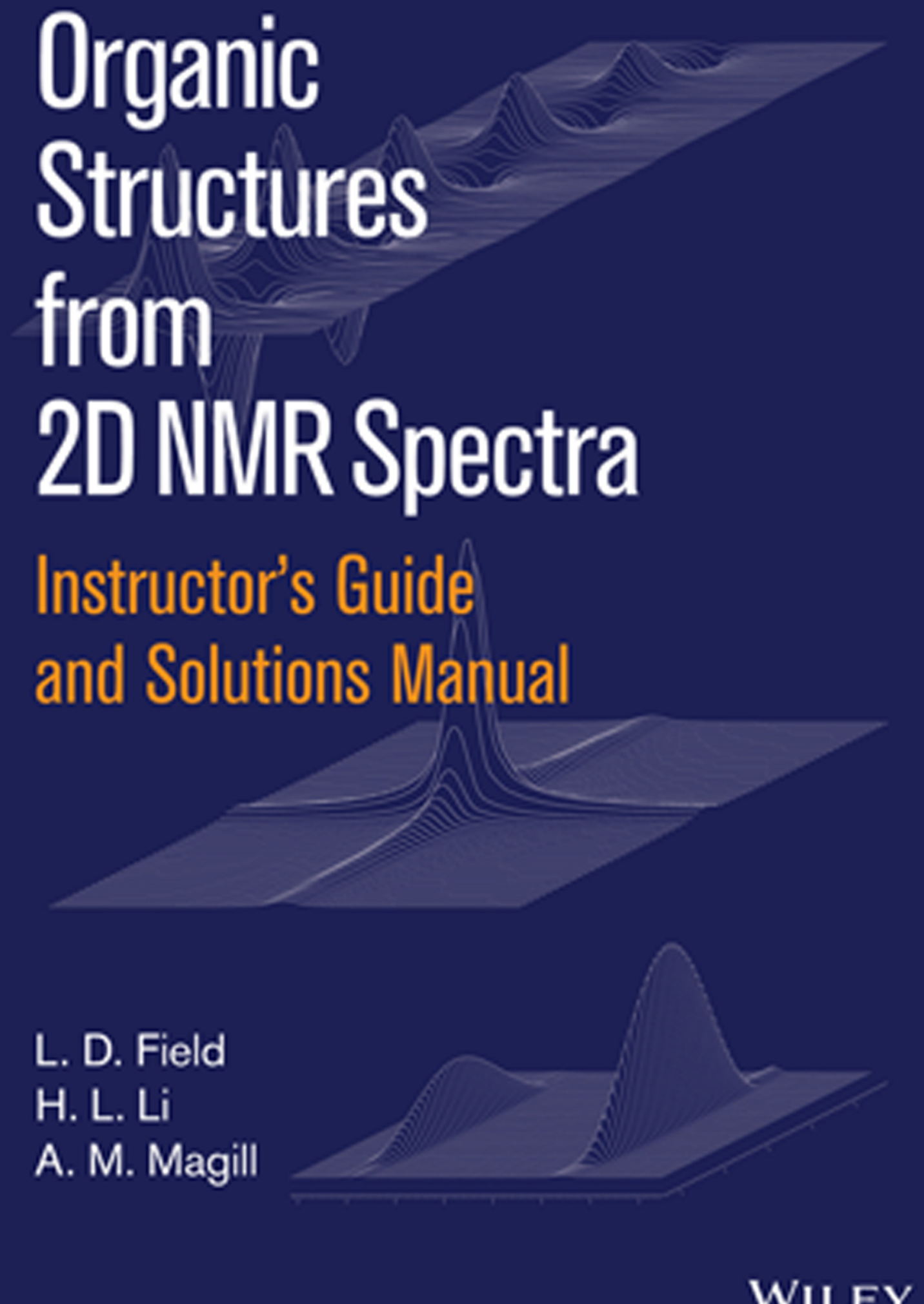


Organic Structures from 2D NMR Spectra



Instructor's Guide and Solutions Manual

L. D. Field
H. L. Li
A. M. Magill

WILEY

Full file at

<https://buklibry.com/download/solutions-manual-organic-structures-from-2d-nmr-spectra-1st-edition-by-field-magill/>

Instructor's Guide and Solutions Manual to Organic Structures from 2D NMR Spectra

Full file at

<https://buklibry.com/download/solutions-manual-organic-structures-from-2d-nmr-spectra-1st-edition-by-field-magill/>

Instructor's Guide and Solutions Manual to Organic Structures from 2D NMR Spectra

L. D. Field, H. L. Li and A. M. Magill

School of Chemistry, University of New South Wales, Australia

WILEY

This edition first published 2015

© 2015 John Wiley & Sons Ltd

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex, PO19 8SQ, United Kingdom

For details of our global editorial offices, for customer services and for information about how to apply for permission to reuse the copyright material in this book please see our website at www.wiley.com.

The right of the author to be identified as the author of this work has been asserted in accordance with the Copyright, Designs and Patents Act 1988.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, except as permitted by the UK Copyright, Designs and Patents Act 1988, without the prior permission of the publisher.

Wiley also publishes its books in a variety of electronic formats. Some content that appears in print may not be available in electronic books.

Designations used by companies to distinguish their products are often claimed as trademarks. All brand names and product names used in this book are trade names, service marks, trademarks or registered trademarks of their respective owners. The publisher is not associated with any product or vendor mentioned in this book.

Limit of Liability/Disclaimer of Warranty: While the publisher and author have used their best efforts in preparing this book, they make no representations or warranties with respect to the accuracy or completeness of the contents of this book and specifically disclaim any implied warranties of merchantability or fitness for a particular purpose. It is sold on the understanding that the publisher is not engaged in rendering professional services and neither the publisher nor the author shall be liable for damages arising herefrom. If professional advice or other expert assistance is required, the services of a competent professional should be sought.

Library of Congress Cataloging-in-Publication Data applied for.

A catalogue record for this book is available from the British Library.

ISBN: 9781119027256

Set in 12/18pt Times New Roman by Aptara Inc., New Delhi, India.

1 2015

CONTENTS

| | |
|--|------------|
| Preface | ix |
| Solutions Summary | 1 |
| Problem 1 (1-iodopropane) | 7 |
| Problem 2 (2-butanone) | 11 |
| Problem 3 (2-hexanone) | 15 |
| Problem 4 (ethyl propionate) | 19 |
| Problem 5 (ethyl 3-ethoxypropionate) | 23 |
| Problem 6 (4-acetylbutyric acid) | 28 |
| Problem 7 (3-ethoxypropionyl chloride) | 32 |
| Problem 8 (ethyl 3-chloropropionate) | 36 |
| Problem 9 (isoamyl acetate) | 40 |
| Problem 10 (<i>trans</i>-4-hexen-3-one) | 45 |
| Problem 11 (<i>trans</i>-2-octen-4-one) | 50 |
| Problem 12 (3-nitrobenzaldehyde) | 55 |
| Problem 13 (3-iodotoluene) | 61 |
| Problem 14 (8-hydroxy-5-nitroquinoline) | 64 |
| Problem 15 (2-bromo-3-picoline) | 69 |
| Problem 16 (<i>trans</i>-anethole) | 72 |
| Problem 17 (<i>cis</i>-2-pentene) | 75 |
| Problem 18 (<i>p</i>-tolyl benzoate) | 79 |
| Problem 19 (phenyl <i>p</i>-toluate) | 86 |
| Problem 20 (4-biphenyl acetate) | 93 |
| Problem 21 (4'-phenoxyacetophenone) | 99 |
| Problem 22 (4'-<i>tert</i>-butylacetophenone) | 106 |

| | |
|---|-----|
| Problem 23 (2,2,4'-trimethylpropiophenone) | 110 |
| Problem 24 (<i>trans</i> -2-methyl-3-phenyl-2-propen-1-ol) | 114 |
| Problem 25 (methyl 4-ethoxybenzoate) | 119 |
| Problem 26 (methyl 3-(<i>p</i> -tolyl)propionate) | 123 |
| Problem 27 (4-(4'-methoxyphenyl)-2-butanone) | 127 |
| Problem 28 (ethyl 6-bromohexanoate) | 132 |
| Problem 29 (piperonal) | 135 |
| Problem 30 (<i>cis</i> -3-hexenyl benzoate) | 139 |
| Problem 31 (<i>trans</i> -2, <i>cis</i> -6-nonadienal) | 146 |
| Problem 32 (allyl glycidyl ether) | 155 |
| Problem 33 (3,4-epoxy-4-methyl-2-pentanone) | 159 |
| Problem 34 (dl-methionine) | 162 |
| Problem 35 (<i>N</i> -acetyl- <i>l</i> -leucine) | 165 |
| Problem 36 (isoamyl valerate) | 170 |
| Problem 37 ((<i>E</i>)-4-methyl-4'-nitrostilbene) | 173 |
| Problem 38 (2- <i>tert</i> -butyl-6-methylphenol) | 181 |
| Problem 39 (2-allyl-6-methylphenol) | 186 |
| Problem 40 (2-hydroxy-4-methoxybenzaldehyde) | 194 |
| Problem 41 (2'-hydroxy-5'-methylacetophenone) | 198 |
| Problem 42 (3'-fluoro-4'-methoxyacetophenone) | 203 |
| Problem 43 (<i>trans</i> -ferulic acid) | 209 |
| Problem 44 (sec-butyl 3-hydroxycinnamate) | 215 |
| Problem 45 (1-benzosuberone) | 221 |
| Problem 46 (dimethyl (3-bromopropyl)phosphonate) | 228 |
| Problem 47 (caffeine) | 233 |
| Problem 48 (benzyloxypropionitrile) | 238 |
| Problem 49 (cineole) | 242 |
| Problem 50 (thymoquinone) | 246 |

| | |
|--|------------|
| Problem 51 (4-bromo-1-indanol) | 251 |
| Problem 52 (1-bromo-4-methylnaphthalene) | 257 |
| Problem 53 (carvacrol) | 264 |
| Problem 54 (acetoacetanilide) | 272 |
| Problem 55 (ethyl acetamidocyanoacetate) | 277 |
| Problem 56 (α-humulene) | 283 |
| Problem 57 (3,4-dihydro-2<i>H</i>-benzopyran-3-carboxylic acid) | 289 |
| Problem 58 (quinidine) | 296 |
| Problem 59 (salbutamol) | 312 |
| Problem 60 (2-hydroxy-1-naphthaldehyde) | 322 |
| Problem 61 (6-methyl-4-chromanone) | 329 |
| Problem 62 (citronellal) | 336 |
| Problem 63 ((+)-<i>cis</i>-2-oxabicyclo-[3.3.0]oct-6-en-3-one) | 344 |
| Problem 64 (melatonin) | 349 |
| Problem 65 (carvone) | 362 |
| Problem 66 (haloperidol) | 370 |

Full file at

<https://buklibry.com/download/solutions-manual-organic-structures-from-2d-nmr-spectra-1st-edition-by-field-magill/>

PREFACE

This book is the Instructor's Guide and Solutions Manual to the problems contained in the text *Organic Structures from 2D NMR Spectra*.

The aim of this book is to teach students to solve structural problems in organic chemistry using NMR spectroscopy and in particular 2D NMR spectroscopy. The basic philosophy of the book is that learning to identify organic structures using spectroscopy is best done by working through examples. This book contains a series of about 60 graded examples ranging from very elementary problems through to very challenging problems at the end of the collection.

We have assumed a working knowledge of basic structural organic chemistry and common functional groups. We also assume a working knowledge of the rudimentary spectroscopic methods which would be applied routinely in characterising and identifying organic compounds including infrared spectroscopy and basic 1D ^{13}C and ^1H NMR spectroscopy.

The Instructor's Guide contains a worked solution to each of the problems contained in *Organic Structures from 2D NMR Spectra*. At the outset, it should be emphasised that there are always many paths to the correct answer – there is no single process to arrive at the correct solution to any of the problems. We do not recommend a mechanical attitude to problem solving – intuition, which comes with experience, has a very important place in solving structures from spectra; however, students often find the following approach useful:

- (i) **Extract as much information as possible from the basic characterisation data which is provided:**
 - (a) **Note the molecular formula** and any restrictions this places on the functional groups that may be contained in the molecule.
 - (b) From the molecular formula, **determine the degree of unsaturation**. The degree of unsaturation can be calculated from the molecular formula for all compounds containing C, H, N, O, S and the halogens using the following three basic steps:
 - 1. Take the molecular formula and replace all halogens by hydrogens.

2. Omit all of the sulfur and/or oxygen atoms.
3. For each nitrogen, omit the nitrogen and omit one hydrogen.

After these three steps, the molecular formula is reduced to C_nH_m , and the degree of unsaturation is given by:

$$\text{Degree of Unsaturation} = n - \frac{m}{2} + 1$$

The degree of unsaturation indicates the number of π bonds and/or rings that the compound contains. For example, if the degree of unsaturation is 1, the molecule can only contain one double bond or one ring. If the degree of unsaturation is 4, the molecule must contain four rings or multiple bonds. An aromatic ring accounts for four degrees of unsaturation (the equivalent of three double bonds and a ring). An alkyne or a $C \equiv N$ accounts for two degrees of unsaturation (the equivalent of two π bonds).

- (c) **Analyse the 1D 1H NMR spectrum** if one is provided and note the relative numbers of protons in different environments and any obvious information contained in the coupling patterns. Note the presence of aromatic protons, exchangeable protons, and/or vinylic protons, all of which provide valuable information on the functional groups which may be present.
 - (d) **Analyse the 1D ^{13}C NMR spectrum** if one is provided and note the number of carbons in different environments. Note also any resonances that would be characteristic of specific functional groups, *e.g.* the presence or absence of a ketone, aldehyde, ester or carboxylic acid carbonyl resonance.
 - (e) **Analyse any infrared data** and note whether there are absorptions characteristic of specific functional groups, *e.g.* $C=O$ or $-OH$ groups.
- (ii) **Extract basic information from the 2D COSY, TOCSY and/or C–H correlation spectra.**
- (a) The COSY will provide obvious coupling partners. If there is one identifiable starting point in a spin system, the COSY will allow the successive identification (*i.e.* the sequence) of all nuclei in the spin system. The COSY cannot jump across breaks in the spin system (such as where there is a heteroatom or a carbonyl group that isolates one spin system from another).

- (b) The TOCSY identifies all groups of protons that are in the same spin system.
- (c) The C–H correlation links the carbon signals with their attached protons and also identifies how many –CH–, –CH₂–, –CH₃ and quaternary carbons are in the molecule.
- (iii) **Analyse the INADEQUATE spectrum** if one is provided, because this can sequentially provide the whole carbon skeleton of the molecule. Choose one signal as a starting point and sequentially work through the INADEQUATE spectrum to determine which carbons are connected to which.
- (iv) **Analyse the HMBC spectrum.** This is perhaps the most useful technique to pull together all of the fragments of a molecule because it gives long-range connectivity.
- (v) **Analyse the NOESY spectrum** to assign any stereochemistry in the structure.
- (vi) **Continually update the list of structural elements** or fragments that have been conclusively identified at each step and start to pull together reasonable possible structures. Be careful not to jump to possible solutions before the evidence is conclusive. Keep assessing and re-assessing all of the options.
- (vii) When you have a final solution which you believe is correct, **go back and confirm that all of the spectroscopic data are consistent with the final structure** and that every peak in every spectrum can be properly rationalised in terms of the structure that you have proposed.

L. D. Field

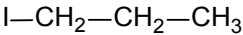
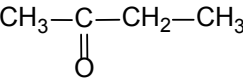
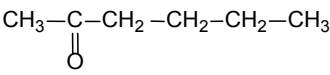
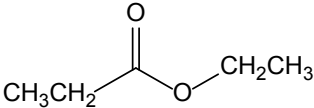
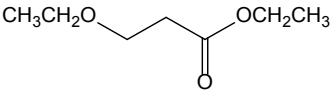
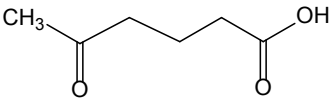
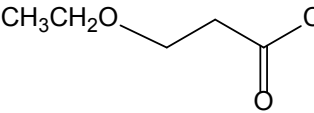
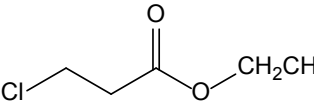
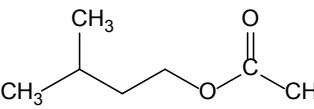
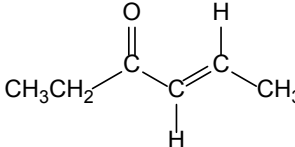
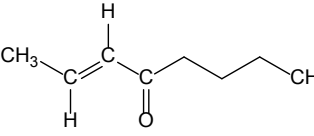
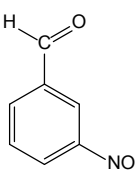
H. L. Li

A. M. Magill

January 2015

Full file at

<https://buklibry.com/download/solutions-manual-organic-structures-from-2d-nmr-spectra-1st-edition-by-field-magill/>

| | | |
|----|---|--|
| 1 |  | LABEL COSY HSQC HMBC INADEQUATE |
| | 1-iodopropane C_3H_7I | |
| 2 |  | LABEL COSY HSQC HMBC INADEQUATE |
| | 2-butanone C_4H_8O | |
| 3 |  | COSY HSQC HMBC |
| | 2-hexanone $C_6H_{12}O$ | |
| 4 |  | SIMULATE COSY HSQC HMBC |
| | ethyl propionate $C_5H_{10}O_2$ | |
| 5 |  | LABEL COSY HSQC HMBC |
| | ethyl 3-ethoxypropionate $C_7H_{14}O_3$ | |
| 6 |  | ASSIGNMENT HSQC HMBC |
| | 4-acetylbutyric acid $C_6H_{10}O_3$ | |
| 7 |  | COSY HSQC HMBC ISOMER (2) |
| | 3-ethoxypropionyl chloride $C_5H_9ClO_2$ | |
| 8 |  | COSY HSQC HMBC ISOMER (2) |
| | ethyl 3-chloropropionate $C_5H_9ClO_2$ | |
| 9 |  | LABEL COSY HSQC HMBC INADEQUATE |
| | isoamyl acetate $C_7H_{14}O_2$ | |
| 10 |  | LABEL COSY HSQC HMBC NOESY |
| | <i>trans</i> -4-hexen-3-one $C_6H_{10}O$ | |
| 11 |  | COSY HSQC HMBC NOESY |
| | <i>trans</i> -2-octen-4-one $C_8H_{14}O$ | |
| 12 |  | LABEL COSY HSQC HMBC NOESY INADEQUATE |
| | 3-nitrobenzaldehyde $C_7H_5NO_3$ | |

Problem 19

Question:

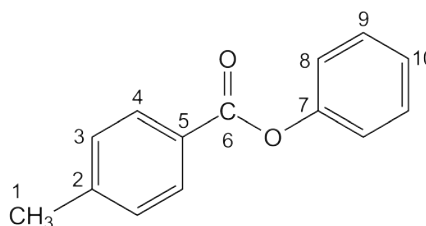
Identify the following compound.

Molecular Formula: $C_{14}H_{12}O_2$

IR: 1720 cm^{-1}

Solution:

Phenyl *p*-toluate



1. The molecular formula is $C_{14}H_{12}O_2$. Calculate the degree of unsaturation from the molecular formula: ignore the O atoms to give an effective molecular formula of $C_{14}H_{12}$ (C_nH_m) which gives the degree of unsaturation as $(n - m/2 + 1) = 14 - 6 + 1 = 9$. The compound contains a combined total of nine rings and/or π bonds.
2. The 1H NMR spectrum indicates that the compound has nine aromatic protons and three aliphatic protons.
3. The presence of nine aromatic protons suggests two aromatic rings.
4. The three aliphatic protons are equivalent and have no visible splitting so these must be an isolated methyl group.
5. IR and 1D NMR spectra establish that the compound is an ester (quaternary ^{13}C resonance at 165.2 ppm).
6. The presence of two aromatic rings and an ester carbonyl satisfies the degree of unsaturation, so there are no more functional groups with double bonds or rings.
7. The methyl resonance in the 1H and ^{13}C spectra (2.44 and 21.7 ppm, respectively) eliminates the possibility of a methyl ester, since for a methoxy group both the 1H and ^{13}C signals would appear significantly further downfield.
8. The 1H NMR spectrum shows five unique signals in the aromatic region.

Problem 39

Question:

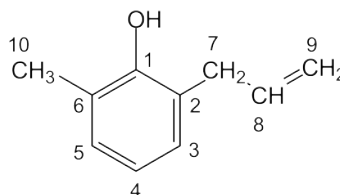
Identify the following compound.

Molecular Formula: $C_{10}H_{12}O$

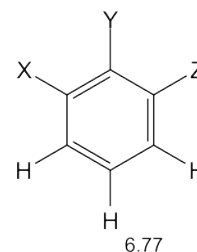
IR: 3600 (br), 1638, 1594, 1469 (s) cm^{-1}

Solution:

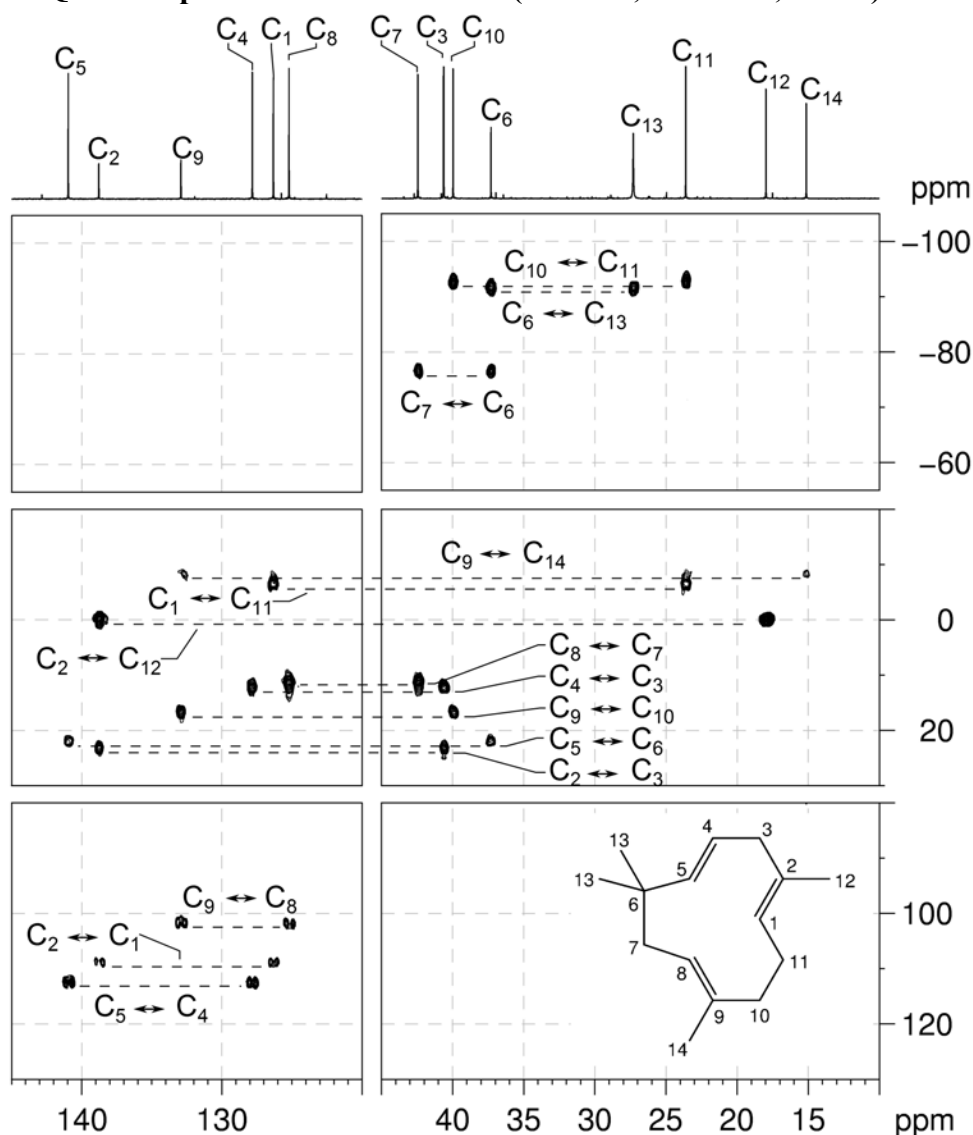
2-Allyl-6-methylphenol



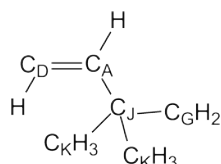
1. The molecular formula is $C_{10}H_{12}O$. Calculate the degree of unsaturation from the molecular formula: ignore the O atom to give an effective molecular formula of $C_{10}H_{12}$ (C_nH_m) which gives the degree of unsaturation as $(n - m/2 + 1) = 10 - 6 + 1 = 5$. The compound contains a combined total of five rings and/or π bonds.
2. 1D spectra establish that the compound is a trisubstituted benzene. The aromatic ring accounts for four degrees of unsaturation and the remaining degree of unsaturation is accounted for by a double bond (alkene 1H resonances at 5.99 and 5.15 ppm).
3. The coupling pattern in the aromatic region of the 1H NMR spectrum shows that the three protons on the aromatic ring must occupy adjacent positions. The proton at 6.77 ppm is the proton at the middle of the spin system since it has two large splittings (*i.e.* it has two *ortho*-protons) whereas the other two aromatic protons each have only one large splitting.
4. The three substituents on the aromatic ring must therefore be in adjacent positions *i.e.* this compound is a “1,2,3-trisubstituted benzene”.
5. 1D spectra establish that two of the substituents are an $-OH$ substituent (1H resonance at 4.99 ppm, exchangeable) and a $-CH_3$ group (three proton resonance at 2.21 ppm).



INADEQUATE spectrum of α -humulene ($C_{15}H_{22}$, 150 MHz, 338 K)



7. We will only work in one direction, so let us work from C_J . This resonance has two further correlations in the INADEQUATE spectrum – one to the resonance at 27.3 ppm (C_K , which, according to the integrations in the 1H NMR spectrum, corresponds to a pair of geminal methyl groups) and the second to the resonance at 42.4 ppm (C_G , a methylene group).



8. C_K has no further correlations as it is a pair of terminal geminal methyl groups.