# *E-Z* isomerization in Suzuki cross-couplings of haloenones: Ligand effects and evidence for a separate catalytic cycle. Supporting Information

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# Contents

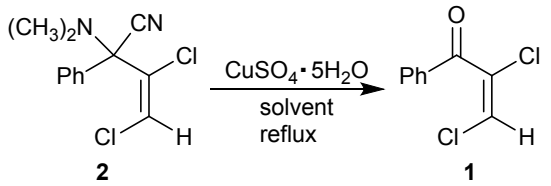
# 1. General Notes

In this Supporting Information, compound numbers correspond to those used in the main article text. Hypothetical structures and computed structures not referenced in the text are labelled with alphabetic designations for convenience within the Supporting Information.

Analytical thin layer chromatography (TLC) was performed on pre-coated (175-225 µm layer thickness) silica gel plates, on aluminium base (TLC Silica gel 60 F254, EMD Millipore Corporation). The eluent system used was hexanes:ethyl acetate = 9:1, unless otherwise mentioned. The plates were visualized under UV light. Preparative flash chromatography was performed using Silicycle Silica-P flash silica gel (230-400 mesh) and the eluant was 97:3 hexanes:ethyl acetate. Melting points were measured using a DigiMelt (Stanford Research systems) apparatus with a ramp rate of 1 °C and starting temperature set at 26 °C, unless otherwise mentioned. Melting points obtained are uncorrected.
$^{1}H$ and $^{13}C$ NMR were recorded at 298 K on either a Bruker Avance 300 spectrometer or a Bruker AvanceIII 500 spectrometer. Chloroform-$d_1$ ($CDCl_3$) containing 99.8 atom % D was used as a NMR solvent unless otherwise noted. The chemical shifts were calibrated with reference to the residual peak of $CDCl_3$ (7.26 ppm for $^{1}H$ and 77.00 ppm for $^{13}C$). NMR spectra were processed using the Spinworks 4 program, written by Dr. Kirk Marat. The abbreviations s, t, m signify singlet, triplet, multiplet and AA'BB', AA'BB'C signify second order splitting patterns where C symbolizes the para proton present in a monosubstituted aromatic ring.
All chemicals were purchased from Sigma-Aldrich and were used as received, unless otherwise mentioned.

# 2. Characterization of (2*E*)-2,3-Dichloro-1-phenylprop-2-en-1-one (1).

As noted in the main text, **1** was prepared by a slight modification of the method reported by Jonczyk and Gierczak.[1] They reported the hydrolysis of the precursor **2** promoted by $CuSO_4 \cdot 5H_2O$ in EtOH but in our hands the reaction under these conditions failed to go to completion. We found that the use of wet THF solvent reliably gave full conversion and consistent isolated yields.




**2** **1**

Solvent: EtOH (Jonczyk and Gierczak)
THF/$H_2O$ (our work)

Jonczyk and Gierczak reported the following characterization data for their product: $^1$H NMR (200 MHz, $CDCl_3$): δ = 6.39 (s, 1 H, =CH), 7.26–7.44 (m, 3 H, ArH), 7.75–7.82 (m, 2 H, ArH). Anal. $C_9H_6Cl_2O$ (201.1): calcd C, 53.75; H, 3.00; Cl, 35.26; found C, 53.60; H, 3.06; Cl, 34.96.

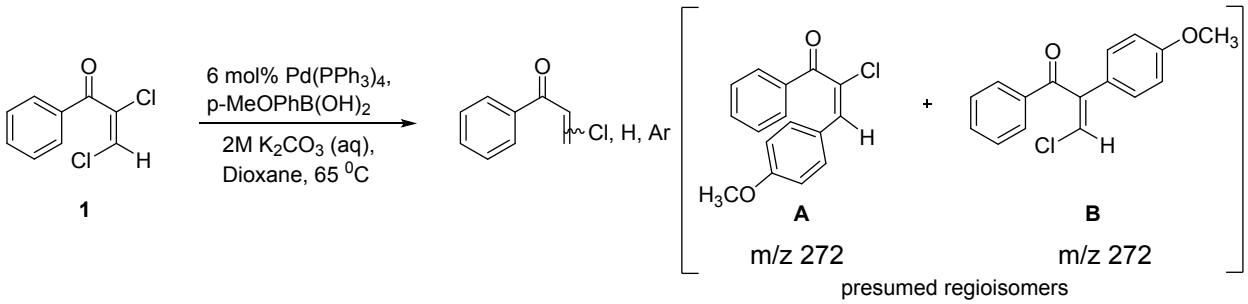
We obtained the following $^1$H NMR data for our sample of **1**: $^1$H NMR (500 MHz, $CDCl_3$) δ 6.69 (s, 1H), 7.51-7.54 (AA'BB', 2H), 7.64-7.67 (AA'BB'**C**, 1H), 7.96-7.97 (AA'BB', 2H) ppm. $^3J_{C,H}$ = 7.0 Hz between the vinylic H and the carbonyl C.

We obtained the *Z*-isomer **6** later in the course of this study. The $^1$H NMR data we obtained for this sample were: $^1$H NMR (500 MHz, $CDCl_3$) δ 7.29 (s, 1H), 7.48-7.51 (AA'BB', 2H), 7.60-7.63 (AA'BB'**C**, 1H), 7.74-7.75 (AA'BB', 2H) ppm. $^3J_{C,H}$ = 2.9 Hz between the vinylic H and the carbonyl C.

Since our spectra were obtained at 500 MHz, we could see the ortho, meta and para protons of the phenyl ring as distinct multiplets (consistent with an AA'BB'C structure although we did not analyse the couplings in detail) whereas Jonczyk and Gierczak's spectrum at 200 MHz apparently merged the signals of the meta and para protons into a single multiplet. Even so, the chemical shifts they quoted are consistently upfield (by some 0.2 – 0.3 ppm) relative to those we observed. We can only surmise that their spectrometer was mis-calibrated because we have verified our spectra and the structures assigned to **1** and **6** using all the NMR techniques at our disposal.

The preparation of a compound of the same general structure as **1** was described in a 1947 US patent,[2] via a Friedel-Crafts reaction of α,β-dichloroacryloyl chloride with benzene. Very little characterization data were reported in this patent and it is unclear whether the product was a single isomer or a mixture.

# 3. Initial Suzuki reaction and identification of products



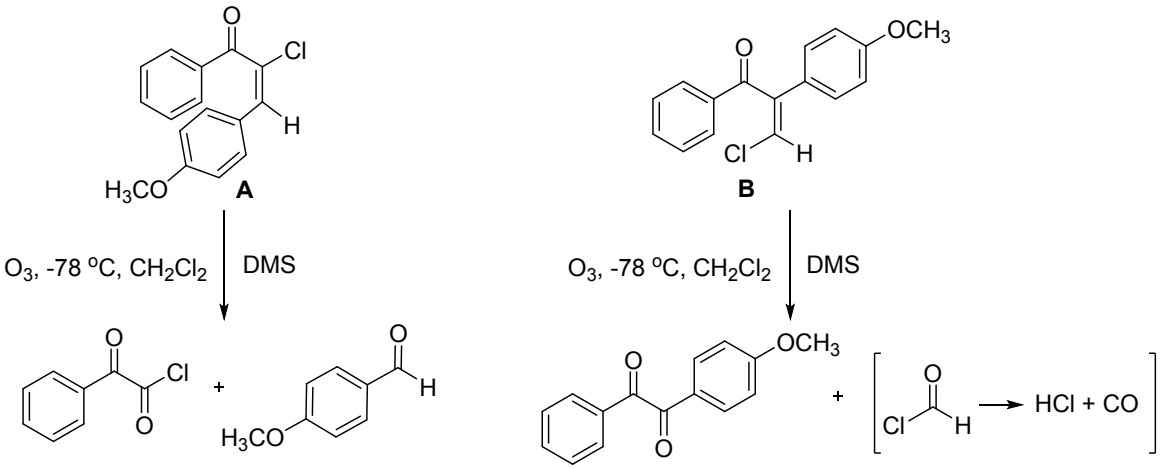

Compound **1** (100.5 mg, 0.5 mmol), $Pd(PPh_3)_4$ (17.33 mg, 0.015 mmol), p-$MeOPhB(OH)_2$ (76.0 mg, 0.5 mmol), and 2M aqueous $K_2CO_3$ (1.0 mL, 2 mmol) were placed in a glass tube with a septum fitted screw cap. Dioxane (5 mL) was added to the glass tube. The stirred solution was heated at 65 °C until tlc analysis indicated full conversion. GC-MS analysis of the reaction mixture revealed two products, both of m/z 272, in the ratio of 26:74. It was presumed that regioisomers (**A** and **B**) might have been formed.

The reaction mixture was cooled to room temperature and ice-cold water was added. The reaction mixture was extracted with ethyl acetate (ca. 6 mL × 3). The combined organic extract was washed with brine (ca. 20 mL) and dried over anhydrous sodium sulphate. After filtration, the filtrate was concentrated and the residue was subjected to silica-gel chromatography, eluting with 97:3 hexanes:ethyl acetate. Two products were isolated.

The $^1H$ and $^{13}C$ NMR spectra of the products were sufficient to identify their general structures but we could not unambiguously assign the location of the *p*-methoxyphenyl substituent based on these spectra alone. We therefore turned to chemical degradation and derivatization.

## 3.1. Ozonolysis

Presuming that the products were regioisomers **A** and **B**, it was evident that ozonolysis would yield characteristic degradation products from each possibility. These could be identified by NMR or GC-MS.

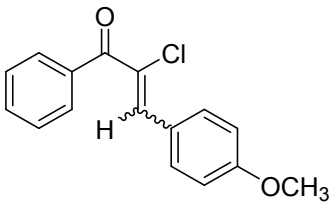


Regioisomer **A** would yield *p*-methoxybenzaldehyde whereas regioisomer **B** would afford 4-methoxybenzil, both of which could be easily identified.

Ozonolysis was performed on both isolated products (presumed regioisomers **A** and **B**) separately.

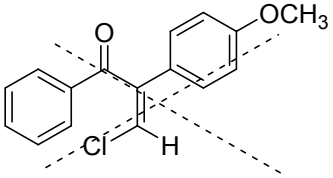
The isolated isomer (50 mg, 0.184 mmol) was dissolved in dichloromethane (0.5 mL). The solution was cooled to -78 °C. Ozone was bubbled through the solution until a persistent blue colour was observed. At this point, the ozone was turned off and the mixture was sparged with air until the blue colour disappeared. The solution was then warmed to the room temperature. Dimethyl sulfide (27 µL, 0.368 mmol) was added to quench the reaction. The crude product mixtures were analyzed by GC-MS. Formation of p-methoxybenzaldehyde was observed from both the isomers.

The formation of p-methoxybenzaldehyde meant that *both* products of the Suzuki coupling had the stereoisomeric chalcone structures **A** or **A'**.




**A (*Z isomer)***

**A' (*E isomer*)**




**B**

## 3.2. Cross coupling with methylboronic acid

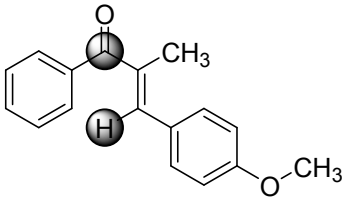
We still had the problem of identifying whether the major product from the Suzuki coupling was **A** or **A'** (eventually identified as **4a** and **3a** respectively). The lack of clearly diagnostic NMR signals made this challenging, but we reasoned that substituting a $CH_3$ group for the remaining Cl would permit nOe experiments to clarify the assignment. A Suzuki cross-coupling with methylboronic acid was performed on an 80:20 mixture of the isomers **A** and **A'**.

The mixture of **A** and **A'** (50.0 mg, 0.183 mmol), methylboronic acid (16.5 mg, 0.275 mmol, 1.5 eq), palladium acetate (1.1 mg, 0.005 mmol, 0.025 eq.), S-phos (3.7 mg, 0.009 mmol, 0.05 eq.), $K_3PO_4$ (77.7 mg, 0.366 mmol, 2 eq.) were added to a tube fitted with a septum screw cap. Anhydrous toluene (2.6 mL) was added to the test tube, and the stirred mixture was boiled under reflux until tlc indicated complete conversion. The reaction mixture was then cooled to room temperature and ice-cold water was added. The mixture was extracted with ethyl acetate (ca. 6 mL × 3). The combined organic extract was washed with brine (ca. 20 mL) and dried over anhydrous sodium sulphate. After filtration, the filtrate was concentrated and the residue was purified by silica-gel chromatography (97:3 hexanes:ethyl acetate). The 89:11 mixture of methylated isomers **C** and **C'** was isolated in 74% combined yield. We could not separate the isomers further so all spectra were obtained using this mixture. Only some of the signals due to the minor isomer could be distinctly observed in the NMR spectra.

Major isomer **C**:

$^{1}$H NMR (500 MHz, $CDCl_3$) δ 2.28 (d, *J* =1.2 Hz, 3H), 3.85 (s, 3H), 6.93-6.96 (AA'BB', 2H), 7.16 (s, 1H), 7.40 - 7.47 (AA'BB', 4H), 7.52-7.55 (AA'BB'**C**, 1H), 7.71-7.72 (AA'BB', 2H) ppm;

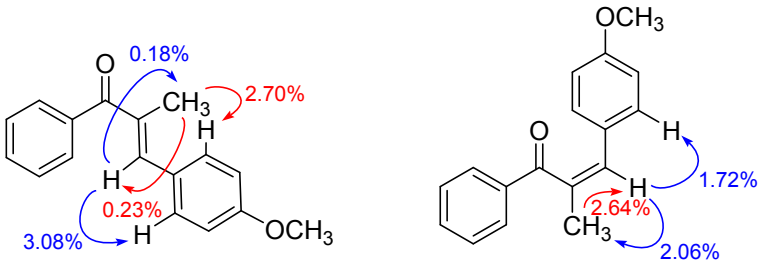
$^{13}$C NMR (75 MHz, $CDCl_3$) δ 14.38, 55.36, 113.99, 128.15, 128.42, 129.41, 131.36, 131.59, 134.90, 138.97, 142.64, 160.00, 199.58 ppm.




$^{3}J_{C,H}$ = 7.0 Hz

*The minor isomer **C'** had* $^{3}J_{C,H}$ *= 10.5 Hz*.

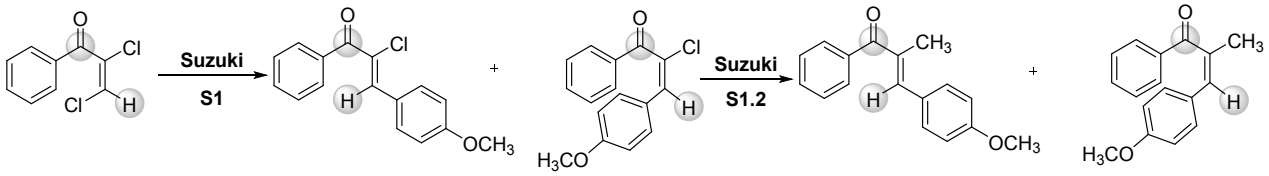
Nuclear Overhauser Effect Measurements
arrows point from irradiated nucleus to observed nucleus




**C** - major isomer **C'** - minor isomer

*There was negligible nOe between the $CH_3$ and the ortho protons in the minor isomer **C'**.*

Based on these observations, we were able to make the following structural assignments. The assignments of **A** and **A'** were later confirmed by X-ray crystallography (see below).




**1**

$^{3}J_{CH}$ = 7.0 Hz
***E* (trans)**

**A**
**major isomer** **76:24**

$^{3}J_{CH}$ = 4.5 Hz
***Z* (C,H cis)**

**A'**
**minor isomer**

$^{3}J_{CH}$ = 11 Hz
***E* (C,H trans)**

**C**
**major isomer** **89:11**

$^{3}J_{CH}$ = 7 Hz
***E* (C,H cis)**

**C'**
**minor isomer**

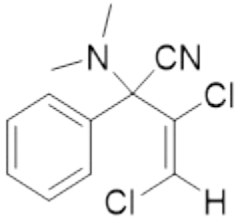
$^{3}J_{CH}$ = 10.5 Hz
***Z* (C,H trans)**

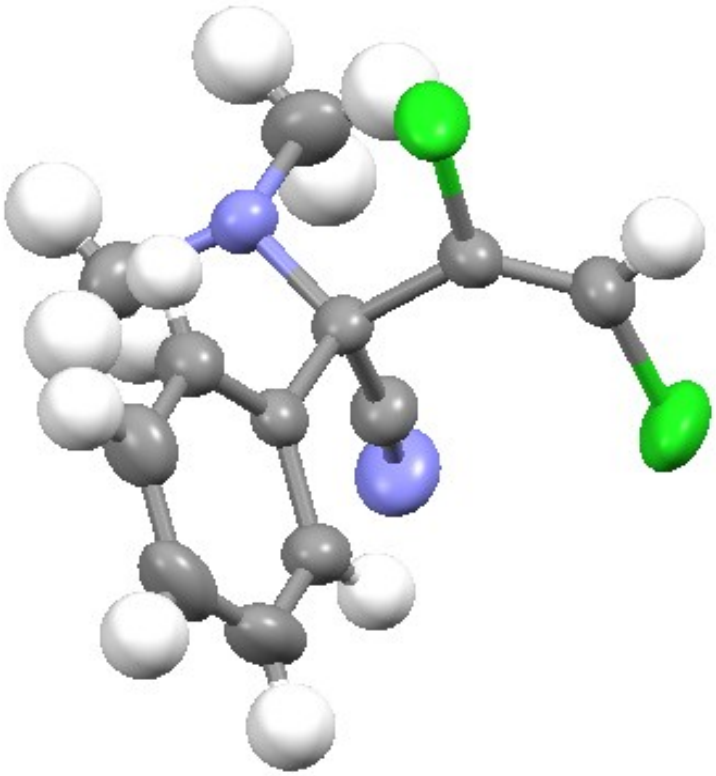
*In the paper, the series of Z products is designated **4a-h** while the series of E products is designated **3a-h**.*

# 4. X-ray crystallography

X-ray diffractograms were acquired on a Bruker D8 three-circle diffractometer with an APEX-II CCD detector, using MoK/α radiation. Data were processed using the APEX2 software suite. The structures were solved using SHELXS-97 and refined using SHELXL-97.

## 4.1. (3*E*)-3,4-dichloro-2-(dimethylamino)-2-phenylbut-3-enenitrile (2)



Selected data:

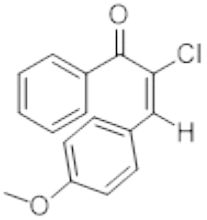
Cl2-C2-C1-Cl1 176.5°

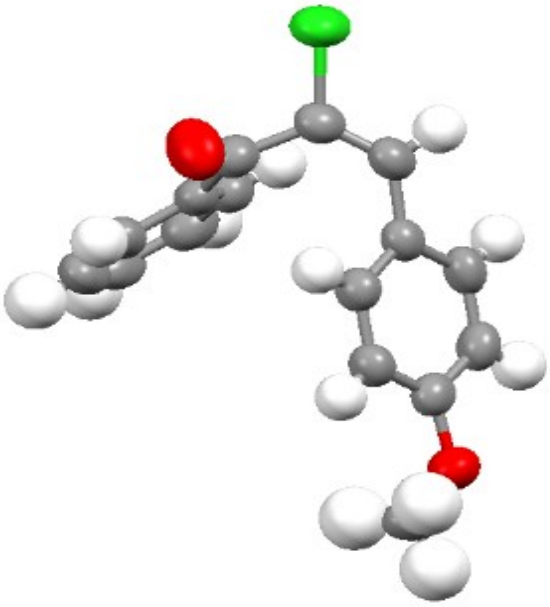
H1-C1-C2-C3 -176.2°

C1-C2 1.315 Å

## 4.2. (2*E*)-2-Chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (3a) and (2*Z*)-2-Chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (4a).

After some effort, we were able to obtain crystals of both **3a** and **4a** suitable for X-ray crystallography. The resulting structures confirmed the conclusions drawn from the NMR data described above, that the major product from the initial Suzuki reaction had the unexpected *Z* configuration.



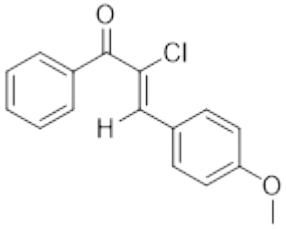



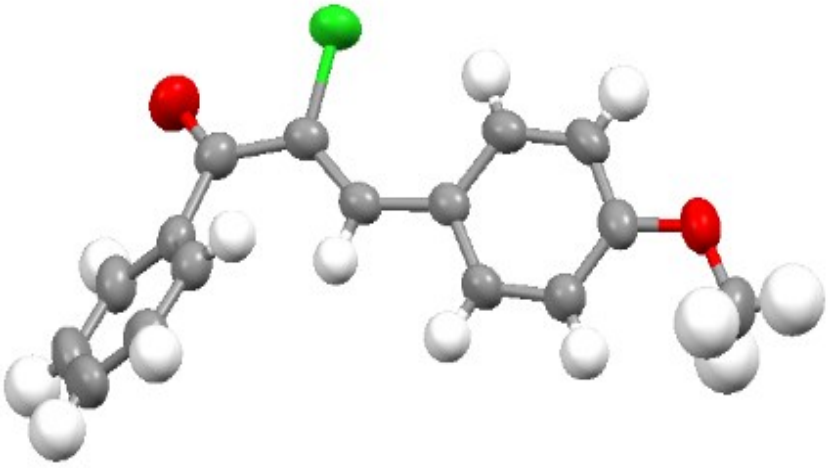
Selected data:

C21-C1-C2-Cl2 172.73°

H1-C1-C2-C3 176.30°

C1-C2 1.330 Å



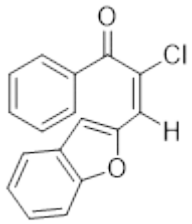
Selected data:

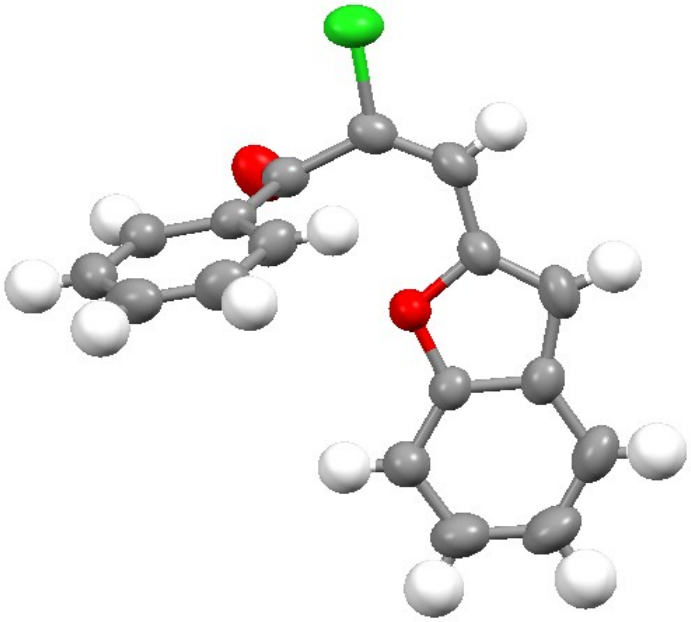
C21-C1-C2-Cl2 3.64°

H1-C1-C2-Cl2 -176.4°

C1-C2 1.341 Å

## 4.3. (2*E*)-3-(Benzofuran-2-yl)-2-chloro-1-phenylprop-2-en-1-one (3f)



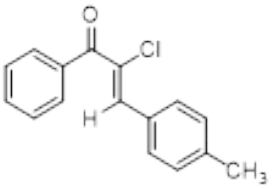
Selected data:

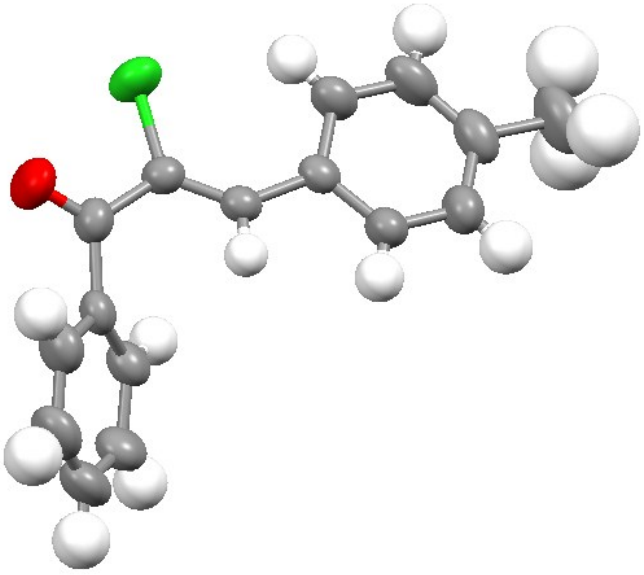
C21-C1-C2-Cl2 178.45°

H1-C1-C2-C3 175.75°

C1-C2 1.320 Å

## 4.4. (2Z)-2-chloro-3-(4-methylphenyl)-1-phenylprop-2-en-1-one (4b)



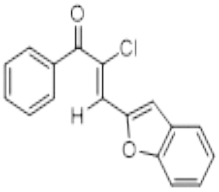
Selected data:

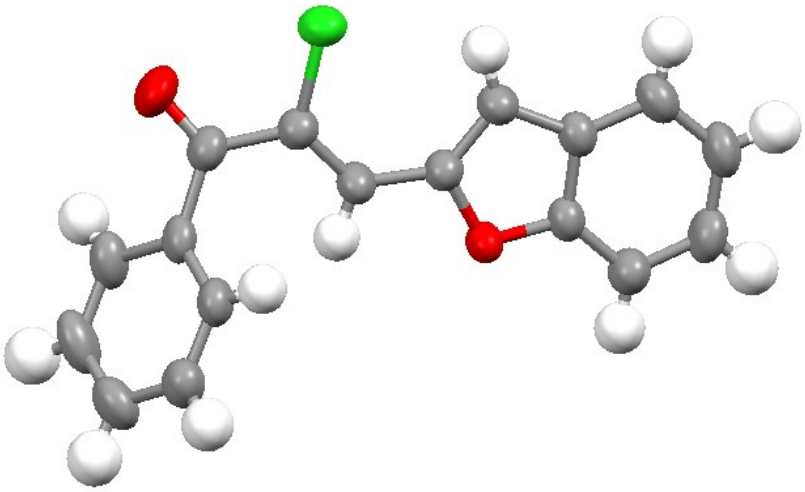
C21-C1-C2-Cl2 -3.88°

H1-C1-C2-C3 0.82°

C1-C2 1.338 Å

### 4.5. (2*Z*)-3-(Benzofuran-2-yl)-2-chloro-1-phenylprop-2-en-1-one (4f)



Selected data:

C21-C1-C2-Cl2 -2.04°

H1-C1-C2-C3 -6.83°

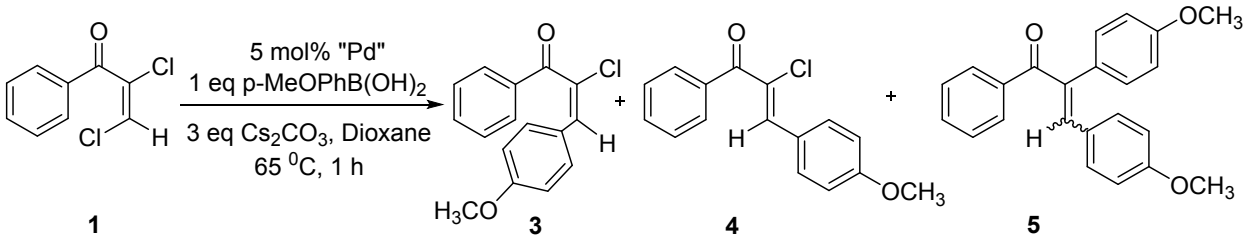
C1-C2 1.339 Å

# 5. Survey of reaction conditions

## 5.1. Effect of various palladium sources

*This experiment was done without a phosphine ligand to determine what effect the Pd source had on the efficiency of the reaction and on the product distribution.*

Compound **1** (50.0 mg, 0.249 mmol, 1 eq.), p-MeOPhB$(OH)_2$ (49.2 mg, 0.324 mmol, 1.3 eq.), palladium catalyst (0.012 mmol, 0.05 eq.) and $Cs_2CO_3$ (243.4 mg, 0.747 mmol, 3 eq.) were placed in a glass tube with a screw cap. Anhydrous dioxane (1.5 mL) was added. The stirred solution was heated at 65 °C for one hour and then cooled. An aliquot was quenched with cold water and extracted with dichloromethane. The dichloromethane extract was analyzed by GC-MS.



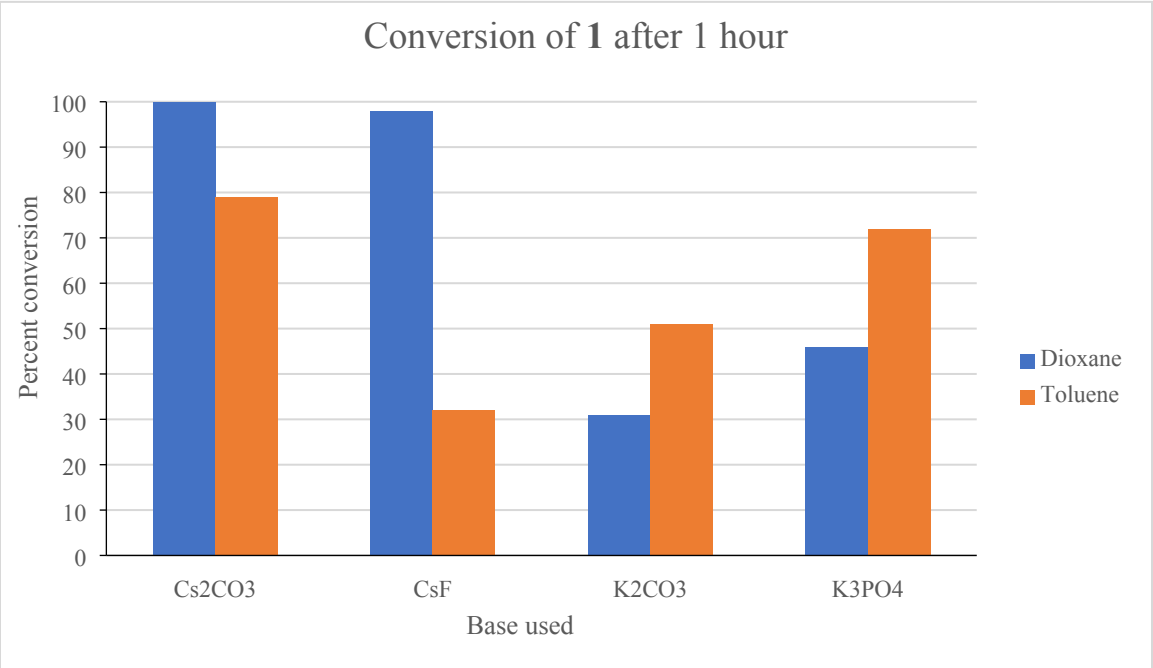

| Entry | "Pd" | Conv. % | **3:4:5** |
|---|---|---|---|
| 1. | $Pd_2(dba)_3$ | 100 | 94:5:1 |
| 2. | $Pd(OAc)_2$ | 100 | 91:9:1 |
| 3. | AllylPd(II)Cl dimer | 88 * | 77:11:0 |
| 4. | $PdCl_2$ | 58 * | 20:38:0 |

** The balance was unreacted **1**.*

## 5.2. Effect of base and solvent

*This experiment was done without a phosphine ligand present. The purpose was simply to observe the conversion of the starting material.*

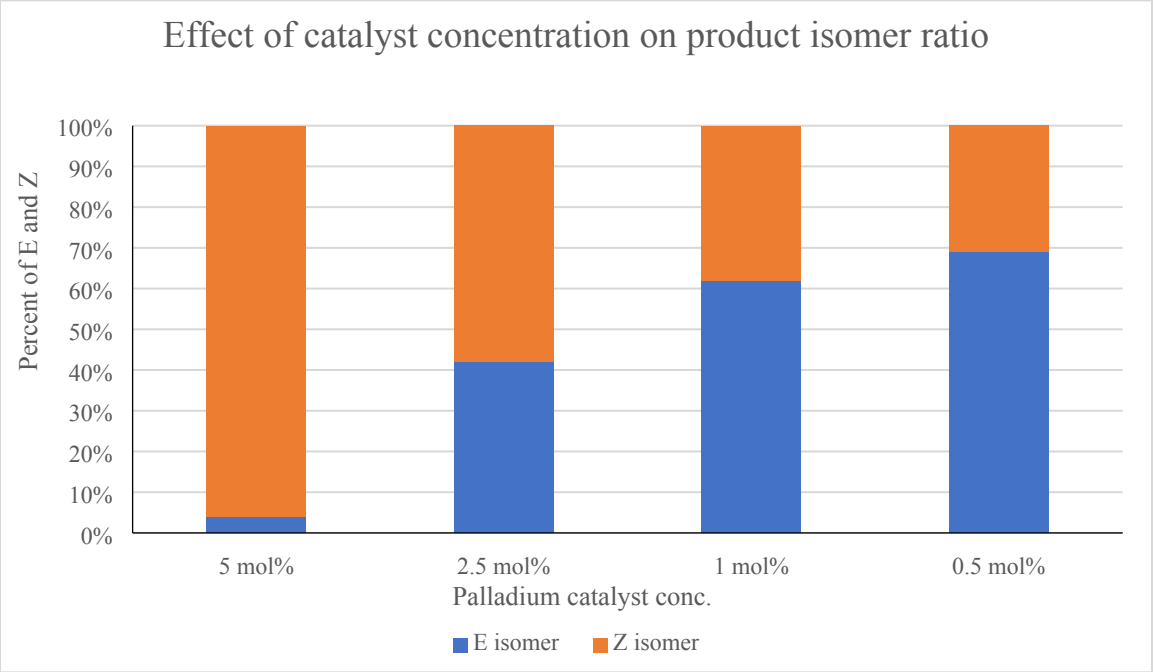
Compound **1** (50 mg, 0.249 mmol, 1 eq.), p-MeOPhB(OH)$_2$ (49.2 mg, 0.324 mmol, 1.3 eq.), $Pd_2(dba)_3$ (11.0 mg, 0.012 mmol, 0.05 eq.) and base (0.747 mmol, 3 eq.) were placed in a glass tube with a screw cap. Anhydrous dioxane or toluene (1.5 mL) was added to the glass tube. The stirred solution was heated at 65 °C for one hour. An aliquot was quenched with cold water and extracted with dichloromethane. The dichloromethane extract was analyzed by GC-MS.



## 5.3. Effect of catalyst loading

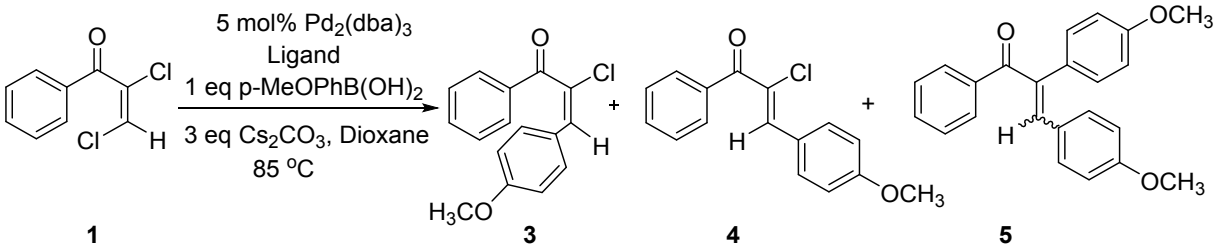
*In this experiment, a phosphine ligand was employed – conditions expected to lead to substantial formation of the "isomerized" product **4a**. We wanted to observe whether the proportion of **3a**:**4a** was dependent on the catalyst concentration.*

Compound **1** (50.0 mg, 0.249 mmol, 1 eq.), p-MeOPhB(OH)$_2$ (37.8 mg, 0.249 mmol, 1 eq.), $Pd_2(dba)_3$ and DPEphos (various amounts, constant 1:2 molar ratio) and $Cs_2CO_3$ (243.4 mg, 0.747 mmol, 3 eq.) were placed in a glass tube with a screw cap. Anhydrous dioxane (1.5 mL) was added to the glass tube. The stirred solution was heated at 85 °C for one hour. An aliquot was quenched with cold water and extracted with dichloromethane. The dichloromethane extract was analyzed by GC-MS.




## 5.4. Survey of phosphine ligands

Compound **1** (50.0 mg, 0.249 mmol, 1 eq.), p-MeOPhB(OH)$_2$ (37.84 mg, 0.249 mmol, 1 eq.), $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol, 0.025 eq.), phosphine ligand (5 mol% for bidentate and 7 mol% for monodentate ligands) and $Cs_2CO_3$ (243.4 mg, 0.747 mmol, 3 eq.) were placed in a glass tube with a screw cap. Anhydrous dioxane (1.5 mL) was added to the glass tube. The stirred solution was heated at 85 °C for one hour. Aliquots were taken after 1 hour and 24 hours. Aliquots were quenched with cold water and extracted with dichloromethane. The dichloromethane extracts were analyzed by GC-MS.



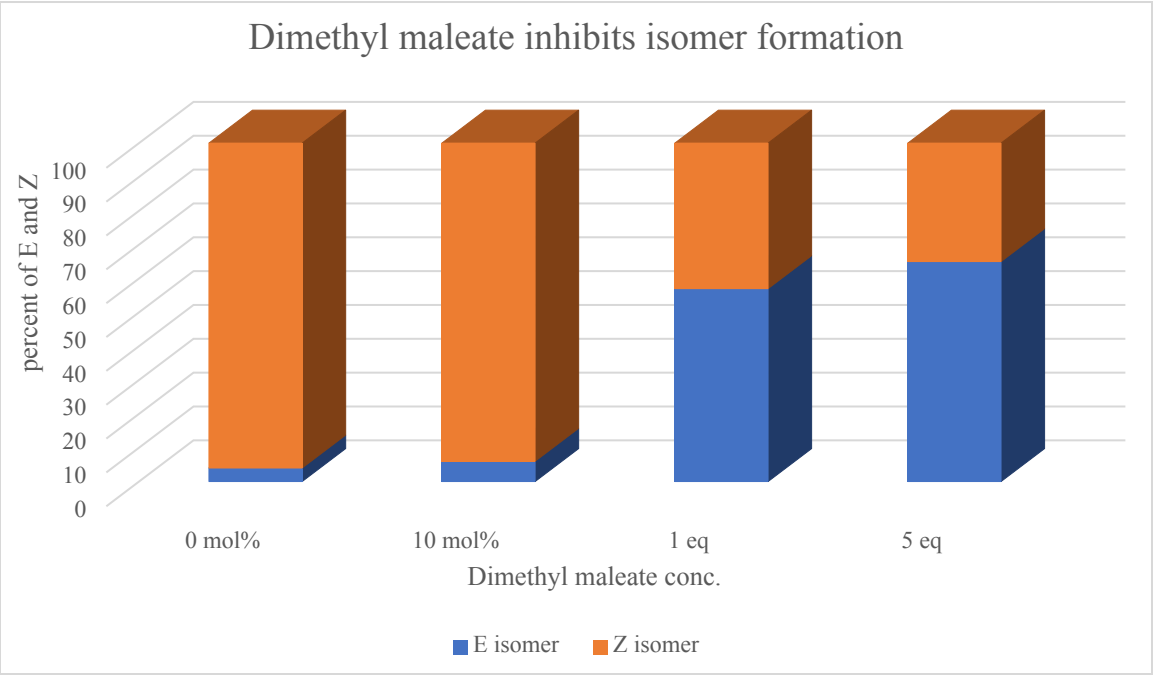

| Entry | Ligand | After 1 hour (**3:4:5**) | After 24 hours (**3:4:5**) |
|---|---|---|---|
| 1. | DPEphos | 4:96 | 4:96 |
| 2. | Xantphos | 6.5:93:0.5 | 4:96 |
| 3. | Davphos | 18:76:6 | 6:88:6 |
| 4. | PhDavePhos | 30:68:2 | 21:76:3 |
| 5. | $P(o\text{-}tol)_3$ | 35:64:1 | 5:93:2 |
| 6. | DIPHOS | 43:57 | 11:88:1 |
| 7. | $(Cy)_3P{\cdot}HBF_4$ | 50:50 | 7:93 |
| 8. | DPPF | 51:49 | 15:85 |
| 9. | $(t\text{-}Bu)_3P{\cdot}HBF_4$ | 70%; 44:23:3 | 100%; 10:80:10 |
| 10. | DPPB | 75:23:2 | 10:89:1 |
| 11. | Q-Phos | 81:19 | 29:67:4 |
| 12. | t-BuDavephos | 74:17:9 | 12:79:9 |
| 13. | t-BuXantphos | 93:5:2 | 5:89:4 |
| 14. | No ligand | 94:5:1 | 55:43:2 |

# 6. Experiments relating to mechanism.

## 6.1. Effect of dimethyl maleate on isomer formation

Compound **1** (50.0 mg, 0.249 mmol, 1 eq.), p-MeOPhB$(OH)_2$ (37.8 mg, 0.249 mmol, 1 eq.), dimethyl maleate (various), $Pd_2(dba)_3$ (5.5 mg, 0.006 mmol, 0.025 eq.), DPEphos (6.7 mg, 0.0125 mmol, 0.05 eq.) and $Cs_2CO_3$ (243.4 mg, 0.747 mmol, 3 eq.) were placed in a glass tube with a screw cap. Anhydrous dioxane (1.5 mL) was added. The stirred solution was heated at 85 °C for one hour. An aliquot was

quenched with cold water and extracted with dichloromethane. The dichloromethane extract was analyzed by GC-MS.




## 6.2. Effect of TEMPO and benzoquinone on isomer formation

The compound **1** (100 mg, 0.5 mmol), p-MeOPhB(OH)$_2$ (75.54 mg, 0.5 mmol), $Pd_2(dba)_3$ (10.99 mg, 0.012 mmol), DPEphos (13.46 mg, 0.025 mmol), TEMPO (1.88 mg, 0.012 mmol) / quinone (1.30 mg, 0.012 mmol) and $Cs_2CO_3$ (485.50 mg, 1.49 mmol) were placed in a glass tube with a screw cap. Anhydrous dioxane (3 ml, 0.166 M with respect to ***E*-1**) was added to the glass tube. The stirred solution was heated at 85 °C until complete consumption of ***E*-1**. The aliquot taken was quenched with cold water and extracted with dichloromethane. The reaction was monitored by GC-MS. The isomerization of 4: 96 (***Z*-2**: ***E*-2**) was observed.

## 6.3. Suzuki cross coupling with organic base

The compound **1 (**50 mg, 0.25 mmol), p-MeOPhB(OH)$_2$ (37.85 mg, 0.25 mmol), $Pd_2(dba)_3$ (5.68 mg, 0.006 mmol), DPEphos (6.73 mg, 0.0125 mmol) and triethyl amine (104 ul, 0.75 mmol) were placed in a glass tube with a screw cap. Anhydrous dioxane (1.5 ml, 0.166 M with respect to **1**) was added to the glass tube. The stirred solution was heated at 85 °C. The aliquot taken was quenched with cold water and extracted with dichloromethane. The sample was analysed by GC-MS. No Suzuki cross coupled product formation was observed.

## 6.4. Effect of triethylamine on isomerization of 3a to 4a

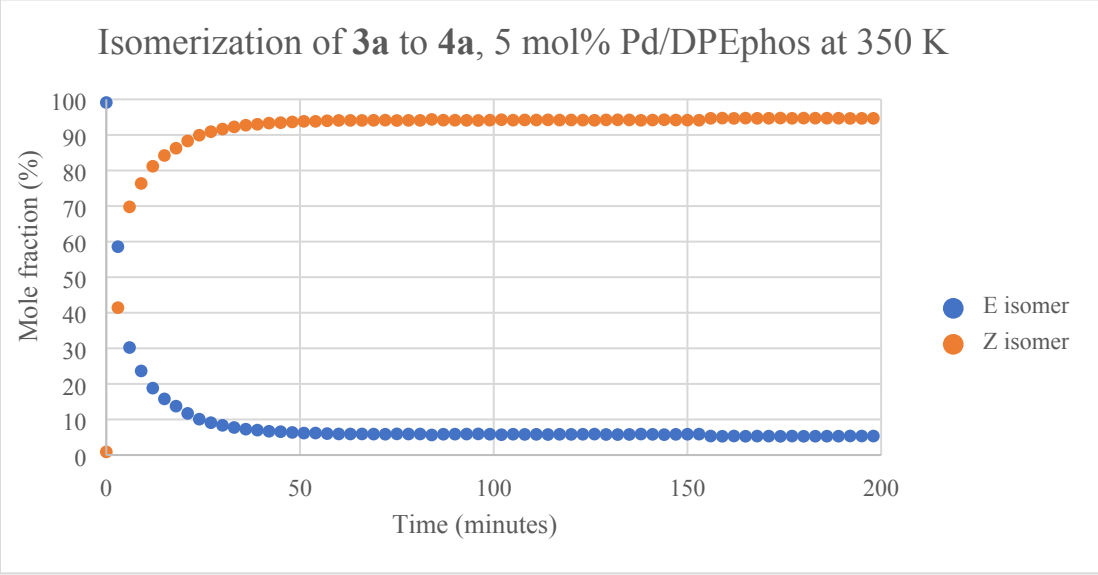
The compound **3a** (50 mg, 0.18 mmol), p-MeOPhB(OH)$_2$ (27.81 mg, 0.18 mmol), $Pd_2(dba)_3$ (4.58 mg, 0.005 mmol), DPEphos (4.85 mg, 0.009 mmol,) and triethyl amine (77 ul, 0.55 mmol) were placed in a

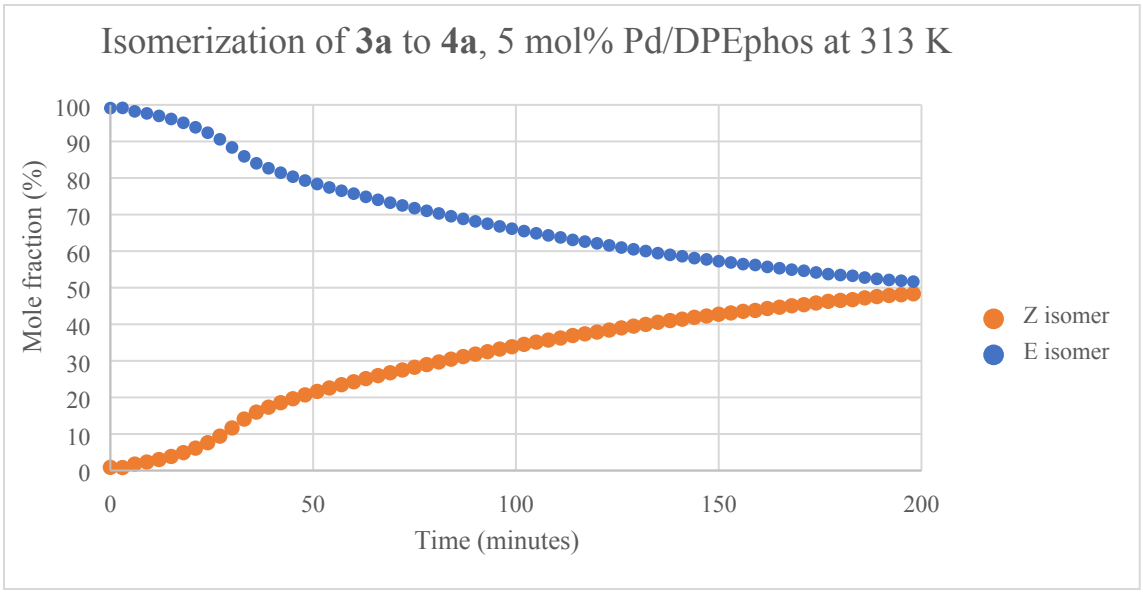
glass tube with a screw cap. Anhydrous dioxane (1.1 ml, 0.166 M with respect to **3a**) was added to the glass tube. The stirred solution was heated at 85 °C for one hour. The aliquot taken was quenched with cold water and extracted with dichloromethane. The sample was analyzed by GC-MS. The formation of **3a**: **4a** = 4: 96 was observed.

## 6.5. VT-NMR monitoring of isomerization of 3a to 4a, 5 mol% Pd/DPEphos

*Isomerization of the kinetic (*E*) product **3a** was monitored by 500 MHz $^1$H NMR in toluene-$d_8$ at 350 K and at 313 K. An automated script acquired spectra every 3 minutes during each experiment. After data processing, the $OCH_3$ signals of **3a** and **4a** were integrated. The ratio of these integrals was taken to be the mole fraction of each isomer at the time the spectrum was acquired.*

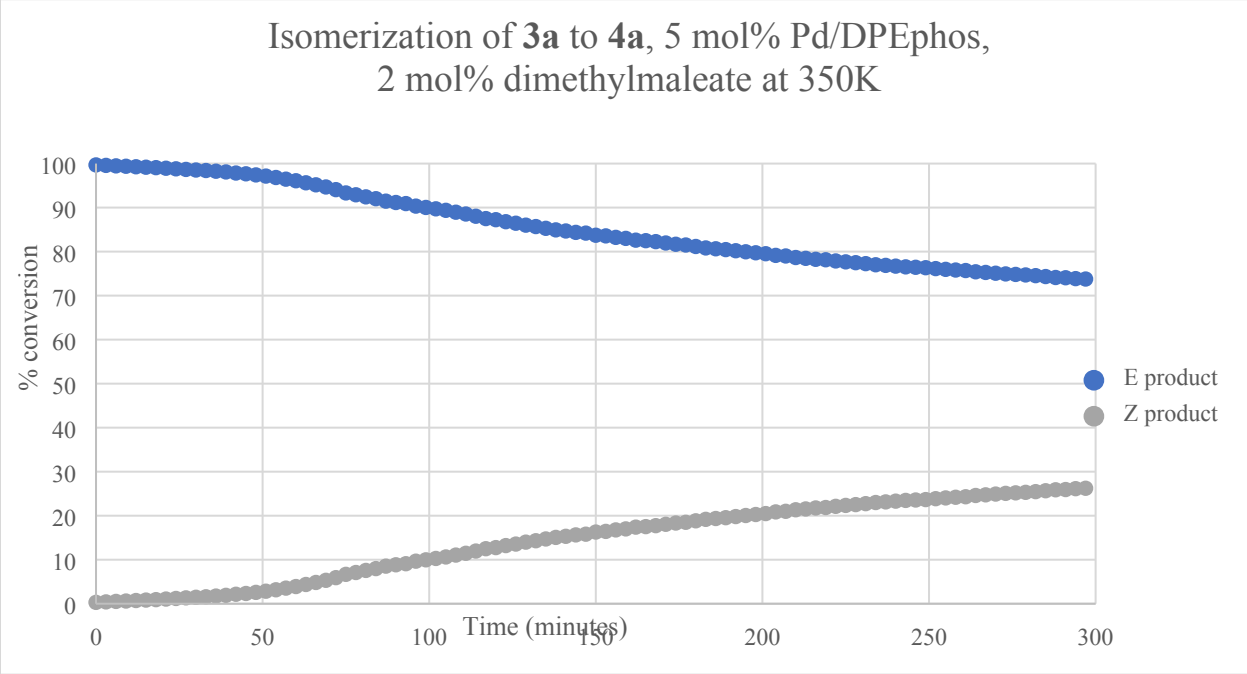
The compound **3a** (27.2 mg, 0.1 mmol, 1 eq.), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 0.025 eq.) and DPEphos (2.7 mg, 0.005 mmol, 0.05 eq.) were dissolved in deuterated toluene (0.6 mL) and were placed in an NMR tube. The probe was equilibrated at the target temperature before inserting the sample tube. $^1$H NMR spectra were acquired at this temperature every 3 minutes.






## 6.6. VT-NMR monitoring of isomerization of 3a to 4a, effect of dimethyl maleate.

Compound **3a** (27.2 mg, 0.1 mmol, 1eq.), dimethyl maleate (0.25 µl, 0.002 mmol, 0.02 eq.), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 0.025 eq.) and DPEphos (2.7 mg, 0.005 mmol, 0.05 eq.) were dissolved in deuterated toluene (0.6 mL) and were placed in a NMR tube. The probe was equilibrated at 350 K before the sample was inserted, and this temperature was maintained throughout the experiment. $^1H$ NMR spectra were acquired every 3 minutes.




*It is evident that the rate of isomerization is greatly slowed in the presence of dimethyl maleate.*

## 6.7. VT-NMR monitoring of *Z*-stilbene with 5 mol% Pd/DPEphos at 350 K

*Z*-Stilbene (17.8 µl, 0.1 mmol, 1 eq.), $Pd_2(dba)_3$ (2.3 mg, 0.0025 mmol, 0.025 eq.) and DPEphos (2.7 mg, 0.005 mmol, 0.05 eq.) were dissolved in deuterated toluene (0.6 mL) and were placed in a NMR tube. $^1H$ NMR spectra of the sample were acquired every 3 minutes for a total of 1.5 hours at 350 K. No isomerization to *E*-stilbene could be observed.

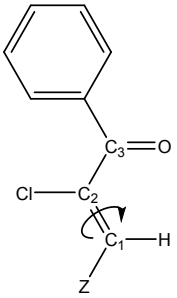
## 6.8. VT-NMR monitoring of isomerization of 3a to 4a, effect of TEMPO at 313 K.

The compound **3a** (27.16 mg, 0.09 mmol), $Pd_2(dba)_3$ (2.29 mg, 0.025 mmol), DPEphos (2.69 mg, 0.005 mmol), Tempo (0.78 mg, 0.005 mmol) in d-toluene (0.6 mL) were placed in a NMR tube. The tube was placed in NMR instrument (at 313 K) and automated script was acquired every 3 minutes. The reaction was allowed to proceed for 3.5 hr. At the end of 3.5 hr, 55% **3a** and 45% **4a** was observed.

# 7. Computational methods

## DFT: Forced rotation around C=C bond

Geometry optimizations for model compounds **D**-**F** were carried out subject to only torsion constraints used to force rotation around the C1=C2 bond: the H-C1-C2-C3 dihedral angle was stepped in increments of 15° from 15° to 165° while at the same time the H-C1-C2-Cl dihedral angle was increased from -165° to -15°. No constraints were put on torsions involving Z. In addition to these constrained optimizations, the beginning and end points of the rotation profile were obtained from unconstrained optimizations. The resulting energy profiles for rotation are shown in Figure S1, below.




**D**: Z = *cis*-Pd(PMe$_3$)$_2$Cl
**E**: Z = *trans*-Pd(PMe$_3$)$_2$Cl
**F**: Z = H

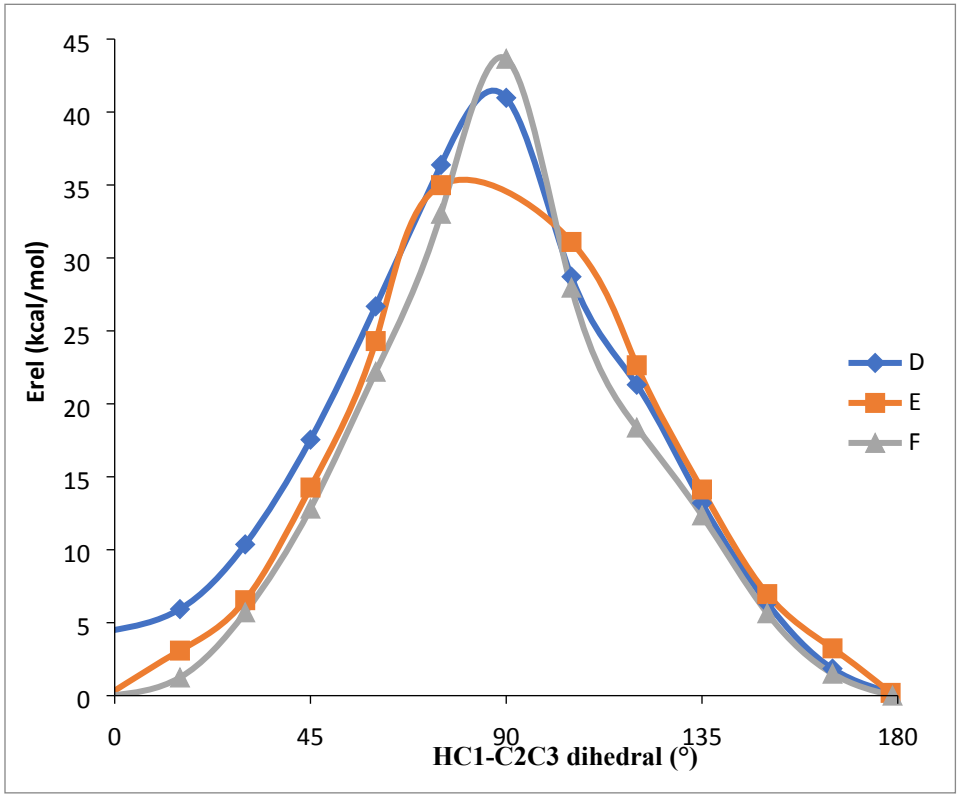



Figure S1. Energy profiles for forced rotation around C=C bond for species **A**-**C**.

Inspection of geometries close to H-C1-C2-C3 = 90° reveals that these constraints do not really enforce rotation around the C=C bond. Instead, all three systems **D**-**F**"escape" by opening up the H-C1-C2 bond angle to nearly ~140° (and simultaneously reducing Z-C1-C2 to ~100°), at which point the dihedral angle constraints can be satisfied by moving H only a small distance out of the C1C2C3Cl plane. The tables below list energies and relevant geometrical parameters for the rotation profiles of **D**-**F**. The Figure shows clearly that the Pd atom does not facilitate rotation: distortion costs the same amount of energy for compound **F** (Z = H) as for the Pd-containing compounds **D** and **E**. The bond lengths in the Tables similarly show no evidence of the shortening of the C1-Pd bond or elongation of the C1-C2 bond that would be expected for a zwitterionic Pd-carbene type structure.

It should be noted that the "top" of the profiles, near 90°, does not correspond to a transition state: as far as we can establish there is no transition state connecting the *cis* and *trans* isomers at the single-determinant DFT level.

**Energy profile and geometric details for forced C=C rotation in compound D**

| | Eelec (h) | Erel (kcal/mol) | HC1C2C3 [a] (°) | Z-C1 (°) | C1-C2 (Å) | H-C1-C2 (Å) | Z-C1-C2 (°) |
|---|---|---|---|---|---|---|---|
| L2PdCl_CCcis (min) | -2392.67804 | 4.45 | -1.05 | 2.022 | 1.335 | 114.5 | 129.3 |
| L2PdCl_CCtrans15 | -2392.67569 | 5.93 | 15 | 2.023 | 1.336 | 114.7 | 127.9 |
| L2PdCl_CCtrans30 | -2392.66861 | 10.37 | 30 | 2.030 | 1.338 | 116.0 | 126.6 |
| L2PdCl_CCtrans45 | -2392.65718 | 17.54 | 45 | 2.038 | 1.341 | 118.6 | 124.0 |
| L2PdCl_CCtrans60 | -2392.64262 | 26.68 | 60 | 2.052 | 1.342 | 123.3 | 120.6 |
| L2PdCl_CCtrans75 | -2392.62716 | 36.38 | 75 | 2.093 | 1.332 | 134.2 | 115.3 |
| L2PdCl_CCtrans90 | -2392.61984 | 40.97 | 90 | 2.213 | 1.298 | 174.6 | 107.5 |
| L2PdCl_CCtrans105 | -2392.63938 | 28.72 | 105 | 2.133 | 1.300 | 149.9 | 107.6 |
| L2PdCl_CCtrans120 | -2392.65118 | 21.31 | 120 | 2.068 | 1.317 | 130.9 | 115.4 |
| L2PdCl_CCtrans135 | -2392.66409 | 13.20 | 135 | 2.047 | 1.322 | 124.4 | 120.3 |
| L2PdCl_CCtrans150 | -2392.67502 | 6.35 | 150 | 2.039 | 1.323 | 121.4 | 122.8 |
| L2PdCl_CCtrans165 | -2392.68218 | 1.85 | 165 | 2.034 | 1.325 | 119.5 | 125.2 |
| L2PdCl_CCtrans (min) | -2392.68514 | 0.00 | 181.39 | 2.034 | 1.326 | 118.8 | 126.0 |

[a] This angle was constrained at the given value, except for the first and last entry.

**Energy profile and geometric details for forced C=C rotation in compound E**

| | Eelec (h) | Erel (kcal/mol) | HC1C2C3 [a] (°) | Z-C1 (°) | C1-C2 (Å) | H-C1-C2 (Å) | Z-C1-C2 (°) |
|---|---|---|---|---|---|---|---|
| LLPdCl_CCcis (min) | -2392.69864 | 0.00 | -1.80 | 1.995 | 1.338 | 113.0 | 130.0 |
| LLPdCl_CCtrans15 | -2392.69372 | 3.09 | 15 | 1.999 | 1.339 | 112.6 | 130.4 |
| LLPdCl_CCtrans30 | -2392.68821 | 6.54 | 30 | 2.000 | 1.339 | 113.8 | 129.3 |
| LLPdCl_CCtrans45 | -2392.67591 | 14.26 | 45 | 2.005 | 1.343 | 116.3 | 126.7 |
| LLPdCl_CCtrans60 | -2392.65991 | 24.30 | 60 | 2.013 | 1.345 | 120.8 | 123.6 |
| LLPdCl_CCtrans75 | -2392.64288 | 34.99 | 75 | 2.051 | 1.333 | 133.0 | 117.9 |
| b | | | 90 | | | | |
| LLPdCl_CCtrans105 | -2392.64908 | 31.10 | 105 | 2.102 | 1.308 | 142.8 | 109.2 |
| LLPdCl_CCtrans120 | -2392.66255 | 22.65 | 120 | 2.053 | 1.322 | 127.9 | 115.9 |
| LLPdCl_CCtrans135 | -2392.67612 | 14.13 | 135 | 2.032 | 1.327 | 122.2 | 120.7 |
| LLPdCl_CCtrans150 | -2392.68755 | 6.96 | 150 | 2.019 | 1.331 | 118.9 | 124.7 |
| LLPdCl_CCtrans165 | -2392.69347 | 3.24 | 165 | 2.012 | 1.337 | 116.3 | 129.1 |
| LLPdCl_CCtrans (min) | -2392.69834 | 0.19 | 178.36 | 2.007 | 1.336 | 116.1 | 129.2 |

[a] This angle was constrained at the given value, except for the first and last entry. [b] Unstable optimization, "flipping" between <90 and >90 torsion values.

**Energy profile and geometric details for forced C=C rotation in compound F**

| | Eelec (h) | Erel (kcal/mol) | HC1C2C3 [a] (°) | Z-C1 (°) | C1-C2 (Å) | H-C1-C2 (Å) | Z-C1-C2 (°) |
|---|---|---|---|---|---|---|---|
| H_CCcis (min) | -882.75249 | 0.00 | -1.06 | 1.082 | 1.329 | 118.7 | 122.3 |
| H_CCtrans15 | -882.75052 | 1.24 | 15 | 1.082 | 1.331 | 118.6 | 122.1 |
| H_CCtrans30 | -882.74340 | 5.71 | 30 | 1.084 | 1.333 | 119.4 | 119.9 |
| H_CCtrans45 | -882.73207 | 12.82 | 45 | 1.088 | 1.338 | 121.2 | 116.8 |
| H_CCtrans60 | -882.71712 | 22.20 | 60 | 1.093 | 1.343 | 124.4 | 112.6 |
| H_CCtrans75 | -882.69987 | 33.03 | 75 | 1.101 | 1.348 | 130.2 | 107.5 |
| H_CCtrans90 | -882.68294 | 43.65 | 90 | 1.116 | 1.341 | 145.9 | 100.0 |
| H_CCtrans105 | -882.70794 | 27.96 | 105 | 1.102 | 1.347 | 131.1 | 106.4 |
| H_CCtrans120 | -882.72322 | 18.37 | 120 | 1.094 | 1.344 | 126.5 | 111.0 |
| H_CCtrans135 | -882.73281 | 12.35 | 135 | 1.090 | 1.332 | 125.3 | 113.3 |
| H_CCtrans150 | -882.74350 | 5.64 | 150 | 1.087 | 1.332 | 123.6 | 116.0 |
| H_CCtrans165 | -882.75010 | 1.50 | 165 | 1.083 | 1.330 | 122.6 | 118.0 |
| H_CCtrans (min) | -882.75250 | 0.00 | 178.79 | 1.084 | 1.329 | 122.4 | 118.8 |

[a] This angle was constrained at the given value, except for the first and last entry.

## DFT: Energies for species on enone-enolate isomerization path

### General

Final free energies were calculated from:

1. Thermal corrections (298 K, 1 bar) from the b-lyp /def-SV(P) level vibrational analysis
2. Single-point energy at TPSSh/def-TZVPP
3. DFT-D dispersion correction

For details, see the main text, "Computational".

All relevant conformations of the five stationary points of the isomerization path (Scheme 4) were optimized without constraints, for all combinations of four substrates (acrolein "Acr", **1** "Nav0", **3a**/**4a** "Nav" and methyl maleate/fumarate "FM") and two ligands (DMPE "PE" and DMPE mono-oxide "PO"). The results are summarized in the following Tables. For each species, "c" and "t" in the name indicate cis/cisoid or trans/transoid orientations around C-C or C-O bonds; "x" and "y" refer to the twist of the (DMPE)Pd or (DMPE-O)Pd chelate ring. "TS" indicates the **9**/**10** and **10**/**11** transition states; "Diyl" indicates the enolate cyclic intermediate. The lowest-energy species for each block is highlighted. "rel" lists free energy (kcal/mol) relative to the most stable species on each path; "bind" is the binding free energy of the relevant enone isomer to the LPd fragment.

**Total and relative energies for degenerate isomerization of acrolein (298 K, 1 bar)**

| Name | HCorr | TSCorr | Eelec | Edisp | G | rel | bind |
|---|---|---|---|---|---|---|---|
| Acr_c | 0.06462 | 0.03175 | -191.99283 | -0.00237 | -191.96232 | 2.07 | |
| Acr_t | 0.06456 | 0.03166 | -191.99629 | -0.00223 | -191.96562 | 0.00 | |
| PE_x | 0.21745 | 0.05653 | -1049.04011 | -0.01892 | -1048.89811 | | |
| PO_x | 0.22254 | 0.05896 | -1124.31645 | -0.02163 | -1124.17450 | | |
| PE_x_AcrDiyl_f | 0.28324 | 0.06809 | -1241.07255 | -0.02692 | -1240.88432 | 16.98 | -29.90 |
| PE_y_AcrDiyl_f | 0.28322 | 0.06824 | -1241.07194 | -0.02689 | -1240.88384 | 17.28 | |
| PE_x_AcrTS_f | 0.28206 | 0.06889 | -1241.05673 | -0.02683 | -1240.87038 | 25.73 | |
| PE_y_AcrTS_f | 0.28207 | 0.06875 | -1241.05712 | -0.02687 | -1240.87067 | 25.55 | |
| PE_x_Acr_fc | 0.28410 | 0.06996 | -1241.09596 | -0.02701 | -1240.90883 | 1.60 | |
| PE_x_Acr_ft | 0.28392 | 0.06992 | -1241.09774 | -0.02716 | -1240.91089 | 0.31 | |
| PE_y_Acr_fc | 0.28410 | 0.06977 | -1241.09611 | -0.02708 | -1240.90886 | 1.58 | |
| PE_y_Acr_ft | 0.28390 | 0.07003 | -1241.09786 | -0.02740 | -1240.91139 | 0.00 | |
| PO_x_AcrDiyl_b | 0.28853 | 0.07027 | -1316.34557 | -0.03054 | -1316.15785 | 14.84 | -25.96 |
| PO_y_AcrDiyl_f | 0.28851 | 0.07031 | -1316.34552 | -0.03053 | -1316.15785 | 14.84 | |
| PO_x_AcrTS_f | 0.28755 | 0.07121 | -1316.33441 | -0.03033 | -1316.14840 | 20.77 | |
| PO_y_AcrTS_f | 0.28754 | 0.07064 | -1316.33605 | -0.03046 | -1316.14961 | 20.01 | |
| PO_x_Acr_fc | 0.28926 | 0.07267 | -1316.36389 | -0.02954 | -1316.17684 | 2.92 | |
| PO_x_Acr_ft | 0.28906 | 0.07283 | -1316.36552 | -0.02932 | -1316.17861 | 1.81 | |
| PO_y_Acr_fc | 0.28923 | 0.07246 | -1316.36696 | -0.03131 | -1316.18150 | 0.00 | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| PO_y_Acr_ft | 0.28911 | 0.07138 | -1316.36735 | -0.03127 | -1316.18087 | 0.39 | |

**Total and relative energies for isomerization of 1 (298 K, 1 bar)**

| Name | HCorr | TSCorr | Eelec | Edisp | G | rel | bind |
|---|---|---|---|---|---|---|---|
| Nav0_cc | 0.13272 | 0.05159 | -1342.39419 | -0.01385 | -1342.32691 | 1.84 | |
| Nav0_ct | 0.13269 | 0.05198 | -1342.39431 | -0.01409 | -1342.32769 | 1.35 | |
| Nav0_tc | 0.13286 | 0.05072 | -1342.39866 | -0.01332 | -1342.32985 | 0.00 | |
| Nav0_tt | 0.13290 | 0.05052 | -1342.39905 | -0.01305 | -1342.32971 | 0.08 | |
| PE_x | 0.21745 | 0.05653 | -1049.04011 | -0.01892 | -1048.89811 | | |
| PO_x | 0.22254 | 0.05896 | -1124.31645 | -0.02163 | -1124.17450 | | |
| PE_x_Nav0_fcc | 0.35200 | 0.08845 | -2391.48819 | -0.04592 | -2391.27054 | 0.81 | |
| PE_x_Nav0_fct | 0.35180 | 0.08828 | -2391.48935 | -0.04600 | -2391.27183 | 0.00 | -28.89 |
| PE_y_Nav0_fcc | 0.35203 | 0.08882 | -2391.48818 | -0.04588 | -2391.27084 | 0.62 | |
| PE_y_Nav0_fct | 0.35183 | 0.08818 | -2391.48924 | -0.04598 | -2391.27157 | 0.16 | |
| PE_x_Nav0TS_fc | 0.35083 | 0.08649 | -2391.47040 | -0.04333 | -2391.24938 | 14.08 | |
| PE_y_Nav0TS_fc | 0.35081 | 0.08635 | -2391.47015 | -0.04331 | -2391.24900 | 14.33 | |
| PE_x_Nav0Diyl_f | 0.35237 | 0.08727 | -2391.49278 | -0.04291 | -2391.27059 | 0.78 | |
| PE_y_Nav0Diyl_f | 0.35247 | 0.08591 | -2391.49407 | -0.04351 | -2391.27102 | 0.51 | |
| PE_x_Nav0TS_ft | 0.35066 | 0.08633 | -2391.46544 | -0.04296 | -2391.24408 | 17.42 | |
| PE_y_Nav0TS_ft | 0.35067 | 0.08581 | -2391.46694 | -0.04314 | -2391.24521 | 16.70 | |
| PE_x_Nav0_ftc | 0.35216 | 0.08826 | -2391.49473 | -0.04539 | -2391.27621 | -2.75 | |
| PE_x_Nav0_ftt | 0.35205 | 0.08856 | -2391.49287 | -0.04513 | -2391.27451 | -1.68 | |
| PE_y_Nav0_ftc | 0.35222 | 0.08830 | -2391.49497 | -0.04534 | -2391.27639 | -2.86 | -30.40 |
| PE_y_Nav0_ftt | 0.35204 | 0.08941 | -2391.49263 | -0.04512 | -2391.27512 | -2.07 | |
| PO_x_Nav0_fcc | 0.35715 | 0.09149 | -2466.76087 | -0.04815 | -2466.54336 | 3.09 | |
| PO_x_Nav0_fct | 0.35686 | 0.09110 | -2466.76141 | -0.04837 | -2466.54401 | 2.68 | |
| PO_y_Nav0_fcc | 0.35714 | 0.09055 | -2466.76392 | -0.05095 | -2466.54829 | 0.00 | -28.92 |
| PO_y_Nav0_fct | 0.35686 | 0.09109 | -2466.75928 | -0.04873 | -2466.54225 | 3.79 | |
| PO_x_Nav0TS_fc | 0.35613 | 0.08849 | -2466.74632 | -0.04602 | -2466.52470 | 14.80 | |
| PO_y_Nav0TS_fc | 0.35608 | 0.08778 | -2466.74909 | -0.04773 | -2466.52852 | 12.41 | |
| PO_x_Nav0Diyl_f | 0.35766 | 0.08885 | -2466.78064 | -0.04581 | -2466.55765 | -5.87 | |
| PO_y_Nav0Diyl_f | 0.35777 | 0.08857 | -2466.76867 | -0.04615 | -2466.54562 | 1.67 | |
| PO_x_Nav0TS_ft | 0.35592 | 0.08905 | -2466.74417 | -0.04669 | -2466.52399 | 15.24 | |
| PO_y_Nav0TS_ft | 0.35599 | 0.08798 | -2466.74551 | -0.04568 | -2466.52318 | 15.75 | |
| PO_x_Nav0_ftc | 0.35731 | 0.09046 | -2466.76824 | -0.04909 | -2466.55048 | -1.38 | |
| PO_x_Nav0_ftt | 0.35715 | 0.09113 | -2466.76575 | -0.04783 | -2466.54756 | 0.45 | |
| PO_y_Nav0_ftc | 0.35727 | 0.09106 | -2466.76950 | -0.04890 | -2466.55220 | -2.45 | -30.02 |
| PO_y_Nav0_ftt | 0.35721 | 0.09188 | -2466.76374 | -0.04726 | -2466.54567 | 1.64 | |

**Total and relative energies for isomerization of 3a/4a (298 K, 1 bar)**

| Name | HCorr | TSCorr | Eelec | Edisp | G | rel | bind |
|---|---|---|---|---|---|---|---|
| Nav_cc | 0.22440 | 0.05938 | -1113.92441 | -0.02070 | -1113.78009 | 2.56 | |
| Nav_cc2 | 0.22441 | 0.05936 | -1113.92440 | -0.02071 | -1113.78006 | 2.58 | |
| Nav_tc | 0.22455 | 0.05937 | -1113.92884 | -0.02030 | -1113.78395 | 0.14 | |
| Nav_tt | 0.22460 | 0.05915 | -1113.92941 | -0.02021 | -1113.78417 | 0.00 | |
| PE_x | 0.21745 | 0.05653 | -1049.04011 | -0.01892 | -1048.89811 | | |
| PO_x | 0.22254 | 0.05896 | -1124.31645 | -0.02163 | -1124.17450 | | |
| PE_x_Nav_fcc | 0.44356 | 0.09700 | -2163.01316 | -0.05517 | -2162.72177 | 0.62 | |
| PE_x_Nav_fct | 0.44291 | 0.09674 | -2163.01207 | -0.05685 | -2162.72275 | 0.00 | -27.96 |
| PE_y_Nav_fcc | 0.44361 | 0.09709 | -2163.01293 | -0.05502 | -2162.72142 | 0.83 | |
| PE_y_Nav_fct | 0.44287 | 0.09681 | -2163.01174 | -0.05667 | -2162.72235 | 0.25 | |
| PE_x_NavTS_fc | 0.44205 | 0.09486 | -2162.98861 | -0.05330 | -2162.69472 | 17.59 | |
| PE_y_NavTS_fc | 0.44211 | 0.09508 | -2162.98832 | -0.05301 | -2162.69430 | 17.85 | |
| PE_x_NavDiyl_b | 0.44328 | 0.09435 | -2163.00934 | -0.05424 | -2162.71465 | 5.08 | |
| PE_y_NavDiyl_f | 0.44339 | 0.09454 | -2163.01092 | -0.05433 | -2162.71640 | 3.99 | |
| PE_x_NavTS_ft | 0.44185 | 0.09533 | -2162.98598 | -0.05325 | -2162.69271 | 18.85 | |
| PE_y_NavTS_ft | 0.44188 | 0.09429 | -2162.98709 | -0.05356 | -2162.69306 | 18.63 | |
| PE_x_Nav_ftt | 0.44341 | 0.09687 | -2163.01842 | -0.05427 | -2162.72615 | -2.13 | |
| PE_x_Nav_tc | 0.44355 | 0.09646 | -2163.02054 | -0.05493 | -2162.72838 | -3.54 | |
| PE_y_Nav_ftc | 0.44360 | 0.09660 | -2163.02103 | -0.05500 | -2162.72902 | -3.94 | -29.33 |
| PE_y_Nav_ftt | 0.44342 | 0.09714 | -2163.01826 | -0.05439 | -2162.72638 | -2.28 | |
| PO_x_Nav_fcc | 0.44853 | 0.09998 | -2238.28573 | -0.05757 | -2237.99475 | 1.27 | |
| PO_x_Nav_fct | 0.44783 | 0.10020 | -2238.28110 | -0.05874 | -2237.99221 | 2.86 | |
| PO_y_Nav_fcc | 0.44872 | 0.09919 | -2238.28673 | -0.05957 | -2237.99677 | 0.00 | -26.47 |
| PO_y_Nav_fct | 0.44799 | 0.09929 | -2238.27866 | -0.05925 | -2237.98921 | 4.74 | |
| PO_x_NavTS_fc | 0.44749 | 0.09774 | -2238.26509 | -0.05599 | -2237.97134 | 15.96 | |
| PO_y_NavTS_fc | 0.44744 | 0.09643 | -2238.26667 | -0.05698 | -2237.97264 | 15.14 | |
| PO_x_NavDiyl_f | 0.44876 | 0.09640 | -2238.28207 | -0.05711 | -2237.98683 | 6.24 | |
| PO_y_NavDiyl_f | 0.44874 | 0.09653 | -2238.28231 | -0.05619 | -2237.98628 | 6.58 | |
| PO_x_NavTS_ft | 0.44739 | 0.09753 | -2238.26607 | -0.05734 | -2237.97354 | 14.58 | |
| PO_y_NavTS_ft | 0.44727 | 0.09714 | -2238.26801 | -0.05657 | -2237.97445 | 14.01 | |
| PO_x_Nav_ftc | 0.44863 | 0.10016 | -2238.29200 | -0.05785 | -2238.00138 | -2.89 | |
| PO_x_Nav_ftt | 0.44857 | 0.09999 | -2238.28897 | -0.05699 | -2237.99738 | -0.38 | |
| PO_y_Nav_ftc | 0.44868 | 0.09965 | -2238.29435 | -0.05848 | -2238.00379 | -4.41 | -28.31 |
| PO_y_Nav_ftt | 0.44858 | 0.10004 | -2238.28758 | -0.05670 | -2237.99574 | 0.64 | |

**Total and relative energies for isomerization of maleate/fumarate (298 K, 1 bar)**

| Name | HCorr | TSCorr | Eelec | Edisp | G | rel | bind |
|---|---|---|---|---|---|---|---|
| FM_cct | 0.14549 | 0.05048 | -534.56757 | -0.01061 | -534.48317 | 4.71 | |
| FM_cct2 | 0.14548 | 0.05051 | -534.56754 | -0.01061 | -534.48318 | 4.71 | |
| FM_tct | 0.14554 | 0.05152 | -534.56562 | -0.01111 | -534.48271 | 5.01 | |
| FM_ctc | 0.14577 | 0.04953 | -534.57718 | -0.00975 | -534.49069 | 0.00 | |
| FM_ctt | 0.14581 | 0.05038 | -534.57593 | -0.00984 | -534.49035 | 0.21 | |
| FM_ttt | 0.14589 | 0.05057 | -534.57505 | -0.00993 | -534.48967 | 0.64 | |
| PE_x | 0.21745 | 0.05653 | -1049.04011 | -0.01892 | -1048.89811 | | |
| PO_x | 0.22254 | 0.05896 | -1124.31645 | -0.02163 | -1124.17450 | | |
| PE_x_FM_fccc | 0.36474 | 0.08890 | -1583.66762 | -0.03936 | -1583.43114 | 0.53 | |
| PE_x_FM_ftcc | 0.36482 | 0.08725 | -1583.66980 | -0.03971 | -1583.43194 | 0.02 | |
| PE_x_FM_ftct | 0.36485 | 0.08729 | -1583.66831 | -0.04017 | -1583.43091 | 0.67 | |
| PE_y_FM_fccc | 0.36479 | 0.08856 | -1583.66766 | -0.03912 | -1583.43056 | 0.89 | |
| PE_y_FM_ftcc | 0.36483 | 0.08829 | -1583.66923 | -0.03929 | -1583.43198 | 0.00 | -31.81 |
| PE_y_FM_ftct | 0.36483 | 0.08782 | -1583.66791 | -0.03983 | -1583.43073 | 0.78 | |
| PE_x_FM_TS_fcc | 0.36267 | 0.08622 | -1583.62574 | -0.04037 | -1583.38966 | 26.56 | |
| PE_x_FM_TS_ftc | 0.36298 | 0.08428 | -1583.62987 | -0.04088 | -1583.39205 | 25.06 | |
| PE_y_FM_TS_fcc | 0.36271 | 0.08592 | -1583.62570 | -0.04046 | -1583.38937 | 26.74 | |
| PE_y_FM_TS_ftc | 0.36285 | 0.08545 | -1583.62838 | -0.04031 | -1583.39130 | 25.53 | |
| PE_x_FMDiyl_fc | 0.36357 | 0.08705 | -1583.62965 | -0.04060 | -1583.39374 | 24.00 | |
| PE_x_FMDiyl_ft | 0.36386 | 0.08623 | -1583.63455 | -0.04039 | -1583.39731 | 21.75 | |
| PE_y_FMDiyl_fc | 0.36362 | 0.08649 | -1583.62990 | -0.04067 | -1583.39343 | 24.19 | |
| PE_y_FMDiyl_ft | 0.36422 | 0.08421 | -1583.64033 | -0.04103 | -1583.40135 | 19.22 | |
| PE_x_FM_TS_bct | 0.36275 | 0.08663 | -1583.63226 | -0.03966 | -1583.39580 | 22.70 | |
| PE_x_FM_TS_btt | 0.36295 | 0.08601 | -1583.63168 | -0.03954 | -1583.39428 | 23.65 | |
| PE_y_FM_TS_bct | 0.36266 | 0.08606 | -1583.63279 | -0.03891 | -1583.39510 | 23.14 | |
| PE_y_FM_TS_btt | 0.36285 | 0.08613 | -1583.63116 | -0.03940 | -1583.39384 | 23.93 | |
| PE_x_FM_fctc | 0.36498 | 0.08892 | -1583.68170 | -0.03845 | -1583.44409 | -7.60 | -34.70 |
| PE_x_FM_fctt | 0.36510 | 0.08772 | -1583.68092 | -0.03895 | -1583.44249 | -6.60 | |
| PE_x_FM_fttt | 0.36515 | 0.08827 | -1583.68040 | -0.03896 | -1583.44247 | -6.59 | |
| PE_y_FM_fctc | 0.36500 | 0.08845 | -1583.68179 | -0.03849 | -1583.44373 | -7.37 | |
| PE_y_FM_fttc | 0.36509 | 0.08750 | -1583.68111 | -0.03882 | -1583.44234 | -6.50 | |
| PE_y_FM_fttt | 0.36513 | 0.08874 | -1583.68068 | -0.03895 | -1583.44323 | -7.06 | |
| PO_x_FM_fccc | 0.36986 | 0.09084 | -1658.93465 | -0.04176 | -1658.69738 | 4.12 | |
| PO_x_FM_ftcc | 0.36989 | 0.08930 | -1658.93939 | -0.04230 | -1658.70110 | 1.78 | |
| PO_x_FM_ftct | 0.36992 | 0.08981 | -1658.93727 | -0.04280 | -1658.69995 | 2.50 | |
| PO_y_FM_fccc | 0.36988 | 0.09044 | -1658.93805 | -0.04341 | -1658.70202 | 1.21 | |
| PO_y_FM_ftcc | 0.36980 | 0.08886 | -1658.94058 | -0.04430 | -1658.70394 | 0.00 | -29.03 |
| PO_y_FM_ftct | 0.36977 | 0.08990 | -1658.93730 | -0.04448 | -1658.70190 | 1.28 | |
| PO_x_FM_TS_fcc | 0.36810 | 0.08765 | -1658.90379 | -0.04385 | -1658.66720 | 23.06 | |
| PO_x_FM_TS_ftc | 0.36840 | 0.08652 | -1658.90715 | -0.04388 | -1658.66915 | 21.84 | |

| Name | HCorr | TSCorr | Eelec | Edisp | G | rel | bind |
|---|---|---|---|---|---|---|---|
| PO_y_FM_TS_fcc | 0.36814 | 0.08648 | -1658.90491 | -0.04548 | -1658.66873 | 22.09 | |
| PO_y_FM_TS_ftc | 0.36827 | 0.08663 | -1658.90714 | -0.04522 | -1658.67073 | 20.84 | |
| PO_x_FMDiyl_fc | 0.36907 | 0.08842 | -1658.90530 | -0.04563 | -1658.67028 | 21.12 | |
| PO_x_FMDiyl_ft | 0.36920 | 0.08754 | -1658.90858 | -0.04538 | -1658.67231 | 19.85 | |
| PO_y_FMDiyl_fc | 0.36897 | 0.08891 | -1658.90523 | -0.04416 | -1658.66934 | 21.72 | |
| PO_y_FMDiyl_ft | 0.36926 | 0.08736 | -1658.91015 | -0.04414 | -1658.67239 | 19.80 | |
| PO_x_FM_TS_bct | 0.36822 | 0.08935 | -1658.90671 | -0.04232 | -1658.67016 | 21.20 | |
| PO_x_FM_TS_btt | 0.36843 | 0.08807 | -1658.90712 | -0.04213 | -1658.66889 | 22.00 | |
| PO_y_FM_TS_bct | 0.36826 | 0.08854 | -1658.90575 | -0.04224 | -1658.66827 | 22.39 | |
| PO_x_FM_fctc | 0.37007 | 0.09002 | -1658.94969 | -0.04253 | -1658.71218 | -5.17 | -29.48 |
| PO_x_FM_fctt | 0.37010 | 0.09092 | -1658.94729 | -0.04198 | -1658.71009 | -3.86 | |
| PO_x_FM_fttt | 0.37026 | 0.09040 | -1658.94795 | -0.04217 | -1658.71026 | -3.96 | |
| PO_y_FM_fctc | 0.37015 | 0.09006 | -1658.94916 | -0.04254 | -1658.71161 | -4.81 | |
| PO_y_FM_fctt | 0.37021 | 0.09010 | -1658.94806 | -0.04270 | -1658.71065 | -4.21 | |
| PO_y_FM_fttt | 0.37020 | 0.09030 | -1658.94713 | -0.04244 | -1658.70966 | -3.59 | |

# 8. NMR Spectra

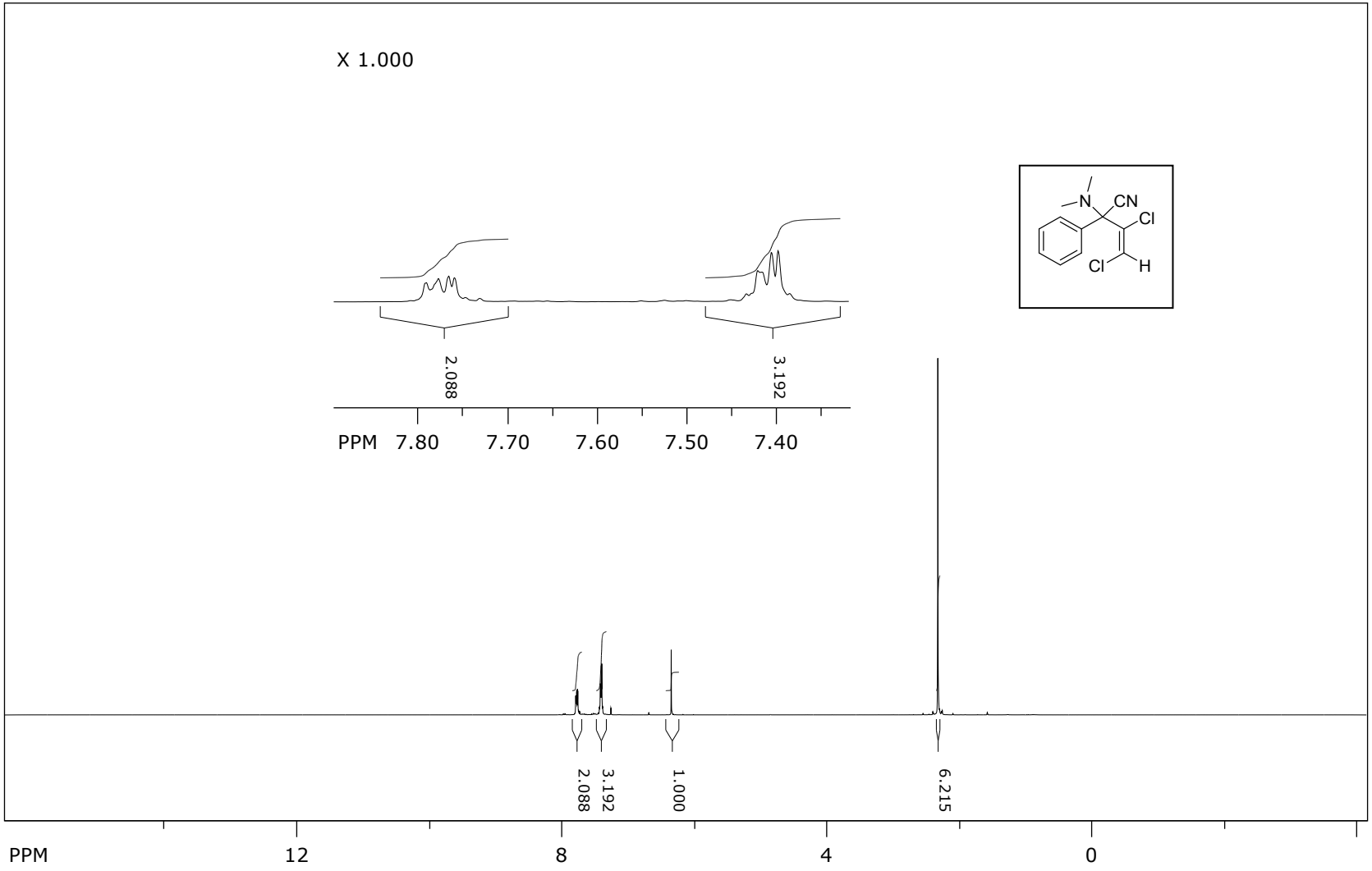
## 8.1. Measurement of three-bond heteronuclear coupling constants ($^3J_{C,H}$)

The 3-bond heteronuclear NMR coupling constant between a vinylic proton and an allylic carbon is known to be sensitive to the *E*/*Z* stereochemical relationship between the nuclei. The value of $^3J_{C,H}$ for the *E* (trans) relationship is greater than $^3J_{C,H}$ for the *Z* (cis) relationship.[3]

These couplings may easily be observed using an HMBC experiment, provided that sufficient digital resolution in the acquisition (time) domain is obtained. Our HMBC spectra were acquired using the Bruker magnitude-mode gradient-enhanced low-pass filtered "hmbcgplpndqf" pulse program on either a 300 MHz or 500 MHz spectrometer. The time domain size and spectral width were typically chosen to give an F2 digital resolution of < 0.5 Hz/pt and the data were generally zero-filled once in F2 before the Fourier transform.

The $^3J_{C,H}$ constants were measured from F2 slices (i.e. $^1$H sub-spectra) at the carbonyl $^{13}$C (F1) frequencies.

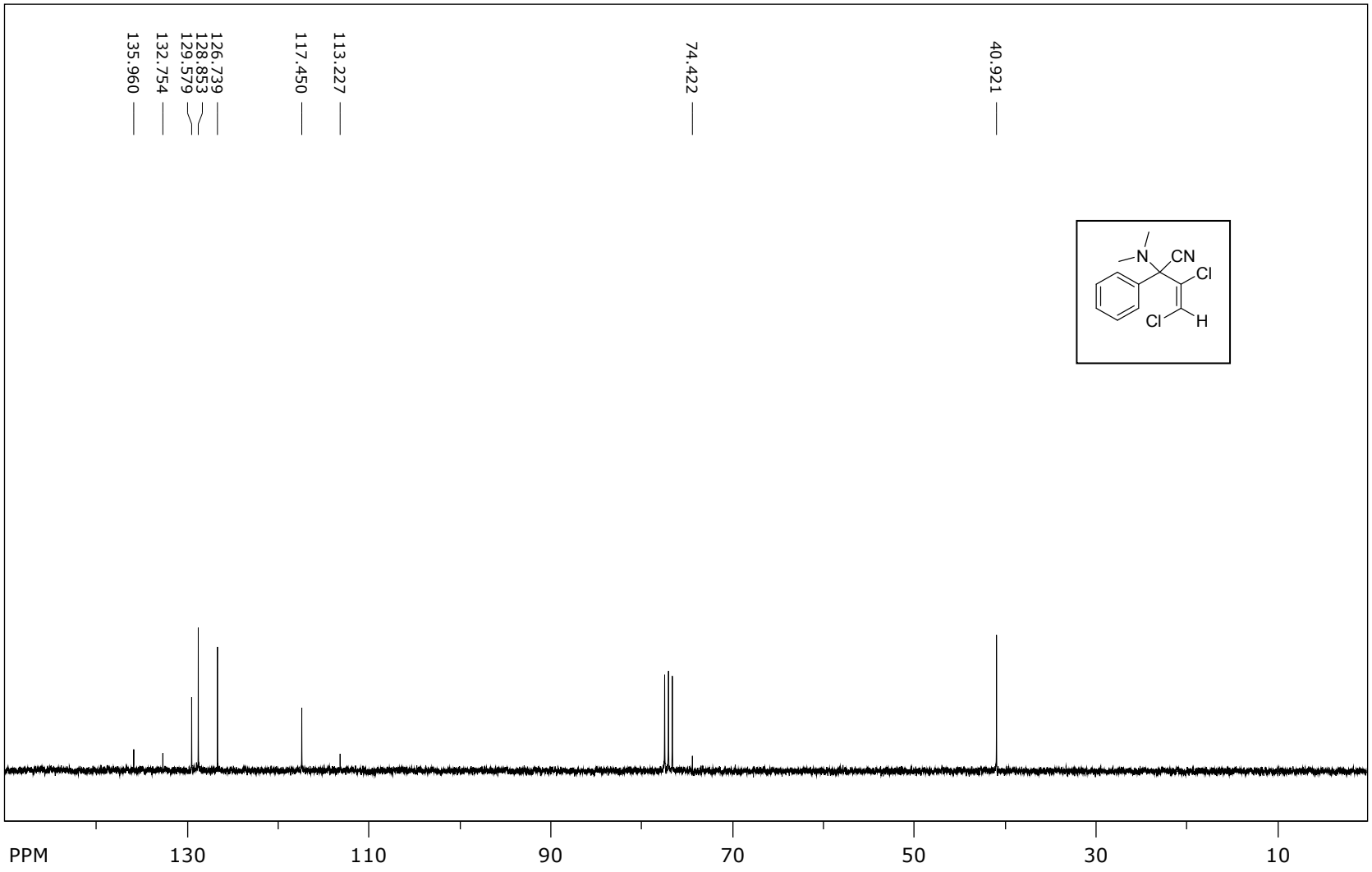
## (*E*)-3,4-Dichloro-2-(dimethylamino)-2-phenylbut-3-enenitrile (2) – $^{1}$H NMR




file: ...\NMR 300\NKC_7_startingmat_2\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130012 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

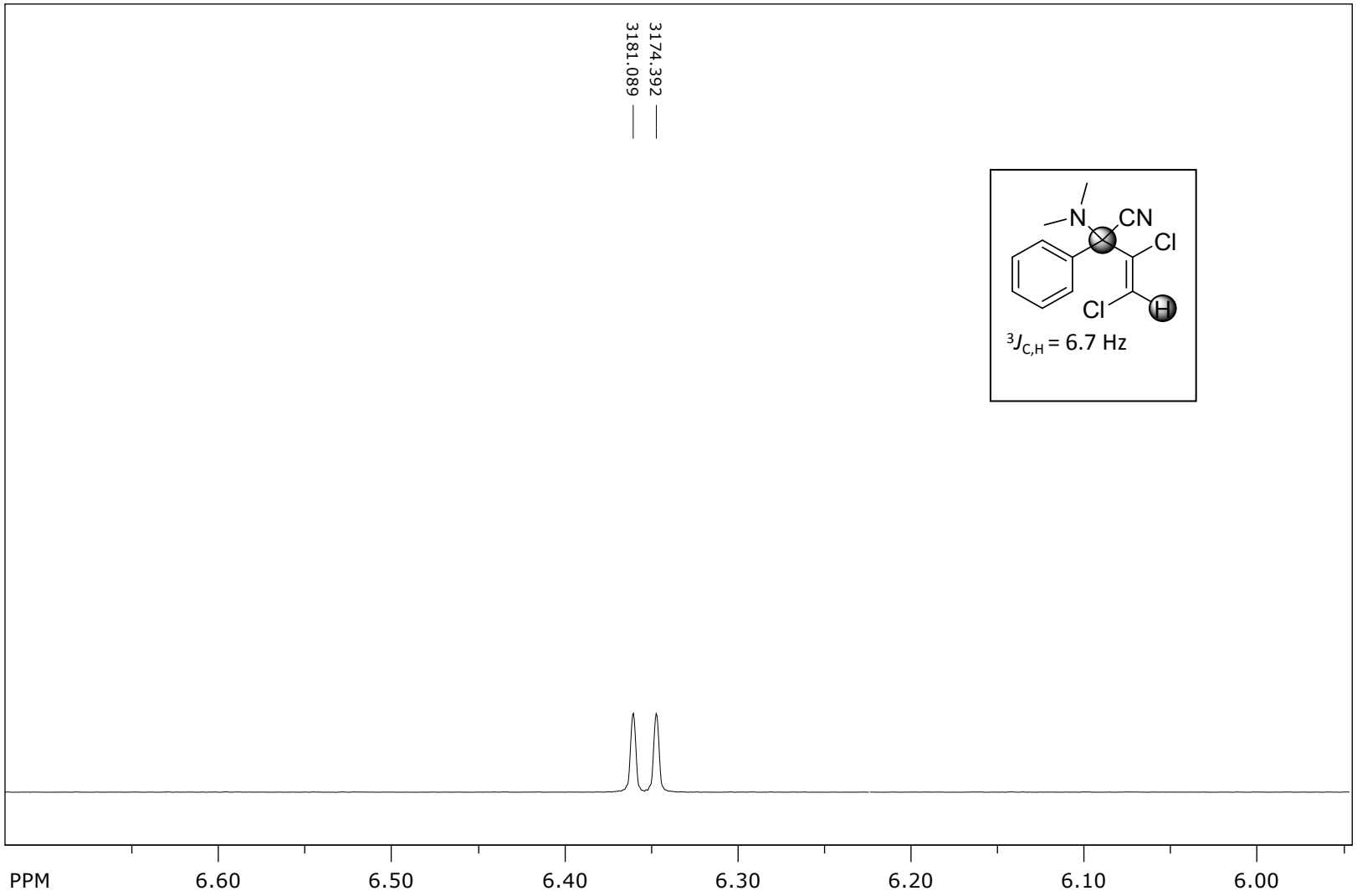
## (*E*)-3,4-Dichloro-2-(dimethylamino)-2-phenylbut-3-enenitrile (2) – $^{13}$C NMR




file: ...\NMR 300\NKC_7_startingmat_2\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 32

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

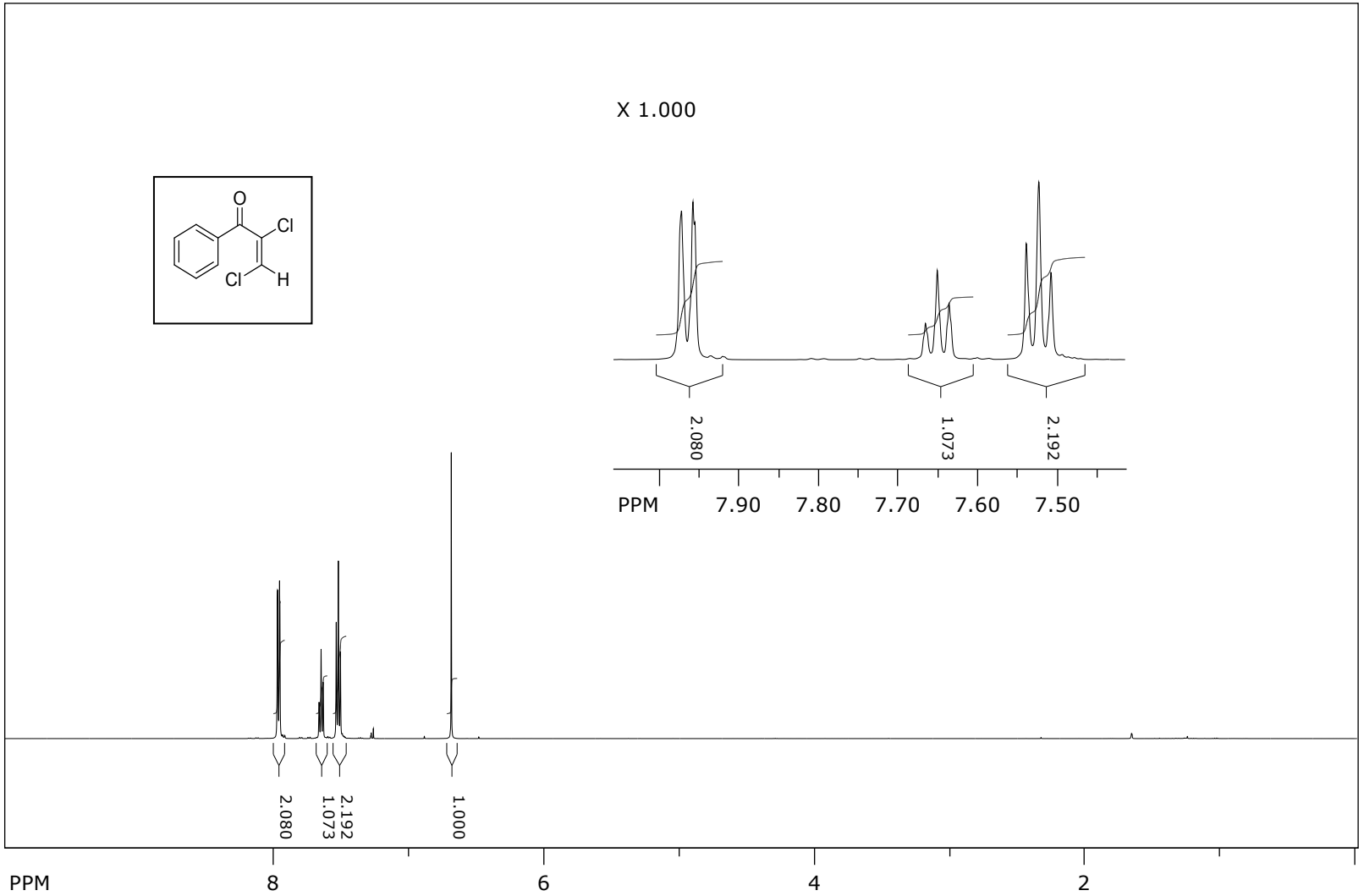
## (*E*)-3,4-Dichloro-2-(dimethylamino)-2-phenylbut-3-enenitrile (2) – $^{3}J_{C,H}$




file: D:\nmr 500\NKC_7_78\2\ser expt: <hmbcgplpndqf>
transmitter freq.: 500.132201 MHz
time domain size: 8192 points
width: 4000.00 Hz = 7.9979 ppm = 0.488281 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 16384 complex points
LB: 0.000 GF: 0.0000

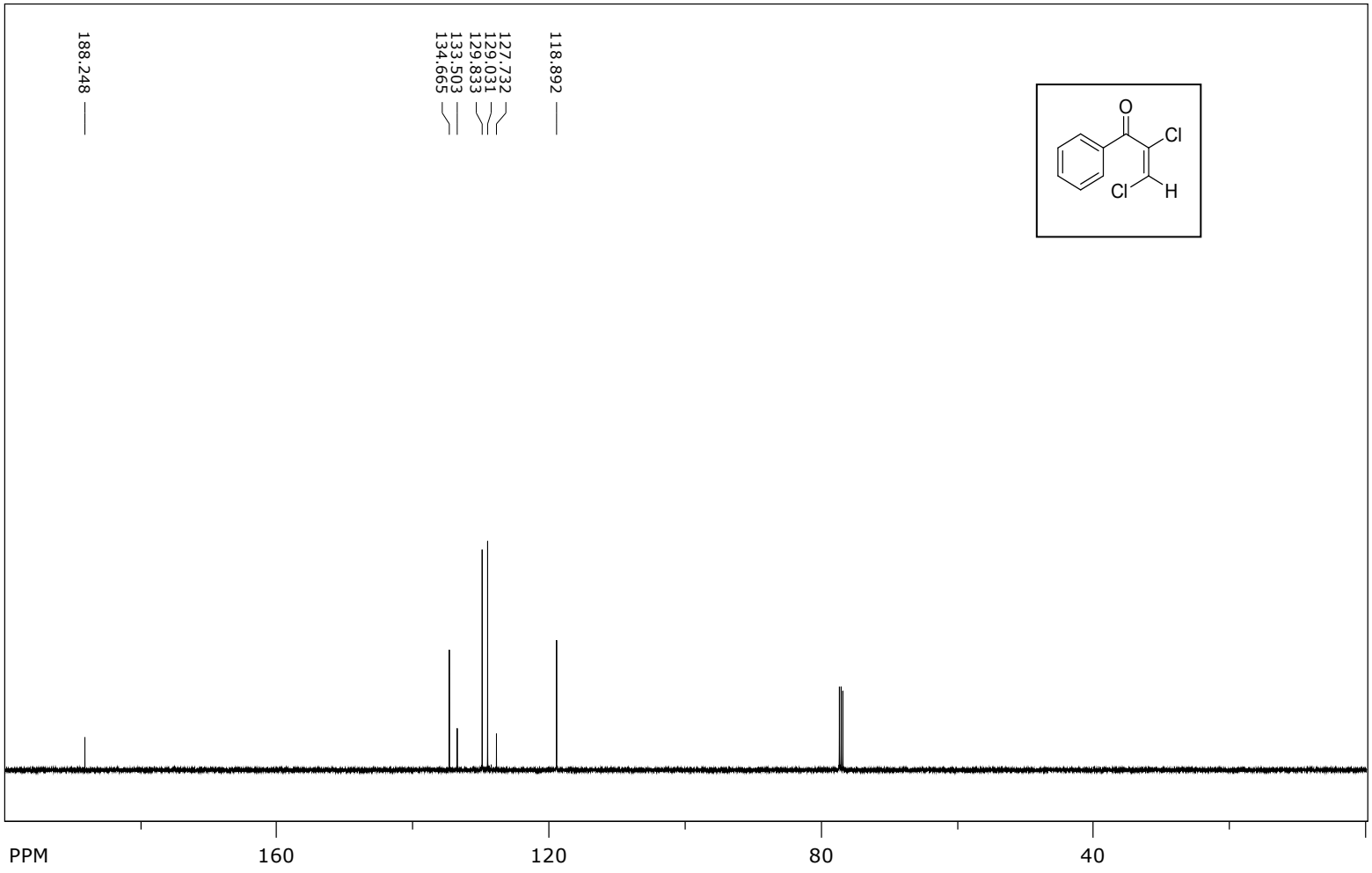
## (2*E*)-2,3-Dichloro-1-phenylprop-2-en-1-one (1) – $^{1}$H NMR




file: D:\nmr 500\NKC_8_65_trans\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

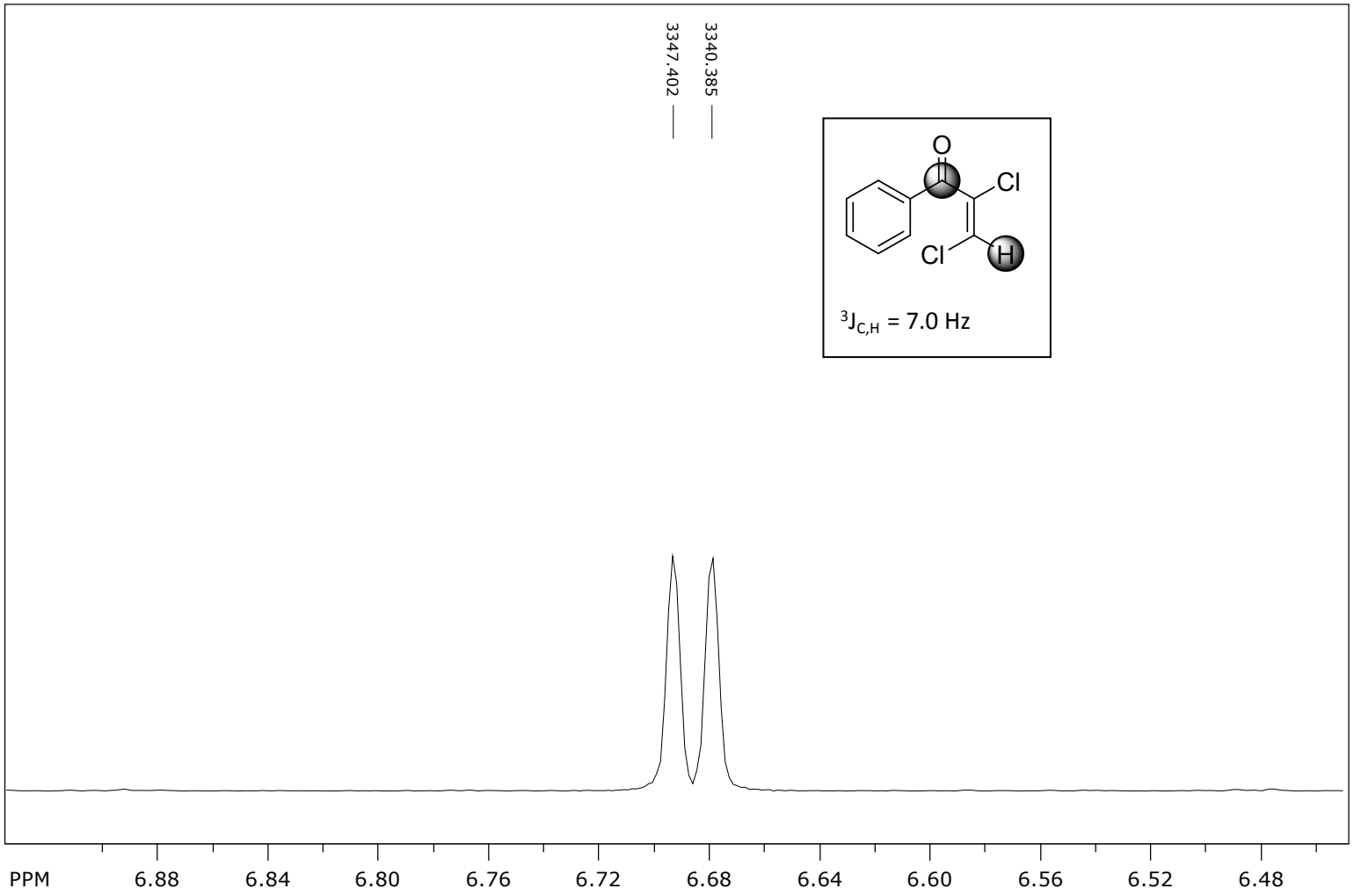
## (2*E*)-2,3-Dichloro-1-phenylprop-2-en-1-one (1) – $^{13}$C NMR




file: D:\nmr 500\NKC_8_65_trans\3\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.90 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 28

freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

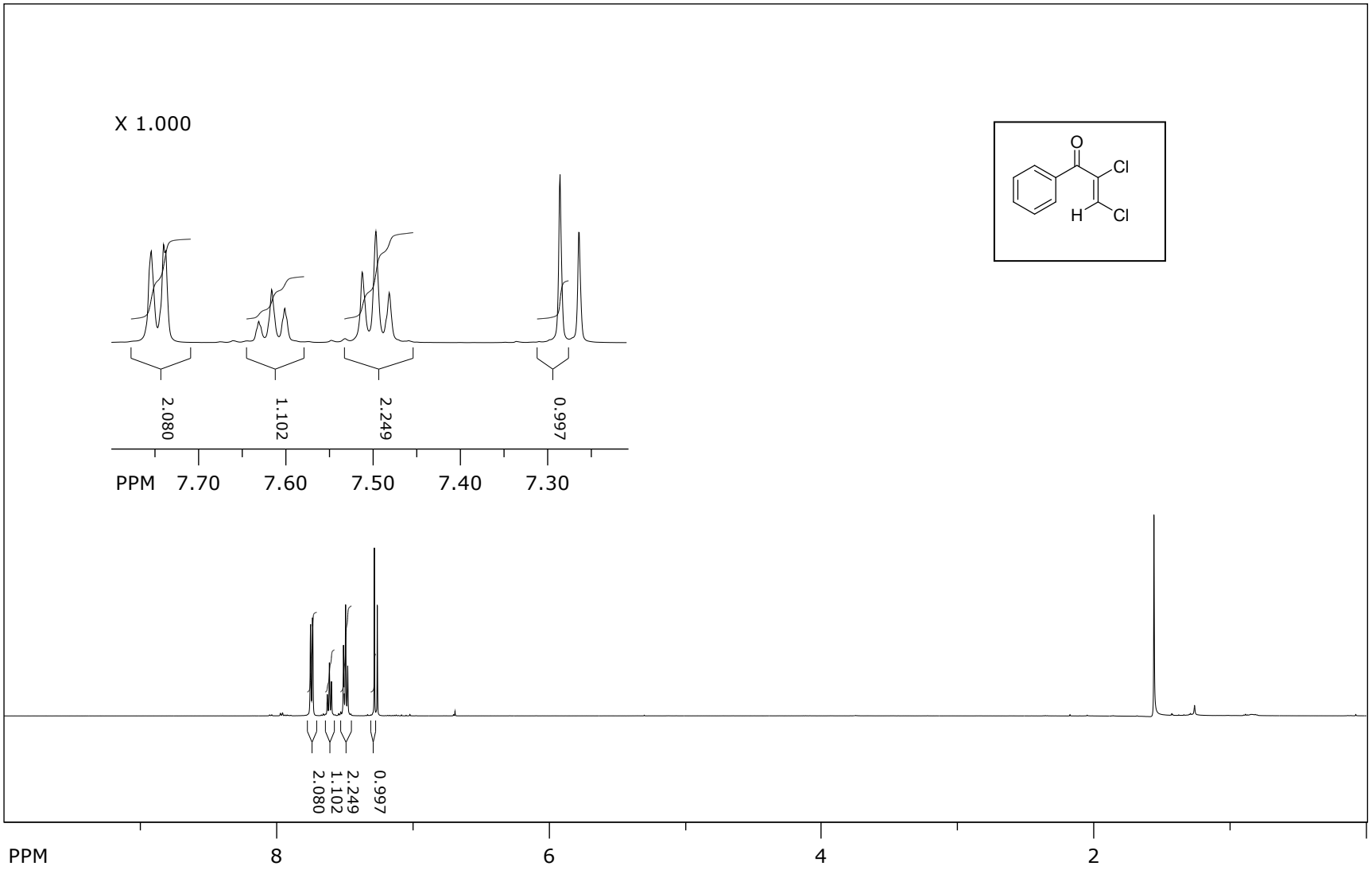
## (2*E*)-2,3-Dichloro-1-phenylprop-2-en-1-one (1) - $^{3}J_{C,H}$




file: D:\nmr 500\NKC_8_65_trans\2\ser expt: <hmbcgplpndqf>
transmitter freq.: 500.132851 MHz
time domain size: 4096 points
width: 3001.20 Hz = 6.0008 ppm = 0.732715 Hz/pt
number of scans: 4

freq. of 0 ppm: 500.130000 MHz
processed size: 4096 complex points
LB: 0.000 GF: 0.0000

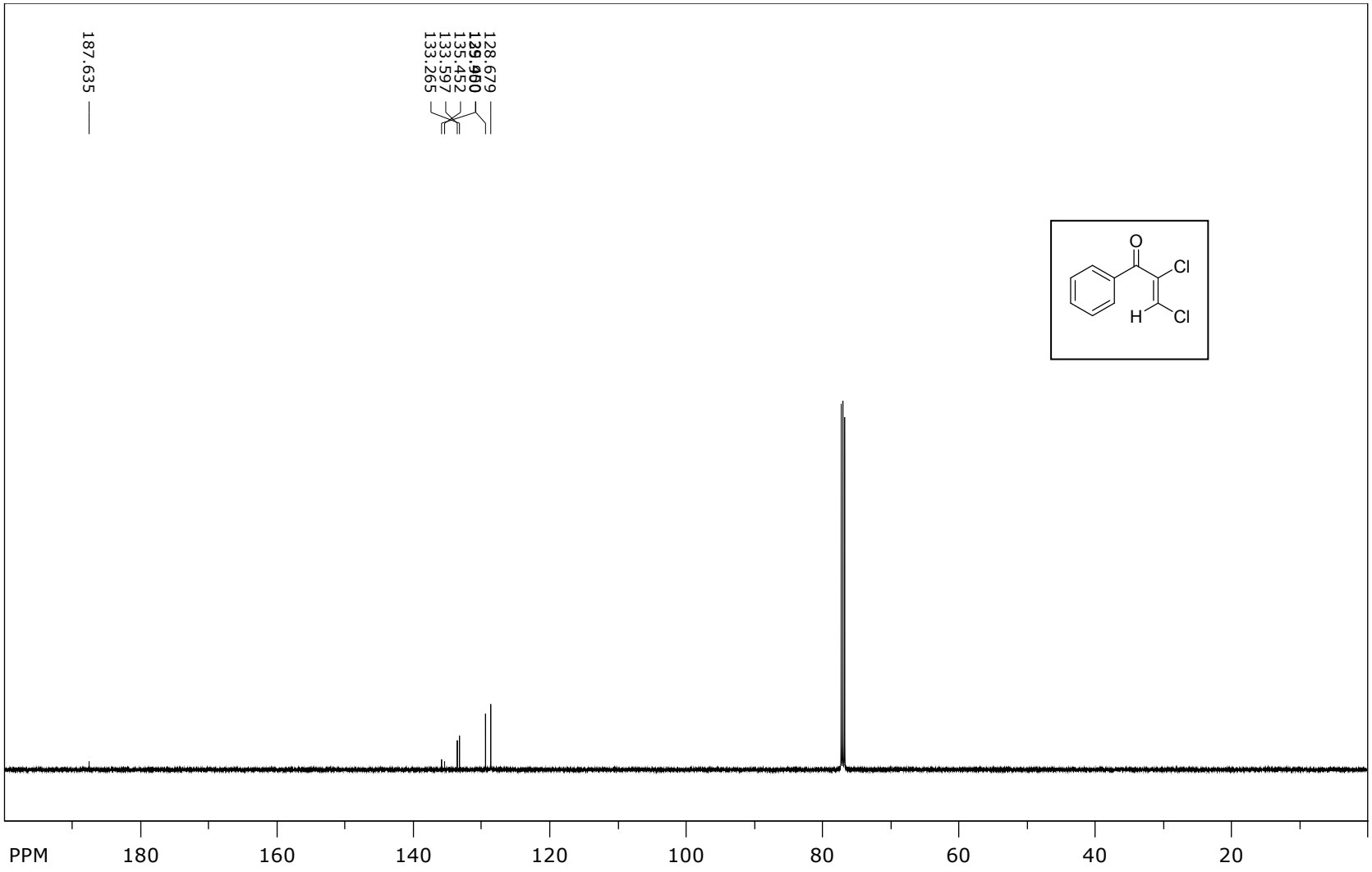
## (2*Z*)-2,3-Dichloro-1-phenylprop-2-en-1-one (6) – $^{1}$H NMR




file: D:\nmr 500\NKC_10_cisisomer\1\fid expt: <zg30>
transmitter freq.: 500.133088 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 128

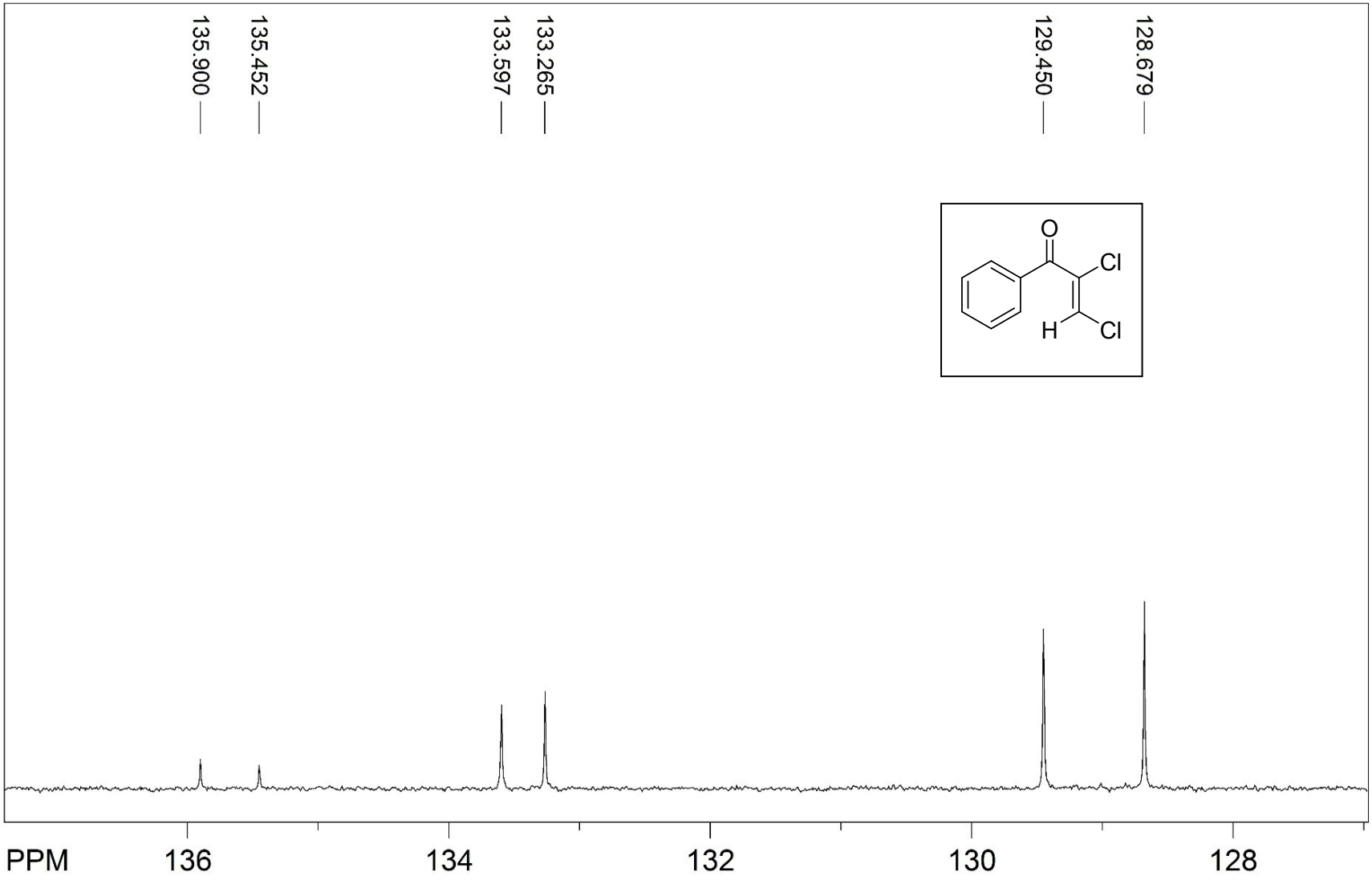
freq. of 0 ppm: 500.130000 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

## (2*Z*)-2,3-Dichloro-1-phenylprop-2-en-1-one (6) – $^{13}$C NMR




file: D:\nmr 500\NKC_10_cisisomer\2\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.90 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 1024

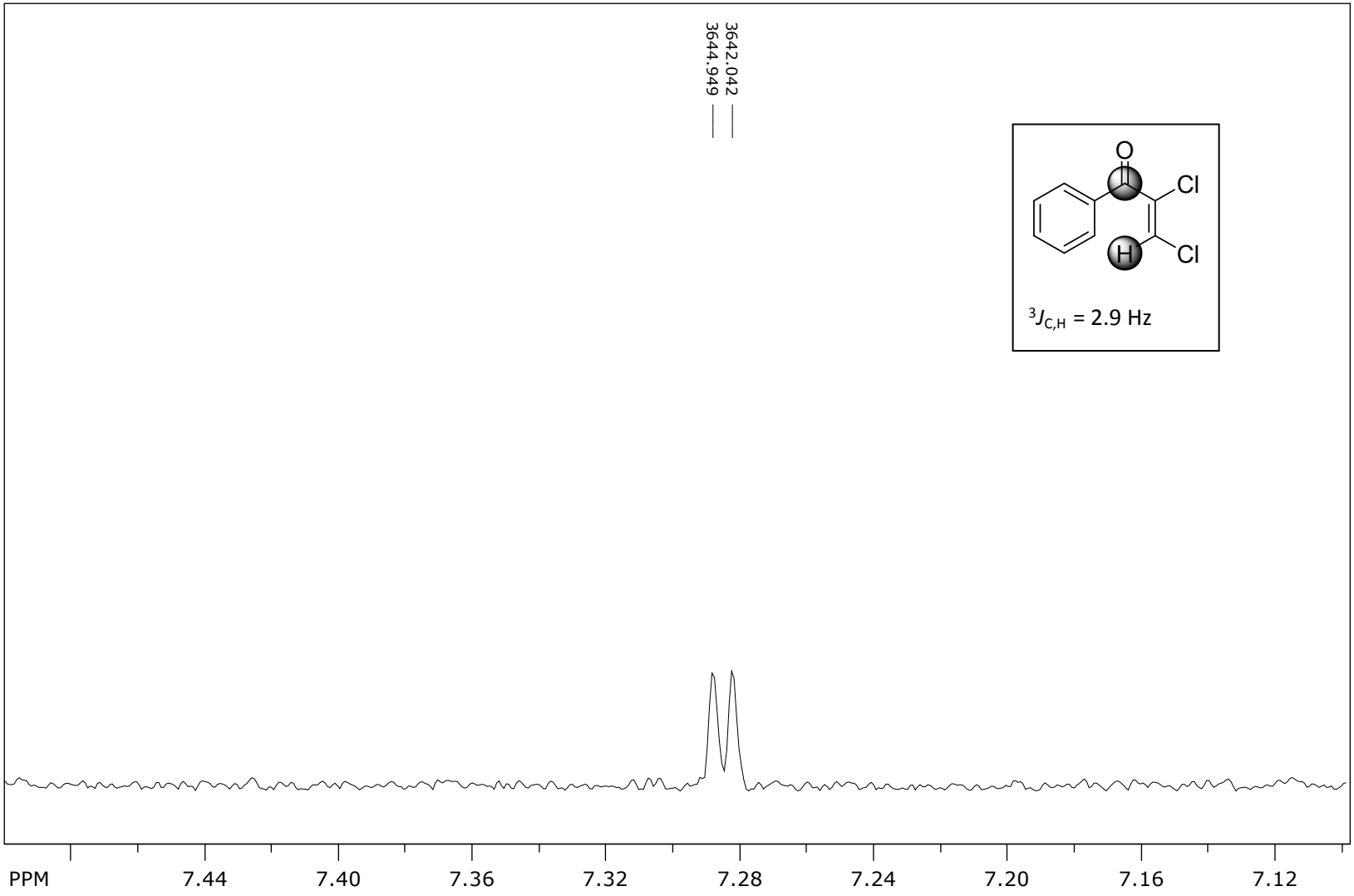
freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000




file: ...hal\Desktop\NKC_10_cisisomer\2\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.91 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 1024

freq of 0 ppm: 125.757789 MHz
processed size: 32768 points
LB: 1.000 GF: 0.0000
Hz/cm: 52.509 ppm/cm: 0.41750

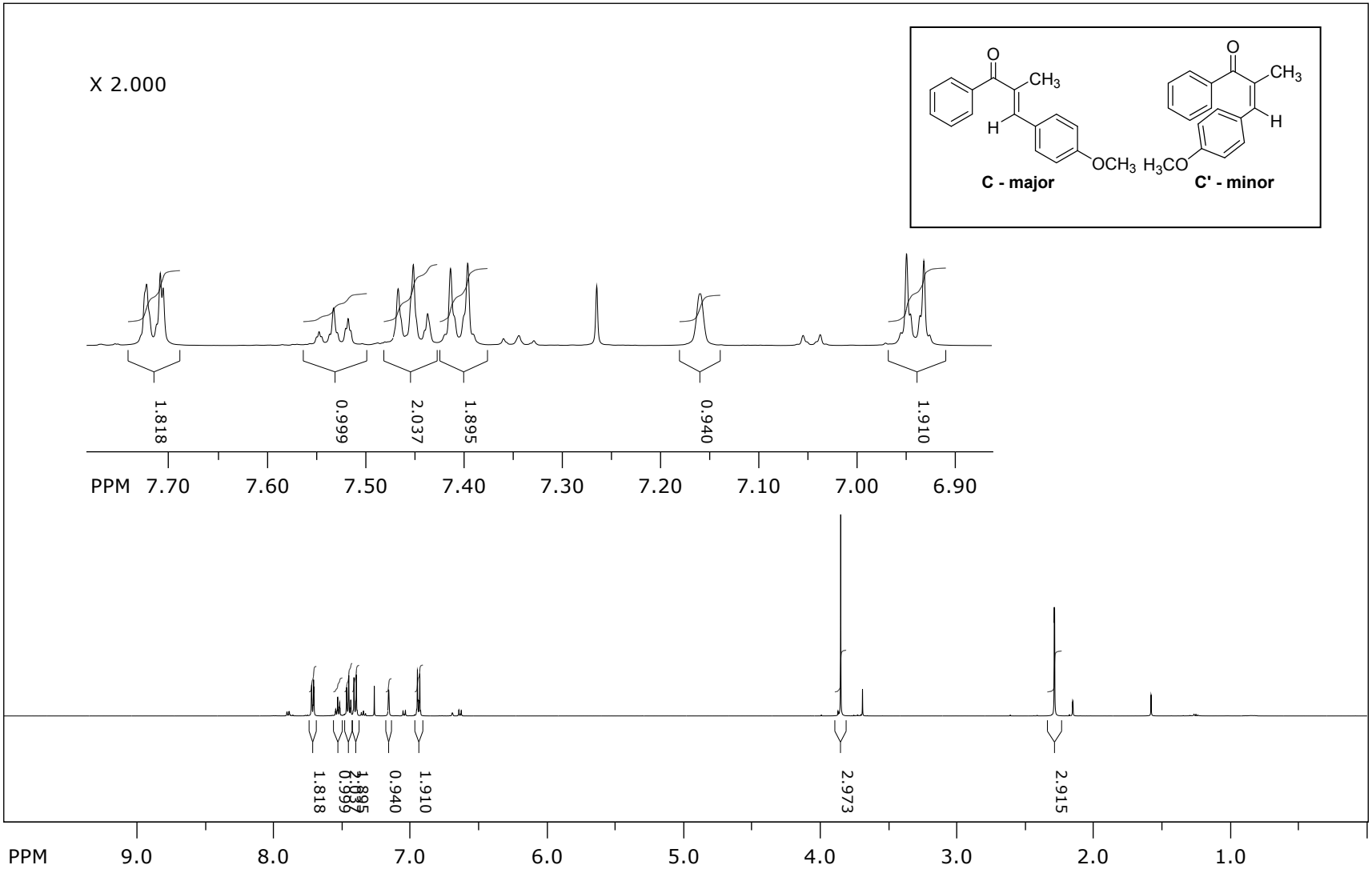
## (2*Z*)-2,3-Dichloro-1-phenylprop-2-en-1-one (6) – $^{3}J_{C,H}$




file: D:\nmr 500\NKC_10_cisisomer\6\ser expt: <hmbcgplpndqf>
transmitter freq.: 500.133651 MHz
time domain size: 4096 points
width: 1500.60 Hz = 3.0004 ppm = 0.366357 Hz/pt
number of scans: 4

freq. of 0 ppm: 500.130000 MHz
processed size: 4096 complex points
LB: 0.000 GF: 0.0000

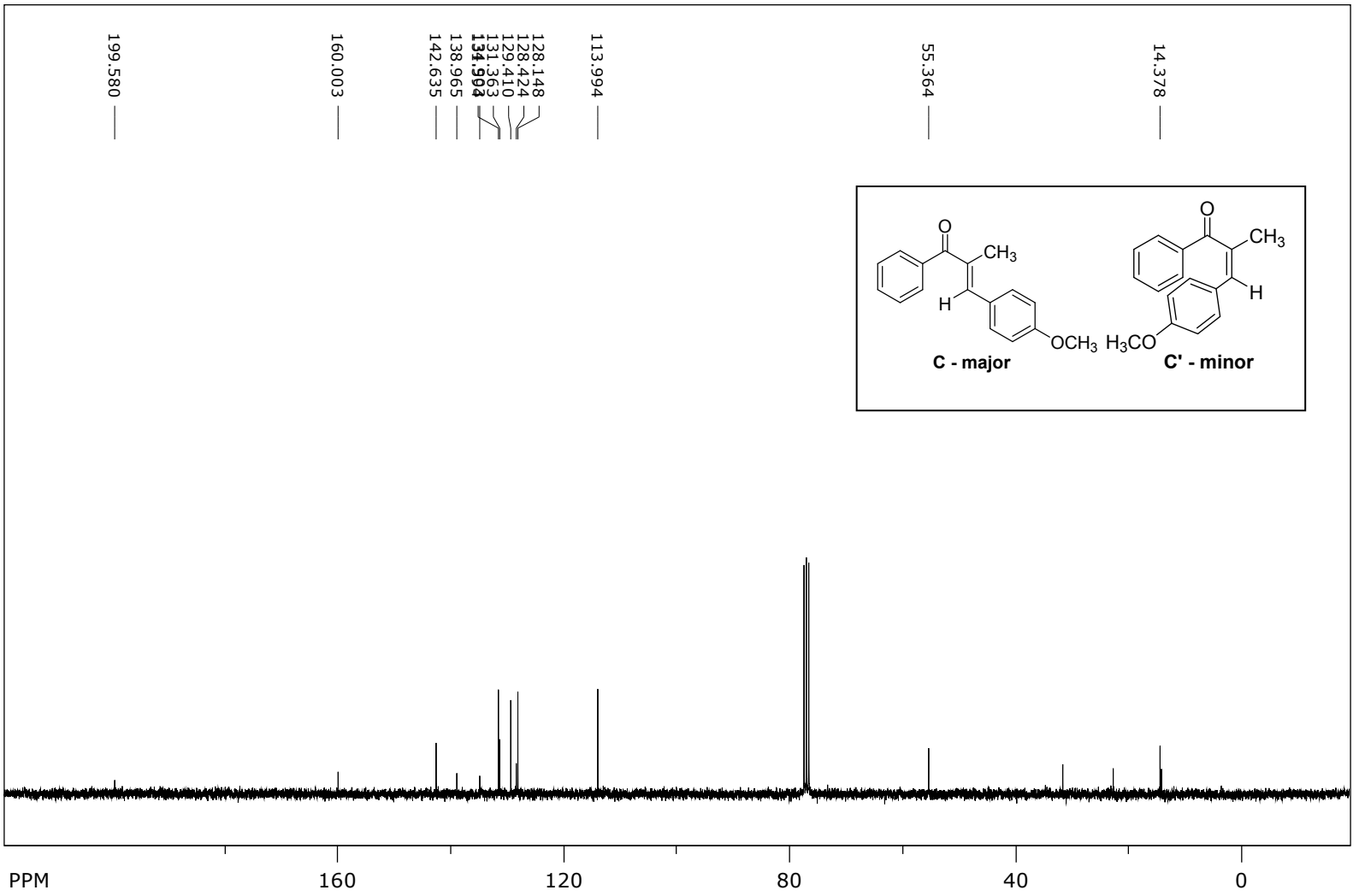
# (2*E*/*Z*)-3-(4-Methoxyphenyl)-2-methyl-1-phenylprop-2-en-1-one (C and C') – $^1$H NMR




file: D:\nmr 500\NKC_7_74\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130000 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

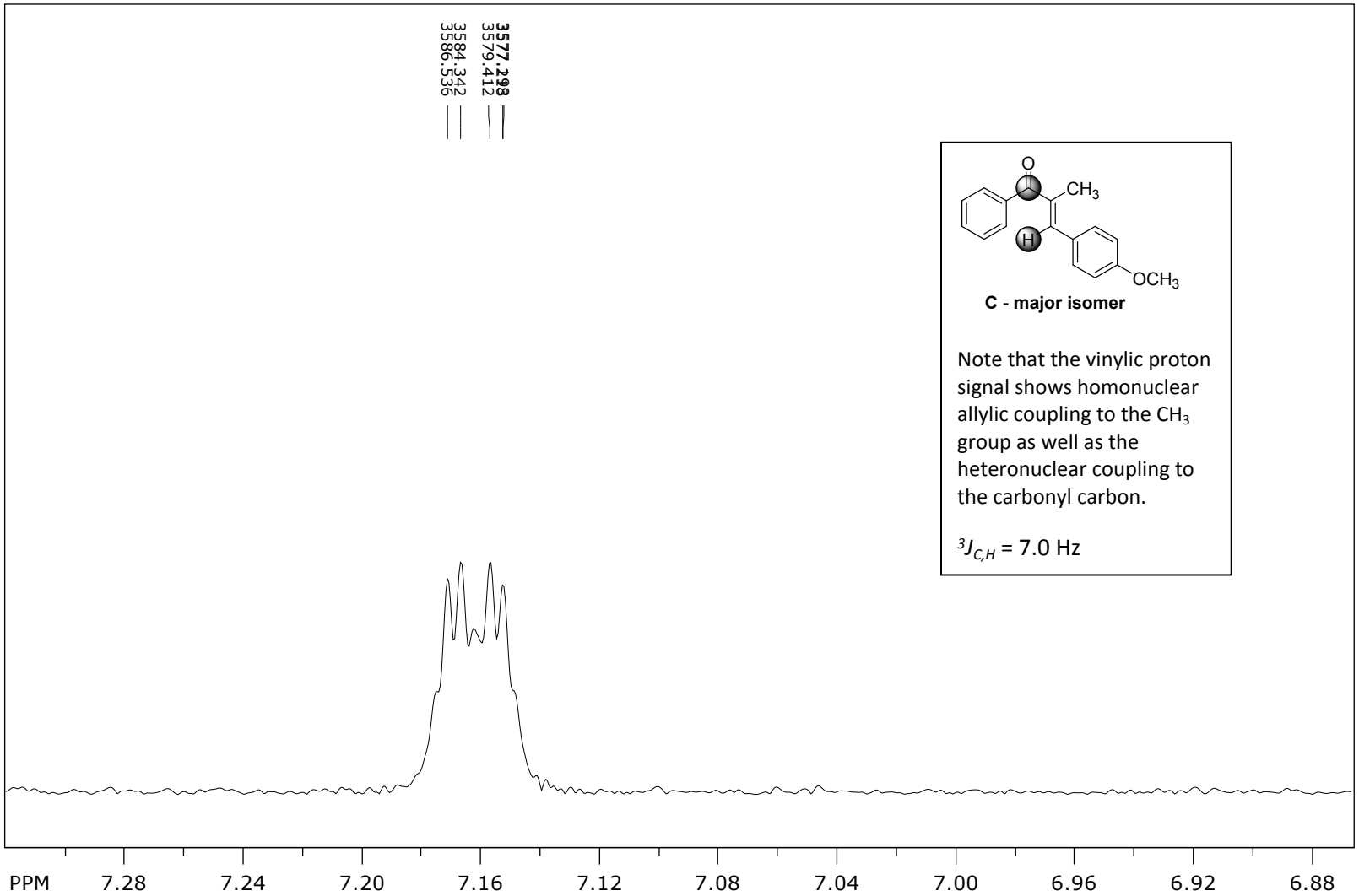
## (2*E/Z*)-3-(4-Methoxyphenyl)-2-methyl-1-phenylprop-2-en-1-one (C and C') – $^{13}$C NMR




file: ...300\NKC_7_74_methyl_purified\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 128

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

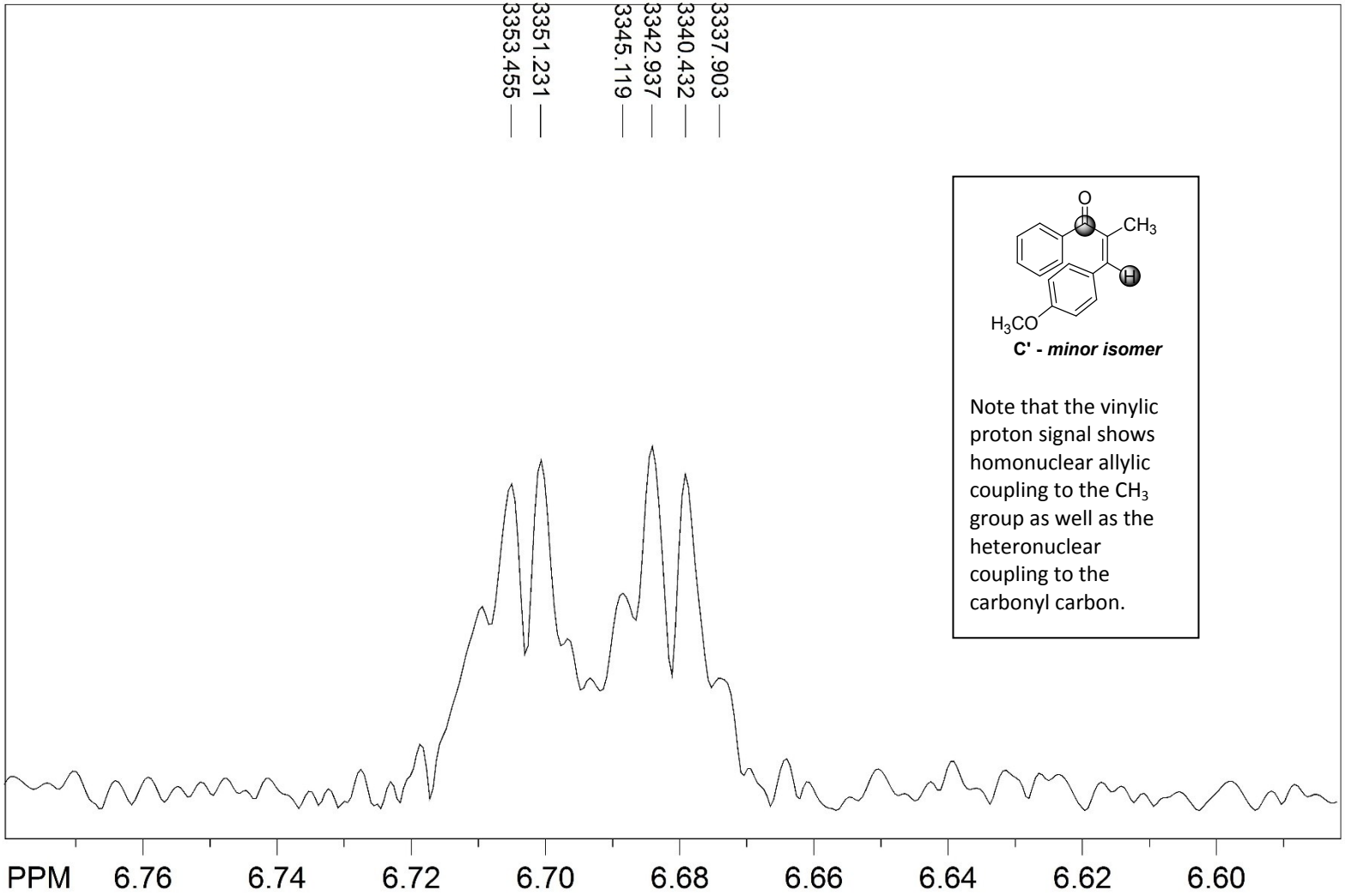
## (2*E/Z*)-3-(4-Methoxyphenyl)-2-methyl-1-phenylprop-2-en-1-one (C and C') – $^{3}J_{C,H}$ at $\delta_H$ = 7.16, $\delta_C$ = 199.6 ppm.




file: D:\nmr 500\NKC_7_81\101\ser expt: <hmbcgplpndqf>
transmitter freq.: 500.132201 MHz
time domain size: 8192 points
width: 4000.00 Hz = 7.9979 ppm = 0.488281 Hz/pt
number of scans: 16

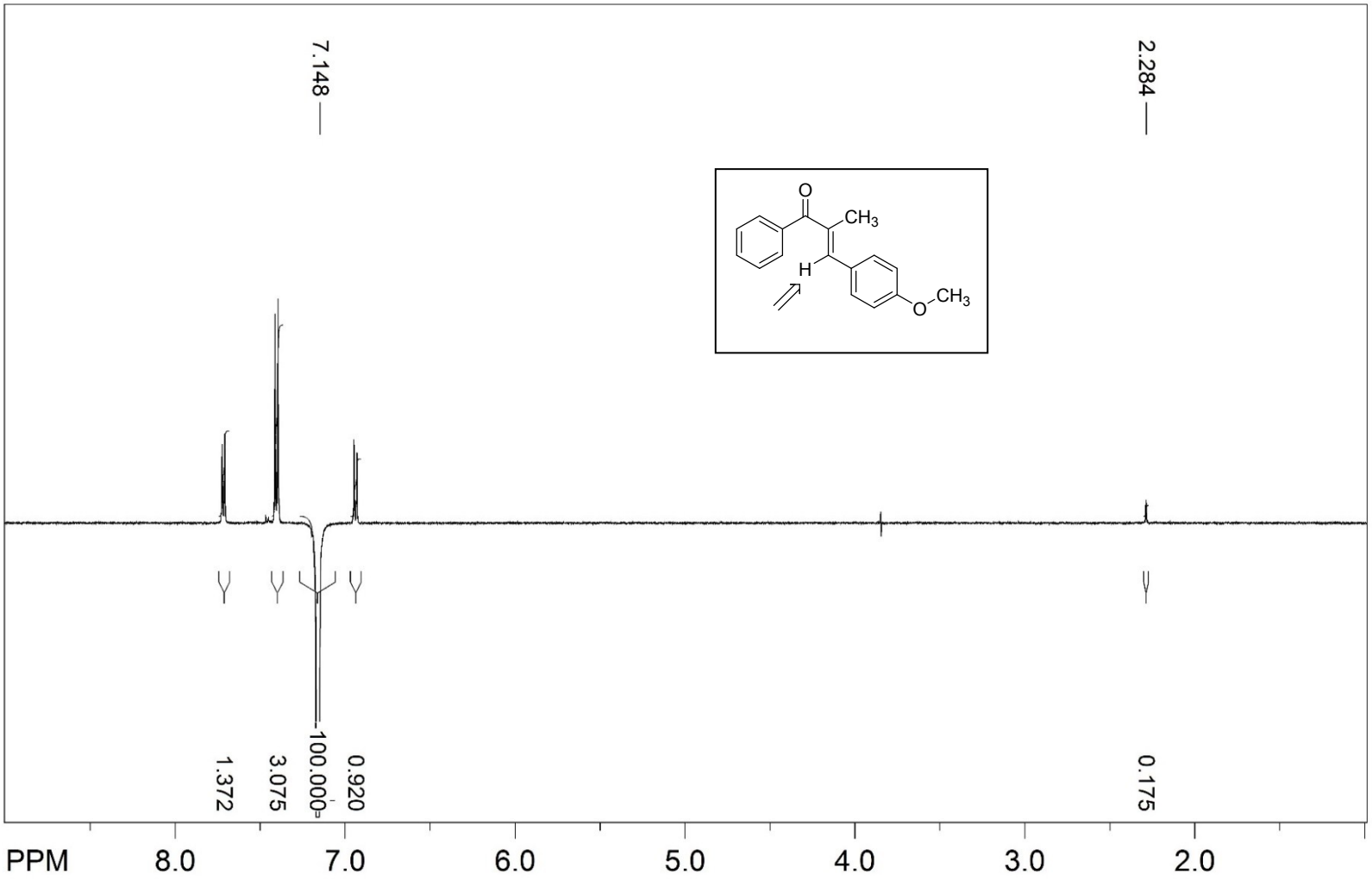
freq. of 0 ppm: 500.130000 MHz
processed size: 16384 complex points
LB: 0.000 GF: 0.0000

**(2*E/Z*)-3-(4-Methoxyphenyl)-2-methyl-1-phenylprop-2-en-1-one (C and C') – $^{3}J_{C,H}$ at $\delta_H$ = 6.69, $\delta_C$ = 201.0 ppm.**



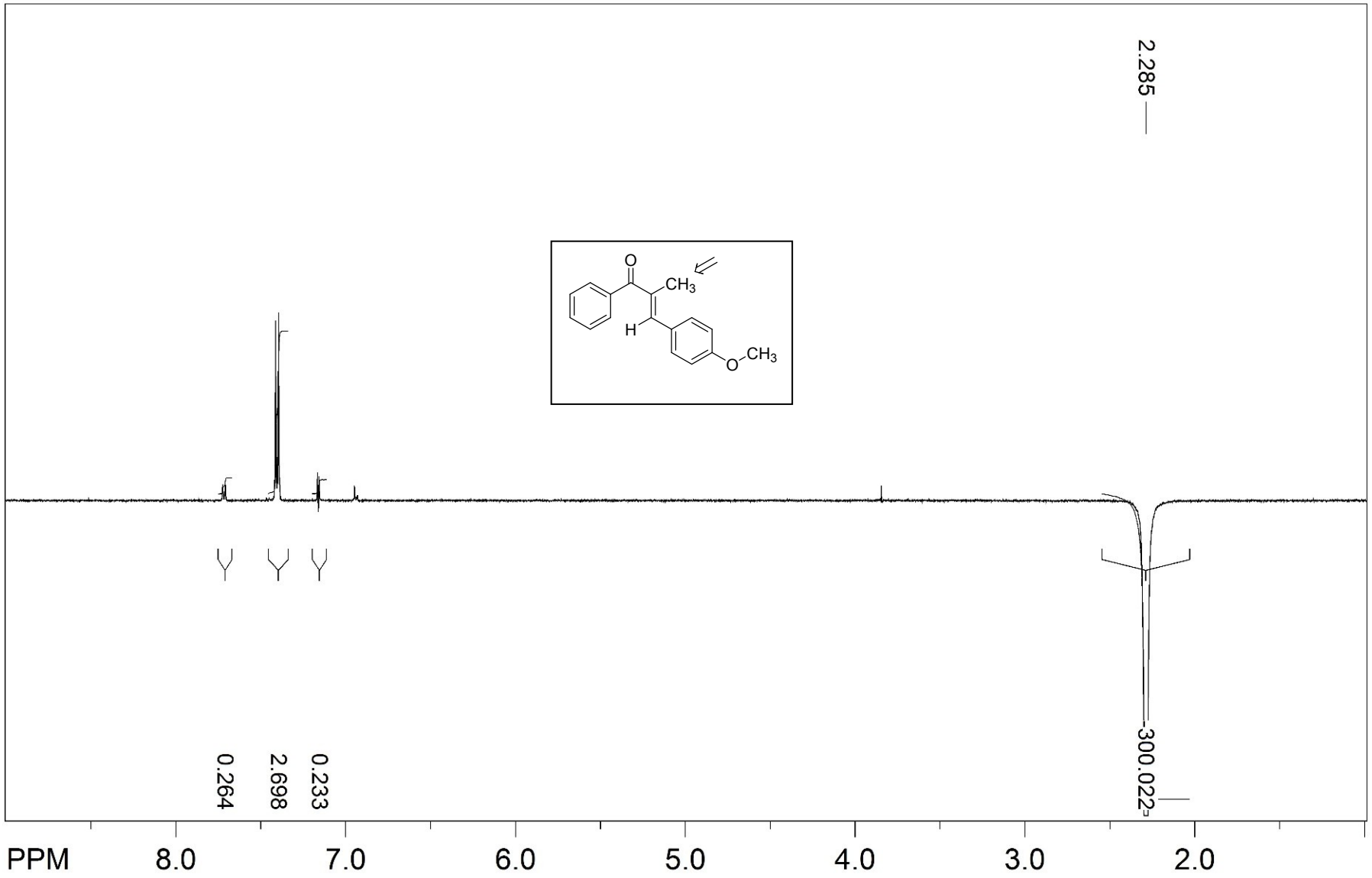

file: ...ers\chehal\Desktop\NKC 7 81\10/ser expt: <hmbcgplpndqfreq of 0 ppm: 500.130000 MHz
transmitter freq.: 500.132201 MHz processed size: 16384 points
time domain size: 8192 points LB: 0.000 GF: 0.0000
width: 4000.00 Hz = 7.9979 ppm = 0.488281 Hz/pt Hz/cm: 4.147 ppm/cm: 0.00829
number of scans: 128

## (2*E*/*Z*)-3-(4-Methoxyphenyl)-2-methyl-1-phenylprop-2-en-1-one (C and C') – NOE experiments



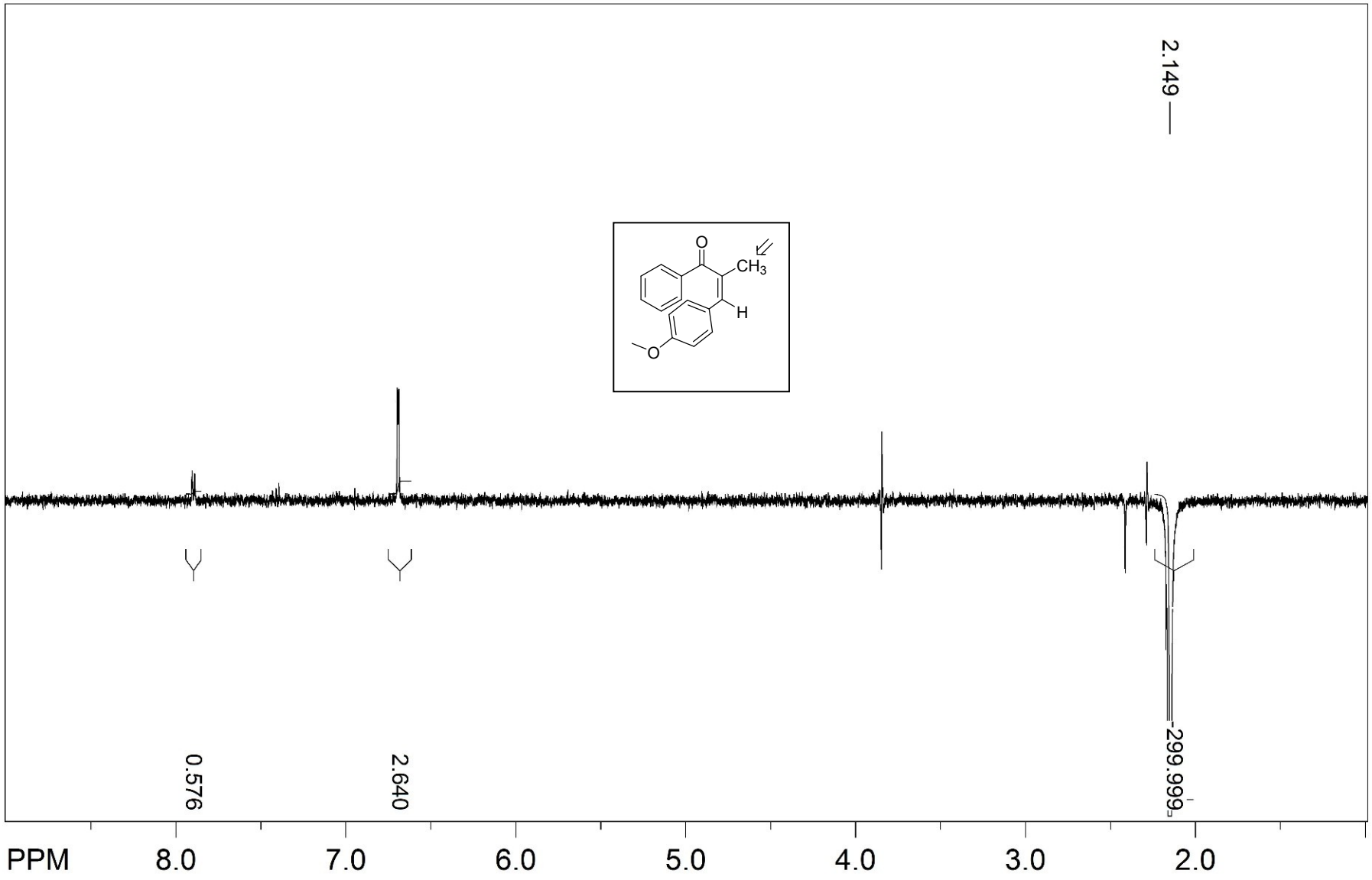

file: ...sers\chehal\Desktop\NKC_7_81\5/fid expt: <selnogp>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 64

freq of 0 ppm: 500.130000 MHz
processed size: 65536 points
LB: 0.300 GF: 0.0000
Hz/cm: 160.466 ppm/cm: 0.32085




file: ...sers\chehal\Desktop\NKC 7 81\7/fid expt: <selnogp>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 64

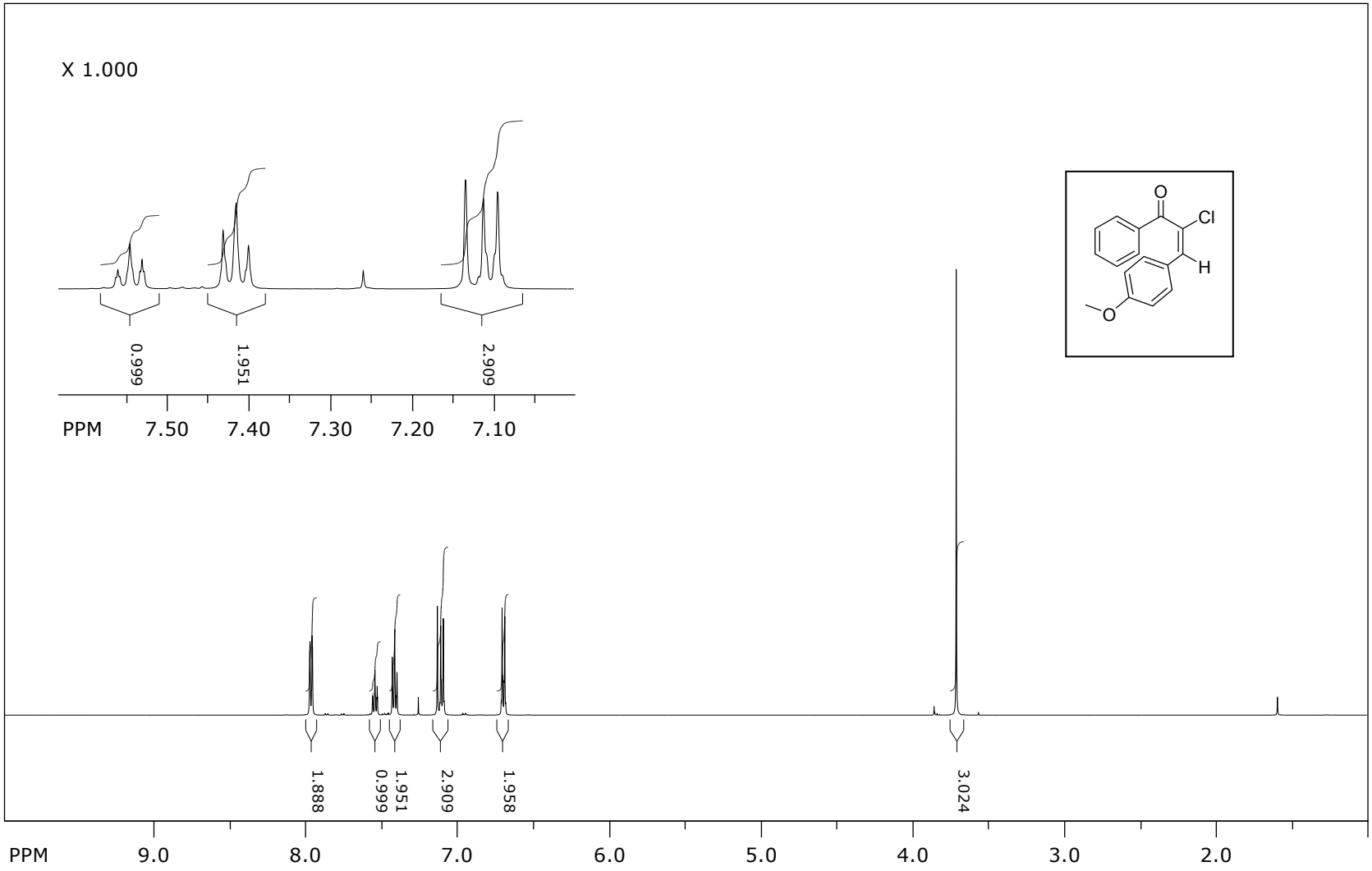
freq of 0 ppm: 500.130000 MHz
processed size: 65536 points
LB: 0.300 GF: 0.0000
Hz/cm: 160.466 ppm/cm: 0.32085




file: ...sers\chehal\Desktop\NKC_7_81\8/fid expt: <selnogp>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 64

freq of 0 ppm: 500.130000 MHz
processed size: 65536 points
LB: 0.300 GF: 0.0000
Hz/cm: 160.466 ppm/cm: 0.32085

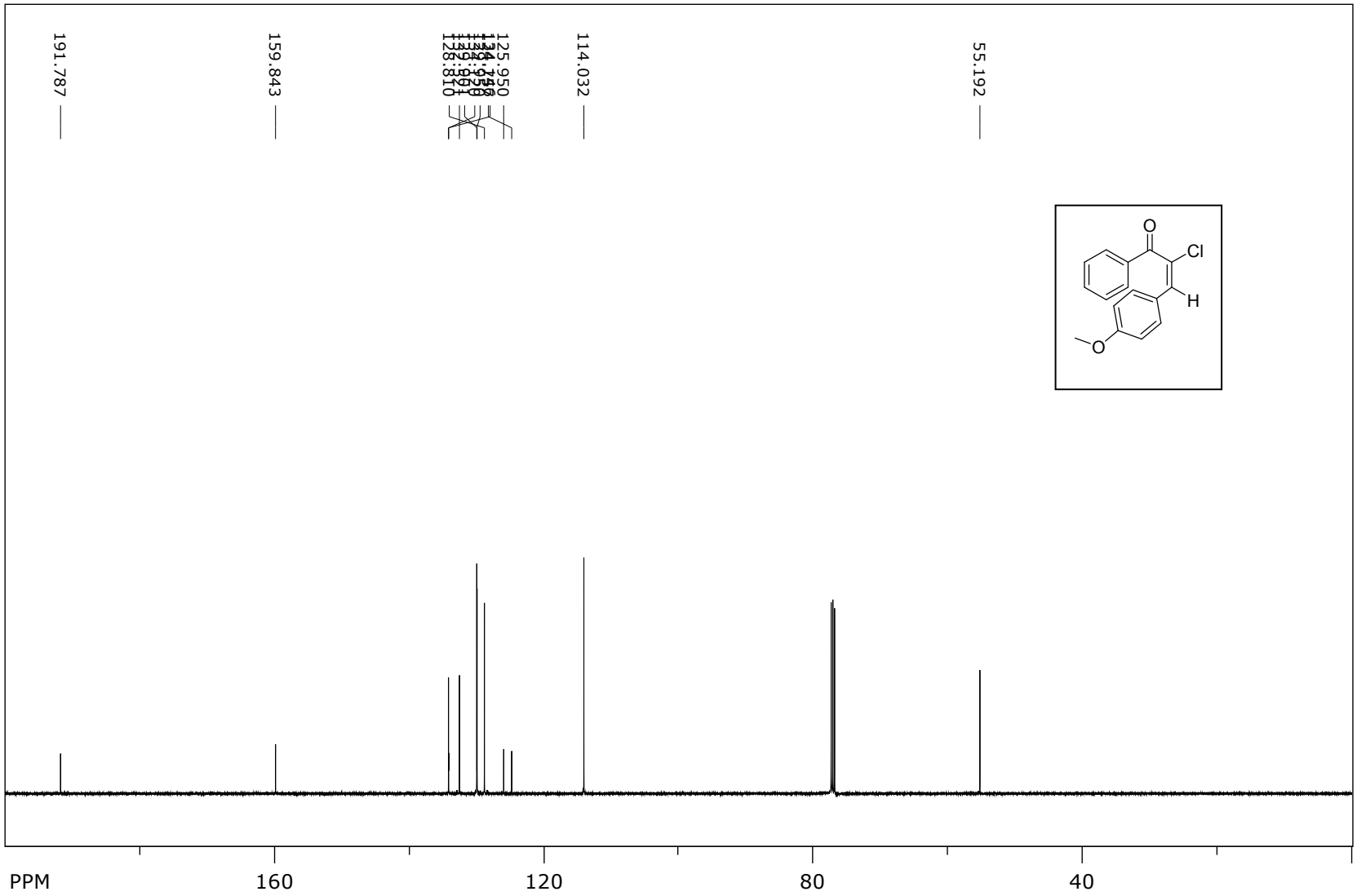
## (E)-2-chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (3a) – $^{1}$H NMR




file: D:\nmr 500\NKC_8_44_F6-14\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 16

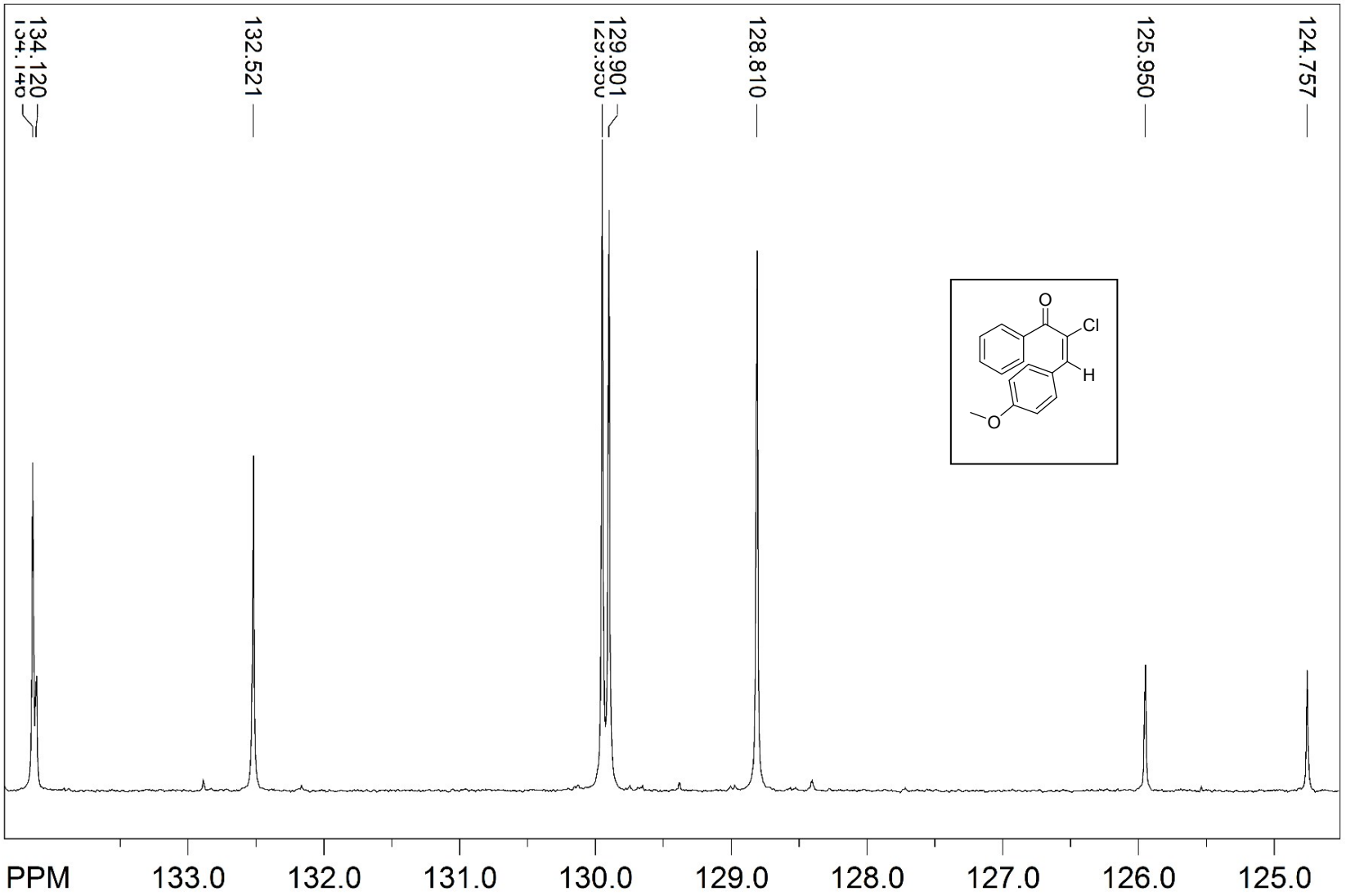
freq. of 0 ppm: 500.130002 MHz
processed size: 65536 complex points
LB: 0.300 GF: 0.0000

## (E)-2-chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (3a) – $^{13}$C NMR




file: D:\nmr 500\NKC_8_44_F6-14\3\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.90 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 1024

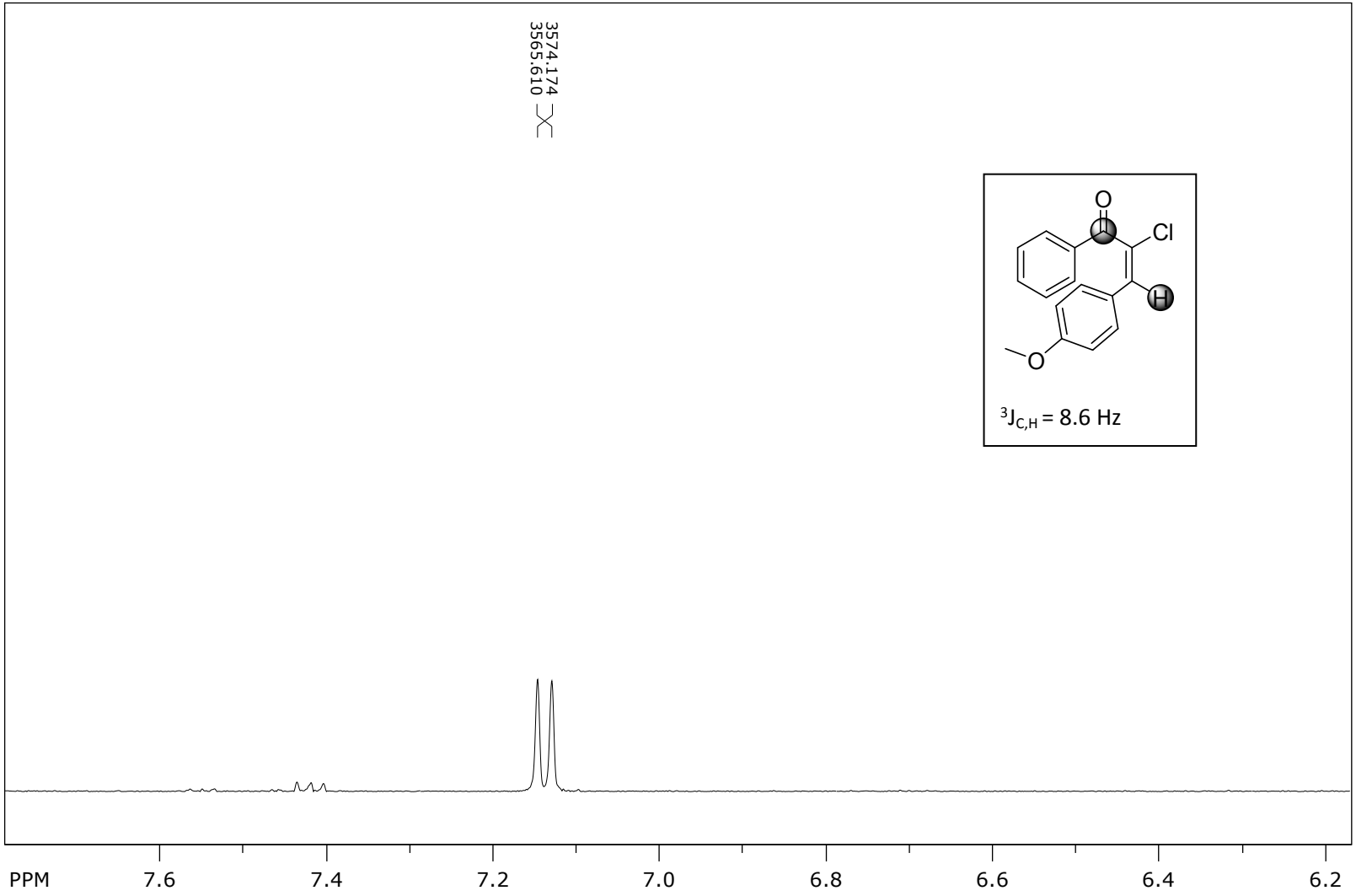
freq. of 0 ppm: 125.757789 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000




file: ...ktop\NMR data\NKC 8 44 F6-14\3\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.90 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 1024

freq of 0 ppm: 125.757789 MHz
processed size: 32768 points
LB: 1.000 GF: 0.0000
Hz/cm: 51.547 ppm/cm: 0.40985

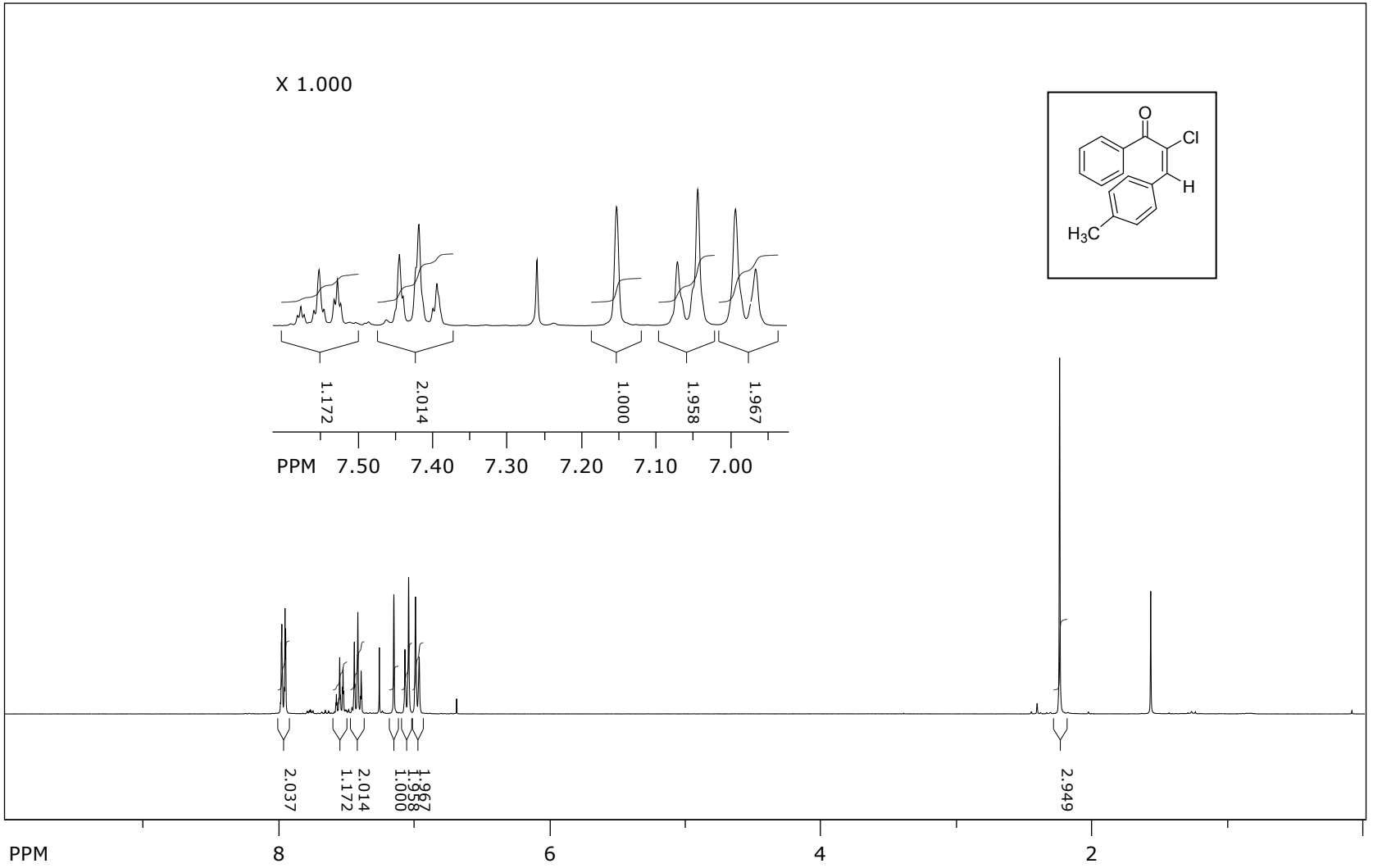
## (E)-2-chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (3a) – $^{3}J_{C,H}$




file: D:\nmr 500\NKC_8_44_F6-14\2\ser expt: <hmbcgplpndqf>
transmitter freq.: 500.132201 MHz
time domain size: 8192 points
width: 4000.00 Hz = 7.9979 ppm = 0.488281 Hz/pt
number of scans: 8

freq. of 0 ppm: 500.130000 MHz
processed size: 16384 complex points
LB: 0.000 GF: 0.0000

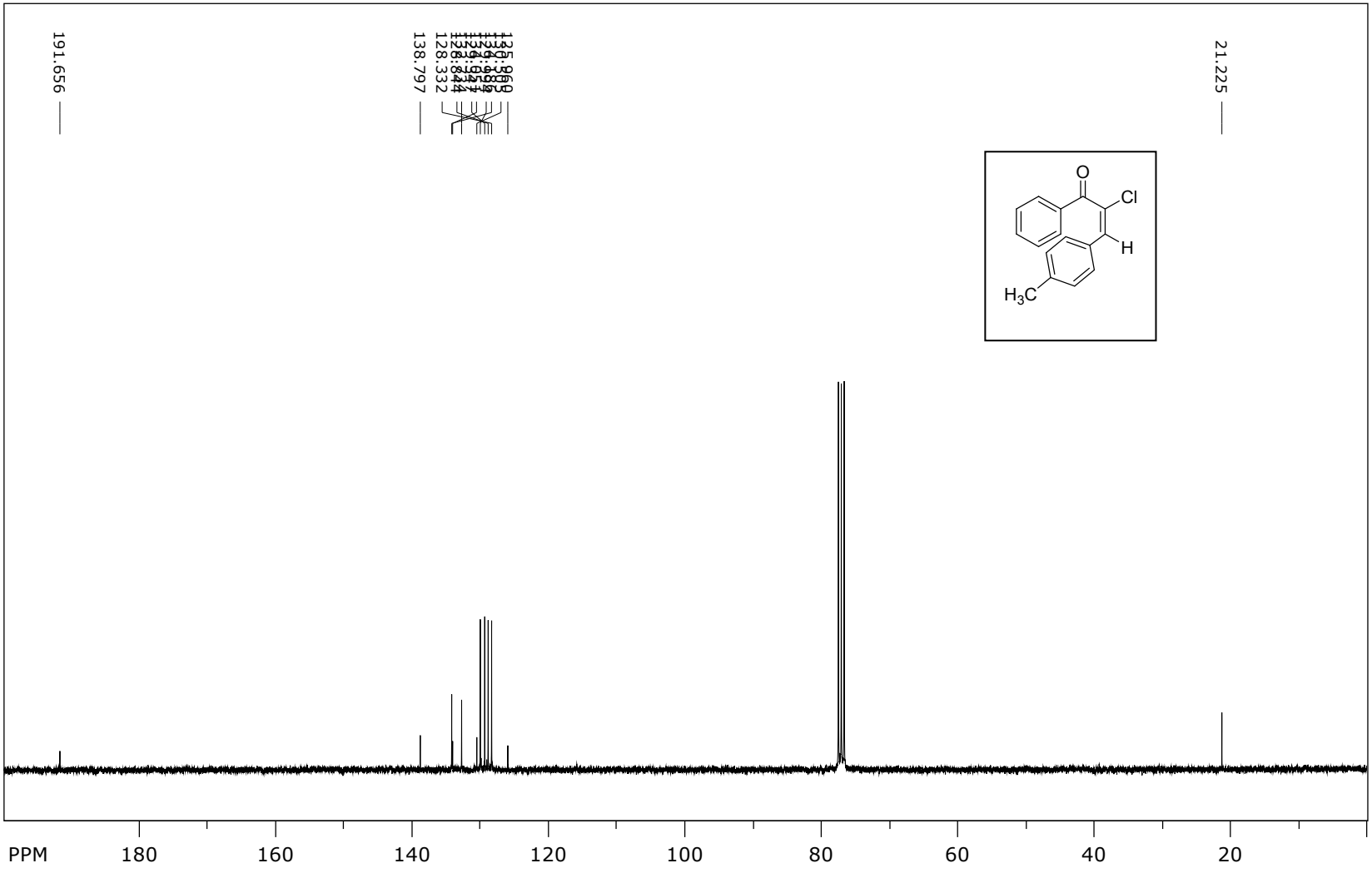
## (E)-2-chloro-3-(4-methylphenyl)-1-phenylprop-2-en-1-one (3b) – $^{1}$H NMR




file: D:\NKC_10_methylphenyltrans\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130012 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

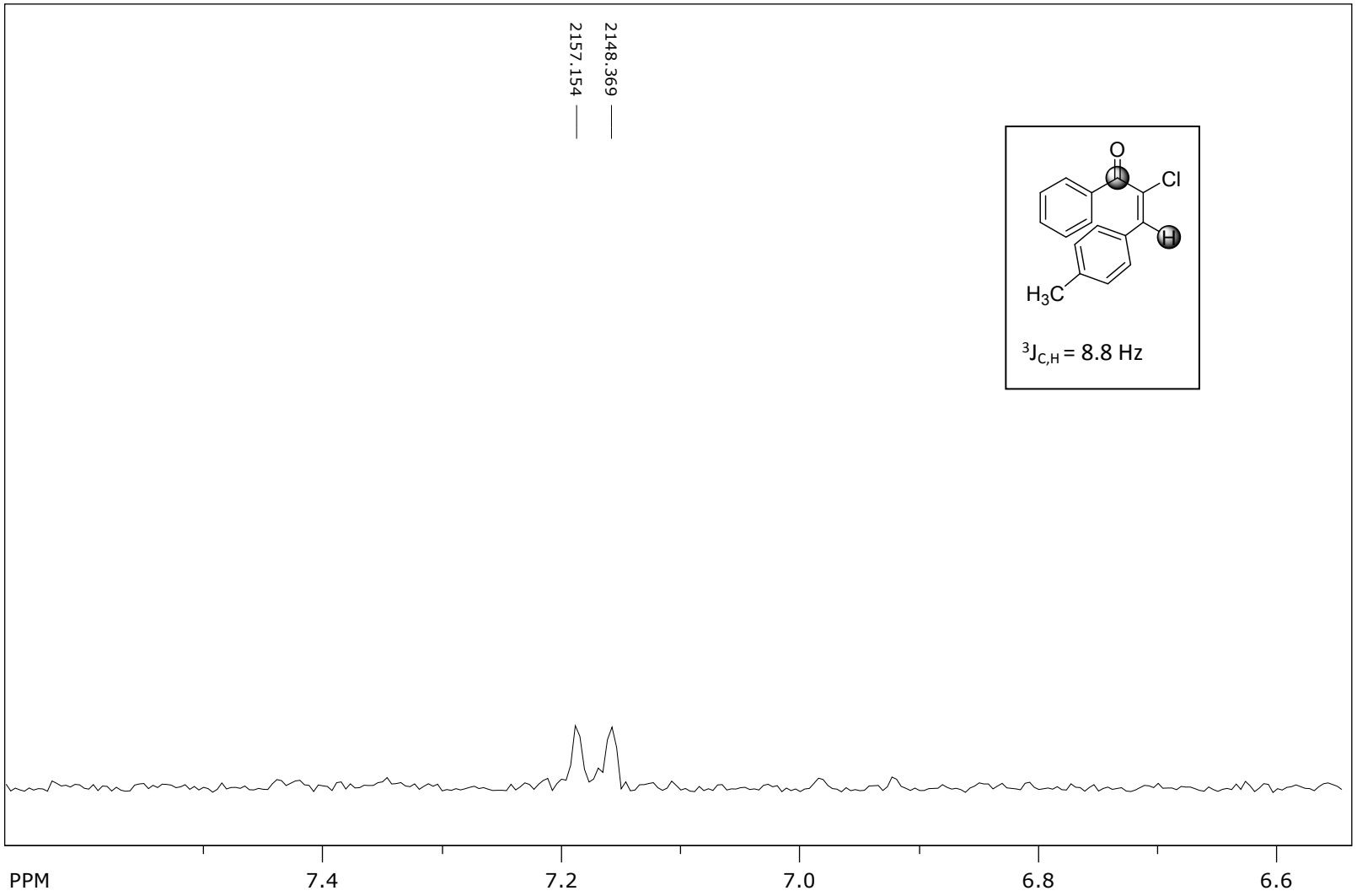
## (E)-2-chloro-3-(4-methylphenyl)-1-phenylprop-2-en-1-one (3b) – $^{13}$C NMR




file: D:\NKC_10_methylphenyltrans\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

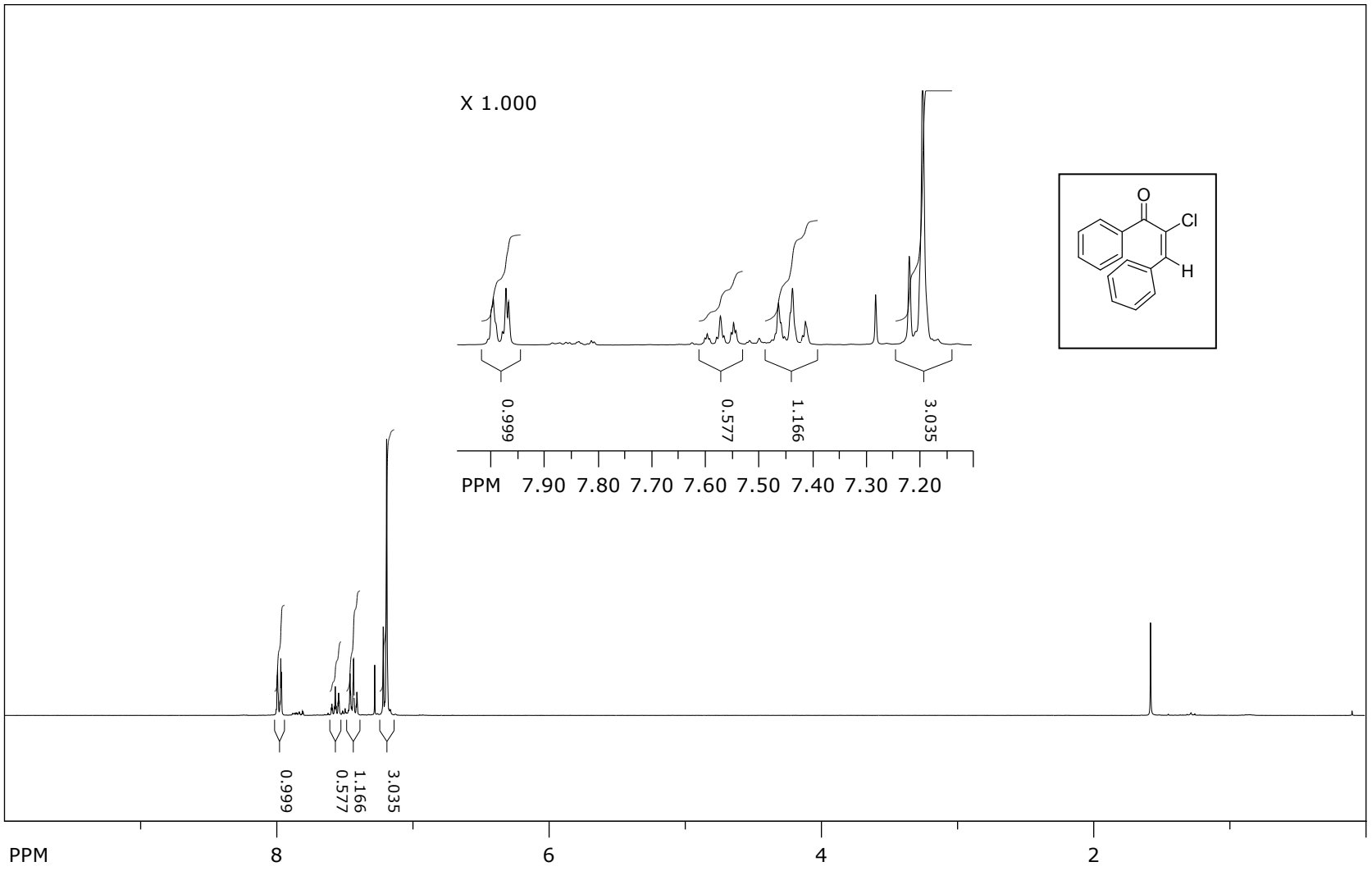
## (E)-2-chloro-3-(4-methylphenyl)-1-phenylprop-2-en-1-one (3b) – $^{3}J_{C,H}$




file: D:\NKC_10_methylphenyltrans\8\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.131409 MHz
time domain size: 4096 points
width: 2367.42 Hz = 7.8880 ppm = 0.577984 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

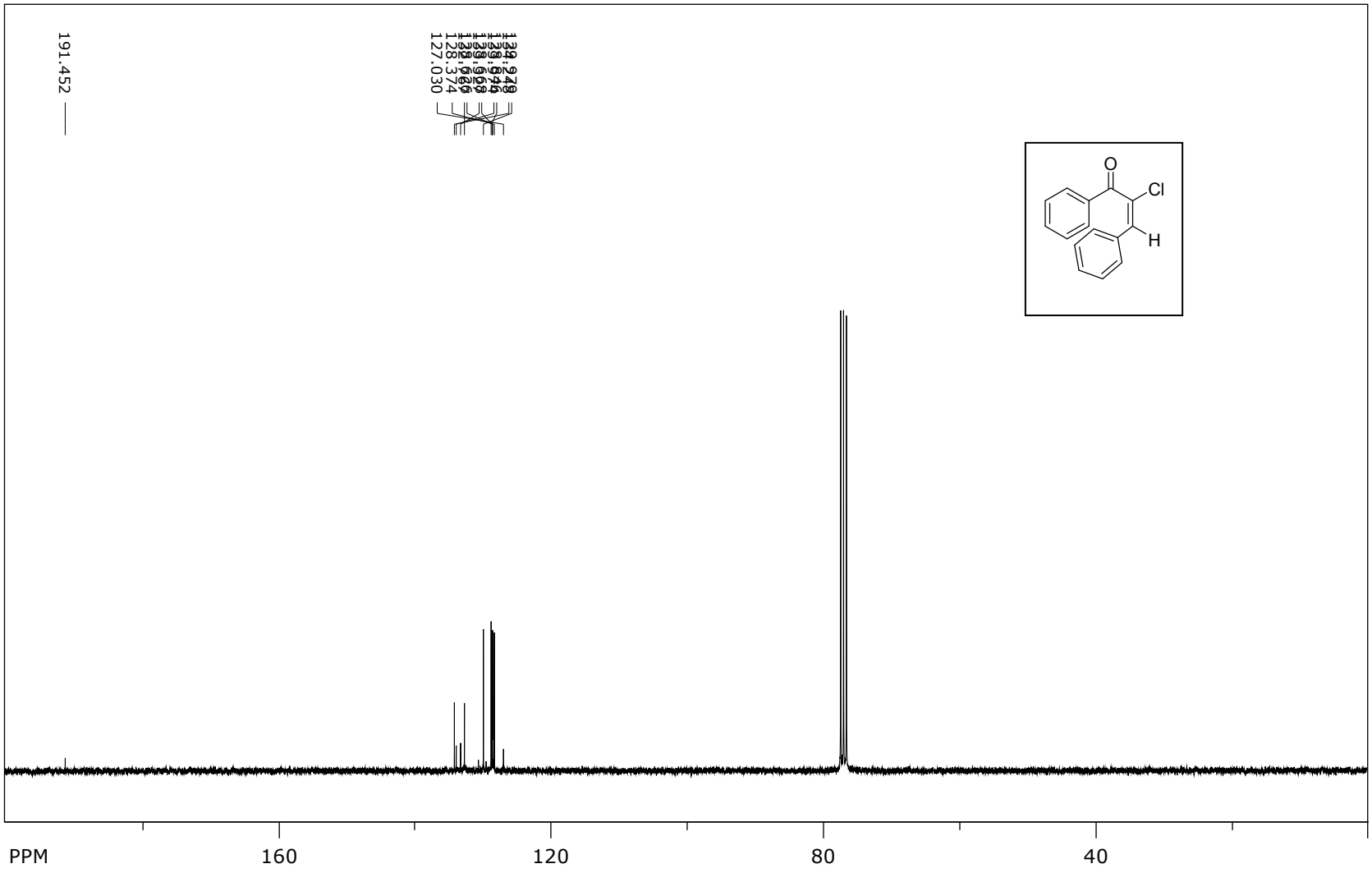
## (E)-2-chloro-3-(phenyl)-1-phenylprop-2-en-1-one (3c) – $^{1}$H NMR




file: D:\NKC_10_phenyltrans\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

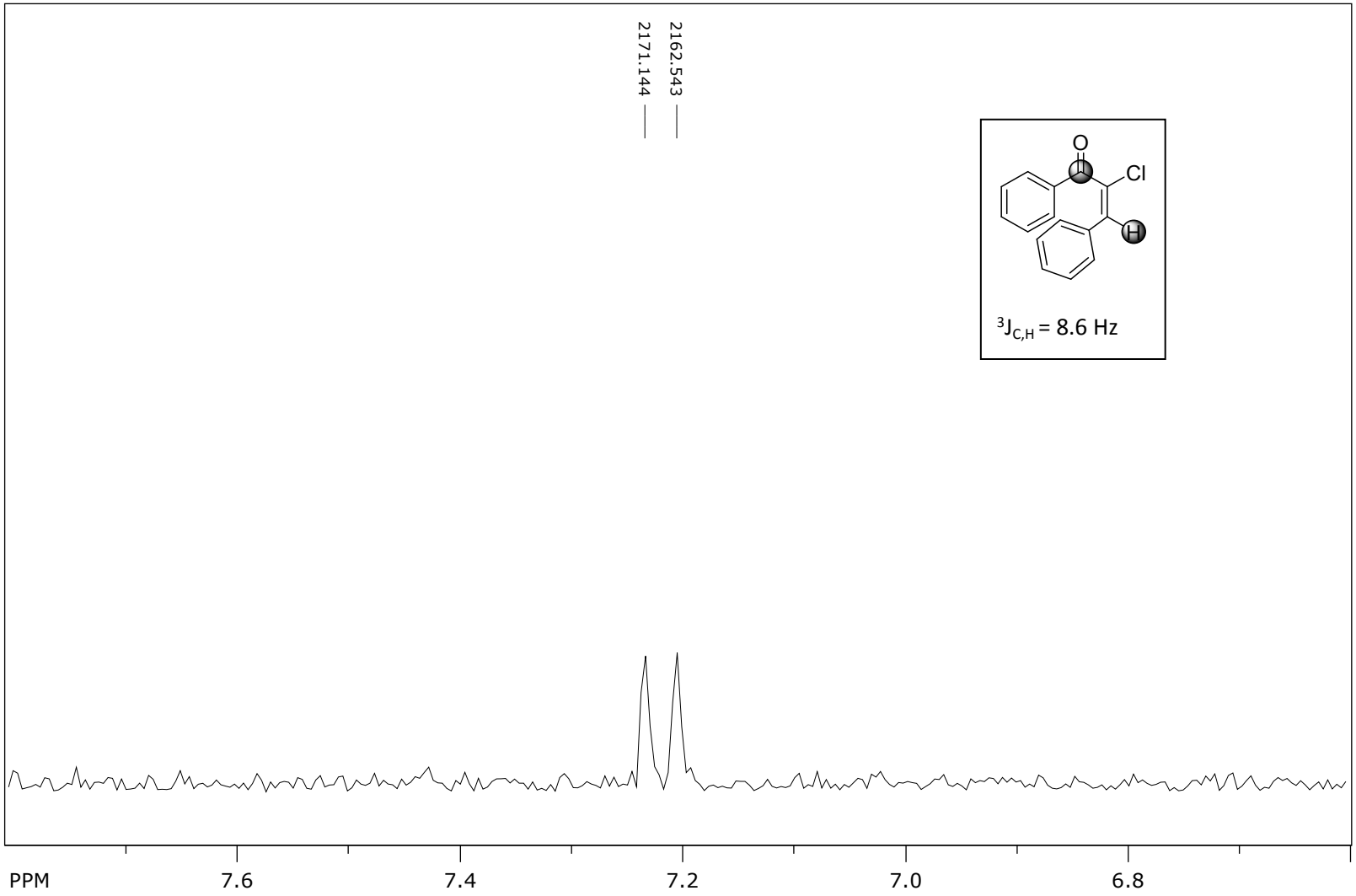
## (E)-2-chloro-3-(phenyl)-1-phenylprop-2-en-1-one (3c) – $^{13}$C NMR




file: D:\NKC_10_phenyltrans\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

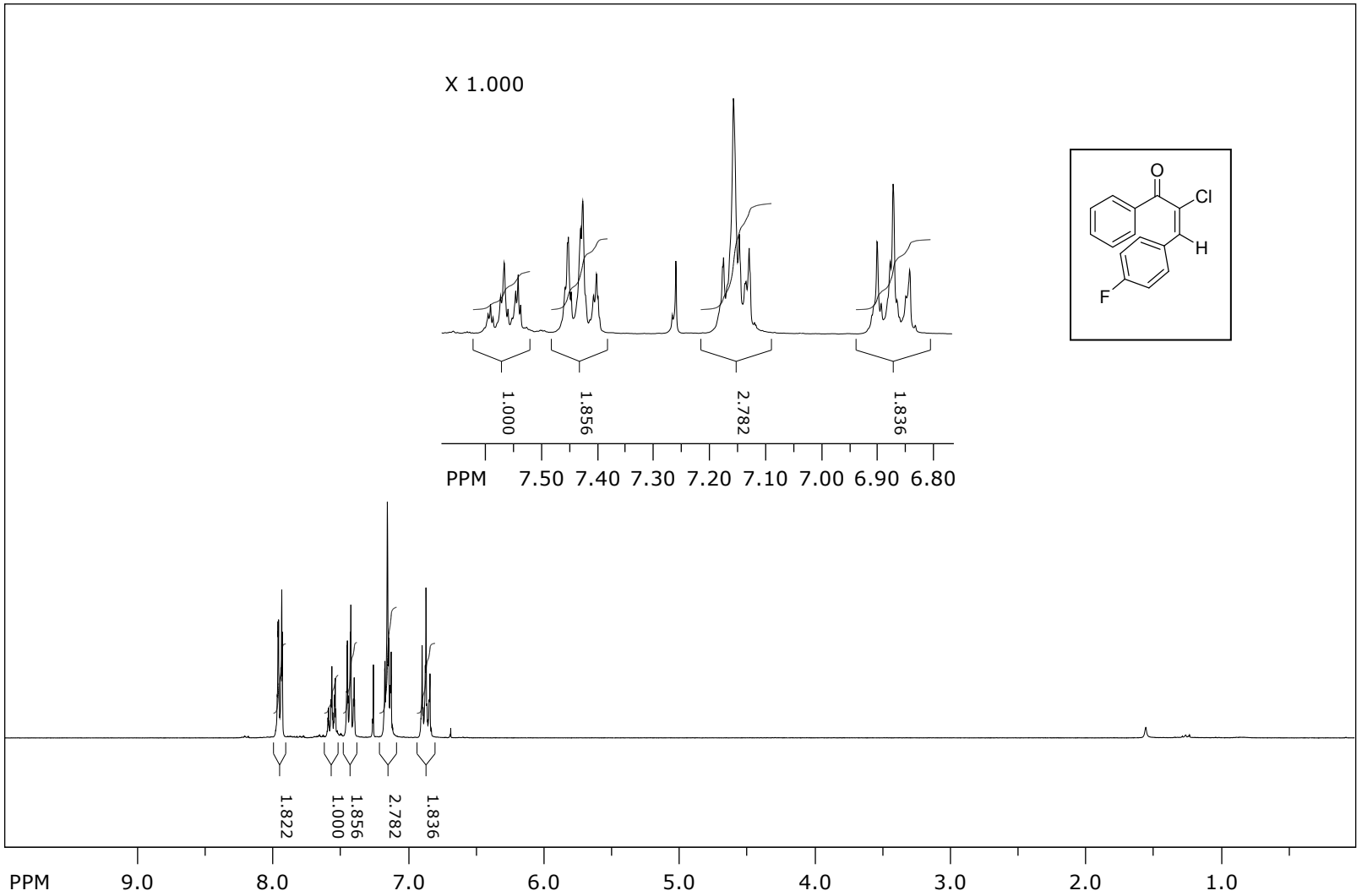
## (E)-2-chloro-3-(phenyl)-1-phenylprop-2-en-1-one (3c) – $^{3}J_{C,H}$




file: D:\NKC_10_phenyltrans\7\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.131346 MHz
time domain size: 4096 points
width: 2495.01 Hz = 8.3131 ppm = 0.609133 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

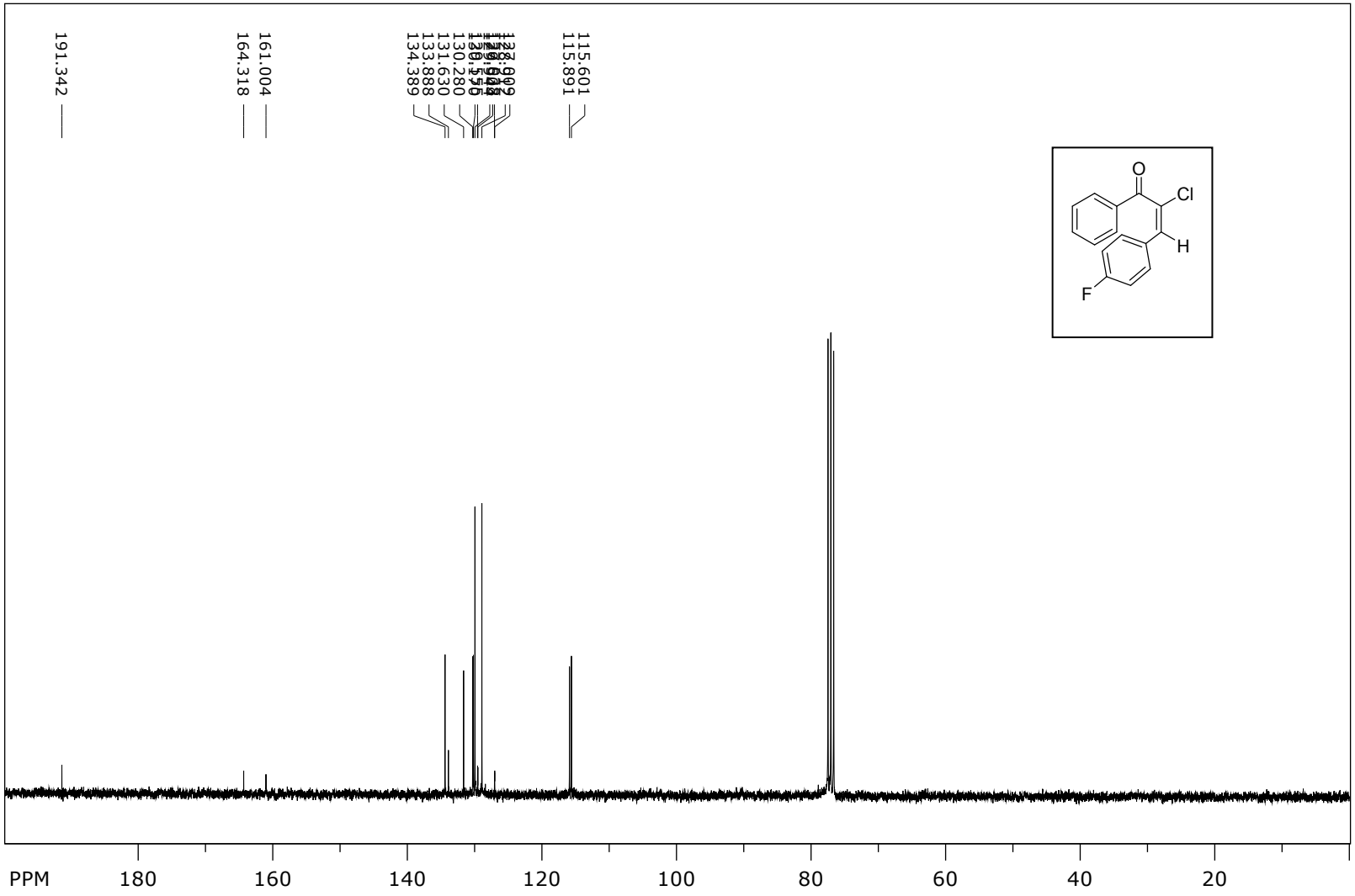
## (E)-2-chloro-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (3d) – $^{1}$H NMR




file: ...:\NMR 300\NKC_9_28_f1_pure_2\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130012 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

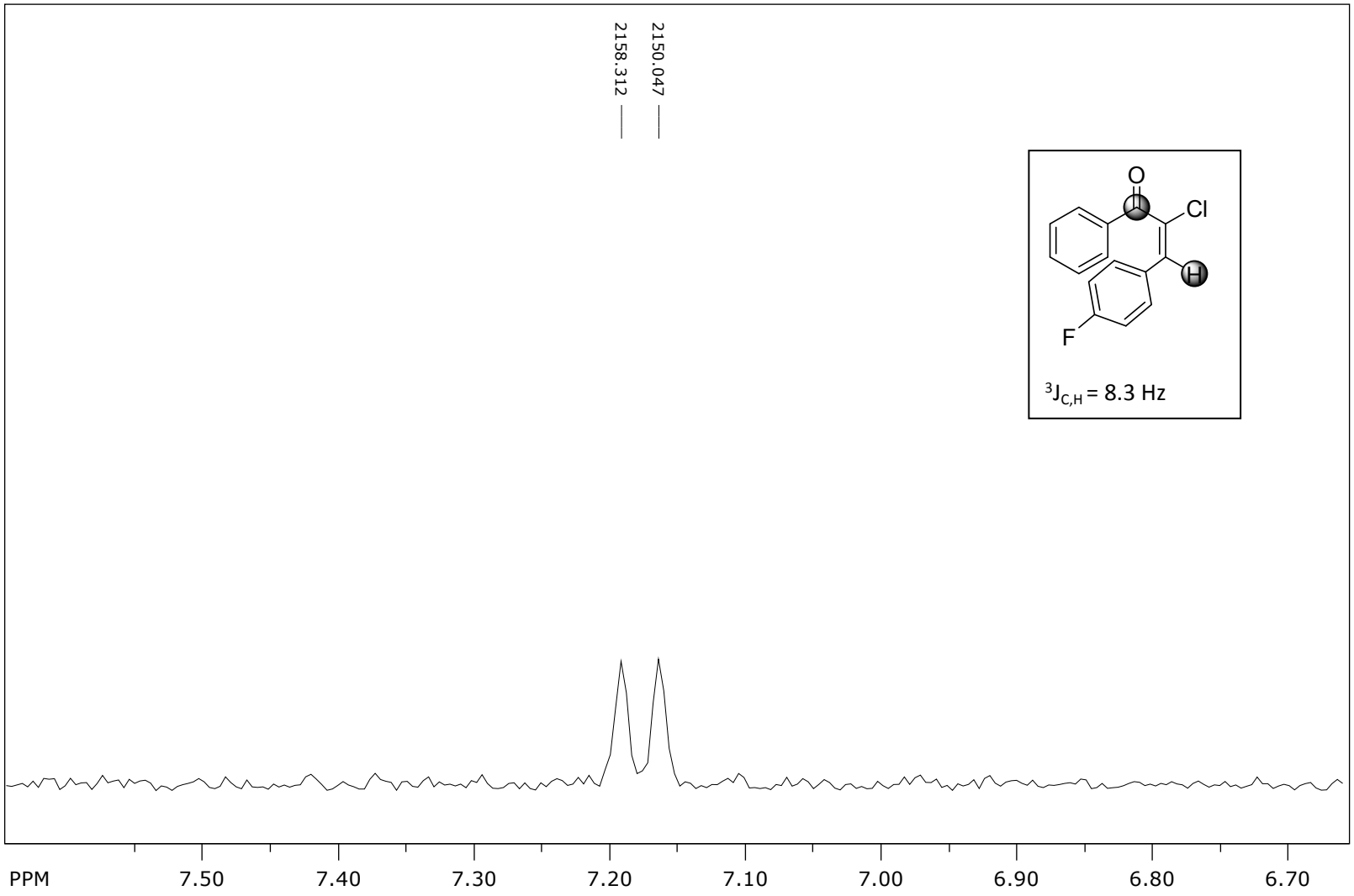
## (E)-2-chloro-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (3d) – $^{13}$C NMR




file: ...:\NMR 300\NKC_9_28_f1_pure_2\9\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 512

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

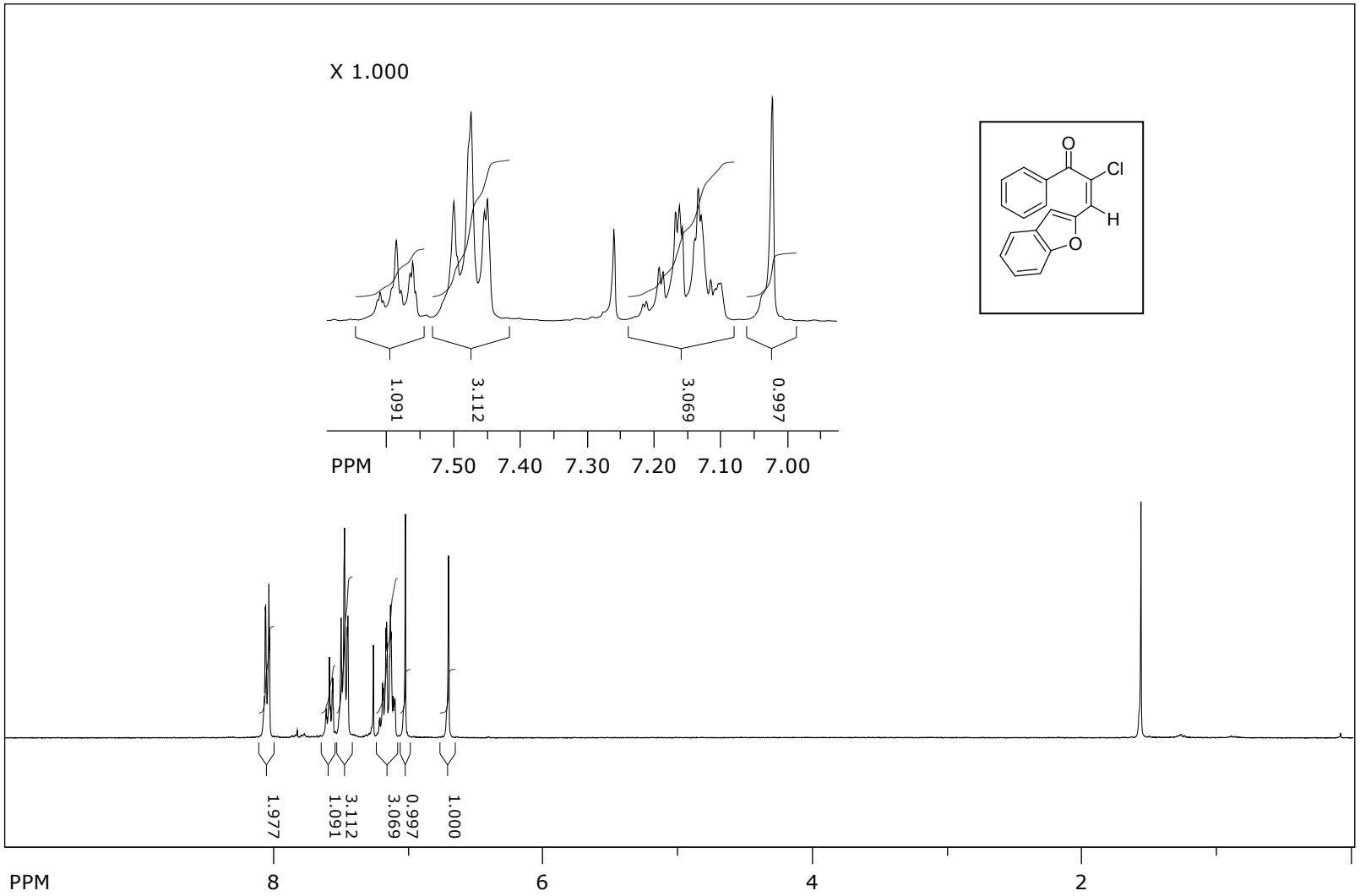
## (E)-2-chloro-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (3d) – $^{3}J_{C,H}$




file: ...:\NMR 300\NKC_9_28_f1_pure_2\4\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.131380 MHz
time domain size: 4096 points
width: 2422.48 Hz = 8.0714 ppm = 0.591426 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

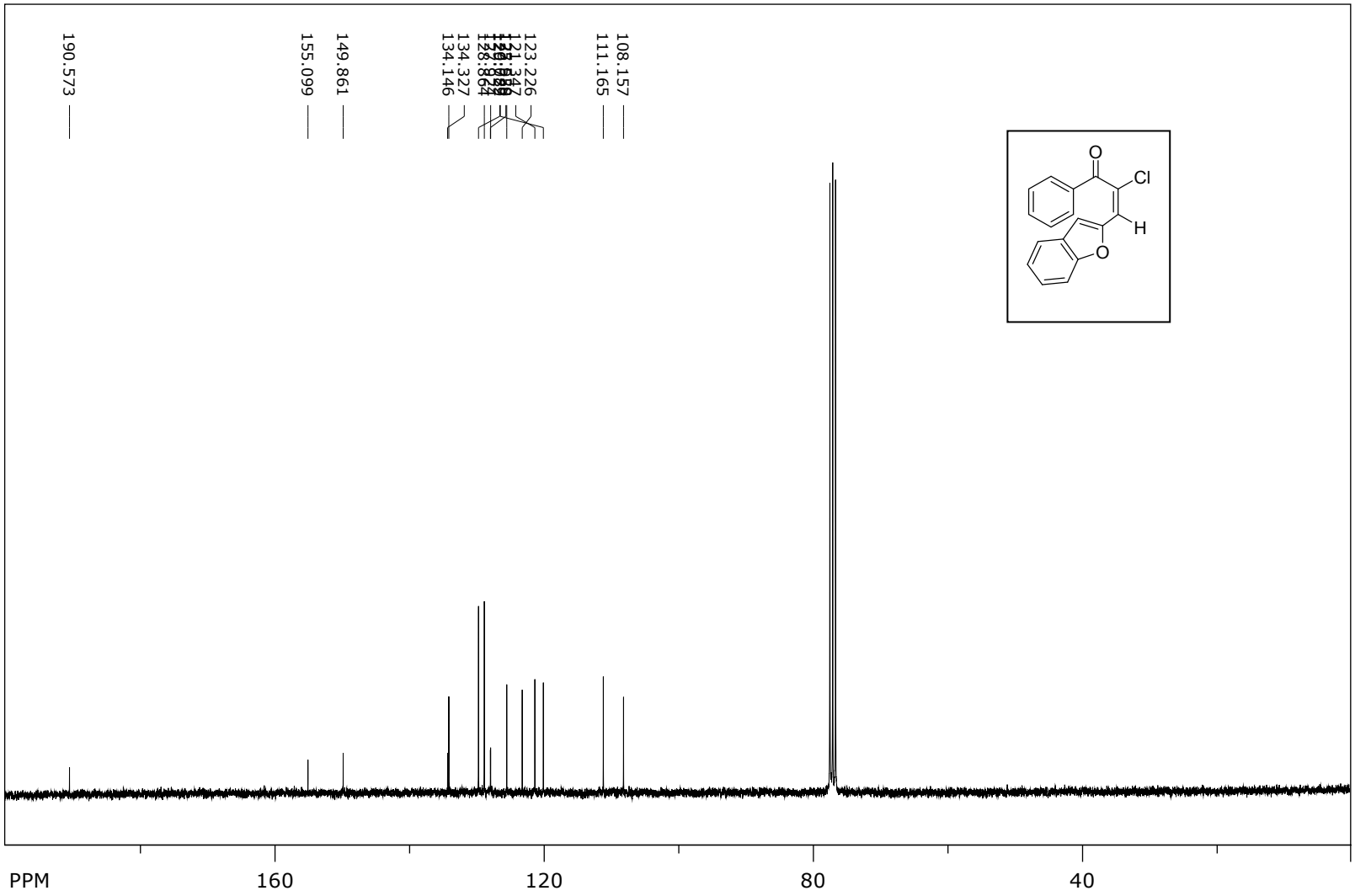
## (2*E*)-3-(Benzofuran-2-yl)-2-chloro-1-phenylprop-2-en-1-one (3f) – $^{1}$H NMR




file: ...:\NMR 300\NKC_10_45_bdftrans\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130012 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

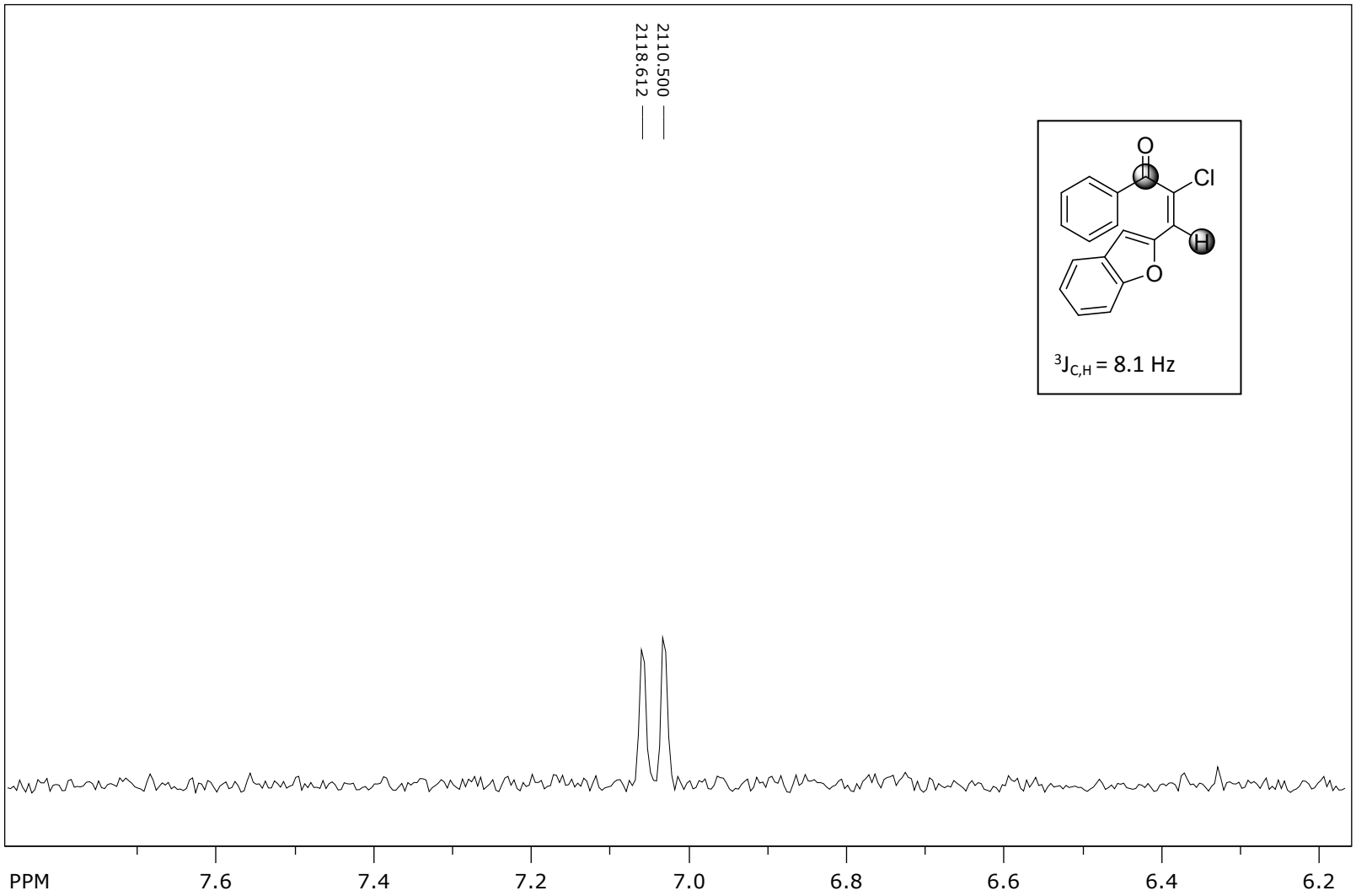
## (2*E*)-3-(Benzofuran-2-yl)-2-chloro-1-phenylprop-2-en-1-one (3f) – $^{13}$C NMR




file: ...:\NMR 300\NKC_10_45_bdftrans\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

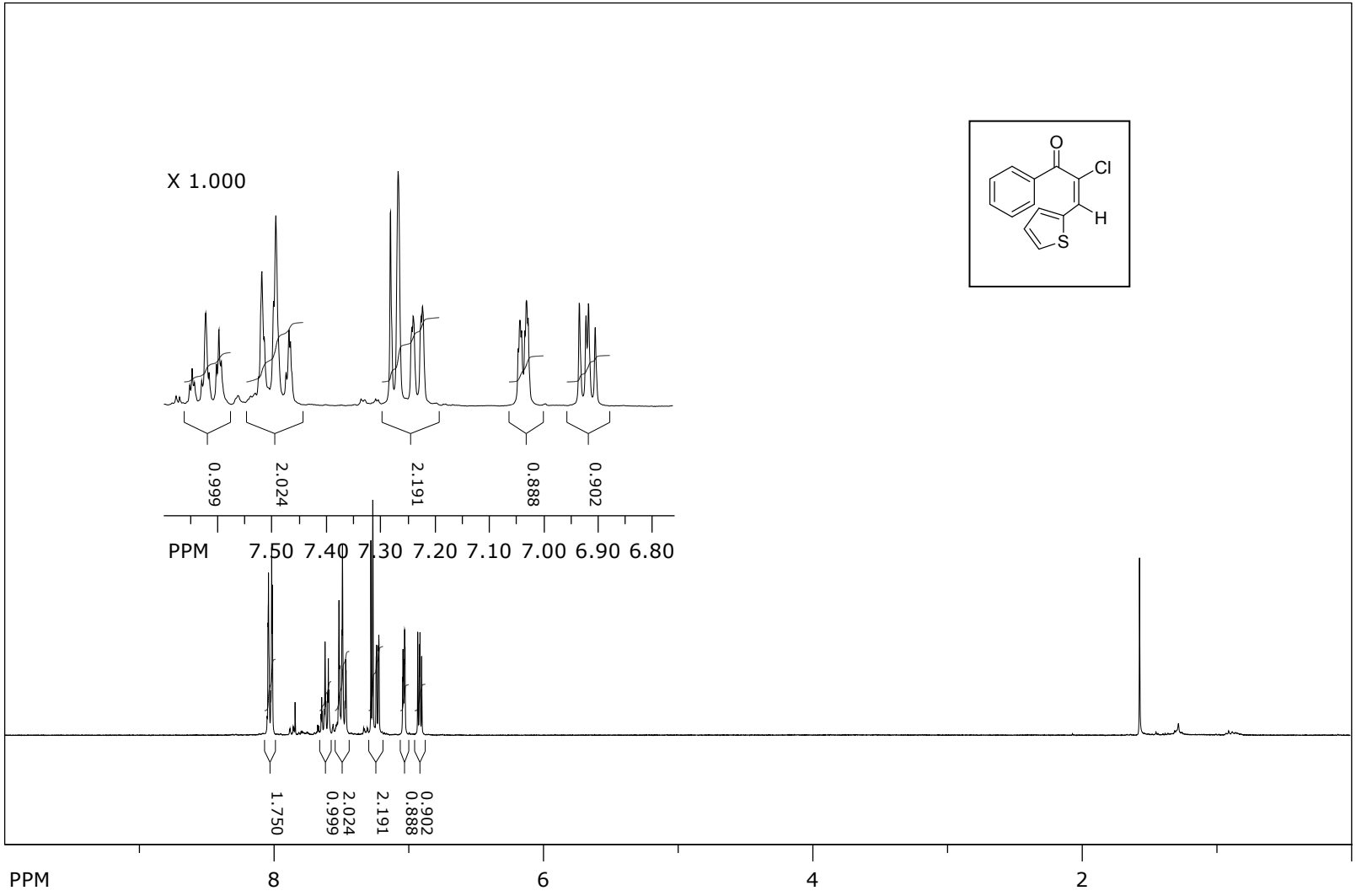
## (2*E*)-3-(Benzofuran-2-yl)-2-chloro-1-phenylprop-2-en-1-one (3f) – $^{3}J_{C,H}$




file: ...:\NMR 300\NKC_10_45_bdftrans\7\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.131418 MHz
time domain size: 4096 points
width: 2367.42 Hz = 7.8880 ppm = 0.577984 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

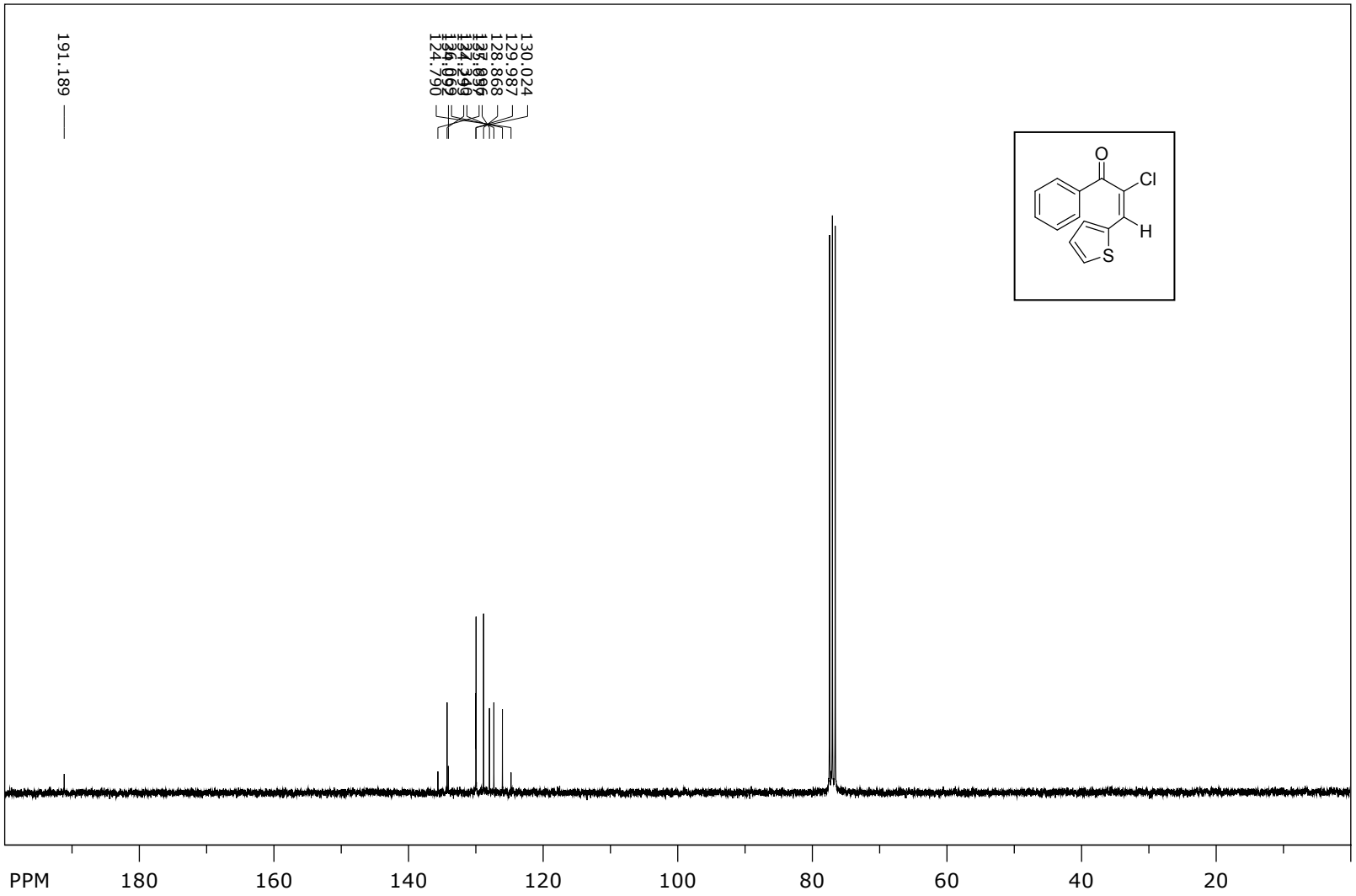
## (E)-2-chloro-3-(2-thienyl)-1-phenylprop-2-en-1-one (3g) – $^{1}$H NMR




file: D:\NKC_10_48_thienyl_trans\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

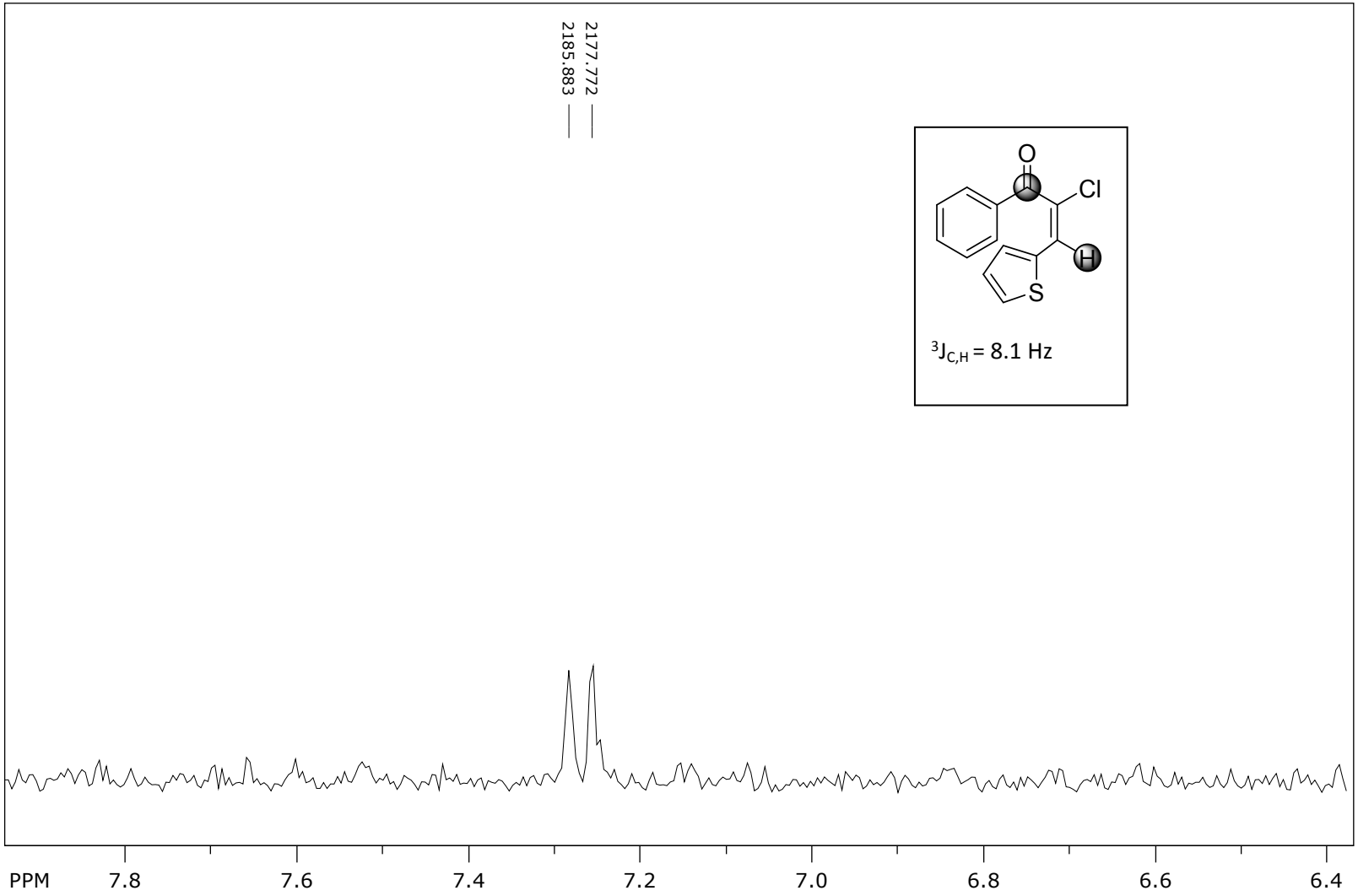
## (E)-2-chloro-3-(2-thienyl)-1-phenylprop-2-en-1-one (3g) – $^{13}$C NMR




file: D:\NKC_10_48_thienyl_trans\3\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

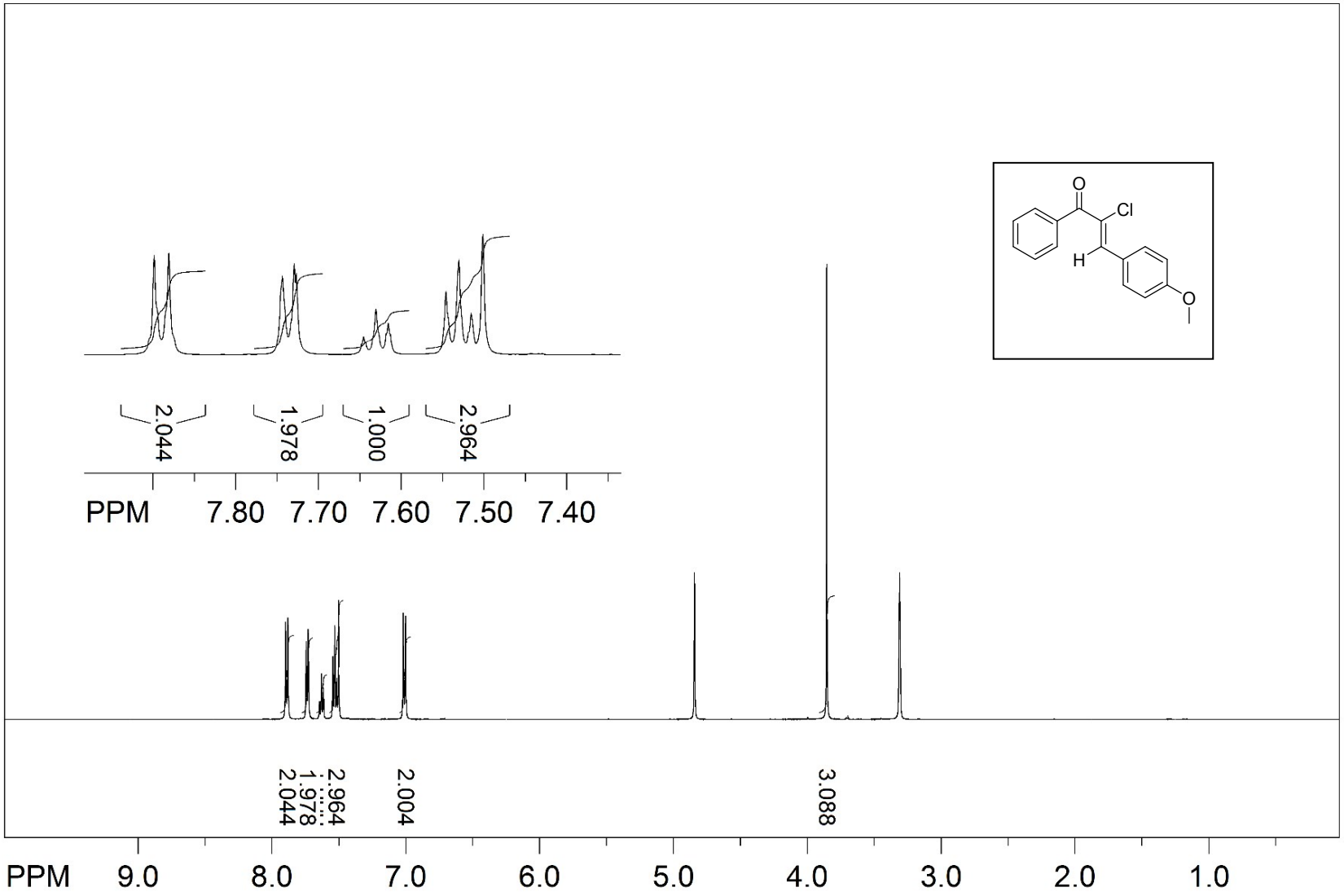
## (E)-2-chloro-3-(2-thienyl)-1-phenylprop-2-en-1-one (3g) – $^{3}J_{C,H}$




file: ... 300\NKC_10_48_thienyl_trans\8\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.131355 MHz
time domain size: 4096 points
width: 2510.04 Hz = 8.3631 ppm = 0.612803 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

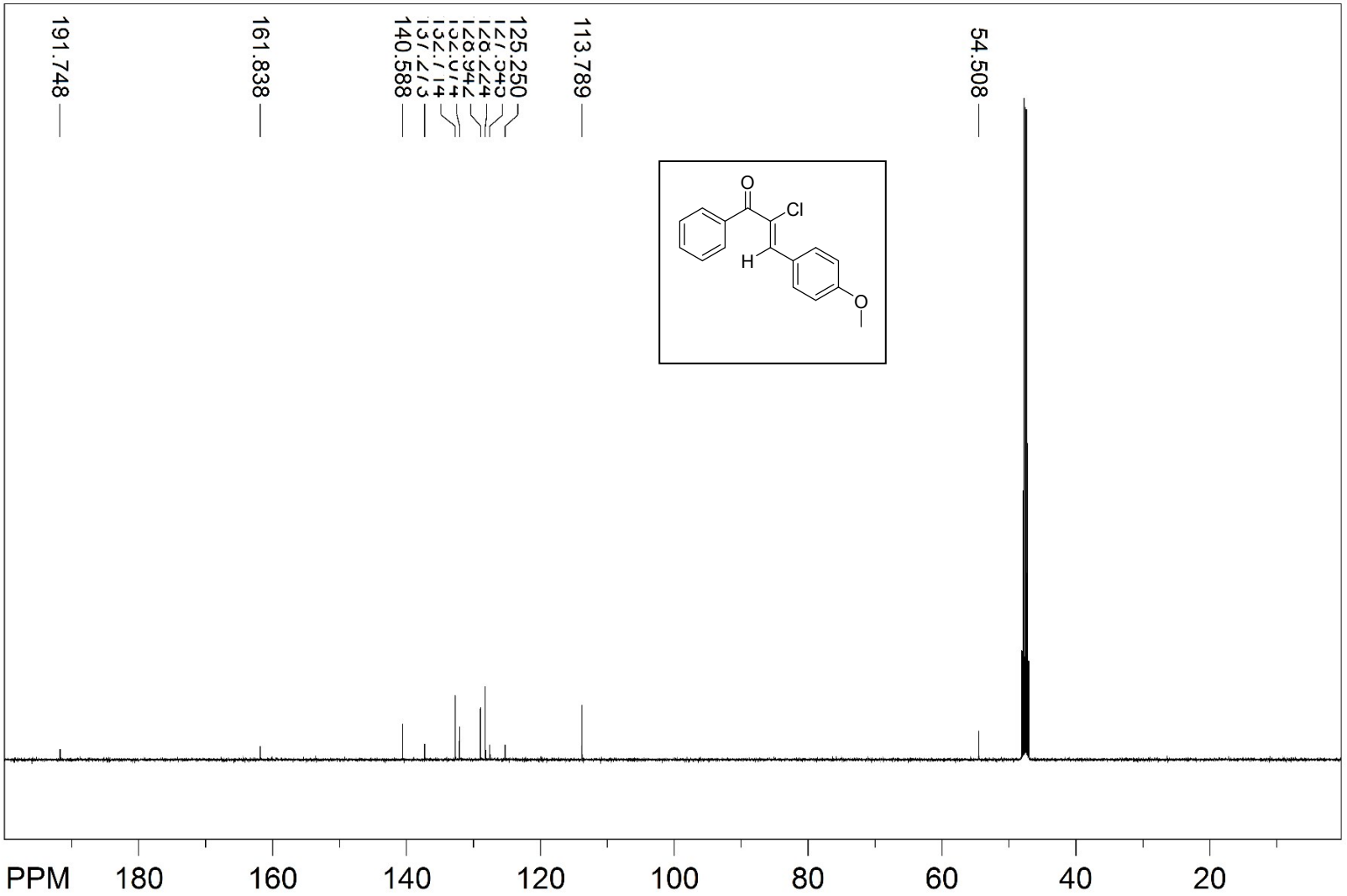
**(Z)-2-chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (4a) – $^{1}$H NMR**




file: ...ers\chehal\Desktop\NKC 12_49\2\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 32

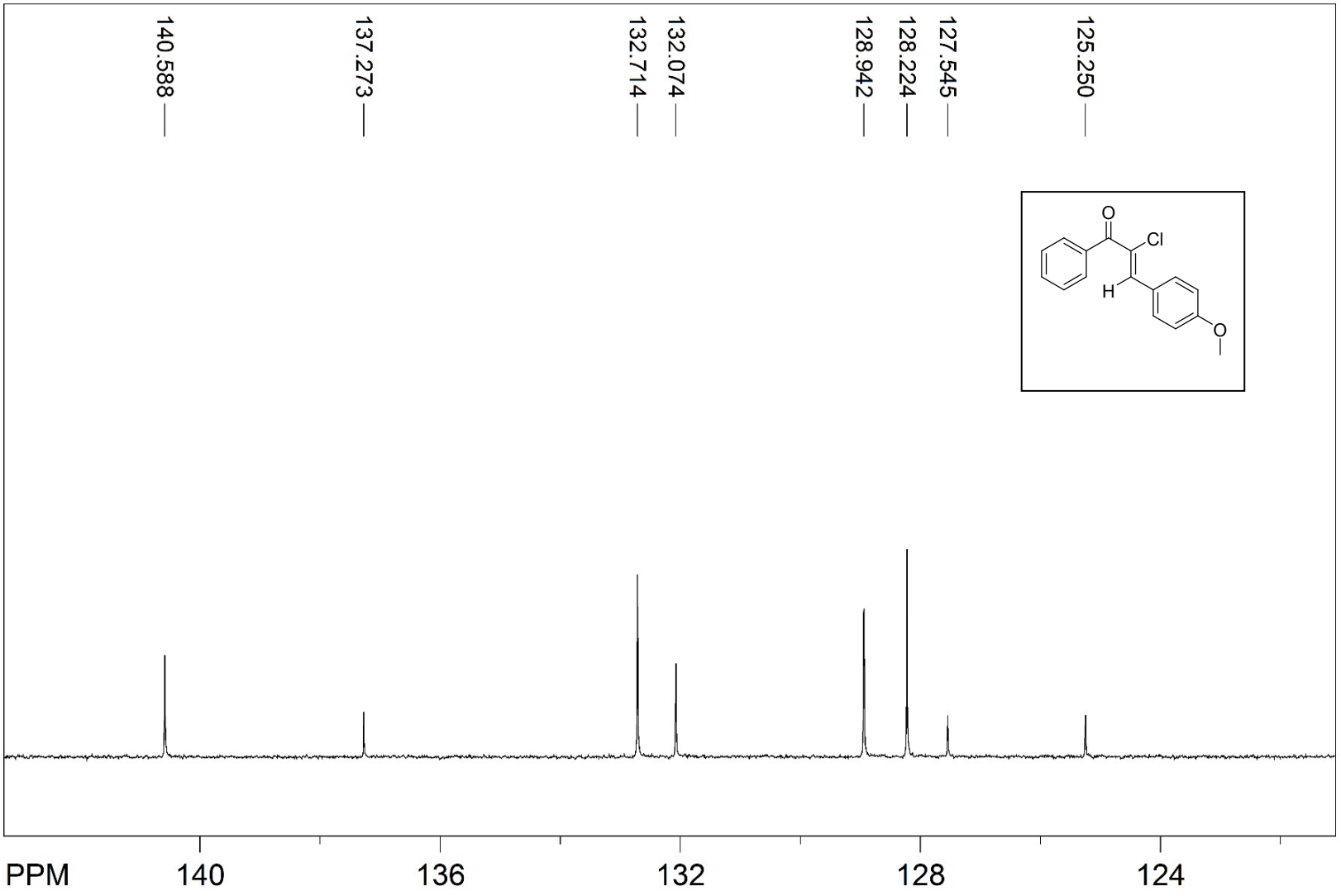
freq of 0 ppm: 500.129994 MHz
processed size: 65536 points
LB: 0.300 GF: 0.0000
Hz/cm: 207.827 ppm/cm: 0.41554

## (Z)-2-chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (4a) – $^{13}$C NMR




file: ...ers\chehal\Desktop\NKC 12 49\1\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.90 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 1024

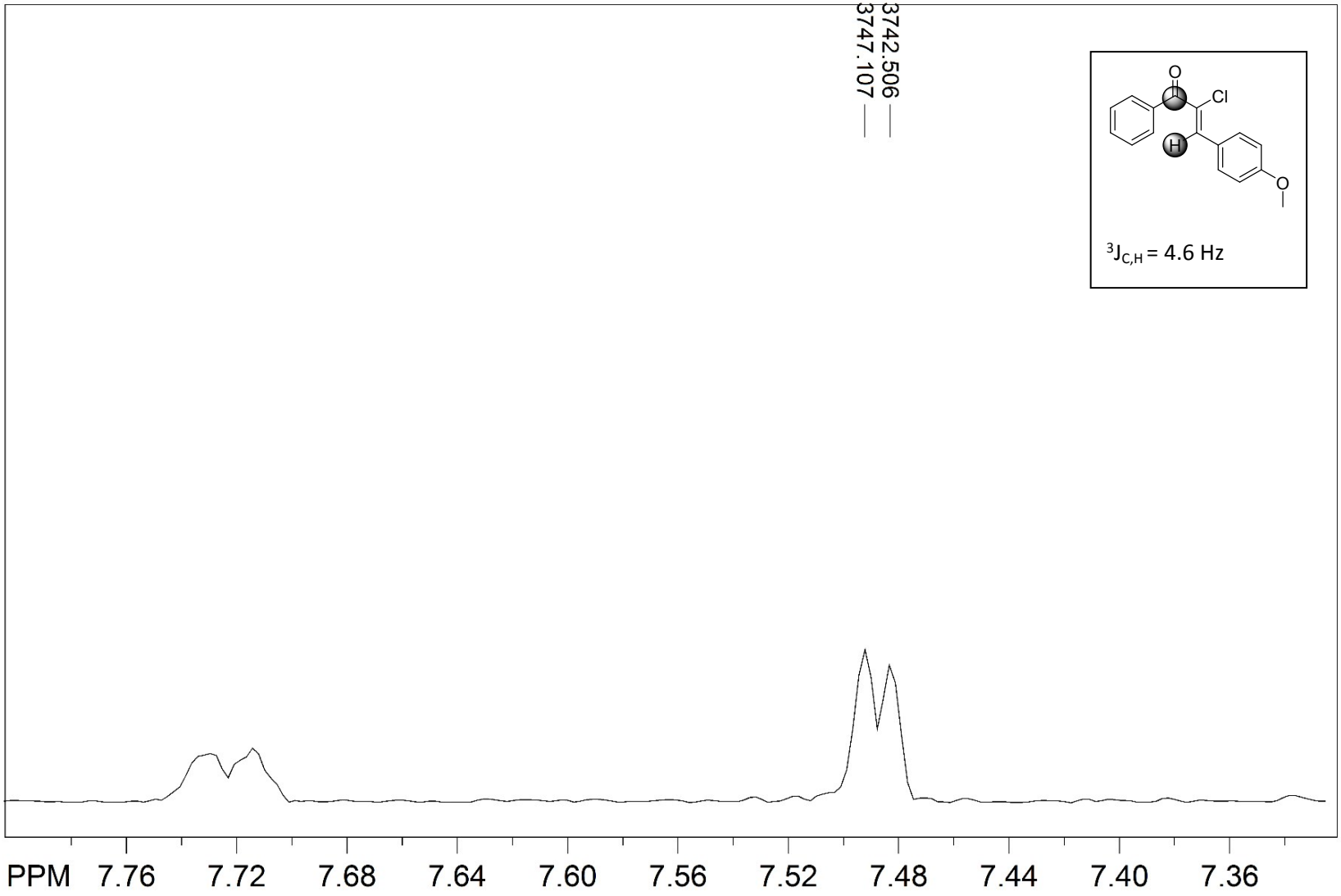
freq of 0 ppm: 125.757789 MHz
processed size: 32768 points
LB: 1.000 GF: 0.0000
Hz/cm: 1046.148 ppm/cm: 8.31792




file: ...ers\chehal\Desktop\NKC_12_49\1\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.90 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 1024

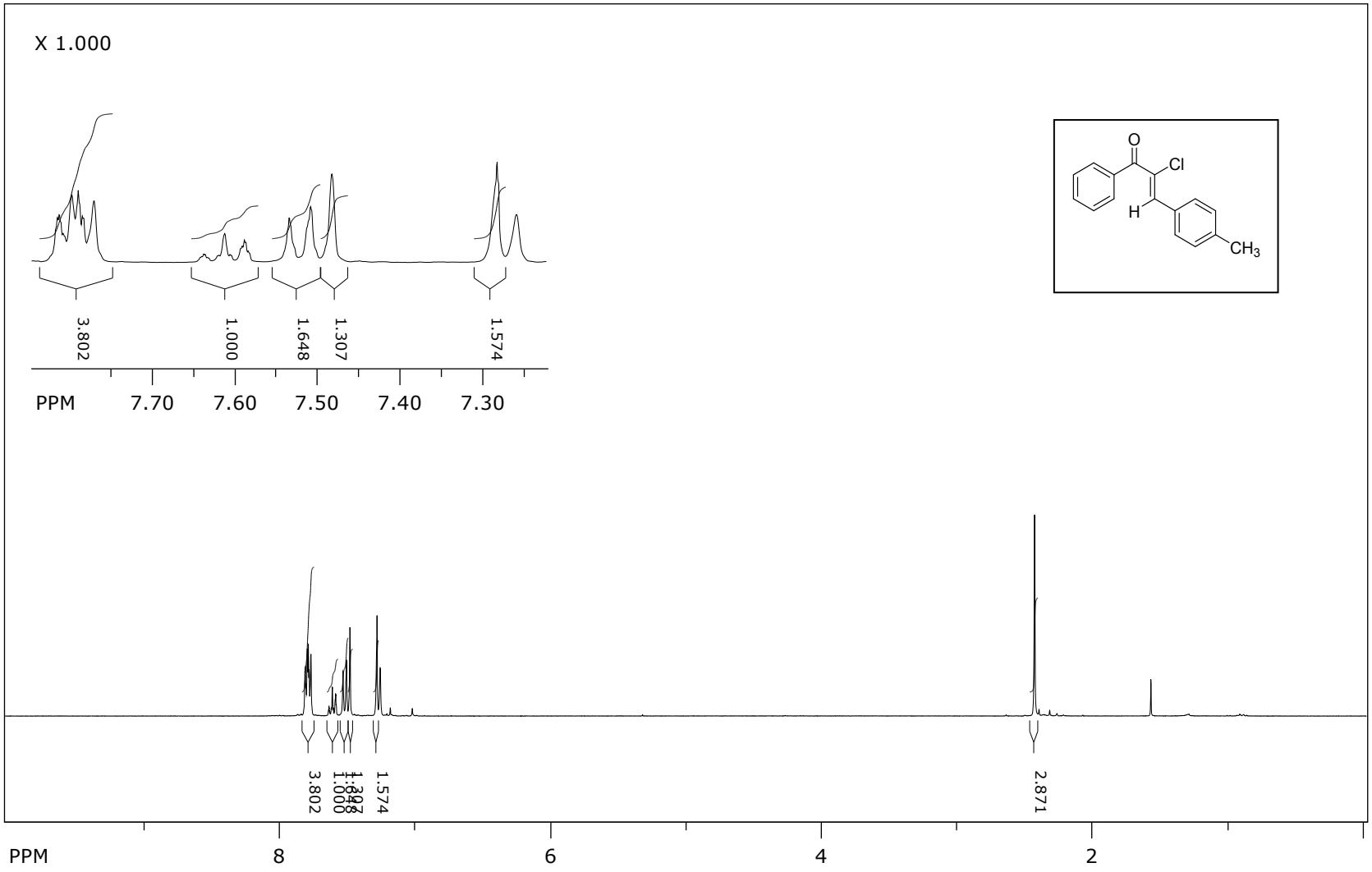
freq of 0 ppm: 125.757789 MHz
processed size: 32768 points
LB: 1.000 GF: 0.0000
Hz/cm: 116.239 ppm/cm: 0.92421

**(Z)-2-chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-one (4a) – $^{3}J_{CH}$**




file: ...ers\chehal\Desktop\NKC_12_49\3\ser expt: <hmbcgplpndqfreq of 0 ppm: 500.130000 MHz
transmitter freq.: 500.132751 MHz processed size: 4096 points
time domain size: 4096 points LB: 0.000 GF: 0.0000
width: 4504.51 Hz = 9.0066 ppm = 1.099733 Hz/pt Hz/cm: 10.065 ppm/cm: 0.02012
number of scans: 8

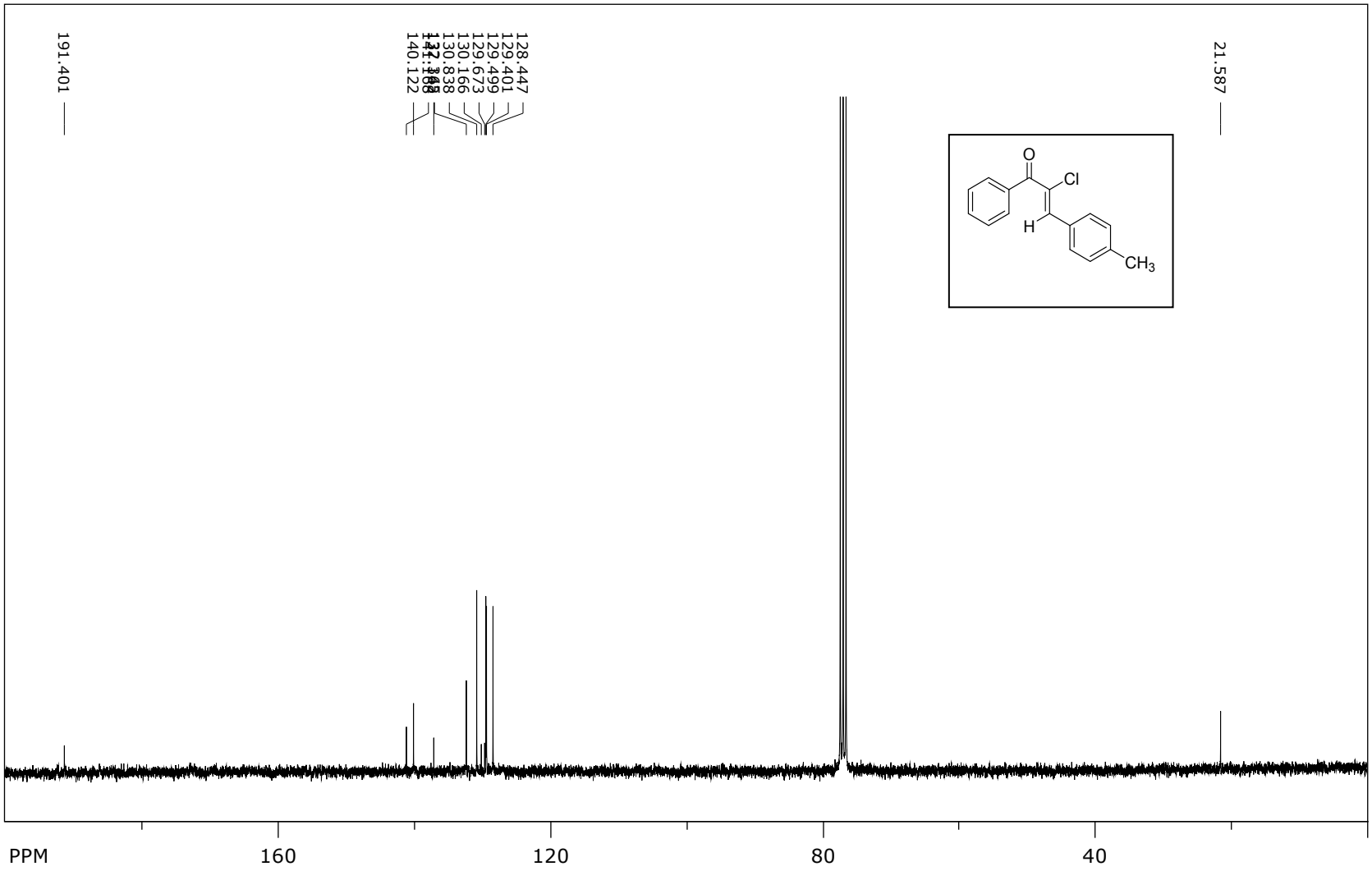
# (Z)-2-chloro-3-(4-methylphenyl)-1-phenylprop-2-en-1-one (4b) – $^{1}$H NMR




file: D:\NKC_10_21_methyl_3\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

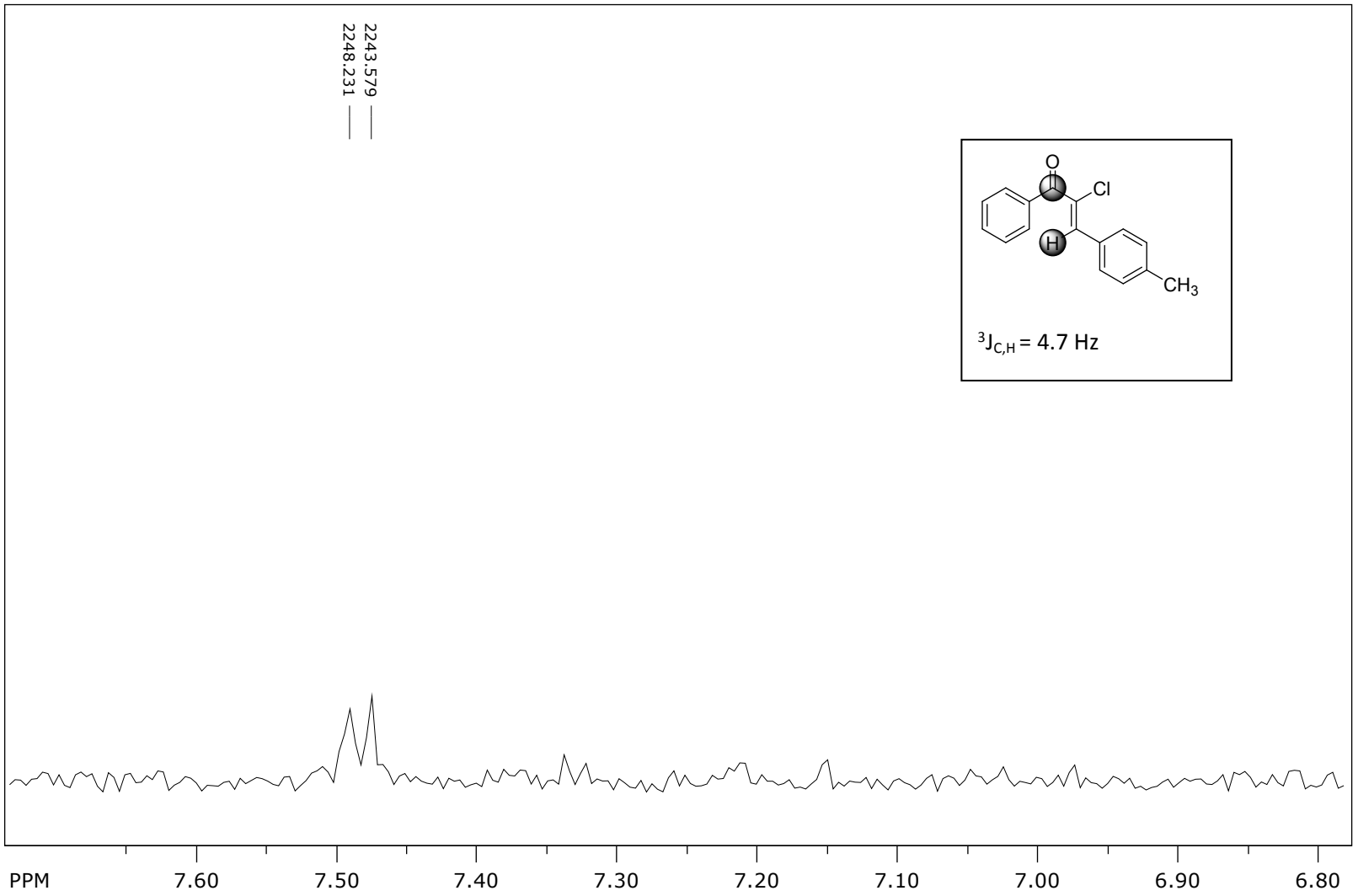
## (Z)-2-chloro-3-(4-methylphenyl)-1-phenylprop-2-en-1-one (4b) – $^{13}$C NMR




file: D:\NKC_10_21_methyl_3\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

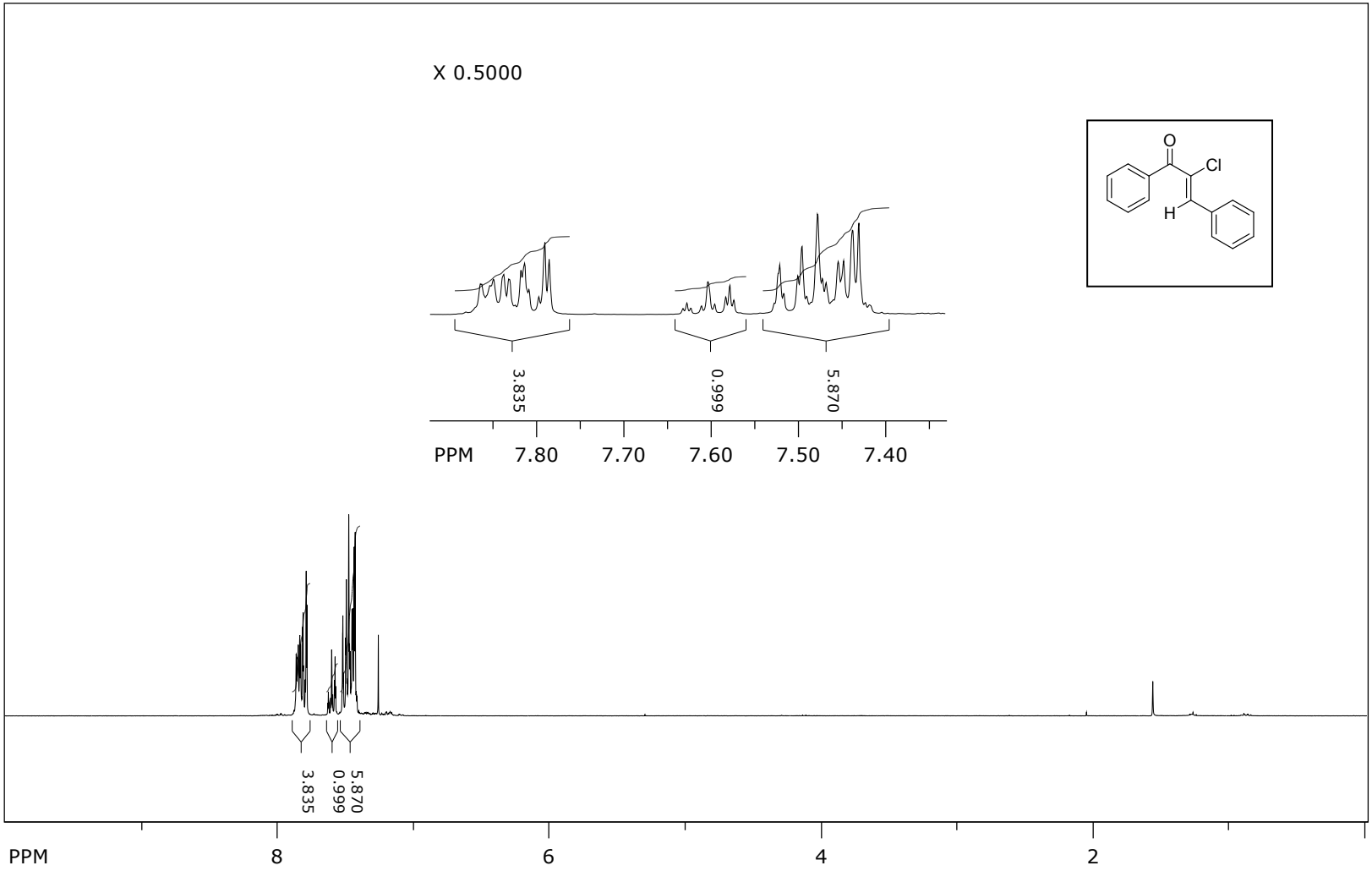
## (Z)-2-chloro-3-(4-methylphenyl)-1-phenylprop-2-en-1-one (4b) – $^{3}J_{CH}$




file: D:\NKC_10_21_methyl_3\3\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.131323 MHz
time domain size: 4096 points
width: 2408.48 Hz = 8.0247 ppm = 0.588007 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

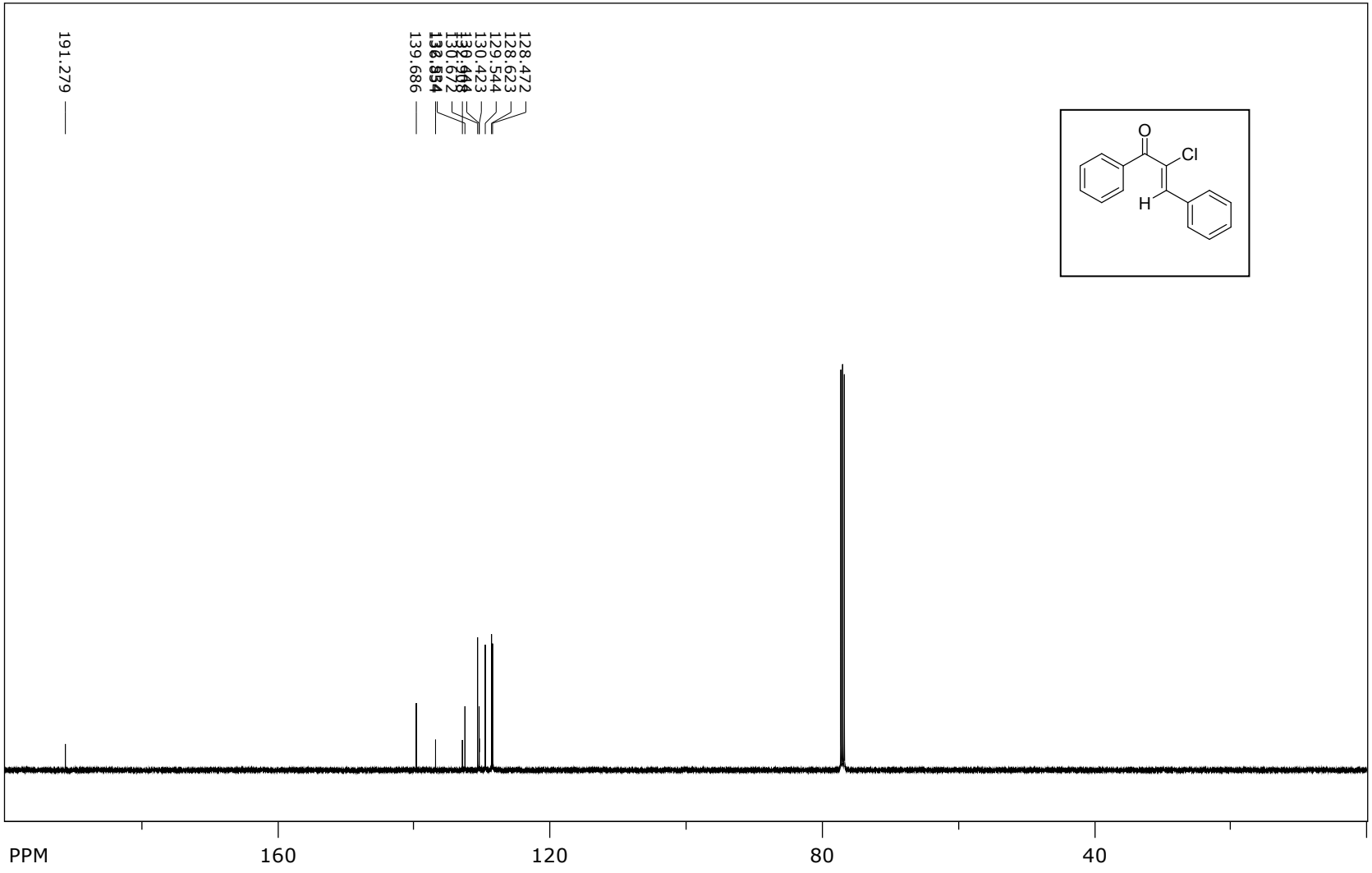
# (Z)-2-chloro-3-(phenyl)-1-phenylprop-2-en-1-one (4c) – $^{1}$H NMR




file: D:\NMR 300\NKC_10_22_phenyl\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130012 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

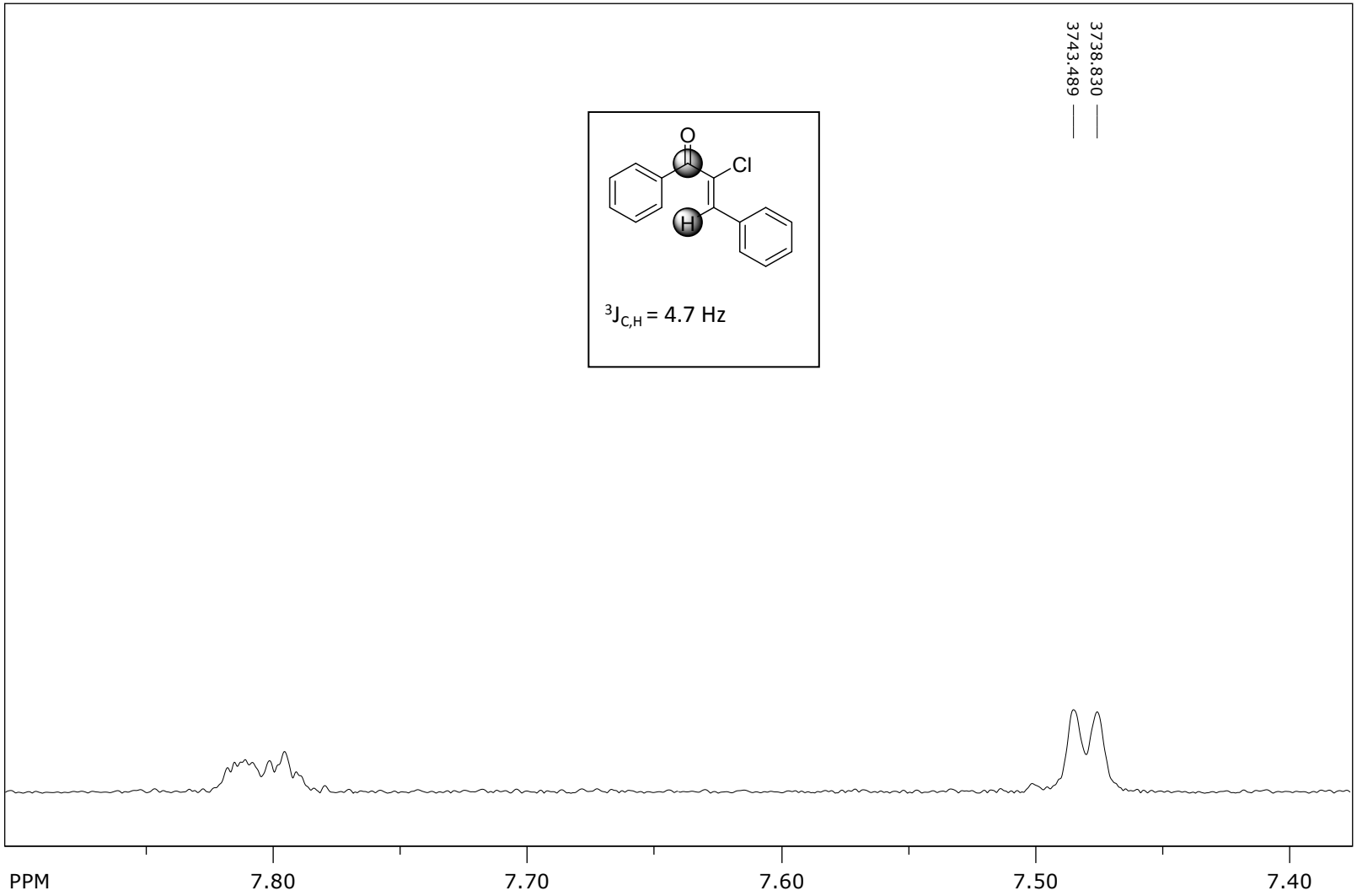
## (Z)-2-chloro-3-(phenyl)-1-phenylprop-2-en-1-one (4c) – $^{13}$C NMR




file: ...C_10_phenyl_longerrelaxdelay\2\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.90 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 323

freq. of 0 ppm: 125.757789 MHz
processed size: 65536 complex points
LB: 1.000 GF: 0.0000

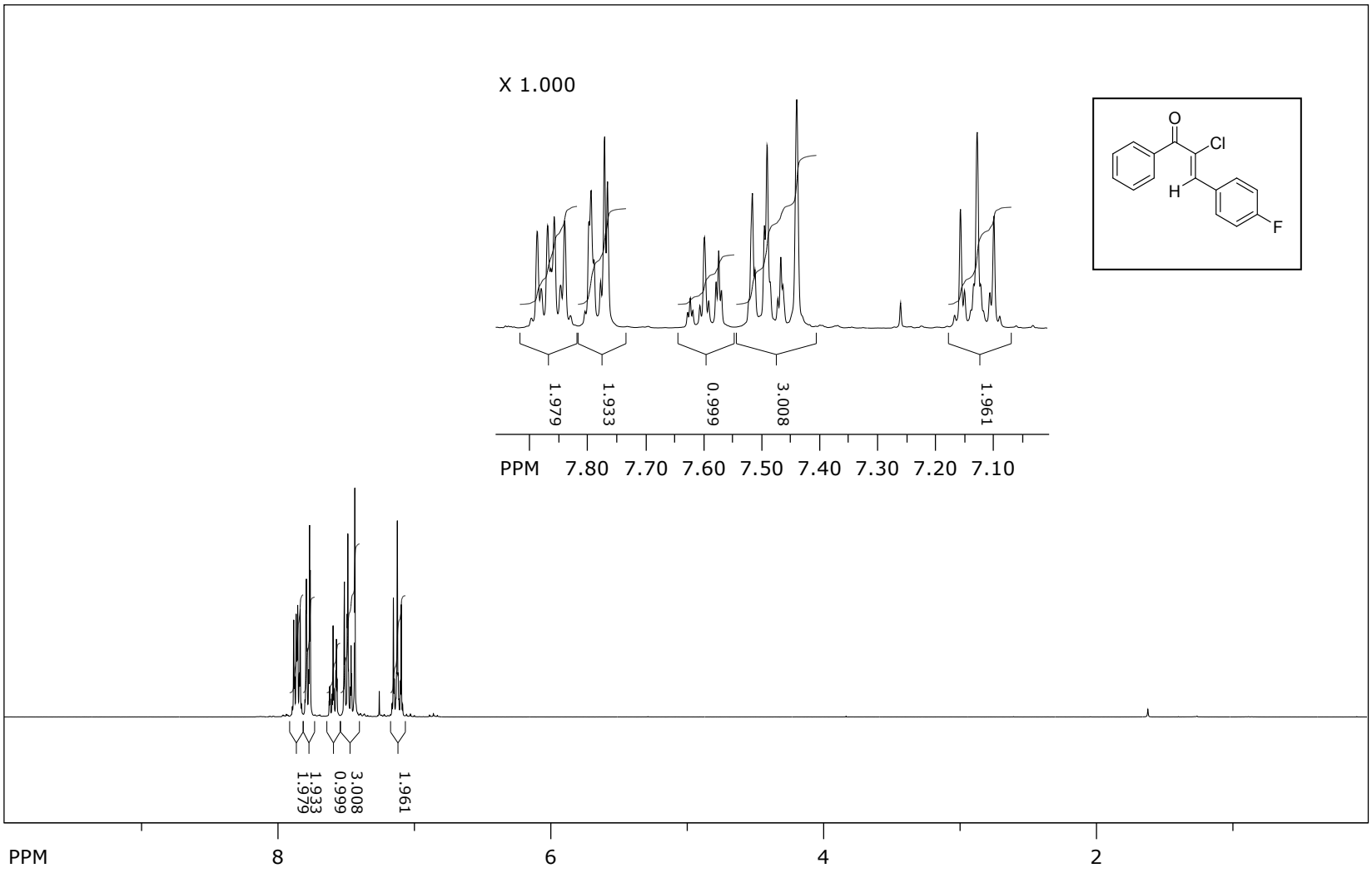
## (Z)-2-chloro-3-(phenyl)-1-phenylprop-2-en-1-one (4c) – $^{3}J_{CH}$




file: ...C_10_phenyl_longerrelaxdelay\3\ser expt: <hmbcgplpndqf>
transmitter freq.: 500.133821 MHz
time domain size: 824 points
width: 265.11 Hz = 0.5301 ppm = 0.321737 Hz/pt
number of scans: 4

freq. of 0 ppm: 500.130000 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

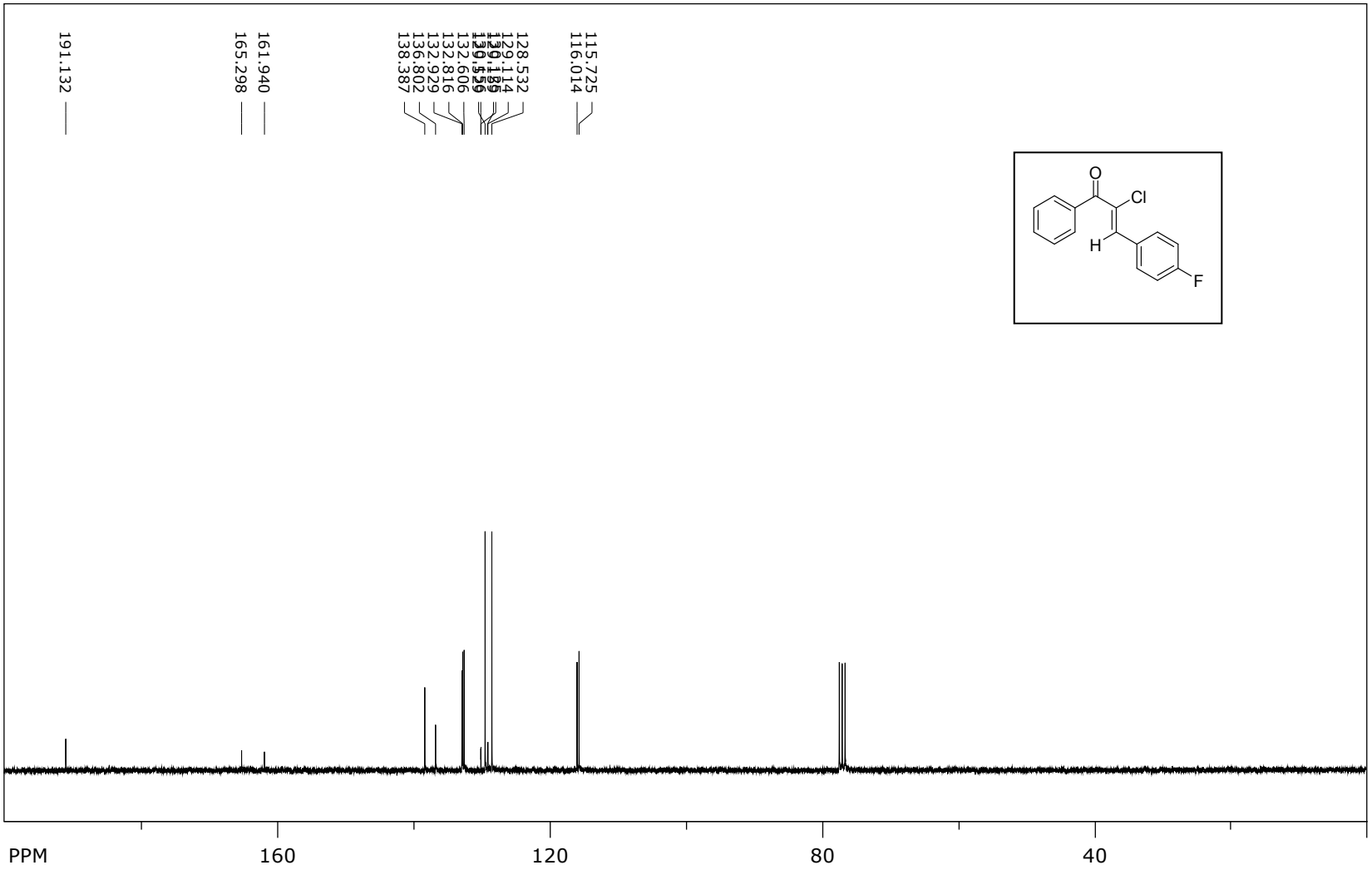
## (2*Z*)-2-Chloro-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (4d) – $^{1}$H NMR




file: D:\NKC_10_23_pfluoro2\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130012 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

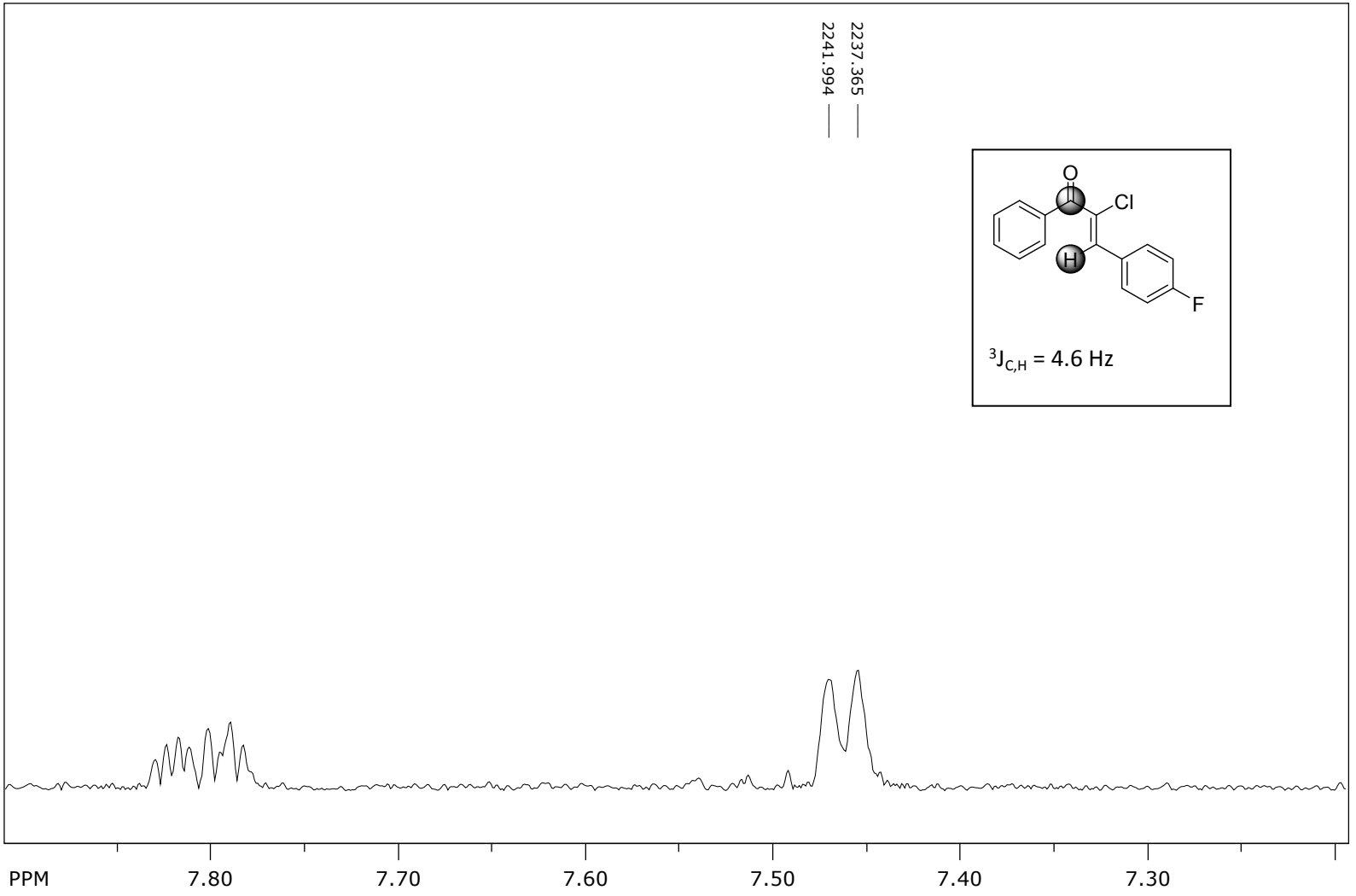
## (2*Z*)-2-Chloro-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (4d) – $^{13}$C NMR




file: D:\NKC_10_23_pfluoro2\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 128

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

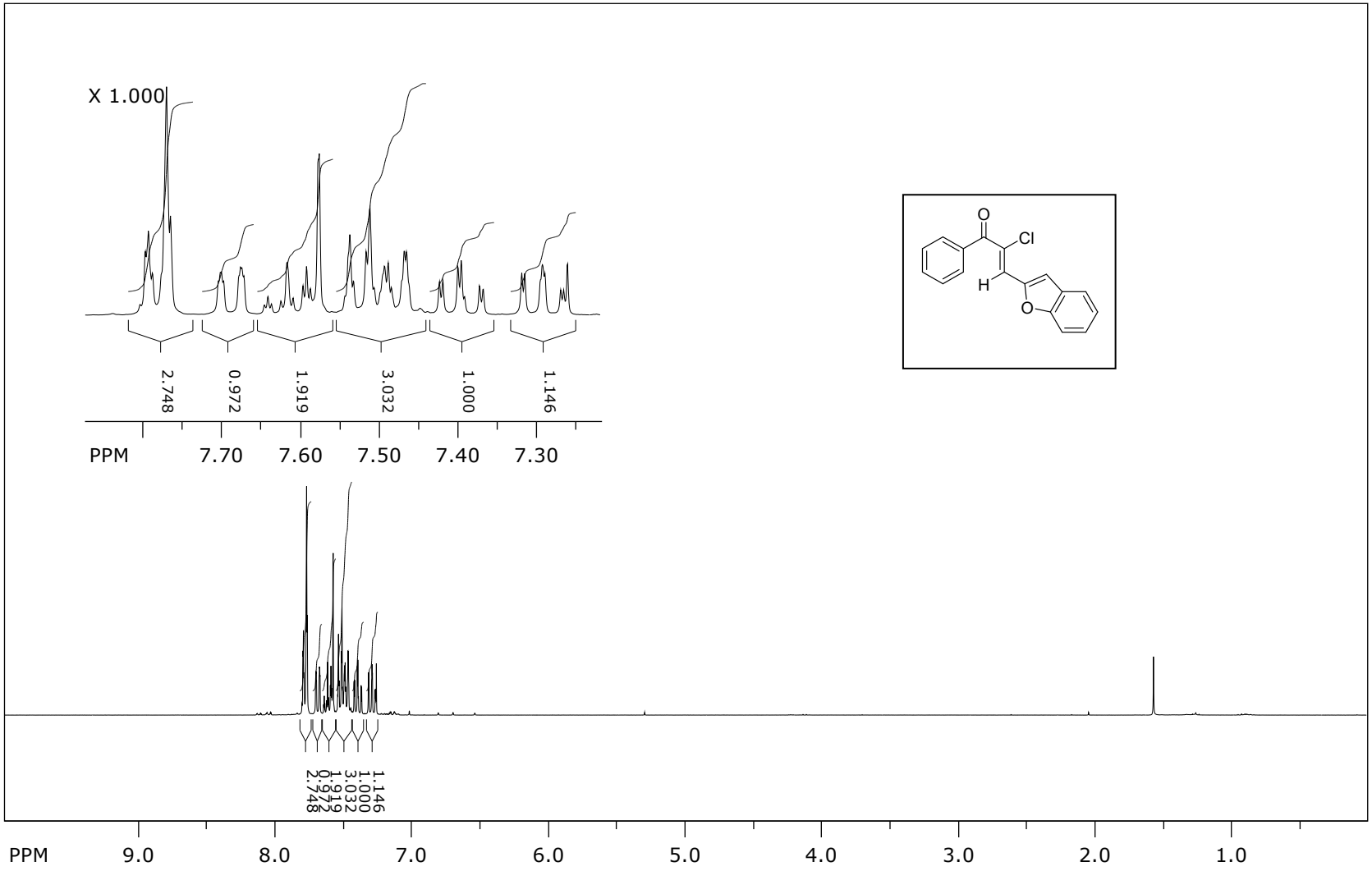
## (2*Z*)-2-Chloro-3-(4-fluorophenyl)-1-phenylprop-2-en-1-one (4d) – $^{3}J_{CH}$




file: D:\NKC_10_23_pfluoro2\4\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.132259 MHz
time domain size: 2008 points
width: 524.33 Hz = 1.7470 ppm = 0.261120 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

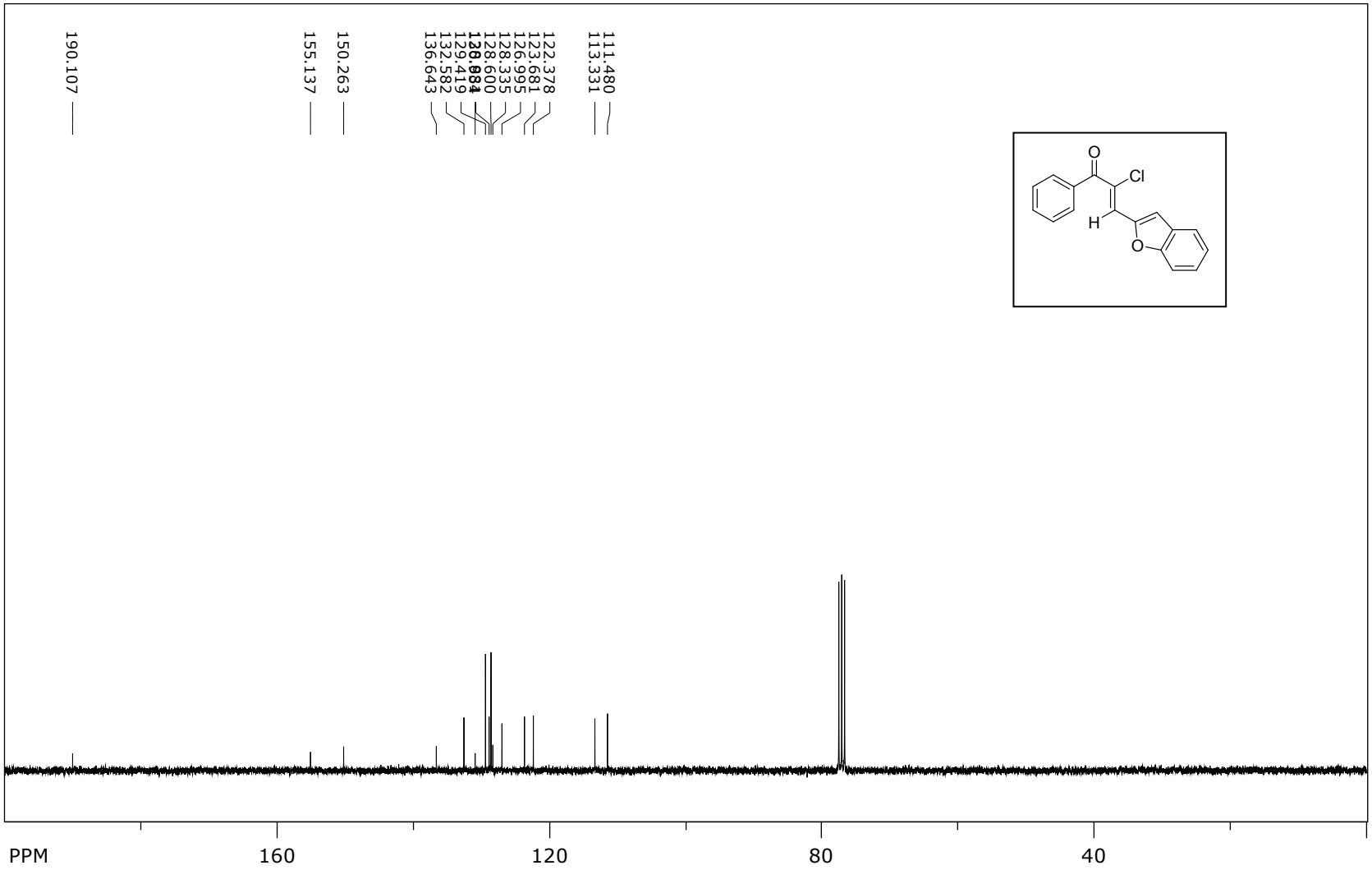
## (2*Z*)-3-(Benzofuran-2-yl)-2-chloro-1-phenylprop-2-en-1-one (4f) – $^{1}$H NMR




file: D:\NKC_10_benzofurancis\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130012 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

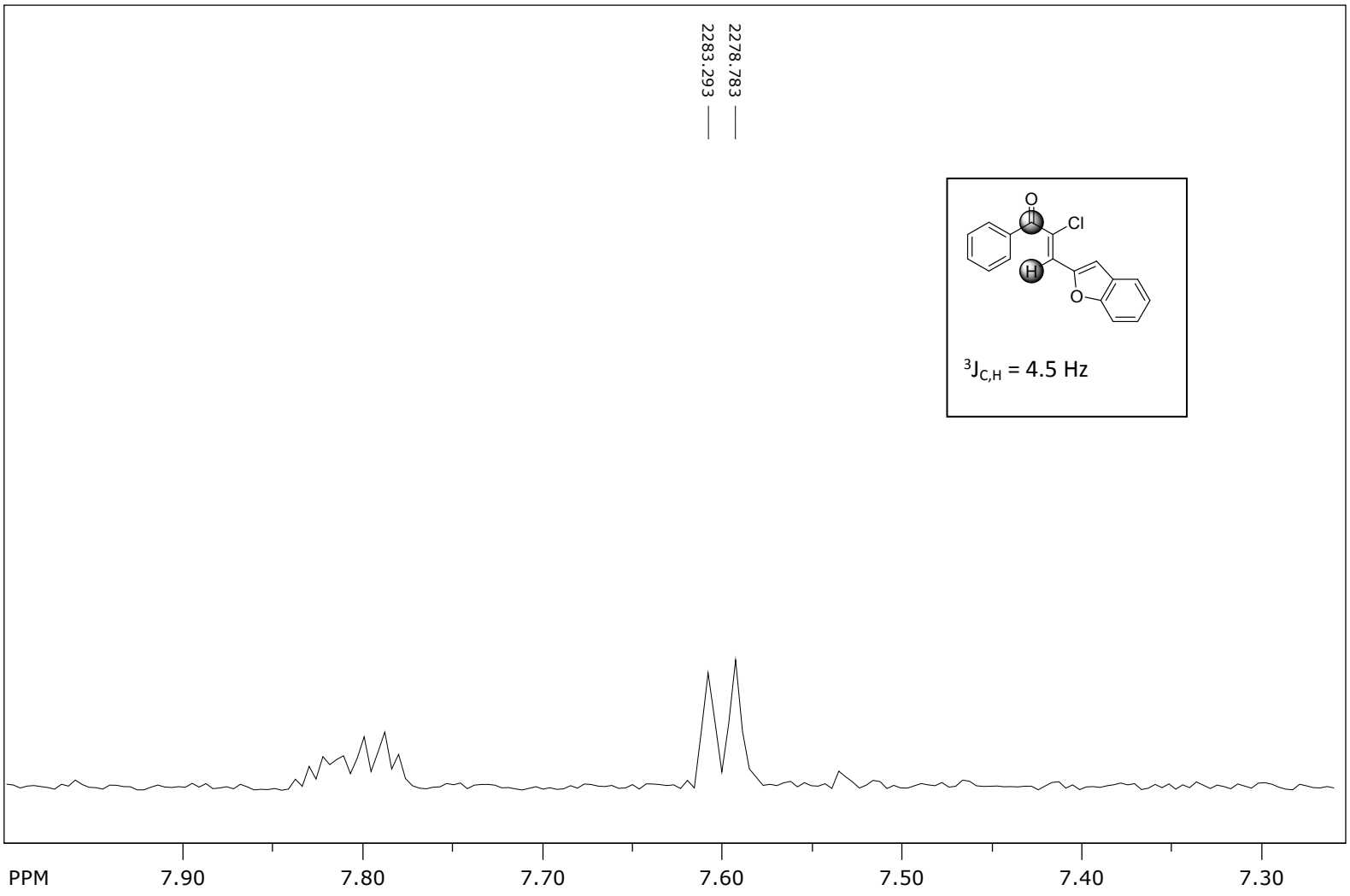
## (2*Z*)-3-(Benzofuran-2-yl)-2-chloro-1-phenylprop-2-en-1-one (4f) – $^{13}$C NMR




file: D:\NKC_10_benzofurancis\2\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 128

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

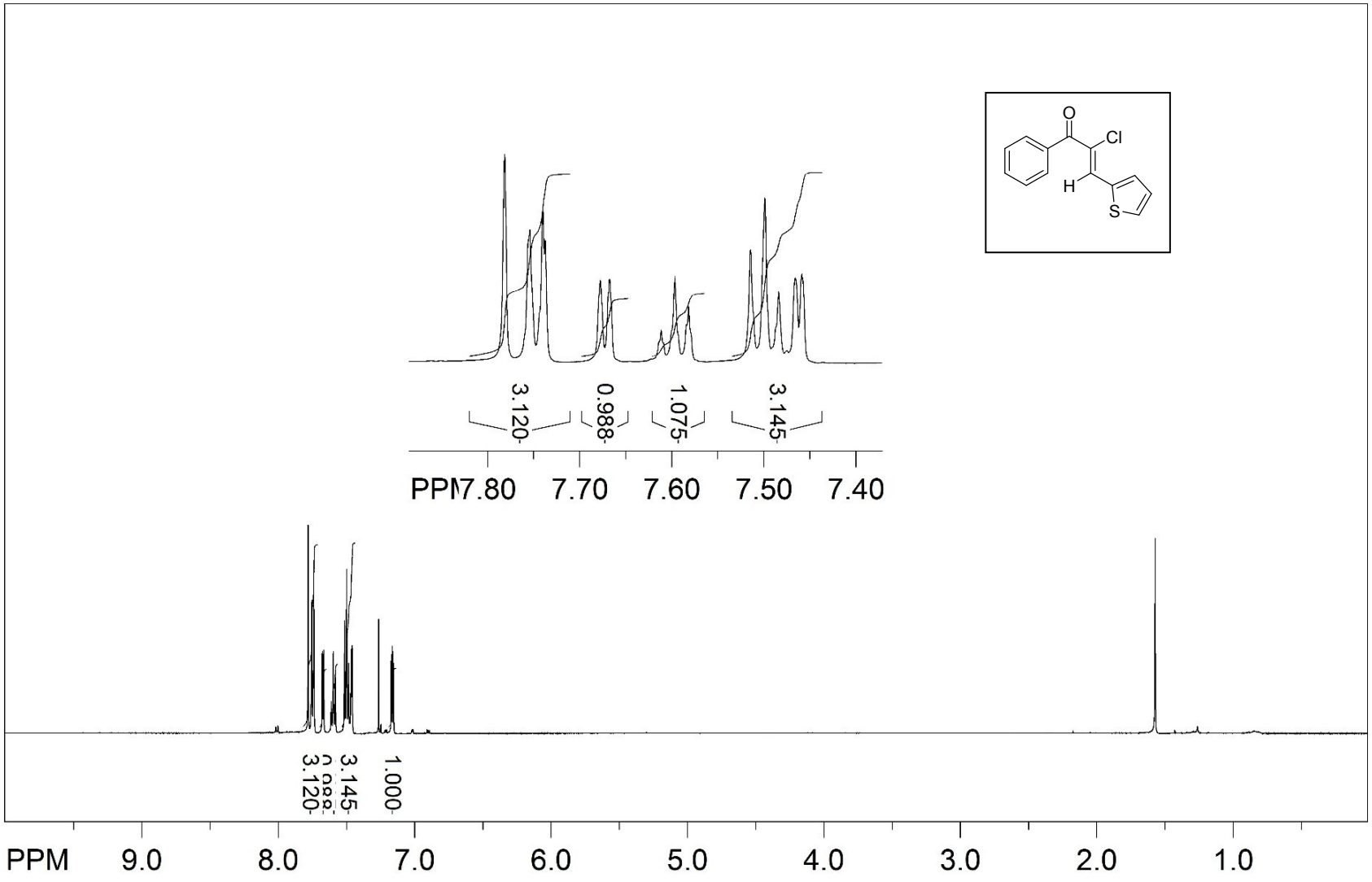
## (2*Z*)-3-(Benzofuran-2-yl)-2-chloro-1-phenylprop-2-en-1-one (4f) – $^{3}J_{CH}$




file: D:\NKC_10_benzofurancis\3\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.131417 MHz
time domain size: 4096 points
width: 2354.05 Hz = 7.8434 ppm = 0.574719 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

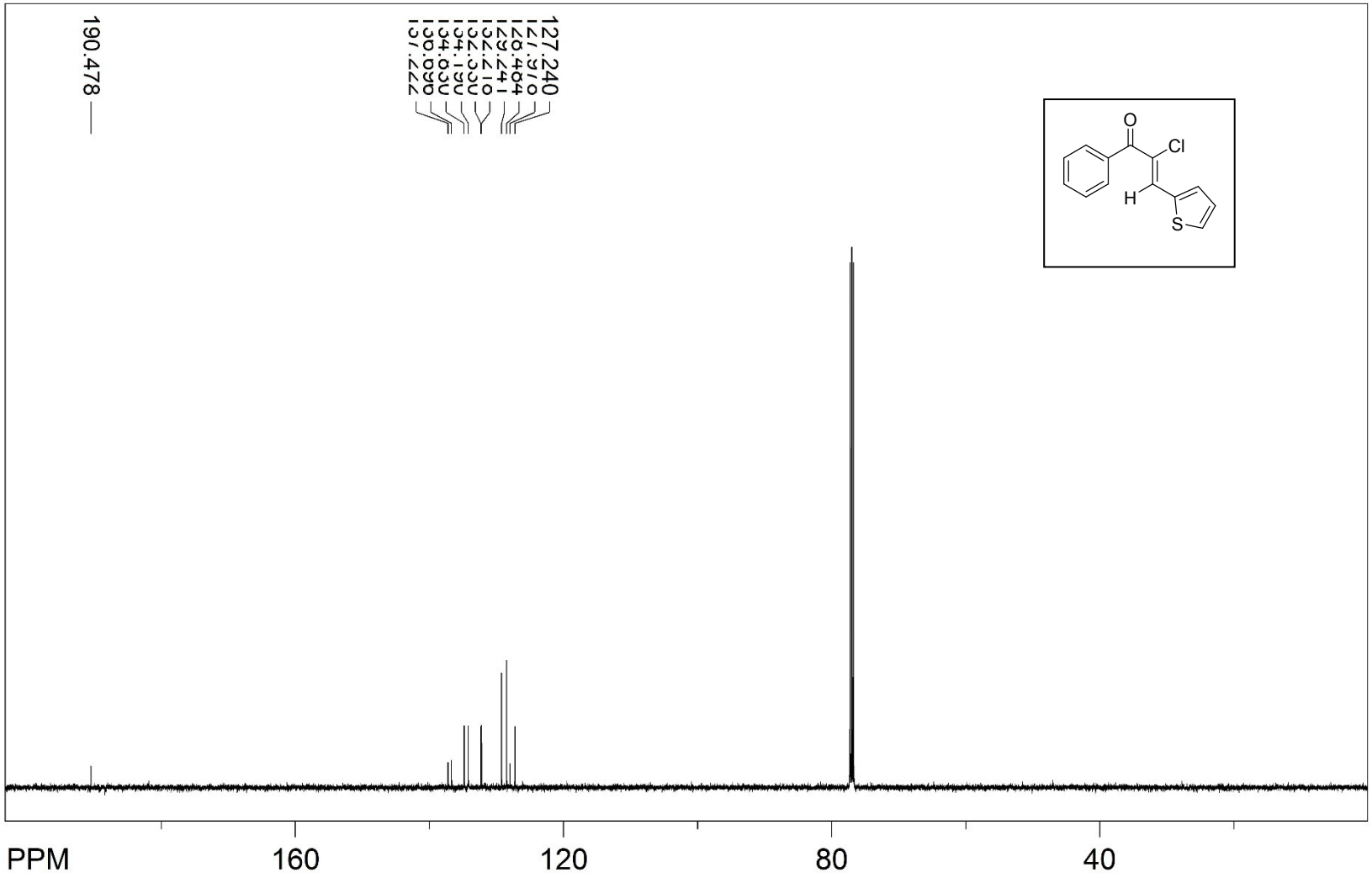
**(2*Z*)-2-Chloro-1-phenyl-3-(2-thienyl)prop-2-en-1-one (4g) – $^{1}$H NMR**




file: ...hal\Desktop\NKC 10 thiophene\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 16

freq of 0 ppm: 500.130000 MHz
processed size: 65536 points
LB: 0.300 GF: 0.0000
Hz/cm: 199.903 ppm/cm: 0.39970

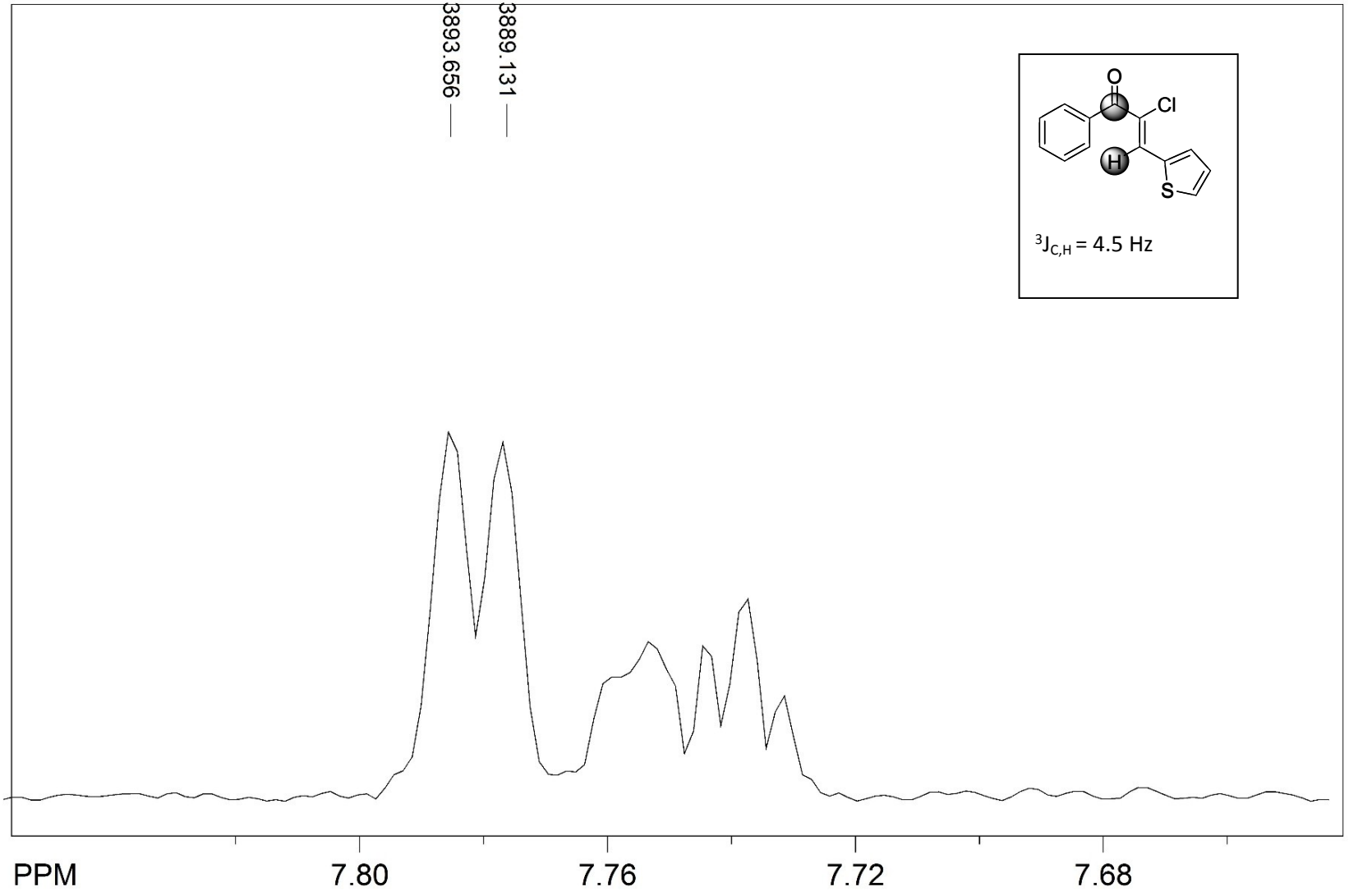
## (2*Z*)-2-Chloro-1-phenyl-3-(2-thienyl)prop-2-en-1-one (4g) – $^{13}$C NMR




file: ...sktop\NKC 10 thiophenecarbon\2\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.90 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 141

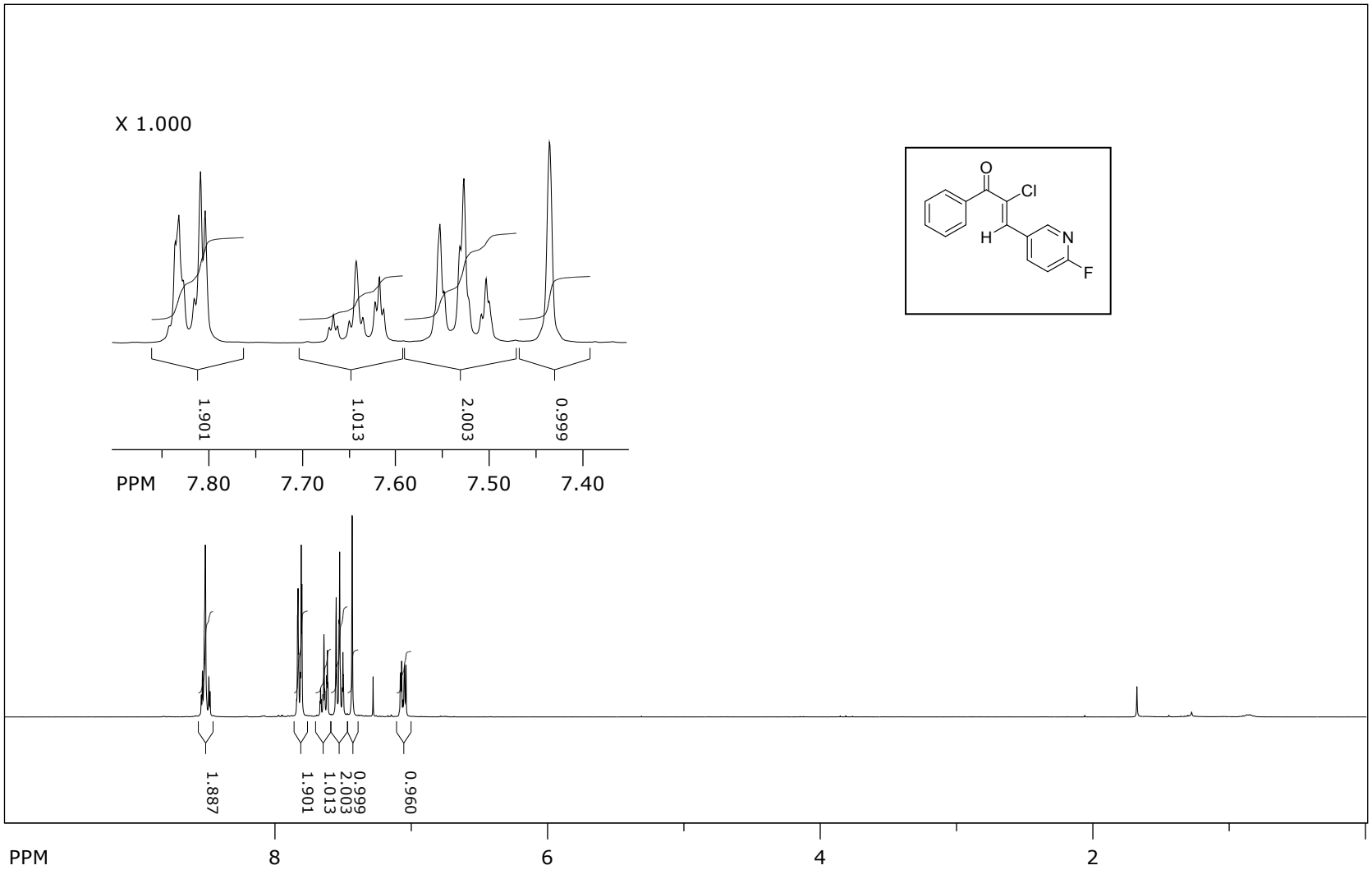
freq of 0 ppm: 125.757789 MHz
processed size: 65536 points
LB: 1.000 GF: 0.0000
Hz/cm: 1022.225 ppm/cm: 8.12771

**(2*Z*)-2-Chloro-1-phenyl-3-(2-thienyl)prop-2-en-1-one (4g) – $^{3}J_{CH}$**




file: ...esktop\NKC 10 thiophene hmbc\3\ser expt: <hmbcgplpndfreq of 0 ppm: 500.130000 MHz
transmitter freq.: 500.133751 MHz processed size: 2048 points
time domain size: 2048 points LB: 0.000 GF: 0.0000
width: 1500.60 Hz = 3.0004 ppm = 0.732715 Hz/pt Hz/cm: 4.477 ppm/cm: 0.00895
number of scans: 8

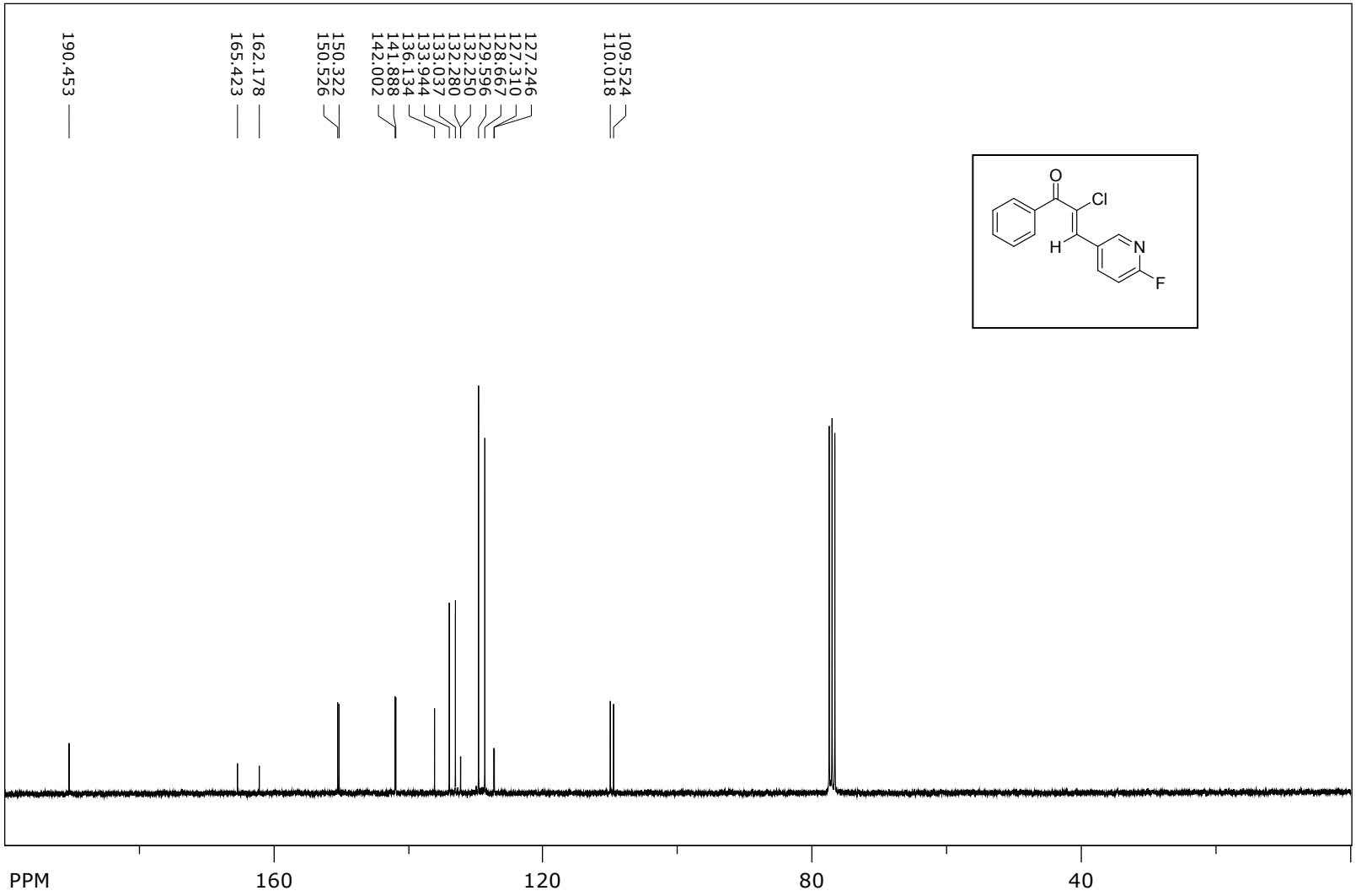
## (2*Z*)-2-Chloro-3-(2-fluoropyridin-4-yl)-1-phenylprop-2-en-1-one (4h) – $^{1}$H NMR




file: ...:\NKC_10_fluoropyridinecis_2\1\fid expt: <zg30>
transmitter freq.: 300.131853 MHz
time domain size: 65536 points
width: 6172.84 Hz = 20.5671 ppm = 0.094190 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130006 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000

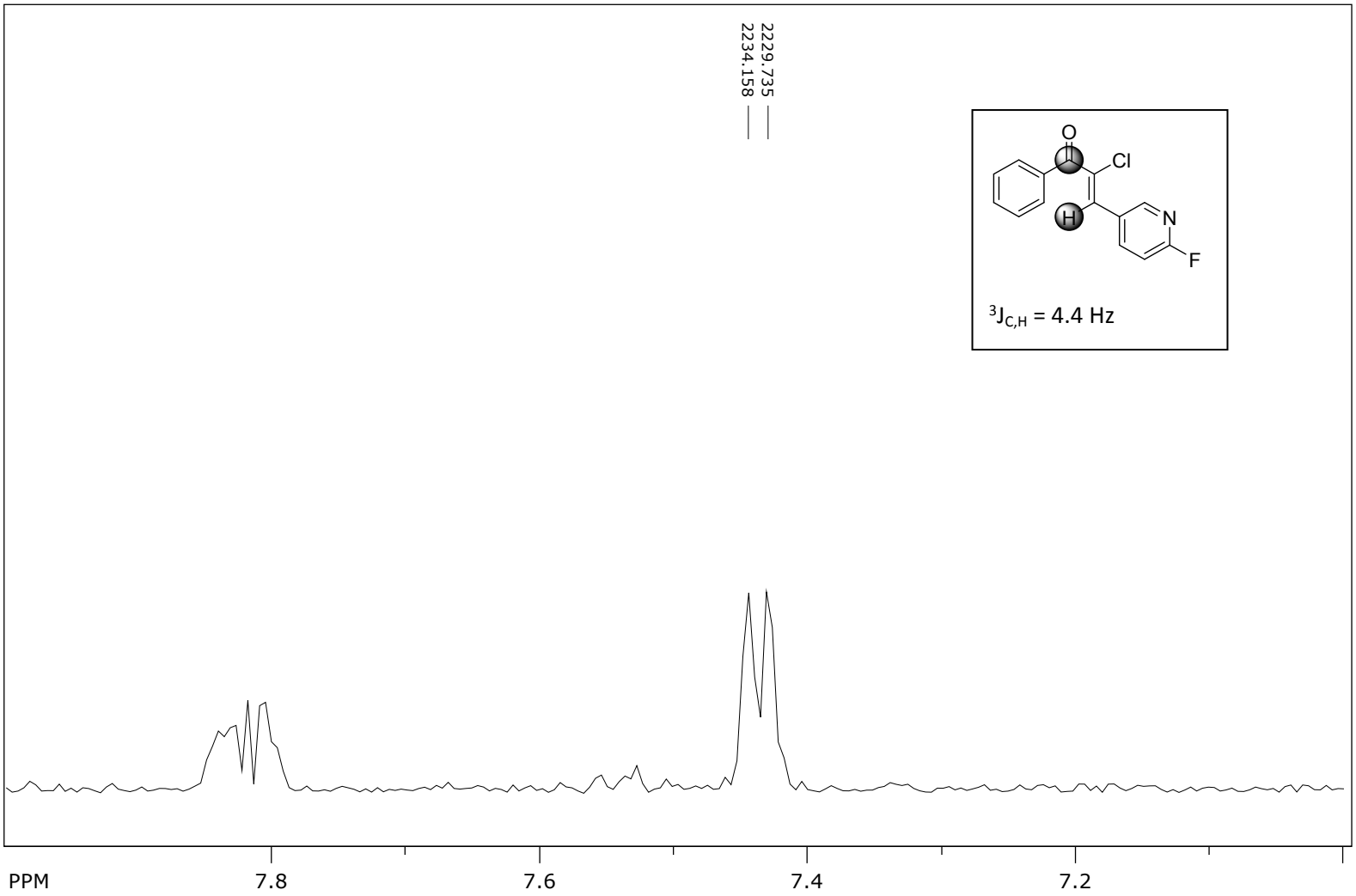
## (2*Z*)-2-Chloro-3-(2-fluoropyridin-4-yl)-1-phenylprop-2-en-1-one (4h) – $^{13}$C NMR




file: ...:\NKC_10_fluoropyridinecis_2\3\fid expt: <zgpg30>
transmitter freq.: 75.475295 MHz
time domain size: 65536 points
width: 17985.61 Hz = 238.2980 ppm = 0.274439 Hz/pt
number of scans: 1024

freq. of 0 ppm: 75.467749 MHz
processed size: 32768 complex points
LB: 1.000 GF: 0.0000

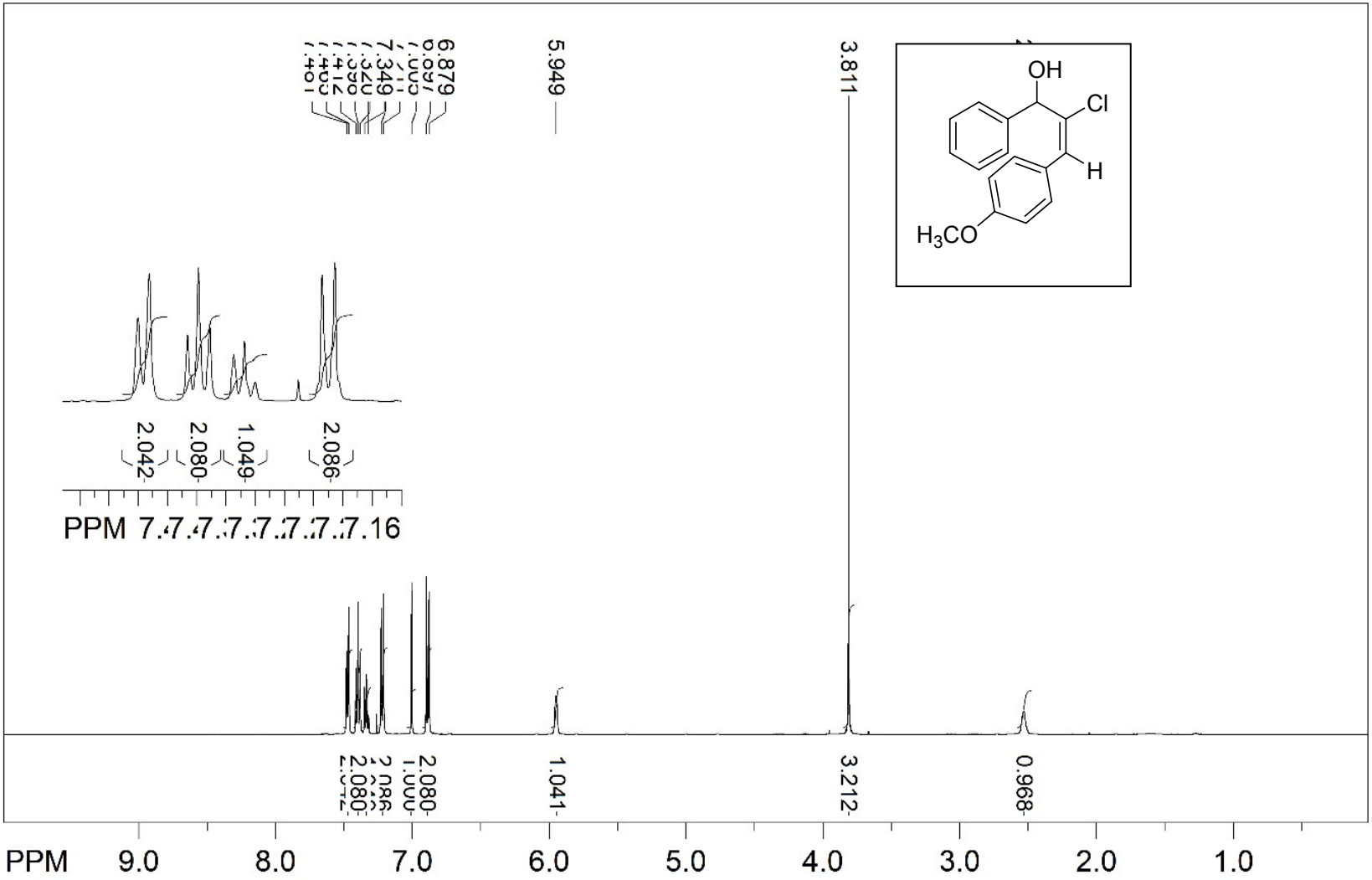
## (2*Z*)-2-Chloro-3-(2-fluoropyridin-4-yl)-1-phenylprop-2-en-1-one (4h) – $^{3}J_{CH}$




file: ...:\NKC_10_fluoropyridinecis_2\2\ser expt: <hmbcgplpndqf>
transmitter freq.: 300.131421 MHz
time domain size: 4096 points
width: 2705.63 Hz = 9.0148 ppm = 0.660554 Hz/pt
number of scans: 8

freq. of 0 ppm: 300.130006 MHz
processed size: 2048 complex points
LB: 0.000 GF: 0.0000

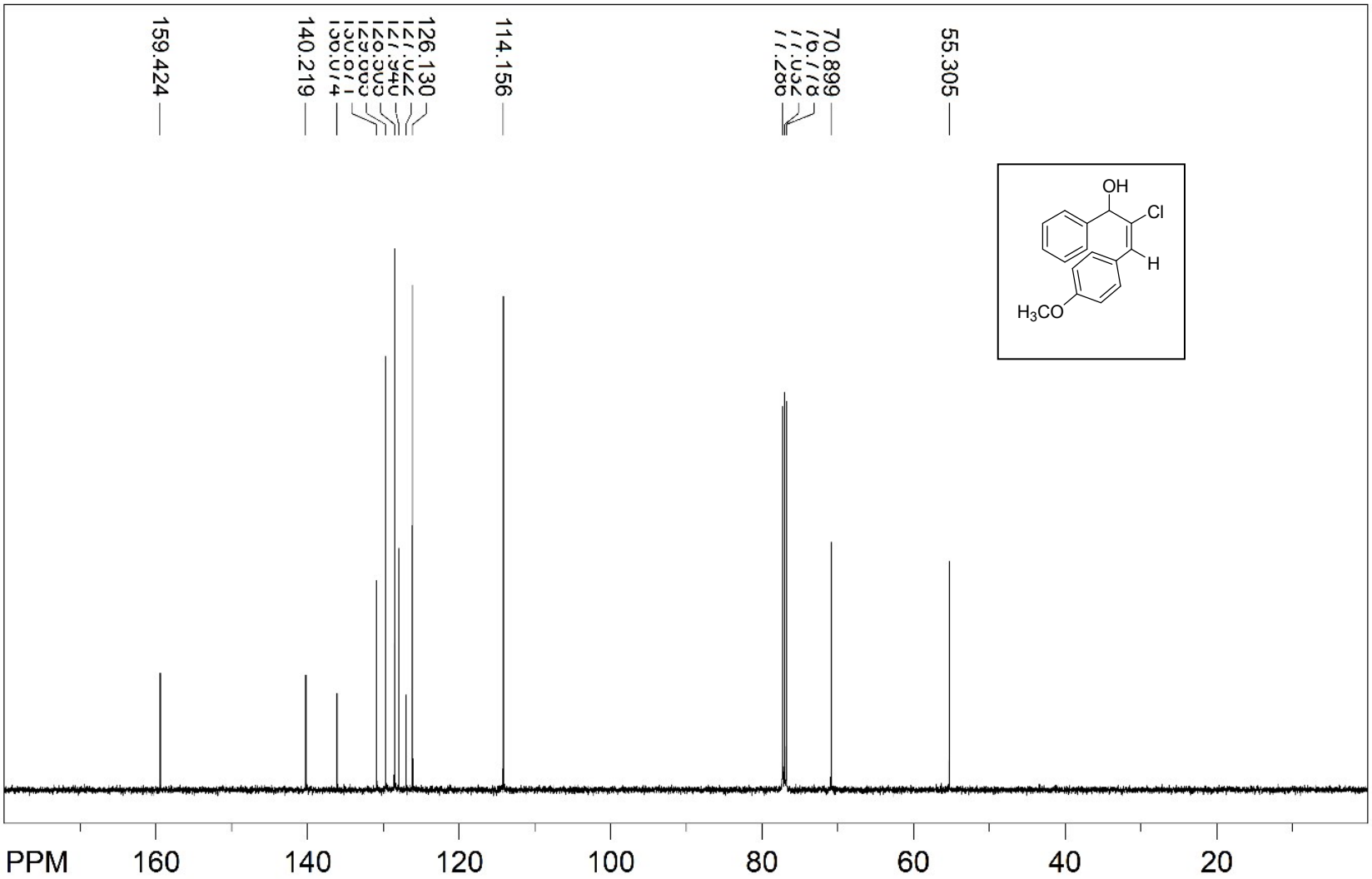
**(2*E*)-2-Chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol (7) – $^{1}$H NMR**




file: ...ehal\Desktop\NKC 12 46 luche\1\fid expt: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10000.00 Hz = 19.9947 ppm = 0.152588 Hz/pt
number of scans: 16

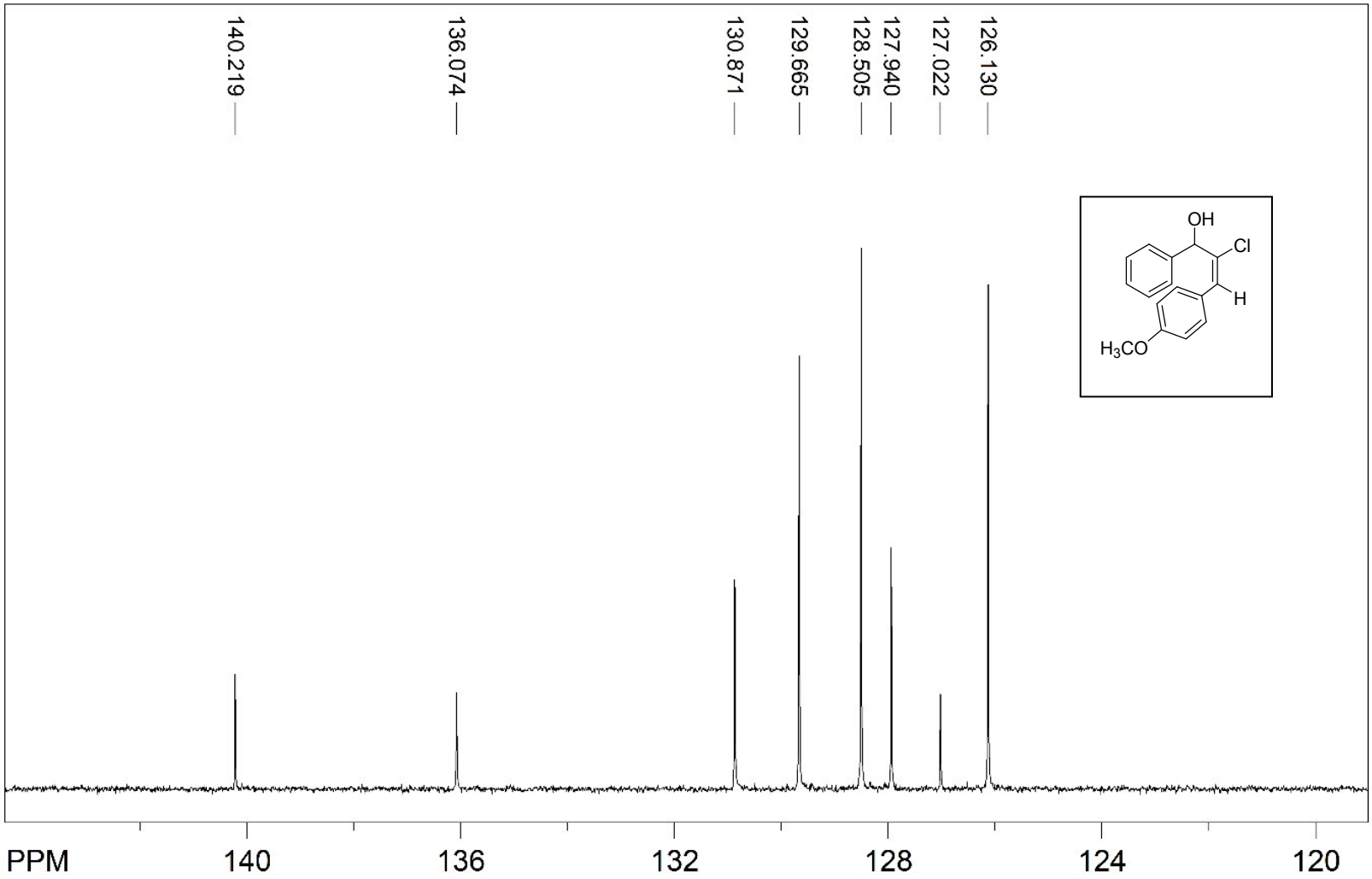
freq of 0 ppm: 500.130000 MHz
processed size: 65536 points
LB: 0.300 GF: 0.0000
Hz/cm: 199.514 ppm/cm: 0.39892

**(2*E*)-2-Chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol (7) – $^{13}$C NMR**




file: ...ehal\Desktop\NKC 12 46 luche\2\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.91 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 183

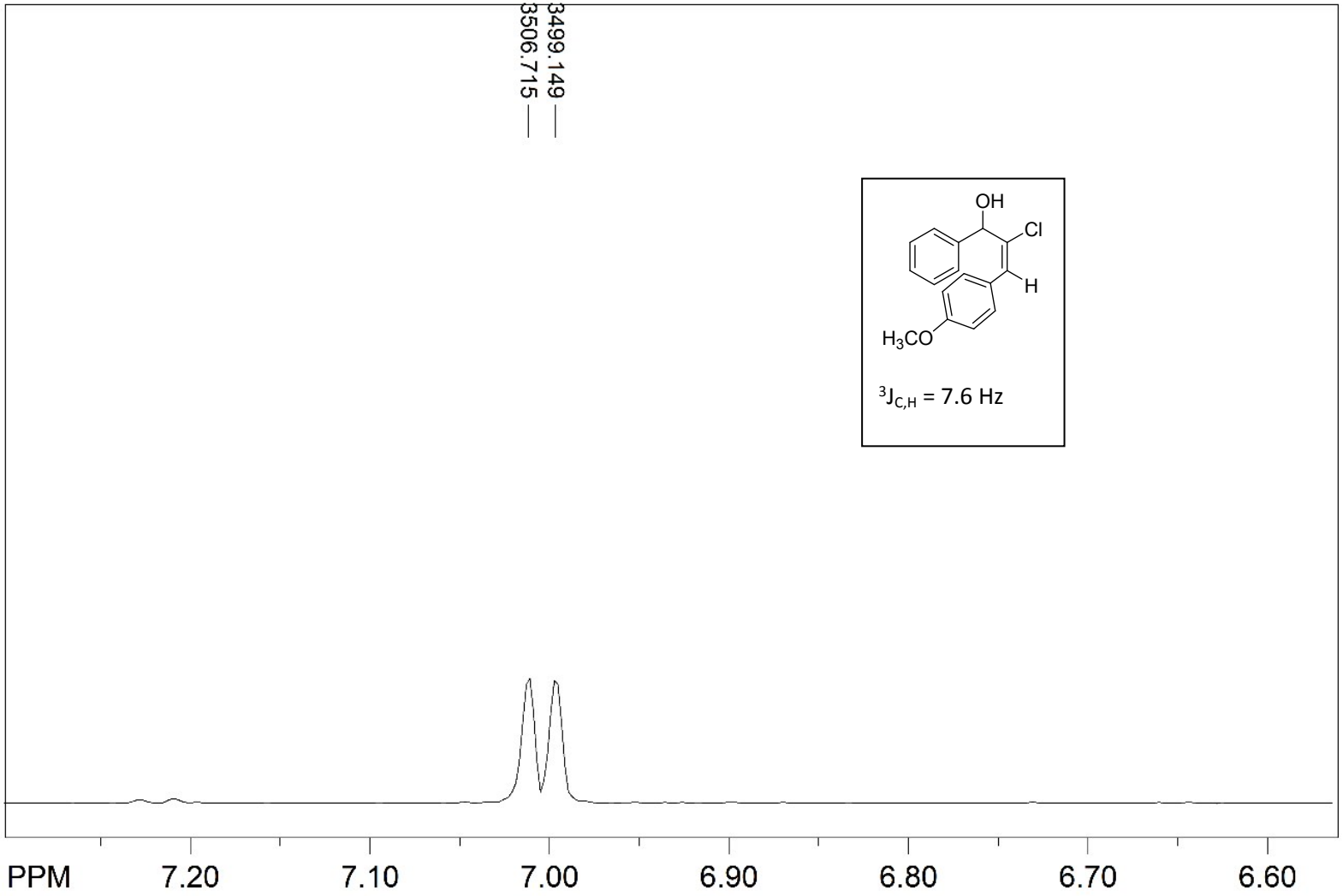
freq of 0 ppm: 125.757789 MHz
processed size: 32768 points
LB: 1.000 GF: 0.0000
Hz/cm: 905.433 ppm/cm: 7.19909




file: ...ehal\Desktop\NKC 12 46 luche\2\fid expt: <zgpg30>
transmitter freq.: 125.770364 MHz
time domain size: 65536 points
width: 29761.91 Hz = 236.6369 ppm = 0.454131 Hz/pt
number of scans: 183

freq of 0 ppm: 125.757789 MHz
processed size: 32768 points
LB: 1.000 GF: 0.0000
Hz/cm: 128.356 ppm/cm: 1.02056

**(2*E*)-2-Chloro-3-(4-methoxyphenyl)-1-phenylprop-2-en-1-ol (7) – $^{3}J_{CH}$**




file: ...ehal\Desktop\NKC 12 46 luche\3\ser expt: <hmbcgplpnd freq of 0 ppm: 500.130000 MHz
transmitter freq.: 500.132001 MHz processed size: 4096 points
time domain size: 4096 points LB: 0.000 GF: 0.0000
width: 4000.00 Hz = 7.9979 ppm = 0.976563 Hz/pt Hz/cm: 15.468 ppm/cm: 0.03093
number of scans: 8

# 9. References

1. A. Jonczyk and A. H. Gierczak, *Synthesis*, 1998, 962-964.
2. *US Pat.,* 2415796, 1947.
3. T. Parella and J. F. Espinosa, *Prog. Nucl. Magn. Reson. Spectrosc.*, 2013, **73**, 17-55.