Intramolecular Heck Couplings of Unactivated Alkyl Electrophiles: Synthetic and Mechanistic Studies

by

Luke Firmansjah

M. Chem., Chemistry
University of Oxford – Oriel College, 2002

Submitted to the Department of
Chemistry in Partial Fulfillment of
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Signature of Author...
Department of Chemistry
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Certified by...
Professor Gregory C. Fu
Thesis Supervisor

Accepted by...
Robert W. Field
Chairman, Departmental Committee on Graduate Students

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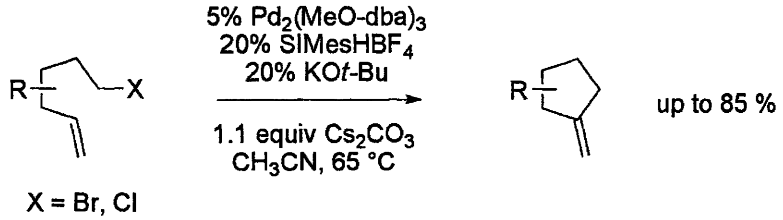
ABSTRACT

A method for the palladium-catalyzed intramolecular Heck coupling of unactivated alkyl bromides and chlorides is described. The optimal catalyst system was composed of $Pd_2(MeO\text{-}dba)_3$ as the metal source and *N*-heterocyclic carbene SIMes as the ligand, and the influence of both parameters is discussed. Reaction of a diastereomerically pure, deuterium-labeled substrate gave only one diastereomer of product, suggesting that the reaction does not proceed through radical pathway, in contrast to processes currently described in the literature.

Mechanistic studies involved the synthesis of novel complex $Pd(SIMes)_2$ and a number of its oxidative addition adducts, which were thought to resemble intermediates along a postulated catalytic cycle. However, the alkylpalladium species thus obtained, which were characterized by X-ray crystallography and which bear freely accessible β hydrogen atoms, are air and moisture-stable compounds that display no tendency for β-hydride elimination, even upon heating. These complexes are therefore not thought to be part of the catalytic cycle. It was further demonstrated that while $Pd(SIMes)_2$ is not itself catalytically competent in the reaction, it may serve as a catalyst precursor. Evidence is provided to suggest that the true active catalyst is composed of a mixed ligand complex involving both SIMes and dba.



Thesis Supervisor: Professor Gregory C. Fu
Title: Professor of Chemistry

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Chapter 1

Intramolecular Heck Reactions of Unactivated Alkyl Halides

1.1. Introduction.

Transition metal-catalyzed cross-coupling reactions (eq 1.1), have achieved widespread use in organic synthesis.[1] Their appeal chiefly derives from the mild conditions that can be employed, which are frequently tolerant of sensitive functional groups, and which can typically furnish the desired products in an efficient and selective manner. One of the metals most commonly-employed for this purpose has been palladium,[1a] and cross-coupling protocols such as the Suzuki, Negishi, and Stille reactions[2] have found, based on this metal source, wide application in both the academic and industrial context.

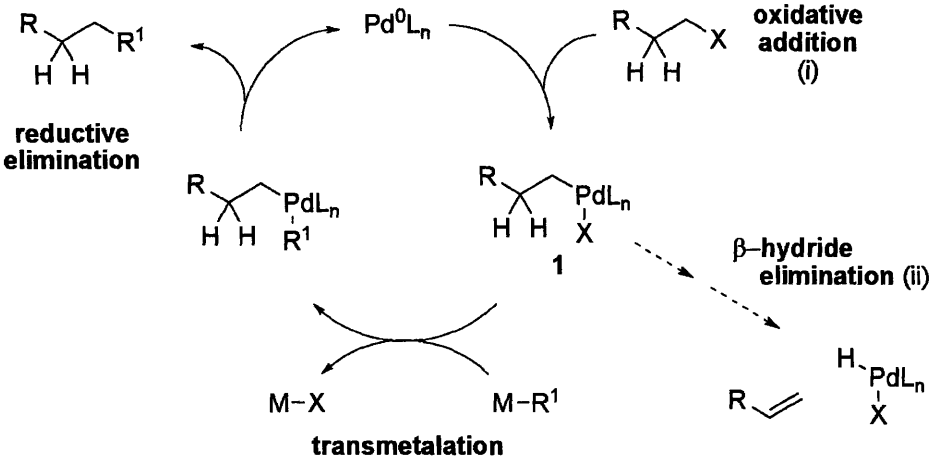
$$\mathrm{R{-}X} \qquad \mathrm{M{-}R^1} \xrightarrow{\substack{\text{Metal Catalyst}\\ \text{Ligand}}} \mathrm{R{-}R^1} \qquad (1.1)$$

R = Ar, alkenyl
benzyl, allyl

X = Hal, OTs, OTf

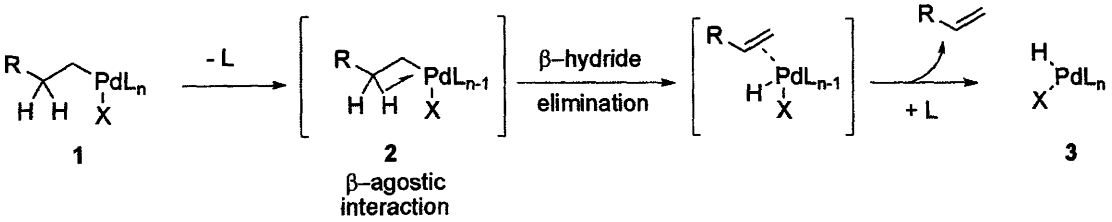
M = BX_2 (Suzuki-Miyaura)
ZnX (Negishi)
SnX_3 (Stille)

The majority of the available literature for cross-coupling chemistry involves the use of sp^2-hybridized electrophiles, i.e., aryl and vinyl compounds. In contrast, the use of sp^3-hybridized electrophiles, i.e., alkyl compounds, has been considerably more scarce.[3] This is often attributed to two main factors in the proposed catalytic cycle (Scheme 1.1): (i) slow oxidative addition of the active catalyst to an alkyl electrophile,[4] leading to inefficient conversions and side reactions, and (ii) rapid sequestering of the incipient alkylmetal species **1**, via an undesired side-pathway known as β-hydride elimination.[5]



Scheme 1.1. General mechanism for palladium-catalyzed cross-coupling reactions.

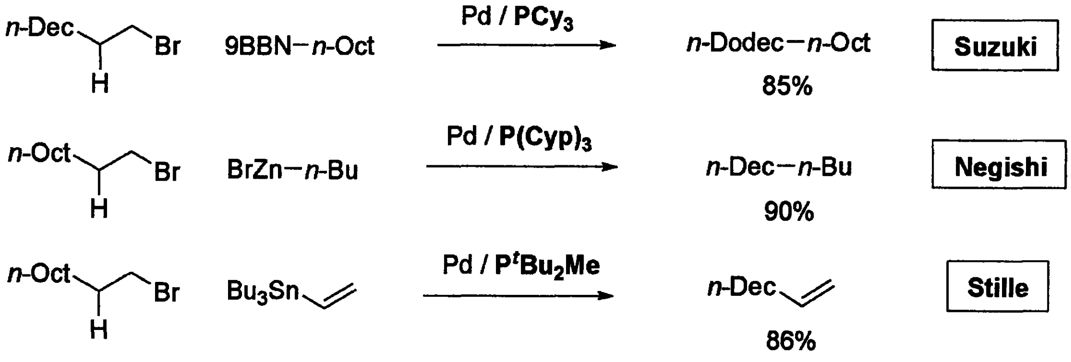
This latter process is believed to operate via the pathway shown in Scheme 1.2. Initial ejection of a ligand from the oxidative addition complex **1** forms a coordinatively unsaturated species (not shown). The vacant coordination site is then filled by an agostic interaction from a C-H bond on the alkyl group that is β- to the alkyl-metal bond. However, the resultant species **2** is often only transient in nature and is prone to rapid collapse, via β-hydride elimination, to form a metal hydride **3** and the olefin side-product.



Scheme 1.2. Proposed pathway for β-hydride elimination.

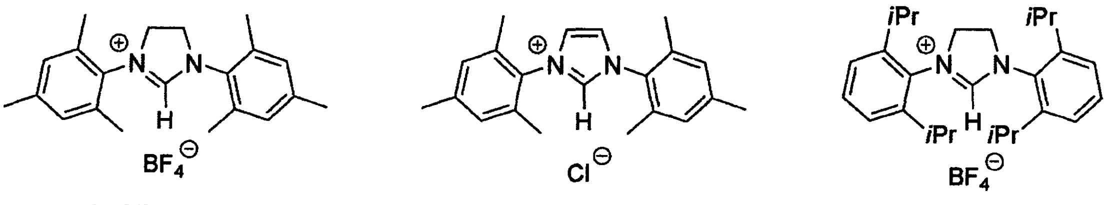
While a number of modifications may be built into the substrate architecture, such as the use of 'activated' alkyl electrophiles[6] that enhance the rate of oxidative addition, or the use of alkyl electrophiles that do not contain accessible β hydrogens[7] (thus avoiding elimination), solutions based upon the nature of the catalyst have appeared only recently.

Fu and coworkers have demonstrated[8] that systems composed of a Pd source and a selection of bulky, electron-rich phosphines (Scheme 1.3) were able to couple various aliphatic, β hydrogen-containing primary electrophiles with a number of organometallic reagents, in an efficient and high-yielding manner. In one instance, the use of an *N*-heterocyclic carbene ligand (vide infra) also proved highly effective.[9]



Scheme 1.3. Examples of phosphine-based cross-couplings for alkyl electrophiles.

Organ and Beller have also subsequently shown that *N*-heterocyclic carbene[10] ligands (NHCs) are also capable of these transformations.[11] Although systems for the cross-couplings of secondary alkyl electrophiles[12] using Ni-based catalysts have since been reported, these latter protocols are believed to proceed via a different mechanistic pathway,[13] and they will not be discussed further.

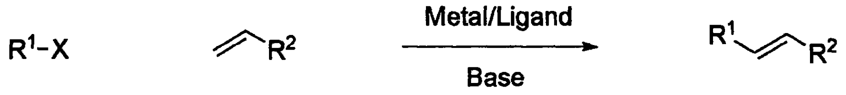


4a SIMes·HBF$_4$ **4b** IMes·HCl **4c** SIPr·HBF$_4$

Figure 1.1. Examples of N-heterocyclic carbenes as their precursor salts.

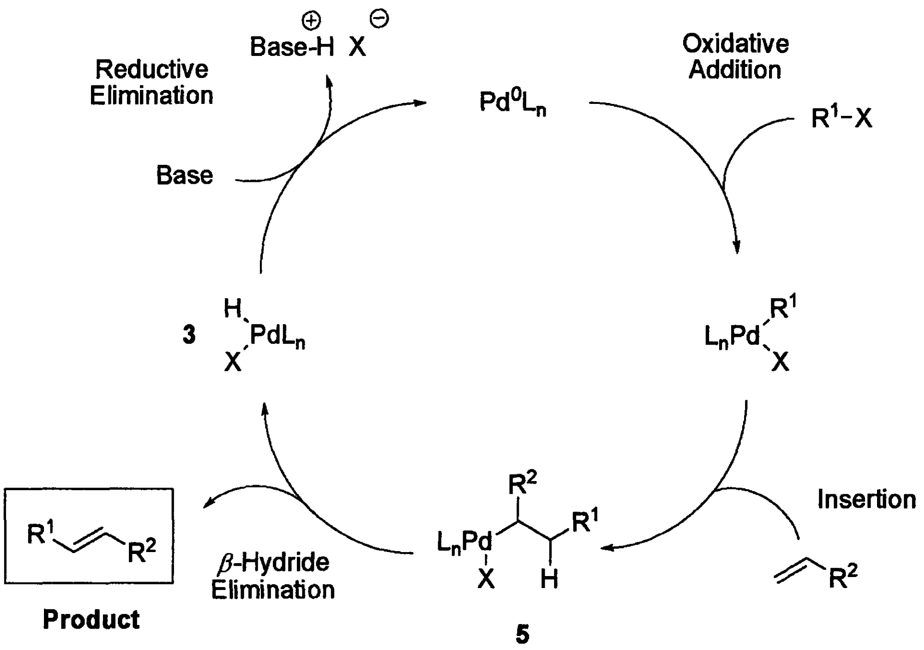
Further mechanistic investigation into the Pd/PR_3 cross-coupling systems described above has revealed that oxidative addition is a relatively fast,[14] well-defined[15] process. Further, the resultant alkylpalladium intermediates (**1**, L = PCy_3, P(*t*-Bu)$_2$Me) are in some cases stable enough to be isolated and characterized.[8] While β-hydride elimination still occurs, it appears to be a greatly attenuated phenomenon. These findings informed our strategy for the new methodology presented herein.

The closely related Heck[16] reaction (eq 2) has evolved into a versatile and widely applicable method in organic synthesis.[17] It shares a number of common features with its cross-coupling counterparts, such as the use of similar transition metal catalysts and the use of an organic electrophile as substrate. However, the Heck reaction employs an *olefin* as a coupling partner, in place of an organometallic reagent.



(1.2)

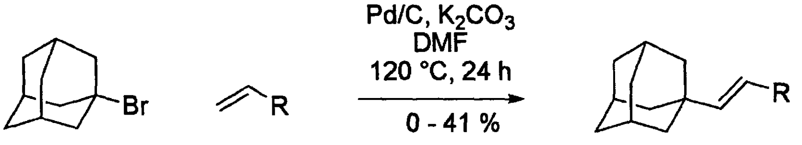
This leads to a mechanistically distinct reaction pathway (Scheme 1.4): the olefin coordinates to the metal center (in exchange for a ligand, not shown) before inserting into the metal-carbon bond to form a transient alkylmetal complex **5**. It should be noted that, in order to generate the desired olefinic product, a β-hydride elimination step is now *required.*[18]



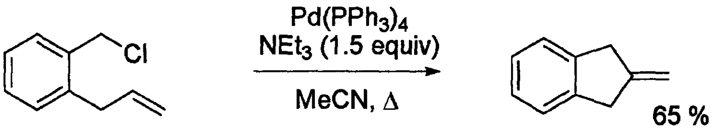
Scheme 1.4. Postulated mechanism of the Heck reaction.

Finally, the active catalyst must be regenerated from the resultant metal-hydride species **3**. A base is typically employed for this purpose,[19] extruding HX and formally reducing the complex.

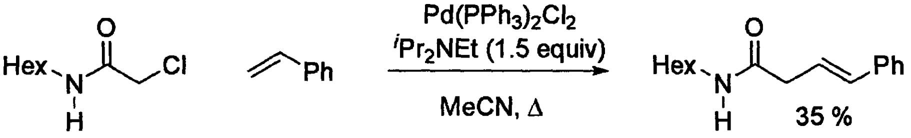
While precedent for the Heck coupling of *aryl* and *vinyl* electrophiles is extensive, examples of the Heck coupling for unactivated *alkyl* electrophiles are less prolific. An initial report from Lebedev and Beletskaya[20] describes a Ni-based protocol, in which a selection of unactivated alkyl electrophiles were coupled to styrene. Oshima[21] and Branchaud[22] have reported cobalt-catalyzed systems, while Kambe has described a titanocene-mediated coupling.[23] In the above cases, however, the postulated carbon-carbon bond-forming step is suspected to proceed through a radical, rather than alkylmetal, intermediate, rendering these processes distinct from a true alkyl-Heck pathway.



(1.3)



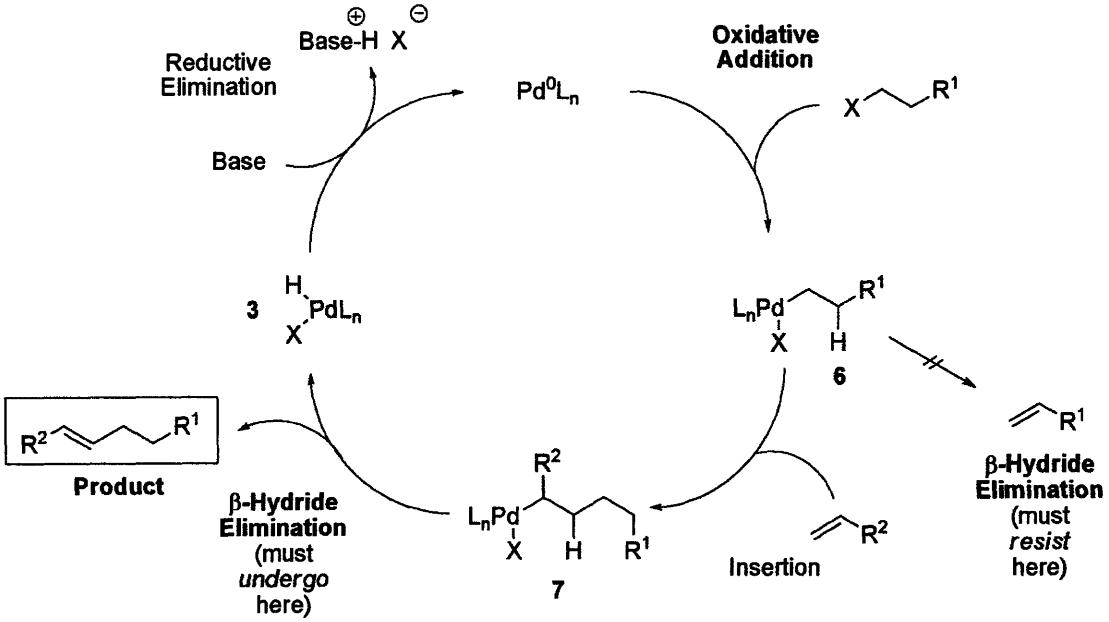
(1.4)



(1.5)

Although the Pd-catalyzed Heck coupling of alkyl halides has been achieved by a number of groups, the electrophiles of interest do not possess accessible β hydrogen atoms.[24] In addition, the electrophiles are typically activated substrates, such as benzylic,[16, 25] allylic,[26] or α-halo carbonyl[27] compounds (eqs 1.3-1.5). To the best of our knowledge, a Pd-catalyzed Heck coupling of unactivated alkyl electrophiles bearing accessible β hydrogen atoms has yet to be described.

Superimposing the requirements of the Heck cycle onto those of the cross-coupling of unactivated alkyl electrophiles, however, reveals what appears to be an impasse (Scheme 1.5): while the initial alkylmetal intermediate **6** that arises from oxidative addition must be *resistant* to β-hydride elimination, the alkylmetal intermediate **7** arising from the next step (insertion) must be able to *undergo* facile β-hydride elimination, in order to furnish the desired product.



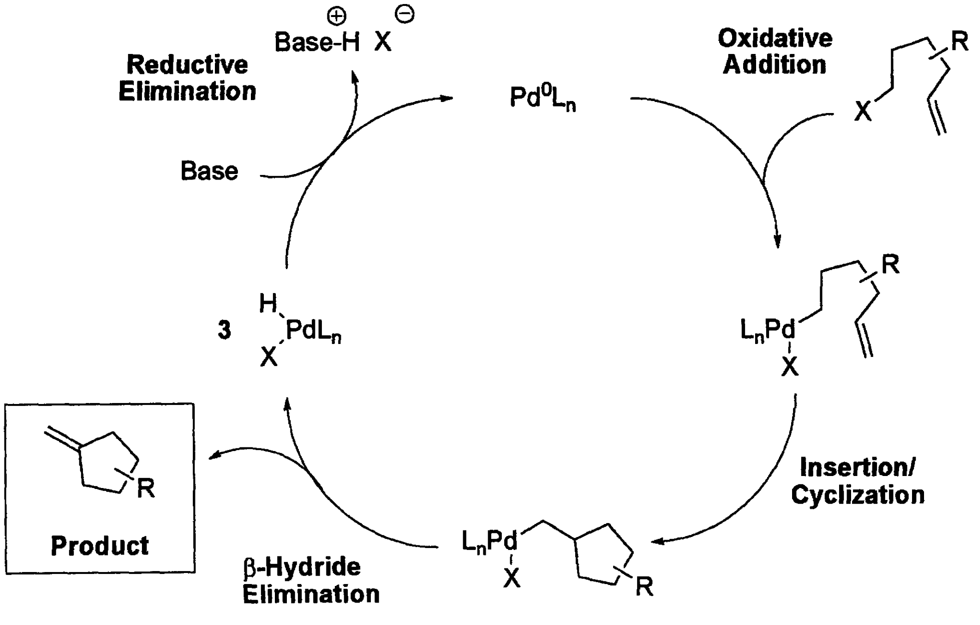
Scheme 1.5. Challenges faced in a hypothetical Pd-catalyzed alkyl-Heck cycle.

Fortunately, if the alkyl groups in each case are sufficiently distinguishable, and, in particular, if the nature of the alkyl group renders the second intermediate far more prone to β-hydride elimination, then a productive selectivity profile between the two intermediates **6** and **7** can be achieved. In many situations this may indeed be the case, as the intermediate following insertion will be branched – the ensuing increase in steric bulk at the metal center may, for example, encourage release of a ligand, and induce the elimination pathway described in Scheme 1.2.

While elegant solutions in the literature, as described above, have been provided by bypassing this mechanistic predicament altogether, for those seeking to develop a Pd-catalyzed system, the challenge remains: β-hydride elimination must be attenuated in a system for which it also a critical step in the cycle. The aim of the current work has been to address this issue.

1.2. Optimization of the Reaction Conditions.

The initial concern was ensuring that insertion into the olefin would out-compete β-hydride elimination from the first alkylpalladium intermediate **6**, as described above. The most obvious solution appeared to be to opt for an *intra*molecular reaction (Scheme 1.6), wherein the the electrophilic and olefinic components are attached to the same molecule. Indeed, Knochel has demonstrated a related Ni-based procedure[3b] in which a coordinated olefin was believed to stabilize the alkyl metal intermediate with respect to elimination (although it should be noted that insertion did not follow).



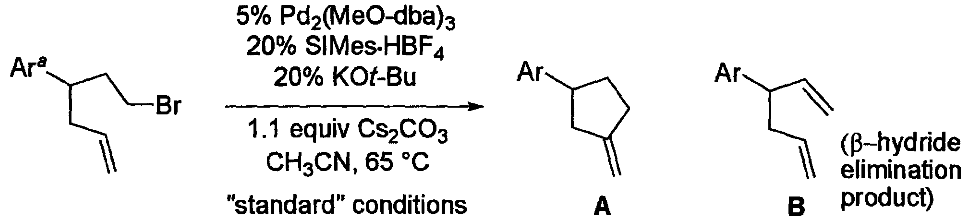
Scheme 1.6. Pathway for a hypothetical Pd-catalyzed intramolecular Heck reaction.

It could be reasonably proposed that, with the appropriate chain length, the chances of an *intra*molecular olefin coordinating prior to β-hydride elimination are somewhat greater than for the analogous *inter*molecular coupling. We reasoned that five-membered rings were sensible targets for what would now be a Heck cyclization, and synthesized our substrates accordingly.

Our metric for success consisted not only of high yield and conversion, but also definitive control over the level of β-hydride elimination. The amount of product isomerization (Scheme 1.7) was also monitored, but did not impinge upon the reaction to any considerable degree (except through specific changes to the reaction conditions).

We subsequently found that a palladium/N-heterocyclic carbene catalyst was highly effective for this intramolecular alkyl-Heck system (Table 1.1). As suggested above, NHC ligands have found great utility as alternatives to phosphine ligands[28] due to their strong σ-donating properties. A survey of NHC ligands suggested that SIMes·HBF_4 **4a** (entry 1) was the optimum ligand source. The popular SIPr·HBF_4[29] **4c** (entry 3) gave significantly lower yields, as did adding an element of unsaturation to the imidazolinium ring (IMes·HBF_4, entry 2). Exchanging the counterion to the less innocuous chloride[30] ion resulted in lower conversion (entry 4) and possible decomposition of the catalyst. Although phosphines were less effective ligands overall, PCy_3 (entry 6) was reasonably efficient at controlling β-hydride elimination. Interestingly, the reaction is somewhat tolerant of the metal:ligand ratio, with a window of largely unchanged reactivity existing between proportions of 1:1 and 1:2 (entry 7).

Table 1.1. Variation of the ligand against the standard conditions.



entry	variation of the ligand	yield of **A** (%)^b	yield of **B** (%)^b	SM^b
1	none	**80**	6	**< 2**
2	20% IMes·HBF_4	**13**	5	**48**
3	20% SIPr·HBF_4	**27**	20	**34**
4	20% SIMes·HCl	**36**	14	**30**
5	20% $P(t\text{-}Bu)_2Me$	**43**	52	**< 2**
6	20% PCy_3	**53**	23	**8**
7	10% SIMes·HBF_4	**77**	7	**< 2**
8	no SIMes·HBF_4	**< 2**	2	**81**

[a] Ar = *p*-anisyl. [b] Determined through analysis by gas chromatography versus a calibrated internal standard (average of two experiments).

The choice of $Pd_2(MeO\text{-}dba)_3$ as metal source arose from a number of observations. While $Pd_2(dba)_3$ performed respectably in the reaction, $Pd(PPh_3)_4$ was completely inactive. Further comparison of commercially available palladium sources revealed that the most successful catalyst precursors were those containing ligands with a capacity for *π*–bonding to the palladium center. Thus, Pd(II) salts such as $[(allyl)PdCl]_2$ and $Pd(COD)_2Cl_2$ were able to furnish desired product in acceptable yields (40-50%) and with some degree of control over the level of β-hydride elimination (up to 3:1 in favor of product).

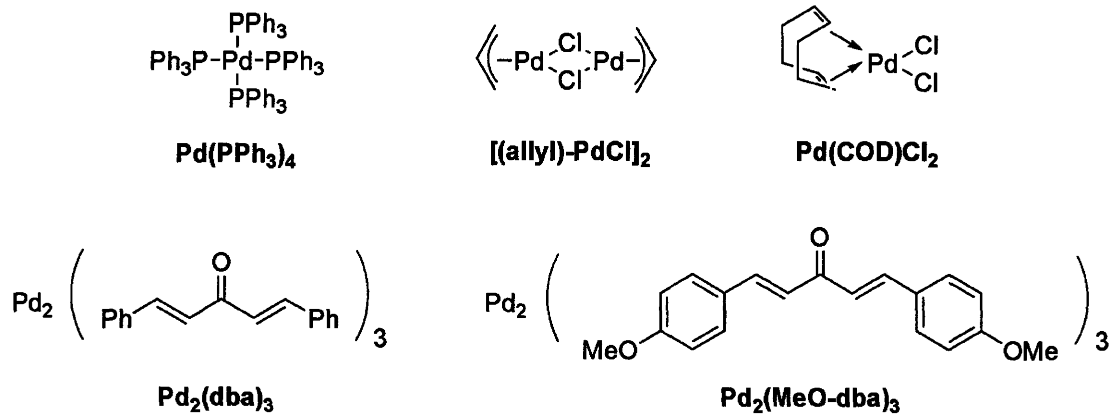


Figure 1.2. A selection of palladium sources tested during optimization.

The dba ligand has been implicated as a 'non-innocent' species in a number of cross-coupling reactions.[31] Fairlamb has subsequently demonstrated that electronic tuning of dba-derivatives and their corresponding palladium complexes can have profound effects in a variety of palladium-mediated coupling reactions.[32] In particular, it was observed that electron-rich variants of dba, such as MeO-dba, offered increased reaction rates. This is attributed to such variants being less tightly-bound (in the Pd(0) state) and generating a more active catalyst (Figure 1.3). As shown in Table 1.1, the complex $Pd_2(MeO\text{-}dba)_3$ indeed provided a significant improvement over $Pd_2(dba)_3$, both in terms of yield and suppression of β-hydride elimination (vide infra). Attempts to synthesize and test the even more electron-rich (and undocumented) $Pd_2(Me_2N\text{-}dba)_3$ complex were, however, unsuccessful.

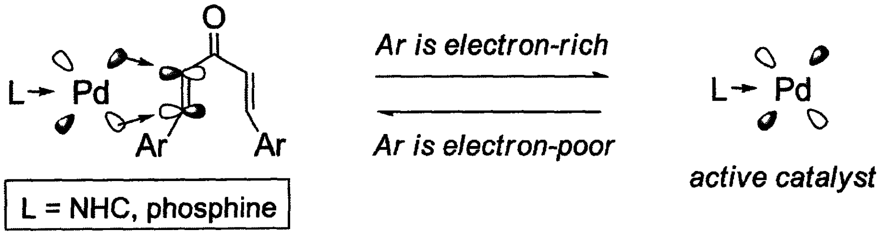


Figure 1.3. Control of active catalyst generation as a function of Ar.

For the purposes of screening, an alternative setup involved the use of $Pd_2(dba)_3$ and addition of a variety of dba variants. The precise effect and trends from this study remain unclear, due in part to reproducibility issues. Addition of the more electron-poor ligand CF_3-dba appears to have little effect, while the addition of Me_2N-dba suggests that it is even more effective than MeO-dba. However, Me_2N-dba is relatively unstable[33] and was considered less reliable than MeO-dba as a standard for optimization.

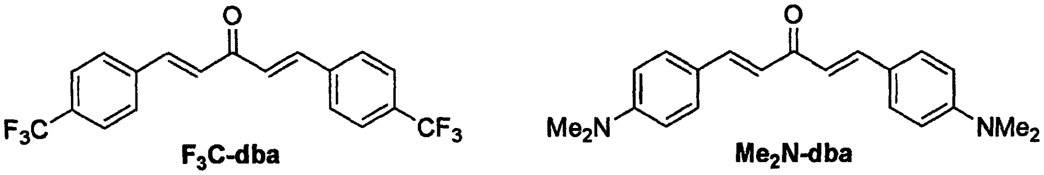


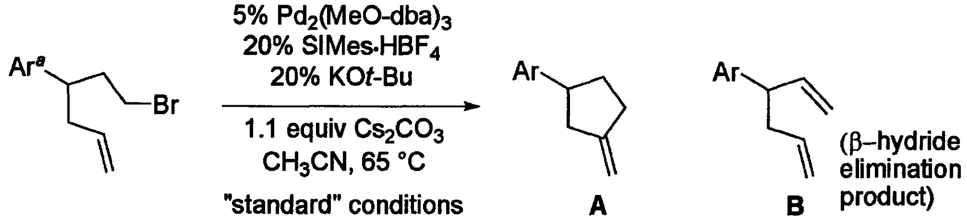
Figure 1.4. Electron-poor and electron-rich variants of dba.

Discernible trends with relation to other reaction parameters were also possible (Table 1.2). While the moderately strong Brønsted base Cs_2CO_3 proved optimal for the alkyl bromides, somewhat stronger bases such as KO*t*-Bu (entry 4) provided almost quantitative elimination. Weaker bases such as K_2CO_3 (entry 2) suffered from inefficient conversion, and were unpredictable in their ability to suppress β-hydride elimination. The use of amine bases (entries 5, 6) generally gave low conversion, and, upon moving to stronger amine bases such as DBU, quantitative elimination was once again observed.

CH_3CN and NMP emerged as the most successful solvents for this reaction. More polar solvents such as DMSO gave large quantities of elimination and isomerization. Less polar solvents such as toluene resulted in lower conversions.

The reaction is sluggish at room temperature, and moreover shows no favorable divergence between the levels of product and elimination. A similar trend was observed in attempting to lower the catalyst loading.

Table 1.2. Variation of the base and other parameters.



entry	variation of base	yield of **A** (%)[b]	yield of **B** (%)[b]	SM[b]
1	none	80	6	< 2
2	K_2CO_3	12	7	65
3	K_3PO_4	37	8	34
4	KO*t*-Bu	< 2	82	< 2
5	NCy_2Me	18	3	68
6	DBU	< 2	77	< 2
7	NMP as solvent	46	15	3
8	room temperature	5	1	83

[a] Ar = *p*-anisyl. [b] Determined through analysis by gas chromatography versus a calibrated internal standard (average of two experiments).

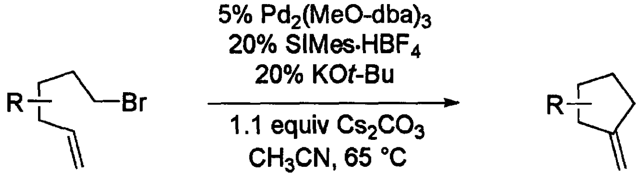
1.3. Substrate Scope and Limitations.

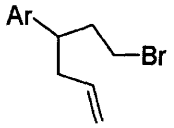
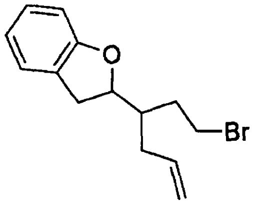
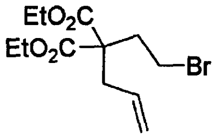
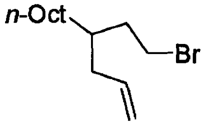
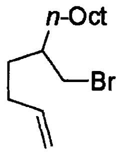
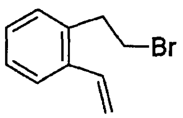
These optimized reaction conditions were shown to be applicable to several classes of substrate (Table 1.3). Unactivated alkyl bromides possessing a variety of aromatic (entries 1-4), heteroaromatic (entry 5), and alkyl (entries 7, 8) substituents were all shown to proceed with comparable yield. Encouragingly, increasing the steric bulk near the electrophilic site (entry 8) still resulted in respectable yields of the desired product (and notable control over β-hydride elimination), although longer reaction times were required. Finally, construction of indenes from styrenyl substrates is also possible with this method (entry 9).

After an appropriate change to the reaction conditions, we were delighted to find that a representative array of unactivated alkyl *chlorides* were also viable substrates for this reaction (Table 1.4). Of particular note is the apparent stability of the hindered electrophile in entry 4 and (by association) its intermediates toward elimination, even at 100 °C.

Despite these successes, the method still suffers from considerable limitations. The olefin acceptor must be terminal and monosubstituted, and attempts to introduce (E)-styrenyl acceptor **8a** furnished little product. Information on acrylate acceptor **8b** (up to 52 %) is more difficult to interpret, as our group has previously reported a metal-free, Heck-type cyclization of such substrates, catalyzed by a free carbene (SIMes itself displays notable reactivity in this system).[34] The degree of contribution from this pathway as opposed to the metal-mediated, 'true Heck' system is unclear. Given this uncertainty, acrylate substrates were not pursued further.

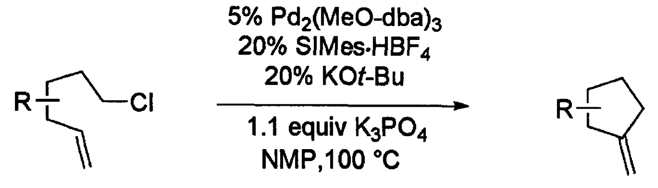
Table 1.3. Alkyl Heck reactions of unactivated alkyl bromides.

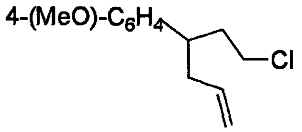
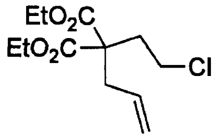
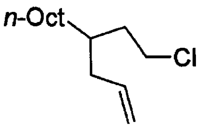
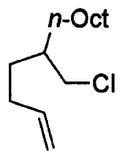


entry	substrate	yield (%)[a]
1	Ar = Ph 	73
2	2-napthyl	78
3	4-(MeO)-C_6H_4	82
4	4-(F_3C)-C_6H_4	79
5		83
6		85
7		75
8		73
9		71 (81)[b]

[a] Isolated yield (average of two experiments). [b] Base used: K_3PO_4. The value in parentheses is the yield according to GC analysis versus a calibrated internal standard (the product is slightly volatile).

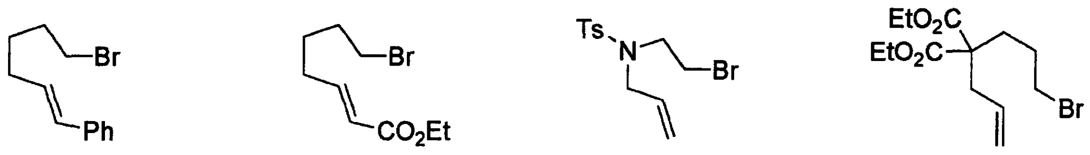
Table 1.4. Alkyl Heck reactions of unactivated alkyl chlorides.



entry	substrate	yield (%)[a]
1		72
2		80
3		71
4		66

[a] Isolated yield (average of two experiments).

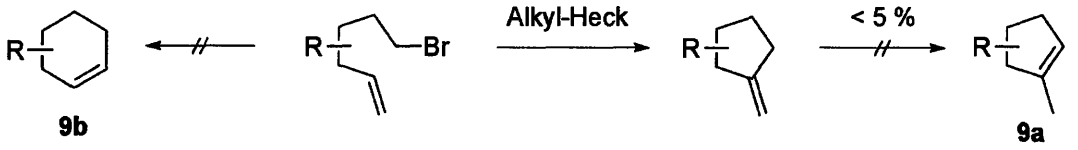
Disappointingly, extending the chain length in the hope of gaining access to six-membered rings was not successful, with **8d** giving < 30 % of desired cyclized product and competitive levels of β-hydride elimination. Heteroallylic substrates (e.g., **8c**) were not tolerated in the reaction, although the chief complication in this case appears to be a rapid deallylation pathway, as opposed to any inherent reluctance to undergo the reaction. Perhaps not surprisingly, secondary alkyl halides are not viable substrates for this system.



8a; < 10 **8b**; [52] **8c**; < 5 **8d** < 30

Figure 1.5. Substrate-based limitations to the system.

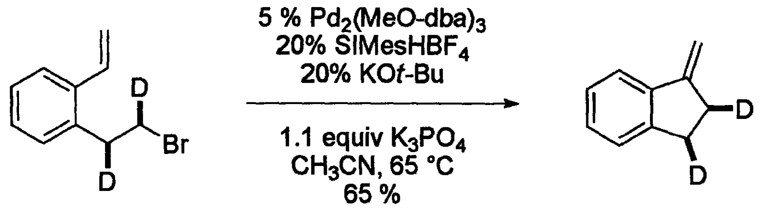
As mentioned above, isomerization from the exocyclic olefin to internal olefin **9a** was typically observed in only small quantities (< 5%). It should also be noted that, for the substrates tested, there were no appreciable levels of 6-*endo*-cyclization to form six-membered rings such as **9b**.



Scheme 1.7. Formation of isomers in the alkyl Heck reaction.

1.4. Deuterium Labeling Experiment – Evidence for a Non-Radical Pathway.

In order to further distinguish our system from previous procedures,[21-23, 35] we sought to determine whether radical species might be intermediates along the reaction pathway. Following the strategy of Whitesides,[36] the diasteromerically pure, deuterium-labeled styrene **10** was prepared and tested (eq 1.6). Under the associated conditions, only diastereomer **11** was obtained after isolation, suggesting that the reaction is stereospecific[37] and involves inversion at the C-Br stereocenter. This observation is evidence against the presence of radical intermediates; moreover, it is consistent with earlier studies on the nature of the oxidative addition of alkyl halides to bis(trialkylphosphine)palladium complexes.[14]



10; one diastereomer

11; one diastereomer

(1.6)

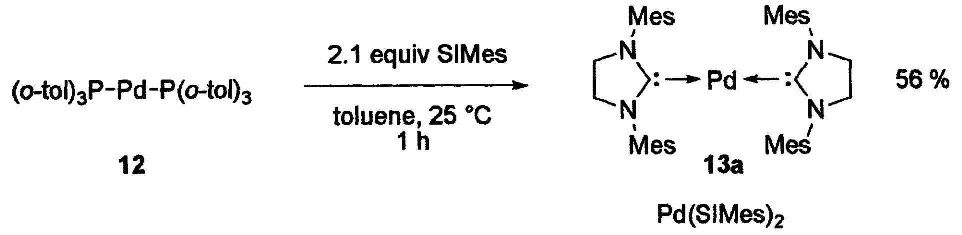
In summary, a catalyst system composed of $Pd_2(MeO\text{-}dba)_3$ and $SIMes{\cdot}HBF_4$ is capable of effecting intramolecular Heck cyclization for a number of alkyl bromides and chlorides in good yields. Deuterium-labeling experiments suggest that the reaction proceeds through a non-radical pathway and that inversion at the C-Br center takes place.

Chapter 2

Mechanistic Studies on Intramolecular Heck Reactions of Unactivated Alkyl Halides

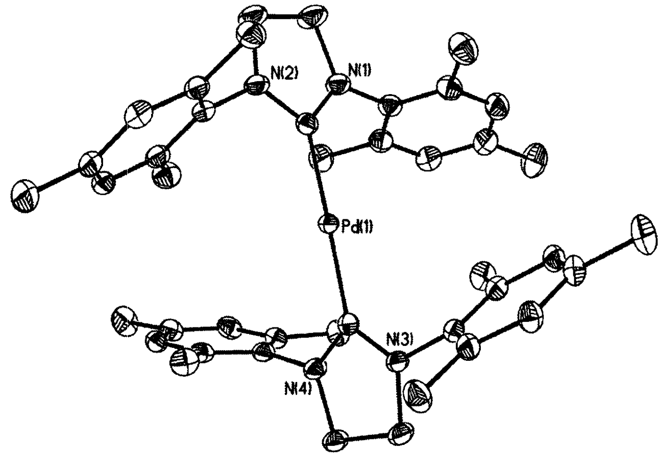
2.1. Synthesis of $Pd(SIMes)_2$.

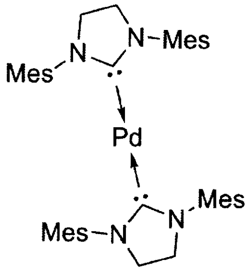
As described in Scheme 1.6, the working model for the alkyl Heck cycle was based upon (i) the analogous cycle for sp^2-hybridized compounds (ii) the demands of the cross-coupling cycle for alkyl electrophiles. Consistent with earlier studies described above,[14] our initial postulate for the active catalytic species was a biscarbene complex, $Pd(SIMes)_2$ (**13a**).[38] A variety of biscarbene complexes of palladium[39] and other metals[40] have been prepared in literature, and they have demonstrated notable activity in catalytic cross-coupling reactions. The synthesis of **13a** was adapted from a procedure by Herrmann,[41] giving the desired product in modest yield (eq 2.1).



(2.1)

Characterization by X-ray analysis confirms the structure of this novel complex (Figure 2.1) and reveals an appreciably non-linear C-Pd-C bond angle of 173.5°. By contrast, the corresponding angle for the related compound $Pd(IMes)_2$ is 178.8°.[42] The origins – and consequences – of this deviation are not clear.



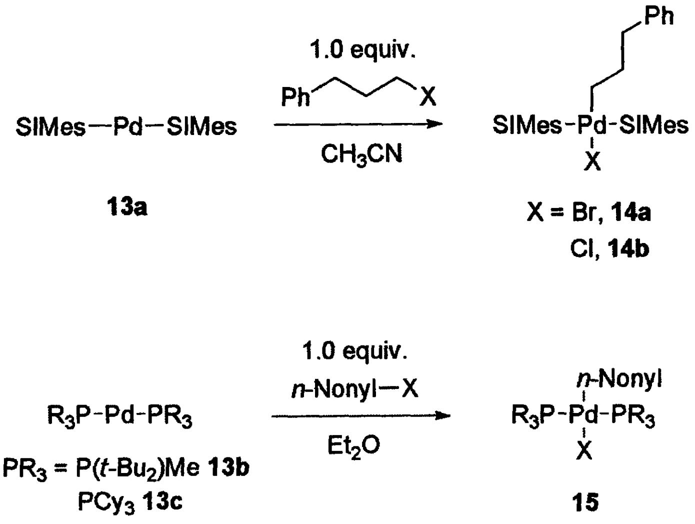


13a

Figure 2.1. X-ray crystal structure of **13a**.

2.2 Reactivity of Pd(SIMes)$_2$ and Derivatives.

Subsequent treatment of **13a** with a variety of alkyl halides revealed an extremely rapid rate of oxidative addition. Side-by-side comparison of simple alkyl bromides, chlorides and tosylates suggested that all were consumed at room temperature within 1 h, to cleanly provide the oxidative addition adducts (Figure 2.2). In particular, the consumption of alkyl bromides is virtually instantaneous, with the reaction complete in less than one minute. These results can be compared to related studies for bisphosphinepalladium complexes **13b** and **13c**,[14] in which oxidative addition of alkyl bromides is a somewhat slower process, and reaction with alkyl chlorides and tosylates required longer reaction times at elevated temperatures.



X	$t_{1/2}$
Br	< 1 min at 20 °C
OTs	10 min at 20 °C
Cl	10 min at 20 °C
F	No reaction

X	$t_{1/2}$
OTs	10.4 h at 40 °C
Cl	2 d at 60 °C
Ph(CH$_2$)$_3$Br	~2 h at 0 °C

Figure 2.2. Comparison of oxidative addition rates for bis-ligated palladium complexes.

Compounds **14a** and **14b** were characterized by X-ray crystallography (Figure 2.3). While Cavell has reported a related complex **16** in which a methyl group is bound to the metal center,[43] it is believed that these structures are the first examples of alkyl(biscarbene)halide complexes in which the alkyl group contains freely accessible β hydrogen atoms.

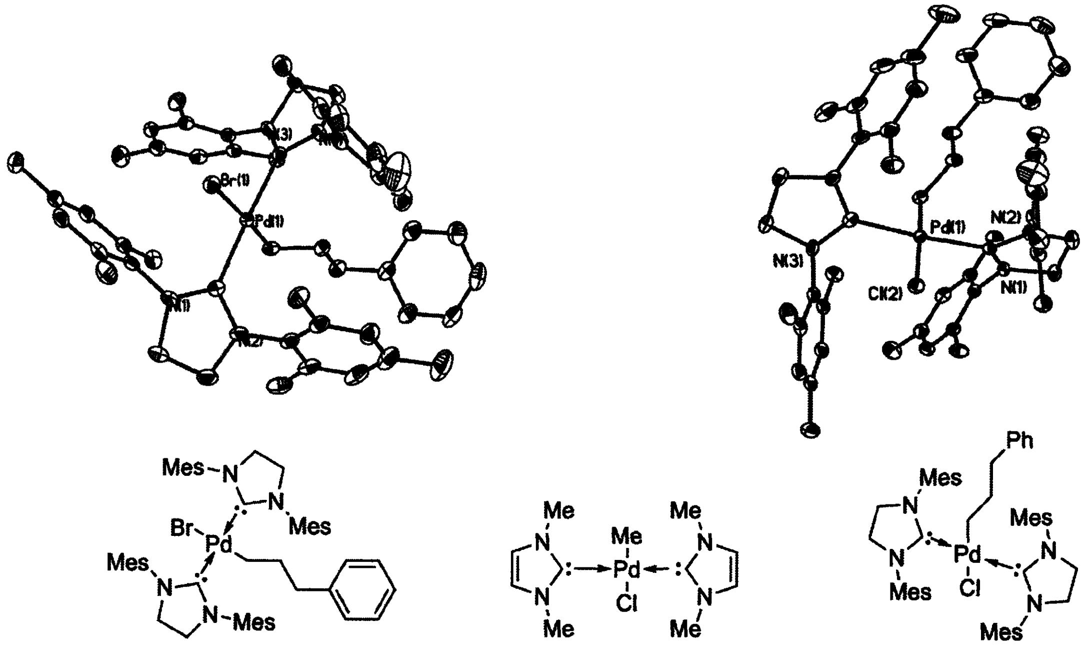
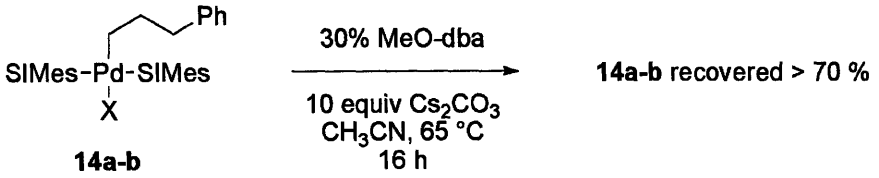


Figure 2.3. X-ray structures for **14a** and **14b**.

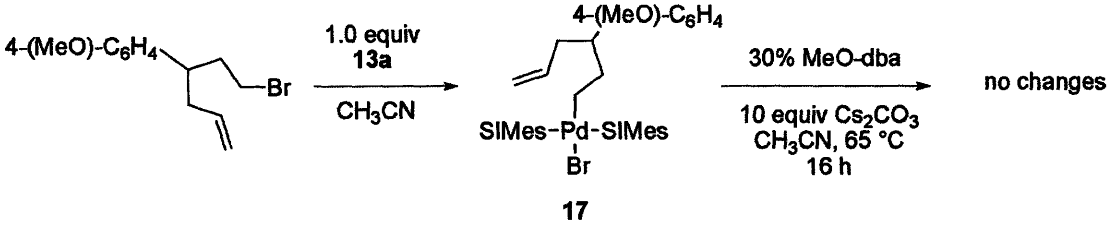
Further contrast with earlier studies could be found in the reactivity profiles of the respective oxidative addition adducts. Whereas complexes such as **15** undergo appreciable levels of β-hydride elimination after several hours, the corresponding adducts **14a-b** are extremely unreactive, showing no detectable proclivity for β-hydride elimination at either ambient or elevated temperatures. Prolonged heating, even under the simulated reaction conditions, evinced no significant changes, and the alkylpalladium complex was recovered in high yields (eq 2.2).



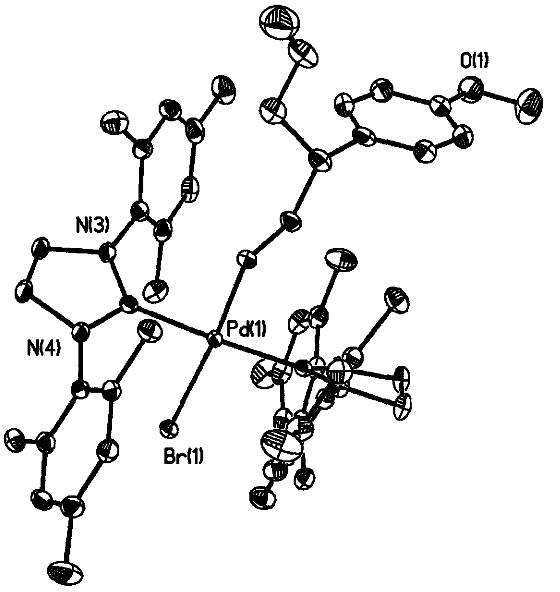
(2.2)

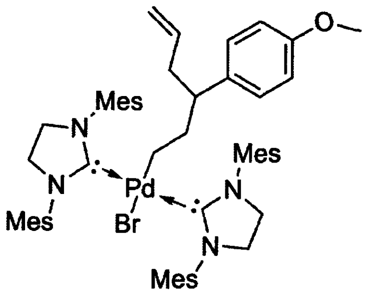
Miscellaneous reactions included (i) unsuccessful attempts to displace SIMes ligands from the complex using trialkylphosphines, and (ii) treatment with an alkylzinc halide, giving slow conversion to an unidentified mixture of products.

Oxidative addition adduct **17**, a working substrate for Heck cyclizations, was then procured and characterized by X-ray crystallography (Figure 2.4). Disappointingly, this adduct was also unreactive (Scheme 2.1), and showed no evidence of β-hydride elimination or cyclization under the simulated reaction conditions. This observation is consistent with the observation by Cavell that complex **15** was resistant to insertion into an unfunctionalized olefin.[43] Moreover, analysis of the crystal structure for **17** showed no special interaction between the olefin and the metal center.



Scheme 2.1. Synthesis and reactivity of **17**.



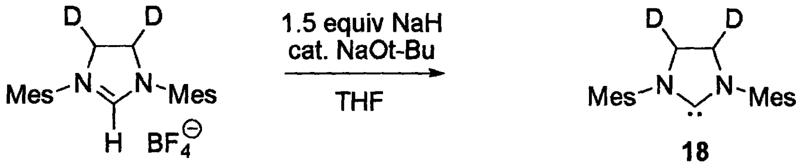


17

Figure 2.4. X-ray structure for **17**.

The accrued data suggest that these alkyl(biscarbene)palladium intermediates, while unprecedented, play no productive role in the catalytic cycle of interest.

Further studies on **13a**, however, furnished important information. While treatment of the complex with deuterated free SIMes **18** suggests that no self-exchange occurs (eq 2.4), the SIMes ligands are rapidly displaced from **13a** by P(*t*-Bu)$_2$Me (eq 2.3), consistent with related observations from Hermann[44] and Cloke.[45] One explanation for these results is that ligand exchange must occur via an associative mechanism (Scheme 2.2), in which approach of a third SIMes ligand is disfavoured on steric grounds. However, approach of P(*t*-Bu)$_2$Me (while still acknowledged as a sterically demanding ligand) appears to be possible. Calculations by Nolan,[46] it should be noted, imply that such bulky trialkylphosphines can be more sterically demanding than NHCs, and so this rationale may be over-simplistic.

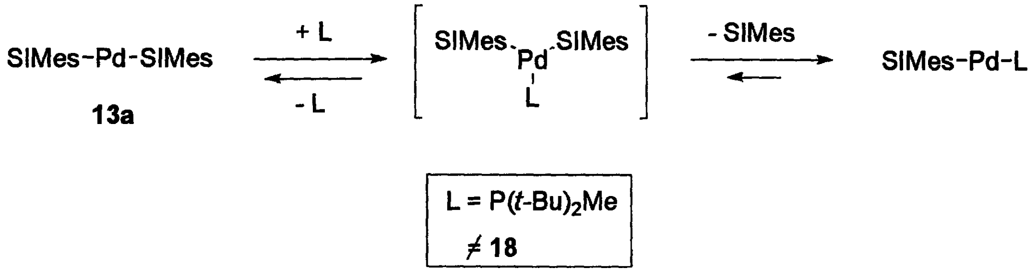


(2.3)

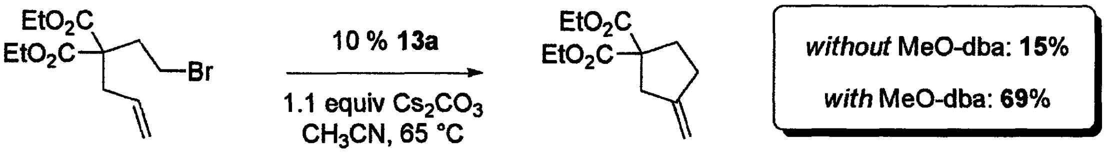
$$\underset{\textbf{13a}}{\text{SIMes-Pd-SIMes}} \xrightarrow[\text{CH}_3\text{CN}]{\text{2.0 equiv } \textbf{18}} \text{no exchange by } {}^2\text{H NMR} \qquad (2.4)$$

$$\underset{\textbf{13a}}{\text{SIMes-Pd-SIMes}} \xrightarrow[\text{CH}_3\text{CN, 5 min}]{\text{1.0 equiv P}(t\text{-Bu})_2\text{Me}} \underset{30\%}{\text{Me}(t\text{-Bu})_2\text{P-Pd-P}(t\text{-Bu})_2\text{Me}} \qquad (2.5)$$

The conclusion that the SIMes ligands on Pd(SIMes)$_2$ are apparently labile under the appropriate conditions led us to test the catalytic competence of this intermediate. As shown in Scheme 2.3, the reaction performed poorly when using only **13a** as the 'catalyst'. This is consistent with the observations above, which suggest that mixing of the substrate and **13a** will lead primarily to an inactive adduct. However, pre-stirring of Pd(SIMes)$_2$ with MeO-dba, followed by addition of the substrate, gave the desired product in yields comparable to the standard reaction conditions.



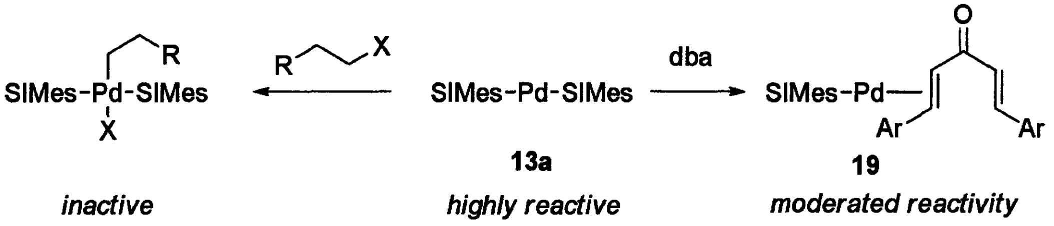
Scheme 2.2. Associative mechanism to rationalize exchange at **13a**.



without MeO-dba: **15%**
with MeO-dba: **69%**

Scheme 2.3. Importance of dba derivatives on catalytic efficiency.

This result emphasizes the importance of the dba derivatives in the reaction and raises the possibility that they are present in the structure of the 'true' active catalyst, e.g., **19**, with dba serving to temper the extremely reactive properties of $Pd(SIMes)_2$ (Scheme 2.4). Although no success was achieved in isolating such intermediates, it should be noted that Pd(NHC)-type species bound to electron-deficient, dba-like olefins (Figure 2.5) have been prepared and isolated, and even employed as catalysts in cross-coupling chemistry.[47,48]



Scheme 2.4. Moderation of the highly reactive complex **13a**.

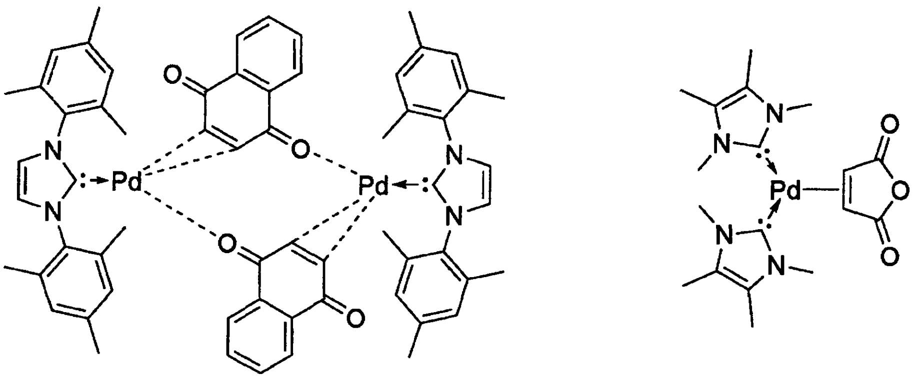
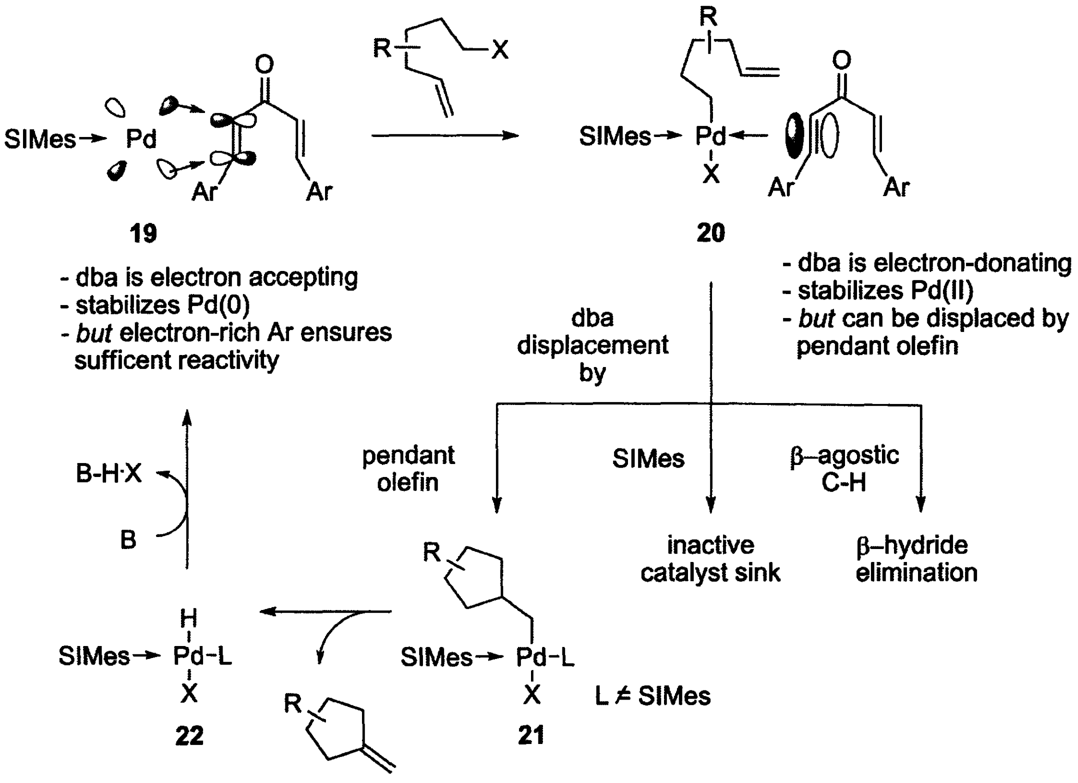


Figure 2.5. Examples of Pd(NHC)(olefin) complexes.

2.3. Conclusion.

In summary, these mechanistic studies reveal that, while (bisphosphine)palladium and alkyl(bisphosphine)palladium complexes may be catalytically competent intermediates for alkyl-alkyl cross-coupling chemistry,[8e] the analogous carbene species do not play such a direct role. Instead, the active catalytic species is more likely a mixed ligand complex, incorporating the strong σ-donating properties of the NHC with more σ-donating/π-accepting nature of the dba species. This dual property, and its potential consequences, can be assessed in the context of a postulated catalytic cycle (Scheme 2.5). Here, the role of dba would be to stabilize the electron-rich Pd(0) (**19**) through π-back donation, yet render it sufficiently active to undergo oxidative addition to form **20**. At this stage, the dba ligand can now stabilize the Pd(II) center by σ-donation. Moreover, the ligand must be tuned such that it is primarily displaced by the pendant olefin, which leads to the next productive step (**21**). Interception by SIMes leads to an inactive complex much like **17** (and may explain the high catalyst loading required). Interception by a β C-H bond results in β-hydride elimination. While the remaining steps **21-19** are more difficult to rationalize, it is reasonable to suggest that only one SIMes ligand should be coordinated at any one time.



- dba is electron accepting
- stabilizes Pd(0)
- *but* electron-rich Ar ensures sufficent reactivity

- dba is electron-donating
- stabilizes Pd(II)
- *but* can be displaced by pendant olefin

Scheme 2.5. Postulated catalytic cycle for the alkyl-Heck reaction.

It is strongly recommended that, in any attempt to broaden the scope of the alkyl-Heck reaction along these lines, due attention be paid to the correct combination of both NHC and dba ligand.

Appendix A

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Appendix B

Experimental

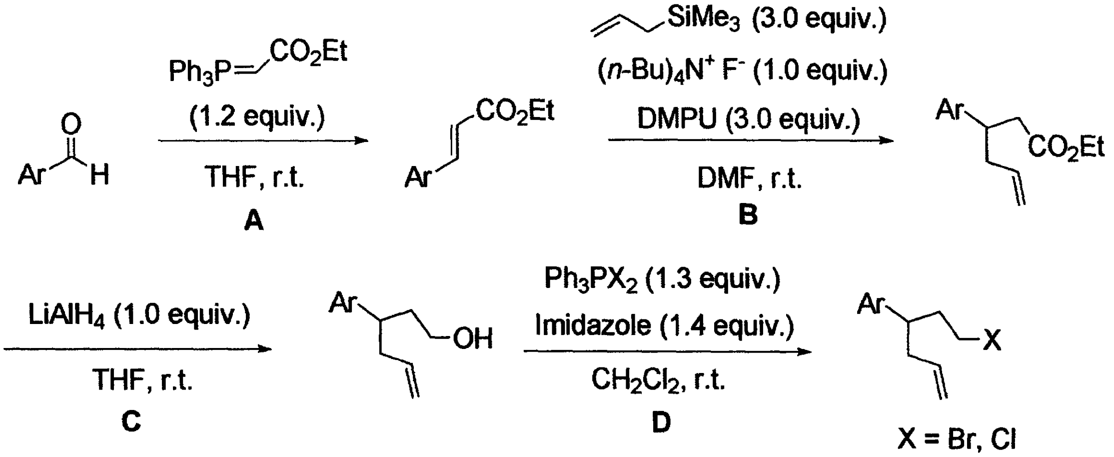
I. General

^1H and ^{13}C nuclear magnetic resonance spectra were recorded on a Varian Unity 300 NMR spectrometer or Varian VXR-500 NMR spectrometer at ambient temperature, except where indicated otherwise. ^2H nuclear magnetic resonance spectra were recorded on a Varian VXR-500 NMR spectrometer at ambient temperature, except where indicated otherwise. ^1H data are reported as follows: chemical shift in parts per million downfield from tetramethylsilane (δ scale), multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dddd = doublet of doublet of doublet of doublets, m = multiplet), integration, and coupling constant (Hz). All ^{13}C spectra were determined with complete proton decoupling.

All reactions were carried out under an atmosphere of nitrogen or argon in oven-dried glassware with magnetic stirring, unless otherwise indicated. THF, Toluene and CH_2Cl_2 were purified by passage through a neutral column. All other solvents were used as received: CH_3CN (Fluka; Sure/Seal), NMP (Fluka; Sure/Seal), DMF (Fluka; Sure/Seal), DMPU (Fluka; Sure/Seal). All other reagents were used as received. $Pd[P(o\text{-}tol)_3]_2$ was prepared following the procedure of Hartwig.[1]

II: Preparation of starting materials

Substrates for Entries **1** – **5** of Table 2 and Entry **1** of Table 3 were typically prepared according to Scheme 1:



Scheme 1.

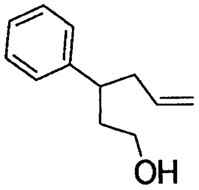
Step A: An oven-dried 250 mL round-bottomed flask was charged with (Ethoxycarbonylmethylene)triphenylphosphorane (12.5 g, 36 mmol, 1.2 equiv.), and purged with argon for 5 min. THF (30 mL) was added, followed by dropwise addition of the aldehyde (30 mmol) in 10 mL THF. The mixture was stirred for 3 – 16 h with monitoring by TLC. Once the reaction was complete, 15.0 g SiO_2 was added and the reaction stirred for 5 min, then concentrated to a dry solid (care! fine powder). The solid was placed atop a column (SiO_2) and eluted with hexanes/Et_2O to furnish the desired product.

Step B: Using a procedure modified from that of Majetich,[2] tetra-*n*-butylammonium fluoride (1.31 g, 5.0 mmol, 1.0 equiv.) was dried *in vacuo* in an oven-dried 50 mL round-bottomed flask for 2 h, then taken up in 3.0 mL dry DMF and transferred by canula to an oven-dried 100 mL round-bottomed flask containing 1.0 g activated 4Å molecular sieves, and stirred for a further 30 min. The ester substrate obtained from step **A** (5.0 mmol) dissolved in 3.0 mL dry DMF was then added, followed by dropwise addition (over 30 min) of a mixture of allyltrimethylsilane (1.71 g, 2.38 mL, 15.0 mmol, 3.0 equiv.) and DMPU (1.92 g, 1.8 mL, 15.0 mmol, 3.0 equiv.) in 3.0 mL dry DMF. After stirring for a further 30 min, the reaction mixture was quenched by addition of 15 mL MeOH, then poured over celite pad, washing with Et_2O (30 mL). To the filtrate was added 100 mL H_2O, and the layers allowed to separate. The aqueous portion was extracted with a further 2 x 30 mL Et_2O, then organic layers combined, wshed with 100 mL H_2O, 50 mL brine, dried (MgSO4), filtered and concentrated to a dark orange oil. The residue was purified by column chromatography (SiO_2, hexanes/Et_2O) to give a mixture of inseparable regioisomers as shown in Figure 1 (with the exceptoion of the precursor for Entry 3), that were submitted to step **C** without further purification.

Figure 1. The mixture of regioisomers from Step **B**.

Step C: The mixture of esters obtained from step **B** was dissolved in 15 mL dry THF, then treated with $LiAlH_4$ (1.0 M soln in Et_2O, 5.0 mL, 5.0 mmol). The reaction mixture was stirred under Argon for 1 h, then quenched by the careful, dropwise addition of (1.0 mL) sat. aq. sodium potassium tartrate (Rochelle's salt). 50 mL Et_2O was then added, followed by a further 50 mL sat. aq. sodium potassium tartrate. The mixture was stirred for 3 h, at which point the layers were allowed to separate. The Et_2O layer was washed with 50 mL brine, dried (MgSO4), filtered and concentrated to a clear residue. Purification by column chromatography (SiO_2, hexanes/Et_2O) successfully separated the regioisomeric alcohol products in each case.

Step D: Triphenylphosphine dihalide (2.6 mmol, 1.3 equiv.) and imidazole (2.8 mmol, 1.4 equiv.) were charged to an oven-dried 100 mL round-bottomed flask and purged with argon for 5 min. 15 mL dry CH_2Cl_2 was added, and the mixture lowered to 0 °C in an ice bath. A solution of the alcohol obtained from step **C** (2.0 mmol) in 10 mL CH_2Cl_2 was added dropwise over 10 min, then the ice bath was removed and the reaction stirred for 3 h. After the reaction was complete by TLC, 1.0 g SiO_2 was added directly to the mixture and stirred for 5 min (mixture may turn orange at this point). After removal of the stir bar, the mixture was concentrated to a dry solid (care! fine powder), then placed atop a pre-packed column (SiO_2) and eluted with hexanes/Et_2O to furnish the desired product.



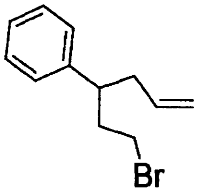
3-Phenylhex-5-en-1-ol [*75834-24-1*] Prepared according to steps **B** and **C** of Scheme 1 from (E)-ethyl cinnamate. Chromatography (7:1 hexanes/ Et_2O) gave 370 mg desired product (42% over two steps) as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.33-7.16 (m, 5H), 5.74-5.59 (m, 1H), 5.01-4.91 (m, 2H), 3.59-3.19 (m, 2H), 2.86-2.74 (m, 1H), 2.41-2.33 (m, 2H), 2.06-1.93 (m, 1H), 1.88-1.72 (m, 1H), 1.19 (bs, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 144.7, 137.0, 128.7, 127.9, 126.6, 116.4, 61.3, 42.5, 41.6, 38.8;

IR (film) 3335, 3076, 3028, 2929, 1640, 1603, 1494, 1453, 1440, 1362, 1047, 1028, 995, 700 cm^{-1};

GCMS (EI) calcd for $C_{12}H_{16}O$ 176 $[M]^+$, found 176, 158 $[M - H_2O]^+$.



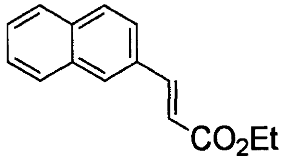
(1-Bromohex-5-en-3-yl)benzene; Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave 428 mg product (85 %) as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.38-7.15 (m, 5H), 5.72-5.59 (m, 1H), 5.02-4.90 (m, 1H), 3.34-3.26 (m, 1H), 3.15-3.05 (m, 1H), 2.93-2.82 (m, 1H), 2.47-2.31 (m, 2H), 2.29-2.17 (m, 1H), 2.15-2.02 (m, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.5, 128.8, 127.9, 126.8, 116.8, 44.2, 41.1, 38.9, 32.2;

IR (film) 2918, 1640, 1494, 1453, 1252, 915, 762, 700 cm^{-1};

GCMS (EI) calcd for $C_{12}H_{15}Br$ 238/240 (1:1) $[M]^+$, found 238/240 (1:1).

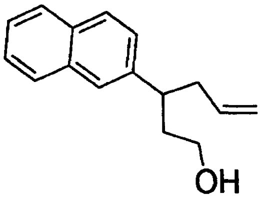


(E)-Ethyl 3-(naphthalen-2-yl)acrylate [*19661-27-27-9, 114833-06-6*] Prepared according to Step **A** in Scheme 1. Chromatography (15:1 hexanes/ Et_2O) gave 6.30 g desired product (93%) as a crystalline white solid.

mp 65 - 66 °C;

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.95 (s, 1H), 7.89-7.82 (m, 2H), 7.84 (d, J = 15.8 Hz, 1H), 7.68 (dd, J = 8.5 Hz, 1.6 Hz, 1H), 7.55-7.50 (m, 2H), 6.57 (d, J = 15.8 Hz, 1H), 4.60 (q, J = 7.1 Hz, 2H), 1.37 (t, J = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.3, 144.9, 134.4, 133.5, 132.2, 130.2, 128.9, 128.8, 128.0, 127.5, 126.9, 123.7, 118.6, 60.8, 14.6.

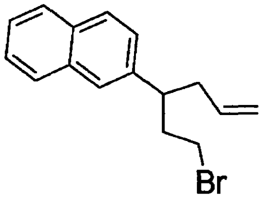


3-(Naphthalen-2-yl)hex-5-en-1-ol Prepared according to steps **B** and **C** of Scheme 1. Chromatography (5:1 hexanes/Et_2O) gave 542 mg desired product (48% over two steps) as a clear oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.84-7.77 (m, 3H), 7.62 (s, 1H), 7.50-7.42 (m, 2H), 7.36 (dd, J = 8.5 Hz, 1.8 Hz, 1H), 5.70 (m, 1H), 5.04-4.92 (m, 2H), 3.62-3.55 (m, 1H), 3.53-3.46 (m, 1H), 3.03-2.96 (m, 1H), 2.49 (td, J = 7.1 Hz, 1.1 Hz, 2H), 2.12-2.05 (m, 1H), 1.97-1.89 (m, 1H), 1.16 (t, J = 5.2 Hz, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.3, 134.2, 133.0, 128.9, 128.3, 128.2, 127.0, 126.7, 126.4, 126.0, 117.0, 100.5, 61.7, 43.1, 42.0, 39.2;

IR (film) 3364, 3055, 2929, 2640, 1601, 1508, 1440, 1046, 913, 855, 819, 747 cm^{-1}.



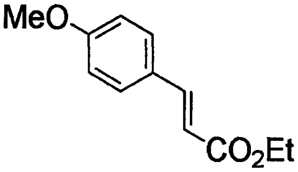
2-(1-Bromohex-5-en-3-yl)naphthalene Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave 607 mg product (88 %) as a clear oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.83-7.79 (m, 3H), 7.63 (d, J = 1.4 Hz, 1H), 7.50-7.43 (m, 2H), 7.33 (dd, J = 8.6 Hz, 1.6 Hz, 1H), 5.78-5.72 (m, 1H), 5.07-4.93 (m, 2H), 3.34-3.28 (m, 1H), 3.16-3.08 (m, 1H), 3.09-3.30 (m, 1H), 2.54-2.44 (m, 2H), 2.35-2.27 (m, 1H), 2.25-2.16 (m, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 140.8, 136.5, 133.7, 132.7, 128.6, 127.9, 127.8, 126.9, 126.3, 125.8, 125.7, 116.9, 44.4, 41.1, 38.9, 32.2;

IR (film) 3055, 2920, 1640, 1600, 1508, 1437, 1254, 911, 855, 819, 747 cm^{-1};

GCMS (EI) calcd for $C_{16}H_{17}Br$ 288/290 (1:1) $[M]^+$, found 288/290 (1:1).

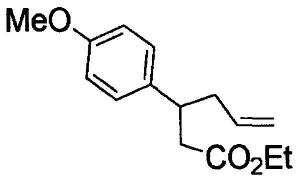


(E)-Ethyl 3-(4-methoxyphenyl)acrylate [*1929-30-2, 2493-56-4, 51507-22-3*] Prepared according to Step **A** in Scheme 1. Chromatography (15:1 hexanes/ Et_2O) gave 5.93 g desired product (96%) as a clear oil, which slowly crystallized to give a colorless solid.

mp 50 – 51 °C;

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.63 (d, *J* = 16.0 Hz, 1H), 7.50-7.44 (m, 2H), 6.92-6.88 (m, 2H), 6.31 (d, *J* = 16.0 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 167.6, 161.5, 144.5, 129.9, 127.4, 115.9, 114.5, 60.6, 55.6, 14.6.



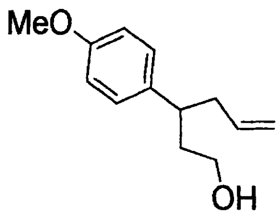
Ethyl 3-(4-methoxyphenyl)hex-5-enoate Prepared according to step **B** of Scheme 1. Chromatography (20:1 hexanes/ Et_2O) furnished 694 mg (56%) of the desired product.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.13-7.08 (m, 2H), 6.85-6.80 (m, 2H), 5.73-5.59 (m, 1H), 5.03-4.93 (m, 2H), 4.02 (dq, *J* = 7.2 Hz, 0.9 Hz, 2H), 3.78 (s, 3H), 3.22-3.11 (m, 1H), 2.64 (dd, *J* = 15.2 Hz, 6.6 Hz, 1H), 2.51 (dd, *J* = 15.2 Hz, 8.6 Hz), 2.36 (tt, *J* = 7.2 Hz, 1.2 Hz, 2H), 1.14 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 173.1, 158.8, 136.8, 136.3, 129.1, 117.5, 114.4, 60.9, 55.9, 41.8, 41.6, 41.5, 14.8;

IR (film) 3078, 2979, 2917, 1734, 1640, 1612, 1584, 1514, 1443, 1249, 1178 cm^{-1};

GCMS (EI) calcd for $C_{15}H_{20}O_3$ 248 $[M]^+$, found 248.



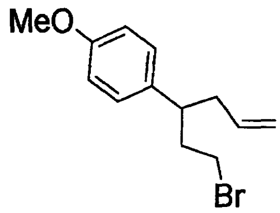
3-(4-Methoxyphenyl)hex-5-en-1-ol Prepared according to step **C** of Scheme 1. Chromatography was not required, and 577 mg desired product (95%) was obtained as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.11-7.07 (m, 2H), 6.87-6.82 (m, 2H), 5.72-5.59 (m, 1H), 5.01-4.91 (m, 2H), 3.78 (s, 3H), 3.61-3.39 (m, 2H), 2.35 (tt, *J* = 7.0 Hz, 1.2 Hz, 2H), 2.02-1.93 (m, 1H), 1.81-1.70 (m, 1H), 1.30 (t, *J* = 5.1 Hz, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.7, 137.5, 137.2, 129.2, 116.8, 114.5;

IR (film) 3363, 3074, 2920, 1640, 1611, 1584, 1513, 1442, 1248, 1178 1036 cm^{-1};

GCMS (EI) calcd for $C_{13}H_{18}O_2$ 206 $[M]^+$, found 206.



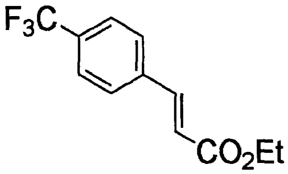
1-(1-Bromohex-5-en-3-yl)-4-methoxybenzene Prepared according to step **D** of Scheme 1. Chromatography (40:1 hexanes/Et_2O) gave 580 mg product (77 %) as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.09 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 8.6 Hz, 2H), 5.78-5.60 (m, 1H), 5.08-4.95 (m, 1H), 3.80 (s, 3H), 3.34-3.26 (m, 1H), 3.14-3.06 (m, 1H), 2.89-2.78 (m, 1H), 2.40-2.32 (m, 2H), 2.27-2.14 (m, 1H), 2.10-1.97 (m, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.4, 136.7, 135.3, 128.8, 116.6, 114.2, 55.5, 43.3, 41.3, 39.1, 32.4;

IR (film) 3079, 2918, 2835, 1640, 1611, 1583, 1513, 1441, 1247, 1178, 1038 cm^{-1};

GCMS (EI) calcd for $C_{13}H_{17}BrO$ 268/270 (1:1) $[M]^+$, found 268/270 (1:1).

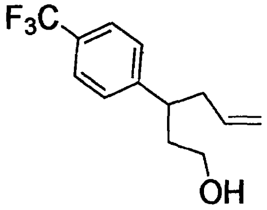


(*E*)-Ethyl 3-(4-(trifluoromethyl)phenyl)acrylate [*101466-85-7, 128408-03-7*] Prepared according to Step **A** in Scheme 1. Chromatography (20:1 hexanes/ Et_2O) gave 6.15 g desired product (84 %) as a crystalline white solid.

mp 36-37 °C;

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.69 (d, *J* = 16.1 Hz, 1H), 7.63 (s, 4H), 6.51 (d, *J* = 16.1 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.1, 143.4, 138.5, 132.4 (q, $J_{C\text{-}F}$ = 32.8 Hz), 128.8, 125.6 (q, *J* = 3.5 Hz), 129.2, 129.1, 125.7, 123.7, 123.5, 116.5, 116.3, 57.0, 56.9.



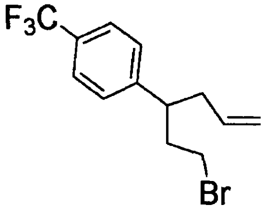
3-(4-(Trifluoromethyl)phenyl)hex-5-en-1-ol Prepared according to steps **B** and **C** of Scheme 1. Chromatography (5:1 hexanes/Et_2O) gave 512 mg desired product (42% over two steps) as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 6.51 (d, *J* = 16.1 Hz, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.1, 143.4, 138.5, 132.4 (q, $J_{C\text{-}F}$ = 32.8 Hz), 128.8, 125.6 (q, *J* = 3.5 Hz), 129.2, 129.1, 125.7, 123.7, 123.5, 116.5, 116.3, 57.0, 56.9;

IR (film) 3345, 3079, 2931, 1642, 1620, 1584, 1421, 327, 1123, 1070, 917, 840 cm^{-1};

GCMS (EI) calcd for $C_{13}H_{15}F_3O$ 244 [M]$^+$, found 226 [M-H_2O]$^+$.



1-(1-Bromohex-5-en-3-yl)-4-(trifluoromethyl)benzene Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave 509 mg product (79 %) as a clear oil.

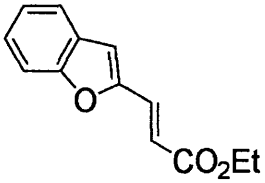
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 3.34-3.29 (m, 1H), 3.10-3.04 (m, 1H), 3.03-2.97 (m, 1H), 2.42 (t, *J* = 7.0 Hz, 1H), 2.31-2.23 (m, 1H), 2.14-2.06 (m, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 147.6, 135.8, 128.3, 125.8 (q, *J* = 3.8 Hz), 117.3, 44.0, 40.8, 38.6, 31.7;

^{19}F NMR ($CDCl_3$, 282 MHz) δ -63.0.

IR (film) 3079, 2919, 1642, 1619, 1439, 1421, 1327, 1165, 1125, 1069, 1018 cm^{-1};

GCMS (EI) calcd for $C_{13}H_{14}BrF_3$ 306/308 (1:1) [M]$^+$, found 306/308 (1:1).

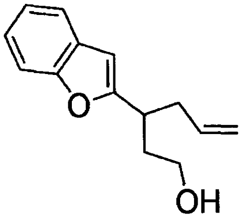


(E)-Ethyl 3-(benzofuran-2-yl)acrylate [41098-05-9, 125482-23-7] Prepared according to Step **A** in Scheme 1. Chromatography (10:1 hexanes/ Et_2O) gave 5.83 g desired product (90%) as a crystalline white solid.

mp 75 – 77 °C;

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.57 (m, 1H), 7.54 (dd, *J* = 15.6 Hz, 0.4 Hz, 1H), 7.46 (m, 1H), 7.35 (m, 1H,), 7.24 (m, 1H), 6.92 (s, 1H), 6.58 (dd, *J* = 15.6 Hz, 0.6 Hz, 1H), 4.28 (q, *J* = 7.1 Hz, 2H), 1.34 (t, *J* = 7.1 Hz, 3H);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 166.9, 155.8, 152.6, 131.5, 128.6, 126.6, 123.5, 122.0, 119.3, 111.6, 111.3, 60.9, 14.6.

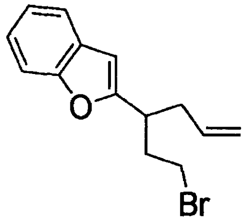


3-(Benzofuran-2-yl)hex-5-en-1-ol Prepared according to steps **B** and **C** of Scheme 1. Chromatography (5:1 hexanes/ Et$_2$O) gave 562 mg desired product (52 % over two steps) as a clear oil.

^{1}H NMR (CDCl$_3$, 500 MHz) δ 7.52-7.49 (m, 1H), 7.45-7.42 (m, 1H), 7.25-7.18 (m, 2H), 6.44 (s, 1H), 5.76 (dddd, *J* = 17.1 Hz, 10.2 Hz, 7.0 Hz, 7.0 Hz), 5.10-4.98 (m, 2H), 3.75-3.65 (m, 1H), 3.16-3.09 (dddd, *J* = 6.3 Hz, 6.3 Hz, 6.3 Hz, 8.0 Hz, 1H), 2.60-2.52 (m, 1H), 2.51-2.44 (m, 1H), 1.38 (bs, 1H);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 160.9, 154.8, 136.0, 128.8, 123.5, 122.7, 120.6, 117.1, 111.1, 102.8, 60.9, 38.5, 36.2, 36.1.

IR (film) 3363, 3076, 2932, 1642, 1584, 1455, 1253, 1045, 917, 801, 751 cm^{-1};



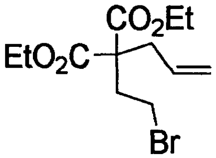
2-(1-Bromohex-5-en-3-yl)benzofuran Prepared according to step **D** of Scheme 1. Chromatography (30:1 hexanes/Et_2O) gave 726 mg product (82 %) as a clear oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.51 (d, J = 7.4 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.28-7.18 (m, 2H), 6.48 (s, 1H), 5.80-5.67 (m, 1H), 5.10-4.99 (m, 2H), 3.47-3.40 (m, 1H), 3.30-3.24 (m, 1H), 3.23-3.16 (m, 1H), 2.62-2.54 (m, 1H), 2.50-2.43 (m, 1H), 2.34-2.26 (m, 1H), 2.28-2.18 (m, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.4, 154.9, 135.6, 128.7, 123.7, 122.8, 120.7, 117.4, 111.2, 103.7, 38.1, 38.0, 36.1, 31.7;

IR (film) 3076, 2918, 1642, 1584, 1455, 1253, 916, 803, 751 cm^{-1};

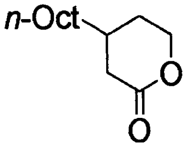
GCMS (EI) calcd for $C_{14}H_{15}BrO$ 278/280 (1:1) $[M]^+$, found 278/280 (1:1).



Diethyl 2-allyl-2-(2-bromoethyl)malonate [*174619-42-2*] An oven-dried 100 mL round-bottomed flask was charged with NaH (60% in mineral oil, 0.76 g, 31.5 mmol, 1.05 equiv.) and flushed with Ar for 3 min. Dry DMF (15 mL) was added, followed by dropwise addition of diethylallylmalonate (6.00 g, 30 mmol). After 0.5 h, H_2 evolution had ceased, and 1,2-dibromoethane (5.92 g, 31.5 mmol, 1.05 equiv.) was added over 10 min. The mixture was stirred overnight, then quenched with sat. aq. NH_4Cl (10 mL). The mixture was extracted with Et_2O (50 mL), then the organic layer washed with brine (30 mL), dried (MgSO4), filtered, and concentrated. The residue was purified by flash column chromatography (SiO_2, 20:1 hexanes/Et_2O) to provide 6.73 g (73%) of the desired product.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.70-5.59 (m, 1H), 5.17-5.11 (m, 2H), 4.23-4.17 (m, 4H), 3.36 (t, J = 8.3 Hz, 2H), 2.66 (d, J = 7.4 Hz, 2H), 2.44 (d, J = 8.3 Hz, 2H), 1.27 (t, J = 7.3 Hz, 6H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.5, 132.0, 120.0, 61.9, 57.7, 38.0, 36.4, 27.3, 14.3.



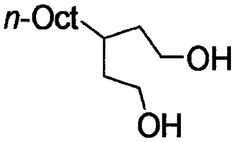
4-Octyltetrahydro-2*H*-pyran-2-one Using the procedure of Cahiez,[3] an oven-dried 100 mL round-bottomed flask was charged with CuCl (59 mg, 0.6 mmol, 0.03 equiv.), and flushed with Ar for 10 min. A solution of 5,6-dihydro-2H-pyran-2-one (1.96 g, 20 mmol) in 20 mL THF was added, followed by Me_3SiCl (3.1 mL, 2.59 g, 24 mmol, 1.2 equiv.). The reaction mixture was cooled to 0 °C in an ice bath and *n*-octylmanesium bromide (2.0 M in THF, 10.4 mL, 20.8 mmol, 1.04 equiv.) was added dropwise over 15 min. The dark purple solution was stirred for a further 1 h, then sat. aq. NH_4Cl (50 mL) was added. The mixture was extracted with 50 mL Et_2O, the organic layer washed with brine (30 mL), dried ($MgSO_4$), filtered and concentrated. The residue was purified by column chromatography (SiO_2, 4:1 hexanes/Et_2O) to provide 2.0 g (47%) of desired product.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.41 (ddd, J = 11.4 Hz, 4.9 Hz, 3.8 Hz, 1H), 4.26 (dt, J = 10.4 Hz, 3.6 Hz, 1H), 2.69 (ddd, J = 17.2 Hz, 5.7 Hz, 1.6 Hz, 1H), 2.14 (dd, J = 17.2 Hz, 10.1 Hz, 1H), 2.01-1.88 (m, 2H), 1.51 (ddt, *J* = 10.4 Hz, 10.8 Hz, 4.2 Hz, 1H), 1.40-1.18 (m, 14H), 0.88 (t, *J* = 7.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.3, 69.3, 37.3, 36.9, 32.5, 32.2, 30.3, 30.2, 29.9, 29.6, 27.1, 23.4, 14.8.

IR (film) 2923, 2854 1742, 1467, 1402, 1256, 1221, 1089, 1074 cm^{-1};

HRMS (ESI) calcd for $C_{13}H_{24}O_2$ 212 $[M]^+$, found

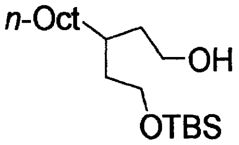


3-Octylpentane-1,5-diol A solution of the lactone (2.0 g, 9.7 mmol) in 10 mL THF was treated with $LiAlH_4$ (1.0 M in Et_2O, 10 mL, 1.0 equiv.) under Ar. After stirring for 6h, 50 mL Et_2O was then added, followed by dropwise addition of 10 mL solution of sodium potassium tartrate (Rochelle's Salt). After stirring overnight, the organic layer was washed with brine (50 mL), dried ($MgSO_4$), filtered and concentrated to give 2.0 g (99%) of the desired product.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.77-3.62 (m, 4H), 1.84 (bs, 2H), 1.66-1.56 (m, 1H), 1.63-1.47 (m, 4H), 1.34-1.18 (m, 14H), 0.92-0.84 (m, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.3, 36.8, 34.7, 32.1, 31.5, 30.3, 29.9, 29.6, 26.8, 22.9, 14.4.

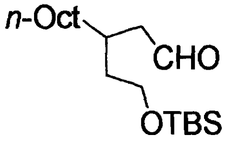
IR (film) 3341, 2923, 2854, 1466, 1378, 1056, 1015 cm^{-1}.



3-(2-(*tert*-Butyldimethylsilyloxy)ethyl)undecan-1-ol An oven-dried round-bottomed 100 mL flask was charged with NaH (60% in mineral oil, 372 mg, 9.3 mmol) and 10 mL THF under Ar. A solution of the diol in 10 mL THF was added slowly to mixture, then the reaction was cooled to 0 °C and stirred for 30 min. Under Ar, *tert*-butyldimethylsilyl chloride (TBSCl) was added in one portion and the reaction stirred a further 2 h at 0 °C. 50 mL H_2O and 30 mL Et_2O were added, and the layers separated. The aqueous layer was extracted with a further 3 x 30 mL Et_2O, the combined organic layers washed with brine, dried ($MgSO_4$), filtered and concentrated. Column chromatography (SiO_2, 3:1 hexanes/Et_2O) furnished an oil that was further purified by fractional distillation to give 1.75 g desired product (57%).

^1H NMR ($CDCl_3$, 500 MHz) δ 3.75-3.60 (m, 4H), 1.63-1.40 (m, 6H), 1.34-1.22 (m, 14H), 0.91-0.83 (m, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 61.0, 60.9, 36.7, 36.7, 34.8, 32.1, 31.3, 30.3, 29.9, 29.6, 26.8, 22.9, 14.4, -13.3.



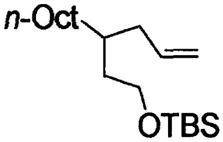
3-(2-(*tert*-Butyldimethylsilyloxy)ethyl)undecanal An oven-dried 100 mL round-bottomed flask was charged with pyridinium chlorochromate (1.60 g, 7.4 mmol, 1.4 equiv.) and flushed with Ar for 5 min. 10 mL CH_2Cl_2 was added, and the mixture cooled to 0 °C. A solution of the alcohol (1.75 g, 5.3 mmol) in 10 mL CH_2Cl_2 was added dropwise, and the reaction stirred a further 4 h. 50 mL Et_2O was then added, and the reaction stirred vigorously for 30 min. 5 g activated carbon was added, and the mixture was stirred for 10 min, then filtered over a pad celite. The pad was washed with 2 x 20 mL Et_2O, and the filtrate concentrated to an orange oil, which was purified by column chromatography (SiO_2, 20:1 hexanes/Et_2O) to give 1.60 g of desired product (95 %).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.76 (t, J = 2.4 Hz, 1H), 3.62 (t, J = 6.4 Hz, 2H), 2.41, (ddd, J = 16.3 Hz, 6.6 Hz, 2.3 Hz, 1H), 2.36, (ddd, J = 16.3 Hz, 6.6 Hz, 2.3 Hz, 1H), 2.13, (septet, J = 6.3 Hz, 1H), 1.61 (septet, J = 6.3 Hz, 1H), 1.48 (septet, J = 6.6 Hz, 1H), 1.38-1.20 (m, 14H), 0.89-0.86 (m, 3H), 0.87 (s, 9H), 0.05 (s, 6H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 203.7, 61.1, 48.8, 37.2, 34.6, 32.1, 30.2, 30.0, 29.8, 29.5, 26.9, 26.2, 22.9, 18.5, 14.4, -5.1, -13.3.

IR (film) 2927, 2856, 1728, 1471, 1256, 1101, 836, 775 cm^{-1};

GCMS (EI) calcd for $C_{19}H_{40}O_2Si$ 328 $[M]^+$, found 327 $[M-1]^+$.



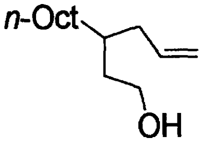
(3-Allylundecyloxy)(*tert*-butyl)dimethylsilane Methyl triphenylphosphonium bromide (2.06 g, 5.8 mmol, 1.05 equiv.) was charged to an oven-dried 100 mL round-bottomed flask, and purged with Ar for 5 min. 10 mL THF was added, followed by dropwise addition of *n*-BuLi (1.0 M in hexanes, 5.8 mL, 5.8 mmol). After 15 min stirring, a solution of the aldehyde (1.60g, 5.2 mmol) in 10 mL THF was added, and the mixture stirred for an additional 2 h at room temperature. The reaction was quenched by addition of 10 mL wet ether, and the mixture concentrated. The resultant residue was taken up in 20 mL CH_2Cl_2, 5g SiO_2 added, then the mixture re-concentrated to a fine orange powder. This was placed atop a pre-packed column (SiO_2) and eluted with 25:1 hexanes/Et_2O to give 1.2 g desired product (67 %).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.81-5.72 (m, 1H), 5.03-4.96 (m, 2H), 3.64 (td, *J* = 7.4 Hz, 1.3 Hz, 2H), 2.04 (t, *J* = 6.2 Hz, 2H), 1.56-1.47 (m, 1H), 1.49 (quintet, *J* = 7.3 Hz, 2H), 1.35-1.20 (m, 14H), 0.91-0.85 (s, 9H), 0.91-0.83 (m, 3H) 0.05 (s, 6H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.5, 116.0, 61.6, 38.4, 36.8, 34.3, 33.7, 32.2, 30.2, 29.9, 29.6, 26.8, 26.2, 22.9, 18.6, 14.4, -5.0, -13.3;

IR (film) 3079, 2979, 2928, 1921, 1642, 1619, 1439, 1421, 1327, 1165, 1125 cm^{-1};

GCMS (EI) calcd for $C_{20}H_{42}OSi$ 327 $[M]^+$, found 327.



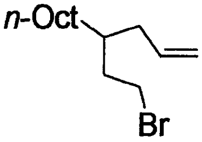
3-Allylundecan-1-ol A solution of the TBS-protected alcohol (1.0 g, 3.1 mmol) in 5 mL THF was treated with tetra-*n*-butylammonium fluoride (1.0 M in THF, 3.7 mL, 3.7 mmol, 1.2 equiv.). The reaction was stirred for 1 h at room temperature, then concentrated to a residue and dissolved in 20 mL CH_2Cl_2, washed successively with sat. aq. NH_4Cl (20 mL), H_2O (30 mL), brine (30 mL), dried (Na_2SO_4) , filtered and concentrated to give 523 mg free alcohol (80 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.82-5.68 (m, 1H), 5.06-4.99 (m, 1H), 3.73-3.63 (m, 2H), 2.15-1.99 (m, 2H), 1.62-1.48 (m, 3H), 1.38-1.18 (m, 14H), 0.93-0.84 (m, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.3, 116.3, 61.3, 38.3, 36.8, 34.4, 33.8, 32.1, 30.2, 29.9, 29.6, 26.8, 22.9, 14.4;

IR (film) 3332, 3076, 2923, 2854, 1640, 1466, 1378, 1057, 994, 910 cm^{-1};

GCMS (EI) calcd for $C_{14}H_{28}O$ 212 $[M]^+$, found 212.



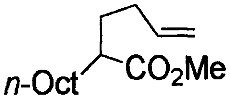
4-(2-Bromoethyl)dodec-1-ene Prepared directly from the TBS-protected alcohol: triphenylphosphine dibromide (1.10 g, 2.6 mmol, 1.3 equiv.) was charged to an oven-dried 100 mL round-bottomed flask and purged with Ar for 5 min. 15 mL dry CH_2Cl_2 was added, and the mixture lowered to 0 °C in an ice bath. A solution of the TBS-protected alcohol (654 mg, 2.0 mmol) in 10 mL CH_2Cl_2 was added dropwise over 10 min, then the ice bath was removed and the reaction stirred for 3 h. After the reaction was complete by TLC, 1.0 g SiO_2 was added directly to the mixture and stirred for 5 min (mixture may turn orange at this point). After removal of the stir bar, the mixture was concentrated to a dry solid (care! fine powder), then placed atop a pre-packed column (SiO_2) and eluted with hexanes to furnish 440 mg (80%) of the desired product.

^1H NMR ($CDCl_3$, 300 MHz) δ 5.81-5.68 (m, 1H), 5.06-4.99 (m, 1H), 3.43 (t, J = 7.3 Hz, 1H), 2.08-2.02 (m, 2H), 1.86-1.78 (m, 2H), 1.64-1.54 (m, 1H), 1.33-1.19 (m, 14H), 0.88 (t, J = 7.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 136.7, 116.9, 37.7, 37.0, 36.4, 33.1, 32.3, 32.1, 30.1, 29.8, 29.6, 26.7, 22.9, 14.4;

IR (film) 3077, 2924, 2854, 1640, 1466, 1255, 994, 913 cm^{-1};

GCMS (EI) calcd for $C_{14}H_{27}Br$ 274/276 (1:1) $[M]^+$, found 274/276 (1:1), 232/234 $[M-allyl]^+$.



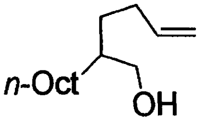
Methyl 2-(but-3-enyl)decanoate A solution of diisopropylamine (0.83 g, 1.15 mL, 8.2 mmol, 1.05 equiv.) in 15 mL THF was cooled to -78 °C in a dry ice/acetone bath. *n*-BuLi (1.6 M in hexanes, 5.1 mL, 8.2 mmol, 1.05 equiv.) was slowly added ad the mixture stirred for 10 min. The reaction was allowed to warm to 0 °C and stirred for 10 min, then cooled back to -78 °C. Methyl hex-5-enoate (1.0 g, 7.8 mmol) was added dropwise, and the mixture stirred for 1 h. *n*-Octyl iodide (1.97 g, 1.48 mL, 1.05 equiv.) was added dropwise and the mixture stirred a further 16 h. After this time, sat. aq. NH_4Cl (20 mL) and Et_2O (50 mL)were added, and the layers allowed to separate. The Et_2O layer was washed with H_2O (75 mL), brine, dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (SiO_2, 50:1 hexanes/ Et_2O) to give 1.3 g product (72%).

^1H NMR ($CDCl_3$, 300 MHz) δ 5.77 (dddd, *J* = 6.6 Hz, 6.6 Hz, 10.2 Hz, 16.9 Hz, 1H), 5.05-4.92 (m, 2H), 3.66 (s, 3H), 2.37 (dddd, *J* = 5.2 Hz, 5.2 Hz, 8.8 Hz, 8.8 Hz, 1H), 2.08-1.97 (m, 2H), 1.78-1.64 (m, 1H), 1.66-1.36 (m, 3H), 1.34-1.16 (m, 14H), 0.90-0.84 (m, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 177.5, 138.632, 115.7, 52.1, 45.7, 33.2, 32.6, 32.3, 32.2, 30.2, 30.1, 29.9, 28.1, 23.4, 14.8;

IR (film) 2925 2855, 1739, 1642, 1455, 1378, 1163, 911 cm^{-1};

GCMS (EI) calcd for $C_{15}H_{28}O_2$ 240 $[M]^+$, found 240.

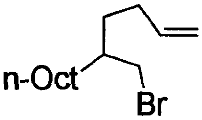


2-(But-3-enyl)decan-1-ol A solution of the ester (800 mg, 3.3 mmol) in 15 mL dry THF was treated with $LiAlH_4$ (1.0 M in Et_2O, 3.3 mL, 3.3 mmol, 1.0 equiv.), and stirred for 1 h at room temperature. 0.5 mL sat. aq. sodium potassium tartrate (Rochelle's salt) was added carefully, then 100 mL Et_2O, followed by a further 10 mL sat. aq. Rochelle's salt. The mixture was stirred overnight, after which the layers were allowed to separate. The Et_2O layer was washed with 100 mL H_2O, brine, dried ($MgSO_4$), filtered and concentrated to give desired product (700mg, 99 %).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.86-5.78 (m, 1H), 5.04-4.94 (m, 2H), 3.56 (td, J = 5.5 Hz, 1.3 Hz, 2H), 2.11-2.06 (m, 2H), 1.54-1.47 (m, 1H), 1.50-1.41 (m, 1H), 1.42-1.33 (m, 1H), 1.35-1.22 (m, 14H), 1.22-1.17 (m, 1H), 0.90-0.86 (m, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 139.3, 114.6, 65.7, 40.2, 32.1, 31.4, 31.0, 30.4, 30.3, 29.8, 29.6, 27.1, 22.9, 14.4;

IR (film) 3346, 3078, 2924, 2854, 1641, 1467, 1036, 994, 909 cm^{-1};



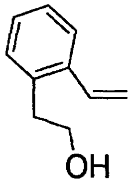
5-(Bromomethyl)tridec-1-ene Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave product (80 %) as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.86-5.73 (m, 1H), 5.07-4.94 (m, 1H), 3.46 (d, J = 4.6 Hz, 2H), 2.11-2.02 (m, 2H), 1.68-1.58 (m, 1H), 1.58-1.36 (m, 2H), 1.42-1.18 (m, 14H), 0.88 (t, J = 7.7 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.7, 115.0, 39.6, 38.9, 32.6, 32.1, 31.9, 31.0, 30.0, 29.8, 29.5, 26.7, 22.9, 14.4;

IR (film) 2925, 2854, 1641, 1455, 911 cm^{-1};

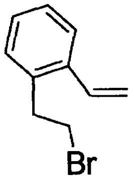
GCMS (EI) calcd for $C_{14}H_{27}Br$ 274/276 (1:1) $[M]^+$, found 195 $[M-80]^+$.



2-(2-Vinylphenyl)ethanol [*55488-94-3*] Following the procedure of Schwarz and Fu,[4] 2-(2-Bromophenyl)ethanol (1.6 g, 7.9 mmol), tributylvinyltin (2.62 g, 8.3 mmol, 1.05 equiv.), Pd_2dba_3 (71 mg, 0.078 mmol, 0.01 equiv.) and $P(t\text{-}Bu)_3$ (35 mg, 0.16 mmol, 0.02 equiv.) were stirred in 8 mL toluene under Ar for 24 h. 5 g KF was then added, followed by 10 mL Et_2O, 5 g activated carbon, and the mixture stirred 5 min. The reaction was filtered over a pad of silica, and washed with 3 x 20 mL Et_2O. The filtrate was concentrated, and the residue purified by column chromatography (SiO_2, 5:1 hexanes/ EtOAc) to give 970 mg product (85 %).

^1H NMR ($CDCl_3$, 300 MHz) δ 11.16 (s, 1H), 8.00 (d, J = 8.8 Hz, 2H), 7.64-7.54 (m, 7H), 7.31 (d, J = 8.9 Hz, 2H), 7.20 (d, J = 8.8 Hz, 2H), 3.89 (s, 3H), 3.84 (s, 3H);

^{13}C NMR ($CDCl_3$, 125 MHz) δ 162.2, 161.9, 154.3, 133.4, 130.4, 130.4, 129.2, 129.1, 125.7, 123.7, 123.5, 116.5, 116.3, 57.0, 56.9.



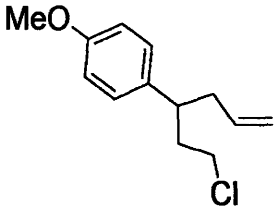
1-(2-Bromoethyl)-2-vinylbenzene [95798-50-8] Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave product (74 %) as a clear oil. This material was stored at 0 °C as a precautionary measure.

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.45-7.55 (m, 1H), 7.31-7.15 (m, 3H), 6.96 (dd, *J* = 17.3 Hz, 10.9 Hz, 1H), 5.68 (dd, *J* = 17.2 Hz, 1.0 Hz, 1H), 5.36 (dd, J = 10.9 Hz, 1.0 Hz 1H), 3.50 (t, *J* = 8.3 Hz, 2H), 3.24 (t, *J* = 8.3 Hz, 1H);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 137.0, 136.4, 134.1, 130.2, 128.3, 127.7, 126.4, 116.9, 37.3, 32.2;

IR (film) 3065, 3015, 2966, 2247, 1626, 1485, 1451, 1262, 1217, 989, 911, 734 cm^{-1};

GCMS (EI) calcd for $C_{10}H_{11}Br$ 210/212 (1:1) [M]$^+$, found 210/212 (1:1).



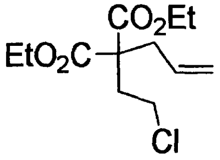
1-(1-Chlorohex-5-en-3-yl)-4-methoxybenzene Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave product (77 %) as a clear oil.

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.10 (d, *J* = 8.7 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 5.75-5.61 (m, 1H), 5.04-4.94 (m, 1H), 3.81 (s, 3H), 3.47-3.40 (m, 1H), 3.30-3.21 (m, 1H), 2.90-2.80 (m, 1H), 2.37 (t, *J* = 7.6 Hz, 2H), 2.20-2.09 (m, 1H), 2.00-1.88 (m, 1H);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 158.4, 136.7, 135.5, 128.8, 116.6, 114.1, 55.4, 43.4, 42.1, 41.3, 39.0;

IR (film) 3076, 2917, 2836, 1640, 1612, 1583, 1513, 1441, 1303, 1249, 1178, 1038 cm^{-1};

GCMS (EI) calcd for $C_{13}H_{17}ClO$ 224/226 (3:1) [M]$^+$, 224/226 (3:1).

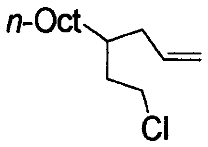


Diethyl 2-allyl-2-(2-chloroethyl)malonate [*174619-41-1*] An oven-dried 100 mL round-bottomed flask was charged with NaH (60% in mineral oil, 0.76 g, 31.5 mmol, 1.05 equiv.) and flushed with Ar for 3 min. Dry DMF (15 mL) was added, followed by dropwise addition of diethylallylmalonate (6.00 g, 30 mmol). After 0.5 h, H_2 evolution had ceased, and 1-bromo-2-chloroethane (4.52 g, 31.5 mmol, 1.05 equiv.) was added over 10 min. The mixture was stirred overnight, then quenched with sat. aq. NH_4Cl (10 mL). The mixture was extracted with Et_2O (50 mL), then the organic layer washed with brine (30 mL), dried (MgSO4), filtered, and concentrated. The residue was purified by flash column chromatography (SiO_2, 20:1 hexanes:Et_2O) to provide 6.16 g (78%) of the desired product.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.68-5.59 (m, 1H), 5.16-5.10 (m, 2H), 4.22-4.16 (m, 4H), 3.52 (t, *J* = 7.2 Hz, 2H), 2.66 (d, *J* = 7.5 Hz, 2H), 2.35 (d, *J* = 7.3 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 6H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 170.6, 132.0, 119.9.0, 61.8, 56.7, 40.1, 38.0, 35.9, 14.3.

IR (film) 3081, 2983, 1732, 1642, 1447, 1368, 1300, 1265, 1096, 1030, 926, 859 cm^{-1}.



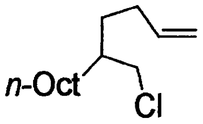
4-(2-Chloroethyl)dodec-1-ene Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave 428 mg product (81 %) as a clear oil.

^{1}H NMR (CDCl$_3$, 300 MHz) δ 5.82-5.68 (m, 1H), 5.06-4.99 (m, 1H), 3.56 (t, J = 7.1 Hz, 1H), 2.09-2.02 (m, 2H), 1.77-1.70 (m, 2H), 1.67-1.60 (m, 1H), 1.33-1.20 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 136.7, 116.6, 43.5, 37.8, 36.7, 35.2, 32.3, 32.1, 30.1, 29.8, 29.6, 26.7, 22.9, 14.4.

IR (film) 3077, 2925, 2855, 1640, 1457, 1378, 994, 911, 736 cm^{-1};

GCMS (EI) calcd for $C_{14}H_{27}Cl$ 230, $[M]^+$, found 230.



5-(Chloromethyl)tridec-1-ene Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave 428 mg product (72 %) as a clear oil.

^{1}H NMR (CDCl$_3$, 300 MHz) δ 5.89-5.73 (m, 1H), 5.08-4.93 (m, 1H), 3.55 (d, J = 4.9 Hz, 2H), 2.16-1.98 (m, 2H), 1.76-1.64 (m, 1H), 1.59-1.37 (m, 2H), 1.48-1.22 (m, 14H), 0.88 (t, J = 7.2 Hz, 3H);

^{13}C NMR (CDCl$_3$, 75 MHz) δ 138.7, 114.9, 48.8, 39.4, 32.1, 31.7, 31.1, 30.9, 30.0, 29.8, 29.5, 26.8, 22.9, 14.4;

IR (film) 3078, 2925, 2855, 1642, 1456, 1378, 1293, 993, 911, 723, 688 cm^{-1};

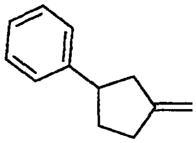
GCMS (EI) calcd for $C_{14}H_{27}Cl$ 230 $[M]^+$, found 230.

II. Synthesis and Characterization of Products

General procedure for alkyl bromides (without a glovebox), Table 2: An oven-dried 25 mL Schlenk flask was thoroughly purged with Ar for 10 min, then charged with $Pd_2(MeO\text{-}dba)_3$ (27.4 mg, 0.025 mmol, 0.05 equiv.), $SIMesHBF_4$ (39.4 mg, 0.1 mmol, 0.2 equiv.), KO*t*-Bu (11.2 mg, 0.1 mmol, 0.2 equiv.), Cs_2CO_3 (179.2 mg, 0.55 mmol, 1.1 equiv. [K_3PO_4 for Entry **9**, 116.6 mg]) and purged with Ar for a further 5 min, with stirring. Dry CH_3CN (5 mL) was then added, and the mixture stirred under Ar for 10 min. [At this point, the reaction mixture should be dark brown-orange. If the mixture is light orange in color, the reaction has failed.] The electrophile was then added via gastight syringe (0.5 mmol), the Schlenk flask sealed, and reaction stirred for 16 h at 60 °C. [Note, the reaction should not be opened to the line, as this led to reproducibility problems.] Entries **1** and **9** were at this point handled separately as shown below, due to their volatility. For Entries **2** – **8**, the mixture was allowed to cool, then filtered over a pad of silica gel, eluting with Et_2O. Concentration of the filtrate furnished an orange-brown residue that was purified using column chromatography (10% w/w $AgNO_3$ on SiO_2 [silver column ref], 10 g/mmol product), to give the desired compound.

For Entries **1** and **9**, the cooled reaction mixture was diluted with 100 mL H_2O and 50 mL pentane, and the layers allowed to separate. The organic layer was passed through a plug of silica gel, eluting with 20 mL pentane. The pentane was then distilled from the filtrate at atmospheric pressure, and the residue purified by chromatography (10% w/w $AgNO_3$ on SiO_2, 100% pentanes) to give the desired product.

General procedure for alkyl chlorides (without a glovebox), Table 3: An oven-dried 25 mL Schlenk flask was thoroughly purged with Ar for 10 min, then charged with $Pd_2(MeO\text{-}dba)_3$ (27.4 mg, 0.025 mmol, 0.05 equiv.), $SIMesHBF_4$ (39.4 mg, 0.1 mmol, 0.2 equiv.), KO*t*-Bu (11.2 mg, 0.1 mmol, 0.2 equiv.), K_3PO_4 (116.6 mg, 0.55 mmol, 1.1 equiv.) and purged with Ar for a further 5 min, with stirring. Dry NMP (5 mL) was then added, and the mixture stirred under Ar for 10 min. The electrophile was then added via gastight syringe (0.5 mmol), the Schlenk flask sealed, and reaction stirred for 16 h at 100 °C. After this time, the mixture was allowed to cool, then 100 mL H_2O and 50 mL Et_2O added, and the layers allowed to separate. The aqueous layer was further extracted (3 x 30 mL), then the combined organic layers washed with 100 mL H_2O, brine (30 mL), dried ($MgSO_4$), filtered and concentrated. The residue was purified by chromatography (10% w/w $AgNO_3$ on SiO_2) to furnish the desired product.



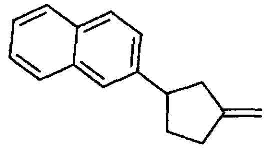
(3-Methylenecyclopentyl)benzene [*122833-99-2*]. Chromatography (100% pentanes) gave 57.7 mg (73 %) product as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.35-7.19 (m, 5H), 4.95-4.85 (m, 2H), 3.21-3.08 (m, 1H), 2.75 (ddt, J = 16.5 Hz, 7.1 Hz, 1.6 Hz, 1H), 2.60-2.45 (m, 1H), 2.43-2.34 (m, 2H), 2.21-2.10 (m, 1H), 1.82-1.67 (m, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.4, 145.2, 128.6, 127.2, 126.3, 105.6, 45.8, 41.4, 34.7, 32.8;

IR (film) 3066, 3029, 2948, 2250, 1657, 1603, 1541, 1494, 1451, 1434, 1265, 1031, 909, 878, 734, 699, 650 cm^{-1};

GCMS (EI) calcd for $C_{12}H_{14}$ 158 [M]$^+$, found 158.



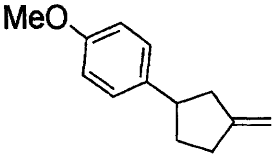
2-(3-Methylenecyclopentyl)naphthalene Chromatography (100% hexanes) gave 81.1 mg (78 %) product as a clear oil.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.83-7.76 (m, 3H), 7.67 (s, 1H), 7.49-7.39 (m, 3H), 5.00-4.96 (m, 1H), 4.96-4.93 (m, 1H), 3.34 (tt, *J* = 10.3 Hz, 7.2 Hz, 1H), 2.84 (dd, *J* = 16.0 Hz, 7.3 Hz, 1H), 2.63-2.55 (m, 1H), 2.79 (dd, *J* = 16.4 Hz, 7.7 Hz, 1H), 2.65-2.55 (m, 1H), 2.56-2.49 (m, 1H), 2.51-2.42 (m, 1H), 2.28-2.21 (m, 1H), 1.88 (dddd, *J* = 12.1 Hz, 10.3 Hz, 10.3 Hz, 8.3 Hz, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 152.8, 143.2, 134.2, 132.9, 128.6, 128.3, 126.7, 126.6, 125.9, 125.6, 106.2, 46.4, 41.8, 35.2, 33.4;

IR (film) 3054, 2919, 2850, 1657, 1633, 1601, 1543, 1508, 1433, 1373, 1269, 1019, 876, 853, 816, 744 cm^{-1};

GCMS (EI) calcd for $C_{16}H_{16}$ 208 [M]$^+$, found 208.



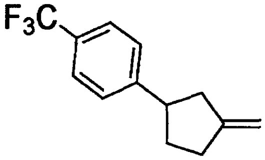
1-Methoxy-4-(3-methylenecyclopentyl)benzene Chromatography (50:1 hexanes:Et_2O) gave 77.1 mg (82 %) product as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21-7.15 (m, 2H), 6.88-6.83 (m, 2H), 4.95-4.91 (m, 1H), 4.92-4.88 (m, 1H), 3.80 (s, 3H), 3.10 (dddd, J = 10.6 Hz, 10.6 Hz, 6.6 Hz, 6.6 Hz, 1H), 2.76-2.70 (m, 1H), 2.56-2.49 (m, 1H), 2.44-2.34 (m, 2H), 2.16-2.10 (m, 1H), 1.72 (dddd, J = 8.7 Hz, 10.7 Hz, 10.7 Hz, 12.5 Hz, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.6, 152.9, 137.8, 128.6, 114.4, 106.0, 56.0, 45.5, 42.0, 35.4, 33.2;

IR (film) 3070, 3033, 2998, 2950, 2907, 2835, 1655, 1612, 1583, 1514, 1464, 1441, 1361, 1304, 1282, 1249, 1179, 1108, 1039, 875, 828, 668 cm^{-1};

GCMS (EI) calcd for $C_{13}H_{16}O$ 188 $[M]^+$, found 188.



1-(3-Methylenecyclopentyl)-4-(trifluoromethyl)benzene Chromatography (100:1 hexanes:Et_2O) gave 89.3 mg (79 %) product as a clear oil.

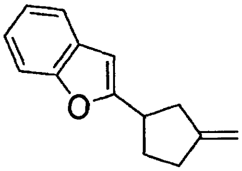
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.55 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 4.96-4.91 (m, 2H), 3.12-3.15 (m, 1H), 2.78 (ddt, J = 17.0 Hz, 7.4 Hz, 1.5 Hz, 1H), 2.62-2.36 (m, 3H), 2.21-2.15 (m, 1H), 1.76 (m, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 151.5, 149.4, 127.6, 125.5 (q, J = 4.0 Hz), 106.1, 45.6, 41.2, 34.6, 32.6. (Note: Not all C atoms could be clearly defined)

^{19}F NMR ($CDCl_3$, 282 MHz) δ -62.9.

IR (film) 2917, 2850, 1659, 1620, 1579, 1543, 1462, 1421, 1327, 1164, 1124, 1069, 1018, 880, 838 cm^{-1};

GCMS (EI) calcd for $C_{13}H_{13}F_3$ 226 $[M]^+$, found 226, 211 $[M-CH_3]^+$.



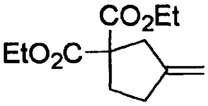
2-(3-Methylenecyclopentyl)benzofuran Chromatography (100:1 hexanes:Et_2O) gave 82.2 mg (83 %) product as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.51-7.47 (m, 1H), 7.44-7.40 (m, 1H), 7.22 (td, *J* = 7.2 Hz, 1.8 Hz, 1H), 7.17 (td, *J* = 7.2 Hz 1.4 Hz, 1H), 6.41 (t, *J* = 1.0 Hz, 1H), 4.97-4.93 (m, 1H), 4.95-4.90 (m, 1H), 3.40-3.29 (m, 1H), 2.79 (dd, *J* = 16.4 Hz, 7.7 Hz, 1H), 2.65-2.35 (m, 3H), 2.24-2.17 (m, 1H), 1.95 (dq, *J* = 12.4 Hz, 8.9 Hz);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.5, 155.3, 151.6, 129.5, 123.9, 123.1, 121.0, 111.5, 106.7, 101.5, 39.8, 39.1, 32.8, 32.5;

IR (film) 3071, 2918, 2850, 1659, 1600, 1586, 1455, 1434, 1254, 1179, 1104, 1011, 965, 926, 909, 881, 797, 750, 739 cm^{-1};

GCMS (EI) calcd for $C_{14}H_{14}O$ 198 $[M]^+$, found 198.



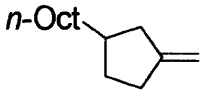
Diethyl 3-methylenecyclopentane-1,1-dicarboxylate [137435-46-2] Chromatography (20:1 hexanes:Et_2O) gave 96.1 mg (85 %) product as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.82-4.95 (m, 2H), 4.18 (q, *J* = 7.1 Hz, 4H), 2.46-2.37 (m, 2H), 2.25 (td, *J* = 7.7 Hz, 0.9Hz, 2H), 1.24 (t, *J* = 7.1 Hz, 6H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 172.0, 148.7, 107.1, 61.7, 60.4, 40.9, 39.9, 31.5, 14.3;

IR (film) 3077, 2984, 2939, 2875, 1732, 1663, 1465, 1446, 1390, 1367, 1299, 1274, 1252, 1203, 1181, 1157, 1097, 1071, 1041, 1019, 934, 882, 862 cm^{-1};

GCMS (EI) calcd for $C_{12}H_{18}O_4$ 226 $[M]^+$, found 226.



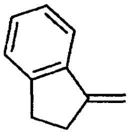
1-Methylene-3-octylcyclopentane Chromatography (100 % hexanes) gave 69.9 mg (72 %) product as a clear oil.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.82 (m, 1H), 4.81 (m, 1H), 2.47-2.44 (m, 1H), 2.39-2.33 (m, 1H), 2.28-2.21 (m, 1H), 1.90-1.83 (m, 3H), 1.34-1.28 (m, 15H), 0.89 (t, J = 7.0 Hz, 3H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 153.5, 104.9, 40.7, 40.2, 35.7, 33.1, 32.6, 32.2, 30.1, 29.9, 29.6, 28.7, 22.9, 14.4.

IR (film) 3071, 2923, 2854, 1755, 1658, 1466, 1433, 1378, 875, 722 cm^{-1};

GCMS (EI) calcd for $C_{14}H_{26}$ 194 $[M]^+$, found 194.



1-Methylene-2,3-dihydro-1*H*-indene [*1194-56-5*] Chromatography (100 % pentanes) gave 44.9 mg (69 %) product as a 20:1 mixture with the product arising from *β*-hydride elimination.

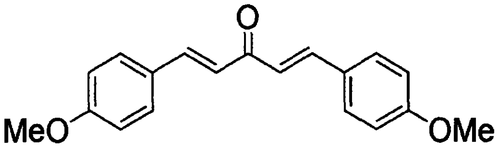
^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54-7.45 (m, 1H), 7.31-7.19 (m, 3H), 5.45 (t, J = 2.5 Hz, 1H), 5.04 (t, J = 2.2 Hz, 1H), 3.02-2.97 (m, 2H), 2.84-2.76 (m, 2H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.8, 147.0, 141.3, 128.5, 126.7, 125.6, 120.9, 102.7, 31.4, 30.2;

IR (film) 3066, 2917, 2850, 1715, 1639, 1462, 1441, 1400, 1381, 1279, 1169, 1017, 1003, 945, 914, 868, 771, 718 cm^{-1};

GCMS (EI) calcd for $C_{10}H_{10}$ 130 $[M]^+$, found 130.

III. Catalyst Synthesis



(1E,4E)-1,5-Bis(4-methoxyphenyl)penta-1,4-dien-3-one [*37951-12-5*] Prepared according to the procedure of Fairlamb.[5] In addition, the material was recrystallized from 1:3 v/v CH_2Cl_2/Et_2O. Yield: 70 %

mp 122 – 123 °C;

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.71 (d, J = 15.8 Hz, 1H), 7.58 (dt, *J* = 8.5 Hz, 1.8 Hz, 2H), 6.97 (d, *J* = 15.9 Hz, 1H), 6.94 (dt, *J* = 8.8 Hz, 2.0 Hz, 2H), 3.86 (s, 3H);

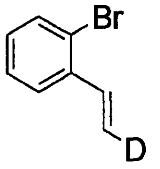
^{13}C NMR ($CDCl_3$, 75 MHz) δ 189.1, 161.8, 142.9, 130.3, 127.8, 123.7, 114.6, 55.7.

Pd_2(MeO-dba)$_3$ [*130610-16-1*] Adapted from the procedure of Beller:[6] Anhydrous NaOAc (1.95 g, 23.8 mmol, 8.0 equiv.) and MeO-dba (2.88 g, 9.8 mmol, 3.3 equiv.) were added to a 250 mL two-neck round-bottom flask, and purged with Ar for 10 min. 70 mL dry MeOH was added and the mixture stirred 10 min at 50 °C. $PdCl_2$ (0.53 g, 2.96 mmol) was then added under high Ar flow, and the mixture stirred at 40 °C for 4 h. The mixture was then cooled to 0 °C in an ice bath, and filtered. The filtered solid was washed with 2 x 15 mL H_2O, 2 x 15 mL acetone, and the dark purple solid dried in vacuo overnight then placed under Ar. Yield: 2.1 g (65 %).

mp 139-141 °C (lit: 141-143 °C);

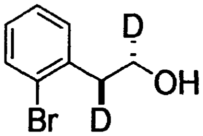
Anal. Calcd. for $C_{57}H_{54}O_9Pd_2$ (1094.18) C 62.47, H 4.97, Pd 19.42; Found, C 65.46, H 5.15, Pd 13.90.

IV. Deuterium Experiment



(E)-1-bromo-2-(2-deuterovinyl)benzene Prepared in the manner of Soderquist.[7]

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.59-7.54 (m, 2H), 7.33-7.26 (m, 1H), 7.16-7.10 (m, 1H), 7.07 (d, J = 17.5 Hz, 1H, note: there is unresolved hyperfine splitting, presumably due to coupling to the vicinal ^{2}H atom), 5.71 (d, J = 17.5 Hz, 1H); ^{2}H incorporation: 94% by ^{1}H NMR. This material is unstable and was used in the next step without further purification or characterization.



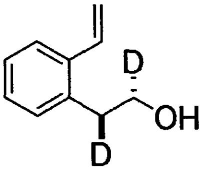
(+/-)-erythro-2-(2-bromophenyl)-1,2-dideuteroethanol $NaBD_4$ (462 mg, 11 mmol) was added to an oven-dried 100 mL round-bottomed flask and purged 5 min. The styrene (1.8 g, 10 mmol) was added as a solution in 20 ml THF. $BF_3.OEt_2$ was added slowly over 10 min, then the mixture heated to 40 °C and stirred for 3 h. The reaction was cooled to 0 °C, and 4.5 mL H_2O was added carefully. 3N NaOH (5 mL) and H_2O_2 (30 %, 5 mL) were subsequently added (slow!), the mixture heated to 50 °C, and stirred for 2 h. The mixture was allowed to cool, and NaCl (4 g) was added, at which point the mixture cleared slightly. 100 mL Et_2O and 50 mL brine were added, and the layers allowed to separate. The Et_2O layer was washed with 50 mL H_2O, dried ($MgSO_4$), filtered and concentrated. The residue was purified by column chromatography (SiO_2, 4:1 hexanes/ Et_2O) to give 800 mg desired product (40 %).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.57 (d, J = 7.8 Hz, 1H), 7.30-7.24 (m, 2H), 7.13-7.09 (m, 1H), 3.88 (t, J = 6.0 Hz, 1H), 3.02 (d, J = 6.5 Hz, 1H), 1.42 (s, 1H)

^{13}C NMR ($CDCl_3$, 75 MHz) δ 138.4, 133.7, 132.0, 128.9, 128.2, 125.4, 62.4 (t, J = 23.0 Hz), 39.6 (t, J = 19.5 Hz);

IR (film) 3356, 3057, 2918, 2165, 1566, 1470, 1437, 1263, 1098, 1022, 746 cm^{-1};

GCMS (EI) calcd for $C_8H_7D_2BrO$ 202/204 $[M]^+$, found 202/204 (1:1).



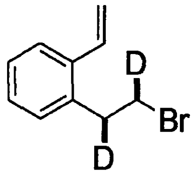
(+/-)-erythro-2-(2-vinylphenyl)-1,2-dideuteroethanol Following the procedure of Schwartz and Fu,[4] the alcohol from the previous step (800 mg, 3.94 mmol), tributylvinyltin (1.31 g, 4.13 mmol, 1.05 equiv.), Pd_2dba_3 (36 mg, 0.039 mmol, 0.01 equiv.) and $P(t\text{-}Bu)_3$ (17.5 mg, 0.08 mmol, 0.02 equiv.) were stirred in 4 mL toluene under Ar for 24 h. 3 g KF was then added, followed by 10 mL Et_2O, 3 g activated carbon, and the mixture stirred 5 min. The reaction was filtered over a pad of silica, and washed with 3 x 20 mL Et_2O. The filtrate was concentrated, and the residue purified by column chromatography (SiO_2, 5:1 hexanes/ EtOAc) to give 520 mg product (88 %).

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.57-7.49 (m, 1H), 7.31-7.18 (m, 3H), 7.02 (dd, J = 17.4 Hz, 11.0 Hz, 1H), 5.66 (dd, J = 17.3 Hz, 1.4 Hz, 1H), 5.32 (dd, J = 11.0 Hz, 1.4 Hz, 1H), 3.79 (t, J = 6.6 Hz, 1H), 2.95 (d, J = 7.0 Hz, 1H), 1.44 (d, J = 6.0 Hz, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.3, 135.9, 134.6, 130.6, 128.1, 127.2, 126.3, 116.3, 63.0 (t, J_{CD} = 21.9 Hz), 36.2 (t, J_{CD} = 19.5 Hz);

IR (film) 3346, 3087, 3063, 3027, 2922, 2166, 1834, 1626, 1484, 1450, 1416, 1332, 1098, 1024, 991, 914, 772 cm^{-1};

GCMS (EI) calcd for $C_{10}H_{10}D_2O$ 150 $[M]^+$, found 150.



(+/-)-syn-1-(2-bromo-1,2-dideuteroethyl)-2-vinylbenzene Prepared according to step **D** of Scheme 1. Chromatography (100% hexanes) gave product (79 %) as a clear oil. This material was stored at 0 °C as a precautionary measure.

^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.54-7.48 (m, 1H), 7.30-7.20 (m, 2H), 7.21-7.15 (m, 1H), 6.96 (dd, J = 17.3 Hz, 11.0 Hz, 1H), 5.69 (dd, J = 17.2 Hz, 1.3 Hz, 1H), 5.37 (dd, J = 11.0 Hz, 1.3 Hz, 1H), 3.48 (d, with hyperfine splitting due to geminal ^{2}H, $^3J_{ab}$ = 5.9 Hz, $^2J_{HD}$ = 1.4 Hz), 3.23 (d, with hyperfine splitting due to geminal ^{2}H, $^3J_{ab}$ = 5.9 Hz, $^2J_{HD}$ = 1.7 Hz);

Decoupling:

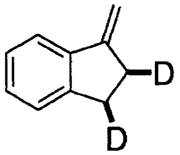
^{1}H {^{2}H } NMR ($CDCl_3$, 500 MHz) irradiation at δ 3.24: 3.48 (d, with hyperfine splitting due to geminal ^{2}H, $^3J_{ab}$ = 5.9 Hz, 1H), 2.78 (d, $^3J_{ab}$ = 5.9 Hz, 1H);

^{1}H {^{2}H } NMR ($CDCl_3$, 500 MHz) irradiation at δ 3.48: 3.48 (d, but with only partial decoupling from geminal ^{2}H, $^3J_{ab}$ = 5.9 Hz, 1H), 2.78 (d, with hyperfine splitting due to geminal ^{2}H, $^3J_{ab}$ = 5.9 Hz, 1H);

^{13}C NMR ($CDCl_3$, 75 MHz) δ 137.0, 136.3, 134.1, 130.2, 128.2, 127.7, 126.4, 116.9, 36.8 (t, J_{CD} = 19.8 Hz), 31.9 (t, J_{CD} = 23.5 Hz);

IR (film) 3087, 3063, 3027, 2211, 1922, 1839, 1626, 1484, 1450, 1417, 1327, 1191, 989, 916, 772, 730, 630 cm^{-1};

GCMS (EI) calcd for $C_{10}H_9D_2Br$ 212/214 $[M]^+$, found 212/214 (1:1).



Isolated according to the procedure given for 1-methylene-2,3-dihydro-1*H*-indene, as a 20:1 mixture with product arising from β-hydride elimination.

^{1}H NMR (CDCl$_3$, 300 MHz) δ 7.54-7.48 (m, 1H), 7.31-7.18 (m, 3H), 5.46 (d, J = 2.5 Hz, 1H), 5.04 (d, J = 2.2 Hz, 1H), 2.97 (d, with hyperfine splitting due to geminal ^{2}H, $^3J_{ab}$ = 9.3 Hz, $^2J_{HD}$ = 2.2 Hz, 1H), 2.78 (d, with hyperfine splitting due to geminal ^{2}H, $^3J_{ab}$ = 9.4 Hz, $^2J_{HD}$ = 2.3 Hz, 1H);

^{2}H NMR (CDCl$_3$, 77 MHz) δ 3.01 (d, J = 2.2 Hz, 1D), 2.83 (d, J = 2.6 Hz, 1D);

Decoupling:

^{2}H {^{1}H } NMR (CDCl$_3$, 77 MHz) irradiation at δ 2.83: 3.01 (d, J = 2.2 Hz, 1D), 2.83 (s, 1D);

^{2}H {^{1}H } NMR (CDCl$_3$, 77 MHz) irradiation at δ 3.01: 3.01 (s, 1D), 2.83 (d, J = 2.6 Hz, 1D);

^{1}H {^{2}H } NMR (CDCl$_3$, 500 MHz) irradiation at δ 2.78: 2.96 (d, J = 9.3 Hz, 1H), 2.78 (d, but only partial decoupling from geminal ^{2}H, J = 2.6 Hz, 1H);

^{1}H {^{2}H } NMR (CDCl$_3$, 500 MHz) irradiation at δ 2.96: 2.96 (d, J = 9.3 Hz, 1H), 2.78 (d, with hyperfine splitting due to geminal ^{2}H, $^3J_{ab}$ = 9.3 Hz, $^2J_{HD}$ = 2.2 Hz, 1H);

The extraction of simple doublets or singlets from these data suggest that only one diastereomer of the product is present. The magnitude of the vicinal coupling constant[8] $J = 9.3$ Hz suggests that these indenyl ring protons are in a *cis* relationship, corresponding to the isomer shown.

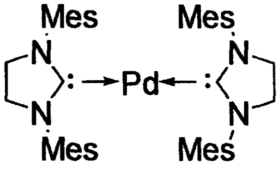
^{13}C NMR ($CDCl_3$, 75 MHz) δ 150.7, 147.1, 141.3, 128.5, 126.7, 125.6, 120.8, 102.7, 31.0 (t, $J_{CD} = 20.2$ Hz), 29.9 (t, $J_{CD} = 19.9$ Hz);

IR (film) 3070, 3020, 2917, 2851, 2169, 1715, 1638, 1462, 1275, 1019, 860, 758 cm^{-1};

GCMS (EI) calcd for $C_{10}H_8D_2$ 132 $[M]^+$, found 132 (1:1).

V. Synthesis of Pd biscarbene complexes.

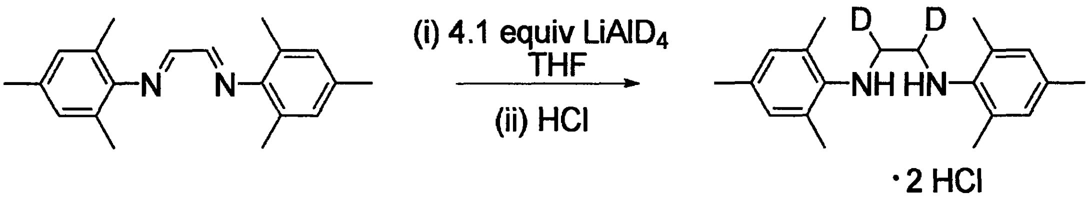
Following the procedure of Nolan,[9] SIMesHBF$_4$ (2.4 g, 6.12 mmol), NaH (219 mg, 9.12 mmol, 1.5 equiv.), and NaO*t*-Bu (11.5 mg, 0.12 mmol, 0.02 equiv.) were dissolved in THF (24 mL) in a glovebox, sealed in a pressure tube, and stirred at 65 °C for 20 h. The cooled mixture was concentrated in vacuo, then hexanes (25 mL) added. The mixture was filtered through an acrodisk™ in the glovebox and concentrated in vacuo to give 1.58 g free carbene as a sticky, partly crystalline material that was used directly in the next step.



Similar to the procedure of Hermann,[10] a solution of free SIMes (1.5 g, 4.9 mmol, 2.14 equiv.) in 20 mL toluene was added dropwise in a glovebox to a stirred suspension of Pd[P(*o*-tol)$_3$]$_2$ (1.5 g, 2.1 mmol) in toluene (20 mL). The reaction mixture changed in color from orange to a deep blood-red solution. The reaction was stirred for a further 1 h, then concentrated in vacuo *to dryness* (important!). The solid was broken up to a powder, and left to dry in vacuo for a further 2 h. The solid was then taken up in hexanes (50 mL) and stirred vigorously for 12 h. The solid was filtered and washed with 10 mL hexanes, and further dried in vacuo to give Pd(SIMes)$_2$ (850 mg, 56 %) as an orange solid. A small quantity of material was recrystallized from a 10:1 mixture of hexanes/CH2Cl2 to provide crystals that were suitable for X-ray diffraction studies (an NMR tube was found to give good-quality crystals).

^{1}H NMR (CD_3CN, 300 MHz) δ 6.81 (s, 8H), 3.44 (s, 8H), 2.30 (s, 12H), 1.99 (s, 24H).

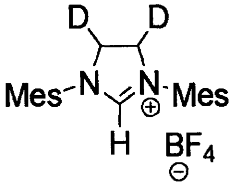
Steps detailing the synthesis of the dideuterated imidazolium tetrafluoroborate salt are analogous to those reported by Arduengo.[11]



An oven-dried 100 mL round-bottomed flask equipped with a side-arm and stir bar was charged with $LiAlD_4$ (1.72 g, 41 mmol, 4.1 equiv) and dry THF (40 mL) under argon. The resulting suspension was cooled to 0 °C, and the bis-imine (2.92 g, 10 mmol) added portionwise over 10 min, under flow of argon. The mixture was stirred for 16 h, then quenched with 40 mL sat. aq. Na_2SO_4 (CARE!), until a white suspension was obtained. After 1 h further stirring, 30 mL EtOAc was added, and the liquid decanted over a celite plug. The solids were stirred in refluxing EtOAc (30 mL) for 2 h, then also poured over celite. To the combined filtrates was added 15 mL 1N HCl, which furnished a white precipitate. After 1 h stirring, the solid was filtered and dried in vacuo to give 3.0 g (81%) of the desired diamine as the dihydrochloride salt.

^{1}H NMR (d_6-DMSO, 300 MHz) δ 6.90 (s, 4H), 3.40 (s, 2H), 2.36 (s, 6H), 2.20 (s, 6H),

^{2}H NMR (d_6-DMSO, 77 MHz) δ 3.40.



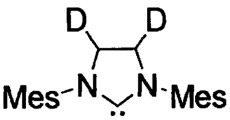
1,3-Bis(2,4,6-trimethylphenyl)-4,5-dideuteroimidazolium tetrafluoroborate

Distillation apparatus was fitted atop a mixture of the preceding diamine salt (3.0 g, 8.1 mmol) in 15 mL triethylorthoformate, with 1-2 drops formic acid. The mixture was stirred at 130 °C, until the theoretical quantity of EtOH had been distilled from the reaction mixture. The cooled white suspension was filtered, the solid dissolved in 30 mL H_2O, and 5 mL 48% wt HBF_4 (aq) was added with stirring. The resultant white suspension was stirred for 1 h, filtered, and washed with 2 x 50 mL distilled H_2O. The solid was dried in vacuo over night to give desired product (2.3 g, 71%) as a white solid. Note: Later study suggests that this material can be recrystallized from hot EtOH.

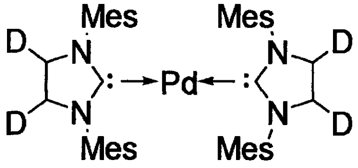
^{1}H NMR (d_6-DMSO, 500 MHz) δ 9.00 (s, 1H), 7.10 (s, 4H), 4.43 (s, 2H), 2.36 (s, 12H), 2.30 (s, 8H).

^{13}C NMR (d_6-DMSO, 125 MHz) δ 160.3, 139.7, 135.4, 131.0, 129.5, 51.0, 39.5 (quintet, $J_{C\text{-}D}$ = 20.8 Hz), 20.6, 17.2;

^{2}H NMR (d_6-DMSO, 77 MHz) δ 4.40.



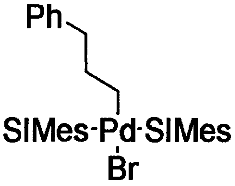
In a glovebox, d_2-SIMesHBF$_4$ (913 mg, 2.3 mmol), NaH (8.3 mg, 3.5 mmol, 1.5 equiv), and NaO*t*-Bu (4.4 mg, 0.05 mmol, 0.02 equiv) were combined in a 100 mL pressure tube with 10 mL THF. The pressure tube was sealed and stirred at 65 °C for 9 h. The cooled mixture was concentrated in vacuo, then taken up in 5 mL hexanes, filtered through an acrodisk™, and re-concentrated to give a beige solid (500 mg, 71 %). This material appears to be unstable, and should be used within 6 h.



Prepared in a manner identical to Pd(SIMes)$_2$. Using Pd[P(*o*-tol)$_3$]$_2$ (542 mg, 0.76 mmol), d_2-SIMes (500 mg, 1.62 mmol, 2.1 equiv) gave 150 mg (28 %) product.

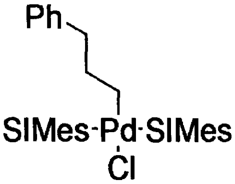
^{1}H NMR (C_6D_6, 500 MHz) δ 6.85 (s, 8H), 2.97 (s, 4H), 2.36 (s, 12H), 2.14 (s, 24H);

^{2}H NMR (CD_3CN, 77 MHz) δ 3.40.



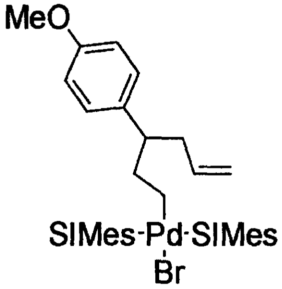
In a glovebox, a solution of Pd(SIMes)$_2$ (14.4 mg, 0.02 mmol) in 0.7 mL CD_3CN was treated with 1-bromo-3-phenylpropane. The red-orange solution became virtually colorless in less than 1 min. After 3 h strring, the mixture was concentrated in vacuo in the NMR tube to give a sticky residue, which was triturated with hexanes and filtered to give the alkyl palladium complex as an air and moisture-stable white solid (18.1 mg, 98 %). The material was dissolved in 0.1 mL CH_2Cl_2 in an NMR tube and 0.6 mL hexanes slowly added. After standing for 12 h, crystals formed that were suitable for X-ray analysis.

^{1}H NMR (CD_3CN, 300 MHz) δ 7.33-7.02 (m, 5H), 7.01 (s, 8H), 3.90-3.60 (bs, 8H), 2.40 (s, 12H), 2.25-2.15 (m, 2H), 1.98 (s, 24H), 0.77-0.58 (m, 2H), 0.62-0.51 (m, 2H).



Furnished according to the above procedure. Pd(SIMes)$_2$ (14.4 mg, 0.02 mmol) and 1-chloro-3-phenylpropane (3.1 mg, 0.02 mmol) gave 15.7 mg (90 %) oxidative addition adduct as a white solid. X-ray quality crystals were obtained from layering 1.2 mL hexanes on 0.05 mL solution of the material in CH_2Cl_2, and leaving the vessel exposed to the atmosphere for slow evaporation.

^{1}H NMR (CD_3CN, 300 MHz) δ 7.31-7.04 (m, 5H), 7.01 (s, 8H), 3.84-3.66 (bs, 8H), 2.41 (s, 12H), 2.24-2.16 (m, 2H), 1.98 (s, 24H), 0.76-0.62 (m, 2H), 0.62-0.52 (m, 2H).



Furnished according to the above procedure. Pd(SIMes)$_2$ (14.4 mg, 0.02 mmol) and 1-(1-Bromohex-5-en-3-yl)-4-methoxybenzene (5.4 mg, 0.02 mmol) gave 18.0 mg (91 %) oxidative addition adduct as an off-white solid. X-ray quality crystals were obtained from layering 0.7 mL hexanes on 0.1 mL solution of the material in CH_2Cl_2.

^{1}H NMR (CD_3CN, 300 MHz) δ 6.98 (s, 8H), 6.97-6.78 (m, 4H), 5.61-5.47 (m, 1H), 4.92-4.79 (m, 2H), 3.79 (s, 3H), 3.68 (s, 8H), 2.40 (s, 12H), 2.42-2.33 (m, 1H), 2.30-2.04 (m, 4H), 1.99 (s, 24H), 0.80-0.72 (m, 2H), 0.65-0.55 (m, 1H), 0.44-0.30 (m, 1H).

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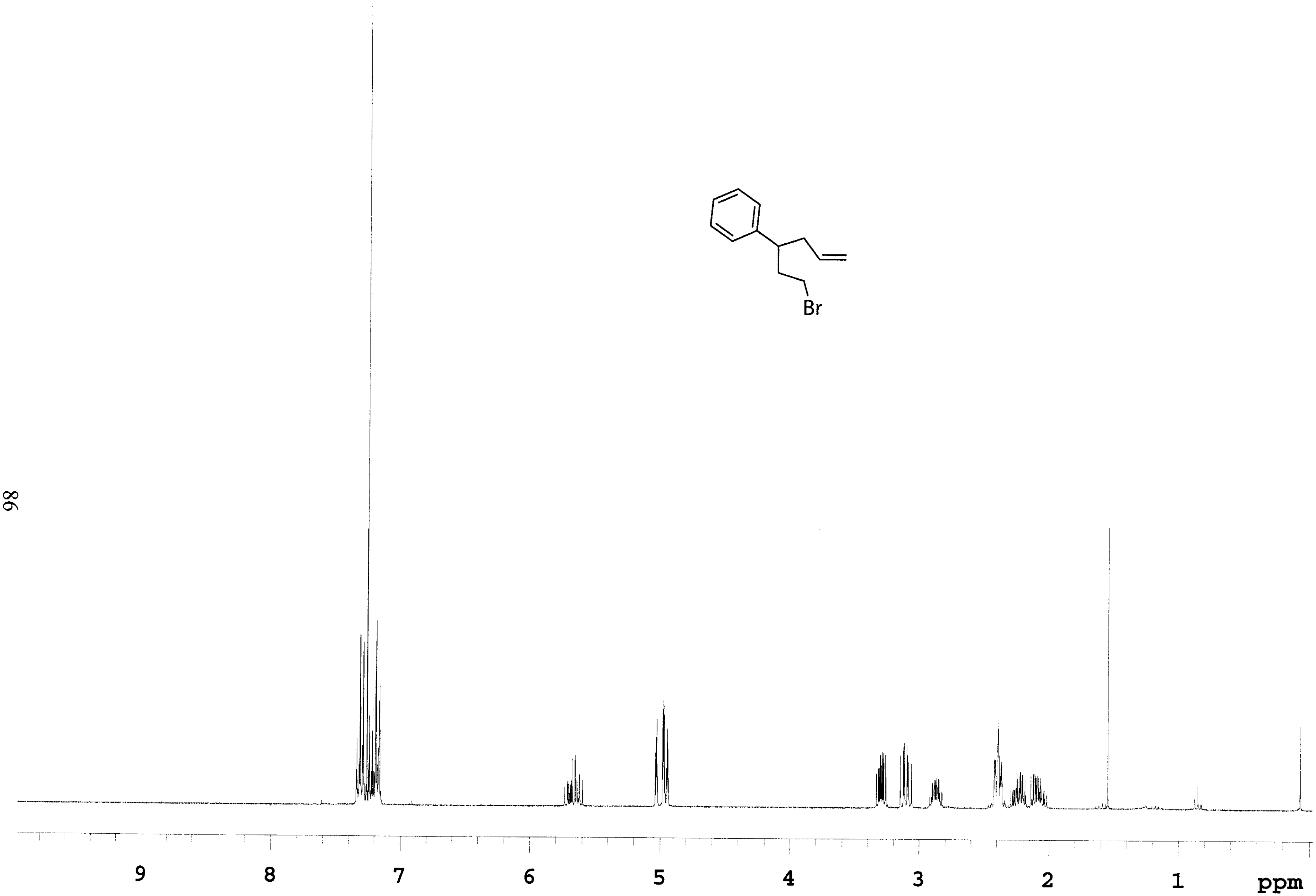
Appendix C

Selected ^{1}H NMR and ^{2}H NMR Spectra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5
4
3
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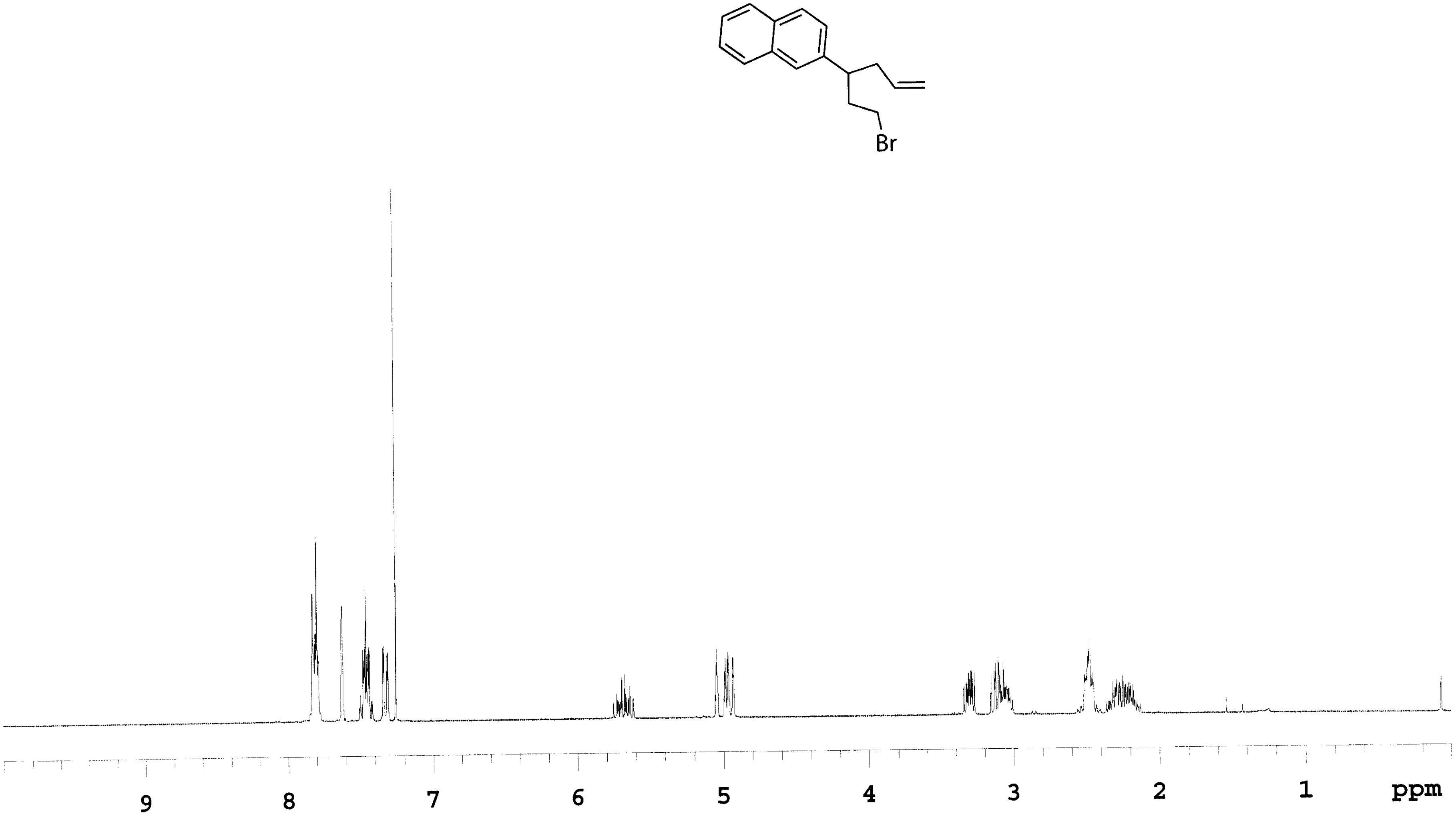
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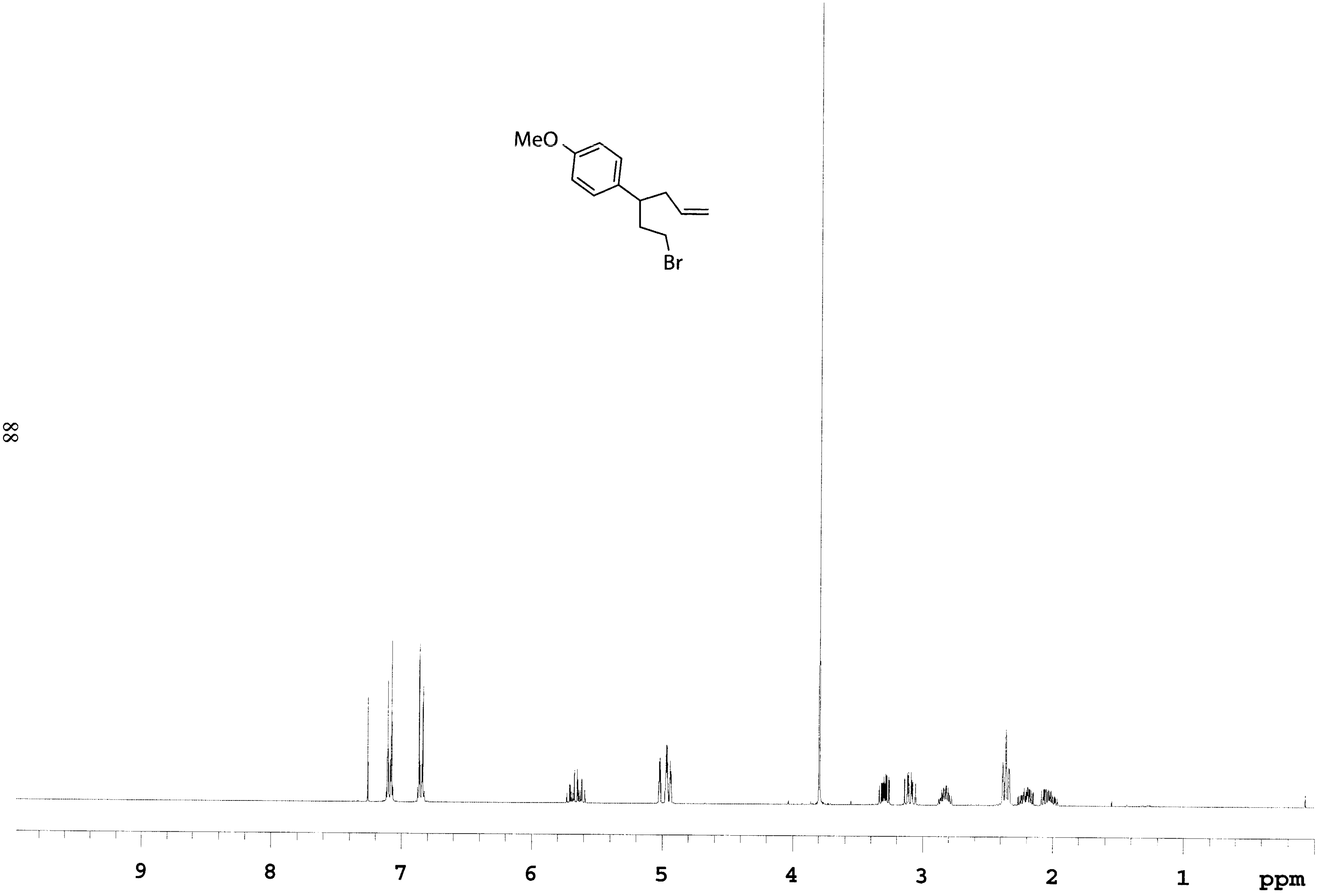
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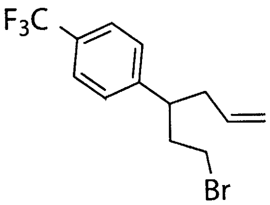
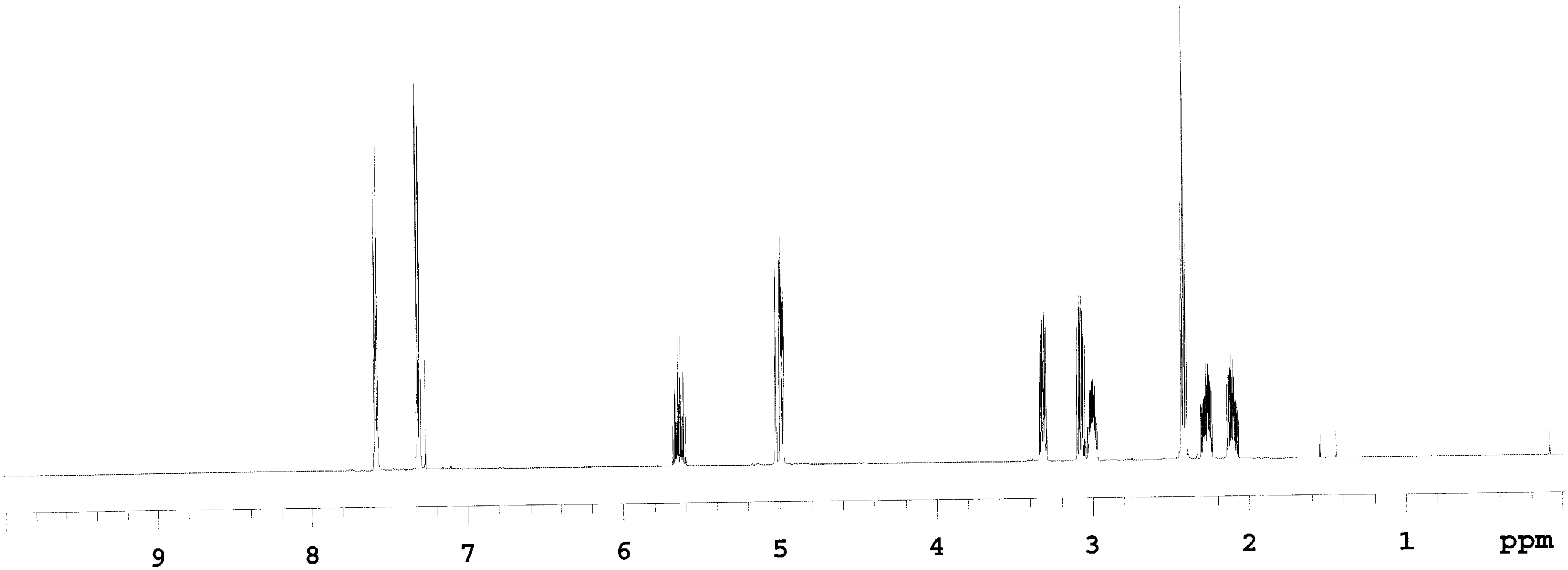
6
5
4
3
2
1
ppm


F3C
Br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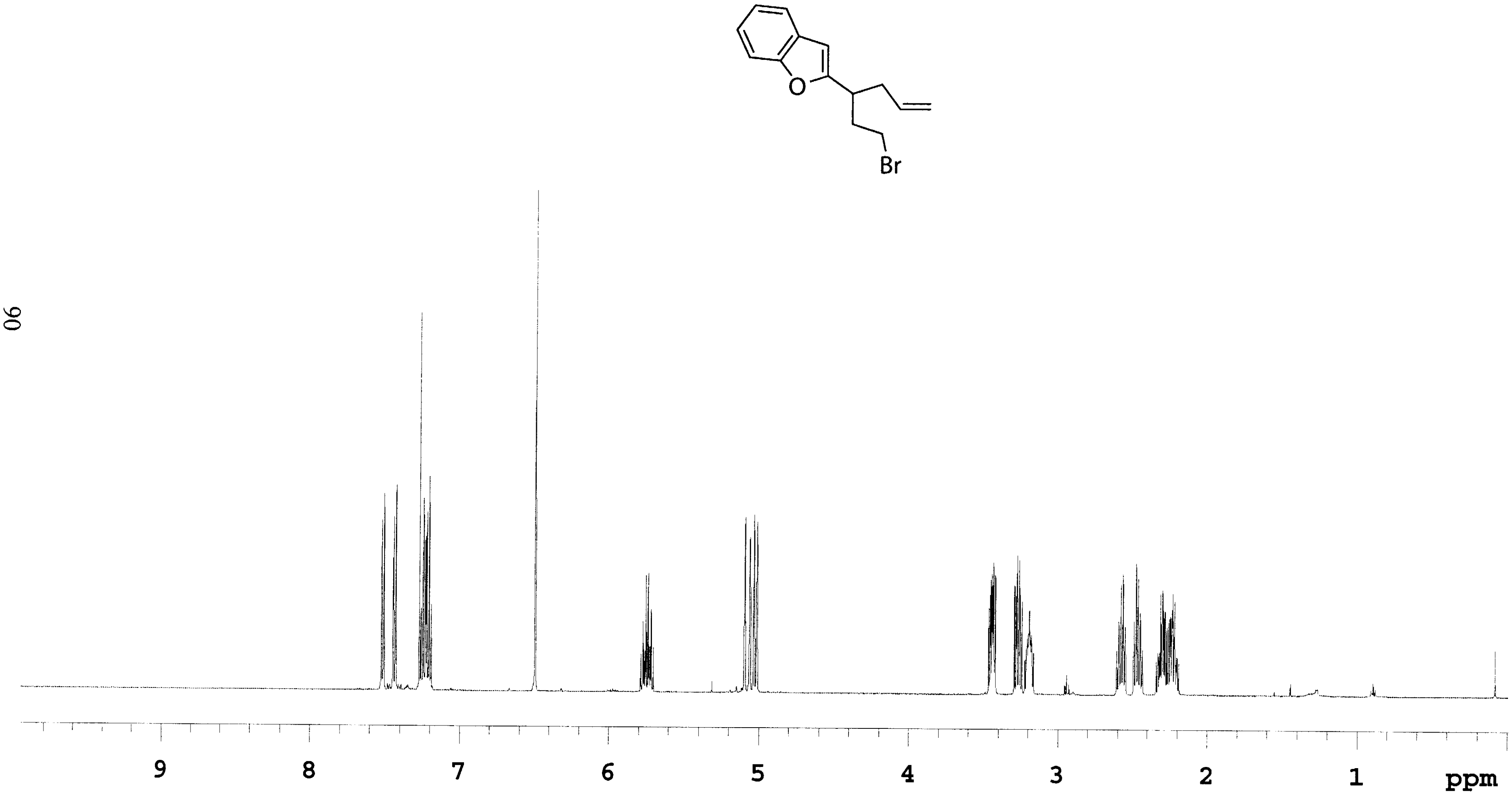
8
7
6
5
4
3
2
1
ppm


O
Br
9
8
7
6
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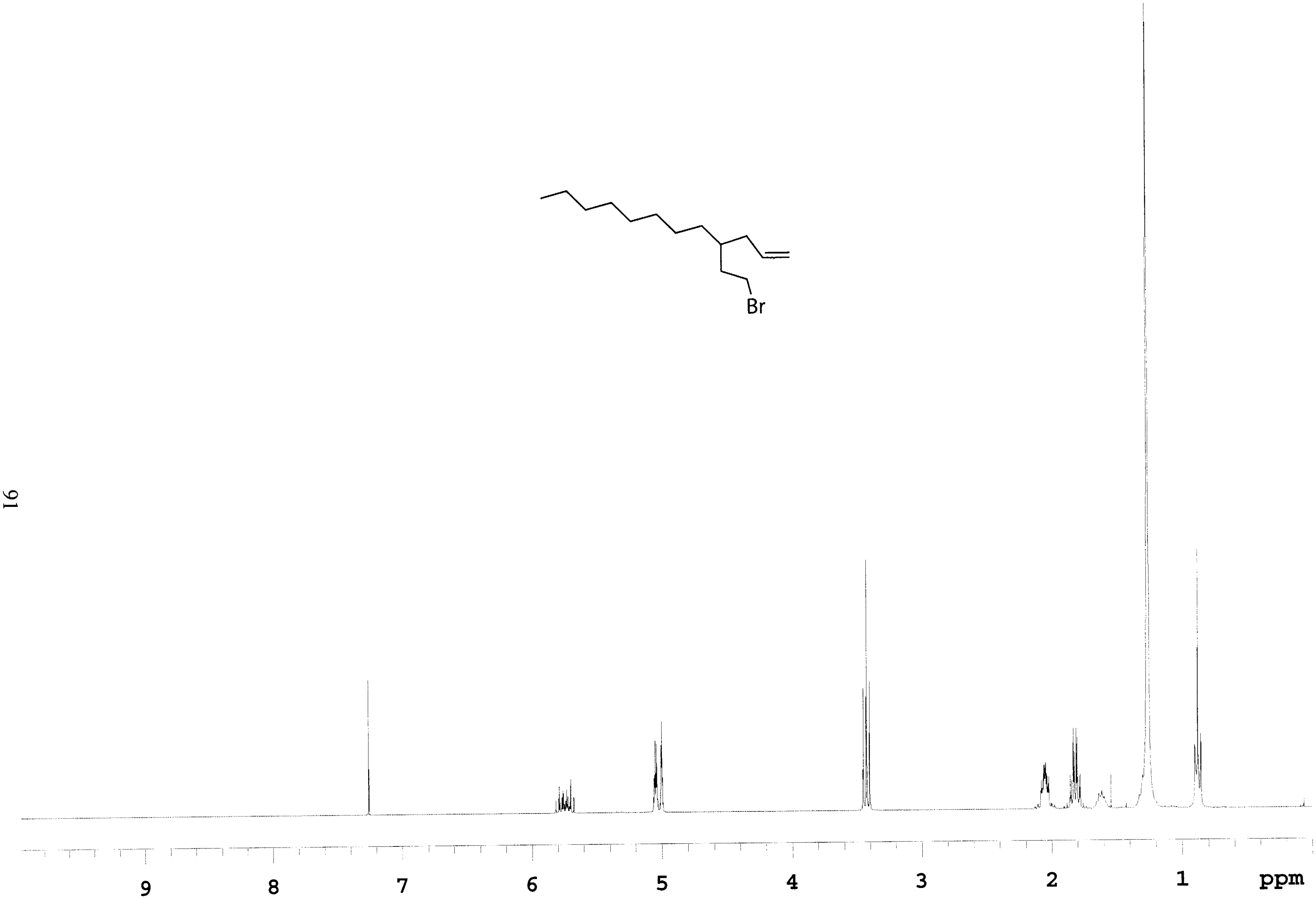
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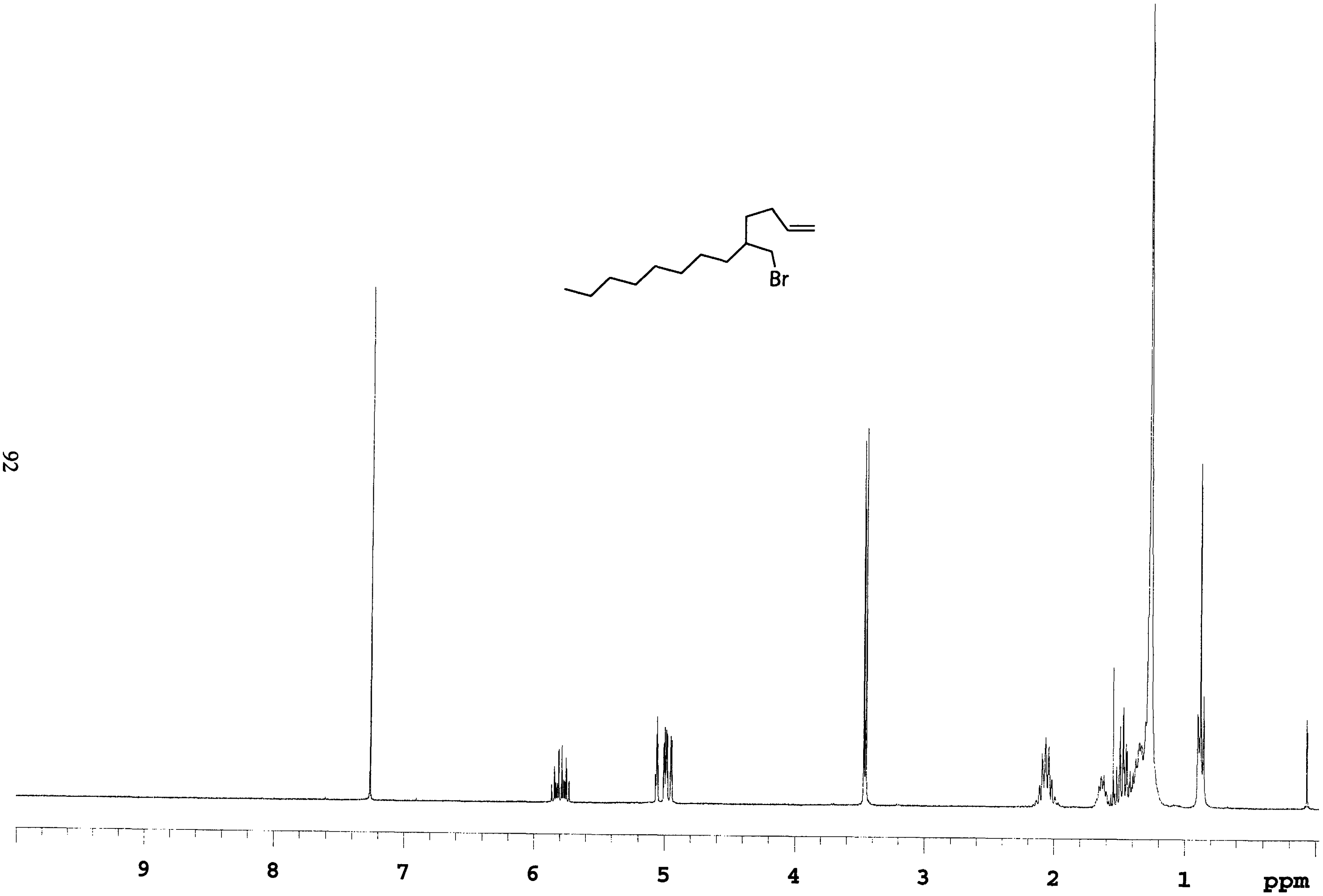
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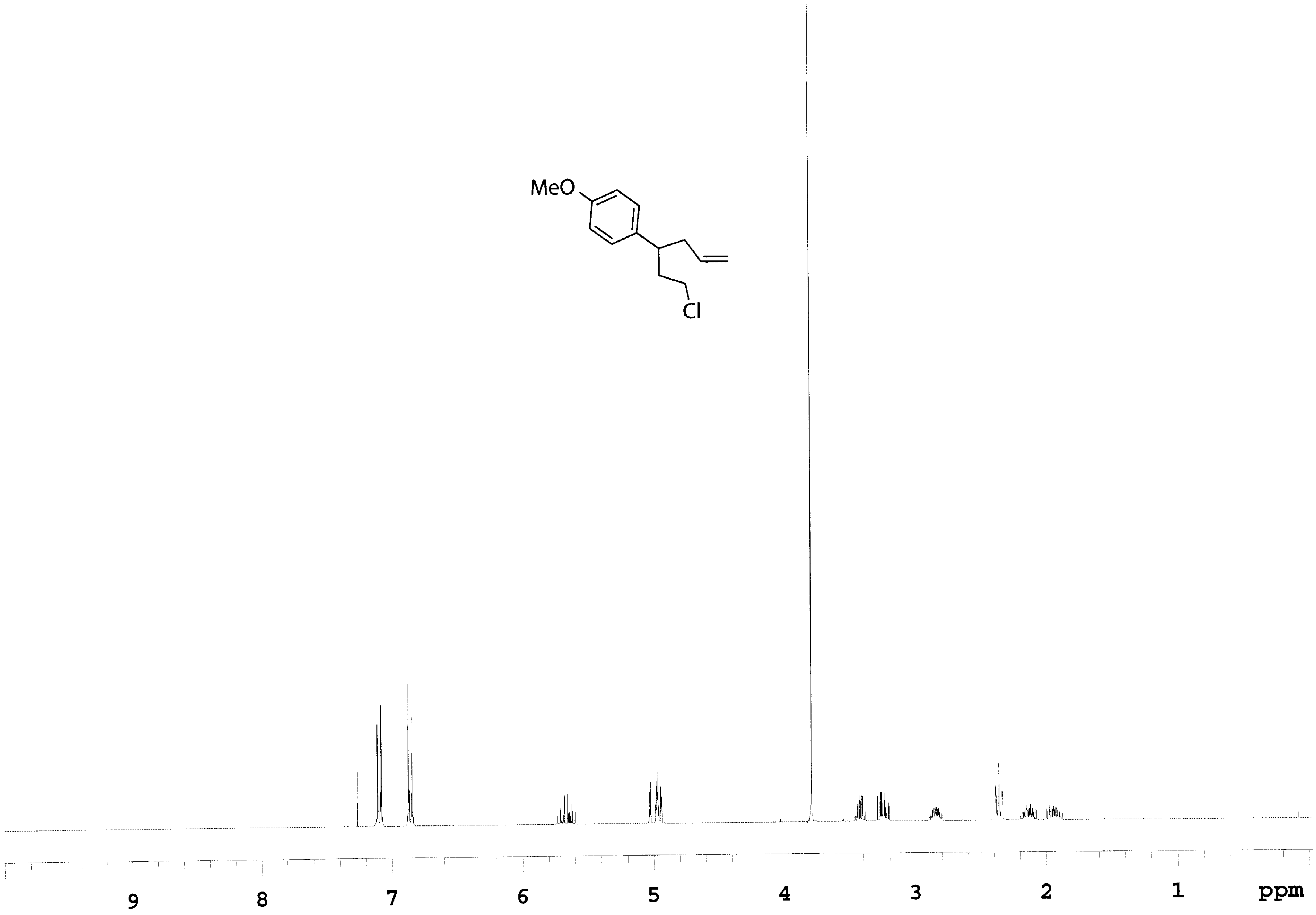
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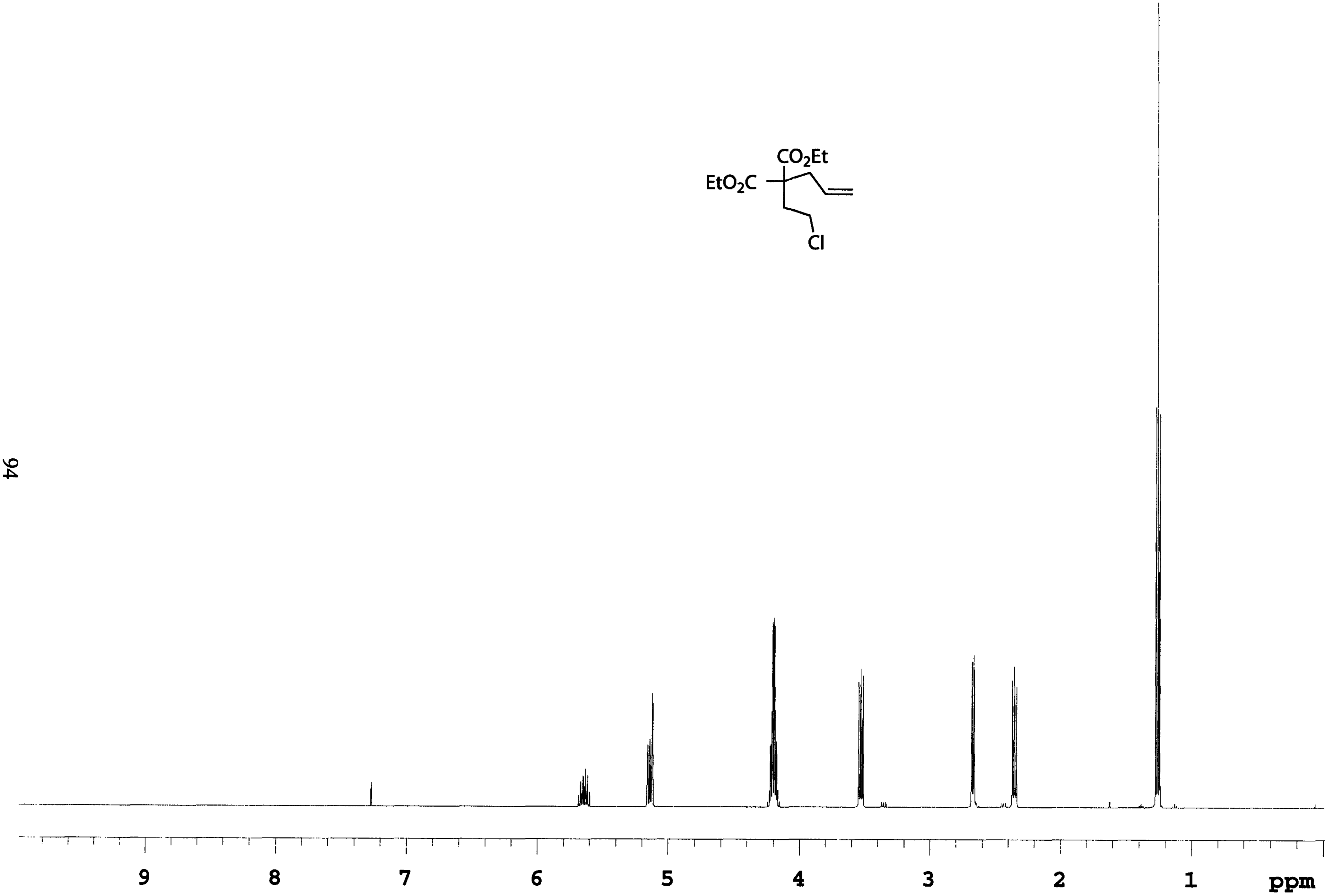
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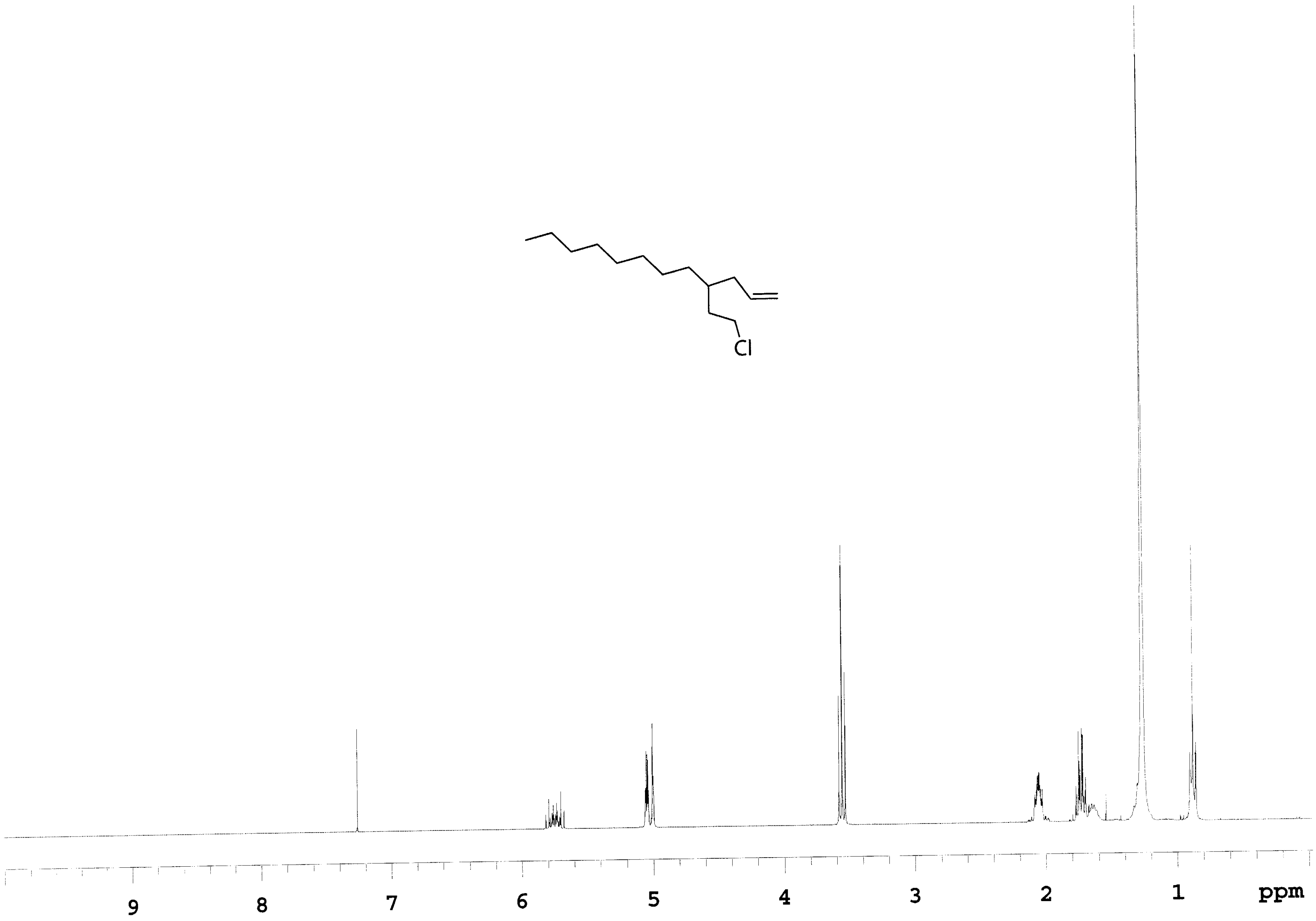
Cl
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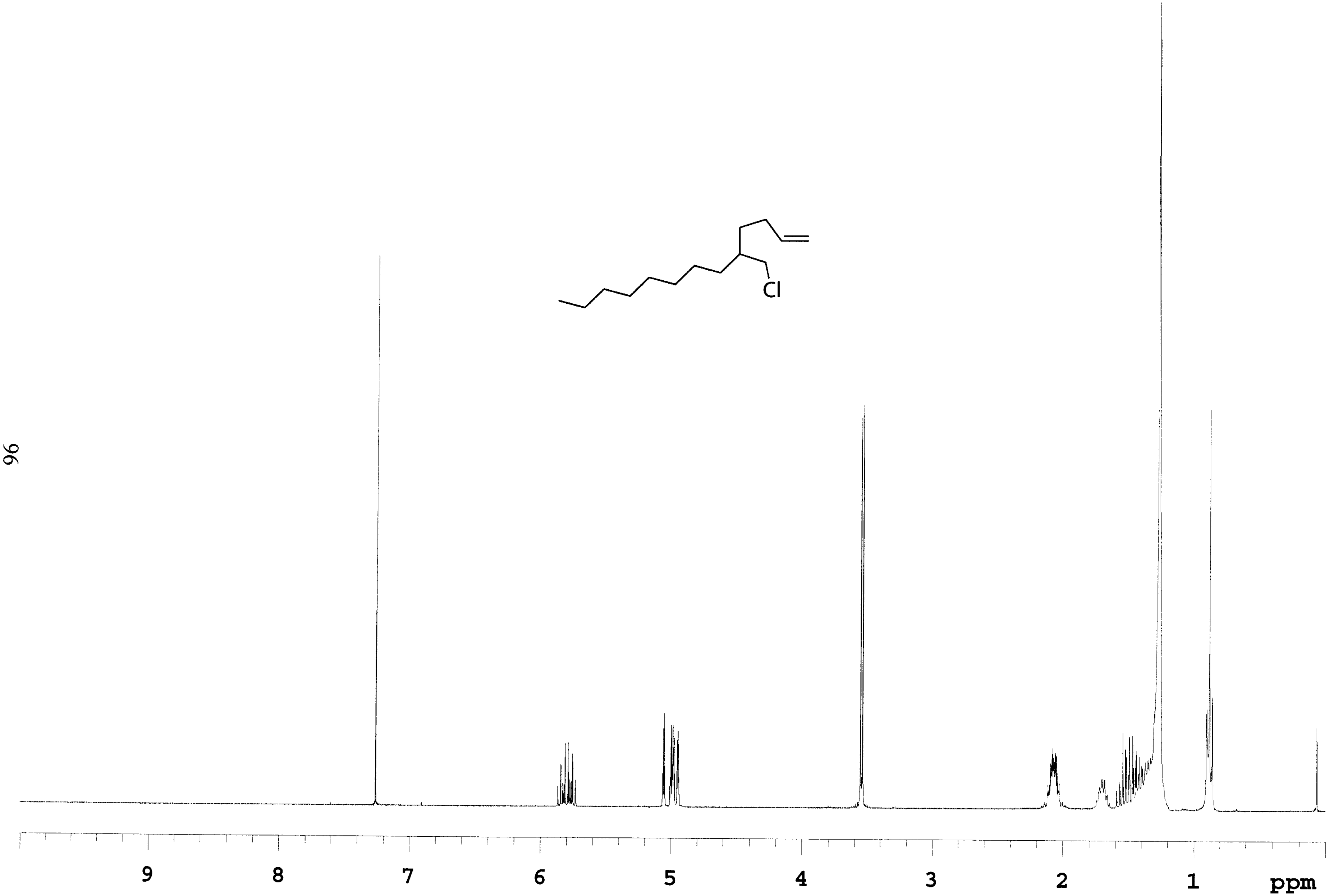
8
7
6
5
4
3
2
1
ppm


Cl
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8
7
6
5
4
3
2
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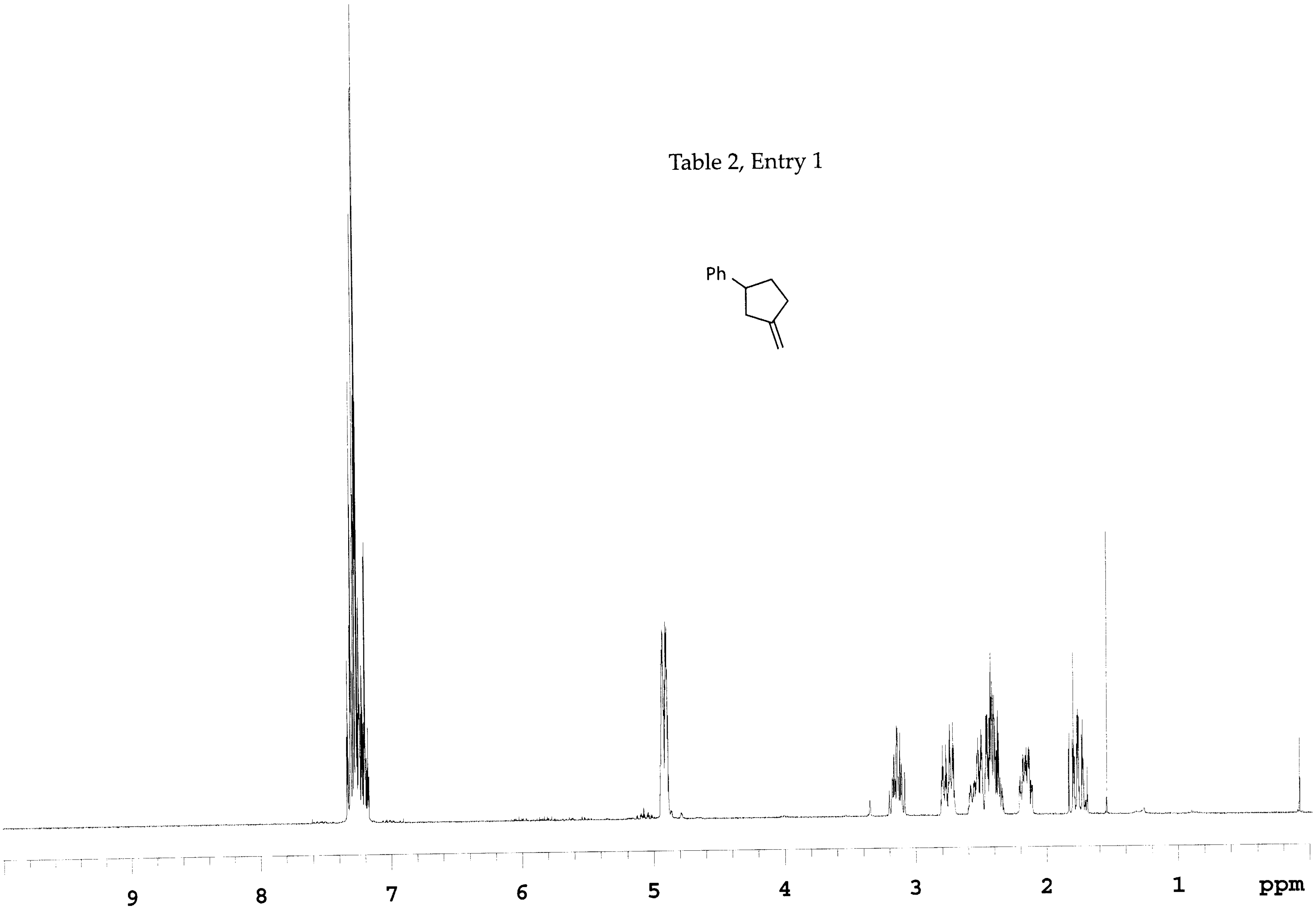
ppm



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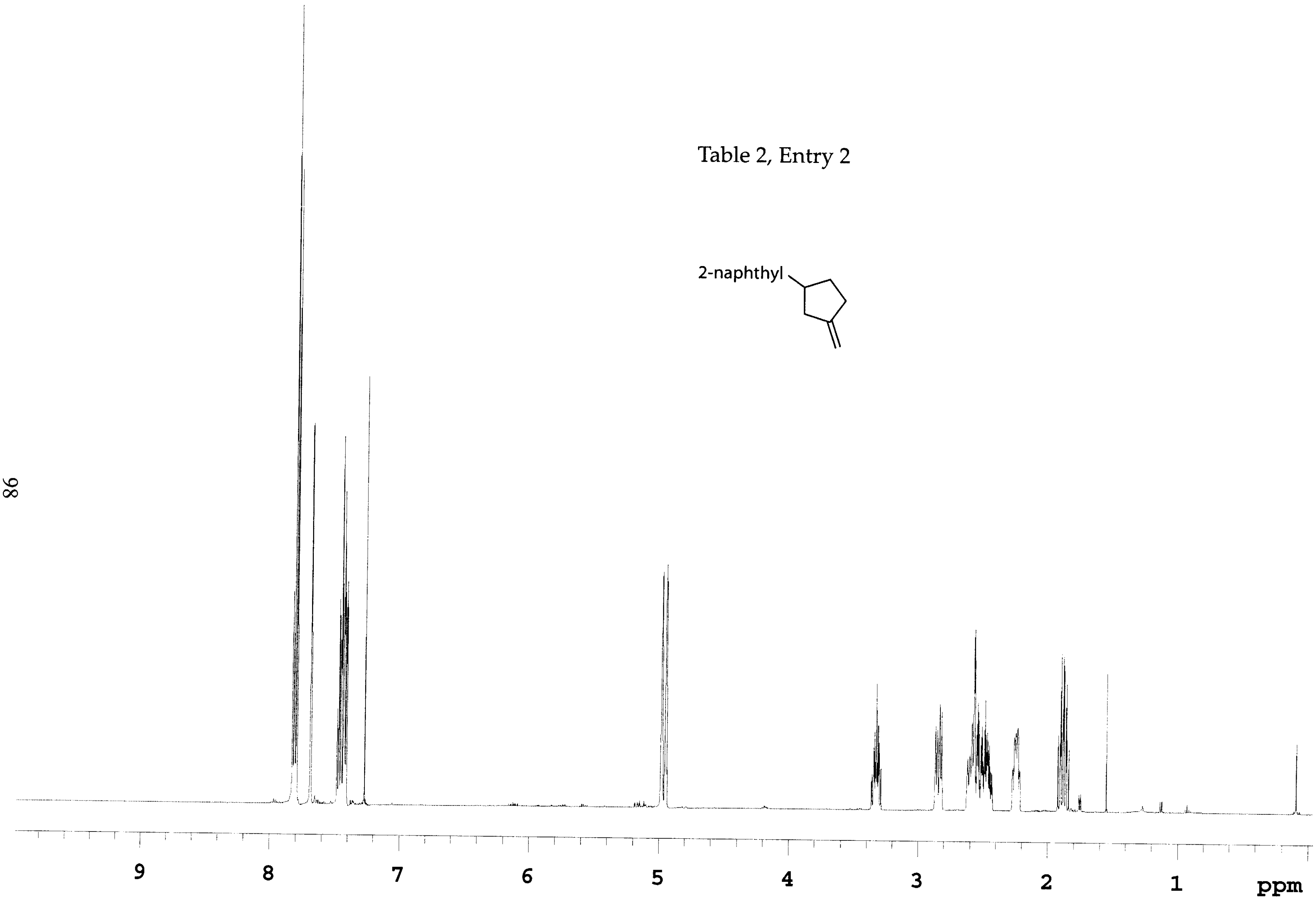

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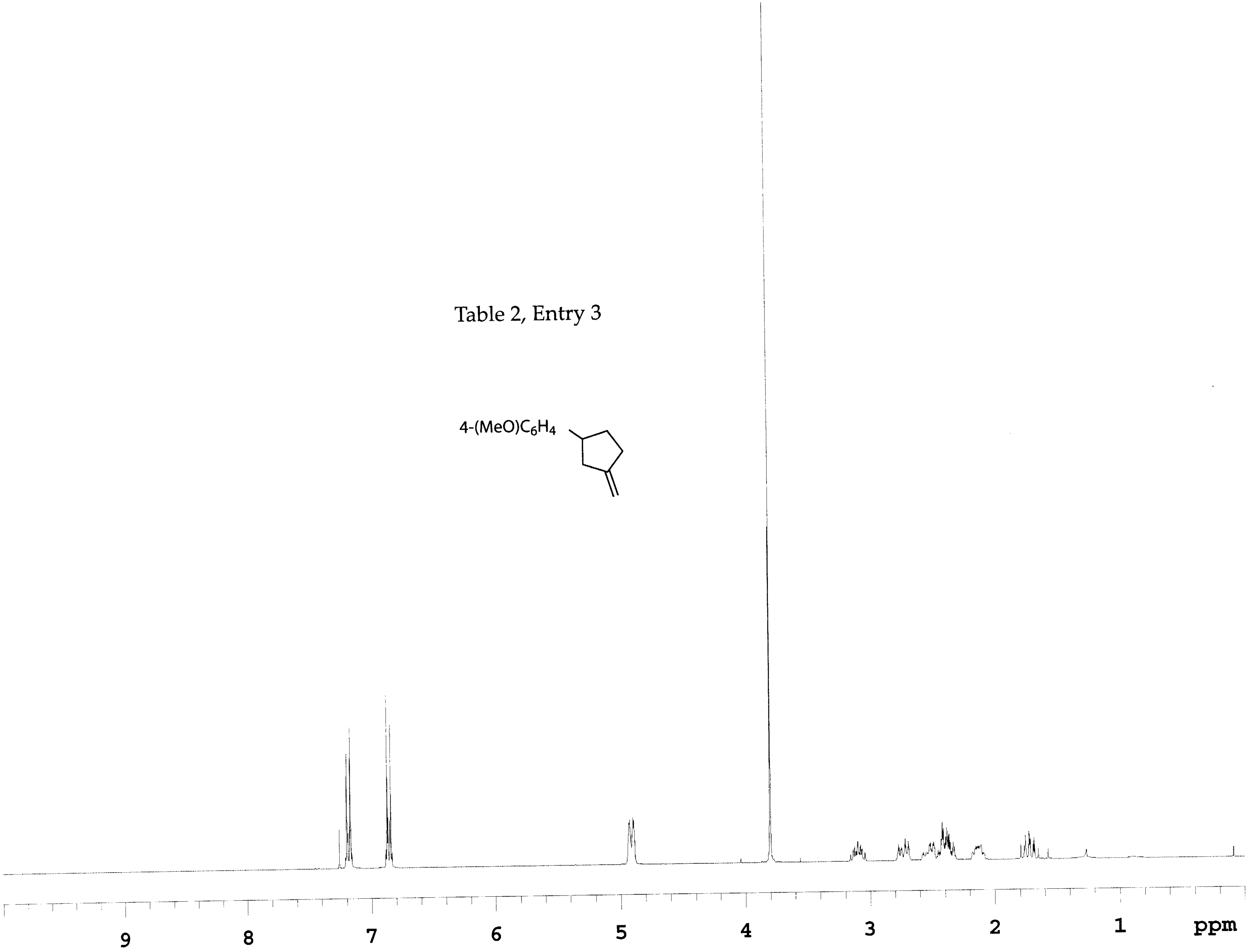
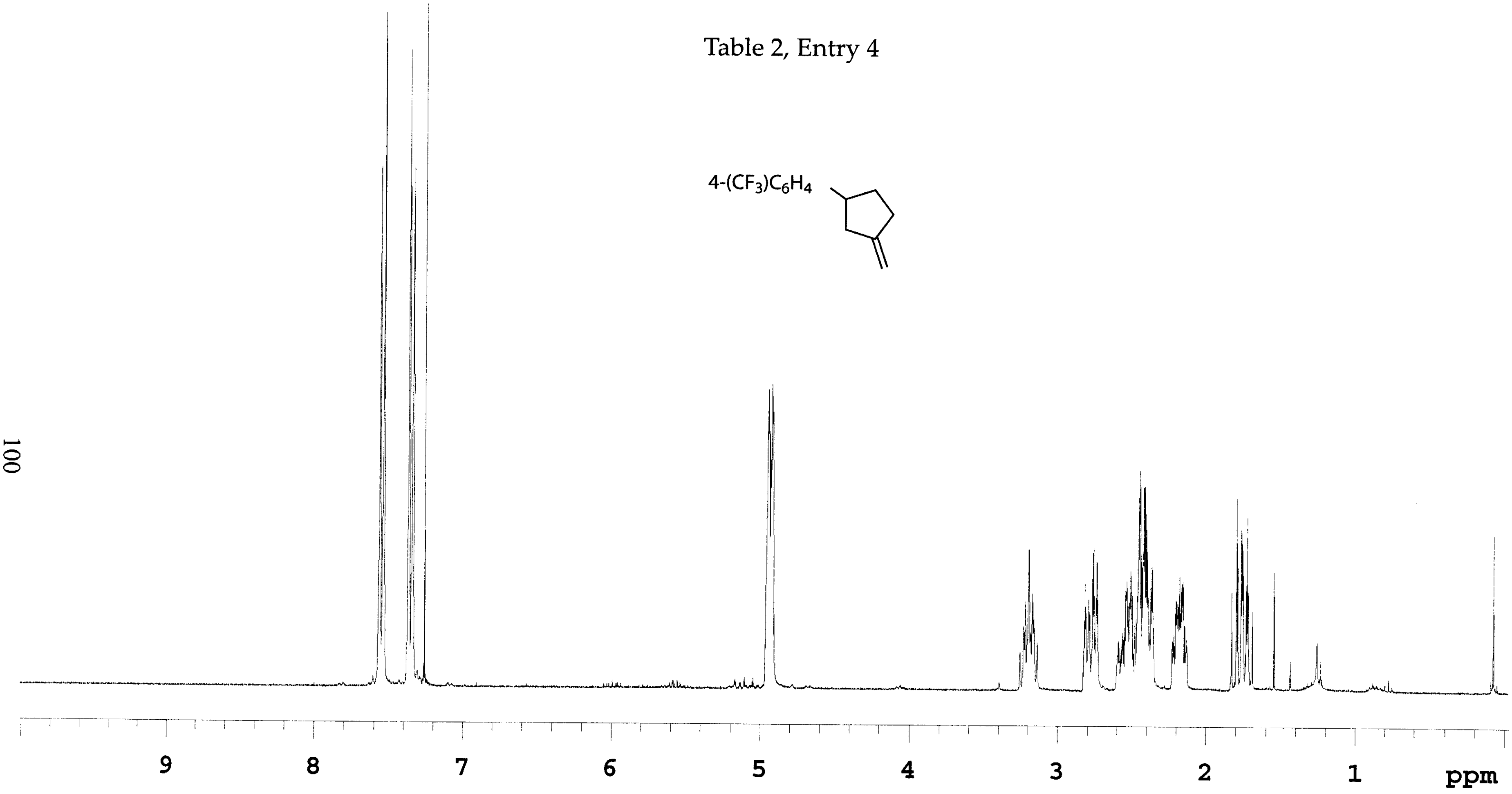


Table 2, Entry 3

Table 2, Entry 4



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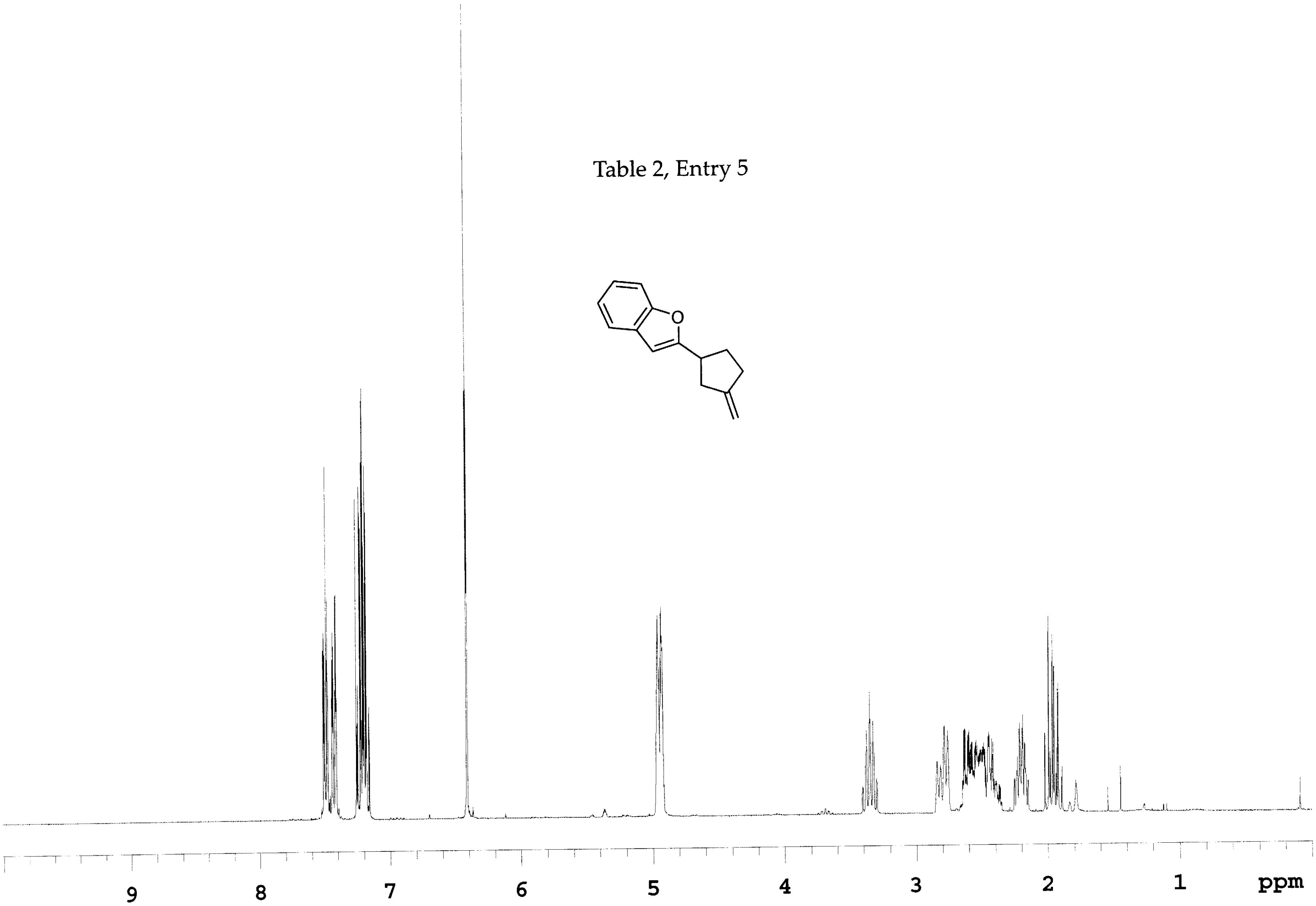

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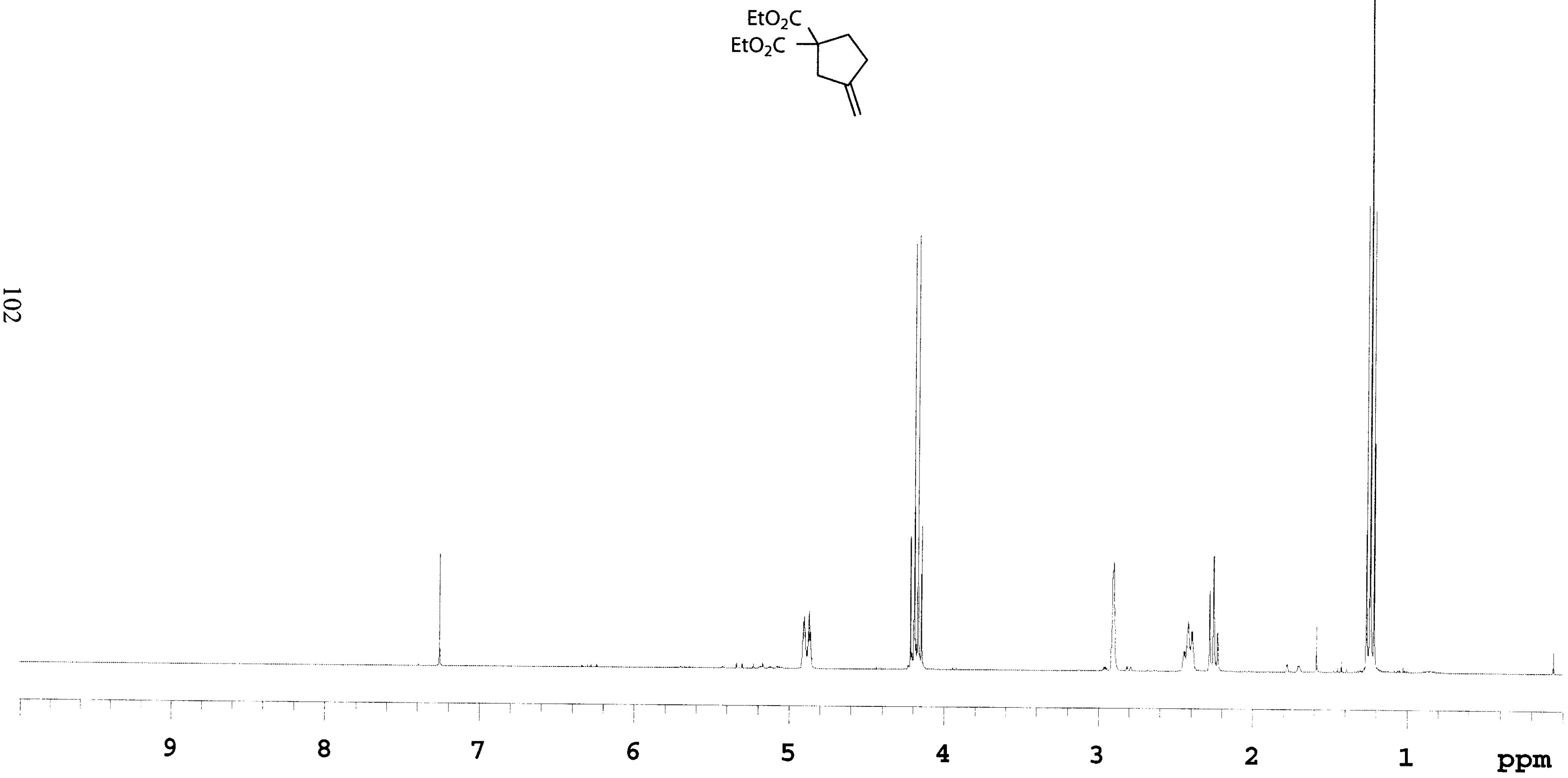

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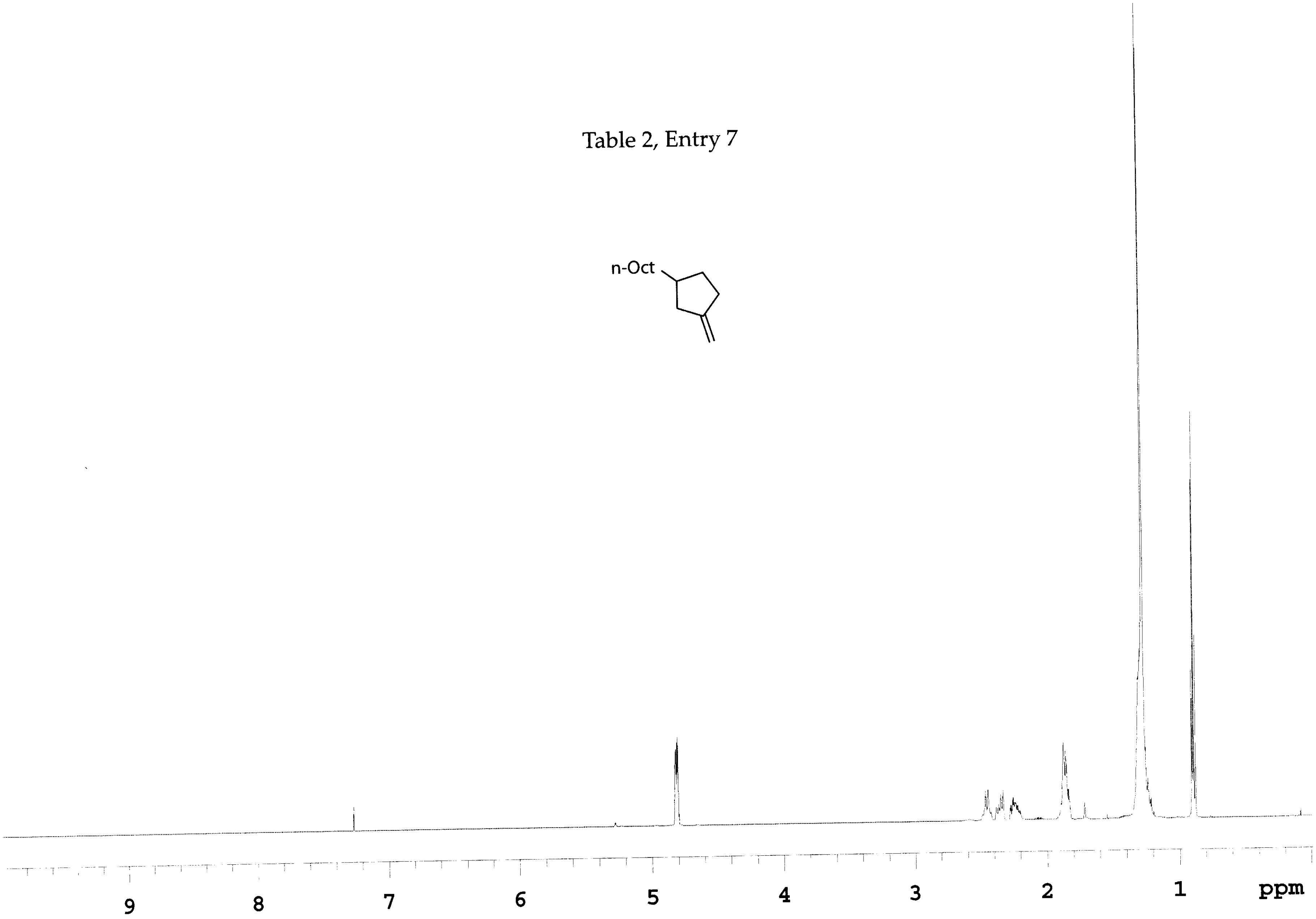

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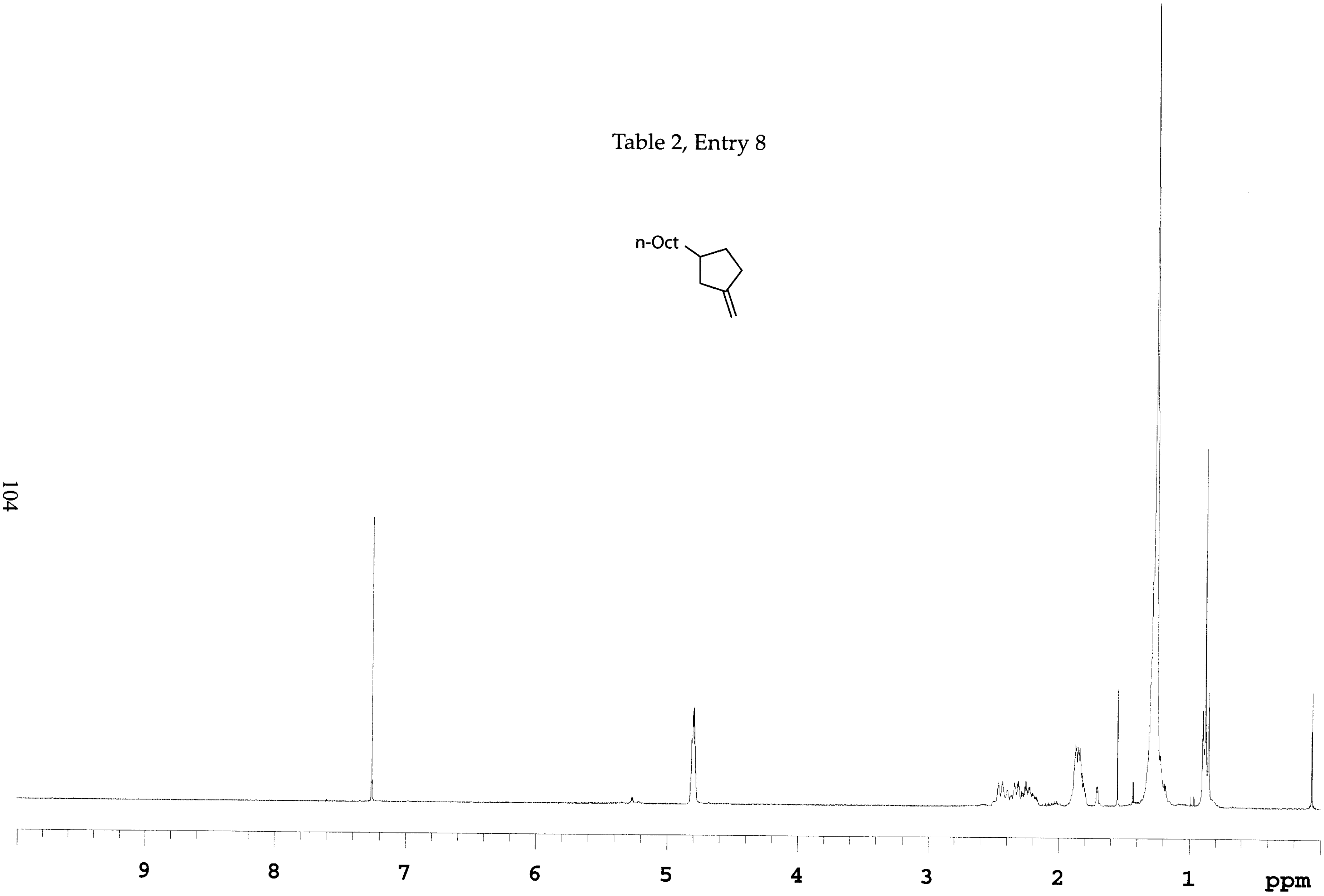

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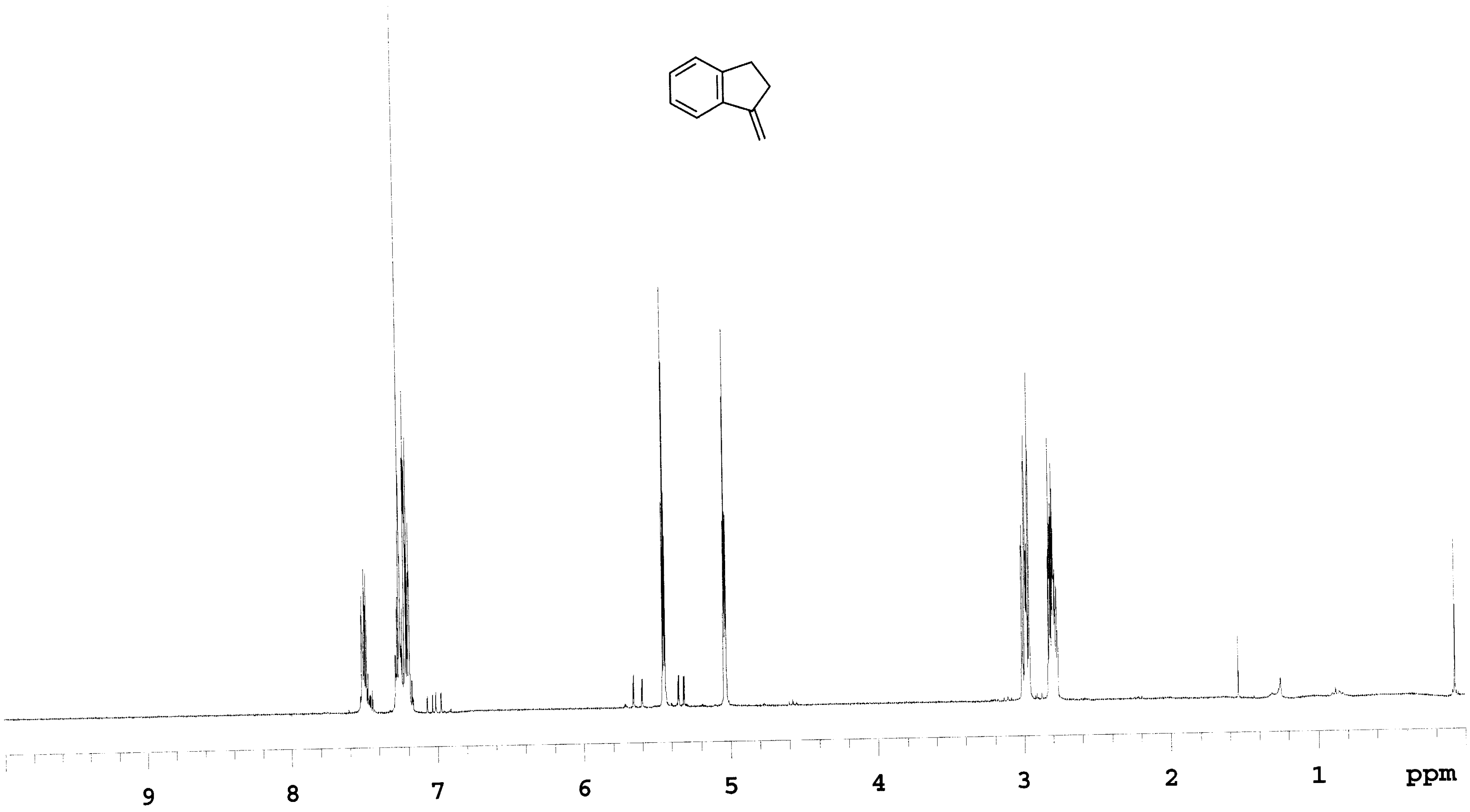

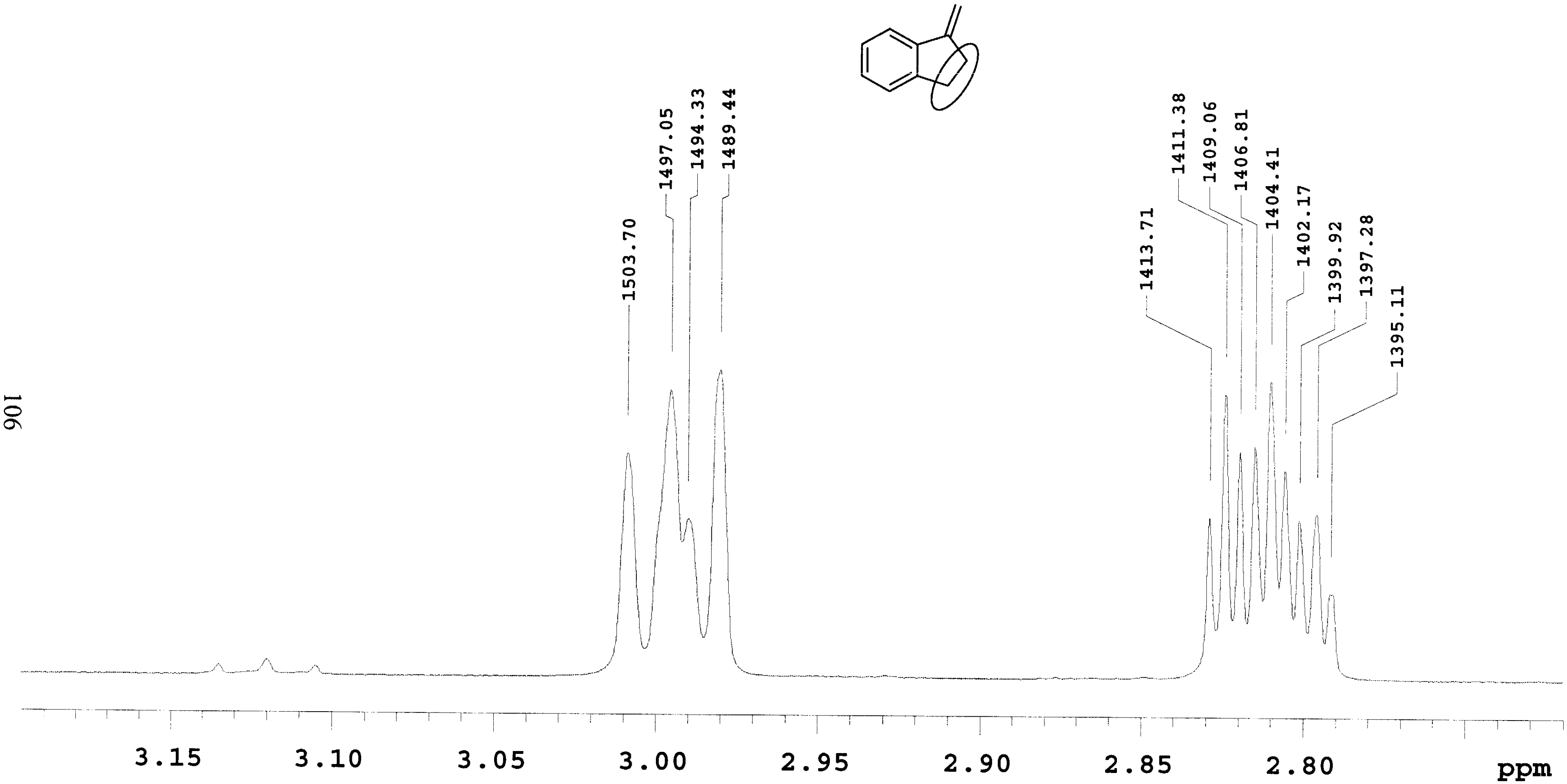
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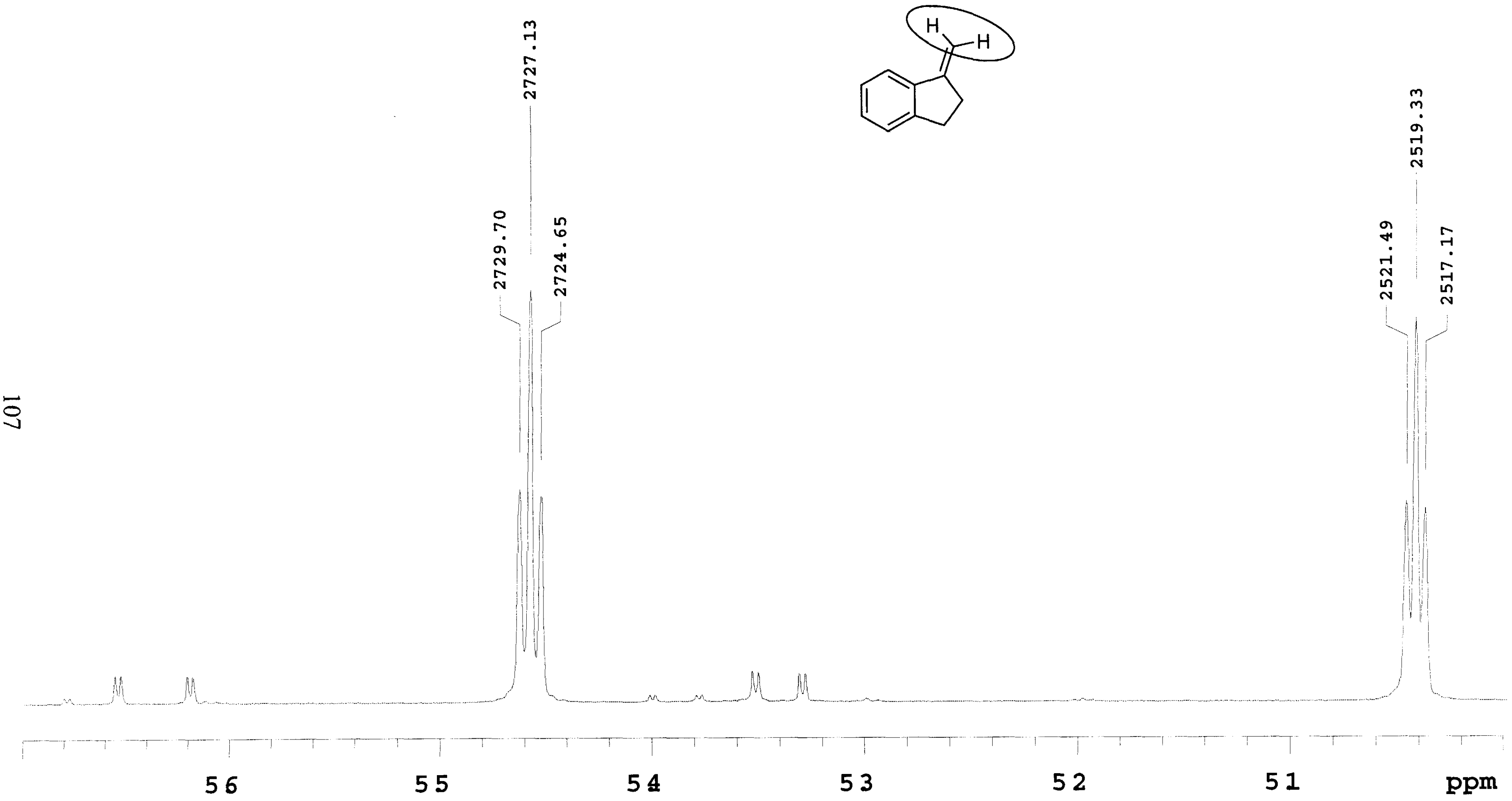
1497.05
1494.33
1489.44
1413.71
1411.38
1409.06
1406.81
1404.41
1402.17
1399.92
1397.28
1395.11
3.15
3.10
3.05
3.00
2.95
2.90
2.85
2.80
ppm



H
H
2729.70
2727.13
2724.65
2521.49
2519.33
2517.17
5 6
5 5
5 4
5 3
5 2
5 1
ppm

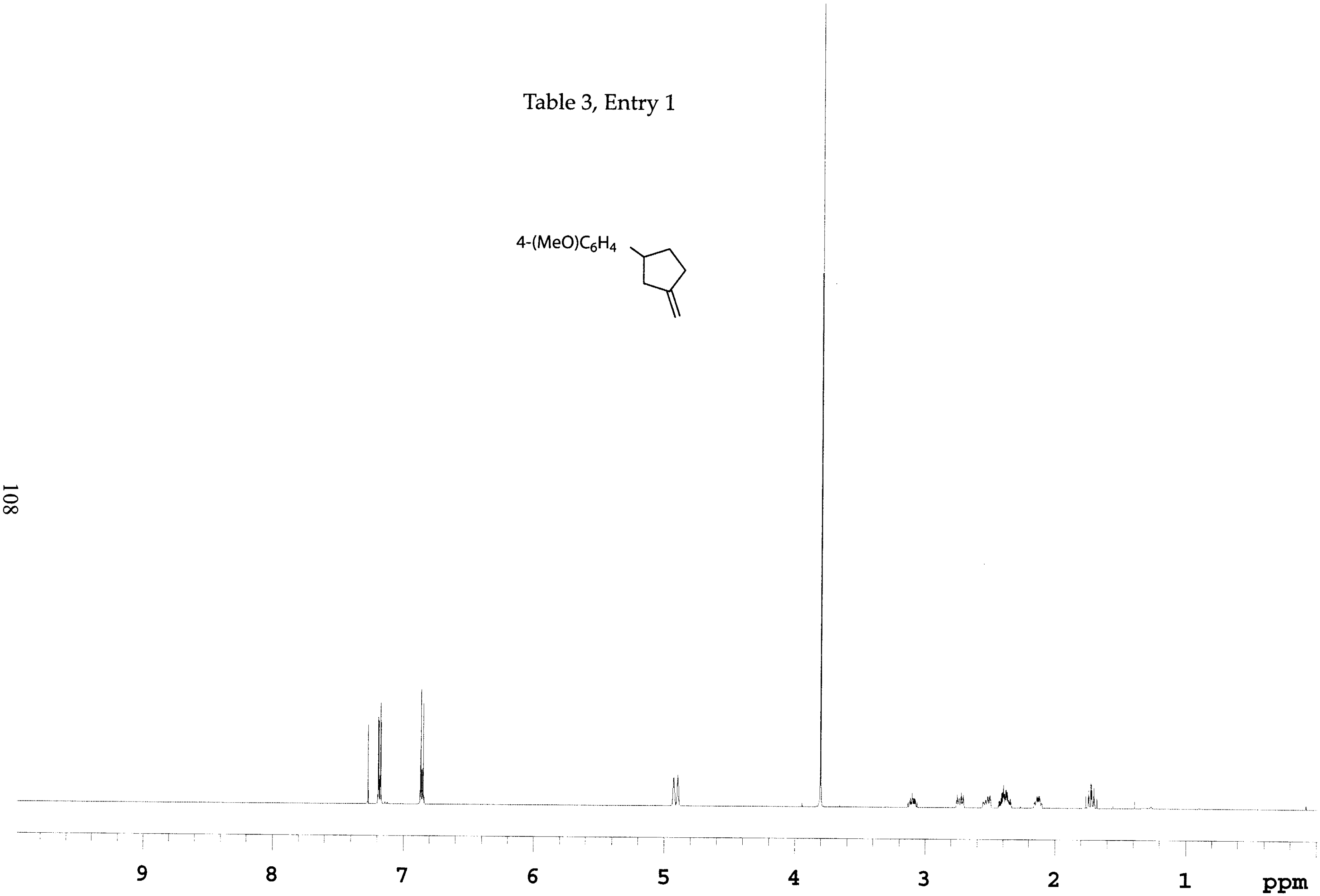
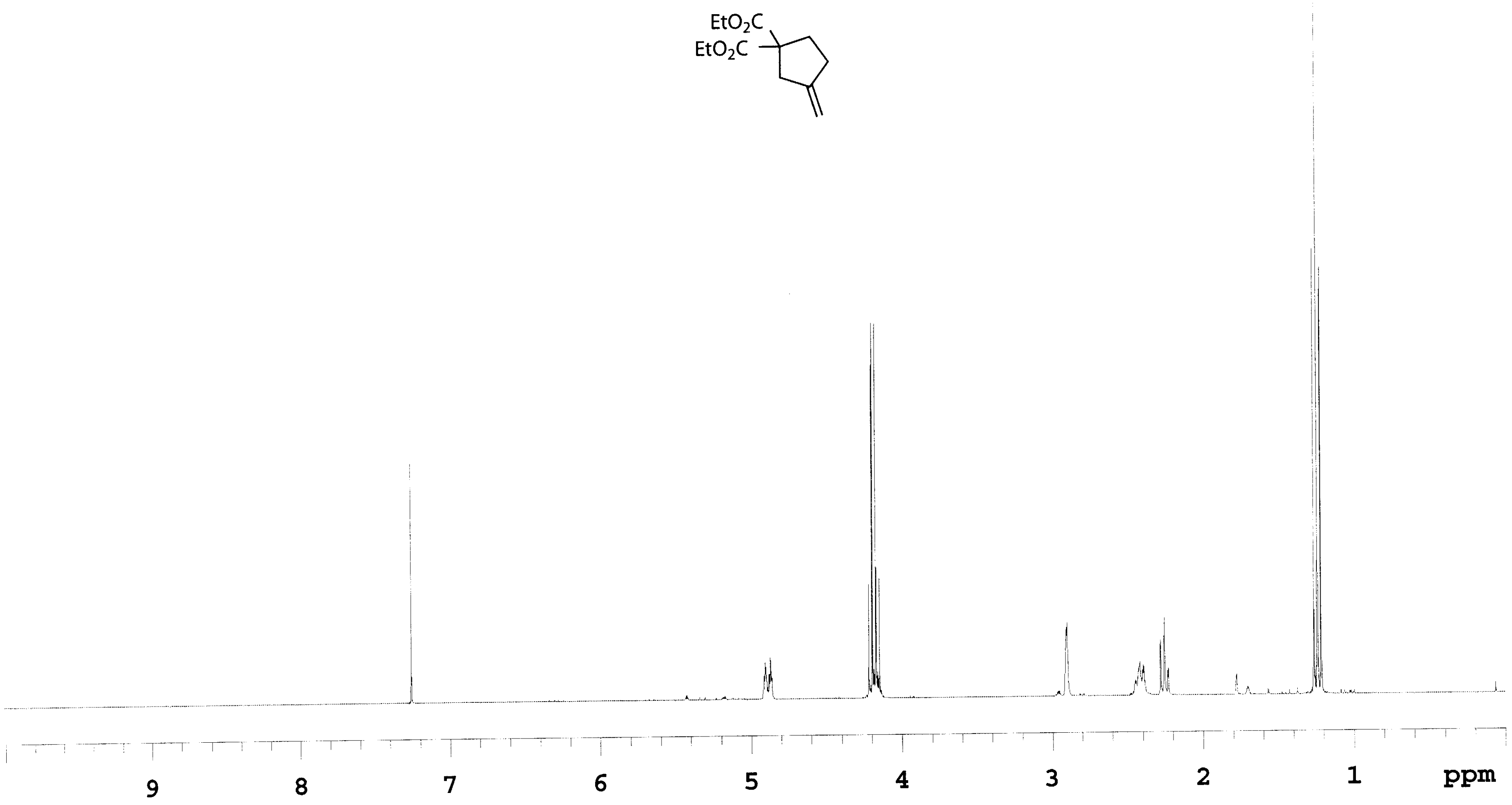


Table 3, Entry 1

Table 3, Entry 2



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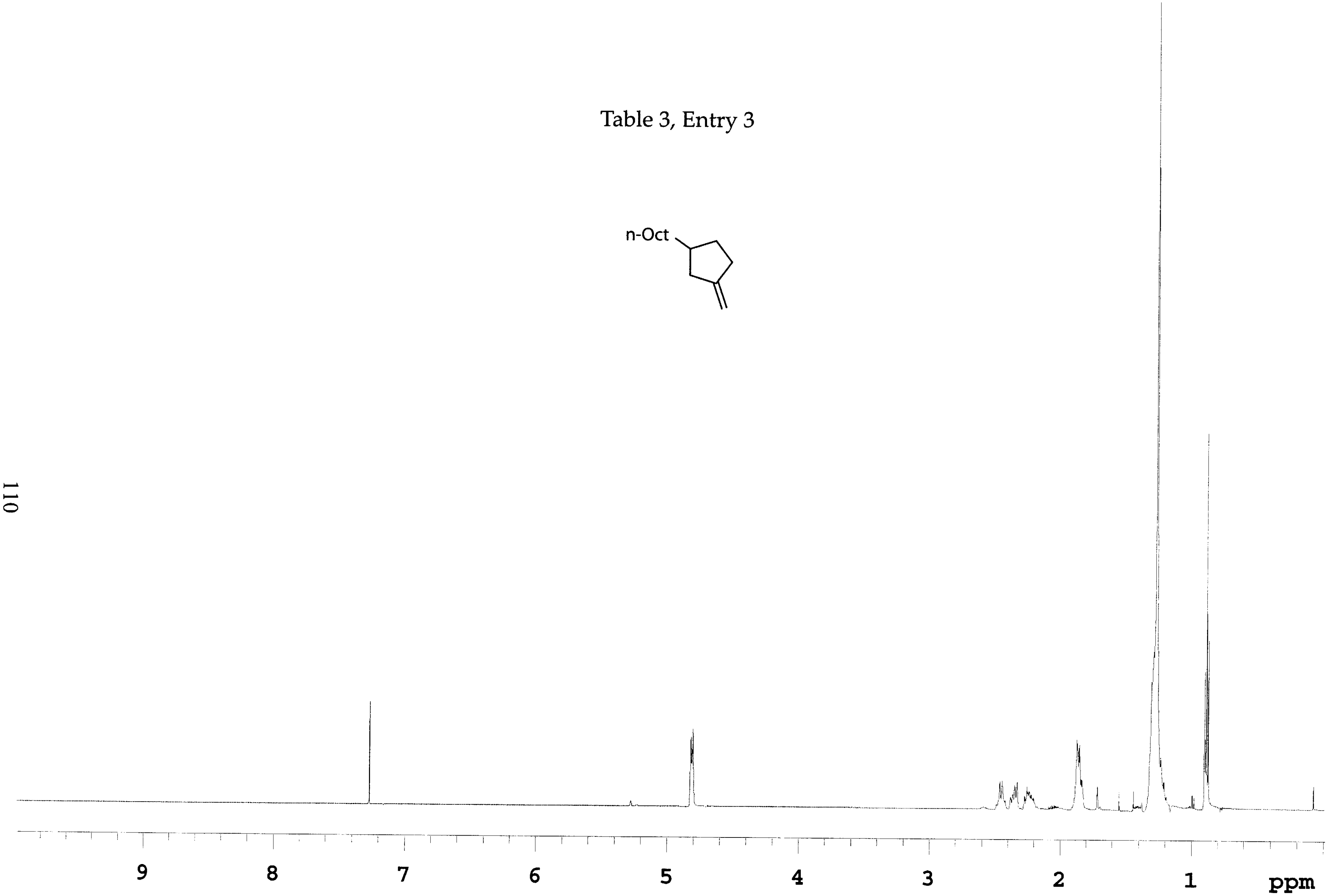

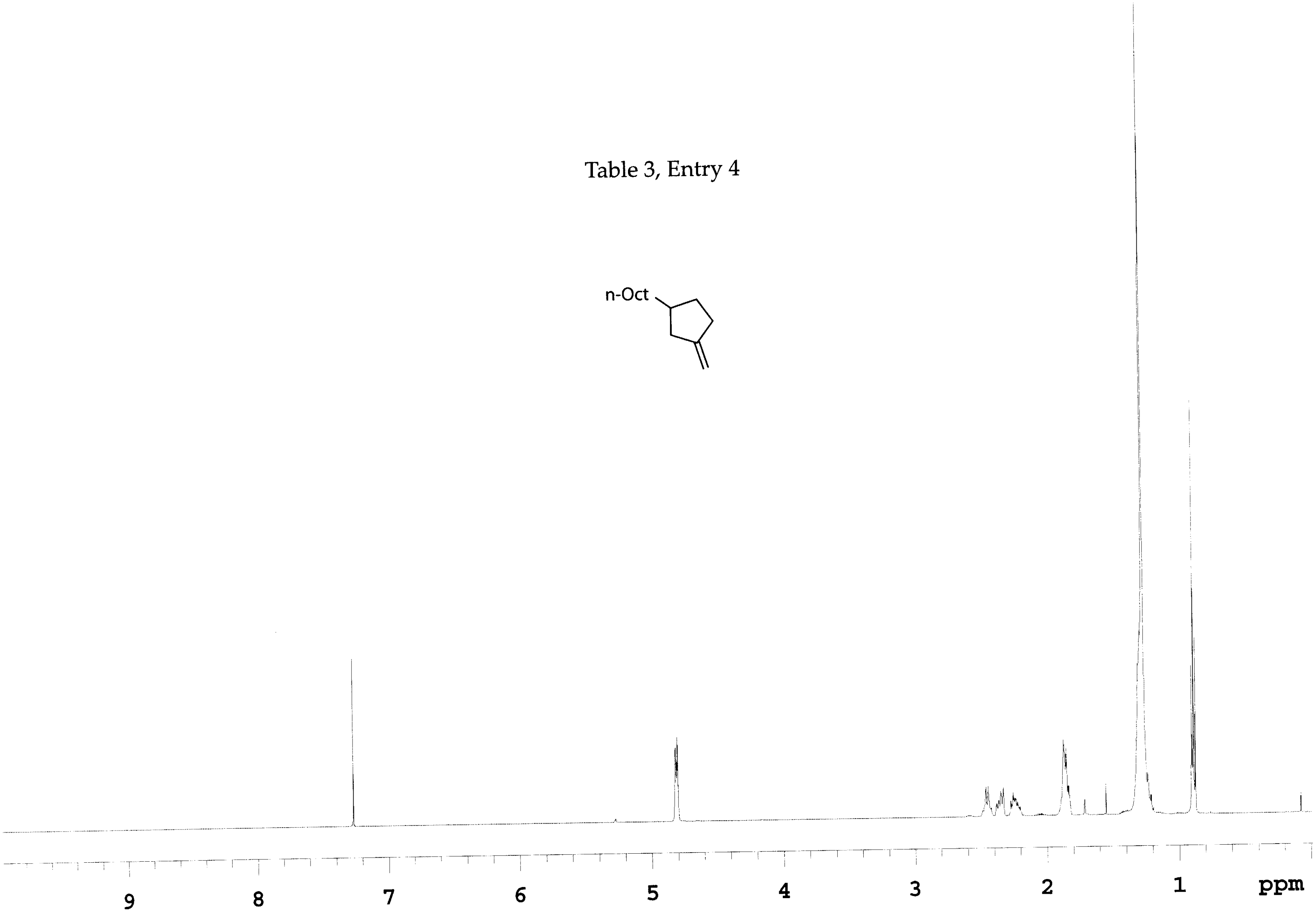

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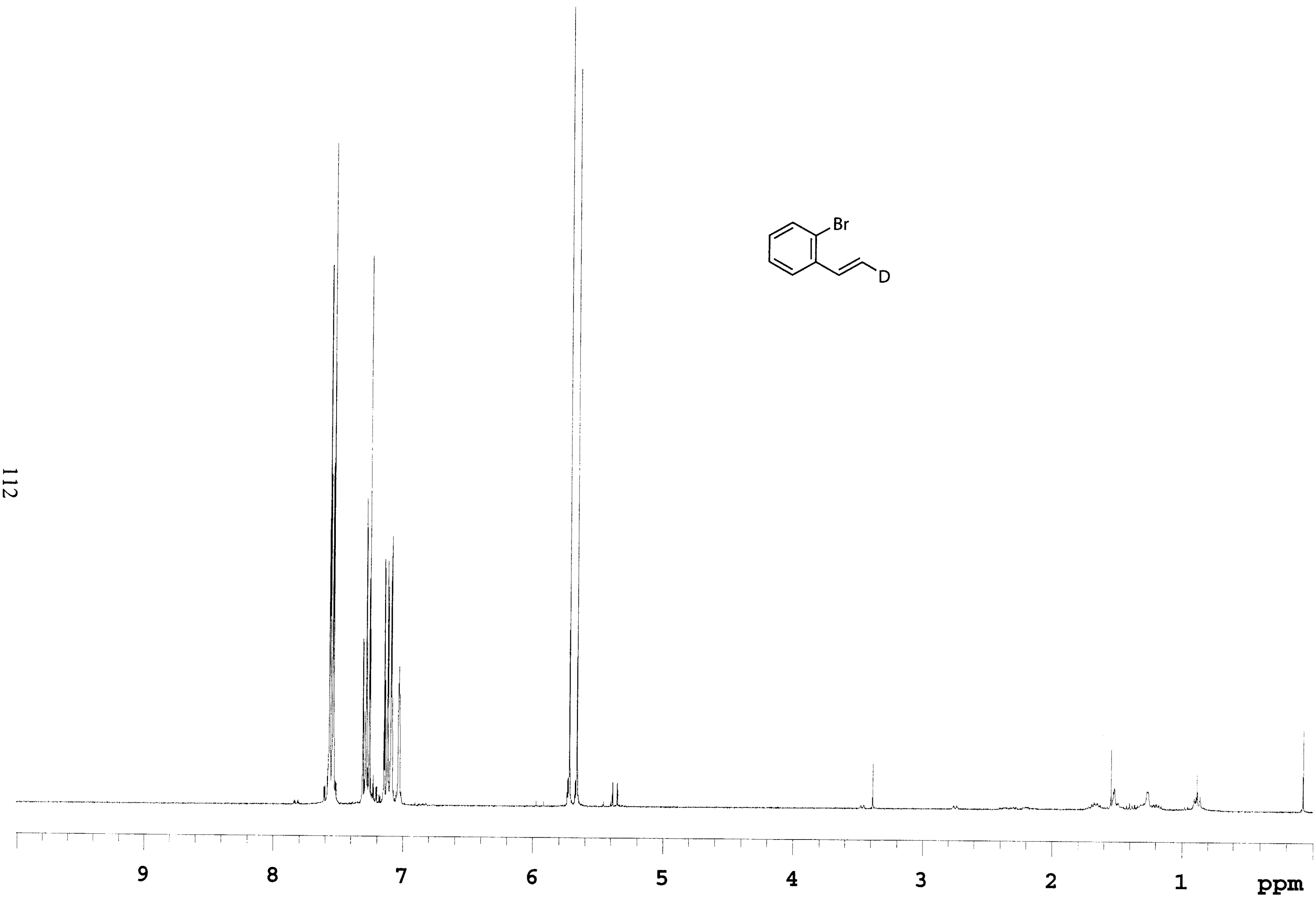
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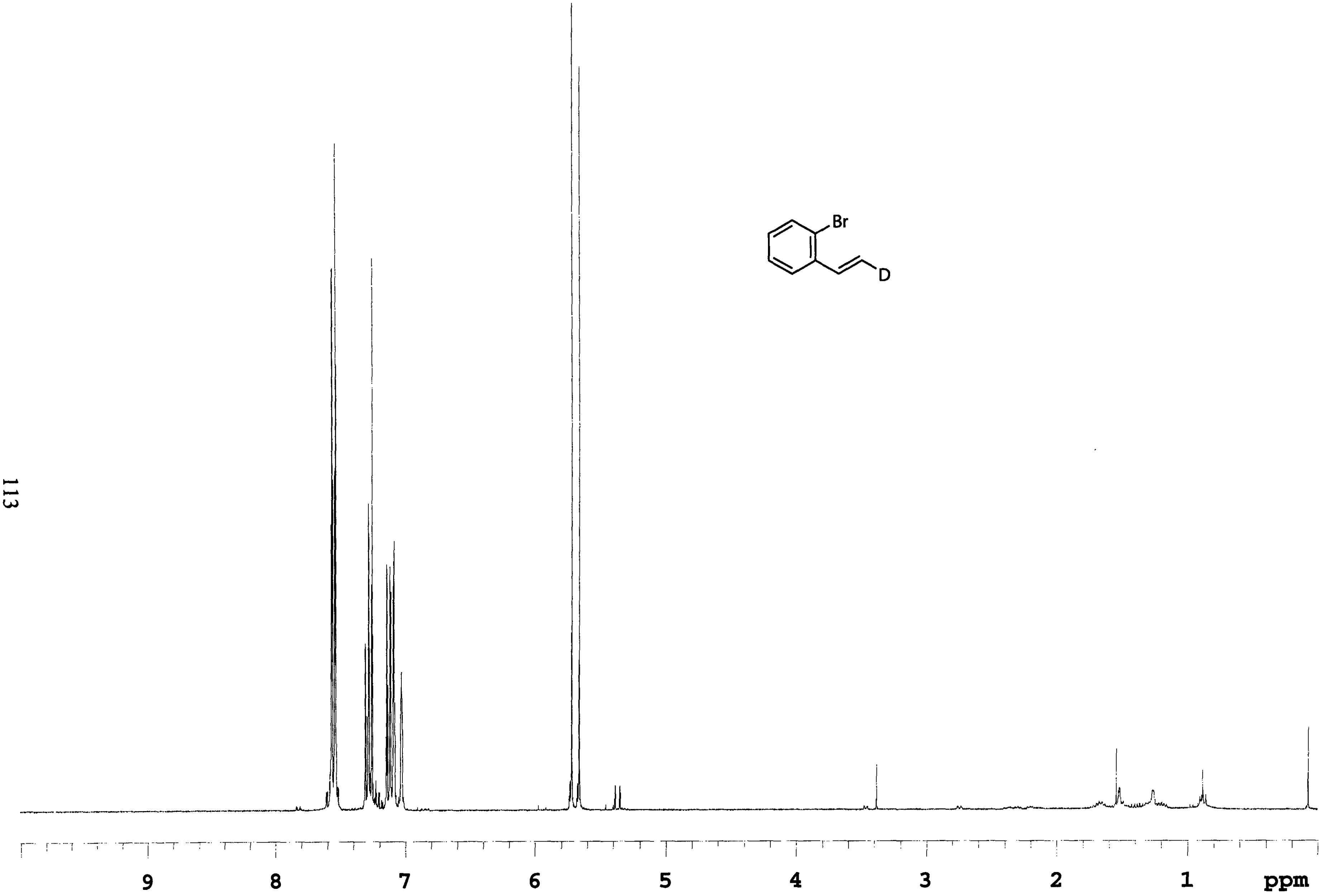
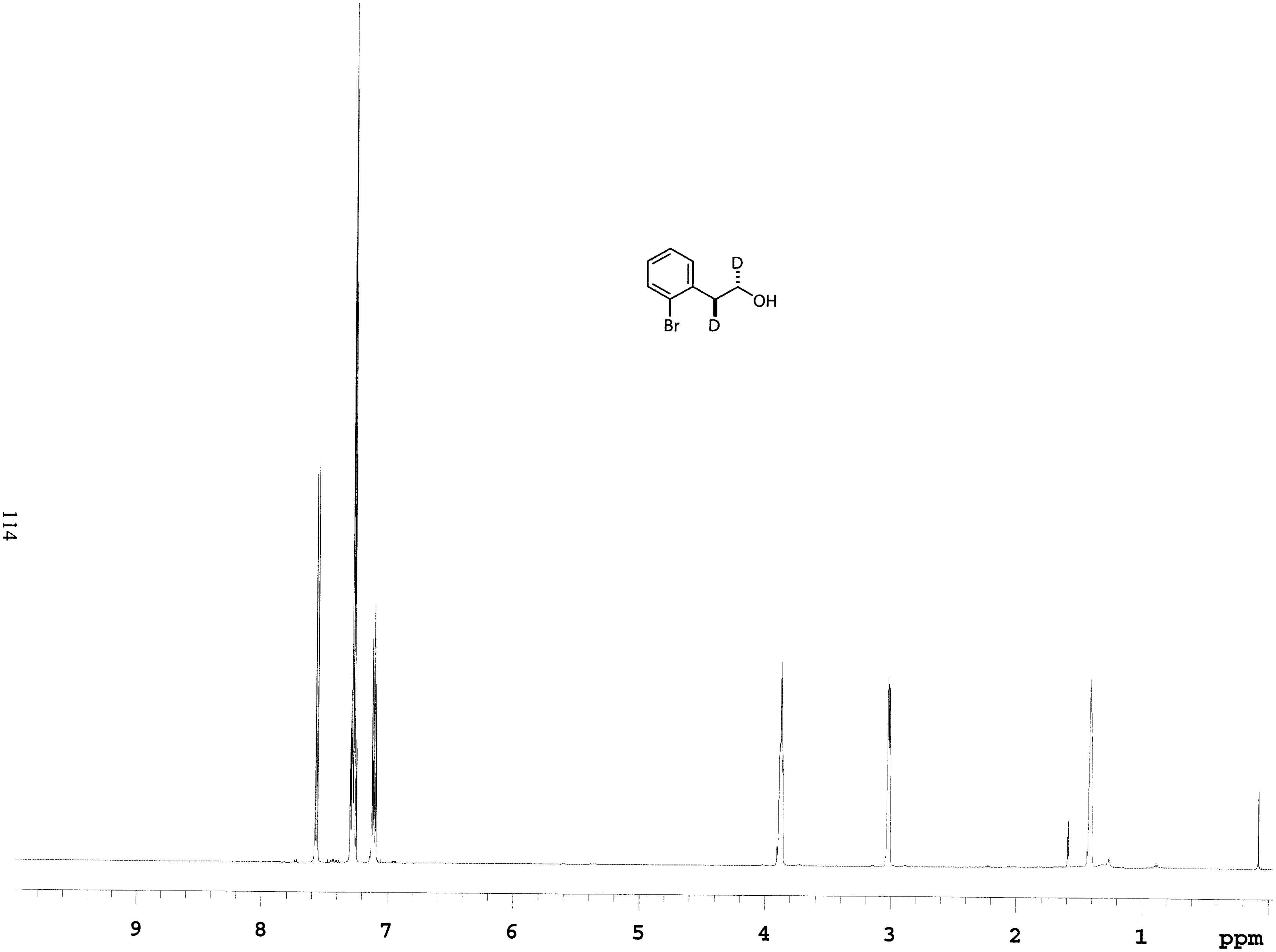
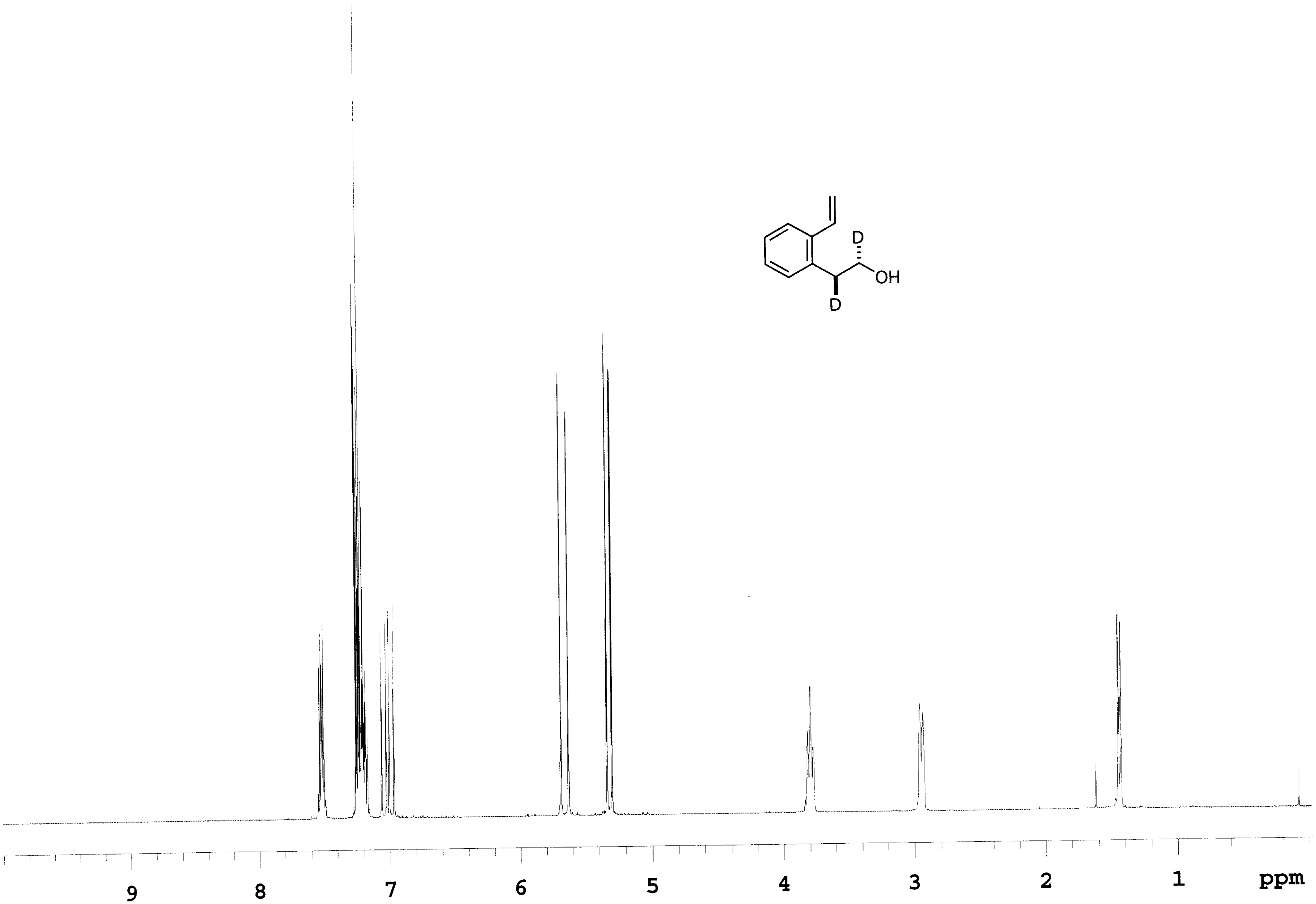
D
9
8
7
6
5
4
3
2
1
ppm


Br
D
9
8
7
6
5
4
3
2
1
ppm


D
OH
Br
D
9
8
7
6
5
4
3
2
1
ppm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OH
D
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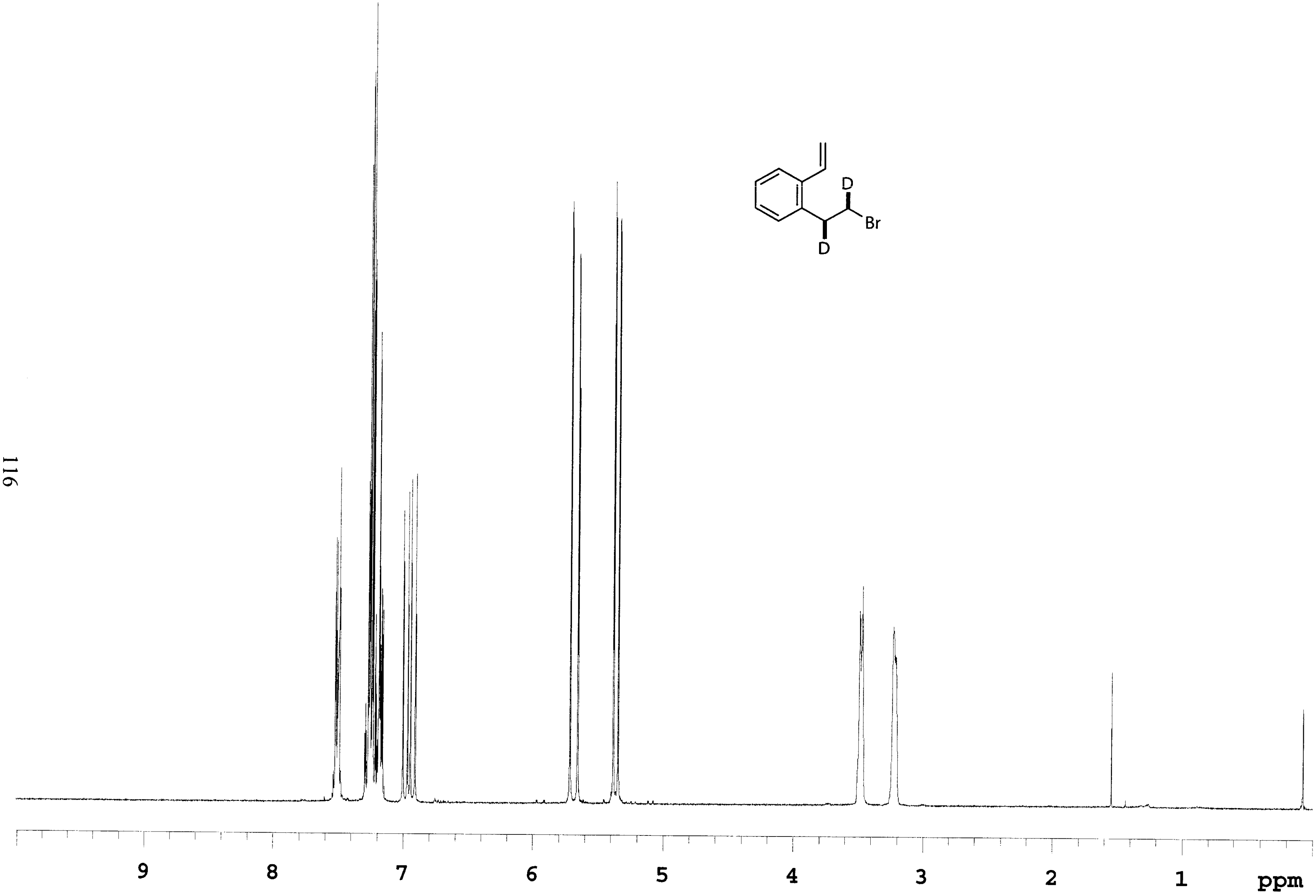
7
6
5
4
3
2
1
ppm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D
Br
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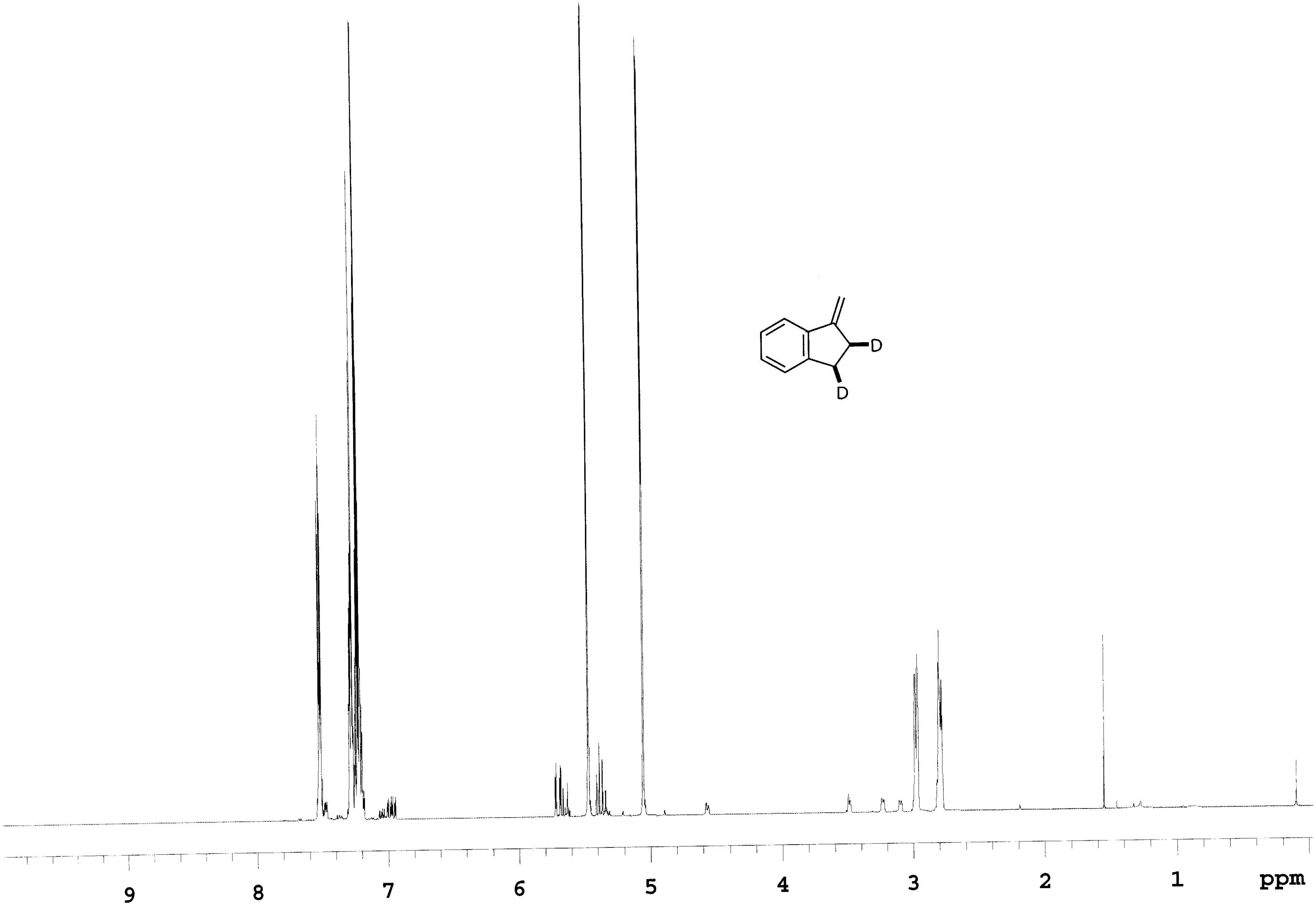
7
6
5
4
3
2
1
ppm


D
D
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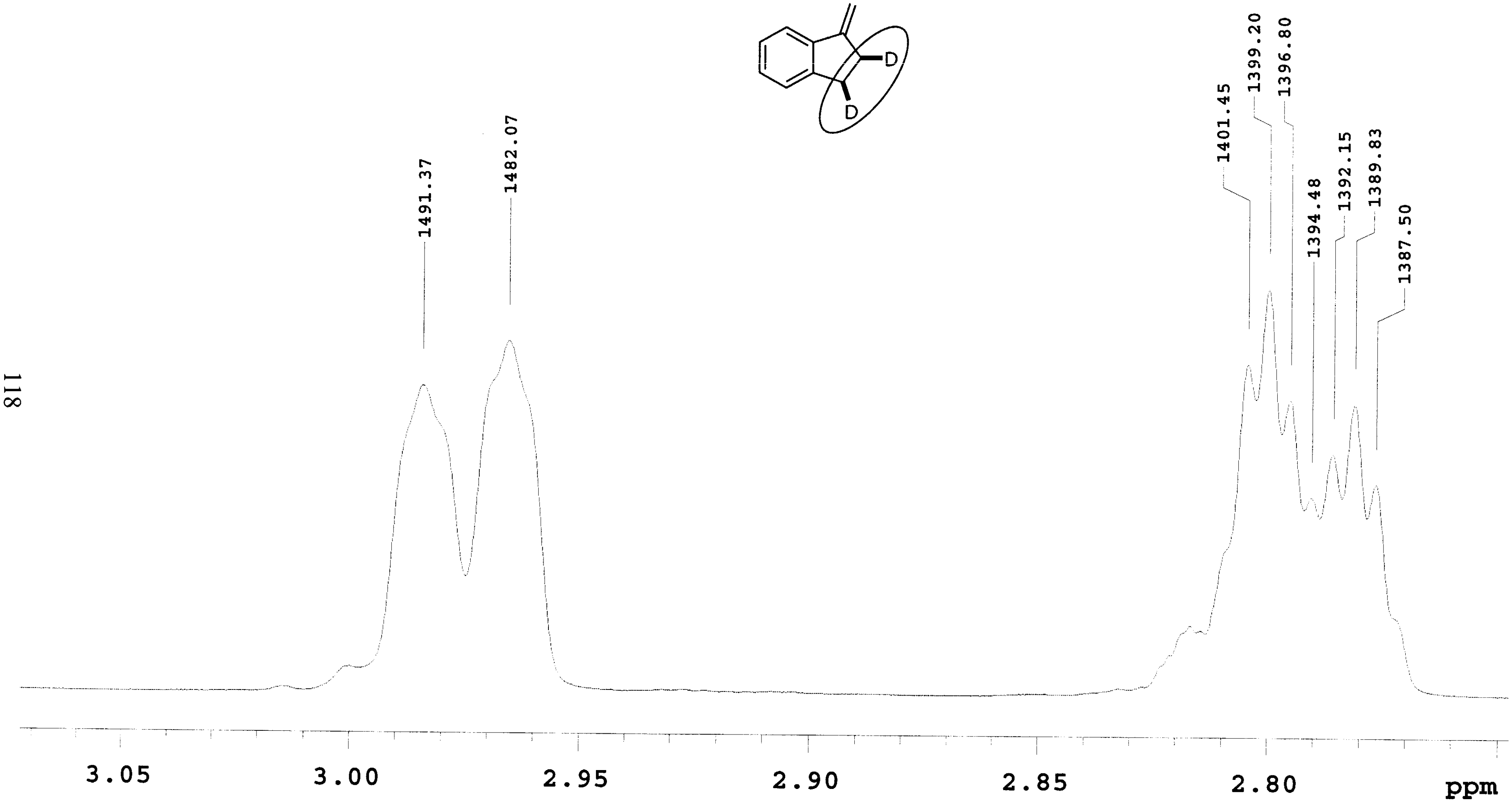
8
7
6
5
4
3
2
1
ppm


D
D
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1482.07
1401.45
1399.20
1396.80
1394.48
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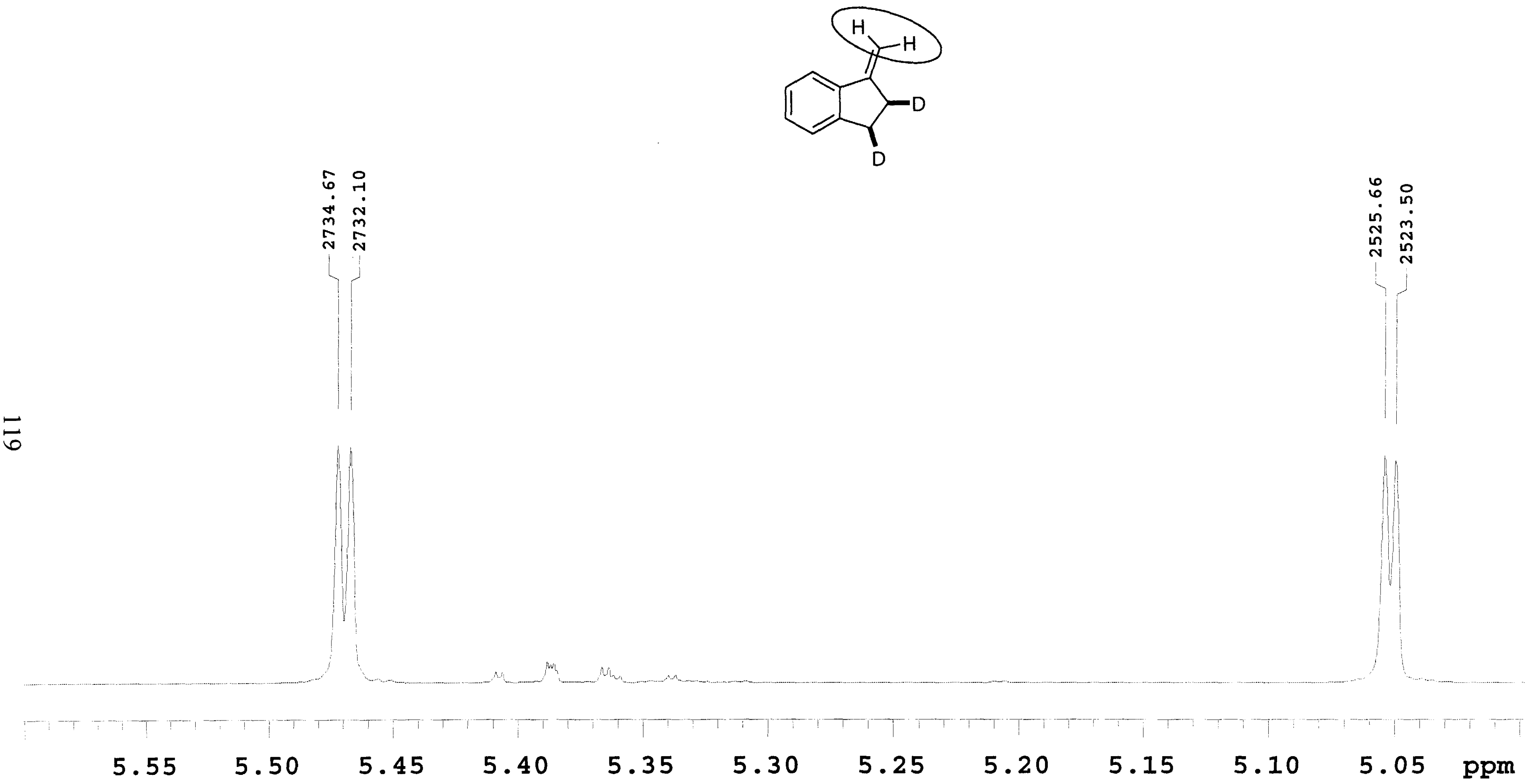
2.85
2.80
ppm


H
H
D
D
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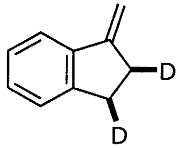
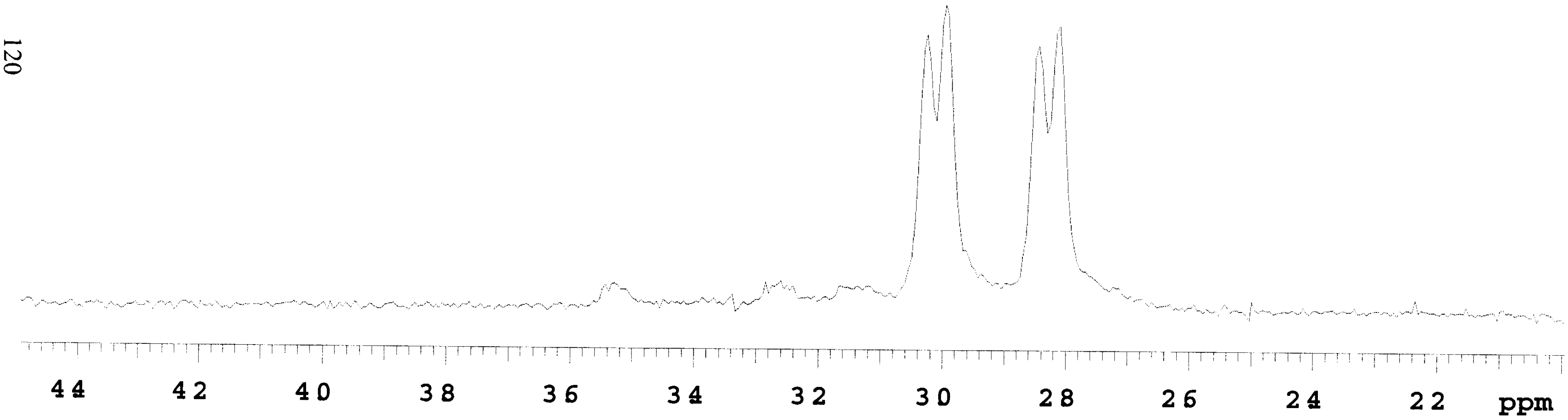
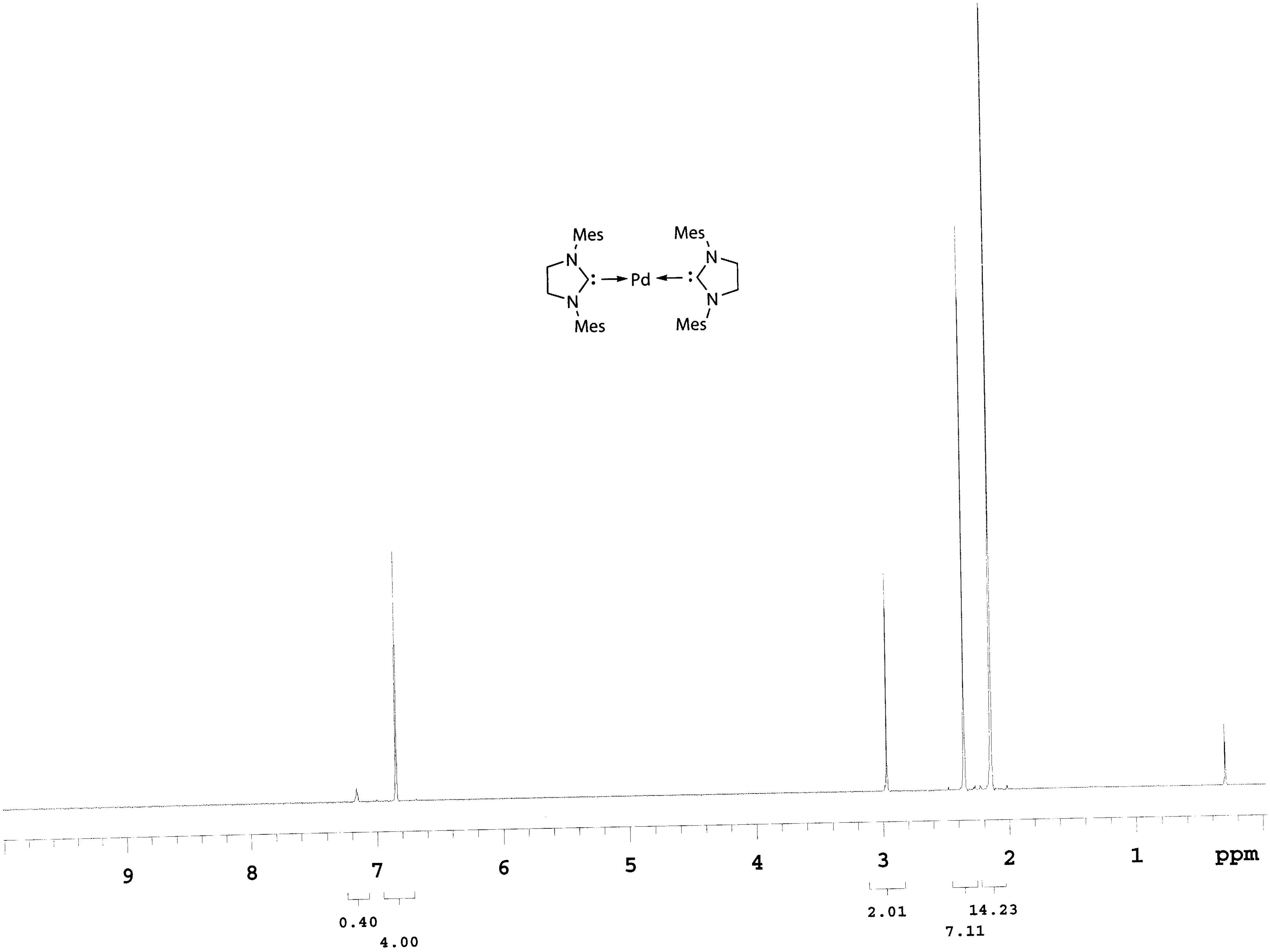
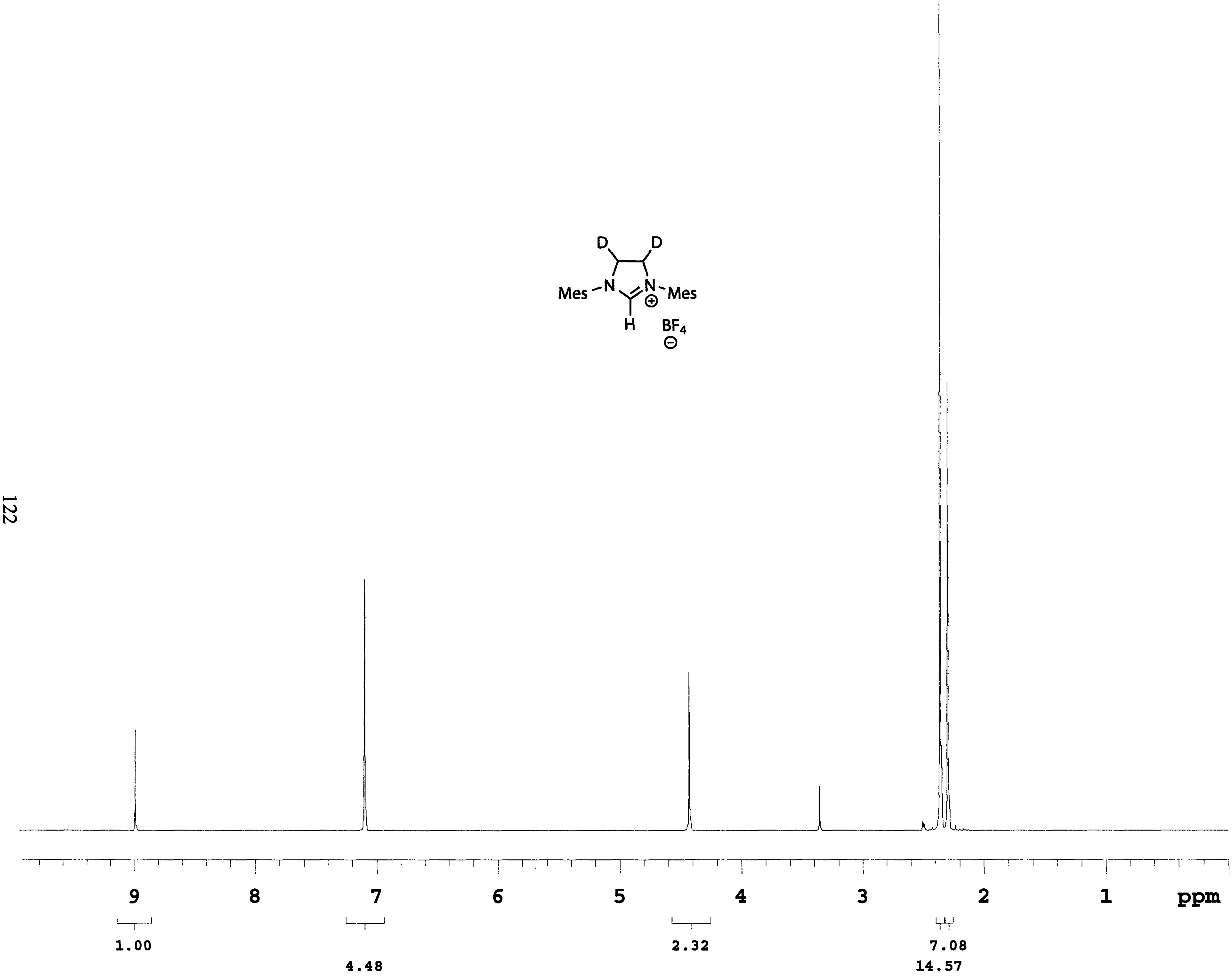
5.30
5.25
5.20
5.15
5.10
5.05
ppm

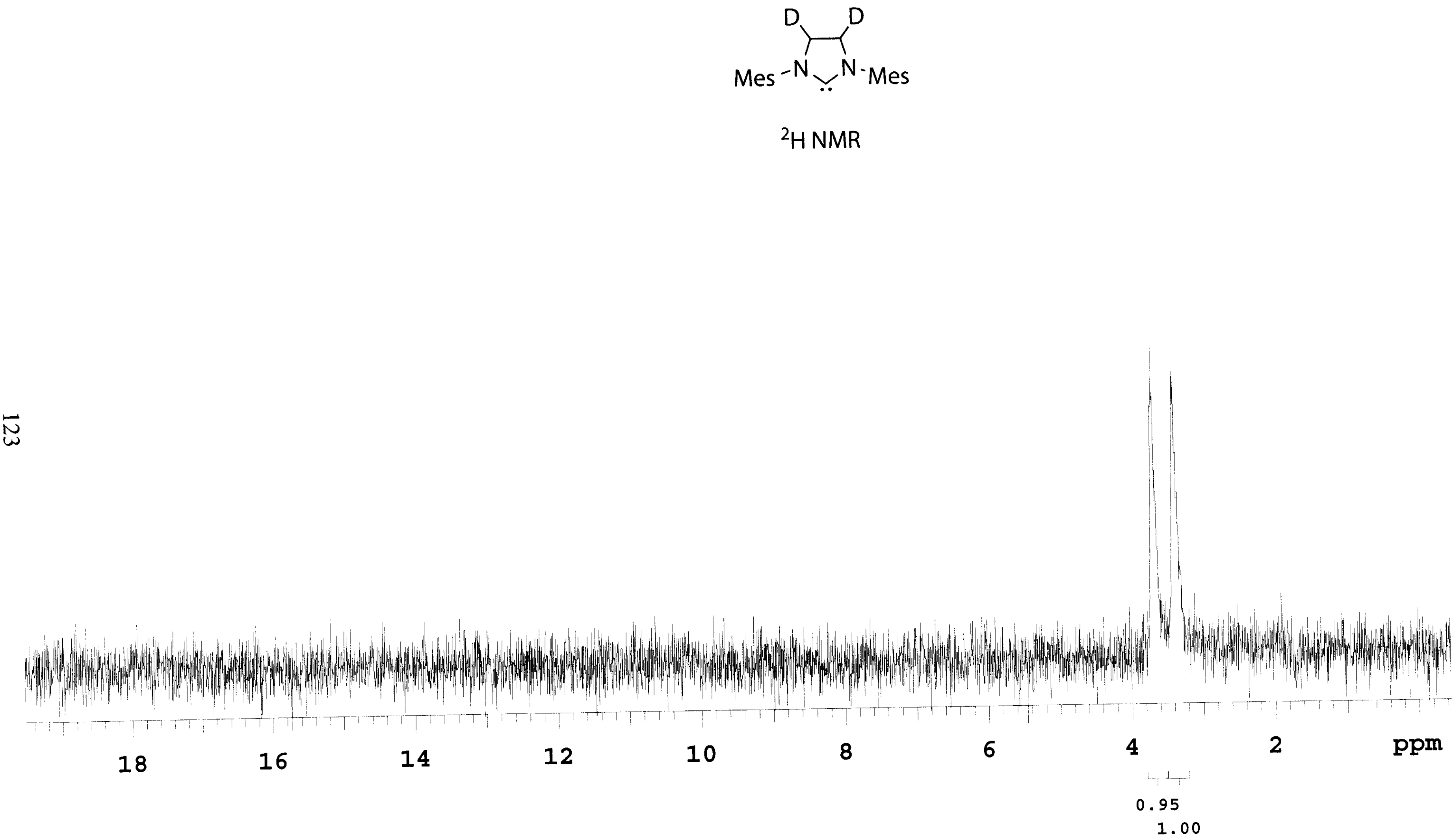


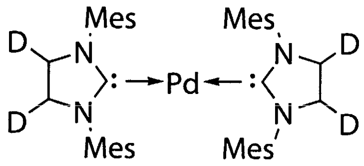
2H NMR
(J = 2.3 Hz)



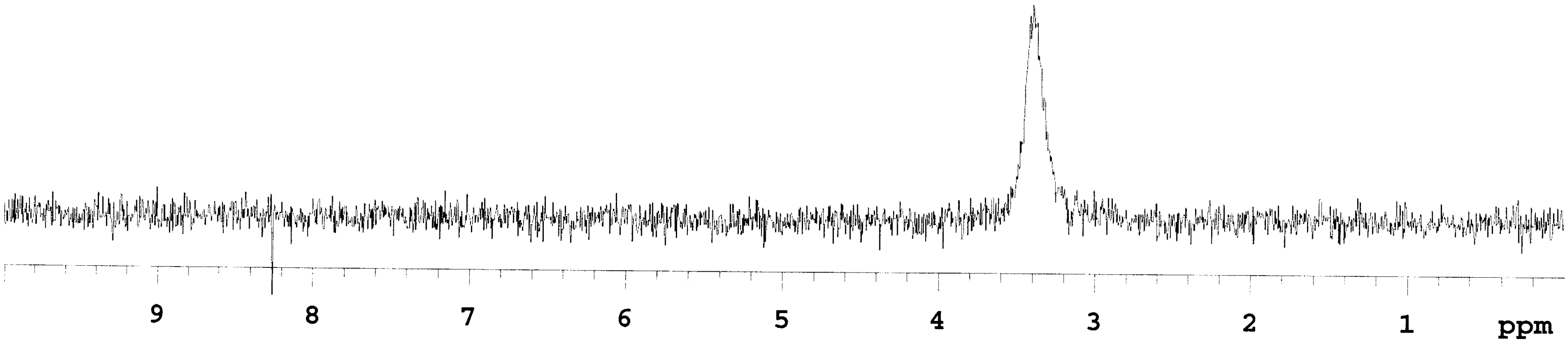

Mes
N
N
Mes
Pd
Mes
N
N
Mes
9
8
7
6
5
4
3
2
1
ppm
0.40
4.00
2.01
7.11
14.23

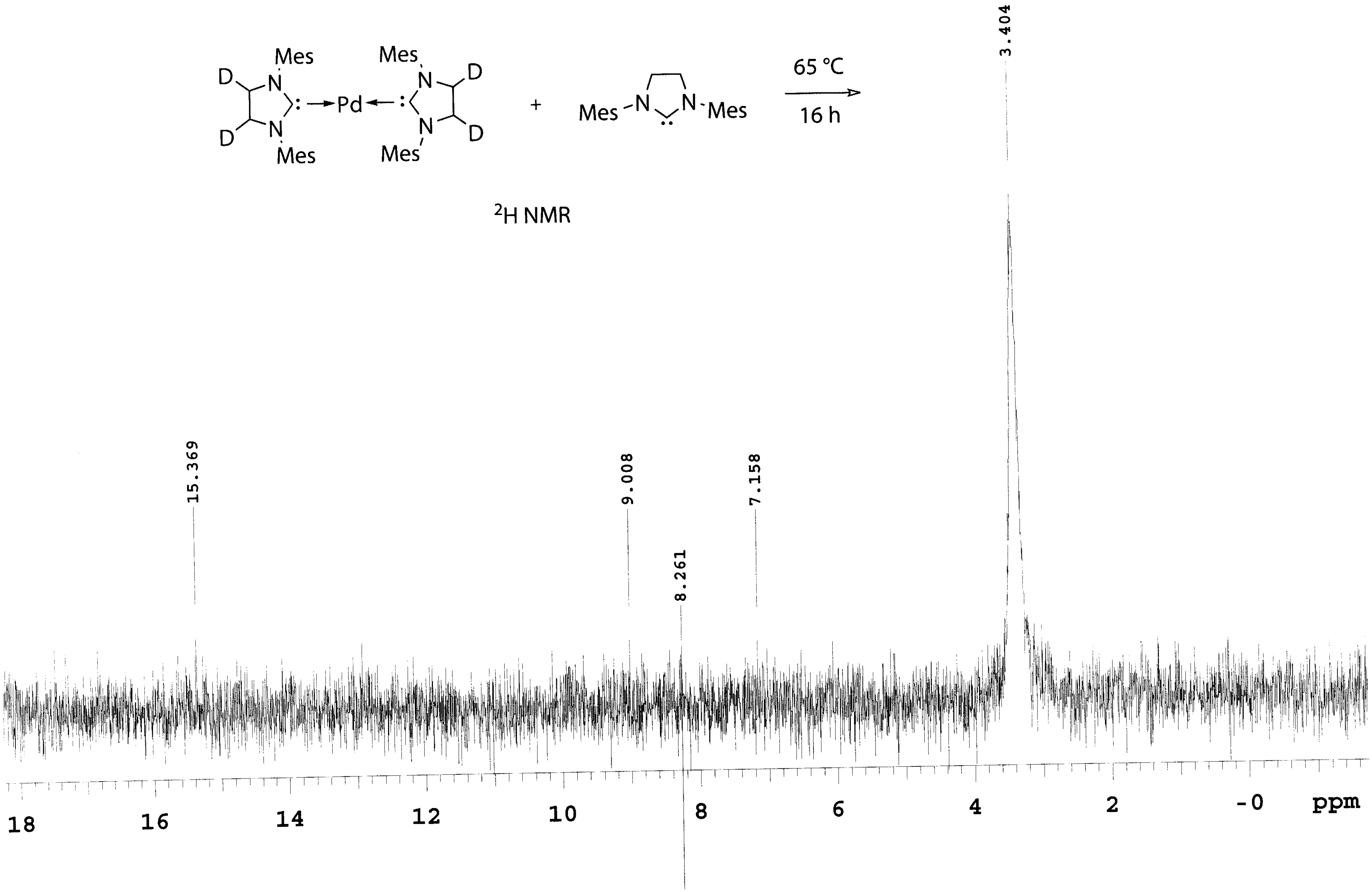

D
D
Mes
N
N
Mes
H
BF4
9
8
7
6
5
4
3
2
1
ppm
1.00
4.48
2.32
7.08
14.57

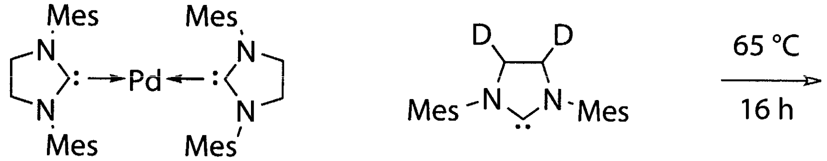

D
D
Mes
N
N
Mes
²H NMR
18
16
14
12
10
8
6
4
2
ppm
0.95
1.00



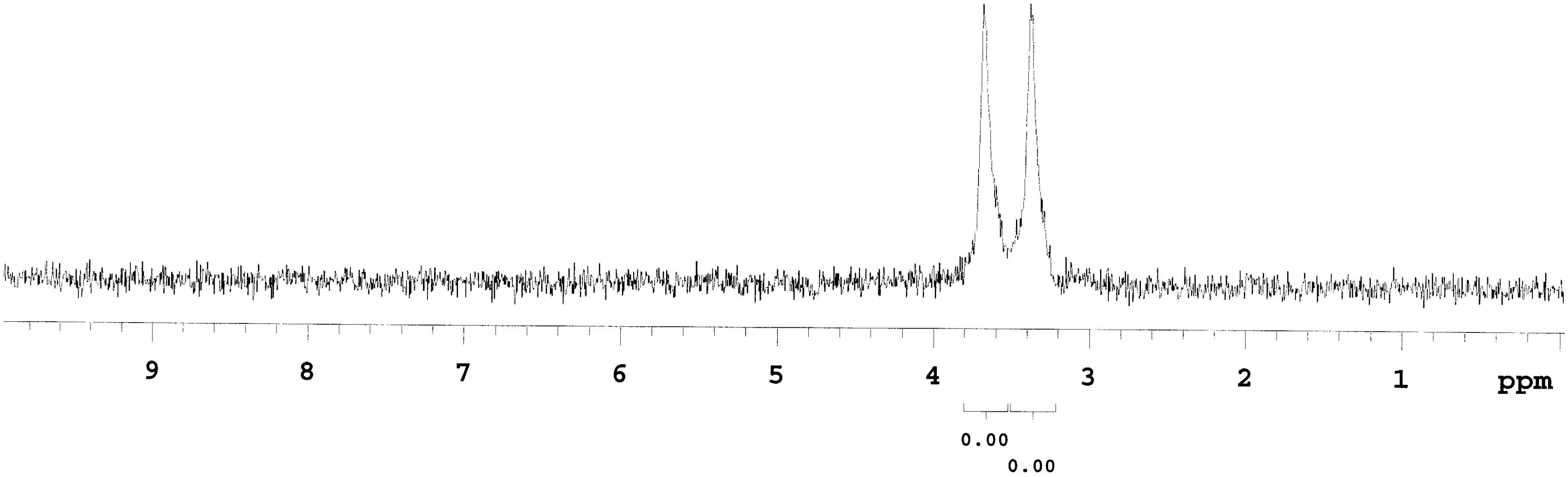
^{2}H NMR

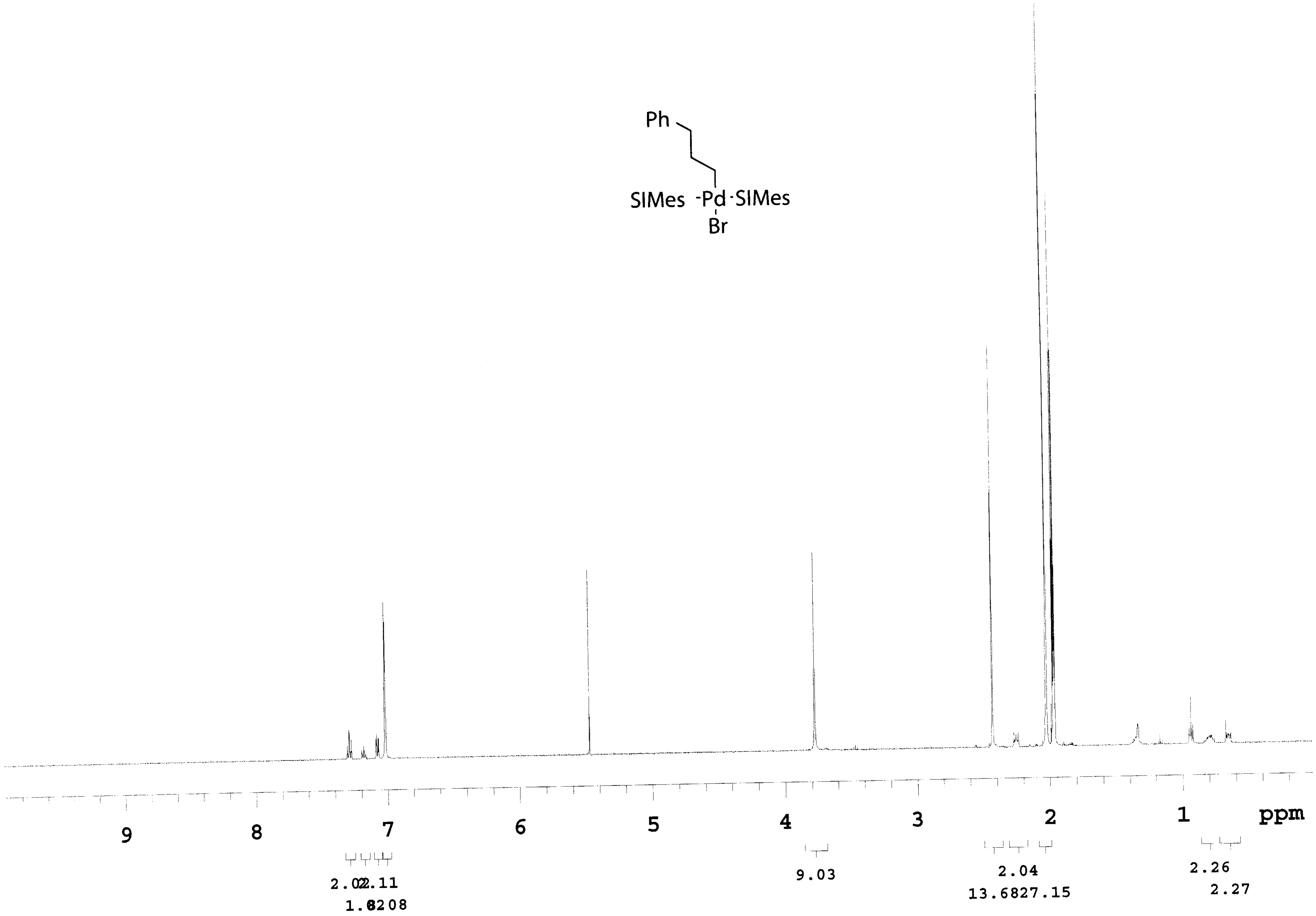


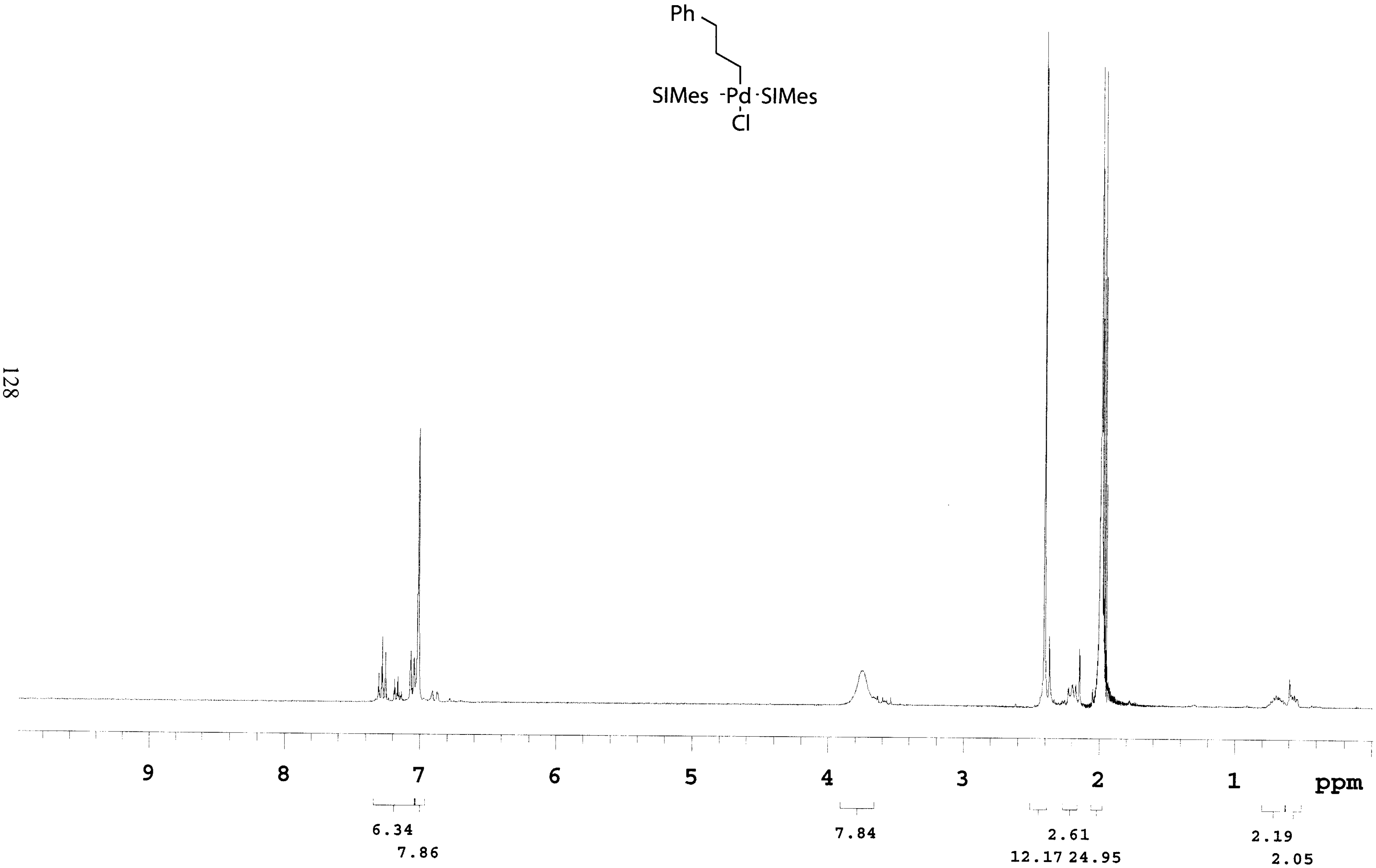

D
Mes
N
Pd
Mes
D
+
Mes
N
N
Mes
65 °C
16 h
^{2}H NMR
3.404
15.369
9.008
8.261
7.158
18
16
14
12
10
8
6
4
2
-0
ppm


Mes
N
N
Mes
Pd
Mes
N
N
Mes
D
D
Mes
N
N
Mes
65 °C
16 h

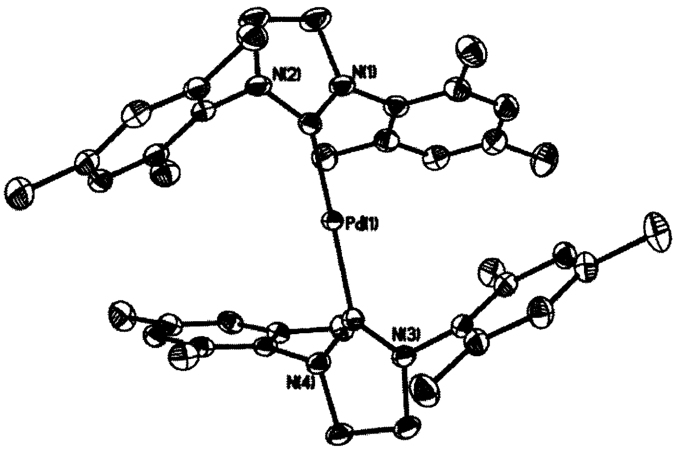
^{2}H NMR


9
8
7
6
5
4
3
2
1
ppm
0.00
0.00


Ph
SIMes
Pd
SIMes
Br
9
8
7
6
5
4
3
2
1
ppm
2.02
2.11
1.82
2.08
9.03
2.04
13.68
27.15
2.26
2.27


Ph
SIMes
Pd
SIMes
Cl
9
8
7
6
5
4
3
2
1
ppm
6.34
7.86
7.84
2.61
12.17
24.95
2.19
2.05

Appendix D
X-ray Crystallographic Data


N(2)
N(1)
Pd(1)
N(3)
N(4)

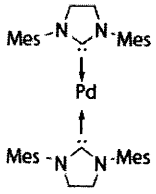

Mes
N
N
Mes
Pd
Mes
N
N
Mes

Table 1. Crystal data and structure refinement for 05182.

Identification code	05182	
Empirical formula	C42 H52 N4 Pd	
Formula weight	719.28	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 17.0206(13) Å	α = 90°.
	b = 10.4322(6) Å	β = 99.180(2)°.
	c = 21.5999(16) Å	γ = 90°.
Volume	3786.2(5) $Å^3$	
Z	4	
Density (calculated)	1.262 Mg/m^3	
Absorption coefficient	0.523 mm^{-1}	
F(000)	1512	
Crystal size	0.16 x 0.15 x 0.14 mm^3	
Theta range for data collection	1.66 to 29.57°.	
Index ranges	-23<=h<=23, -14<=k<=14, -29<=l<=29	
Reflections collected	83020	
Independent reflections	10633 [R(int) = 0.0268]	
Completeness to theta = 29.57°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9303 and 0.9209	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10633 / 0 / 436	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0677	
R indices (all data)	R1 = 0.0289, wR2 = 0.0702	
Largest diff. peak and hole	0.728 and -0.244 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 05182. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	8072(1)	6923(1)	369(1)	18(1)
N(1)	6938(1)	4759(1)	33(1)	26(1)
N(2)	7896(1)	4640(1)	-511(1)	25(1)
N(3)	8778(1)	8896(1)	1341(1)	24(1)
N(4)	8260(1)	9732(1)	454(1)	26(1)
C(1)	7624(1)	5325(1)	-61(1)	22(1)
C(2)	6724(1)	3621(2)	-356(1)	40(1)
C(3)	7371(1)	3580(2)	-768(1)	34(1)
C(4)	8403(1)	8608(1)	754(1)	21(1)
C(5)	8811(1)	10281(1)	1475(1)	31(1)
C(6)	8603(1)	10855(1)	818(1)	29(1)
C(11)	6460(1)	5194(1)	478(1)	25(1)
C(12)	6541(1)	4608(1)	1066(1)	28(1)
C(13)	6050(1)	5004(2)	1487(1)	31(1)
C(14)	5507(1)	5993(2)	1342(1)	31(1)
C(15)	5454(1)	6581(2)	758(1)	30(1)
C(16)	5912(1)	6181(1)	314(1)	27(1)
C(17)	7161(1)	3591(2)	1252(1)	38(1)
C(18)	4995(1)	6428(2)	1811(1)	45(1)
C(19)	5827(1)	6809(2)	-319(1)	35(1)
C(21)	8567(1)	4998(1)	-794(1)	22(1)
C(22)	9270(1)	4293(1)	-657(1)	23(1)
C(23)	9915(1)	4633(1)	-948(1)	26(1)
C(24)	9870(1)	5660(1)	-1361(1)	26(1)
C(25)	9163(1)	6344(1)	-1487(1)	26(1)
C(26)	8499(1)	6023(1)	-1217(1)	24(1)
C(27)	9341(1)	3195(1)	-202(1)	30(1)
C(28)	10582(1)	6026(2)	-1657(1)	38(1)
C(29)	7731(1)	6758(2)	-1369(1)	32(1)

C(31)	8922(1)	7995(1)	1843(1)	21(1)
C(32)	9710(1)	7725(1)	2110(1)	24(1)
C(33)	9846(1)	6889(1)	2617(1)	25(1)
C(34)	9226(1)	6295(1)	2852(1)	25(1)
C(35)	8450(1)	6576(1)	2575(1)	23(1)
C(36)	8282(1)	7436(1)	2080(1)	22(1)
C(37)	10403(1)	8302(2)	1854(1)	32(1)
C(38)	9391(1)	5362(2)	3389(1)	35(1)
C(39)	7434(1)	7748(2)	1811(1)	29(1)
C(41)	7859(1)	9882(1)	-176(1)	22(1)
C(42)	7039(1)	10113(1)	-275(1)	25(1)
C(43)	6660(1)	10356(1)	-883(1)	28(1)
C(44)	7074(1)	10368(1)	-1387(1)	27(1)
C(45)	7881(1)	10096(1)	-1276(1)	25(1)
C(46)	8286(1)	9840(1)	-676(1)	23(1)
C(47)	6579(1)	10058(2)	263(1)	34(1)
C(48)	6660(1)	10676(2)	-2041(1)	40(1)
C(49)	9148(1)	9460(2)	-577(1)	30(1)

Table 3. Bond lengths [Å] and angles [°] for 05182.

Pd(1)-C(4)	1.9874(13)
Pd(1)-C(1)	1.9999(13)
N(1)-C(1)	1.3513(17)
N(1)-C(11)	1.4282(18)
N(1)-C(2)	1.4664(19)
N(2)-C(1)	1.3466(17)
N(2)-C(21)	1.4294(17)
N(2)-C(3)	1.4728(17)
N(3)-C(4)	1.3581(16)
N(3)-C(31)	1.4273(16)
N(3)-C(5)	1.4730(17)
N(4)-C(4)	1.3428(17)
N(4)-C(41)	1.4306(16)
N(4)-C(6)	1.4782(17)
C(2)-C(3)	1.524(2)
C(5)-C(6)	1.5294(19)
C(11)-C(16)	1.396(2)
C(11)-C(12)	1.398(2)
C(12)-C(13)	1.392(2)
C(12)-C(17)	1.506(2)
C(13)-C(14)	1.387(2)
C(14)-C(15)	1.392(2)
C(14)-C(18)	1.509(2)
C(15)-C(16)	1.392(2)
C(16)-C(19)	1.502(2)
C(21)-C(22)	1.3961(19)
C(21)-C(26)	1.3976(18)
C(22)-C(23)	1.394(2)
C(22)-C(27)	1.5021(19)
C(23)-C(24)	1.389(2)
C(24)-C(25)	1.388(2)
C(24)-C(28)	1.506(2)
C(25)-C(26)	1.393(2)
C(26)-C(29)	1.506(2)

C(31)-C(36)	1.4009(19)
C(31)-C(32)	1.4024(19)
C(32)-C(33)	1.3892(19)
C(32)-C(37)	1.5057(19)
C(33)-C(34)	1.3890(19)
C(34)-C(35)	1.3915(19)
C(34)-C(38)	1.5047(19)
C(35)-C(36)	1.3900(18)
C(36)-C(39)	1.5038(19)
C(41)-C(46)	1.3944(19)
C(41)-C(42)	1.399(2)
C(42)-C(43)	1.3912(19)
C(42)-C(47)	1.503(2)
C(43)-C(44)	1.387(2)
C(44)-C(45)	1.387(2)
C(44)-C(48)	1.5097(19)
C(45)-C(46)	1.3951(18)
C(46)-C(49)	1.5010(19)

C(4)-Pd(1)-C(1)	173.48(5)
C(1)-N(1)-C(11)	124.05(11)
C(1)-N(1)-C(2)	114.21(12)
C(11)-N(1)-C(2)	121.73(12)
C(1)-N(2)-C(21)	124.11(11)
C(1)-N(2)-C(3)	114.39(11)
C(21)-N(2)-C(3)	120.84(11)
C(4)-N(3)-C(31)	124.22(11)
C(4)-N(3)-C(5)	113.43(11)
C(31)-N(3)-C(5)	119.95(11)
C(4)-N(4)-C(41)	125.23(11)
C(4)-N(4)-C(6)	114.21(11)
C(41)-N(4)-C(6)	120.45(11)
N(2)-C(1)-N(1)	106.31(11)
N(2)-C(1)-Pd(1)	128.91(10)
N(1)-C(1)-Pd(1)	124.69(10)
N(1)-C(2)-C(3)	102.69(12)

N(2)-C(3)-C(2)	102.14(12)
N(4)-C(4)-N(3)	106.22(11)
N(4)-C(4)-Pd(1)	123.58(9)
N(3)-C(4)-Pd(1)	130.18(9)
N(3)-C(5)-C(6)	101.88(11)
N(4)-C(6)-C(5)	101.27(11)
C(16)-C(11)-C(12)	121.12(13)
C(16)-C(11)-N(1)	119.61(13)
C(12)-C(11)-N(1)	119.26(13)
C(13)-C(12)-C(11)	118.83(14)
C(13)-C(12)-C(17)	120.24(14)
C(11)-C(12)-C(17)	120.90(14)
C(14)-C(13)-C(12)	121.36(14)
C(13)-C(14)-C(15)	118.48(14)
C(13)-C(14)-C(18)	120.45(15)
C(15)-C(14)-C(18)	121.06(15)
C(16)-C(15)-C(14)	121.95(14)
C(15)-C(16)-C(11)	118.19(14)
C(15)-C(16)-C(19)	120.82(14)
C(11)-C(16)-C(19)	120.99(14)
C(22)-C(21)-C(26)	121.34(12)
C(22)-C(21)-N(2)	119.19(12)
C(26)-C(21)-N(2)	119.45(12)
C(23)-C(22)-C(21)	118.70(12)
C(23)-C(22)-C(27)	120.13(13)
C(21)-C(22)-C(27)	121.17(13)
C(24)-C(23)-C(22)	121.24(13)
C(25)-C(24)-C(23)	118.68(13)
C(25)-C(24)-C(28)	121.19(14)
C(23)-C(24)-C(28)	120.13(14)
C(24)-C(25)-C(26)	122.01(13)
C(25)-C(26)-C(21)	118.02(13)
C(25)-C(26)-C(29)	121.32(13)
C(21)-C(26)-C(29)	120.66(13)
C(36)-C(31)-C(32)	120.97(12)
C(36)-C(31)-N(3)	120.17(12)

C(32)-C(31)-N(3)	118.81(12)
C(33)-C(32)-C(31)	118.57(12)
C(33)-C(32)-C(37)	119.96(13)
C(31)-C(32)-C(37)	121.47(12)
C(34)-C(33)-C(32)	121.86(13)
C(33)-C(34)-C(35)	118.19(12)
C(33)-C(34)-C(38)	120.74(13)
C(35)-C(34)-C(38)	121.07(13)
C(36)-C(35)-C(34)	122.14(12)
C(35)-C(36)-C(31)	118.22(12)
C(35)-C(36)-C(39)	120.22(12)
C(31)-C(36)-C(39)	121.57(12)
C(46)-C(41)-C(42)	121.21(12)
C(46)-C(41)-N(4)	120.28(12)
C(42)-C(41)-N(4)	118.47(12)
C(43)-C(42)-C(41)	118.46(13)
C(43)-C(42)-C(47)	121.09(14)
C(41)-C(42)-C(47)	120.43(13)
C(44)-C(43)-C(42)	121.70(13)
C(45)-C(44)-C(43)	118.47(12)
C(45)-C(44)-C(48)	120.35(14)
C(43)-C(44)-C(48)	121.18(14)
C(44)-C(45)-C(46)	121.88(13)
C(41)-C(46)-C(45)	118.20(13)
C(41)-C(46)-C(49)	121.11(12)
C(45)-C(46)-C(49)	120.61(13)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 05182. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

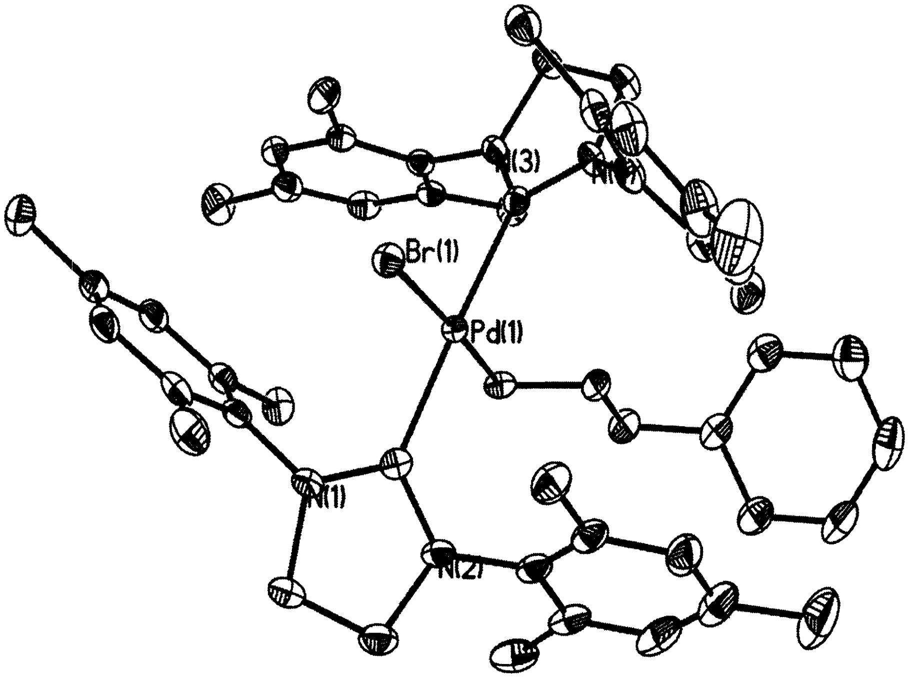
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	23(1)	15(1)	18(1)	-1(1)	2(1)	-2(1)
N(1)	27(1)	22(1)	31(1)	-7(1)	9(1)	-7(1)
N(2)	28(1)	19(1)	30(1)	-7(1)	8(1)	-7(1)
N(3)	33(1)	17(1)	19(1)	0(1)	-1(1)	-3(1)
N(4)	39(1)	18(1)	18(1)	0(1)	-3(1)	-2(1)
C(1)	24(1)	18(1)	22(1)	1(1)	3(1)	-1(1)
C(2)	41(1)	34(1)	49(1)	-20(1)	18(1)	-19(1)
C(3)	34(1)	27(1)	41(1)	-15(1)	11(1)	-13(1)
C(4)	25(1)	19(1)	19(1)	1(1)	1(1)	-2(1)
C(5)	50(1)	18(1)	23(1)	-3(1)	-3(1)	-3(1)
C(6)	42(1)	17(1)	24(1)	-1(1)	-4(1)	-2(1)
C(11)	23(1)	23(1)	30(1)	-3(1)	6(1)	-6(1)
C(12)	26(1)	26(1)	33(1)	1(1)	6(1)	-3(1)
C(13)	30(1)	34(1)	30(1)	1(1)	7(1)	-5(1)
C(14)	25(1)	36(1)	32(1)	-6(1)	7(1)	-4(1)
C(15)	23(1)	31(1)	35(1)	-4(1)	3(1)	0(1)
C(16)	24(1)	27(1)	30(1)	-2(1)	2(1)	-4(1)
C(17)	38(1)	35(1)	44(1)	8(1)	11(1)	7(1)
C(18)	40(1)	58(1)	39(1)	-6(1)	14(1)	6(1)
C(19)	37(1)	35(1)	32(1)	3(1)	4(1)	2(1)
C(21)	26(1)	18(1)	21(1)	-4(1)	5(1)	-4(1)
C(22)	29(1)	18(1)	21(1)	-3(1)	2(1)	-1(1)
C(23)	27(1)	24(1)	27(1)	-5(1)	3(1)	1(1)
C(24)	32(1)	26(1)	22(1)	-7(1)	8(1)	-8(1)
C(25)	38(1)	21(1)	18(1)	-1(1)	3(1)	-6(1)
C(26)	29(1)	20(1)	21(1)	-3(1)	0(1)	-1(1)
C(27)	39(1)	22(1)	29(1)	3(1)	2(1)	2(1)
C(28)	41(1)	40(1)	36(1)	-8(1)	16(1)	-13(1)
C(29)	35(1)	26(1)	34(1)	2(1)	0(1)	4(1)
C(31)	27(1)	19(1)	16(1)	0(1)	1(1)	-1(1)
C(32)	24(1)	26(1)	21(1)	0(1)	5(1)	-3(1)

C(33)	22(1)	31(1)	22(1)	3(1)	2(1)	1(1)
C(34)	28(1)	28(1)	19(1)	4(1)	5(1)	2(1)
C(35)	24(1)	26(1)	21(1)	1(1)	7(1)	-1(1)
C(36)	22(1)	23(1)	20(1)	-2(1)	2(1)	1(1)
C(37)	28(1)	37(1)	33(1)	5(1)	8(1)	-7(1)
C(38)	34(1)	44(1)	28(1)	14(1)	6(1)	3(1)
C(39)	23(1)	34(1)	30(1)	0(1)	1(1)	3(1)
C(41)	30(1)	16(1)	20(1)	1(1)	-3(1)	-3(1)
C(42)	30(1)	20(1)	26(1)	1(1)	5(1)	-4(1)
C(43)	23(1)	26(1)	32(1)	4(1)	-2(1)	-4(1)
C(44)	29(1)	25(1)	23(1)	5(1)	-5(1)	-6(1)
C(45)	29(1)	22(1)	22(1)	2(1)	1(1)	-5(1)
C(46)	26(1)	17(1)	24(1)	1(1)	-2(1)	-3(1)
C(47)	38(1)	35(1)	32(1)	0(1)	12(1)	-5(1)
C(48)	37(1)	49(1)	28(1)	11(1)	-8(1)	-6(1)
C(49)	27(1)	28(1)	32(1)	0(1)	-2(1)	2(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 05182.

	x	y	z	U(eq)
H(2A)	6190	3715	-612	48
H(2B)	6732	2838	-96	48
H(3A)	7657	2750	-728	41
H(3B)	7148	3729	-1214	41
H(5A)	9348	10546	1680	37
H(5B)	8416	10529	1744	37
H(6A)	8211	11558	807	34
H(6B)	9083	11178	663	34
H(13)	6087	4588	1882	37
H(15)	5095	7275	659	36
H(17A)	7307	3577	1710	57
H(17B)	7634	3781	1062	57
H(17C)	6947	2753	1106	57
H(18A)	4719	5687	1955	67
H(18B)	4602	7050	1613	67
H(18C)	5330	6828	2170	67
H(19A)	6334	7206	-372	52
H(19B)	5412	7467	-350	52
H(19C)	5680	6163	-646	52
H(23)	10395	4154	-861	31
H(25)	9131	7054	-1765	31
H(27A)	9066	2443	-406	46
H(27B)	9098	3434	164	46
H(27C)	9904	2990	-67	46
H(28A)	10413	6189	-2105	57
H(28B)	10970	5324	-1603	57
H(28C)	10826	6801	-1454	57
H(29A)	7293	6159	-1502	48

H(29B)	7770	7366	-1709	48
H(29C)	7631	7226	-996	48
H(33)	10378	6718	2807	30
H(35)	8021	6166	2728	28
H(37A)	10480	9190	1998	48
H(37B)	10294	8285	1394	48
H(37C)	10885	7805	2001	48
H(38A)	8888	4995	3473	53
H(38B)	9656	5809	3764	53
H(38C)	9736	4674	3279	53
H(39A)	7301	7363	1393	44
H(39B)	7368	8680	1778	44
H(39C)	7079	7403	2086	44
H(43)	6104	10517	-955	33
H(45)	8167	10084	-1620	29
H(47A)	6606	9189	438	52
H(47B)	6022	10284	114	52
H(47C)	6808	10665	589	52
H(48A)	6783	11560	-2147	59
H(48B)	6084	10581	-2061	59
H(48C)	6846	10087	-2341	59
H(49A)	9301	9220	-980	45
H(49B)	9231	8729	-289	45
H(49C)	9475	10184	-398	45


N(3)
Br(1)
Pd(1)
N(1)
N(2)

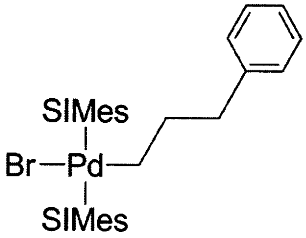

SIMes
Br
Pd
SIMes

Table 1. Crystal data and structure refinement for 05185.

Identification code	05185	
Empirical formula	C55 H72 Br Cl2 N4 Pd	
Formula weight	1046.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.348(4) Å	α = 90°.
	b = 14.872(6) Å	β = 98.509(12)°.
	c = 29.172(12) Å	γ = 90°.
Volume	5298(3) Å^{3}	
Z	4	
Density (calculated)	1.312 Mg/m^{3}	
Absorption coefficient	1.244 mm^{-1}	
F(000)	2180	
Crystal size	0.15 x 0.10 x 0.06 mm^{3}	
Theta range for data collection	1.90 to 29.58°.	
Index ranges	-17<=h<=17, -20<=k<=20, -40<=l<=40	
Reflections collected	113022	
Independent reflections	14864 [R(int) = 0.0881]	
Completeness to theta = 29.58°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9291 and 0.8354	
Refinement method	Full-matrix least-squares on F^{2}	
Data / restraints / parameters	14864 / 7 / 608	
Goodness-of-fit on F^{2}	1.014	
Final R indices [I>2sigma(I)]	R1 = 0.0395, wR2 = 0.0868	
R indices (all data)	R1 = 0.0642, wR2 = 0.0974	
Largest diff. peak and hole	1.778 and -0.534 e.Å^{-3}	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 05185. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	2987(1)	10743(1)	1757(1)	20(1)
Pd(1)	4150(1)	9311(1)	1722(1)	14(1)
C(1)	5052(2)	9966(2)	1290(1)	18(1)
N(1)	5647(2)	10733(1)	1383(1)	21(1)
C(11)	5884(2)	11195(2)	1822(1)	19(1)
C(12)	6581(2)	10795(2)	2193(1)	20(1)
C(13)	6815(2)	11283(2)	2610(1)	22(1)
C(14)	6400(2)	12145(2)	2660(1)	24(1)
C(15)	5744(2)	12533(2)	2278(1)	24(1)
C(16)	5474(2)	12078(2)	1856(1)	22(1)
C(17)	7079(2)	9870(2)	2154(1)	25(1)
C(18)	6645(2)	12641(2)	3121(1)	33(1)
C(19)	4737(2)	12518(2)	1455(1)	31(1)
C(2)	6304(2)	10971(2)	1010(1)	31(1)
C(3)	5749(2)	10393(2)	605(1)	29(1)
N(2)	5164(2)	9715(1)	851(1)	22(1)
C(21)	4585(2)	8987(2)	591(1)	23(1)
C(22)	5203(2)	8267(2)	447(1)	29(1)
C(23)	4641(3)	7576(2)	183(1)	36(1)
C(24)	3504(3)	7577(2)	61(1)	38(1)
C(25)	2921(2)	8312(2)	195(1)	31(1)
C(26)	3442(2)	9031(2)	457(1)	25(1)
C(27)	6443(2)	8224(2)	564(1)	37(1)
C(28)	2909(3)	6794(2)	-202(1)	58(1)
C(29)	2772(2)	9830(2)	572(1)	28(1)
C(4)	3313(2)	8563(2)	2152(1)	16(1)
N(3)	3760(2)	8245(1)	2575(1)	17(1)
C(31)	4807(2)	8505(2)	2832(1)	17(1)
C(32)	4958(2)	9374(2)	3018(1)	19(1)

C(33)	5987(2)	9589(2)	3271(1)	21(1)
C(34)	6854(2)	8969(2)	3334(1)	24(1)
C(35)	6657(2)	8100(2)	3161(1)	23(1)
C(36)	5642(2)	7847(2)	2915(1)	19(1)
C(37)	4060(2)	10082(2)	2961(1)	24(1)
C(38)	7971(2)	9255(2)	3580(1)	34(1)
C(39)	5439(2)	6880(2)	2760(1)	26(1)
C(5)	2963(2)	7740(2)	2813(1)	22(1)
C(6)	2054(2)	7538(2)	2409(1)	23(1)
N(4)	2285(2)	8212(1)	2056(1)	19(1)
C(41)	1416(2)	8545(2)	1707(1)	22(1)
C(42)	793(2)	9281(2)	1827(1)	24(1)
C(43)	5(2)	9650(2)	1480(1)	31(1)
C(44)	-189(2)	9297(2)	1032(1)	33(1)
C(45)	366(2)	8519(2)	938(1)	30(1)
C(46)	1166(2)	8121(2)	1273(1)	24(1)
C(47)	956(2)	9674(2)	2312(1)	27(1)
C(48)	-998(3)	9743(2)	651(1)	52(1)
C(49)	1687(2)	7243(2)	1156(1)	30(1)
C(7)	5142(2)	8180(2)	1678(1)	19(1)
C(8)	4518(2)	7341(2)	1477(1)	21(1)
C(9)	5247(2)	6515(2)	1429(1)	24(1)
C(91)	4597(2)	5727(2)	1192(1)	24(1)
C(92)	3733(2)	5331(2)	1384(1)	31(1)
C(93)	3093(3)	4646(2)	1155(1)	37(1)
C(94)	3327(3)	4325(2)	727(1)	40(1)
C(95)	4195(3)	4698(2)	535(1)	37(1)
C(96)	4812(2)	5392(2)	763(1)	31(1)
C(1S)	3996(9)	6635(9)	4209(3)	39(2)
Cl(1S)	3634(6)	7089(4)	4704(2)	66(1)
Cl(2S)	5043(5)	7248(4)	4004(2)	62(1)
C(1T)	3782(11)	6880(13)	4115(4)	68(6)
Cl(1T)	3412(8)	7137(3)	4638(3)	68(2)
Cl(2T)	4933(8)	7406(9)	3976(2)	94(3)
C(1H)	1571(3)	3911(2)	-608(1)	41(1)
C(2H)	354(3)	4620(3)	-58(1)	54(1)

C(3H)	844(4)	4682(3)	-496(1)	58(1)

Table 3. Bond lengths [Å] and angles [°] for 05185.

Br(1)-Pd(1)	2.5795(8)
Pd(1)-C(1)	2.046(2)
Pd(1)-C(4)	2.066(2)
Pd(1)-C(7)	2.095(2)
C(1)-N(2)	1.361(3)
C(1)-N(1)	1.361(3)
N(1)-C(11)	1.445(3)
N(1)-C(2)	1.492(3)
C(11)-C(12)	1.409(3)
C(11)-C(16)	1.417(3)
C(12)-C(13)	1.409(3)
C(12)-C(17)	1.518(3)
C(13)-C(14)	1.397(4)
C(14)-C(15)	1.402(4)
C(14)-C(18)	1.525(4)
C(15)-C(16)	1.401(4)
C(16)-C(19)	1.519(4)
C(2)-C(3)	1.538(4)
C(3)-N(2)	1.486(3)
N(2)-C(21)	1.449(3)
C(21)-C(26)	1.410(4)
C(21)-C(22)	1.414(4)
C(22)-C(23)	1.404(4)
C(22)-C(27)	1.520(4)
C(23)-C(24)	1.396(5)
C(24)-C(25)	1.396(4)
C(24)-C(28)	1.523(4)
C(25)-C(26)	1.412(4)
C(26)-C(29)	1.514(4)
C(4)-N(3)	1.359(3)
C(4)-N(4)	1.363(3)
N(3)-C(31)	1.448(3)
N(3)-C(5)	1.489(3)
C(31)-C(32)	1.404(3)

C(31)-C(36)	1.416(3)
C(32)-C(33)	1.409(3)
C(32)-C(37)	1.519(3)
C(33)-C(34)	1.405(4)
C(34)-C(35)	1.395(4)
C(34)-C(38)	1.517(3)
C(35)-C(36)	1.401(3)
C(36)-C(39)	1.517(3)
C(5)-C(6)	1.531(3)
C(6)-N(4)	1.495(3)
N(4)-C(41)	1.452(3)
C(41)-C(46)	1.407(4)
C(41)-C(42)	1.411(4)
C(42)-C(43)	1.408(4)
C(42)-C(47)	1.518(4)
C(43)-C(44)	1.396(4)
C(44)-C(45)	1.393(4)
C(44)-C(48)	1.529(4)
C(45)-C(46)	1.413(4)
C(46)-C(49)	1.516(4)
C(7)-C(8)	1.537(3)
C(8)-C(9)	1.541(3)
C(9)-C(91)	1.527(4)
C(91)-C(92)	1.406(4)
C(91)-C(96)	1.407(4)
C(92)-C(93)	1.398(4)
C(93)-C(94)	1.405(4)
C(94)-C(95)	1.394(5)
C(95)-C(96)	1.393(4)
C(1S)-Cl(1S)	1.711(8)
C(1S)-Cl(2S)	1.757(8)
C(1T)-Cl(1T)	1.701(11)
C(1T)-Cl(2T)	1.721(11)
C(1H)-C(3H)	1.522(5)
C(2H)-C(3H)	1.494(5)
C(2H)-C(2H)#1	1.499(7)

C(1)-Pd(1)-C(4)	175.58(9)
C(1)-Pd(1)-C(7)	88.19(9)
C(4)-Pd(1)-C(7)	87.39(9)
C(1)-Pd(1)-Br(1)	89.31(7)
C(4)-Pd(1)-Br(1)	95.10(7)
C(7)-Pd(1)-Br(1)	177.48(7)
N(2)-C(1)-N(1)	106.8(2)
N(2)-C(1)-Pd(1)	126.08(18)
N(1)-C(1)-Pd(1)	127.11(17)
C(1)-N(1)-C(11)	127.37(19)
C(1)-N(1)-C(2)	112.9(2)
C(11)-N(1)-C(2)	118.2(2)
C(12)-C(11)-C(16)	121.4(2)
C(12)-C(11)-N(1)	120.0(2)
C(16)-C(11)-N(1)	118.4(2)
C(13)-C(12)-C(11)	117.9(2)
C(13)-C(12)-C(17)	119.8(2)
C(11)-C(12)-C(17)	122.2(2)
C(14)-C(13)-C(12)	122.2(2)
C(13)-C(14)-C(15)	118.0(2)
C(13)-C(14)-C(18)	120.6(2)
C(15)-C(14)-C(18)	121.3(2)
C(16)-C(15)-C(14)	122.4(2)
C(15)-C(16)-C(11)	117.9(2)
C(15)-C(16)-C(19)	120.4(2)
C(11)-C(16)-C(19)	121.7(2)
N(1)-C(2)-C(3)	101.5(2)
N(2)-C(3)-C(2)	101.5(2)
C(1)-N(2)-C(21)	125.9(2)
C(1)-N(2)-C(3)	113.2(2)
C(21)-N(2)-C(3)	119.4(2)
C(26)-C(21)-C(22)	121.0(2)
C(26)-C(21)-N(2)	120.5(2)
C(22)-C(21)-N(2)	118.3(2)
C(23)-C(22)-C(21)	118.2(3)

C(23)-C(22)-C(27)	119.5(3)
C(21)-C(22)-C(27)	122.4(3)
C(24)-C(23)-C(22)	122.4(3)
C(23)-C(24)-C(25)	118.0(3)
C(23)-C(24)-C(28)	121.3(3)
C(25)-C(24)-C(28)	120.6(3)
C(24)-C(25)-C(26)	122.1(3)
C(21)-C(26)-C(25)	118.2(2)
C(21)-C(26)-C(29)	122.1(2)
C(25)-C(26)-C(29)	119.7(3)
N(3)-C(4)-N(4)	107.15(19)
N(3)-C(4)-Pd(1)	124.47(16)
N(4)-C(4)-Pd(1)	128.00(16)
C(4)-N(3)-C(31)	126.12(19)
C(4)-N(3)-C(5)	112.99(19)
C(31)-N(3)-C(5)	119.58(18)
C(32)-C(31)-C(36)	121.2(2)
C(32)-C(31)-N(3)	120.2(2)
C(36)-C(31)-N(3)	118.4(2)
C(31)-C(32)-C(33)	118.0(2)
C(31)-C(32)-C(37)	122.8(2)
C(33)-C(32)-C(37)	119.2(2)
C(34)-C(33)-C(32)	122.1(2)
C(35)-C(34)-C(33)	118.1(2)
C(35)-C(34)-C(38)	121.9(2)
C(33)-C(34)-C(38)	120.0(2)
C(34)-C(35)-C(36)	122.0(2)
C(35)-C(36)-C(31)	118.4(2)
C(35)-C(36)-C(39)	120.2(2)
C(31)-C(36)-C(39)	121.3(2)
N(3)-C(5)-C(6)	101.55(19)
N(4)-C(6)-C(5)	101.91(18)
C(4)-N(4)-C(41)	125.6(2)
C(4)-N(4)-C(6)	112.39(19)
C(41)-N(4)-C(6)	121.06(19)
C(46)-C(41)-C(42)	121.1(2)

C(46)-C(41)-N(4)	121.2(2)
C(42)-C(41)-N(4)	117.6(2)
C(43)-C(42)-C(41)	117.9(2)
C(43)-C(42)-C(47)	120.2(2)
C(41)-C(42)-C(47)	121.9(2)
C(44)-C(43)-C(42)	122.1(3)
C(45)-C(44)-C(43)	118.4(2)
C(45)-C(44)-C(48)	120.3(3)
C(43)-C(44)-C(48)	121.4(3)
C(44)-C(45)-C(46)	121.7(3)
C(41)-C(46)-C(45)	118.2(2)
C(41)-C(46)-C(49)	123.0(2)
C(45)-C(46)-C(49)	118.8(2)
C(8)-C(7)-Pd(1)	114.27(16)
C(7)-C(8)-C(9)	114.5(2)
C(91)-C(9)-C(8)	112.2(2)
C(92)-C(91)-C(96)	117.5(2)
C(92)-C(91)-C(9)	121.3(2)
C(96)-C(91)-C(9)	121.2(2)
C(93)-C(92)-C(91)	121.4(3)
C(92)-C(93)-C(94)	119.8(3)
C(95)-C(94)-C(93)	119.5(3)
C(96)-C(95)-C(94)	120.1(3)
C(95)-C(96)-C(91)	121.6(3)
Cl(1S)-C(1S)-Cl(2S)	112.3(6)
Cl(1T)-C(1T)-Cl(2T)	116.7(9)
C(3H)-C(2H)-C(2H)#1	118.2(4)
C(2H)-C(3H)-C(1H)	117.6(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x,-y+1,-z

Table 4. Anisotropic displacement parameters ($Å^2 x 10^3$) for 05185. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	21(1)	18(1)	22(1)	0(1)	5(1)	3(1)
Pd(1)	15(1)	15(1)	14(1)	0(1)	3(1)	1(1)
C(1)	17(1)	21(1)	16(1)	2(1)	1(1)	5(1)
N(1)	22(1)	23(1)	19(1)	4(1)	7(1)	-2(1)
C(11)	16(1)	22(1)	20(1)	2(1)	7(1)	-4(1)
C(12)	16(1)	21(1)	24(1)	1(1)	6(1)	-2(1)
C(13)	18(1)	25(1)	24(1)	2(1)	4(1)	-5(1)
C(14)	18(1)	27(1)	29(1)	-5(1)	9(1)	-6(1)
C(15)	17(1)	20(1)	38(2)	-3(1)	11(1)	-3(1)
C(16)	17(1)	18(1)	31(1)	7(1)	8(1)	-2(1)
C(17)	21(1)	24(1)	30(1)	0(1)	2(1)	4(1)
C(18)	33(2)	34(2)	35(2)	-12(1)	7(1)	-10(1)
C(19)	28(1)	26(1)	39(2)	9(1)	5(1)	1(1)
C(2)	36(2)	33(2)	26(1)	3(1)	16(1)	-7(1)
C(3)	36(2)	33(2)	20(1)	5(1)	10(1)	-1(1)
N(2)	26(1)	25(1)	15(1)	3(1)	7(1)	1(1)
C(21)	34(1)	22(1)	14(1)	3(1)	7(1)	2(1)
C(22)	43(2)	29(2)	17(1)	3(1)	11(1)	10(1)
C(23)	63(2)	27(2)	21(1)	0(1)	8(1)	16(1)
C(24)	65(2)	27(2)	21(1)	-1(1)	2(1)	1(1)
C(25)	39(2)	32(2)	21(1)	2(1)	-1(1)	-4(1)
C(26)	36(2)	25(1)	14(1)	3(1)	4(1)	3(1)
C(27)	42(2)	44(2)	30(2)	5(1)	17(1)	17(1)
C(28)	89(3)	37(2)	43(2)	-15(2)	-4(2)	-6(2)
C(29)	29(1)	32(2)	23(1)	-2(1)	1(1)	6(1)
C(4)	15(1)	15(1)	17(1)	-2(1)	3(1)	2(1)
N(3)	17(1)	18(1)	18(1)	1(1)	4(1)	-3(1)
C(31)	17(1)	22(1)	14(1)	3(1)	3(1)	-1(1)
C(32)	20(1)	21(1)	16(1)	3(1)	5(1)	1(1)
C(33)	24(1)	24(1)	18(1)	-1(1)	4(1)	-4(1)
C(34)	20(1)	34(1)	17(1)	2(1)	1(1)	-2(1)

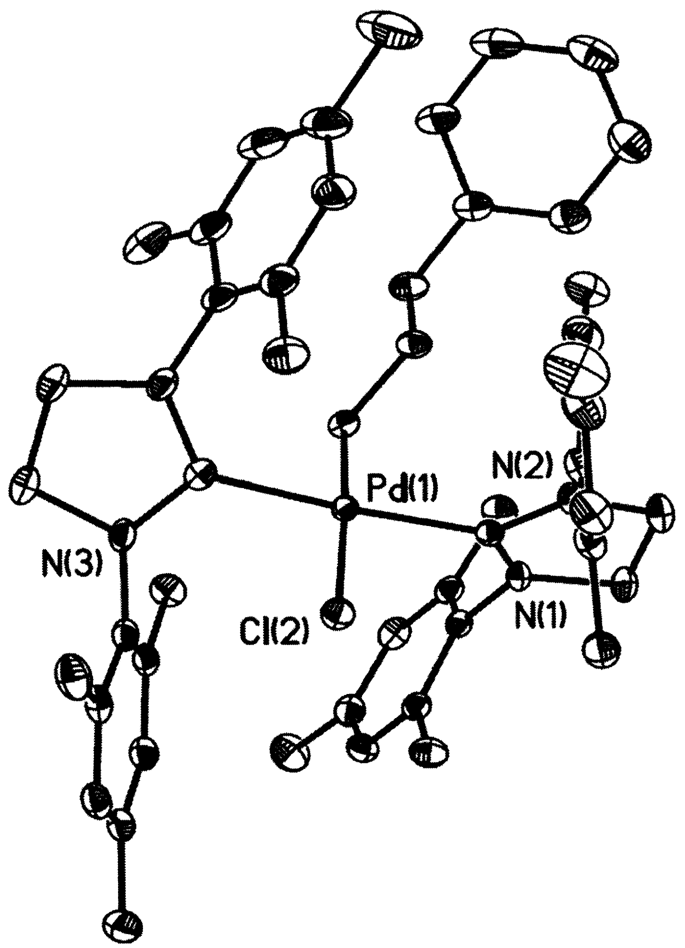
C(35)	19(1)	30(1)	21(1)	4(1)	4(1)	6(1)
C(36)	21(1)	20(1)	17(1)	3(1)	6(1)	1(1)
C(37)	26(1)	22(1)	23(1)	-2(1)	3(1)	5(1)
C(38)	22(1)	42(2)	35(2)	-1(1)	-5(1)	-1(1)
C(39)	30(1)	21(1)	25(1)	2(1)	3(1)	4(1)
C(5)	22(1)	23(1)	23(1)	6(1)	6(1)	-5(1)
C(6)	19(1)	22(1)	28(1)	6(1)	4(1)	-4(1)
N(4)	17(1)	17(1)	24(1)	4(1)	3(1)	-2(1)
C(41)	15(1)	21(1)	28(1)	5(1)	0(1)	0(1)
C(42)	18(1)	22(1)	33(1)	-1(1)	2(1)	-4(1)
C(43)	19(1)	25(1)	47(2)	2(1)	-1(1)	3(1)
C(44)	23(1)	32(2)	40(2)	5(1)	-10(1)	0(1)
C(45)	24(1)	35(2)	30(1)	0(1)	-3(1)	-3(1)
C(46)	19(1)	24(1)	29(1)	0(1)	3(1)	-2(1)
C(47)	23(1)	24(1)	35(2)	-1(1)	7(1)	1(1)
C(48)	43(2)	52(2)	53(2)	1(2)	-22(2)	12(2)
C(49)	26(1)	33(2)	31(2)	-6(1)	1(1)	1(1)
C(7)	20(1)	24(1)	15(1)	2(1)	4(1)	4(1)
C(8)	23(1)	20(1)	19(1)	-2(1)	4(1)	2(1)
C(9)	24(1)	23(1)	24(1)	-2(1)	3(1)	7(1)
C(91)	28(1)	20(1)	22(1)	-1(1)	0(1)	9(1)
C(92)	39(2)	23(1)	30(2)	-1(1)	6(1)	5(1)
C(93)	43(2)	24(2)	44(2)	2(1)	5(1)	-1(1)
C(94)	48(2)	25(2)	41(2)	-5(1)	-12(1)	0(1)
C(95)	55(2)	33(2)	22(1)	-7(1)	-1(1)	5(1)
C(96)	38(2)	28(1)	26(1)	-1(1)	3(1)	7(1)
C(1S)	36(4)	57(5)	25(5)	-12(4)	10(4)	-18(4)
Cl(1S)	97(3)	80(3)	25(2)	-7(1)	25(2)	-41(2)
Cl(2S)	61(2)	59(2)	75(3)	-16(2)	39(2)	-23(2)
C(1T)	53(7)	133(15)	15(4)	2(6)	-6(4)	-27(8)
Cl(1T)	87(3)	30(2)	100(4)	-18(2)	57(3)	1(2)
Cl(2T)	98(4)	158(6)	28(2)	3(3)	15(2)	-78(4)
C(1H)	55(2)	39(2)	33(2)	13(1)	15(1)	16(2)
C(2H)	66(3)	52(2)	48(2)	7(2)	17(2)	14(2)
C(3H)	84(3)	45(2)	50(2)	5(2)	27(2)	9(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 05185.

	x	y	z	U(eq)
H(13)	7270	11017	2865	27
H(15)	5474	13125	2306	29
H(17A)	7749	9818	2379	38
H(17B)	7256	9786	1840	38
H(17C)	6554	9409	2218	38
H(18A)	6172	13172	3115	50
H(18B)	7414	12830	3172	50
H(18C)	6507	12241	3373	50
H(19A)	4440	13079	1561	47
H(19B)	4133	12110	1341	47
H(19C)	5161	12648	1204	47
H(2A)	7084	10806	1098	37
H(2B)	6248	11620	935	37
H(3A)	5233	10753	386	35
H(3B)	6296	10107	435	35
H(23)	5049	7091	84	44
H(25)	2150	8330	106	38
H(27A)	6678	7594	589	56
H(27B)	6677	8530	860	56
H(27C)	6775	8520	319	56
H(28A)	3426	6450	-357	87
H(28B)	2319	7026	-434	87
H(28C)	2599	6402	16	87
H(29A)	2603	9767	889	42
H(29B)	2089	9857	354	42
H(29C)	3191	10384	549	42
H(33)	6098	10172	3403	26
H(35)	7229	7668	3211	28

H(37A)	4079	10413	2672	36
H(37B)	4176	10500	3223	36
H(37C)	3346	9788	2950	36
H(38A)	8335	8740	3747	51
H(38B)	7883	9737	3800	51
H(38C)	8416	9471	3351	51
H(39A)	6137	6596	2722	38
H(39B)	4948	6869	2463	38
H(39C)	5102	6551	2993	38
H(5A)	2690	8111	3053	27
H(5B)	3289	7180	2956	27
H(6A)	2108	6915	2294	27
H(6B)	1320	7630	2499	27
H(43)	-408	10156	1553	37
H(45)	202	8249	641	36
H(47A)	1143	9192	2539	40
H(47B)	278	9968	2370	40
H(47C)	1550	10116	2342	40
H(48A)	-1432	10191	790	78
H(48B)	-1486	9285	492	78
H(48C)	-593	10037	428	78
H(49A)	2264	7367	967	45
H(49B)	1130	6856	982	45
H(49C)	2006	6940	1442	45
H(7A)	5706	8331	1482	23
H(7B)	5525	8036	1991	23
H(8A)	4115	7491	1167	25
H(8B)	3970	7178	1679	25
H(9A)	5832	6684	1247	29
H(9B)	5602	6325	1740	29
H(92)	3580	5534	1677	37
H(93)	2502	4397	1287	45
H(94)	2898	3858	569	48
H(95)	4365	4478	249	45
H(96)	5393	5646	626	37
H(1S1)	3346	6619	3966	46

H(1S2)	4245	6008	4272	46
H(1T1)	3160	7028	3871	81
H(1T2)	3899	6223	4103	81
H(1H1)	1833	4031	-904	62
H(1H2)	1151	3350	-632	62
H(1H3)	2199	3855	-362	62
H(2H1)	962	4551	202	65
H(2H2)	-86	4062	-72	65
H(3H1)	1279	5242	-484	70
H(3H2)	237	4743	-757	70


Pd(1)
N(2)
N(3)
Cl(2)
N(1)

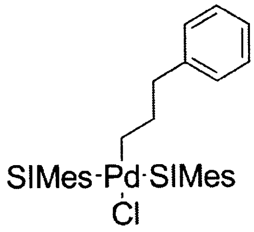

SIMes·Pd·SIMes
Cl

Table 1. Crystal data and structure refinement for 05222.

Identification code	05222	
Empirical formula	C55 H72 Cl3 N4 Pd	
Formula weight	1001.92	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.1896(3) Å	α = 90°.
	b = 14.6636(3) Å	β = 98.3640(10)°.
	c = 28.8537(7) Å	γ = 90°.
Volume	5102.6(2) $Å^3$	
Z	4	
Density (calculated)	1.304 Mg/m^3	
Absorption coefficient	0.560 mm^{-1}	
F(000)	2108	
Crystal size	0.25 x 0.25 x 0.20 mm^3	
Theta range for data collection	1.93 to 29.57°.	
Index ranges	-16<=h<=16, -20<=k<=20, -40<=l<=40	
Reflections collected	113115	
Independent reflections	14313 [R(int) = 0.0598]	
Completeness to theta = 29.57°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8962 and 0.8726	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14313 / 0 / 581	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0413, wR2 = 0.1013	
R indices (all data)	R1 = 0.0565, wR2 = 0.1093	
Largest diff. peak and hole	0.879 and -1.541 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for 05222. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(2S)	6573(3)	3901(2)	4404(1)	45(1)
C(4S)	5364(3)	4617(2)	4946(1)	45(1)
Pd(1)	4140(1)	5676(1)	1730(1)	13(1)
Cl(2)	3032(1)	4295(1)	1771(1)	18(1)
N(3)	5644(2)	4243(1)	1395(1)	18(1)
C(16)	4948(2)	5643(2)	3019(1)	17(1)
N(2)	2284(2)	6822(1)	2047(1)	17(1)
N(1)	3748(2)	6781(1)	2575(1)	15(1)
C(32)	6588(2)	4193(2)	2204(1)	18(1)
C(22)	820(2)	5720(2)	1812(1)	20(1)
C(24)	-170(2)	5711(2)	1018(1)	28(1)
C(4)	5049(2)	5009(2)	1301(1)	16(1)
C(53)	4598(2)	9272(2)	1186(1)	22(1)
N(4)	5164(2)	5259(1)	859(1)	20(1)
C(1)	3306(2)	6452(1)	2152(1)	14(1)
C(41)	4579(2)	5990(2)	598(1)	22(1)
C(15)	5976(2)	5426(2)	3270(1)	21(1)
C(11)	4796(2)	6524(2)	2832(1)	15(1)
C(35)	5728(2)	2454(2)	2303(1)	22(1)
C(31)	5876(2)	3787(2)	1838(1)	18(1)
C(33)	6830(2)	3712(2)	2624(1)	20(1)
C(12)	5636(2)	7178(2)	2914(1)	18(1)
C(2)	2949(2)	7316(2)	2804(1)	21(1)
C(36)	5449(2)	2911(2)	1881(1)	20(1)
C(42)	3428(2)	5946(2)	470(1)	24(1)
C(51)	4504(2)	7650(2)	1475(1)	19(1)
C(21)	1422(2)	6479(2)	1697(1)	19(1)
C(34)	6404(2)	2849(2)	2682(1)	22(1)
C(14)	6847(2)	6044(2)	3334(1)	21(1)

C(17)	5446(2)	8146(2)	2755(1)	22(1)
C(26)	1160(2)	6915(2)	1264(1)	22(1)
C(18)	7973(2)	5765(2)	3583(1)	32(1)
C(56)	3336(3)	10691(2)	725(1)	37(1)
C(23)	37(2)	5341(2)	1465(1)	27(1)
C(27)	1002(2)	5316(2)	2296(1)	23(1)
C(29)	1663(2)	7811(2)	1152(1)	28(1)
C(52)	5247(2)	8479(2)	1422(1)	23(1)
C(3)	2050(2)	7514(2)	2394(1)	22(1)
C(13)	6656(2)	6925(2)	3159(1)	21(1)
C(6)	6303(2)	3996(2)	1022(1)	27(1)
C(54)	4820(2)	9606(2)	758(1)	29(1)
C(5)	5752(2)	4569(2)	615(1)	27(1)
C(45)	4630(3)	7402(2)	184(1)	36(1)
C(49)	6444(3)	6748(2)	560(1)	37(1)
C(38)	4686(2)	2473(2)	1487(1)	27(1)
C(25)	364(2)	6506(2)	929(1)	27(1)
C(58)	3735(2)	9671(2)	1383(1)	28(1)
C(43)	2907(3)	6663(2)	210(1)	31(1)
C(47)	2763(2)	5148(2)	595(1)	28(1)
C(28)	-967(3)	5253(2)	635(1)	43(1)
C(44)	3486(3)	7402(2)	69(1)	38(1)
C(46)	5200(2)	6711(2)	449(1)	28(1)
C(37)	6659(2)	2358(2)	3145(1)	30(1)
C(57)	3100(3)	10369(2)	1151(1)	35(1)
C(55)	4197(3)	10312(2)	533(1)	38(1)
C(48)	2885(4)	8188(2)	-196(1)	58(1)
C(19)	4044(2)	4934(2)	2957(1)	22(1)
C(39)	7099(2)	5119(2)	2158(1)	22(1)
C(50)	5127(2)	6808(2)	1678(1)	17(1)
Cl(1S)	3455(1)	7894(1)	4657(1)	64(1)
Cl(2S)	4937(1)	7708(1)	3964(1)	71(1)
C(1S)	3828(3)	8293(3)	4134(1)	63(1)
C(3S)	5834(3)	4676(2)	4497(1)	47(1)

Table 3. Bond lengths [Å] and angles [°] for 05222.

C(2S)-C(3S)	1.498(5)
C(4S)-C(4S)#1	1.492(6)
C(4S)-C(3S)	1.495(4)
Pd(1)-C(4)	2.028(2)
Pd(1)-C(1)	2.044(2)
Pd(1)-C(50)	2.068(2)
Pd(1)-Cl(2)	2.4462(5)
N(3)-C(4)	1.343(3)
N(3)-C(31)	1.434(3)
N(3)-C(6)	1.479(3)
C(16)-C(15)	1.390(3)
C(16)-C(11)	1.401(3)
C(16)-C(19)	1.507(3)
N(2)-C(1)	1.352(3)
N(2)-C(21)	1.439(3)
N(2)-C(3)	1.482(3)
N(1)-C(1)	1.348(3)
N(1)-C(11)	1.431(3)
N(1)-C(2)	1.478(3)
C(32)-C(33)	1.394(3)
C(32)-C(31)	1.399(3)
C(32)-C(39)	1.508(3)
C(22)-C(23)	1.393(3)
C(22)-C(21)	1.399(3)
C(22)-C(27)	1.505(3)
C(24)-C(25)	1.377(4)
C(24)-C(23)	1.390(4)
C(24)-C(28)	1.517(4)
C(4)-N(4)	1.354(3)
C(53)-C(54)	1.391(3)
C(53)-C(58)	1.395(4)
C(53)-C(52)	1.510(3)
N(4)-C(41)	1.437(3)
N(4)-C(5)	1.477(3)

C(41)-C(42)	1.400(4)
C(41)-C(46)	1.404(3)
C(15)-C(14)	1.389(3)
C(11)-C(12)	1.398(3)
C(35)-C(36)	1.388(3)
C(35)-C(34)	1.397(4)
C(31)-C(36)	1.398(3)
C(33)-C(34)	1.388(3)
C(12)-C(13)	1.388(3)
C(12)-C(17)	1.501(3)
C(2)-C(3)	1.519(3)
C(36)-C(38)	1.505(3)
C(42)-C(43)	1.391(4)
C(42)-C(47)	1.498(4)
C(51)-C(50)	1.521(3)
C(51)-C(52)	1.536(3)
C(21)-C(26)	1.398(3)
C(34)-C(37)	1.508(3)
C(14)-C(13)	1.395(3)
C(14)-C(18)	1.509(3)
C(26)-C(25)	1.402(3)
C(26)-C(29)	1.505(4)
C(56)-C(55)	1.374(5)
C(56)-C(57)	1.385(4)
C(6)-C(5)	1.519(4)
C(54)-C(55)	1.388(4)
C(45)-C(44)	1.386(5)
C(45)-C(46)	1.391(4)
C(49)-C(46)	1.505(4)
C(58)-C(57)	1.394(4)
C(43)-C(44)	1.386(4)
C(44)-C(48)	1.512(4)
Cl(1S)-C(1S)	1.739(4)
Cl(2S)-C(1S)	1.732(4)

C(4S)#1-C(4S)-C(3S)	116.8(4)

C(4)-Pd(1)-C(1)	174.75(8)
C(4)-Pd(1)-C(50)	88.15(9)
C(1)-Pd(1)-C(50)	86.62(8)
C(4)-Pd(1)-Cl(2)	89.18(6)
C(1)-Pd(1)-Cl(2)	96.06(6)
C(50)-Pd(1)-Cl(2)	177.30(6)
C(4)-N(3)-C(31)	126.97(19)
C(4)-N(3)-C(6)	113.10(19)
C(31)-N(3)-C(6)	118.45(19)
C(15)-C(16)-C(11)	118.1(2)
C(15)-C(16)-C(19)	119.4(2)
C(11)-C(16)-C(19)	122.4(2)
C(1)-N(2)-C(21)	124.87(19)
C(1)-N(2)-C(3)	112.67(18)
C(21)-N(2)-C(3)	121.42(18)
C(1)-N(1)-C(11)	125.64(18)
C(1)-N(1)-C(2)	113.06(18)
C(11)-N(1)-C(2)	120.29(18)
C(33)-C(32)-C(31)	118.0(2)
C(33)-C(32)-C(39)	119.6(2)
C(31)-C(32)-C(39)	122.4(2)
C(23)-C(22)-C(21)	118.4(2)
C(23)-C(22)-C(27)	120.2(2)
C(21)-C(22)-C(27)	121.5(2)
C(25)-C(24)-C(23)	118.5(2)
C(25)-C(24)-C(28)	120.6(3)
C(23)-C(24)-C(28)	120.9(3)
N(3)-C(4)-N(4)	106.86(19)
N(3)-C(4)-Pd(1)	127.35(16)
N(4)-C(4)-Pd(1)	125.78(17)
C(54)-C(53)-C(58)	117.9(2)
C(54)-C(53)-C(52)	121.0(2)
C(58)-C(53)-C(52)	121.1(2)
C(4)-N(4)-C(41)	125.7(2)
C(4)-N(4)-C(5)	112.8(2)
C(41)-N(4)-C(5)	119.98(19)

N(1)-C(1)-N(2)	107.02(18)
N(1)-C(1)-Pd(1)	124.84(16)
N(2)-C(1)-Pd(1)	127.69(16)
C(42)-C(41)-C(46)	121.2(2)
C(42)-C(41)-N(4)	120.4(2)
C(46)-C(41)-N(4)	118.3(2)
C(14)-C(15)-C(16)	122.3(2)
C(12)-C(11)-C(16)	120.9(2)
C(12)-C(11)-N(1)	118.9(2)
C(16)-C(11)-N(1)	120.1(2)
C(36)-C(35)-C(34)	121.9(2)
C(36)-C(31)-C(32)	121.5(2)
C(36)-C(31)-N(3)	118.6(2)
C(32)-C(31)-N(3)	119.7(2)
C(34)-C(33)-C(32)	122.2(2)
C(13)-C(12)-C(11)	118.9(2)
C(13)-C(12)-C(17)	119.7(2)
C(11)-C(12)-C(17)	121.4(2)
N(1)-C(2)-C(3)	101.63(18)
C(35)-C(36)-C(31)	118.3(2)
C(35)-C(36)-C(38)	120.2(2)
C(31)-C(36)-C(38)	121.5(2)
C(43)-C(42)-C(41)	118.0(2)
C(43)-C(42)-C(47)	120.1(2)
C(41)-C(42)-C(47)	121.9(2)
C(50)-C(51)-C(52)	114.34(19)
C(26)-C(21)-C(22)	121.1(2)
C(26)-C(21)-N(2)	121.1(2)
C(22)-C(21)-N(2)	117.8(2)
C(33)-C(34)-C(35)	118.0(2)
C(33)-C(34)-C(37)	120.8(2)
C(35)-C(34)-C(37)	121.2(2)
C(15)-C(14)-C(13)	118.1(2)
C(15)-C(14)-C(18)	120.8(2)
C(13)-C(14)-C(18)	121.1(2)
C(21)-C(26)-C(25)	117.7(2)

C(21)-C(26)-C(29)	123.0(2)
C(25)-C(26)-C(29)	119.2(2)
C(55)-C(56)-C(57)	119.3(3)
C(24)-C(23)-C(22)	121.6(2)
C(53)-C(52)-C(51)	112.1(2)
N(2)-C(3)-C(2)	101.86(18)
C(12)-C(13)-C(14)	121.5(2)
N(3)-C(6)-C(5)	101.63(19)
C(55)-C(54)-C(53)	121.0(3)
N(4)-C(5)-C(6)	101.59(19)
C(44)-C(45)-C(46)	122.4(3)
C(24)-C(25)-C(26)	122.2(2)
C(57)-C(58)-C(53)	120.8(3)
C(44)-C(43)-C(42)	122.5(3)
C(43)-C(44)-C(45)	117.9(3)
C(43)-C(44)-C(48)	120.9(3)
C(45)-C(44)-C(48)	121.2(3)
C(45)-C(46)-C(41)	118.0(3)
C(45)-C(46)-C(49)	119.8(3)
C(41)-C(46)-C(49)	122.2(3)
C(56)-C(57)-C(58)	120.2(3)
C(56)-C(55)-C(54)	120.7(3)
C(51)-C(50)-Pd(1)	114.62(15)
Cl(2S)-C(1S)-Cl(1S)	113.1(2)
C(4S)-C(3S)-C(2S)	115.3(3)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+1

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 05222. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(2S)	55(2)	45(2)	35(2)	6(1)	11(2)	9(2)
C(4S)	53(2)	42(2)	43(2)	6(1)	14(2)	11(2)
Pd(1)	14(1)	12(1)	12(1)	0(1)	3(1)	-1(1)
Cl(2)	19(1)	15(1)	21(1)	0(1)	5(1)	-3(1)
N(3)	20(1)	18(1)	18(1)	-4(1)	7(1)	2(1)
C(16)	20(1)	17(1)	15(1)	-1(1)	5(1)	-1(1)
N(2)	15(1)	15(1)	22(1)	-2(1)	3(1)	2(1)
N(1)	16(1)	14(1)	17(1)	-2(1)	4(1)	2(1)
C(32)	15(1)	16(1)	23(1)	-1(1)	6(1)	2(1)
C(22)	15(1)	18(1)	28(1)	0(1)	2(1)	2(1)
C(24)	20(1)	29(1)	34(1)	-2(1)	-5(1)	1(1)
C(4)	17(1)	17(1)	15(1)	-3(1)	3(1)	-4(1)
C(53)	28(1)	18(1)	19(1)	0(1)	0(1)	-8(1)
N(4)	26(1)	22(1)	14(1)	-3(1)	6(1)	1(1)
C(1)	15(1)	11(1)	18(1)	2(1)	5(1)	-2(1)
C(41)	33(1)	22(1)	12(1)	-2(1)	5(1)	-2(1)
C(15)	24(1)	20(1)	18(1)	2(1)	2(1)	3(1)
C(11)	17(1)	17(1)	13(1)	-2(1)	3(1)	0(1)
C(35)	18(1)	16(1)	36(1)	1(1)	10(1)	1(1)
C(31)	16(1)	18(1)	20(1)	-1(1)	6(1)	3(1)
C(33)	17(1)	21(1)	22(1)	-1(1)	3(1)	3(1)
C(12)	23(1)	17(1)	16(1)	-2(1)	6(1)	-2(1)
C(2)	22(1)	20(1)	21(1)	-6(1)	6(1)	3(1)
C(36)	16(1)	17(1)	27(1)	-5(1)	6(1)	2(1)
C(42)	33(1)	24(1)	15(1)	-2(1)	3(1)	-1(1)
C(51)	23(1)	16(1)	18(1)	2(1)	2(1)	-4(1)
C(21)	15(1)	16(1)	25(1)	-2(1)	0(1)	3(1)
C(34)	20(1)	21(1)	27(1)	3(1)	8(1)	7(1)
C(14)	19(1)	26(1)	17(1)	-2(1)	1(1)	2(1)
C(17)	25(1)	17(1)	24(1)	0(1)	2(1)	-5(1)
C(26)	18(1)	22(1)	26(1)	1(1)	3(1)	4(1)

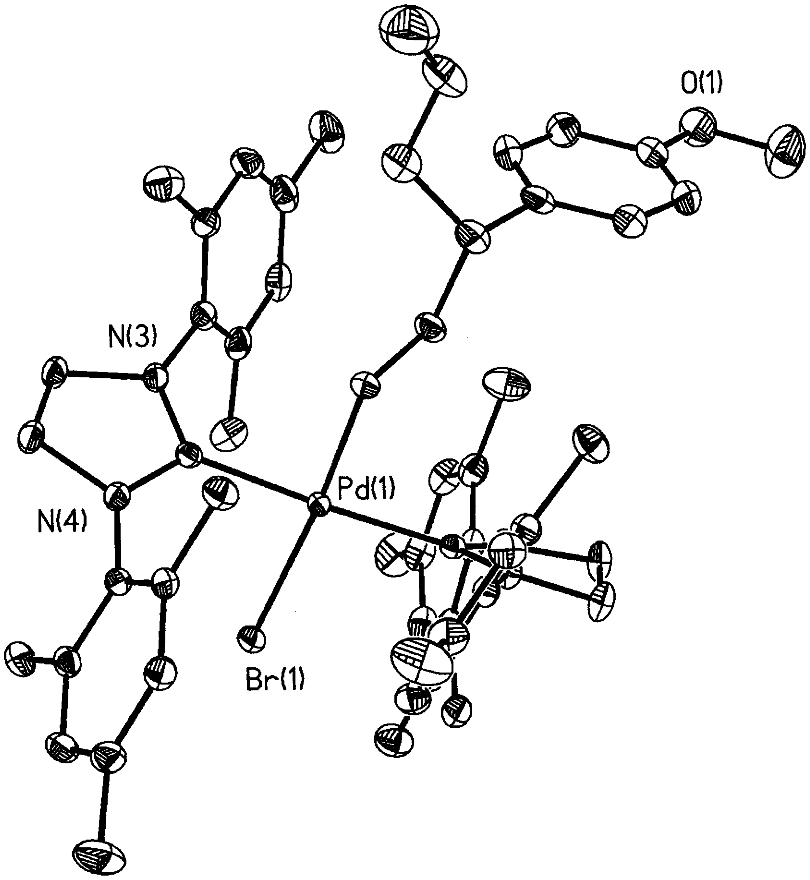
C(18)	23(1)	36(2)	32(1)	1(1)	-5(1)	2(1)
C(56)	49(2)	21(1)	37(2)	4(1)	-11(1)	0(1)
C(23)	20(1)	23(1)	37(1)	-1(1)	1(1)	-3(1)
C(27)	22(1)	20(1)	29(1)	1(1)	6(1)	-2(1)
C(29)	27(1)	26(1)	30(1)	7(1)	0(1)	0(1)
C(52)	25(1)	21(1)	22(1)	4(1)	2(1)	-7(1)
C(3)	19(1)	20(1)	28(1)	-5(1)	5(1)	3(1)
C(13)	19(1)	24(1)	20(1)	-4(1)	3(1)	-5(1)
C(6)	31(1)	30(1)	23(1)	-3(1)	13(1)	7(1)
C(54)	40(2)	26(1)	22(1)	3(1)	5(1)	-7(1)
C(5)	34(1)	30(1)	19(1)	-6(1)	10(1)	3(1)
C(45)	69(2)	23(1)	18(1)	0(1)	11(1)	-9(1)
C(49)	47(2)	40(2)	28(1)	-6(1)	17(1)	-17(1)
C(38)	24(1)	21(1)	37(1)	-8(1)	3(1)	-1(1)
C(25)	22(1)	30(1)	26(1)	2(1)	-2(1)	4(1)
C(58)	36(2)	19(1)	29(1)	2(1)	5(1)	-5(1)
C(43)	41(2)	32(1)	18(1)	-1(1)	-1(1)	6(1)
C(47)	28(1)	31(1)	23(1)	1(1)	-1(1)	-4(1)
C(28)	35(2)	46(2)	43(2)	-3(1)	-15(1)	-10(1)
C(44)	67(2)	26(1)	18(1)	2(1)	1(1)	3(1)
C(46)	44(2)	26(1)	16(1)	-4(1)	10(1)	-8(1)
C(37)	30(1)	30(1)	31(1)	11(1)	7(1)	7(1)
C(57)	40(2)	22(1)	44(2)	-2(1)	2(1)	-1(1)
C(55)	58(2)	30(1)	24(1)	8(1)	-2(1)	-6(1)
C(48)	91(3)	37(2)	40(2)	14(2)	-6(2)	10(2)
C(19)	24(1)	18(1)	23(1)	3(1)	2(1)	-4(1)
C(39)	21(1)	19(1)	27(1)	0(1)	2(1)	-4(1)
C(50)	20(1)	17(1)	15(1)	0(1)	3(1)	-3(1)
Cl(1S)	95(1)	45(1)	59(1)	13(1)	41(1)	16(1)
Cl(2S)	74(1)	91(1)	52(1)	9(1)	26(1)	39(1)
C(1S)	57(2)	94(3)	41(2)	24(2)	20(2)	34(2)
C(3S)	61(2)	36(2)	47(2)	6(1)	22(2)	6(2)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 05222.

	x	y	z	U(eq)
H(2S1)	7243	3906	4637	67
H(2S2)	6780	3966	4090	67
H(2S3)	6179	3323	4424	67
H(4S1)	4933	4044	4943	54
H(4S2)	5989	4570	5206	54
H(15)	6086	4833	3402	25
H(35)	5451	1855	2334	27
H(33)	7301	3984	2877	24
H(2A)	3288	7885	2943	25
H(2B)	2658	6956	3049	25
H(51A)	3952	7821	1679	23
H(51B)	4094	7494	1163	23
H(17A)	4950	8157	2456	34
H(17B)	6156	8427	2715	34
H(17C)	5108	8488	2990	34
H(18A)	7884	5313	3825	47
H(18B)	8360	6301	3728	47
H(18C)	8407	5499	3356	47
H(56)	2907	11169	567	45
H(23)	-366	4818	1537	32
H(27A)	321	5013	2358	35
H(27B)	1196	5802	2527	35
H(27C)	1607	4870	2320	35
H(29A)	2002	8105	1443	42
H(29B)	1084	8207	989	42
H(29C)	2232	7704	950	42
H(52A)	5612	8671	1736	28
H(52B)	5833	8302	1236	28

H(3A)	1301	7431	2482	27
H(3B)	2116	8141	2273	27
H(13)	7236	7363	3209	25
H(6A)	6245	3336	949	33
H(6B)	7093	4161	1110	33
H(54)	5407	9348	618	35
H(5A)	6308	4854	442	32
H(5B)	5229	4202	395	32
H(45)	5041	7891	79	44
H(49A)	6773	6440	312	56
H(49B)	6682	6443	860	56
H(49C)	6686	7386	581	56
H(38A)	4069	2887	1381	41
H(38B)	4396	1902	1596	41
H(38C)	5096	2345	1226	41
H(25)	187	6786	630	32
H(58)	3577	9464	1678	34
H(43)	2124	6646	125	37
H(47A)	2639	5203	922	41
H(47B)	3167	4582	555	41
H(47C)	2047	5136	391	41
H(28A)	-1366	5720	433	65
H(28B)	-1499	4883	777	65
H(28C)	-551	4861	448	65
H(37A)	6235	2635	3372	45
H(37B)	7453	2405	3261	45
H(37C)	6453	1714	3103	45
H(57)	2503	10625	1286	42
H(55)	4369	10535	243	46
H(48A)	2291	7951	-430	86
H(48B)	3408	8539	-352	86
H(48C)	2566	8584	24	86
H(19A)	4041	4625	2655	33
H(19B)	3325	5229	2963	33
H(19C)	4178	4487	3211	33
H(39A)	7256	5201	1837	33

H(39B)	7791	5165	2377	33
H(39C)	6583	5592	2231	33
H(50A)	5517	6959	1994	20
H(50B)	5697	6650	1479	20
H(1S1)	3183	8241	3885	75
H(1S2)	4023	8948	4170	75
H(3S1)	6261	5251	4497	56
H(3S2)	5213	4711	4235	56


O(1)
N(3)
Pd(1)
N(4)
Br(1)

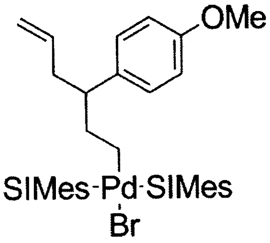

OMe
SIMes-Pd-SIMes
Br

Table 1. Crystal data and structure refinement for 05197.

Identification code	05197	
Empirical formula	C56 H71 Br Cl2 N4 O Pd	
Formula weight	1073.38	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 12.5782(18) Å	$\alpha = 90°$.
	b = 15.1298(18) Å	$\beta = 92.924(5)°$.
	c = 29.463(4) Å	$\gamma = 90°$.
Volume	5599.7(13) $Å^3$	
Z	4	
Density (calculated)	1.273 Mg/m^3	
Absorption coefficient	1.180 mm^{-1}	
F(000)	2232	
Crystal size	0.20 x 0.20 x 0.15 mm^3	
Theta range for data collection	1.93 to 29.57°.	
Index ranges	-17<=h<=17, -21<=k<=21, -40<=l<=40	
Reflections collected	114751	
Independent reflections	15714 [R(int) = 0.0528]	
Completeness to theta = 29.57°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8429 and 0.7983	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15714 / 7 / 611	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0475, wR2 = 0.1404	
R indices (all data)	R1 = 0.0596, wR2 = 0.1487	
Largest diff. peak and hole	2.366 and -1.397 e.$Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 05197. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pd(1)	707(1)	1219(1)	1653(1)	13(1)
Br(1)	1920(1)	-144(1)	1790(1)	19(1)
C(1)	-348(2)	2259(2)	1505(1)	18(1)
C(2)	186(3)	3057(2)	1300(1)	22(1)
C(3)	-561(3)	3879(2)	1203(1)	32(1)
C(4)	-1523(3)	3701(2)	885(1)	33(1)
C(5)	-2248(3)	4467(2)	829(1)	35(1)
C(6)	-3277(4)	4408(4)	816(2)	61(1)
C(51)	181(3)	4613(2)	1038(1)	32(1)
C(52)	543(4)	4643(2)	597(1)	36(1)
C(53)	1287(4)	5263(3)	468(1)	36(1)
C(54)	1704(3)	5880(2)	785(1)	28(1)
C(55)	1353(3)	5864(2)	1223(1)	29(1)
C(56)	597(3)	5234(2)	1344(1)	29(1)
O(1)	2426(2)	6469(2)	623(1)	38(1)
C(57)	2894(4)	7079(3)	938(2)	54(1)
C(7)	1555(2)	2059(2)	2086(1)	14(1)
C(71)	2764(3)	3158(2)	2365(1)	23(1)
C(72)	1963(3)	2977(2)	2723(1)	23(1)
N(1)	2508(2)	2445(2)	2031(1)	18(1)
C(11)	3333(2)	2138(2)	1742(1)	19(1)
C(12)	3512(3)	2557(2)	1329(1)	23(1)
C(13)	4332(3)	2237(3)	1071(1)	27(1)
C(14)	4987(3)	1547(3)	1219(1)	29(1)
C(15)	4827(3)	1177(2)	1644(1)	26(1)
C(16)	4018(2)	1468(2)	1914(1)	21(1)
C(17)	2877(3)	3347(3)	1157(1)	37(1)
C(18)	5896(3)	1245(3)	940(2)	43(1)
C(19)	3913(3)	1080(2)	2381(1)	24(1)

N(2)	1180(2)	2408(2)	2469(1)	17(1)
C(21)	221(2)	2175(2)	2688(1)	17(1)
C(22)	-582(2)	2815(2)	2714(1)	19(1)
C(23)	-1486(3)	2606(2)	2948(1)	22(1)
C(24)	-1595(3)	1790(2)	3160(1)	23(1)
C(25)	-768(3)	1181(2)	3143(1)	21(1)
C(26)	150(2)	1352(2)	2909(1)	19(1)
C(27)	-473(3)	3725(2)	2509(1)	25(1)
C(28)	-2599(3)	1567(3)	3401(2)	39(1)
C(29)	1021(3)	669(2)	2902(1)	25(1)
C(8)	-203(2)	461(2)	1219(1)	15(1)
C(81)	-889(3)	-206(2)	545(1)	21(1)
C(82)	-1425(3)	-618(2)	944(1)	21(1)
N(3)	-350(2)	567(2)	764(1)	17(1)
C(31)	93(3)	1243(2)	486(1)	18(1)
C(32)	-622(3)	1788(2)	231(1)	21(1)
C(33)	-209(3)	2422(2)	-60(1)	27(1)
C(34)	878(3)	2529(2)	-98(1)	29(1)
C(35)	1562(3)	1967(2)	150(1)	26(1)
C(36)	1192(3)	1307(2)	438(1)	22(1)
C(37)	-1812(3)	1716(3)	259(1)	31(1)
C(38)	1307(4)	3235(3)	-407(1)	40(1)
C(39)	1972(3)	680(2)	666(1)	28(1)
N(4)	-760(2)	-266(2)	1331(1)	17(1)
C(41)	-910(2)	-613(2)	1776(1)	16(1)
C(42)	-1516(2)	-150(2)	2085(1)	18(1)
C(43)	-1680(2)	-543(2)	2507(1)	20(1)
C(44)	-1278(3)	-1375(2)	2622(1)	23(1)
C(45)	-694(2)	-1825(2)	2304(1)	21(1)
C(46)	-497(2)	-1461(2)	1880(1)	18(1)
C(47)	-2011(3)	744(2)	1981(1)	22(1)
C(48)	-1509(4)	-1801(3)	3069(1)	37(1)
C(49)	151(3)	-1972(2)	1552(1)	23(1)
C(1S)	4000(4)	9328(3)	953(2)	43(1)
Cl(1S)	4316(1)	9291(1)	375(1)	61(1)
Cl(2S)	4915(1)	8702(1)	1294(1)	56(1)

Table 3. Bond lengths [Å] and angles [°] for 05197.

Pd(1)-C(8)	2.026(3)
Pd(1)-C(7)	2.060(3)
Pd(1)-C(1)	2.089(3)
Pd(1)-Br(1)	2.5839(4)
C(1)-C(2)	1.522(4)
C(2)-C(3)	1.576(5)
C(3)-C(4)	1.518(5)
C(3)-C(51)	1.544(5)
C(4)-C(5)	1.479(5)
C(5)-C(6)	1.296(7)
C(51)-C(56)	1.384(5)
C(51)-C(52)	1.401(6)
C(52)-C(53)	1.391(6)
C(53)-C(54)	1.401(5)
C(54)-O(1)	1.374(4)
C(54)-C(55)	1.385(5)
C(55)-C(56)	1.405(5)
O(1)-C(57)	1.417(5)
C(7)-N(1)	1.350(4)
C(7)-N(2)	1.354(4)
C(71)-N(1)	1.486(4)
C(71)-C(72)	1.519(4)
C(72)-N(2)	1.481(4)
N(1)-C(11)	1.450(4)
C(11)-C(12)	1.401(4)
C(11)-C(16)	1.409(4)
C(12)-C(13)	1.398(4)
C(12)-C(17)	1.511(5)
C(13)-C(14)	1.386(5)
C(14)-C(15)	1.397(5)
C(14)-C(18)	1.512(5)
C(15)-C(16)	1.394(4)
C(16)-C(19)	1.509(4)
N(2)-C(21)	1.439(4)

C(21)-C(22)	1.403(4)
C(21)-C(26)	1.411(4)
C(22)-C(23)	1.395(4)
C(22)-C(27)	1.513(4)
C(23)-C(24)	1.393(4)
C(24)-C(25)	1.393(4)
C(24)-C(28)	1.518(5)
C(25)-C(26)	1.400(4)
C(26)-C(29)	1.507(4)
C(8)-N(4)	1.353(4)
C(8)-N(3)	1.355(4)
C(81)-N(3)	1.483(4)
C(81)-C(82)	1.520(4)
C(82)-N(4)	1.477(4)
N(3)-C(31)	1.439(4)
C(31)-C(36)	1.400(5)
C(31)-C(32)	1.409(4)
C(32)-C(33)	1.402(4)
C(32)-C(37)	1.507(5)
C(33)-C(34)	1.387(5)
C(34)-C(35)	1.391(5)
C(34)-C(38)	1.520(5)
C(35)-C(36)	1.404(4)
C(36)-C(39)	1.498(5)
N(4)-C(41)	1.436(4)
C(41)-C(42)	1.402(4)
C(41)-C(46)	1.412(4)
C(42)-C(43)	1.402(4)
C(42)-C(47)	1.514(4)
C(43)-C(44)	1.392(4)
C(44)-C(45)	1.396(5)
C(44)-C(48)	1.508(4)
C(45)-C(46)	1.398(4)
C(46)-C(49)	1.510(4)
C(1S)-Cl(2S)	1.763(5)
C(1S)-Cl(1S)	1.768(5)

C(8)-Pd(1)-C(7)	175.98(11)
C(8)-Pd(1)-C(1)	87.86(11)
C(7)-Pd(1)-C(1)	88.13(11)
C(8)-Pd(1)-Br(1)	87.55(8)
C(7)-Pd(1)-Br(1)	96.46(8)
C(1)-Pd(1)-Br(1)	175.41(8)
C(2)-C(1)-Pd(1)	113.1(2)
C(1)-C(2)-C(3)	115.3(3)
C(4)-C(3)-C(51)	114.2(3)
C(4)-C(3)-C(2)	114.9(3)
C(51)-C(3)-C(2)	105.1(3)
C(5)-C(4)-C(3)	113.4(3)
C(6)-C(5)-C(4)	123.9(4)
C(56)-C(51)-C(52)	116.8(3)
C(56)-C(51)-C(3)	119.9(4)
C(52)-C(51)-C(3)	123.1(3)
C(53)-C(52)-C(51)	122.0(3)
C(52)-C(53)-C(54)	120.1(4)
O(1)-C(54)-C(55)	125.6(3)
O(1)-C(54)-C(53)	115.6(3)
C(55)-C(54)-C(53)	118.8(3)
C(54)-C(55)-C(56)	120.0(3)
C(51)-C(56)-C(55)	122.3(4)
C(54)-O(1)-C(57)	117.1(3)
N(1)-C(7)-N(2)	106.4(2)
N(1)-C(7)-Pd(1)	128.8(2)
N(2)-C(7)-Pd(1)	124.5(2)
N(1)-C(71)-C(72)	101.5(2)
N(2)-C(72)-C(71)	101.7(2)
C(7)-N(1)-C(11)	126.8(2)
C(7)-N(1)-C(71)	113.4(2)
C(11)-N(1)-C(71)	118.9(2)
C(12)-C(11)-C(16)	121.0(3)
C(12)-C(11)-N(1)	121.1(3)
C(16)-C(11)-N(1)	117.6(3)

C(13)-C(12)-C(11)	118.2(3)
C(13)-C(12)-C(17)	118.9(3)
C(11)-C(12)-C(17)	122.9(3)
C(14)-C(13)-C(12)	122.2(3)
C(13)-C(14)-C(15)	118.2(3)
C(13)-C(14)-C(18)	120.7(3)
C(15)-C(14)-C(18)	120.9(4)
C(16)-C(15)-C(14)	121.9(3)
C(15)-C(16)-C(11)	118.3(3)
C(15)-C(16)-C(19)	119.9(3)
C(11)-C(16)-C(19)	121.8(3)
C(7)-N(2)-C(21)	127.8(2)
C(7)-N(2)-C(72)	113.3(2)
C(21)-N(2)-C(72)	117.9(2)
C(22)-C(21)-C(26)	121.4(3)
C(22)-C(21)-N(2)	118.5(3)
C(26)-C(21)-N(2)	119.8(3)
C(23)-C(22)-C(21)	118.5(3)
C(23)-C(22)-C(27)	119.7(3)
C(21)-C(22)-C(27)	121.7(3)
C(24)-C(23)-C(22)	121.6(3)
C(23)-C(24)-C(25)	118.7(3)
C(23)-C(24)-C(28)	120.7(3)
C(25)-C(24)-C(28)	120.6(3)
C(24)-C(25)-C(26)	122.1(3)
C(25)-C(26)-C(21)	117.6(3)
C(25)-C(26)-C(29)	119.9(3)
C(21)-C(26)-C(29)	122.4(3)
N(4)-C(8)-N(3)	106.9(2)
N(4)-C(8)-Pd(1)	126.1(2)
N(3)-C(8)-Pd(1)	127.0(2)
N(3)-C(81)-C(82)	101.4(2)
N(4)-C(82)-C(81)	101.1(2)
C(8)-N(3)-C(31)	127.6(2)
C(8)-N(3)-C(81)	111.9(2)
C(31)-N(3)-C(81)	119.7(2)

C(36)-C(31)-C(32)	120.7(3)
C(36)-C(31)-N(3)	121.3(3)
C(32)-C(31)-N(3)	117.7(3)
C(33)-C(32)-C(31)	118.7(3)
C(33)-C(32)-C(37)	118.9(3)
C(31)-C(32)-C(37)	122.4(3)
C(34)-C(33)-C(32)	121.9(3)
C(33)-C(34)-C(35)	118.1(3)
C(33)-C(34)-C(38)	120.8(4)
C(35)-C(34)-C(38)	121.1(4)
C(34)-C(35)-C(36)	122.5(3)
C(31)-C(36)-C(35)	118.1(3)
C(31)-C(36)-C(39)	122.5(3)
C(35)-C(36)-C(39)	119.4(3)
C(8)-N(4)-C(41)	127.8(2)
C(8)-N(4)-C(82)	112.7(2)
C(41)-N(4)-C(82)	118.5(2)
C(42)-C(41)-C(46)	121.3(3)
C(42)-C(41)-N(4)	120.7(3)
C(46)-C(41)-N(4)	117.8(3)
C(41)-C(42)-C(43)	118.2(3)
C(41)-C(42)-C(47)	123.1(3)
C(43)-C(42)-C(47)	118.7(3)
C(44)-C(43)-C(42)	122.1(3)
C(43)-C(44)-C(45)	118.3(3)
C(43)-C(44)-C(48)	121.1(3)
C(45)-C(44)-C(48)	120.6(3)
C(44)-C(45)-C(46)	122.0(3)
C(45)-C(46)-C(41)	118.1(3)
C(45)-C(46)-C(49)	119.8(3)
C(41)-C(46)-C(49)	122.1(3)
Cl(2S)-C(1S)-Cl(1S)	111.1(3)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2$x 10^3) for 05197. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Pd(1)	16(1)	11(1)	12(1)	0(1)	0(1)	-1(1)
Br(1)	20(1)	15(1)	23(1)	1(1)	-4(1)	2(1)
C(1)	23(1)	15(1)	17(1)	3(1)	-1(1)	0(1)
C(2)	31(2)	16(1)	18(1)	3(1)	3(1)	1(1)
C(3)	39(2)	19(2)	37(2)	7(1)	-8(2)	-4(1)
C(4)	34(2)	29(2)	35(2)	2(1)	0(2)	2(1)
C(5)	42(2)	25(2)	39(2)	5(2)	13(2)	8(2)
C(6)	51(3)	55(3)	76(4)	12(3)	-8(3)	5(2)
C(51)	39(2)	17(1)	37(2)	10(1)	-12(2)	-1(1)
C(52)	55(2)	19(2)	33(2)	-2(1)	-13(2)	-2(2)
C(53)	56(3)	28(2)	24(2)	0(1)	-4(2)	2(2)
C(54)	35(2)	20(1)	28(2)	4(1)	-3(1)	0(1)
C(55)	38(2)	20(2)	29(2)	1(1)	-5(1)	-6(1)
C(56)	36(2)	23(2)	28(2)	3(1)	-4(1)	-3(1)
O(1)	45(2)	34(1)	34(1)	6(1)	1(1)	-10(1)
C(57)	66(3)	51(3)	45(2)	0(2)	5(2)	-31(2)
C(7)	15(1)	14(1)	15(1)	1(1)	0(1)	1(1)
C(71)	21(2)	22(1)	26(2)	-10(1)	5(1)	-7(1)
C(72)	20(2)	27(2)	20(1)	-9(1)	2(1)	-7(1)
N(1)	16(1)	19(1)	19(1)	-5(1)	2(1)	-2(1)
C(11)	16(1)	21(1)	20(1)	-5(1)	3(1)	-2(1)
C(12)	19(1)	27(2)	23(1)	-2(1)	2(1)	-4(1)
C(13)	22(2)	39(2)	22(2)	-2(1)	5(1)	-6(1)
C(14)	21(2)	37(2)	28(2)	-10(1)	6(1)	-2(1)
C(15)	20(2)	27(2)	31(2)	-7(1)	3(1)	2(1)
C(16)	16(1)	22(1)	24(1)	-4(1)	0(1)	-3(1)
C(17)	34(2)	41(2)	36(2)	16(2)	11(2)	6(2)
C(18)	31(2)	61(3)	40(2)	-8(2)	16(2)	7(2)
C(19)	24(2)	25(2)	23(1)	-2(1)	-1(1)	-2(1)
N(2)	17(1)	18(1)	16(1)	-4(1)	2(1)	-3(1)
C(21)	17(1)	17(1)	15(1)	-2(1)	2(1)	-1(1)

C(22)	22(1)	18(1)	17(1)	-1(1)	1(1)	1(1)
C(23)	22(2)	24(2)	21(1)	0(1)	4(1)	4(1)
C(24)	22(2)	27(2)	21(1)	3(1)	6(1)	-1(1)
C(25)	25(2)	22(1)	16(1)	3(1)	3(1)	-1(1)
C(26)	20(1)	21(1)	15(1)	-2(1)	1(1)	1(1)
C(27)	31(2)	19(1)	27(2)	1(1)	10(1)	3(1)
C(28)	32(2)	45(2)	41(2)	16(2)	20(2)	4(2)
C(29)	27(2)	24(2)	25(2)	3(1)	4(1)	7(1)
C(8)	17(1)	14(1)	14(1)	1(1)	1(1)	1(1)
C(81)	28(2)	20(1)	14(1)	-3(1)	-1(1)	-6(1)
C(82)	24(2)	21(1)	18(1)	-2(1)	-3(1)	-7(1)
N(3)	22(1)	15(1)	15(1)	0(1)	1(1)	-4(1)
C(31)	25(2)	17(1)	13(1)	-2(1)	3(1)	-1(1)
C(32)	30(2)	20(1)	13(1)	-3(1)	0(1)	3(1)
C(33)	43(2)	21(2)	16(1)	2(1)	1(1)	3(1)
C(34)	49(2)	20(2)	19(1)	-2(1)	8(1)	-7(1)
C(35)	32(2)	26(2)	21(1)	-5(1)	7(1)	-12(1)
C(36)	28(2)	23(2)	16(1)	-4(1)	3(1)	-5(1)
C(37)	33(2)	34(2)	26(2)	2(1)	1(1)	6(2)
C(38)	63(3)	29(2)	28(2)	4(2)	11(2)	-12(2)
C(39)	23(2)	37(2)	23(2)	0(1)	3(1)	1(1)
N(4)	20(1)	17(1)	14(1)	0(1)	0(1)	-3(1)
C(41)	16(1)	15(1)	16(1)	2(1)	-1(1)	-3(1)
C(42)	18(1)	16(1)	18(1)	1(1)	-1(1)	-4(1)
C(43)	21(1)	21(1)	18(1)	-1(1)	2(1)	-3(1)
C(44)	24(2)	25(2)	21(1)	6(1)	-1(1)	-5(1)
C(45)	20(1)	17(1)	26(2)	6(1)	-1(1)	-1(1)
C(46)	16(1)	16(1)	23(1)	1(1)	0(1)	-2(1)
C(47)	23(2)	20(1)	23(1)	2(1)	2(1)	3(1)
C(48)	49(2)	35(2)	26(2)	13(2)	7(2)	5(2)
C(49)	23(2)	17(1)	28(2)	-1(1)	3(1)	1(1)
C(1S)	47(3)	46(2)	37(2)	0(2)	-2(2)	3(2)
Cl(1S)	60(1)	88(1)	34(1)	4(1)	2(1)	13(1)
Cl(2S)	66(1)	57(1)	42(1)	4(1)	-11(1)	10(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10 ^{3}) for 05197.

	x	y	z	U(eq)
H(1A)	-670(30)	2410(30)	1796(9)	22
H(1B)	-950(20)	2020(20)	1301(11)	22
H(2A)	780(20)	3280(30)	1494(12)	26
H(2B)	540(30)	2890(30)	1022(9)	26
H(3)	-830	4075	1501	38
H(4A)	-1276	3531	583	39
H(4B)	-1924	3195	1003	39
H(5)	-1941	5037	800	42
H(6A)	-3607	3847	843	73
H(6B)	-3701	4925	779	73
H(52)	273	4228	379	43
H(53)	1513	5269	166	43
H(55)	1624	6278	1441	35
H(56)	364	5234	1645	35
H(57A)	2349	7490	1036	81
H(57B)	3455	7410	794	81
H(57C)	3202	6759	1203	81
H(71A)	2658	3751	2228	27
H(71B)	3505	3108	2494	27
H(72A)	2297	2664	2989	27
H(72B)	1631	3530	2826	27
H(13)	4444	2501	785	33
H(15)	5283	715	1753	31
H(17A)	3335	3736	986	55
H(17B)	2608	3671	1415	55
H(17C)	2277	3147	958	55
H(18A)	5780	1455	627	65
H(18B)	5930	598	942	65

H(18C)	6567	1486	1071	65
H(19A)	3288	693	2379	36
H(19B)	3830	1558	2601	36
H(19C)	4553	737	2468	36
H(23)	-2040	3029	2962	27
H(25)	-829	631	3296	25
H(27A)	-1180	3949	2411	38
H(27B)	-28	3690	2246	38
H(27C)	-142	4126	2736	38
H(28A)	-2831	2087	3568	58
H(28B)	-2454	1079	3613	58
H(28C)	-3162	1393	3176	58
H(29A)	945	251	3152	38
H(29B)	1716	961	2936	38
H(29C)	969	349	2612	38
H(81A)	-370	-617	416	25
H(81B)	-1416	-22	302	25
H(82A)	-2175	-423	957	25
H(82B)	-1399	-1271	933	25
H(33)	-686	2787	-235	32
H(35)	2308	2031	124	31
H(37A)	-2140	2291	192	46
H(37B)	-1980	1529	565	46
H(37C)	-2088	1279	37	46
H(38A)	1562	3739	-224	60
H(38B)	739	3429	-624	60
H(38C)	1896	2990	-573	60
H(39A)	2142	880	978	41
H(39B)	2623	664	498	41
H(39C)	1659	88	672	41
H(43)	-2078	-231	2721	24
H(45)	-423	-2396	2378	25
H(47A)	-1553	1210	2114	33
H(47B)	-2713	775	2109	33
H(47C)	-2088	827	1651	33
H(48A)	-1980	-2310	3014	55

H(48B)	-1857	-1372	3261	55
H(48C)	-841	-1999	3222	55
H(49A)	596	-2406	1719	34
H(49B)	605	-1564	1391	34
H(49C)	-329	-2279	1332	34
H(1S1)	4011	9949	1059	52
H(1S2)	3273	9092	985	52