	2.33	23.03
	2.13[b]	
6	2.19-2.09[b]	24.75
	1.75	
7	6.33	139.27
8	5.06	110.83
	4.98	
9		181.58

[a] The carbon atom label of acid **7** are as follows:



[b] The ^{1}H NMR assignment may be reversed due to the overlap of their signals.

Discussion

The improved preparation by FVP of acetate **4** provides triene **1** in good to high yields for quantities of up to 5 g. For preparations of one gram or less, the overall yields are very high (95%). As larger quantities are prepared, yields are more modest (65%) as triene **1** is lost to the formation of carbon deposits on the pyrolysis tube and slightly larger amounts of

dimer in the product mixture. The improved preparation also provides triene **1** with fewer by-products such as acetic acid, acetic anhydride, benzene, dimer, and oligomers.

The Diels-Alder reaction of triene 1 and methyl acrylate proceeds under mild conditions in high yield (*ca.* 85%) and with high regioselectivity (93/7) in favor of the '*para*' 1:1 adduct. The mildness of the reaction allows for very little side-product formation such as dimer, oligomers, and 2:1 adducts. Formation of 2:1 adducts with methyl acrylate requires higher reaction temperatures or extended reactions times.

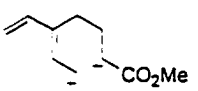
Direct use of triene **1** with unsymmetrical dieneophile yielded products with greater regioselectivity compared to the two synthetic equivalents: 3-methylene-5-phenylsulfinyl-1-pentane (**2**) and 2-trimethylsilylethyl-1,3-butadiene (**3**). The Diels-Alder reaction of triene synthetic equivalent **2** with methyl acrylate yielded only moderate regioselectivity for the '*para*' 1:1 adduct (69:31).[8] Triene synthetic equivalent **3** yielded only slightly better regoiselectivity for the '*para*' 1:1 adduct (73:27).[9]

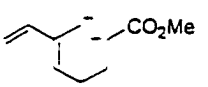
This high regioselectivity is consistent with the analysis based on frontier molecular orbital theory.[1,11,12] This Diels-Alder reaction involves a "normal electron demand" because the vinyl group on the diene is a donating group and the methyl carboxylate on the dieneophile is an accepting group. By bringing together the largest coefficients of the HOMO of the diene and LUMO of the dieneophile, the "*para*" regio-isomer is predicted.

Kahn and Hehre have proposed an alternative method for predicting the regioselectivity of cycloaddition reactions, based on matching complementary (electrophilic and nucleophilic) reactivity surfaces calculated at the Hartree-Fock level (3-21G/3-21G$^{(*)}$)

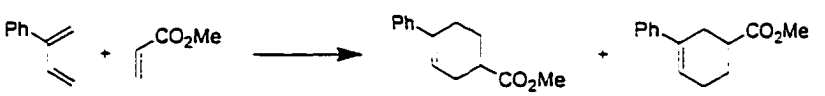
and obtained independently for each of the two reactants.[12] This chemical reactivity modeling procedure uses a "test" electrophile, H^-, to probe the diene and a "test" nucleophile, H^-, to probe the dienophile. In the case of the hydride probe, reactivity surfaces are constructed by treating the hydride as a nondeformable "ball" which then "rolls around" on the top of the electron-density surface of the dienophile and the potential energy of interaction is evaluated at each point of contact.[12] The preferred regiochemistry of the Diels-Alder reaction is one in which the diene terminus with the larger reactivity towards electrophiles aligns with the ethylene carbon of the dienophile with the larger reactivity towards nucleophiles. Using this method, the "*meta*" 1:1 adduct is predicted to be favored.[12]

Consideration of a dipolar resonance structure of the transition states also leads to the conclusion that the '*para*' 1:1 adduct is favored. Triene 1 is analogous to 2-phenylbutadiene





and the reaction of this diene and methyl acrylate also produces more of the '*para*' adduct ('*para*'/'*meta*' = 82/18).[13]



Conclusion

3-Methylene-1,4-pentadiene (**1**) can be prepared with few impurities by flash vacuum pyrolysis (FVP) in good to high yields (65-95%). The ^{13}C NMR spectrum of triene **1** was clarified with the use of HETCOR NMR spectroscopy. The Diels-Alder reaction of triene **1** and methyl acrylate produces 1:1 adducts in 85% yield with dimer and 2:1 adducts as the

primary impurities. The reaction is regioselective favoring methyl 4-vinyl-3-cyclohexenecarboxylate (**5**), the '*para*' 1:1 adduct, over methyl 3-vinyl-3-cyclohexenecarboxylate (**6**), the '*meta*' 1:1 adduct by 93/7. This selectivity is consistent with frontier molecular orbital theory and dipole resonance structures of the transition states. The "*para*" selectivity is inconsistent with Kahn-Hehre reactivity modeling procedure.

Experimental Section

Methods and Materials. Some general methods have been described previously.[14] All materials were commercially available and used as received, except where indicated. ^{1}H NMR spectra were 300 MHz unless noted otherwise. ^{13}C NMR spectra were recorded at 75.47 MHz unless noted otherwise.. For both the GC and the GC/MS analysis, a DB-5 column (30m, I.D. 0.32 mm, 0.25μ film thickness) was used. Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN.

1,5-Diacetoxy-3-(acetoxymethyl)pentane (4) was prepared by a procedure similar to the procedure of Bailey and Economy.[3] The crude product was distilled twice (short-path) to give a light yellow distillate, bp 120 °C (0.07 mm) (lit.[3] 120 °C (0.5 mm)). Analysis of the material by capillary GC indicated it was > 99 % pure. ^{13}C NMR (75.47 MHz, $CDCl_3$) δ (multiplicity when off-resonance decoupled) 170.36 (s), 170.28 (s), 65.74 (t), 61.62 (t), 31.50 (d), 29.64 (t), 20.34 (q), 20.27 (q).

3-Methylene-1,4-pentadiene (1) was prepared by FVP[14] of 5.00g (19.2 mmol) of 1,5-diacetoxy-3-(acetoxymethyl)pentane (**4**) by a procedure similar to that reported[5, 6] with the following changes: a) No quartz chips were used in the pyrolysis tube. b) 15 mL of CCl_4

was added to the trap instead of benzene. c) Pyrolysis oven was heated to 850 °C. d) Sample chamber was heated to 90 °C.

A significantly different workup was used. The product solution was transferred to a separatory funnel with an additional 5 mL of CCl_4 as rinse. The CCl_4 solution was washed with saturated $NaHCO_3$ (4 x 10 mL). The basic wash layers were combined and back extracted with an additional 5 mL of CCl_4. The CCl_4 layers were combined, washed with saturated NaCl (10 mL), and dried ($MgSO_4$). Known volumes of the product solution were transferred into vials for storage at –80°C.

A vial of triene **1** solution was allowed to warm to room temperature. The concentration of the triene **1** solution was determined by NMR spectroscopy (1,1,2,2-tetrachlororethane, internal standard) to be 0.54 M. The yield was 61%. GC and NMR analyses indicates little or no acetic acid and acetic anhydride. ^{1}H NMR (benzene-d_6) δ 6.36 (dd, *J*=17.4 *Hz*, *J'*=10.8 Hz, 2H), 5.32 (dd, *J*=17.1 *Hz*, *J'*=1.2 Hz, 2H), 5.03 (s, 2H), 4.98 (dd, *J*=10.9 *Hz*, *J'*= 1.1 Hz, 2H); lit.[6] ^{1}H NMR (benzene-d_6, 298 K) δ 6.33 (dd, *J*=17.4 *Hz*, *J'*=10.8 Hz, 2H), 5.30 (dd, *J*=17.5 Hz, *J'*=1.5 Hz, 2H), 4.99 (s, 2H), 4.95 (dd, *J*=10.9 Hz, *J'*=1.6 Hz, 2H)); ^{13}C NMR (75.47 MHz, CD_2Cl_2 and CCl_4) δ 144.74, 135.93, 115.63, 115.44; ^{13}C NMR (75.47 MHz, benzene-d_6) δ (multiplicity when off resonance decoupled) 145.08 (s), 136.16 (d), 115.70 (dd), 115.64 (t); lit.[10] ^{13}C NMR (CD_2Cl_2, 203 K) δ 144.55,136.09, 116.27, 116.17; lit.[7] ^{13}C NMR ($CDCl_3$, DEPT) δ 135.62, 115.38, 115.35; lit.[6] ^{13}C NMR (75.47 MHz, benzene-d_6 298 K) δ (multiplicity when off resonance decoupled) 166.14 (s, (low intensity)), 145.18 (t), 136.26 (d), 115.77 (t).

Methyl 4-Vinyl-3-cyclohexenecarboxylate (5), Methyl 3-Vinyl-3-cyclohexenecarboxylate (6), and 4-Vinyl-3-cyclohexenecarboxylic Acid (7). To a 10-mL round-bottom flask was added 0.0197g (1.277×10^{-4} mol) of biphenyl. A vial containing one mL of 0.49 M solution of triene 1 (4.9×10^{-4} mol) in CCl_4 was warmed from storage at -80°C to room temperature. The triene **1** solution, one mL of CCl_4, and two mL of methyl acrylate (1.9g, 2.2×10^{-2} mol) were added to the flask. A water-cooled condenser was placed on the flask. The flask was heated to 40°C. The reaction was followed by GC and after 18 h, the triene **1** was consumed. Analysis of the crude product mixture by GC and GC/MS revealed two major products, methyl 4-vinyl-3-cyclohexenecarboxylate (**5**) and methyl 3-vinyl-3-cyclohexenecarboxylate (**6**), and several minor products, dimer (*ca.* 6%) and 2:1 adducts (*ca.* 2%). From the GC analysis the '*para*' to '*meta*' regioselectivity (the ratio of **5** to **6**) was determined to be 93:7. The product mixture was concentrated under reduced pressure to yield viscous oil (0.082g). Isolation of esters **5** and **6** was attempted by column chromatography on silica gel (toluene) but failed to resolve the two regioisomers although the dimer and 2:1 adducts were removed. With this mixture of the two regioisomers **5** and **6**, ^1H and ^{13}C NMR spectra were obtained.

5: ^1H NMR ($CDCl_3$) δ 6.34 (dd, J=17.4 Hz, J'=10.5 Hz, 1 H), 5.74 (broad s, 1 H), 5.08 (d, J=17.4 Hz, 1H), 4.94 (d, J=10.8, 1 H), 3.70 (s, 3 H), 2.56 (m, 1 H), 2.38 (m, 2 H), 2.30 (m, 1 H), 2.11 (m, 2H), 1.73 (m, 1H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 176.03, 139.27, 135.55, 127.28, 110.60, 51.66, 39.29, 28.03, 24.95, 23.12; MS (70 eV) 166 (M^+) (17), 137 (2), 135 (2), 107 (30), 106 (87), 105 (41), 92 (15), 91 (100), 80 (14), 79 (75), 78 (50), 77 (39), 65 (10), 51 (12).

6: MS (70 eV) 166 (M^+) (<1), 137 (2), 107 (18), 106 (14), 105 (13), 91 (63), 79 (100), 78 (28), 77(22), 65 (11), 51 (10), 50 (5).

To the crude mixture of esters **5** and **6** (114mg, 0.69 mmol) was added 3 mL of 1 M NaOH and 10 mL of H_2O. The mixture was stirred rapidly and warmed to near boiling for about 1 h. The solution was washed with hexanes (3 x 10 mL). The aqueous layer was slowly acidified with 1 M HCl to a pH of less than one. The solid was recrystallized in $AcOH/H_2O$. Acid **7** was sublimed at 50°C (0.01 mm) to yield 51 mg (0.34 mmol) of a finely divided, white solid: mp 75.5-76.2°C; ^1H NMR ($CDCl_3$) δ 6.33 (dd, J=17.4 Hz, J'=10.8 Hz, 1 H), 5.72 (broad s, 1 H), 5.07 (d, J=17.7 Hz, 1H), 4.93 (d, J=10.8, 1 H), 2.59 (m, 1 H), 2.40 (m, 2 H), 2.30 (m, 1 H), 2.15 (m, 2H), 1.74 (m, 1H); ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 181.32, 139.21, 135.63, 129.98, 110.78, 39.07, 27.75, 24.72, 23.00; Anal. Cald for $C_9H_{12}O_2$: C, 71.03; H,7.94. Found: C, 71.20; H, 7.94.

Forty mg (0.26 mmol) of acid **7** was dissolved in methanol with a trace of H_2SO_4. The solution was heated to reflux for about 10 h. Solid $NaHCO_3$ was added and then the methanol was evaporated under reduced pressure. The product was dissolved in 10 mL of ether and the solution was washed successively with of H_2O (3 x 10 mL), saturated NaCl solution, and then dried ($MgSO_4$). Ester **5** was found to be 98% pure (GC) and concentrated to give 38 mg of an oil (0.23 mmol, 87% yield). Three solutions of purified ester **5** ($1x\ 10^{-4}$ mol) and biphenyl (2.65×10^{-5} mol, internal standard) in 0.600 mL of CCl_4 and 0.400 mL of CD_2Cl_2 were prepared. By comparison of NMR quantification (10 s pulse delay) of ester **5** in the three samples and GC peak area (biphenyl, internal standard), a GC correction factor of 1.68 $g_{ester}\ \%_{biphenyl}\ g_{biphenyl}^{-1}\ \%_{ester}^{-1}$ was calculated.[15] With this GC correction factor and the data collected from the above preparation of esters **5** and **6**, the yields can be calculated to

be 79% and 6%, respectively. A ^{1}H NMR spectrum of purified ester **5** was obtained and was consistent with the major component of the ^{1}H NMR spectrum of the mixture of esters **5** and **6**.

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Appendix

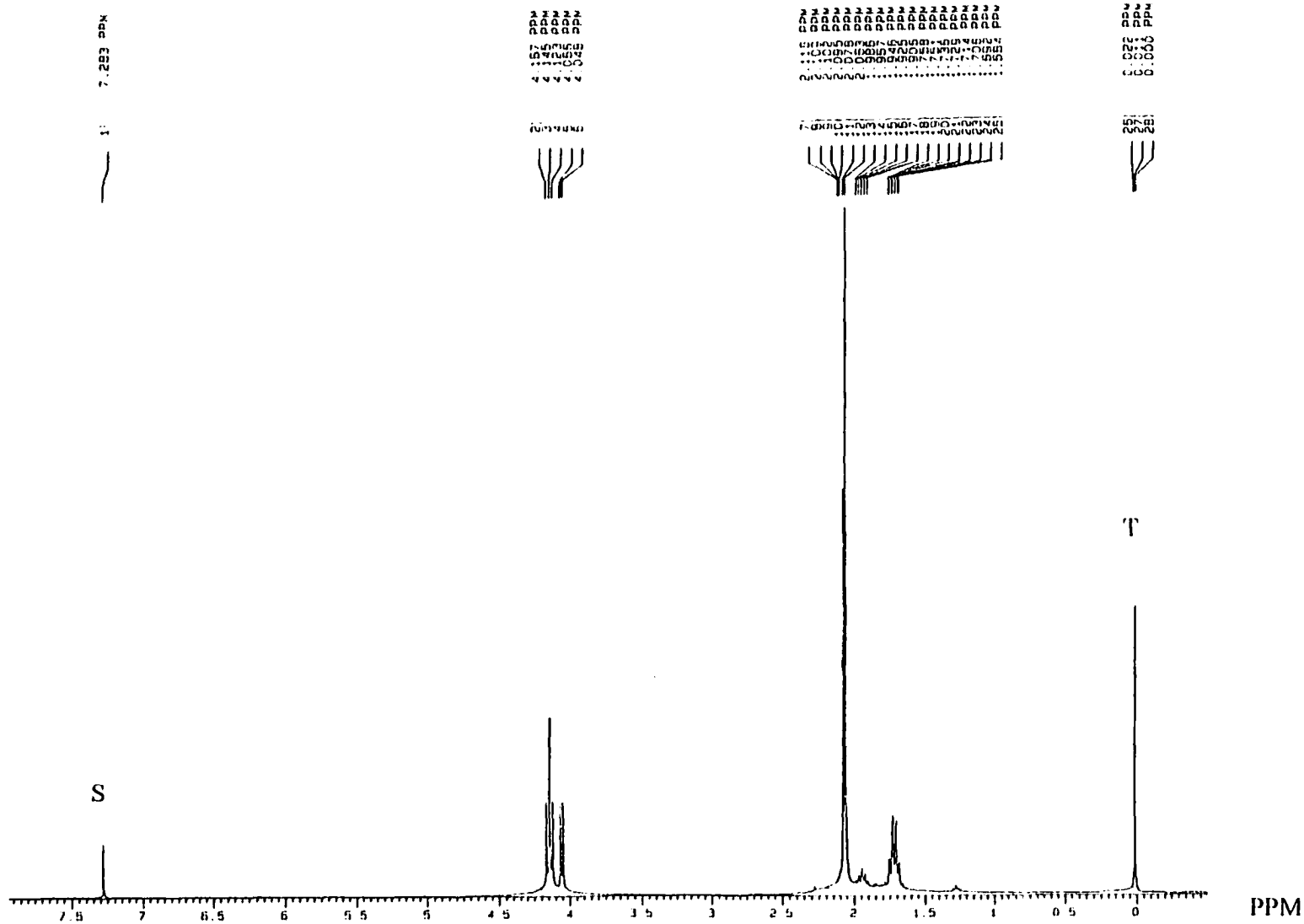


Figure A-1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 1,5-diacetoxy-3-(acetoxymethyl)pentane (4). (S: chloroform, T: TMS)

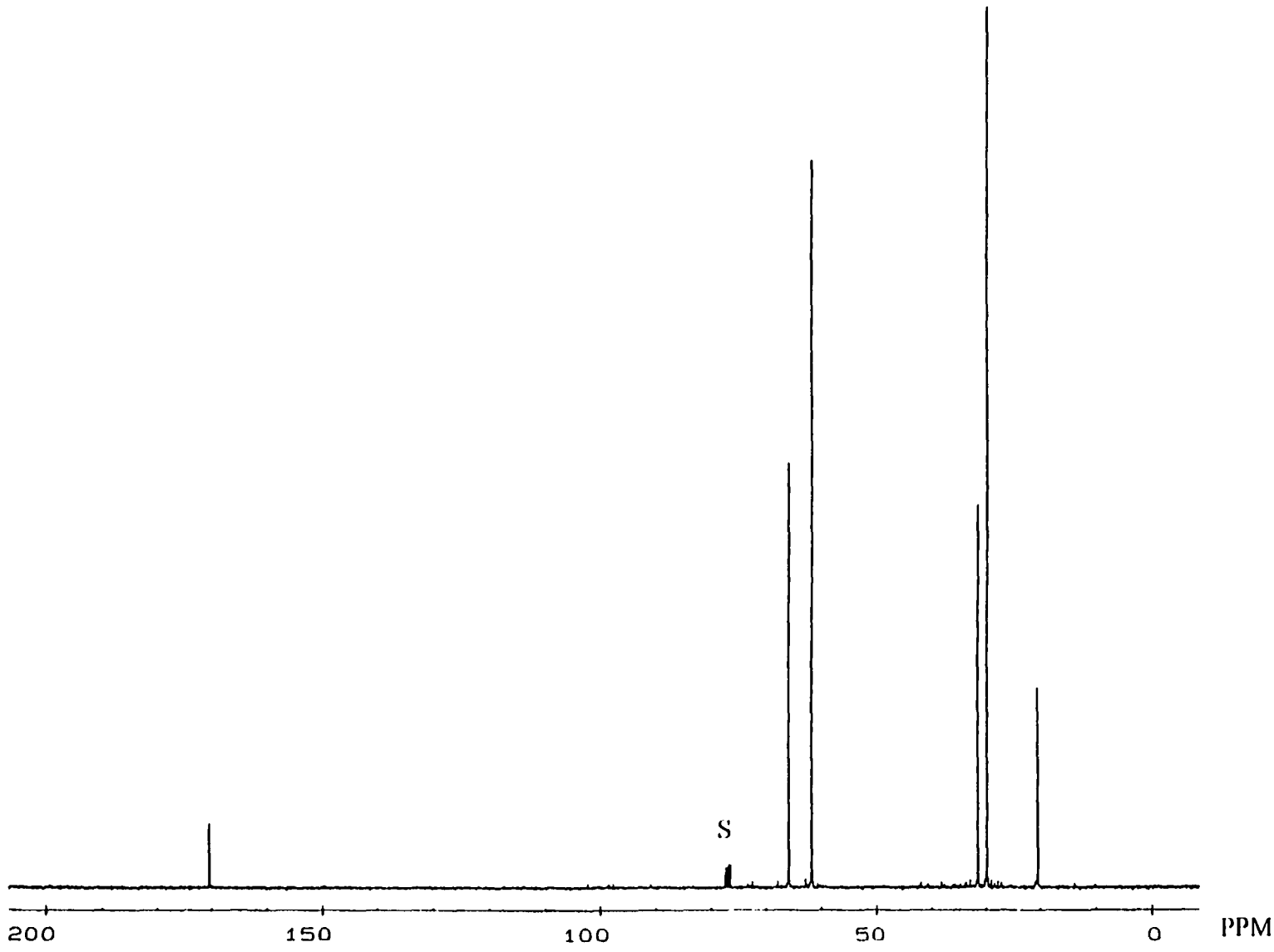


Figure A-2. ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$) of 1,5-diacetoxy-3-(acetoxymethyl)pentane (4). (S: chloroform)

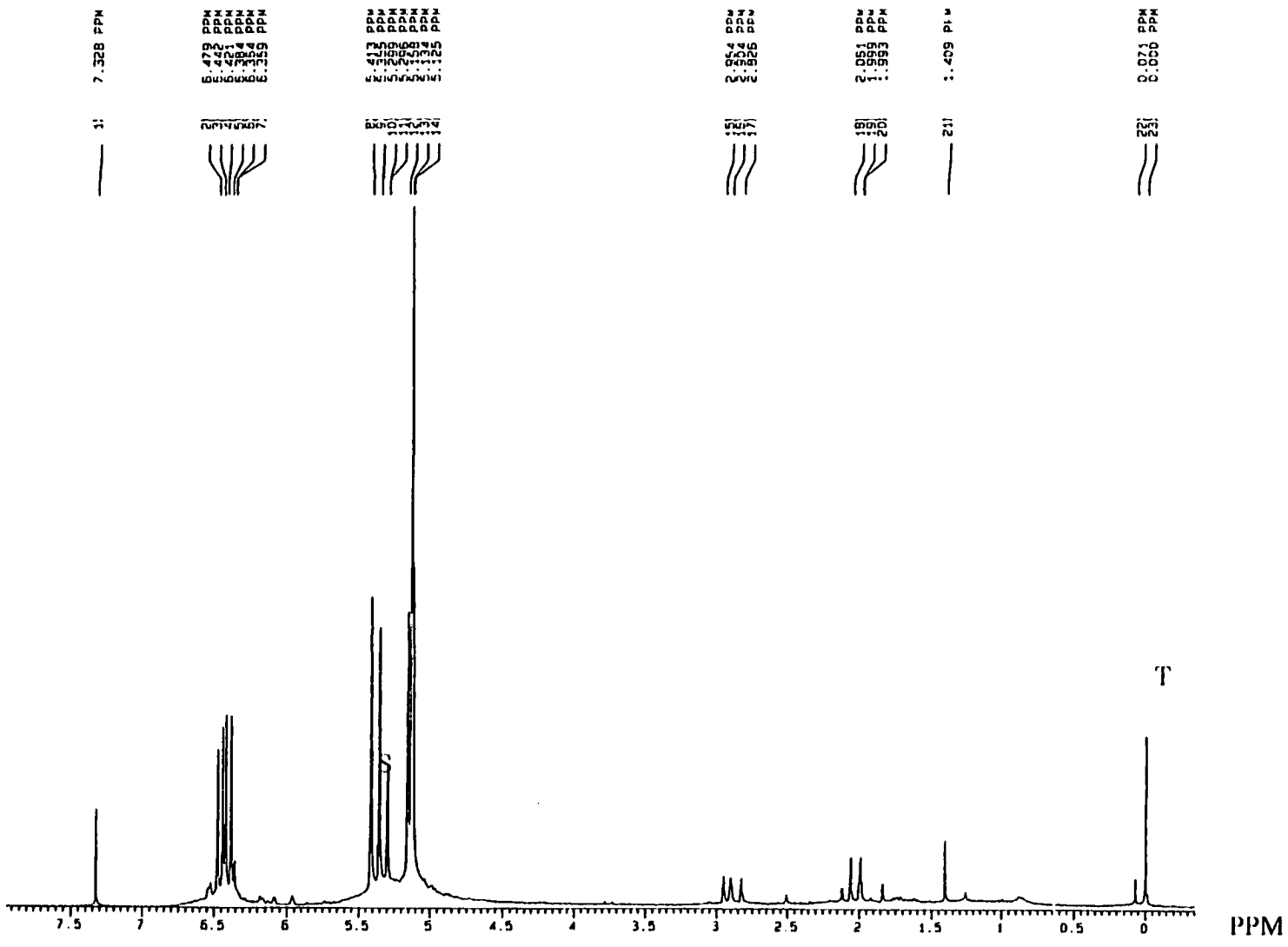


Figure A-3. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2 and CCl_4) of 3-methylene-1,4-pentadiene (1). (S: methylene chloride, T: TMS)

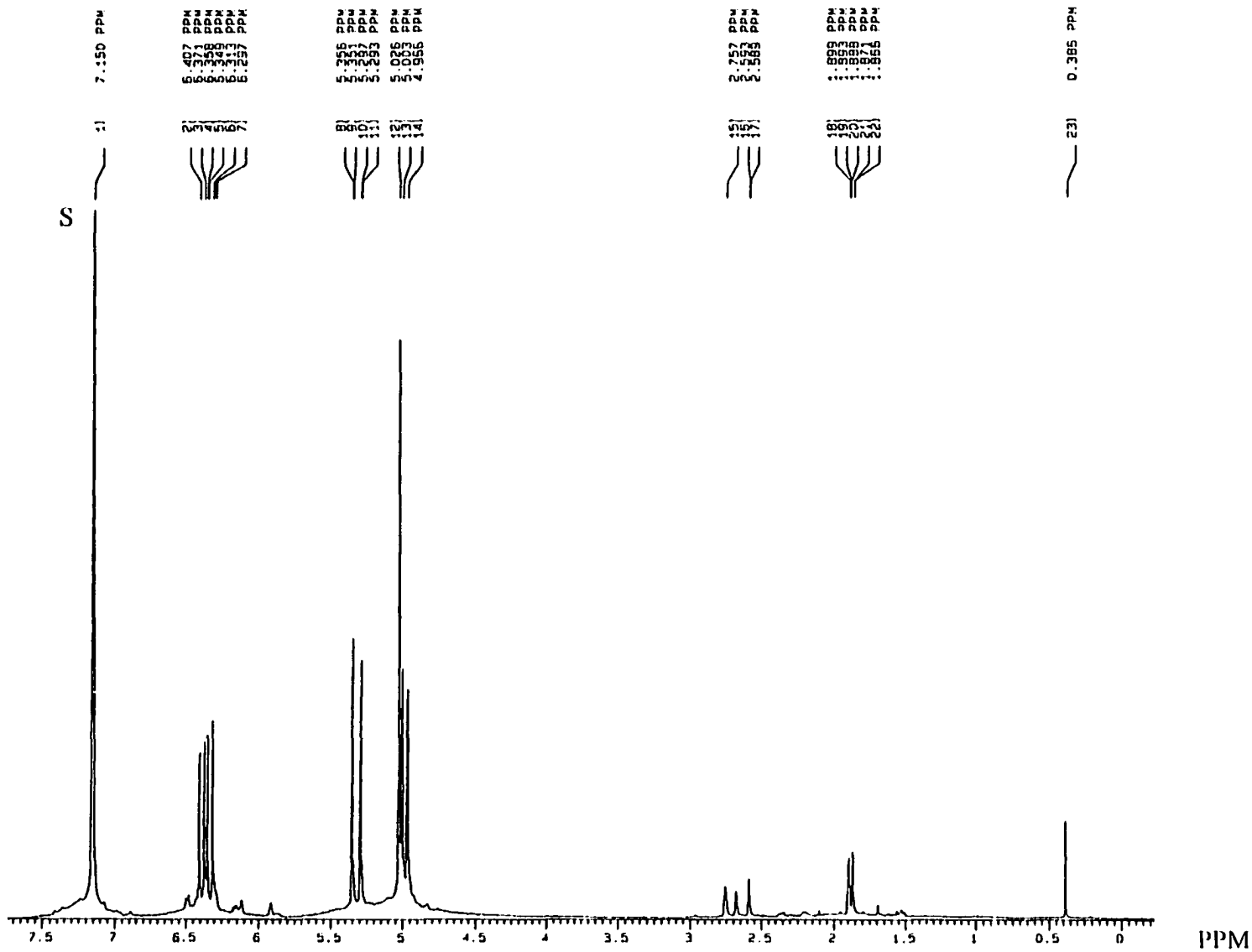


Figure A-4. ^{1}H NMR spectrum (300 MHz, benzene-d_6) of 3-methylene-1,4-pentadiene (**1**). (S: benzene)

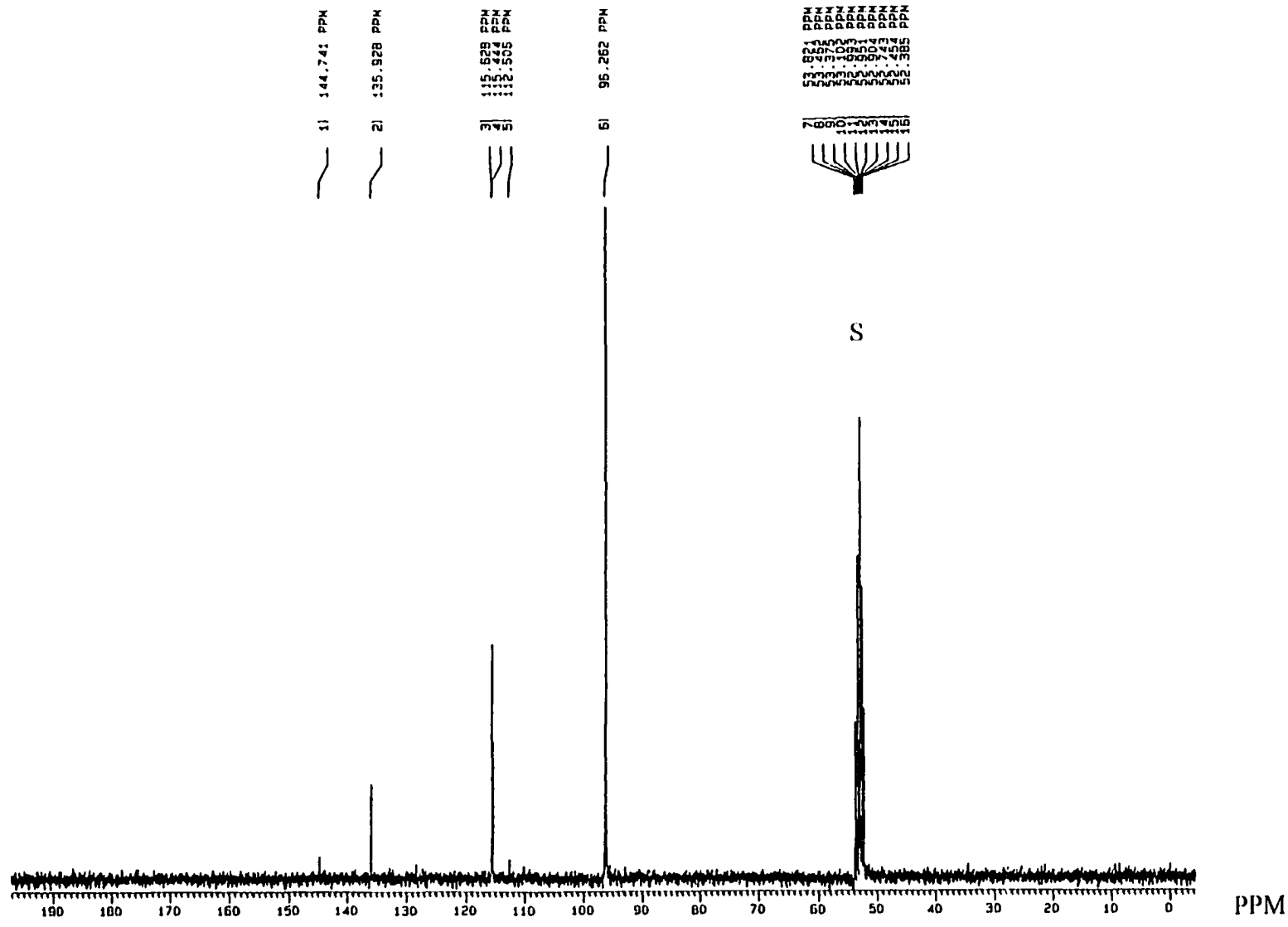


Figure A-5. ^{13}C NMR spectrum (75.47 MHz, CD_2Cl_2 and CCl_4) of 3-methylene-1,4-pentadiene (**1**). (S: methylene chloride)

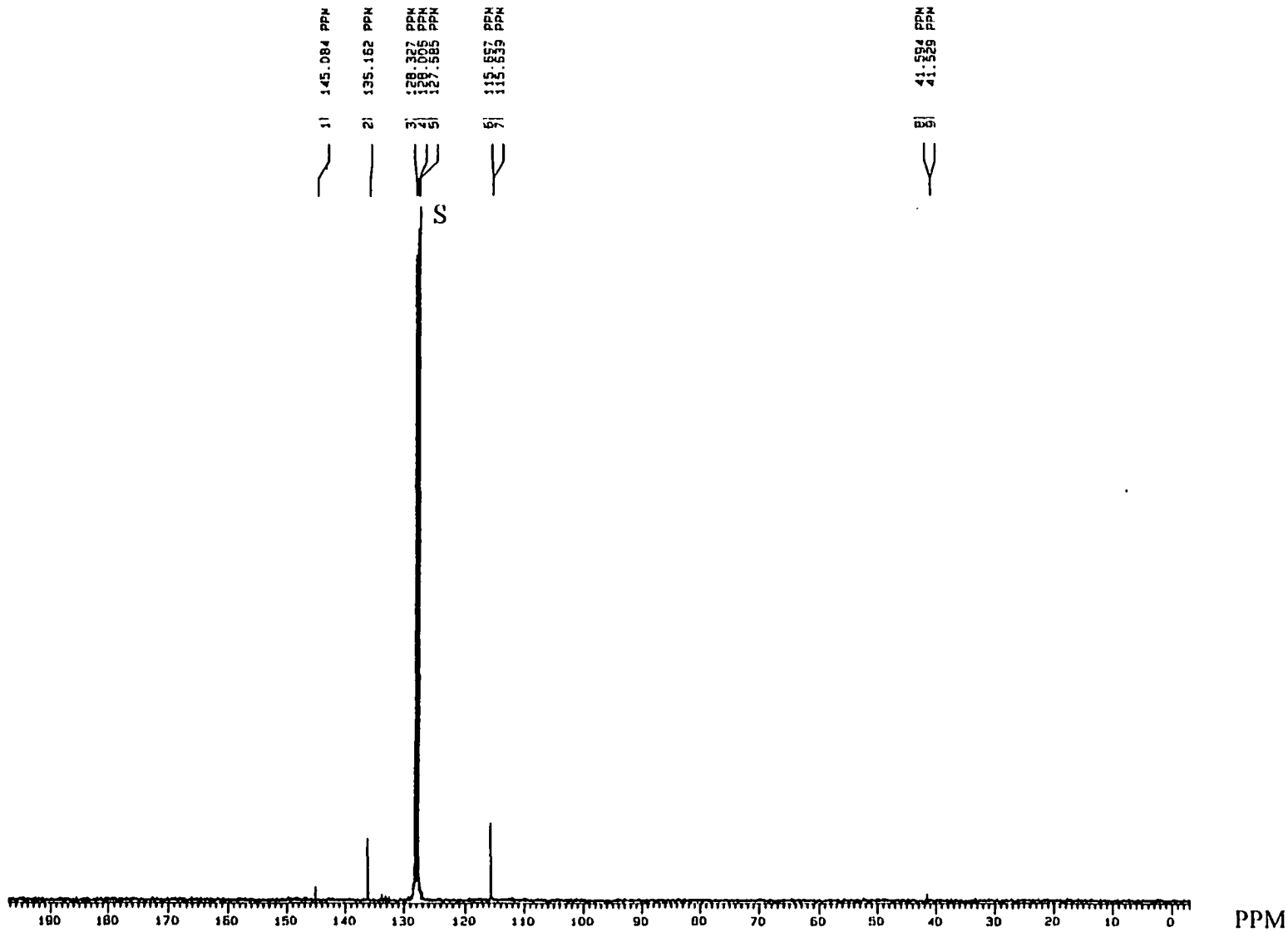


Figure A-6. ^{13}C NMR spectrum (75.47 MHz, benzene-d_6) of 3-methylene-1,4-pentadiene (**1**). (S: benzene)

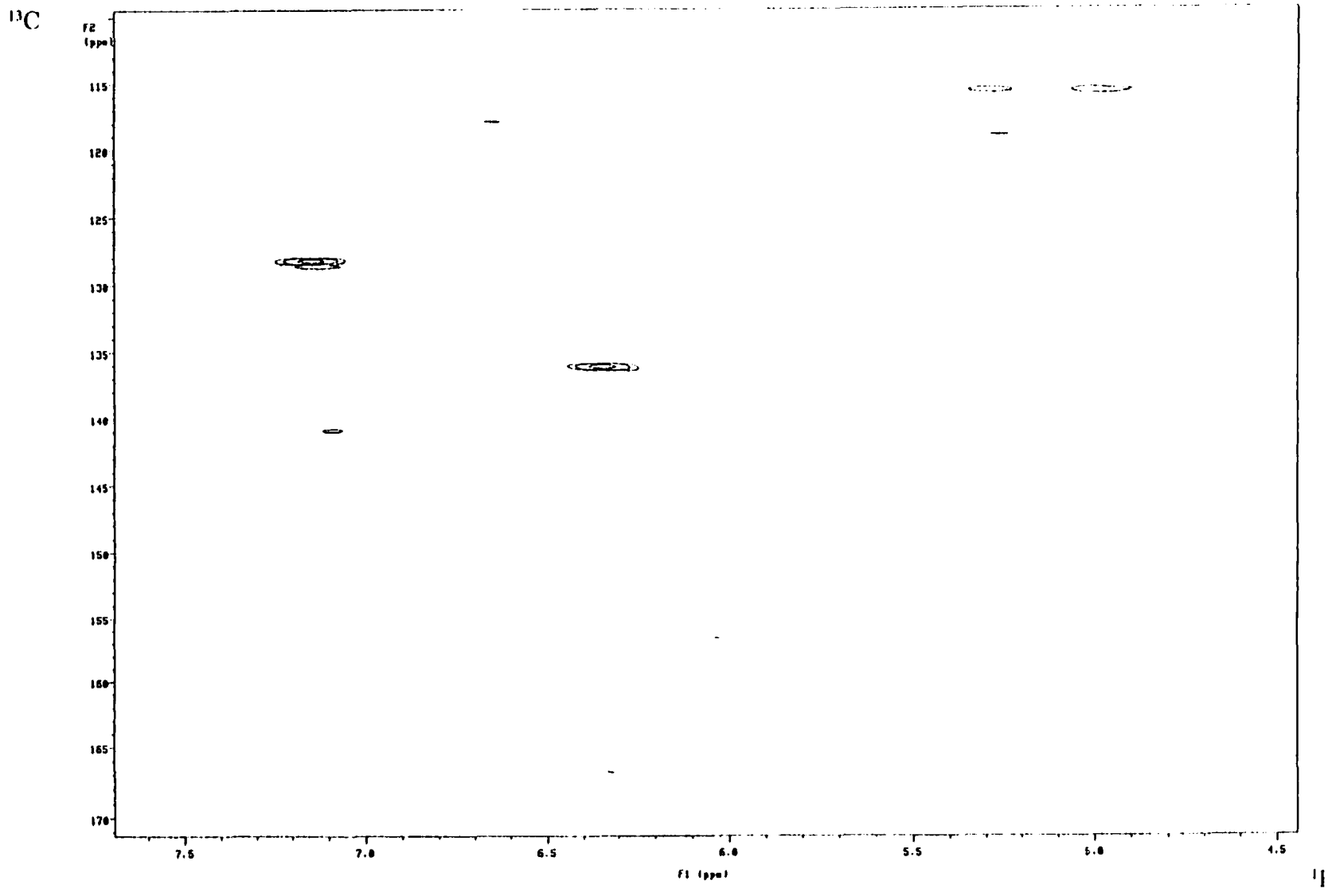


Figure A-7. HETCOR spectrum (benzene-d_6) of 3-methylene-1,4-pentadiene (**1**).

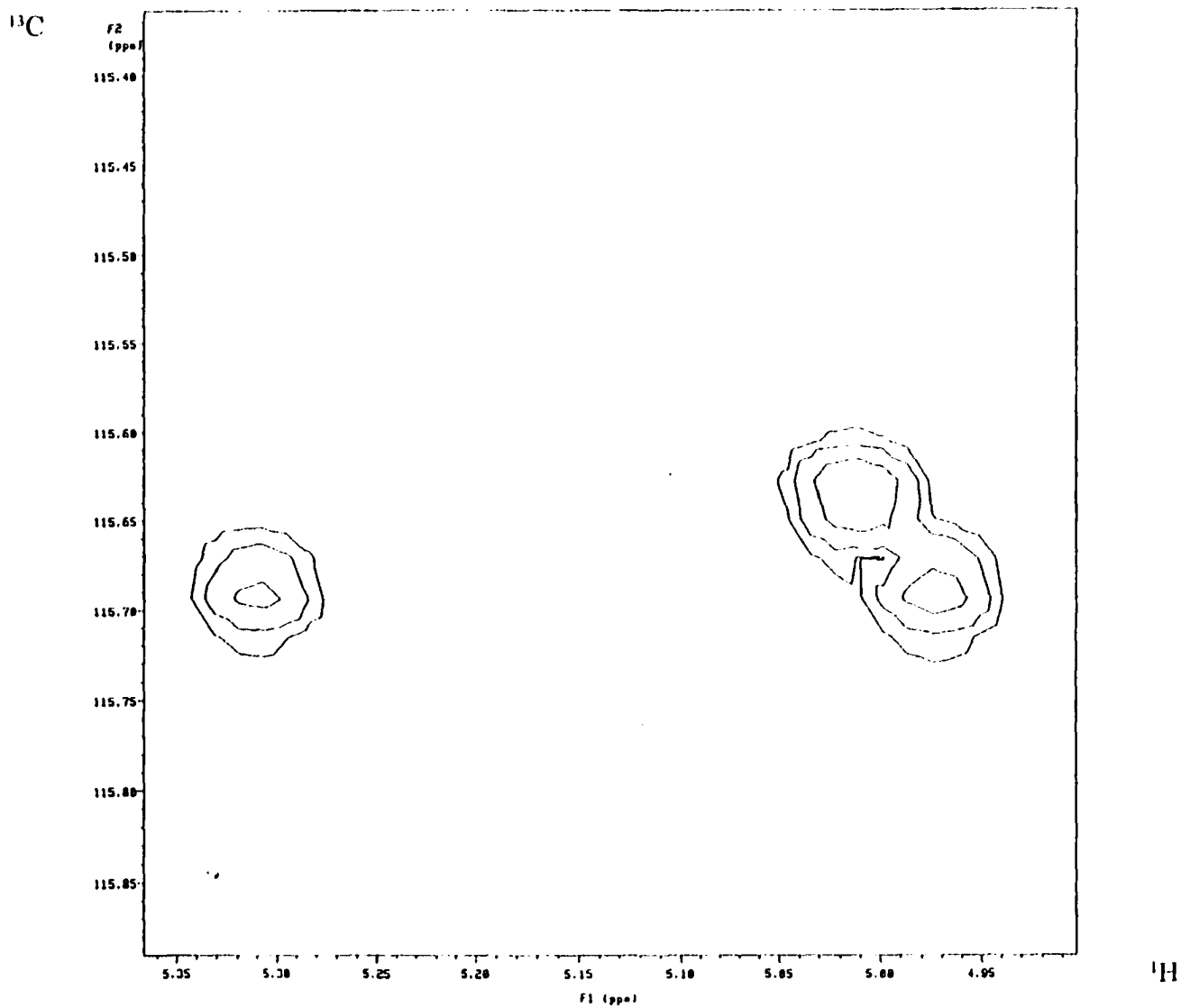


Figure A-8. Expansion of Figure A-7. HETCOR spectrum (benzene-d_6) of 3-methylene-1,4-pentadiene (1).

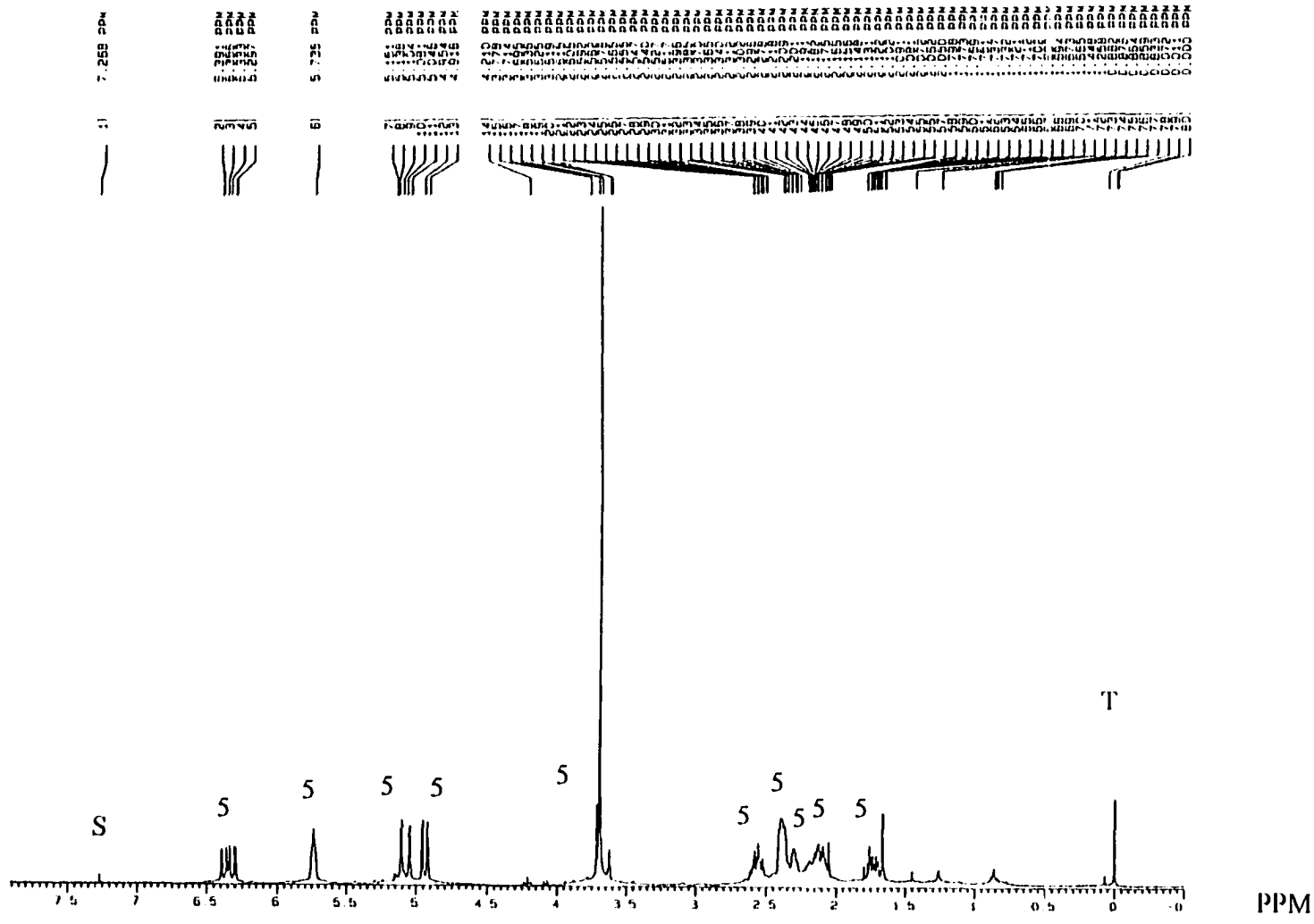


Figure A-9. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of methyl 4-vinyl-3-cyclohexenecarboxylate (**5**) and methyl 3-vinyl-3-cyclohexenecarboxylate (**6**). (S: chloroform, T: TMS)

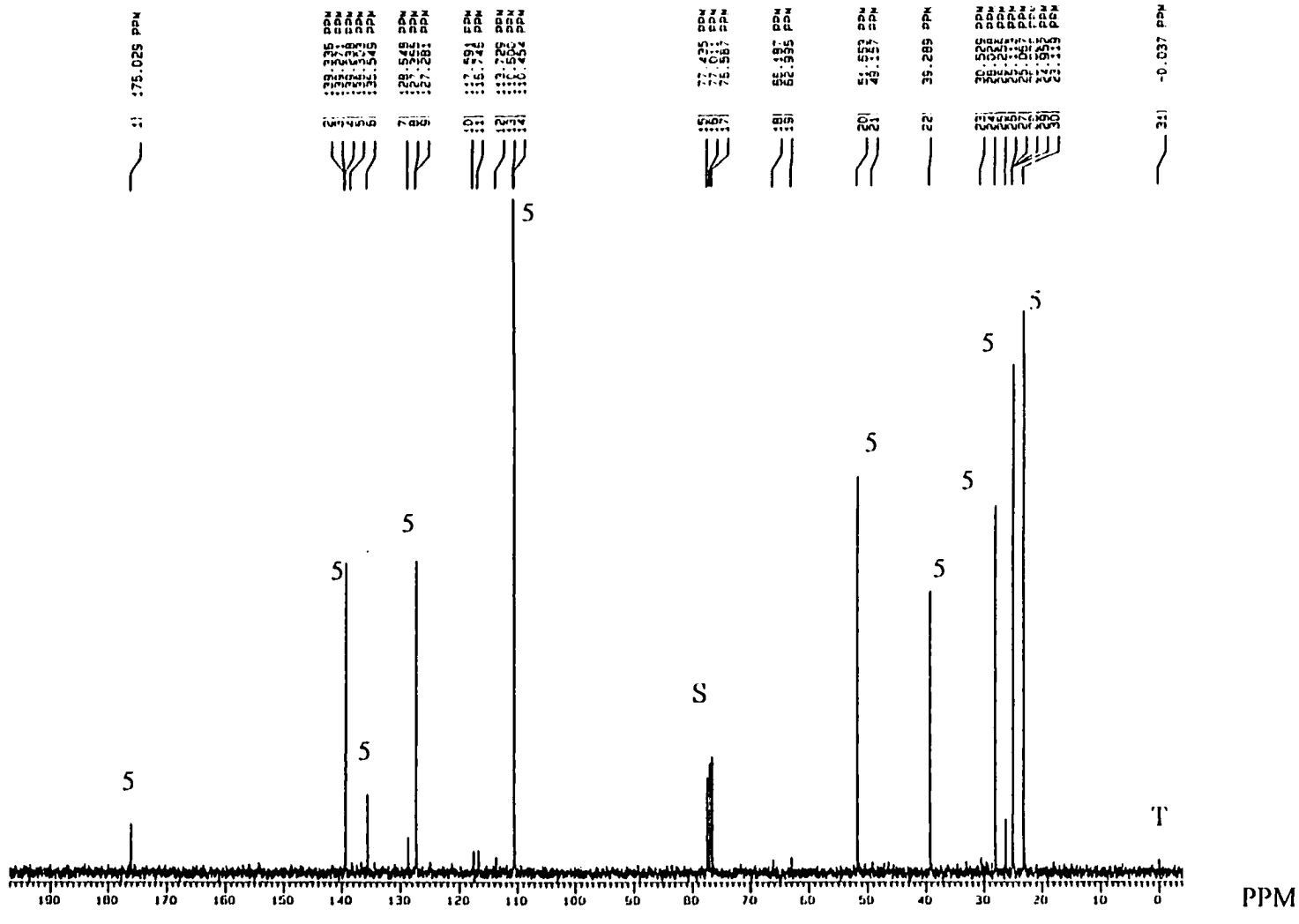


Figure A-10. ^{13}C NMR spectrum (75.47 MHz, $CDCl_3$) of methyl 4-vinyl-3-cyclohexenecarboxylate (**5**) and methyl 3-vinyl-3-cyclohexenecarboxylate (**6**). (S: chloroform, T: TMS)

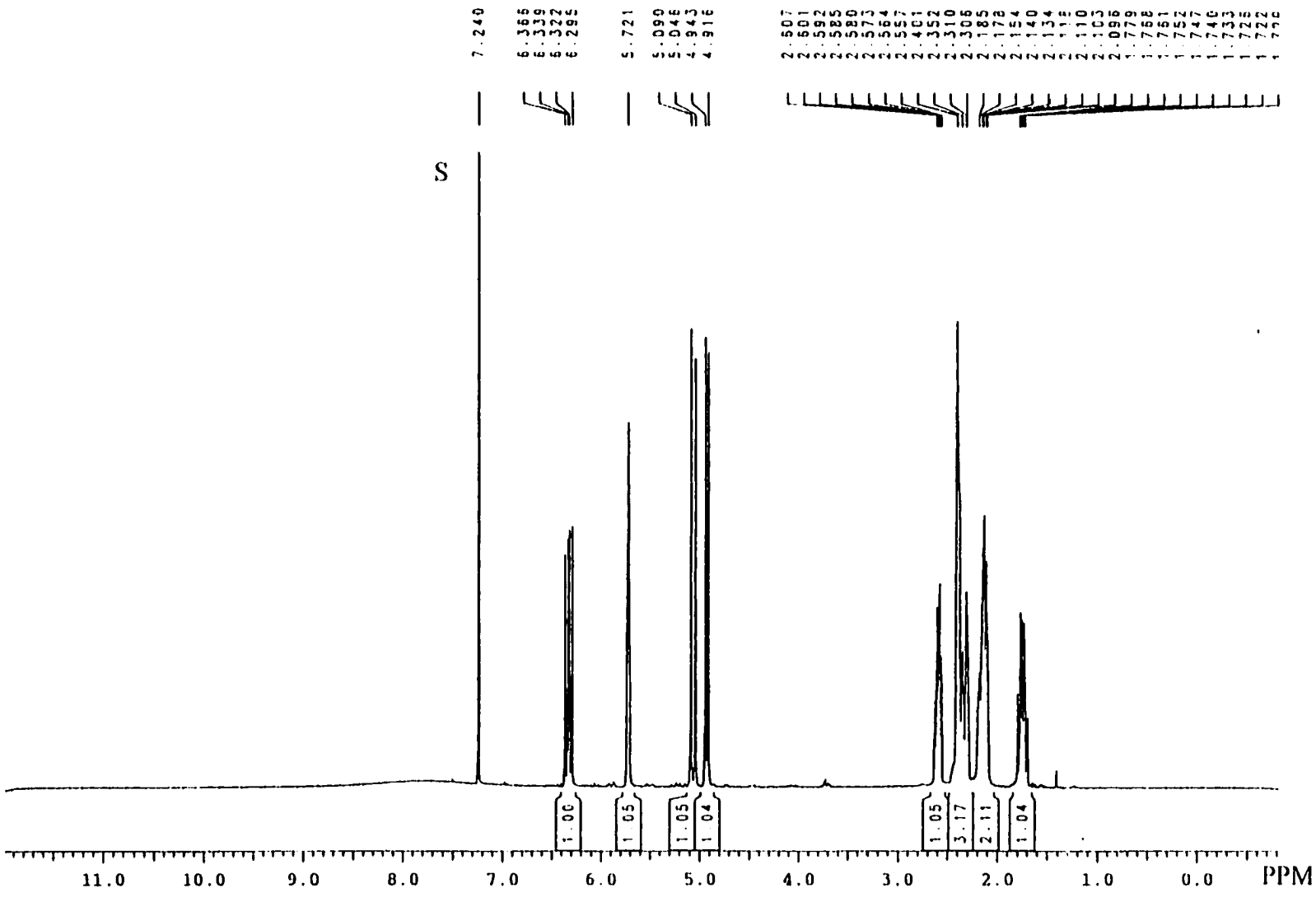


Figure A-11. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7). (S: chloroform)

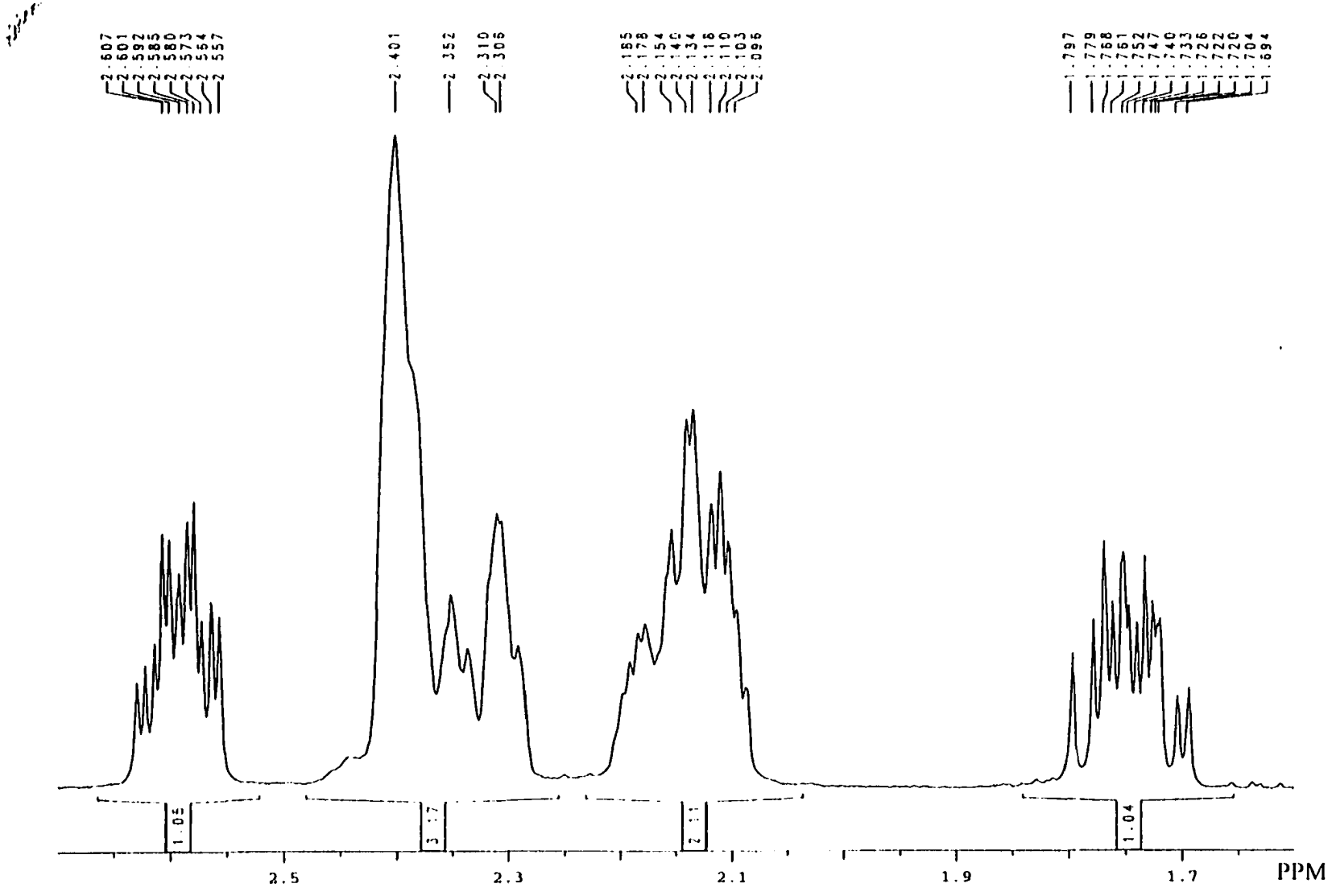


Figure A-12. Expansion of Figure A-11. ^1H NMR spectrum (400 MHz, $CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7).

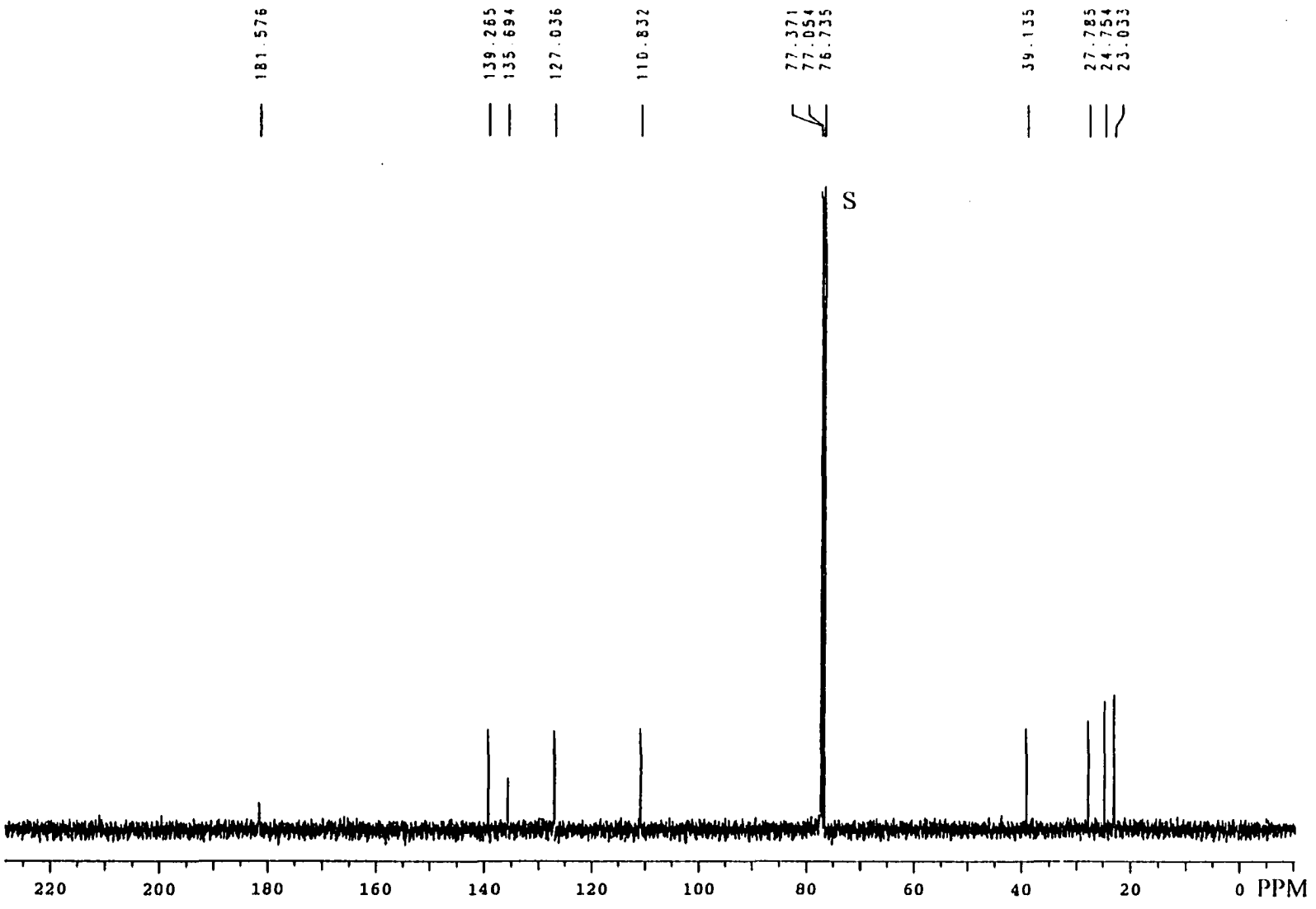


Figure A-13. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7). (S: chloroform)

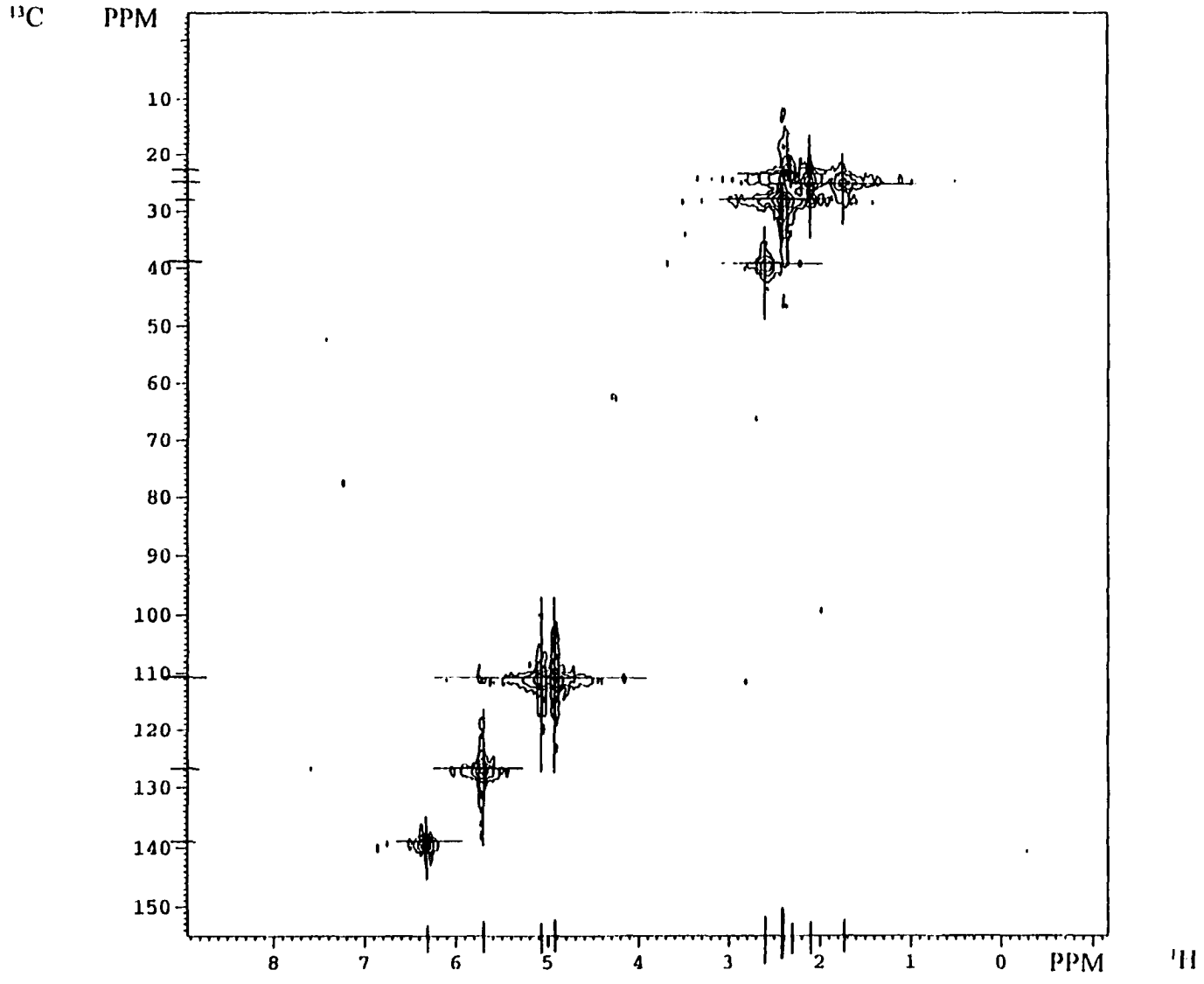


Figure A-14. HETCOR spectrum ($CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7).

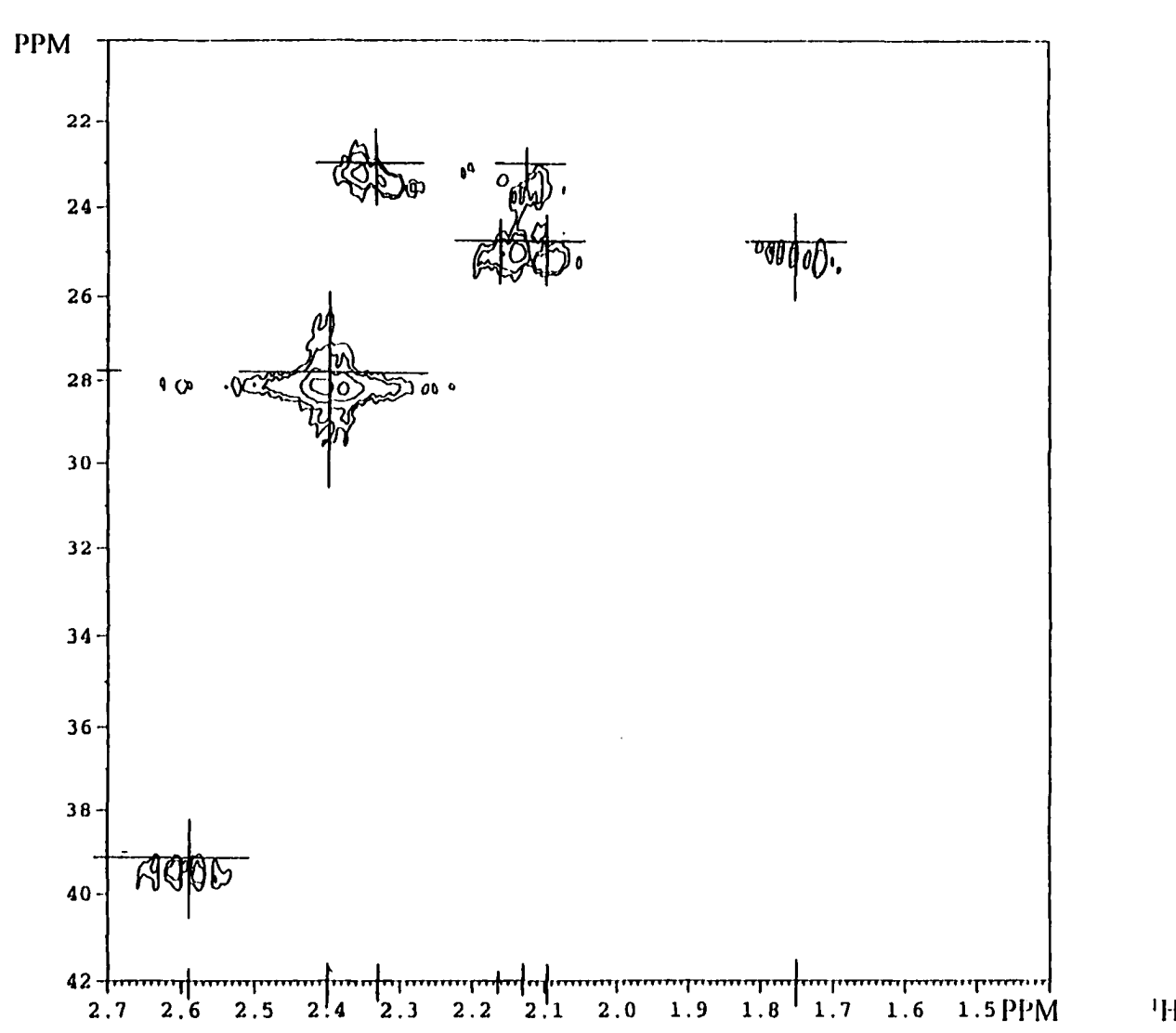
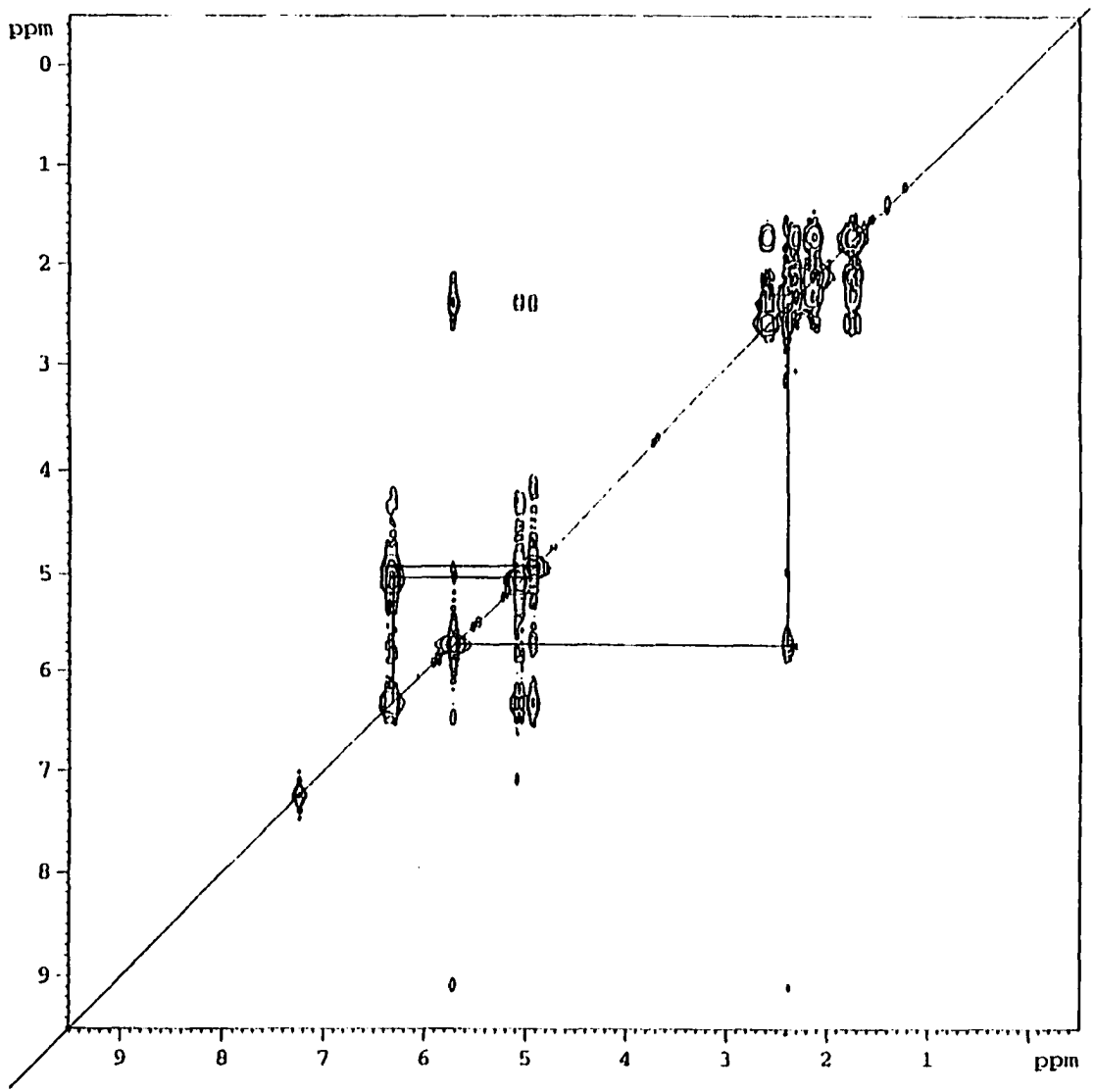


Figure A-15. Expansion of Figure A-14. HETCOR spectrum ($CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7).



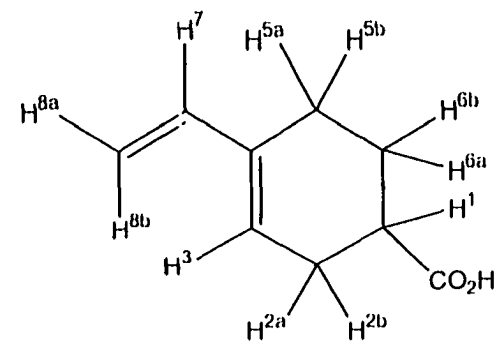
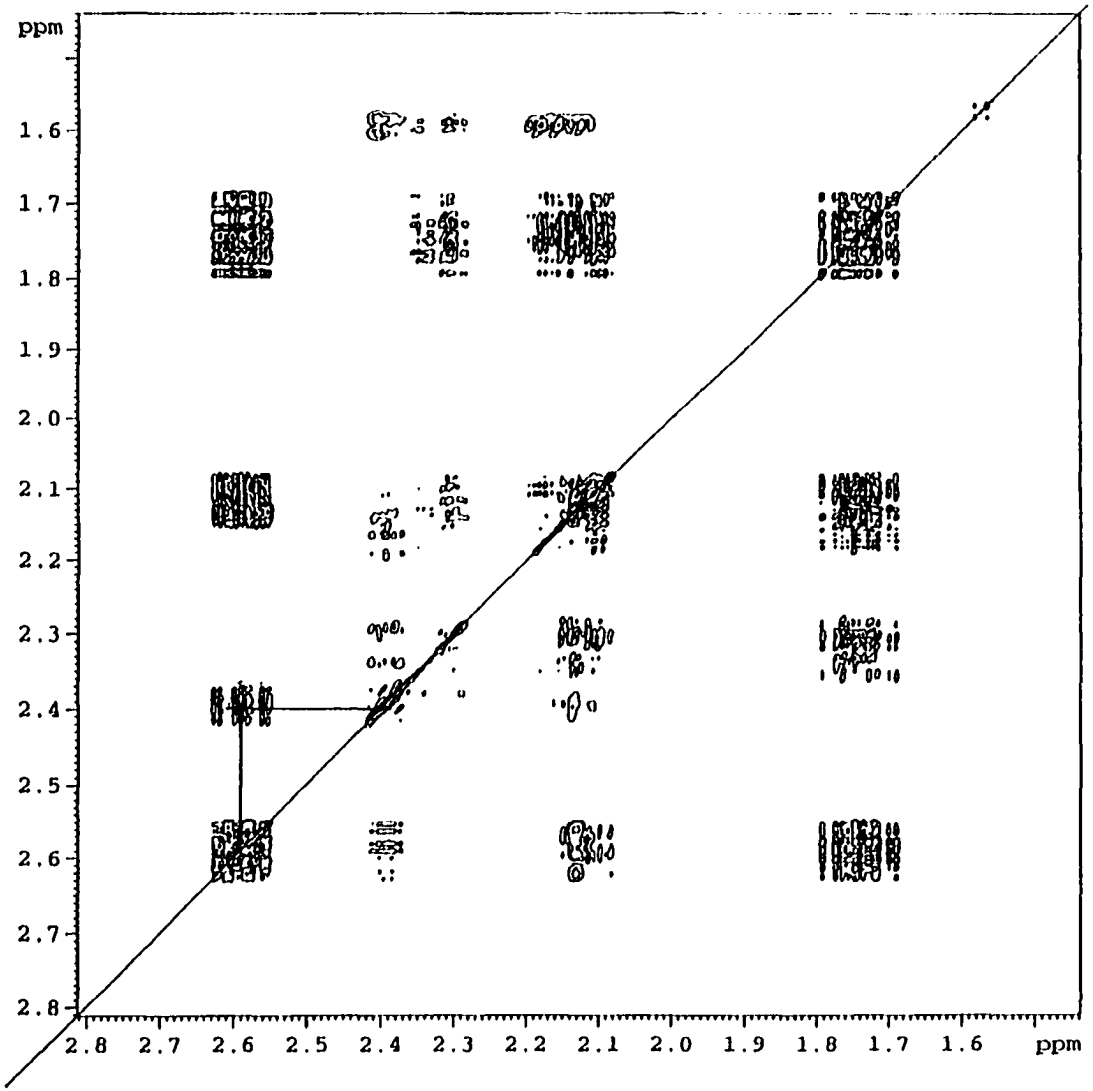


Figure A-16. COSY spectrum ($CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7) with H^{8a} & H^{8b} interaction with H^7 and H^3 interaction with H^{2a} & H^{2b} highlighted.



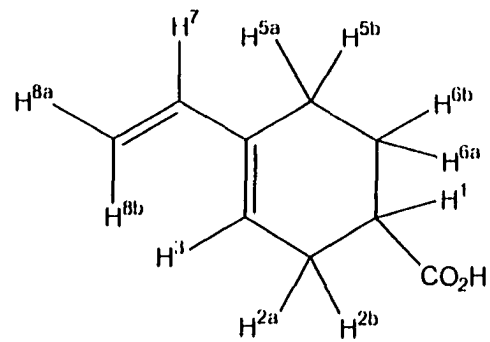
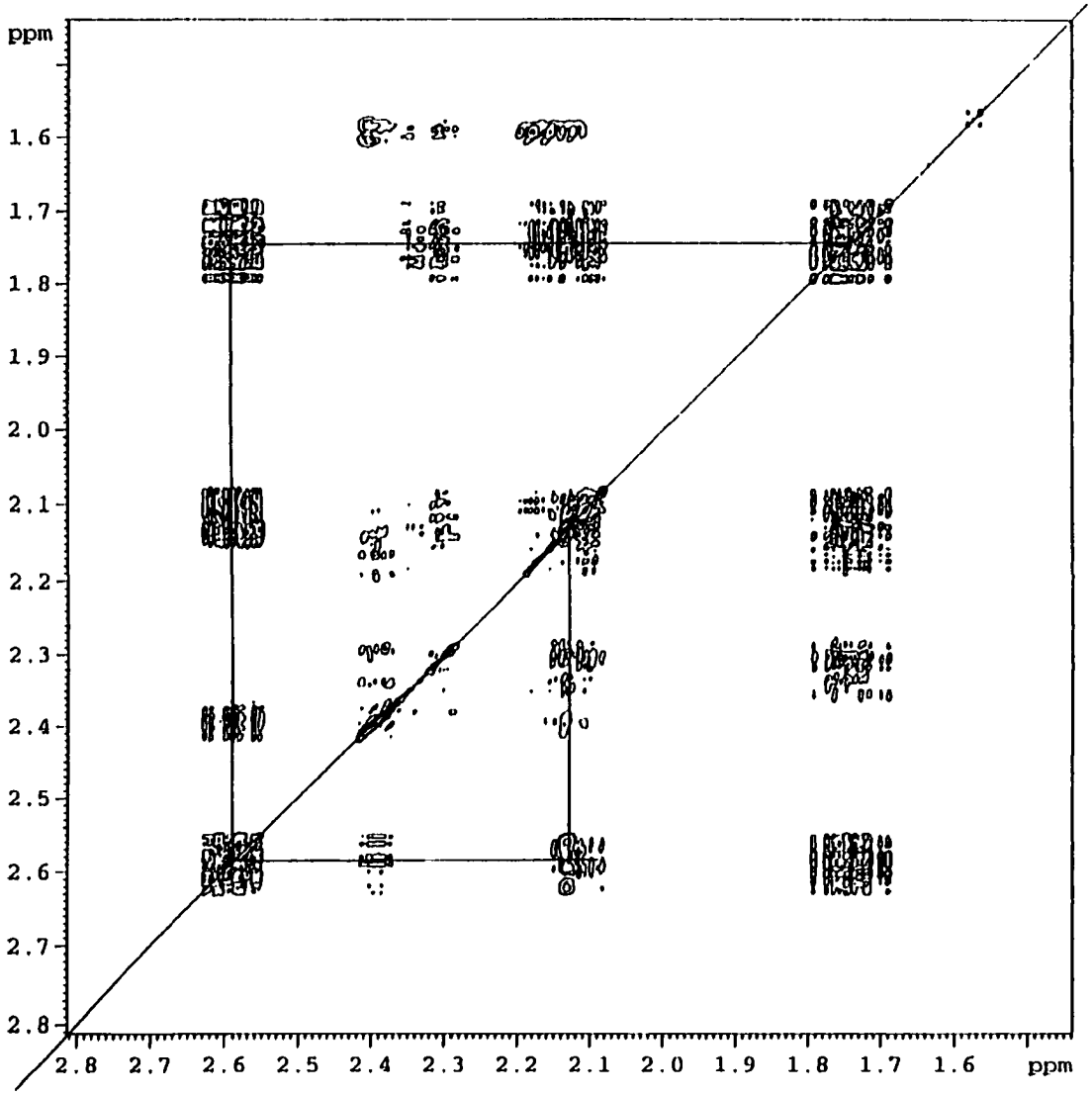


Figure A-17. COSY spectrum ($CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7) with H^{2a} & H^{2b} interaction with H^1 highlighted.



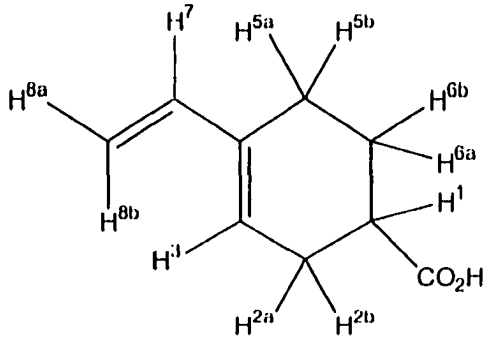
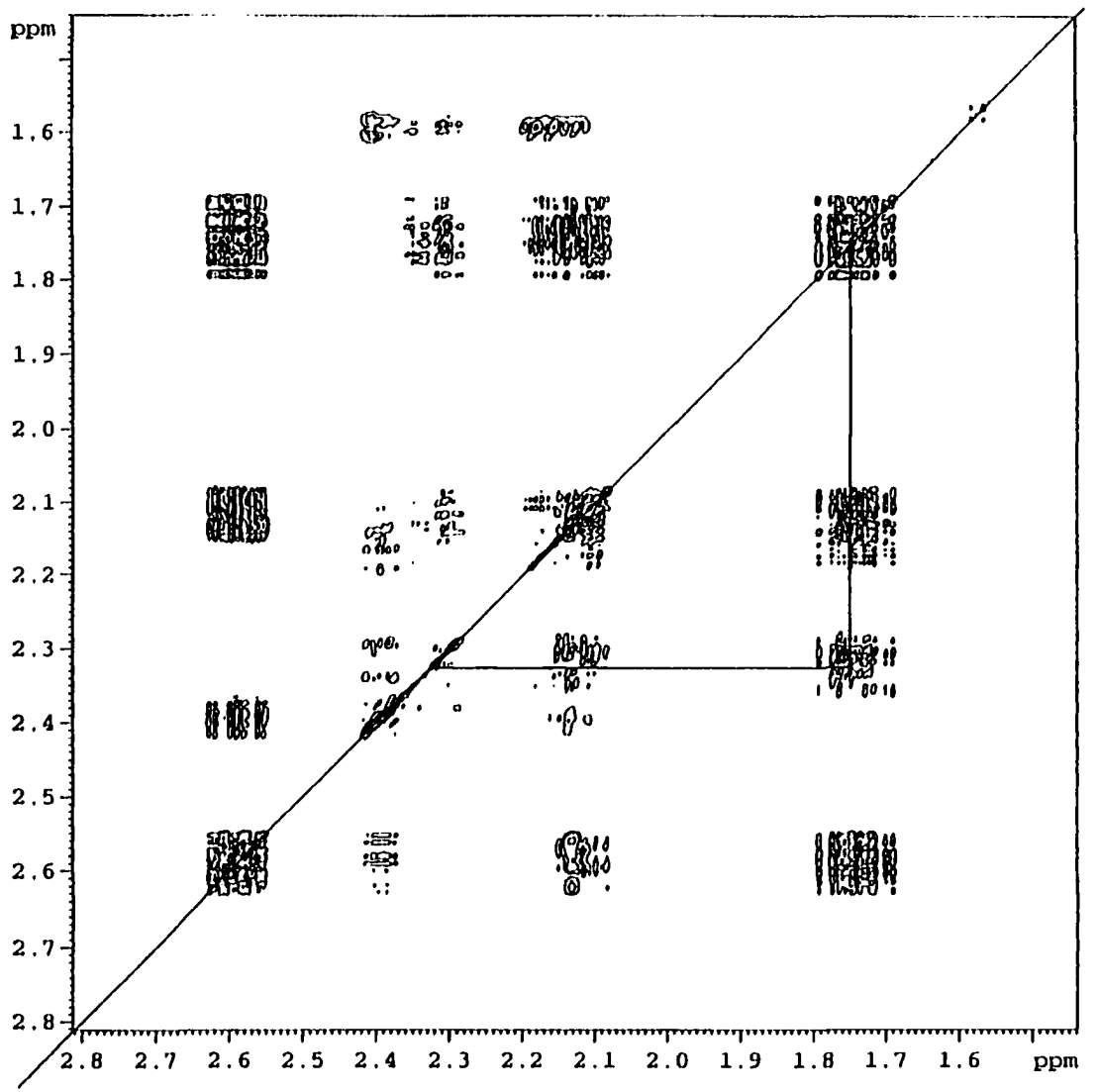


Figure A-18. COSY spectrum ($CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7) with H^1 interaction with H^{6a} and H^1 interaction with H^{6b} highlighted.



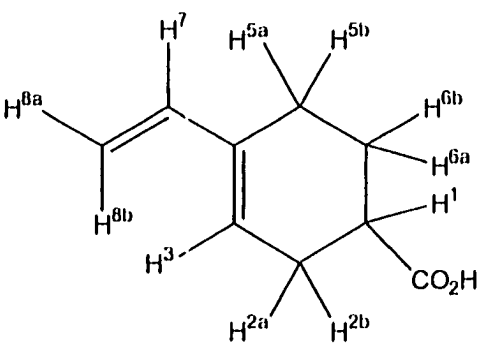


Figure A-19. COSY spectrum ($CDCl_3$) of 4-vinyl-3-cyclohexenecarboxylic acid (7) with H^6 interaction with H^5 highlighted.

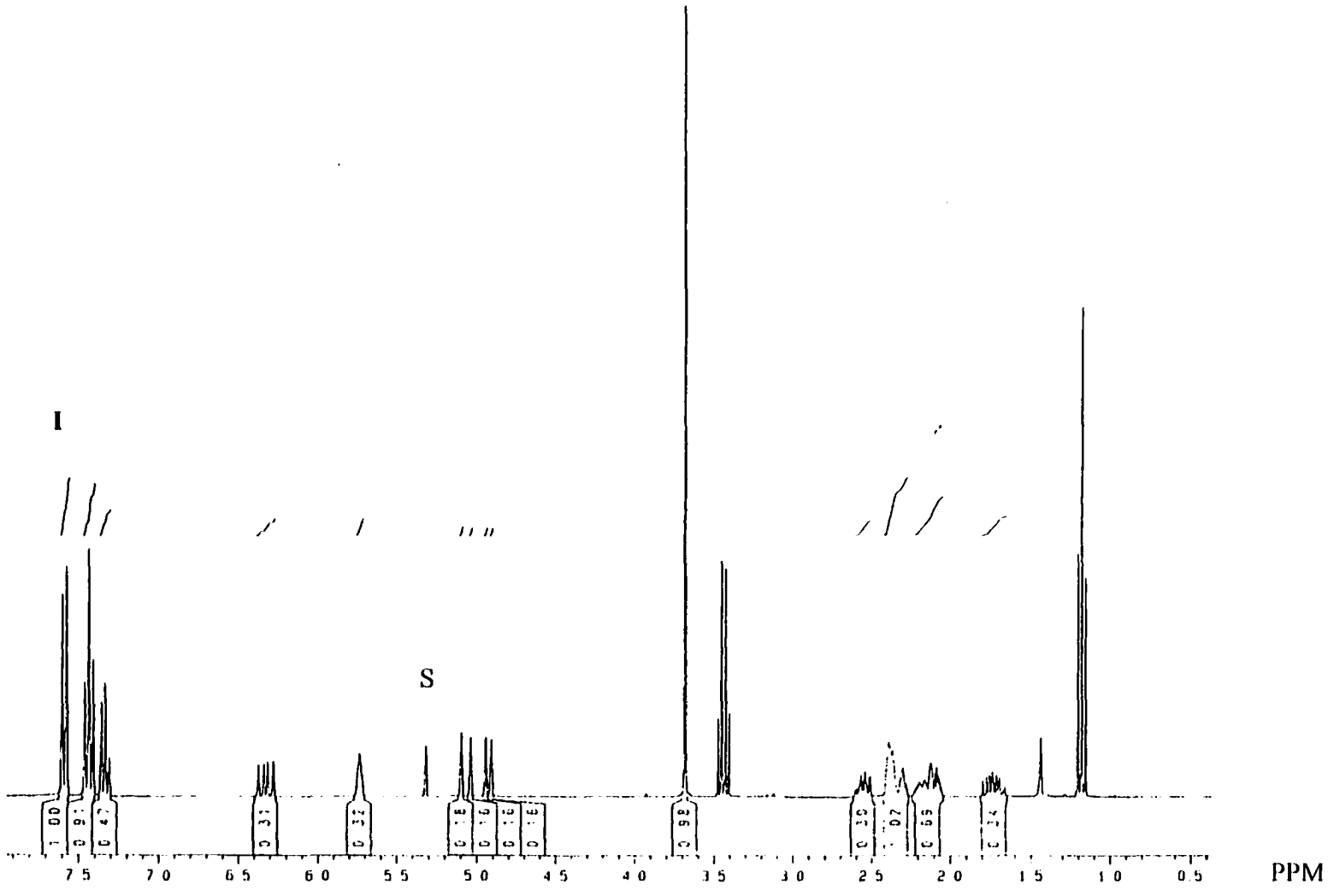


Figure A-20. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of methyl 4-vinyl-3-cyclohexenecarboxylate (**5**). (**I**: interal standard, biphenyl, **S**: methylene chloride)

CHAPTER 2. LITERATURE REVIEW OF SIMPLE BENZENE-BASED *p*-QUINODIMETHANE'S

Introduction

p-Quinodimethanes (*p*-QDM's) are reactive, cross-conjugated cyclic molecules that have been invoked as transient intermediates in a number of reactions.[1,2] *p*-Xylylene (**1**), the parent benzenoid *p*-QDM, is considerably less reactive than its isomeric counterpart *o*-xylylene (**2**),[3,4] the simplest *o*-quinodimethanes (*o*-QDM's).[5] *p*-QDM and *o*-QDM are structurally related to two other classes of cross-conjugated cyclic molecules, *p*- and *o*-quinone methides[6] (**3** and **4**) and *p*- and *o*-quinones[7] (**5** and **6**).

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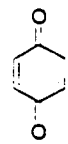
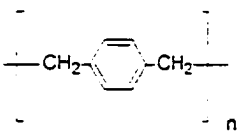


5

6

p-QDM's are important monomers for the vapor-coating polymerization of poly-*p*-QDM's which was originally developed by Union Carbide Corporation and now is used by dozens of specialized companies.[8] Poly-*p*-QDM's are sold under the trade names "Parylene" and "Galxyl"; Parylene N refers to unsubstituted poly-*p*-xylylene (**7**), Parylene C to poly-2-chloro-*p*-xylylene (**8**) and Parylene D to poly-2,5-dichloro-*p*-xylylene (**9**).[8] The physical properties of low-gas and moisture permeability, high dielectric strength, high



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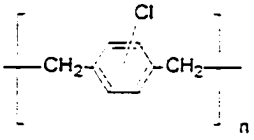

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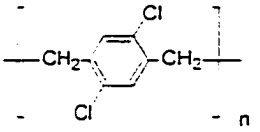

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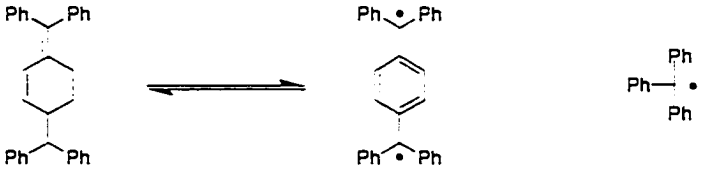
dielectric constants and the method of vapor-coating makes Parylene suitable for the surface coating of critical electrical assemblies.[8] The film deposited on the surface can be adjusted to a thickness of several submicrons to several millimeters.[8] The solvent-free, pinhole-free, and stress-free vapor coating process of Parylene is also ideal for the protective coating of biomedical implants and restoration of paper documents by encapsulation of individual fibers to prevent them from fracturing.[9]

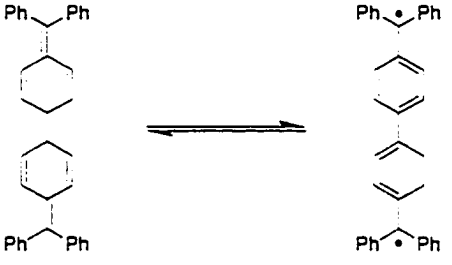
Another area of current interest in poly-*p*-QDM's is their use as precursor polymers for poly(*p*-phenylenevinylene) (PPV's).[10] PPV's display a variety of interesting properties, such as electrical conductivity upon doping, nonlinear optical response, electro- and photoluminescence.[11] Although *p*-quinodimethanes have been identified as an intermediate product in the formation of poly-*p*-QDM's, the mechanism of initiation and chain propagation is still open to discussion.[11] Many *p*-QDM's polymerizes spontaneously at room temperature upon condensation on a solid surface.

Thiele and Balhorn attempted to prepare *p*-QDM 1 by debromination of 7,8-dibromo-*p*-xylene but instead obtained an insoluble white powder which they described as poly-*p*-QDM 7.[12] Thiele[12] and Staudinger[13] were able to isolate a relatively stable tetraphenyl derivative of *p*-QDM 1, 7,7,8,8-tetraphenyl-*p*-xylylene (**10**). This research was motivated by Gomberg's discovery of the stable triphenylmethyl radical (**11**) which led to the question does *p*-QDM **10** exist in the quinoid form or as a biradical **12**. Early investigations

indicated that **10** consisted of less than 0.2 % biradical **12**, but Chichibabin's hydrocarbon, **13**, was 5-10% biradical **14** based on ESR.[14]



10 **12** **11**



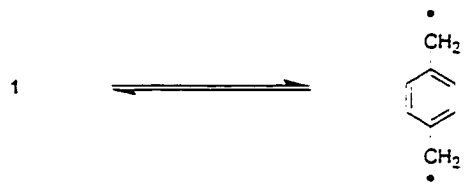
13 **14**

p-Xylylene (**1**) was first isolated as a solution and properly characterized by Szwarc who obtained it by the pyrolysis of *p*-xylene.[15] Although the monomer is stable in the vapor phase, in the condensed phase at low temperature it polymerizes spontaneously to poly-*p*-xylylene (**7**) as well as the cyclic dimer ([2.2]paracyclophane) (**15**) and other side-products. Subsequently this material has been extensively studied on account of its

15

unusual chemical and physical properties.[16,17,18,19,20] The energy difference of the *p*-QDM molecule between the singlet ground state, **1**, and the triplet excited state, **16**, has been

calculated to be as small as 8-9 kcal mol^{-1} (33-38 kJ/mol) by Coulson and coworkers[21] and as large as 0.93 eV (90 kJ/mol) by Dohnert[22]. The corresponding value for ethylene was



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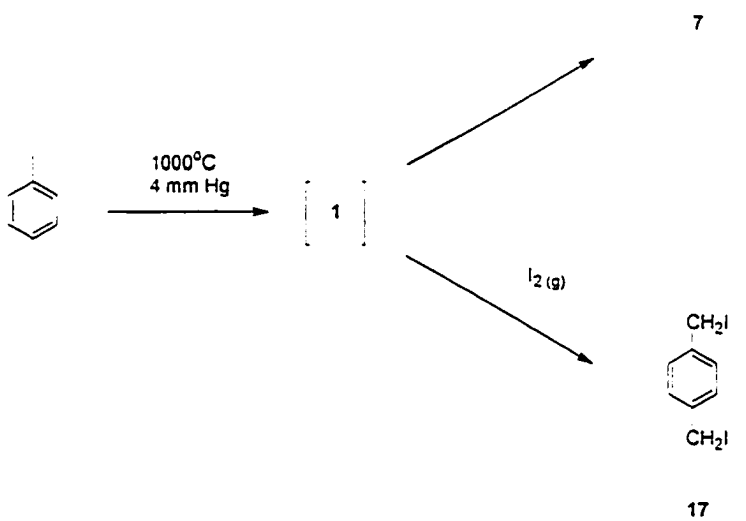
determined by Waser[23] to be 82 kcal mol^{-1} (343 kJ/mol). This unusually low energy difference of *p*-QDM 1 is responsible for the very high reactivity and thusly, *p*-QDM 1 is so reactive that, when prepared, it polymerizes spontaneously even at -78°C and it cannot be isolated pure under normal conditions.[4,24] Coppinger and Bauer have defined the relative stability of quinonoid systems as the energy difference between the quinonoid ground state and the benzenoid excited state; they pointed out that the stability increases with increasing electronegativity of the exocyclic groups. That is, an increase in electronegativity of the exocyclic atom results in a decrease of the highest occupied bonding energy level and in an increase of the lowest unoccupied antibonding energy level. This leads to an increase in energy difference between ground and transition states and the large stability of the compound. *p*-Benzoquinone (**5**) is a typical example of quinonoid compounds isolable at room temperature.

When electron-withdrawing substituents such as the cyano group are introduced at the 7 and 8 positions of the unsubstituted quinodimethane, the electronegativity of its exocyclic positions increase, leading to stablilization of quinodimethanes. Therefore, substituted quinodimethanes become more stable and more easily obtained as crystals at room temperature. Many substituted quinodimethanes like 7,7,8,8-tetracyano-*p*-quino-

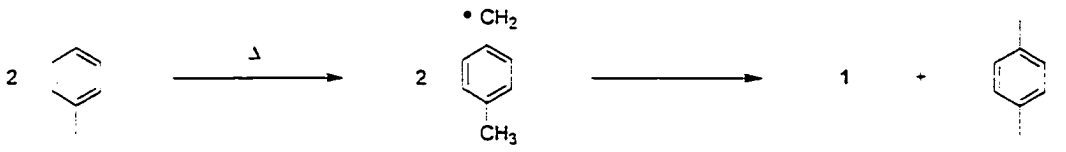
dimethane have been prepared as isolable crystalline compounds. Consequently, substituted quinodimethanes, isolable as pure crystalline and highly conjugated (reactive) monomers, are expected to exhibit novel and unique polymerization behavior beyond the scope of conventional polymer chemistry established on the basis of vinyl polymerizations of ethylenes.

Pyrolytic Preparation

In 1947 Szwarc prepared a white polymeric material by a rapid flow (flash) pyrolysis of *p*-xylene under reduced pressure.[15] Since *p*-xylylene diiodide (17) was detected among the pyrolysis products when iodine gas[25] was mixed with the pyrolysis gas, he proposed the formation of *p*-xylylene (1) in this pyrolysis.[15,26] He claimed the polymeric material to be poly-*p*-xylylene[15] (7) and proposed a mechanism for its formation[25] which involves thermal



cleavage of carbon-hydrogen bonds of *p*-xylene to yield *p*-xylyl radicals **18**, which in turn collide with each other to give *p*-xylene and *p*-QDM **1** through disproportionation. *p*-QDM **1** condenses and polymerizes to produce poly-*p*-QDM **7**, a high melting point substance



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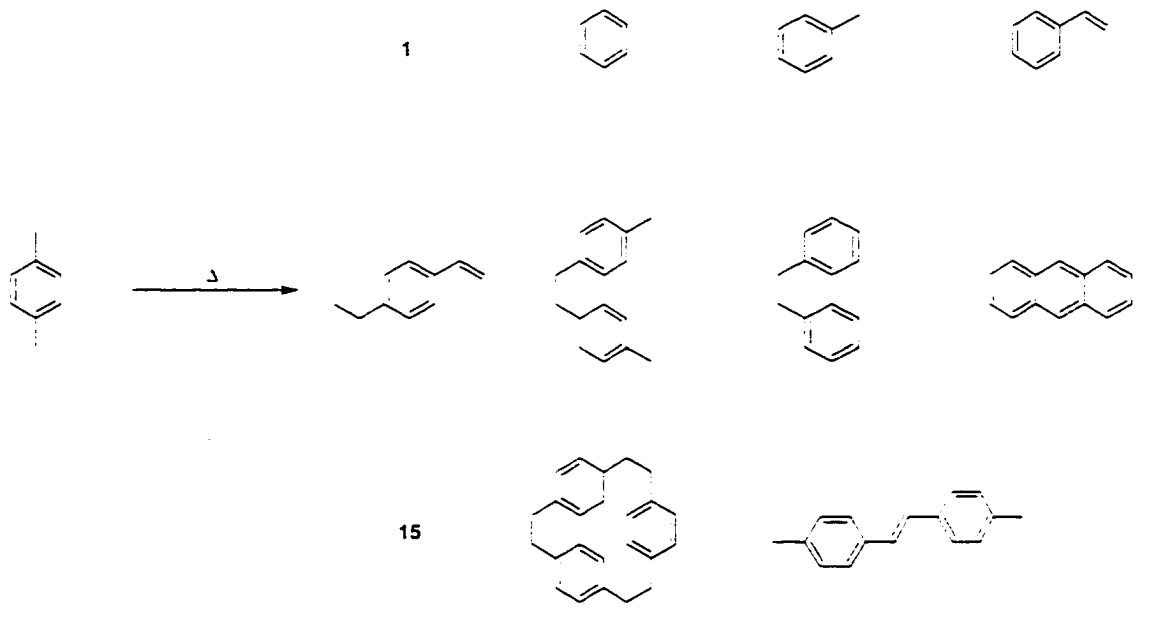
which is inert to organic and inorganic reagents. Further side reactions causing crosslinking are indicated by the insolubility in high boiling solvents at high temperatures of poly-*p*-xylylene prepared from the pyrolysis of *p*-QDM **1**.[17,18]

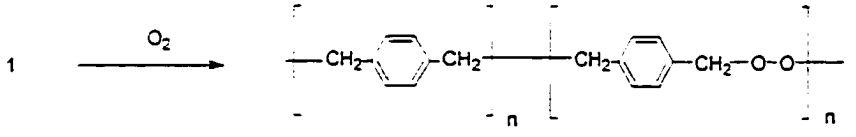
The rapid flow pyrolysis of *p*-xylene was carried out under reduced pressure of 4 mm Hg at 1000°C and the pyrolysis products were condensed at -78°C to obtain solutions of monomeric *p*-QDM up to 0.12 M concentration.[27] In addition to *p*-QDM **1**, benzene, toluene, styrene, *p*-ethylstyrene, 1,2-di(*p*-tolyl)ethane, a diarylmethane, anthracene, cyclophane **15**, [2.2.2]paracyclophane (cyclic trimer , **19**), and 4,4'-dimethylstilbene were produced as by-products.[15, 16, 17, 18,19,20,28] Even when kept at -78°C the solution of the pyrolysis product polymerizes very slowly. When an aliquot is drawn up into a warm pipet and allowed to flow back into the solution, the polymerization rate is significantly increased, presumably due to formation of diradicals with n-mers. The polymerization of *p*-QDM 1 is believed to take place by successive additions of *p*-QDM monomer until all the monomer is consumed or the polymeric free radical ends are entrapped in the polymer mesh. Errede and coworkers[29] have found that solutions which polymerize with apparent first-order rate constants of $9\pm1 \times 10^{-6}$ s^{-1} could be reproduced fairly consistently if the solution of the



pyrolysis was filtered through a bed of crystalline *p*-xylene using an apparatus that was prechilled to -78°C. Such solutions were used to determine the rate of polymerization at various temperatures above -78°C. The rates were found to obey a first-order law with respect to monomer. The kinetic plot of the apparent first-order rate constants was linear for the first 10 h but the deviation from the first-order kinetics become appreciable at longer reaction times, corresponding to the slow but steady decrease in apparent rate constants. A plot of the reciprocal of the apparent rate constant against time is linear, indicating that the disappearance of the polymerization active sites is second-order with respect to the sites.[30] This treatment gives the ratio of apparent rate constant of disappearance of the polymerization active site to that of the polymerization to be 0.45, in sharp contrast to the conventional free radical vinyl polymerization in which termination is about $\sim 10^4 - 10^6$ times faster than propagation. One interesting characteristic of *p*-QDM **1** polymerization is that the propagation, a radical addition reaction between a very stable polymer radical and a very

reactive monomer, takes place with a rate similar to that of the termination. This is a radical coupling reaction between very stable polymer radicals. When a solution of *p*-QDM **1** is heated to a temperature higher than -78°C, in addition to the insoluble high molecular weight polymer, some soluble low molecular weight products such as a cyclophane **15**, cyclic trimer **19**, cyclic tetramer, 1,4-bis(2'-*p*-tolylethyl)benzene and oligomers are obtained.[29] Furthermore, when a solution of *p*-QDM **1** at -78°C is added dropwise to a hot inert solvent such as toluene at 100°C a cyclophane **15** is obtained in a good yield.[29]

p-QDM **1** does not copolymerize with conventional olefinic monomers at -78°C in the usual way that both monomers are mixed, but the homopolymers of *p*-QDM **1** and the conventional monomer are obtained.[31] However, when a solution of *p*-QDM **1** at -78°C is added to a solution of a conventional monomer maintained at about 100°C, a copolymer can be produced.[31] When oxygen or air is bubbled through a solution of *p*-QDM **1**, *p*-QDM **1** is copolymerized with oxygen to yield poly-*p*-QDM peroxide **20** with an oxygen content ranging from 1 to 23% molar ratio of *p*-QDM to oxygen from 31:1 up to 1:1).[32] The



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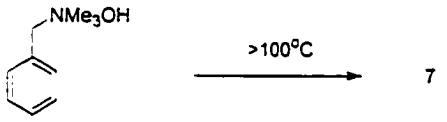
polymerization of *p*-QDM **1** is not influenced by conventional chain transfer agents such as carbon tetrachloride, chloroform, *p*-cumene, nitrobenzene, and hydroquinone.[31] When a three-fold excess of thiophenol, a highly reactive chain transfer agent, is added to a solution of *p*-QDM **1**, a telomer with a 21:1 ratio of *p*-QDM **1** to thiophenol units is obtained.[31]

It was pointed out that the flash pyrolysis method of *p*-xylene has several limitations[33], i.e. (1) at most 25% yields of *p*-QDM 1 are obtained the extreme pyrolysis temperature of 1150°C[16]; (2) the polymers obtained are loosely cross-linked,[17,18] and (3) the vapor-deposited polymeric products formed by this method are contaminated with 10-20% of low molecular weight by-products.[16,18]

As an alternative to the pyrolysis of *p*-xylene, Fawcett found that degradation of *p*-xylyltrimethylammonium hydroxide (**21**) can take place at temperatures as low as 100°C, and the immediate and concurrent polymerization of the monomer affords linear, soluble



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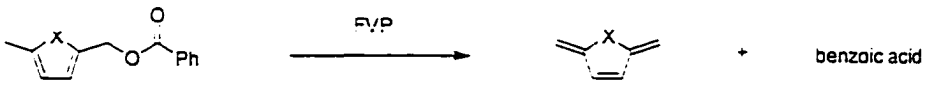
poly-*p*-QDM **7** in high yields.[34] This method was successfully applied to 5-methyl-2furfuryltrimethylammonium hydroxide (**22a**) and 5-methyl-2-thienyltrimethylammonium hydroxide (**22b**) to obtain 2,5-dimethylene-2,5-dihydrofuran (**23a**) and 2,5-dimethylene-2,5-dihydrothiophene (**23b**), respectively.[35] Both monomers are very

22a: X=O
22b: X=S

23a: X=O
23b: X=S

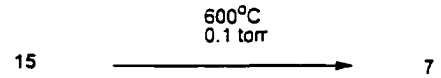
reactive and they either polymerized or form a heterocyclophane, crystalline cyclic dimer.[35] This method is widely applicable to the synthesis of other *p*-QDM polymers substituted with groups which are insensitive to the strongly basic medium, e.g. poly-2,5-dimethoxy-*p*-xylylene, which can be hydrolyzed to poly-2,5-dihydroxy-*p*-xylylene.[36] An alternative

preparation of both the furan monomer **23a** and the thiophene monomer **23b** by flash vacuum pyrolysis (FVP) from their corresponding benzoates was developed by Trahanovsky and workers[37]. Both the furan monomer **23a** [35,37] and the thiophene monomer **23b**[37] can be isolated at -78°C.



23a: X=O
23b: X=S

A much better method for preparing poly-*p*-xylylene (**7**) was subsequently developed by Gorham in which [2.2]paracyclophane (**15**) is pyrolyzed in a vacuum (~0.1 torr) at 600°C and the pyrolyzed gas is condensed on a glass or metal surface maintained below 30°C to



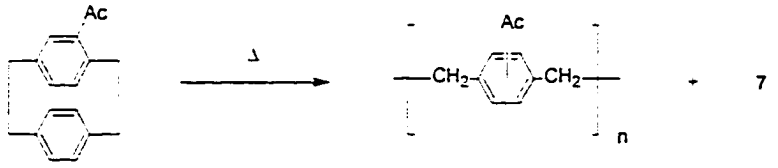
yield a tough, transparent polymeric film.[33,38] This pyrolysis of cyclophane **15** under milder and more readily controlled conditions, was described by Szwarc and Errede which resulted in almost a quantitative preparation of the polymer containing less than 1% carbon tetrachloride extractable material, most of which is unreacted dimer **15**. The polymer film obtained is readily soluble in chlorinated biphenyls and benzyl benzoate at temperatures above 200°C, indicating that it is linear and free from cross-linking. This process has much greater advantages than the Szwarc-Errede pyrolysis of *p*-xylene. Due to the milder pyrolysis temperature the vapor-coating process may be applied to the preparation of a variety of substituted *p*-QDM polymers.

The best laboratory preparation for cyclophane **15** is probably the pyrolysis of *p*-xylyltrimethylammonium hydroxide (**21**) as described by Weinberg and Fawcett.[39] Pollart

had developed a solvent quenching technique for the synthesis of cyclophane **15**.[40] The condensation of *p*-QDM **1** vapor directly into an organic solvent at a temperature of 50-200°C results in the formation of cyclophane **15** in a yield higher than 90%. [40] Commercially, Union Carbide makes cyclophane **15** by the 900°C rapid pyrolysis of *p*-xylene in the presents of steam followed by condensation of the vapor in an organic solvent such as *p*-xylene at 50°C to produce cyclophane **15** in 8-10% yield with only 0.1% polymeric material.[40, 41]

Gorham prepared about 30 types of substituted paracyclophanes including the dichloro, dibromo, dicyano, dimethyl, diethyl, and tetrachloro derivatives for the preparation of polymers of the respective substituted *p*-QDM's.[33] The various substituted *p*-QDM monomers condense and polymerize on the surface at temperatures lower than the threshold condensation temperature which is related to the molecular weight and volatility of the respective monomer. The threshold condensation temperature is defined as the highest temperature of the surface on which the *p*-QDM monomers condense and polymerize at an appreciable rate. At normal pressure (about 0.1 mm Hg) the threshold temperatures are 30°C for *p*-QDM **1**, 60°C for 2-methyl-*p*-xylylene, 90°C for 2-ethyl- and 2-chloro-*p*-xylylene and 130°C for 2-cyano-, 2-bromo-, and dichloro-*p*-xylylene.

The mechanism of the vapor-coating process of unsymmetrical cyclophane has been studied.[33] The pyrolysis gas from mono-acetyl-cyclophane **24** is initially led through a glass tube maintained at 90°C and subsequently through another glass tube kept at 20°C. The polymer deposited at 90°C has been identified as poly-acetyl-*p*-xylylene **25** and the polymer deposited at 20°C has been identified as poly-*p*-QDM **7** on the basis of its elemental analysis



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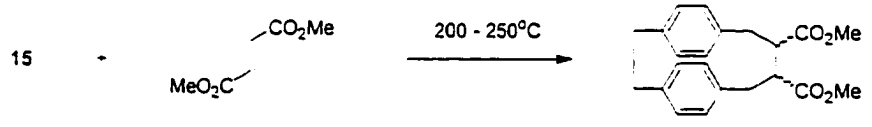
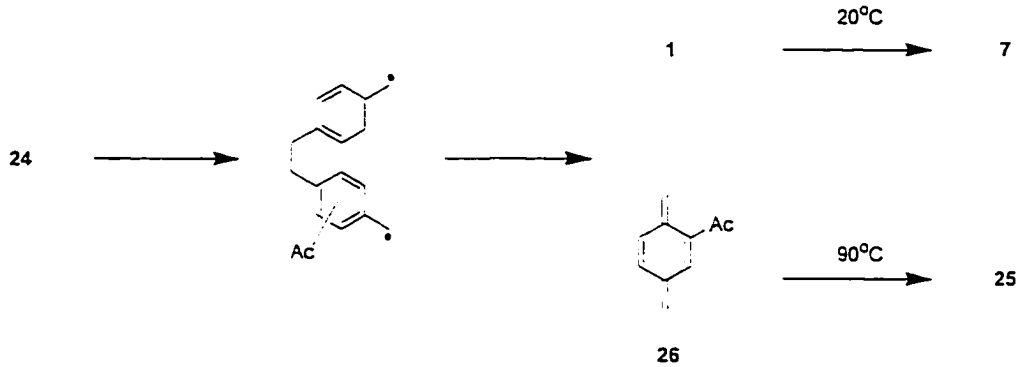
and IR spectrum and by properties such as their melting point and solubility in organic solvents. The enhanced reactivity of paracyclophane can be seen as the result of its ring strain. However, the ringstrain is released as soon as the bond on one side is broken. Gorham acknowledges that this does not answer the question as to whether both bonds in the cyclophane are broken simultaneously or sequentially. In fact, it should be pointed out that by pyrolyzing cyclophane **15** at 200-250°C, Cram has established unequivocal evidence for the breakage of only one bond.[42] It should also be pointed out that the concerted cleavage



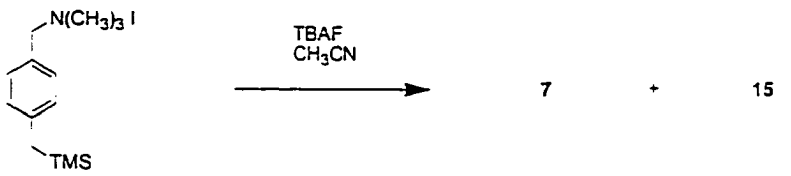
of cyclophane **15** to the *p*-quinodimethane is a [π^6s +π^6s] process which is orbital symmetry forbidden.[43] These results reasonably suggest that the acetyl-cyclophane **24** is cleaved to a ring-open biradical then to *p*-QDM **1** and acetyl-*p*-QDM **26**. The subsequent fractional polymerization which then take place depends upon the threshold condensation temperatures of these fragments.



The polymerization has a "living" character, which does not mean that this polymerization is truly a living polymer but the growing polymer chains are terminated by radical species with lifetimes of days, depending on the monomer structure, as proved by ESR spectroscopy. For example, the apparent half-life of poly-*p*-xylylene (**7**) radical is 20 min and of poly-2,5-dichloro-*p*-xylylene (**9**) radical is 21 h.[44] Immediately after its preparation by the vapor-coating process, the poly-*p*-xylylene was found to be paramagnetic (radical concentration of 5-10 x 10^{-4} mol g^{-1}).[33] The mechanical properties of poly-*p*-xylylenes, such as tensile strength and tensile modulus, can be improved by termination of radical chain ends by chain transfer agents or annealing before contact with oxygen.[44,45,46]

Non-Pyrolytic Preparation

p-[(Trimethylsilyl)methyl]benzyltrimethylammonium iodide (**27**) can be decomposed at room temperature with tetrabutylammonium fluoride (TBAF) in acetonitrile to give poly-*p*-QDM **7** (51% yield) and cyclophane **15** (6% yield), or at refluxing temperature to give 50% cyclophane **15**.[47]



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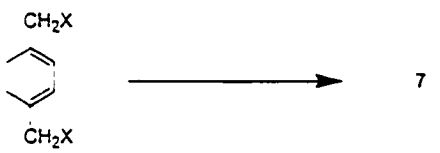
Amorphous, low molecular weight (~3000) poly-*p*-QDM (**7**) was synthesized by Wurtz-type coupling reaction of 1,4-bis(halomethyl)benzenes **28** and different coupling reagents in solution. Zinc[12], magnesium[48], sodium[49,50,51], phenyllithium[52], iron or nickel or cobalt or zinc suspended in water or Urushibara Nickel[53], chromium(II) chloride[54], or naphthalene alkali[55] was used as the coupling reagent. Molecular weights of poly-*p*-QDM's



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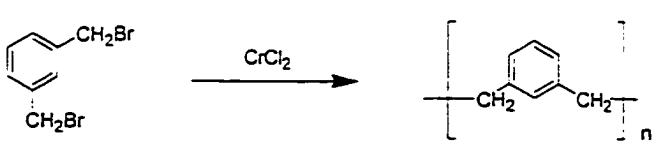
obtained by this route are limited by the insolubility of poly-*p*-QDM **7** at moderate temperatures. This reaction was improved in various ways to give satisfactory yields of the crystalline polymer.[20,56] The role of *p*-QDM **1** as an intermediate in these coupling reactions was already recognized by Thiele and Balhorn.[12]

Interestingly, poly-*m*-xylylene (**29**) was obtained by reaction of 1,3-bis(bromomethyl)benzene (**30**) with $CrCl_2$ as well as copolymers by reaction with 1,4-bis(bromomethyl)benzene, which indicates that the reaction does not essentially proceed via a quinoid species as



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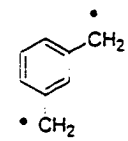
intermediate since *m*-xylylene (**31**) can not form a quinodimethane.[54] This would implicate a stepwise growth mechanism via poly-recombination of benzylic radical species. Further



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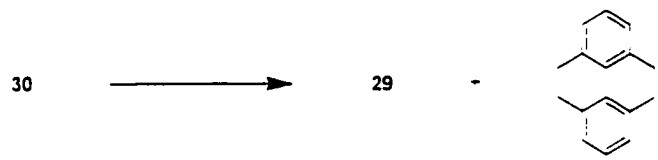
evidence was obtained by previous reactions of **30** in the presence of sodium and the formation of poly-*m*-QDM **29**.[57] Similarly, poly-*m*-QDM **29** was obtained by reaction of **30** in the presence of reduced iron suspended in water. Small amounts of [2.2]metacyclophane (**32**) were obtained as side product.[51]



32

Direct Observation

More recently the question of biradical **16** verses quinoid **1** structure was examined with regard to *p*-xylylene. Low temperature (-80°C) solution spectra[58] (IR, UV, NMR) indicate that the quinoid structure is predominant and that the biradical, if formed, is very short-lived. No ESR signals were obtained and the NMR signals were not broadened. In addition the solid state photoelectron spectrum of *p*-QDM **1** were consistent with the quinoid structure.[59, 60]

Other reactive *p*-QDM's have been spectroscopically observed. 1,4-Naphthaquinodimethane and 9,10-anthraquinodimethane were observed by ^{1}H NMR, UV, and IR spectroscopy using methods similar to the one used for *p*-QDM **1**.[58] Photoelectron spectra

were obtained of 2,3-dimethyl-*p*-xylylene[61] and 2,5-dimethyl-*p*-xyl-ylene.[61,62] The IR spectrum of 7,8-dichloro-*p*-xylylene was acquired by trapping the *p*-QDM on a N_2 matrix.[63] Both the IR and UV spectra were obtained for 7,7,8,8-tetra-chloro-*p*-xyl-ylene.[64] 7,7-Diphenyl-*p*-xylylene was prepared by basic elimination of hydrogen chloride or hydrogen bromide using pyridine. As a dilute solution, an UV/Vis spectrum was obtained.[65]

Summary

p-Quinodimethanes, in particularly *p*-xylylene (**1**), have received considerable attention in the literature concerning its reactivity and their use as a monomers for the commercial polymer Parylene. *p*-QDM's have been prepared by pyrolysis or by elimination reactions. The most common method of preparing *p*-QDM's is the pyrolysis of [2.2]paracyclophanes. Many *p*-QDM's are reactive and form polymers upon condensation of a surface. Although the mechanism of polymerization is uncertain, it is believe to involve a dimeric diradical. *p*-QDM **1** and several other reactive *p*-QDM's have been directly observed by IR, UV, and ^{1}H NMR spectroscopy.

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CHAPTER 3. ROOM TEMPERATURE OBSERVATION OF *p*-XYLYLENES BY ^{1}H NMR AND EVIDENCE FOR DIRADICAL INTERMEDIATES IN THEIR OLIGOMERIZATION[1]

A paper to be submitted to the Journal of Organic Chemistry

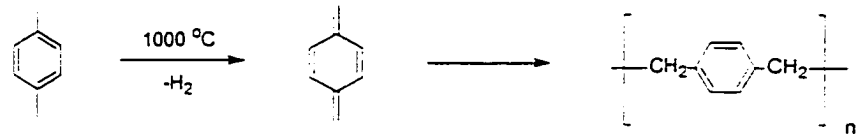
Steven P. Lorimor and Walter S. Trahanovsky

Abstract

p-Quinodimethanes (*p*-QDM's) are reactive molecules that have been invoked as transient intermediates in a number of reactions. Dilute solutions of benzene-based *p*-QDM's, *p*-xylylene (**1**), α-methyl-*p*-xylylene (**11**), and 2,5-dimethyl-*p*-xylylene (**12**), can be prepared by fluoride-induced elimination of trimethylsilyl acetate from the appropriate precursor. It has been found that these solutions are stable enough to allow these reactive *p*-QDM's to be observed by ^{1}H NMR spectroscopy at room temperature. For the first time, the ^{13}C NMR spectrum of *p*-QDM **1** was observed. After several hours at room temperature, these *p*-QDM's form dimers, trimers, and insoluble oligomers. Formation of trimers provides evidence that *p*-QDM's **1**, **11**, and **12** dimerize by a stepwise mechanism involving dimeric diradicals as intermediates.

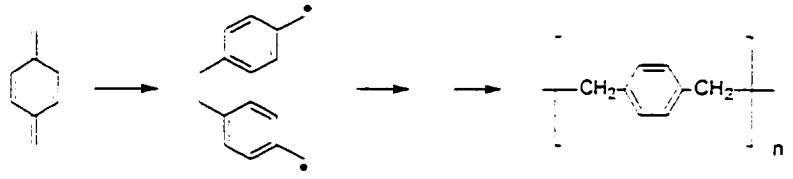
Introduction

p-Quinodimethanes (*p*-QDM's) are reactive molecules that have been invoked as transient intermediates in a number of reactions. *p*-Xylylene (**1**), the parent benzene-based *p*-QDM, was first proposed as an intermediate in the pyrolysis of *p*-xylene that yielded poly-*p*-xylylene.[2] Errede was able to prepare solutions of *p*-QDM **1** at -78°C by



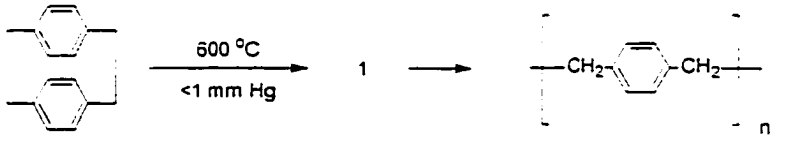
1

dissolving the *p*-xylene pyrolyzate in a cold, well-stirred solvent.[3] Errede and Szwarc[4] suggested that the polymerization of *p*-QDM **1** occurs via the initially formed diradical **2**.



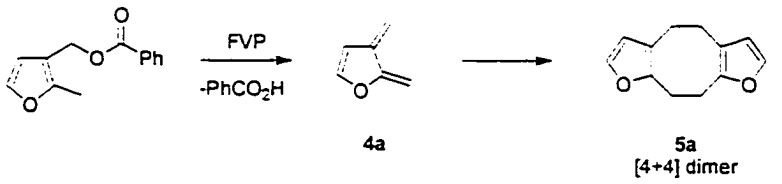
1 2

Gorham found that heating [2.2]paracyclophane, dimer **3**, in the gas phase formed what he suspected to be *p*-QDM **1** and when this vapor was allowed to condense on a cool surface, it formed polymer.[5]



3

Over the past several decades our group has studied the mechanism of oligomerization of other *o*- and *p*-QDM's including ones based on furan and ones based on thiophene. Furan-based *o*-QDM **4a** can be prepared by flash vacuum pyrolysis (FVP) of 2-methyl-3-furylmethyl benzoate.[6] Upon standing, furan-based *o*-QDM **4a** dimerizes nearly quantitatively to the head-to-head, [4 ÷ 4] dimer **5a**.[6] Chou and Trahanovsky probed the mechanism of dimerization with deuterium labeling of the α-positions and found that

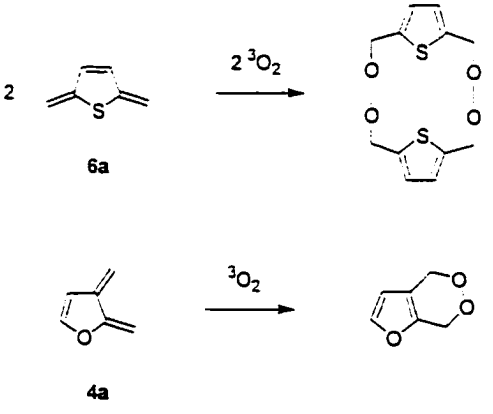


a significant inverse isotope effect at the 3-methylene position which supports a step wise mechanism involving diradicals at the 2-methylene.[7]

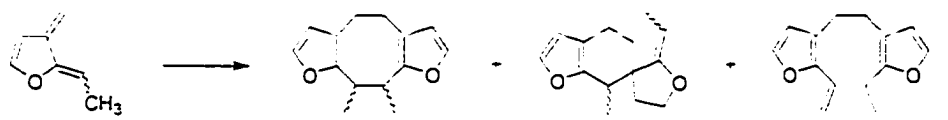
By substitution of a bulky *tert*-butyl group at either of the α-positions, Trahanovsky was able to demonstrate that the 3-methylene is more reactive than the 2-methylene.[8] The 2-substituted *o*-QDM **4b** has a similar rate of dimerization to the unsubstituted *o*-QDM **4a**. The 3-substituted *o*-QDM **4c** does not form dimers and is stable for days at room temperature.

4b **4c**

Although triplet oxygen is normally slow to react with olefins, thiophene-based *p*-QDM **6a** [9] and furan-based *o*-QDM **4a**[10] have been shown to react rapidly with $^3O_2$ to give cyclic products.

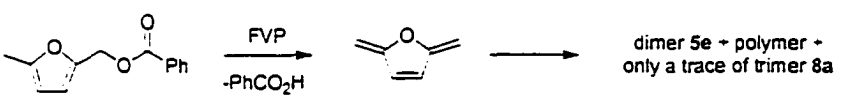


Leung and Trahanovsky[11] reported that 2-ethylidene-3-methylene-2,3-dihydrofuran (**4d**) dimerizes to give rise to two [4+4] dimers **5b**, four [4+2] dimers **5c**, and one intramolecular disproportionation dimer **5d**. Identification of the intramolecular disproportionation product **5d** provides additional support for the diradical intermediate.



4d 5b ~30% 5c ~67% 5d ~2%

Furan-based *p*-QDM **7** can be prepared by FVP of 5-methylfurfuryl benzoate.[12, 13] Upon standing furan-based *p*-QDM **7** forms dimer **5e**, polymer, and only a trace amount of trimer **8a**.[13] One proposed explanation for the low yield of trimer **8a** is that once the dimeric



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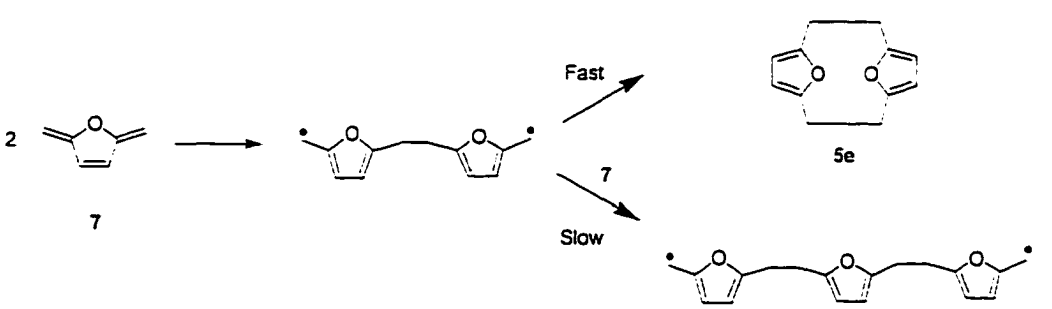
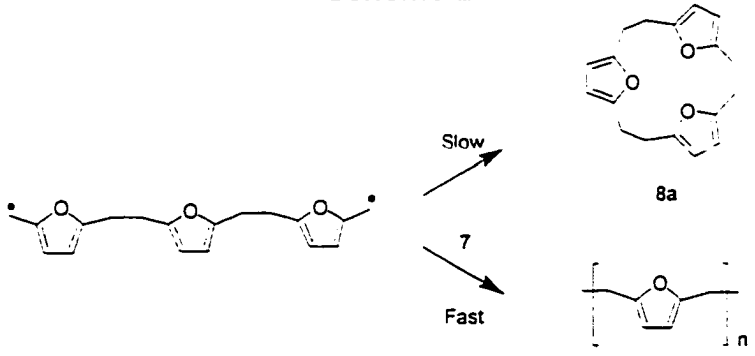
diradical is formed, it rapidly closes to dimer **5e** rather than reacting with a third molecule of *p*-QDM **7** to form a trimeric diradical (Scheme 1). Another explanation is the trimeric

Scheme 1

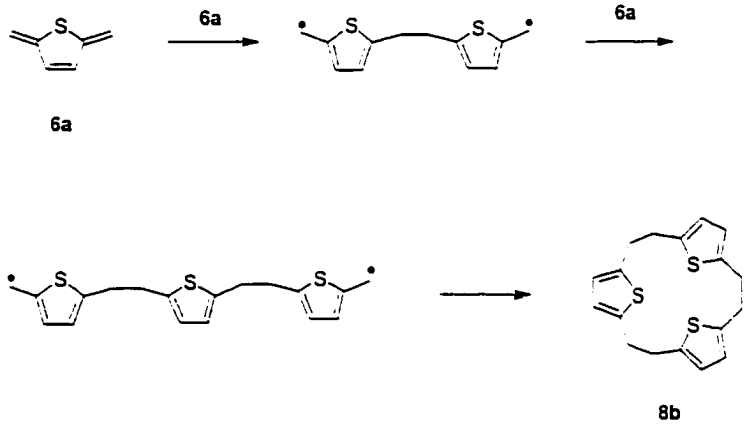


diradical reacts with another molecule of monomer to form polymer faster than closing to trimer **8a** (Scheme 2).[13]

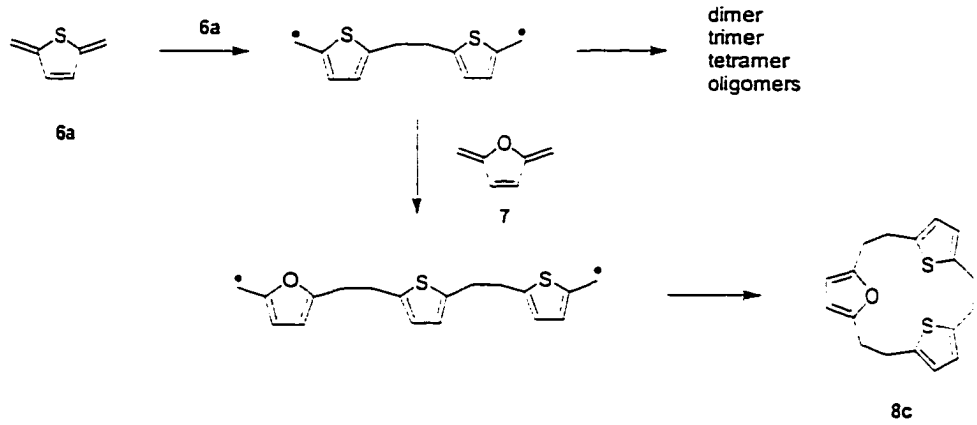
Scheme 2



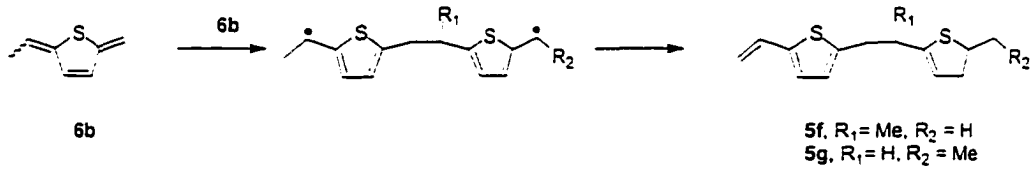
2,5-Dimethylene-2, 3-dihydrothiophene, thiophene-based *p*-QDM **6a**, can be prepared from the flash vacuum pyrolysis (FVP) of 5-methyl-2-thiophenemethyl benzoate.[13] Upon standing thiophene-based *p*-QDM **6a** forms dimer (14.7%), trimer **8b** (44.3%), tetramer (0.68%), and oligomers. It has been proposed that trimer formation provides firm evidence for the existence of dimeric diradicals.[13]



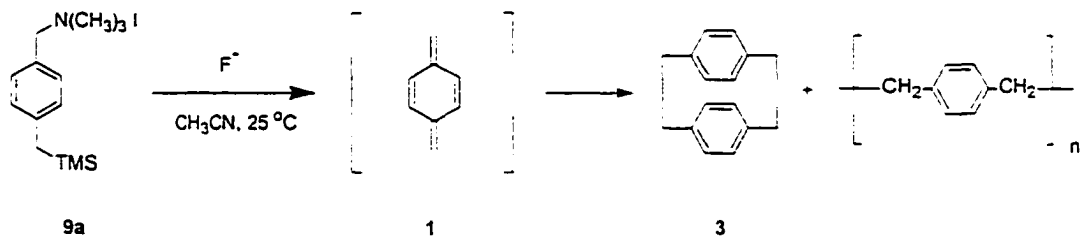
Further evidence for a dimeric diradical was found in trapping with the furan-based *p*-QDM **7** to form a mixed trimer **8c**.[14]



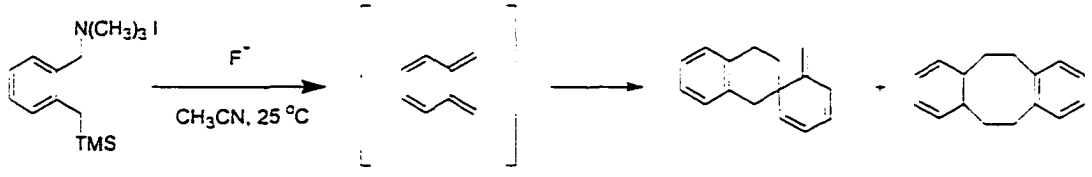
From the methyl derivative **6b,** prepared by FVP of 5-ethyl-2-thiophenemethyl benzoate, acyclic dimers **5f** and **5g** were observed.[13] Their formation is reasonably explained by intramolecular disproportionation of dimeric diradicals. This provides additional evidence for the dimeric diradicals.



Ito used a fluoride induce 1,6-elimination of trimethylsilyl iodide and trimethylamine from [*p*-[(trimethylsilyl)methyl]benzyl]trimethylammonium iodide (**9a**) to yield dimer 3 and polymer.[14] *o*-Xylylene (**10**) can be generated also by a fluoride induced 1, 4-elimination of

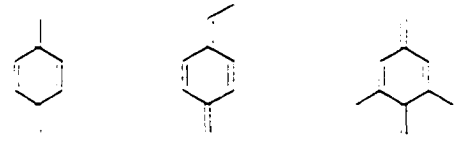


trimethylsilyl iodide and trimethylamine from [*o*-[(trimethylsilyl)methyl]benzyl]trimethyl ammonium iodide (**9b**).[15] *o*-QDM **10** rapidly dimerizes to [4 + 2] dimer **5h** and [4 + 4] dimer **5i** in a ratio of 11:1.[15a]



9b 10 5h 5i

In order to more fully investigate the possibility of a dimeric diradical intermediate in the oligomerization of benzene-based *p*-QDM's, dilute solutions of *p*-QDM 1, α-methyl-*p*-xylylene (**11**), and 2,6-dimethyl-*p*-xylylene (**12**) were prepared and their oligomerization was studied.

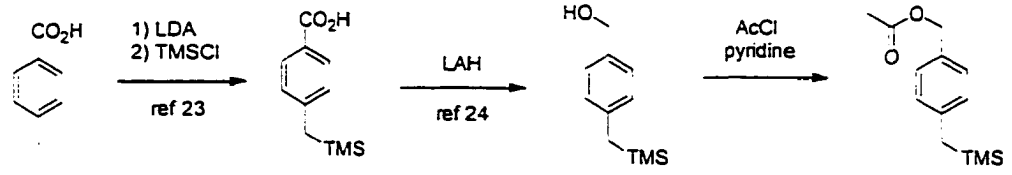


1 11 12

Results

***p*-Xylylene (1) Oligomerization Studies.** [*p*-((Trimethylsilyl)methyl)phenyl]methyl acetate (**13**) was prepared from *p*-tolulic acid by reactions shown in Scheme 3.

Scheme 3



13

p-Xylylene (**1**) was prepared as a dilute solution in CD_3CN (ca. 10^{-3} M) by the fluoride induced elimination[14] of trimethylsilyl acetate from acetate **13**. Due to the stability of this dilute solution, we were able to obtain the ^1H NMR spectrum (Figure 1) at room

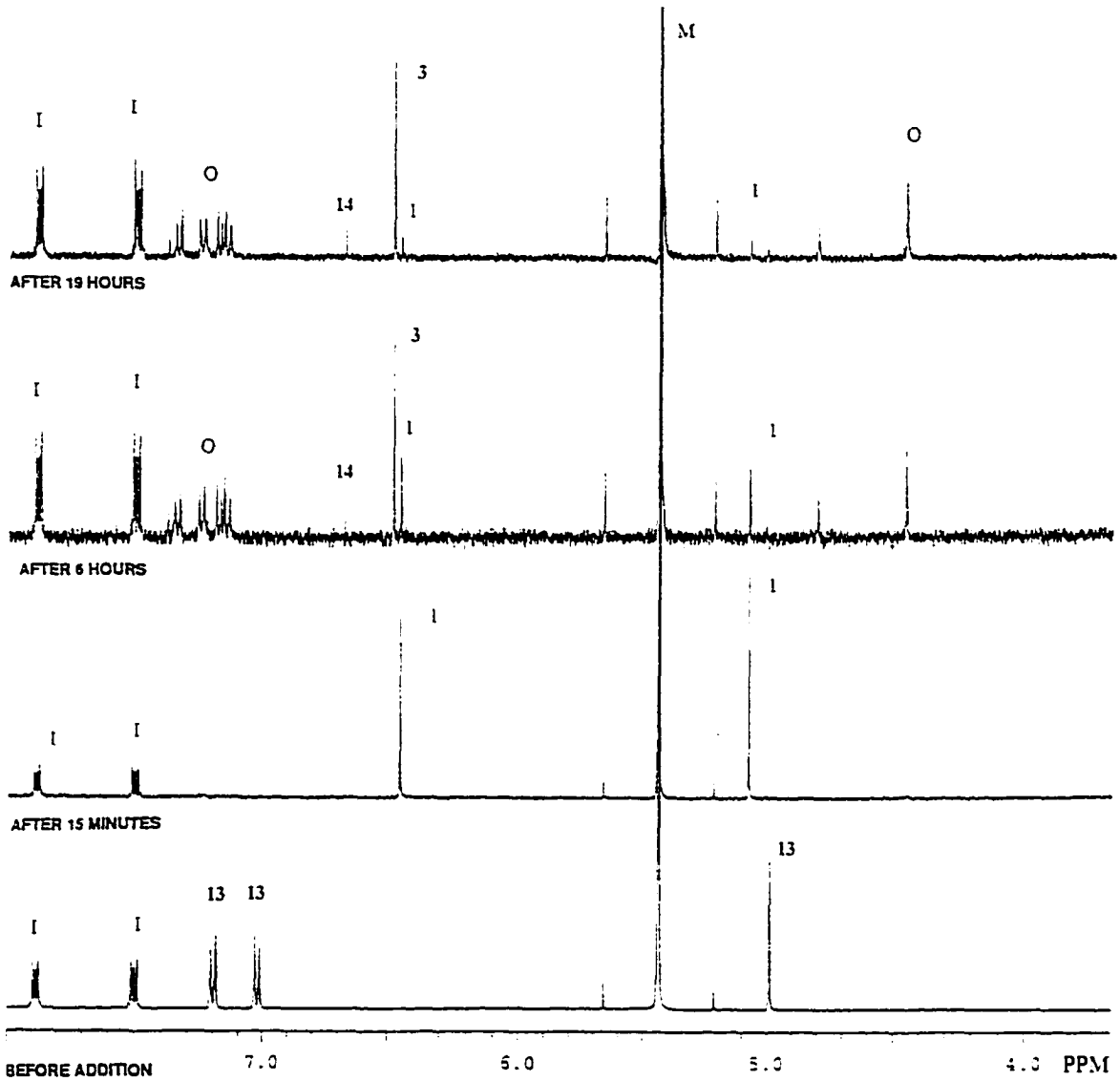
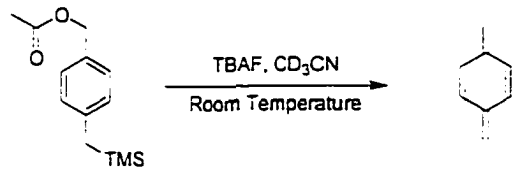


Figure 1. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-xylylene (1) in degassed CD_3CN. (3, 13, and 14 are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride, **O**: oligomers)



13 1

temperature[16] whereas the previous reports were obtained at about -80 °C.[17] By studying the ^{1}H NMR spectrum over time, we were able to estimate the first half-life to be approximately 4 h. With a more concentrated solutions of *p*-QDM **1** (~10^{-2} M) and reduced temperature (-40°C), an ^{13}C NMR spectrum of *p*-QDM **1** was obtained for the first time.

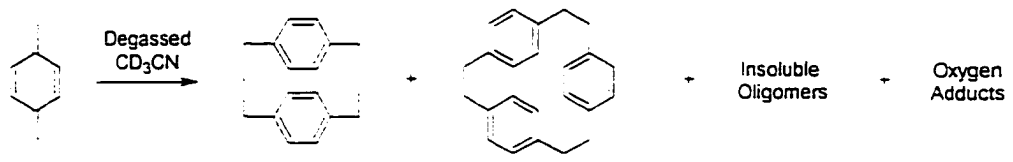
The product mixture that forms from the solution of *p*-QDM **1** varies based on the care taken to exclude oxygen (Table 1). Under standard freeze-pump-thaw degassing conditions, dimer **3**, [2.2.2]paracyclophane, trimer **14**, products that appear

Table 1. Yields of [2.2]Paracyclophane (3) and [2.2.2]Paracyclophane (14) from *p*-Xylylene (1).

μmol **1**	μmol **3**	% yield	μmol **14**	% yield	Oxygen adducts
1.1[a]	0.077	7	0.00015	0.4	Present
1.5[a]	0.11	15	0.025	5	Present
1.3[b]	0.23	35	0.031	7	Trace

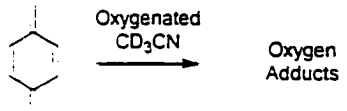
[a]Results of *p*-xylylene **1** in degassed CD_3CN.

[b]Result of *p*-xylylene **1** in deoxygenated CD_3CN.



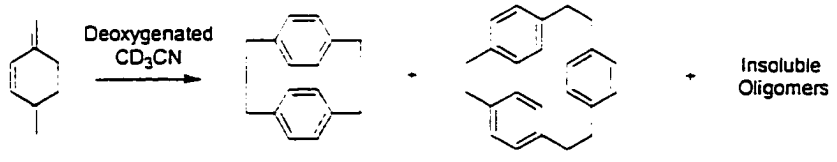
1 3 14

to be oxygen adducts, and insoluble oligomers were observed. The ^{1}H NMR spectrum of the oxygen adducts (Figure 2) was compared to the products prepared in an oxygenated solvent. ^{1}H NMR spectra of both products mixtures showed signals near δ4.5.



1

When *p*-QDM 1 is prepared in a solution that was rigorously freed of oxygen, its product mixture contained dimer 3, trimer 14, and what appear to be insoluble oligomers of *p*-QDM 1 (Table 1). The ^{1}H NMR spectrum (Figure 3) of this mixture did not contain signals at δ 4.5.



1 3 14

α-Methyl-*p*-xylylene (11) Oligomerization Studies. In an attempt to obtain additional evidence for dimeric diradical intermediates, the methyl derivative, α-methyl-*p*-xylylene (11) was studied. 1-[*p*-((Trimethylsilyl)methyl)phenyl]ethyl acetate (15) was prepared from 4-[(trimethylsilyl)methyl]benzyl alcohol by reactions shown in Scheme 4.

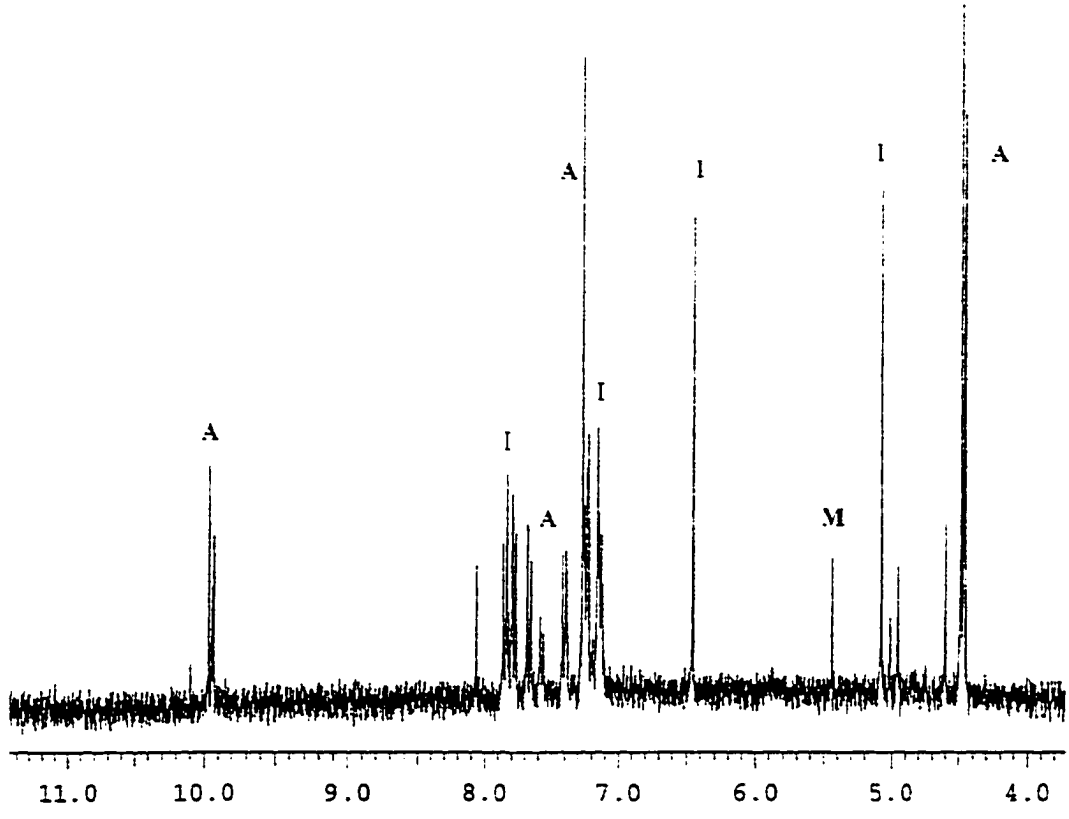


Figure 2. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (**1**) and oligomerization products in oxygenated CD_3CN. (**A**: oxygen adducts, **I**: internal standard, naphthalene, **M**: methylene chloride)

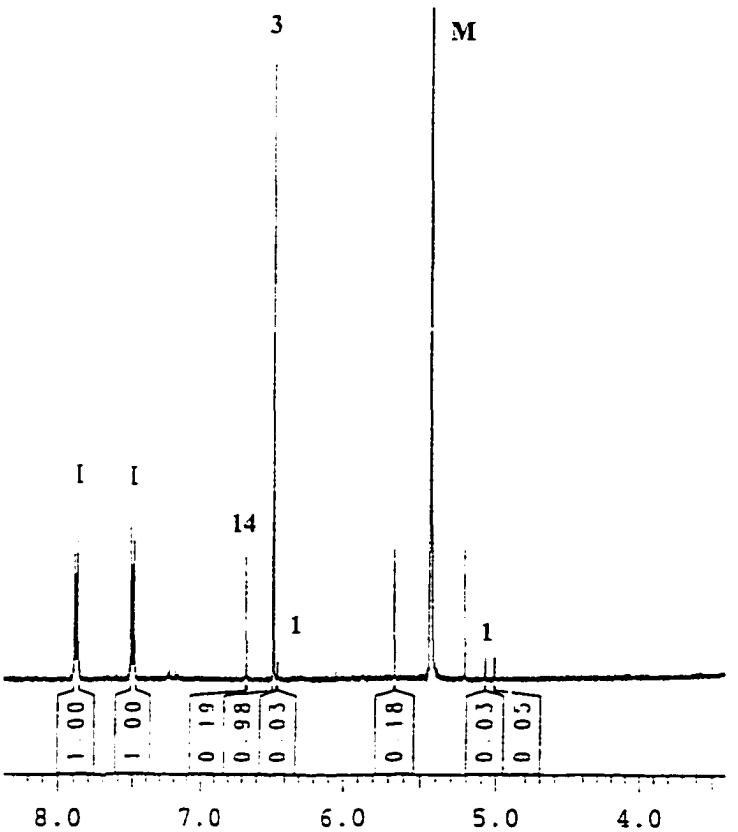
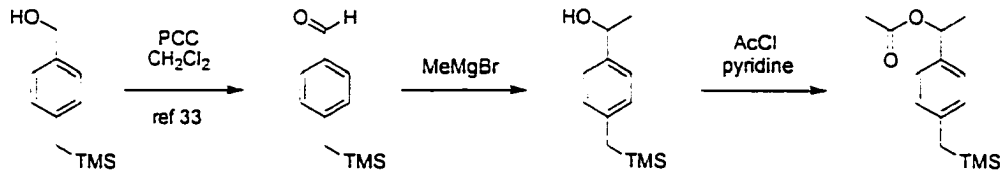


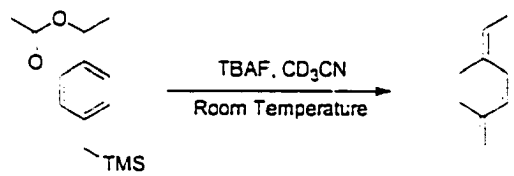
Figure 3. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (**1**) products in deoxygenated CD_3CN. (**3** and **14** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride)

Scheme 4



15

A dilute solution (10^{-3} M) of *p*-QDM **11** was prepared by a similar fluoride-induced elimination from acetate **15**. The ^{1}H NMR spectrum of *p*-QDM **10** was also obtained at



15 11

room temperature (Figure 4). Similar to the parent system, the presence of oxygen in the sample has a notable effect. When solutions of *p*-QDM **11** are prepared in the degassed CD_3CN and analyzed by ^{1}H NMR spectroscopy (Figure 5), cyclic dimers, cyclic trimers, and oxygen containing products are observed. When samples of *p*-QDM **11** were prepared with careful exclusion of oxygen (Figure 6), the products are cyclic dimers **16** (14.9 % yield), cyclic trimers **17** (14.9 % yield), and insoluble oligomers (Scheme 5). We did not observe any evidence of an acyclic dimers **18** by NMR spectroscopy or GC/MS.

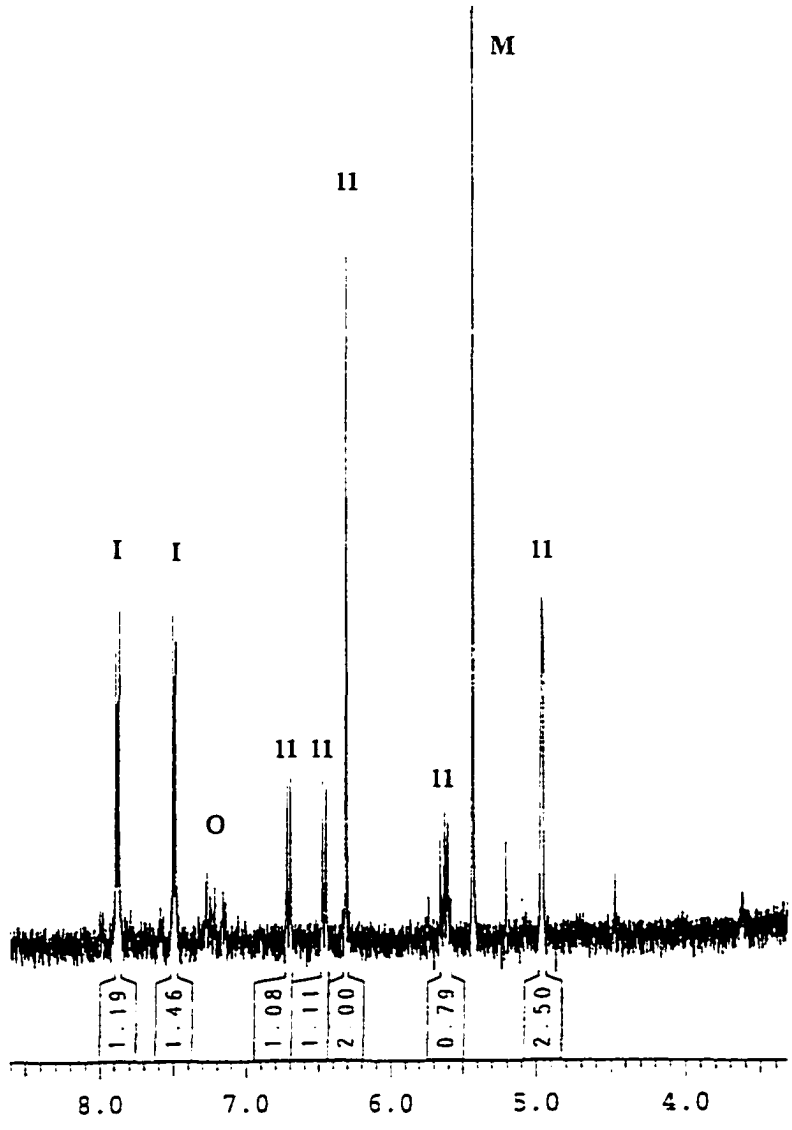


Figure 4. ^{1}H NMR spectrum (400 MHz, CD_3CN) of α-methyl-*p*-xylylene (**11**) in degassed CD_3CN. α-Methyl not shown. (**I**: internal standard, naphthalene, **M**: methylene chloride, **O**: oligomers)

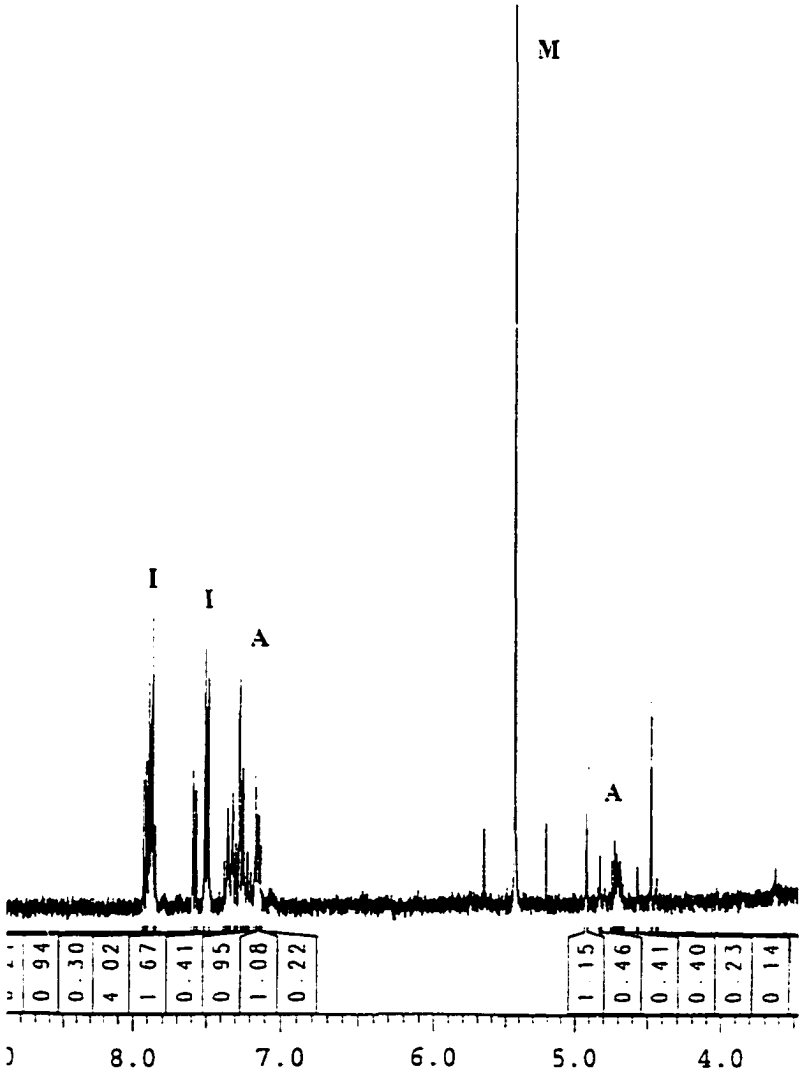


Figure 5. ^{1}H NMR spectrum (400 MHz, CD_3CN) of product mixture of α-methyl-*p*-xylylene (**11**) in degassed CD_3CN. (**A**: oxygen adducts, **I**: internal standard, naphthalene, **M**: methylene chloride)

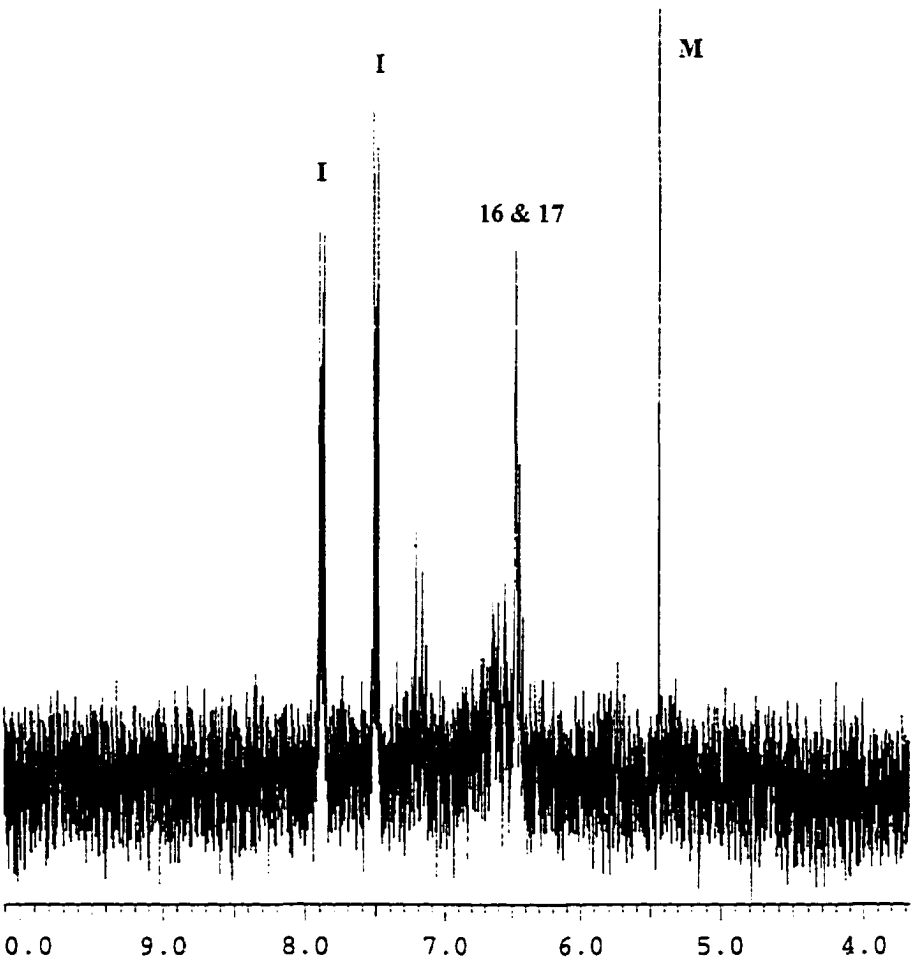
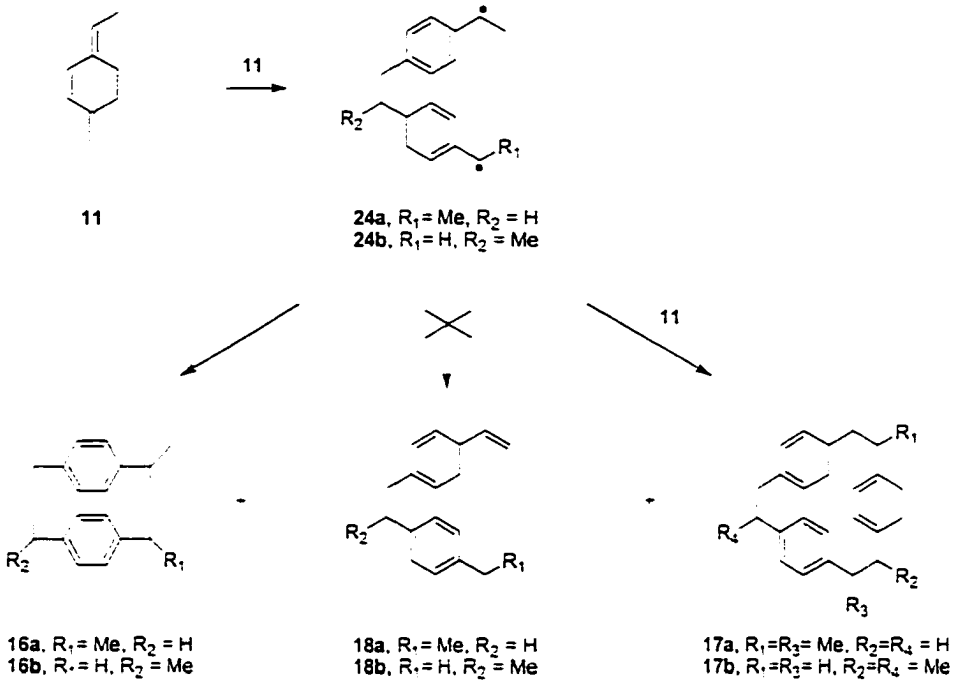
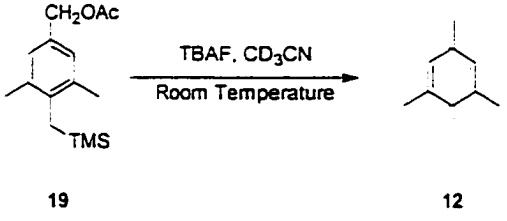


Figure 6. ^{1}H NMR spectrum (400 MHz, CD_3CN) of product mixture of α-methyl-*p*-xylylene (**11**) in deoxygenated CD_3CN. (**1** and **14** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride)

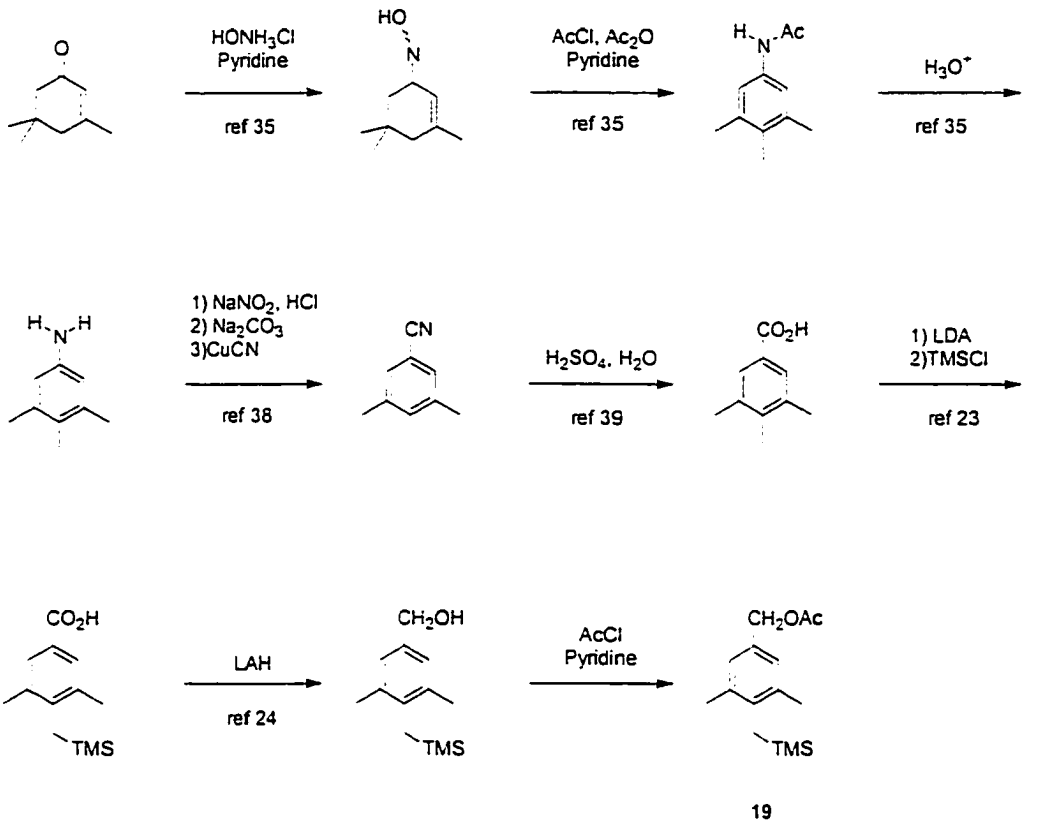
Scheme 5



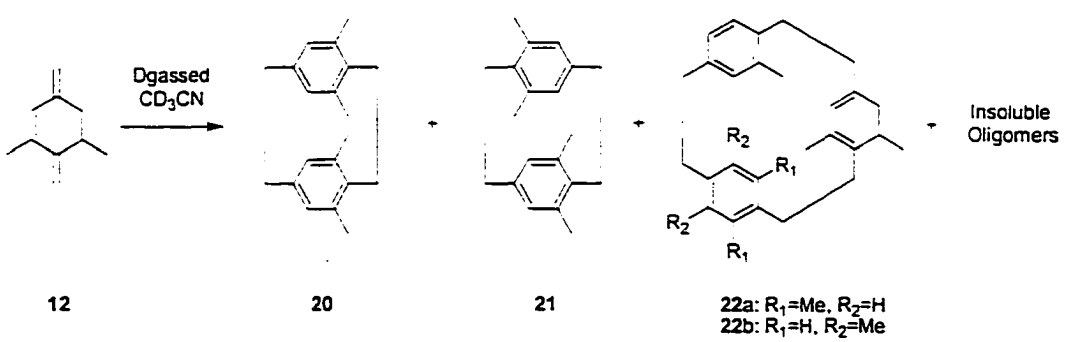
2,6-Dimethyl-*p*-xylylene (12) Oligomerization Studies. [3,5-Dimethyl-4-((trimethylsilyl)methyl)phenyl]methyl acetate (**19**) was prepared from isophorone by reactions shown in Scheme 6. A fluoride induced elimination of trimethylsilyl acetate from acetate **19** yielded 2,6-dimethyl-*p*-xylylene (**12**). The ^{1}H NMR spectrum of *p*-QDM **12** was obtained in



Scheme 6



degassed acetonitrile-d_3 at room temperature (Figure 7). Upon standing, nearly equal amounts of head-to-head dimer **20** (7.7 % yield) and head-to-tail dimer **21** (7.3 % yield) were formed along with insoluble oligomers and a trace (1.3 % yield) of trimer **22a** (Figure 8).



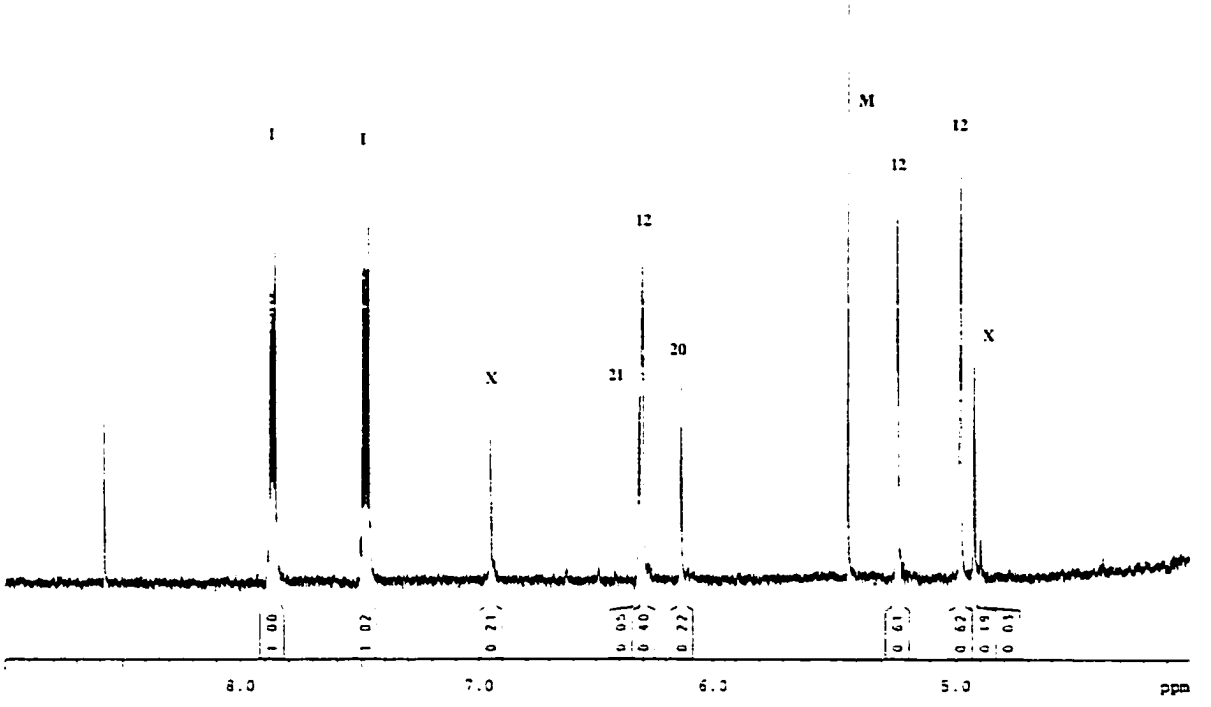


Figure 7. ^{1}H NMR spectrum (400 MHz, CD_3CN) of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**20** and **21** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride, **X**: impurity)

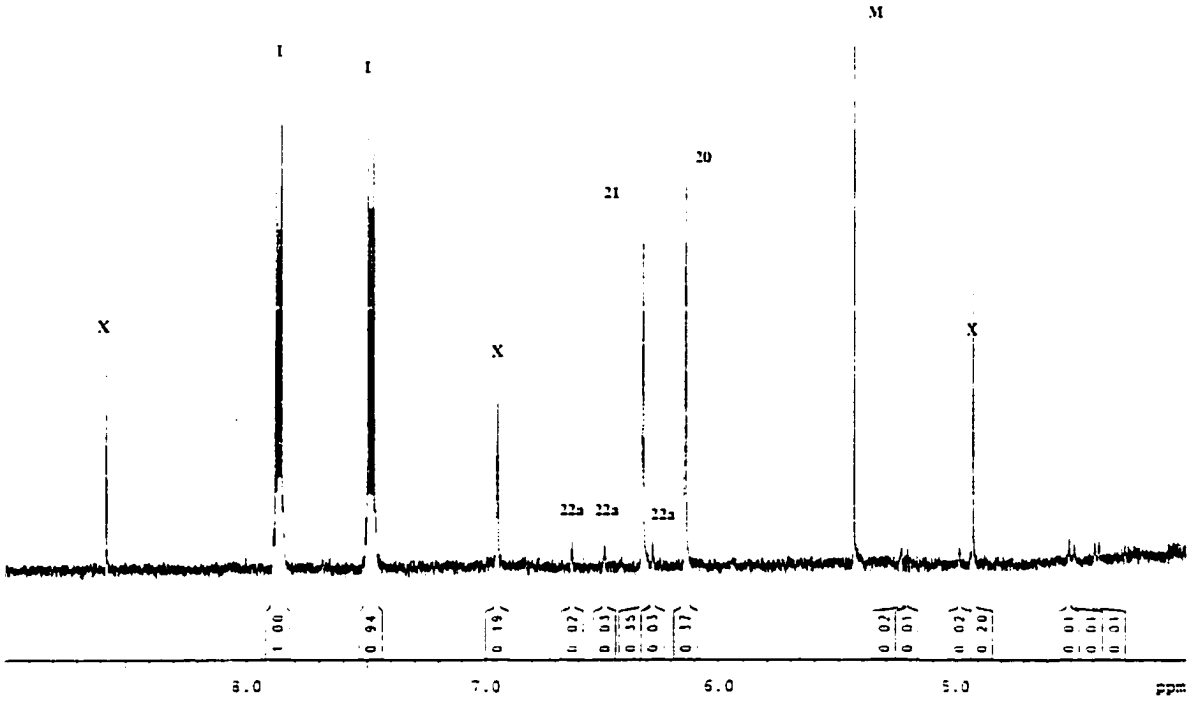


Figure 8. ^{1}H NMR spectrum (400 MHz, CD_3CN) of product mixture of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**20**, **21** and **22a** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride, **X**: impurity)

Only one trimer was found in the GC\MS of the product mixture. Based on the ^{1}H NMR spectrum, which shows three signals for aromatic hydrogens rather than just one, it can be concluded that trimer **22a**, was formed.

***p*-Xylylene (1) and 2,6-Dimethyl-*p*-xylylene (12) Co-oligomerization Studies.** A mixture of *p*-QDM's 1 and 12 were prepared by fluoride induced eliminations from their respective acetates 13 and 19. The ^{1}H NMR spectrum (Figure 9) of the mixture clearly shows the ratio of *p*-QDM's 1 to 12 as being nearly 1 to 4. Upon standing,

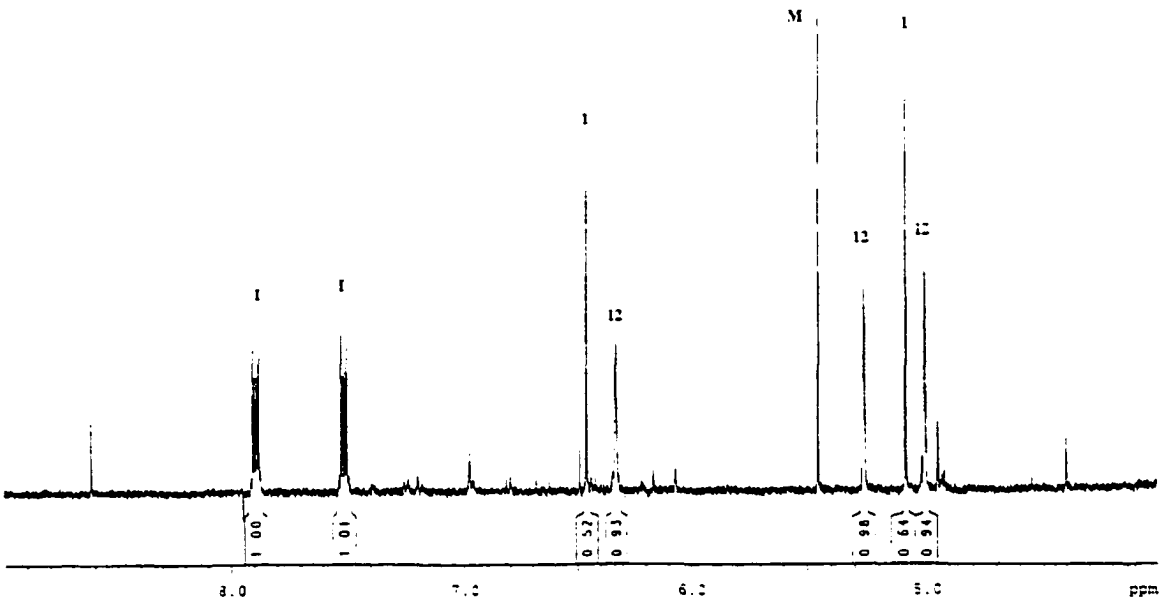
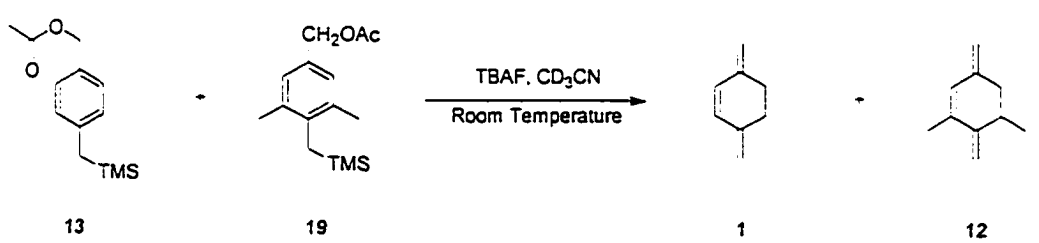


Figure 9. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (**1**) and 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**I**: internal standard, naphthalene, **M**: methylene chloride)



p-xylylene dimer **3**, mixed dimer **23**, head-to-head dimer **20**, head-to-tail dimer **21**, and insoluble oligomers were formed. We did not observe any evidence of trimers by ^{1}H NMR spectrum (Figure 10) or GC/MS.

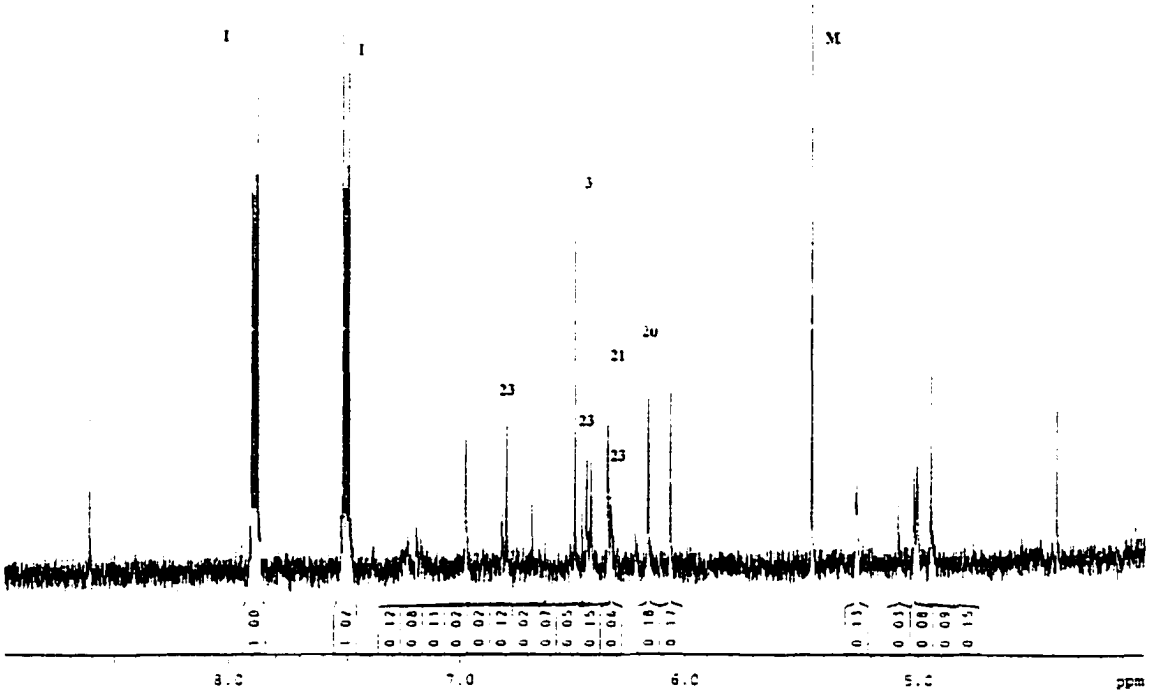
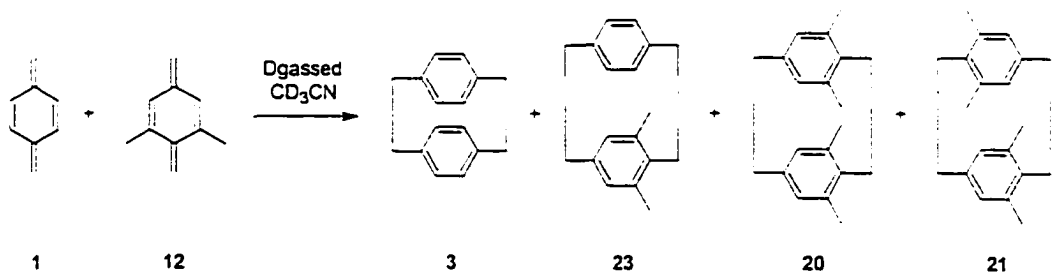


Figure 10. ^{1}H NMR spectrum (400 MHz, CD_3CN) of product mixture of *p*-xylylene (1) and 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**3**, **20**, **21**, and **23** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride)



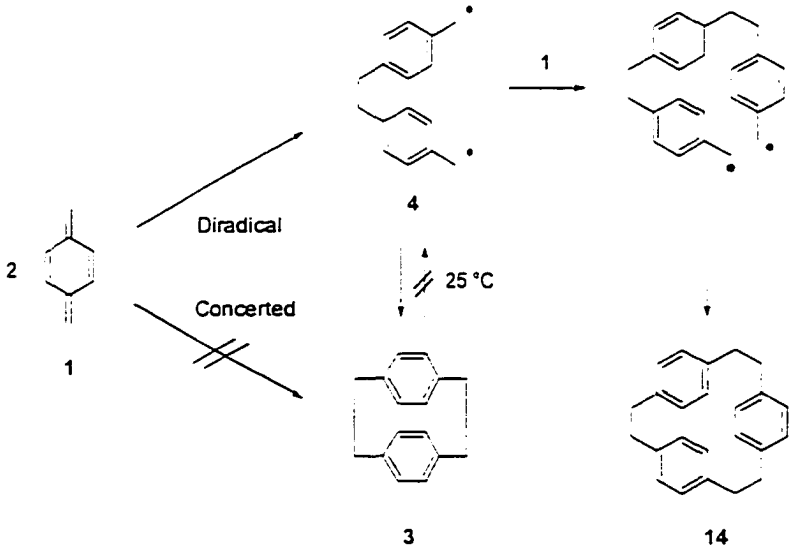
Discussion

***p*-Xylylene (1) Oligomerization Studies.** The fluoride induced elimination of trimethylsilyl acetate has proven to be an effective and mild means of preparing *p*-QDM's.

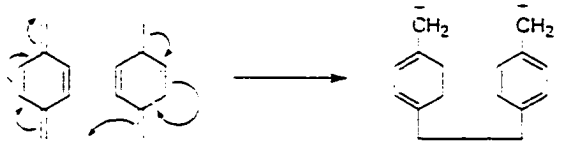
Under these mild conditions, *p*-xylylene (**1**) can be prepared as a dilute solution that persists for several hours at room temperature. With relatively stable solutions of *p*-QDM's at room temperature, other reactions could be studied that might be unfavorable at reduce temperatures. In contrast to the pyrolysis preparations, reaction products are free of side products resulting from the pyrolysis of oligomers.

Two pathways could form dimer **3**: a concerted [6 + 6] cycloaddition of two molecules of *p*-QDM **1** or formation of an initial dimeric diradical **2** followed by closure of the diradical. Formation of trimer **14** at room temperature is consistent with the trapping of diradical **2** by *p*-QDM **1**. Since dimer **3** does not open to diradical **2** at room temperature,[18] formation of dimer **2** must be stepwise, not concerted (Scheme 7).

Scheme 7



Zwitterionic Intermediates. An alternative to the stepwise diradical mechanism is a stepwise mechanism involving zwitterionic intermediate **24**.[19] It is known that reactions



1 1 24

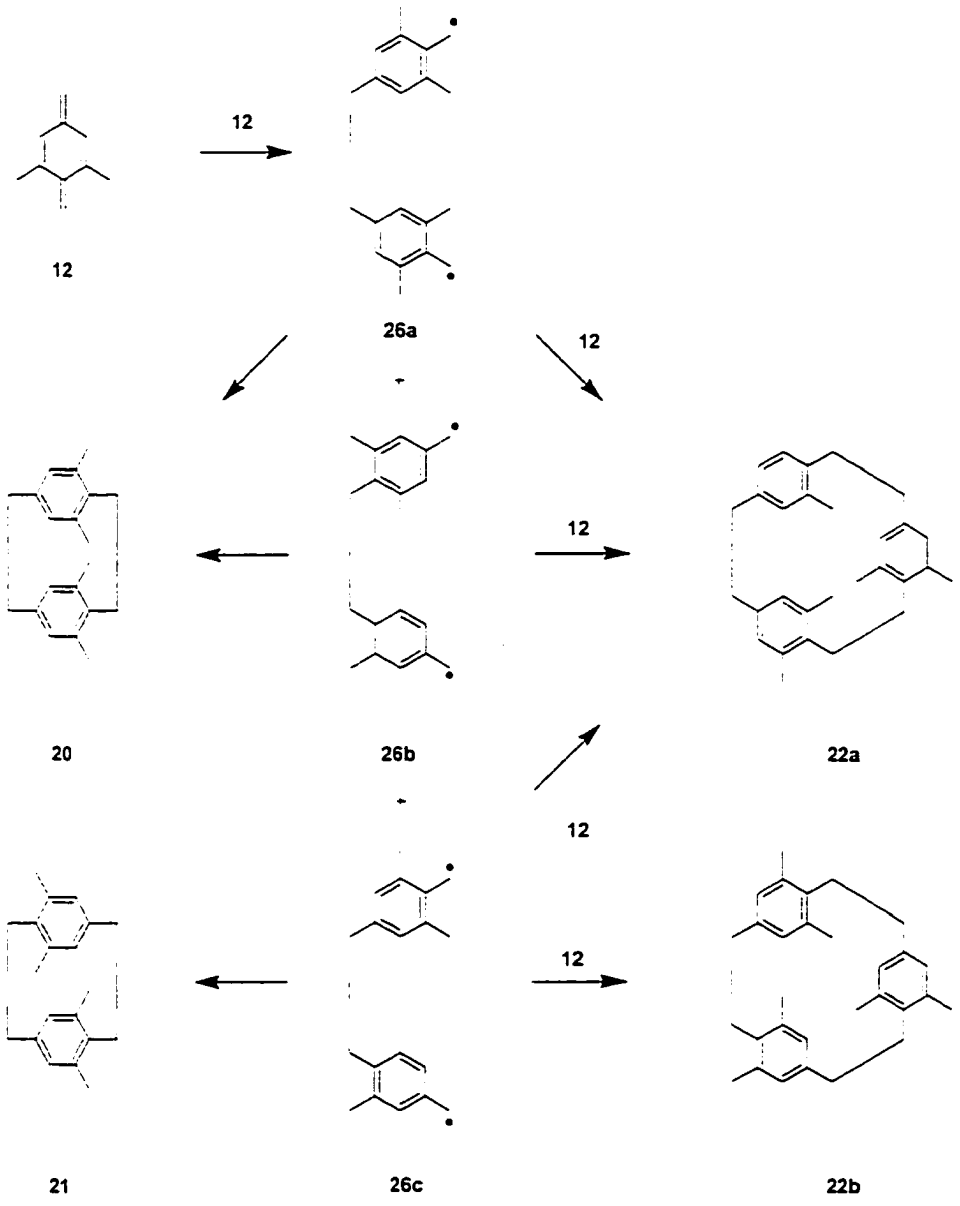
involving zwitterionic intermediate are sensitive to changes in solvent polarity.[20] Although acetonitrile-d_3 was the only solvent used in this study, solutions of *p*-QDM 1 in hexane, prepared from the pyrolysis of p-xylene, is known to form a trace amount of dimer 3.[21] There is no evidence of products resulting from the zwitterionic intermediates reacting with the solvent. Furan-based *o*-QDM **4a** is thought to dimerize by a diradical intermediate rather than a zwitterionic intermediate because it exhibited no change in rate of dimerization when the polarity of solvent was changed.[7]

Further evidence against a zwitterionic intermediate is that unsymmetrical *p*-QDM 11 forms both head-to-head **16a** and head-to-tail **16b** dimers. Unsymmetrical molecules that dimerize by a zwitterionic intermediates often form head-to-tail dimers. It has been proposed that this occurs because the positive end of one molecule would be expected to attack the negative end of the other.[22]

α-Methyl-*p*-xylylene (11) Oligomerization Studies. α-Methyl-*p*-xylylene (11) has a half-life similar or slightly longer than that of *p*-xylylene (1). Observation of trimers **17** again support the existence of a dimeric diradical **25**. Due to the large number of isomers, it is difficult to determine if the reaction is regioselective.

2,6-Dimethyl-*p*-xylylene (12) Oligomerization Studies. Dimers **20** and **21** were formed in near equal amounts. Dimer **20** can arise from either dimeric diradical **26a** or **26b** whereas dimer **21** can only be formed from dimeric diradical **26c** (Scheme 8). With its two

Scheme 8



flanking methyl groups, 2,6-dimethyl-*p*-xylylene (**12**) has one exocyclic methylene that is sterically hindered. This could have limited the possible dimeric diradicals that could form to the tail-to-tail diradical **26a** because head-to-head diradical **26b** and head-to-tail diradical **26c** would have too much steric hinderance to form. Since dimers **20** and **21** were formed in

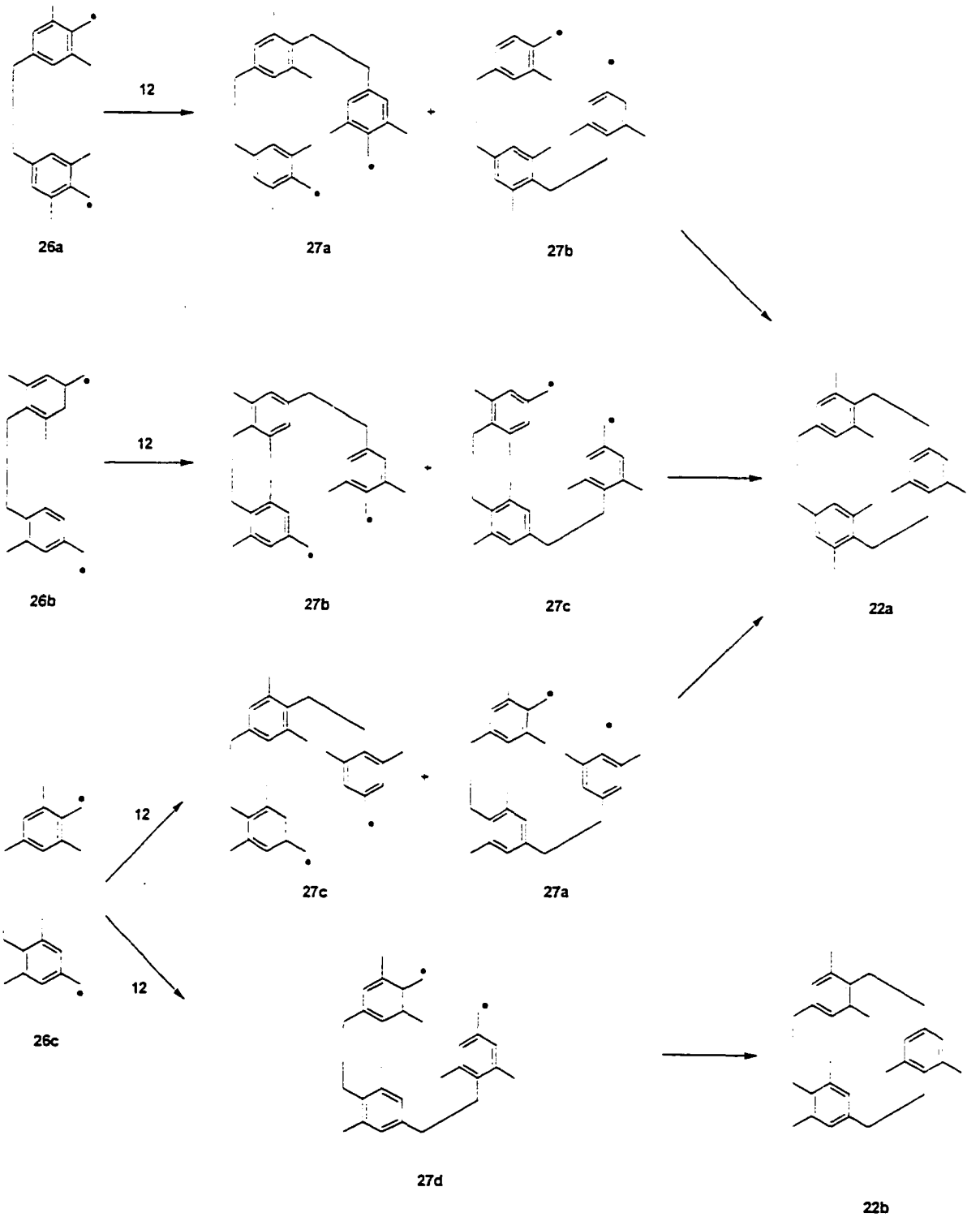
nearly equal amounts, the steric hinderance of the two methyl groups must be minimal. Trimer **22a** was observed by ^{1}H NMR spectroscopy and GC\MS but evidence for trimer **22b** was not found. Trimer **22b** can only be formed from dimeric diradical **26c,** were as trimer **22a** can form from either dimeric diradical **26a** , **26b** or **26c** (Scheme 9). Dimeric diradical **26c** must close to dimer **21** faster than being trapped as trimers **22a** or **22b**.

***p*-Xylylene (1) and 2,6-Dimethyl-*p*-xylylene (12) Co-oligomerization Studies.** Both *p*-QDM's 1 and **12** oligomerized at a similar rate and produced a mixed dimer **23**. This supports the theory that the flanking methyl groups of *p*-QDM **12** are having little effect on its reactivity. It is unclear why trimers were not observed from the mixed *p*-QDM's studies, where as trimers were observed in both of the isolated studies of *p*-QDM's 1 and **12**.

Conclusion

^{1}H NMR spectra of *p*-xylylene (**1**), α-methyl-*p*-xylylene (**11**), and 2,6-dimethyl-*p*-xylylene (**12**) have been observed at room temperature, which will possibly allow a more detailed study of their chemistry. For the first time, ^{13}C NMR spectrum of *p*-QDM 1 has been observed. The trapping of diradicals **2**, **25**, and **26** as their respective trimers is strong evidence that *p*-QDM's **1**, **11**, and **12** dimerize by a stepwise mechanism. The absence of acyclic dimer **18**, which was present in the thiophene-based *p*-QDM **6b** and furan-based *o*-QDM **4d**, can be explained by the conformational limitations found in the benzene-based *p*-QDM's. Reactivity of *p*-QDM's **1** and **12** are similar. The flanking methyl groups do not appear to reduce the reactivity of the *p*-QDM **12**.

Scheme 9



Experimental Section

Methods and Materials. All materials were commercially available and used as received, except where indicated. ^{1}H NMR spectra were recorded at 400 MHz unless noted otherwise. ^{13}C NMR spectra were recorded at 100 MHz unless noted otherwise. The residual CHD_2CN was used as the internal reference for all ^{1}H NMR spectra unless noted otherwise. Both the GC and the GC/MS analysis were done using a DB-5 column (30m, I.D. 0.32 mm, 0.25μ film thickness). Elemental analyses were performed by Iowa State University Instrumental Services, Ames, IA.

4-[(Trimethylsilyl)methyl]benzoic Acid was prepared in a 25% yield from *p*-toluic acid (29 mmol) as described by Stern and Swenton.[23] ^{1}H NMR (400 MHz, CD_3CN) δ 9.293 (br s), 7.833 and 7.115 (AA'BB'q, *J*=8.4Hz), 2.207 (s), -0.032 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 and 7.07 (AA'BB'q, *J*=12Hz, 4H), 2.17 (s, 2H), -0.02 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 168.0, 148.4, 130.5, 129.0, 126.5, 28.0, -2.0.

4-[(Trimethylsilyl)methyl]benzyl Alcohol was prepared in a 94% yield by lithium aluminum hydride (4 mmol) reduction of 4-[(trimethylsilyl)methyl]benzoic acid (1.8 mmol)with a procedure similar to the procedure outlined by Nystrom and Brown[24] for the reduction of phenylacetic acid to β-phenylethanol. ^{1}H NMR (400 MHz, CD_3CN) δ 7.191 and 7.009 (AA'BB'q, *J*=7.6Hz), 4.507 (s), 3.320 (br s),2.107 (s), 0.001 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 and 6.97 (AA'BB'q, *J*=8Hz, 4H), 4.61 (s, 2H), 2.06 (s, 2H), 1.56 (br s, 1H), -0.03 (s, 9H).[lit[25] ^{1}H NMR ($CDCl_3$) δ 7.22 and 7.00 (ABq, *J*=8.0Hz, 4H, arom), 4.6 (s, 2H, CH_2), 2.12 (s, 2H, CH_2), 0.02 (s, 9H, $SiMe_3$)]; ^{13}C NMR (100 MHz, CD_3CN) δ 140.3,

138.4, 128.8, 127.8, 64.7, 26.9, -1.8. Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 68.14; H, 9.47.

[*p*-((Trimethylsilyl)methyl)phenyl]methyl Acetate (13). A solution of 109 mg of 4-[(trimethylsilyl)methyl]benzyl alcohol (0.56 mmol) and 0.3 mL of pyridine (3.7 mmol) in 2 mL dry THF was prepared in a 10-mL flask. An argon atmosphere was placed over the solution. The solution was cooled to 0°C and stirred. A solution of 0.125 mL acetyl chloride (1.76 mmol) in 1 mL of dry THF was added dropwise to the alcohol solution by a syringe. The reaction mixture was allowed to warm to room temperature and was stirred for 2 h. The reaction mixture was added to 10 mL of ether. The ether solution was washed with brine twice then with a saturated solution of $NaHCO_3$ and finally with brine again. The ether solution was dried with $MgSO_4$ and concentrated under reduced pressure to get 115 mg (87%) of viscous oil. ^{1}H NMR (400 MHz, CD_3CN) δ 7.193 and 7.012 (AA'BB'q, *J*=8Hz, 4H), 4.985 (s, 2H), 2.160 (s, 2H), 2.006 (s, 3H), -0.047 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 171.6, 141.8, 132.9, 129.2, 129.1, 66.8, 22.4, 21.1, -2.0.

Drying and Initial Degassing of CD_3CN. Prior to use as a solvent in the preparation of *p*-QDM's, the CD_3CN was distilled from P_2O_5 under argon then degassed by repeated freeze-pump-thaw cycles, except where indicated.[26]

***p*-Xylylene (1) in Degassed CD_3CN.** To a tear-shaped flask was added 7.6 mg of TBAF (24 μmol). To a second tear-shaped flask was added 9.5 μL of a 5.0 x 10^{-2} M solution of naphthalene in CH_2Cl_2 (0.48 μmol) and 9 μL of an approximately 0.1 M solution of **13** in CH_2Cl_2 (~1 μmol). The CH_2Cl_2 was removed at reduced pressures. The two flasks were placed into a nitrogen-filled glove bag. To the acetate flask was added about 0.8 mL of degassed CD_3CN. The acetate solution was transferred to an NMR tube and the acetate was

quantified by ^{1}H NMR. The NMR tube was returned to the glove bag. To the TBAF flask was added about 0.2 mL of degassed CD_3CN. The TBAF solution was added to the NMR tube. The sample was protected from light. The NMR tube was periodically removed from the glove bag for analysis by ^{1}H NMR spectroscopy. ^{1}H NMR (400 MHz, CD_3CN, 20°C) δ 6.452 (s, 4H), 5.007 (s, 4H). [lit[17] ^{1}H NMR (60 MHz, THF-d_8, -80°C) δ 6.49, 5.10].

As the solution is allowed to stand, the *p*-xylylene (**1**) was consumed and [2.2]paracyclophane (**3**) (7 % yield), [2.2.2]paracyclophane (**14**) (0.4% yield) and insoluble oligomers were formed. **3:** ^{1}H NMR (400 MHz, CD_3CN) δ 6.484 (s, 8H), 3.046 (s, 8H).). [lit[27] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.48, 3.08]; GC/MS m/z (relative intensity) 209 (5), 208 (35), M$^+$), 105 (5), 104 (100), 78 (8), 77 (4). [lit[28] GC/MS m/z (relative intensity) 208 (16), 104 (100), 103 (100)]. **14:** ^{1}H NMR (400 MHz, CD_3CN, 20°C) δ 6.678 (s, 12H), 2.903 (s, 12H). [lit[29] ^{1}H NMR (100 MHz, $CDCl_3$) δ 6.68 (Ar), 2.92 (CH_2), ^{1}H NMR (100 MHz, CD_3OD) δ 6.23 (Ar), 2.47 (CH_2)]; GC/MS m/z (relative intensity) 313 (15), 312 (77), 207 (14), 195 (12), 193 (31), 104 (100). [lit[30] GC/MS m/z (relative intensity) 312 (44), 118 (32). 117 (100), 115 (59), 105 (90), 104 (83), 91 (54), 77(35)].

^{13}C NMR Spectrum of 1 at -40°C. The sample was prepared in a manner similar to the one reported above for the degassed CD_3CN preparation of **1** except: (A) No naphthalene was added; (B) 7mg of $Cr(acac)_3$ was added[31]; (C) 35 mg of TBAF (111 μmol) was used; (D) 100 μL of 0.1 M solution of **13** (~10 μmol) was used; (E) 30 s after the TBAF solution was added, the NMR tube was placed into a CH_3CN/dry ice bath. ^{13}C NMR (100 MHz, CD_3CN, -40°C) δ 140.3, 129.8, 115.5.

***p*-Xylylene (1) in Deoxygenated CD_3CN.** To a tear-shaped flask was added 7 mg of tetrabutylammonium fluoride trihydrate (TBAF) (22.2 μmol). To a second tear-shaped flask was added 10 μL of a 4.7 x 10^{-2} M solution of naphthalene in CH_2Cl_2 and 10 μL of an approximately 0.1 M solution of **13** in CH_2Cl_2. The CH_2Cl_2 was removed at reduced pressure. The two flasks were placed into a nitrogen filled glove bag. To the acetate flask was added about 0.8 mL of degassed CD_3CN and to the TBAF was added about 0.2 mL of degassed CD_3CN. The acetate solution was transferred to an NMR tube and the acetate was quantified by NMR. The NMR tube was returned to the glove bag. The acetate solution was poured into one tube of a two-tube reaction cell[32]. The TBAF solution was added to the other tube of the cell. The cell was connected to a valved vacuum adapter. The two solutions were deoxygenated by two series of argon purging followed by three freeze-pump-thaw cycles. Once the cell had returned to room temperature, the cell was tipped to allow the TBAF solution to be added to the acetate solution. While still under a vacuum, the cell was wrapped in foil and placed into the glove bag. After 18 h, the reaction mixture, that contained some precipitate, was transferred to an NMR tube. The soluble products, **3** (35% yield) and **14** (7% yield), were quantified by NMR.

***p*-Xylylene (1) in Oxygenated CD_3CN.** The CD_3CN was distilled from P_2O_5 under dry air then oxygen was bubbled through the CD_3CN for 30 s. To a tear-shaped flask was added 7 mg of TBAF (22 μmol). To a second tear-shaped flask was added 10 μL of an approximately 0.1 M solution of **11** in CH_2Cl_2. The CH_2Cl_2 was removed at reduced pressure. The dried CD_3CN was added to the acetate flask and the TBAF flask, 0.8 mL and 0.2 mL, respectively. Both solutions were transferred to an NMR tube.

4-[(Trimethylsilyl)methyl]benzaldehyde was prepared in a 96% yield from 4-[(trimethylsilyl)methyl]benzyl alcohol (3.93 mmol) with a procedure similar to the procedure outlined by Corey and Suggs.[33] ^{1}H NMR (400 MHz, CD_3CN) δ 9.889 (s), 7.727 and 7.198 (AA'BB'q, *J*=8Hz), 2.238 (s), -0.017 (s). ^{1}H NMR in $CDCl_3$ data are in good accord with published values.[34] ^{13}C NMR (100 MHz, CD_3CN) δ 192.9, 150.2, 134.1, 130.5, 129.5, 28.4, -2.0.

1-[*p*-((Trimethylsilyl)methyl)phenyl]ethanol. To a solution of 209 mg of 4-[(trimethylsilyl)methyl]benzaldehyde (1.09 mmol) in 3 mL of dry ether was added 0.4 mL of 3 M MeMgBr (1.2 mmol), dropwise. The reaction mixture was heated to reflux for 30 min. The reaction mixture was worked up in the normal manner to yield 197 mg (95%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.186 and 6.975 (AA'BB'q, *J*=8Hz), 4.727 (q, *J*=6.4Hz), 2.073 (s), 1.353 (d, *J*=6.4Hz), -0.034 (s); ^{13}C NMR (100 MHz, CD_3CN) δ 143.3, 140.1, 128.7, 126.2, 69.9, 26.7, 25.9, -1.9. Anal. Calcd for $C_{12}H_{20}OSi$: C, 69.17; H, 9.67. Found: C, 69.29; H, 9.95.

1-[*p*-((Trimethylsilyl)methyl)phenyl]ethyl Acetate (15) was prepared in an 87% yield from 1-[*p*-((trimethylsilyl)methyl)phenyl]ethanol (50 mg, 0.24 mmol) with the procedure used for the above preparation of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate. ^{1}H NMR (400 MHz, CD_3CN) δ 7.196 and 7.002 (AA'BB'q, *J*=8Hz, 4H), 5.763 (q, *J*=6.8Hz, 1H), 2.085 (s, 2H), 1.991 (s, 3H),1.456 (d, *J*=6.8Hz, 3H), -0.038 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 171.0, 141.3, 138.5, 129.0, 126.8, 72.8, 26.9, 22.4, 21.5, −1.9.

α-Methyl-*p*-xylylene (11) in Degassed CD_3CN was prepared from acetate **15** (1.2 μmol), TBAF (25 μmol), and naphthalene (0.30 μmol) with the procedure used for the above

preparation of *p*-xylylene (**1**) in degassed CD_3CN. ^1H NMR (400 MHz, CD_3CN) δ 6.713 (br d, *J*=9.6Hz, 1H), 6.466 (br d, *J*=9.6Hz, 1H), 6.314 (br s, 2H) 5.619 (q, *J*=8Hz, 1H), 4.963 (br s, 2H), 1.848 (d, *J*=8Hz, 3H).

α-Methyl-*p*-xylylene (11) in Deoxygenated CH_3CN was prepared from acetate **15** (20 μmol), TBAF (45 μmol) in 20 mL of CH_3CN with the procedure used for the above preparation of *p*-xylylene (**1**) in deoxygenated CD_3CN. As the solution is allowed to stand, the α-methyl-*p*-xylylene (**11**) was consumed and three dimers **16**, four trimers **17**, and insoluble oligomers were formed. Dimer A **16** (7.3 % yield): GC/MS m/z (relative intensity) 237 (6), 236 (31) M^+, 119 (29), 118 (100), 117 (66), 115 (24), 113 (3), 105 (2), 103 (3), 102 (3), 89 (7), 88 (6). Dimer B **16** (2.6 % yield): GC/MS m/z (relative intensity) 237 (2), 236 (3) M^+, 119 (58), 118 (100), 117 (93), 115 (26), 103 (3), 90 (6), 89 (9), 88 (8). Dimer C **16** (5.0% yield): GC/MS m/z (relative intensity) 236 (9) M^+, 120 (3), 119 (36), 118 (97), 117 (100), 115 (24), 103 (3), 89 (12), 88 (7), 86 (6). Trimer A **17** (1.3 % yield): GC/MS m/z (relative intensity) 354 (2) M^+, 238 (16), 237 (100), 236 (60), 189 (2), 131 (2), 129 (2), 128 (3), 119 (42), 118 (56), 117 (99), 115 (34), 107 (2), 103 (3), 90 (6), 89 (10), 88 (10), 86 (4). Trimer B **17** (2.2 % yield): GC/MS m/z (relative intensity) 354 (6) M^+, 238 (15), 237 (100), 236 (51), 232 (2), 189 (2), 131 (2), 129 (2), 128 (2), 122 (4), 118 (60), 117 (89), 115 (35), 106 (2), 105 (2), 103 (3), 89 (9), 87 (4), 86 (3), 77 (3), 75 (2), 74 (3). Trimer C **17** (1.1 % yield): GC/MS m/z (relative intensity) 354 (2) M^+, 238 (15), 237 (92), 236 (57), 131 (2), 128 (3), 119 (41), 118 (56), 117 (100), 115 (37), 103 (2), 91 (4), 89 (12), 88 (10), 87 (5), 86 (4). Trimer D **17** (2.4 % yield): GC/MS m/z (relative intensity) 355 (2), 354 (7) M^+, 353 (2), 239(2), 238 (15), 237 (97), 236 (36), 233(4), 232 (3), 189 (2), 131 (2), 128 (3), 119

(38), 118 (569), 117 (100), 115 (39), 112 (2), 108 (2), 105 (2), 103 (2), 91 (6), 90 (7), 89 (10), 88 (9), 86 (3), 77 (4), 76 (3), 74 (2).

Isophorone Oxime was prepared in a 98% yield from isophorone (200 mmol) as described by Beringer and Ugelow.[35] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.601 (s, 1H), 2.103 (s, 2H), 1.996 (s, 2H) 1.855 (s, 3H), 0.960 (s, 6H). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.906 (s, 1H), 2.363 (s, 2H), 1.945 (s, 2H) 1.807 (s, 3H), 0.971 (s, 6H). [lit[36] ^{1}H NMR (300 MHz, $CDCl_3$) *E* isomer δ 5.92, 2.38, 1.94, 1.81, 0.98; *Z* isomer δ 6.63, 2.09, 1.98, 1.85, 0.97]

3',4',5'-Trimethylacetanilide was prepared in a 20% yield from isophorone oxime (200 mmol) as described by Beringer and Ugelow.[35] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.112 (s, 2H), 2.235 (s, 6H), 2.123 (s, 3H) 2.099 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 168.2, 137.0, 134.9, 131.2, 119.3, 24.4, 20.6, 14.9.

3,4,5-Trimethylaniline was prepared in a 91% yield from 3',4',5'-trimethylacetanilide (34 mmol) as described by Beringer and Ugelow.[35] ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.383 (s, 2H), 3.434 (br s), 2.182 (s, 6H) 2.048 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.5, 137.3, 125.0, 114.7, 20.6, 14.4. [lit[37] ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.4 (s, 2H), 3.5 (s, 2H), 2.2 (s, 6H) 2.15 (s, 3H)].

3,4,5-Trimethylbenzonitrile was prepared in 66 % yield by the Sandmeyer reaction from 3,4,5-trimethylaniline (13.6 mmol) with a procedure similar to the procedure outlined by Clarke and Read[38] for the reaction of *o*-toluidine to *o*-tolunitrile. IR (neat) 2930, 2210,1610,1560 cm^{-1}.

3,4,5-Trimethylbenzoic Acid was prepared in a 61 % yield by acid-catalyzed hydrolysis of 3,4,5-trimethylbenzonitrile (8.56 mmol) following a procedure similar to that

outlined by Clarke and Taylor[39] for the acid-catalyzed hydrolysis of *o*-tolunitrile acid to *o*-toluic acid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.726 (s, 2H), 2.319 (s, 6H), 2.218 (s, 3H) [lit[37] ^{1}H NMR (90 MHz, $CDCl_3$) δ 9.2 (s, 1H), 7.6 (s, 2H), 2.33 (s, 6H), 2.25 (s, 3H)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 142.0, 136.7, 129.2, 126.0, 20.6, 16.0. [lit[40] ^{13}C NMR (25 MHz, $CDCl_3$) aromatic carbons only δ 141.9, 136.8, 129.2, 126.1]

3,5-Dimethyl-4-[(trimethylsilyl)methyl]benzoic Acid was prepared in a 60 % yield from 3,4,5-trimethylbenzoic acid (2.01 mmol) as described by Stern and Swenton.[23] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.707 (s, 2H), 2.266 (s, 6H), 2.233 (s, 2H) 0.015 (s, 9H) [lit[23] ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.74 (s, 2H), 2.29 (s, 6H), 2.26 (s, 2H) 0.04 (s, 9H)]

3,5-Dimethyl-4-[(trimethylsilyl)methyl]benzyl Alcohol was prepared in a 92% yield by lithium aluminum hydride (1.23 mmol) reduction of 3,5-dimethyl-4-[(trimethylsilyl)methyl]benzoic acid (0.5 mmol) following a procedure similar to that outlined by Nystrom and Brown[24] for the reduction of phenylacetic acid to β-phenylethanol that was used above for 4-[(trimethylsilyl)methyl]benzyl alcohol. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.967 (s, 2H), 4.538 (s, 2H), 2.224 (s, 6H), 2.138 (s, 2H) 0.014 (s, 9H)

[3,5-Dimethyl-4-((trimethylsilyl)methyl)phenyl]methyl Acetate (19) was prepared in an 85% yield from 3,5-dimethyl-4-[(trimethylsilyl)methyl]benzyl alcohol (0.4 mmol) following the procedure used for the above preparation of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.954 (s, 2H), 4.925 (s, 2H), 2.209 (s, 6H), 2.170 (s, 2H)), 2.008 (s, 3H) -0.003 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.7, 138.5, 131.4, 127.8, 117.4, 66.0, 20.4,20.2, 19.4,-1.1. GC/MS m/z (relative intensity) 264 (2) M^+, 249 (5), 207(5), 206 (14), 205 (100), 202 (9), 201 (6),

197 (3), 195 (2), 135 (3), 132(20), 130 (15), 128 (13), 125 (7), 117 (2), 115 (4), 113 (2), 112 (2).

2,6-Dimethyl-*p*-xylylene (12) in Degassed CD_3CN was prepared from [3,5-dimethyl-4-((trimethylsilyl)methyl)phenyl]methyl acetate (**19**) (1.6 μmol), TBAF (25 μmol) and naphthalene (0.47 μmol) following the procedure used for the above preparation of *p*-xylylene (**1**) in degassed CD_3CN. ^1H NMR (400 MHz, $CDCl_3$) δ 6.331 (s, 2H), 5.262 (s, 2H), 5.007 (s, 2H), 1.997 (s, 6H) . As the solution is allowed to stand, the 2,6-dimethyl-*para*-xylylene (**12**) was consumed and head-to-head dimer **20** (7.7 % yield), head-to-tail dimer **21** (7.3% yield), trimer **22a** (1.3% yield), and insoluble oligomers were formed. Dimer **20**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.166 (s, 4H), 3.292 (s, 4H), 2.850 (s, 4H), 2.020 (s, 12H); GC/MS m/z (relative intensity) 264 (13) M^+, 249 (10), 133 (19), 132 (100), 129 (19), 128 (13), 117 (18), 115 (26), 114 (12). Dimer **21**: ^1H NMR (400 MHz, $CDCl_3$) δ 6.348 (s, 4H), 2.97-2.93 (m, 4H), 2.85-2.80 (m, 4H), 2.210 (s, 12H); GC/MS m/z (relative intensity) 264 (18) M^+, 249 (5), 133 (23), 132 (100), 129 (12), 128 (10), 117 (47), 115 (44). Trimer **22a**: ^1H NMR[41] (400 MHz, $CDCl_3$) δ 6.630 (s, 2H), 6.489 (s, 2H), 6.278(s, 2H); GC/MS m/z (relative intensity) 397 (2), 396 (6) M^+, 147 (4), 146 (2), 145 (2), 143 (2), 134 (3), 133 (26), 132 (100), 129 (9), 128 (6), 127 (3), 126 (2), 117 (19), 115 (21), 111 (2), 103 (2), 89 (5), 88 (10), 86 (2), 85 (2), 53 (2).

***p*-Xylylene (1) and 2,6-Dimethyl-*p*-xylylene (12) in Degassed CD_3CN** was prepared from [*p*-((Trimethylsilyl)methyl)phenyl]methyl acetate (**13**) (0.67 μmol), [3,5-dimeth-yl-4-((trimethylsilyl)methyl)phenyl]methyl acetate (**19**) (1.5 μmol), TBAF (50 μmol) and naphthalene (0.47 μmol) following the procedure used for the above preparation of

p-xylylene (**1**) in degassed CD_3CN. As the solution is allowed to stand, the *p*-xylylene and 2,6-dimethyl-*para*-xylylene (**12**) was consumed and *p*-xylylene dimer **3** (2.8×10^{-8} mol), head-to-head dimers **20** (1.1×10^{-7} mol), head-to-tail dimer **21** (9.1×10^{-8} mol), mixed dimer **23** (1.6×10^{-7} mol), and insoluble oligomers were formed. Mixed dimer **23**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.811 (d, *J*=8Hz, 2H), 6.433 (d, *J*=8Hz, 2H), 6.348 (s, 2H), 3.005 (s, 4H), 2.97-2.93 (m, 2H), 2.85-2.80 (m, 2H), 2.053 (s, 6H); GC/MS m/z (relative intensity) 236 (64) M$^+$, 233 (5), 132 (100), 131 (30), 129 (24), 126 (7), 117 (17), 115 (23), 114 (17), 113 (13), 112 (9), 111 (5).

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Appendix

4-[(Trimethylsilyl)methyl]benzoic Acid was prepared from *p*-toluic acid as described by Stern and Swenton.[23] All equipment was dried in a vacuum oven prior to use. To a dry 250 mL 3-necked round-bottomed flask was added 80 mL of dry THF and 12 mL of diisopropylamine (84 mmol). To one neck was added an addition funnel, to another a glass stopper, and to the last a rubber septum. The flask and its contents were cooled to –78 °C with an IPA/CO_2 bath. Thirty-two milliliters of 2.5 M *n*-butyl lithium in hexanes (80 mmol) was placed into the addition funnel. The *n*-butyl lithium was added dropwise while the solution was being stirred. The dark yellow LDA solution was stored at –78 °C. To a dry 500-mL round-bottomed flask was added 4.032g of *p*-toluic acid (29 mmol). A stirbar and 100 mL of dry THF was added to the flask then a rubber septum was placed over the mouth. HMPA (11 mL) was added to the flask via a syringe. The flask was cooled to –78 °C with an IPA/CO_2 bath. After the flask had cooled for approximately 20 min, a canula was placed between the 500-mL flask and the flask that contained the LDA solution. The LDA solution was slowly transferred. After the LDA solution was added, the reaction mixture was stirred for 20 min. Freshly distilled chlorotrimethylsilane (8 mL, 60 mmol) was added slowly by syringe. The IPA/CO_2 bath was removed and the solution was allowed to warm to room temperature. As the solution warmed, it changed from an orange to a light yellow color. The solution was poured into 150 mL of water. The two layers were separated. The water layer was acidified with 6 M HCl and then extracted with 50 mL of ether three times. The combined ether layers was extracted three times with 50 mL of 5% Na_2CO_3. The basic extract was acidified with 6 M HCl and then extracted with three portions of 50 mL of ether. The ether extract was washed with a saturated NaCl solution then dried with anhydrous $MgSO_4$. The ether was removed under reduced pressures to yield 4.65g of crude product. The product was repeatedly recrystalized from methanol/H_2O to yield 1.273g of white product (25% yield; 99% pure by GC). Addition product was recovered from the mother liquor. ^{1}H NMR (400 MHz, CD_3CN) δ 9.293 (bs), 7.833 and 7.115 (AA'BB'q, *J*=8.4Hz),

2.207 (s), -0.032 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 and 7.07 (AA'BB'q, *J*=12Hz, 4H), 2.17 (s, 2H), -0.02 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 168.0, 148.4, 130.5, 129.0, 126.5, 28.0, -2.0.

4-[(Trimethylsilyl)methyl]benzyl Alcohol was prepared by lithium aluminum hydride reduction of 4-[(trimethylsilyl)methyl]benzoic acid with a procedure similar to the procedure outlined by Nystrom and Brown[24] for the reduction of phenylacetic acid to β-phenylethanol. LAH (150 mg, 4 mmol) was weighed into a 50-mL three-necked flask. About 4 mL of dry ether was added to the dropping funnel. The flask was cooled with an ice bath. The ether was added to the flask. The 4-[(trimethylsilyl)methyl]benzoic acid was weighed into a flask (401mg, 1.8 mmol) and dissolved in about 8 mL of dry ether. The acid solution was transferred to the dropping funnel. The acidic solution was added dropwise to the LAH mixture. After the addition was complete, the reaction mixture was heated to reflux for 15 min. The flask was cooled with an ice-water bath. One milliliter of water was added dropwise to neutralize the remaining LAH. Three milliliters of 10% H_2SO_4 was added to the reaction mixture. The ether layer was separated, washed with water, and then dried with anhydrous $MgSO_4$. The ether was removed under reduced pressure to yield 335mg of the desired alcohol. (1.7 mmol, 94% yield). ^{1}H NMR (400 MHz, CD_3CN) δ 7.191 and 7.009 (AA'BB'q, *J*=7.6Hz), 4.507 (s), 3.320 (bs),2.107 (s), 0.001 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 and 6.97 (AA'BB'q, *J*=8Hz, 4H), 4.61 (s, 2H), 2.06 (s, 2H), 1.56 (bs, 1H), -0.03 (s, 9H).[lit[25] ^{1}H NMR ($CDCl_3$) δ 7.22 and 7.00 (ABq, *J*=8.0Hz, 4H, arom), 4.6 (s, 2H, CH_2), 2.12 (s, 2H, CH_2), 0.02 (s, 9H, $SiMe_3$)]; ^{13}C NMR (100 MHz, CD_3CN) δ 140.3, 138.4, 128.8, 127.8, 64.7, 26.9, -1.8. Anal. Calcd for $C_{11}H_{18}OSi$: C, 67.98; H, 9.34. Found: C, 68.14; H, 9.47.

4-[(Trimethylsilyl)methyl]benzaldehyde was prepared from 4-[(trimethylsilyl)methyl]benzyl alcohol with a procedure similar to the procedure outlined by Corey and Suggs.[33] To a 100-mL roumd-bottomed flask was added 1.307 g of PCC (6 mmol) and 8 mL of dry

CH_2Cl_2. The reaction mixture was place beneath a nitrogen atomosphere. A solution of 0.763 g of 4-[(trimethylsilyl)methyl]benzyl alcohol (3.93 mmol) in 4 mL of CH_2Cl_2 was added to the PCC solution. After the mixture was stirred for 2 h, 20 mL of ether was added to the flask. The liquid was removed from the flask. The flask and the solid were rinsed twice with additional ether. The ether solution was filtered through diatomaous earth. The solvent was removed under reduced pressures to yield 0.726 g of an oil (3.76 mmol, 96% yield) ^{1}H NMR (400 MHz, CD_3CN) δ 9.889 (s), 7.727 and 7.198 (AA'BB'q, *J*=8Hz), 2.238 (s), -0.017 (s). ^{1}H NMR in $CDCl_3$ data are in good accord with published values.[34] ^{13}C NMR (100 MHz, CD_3CN) δ 192.9, 150.2, 134.1, 130.5, 129.5, 28.4, -2.0.

Isophorone Oxime was prepared from isophorone as described by Beringer and Ugelow.[35] To a 250-mL round-bottomed flask was added 30.0 mL of isophone (27.7 g, 0.200 mol), 17.0 g of hydroxylamine hydrochloride (0.24 mol), 17 mL of dry pyridine and 20 ml of methanol. The mixture was stirred until homogeneous and then stirred for 24 h. The reaction solution was then slowly poured into a beaker with approximately 50 mL of water, which was being stirred. About 50 g of crushed ice was added to the mixture. After the ice had melted, the precipitate was filtered and rinsed with approximately 150 mL of water. The wet solid was dissolved in ether and then placed in a separatory funnel. The water layer was removed and back extracted with additional ether. The ether layers were combined and dried with anhydrous sodium sulfate. The dried ether solution was placed into a 500-mL round-bottomed flask and the ether was remove under reduce pressures. A mixed of the *E* and *Z* isomers of isophone oxime (1.93 : 1) was with a final mass of 29.970 g (0.196, 98%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.601 (s, 1H), 2.103 (s, 2H), 1.996 (s, 2H) 1.855 (s, 3H), 0.960 (s, 6H). ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.906 (s, 1H), 2.363 (s, 2H), 1.945 (s, 2H) 1.807 (s, 3H), 0.971 (s, 6H). [lit[36] ^{1}H NMR (300 MHz, $CDCl_3$) *E* isomer δ 5.92, 2.38, 1.94, 1.81, 0.98; *Z* isomer δ 6.63, 2.09, 1.98, 1.85, 0.97]

3',4',5'-Trimethylacetanilide was prepared from isophorone oxime as described by

Beringer and Ugelow.[35] A chilled solution of 29.554 g of isophorone oxime (0.192 mol) in 100 mL of acetic anhydride and 16.1 mL of pyridine (0.20 mol) was prepared in a 500-mL round-bottomed flask. A solution of 14.2 mL of acetyl chloride (0.2 mol) in 10 mL of acetic anhydride was added to the flask and resulted in the formation of a solid. A condenser was added to the flask. A water bath was placed around the flask and the mixture was stirred. The water bath was heated to approximately 65°C and held there until the mixture became homogeneous. The temperature of the water bath was then increased until the water boiled. As the reaction progressed the mixture changed from a light orange to a nearly black. After 1 h at 100°C, the hot water bath was removed and 125 mL of water was slowly added to the reaction mixture though the condenser. The dark reaction mixture was transfered to an Erlenmeyer flask and the round-bottomed flask was rinsed with an additional 50 mL of water, which was added to the Erlenmeyer flask. At this point some crystals were beginning to form. The flask containing the crude product mixture was place in the refrigerator overnight. The cold mixture was then filtered and then recrystalized from methanol to produce 6.679 g of 3',4',5'-trimethylacetanilide (0.038 mol, 20%). Additional product was obtained by extracting the aqueous mother liquor with ether and then removing the ether under reduced pressures. The product obtain from extraction was a solid suspended in a thick oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.112 (s, 2H), 2.235 (s, 6H), 2.123 (s, 3H) 2.099 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 168.2, 137.0, 134.9, 131.2, 119.3, 24.4, 20.6, 14.9.

3,4,5-Trimethylaniline was prepared from 3',4',5'-trimethylacetanilide as described by Beringer and Ugelow.[35] A mixture of 6.001 g of 3',4',5'-trimethylacetanilide (0.034 mol) in 10 mL of 20% H_2SO_4 was heated to reflux for 2 h. The mixture was allowed to cool to room temperature and then made basic with sodium hydroxide solution. After the mixed was chilled in an ice bath, it was filtered. The product was recrystalized from hexanes to yield 4.243 g of 3,4,5-trimethylaniline (0.031 mol, 91 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.383 (s, 2H), 3.434 (bs), 2.182 (s, 6H) 2.048 (s, 3H); ^{13}C NMR (75.4 MHz, $CDCl_3$) δ 143.5, 137.3,

125.0, 114.7, 20.6, 14.4. [lit[37] ^{1}H NMR (90 MHz, $CDCl_3$) δ 6.4 (s, 2H), 3.5 (s, 2H), 2.2 (s, 6H) 2.15 (s, 3H)].

3,4,5-Trimethylbenzonitrile was prepared by the Sandmeyer reaction from 3,4,5-trimethylaniline with a procedure similar to the procedure outlined by Clarke and Read[38] for the reaction of *o*-toluidine to *o*-tolunitrile. In a 100-mL round-bottomed flask, a cuprous cyanide solution was prepared from cuprous chloride (1.75 g, 17.7 mmol), sodium cyanide (2.2 g, 45 mmol), and 12 mL of water. The solution was chilled in an ice-water bath then 10 mL of toluene was added to the flask. While the cuprous cyanide solution was cooling, to another 100-mL round-bottomed flask was added 1.85 g of 3,4,5-trimethylaniline (13.6 mmol), 18 mL of water, and 3.5 mL of concentrated hydrochloric acid. The mixture was chilled in an ice-water bath until its temperature was below 5°C. A solution of sodium nitrite (960 mg, 13.9 mmol) in 3 mL of water was added slowly over 10 min to the stirred mixture of 3,4,5-trimethylaniline hydrochloride. The mixture was tested with starch-iodide paper to ensure that enough sodium nitrite was added. Solid carbonate was slowly added to the mixture until neutral with litmus paper. The cold diazonium solution was slowly added to the rapidly stirred cuprous cyanide solution. The mixture was stirred for an additional 30 min while maintaining the temperature below 5°C. The stirring was continued as the mixture was allowed to slowly warm to room temperatures over a period of 5 h. The mixture was warmed with a 50°C-water bath for 20 min. The mixture was allowed to cool to room temperature and then placed into a separatory funnel. The organic layer was separated, washed with water, and then dried with sodium sulfate. The toluene was removed under reduced pressures. The mass of the crude oil product was 1.267 g (8.72 mmol, 66 %). IR (neat) 2930, 2210,1610,1560 cm^{-1}.

3,4,5-Trimethylbenzoic Acid was prepared by acid-catalyzed hydrolysis of 3,4,5-trimethylbenzonitrile following a procedure similar to that outlined by Clarke and Taylor[39] for the acid-catalyzed hydrolysis of *o*-tolunitrile acid to *o*-toluic acid. In a 10-mL

round-bottomed flask, equipped with a stir bar and condenser, are placed 1 mL of water and 3 mL of concentrated sulfuric acid. The 75% sulfuric acid solution was heated to 150°C by an oil bath. The oily 3,4,5-trimethylbenzonitrile (1.243 g, 8.56 mmol) from above was slowly added dropwise into the reaction mixture through the condenser. The temperature of the oil bath was raised to 190°C and stirring was continued for 150 min. The oil bath was then removed and the mixture was allowed to cool. The mixture was then poured into a beaker containing ice chips. The crude product was filtered and then dissolved in 1M sodium hydroxide solution. The aqueous layer was washed with hexanes and then acidified with dilute hydrochloric acid. The resulting solid was filtered, dried, and recrystallized (methanol-water) to yield 858 mg of 3,4,5-trimethylbenzoic acid (5.23 mmol, 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.726 (s, 2H), 2.319 (s, 6H), 2.218 (s, 3H) [lit[37] ^{1}H NMR (90 MHz, $CDCl_3$) δ 9.2 (s, 1H), 7.6 (s, 2H), 2.33 (s, 6H), 2.25 (s, 3H)]; ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6, 142.0, 136.7, 129.2, 126.0, 20.6, 16.0. [lit[42] ^{1}H NMR (MHz, $CDCl_3$) δ.]

3,5-Dimethyl-4-[(trimethylsilyl)methyl]benzoic Acid was prepared from 3,4,5-trimethylbenzoic acid as described by Stern and Swenton.[23] A solution of 3,4,5-trimethylbenzoic acid (330 mg, 2.01 mmol) in 14 mL of dry THF and 0.70 mL of HMPA was prepared in a 50-mL round-bottomed flask then chilled to –78°C in a IPA/CO_2 bath. *tert*-Butyllithium (2.4 mL, 1.7 M in pentane, 4.08 mmol) was slowly added to the reaction mixture and then the mixture was stirred for 2 min. Freshly distilled chlorotrimethylsilane (0.5 mL, 3.94 mmol) was rapidly added. The mixture was allowed to warm to room temperature and then stirred for 2 h. The THF was removed under reduced pressures and then worked up in the same manor as that described above for 4-[(trimethylsilyl)methyl]benzoic acid to yield 284 mg of 3,5-dimethyl-4-[(trimethylsilyl)methyl]benzoic acid (1.2 mmol, 60% yield) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.707 (s, 2H), 2.266 (s, 6H), 2.233 (s, 2H) 0.015 (s, 9H) [lit[23] ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.74 (s, 2H), 2.29 (s, 6H), 2.26 (s, 2H) 0.04 (s, 9H)]

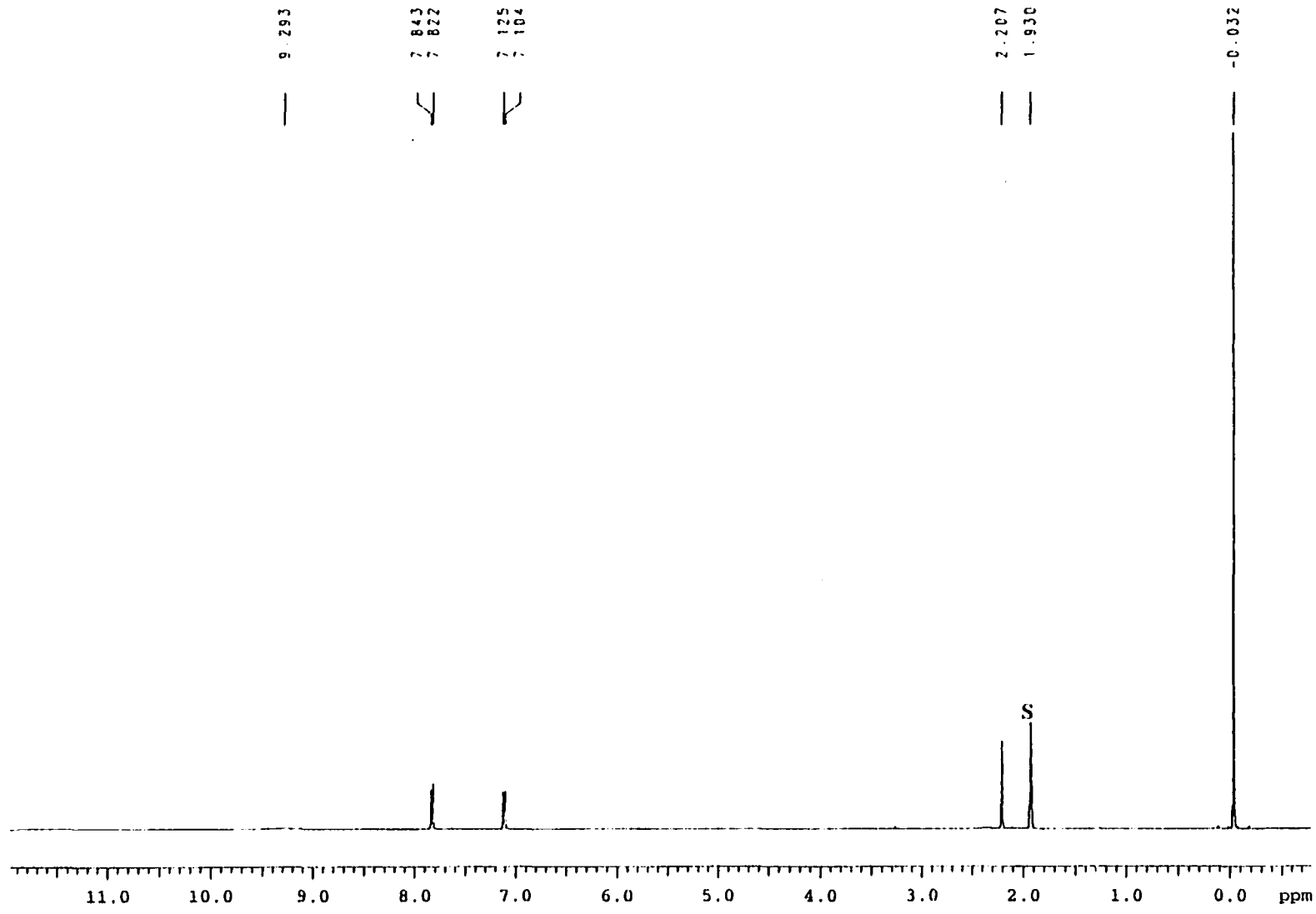


Figure A-1. ^{1}H NMR spectrum (400 MHz, CD_3CN) of 4-[(trimethylsilyl)methyl]benzoic acid. (S: acetonitrile)

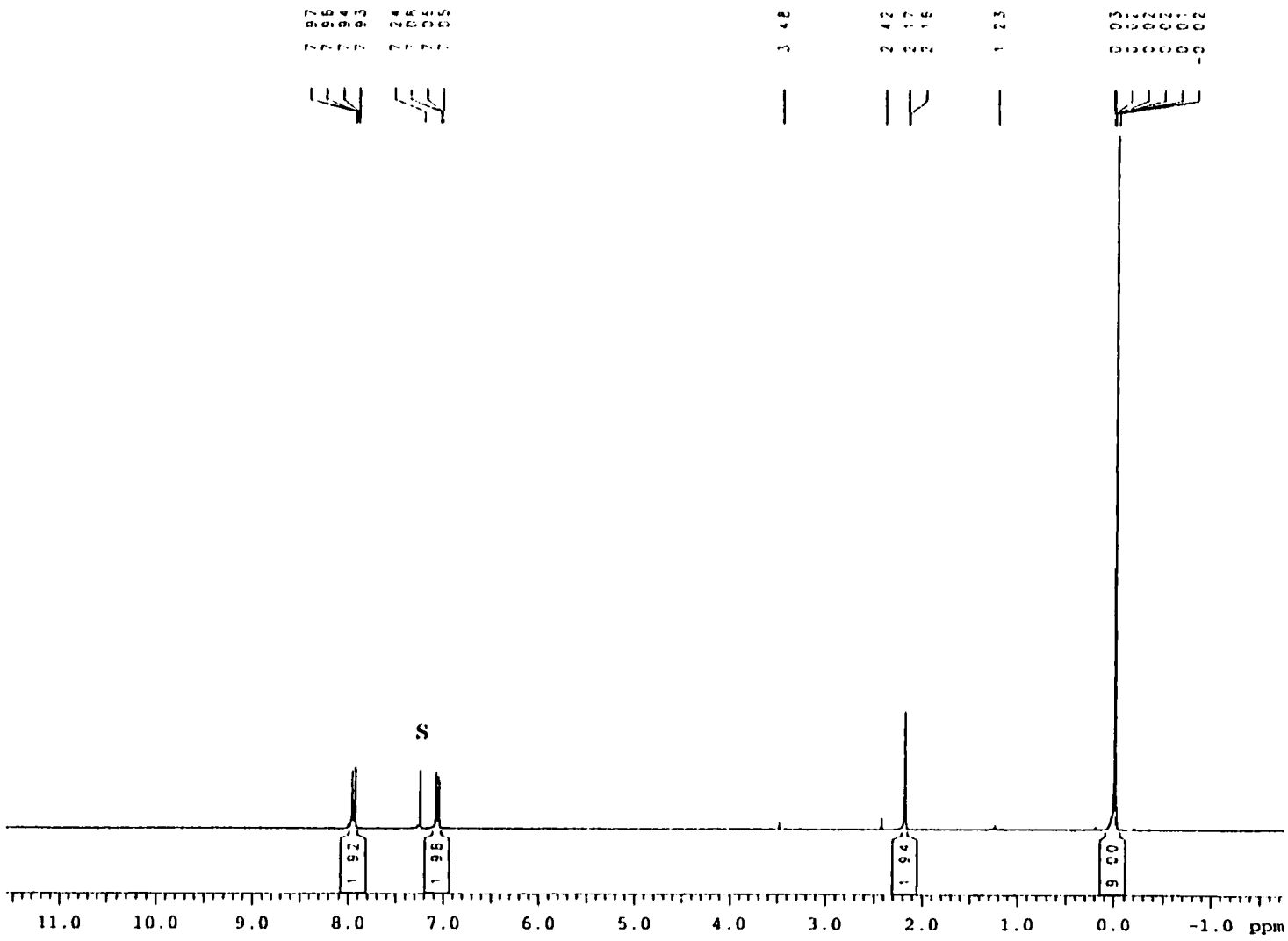


Figure A-2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-[(trimethylsilyl)methyl]benzoic acid. (S: chloroform)

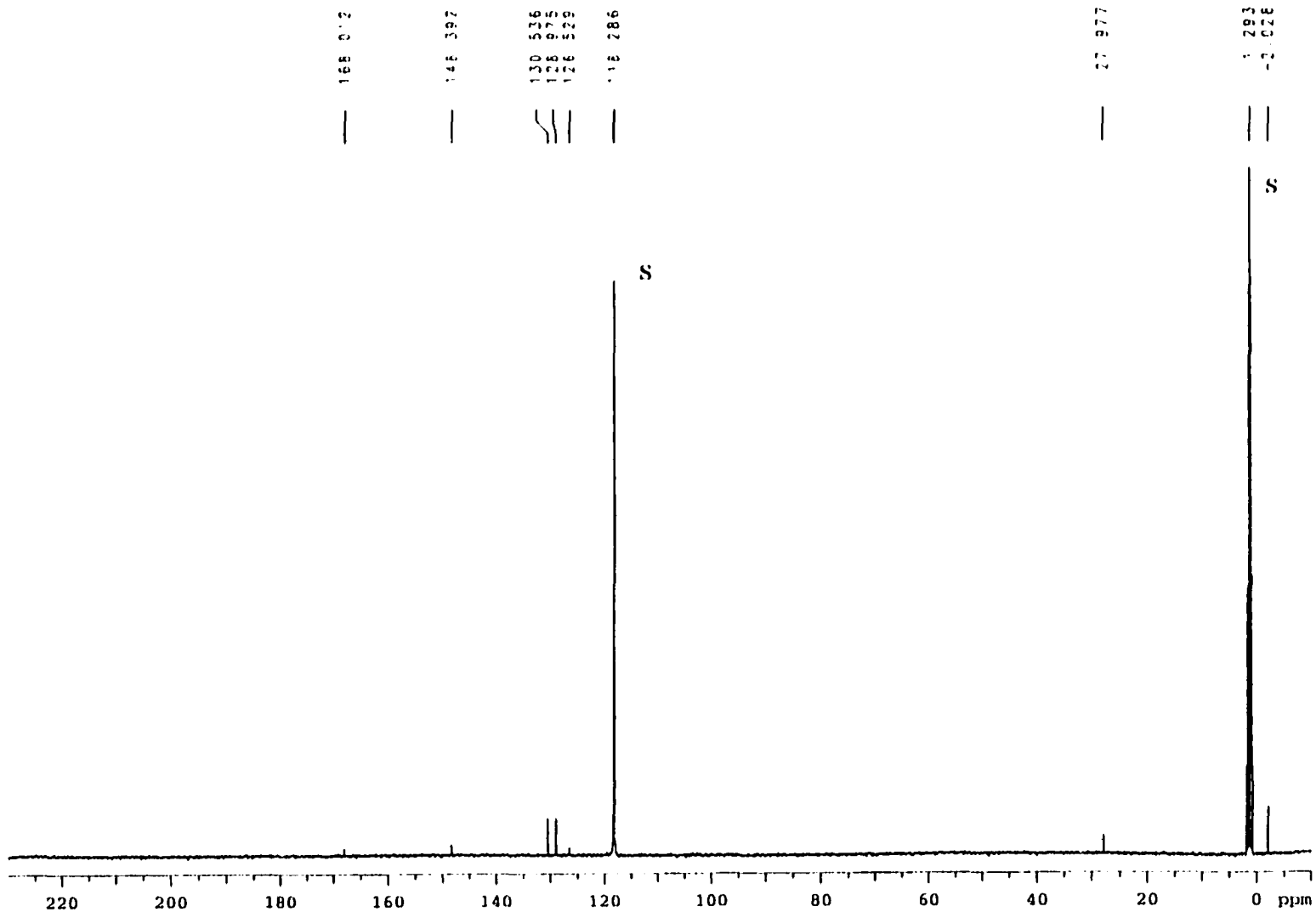


Figure A-3. ^{13}C NMR spectrum (100 MHz, CD_3CN) of 4-[(trimethylsilyl)methyl]benzoic acid. (S: acetonitrile)

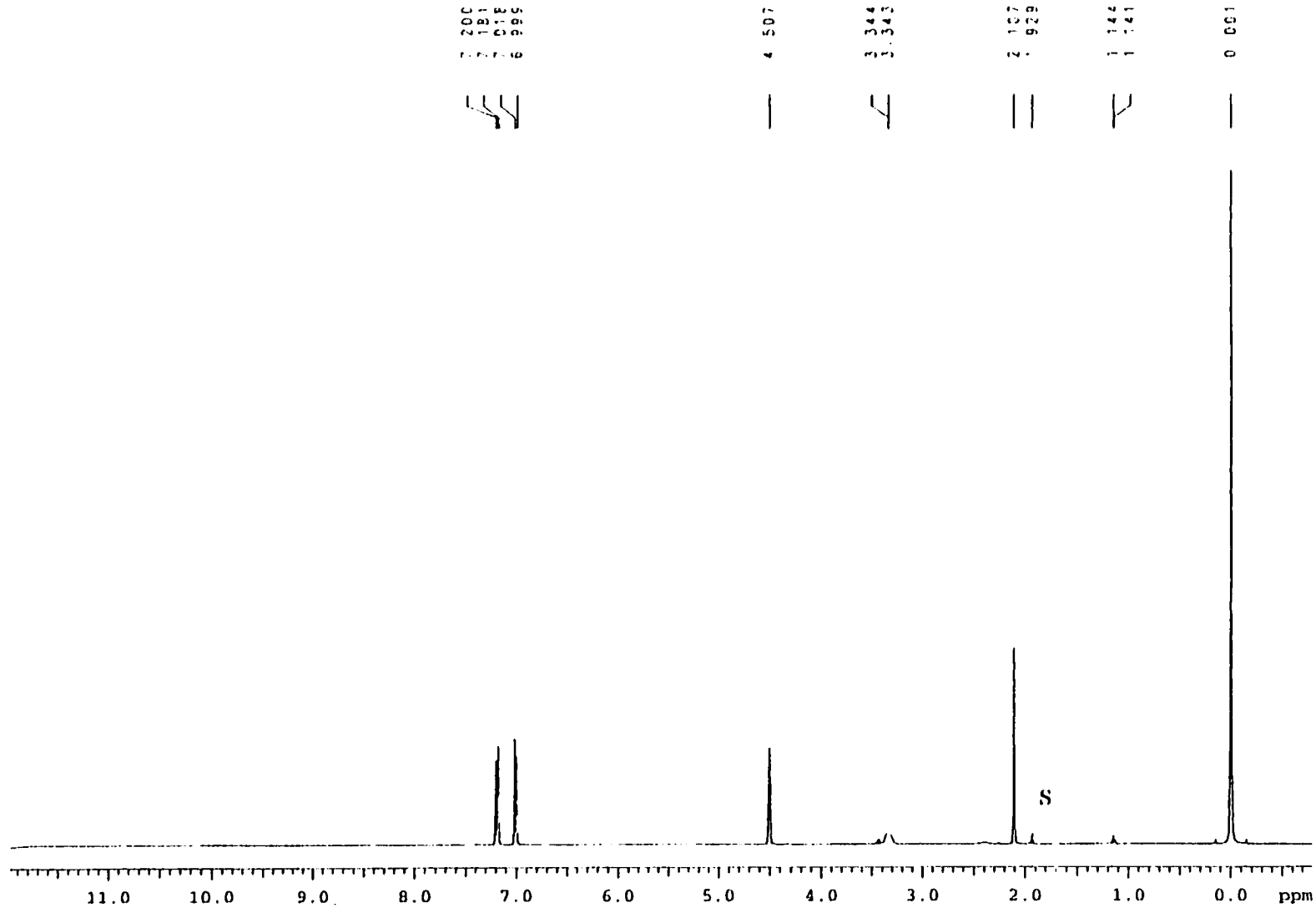


Figure A-4. ^{1}H NMR spectrum (400 MHz, CD_3CN) of 4-[(trimethylsilyl)methyl]benzyl alcohol. (S: acetonitrile)

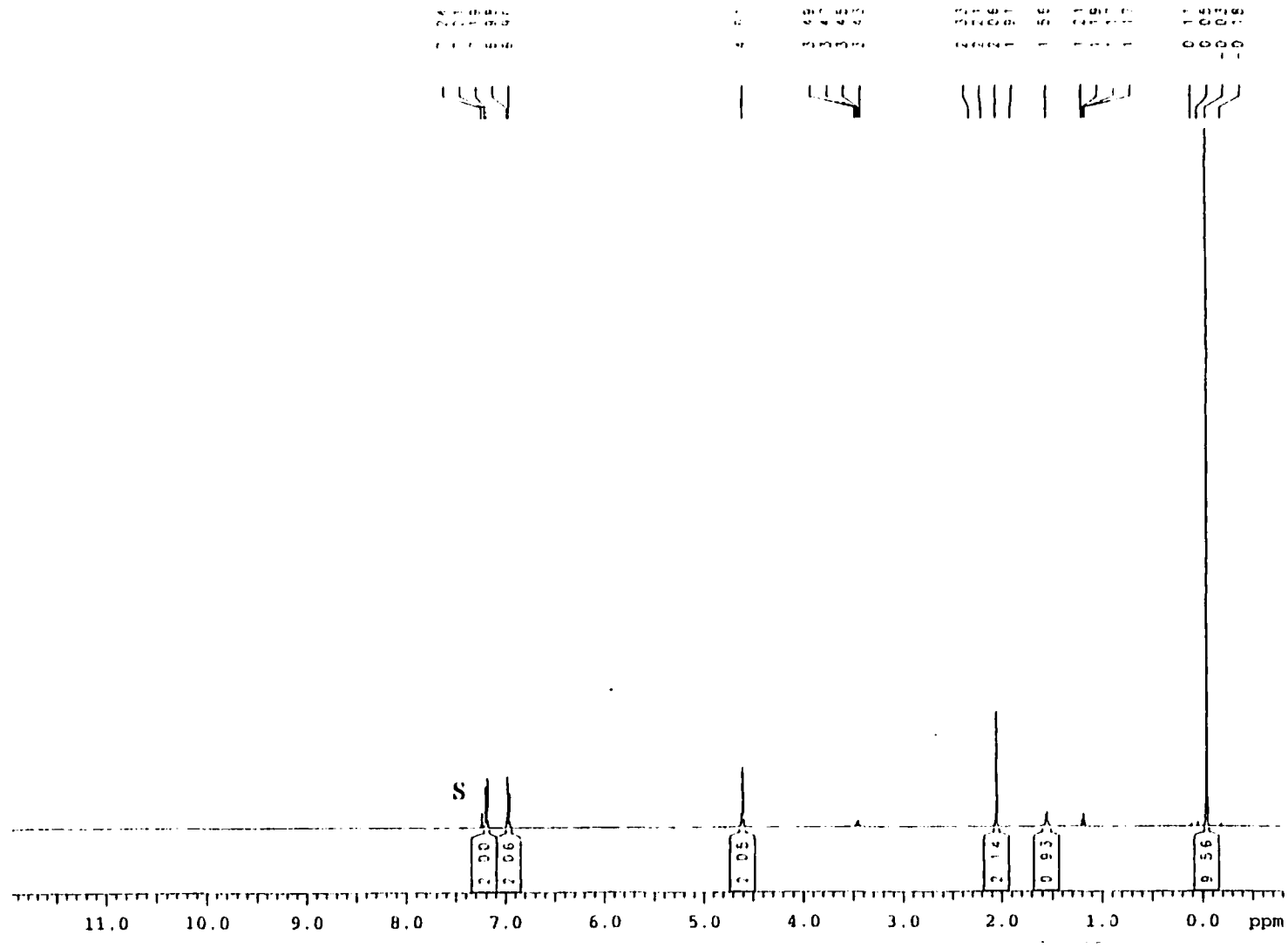


Figure A-5. ^1H NMR spectrum (400 MHz, $CDCl_3$) of 4-[(trimethylsilyl)methyl]benzyl alcohol. (S: chloroform)

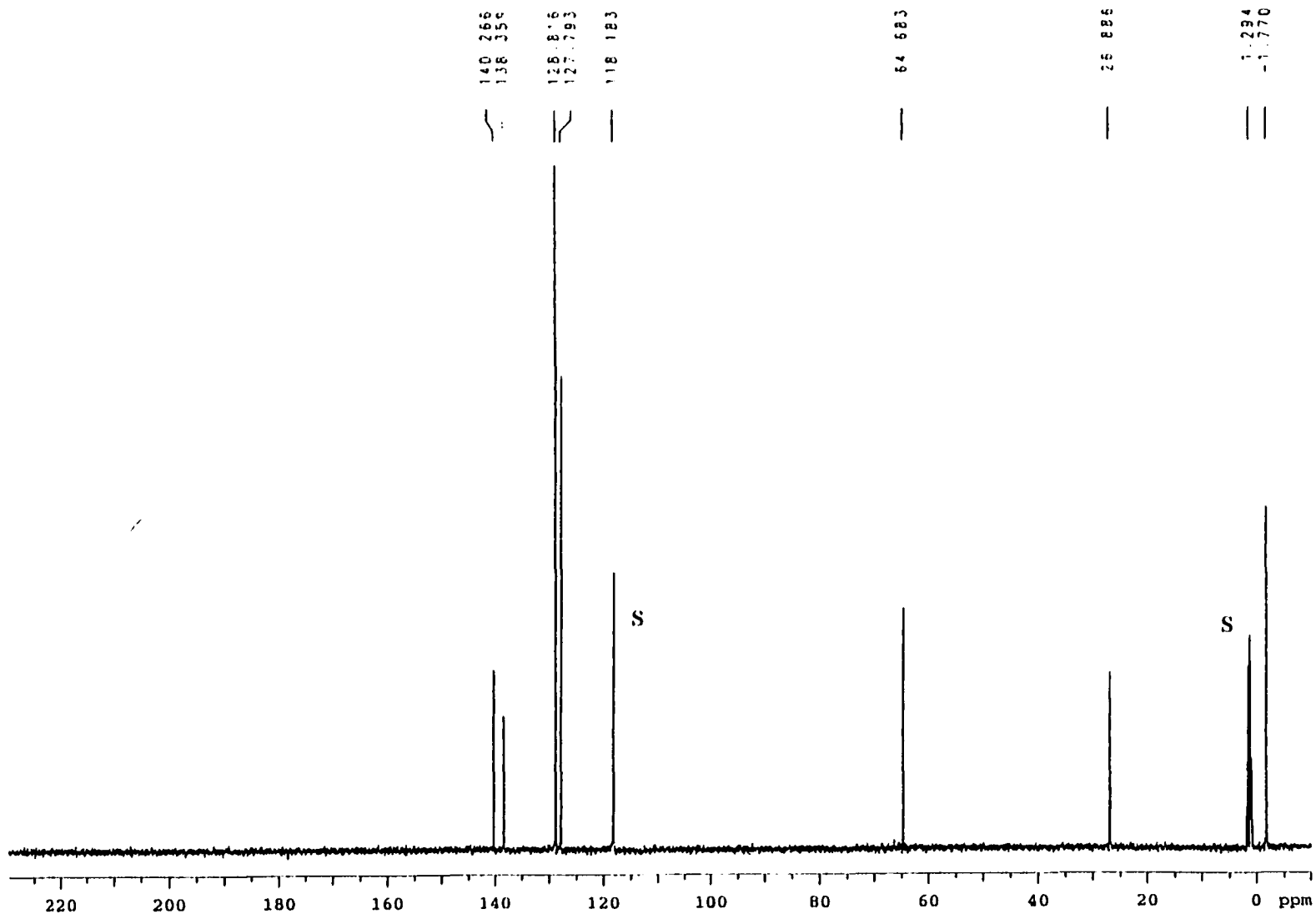


Figure A-6. ^{13}C NMR spectrum (100 MHz, CD_3CN) of 4-[(trimethylsilyl)methyl]benzyl alcohol. (S: acetonitrile)

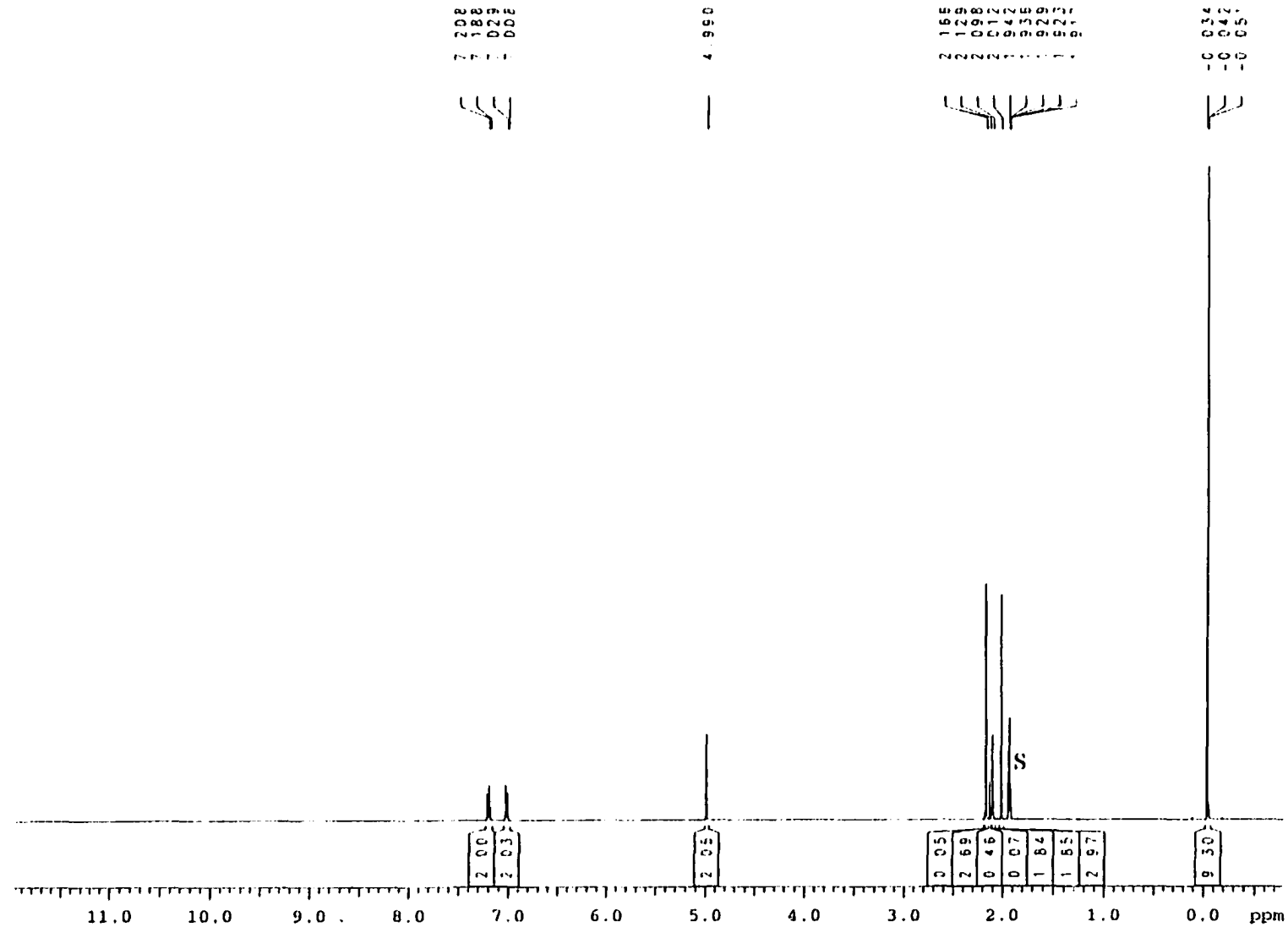


Figure A-7. ^{1}H NMR spectrum (400 MHz, CD_3CN) of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**13**). (S: acetonitrile)

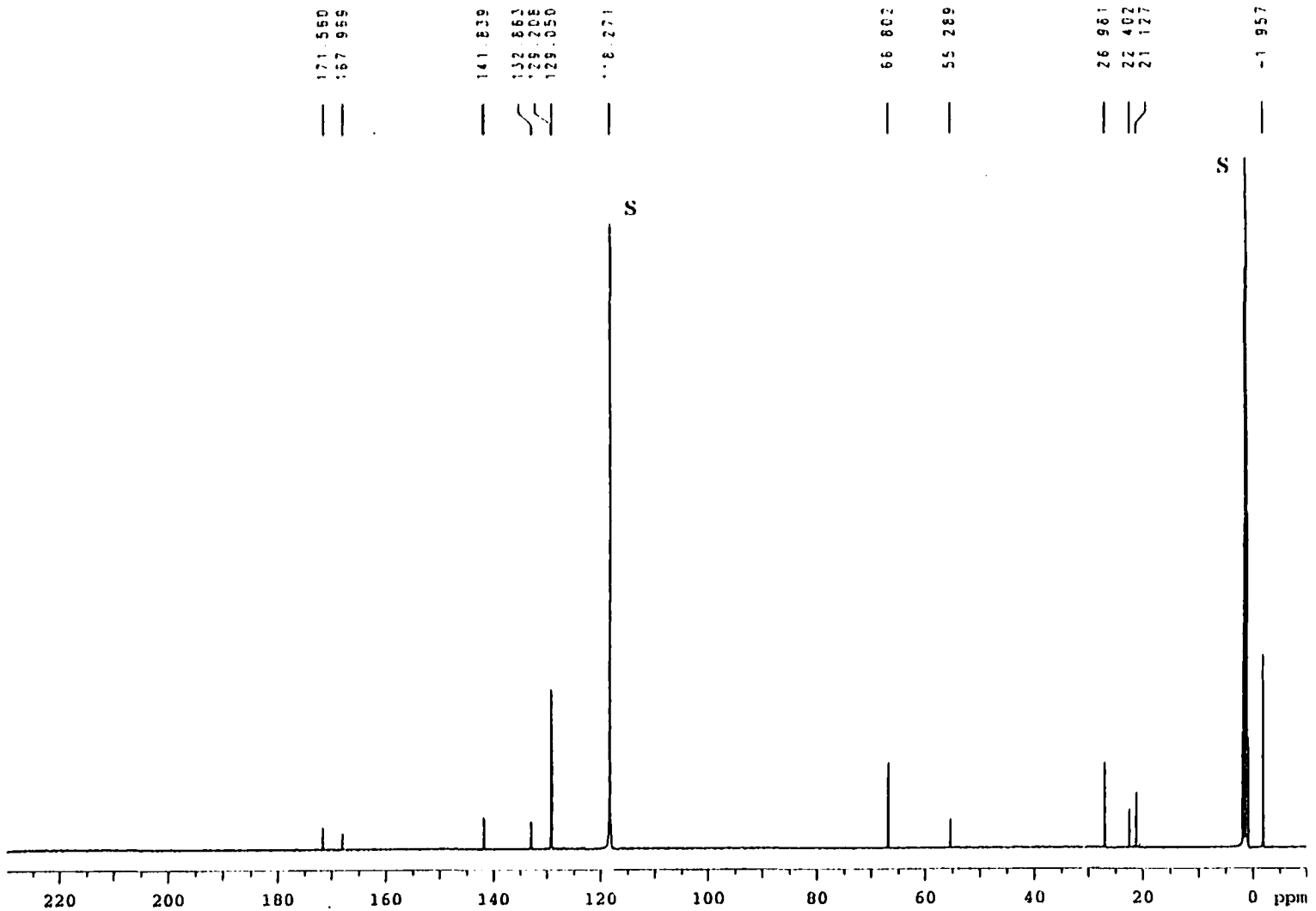


Figure A-8. ^{13}C NMR spectrum (100 MHz, CD_3CN) of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**13**). (S: acetonitrile)

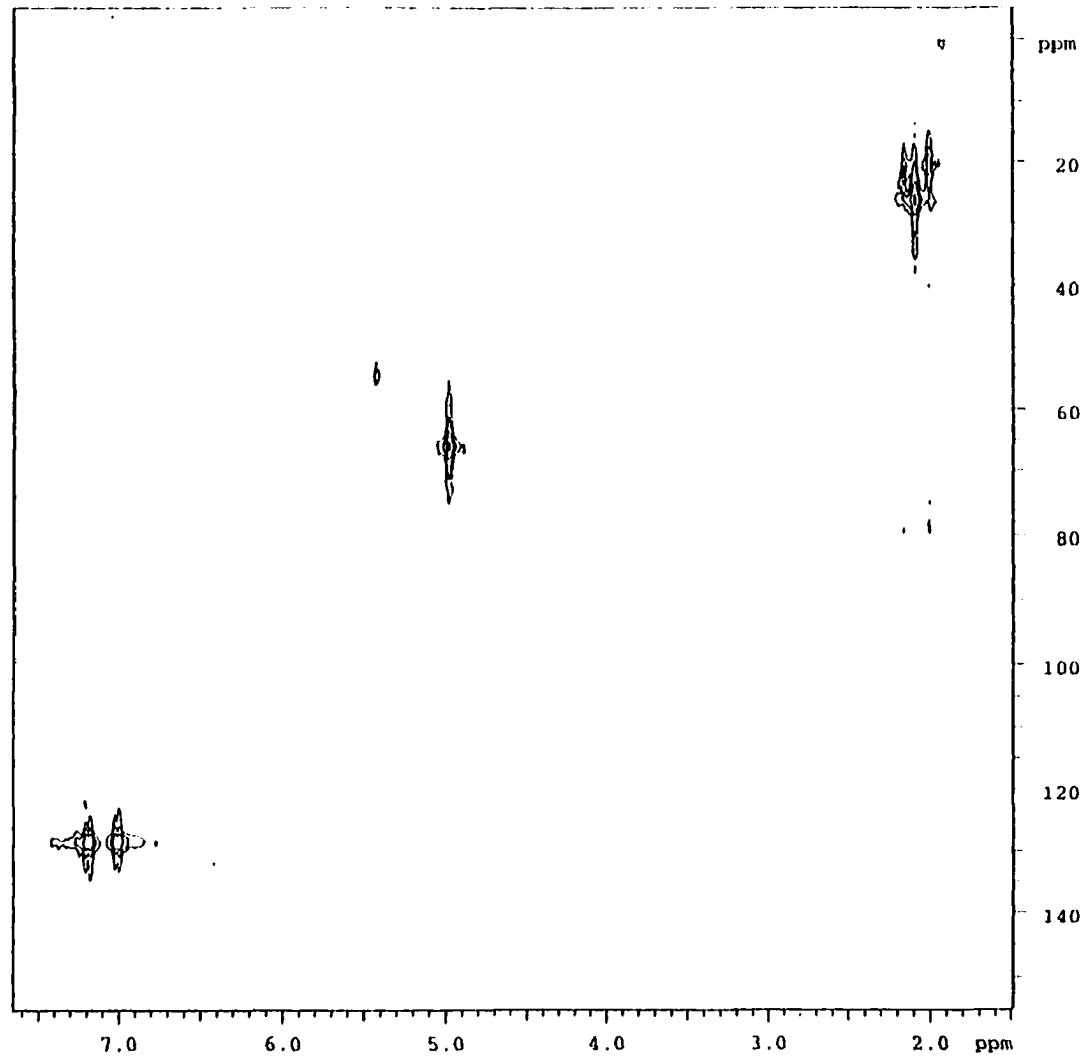


Figure A-9. HETCOR spectrum (CD_3CN) of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**13**).

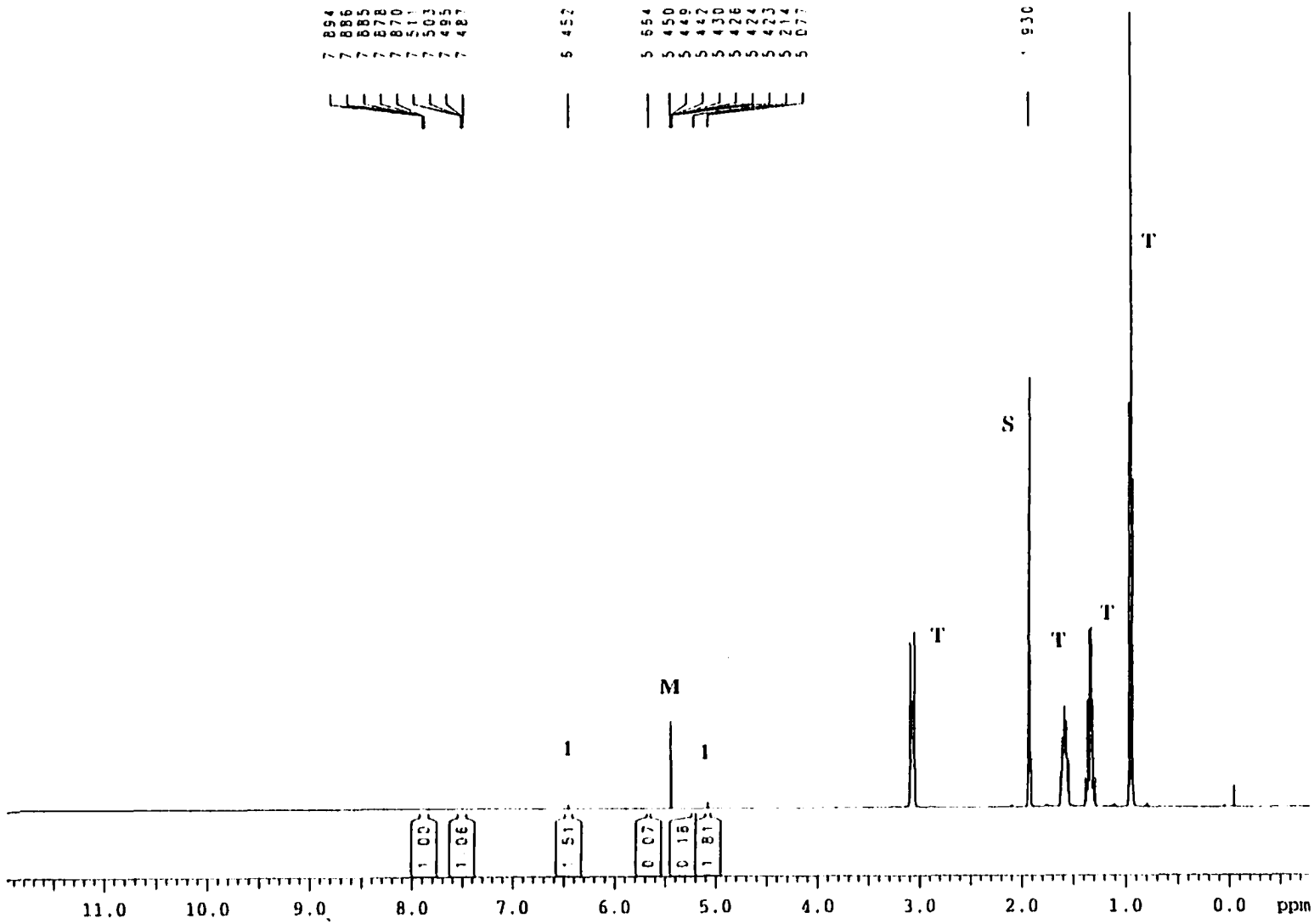


Figure A-10. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (**1**) in degassed CD_3CN. (**M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

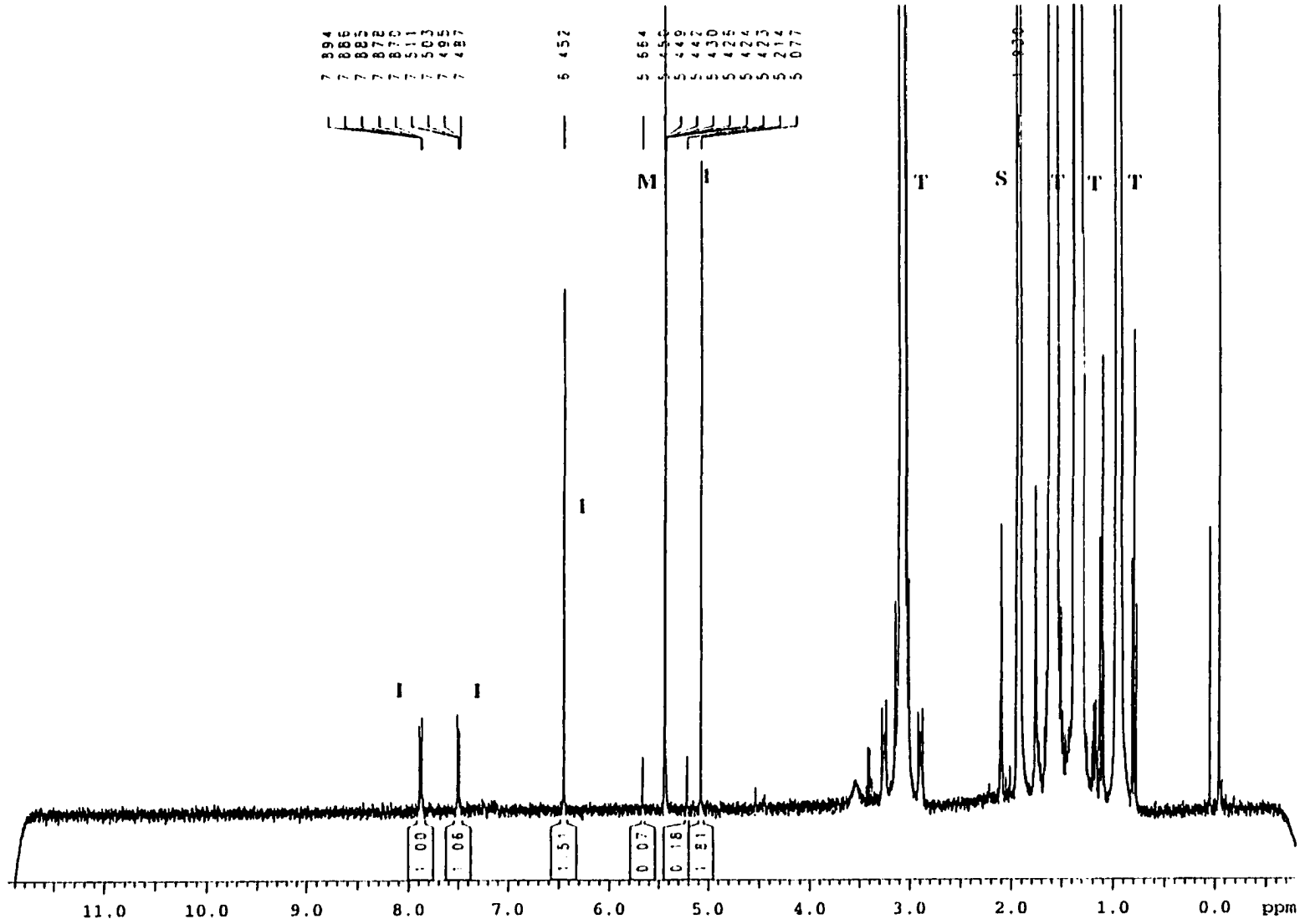


Figure A-11. Enlargement of Figure A-10 from 12 to -0.7 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (**1**) in degassed CD_3CN. (**I**: internal standard, naphthalene **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

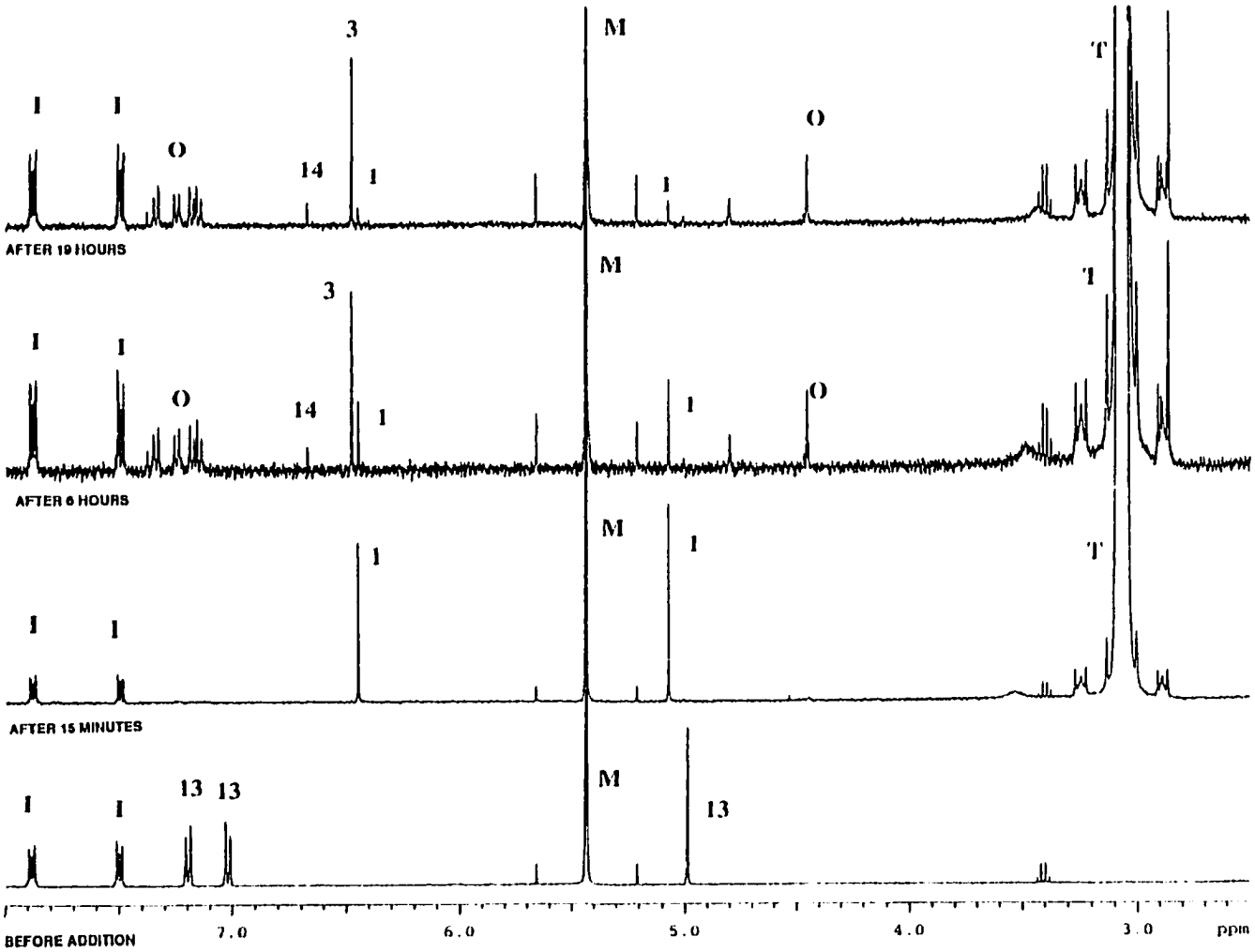


Figure A-12. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-xylylene (**1**) in degassed CD_3CN. (**1**, **3**, **13** and **14** are compound numbers given in the text, **I**: internal standard, naphthalene **M**: methylene chloride, **O**: oligomers, **T**: TBAF)

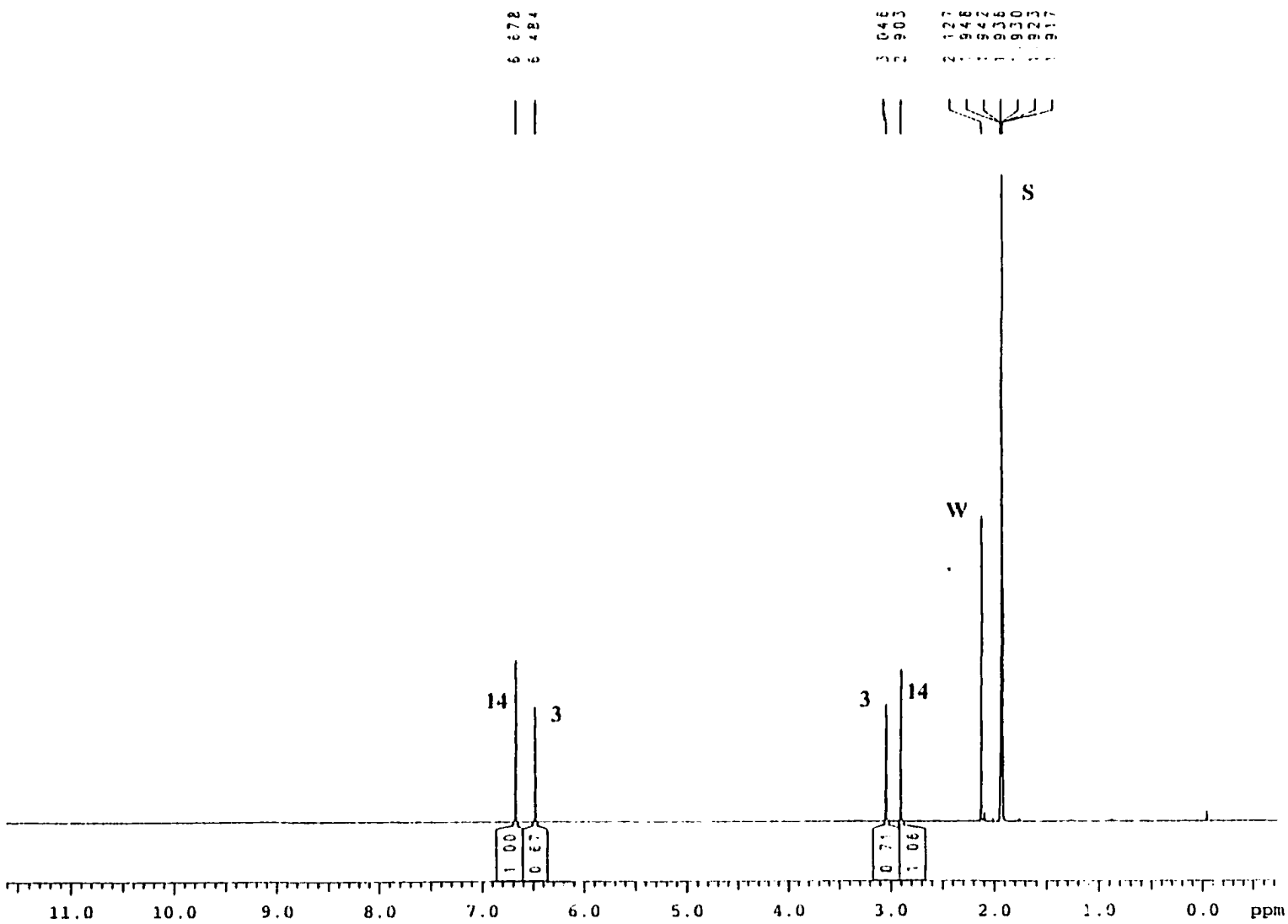


Figure A-13. ^{1}H NMR spectrum (400 MHz, CD_3CN) of [2.2]paracyclophane (**3**) and [2.2.2]paracyclophane (**14**). (S: acetonitrile, W: water)

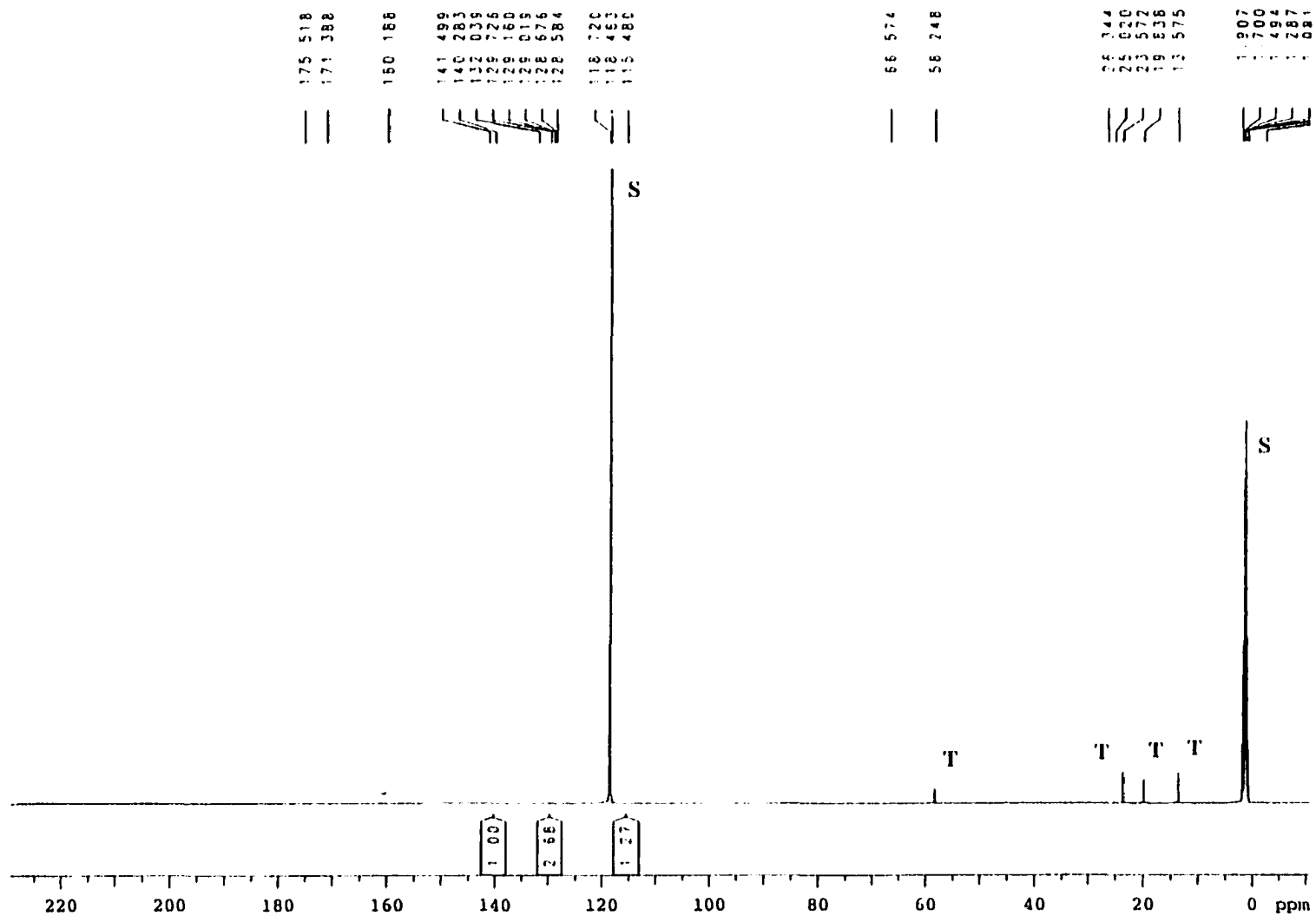


Figure A-14. ^{13}C NMR spectrum (100 MHz, CD_3CN) of *p*-xylylene (**1**) with $Cr(acac)_3$. (S: acetonitrile, T: TBAF)

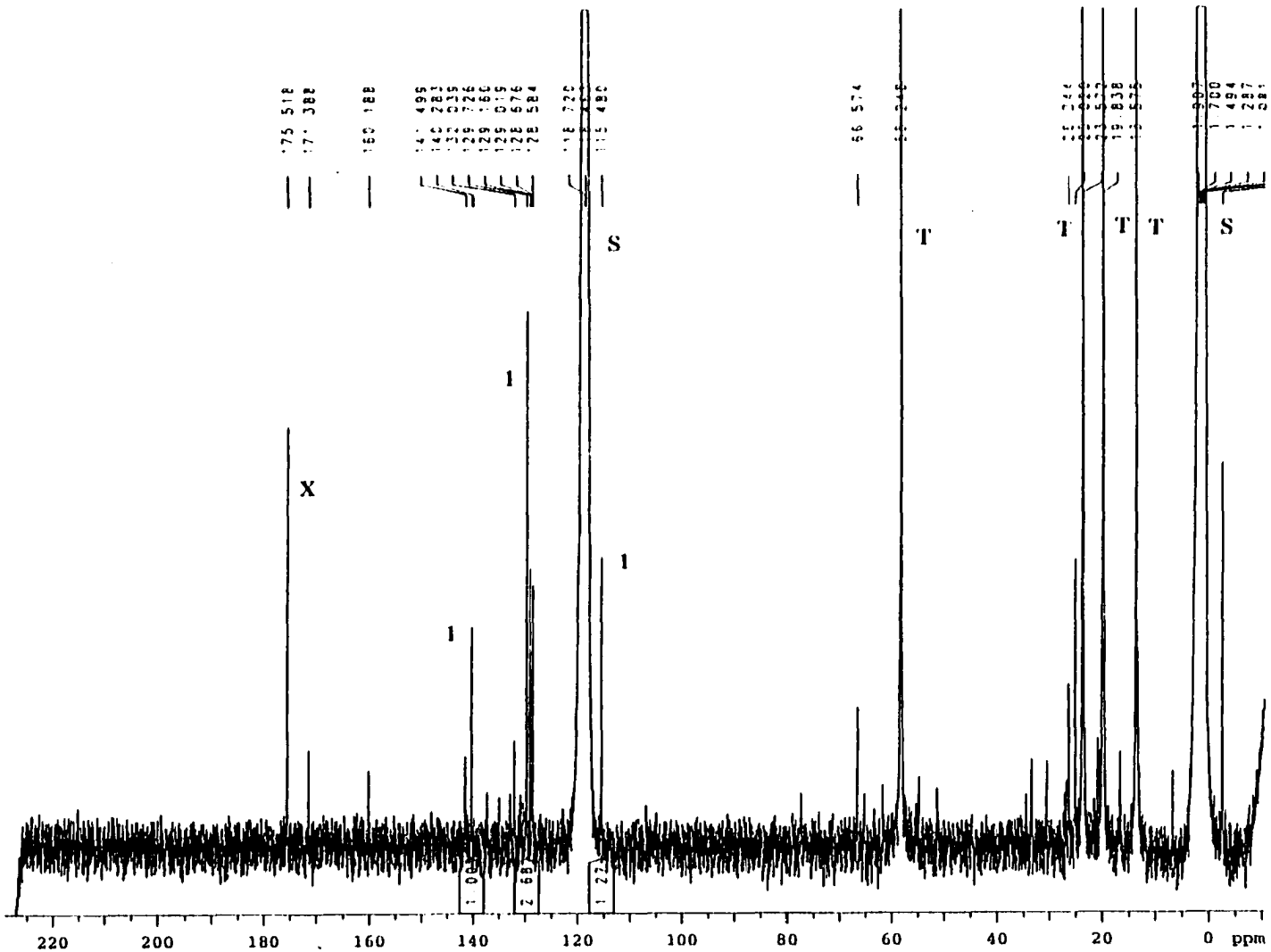


Figure A-15. Enlargement of Figure A-14 from 230 to -10 ppm. ^{13}C NMR spectrum (100 MHz, CD_3CN) of *p*-xylylene (1) with $Cr(acac)_3$. (**S**: acetonitrile, **T**: TBAF, **X**: acetate)

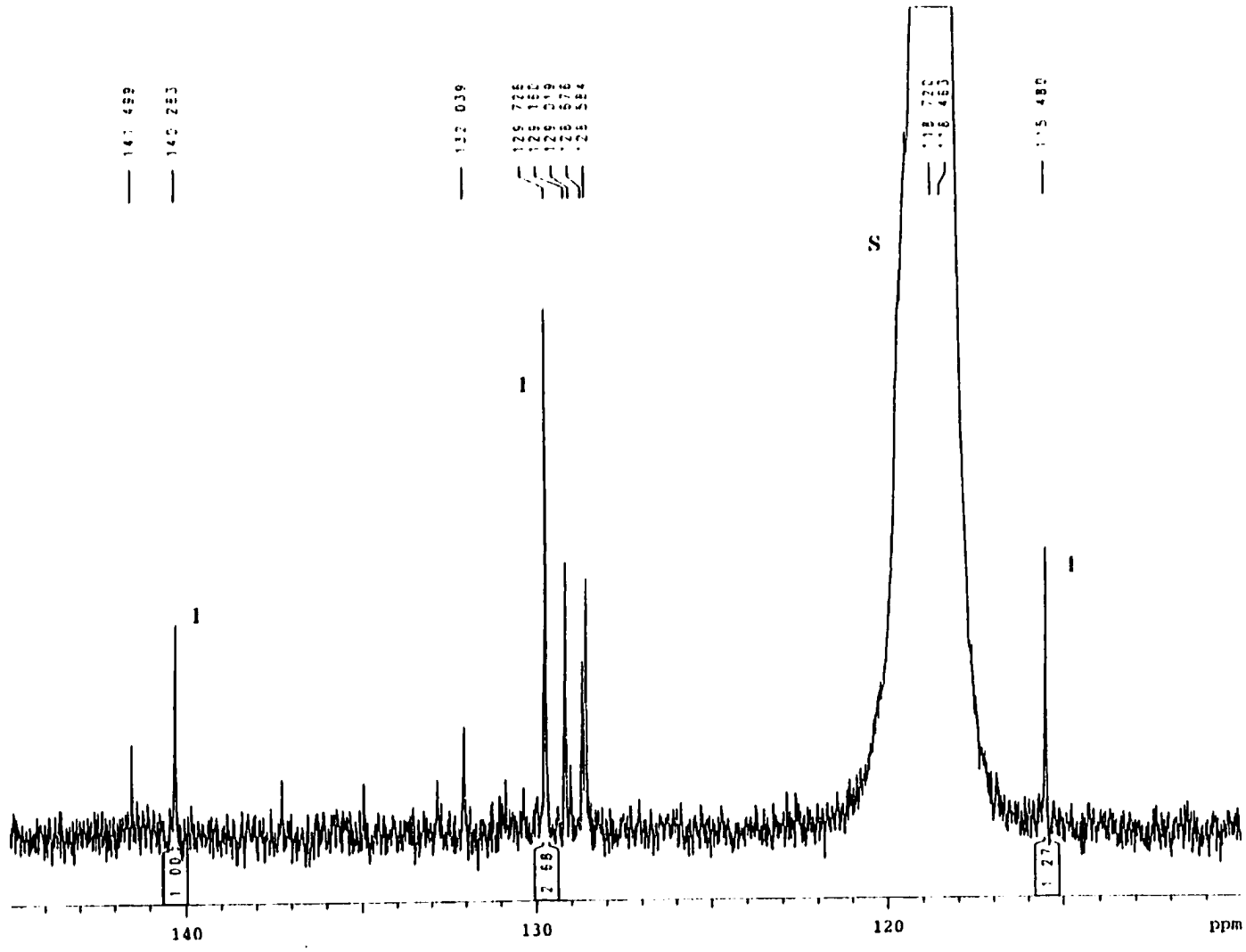


Figure A-16. Enlargement of Figure A-14 from 145–110 ppm. ^{13}C NMR spectrum (100 MHz, CD_3CN) of *p*-xylylene (**1**) with $Cr(acac)_3$. (**S**: acetonitrile)

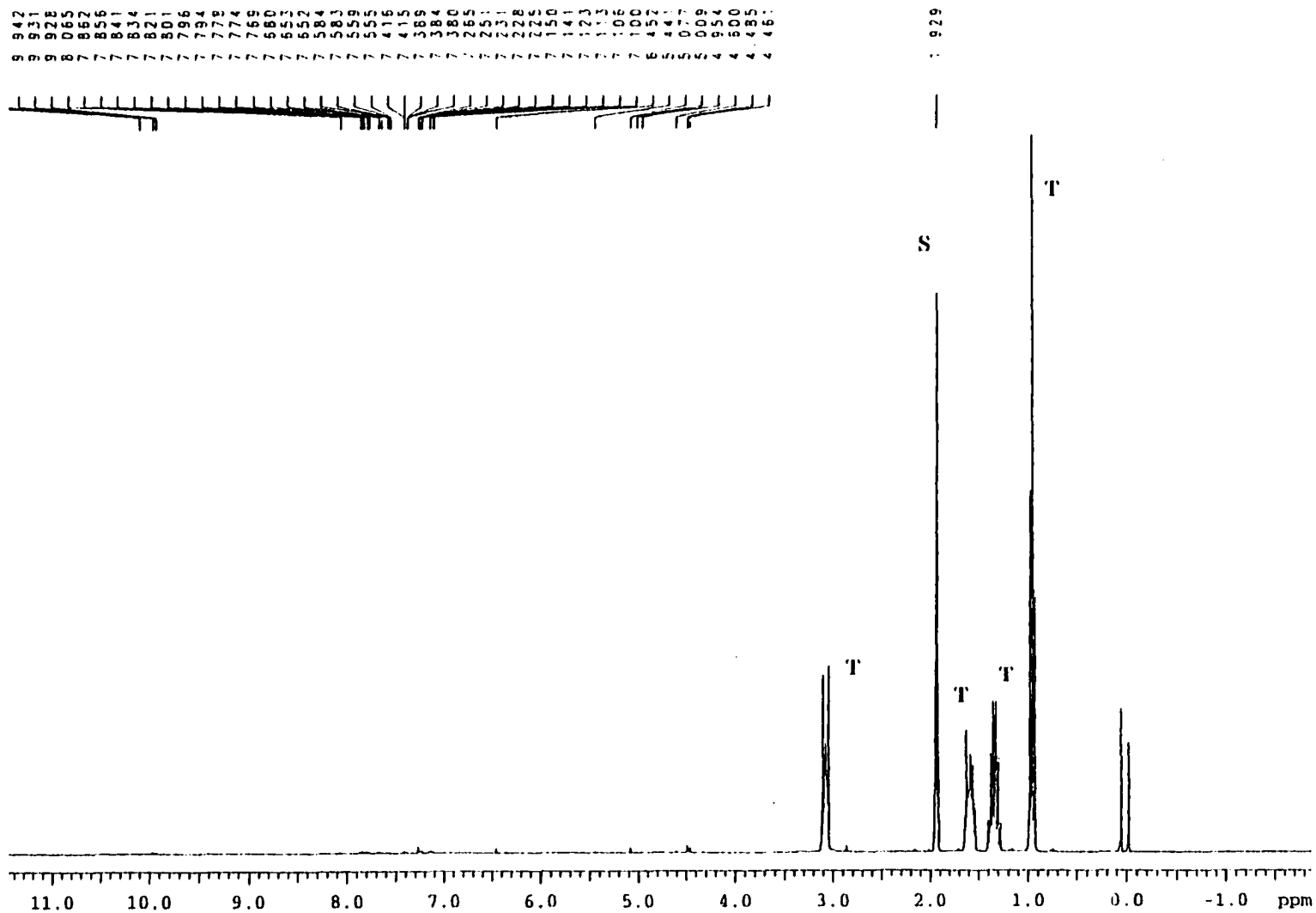


Figure A-17. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (**1**) and oligomerization products in oxygenated CD_3CN. (**S**: acetonitrile, **T**: TBAF)

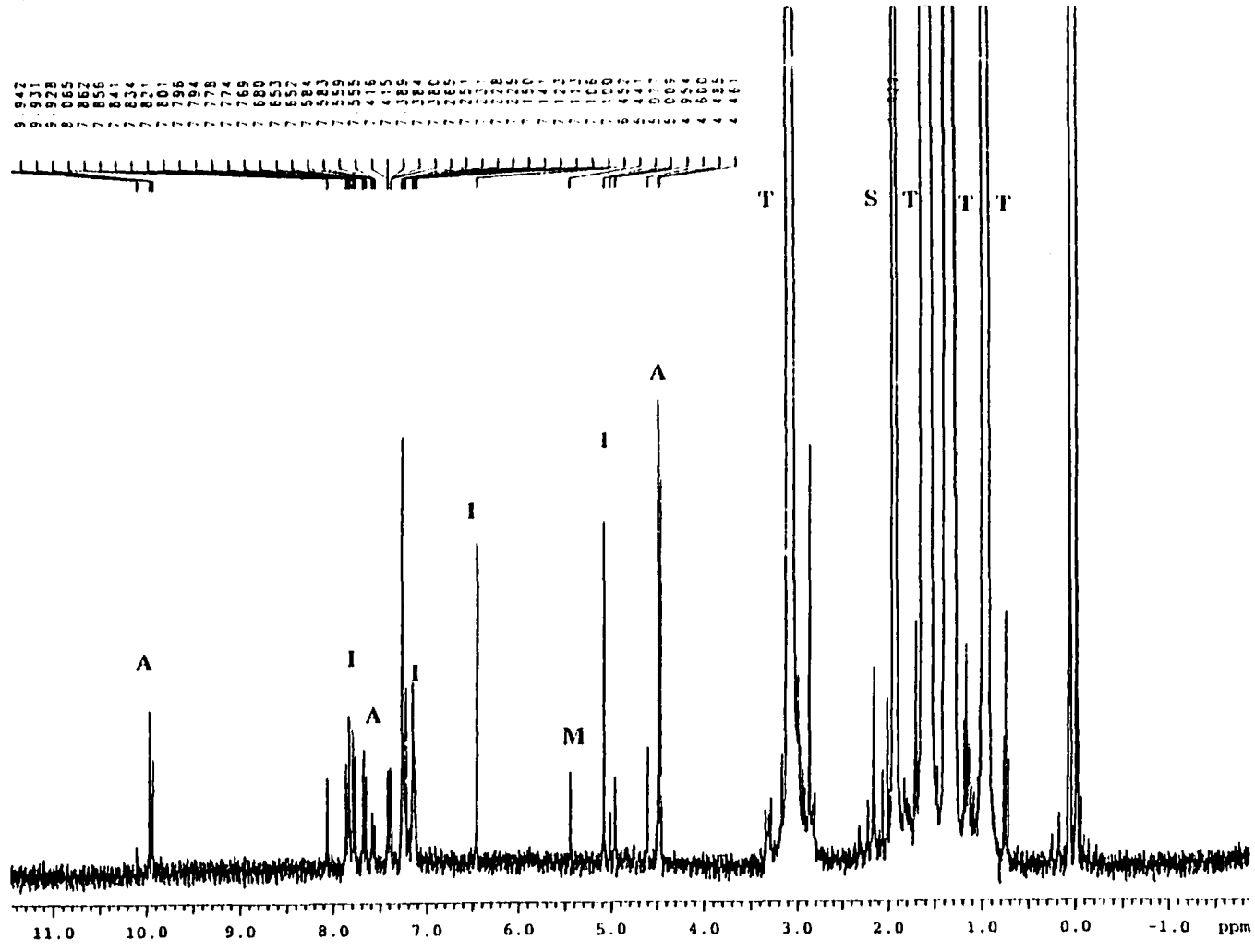


Figure A-18. Enlargement of Figure A-17 from 11.5 to -1.8 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (**1**) and oligomerization products in oxygenated CD_3CN. (**A**: oxygen adducts, **I**: internal standard, naphthalene, **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

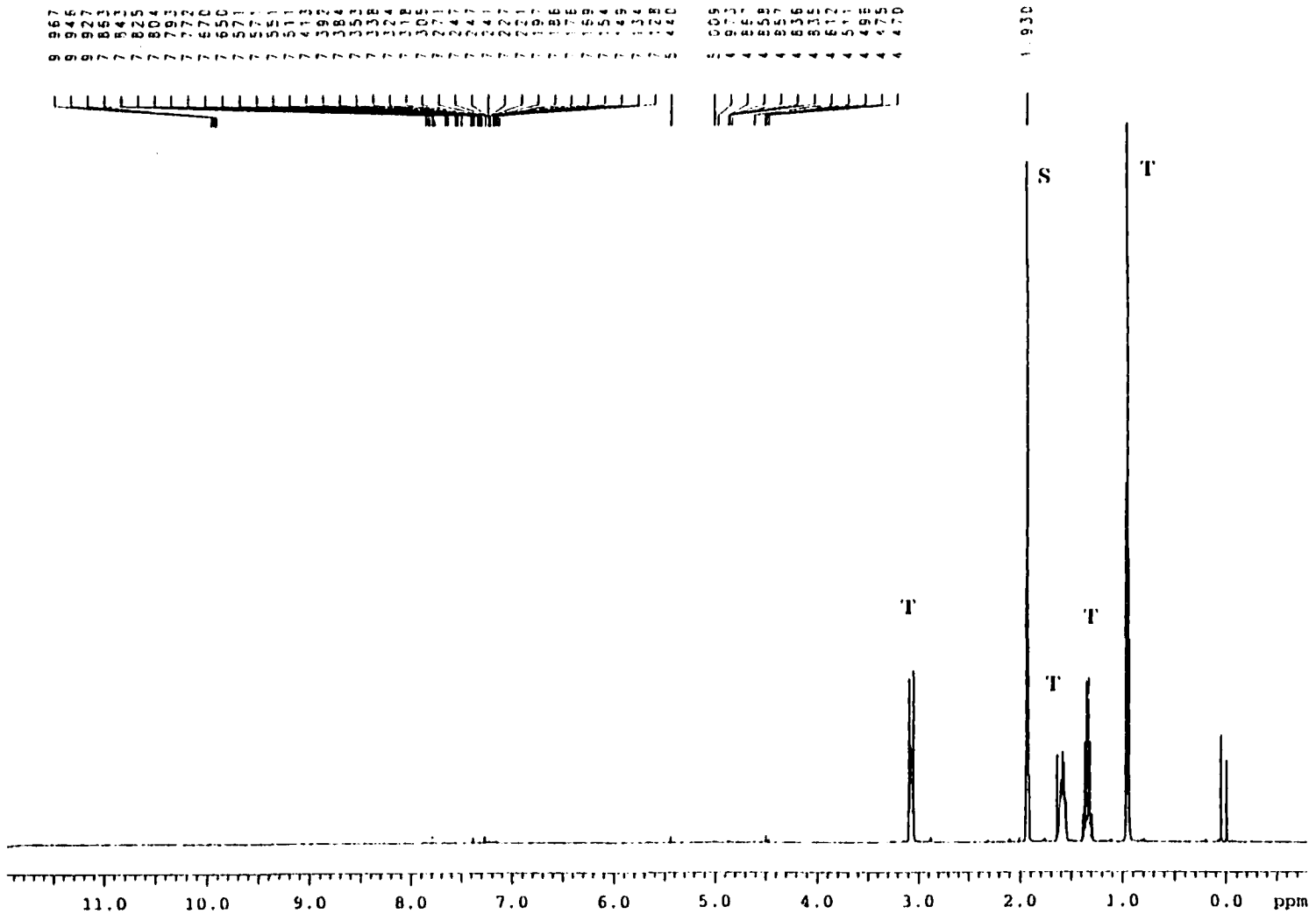


Figure A-19. ^{1}H NMR spectrum (400 MHz, CD_3CN) of products of *p*-xylylene (**1**) and oxygen. (S: acetonitrile, T: TBAF)

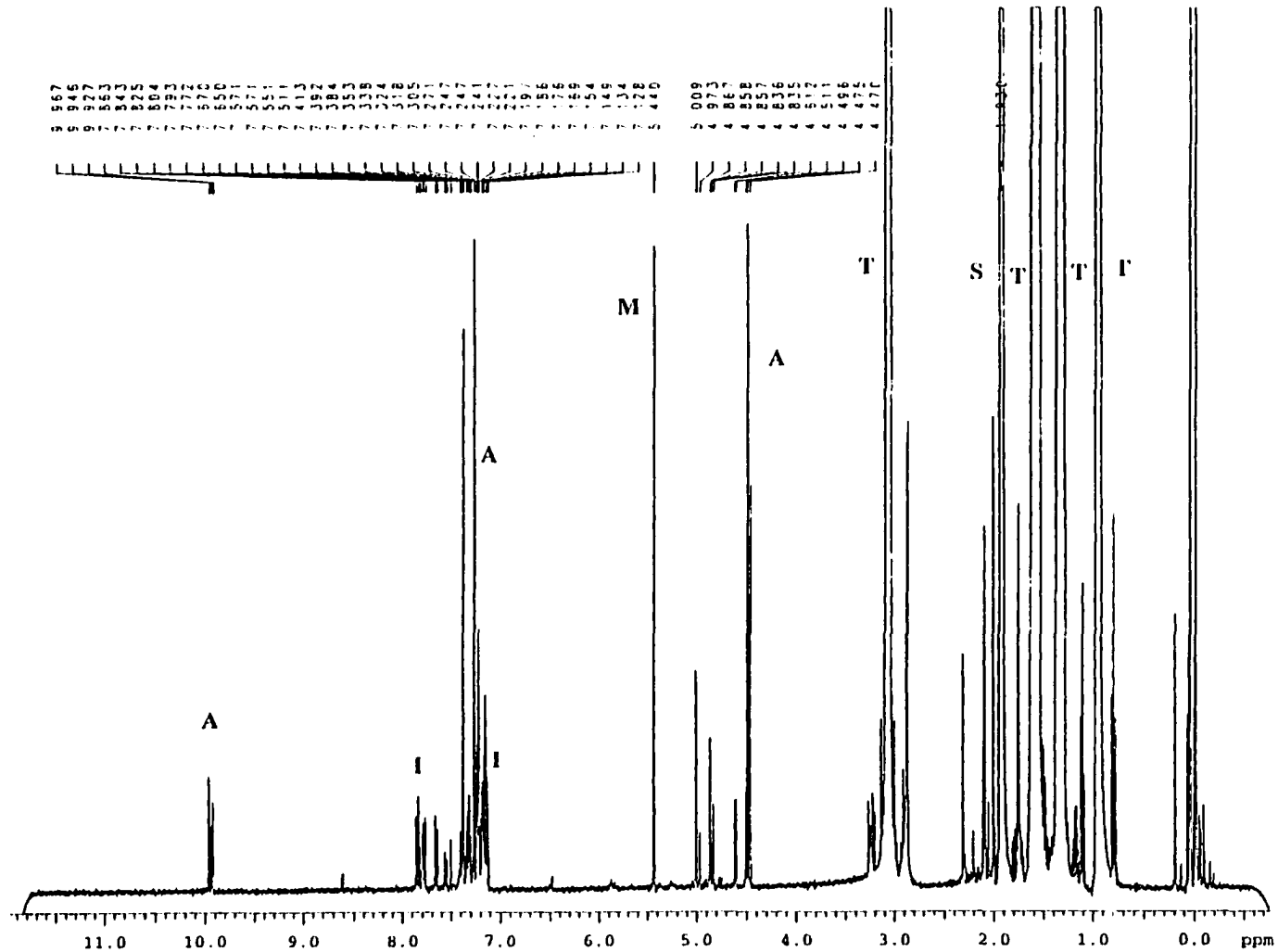


Figure A-20. Enlargement of Figure A-19 from 12 to -0.7 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of products of *p*-xylylene (**1**) and oxygen. (**A**: oxygen adducts, **I**: internal standard, naphthalene, **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

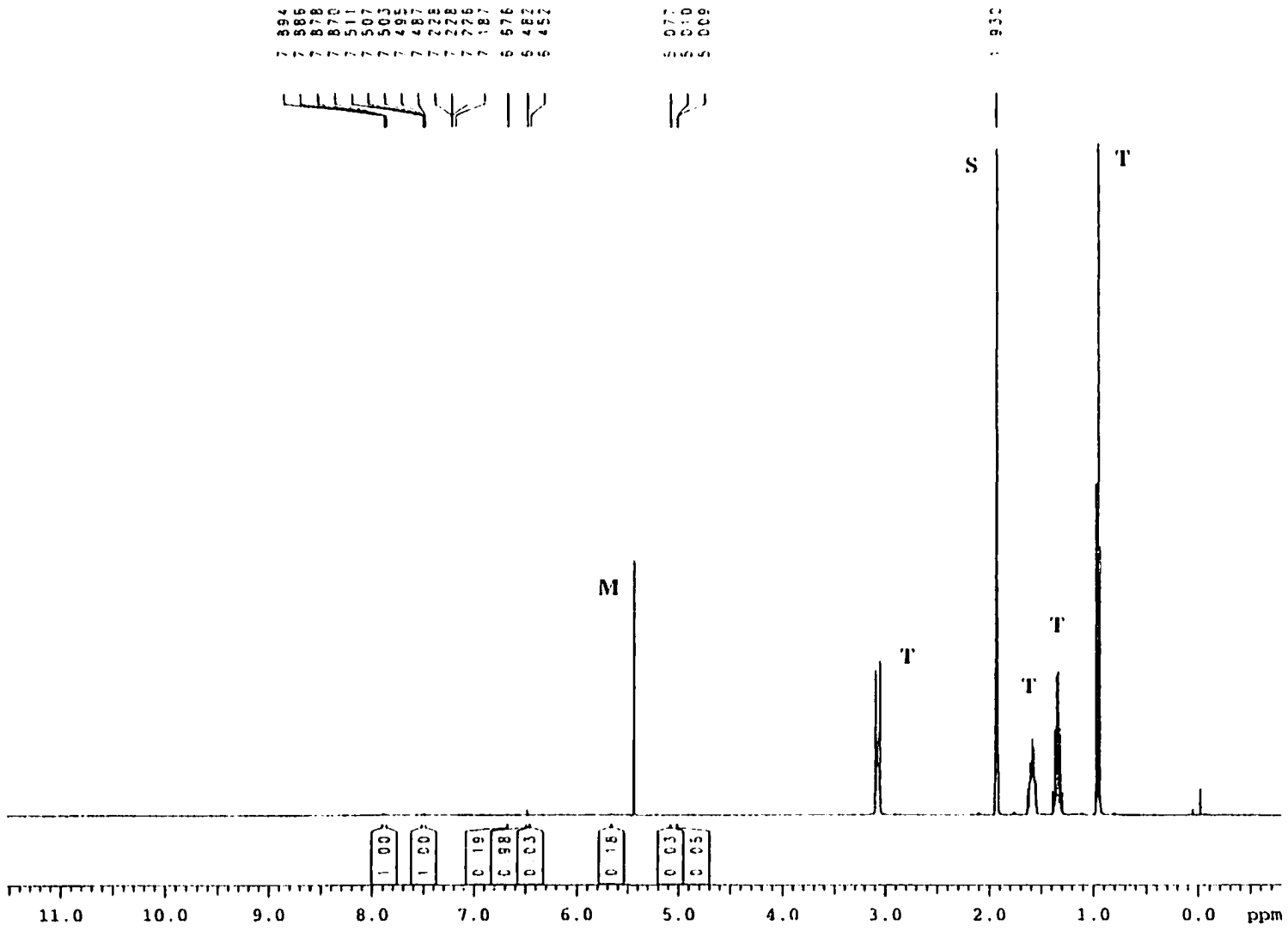


Figure A-21. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (1) products in deoxygenated CD_3CN. (**M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

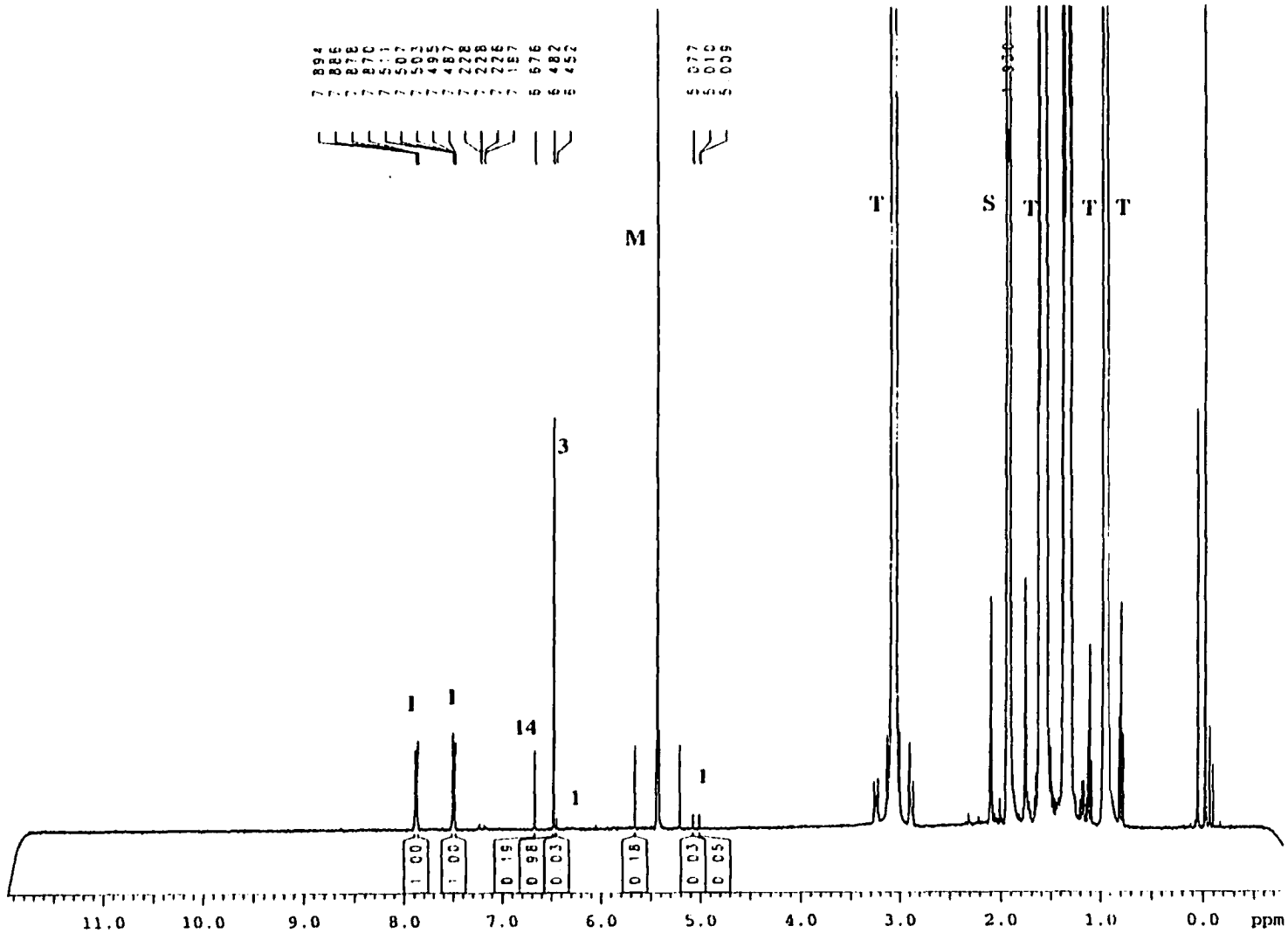


Figure A-22. Enlargement of Figure A-21 from 12 to -0.7 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-xylylene (**1**) products in deoxygenated CD_3CN. (**3** and **14** are compound numbers given in the text, **I**: internal standard, naphthalene **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

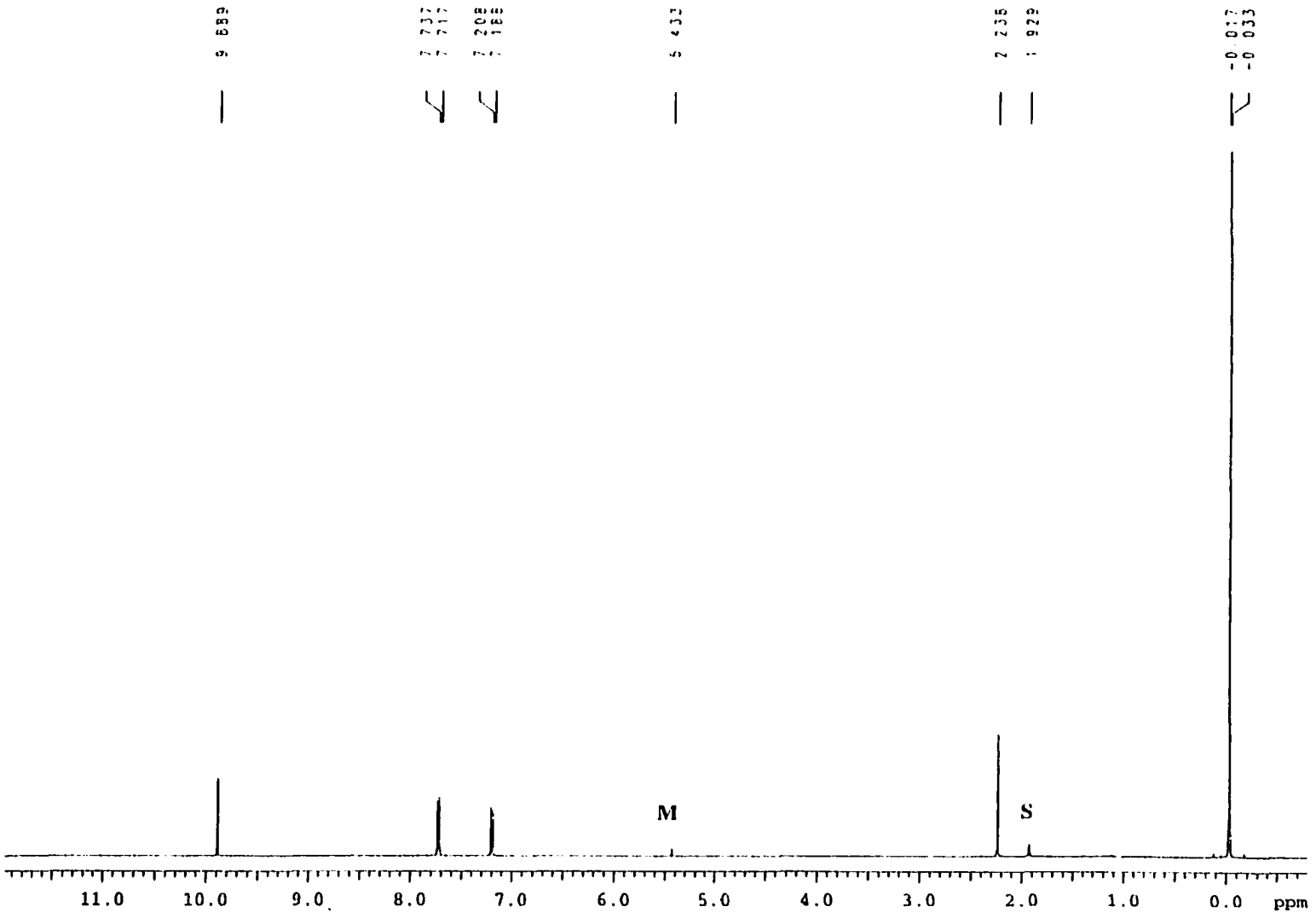


Figure A-23. ^{1}H NMR spectrum (400 MHz, CD_3CN) of 4-[(trimethylsilyl)methyl]benzaldehyde. (**M**: methylene chloride, **S**: acetonitrile)

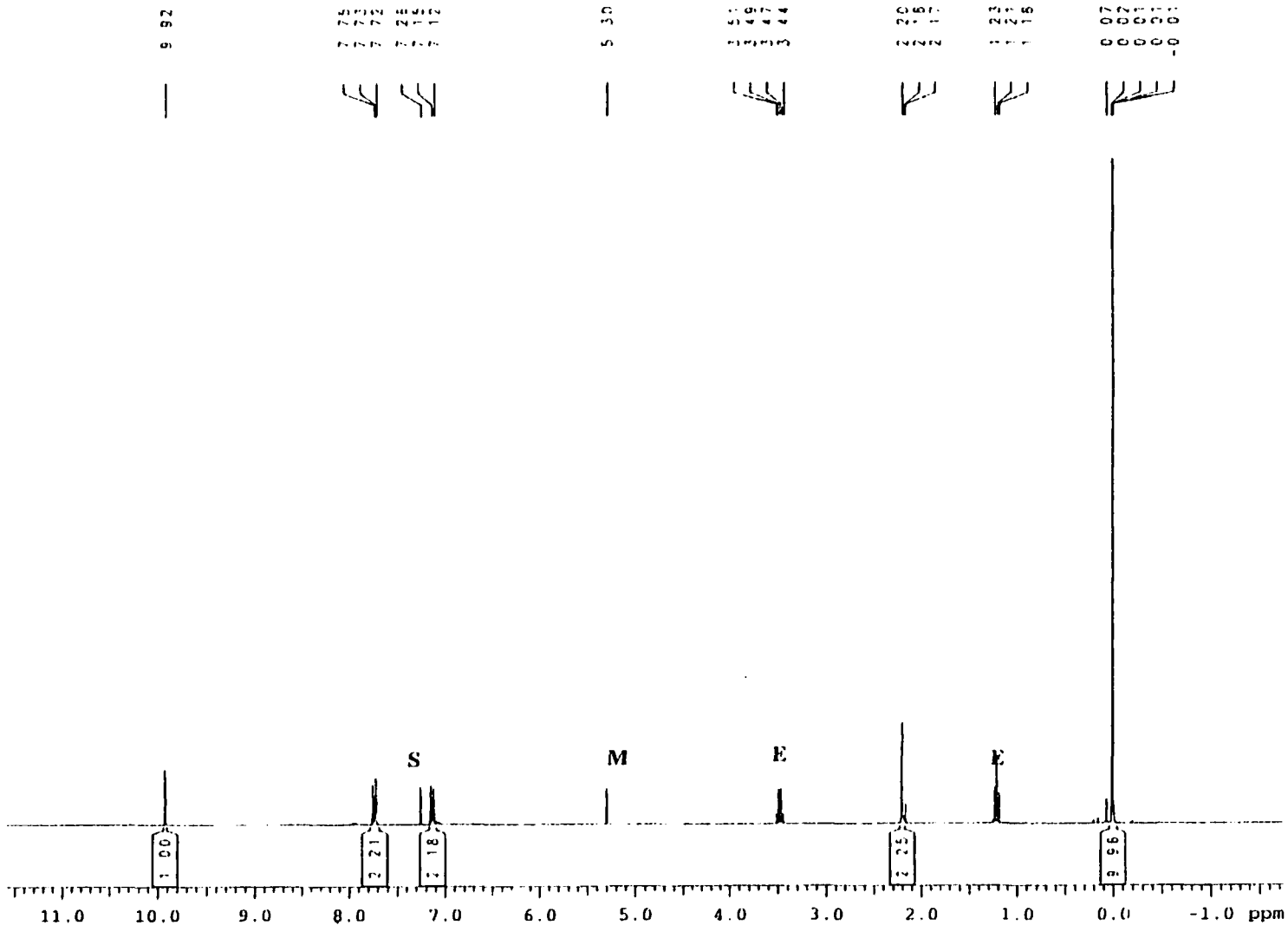


Figure A-24. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4-[(trimethylsilyl)methyl]benzaldehyde. (E: ethyl ether, M: methylene chloride, S: acetonitrile)

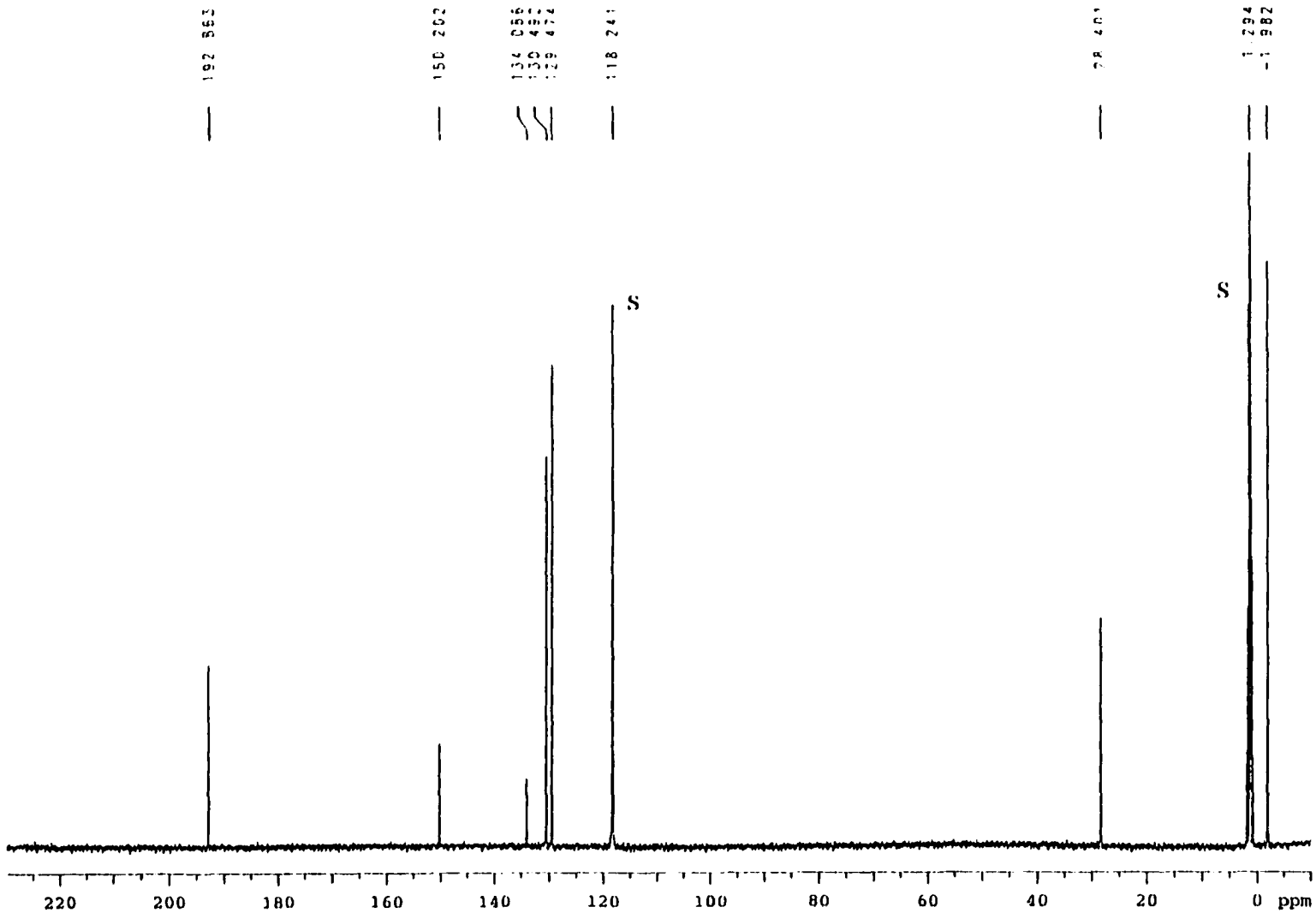


Figure A-25. ^{13}C NMR spectrum (100 MHz, CD_3CN) of 4-[(trimethylsilyl)methyl]benzaldehyde. (S: acetonitrile)

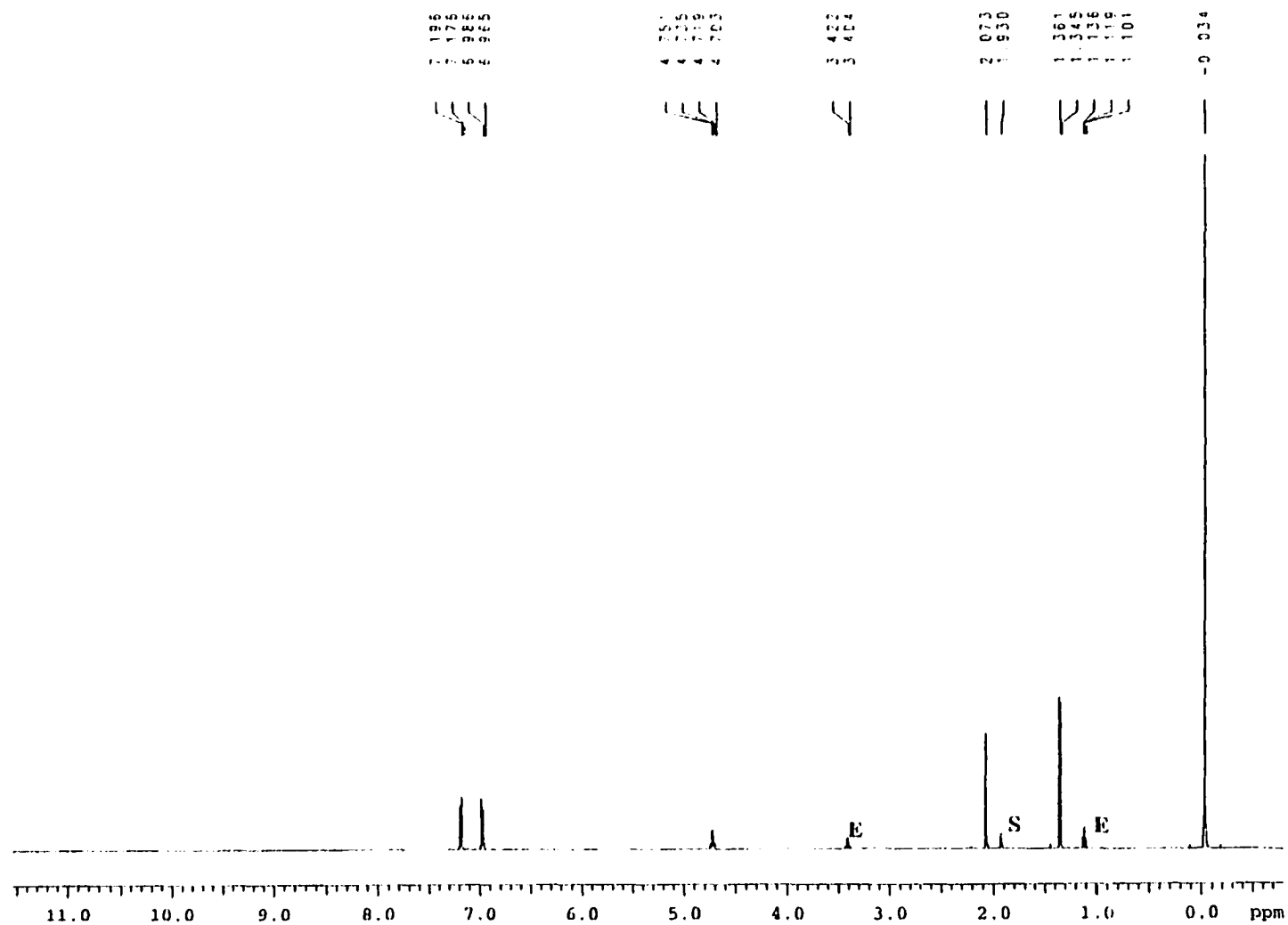


Figure A-26. ^{1}H NMR spectrum (400 MHz, CD_3CN) of 1-[*p*-((trimethylsilyl)methyl)phenyl]ethanol. (E: ethyl ether, S: acetonitrile)

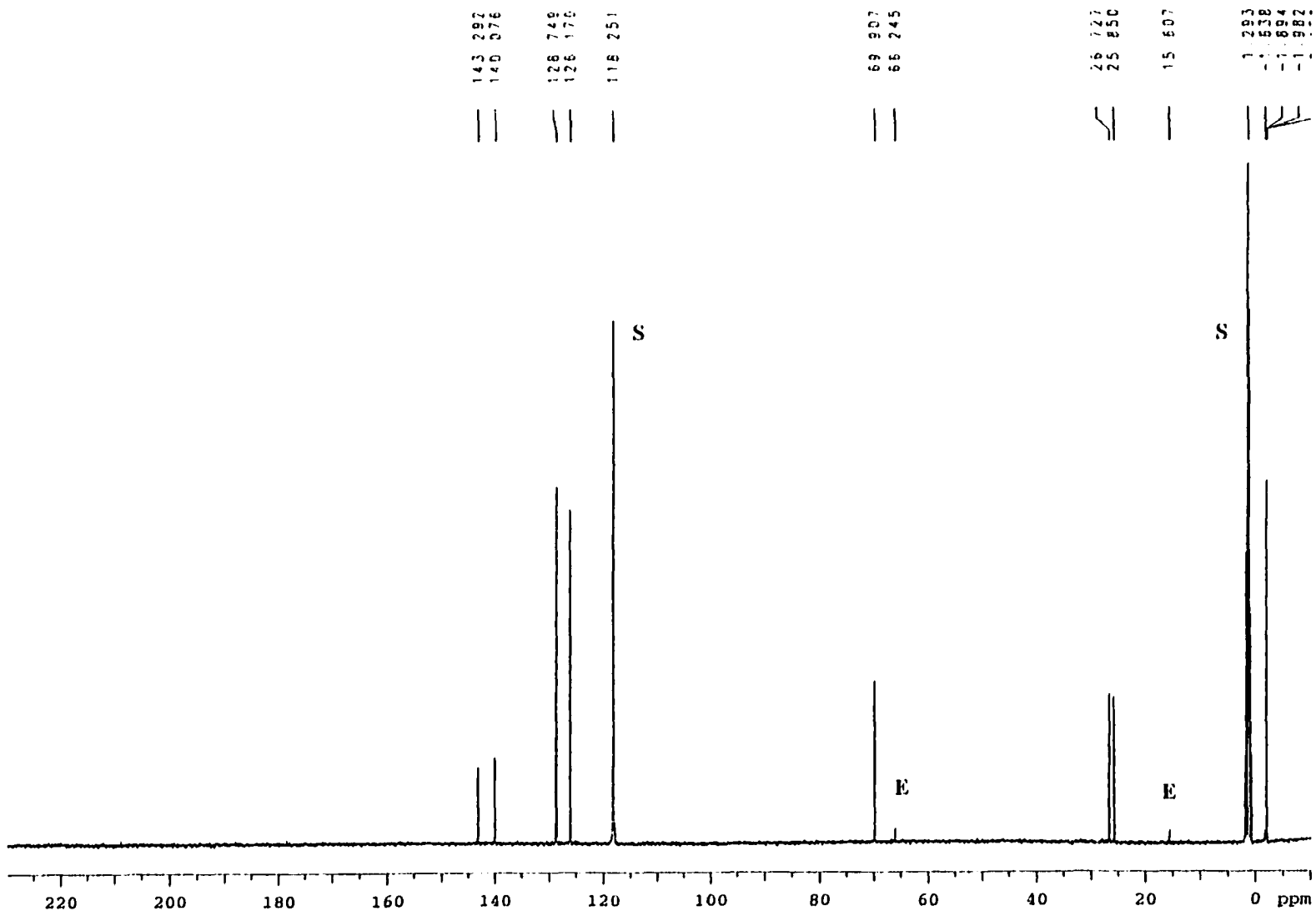


Figure A-27. ^{13}C NMR spectrum (100 MHz, CD_3CN) of 1-[*p*-((trimethylsilyl)methyl)phenyl]ethanol. (**E**: ethyl ether, **S**: acetonitrile)

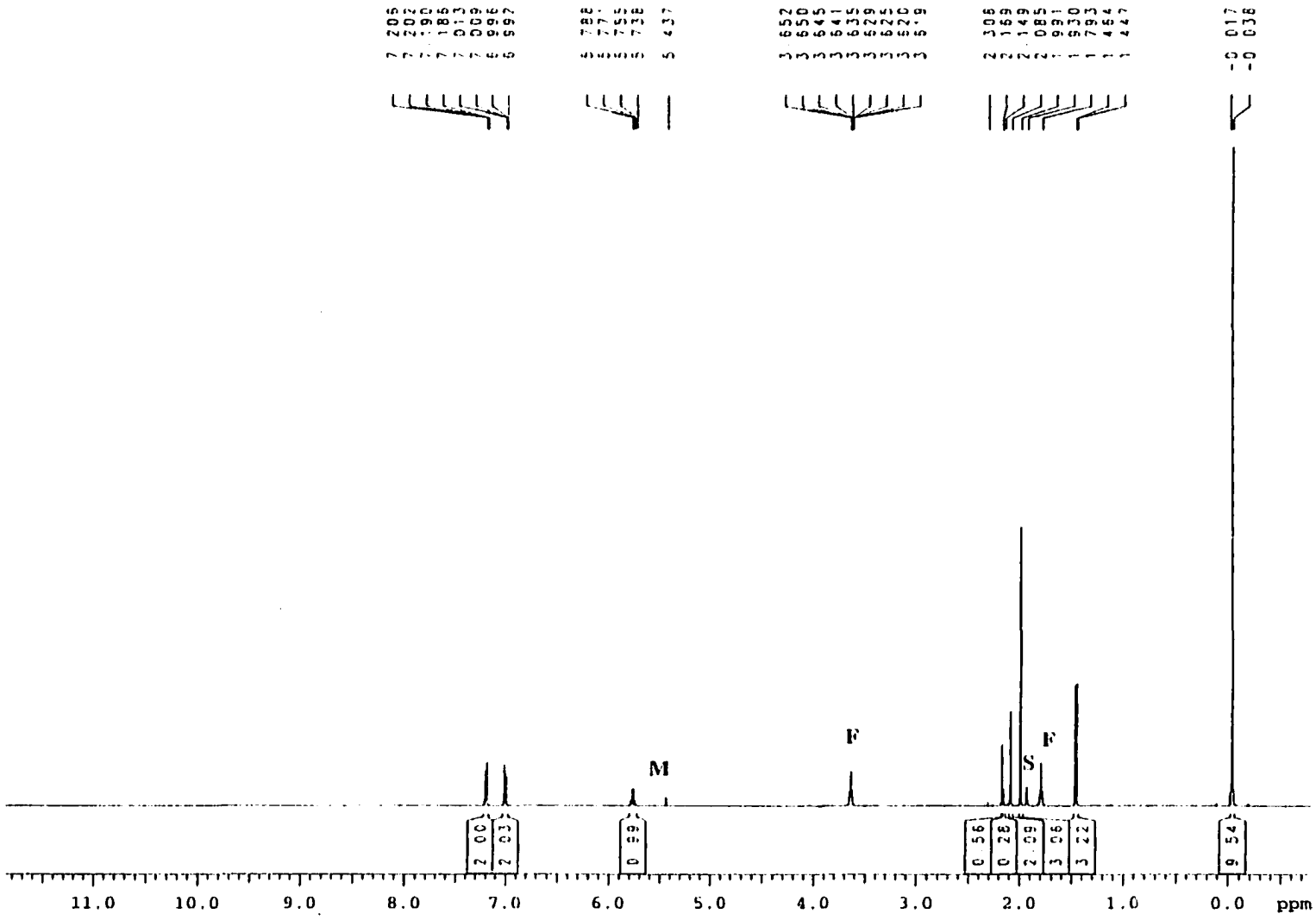


Figure A-28. ^{1}H NMR spectrum (400 MHz, CD_3CN) of 1-[*p*-((trimethylsilyl)methyl)phenyl]ethyl acetate (**15**). (**F**: THF, **M**: methylene chloride, **S**: acetonitrile)

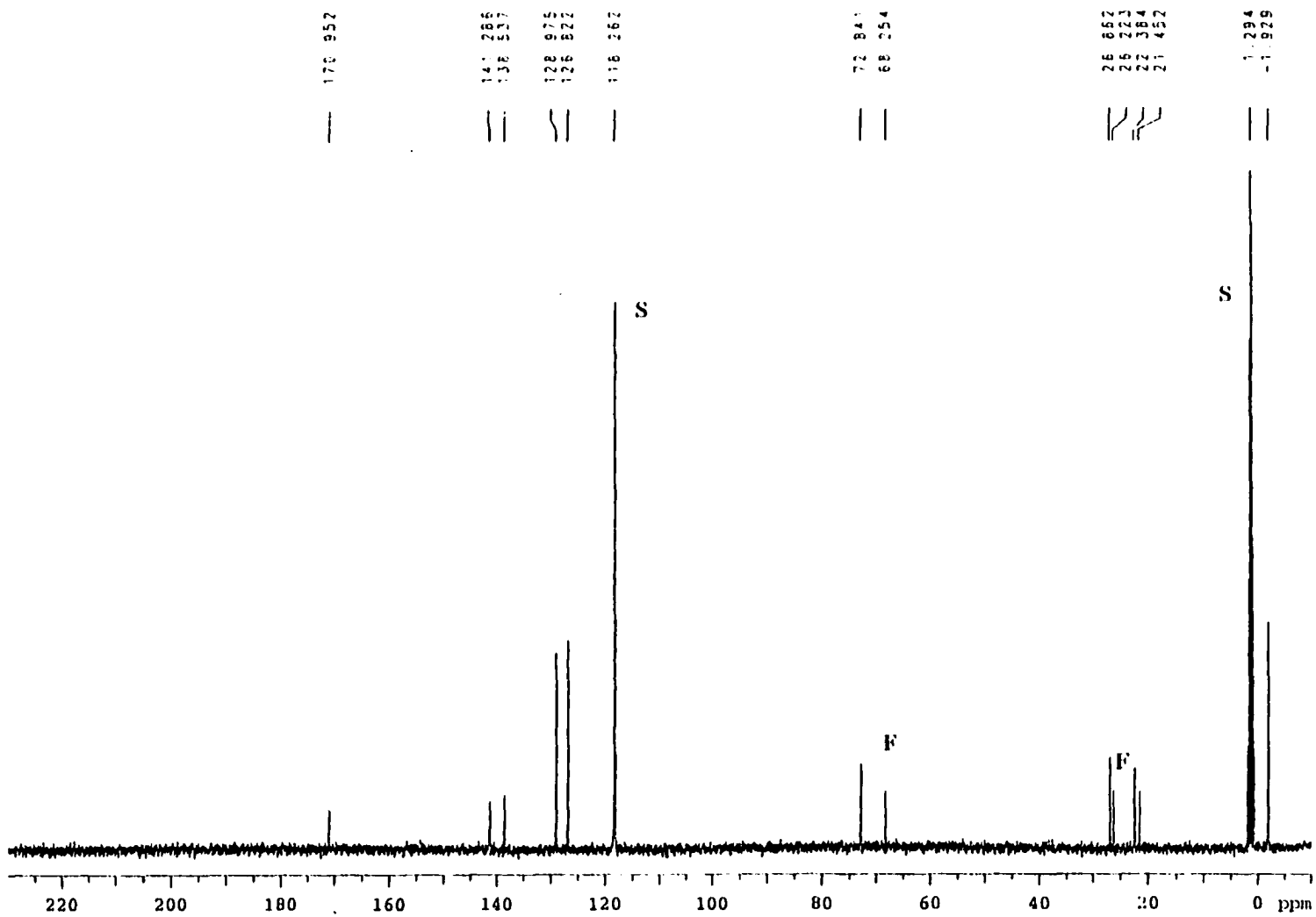


Figure A-29. ^{13}C NMR spectrum (100 MHz, CD_3CN) of 1-[*p*-((trimethylsilyl)methyl)phenyl]ethyl acetate (**15**). (F: THF, S: acetonitrile)

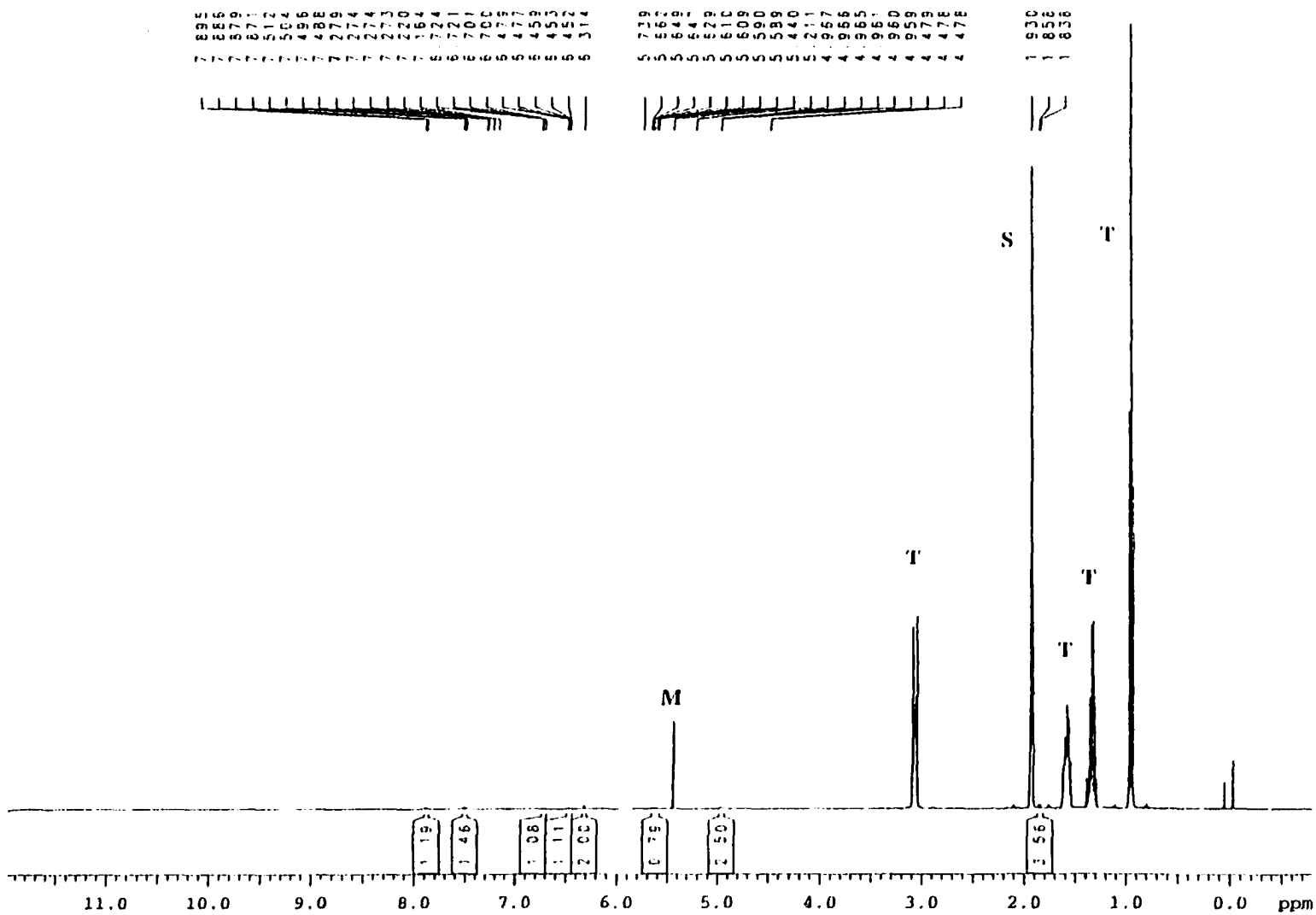


Figure A-30. ^{1}H NMR spectrum (400 MHz, CD_3CN) of α-methyl-*p*-xylylene (**11**) in degassed CD_3CN. (**M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

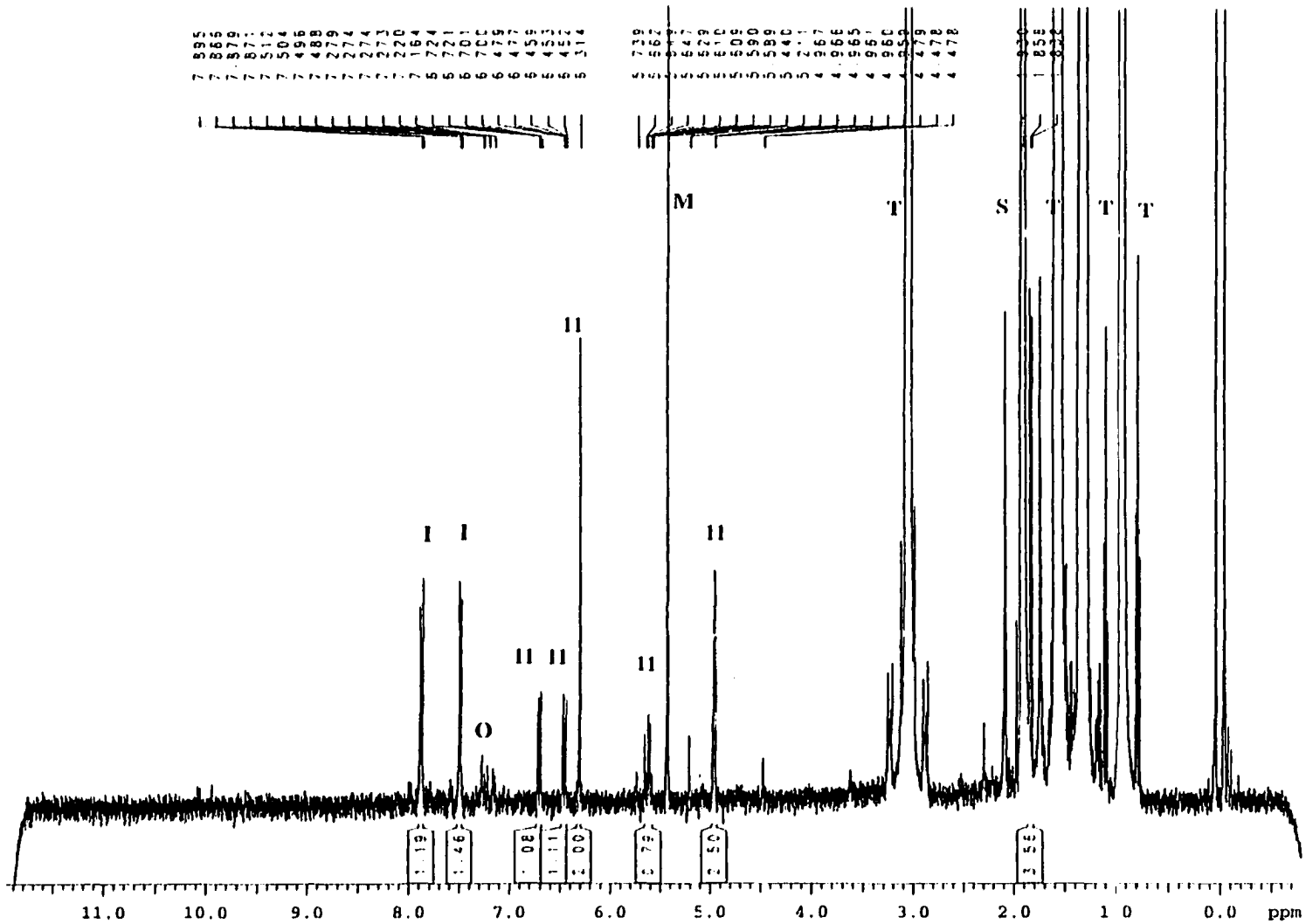


Figure A-31. Enlargement of Figure A-30 from 12 to -0.7 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of α-methyl-*p*-xylylene (**11**) in degassed CD_3CN. (**I**: internal standard, naphthalene, **M**: methylene chloride, **O**: oligomers, **S**: acetonitrile, **T**: TBAF)

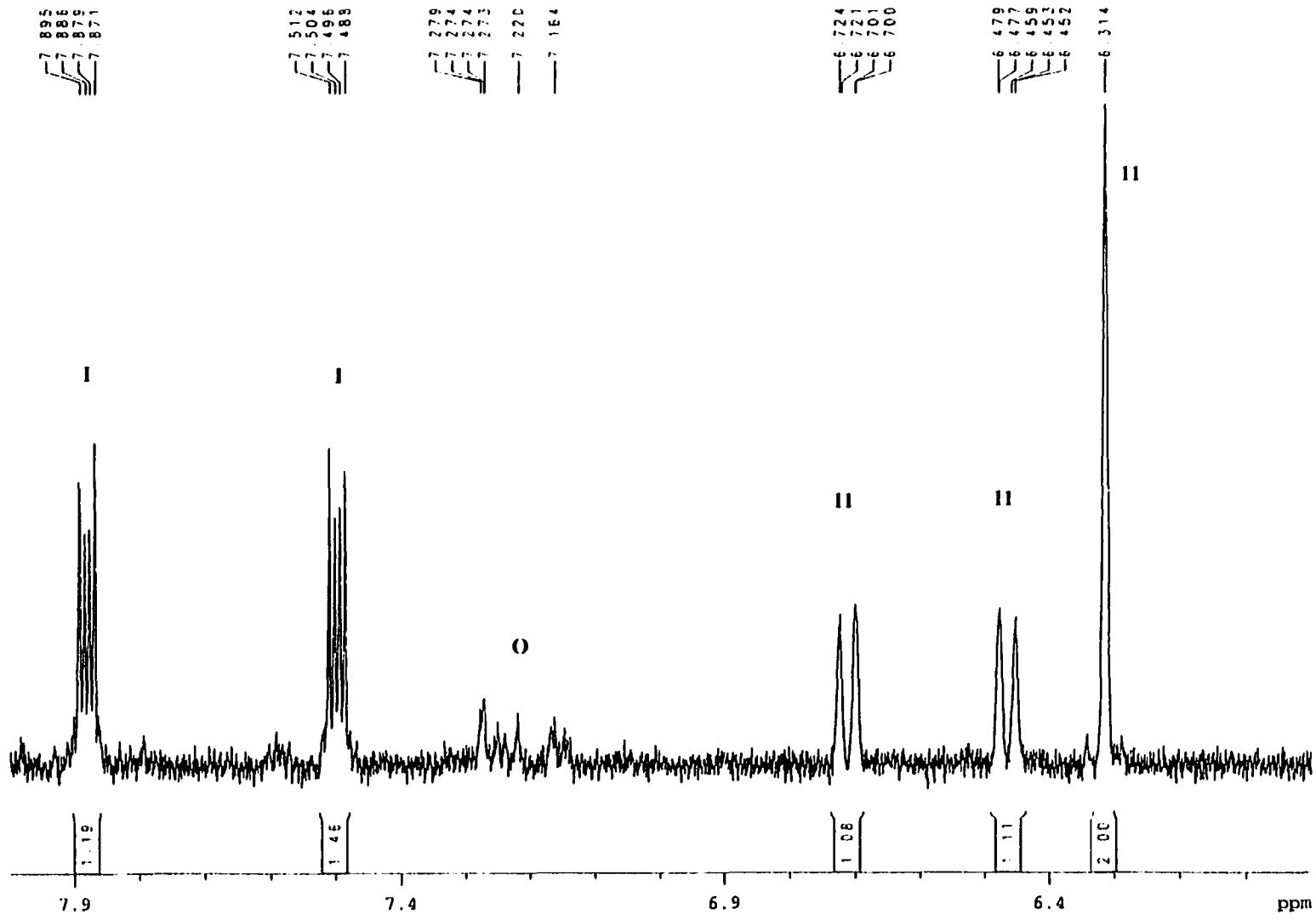


Figure A-32. Enlargement of Figure A-30 from 8–6 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of α-methyl-*p*-xylylene (**11**) in degassed CD_3CN. (**I**: internal standard, naphthalene, **O**: oligomers)

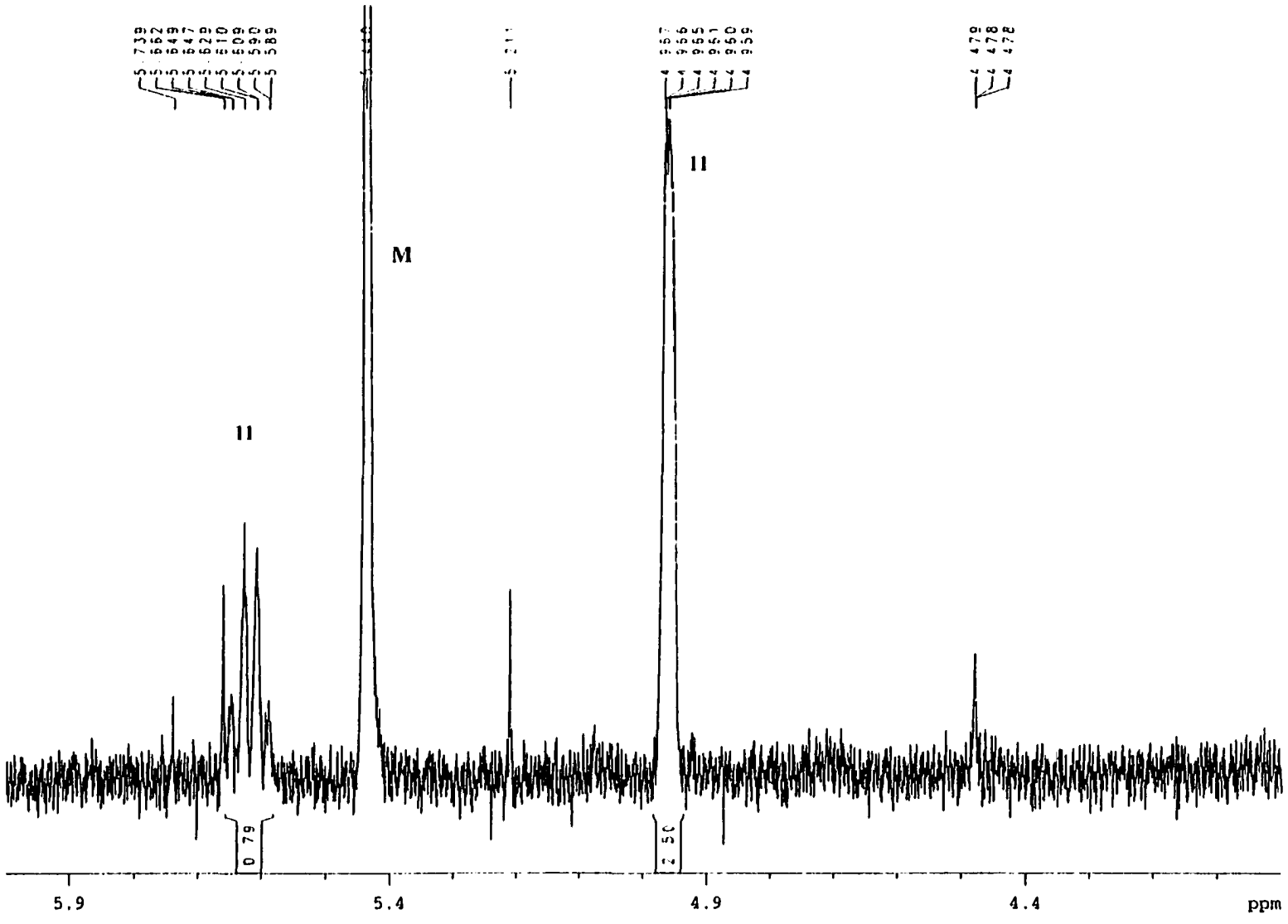


Figure A-33. Enlargement of Figure A-30 from 6–4 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of α-methyl-*p*-xylylene (**11**) in degassed CD_3CN. (**M**: methylene chloride)

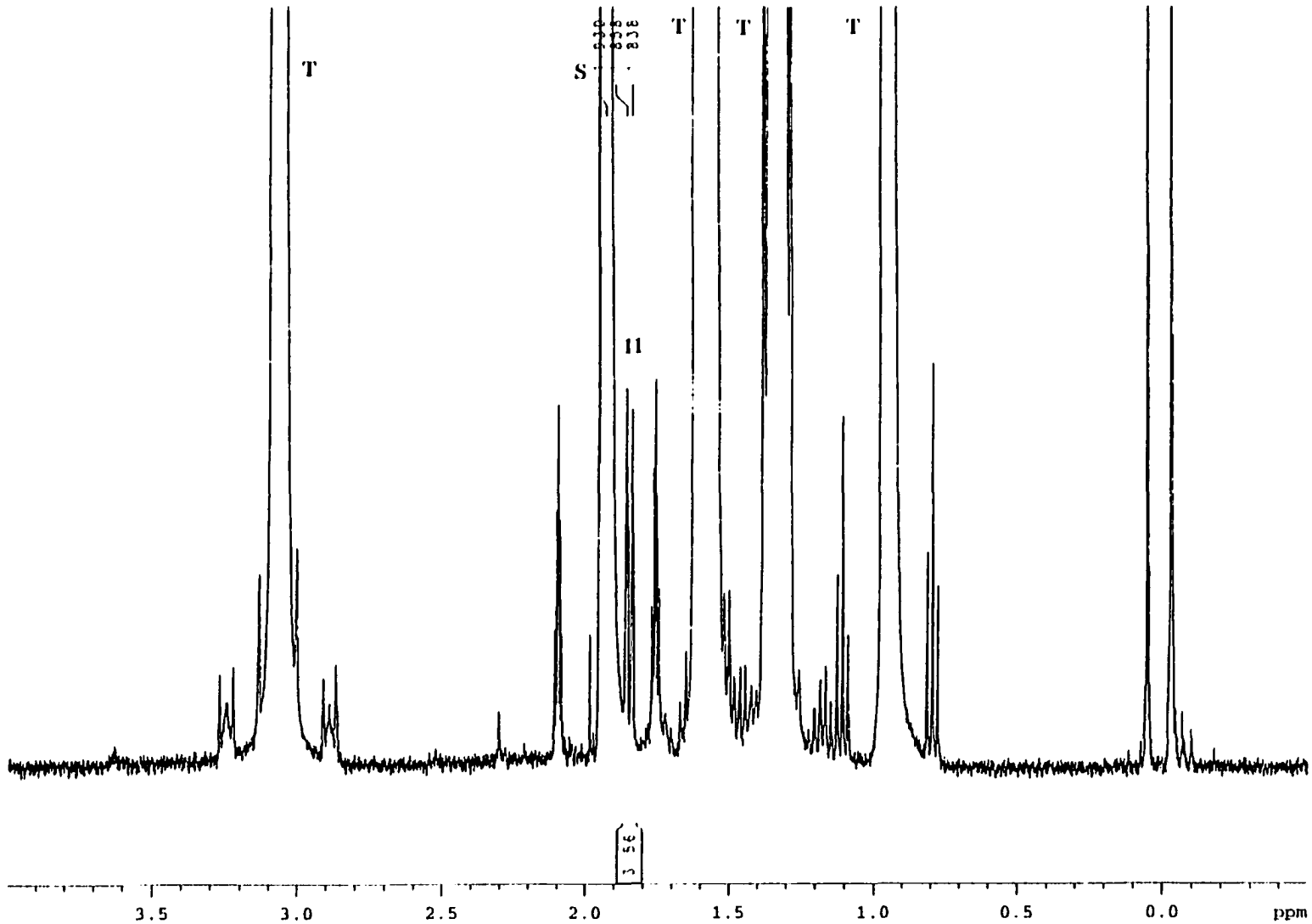


Figure A-34. Enlargement of Figure A-30 from 4 to -0.5 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of α-methyl-*p*-xylylene (11) in degassed CD_3CN. (S: acetonitrile, T: TBAF)

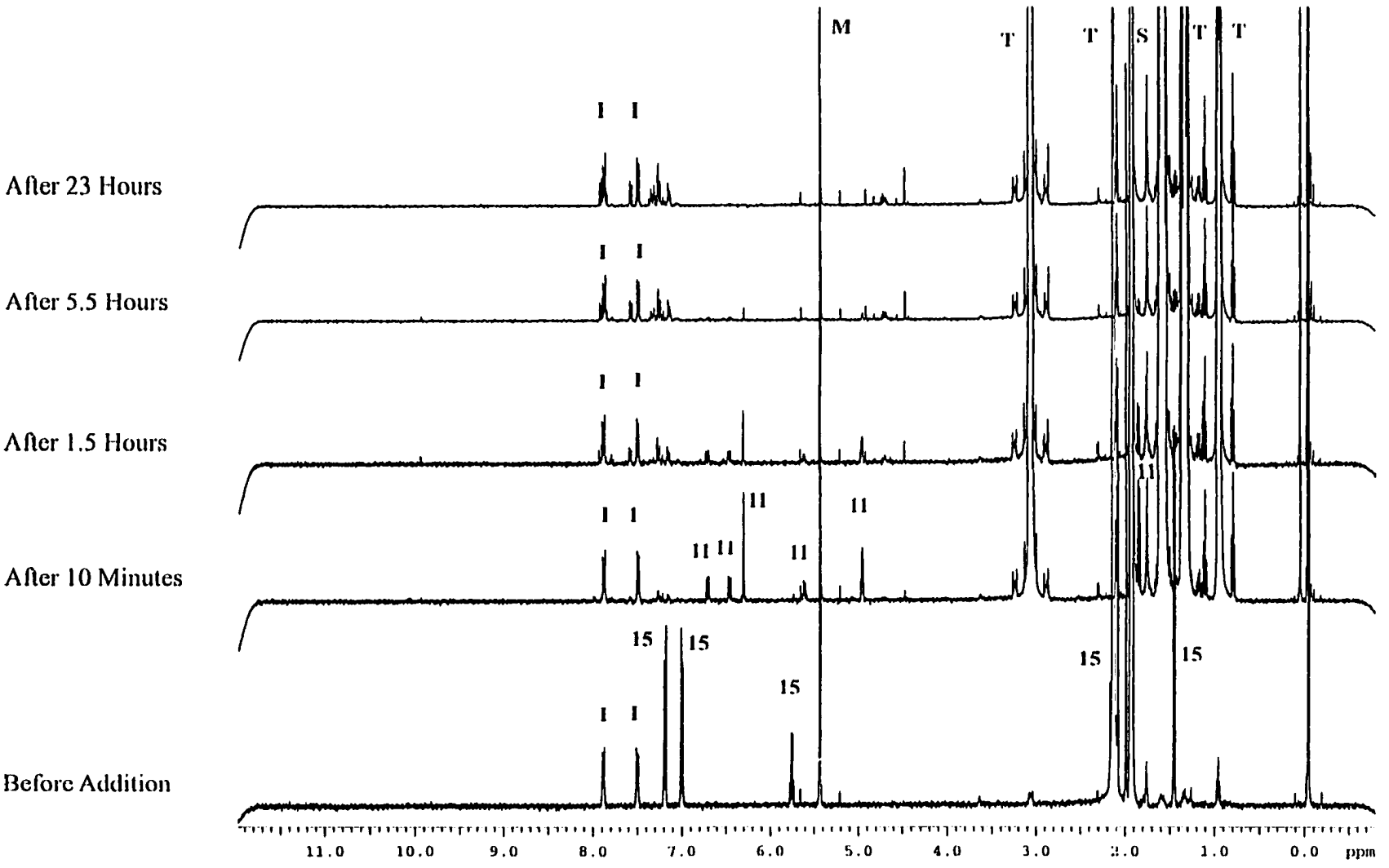


Figure A-35. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of α-methyl-*p*-xylylene (**11**) in degassed CD_3CN. (**15** is a compound number given in the text, **I**: internal standard, naphthalene **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

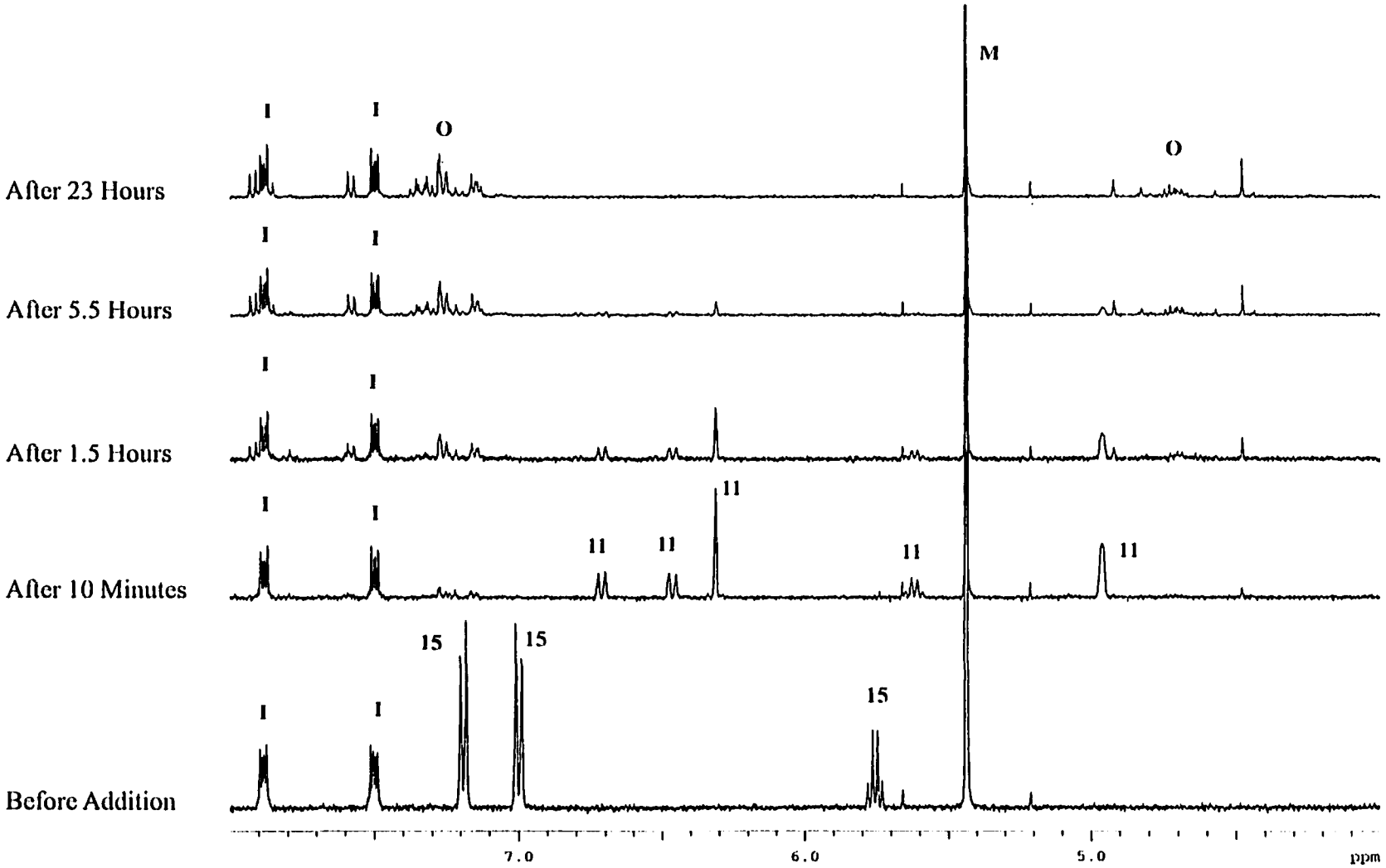


Figure A-36. Enlargement of Figure A-35 from 8–4 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of α-methyl-*p*-xylylene (**11**) in degassed CD_3CN. (**15** is a compound number given in the text, **I**: internal standard, naphthalene **M**: methylene chloride, **O**: oligomers)

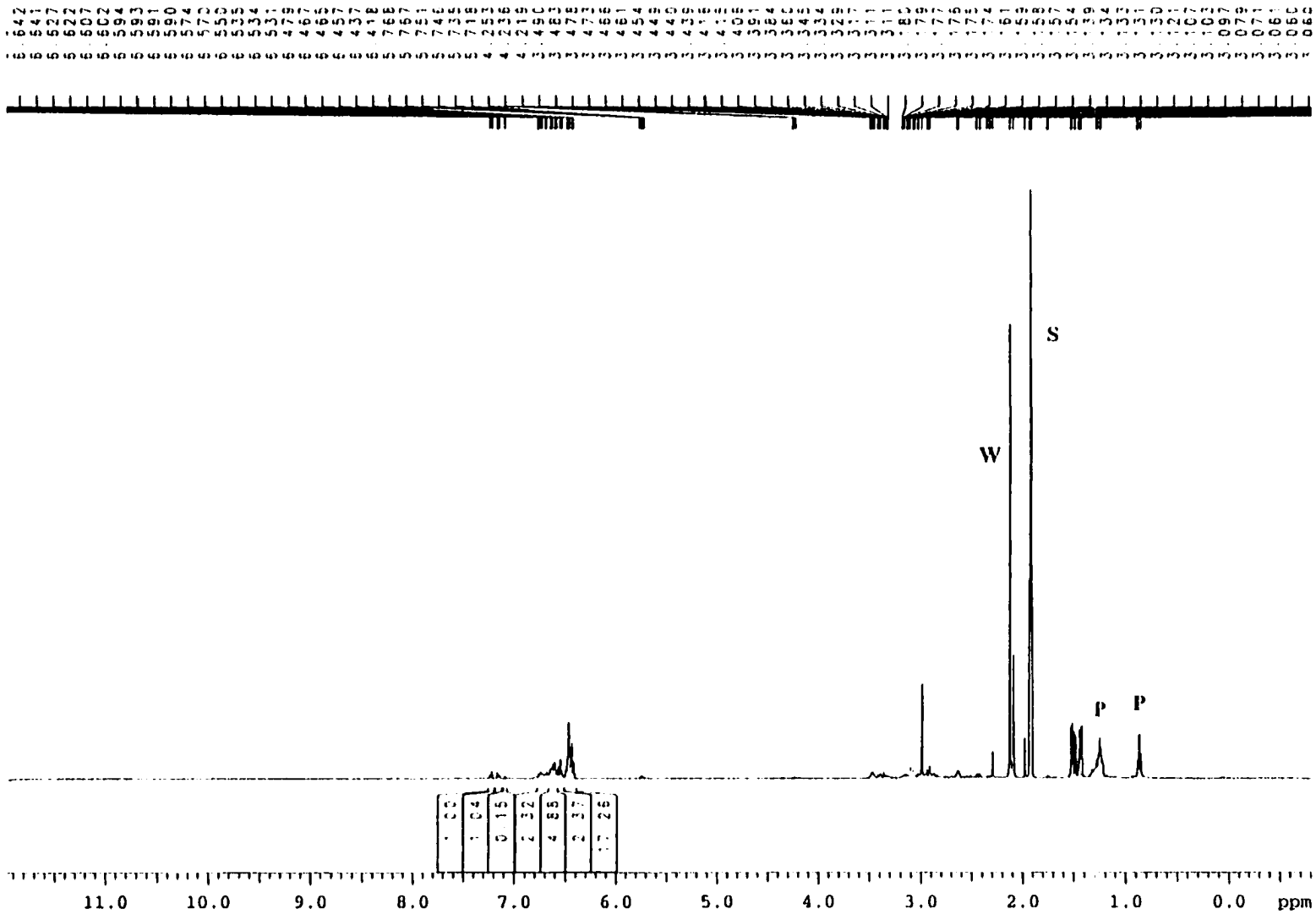


Figure A-37. ^{1}H NMR spectrum (400 MHz, CD_3CN) of pentane extraction of product mixture of α-methyl-*p*-xylylene (**11**) in deoxygenated CD_3CN. (**P**: pentane, **S**: acetonitrile, **W**: water)

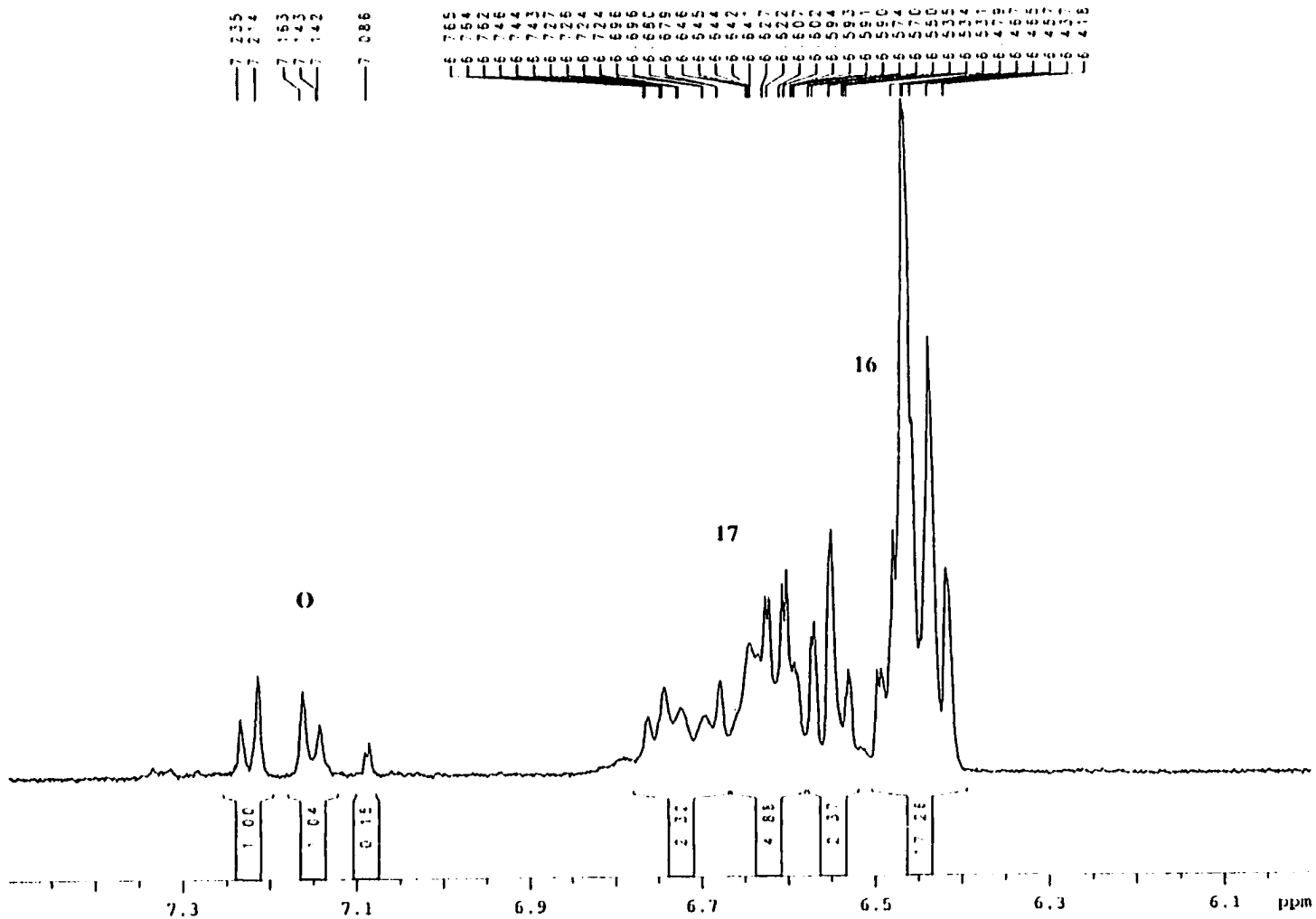


Figure A-38. Enlargement of Figure A-37 from 7.5 6.0 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of pentane extraction of product mixture of α-methyl-*p*-xylylene (**11**) in deoxygenated CD_3CN. (**16** and **17** are compound numbers given in the text, **O**: oligomers)

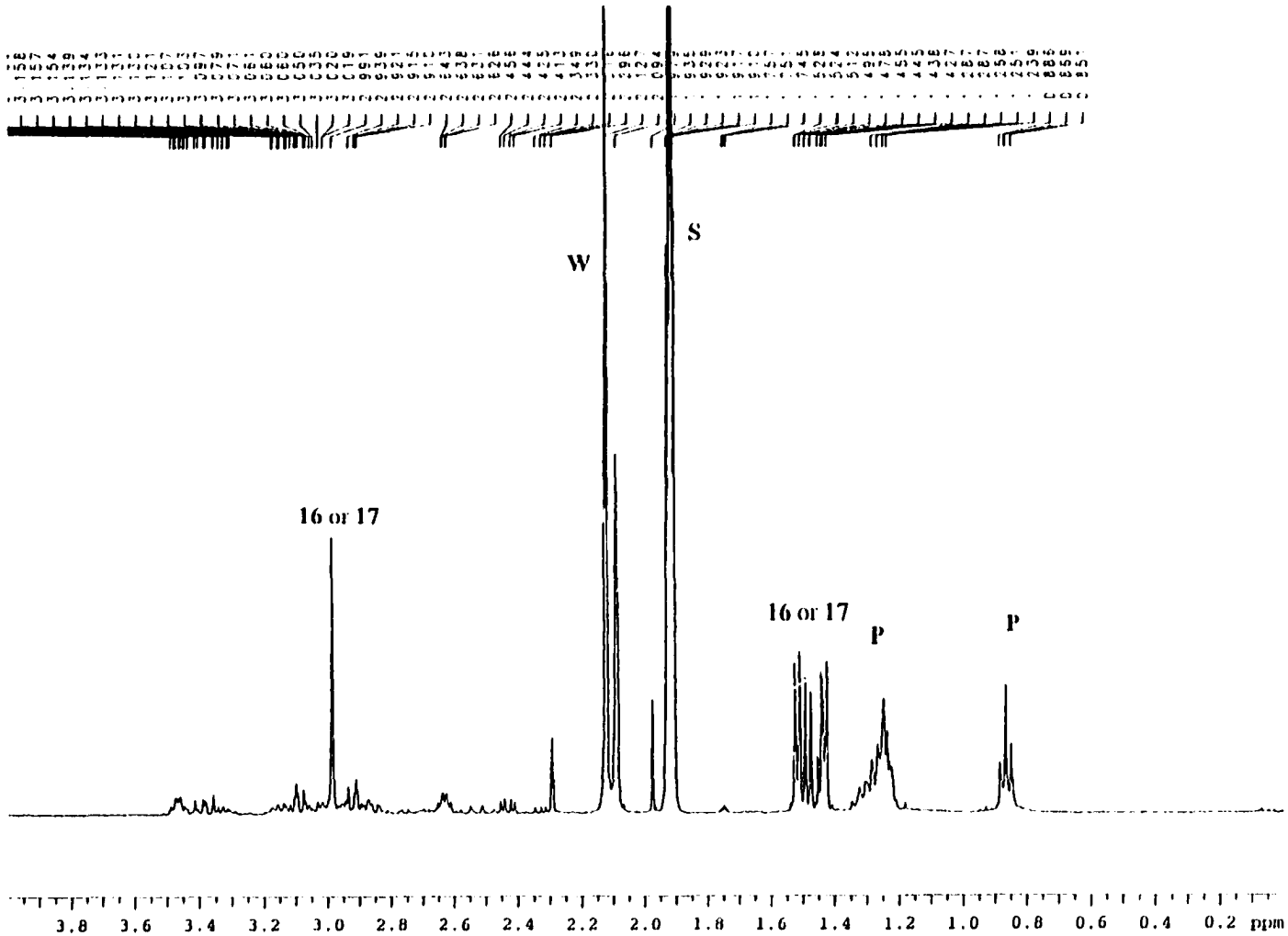


Figure A-39. Enlargement of Figure A-37 from 4–0 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of pentane extraction of product mixture of α-methyl-*p*-xylylene (**11**) in deoxygenated CD_3CN. (**16** and **17** are compound numbers given in the text, **P**: pentane, **S**: acetonitrile, **W**: water)

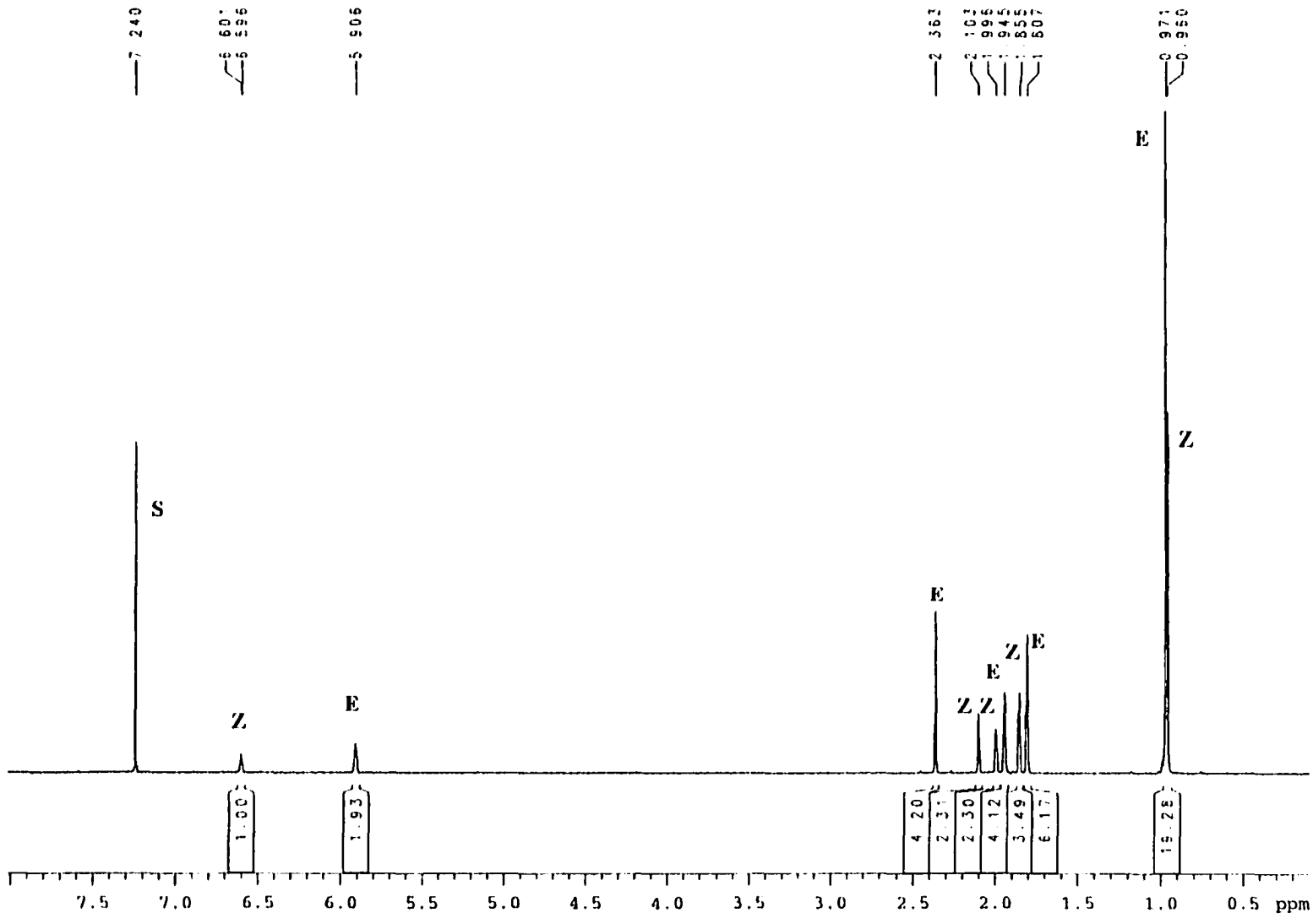


Figure A-40. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of isophorone oxime. (**E**: *E* isomer, **S**: chloroform, **Z**: *Z* isomer)

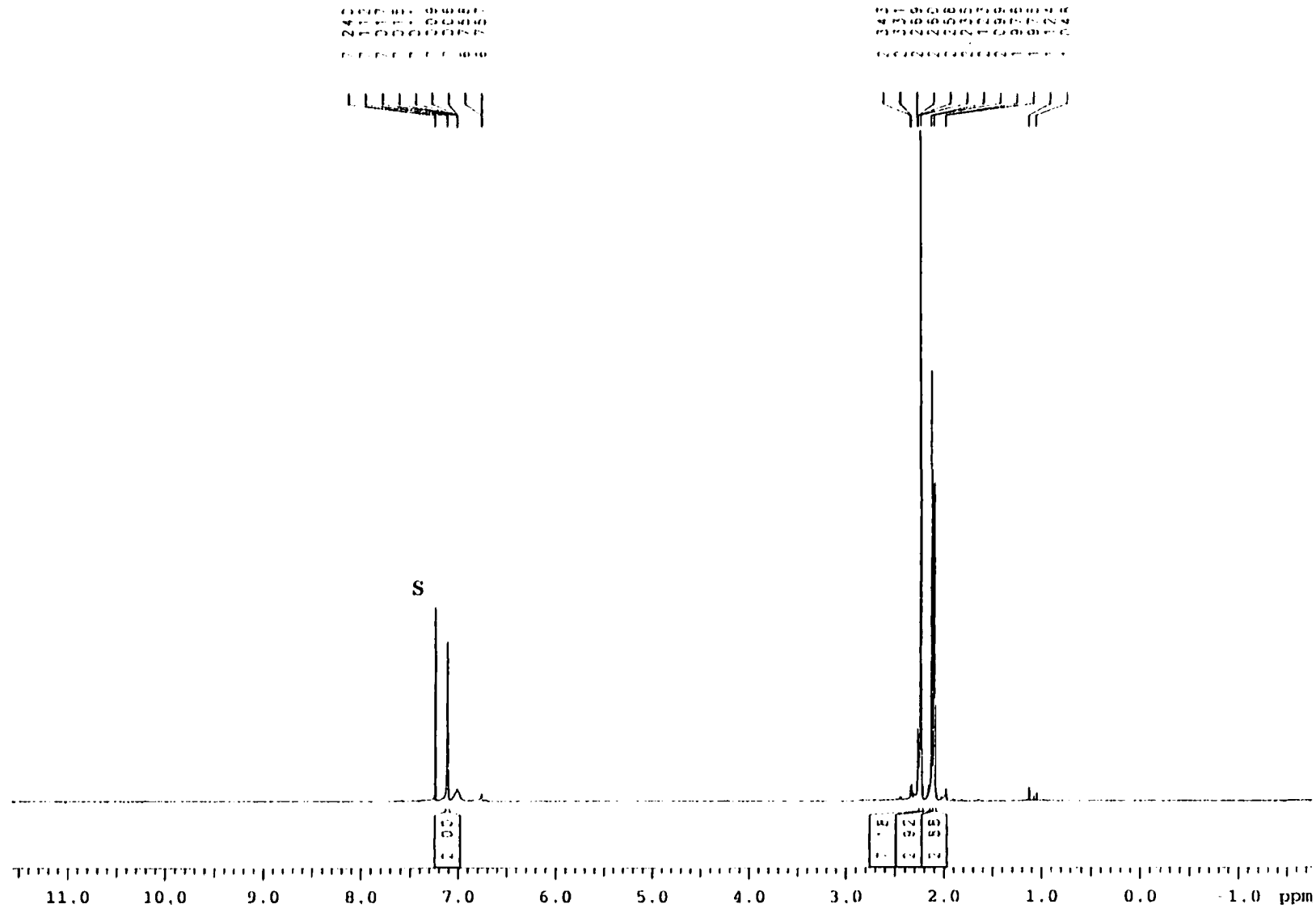


Figure A-41. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 3',4',5'-trimethylacetanilide. (**S**: chloroform)

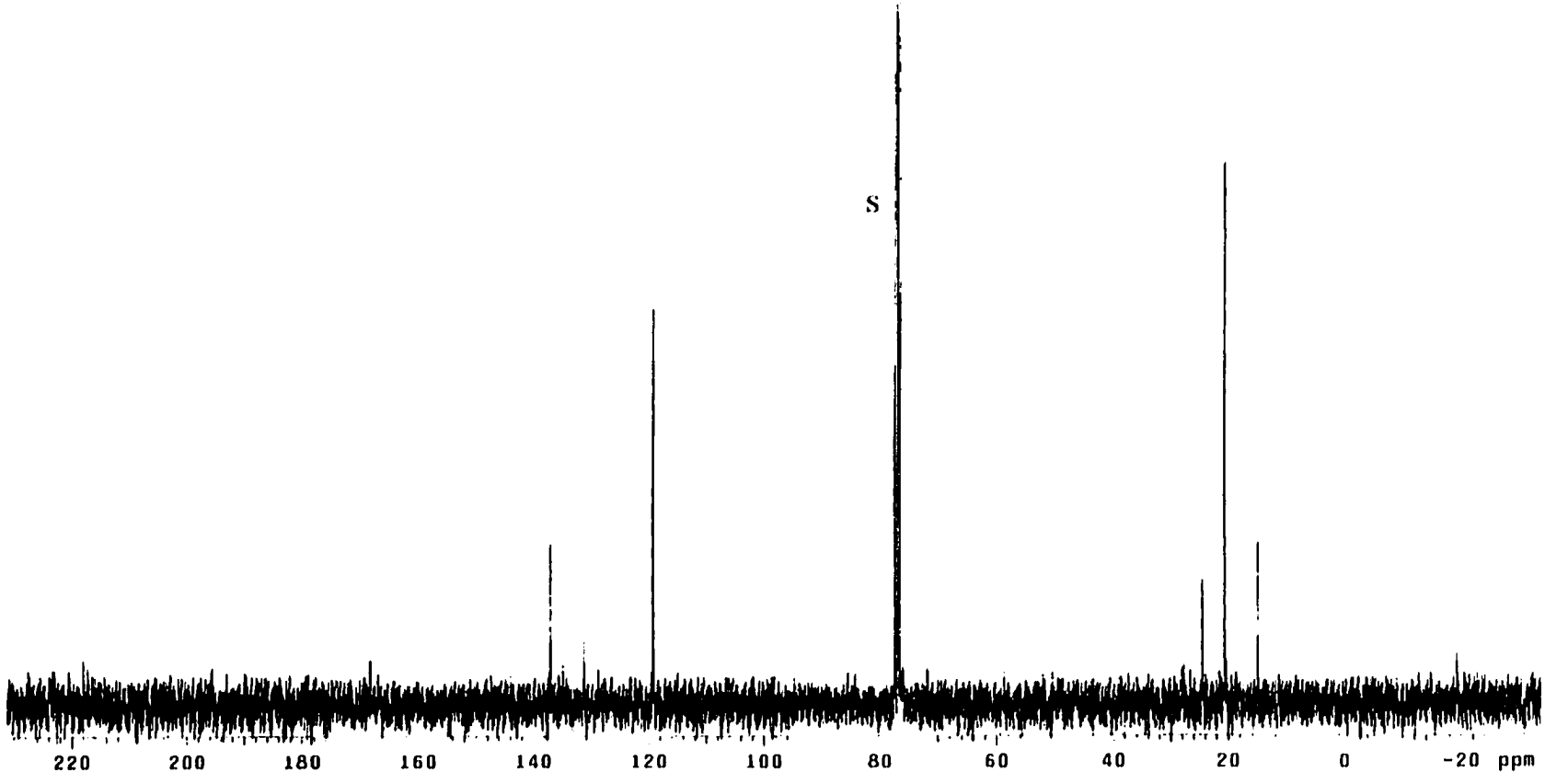


Figure A-42. ^{13}C NMR spectrum (75.4 MHz, $CDCl_3$) of 3',4',5'-trimethylacetanilide. (S: chloroform)

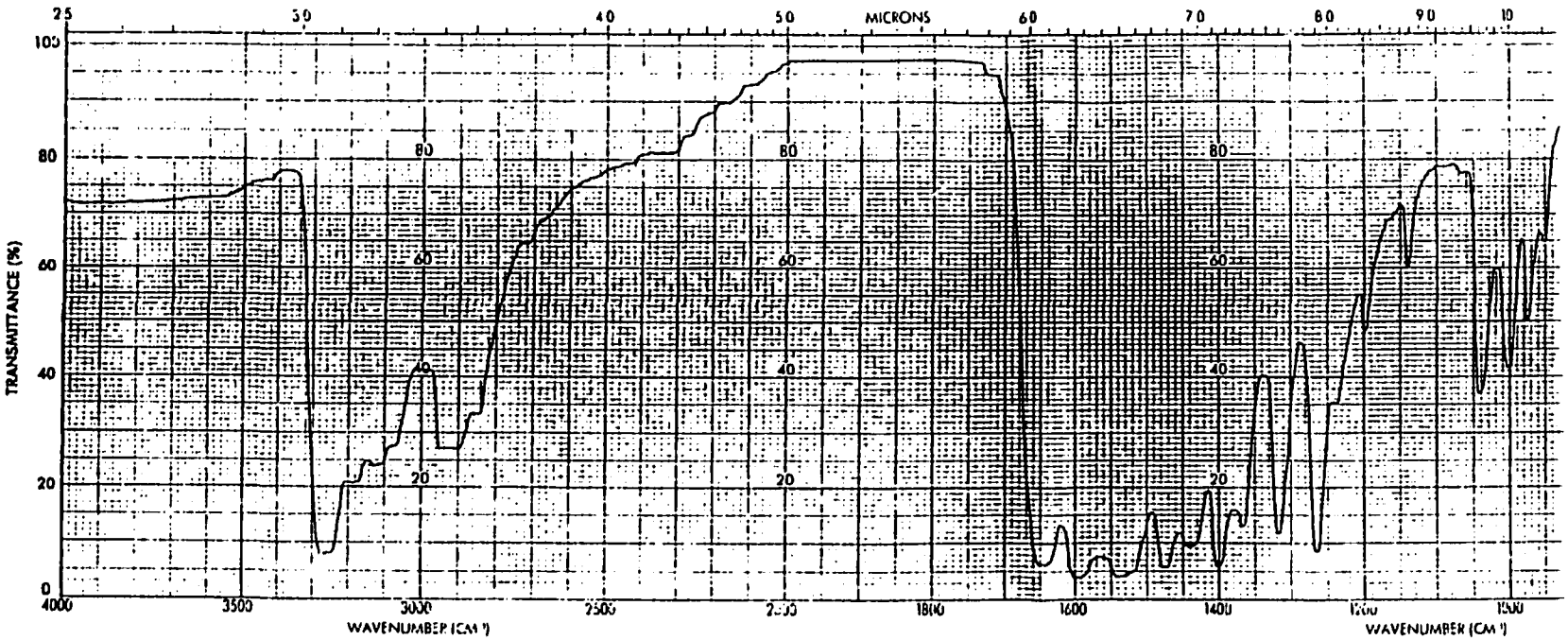


Figure A-43. Infrared spectrum of 3',4',5'-trimethylacetanilide.

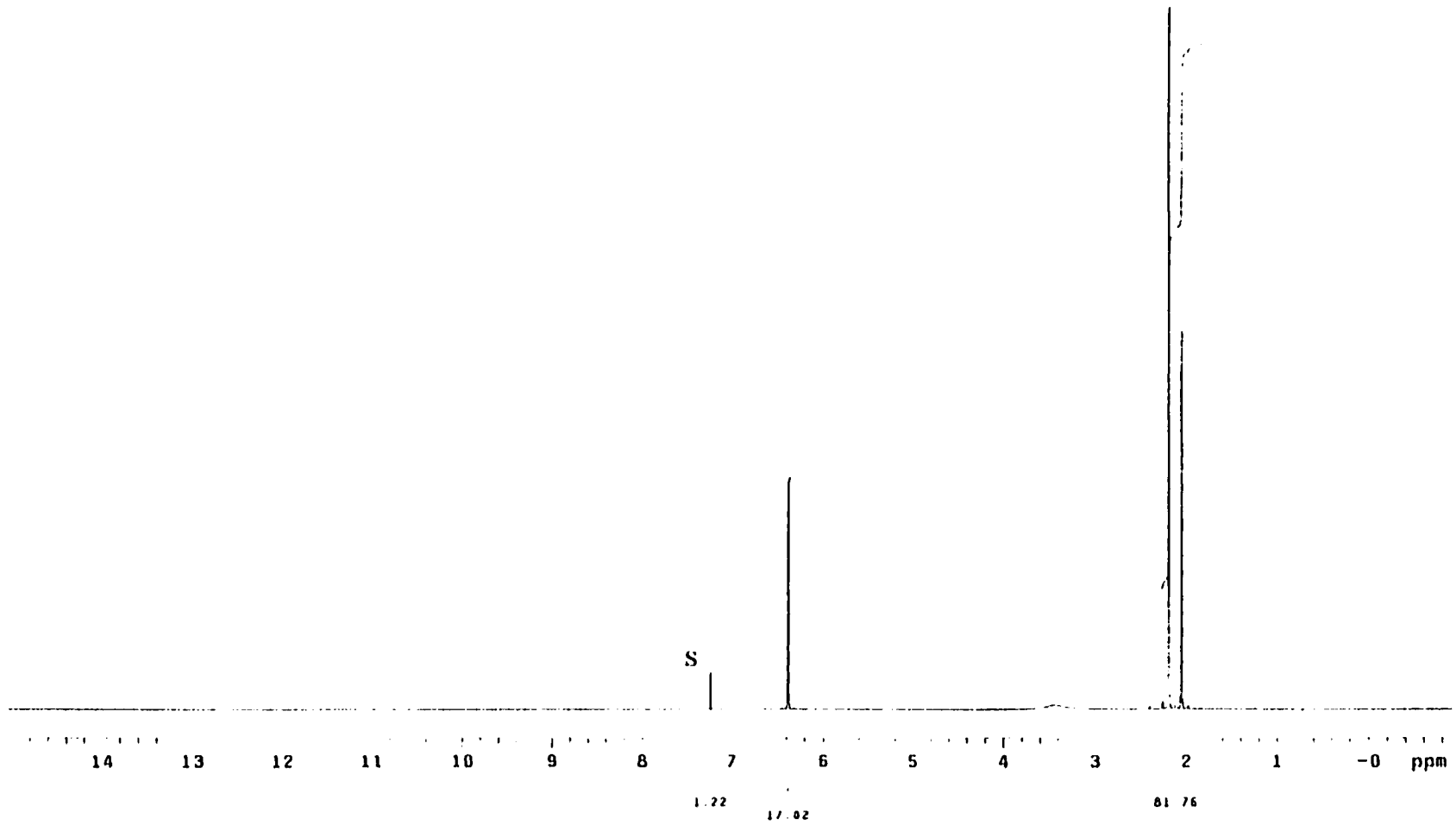


Figure A-44. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 3,4,5-trimethylaniline. (S: chloroform)

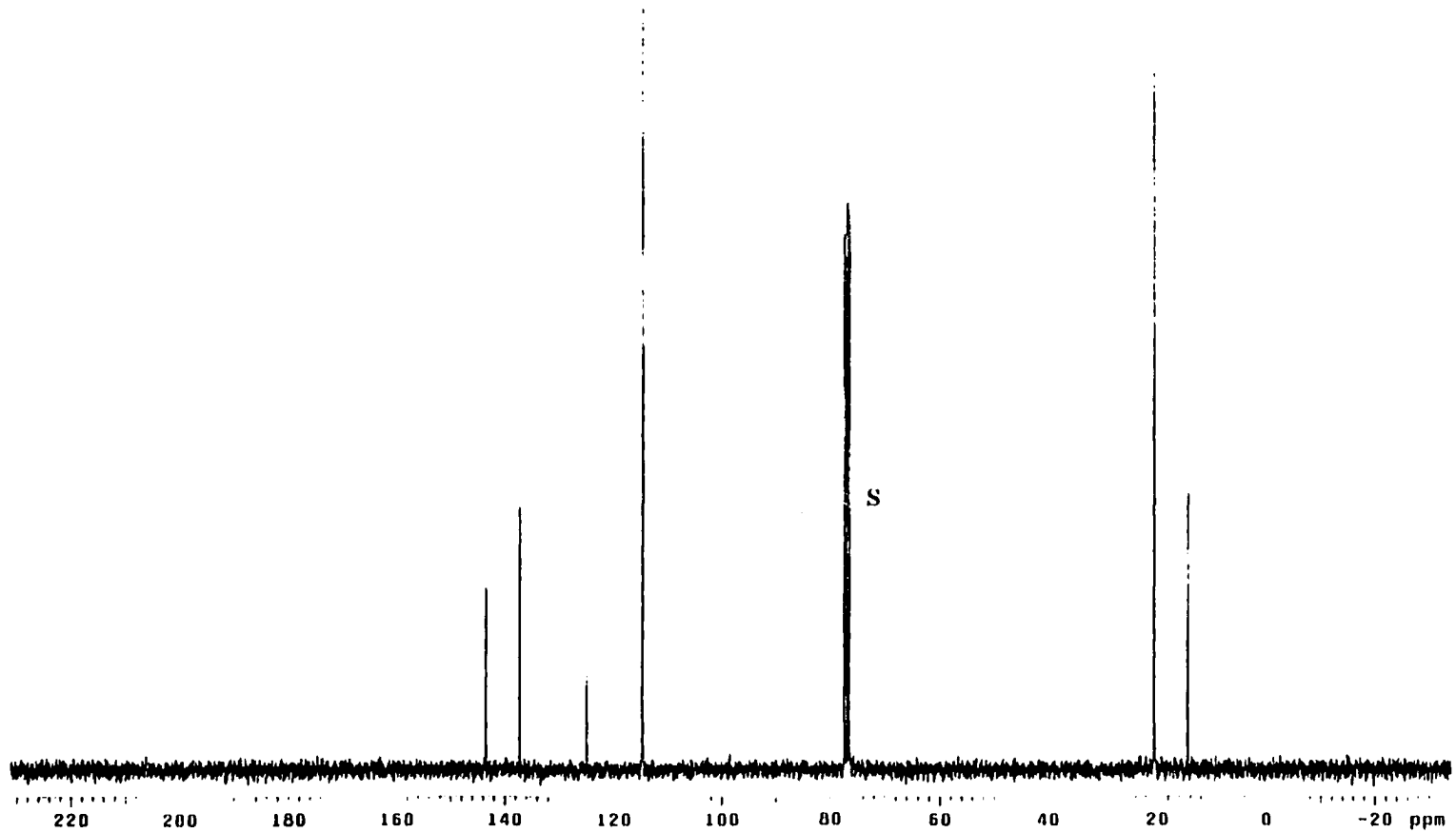


Figure A-45. ^{13}C NMR spectrum (75.4 MHz, $CDCl_3$) of 3,4,5-trimethylaniline. (S: chloroform)

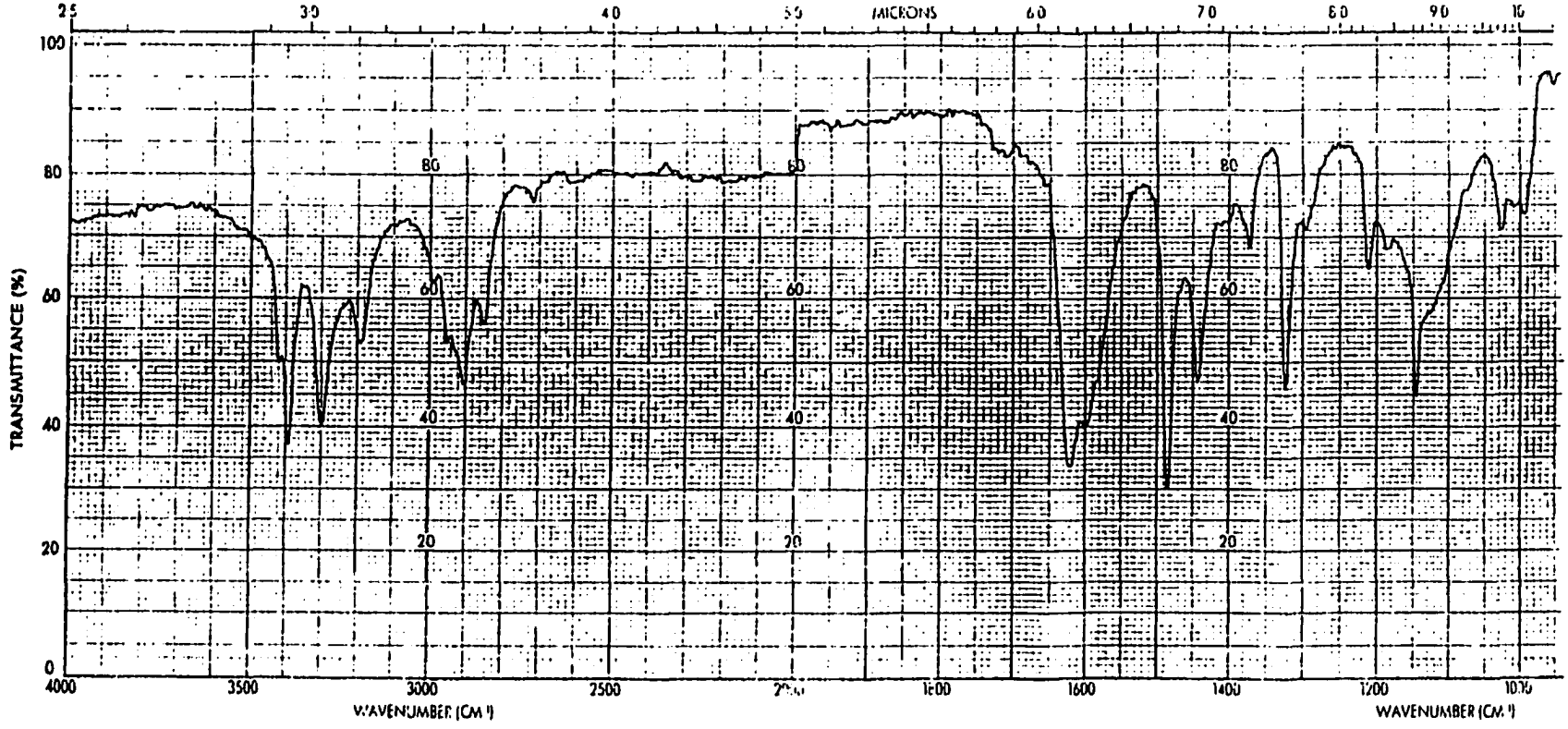


Figure A-46. Infrared spectrum of 3,4,5-trimethylaniline.

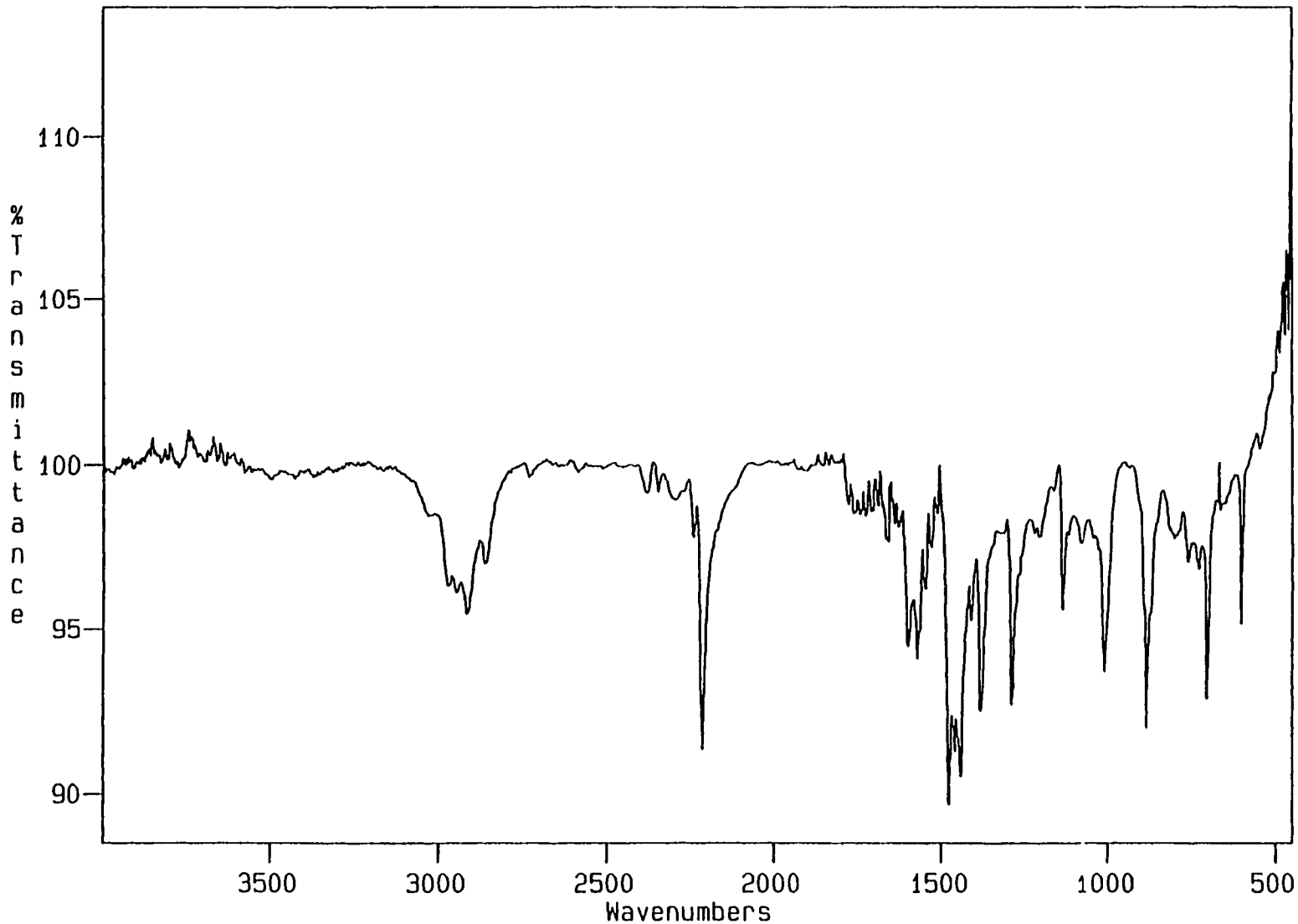


Figure A-47. Infrared spectrum of 3,4,5-trimethylbenzonitrile.

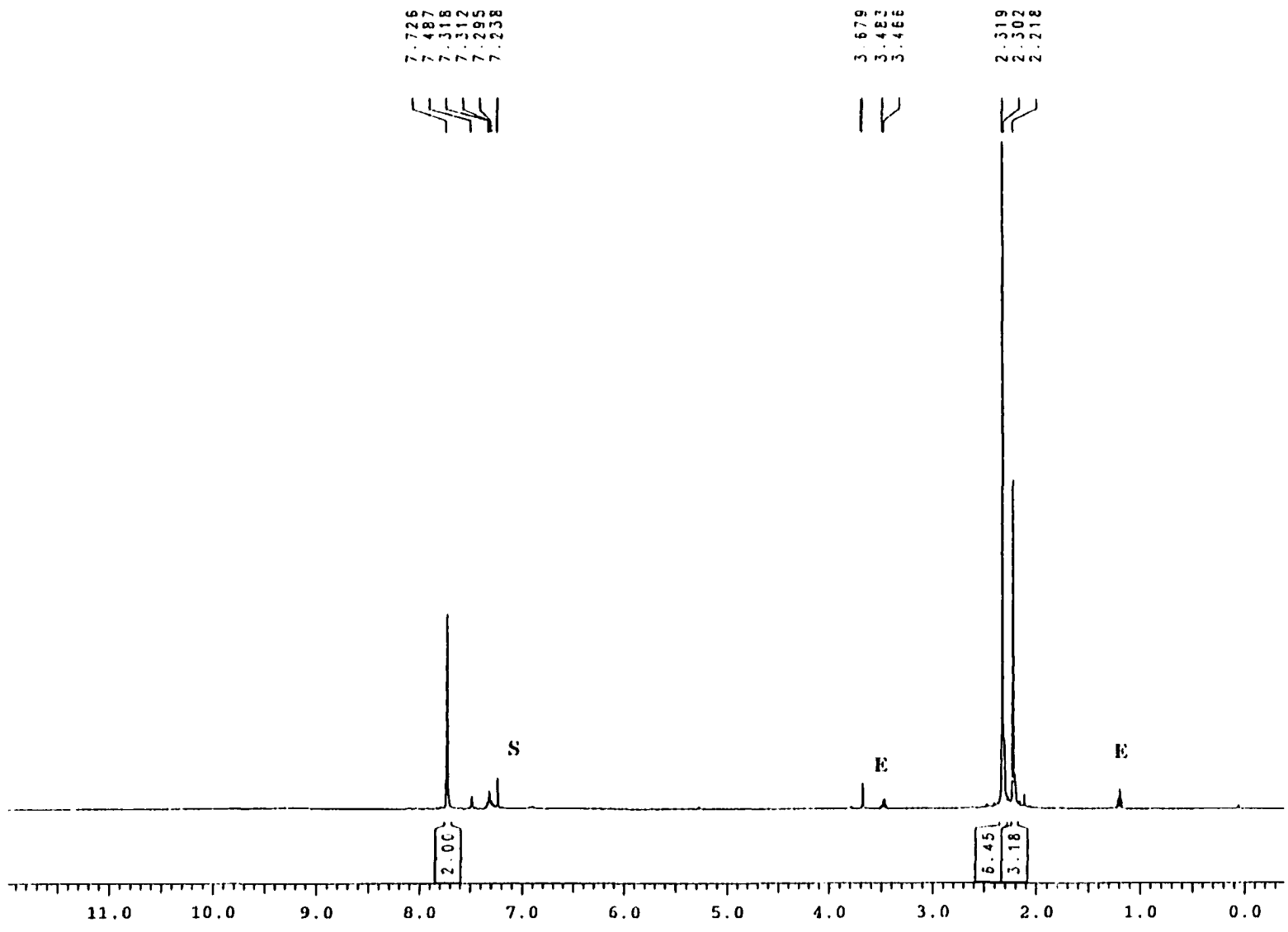


Figure A-48. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3,4,5-trimethylbenzoic acid. (E: ethyl ether, S: chloroform)

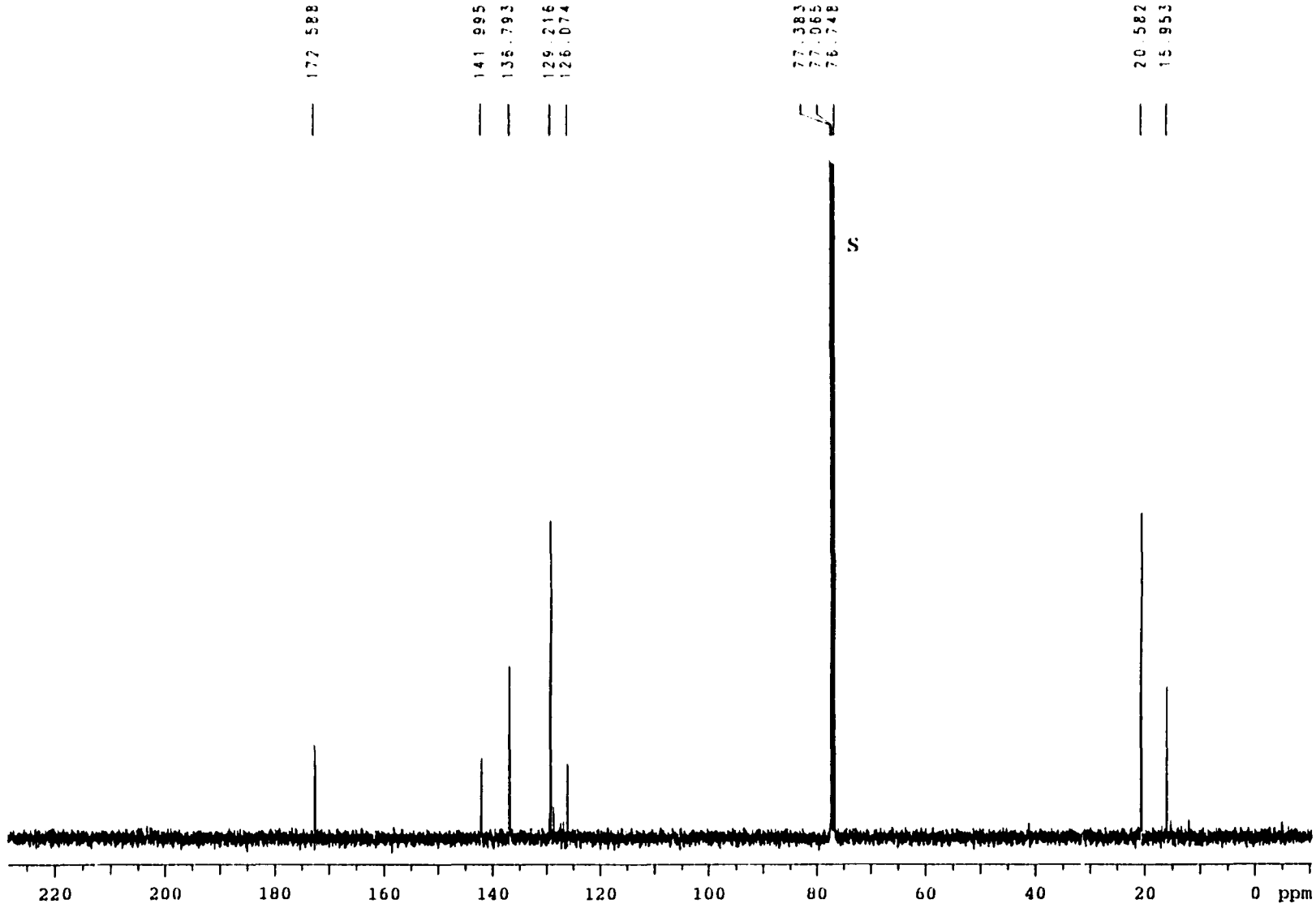


Figure A-49. ^{13}C NMR spectrum (100 MHz, CD_3CN) of 3,4,5-trimethylbenzoic acid. (S: chloroform)

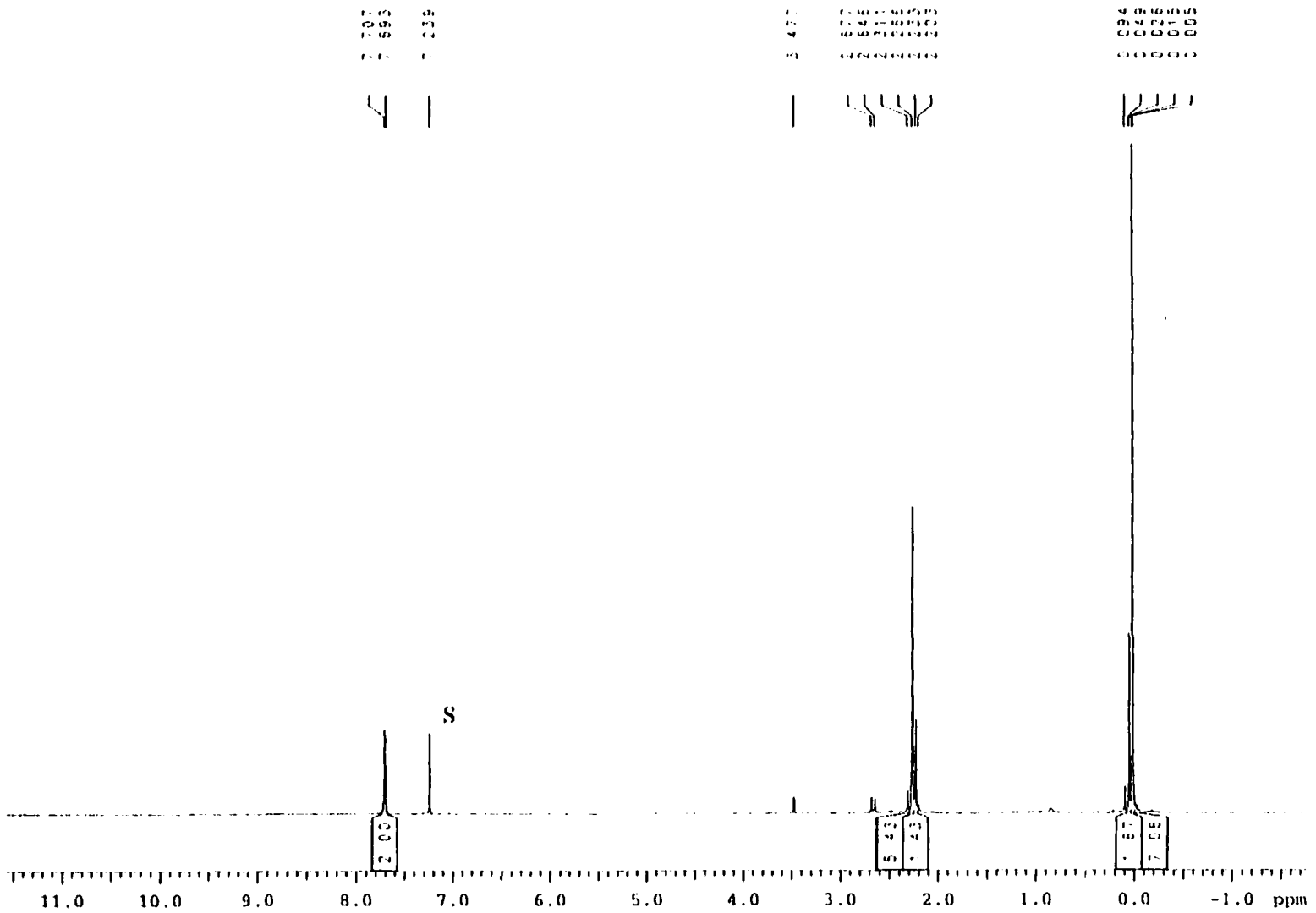


Figure A-50. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 3,5-dimethyl-4-[(trimethylsilyl)methyl]benzoic acid. (S: chloroform)

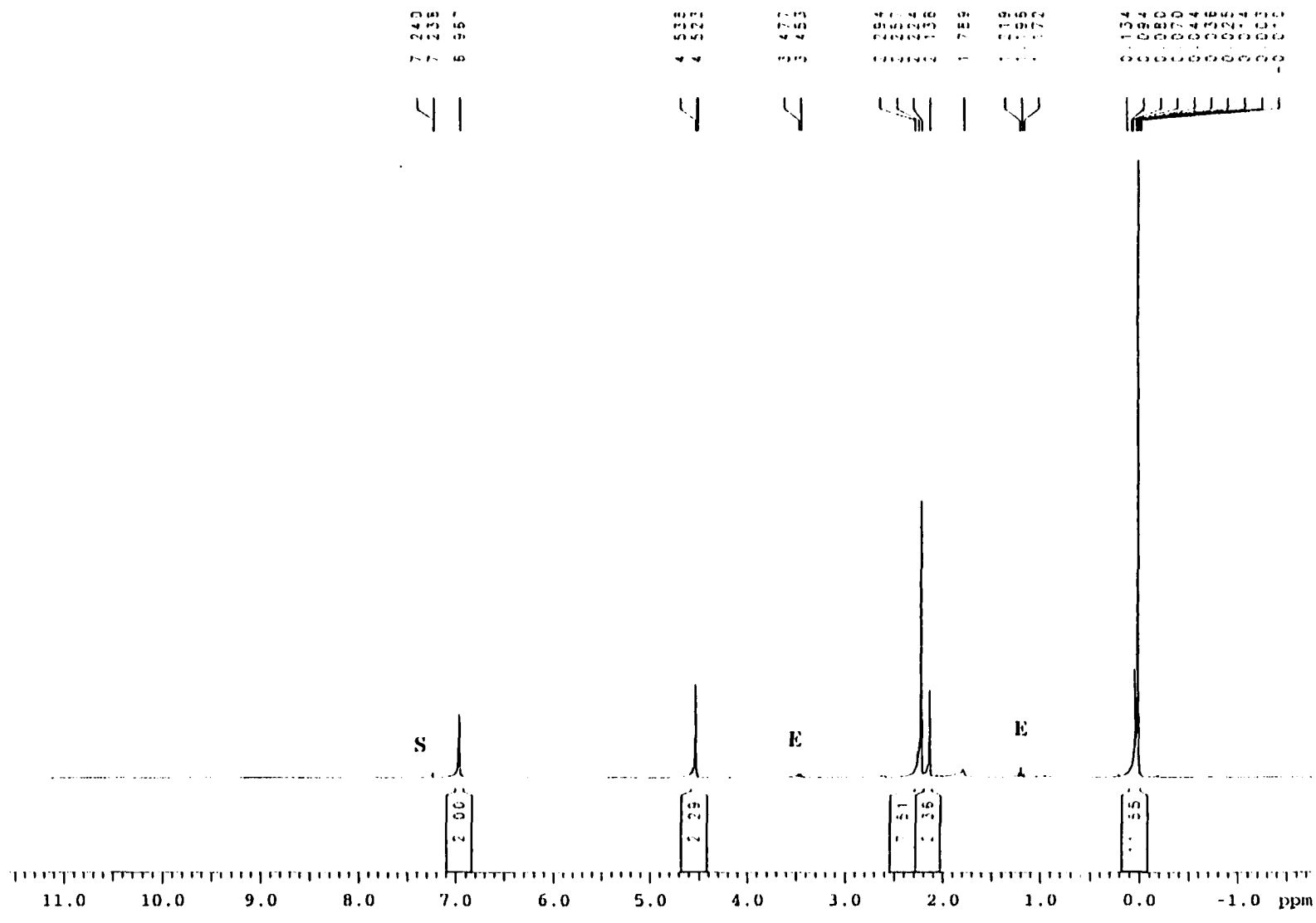


Figure A-51. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of 3,5-dimethyl-4-[(trimethylsilyl)methyl]benzyl alcohol. (E: ethyl ether, S: chloroform)

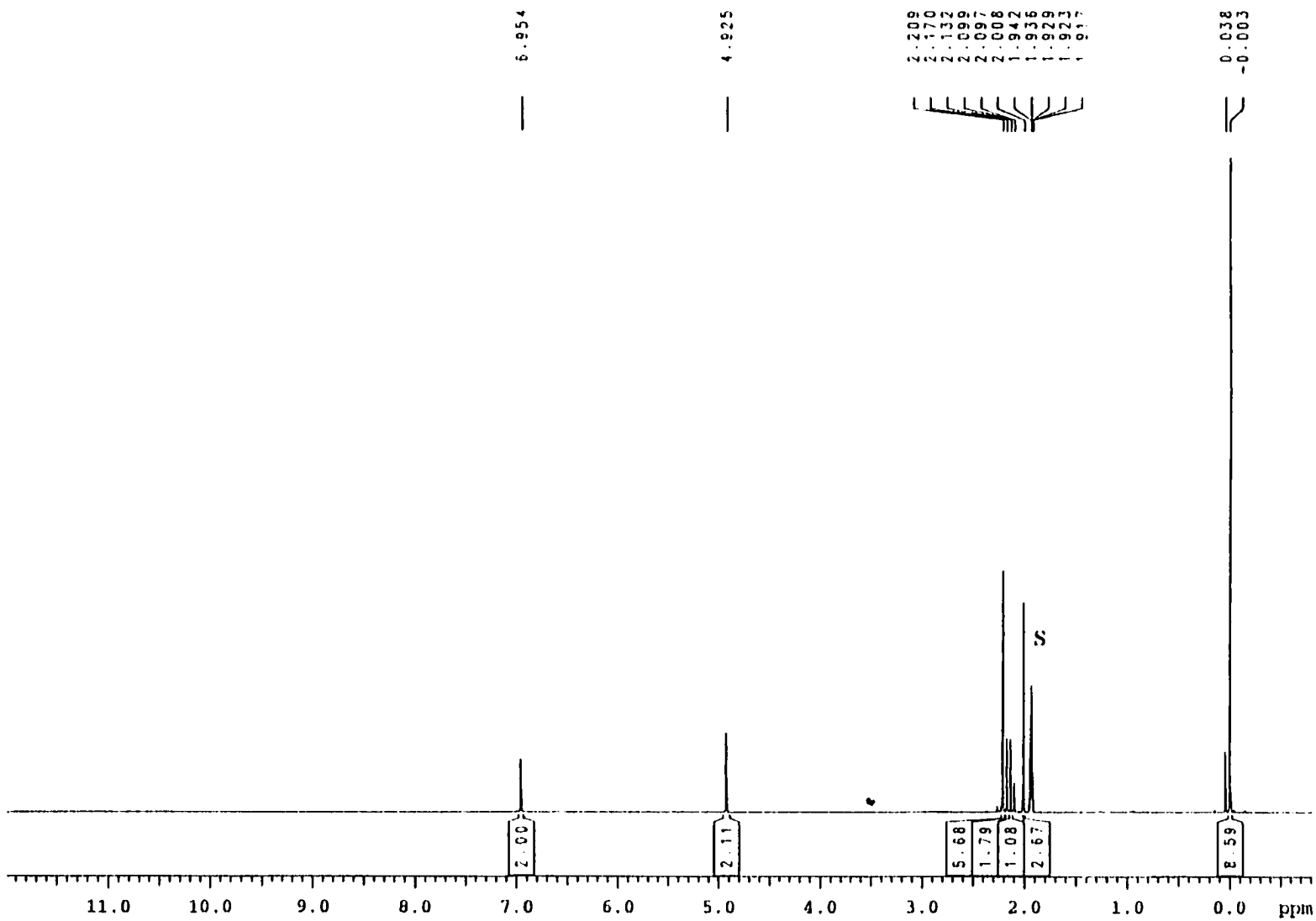


Figure A-52. ^{1}H NMR spectrum (400 MHz, CD_3CN) of [3,5-dimethyl-4-((trimethylsilyl)methyl)phenyl]methyl acetate (**19**). (**S**: acetonitrile)

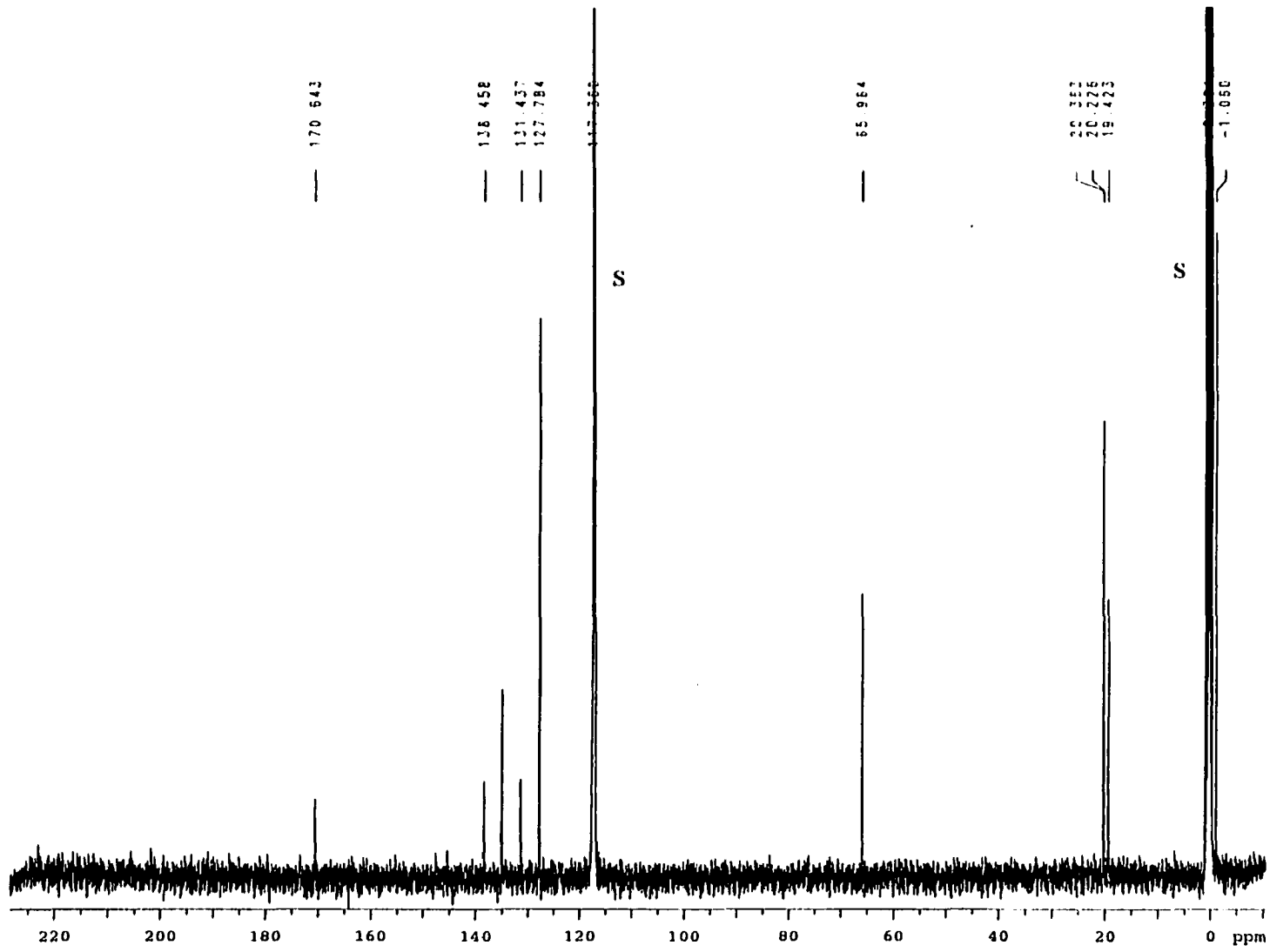


Figure A-53. ^{13}C NMR spectrum (100 MHz, CD_3CN) of [3,5-dimethyl-4-((trimethylsilyl)methyl)phenyl]methyl acetate (**19**). (S: acetonitrile)

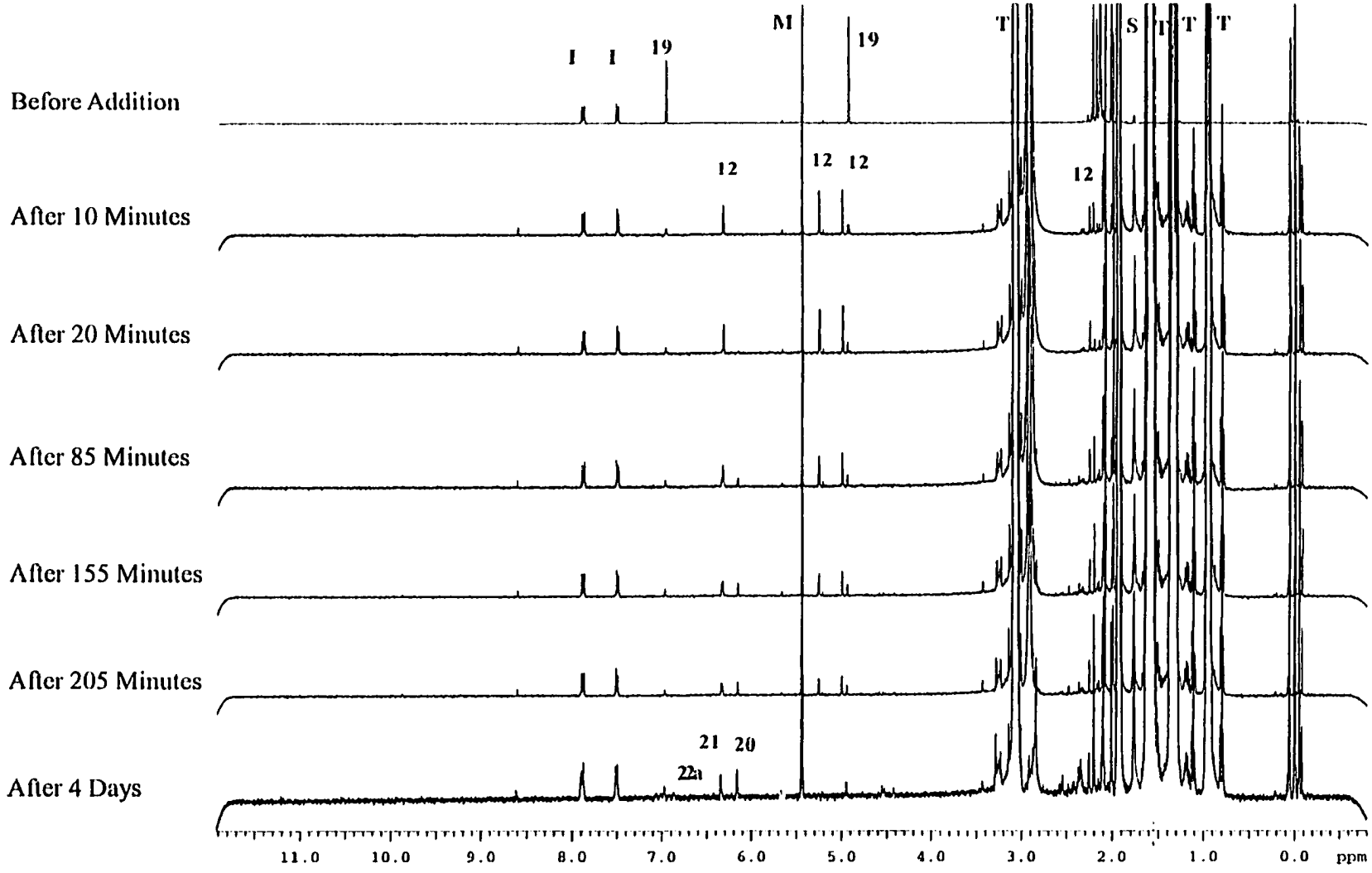


Figure A-54. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**19**, **20**, **21**, and **22a** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

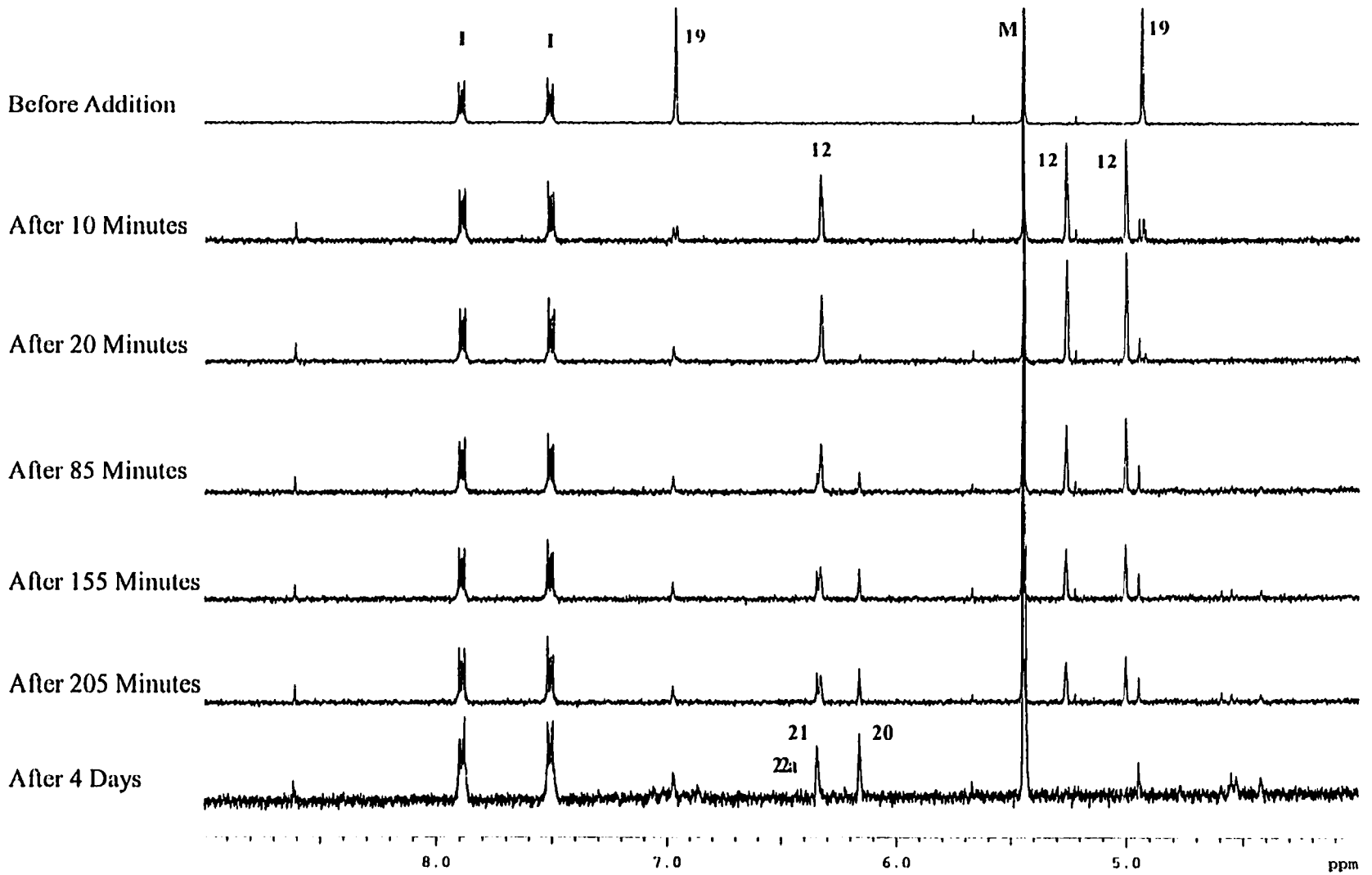


Figure A-55. Enlargement of Figure A-54 from 9–4 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**19**, **20**, **21**, and **22a** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride)

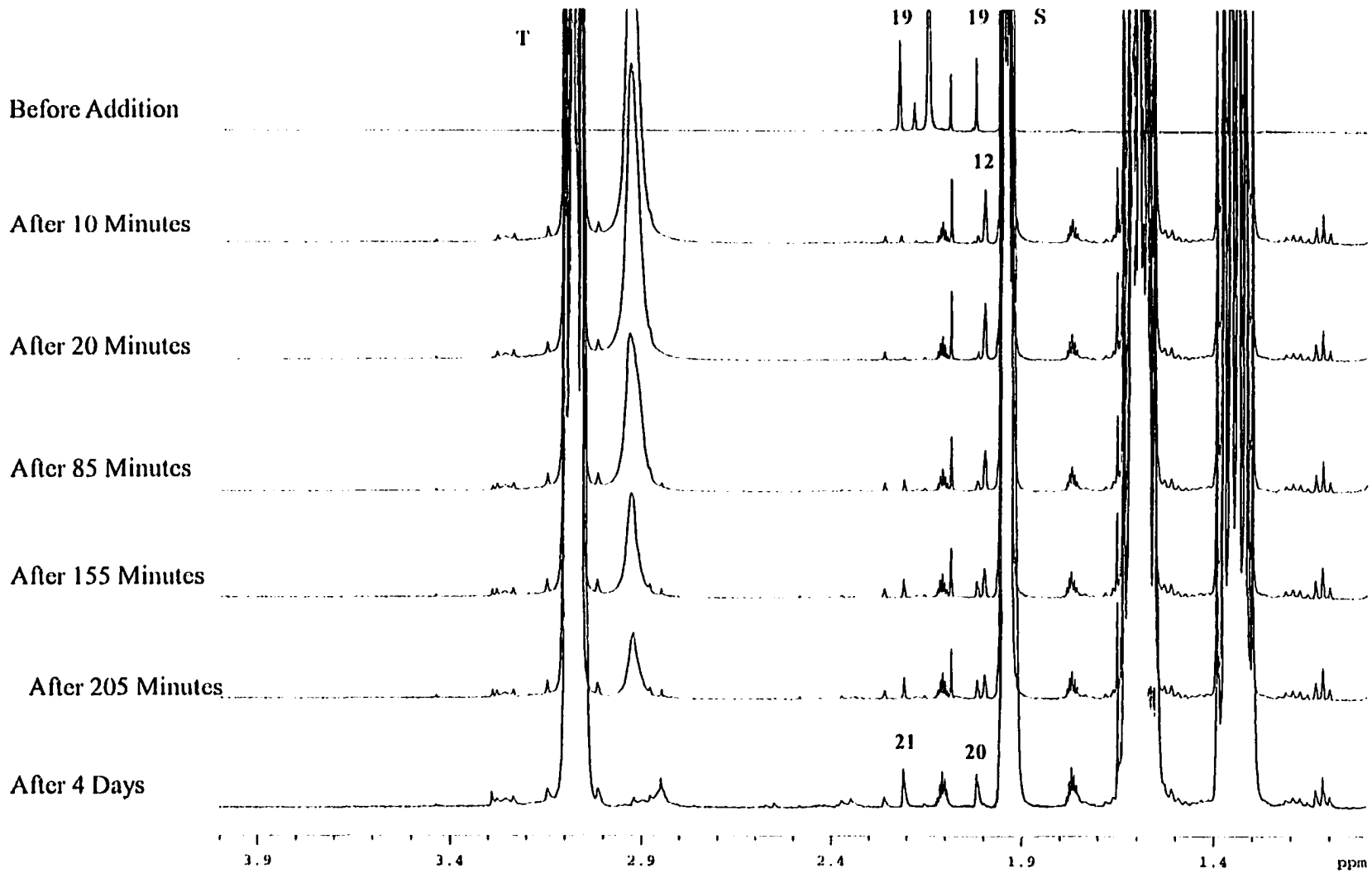


Figure A-56. Enlargement of Figure A-54 from 4–1 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**19**, **20**, and **21** are compound numbers given in the text, **S**: acetonitrile, **T**: TBAF)

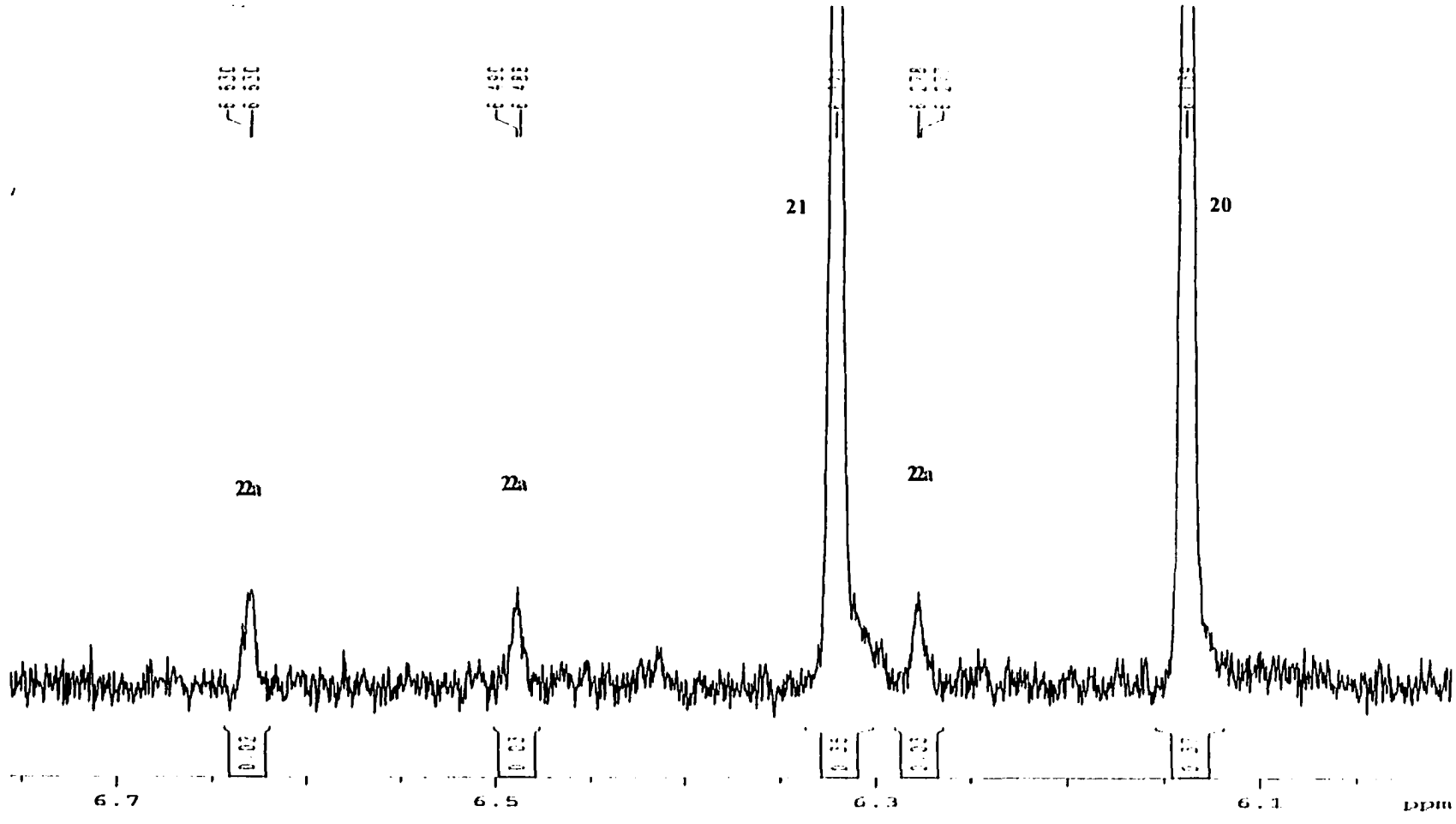


Figure A-57. Enlargement of Figure A-54 from 6.75 -6 ppm (After 4 Days only). ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**20**, **21**, and **22a** are compound numbers given in the text)

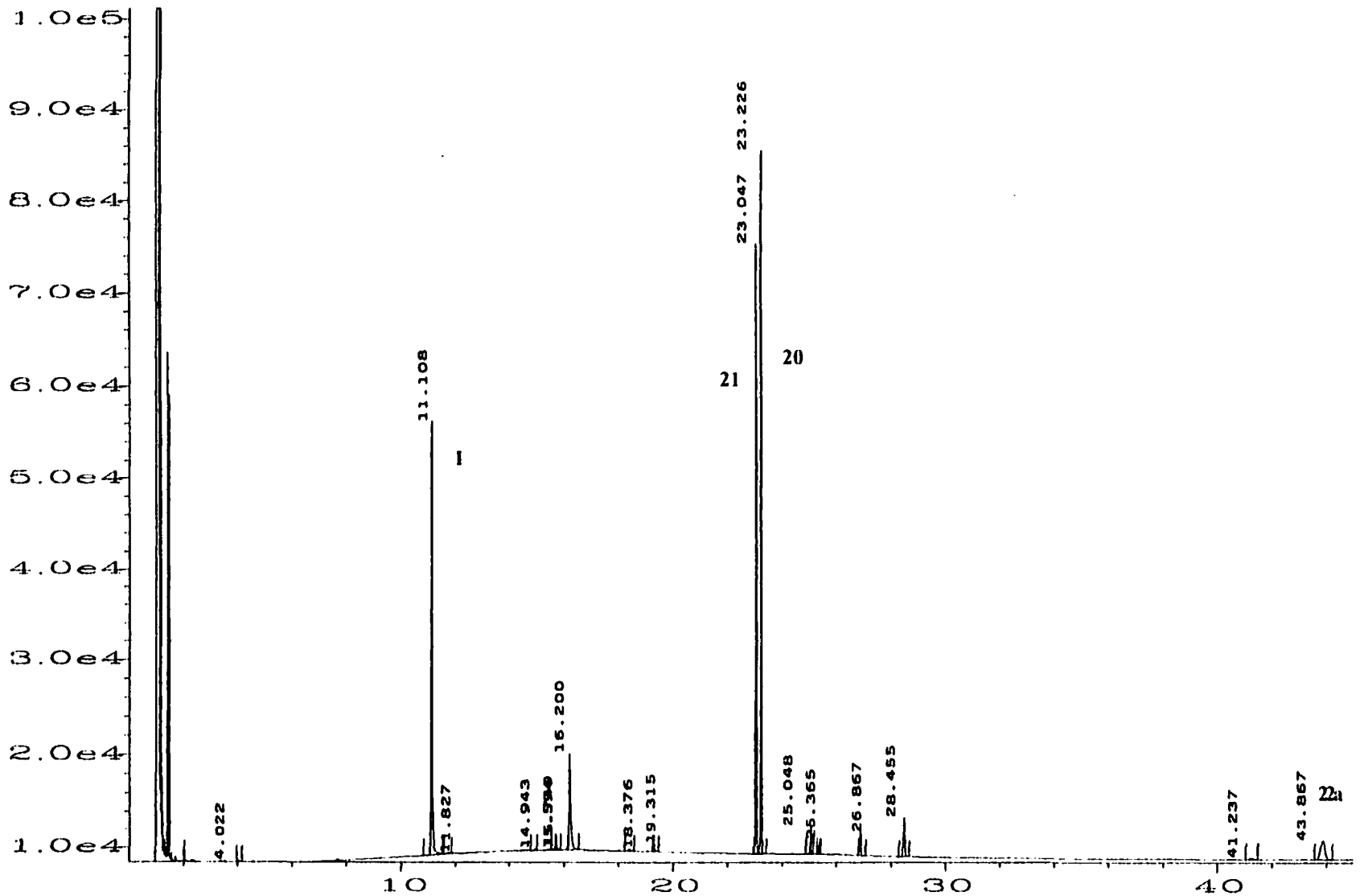


Figure A-58. GC chromatogram of the pentane extraction of product mixture of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**20**, **21**, and **22a** are compound numbers given in the text, **I**: internal standard, naphthalene)

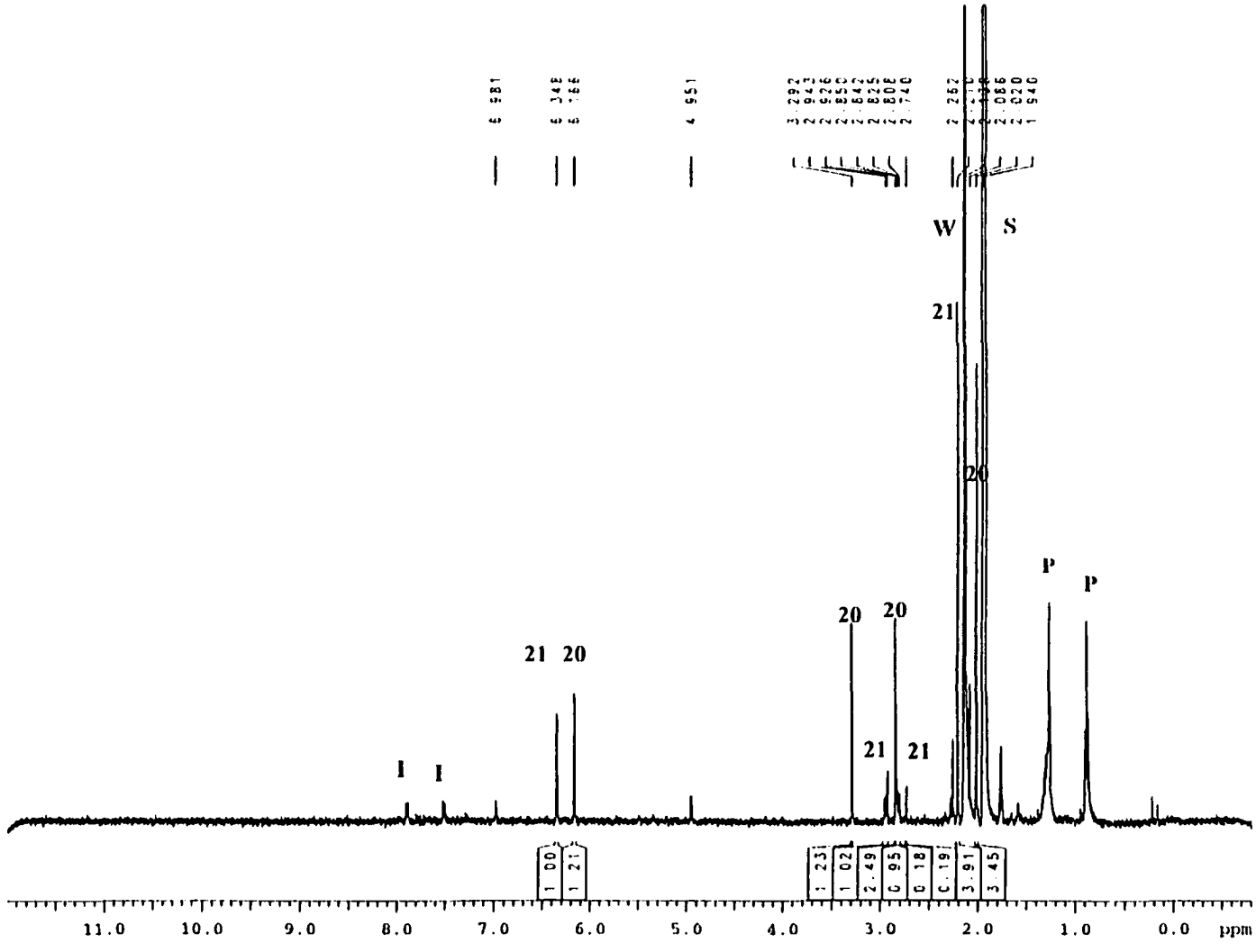


Figure A-59. ^{1}H NMR spectrum (400 MHz, CD_3CN) of pentane extraction of product mixture of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**20** and **21** are compound numbers given in the text, **I**: internal standard, naphthalene, **P**: pentane, **S**: acetonitrile, **W**: water)

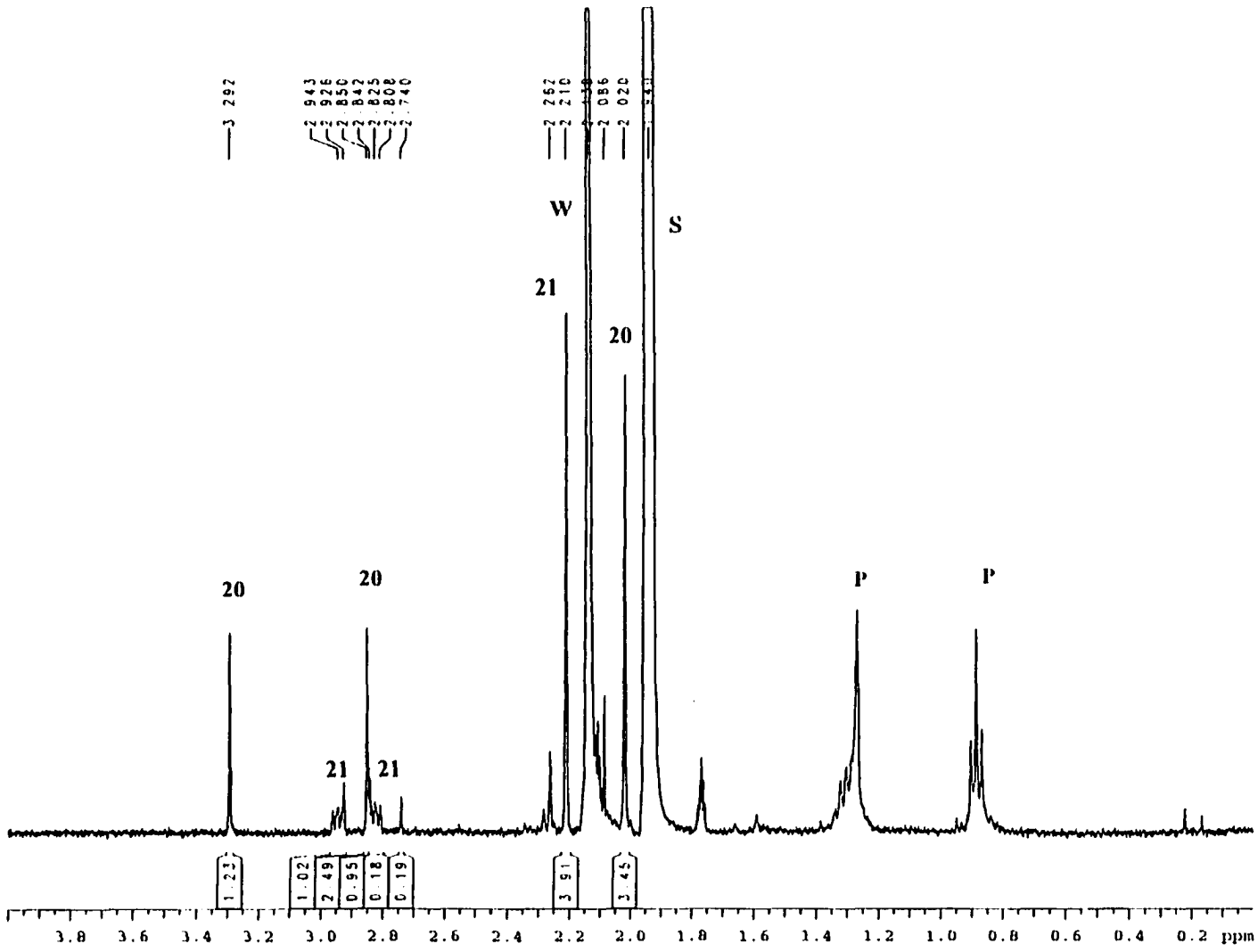


Figure A-60. Enlargement of Figure A-59 from 4–0 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of pentane extraction of product mixture of 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**20** and **21** are compound numbers given in the text, **P**: pentane, **S**: acetonitrile, **W**: water)

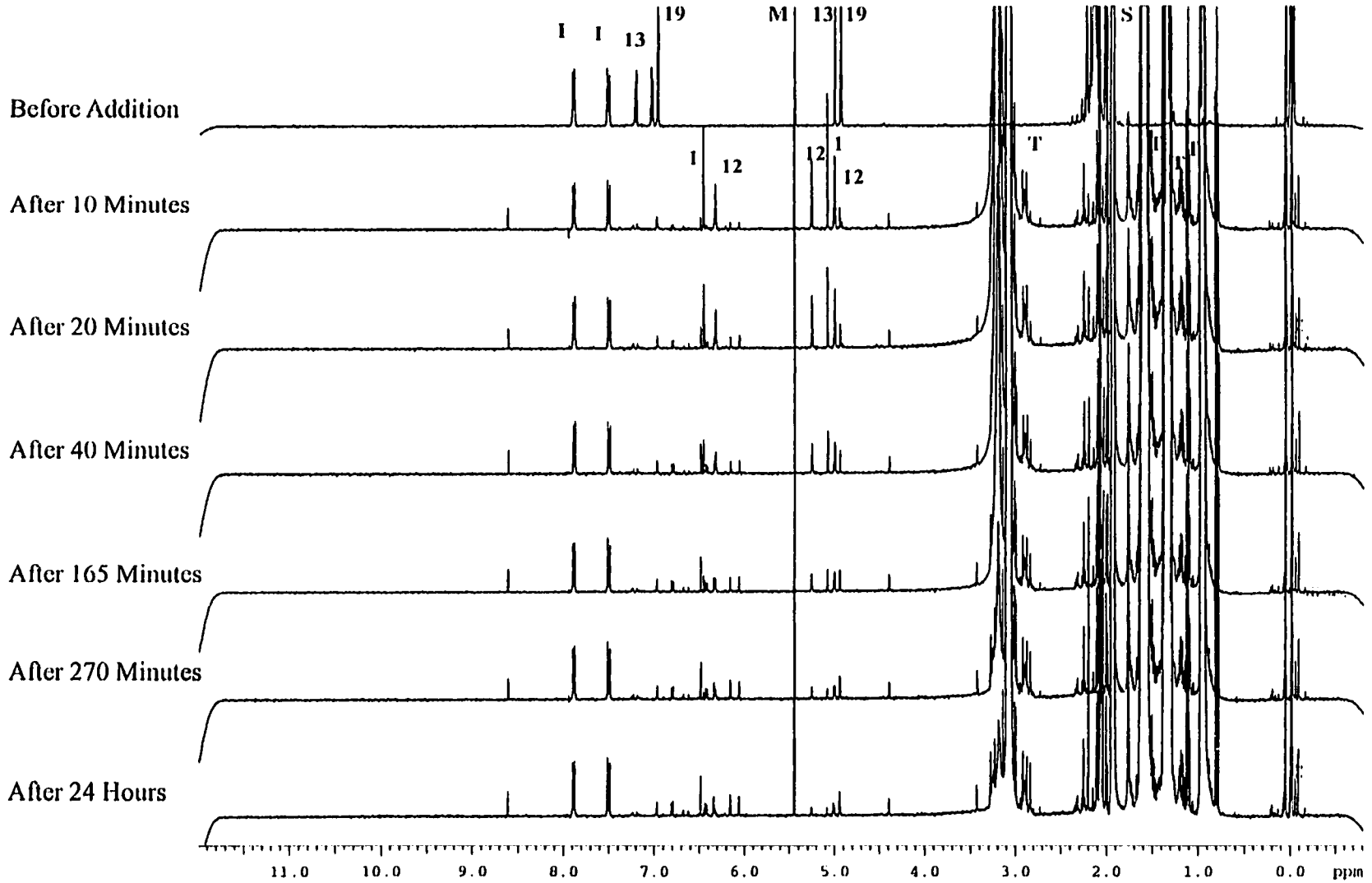


Figure A-61. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-xylylene (**1**) and 2,6-dimethyl- *p*-xylylene (**12**) in degassed CD_3CN. (**13** and **19** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF)

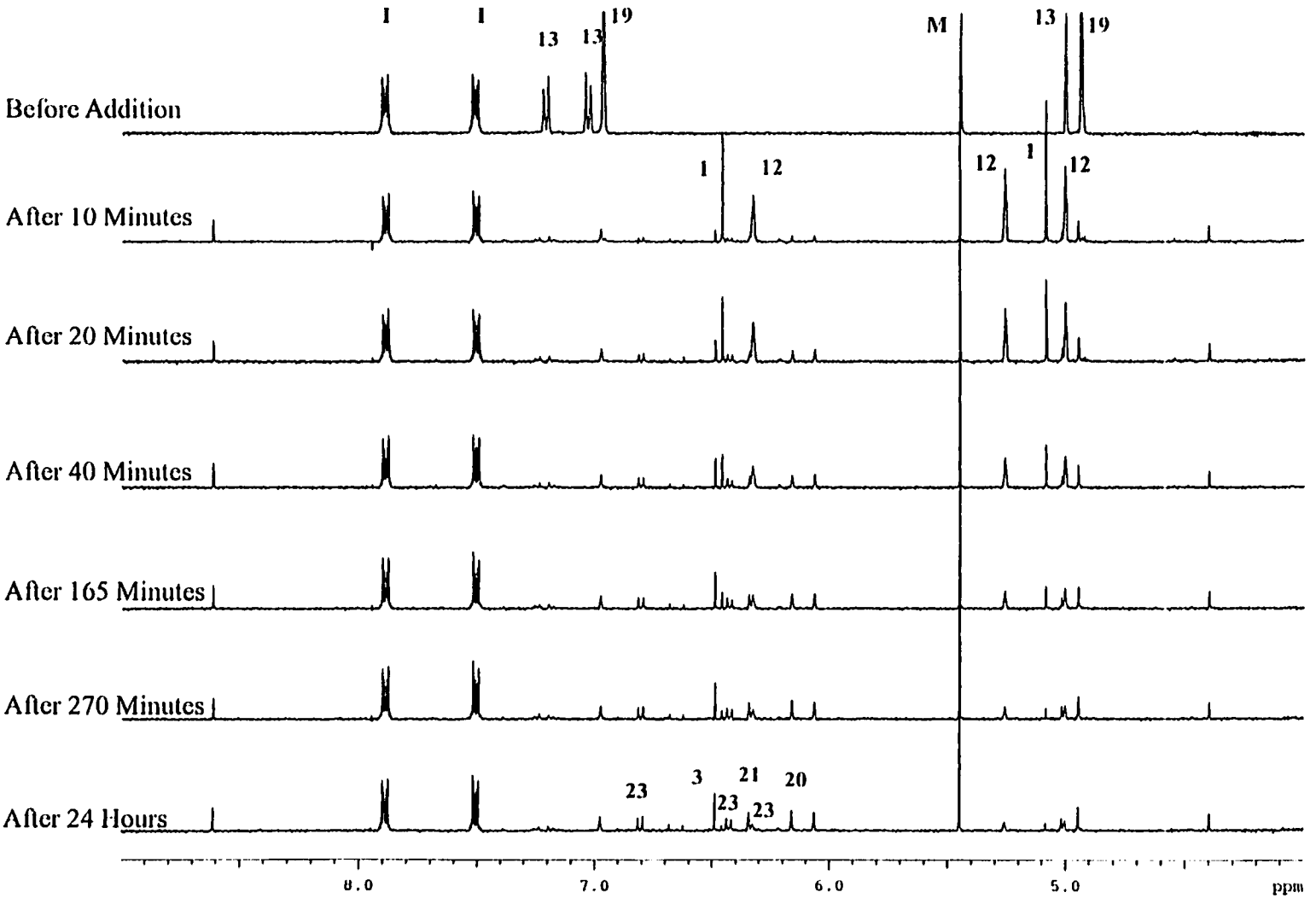


Figure A-62. Enlargement of Figure A-61 from 9-4 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-xylylene (**1**) and 2,6-dimethyl-*p*-xylylene (**12**) in degassed CD_3CN. (**3**, **13**, **19**, **20**, **21**, and **23** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride)

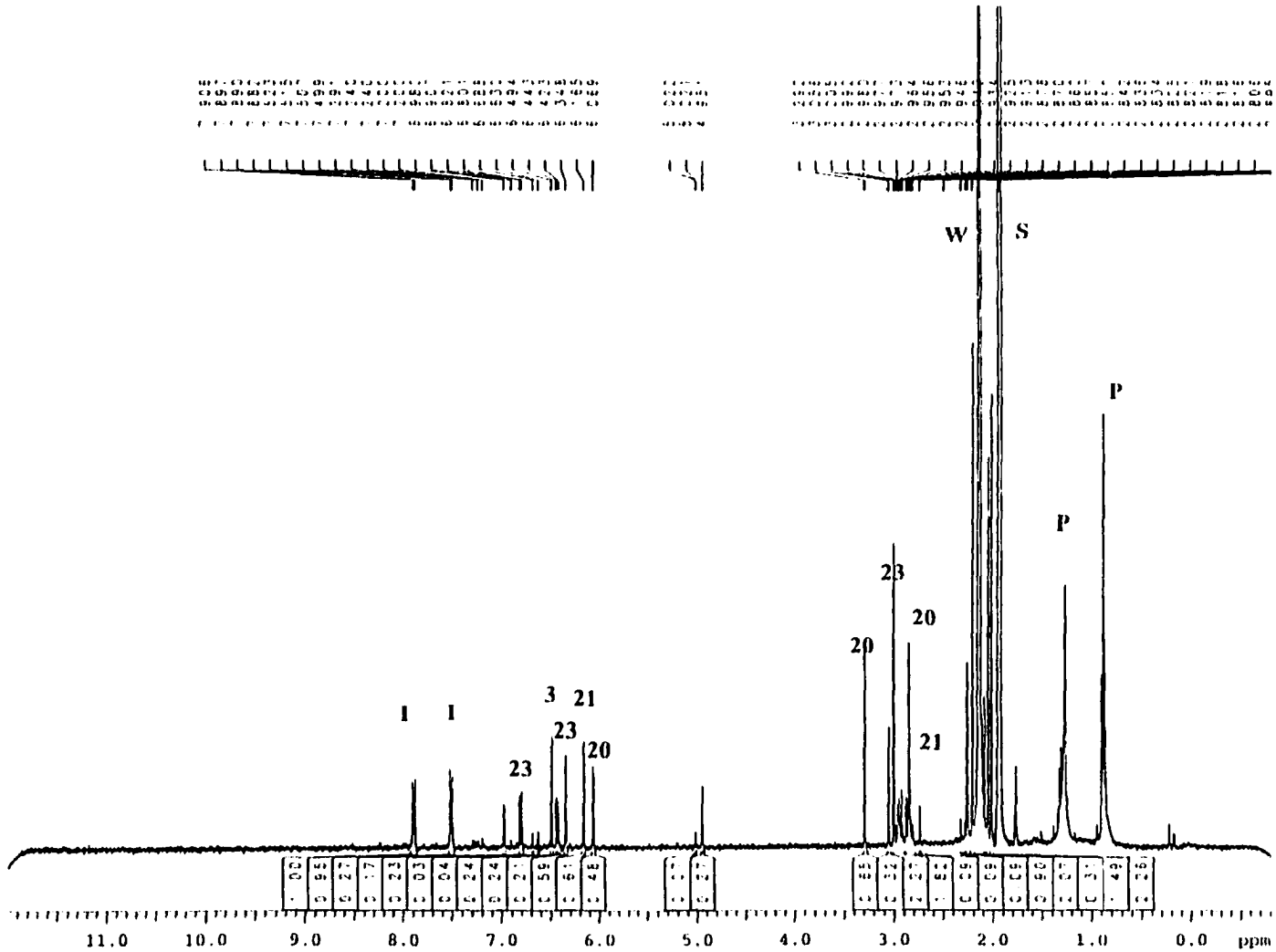


Figure A-63. ^{1}H NMR spectrum (400 MHz, CD_3CN) of pentane extraction of product mixture of *p*-xylylene (**1**) and 2,6-dimethyl- *p*-xylylene (**12**) in degassed CD_3CN. (**3**, **20**, **21**,and **23** are compound numbers given in the text, **I**: internal standard, naphthalene, **P**: pentane, **S**: acetonitrile, **W**: water)

CHAPTER 4. EFFECTS OF α-PHENYL AND α-METHYL SUBSTITUTION ON THE STABILITY OF *p*-XYLYLENES

Written in the style suitable for publication in the professional journals published by the American Chemical Society

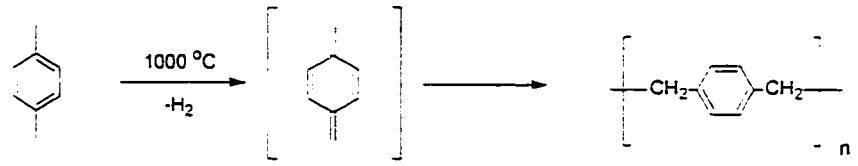
Steven P. Lorimor and Walter S. Trahanovsky

Abstract

Four reactive *p*-quinodimethanes (*p*-QDM's), *p*-xylylene (**1**), α-methyl-*p*-xylylene (**4**), α-phenyl-*p*-xylylene (**8**), and α,α-diphenyl-*p*-xylylene (**6**), were prepared as dilute solutions by fluoride induced elimination. These *p*-QDM's are stable enough in solution to be observed by ^{1}H NMR spectroscopy at room temperature. For the first time, ^{1}H NMR spectra of *p*-QDM's **6** and **8** were observed. All four *p*-QDM's were found to form dimers and insoluble oligomers. Rate constants were determined for their decomposition in order to approximate their relative stabilities. In most of the kinetic studies, both first- and second-order decompositions were occurring resulting from polymerization and dimerization, respectively. *p*-QDM **4** was found to be less reactive than the parent *p*-QDM **1**. *p*-QDM **6** was found to be the most reactive in the series followed by *p*-QDM **8**.

Introduction

p-Xylylene (**1**), the parent benzene-based *p*-quinodimethane (*p*-QDM)[1], is a reactive molecule that was first proposed as an intermediate in the pyrolysis of *p*-xylene (**2**) that yielded poly-*p*-xylylene (**3**).[2] Polymers from *p*-QDM **1** and other substituted *p*-QDM's are



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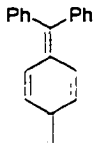
commercially useful as protective coatings.[3] Recently our research group prepared *p*-xylylene (1), α-methyl-*p*-xylylene (4), and 2,5-dimethyl-*p*-xylylene (5) as dilute solutions by fluoride induced elimination of trimethylsilyl acetate.[4] Trimers of *p*-QDM's 1, 4, and 5

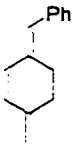
4 5

were observed which is strong evidence that they dimerize and oligomerize via a dimeric diradical intermediate. Although the trimer is good evidence of the existence of the dimeric diradical, no direct evidence was observed in the ^{1}H NMR spectrum.

In an attempt to obtain direct evidence of diradical intermediates, α,α-diphenyl-*p*-xylylene (6) was prepared. The stability of the dimeric diradical in the oligomerization of *p*-QDM 6 was expected to be similar to that of the trityl radical 7.[5] The initial experimental work found no evidence of a stable dimeric diradical intermediate but did find a substantial increased reactivity of *p*-QDM 6 compared to *p*-QDM 1. When α-phenyl-*p*-xylylene (8) was prepared, it also appeared to be more reactive than *p*-QDM 1 but less reactive than *p*-QDM 6. These results are contrary to the decreased reactivity of α-methyl-*p*-xylylene (4) when compared to the parent *p*-QDM 1.[4]



6



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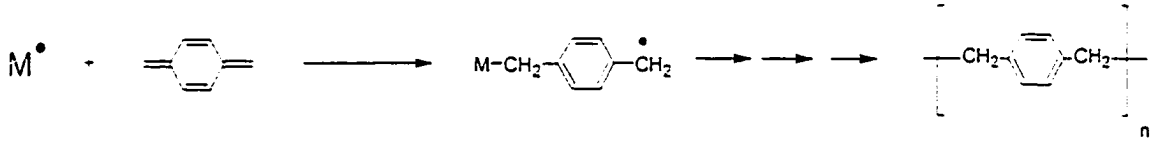
Based on previous product studies, the two major reactions that consume the *p*-QDM's are polymerization and dimerization. Errede[6] reported that solutions of *p*-QDM **1** at −78 °C polymerize by an apparent first-order process.



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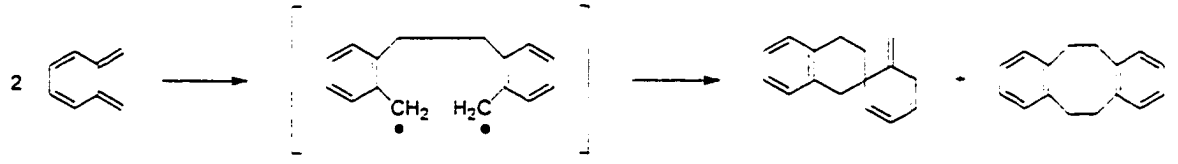
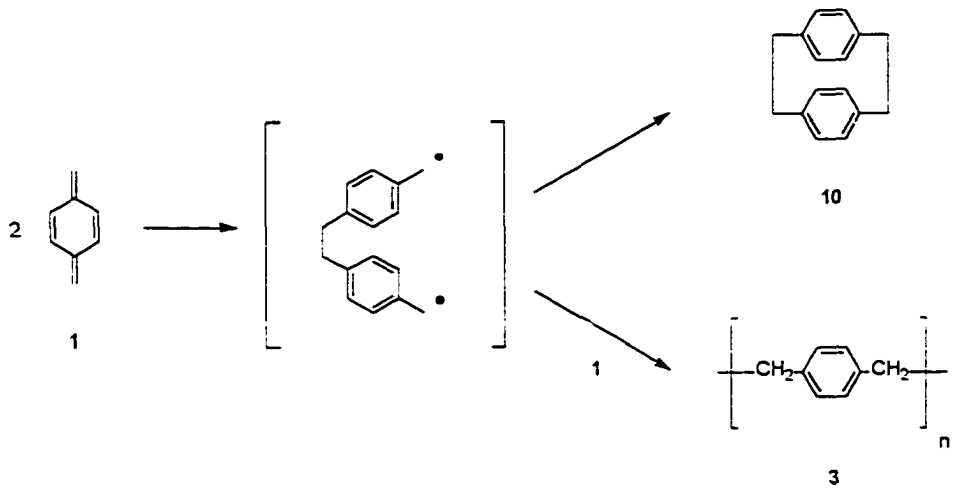
Trahanovsky and Macias[7] reported that *o*-xylylene dimerizes by a second-order process via a proposed stepwise mechanism involving a diradical intermediate.

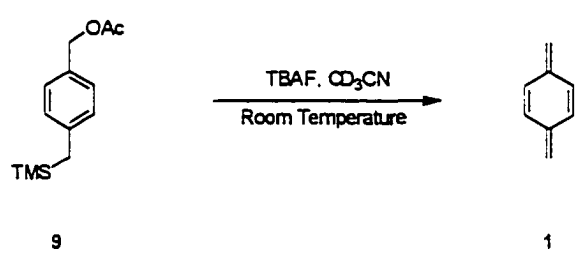


This dimerization is similar to the *p*-QDM dimerization. It can be expected that in the *para*- reaction the formation of dimeric diradical would also occur by a second-order process. Given the complex nature of the oligomerization reactions of *p*-QDM's, a feasible means of comparing their overall reactivity would be to compare their estimated second-order rate constants. In order to study the relationship between α-substituents and stability, the rate constants for the decomposition of *p*-QDM's **1**, **4**, **6**, and **8** at 20 °C were determined. The rate constants presented in this paper are approximations and are intended to be a means of estimating the relative reactivity of the four *p*-xylylenes.



Results

***p*-Xylylene (1) Long-term Kinetics Studies.** *p*-Xylylene (**1**) was prepared as a dilute solution by the fluoride induced elimination of trimethylsilyl acetate from [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**9**) and analyzed by ^{1}H NMR spectroscopy (Figure 1).



9 **1**

By comparison with naphthalene's peak integration, an internal standard, and the *p*-xylylene's (**1**) peak integration, the concentration of *p*-QDM **1** was calculated for each ^{1}H NMR spectrum taken over time. The results are presented in Table A-1. Attempts to obtain either a first-order rate constant, by plotting the natural log of the concentration verses time,

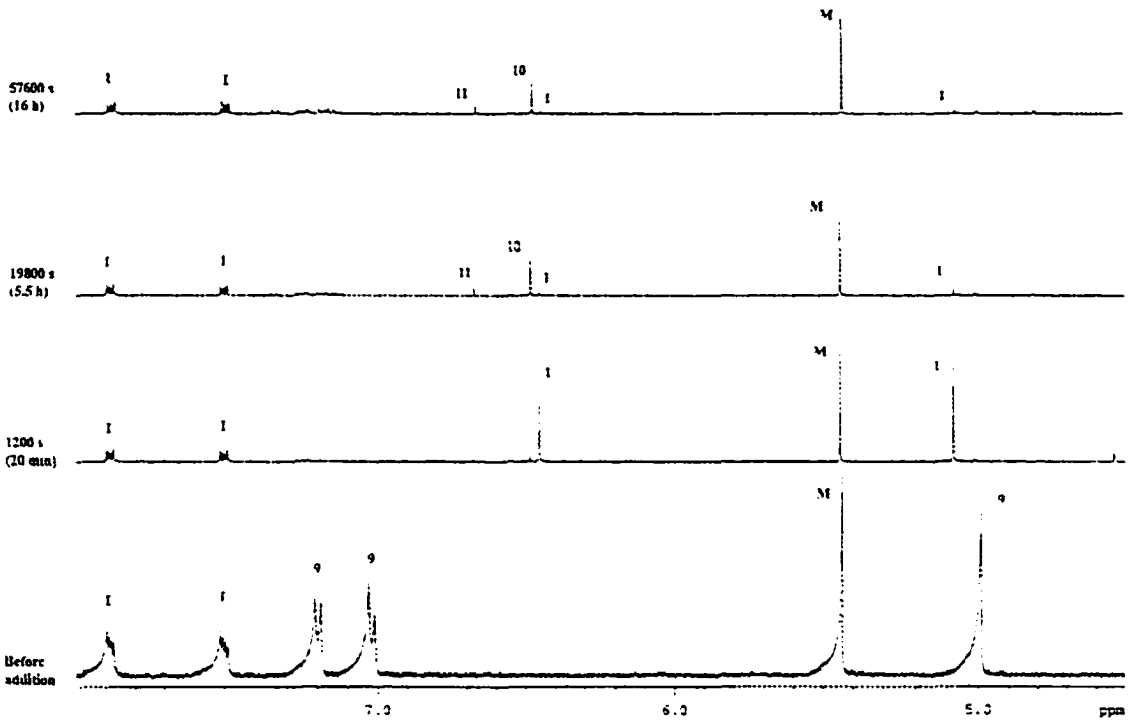


Figure 1. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress for long-term kinetics experiment of *p*-xylylene (**1**) in deoxygenated CD_3CN. (**9**, **10**, and **11** are compound numbers given in the text, **I**: internal standard, naphthalene, **M**: methylene chloride)

or second-order rate constants, by plotting the inverse concentration verses time, are shown in Figures 2 and 3. The ^{1}H NMR spectrum of the oligimerization products are consistent with [2.2]paracyclophane,[8] dimer **10**, and [2.2.2]paracyclophane,[9] trimer **11**. Consistent with the observations made earlier, the NMR tube contained precipitate.

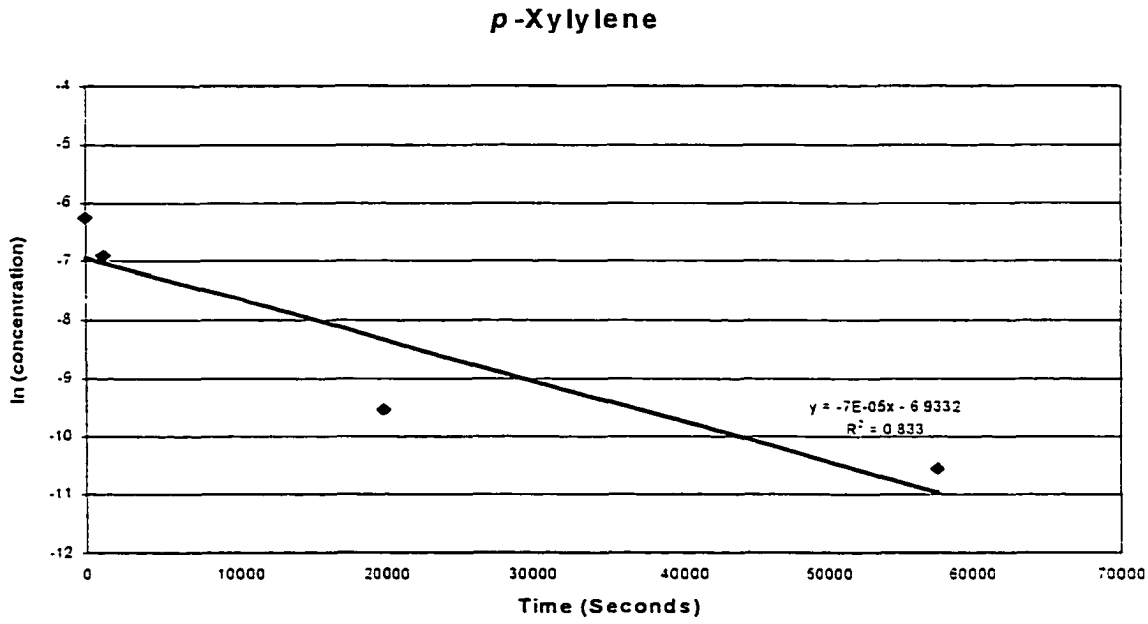


Figure 2. Plot of ln[1] vs time for long-term kinetics experiment.

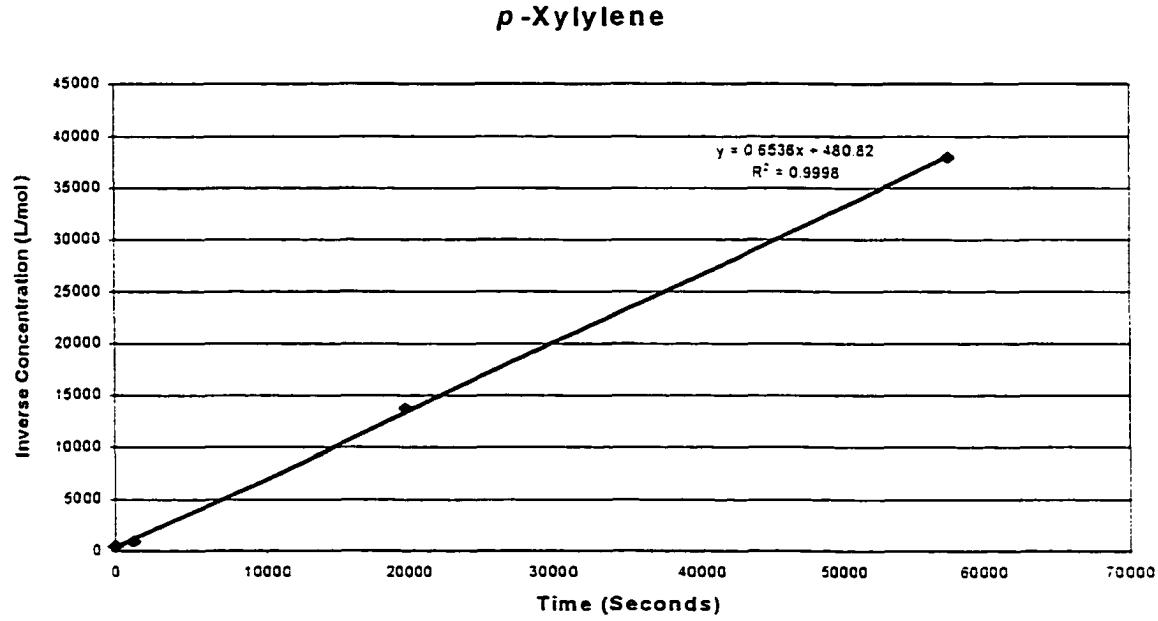
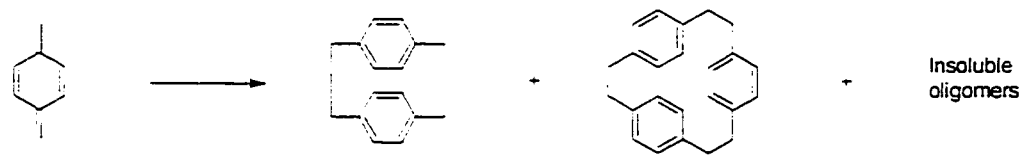
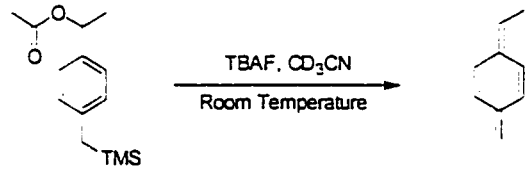


Figure 3. Plot of $[1]^{-1}$ vs time for long-term kinetics experiment.



1 10 11

α-Methyl-*p*-xylylene (4) Long-term Kinetics Studies. α-Methyl-*p*-xylylene (4) was prepared as a dilute solution by the fluoride induced elimination of trimethylsilylacetate from 1-[*p*-((trimethylsilyl)methyl)phenyl]ethyl acetate (**12**) and analyzed by ^{1}H NMR



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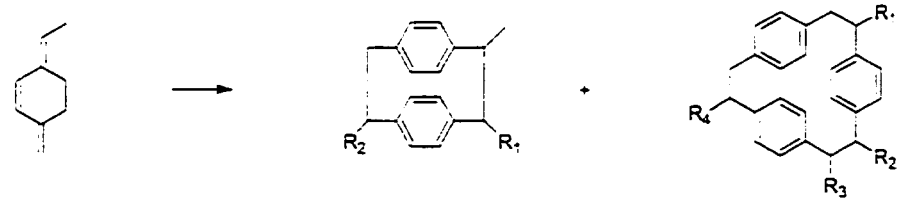
spectroscopy (Figure 4). The concentration of *p*-QDM **4** was calculated using the internal standard naphthalene and the results are presented in Table A-2. First- and second-order kinetic plots were prepared (Figures 5 and 6). The oligomerization products observed in the ^{1}H NMR spectrum are consistent with cyclic dimers **13** and trimers **14** observed in product studies.[10,11]



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13a, R_1= Me, R_2 = H
13b, R_1= H, R_2 = Me

14a, R_1=R_3= Me, R_2=R_4 = H
14b, R_1=R_3= H, R_2=R_4 = Me

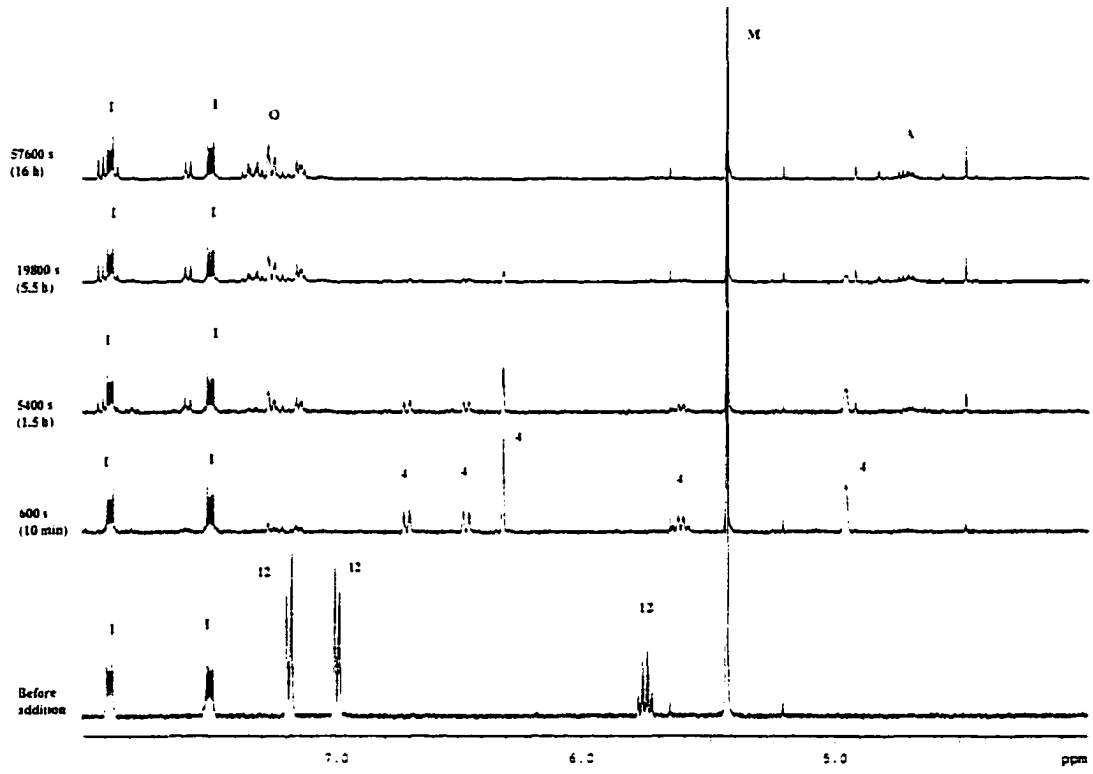


Figure 4. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress for long-term kinetics experiment of α-methyl-*p*-xylylene (**4**) in deoxygenated CD_3CN. (**12** is a compound number given in the text, **A**: oxygen adducts, **I**: internal standard, naphthalene, **M**: methylene chloride, **O**: oligomers)

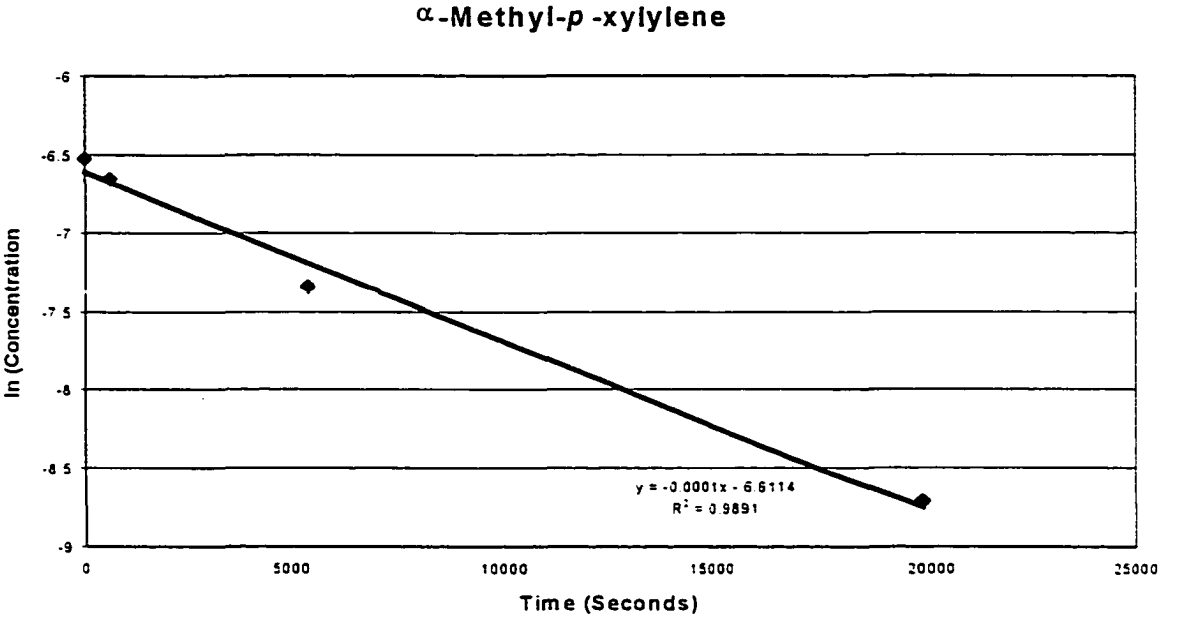


Figure 5. Plot of ln [4] vs time for long-term kinetics experiment.

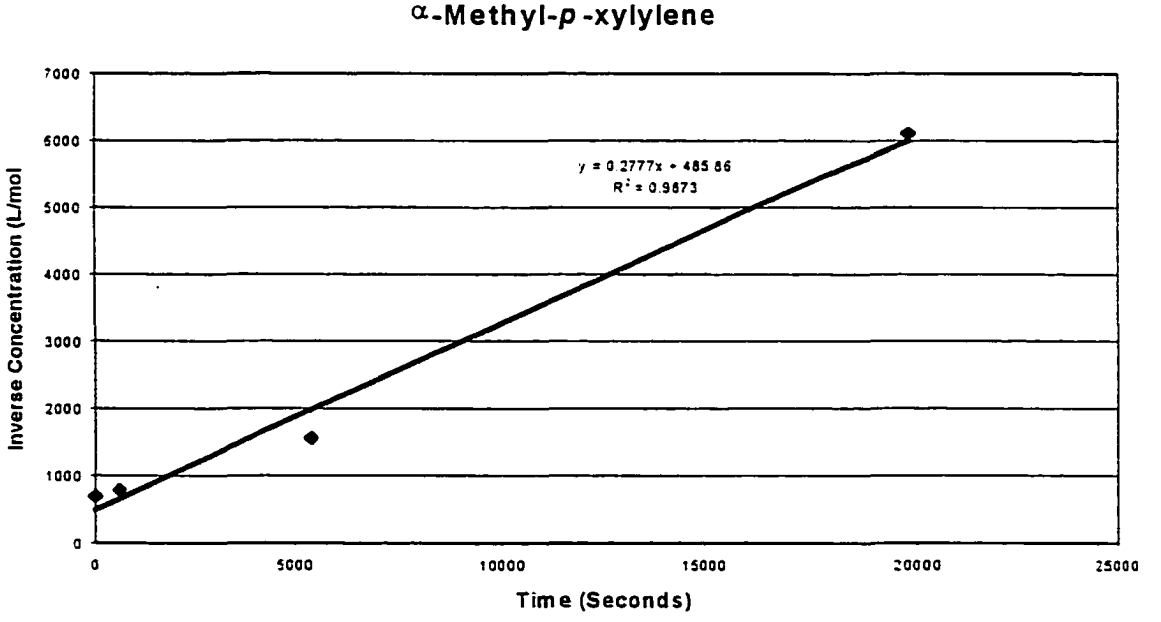


Figure 6. Plot of $[4]^{-1}$ vs time for long-term kinetics experiment.

***p*-Xylylene (1) Short-term Kinetics Studies.** *p*-Xylylene (1) was prepared the same way as above and analyzed by ^{1}H NMR spectroscopy (Figure 7). Using the same means of comparison of the naphthalene standard peaks to the *p*-xylylene peaks in the ^{1}H NMR spectra, the concentration of *p*-QDM **1** was calculated. The results are presented in Table A-3. First- and second-order kinetic plots were prepared (Figures 8 and 9).

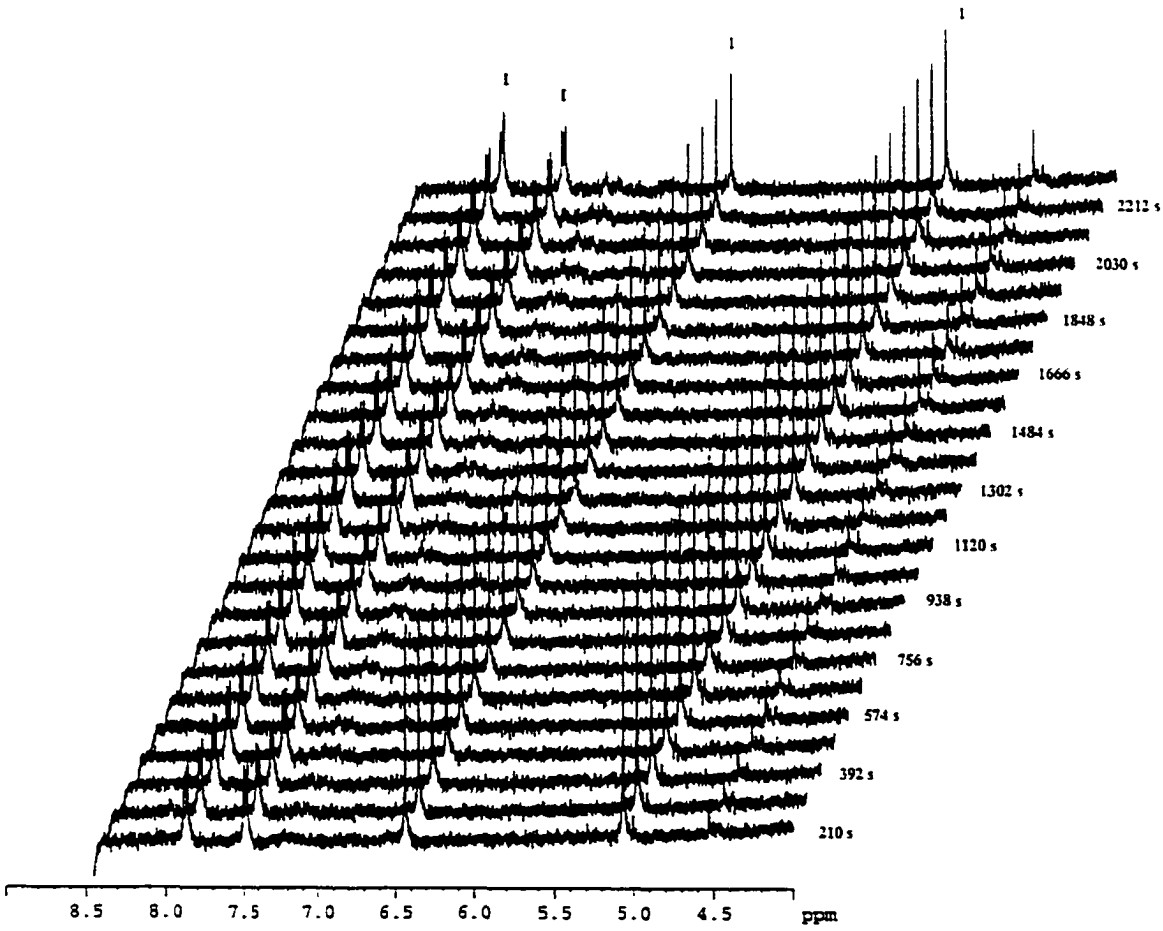


Figure 7. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress for short-term kinetics experiment of *p*-xylylene (1) in degassed CD_3CN. (**I**: internal standard, naphthalene)

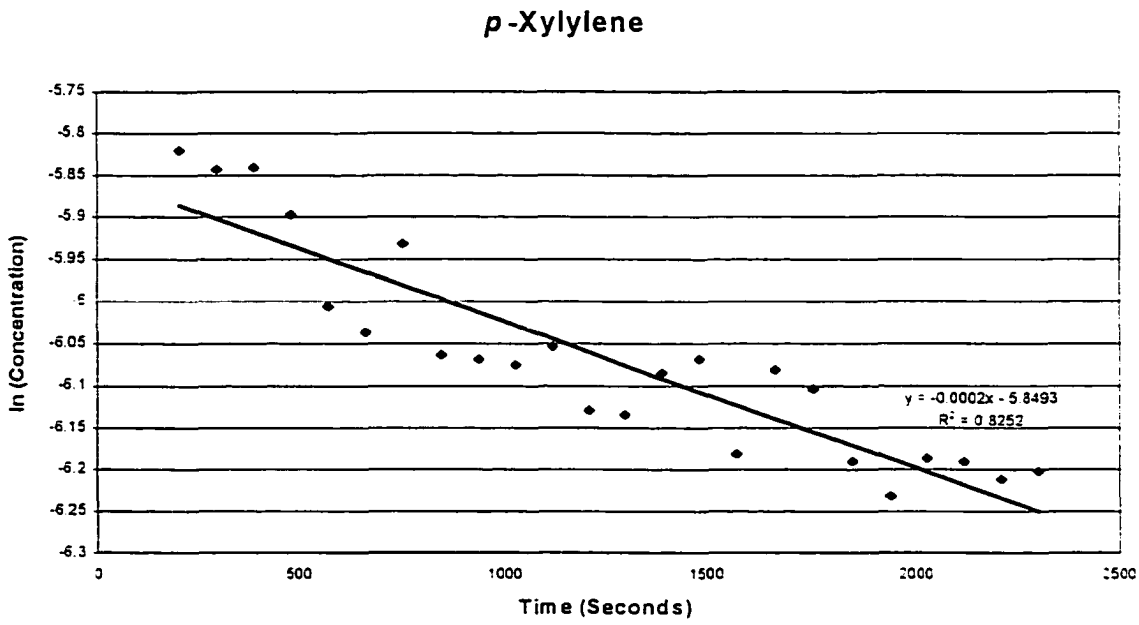


Figure 8. Plot of ln [1] vs time for short-term kinetics experiment.

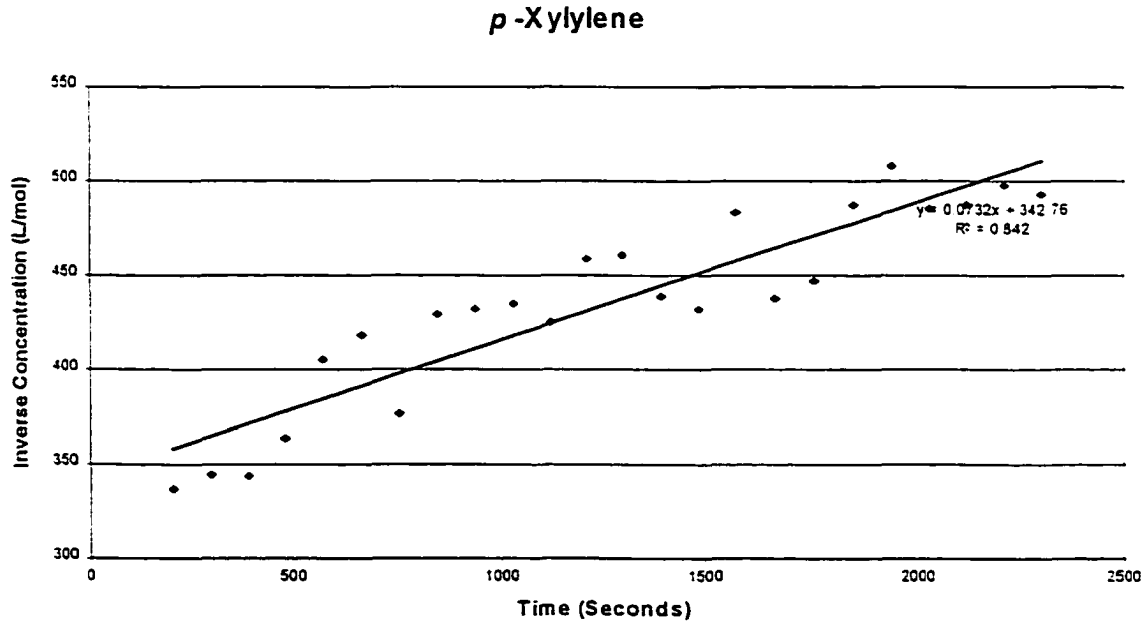
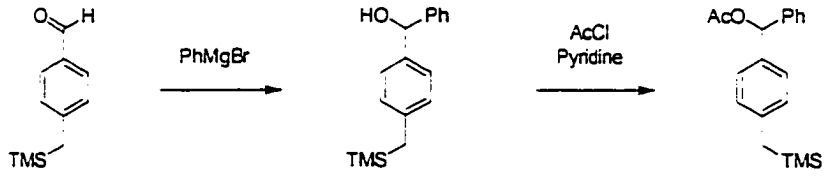


Figure 9. Plot of $[1]^{-1}$ vs time for short-term kinetics experiment.

Within the time span of this kinetic experiment only traces of dimer were formed. After standing overnight, the reaction mixture showed NMR peaks for both dimer **10** and trimer **11** contained a precipitate.

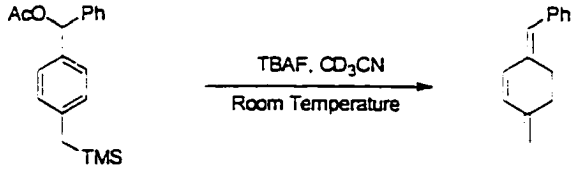
Generation and Oligomerization of α-Phenyl-*p*-xylylene (8). (4-[(Trimethylsilyl)methyl]phenyl)phenylmethyl acetate (**15**) was prepared from 4-[(trimethylsilyl)methyl]benzaldehyde (**16**) as shown in Scheme 1. α-Phenyl-*p*-xylylene (**8**) was prepared as a

Scheme 1



16 **17** **15**

dilute solution by the fluoride induced elimination of trimethylsilylacetate from (4-[(trimethylsilyl)methyl]phenyl)phenylmethyl acetate (**15**). The ^{1}H NMR spectra are



15 **8**

presented in Figure 10. Using the same means of comparison of the naphthalene standard peaks to *p*-QDM **8** peaks in the ^{1}H NMR spectra, the concentration of *p*-QDM **8** was calculated and the results are presented in Table A-4. First- and second-order kinetic plots were prepared (Figures 11 and 12).

α-Phenyl-*p*-xylylene (**8**) was prepared on a larger scale with non-deuterated solvents.

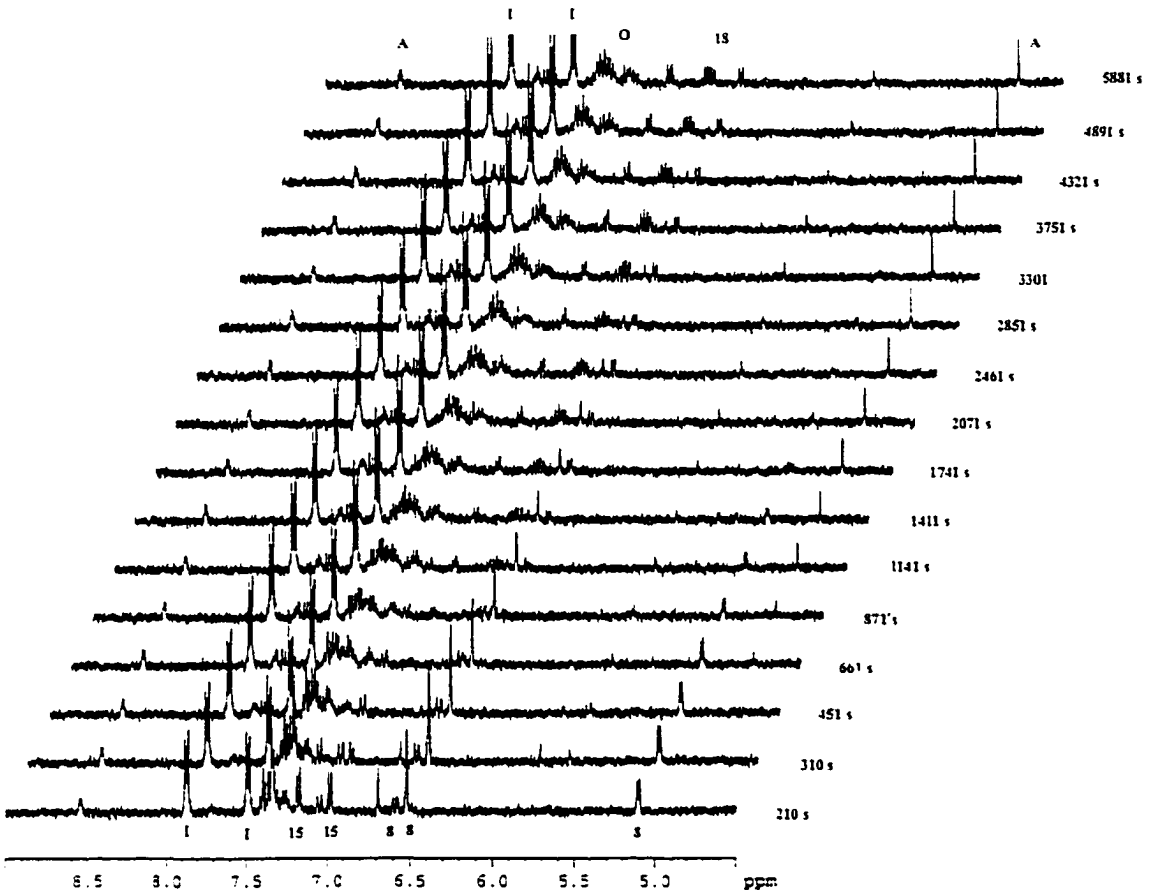


Figure 10. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress for kinetics experiment of α-phenyl-*p*-xylylene (**8**) in degassed CD_3CN. (**15** and **18** are compound numbers given in the text, **A**: oxygen adducts, **I**: internal standard, naphthalene, **O**: oligomers, **X**: impurity)

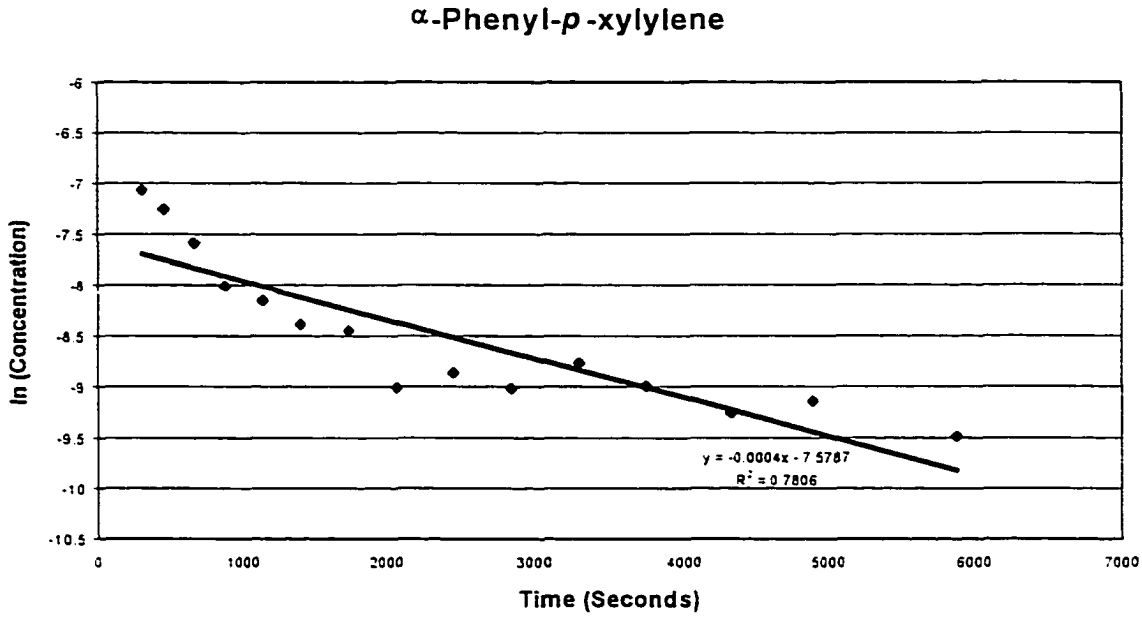


Figure 11. Plot of ln [8] vs time for kinetics experiment.

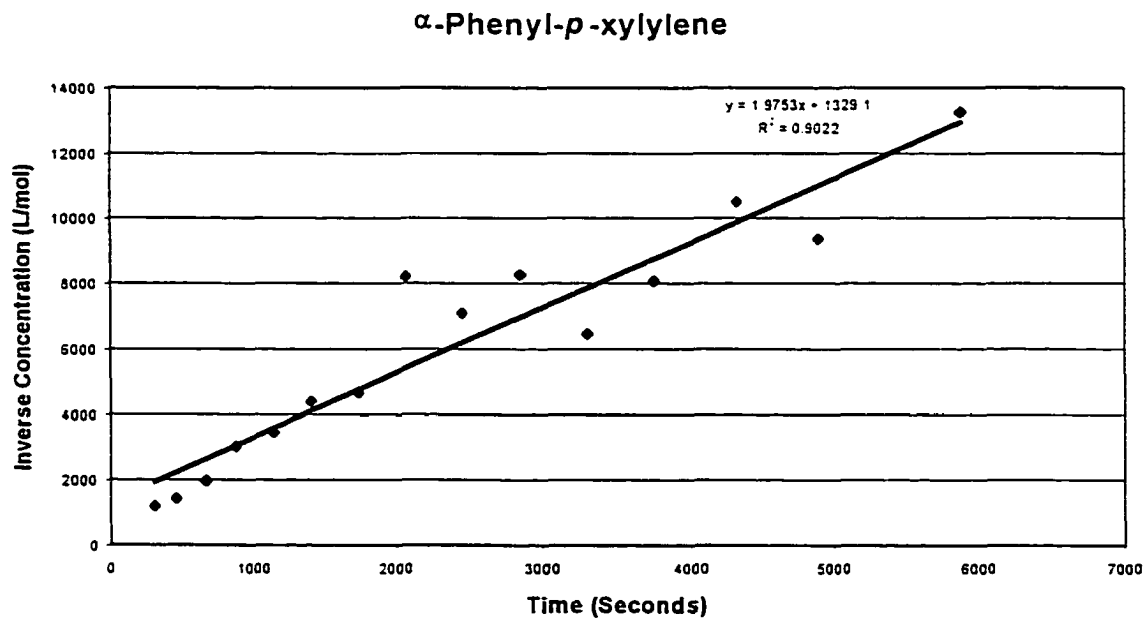
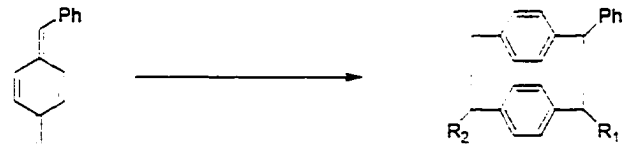


Figure 12. Plot of $[8]^{-1}$ vs time for kinetics experiment.

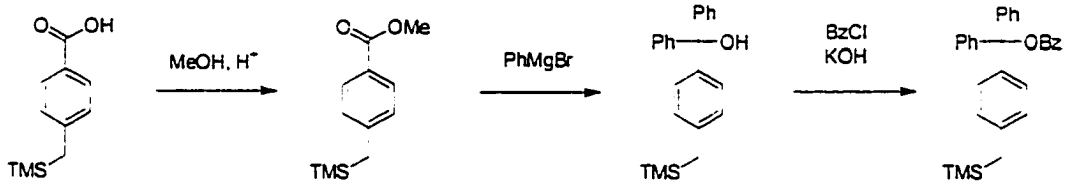
The major oligomer, that was isolated and analyzed by ^{1}H NMR spectroscopy (Figure 13) and mass spectroscopy (Figure 14), was consistent with dimers **18**.



8 **18a**, R_1 = Ph, R_2 = H
18b, R_1 = H, R_2 = Ph

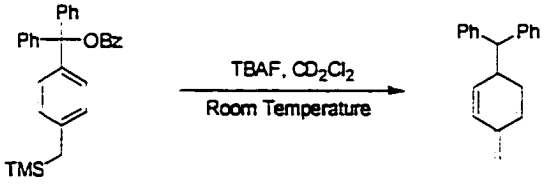
Generation and Oligomerization of α,α-Diphenyl-*p*-xylylene (6). (4-[(Trimethylsilyl)methyl]phenyl)diphenylmethyl benzoate (**19**) was prepared from 4-[(trimethylsilyl)methyl]benzoic acid (**20**) as shown in Scheme 2. Benzoate **19** was found to be only

Scheme 2



20 **21** **22** **19**

slightly soluble in acetonitrile, therefore the oligomerization studies were conducted in deuterated methylene chloride. α,α-Diphenyl-*p*-xylylene (**6**) was prepared as a dilute solution in CD_2Cl_2 by a fluoride induced elimination of trimethylsilyl benzoate from benzoate **19** and analyzed by ^{1}H NMR spectroscopy (Figure 15). Due to its higher reactivity,



19 **6**

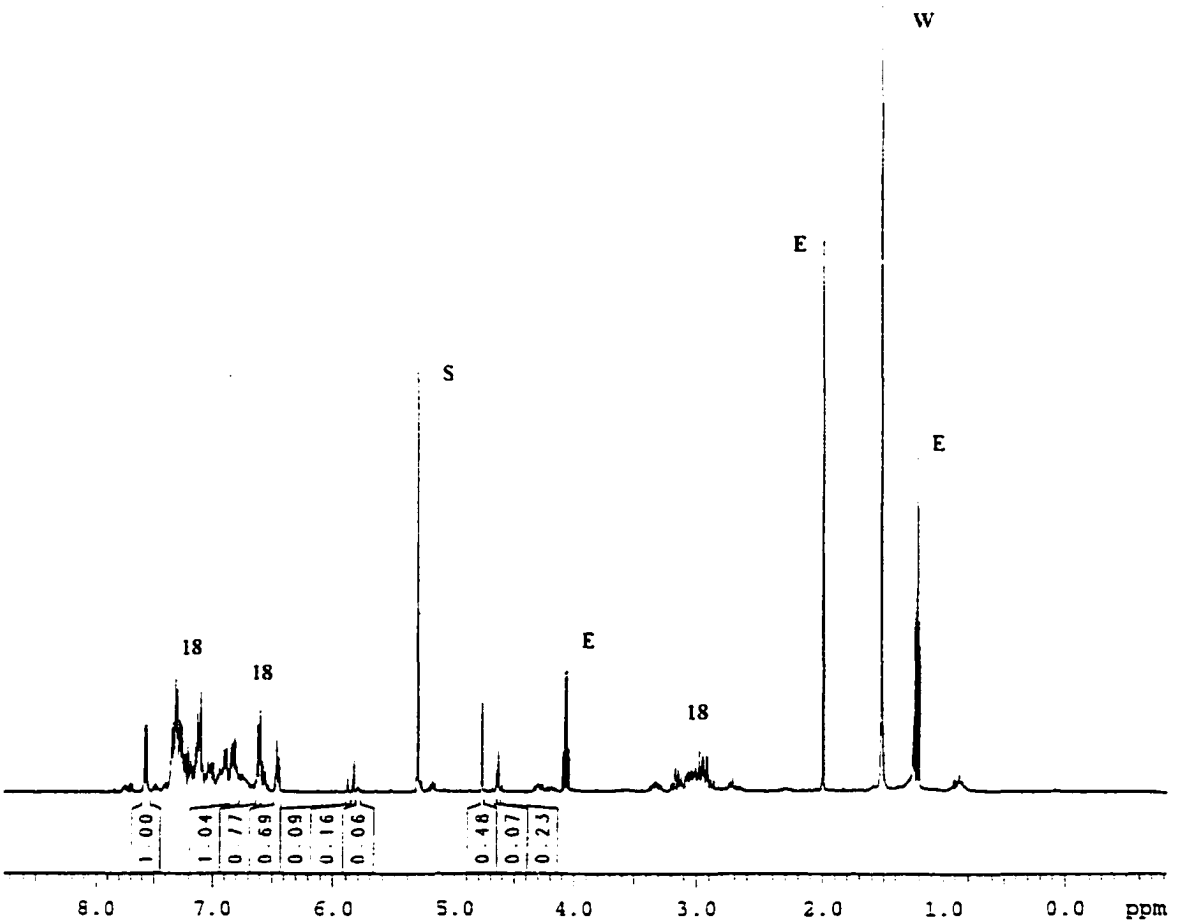


Figure 13. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ethyl acetate extracted TLC spot of α-phenyl-*p*-xylylene (**8**) products. (**18** is a compound number given in the text, **E**: ethyl acetate, **S**: methylene chloride, **W**: water)

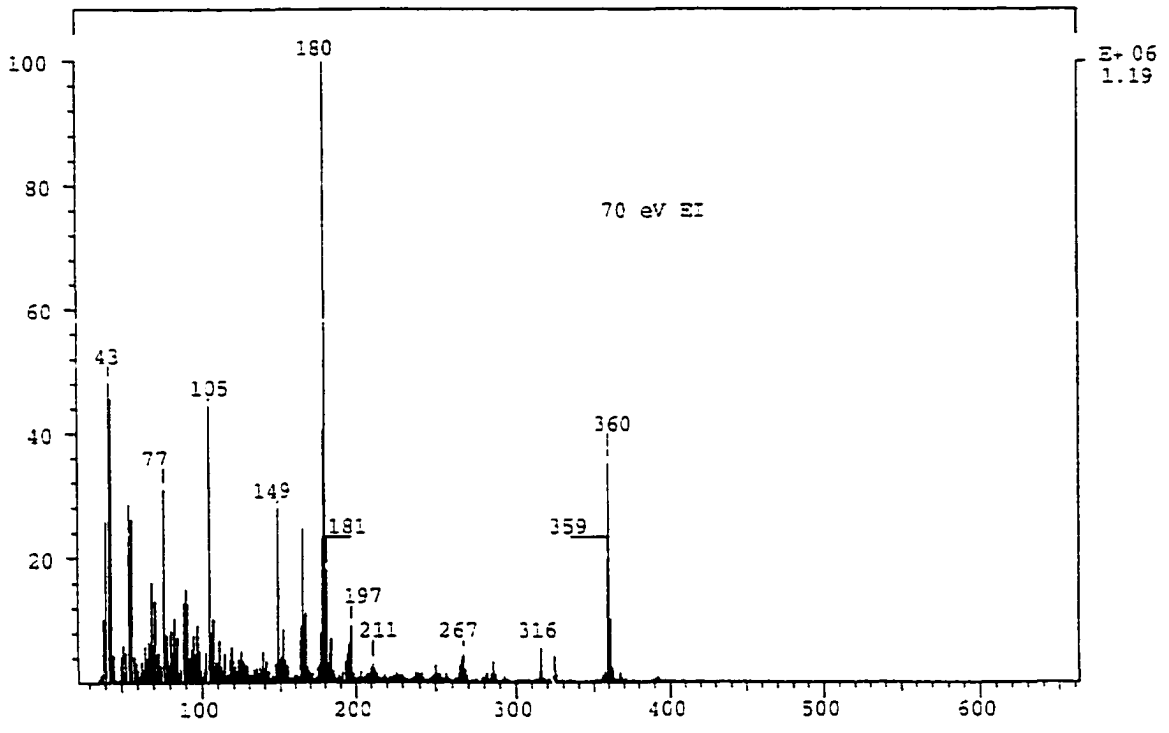


Figure 14. Mass spectrum (EI) of ethyl acetate extracted TLC spot of α-phenyl-*p*-xylylene (**8**) products.

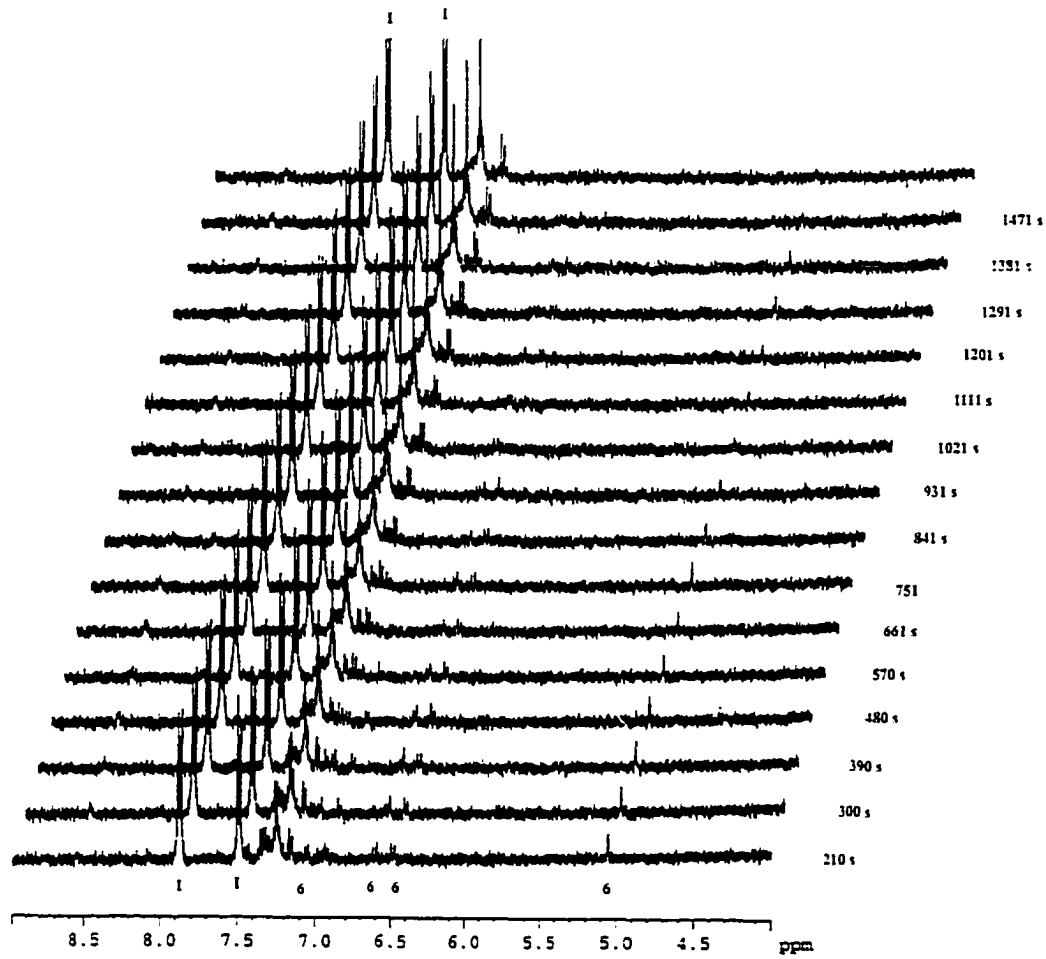


Figure 15. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of reaction progress for kinetics of α,α-diphenyl-*p*-xylylene (**6**). (**I**: internal standard, naphthalene)

a higher dilution of *p*-QDM **6** had to be used so it could be observed prior to formation of its oligomers. Using the same means of comparison of the naphthalene standard peaks to that of the *p*-QDM **6** peaks in the ^{1}H NMR spectra, the concentrations of *p*-QDM **6** was calculated and the results are presented in Table A-5. First- and second-order kinetic plots were prepared (Figures 16 and 17).

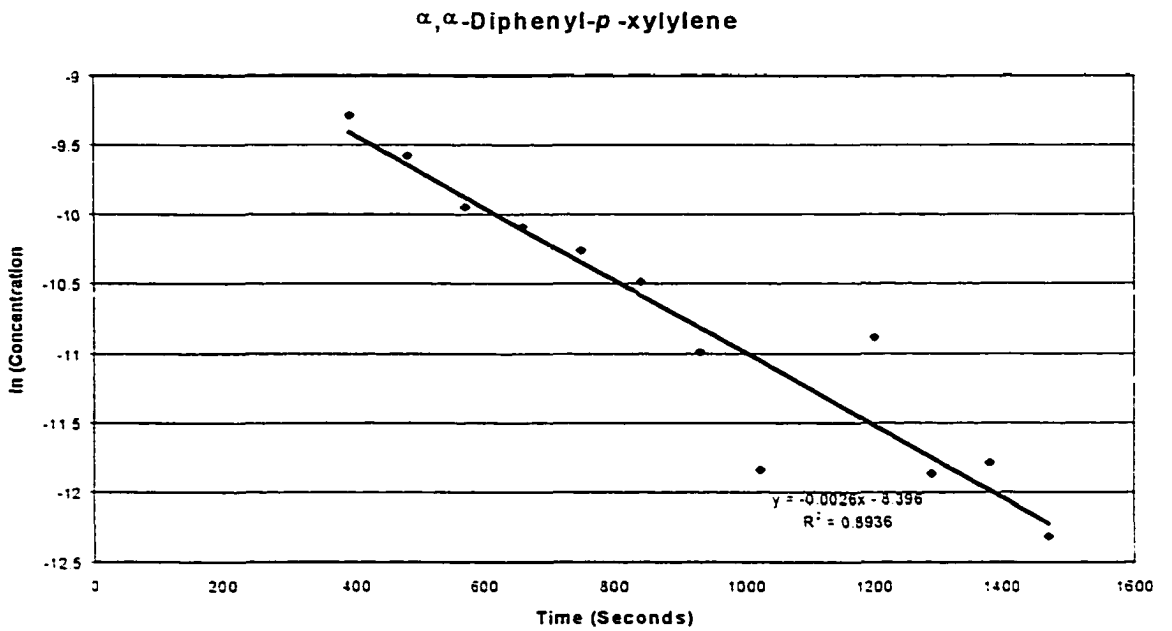


Figure 16. Plot of ln [**6**] vs time for kinetics experiment.

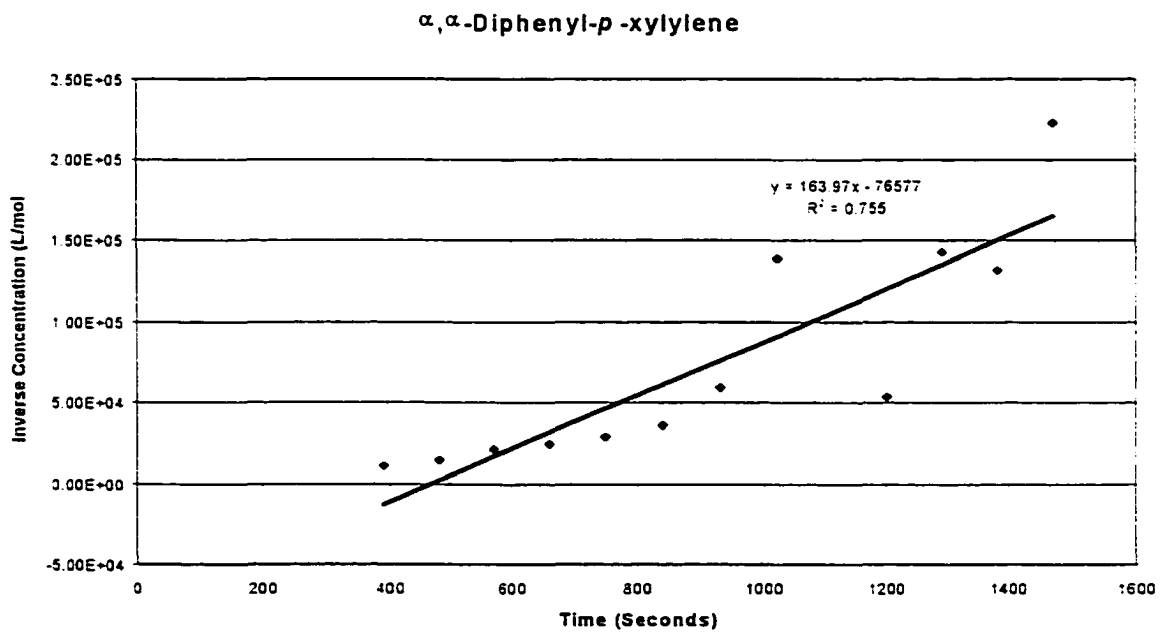
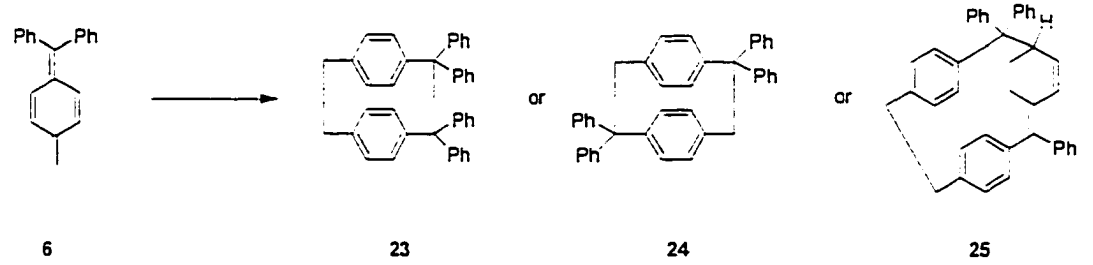


Figure 17. Plot of $[\mathbf{6}]^{-1}$ vs time for kinetics experiment.

α,α-Diphenyl-*p*-xylylene (**6**) was prepared on a larger scale with non-deuterated solvents. The major oligomer, that was isolated and analyzed by ^{1}H NMR spectroscopy (Figure 18) and mass spectroscopy (Figure 19), was consistent with any of the three dimers, **23**, **24**, or **25**.



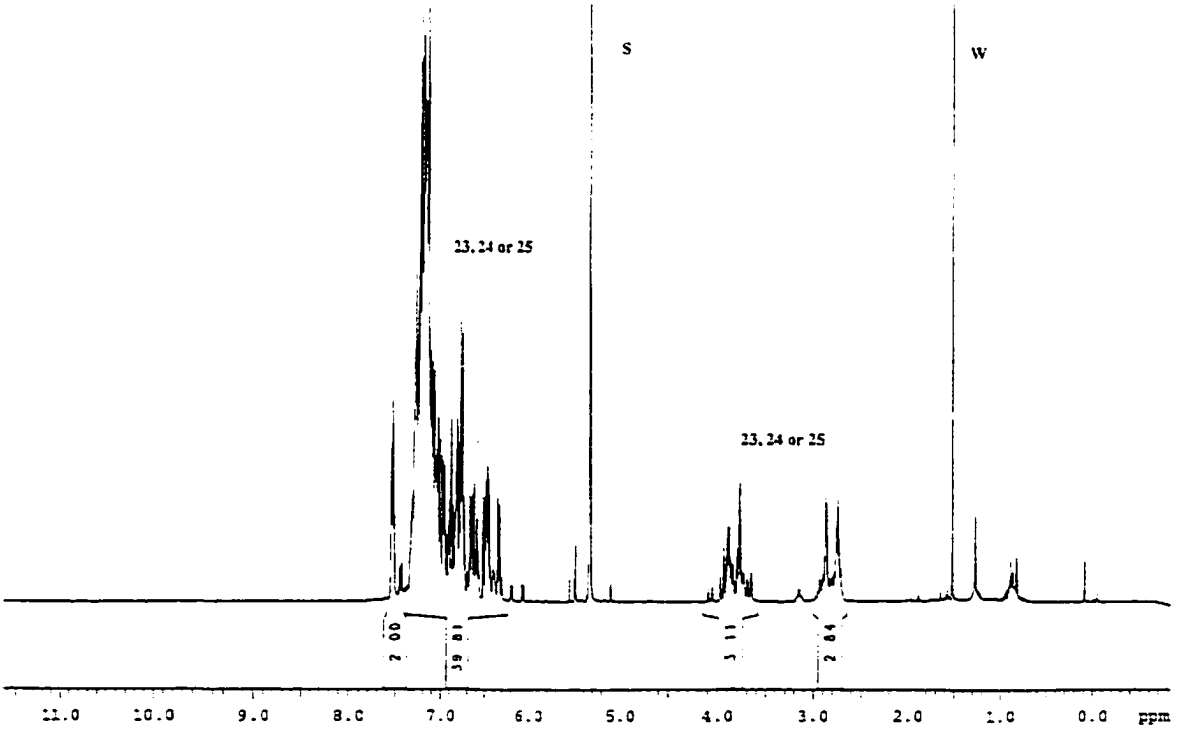


Figure 18. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of methylene chloride extracted TLC spot of α,α-diphenyl-*p*-xylylene (**6**) products. (**23**, **24**, and **25** are compound numbers given in the text, **S**: methylene chloride, **W**: water)

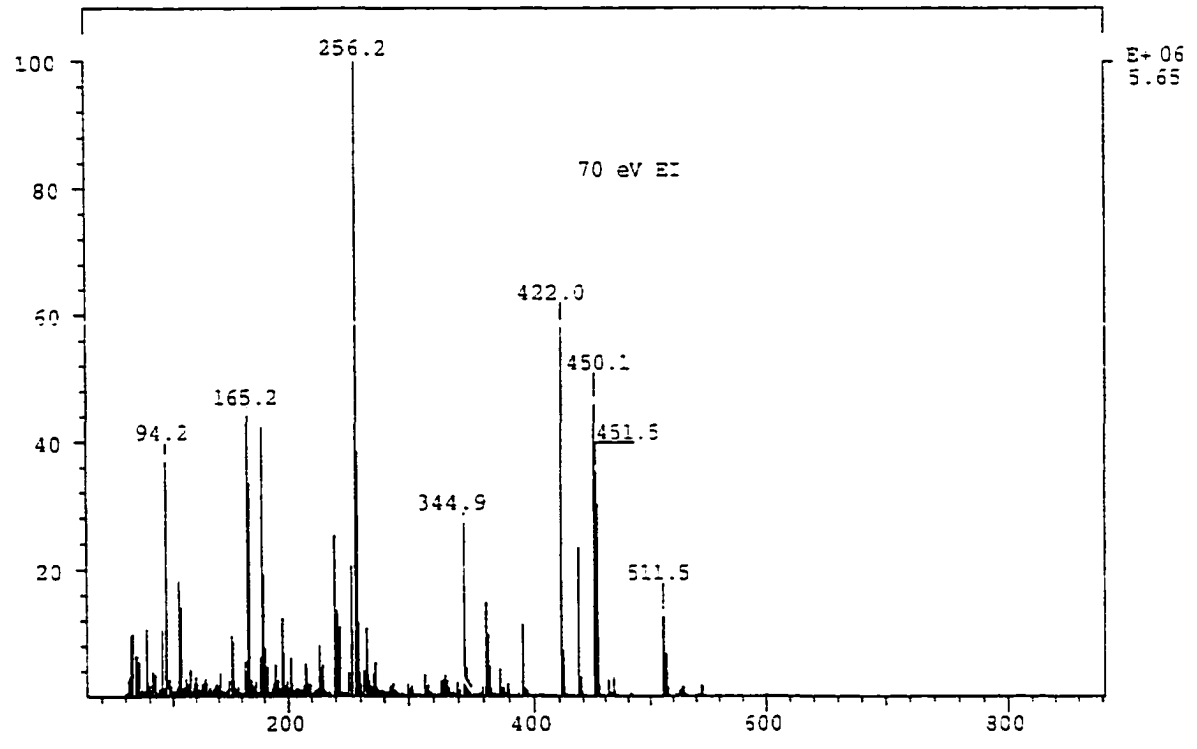
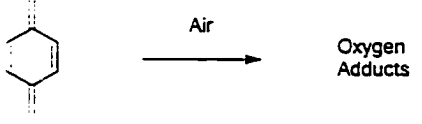


Figure 19. Mass spectrum (EI) of ethyl acetate extracted TLC spot of α,α-diphenyl-*p*-xylylene (**6**) products.

***p*-Xylylene (1) with Air Kinetics Studies.** *p*-Xylylene (**1**) was prepared the same way as above except that a small amount of air was introduced along with the TBAF solution. The ^{1}H NMR spectra are presented in Figure 20. Using the same means of comparison of the naphthalene standard peaks to that of the *p*-xylylene peaks in the ^{1}H NMR



1

spectra, the concentration of *p*-QDM **1** was calculated and summarized in Table A-6. First- and second-order kinetic plots were prepared (Figures 21 and 22). Within the ^{1}H NMR

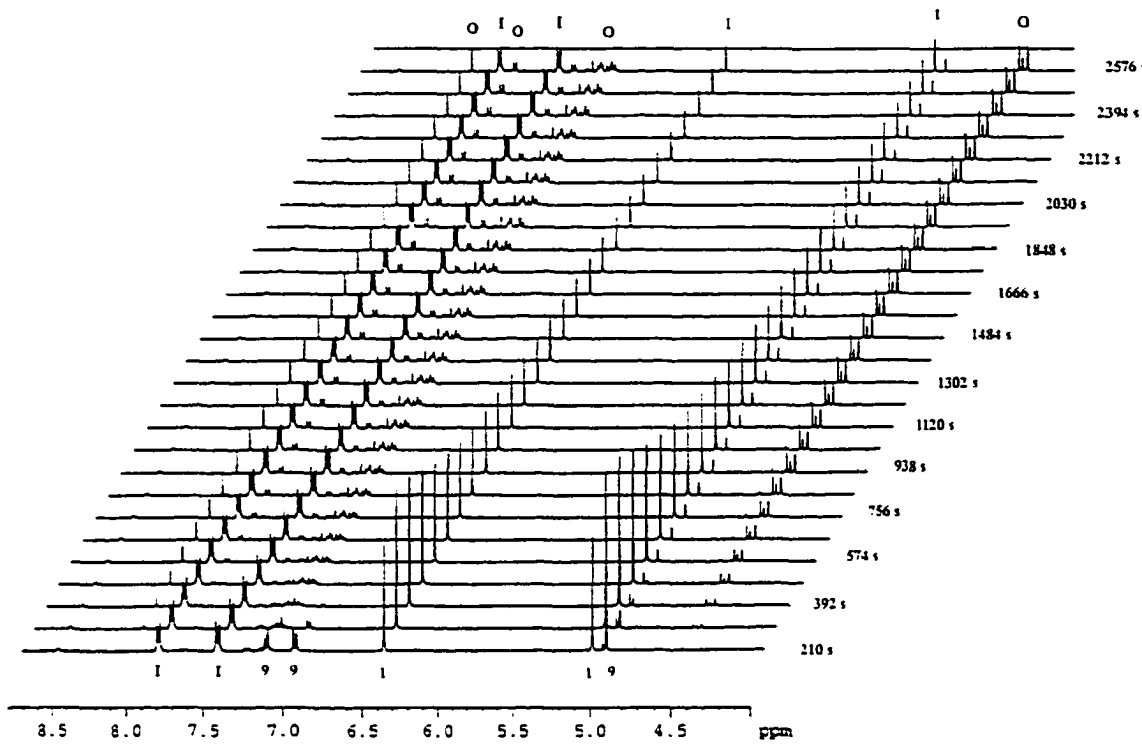


Figure 20. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress for short-term kinetics experiment of *p*-xylylene (**1**) with oxygen in CD_3CN. (**1** is a compound number given in the text, **I**: internal standard, naphthalene, **O**: oligomers)

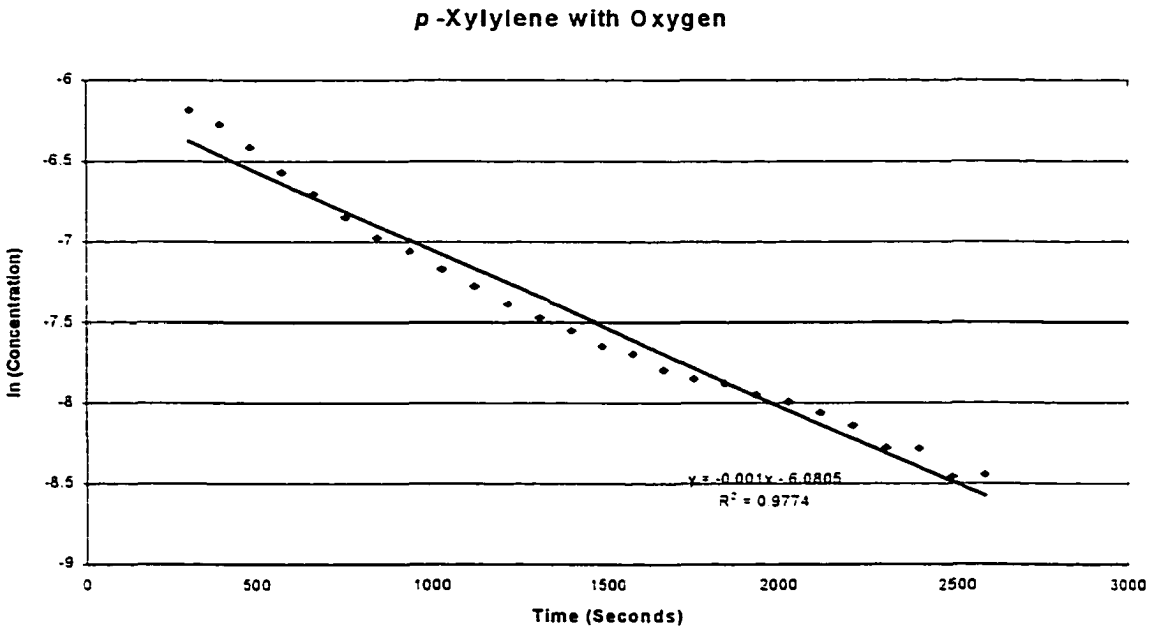


Figure 21. Plot of ln [1] with oxygen vs time for kinetics experiment.

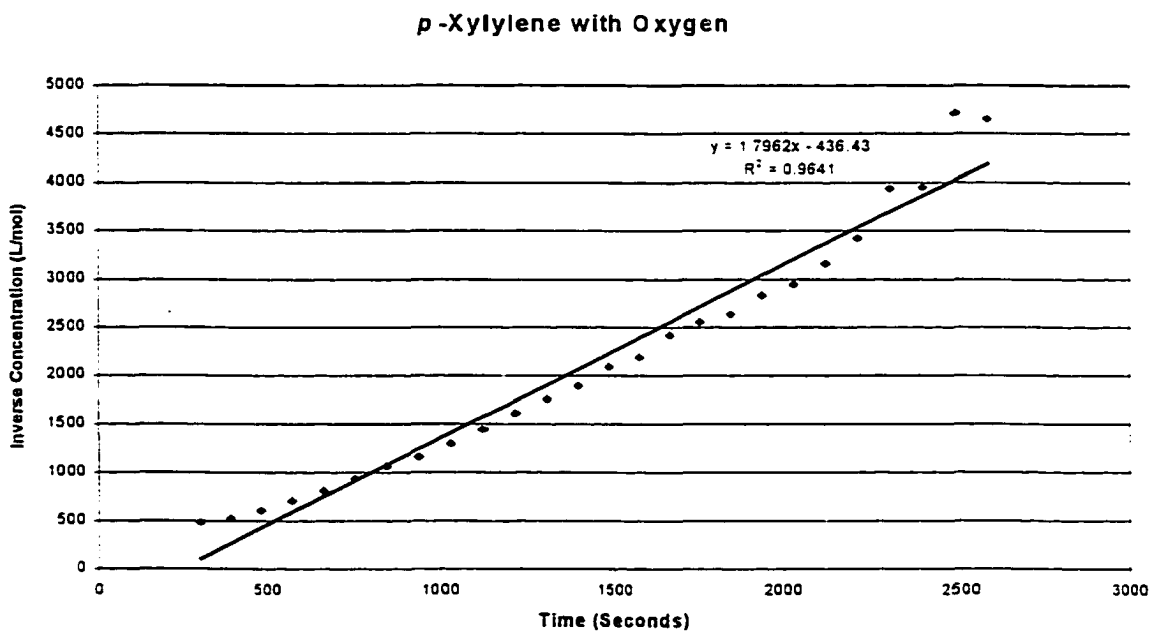


Figure 22. Plot of $[1]^{-1}$ with oxygen vs time for kinetics experiment.

spectra there were peaks consistent with oxygen adducts. The ^{1}H NMR spectra of the final products were free of peaks that can be associated with the dimer or trimer.

Determination of Rate Constants. It is clear from the product mixtures that more than a single reaction is consuming the *p*-QDM's. Two known reactions consuming *p*-QDM's are dimerization and polymerization. Given the kinetic data in Figures 2-22, a single, simple first- or second-order process is not responsible for the decomposition of the *p*-QDM's. Therefore trying to overinterpret the rate constants obtained from the plots is not constructive. However, we can at least use the data to get a qualitative picture of the relative reactivity of the four *p*-QDM's. The results of linear regressions performed on the first- and second-order kinetic plots are summarized in Table 1.

Table 1. Estimated First- and Second-order Rate Constants[a]

p-QDM	First-order Rate Constant (s^{-1})	R^2	Second-order Rate Constant (L mol^{-1} s^{-1})	R^2
Long –term *p*-Xylylene (**1**)	7.0×10^{-5}	0.8329	0.6527	0.998
Long –term α-Methyl-*p*-xylylene (**4**)	1.1×10^{-4}	0.989	0.277	0.9874
p-Xylylene (**1**)	2.0×10^{-4}	0.8251	0.0731	0.842
α-Phenyl-*p*-xylylene (**8**)	3.9×10^{-4}	0.8011	1.98	0.9104
α,α-Diphenyl-*p*-xylylene (**6**)	2.3×10^{-3}	0.8608	137.15	0.7235
p-Xylylene (**1**) with oxygen	8.2×10^{-4}	0.9845	2.29	0.9687

[a]Rate constants were determined at 20 °C

Discussion

Errede[10] determined that solutions of *p*-QDM **1** at –78°C polymerized with an apparent first-order rate constant of $9\pm1 \times 10^{-6}$ s^{-1}. The concentration of *p*-QDM **1**, as a function of time, was determined by removing small aliquots and titrating them with iodine. Other similar solutions of *p*-QDM **1** were used at temperatures above –78°C to determine additional rate constants. With the rate constants for the solutions at different temperatures, Errede was able to determine an energy of activation for this reaction to be 8.7 kcal mol^{-1}. Using Errede's first-order rate constants at –78°C and energy of activation, a first-order rate constant at 20°C can be calculated to be 1.6×10^{-2} s^{-1}.

The data gathered from our *p*-QDM **1** short-term kinetic experiment were unclear as to whether the reaction was following first- or second-order kinetics or some combination thereof. From plots of ln [**1**] verses time (Figure 5) and $[\mathbf{1}]^{-1}$ verses time (Figure 6), the first-order rate constant was 2.0×10^{-4} s^{-1} and the second-order rate constant was 0.0731 L mol^{-1} s^{-1}. Both plots yielded poor linearity. This first-order rate constant is nearly two orders of magnitude from the room temperature rate constant calculated from Errede's data.

The data gathered from *p*-QDM **1** long-term kinetic experiment appear to show the reaction to be proceding primarily by a second-order process with a rate constant of 0.6527 L mol^{-1} s^{-1} and was reasonably linear in the plot of $[\mathbf{1}]^{-1}$ verses time (Figure 3). A plot ln [**1**] verses time (Figure 2) clearly shows that the reaction is not first-order in nature.

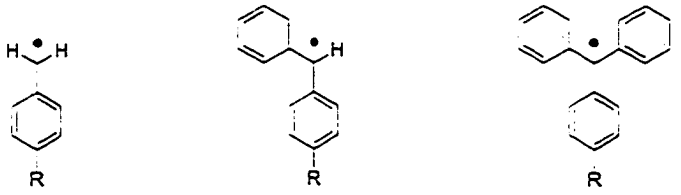
The difference between Errede's results and the results presented here can be rationalized by considering the conditions of the reaction and the products formed. Errede's experiments were conducted with solutions of *p*-QDM **1** were 40 to 100 times more concentrated than the ones used in this study. Higher concentrations lead to higher relative

yields of polymers verses dimer and trimer. The reactions were also done at temperatures near or at –78°C. It has been found that higher temperatures favor the formation of dimer.[12]

Given the complex nature of the oligomerization reactions, a feasible means of comparing the overall reactivity of *p*-QDM's is to compare their estimated second-order rate constants as long as the concentrations are approximately the same. This comparison can be justified because both dimerization and polymerization began when two monomers react to form a dimeric diradical. Comparing the second-order rate constants for the long-term experiment for *p*-QDM's **1** and **4**, we can see evidence that α-methyl-*p*-QDM **4** is less reactive than the parent, *p*-QDM **1**. The second-order rate constants also show the tread that the α,α-diphenyl-*p*-QDM (**6**) was found to be the most reactive of the series followed by the α-phenyl-*p*-QDM (**8**), and *p*-xylylene (**1**).

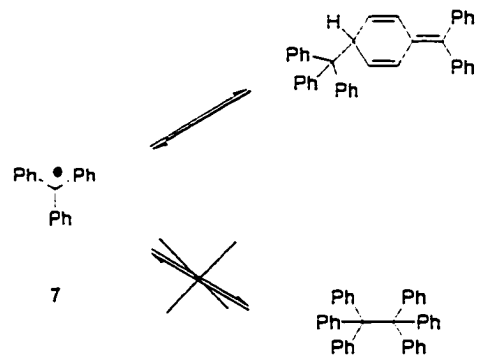
There appears to be two opposing effects controlling the rate of decomposition of these *p*-QDM's: (a) the steric effect that the groups has of blocking one of the two exocyclic methylenes which has the effect of reducing the reactivity and (b) the stabilizing effects the substituents have on the diradical intermediate which has the effect of increasing the reactivity. α-Methyl-*p*-xylylene (**4**) appears to be slightly less reactive than *p*-xylylene, the parent *p*-QDM **1**. Although the methyl groups should stabilize the radical sites of the intermediate, the methyl must be slowing the reaction by blocking one of the methylene groups from attack. α-Phenyl-*p*-xylylene (**8**) is more reactive that *p*-QDM **1**. The dimeric diradical produced from *p*-QDM **8** is should be significantly more stable than the diradical formed for the parent system. Apparently the steric effect of the phenyl group blocking one of the two exocyclic methylenes is not great enough to offset the increase of reactivity caused

by the stabilizing of the diradical. α,α-Diphenyl-*p*-xylylene (**6**) is more reactive than the other *p*-QDM's studied here. The two phenyl groups will significantly stabilize each radical site of the intermediate. It appears that the increase of reactivity caused by stabilizing the diradical cannot be offset by the steric effect of even two phenyl groups thoroughly blocking one of the methylene groups. Although calculating the rate-constants with a great amount of certainty for the oligomerization of *p*-QDM would be difficult even with additional experimental data, it can be seen that the reactivity of *p*-QDM's varies with the different α-substituents.



As stated above for the rate constants for decomposition of *p*-QDM's to be comparable to each other, the conditions of the reaction and the products formed must be similar. *p*-QDM's **1** and **4** under these conditions form dimers, trimers, and oligomers. The products formed from *p*-QDM **8** are not completely characterized. Their ^{1}H NMR spectra are similar to the spectra of products formed for *p*-QDM **4**. The major component of the oligomerization products of *p*-QDM **8** has a ^{1}H NMR spectrum and mass spectrum consistent with a cyclic dimer. The products of *p*-QDM **6** appear to be dimers. Cyclophane dimers seem unlikely products because in a head to head dimer, the product would be similar to the proposed hexaphenylethane which is not formed in the coupling of two trityl radicals **7**.[5] A head to tail cyclophane dimer would have to overcome the steric effects of the two phenyl

groups. A possible product is an olefinic product from a para attack onto one of the phenyl groups.



Small amount of oxygen dissolved in the solutions of *p*-QDM's can have a dramatic effect on the products observed. When a small amount of air is allowed to leak into a NMR tube containing a deoxygenated solution of *p*-QDM precursor, in many cases oxygenated products form exclusively. By comparing the second-order rate constants for the oligomerization of *p*-xylylene (**1**) and the reaction of *p*-QDM **1** with oxygen, it was found that even small concentrations oxygen can consume *p*-QDM's rapidly. Examination of both the first- and second-order kinetics plot (Figures 21 and 22) finds that this consummation by oxygen is neither a solely first or second-order process.

Conclusions

Four reactive *p*-QDM's, *p*-xylylene (**1**), α-methyl-*p*-xylylene (**4**), α-phenyl-*p*-xylylene (**8**), and α,α-diphenyl-*p*-xylylene (**6**), were prepared by fluoride induced elimination and characterized by ^{1}H NMR spectroscopy. This was the first report of the ^{1}H NMR spectra of *p*-QDM's **6** and **8**. All four *p*-QDM's were found to form dimers and insoluble oligomers.

First- and second –order rate constants were estimated for the decomposition of the four *p*-QDM's. Using the estimated rate constants, the α,α-diphenyl-*p*-QDM (**6**) was found to be the most reactive of the series followed by the α-phenyl-*p*-QDM (**8**), *p*-xylylene (**1**), and the α-methyl-*p*-QDM (**4**). The long-term kinetic study of *p*-QDM **1** was found to decompose primarily by a second-order process, possibly dimerization.[7] This is in contrast to the first-order results observed by Errede for the polymerization of *p*-QDM **1**.[6] The other kinetic studies, including the short-term study of *p*-QDM **1**, found that both first- and second-order decomposition was occurring. A probable explanation is that polymerization, a first-order process, and dimerization, a second-order process, are occurring at comparable rate. The reaction of *p*-QDM **1** with oxygen was found to be rapid in comparison with its oligomerization.

Experimental Section

Methods and Materials. All materials were commercially available and used as received, except where indicated. ^{1}H NMR spectra were recorded at 400 MHz and at 20 °C unless noted otherwise. ^{13}C NMR spectra were recorded at 100 MHz unless noted otherwise. The residual CHD_2CN was used as the internal reference for all ^{1}H NMR spectra unless noted otherwise. Both the GC and the GC/MS analysis were done using a DB-5 column (30m, I.D. 0.32 mm, 0.25μ film thickness). Elemental analyses were performed by Iowa State University Instrumental Services, Ames, IA.

Drying and Initial Degassing of Acetonitrile-d_3 and Methylene Chloride-d_2.[13] Prior to use as a solvent in the preparation of *p*-QDM's, acetonitrile-d_3 was distilled from P_2O_5 under argon and methylene chloride from calcium hydride under argon. The solvents were initially degassed by repeated freeze-pump-thaw cycles, except where indicated.

***p*-Xylylene (1) Long-term Kinetics.** To a 5-mL tear-shaped flask 17 mg of TBAF (54 μmol) was added. To a second tear-shaped flask was added 8.5 μL of a 5.0 x 10^{-2} M solution of naphthalene in CH_2Cl_2 (0.48 μmol) and 18 μL of an approximately 0.1 M solution of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**9**)[14] in CH_2Cl_2 (~2.2 μmol). The CH_2Cl_2 was removed at reduced pressures. The two flasks were placed into a nitrogen filled glove bag. To the acetate flask was added about 0.6 mL of degassed CD_3CN. The acetate solution was transferred to an NMR tube and the acetate was quantified by ^1H NMR spectroscopy. The NMR tube was returned to the glove bag. To the TBAF flask was added about 0.2 mL of degassed CD_3CN. The TBAF solution was added to the NMR tube. The sample was protected from light. The NMR tube was periodically removed from the glove bag for analysis by ^1H NMR spectroscopy. The kinetic data are summarized in Table A-1. ^1H NMR (400 MHz, CD_3CN, 20°C) δ 6.452 (s, 4H), 5.007 (s, 4H). [lit[15] ^1H NMR (60 MHz, THF-d_8, -80°C) δ 6.49, 5.10]. As the solution is allowed to stand, the *p*-xylylene (**1**) was consumed and [2.2]paracyclophane (**10**)[8], [2.2.2]paracyclophane (**11**)[8], and insoluble oligomers were formed.

α-Methyl-*p*-xylylene (4) Long-term Kinetics. α-Methyl-*p*-xylylene (**4**) was prepared from 1-[*p*-((trimethylsilyl)methyl)phenyl]ethyl acetate[16] (**12**, 1.2 μmol), TBAF (25 μmol) and naphthalene (0.30 μmol) with the procedure used from the above preparation of *p*-xylylene (**1**) in degassed CD_3CN. The kinetic data are summarized in Table A-2. ^1H NMR (400 MHz, CD_3CN) δ 6.713 (br d, *J*=9.6Hz, 1H), 6.466 (br d, *J*=9.6Hz, 1H), 6.314 (br s, 2H) 5.619 (q, *J*=8Hz, 1H), 4.963 (br s, 2H), 1.848 (d, *J*=8Hz, 3H). As the solution is allowed to

stand, the α-methyl-*p*-xylylene (**4**) was consumed and dimers **13**[8], timers **14**[11], and insoluble oligomers were formed.

***p*-Xylylene (1) Short-term Kinetics.** An NMR tube was charged with 25 μL of a 0.068 M solution of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**9**) in CD_3CN (1.7 μmol), 8.0 μL of a 0.101 M solution of naphthalene in CD_3CN (0.81 μmol), and 0.75 mL of CD_3CN. A solution of TBAF (6 mg, 20 μmol) in 0.25 mL of CD_3CN was prepared in a tear-shaped flask. Both solutions were degassed by repeated freeze-pump-thaw cycles then stored under argon. A ^1H NMR spectrum was taken of the deoxygenated acetate **9** solution. The kinetic experiment began by the addition of the TBAF solution to the NMR tube via a syringe through its rubber septum cap. The kinetic data are summarized in Table A-3. The products after standing are similar to the long-term kinetics experiment.

4-[(Trimethylsilyl)methyl]benzhydrol (17) was prepared by a Gridnard reaction of 4-[(trimethylsilyl)methyl]benzaldehyde (**16**)[17] (208 mg, 1.08 mmol) with phenylmagnesium bromide (1.1 mmol). The reaction was quenched with saturated NH_4Cl. Water and ether were added, and the separated ether layer was washed with saturated $NaHCO_3$ then saturated NaCl. The organic phase was dried with anhydrous Na_2SO_4, filtered, freed of solvent, and chromatographed on silica gel (elution with 4:1 hexanes-ether) to afford alcohol **17** (173 mg, 0.64 mmol, 59%) as a colorless oil: ^1H NMR (400 MHz, CD_3CN) δ 7.4-7.2 (m, 5H), 7.182 and 6.952 (AA'BB'q, 4H, *J*=8.0 Hz), 5.690 (d, 1H, *J*=4.0 Hz), 3.666 (d, 1H, *J*=4.0 Hz), 2.045 (s, 2H), -0.067 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 145.54, 140.75, 139.56, 128.27,127.93, 126.98, 126.25, 75.09, 25.88, -2.80. Anal. Calcd for $C_{17}H_{22}OSi$: C, 75.50; H, 8.20. Found: C, 75.41; H, 8.45.

(4-[(Trimethylsilyl)methyl]phenyl)phenylmethyl Acetate (15). A 10-mL round-bottomed flask was charged with alcohol **17** (27 mg, 0.10 mmol), 1 mL dry THF, and 10 drops of dry pyridine. A solution of 0.2 ml acetyl chloride in 1 mL dry THF was added dropwise to the well stirred alcohol solution. The reaction was stirred to 36 h at room temperature. Ether (10 mL) and brine (10 mL) were added to the reaction mixture. The separated organic phase was washed with additional brine, saturated $NaHCO_3$, brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure and the resulting oil was chromatographed on triethylamine treated silica gel (elution with 4:1 hexanes-ether) to afford acetate **15** (24 mg, 0.077 mmol, 77%) as a colorless oil: ^{1}H NMR (400 MHz, CD_3CN) δ 7.37-7.25 (m, 5H), 7.190 and 6.990 (AA'BB'q, 4H, *J*=8.0 Hz), 6.703 (s, 1H), 2.088 (s, 3H), 2.065 (s, 2H), -0.062 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 169.91, 141.24, 140.65, 136.27, 128.56, 128.15, 127.72, 126.73, 126.55,76.85, 25.96, 20.44, -2.88.

α-Phenyl-*p*-xylylene (8) Kinetics. An NMR tube was charged with 16 μL of a 0.077 M solution of acetate **15** in CD_3CN (1.2 μmol), 8.0 μL of a 0.101 M solution of naphthalene in CD_3CN (0.81 μmol), and 0.75 mL of CD_3CN. A solution of TBAF (6 mg, 20 μmol) in 0.25 mL of CD_3CN was prepared in a tear-shaped flask. Both solutions were degassed by repeated freeze-pump-thaw cycles then stored under argon. A ^{1}H NMR spectrum was taken of the deoxygenated acetate **15** solution. The kinetic experiment began by the addition of the TBAF solution to the NMR tube via a syringe through its rubber septum cap. ^{1}H NMR (400 MHz, CD_3CN) δ 7.045 (d, *J*=14 Hz), 6.586 (d, *J*=14 Hz), 6.519 (s), 5.102 (d, *J*=14 Hz). The kinetic data are summarized in Table A-4.

α-Phenyl-*p*-xylylene (8) Oligomers. Fifteen milliliters of a 1.28 mM solution of acetate **15** (19.2 μmol) in CH_3CN was added to a 50-mL round-bottomed flask. A solution of TBAF (63 mg, 190 μmol) was prepared in a 25-mL tear-shaped flask with 5 mL CH_3CN. Both solutions were degassed by repeated freeze-pump-thaw cycles then stored under argon. Inside of a nitrogen-filled glovebag, the TBAF solution was transferred to the acetate solution via a 10-mL syringe. The reaction mixture was swirled then allowed to stand for 4 h. The CH_3CN was removed under reduced pressure and the resulting residue was dissolved in CD_3CN. A ^1H NMR spectrum was taken and was similar to the NMR spectrum observed for the kinetics experiment. The CD_3CN was removed under reduced pressure and the residue was dissolved in 5 mL of CH_2Cl_2. The methylene chloride solution was washed with 5 mL of water twice, dried with Na_2SO_4, and the solvent was removed under reduced pressure. The residue was dissolved in CD_2Cl_2 and a ^1H NMR spectrum was taken. TLC with CH_2Cl_2 as the elutent revealed at least 11 components with the three major occurring at R_f of 0.89, 0.36, and 0.21. The three major spots were scraped individually from the plate and extracted with ethyl acetate. The solvent from the filtered ethyl acetate solution was removed from each under reduced pressure. Only the 0.89 Rf spot had any visible residue. CD_2Cl_2 was added to each sample and ^1H NMR spectra was taken of each. The ^1H NMR spectra of the 0.36 and 0.21 Rf contained only solvent peaks. The ^1H NMR spectrum of the 0.89 spot was subset of the peaks observed for the extracted product mixture. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.570 (d, J=8.0 Hz), 7.35-6.68 (m), 6.64-6.52 (m), 6.452 (dd, J=8.0 Hz, J'=1.6), 5.884 (s), 5.839 (s), 5.8 (s), 4.772 (s), 4.69-4.60 (m), 4.35-4.15 (m), 3.37-2.62 (m). A mass spectra was taken of the 0.89 Rf residue. MS (EI) m/z (relative intensity) 361 (10), 360 (35), 359 (20), 181 (18), 180 (100), 179 (41), 178 (23), 167 (11), 166 (11), 165 (25).

Methyl 4-[(Trimethylsilyl)methyl]benzoate (21) was prepared by a Fischer esterification of 4-[(trimethylsilyl)methyl]benzoic acid[17] (**20**; 2.29 g, 11.0 mmol) with methanol (50 mL) and H_2SO_4 (1 mL). After refluxing for 4 h, the reaction mixture was worked up in the normal manner to yield ester **21** (2.398 g, 10.8 mmol, 98 %) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.869 and 7.025 (AA'BB'q, 4H, *J*=8.4 Hz), 3.867 (s, 3H), 2.141 (s, 2H), -0.028 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.34, 146.81, 129.58, 127.85, 125.95, 51.83, 27.92, -1.96.

(4-[(Trimethylsilyl)methyl]phenyl)diphenylmethanol (22) was prepared by a Grignard reaction of ester **21** (953 mg, 4.5 mmol) with phenylmagnesium bromide (10.3 mmol). After the normal work up, purification was achieved by crystallization from hexanes to give alcohol **22** (486 mg, 1.4 mmol, 31%): mp 92.4-93.7 °C; ^{1}H NMR (400 MHz, CD_3CN) δ 7.3-7.2 (m, 10H), 7.043 and 6.954 (AA'BB'q, 4H, *J*=8.4 Hz), 4.186 (s, 1H), 2.080 (s, 2H), -0.042 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 148.65, 143.84, 140.39, 128.62,128.55, 128.52, 128.17, 127.72, 82.03, 26.60, -2.02. Anal. Calcd for $C_{23}H_{26}OSi$: C, 79.72; H, 7.56. Found: C, 79.99; H, 7.69.

(4-[(Trimethylsilyl)methyl]phenyl)diphenylmethyl Benzoate (19).[18] To a 25-mL tear-shaped flask was added 120 mg of 35% potassium hydride dispersion in mineral oil. The potassium hydride was washed three times with dry pentane to remove the mineral oil. Dry THF (2 mL) was added to the flask. A solution of alcohol **22** (111 mg, 0.32 mmol) in 2 mL dry THF was added dropwise to the reaction mixture then stirred for 1 h. A solution of benzoyl chloride (37 uL, 0.32 mmol) in 1 mL dry THF was added slowly to the reaction mixture. After stirring to 2 h, the reaction mixture was filtered though a glass wool plug to remove excess potassium hydride. Methylene chloride (10 mL) and saturated $NaHCO_3$ (10

mL) solution were added to the reaction solution. The separated organic phase was washed with brine (3x), dried ($MgSO_4$), and concentrated under reduced pressure to yield benzoate **19** as a colorless oil (59 mg, 0.13 mmol, 41%). Neat sample of benzoate **19** was found to quickly decompose. All samples of benzoate **19** were stored as a solution in methylene chloride-d_2 (the solubility of the benzoate was poor in acetonitrile-d_3). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.131 and 6.979 (AA'BB'q, 4H, J=9.0 Hz), 7.63-7.57 (m, 1H),), 7.52-7.45 (m, 5H),), 7.36-7.27 (m, 9H), 2.093 (s, 2H), 0.012 (s, 9H); ^{13}C NMR (75 MHz, CD_2Cl_2) δ 164.89, 144.45, 140.62, 139.34,133.55, 131.95, 130.23, 129.02, 128.95, 128.76, 128.38, 128.35, 128.32, 128.09, 127.94, 127.72, 127.58, 27.073, -1.66.

α,α-Diphenyl-*p*-xylylene (6) Kinetics. An NMR tube was charged with 100 μL of a 0.011 M solution of benzoate **19** in CD_2Cl_2 (1.1 μmol), 8.0 μL of a 0.101 M solution of naphthalene in CD_2Cl_2 (0.81 μmol), and 0.65 mL of CD_2Cl_2. A solution of TBAF (6 mg, 20 μmol) in 0.25 mL of CD_2Cl_2 was prepared in a tear-shaped flask. Both solutions were degassed by repeated freeze-pump-thaw cycles then stored under argon. A ^{1}H NMR spectrum was taken of the deoxygenated benzoate **19** solution. The kinetic experiment began by at the addition of the TBAF solution to the NMR tube via a syringe through its rubber septum cap. ^{1}H NMR (400 MHz, CD_3CN) δ 7.164 (d, J=14 Hz), 6.604 (d, J=14 Hz), 6.483 (d, J=14 Hz), 5.055 (s). The kinetic data are summarized in Table A-5.

α,α-Diphenyl-*p*-xylylene (6) Oligomers. Fifteen milliliters of a 0.95 mM solution of benzoate **19** (14.2 μmol) in CH_2Cl_2 was added to a 50-mL round-bottomed flask. A solution of TBAF (50 mg, 145 μmol) was prepared in a 25-mL tear-shaped flask with 5 mL CH_2Cl_2. Both solutions were degassed by repeated freeze-pump-thaw cycles then stored under argon.

Inside the nitrogen filled glovebag, the TBAF solution was transferred to the acetate solution via a 10-mL syringe. The reaction mixture was swirled then allowed to stand for 4 h. The CH_2Cl_2 was removed under reduced pressure and the resulting residue was dissolved in CD_2Cl_2. A ^1H NMR spectrum was taken and was similar to the NMR spectrum observed during the kinetics experiment. The CD_2Cl_2 was added to 4 mL of CH_2Cl_2 and the methylene chloride solution was washed with 5 mL of water twice, dried with Na_2SO_4, and the solution was concentrated under reduced pressure. The concentrated solution was analyzed by TLC with CH_2Cl_2 as the elutent revealed at least 8 components with the major product occurring at R_f of 0.86. The major spot was scraped from the plate and extracted with methylene chloride. The mixture was filtered and the solvent was removed under reduced pressure. The ^1H NMR, ^{13}C NMR, and mass spectrum were taken of the residue. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.55-7.4 (m, 2.00H), 7.35-6.25 (m, 39.81H), 4.14-4.64 (m, 3.11H), 2.97-2.68 (m, 2.84H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 131.44, 131.37, 130.35, 129.60, 128.54, 128.15, 128.06, 126.33, 126.26. MS (EI) m/z (relative intensity) 512 (13), 453 (30), 452 (35), 450 (46), 436 (23), 422 (58), 391 (12), 362 (15), 350 (27), 265 (11), 259 (12), 258 (38), 256 (100), 254 (11), 252 (21), 244 (11), 243 (11), 242 (13), 241 (14), 239 (25), 195 (12), 180 (19), 178 (42), 167 (34), 165 (44), 107 (14), 105 (18), 94 (37), 91 (10), 77 (11).

***p*-Xylylene (1) with Oxygen Kinetics.** An NMR tube was charged with 25 μL of a 0.068 M solution of [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate (**9**) in CD_3CN (1.7 μmol), 8.0 μL of a 0.101 M solution of naphthalene in CD_3CN (0.81 μmol), and 0.75 mL of CD_3CN. A solution of TBAF (6 mg, 20 μmol) in 0.25 mL of CD_3CN was prepared in a tear-shaped flask. Both solutions were degassed by repeated freeze-pump-thaw cycles then stored under argon. A ^1H NMR spectrum was taken of the deoxygenated acetate **9** solution.

The kinetic experiment began by the addition of the TBAF solution and approximately 0.3 mL of air to the NMR tube via a syringe through its rubber septum cap. The kinetic data are summarized in Table A-6. The products that formed are consistent with oxygen adducts.

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Appendix

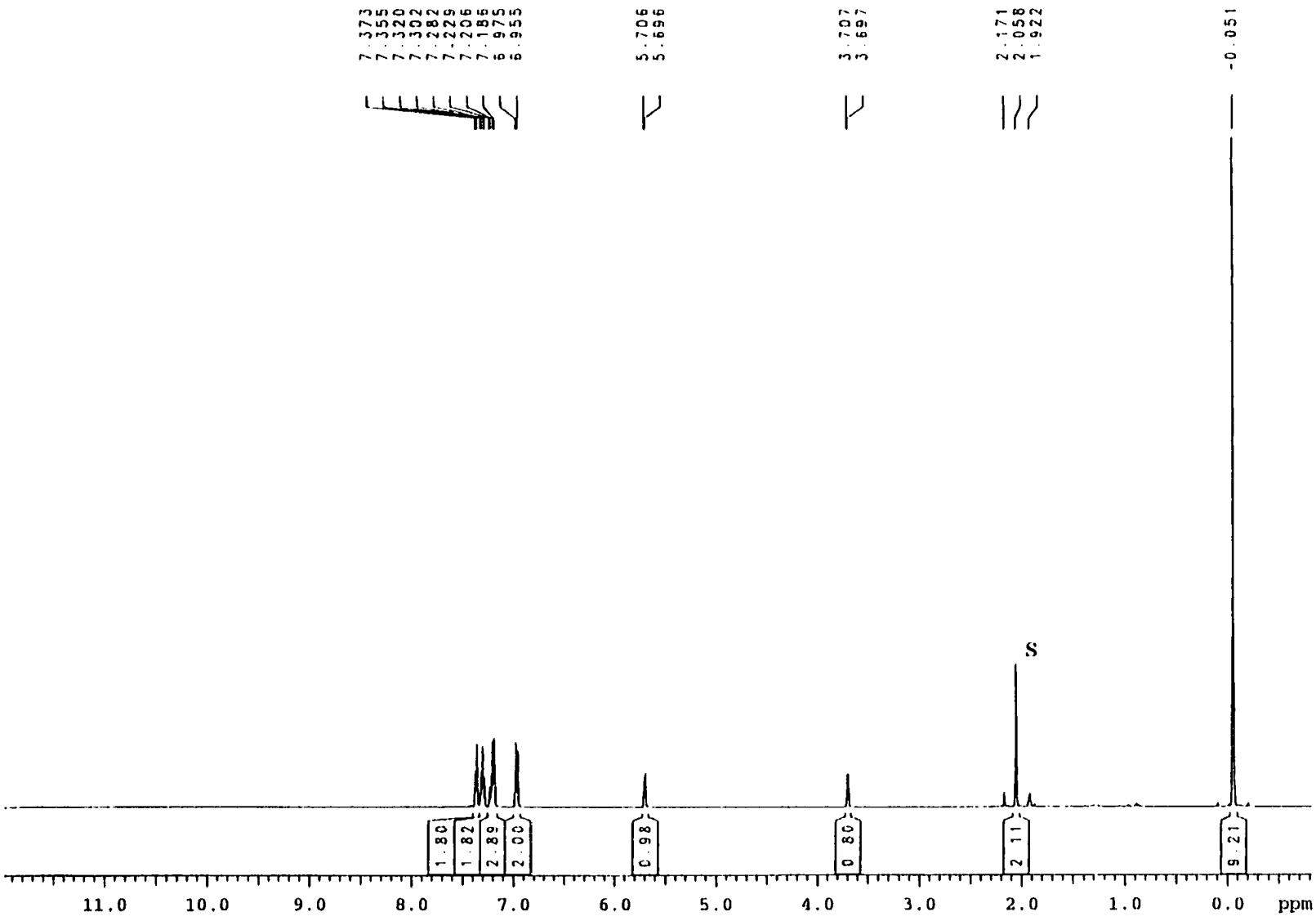


Figure A-1. ^{1}H NMR spectrum (400 MHz, CD_3CN) of 4-[(trimethylsilyl)methyl]benzhydrol (17). (S: acetonitrile)

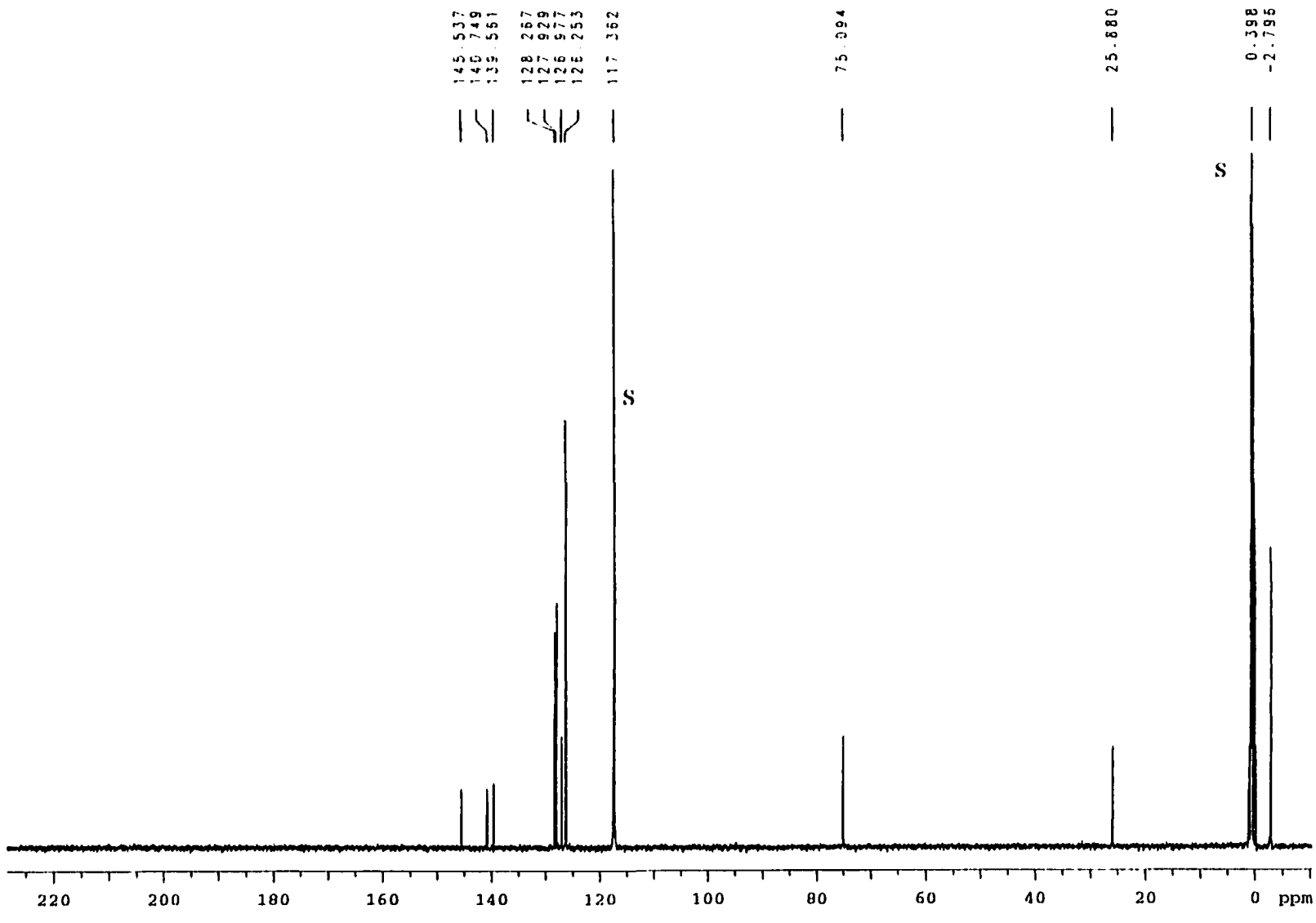


Figure A-2. ^{13}C NMR spectrum (100 MHz, CD_3CN) of 4-[(trimethylsilyl)methyl]benzhydrol (17). (S: acetonitrile)

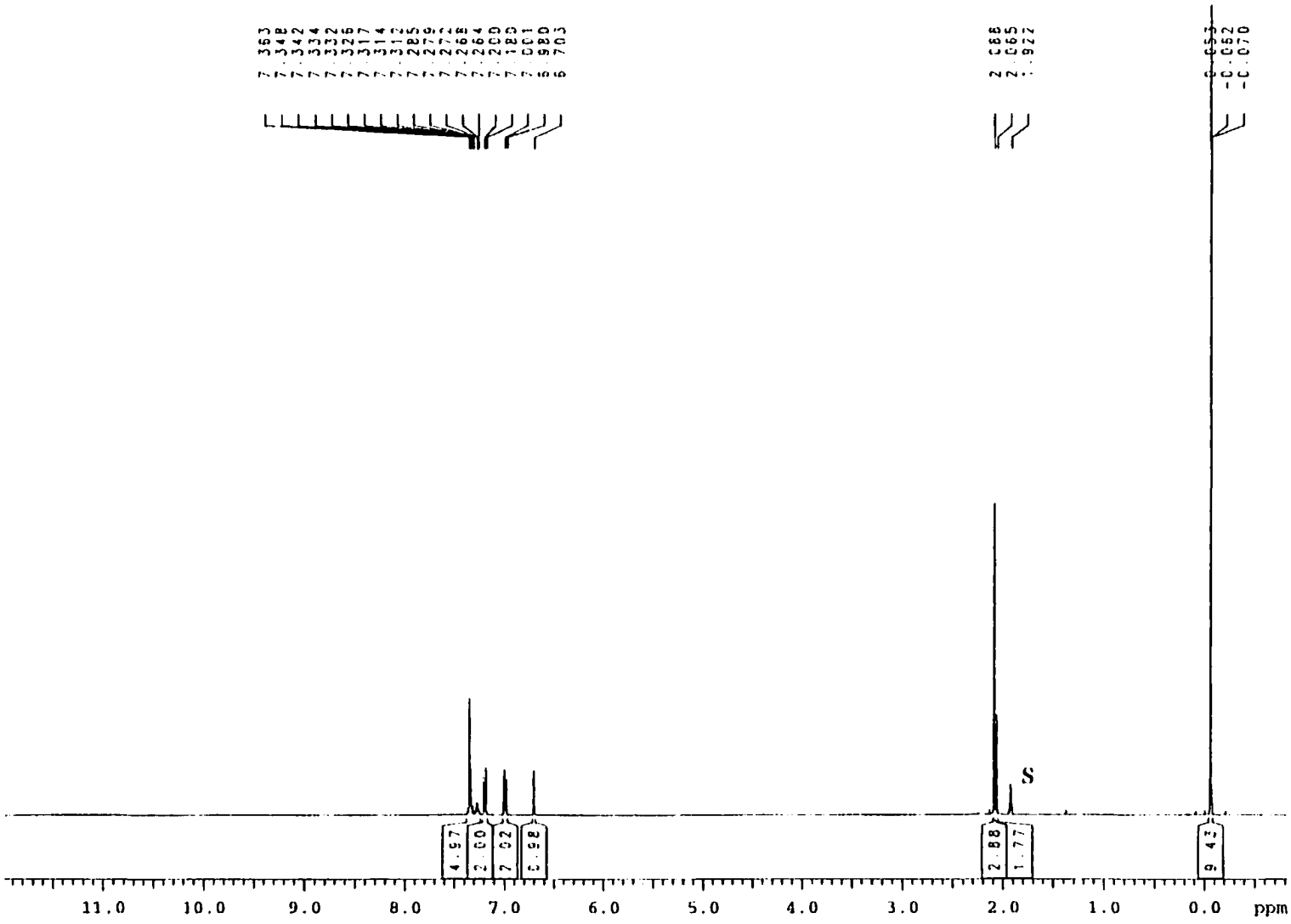


Figure A-3. ^{1}H NMR spectrum (400 MHz, CD_3CN) of (4-[(trimethylsilyl)methyl]phenyl)phenylmethyl acetate (**15**). (S: acetonitrile)

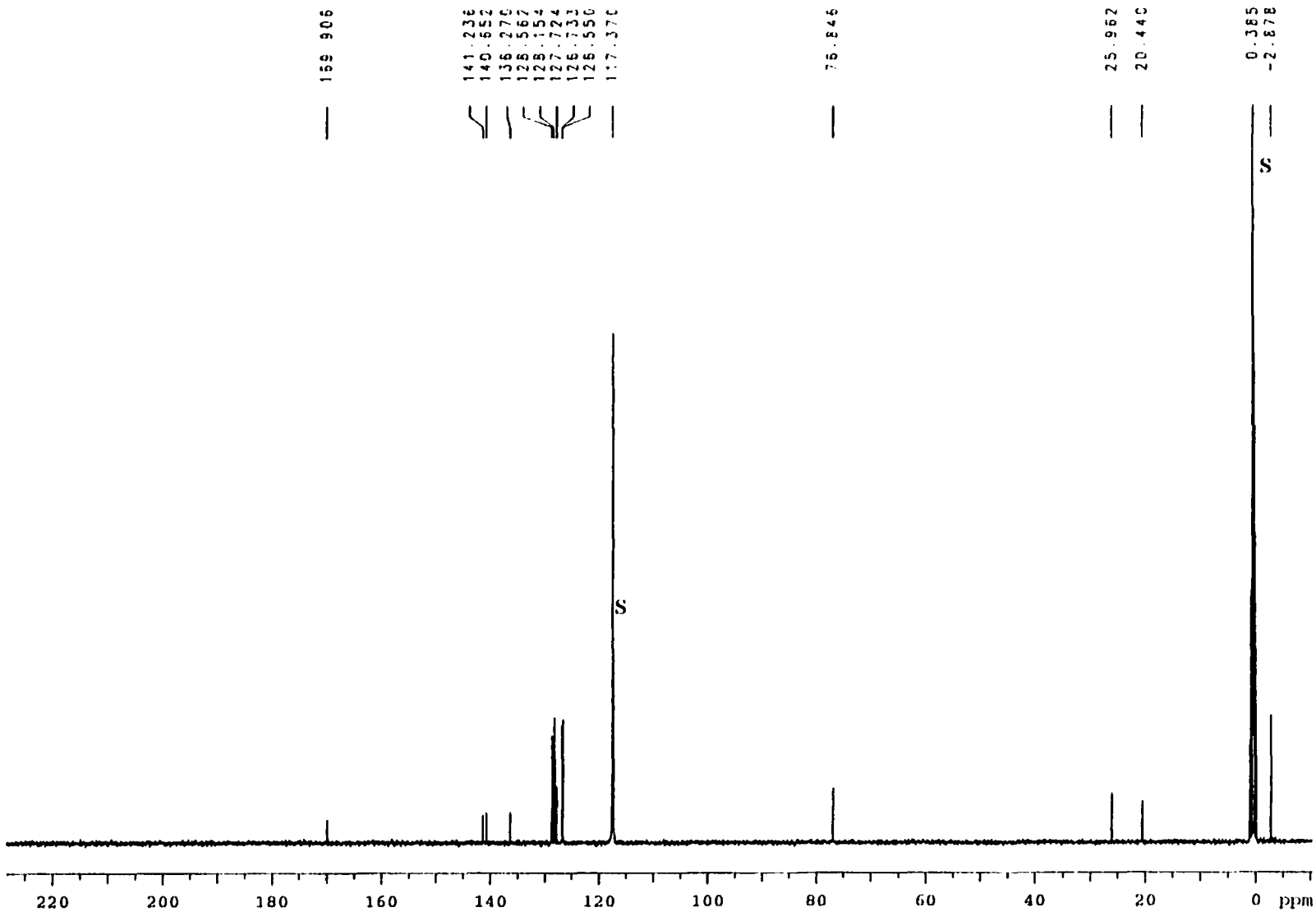


Figure A-4. ^{13}C NMR spectrum (100 MHz, CD_3CN) of (4-[(trimethylsilyl)methyl]phenyl)phenylmethyl acetate (**15**). (S: acetonitrile)

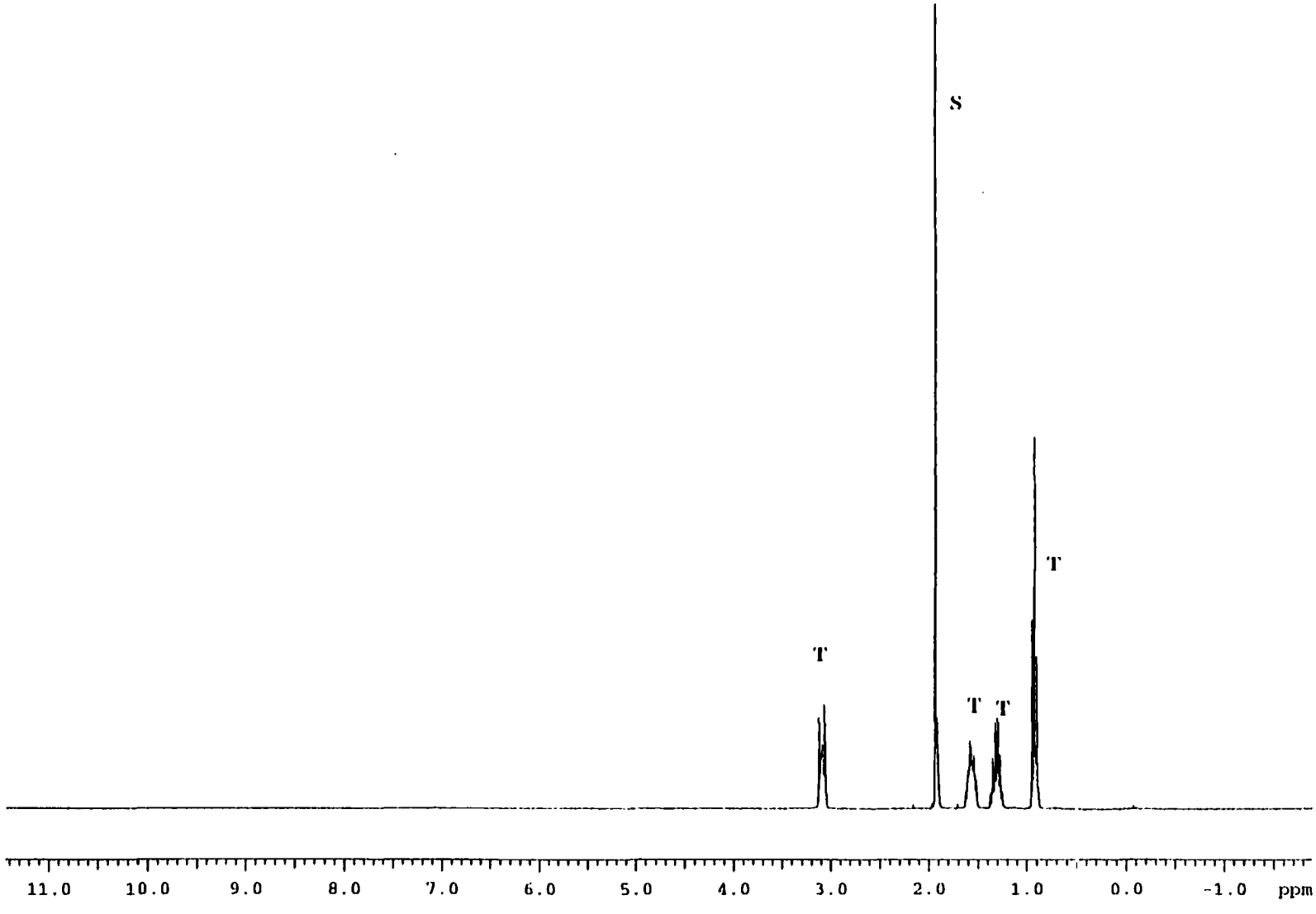


Figure A-5. ^{1}H NMR spectrum (400 MHz, CD_3CN) of α-phenyl-*p*-xylylene (**8**) products with TBAF. (S: acetonitrile, **T**: TBAF)

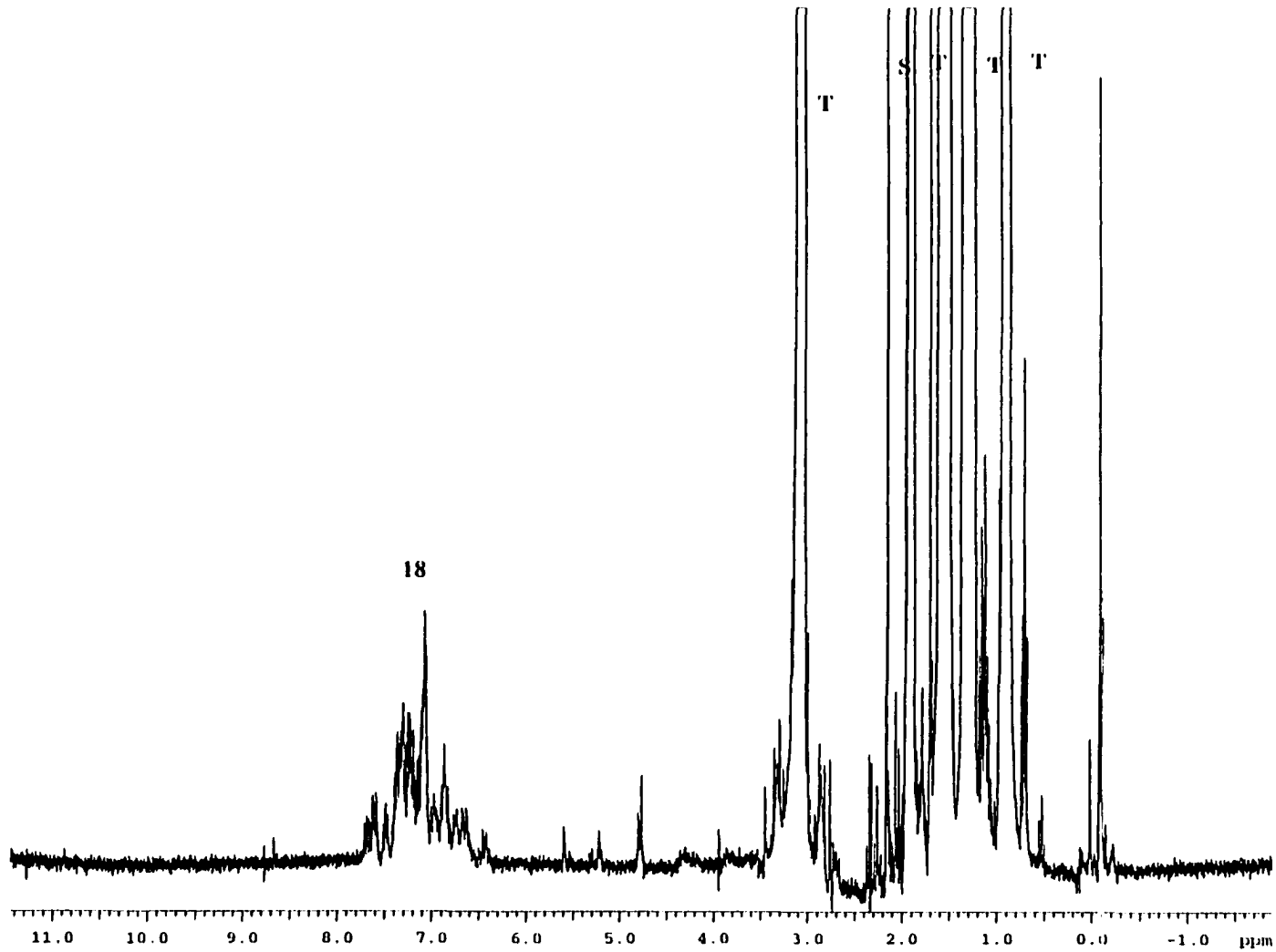


Figure A-6. Enlargement of Figure A-5. ^{1}H NMR spectrum (400 MHz, CD_3CN) of α-phenyl-*p*-xylylene (**8**) products with TBAF. (**18** is a compound number given in the text, S: acetonitrile, T: TBAF)

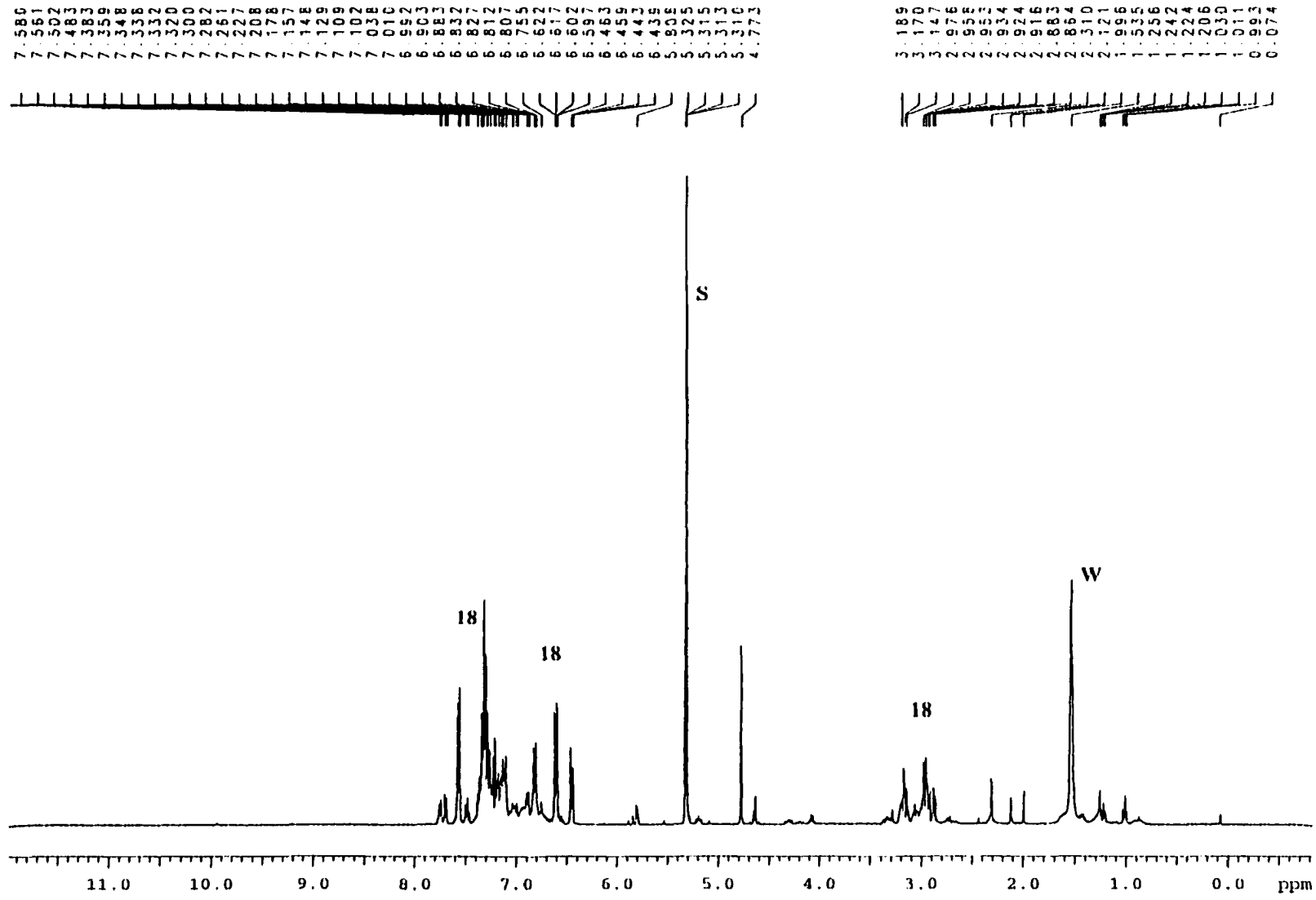


Figure A-7. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of methylene chloride extract of α-phenyl-*p*-xylylene (**8**) products. (**18** is a compound number given in the text, S: methylene chloride, W: water)

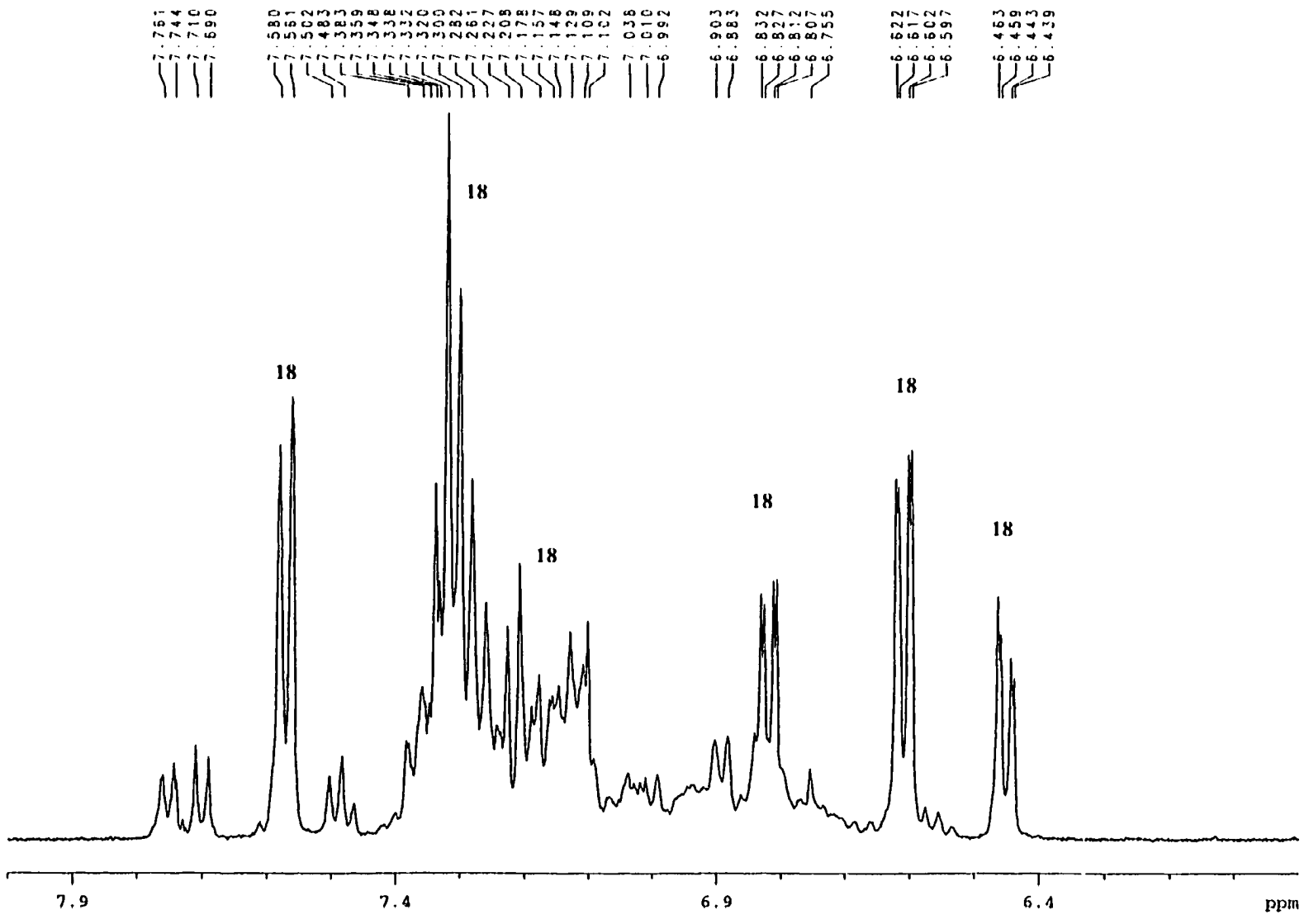


Figure A-8. Enlargement of Figure A-7 from 8–6 ppm. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of methylene chloride extract of α-phenyl-*p*-xylylene (**8**) products. (**18** is a compound number given in the text)

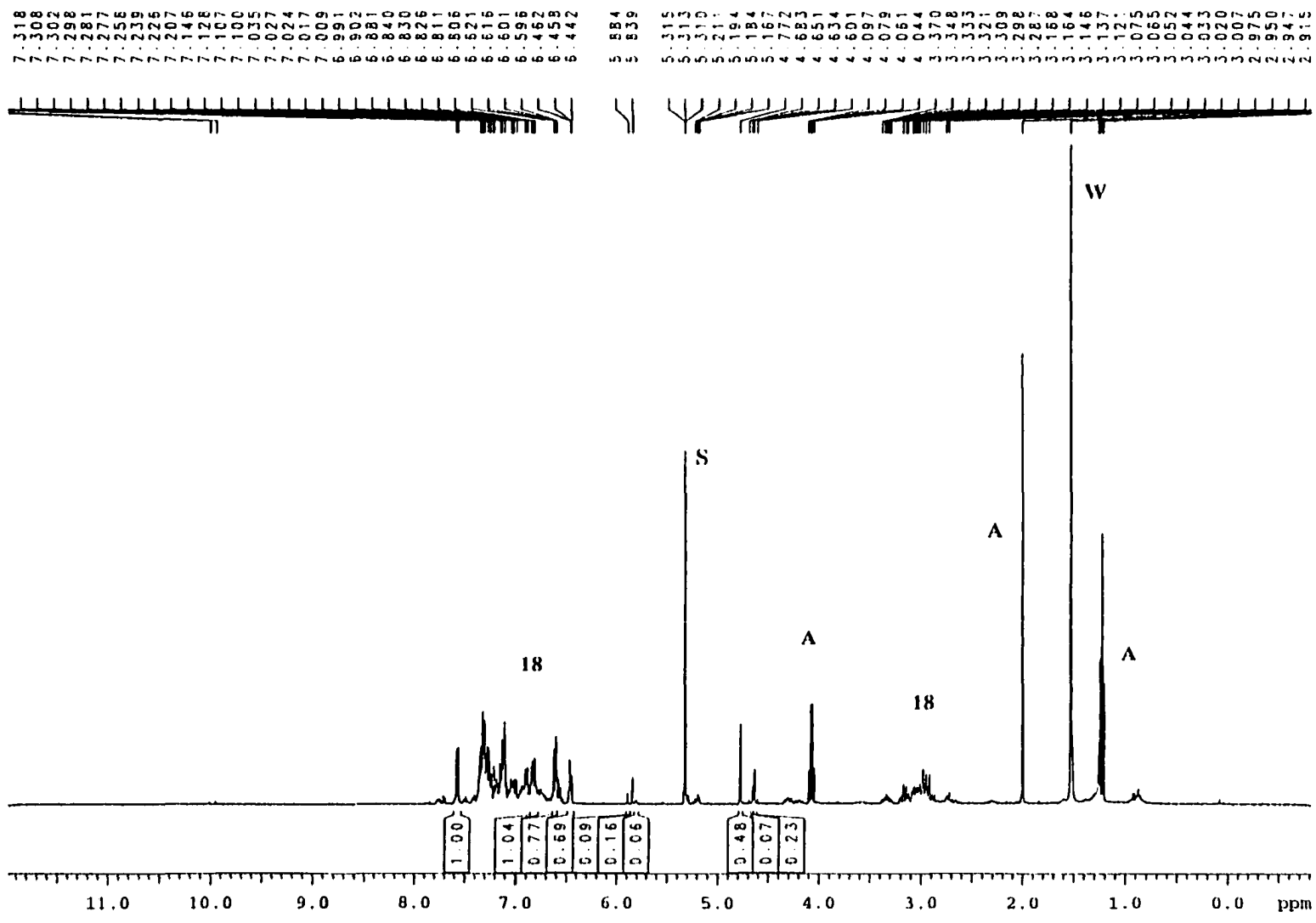


Figure A-9. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ethyl acetate extracted TLC spot of α-phenyl-*p*-xylylene (**8**) products. (**18** is a compound number given in the text, **A**: ethyl acetate, **S**: methylene chloride, **W**: water)

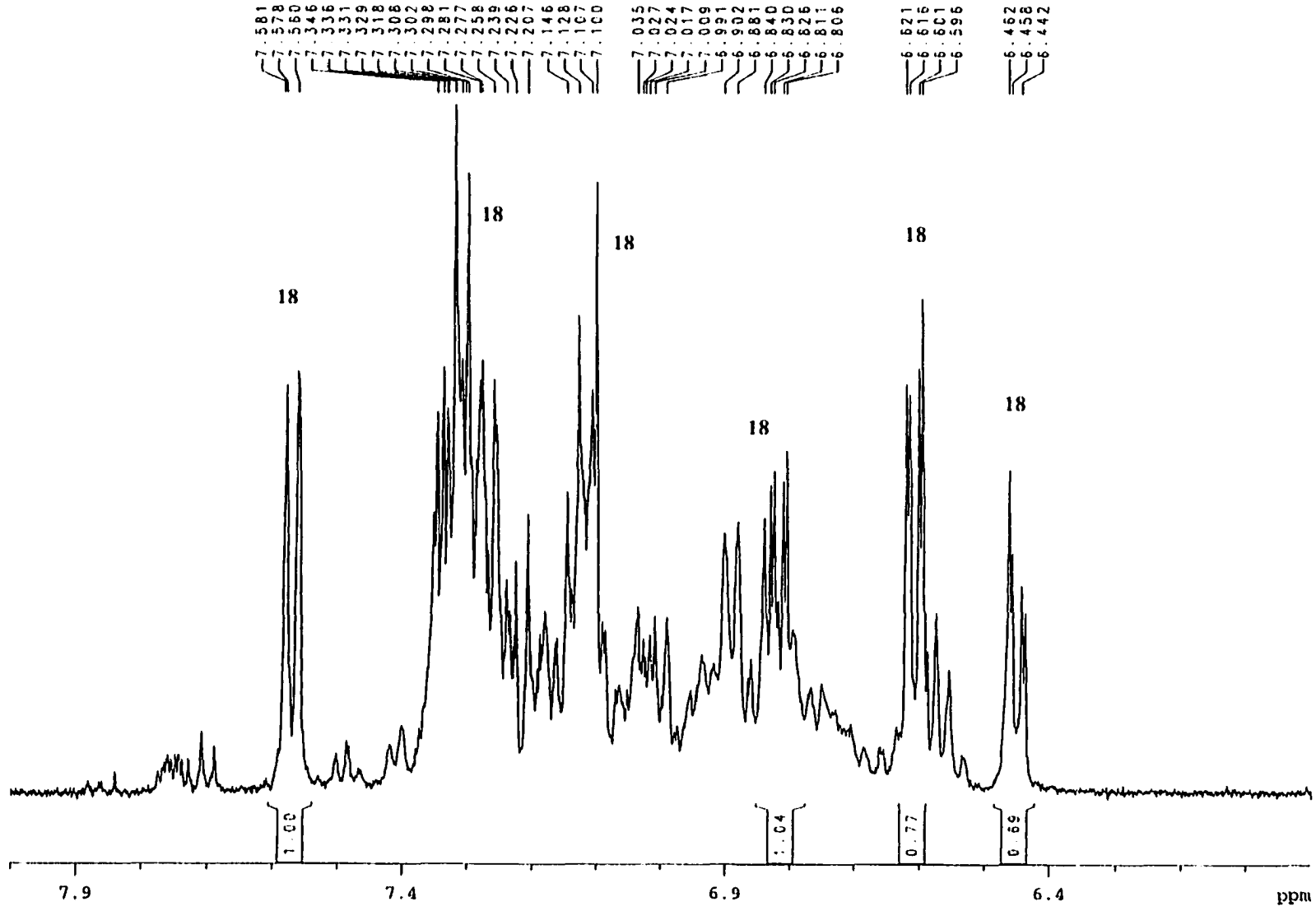


Figure A-10. Enlargement of Figure A-9 from 8–6 ppm. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of ethyl acetate extracted TLC spot of α-phenyl-*p*-xylylene (**8**) products. (**18** is a compound number given in the text)

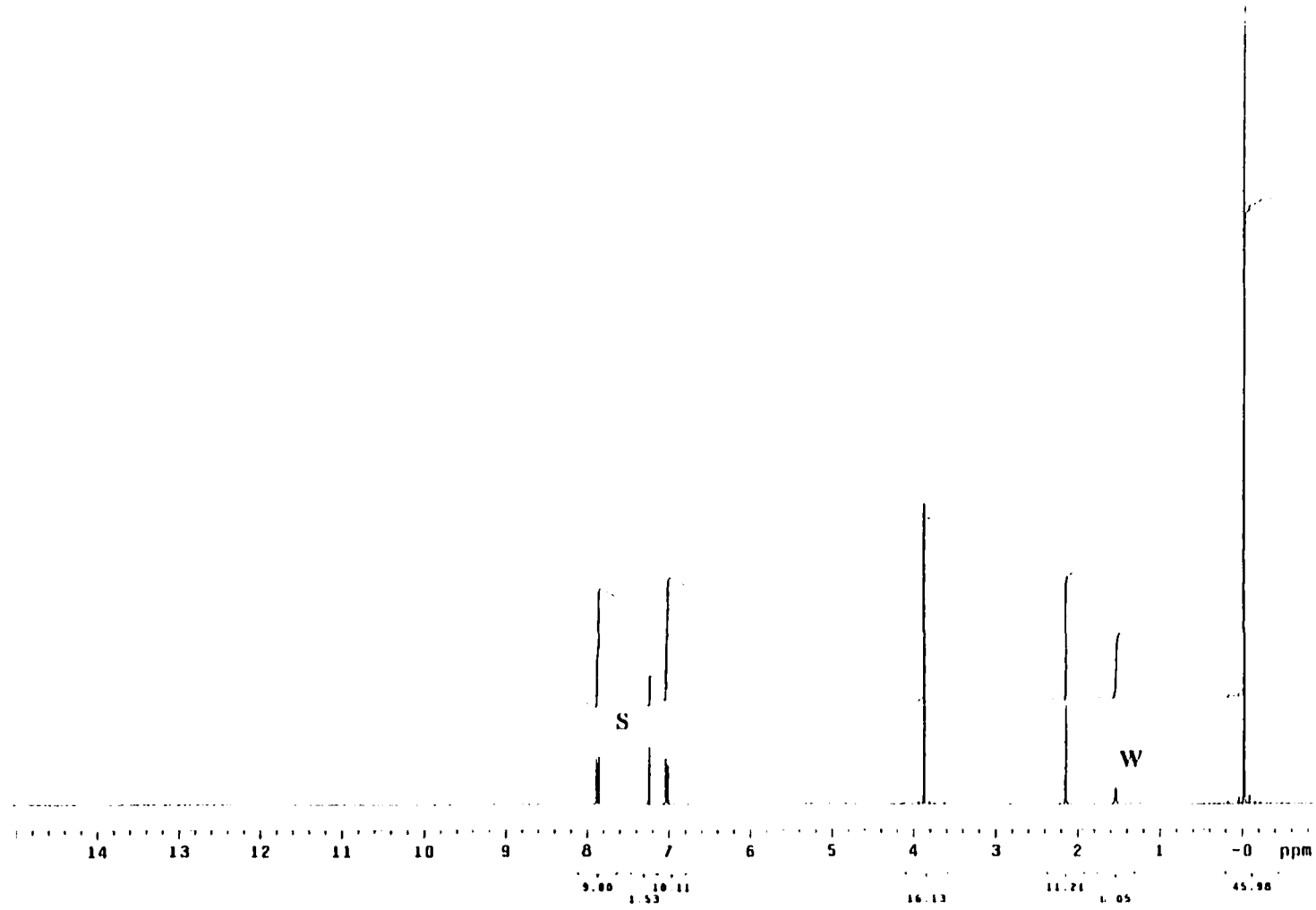


Figure A-11. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of methyl 4-[(trimethylsilyl)methyl]benzoate (**21**). (S: chloroform, W: water)

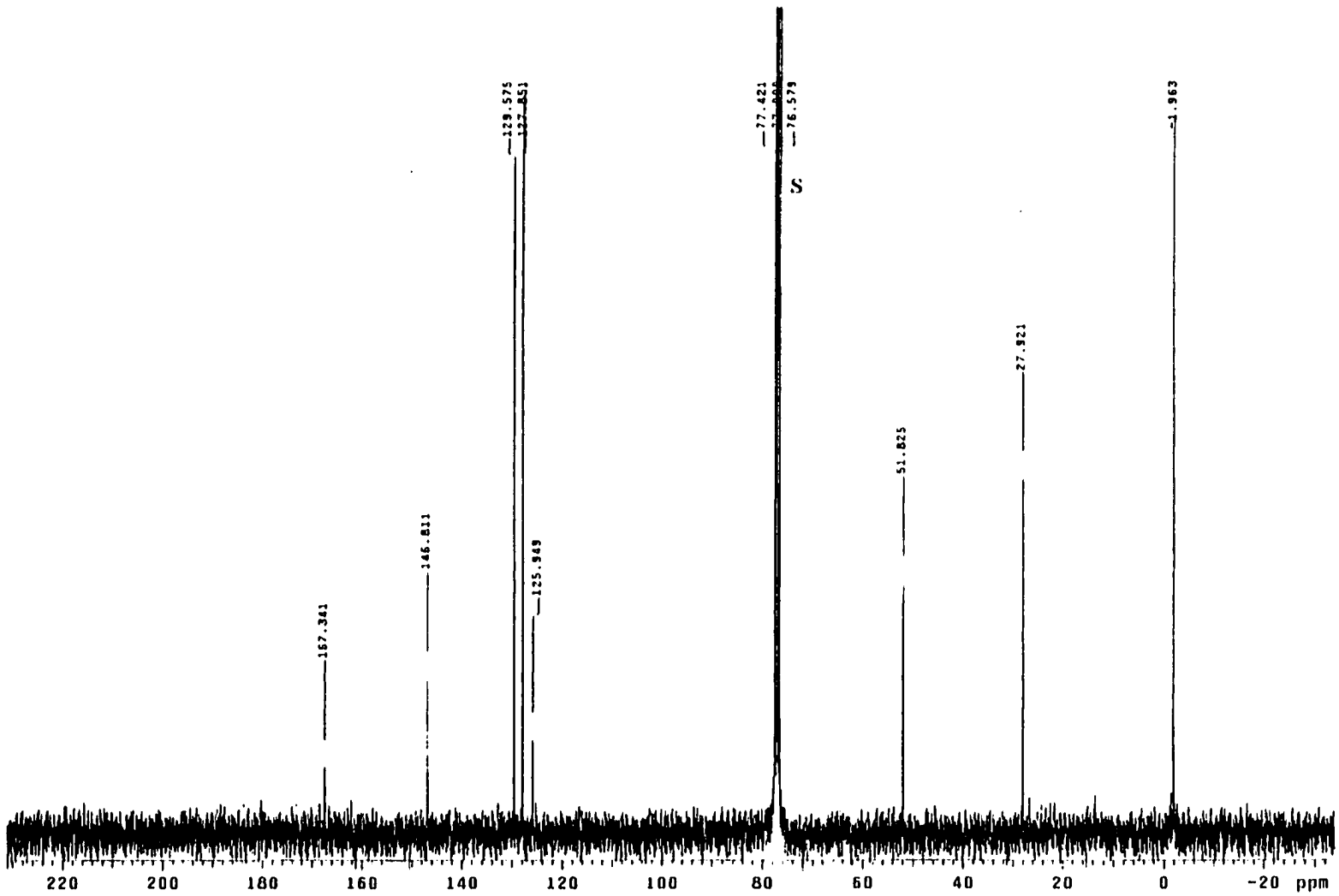


Figure A-12. ^{13}C NMR spectrum (75 MHz, $CDCl_3$) of methyl 4-[(trimethylsilyl)methyl]benzoate (**21**). (S: chloroform)

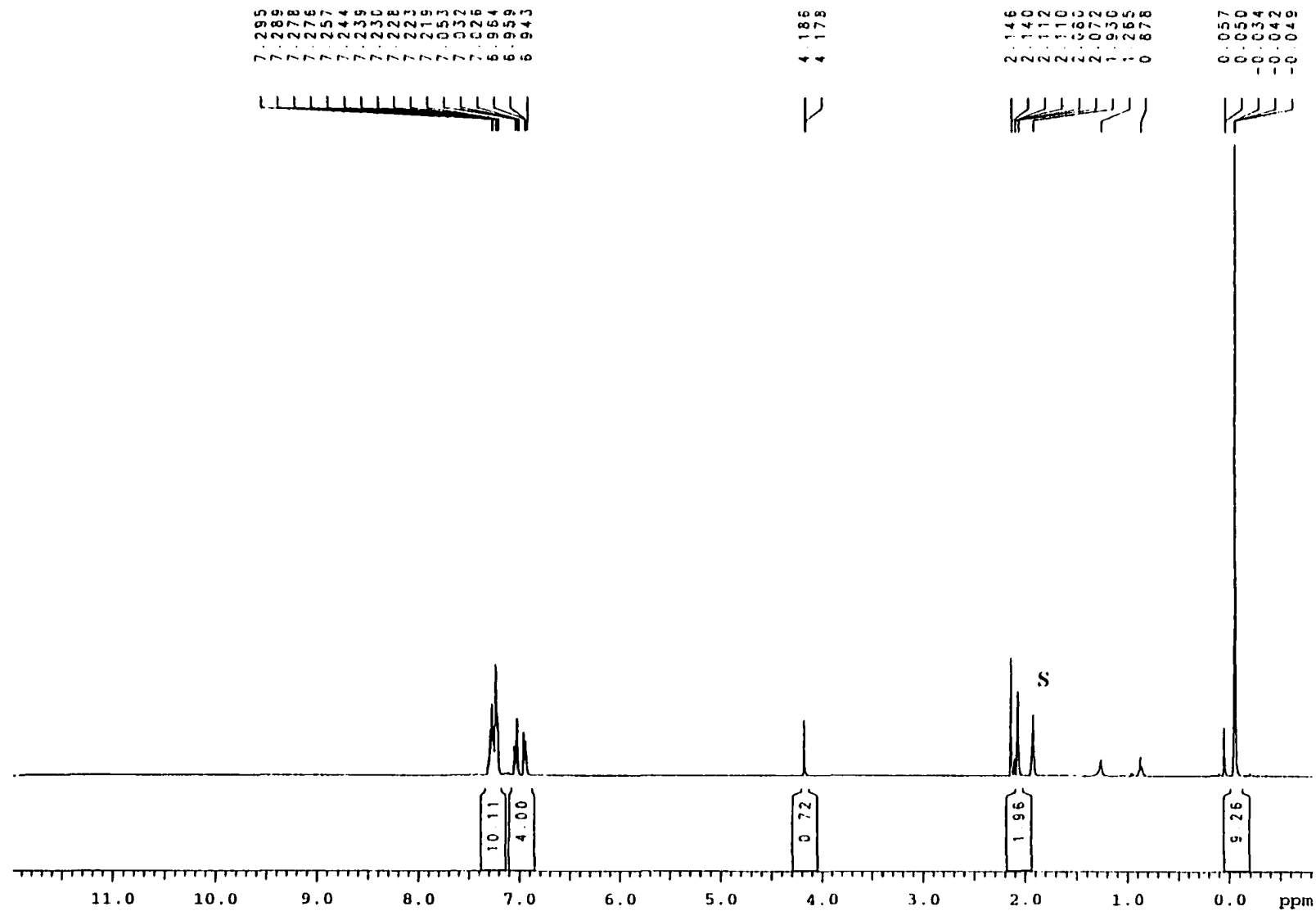


Figure A-13. ^{1}H NMR spectrum (400 MHz, CD_3CN) of (4-[(trimethylsilyl)methyl]phenyl)diphenylmethanol (**22**). (S: acetonitrile)

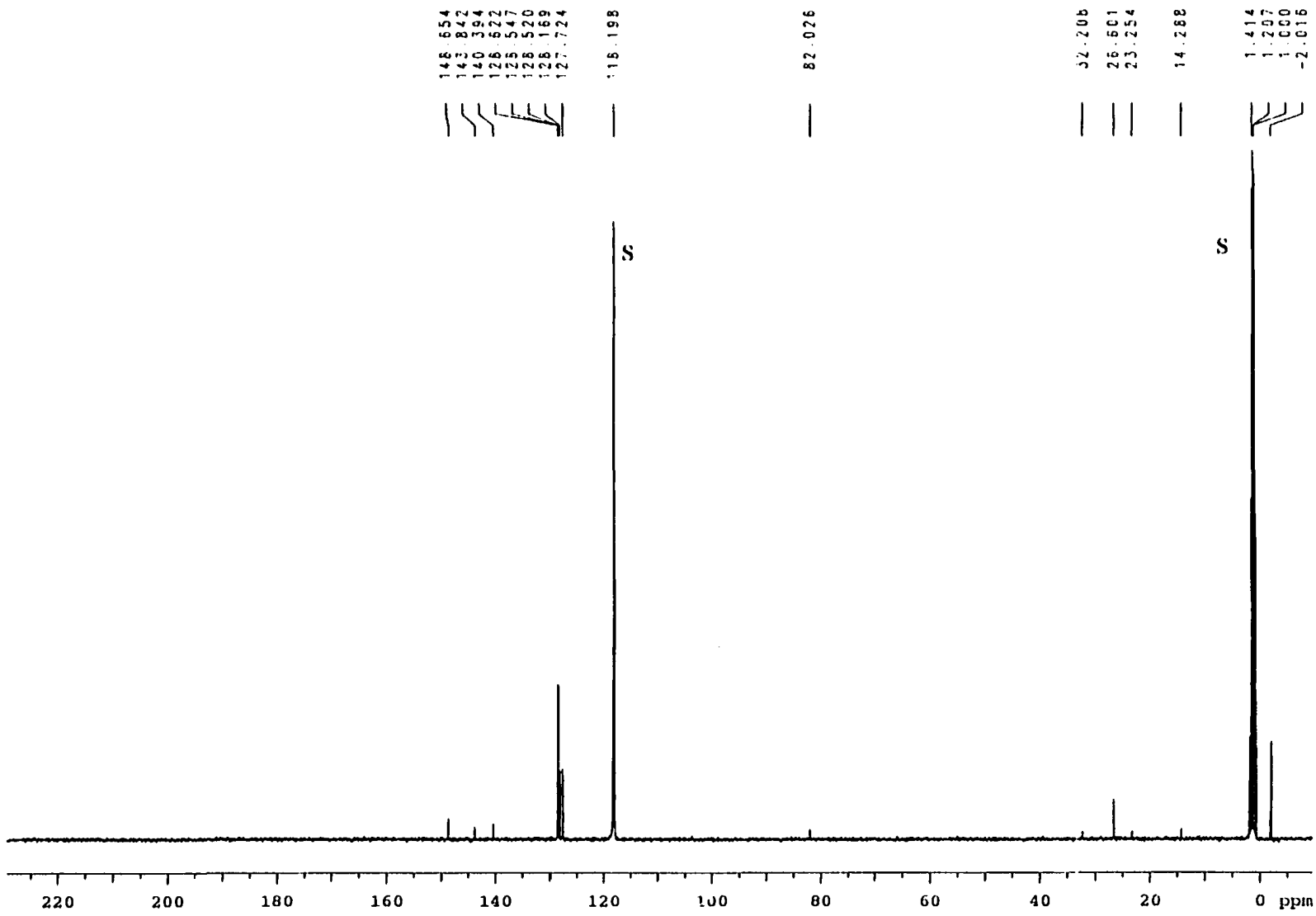


Figure A-14. ^{13}C NMR spectrum (100 MHz, CD_3CN) of (4-[(trimethylsilyl)methyl]phenyl)diphenylmethanol (22). (S: acetonitrile)

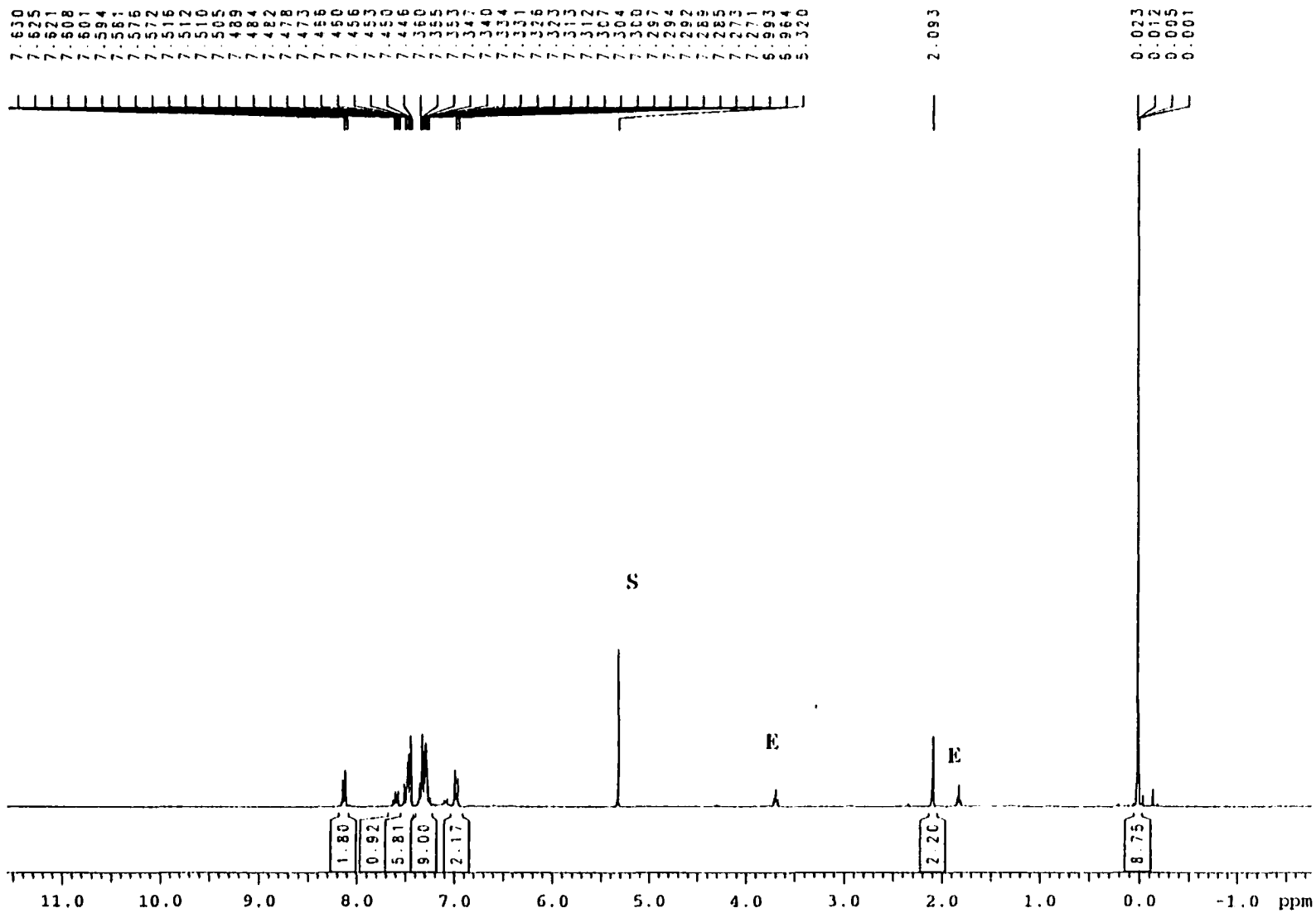


Figure A-15. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of (4-[(trimethylsilyl)methyl]phenyl)diphenylmethyl benzoate (**19**). (E: ethyl ether, S: methylene chloride)

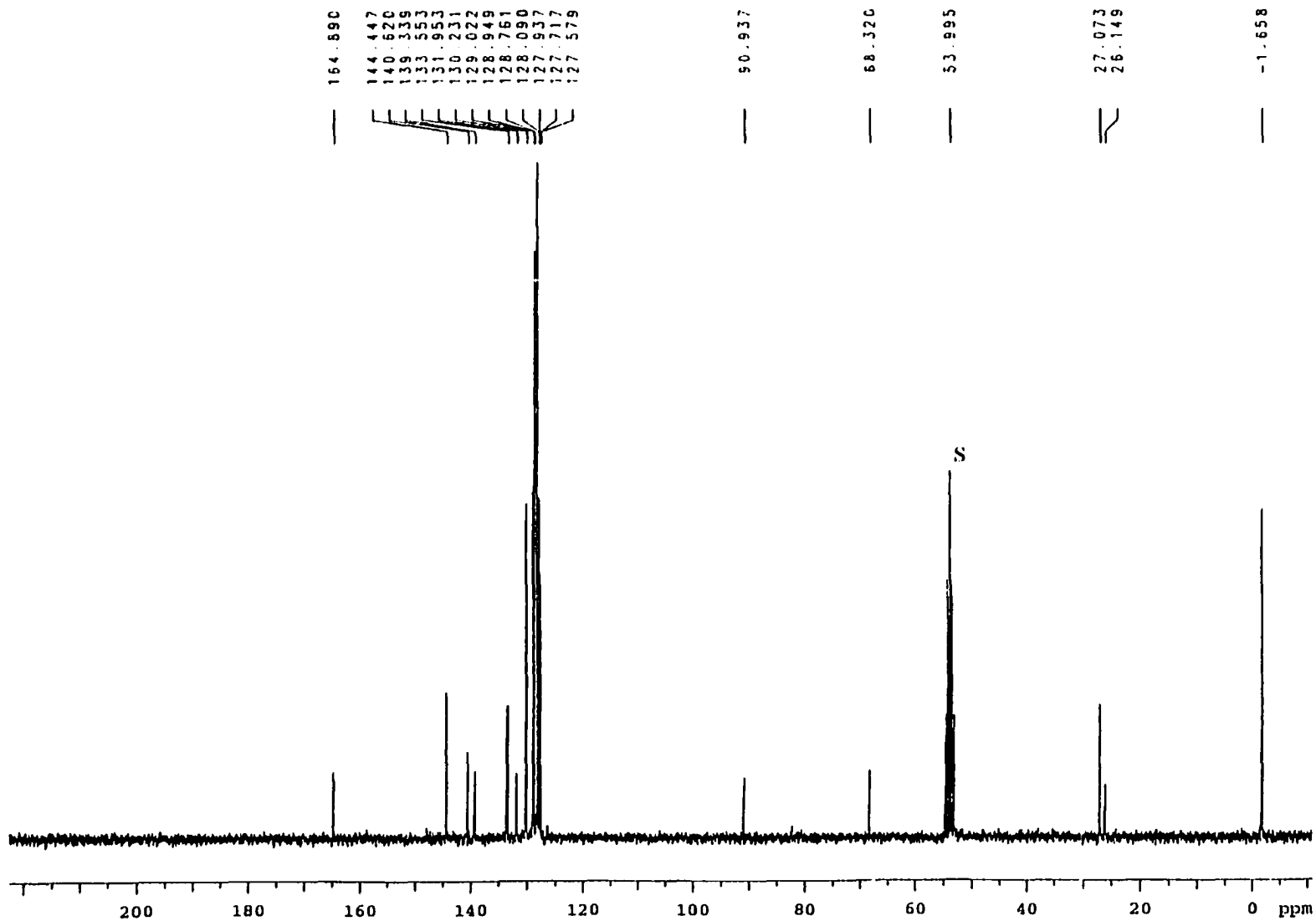


Figure A-16. ^{13}C NMR spectrum (75 MHz, CD_2Cl_2) of (4-[(trimethylsilyl)methyl]phenyl)diphenylmethyl benzoate (**19**). (S: methylene chloride)

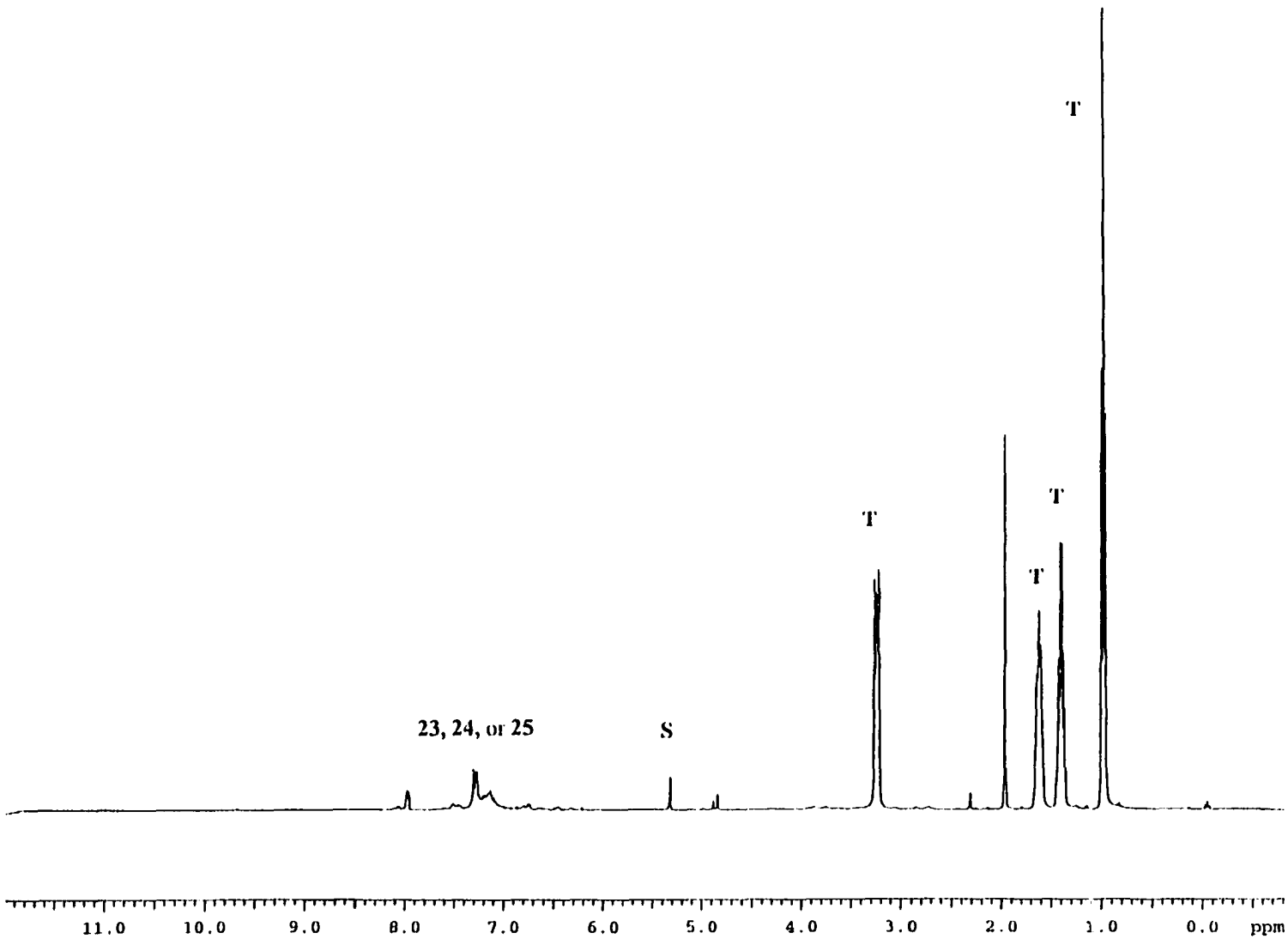


Figure A-17. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of α,α-diphenyl-*p*-xylylene (**6**) products with TBAF. (**23**, **24**, and **25** are compound numbers given in the text, **S**: methylene chloride, **T**: TBAF)

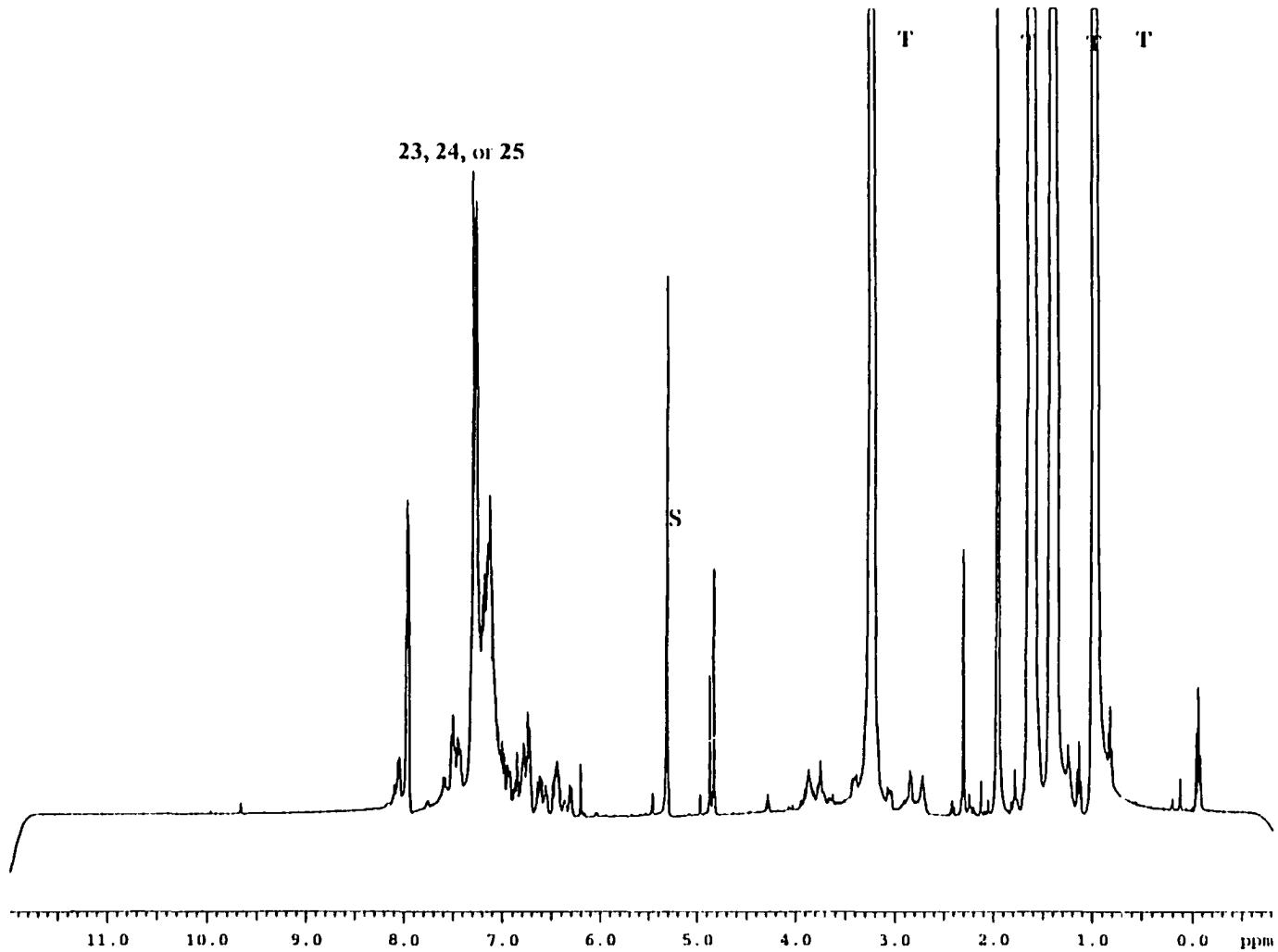


Figure A-18. Enlargement of Figure A-17 from 12 to -1 ppm. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of α,α-diphenyl-*p*-xylylene (**6**) products with TBAF. (**23, 24**, and **25** are compound numbers given in the text, **S**: methylene chloride, **T**: TBAF)

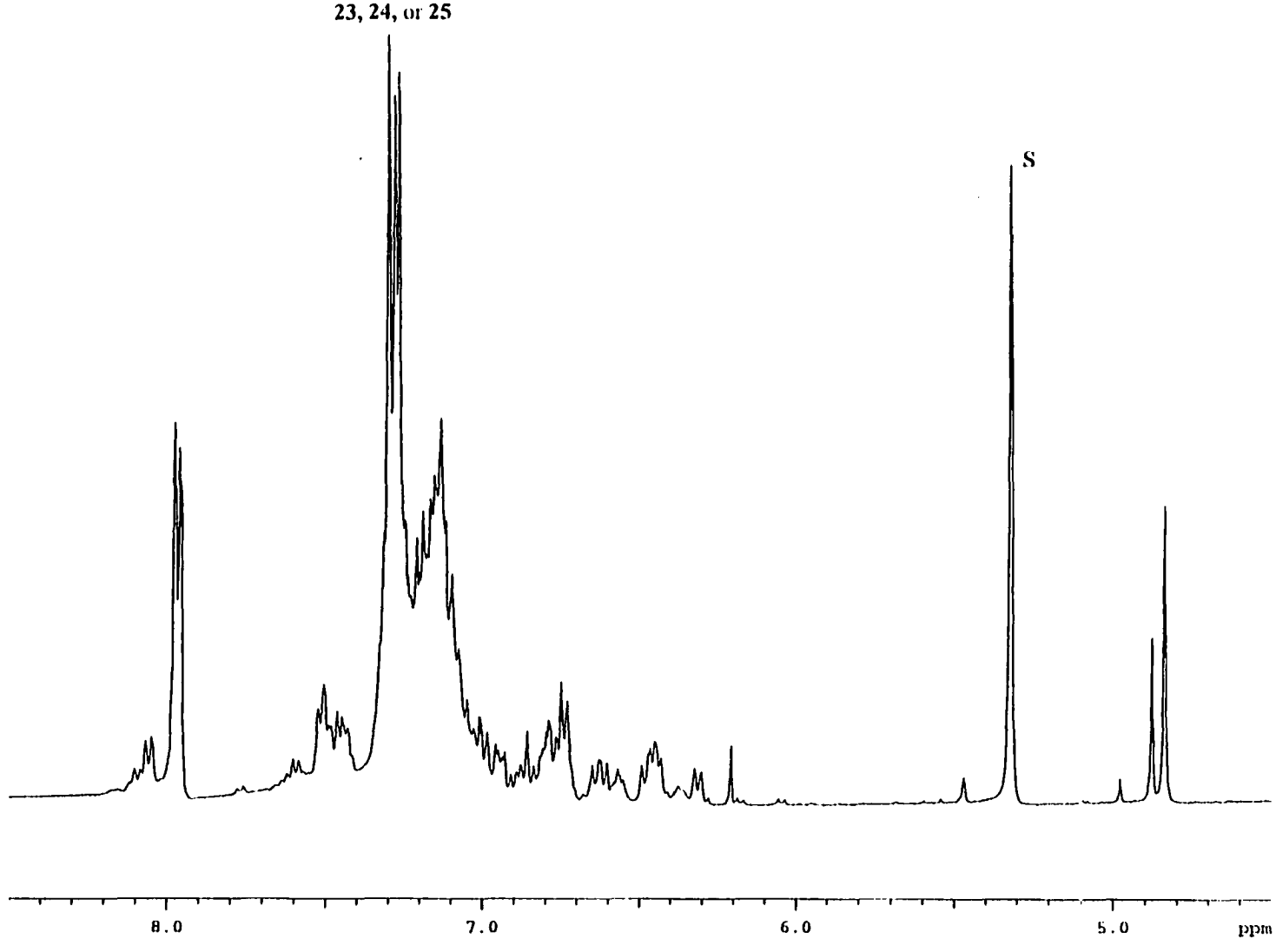


Figure A-19. Enlargement of Figure A-17 from 8.5– 4.5 ppm. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of α,α-diphenyl-*p*-xylylene (**6**) products with TBAF. (**23**, **24**, and **25** are compound numbers given in the text, **S**: methylene chloride)

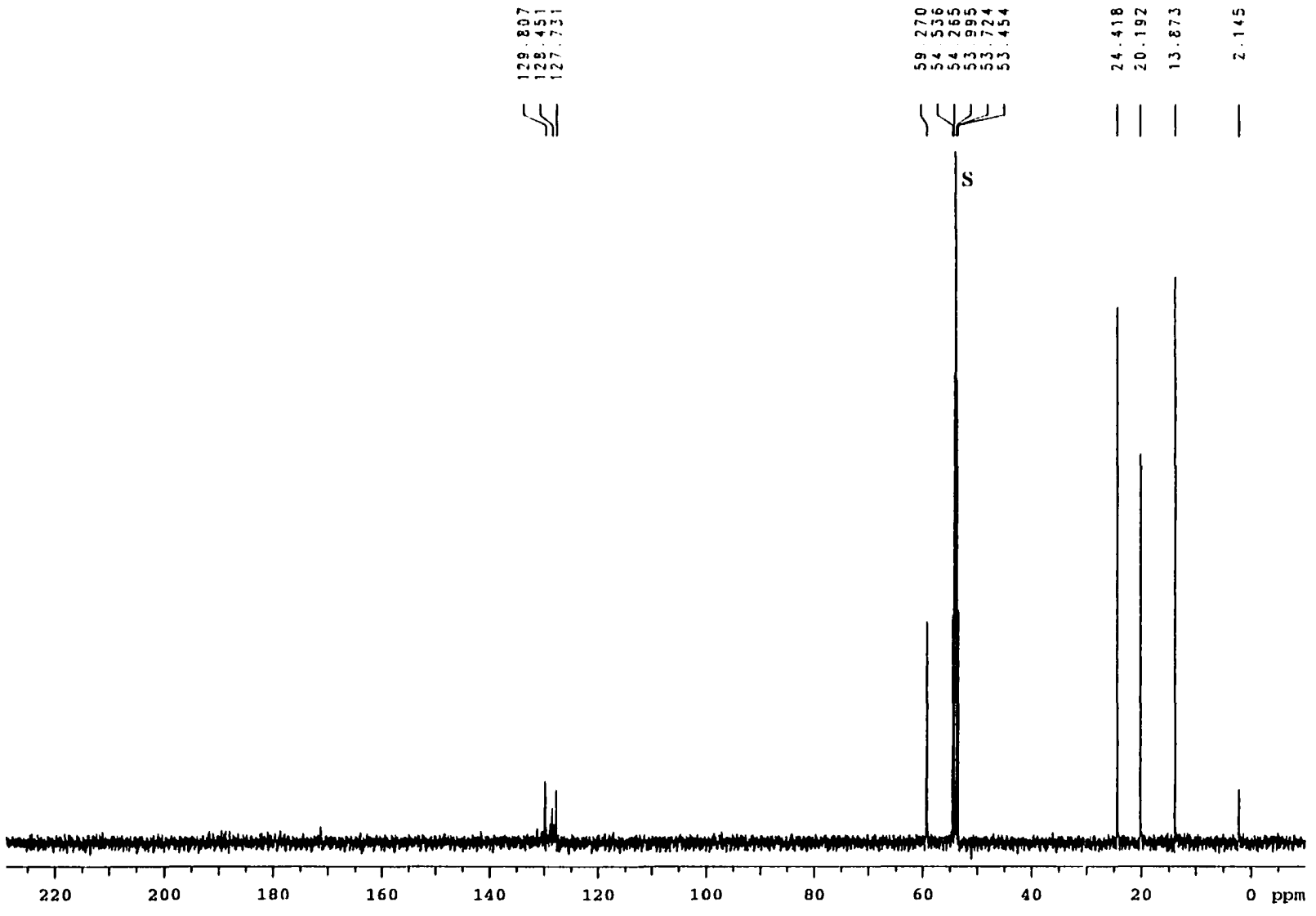


Figure A-20. ^{13}C NMR spectrum (75 MHz, CD_2Cl_2) of α,α-diphenyl-*p*-xylylene (**6**) products with TBAF. (S: methylene chloride)

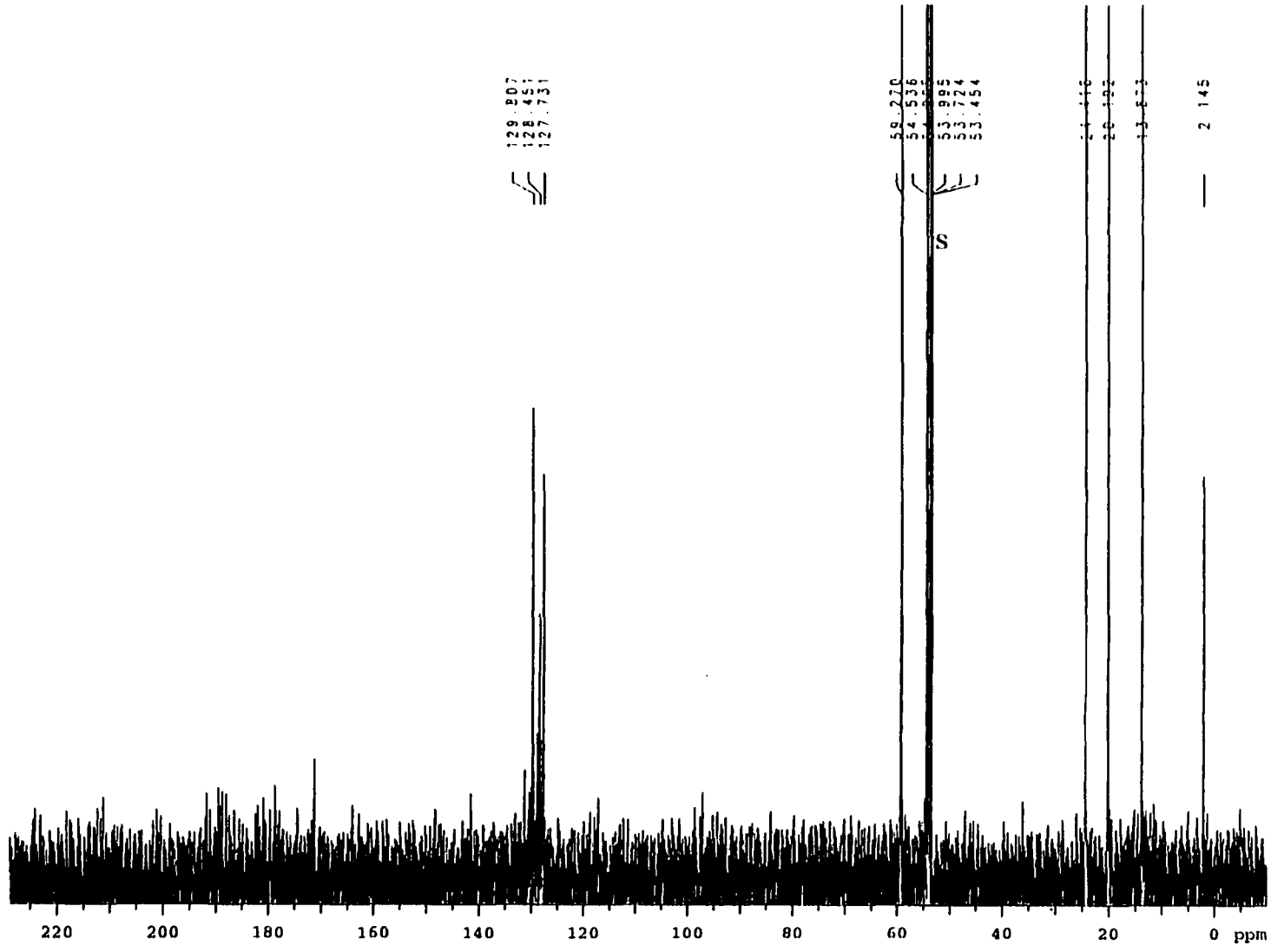


Figure A-21. Enlargement of Figure A-20 from 230 to -10 ppm. ^{13}C NMR spectrum (75 MHz, CD_2Cl_2) of α,α-diphenyl-*p*-xylylene (**6**) products with TBAF. (S: methylene chloride)

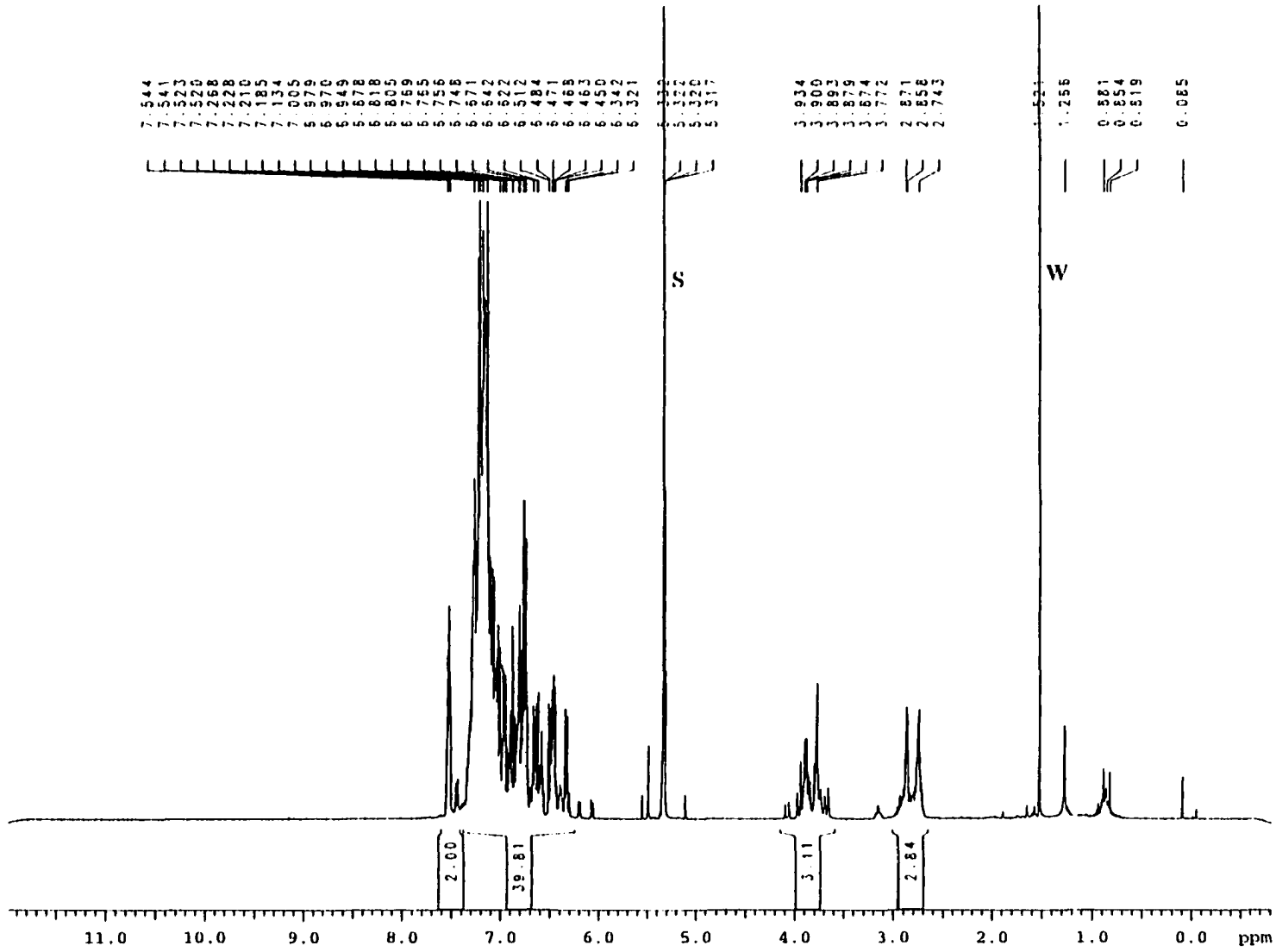


Figure A-22. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of methylene chloride extracted TLC spot of α,α-diphenyl-*p*-xylylene (**6**) products. (**S**: methylene chloride, **W**: water)

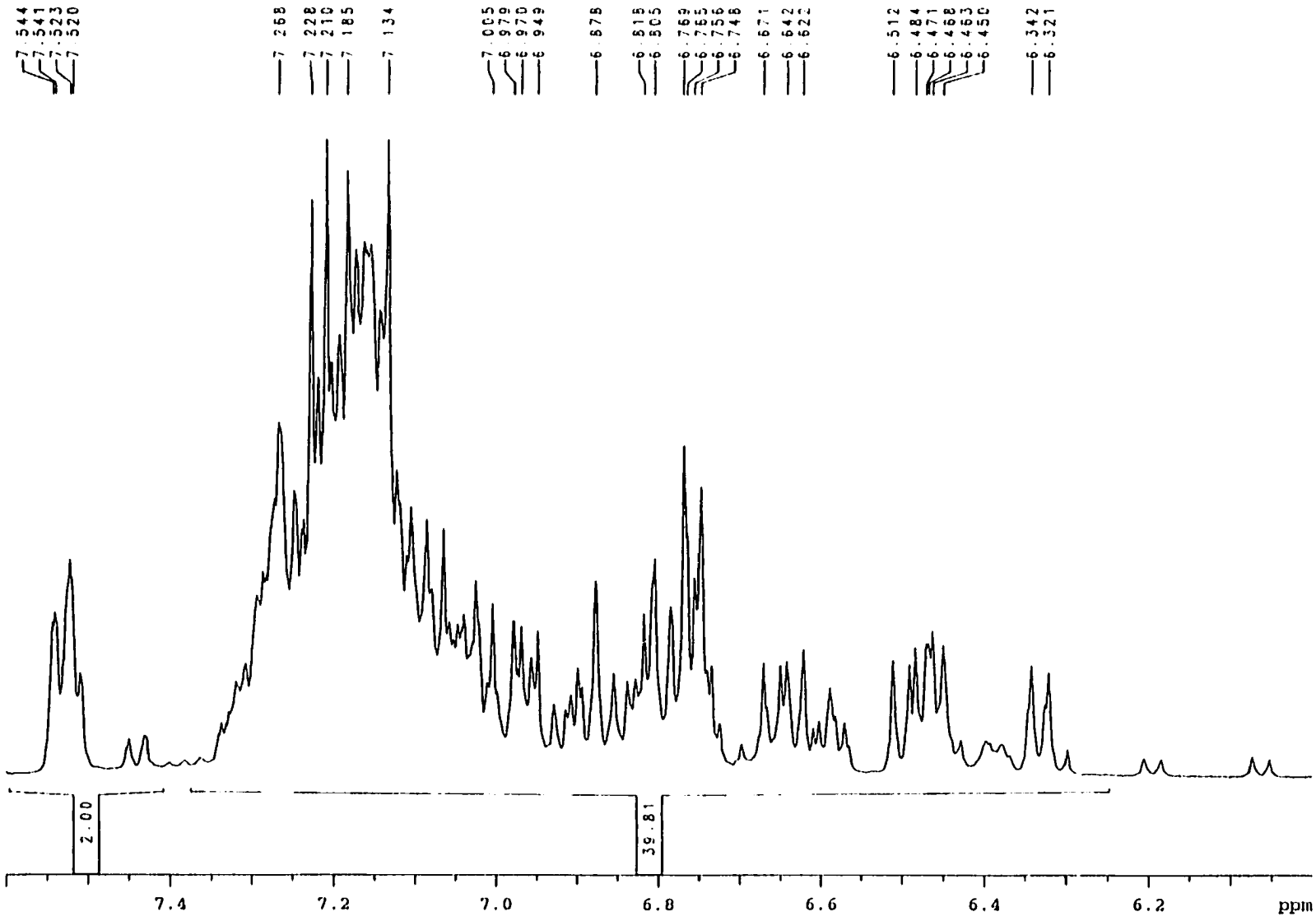


Figure A-23. Enlargement of Figure A-22 from 7.6 -6 ppm. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of methylene chloride extracted TLC spot of α,α-diphenyl-*p*-xylylene (**6**) products.

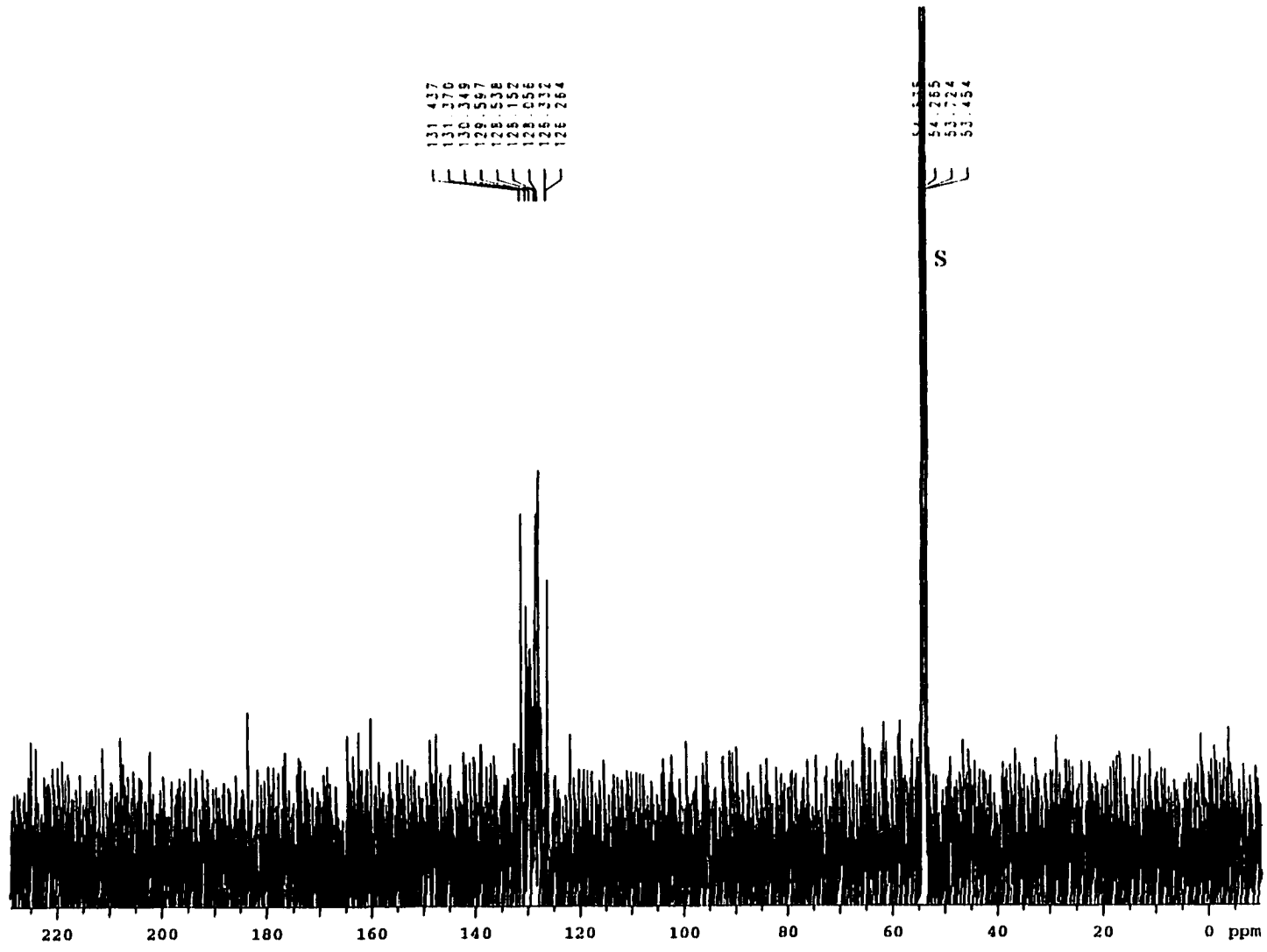


Figure A-24. ^{13}C NMR spectrum (75 MHz, CD_2Cl_2) of methylene chloride extracted TLC spot of α,α-diphenyl-*p*-xylylene (**6**) products. (S: methylene chloride)

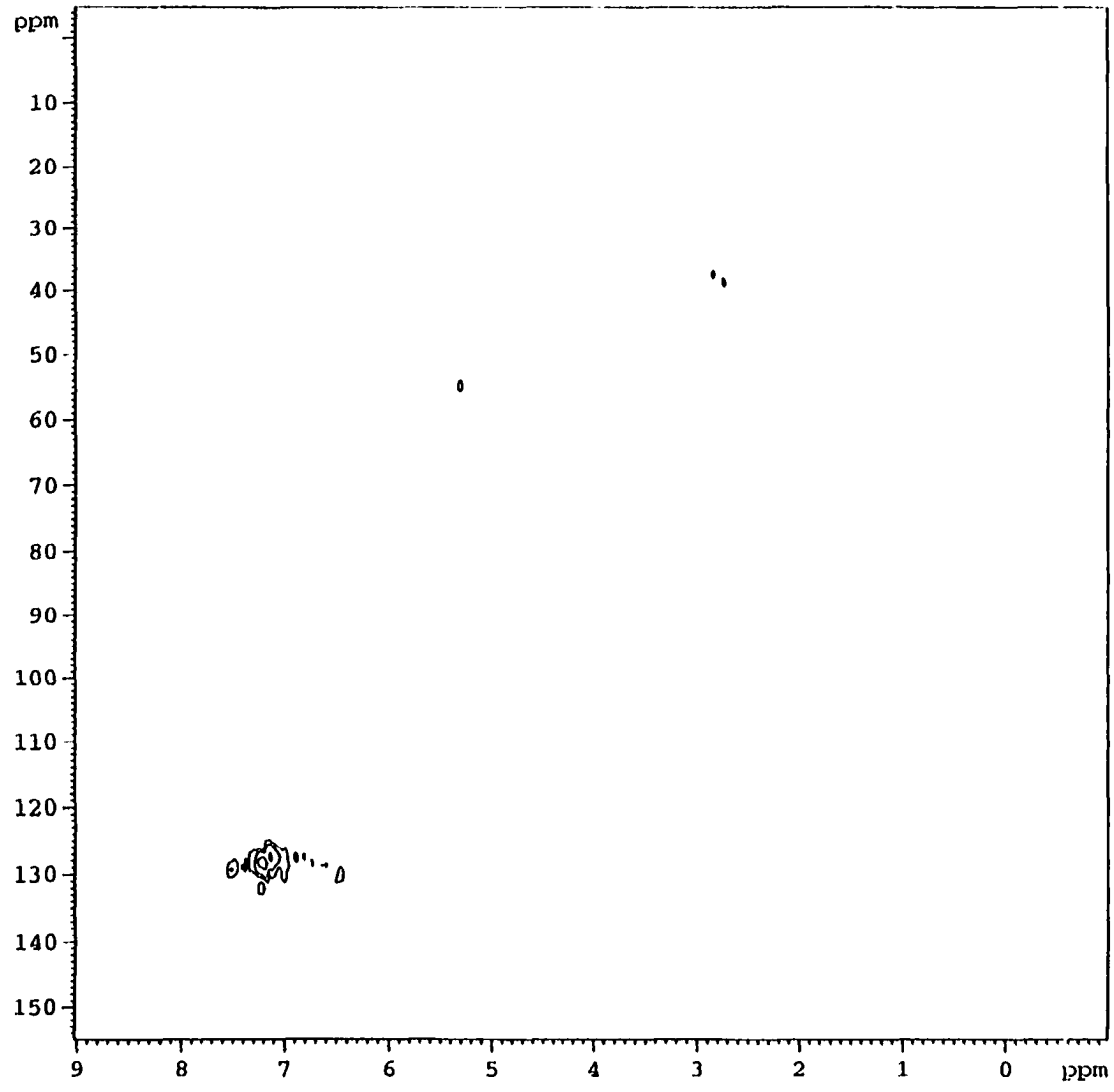


Figure A-25. HETCOR spectrum (CD_2Cl_2) of methylene chloride extracted TLC spot of α,α-diphenyl-*p*-xylylene (**6**) products.

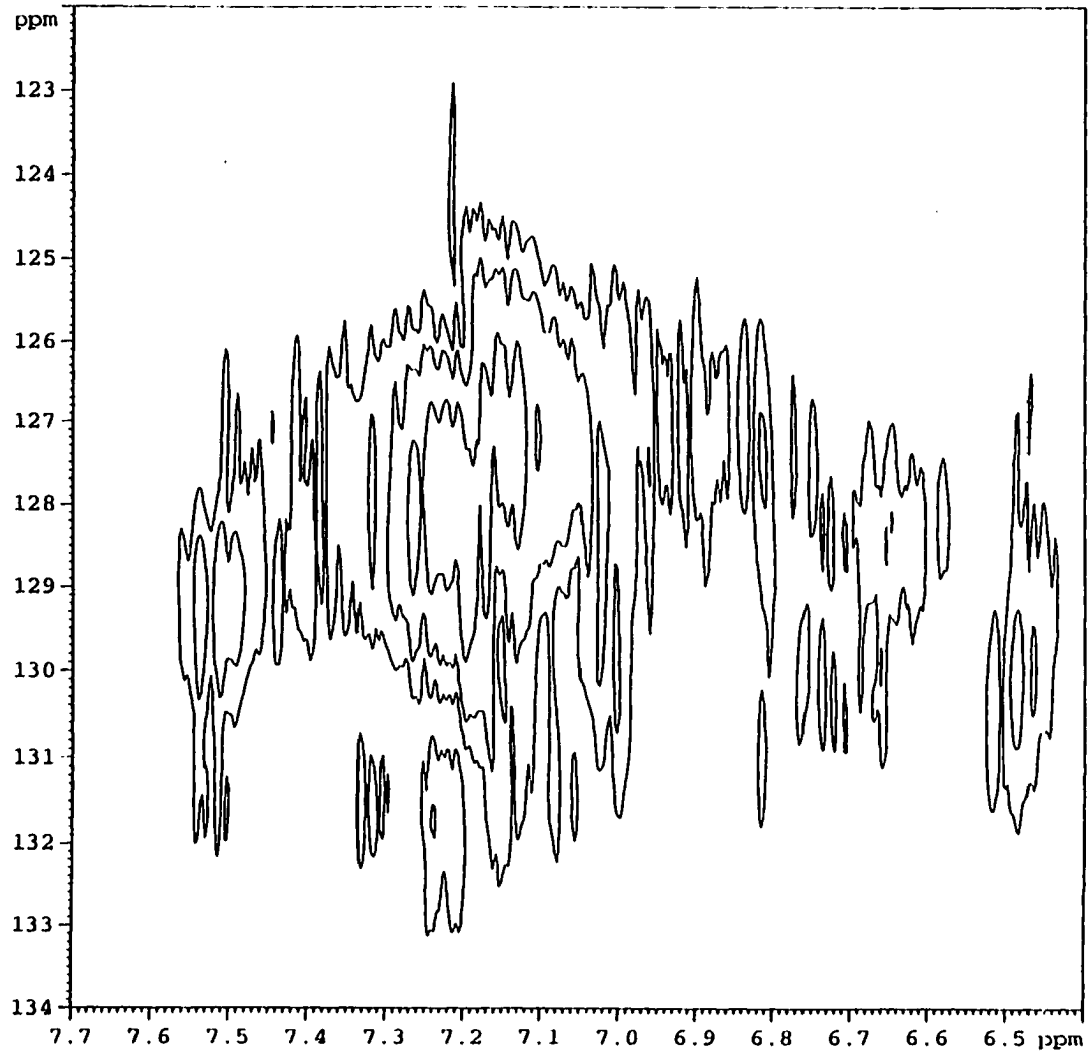


Figure A-26. Enlargement of Figure A-25. HETCOR spectrum (CD_2Cl_2) of methylene chloride extracted TLC spot of α,α-diphenyl-*p*-xylylene (**6**) products.

Table A-1. ^{1}H NMR and Kinetic Data for *p*-Xylylene (1).

	relative area of peak integration						
Time, s	δ7.91-7.83[a]	δ 7.53-7.45[a]	δ 7.30-7.16[b]	δ 7.14-7.00[b]	δ 6.47-6.43[c]	δ5.10-5.03[c]	[1], M
1	1.00	0.89	1.48	1.56			0.00193
1200	1.00	1.01			1.44	1.93	0.001006
19800	1.00	0.90			0.10	0.13	7.26E-05
57600	1.00	1.05			0.04	0.05	2.63E-05

[a] Naphthalene, internal standard. [b] Starting acetate **9**. [c] *p*-QDM **1**.

Table A-2. ^{1}H NMR and Kinetic Data for α-Methyl-*p*-xylylene (4).

	relative area of peak integration						
Time, s	δ7.91-7.83[a]	δ 7.53-7.45[a]	δ 7.30-7.16[b]	δ 7.14-7.00[b]	δ 6.47-6.43[c]	δ5.99-5.50[c]	[4], M
0.1	1.01	1.01	2.00	1.91			0.001469
600	1.19	1.46			2.00	2.50	0.001289
5400	2.43	2.59			2.00	2.25	0.000644
19800	8.46	8.40			1.60	2.05	0.000164

[a] Naphthalene, internal standard. [b] Starting acetate **12**. [c] *p*-QDM **4**.

Table A-3. ^{1}H NMR and Kinetic Data for *p*-Xylylene (1).

	relative area of peak integration				
Time, s	δ7.93-7.80[a]	δ 7.53-7.44[a]	δ 6.46-6.42[b]	δ5.10-5.03[b]	[1], M
210	0.048294	0.251352	0.7337	0.906805	0.002968
301	0.001696	0.163426	0.710012	0.893408	0.002901
392	0.020532	0.103578	0.707207	0.89927	0.002907
483	-0.02625	0.22485	0.607098	0.911598	0.002748
574	0.067598	0.170469	0.547379	0.81587	0.002466
665	-0.03523	0.395089	0.616911	0.704518	0.002391
756	-0.02497	0.248015	0.624218	0.843609	0.002656
847	-0.00668	0.265821	0.517171	0.768882	0.002327
938	-0.04449	0.3761	0.417877	0.861698	0.002315
1029	0.010344	0.282544	0.532707	0.738289	0.0023
1120	0.008533	0.272811	0.514482	0.78481	0.002351
1211	0.040049	0.26137	0.433708	0.770473	0.002179
1302	-0.00099	0.374713	0.476467	0.721932	0.002168
1393	0.008024	0.268993	0.47085	0.7883	0.002278
1484	0.022874	0.227467	0.560201	0.71936	0.002315
1575	-0.0862	0.226261	0.47046	0.672973	0.002069
1666	-0.03608	0.258866	0.531499	0.731743	0.002286
1757	0.070908	0.252365	0.512628	0.722891	0.002235
1848	-0.02935	0.33479	0.47993	0.653678	0.002051
1939	-0.15258	0.299196	0.479755	0.607356	0.001967
2030	-0.08805	0.146113	0.401155	0.736442	0.002058
2121	-0.08961	0.158234	0.47838	0.65446	0.00205
2212	0.027896	0.149039	0.500584	0.608838	0.002007
2303	0.143587	0.256084	0.385533	0.734845	0.002027

[a] Naphthalene, internal standard. [b] *p*-QDM 1.

Table A-4. ^{1}H NMR and Kinetic Data for α-Phenyl-*p*-xylylene (8).

	relative area of peak integration						
Time, s	δ7.91-7.83[a]	δ 7.53-7.45[a]	δ 7.08-7.01[b]	δ 6.62-6.56[b]	δ 6.55-6.49[b]	δ5.13-5.07[b]	[8], M
210	100	99.9998	18.0371	18.0907	48.0001	39.1927	0.000635
301	83.3373	84.6375	23.9578	22.6364	59.1395	44.0005	0.000849
451	95.2146	99.8187	20.1228	18.6057	53.2802	42.4276	0.000705
661	95.0835	99.3803	16.1206	16.7088	40.9705	30.5409	0.000509
871	99.4667	106.241	11.9976	13.0714	27.7277	20.9891	0.000331
1141	94.4742	97.7418	9.99881	11.1183	19.2935	17.1222	0.000289
1411	98.2714	100.989	8.33601	7.62207	15.6353	14.0329	0.000228
1741	91.6172	103.173	7.48672	8.33998	11.4426	12.85	0.000214
2071	98.0135	105.306	7.25946	9.32331	7.88067	7.63913	0.000122
2461	99.4872	104.451	5.35352	8.69119	6.64913	8.86125	0.000141
2851	95.1114	109.173	4.24915	10.3047	2.8963	7.61194	0.000121
3301	99.2261	105.859	5.96816	8.52456	2.83161	9.78493	0.000155
3751	95.5595	110.601	3.52814	5.74849	1.26516	7.86371	0.000124
4321	98.2964	109.426	7.56926	8.01077	1.64412	6.1071	9.53E-05
4891	99.79	108.541	5.36589	4.36513	-2.45295	6.9077	0.000107
5881	96.5816	106.442	1.60303	6.60123	-3.82929	4.7301	7.55E-05

[a] Naphthalene, internal standard. [b] *p*-QDM 8.

Table A-5. ^{1}H NMR and Kinetic Data for α,α-Diphenyl-*p*-xylylene (6).

	relative area of peak integration					
Time, s	δ7.91-7.83[a]	δ 7.53-7.45[a]	δ 7.08-7.01[b]	δ 6.62-6.56[b]	δ 6.55-6.49[b]	[6], M
210	20.5049	19.1465	0.835799	0.776624	0.209931	4.96E-05
300.1	20.1638	16.7548	1.09792	1.02767	0.538339	7.79E-05
390.2	19.4372	16.5002	1.2729	1.22946	0.578094	9.26E-05
480.3	19.2173	16.4116	1.25765	0.796675	0.226992	6.92E-05
570.4	19.5417	17.1102	1.04375	0.79158	-0.21302	4.78E-05
660.5	18.9346	16.6177	0.81566	0.72203	-0.17734	4.13E-05
750.6	18.6361	16.9156	0.861598	0.334138	-0.04333	3.5E-05
840.7	19.0949	16.7031	0.584589	0.50279	-0.16212	2.79E-05
930.8	18.5741	16.2915	0.560523	0.563514	-0.5781	1.69E-05
1020.9	19.1205	16.8079	0.72211	-0.01118	-0.47119	7.21E-06
1111	18.7689	16.2412	0.596938	0.081959	-0.64995	8.93E-07
1201.1	19.3051	17.1376	0.428173	0.62909	-0.42285	1.88E-05
1291.2	19.5347	16.483	0.52933	0.197085	-0.4926	7.01E-06
1381.3	19.6415	16.6144	0.446632	0.173063	-0.36503	7.59E-06
1471.4	18.8405	16.781	0.602632	0.246199	-0.70088	4.49E-06

[a] Naphthalene, internal standard. [b] *p*-QDM 6.

Table 6. ^{1}H NMR and Kinetic Data for *p*-Xylylene (1) with Oxygen.

	relative area of peak integration				
Time, s	δ7.93-7.84[a]	δ 7.53-7.44[a]	δ 6.43-6.42[b]	δ5.10-5.03[b]	[1], M
210	99.999	99.9989	90.746	102.453	0.001646
301	92.7318	92.7624	112.678	128.989	0.002073
392	89.1111	88.6605	101.155	117.85	0.001894
483	85.8708	85.7835	87.3853	102.327	0.001644
574	84.5299	83.6038	73.2834	87.6173	0.001408
665	81.0243	80.1458	62.4669	76.3488	0.001227
756	79.2797	78.2923	54.0955	66.1386	0.001063
847	78.2583	77.4999	48.7108	58.2442	0.000936
938	77.9478	76.7228	42.9164	53.6728	0.000862
1029	75.6927	74.6874	38.0938	47.9285	0.00077
1120	76.2125	73.8117	34.3869	43.0425	0.000692
1211	73.2002	72.4405	31.1945	38.7838	0.000623
1302	72.7645	72.193	26.9175	35.4559	0.00057
1393	72.8403	71.3073	26.1364	32.8522	0.000528
1484	72.5571	71.0015	22.8624	29.7907	0.000479
1575	71.7064	70.3724	21.8349	28.4492	0.000457
1666	70.6171	70.218	20.6766	25.6753	0.000413
1757	70.8347	70.5084	19.1845	24.3578	0.000391
1848	71.6326	70.4296	17.7603	23.6037	0.000379
1939	71.7427	68.2428	17.0154	21.9963	0.000353
2030	71.3134	68.7554	16.0637	21.092	0.000339
2121	69.7382	68.0428	14.9259	19.6365	0.000316
2212	69.2637	67.8416	14.4181	18.1873	0.000292
2303	69.1268	67.1357	13.3439	15.8301	0.000254
2394	68.5809	65.4466	11.5931	15.7678	0.000253
2485	67.4901	66.6011	10.306	13.1747	0.000212
2576	67.5058	65.3199	10.1765	13.387	0.000215

[a] Napthalene, internal standard. [b] p-QDM 1.

CHAPTER 5. EVIDENCE FOR THE GENERATION OF *p*-DIPHENOQUINODIMETHANE

Written in the style suitable for publication in the professional journals published by the American Chemical Society

Steven P. Lorimor and Walter S. Trahanovsky

Abstract

p-Diphenoquinodimethane (**5**), a biphenyl-based reactive *p*-quinodimethane (*p*-QDM), is a highly reactive, cross-conjugated molecule. (4-[4'-((Trimethylsilyl)methyl)phenyl]benzyl)diisopropylmethylammonium iodide (**13**) was prepared which yields *p*-QDM **5** upon fluoride induced elimination of trimethylsilyl iodide and diisopropylmethylamine. Although *p*-QDM **5** was not directly observed by ^{1}H NMR spectroscopy, evidence of its formation was found in the products formed from its reaction with oxygen or in its oligomerization products. Upon reacting ammonium salt **13** with TBAF in the presence of oxygen, products consistent with aldehydes and peroxides were observed by ^{1}H NMR spectroscopy. With careful exclusion of oxygen, ammonium salt **13** reacts with TBAF to form several products possibly including [2.2]-(4,4')-biphenylophane, cyclophane **7**.

Introduction

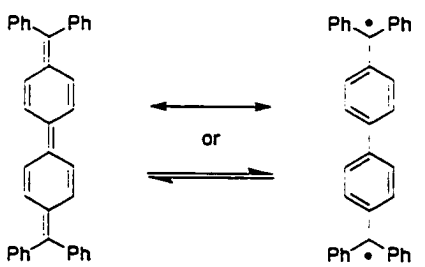
p-Quinodimethanes (*p*-QDM's) are reactive, cross-conjugated cyclic molecules that have been invoked as transient intermediates in a number of reactions and interesting fundamental molecules.[1] Commercially useful polymers have been developed from *p*-QDM's.[2] *p*-Xylylene (**1**), the parent benzene-based *p*-QDM, was first proposed as an intermediate in the pyrolysis of *p*-xylene that yielded poly-*p*-xylylene.[3] Our research group

found that *p*-xylylene and several other simple, reactive *p*-QDM's can be observed at room temperature by ^{1}H NMR spectroscopy by preparing them as dilute solutions.[4,5] Trimers of the *p*-QDM's were observed which is strong evidence that they dimerize via a dimerical diradical in a stepwise mechanism.

The first isolable derivative of *p*-QDM **1** was 7,7,8,8-tetraphenyl-*p*-xylylene, Thiele's hydrocarbon (**2**).[6] Although *p*-QDM **2** does react with oxygen, few precautions must be

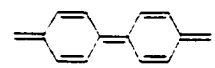
1 **2**

taken in its manipulation.[7] In 1907 Chichibabin prepared the more reactive [1,1'-biphenyl]-4,4'-diylbis[diphenylmethyl], Chichibabin's hydrocarbon (**3**), in an attempt to synthesize diradical **4**.[8] The *p*-QDM **3** readily yields polymeric peroxides when exposed to



3 **4**

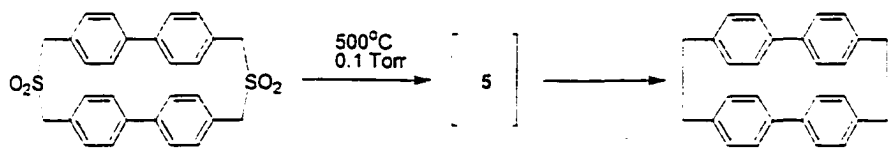
air.[7] The unsubstituted analog of *p*-QDM **3** is *p*-diphenoquinodimethane (**5**).[9] *p*-QDM **5** is expected to be highly reactive[10] and has received a moderate amount of attention by theoretical chemists.[11]



5

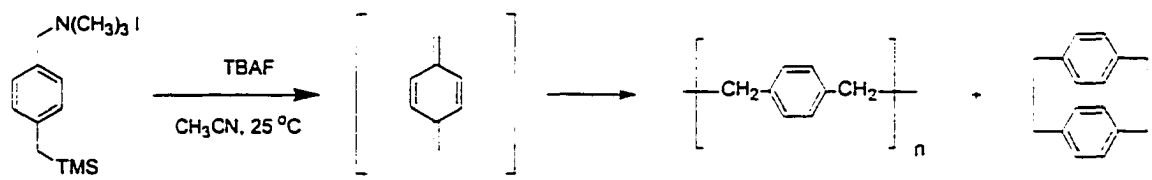
p-QDM **5** has been proposed as an intermediate in several reactions. *p*-QDM **5** is a probable intermediate in the pyrolysis of disulfone **6** that yields [2.2]-(4,4')-biphenylophane, cyclophane **7** (Scheme 1).[12] Polymers of *p*-QDM **5** have been prepared by elimination of hydrogen chloride with potassium *t*-butoxide from 4-chloromethyl-4'-methylbiphenyl[13] and by cathodic elimination of bromine from 4,4'-bis(bromomethyl)biphenyl.[14]

Scheme 1



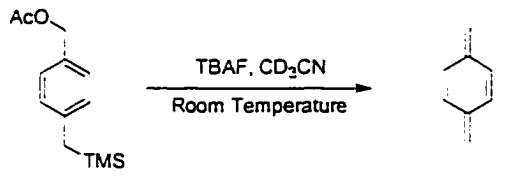
6 7

To prepare *p*-QDM **5**, a precursor compound with the proper leaving group must be prepared. Ito prepared poly-*p*-xylylene and [2.2]paracyclophane from ammonium salt **8** by a fluoride induced elimination.[15] Our group prepared dilute solutions of *p*-QDM **1** by fluoride



8 1

induced elimination of trimethylsilyl acetate from [*p*-((trimethylsilyl)methyl)phenyl]methyl acetate.[4] Once *p*-QDM **5** has been prepared as a dilute solution, ^{1}H NMR studies can be



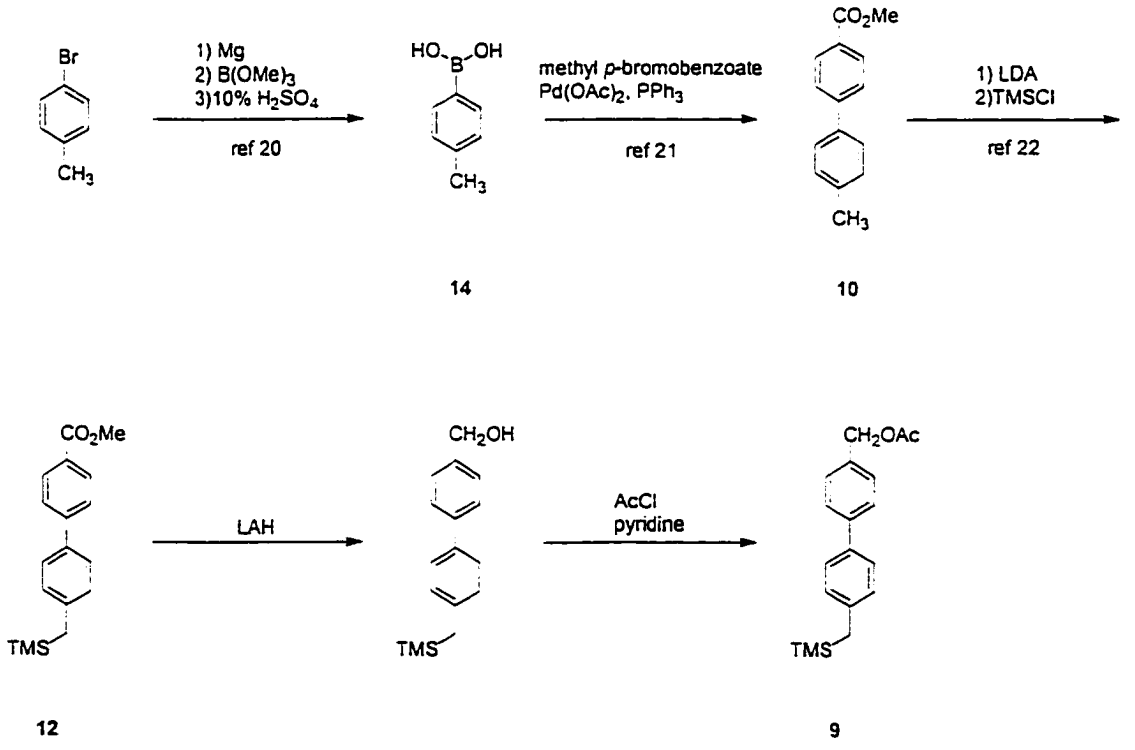
1

preformed. By analyzing the products produced in the reaction, a better understanding of *p*-QDM **5** can be established by comparing it to the products of *p*-xylylene (**1**). In this paper we report the synthesis of a precursor to *p*-QDM **5**, attempts to observe *p*-QDM **5** by ^1H NMR spectroscopy, and characterization of reaction products.

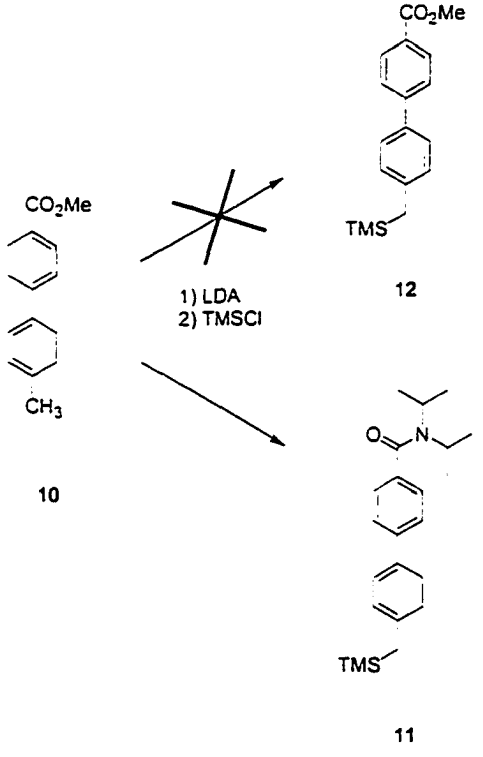
Results

Preparation of a Precursor to *p*-Diphenoquinodimethane (5). The preparation of acetate **9**, a possible precursor of *p*-QDM **5**, was attempted by the sequence of reactions outlined in Scheme 2. When methyl 4'-methyl-4-biphenylcarboxylate (**10**) was reacted with

Scheme 2



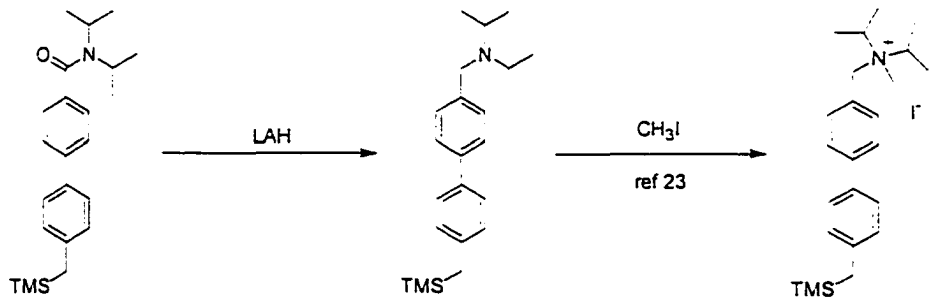
LDA and trimethylsilyl chloride, *N*,*N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzamide (**11**) was formed instead of the intended product, methyl 4-[4'-((trimethylsilyl)methyl)phenyl]benzoate (**12**). The synthesis of acetate **9** was abandoned for the



synthesis of (4-[4'-((trimethylsilyl)methyl)phenyl]benzyl)diisopropylmethylammonium iodide (**13**), an alterative precursor to *p*-QDM **5**. Ammonium salt **13** was prepared from amide **11** by the method outlined in Scheme 3.

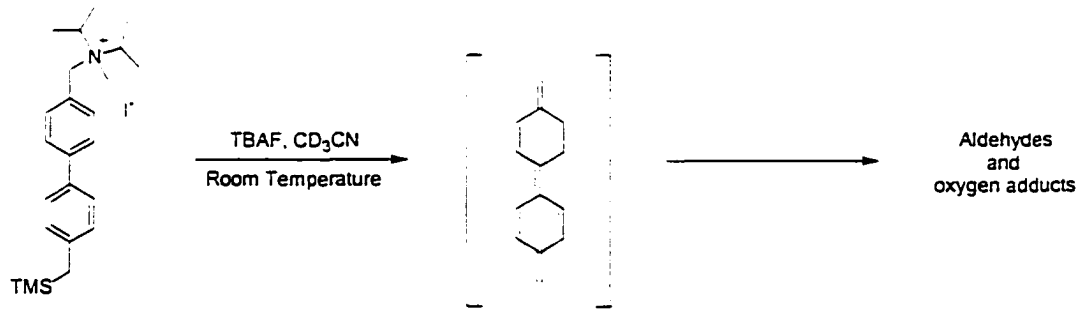
Reaction of *p*-Diphenoquinodimethane (5) with Oxygen. A dilute solution of ammonium salt **13** was prepared in dry acetonitrile-d_3 and was analyzed by ^{1}H NMR spectroscopy. The diluted solution of ammonium salt **13** was reacted with a solution of TBAF (Scheme 4).

Scheme 3



11 16 13

Scheme 4



13 5

The solution was then analyzed by ^{1}H NMR spectroscopy. The two spectra are presented in Figure 1. Although there are no peaks assignable to *p*-QDM **5**, the spectrum of the products show signals for aldehydes (~ δ 10) and benzylic methylenes adjacent to oxygen atom(~ δ 4.5). All of the aromatic signals are downfield of δ 7.2, which is consistent with peroxide products.

Oligomerization of *p*-Diphenoquinodimethane (5). A dilute solution of ammonium salt **13** was prepared in dry deoxygenated acetonitrile-d_3 and was analyzed by ^{1}H NMR spectroscopy. The solution of ammonium salt **13** was reacted with a solution of TBAF (Scheme 5). The resulting solution was analyzed by ^{1}H NMR spectroscopy after 10 min.

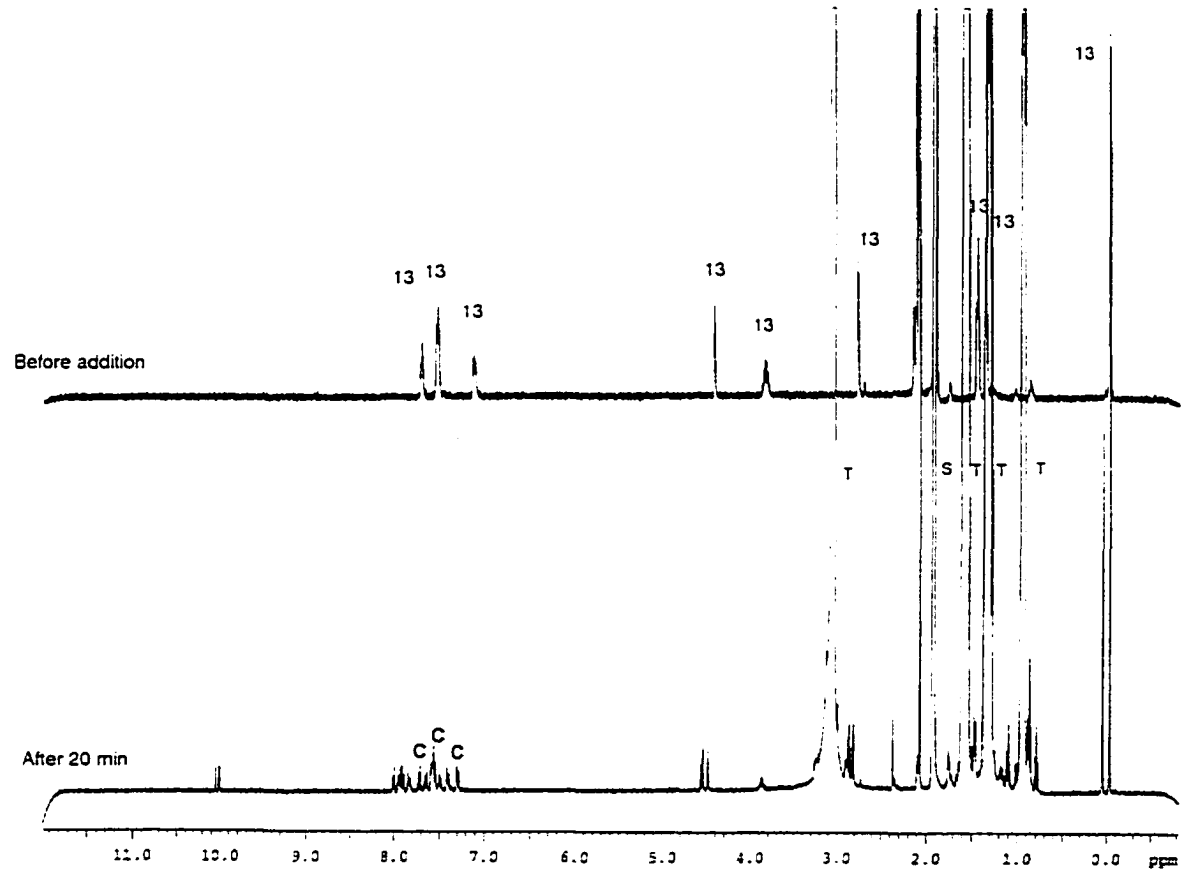
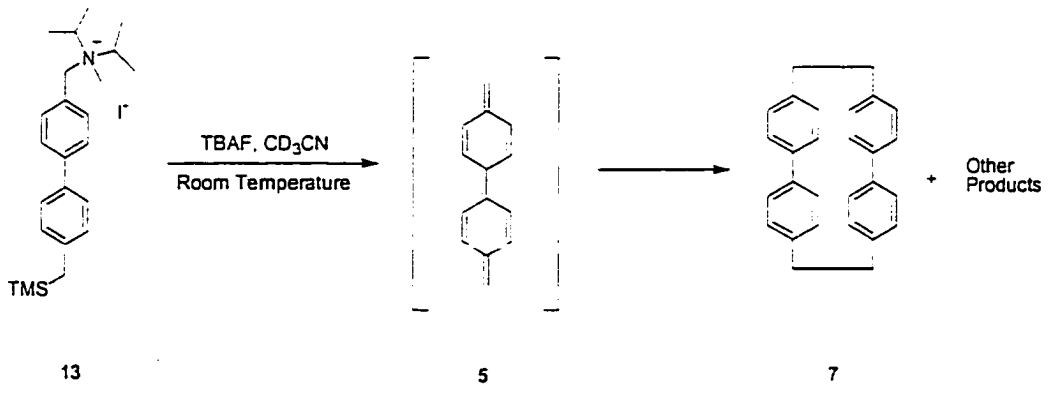


Figure 1. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-diphenoquinodimethane (**5**) in non-deoxygenated acetonitrile-d_3. (**13** is a possible precursor of *p*-QDM **5**, **C**: common product that appears in both the non-deoxygenated and deoxygenated experiments, **S**: acetonitrile, **T**: TBAF)

Scheme 5



13 5 7

The solution was stored carefully to exclude oxygen for 2 h then analyzed again by ^{1}H NMR spectroscopy. The spectra obtained in this NMR study are presented in Figure 2. Although the ^{1}H NMR spectra does not show peaks assignable to *p*-QDM **5**, the reaction produces a limited number of products. One product that can be tentatively assigned by ^{1}H NMR spectroscopy, based on its match of known literature values,[12] is cyclophane **7**. Based on similar peaks in the spectra of oxygenated and deoxygenated samples, the peaks downfield could be unreacted starting material or some other impurity. The remaining peaks have not been assigned.

The sample was extracted using methylene chloride and then the extract was concentrated under reduced pressure. The resulting residue was analyzed by ^{1}H NMR spectroscopy (Figure 3). In this spectrum, the downfield peaks seen in Figure 2, possibly assignable to starting material or oligomers, are no longer present. The peaks assignable to the cyclophane products remain along with what appears to be an AA'BB' system. An unusual observation was noted that both the AA'BB' system tentatively assigned to cyclophane **7** and the unknown's AA'BB' system have similar integrations.

Discussion

It is unclear why *N*,*N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzamide (**11**) was formed instead of the intended product, methyl 4-[4'-((trimethylsilyl)methyl)phenyl]benzoate (**12**) when methyl 4'-methyl-4-biphenylcarboxylate (**10**) was reacted with LDA and trimethylsilyl chloride. Many methyl esters are not considered to be very reactive towards the conversion to *N*, *N*-dialkyl amides,[16] but strongly basic conditions have been known to catalyze the reaction.[17]

Although *p*-QDM **5** was not observed directly by ^{1}H NMR spectroscopy, there is strong evidence that it was formed by the fluoride induced elimination of trimethylsilyl iodide and diisopropylmethylamine. *p*-QDM **5** forms similar products to *p*-xylylene **1** when it is allowed to react with oxygen. The ^{1}H NMR spectra of both product mixtures contain peaks with similar chemical shifts (~ δ 10, 4.5).[4]

The ^{1}H NMR spectrum of the product mixture produced in the deoxygenated acetonitrile-d_3 is consistent with there being four or fewer products. One product is likely to be the cyclophane **7** because of its match with the literature values.[12] The downfield peaks (labeled **C** in figures 1 and 2) which were not extracted into the methylene chloride layer could be polymeric, non-cyclophane addition products, or starting material with its chemical shift altered because of the addition of TBAF. The remaining AA'BB' signals (labeled **U** in figures 2 and 3) are difficult to interpret because they are shifted up field compared to most aromatic protons. This shift upfield is consistent with a cyclophane product, similar to a cyclic trimer, with a distorted aromatic ring but one that is not as much as distorted as that of cyclophane **7**. The fact that the unassigned aromatic signals have similar integrations to

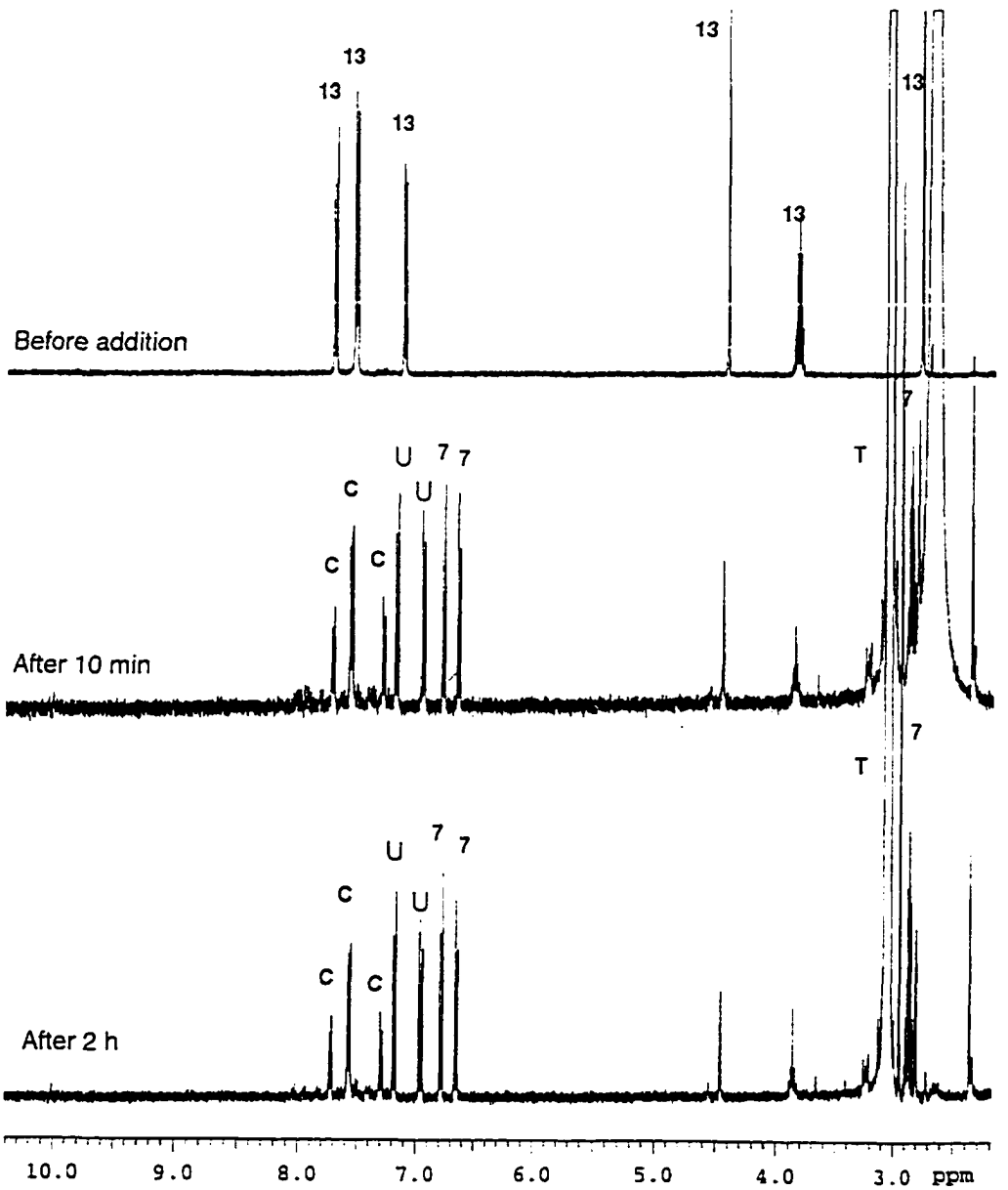


Figure 2. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-diphenoquinodimethane (**5**) in deoxygenated acetonitrile-d_3. (7 and 13 are compound numbers given in the text, **C**: common product that appears in both the non-deoxygenated and deoxygenated experiments, **T**: TBAF, **U**: unknown compound)

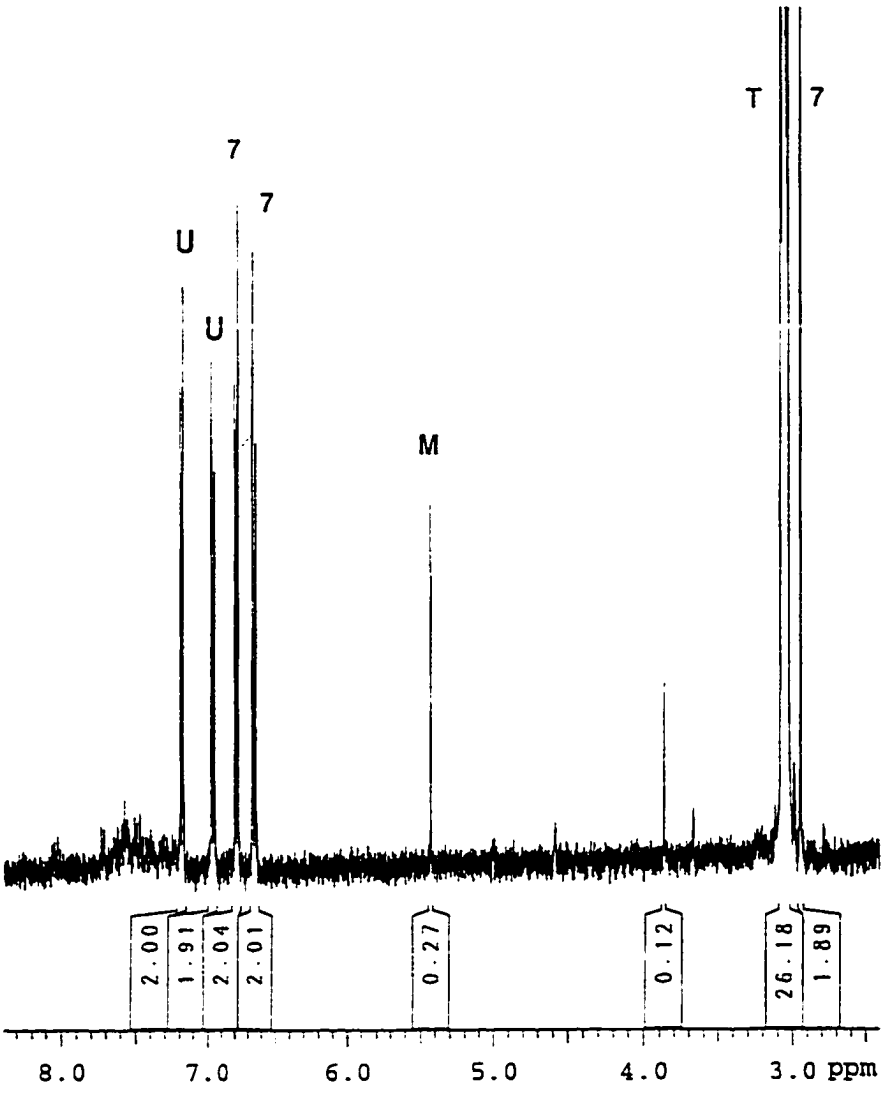


Figure 3. ^{1}H NMR spectrum (400 MHz, CD_3CN) of methylene chloride extract of *p*-diphenoquinodimethane (**5**) products in deoxygenated acetonitrile-d_3. (**7** is a compound number given in the text, **M**: methylene chloride, **T**: TBAF, **U**: unknown compound)

those of the peaks tentatively assigned to cyclophane **7** leads one to question whether or not the assignment of the peaks to cyclophane **7** is correct.

A probable next step is to attempt to prepared *p*-QDM **5** as a similarly dilute solution but on a larger scale. If the reaction was carried out on a larger scale, the products might be less difficulty to isolated and characterized. Once the products are firmly determined, focused efforts could be made in order to observe *p*-QDM **5** directly.

Because the fluoride induced elimination is both facile and mild, further studies may allow direct observation of *p*-QDM **5**. High dilution studies similar to the one used for α,α-diphenyl-*p*-xylylene[5] could be used to observe *p*-QDM **5** by ^{1}H NMR. Flow NMR has been used to observe reactive molecules such as benzocyclobutadiene[18], 1,2-dimethylene-1,2-dihydronaphthalene,[19] and *o*-xylylene[19] using a similar fluoride induced elimination as a means of preparation.

Conclusion

The preparation of *p*-diphenoquinodimethane (**5**) by fluoride induced elimination of trimethylsilyl iodide and diisopropylmethylamine from ammonium salt **13** is probable based on the products observed. When exposed to oxygen, the product's ^{1}H NMR spectrum was similar to that of *p*-xylylene **1** with signals from aldehydes and peroxides. With careful avoidance of oxygen in the solution, evidence for [2.2]-(4,4')-biphenylophane (**7**), which is analogous to the [2.2]cyclophane found in the oligomerization of *p*-xylylene (**1**), was obtained.

Experimental Section

Methods and Materials. All materials were commercially available and used as received, except where indicated. Prior to use as a solvent in the preparation of *p*-QDM **5**,

acetonitrile-d_3 was distilled from P_2O_5 under argon and initially degassed by repeated freeze-pump-thaw cycles, except where indicted. ^{1}H NMR spectra were recorded at 400 MHz unless noted otherwise. ^{13}C NMR spectra were recorded at 100 MHz unless noted otherwise. The residual CHD_2CN was used as the internal reference for all ^{1}H NMR spectra unless noted otherwise. Both the GC and the GC/MS analysis were done using a DB-5 column (30m, I.D. 0.32 mm, 0.25μ film thickness). Elemental analyses were performed by Iowa State University Instrumental Services, Ames, IA.

***p*-Tolylboronic Acid (14)** was prepared in a 65 % yield by the method of Matsubara[20] but on a 0.131 mole scale. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.136 and 7.322 (AA'BB'q, *J*=7.8Hz, 4H), 2.454 (s, 3H); mp 247.5-250.3 °C (lit.[20] mp 245-247 °C).

Methyl 4'-Methyl-4-biphenylcarboxylate (10) was prepared in a 61% yield on 8.5 mmol scale using a method similar to the method used by Huff[21] for the synthesis of unsymmetrical biaryls using a modified Suzuki cross-coupling: 4-biphenylcarboxaldehyde. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.071 and 7.627 (AA'BB'q, *J*=8.8 Hz, 4H), 7.510 and 7.256(AA'BB'q, *J*=8.8 Hz, 4H), 3.918 (s, 3H), 2.389 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 145.6, 138.2, 137.1, 130.1, 129.7, 128.6, 127.1, 126.8, 52.1 , 21.2.

***N,N*-Diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzamide (11)** was prepared in a 21% yield from *N,N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzlamine (0.14 mmol) by a method similar to the method used by Leung[22] to prepare methyl 2-[(trimethylsilyl)methyl]benzoate. The preparation was intended to prepare methyl 4-[4'-((trimethylsilyl)methyl)phenyl]benzoate (**12**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.569 and 7.345 (AA'BB'q, *J*=8 Hz, 4H), 7.441 and 7.051 (AA'BB'q, *J*=8 Hz, 4H), 3.92 (br s), 3.466 (br s), 2.104 (s, 2H), 1.475 (br s), 1.205 (br s), -0.002 (s, 9H); IR (neat, cm^{-1}) 2958,

1628,1436,1337; GC/MS m/z (relative intensity) 442 (6), 441 (14), 370 (6), 369 (13), 368 (25), 367 (7) M^+, 366 (9), 270 (7), 269 (22), 268 (51), 267 (100), 266 (17), 265 (18), 264 (10), 263 (11), 262 (6), 251 (6), 188 (5), 165 (25).

***N,N*-Diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzylamine (16).** A 100 mL three-necked round-bottomed flask with a stir bar, condenser, addition funnel, and argon gas inlet was charged with lithium aluminum hydride (80 mg, 2.1 mmol) and 5 mL of dry ether. A solution of *N,N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzamide (11, 280 mg, 0.76 mmol) in 15 mL of ether was added dropwise to the LAH mixture. After the addition was complete, the mixture was heated to reflux for 1 h. After the normal workup, amide **11** (210 mg, 0.59 mmol, 78%) was isolated as an oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.521 and 7.443 (AA'BB'q, *J*=8.0 Hz, 4H), 7.477 and 7.085(AA'BB'q, *J*=8.4 Hz, 4H), 3.690 (s, 2H), 3.040 (sept, *J*=6.4 Hz, 2H), 2.140 (s, 2H), 1.061 (d, *J*=6.4 Hz, 12H), 0.038 (s, 9H); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 142.6, 140.1, 139.5, 137.2, 129.0, 128.9, 127.1,126.7, 49.1, 48.3, 27.1, 21.1, -1.7. Anal. Calcd for $C_{23}H_{35}NSi$: C, 78.12; H, 9.98; N, 3.96. Found: C, 78.18; H, 9.87; N, 3.90.

(4-[4'-((Trimethylsilyl)methyl)phenyl]benzyl)diisopropylmethylammonium Iodide (13) was prepared in a 14 % yield by a method similar to the method used by Ito[23] to prepare [*o*-[1-(trimethylsilyl)pentyl]benzyl]trimethylammonium iodide from [*o*-[1-(trimethylsilyl)pentyl]benzyl]dimethylamine. ^{1}H NMR (400 MHz, CD_3CN) δ 7.718 and 7.540 (AA'BB'q, *J*=8.4 Hz, 4H), 7.555 and 7.131(AA'BB'q, *J*=8.0 Hz, 4H), 3.690 (s, 2H), 4.451 (s, 2H), 3.040 (sept, *J*=6.8 Hz, 2H), 2.794 (s, 3H), 1.460 (d, *J*=6.4 Hz, 6H), 1.370 (d, *J*=6.8 Hz, 6H), -0.017 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 142.7, 141.3, 134.9, 133.3, 128.8, 127.1, 127.0,126.7, 63.9, 60.9, 26.1, 17.5, 17.4, -2.5.

Oxygen Trapping of *p*-Diphenoquinodimethane (5). An NMR tube was charged with (4-[4'-((trimethylsilyl)methyl)phenyl]benzyl)diisopropylmethylammonium iodide (**13**, 0.5 mg, 1.0 μmol) and 0.7 mL of CD_3CN. A ^1H NMR spectrum was taken of the quaternary ammonium salt **13**. A solution of TBAF (6 mg, 17 mmol) in 0.2 mL of CD_3CN was added to the NMR tube. After allowing the reaction solution to stand for 20 min, a ^1H NMR was taken. ^1H NMR (400 MHz, CD_3CN) δ 10.048 (s), 10.007 (s), 8.01 (d), 7.94 (d), 7.90 (d), 7.83 (d), 7.721 (d, *J*=8.0 Hz), 7.64 (d), 7.59-7.52 (m), 7.49 (d), 7.41 (d), 7.29 (d), 4.566 (s), 4.541 (s), 4.481 (s), 2.9-2.8 (m), 2.067 (s).

Oligomerization of *p*-Diphenoquinodimethane (5). An NMR tube was charged with 0.1 mL of a 0.012 M solution of (4-[4'-((trimethylsilyl)methyl)phenyl]benzyl)diisopropylmethylammonium iodide (**13**, 1.2 μmol) in CD_3CN and 0.60 mL of CD_3CN. A solution of TBAF (7 mg, 20 μmol) in 0.3 mL of CD_3CN was prepared in a tear-shaped flask. Both solutions were deoxygentated by repeated freeze-pump-thaw cycles then stored under argon. A ^1H NMR spectrum was taken of the deoxygenated quaternary ammonium salt **13** solution. The NMR tube was returned to the glove bag. The TBAF solution was added to the NMR tube. The sample was protected from light. The NMR tube was periodically removed from the glove bag for analysts by ^1H NMR spectroscopy. After 21 h the last ^1H NMR spectrum was taken of the reaction solution. ^1H NMR (400 MHz, CD_3CN) δ 7.735 (d, *J*=8.0 Hz, 2.0H), 7.571 (d, *J*=8.0 Hz, 3.9H), 7.296 (d, *J*=8.0 Hz, 2.1H), 7.158 (d, *J*=8.4 Hz, 3.4H), 6.960 (d, *J*=8.4 Hz, 3.1H), 4.463 (d, 1.6H), 2.38 (s, 2.2), 2.07 (s, 6.8H), 0.06 (s, 14.2H), -0.02 (s, 12.7H). **7**: ^1H NMR (400 MHz, CD_3CN) δ 6.85 and 6.652 (AA'BB'q, *J*=8.0 Hz, 6.4H),

2.96 (s, 3.2H); (lit.[12] ^{1}H NMR (60 MHz, CDCl) τ 7.04(s), 3.39 and 3.23 (AA'BB'q, J=8.0 Hz))

The reaction mixture was extracted with methylene chloride and the combined organic layers were dried with Na_2SO_4. The organic solvent was removed under reduced pressure and the resulting residue was dissolved in CD_3CN. ^{1}H NMR (400 MHz, CD_3CN) δ 7.186 (d, J=8.4 Hz, 2.0H), 6.960 (d, J=8.0 Hz, 1.9H), 6.786 (d, J=8.4 Hz, 2.0H), 6.653 (d, J=8.4 Hz, 2.0H), 2.948 (s, 1.9H). The tetrabutylammonium salts were not completely removed by the extraction process.

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Appendix

***p*-Tolylboronic Acid (14)** was prepared by the method of Matsubara[20] but on a 13.1 molar scale. A 25-mL tear-shaped flask fitted with a condenser was charged with magnesium (0.342 g, 114 mmol) and 5 mL of dry THF. A solution of *p*-bromotoluene (2.24 g, 13.1 mmol) in 10 mL of dry THF was added slowly through the condenser to maintain a reflux. The mixture was heated to reflux for an additional 30 min and then allowed to cool to room temperature. In a 50-ml flask, a solution of trimethoxyborane (2.04 g, 2.2 mL, 19.4 mmol) in 10 mL of dry THF was cooled to –78°C. The Grignard reagent solution was transferred slowly to the chilled solution. The reaction mixture was stirred for 1 h at low temperature. While still cool, 10 mL of 10% H_2SO_4 was added and the mixture was allowed to warm to room temperature. The mixture was filtered and was extracted with ether. The ether combined layers was washed with water then dried with sodium sulfate. The ether was removed under reduced pressures. The resulting white solid was washed with hexane and water to yield acid 14 (1.15 g, 84.5 mmol, 65 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.136 and 7.322 (AA'BB'q, *J*=7.8Hz, 4H), 2.454 (s, 3H); mp 247.5-250.3 °C (lit.[20] mp 245-247 °C).

Methyl 4'-Methyl-4-biphenylcarboxylate (10) was prepared on 8.5 mmol scale using a method similar to the method used by Huff[21] for the synthesis of unsymmetrical biaryls using a modified Suzuki cross-coupling: 4-biphenylcarboxaldehyde. A 100-mL three-necked round-bottom flask with a stir bar, condenser, and argon gas inlet was charged with 1.150 g of *p*-tolylboronic acid (**14**, 8.46 mmol), 1.91 g of methyl *p*-bromobenzoate (**15**, 8.87 mmol) and 20 mL of 1-propanol. The mixture was stirred until the solids dissolved. To the solution was added 6 mg of $Pd(OAc)_2$ (0.025 mmol), 20 mg of PPh_3 (0.076 mmol), and 1 g Na_2CO_3 (10.1 mmol) in 8 mL H_2O. The mixture was heated to reflux for 1 h. Water (10 mL) was added to the mixture while it was still hot. The reaction vessel was opened to the air and stirred overnight. Ethyl acetate (20 mL) was added to the reaction mixture and the layers were separated. The aqueous layer was extracted twice with 10 mL of ethyl acetate. The combined ethyl acetate layers was washed with 5% sodium bicarbonate solution then with

brine. The organic solution was transferred to an Erlenmeyer flask. Carbon (0.8 g) was added to the flask and the mixture was stirred for 30 min. The mixture was filtered through Florisil on a Celite pad with additional ethyl acetate to rinse the pad. The solvent was removed under reduced pressure to yield a crude solid product which was recrystallized from hexanes and methanol. (1.180 g, 5.22 mmol, 61%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.071 and 7.627 (AA'BB'q, *J*=8.8 Hz, 4H), 7.510 and 7.256(AA'BB'q, *J*=8.8 Hz, 4H), 3.918 (s, 3H), 2.389 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 145.6, 138.2, 137.1, 130.1, 129.7, 128.6,127.1, 126.8, 52.1 , 21.2.

***N,N*-Diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzamide (11)** was prepared by a method similar to the method used by Leung[22] to prepare methyl 2-[(trimethylsilyl)methyl]benzoate. The preparation was intended to prepare methyl 4-[4'-((trimethylsilyl)methyl)phenyl]benzoate (**12**). A solution of LDA was prepared at –78°C with diisopropylamine (1.5 mL, 10.4 mmol), *n*-butyllithium in hexanes (4.15 mL, 2.5 M, 10.4 mmol) in 10 mL of THF. A solution of methyl 4'-methyl-4-biphenylcarboxylate (**10**, 1.18 g, 5.2 mmol) and chlorotrimethylsilane (0.7 mL, 5.5 mmol) in 10 mL of dry THF was added to the cold LDA solution over 10 min. After the solution was stirred for 30 min, the reaction was quenched with the addition of water. Once the reaction mixture had warmed to room temperature, it was extracted with ether. The combined ether extracts was dried with Na_2SO_4 and the solvent was removed under reduced pressure to yield a crude oily product. Flash column chromatography on silica gel (elution with 4:1 hexanes-ether) to afford amide **11** (408 mg, 1.1 mmol, 21%) as a white solid: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.569 and 7.345 (AA'BB'q, *J*=8 Hz, 4H), 7.441 and 7.051 (AA'BB'q, *J*=8 Hz, 4H), 3.92 (b), 3.466 (b), 2.104 (s, 2H), 1.475 (b), 1.205 (b), -0.002 (s, 9H); IR (neat, cm^{-1}) 2958, 1628,1436,1337; GC/MS m/z (relative intensity) 442 (6), 441 (14), 370 (6), 369 (13), 368 (25), 367 (7) M^+, 366 (9),

270 (7), 269 (22), 268 (51), 267 (100), 266 (17), 265 (18), 264 (10), 263 (11), 262 (6), 251 (6), 188 (5), 165 (25).

(4-[4'-((Trimethylsilyl)methyl)phenyl]benzyl)diisopropylmethylammonium Iodide (13) was prepared by a method similar to the method used by Ito[23] to prepare [*o*-[1-(trimethylsilyl)pentyl]benzyl]trimethylammonium iodide from [*o*-[1-(trimethylsilyl)pentyl]benzyl]dimethylamine. A 5-mL tear-shaped flask with a stir bar, condenser, and argon gas inlet was charged with *N,N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzlamine (**16**, 50 mg, 0.14 mmol), 1 mL of acetonitrile, and methyl iodide (0.2 mL, 0.456 g, 3.2 mmol). The reaction solution was stirred for 1 h, heated to reflux for 1 h, and allowed to cool to room temperature. Pentane was added to the reaction solution, and the precipitate was collected. The crude solid was recrystallized from acetone-pentane to yield the quaternary ammonium salt **13** (10 mg, 20 μmol, 14%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.718 and 7.540 (AA'BB'q, *J*=8.4 Hz, 4H), 7.555 and 7.131(AA'BB'q, *J*=8.0 Hz, 4H), 3.690 (s, 2H), 4.451 (s, 2H), 3.040 (sept, *J*=6.8 Hz, 2H), 2.794 (s, 3H), 1.460 (d, *J*=6.4 Hz, 6H), 1.370 (d, *J*=6.8 Hz, 6H), -0.017 (s, 9H); ^{13}C NMR (100 MHz, CD_3CN) δ 142.7, 141.3, 134.9, 133.3, 128.8, 127.1, 127.0,126.7, 63.9, 60.9, 26.1, 17.5, 17.4, -2.5.

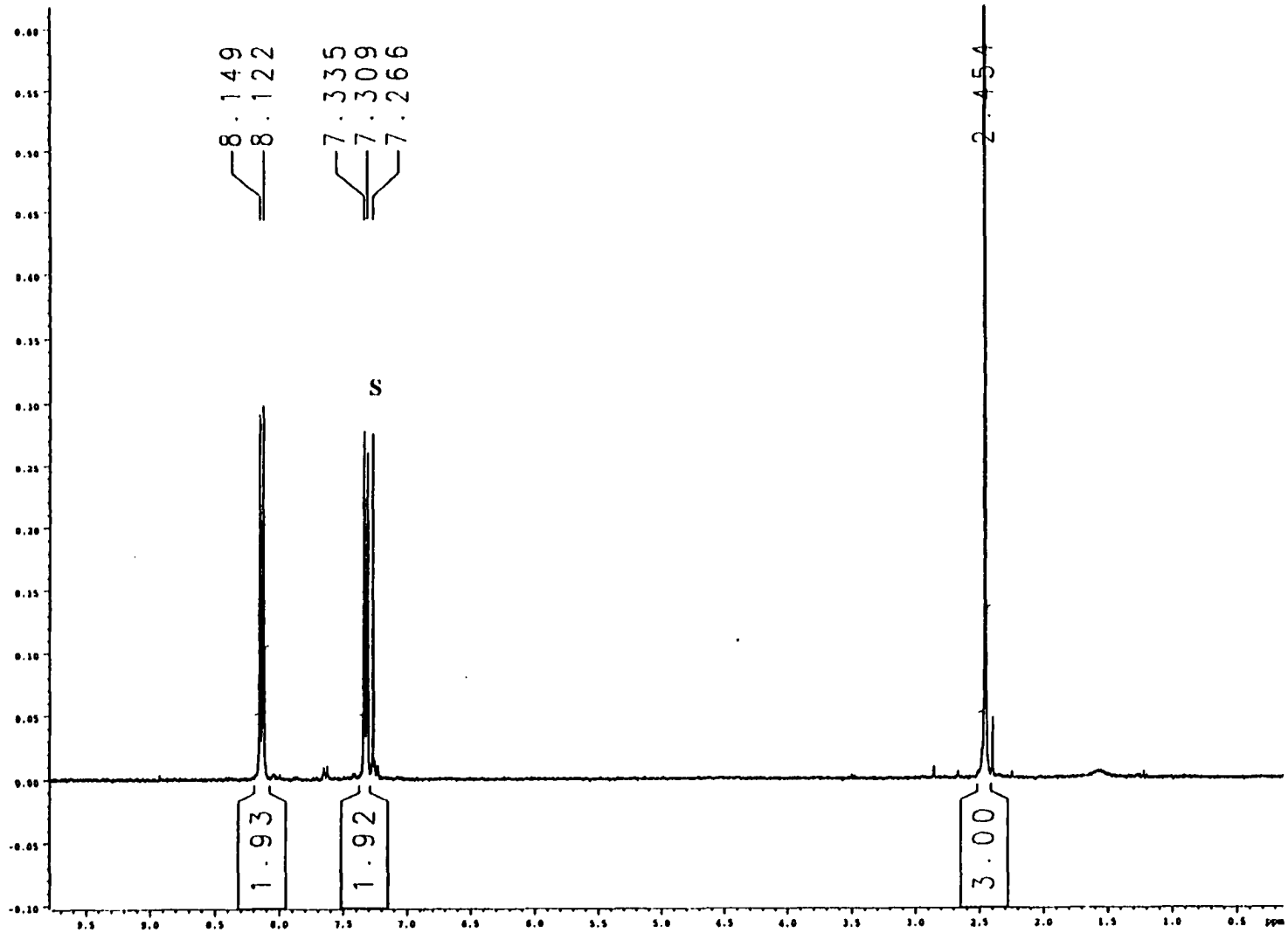

Figure A-1. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of *p*-tolylboronic acid (**14**). (S: chloroform)

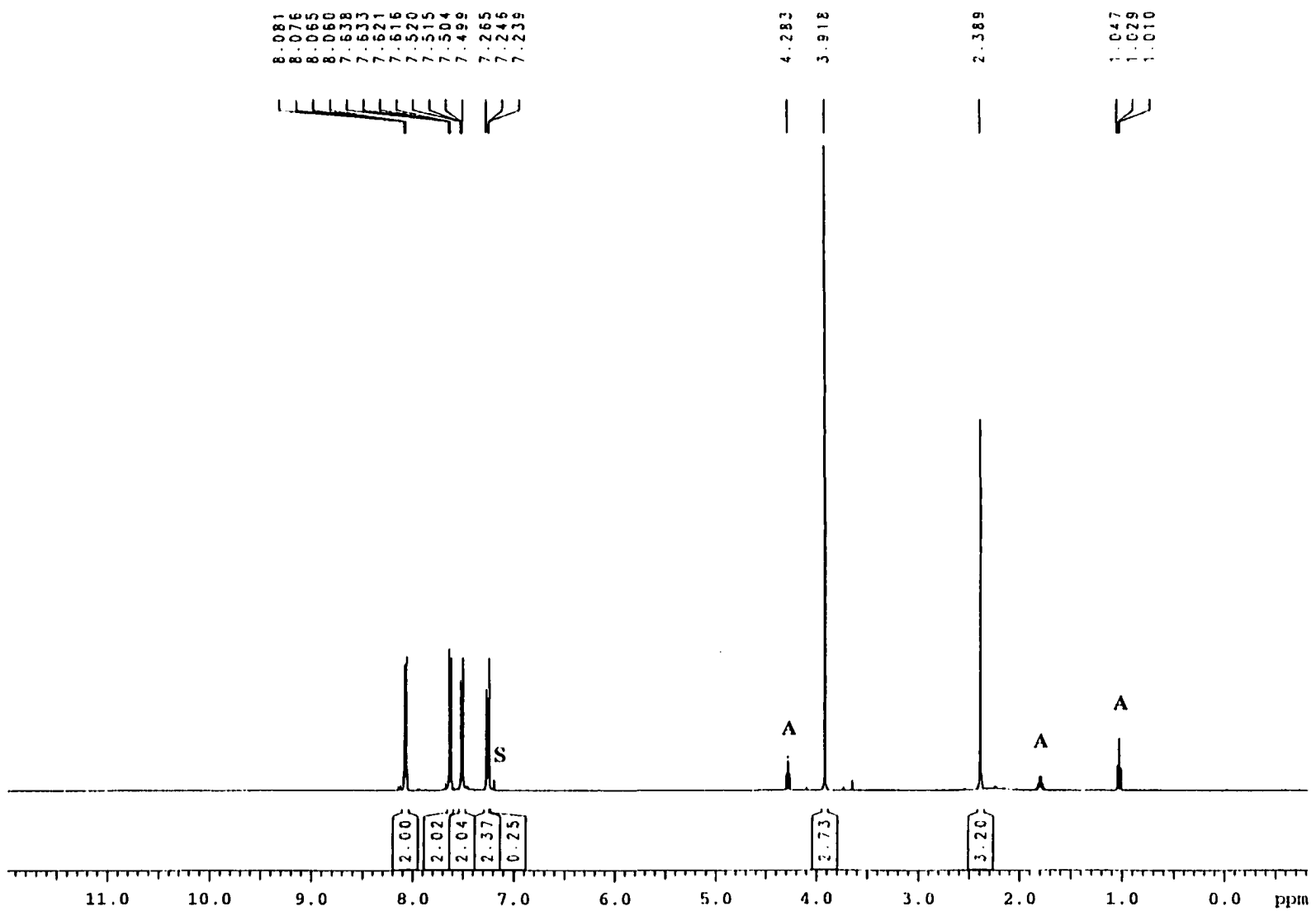

Figure A-2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of methyl 4'-methyl-4-biphenylcarboxylate (**10**). (**A**: ethyl acetate, **S**: chloroform)

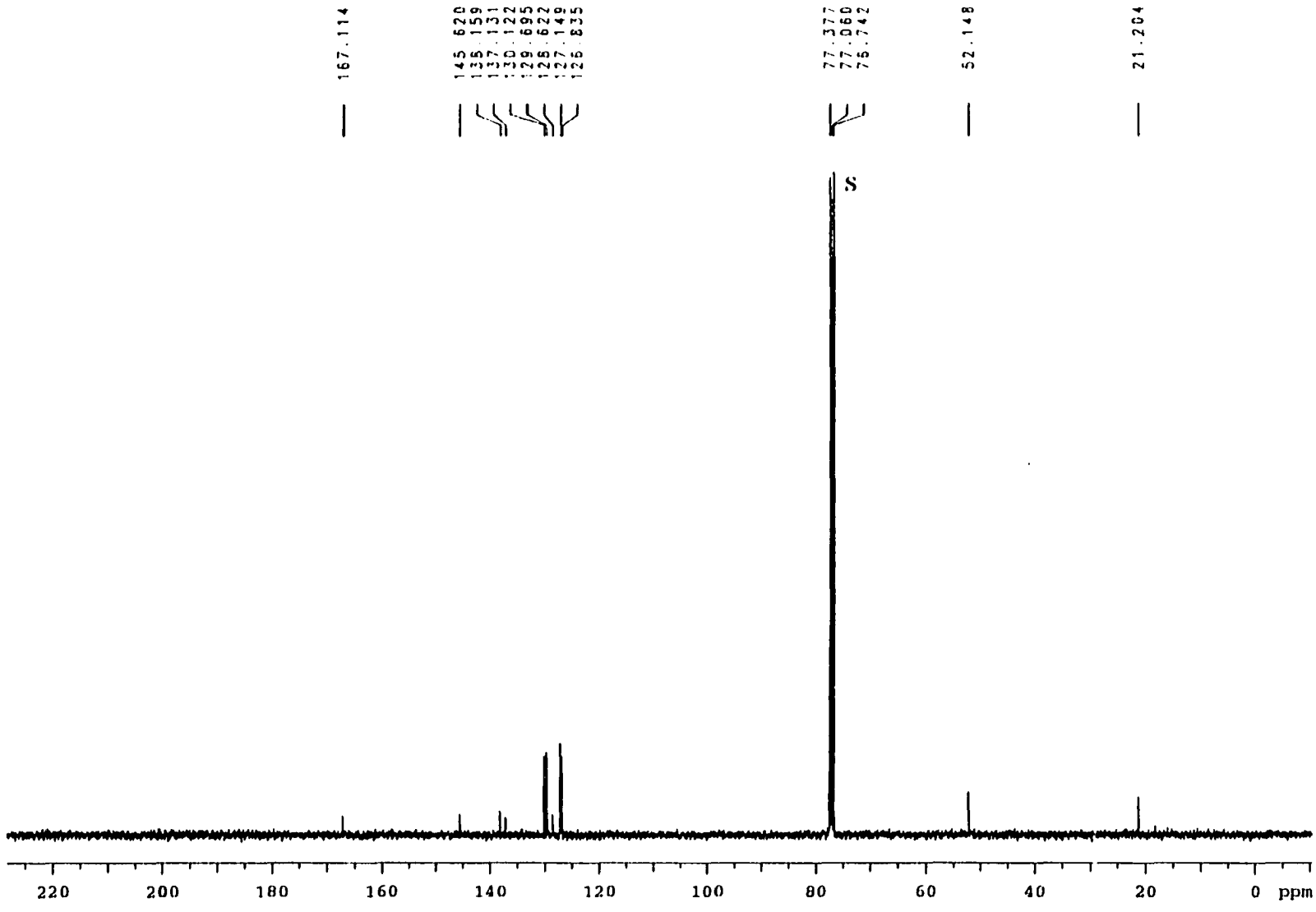

Figure A-3. ^{13}C NMR spectrum (100 MHz, $CDCl_3$) of methyl 4'-methyl-4-biphenylcarboxylate (**10**). (**S**: chloroform)

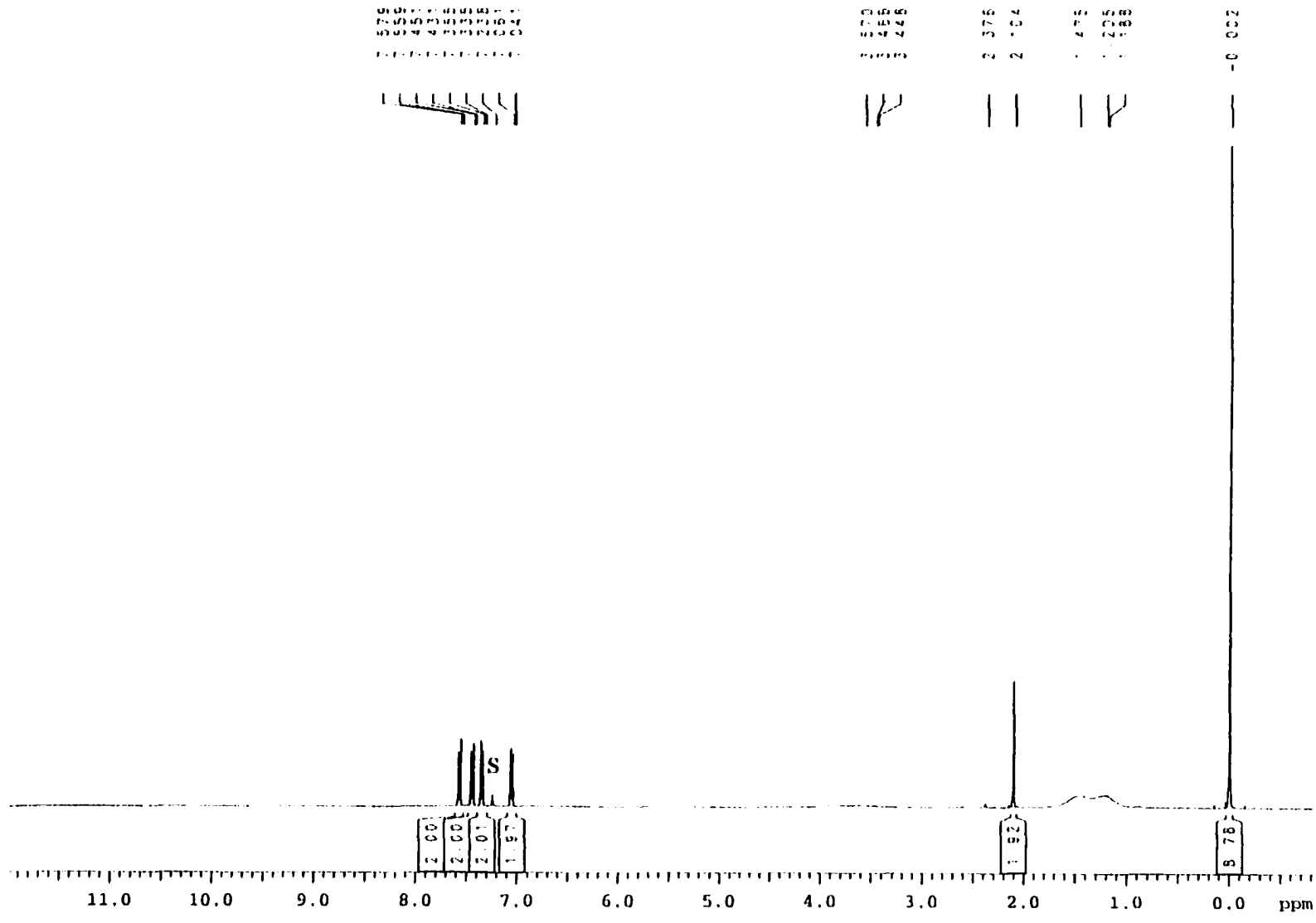

Figure A-4. ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of *N,N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzamide (**11**). (S: chloroform)

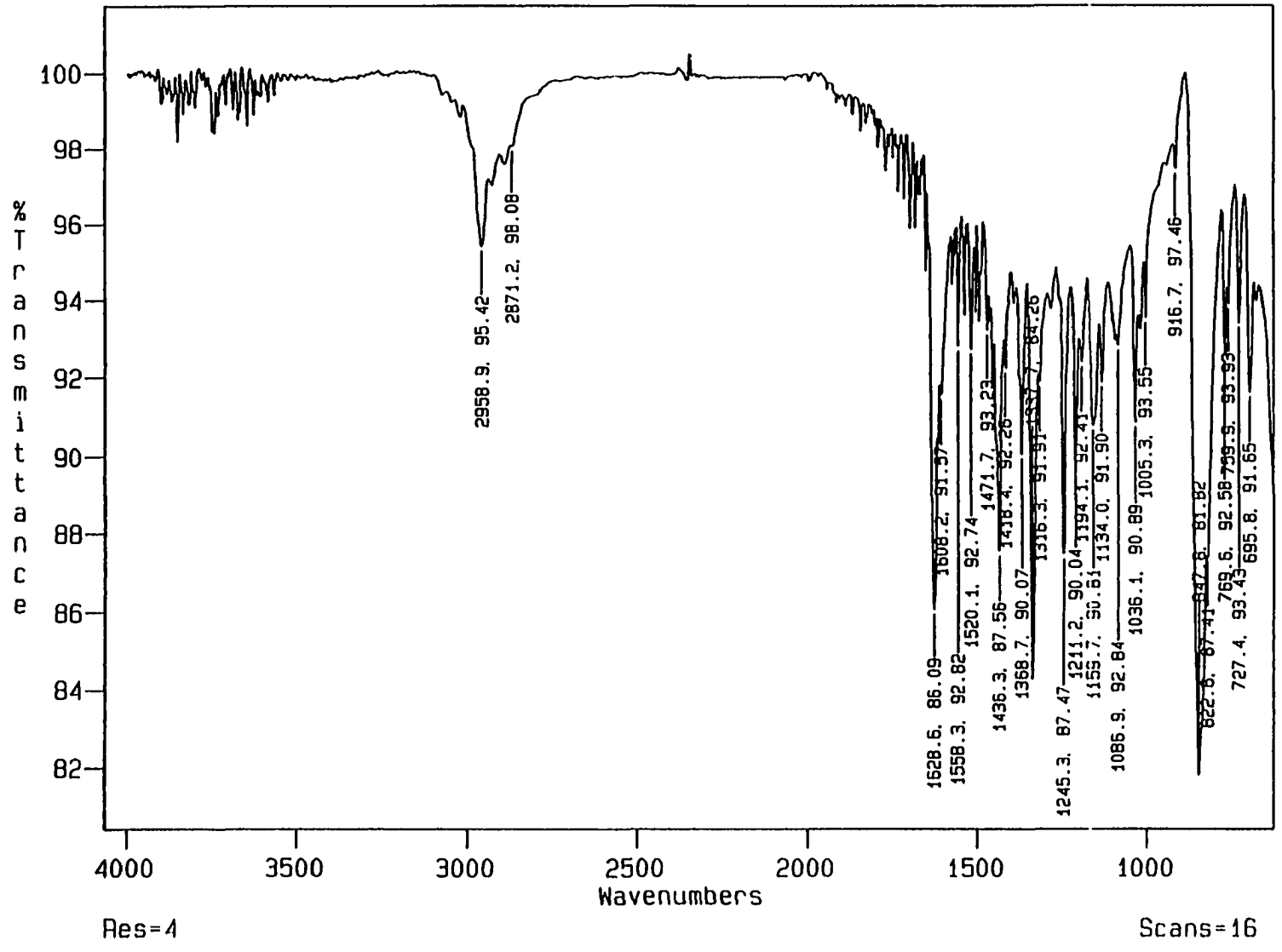

Figure A-5. Infrared spectrum of *N,N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzamide (**11**).

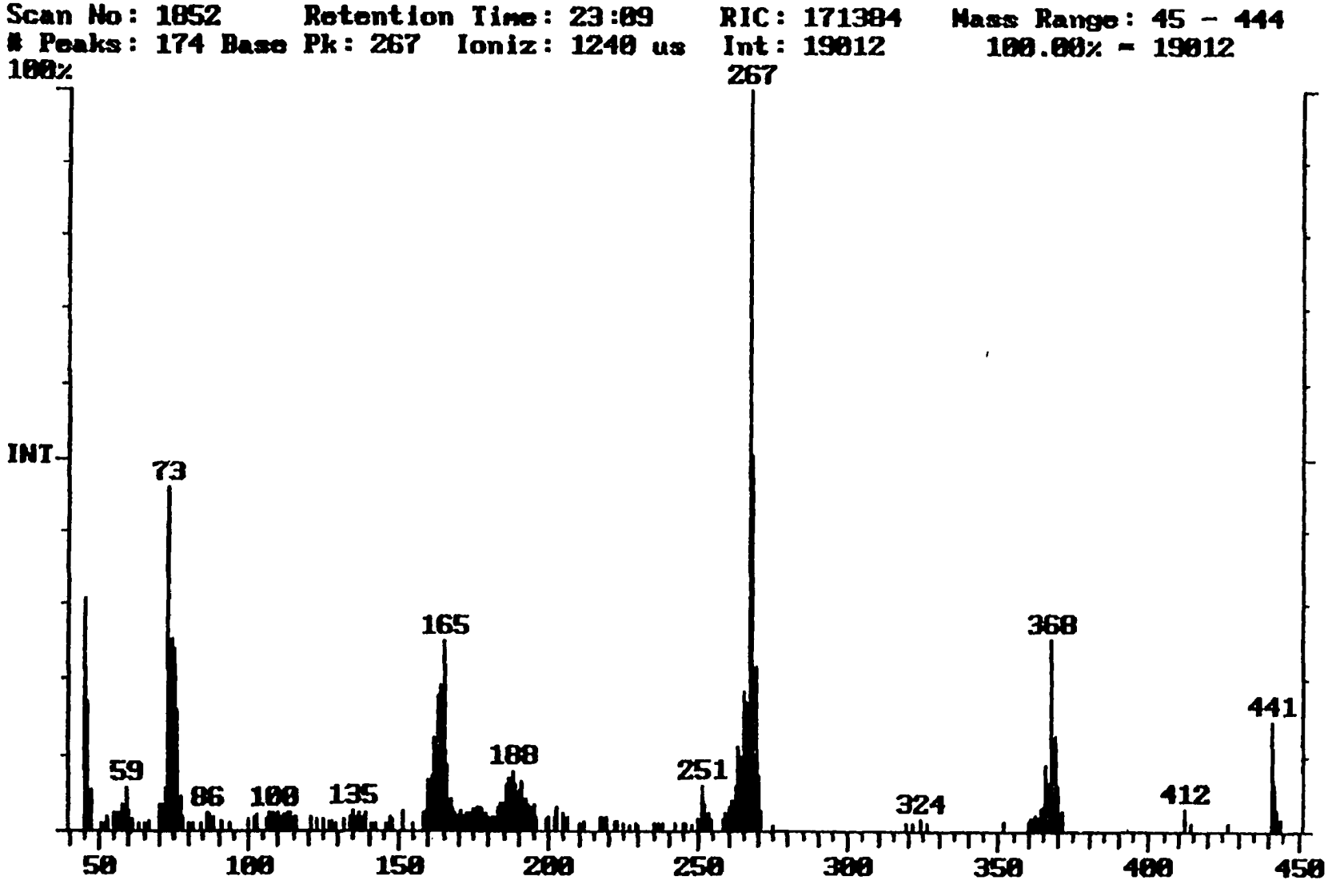

Figure A-6. Mass spectrum (EI) of *N,N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzamide (11).

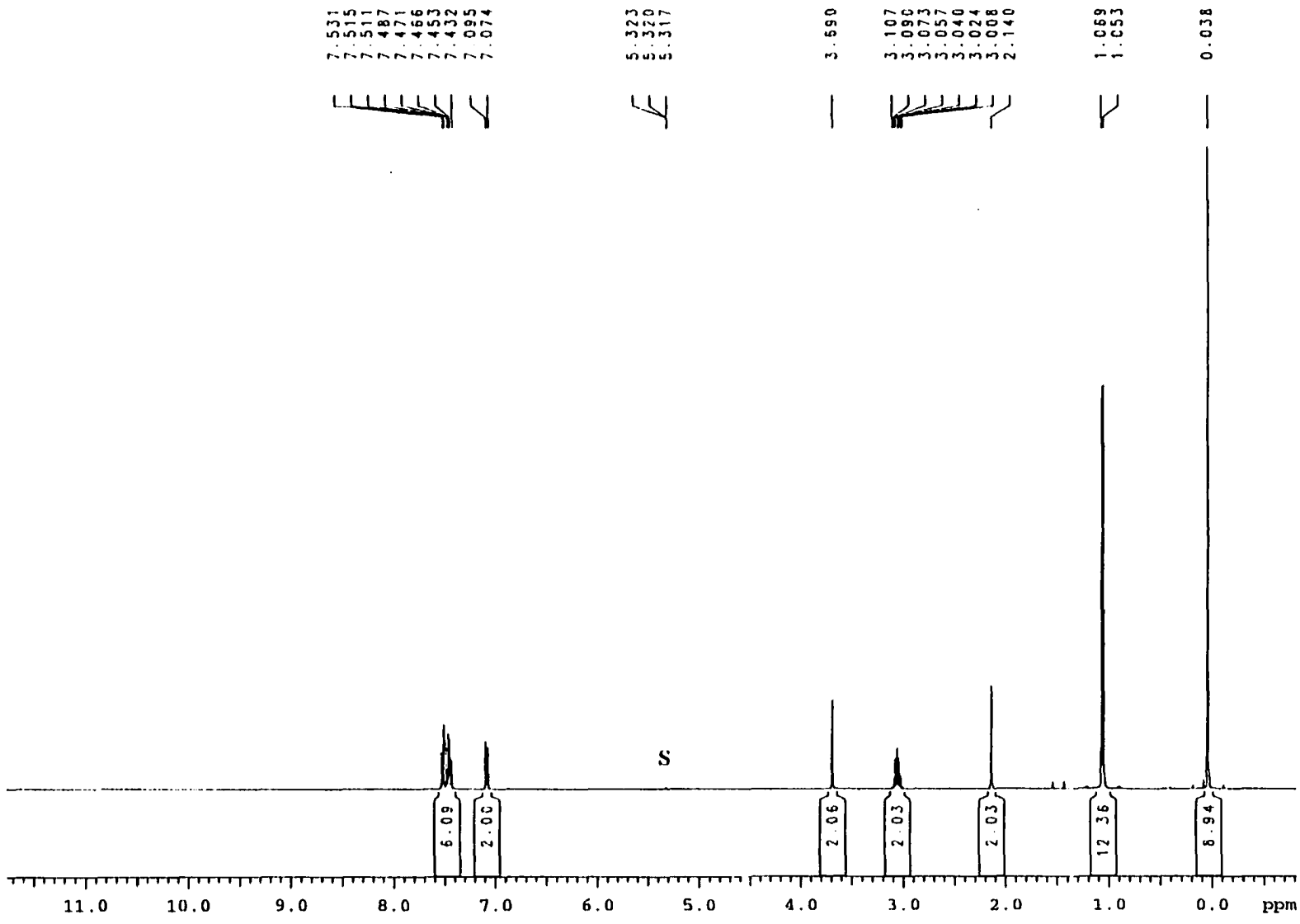

Figure A-7. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2) of *N,N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzylamine (**16**). (S: methylene chloride)

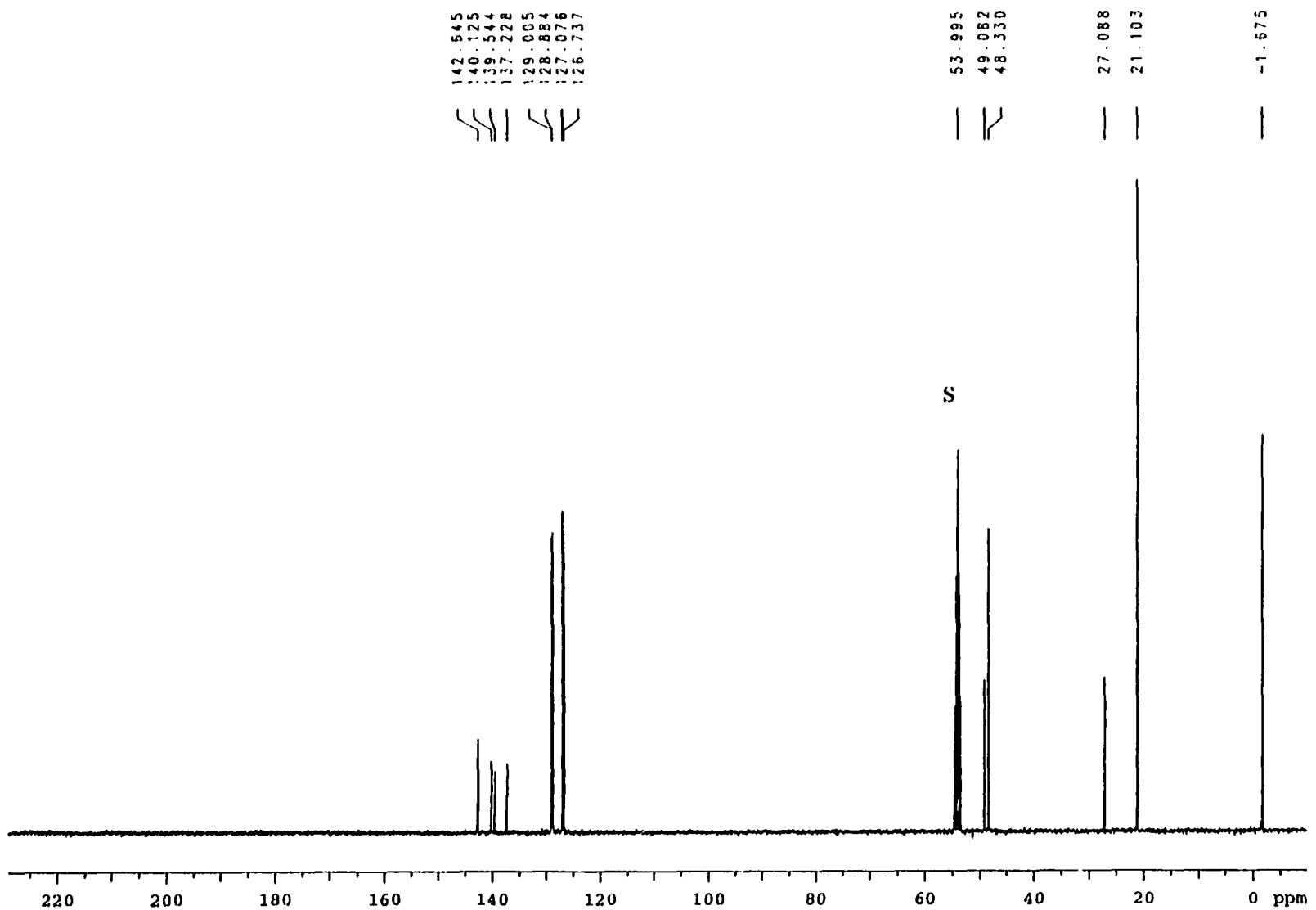

Figure A-8. ^{13}C NMR spectrum (100 MHz, CD_2Cl_2) of *N,N*-diisopropyl-4-[4'-((trimethylsilyl)methyl)phenyl]benzylamine (**16**). (S: methylene chloride)

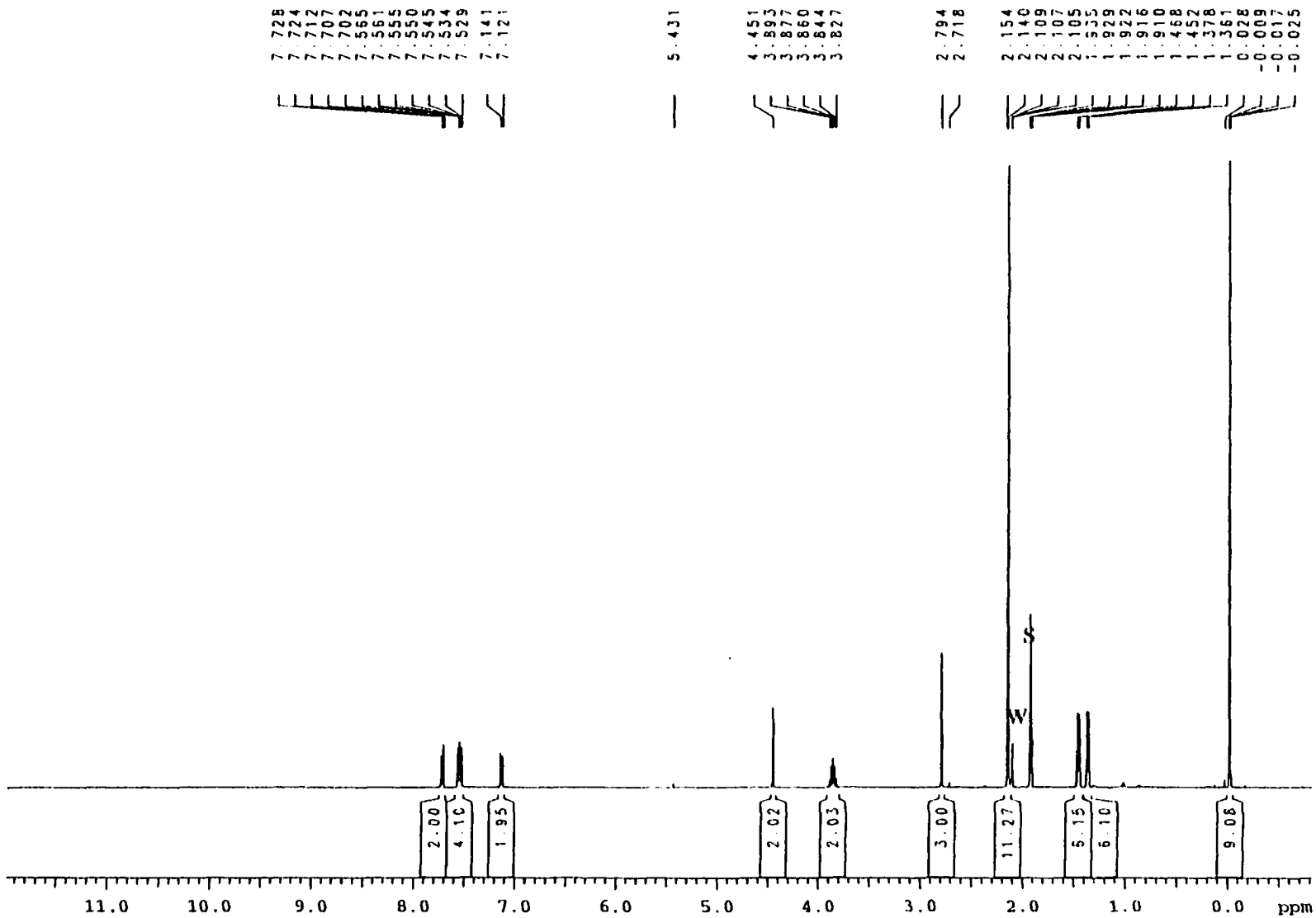

Figure A-9. ^{1}H NMR spectrum (400 MHz, CD_3CN) of (4-[4'-((trimethylsilyl)methyl)phenyl]benzyl)diisopropylmethylammonium iodide (**13**). (**S**: acetonitrile, **W**: water)

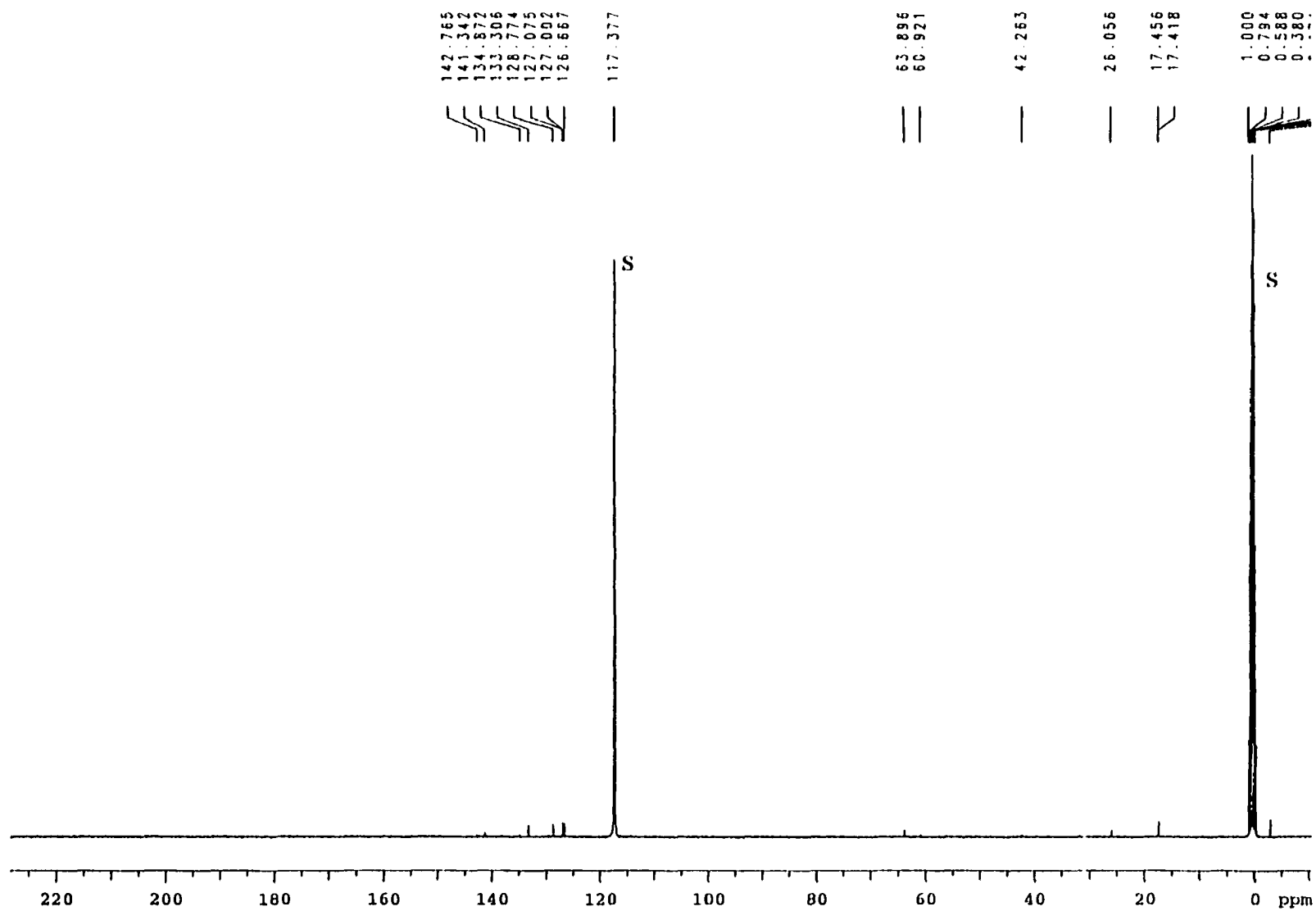

Figure A-10. ^{13}C NMR spectrum (100 MHz, CD_3CN) of 4-[4'-((trimethylsilyl)methyl)phenyl]benzyl)diisopropylmethylammonium iodide (**13**). (S: acetonitrile)

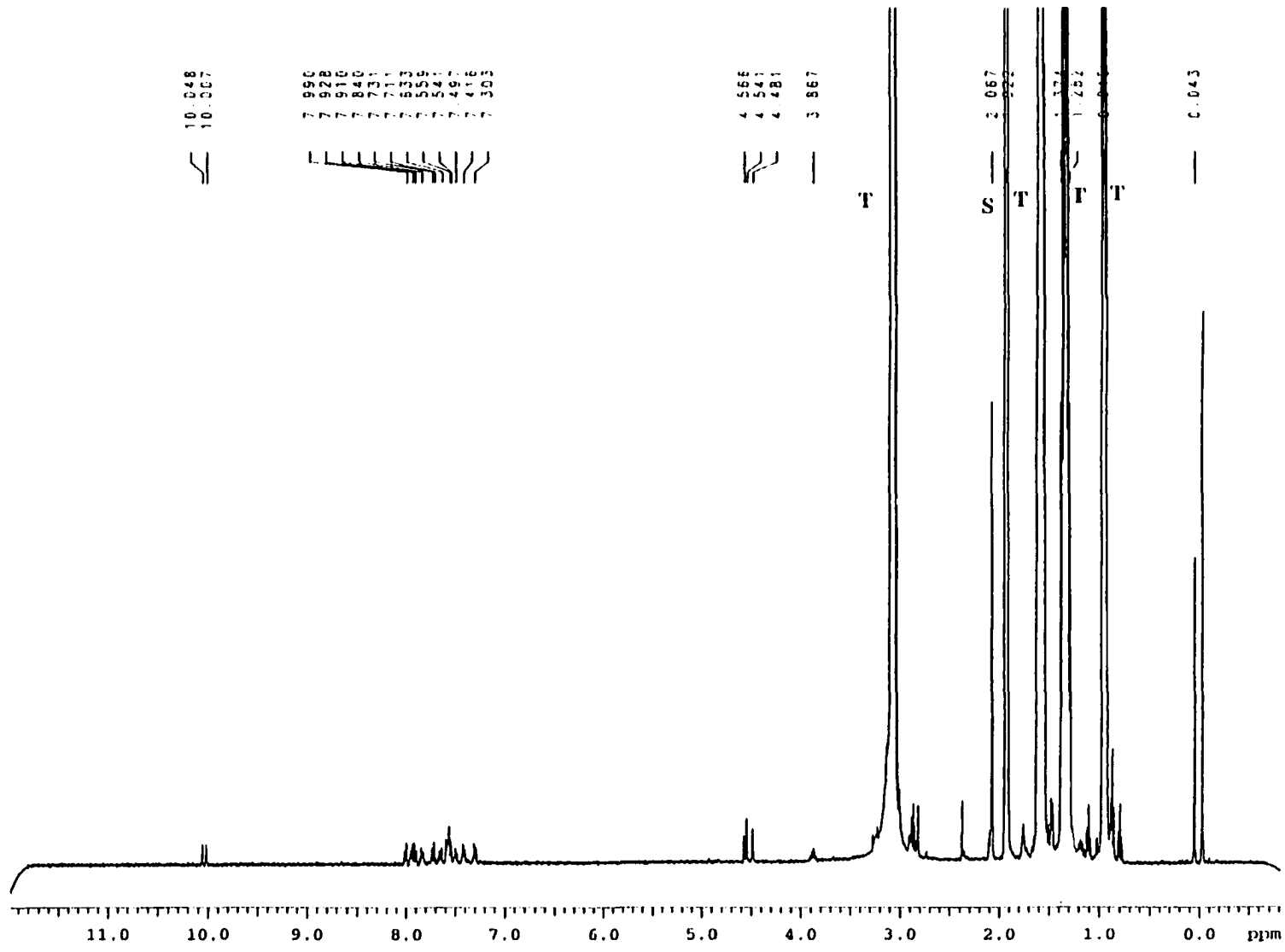

Figure A-11. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-dibenzoquinodimethane (**5**) products in non-deoxygenated acetonitrile after 20 min. (S: acetonitrile, T: TBAF)

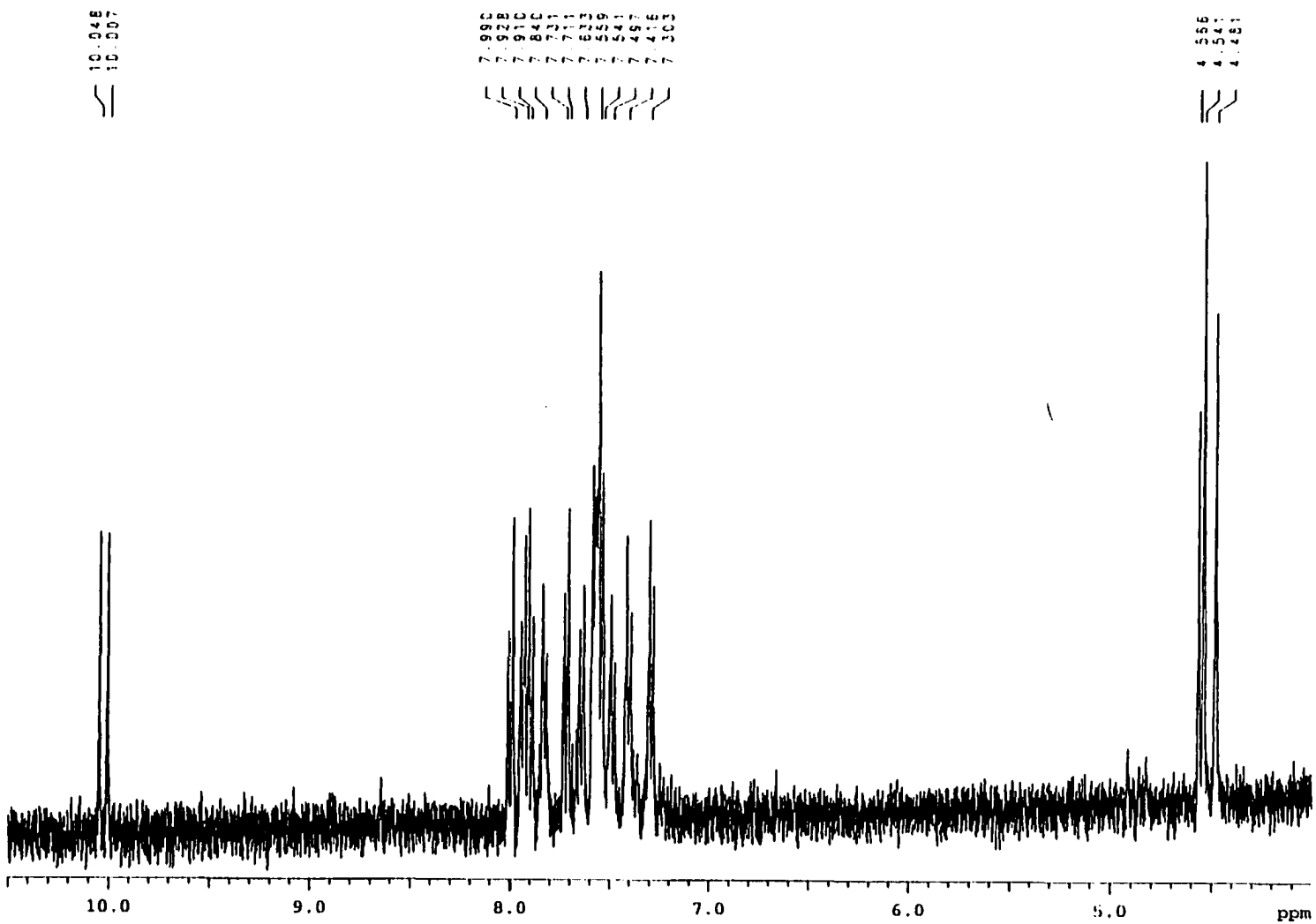

Figure A-12. Enlargement of Figure A-11 from 10.5– 4 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-dibenzoquinodimethane (5) products in non-deoxygenated acetonitrile after 20 min.

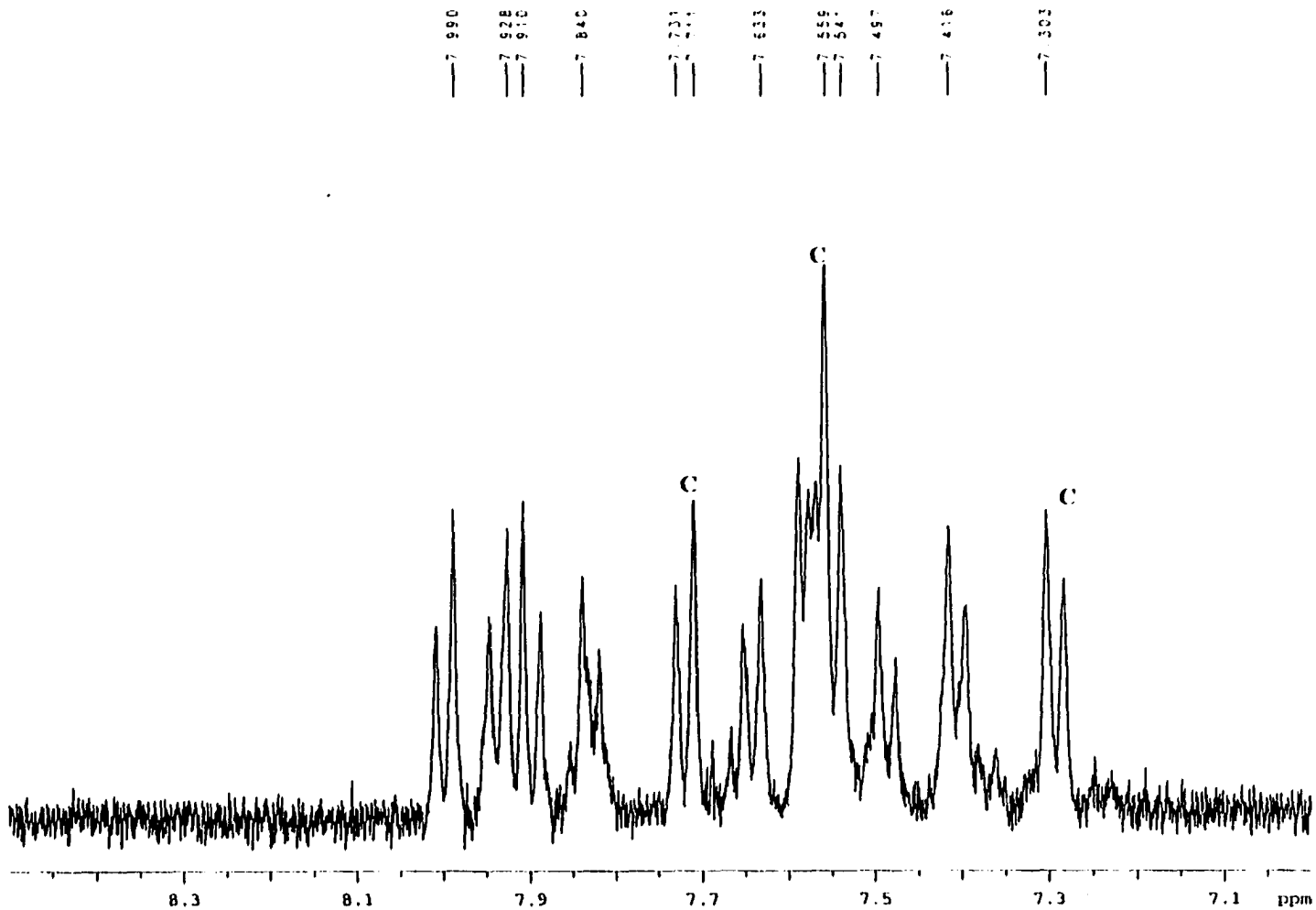

Figure A-13. Enlargement of Figure A-11 from 8.5– 7 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-dibenzoquinodimethane (**5**) products in non-deoxygenated acetonitrile after 20 min. (**C**: common product that appears in both experiments)

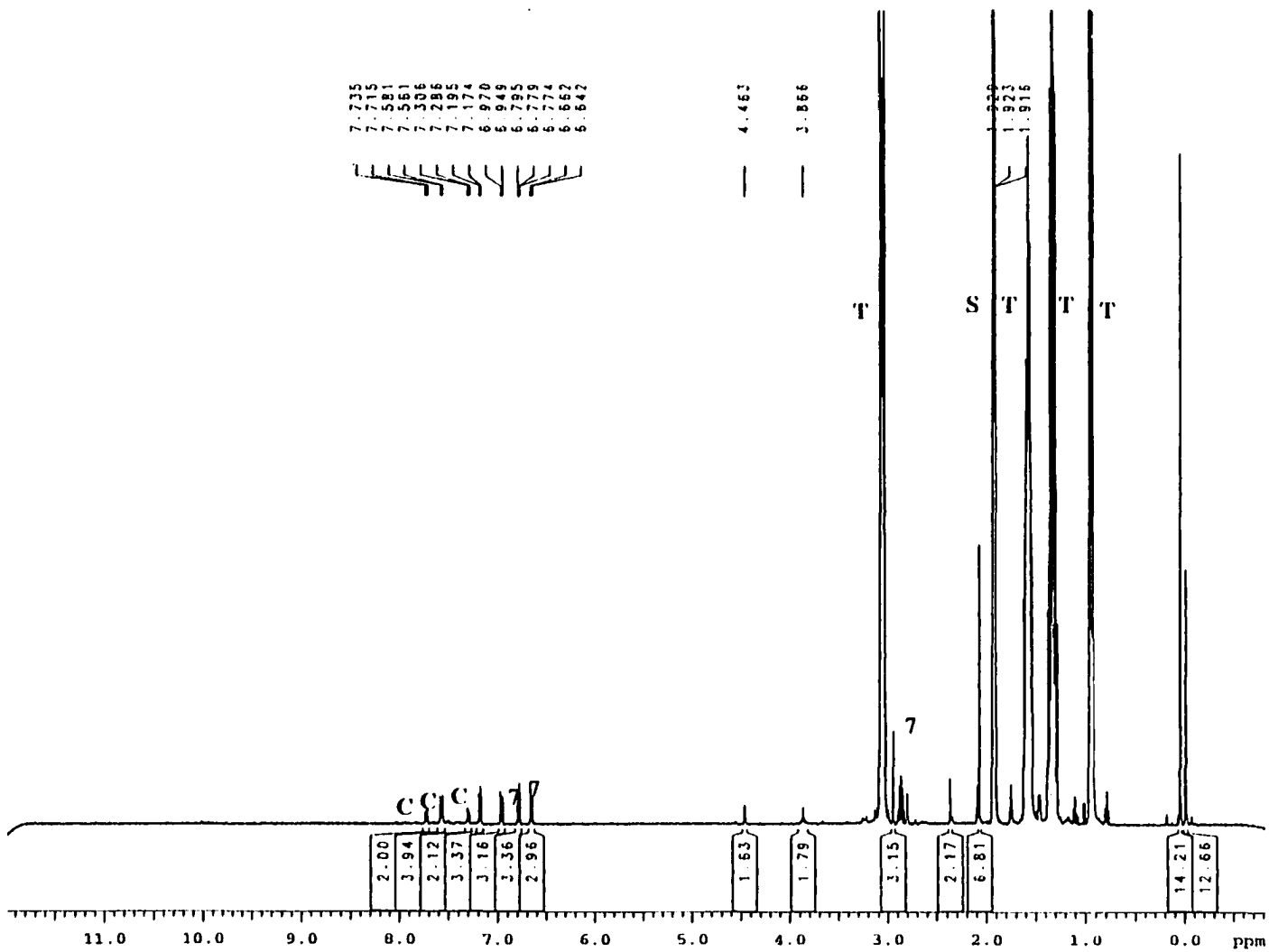

Figure A-14. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-dibenzoquinodimethane (**5**) products in deoxygenated acetonitrile after 2 h. (**7** is a compound number given in the text, **C**: common product that appears in both experiments, **S**: acetonitrile, **T**: TBAF)

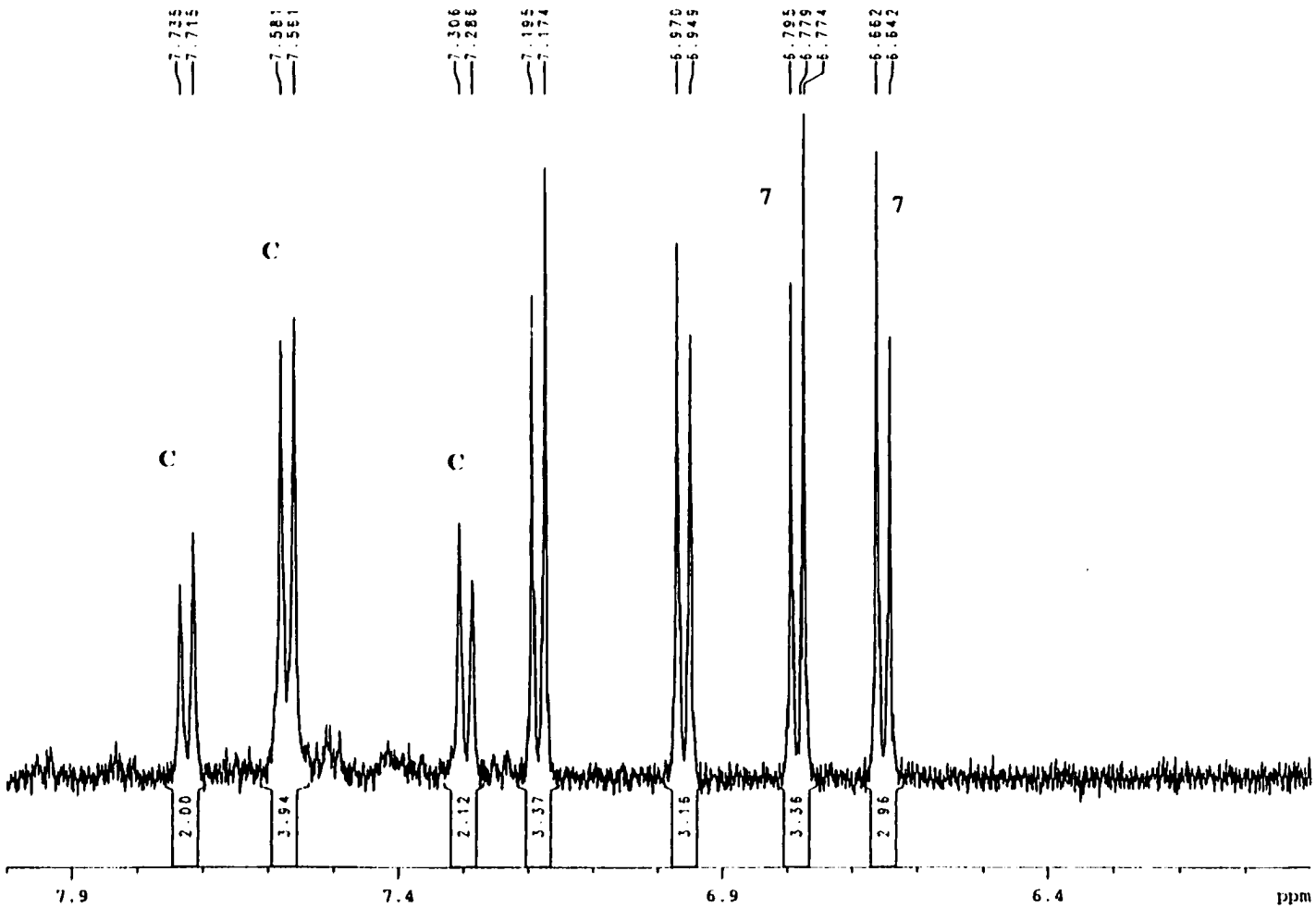

Figure A-15. Enlargement of Figure A-13 from 8 – 6 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of *p*-dibenzoquinodimethane (**5**) products in deoxygenated acetonitrile after 2 h. (**7** is a compound number given in the text, **C**: common product that appears in both experiments)

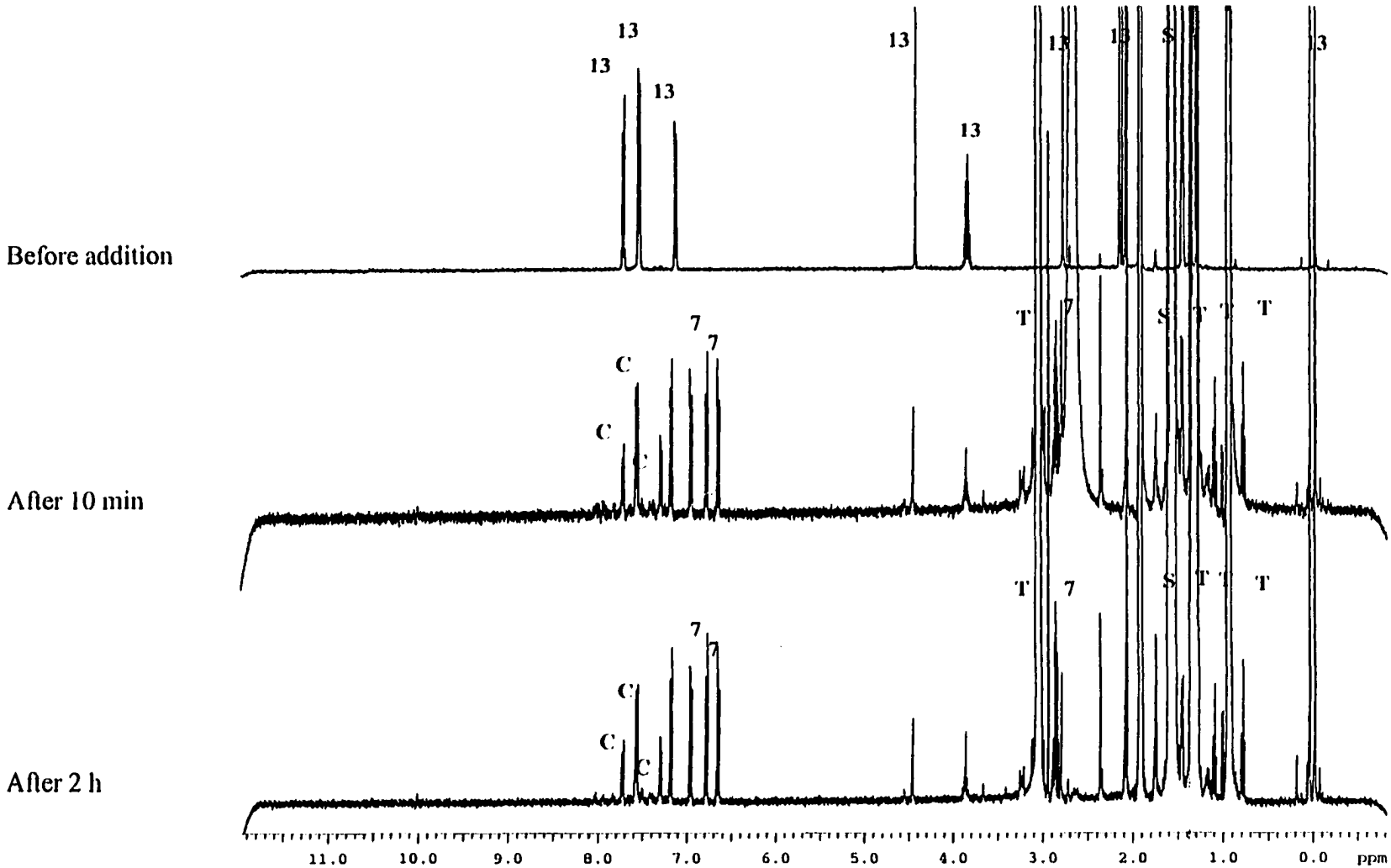

Figure A-16. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-dibenzoquinodimethane (**5**) in deoxygenated acetonitrile. (**7** and **13** are compound numbers given in the text, **C**: common product that appears in both experiments, **S**: acetonitrile, **T**: TBAF)

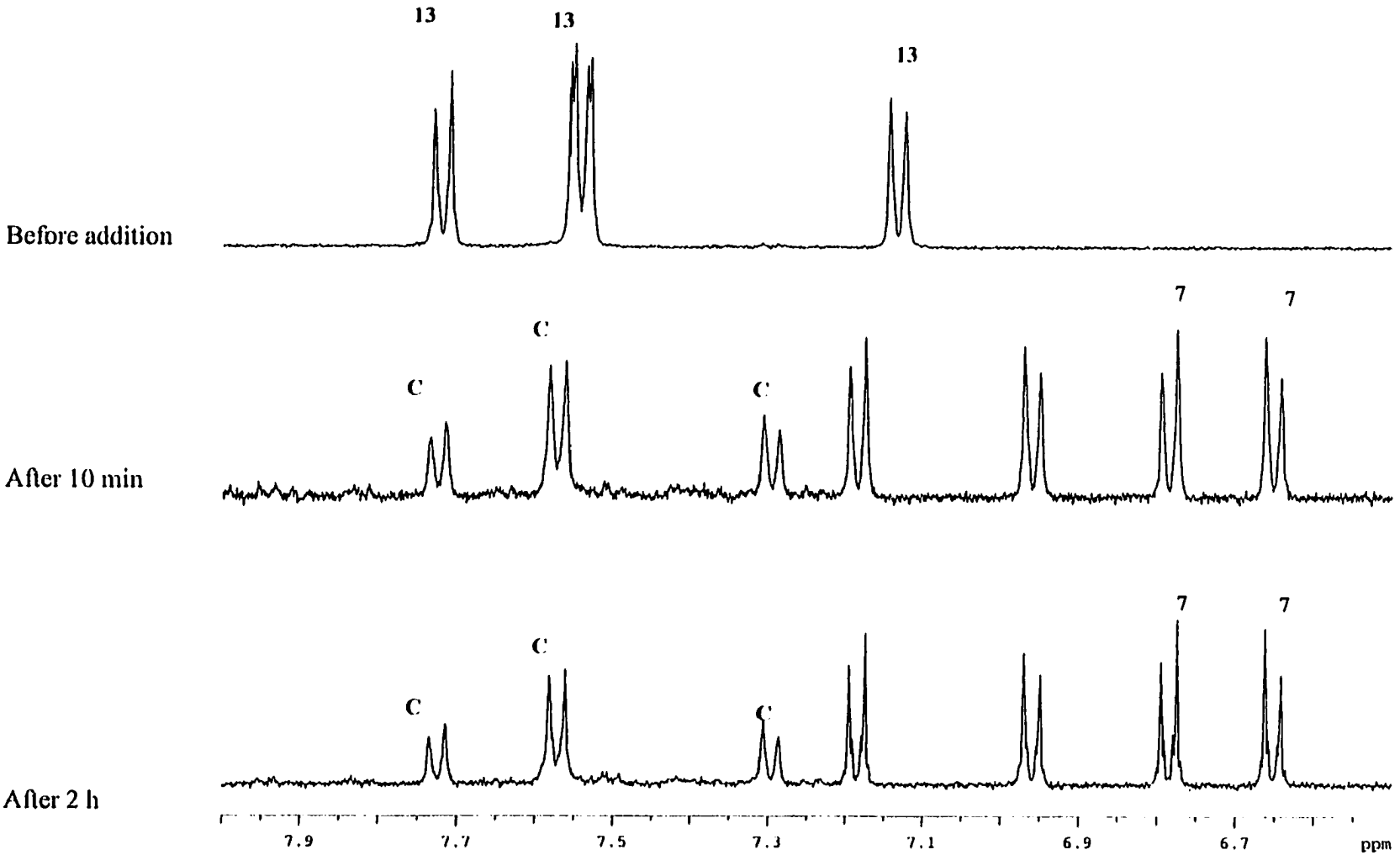

Figure A-17. Enlargement of Figure A-16 from 8 – 6.5 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of reaction progress of *p*-dibenzoquinodimethane (**5**)in deoxygenated acetonitrile. (**7** and **13** are compound numbers given in the text, **C**: common product that appears in both experiments)

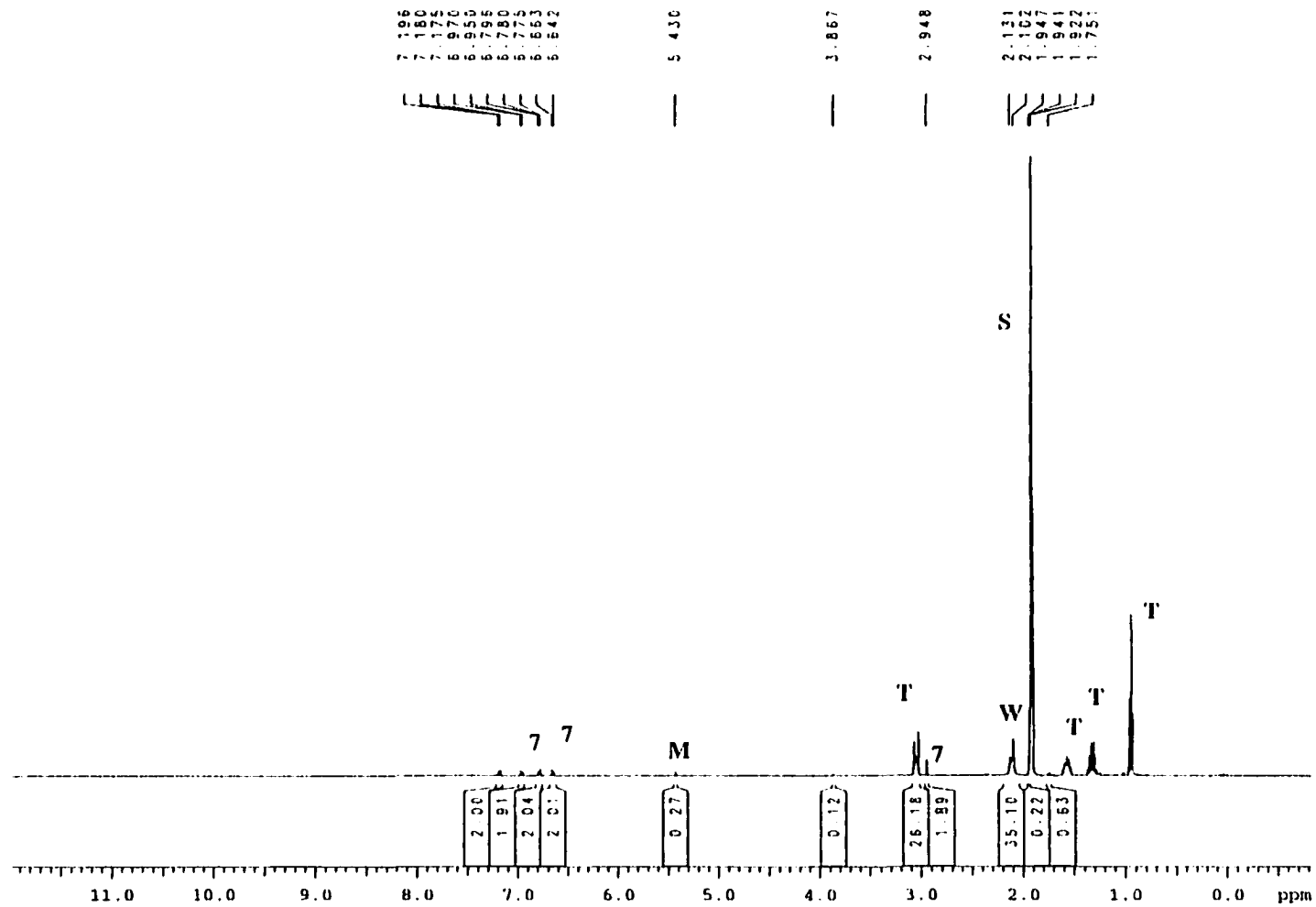

Figure A-18. ^{1}H NMR spectrum (400 MHz, CD_3CN) of methylene chloride extract of *p*-dibenzoquinodimethane (**5**) products in deoxygenated acetonitrile. (**7** is a compound number given in the text, **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF, **W**: water)

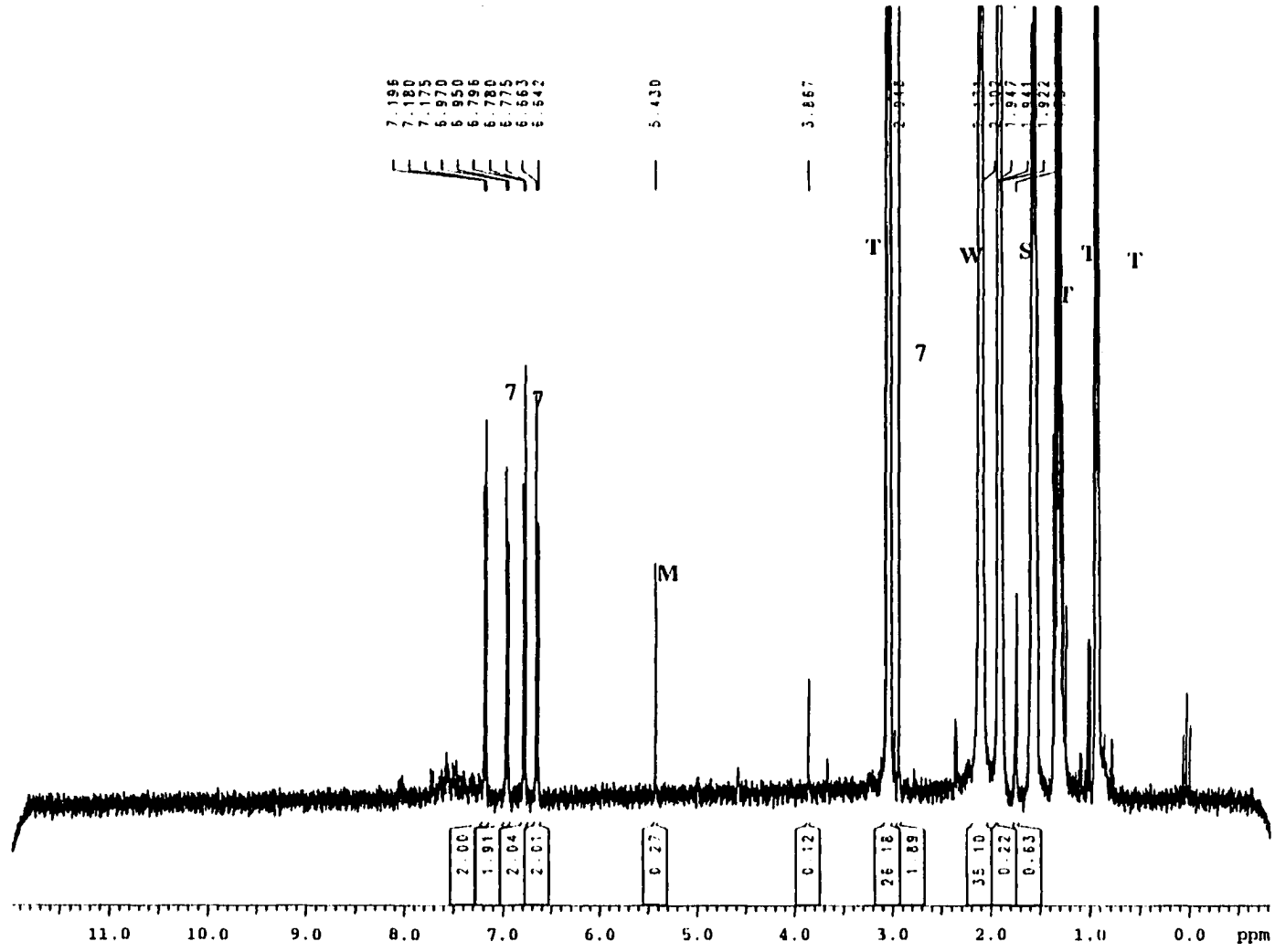

Figure A-19. Enlargement of Figure A-18. ^{1}H NMR spectrum (400 MHz, CD_3CN) of methylene chloride extract of *p*-dibenzoquinodimethane (**5**) products in deoxygenated acetonitrile. (**7** is a compound number given in the text, **M**: methylene chloride, **S**: acetonitrile, **T**: TBAF, **W**: water)

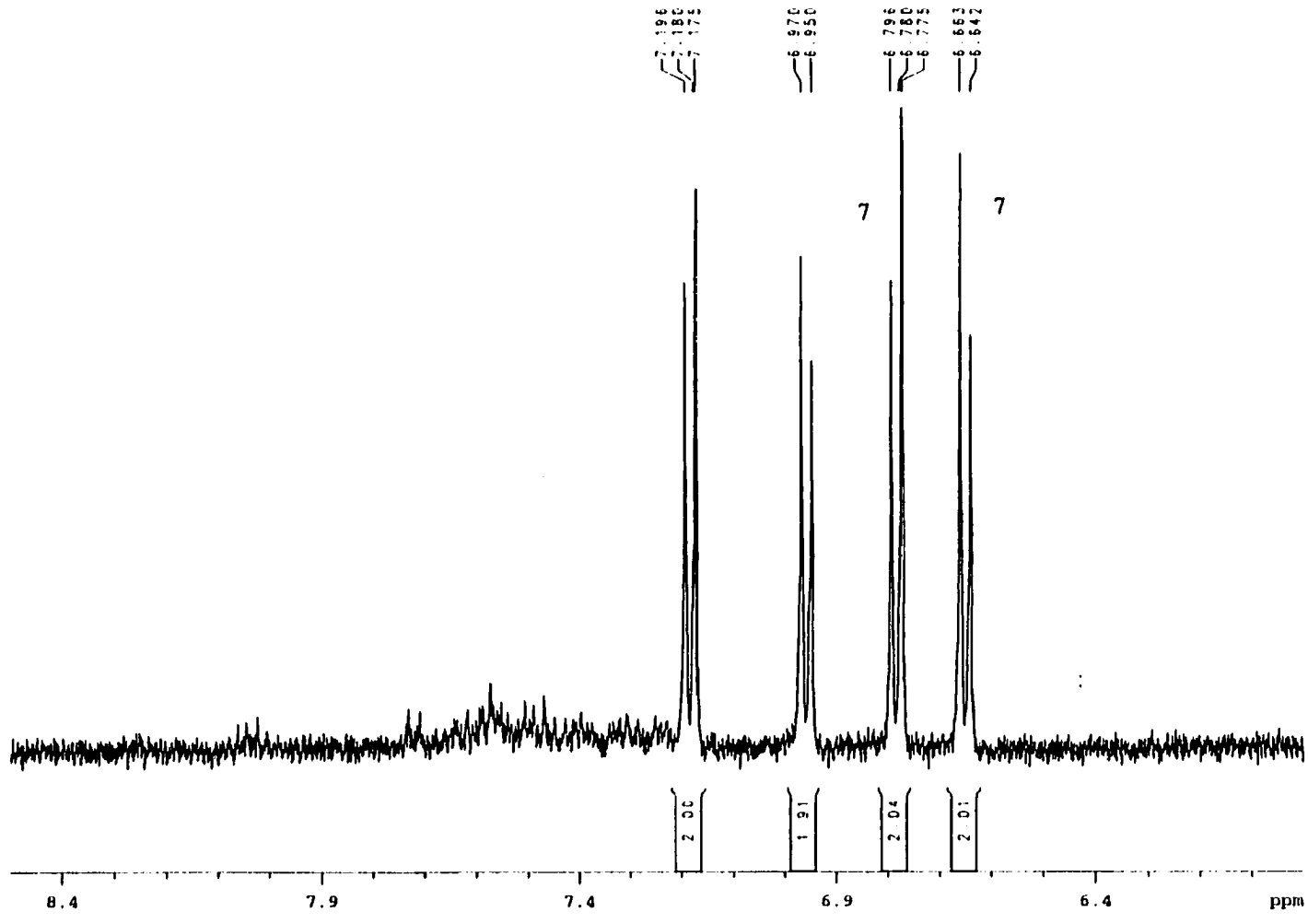

Figure A-20. Enlargement of Figure A-18 from 8.5 – 6 ppm. ^{1}H NMR spectrum (400 MHz, CD_3CN) of methylene chloride extract of *p*-dibenzoquinodimethane (**5**) products in deoxygenated acetonitrile. (**7** is a compound number given in the text.)

GENERAL CONCLUSION

The research presented in this dissertation demonstrates that molecules generally considered highly reactive can be prepared in such a manner that they are relatively stable at room temperature. Once prepared, these compounds can be observed at room temperature by spectroscopic means including ^{1}H NMR spectroscopy. Their relative stability also allows their chemistry to be studied and mechanisms to be examined.

The first chapter of the dissertation describes the preparation of the smallest possible cross-conjugated polyene, 3-methylene-1,4-pentadiene, by flash vacuum pyrolysis (FVP). The triene was characterized by ^{1}H, ^{13}C, and heteronuclear chemical shift correlation (HETCOR) NMR spectroscopy. The Diels-Alder reaction of the cross-conjugated triene and methyl acrylate under mild conditions produces methyl 4-vinyl-3-cyclohexenecarboxylate, the '*para*' 1:1 adduct, as the major product and methyl 3-vinyl-3-cyclohexenecarboxylate, the '*meta*' 1:1 adduct, as the minor product. The '*para*' regioselectivity observed in this reaction is consistent with frontier molecular orbital theory. Under the mild conditions used for this Diels-Alder reaction, only traces of 2:1 adducts are produced. It can be concluded that there is a large difference in the reactivity toward dienophiles of the initial triene and the 1:1 adducts. An area of further work is the issue of the regioselectivity of the addition of a second dienophile to form the 2:1 adducts.

Chapter two is a literature review of simple *p*-QDM's. It describes the relative reactivity, a number of methods of generating by pyrolylic and non-pyrolylic methods, and spectral observation of simple *p*-QDM's.

Chapters three and four describe the preparation by fluoride induced elimination of trimethylsilyl acetate and the room temperature characterization by ^{1}H NMR spectroscopy of

five reactive *p*-QDM's: *p*-xylylene, α-methyl-*p*-xylylene, 2,6-dimethyl-*p*-xylylene, α-phenyl-*p*-xylylene, and α,α-diphenyl-*p*-xylylene. The ^{13}C NMR spectrum of *p*-xylylene was observed for the first time. Trimers of three *p*-QDM's, *p*-xylylene, α-methyl-*p*-xylylene, and 2,6-dimethyl-*p*-xylylene, were observed which is strong evidence that they dimerize via a dimerical diradical in a stepwise mechanism. Rate constants were determined for the decomposition of *p*-xylylene, α-methyl-*p*-xylylene, α-phenyl-*p*-xylylene, and α,α-diphenyl-*p*-xylylene. The long-term kinetic study of *p*-xylylene found that it primarily decomposes by a second-order process like dimerization. The other kinetic studies, including the short-term study of *p*-xylylene, found that both first- and second-order decomposition was occurring. A probable explanation is that polymerization, a first-order process, and dimerization, a second-order process, are occurring at an appreciable rate. The α,α-diphenyl derivative was found to be the most reactive of the series followed by the α-phenyl derivative, *p*-xylylene, and the α-methyl derivative.

Chapter five discusses the attempted preparation of *p*-diphenoquinodimethane by fluoride induced elimination. The biphenyl-based *p*-QDM is believed to be form based on the similarities of its products and that of other *p*-QDM. When exposed to oxygen, the product's ^{1}H NMR spectrum with signals from aldehydes and peroxides was similar to that obtained with *p*-xylylene. With careful avoidance of oxygen in the solution, evidence was obtained for [2.2]-(4,4')-biphenylophane, which is analogous to the [2.2]cyclophane found in the oligomerization of *p*-xylylene.

ACKNOWLEDGEMENTS

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