


## A Mixed N-Heterocyclic Carbene/Triphenylphosphine Palladium(II) Complex for Suzuki-Miyaura Cross-Coupling Reactions

Deniz Demir Atlı<sup>1\*</sup> 

<sup>1</sup>Manisa Celal Bayar University, Faculty of Science and Letters, 45140, Manisa, Turkey

\*[deniz.demir@cbu.edu.tr](mailto:deniz.demir@cbu.edu.tr)

\*Orcid: 0000-0001-8442-4916

Received: 24 May 2021

Accepted: 23 November 2021

DOI: 10.18466/cbayarfbe.941916

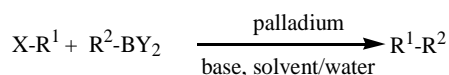
### Abstract

In this work, a novel compound, 1-(2,5-dimethylbenzyl)benzimidazole (**1**) was prepared by N-alkylation of benzimidazole with 2,5-dimethylbenzyl chloride in the presence of KOH base. Quaternization of **1** with 2,5-dimethylbenzyl chloride gave 1,3-bis(2,5-dimethylbenzyl)benzimidazolium chloride (**2**) salt. The reaction of **2** with palladium(II) acetate, PPh<sub>3</sub>, LiCl and Et<sub>3</sub>N gave [PdCl<sub>2</sub>{1,3-bis(2,5-dimethylbenzyl)benzimidazolium-2-ylidene}(PPh<sub>3</sub>)] (**3**) complex. The prepared compounds were characterized by spectroscopic methods and elemental analysis. The palladium complex **3** was used as catalyst in Suzuki–Miyaura cross-coupling reactions of some aryl bromides and chlorides with phenylboronic acid. In the reactions of the all aryl bromides, the catalyst displayed excellent activity and biphenyl compounds were achieved in >99% yields. High activity was observed with some aryl chlorides.

**Keywords:** Benzimidazolium, N-heterocyclic carbene, palladium, Suzuki-Miyaura cross-coupling

### 1. Introduction

Cross-coupling reaction is one of the most important reactions in organic chemistry. A carbon-carbon bond is formed in this reaction that takes place between an organo(pseudo)halide electrophile and an organometallic nucleophile. It is differently called depending on the nucleophile used. The reaction of a halide with a stable organoboron compound in the presence of a base and a palladium catalyst, known Suzuki-Miyaura cross-coupling reaction, was firstly performed in 1979 (Scheme 1) [1-3]. Since then, numerous studies on these type reactions using palladium, nickel, cobalt, iron, ruthenium and rhodium catalysts have been reported [4-9].



R<sup>1</sup> = aryl, alkenyl, alkynyl; X = halide;

R<sup>2</sup> = aryl, alkyl; Y = organic group

**Scheme 1.** Palladium catalyzed Suzuki-Miyaura cross-coupling reaction.

N-heterocyclic carbenes (NHCs) are among the most interesting ligands in organometallic chemistry.

Due to strong  $\sigma$ -donor and weak  $\pi$ -acceptor features, they compose stable transition metal complexes. Palladium NHC complexes have been intensely studied as efficient cross-coupling catalysts [10-13]. PPh<sub>3</sub> is inexpensive and air-stable chemical. Besides the NHC, a labile phosphine ligand contributes to the stability of a mixed NHC/phosphine palladium(II) complex. Such compounds can be prepared by different methods. The most commonly used one is the reaction of dimeric halide bridged [(NHC)PdX<sub>2</sub>]<sub>2</sub> complex with a phosphine ligand [14]. Another method is the reaction of [(NHC)PdX<sub>2</sub>(py)] with phosphine and an alkali halide [15]. Also, the reaction of a NHC precursor with a palladium(II) compound, phosphine, a base and an alkali halide can be used to prepare NHC/phosphine Pd(II) complexes [16]. They have been employed as efficient catalysts in many reactions such as Suzuki coupling, telomerization of butadiene, C-S bond formation and Mizoroki-Heck reaction [17-20].

In this study, a 1-alkylbenzimidazole, a benzimidazolium salt and a palladium(II) complex containing NHC and PPh<sub>3</sub> ligands were synthesized for the first time. The prepared compounds were characterized. Also, the catalytic activity of NHC-

Pd(II) complex in Suzuki coupling reactions of some aryl bromides and chlorides with phenylboronic acid was tested.

## 2. Experimental

### 2.1. General Remarks

All experimental studies were performed in air. The chemical agents were employed as purchased. Elemental analysis, NMR, FT-IR and LC-MSMS measurements were carried through CHNS-932 (LECO) elemental analyzer, Varian 400 MHz NMR spectrophotometer, Perkin Elmer spectrophotometer and SHIMADZU LC-MSMS-8040 mass spectrometer, respectively.

### 2.2. Synthesis of the compounds

#### 2.2.1. 1-(2,5-dimethylbenzyl)benzimidazole (1)

KOH (1.91 g, 34.03 mmol) was added to an ethanolic solution of benzimidazole (4.02 g, 34.03 mmol) and the mixture was stirred at room temperature for 2h. Then, 2,5-dimethylbenzyl chloride (5.1 mL, 34.03 mmol) was added. It was refluxed for 24h. After filtration, EtOH was removed. Water (100 mL) was added. The product was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3x30 mL). Organic part was dried by adding Na<sub>2</sub>SO<sub>4</sub>. After filtration, the filtrate was concentrated. The product was crystallized by adding n-hexane. Yield: 6.60 g, 82%.  $\nu_{\text{CN}}$ : 1495 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.84 (dd, J = 6.5, 2.5 Hz, 1H, Ar-H), 7.79 (s, 1H, NCHN), 7.35 – 7.24 (m, 3H, Ar-H), 7.11 (d, J = 7.6 Hz, 1H, Ar-H), 7.06 (d, J = 7.5 Hz, 1H, Ar-H), 6.76 (s, 1H, Ar-H), 5.26 (s, 2H, NCH<sub>2</sub>), 2.25 (s, 3H, Me), 2.23 (s, 3H, Me) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.01, 143.25, 136.34, 134.23, 133.00, 132.94, 130.88, 129.29, 128.81, 123.12, 122.35, 120.53, 110.00, 47.09, 21.07, 18.76 ppm. Anal. Calcd. for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>(%): C, 81.31; H, 6.84; N, 11.86. Found: C, 81.29; H, 6.83; N, 11.99.

#### 2.2.2. 1,3-bis(2,5-dimethylbenzyl)benzimidazolium chloride (2)

The mixture of 2,5-dimethylbenzyl chloride (0.51 mL, 3.36 mmol) and **1** (0.72 g, 3.05 mmol) in DMF (2 mL) was stirred at 80 °C for 5h. White solids were precipitated by adding excess Et<sub>2</sub>O. The product was recrystallized from EtOH/Et<sub>2</sub>O (1/3). Yield: 1.08 g, 91%.  $\nu_{\text{CN}}$ : 1563 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 11.98 (s, 1H, NCHN), 7.43 (dt, J = 7.0, 3.5 Hz, 2H, Ar-H), 7.41 – 7.34 (m, 2H, Ar-H), 7.06 (q, J = 7.7 Hz, 4H, Ar-H), 6.88 (s, 2H, Ar-H), 5.86 (s, 4H, NCH<sub>2</sub>), 2.34 (s, 6H, Me), 2.22 (s, 6H, Me) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 144.88, 136.56, 133.32, 131.66, 131.36, 130.42, 130.12, 128.82, 127.20, 113.96, 51.54, 22.00, 19.19 ppm. Anal. Calcd. for C<sub>25</sub>H<sub>27</sub>N<sub>2</sub>Cl(%): C, 76.79; H, 6.98; N, 7.17. Found: C, 75.78; H, 6.91; N, 7.42.

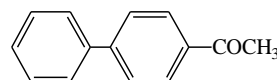
#### 2.2.3. [PdCl<sub>2</sub>{1,3-bis(2,5 dimethylbenzyl) benzimidazolin -2-ylidene}(PPh<sub>3</sub>)] (3)

The mixture of **2** (0.22 g, 0.58 mmol), PPh<sub>3</sub> (0.15 g, 0.58 mmol), LiCl (0.74 g, 17.4 mmol), Pd(OAc)<sub>2</sub> (0.13 g, 0.58 mmol) and Et<sub>3</sub>N (0.4 mL, 2.9 mmol) in MeCN (10 mL) was stirred at 70 °C overnight. The precipitated solid was isolated with filtration and washing excess water. It was recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/n-pentane (1/3). Yield: 0.33 g, 72%.  $\nu_{\text{CN}}$ : 1436 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 7.47 (dd, J = 12.0, 7.7 Hz, 6H, Ar-H), 7.39 – 7.33 (m, 3H, Ar-H), 7.19 (td, J = 7.6, 2.5 Hz, 6H, Ar-H), 7.04 (dd, J = 6.1, 3.1 Hz, 2H, Ar-H), 6.97 (d, J = 7.6 Hz, 4H, Ar-H), 6.87 (d, J = 8.0 Hz, 2H, Ar-H), 6.75 (dd, J = 6.1, 3.1 Hz, 2H, Ar-H), 5.88 (d, J = 15.8 Hz, 2H, NCH<sub>2</sub>), 5.02 (d, J = 15.5 Hz, 2H, NCH<sub>2</sub>), 2.33 (s, 6H, Me), 2.08 (s, 6H, Me) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  = 176.55 (C<sub>carbene</sub>), 136.17, 134.64, 134.35, 134.24, 131.88, 131.24, 130.38, 130.01, 129.48, 128.91, 128.67, 128.47, 128.35, 123.48, 112.43, 50.99, 21.06, 19.39 ppm. Anal. Calcd. for C<sub>43</sub>H<sub>41</sub>N<sub>2</sub>PPdCl<sub>2</sub>(%): C, 65.03; H, 5.21; N, 3.53. Found: C, 64.30; H, 5.72; N, 3.68.

### 2.3. General catalytic procedure

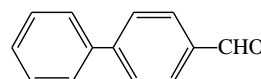
Catalyst (7.9 mg, 0.01 mmol), aryl halide (1 mmol), K<sub>2</sub>CO<sub>3</sub> (0.21 g, 1.5 mmol), phenylboronic acid (0.18 g, 1.5 mmol) were introduced in a flask. DMF (2mL) and water (2 mL) were added. The mixture was stirred at 80 °C for 2h. It was diluted with water (20 mL). After extraction with CH<sub>2</sub>Cl<sub>2</sub> (3x10 mL), drying with Na<sub>2</sub>SO<sub>4</sub>, and filtration procedures, the solvent was removed under reduced pressure. The known cross-coupling products were purely obtained by column chromatography and defined by <sup>1</sup>H NMR.

#### 4-acetylbiphenyl (4a)



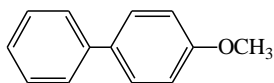
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 8.07-8.00 (m, 2H, Ar-H), 7.72-7.66 (m, 2H, Ar-H), 7.67-7.60 (m, 2H, Ar-H), 7.52-7.37 (m, 3H, Ar-H), 2.64 (s, 3H, Me) ppm [21].

#### Biphenyl-4-carbaldehyde (4b)



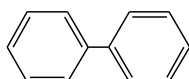
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  = 10.05 (s, 1H, COH), 7.96-7.93 (m, 2H, Ar-H), 7.76-7.73 (m, 2H, Ar-H), 7.64-7.61 (m, 2H, Ar-H), 7.50-7.45 (m, 2H, Ar-H), 7.43-7.40 (m, 1H, Ar-H) ppm [22].

#### 4-Methoxybiphenyl (4c)

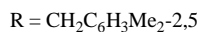
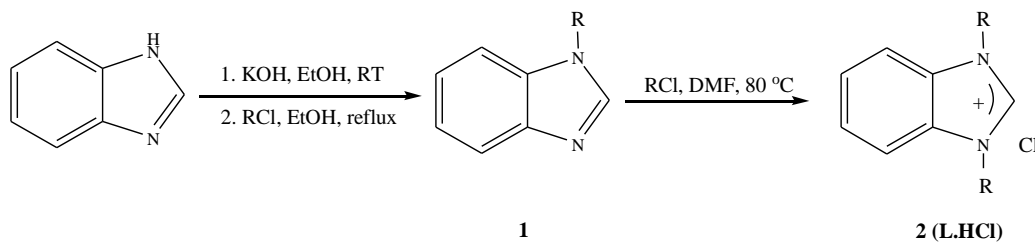


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.58\text{-}7.53$  (m, 4H, Ar-H), 7.45-7.41 (m, 2H, Ar-H), 7.34-7.29 (m, 1H, Ar-H), 7.01-6.98 (m, 2H, Ar-H), 3.87 (s, 3H, Me) ppm [22].

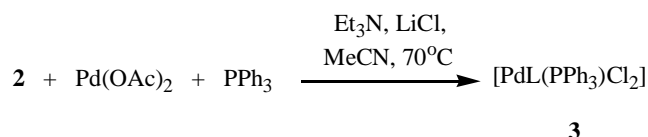
#### Biphenyl (4d)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.64\text{-}7.61$  (m, 4H, Ar-H), 7.49-7.44 (m, 4H, Ar-H), 7.39-7.35 (m, 2H, Ar-H) ppm [22].



**Scheme 2.** Synthesis of **1** and **2**.



**Scheme 3.** Synthesis of **3**.

The all prepared compounds were characterized by elemental analysis, NMR and FT-IR. According to the elemental analysis data, **1-3** have the anticipated formulations. NMR spectra validate the expected structures (Figures 1-3). In  $^1\text{H}$  NMR spectra of the **1-3**, aromatic proton and methyl signals appear at 6.75-7.84 ppm and 2.08-2.34 ppm, respectively. NCHN signal was observed at 7.79 ppm for **1**. The same signal for **2**, a salt compound, appeared at 11.98 ppm. It is characteristic that a singlet signal is present in the low field in  $^1\text{H}$  NMR spectrum for the acidic proton of the benzimidazolium salt. This low field signal disappears for **3**. This signifies that deprotonation takes place [25]. The number of phenyl proton peaks in the range of 7.0-8.0 ppm increases due to the presence of  $\text{PPh}_3$  ligands in **3** [15]. The singlet signals of the methylene protons at 5.86 ppm in the  $^1\text{H}$  NMR

### 3. Results and Discussion

Synthetic procedures for **1** and **2** are included in scheme 2. The benzimidazolium salt **2** was prepared in two steps using existing methods in the literature [23, 24]. Firstly, the compound **1** was obtained by N-alkylation of benzimidazole with 2,5-dimethylbenzyl chloride using KOH base in ethanolic medium. The reaction of **1** with 2,5-dimethylbenzyl chloride in DMF gave **2** in high yield.

The mixed  $\text{PPh}_3/\text{NHC}$  palladium(II) complex (**3**) was prepared by modifying the method used by Chan et al. [16]. The reaction of palladium(II) acetate with **2**,  $\text{PPh}_3$  and LiCl in the presence of  $\text{Et}_3\text{N}$  in MeCN gave the expected product in 72% yield (Scheme 3). As far as is known, palladium(II) acetate has not been previously used for this method. This route has the advantage that the desired phosphine complexes can be obtained from NHC precursors without isolating any intermediates. **3** is soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , dmsO, dmf and insoluble in MeCN, pentane, water and  $\text{Et}_2\text{O}$ . The all compounds are stable in air.

spectrum of **2** become dublet signals at 5.02 and 5.88 ppm in that of **3**. So, the methylene protons are diastereotopic as mentioned previously [22, 26]. In  $^{13}\text{C}$  NMR spectrum of **3**, carbene carbon signal was observed at 176.55 ppm [15, 27]. The peaks observed in LC-MSMS at 723.30 and 355.25 show  $[\text{M}-2\text{Cl}]^+$  and  $[\text{M}-2\text{Cl}-\text{PPh}_3-\text{Pd}]^+$  fragments, respectively (Figure 4).  $\nu_{\text{CN}}$  peaks were monitored at 1495, 1563 and 1436  $\text{cm}^{-1}$  in FT-IR spectra of **1-3**.

The preliminary catalytic tests of NHC palladium(II) complex **3** were done for Suzuki-Miyaura coupling reactions of some aryl bromides and chlorides with phenylboronic acid. The experiments were performed by using 1% mol catalyst in DMF/water (1/1) at 80 °C for 2h.  $\text{K}_2\text{CO}_3$  was employed as base. No optimization study was done. The cross-coupling products were

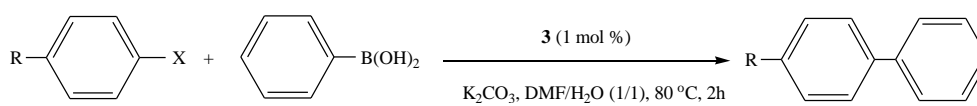
isolated by purifying with column chromatography and percentage yields were calculated. <sup>1</sup>H NMR spectra of them are given in figures 5-8. When aryl bromides were used, each biphenyl compound was obtained in >99% yield. Complex **3** exhibited excellent activity for aryl bromides under the studied conditions (Table 1, entries 1,3,5,7). Catalytic activity was also studied with aryl chlorides. The studied all aryl chlorides led to lower yields than the aryl bromides. It has been previously reported that this is due to the slow oxidative addition of aryl chlorides to palladium [28]. 4'-chloroacetophenone and 4-chlorobenzaldehyde bearing electron withdrawing groups led to the biaryls in good yields (Table 1, entries 2 and 4). While chlorobenzene formed biphenyl in 30% yield, the yield was only 5% with 4-

chloroanisole bearing donating methoxy group (Table 1, entries 6 and 8). It is understood from these results that decrease in electron density on aryl chlorides causes increase in activity. These results are consistent with the literature [29,30].

#### 4. Conclusion

In this study, 1-(2,5-dimethylbenzyl)benzimidazole, 1,3-bis(2,5-dimethylbenzyl)benzimidazolium chloride and [PdCl<sub>2</sub>{1,3-bis(2,5-dimethylbenzyl)benzimidazol-2-ylidene}(PPh<sub>3</sub>)] compounds were successfully prepared and characterized. Palladium(II) complex was tested as catalyst in the Suzuki-Miyaura cross-coupling reactions of some aryl bromides and chlorides with phenylboronic acid in aqueous media.

**Table 1.** Suzuki-Miyaura cross-coupling reactions catalyzed by **3**.



Entry	R	X	Product	Yield(%)
1	-COCH <sub>3</sub>	Br	<b>4a</b>	>99
2	-COCH <sub>3</sub>	Cl	<b>4a</b>	76
3	-CHO	Br	<b>4b</b>	>99
4	-CHO	Cl	<b>4b</b>	77
5	-OCH <sub>3</sub>	Br	<b>4c</b>	>99
6	-OCH <sub>3</sub>	Cl	<b>4c</b>	5
7	-H	Br	<b>4d</b>	>99
8	-H	Cl	<b>4d</b>	29

#### Author's Contributions

Deniz DEMİR ATLI: Performed the experiments and wrote the manuscript.

#### Ethics

There are no ethical issues after the publication of this manuscript.

#### References

- Miyaura, N, Yamada, K, Suzuki, A. 1979. A new stereospecific cross-coupling by the palladium-catalyzed reaction of 1-alkenylboranes with 1-alkenyl or 1-alkynyl halides. *Tetrahedron Letters*; 20(36): 3437-3440.
- Miyaura, N, Suzuki, A. 1979. Stereoselective synthesis of arylated (E)-alkenes by the reaction of alk-1-enylboranes with aryl halides in the presence of palladium catalyst. *Journal of the Chemical Society, Chemical Communications*; 19: 866-867.
- Pagett, AB, Lloyd-Jones, GC. Suzuki-Miyaura cross-coupling. In: Denmark SE et al. (ed.) *Organic Reactions*, Wiley, UK, 2019, pp 547-620.
- Talukder, MM, Cue, JMO, Miller, JT, Gamage, PL, Aslam, A, McCandless, GT, Biewer, MC, Stefan, MC. 2020. Ligand steric effects of  $\alpha$ -diimine nickel(II) and palladium(II) complexes in the Suzuki-Miyaura cross-coupling reaction. *ACS Omega*; 5(37): 24018-24032.
- D'Accriscio, F, Ohleier, A, Nicolas, E, Demange, M, Boullay, OTD, Saffon-Merceron, N, Fustier-Boutignon, M, Rezabal, E, Frison, G, Nebra, N, Mezaillies, N. 2020. [(dcp)Ni( $\eta$ 2-



- Arene)] precursors: Synthesis, reactivity, and catalytic application to the Suzuki–Miyaura reaction. *Organometallics*; 39(10): 1688-1699.
6. Ansari, RM, Kumar, LM, Bhat, BR. 2018. Air-stable cobalt(II) and nickel(II) Complexes with schiff base Ligand for catalyzing Suzuki–Miyaura cross-coupling reaction. *Russian Journal of Coordination Chemistry*; 44: 1-8.
  7. Key, RJ, Tengco, JMM, Smith, MD, Vannucci, AK. 2019. A molecular/heterogeneous nickel catalyst for Suzuki–Miyaura coupling. *Organometallics*; 38(9): 2007-2014.
  8. Ansari, RM, Bhat, BR. 2017. Schiff base transition metal complexes for Suzuki–Miyaura cross-coupling reaction. *Journal of Chemical Sciences*; 129: 1483-1490.
  9. Kadu, BS. 2021. Suzuki–Miyaura cross coupling reaction: recent advancements in catalysis and organic synthesis. *Catalysis Science&Technology*; 11(4): 1186-1221.
  10. Pirkel, N, Grosso, AD, Mallick, B, Doppiu, A, Gooben LJ. 2019. Dihalogen-bridged NHC–palladium(I) dimers: synthesis, characterisation and applications in cross-coupling reactions. *Chemical Communications*; 55(36): 5275-5278.
  11. Kaloğlu, N, Özdemir, İ. 2019. PEPPSI-Pd-NHC catalyzed Suzuki–Miyaura cross-coupling reactions in aqueous media. *Tetrahedron*; 75(15): 2306-2313.
  12. Sharma, KN, Satrawala, N, Srivastava, AK, Ali, M, Joshi, RK. 2019. Palladium(II) ligated with selenated NHC based (Se, CNHC, N<sup>-</sup>) type pincer: An efficient catalyst for Mizoroki–Heck and Suzuki Miyaura coupling in water. *Organic&Biomolecular Chemistry*; 17(40): 8969-8976.
  13. Vaishya, V, Patider, S, Plania, M. 2021. Imidazolium/triazolium based NHC–Palladium complexes and their application in catalysis. *Materials Today: Proceedings*; 43: 3181-3187.
  14. Schmid, TE, Jones, DC, Songis, O, Furst, MRL, Slawin, AMZ, Cazin, CSJ. 2013. Mixed phosphine/N-heterocyclic carbene palladium complexes: synthesis, characterization and catalytic use in aqueous Suzuki–Miyaura reactions. *Dalton Transactions*; 42(20): 7345-7353.
  15. Aktaş, A, Erdemir, F, Celepci, DB, Gök, Y, Aygün, M. 2019. Mixed phosphine/N- heterocyclic carbene–palladium complexes: synthesis, characterization, crystal structure and application in the Sonogashira reaction in aqueous media. *Transition Metal Chemistry*; 44: 229-236.
  16. Chan, KT, Tsai, YH, Lin, WS, Wu, JR, Chen, SJ, Liao, FX, Hu, CH, Lee, HM. 2009. Palladium complexes with carbene and phosphine ligands: Synthesis, structural characterization, and direct arylation reactions between aryl halides and alkynes. *Organometallics*; 29(2): 463-472.
  17. Liao, CY, Chan, KT, Tu, CY, Chang, YW, Hu, CH, Lee, HM. 2009. Robust and electron-rich cis-palladium(II) complexes with phosphine and carbene ligands as catalytic precursors in Suzuki coupling reactions. *Chemistry-A European Journal*; 2009(15): 405-417.
  18. Mesnager, J, Lammel, P, Jeanneau, E, Pinel, C. 2009. Mixed N-heterocyclic carbene and phosphine palladium complexes for telomerization of butadiene with methanol. *Applied Catalysis A- General*; 368(1-2): 22-28.
  19. Fu, CF, Liu, YH, Peng, SM, Liu, ST. 2010. C–S bond formation catalyzed by N-heterocyclic carbene palladium phosphine complexes. *Tetrahedron*; 66(12): 2119-2122.
  20. Pytkowicz, J, Roland, S, Mangeney, P, Meyer, G, Jutand, A. 2003. Chiral diaminocarbene palladium(II) complexes: synthesis, reduction to Pd(0) and activity in the Mizoroki–Heck reaction as recyclable catalysts. *Journal of Organometallic Chemistry*; 678(1-2): 166-179.
  21. Zhang, J, Zhang, W, wang, Y, Zhang, M. 2008. Palladium-iminodiacetic acid immobilized on pH-responsive polymeric microspheres: Efficient quasi-homogeneous catalyst for Suzuki and Heck reactions in aqueous solution. *Advanced Synthesis & Catalysis*; 350(13): 2065-2076.
  22. Demir Atlı, D. 2020. Synthesis and catalytic application of cyclopentadienyl nickel(II) N-heterocyclic carbene complexes. *Journal of Coordination Chemistry*; 73(10): 1530-1537.
  23. Özdemir, İ, Şahin, N, Gök, Y, Demir, S, Çetinkaya, B. 2005. In situ generated 1-alkylbenzimidazole–palladium catalyst for the Suzuki coupling of aryl chlorides. *Journal of Molecular Catalysis A: Chemical*; 234(1-2): 181-185.
  24. Yıldırım, I, Aktaş, A, Celepci, DB, Kırbağ, S, Kutlu, T, Gök, Y, Aygün, M. 2017. Synthesis, characterization, crystal structure, and antimicrobial studies of 2-morpholinoethylsubstituted benzimidazolium salts and their silver(I)-N-heterocyclic carbene complexes. *Research on Chemical Intermediates*; 43: 6379-6393.
  25. Achar, G, Agarwal, P, Brinda, KN, Malecki, JG, Keri, RS, Budagumpi, S. 2018. Ether and coumarin-functionalized (benz)imidazolium salts and their silver(I)-N-heterocyclic carbene complexes: Synthesis, characterization, crystal structures and antimicrobial studies. *Journal of Organometallic Chemistry*; 854: 64-75.
  26. Kandil, S, Kariuki, BM, McGuian, C, Westwell, AD. 2021. Synthesis, biological evaluation and X-ray analysis of bicalutamide sulfoxide analogues for the potential treatment of prostate cancer. *Bioorganic & Medicinal Chemistry Letters*; 36: 127817.
  27. Mansour, W, Suleiman, R, Fettouhi, M, Ali, BE. 2020. Soft heteroleptic N-heterocyclic carbene palladium(II) species for efficient catalytic routes to alkyneones via carbonylative Sonogashira coupling. *ACS Omega*; 5(37): 23687-23702.
  28. Doucet, H. 2008. Suzuki–Miyaura cross-coupling reactions of alkylboronic acid derivatives or alkyltrifluoroborates with aryl, alkenyl or alkyl halides and triflates. *European Journal of Organic Chemistry*; 2008(12): 2013-2030.
  29. Zhou, YB, Li, CY, Lin, M, Ding, YJ, Zhan, ZP. 2015. A polymer-bound monodentate-P-ligated palladium complex as a recyclable catalyst for the Suzuki–Miyaura coupling reaction of aryl chlorides. *Advanced Synthesis & Catalysis*; 357(11): 2503-2508.
  30. Shahnaz, N, Banik, B, Das, P. 2013. A highly efficient schiff-base derived palladium catalyst for the Suzuki–Miyaura reactions of aryl chlorides. *Tetrahedron Letters*; 54: 2886-2889.

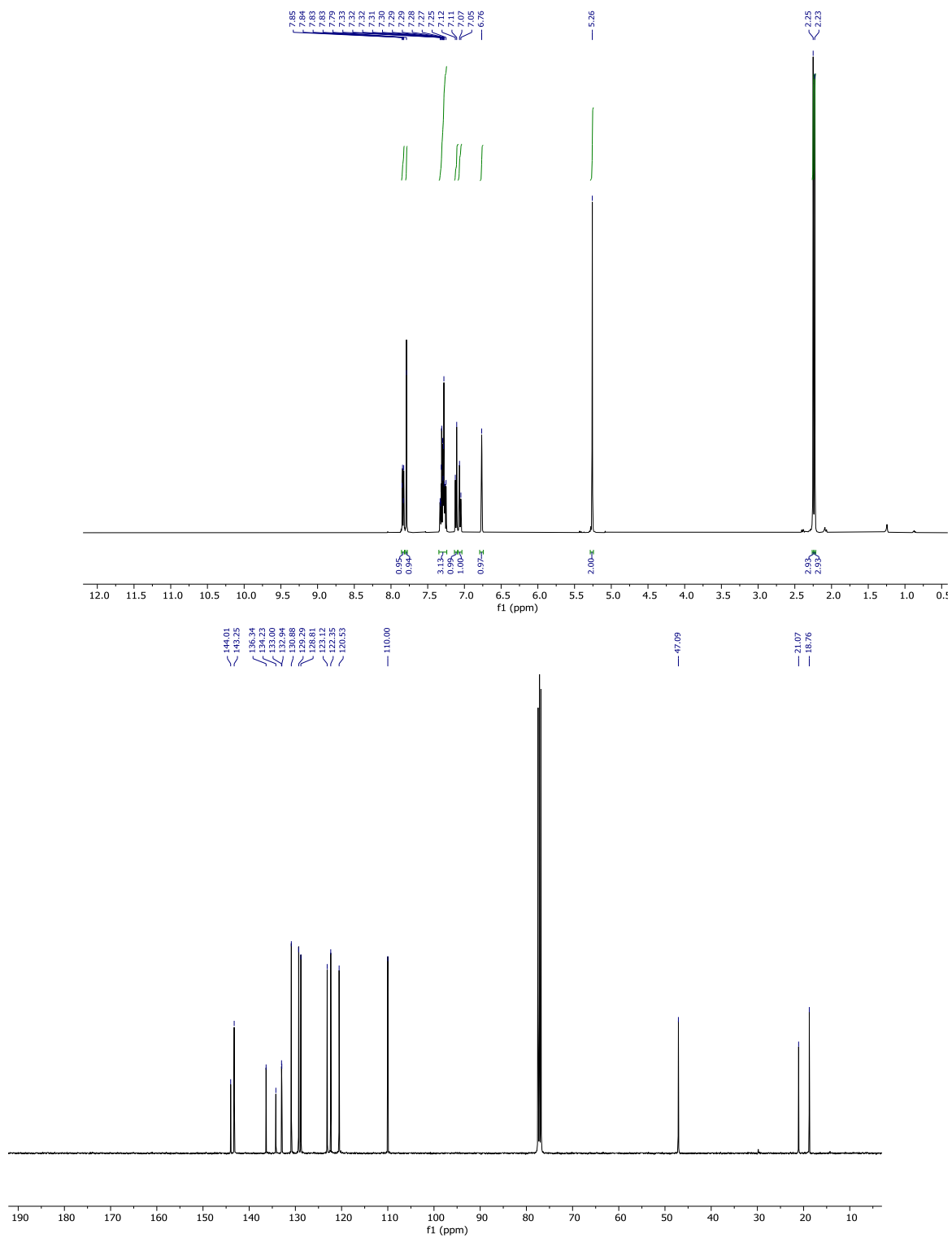


Figure 1.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 1.



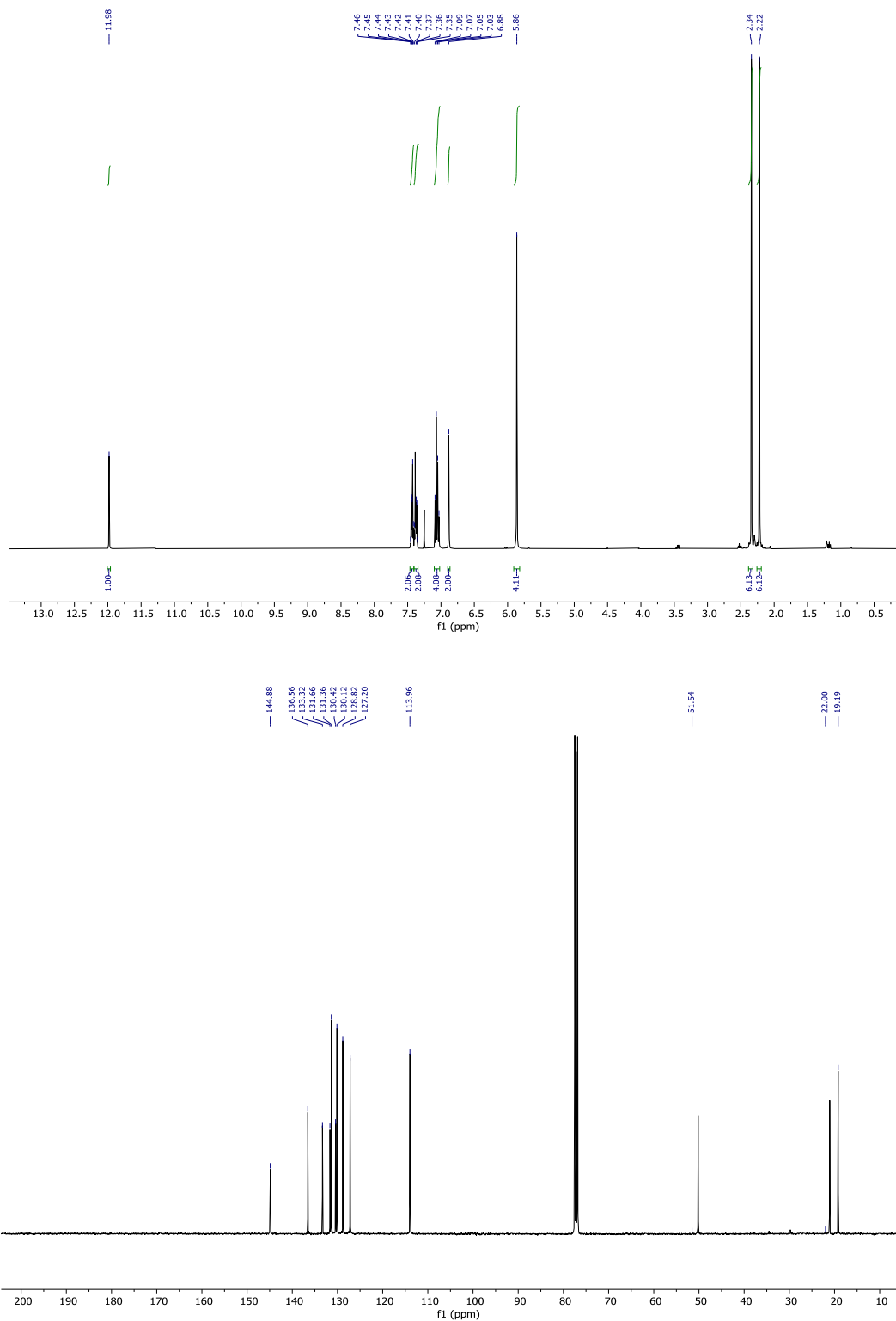


Figure 2.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 2.

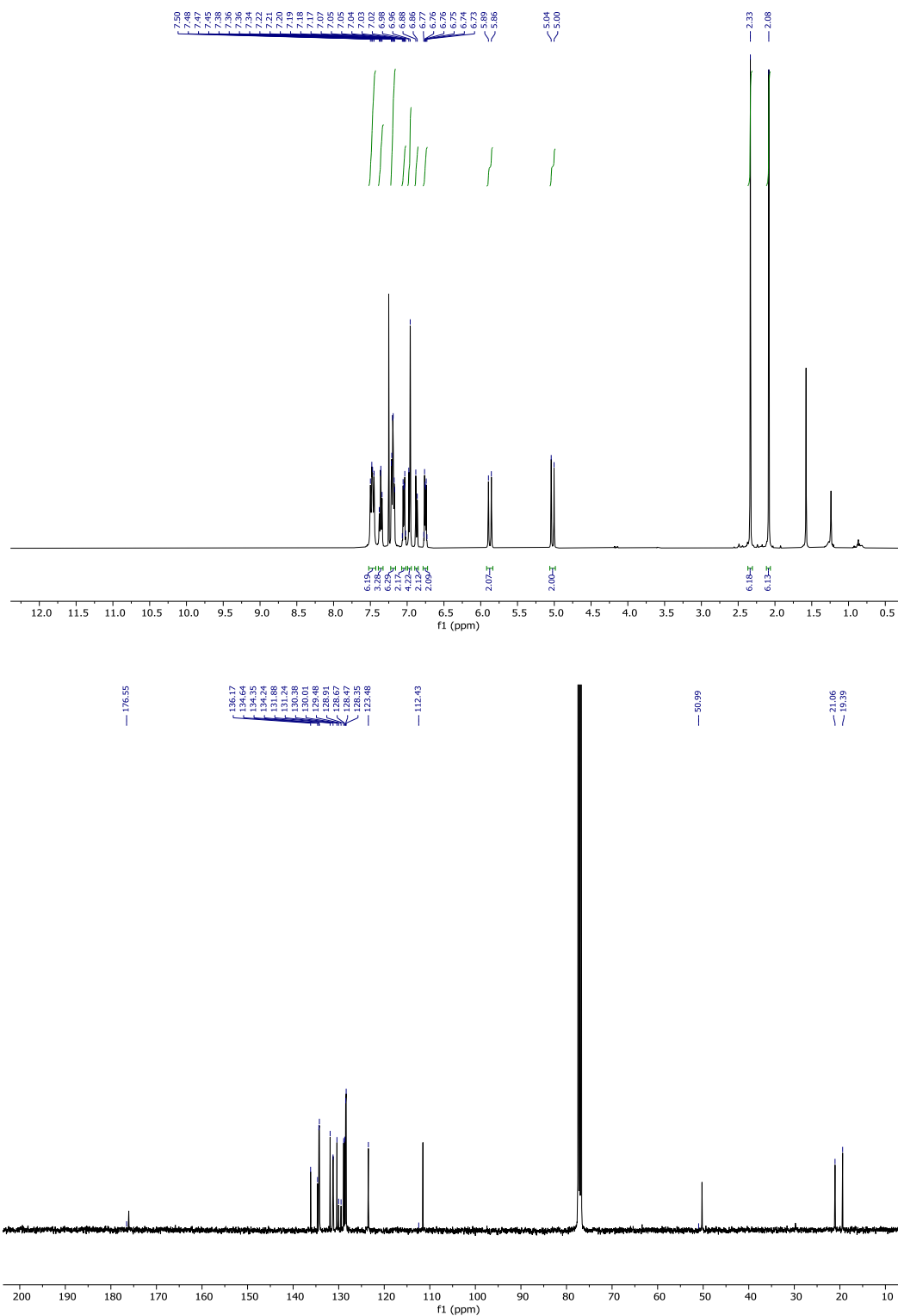


Figure 3.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 3.



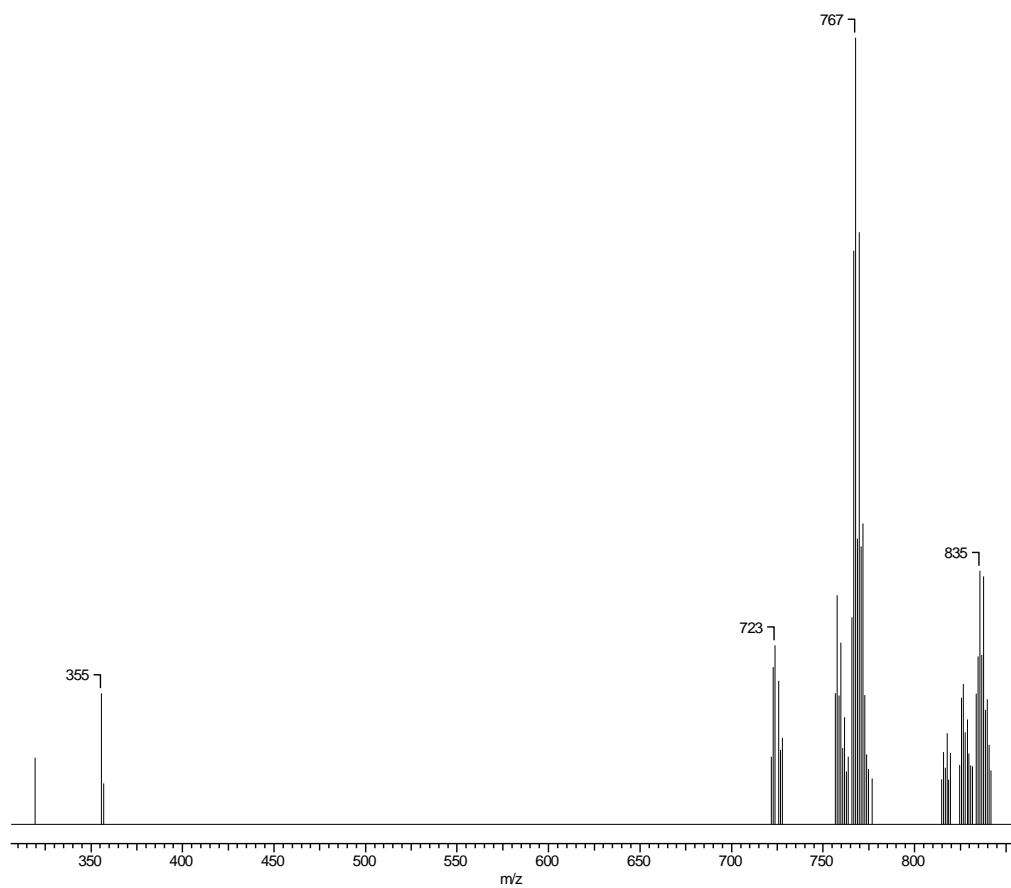


Figure 4. LC-MSMS spectrum of **3**.

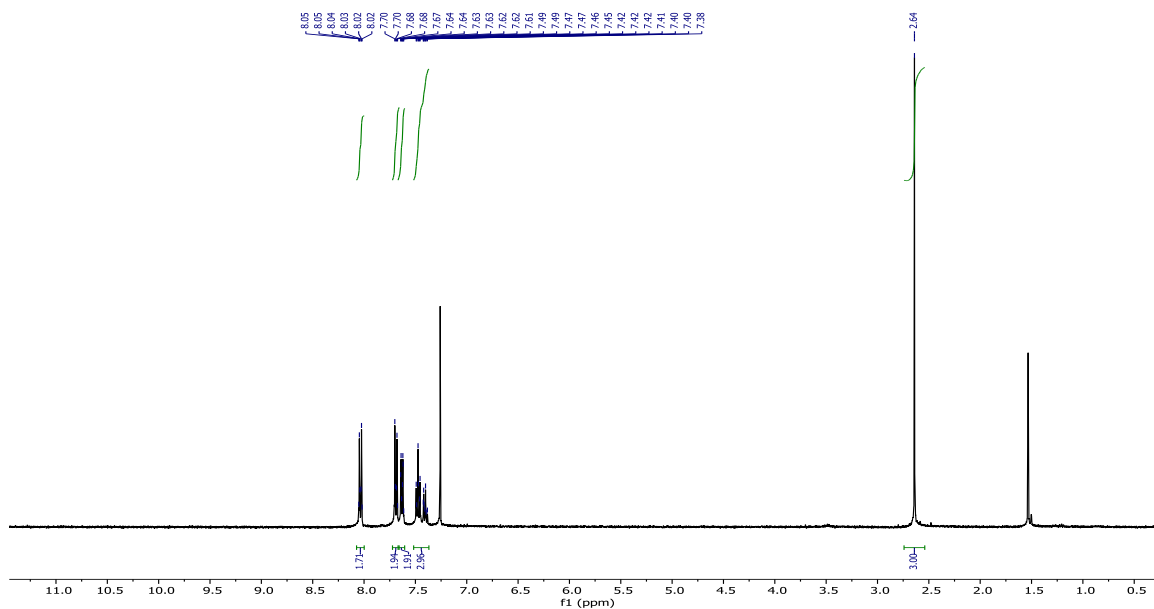


Figure 5. <sup>1</sup>H NMR spectrum of 4-acetylbiphenyl.

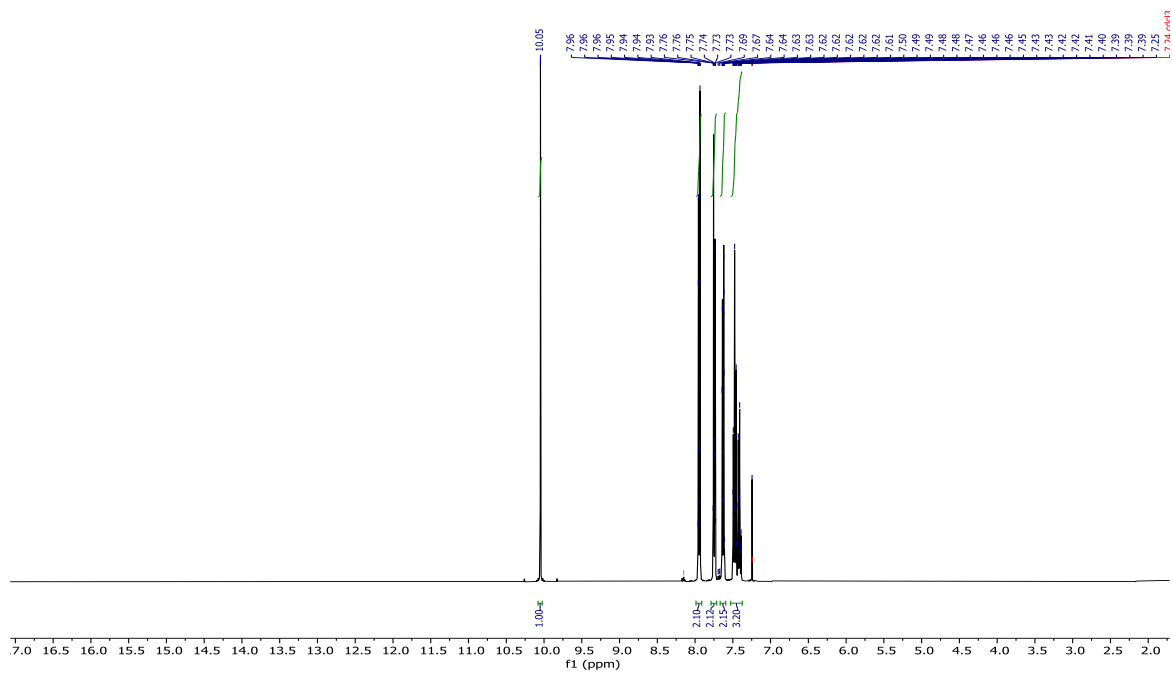


Figure 6.  $^1\text{H}$  NMR spectrum of biphenyl-4-carbaldehyde.

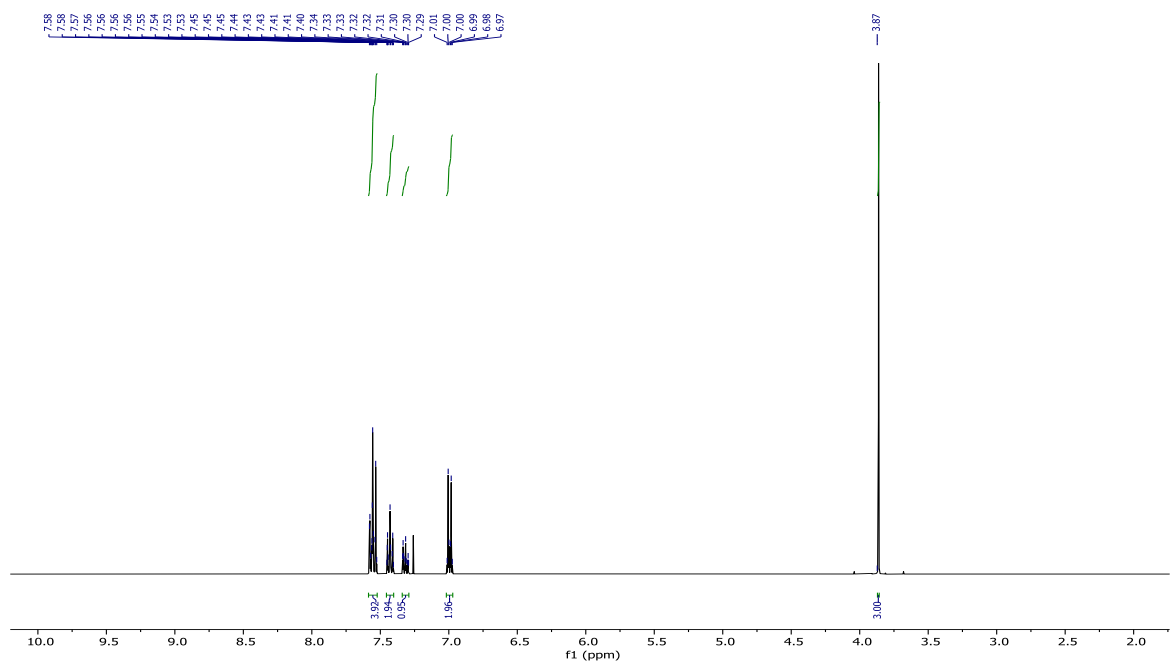


Figure 7.  $^1\text{H}$  NMR spectrum of 4-methoxybiphenyl.

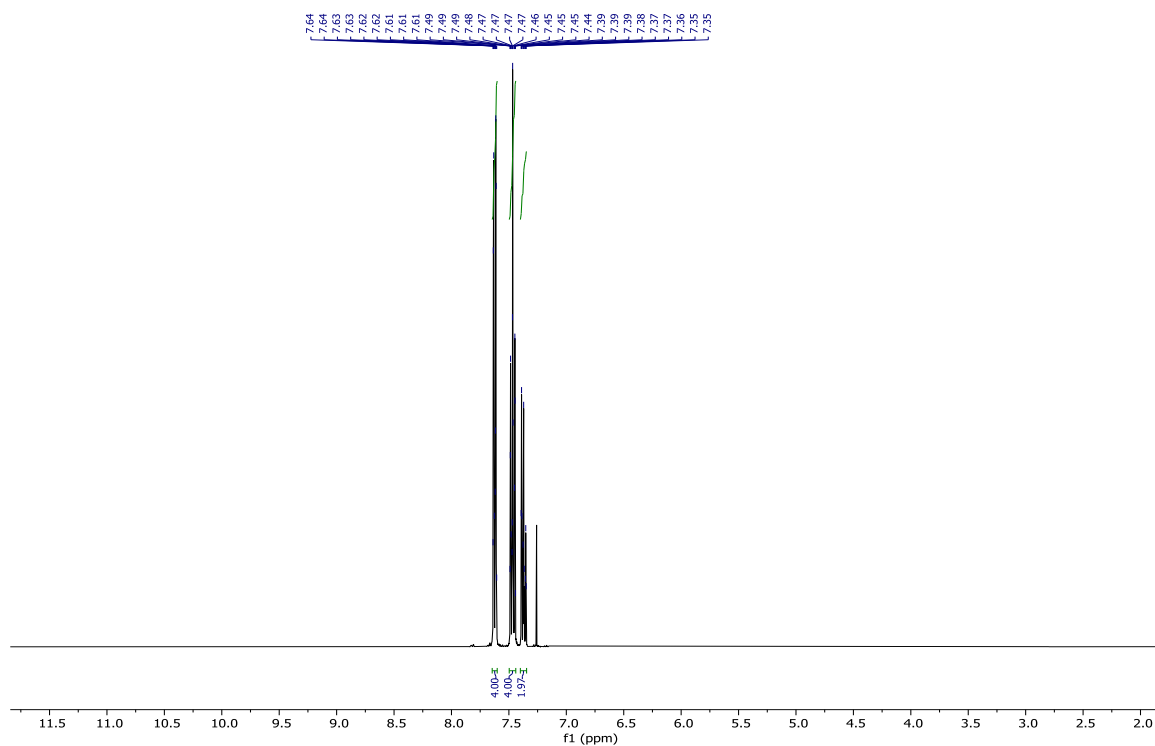


Figure 8. <sup>1</sup>H NMR spectrum of biphenyl.