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# Synthesis and Catalytic Activity of -NHC Group 9 Metal Pincer Complexes

Sean William Reilly

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Synthesis and catalytic activity of CCC-NHC group 9 metal pincer complexes

By

Sean William Reilly

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Synthesis and catalytic activity of CCC-NHC group 9 metal pincer complexes

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*N*-Heterocyclic carbenes (NHCs) are one of the few ligand systems that can finely tune transition metal catalysts via sterics and electronics. The strong sigma-donating properties of these ancillary ligands allow the development of robust tridentate NHC pincer framework, which has emerged as an alternative to the phosphine pincer ligands. The combination of NHC and pincer systems has resulted in a new generation of catalytically active organometallic complexes reported throughout the literature.

CCC-NHC Rh pincer complexes were found to be catalytically active in C-C and C-B bond formation via 1,4-addition reactions. In addition, the *in-situ* generated CCC-NHC Ir(H) pincer complex demonstrated catalytic activity in borylation of arene C-H bonds. Preliminary results are comparable to the C-H borylation results published by Hartwig and co-workers. The CCC-NHC Ir(H) pincer complex may also prove to be a suitable catalyst for alkane dehydrogenation, due to framework similarities of the highly active and durable PCP and POCOP pincer hydride systems.

Expansion of group 9 metal sources for transmetalation of the CCC-NHC Zr pincer complex afforded the development of CCC-NHC Rh(CO) and CCC-NHC Co

complexes. Group 9 metal carbonyl complexes have been reported as active catalysts in photocatalytic C-H activation of small molecules. Testing of Co sources for transmetalation afforded three rare Co pincer complexes, and the first examples of CCC-NHC Co pincer complexes to date. Development of CCC-NHC pincer complexes with base metals provide cost-effect alternatives to pincer systems with precious metal centers, and is reported herein.

DEDICATION

This dissertation is dedicated to my mom and dad who have been supportive and encouraging throughout my time in graduate school.

## ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

## 1.1    *N*-Heterocyclic Carbenes (NHCs)

Carbenes are a widely researched class of neutral compounds containing a divalent carbon atom with six electrons in their valence shells.[1,2] Singlet carbenes (Figure 1.1) contain a lone pair of electrons in the $sp^2$ hybridized orbital of the carbon atom resulting in a vacant p orbital. This electron occupancy differs from the triplet carbene, in which each two electron resides in an individual in a degenerate p orbital.
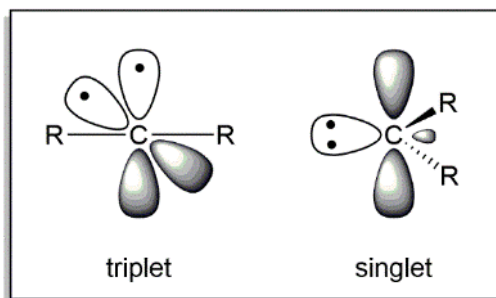


Figure 1.1    Triplet carbenes vs. singlet carbenes

Figure adapted from ref. 3

The competing electronic states of these two carbene classes is driven by the singlet-triplet $\sigma$-$p_\pi$ gap (Figure 1.2). The linear geometry of the triplet carbene results in two nonbonding degenerate p orbitals ($p_x$ and $p_y$) on the divalent carbon, commonly regarded as a diradical system. The singlet carbene, however, contains a bent geometry

resulting in a sp$^2$ hybridization thereby breaking the degeneracy of the $p_x$ and $p_y$ orbitals.

This change in geometry fosters two new inequivalent $p_\pi$ and $\sigma$ orbitals, resulting from

the former $p_y$ (remains mostly unchanged), and the $p_x$ (acquires s character),

respectively.[2] The $\sigma$-$p_\pi$ gap in the singlet ground-state is heavily favored with $\sigma$-electron

withdrawing substituents on the carbene carbon thereby stabilizing the non-bonding $\sigma$

orbital. In contrast, $\sigma$-electron donating groups decrease the $\sigma$-$p_\pi$ energy gap, favoring the

carbene in the singlet ground state.[3,4]
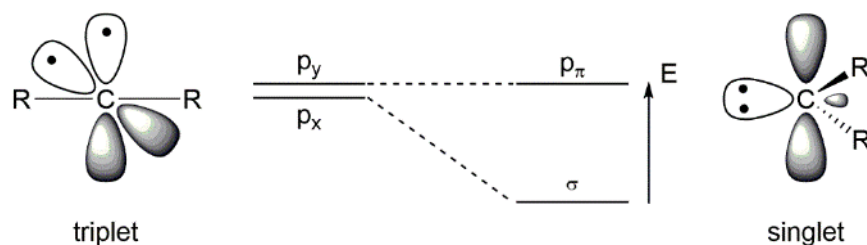


Figure 1.2     Triplet vs singlet carbene energy diagram

Figure adapted from ref. 2

NHCs are a specific class of carbenes which include increased electronic stability

due to the nitrogen atoms.[5] The inductive $\sigma$-electron withdrawing and $\pi$-electron donating

ability of the nitrogen atom decreases the electron density on the carbene carbon thereby

inducing stabilization of the NHC (Figure 1.3).[6] Furthermore, *N*-substituents allow for

manipulation of carbene stabilization from steric bulk through kinetic stability and

electronic stabilization by incorporation of electron withdrawing and/or donating groups.[6]
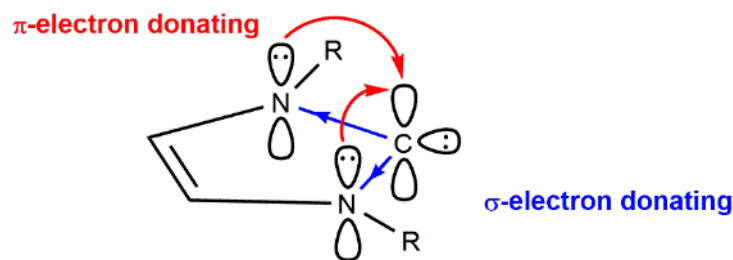
Figure 1.3     Electronic stabilization of NHC in imidazole-2-ylidene scaffold

Figure adapted from ref. 6

The increased stabilization and electronic tuning abilities of the NHC ligands have led to a substantial increase of reports demonstrating their catalytic applications with transition metals, rivaling the phosphine and cyclopentadienyl ligands.[7,8] While NHCs and the phosphine congeners both bind to metal centers via dative coordination by their respective lone pairs, the strong σ donating capabilities make NHC ligands more attractive than their phosphine counterparts in many applications. The increased electron-donating properties of NHC ligands leads to thermodynamically stronger C–M bonds in NHC complexes represented by greater bond disassociation energies along with decreased bond lengths compared to the metal–ligand binding in phosphine complexes.[9] This durability has allowed NHC complexes to be pertinent in many other chemical applications as well (Figure 1.4).[5,10-15]
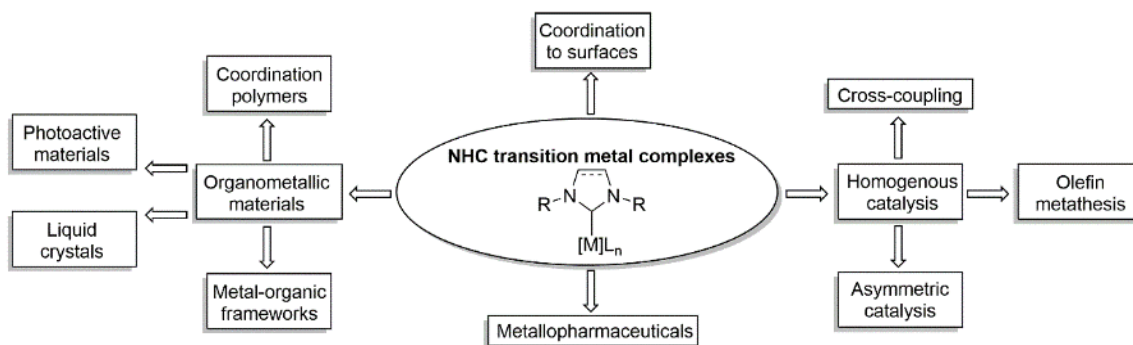
Figure 1.4    Applications of NHC complexes

Figure adapted from ref. 6

## 1.2    Pincer Ligands

Pincer ligands are tridentate chelators which coordinate in a meridional tridentate fashion thereby increasing the stability of organometallic complexes.[16] This ligand architecture allows Shaw and co-workers were the first to introduce pincer-ligated transition metal complexes in the 1970's.[17-19] Since then, there has been an enormous amount of development due to the variation that is allowed in pincer architectures (Figure 1.5).[20-25]



| Group | Variation Effects |
|---|---|
| Z | -remote control of electron density<br>-solubility control |
| X | -electronic effect<br>-*trans* influence |
| Y | -control of electron density<br>-indirect control on steric properties |
| LR$_n$ | -steric control *via* substituent variation<br>-control of electron density<br>-lability |

PINCER LIGAND ARCHITECHTURE
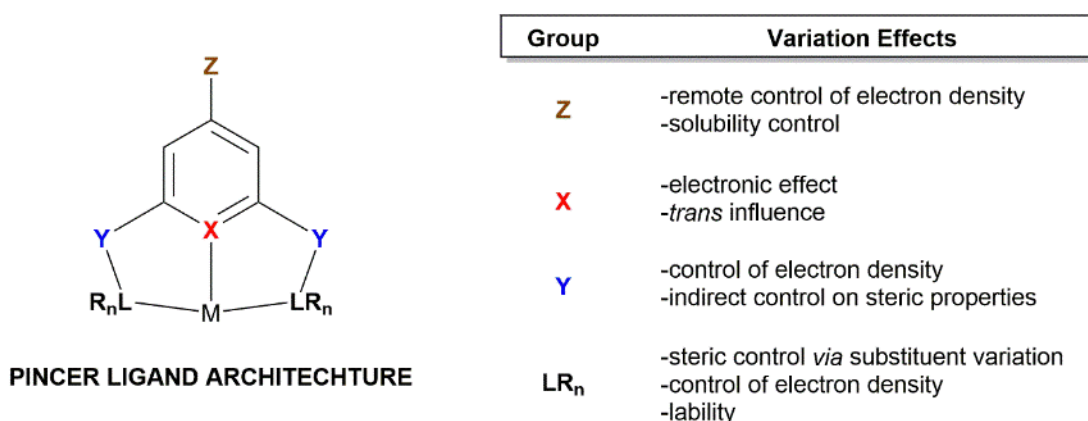
Figure 1.5    Generic pincer ligand design

Figure adapted from ref. 20

Pincer ligand architecture has led to high or unparalleled catalytic activity in many application including small molecule activation.[16,26-28] In fact, the first report demonstrating the activation of an unstrained C–C bond in solution was catalyzed with a PCP pincer Rh complex.[29] The tridentate coordination of the pincer ligand to the metal center allows for increased kinetic stability in ligand–metal chelation. This robust and rigid ligand framework results in thermal stabilization of pincer complexes. Thus, pincer systems are suitable catalysts for endothermic reactions requiring high temperatures such as C–H bond functionalization, most notably alkane dehydrogenation.[20,30-36]

## 1.3    CCC-NHC Pincer Ligands

Incorporation of NHCs into pincer architecture has been demonstrated in four different types of ligand design (Figure 1.6). (The common pincer nomenclature is based on the ligand coordinating atoms to the metal center; thus Type **A** and **C** are CNC and CCC, respectively.) Carbon and nitrogen are the two prevalent central atom donors to the metal centers, flanked with or without methylene spacers between the aryl and lateral NHC ligands (methylene spacer represented with a "^"). Since the seminal report of Type **C** CCC-NHC pincer complex,[37] groups worldwide have continued develop and expand on this class of ligand system.[16,38-48]
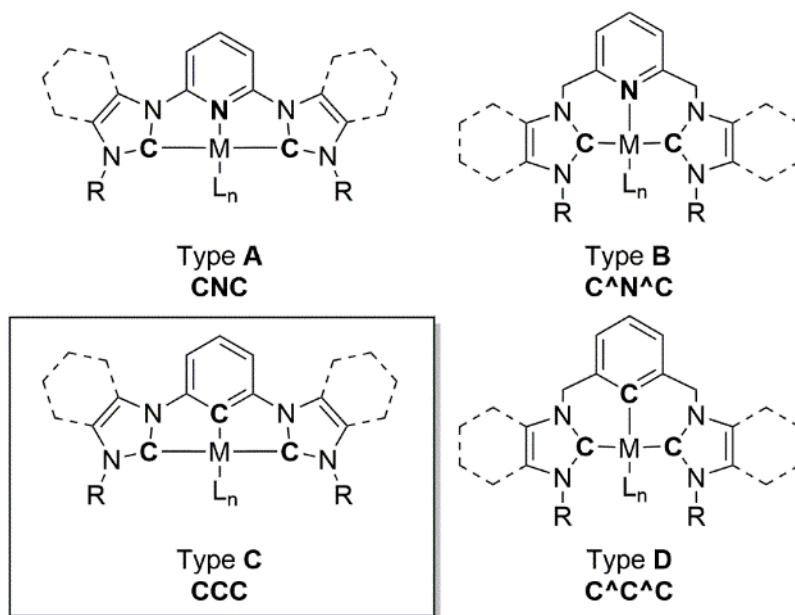
Figure 1.6    Type of NHC pincer framework

Type **C** framework was developed with the intention of being applicable for endothermic reactions, such as dehydrogenation of alkanes, due to the inherent thermal stability of the NHC pincer ligand architecture. Dehydrogenation reactions are favorable for Ir pincer framework due to the three-coordinate chelation, with two $LR_2$ (see Figure 1.5) groups (NHC for Type **C**) linked to the central coordinating group, leaving the *trans* site to the central group vacant.[20] This lack of congestion and three-coordinate $d^8$ Ir metal center allows for C–H oxidative addition and subsequent *β*-hydride elimination of the hydrocarbon substrate. With greater C–M bond strengths in NHC ligands, compared to the phosphine analogues, the CCC-NHC Ir pincer complex could offer increased stability at higher reaction temperatures compared to the active PCP and POCOP pincer reported by Jensen[35] and Brookhart,[32,49] respectively (Figure 1.7).
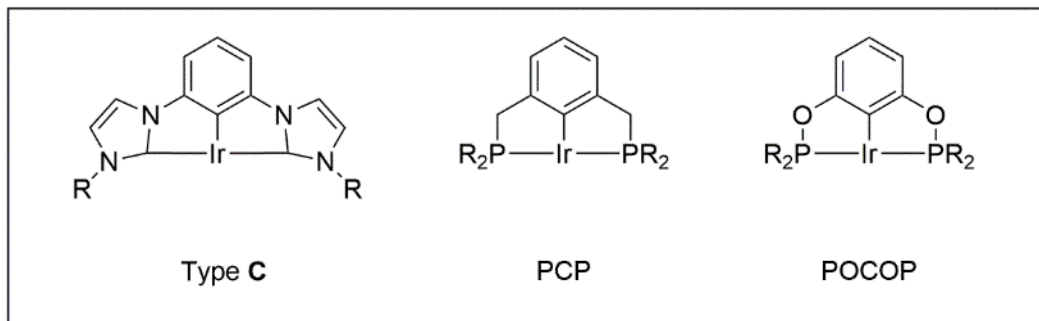
Figure 1.7    Type **C**, PCP, and POCOP pincer framework

The synthesis of CCC-NHC (Type **C)** ligand precursors begins with a Cu-catalyzed coupling of the desired heterocycle and 1,3-dibromobenzene, followed by alkylation affording the salt precursors for generation of CCC-NHC pincer complexes.[50,51]
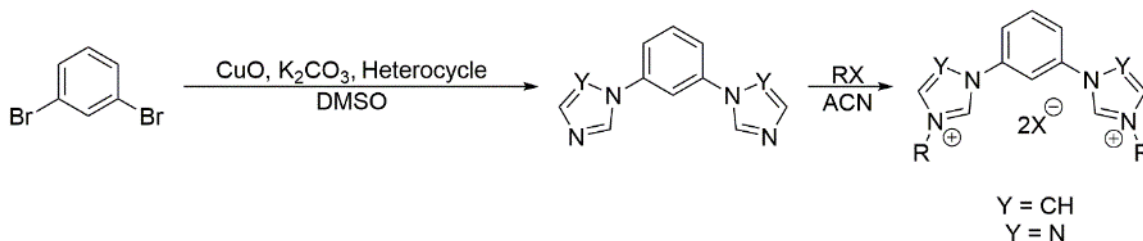


Figure 1.8    General synthesis of CCC-NHC ligand precursors

In preparation of CCC-NHC Rh and Ir pincer complexes, the Hollis group reported transmetalation of a CCC-NHC Zr pincer complex with Rh and Ir sources (Figure 1.9).[37,52] $Zr(NMe_2)_4$ serves the two-fold purpose of acting as a base to generate the NHC's, and activating the aryl C–H bond via the electrophilic Zr center.
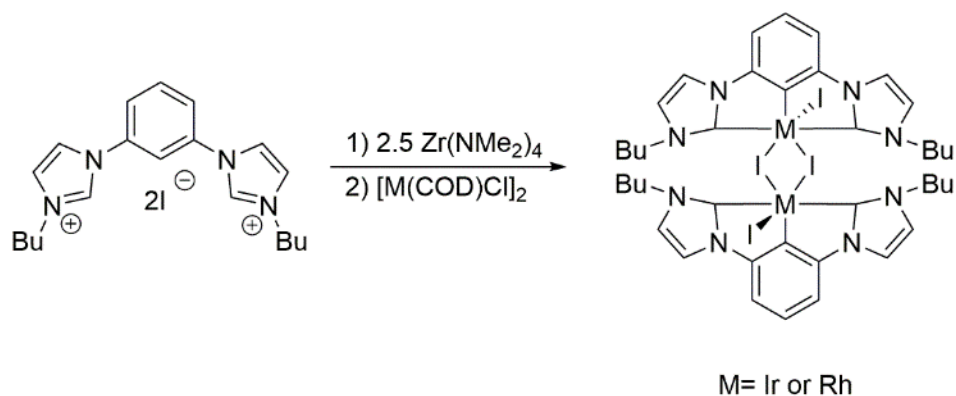
Figure 1.9    General synthesis of CCC-NHC Ir and Rh pincer complexes

Aside from screening the CCC-NHC Rh and Ir pincer complex for catalytic activity in intramolecular hydroamination/cyclization,[52] studies of these pincer complexes have been limited. The work herein discusses the applicability of the CCC-NHC Rh pincer complex in synthetically useful C–C and C–B bond forming reactions, including room temperature β-boration catalysis. Preliminary studies show catalytic activity of the CCC-NHC Ir pincer complex activating aryl C–H bonds. Furthermore, the development of CCC-NHC pincer complexes with Co was explored, resulting in the first CCC-NHC Co pincer complexes to date. Finally, synthesis for CCC-NHC Rh(CO) complexes will also be reviewed, along with their potential role as a catalyst for photocatalytic C–H bond functionalization.

CHAPTER II

SYNTHESIS OF AIR-STABLE CCC-NHC PINCER COBALT COMPLEXES

## 2.1    Introduction

Pincer ligands have played a significant role in the development of homogenous

catalysis ever since their introduction in the 1970's.[26,53-55] The tridentate meridional

architecture of the pincer ligand is a durable framework for various transition metal

catalysis, most notably C–C bond formation,[31,56-61] C–H bond activation,[20,31,36,56,57,62-66] as

well as small molecule activation[66,67] including $NH_3$,[67,68] $CO_2$,[31,57,69-71] $H_2O$,[56,72] and $N_2$

fixation.[73,74] N-Heterocyclic carbenes (NHCs) increase the durability of these resilient

ligand systems due to their strong σ-electron-donating properties, resulting in pincer

scaffolds with profound metal–NHC bond strengths.[5,12,16,55,75] As a result, these σ donors

have become an attractive ligand to implement into catalytic systems with base metal

centers such as Fe, Ni, and Co.[76-84]

Numerous NHC base metal pincer complexes have been reported with a CNC-

NHC framework (refer to Figure 1.6).[85-95] Danopoulos et al. reported some of the first

examples of CNC-NHC pincers with low valent Fe and Co centers.[85,86] Chirik and co-

workers have illustrated several examples of catalytically active CNC-NHC Fe and Co

complexes in hydrogenation[96,97] and hydroboration.[98] More specifically, Co pincer

complexes have shown to be effective in various catalysis such as alkene[99-101] and

nitrile[102,103] hydrogenation, alcohol dehydrogenation,[104] $CO_2$ activation,[71,105] alkene hydroboration[106,107] and silylation,[108] and C–H borylation.[65]

Despite the increasing reported examples of base metal pincer complexes, the CCC-NHC variants are exceedingly rare. In fact, the only reported CCC-NHC late transition base metal complexes to date are the bis(diisopropylphenylimidazol-2-ylidene)phenyl ($^{DIPP}$CCC)Ni complexes recently reported by Fout and co-workers.[109] Prior to that report, the only other late transition metal monoanionic tridentate pincers in the literature are the bis(arylimidazol-2-ylidene)pyridine ($^{iPr}$CNC)Co complexes, published by Chirik and co-workers in 2013.[96] In order to promote metalation of the CCC imidazolium salt pre-cursor, activation of both the aryl C–H bond and the NHC protons of the CCC-NHC pro-ligand are required. The need for an electrophile to activate the aryl C–H bond, compounded with the inherently weak nature of M–C bonds of first row metals, has hindered the advance in CCC-NHC base metal complexes. However, use of early transition-metal amido starting materials have been effective in activating ligand pre-cursors in order to access multidentate complexes.[110-114] The electrophilic nature of the $d^0$ metal center along with the basicity of the amidos serves the two fold purpose needed to synthesize CCC-NHC pincer complexes. This also allows a synthetic route to late transition metal CCC-NHC pincer complexes through transmetalation. In 2005 and 2008, the Hollis group utilized this methodology to generate CCC-NHC Rh[37] and Ir[52] pincer complexes, respectively. Herein, we extend this methodology to Co and discuss the synthesis of the first reported CCC-NHC Co pincer complexes.

## 2.2    Results and Discussion

The Hollis group has reported the synthesis of CCC-NHC Rh[37] and Ir[52] pincer

complexes via transmetalation of a CCC-NHC Zr complex with [Rh(COD)Cl]$_2$ and

[Ir(COD)Cl]$_2$, respectively. Due to the successful formation of these group 9 pincer

complexes, several Co transmetalating sources were screened with CCC-NHC Zr pincer

complexes **1** and **2** (Figure 2.1) in order to access CCC-NHC Co complexes.
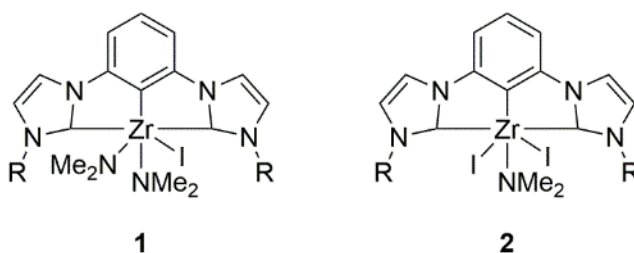


Figure 2.1    CCC-NHC pincer Zr complexes as transmetalating reagents


Initially, Co(acac)$_3$ was examined as a viable Co source for transmetalation.

Investigation began with addition of 2.5 equiv of Zr(NMe$_2$)$_4$ to the (1,3-bis(3-

butylimidazol-1-yl)benzene diiodide ligand precursor (**3**) to generate the Zr diamido

complex (**1**) *in-situ* in dichloromethane, followed by addition of Co(acac)$_3$ (Scheme 2.1).

The $^1$H NMR spectrum indicated an absence of imidazolium proton signals at □ 11.27,

however, various indistinguishable chemical species also appeared in the $^1$H NMR

spectrum (see Figure A. 1). A single red crystal was retrieved from the reaction mixture,

which also included several blue and clear crystals, and identified as **4** from X-ray

analysis.
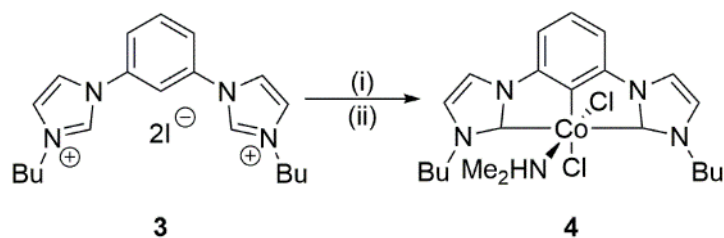
Scheme 2.1    Synthesis of **4**

Conditions: (i) 2.5 equiv Zr(NMe$_2$)$_4$, CH$_2$Cl$_2$, rt, 1h; (ii) 1.1 equiv Co(acac)$_3$, CH$_2$Cl$_2$, 12 h

An ORTEP plot of **4** is presented in Figure 2.2 with selected metric data in Table 2.1. Due to the meridional coordination and rigidity of the CCC-NHC tridentate ligand, Co complex **4** contains a distorted-octahedral center resulting in a (C$_{NHC}$)–Co–(C$_{NHC}$) bond angle of 145.6°.  The (C$_{NHC}$)–Co bonds length is 2.175 Å, which is 0.213 Å longer than the (C$_{NHC}$)–Co bond length of the Co(CNC)Br$_3$ pincer reported by Danopoulos in 2004.[85] This trend of (C$_{NHC}$)–Co increased bond length is also observed when compared to Chirik's (4-CPh$_2$CH$_3$-$^{iPr}$CNC)-CoN$_2$ pincer complex.[96] Although imidazolium pro-ligand **3** contained iodide halogens, complex **4** contained two coordinated chloride atoms, signifying halide exchange with dichloromethane.

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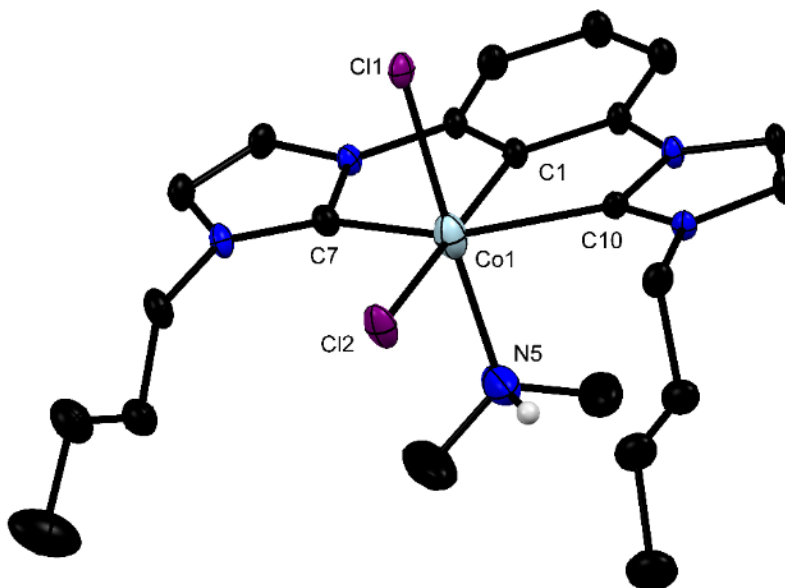
Figure 2.2    X-ray molecular structure of **4**

All but amine hydrogen are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 2.1    Selected Bond Lengths (Å) and Angles (°) for **4**

| length (Å) | | angle (°) | |
|---|---|---|---|
| Co(1)–Cl(1) | 2.411(1) | C(1)–Co(1)–C(7) | 72.7(2) |
| Co(1)–Cl(2) | 2.360(1) | C(1)–Co(1)–C(10) | 73.0(2) |
| Co(1)–N(5) | 2.135(5) | C(7)–Co(1)–C(10) | 145.6(2) |
| Co(1)–C(1) | 2.107(4) | Cl(2)–Co(1)–Cl(1) | 90.06(4) |
| Co(1)–C(7) | 2.202(4) | N(5)–Co(1)–Cl(2) | 87.63(13) |
| Co(1)–C(10) | 2.175(4) | C(10)–Co(1)–Cl(2) | 106.04(10) |

With many recent Co pincer reports exhibiting a chloride coordinated to the Co center,[103,106,115-117] it was hypothesized the chloride imidazolium pro-ligand would be a more appropriate ligand pre-cursor in order to synthesize the desired Co complex **4** in high yield. In addition, CoCl$_2$ was examined as a Co source in hopes of further favoring the formation of **4**. However, the reaction outlined in Scheme 2.2 resulted in the

formation of a single product, a presumed bis-coordination of two CCC-NHC ligands to the Co center (**6**).
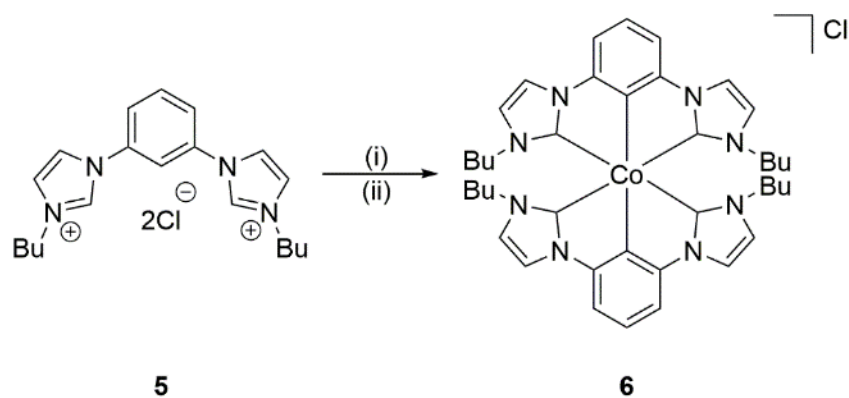


**Scheme 2.2    Synthesis of 6**

Conditions: (i) 2.5 equiv Zr(NMe$_2$)$_4$, CH$_2$Cl$_2$, rt, 1h; (ii) 1.1 equiv CoCl$_2$, CH$_2$Cl$_2$, 12 h

Accurate mass measurements of **6** contained the correct isotopic distribution pattern at $m/z$ = 701.3463 to match the formulation of M = C$_{40}$H$_{50}$CoN$_8$Cl ([M-Cl]$^+$) as the major product (see Figure A.2-4). Further evidence of **6** was observed in the $^1$H NMR spectrum with a single methylene peak shifted upfield at $\square$ 2.80, dissimilar to the diastereotopic methylene peaks shift of around $\square$ 4.5-5.5 commonly observed in our previously reported mono-ligated CCC-NHC pincer complexes.[118-120] In addition, the butyl chain peaks of **6** overlapped and were also shifted upfield at $\square$ 0.66-0.73. The C$_{NHC}$ and the Co–C$_{aryl}$ peak were observed in the $^{13}$C NMR spectrum at $\square$ 183.9 and $\square$ 176.0, respectively, verifying metalation to the Co center. It should also be noted this hexacoordination has also been reported with several CNC and scorpionato type Fe NHC complexes.[76] While further studies continue on air-stable **6**, investigation was continued

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to into developing a facile methodology that would allow access to a single, mono-coordinated CCC-NHC Co complex.

Despite numerous experimental designs to directly access a single mono-coordinated CCC-NHC Co pincer complex, incomplete metalation or product mixtures continuously occurred. It was then surmised that the *in-situ* formed Zr diamido species **1** could be correlated to these experimental shortcomings. Zr diiodo complex **2** was then considered as a transmetalating reagent in hopes of accessing the desired mono-coordinated product in high yield. Ultimately, Zr diiodo complex **2** was found to be a competent transmetalating reagent resulting in the formation of a single product (**7**) (Scheme 2.3). Due to the lower solubility of complex **2**, compared to that of **1**, increased reaction temperatures were required to carry out the reaction in Scheme 2.3.
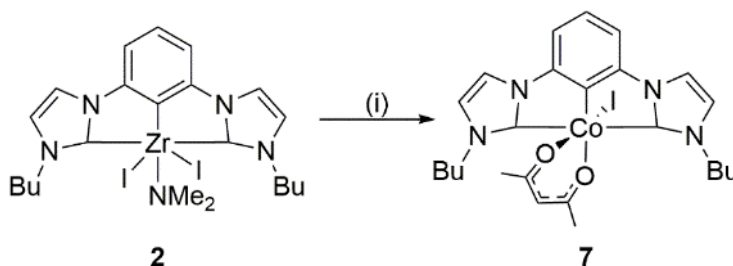


Scheme 2.3     Synthesis of **7**

Conditions: (i) 1.1 equiv Co(acac)$_3$, toluene, 90 °C, 12 h

$^1$H NMR spectrum of **7** reveals the diastereotopic methylene signals indicating the octahedral geometry that is also observed in our reported CCC-NHC Rh and Ir pincer complexes. The unique Co-acac six-membered chelate ring is easily identifiable in the $^1$H NMR spectrum with two distinct singlets at ☐ 2.29 and ☐ 1.19 representing the methyl groups of the bidentate acac ligand. The carbene and Co–C$_{aryl}$ signals at ☐ 183.9 and

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175.9, respectively, in the $^{13}$C spectrum were also consistent with successful metalation.

X-ray quality crystals were grown by recrystallization using a DCM/hexane solvent system. The chelation of the acac ligand was further confirmed through X-ray analysis along with a coordinated iodide atom to the Co metal center. An ORTEP plot of Co complex **7** is displayed in Figure 2.3 along with selected metric data in Table 2.2. Compared to **4**, Co complex **7** adopts a less distorted octahedral geometry due to the chelation of the bidentate acac. The (C$_{aryl}$)–Co bond length in **7** was measured at 1.874 Å (Table 2.2), noticeably shorter to the analogous bond distance in **4**.
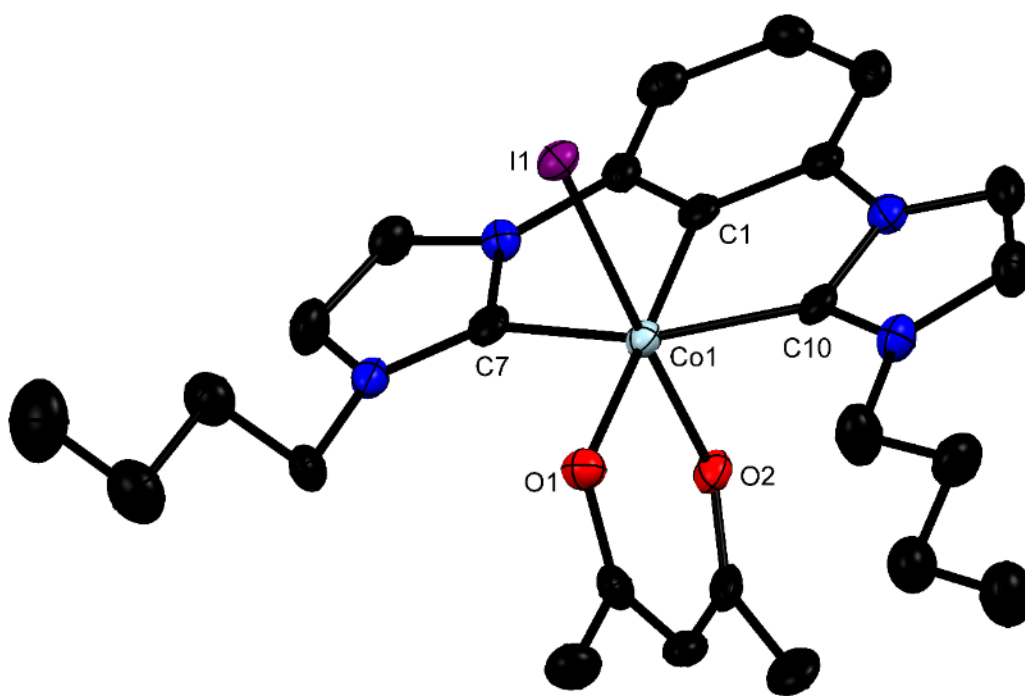


Figure 2.3    X-ray molecular structure of **7**

The hydrogens and one dichloromethane molecule were omitted for clarity. Thermal ellipsoids are shown at 50% probability.

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Table 2.2    Selected Bond Lengths (Å) and Angles (°) for **7**

| length (Å) | | angle (°) | |
|---|---|---|---|
| Co(1)–C(1) | 1.874(5) | C(1)–Co(1)–C(10) | 80.09(19) |
| Co(1)–O(2) | 1.941(3) | C(1)–Co(1)–C(7) | 79.84(19) |
| Co(1)–C(10) | 1.965(4) | C(10)–Co(1)–C(7)) | 159.9(2) |
| Co(1)–C(7) | 1.971(4) | O(2)–Co(1)–O(1) | 92.81(13) |
| Co(1)–O(1) | 2.002(3) | C(1)–Co(1)–O(2) | 89.48(16) |
| Co(1)–I(1) | 2.5685(6) | C(1)–Co(1)–I(1) | 89.73(12) |

## 2.3    Conclusion

In conclusion, air stable CCC-NHC Co pincer complexes have been synthesized via transmetalation of CCC-NHC Zr pincer complexes **1** and **2**. Furthermore, this facile methodology could potentially allow access to more economic catalyst development, an attractive alternative to costly precious metals systems. This synthetic route resulted in complexes **4**, **6**, and **7**, the first monoanionic CCC Co pincer complexes reported to date. Due to previous reports of Co(III) complexes being active catalysts in C–H activation,[121-124] studies are currently ongoing in identifying the reactivity of Co complexes **4**, **6**, and **7**, as well as employing this methodology to access various oxidation states of the Co metal center.

## 2.4    Experimental

### 2.4.1    General Considerations

All NMR spectra were taken on a Bruker Advance III 600 MHz. High-resolution mass spectrometer (HRMS) data was acquired using ESI on a Bruker UHPLC-Micro-Q/T OF-MS/MS. Standard inert-atmosphere techniques were used unless otherwise noted. Synthesis of **1**, **2**, **3**, and **5** were prepared from previously reported literature procedures.[37,51,125] Solvents were dried using molecular sieves and the SP-1 Solvent

System from LC Technology Solutions Inc. All commercial reagents were used as received. Chemical shifts ($\delta$) in the NMR spectra ($^1$H and $^{13}$C) were referenced by assigning the residual solvent peaks.

### 2.4.2 Synthesis of CCC-NHC Pincer Cobalt Complex 4

1,3-Bis(3-butylimidazol-1-yl)benzene diiodide (**3**) (0.200 g, 0.350 mmol), $Zr(NMe_2)_4$ (0.230 g, 0.870 mmol), and $CH_2Cl_2$ (15.0 mL) were combined in a 50 mL flask and stirred at room temperature (22 °C) for 1 h or until a light yellow homogenous solution appeared. Upon reaction mixture homogeneity, $Co(acac)_3$ (0.137 g, 0.385 mmol) was added to the flask to afford an instantaneous dark blue homogenous solution, and stirring continued at room temperature for 12 h. Deionized water (1 mL) was added, and it was stirred vigorously for 10 minutes providing a white precipitate and a dark red supernatant. The red supernatant was filtered and the solvent was removed under reduced pressure affording a light brown solid. The solid was washed with hexanes (25 mL) and ether (25 mL) yielding a red/brown solid. The red/brown solid was dissolved in $CH_2Cl_2$ and hexanes was diffused into the saturated solution resulting in several red crystals (**4**).

### 2.4.3 Synthesis of CCC-NHC Pincer Cobalt Complex 6

1,3-Bis(3-butylimidazol-1-yl)benzene diichloride (**5**) (0.275 g, 0.698 mmol), $Zr(NMe_2)_4$ (0.190 g, 0.712 mmol), and $CH_2Cl_2$ (15.0 mL) were combined in a 50 mL flask and stirred at room temperature (22 °C) for 1 h or until a light yellow homogenous solution appeared. Upon reaction mixture homogeneity, $Co(Cl)_2$ (0.099 g, 0.767 mmol) was added to the flask to afford an instantaneous dark blue homogenous solution, and stirring continued at room temperature for 6 h. Deionized water (1 mL) was added, and it

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was stirred vigorously for 10 minutes providing a white precipitate and a dark red supernatant. The red supernatant was filtered and the solvent was removed under reduced pressure yielding a red/brown solid. The solid was washed with hexanes (25 mL) and (10 mL) of deionized water to remove unreacted **5** and $Co(Cl)_2$. The resulting brown/red supernatant was decanted resulting in an opaque green solid (0.180 g, 57%).) $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.64 (s, 4H), 7.44-7.43 (t, $J$ = 7.50 Hz, 2H), 7.34-7.33 (d, $J$ = 7.50, 4H), 6.79 (s, 4H), 2.81-2.79 (m, 8H), 0.73-0.69 (m, 16H), 0.67-0.66 (m, 9H). $^{13}$C (150 MHz, $CDCl_3$): $\delta$ 183.9, 175.9, 148.1, 124.8, 123.2, 115.0, 107.3, 48.9, 33.7, 19.6, 13.9 HRMS-ESI (m/z): [M-Cl]$^+$ calcd for $C_{40}H_{50}CoN_8$, 701.3485; found, 701.3463.

### 2.4.4 Synthesis of CCC-NHC Pincer Cobalt Complex 7

2-(1,3-Bis(30-butyl-imidazol-20-ylidene)phenylene)(dimethylamido)diiodo zirconium (IV) (**2**) (0.100 g, 0.141 mmol), $Co(acac)_3$ (0.063 g, 0.1555 mmol) and toluene (15.0 mL) were combined in a 50 mL sealed vessel and stirred at 90 °C for 12 h. After cooling to room temperature, unreacted **2** conveniently precipitated out of the dark blue solution. The reaction mixture was then filtered, followed by solvent removal under reduced pressure. The resulting dark blue solid was heated under vacuum at 100 ˚C, to remove impurities, resulting in a black solid (0.070 g, 82%). X-ray quality crystals of **7** were grown by vapor diffusion of hexane into a saturated solution of $CH_2Cl_2$. $^1$H NMR (600 MHz, $CDCl_3$): $\delta$ 7.69-7.68 (d, $J$ = 1.50 Hz, 2H), 7.16-7.14 (t, $J$ = 7.8 Hz, 1H), 7.09-7.08 (d, $J$ = 7.50 Hz, 2H), 7.05-7.04 (d, $J$ = 1.50 Hz, 2H), 5.17 (s, 1H), 4.73-4.68 (m, 2H), 4.52-4.47 (m, 2H), 2.29 (s, 1H), 2.20-1.97 (m, 4H), 1.92 (s, 1H), 1.00-0.98 (t, $J$ = 7.52 Hz, 6H). $^{13}$C (150 MHz, $CDCl_3$): $\delta$188.6, 188.04, 187.6, 160.6, 149.7, 124.3, 121.6,

116.2, 107.7, 97.5, 49.5, 33.4, 28.4, 27.3, 20.3, 13.4. HRMS-ESI (m/z): [M-I]$^+$ calcd for

C$_{25}$H$_{32}$CoN$_4$O$_2$, 479.1852; found, 479.1836.

CHAPTER III

1,4-ADDITION OF ARYL BORONIC ACIDS TO α,β-UNSATURATED KETONES

CATALYZED BY A CCC-NHC PINCER RHODIUM COMPLEX

## 3.1    Introduction

Catalytic formation of C–C bonds has been a major focus in organic synthesis for decades.[126-130] A wide range of transition metals have been reported to induce C–C bond-forming reactions.[131-138] Two traditional metals used in C–C bond formations are Cu[128,139-142] and Pd.[131,143-150] Many cross coupling reactions are catalyzed by Pd, such as couplings with carbonyl groups at site-specific β-positions and desulfitative conjugate addition of aryl sulfonic acids.[151] In 1997, Miyaura reported an innovative method for C–C bond formation utilizing Rh in a catalytic 1,4-addition of aryl boronic acids to electron deficient olefins,[152] which produced C–C bonds, chiral centers, and biologically-active structural motifs.[153-160] Due to air- and water-stability and wider substrate scope in 1,4-addition reactions with aryl boronic acids, Rh catalysts provided an attractive alternative to Cu and diorganozinc.[136,155,161-167] Most reports of Rh catalyzed 1,4-addition have employed the use of phosphine ligands,[152,153,155,158,159,160,162,164,168-185] which have exhibited broad applicability to a variety of Michael acceptors including enantioselective variants.[158,176-178,184,186-189] However, reports using alternative ligands are sparse.[157,163,167,189,190] Many of these methods used co-solvents that are less environmentally-friendly such as DME, toluene, THF, and dioxane.[155,163,164,175,191-194]

The Hollis group reported an air- and water- stable CCC–NHC pincer Rh complex that catalyzed the hydroamination/cyclization of unactivated alkene amines to produce five- and six-membered nitrogen heterocycles in high yields (>98%) while utilizing environmentally-friendly aqueous solvent.[52] While excellent yields were obtained for cyclization, intermolecular hydroamination trials gave no reaction. The lack of reactivity was attributed to poor binding of the electron rich alkene to the electron rich metal center, therefore, reactivity with electron deficient alkenes was sought. With the goal of catalyzing an intermolecular reaction and extending the applicability of these complexes to other important catalytic reactions, 1,4-addition of aryl boronic acids to enones was examined. We report herein the coupling of α,β-unsaturated enones with aryl boronic acids catalyzed by a CCC–NHC pincer Rh complex in environmentally-friendly alcohol/water solvents.

## 3.2    Results and Discussion

Initial catalytic trials using freshly isolated **9** (Scheme 3.1) for the coupling of 2-cyclohexenone with 1.2 equiv of $PhB(OH)_2$ at 50 °C in $MeOH/H_2O$ produced >99% yield in 1 h (Table 3.1, entry 2). In time the catalytic activity of **9** was observed to decline, since **9** was believed to dimerize[37] and lose $NHMe_2$, which could be detected over the isolated complex. Addition of $NHMe_2$ to the reactions was found to consistently generate a catalytically active species (Table 3.1, entries 2-4). The mol% of added $NHMe_2$ was varied and 3 mol% was found to be a good compromise that gave excellent yields and reproducibility. In the absence of the Rh complex, no product was formed (entry 5). A variety of protic and aprotic solvents were also screened. The reaction proceeded in a variety of "green" protic solvents.[195] Limited conversion was observed in

purely aprotic solvents such as benzene or methylene chloride (entries 17 and 18).

Conveniently, a 1:1 MeOH/$H_2O$ mixture (entry 10) was found to give high yields

comparable with 10:1 solvent mixtures, and was, therefore, chosen for further catalytic

trials. It should be noted, with extended reaction times, biphenyl was observed in the GC-

MS spectra in minor amounts (<3%, entries 12-16).
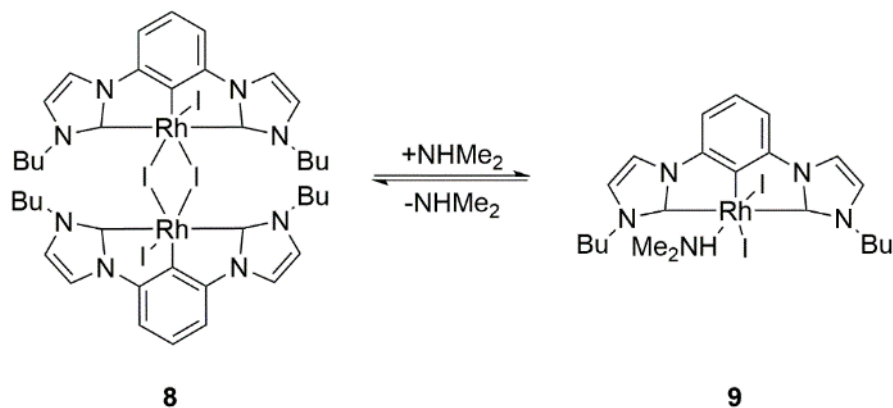


Scheme 3.1    Equilibrium of CCC-NHC Rh iodo-bridged dimer (**8**) and amine adduct
(**9**)

Table 3.1      Optimization of **8** with Cylohexenone and PhB(OH)$_2$
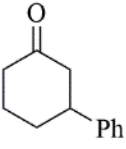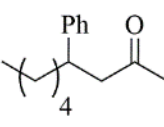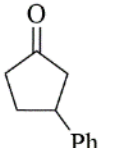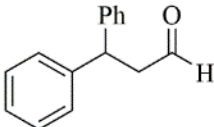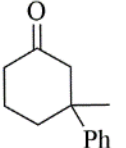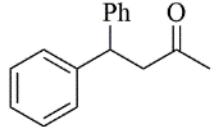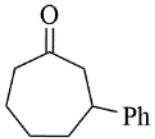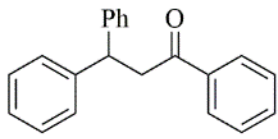


| entry | solvent | cat. | mol % NHMe$_2$ | time | yield$^a$ |
|---|---|---|---|---|---|
| 1 | 10:1 MeOH/H$_2$O | 8 | -- | 1h | 0 |
| 2 | 10:1 MeOH/H$_2$O | 8 | 0.6 | 1h | >98 |
| 3 | 10:1 MeOH/H$_2$O | 8 | 3.0 | 1h | >98 |
| 4 | 10:1 MeOH/H$_2$O | 8 | 11.0 | 1h | >98 |
| 5 | 10:1 MeOH/H$_2$O | -- | 12.0 | 1h | 0 |
| 6 | H$_2$O | 8 | 3.0 | 1h | >98 |
| 7 | MeOH | 8 | 3.0 | 1h | >98 |
| 8 | EtOH | 8 | 3.0 | 1h | >98 |
| 9 | 10:1 EtOH/H$_2$O | 8 | 3.0 | 1h | >98 |
| 10 | 1:1 MeOH/H$_2$O | 8 | 3.0 | 1h | >98 |
| 11 | 10:1 Dioxane/H$_2$O | 8 | 3.0 | 1h | >98 |
| 12 | 10:1 Dioxane/H$_2$O | -- | -- | 48h | 0 |
| 13 | H$_2$O | -- | -- | 20h | 0 |
| 14 | 10:1 EtOH/H$_2$O | [Rh(COD)Cl]$_2$ | -- | 20h | 51 |
| 15 | 10:1 EtOH/H$_2$O | -- | 3.0 | 20h | 0 |
| 16 | 10:1 EtOH/H$_2$O | 8 | -- | 16h | 0 |
| 17 | CH$_2$Cl$_2$ | 8 | 3.0 | 1h | 0 |
| 18 | Benzene | 8 | 3.0 | 1h | 10 |

$^a$Yields were determined by $^1$H NMR and identified by GC-MS

Once the reaction conditions were optimized, the catalyst loading was lowered to 1 and 0.1 mol% (Table 3.2, entry 1). Even at the reduced loading, moderate conversion was seen within 1 h, although not at the level seen with 2 mol%. Therefore, all remaining reactions were carried out with 2 mol% of the catalyst. While good to moderate yields (≥77%) were obtained at 50 °C (entries 5 and 7) and even room temperature (entry 1), low yields were observed for several substrates at these temperatures (entries 4 and 6). Therefore a higher temperature of 80 °C was evaluated and found to produce consistently higher yields. The screening of cyclic enones also included 2-cyclopentenone to examine 5-membered rings, (entry 2) which also produced a high yield with PhB(OH)$_2$. 3-Methylcyclohexenone (entry 3) reacted much slower, which was attributed to the methyl group at the β-position creating steric hindrance. All acyclic Michael acceptors screened

in Table 3.2 demonstrated excellent yields with PhB(OH)$_2$ including the enal

cinnamaldehyde (entry 6). High yields were also obtained with chalcone (entry 8), a

Michael acceptor with medicinal significance due to its cytotoxic, anticancer, and other

therapeutic characteristics.[196] Since consistently high yields were obtained at 80 °C with

α,β-unsaturated enones and enals, this temperature was adopted for further studies.

Table 3.2    Scope of Michael Acceptors with PhB(OH)$_2$[a]
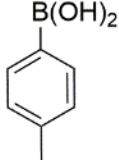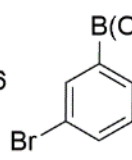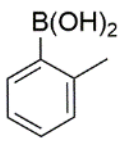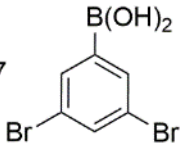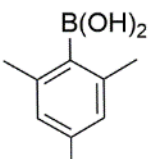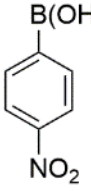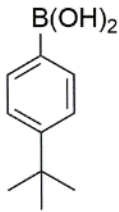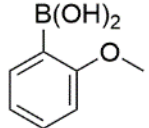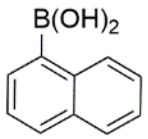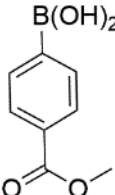
| entry | product | yield[b] (mol%, time, temp.) | entry | product | yield[b] (mol%, time, temp.) |
|---|---|---|---|---|---|
| 1 | | 92 (2,1h,80 °C)[c] 99(2,24h,rt) 99(2,1h,50 °C) 86 (1,1h,50 °C) 69 (0.1,1h,50 °C) | 5 | | 68(2,1h,80 °C)[c] 86(2,1h,50 °C) 96(2,1h,80 °C) |
| 2 | | 78(2,1h,80 °C)[c] 99(2,1h, 80 °C) | 6 | | 40(2,1h,80 °C)[c] 20(2,1h,50 °C) 99(2,1h,80 °C) |
| 3 | | 21(2,72h,80 °C)[c] 57(2,72h,80 °C) | 7 | | 91(2,1h,80 °C)[c] 77(2,1h,50 °C) 99(2,1h,80 °C) |
| 4 | | 94(2,1h,80 °C)[c] 15(2,1h,50 °C) 99(2,1h,80 °C) | 8 | | 93(2,1h,80 °C)[c] 99(2,1h,80 °C) |

[a]Substrate (0.0735 mmol), PhB(OH)$_2$ (0.0880 mmol), NHMe$_2$ (0.002 mmol), **8** (0.00150 mmol), and 0.700 mL of solvent were heated at 80 °C. [b]% yield determined by ^{1}H NMR spectrum and  product ion peaks were observed by GC-MS. [c]Isolated yield.

    The scope of reaction with aryl boronic acids was examined (Table 3.3). Utilizing

previously optimized conditions of 1.2 equiv of PhB(OH)$_2$, initial catalytic trials with

substituted-aryl boronic acids with 2-cyclohexenone produced low yields (entries 6 and

8). Upon careful observation of the $^1$H NMR spectra and GC-MS data, deborylated aryl compounds could be observed, indicating deborylation of the boronic acid. This observation is consistent with previously reported literature, stating hydrolysis of boronic acids occurs as a competing side reaction under basic conditions and/or elevated temperatures.[197] Previous reports had overcome this loss of boronic acid due by increasing the boronic acid equivalents, which resulted in higher yields of product.[198] Therefore, 2.5 equiv of all aryl boronic acids were evaluated and found to produce excellent yields. Many of the boronic acids with electron rich substituents generated yields >97% in 1 h (entries 1, 2, and 4). A high yield was obtained using napthalene boronic acid (entry 5), which is noteworthy due to napthalene's importance in the production of plastic, dyes, and insecticides.[199,200] It has been reported that aryl boronic acids with *ortho*-substituents drastically slow the rate of 1,4-addition,[152] which held true for 2,4,6-trimethylphenyl boronic acid (entry 3). However, 2-methylphenyl and 2-methoxyphenyl boronic acid (entries 2 and 9) resulted in high yields in just 1 h. While longer reaction times were required to obtain high yields with boronic acids containing strong electron withdrawing substituents (entries 6 and 8), no yield was obtained when using 1,3-dibromophenyl boronic acid (entry 7). Boronic acids containing moderate electron withdrawing groups, (entries 9 and 10), produced yields of >99% in just 1 h.

Table 3.3    Scope of Cyclohexenone with ArB(OH)$_2$[a]

| entry | yield[b] (mol%, time, temp.) | entry | yield[b] (mol%, time, temp.) |
|---|---|---|---|
| 1 | 77(2,1h,80°C)[c] 97(2,1h, 80°C) | 6 | 64(2,1h, 80°C)[c] 62(2,72h,80°C)[d] 99(2,7h,80°C) |
| 2 | 70 (2,1h, 80°C)[c] 99(2,1h, 80°C) | 7 | NR(2,63h,80°C) |
| 3 | 76(2,1h, 80°C)[c] 99(2,24h,80°C) | 8 | 34(2,1h, 80°C)[c] 22(2,72h,80°C)[d] 46(2,72h,80°C) |
| 4 | 81(2,1h, 80°C)[c] 98(2,1h, 80°C) | 9 | 92(2,1h, 80°C)[c] 99(2,1h, 80°C) |
| 5 | 80 (2,1h,80°C)[c] 99(2,1h,80°C) | 10 | 92(2,1h,80°C)[c] 99(2,1h, 80°C) |

[a]Substrate (0.0735 mmol), PhB(OH)$_2$ (0.0880 mmol), NHMe$_2$ (0.002 mmol), **8** (0.00150 mmol), and 0.700 mL of solvent were heated at 80 °C. [b]% yield determined by $^1$H NMR spectrum and product ion peaks were observed by GC-MS. [c]Isolated yield. [d]% yield when using 1.2 equiv (0.088 mmol) of ArB(OH)$_2$.
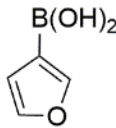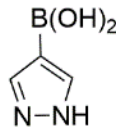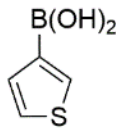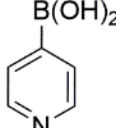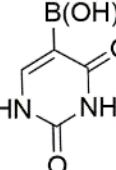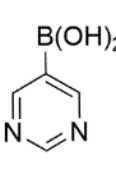
Nitrogen heterocycles such as pyrazole and pyridine are some of the most common heterocycles in biologically- and medicinally-active compounds.[201-203] Pyrimidine is an important pharmacophore and plays a vital role in the synthesis of nucleic acids and the HIV drug zidovudine.[204] 5-Fluorouracil (5-FU) is an important chemotherapy agent and has shown inhibitory effects on human gastric carcinoma cell

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growth.[205] Sulfur heterocycles such as thiophenes, can be coupled to produce

polythiophenes electron acceptors which have attracted considerable attention due to their

outstanding electrical, optical, and magnetic properties.[206,207] Polysubstituted furans are

also important building block throughout synthetic chemistry, and widely seen

throughout pharmaceutical and natural products.[208] The scope of reaction with

heterocyclic boronic acids was examined with 2-cyclohexenone as the Michael acceptor

(Table 3.4).

Deborylation products were also observed in the early screenings of heterocyclic

boronic acid, therefore 2.5 equiv of boronic acid were employed. With this increase,

higher yields were obtained for many 1,4-addition products. It was found longer reaction

times were required compared to many of the aryl boronic acids to produce moderate to

high yields for most of the heterocycles screened in Table 3.4. With extended reaction

times, a yield of 77% was obtained with furan-3-boronic acid (entry 1). Thiophene-3-

boronic acid (entry 2) produced moderate conversion, while no conversion was observed

when using uracil-5-boronic acid (entry 3). Nitrogen heterocycles, 3-pyrazole boronic

acid and 4-pyridine boronic acid, were successfully coupled to 2-cyclohexenone in high

yields (entries 4 and 5). Pyrimidine boronic acid showed no conversion despite the

increase in equivalents and extended reaction times (entry 6).

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Table 3.4    Scope of Cyclohexenone with Heterocycle Boronic Acids[a]

| entry | yield[b] (mol%, time, temp.) | entry | yield[b] (mol%, time, temp.) |
|---|---|---|---|
| 1 | 26(2,72h,80°C)[c] 77(2,72h,80°C) | 4 | 87(2,7h,80°C)[c] 99(2,7h,80°C) |
| 2 | 46(2,72h,80°C)[c] 69(2,72h,80°C) | 5 | 36(2,72h,80°C)[c] 83(2,7h,80°C) |
| 3 | NR(72h) | 6 | NR(72h) |

[a]2-Cyclohexenone (0.0735 mmol), heterocycle boronic acid (0.184 mmol), NHMe$_2$ (0.002 mmol), **8** (0.00150 mmol), and 0.700 mL of solvent were heated at 80 $^\circ$C. [b]% yield determined by $^1$H NMR and the product was observed by GC-MS. [c]Isolated yield.

## 3.3    Conclusion

A CCC–NHC pincer Rh complex has been reported to catalyze the coupling of aryl and heterocyclic boronic acids to cyclic and acyclic α,β-unsaturated enones and enals in high yields without the exclusion of air and water. Promising results were observed in the 1,4-addition of nitrogen heterocycles, which are commonly seen in medicinal- and biologically-active compounds.[201-203] Additionally, high yields were observed while utilizing solely environmentally "green" alcohol/water solvents.  Further development of the scope and limitations of this methodology is underway.

### 3.4    Experimental

### 3.4.1    General Consideration

Gas chromatography mass spectrometer (GC-MS) data was collected on a Shimadzu GCMS-QP2010 plus. All NMR spectra were taken on a Bruker Avance III 300 or 600 MHz. High-resolution mass spectrometer (HRMS) were acquired using ESI technique on a Bruker UHPLC-Micro-Q/T of MS/MS. IR spectrum was collected using Thermo Scientific Nicolet iS 5 FT-IR.

### 3.4.2    General Procedure for Catalytic Trials

On a bench top, a NMR tube was charged with enone (0.0735 mmol), boronic acid (0.1836 mmol), catalyst **8** (0.00150 mmol), 2M NHMe$_2$ (0.002 mmol), H$_2$O (0.350 mL), and MeOH (0.350 mL). The NMR tube was closed and heated to 80 °C. The reaction was monitored by $^1$H NMR spectroscopy. The crude reaction mixture was then filtered through a plug of celite to remove any insolubles. Volatiles from the filtered reaction mixture were then removed under reduced pressure resulting in an oil. 5 mL of CHCl$_3$ was added to the oil and the resultant mixture was passed through a second plug of celite. The solvent was removed under reduced pressure to afford the crude product.

### 3.4.3    Synthesis of 3-(1H-pyrazol-4-yl)cyclohexan-1-one

*3-(1H-pyrazol-4-yl)cyclohexan-1-one* (Table 3.4, entry 4): The title compound was prepared according to the general procedure using H$_2$O and MeOH.  Volatiles were removed under reduced pressure resulting in a yellow oil, which was passed through a short plug of silica with 1×25 mL CH$_2$Cl$_2$ and concentrated again.  Purification by column chromatography (silica gel) eluting with CH$_2$Cl$_2$, (5 mL), CH$_2$Cl$_2$:*i*Pr*O*H (10 mL,

20:1), and CH$_2$Cl$_2$:$i$PrOH (15 mL, 10:1) gave a yellow solid (10.9 mg, 87%). Due to volatility trace solvents remained observable in the $^1$H NMR spectrum. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.51 (d, $J$ = 1.63 Hz, 1H), 7.39 (d, $J$ = 2.31 Hz, 1H), 6.22 (t, $J$ = 2.12 Hz, 1H), 4.52 (m, 1H), 3.00 (dd, $J_1$ = 10.16 Hz, $J_2$ = 10.26 Hz, 1H), 2.82 (dd, $J_1$ = 5.13 Hz, $J_2$ = 4.96 Hz, 1H), 2.41 (m, 1H), 2.2 (m, 2H), 2.04 (m, 1H), 1.71 (m, 1H); $^{13}$C NMR (600 MHz, CDCl$_3$) δ 208.02, 139.55, 139.49, 127.56, 105.42, 59.80, 47.40, 31.85, 21.81; HRMS (ESI) C$_9$H$_{13}$N$_2$O$^+$ [M+H]$^+$ calculated m/z = 165.1022, found 165.1022.

### 3.4.4 Product Characterization

For Michael Addition products known from previous literature (Table 3.2, Entries 1-8), (Table 3.3, Entries 1-6,8-10), and (Table 3.4, Entries 1-3,5), $^1$H NMR spectra are provided. Full characterization data are provided for (Table 3.4, Entry 4).

*3-phenylcyclohexan-1-one* (Table 3.2, Entry 1):[151] $^1$H NMR (600 MHz, CDCl$_3$) δ 7.33 (m, 2H), 7.23 (m, 3H), 3.01 (t, $J$ = 11.7 Hz, 1H), 2.61 (m, 1H), 2.59 (m, 1H), 2.45 (m, 1H), 2.39 (m, 1H), 2.16 (m, 1H), 2.10 (m, 1H), 1.83 (m, 2H).

*3-phenylcyclopentan-1-one* (Table 3.2, Entry 2):[209] $^1$H NMR (300 MHz, CDCl$_3$) δ 7.30 (m, 2H), 7.25 (m, 3H), 3.33 (m, 1H), 2.65 (m, 1H), 2.43 (m, 4H), 1.95 (m, 1H)

*3-methyl-3-phenylcyclohexan-1-one* (Table 3.2, Entry 3):[210] $^1$H NMR (300 MHz, CDCl$_3$) δ 7.31 (m, 5H), 2.91 (d, $J$ = 14.22 Hz, 1H), 2.32 (t, $J$ = 7.24 Hz, 2H), 2.19 (m, 1H), 1.89 (m, 2H), 1.71 (m, 1H).

*3-phenylcycloheptan-1-one* (Table 3.2, Entry 4):[211] $^1$H NMR (600 MHz, CDCl$_3$) δ 7.30 (m, 2H), 7.18 (m, 3H), 2.91 (m, 2H), 2.66 (d, $J$ = 11.1 Hz, 1H), 2.58 (m, 2H), 2.10 (m, 2H), 2.02 (m, 1H), 1.73 (m, 2H), 1.51 (m, 1H).

*4-phenylnonan-2-one* (Table 3.2, Entry 5):[209] ^{1}H NMR (600 MHz, CDCl₃) δ 7.29 (m, 2H), 7.17 (m, 3H), 3.10 (m, 1H), 2.71 (m, 2H), 2.01 (s, 3H), 1.58 (m, 2H), 1.21 (m, 6H), 0.82 (t, $J = 6.68$ Hz, 1H).

*3,3-diphenylpropanal* (Table 3.2, Entry 6):[212] ^{1}H NMR (300 MHz, CDCl₃) δ 9.77 (t, $J = 1.89$ Hz, 1H), 7.31 (m, 10H), 4.66 (m, 1H), 3.22 (dd, $J_1 = 1.90$ Hz, $J_2 = 1.88$ Hz, 2H).

*4,4-diphenylbutan-2-one* (Table 3.2, Entry 7):[213] ^{1}H NMR (300 MHz, CDCl₃) δ 7.25 (m, 10H), 4.59 (t, $J = 7.51$ Hz, 1H), 3.18 (d, $J = 7.61$ Hz, 3H).

*1,3,3-triphenylpropan-1-one* (Table 3.2, entry 8):[214] ^{1}H NMR (600 MHz, CDCl₃) δ 7.93 (d, $J = 6.83$ Hz, 2H), 7.53 (t, $J = 7.21$ Hz, 1H), 7.43 (t, $J = 7.67$ Hz, 2H), 7.27 (m, 8H), 4.83 (t, $J = 7.29$ Hz, 1H), 3.74 (d, $J = 7.35$ Hz, 2H).

*3-(p-tolyl)cyclohexan-1-one* (Table 3.3, Entry 1):[151] ^{1}H NMR (300 MHz, CDCl₃) δ 7.11 (m, 4H), 2.98 (m, 1H), 2.57 (m, 2H), 2.48 (m, 2H), 2.36 (s, 3H), 2.15 (m, 2H), 1.82 (m, 2H).

*3-(o-tolyl)cyclohexan-1-one* (Table 3.3, Entry 2):[151] ^{1}H NMR (300 MHz, CDCl₃) δ 7.24 (m, 2H), 7.16 (m, 2H), 3.21 (m, 1H), 2.53 (m, 2H), 2.46 (m, 1H), 2.32 (s, 3H), 2.19 (m, 1H), 2.00 (m, 1H), 1.81 (m, 2H).

*3-mesitylcyclohexan-1-one* (Table 3.3, Entry 3):[179] ^{1}H NMR (600 MHz, CDCl₃) δ 6.84 (s, 2H), 3.40 (m, 1H), 2.94 (t, $J = 14.05$ Hz, 1H), 2.32 (m, 14H), 1.88 (m, 1H), 1.75 (m, 1H).

*3-(4-(tert-butyl)phenyl)cyclohexan-1-one* (Table 3.3, Entry 4):[209] ^{1}H NMR (300 MHz, CDCl₃) δ 7.36 (m, 2H), 7.16 (m, 2H), 2.99 (m, 1H), 2.50 (m, 4H), 2.16 (m, 2H), 2.14 (m, 2H), 1.32 (s, 9H).

*3-(naphthalen-1-yl)cyclohexan-1-one* (Table 3.3, Entry 5):[151] ^{1}H NMR (600 MHz, CDCl$_3$) δ 8.05 (d, *J* = 8.75 Hz, 1H), 7.89 (d, *J* = 7.90 Hz, 1H), 7.75 (d, *J* = 8.40 Hz, 1H), 7.50 (m, 1H), 7.55 (m, 1H), 7.53 (m, 2H), 7.41 (m, 1H), 3.86 (m, 1H), 2.76 (m, 1H), 2.67 (t, *J* = 12.52 Hz, 1H), 2.57 (m, 1H), 2.50 (m, 1H), 2.25 (m, 2H), 2.03 (m, 1H), 1.96 (m, 1H).

*3-(3-bromophenyl)cyclohexan-1-one* (Table 3.3, Entry 6):[215] ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.37 (d, *J* = 7.02 Hz, 2H), 7.21 (t, *J* = 7.40 Hz, 1H), 7.14 (d, *J* = 7.09 Hz, 1H), 2.98 (m, 1H), 2.59 (m, 1H), 2.51 (m, 2H), 2.39 (m, 1H), 2.16 (m, 1H), 2.06 (m, 1H), 1.76 (m, 2H).

*3-(4-nitrophenyl)cyclohexan-1-one* (Table 3.3, Entry 8):[151] ^{1}H NMR (600 MHz, CDCl$_3$) ) δ 8.21 (d, *J* = 8.32 Hz, 2H), 7.40 (d, *J* = 8.37 Hz, 2H), 3.14 (m, 1H), 2.63 (m, 1H), 2.53 (m, 2H), 2.41 (m, 1H), 2.20 (m, 1H), 2.11 (m, 1H), 1.86 (m, 2H).

*3-(2-methoxyphenyl)cyclohexan-1-one* (Table 3.3, Entry 9):[151] ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.22 (m, 2H), 7.19 (t, *J* = 7.78 Hz, 1H), 6.88 (d, *J* = 7.66 Hz, 1H), 3.82 (s, 3H), 3.43 (m, 1H), 2.59 (m, 1H), 2.53 (m,1H), 2.45 (m, 1H), 2.35 (m, 1H), 2.11 (m, 1H), 2.01 (m, 1H), 1.82 (m, 2H).

*methyl 4-(3-oxocyclohexyl)benzoate* (Table 3.3, Entry 10):[151] ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.02 (m, 2H), 7.32 (m, 2H), 3.93 (s, 3H), 3.10 (m, 1H), 2.58 (m, 4H), 2.19 (m, 2H), 1.79 (m, 2H).

*3-(furan-3-yl)cyclohexan-1-one* (Table 3.4, Entry 1):[216] ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.37 (m, 1H), 7.23 (m, 1H), 6.30 (m, 1H), 3.00 (m, 1H), 2.62 (m, 1H), 2.42 (m, 3H), 2.30 (m, 2H), 1.75 (m, 2H).

*3-(thiophen-3-yl)cyclohexan-1-one* (Table 3.4, Entry 2):[166] ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.29 (m, 1H), 6.98 (m, 2H), 3.16 (m, 1H), 2.72 (m, 1H), 2.66 (m, 3H), 2.16 (m, 2H), 1.78 (m, 2H),

*3-(pyridin-4-yl)cyclohexan-1-one* (Table 3.4, Entry 5):[217] ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.56 (m, 2H), 7.14 (m, 2H), 3.03 (m, 1H), 2.58 (m, 4H), 2.16 (m, 2H), 1.84 (m, 2H).

CHAPTER IV

ROOM TEMPERATURE β-BORATION OF α,β-UNSATURATED CARBONYL

COMPOUNDS CATALYZED BY CCC-NHC PINCER

RHODIUM COMPLEXES

**4.1     Introduction**

Organoborane compounds are highly sought after intermediates in organic

synthesis. The facile transformation of the C–B bond into other functional groups such as

alcohols, amines, and alkenes allows direct access to a wide range of organic

molecules.[218-220] In 1997, a Pt catalyst was utilized in the first report of β-boration of α,β-

unsaturated carbonyl compounds using a diboron reagent.[221] To date, the boration of α,β-

unsaturated carbonyl compounds has been catalyzed with Pt,[221-224] Pd,[225,226]

Rh,[173,188,227,228] Cu,[229-254] Ni,[226,255,256] Fe,[257] metal-free phosphines,[258-260] and NHCs.[261-263]

Subsequently, β-boration of α,β-unsaturated carbonyl compounds has become very useful

due to the additional carbonyl contained in the product.[222,227,231-236,255,257] Oxidation of the

product provides access to β-hydroxy compounds as an alternative to the aldol reaction or

reduction of β-keto carbonyl compounds. β-Hydroxy carbonyl compounds are found

widely in natural products and pharmaceuticals.[264,265] Additionally, β-boro-carbonyl

compounds have been reported as being effective therapeutic agents in cancer

treatment.[266,267]

Cu systems have been the most commonly applied catalysts for β-boration of α,β-unsaturated carbonyl compounds. Noteworthy examples have been reported using strictly protic solvents such as MeOH[240] and $H_2O$.[250,251,268-271] In 2009, Santos reported the synthesis of an innovative $sp^2$–$sp^3$ diboron reagent and demonstrated its application in a Cu catalyzed β-boration of acyclic substrates.[246] In 2008, the first asymmetric catalysis for β-boration of acyclic compounds was reported using a chiral Cu phosphine complex,[229] opening the path for innovative work such as asymmetric β-borations conducted in water.[251,268-270] Subsequently, other examples of asymmetric catalysis have been reported with Ni,[226] Pd,[226] Rh,[188,227,228] and Cu. [232,235,236,241-244,247-249,253,254,271-273] Metal free-catalysis has also been developed, including asymmetric variants,[260,262] such as a chiral NHC salt reported by Hoveyda.[262,263] Suprisingly, only a few examples in the literature have utilized Rh. In 2002, Kabalka[173] reported the first Rh catalyzed β-boration of α,β-unsaturated electron deficient olefins. Then in 2009 several enantioselective Rh catalyzed examples were reported using Rh(Phebox).[228] Despite many reports utilizing various transition metals, base additives or high temperatures have been required for efficient rates, and limitations to acyclic α,β-unsaturated carbonyl substrates have been noted. In addition, very few cyclic products with boron-substituted quaternary carbon centers have been reported.[261] A catalyst that provides cyclic β-boro-carbonyl compounds containing quarternary carbon centers and can operate at room temperature will be an advance in the formation of C–B bonds as well as β-hydroxy carbonyl compound derived thereof.

Previously, we had reported a mixture of the CCC-NHC pincer Rh complexes **8/9** (refer to Scheme 3.1) that efficiently catalyzed 1,4-addition of aryl boronic acids to

electron-deficient alkenes.[274] CCC-NHC pincer Rh complexes **8/9** with added NHMe₂,

produced excellent yields (>90%) with various Michael acceptors and arylboronic acids

in protic solvents.[274] Upon further attempts to optimize the synthesis of **9**, a crude isolate

(**10**) that was orange in color was obtained reproducibly (Figure 4.1). We report herein

the results of screening material **10** in the β-boration of cyclic and acyclic α,β-

unsaturated, electron-deficient alkenes and a partial characterization of the mixture **10**.

To our knowledge, this is the first report of a CCC-NHC pincer Rh complex catalyzing

1,4-addition reactions at room temperature.



**9**

**10**
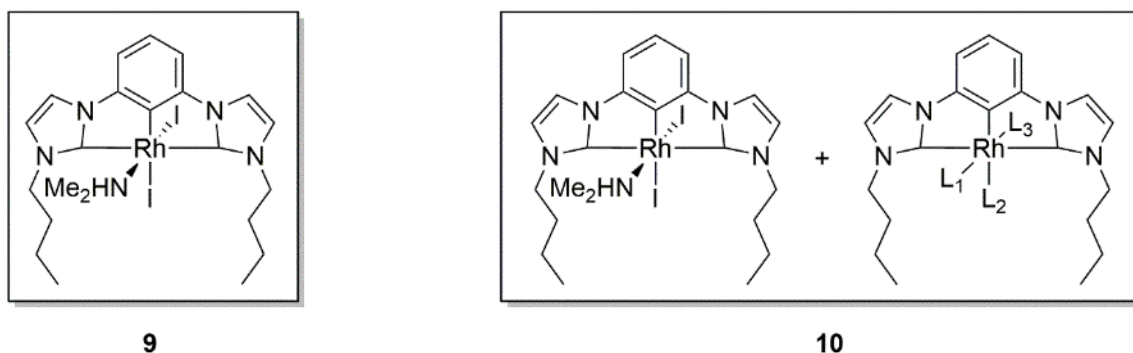
Figure 4.1    CCC-NHC Rh amine adduct (**9**) and crude isolate (**10**)

## 4.2    Results and Discussion

Because high yields were observed previously for Michael addition products in a

H₂O/MeOH solvent mixture,[274] pre-catalyst loading optimization of **10** in β-boration

reactions was conducted in MeOH with *trans*-3-nonen-2-one and B₂pin₂ (Table 4.1).

Although the material **10** is a mixture, 2 mg (~4 mol %) were typically used in a catalytic

trial.  The molecular weight of amine adduct **9** (722.98 g/mol) was used as a surrogate for

the entire sample to calculate pre-catalyst loading (mol %) for comparative purposes.

Table 4.1     Optimization of β-Boration Reaction Conditions[a]
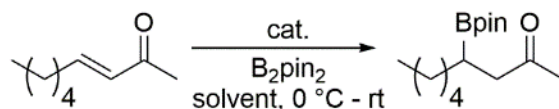


| entry | solvent | cat. (mol %) | B$_2$pin$_2$ (equiv) | time | conv %[b] |
|---|---|---|---|---|---|
| 1 | MeOH | **10** (4) | 1.5 | 1 h | 34 |
| 2 | MeOH | **10** (4) | 2.5 | 1 h | >99 |
| 3 | MeOH | -------- | 2.5 | 1 h | 0 |
| 4 | MeOH | [Rh(COD)Cl]$_2$ (4) | 2.5 | 1 h | 9 |
| 5 | MeOH | NHMe$_2$ (4) | 2.5 | 1 h | <3 |
| 6 | MeOH | **10** (2) | 2.5 | 1.5 h | >99 |
| 7 | MeOH | **10** (4) | 2.5 | 1 h | 60[c] |
| 8 | EtOH | **10** (4) | 2.5 | 1 h | 93 |
| 9 | H$_2$O | **10** (4) | 2.5 | 1 h | >99 |

[a]trans-3-nonen-2-one (0.0735 mmol), B₂pin₂, cat **10** ( 2.00 mg, ~2.94 µmol), and solvent (0.700 mL) were added to a 1 dram vial with a magnetic stir bar, sonicated for 1 min and stirred for 1 h at rt. [b]Conversion was determined by GC-MS analysis. [c]Reaction was conducted at 0 ˚C.
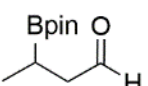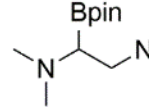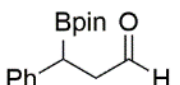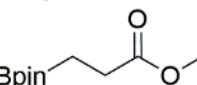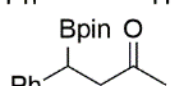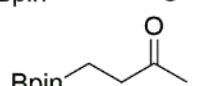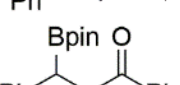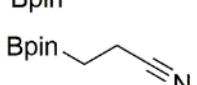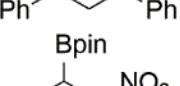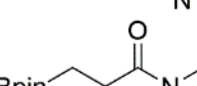
Initially, 1.5 equiv of B₂pin₂ were used with *trans*-3-nonen-2-one, and a 34%

conversion to the borated product was observed (entry 1). Previously, using 2.5 equiv of

aryl boronic acids with α,β-unsaturated carbonyl compounds in 1,4-additions gave higher

conversion. Therefore, the B₂pin₂ concentration was increased to 2.5 equiv, and as

expected, conversion to the borated *trans*-3-nonen-2-one of >99% was observed in 1 h

(entry 2). A control experiment without added **10** (entry 3) resulted in no reaction.

Evaluating 4 mol % [Rh(COD)Cl]₂ dimer as a potential catalyst (entry 4) provided only 1

turnover (8-atom mol % Rh and 9% yield) in 1 h, thus eliminating extraneous starting

material as the active catalyst. To demonstrate that the amine base was not the active

catalyst, 4 mol % of NHMe₂ only produced <3% conversion (entry 5). The catalyst

loading was lowered to examine the efficiency of **10** (entries 6 vs. 7). At 2 mol % (1 mg)

pre-catalyst loading (entry 6), >99% conversion was observed in 1.5 h. The reaction was

also conducted at 0 ˚C to determine the efficiency of the catalyst below rt (entry 7),

which resulted in a respectable 60% conversion in only one hour. High conversion was

also observed using eco-friendly solvents, $H_2O$ (>99%) and EtOH (>93%) (entries 8 and

9). These results are consistent with previous work of Yun and co-workers [240] and

Fernández and co-workers,[259] in which both demonstrated an enhanced rate of β-boration

of α,β-unsaturated carbonyl compounds with the use of alcohol additives such as MeOH.

Moreover, Santos clearly demonstrated, through detailed mechanistic studies, the ability

of the amine base to activate a nucleophilic water molecule generating the $sp^2$–$sp^3$ diboryl

adduct that participates in transmetalation.[250] Protic solvents MeOH and EtOH were used

throughout the screening of activated acyclic and cyclic alkenes to evaluate the effect on

the rate of conversion. Because >99% conversion was observed in 1 h with 4 mol % of **10**

(entry 2, Table 4.1), the scope and limitations studies were conducted under these

optimized conditions.

      Utilizing the optimized reaction conditions, activated acyclic alkenes were

examined (Table 4.2). Excellent conversions (>99%) of the aldehyde substrates

(crotonaldehyde and cinnamaldehyde, entries 1 and 2) were observed in both MeOH and

EtOH. *trans*-4-Phenyl-3-buten-2-one (entry 3) and chalcone (entry 4) had the least

conversion in 1 h.

Table 4.2    Scope of Acyclic Substrate Reactivity in the β-Boration with B$_2$pin$_2$[a]



R = H, CH$_3$, Ph, NR$_2$    EWG = ald, ket, ester, amide, nitrile

| entry | product | MeOH conv%[b] (yield%)[c] | EtOH | entry | product | MeOH conv%[b] (yield%)[c] | EtOH |
|---|---|---|---|---|---|---|---|
| 1 | | >99 (86) | >99 (81) | 6 | | 0[d] | 0[d] |
| 2 | | >99 (86) | >99 (84) | 7 | | >99 (90) | >99 (94) |
| 3 | | 96 (82) | 84 (61) | 8 | | >99 (93) | >99 (96) |
| 4 | | 81 (66) | 49 (22) | 9 | | 0[d] | 0[d] |
| 5 | | 0[d] | 0[d] | 10 | | >99 (84) | >99 (83) |

[a]Acyclic α,β-unsaturated compound (0.0735 mmol), bis(pinacolato)diboron (0.184 mmol), **10** (2.00 mg, ~2.94 µmol), and 0.700 mL of MeOH were added to a 1 dram vial with a magnetic stir bar, and stirred for 1h at rt. [b]Conversion was determined by GC-MS analysis. [c]Isolated yield. [d]After 24 h reaction time.

Due to lack of reported borated products containing nitro functionalities, *trans*-β-nitro styrene (entry 5) and 1-(dimethylamino)-2-nitroethylene (entry 6) were both screened. No product was observed for any of the nitro-containing substrates despite extended reaction time of 24 h. Ethyl acrylate (entry 7) exhibited excellent conversion (>99%) in both MeOH and EtOH. Methyl vinyl ketone (entry 8) was another acyclic substrate to show high conversion in MeOH and EtOH. Acrylonitrile (entry 9) was evaluated but no product was observed. Boration of *N,N*-dimethylacrylamide (entry 10) was successful (>99% conversion) in both MeOH and EtOH.

Previously, little success has been reported in borating cyclic enones with Rh catalysts. Reports include Rh(Phebox)[227] with 0% conversion of cyclohexenone and Wilkinson's catalyst with extended reactions times (12-13 h) and elevated temperature (80 °C) for the boration of cyclohexenone (78%) and cycloheptenone (75%) in good yields.[173] Thus, cyclic enones were evaluated under the optimized conditions with 4 mol % (2.00 mg) of **10**, and the results are presented in Table 4.3. Conversions of >99% in just 1 h were observed for all three non-substituted cyclic substrates (entries 1-3) in MeOH and EtOH. This rate of conversion of cyclohexenone is comparable to catalytic reports with Cu (99%, 1 h)[250] and an NHC (91%, 1 h)[261] catalysts. The rate of product formation with cyloheptenone (entry 3, >93%), in all solvents, is also comparable or faster than the best previous reports.[173,261] Only modest conversions were observed for the α-substituted, 2-methylcyclopent-2-en-1-one (entry 4) in 1h, but upon extended reaction times improved conversions to the borated product were obtained. No significant diastereoselectivity was observed in the reactions with 2-methylcyclopent-2-en-1-one (entry 4). Excellent conversions have been reported for sterically hindered β-substituted cyclic enones in 1 h reaction times with Cu or NHC catalysts.[250,261,262] However, extended reaction times were required when pre-catalyst **10** was employed for both 2-methyl cyclopentenone (entry 5) and 2-methyl cyclohexenone (entry 6) in ethanol and methanol, resulting in only fair to good conversions. After 1 h, moderate conversion (70%) was observed when using MeOH as a solvent for 3-methyl-2-cyclopentenone (entry 6), while less was observed in EtOH (57%). A drastic reduction in conversion rate was observed for 3-methyl-2-cyclohexenone (entry 6). This observation is consistent with

Nishiyama[227] and co-workers' proposed catalytic cycle, which suggests that the steric congestion due to the methyl group hinders the boryl-insertion at the β-position.

Table 4.3    Scope of Cyclic Substrate Reactivity in the β-Boration with B$_2$pin$_2$[a]



n = 0, 1, 2
R, R' = H, CH$_3$
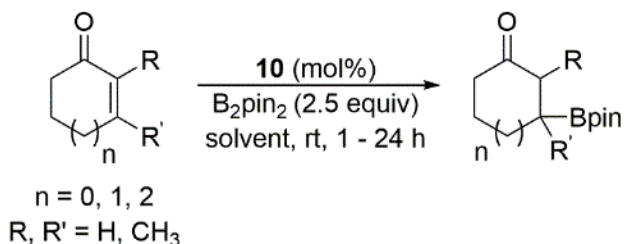
| entry | product | MeOH conv%[b] (yield%)[c] | EtOH conv%[b] (yield%)[c] | entry | product | MeOH conv%[b] (yield%)[c] | EtOH conv%[b] (yield%)[c] |
|---|---|---|---|---|---|---|---|
| 1 | | >99 (90), 1 h | >99 (70) 1 h | 4 | | 75, 1 h (dr = 1.1:1) 93 (71), 24 h (dr = 1:1) | 70, 1 h (dr = 1.7:1) 80 (51), 24 h (dr = 1.6:1) |
| 2 | | >99 (88), 1 h | >99 (84) 1 h | 5 | | 70, 1 h 86 (51), 24 h | 57, 1 h 63 (40), 24 h |
| 3 | | >99 (91), 1h | 94 (90) 1h | 6 | | 40, 1 h 51 (40), 24 h | 26, 1 h 38 (25), 24 h |

[a]Cyclic α,β-unsaturated compound (0.0735 mmol), bis(pinacolato)diboron (0.184 mmol), **10** (2.00 mg, ~2.94 μmol), and 0.700 mL of MeOH were added to a 1 dram vial with a magnetic stir bar, stirred for 1 or 24 h at rt. [b]Conversion was determined by GC-MS analysis. [c]Isolated yield.

    It was noted that if isolate **10** was "aged" (i.e. was stored for several months) there was an impact on its catalytic efficiency.  Thus, using a five month old sample of **10** for the boration of cylcohexenone only an 83% conversion was found in 1 h, compared to Table 4.3, entry 2, which was quantitatively converted in 1 h with freshly prepared **10**. While 83% conversion is still very good, freshly isolated pre-catalyst **10** is best for optimum catalytic activity.

Spectroscopic data indicated that orange mixture **10** consisted of primarily two

CCC-NHC pincer Rh complexes. However, many peaks in the $^1$H NMR spectrum

overlapped (see Figure A. 34). While full characterization is currently ongoing, partial

characterization can be presented. Fortunately, several sets of signals in the spectroscopic

data have led to partial characterization, thus indicating similarities between the two

complexes. Two sets of diastereotopic methylene peaks indicating a mixture of CCC-

NHC pincer Rh complexes. x and x′ indicate signals due to CCC-NHC pincer Rh amine

adduct **9** (Figure 4.2).
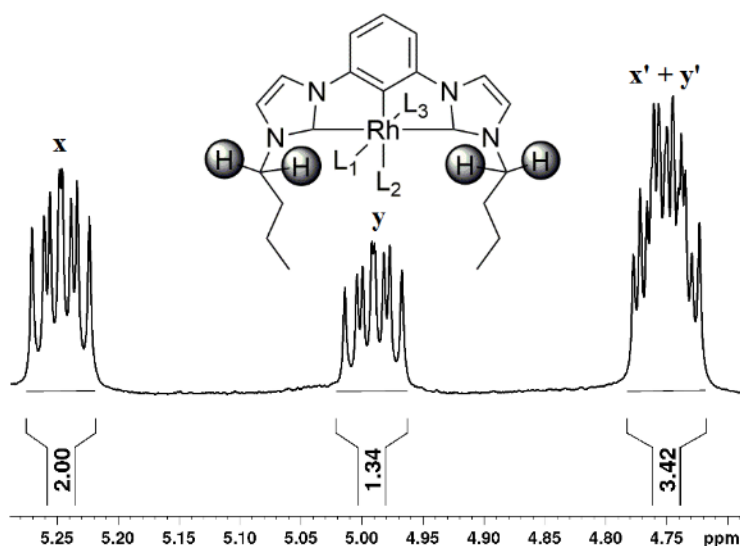


Figure 4.2     Diastereotopic methylene peaks of **10** observed in $^1$H NMR spectrum

Two sets of diastereotopic methylene peaks indicating a mixture of CCC-NHC pincer Rh
complexes. **x** and **x′** indicate signals due to CCC-NHC pincer Rh amine adduct **9**.

For example, an integration value of 2 was set for the multiplet at 5.20 ppm

(Figure 4.2, **x**), a signal observed for diastereotopic methylene peaks, yet an integration

value of 3.42 is observed for the other corresponding diastereotopic methylene signal at

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4.75 ppm. This integral intensity is due to overlapping diastereotopic methylene peaks (**x',y'**, see Figure 4.2) at 4.75 ppm, while the other diastereotopic peak (**y**) corresponding to the minor complex is slightly downfield at 4.95 ppm. Two doublets of doublets were observed at 1.59 and 1.64 ppm with identical coupling values (dd, $^3J_{H-H}$ = 1.2 Hz, $^3J_{Rh-H}$ = 6.3 Hz) in the $^1$H NMR spectrum (see Figure A. 34) due to the unique heteronuclear coupling of NMR active[103] Rh to coordinated NHMe$_2$.

Two Rh–$C_{aromatic}$ and Rh–$C_{carbene}$ doublets (Figure 4.3) observed in the $^{13}$C NMR spectrum further advances our assignment of structural similarities between the two species. Identical coupling values are observed for the Rh–$C_{carbene}$ and the Rh–$C_{aromatic}$ doublets ($^1J$ = 39 Hz and $J$ = 29 Hz, respectively).
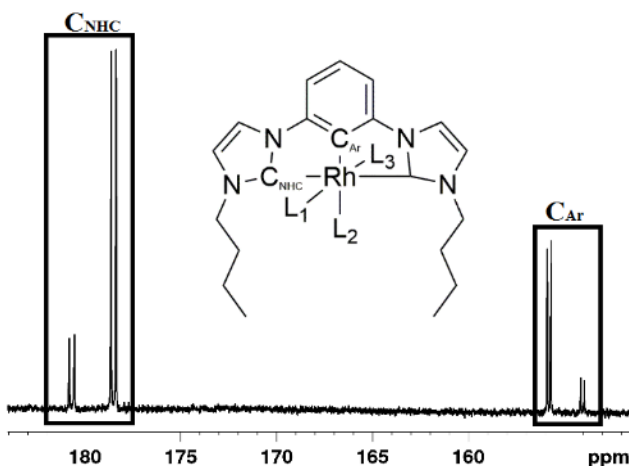


Figure 4.3     Rh–$C_{aromatic}$ and Rh–$C_{carbene}$ doublets of **10** observed in $^{13}$C spectrum

Partial chromatographic separation of **10** was accomplished using silica gel. The main component isolated was a dark orange solid in 26% yield. Analysis of the spectroscopic data of this component leads to the assignment of axial amine adduct **9** as

the structure,[37] which has NMR peaks coincident with the major component of mixture **9**.

Additionally, orange X-ray quality crystals were grown by vapor diffusion

(toluene/DCM) from mixture **9**. X-ray crystal structure analysis determined molecular

structure **9** (Figure 4.4) was indeed the axial isomer.[275] The equatorial isomer of **9** may be

ruled out as the other component of the mixture because it would not be expected to give

rise to diastereotopic signals as observed for **y** (Figure 4.2). The molecular structure was

observed to be a distorted octahedral geometry with the amine ligand in an axial position.

The metric data (bond distances and angles) are normal for this ligand system (Table 4.4).

A catalytic trial was performed under optimized reaction conditions using 2 mg of **9** with

cyclohexenone. However, only a 72% conversion to the borated product was observed in

1 h (compared to >99% in Table 3, entry 2), indicating that **8** alone was not as

catalytically active as the mixture **10**.
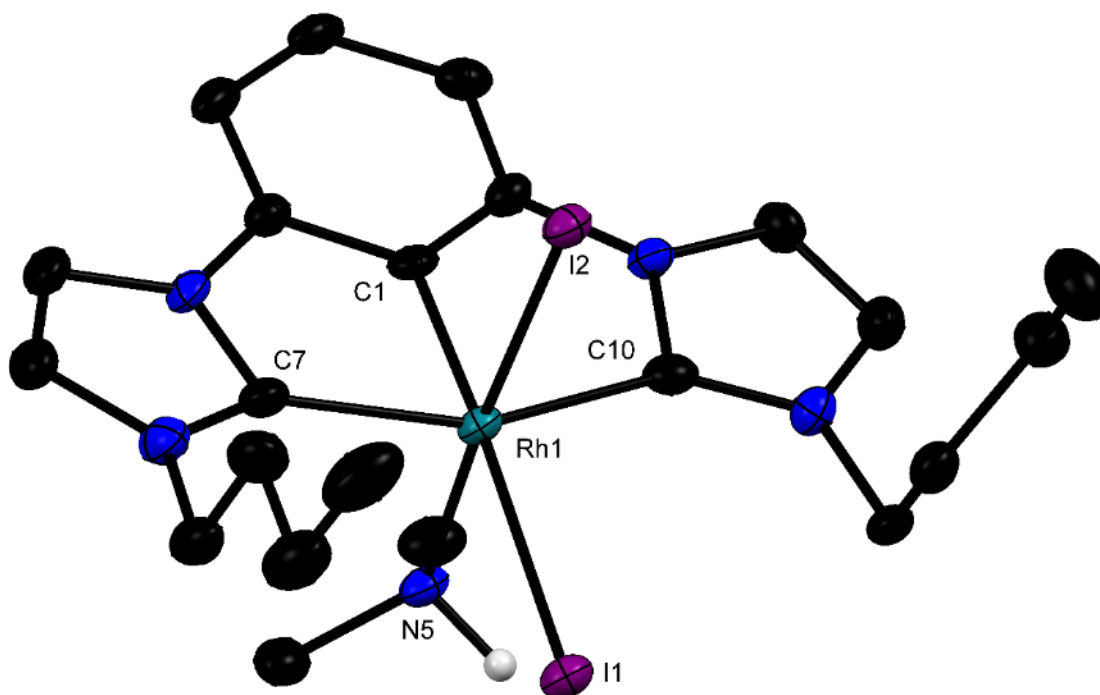
Figure 4.4    X-ray molecular structure of **9**

All but amine hydrogens are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 4.4    Selected Bond Lengths (Å) and Angles (°) for **9**

| length (Å) | | angle (°) | |
|---|---|---|---|
| Rh(1)–C(1) | 1.948(4) | C(1)–Rh(1)–C(10) | 78.41(15) |
| Rh(1)–C(7) | 2.083(4) | C(1)–Rh(1)–C(7) | 78.48(14) |
| Rh(1)–N(5) | 2.136(3) | C(10)–Rh(1)–C(7)) | 156.61(14) |
| Rh(1)–I(1) | 2.856(4) | N(5)–Rh(1)–I(1) | 83.80(8) |

## 4.3    Conclusion

In conclusion, the CCC-NHC pincer Rh complex mixture **10** catalyzed the β-boration of α,β-unsaturated activated alkenes at room temperature in quantitative yield, typically in only 1 h, producing tertiary and quaternary carbon centers. The reported method does not require the exclusion of air or $H_2O$ due to the stability of pre-catalyst **10**.

To our knowledge, this is the first report of β-boration using a CCC pincer complex catalyst to produce tertiary and quaternary β-substituted carbon centers using MeOH and EtOH as the solvent. The rates obtained with **9** for β-boration are comparable to the best reported.[250,261] Separating and identifying the remaining component of pre-catalyst **10**, its reactivity and synergy with **9**, and identifying the precipitate observed during the catalytic trials and the catalytically active species will be the subject of future work.

## 4.4    Experimental

### 4.4.1    General Consideration

All NMR spectra were taken on a Bruker Advance III 300 or 600 MHz. High-resolution mass spectrometer (HRMS) data was acquired using ESI technique on a Bruker UHPLC-Micro-Q/T OF-MS/MS. Gas chromatography mass spectrometer (GC-MS) data was collected on a Shimadzu GCMS-QP2010 plus. A Zebron capillary GC column was used with the following dimensions: length - 30 m: I.D. - 0.25 mm: film thickness - 0.25μm. The following method, Table 4.5, was employed on the GC-MS for all catalysis trials:

Table 4.5    GC-MS Method for β-Boration Catalysis

| | |
|---|---|
| Column Oven Temp. | 50.0 ˚C |
| Injection Temp. | 250.0 ˚C |
| Injection Mode | Split |
| Flow Control Mode | Linear Velocity |
| Pressure | 53.6 kPa |
| Total Flow | 102.0 mL/min |
| Column FLow | 1.00 mL/min |
| Linear Velocity | 36.3 cm/sec |
| Purge Flow | 1.0 mL/min |
| Split Ratio | 100.0 |
| High Pressure Injection | OFF |
| Carrier Gas Saver | ON |
| Carrier Gas Saver Split Ratio | 5.0 |
| Carrier Gas Saver Time | 1.00 min |
| Splitter Hold | OFF |
| Oven Temp. Program | |

| **Rate** | **Temperature (˚C) : Hold Time (min)** |
|---|---|
| -- | 50.0 : 0 |
| 10.00 | 250.0 : 5.00 |

## 4.4.2    Synthesis of CCC-NHC Pincer Rhodium Complexes 10

1, 3-bis (1-butylimidazolium-3-yl) benzene iodide (**3**) (0.150 g, 0.260 mmol), and

tetrakis(dimethylamido)zirconium (0.173 g, 0.650 mmol) were weighed in under inert

atmosphere  and dry THF (15 ml) was added into a 50 mL flask. The mixture was stirred

at room temperature for approximately 1 hour or until a light yellow homogenous

solution was obtained. Once the solution became homogeneous, [Rh(COD)Cl]$_2$ (0.128 g,

0.260 mmol) was added to the flask and stirring continued at room temperature for

another 12 hours. Deionized water (1 mL) was added, and it was stirred vigorously for 10

minutes providing a white precipitate and a bright orange supernatant. The orange

supernatant was filtered and the solvent was removed under reduced pressure yielding a

dark orange solid. The solid was washed with hexanes (25 mL) and ether (25 mL) and

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dried to obtain dark orange/red solid (0.128 g, 68 %). Orange X- ray quality crystals of **9** were grown by vapor diffusion (toluene/DCM). Catalyst **10** mixture (Two components: ratio ~1.6:1) $^1$H NMR (600 MHz, CDCl$_3$): δ 7.61-7.60 (m, 3H), 7.27-7.13 (m, 5.1H), 7.11-7.07 (m, 3.1H), 5.25-5.21 (m, 2H), 4.97-4.94 (m, 1.2H), 4.79-4.74 (m, 3.2H), 3.72 (m, 1H), 3.69 (m, 0.6H), 2.05-1.99 (m, 6.4H), 1.65-1.63 (dd, $^3$J H–H = 1.2 Hz, $^3$J Rh–H = 6.3 Hz, 3.3H), 1.60-1.59 (dd, $^3$J H–H = 1.2 Hz, $^3$J Rh–H = 6.3 Hz, 5.8H), 1.57-1.51 (m, 6.5H), 1.02-0.99 (m, 9.4H). $^{13}$C (150 MHz, CDCl$_3$): δ 180.6 (d, J = 39 Hz, Rh–C$_{carbene}$), 178.4 (d, J = 39 Hz, Rh–C$_{carbene}$), 155.7 (d, J = 29 Hz, Rh–C$_{aromatic}$), 153.9 (d, J = 29 Hz, Rh–C$_{aromatic}$), 145.8, 145.5, 124.0, 123.7, 121.6, 121.1, 115.8, 115.5, 108.6, 108.5, 51.7, 49.8, 44.6, 44.5, 33.6, 33.2, 20.1, 19.9, 14.1, 14.0. HRMS-ESI (m/z): [M-I]$^+$ calcd for C$_{22}$H$_{32}$IN$_5$Rh, 596.0752; found, 596.0740; [M-I-NHMe$_2$]$^+$ calcd for C$_{20}$H$_{25}$IN$_4$Rh, 551.0173; found, 551.0163.

### 4.4.3    General Procedure for Catalytic Trials

A 1 dram vial with a magnetic stir bar was charged with α,β–unsaturated compound (0.0735 mmol), bis(pinacolato)diboron (0.184 mmol), pre-catalyst **10** (2.00 mg, 2.94 µmol), and solvent (0.700 mL). The vial was closed and stirred vigorously for 1 h at rt during which time a dark precipitate was observed to form. After 1 h, a 10 µL aliquot was passed through a short plug of celite and a 0.45 um PTFE filter and was injected into the GC-MS to determine conversion. The crude reaction mixture was then filtered through a plug of celite to remove insolubles. Volatiles from the filtered reaction mixture were then removed under reduced pressure resulting in an oil. $^1$H NMR and HRMS was then taken of the crude product to confirm the borylated product. The crude product was then purified by silica gel chromatography to determine an isolated yield.

### 4.4.4    Product Characterization

Borated Products: Table 4.1, Entry 2; Table 4.2, Entries 1-5,7; and Table 4.3, Entries 1-7.

*4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nonan-2-one* (Table 4.1, Entry2): Colorless oil, eluted with 1:10 / EtOAc:Hexanes, $R_f$ 0.25. $^1$H and $^{13}$C NMR match previously reported literature.[250] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{15}H_{30}BO_3$, 269.2285; found 269.2297.

*3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanal* (Table 4.2, Entry 1): Colorless oil, eluted with 1:10 / Et$_2$O:Hexanes, $R_f$ 0.27. $^1$H and $^{13}$C NMR match previously reported literature.[234] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{10}H_{19}BO_3$, 199.1502; found, 199.1506; [M+Na]$^+$ calcd for $C_{10}H_{19}BO_3Na$, 221.1321; found 221.1318.

*3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanal* (Table 4.2, Entry 2): Colorless oil, eluted with 1:15 / EtOAc:Hexanes, $R_f$ 0.24. $^1$H and $^{13}$C NMR match previously reported literature.[234] HRMS-ESI (*m/z*): [M-OH]$^+$ calcd for $C_{15}H_{20}BO_2$, 243.1554; found 243.1559; [M+Na]$^+$ calcd for $C_{15}H_{21}BO_3Na$,  283.1479; found 283.1483.

*4-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one* (Table 4.2, Entry 3): Colorless oil, eluted with 1:10 / EtOAc:Hexanes, $R_f$ 0.25. $^1$H and $^{13}$C NMR match previously reported literature.[234] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{16}H_{24}BO_3$, 275.1816; found 275.1812;  [M+Na]$^+$ calcd for $C_{16}H_{23}BO_3Na$ 297.1635; found 297.1632.

*1,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one* (Table 4.2, Entry 4): Colorless oil, eluted with 1:15 / EtOAc:Hexanes, $R_f$ 0.29. $^1$H and $^{13}$C NMR

match previously reported literature.[234] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{25}H_{26}BO_3$, 337.1970; found 337.1973; [M+Na]$^+$ calcd for $C_{21}H_{25}BO_3Na$, 359.1793; found 359.1789.

*ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate* (Table 4.2, Entry 7): Colorless oil, eluted with 1:10 / EtOAc:Hexanes, R$_f$ 0.32. $^1$H and $^{13}$C NMR match previously reported literature.[246] HRMS-ESI (m/*z*): [M+H]$^+$ calcd for $C_{11}H_{22}BO_4$, 229.1608; found 229.1597; [M+Na]$^+$ calcd for $C_{11}H_{21}BO_4Na$, 251.1425; found 251.1427.

*4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one* (Table 4.2, Entry 8): Colorless oil, eluted with 1:10 / EtOAc:Hexanes, R$_f$ 0.36. $^1$H and $^{13}$C NMR match previously reported literature.[234] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{10}H_{20}BO_3$, 199.1502; found 199.1502; [M+Na]$^+$ $C_{10}H_{19}BO_3Na$, 221.1321; found 221.1324

*N,N-dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanamide* (Table 4.2, Entry 10): Yellow oil, eluted with 1:10 / Hexanes:EtOAc, R$_f$ 0.10. $^1$H and $^{13}$C NMR match previously reported literature.[246] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{11}H_{23}BNO_3$, 228.1768; found 228.1767; [M+Na]$^+$ calcd for $C_{11}H_{22}BNO_3Na$, 250.1587; found 250.1587.

*3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentan-1-one* (Table 4.3, Entry 1): Colorless oil, eluted with 1:10 / EtOAc:Hexanes, R$_f$ 0.33. $^1$H and $^{13}$C NMR match previously reported literature.[261] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{11}H_{20}BO_3$, 211.1502; found 211.1503.

*3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-one* (Table 4.3, Entry 2): Colorless oil, eluted with 1:15 / EtOAc:Hexanes, R$_f$ 0.23. $^1$H and $^{13}$C NMR match previously reported literature.[173] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{12}H_{22}BO_3$, 225.1659; found 225.1653.

*3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cycloheptan-1-one* (Table 4.3, Entry 3): Colorless oil, eluted with 1:15 / EtOAc:Hexanes, $R_f$ 0.27. $^1$H and $^{13}$C NMR match previously reported literature.[276] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{32}H_{23}BO_3$, 239.1815; found 239.1820; [M+Na]$^+$ calcd for $C_{32}H_{23}BO_3Na$, 261.1635; found 261.1641.

*2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentan-1-one* (Table 4.3, Entry 4): Colorless oil, eluted with 1:15 / EtOAc:Hexanes, $R_f$ 0.32. $^1$H and $^{13}$C NMR match previously reported literature.[261] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{12}H_{22}BO_3$, 225.1659; found 225.1655.

*3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopentan-1-one* (Table 4.3, Entry 5): Colorless oil, eluted with 1:15 / EtOAc:Hexanes, $R_f$ 0.33. $^1$H and $^{13}$C NMR match previously reported literature.[261] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{12}H_{22}BO_3$, 225.1659; found 225.1658.

*3-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexan-1-one* (Table 4.3, Entry 6): Colorless oil, eluted with 1:15 / EtOAc:Hexanes, $R_f$ 0.26. $^1$H and $^{13}$C NMR match previously reported literature.[261] HRMS-ESI (*m/z*): [M+H]$^+$ calcd for $C_{13}H_{24}BO_3$, 39.1815; found 239.1810.

CHAPTER V

DEVELOPMENT OF CCC-NHC Ir AND Rh PINCER COMPLEXES FOR

BORYLATION OF ARENE AND ALKANE C–H BONDS

## 5.1    Introduction

Organoboron compounds are valuable synthetic intermediates for development of

many pharmaceuticals, agrochemicals, and materials science products.[218,220,277,278] In

addition, aryl organoborates are essential building blocks for synthesis of C–C bonds in

the Suszuki Coupling reaction.[145,146] Direct access to these versatile aryl boronate esters

were reported by Miyaura demonstrating Pd catalyzed borylation of aryl halides.[279] In

1995, Hartwig and co-workers reported the first borylation of arenes and alkenes with

well-defined metal–boryl catalysts, producing free boronate ester products in high

yield.[280] This direct borylation methodology does not require the use of aryl halides or

pseudohalides, in contrast to Miyaura's report, allowing for a more facile synthetic

pathway with fewer steps.

Ir catalyzed C–H borylation has been the most efficient method in the formation

of arylboronate compounds using bis(pinacolato)diboron (B$_2$pin$_2$) and pinacolborane

(HBpin) reagents.[277,278,281-283] Recently, high turnovers have also been reported in Ir

catalyzed borylation of heteroarene substrates.[284-287] Furthermore, mono- and bidentate

Ir-NHC complexes have shown to be applicable in the synthesis of boronic acid esters

*via* C–H functionalization with diboryl agents.[41,288,289] Inspired by these reports, we

investigated CCC-NHC Ir pincer complex **11** (Scheme 5.1) as a potential catalyst in C–H

borylation reactions.[52]
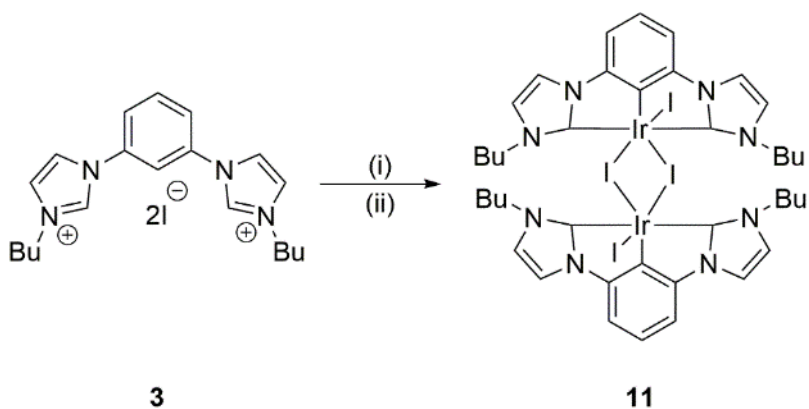


Scheme 5.1    Synthesis of **11**
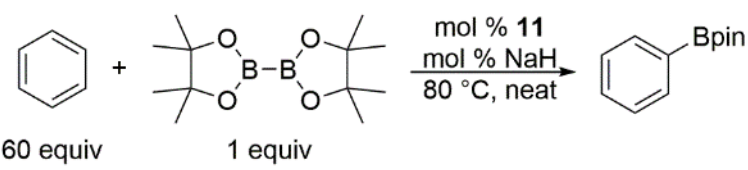
Conditions: (i) 2.5 equiv Zr(NMe$_2$)$_4$, THF, rt, 1h; (ii) 1 equiv [Ir(COD)Cl]$_2$, THF, 6 h

## 5.2    **Results and Discussion**

Following the optimization conditions for borylation of arenes reported by

Hartwig and co-workers,[290] complex **11** was tested for activity in functionalization of

benzylic C-H bonds outlined in Table 5.1. Initially, complex **11** was evaluated with

B$_2$pin$_2$ in benzene resulting in minimal conversion (entry 1). It was then surmised a

possible hydride source could advance the sluggish results due to Smith and co-workers

report outlining an active Ir$^{III}$(H) intermediate in their proposed catalytic cycle of arene

borylation.[291] Indeed, upon addition of excess NaH (entry 2), the boryl source was

completely consumed in 6 h giving the benzene ester product. This result is competitive

with Hartwig and Miyaura's 2002 publication, in which they reported a 96% yield at 80

°C, with similar catalyst loading at 16 h.[290] Conversions held steady when lowering the

NaH loading from 50% to 15% in catalytic trials 3 and 4. However, when limiting the

amount of added NaH (entries 5 and 6) conversions dropped drastically, indicating **11** acts as a pre-catalyst to a hypothesized CCC-NHC Ir(H) adduct. [Ir(COD)Cl]₂, a common catalyst precursor in many arene borylation reports,[277] was also screened resulting in minimal conversion (entry 8). Lower conversions were also observed in shorter time periods (entries 9 and 10), although a respectable 92% conversion was still obtained at 4 h (entry 9).

Table 5.1    Benzene C–H Borylation Optimization[a]



| entry | 11 mol%[a] | NaH mol%[b] | time (h) | conv (%) |
|---|---|---|---|---|
| 1 | 1.5 | - | 6 | 4 |
| 2 | 1.5 | 50 | 6 | >99 |
| 3 | 1.5 | 30 | 6 | >99 |
| 4 | 1.5 | 15 | 6 | >99 |
| 5 | 1.5 | 8 | 6 | 53 |
| 6 | 1.5 | 4 | 6 | 5 |
| 7 | - | 15 | 6 | 0 |
| 8 | -[c] | 15 | 6 | 9 |
| 9 | 1.5 | 15 | 4 | 92 |
| 10 | 1.5 | 15 | 2 | 64 |

[a]mol % of **11** and NaH calculated from mmol of B₂pin₂ (0.187 mmol). [b]% conv based on boron atom in B₂pin₂ determined by GC-MS. [c]1.5 mol% of [Ir(COD)Cl]₂ used as catalyst.

Hartwig and Miyaura illustrated through kinetic and computational studies how electron rich arenes formed stable $\eta^2$-arene Ir intermediate complexes that precede oxidative addition, thereby resulting in lower conversions compared to electron poor aryl derivatives.[292] Therefore, *o*-xylene and chlorobenzene were screened (Table 5.2) to observe if the *in-situ* generated active catalyst followed this reported trend.

Table 5.2    Arenes Substrates for C–H Borylation[a]



| entry | product | time (h) | conv (%)[b] | isomer ratio[c] |
|---|---|---|---|---|
| 1 | Bpin (o-xylene Bpin product) | 2<br>4<br>7<br>15 | 18<br>46<br>53<br>76 | 60:40 |
| 2 | Bpin Cl (chlorobenzene product) | 2<br>4 | 83<br>94 | 75:25 |
| 3 | Bpin N (pyridine product) | 2 | 41 | 60:40 |

[a]All reactions were conducted in a 1 dram vial with B$_2$pin$_2$ (1.0 equiv), arene (60 equiv), **11** (1.5 mol %), and NaH (15 mol %) neat. [b]Conversion was determined by GC-MS analysis. [c]Isomer ratio determined by GC-MS.

Indeed, lower conversion was observed with o-xylene (entry 1) compared to the electron poor chlorobenzene (entry 2). Borylation of heteroarenes could allow development in new synthetic pathways to important pharmaceutical and natural products. While the scope is still limited in the application of heteroarene borylation, a recent report by Hartwig and co-workers, revealing mechanistic studies and regioselectivity of C–H functionalization of heteroarenes, may help in furthering the development of synthetically useful heteroaryl boronate esters.[284] Pyridine (entry 3) was examined and observed a 41% conversion observed in 2 h. While this result, along with results of entries 1 and 2, are preliminary, they are nevertheless encouraging, as the basicity of the non-bonding electrons on nitrogen in many heterocycles have been reported to poison many catalytic systems in C–H functionalization of heteroarenes.[284]

Intrigued by the results discussed in Tables 5.1 and 5.2, investigation was turned to determining the identity of the active catalyst in the borylation reactions. Following the conditions outlined in Scheme 5.2, 50 equiv of NaH was added to **11** in THF at room temperature, resulting in a brown heterogeneous mixture that was left standing for 12 h. Afterwards, a single opaque X-ray quality crystal was retrieved from the reaction mixture and was identified as a H–Ir(μ-H)$_2$Ir–H bridged dimer (**12**) upon X-ray analysis. An ORTEP plot of **12** is displayed in Figure 5.1 along with selected metric data in Table 5.3. While further studies are currently ongoing, complex **12** is believed to be the active species in Tables 5.1 and 5.2. Furthermore, complex **12** is presently being evaluated for activity in alkane dehydrogenation studies due to the similar framework of the active PCP hydride pincer catalysts reported,[20] most notably by Jensen[34,35] and Goldman.[33,293]
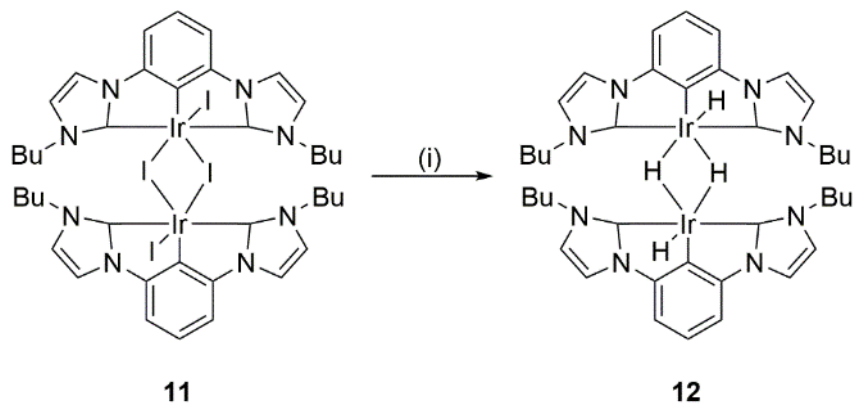


Scheme 5.2    Synthesis of **12**

Conditions: (i) 50 equiv of NaH, THF, rt, 12 h;
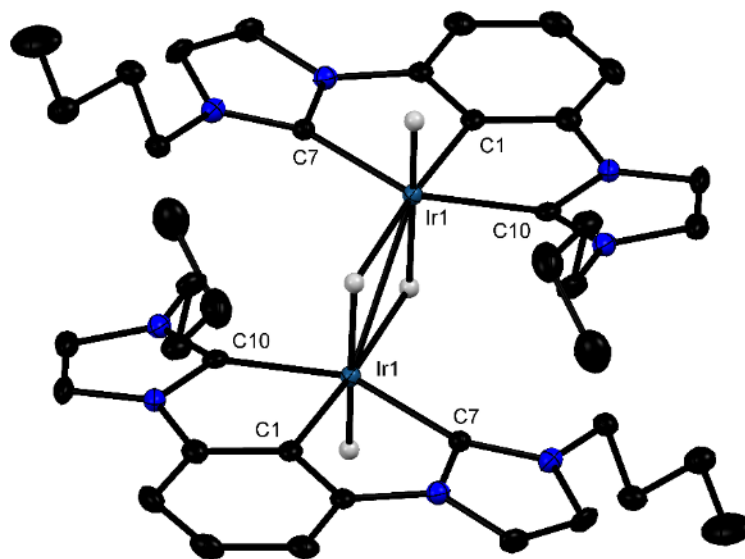
Figure 5.1    X-ray structure of **12**

Excluding Ir–H's, hydrogens are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 5.3    Selected Bond Lengths (Å) and Angles (°) for **12**

| length (Å) | | angle (°) | |
|---|---|---|---|
| Ir(1)–C(1) | 1.967(3) | C(1)–Ir(1)–C(10) | 77.99(12) |
| Ir(1)–C(10) | 2.035(3) | C(1)–Ir(1)–C(7) | 78.10(12) |
| Ir(1)–C(7) | 2.035(3) | C(10)–Ir(1)–C(7)) | 154.55(12) |
| Ir(1)–Ir'(1) | 2.7837(2) | C(2)–C(1)–Ir(1) | 120.8(2) |

With promising preliminary results obtained in C–H borylation of arenes utilizing

presumed catalyst **12**, a potentially more reactive second row CCC-NHC Rh pincer

variant was pursued for possible activation of alkyl C–H bonds. Hartwig and co-workers

pioneered the first selective catalytic C–H functionalization of alkanes at the terminal

position with Cp*Rh(R)$_x$ (Cp* C$_5$Me$_5$H, Me = CH$_3$) complexes.[294] Harris and Bergman

developed Tp*Rh (CO)$_2$ (Tp* 5 HB–Pz3*, Pz* = 3,5-dimethylpyrazolyl) photocatalytic

catalysts which activated alkyl C–H bonds at room temperature.[295,296] It was reasoned a

CCC-NHC Rh pincer complex with a CO ligand could provide access to an unsaturated CCC-NHC Rh species by simple halide abstraction, generating a 16 e⁻ square planar species with a $d^8$ metal center (Figure 5.2). This resulting complex would provide a pathway to a further coordinatively unsaturated 14 e⁻ $d^8$ metal complex *via* photolysis of the CO ligand. These systems have been reported as active intermediates in C-H activation, and can be stabilized by NHC ligand systems.[297,298]



coordinatively unsaturated 16 e⁻ complex
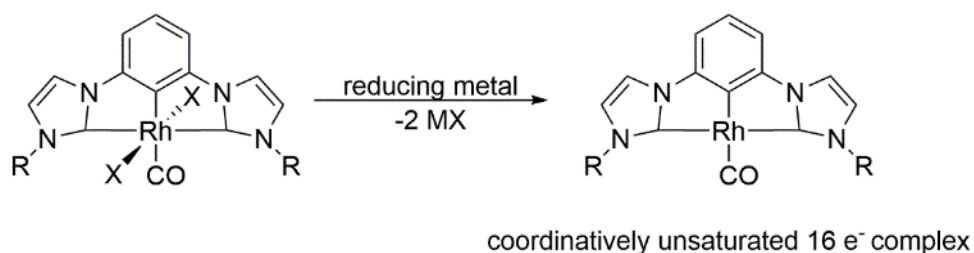
Figure 5.2    Coordinatively unsaturated CCC-NHC Rh(CO) pincer complex

CCC-NHC Zr pincer complex **2** was explored as a transmetalating reagent in order to access a single CCC-NHC Rh(CO) variant due to the successful formation of complex CCC-NHC Co pincer complex **7** in high yield, using the Zr diiodo species (refer to Scheme 2.3). Fortunately, upon addition of 1.2 equiv of [Rh(CO)$_2$Cl]$_2$ to Zr complex **2** (Scheme 5.3), complex **13** was formed and confirmed by $^1$H and $^{13}$C NMR along with DEPT 135 (see Figure A.99-101).
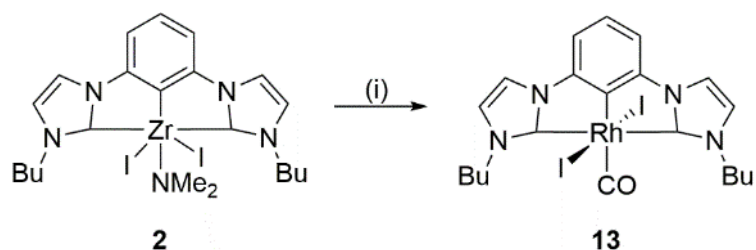
Scheme 5.3    Synthesis of **13**

Conditions: 1.2 equiv [Rh(CO)$_2$Cl]$_2$, CH$_2$Cl$_2$, rt, 12 h

Orange crystals suitable for single crystal X-ray diffraction of **13** were grown by vapor diffusion of hexane into a saturated solution CH$_2$Cl$_2$ and further confirmed through X-ray analysis. An ORTEP plot of **13** is displayed in Figure 5.2 along with selected metric data in Table 5.4. Complex **13** will provide access to the desired 16e$^-$ square planar CCC-NHC Rh(I)(CO) species, outlined in Figure 5.2, to generate the coordinatively unsaturated 14 e$^-$ d$^8$ metal complex via photolysis of the CO ligand.
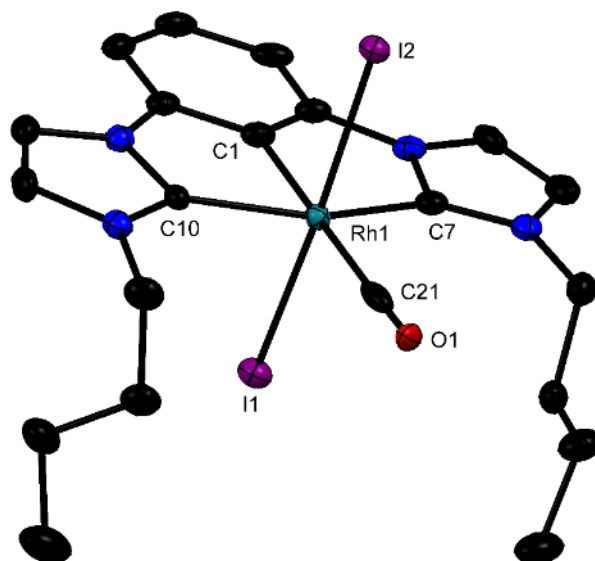


Figure 5.3    X-ray structure of **13**

Hydrogens are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 5.4    Selected Bond Lengths (Å) and Angles (°) for **13**

| length (Å) | | angle (°) | |
|---|---|---|---|
| I(1)–Rh(1) | 2.6685(3) | C(1)–Rh(1)–I(1) | 87.12(9) |
| Rh(1)–C(10) | 2.061(3) | C(1)–Rh(1)–C(21) | 178.53(13) |
| Rh(1)–C(7) | 2.057(3) | O(1)–C(21)–Rh(1) | 178.6(3) |
| Rh(1)–C(21) | 1.999(4) | N(2)–C(1O)–Rh(1) | 140.9(2) |

With the successful formation of complex **13**, a CCC-NHC Rh(CO) hydride variant was then sought due extensive reports of Rh(H)(CO) complexes active in catalytic carbonylation of olefins.[299] Moreover, Marder and co-workers reported catalytic C–H bond activation occurring directly from Rh–H complexes.[300-302] Following similar reaction conditions outlined in Scheme 5.3, attempts to synthesize a CCC-NHC Rh(CO) hydride species with various hydride sources were pursued. However, no product formation was observed for the desired Rh–H complex. Therefore, Rh(CO)$_2$(acac) was examined as an alternative Rh transmetalating reagent, along with LiAlH$_4$ as a hydride source, resulting in the unexpected formation of **14**, demonstrated in Scheme 5.4.
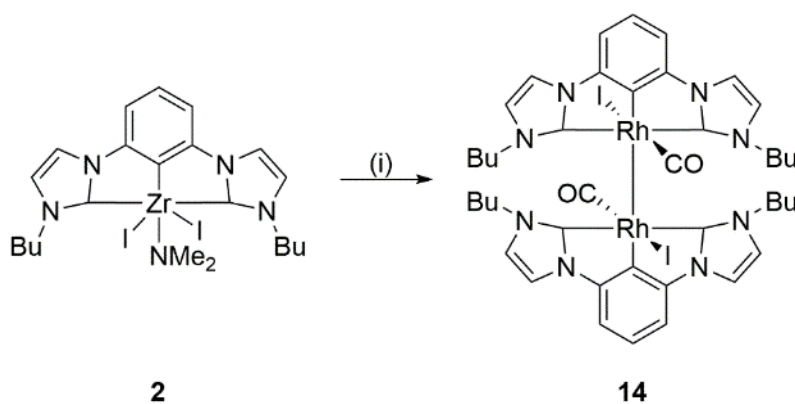


Scheme 5.4    Synthesis of **14**

Conditions: 1.2 equiv Rh(CO)$_2$(acac), 5.0 equiv LiAlH$_4$, CH$_2$Cl$_2$, rt, 12 h

Several crystals precipitated from the reaction mixture and were solved by X-ray analysis, characterizing complex **14** as a bimetallic Rh(II)(CO)–Rh(II)(CO) complex (Figure 5.4). Selected bond lengths and angles for **14** are given in Table 5.5.
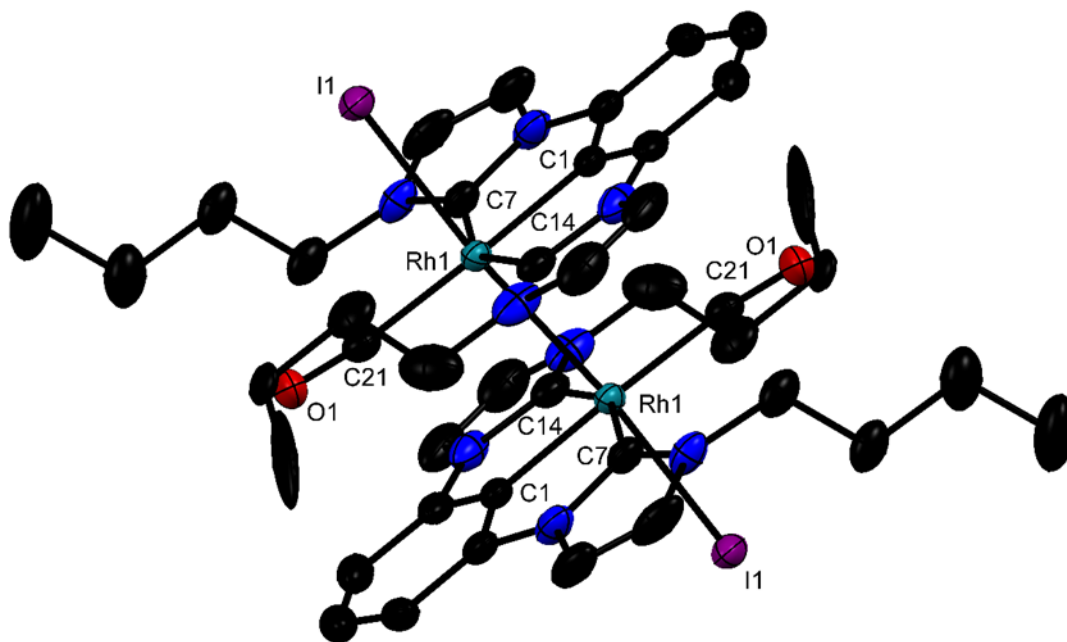


Figure 5.4    X-ray structure of **14**

Hydrogens are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

Table 5.5    Selected Bond Lengths (Å) and Angles (°) for **14**

| length (Å) | | angle (°) | |
|---|---|---|---|
| Rh(1)–Rh(1) | 2.8102(5) | C(1)–Rh(1)–I(1) | 89.77(10) |
| Rh(1)–C(1) | 1.984(4) | C(1)–Rh(1)–C(21) | 177.91(14) |
| Rh(1)–C(21) | 1.949(4) | O(1)–C(21)–Rh(1) | 173.1(3) |
| C(21)–O(1) | 1.136(5) | C(21)–Rh(1)–Rh(1) | 96.60(11) |

## 5.3    Conclusions

The formation of a CCC-NHC Ir(H) pincer complex (**12**) has been successfully demonstrated, the surmised active catalyst in our preliminary trials in C–H borylation of

arenes. Furthermore, we present a direct synthetic pathway in developing CCC-NHC

Rh(III)(CO) and CCC-NHC Rh(II)(CO) pincer complexes, potential pre-catalysts for

photocatalytic C–H bond activation of alkyl derivatives. Further studies are ongoing in

expanding the scope of our studies outlined in Table 5.2, along with providing full

spectroscopic characterization of CCC-NHC pincer complexes **12-14**.

## 5.4     Experimental

### 5.4.1      General Considerations

All NMR spectra were taken on a Bruker Advance III 600 MHz. High-resolution

mass spectrometer (HRMS) data was acquired using ESI technique on a Bruker UHPLC-

Micro-Q/T OF-MS/MS. Standard inert-atmosphere techniques were used unless

otherwise noted. Synthesis of **2** and **11** were prepared from previously reported literature

procedures.[37,51,125] $CH_2Cl_2$, THF, and toluene were dried by using molecular sieves and

the SP-1 Solvent System from LC Technology Solutions Inc. All commercial reagents

were used as received. Chemical shifts ($\delta$) in the NMR spectra ($^1$H and $^{13}$C) were

referenced by assigning the residual solvent peaks. Gas chromatography mass

spectrometer (GC-MS) data was collected on a Shimadzu GCMS-QP2010 plus. A Zebron

capillary GC column was used with the following dimensions: length - 30 m: I.D. - 0.25

mm: film thickness - 0.25µm. The following method, Table 5.2, was employed on the

GC-MS for all catalysis trials:

Table 5.6    GC-MS Method for C–H Borylation Catalysis

| | |
|---|---|
| Column Oven Temp. | 50.0 ˚C |
| Injection Temp. | 250.0 ˚C |
| Injection Mode | Split |
| Flow Control Mode | Linear Velocity |
| Pressure | 53.6 kPa |
| Total Flow | 102.0 mL/min |
| Column FLow | 1.00 mL/min |
| Linear Velocity | 36.3 cm/sec |
| Purge Flow | 1.0 mL/min |
| Split Ratio | 100.0 |
| High Pressure Injection | OFF |
| Carrier Gas Saver | ON |
| Carrier Gas Saver Split Ratio | 5.0 |
| Carrier Gas Saver Time | 1.00 min |
| Splitter Hold | OFF |
| Oven Temp. Program | |

| **Rate** | **Temperature (˚C) : Hold Time (min)** |
|---|---|
| -- | 50.0 : 0 |
| 10.00 | 250.0 : 5.00 |

## 5.4.2    Synthesis of CCC-NHC Iridium Pincer Complex 12

1, 3-bis(imidazolene-3-yl)benzene tetra(iodo)-di(iridium)(III) complex (**11**) (0.020 g, 0.016 mmol), sodium hydride (NaH) (0.019 g, 0.780 mmol) and THF (0.50 mL) were combined in a one dram vial at room temperature (22 °C). Reaction mixture became a brown heterogeneous mixture and allowed to sit at room temperature for 12 h. A single opaque x-ray quality crystal of **12** was retrieved out of the reaction mixture.

## 5.4.3    Synthesis of CCC-NHC Rhodium Pincer Complex 13

2-(1,3-Bis(30-butyl-imidazol-20-ylidene)phenylene)(dimethylamido)diiodo zirconium(IV) complex (**2**) (0.025 g, 0.035 mmol), [Rh(CO)$_2$Cl]$_2$ (0.017 g, 0.043 mmol) and CH$_2$Cl$_2$ (0.50 mL) were combined in a one dram vial at room temperature (22 °C). Reaction mixture immediately became a red homogeneous mixture and was allowed to sit

at room temperature for 12 h. Orange x-ray quality crystals of **13** were grown by vapor diffusion of hexane into a saturated solution of $CH_2Cl_2$. $^1H$ NMR (600 MHz, $CDCl_3$): δ 7.61-7.60 (d, $J = 1.83$ Hz, 2H), 7.19 (s, 3H), 7.04-7.03 (d, $J = 1.83$ Hz, 2H), 4.32-4.29 (t, $J = 7.96$ Hz, 4H), 1.55-1.49 (m, 4H), 1.52-1.50 (m, 4H), 1.05-0.99 (t, $J = 7.28$ Hz, 6H). $^{13}C$ (150 MHz, $CDCl_3$): δ188.6 (d, $J = 42$ Hz, Rh–$C_{NHC}$), 180.1 (d, $J = 69$ Hz, Rh–$C_{CO}$), 180.1 (d, $J = 35$ Hz, Rh–$C_{aryl}$), 145.3, 125.4, 121.2, 116.4, 109.0, 51.8, 32.8, 20.0, 13.7.

### 5.4.4 Synthesis of CCC-NHC Rhodium Pincer Complex 14

2-(1,3-Bis(30-butyl-imidazol-20-ylidene)phenylene)(dimethylamido)diiodo zirconium(IV) complex (**2**) (0.025 g, 0.035 mmol), lithium aluminum hydride (LAH) (0.007 g, 0.176 mmol) (acetylacetonato)dicarbonylrhodium(I) (0.011 g, 0.043 mmol) and $CH_2Cl_2$ (0.50 mL) were combined in a one dram vial at room temperature (22 °C). Reaction mixture immediately became a dark red homogenous mixture and was allowed to sit at room temperature for 12 h. Orange x-ray quality crystals of **14** were grown by vapor diffusion of hexane into a saturated solution of $CH_2Cl_2$.

### 5.4.5 General Procedure for Catalytic Trials

A 1 dram vial with a magnetic stir bar was charged with arene (1.0 mL), bis(pinacolato)diboron (60 equiv), **11** (1.5 mol%), NaH (15 mol %) and was conducted neat. The vial was closed and stirred vigorously for at 80 °C. After 6 h, a 10 μL aliquot was passed through a short plug of celite and a 0.45 um PTFE filter and was injected into the GC-MS to determine conversion.

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APPENDIX A

SPECTROSCOPIC DATA

# A.1 Chapter II Compounds
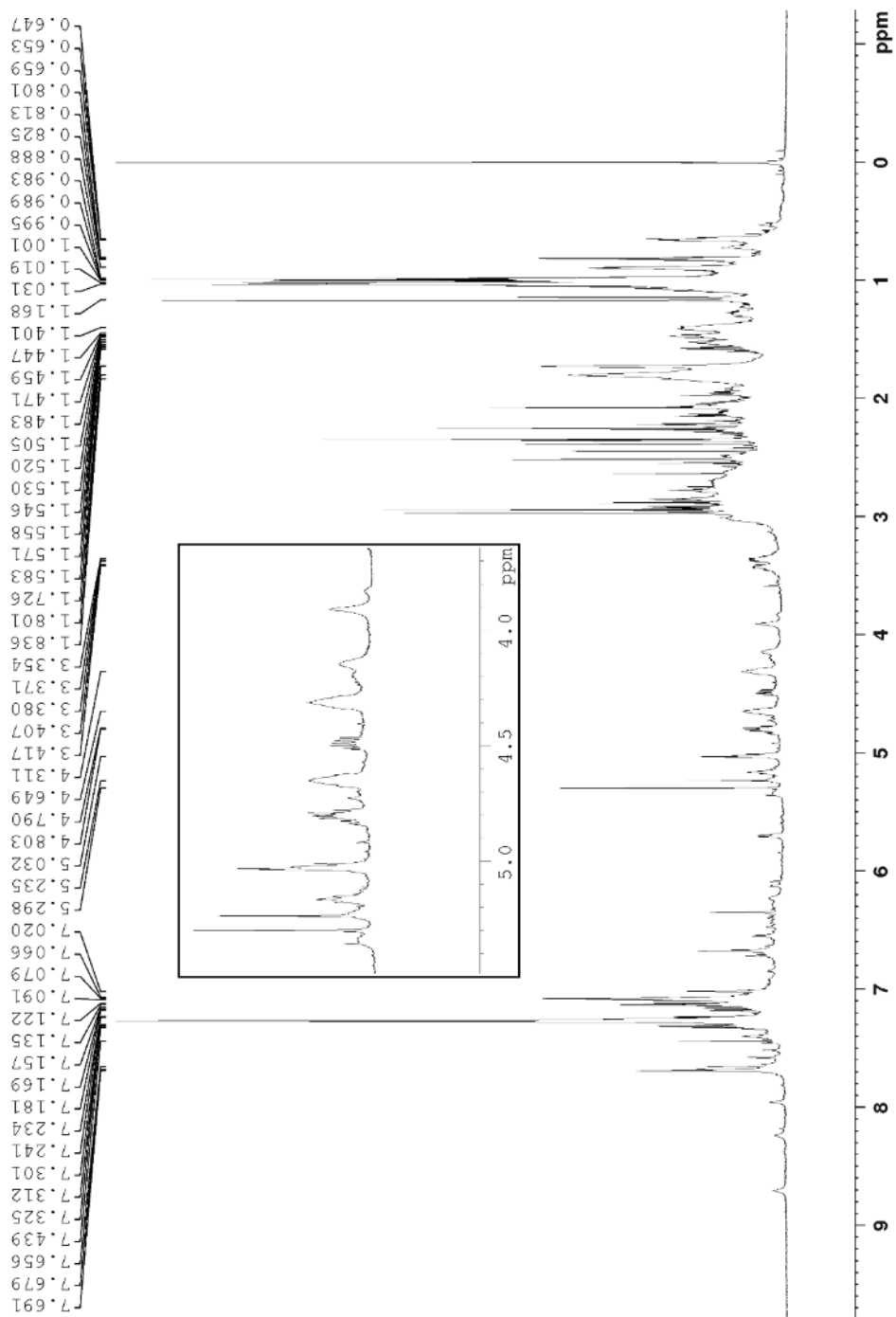


Figure A.1 $^1$H NMR (600 MHz, CDCl$_3$) spectrum of reaction mixture (Scheme 2.1)

0.657
0.666
0.691
0.703
0.726

2.791
2.803
2.814

6.788
7.331
7.343
7.428
7.441
7.637

9.47
16.36

8.21

4.24
4.03
2.11
4.00

ppm
0
1
2
3
4
5
6
7
8
9
10
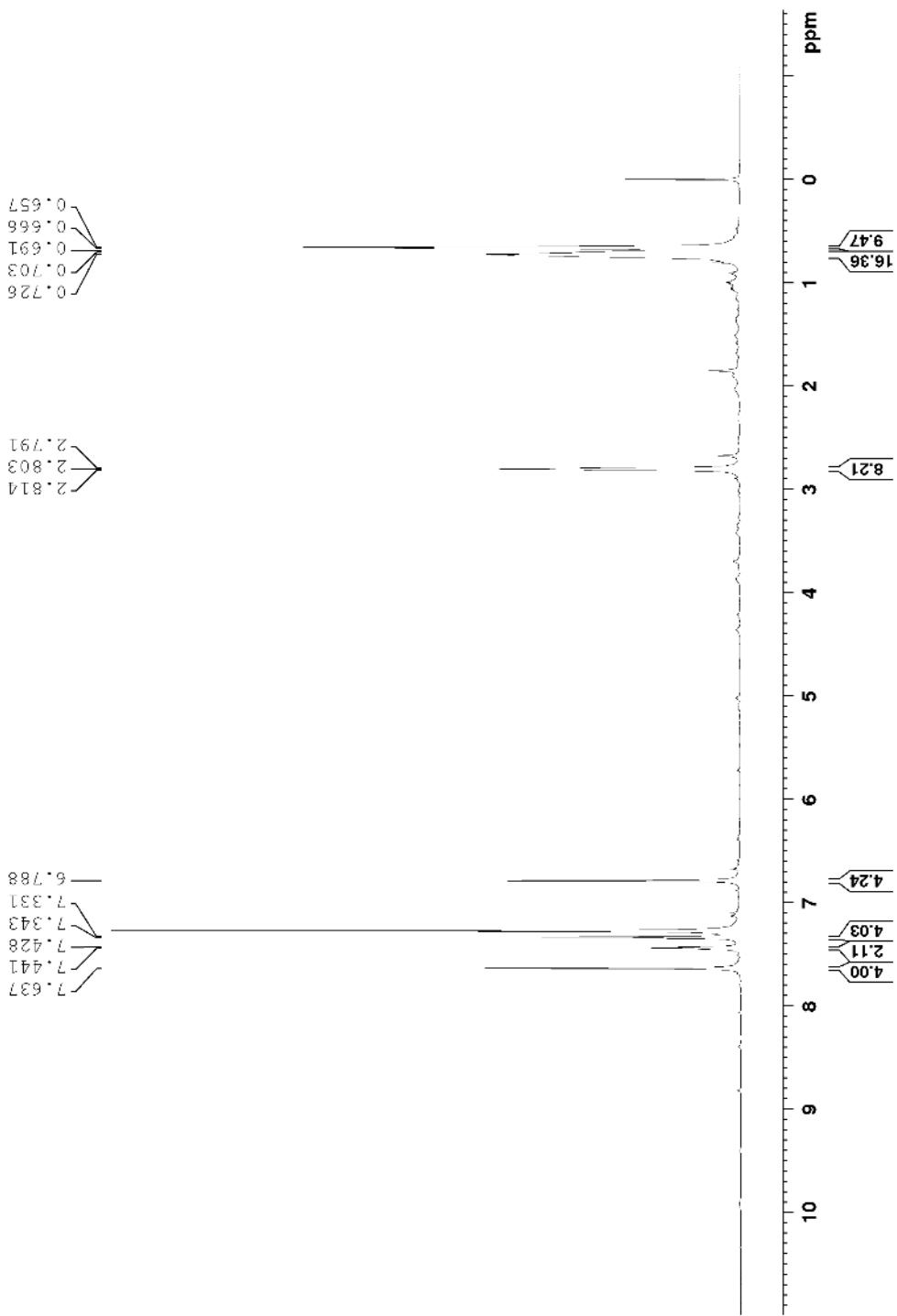
Figure A.2    $^1$H NMR (600 MHz, CDCl$_3$) spectrum of **6**
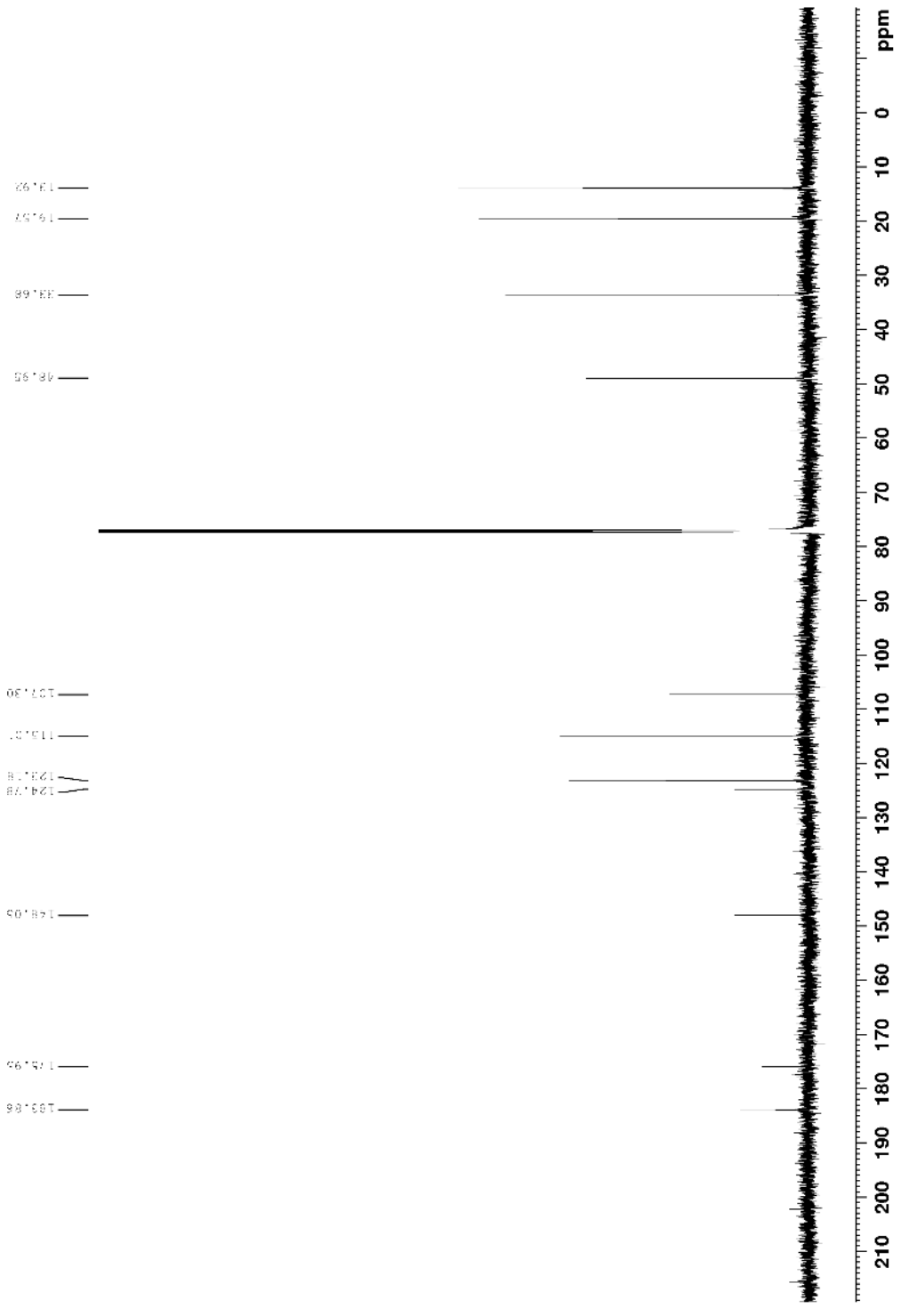
Figure A.3    $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of **6**

86
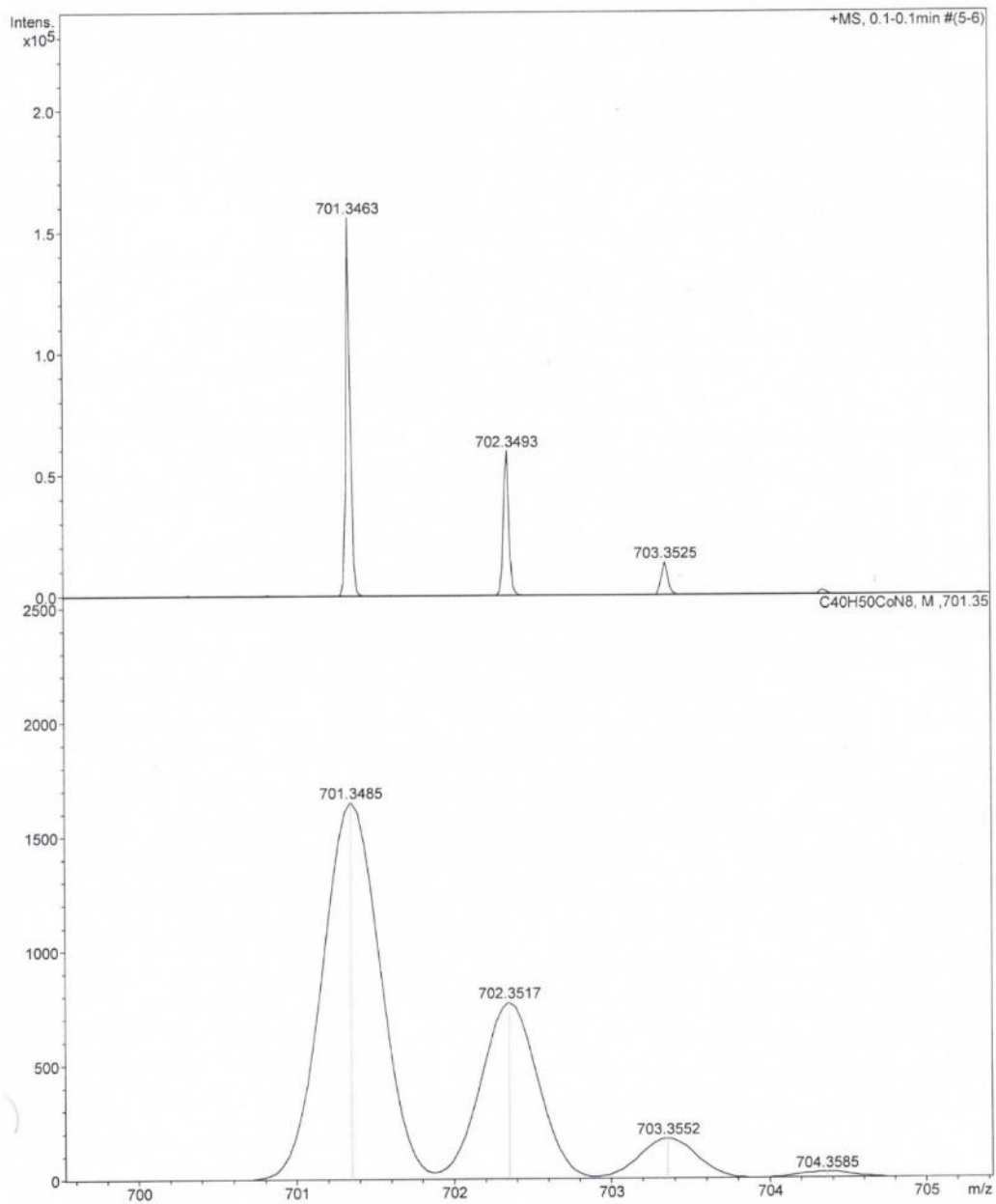
Figure A.4    HRMS spectrum of **6**

HRMS-ESI (m/z): [M-Cl]$^+$ calcd (bottom) for C$_{40}$H$_{50}$CoN$_8$, 701.3485; found (top),701.3463

0.976
0.989
1.001
1.192
1.455
1.468
1.480
1.493
1.971
1.985
1.999
2.012
2.023
2.286

4.469
4.480
4.484
4.492
4.502
4.506
4.516
4.682
4.693
4.697
4.705
4.708
4.716
4.719
4.730
5.171

7.047
7.049
7.055
7.077
7.089
7.143
7.156
7.682
7.685

6.08
3.03
4.03
4.18
3.08
2.06
2.15
1.07
1.93
1.91
1.19
2.00

ppm
0  1  2  3  4  5  6  7  8  9  10
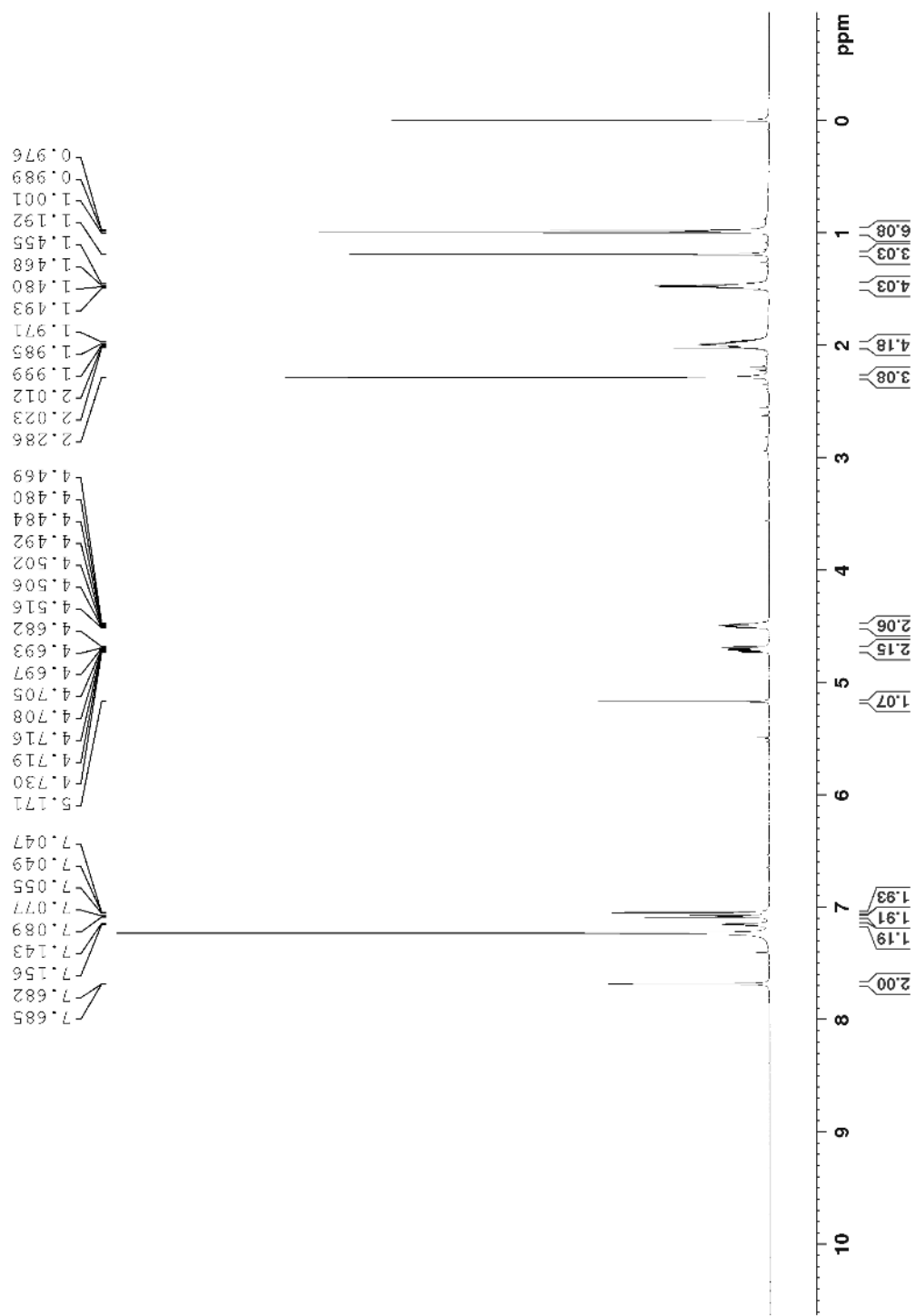
Figure A.5    $^1$H NMR (600 MHz, CDCl$_3$) spectrum of **7**
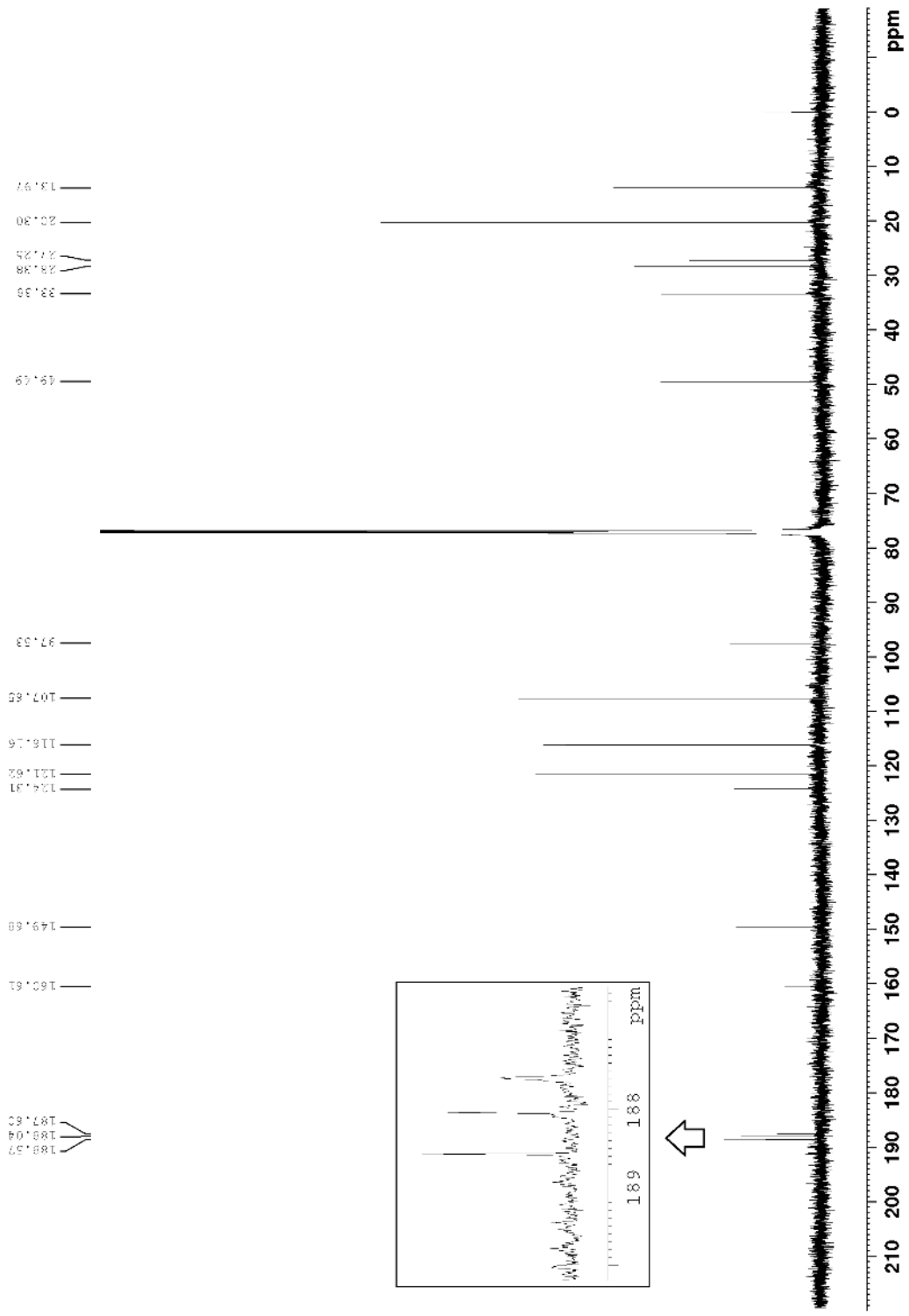
Figure A.6 $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of **7**
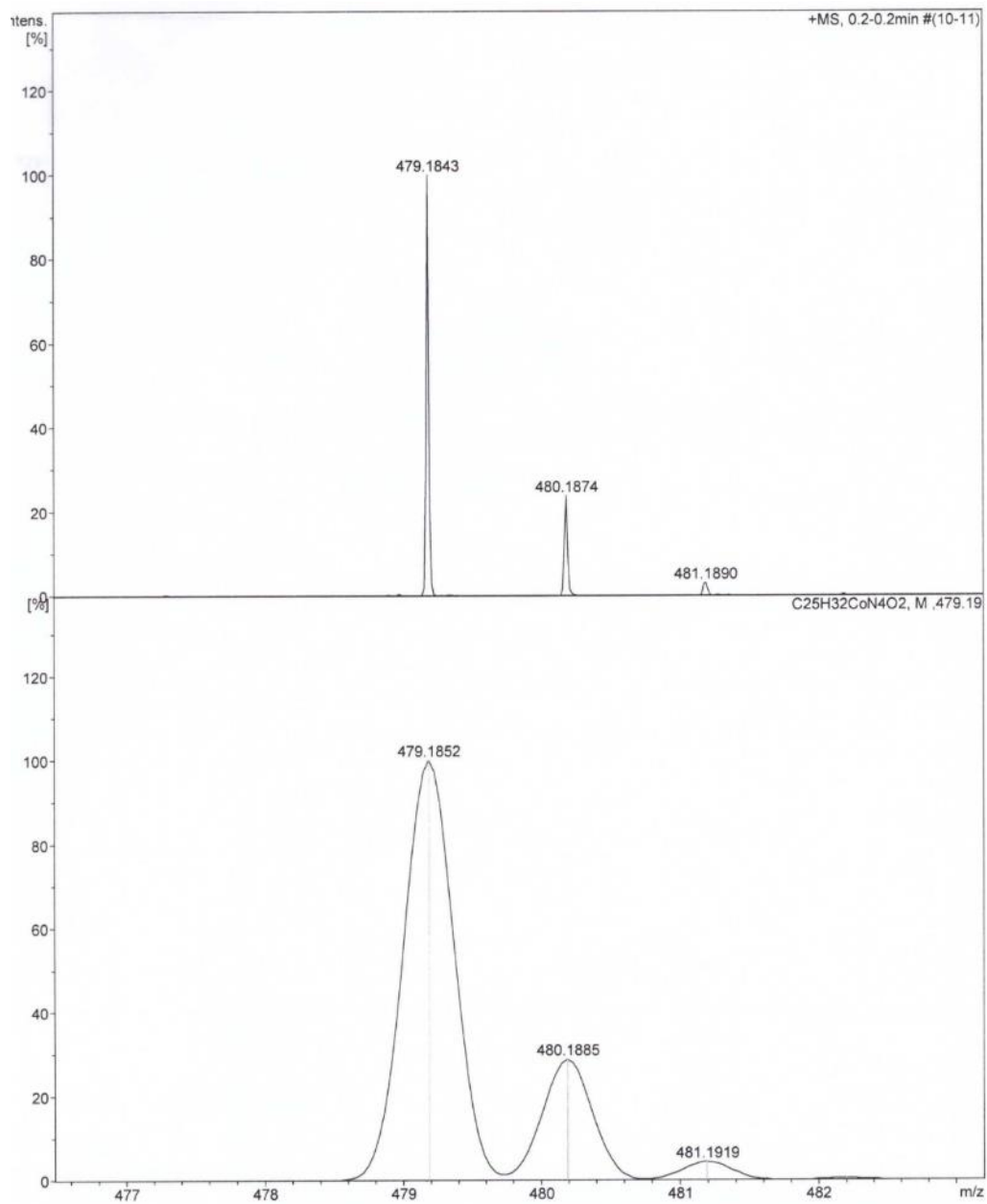
Figure A.7     HRMS spectrum of **7**

HRMS-ESI (m/z): [M-I]$^+$ calcd (bottom) for C$_{25}$H$_{32}$CoN$_4$O$_2$, 479.1852; found (top), 479.1836
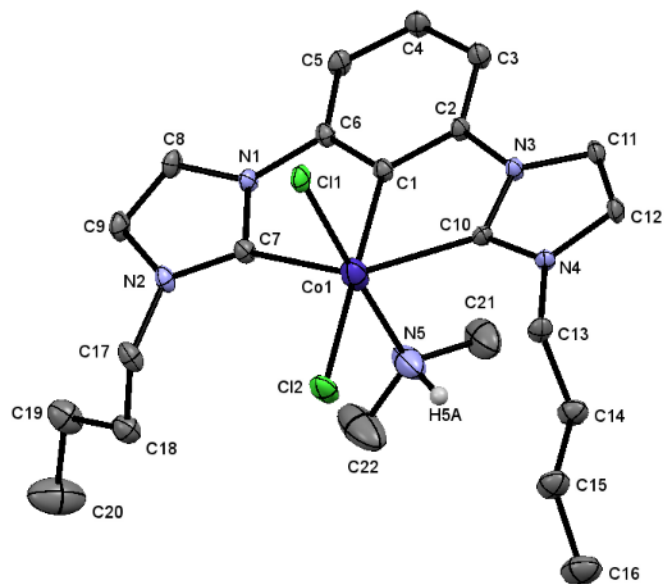
Figure A.8    X-ray molecular structure of **4**

Table A.1    Crystal Data and Structure Refinement for 4

| | |
|---|---|
| Empirical formula | $C_{22}H_{32}Cl_2CoN_5$ |
| Formula weight | 496.35 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| Unit cell dimensions | $a = 12.0081(2)$ Å          $\alpha = 90°$ |
| | $b = 13.2257(2)$ Å          $\beta = 94.0720(10)°$ |
| | $c = 15.1254(2)$ Å          $\gamma = 90°$ |
| Volume | 2396.08(6) Å$^3$ |
| Z | 4 |
| Density (calculated) | 1.376 g.cm$^{-3}$ |
| Absorption coefficient ($\mu$) | 0.958 mm$^{-1}$ |
| F(000) | 1040 |
| Crystal color, habit | Colorless, Plates |
| Crystal size | $0.35 \times 0.065 \times 0.042$ mm$^3$ |
| $\theta$ range for data collection | 2.048 to 27.884° |
| Index ranges | $-14 \le h \le 15, -17 \le k \le 17, -19 \le l \le 17$ |
| Reflections collected | 17925 |
| Independent reflections | 5607 [$R_{int} = 0.0316$] |
| Completeness to $\theta = 26.000°$ | 99.7 % |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 5607 / 0 / 275 |
| Goodness-of-fit on F$^2$ | 1.076 |
| Final R indices [I>2$\sigma$(I)] | $R_1 = 0.0670$, $wR_2 = 0.2089$ |
| R indices (all data) | $R_1 = 0.0811$, $wR_2 = 0.2205$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.006 and -1.863 e$^-$.Å$^{-3}$ |

Table A.2    Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{Å}^2$) for **4**

|        | x            | y            | z            | U(eq)     |
|--------|--------------|--------------|--------------|-----------|
| Co(1)  | 0.26871(5)   | 0.35802(5)   | 0.60172(4)   | 0.026(1)  |
| Cl(1)  | 0.12381(7)   | 0.36043(6)   | 0.70418(6)   | 0.016(1)  |
| Cl(2)  | 0.14811(9)   | 0.27212(8)   | 0.49708(7)   | 0.024(1)  |
| N(1)   | 0.3052(3)    | 0.5838(2)    | 0.6397(2)    | 0.013(1)  |
| N(2)   | 0.1863(3)    | 0.5865(2)    | 0.5272(2)    | 0.015(1)  |
| N(3)   | 0.4311(2)    | 0.2723(2)    | 0.7469(2)    | 0.013(1)  |
| N(4)   | 0.3622(2)    | 0.1396(2)    | 0.6835(2)    | 0.012(1)  |
| N(5)   | 0.3958(4)    | 0.3440(4)    | 0.5107(3)    | 0.037(1)  |
| C(1)   | 0.3755(3)    | 0.4323(3)    | 0.6974(2)    | 0.013(1)  |
| C(2)   | 0.4410(3)    | 0.3784(3)    | 0.7603(2)    | 0.013(1)  |
| C(3)   | 0.5055(3)    | 0.4240(3)    | 0.8292(3)    | 0.017(1)  |
| C(4)   | 0.5048(3)    | 0.5298(3)    | 0.8333(3)    | 0.018(1)  |
| C(5)   | 0.4414(3)    | 0.5880(3)    | 0.7715(3)    | 0.015(1)  |
| C(6)   | 0.3778(3)    | 0.5363(3)    | 0.7056(2)    | 0.013(1)  |
| C(7)   | 0.2498(3)    | 0.5217(3)    | 0.5784(2)    | 0.014(1)  |
| C(8)   | 0.2753(3)    | 0.6845(3)    | 0.6278(3)    | 0.016(1)  |
| C(9)   | 0.2002(3)    | 0.6858(3)    | 0.5568(3)    | 0.017(1)  |
| C(10)  | 0.3564(3)    | 0.2414(3)    | 0.6805(2)    | 0.013(1)  |
| C(11)  | 0.4828(3)    | 0.1912(3)    | 0.7900(2)    | 0.015(1)  |
| C(12)  | 0.4395(3)    | 0.1077(3)    | 0.7501(2)    | 0.014(1)  |
| C(13)  | 0.2946(3)    | 0.0711(3)    | 0.6251(3)    | 0.015(1)  |
| C(14)  | 0.3534(3)    | 0.0385(3)    | 0.5443(3)    | 0.021(1)  |
| C(15)  | 0.2737(4)    | -0.0180(4)   | 0.4793(3)    | 0.025(1)  |
| C(16)  | 0.3252(4)    | -0.0500(4)   | 0.3948(3)    | 0.035(1)  |
| C(17)  | 0.1152(3)    | 0.5583(3)    | 0.4480(3)    | 0.018(1)  |
| C(18)  | 0.1677(3)    | 0.5817(3)    | 0.3619(3)    | 0.023(1)  |
| C(19)  | 0.1845(4)    | 0.6940(4)    | 0.3428(3)    | 0.029(1)  |
| C(20)  | 0.2222(6)    | 0.7106(5)    | 0.2503(4)    | 0.055(2)  |
| C(21)  | 0.5141(4)    | 0.3295(5)    | 0.5432(4)    | 0.043(1)  |
| C(22)  | 0.3829(6)    | 0.3847(7)    | 0.4259(4)    | 0.067(2)  |
| H(5A)  | 0.3805       | 0.2736       | 0.4939       | 0.044     |
| H(3)   | 0.5475       | 0.3857       | 0.8710       | 0.020     |

Table A.2 (Continued)

| | | | | |
|---|---|---|---|---|
| H(4) | 0.5477 | 0.5621 | 0.8784 | 0.021 |
| H(5) | 0.4417 | 0.6583 | 0.7742 | 0.018 |
| H(8) | 0.3014 | 0.7394 | 0.6615 | 0.019 |
| H(9) | 0.1644 | 0.7427 | 0.5322 | 0.021 |
| H(11) | 0.5368 | 0.1937 | 0.8371 | 0.018 |
| H(12) | 0.4579 | 0.0412 | 0.7645 | 0.017 |
| H(13A) | 0.2253 | 0.1046 | 0.6057 | 0.018 |
| H(13B) | 0.2761 | 0.0115 | 0.6585 | 0.018 |
| H(14A) | 0.4160 | -0.0049 | 0.5626 | 0.025 |
| H(14B) | 0.3822 | 0.0975 | 0.5155 | 0.025 |
| H(15A) | 0.2097 | 0.0248 | 0.4638 | 0.031 |
| H(15B) | 0.2469 | -0.0778 | 0.5083 | 0.031 |
| H(16A) | 0.2681 | -0.0767 | 0.3536 | 0.052 |
| H(16B) | 0.3806 | -0.1011 | 0.4084 | 0.052 |
| H(16C) | 0.3594 | 0.0074 | 0.3689 | 0.052 |
| H(17A) | 0.0448 | 0.5942 | 0.4486 | 0.022 |
| H(17B) | 0.0993 | 0.4865 | 0.4503 | 0.022 |
| H(18A) | 0.1210 | 0.5528 | 0.3134 | 0.027 |
| H(18B) | 0.2396 | 0.5482 | 0.3631 | 0.027 |
| H(19A) | 0.1149 | 0.7298 | 0.3487 | 0.035 |
| H(19B) | 0.2399 | 0.7215 | 0.3859 | 0.035 |
| H(20A) | 0.1658 | 0.6864 | 0.2074 | 0.082 |
| H(20B) | 0.2905 | 0.6744 | 0.2440 | 0.082 |
| H(20C) | 0.2342 | 0.7814 | 0.2411 | 0.082 |
| H(21A) | 0.5439 | 0.3922 | 0.5665 | 0.064 |
| H(21B) | 0.5563 | 0.3078 | 0.4951 | 0.064 |
| H(21C) | 0.5186 | 0.2792 | 0.5890 | 0.064 |
| H(22A) | 0.3049 | 0.3888 | 0.4074 | 0.100 |
| H(22B) | 0.4199 | 0.3423 | 0.3856 | 0.100 |
| H(22C) | 0.4150 | 0.4512 | 0.4261 | 0.100 |

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table A.3    Anisotropic Displacement Parameters (Å$^2$) for **4**

| | U$_{11}$ | U$_{22}$ | U$_{33}$ | U$_{23}$ | U$_{13}$ | U$_{12}$ |
|---|---|---|---|---|---|---|
| Co(1) | 0.0307(4) | 0.0184(3) | 0.0281(4) | 0.0003(2) | -0.0083(3) | 0.0008(2) |
| Cl(1) | 0.0187(4) | 0.0091(4) | 0.0204(5) | 0.0018(3) | -0.0012(3) | 0.0021(3) |
| Cl(2) | 0.0310(5) | 0.0180(5) | 0.0217(5) | -0.0030(4) | -0.0128(4) | -0.0015(4) |
| N(1) | 0.0165(14) | 0.0076(14) | 0.0137(14) | 0.0013(11) | -0.0009(11) | 0.0002(11) |
| N(2) | 0.0159(14) | 0.0111(15) | 0.0165(15) | 0.0043(12) | -0.0022(11) | -0.0001(12) |
| N(3) | 0.0145(14) | 0.0082(14) | 0.0144(15) | 0.0000(11) | -0.0036(11) | 0.0007(11) |
| N(4) | 0.0126(14) | 0.0097(15) | 0.0133(14) | -0.0021(11) | -0.0032(11) | 0.0000(11) |
| N(5) | 0.030(2) | 0.056(3) | 0.024(2) | 0.0080(19) | 0.0000(16) | 0.0083(19) |
| C(1) | 0.0129(15) | 0.0107(17) | 0.0140(17) | 0.0009(13) | -0.0008(12) | -0.0002(13) |
| C(2) | 0.0139(16) | 0.0082(16) | 0.0153(17) | 0.0000(13) | -0.0025(13) | 0.0000(12) |
| C(3) | 0.0178(17) | 0.0129(18) | 0.0191(18) | -0.0002(14) | -0.0045(14) | -0.0001(14) |
| C(4) | 0.0175(17) | 0.0146(19) | 0.0205(19) | -0.0031(15) | -0.0054(14) | -0.0011(14) |
| C(5) | 0.0172(16) | 0.0087(16) | 0.0195(18) | -0.0008(14) | -0.0013(14) | -0.0025(13) |
| C(6) | 0.0125(15) | 0.0104(17) | 0.0143(17) | 0.0021(13) | -0.0007(12) | 0.0000(12) |
| C(7) | 0.0145(16) | 0.0116(17) | 0.0140(17) | 0.0014(13) | -0.0015(13) | -0.0021(13) |
| C(8) | 0.0197(17) | 0.0068(17) | 0.0211(19) | 0.0016(14) | 0.0015(14) | 0.0008(13) |
| C(9) | 0.0208(18) | 0.0093(17) | 0.0218(19) | 0.0038(14) | -0.0002(14) | 0.0019(14) |
| C(10) | 0.0143(16) | 0.0105(17) | 0.0126(17) | -0.0025(13) | -0.0014(13) | 0.0018(13) |
| C(11) | 0.0156(16) | 0.0134(18) | 0.0157(18) | 0.0027(14) | -0.0039(13) | 0.0036(13) |
| C(12) | 0.0160(16) | 0.0096(17) | 0.0171(18) | 0.0030(14) | -0.0031(13) | 0.0031(13) |
| C(13) | 0.0141(16) | 0.0105(17) | 0.0205(18) | -0.0040(14) | -0.0027(13) | -0.0023(13) |
| C(14) | 0.0173(18) | 0.023(2) | 0.022(2) | -0.0069(16) | -0.0015(15) | -0.0034(15) |
| C(15) | 0.023(2) | 0.025(2) | 0.027(2) | -0.0105(18) | -0.0023(16) | -0.0025(17) |
| C(16) | 0.036(2) | 0.039(3) | 0.030(2) | -0.014(2) | -0.0013(19) | -0.005(2) |
| C(17) | 0.0171(17) | 0.0165(19) | 0.0193(18) | 0.0056(15) | -0.0054(14) | -0.0033(14) |
| C(18) | 0.0230(19) | 0.024(2) | 0.020(2) | 0.0003(16) | -0.0022(15) | -0.0014(16) |
| C(19) | 0.032(2) | 0.027(2) | 0.027(2) | 0.0049(19) | -0.0025(18) | -0.0082(18) |
| C(20) | 0.087(5) | 0.044(4) | 0.035(3) | 0.001(3) | 0.012(3) | -0.028(3) |
| C(21) | 0.024(2) | 0.068(4) | 0.037(3) | 0.006(3) | 0.005(2) | 0.008(2) |
| C(22) | 0.042(3) | 0.124(7) | 0.035(3) | 0.025(4) | 0.009(3) | 0.014(4) |

$$2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}] \tag{A.1}$$

Table A.4    Bond Lengths [Å] for **4**

| atom-atom | distance | atom-atom | distance |
|---|---|---|---|
| Co(1)-C(1) | 2.107(4) | Co(1)-N(5) | 2.134(4) |
| Co(1)-C(10) | 2.174(4) | Co(1)-C(7) | 2.203(4) |
| Co(1)-Cl(2) | 2.3596(11) | Co(1)-Cl(1) | 2.4111(11) |
| N(1)-C(7) | 1.374(5) | N(1)-C(8) | 1.388(5) |
| N(1)-C(6) | 1.423(5) | N(2)-C(7) | 1.354(5) |
| N(2)-C(9) | 1.394(5) | N(2)-C(17) | 1.469(5) |
| N(3)-C(10) | 1.361(5) | N(3)-C(11) | 1.380(5) |
| N(3)-C(2) | 1.423(5) | N(4)-C(10) | 1.349(5) |
| N(4)-C(12) | 1.386(5) | N(4)-C(13) | 1.469(5) |
| N(5)-C(22) | 1.390(7) | N(5)-C(21) | 1.482(6) |
| N(5)-H(5A) | 0.9800 | C(1)-C(6) | 1.381(5) |
| C(1)-C(2) | 1.388(5) | C(2)-C(3) | 1.391(5) |
| C(3)-C(4) | 1.401(5) | C(3)-H(3) | 0.9300 |
| C(4)-C(5) | 1.394(5) | C(4)-H(4) | 0.9300 |
| C(5)-C(6) | 1.392(5) | C(5)-H(5) | 0.9300 |
| C(8)-C(9) | 1.352(5) | C(8)-H(8) | 0.9300 |
| C(9)-H(9) | 0.9300 | C(11)-C(12) | 1.345(5) |
| C(11)-H(11) | 0.9300 | C(12)-H(12) | 0.9300 |
| C(13)-C(14) | 1.518(5) | C(13)-H(13A) | 0.9700 |
| C(13)-H(13B) | 0.9700 | C(14)-C(15) | 1.519(5) |
| C(14)-H(14A) | 0.9700 | C(14)-H(14B) | 0.9700 |
| C(15)-C(16) | 1.519(6) | C(15)-H(15A) | 0.9700 |
| C(15)-H(15B) | 0.9700 | C(16)-H(16A) | 0.9600 |
| C(16)-H(16B) | 0.9600 | C(16)-H(16C) | 0.9600 |
| C(17)-C(18) | 1.518(6) | C(17)-H(17A) | 0.9700 |
| C(17)-H(17B) | 0.9700 | C(18)-C(19) | 1.530(6) |
| C(18)-H(18A) | 0.9700 | C(18)-H(18B) | 0.9700 |
| C(19)-C(20) | 1.516(7) | C(19)-H(19A) | 0.9700 |
| C(19)-H(19B) | 0.9700 | C(20)-H(20A) | 0.9600 |
| C(20)-H(20B) | 0.9600 | C(20)-H(20C) | 0.9600 |
| C(21)-H(21A) | 0.9600 | C(21)-H(21B) | 0.9600 |
| C(21)-H(21C) | 0.9600 | C(22)-H(22A) | 0.9600 |
| C(22)-H(22B) | 0.9600 | C(22)-H(22C) | 0.9600 |

Symmetry transformations used to generate equivalent atoms.

Table A.5     Bond Angles [°] for **4**

| atom-atom-atom | angle | atom-atom-atom | angle |
|---|---|---|---|
| C(1)-Co(1)-N(5) | 93.18(16) | C(1)-Co(1)-C(10) | 72.95(14) |
| N(5)-Co(1)-C(10) | 87.22(15) | C(1)-Co(1)-C(7) | 72.70(14) |
| N(5)-Co(1)-C(7) | 92.99(17) | C(10)-Co(1)-C(7) | 145.61(14) |
| C(1)-Co(1)-Cl(2) | 178.66(11) | N(5)-Co(1)-Cl(2) | 87.63(13) |
| C(10)-Co(1)-Cl(2) | 106.04(10) | C(7)-Co(1)-Cl(2) | 108.33(10) |
| C(1)-Co(1)-Cl(1) | 89.07(10) | N(5)-Co(1)-Cl(1) | 175.78(15) |
| C(10)-Co(1)-Cl(1) | 90.02(10) | C(7)-Co(1)-Cl(1) | 91.09(10) |
| Cl(2)-Co(1)-Cl(1) | 90.06(4) | C(7)-N(1)-C(8) | 112.1(3) |
| C(7)-N(1)-C(6) | 116.9(3) | C(8)-N(1)-C(6) | 130.9(3) |
| C(7)-N(2)-C(9) | 111.3(3) | C(7)-N(2)-C(17) | 125.3(3) |
| C(9)-N(2)-C(17) | 123.4(3) | C(10)-N(3)-C(11) | 111.5(3) |
| C(10)-N(3)-C(2) | 116.4(3) | C(11)-N(3)-C(2) | 132.0(3) |
| C(10)-N(4)-C(12) | 111.0(3) | C(10)-N(4)-C(13) | 124.8(3) |
| C(12)-N(4)-C(13) | 124.2(3) | C(22)-N(5)-C(21) | 113.4(5) |
| C(22)-N(5)-Co(1) | 121.6(4) | C(21)-N(5)-Co(1) | 120.7(3) |
| C(22)-N(5)-H(5A) | 96.9 | C(21)-N(5)-H(5A) | 96.9 |
| Co(1)-N(5)-H(5A) | 96.9 | C(6)-C(1)-C(2) | 116.3(3) |
| C(6)-C(1)-Co(1) | 122.2(3) | C(2)-C(1)-Co(1) | 121.3(3) |
| C(1)-C(2)-C(3) | 123.4(3) | C(1)-C(2)-N(3) | 111.8(3) |
| C(3)-C(2)-N(3) | 124.8(3) | C(2)-C(3)-C(4) | 117.4(4) |
| C(2)-C(3)-H(3) | 121.3 | C(4)-C(3)-H(3) | 121.3 |
| C(5)-C(4)-C(3) | 121.8(4) | C(5)-C(4)-H(4) | 119.1 |
| C(3)-C(4)-H(4) | 119.1 | C(6)-C(5)-C(4) | 117.0(3) |
| C(6)-C(5)-H(5) | 121.5 | C(4)-C(5)-H(5) | 121.5 |
| C(1)-C(6)-C(5) | 124.1(3) | C(1)-C(6)-N(1) | 111.7(3) |
| C(5)-C(6)-N(1) | 124.2(3) | N(2)-C(7)-N(1) | 103.6(3) |
| N(2)-C(7)-Co(1) | 139.6(3) | N(1)-C(7)-Co(1) | 116.1(2) |
| C(9)-C(8)-N(1) | 105.6(3) | C(9)-C(8)-H(8) | 127.2 |
| N(1)-C(8)-H(8) | 127.2 | C(8)-C(9)-N(2) | 107.5(3) |
| C(8)-C(9)-H(9) | 126.3 | N(2)-C(9)-H(9) | 126.3 |
| N(4)-C(10)-N(3) | 104.2(3) | N(4)-C(10)-Co(1) | 138.4(3) |
| N(3)-C(10)-Co(1) | 117.4(3) | C(12)-C(11)-N(3) | 106.2(3) |

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Table A.5 (Continued)

| | | | |
|---|---|---|---|
| C(12)-C(11)-H(11) | 126.9 | N(3)-C(11)-H(11) | 126.9 |
| C(11)-C(12)-N(4) | 107.1(3) | C(11)-C(12)-H(12) | 126.4 |
| N(4)-C(12)-H(12) | 126.4 | N(4)-C(13)-C(14) | 113.0(3) |
| N(4)-C(13)-H(13A) | 109.0 | C(14)-C(13)-H(13A) | 109.0 |
| N(4)-C(13)-H(13B) | 109.0 | C(14)-C(13)-H(13B) | 109.0 |
| H(13A)-C(13)-H(13B) | 107.8 | C(13)-C(14)-C(15) | 110.7(3) |
| C(13)-C(14)-H(14A) | 109.5 | C(15)-C(14)-H(14A) | 109.5 |
| C(13)-C(14)-H(14B) | 109.5 | C(15)-C(14)-H(14B) | 109.5 |
| H(14A)-C(14)-H(14B) | 108.1 | C(14)-C(15)-C(16) | 113.9(4) |
| C(14)-C(15)-H(15A) | 108.8 | C(16)-C(15)-H(15A) | 108.8 |
| C(14)-C(15)-H(15B) | 108.8 | C(16)-C(15)-H(15B) | 108.8 |
| H(15A)-C(15)-H(15B) | 107.7 | C(15)-C(16)-H(16A) | 109.5 |
| C(15)-C(16)-H(16B) | 109.5 | H(16A)-C(16)-H(16B) | 109.5 |
| C(15)-C(16)-H(16C) | 109.5 | H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 | N(2)-C(17)-C(18) | 113.3(3) |
| N(2)-C(17)-H(17A) | 108.9 | C(18)-C(17)-H(17A) | 108.9 |
| N(2)-C(17)-H(17B) | 108.9 | C(18)-C(17)-H(17B) | 108.9 |
| H(17A)-C(17)-H(17B) | 107.7 | C(17)-C(18)-C(19) | 115.4(4) |
| C(17)-C(18)-H(18A) | 108.4 | C(19)-C(18)-H(18A) | 108.4 |
| C(17)-C(18)-H(18B) | 108.4 | C(19)-C(18)-H(18B) | 108.4 |
| H(18A)-C(18)-H(18B) | 107.5 | C(20)-C(19)-C(18) | 111.6(4) |
| C(20)-C(19)-H(19A) | 109.3 | C(18)-C(19)-H(19A) | 109.3 |
| C(20)-C(19)-H(19B) | 109.3 | C(18)-C(19)-H(19B) | 109.3 |
| H(19A)-C(19)-H(19B) | 108.0 | C(19)-C(20)-H(20A) | 109.5 |
| C(19)-C(20)-H(20B) | 109.5 | H(20A)-C(20)-H(20B) | 109.5 |
| C(19)-C(20)-H(20C) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 | N(5)-C(21)-H(21A) | 109.5 |
| N(5)-C(21)-H(21B) | 109.5 | H(21A)-C(21)-H(21B) | 109.5 |
| N(5)-C(21)-H(21C) | 109.5 | H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 | N(5)-C(22)-H(22A) | 109.5 |
| N(5)-C(22)-H(22B) | 109.5 | H(22A)-C(22)-H(22B) | 109.5 |
| N(5)-C(22)-H(22C) | 109.5 | H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 | | |

Symmetry transformations used to generate equivalent atoms.

Table A.6    Torsion Angles [°] for **4**

| atom-atom-atom-atom | angle | atom-atom-atom-atom | angle |
|---|---|---|---|
| C(6)-C(1)-C(2)-C(3) | 0.7(5) | Co(1)-C(1)-C(2)-C(3) | -174.4(3) |
| C(6)-C(1)-C(2)-N(3) | 178.9(3) | Co(1)-C(1)-C(2)-N(3) | 3.8(4) |
| C(10)-N(3)-C(2)-C(1) | -3.9(5) | C(11)-N(3)-C(2)-C(1) | 177.1(4) |
| C(10)-N(3)-C(2)-C(3) | 174.3(3) | C(11)-N(3)-C(2)-C(3) | -4.7(6) |
| C(1)-C(2)-C(3)-C(4) | -1.3(6) | N(3)-C(2)-C(3)-C(4) | -179.2(4) |
| C(2)-C(3)-C(4)-C(5) | 0.6(6) | C(3)-C(4)-C(5)-C(6) | 0.5(6) |
| C(2)-C(1)-C(6)-C(5) | 0.5(5) | Co(1)-C(1)-C(6)-C(5) | 175.6(3) |
| C(2)-C(1)-C(6)-N(1) | -178.2(3) | Co(1)-C(1)-C(6)-N(1) | -3.1(4) |
| C(4)-C(5)-C(6)-C(1) | -1.1(6) | C(4)-C(5)-C(6)-N(1) | 177.4(3) |
| C(7)-N(1)-C(6)-C(1) | -2.5(4) | C(8)-N(1)-C(6)-C(1) | 174.2(3) |
| C(7)-N(1)-C(6)-C(5) | 178.8(3) | C(8)-N(1)-C(6)-C(5) | -4.5(6) |
| C(9)-N(2)-C(7)-N(1) | -1.0(4) | C(17)-N(2)-C(7)-N(1) | 176.3(3) |
| C(9)-N(2)-C(7)-Co(1) | 167.5(3) | C(17)-N(2)-C(7)-Co(1) | -15.1(6) |
| C(8)-N(1)-C(7)-N(2) | 1.0(4) | C(6)-N(1)-C(7)-N(2) | 178.3(3) |
| C(8)-N(1)-C(7)-Co(1) | -170.7(2) | C(6)-N(1)-C(7)-Co(1) | 6.6(4) |
| C(7)-N(1)-C(8)-C(9) | -0.6(4) | C(6)-N(1)-C(8)-C(9) | -177.4(4) |
| N(1)-C(8)-C(9)-N(2) | 0.0(4) | C(7)-N(2)-C(9)-C(8) | 0.7(4) |
| C(17)-N(2)-C(9)-C(8) | -176.7(3) | C(12)-N(4)-C(10)-N(3) | -0.3(4) |
| C(13)-N(4)-C(10)-N(3) | 178.7(3) | C(12)-N(4)-C(10)-Co(1) | 177.9(3) |
| C(13)-N(4)-C(10)-Co(1) | -3.0(6) | C(11)-N(3)-C(10)-N(4) | 0.3(4) |
| C(2)-N(3)-C(10)-N(4) | -178.8(3) | C(11)-N(3)-C(10)-Co(1) | -178.4(2) |
| C(2)-N(3)-C(10)-Co(1) | 2.5(4) | C(10)-N(3)-C(11)-C(12) | -0.2(4) |
| C(2)-N(3)-C(11)-C(12) | 178.8(4) | N(3)-C(11)-C(12)-N(4) | 0.0(4) |
| C(10)-N(4)-C(12)-C(11) | 0.2(4) | C(13)-N(4)-C(12)-C(11) | -178.9(3) |
| C(10)-N(4)-C(13)-C(14) | 94.6(4) | C(12)-N(4)-C(13)-C(14) | -86.5(4) |
| N(4)-C(13)-C(14)-C(15) | -170.9(3) | C(13)-C(14)-C(15)-C(16) | 177.9(4) |
| C(7)-N(2)-C(17)-C(18) | -100.7(4) | C(9)-N(2)-C(17)-C(18) | 76.3(5) |
| N(2)-C(17)-C(18)-C(19) | -66.0(5) | C(17)-C(18)-C(19)-C(20) | -172.2(4) |

Symmetry transformations used to generate equivalent atoms.

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### A.1.1 Crystal Summary for 4

Crystal data for $C_{22}H_{32}Cl_2CoN_5$; $M_r = 496.35$; Monoclinic; space group $P2_1/n$; $a = 12.0081(2)$ Å; $b = 13.2257(2)$ Å; $c = 15.1254(2)$ Å; $\alpha = 90°$; $\beta = 94.0720(10)°$; $\gamma = 90°$; $V = 2396.08(6)$ Å$^3$; $Z = 4$; $T = 100(2)$ K; $\lambda$(Mo-K$\alpha$) = 0.71073 Å; $\mu$(Mo-K$\alpha$) = 0.958 mm$^{-1}$; $d_{calc} = 1.376$g.cm$^{-3}$; 17925 reflections collected; 5607 unique ($R_{int} = 0.0316$); giving $R_1 = 0.0670$, $wR_2 = 0.2089$ for 4540 data with [$I > 2\sigma(I)$] and $R_1 = 0.0811$, $wR_2 = 0.2205$ for all 5607 data. Residual electron density (e$^-$.Å$^{-3}$) max/min: 1.006/-1.863.

An arbitrary sphere of data were collected on a Colorless Plates-like crystal, having approximate dimensions of $0.35 \times 0.065 \times 0.042$ mm, on a Bruker APEX-II diffractometer using a combination of $\omega$- and $\varphi$-scans of $0.5°$.[303] Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by vecmap methods and expanded routinely.[304] The model was refined by full-matrix least-squares analysis of $F^2$ against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

Figure A.9    X-ray molecular structure of **7**

Table A.7    Crystal Data and Structure Refinement for **7**

| | |
|---|---|
| Empirical formula | $C_{26}H_{33}Cl_3CoIN_4O_2$ |
| Formula weight | 725.74 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a = 8.4464(3)$ Å $\quad\alpha = 94.144(2)°$ |
| | $b = 10.4389(4)$ Å $\quad\beta = 99.879(2)°$ |
| | $c = 18.6009(7)$ Å $\quad\gamma = 110.932(2)°$ |
| Volume | 1493.13(10) Å$^3$ |
| Z | 2 |
| Density (calculated) | 1.614 g.cm$^{-3}$ |
| Absorption coefficient ($\mu$) | 1.907 mm$^{-1}$ |
| F(000) | 728 |
| Crystal color, habit | ?, Tablet |
| Crystal size | $0.347 \times 0.194 \times 0.060$ mm$^3$ |
| $\theta$ range for data collection | 2.111 to 26.036° |
| Index ranges | $-10 \leq h \leq 10, -12 \leq k \leq 8, -18 \leq l \leq 22$ |
| Reflections collected | 8785 |
| Independent reflections | 5318 [$R_{int} = 0.0273$] |
| Completeness to $\theta = 25.242°$ | 92.3 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9635 and 0.7253 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 5318 / 0 / 334 |
| Goodness-of-fit on F$^2$ | 1.042 |
| Final R indices [I>2$\sigma$(I)] | $R_1 = 0.0393$, $wR_2 = 0.0907$ |
| R indices (all data) | $R_1 = 0.0474$, $wR_2 = 0.0962$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.645 and -1.174 e$^-$.Å$^{-3}$ |

Table A.8    Atomic Coordinates and Equivalent Isotropic Displacement Parameters
($\text{Å}^2$) for **7**

|        | x | y | z | U(eq) |
|--------|---|---|---|-------|
| Co(1)  | 1.21787(7)   | 0.67590(6)    | 0.83772(3)   | 0.015(1) |
| Cl(1)  | -0.3209(2)   | 0.11226(17)   | 0.44437(9)   | 0.048(1) |
| Cl(2)  | 0.03891(19)  | 0.20982(17)   | 0.43630(9)   | 0.052(1) |
| Cl(3)  | -0.1920(2)   | -0.06629(15)  | 0.36796(9)   | 0.051(1) |
| I(1)   | 1.17610(4)   | 0.90212(3)    | 0.81356(2)   | 0.019(1) |
| O(1)   | 1.2237(4)    | 0.6427(3)     | 0.73104(17)  | 0.021(1) |
| O(2)   | 1.2439(4)    | 0.5034(3)     | 0.85687(18)  | 0.021(1) |
| N(1)   | 0.9141(5)    | 0.5965(4)     | 0.8956(2)    | 0.020(1) |
| N(2)   | 0.8163(5)    | 0.5248(4)     | 0.7796(2)    | 0.022(1) |
| N(3)   | 1.5036(4)    | 0.8159(4)     | 0.9557(2)    | 0.018(1) |
| N(4)   | 1.6227(4)    | 0.8200(4)     | 0.8627(2)    | 0.019(1) |
| C(1)   | 1.2085(6)    | 0.7126(4)     | 0.9367(2)    | 0.017(1) |
| C(2)   | 1.0512(6)    | 0.6640(4)     | 0.9582(3)    | 0.020(1) |
| C(3)   | 1.0400(6)    | 0.6804(5)     | 1.0312(3)    | 0.025(1) |
| C(4)   | 1.1934(6)    | 0.7504(5)     | 1.0830(3)    | 0.024(1) |
| C(5)   | 1.3549(6)    | 0.8014(5)     | 1.0637(3)    | 0.023(1) |
| C(6)   | 1.3576(5)    | 0.7797(4)     | 0.9902(3)    | 0.018(1) |
| C(7)   | 1.4662(6)    | 0.7781(4)     | 0.8810(3)    | 0.019(1) |
| C(8)   | 1.6815(6)    | 0.8811(5)     | 0.9837(3)    | 0.023(1) |
| C(9)   | 1.7549(6)    | 0.8829(5)     | 0.9249(3)    | 0.025(1) |
| C(10)  | 0.9664(6)    | 0.5895(4)     | 0.8305(3)    | 0.018(1) |
| C(11)  | 0.7372(6)    | 0.5395(5)     | 0.8857(3)    | 0.026(1) |
| C(12)  | 0.6752(6)    | 0.4938(5)     | 0.8136(3)    | 0.026(1) |
| C(13)  | 0.8123(6)    | 0.4956(6)     | 0.7009(3)    | 0.031(1) |
| C(14)  | 0.6365(6)    | 0.4245(5)     | 0.6527(3)    | 0.031(1) |
| C(15)  | 0.6463(7)    | 0.3932(6)     | 0.5733(3)    | 0.034(1) |
| C(16)  | 0.4723(7)    | 0.3217(6)     | 0.5221(3)    | 0.040(1) |
| C(17)  | 1.6517(6)    | 0.8119(5)     | 0.7880(3)    | 0.023(1) |
| C(18)  | 1.6904(7)    | 0.9512(5)     | 0.7600(3)    | 0.030(1) |
| C(19)  | 1.7342(7)    | 0.9488(6)     | 0.6847(3)    | 0.038(1) |
| C(20)  | 1.7703(8)    | 1.0890(7)     | 0.6567(4)    | 0.051(2) |
| C(21)  | 1.2130(6)    | 0.5291(5)     | 0.6984(3)    | 0.022(1) |

Table A.8 (Continued)

| | | | |
|---|---|---|---|
| C(22) | 1.2321(5) | 0.4100(5) | 0.8085(3) | 0.021(1) |
| C(23) | 1.2135(6) | 0.4137(5) | 0.7324(3) | 0.023(1) |
| C(24) | 1.1981(7) | 0.5197(5) | 0.6156(3) | 0.030(1) |
| C(25) | 1.2414(7) | 0.2789(5) | 0.8361(3) | 0.032(1) |
| C(26) | -0.1721(7) | 0.1068(5) | 0.3897(3) | 0.033(1) |
| H(3A) | 0.9316 | 0.6451 | 1.0455 | 0.030 |
| H(4A) | 1.1880 | 0.7641 | 1.1335 | 0.029 |
| H(5A) | 1.4584 | 0.8491 | 1.0999 | 0.027 |
| H(8A) | 1.7387 | 0.9167 | 1.0337 | 0.027 |
| H(9A) | 1.8756 | 0.9205 | 0.9256 | 0.030 |
| H(11A) | 0.6713 | 0.5336 | 0.9228 | 0.031 |
| H(12A) | 0.5565 | 0.4484 | 0.7899 | 0.032 |
| H(13A) | 0.8809 | 0.4374 | 0.6951 | 0.038 |
| H(13B) | 0.8704 | 0.5843 | 0.6833 | 0.038 |
| H(14A) | 0.5686 | 0.4842 | 0.6556 | 0.037 |
| H(14B) | 0.5754 | 0.3369 | 0.6706 | 0.037 |
| H(15A) | 0.7087 | 0.4812 | 0.5560 | 0.041 |
| H(15B) | 0.7149 | 0.3340 | 0.5710 | 0.041 |
| H(16A) | 0.4884 | 0.3047 | 0.4719 | 0.060 |
| H(16B) | 0.4107 | 0.2333 | 0.5380 | 0.060 |
| H(16C) | 0.4045 | 0.3806 | 0.5231 | 0.060 |
| H(17A) | 1.5474 | 0.7416 | 0.7549 | 0.028 |
| H(17B) | 1.7503 | 0.7822 | 0.7870 | 0.028 |
| H(18A) | 1.5881 | 0.9773 | 0.7577 | 0.036 |
| H(18B) | 1.7889 | 1.0228 | 0.7953 | 0.036 |
| H(19A) | 1.6364 | 0.8764 | 0.6493 | 0.045 |
| H(19B) | 1.8376 | 0.9241 | 0.6870 | 0.045 |
| H(20A) | 1.7981 | 1.0832 | 0.6078 | 0.076 |
| H(20B) | 1.6674 | 1.1129 | 0.6534 | 0.076 |
| H(20C) | 1.8685 | 1.1606 | 0.6910 | 0.076 |
| H(23A) | 1.2003 | 0.3322 | 0.7017 | 0.027 |
| H(24A) | 1.1905 | 0.4277 | 0.5957 | 0.045 |
| H(24B) | 1.0937 | 0.5346 | 0.5929 | 0.045 |

Table A.8 (Continued)

| | | | | |
|---|---|---|---|---|
| H(24C) | 1.3005 | 0.5907 | 0.6049 | 0.045 |
| H(25A) | 1.2310 | 0.2117 | 0.7942 | 0.047 |
| H(25B) | 1.3527 | 0.3014 | 0.8704 | 0.047 |
| H(25C) | 1.1465 | 0.2390 | 0.8616 | 0.047 |
| H(26A) | -0.1994 | 0.1435 | 0.3429 | 0.040 |

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table A.9     Anisotropic Displacement Parameters ($\text{Å}^2$) for **7**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Co(1) | 0.0160(3) | 0.0117(3) | 0.0176(3) | 0.0028(2) | 0.0034(2) | 0.0047(2) |
| Cl(1) | 0.0473(8) | 0.0577(10) | 0.0471(9) | 0.0090(8) | 0.0184(7) | 0.0251(8) |
| Cl(2) | 0.0355(8) | 0.0519(9) | 0.0544(10) | 0.0011(8) | -0.0022(7) | 0.0075(7) |
| Cl(3) | 0.0772(11) | 0.0288(7) | 0.0505(10) | 0.0096(7) | 0.0288(8) | 0.0173(7) |
| I(1) | 0.0217(2) | 0.0143(2) | 0.0203(2) | 0.0042(1) | 0.0027(1) | 0.0073(1) |
| O(1) | 0.0235(16) | 0.0202(17) | 0.0197(17) | 0.0025(14) | 0.0053(13) | 0.0091(13) |
| O(2) | 0.0204(16) | 0.0145(16) | 0.0274(19) | 0.0062(15) | 0.0070(13) | 0.0052(13) |
| N(1) | 0.0207(19) | 0.0160(19) | 0.025(2) | 0.0047(17) | 0.0072(16) | 0.0073(16) |
| N(2) | 0.0172(19) | 0.020(2) | 0.024(2) | 0.0026(17) | 0.0015(16) | 0.0035(16) |
| N(3) | 0.0169(18) | 0.0182(19) | 0.018(2) | 0.0056(16) | 0.0035(15) | 0.0074(15) |
| N(4) | 0.0157(18) | 0.0154(19) | 0.026(2) | 0.0033(17) | 0.0037(16) | 0.0054(15) |
| C(1) | 0.024(2) | 0.010(2) | 0.019(2) | 0.0054(18) | 0.0054(18) | 0.0083(18) |
| C(2) | 0.026(2) | 0.013(2) | 0.024(3) | 0.0040(19) | 0.0087(19) | 0.0086(18) |
| C(3) | 0.030(3) | 0.019(2) | 0.028(3) | 0.010(2) | 0.012(2) | 0.009(2) |
| C(4) | 0.033(3) | 0.022(2) | 0.021(3) | 0.005(2) | 0.009(2) | 0.013(2) |
| C(5) | 0.032(3) | 0.018(2) | 0.019(3) | 0.006(2) | 0.0022(19) | 0.011(2) |
| C(6) | 0.018(2) | 0.014(2) | 0.023(3) | 0.0057(19) | 0.0052(18) | 0.0073(17) |
| C(7) | 0.022(2) | 0.012(2) | 0.023(3) | 0.0071(19) | 0.0041(18) | 0.0081(18) |
| C(8) | 0.020(2) | 0.021(2) | 0.023(3) | 0.003(2) | -0.0023(19) | 0.0067(19) |
| C(9) | 0.018(2) | 0.024(3) | 0.029(3) | 0.006(2) | 0.0003(19) | 0.0025(19) |
| C(10) | 0.021(2) | 0.010(2) | 0.022(3) | 0.0043(19) | 0.0028(18) | 0.0050(17) |
| C(11) | 0.022(2) | 0.022(2) | 0.038(3) | 0.011(2) | 0.013(2) | 0.008(2) |
| C(12) | 0.016(2) | 0.027(3) | 0.033(3) | 0.008(2) | 0.002(2) | 0.005(2) |

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Table A.9 (Continued)

| | | | | | | |
|---|---|---|---|---|---|---|
| C(13) | 0.024(3) | 0.039(3) | 0.025(3) | 0.005(2) | 0.003(2) | 0.005(2) |
| C(14) | 0.026(3) | 0.027(3) | 0.032(3) | 0.000(2) | 0.000(2) | 0.005(2) |
| C(15) | 0.028(3) | 0.032(3) | 0.038(3) | 0.005(3) | 0.009(2) | 0.008(2) |
| C(16) | 0.034(3) | 0.044(3) | 0.038(3) | 0.007(3) | 0.007(2) | 0.009(3) |
| C(17) | 0.016(2) | 0.026(3) | 0.028(3) | 0.003(2) | 0.0084(19) | 0.0066(19) |
| C(18) | 0.033(3) | 0.033(3) | 0.026(3) | 0.009(2) | 0.009(2) | 0.014(2) |
| C(19) | 0.039(3) | 0.050(4) | 0.030(3) | 0.015(3) | 0.011(2) | 0.020(3) |
| C(20) | 0.050(4) | 0.054(4) | 0.047(4) | 0.028(3) | 0.011(3) | 0.013(3) |
| C(21) | 0.014(2) | 0.025(3) | 0.027(3) | 0.003(2) | 0.0074(18) | 0.0074(19) |
| C(22) | 0.014(2) | 0.014(2) | 0.036(3) | 0.009(2) | 0.0063(19) | 0.0041(17) |
| C(23) | 0.024(2) | 0.015(2) | 0.030(3) | 0.000(2) | 0.007(2) | 0.0081(19) |
| C(24) | 0.035(3) | 0.029(3) | 0.024(3) | -0.001(2) | 0.004(2) | 0.012(2) |
| C(25) | 0.041(3) | 0.017(2) | 0.042(3) | 0.010(2) | 0.012(2) | 0.014(2) |
| C(26) | 0.042(3) | 0.030(3) | 0.029(3) | 0.004(2) | 0.007(2) | 0.015(2) |

$$-2\pi^2[h^2a^{*2}U_{11} + ... +2hka^*b^*U_{12}] \qquad (A.2)$$

Table A.10    Bond Lengths [Å] for **7**

| atom-atom | distance | atom-atom | distance |
|---|---|---|---|
| Co(1)-C(1) | 1.874(5) | Co(1)-O(2) | 1.941(3) |
| Co(1)-C(10) | 1.965(4) | Co(1)-C(7) | 1.971(4) |
| Co(1)-O(1) | 2.002(3) | Co(1)-I(1) | 2.5685(6) |
| Cl(1)-C(26) | 1.760(6) | Cl(2)-C(26) | 1.746(6) |
| Cl(3)-C(26) | 1.764(5) | O(1)-C(21) | 1.258(6) |
| O(2)-C(22) | 1.243(6) | N(1)-C(10) | 1.364(6) |
| N(1)-C(11) | 1.370(6) | N(1)-C(2) | 1.424(6) |
| N(2)-C(10) | 1.359(6) | N(2)-C(12) | 1.392(6) |
| N(2)-C(13) | 1.465(6) | N(3)-C(7) | 1.368(6) |
| N(3)-C(8) | 1.393(6) | N(3)-C(6) | 1.430(6) |
| N(4)-C(7) | 1.348(6) | N(4)-C(9) | 1.393(6) |
| N(4)-C(17) | 1.453(6) | C(1)-C(6) | 1.380(6) |
| C(1)-C(2) | 1.383(6) | C(2)-C(3) | 1.380(7) |

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Table A.10 (Continued)

| | | | |
|---|---|---|---|
| C(3)-C(4) | 1.391(7) | C(3)-H(3A) | 0.9500 |
| C(4)-C(5) | 1.396(7) | C(4)-H(4A) | 0.9500 |
| C(5)-C(6) | 1.377(7) | C(5)-H(5A) | 0.9500 |
| C(8)-C(9) | 1.345(7) | C(8)-H(8A) | 0.9500 |
| C(9)-H(9A) | 0.9500 | C(11)-C(12) | 1.337(7) |
| C(11)-H(11A) | 0.9500 | C(12)-H(12A) | 0.9500 |
| C(13)-C(14) | 1.490(7) | C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 | C(14)-C(15) | 1.512(8) |
| C(14)-H(14A) | 0.9900 | C(14)-H(14B) | 0.9900 |
| C(15)-C(16) | 1.502(7) | C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 | C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 | C(16)-H(16C) | 0.9800 |
| C(17)-C(18) | 1.523(6) | C(17)-H(17A) | 0.9900 |
| C(17)-H(17B) | 0.9900 | C(18)-C(19) | 1.509(7) |
| C(18)-H(18A) | 0.9900 | C(18)-H(18B) | 0.9900 |
| C(19)-C(20) | 1.534(8) | C(19)-H(19A) | 0.9900 |
| C(19)-H(19B) | 0.9900 | C(20)-H(20A) | 0.9800 |
| C(20)-H(20B) | 0.9800 | C(20)-H(20C) | 0.9800 |
| C(21)-C(23) | 1.402(6) | C(21)-C(24) | 1.516(7) |
| C(22)-C(23) | 1.401(7) | C(22)-C(25) | 1.520(6) |
| C(23)-H(23A) | 0.9500 | C(24)-H(24A) | 0.9800 |
| C(24)-H(24B) | 0.9800 | C(24)-H(24C) | 0.9800 |
| C(25)-H(25A) | 0.9800 | C(25)-H(25B) | 0.9800 |
| C(25)-H(25C) | 0.9800 | C(26)-H(26A) | 1.0000 |

Symmetry transformations used to generate equivalent atoms

Table A.11    Bond Angles [°] for **7**

| atom-atom-atom | angle | atom-atom-atom | angle |
|---|---|---|---|
| C(1)-Co(1)-O(2) | 89.48(16) | C(1)-Co(1)-C(10) | 80.09(19) |
| O(2)-Co(1)-C(10) | 90.68(15) | C(1)-Co(1)-C(7) | 79.84(19) |
| O(2)-Co(1)-C(7) | 89.85(15) | C(10)-Co(1)-C(7) | 159.9(2) |
| C(1)-Co(1)-O(1) | 177.62(15) | O(2)-Co(1)-O(1) | 92.81(13) |
| C(10)-Co(1)-O(1) | 99.20(16) | C(7)-Co(1)-O(1) | 100.83(16) |

Table A.11 (Continued)

| | | | |
|---|---|---|---|
| C(1)-Co(1)-I(1) | 89.73(12) | O(2)-Co(1)-I(1) | 178.52(9) |
| C(10)-Co(1)-I(1) | 87.96(12) | C(7)-Co(1)-I(1) | 91.23(12) |
| O(1)-Co(1)-I(1) | 87.98(9) | C(21)-O(1)-Co(1) | 124.1(3) |
| C(22)-O(2)-Co(1) | 124.7(3) | C(10)-N(1)-C(11) | 111.6(4) |
| C(10)-N(1)-C(2) | 114.6(4) | C(11)-N(1)-C(2) | 133.7(4) |
| C(10)-N(2)-C(12) | 110.0(4) | C(10)-N(2)-C(13) | 122.6(4) |
| C(12)-N(2)-C(13) | 127.4(4) | C(7)-N(3)-C(8) | 111.8(4) |
| C(7)-N(3)-C(6) | 115.7(4) | C(8)-N(3)-C(6) | 132.5(4) |
| C(7)-N(4)-C(9) | 110.8(4) | C(7)-N(4)-C(17) | 125.3(4) |
| C(9)-N(4)-C(17) | 123.7(4) | C(6)-C(1)-C(2) | 118.6(4) |
| C(6)-C(1)-Co(1) | 121.2(3) | C(2)-C(1)-Co(1) | 120.0(3) |
| C(3)-C(2)-C(1) | 121.8(4) | C(3)-C(2)-N(1) | 128.0(4) |
| C(1)-C(2)-N(1) | 110.2(4) | C(2)-C(3)-C(4) | 117.5(4) |
| C(2)-C(3)-H(3A) | 121.2 | C(4)-C(3)-H(3A) | 121.2 |
| C(3)-C(4)-C(5) | 122.5(5) | C(3)-C(4)-H(4A) | 118.8 |
| C(5)-C(4)-H(4A) | 118.8 | C(6)-C(5)-C(4) | 117.1(4) |
| C(6)-C(5)-H(5A) | 121.4 | C(4)-C(5)-H(5A) | 121.4 |
| C(5)-C(6)-C(1) | 122.4(4) | C(5)-C(6)-N(3) | 128.8(4) |
| C(1)-C(6)-N(3) | 108.8(4) | N(4)-C(7)-N(3) | 104.1(4) |
| N(4)-C(7)-Co(1) | 141.4(4) | N(3)-C(7)-Co(1) | 114.4(3) |
| C(9)-C(8)-N(3) | 105.3(4) | C(9)-C(8)-H(8A) | 127.4 |
| N(3)-C(8)-H(8A) | 127.4 | C(8)-C(9)-N(4) | 107.9(4) |
| C(8)-C(9)-H(9A) | 126.0 | N(4)-C(9)-H(9A) | 126.0 |
| N(2)-C(10)-N(1) | 104.2(4) | N(2)-C(10)-Co(1) | 140.7(4) |
| N(1)-C(10)-Co(1) | 115.0(3) | C(12)-C(11)-N(1) | 106.6(4) |
| C(12)-C(11)-H(11A) | 126.7 | N(1)-C(11)-H(11A) | 126.7 |
| C(11)-C(12)-N(2) | 107.6(4) | C(11)-C(12)-H(12A) | 126.2 |
| N(2)-C(12)-H(12A) | 126.2 | N(2)-C(13)-C(14) | 115.5(4) |
| N(2)-C(13)-H(13A) | 108.4 | C(14)-C(13)-H(13A) | 108.4 |
| N(2)-C(13)-H(13B) | 108.4 | C(14)-C(13)-H(13B) | 108.4 |
| H(13A)-C(13)-H(13B) | 107.5 | C(13)-C(14)-C(15) | 111.6(4) |
| C(13)-C(14)-H(14A) | 109.3 | C(15)-C(14)-H(14A) | 109.3 |
| C(13)-C(14)-H(14B) | 109.3 | C(15)-C(14)-H(14B) | 109.3 |

Table A.11 (Continued)

| | | | |
|---|---|---|---|
| H(14A)-C(14)-H(14B) | 108.0 | C(16)-C(15)-C(14) | 113.8(5) |
| C(16)-C(15)-H(15A) | 108.8 | C(14)-C(15)-H(15A) | 108.8 |
| C(16)-C(15)-H(15B) | 108.8 | C(14)-C(15)-H(15B) | 108.8 |
| H(15A)-C(15)-H(15B) | 107.7 | C(15)-C(16)-H(16A) | 109.5 |
| C(15)-C(16)-H(16B) | 109.5 | H(16A)-C(16)-H(16B) | 109.5 |
| C(15)-C(16)-H(16C) | 109.5 | H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 | N(4)-C(17)-C(18) | 111.4(4) |
| N(4)-C(17)-H(17A) | 109.3 | C(18)-C(17)-H(17A) | 109.3 |
| N(4)-C(17)-H(17B) | 109.3 | C(18)-C(17)-H(17B) | 109.3 |
| H(17A)-C(17)-H(17B) | 108.0 | C(19)-C(18)-C(17) | 112.6(4) |
| C(19)-C(18)-H(18A) | 109.1 | C(17)-C(18)-H(18A) | 109.1 |
| C(19)-C(18)-H(18B) | 109.1 | C(17)-C(18)-H(18B) | 109.1 |
| H(18A)-C(18)-H(18B) | 107.8 | C(18)-C(19)-C(20) | 112.0(5) |
| C(18)-C(19)-H(19A) | 109.2 | C(20)-C(19)-H(19A) | 109.2 |
| C(18)-C(19)-H(19B) | 109.2 | C(20)-C(19)-H(19B) | 109.2 |
| H(19A)-C(19)-H(19B) | 107.9 | C(19)-C(20)-H(20A) | 109.5 |
| C(19)-C(20)-H(20B) | 109.5 | H(20A)-C(20)-H(20B) | 109.5 |
| C(19)-C(20)-H(20C) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 | O(1)-C(21)-C(23) | 125.3(4) |
| O(1)-C(21)-C(24) | 115.9(4) | C(23)-C(21)-C(24) | 118.8(4) |
| O(2)-C(22)-C(23) | 127.2(4) | O(2)-C(22)-C(25) | 115.4(4) |
| C(23)-C(22)-C(25) | 117.4(4) | C(22)-C(23)-C(21) | 124.6(4) |
| C(22)-C(23)-H(23A) | 117.7 | C(21)-C(23)-H(23A) | 117.7 |
| C(21)-C(24)-H(24A) | 109.5 | C(21)-C(24)-H(24B) | 109.5 |
| H(24A)-C(24)-H(24B) | 109.5 | C(21)-C(24)-H(24C) | 109.5 |
| H(24A)-C(24)-H(24C) | 109.5 | H(24B)-C(24)-H(24C) | 109.5 |
| C(22)-C(25)-H(25A) | 109.5 | C(22)-C(25)-H(25B) | 109.5 |
| H(25A)-C(25)-H(25B) | 109.5 | C(22)-C(25)-H(25C) | 109.5 |
| H(25A)-C(25)-H(25C) | 109.5 | H(25B)-C(25)-H(25C) | 109.5 |
| Cl(2)-C(26)-Cl(1) | 110.1(3) | Cl(2)-C(26)-Cl(3) | 110.6(3) |
| Cl(1)-C(26)-Cl(3) | 109.4(3) | Cl(2)-C(26)-H(26A) | 108.9 |
| Cl(1)-C(26)-H(26A) | 108.9 | Cl(3)-C(26)-H(26A) | 108.9 |

Symmetry transformations used to generate equivalent atoms

Table A.12    Torsion Angles [°] for **7**

| atom-atom-atom-atom | angle | atom-atom-atom-atom | angle |
|---|---|---|---|
| O(2)-Co(1)-C(1)-C(6) | 87.3(3) | C(10)-Co(1)-C(1)-C(6) | 178.1(4) |
| C(7)-Co(1)-C(1)-C(6) | -2.7(3) | I(1)-Co(1)-C(1)-C(6) | -94.0(3) |
| O(2)-Co(1)-C(1)-C(2) | -88.3(3) | C(10)-Co(1)-C(1)-C(2) | 2.5(3) |
| C(7)-Co(1)-C(1)-C(2) | -178.3(4) | I(1)-Co(1)-C(1)-C(2) | 90.4(3) |
| C(6)-C(1)-C(2)-C(3) | -0.3(6) | Co(1)-C(1)-C(2)-C(3) | 175.4(3) |
| C(6)-C(1)-C(2)-N(1) | -179.1(4) | Co(1)-C(1)-C(2)-N(1) | -3.4(5) |
| C(10)-N(1)-C(2)-C(3) | -176.3(4) | C(11)-N(1)-C(2)-C(3) | 6.2(8) |
| C(10)-N(1)-C(2)-C(1) | 2.5(5) | C(11)-N(1)-C(2)-C(1) | -175.0(4) |
| C(1)-C(2)-C(3)-C(4) | 1.2(6) | N(1)-C(2)-C(3)-C(4) | 179.8(4) |
| C(2)-C(3)-C(4)-C(5) | -1.1(7) | C(3)-C(4)-C(5)-C(6) | 0.0(7) |
| C(4)-C(5)-C(6)-C(1) | 1.0(6) | C(4)-C(5)-C(6)-N(3) | -177.5(4) |
| C(2)-C(1)-C(6)-C(5) | -0.9(6) | Co(1)-C(1)-C(6)-C(5) | -176.5(3) |
| C(2)-C(1)-C(6)-N(3) | 177.9(4) | Co(1)-C(1)-C(6)-N(3) | 2.3(5) |
| C(7)-N(3)-C(6)-C(5) | 178.7(4) | C(8)-N(3)-C(6)-C(5) | 0.2(8) |
| C(7)-N(3)-C(6)-C(1) | 0.0(5) | C(8)-N(3)-C(6)-C(1) | -178.5(4) |
| C(9)-N(4)-C(7)-N(3) | -0.1(5) | C(17)-N(4)-C(7)-N(3) | -175.4(4) |
| C(9)-N(4)-C(7)-Co(1) | -175.1(4) | C(17)-N(4)-C(7)-Co(1) | 9.7(7) |
| C(8)-N(3)-C(7)-N(4) | 0.2(5) | C(6)-N(3)-C(7)-N(4) | -178.5(3) |
| C(8)-N(3)-C(7)-Co(1) | 176.8(3) | C(6)-N(3)-C(7)-Co(1) | -2.0(5) |
| C(7)-N(3)-C(8)-C(9) | -0.2(5) | C(6)-N(3)-C(8)-C(9) | 178.2(4) |
| N(3)-C(8)-C(9)-N(4) | 0.1(5) | C(7)-N(4)-C(9)-C(8) | 0.0(5) |
| C(17)-N(4)-C(9)-C(8) | 175.3(4) | C(12)-N(2)-C(10)-N(1) | 0.3(5) |
| C(13)-N(2)-C(10)-N(1) | 180.0(4) | C(12)-N(2)-C(10)-Co(1) | -176.9(4) |
| C(13)-N(2)-C(10)-Co(1) | 2.7(7) | C(11)-N(1)-C(10)-N(2) | -0.7(5) |
| C(2)-N(1)-C(10)-N(2) | -178.8(3) | C(11)-N(1)-C(10)-Co(1) | 177.4(3) |
| C(2)-N(1)-C(10)-Co(1) | -0.7(5) | C(10)-N(1)-C(11)-C(12) | 0.8(5) |
| C(2)-N(1)-C(11)-C(12) | 178.4(4) | N(1)-C(11)-C(12)-N(2) | -0.6(5) |
| C(10)-N(2)-C(12)-C(11) | 0.2(5) | C(13)-N(2)-C(12)-C(11) | -179.4(4) |
| C(10)-N(2)-C(13)-C(14) | -179.7(4) | C(12)-N(2)-C(13)-C(14) | -0.1(7) |
| N(2)-C(13)-C(14)-C(15) | -177.4(4) | C(13)-C(14)-C(15)-C(16) | -179.9(5) |
| C(7)-N(4)-C(17)-C(18) | 99.7(5) | C(9)-N(4)-C(17)-C(18) | -74.9(5) |
| N(4)-C(17)-C(18)-C(19) | 175.8(4) | C(17)-C(18)-C(19)-C(20) | 179.2(5) |

Table A.12 (Continued)

| | | | |
|---|---|---|---|
| Co(1)-O(1)-C(21)-C(23) | -7.0(6) | Co(1)-O(1)-C(21)-C(24) | 172.9(3) |
| Co(1)-O(2)-C(22)-C(23) | 6.0(6) | Co(1)-O(2)-C(22)-C(25) | -174.8(3) |
| O(2)-C(22)-C(23)-C(21) | 3.1(8) | C(25)-C(22)-C(23)-C(21) | -176.1(4) |
| O(1)-C(21)-C(23)-C(22) | -2.3(7) | C(24)-C(21)-C(23)-C(22) | 177.8(4) |

Symmetry transformations used to generate equivalent atoms.

## A.1.2 Crystal Summary for 7

Crystal data for $C_{26}H_{33}Cl_3CoIN_4O_2$; $M_r = 725.74$; Triclinic; space group P-1; $a = 8.4464(3)$ Å; $b = 10.4389(4)$ Å; $c = 18.6009(7)$ Å; $\alpha = 94.144(2)°$; $\beta = 99.879(2)°$; $\gamma = 110.932(2)°$; $V = 1493.13(10)$ Å$^3$; $Z = 2$; $T = 100(2)$ K; $\lambda$(Mo-K$\alpha$) = 0.71073 Å; $\mu$(Mo-K$\alpha$) = 1.907 mm$^{-1}$; $d_{calc} = 1.614$g.cm$^{-3}$; 8785 reflections collected; 5318 unique ($R_{int}$ = 0.0273); giving $R_1 = 0.0393$, $wR_2 = 0.0907$ for 4578 data with [I>2$\sigma$(I)] and $R_1 = 0.0474$, $wR_2 = 0.0962$ for all 5318 data. Residual electron density (e$^-$.Å$^{-3}$) max/min: 0.645/-1.174.

An arbitrary sphere of data were collected on a Tablet-like crystal, having approximate dimensions of 0.347 × 0.194 × 0.060 mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5°.[303] Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by vecmap methods and expanded routinely.[304] The model was refined by full-matrix least-squares analysis of F$^2$ against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

**A.2    Chapter III Compounds**
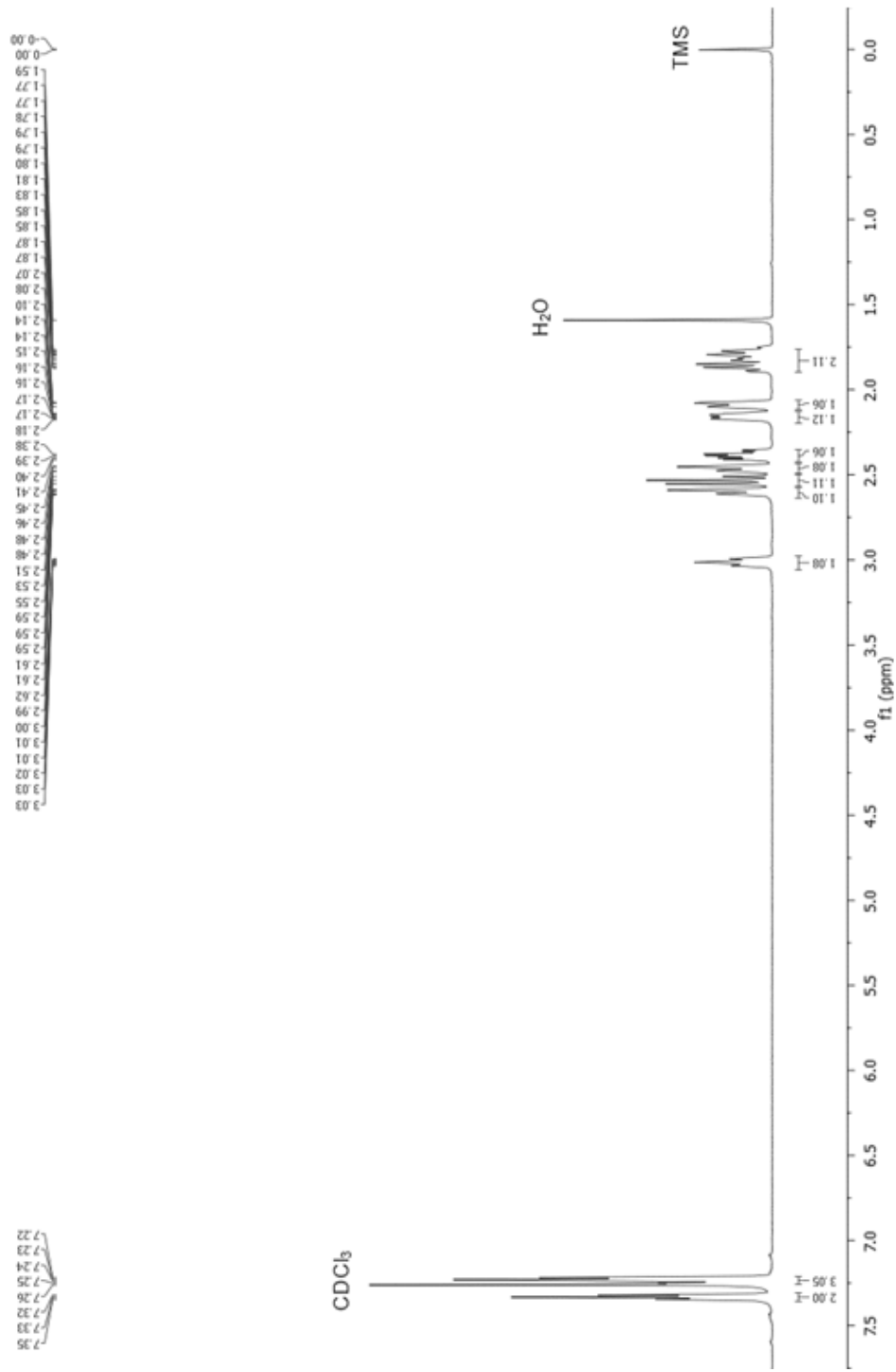


Figure A.10   $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 3.2, Entry 1)
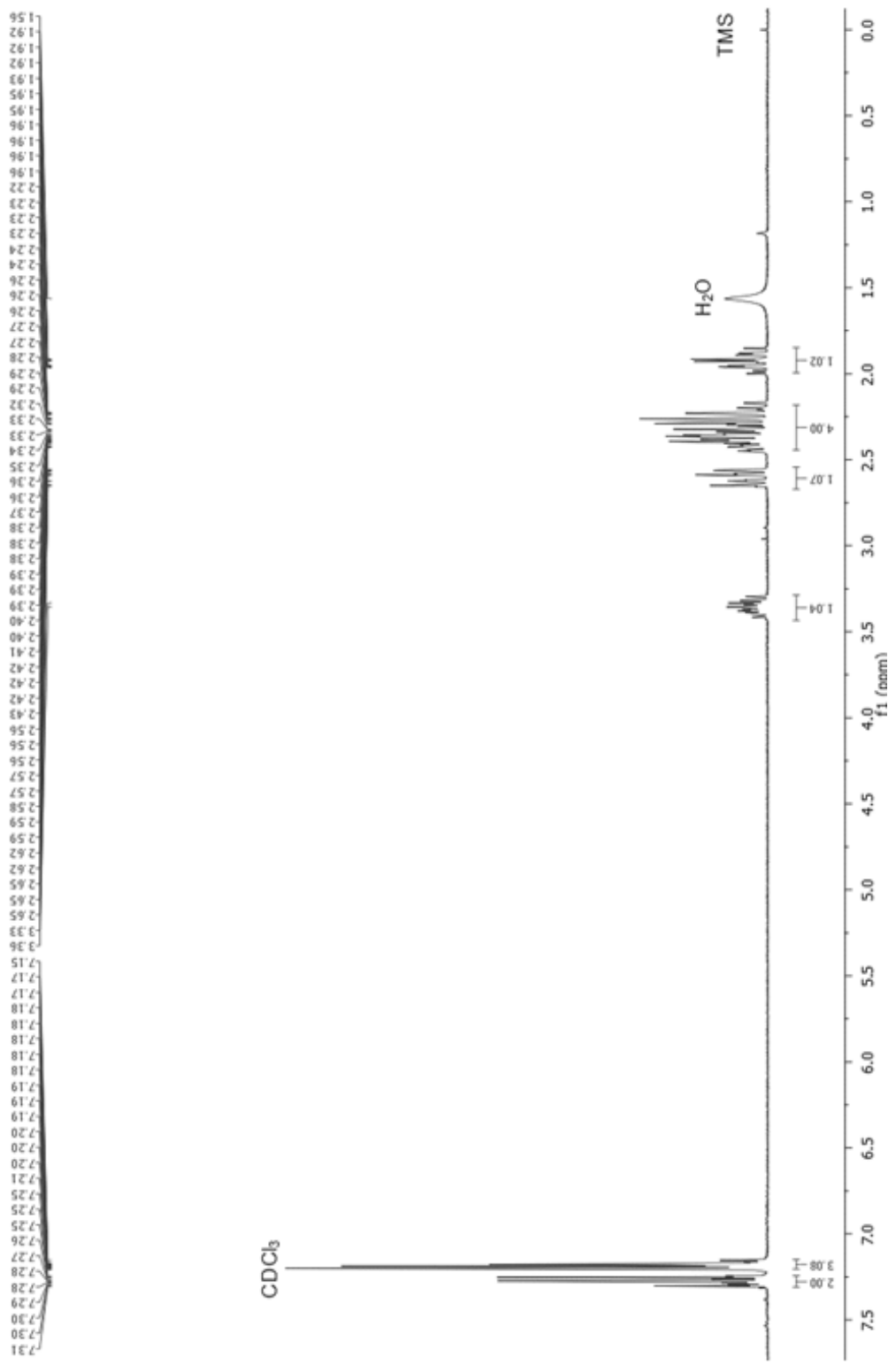
Figure A.11  $^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.2, Entry 2)

Figure A.12   $^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.2, Entry 3)

114

Figure A.13   $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 3.2, Entry 4)

Figure A.14  ¹H NMR (600 MHz, CDCl₃) spectrum of isolated product (Table 3.2, Entry 5)
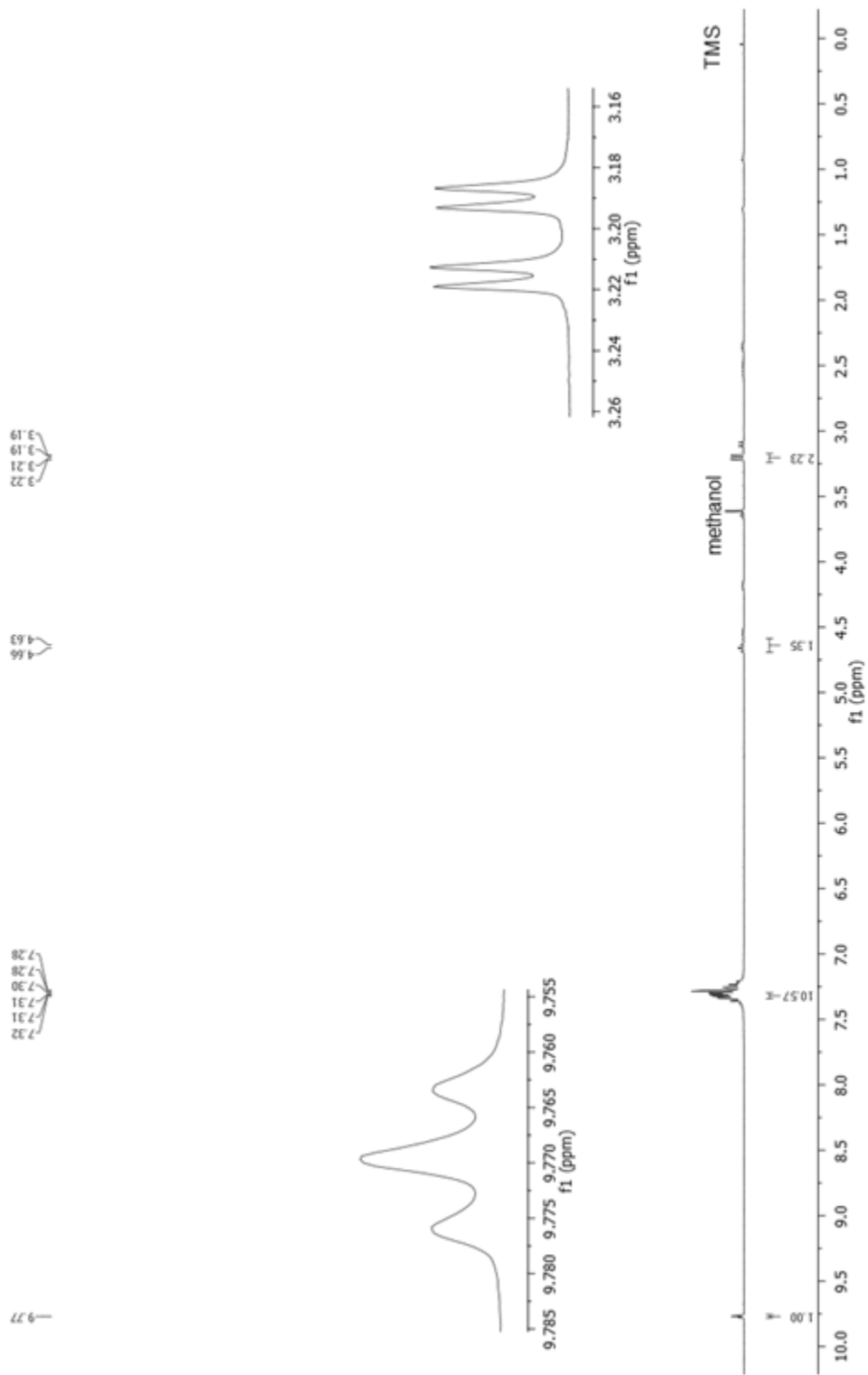
Figure A.15  ¹H NMR (300 MHz, CDCl₃) spectrum of isolated product (Table 3.2, Entry 6)

117
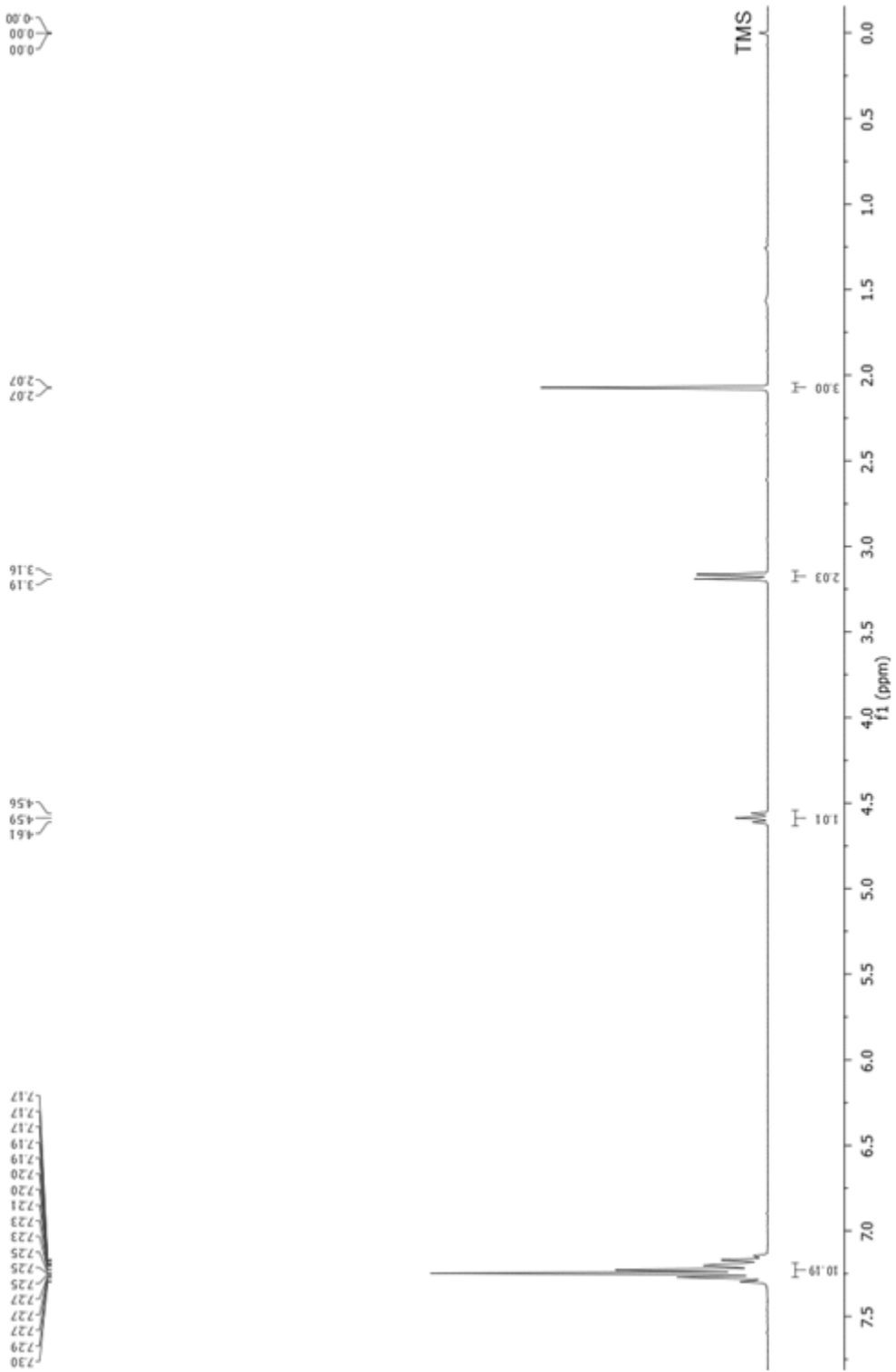
Figure A.16　$^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.2, Entry 7)
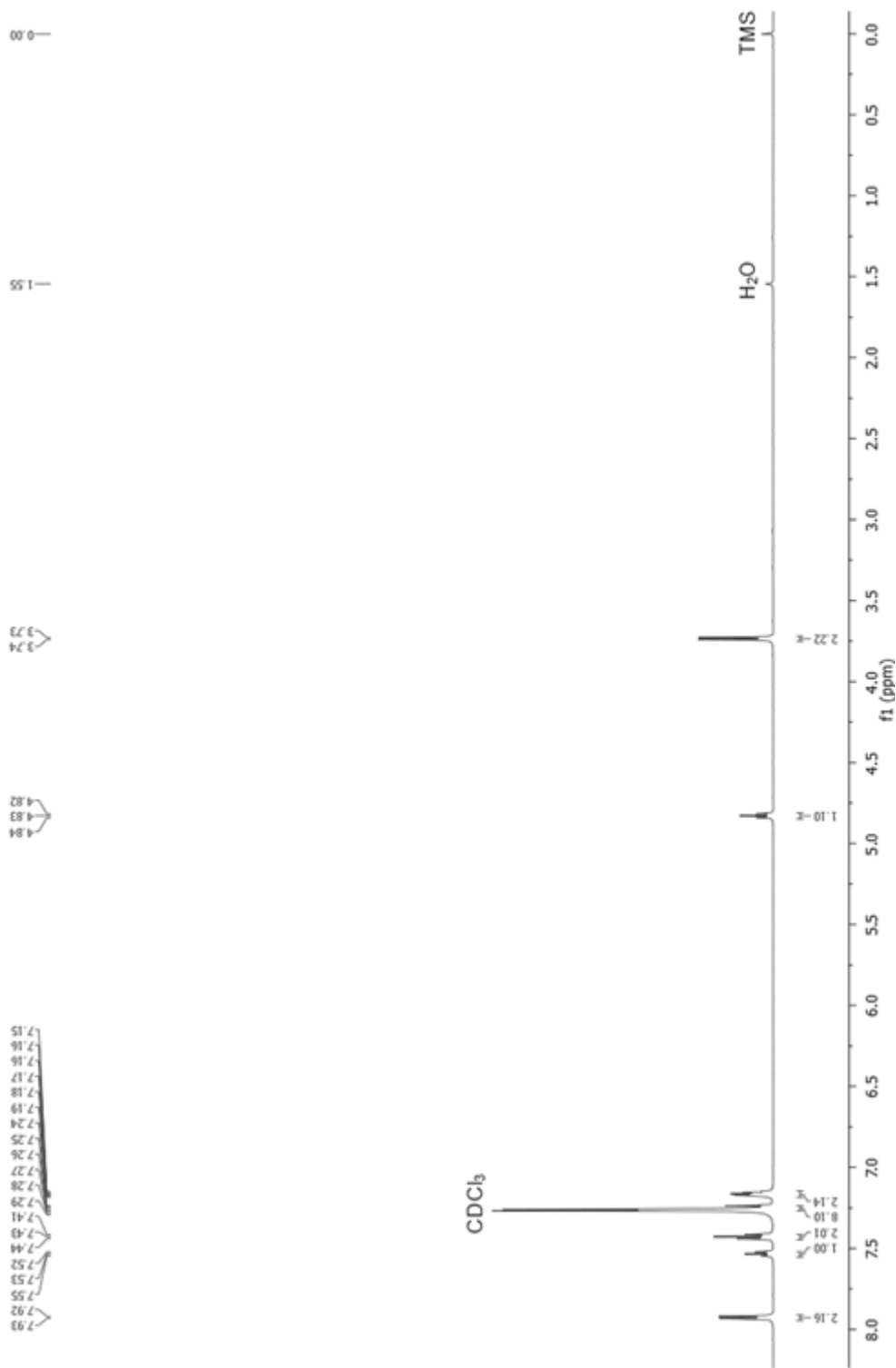
Figure A.17    $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 3.2, Entry 8)
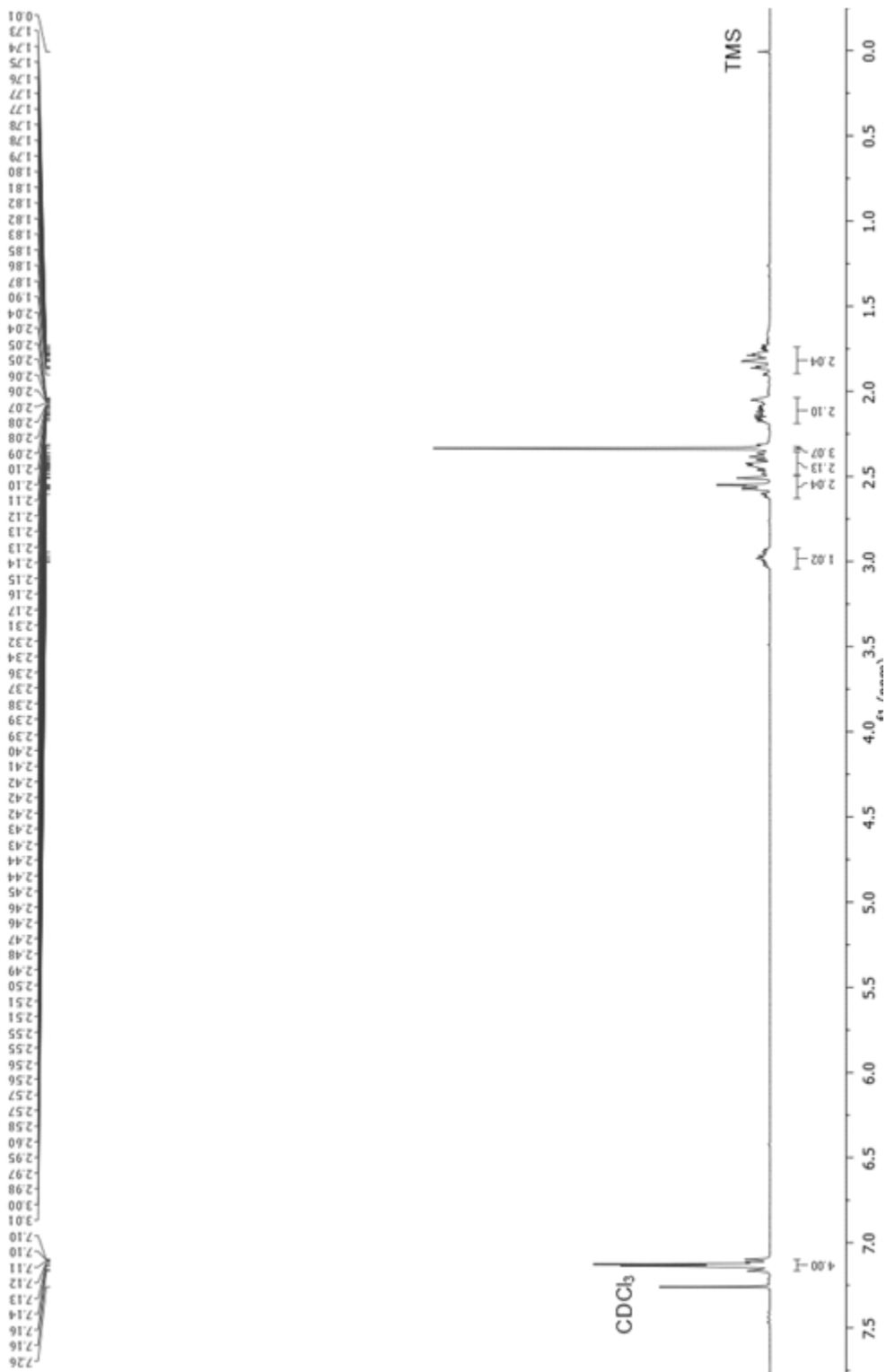
Figure A.18    $^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.3, Entry 1)
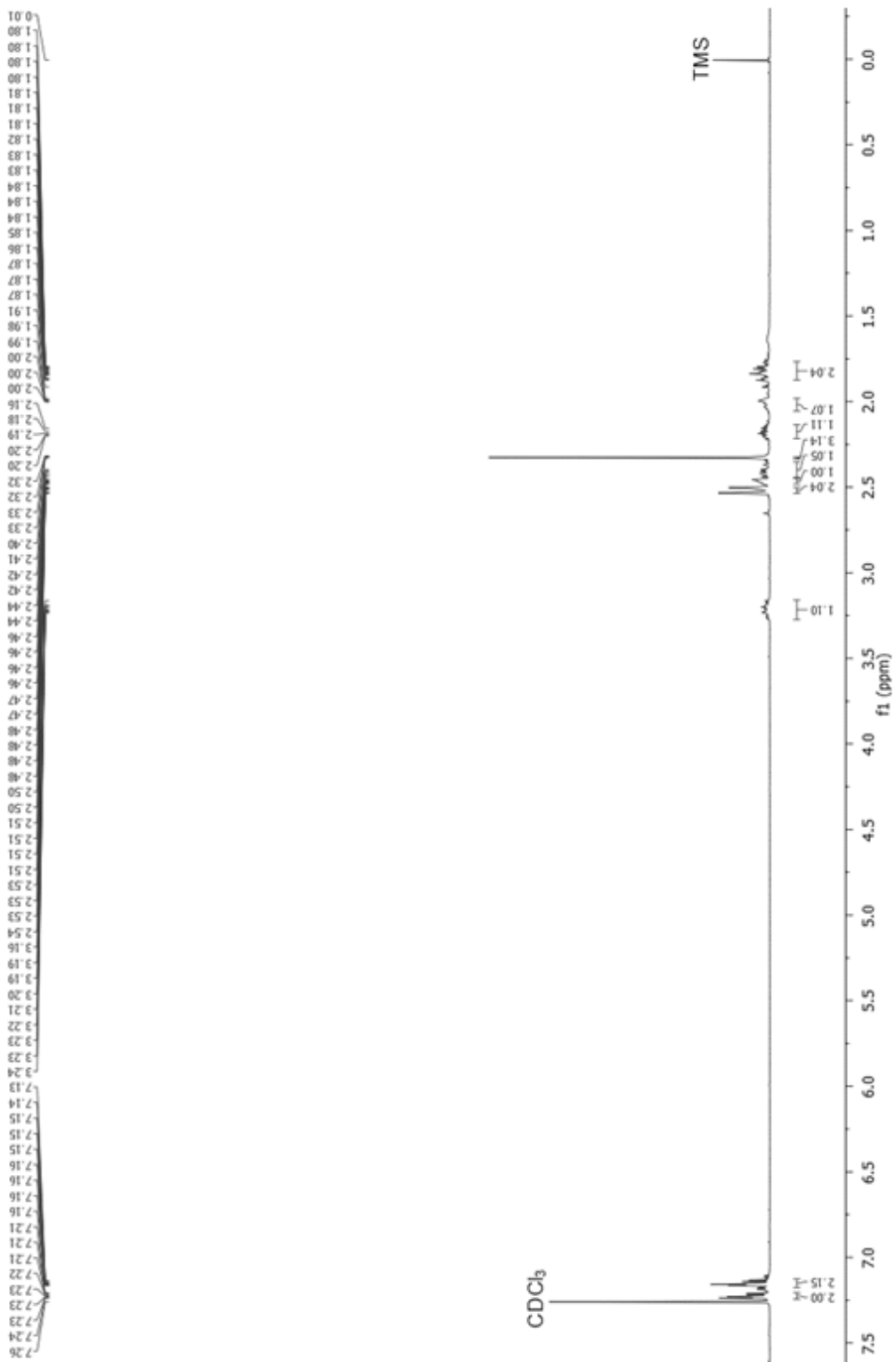
Figure A.19  $^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.3, Entry 2)
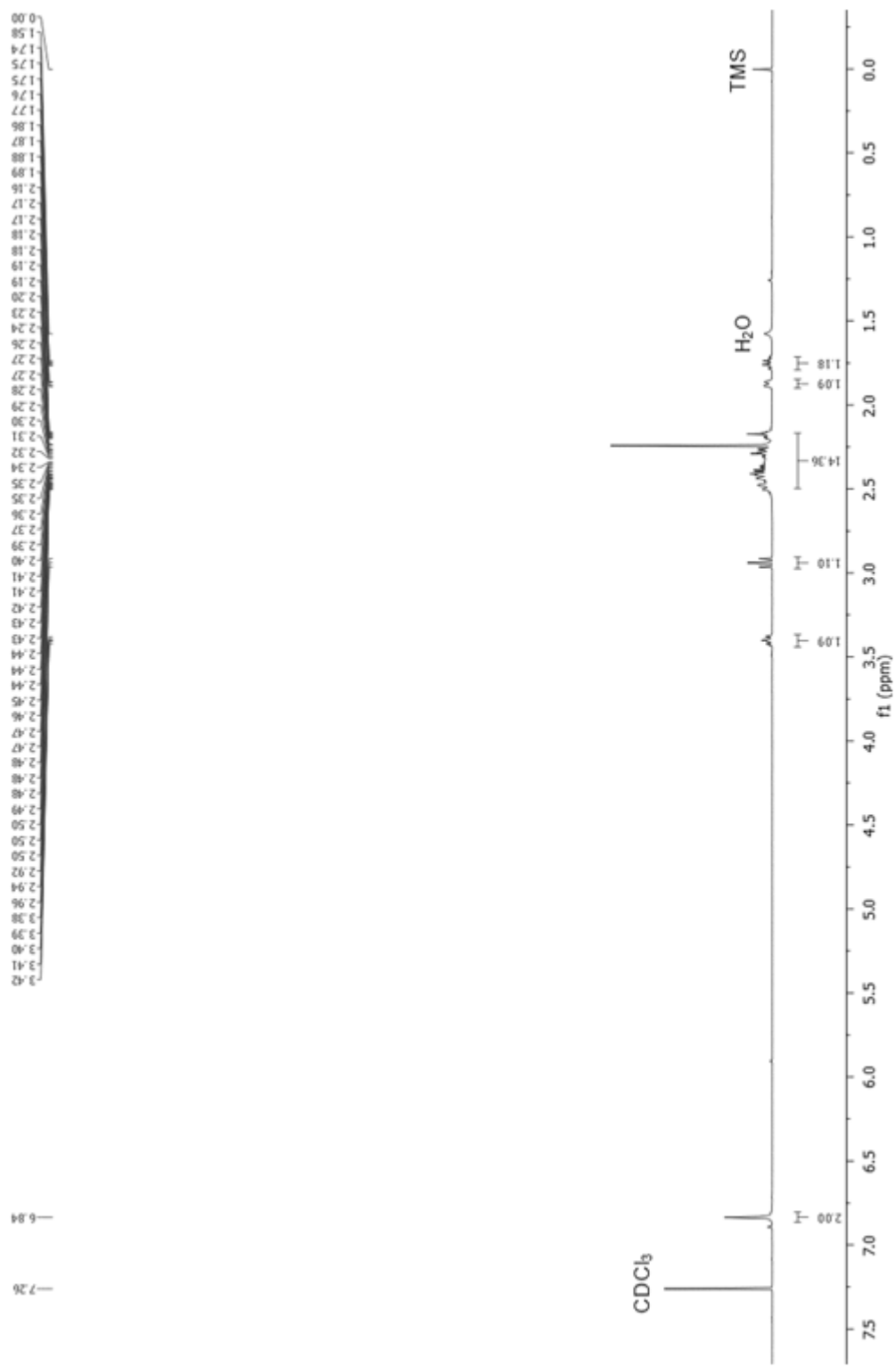
Figure A.20  $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 3.3, Entry 3)

Figure A.21  $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 3.3, Entry 4)

Figure A.22  $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 3.3, Entry 5)

Figure A.23   $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 3.3, Entry 6)

125
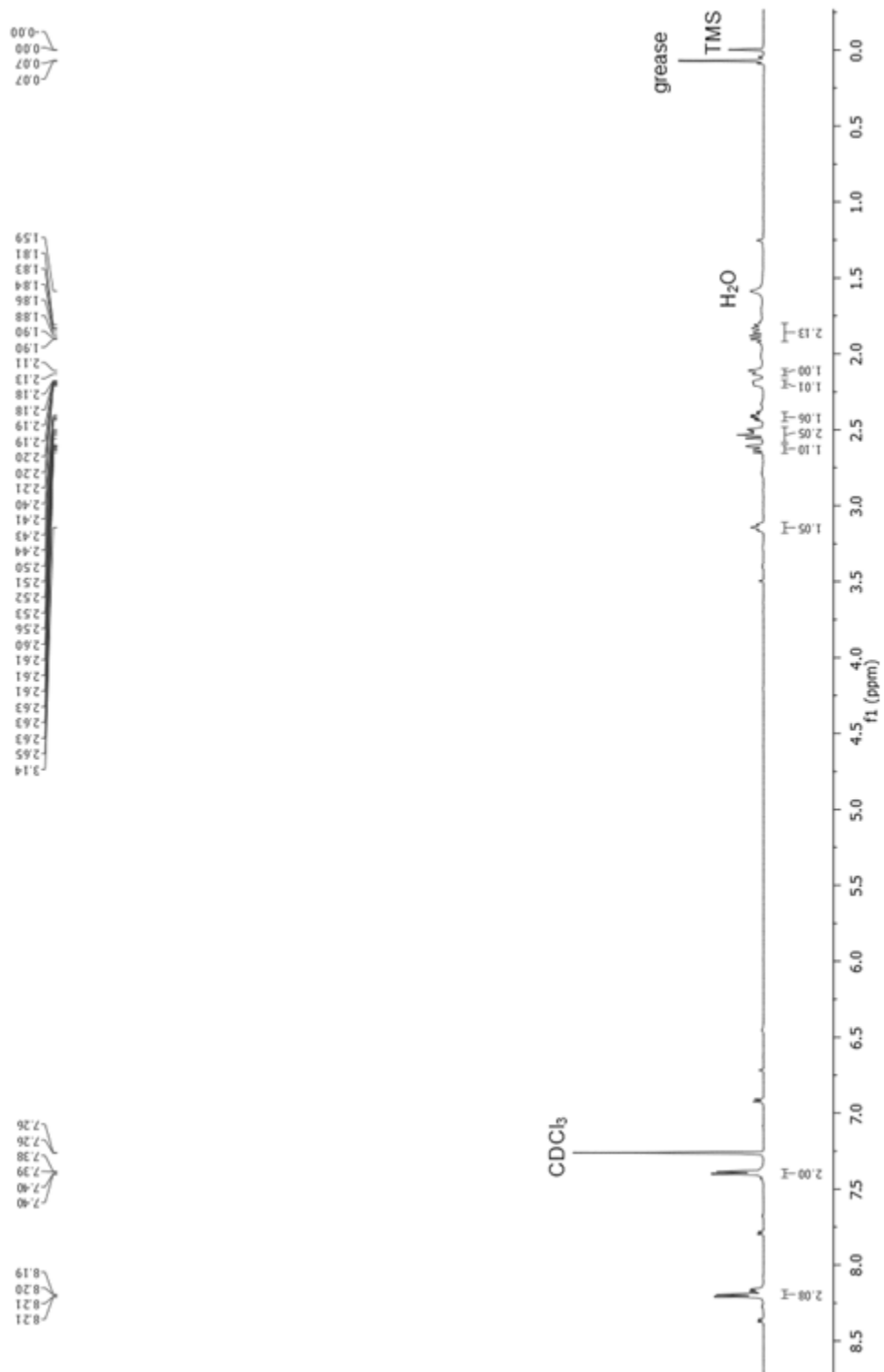
Figure A.24  ¹H NMR (600 MHz, CDCl₃) spectrum of isolated product (Table 3.3, Entry 8)
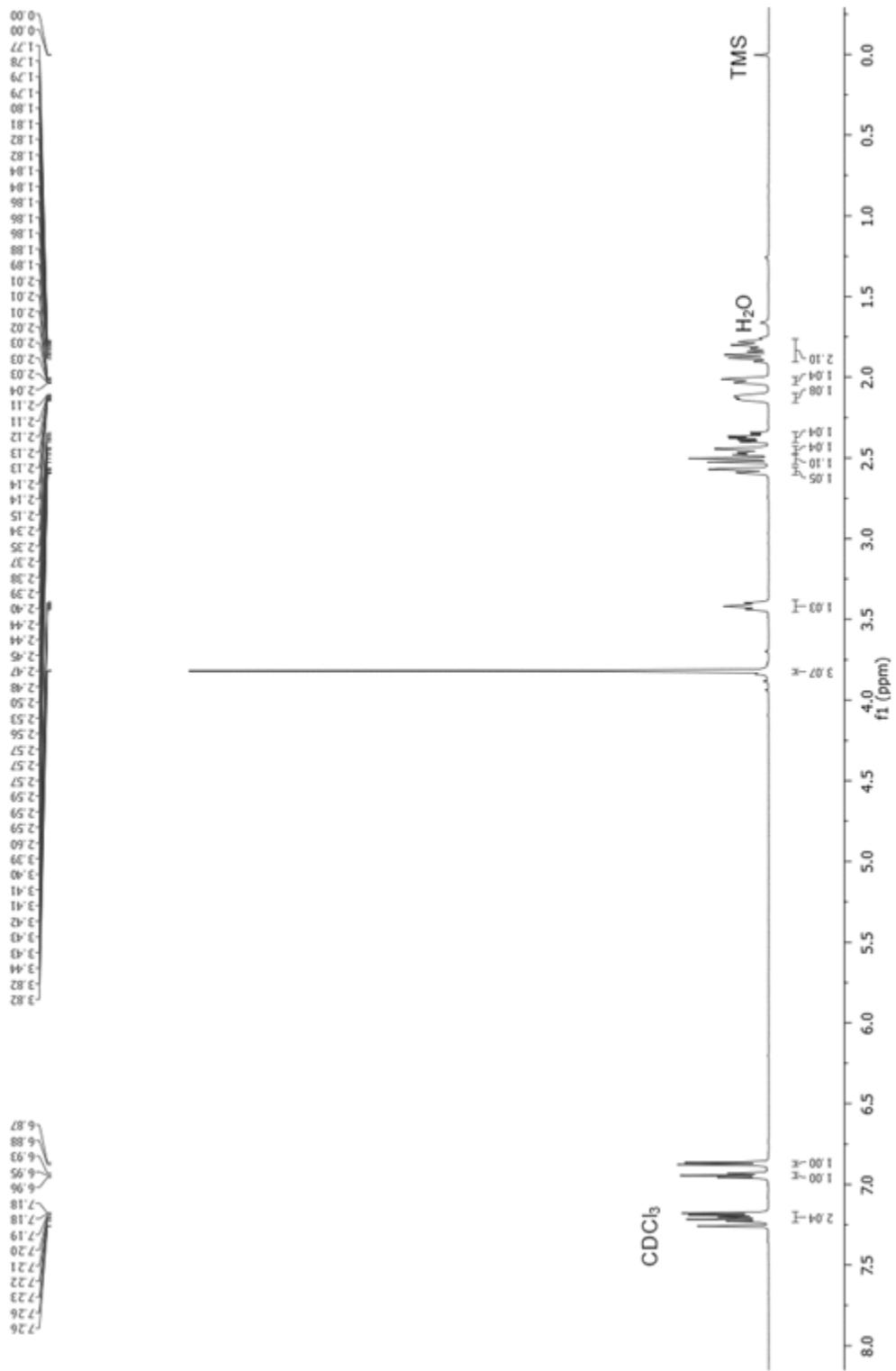
Figure A.25 $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 3.3, Entry 9)

Figure A.26  $^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.3, Entry 10)

Figure A.27  ¹H NMR (300 MHz, CDCl₃) spectrum of isolated product (Table 3.4, Entry 1)

Figure A.28   $^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.4, Entry 2)

Figure A.29  $^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.4, Entry 5)
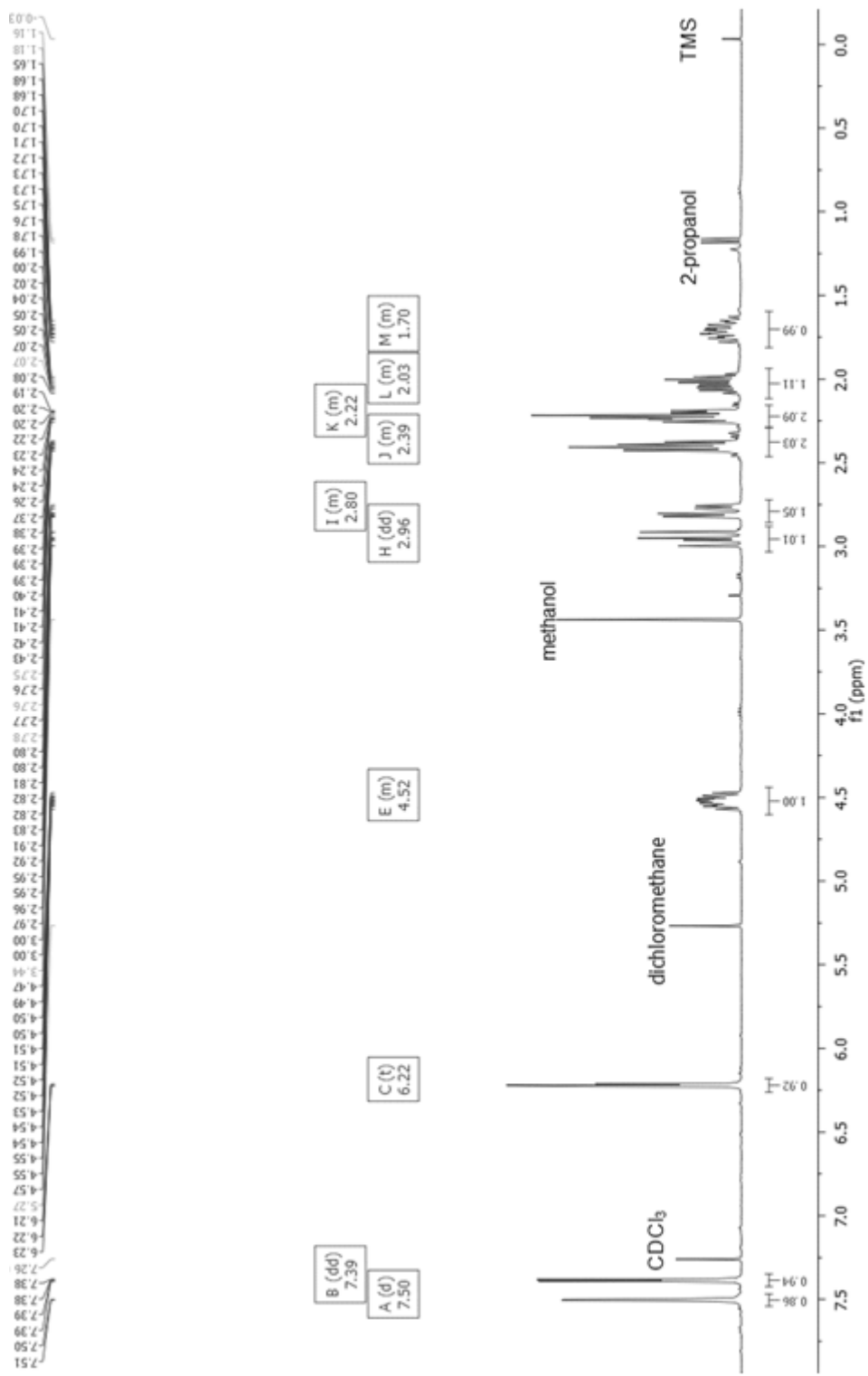
Figure A.30   $^1$H NMR (300 MHz, CDCl$_3$) spectrum of isolated product (Table 3.4, Entry 4)

21.81
31.85
40.70
47.74
59.80
76.95
77.16
77.37
CDCl₃
105.42
127.56
139.49
208.02

Figure A.31 ¹³C NMR (150 MHz, CDCl₃) spectrum of isolated product (Table 3.4, Entry 4)
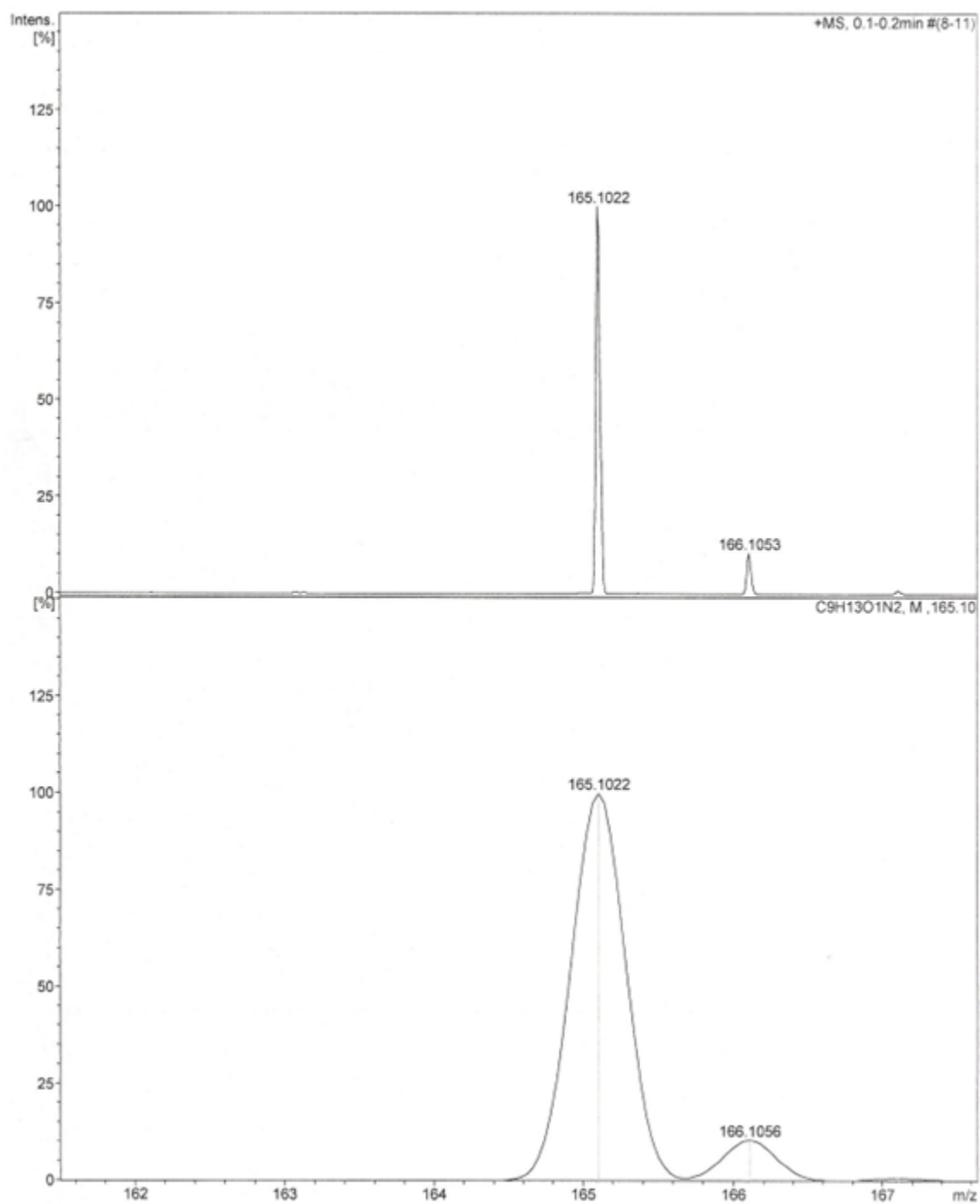
Figure A.32   HRMS of isolated product (Table 3.4, Entry 4)

HRMS-ESI (m/z): [M+H]$^+$ calcd (bottom) for C$_9$H$_{13}$N$_2$O, 165.1022, found (top) 165.1022
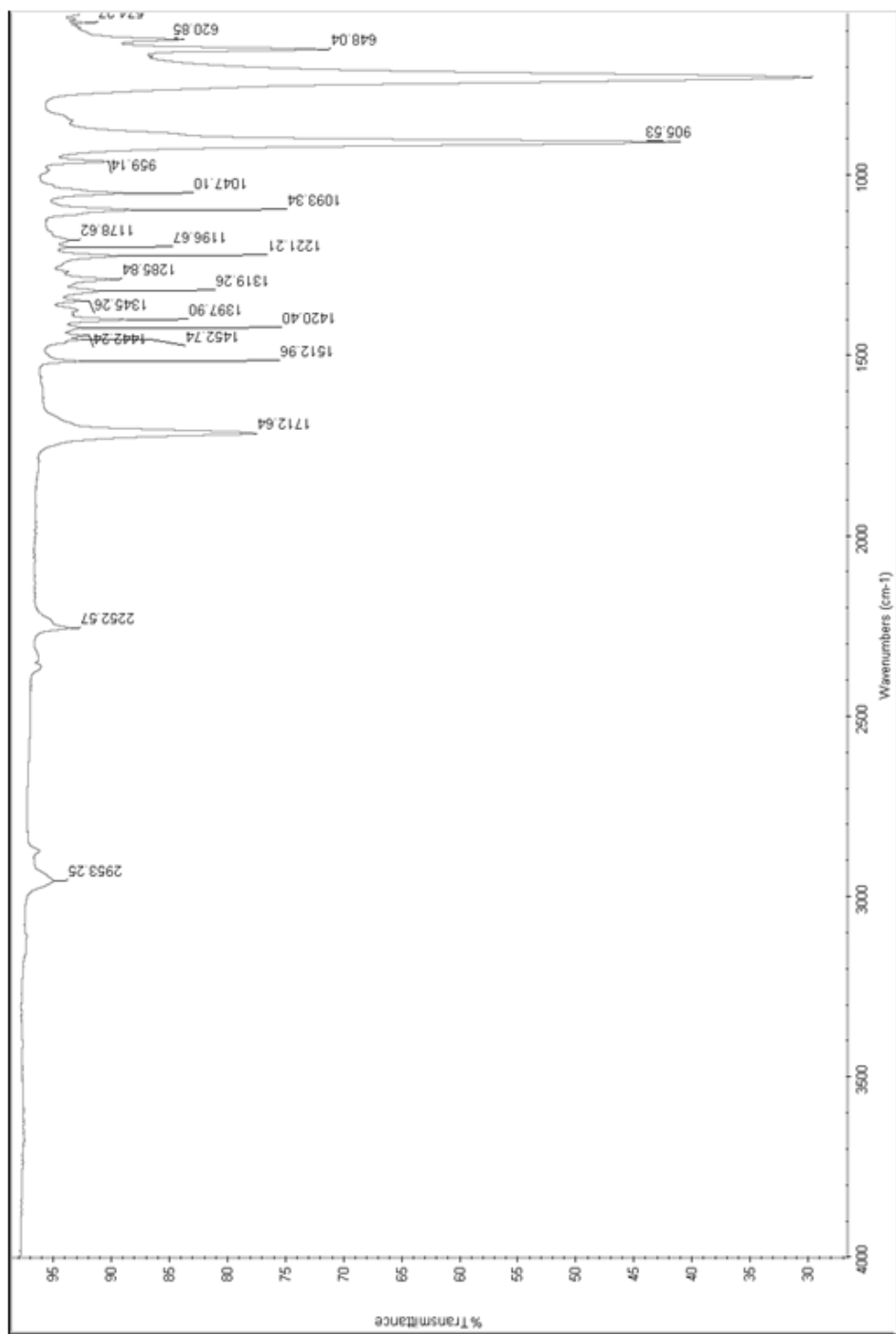
Figure A.33   IR spectrum of isolated product (Table 3.4, Entry 4)

**A.3    Chapter IV Compounds**
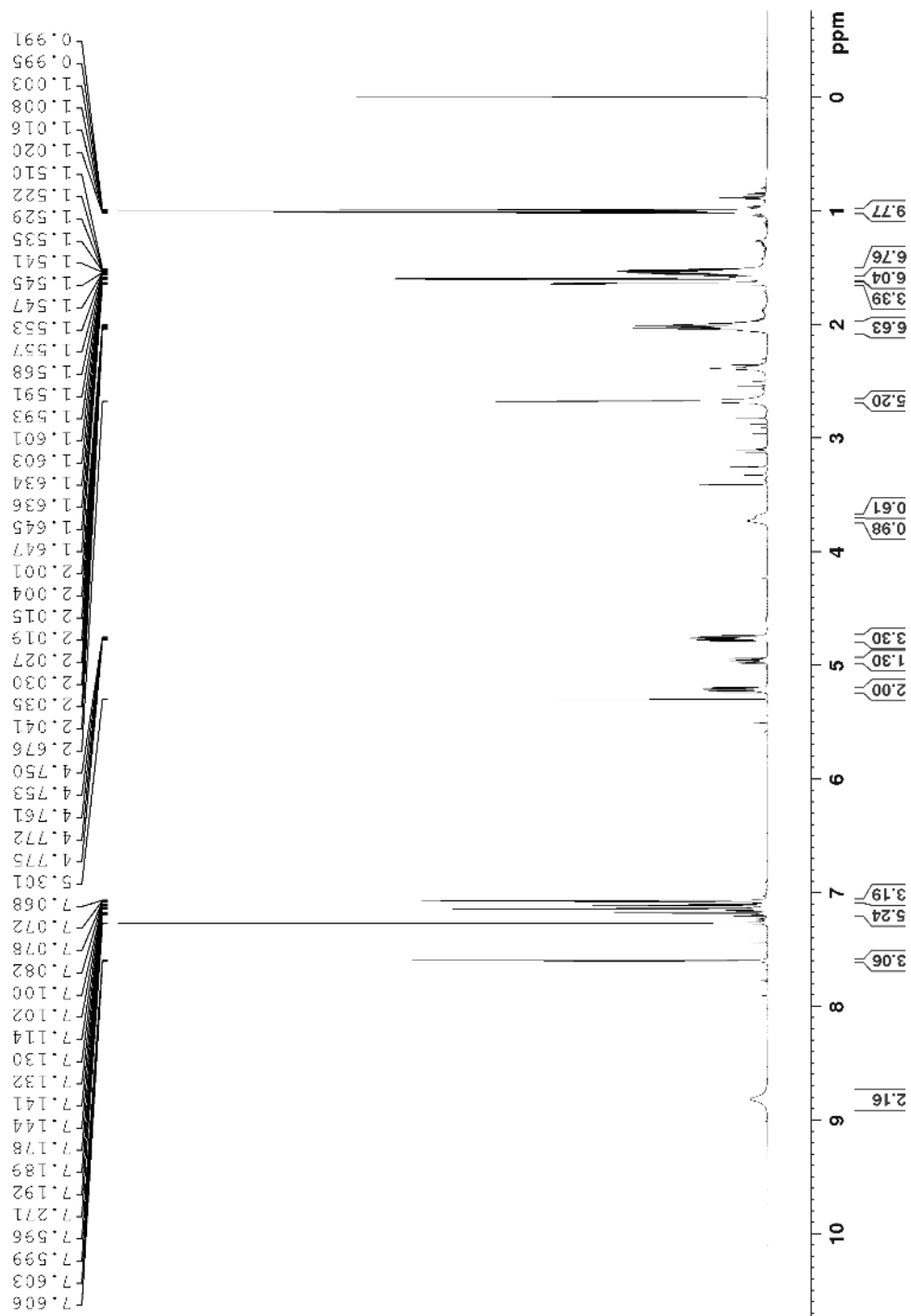


Figure A.34  ¹H NMR (600 MHz, CDCl₃) spectrum of **10**
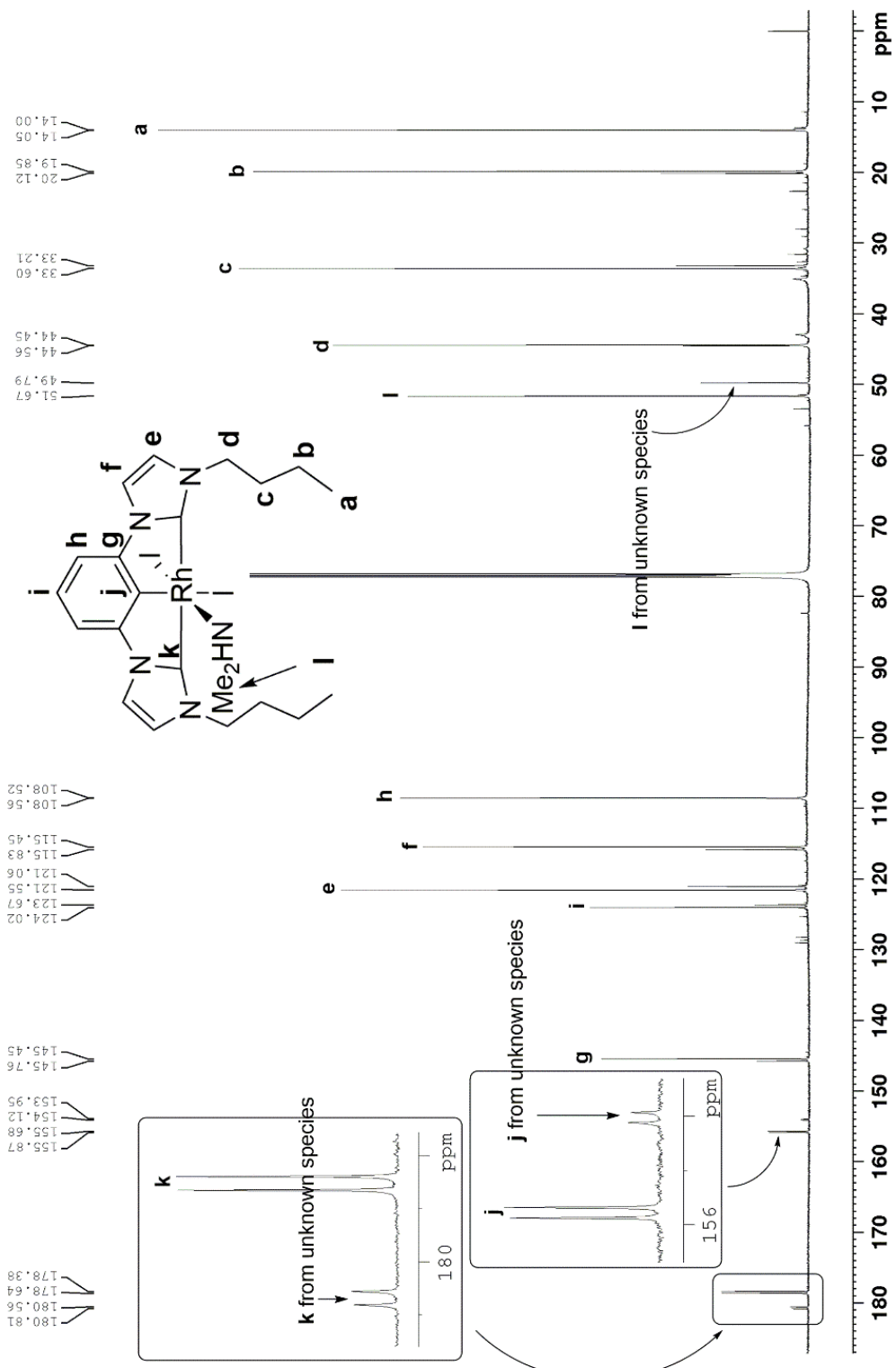
Figure A.35  $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of **10**
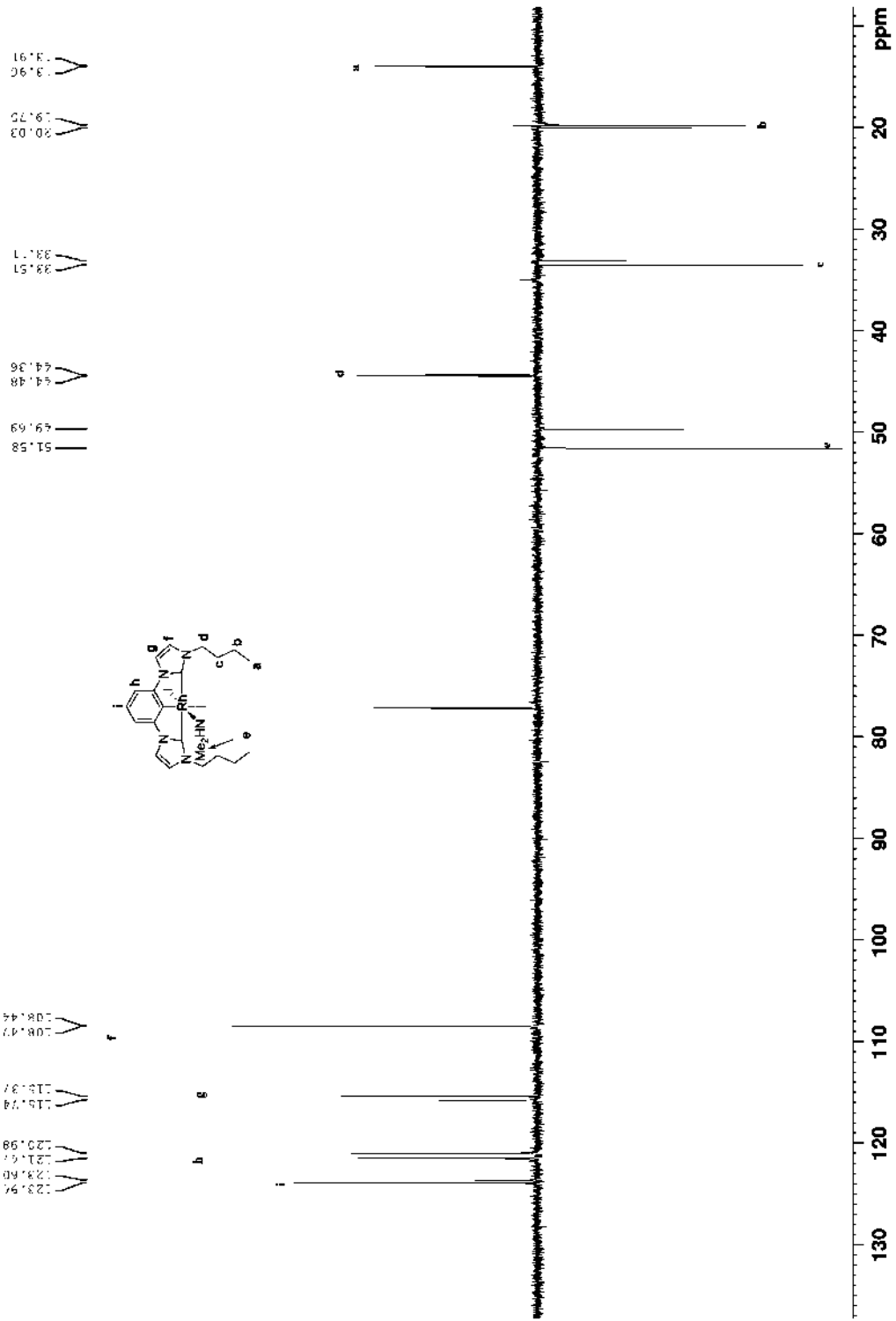
Figure A.36  $^{13}$C DEPT 135 NMR (150 MHz, CDCl$_3$) spectrum of **10**
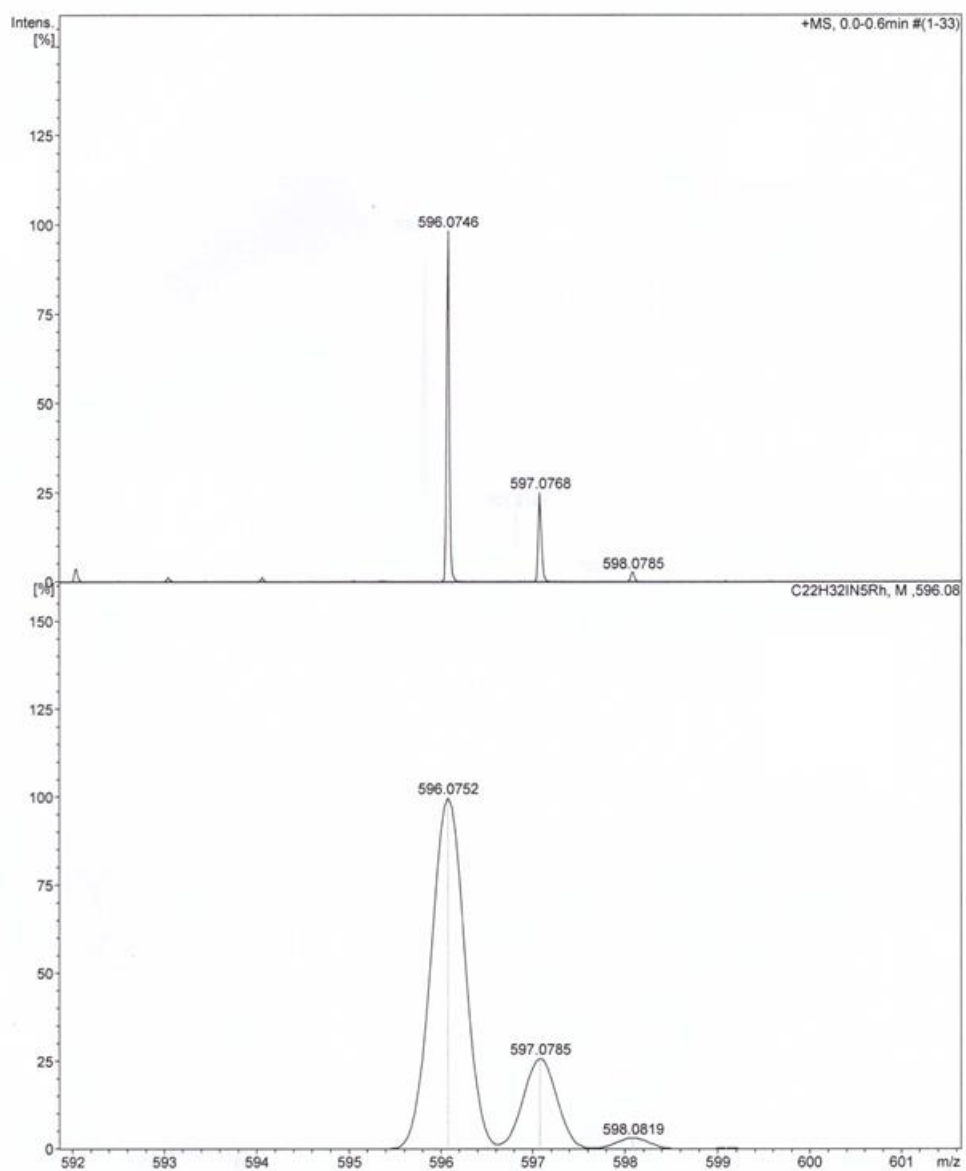
Figure A.37   HRMS of **10**

HRMS-ESI (m/z): [M-I]$^+$ calcd (bottom) for C$_{22}$H$_{32}$IN$_5$Rh, 596.0752; found (top), 596.0740

Figure A.38   GC-MS chromatogram spectrum of catalytic trial (Table 4.1, Entry 2)

140
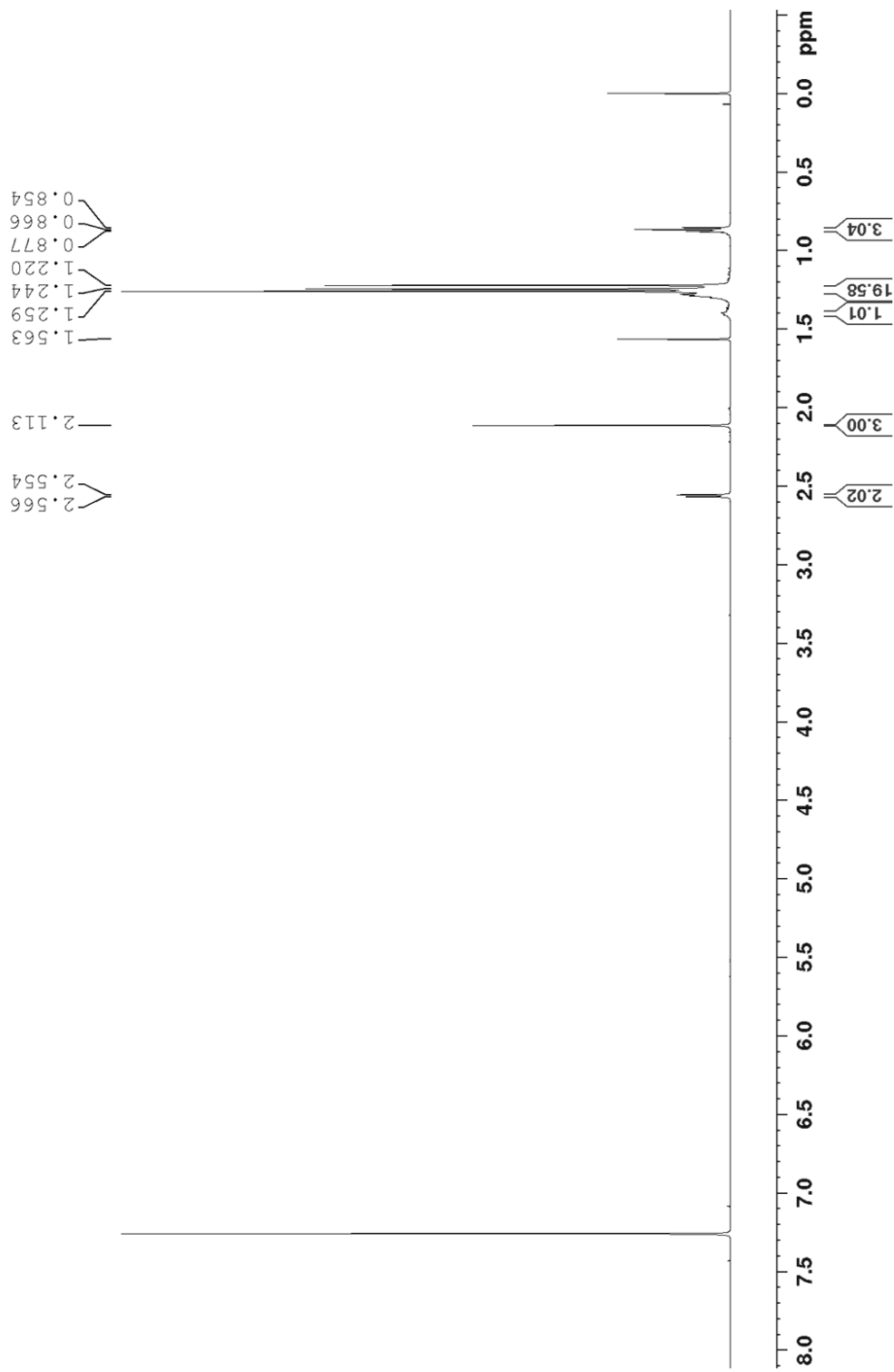
Figure A.39  $^1$H NMR spectrum (600 MHz, CDCl$_3$) of isolated product (Table 4.1, Entry 2)

141

Figure A.40  $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.1, Entry 2)

142
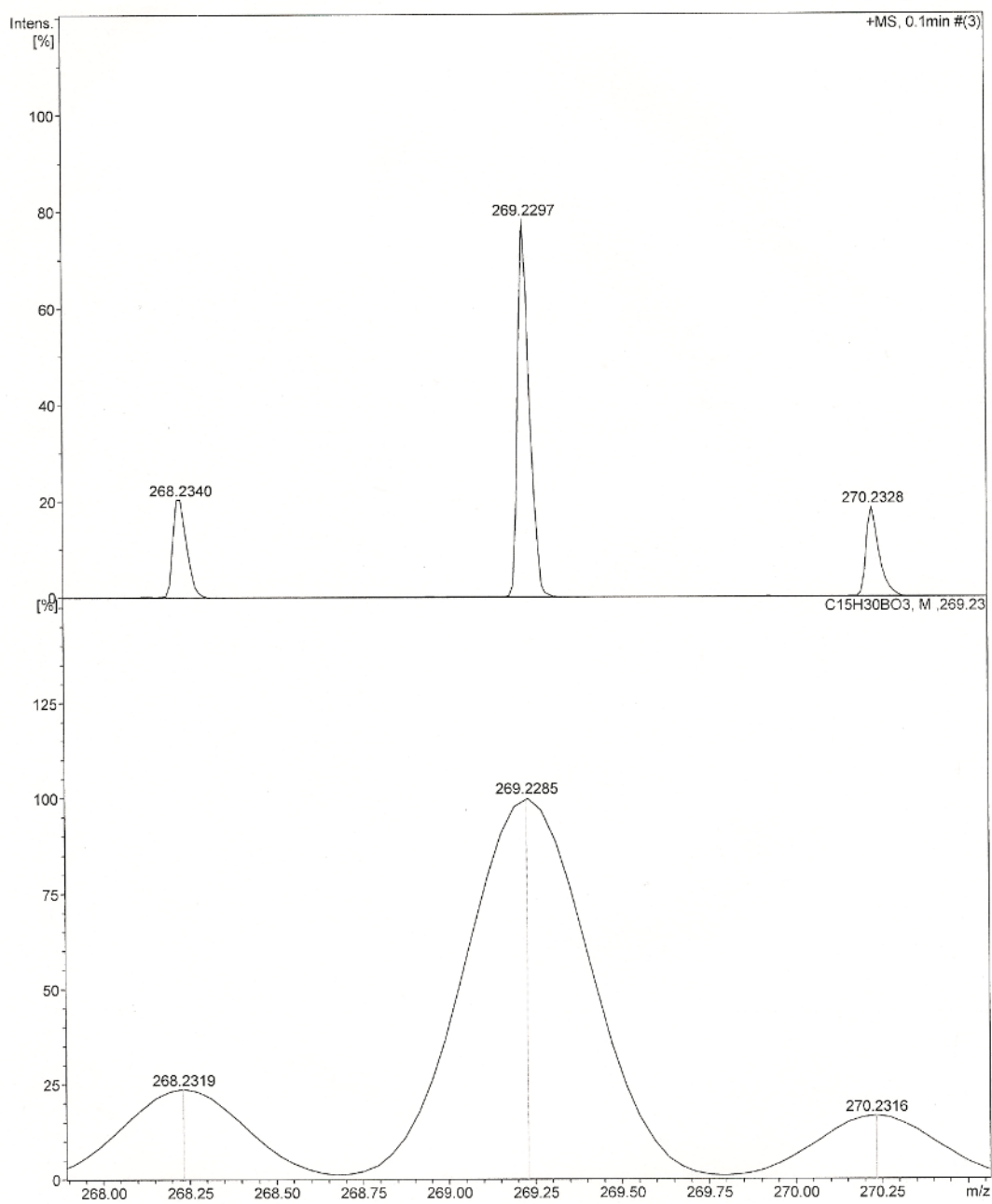
Figure A.41   HRMS of product (Table 4.1, Entry 2)

HRMS-ESI (m/z): [M+H]$^+$ calcd (bottom) for $C_{15}H_{30}BO_3$, 269.2285; found (top) 269.2297
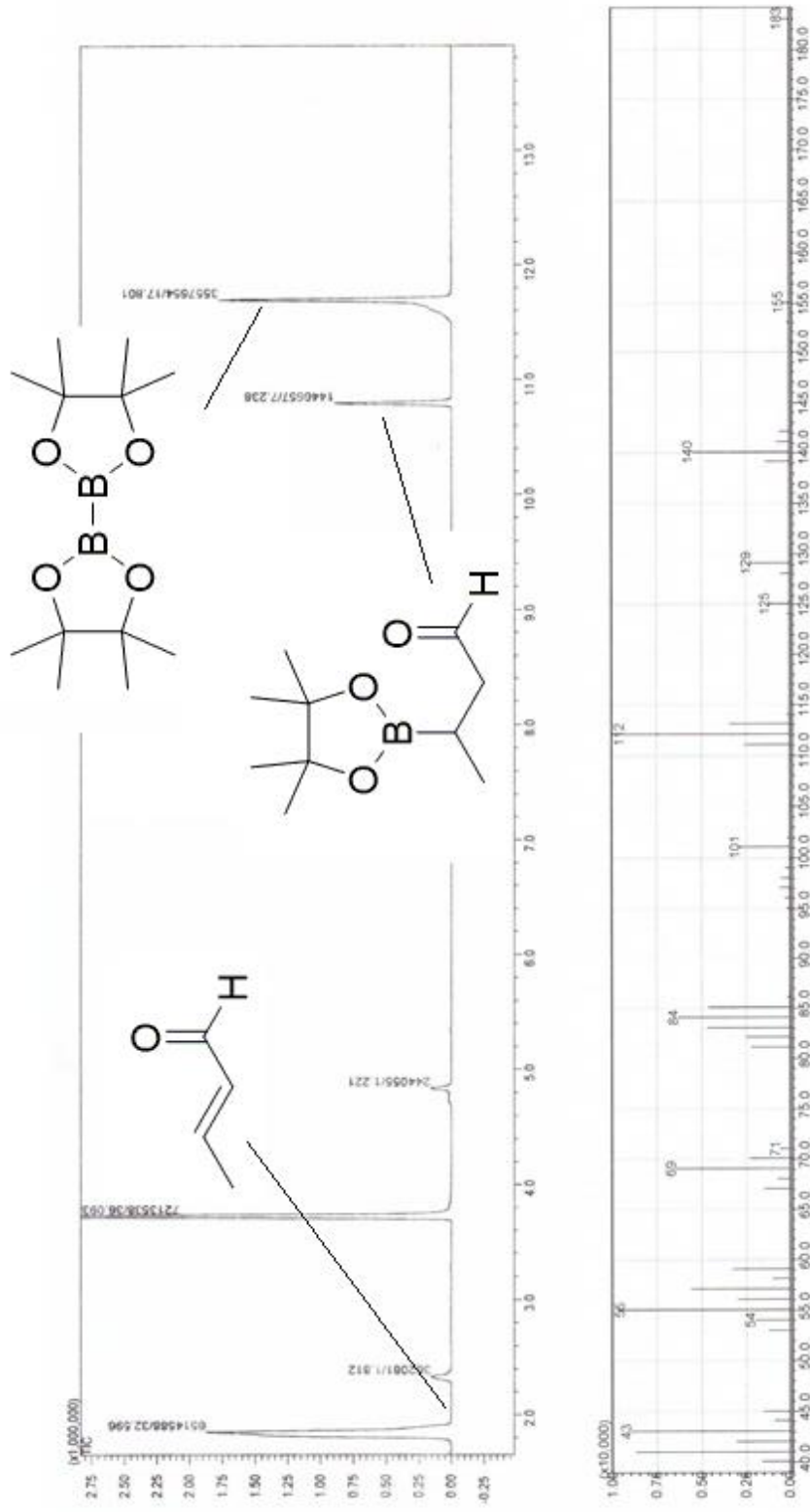
Figure A.42   GC-MS chromatogram spectrum of catalytic trial (Table 4.2, Entry 1)
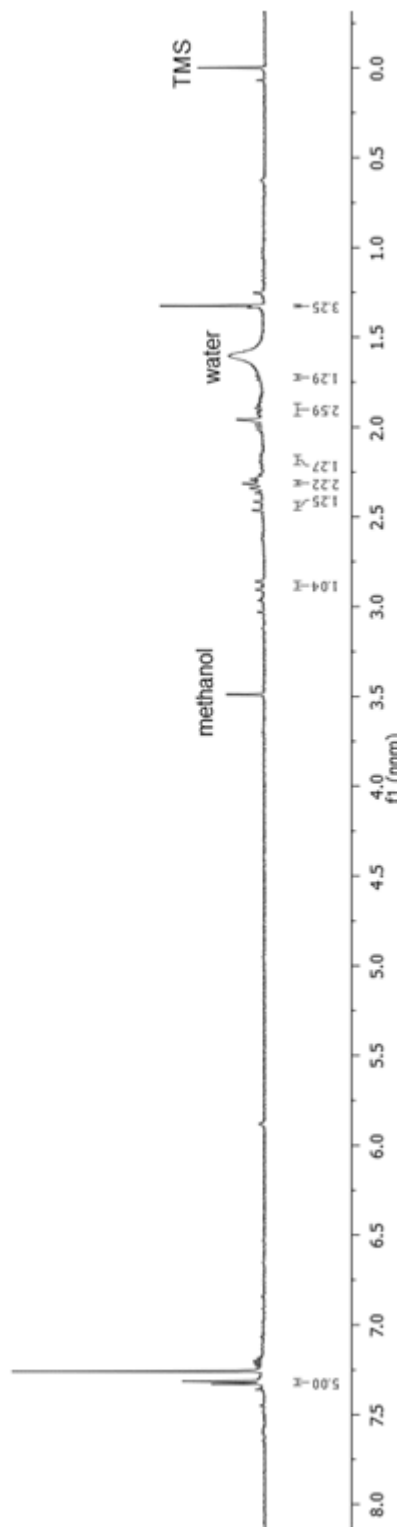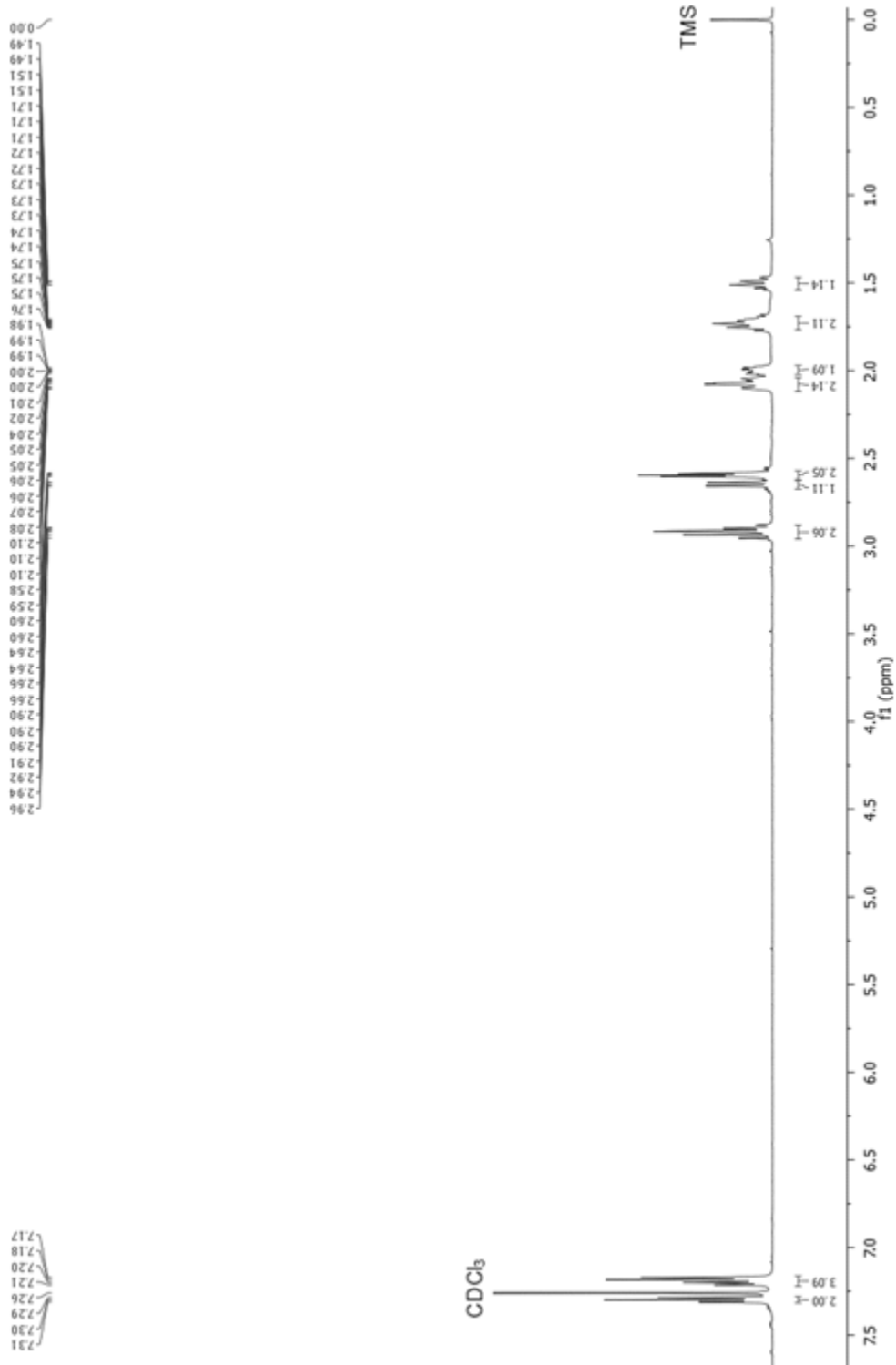
144
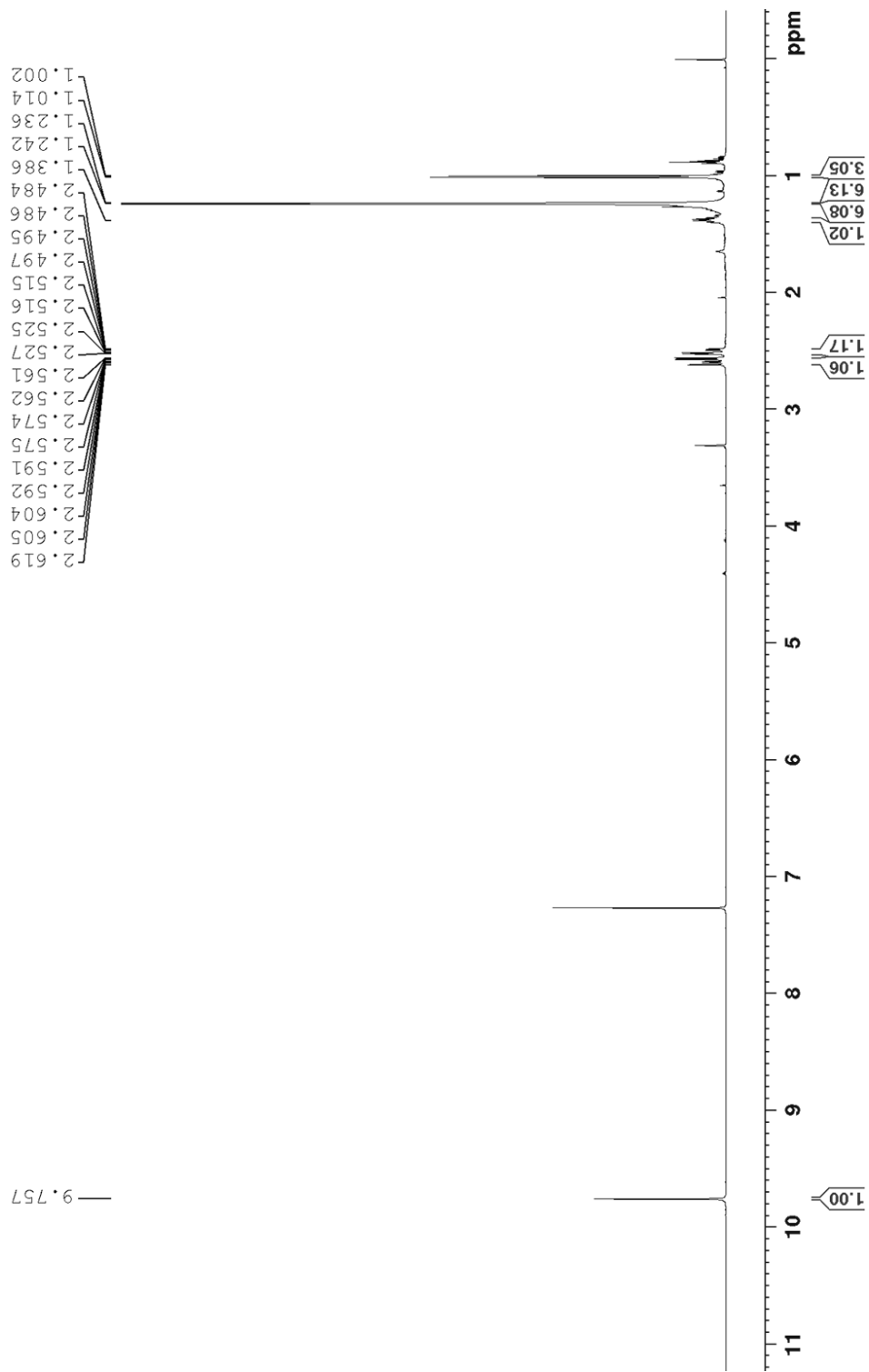
Figure A.43  $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 1)
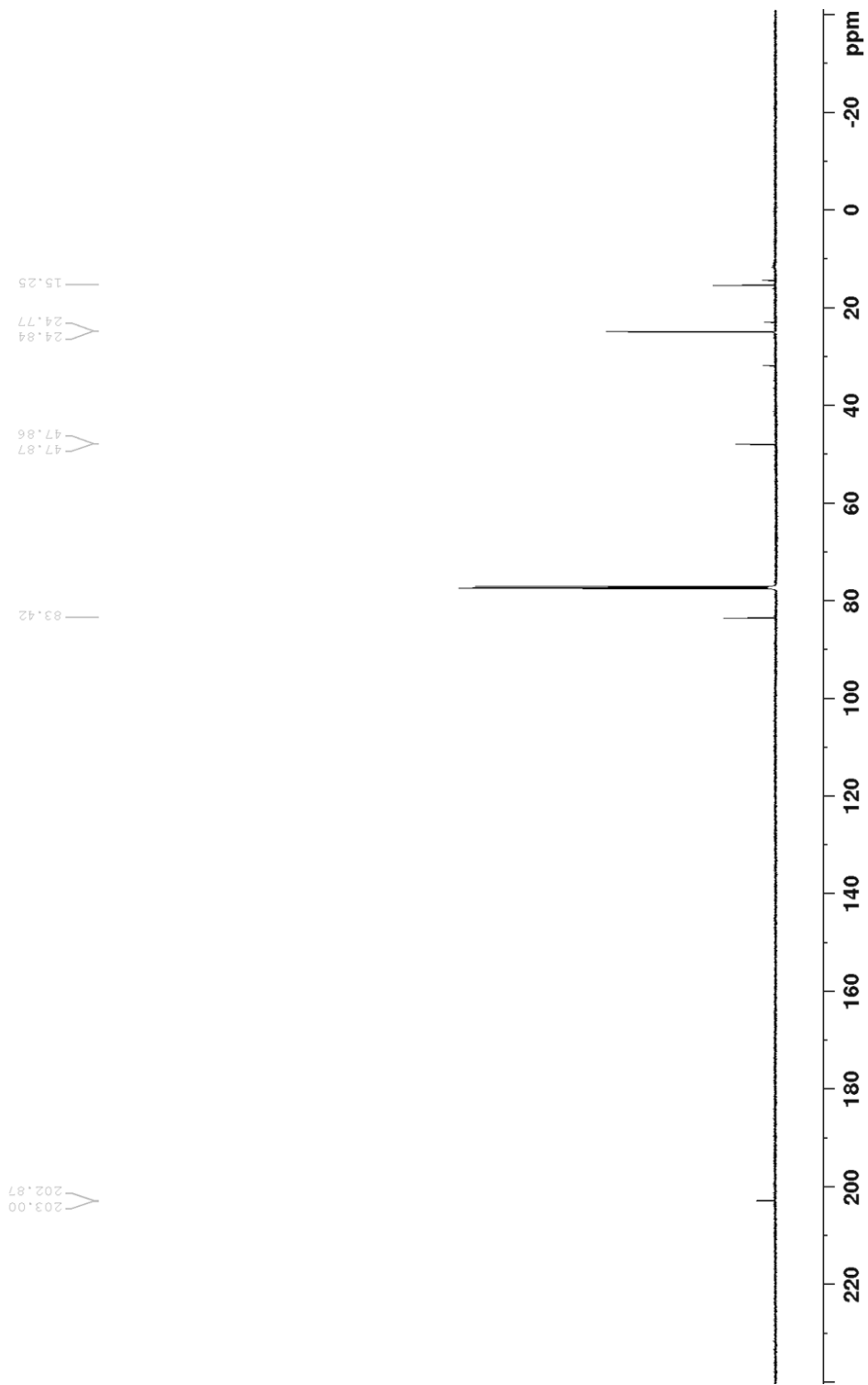
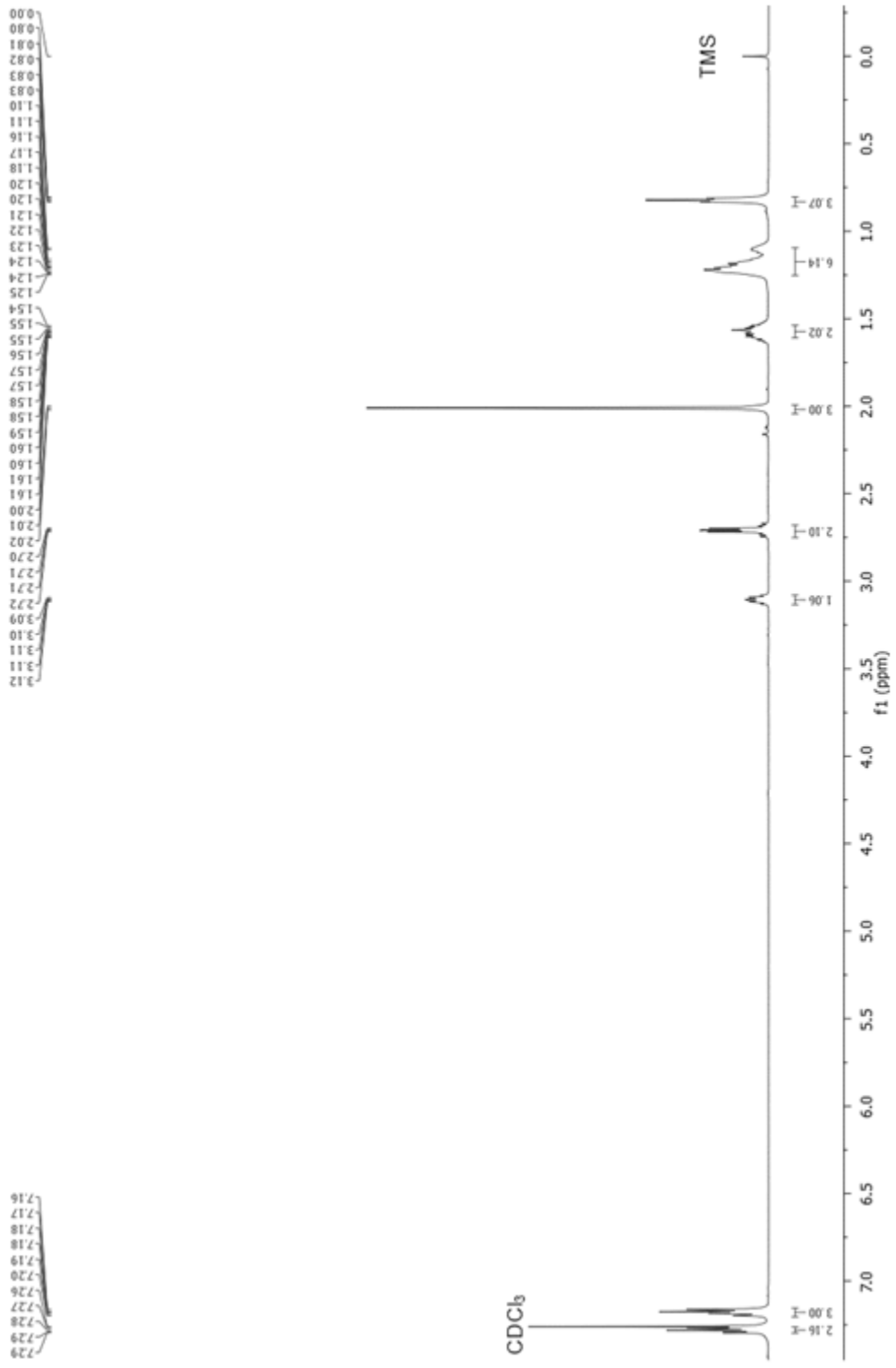Figure A.44  $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 1)
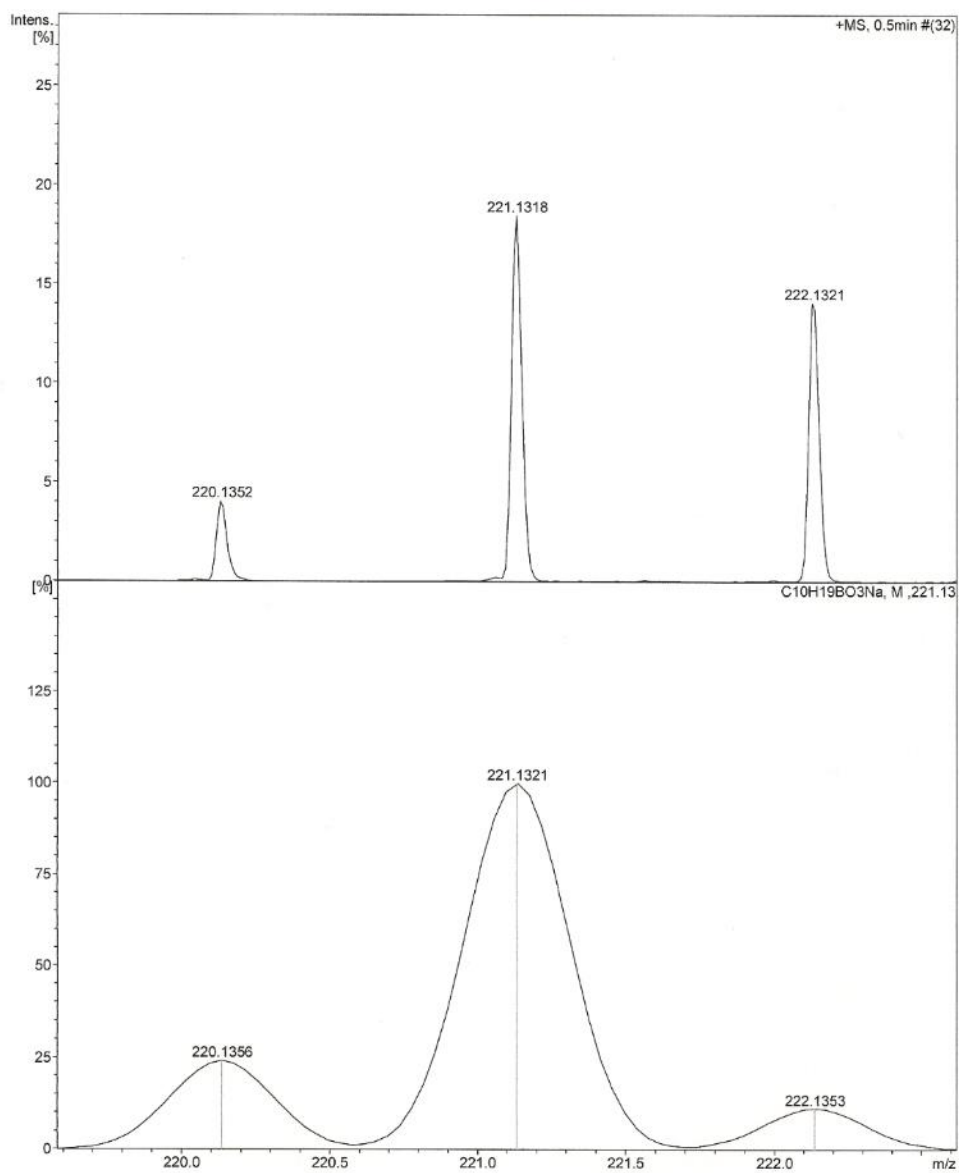
Figure A.45   HRMS of product (Table 4.2, Entry 1)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (B) for C$_{10}$H$_{19}$BO$_3$, 199.1502; found (A), 199.1506
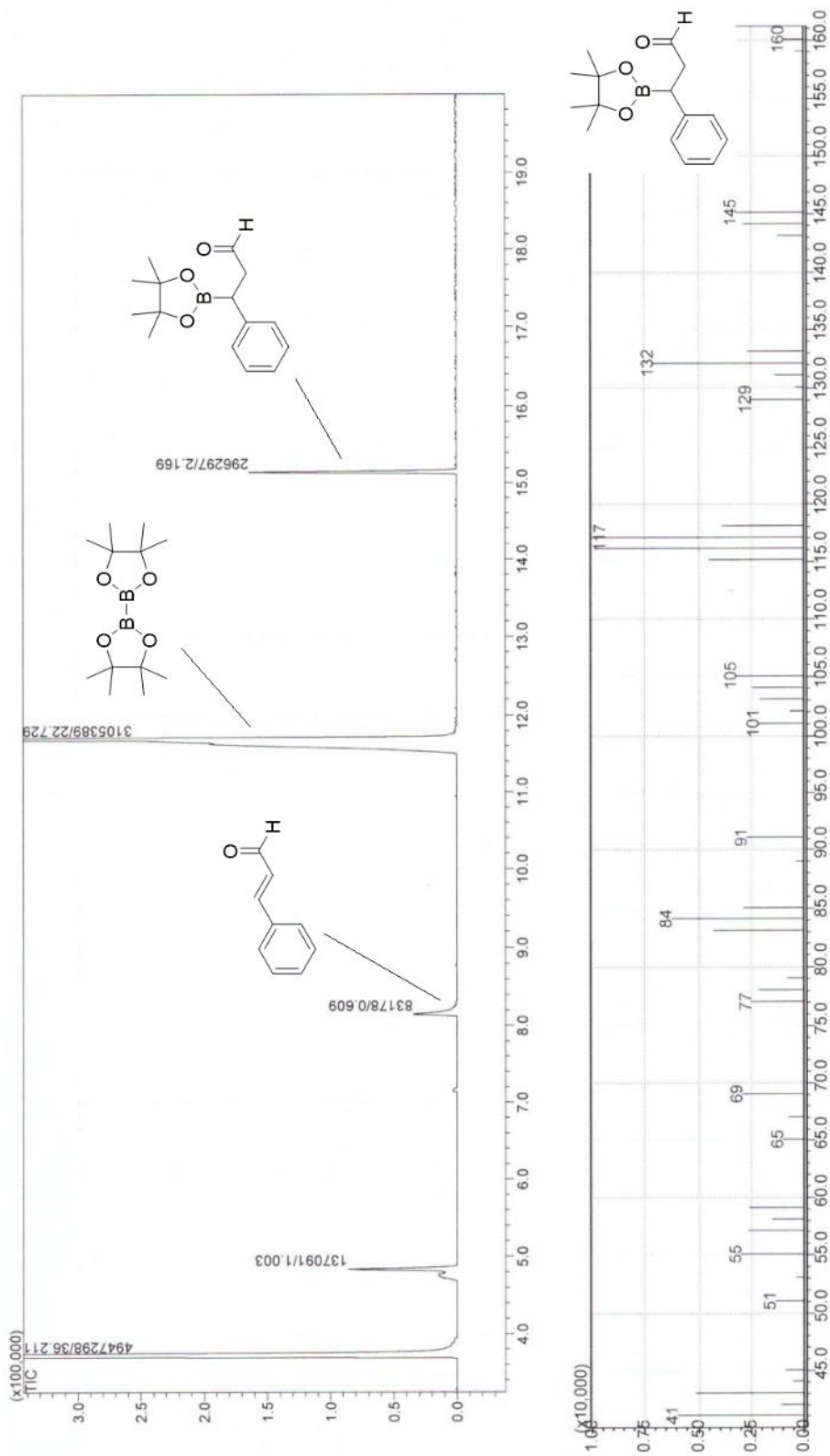
Figure A.46   GC-MS chromatogram spectrum of catalytic trial (Table 4.2, Entry 2)

148
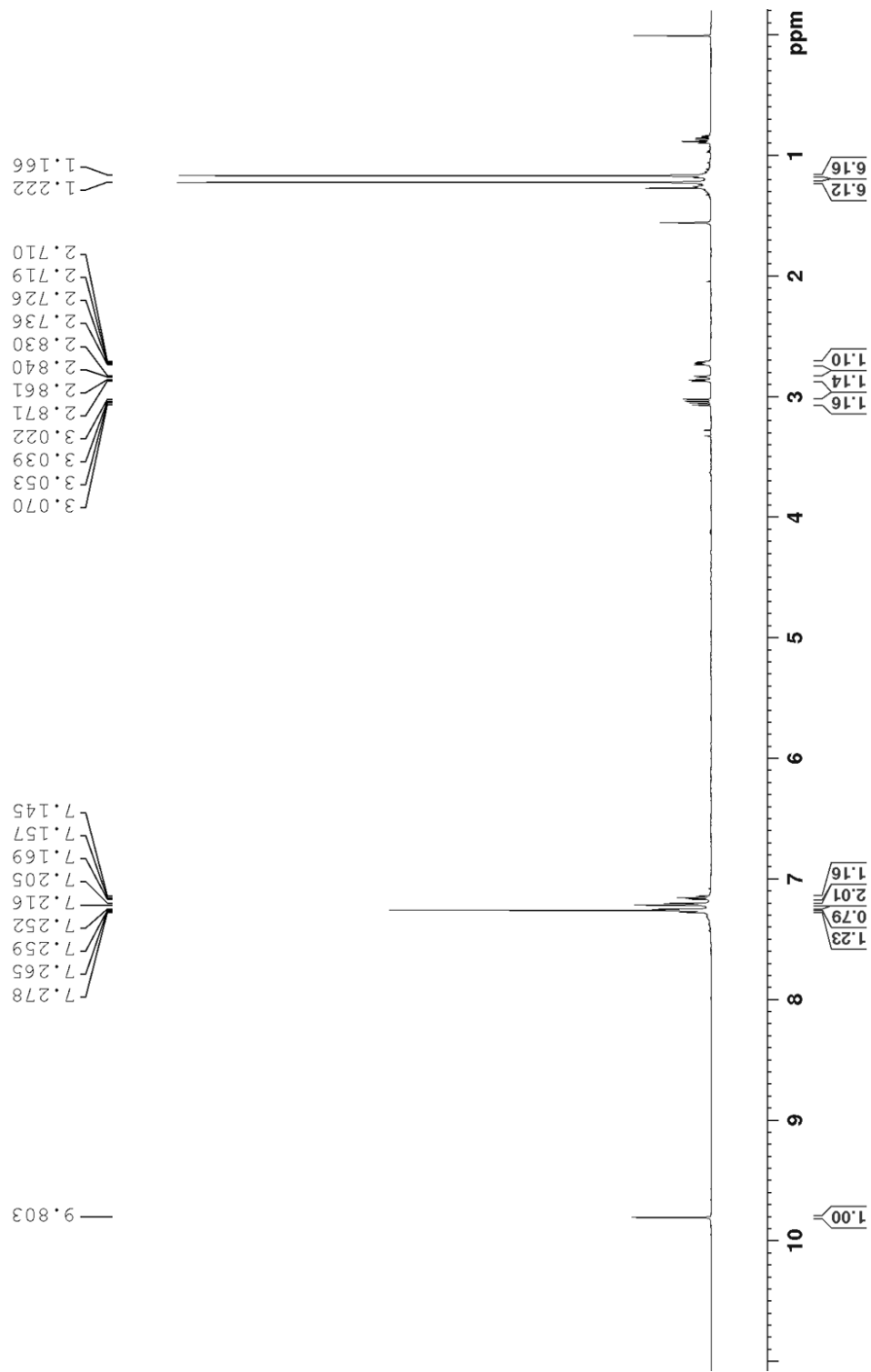
Figure A.47 $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 2)

24.63
24.70

47.70
47.72

83.81

125.88
128.34
128.74

141.35

201.93
202.07

220  200  180  160  140  120  100  80  60  40  20  0  -20  ppm
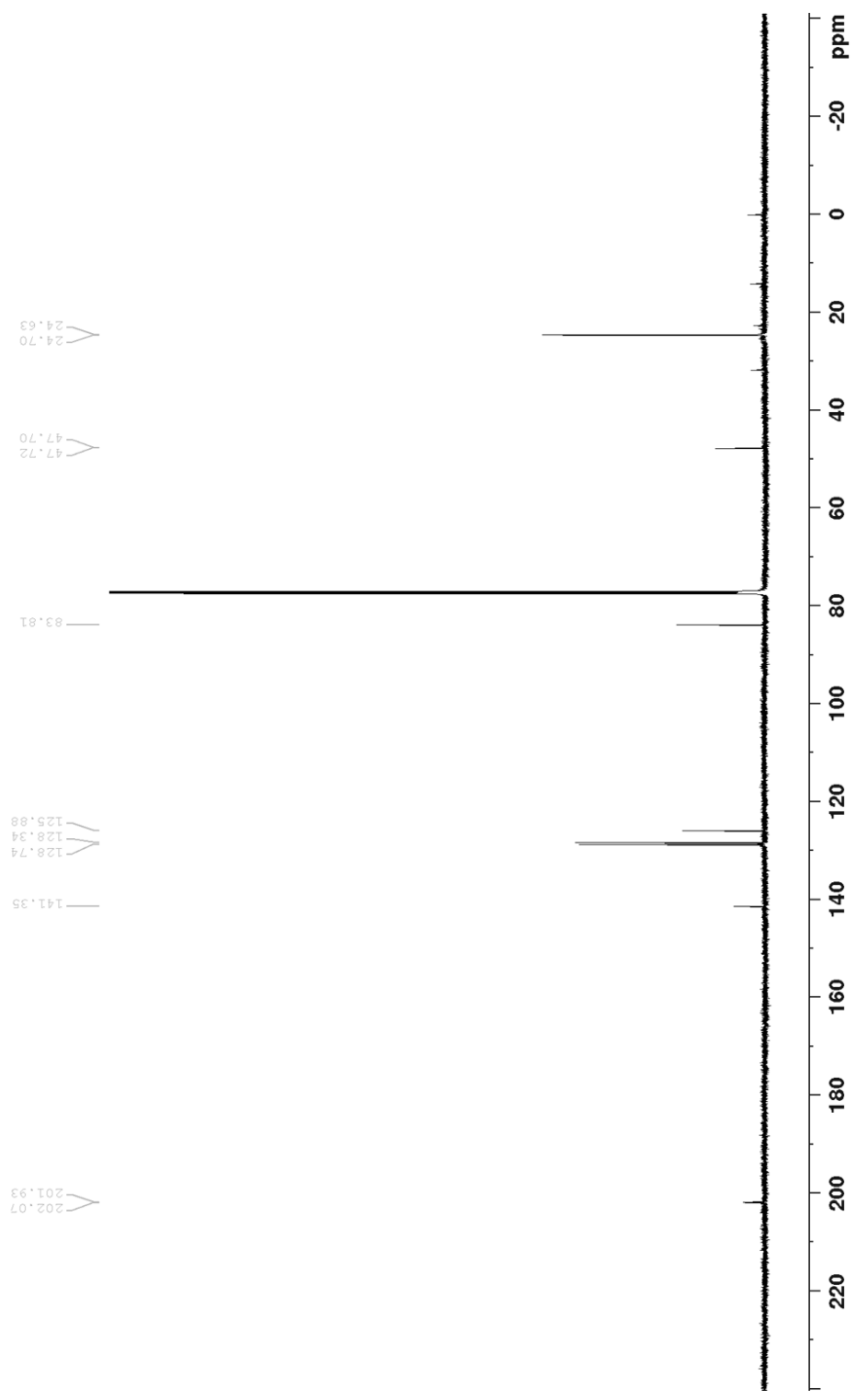
Figure A.48    $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 2)

150
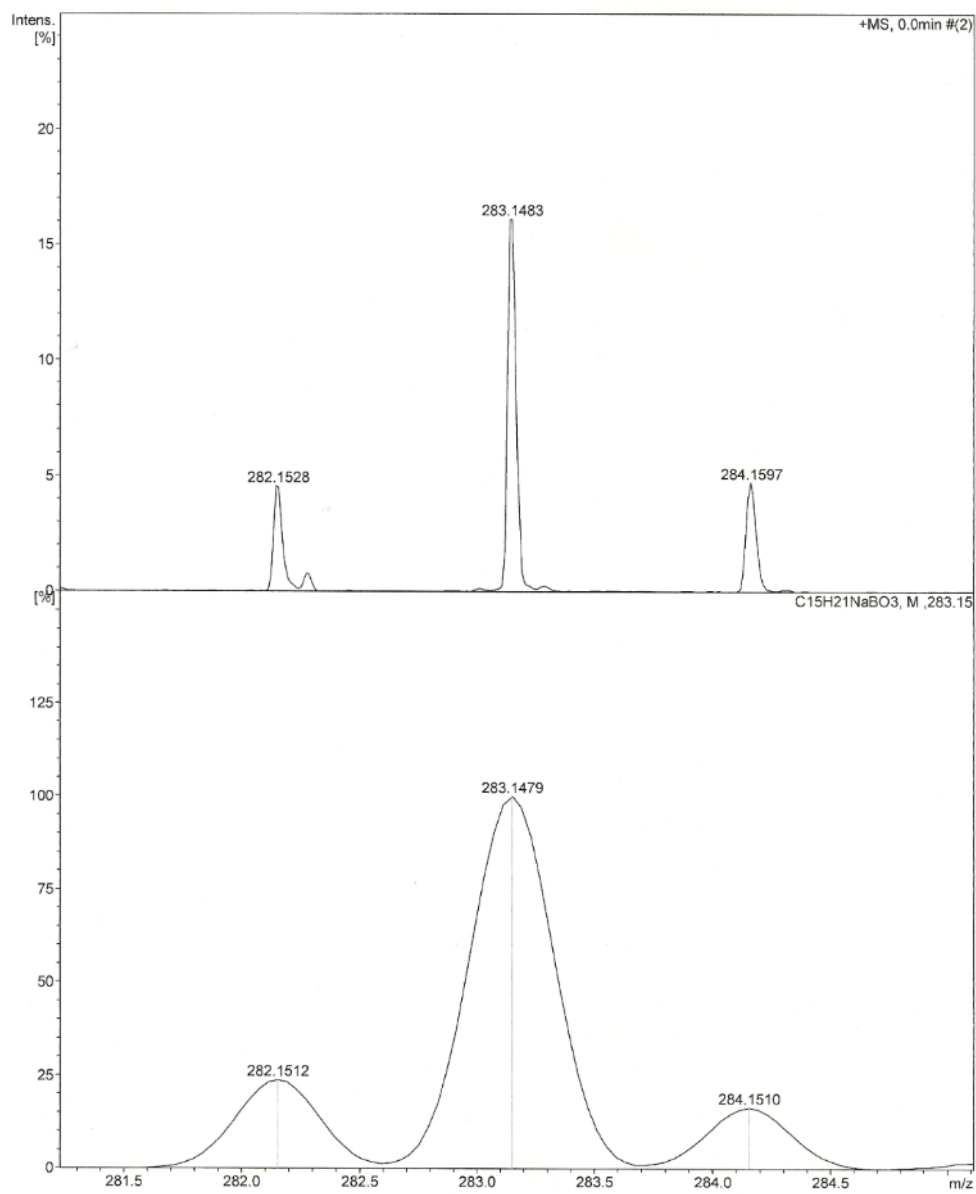
Figure A.49   HRMS of product (Table 4.2, Entry 2)

HRMS-ESI (*m/z*): [M-OH]$^+$ calcd (bottom) for C$_{15}$H$_{20}$BO$_2$, 243.1554; found (top) 243.1559
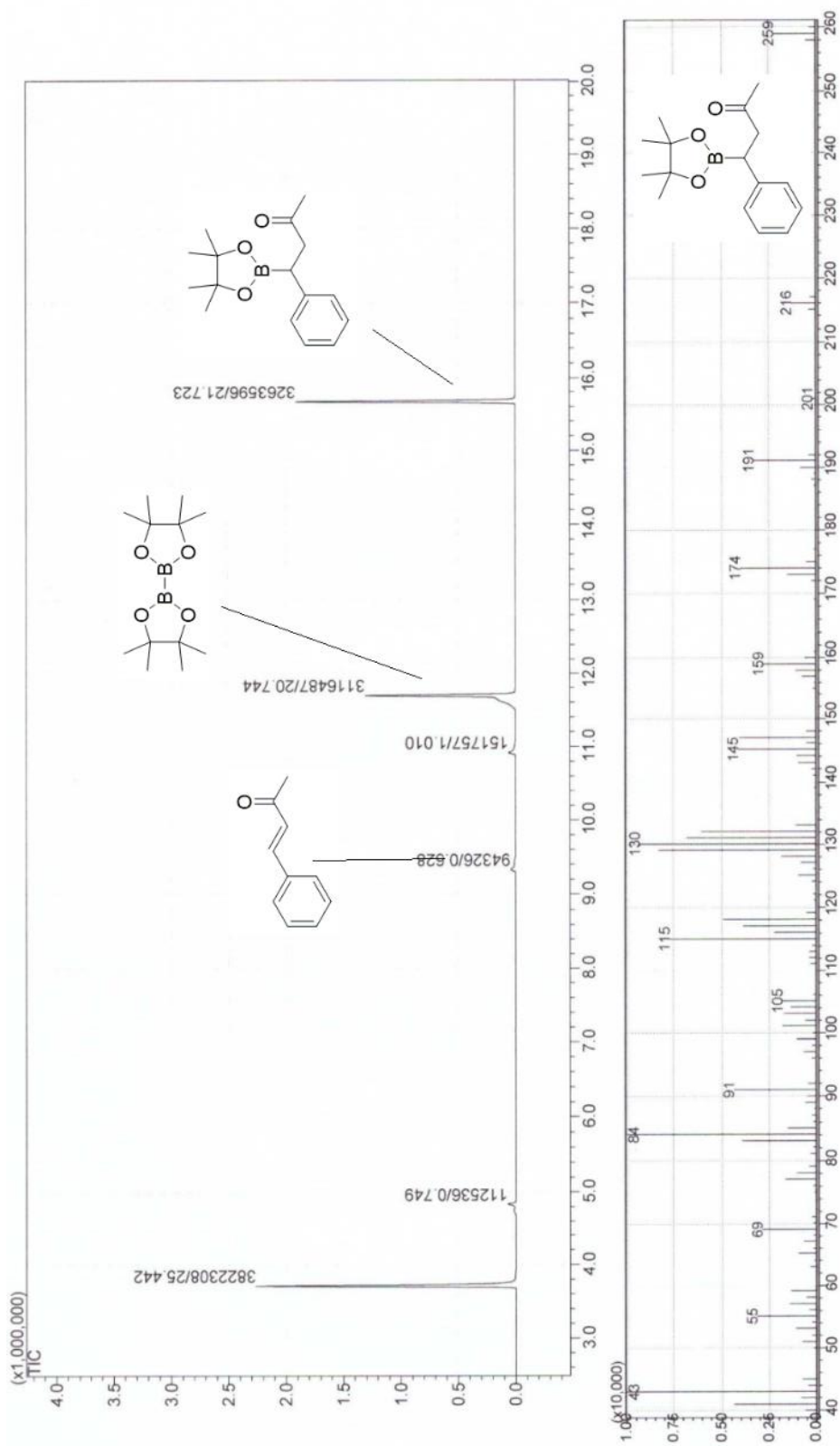
Figure A.50   GC-MS chromatogram spectrum of catalytic trial (Table 4.2, Entry 3)

152
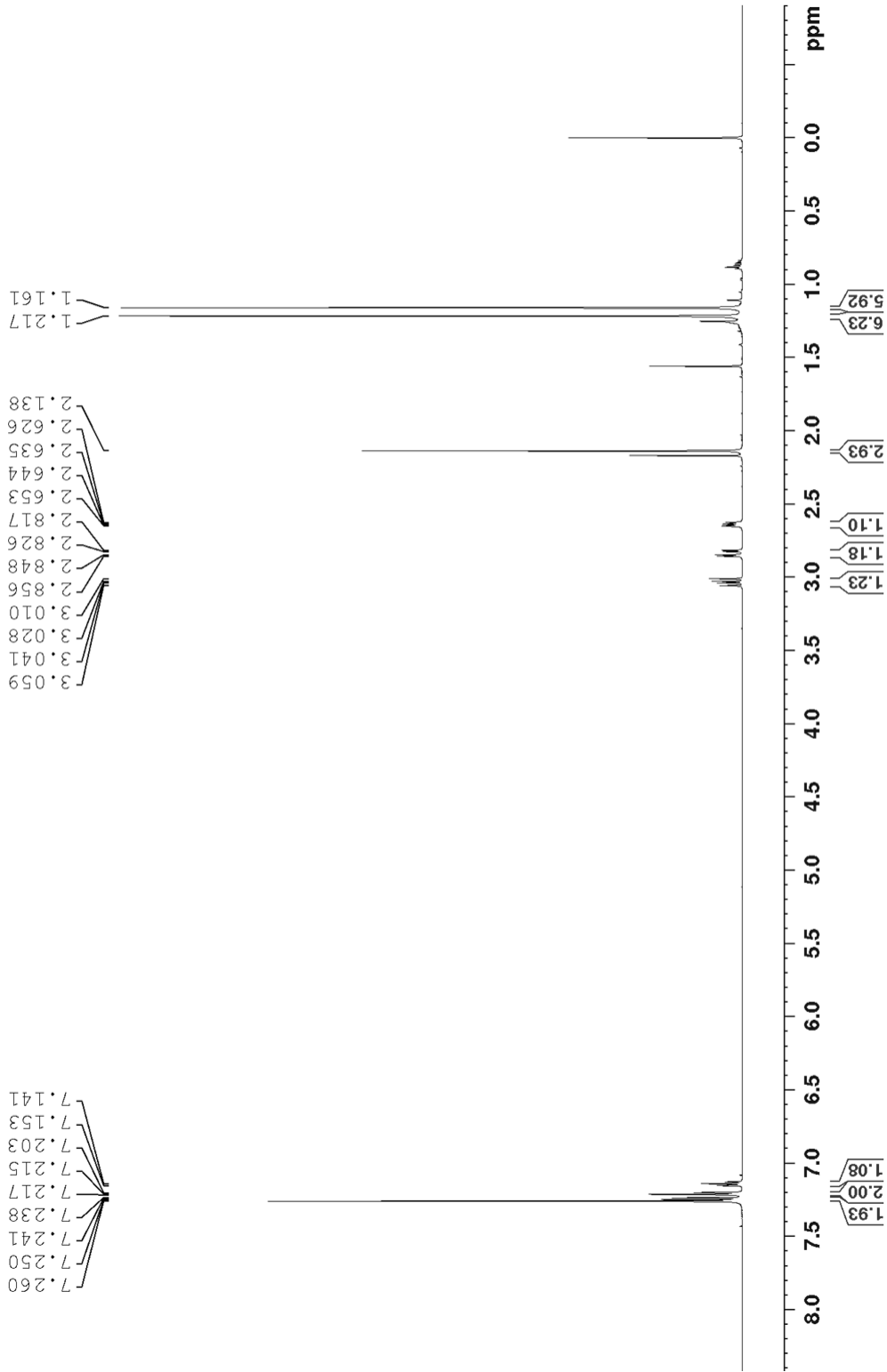
Figure A.51　$^{1}$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 3)

153

208.52
141.82
128.62
128.34
125.69
83.55
47.67
29.76
24.67
24.65
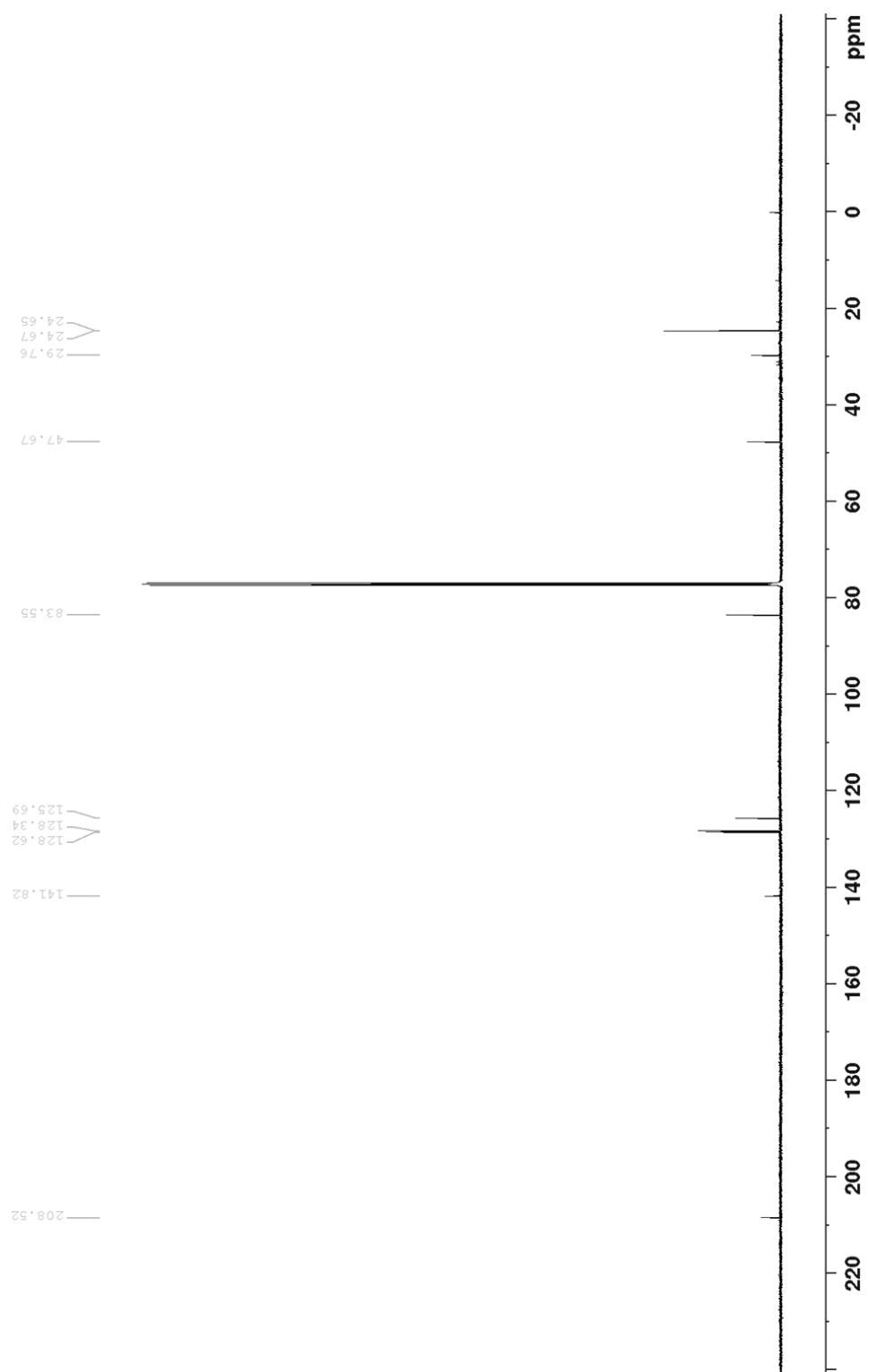
Figure A.52  $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 3)

154
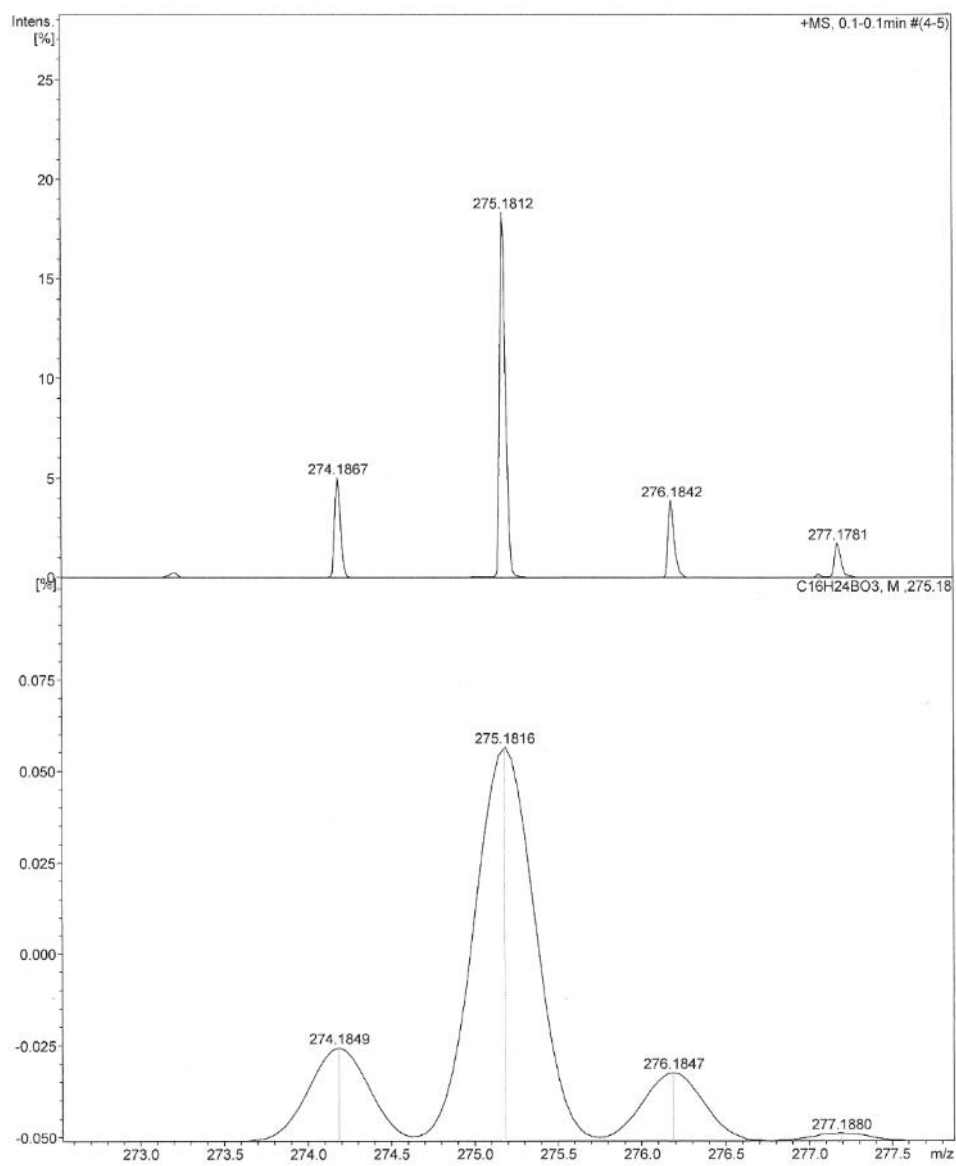
Figure A.53   HRMS of product (Table 4.2, Entry 3)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for C$_{16}$H$_{24}$BO$_3$, 275.1816; found (top) 275.1812
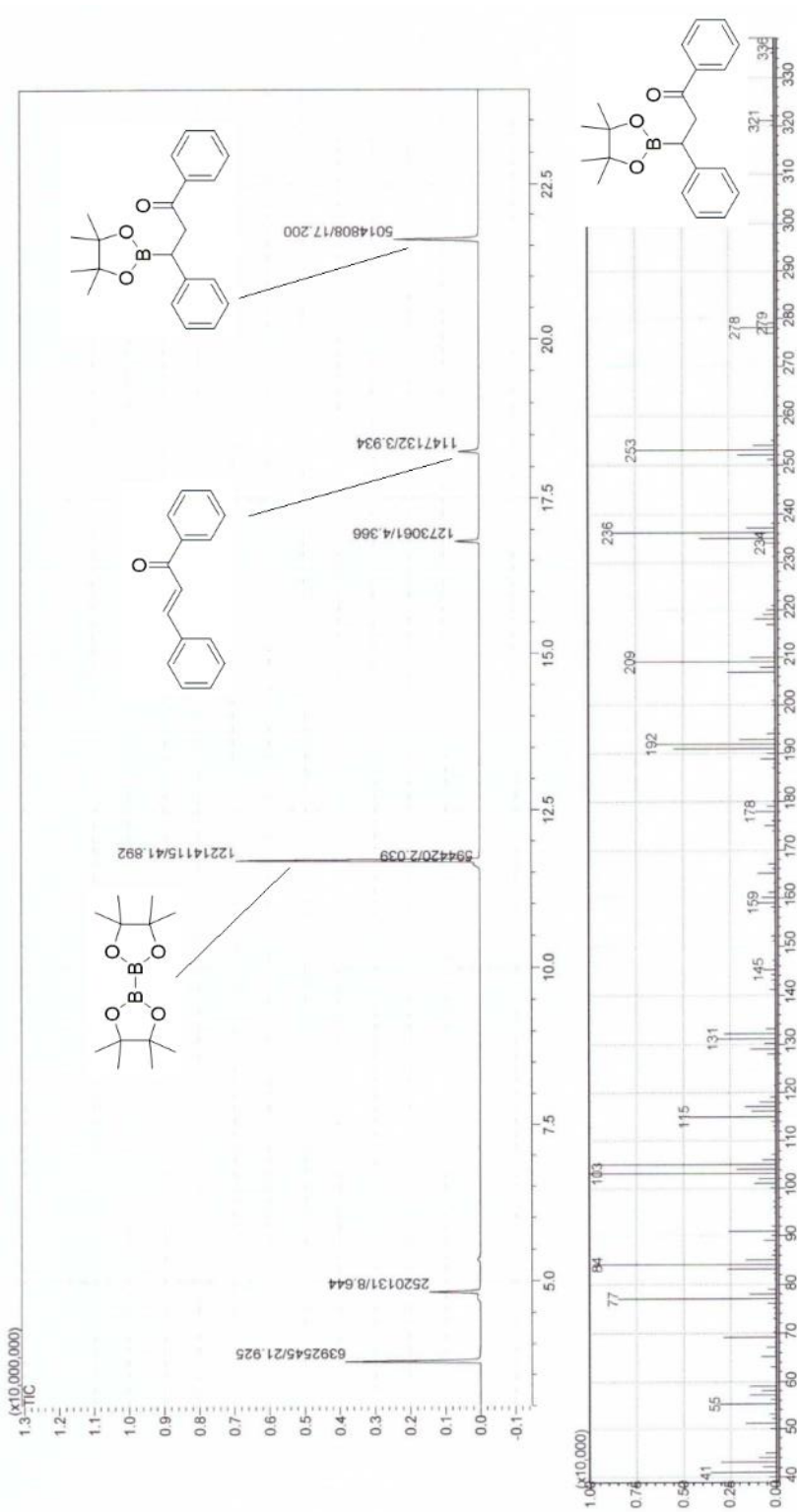
Figure A.54  GC-MS chromatogram spectrum of catalytic trial (Table 4.2, Entry 4)
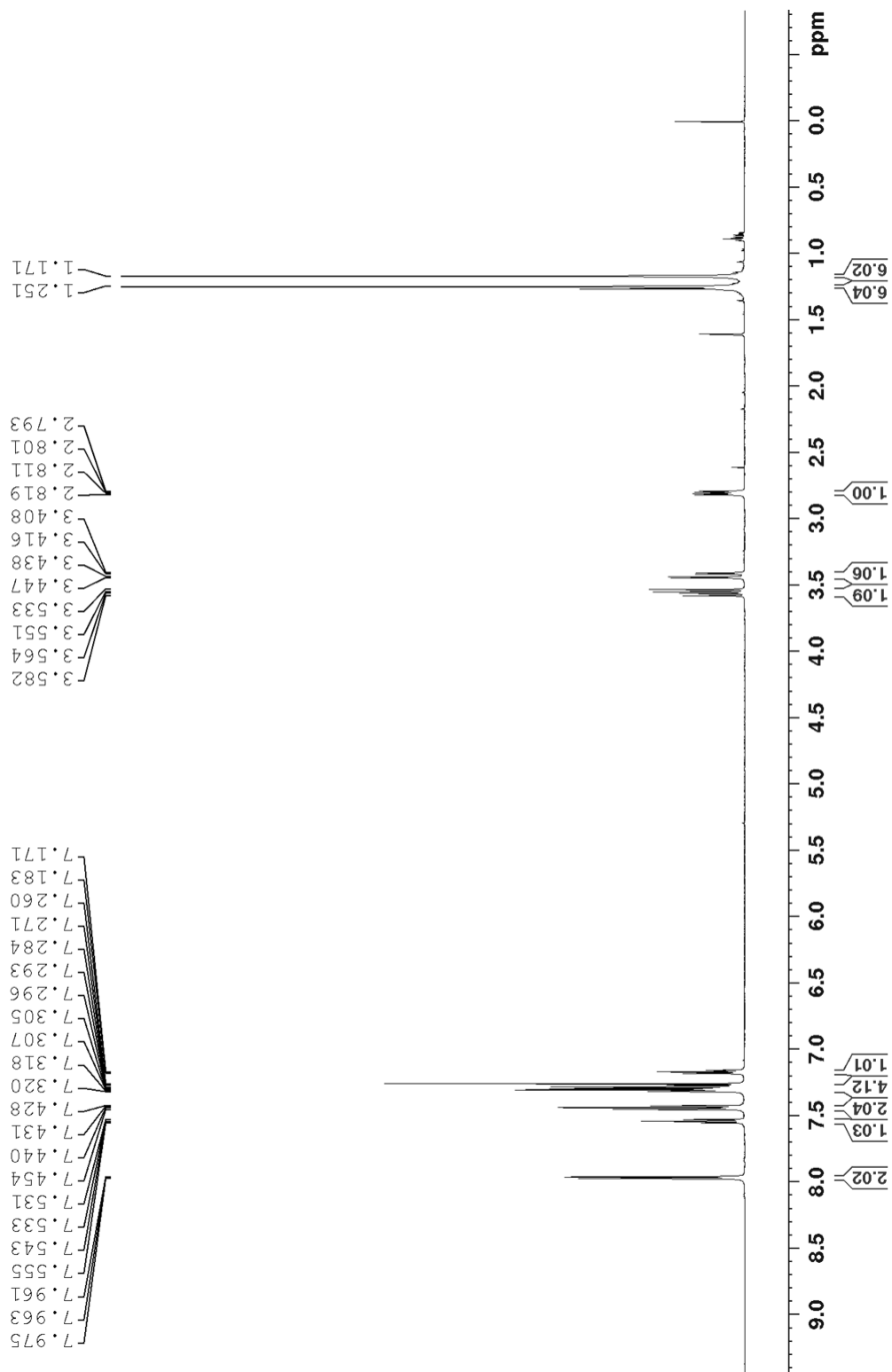
Figure A.55 $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 4)
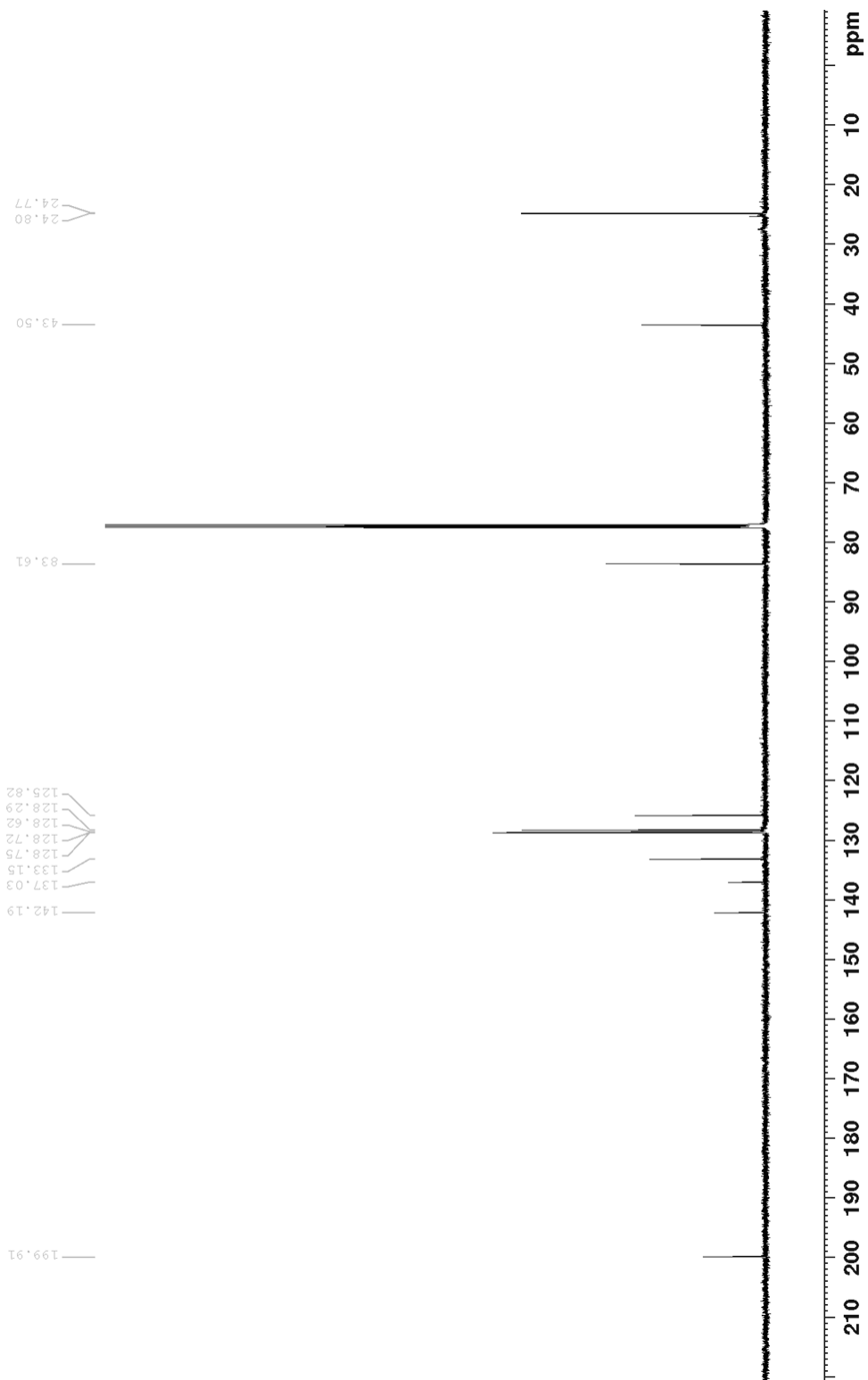
Figure A.56  $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 4)
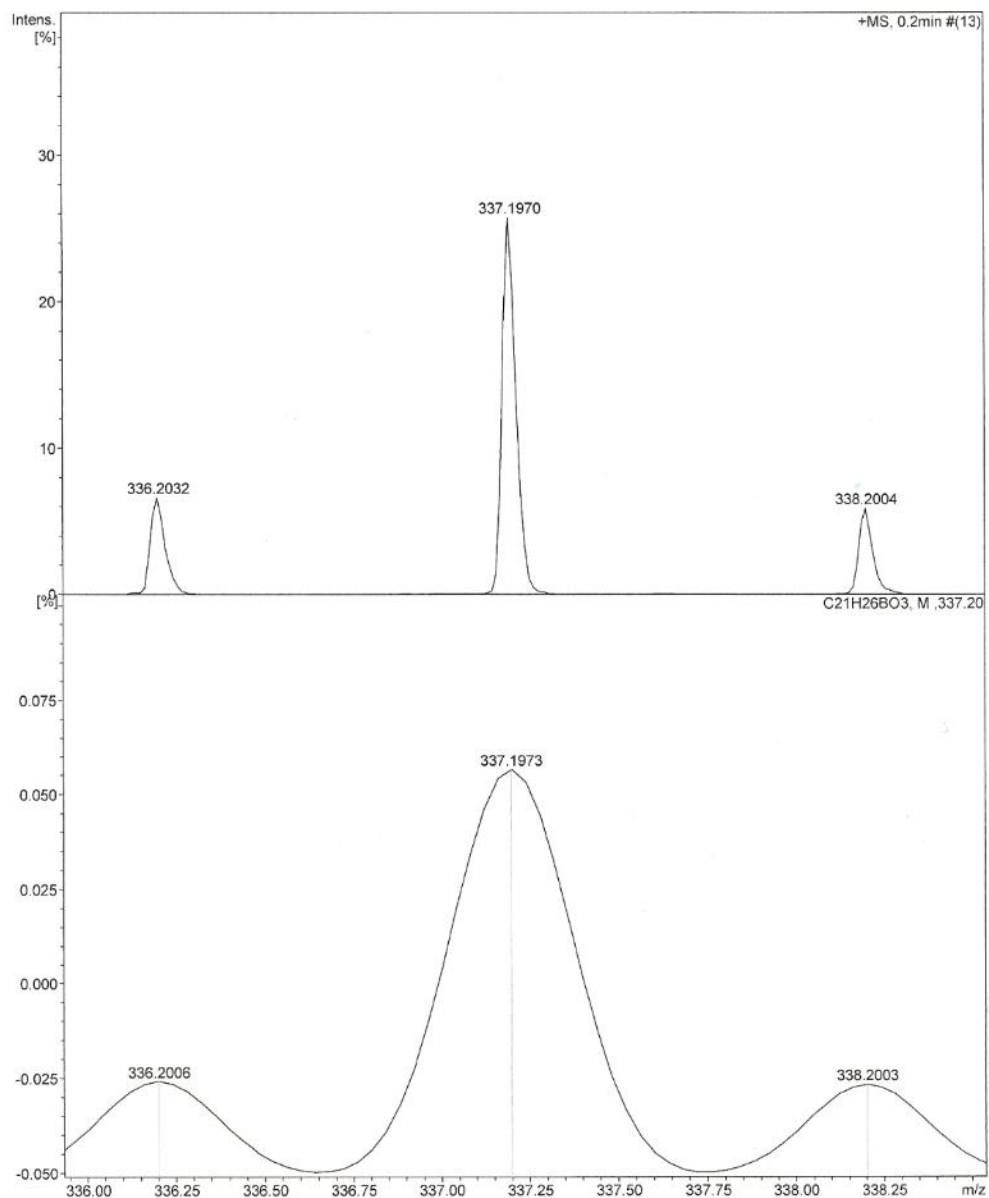
Figure A.57   HRMS of product (Table 4.2, Entry 4)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for C$_{25}$H$_{26}$BO$_3$, 337.1970; found (top) 337.1973

159
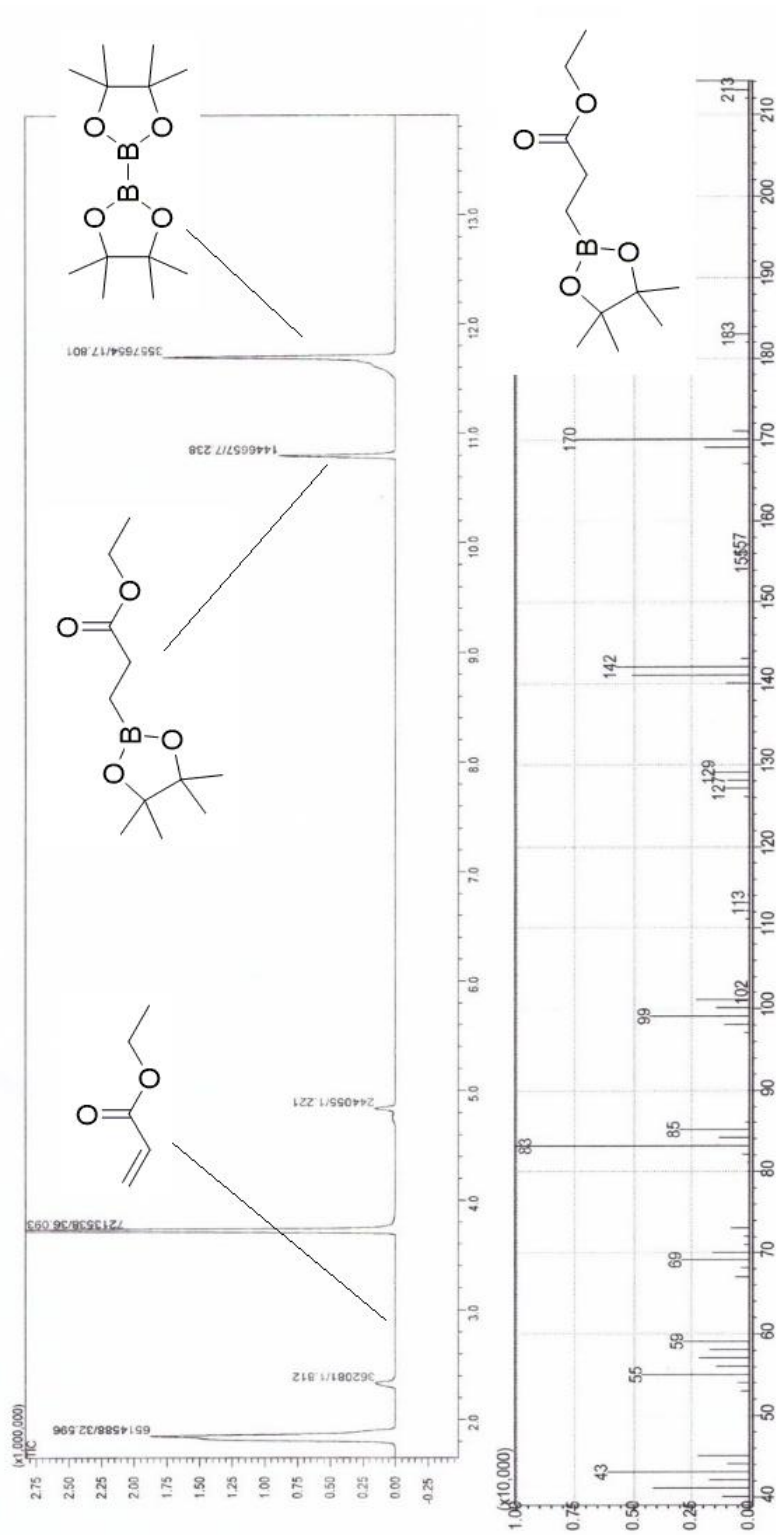
Figure A.58   GC-MS chromatogram spectrum of catalytic trial (Table 4.2, Entry 7)
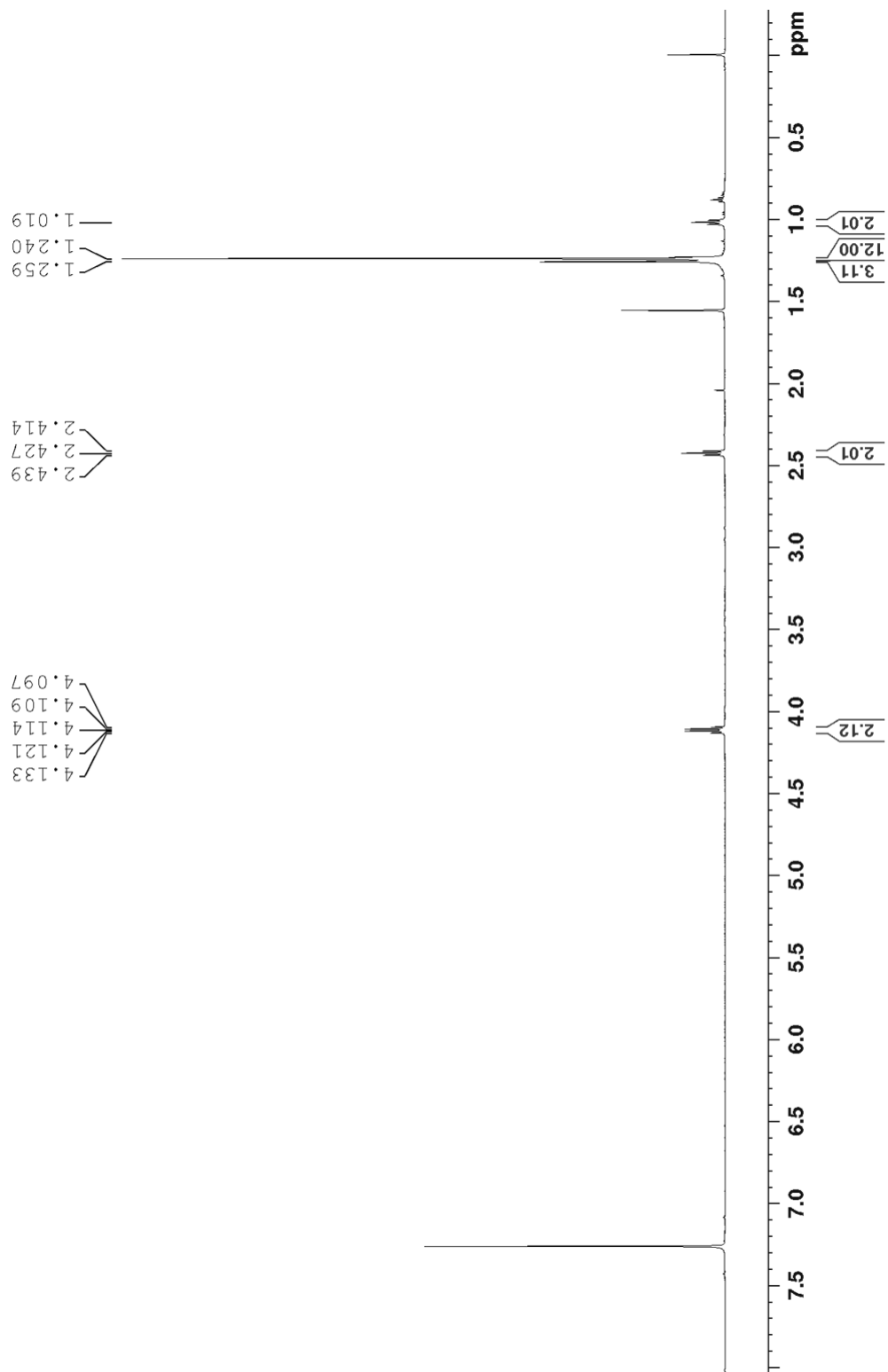
Figure A.59   ¹H NMR (600 MHz, CDCl₃) spectrum of isolated product (Table 4.2, Entry 7)

14.51
25.01
25.27
29.09
60.48
83.45
174.92

ppm
-20
0
20
40
60
80
100
120
140
160
180
200
220
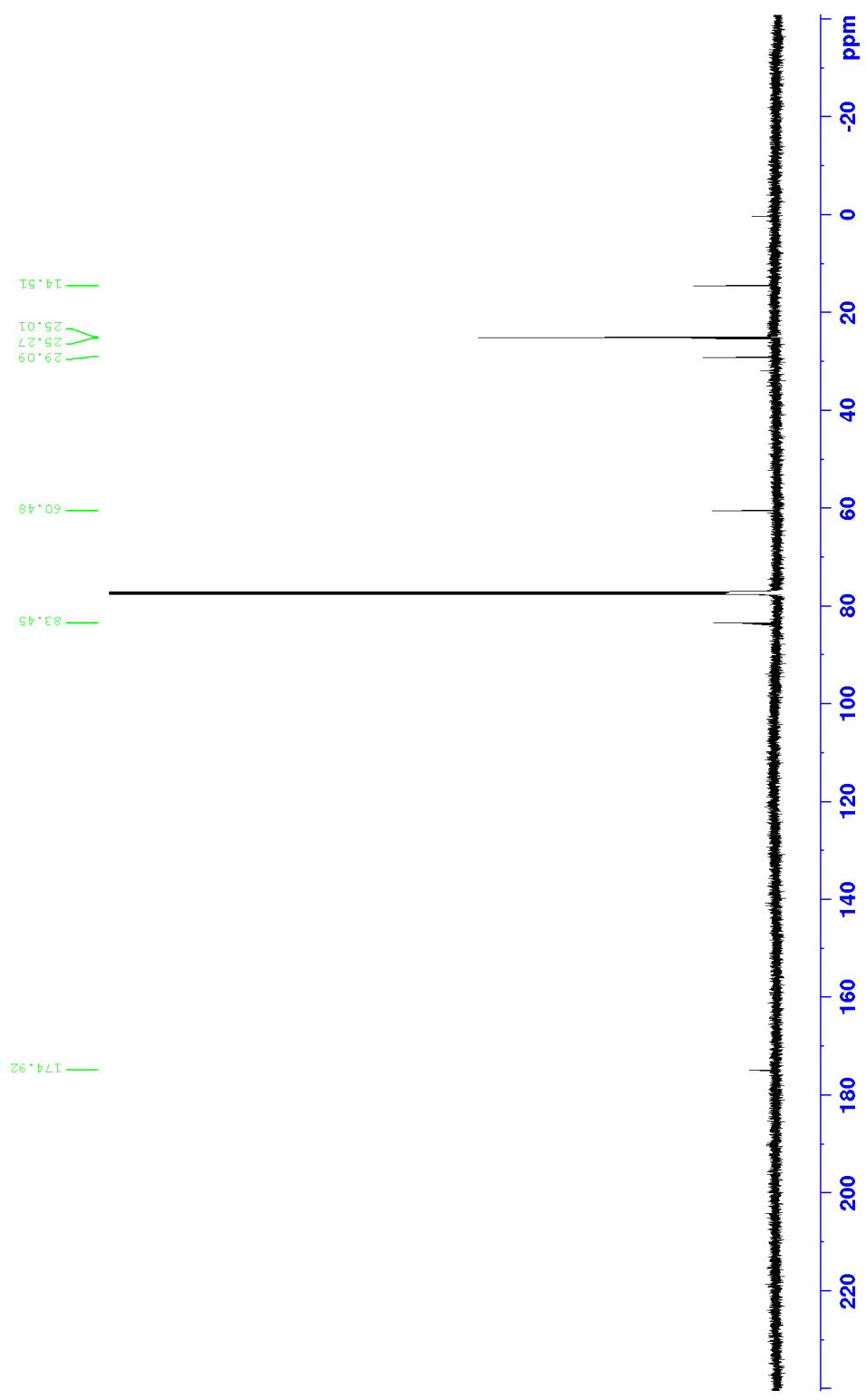
Figure A.60  $^{13}$C NMR spectrum (150 MHz, CDCl$_3$) of isolated product (Table 4.2, Entry 7)

162
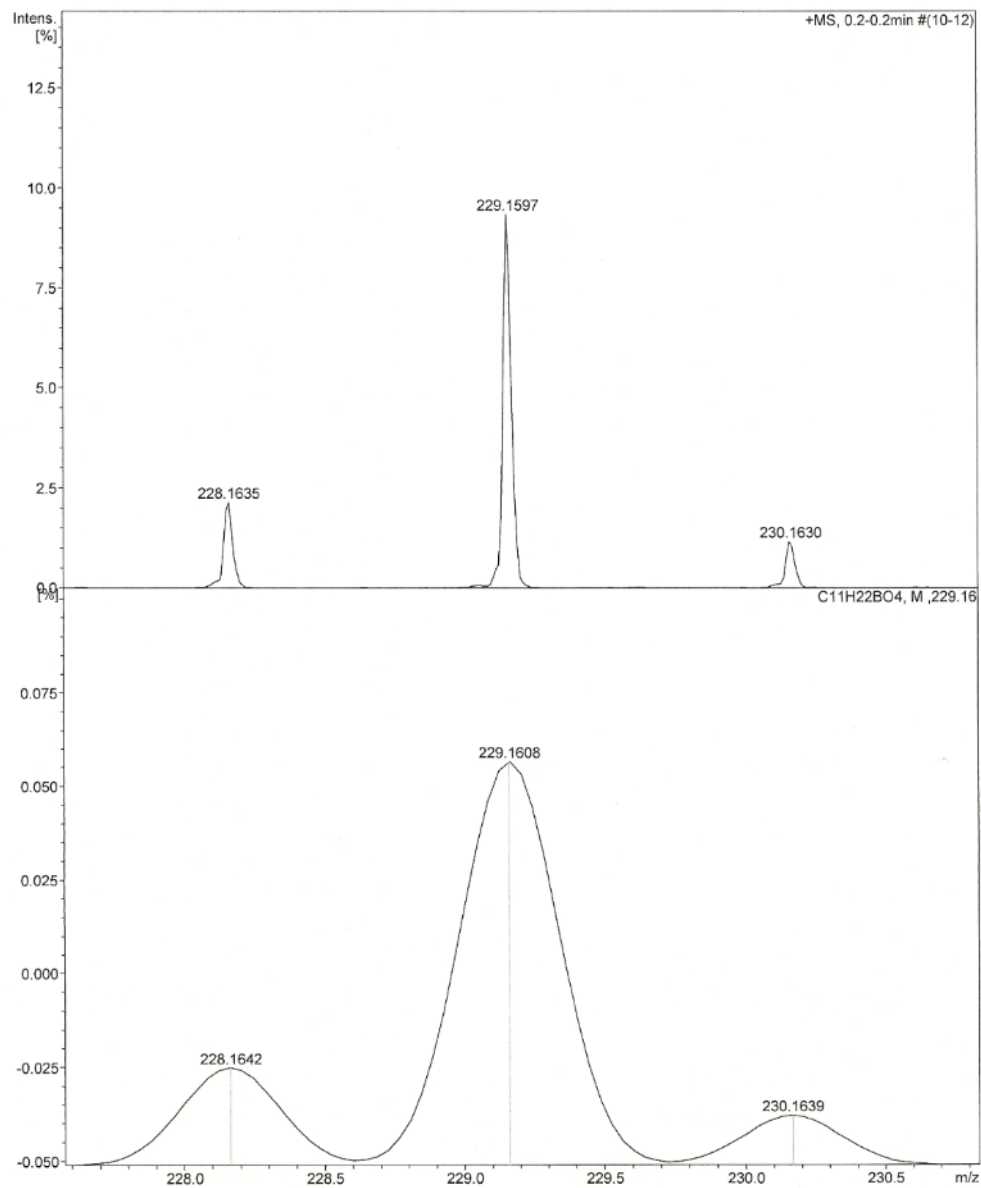
Figure A.61   HRMS of product (Table 4.2, Entry 7)

HRMS-ESI (m/*z*): [M+H]⁺ calcd (bottom) for $C_{11}H_{22}BO_4$, 229.1608; found (top) 229.1597
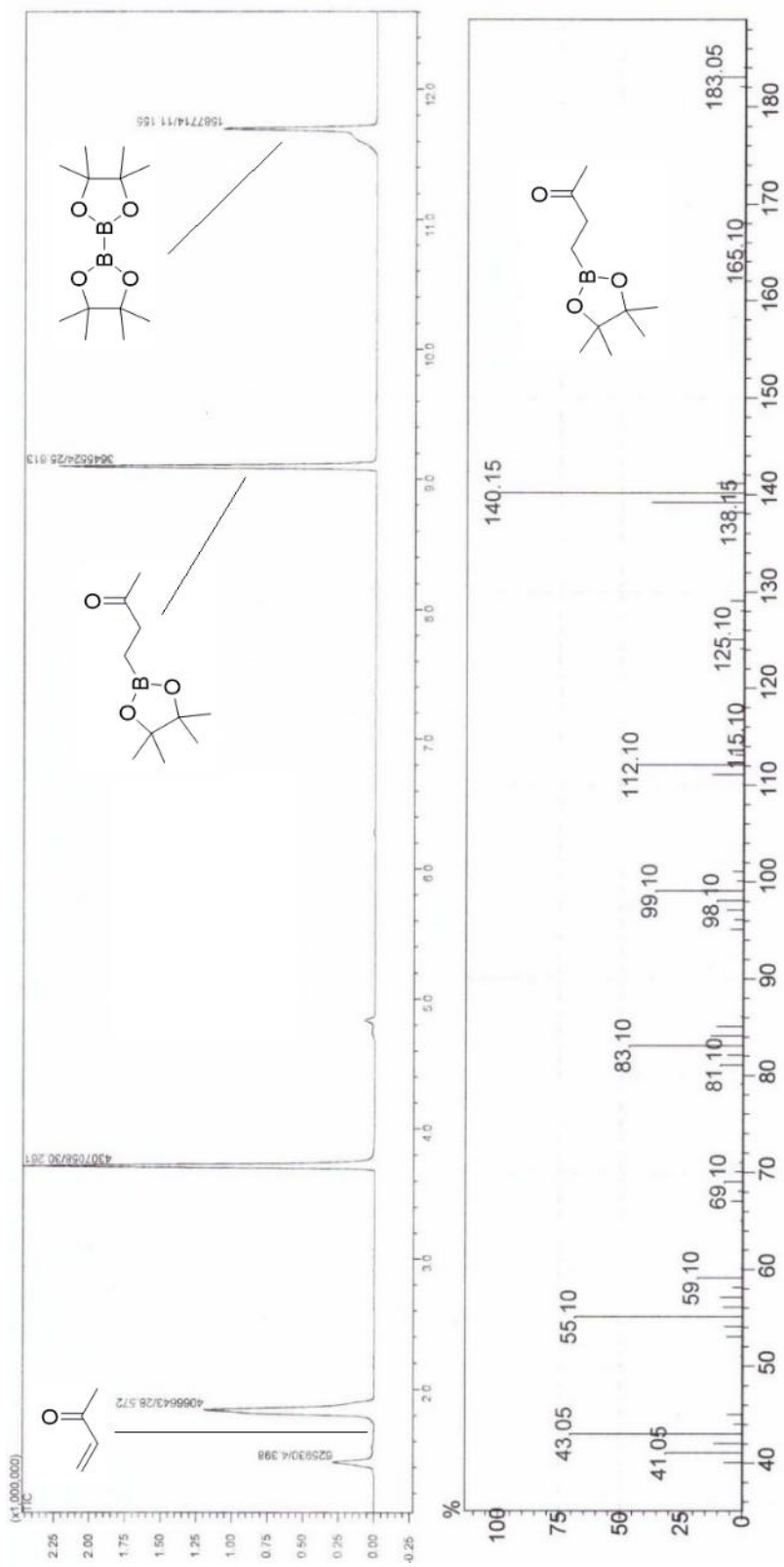
Figure A.62   GC-MS chromatogram spectrum of catalytic trial (Table 4.2, Entry 8)
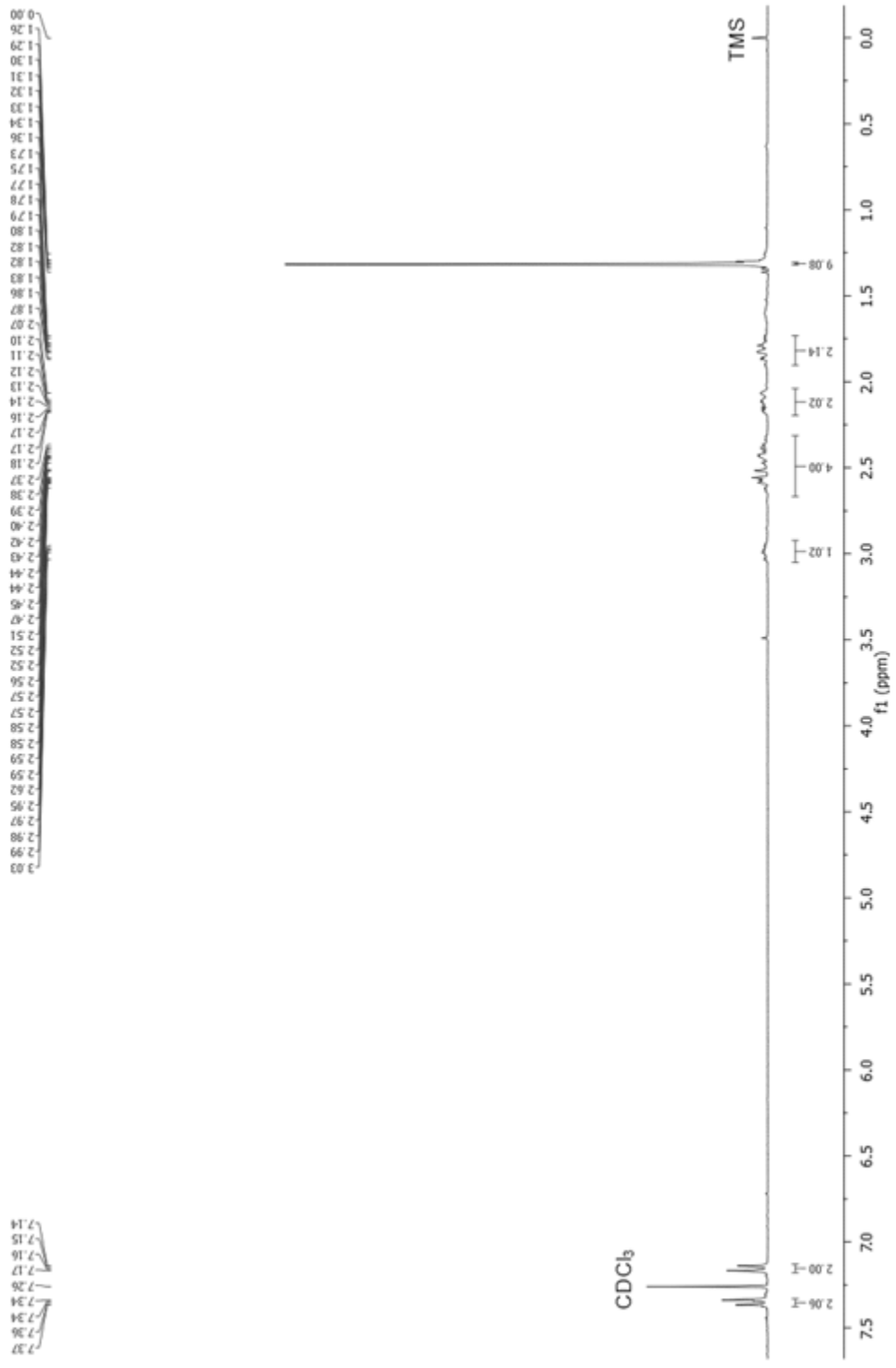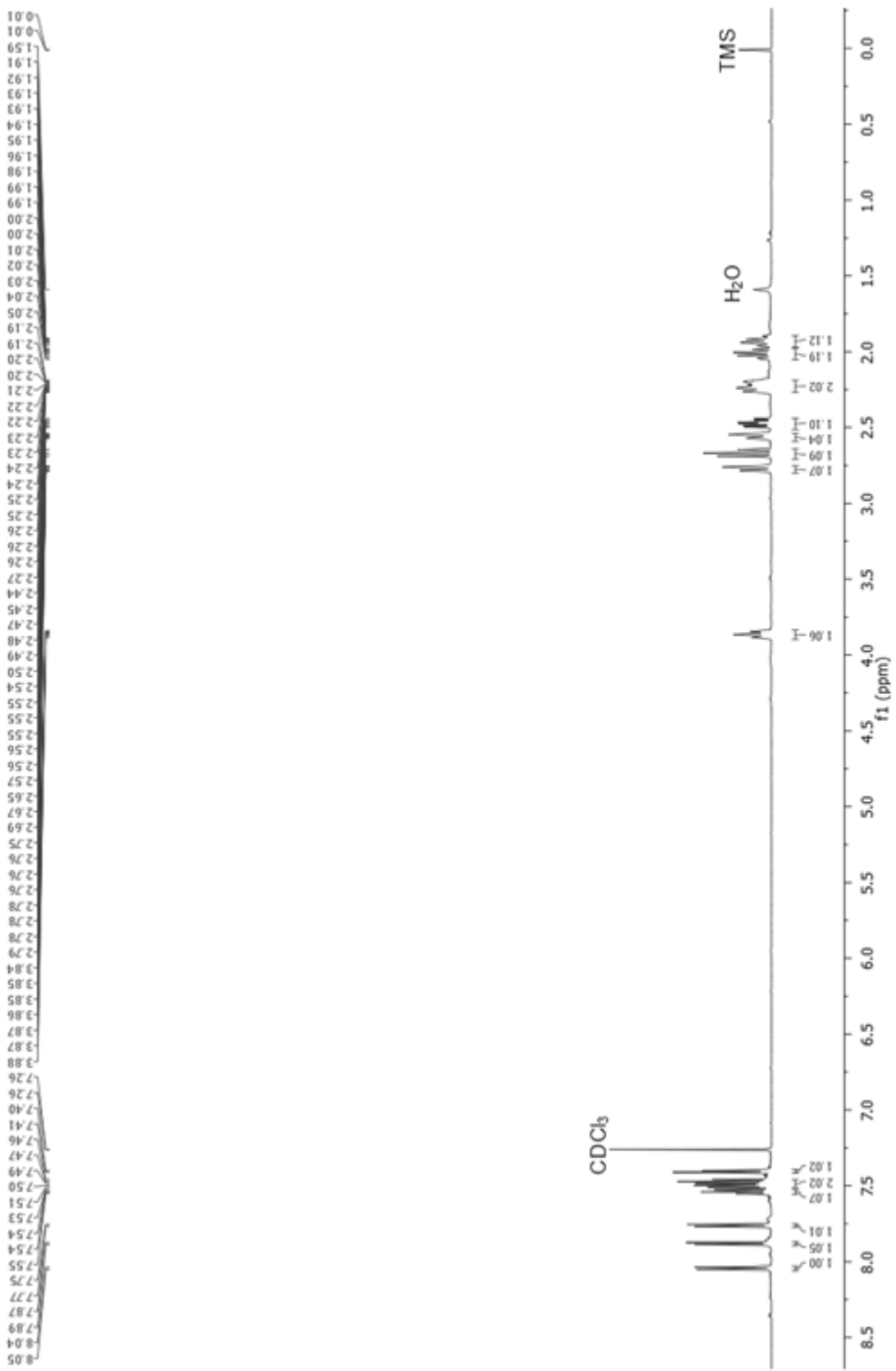
164
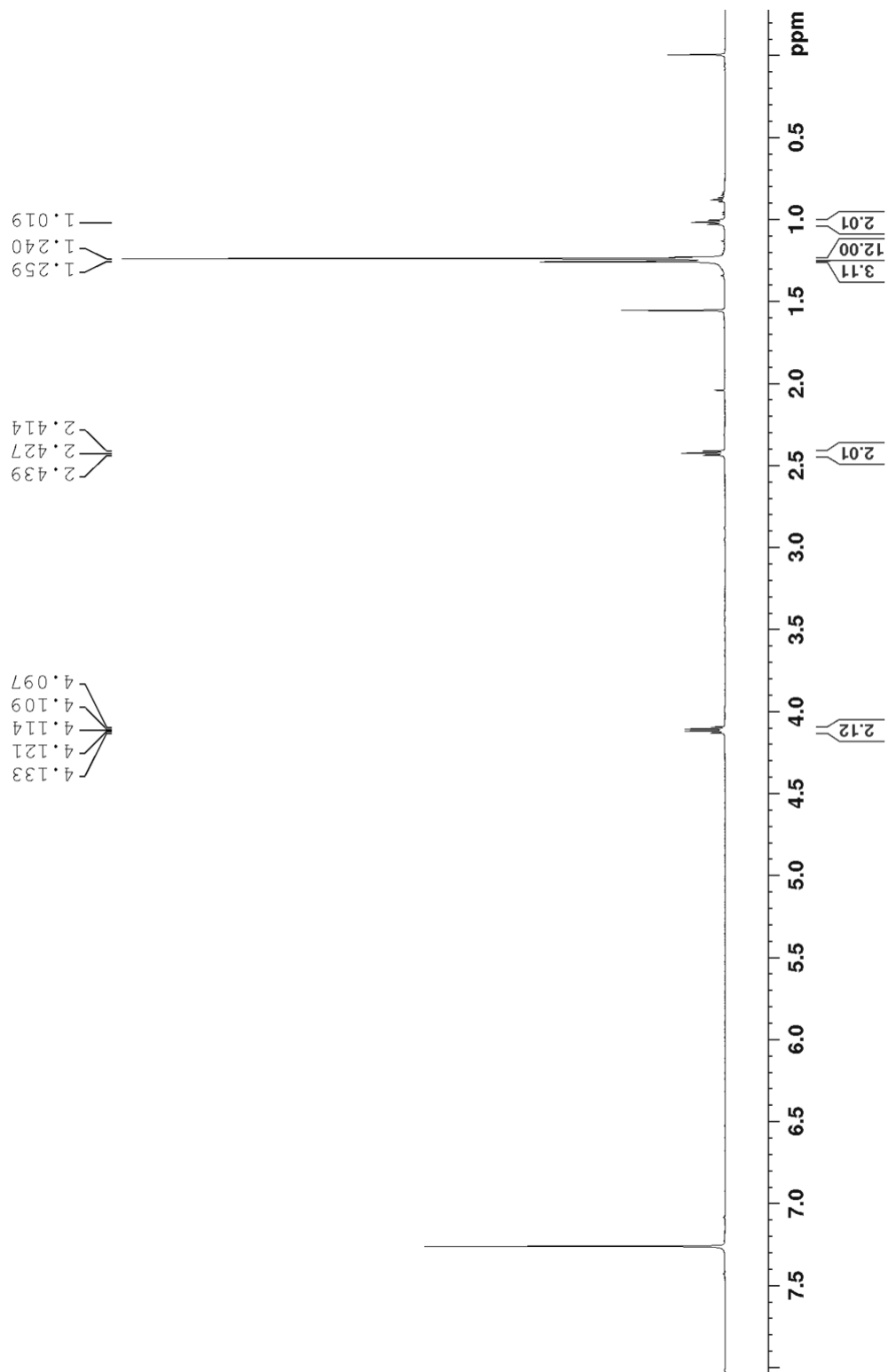
Figure A.63  $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 8)
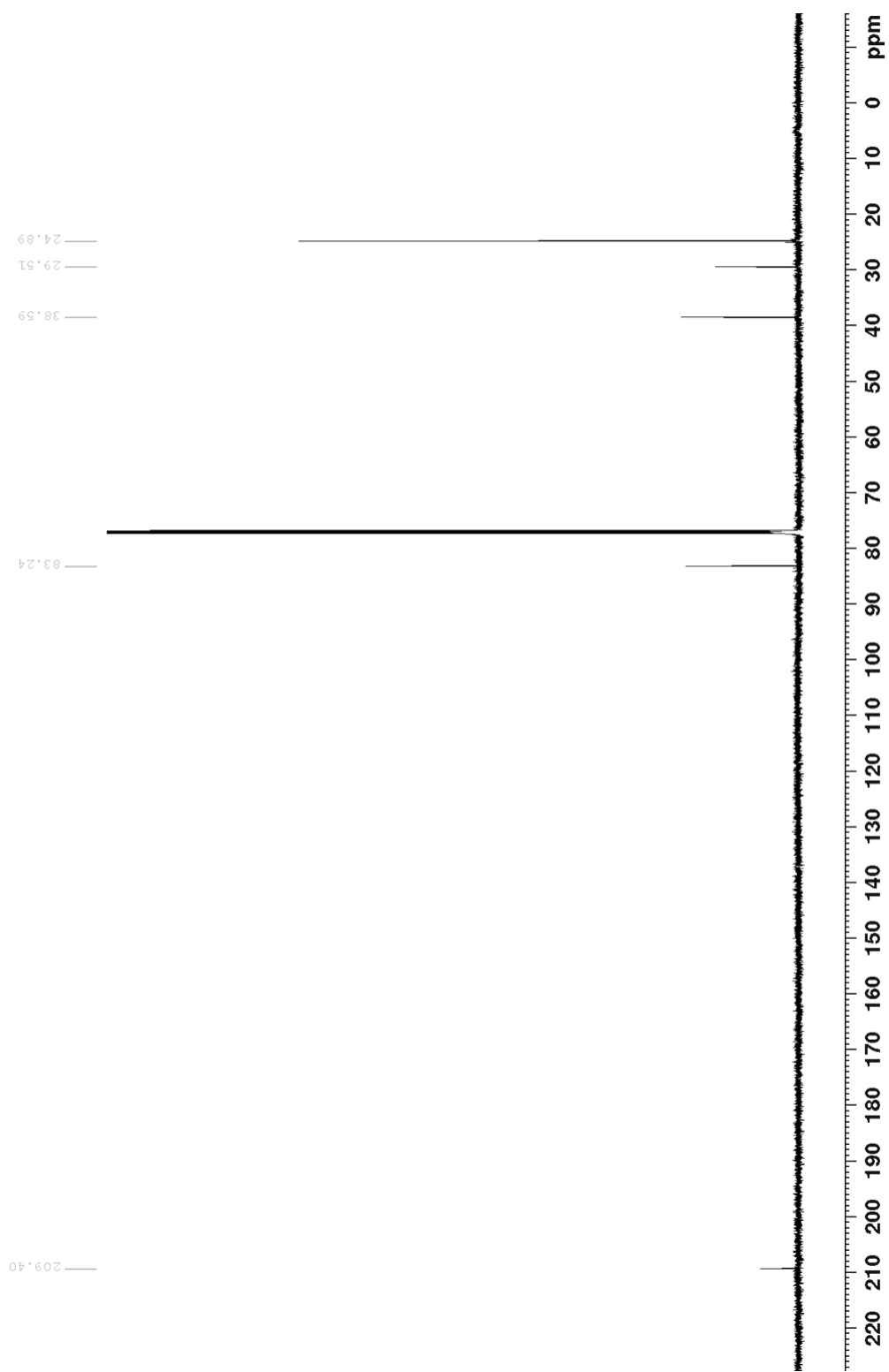
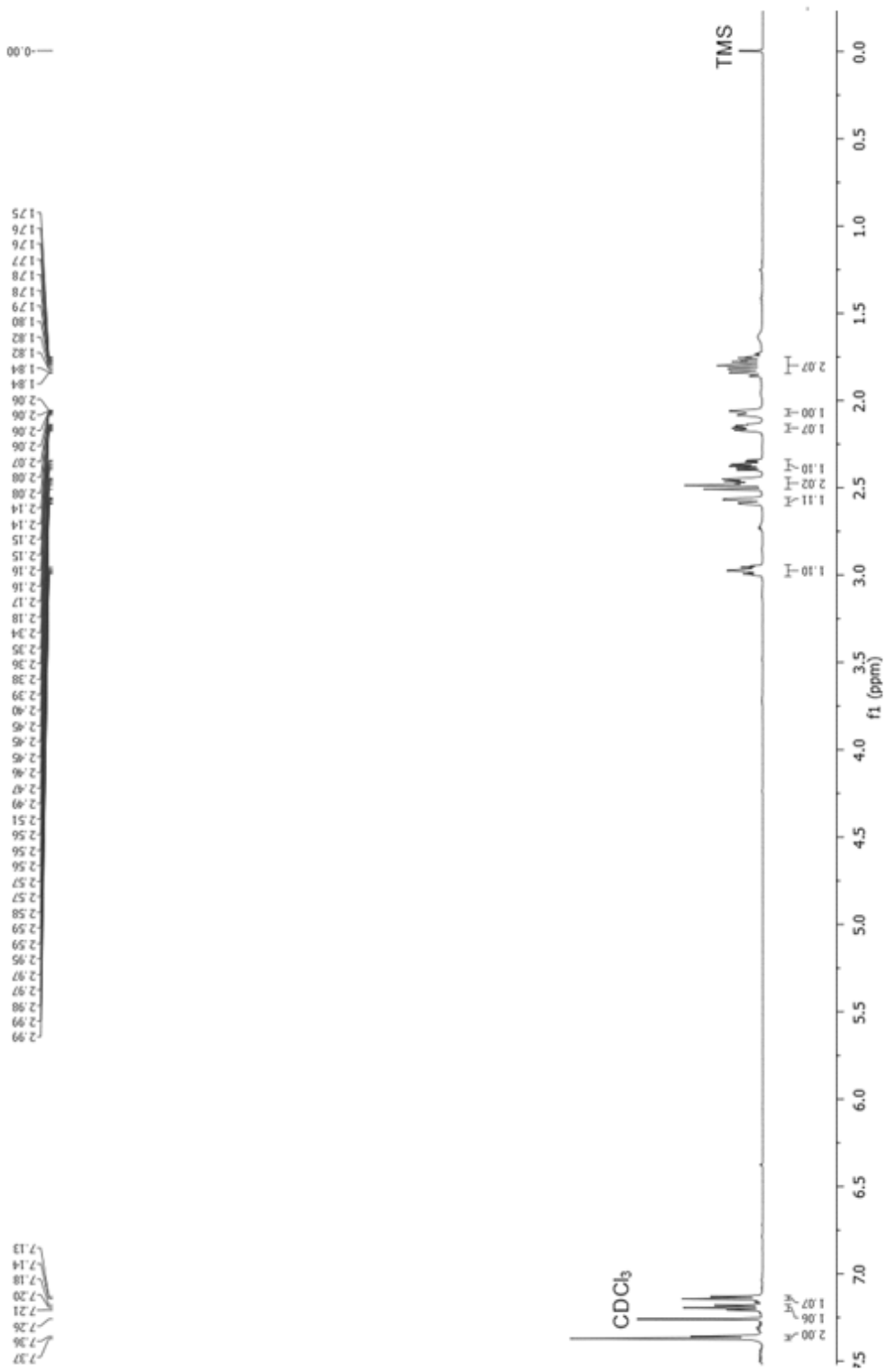Figure A.64  $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 8)

209.40

83.24

38.59

29.51

24.89
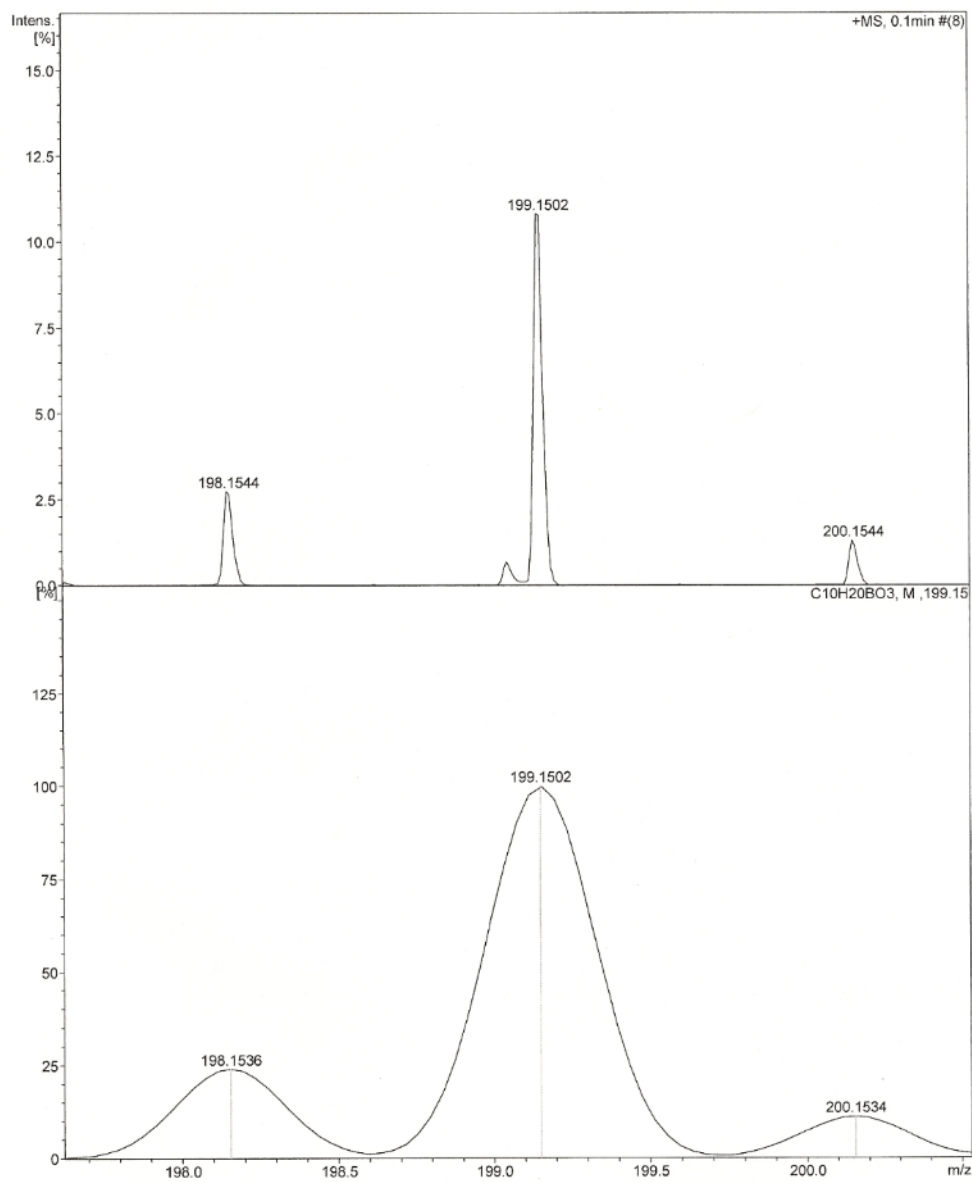
Figure A.65   HRMS of product (Table 4.2, Entry 8)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for C$_{10}$H$_{20}$BO$_3$, 199.1502; found (top) 199.1502
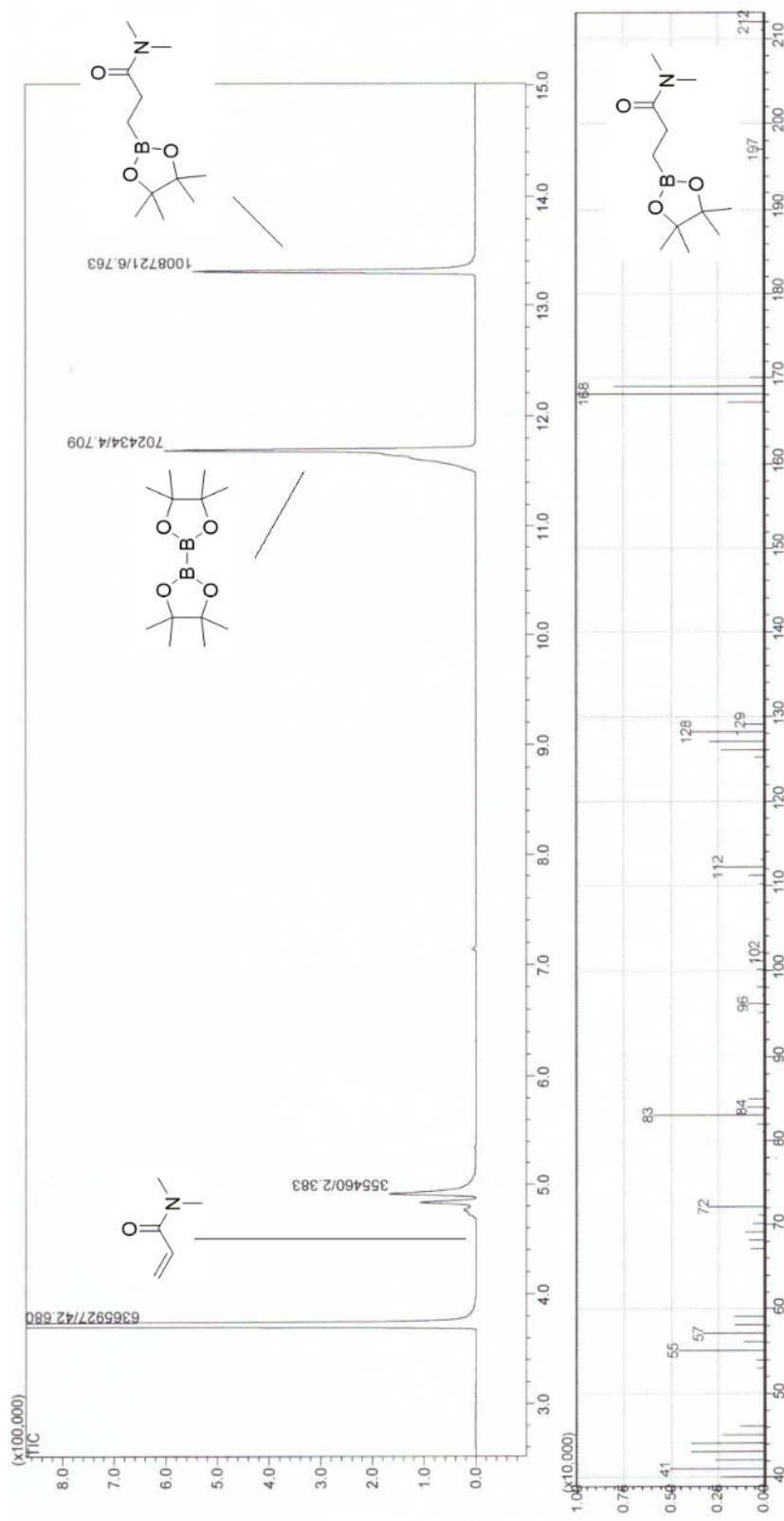
Figure A.66   GC–MS chromatogram spectrum of catalytic trial (Table 4.2, Entry 9)

168
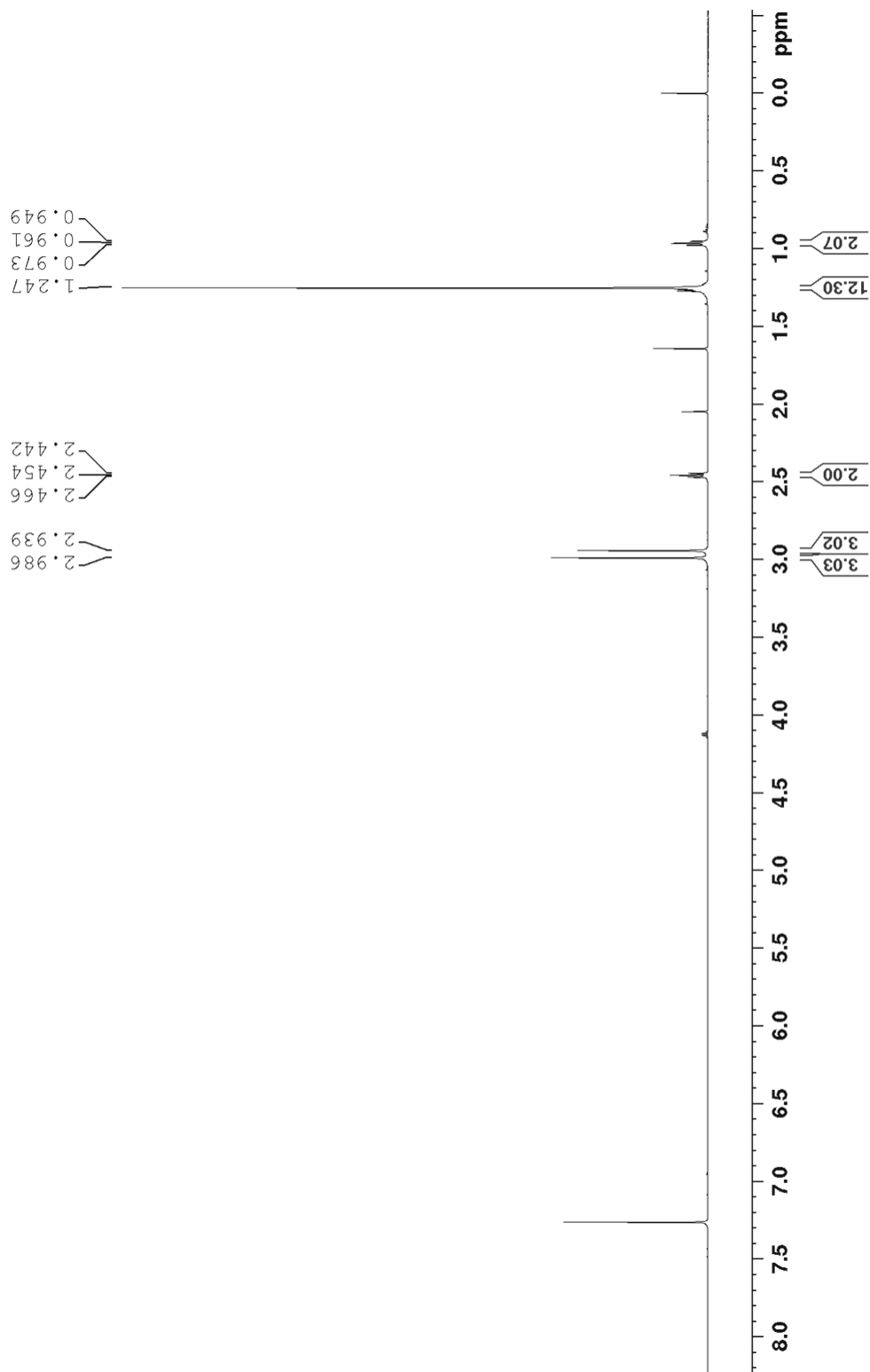
Figure A.67  $^{1}$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 10)

169
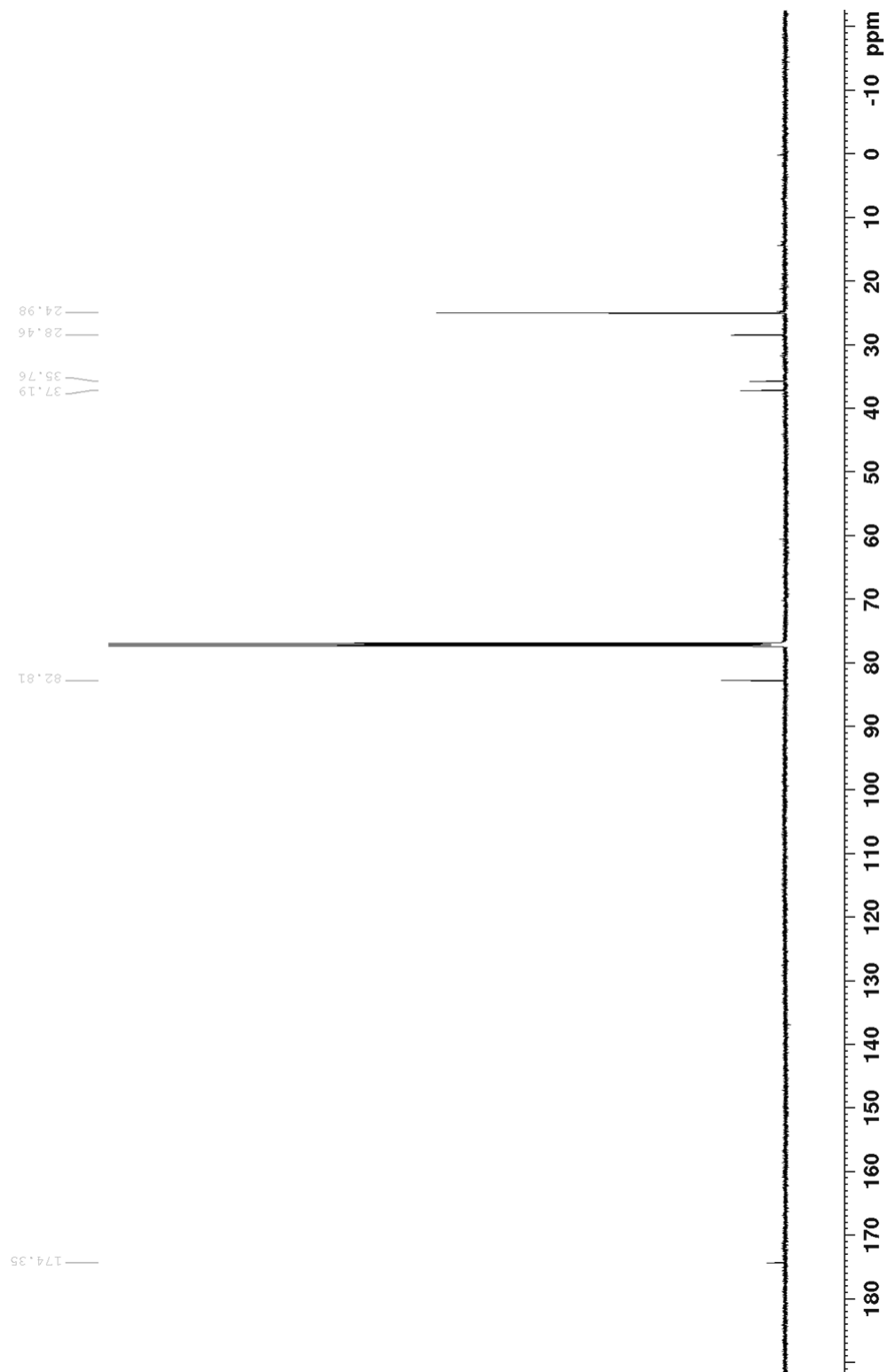
Figure A.68 $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.2, Entry 10)
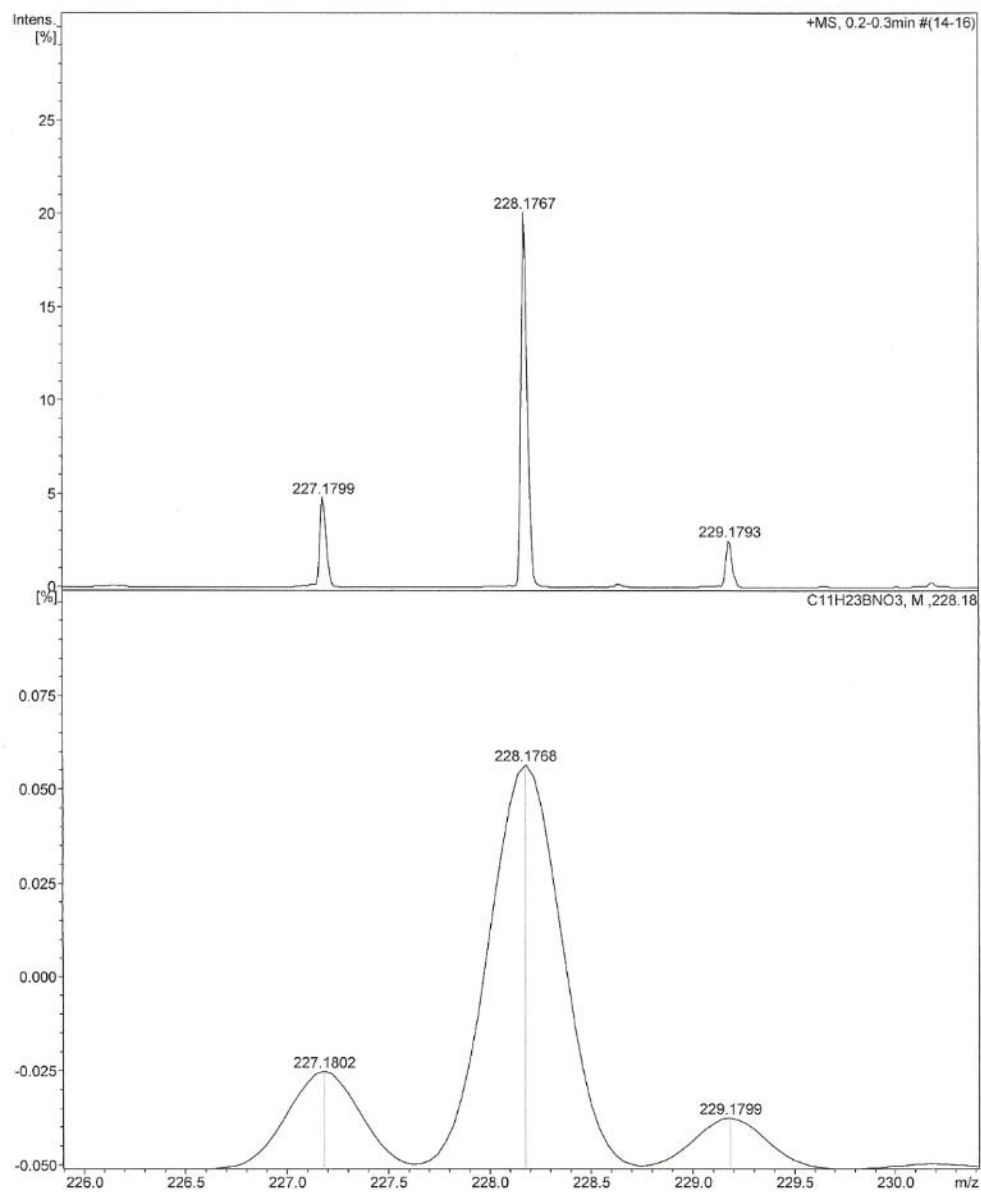
Figure A.69   HRMS of product (Table 4.2, Entry 10)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for $C_{11}H_{23}BNO_3$, 228.1768; found (top) 228.1767
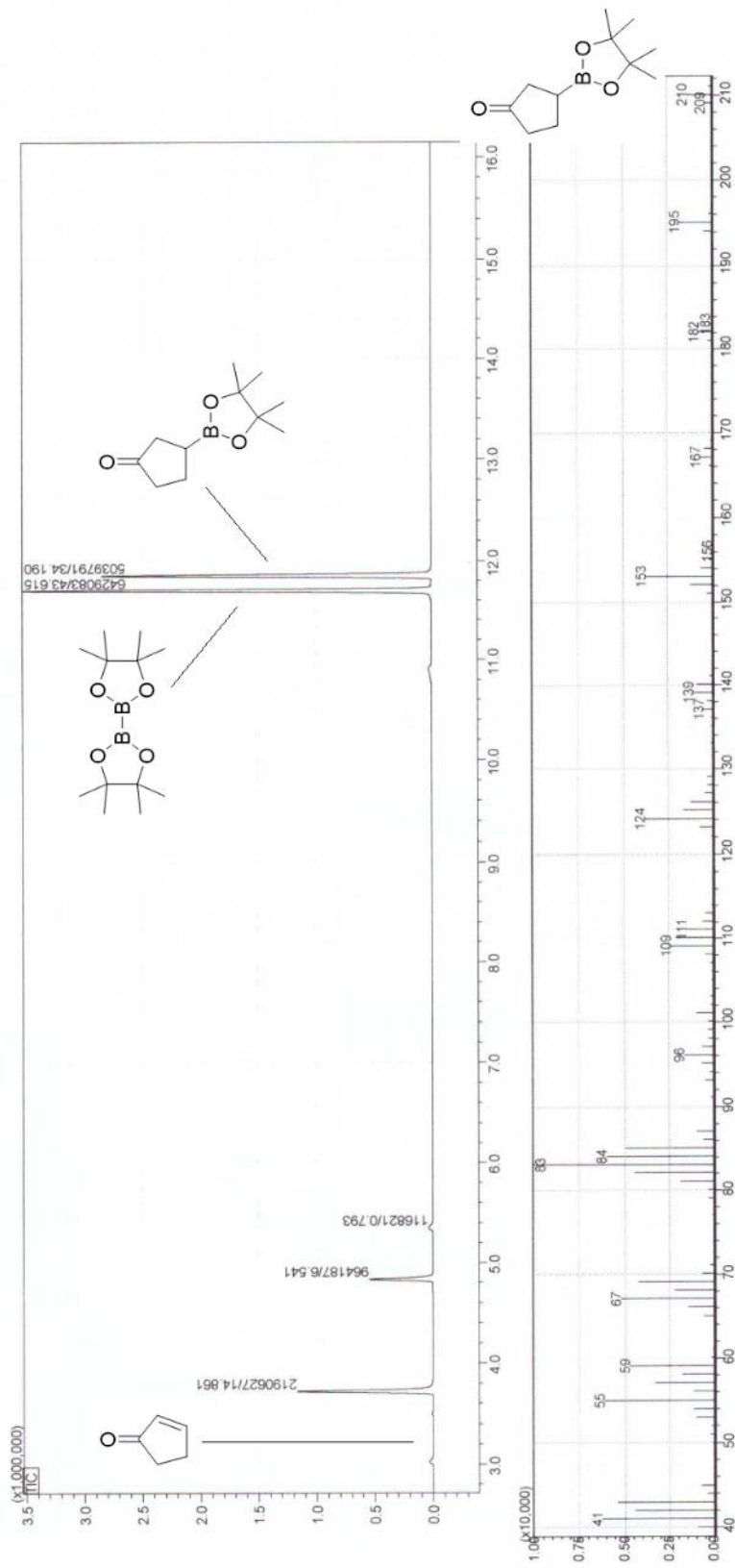
Figure A.70   GC-MS chromatogram spectrum of catalytic trial (Table 4.3, Entry 1 )

172

1.245
1.614
1.624
1.638
1.649
1.667
1.829
1.842
1.846
1.850
1.859
1.864
1.873
1.879
2.087
2.101
2.114
2.129
2.136
2.150
2.225
2.239
2.251
2.268
2.282
2.299
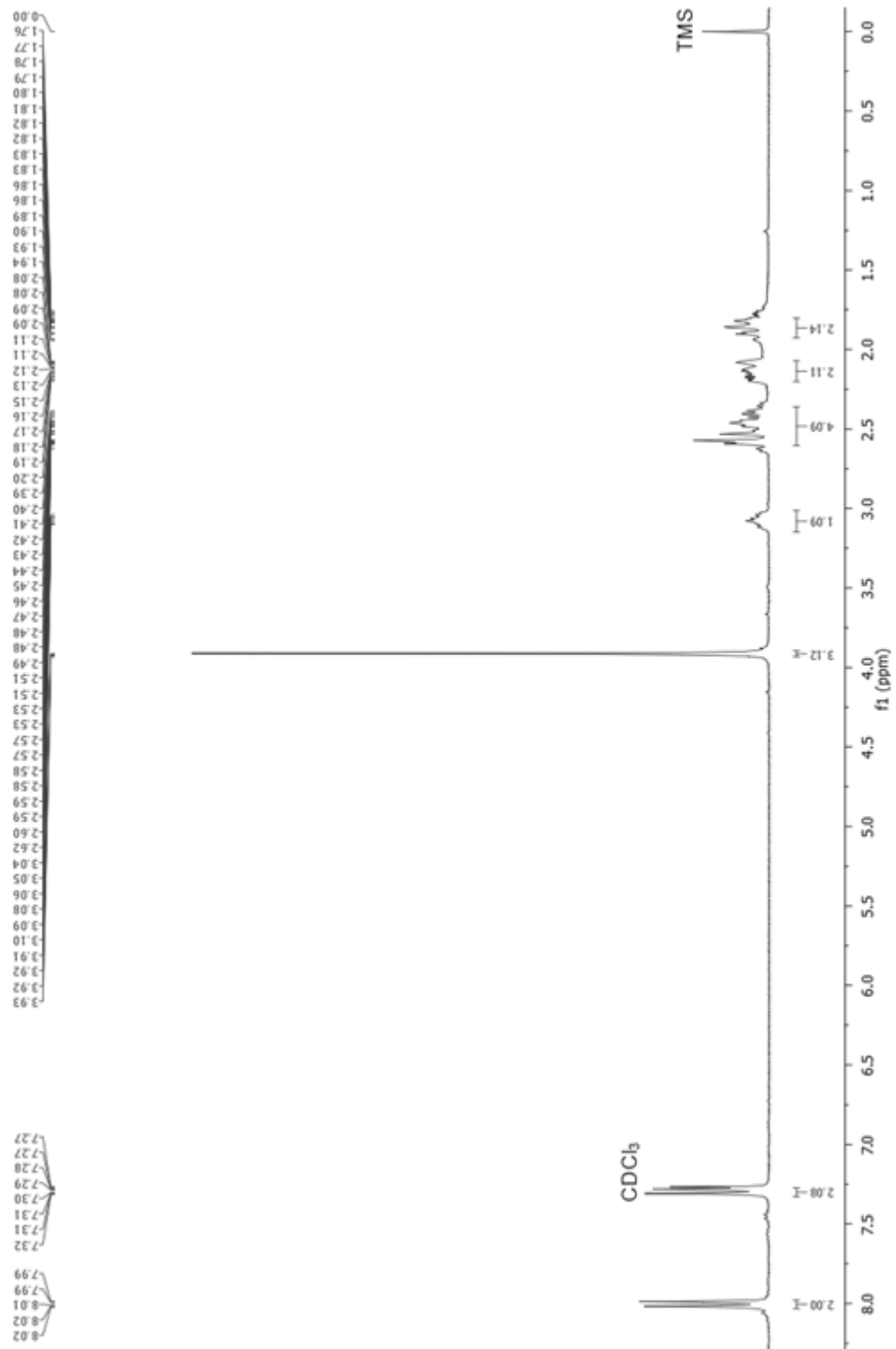2.313

12.24

1.14

1.00

3.00
2.02
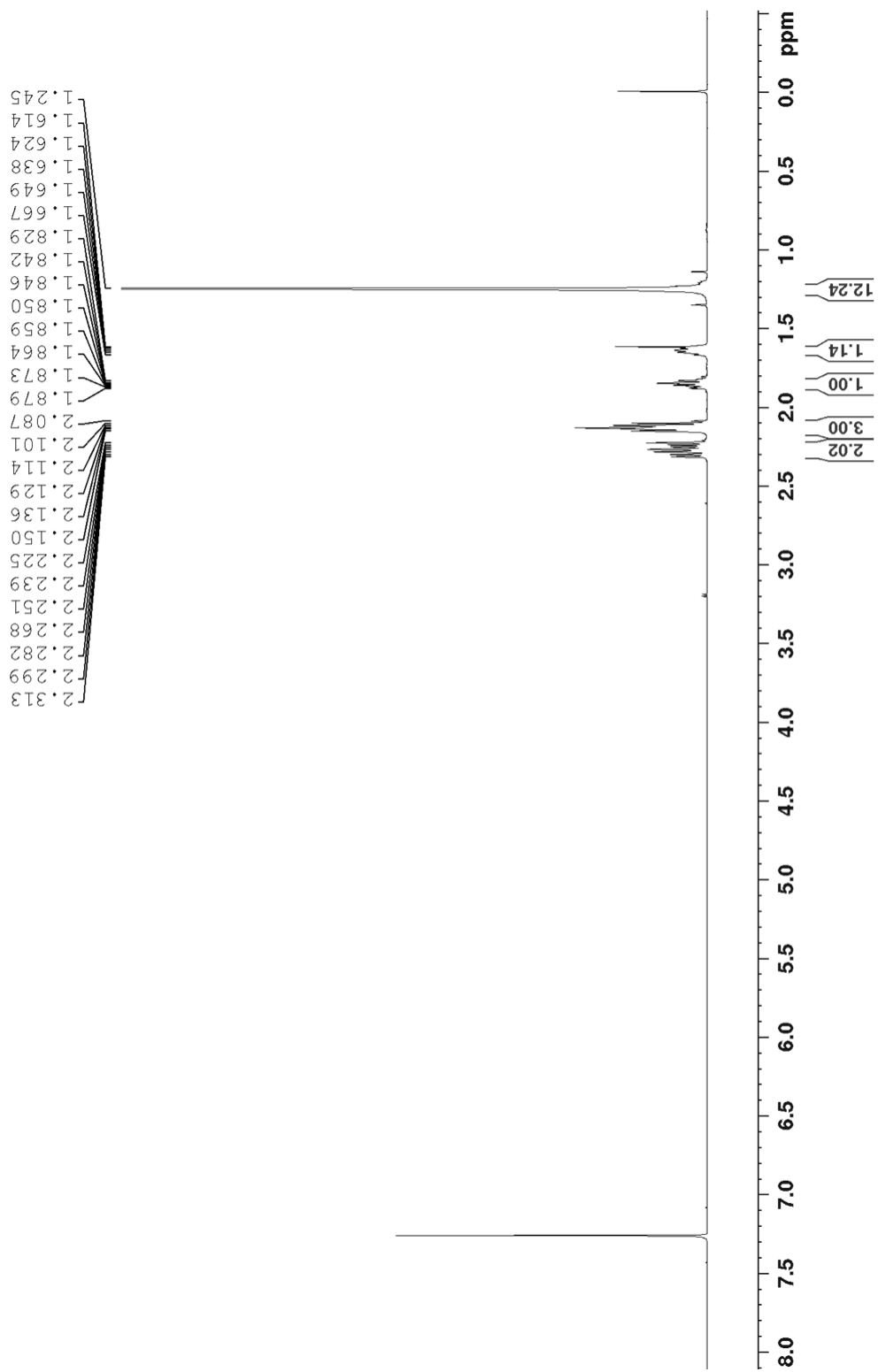
Figure A.71   $^{1}$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 1)
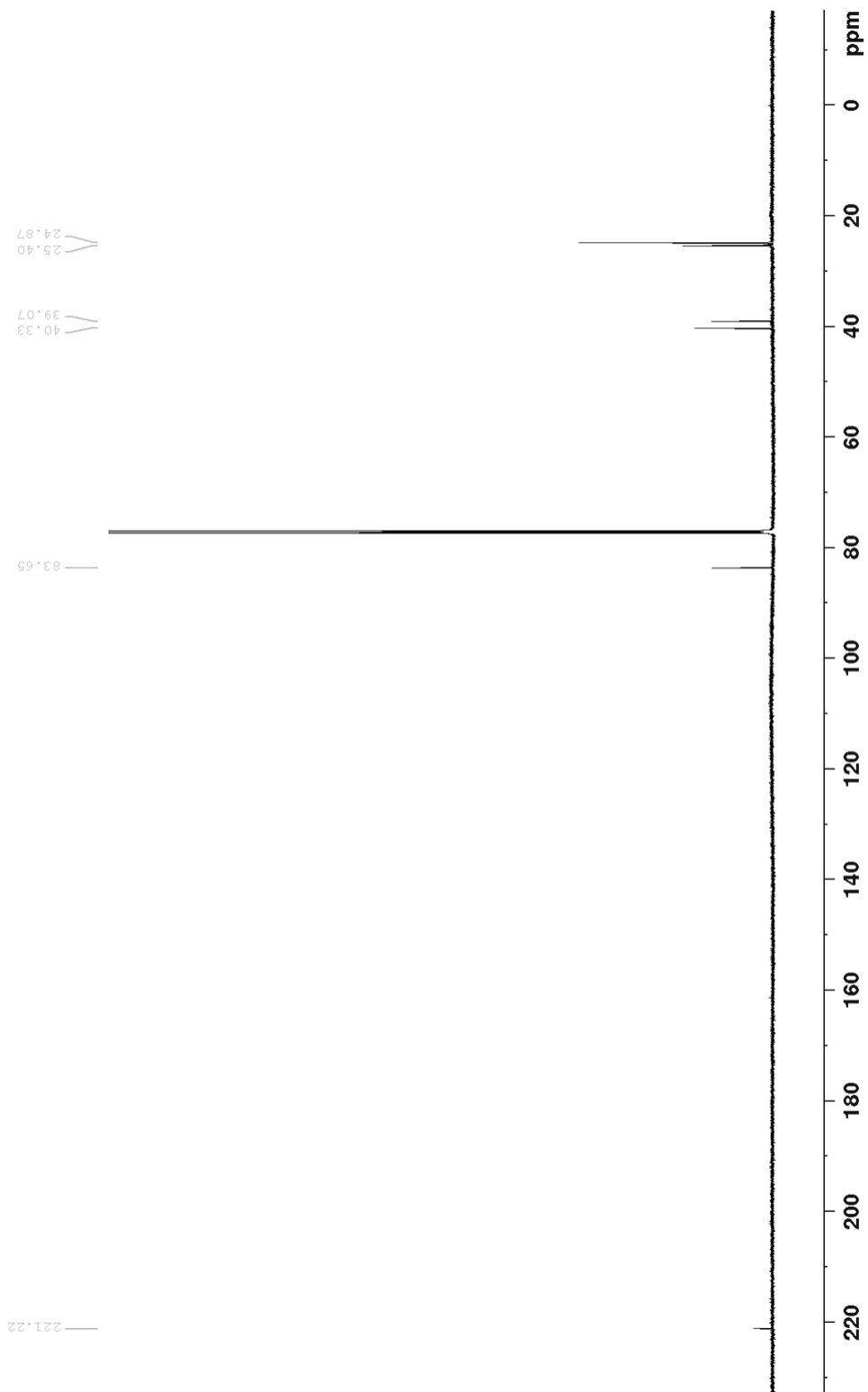
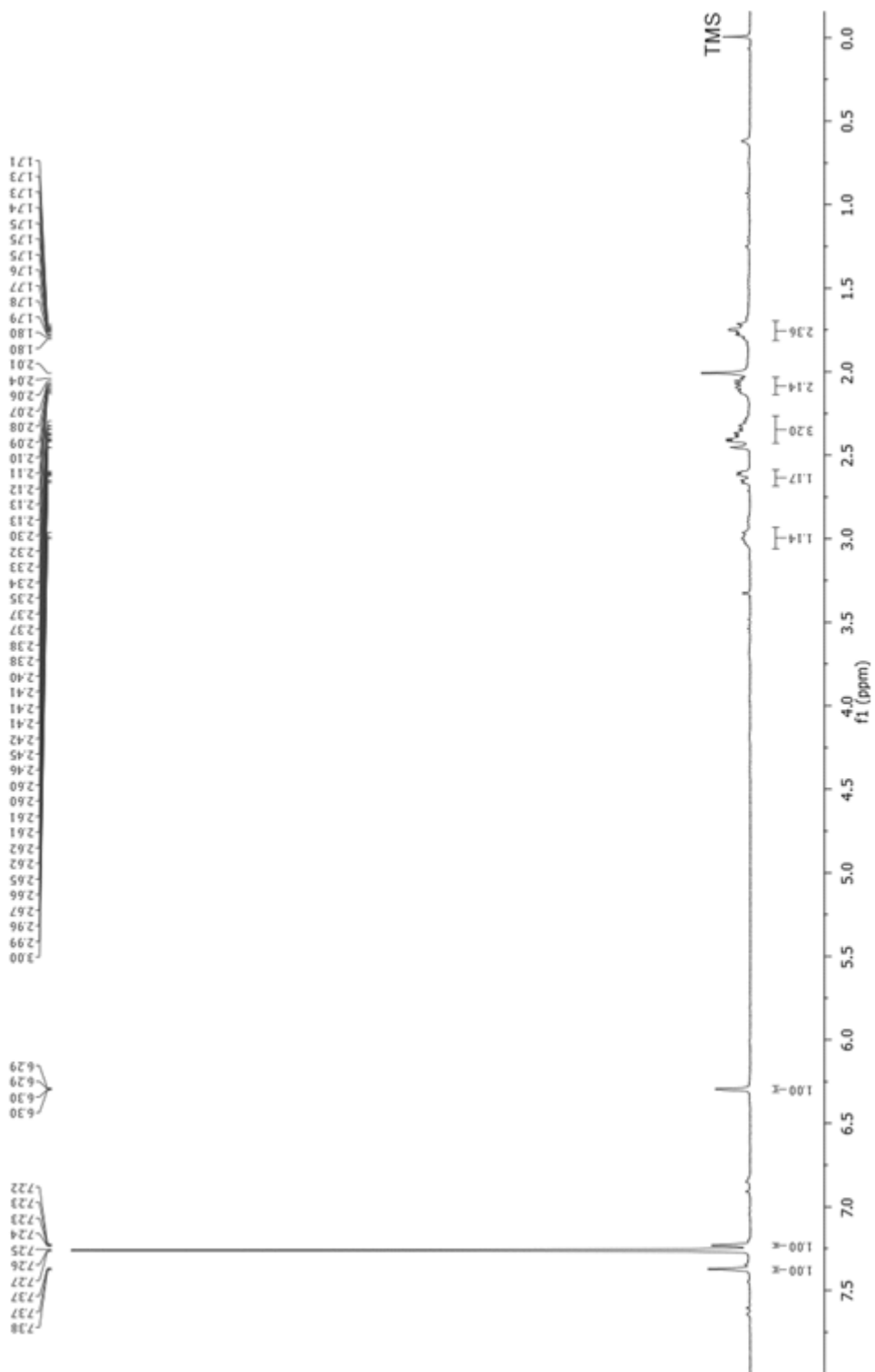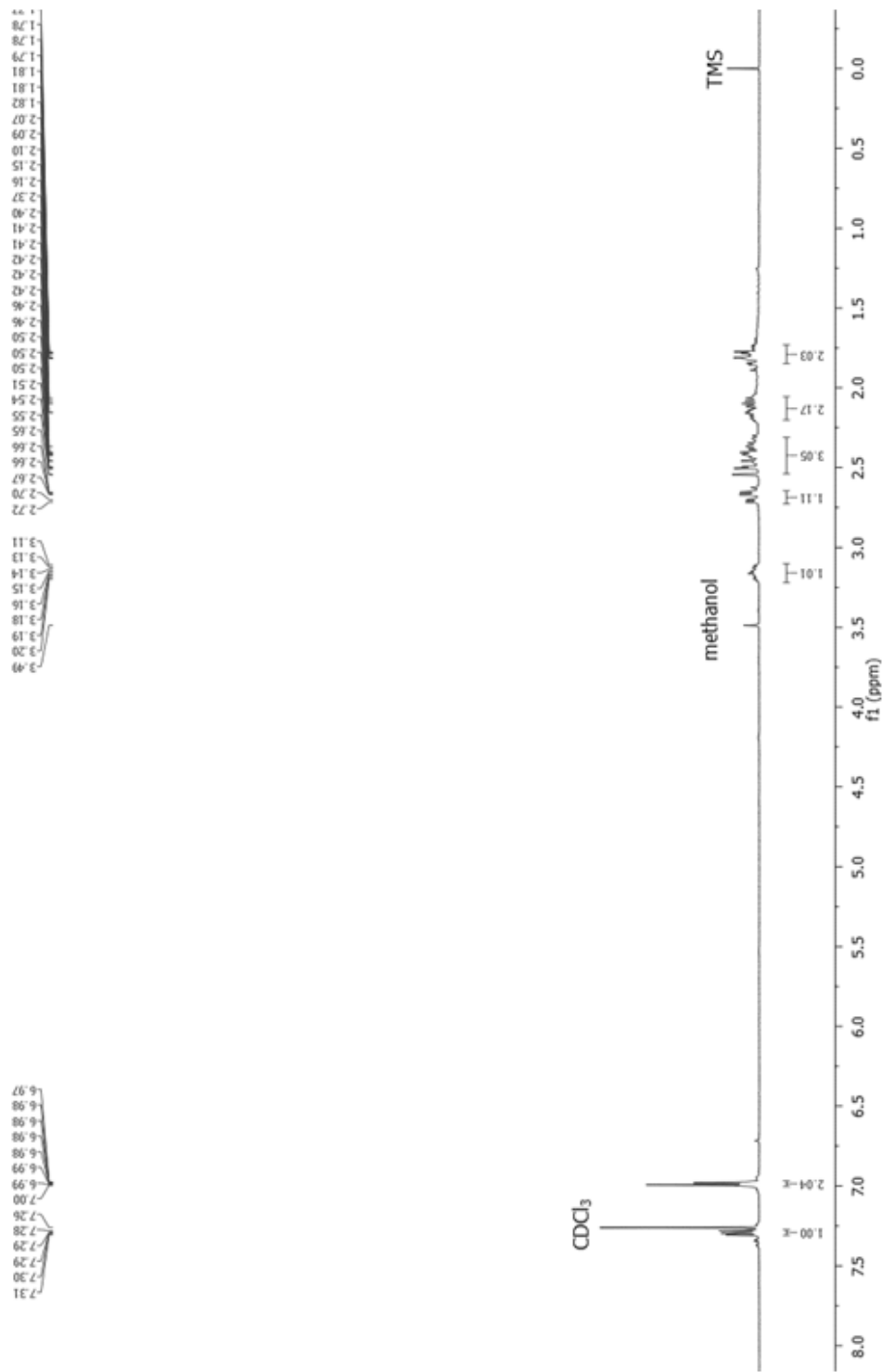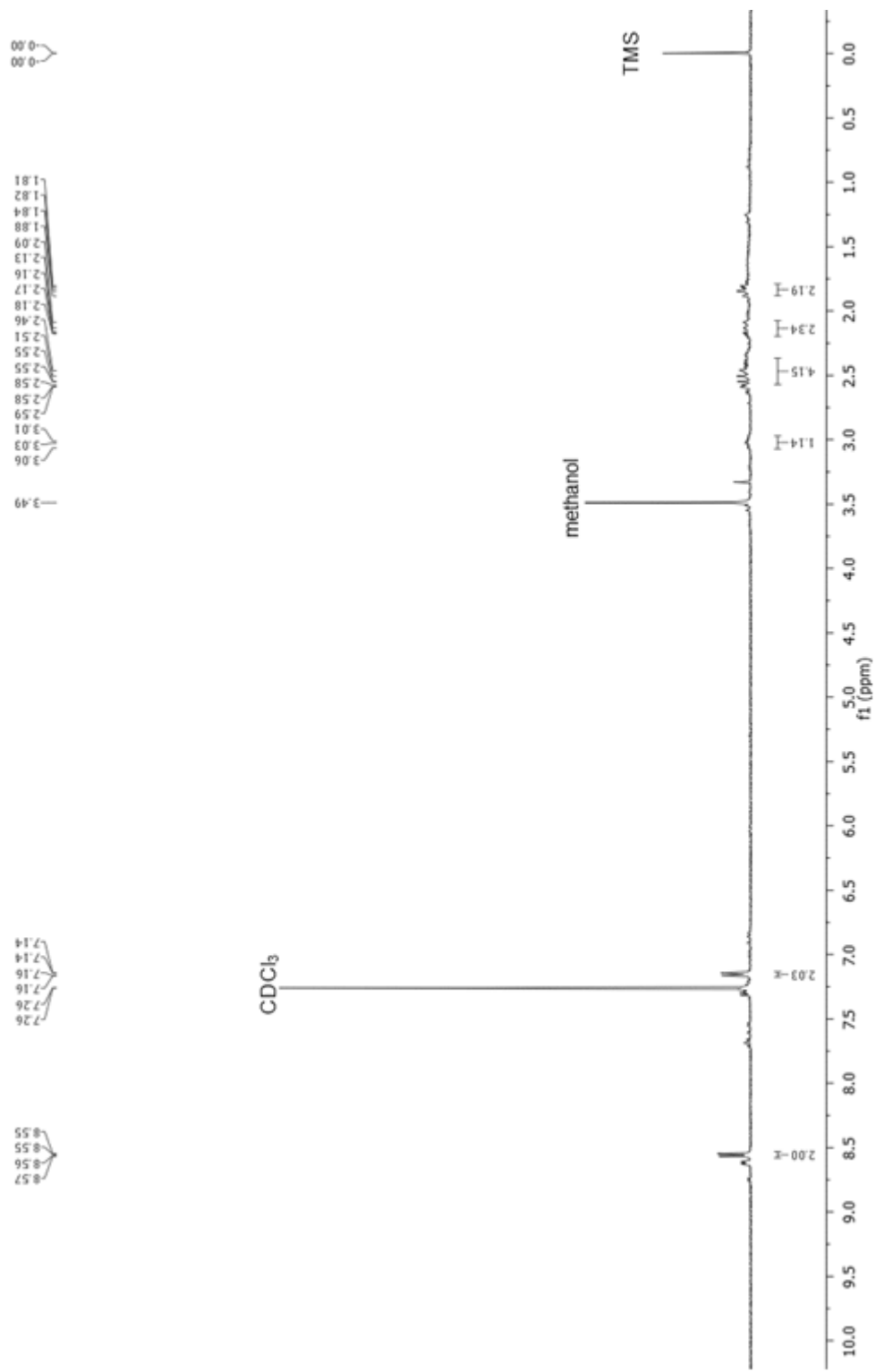Figure A.72   $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 1)
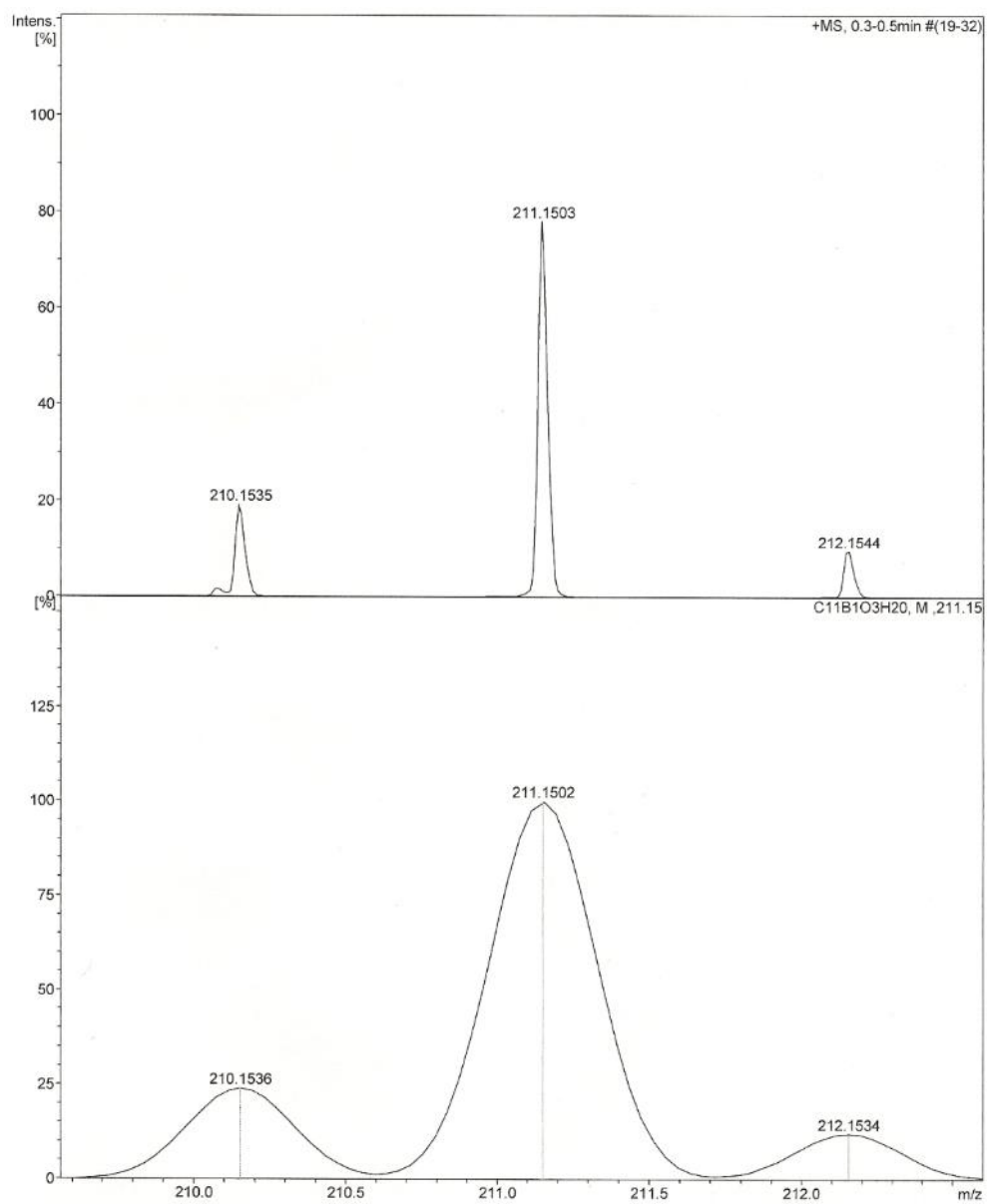
Figure A.73   HRMS of product (Table 4.3, Entry 1)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for C$_{11}$H$_{20}$BO$_3$, 211.1502; found (top) 211.1503
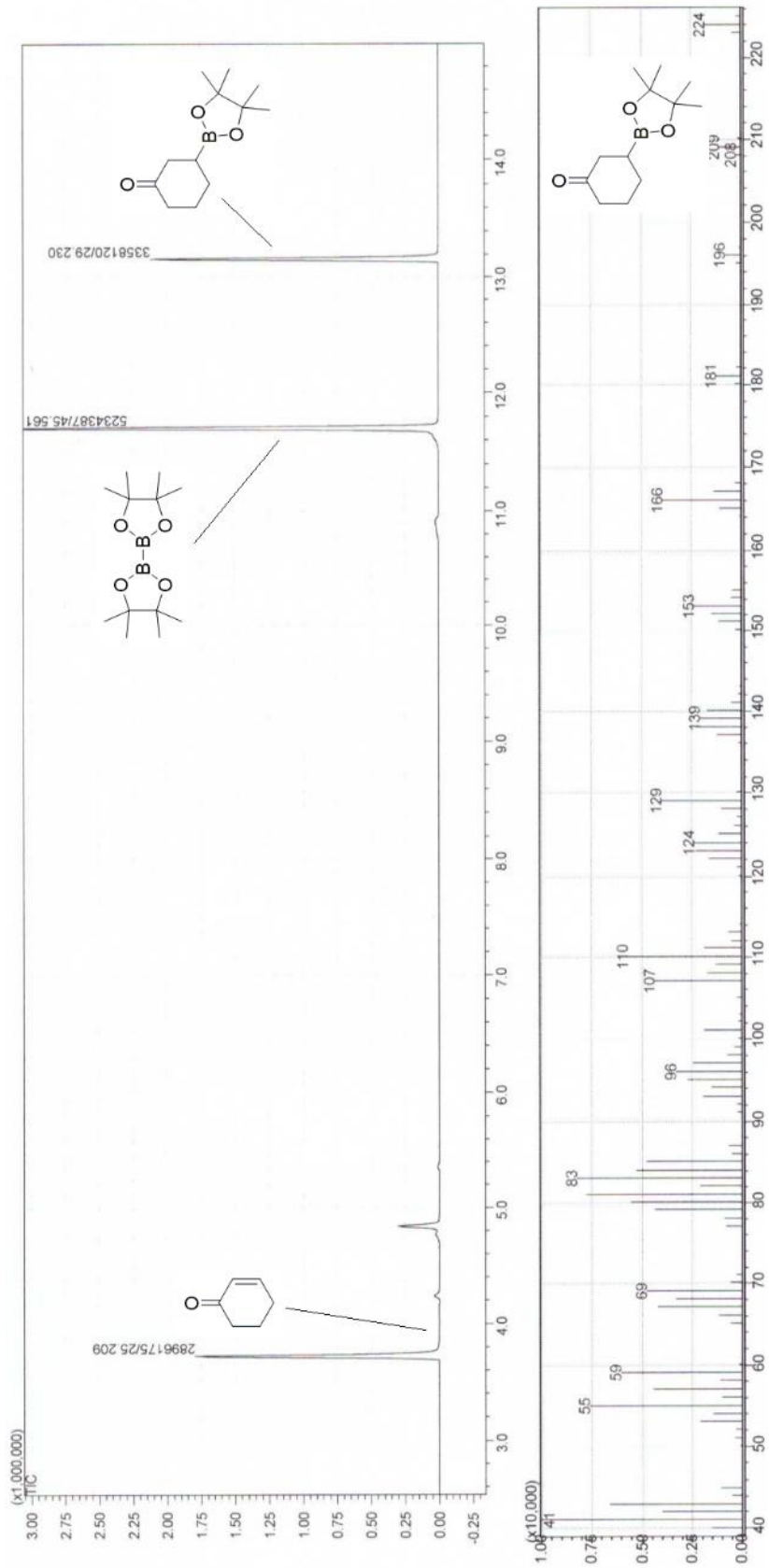
Figure A.74   GC-MS chromatogram spectrum of catalytic trial (Table 4.3, Entry 2)
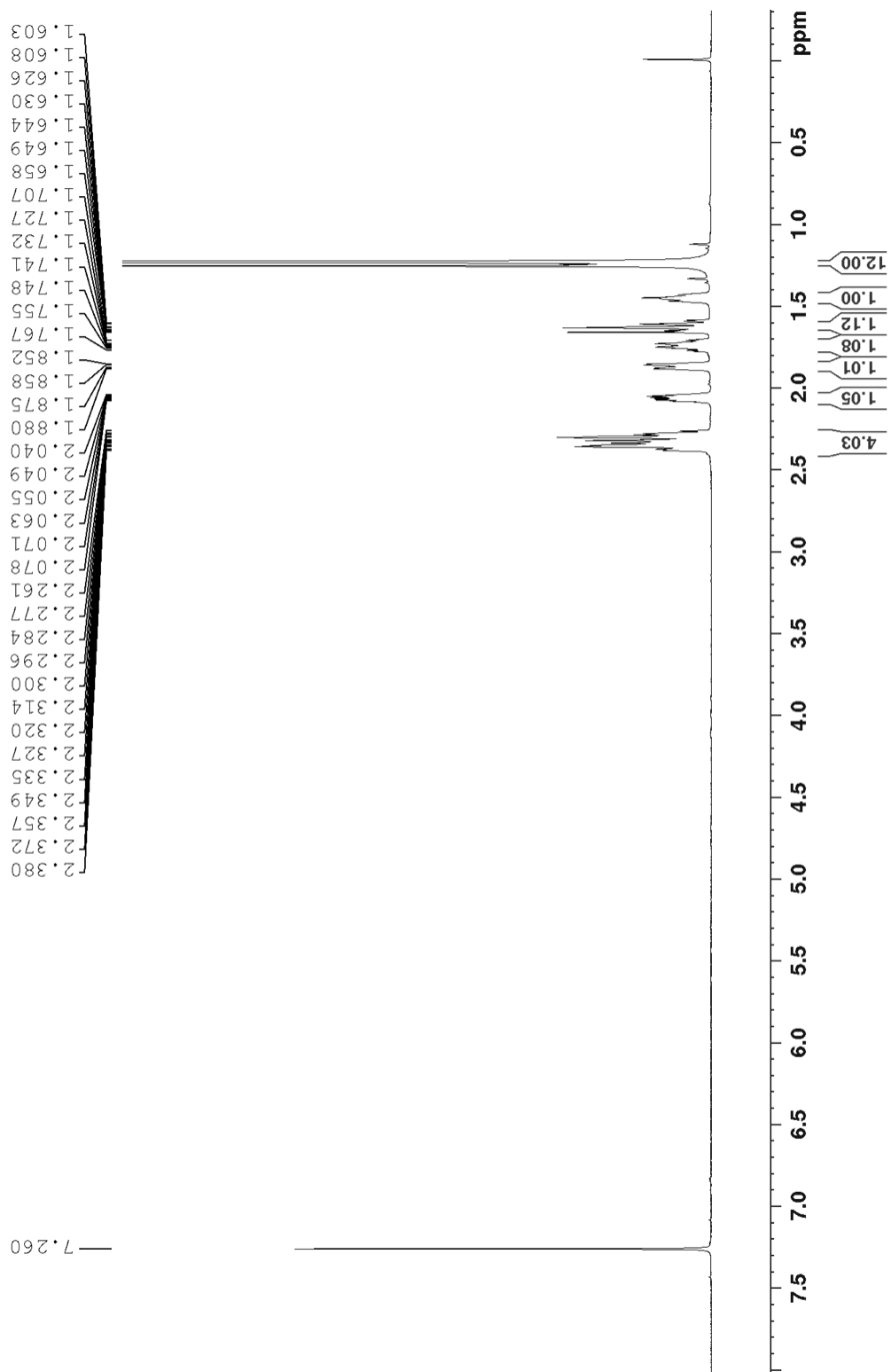
Figure A.75  $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 2)

Peak labels (ppm): 1.603, 1.608, 1.626, 1.630, 1.644, 1.649, 1.658, 1.707, 1.727, 1.732, 1.741, 1.748, 1.755, 1.767, 1.852, 1.858, 1.875, 1.880, 2.040, 2.049, 2.055, 2.063, 2.071, 2.078, 2.261, 2.277, 2.284, 2.296, 2.300, 2.314, 2.320, 2.327, 2.335, 2.349, 2.357, 2.372, 2.380, 7.260

Integrations: 12.00, 1.00, 1.12, 1.08, 1.01, 1.05, 4.03
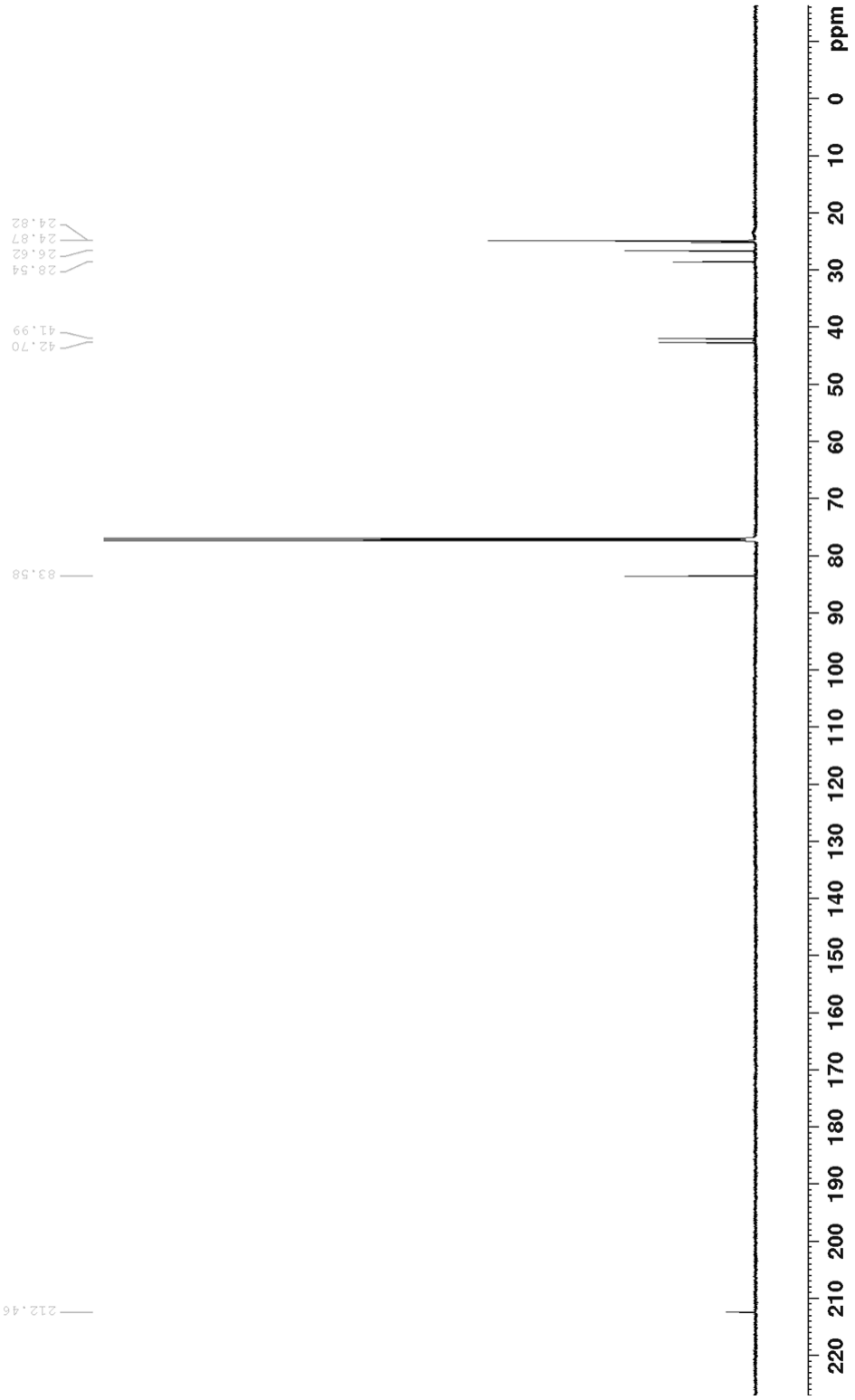
Figure A.76 $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 2)

178
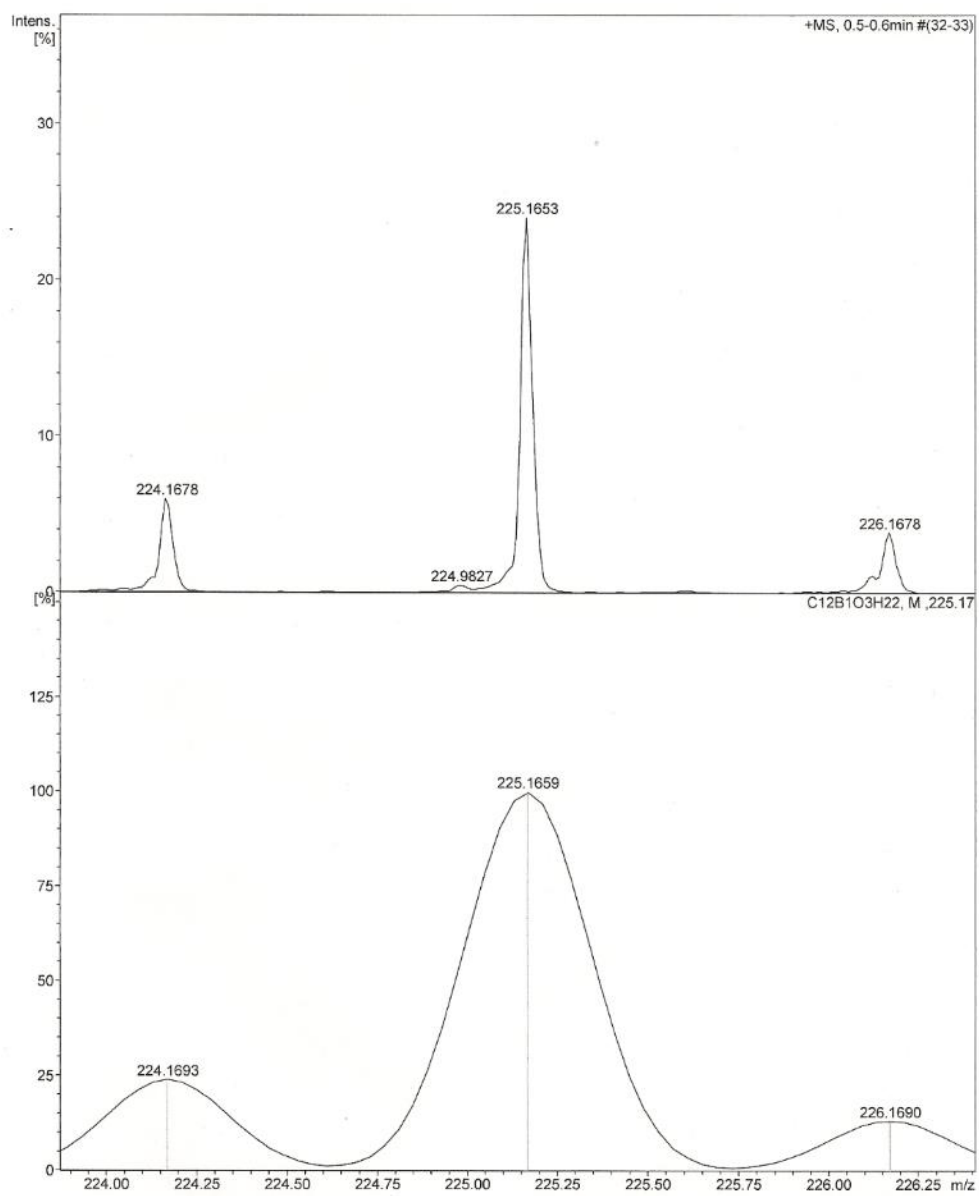
Figure A.77   HRMS of product (Table 4.3, Entry 2)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for $C_{12}H_{22}BO_3$, 225.1659; found (top) 225.1653
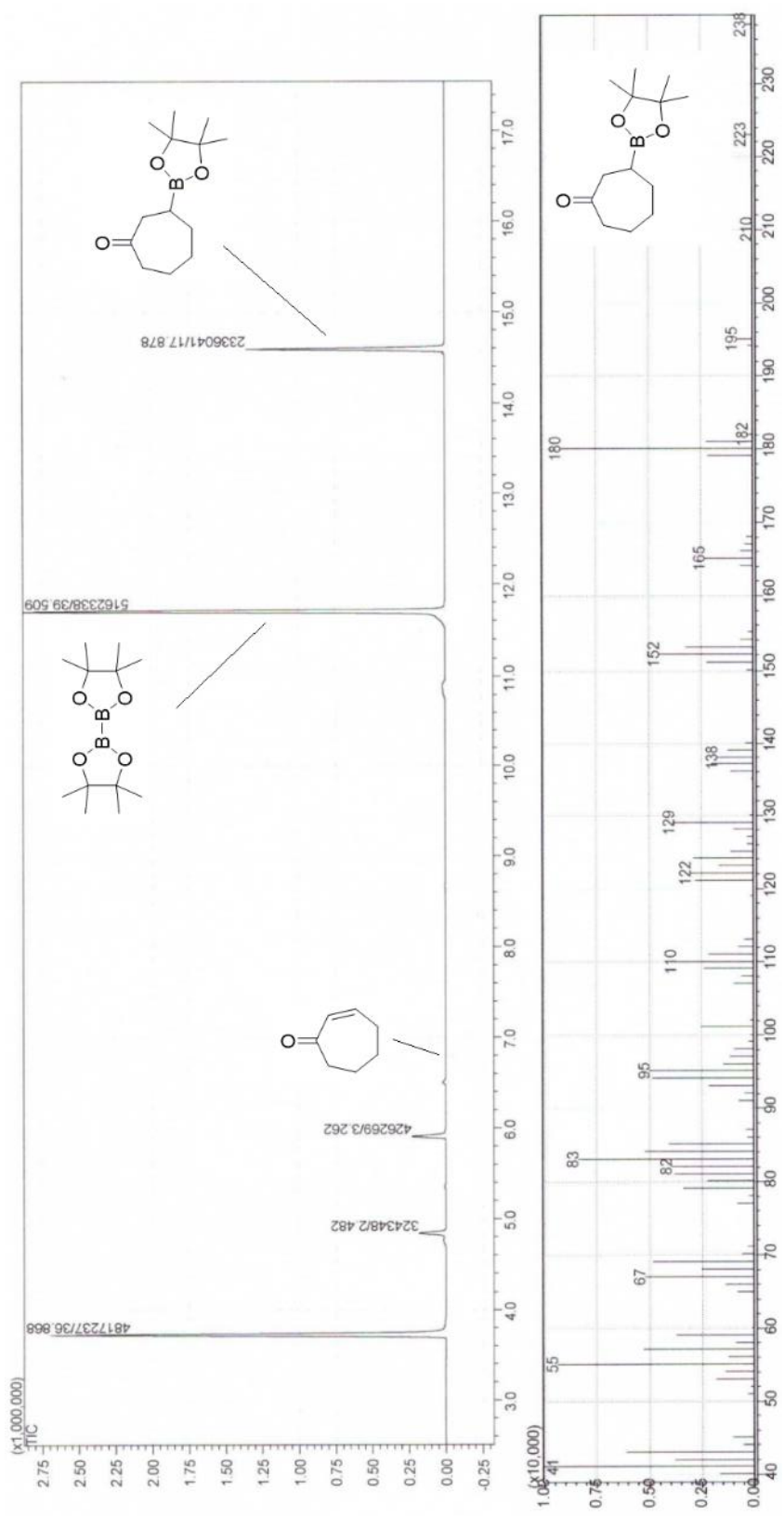
Figure A.78   GC-MS chromatogram spectrum of catalytic trial (Table 4.3, Entry 3)
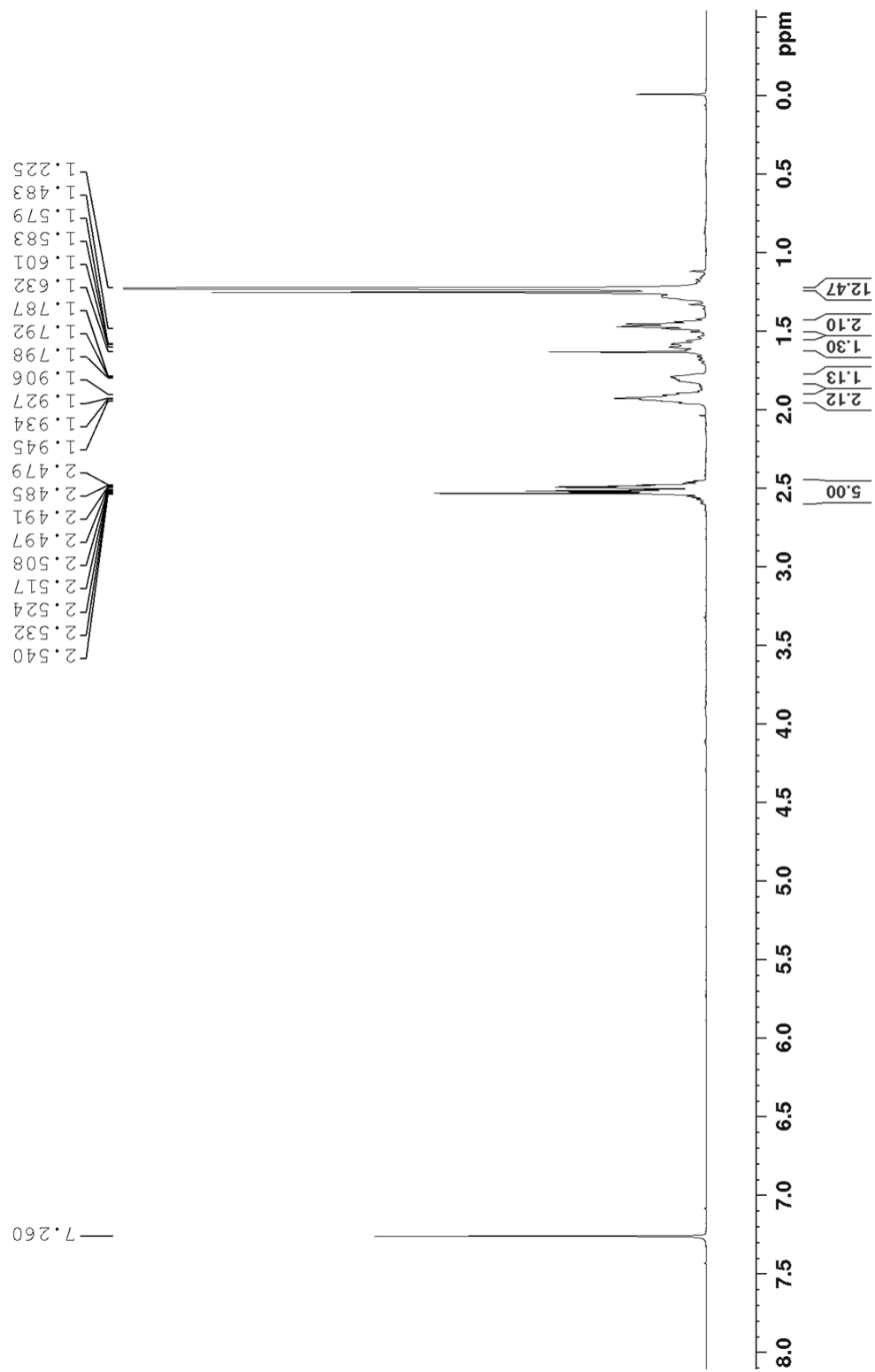
Figure A.79  $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 3)
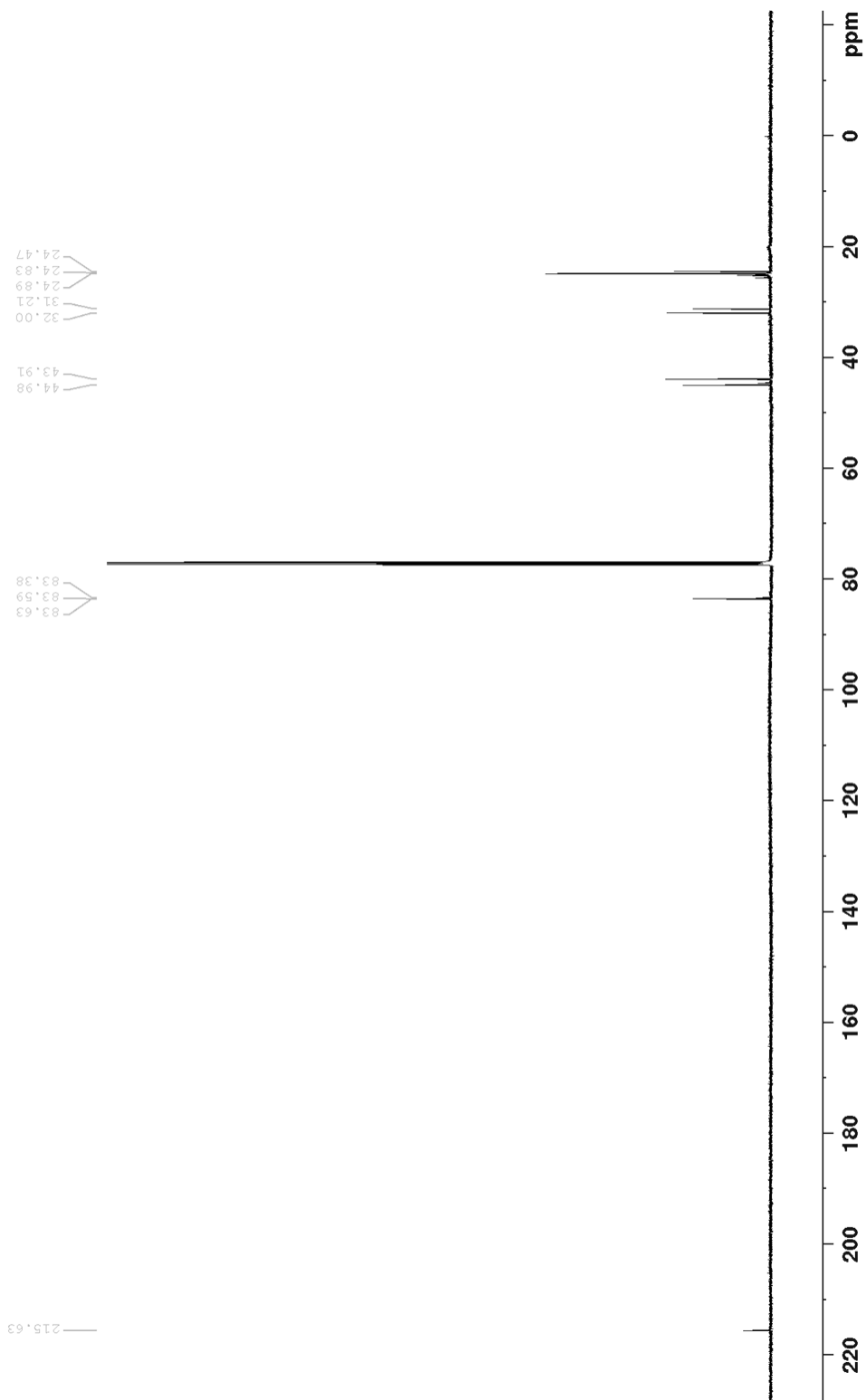
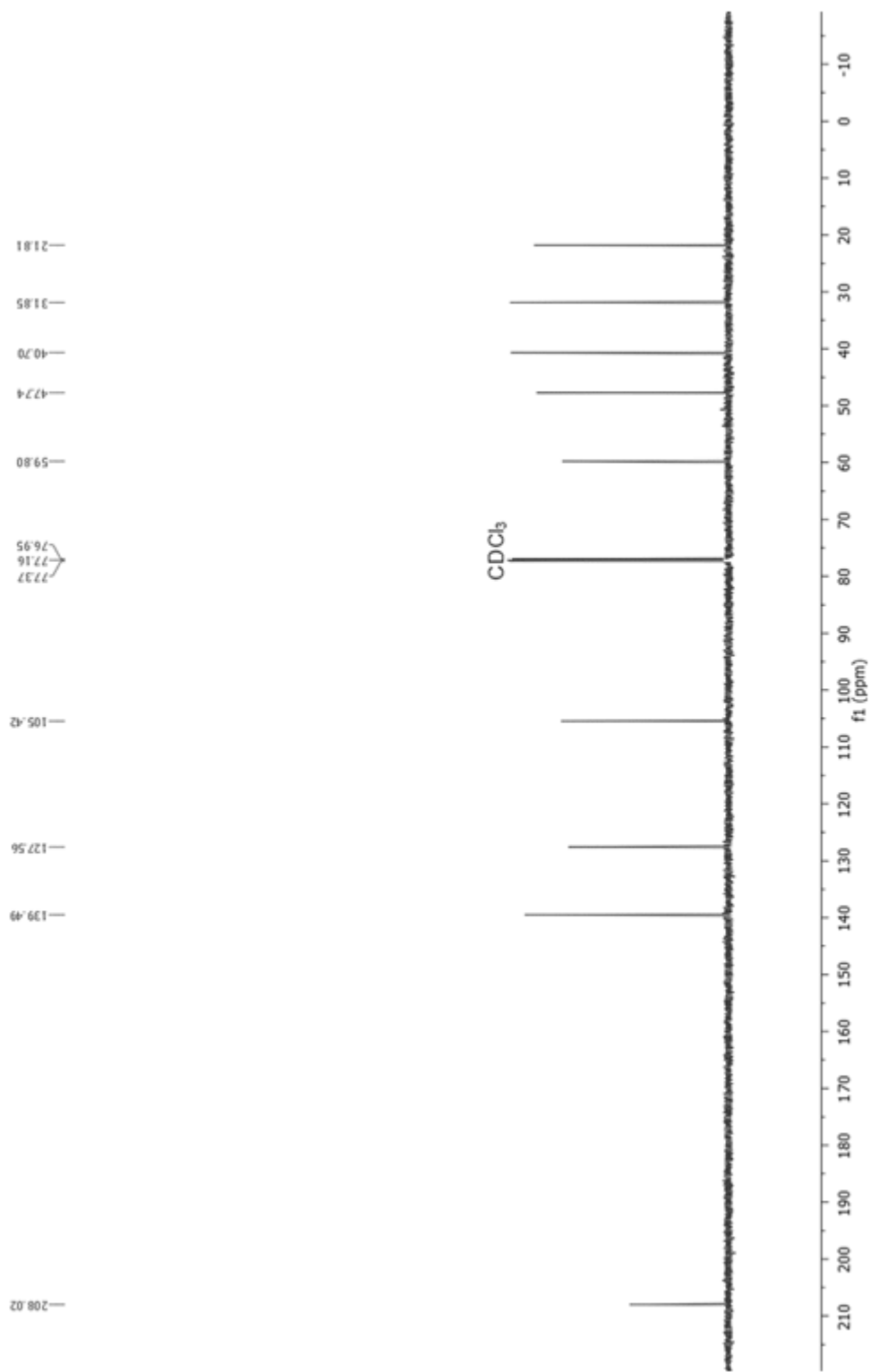Figure A.80 $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 3)
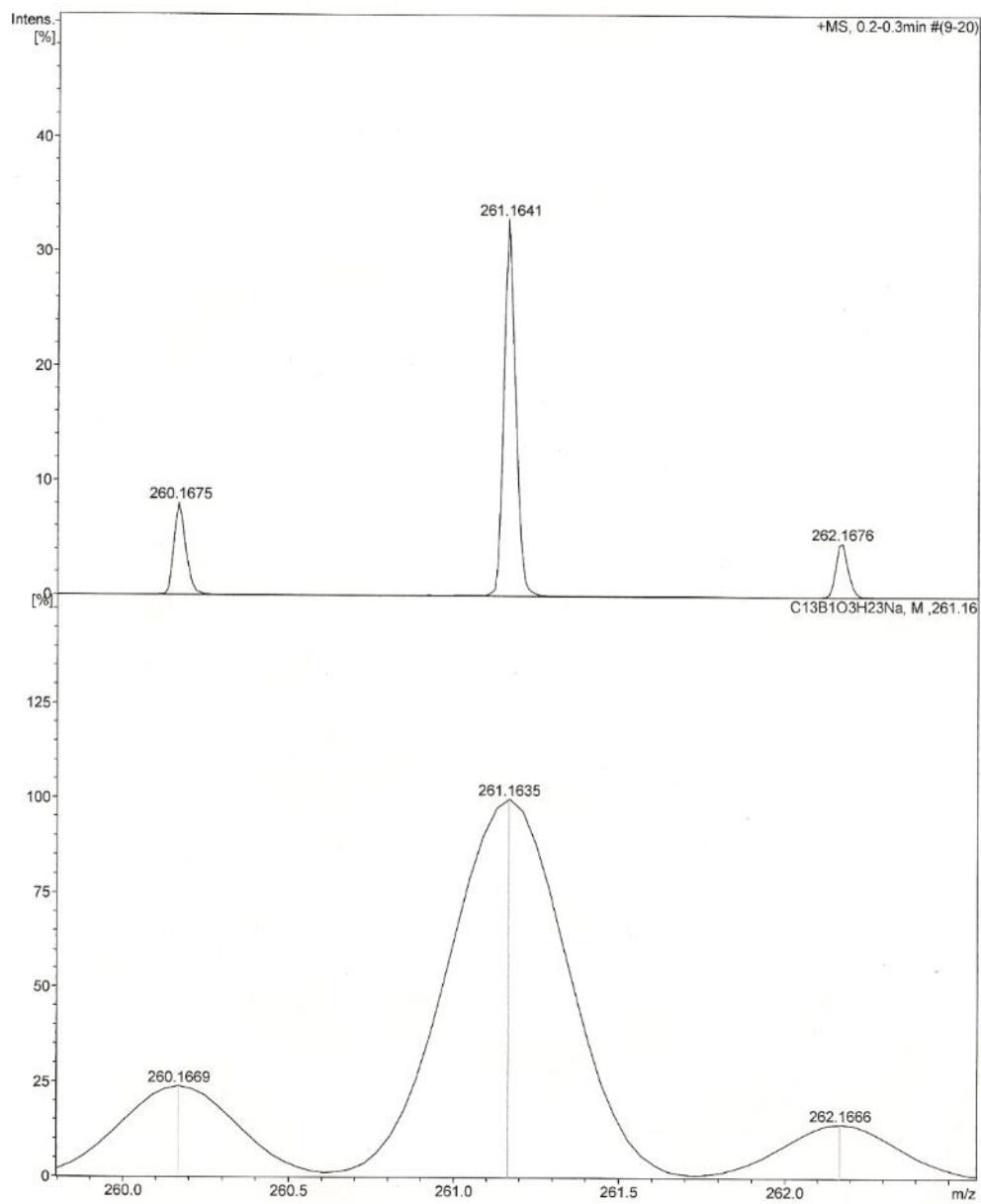
Figure A.81   HRMS of product (Table 4.3, Entry 3)

HRMS-ESI (*m*/*z*): [M+H]$^+$ calcd (bottom) for C$_{32}$H$_{23}$BO$_3$, 239.1815; found (top) 239.1820
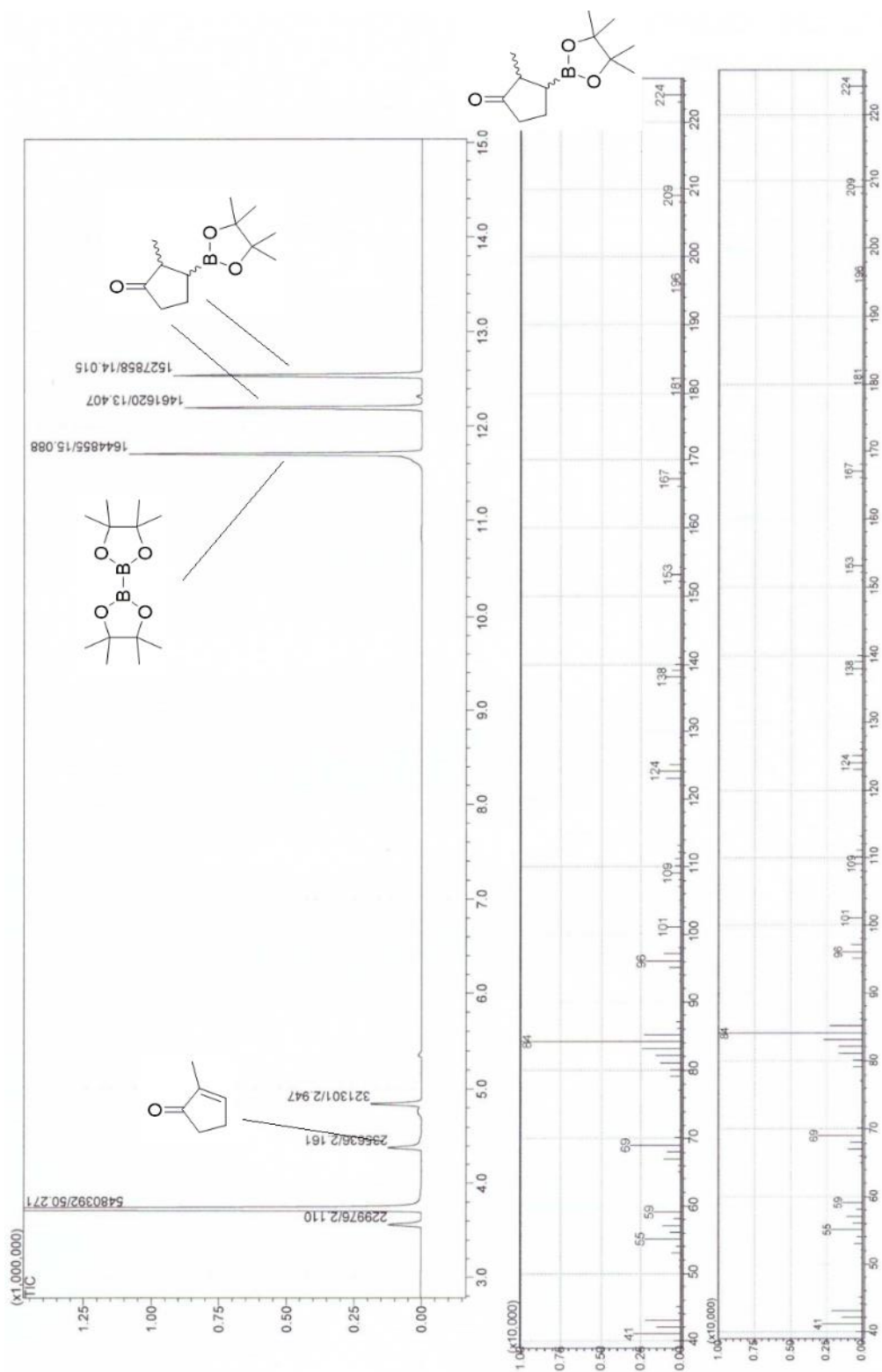
Figure A.82   GC-MS chromatogram spectrum of catalytic trial (Table 4.3, Entry 4)

184
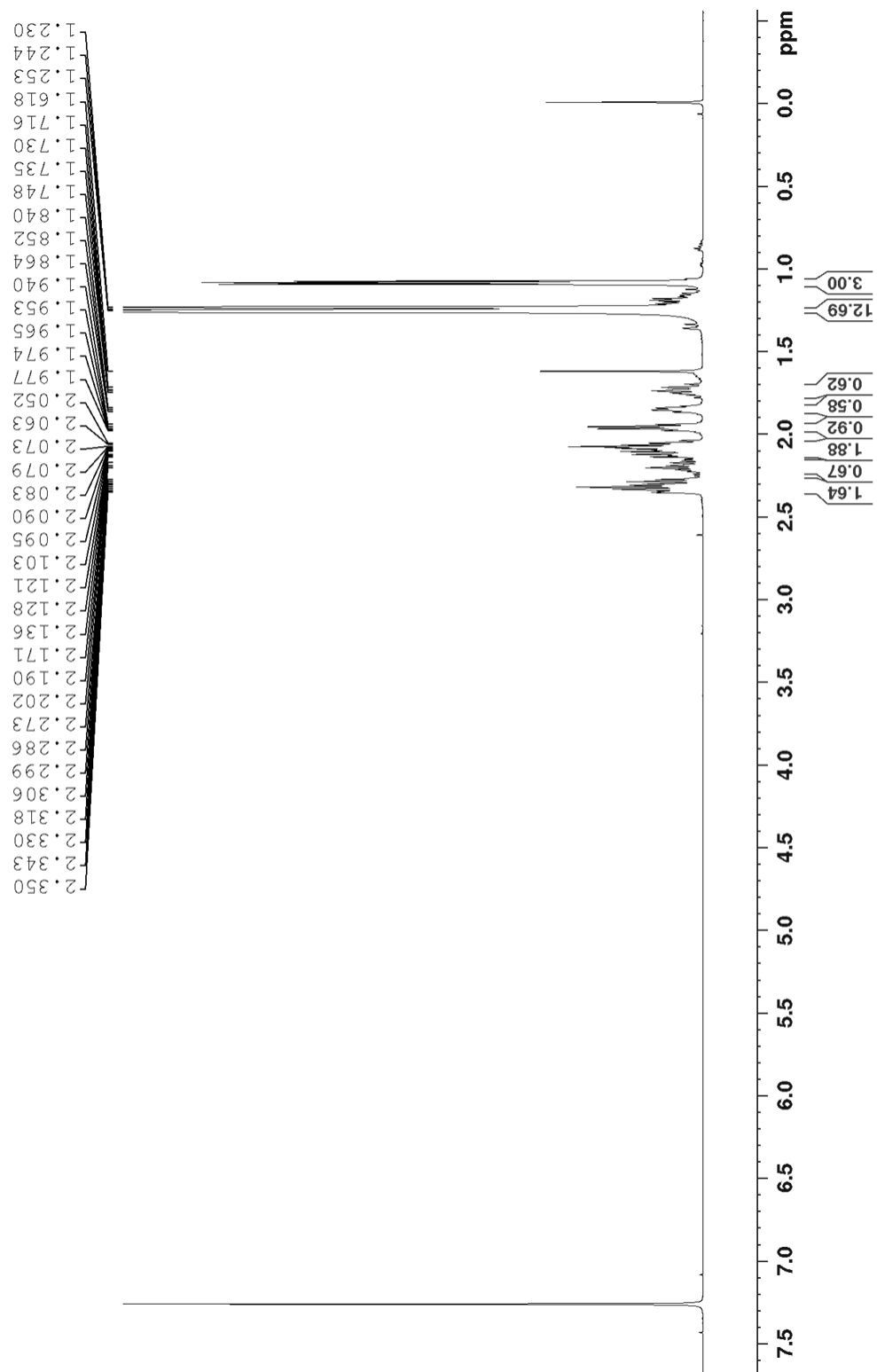
Figure A.83 ¹H NMR (600 MHz, CDCl₃) spectrum of isolated product (Table 4.3, Entry 4)
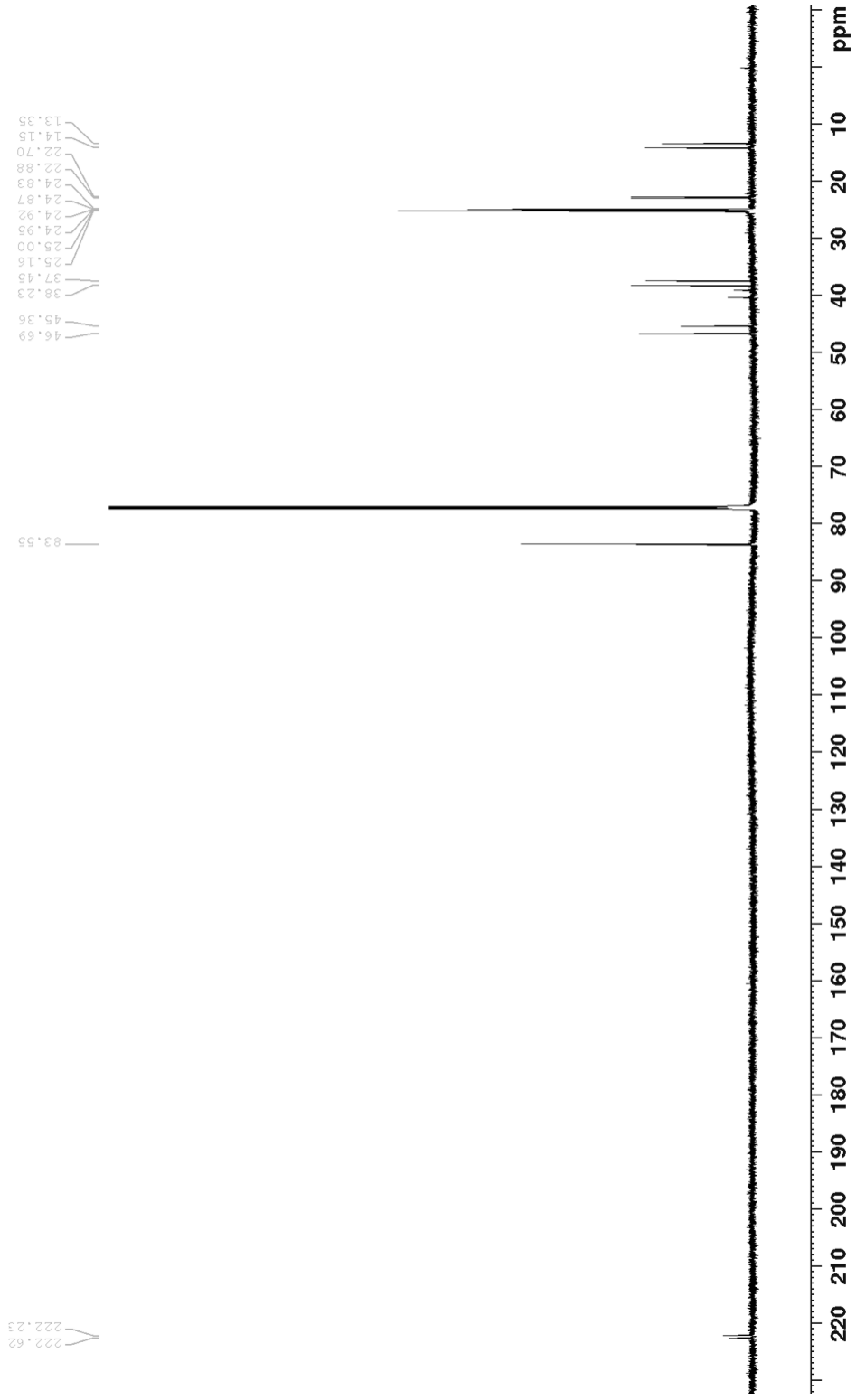
Figure A.84   $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 4)

186
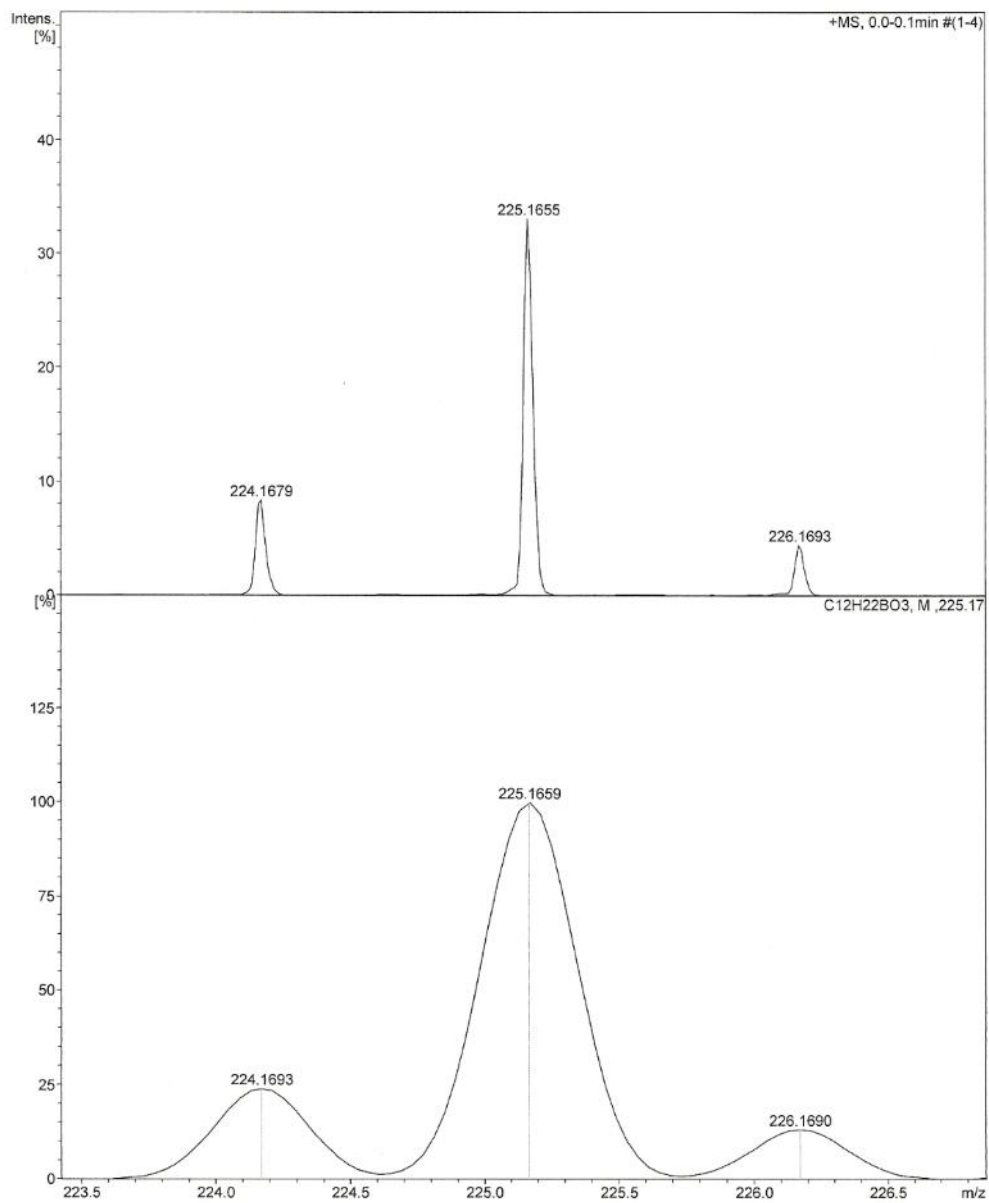
Figure A.85   HRMS of product (Table 4.3, Entry 4)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for C$_{12}$H$_{22}$BO$_3$, 225.1659; found (top) 225.1655
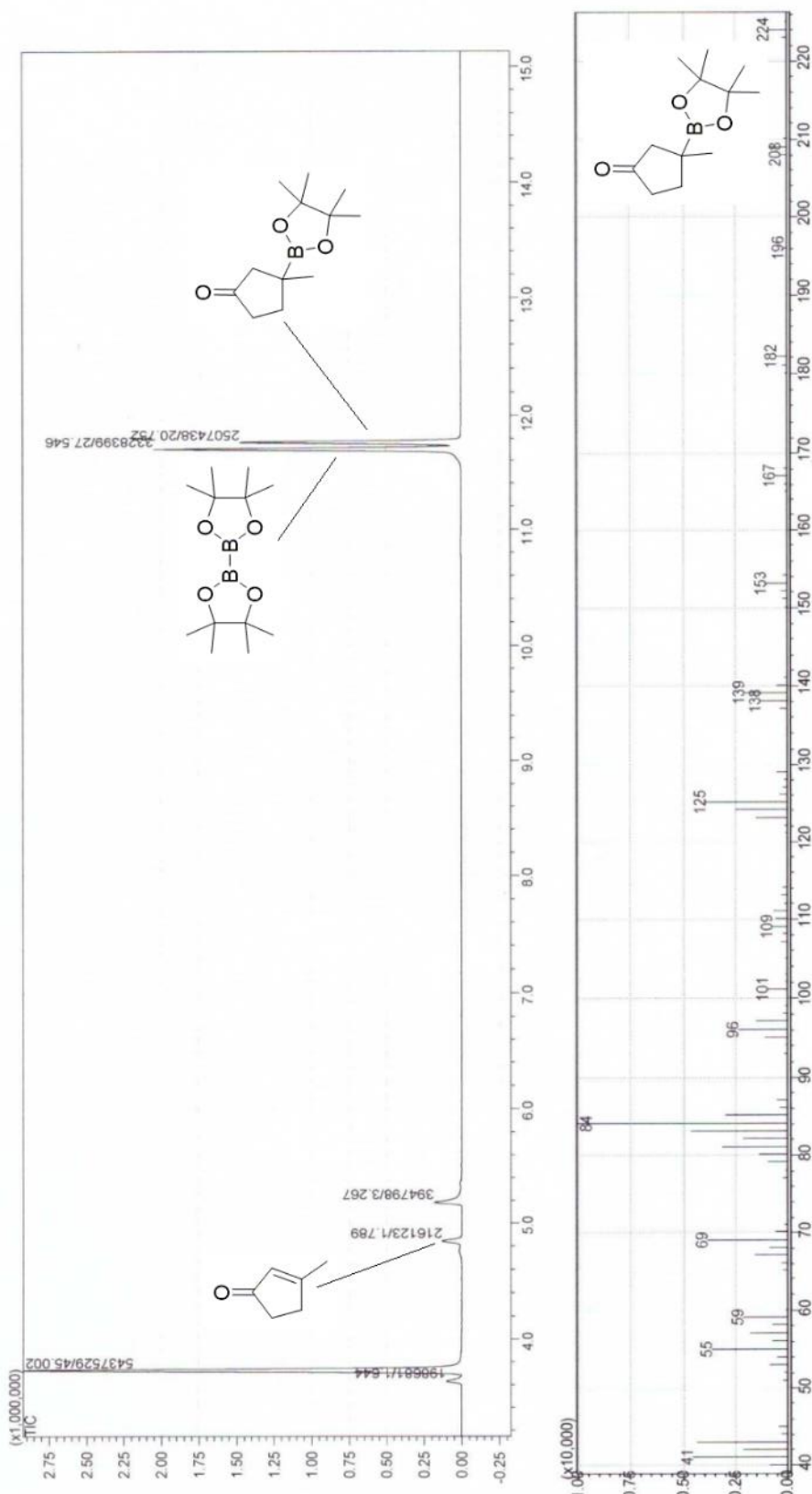
Figure A.86   GC-MS chromatogram spectrum of catalytic trial (Table 4.3, Entry 5)
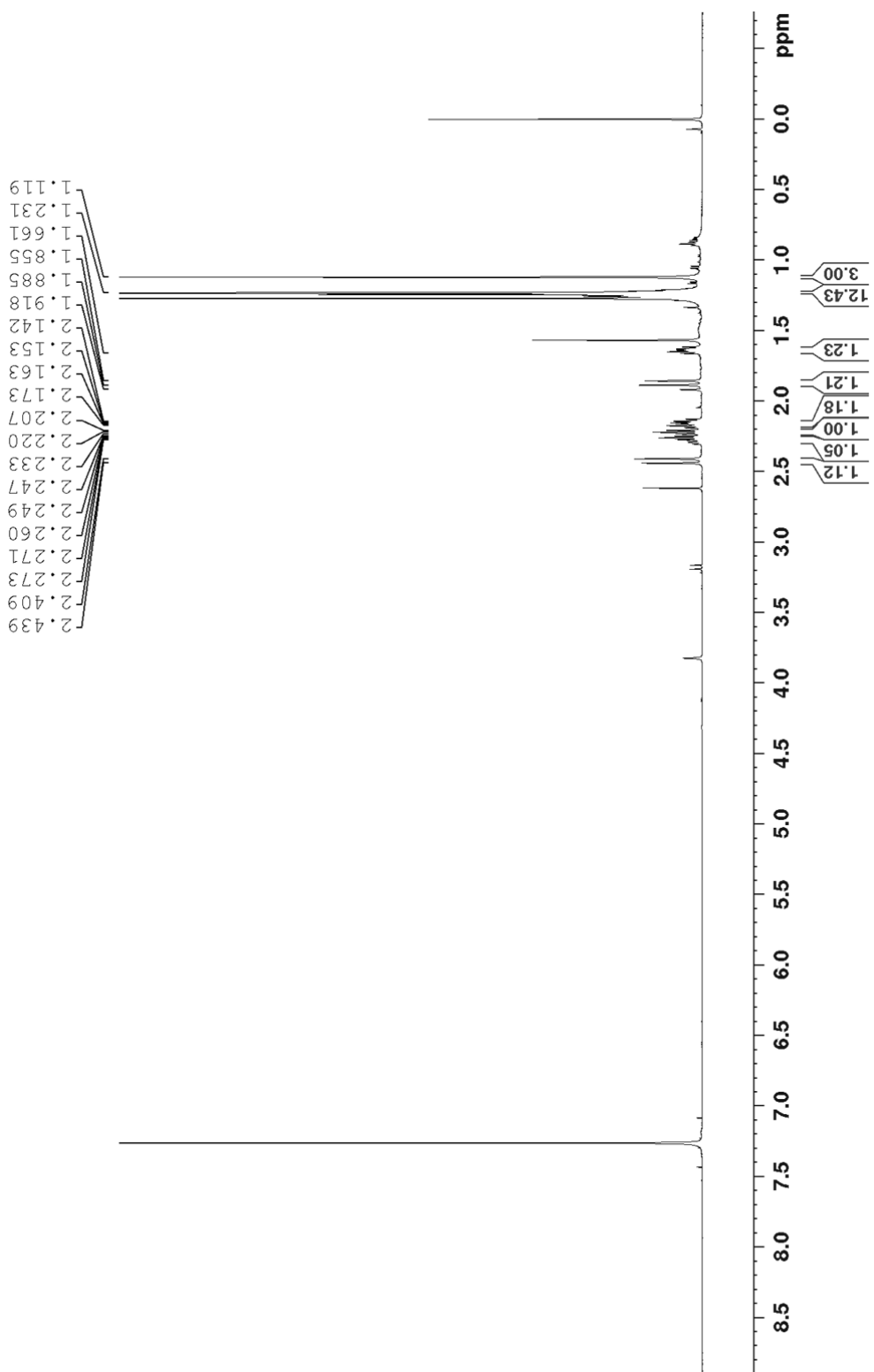
Figure A.87  ¹H NMR (600 MHz, CDCl₃) spectrum of isolated product (Table 4.3, Entry 5)

189
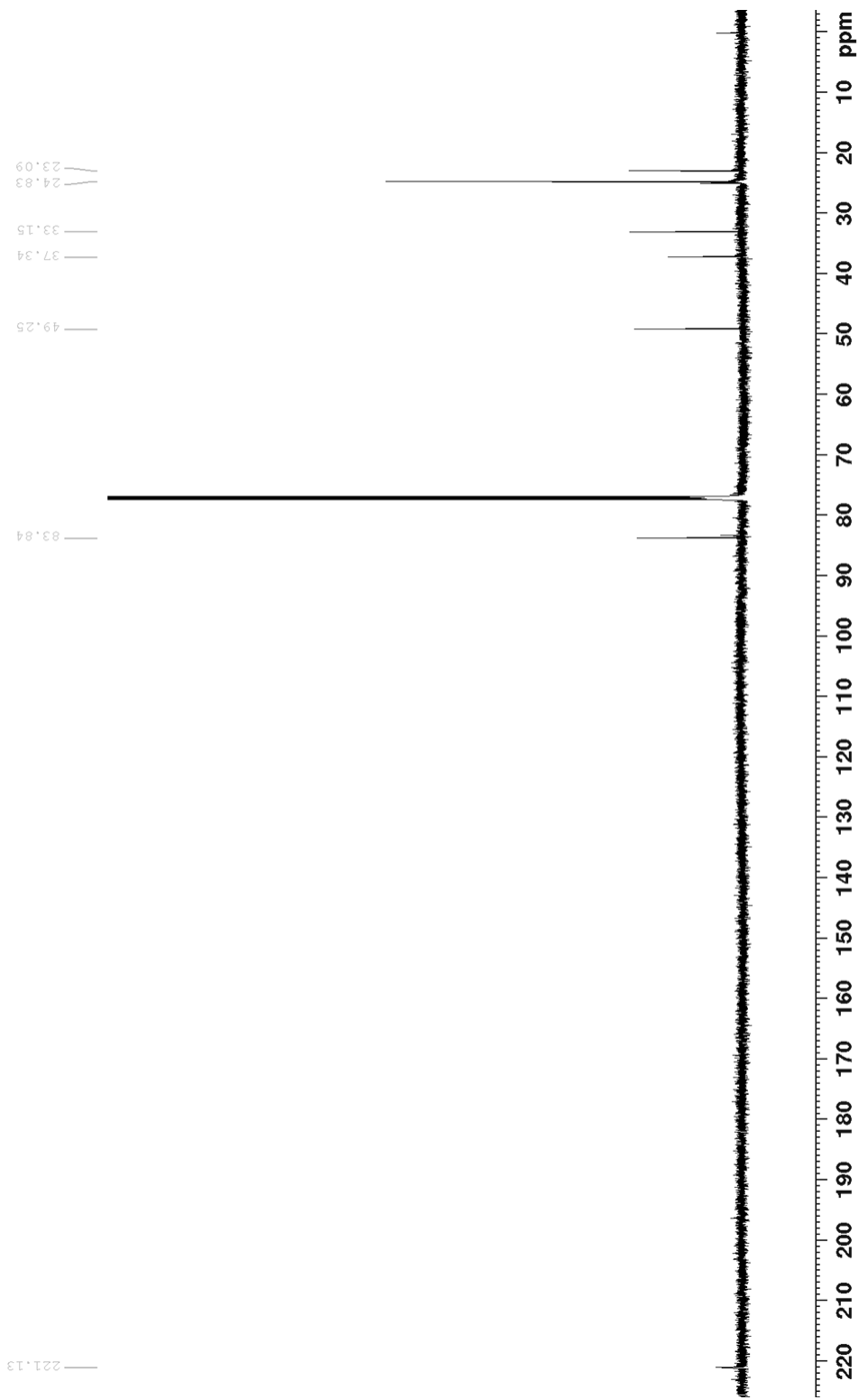
Figure A.88  $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 5)

190
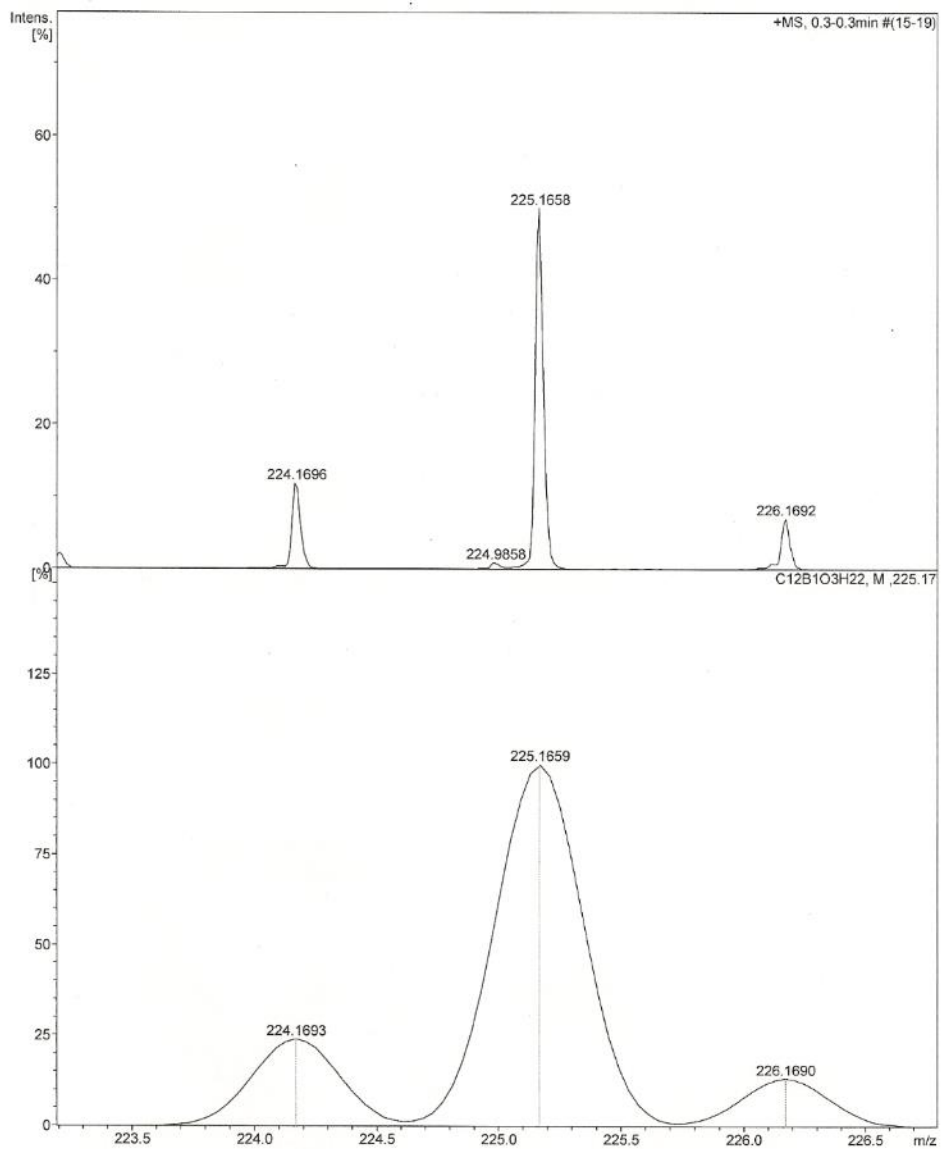
Figure A.89  HRMS of product (Table 4.3, Entry 5)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for $C_{12}H_{22}BO_3$, 225.1659; found (top) 225.1658
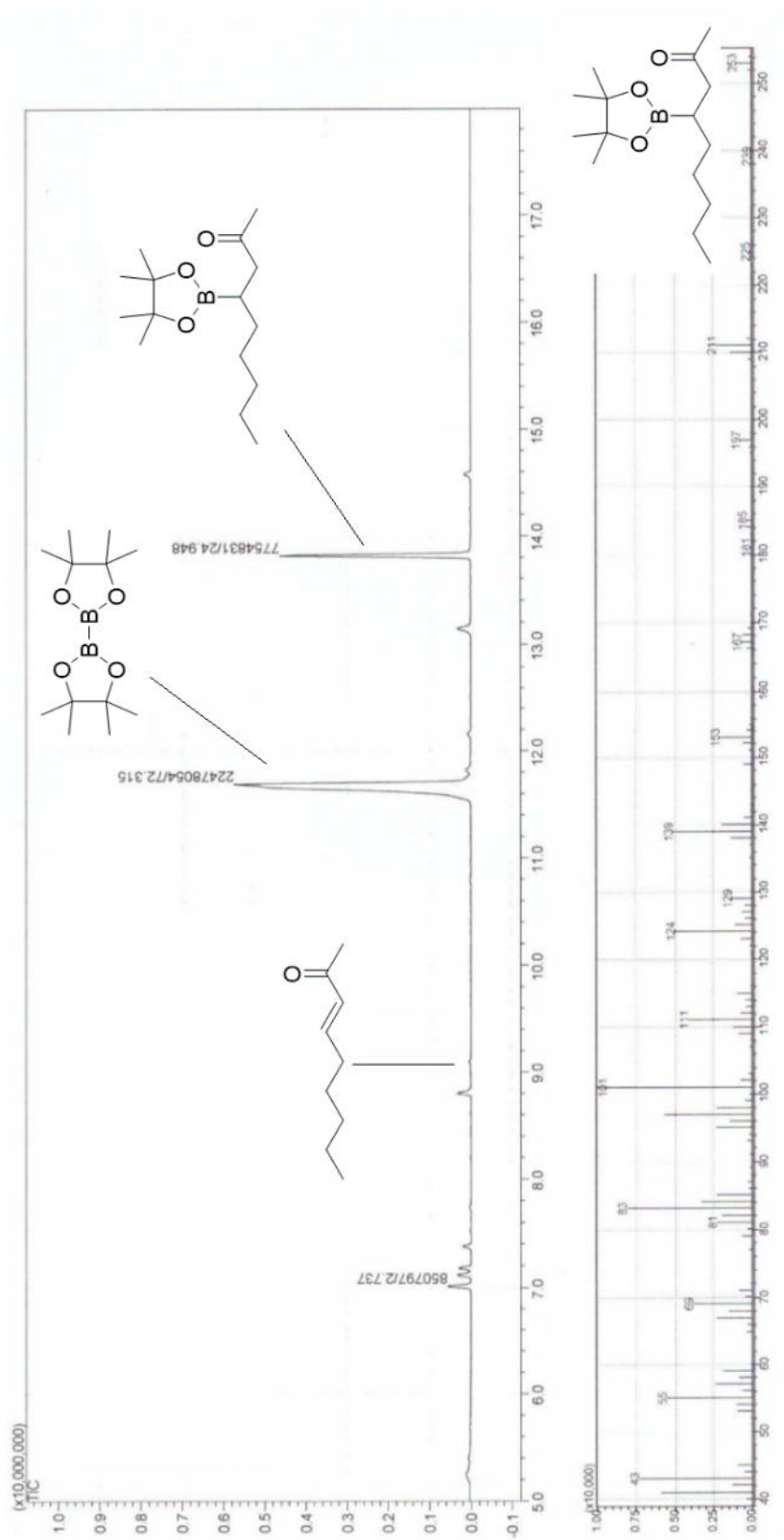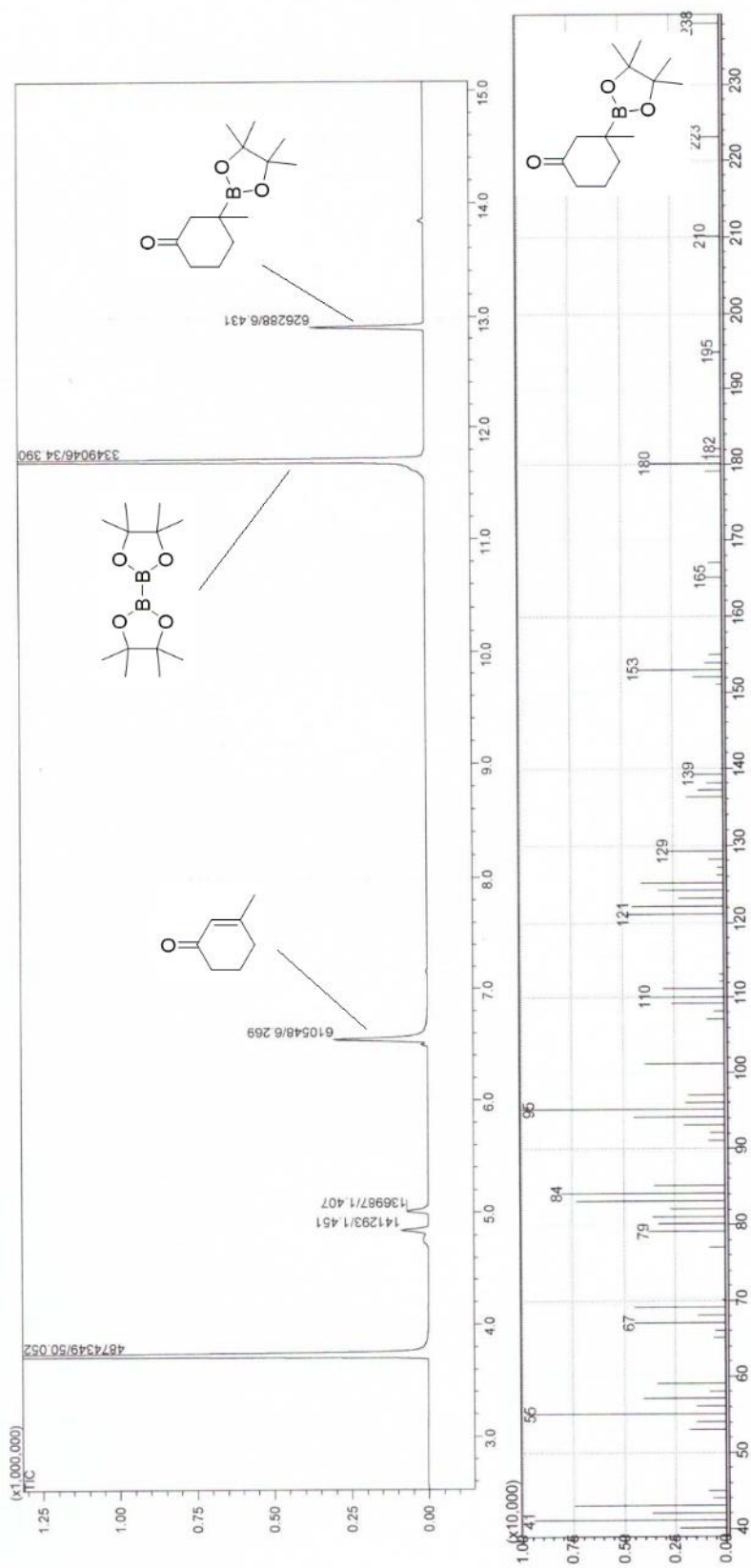
Figure A.90   GC-MS chromatogram spectrum of catalytic trial (Table 4.3, Entry 6)
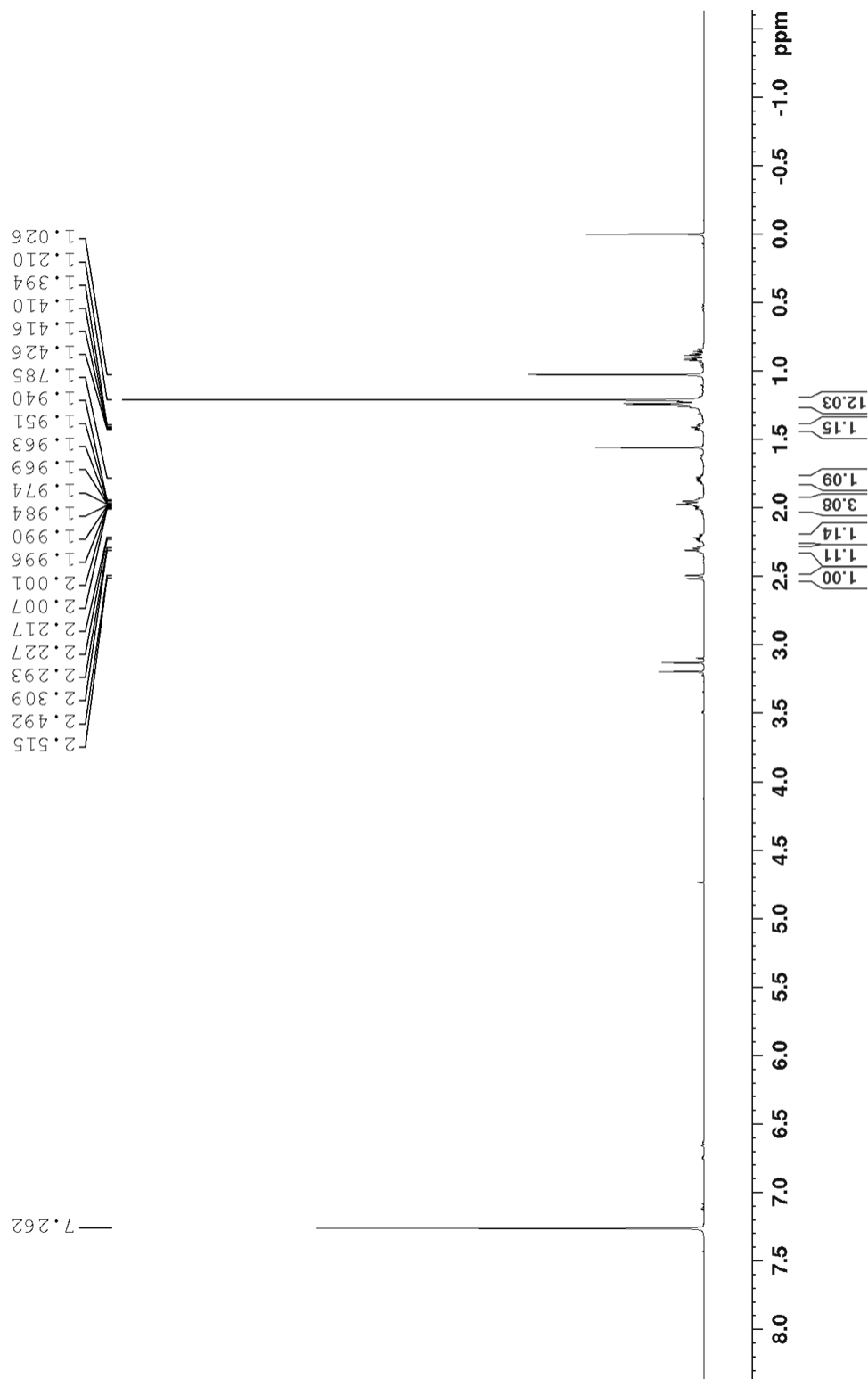
Figure A.91   $^1$H NMR (600 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 6)
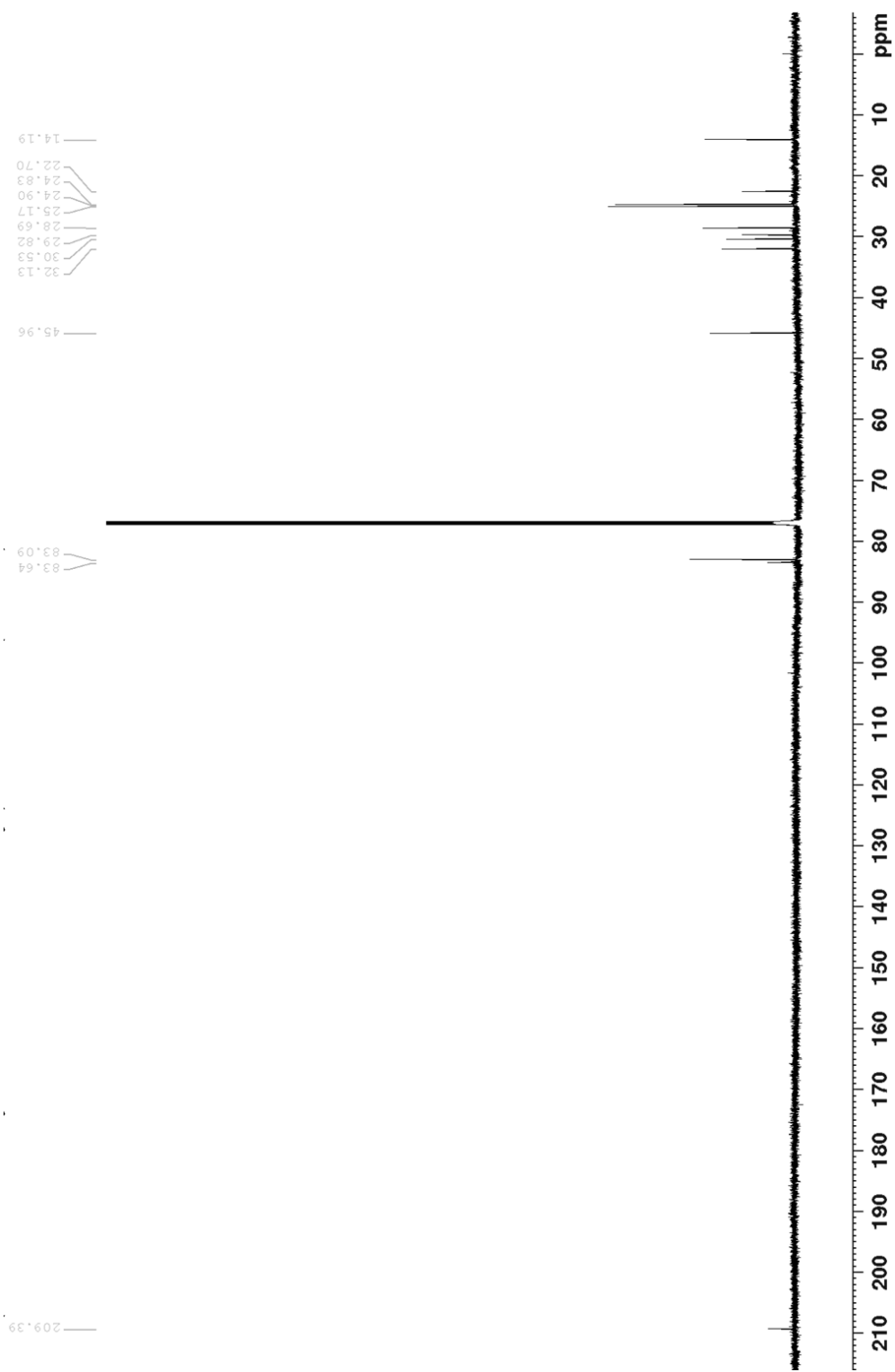
193
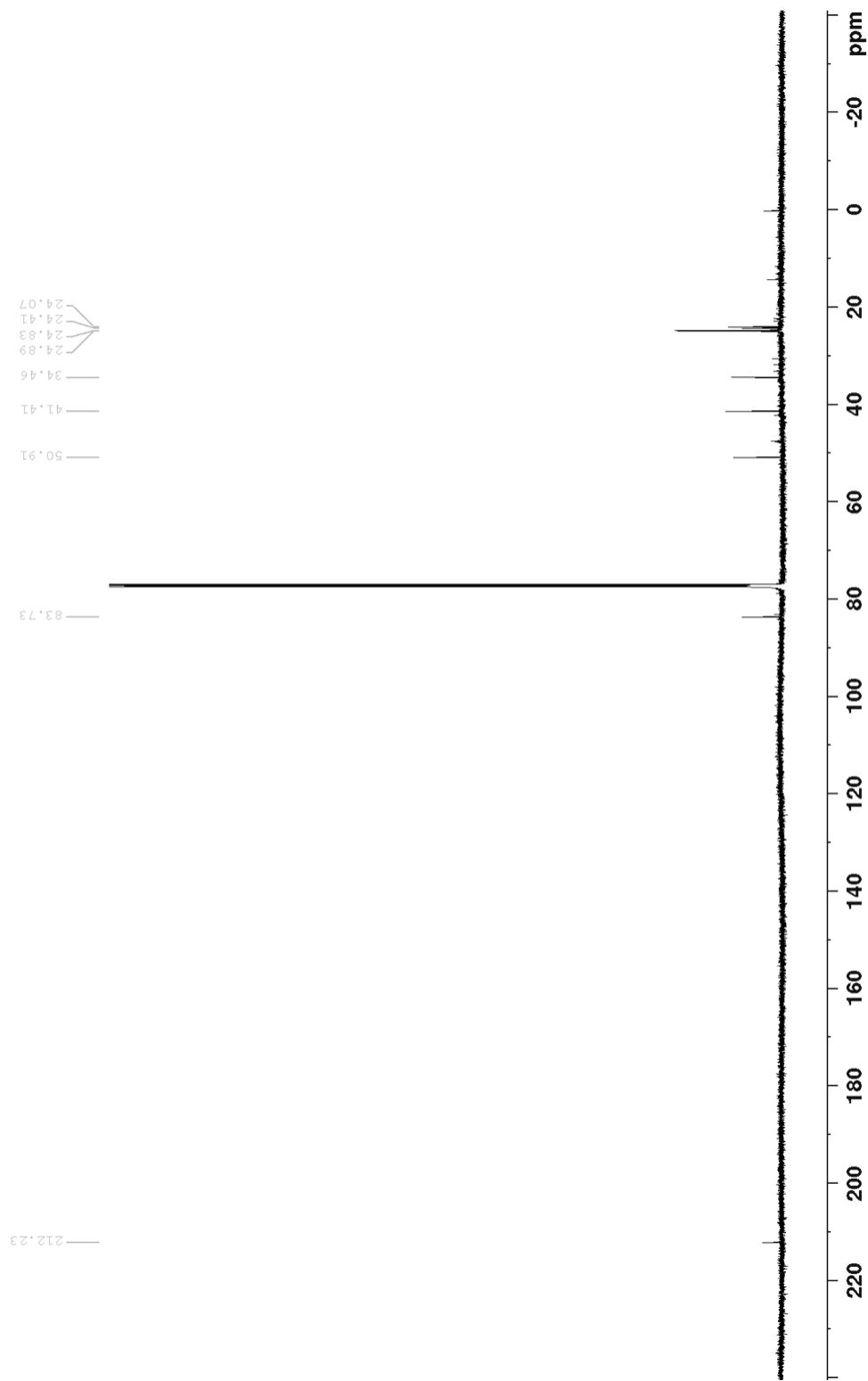
Figure A.92  $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of isolated product (Table 4.3, Entry 6)

194
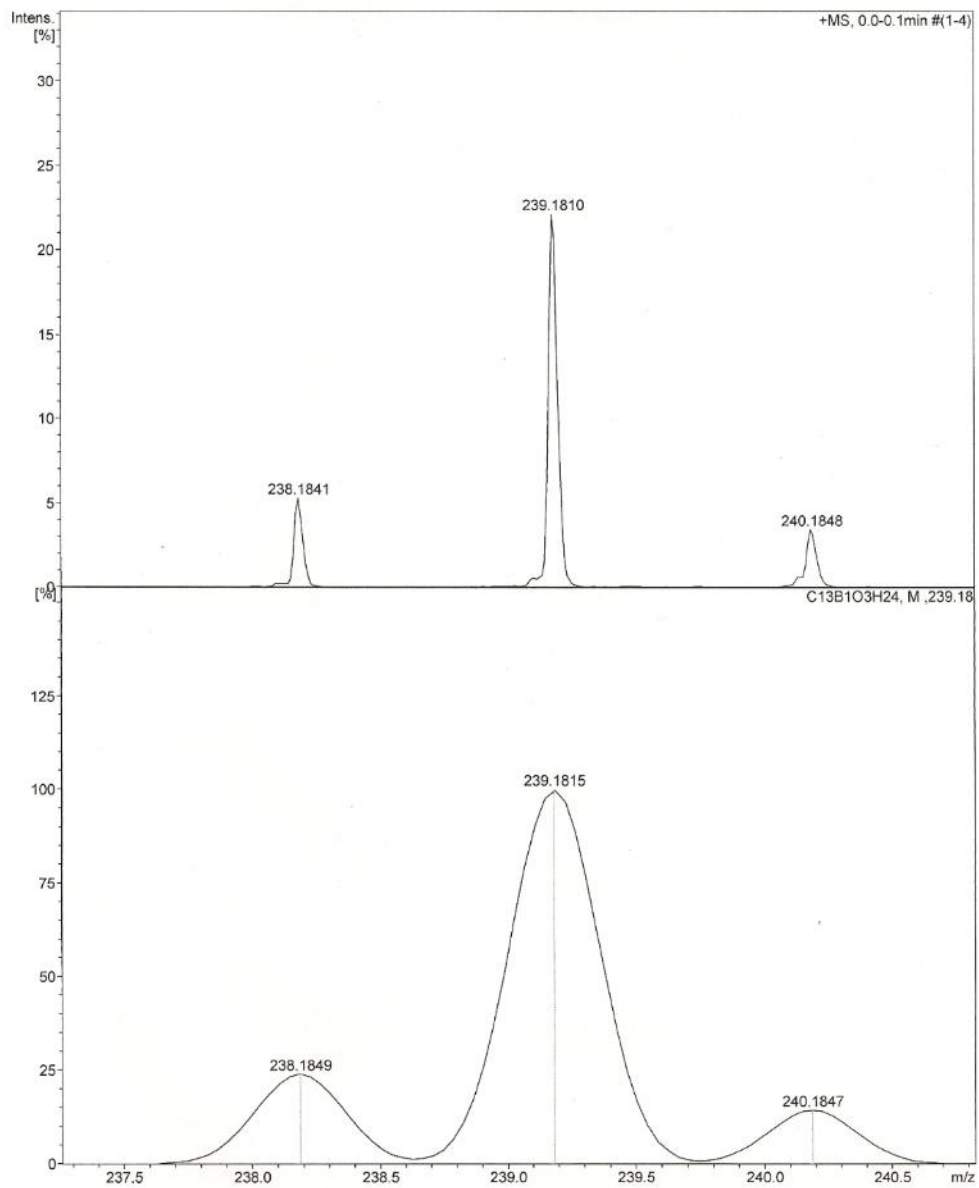
Figure A.93   HRMS of product (Table 4.3, Entry 6)

HRMS-ESI (*m/z*): [M+H]$^+$ calcd (bottom) for C$_{13}$H$_{24}$BO$_3$, 39.1815; found (top) 239.1810
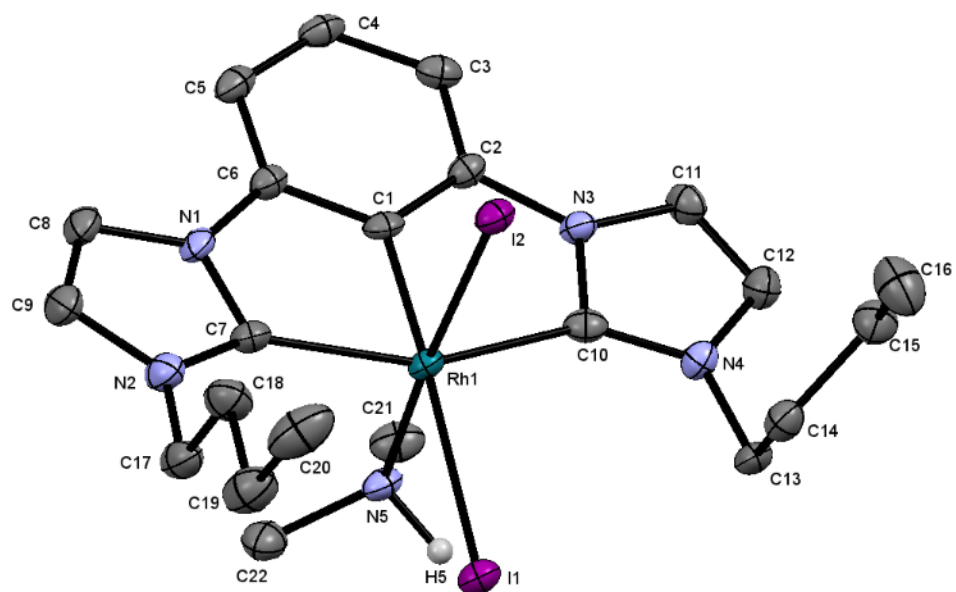
Figure A.94   X-ray molecular structure of **9**

Table A.13    Crystal Data and Structure Refinement for **9**

| | |
|---|---|
| Empirical formula | $C_{22} H_{32} I_2 N_5 Rh$ |
| Formula weight | 723.23 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | $a = 15.6046(11)$ Å      $\alpha = 90°$ |
| | $b = 11.3102(8)$ Å      $\beta = 108.373(4)°$ |
| | $c = 15.4899(11)$ Å      $\gamma = 90°$ |
| Volume | 2594.5(3) Å$^3$ |
| Z | 4 |
| Density (calculated) | 1.852 g.cm$^{-3}$ |
| Absorption coefficient ($\mu$) | 3.056 mm$^{-1}$ |
| F(000) | 1400 |
| Crystal color, habit | ?, ? |
| Crystal size | $0.20 \times 0.20 \times 0.20$ mm$^3$ |
| $\theta$ range for data collection | 1.375 to 27.984° |
| Index ranges | $-20 \le h \le 20, -14 \le k \le 14, -20 \le l \le 20$ |
| Reflections collected | 22210 |
| Independent reflections | 6172 [$R_{int} = 0.0346$] |
| Completeness to $\theta = 26.000°$ | 99.8 % |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 6172 / 0 / 275 |
| Goodness-of-fit on F$^2$ | 1.051 |
| Final R indices [I>2$\sigma$(I)] | $R_1 = 0.0301$, wR$_2 = 0.0657$ |
| R indices (all data) | $R_1 = 0.0388$, wR$_2 = 0.0704$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 2.326 and -1.183 e$^-$.Å$^{-3}$ |

Table A.14   Atomic Coordinates and Equivalent Isotropic Displacement Parameters
(Å²) for **9**

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| Rh(1) | 0.26891(2) | 0.48238(2) | 0.46866(2) | 0.015(1) |
| I(1) | 0.39244(2) | 0.48305(2) | 0.36634(2) | 0.019(1) |
| I(2) | 0.15535(2) | 0.32681(2) | 0.36317(2) | 0.019(1) |
| N(1) | 0.1201(2) | 0.6461(3) | 0.4476(2) | 0.019(1) |
| N(2) | 0.1581(2) | 0.6895(3) | 0.3299(2) | 0.024(1) |
| N(3) | 0.2682(2) | 0.3325(3) | 0.62030(19) | 0.017(1) |
| N(4) | 0.3776(2) | 0.2575(3) | 0.58261(19) | 0.019(1) |
| N(5) | 0.3652(2) | 0.5986(3) | 0.55695(19) | 0.019(1) |
| C(1) | 0.1884(2) | 0.4918(3) | 0.5423(2) | 0.018(1) |
| C(2) | 0.1971(2) | 0.4138(3) | 0.6123(2) | 0.017(1) |
| C(3) | 0.1410(3) | 0.4185(3) | 0.6665(2) | 0.021(1) |
| C(4) | 0.0751(3) | 0.5073(3) | 0.6468(2) | 0.021(1) |
| C(5) | 0.0646(2) | 0.5883(3) | 0.5771(2) | 0.022(1) |
| C(6) | 0.1223(2) | 0.5783(3) | 0.5248(2) | 0.018(1) |
| C(7) | 0.1817(2) | 0.6174(3) | 0.4035(2) | 0.019(1) |
| C(8) | 0.0609(3) | 0.7330(3) | 0.4012(3) | 0.024(1) |
| C(9) | 0.0846(3) | 0.7583(4) | 0.3268(3) | 0.027(1) |
| C(10) | 0.3161(2) | 0.3447(3) | 0.5597(2) | 0.020(1) |
| C(11) | 0.3014(3) | 0.2398(3) | 0.6797(2) | 0.021(1) |
| C(12) | 0.3697(3) | 0.1933(3) | 0.6555(3) | 0.025(1) |
| C(13) | 0.4421(2) | 0.2295(3) | 0.5338(2) | 0.021(1) |
| C(14) | 0.3979(3) | 0.1586(3) | 0.4479(2) | 0.023(1) |
| C(15) | 0.3620(3) | 0.0389(3) | 0.4636(3) | 0.027(1) |
| C(16) | 0.3162(4) | -0.0256(4) | 0.3750(3) | 0.039(1) |
| C(17) | 0.1969(3) | 0.6836(3) | 0.2545(3) | 0.026(1) |
| C(18) | 0.1471(3) | 0.5941(4) | 0.1832(3) | 0.030(1) |
| C(19) | 0.1882(3) | 0.5841(4) | 0.1057(3) | 0.035(1) |
| C(20) | 0.1407(3) | 0.4915(5) | 0.0360(3) | 0.044(1) |
| C(21) | 0.3726(3) | 0.5986(4) | 0.6548(2) | 0.027(1) |
| C(22) | 0.3601(3) | 0.7217(3) | 0.5242(3) | 0.026(1) |
| H(5) | 0.4251 | 0.5693 | 0.5553 | 0.023 |
| H(3) | 0.1471 | 0.3639 | 0.7147 | 0.025 |

Table A.14 (Continued)

| | | | | |
|---|---|---|---|---|
| H(4) | 0.0359 | 0.5123 | 0.6828 | 0.025 |
| H(5A) | 0.0198 | 0.6483 | 0.5654 | 0.026 |
| H(8) | 0.0132 | 0.7677 | 0.4183 | 0.029 |
| H(9) | 0.0558 | 0.8136 | 0.2806 | 0.032 |
| H(11) | 0.2803 | 0.2143 | 0.7278 | 0.026 |
| H(12) | 0.4060 | 0.1278 | 0.6835 | 0.029 |
| H(13A) | 0.4931 | 0.1837 | 0.5742 | 0.025 |
| H(13B) | 0.4667 | 0.3039 | 0.5174 | 0.025 |
| H(14A) | 0.3475 | 0.2055 | 0.4077 | 0.027 |
| H(14B) | 0.4427 | 0.1468 | 0.4153 | 0.027 |
| H(15A) | 0.3182 | 0.0496 | 0.4973 | 0.032 |
| H(15B) | 0.4125 | -0.0099 | 0.5016 | 0.032 |
| H(16A) | 0.2694 | 0.0252 | 0.3350 | 0.059 |
| H(16B) | 0.2885 | -0.0986 | 0.3878 | 0.059 |
| H(16C) | 0.3611 | -0.0450 | 0.3449 | 0.059 |
| H(17A) | 0.2614 | 0.6613 | 0.2788 | 0.031 |
| H(17B) | 0.1932 | 0.7625 | 0.2259 | 0.031 |
| H(18A) | 0.0830 | 0.6178 | 0.1578 | 0.036 |
| H(18B) | 0.1493 | 0.5157 | 0.2123 | 0.036 |
| H(19A) | 0.1840 | 0.6618 | 0.0752 | 0.042 |
| H(19B) | 0.2529 | 0.5633 | 0.1313 | 0.042 |
| H(20A) | 0.1477 | 0.4136 | 0.0652 | 0.066 |
| H(20B) | 0.1673 | 0.4902 | -0.0134 | 0.066 |
| H(20C) | 0.0763 | 0.5109 | 0.0113 | 0.066 |
| H(21A) | 0.3174 | 0.6316 | 0.6624 | 0.041 |
| H(21B) | 0.4245 | 0.6467 | 0.6888 | 0.041 |
| H(21C) | 0.3809 | 0.5173 | 0.6780 | 0.041 |
| H(22A) | 0.3620 | 0.7225 | 0.4616 | 0.040 |
| H(22B) | 0.4113 | 0.7668 | 0.5633 | 0.040 |
| H(22C) | 0.3035 | 0.7576 | 0.5260 | 0.040 |

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table A.15    Anisotropic Displacement Parameters (Å$^2$) for **9**

|  | U$_{11}$ | U$_{22}$ | U$_{33}$ | U$_{23}$ | U$_{13}$ | U$_{12}$ |
|---|---|---|---|---|---|---|
| Rh(1) | 0.0105(1) | 0.0186(1) | 0.0167(1) | 0.0000(1) | 0.0041(1) | 0.0007(1) |
| I(1) | 0.0140(1) | 0.0253(1) | 0.0190(1) | -0.0010(1) | 0.0059(1) | 0.0001(1) |
| I(2) | 0.0141(1) | 0.0223(1) | 0.0209(1) | -0.0029(1) | 0.0051(1) | -0.0009(1) |
| N(1) | 0.0107(15) | 0.0203(15) | 0.0239(15) | 0.0006(12) | 0.0025(12) | 0.0028(12) |
| N(2) | 0.0168(16) | 0.0273(17) | 0.0278(16) | 0.0073(13) | 0.0058(13) | 0.0025(14) |
| N(3) | 0.0136(15) | 0.0213(15) | 0.0171(13) | 0.0024(11) | 0.0060(12) | 0.0007(12) |
| N(4) | 0.0175(16) | 0.0210(15) | 0.0181(14) | 0.0005(11) | 0.0047(12) | 0.0028(13) |
| N(5) | 0.0117(15) | 0.0237(15) | 0.0222(15) | -0.0033(12) | 0.0052(12) | -0.0011(13) |
| C(1) | 0.0108(17) | 0.0220(17) | 0.0214(16) | -0.0019(14) | 0.0048(14) | -0.0042(14) |
| C(2) | 0.0140(17) | 0.0209(17) | 0.0162(15) | -0.0023(13) | 0.0038(13) | 0.0003(14) |
| C(3) | 0.020(2) | 0.0233(18) | 0.0200(17) | -0.0034(14) | 0.0078(15) | -0.0065(16) |
| C(4) | 0.0149(18) | 0.0264(19) | 0.0234(17) | -0.0102(14) | 0.0089(15) | -0.0034(15) |
| C(5) | 0.0137(18) | 0.0227(18) | 0.0273(18) | -0.0089(15) | 0.0056(15) | -0.0005(15) |
| C(6) | 0.0142(18) | 0.0199(17) | 0.0190(16) | -0.0027(13) | 0.0052(14) | -0.0006(14) |
| C(7) | 0.0136(18) | 0.0216(18) | 0.0223(17) | 0.0002(14) | 0.0072(14) | -0.0011(15) |
| C(8) | 0.0150(19) | 0.0227(19) | 0.0309(19) | 0.0012(15) | 0.0032(16) | 0.0033(16) |
| C(9) | 0.018(2) | 0.0257(19) | 0.034(2) | 0.0072(16) | 0.0037(17) | 0.0029(16) |
| C(10) | 0.0164(18) | 0.0239(18) | 0.0175(16) | -0.0027(14) | 0.0042(14) | -0.0049(15) |
| C(11) | 0.023(2) | 0.0224(18) | 0.0176(16) | 0.0054(14) | 0.0042(15) | -0.0004(16) |
| C(12) | 0.022(2) | 0.0222(19) | 0.0280(19) | 0.0041(15) | 0.0060(16) | 0.0027(16) |
| C(13) | 0.0137(18) | 0.0221(18) | 0.0292(18) | 0.0034(15) | 0.0100(15) | 0.0021(15) |
| C(14) | 0.020(2) | 0.0263(19) | 0.0224(17) | 0.0011(15) | 0.0080(15) | 0.0041(16) |
| C(15) | 0.026(2) | 0.026(2) | 0.0270(19) | -0.0021(16) | 0.0062(17) | -0.0006(17) |
| C(16) | 0.047(3) | 0.030(2) | 0.034(2) | 0.0025(18) | 0.002(2) | -0.004(2) |
| C(17) | 0.020(2) | 0.032(2) | 0.0268(18) | 0.0115(16) | 0.0086(16) | 0.0034(17) |
| C(18) | 0.030(2) | 0.033(2) | 0.030(2) | 0.0070(17) | 0.0141(18) | -0.0006(19) |
| C(19) | 0.028(2) | 0.049(3) | 0.029(2) | 0.0083(19) | 0.0106(18) | 0.005(2) |
| C(20) | 0.030(3) | 0.070(4) | 0.033(2) | -0.006(2) | 0.011(2) | 0.006(2) |
| C(21) | 0.022(2) | 0.038(2) | 0.0207(18) | -0.0062(16) | 0.0048(16) | -0.0057(18) |
| C(22) | 0.021(2) | 0.0247(19) | 0.033(2) | -0.0039(16) | 0.0071(17) | -0.0040(17) |

$$-2\pi^2[h^2a*^2U_{11} + ... + 2hka*b*U_{12}] \qquad (A.3)$$

Table A.16    Bond Lengths [Å] for **9**

| atom-atom | distance | atom-atom | distance |
|---|---|---|---|
| Rh(1)-C(1) | 1.948(4) | Rh(1)-C(10) | 2.074(4) |
| Rh(1)-C(7) | 2.083(4) | Rh(1)-N(5) | 2.136(3) |
| Rh(1)-I(2) | 2.6610(4) | Rh(1)-I(1) | 2.8555(4) |
| N(1)-C(7) | 1.382(4) | N(1)-C(8) | 1.385(5) |
| N(1)-C(6) | 1.411(4) | N(2)-C(7) | 1.355(5) |
| N(2)-C(9) | 1.374(5) | N(2)-C(17) | 1.477(5) |
| N(3)-C(10) | 1.379(4) | N(3)-C(11) | 1.383(4) |
| N(3)-C(2) | 1.416(4) | N(4)-C(10) | 1.344(5) |
| N(4)-C(12) | 1.380(5) | N(4)-C(13) | 1.472(4) |
| N(5)-C(22) | 1.475(5) | N(5)-C(21) | 1.484(4) |
| N(5)-H(5) | 1.0000 | C(1)-C(2) | 1.371(5) |
| C(1)-C(6) | 1.385(5) | C(2)-C(3) | 1.392(5) |
| C(3)-C(4) | 1.401(5) | C(3)-H(3) | 0.9500 |
| C(4)-C(5) | 1.386(5) | C(4)-H(4) | 0.9500 |
| C(5)-C(6) | 1.393(5) | C(5)-H(5A) | 0.9500 |
| C(8)-C(9) | 1.348(5) | C(8)-H(8) | 0.9500 |
| C(9)-H(9) | 0.9500 | C(11)-C(12) | 1.344(5) |
| C(11)-H(11) | 0.9500 | C(12)-H(12) | 0.9500 |
| C(13)-C(14) | 1.520(5) | C(13)-H(13A) | 0.9900 |
| C(13)-H(13B) | 0.9900 | C(14)-C(15) | 1.514(5) |
| C(14)-H(14A) | 0.9900 | C(14)-H(14B) | 0.9900 |
| C(15)-C(16) | 1.520(6) | C(15)-H(15A) | 0.9900 |
| C(15)-H(15B) | 0.9900 | C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 | C(16)-H(16C) | 0.9800 |
| C(17)-C(18) | 1.519(6) | C(17)-H(17A) | 0.9900 |
| C(17)-H(17B) | 0.9900 | C(18)-C(19) | 1.532(5) |
| C(18)-H(18A) | 0.9900 | C(18)-H(18B) | 0.9900 |
| C(19)-C(20) | 1.519(7) | C(19)-H(19A) | 0.9900 |
| C(19)-H(19B) | 0.9900 | C(20)-H(20A) | 0.9800 |
| C(20)-H(20B) | 0.9800 | C(20)-H(20C) | 0.9800 |
| C(21)-H(21A) | 0.9800 | C(21)-H(21B) | 0.9800 |
| C(21)-H(21C) | 0.9800 | C(22)-H(22A) | 0.9800 |
| C(22)-H(22B) | 0.9800 | C(22)-H(22C) | 0.9800 |

Symmetry transformations used to generate equivalent atoms.

Table A.17    Bond Angles [°] for **9**

| atom-atom-atom | angle | atom-atom-atom | angle |
|---|---|---|---|
| C(1)-Rh(1)-C(10) | 78.41(15) | C(1)-Rh(1)-C(7) | 78.48(14) |
| C(10)-Rh(1)-C(7) | 156.61(14) | C(1)-Rh(1)-N(5) | 92.55(13) |
| C(10)-Rh(1)-N(5) | 89.97(12) | C(7)-Rh(1)-N(5) | 94.56(13) |
| C(1)-Rh(1)-I(2) | 88.20(10) | C(10)-Rh(1)-I(2) | 86.90(10) |
| C(7)-Rh(1)-I(2) | 88.86(10) | N(5)-Rh(1)-I(2) | 176.57(8) |
| C(1)-Rh(1)-I(1) | 176.12(10) | C(10)-Rh(1)-I(1) | 102.84(10) |
| C(7)-Rh(1)-I(1) | 100.46(10) | N(5)-Rh(1)-I(1) | 83.80(8) |
| I(2)-Rh(1)-I(1) | 95.525(11) | C(7)-N(1)-C(8) | 111.4(3) |
| C(7)-N(1)-C(6) | 117.1(3) | C(8)-N(1)-C(6) | 131.2(3) |
| C(7)-N(2)-C(9) | 111.8(3) | C(7)-N(2)-C(17) | 124.6(3) |
| C(9)-N(2)-C(17) | 122.9(3) | C(10)-N(3)-C(11) | 111.0(3) |
| C(10)-N(3)-C(2) | 117.0(3) | C(11)-N(3)-C(2) | 132.0(3) |
| C(10)-N(4)-C(12) | 111.2(3) | C(10)-N(4)-C(13) | 124.7(3) |
| C(12)-N(4)-C(13) | 124.0(3) | C(22)-N(5)-C(21) | 109.3(3) |
| C(22)-N(5)-Rh(1) | 114.2(2) | C(21)-N(5)-Rh(1) | 117.8(2) |
| C(22)-N(5)-H(5) | 104.7 | C(21)-N(5)-H(5) | 104.7 |
| Rh(1)-N(5)-H(5) | 104.7 | C(2)-C(1)-C(6) | 119.5(3) |
| C(2)-C(1)-Rh(1) | 120.4(3) | C(6)-C(1)-Rh(1) | 120.1(3) |
| C(1)-C(2)-C(3) | 121.9(3) | C(1)-C(2)-N(3) | 111.5(3) |
| C(3)-C(2)-N(3) | 126.6(3) | C(2)-C(3)-C(4) | 117.0(3) |
| C(2)-C(3)-H(3) | 121.5 | C(4)-C(3)-H(3) | 121.5 |
| C(5)-C(4)-C(3) | 122.8(3) | C(5)-C(4)-H(4) | 118.6 |
| C(3)-C(4)-H(4) | 118.6 | C(4)-C(5)-C(6) | 117.4(3) |
| C(4)-C(5)-H(5A) | 121.3 | C(6)-C(5)-H(5A) | 121.3 |
| C(1)-C(6)-C(5) | 121.4(3) | C(1)-C(6)-N(1) | 111.6(3) |
| C(5)-C(6)-N(1) | 126.9(3) | N(2)-C(7)-N(1) | 103.2(3) |
| N(2)-C(7)-Rh(1) | 144.2(3) | N(1)-C(7)-Rh(1) | 112.5(2) |
| C(9)-C(8)-N(1) | 106.0(3) | C(9)-C(8)-H(8) | 127.0 |
| N(1)-C(8)-H(8) | 127.0 | C(8)-C(9)-N(2) | 107.5(3) |
| C(8)-C(9)-H(9) | 126.2 | N(2)-C(9)-H(9) | 126.2 |
| N(4)-C(10)-N(3) | 104.0(3) | N(4)-C(10)-Rh(1) | 143.3(3) |
| N(3)-C(10)-Rh(1) | 112.7(3) | C(12)-C(11)-N(3) | 106.0(3) |

Table A.17 (Continued)

| | | | |
|---|---|---|---|
| C(12)-C(11)-H(11) | 127.0 | N(3)-C(11)-H(11) | 127.0 |
| C(11)-C(12)-N(4) | 107.8(3) | C(11)-C(12)-H(12) | 126.1 |
| N(4)-C(12)-H(12) | 126.1 | N(4)-C(13)-C(14) | 111.6(3) |
| N(4)-C(13)-H(13A) | 109.3 | C(14)-C(13)-H(13A) | 109.3 |
| N(4)-C(13)-H(13B) | 109.3 | C(14)-C(13)-H(13B) | 109.3 |
| H(13A)-C(13)-H(13B) | 108.0 | C(15)-C(14)-C(13) | 114.8(3) |
| C(15)-C(14)-H(14A) | 108.6 | C(13)-C(14)-H(14A) | 108.6 |
| C(15)-C(14)-H(14B) | 108.6 | C(13)-C(14)-H(14B) | 108.6 |
| H(14A)-C(14)-H(14B) | 107.5 | C(14)-C(15)-C(16) | 112.1(3) |
| C(14)-C(15)-H(15A) | 109.2 | C(16)-C(15)-H(15A) | 109.2 |
| C(14)-C(15)-H(15B) | 109.2 | C(16)-C(15)-H(15B) | 109.2 |
| H(15A)-C(15)-H(15B) | 107.9 | C(15)-C(16)-H(16A) | 109.5 |
| C(15)-C(16)-H(16B) | 109.5 | H(16A)-C(16)-H(16B) | 109.5 |
| C(15)-C(16)-H(16C) | 109.5 | H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 | N(2)-C(17)-C(18) | 111.2(3) |
| N(2)-C(17)-H(17A) | 109.4 | C(18)-C(17)-H(17A) | 109.4 |
| N(2)-C(17)-H(17B) | 109.4 | C(18)-C(17)-H(17B) | 109.4 |
| H(17A)-C(17)-H(17B) | 108.0 | C(17)-C(18)-C(19) | 112.0(3) |
| C(17)-C(18)-H(18A) | 109.2 | C(19)-C(18)-H(18A) | 109.2 |
| C(17)-C(18)-H(18B) | 109.2 | C(19)-C(18)-H(18B) | 109.2 |
| H(18A)-C(18)-H(18B) | 107.9 | C(20)-C(19)-C(18) | 112.1(4) |
| C(20)-C(19)-H(19A) | 109.2 | C(18)-C(19)-H(19A) | 109.2 |
| C(20)-C(19)-H(19B) | 109.2 | C(18)-C(19)-H(19B) | 109.2 |
| H(19A)-C(19)-H(19B) | 107.9 | C(19)-C(20)-H(20A) | 109.5 |
| C(19)-C(20)-H(20B) | 109.5 | H(20A)-C(20)-H(20B) | 109.5 |
| C(19)-C(20)-H(20C) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 | N(5)-C(21)-H(21A) | 109.5 |
| N(5)-C(21)-H(21B) | 109.5 | H(21A)-C(21)-H(21B) | 109.5 |
| N(5)-C(21)-H(21C) | 109.5 | H(21A)-C(21)-H(21C) | 109.5 |
| H(21B)-C(21)-H(21C) | 109.5 | N(5)-C(22)-H(22A) | 109.5 |
| N(5)-C(22)-H(22B) | 109.5 | H(22A)-C(22)-H(22B) | 109.5 |
| N(5)-C(22)-H(22C) | 109.5 | H(22A)-C(22)-H(22C) | 109.5 |
| H(22B)-C(22)-H(22C) | 109.5 | | |

Symmetry transformations used to generate equivalent atoms.

Table A.18    Torsion Angles [°] for **9**

| atom-atom-atom-atom | angle | atom-atom-atom-atom | angle |
|---|---|---|---|
| C(6)-C(1)-C(2)-C(3) | 0.3(5) | Rh(1)-C(1)-C(2)-C(3) | 179.7(3) |
| C(6)-C(1)-C(2)-N(3) | -179.7(3) | Rh(1)-C(1)-C(2)-N(3) | -0.3(4) |
| C(10)-N(3)-C(2)-C(1) | 0.7(4) | C(11)-N(3)-C(2)-C(1) | 179.9(3) |
| C(10)-N(3)-C(2)-C(3) | -179.3(3) | C(11)-N(3)-C(2)-C(3) | -0.1(6) |
| C(1)-C(2)-C(3)-C(4) | -0.4(5) | N(3)-C(2)-C(3)-C(4) | 179.6(3) |
| C(2)-C(3)-C(4)-C(5) | -0.1(5) | C(3)-C(4)-C(5)-C(6) | 0.6(5) |
| C(2)-C(1)-C(6)-C(5) | 0.3(5) | Rh(1)-C(1)-C(6)-C(5) | -179.1(3) |
| C(2)-C(1)-C(6)-N(1) | -176.8(3) | Rh(1)-C(1)-C(6)-N(1) | 3.8(4) |
| C(4)-C(5)-C(6)-C(1) | -0.7(5) | C(4)-C(5)-C(6)-N(1) | 175.9(3) |
| C(7)-N(1)-C(6)-C(1) | -0.2(4) | C(8)-N(1)-C(6)-C(1) | 173.3(3) |
| C(7)-N(1)-C(6)-C(5) | -177.1(3) | C(8)-N(1)-C(6)-C(5) | -3.6(6) |
| C(9)-N(2)-C(7)-N(1) | -1.1(4) | C(17)-N(2)-C(7)-N(1) | -172.5(3) |
| C(9)-N(2)-C(7)-Rh(1) | 175.9(4) | C(17)-N(2)-C(7)-Rh(1) | 4.5(7) |
| C(8)-N(1)-C(7)-N(2) | 0.3(4) | C(6)-N(1)-C(7)-N(2) | 175.1(3) |
| C(8)-N(1)-C(7)-Rh(1) | -177.8(2) | C(6)-N(1)-C(7)-Rh(1) | -3.0(4) |
| C(7)-N(1)-C(8)-C(9) | 0.6(4) | C(6)-N(1)-C(8)-C(9) | -173.2(4) |
| N(1)-C(8)-C(9)-N(2) | -1.3(4) | C(7)-N(2)-C(9)-C(8) | 1.6(5) |
| C(17)-N(2)-C(9)-C(8) | 173.1(3) | C(12)-N(4)-C(10)-N(3) | -0.6(4) |
| C(13)-N(4)-C(10)-N(3) | 176.3(3) | C(12)-N(4)-C(10)-Rh(1) | -179.2(3) |
| C(13)-N(4)-C(10)-Rh(1) | -2.3(6) | C(11)-N(3)-C(10)-N(4) | 0.8(4) |
| C(2)-N(3)-C(10)-N(4) | -179.9(3) | C(11)-N(3)-C(10)-Rh(1) | 179.9(2) |
| C(2)-N(3)-C(10)-Rh(1) | -0.8(4) | C(10)-N(3)-C(11)-C(12) | -0.6(4) |
| C(2)-N(3)-C(11)-C(12) | -179.9(3) | N(3)-C(11)-C(12)-N(4) | 0.2(4) |
| C(10)-N(4)-C(12)-C(11) | 0.3(4) | C(13)-N(4)-C(12)-C(11) | -176.7(3) |
| C(10)-N(4)-C(13)-C(14) | -79.2(4) | C(12)-N(4)-C(13)-C(14) | 97.4(4) |
| N(4)-C(13)-C(14)-C(15) | -62.2(4) | C(13)-C(14)-C(15)-C(16) | 178.2(4) |
| C(7)-N(2)-C(17)-C(18) | 85.9(4) | C(9)-N(2)-C(17)-C(18) | -84.5(4) |
| N(2)-C(17)-C(18)-C(19) | -178.4(3) | C(17)-C(18)-C(19)-C(20) | 178.0(4) |

Symmetry transformations used to generate equivalent atoms.

Table A.19    Hydrogen Bonds for **9**

D-H...A  d(D-H)  d(H...A)  d(D...A)  <(DHA)


### A.3.1    Crystal Summary for 9

X-Ray Intensity data were collected at 100 K on a Bruker AXS diffractometer using MoKα radiation ($\lambda$ = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by program SAINT[1] and integrated using 3D profiling algorithms.  The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations.  The data were corrected using multi-scan absorption correction through the APEX2[305] crystallographic software suite.

The structure was solved using ShelXS[306] and refined using ShelXL[307] full-matrix least-squares refinement.  Molecular drawings and reports were generated using Olex2.[308] The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. In the final cycle of refinement, 22210 reflections (of which 6172 are observed with I > 2σ(I)) were used to refine 275 parameters and the resulting $R_1$, $wR_2$ and S (goodness of fit) were 3.01%, 6.50% respectively.  The refinement was carried out by minimizing the $wR_2$ function using $F^2$ rather than F values. $R_1$ is calculated to provide a reference to the conventional R value but its function is not minimized.

The size of the crystal was 0.20 x 0.20 x 0.20 mm at the time of data collection. The structure presented shows the expected, complete molecule in the asymmetric unit as indicated by the chemist who grew the molecule. Bond distances should be treated as a close approximation until better data can be acquired.

The model was refined by full-matrix least-squares analysis of $F^2$ against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded ($1.5 \times$ for methyl, $1.2 \times$ for all others).

## A.4 Chapter V Compounds
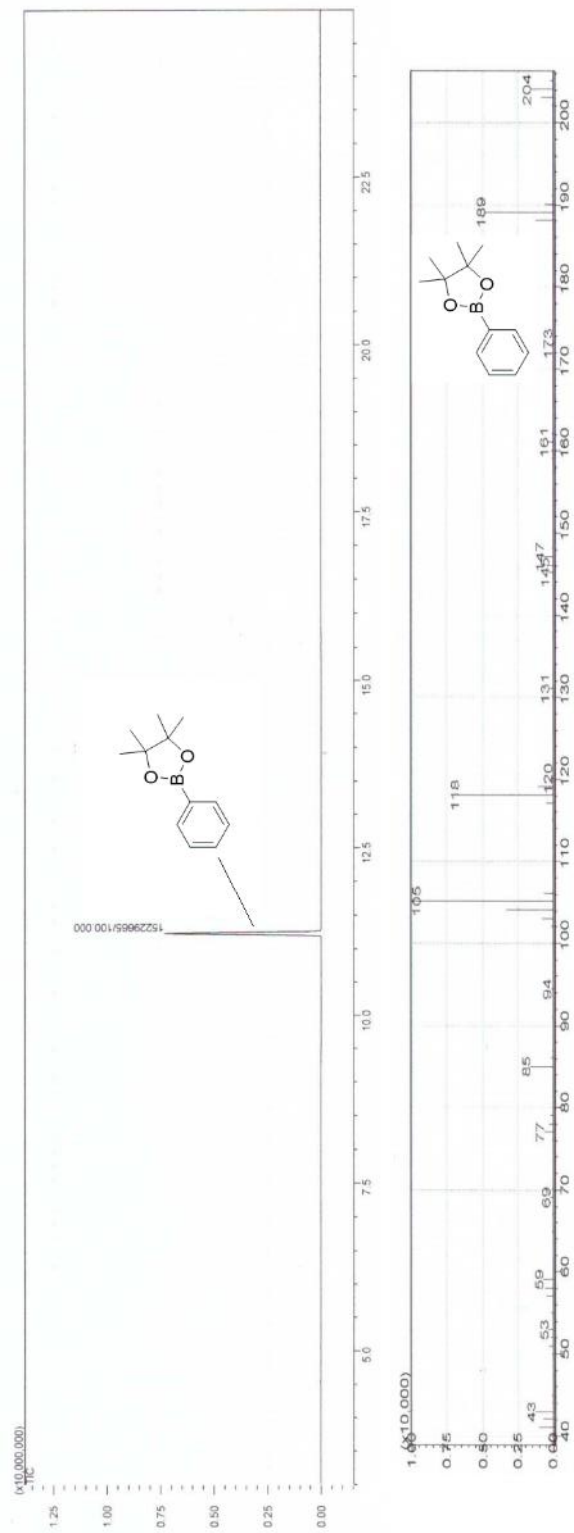


Figure A.95 GC-MS chromatogram spectrum of catalytic trial (Table 5.1, Entry 4)
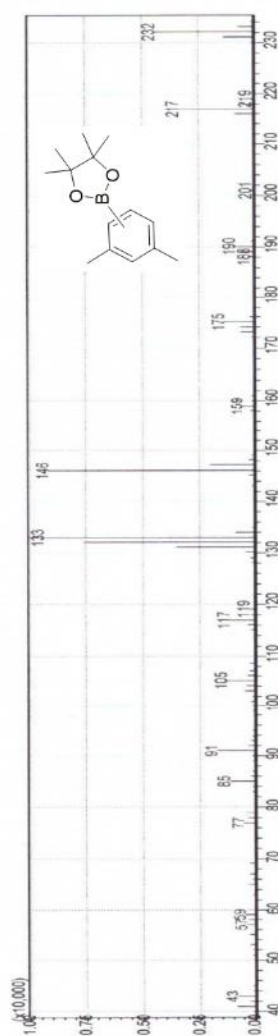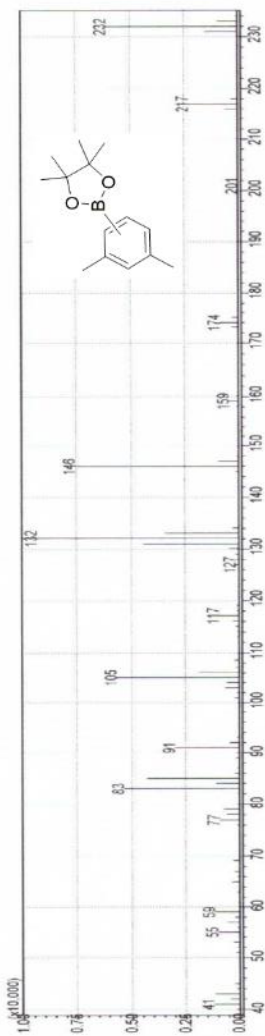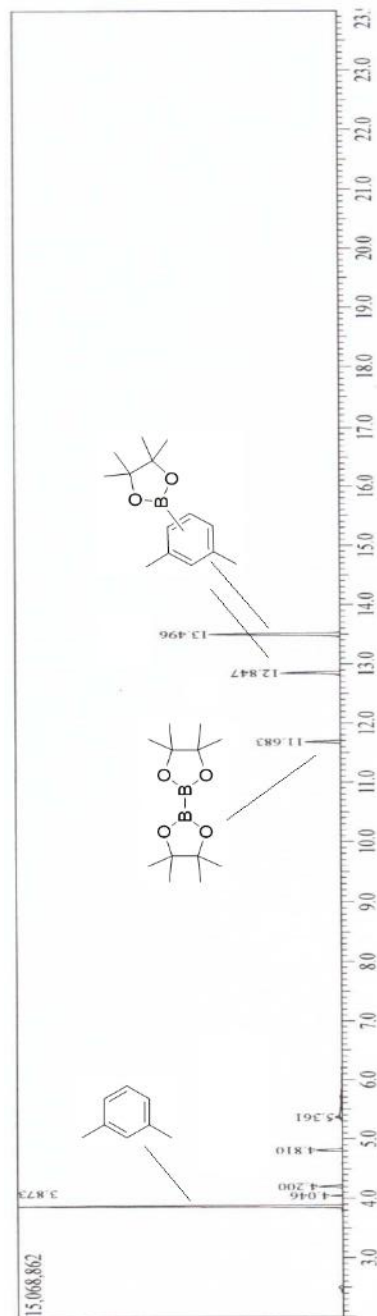
Figure A.96   GC-MS chromatogram spectrum of catalytic trial (Table 5.2, Entry 1)
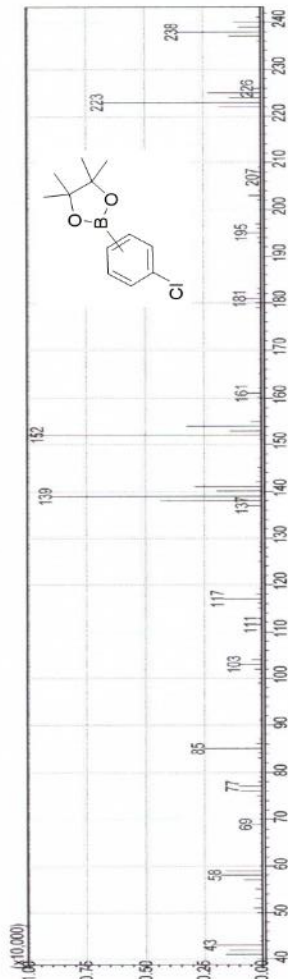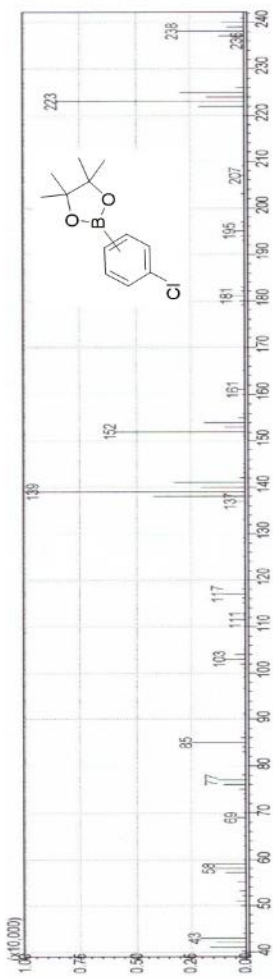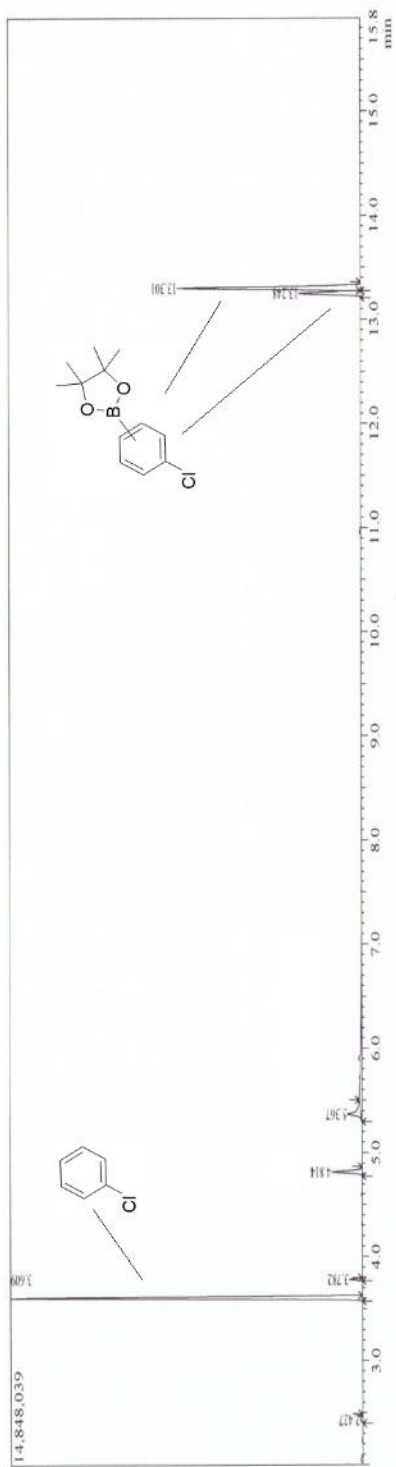
Figure A.97   GC-MS chromatogram spectrum of catalytic trial (Table 5.2, Entry 2)
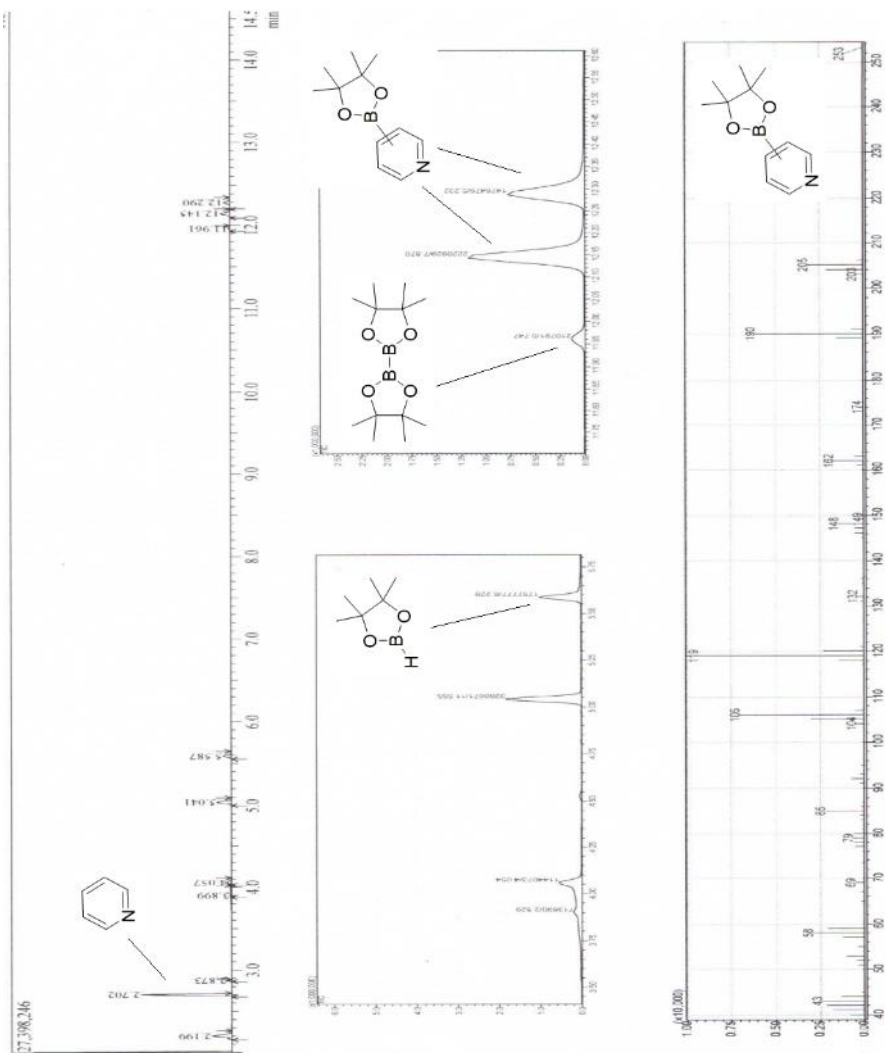
Figure A.98   GC-MS chromatogram spectrum of catalytic trial (Table 5.2, Entry 3)

0.995
1.023
1.035
1.047
1.486
1.498
1.511
1.523
1.536
1.548
2.077
2.090
2.102
2.115
2.127

4.292
4.304
4.317

7.039
7.042
7.186
7.260
7.600
7.603

6.51
4.45
4.23
4.10
1.82
2.97
2.00

ppm
0
1
2
3
4
5
6
7
8
9
10
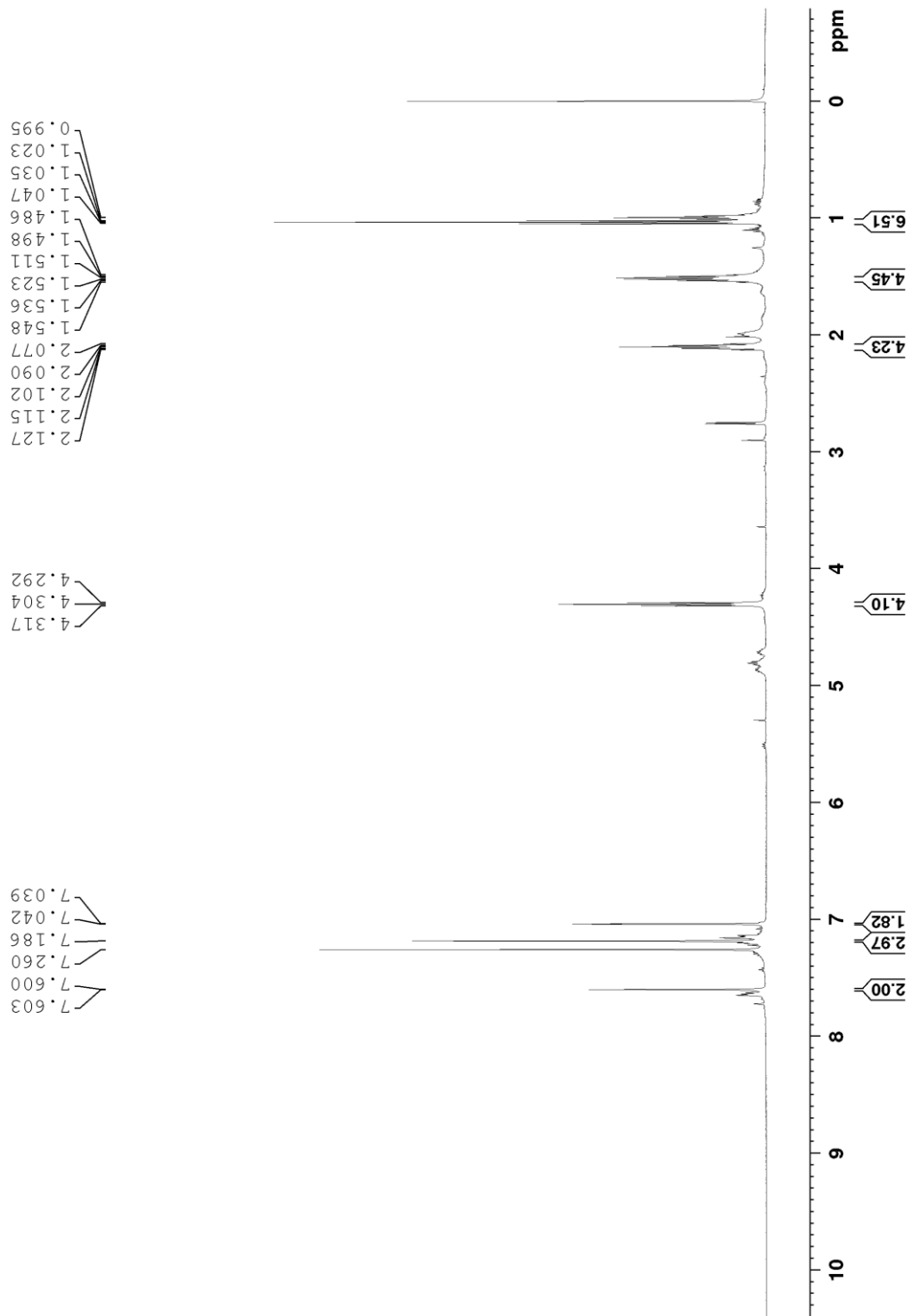
Figure A.99  $^1$H NMR (600 MHz, CDCl$_3$) spectrum of **13**

211

13.70
20.01
32.82
51.75
109.02
116.38
121.16
125.38
145.32
174.03
174.26
179.67
180.12
185.73
186.00

185
180
175
ppm

220    200    180    160    140    120    100    80    60    40    20    0    -20    ppm
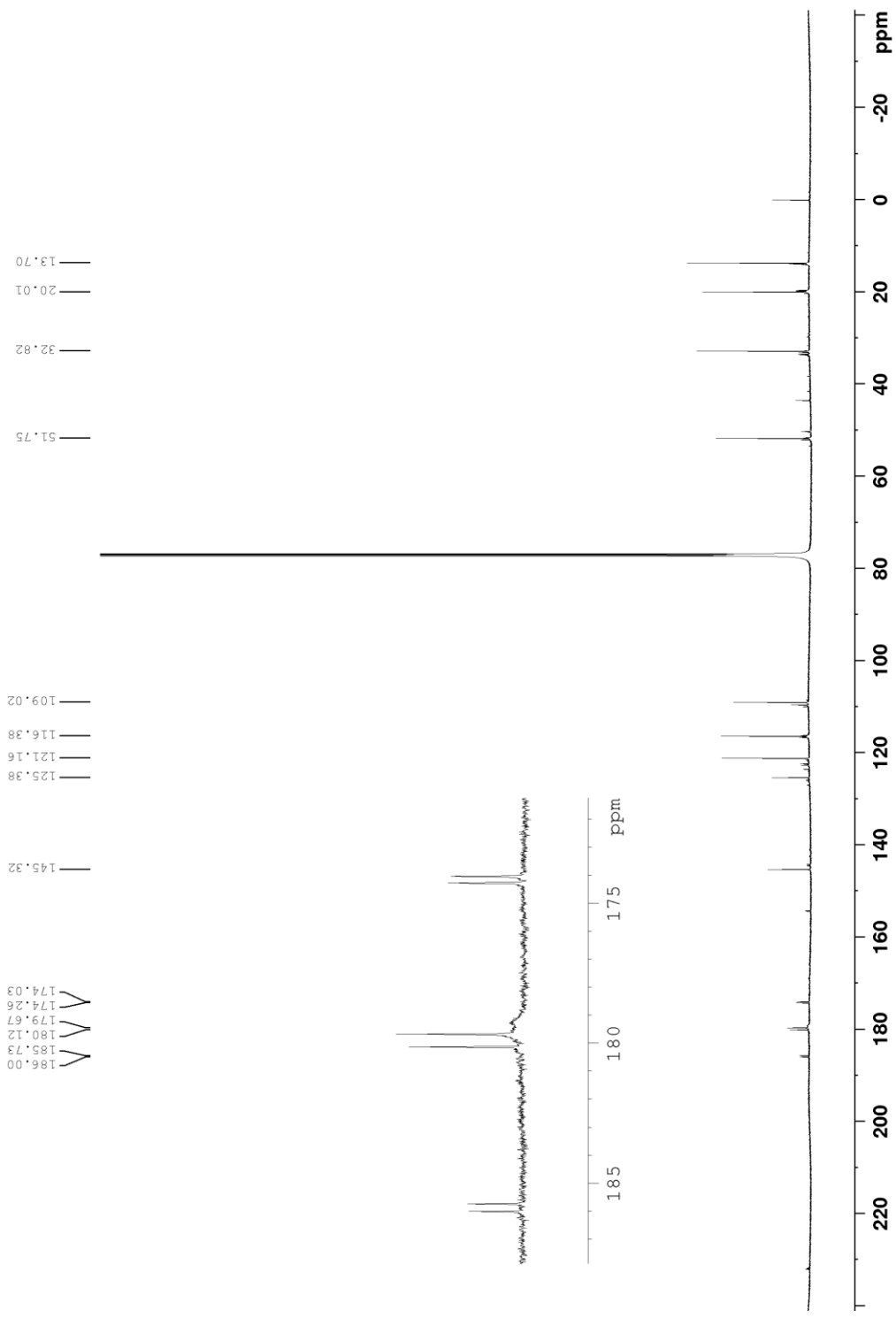
Figure A.100 $^{13}$C NMR (150 MHz, CDCl$_3$) spectrum of **13**

212
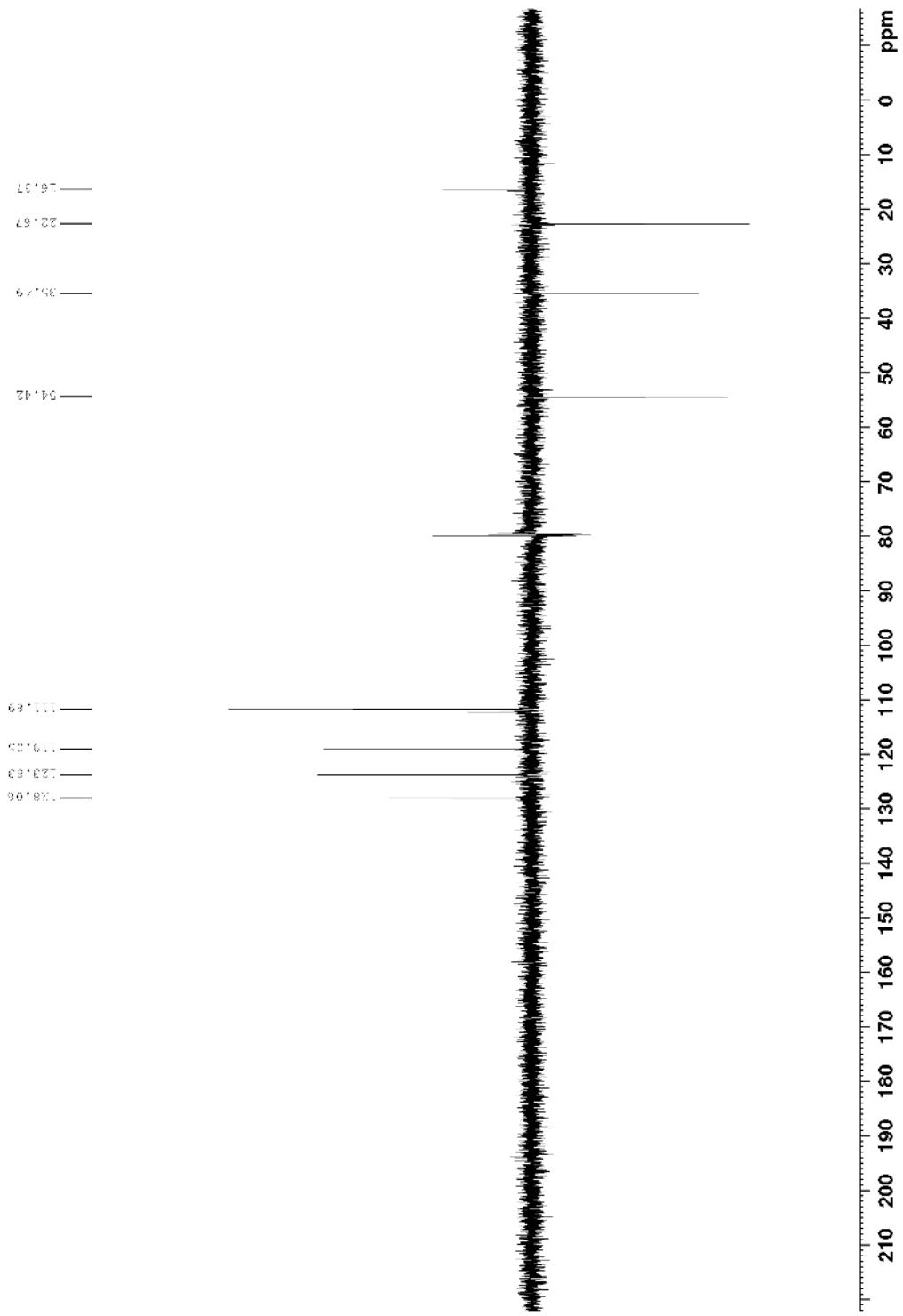
Figure A.101 $^{13}$C DEPT 135 NMR (150 MHz, CDCl$_3$) spectrum of **13**

213
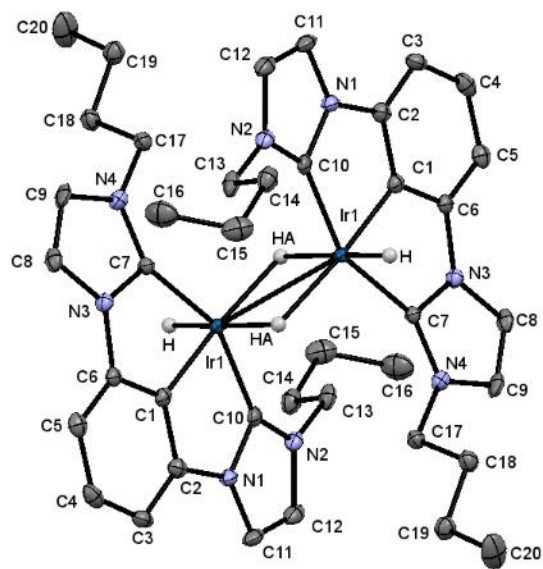
Figure A.102 X-ray molecular structure of **12**

Table A.20    Crystal Data and Structure Refinement for **12**

| | |
|---|---|
| Empirical formula | $C_{20}H_{25}IrN_4$ |
| Formula weight | 513.64 |
| Temperature | 100(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| Unit cell dimensions | $a$ = 10.9713(3) Å        $\alpha$ = 90° |
| | $b$ = 16.1248(4) Å        $\beta$ = 113.3340(10)° |
| | $c$ = 11.6392(3) Å        $\gamma$ = 90° |
| Volume | 1890.68(9) Å$^3$ |
| Z | 4 |
| Density (calculated) | 1.804 g.cm$^{-3}$ |
| Absorption coefficient ($\mu$) | 7.071 mm$^{-1}$ |
| F(000) | 1000 |
| Crystal color, habit | Brown, Tablet |
| Crystal size | $0.202 \times 0.150 \times 0.098$ mm$^3$ |
| $\theta$ range for data collection | 2.022 to 27.984° |
| Index ranges | $-14 \le h \le 14$, $-21 \le k \le 20$, $-15 \le l \le 15$ |
| Reflections collected | 15540 |
| Independent reflections | 4513 [$R_{int}$ = 0.0392] |
| Completeness to $\theta$ = 25.242° | 99.8 % |
| Absorption correction | Numerical |
| Max. and min. transmission | 0.5749 and 0.4294 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 4513 / 0 / 226 |
| Goodness-of-fit on $F^2$ | 1.042 |
| Final R indices [$I>2\sigma(I)$] | $R_1$ = 0.0213, $wR_2$ = 0.0530 |
| R indices (all data) | $R_1$ = 0.0251, $wR_2$ = 0.0552 |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 0.878 and -1.201 e$^-$.Å$^{-3}$ |

Table A.21   Atomic Coordinates and Equivalent Isotropic Displacement Parameters
(Å²) for **12**

|  | x | y | z | U(eq) |
|---|---|---|---|---|
| Ir(1) | 0.52974(2) | 0.55649(2) | 0.59778(2) | 0.010(1) |
| N(1) | 0.7165(2) | 0.68641(15) | 0.6063(2) | 0.014(1) |
| N(2) | 0.5511(3) | 0.70914(16) | 0.4309(2) | 0.015(1) |
| N(3) | 0.6361(2) | 0.48540(16) | 0.8462(2) | 0.013(1) |
| N(4) | 0.4382(3) | 0.43500(15) | 0.7671(3) | 0.014(1) |
| C(1) | 0.6955(3) | 0.58674(19) | 0.7386(3) | 0.013(1) |
| C(2) | 0.7776(3) | 0.64793(19) | 0.7254(3) | 0.014(1) |
| C(3) | 0.8989(3) | 0.6666(2) | 0.8213(3) | 0.018(1) |
| C(4) | 0.9365(3) | 0.6204(2) | 0.9318(3) | 0.019(1) |
| C(5) | 0.8567(3) | 0.55784(18) | 0.9480(3) | 0.017(1) |
| C(6) | 0.7366(3) | 0.54248(18) | 0.8498(3) | 0.013(1) |
| C(7) | 0.5230(3) | 0.48289(18) | 0.7372(3) | 0.011(1) |
| C(8) | 0.6217(3) | 0.43857(18) | 0.9400(3) | 0.016(1) |
| C(9) | 0.4978(3) | 0.4068(2) | 0.8900(3) | 0.018(1) |
| C(10) | 0.5924(3) | 0.65565(19) | 0.5276(3) | 0.015(1) |
| C(11) | 0.7492(3) | 0.7567(2) | 0.5554(3) | 0.019(1) |
| C(12) | 0.6465(3) | 0.7707(2) | 0.4464(3) | 0.020(1) |
| C(13) | 0.4208(3) | 0.7066(2) | 0.3284(3) | 0.018(1) |
| C(14) | 0.3326(3) | 0.7776(2) | 0.3368(3) | 0.021(1) |
| C(15) | 0.1914(3) | 0.7739(2) | 0.2367(4) | 0.026(1) |
| C(16) | 0.1833(4) | 0.7821(3) | 0.1040(4) | 0.032(1) |
| C(17) | 0.3011(3) | 0.4160(2) | 0.6827(3) | 0.015(1) |
| C(18) | 0.1984(3) | 0.4568(2) | 0.7217(3) | 0.018(1) |
| C(19) | 0.0593(3) | 0.4261(2) | 0.6421(3) | 0.019(1) |
| C(20) | -0.0494(4) | 0.4673(3) | 0.6722(4) | 0.036(1) |
| H(3A) | 0.9531 | 0.7084 | 0.8124 | 0.021 |
| H(4A) | 1.0177 | 0.6318 | 0.9968 | 0.023 |
| H(5A) | 0.8833 | 0.5277 | 1.0220 | 0.020 |
| H(8A) | 0.6846 | 0.4307 | 1.0210 | 0.020 |
| H(9A) | 0.4593 | 0.3722 | 0.9303 | 0.022 |
| H(11A) | 0.8267 | 0.7877 | 0.5900 | 0.023 |
| H(12A) | 0.6397 | 0.8138 | 0.3910 | 0.024 |

Table A.21 (Continued)

| | | | | |
|---|---|---|---|---|
| H(13A) | 0.3784 | 0.6541 | 0.3303 | 0.021 |
| H(13B) | 0.4310 | 0.7101 | 0.2495 | 0.021 |
| H(14A) | 0.3288 | 0.7765 | 0.4186 | 0.025 |
| H(14B) | 0.3726 | 0.8298 | 0.3291 | 0.025 |
| H(15A) | 0.1516 | 0.7216 | 0.2443 | 0.032 |
| H(15B) | 0.1397 | 0.8180 | 0.2522 | 0.032 |
| H(16A) | 0.0921 | 0.7793 | 0.0462 | 0.048 |
| H(16B) | 0.2203 | 0.8344 | 0.0948 | 0.048 |
| H(16C) | 0.2323 | 0.7379 | 0.0869 | 0.048 |
| H(17A) | 0.2884 | 0.3564 | 0.6800 | 0.018 |
| H(17B) | 0.2867 | 0.4343 | 0.5989 | 0.018 |
| H(18A) | 0.2189 | 0.4445 | 0.8090 | 0.021 |
| H(18B) | 0.2020 | 0.5165 | 0.7131 | 0.021 |
| H(19A) | 0.0559 | 0.3667 | 0.6537 | 0.023 |
| H(19B) | 0.0417 | 0.4358 | 0.5547 | 0.023 |
| H(20A) | -0.1341 | 0.4450 | 0.6187 | 0.053 |
| H(20B) | -0.0342 | 0.4568 | 0.7580 | 0.053 |
| H(20C) | -0.0484 | 0.5260 | 0.6589 | 0.053 |

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table A.22    Anisotropic Displacement Parameters ($\text{Å}^2$) for **12**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| Ir(1) | 0.0110(1) | 0.0097(1) | 0.0100(1) | 0.0002(1) | 0.0052(1) | -0.0003(1) |
| N(1) | 0.0174(12) | 0.0114(13) | 0.0167(13) | -0.0023(10) | 0.0104(11) | -0.0035(10) |
| N(2) | 0.0224(13) | 0.0108(13) | 0.0172(13) | 0.0007(10) | 0.0121(11) | -0.0001(10) |
| N(3) | 0.0153(12) | 0.0122(13) | 0.0126(13) | 0.0001(10) | 0.0063(10) | 0.0006(10) |
| N(4) | 0.0145(12) | 0.0140(13) | 0.0137(13) | 0.0014(10) | 0.0071(11) | 0.0012(10) |
| C(1) | 0.0155(14) | 0.0106(14) | 0.0161(15) | -0.0016(12) | 0.0099(12) | 0.0012(11) |
| C(2) | 0.0134(13) | 0.0134(15) | 0.0181(16) | -0.0025(12) | 0.0076(12) | 0.0011(11) |
| C(3) | 0.0154(14) | 0.0161(16) | 0.0235(17) | -0.0067(13) | 0.0092(13) | -0.0046(12) |
| C(4) | 0.0140(14) | 0.0206(17) | 0.0178(16) | -0.0058(13) | 0.0022(13) | 0.0015(12) |
| C(5) | 0.0194(15) | 0.0144(16) | 0.0174(17) | -0.0019(12) | 0.0079(14) | 0.0045(12) |
| C(6) | 0.0150(14) | 0.0127(14) | 0.0137(15) | -0.0029(11) | 0.0082(13) | 0.0005(11) |
| C(7) | 0.0112(13) | 0.0109(14) | 0.0101(14) | -0.0002(11) | 0.0040(11) | 0.0001(11) |
| C(8) | 0.0240(16) | 0.0144(16) | 0.0105(15) | 0.0026(11) | 0.0065(13) | 0.0026(12) |
| C(9) | 0.0287(16) | 0.0189(17) | 0.0119(15) | 0.0041(12) | 0.0127(14) | 0.0011(13) |
| C(10) | 0.0198(14) | 0.0136(15) | 0.0144(15) | -0.0022(12) | 0.0107(13) | 0.0003(12) |
| C(11) | 0.0263(16) | 0.0134(16) | 0.0266(18) | -0.0019(13) | 0.0192(15) | -0.0055(13) |
| C(12) | 0.0298(17) | 0.0116(15) | 0.0273(18) | -0.0025(13) | 0.0202(15) | -0.0027(13) |
| C(13) | 0.0255(16) | 0.0164(16) | 0.0129(15) | 0.0037(12) | 0.0097(13) | 0.0051(13) |
| C(14) | 0.0269(17) | 0.0184(17) | 0.0220(17) | -0.0007(14) | 0.0147(15) | 0.0033(14) |
| C(15) | 0.0227(17) | 0.0182(18) | 0.042(2) | 0.0022(16) | 0.0161(16) | 0.0033(14) |
| C(16) | 0.0228(17) | 0.034(2) | 0.034(2) | 0.0024(17) | 0.0044(16) | -0.0019(16) |
| C(17) | 0.0155(14) | 0.0151(15) | 0.0155(15) | -0.0039(12) | 0.0075(12) | -0.0023(12) |
| C(18) | 0.0178(15) | 0.0192(16) | 0.0176(17) | -0.0049(13) | 0.0081(14) | -0.0010(12) |
| C(19) | 0.0179(15) | 0.0228(17) | 0.0188(17) | -0.0011(14) | 0.0085(14) | 0.0014(13) |
| C(20) | 0.0191(17) | 0.057(3) | 0.032(2) | -0.011(2) | 0.0116(17) | 0.0087(18) |

$$-2\pi^2[h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}] \qquad (A.4)$$

Table A.23    Bond Lengths [Å] for **12**

| atom-atom | distance | atom-atom | distance |
|-----------|----------|-----------|----------|
| Ir(1)-C(1) | 1.967(3) | Ir(1)-C(7) | 2.035(3) |
| Ir(1)-C(10) | 2.035(3) | Ir(1)-Ir(1)#1 | 2.7837(2) |
| N(1)-C(11) | 1.390(4) | N(1)-C(10) | 1.397(4) |
| N(1)-C(2) | 1.421(4) | N(2)-C(10) | 1.346(4) |
| N(2)-C(12) | 1.401(4) | N(2)-C(13) | 1.455(4) |
| N(3)-C(7) | 1.379(4) | N(3)-C(8) | 1.387(4) |
| N(3)-C(6) | 1.425(4) | N(4)-C(7) | 1.357(4) |
| N(4)-C(9) | 1.393(4) | N(4)-C(17) | 1.466(4) |
| C(1)-C(2) | 1.385(4) | C(1)-C(6) | 1.388(4) |
| C(2)-C(3) | 1.390(4) | C(3)-C(4) | 1.400(5) |
| C(4)-C(5) | 1.397(4) | C(5)-C(6) | 1.382(5) |
| C(8)-C(9) | 1.350(5) | C(11)-C(12) | 1.341(5) |
| C(13)-C(14) | 1.527(4) | C(14)-C(15) | 1.526(5) |
| C(15)-C(16) | 1.518(5) | C(17)-C(18) | 1.521(4) |
| C(18)-C(19) | 1.521(4) | C(19)-C(20) | 1.522(4) |

Table A.24    Bond Angles [°] for **12**

| atom-atom-atom | angle | atom-atom-atom | angle |
|---|---|---|---|
| C(1)-Ir(1)-C(7) | 78.10(12) | C(1)-Ir(1)-C(10) | 77.99(12) |
| C(7)-Ir(1)-C(10) | 154.55(12) | C(1)-Ir(1)-Ir(1)#1 | 133.10(8) |
| C(7)-Ir(1)-Ir(1)#1 | 101.52(8) | C(10)-Ir(1)-Ir(1)#1 | 101.12(8) |
| C(11)-N(1)-C(10) | 111.1(3) | C(11)-N(1)-C(2) | 132.0(3) |
| C(10)-N(1)-C(2) | 116.4(2) | C(10)-N(2)-C(12) | 111.1(3) |
| C(10)-N(2)-C(13) | 124.3(3) | C(12)-N(2)-C(13) | 124.5(3) |
| C(7)-N(3)-C(8) | 111.5(2) | C(7)-N(3)-C(6) | 116.7(2) |
| C(8)-N(3)-C(6) | 131.1(3) | C(7)-N(4)-C(9) | 111.0(3) |
| C(7)-N(4)-C(17) | 125.0(3) | C(9)-N(4)-C(17) | 124.0(3) |
| C(2)-C(1)-C(6) | 119.0(3) | C(2)-C(1)-Ir(1) | 120.8(2) |
| C(6)-C(1)-Ir(1) | 120.1(2) | C(3)-C(2)-C(1) | 121.6(3) |
| C(3)-C(2)-N(1) | 128.3(3) | C(1)-C(2)-N(1) | 110.1(3) |
| C(2)-C(3)-C(4) | 117.5(3) | C(5)-C(4)-C(3) | 122.4(3) |
| C(6)-C(5)-C(4) | 117.5(3) | C(5)-C(6)-C(1) | 122.0(3) |
| C(5)-C(6)-N(3) | 127.8(3) | C(1)-C(6)-N(3) | 110.1(3) |
| N(4)-C(7)-N(3) | 103.9(2) | N(4)-C(7)-Ir(1) | 141.4(2) |
| N(3)-C(7)-Ir(1) | 114.40(19) | C(9)-C(8)-N(3) | 106.0(3) |
| C(8)-C(9)-N(4) | 107.6(3) | N(2)-C(10)-N(1) | 103.8(2) |
| N(2)-C(10)-Ir(1) | 141.6(2) | N(1)-C(10)-Ir(1) | 114.3(2) |
| C(12)-C(11)-N(1) | 106.2(3) | C(11)-C(12)-N(2) | 107.9(3) |
| N(2)-C(13)-C(14) | 111.6(3) | C(15)-C(14)-C(13) | 113.6(3) |
| C(16)-C(15)-C(14) | 113.9(3) | N(4)-C(17)-C(18) | 113.2(2) |
| C(19)-C(18)-C(17) | 111.1(3) | C(18)-C(19)-C(20) | 113.9(3) |

Table A.25    Torsion Angles [°] for **12**

| atom-atom-atom-atom | angle | atom-atom-atom-atom | angle |
|---|---|---|---|
| C(6)-C(1)-C(2)-C(3) | -0.9(4) | Ir(1)-C(1)-C(2)-C(3) | -176.0(2) |
| C(6)-C(1)-C(2)-N(1) | -179.0(2) | Ir(1)-C(1)-C(2)-N(1) | 5.8(3) |
| C(11)-N(1)-C(2)-C(3) | -7.8(5) | C(10)-N(1)-C(2)-C(3) | -179.2(3) |
| C(11)-N(1)-C(2)-C(1) | 170.2(3) | C(10)-N(1)-C(2)-C(1) | -1.2(3) |
| C(1)-C(2)-C(3)-C(4) | 1.0(4) | N(1)-C(2)-C(3)-C(4) | 178.8(3) |
| C(2)-C(3)-C(4)-C(5) | -0.5(4) | C(3)-C(4)-C(5)-C(6) | -0.1(4) |
| C(4)-C(5)-C(6)-C(1) | 0.2(4) | C(4)-C(5)-C(6)-N(3) | -176.5(3) |
| C(2)-C(1)-C(6)-C(5) | 0.3(4) | Ir(1)-C(1)-C(6)-C(5) | 175.5(2) |
| C(2)-C(1)-C(6)-N(3) | 177.5(2) | Ir(1)-C(1)-C(6)-N(3) | -7.3(3) |
| C(7)-N(3)-C(6)-C(5) | 178.6(3) | C(8)-N(3)-C(6)-C(5) | 9.1(5) |
| C(7)-N(3)-C(6)-C(1) | 1.6(3) | C(8)-N(3)-C(6)-C(1) | -168.0(3) |
| C(9)-N(4)-C(7)-N(3) | -1.5(3) | C(17)-N(4)-C(7)-N(3) | 177.6(3) |
| C(9)-N(4)-C(7)-Ir(1) | -173.6(3) | C(17)-N(4)-C(7)-Ir(1) | 5.6(5) |
| C(8)-N(3)-C(7)-N(4) | 1.3(3) | C(6)-N(3)-C(7)-N(4) | -170.3(2) |
| C(8)-N(3)-C(7)-Ir(1) | 175.83(19) | C(6)-N(3)-C(7)-Ir(1) | 4.3(3) |
| C(7)-N(3)-C(8)-C(9) | -0.5(3) | C(6)-N(3)-C(8)-C(9) | 169.4(3) |
| N(3)-C(8)-C(9)-N(4) | -0.4(3) | C(7)-N(4)-C(9)-C(8) | 1.3(3) |
| C(17)-N(4)-C(9)-C(8) | -177.9(3) | C(12)-N(2)-C(10)-N(1) | 1.0(3) |
| C(13)-N(2)-C(10)-N(1) | -174.9(2) | C(12)-N(2)-C(10)-Ir(1) | 174.6(3) |
| C(13)-N(2)-C(10)-Ir(1) | -1.3(5) | C(11)-N(1)-C(10)-N(2) | -1.0(3) |
| C(2)-N(1)-C(10)-N(2) | 172.2(2) | C(11)-N(1)-C(10)-Ir(1) | -176.60(19) |
| C(2)-N(1)-C(10)-Ir(1) | -3.4(3) | C(10)-N(1)-C(11)-C(12) | 0.6(3) |
| C(2)-N(1)-C(11)-C(12) | -171.2(3) | N(1)-C(11)-C(12)-N(2) | 0.1(3) |
| C(10)-N(2)-C(12)-C(11) | -0.7(3) | C(13)-N(2)-C(12)-C(11) | 175.2(3) |
| C(10)-N(2)-C(13)-C(14) | 107.5(3) | C(12)-N(2)-C(13)-C(14) | -67.8(3) |
| N(2)-C(13)-C(14)-C(15) | -175.7(3) | C(13)-C(14)-C(15)-C(16) | -63.1(4) |
| C(7)-N(4)-C(17)-C(18) | -110.9(3) | C(9)-N(4)-C(17)-C(18) | 68.1(4) |
| N(4)-C(17)-C(18)-C(19) | -172.3(3) | C(17)-C(18)-C(19)-C(20) | -177.4(3) |

## A.4.1    Crystal Summary for 12

Crystal data for $C_{20}H_{27}IrN_4$; $M_r$ = 513.64; Monoclinic; space group P2$_1$/c; $a$ = 10.9713(3) Å; $b$ = 16.1248(4) Å; $c$ = 11.6392(3) Å; $\alpha$ = 90°; $\beta$ = 113.3340(10)°; $\gamma$ = 90°; V = 1890.68(9) Å$^3$; Z = 4; T = 100(2) K; $\lambda$(Mo-K$\alpha$) = 0.71073 Å; $\mu$(Mo-K$\alpha$) = 7.071 mm$^{-1}$; d$_{calc}$ = 1.804g.cm$^{-3}$; 15540 reflections collected; 4513 unique (R$_{int}$ = 0.0392); giving R$_1$ = 0.0213, wR$_2$ = 0.0530 for 4050 data with [I>2$\sigma$(I)] and R$_1$ = 0.0251, wR$_2$ = 0.0552 for all 4513 data. Residual electron density (e$^-$.Å$^{-3}$) max/min: 0.878/-1.201.

An arbitrary sphere of data were collected on a Brown Tablet-like crystal, having approximate dimensions of 0.202 × 0.150 × 0.098 mm, on a Bruker APEX-II diffractometer using a combination of $\omega$- and $\varphi$-scans of 0.5°.[303] Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by vecmap methods and expanded routinely.[304] The model was refined by full-matrix least-squares analysis of F$^2$ against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).

Figure A.103 X-ray molecular structure of **13**

Table A.26    Crystal Data and Structure Refinement for **13**

| | |
|---|---|
| Empirical formula | $C_{21}H_{25}I_2N_4ORh$ |
| Formula weight | 706.16 |
| Temperature | 99.99 K |
| Wavelength | 0.71073 Å |
| Crystal system | Triclinic |
| Space group | P-1 |
| Unit cell dimensions | $a = 8.2638(2)$ Å          $\alpha = 88.0310(10)°$ |
| | $b = 8.4439(2)$ Å          $\beta = 84.8720(10)°$ |
| | $c = 16.8412(3)$ Å          $\gamma = 83.4470(10)°$ |
| Volume | 1162.46(4) Å$^3$ |
| Z | 2 |
| Density (calculated) | 2.017 g.cm$^{-3}$ |
| Absorption coefficient ($\mu$) | 3.410 mm$^{-1}$ |
| F(000) | 676 |
| Crystal color, habit | Orange, Plates |
| Crystal size | $0.32 \times 0.261 \times 0.257$ mm$^3$ |
| $\theta$ range for data collection | 1.214 to 27.877° |
| Index ranges | $-10 \leq h \leq 10$, $-11 \leq k \leq 11$, $-22 \leq l \leq 22$ |
| Reflections collected | 19052 |
| Independent reflections | 5399 [$R_{int} = 0.0236$] |
| Completeness to $\theta = 26.000°$ | 98.7 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.7844 and 0.5599 |
| Refinement method | Full-matrix least-squares on F$^2$ |
| Data / restraints / parameters | 5399 / 0 / 265 |
| Goodness-of-fit on F$^2$ | 1.147 |
| Final R indices [I>2σ(I)] | $R_1 = 0.0227$, $wR_2 = 0.0556$ |
| R indices (all data) | $R_1 = 0.0244$, $wR_2 = 0.0643$ |
| Extinction coefficient | 0.00035(14) |
| Largest diff. peak and hole | 1.081 and -1.133 e$^-$.Å$^{-3}$ |

Table A.27    Atomic Coordinates and Equivalent Isotropic Displacement Parameters
            (Å$^2$) for **13**

|        | x | y | z | U(eq) |
|--------|-----------|-----------|-------------|----------|
| I(1)   | 0.58445(3) | 0.17770(3) | 0.66374(2) | 0.020(1) |
| I(2)   | 0.24862(2) | 0.42658(2) | 0.92496(2) | 0.016(1) |
| Rh(1)  | 0.40734(3) | 0.31112(3) | 0.78936(2) | 0.013(1) |
| O(1)   | 0.1627(3) | 0.5047(3) | 0.69051(14) | 0.021(1) |
| N(1)   | 0.7061(3) | 0.4096(3) | 0.84159(16) | 0.016(1) |
| N(2)   | 0.6217(3) | 0.6069(3) | 0.76610(16) | 0.017(1) |
| N(3)   | 0.3920(3) | -0.0082(3) | 0.85819(16) | 0.016(1) |
| N(4)   | 0.1708(3) | 0.0324(3) | 0.79806(16) | 0.019(1) |
| C(1)   | 0.5661(4) | 0.1880(4) | 0.85714(19) | 0.017(1) |
| C(2)   | 0.7008(4) | 0.2541(4) | 0.87652(19) | 0.016(1) |
| C(3)   | 0.8150(4) | 0.1704(4) | 0.92297(19) | 0.020(1) |
| C(4)   | 0.7860(4) | 0.0151(4) | 0.94787(19) | 0.022(1) |
| C(5)   | 0.6505(4) | -0.0547(4) | 0.92935(19) | 0.020(1) |
| C(6)   | 0.5394(4) | 0.0351(4) | 0.88336(19) | 0.017(1) |
| C(7)   | 0.3042(4) | 0.1019(4) | 0.81198(18) | 0.016(1) |
| C(8)   | 0.3126(4) | -0.1440(4) | 0.8727(2) | 0.020(1) |
| C(9)   | 0.1757(5) | -0.1179(4) | 0.8346(2) | 0.023(1) |
| C(10)  | 0.5825(4) | 0.4646(4) | 0.79491(18) | 0.014(1) |
| C(11)  | 0.8208(4) | 0.5179(4) | 0.8413(2) | 0.021(1) |
| C(12)  | 0.7669(4) | 0.6402(4) | 0.7938(2) | 0.021(1) |
| C(13)  | 0.5309(5) | 0.7080(4) | 0.7085(2) | 0.022(1) |
| C(14)  | 0.5662(5) | 0.6520(4) | 0.6235(2) | 0.024(1) |
| C(15)  | 0.7432(5) | 0.6495(6) | 0.5900(2) | 0.034(1) |
| C(16)  | 0.7654(6) | 0.5933(6) | 0.5039(3) | 0.043(1) |
| C(17)  | 0.0431(4) | 0.1046(4) | 0.7485(2) | 0.022(1) |
| C(18)  | 0.0984(4) | 0.1005(4) | 0.6596(2) | 0.021(1) |
| C(19)  | 0.1293(5) | -0.0658(5) | 0.6266(2) | 0.030(1) |
| C(20)  | 0.2061(6) | -0.0675(6) | 0.5410(2) | 0.036(1) |
| C(21)  | 0.2474(5) | 0.4390(4) | 0.7235(2) | 0.024(1) |
| H(3)   | 0.9079 | 0.2163 | 0.9371 | 0.024 |
| H(4)   | 0.8629 | -0.0452 | 0.9789 | 0.026 |
| H(5)   | 0.6338 | -0.1599 | 0.9474 | 0.024 |

Table A.27 (Continued)

| | | | | |
|---|---|---|---|---|
| H(8) | 0.3479 | -0.2362 | 0.9031 | 0.025 |
| H(9) | 0.0958 | -0.1899 | 0.8330 | 0.027 |
| H(11) | 0.9170 | 0.5076 | 0.8688 | 0.025 |
| H(12) | 0.8193 | 0.7335 | 0.7814 | 0.026 |
| H(13A) | 0.5592 | 0.8184 | 0.7109 | 0.026 |
| H(13B) | 0.4123 | 0.7097 | 0.7241 | 0.026 |
| H(14A) | 0.4971 | 0.7226 | 0.5888 | 0.029 |
| H(14B) | 0.5337 | 0.5431 | 0.6211 | 0.029 |
| H(15A) | 0.8136 | 0.5770 | 0.6233 | 0.040 |
| H(15B) | 0.7775 | 0.7578 | 0.5919 | 0.040 |
| H(16A) | 0.6900 | 0.6605 | 0.4718 | 0.064 |
| H(16B) | 0.7422 | 0.4822 | 0.5028 | 0.064 |
| H(16C) | 0.8782 | 0.6014 | 0.4820 | 0.064 |
| H(17A) | 0.0117 | 0.2167 | 0.7640 | 0.026 |
| H(17B) | -0.0547 | 0.0469 | 0.7588 | 0.026 |
| H(18A) | 0.0137 | 0.1633 | 0.6299 | 0.026 |
| H(18B) | 0.2001 | 0.1526 | 0.6501 | 0.026 |
| H(19A) | 0.0244 | -0.1126 | 0.6289 | 0.036 |
| H(19B) | 0.2026 | -0.1333 | 0.6606 | 0.036 |
| H(20A) | 0.1345 | -0.0002 | 0.5071 | 0.054 |
| H(20B) | 0.2206 | -0.1770 | 0.5219 | 0.054 |
| H(20C) | 0.3127 | -0.0264 | 0.5388 | 0.054 |

$U(eq)$ is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table A.28    Anisotropic Displacement Parameters (Å$^2$) for **13**

|       | U$_{11}$ | U$_{22}$ | U$_{33}$ | U$_{23}$ | U$_{13}$ | U$_{12}$ |
|-------|----------|----------|----------|----------|----------|----------|
| I(1)  | 0.0220(1) | 0.0206(1) | 0.0170(1) | -0.0006(1) | 0.0016(1) | -0.0015(1) |
| I(2)  | 0.0178(1) | 0.0161(1) | 0.0144(1) | -0.0006(1) | 0.0004(1) | -0.0010(1) |
| Rh(1) | 0.0128(1) | 0.0126(1) | 0.0121(1) | 0.0008(1) | -0.0006(1) | -0.0014(1) |
| O(1)  | 0.0121(10) | 0.0369(14) | 0.0147(11) | 0.0010(10) | -0.0035(9) | -0.0039(10) |
| N(1)  | 0.0157(12) | 0.0169(13) | 0.0145(13) | -0.0018(10) | -0.0007(10) | -0.0004(10) |
| N(2)  | 0.0199(13) | 0.0164(13) | 0.0157(13) | -0.0011(10) | 0.0011(11) | -0.0029(11) |
| N(3)  | 0.0229(14) | 0.0136(12) | 0.0128(12) | 0.0001(10) | -0.0008(11) | -0.0020(11) |
| N(4)  | 0.0193(13) | 0.0215(14) | 0.0145(13) | -0.0038(11) | 0.0015(11) | -0.0035(11) |
| C(1)  | 0.0190(15) | 0.0181(15) | 0.0129(14) | -0.0003(12) | -0.0016(12) | 0.0034(12) |
| C(2)  | 0.0186(15) | 0.0180(15) | 0.0119(14) | -0.0027(11) | -0.0001(12) | 0.0026(12) |
| C(3)  | 0.0178(15) | 0.0271(17) | 0.0138(15) | -0.0037(13) | -0.0025(12) | 0.0025(13) |
| C(4)  | 0.0241(16) | 0.0253(17) | 0.0126(15) | -0.0007(13) | -0.0027(13) | 0.0098(14) |
| C(5)  | 0.0302(18) | 0.0165(15) | 0.0112(14) | -0.0006(12) | 0.0001(13) | 0.0055(13) |
| C(6)  | 0.0223(16) | 0.0153(14) | 0.0125(14) | -0.0008(11) | -0.0010(12) | 0.0030(12) |
| C(7)  | 0.0195(15) | 0.0173(15) | 0.0116(14) | -0.0016(11) | -0.0002(12) | 0.0001(12) |
| C(8)  | 0.0287(18) | 0.0155(15) | 0.0171(15) | -0.0006(12) | 0.0060(13) | -0.0087(13) |
| C(9)  | 0.0291(18) | 0.0211(16) | 0.0186(16) | -0.0050(13) | 0.0033(14) | -0.0077(14) |
| C(10) | 0.0149(14) | 0.0141(14) | 0.0129(14) | -0.0010(11) | 0.0018(11) | -0.0034(11) |
| C(11) | 0.0174(15) | 0.0264(17) | 0.0193(16) | -0.0052(13) | 0.0002(13) | -0.0062(13) |
| C(12) | 0.0209(16) | 0.0197(16) | 0.0248(17) | -0.0017(13) | 0.0014(13) | -0.0105(13) |
| C(13) | 0.0265(17) | 0.0163(15) | 0.0212(17) | 0.0039(13) | -0.0013(14) | 0.0038(13) |
| C(14) | 0.0291(18) | 0.0229(17) | 0.0201(17) | 0.0048(13) | -0.0030(14) | 0.0011(15) |
| C(15) | 0.0263(19) | 0.049(3) | 0.0246(19) | 0.0051(17) | 0.0031(15) | -0.0051(18) |
| C(16) | 0.041(2) | 0.058(3) | 0.025(2) | 0.006(2) | 0.0049(18) | 0.008(2) |
| C(17) | 0.0171(15) | 0.0261(17) | 0.0230(17) | -0.0040(14) | -0.0015(13) | -0.0024(13) |
| C(18) | 0.0159(15) | 0.0274(18) | 0.0212(17) | 0.0008(13) | -0.0014(13) | -0.0047(13) |
| C(19) | 0.035(2) | 0.033(2) | 0.0214(18) | -0.0057(15) | -0.0065(16) | 0.0022(17) |
| C(20) | 0.039(2) | 0.045(2) | 0.0215(19) | -0.0084(17) | -0.0055(17) | 0.0064(19) |
| C(21) | 0.0295(19) | 0.0212(17) | 0.0200(17) | -0.0057(14) | 0.0124(15) | -0.0112(15) |

$$-2\pi^2[h^2a*^2U_{11} + ... + 2hka*b*U_{12}] \qquad (A.5)$$

Table A.29    Bond Lengths [Å] for **13**

| atom-atom | distance | atom-atom | distance |
|---|---|---|---|
| I(1)-Rh(1) | 2.6685(3) | I(2)-Rh(1) | 2.6854(3) |
| Rh(1)-C(1) | 1.995(3) | Rh(1)-C(7) | 2.057(3) |
| Rh(1)-C(10) | 2.061(3) | Rh(1)-C(21) | 1.999(4) |
| O(1)-C(21) | 1.032(5) | N(1)-C(2) | 1.424(4) |
| N(1)-C(10) | 1.374(4) | N(1)-C(11) | 1.389(4) |
| N(2)-C(10) | 1.343(4) | N(2)-C(12) | 1.387(4) |
| N(2)-C(13) | 1.469(4) | N(3)-C(6) | 1.415(4) |
| N(3)-C(7) | 1.376(4) | N(3)-C(8) | 1.388(4) |
| N(4)-C(7) | 1.349(4) | N(4)-C(9) | 1.389(5) |
| N(4)-C(17) | 1.468(4) | C(1)-C(2) | 1.370(5) |
| C(1)-C(6) | 1.386(5) | C(2)-C(3) | 1.394(4) |
| C(3)-H(3) | 0.9500 | C(3)-C(4) | 1.403(5) |
| C(4)-H(4) | 0.9500 | C(4)-C(5) | 1.387(5) |
| C(5)-H(5) | 0.9500 | C(5)-C(6) | 1.394(4) |
| C(8)-H(8) | 0.9500 | C(8)-C(9) | 1.343(5) |
| C(9)-H(9) | 0.9500 | C(11)-H(11) | 0.9500 |
| C(11)-C(12) | 1.343(5) | C(12)-H(12) | 0.9500 |
| C(13)-H(13A) | 0.9900 | C(13)-H(13B) | 0.9900 |
| C(13)-C(14) | 1.517(5) | C(14)-H(14A) | 0.9900 |
| C(14)-H(14B) | 0.9900 | C(14)-C(15) | 1.518(5) |
| C(15)-H(15A) | 0.9900 | C(15)-H(15B) | 0.9900 |
| C(15)-C(16) | 1.530(6) | C(16)-H(16A) | 0.9800 |
| C(16)-H(16B) | 0.9800 | C(16)-H(16C) | 0.9800 |
| C(17)-H(17A) | 0.9900 | C(17)-H(17B) | 0.9900 |
| C(17)-C(18) | 1.527(5) | C(18)-H(18A) | 0.9900 |
| C(18)-H(18B) | 0.9900 | C(18)-C(19) | 1.514(5) |
| C(19)-H(19A) | 0.9900 | C(19)-H(19B) | 0.9900 |
| C(19)-C(20) | 1.523(5) | C(20)-H(20A) | 0.9800 |
| C(20)-H(20B) | 0.9800 | C(20)-H(20C) | 0.9800 |

Symmetry transformations used to generate equivalent atoms.

Table A.30    Bond Angles [°] for **13**

| atom-atom-atom | angle | atom-atom-atom | angle |
|---|---|---|---|
| I(1)-Rh(1)-I(2) | 174.272(12) | C(1)-Rh(1)-I(1) | 87.12(9) |
| C(1)-Rh(1)-I(2) | 87.17(9) | C(1)-Rh(1)-C(7) | 77.84(14) |
| C(1)-Rh(1)-C(10) | 77.54(14) | C(1)-Rh(1)-C(21) | 178.53(13) |
| C(7)-Rh(1)-I(1) | 89.21(9) | C(7)-Rh(1)-I(2) | 89.06(9) |
| C(7)-Rh(1)-C(10) | 155.36(13) | C(10)-Rh(1)-I(1) | 88.63(8) |
| C(10)-Rh(1)-I(2) | 90.68(8) | C(21)-Rh(1)-I(1) | 94.12(10) |
| C(21)-Rh(1)-I(2) | 91.59(10) | C(21)-Rh(1)-C(7) | 102.94(14) |
| C(21)-Rh(1)-C(10) | 101.70(13) | C(10)-N(1)-C(2) | 116.8(3) |
| C(10)-N(1)-C(11) | 111.1(3) | C(11)-N(1)-C(2) | 132.0(3) |
| C(10)-N(2)-C(12) | 110.4(3) | C(10)-N(2)-C(13) | 125.0(3) |
| C(12)-N(2)-C(13) | 124.4(3) | C(7)-N(3)-C(6) | 117.0(3) |
| C(7)-N(3)-C(8) | 111.1(3) | C(8)-N(3)-C(6) | 132.0(3) |
| C(7)-N(4)-C(9) | 110.3(3) | C(7)-N(4)-C(17) | 124.1(3) |
| C(9)-N(4)-C(17) | 125.6(3) | C(2)-C(1)-Rh(1) | 120.0(2) |
| C(2)-C(1)-C(6) | 120.7(3) | C(6)-C(1)-Rh(1) | 119.3(3) |
| C(1)-C(2)-N(1) | 111.2(3) | C(1)-C(2)-C(3) | 121.3(3) |
| C(3)-C(2)-N(1) | 127.4(3) | C(2)-C(3)-H(3) | 121.6 |
| C(2)-C(3)-C(4) | 116.8(3) | C(4)-C(3)-H(3) | 121.6 |
| C(3)-C(4)-H(4) | 118.4 | C(5)-C(4)-C(3) | 123.1(3) |
| C(5)-C(4)-H(4) | 118.4 | C(4)-C(5)-H(5) | 121.2 |
| C(4)-C(5)-C(6) | 117.7(3) | C(6)-C(5)-H(5) | 121.2 |
| C(1)-C(6)-N(3) | 111.4(3) | C(1)-C(6)-C(5) | 120.4(3) |
| C(5)-C(6)-N(3) | 128.2(3) | N(3)-C(7)-Rh(1) | 114.5(2) |
| N(4)-C(7)-Rh(1) | 140.9(2) | N(4)-C(7)-N(3) | 104.6(3) |
| N(3)-C(8)-H(8) | 127.1 | C(9)-C(8)-N(3) | 105.7(3) |
| C(9)-C(8)-H(8) | 127.1 | N(4)-C(9)-H(9) | 125.8 |
| C(8)-C(9)-N(4) | 108.3(3) | C(8)-C(9)-H(9) | 125.8 |
| N(1)-C(10)-Rh(1) | 114.4(2) | N(2)-C(10)-Rh(1) | 140.9(2) |
| N(2)-C(10)-N(1) | 104.7(3) | N(1)-C(11)-H(11) | 127.2 |
| C(12)-C(11)-N(1) | 105.5(3) | C(12)-C(11)-H(11) | 127.2 |
| N(2)-C(12)-H(12) | 125.8 | C(11)-C(12)-N(2) | 108.3(3) |
| C(11)-C(12)-H(12) | 125.8 | N(2)-C(13)-H(13A) | 108.9 |

Table A.30 (Continued)

| | | | |
|---|---|---|---|
| N(2)-C(13)-H(13B) | 108.9 | N(2)-C(13)-C(14) | 113.2(3) |
| H(13A)-C(13)-H(13B) | 107.7 | C(14)-C(13)-H(13A) | 108.9 |
| C(14)-C(13)-H(13B) | 108.9 | C(13)-C(14)-H(14A) | 108.5 |
| C(13)-C(14)-H(14B) | 108.5 | C(13)-C(14)-C(15) | 115.0(3) |
| H(14A)-C(14)-H(14B) | 107.5 | C(15)-C(14)-H(14A) | 108.5 |
| C(15)-C(14)-H(14B) | 108.5 | C(14)-C(15)-H(15A) | 109.5 |
| C(14)-C(15)-H(15B) | 109.5 | C(14)-C(15)-C(16) | 110.8(4) |
| H(15A)-C(15)-H(15B) | 108.1 | C(16)-C(15)-H(15A) | 109.5 |
| C(16)-C(15)-H(15B) | 109.5 | C(15)-C(16)-H(16A) | 109.5 |
| C(15)-C(16)-H(16B) | 109.5 | C(15)-C(16)-H(16C) | 109.5 |
| H(16A)-C(16)-H(16B) | 109.5 | H(16A)-C(16)-H(16C) | 109.5 |
| H(16B)-C(16)-H(16C) | 109.5 | N(4)-C(17)-H(17A) | 109.1 |
| N(4)-C(17)-H(17B) | 109.1 | N(4)-C(17)-C(18) | 112.6(3) |
| H(17A)-C(17)-H(17B) | 107.8 | C(18)-C(17)-H(17A) | 109.1 |
| C(18)-C(17)-H(17B) | 109.1 | C(17)-C(18)-H(18A) | 108.8 |
| C(17)-C(18)-H(18B) | 108.8 | H(18A)-C(18)-H(18B) | 107.7 |
| C(19)-C(18)-C(17) | 113.9(3) | C(19)-C(18)-H(18A) | 108.8 |
| C(19)-C(18)-H(18B) | 108.8 | C(18)-C(19)-H(19A) | 109.1 |
| C(18)-C(19)-H(19B) | 109.1 | C(18)-C(19)-C(20) | 112.6(4) |
| H(19A)-C(19)-H(19B) | 107.8 | C(20)-C(19)-H(19A) | 109.1 |
| C(20)-C(19)-H(19B) | 109.1 | C(19)-C(20)-H(20A) | 109.5 |
| C(19)-C(20)-H(20B) | 109.5 | C(19)-C(20)-H(20C) | 109.5 |
| H(20A)-C(20)-H(20B) | 109.5 | H(20A)-C(20)-H(20C) | 109.5 |
| H(20B)-C(20)-H(20C) | 109.5 | O(1)-C(21)-Rh(1) | 178.6(3) |

Symmetry transformations used to generate equivalent atoms.

Table A.31    Torsion Angles [°] for **13**

| atom-atom-atom-atom | angle | atom-atom-atom-atom | angle |
|---|---|---|---|
| Rh(1)-C(1)-C(2)-N(1) | -0.9(4) | Rh(1)-C(1)-C(2)-C(3) | -179.2(2) |
| Rh(1)-C(1)-C(6)-N(3) | -2.1(4) | Rh(1)-C(1)-C(6)-C(5) | 178.6(2) |
| N(1)-C(2)-C(3)-C(4) | -177.3(3) | N(1)-C(11)-C(12)-N(2) | 0.2(4) |
| N(2)-C(13)-C(14)-C(15) | -60.9(4) | N(3)-C(8)-C(9)-N(4) | -0.5(4) |
| N(4)-C(17)-C(18)-C(19) | 66.1(4) | C(1)-C(2)-C(3)-C(4) | 0.8(5) |
| C(2)-N(1)-C(10)-Rh(1) | 2.6(3) | C(2)-N(1)-C(10)-N(2) | -176.4(3) |
| C(2)-N(1)-C(11)-C(12) | 175.5(3) | C(2)-C(1)-C(6)-N(3) | 178.7(3) |
| C(2)-C(1)-C(6)-C(5) | -0.6(5) | C(2)-C(3)-C(4)-C(5) | -1.0(5) |
| C(3)-C(4)-C(5)-C(6) | 0.4(5) | C(4)-C(5)-C(6)-N(3) | -178.8(3) |
| C(4)-C(5)-C(6)-C(1) | 0.4(5) | C(6)-N(3)-C(7)-Rh(1) | -0.4(3) |
| C(6)-N(3)-C(7)-N(4) | -178.9(3) | C(6)-N(3)-C(8)-C(9) | 178.9(3) |
| C(6)-C(1)-C(2)-N(1) | 178.4(3) | C(6)-C(1)-C(2)-C(3) | 0.0(5) |
| C(7)-N(3)-C(6)-C(1) | 1.5(4) | C(7)-N(3)-C(6)-C(5) | -179.3(3) |
| C(7)-N(3)-C(8)-C(9) | 0.5(4) | C(7)-N(4)-C(9)-C(8) | 0.5(4) |
| C(7)-N(4)-C(17)-C(18) | 74.0(4) | C(8)-N(3)-C(6)-C(1) | -176.8(3) |
| C(8)-N(3)-C(6)-C(5) | 2.4(6) | C(8)-N(3)-C(7)-Rh(1) | 178.3(2) |
| C(8)-N(3)-C(7)-N(4) | -0.2(3) | C(9)-N(4)-C(7)-Rh(1) | -178.0(3) |
| C(9)-N(4)-C(7)-N(3) | -0.2(3) | C(9)-N(4)-C(17)-C(18) | -103.4(4) |
| C(10)-N(1)-C(2)-C(1) | -1.2(4) | C(10)-N(1)-C(2)-C(3) | 177.1(3) |
| C(10)-N(1)-C(11)-C(12) | -0.1(4) | C(10)-N(2)-C(12)-C(11) | -0.3(4) |
| C(10)-N(2)-C(13)-C(14) | -77.9(4) | C(11)-N(1)-C(2)-C(1) | -176.6(3) |
| C(11)-N(1)-C(2)-C(3) | 1.6(5) | C(11)-N(1)-C(10)-Rh(1) | 178.9(2) |
| C(11)-N(1)-C(10)-N(2) | -0.1(3) | C(12)-N(2)-C(10)-Rh(1) | -178.3(3) |
| C(12)-N(2)-C(10)-N(1) | 0.2(3) | C(12)-N(2)-C(13)-C(14) | 97.2(4) |
| C(13)-N(2)-C(10)-Rh(1) | -2.6(5) | C(13)-N(2)-C(10)-N(1) | 175.9(3) |
| C(13)-N(2)-C(12)-C(11) | -176.0(3) | C(13)-C(14)-C(15)-C(16) | -179.3(3) |
| C(17)-N(4)-C(7)-Rh(1) | 4.2(5) | C(17)-N(4)-C(7)-N(3) | -177.9(3) |
| C(17)-N(4)-C(9)-C(8) | 178.2(3) | C(17)-C(18)-C(19)-C(20) | -172.2(3) |

Symmetry transformations used to generate equivalent atoms.

### A.4.2 Crystal Summary for 13

Crystal data for $C_{21}H_{25}I_2N_4ORh$; $M_r = 706.16$; Triclinic; space group P-1; $a = 8.2638(2)$ Å; $b = 8.4439(2)$ Å; $c = 16.8412(3)$ Å; $\alpha = 88.0310(10)°$; $\beta = 84.8720(10)°$; $\gamma = 83.4470(10)°$; $V = 1162.46(4)$ Å$^3$; $Z = 2$; $T = 99.99$ K; $\lambda$(Mo-K$\alpha$) $= 0.71073$ Å; $\mu$(Mo-K$\alpha$) $= 3.410$ mm$^{-1}$; $d_{calc} = 2.017$g.cm$^{-3}$; 19052 reflections collected; 5399 unique ($R_{int} = 0.0236$); giving $R_1 = 0.0227$, $wR_2 = 0.0556$ for 5152 data with [I>2σ(I)] and $R_1 = 0.0244$, $wR_2 = 0.0643$ for all 5399 data. Residual electron density (e$^-$.Å$^{-3}$) max/min: 1.081/-1.133.

An arbitrary sphere of data were collected on a orange plate-like crystal, having approximate dimensions of $0.32 \times 0.261 \times 0.257$ mm, on a Bruker APEX-II diffractometer using a combination of ω- and φ-scans of 0.5°.[303] Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by direct methods and expanded routinely.[304] The model was refined by full-matrix least-squares analysis of $F^2$ against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).
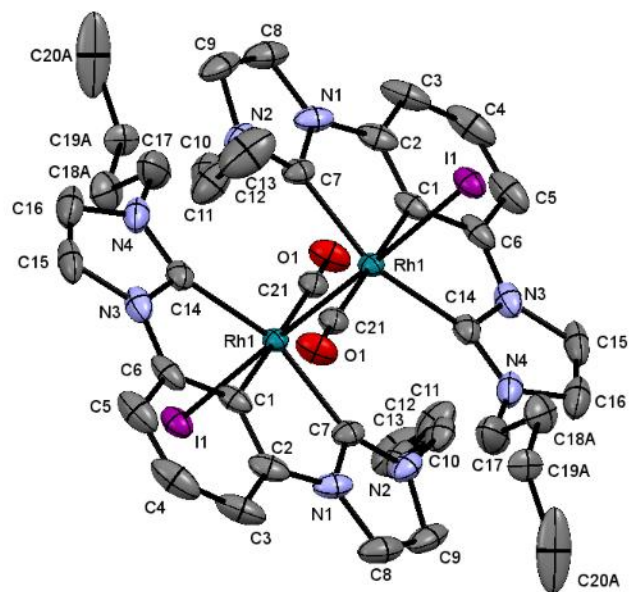
Figure A.104 X-ray molecular structure of **14**

Table A.32    Crystal Data and Structure Refinement **14**

| | |
|---|---|
| Empirical formula | $C_{21.62}H_{26.24}ClIN_4ORh$ |
| Formula weight | 623.44 |
| Temperature | 100.0 K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | P 1 21/n 1 |
| Unit cell dimensions | $a = 13.0363(3)$ Å $\quad\quad$ $\alpha = 90°$ |
| | $b = 10.3210(3)$ Å $\quad\quad$ $\beta = 108.0290(10)°$ |
| | $c = 18.0439(5)$ Å $\quad\quad$ $\gamma = 90°$ |
| Volume | 2308.56(11) Å$^3$ |
| Z | 4 |
| Density (calculated) | 1.794 g.cm$^{-3}$ |
| Absorption coefficient ($\mu$) | 2.213 mm$^{-1}$ |
| F(000) | 1228 |
| Crystal color, habit | red, Tablet |
| Crystal size | $0.315 \times 0.256 \times 0.17$ mm$^3$ |
| $\theta$ range for data collection | 2.303 to 27.883° |
| Index ranges | $-17 \leq h \leq 14, -13 \leq k \leq 13, -23 \leq l \leq 23$ |
| Reflections collected | 21056 |
| Independent reflections | 5503 [$R_{int} = 0.0348$] |
| Completeness to $\theta = 26.000°$ | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Max. and min. transmission | 0.9484 and 0.8248 |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 5503 / 0 / 311 |
| Goodness-of-fit on $F^2$ | 1.074 |
| Final R indices [$I>2\sigma(I)$] | $R_1 = 0.0357$, $wR_2 = 0.0936$ |
| R indices (all data) | $R_1 = 0.0456$, $wR_2 = 0.1002$ |
| Extinction coefficient | n/a |
| Largest diff. peak and hole | 1.384 and -1.406 e$^-$.Å$^{-3}$ |

Table A.33 Atomic Coordinates and Equivalent Isotropic Displacement Parameters ($\text{Å}^2$) for **14**

|        | x           | y           | z            | U(eq)      |
|--------|-------------|-------------|--------------|------------|
| I(1)   | 0.24316(2)  | 0.23880(2)  | 0.43723(2)   | 0.030(1)   |
| Rh(1)  | 0.41129(2)  | 0.41532(2)  | 0.48194(2)   | 0.020(1)   |
| O(1)   | 0.2846(2)   | 0.5389(3)   | 0.58230(18)  | 0.037(1)   |
| N(1)   | 0.3869(3)   | 0.4654(4)   | 0.3191(2)    | 0.032(1)   |
| N(2)   | 0.2753(3)   | 0.5990(3)   | 0.3434(2)    | 0.030(1)   |
| N(3)   | 0.5550(3)   | 0.1927(3)   | 0.5218(2)    | 0.034(1)   |
| N(4)   | 0.5090(3)   | 0.2206(3)   | 0.6253(2)    | 0.037(1)   |
| C(1)   | 0.4834(3)   | 0.3254(4)   | 0.4144(2)    | 0.028(1)   |
| C(2)   | 0.4628(3)   | 0.3618(4)   | 0.3380(2)    | 0.034(1)   |
| C(3)   | 0.5136(4)   | 0.2989(5)   | 0.2901(3)    | 0.045(1)   |
| C(4)   | 0.5845(4)   | 0.1969(6)   | 0.3235(4)    | 0.053(2)   |
| C(5)   | 0.6030(3)   | 0.1547(5)   | 0.3990(3)    | 0.045(1)   |
| C(6)   | 0.5508(3)   | 0.2204(4)   | 0.4441(3)    | 0.035(1)   |
| C(7)   | 0.3500(3)   | 0.5093(4)   | 0.3783(2)    | 0.027(1)   |
| C(8)   | 0.3356(4)   | 0.5270(5)   | 0.2498(3)    | 0.042(1)   |
| C(9)   | 0.2660(4)   | 0.6115(5)   | 0.2646(3)    | 0.044(1)   |
| C(10)  | 0.2096(3)   | 0.6690(4)   | 0.3827(3)    | 0.034(1)   |
| C(11)  | 0.1062(3)   | 0.5995(4)   | 0.3794(3)    | 0.036(1)   |
| C(12)  | 0.0422(4)   | 0.6758(5)   | 0.4228(3)    | 0.049(1)   |
| C(13)  | -0.0670(4)  | 0.6142(7)   | 0.4146(4)    | 0.069(2)   |
| C(14)  | 0.4972(3)   | 0.2731(4)   | 0.5548(2)    | 0.028(1)   |
| C(15)  | 0.6004(3)   | 0.0911(4)   | 0.5735(3)    | 0.044(1)   |
| C(16)  | 0.5717(4)   | 0.1096(4)   | 0.6364(3)    | 0.046(1)   |
| C(17)  | 0.4545(5)   | 0.2661(5)   | 0.6796(3)    | 0.053(1)   |
| C(18A) | 0.3626(7)   | 0.1873(9)   | 0.6792(6)    | 0.042(2)   |
| C(19A) | 0.3092(9)   | 0.2320(12)  | 0.7401(7)    | 0.027(2)   |
| C(20A) | 0.3749(18)  | 0.2078(18)  | 0.8262(19)   | 0.092(10)  |
| C(18B) | 0.4568(9)   | 0.2071(12)  | 0.7517(8)    | 0.032(3)   |
| C(19B) | 0.3859(16)  | 0.2626(18)  | 0.8011(13)   | 0.057(5)   |
| C(20B) | 0.4154(17)  | 0.429(3)    | 0.8285(12)   | 0.107(11)  |
| C(21)  | 0.3360(3)   | 0.4995(4)   | 0.5468(2)    | 0.027(1)   |
| Cl(1)  | 0.3241(4)   | 0.5621(4)   | 0.8487(4)    | 0.106(2)   |

Table A.33 (Continued)

| | | | | |
|---|---|---|---|---|
| Cl(2) | 0.5304(5) | 0.4629(6) | 0.9526(5) | 0.161(3) |
| C(22) | 0.3946(13) | 0.5138(16) | 0.9557(10) | 0.064(6) |
| H(3) | 0.5007 | 0.3240 | 0.2373 | 0.053 |
| H(4) | 0.6215 | 0.1549 | 0.2924 | 0.063 |
| H(5) | 0.6495 | 0.0837 | 0.4193 | 0.054 |
| H(8) | 0.3471 | 0.5125 | 0.2010 | 0.050 |
| H(9) | 0.2193 | 0.6689 | 0.2283 | 0.052 |
| H(10A) | 0.1917 | 0.7554 | 0.3584 | 0.041 |
| H(10B) | 0.2525 | 0.6821 | 0.4380 | 0.041 |
| H(11A) | 0.1233 | 0.5125 | 0.4030 | 0.043 |
| H(11B) | 0.0618 | 0.5883 | 0.3243 | 0.043 |
| H(12A) | 0.0845 | 0.6806 | 0.4787 | 0.059 |
| H(12B) | 0.0311 | 0.7654 | 0.4022 | 0.059 |
| H(13A) | -0.1032 | 0.6626 | 0.4461 | 0.104 |
| H(13B) | -0.0565 | 0.5242 | 0.4327 | 0.104 |
| H(13C) | -0.1116 | 0.6161 | 0.3598 | 0.104 |
| H(15) | 0.6436 | 0.0223 | 0.5646 | 0.052 |
| H(16) | 0.5906 | 0.0562 | 0.6815 | 0.055 |
| H(17A) | 0.5065 | 0.2665 | 0.7329 | 0.064 |
| H(17B) | 0.4301 | 0.3563 | 0.6661 | 0.064 |
| H(17C) | 0.4798 | 0.3561 | 0.6928 | 0.064 |
| H(17D) | 0.3772 | 0.2725 | 0.6489 | 0.064 |
| H(18A) | 0.3862 | 0.0961 | 0.6899 | 0.051 |
| H(18B) | 0.3087 | 0.1907 | 0.6267 | 0.051 |
| H(19A) | 0.2389 | 0.1873 | 0.7293 | 0.032 |
| H(19B) | 0.2943 | 0.3261 | 0.7330 | 0.032 |
| H(20A) | 0.3396 | 0.2512 | 0.8601 | 0.138 |
| H(20B) | 0.4479 | 0.2425 | 0.8364 | 0.138 |
| H(20C) | 0.3788 | 0.1145 | 0.8367 | 0.138 |
| H(18C) | 0.5328 | 0.2081 | 0.7857 | 0.039 |
| H(18D) | 0.4364 | 0.1151 | 0.7406 | 0.039 |
| H(19C) | 0.3982 | 0.2096 | 0.8488 | 0.068 |
| H(19D) | 0.3088 | 0.2548 | 0.7704 | 0.068 |

Table A.33 (Continued)

| | | | | |
|---|---|---|---|---|
| H(20D) | 0.4337 | 0.4368 | 0.8852 | 0.161 |
| H(20E) | 0.3521 | 0.4821 | 0.8032 | 0.161 |
| H(20F) | 0.4765 | 0.4575 | 0.8119 | 0.161 |
| H(22A) | 0.3997 | 0.5882 | 0.9914 | 0.077 |
| H(22B) | 0.3565 | 0.4416 | 0.9721 | 0.077 |

U(eq) is defined as one third of the trace of the orthogonalized $U_{ij}$ tensor.

Table A.34    Anisotropic Displacement Parameters ($\text{Å}^2$) for **14**

| | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| I(1) | 0.0210(1) | 0.0297(1) | 0.0373(2) | -0.0094(1) | 0.0043(1) | -0.0015(1) |
| Rh(1) | 0.0167(1) | 0.0207(1) | 0.0205(2) | -0.0023(1) | 0.0020(1) | 0.0016(1) |
| O(1) | 0.0281(14) | 0.0496(18) | 0.0364(17) | -0.0138(14) | 0.0158(12) | -0.0045(13) |
| N(1) | 0.0226(16) | 0.050(2) | 0.0223(17) | -0.0013(15) | 0.0031(12) | -0.0081(14) |
| N(2) | 0.0212(15) | 0.0357(17) | 0.0278(18) | 0.0084(14) | 0.0009(12) | -0.0026(13) |
| N(3) | 0.0219(16) | 0.0235(15) | 0.049(2) | -0.0042(15) | 0.0004(14) | 0.0032(13) |
| N(4) | 0.0322(18) | 0.0226(15) | 0.046(2) | 0.0065(15) | -0.0009(15) | -0.0028(13) |
| C(1) | 0.0168(16) | 0.0337(19) | 0.033(2) | -0.0143(16) | 0.0050(14) | -0.0043(14) |
| C(2) | 0.0199(18) | 0.049(2) | 0.032(2) | -0.0146(19) | 0.0058(15) | -0.0107(17) |
| C(3) | 0.030(2) | 0.069(3) | 0.036(3) | -0.028(2) | 0.0143(18) | -0.017(2) |
| C(4) | 0.031(2) | 0.064(3) | 0.067(4) | -0.039(3) | 0.022(2) | -0.013(2) |
| C(5) | 0.025(2) | 0.042(2) | 0.068(4) | -0.026(2) | 0.013(2) | -0.0023(18) |
| C(6) | 0.0208(18) | 0.0312(19) | 0.049(3) | -0.0198(19) | 0.0055(17) | -0.0041(15) |
| C(7) | 0.0197(17) | 0.0344(19) | 0.0238(19) | 0.0003(15) | 0.0013(14) | -0.0032(14) |
| C(8) | 0.031(2) | 0.067(3) | 0.024(2) | 0.002(2) | 0.0028(16) | -0.016(2) |
| C(9) | 0.032(2) | 0.060(3) | 0.028(2) | 0.016(2) | -0.0072(17) | -0.016(2) |
| C(10) | 0.0234(19) | 0.032(2) | 0.042(3) | 0.0099(18) | 0.0006(16) | 0.0025(15) |
| C(11) | 0.0232(19) | 0.039(2) | 0.042(3) | 0.0150(19) | 0.0038(17) | 0.0031(16) |
| C(12) | 0.035(2) | 0.060(3) | 0.053(3) | 0.021(3) | 0.014(2) | 0.013(2) |
| C(13) | 0.034(3) | 0.109(5) | 0.068(4) | 0.031(4) | 0.020(3) | 0.011(3) |
| C(14) | 0.0224(18) | 0.0230(17) | 0.034(2) | -0.0022(15) | 0.0003(15) | -0.0029(14) |
| C(15) | 0.027(2) | 0.0185(18) | 0.075(4) | 0.002(2) | 0.000(2) | 0.0020(15) |
| C(16) | 0.036(2) | 0.027(2) | 0.063(4) | 0.013(2) | 0.000(2) | -0.0007(18) |
| C(17) | 0.080(4) | 0.038(2) | 0.043(3) | 0.001(2) | 0.023(3) | -0.018(2) |
| C(18A) | 0.039(5) | 0.038(5) | 0.050(6) | 0.003(4) | 0.015(4) | -0.017(4) |
| C(19A) | 0.019(5) | 0.039(6) | 0.029(6) | 0.002(5) | 0.015(4) | -0.011(4) |
| C(20A) | 0.071(13) | 0.043(10) | 0.21(3) | 0.034(14) | 0.114(18) | 0.015(9) |
| C(18B) | 0.025(6) | 0.031(6) | 0.037(7) | 0.014(5) | 0.003(5) | 0.000(5) |
| C(19B) | 0.052(11) | 0.053(11) | 0.078(14) | 0.024(9) | 0.038(9) | 0.019(9) |
| C(20B) | 0.069(13) | 0.22(3) | 0.050(11) | 0.039(15) | 0.050(10) | 0.078(17) |
| C(21) | 0.0237(18) | 0.0259(17) | 0.027(2) | -0.0017(15) | 0.0021(14) | -0.0034(14) |
| Cl(1) | 0.093(3) | 0.069(2) | 0.173(5) | -0.002(3) | 0.068(3) | -0.004(2) |
| Cl(2) | 0.155(5) | 0.126(4) | 0.259(8) | 0.094(5) | 0.147(6) | 0.092(4) |
| C(22) | 0.056(9) | 0.056(9) | 0.061(11) | -0.017(8) | -0.010(8) | 0.054(8) |

$$-2\pi^2[h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}] \qquad (A.6)$$

Table A.35    Bond Lengths [Å] for **14**

| atom-atom | distance | atom-atom | distance |
|-----------|----------|-----------|----------|
| I(1)-Rh(1) | 2.7711(3) | Rh(1)-Rh(1)#1 | 2.8102(5) |
| Rh(1)-C(1) | 1.984(4) | Rh(1)-C(7) | 2.037(4) |
| Rh(1)-C(14) | 2.056(4) | Rh(1)-C(21) | 1.949(4) |
| O(1)-C(21) | 1.136(5) | N(1)-C(2) | 1.425(6) |
| N(1)-C(7) | 1.377(5) | N(1)-C(8) | 1.377(6) |
| N(2)-C(7) | 1.350(5) | N(2)-C(9) | 1.396(6) |
| N(2)-C(10) | 1.461(6) | N(3)-C(6) | 1.415(6) |
| N(3)-C(14) | 1.375(6) | N(3)-C(15) | 1.406(5) |
| N(4)-C(14) | 1.347(6) | N(4)-C(16) | 1.385(6) |
| N(4)-C(17) | 1.455(7) | C(1)-C(2) | 1.373(6) |
| C(1)-C(6) | 1.394(6) | C(2)-C(3) | 1.401(6) |
| C(3)-H(3) | 0.9500 | C(3)-C(4) | 1.408(8) |
| C(4)-H(4) | 0.9500 | C(4)-C(5) | 1.378(8) |
| C(5)-H(5) | 0.9500 | C(5)-C(6) | 1.388(6) |
| C(8)-H(8) | 0.9500 | C(8)-C(9) | 1.343(8) |
| C(9)-H(9) | 0.9500 | C(10)-H(10A) | 0.9900 |
| C(10)-H(10B) | 0.9900 | C(10)-C(11) | 1.512(6) |
| C(11)-H(11A) | 0.9900 | C(11)-H(11B) | 0.9900 |
| C(11)-C(12) | 1.528(7) | C(12)-H(12A) | 0.9900 |
| C(12)-H(12B) | 0.9900 | C(12)-C(13) | 1.525(7) |
| C(13)-H(13A) | 0.9800 | C(13)-H(13B) | 0.9800 |
| C(13)-H(13C) | 0.9800 | C(15)-H(15) | 0.9500 |
| C(15)-C(16) | 1.315(8) | C(16)-H(16) | 0.9500 |
| C(17)-H(17A) | 0.9900 | C(17)-H(17B) | 0.9900 |
| C(17)-H(17C) | 0.9900 | C(17)-H(17D) | 0.9900 |
| C(17)-C(18A) | 1.446(10) | C(17)-C(18B) | 1.428(13) |
| C(18A)-H(18A) | 0.9900 | C(18A)-H(18B) | 0.9900 |
| C(18A)-C(19A) | 1.543(15) | C(19A)-H(19A) | 0.9900 |
| C(19A)-H(19B) | 0.9900 | C(19A)-C(20A) | 1.54(3) |
| C(20A)-H(20A) | 0.9800 | C(20A)-H(20B) | 0.9800 |
| C(20A)-H(20C) | 0.9800 | C(18B)-H(18C) | 0.9900 |
| C(18B)-H(18D) | 0.9900 | C(18B)-C(19B) | 1.58(2) |
| C(19B)-H(19C) | 0.9900 | C(19B)-H(19D) | 0.9900 |
| C(19B)-C(20B) | 1.79(3) | C(20B)-H(20D) | 1.0543 |
| C(20B)-H(20E) | 1.0537 | C(20B)-H(20F) | 1.0556 |
| Cl(1)-C(22) | 1.930(18) | Cl(2)-C(22) | 1.865(16) |
| C(22)-H(22A) | 0.9900 | C(22)-H(22B) | 0.9900 |

Table A.36    Bond Angles [°] for **14**

| atom-atom-atom | angle | atom-atom-atom | angle |
|---|---|---|---|
| I(1)-Rh(1)-Rh(1)#1 | 175.211(18) | C(1)-Rh(1)-I(1) | 89.77(10) |
| C(1)-Rh(1)-Rh(1)#1 | 85.47(10) | C(1)-Rh(1)-C(7) | 77.58(17) |
| C(1)-Rh(1)-C(14) | 77.92(18) | C(7)-Rh(1)-I(1) | 89.75(10) |
| C(7)-Rh(1)-Rh(1)#1 | 88.71(10) | C(7)-Rh(1)-C(14) | 155.25(17) |
| C(14)-Rh(1)-I(1) | 86.68(10) | C(14)-Rh(1)-Rh(1)#1 | 92.83(10) |
| C(21)-Rh(1)-I(1) | 88.15(11) | C(21)-Rh(1)-Rh(1)#1 | 96.60(11) |
| C(21)-Rh(1)-C(1) | 177.91(14) | C(21)-Rh(1)-C(7) | 102.21(16) |
| C(21)-Rh(1)-C(14) | 102.14(17) | C(7)-N(1)-C(2) | 116.4(3) |
| C(8)-N(1)-C(2) | 132.1(4) | C(8)-N(1)-C(7) | 111.3(4) |
| C(7)-N(2)-C(9) | 111.2(4) | C(7)-N(2)-C(10) | 124.0(3) |
| C(9)-N(2)-C(10) | 124.7(4) | C(14)-N(3)-C(6) | 116.7(3) |
| C(14)-N(3)-C(15) | 109.7(4) | C(15)-N(3)-C(6) | 133.4(4) |
| C(14)-N(4)-C(16) | 111.0(4) | C(14)-N(4)-C(17) | 124.7(4) |
| C(16)-N(4)-C(17) | 124.0(4) | C(2)-C(1)-Rh(1) | 120.4(3) |
| C(2)-C(1)-C(6) | 120.1(4) | C(6)-C(1)-Rh(1) | 119.4(3) |
| C(1)-C(2)-N(1) | 110.5(4) | C(1)-C(2)-C(3) | 120.7(4) |
| C(3)-C(2)-N(1) | 128.7(4) | C(2)-C(3)-H(3) | 121.5 |
| C(2)-C(3)-C(4) | 117.1(5) | C(4)-C(3)-H(3) | 121.5 |
| C(3)-C(4)-H(4) | 118.3 | C(5)-C(4)-C(3) | 123.4(5) |
| C(5)-C(4)-H(4) | 118.3 | C(4)-C(5)-H(5) | 121.4 |
| C(4)-C(5)-C(6) | 117.3(5) | C(6)-C(5)-H(5) | 121.4 |
| C(1)-C(6)-N(3) | 111.3(4) | C(5)-C(6)-N(3) | 127.4(4) |
| C(5)-C(6)-C(1) | 121.3(5) | N(1)-C(7)-Rh(1) | 115.1(3) |
| N(2)-C(7)-Rh(1) | 140.9(3) | N(2)-C(7)-N(1) | 103.8(3) |
| N(1)-C(8)-H(8) | 126.6 | C(9)-C(8)-N(1) | 106.8(4) |
| C(9)-C(8)-H(8) | 126.6 | N(2)-C(9)-H(9) | 126.5 |
| C(8)-C(9)-N(2) | 106.9(4) | C(8)-C(9)-H(9) | 126.6 |
| N(2)-C(10)-H(10A) | 108.9 | N(2)-C(10)-H(10B) | 108.9 |
| N(2)-C(10)-C(11) | 113.3(4) | H(10A)-C(10)-H(10B) | 107.7 |
| C(11)-C(10)-H(10A) | 108.9 | C(11)-C(10)-H(10B) | 108.9 |
| C(10)-C(11)-H(11A) | 109.5 | C(10)-C(11)-H(11B) | 109.5 |
| C(10)-C(11)-C(12) | 110.9(4) | H(11A)-C(11)-H(11B) | 108.0 |

Table A.36 (Continued)

| | | | |
|---|---|---|---|
| C(12)-C(11)-H(11A) | 109.5 | C(12)-C(11)-H(11B) | 109.5 |
| C(11)-C(12)-H(12A) | 109.2 | C(11)-C(12)-H(12B) | 109.2 |
| H(12A)-C(12)-H(12B) | 107.9 | C(13)-C(12)-C(11) | 112.1(5) |
| C(13)-C(12)-H(12A) | 109.2 | C(13)-C(12)-H(12B) | 109.2 |
| C(12)-C(13)-H(13A) | 109.5 | C(12)-C(13)-H(13B) | 109.5 |
| C(12)-C(13)-H(13C) | 109.5 | H(13A)-C(13)-H(13B) | 109.5 |
| H(13A)-C(13)-H(13C) | 109.5 | H(13B)-C(13)-H(13C) | 109.5 |
| N(3)-C(14)-Rh(1) | 114.7(3) | N(4)-C(14)-Rh(1) | 140.5(3) |
| N(4)-C(14)-N(3) | 104.4(3) | N(3)-C(15)-H(15) | 126.5 |
| C(16)-C(15)-N(3) | 106.9(4) | C(16)-C(15)-H(15) | 126.6 |
| N(4)-C(16)-H(16) | 126.0 | C(15)-C(16)-N(4) | 107.9(4) |
| C(15)-C(16)-H(16) | 126.0 | N(4)-C(17)-H(17A) | 109.0 |
| N(4)-C(17)-H(17B) | 109.0 | N(4)-C(17)-H(17C) | 105.6 |
| N(4)-C(17)-H(17D) | 105.6 | H(17A)-C(17)-H(17B) | 107.8 |
| H(17C)-C(17)-H(17D) | 106.1 | C(18A)-C(17)-N(4) | 113.0(6) |
| C(18A)-C(17)-H(17A) | 109.0 | C(18A)-C(17)-H(17B) | 109.0 |
| C(18B)-C(17)-N(4) | 126.8(7) | C(18B)-C(17)-H(17C) | 105.6 |
| C(18B)-C(17)-H(17D) | 105.6 | C(17)-C(18A)-H(18A) | 109.1 |
| C(17)-C(18A)-H(18B) | 109.1 | C(17)-C(18A)-C(19A) | 112.6(8) |
| H(18A)-C(18A)-H(18B) | 107.8 | C(19A)-C(18A)-H(18A) | 109.1 |
| C(19A)-C(18A)-H(18B) | 109.1 | C(18A)-C(19A)-H(19A) | 108.3 |
| C(18A)-C(19A)-H(19B) | 108.3 | C(18A)-C(19A)-C(20A) | 115.9(11) |
| H(19A)-C(19A)-H(19B) | 107.4 | C(20A)-C(19A)-H(19A) | 108.3 |
| C(20A)-C(19A)-H(19B) | 108.3 | C(19A)-C(20A)-H(20A) | 109.5 |
| C(19A)-C(20A)-H(20B) | 109.5 | C(19A)-C(20A)-H(20C) | 109.5 |
| H(20A)-C(20A)-H(20B) | 109.5 | H(20A)-C(20A)-H(20C) | 109.5 |
| H(20B)-C(20A)-H(20C) | 109.5 | C(17)-C(18B)-H(18C) | 107.2 |
| C(17)-C(18B)-H(18D) | 107.2 | C(17)-C(18B)-C(19B) | 120.6(11) |
| H(18C)-C(18B)-H(18D) | 106.8 | C(19B)-C(18B)-H(18C) | 107.2 |
| C(19B)-C(18B)-H(18D) | 107.2 | C(18B)-C(19B)-H(19C) | 109.0 |
| C(18B)-C(19B)-H(19D) | 109.0 | C(18B)-C(19B)-C(20B) | 112.9(13) |
| H(19C)-C(19B)-H(19D) | 107.8 | C(20B)-C(19B)-H(19C) | 108.9 |
| C(20B)-C(19B)-H(19D) | 109.1 | C(19B)-C(20B)-H(20D) | 115.4 |

Table A.36 (Continued)

| | | | |
|---|---|---|---|
| C(19B)-C(20B)-H(20E) | 115.4 | C(19B)-C(20B)-H(20F) | 115.7 |
| H(20D)-C(20B)-H(20E) | 102.9 | H(20D)-C(20B)-H(20F) | 102.8 |
| H(20E)-C(20B)-H(20F) | 102.8 | O(1)-C(21)-Rh(1) | 173.1(3) |
| Cl(1)-C(22)-H(22A) | 111.4 | Cl(1)-C(22)-H(22B) | 111.4 |
| Cl(2)-C(22)-Cl(1) | 101.8(10) | Cl(2)-C(22)-H(22A) | 111.4 |
| Cl(2)-C(22)-H(22B) | 111.4 | H(22A)-C(22)-H(22B) | 109.3 |

Table A.37    Torsion Angles [°] for **14**

| atom-atom-atom-atom | angle | atom-atom-atom-atom | angle |
|---|---|---|---|
| Rh(1)-C(1)-C(2)-N(1) | -0.3(4) | Rh(1)-C(1)-C(2)-C(3) | 179.9(3) |
| Rh(1)-C(1)-C(6)-N(3) | 1.2(4) | Rh(1)-C(1)-C(6)-C(5) | -179.9(3) |
| N(1)-C(2)-C(3)-C(4) | -178.9(4) | N(1)-C(8)-C(9)-N(2) | -0.6(5) |
| N(2)-C(10)-C(11)-C(12) | 178.8(3) | N(3)-C(15)-C(16)-N(4) | 0.1(5) |
| N(4)-C(17)-C(18A)-C(19A) | 176.9(7) | N(4)-C(17)-C(18B)-C(19B) | -175.2(11) |
| C(1)-C(2)-C(3)-C(4) | 0.9(6) | C(2)-N(1)-C(7)-Rh(1) | -0.4(4) |
| C(2)-N(1)-C(7)-N(2) | -175.9(3) | C(2)-N(1)-C(8)-C(9) | 175.3(4) |
| C(2)-C(1)-C(6)-N(3) | -175.5(3) | C(2)-C(1)-C(6)-C(5) | 3.4(6) |
| C(2)-C(3)-C(4)-C(5) | 2.0(7) | C(3)-C(4)-C(5)-C(6) | -2.1(7) |
| C(4)-C(5)-C(6)-N(3) | 178.1(4) | C(4)-C(5)-C(6)-C(1) | -0.6(6) |
| C(6)-N(3)-C(14)-Rh(1) | 2.0(4) | C(6)-N(3)-C(14)-N(4) | 175.9(3) |
| C(6)-N(3)-C(15)-C(16) | -174.7(4) | C(6)-C(1)-C(2)-N(1) | 176.3(3) |
| C(6)-C(1)-C(2)-C(3) | -3.5(6) | C(7)-N(1)-C(2)-C(1) | 0.4(5) |
| C(7)-N(1)-C(2)-C(3) | -179.8(4) | C(7)-N(1)-C(8)-C(9) | 0.5(5) |
| C(7)-N(2)-C(9)-C(8) | 0.6(5) | C(7)-N(2)-C(10)-C(11) | -88.3(4) |
| C(8)-N(1)-C(2)-C(1) | -174.2(4) | C(8)-N(1)-C(2)-C(3) | 5.6(7) |
| C(8)-N(1)-C(7)-Rh(1) | 175.3(3) | C(8)-N(1)-C(7)-N(2) | -0.2(4) |
| C(9)-N(2)-C(7)-Rh(1) | -173.8(4) | C(9)-N(2)-C(7)-N(1) | -0.3(4) |
| C(9)-N(2)-C(10)-C(11) | 88.6(5) | C(10)-N(2)-C(7)-Rh(1) | 3.5(6) |
| C(10)-N(2)-C(7)-N(1) | 177.1(3) | C(10)-N(2)-C(9)-C(8) | -176.7(4) |
| C(10)-C(11)-C(12)-C(13) | 175.1(4) | C(14)-N(3)-C(6)-C(1) | -2.0(5) |
| C(14)-N(3)-C(6)-C(5) | 179.1(4) | C(14)-N(3)-C(15)-C(16) | -0.4(5) |
| C(14)-N(4)-C(16)-C(15) | 0.2(5) | C(14)-N(4)-C(17)-C(18A) | 101.2(6) |
| C(14)-N(4)-C(17)-C(18B) | 174.1(7) | C(15)-N(3)-C(6)-C(1) | 172.0(4) |
| C(15)-N(3)-C(6)-C(5) | -6.8(7) | C(15)-N(3)-C(14)-Rh(1) | -173.4(3) |
| C(15)-N(3)-C(14)-N(4) | 0.5(4) | C(16)-N(4)-C(14)-Rh(1) | 170.8(3) |
| C(16)-N(4)-C(14)-N(3) | -0.4(4) | C(16)-N(4)-C(17)-C(18A) | -72.3(7) |
| C(16)-N(4)-C(17)-C(18B) | 0.6(10) | C(17)-N(4)-C(14)-Rh(1) | -3.4(7) |
| C(17)-N(4)-C(14)-N(3) | -174.7(4) | C(17)-N(4)-C(16)-C(15) | 174.5(4) |
| C(17)-C(18A)-C(19A)-C(20A) | -70.2(14) | C(17)-C(18B)-C(19B)-C(20B) | -58.6(18) |

### A.4.3 Crystal Summary for 14

Crystal data for $C_{21}H_{26}ClIN_4ORh$; $M_r$ = 623.44; Monoclinic; space group P 1 21/n 1; $a$ = 13.0363(3) Å; $b$ = 10.3210(3) Å; $c$ = 18.0439(5) Å; $\alpha$ = 90°; $\beta$ = 108.0290(10)°; $\gamma$ = 90°; V = 2308.56(11) Å$^3$; Z = 4; T = 100.0 K; $\lambda$(Mo-K$\alpha$) = 0.71073 Å; $\mu$(Mo-K$\alpha$) = 2.213 mm$^{-1}$; $d_{calc}$ = 1.794g.cm$^{-3}$; 21056 reflections collected; 5503 unique ($R_{int}$ = 0.0348); giving $R_1$ = 0.0357, $wR_2$ = 0.0936 for 4663 data with [I>2$\sigma$(I)] and $R_1$ = 0.0456, $wR_2$ = 0.1002 for all 5503 data. Residual electron density (e$^-$.Å$^{-3}$) max/min: 1.384/-1.406.

An arbitrary sphere of data were collected on a red Tablet-like crystal, having approximate dimensions of 0.315 × 0.256 × 0.17 mm, on a Bruker APEX-II CCD diffractometer using a combination of $\omega$- and $\varphi$-scans of 0.5°.[303] Data were corrected for absorption and polarization effects and analyzed for space group determination. The structure was solved by methods and expanded routinely.[304] The model was refined by full-matrix least-squares analysis of F$^2$ against all reflections. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters. Unless otherwise noted, hydrogen atoms were included in calculated positions. Thermal parameters for the hydrogens were tied to the isotropic thermal parameter of the atom to which they are bonded (1.5 × for methyl, 1.2 × for all others).