Sterically Encumbered Tetraarylimidazolium Carbenes Pd-PEPPSI Complexes: Highly Efficient Direct Arylation of Imidazoles with Aryl Bromides under Aerobic Conditions

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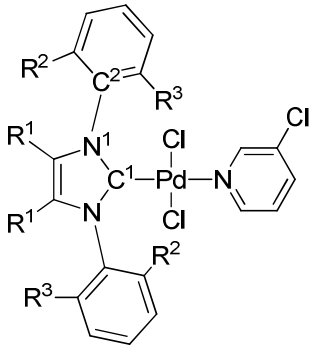
6. NMR spectrums of the arylated cross-coupling products S18

Table S1. Selected distances [Å] and angles [°] for the crystal structures and optimized structures of **C1**, **C2**, and **GADKIH**.



C1: R^1 = Ph, R^2 = Me, R^3 = Me
C2: R^1 = Ph, R^2 = Et, R^3 = Et
GADKIH: R^1 = H, R^2 = Et, R^3 = Et

C1	Crystal structure	DFT Optimized Structure
d(Pd1-C29)	1.957	1.967
∠Pd1-C29-N1	125.0	127.0
∠C29-N1-C1	123.0	123.0
C2		
d(Pd1-C16)	1.979	1.993
∠Pd1-C16-N1	127.2	127.3
∠C29-N1-C1	124.3	124.3
GADKIH		
d(Pd1-C16)	1.971	1.987
∠Pd1-C16-N1	128.4	127.7
∠C29-N1-C1	126.9	126.9

Procedure of mechanism experiments

The capture by oxidant experiment was carried out in flask equipped with a magnetic stirrer. **C3** (0.01 mmol), phenyl bromide (1.0 mmol), 1-methyl-1*H*-imidazole (1.0 mmol), K_2CO_3 (2.0 mmol), PivOH (0.3 mmol) and 3 mL of DMAc were added into the reactor. The reaction mixture was carried out at 130 ^oC for 12 h in the presence of 1 atm of oxygen or 2 equiv of $Cu(OAc)_2$ or 1 equiv of TEMPO. The treatment of the mixture was according to the standard direct arylation.

One-pot competition study on 2-chlorothiophene and 2-methylthiophene with phenyl bromides was performed. **C3** (0.01 mmol), phenyl bromide (1.0 mmol), 2-chlorothiophene (1.0 mmol), 2-methylthiophene (1.0 mmol), K_2CO_3 (2.0 mmol), PivOH (0.3 mmol) and 3 mL of DMAc were added to a flask and the reaction was heated to 130 ºC for 7 min. When reaching the setting time, 20 mL of water was added. The mixture was diluted with Et_2O (5 mL), followed by extraction three times (3 × 5 mL) with Et_2O and the added. The resulting mixture was analyzed by GC-MS with the (trifluoromethyl)benzene as internal standard.

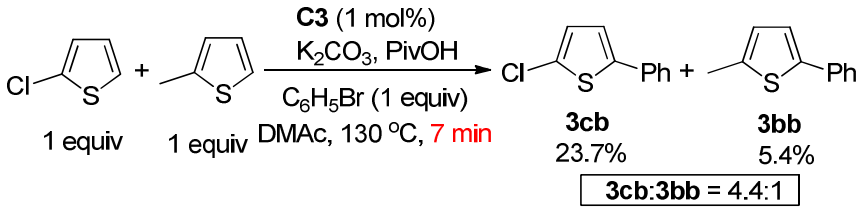
Mechanism discussion

We were then interested to gain some insights into the possible mechanism. The direct reaction between 1-methyl-1*H*-imidazole (**7a**) and 1-bromo-4-chlorobenzene (**8a**) in the presence of 1 equiv of 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) as radical scavenger was performed. The GC yields of **9aa** were obtained in 86%, which

ruled out the possibility of radical process in the arylation.[S1] The Heck-type mechanism seems like impossible, because its involving of insertion and β-H elimination pathway would favor the generation of C4-arylation product.[S2] On the other hand, the reaction was carried out in the presence of 1 atm of oxygen as oxidant, which delivered a much less efficiency of 19% GC yield. Moreover, none arylated product was found when strong oxidant of $Cu(OAc)_2$ was used. These results suggest the Pd(0) would be captured by the strong oxidant, which impeded the arylation reaction.

To provide additional evidence for this process or not, a one-pot competition experiment performed with an equimolar mixture of 2-chlorothiophene and 2-methylthiophene was conducted. The experiment showed that arylation of the more electron deficient 2-chlorothiophene was favored over the more nucleophilic 2-methylthiophene in a 4.4:1 ratio (**Scheme S1**). This outcome excludes a competitive S_EAr pathway[3] but supported the CMD mechanism for which arylation of the electron deficient substrate was favored.[S3]

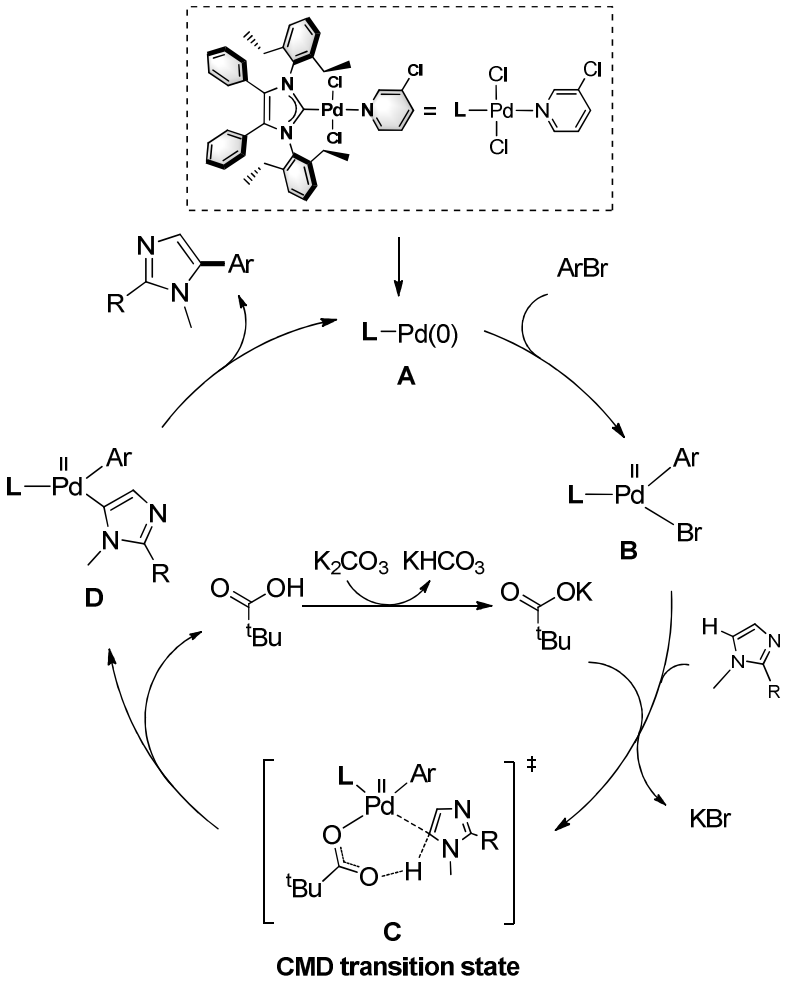
Scheme S1. One-Pot Competition Study



Considered the result obtained above as well as the indispensable role of the PivOH for the cross-coupling reaction, a concerted metalation deprotonation (CMD)

pathway would occur in the catalytic process(**Scheme S2**), which is in accordance with the Pd-catalyzed C-H functionalization arylation by Fagnou and our previous investigations.[S4, S5]

Scheme S2. Proposed Catalytic Cycle for Pd-PEPPSI Catalyzed Direct Arylation of Imidazoles with Aryl Bromides



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(S4) Gorelsky, S. I.; Lapointe, D.; Fagnou, K. *J. Org. Chem.* **2012**, *77*, 658-668.

(S5) Luo, B.-T.; Liu, H.; Lin, Z.-J.; Jiang, J.; Shen, D.-S.; Liu, R.-Z.; Ke, Z.; Liu, F.-S. *Organometallics* **2015**, *34*, 4881-4894.

Figure **S1**. The NMR spectrums of the α-diimine compound of **1**.

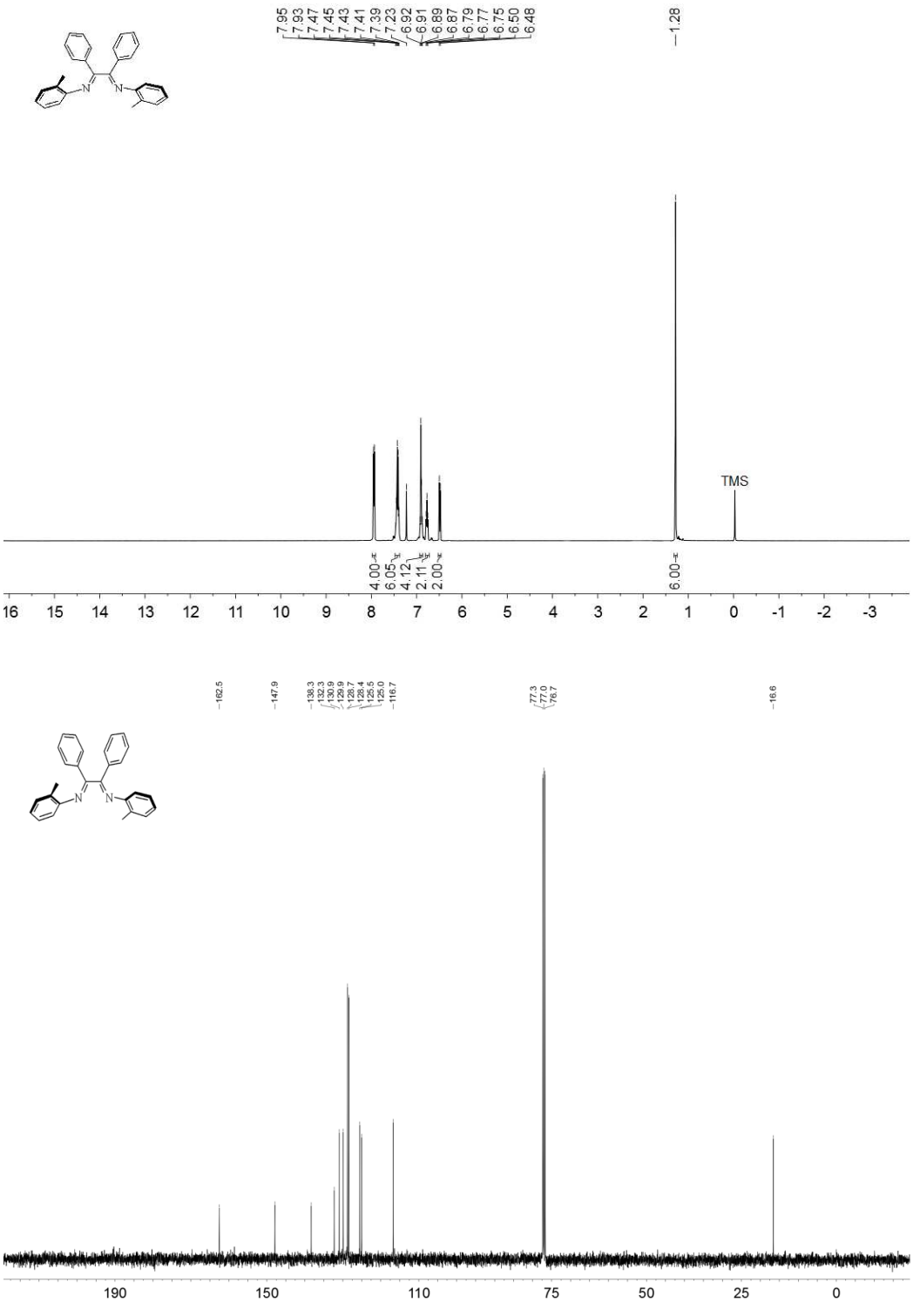


Figure **S2**. The NMR spectrums of the α-diimine compound of **3**.

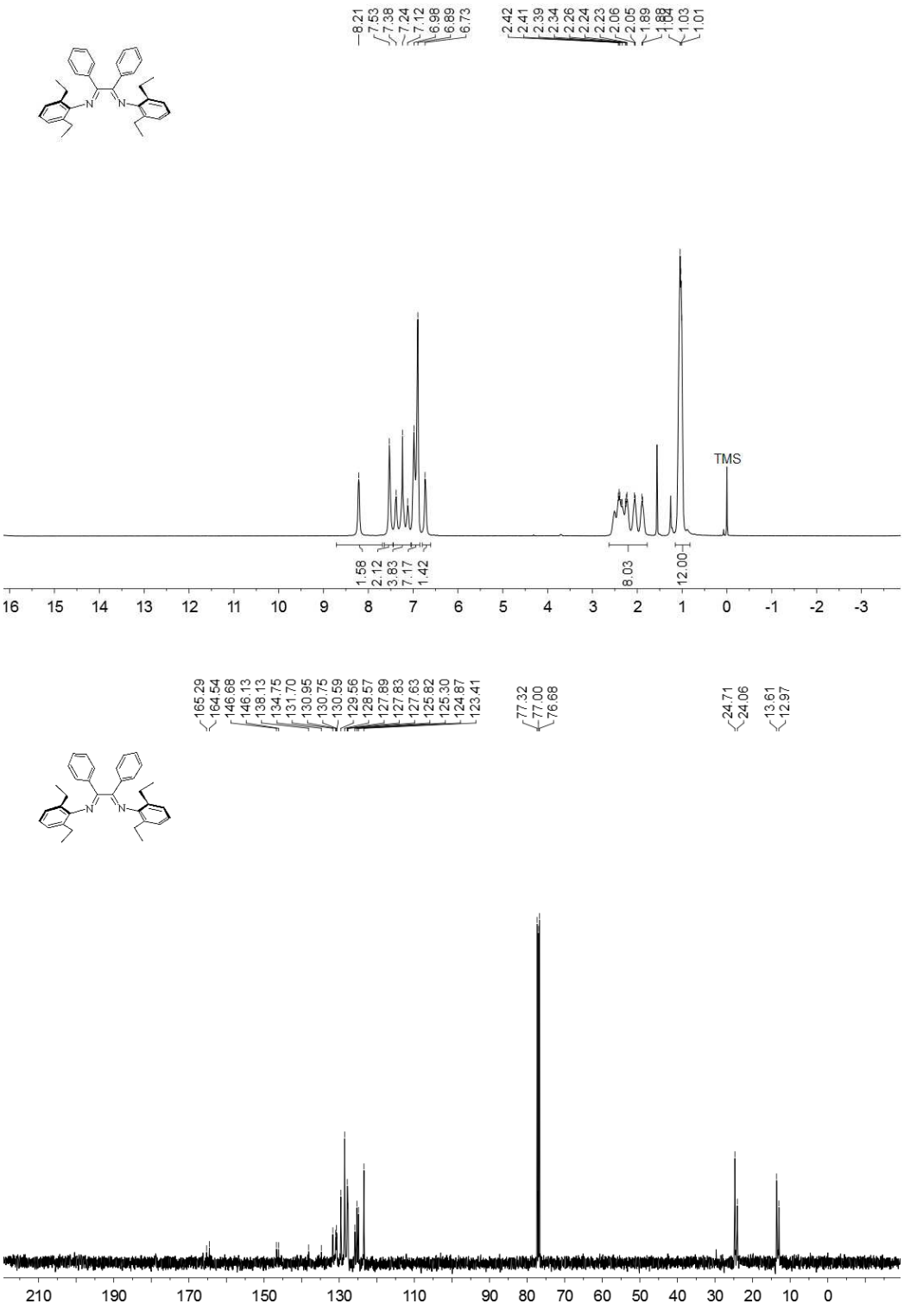


Figure **S3**. The NMR spectrums of the imidazolium salts compound of **L1**.

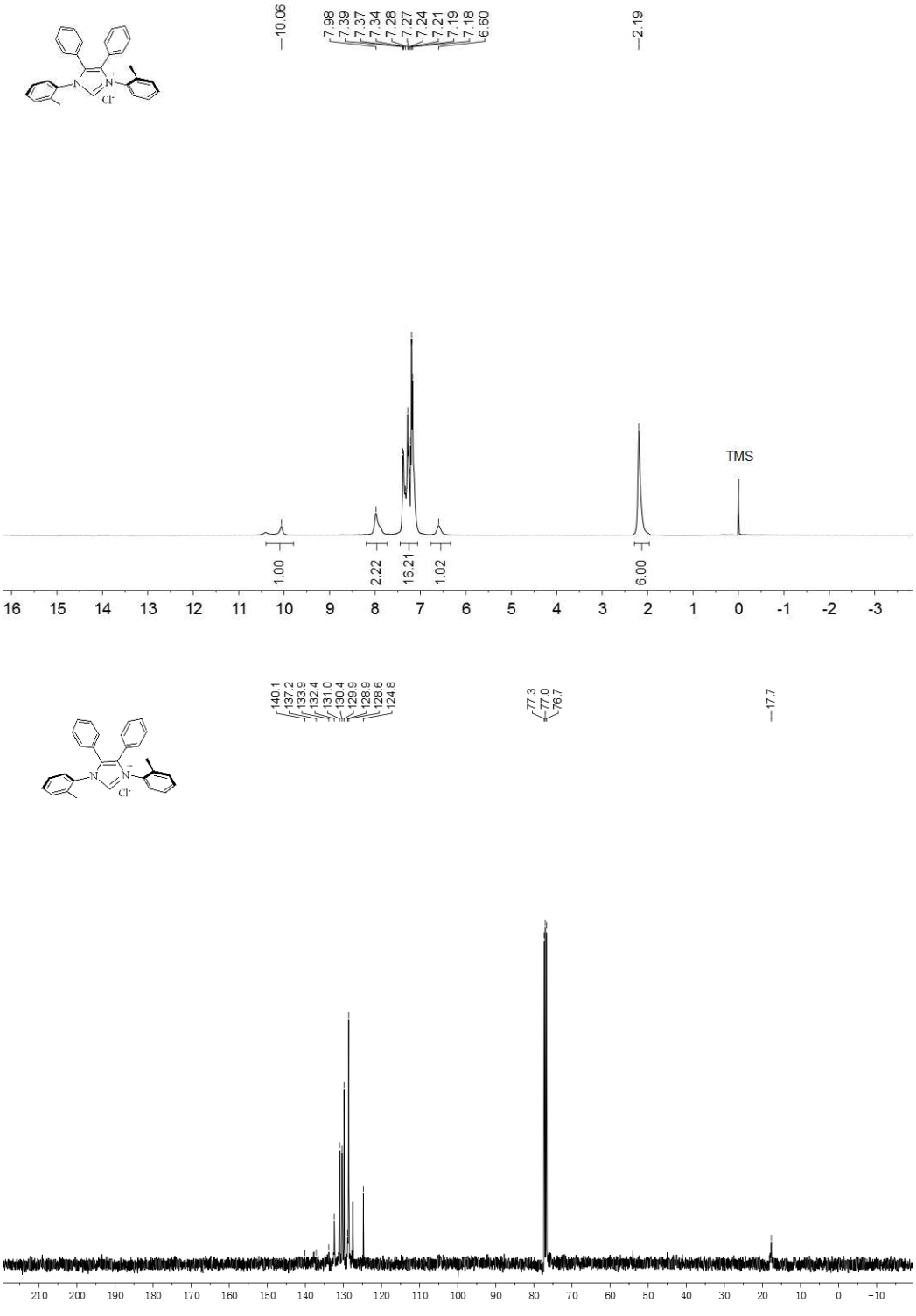
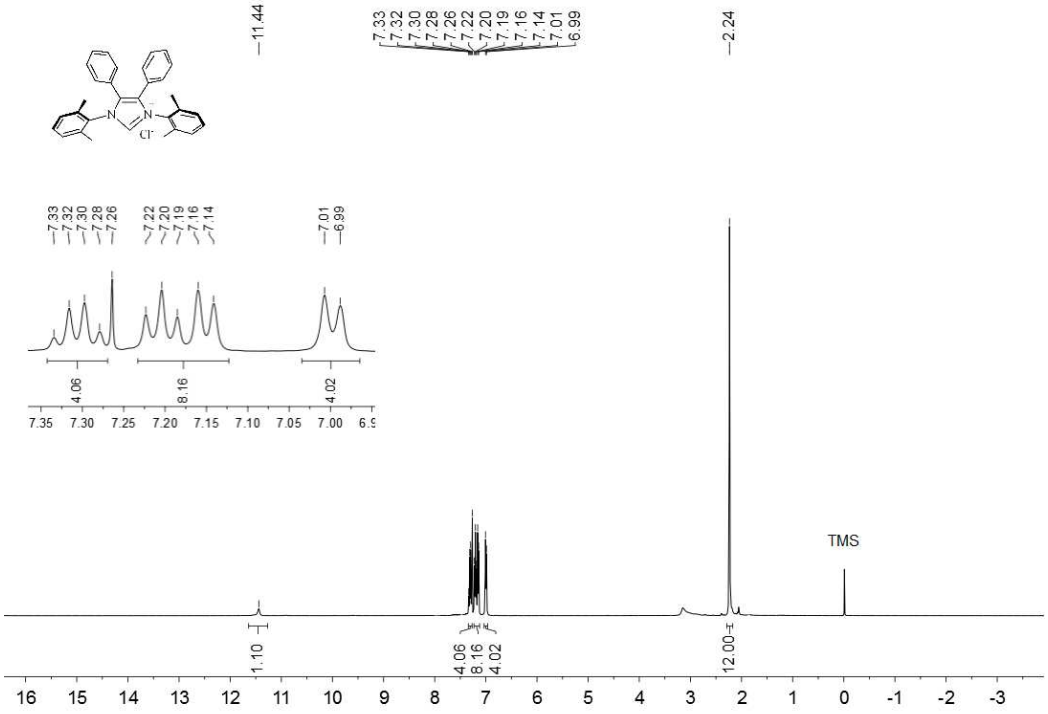


Figure **S4**. The NMR spectrums of the imidazolium salts compound of **L2**.



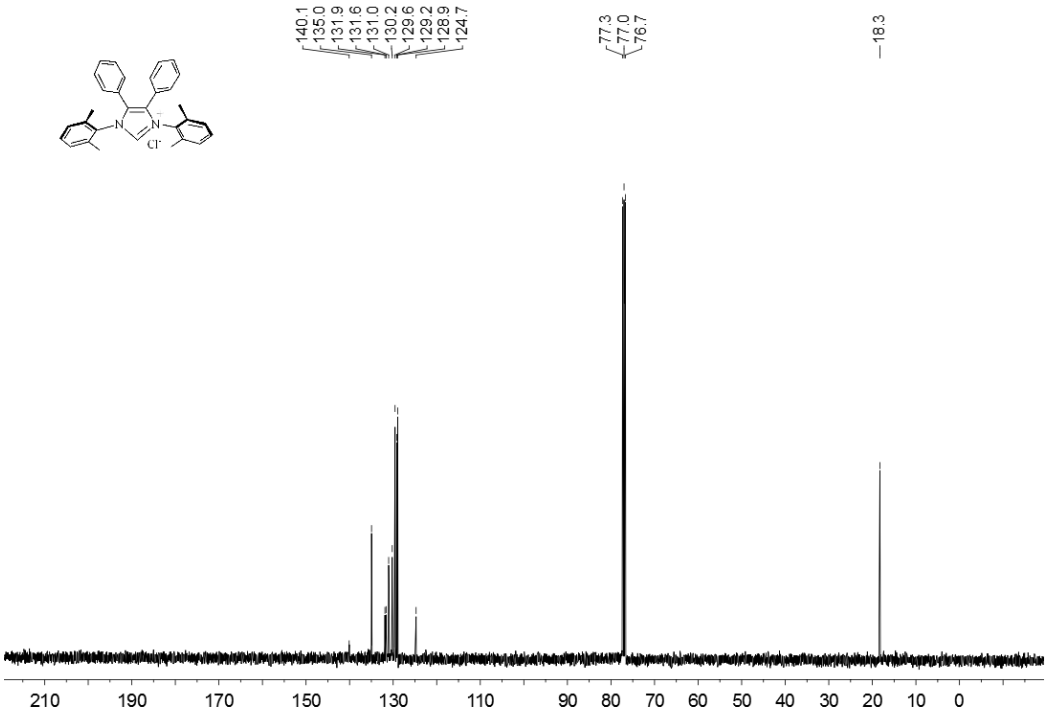


Figure **S5**. The NMR spectrums of the imidazolium salts compound of **L3**.

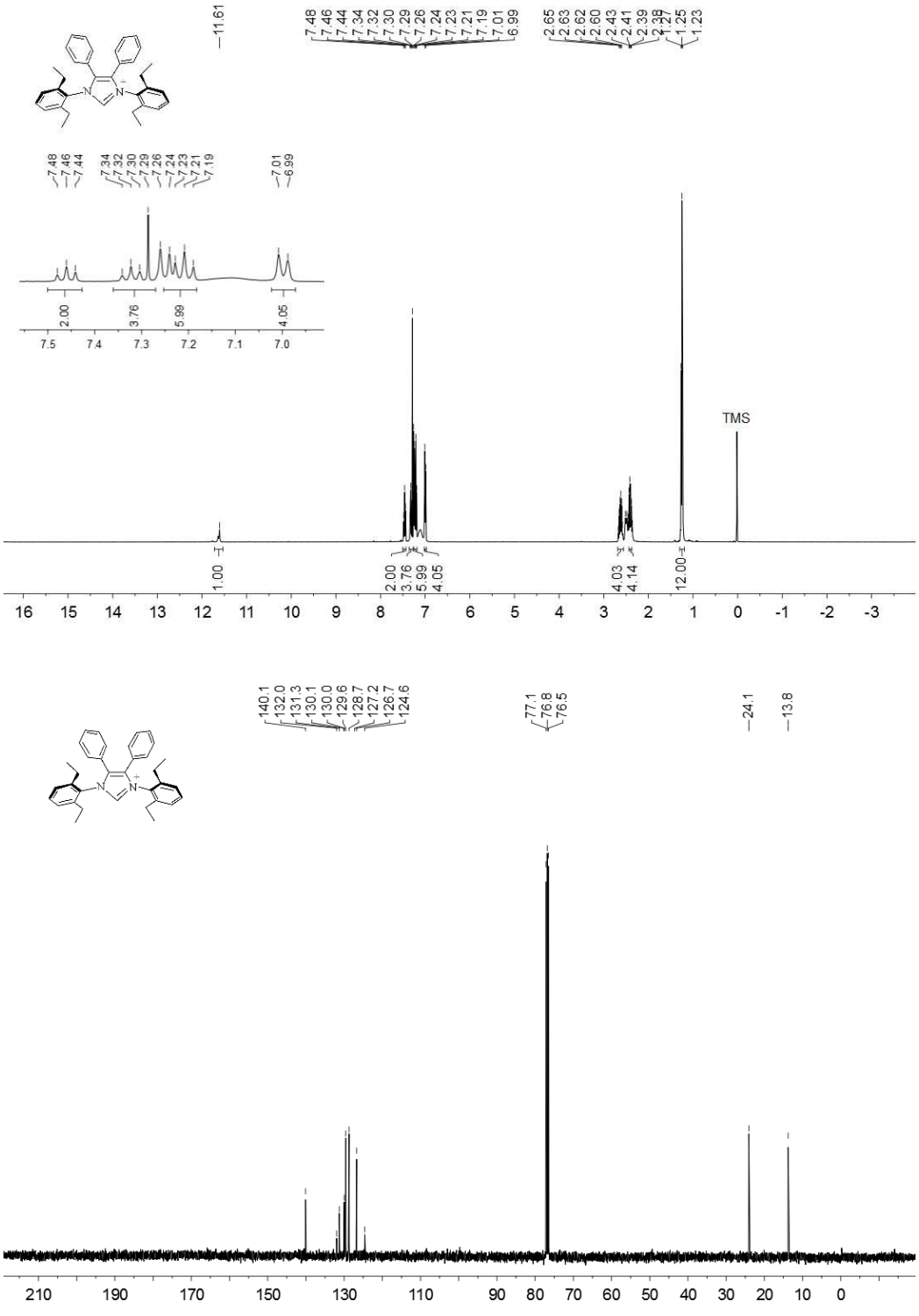


Figure **S6**. The NMR spectrums of the Pd-PEPPSI complex of **C1**.

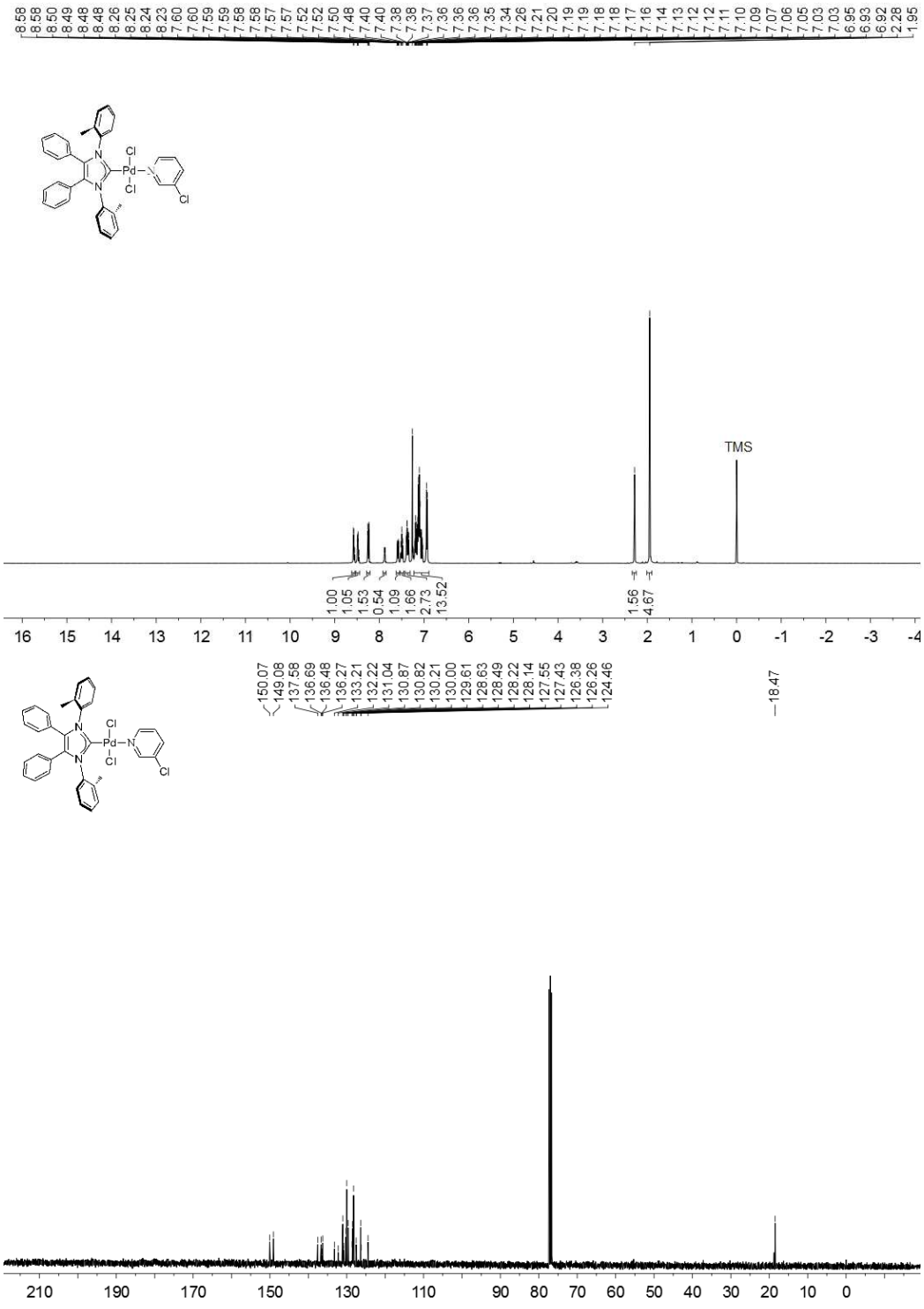


Figure **S7**. The NMR spectrums of the Pd-PEPPSI complex of **C2**.

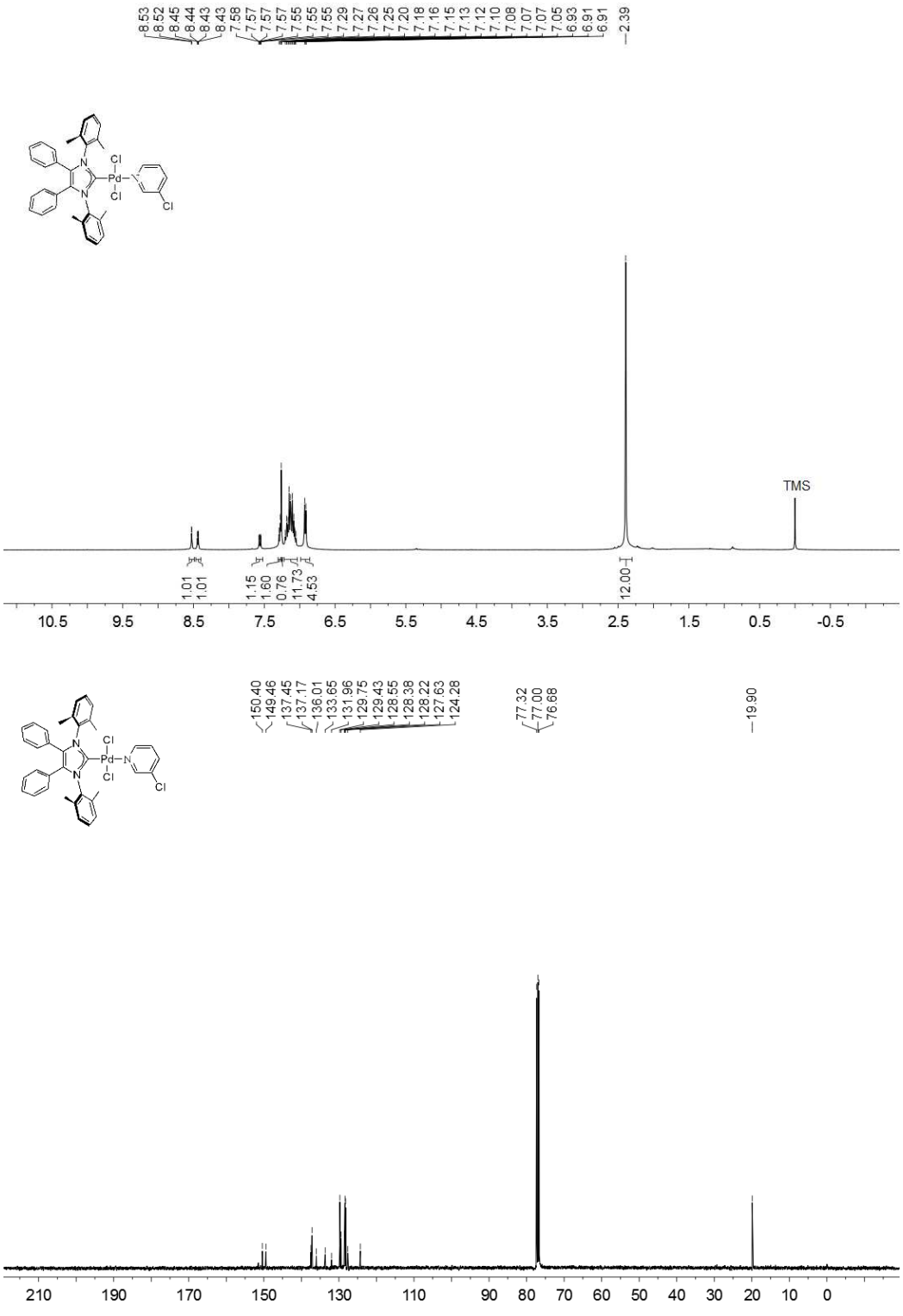


Figure **S8**. The NMR spectrums of the Pd-PEPPSI complex of **C3**.

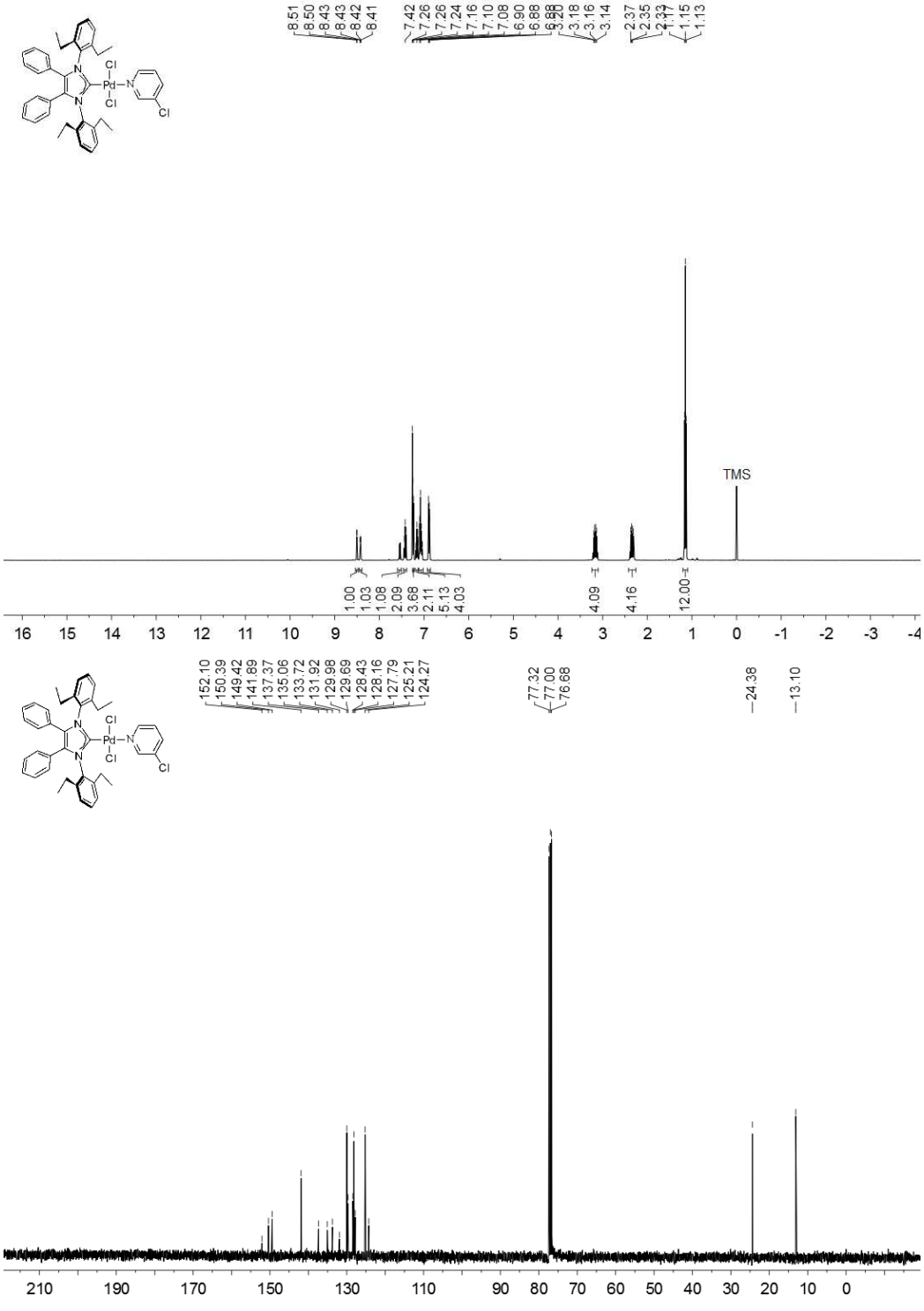


Figure **S9**. The NMR spectrums of the Pd-PEPPSI complex of **C4**.

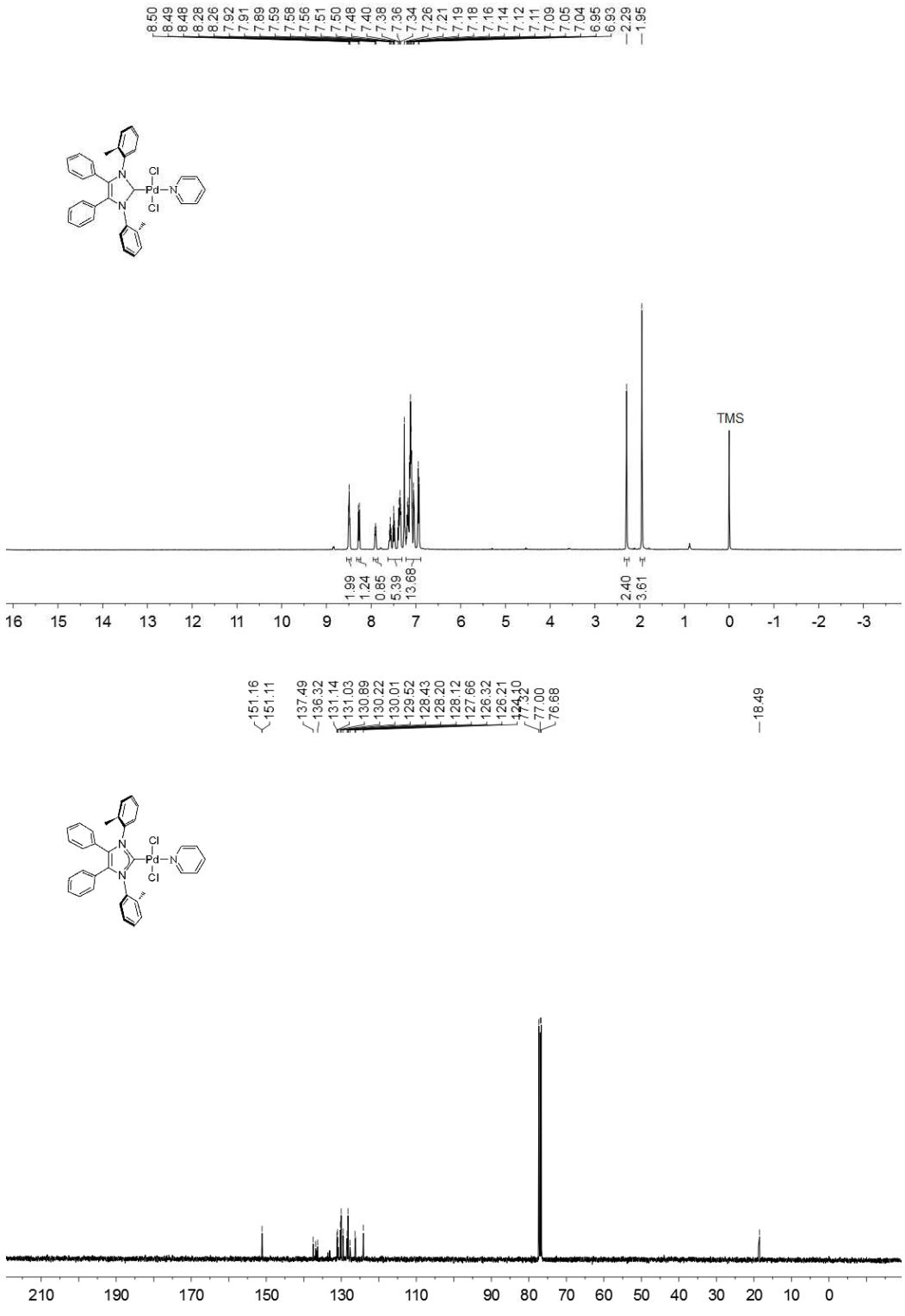


Figure **S10**. The NMR spectrums of the Pd-PEPPSI complex of **C5**.

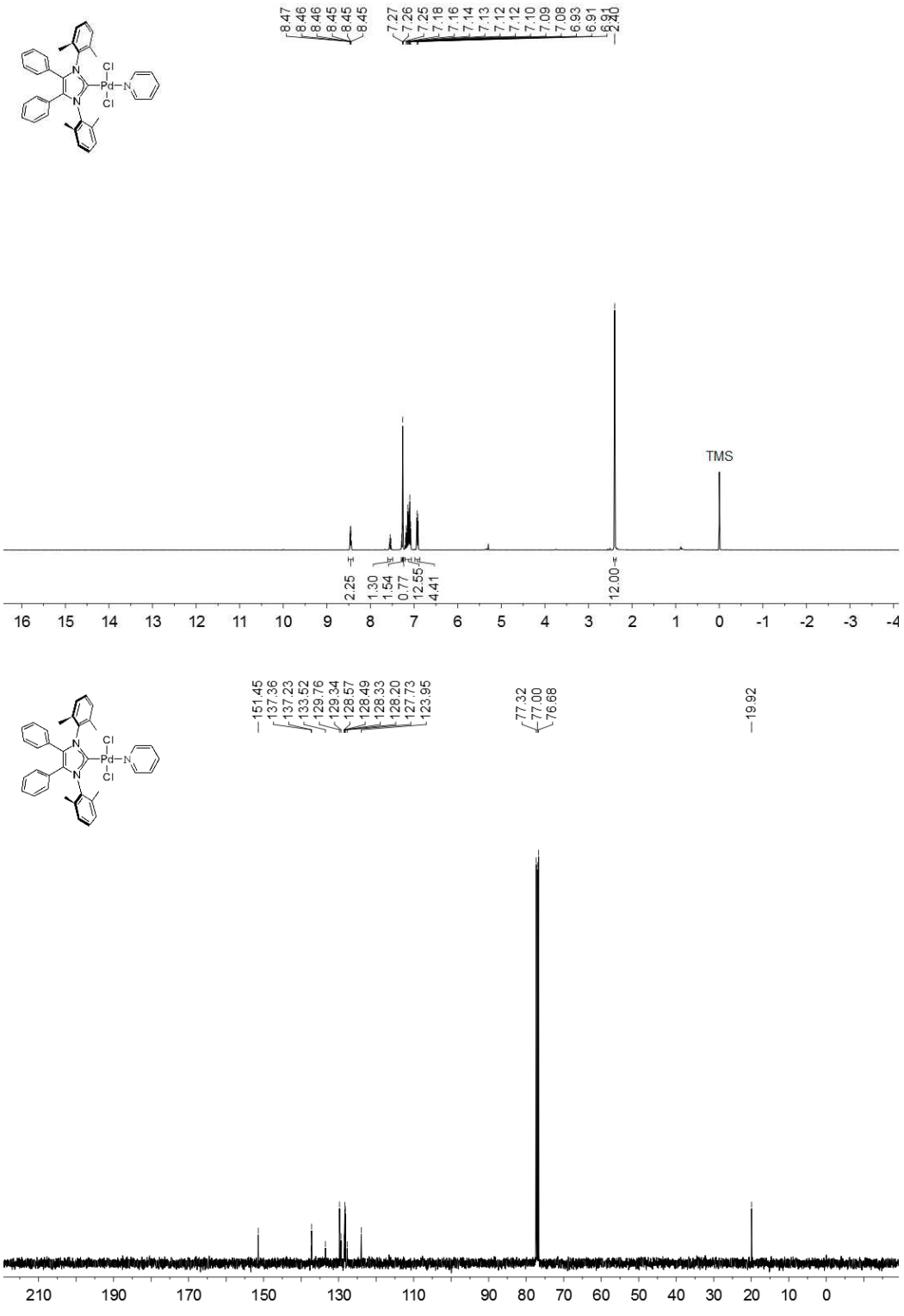


Figure **S11**. The NMR spectrums of the Pd-PEPPSI complex of **C6**.

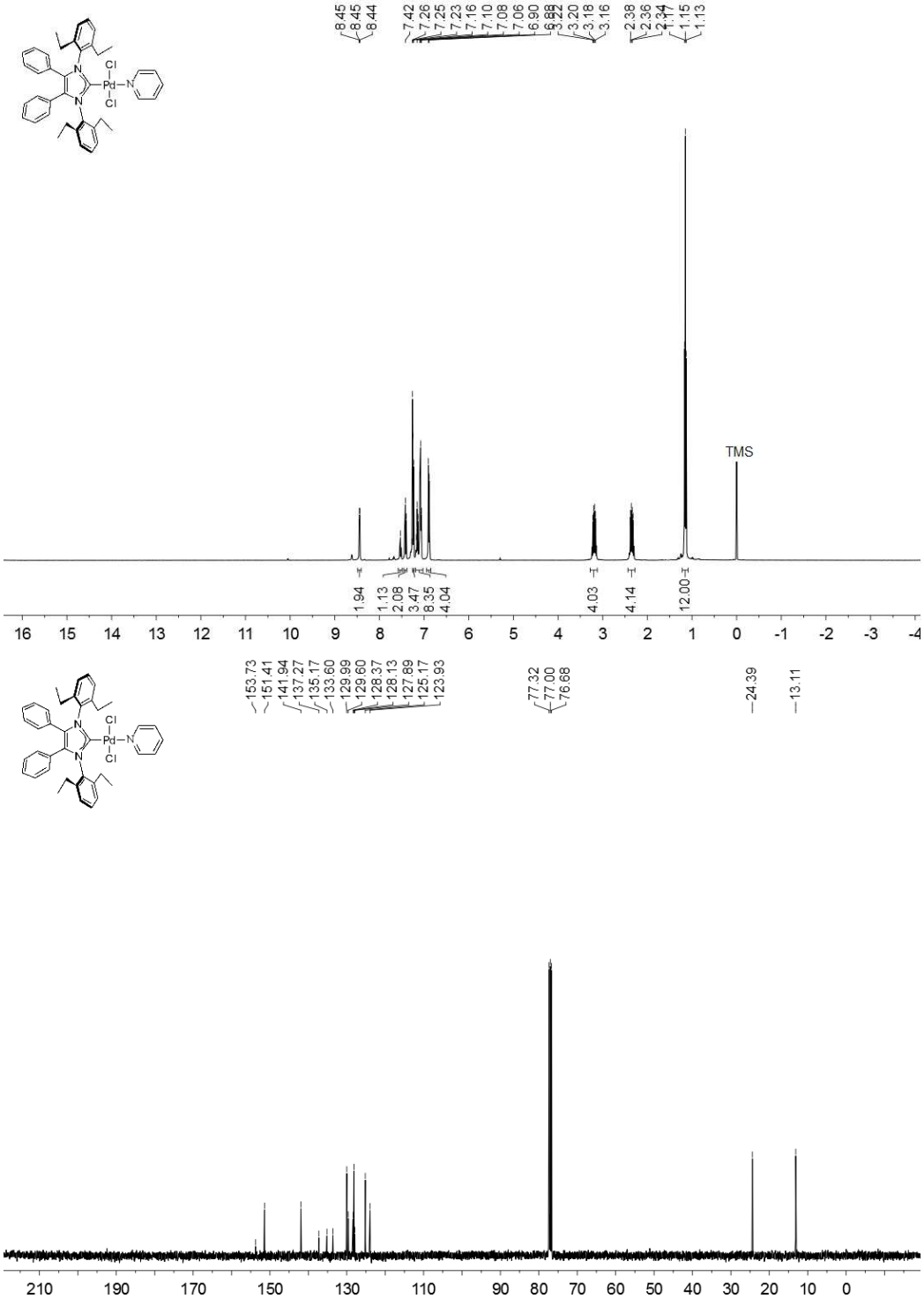


Figure **S12**. The NMR spectrums of 5-(4-chlorophenyl)-1-methyl-1H-imidazole (**9aa**)

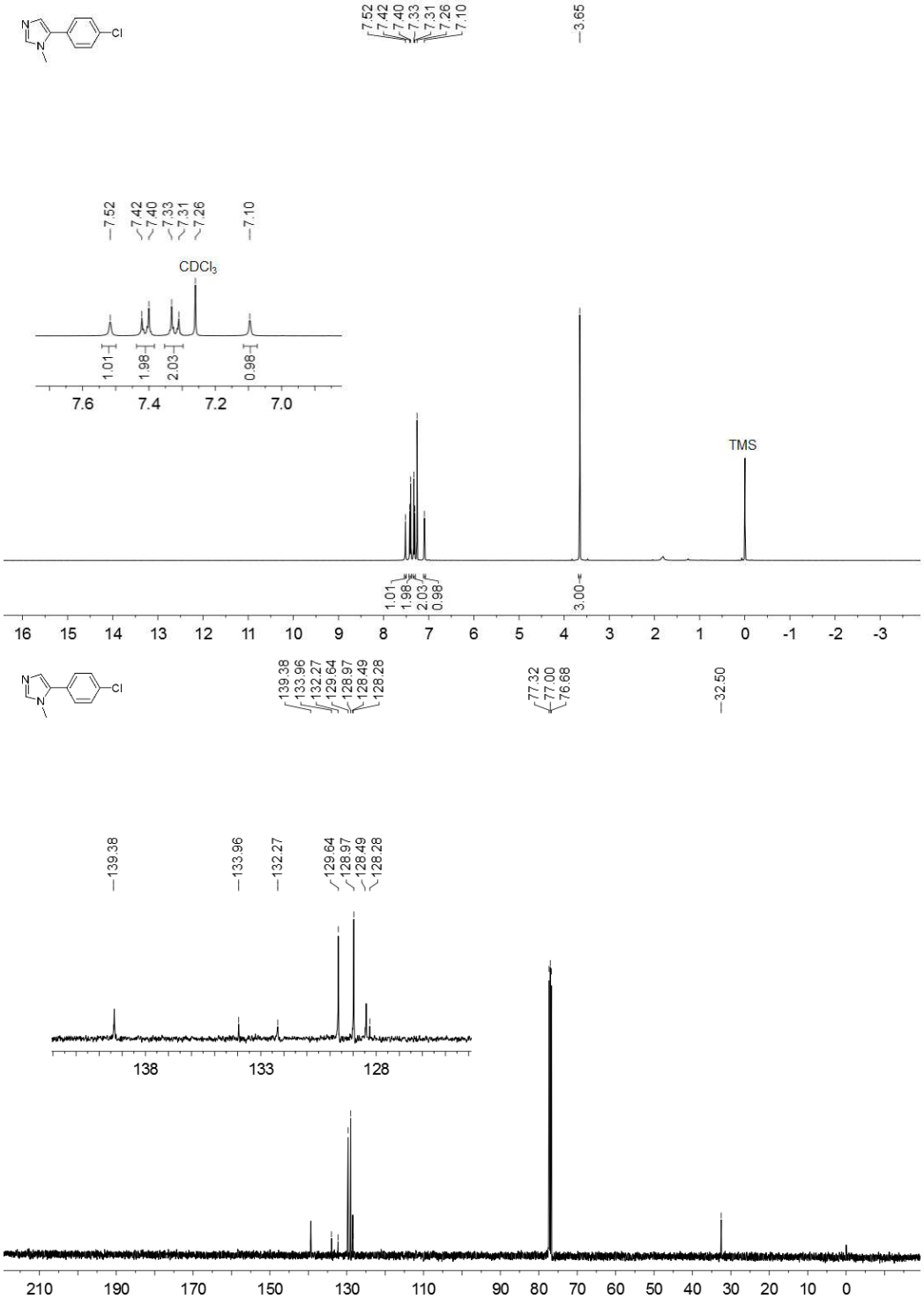


Figure **S13**. The NMR spectrums of methyl 4-(1-methyl-1H-imidazol-5-yl)benzoate (**9ab**)

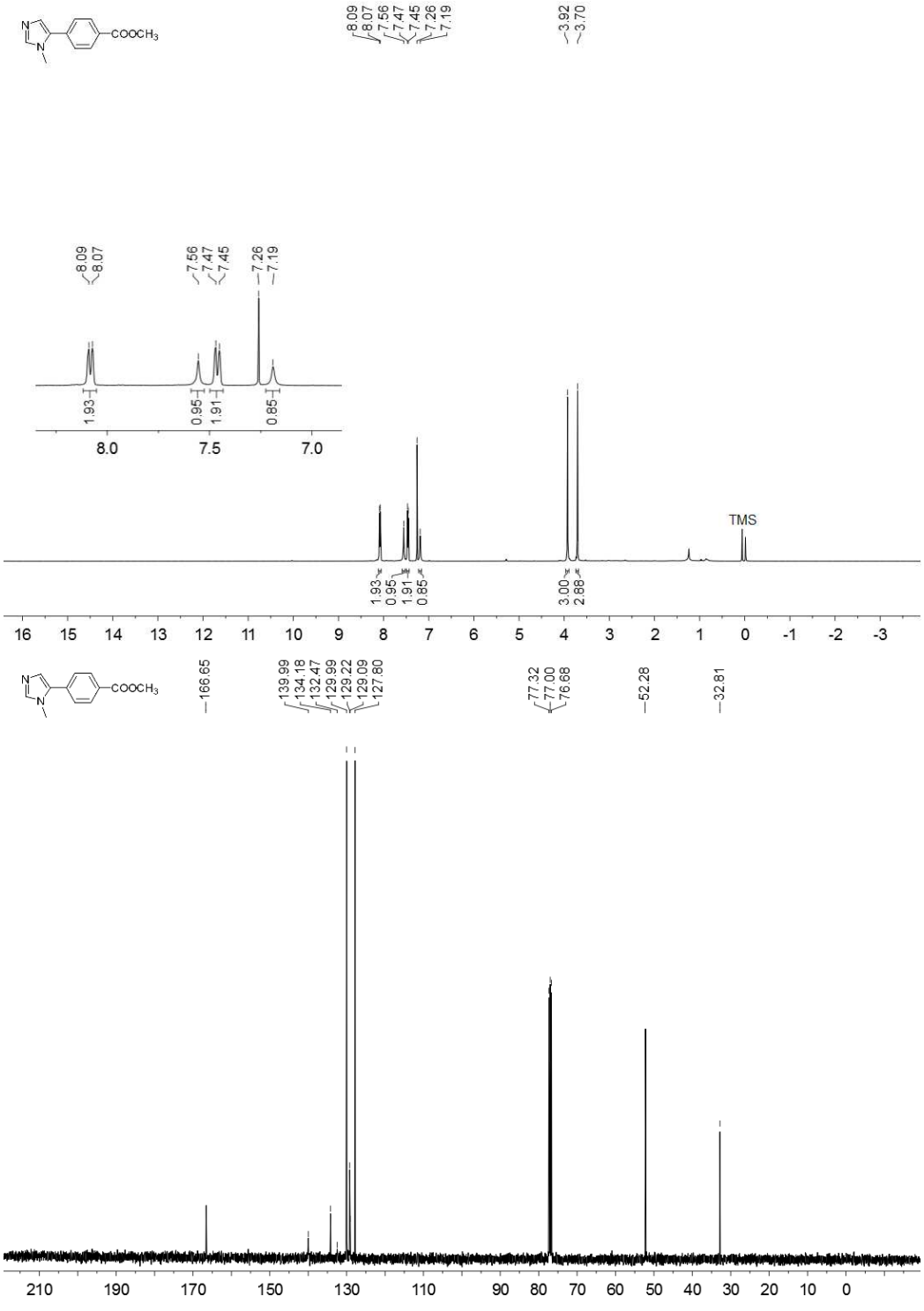


Figure **S14**. The NMR spectrums of 1-methyl-5-(4-nitrophenyl)-1H-imidazole (**9ac**)

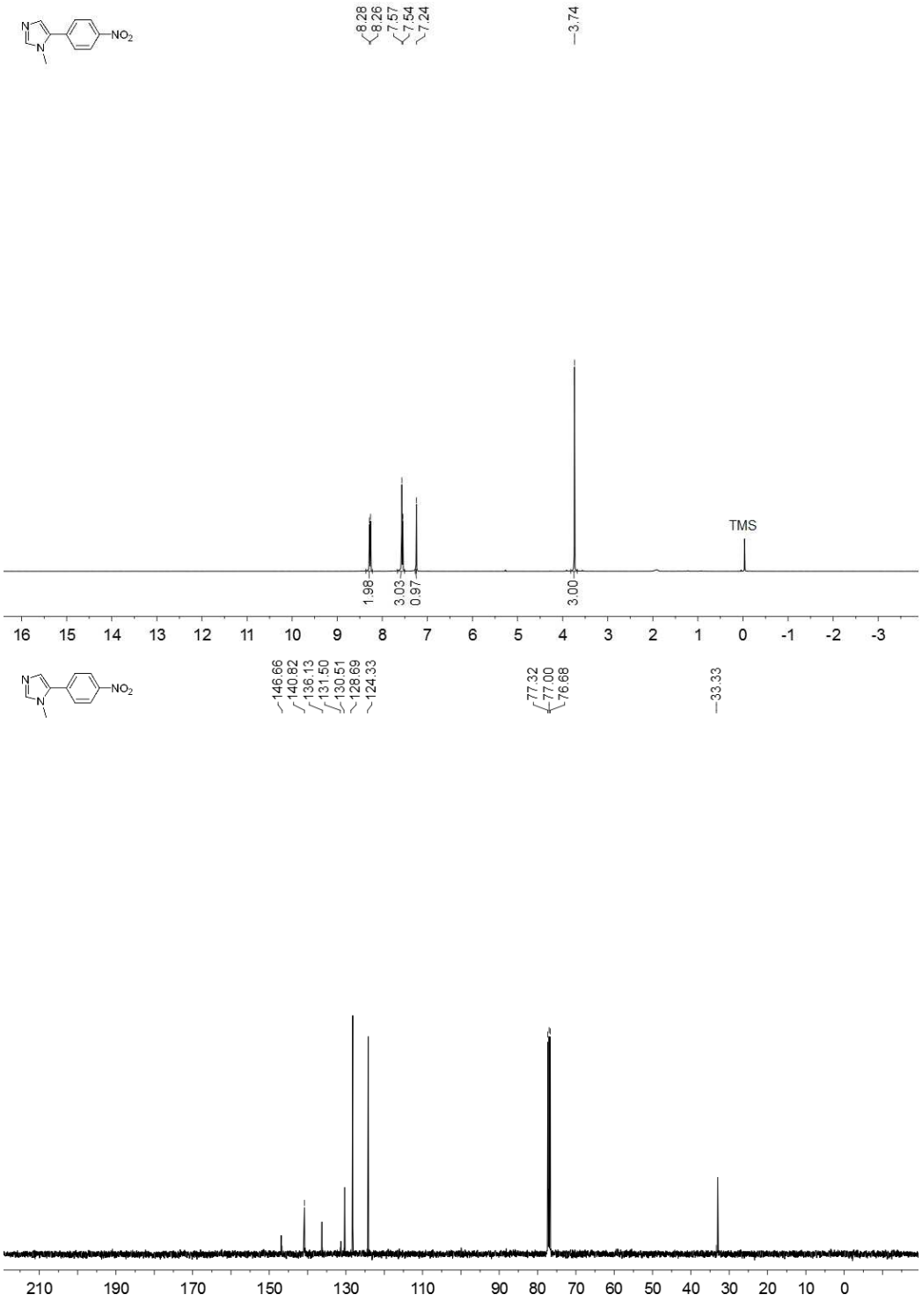


Figure **S15**. The NMR spectrums of 4-(1-methyl-1H-imidazol-5-yl)benzonitrile (**9ad**)

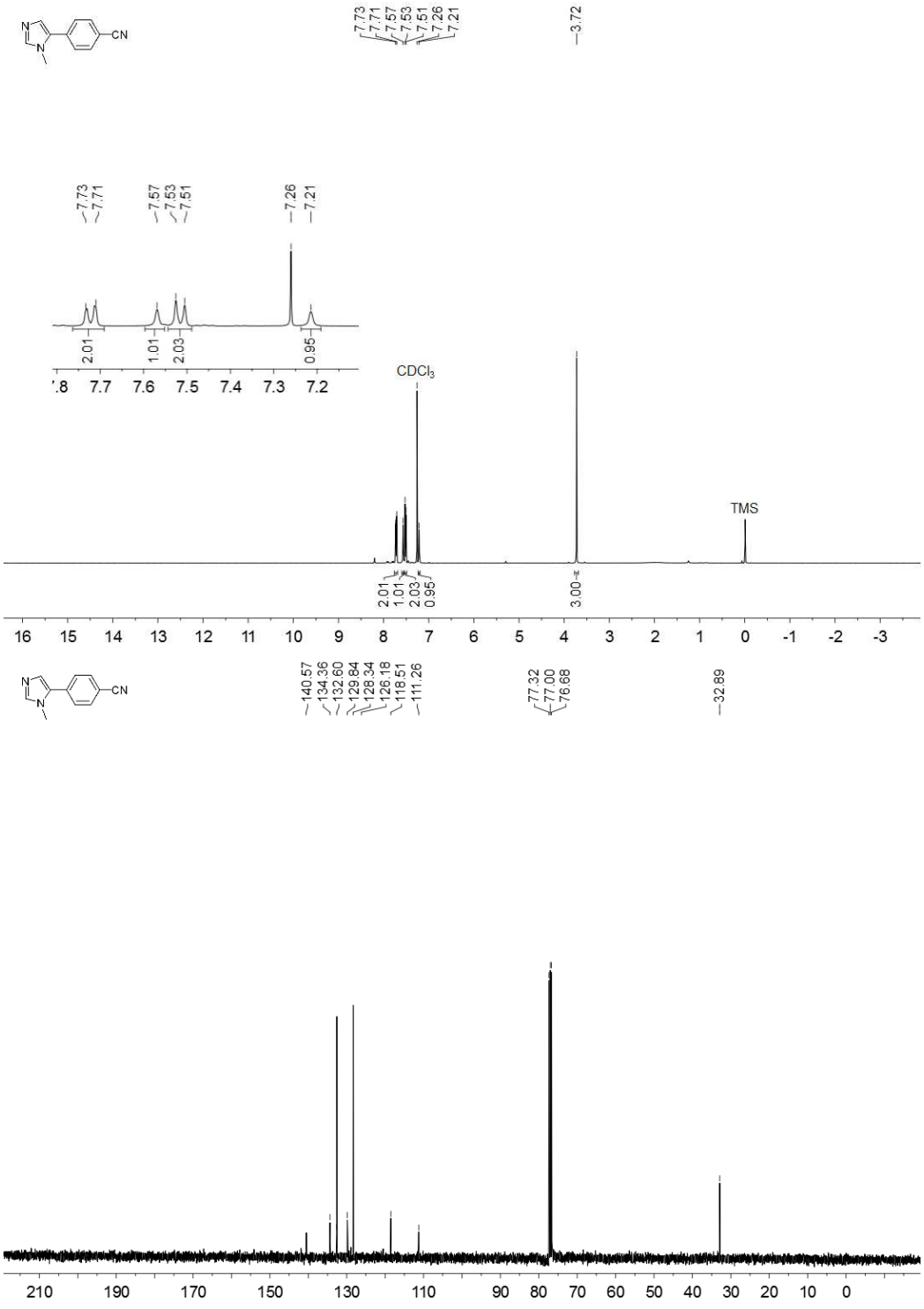


Figure **S16**. The NMR spectrums of 4-(1-methyl-1H-imidazol-5-yl)benzaldehyde (**9ae**)

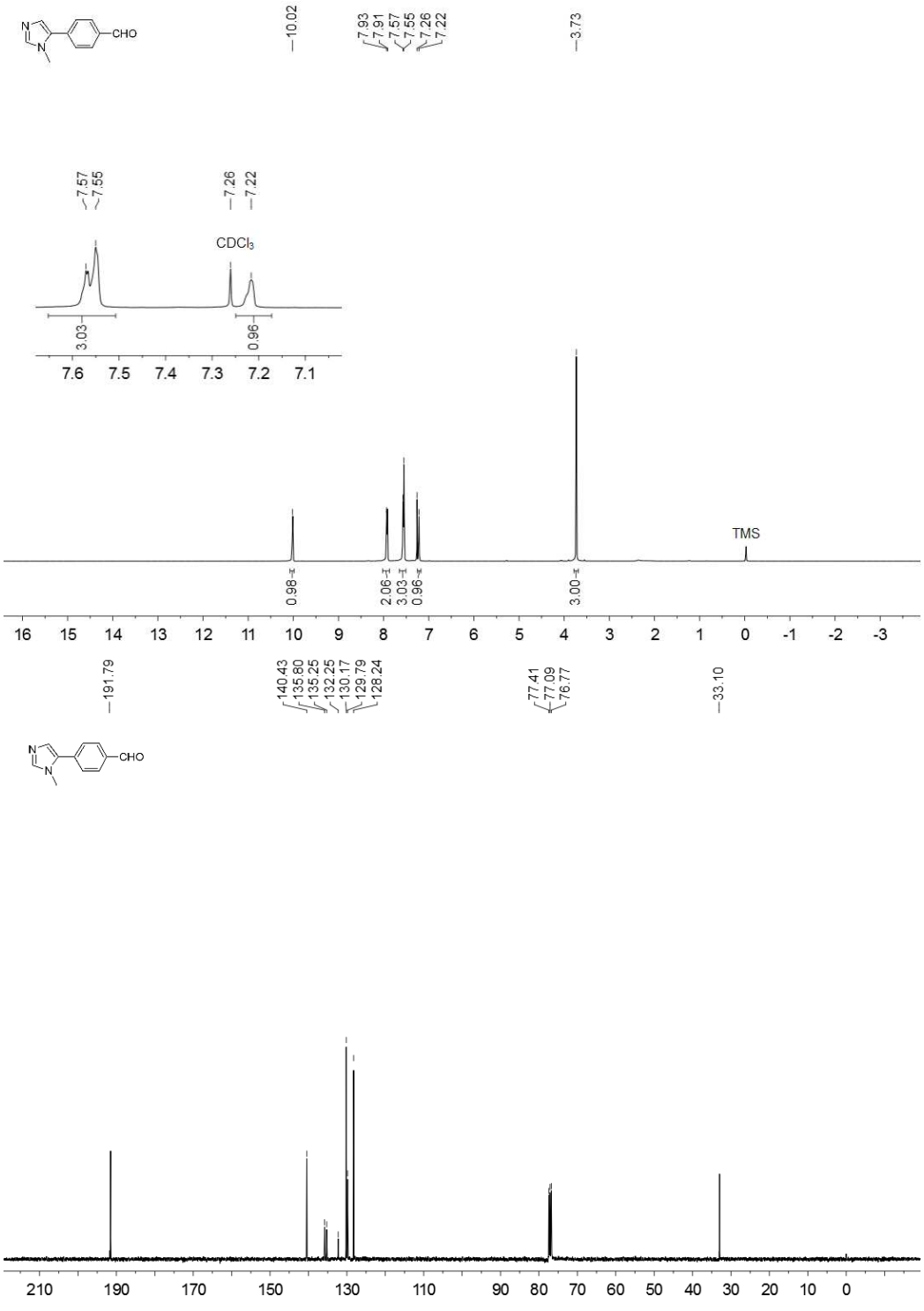


Figure **S17**. The NMR spectrums of 1-(4-(1-methyl-1H-imidazol-5-yl)phenyl)ethanone (**9af**)

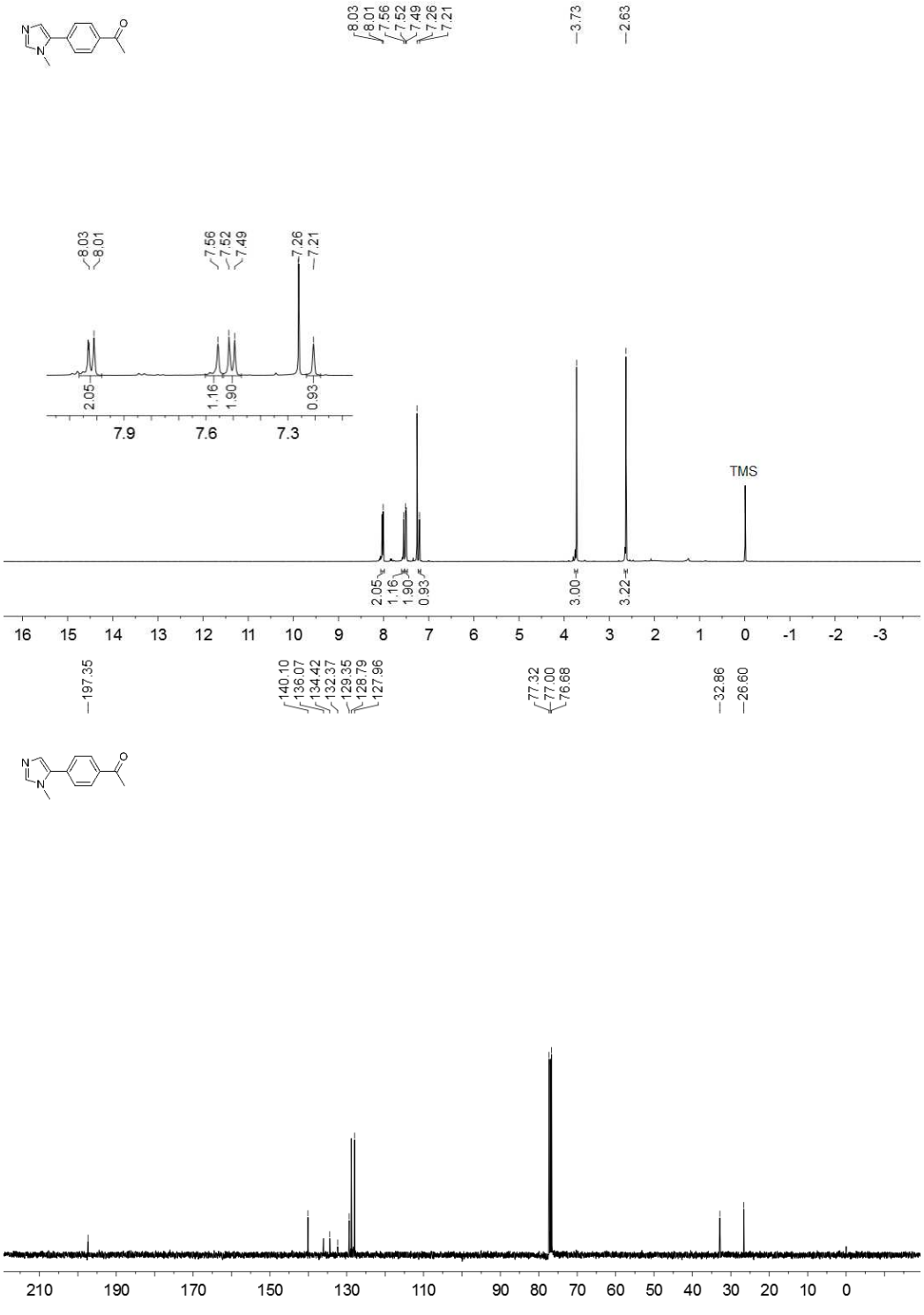


Figure **S18**. The NMR spectrums of 1-methyl-5-(4-(trifluoromethyl)phenyl)-1H-imidazole (**9ag**)

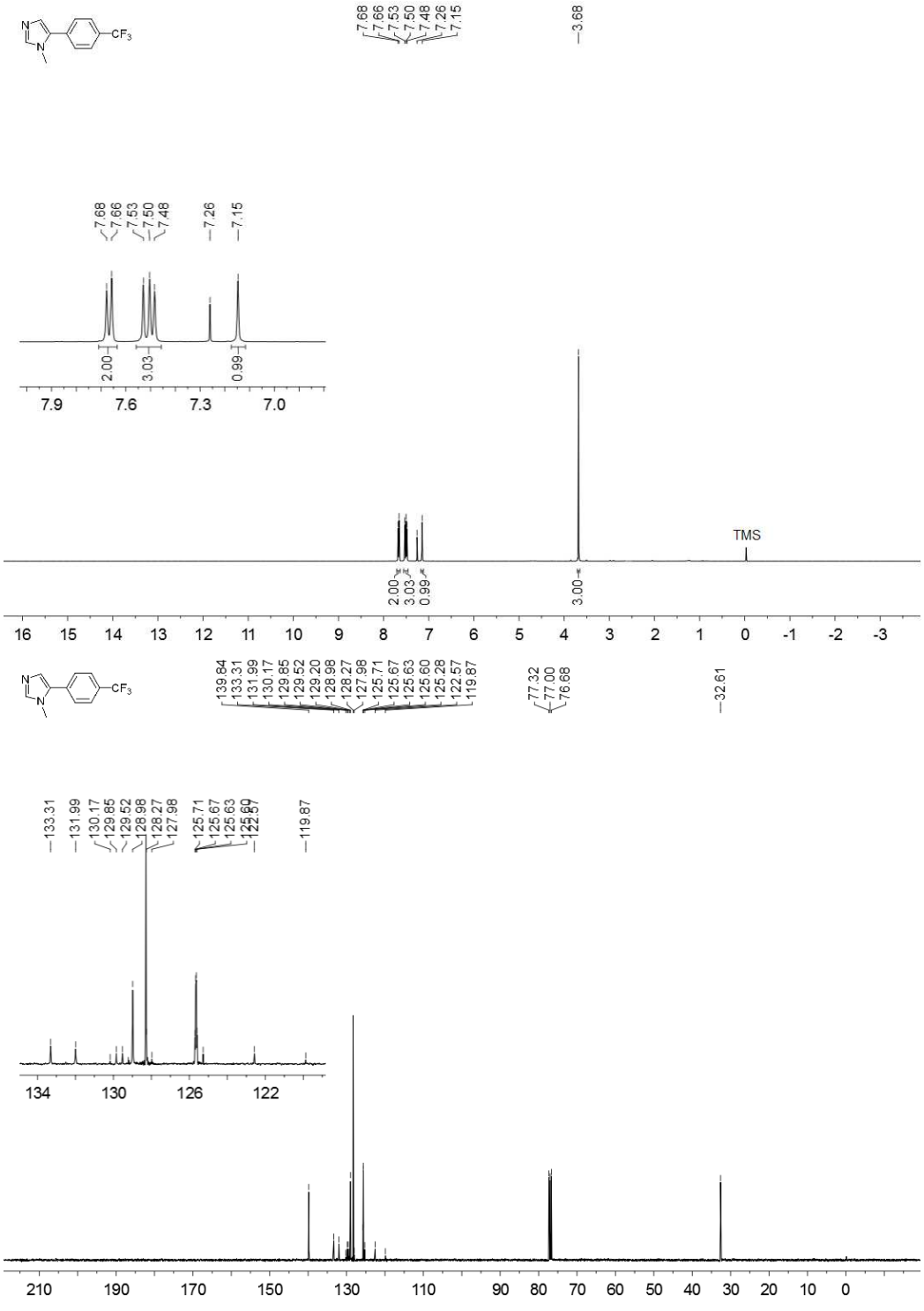


Figure **S19**. The NMR spectrums of 5-(4-fluorophenyl)-1-methyl-1H-imidazole (**9ah**)

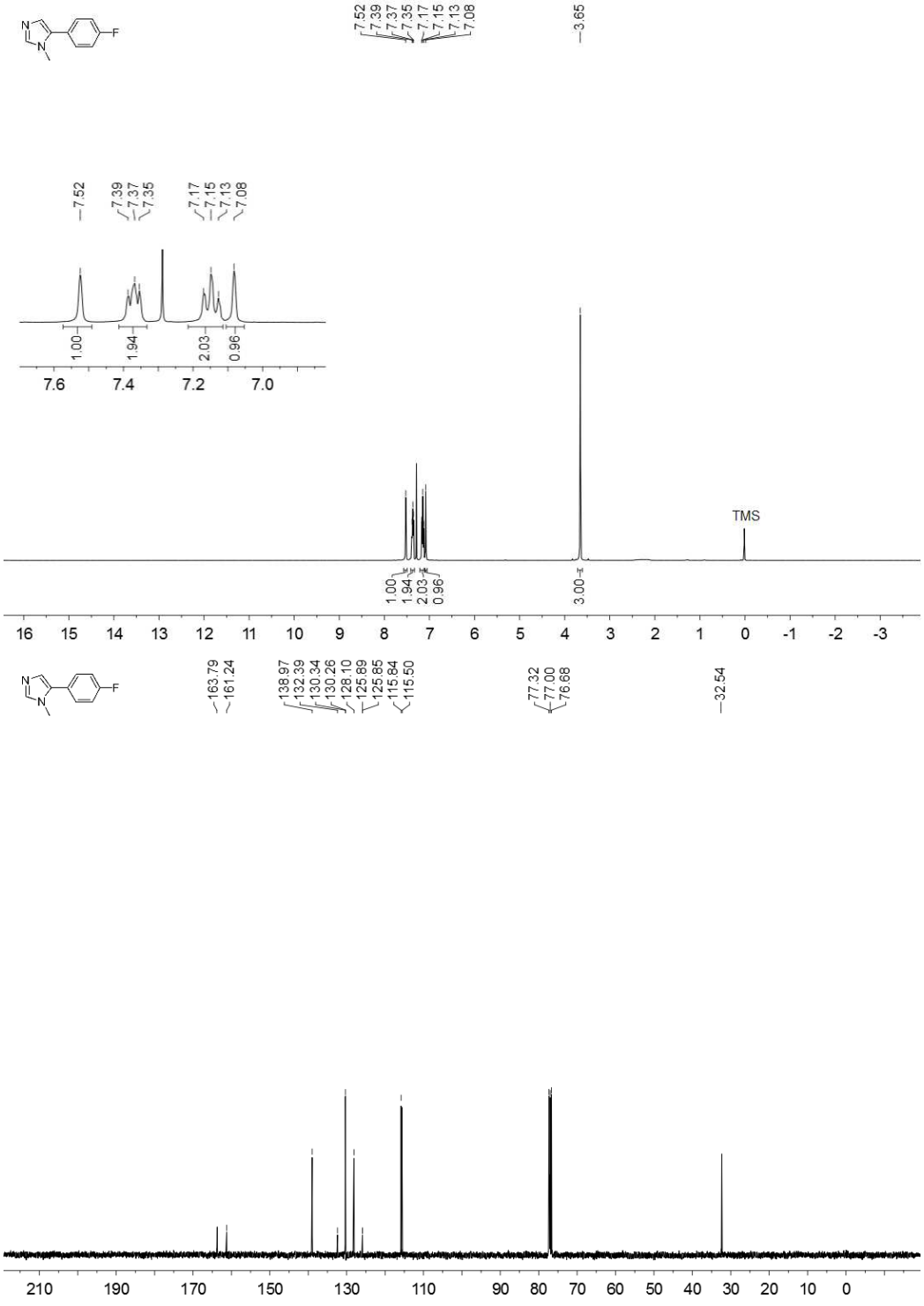


Figure **S20**. The NMR spectrums of 1-methyl-5-phenyl-1H-imidazole (**9ai**)

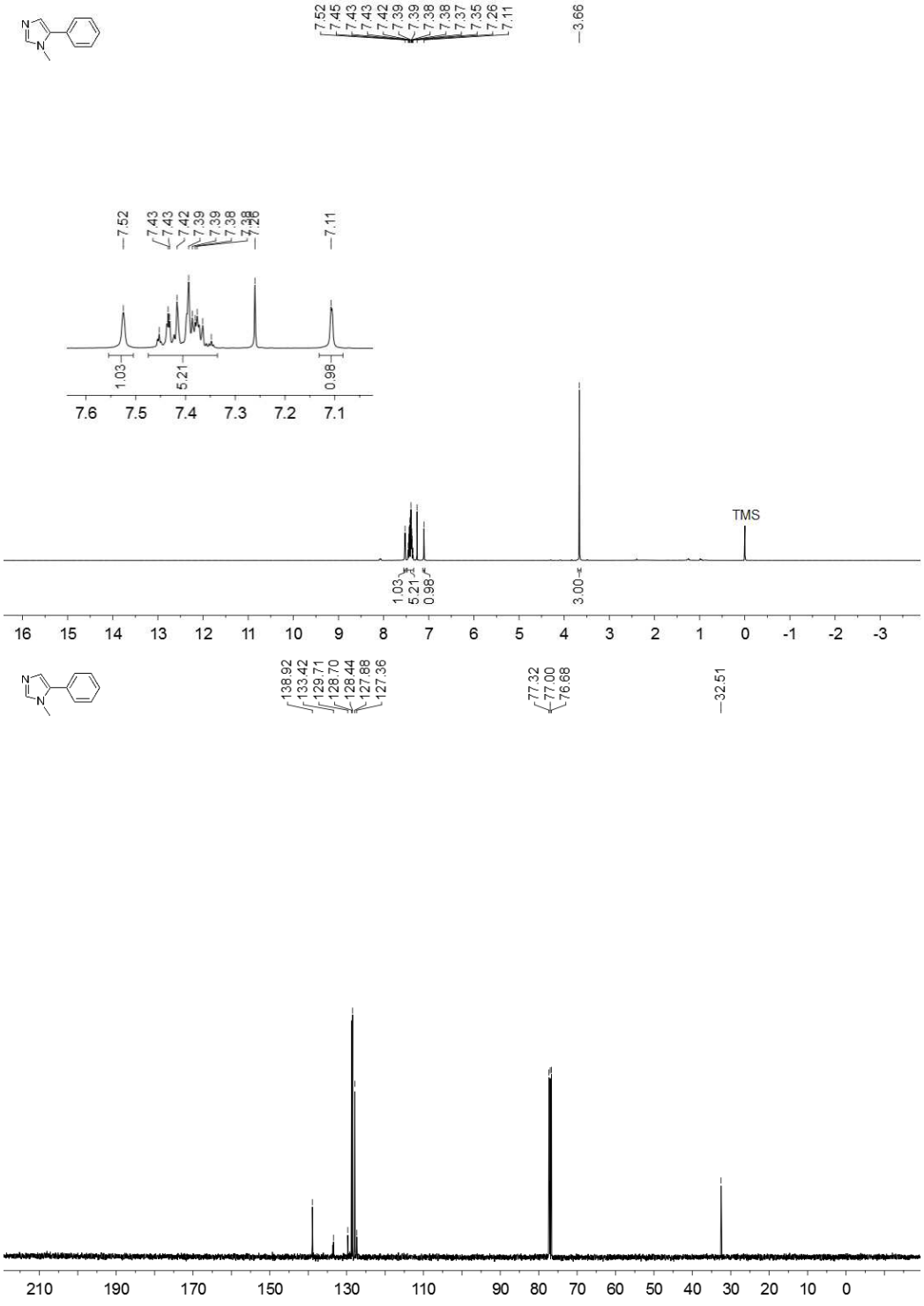


Figure **S21**. The NMR spectrums of 1-methyl-5-(naphthalen-1-yl)-1H-imidazole (**9aj**)

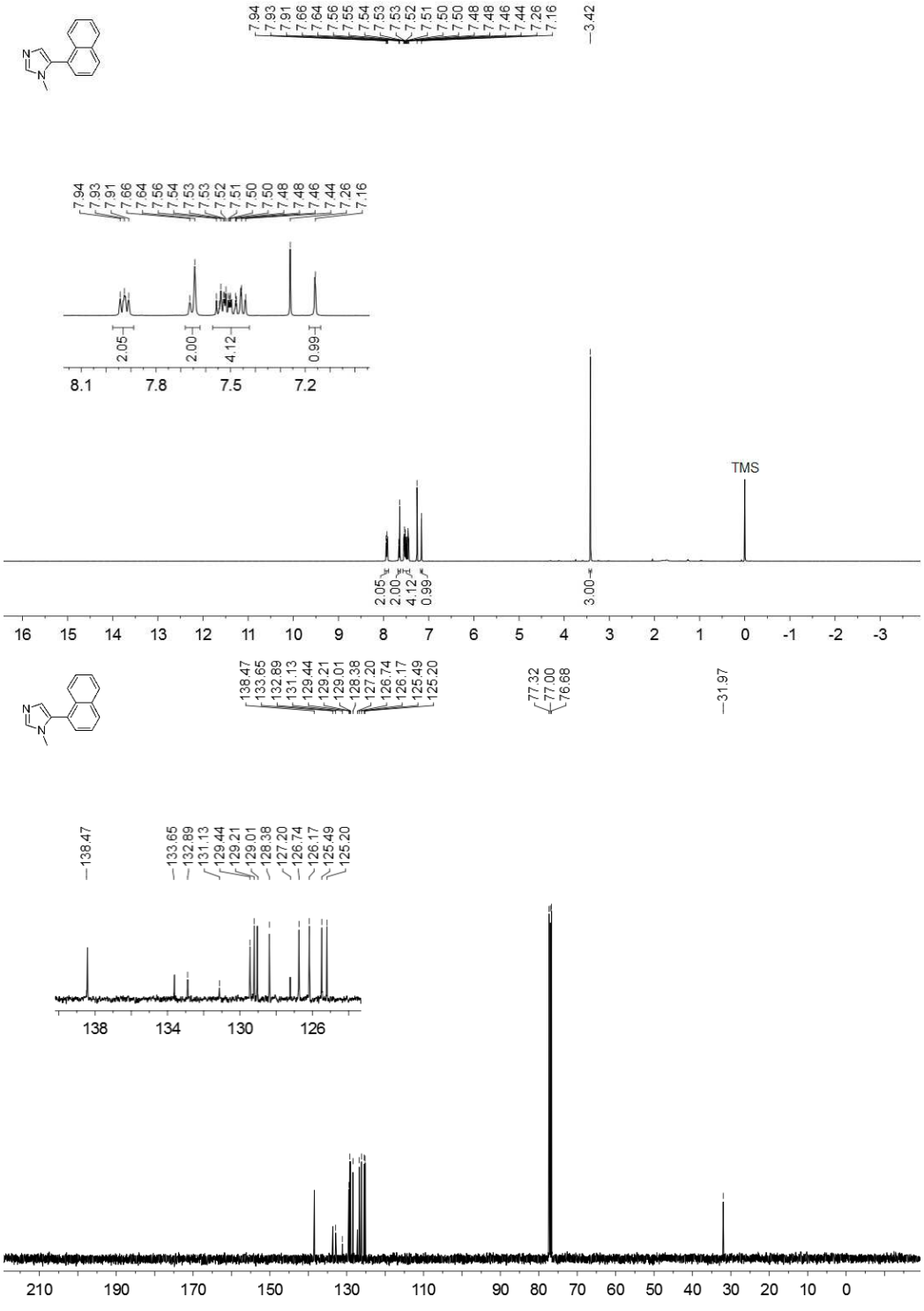


Figure **S22**. The NMR spectrums of 5-(3-methoxyphenyl)-1-methyl-1H-imidazole (**9ak**)

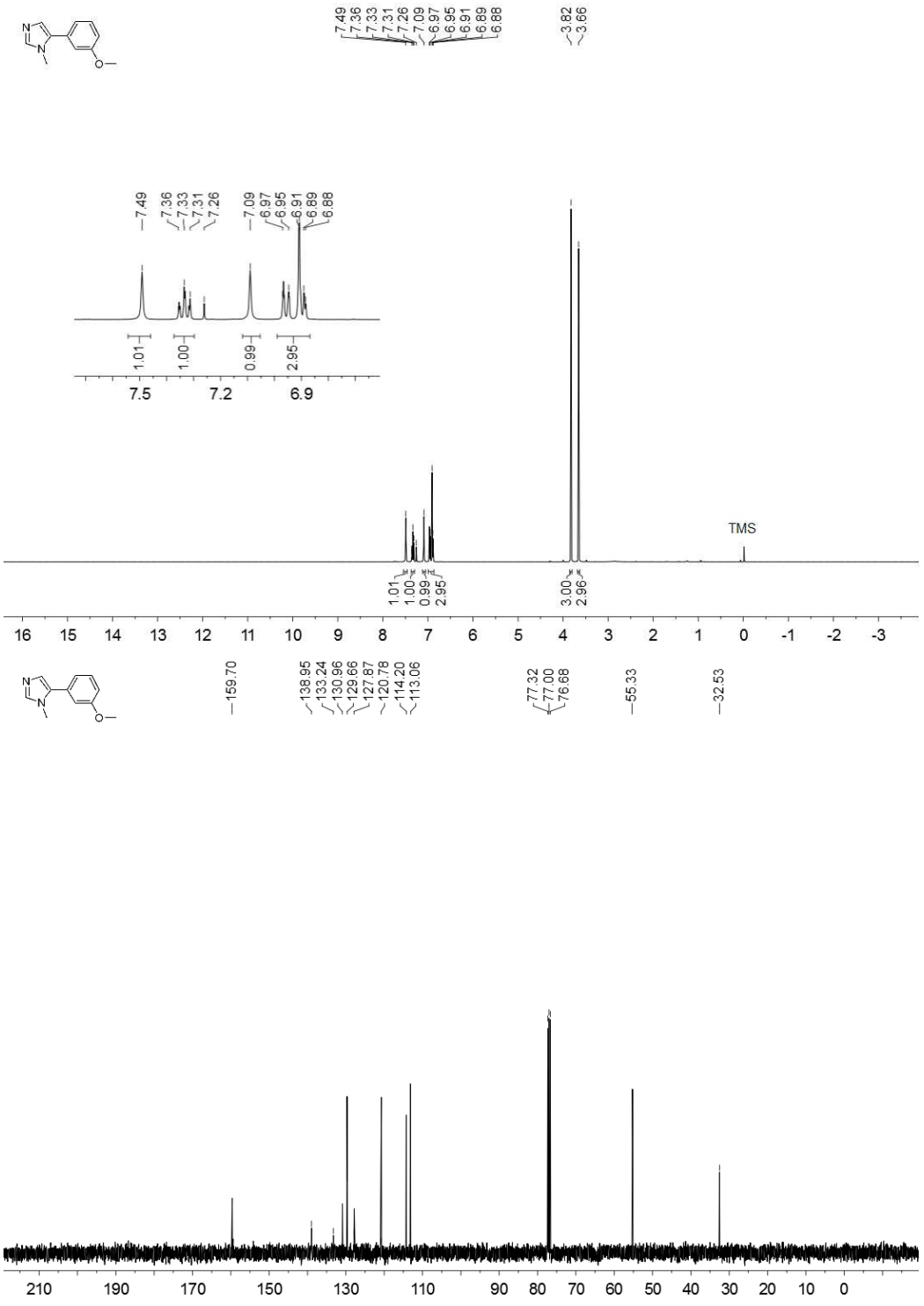


Figure **S23**. The NMR spectrums of 4-(1-methyl-1H-imidazol-5-yl)isoquinoline (**9al**)

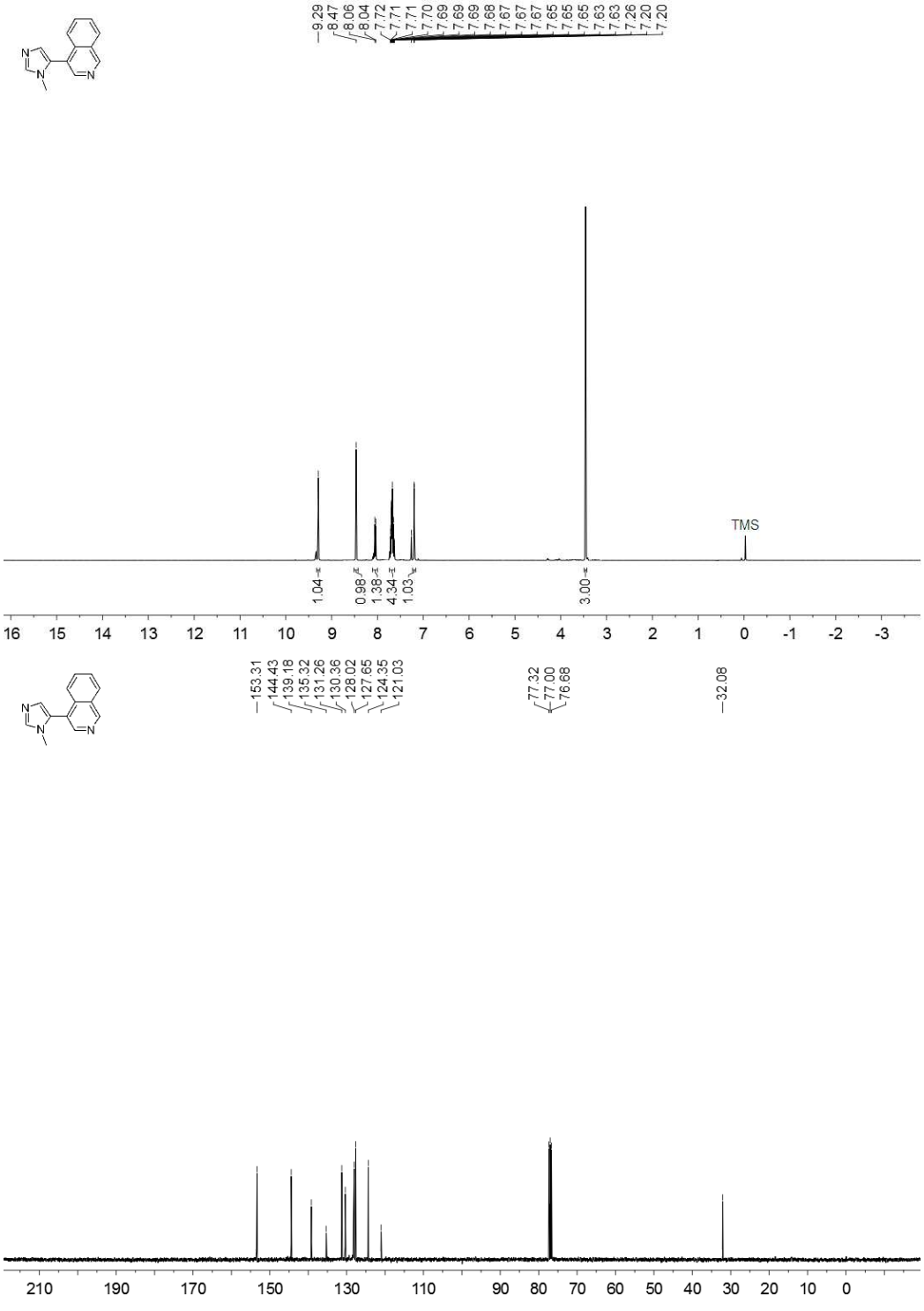


Figure **S24**. The NMR spectrums of 5-(4-chlorophenyl)-1,2-dimethyl-1H-imidazole (**9ba**)

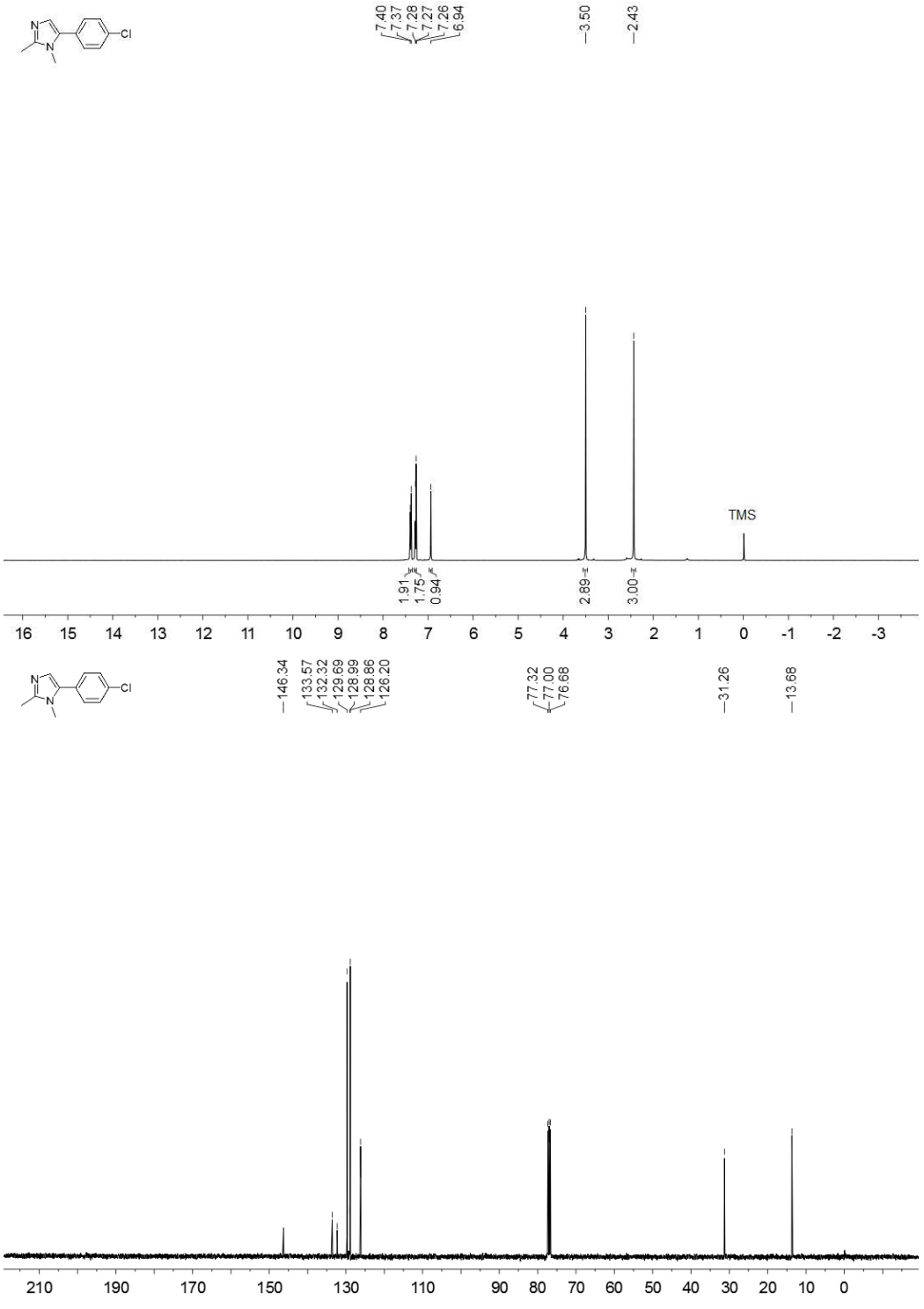


Figure **S25**. The NMR spectrums of methyl 4-(1,2-dimethyl-1H-imidazol-5-yl)benzoate (**9bb**)

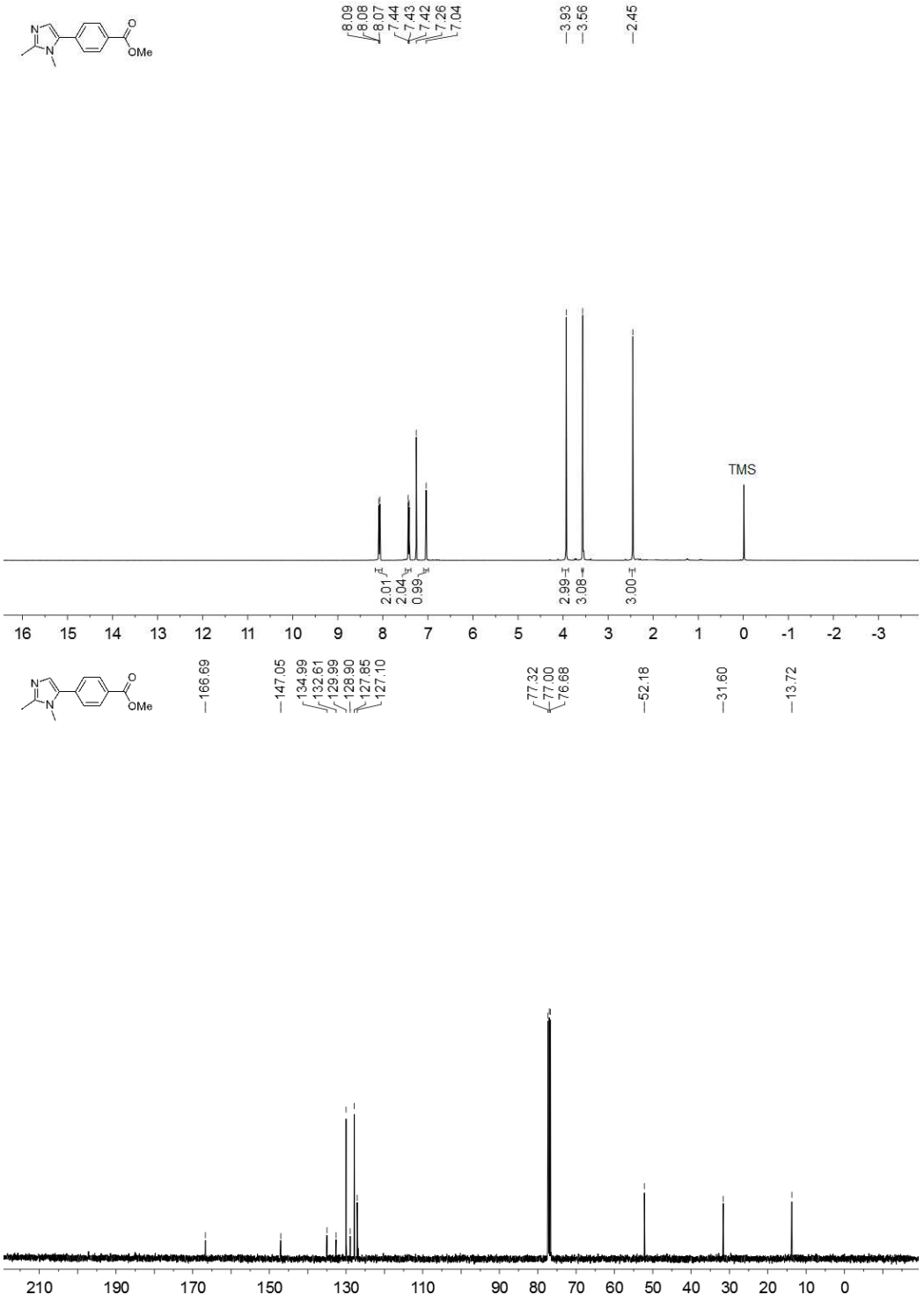


Figure **S26**. The NMR spectrums of methyl 1,2-dimethyl-5-(4-nitrophenyl)-1H-imidazole (**9bc**)

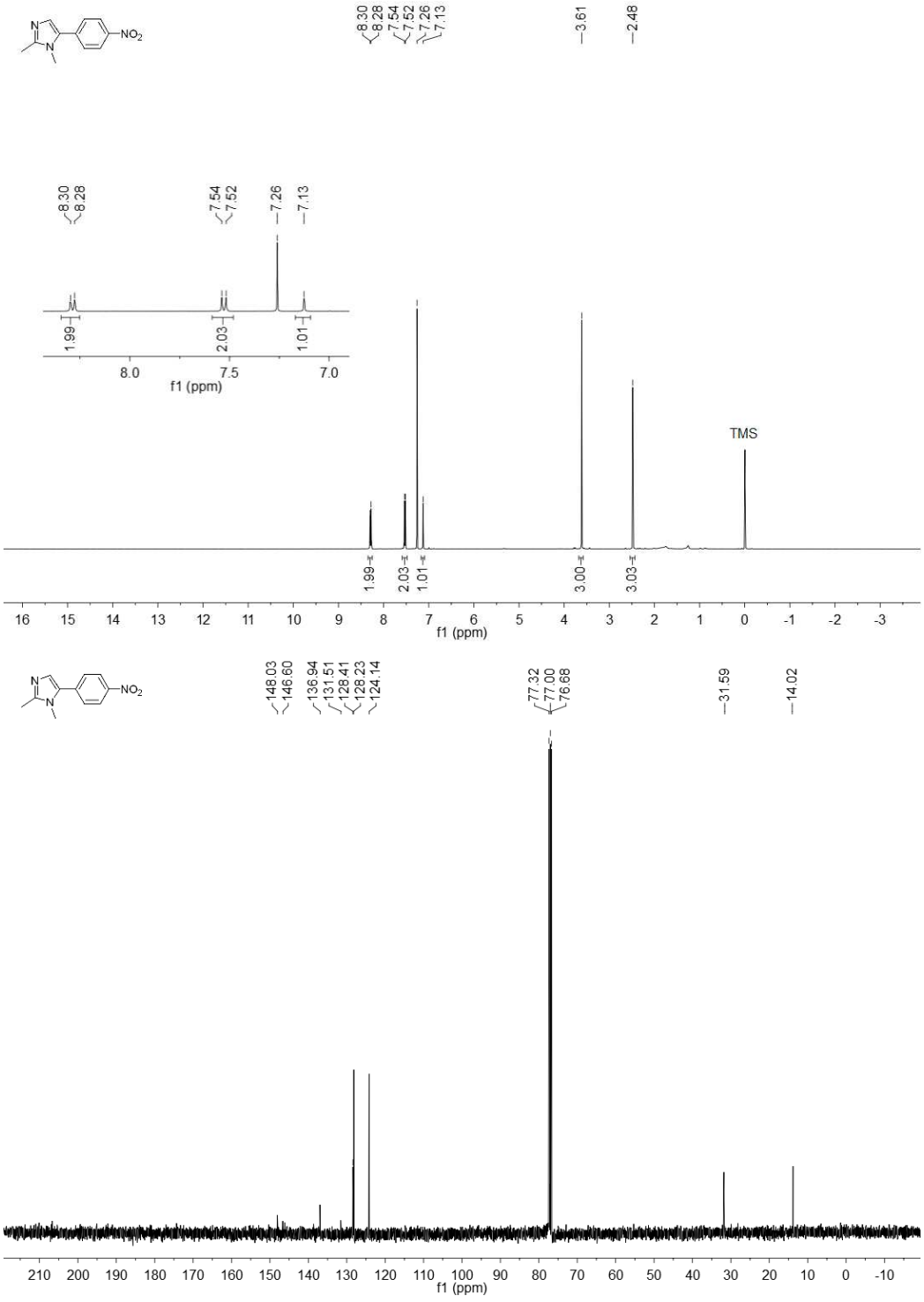


Figure **S27**. The NMR spectrums of methyl 4-(1,2-dimethyl-1H-imidazol-5-yl)benzonitrile (**9bd**)

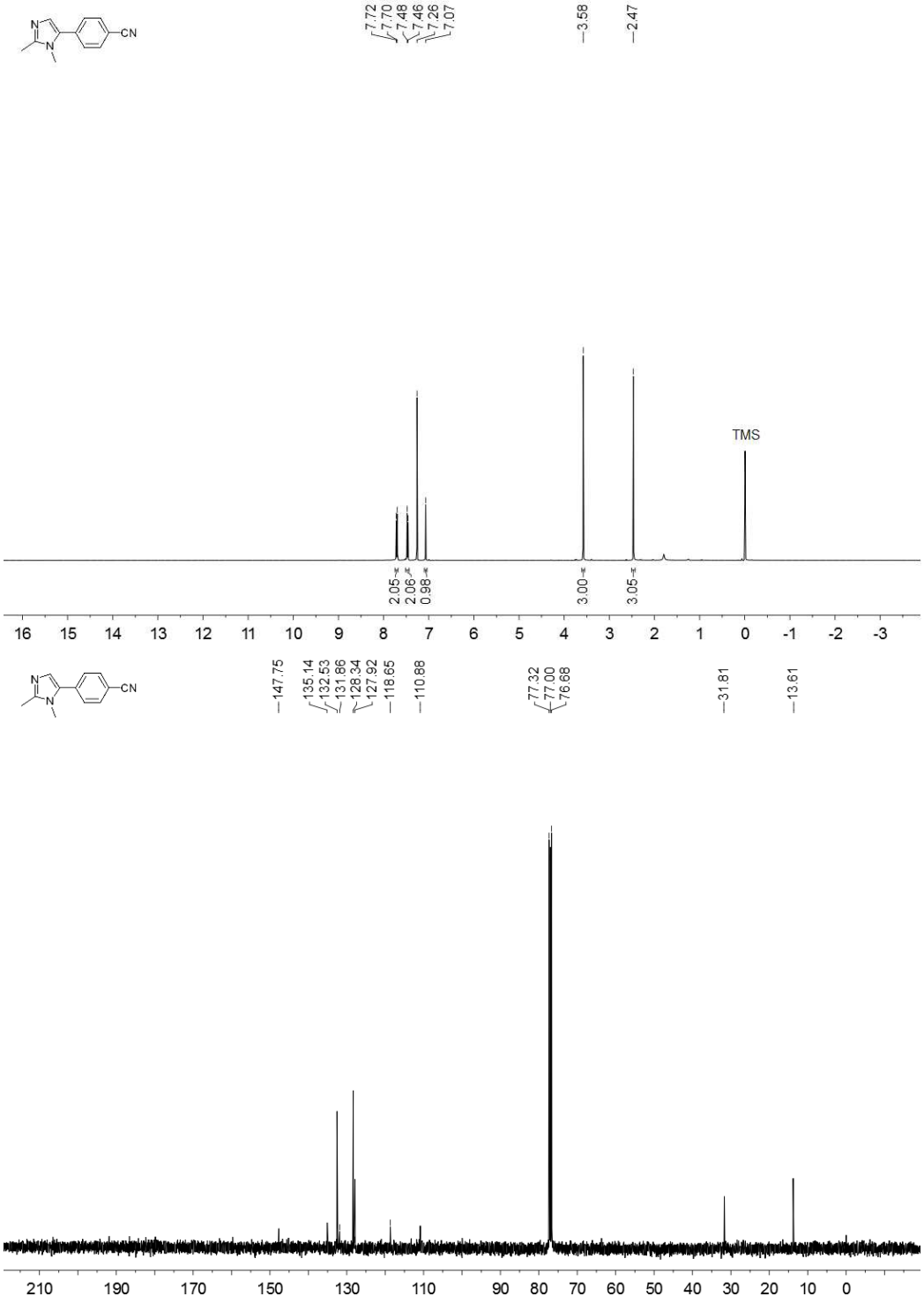


Figure **S28**. The NMR spectrums of 4-(1,2-dimethyl-1H-imidazol-5-yl)benzaldehyde (**9be**)

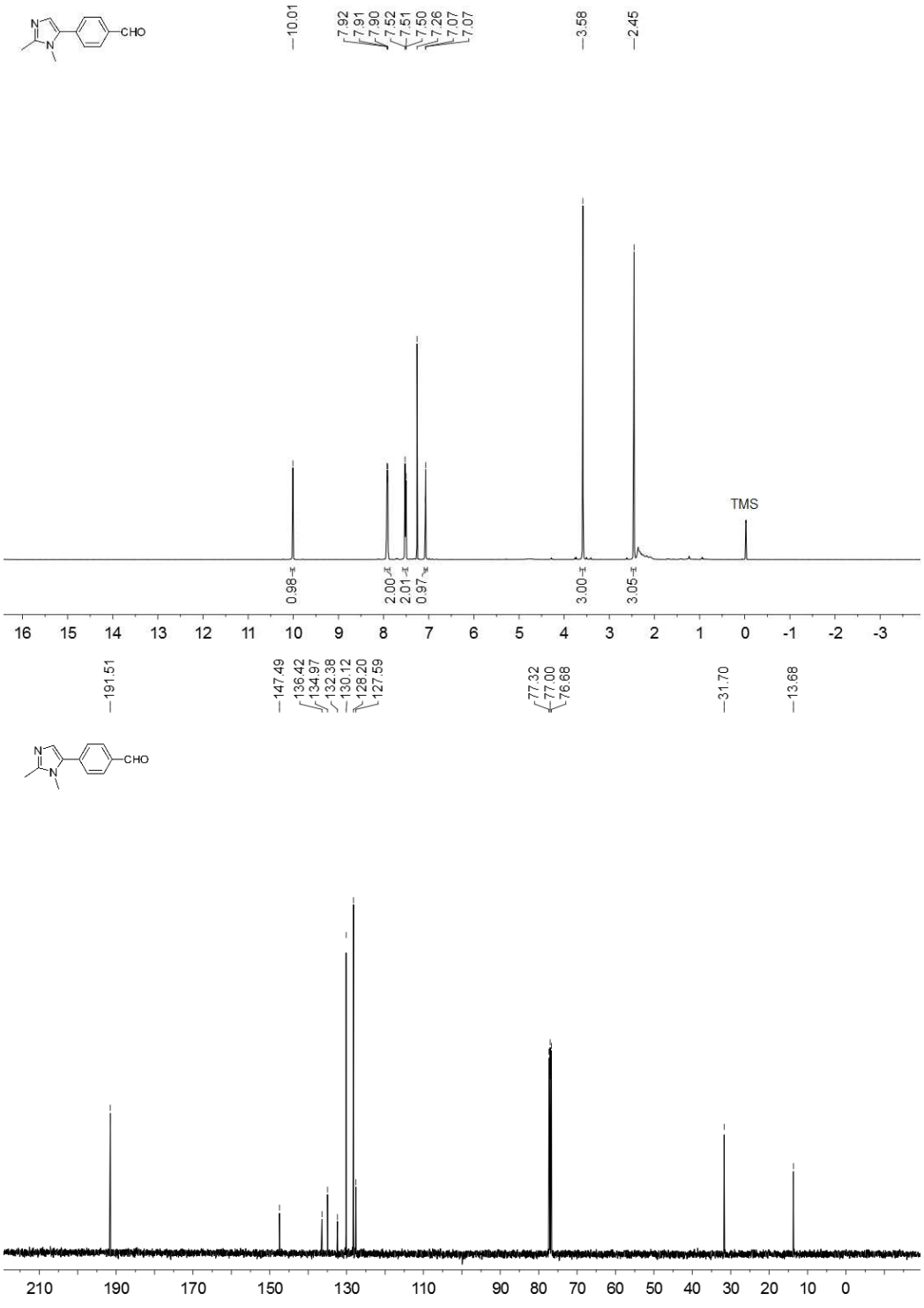


Figure **S29**. The NMR spectrums of 1-(4-(1,2-dimethyl-1H-imidazol-5-yl)phenyl)ethanone (**9bf**)

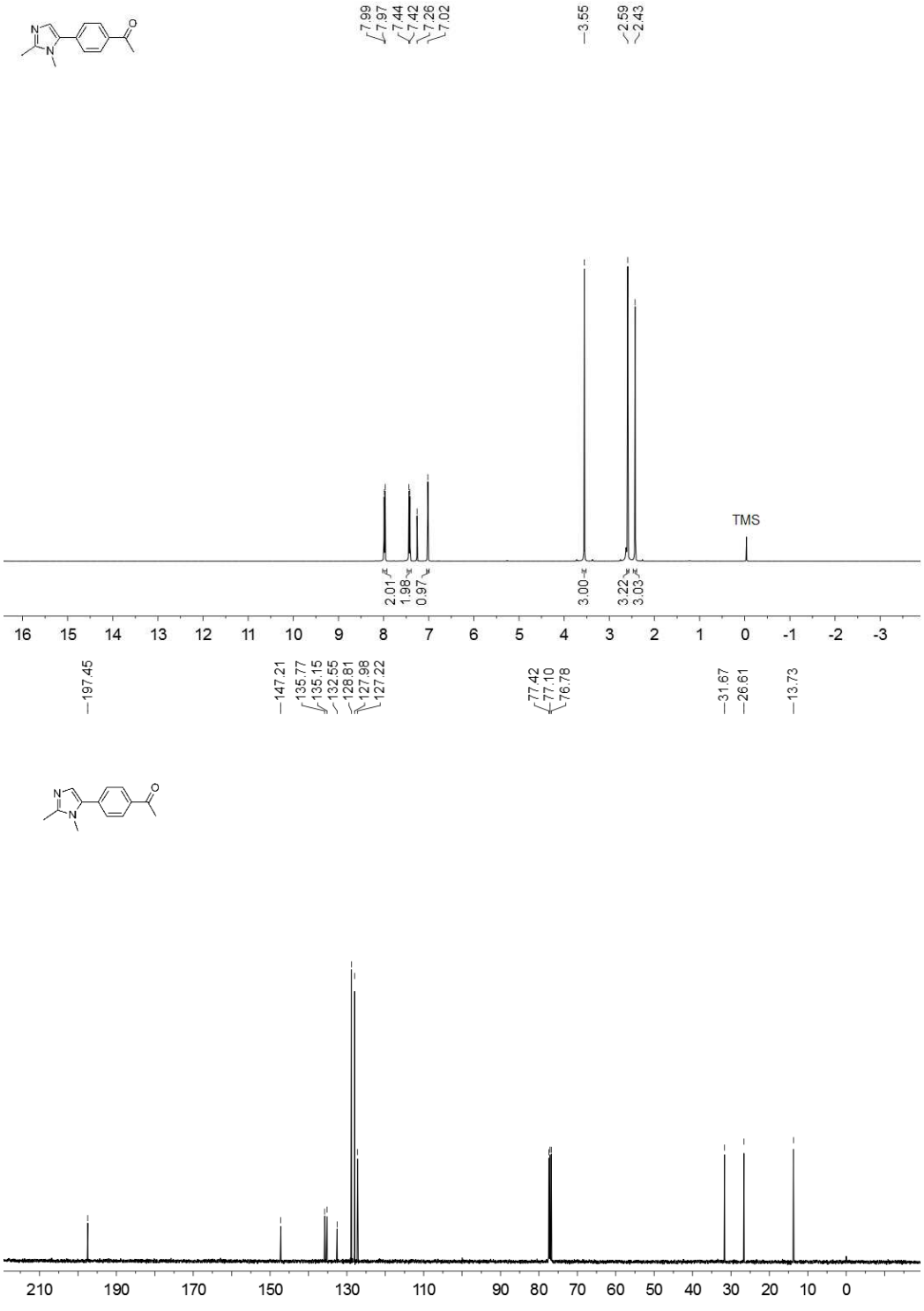


Figure **S30**. The NMR spectrums of 1,2-dimethyl-5-(4-(trifluoromethyl)phenyl)-1H-imidazole (**9bg**)

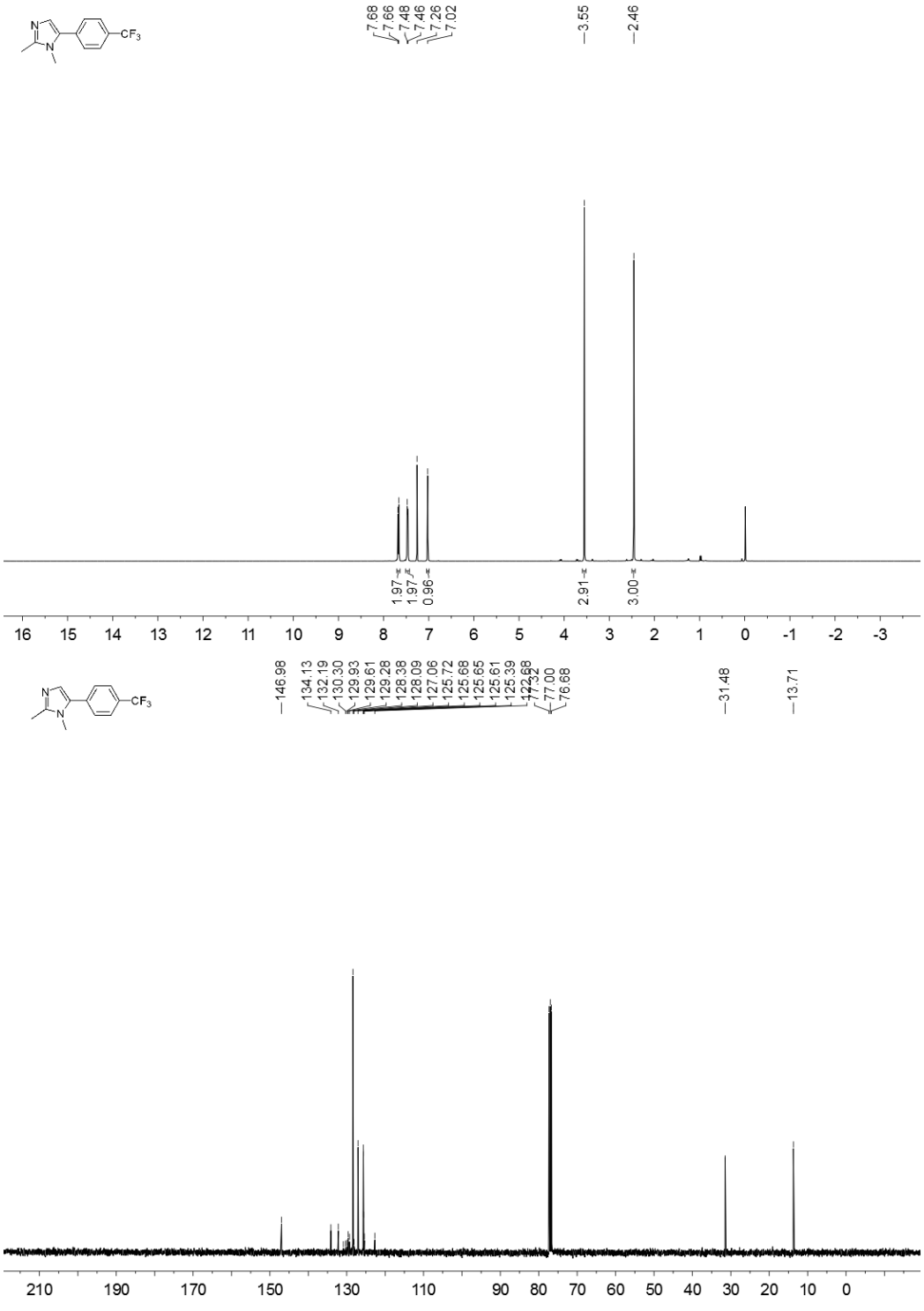


Figure **S31**. The NMR spectrums of 5-(4-fluorophenyl)-1,2-dimethyl-1H-imidazole (**9bh**)

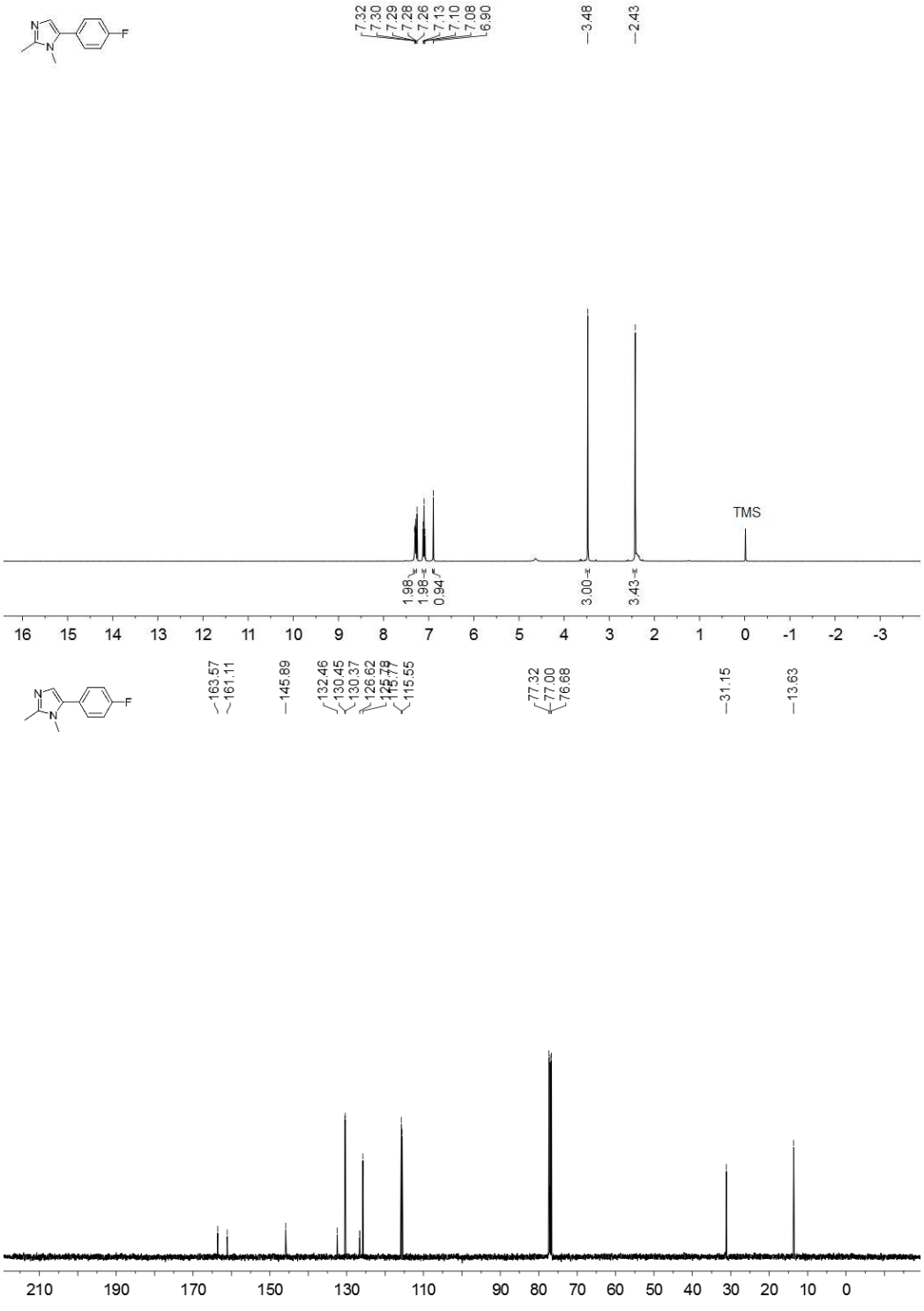


Figure **S32**. The NMR spectrums of 1,2-dimethyl-5-phenyl-1H-imidazole (**9bi**)

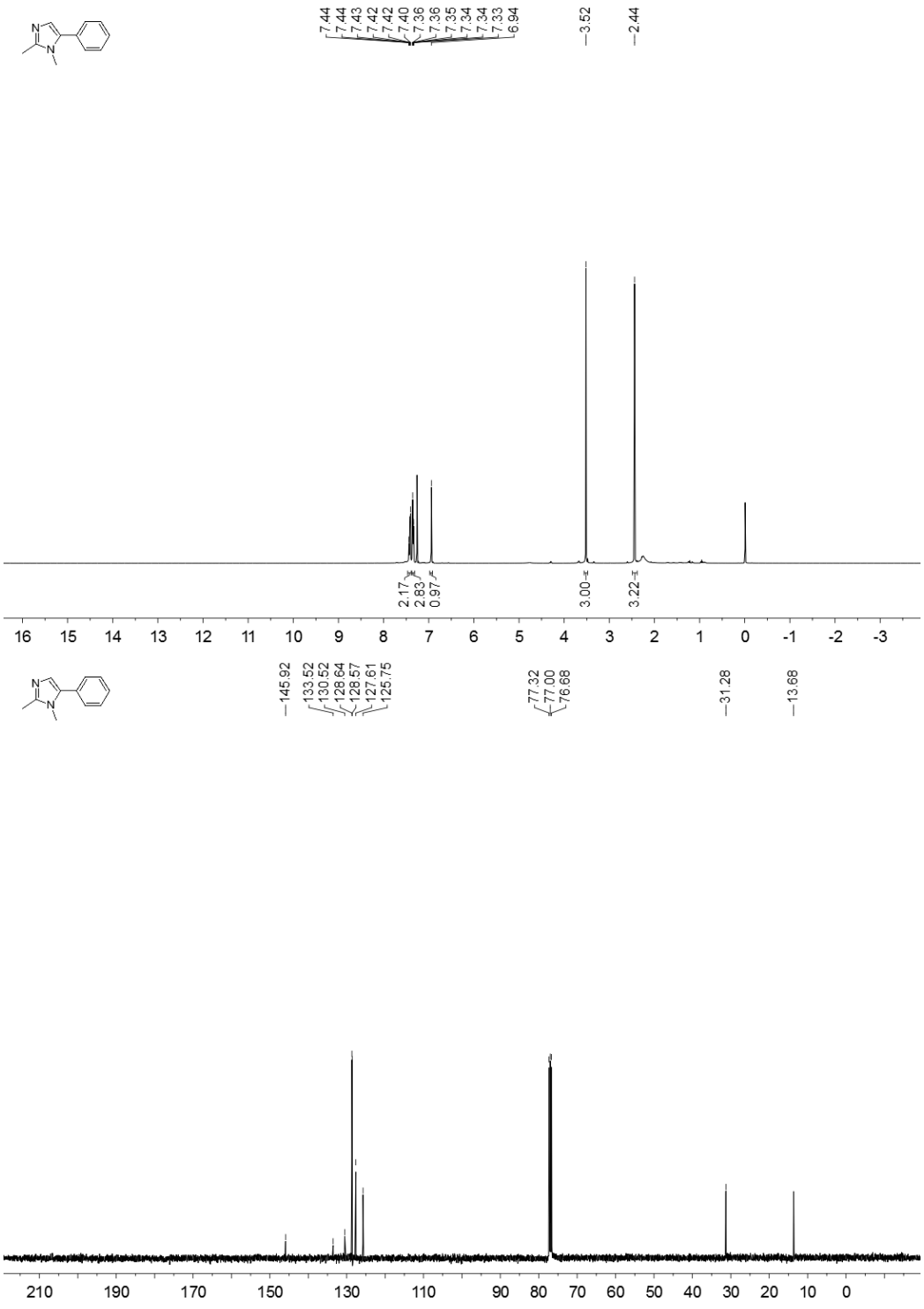


Figure **S33**. The NMR spectrums of 1,2-dimethyl-5-(naphthalen-1-yl)-1H-imidazole (**9bj**)

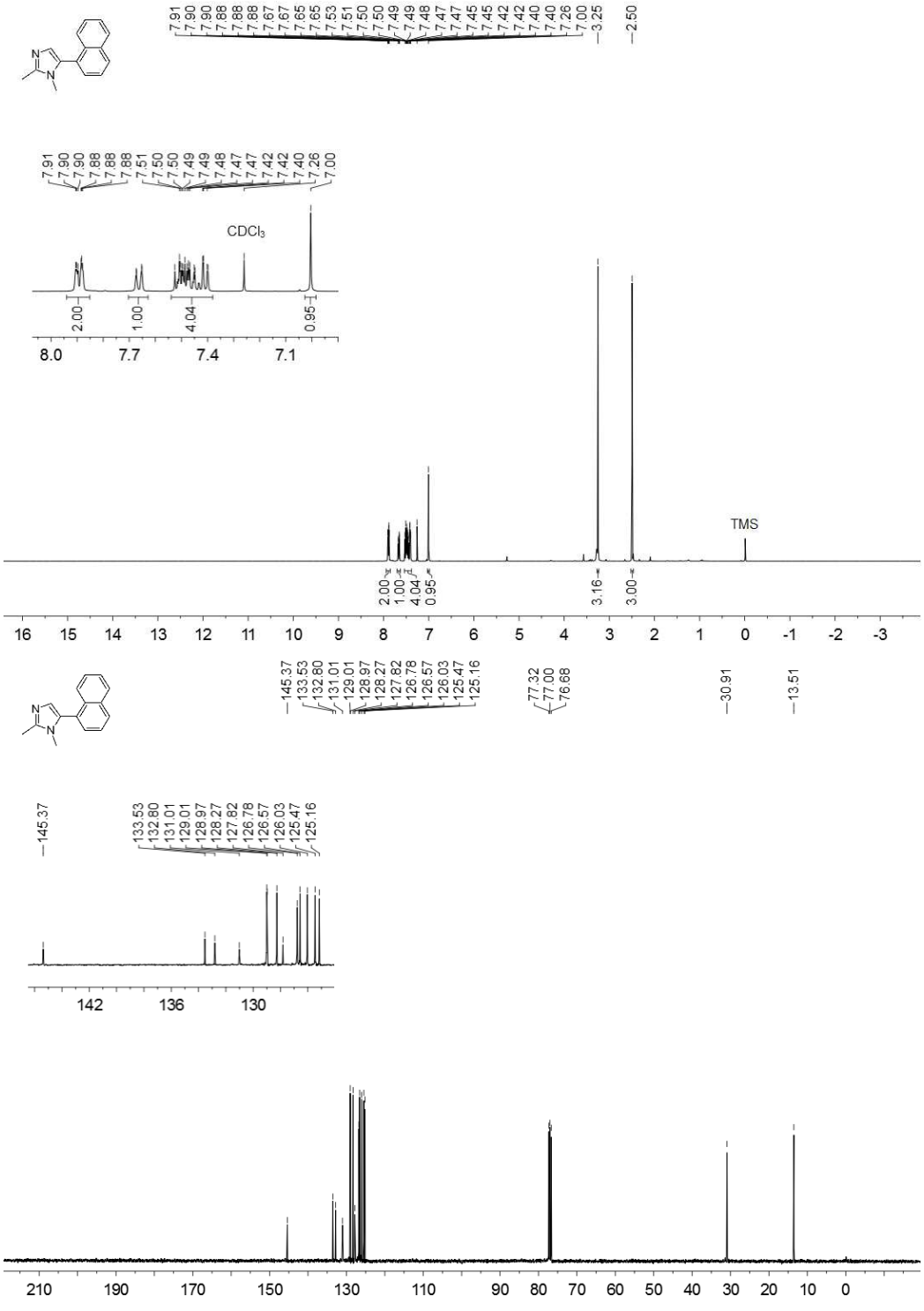
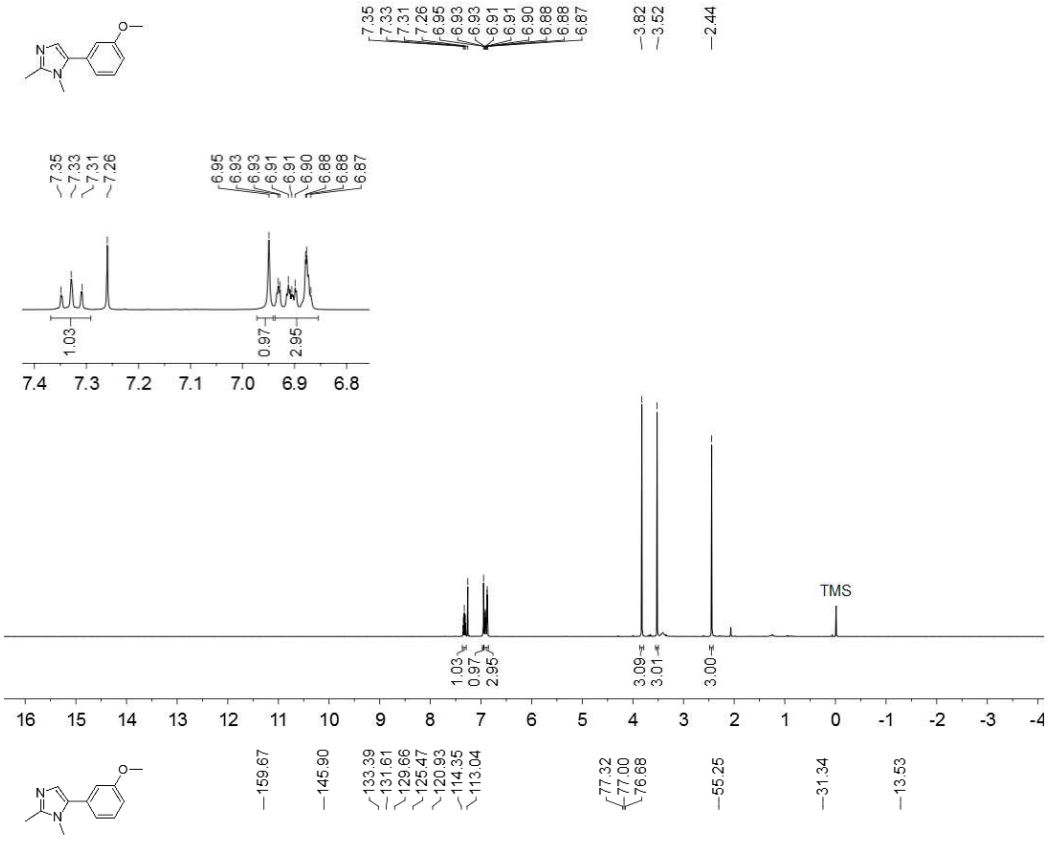


Figure **S34**. The NMR spectrums of 5-(3-methoxyphenyl)-1,2-dimethyl-1H-imidazole (**9bk**)



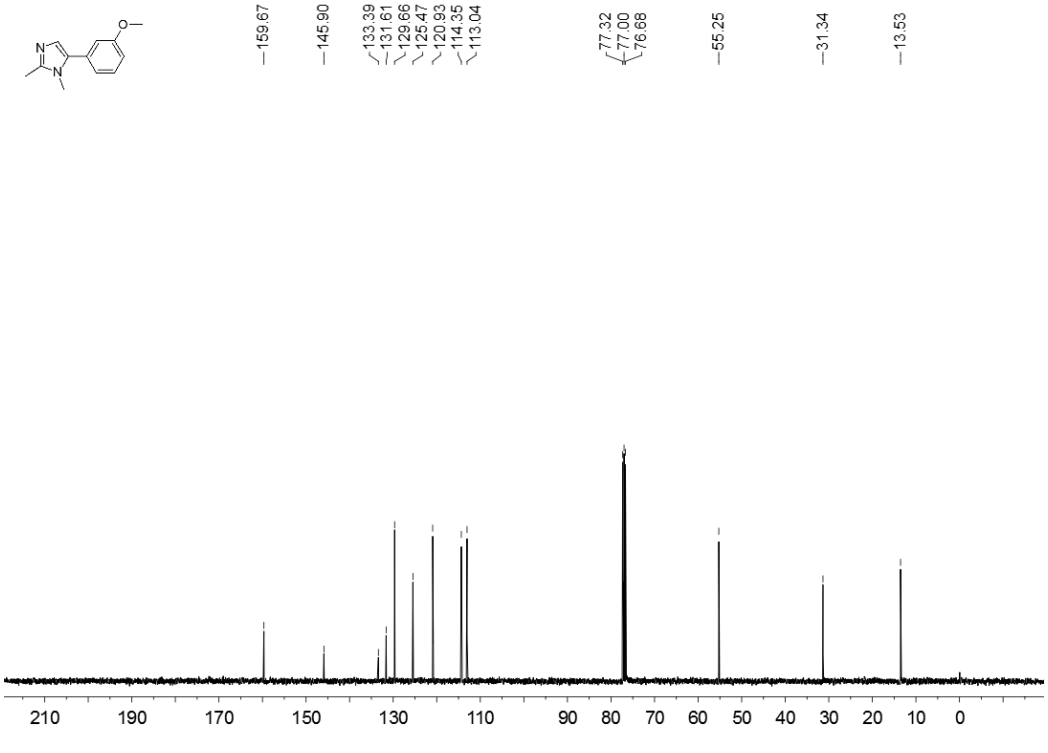


Figure **S35**. The NMR spectrums of 4-(1,2-dimethyl-1H-imidazol-5-yl)isoquinoline (**9bl**)