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Graphical Abstract

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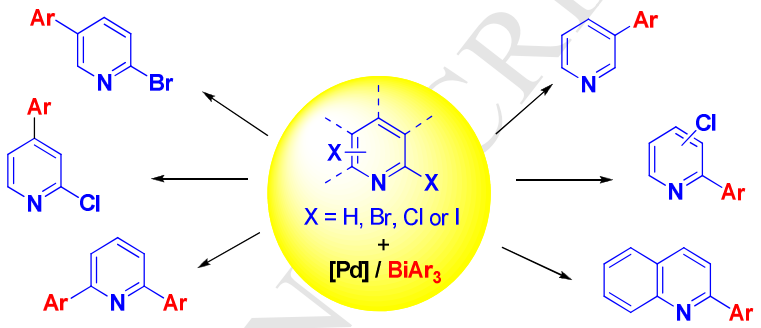

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Cross-coupling study of iodo/chloropyridines and 2-chloroquinoline with atom-economic triarylbismuth reagents under Pd-catalysis

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ABSTRACT

This study describes the palladium-catalyzed couplings of iodopyridines, chloropyridines and chloroquinoline with atom-economic $BiAr_3$ reagents in sub-stoichiometric loadings. Mono-arylations of iodo and chloropyridines produced 2-arylpyridines in high yields. The couplings addressed with dihalopyridines have afforded chemo- and regio-selective coupling products. Arylations of 2-chloroquinoline with different triarylbismuth reagents demonstrated fruitful coupling reactivity under the established conditions. This sumptuous study demonstrates the remarkable cross-coupling reactivity of iodo/chloropyridines and chloroquinoline with triarylbismuth reagents.

1. Introduction

Organometallic reagents exemplify a novel class of nucleophilic partners in cross-coupling reactions with high profile reactivity and synthetic applicability.[1] In particular, coupling partners such as organobismuth compounds are non-toxic and serve as green organometallic reagents.[2,3] More so, triarylbismuths as lead reagents offer threefold coupling reactivity with three aryl groups under metal catalyzed conditions.[4] Importantly, preparation of these compounds using organo-magnesium, -lithium or -zinc reagents and bismuth salts is simple and straightforward.[5] The stable and robust nature of triarylbismuths is added advantage with these reagents.

Our determined efforts in recent years have contributed immensely to the success of triarylbismuths as threefold coupling reagents in organic synthesis.[4,6] In this process, the synthetic potential of triarylbismuths as threefold coupling reagents was evaluated in sub-stoichiometric loading in reactions with different organic electrophiles including aryl and heteroaryl substrates under palladium reaction conditions.[6] In this drive, we have recently enumerated the facile couplings of triarylbismuth reagents with bromopyridines.[7] The brief couplings of chloro-[8] and iodopyridines[9] and other dihalo heteroaromatic systems[10a] known with different bismuth reagents did not establish the broad reactivity.

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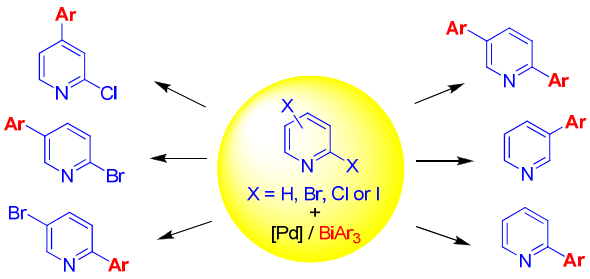
The significance of functionalized arylated heteroaryl systems is well documented in the literature with broader applications in medicinal and in other fields of chemistry.[10] This made us to further explore and elaborate the studies with chloro-/iodopyridines and 2-chloroquinoline in continuation of our interest in halopyridine couplings.[7] The present study thus devoted to establish the general reactivity with special emphasis on chemo- and regio-selective couplings as illustrated in Scheme 1.



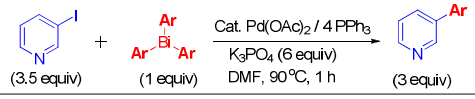
Scheme 1. Representative pyridine couplings with $BiAr_3$ reagents

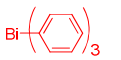
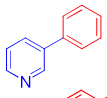
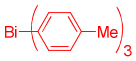
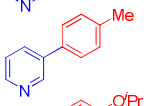
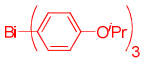
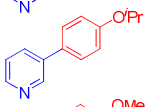
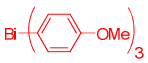
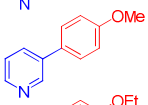
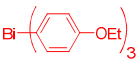
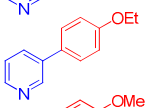
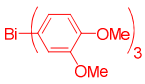
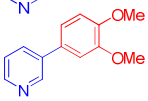
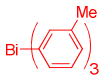
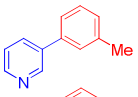
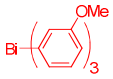
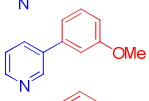
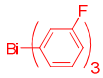
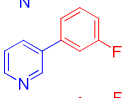
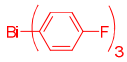
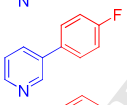
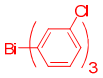
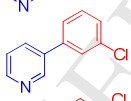
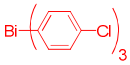
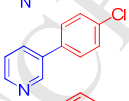
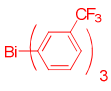
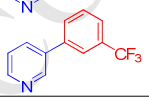
2. Results and Discussion

Our coupling study was commenced with 3-iodopyridine and it was explored with $Pd(OAc)_2/PPh_3$ and K_3PO_4 in DMF at 90 °C conditions.[7] Under these conditions, we have seen facile couplings of 3-iodopyridine with different $BiAr_3$ reagents as given in Table 1. Amazingly, this study furnished

very high yields of 3-arylpyridines demonstrating the broader applicability of electronically different triarylbismuth reagents. The cross-couplings of various triphenylbismuth reagents functionalized with alkoxy, halo, methyl and trifluoromethyl groups showed excellent reactivity to afford the corresponding 3-arylpyridines (Table 1, **1.1**-**1.13**) in 74-99% yields.

Table 1. Cross-couplings with 3-iodopyridine[a,b,c]



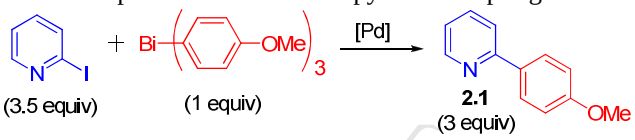
Entry	$BiAr_3$	3-Arylpyridine		Yield (%)
1			**1.1**	98
2			**1.2**	99
3			**1.3**	97
4			**1.4**	99
5			**1.5**	99
6			**1.6**	97
7			**1.7**	95
8			**1.8**	95
9			**1.9**	92
10			**1.10**	88
11			**1.11**	89
12			**1.12**	95
13			**1.13**	74

[a] Conditions: 3-Iodopyridine (0.875 mmol, 3.5 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), $Pd(OAc)_2$ (0.025 mmol, 10 mol%), PPh_3 (0.1 mmol, 40 mol%), K_3PO_4 (1.5 equiv, 6 equiv), DMF, 90 °C, 1 h.[b] Isolated yields based on three aryl couplings from $BiAr_3$. [c] Biaryls formed up to 5%.

This was a phenomenal coupling reactivity and is more convenient in comparison to similar couplings known in literature with other organometallic reagents.[11] In general, electronically rich organometallic nucleophiles are expected to show facile reactivity with good yields, while electronically deficient ones are known to provide poor to moderate coupling yields. Here, we observed a general and facile coupling reactivity employing different functionalized triphenylbismuth reagents in good to high yields.

We further examined the couplings with 2-iodopyridine (Table 2). It was tested under the conditions of 3-iodopyridine and this resulted in poor coupling reactivity with the formation of 2-(*p*-anisyl)pyridine **2.1** in 24% yield (Table 2, entry 1). Hence, this was studied under different conditions to improve the yield.

Table 2. Optimization for 2-iodopyridine couplings[a,b,c]



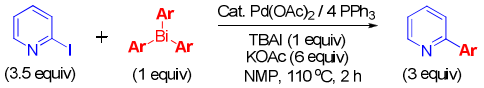
Entry	Base (equiv)	Additives (equiv)	Solvent	Time (°C)	Yield (%)
1	K_3PO_4 (6)	--	DMF	90	24[d]
2	KOAc (6)	---	NMP	110	71
3	KOAc (6)	---	NMP	90	49
4	KOAc (6)	---	NMP	60	31
5	KOAc (6)	TBAB (1)	NMP	110	76
6	KOAc (6)	TBAI (1)	NMP	110	86
7	KOAc (6)	TBAI (1)	NMP	90	59
8	KOAc (4)	TBAI (1)	NMP	110	66
9	No base	TBAI (1)	NMP	110	25
10	KOAc (6)	TBAI (1)	NMP	110	--[e]

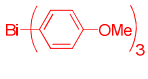
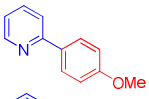
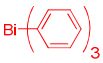
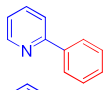
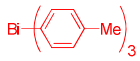
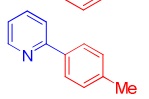
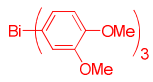
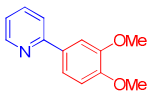
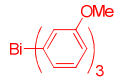
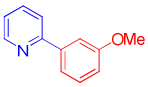
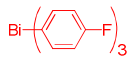
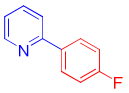
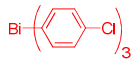
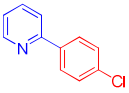
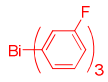
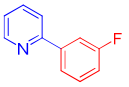
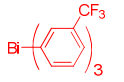
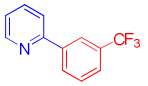
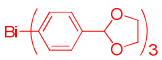
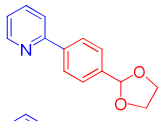
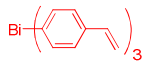
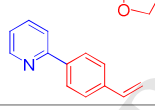
[a] Conditions: 2-Iodopyridine (0.875 mmol, 3.5 equiv), Bi(*p*-anisyl)$_3$ (0.25 mmol, 1 equiv), $Pd(OAc)_2$ (0.0125 mmol, 5 mol%), PPh_3 (0.05 mmol, 20 mol%), KOAc (1.5 equiv, 6 equiv), NMP (3 mL), temp, 2 h; [b] Isolated yields.[c] Bianisyl formed in minor amounts. [d] $Pd(OAc)_2$ (0.025 mmol, 10 mol%), PPh_3 (0.1 mmol, 40 mol%), base, DMF (3 mL), temp, 1 h. [e] without catalyst.

The coupling of 2-iodopyridine carried out using 6 equiv of KOAc at 110 °C delivered **2.1** in 71% yield (Table 2, entry 2). This reaction at 90 °C and 60 °C furnished 49% and 31% yields (Table 2, entries 3 and 4). Coupling with additives such as tetrabutylammonium bromide (TBAB) or iodide (TBAI) showed improved yield and it was high up to 86% with TBAI (Table 2, entries 5 and 6). Again, this condition with TBAI was studied at 90 °C (Table 2, entry 7) or with four equiv of base produced lowered yields (Table 2, entry 8). Further control without base proved to be low yielding (Table 2, entry 9) and the coupling was ineffective in the absence of catalyst (Table 2, entry 10). The conditions thus comprising $Pd(OAc)_2$ (5 mol%)/PPh_3 (20 mol%), KOAc (6 equiv) and TBAI (1 equiv) in NMP at 110 °C proved to be effective for 2-iodopyridine coupling (Table 2, entry 6).

The coupling of 2-iodopyridine was further examined with different bismuth reagents (Table 3). To start with, the coupling carried out with Bi(*p*-anisyl)$_3$ delivered 86% yield (Table 3, **2.1**) and $BiPh_3$ reagent furnished 2-phenylpyridine in 78% yield (Table 3, **2.2**). The couplings of $BiPh_3$ reagent enriched with 4-methyl, 3,4-dimethoxy or 3-methoxy groups provided cross-coupled products in 76-85% yields (Table 3, **2.3**-**2.5**). Similar study of $BiPh_3$ functionalized with deactivating 4-fluoro, 4-chloro, 3-fluoro and 3-trifluoromethyl groups furnished 2-arylpyridines in 60-71% yields (Table 3, **2.6**-**2.9**). The coupling reactivity of $BiPh_3$ with vinyl or protected formyl group also delivered good yields (Table 3, **2.10**-**2.11**).

Table 3. Cross-couplings of 2-iodopyridine[a,b,c]



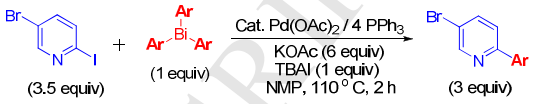
Entry	$BiAr_3$	2-Arylpyridine		Yield (%)
1			**2.1**	86
2			**2.2**	78
3			**2.3**	82
4			**2.4**	85
5			**2.5**	76
6			**2.6**	71
7			**2.7**	65
8			**2.8**	66
9			**2.9**	60
10			**2.10**	65
11			**2.11**	64

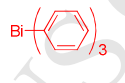
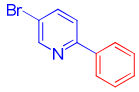
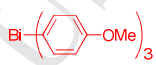
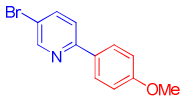
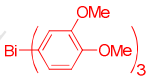
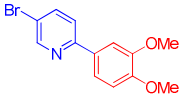
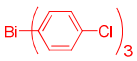
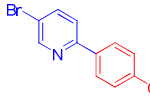
[a] Conditions: 2-Iodopyridine (0.875 mmol, 3.5 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), $Pd(OAc)_2$ (0.0125 mmol, 5 mol%), PPh_3 (0.05 mmol, 20 mol%), KOAc (1.5 mmol, 6 equiv), TBAI (0.25 mmol, 1 equiv), NMP, 110 °C, 2 h. [b] Isolated yields based on three aryl couplings from $BiAr_3$. [c] Biaryls formed up to 10%.

This combined study of Pd-catalyzed cross-couplings of 2-iodo and 3-iodopyridines demonstrated appreciable general coupling reactivity with triarylbismuth reagents. In fact, these conditions are more advantageous in comparison to similar couplings known with either bismuth[9] or indium reagents.[11a]

In our previous study with bromopyridines,[7] one of the focus was to establish the site- and regio-selective couplings with dibromopyridines. Here, our attempt was to explore the chemo-selective couplings in view of the facile couplings known with iodo- and bromo-pyridines. At the outset, it was a challenging task as the established couplings of both iodo and bromopyridines are quite similar with high reactivity. Despite this difficulty, we started the competitive chemoselective couplings using 2-iodo-5-bromopyridine as given in Table 4. This was to check the differential reactivity of 2-iodo *vs* 5-bromo position. It was executed with sub-stoichiometric loading of bismuth reagent towards mono arylation. It was reassuring to see the selective mono-arylations at the more reactive 2-iodo position to give 5-bromo-2-arylpyridines as chemoselective products in 70-85% yields (Table 4, **2.12-2.15**). It is to be noted that these chemoselective couplings are relatively simpler in comparison to the corresponding functionalizations reported with organozinc[12a] and organoboron[12b] reagents. If required, further arylation of 5-bromo-2-arylpyridines at 5-bromo position to obtain bis-arylated 2,5-diarylpyridine is easy with $BiAr_3$ reagent under palladium coupling conditions as reported by us earlier.[7]

Table 4. Chemoselective couplings of 2-iodo-5-bromopyridine with $BiAr_3$ reagents[a,b,c]



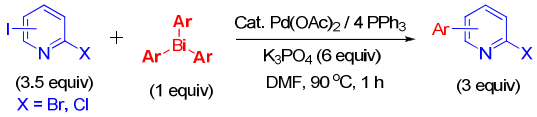
Entry	$BiAr_3$	2-Aryl-5-bromopyridine		Yield (%)
1			**2.12**	81
2			**2.13**	78
3			**2.14**	85
4			**2.15**	70

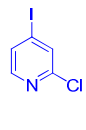
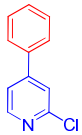
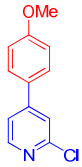
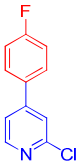
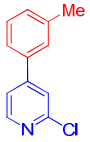
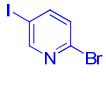
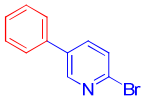
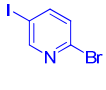
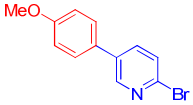
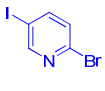
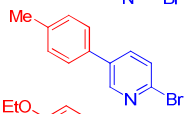
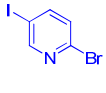
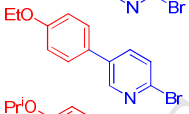
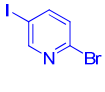
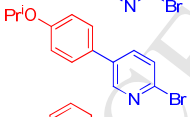
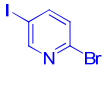
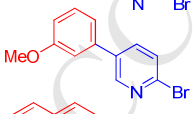
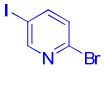
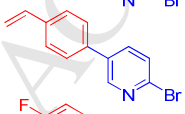
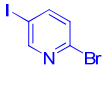
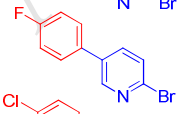
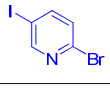
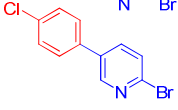
[a] Conditions: 2-Iodo-5-bromopyridine (0.875 mmol, 3.5 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), $Pd(OAc)_2$ (0.0125 mmol, 5 mol%), PPh_3 (0.05 mmol, 20 mol%), KOAc (1.5 mmol, 6 equiv), TBAI (0.25 mmol, 1 equiv), NMP, 110 °C, 2 h. [b] Isolated yields based on three aryl couplings from $BiAr_3$. [c] Biaryls formed up to 10%.

The cross-coupling study was continued with iodopyridine derivatives like 2-chloro-3,4-diiodopyridine[13] and 2-bromo-5-iodopyridine as illustrated in Table 5. The reactivity of 2-chloro-4-iodopyridine was tested using the conditions employed in 3-iodopyridine couplings. It was done with catalytic $Pd(OAc)_2$ in 1 h and this proved to be useful with the formation of chemo-selective 4-aryl-2-chloropyridines in 89-97% yields (Table 5, **3.1-3.4**). The observed reactivity is very inspiring in comparison to couplings known with arylboronic acids which require 20 h reflux conditions.[13]

We further elaborated the study with more competitive substrate such as 2-bromo-5-iodopyridine. This exploration resulted in the realization of the high profile chemoselective couplings at 5-iodo position and the corresponding 5-aryl-2-bromopyridines were obtained in 66-94% yields (Table 5, **4.1-4.9**). This endeavor employing 2-chloro-4-iodopyridine and 2-bromo-5-iodopyridine showed generalized coupling reactivity in delivering high yields.

Table 5. Chemoselective couplings of dihalopyridines[a,b,c]

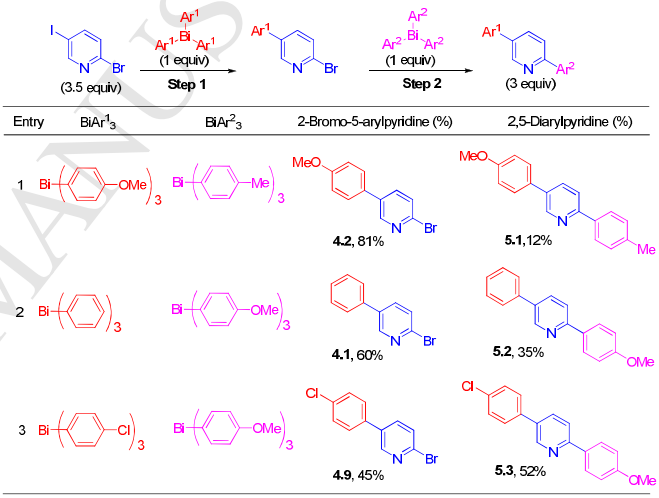


Entry	Dihalopyridine	Arylpyridine		Yield (%)
1			**3.1**	96
2			**3.2**	97
3			**3.3**	93
4			**3.4**	89
5			**4.1**	88
6			**4.2**	89
7			**4.3**	94
8			**4.4**	83
9			**4.5**	85
10			**4.6**	79
11			**4.7**	72
12			**4.8**	66
13			**4.9**	75

[a] Conditions: 4-Iodo-2-chloropyridine/5-Iodo-2-bromopyridine (0.875 mmol, 3.5 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), $Pd(OAc)_2$ (0.02 mmol, 8 mol%), PPh_3 (0.08 mmol, 32 mol%), K_3PO_4 (1.5 mmol, 6 equiv), DMF, 90 °C, 1 h. [b] Isolated yields based on three aryl couplings from $BiAr_3$. [c] Biaryls formed up to 10%.

Attempts were made to understand the electronic effect of aryl substitution in a two-step bis-arylation process (Table 6). This was checked in the second step with electronically different bismuth reagents. The bis-arylation study of 5-iodo-2-bromopyridine was carried out in conjunction with four electronically different triarylbismuth reagents. It was examined in a one-pot operation with a stepwise addition of bismuth reagents. After the step 1, second bismuth reagent was added along with K_3PO_4 (4 equiv) and DMF for step 2 and the reaction was continued at 90 °C for 2 h. As given in Table 6, this study of different combination of bismuth reagents indicated some variation in coupling reactivity. For example, entry 1 shows the arylation in step 1 carried out with tri(*p*-anisyl)bismuth followed by tri(*p*-tolyl)bismuth reagent in step 2. In this case, the donating nature of methoxy substitution in 5-aryl group was found to have some detrimental effect in the second arylation as this made pyridine ring more electron rich leading to poor couplings at 2-bromo position. Here, we have isolated unsymmetrically substituted 2,5-diarylpyridine **5.1** along with unreacted 5-aryl-2-bromopyridine **4.2** after step 2.

Table 6. Bis-couplings with dihalopyridine [a,b,c]



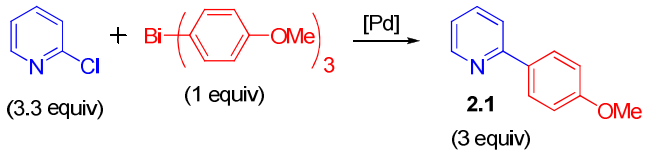
[a] Conditions for **step 1**: 2-Bromo-5-iodopyridine (0.875 mmol, 3.5 equiv), $BiAr^1_3$ (0.25 mmol, 1 equiv), $Pd(OAc)_2$ (0.02 mmol, 8 mol%), PPh_3 (0.08 mmol, 32 mol%), K_3PO_4 (1.5 mmol, 6 equiv), DMF, 90 °C, 1 h; Conditions for **step 2**: $BiAr^2_3$ (0.25 mmol, 1 equiv), K_3PO_4 (1 mmol, 4 equiv), DMF, 90 °C, 2 h. [b] Isolated yields based on three aryl couplings from $BiAr_3$. [c] Biaryls formed up to 10%.

Further experimentation was carried out with electronically different $BiAr_3$ combination (Table 6, entries 2 and 3). In these cases, we have seen an increase in the formation of 2,5-diarylated products (**5.2** and **5.3)** after the step 2 along with isolation of unreacted mono-arylated (**4.1** and **4.9)** products. This increase in the bis-arylation yield could be attributed to the presence of electronically neutral phenyl or deficient 4-chlorophenyl in 5-position to afford a better coupling reactivity at 2-bromo position. This effort thus uncovered the preferential couplings associated with differential reactivity of electronically variant 5-aryl-2-bromopyridines in bis-arylations.

Having seen the encouraging coupling reactivity with iodo and dihalopyridines, it was time to expedite the study with less reactive 2-chloropyridine.[8,14] The coupling of 2-chloropyridine was screened for its reactivity as given in Table 7. The initial coupling performed using conditions employed for 2-

bromopyridine[7] couplings failed to deliver the desired product (Table 7, entry 1). Similar attempt was made with 2-iodopyridine conditions in the presence of TBAI. In this case, we have obtained **2.1** in 5% yield (Table 7, entry 2). Hence, it was realized that the conditions employed in either 2-bromo or 2-iodopyridine couplings are not suitable for 2-chloropyridine substrate.

Table 7. Screening for 2-chloropyridine couplings[a,b,c]



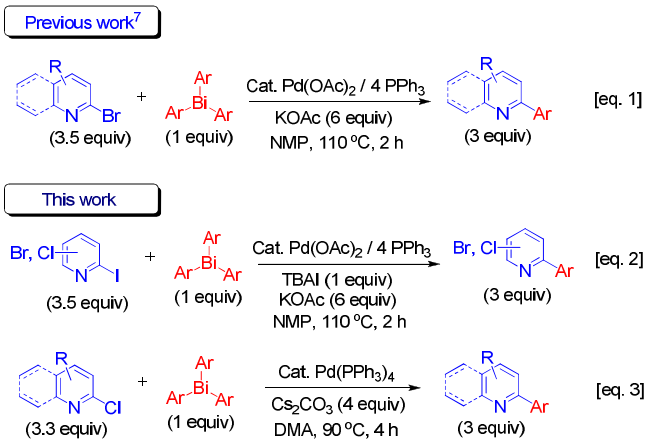
Entry	Catalyst (equiv)	Base (equiv)	Solvent	Time (*h*)	*T* (°C)	Yield (%)
1	$Pd(OAc)_2$ / 4 PPh_3	KOAc (6)	NMP	2	110	--[d]
2	$Pd(OAc)_2$ / 4 PPh_3	KOAc (6)	NMP	2	110	5[d,e]
3	$Pd(OAc)_2$ / 4 PPh_3	KOAc (4)	DMA	2	90	20
4	$Pd(PPh_3)_4$	KOAc (4)	NMP	2	90	41
5	$Pd(PPh_3)_4$	KOAc (4)	DMA	2	90	67
6	$Pd(PPh_3)_4$	Cs_2CO_3 (4)	DMA	4	90	81
7	$Pd(PPh_3)_4$	Cs_2CO_3 (6)	DMA	4	90	76
8	$Pd(PPh_3)_4$	Cs_2CO_3 (4)	DMF	4	90	40
9	$Pd(PPh_3)_4$	Cs_2CO_3 (4)	NMP	4	90	60
10	$Pd(PPh_3)_4$	Cs_2CO_3 (4)	DMA	3	90	68
11	$Pd(PPh_3)_4$	Cs_2CO_3 (4)	DMA	4	60	32
12	None	Cs_2CO_3 (4)	DMA	4	90	--
13	$Pd(PPh_3)_4$	No base	DMA	4	60	10

[a] Conditions: 2-Chloropyridine (0.825 mmol, 3.3 equiv), Bi(*p*-anisyl)$_3$ (0.25 mmol, 1 equiv), base (equiv), catalyst (0.0225 mmol, 9 mol%), solvent (3 mL), temp °C, 2 h. [b] Isolated yields based on three aryl couplings from $BiAr_3$. [c] Bianisyl formed in minor amounts. [d] $Pd(OAc)_2$ (5 mol%). [e] TBAI (0.25 mmol, 1 equiv).

Thus, further investigation was carried out under different conditions (Table 7, entries 3-5) and encouragingly this search provided the desired product up to 67% yield using $Pd(PPh_3)_4$ in DMA with KOAc (Table 7, entry 5) and it was improved to 81% in the presence of Cs_2CO_3 (Table 7, entry 6). Again, additional amount of base did not show further improvement (Table 7, entry 7). While, investigations with the change of solvent (Table 7, entries 8 and 9), reaction time up to 3 h (Table 7, entry 10) or heating at 60 °C proved to be ineffective (Table 7, entry 11). A control without catalyst did not furnish the desired coupling and absence of the base delivered poor yield (Table 7, entries 12 and 13). Thus, the efficient couplings of 2-chloropyridine could be obtained with $Pd(PPh_3)_4$ and Cs_2CO_3 in DMA at 90 °C with 4 h conditions (Table 7, entry 6) and it was considered as our optimized protocol for further study.

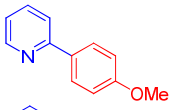
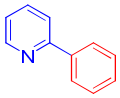
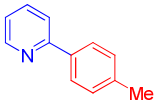
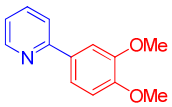
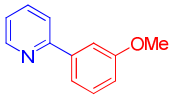
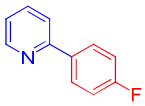
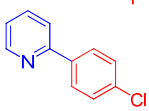
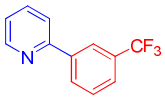
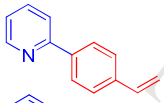
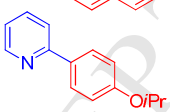
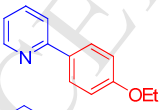
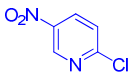
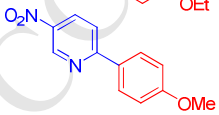
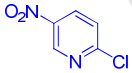
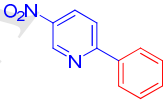
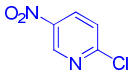
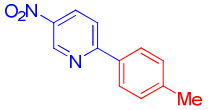
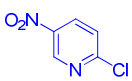
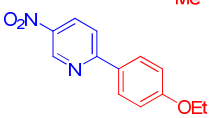
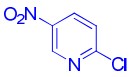
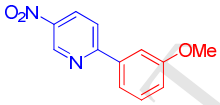
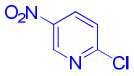
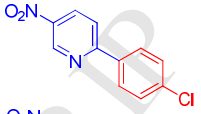
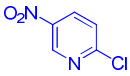
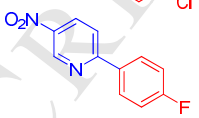
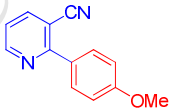
The cross-coupling of 2-chloropyridine was then examined with other $BiAr_3$ reagents. The optimized conditions employed for this study were proved to be very efficient for different couplings with 2-chloropyridine and produced 2-arylpyridines in 52-92% yields (Table 8, entries 1-11). We have seen some difference in the coupling reactivity with electronically variant $BiAr_3$ reagents. However, the overall outcome amply indicated the facile coupling reactivity of 2-chloropyridine with our optimized conditions. Further elaboration with functionalized 2-chloropyridines substituted with 5-nitro (Table 8, entries 12-18), 3-cyano (Table 8, entries 19-21), 5-methyl (Table 8, entry 22) groups was carried out to check their reactivity. This examination delivered functionalized 2-arylpyridines in 68-98% yields (Table 8, entries 12-22). At this stage, a brief attention was paid to investigate the regioselective couplings with differently substituted dichloropyridines. These reactions employing different substrates gave selective arylations at C-2 position with good to excellent yields (Table 8, entries 23-39). Overall, the electronic influence of various groups in 2-chloropyridine couplings was positive under the established conditions. Additionally, a few symmetrical bis-couplings carried out with 2,6-dichloropyridine gave 2,6-diarylpyridines in 75-82% yields (Table 8, entries 40-42). This elaborate examination with electronically variant 2-chloropyridines demonstrated high cross-couplings reactivity. In fact, the earlier known couplings of 2-chloropyridine with organobismuth alkoxides[8a] or with triarylbismuth[8b] reagents required either higher heating conditions or longer time durations. Whereas, the present protocol demonstrated robust reactivity under relatively easier coupling conditions.

In our earlier study, we explored the general coupling reactivity along with regioselective couplings of variously substituted dibromopyridines. This had established the novel coupling ability of triarylbismuths both in mono and bis-arylations with bromopyridines.[7] In this study, the coupling reactivity of bismuth reagents was extended to both iodo and chloropyridines. These substrates also participated with facile coupling reactivity as illustrated in eqs. 1-3.

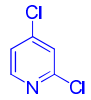
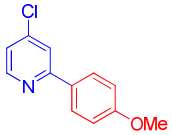
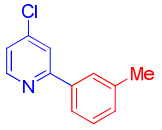
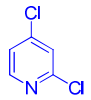
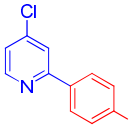
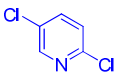
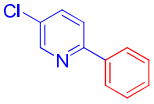
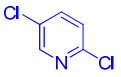
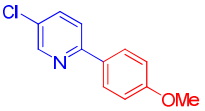
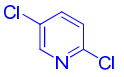
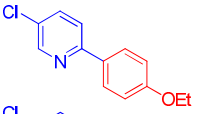
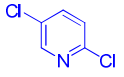
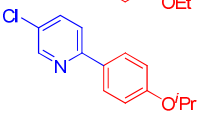


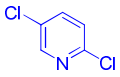
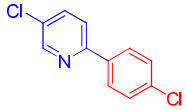
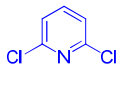
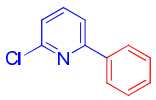
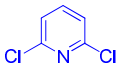
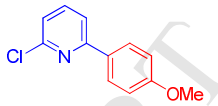
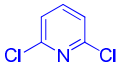
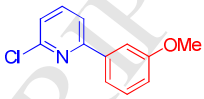
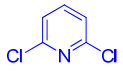
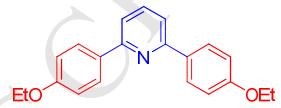
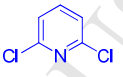
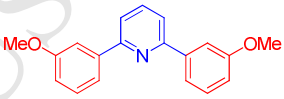
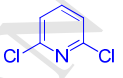
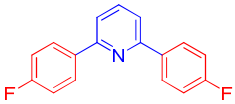
For comparison, the couplings of 2-bromopyridine (eq. 1) or 2-iodopyridine (eq. 2) were affected at 110 °C, 2 h condition while, the couplings with 2-chloropyridine just needed 90 °C for 4 h (eq. 3) under palladium coupling conditions. Thus we have established the overall facile coupling reactivity of various 2-halopyridines with triarylbismuth reagents. Significantly, the chemo- and regio-selective coupled products obtained in this study are useful to prepare scaffolds for medicinal,[15] photophysical[16] and other studies.[17]

Table 8. Couplings of chloropyridines with $BiAr_3$ reagents[a,b,c]

Entry	2-Chloropyridine	2-Arylpyridine		Yield (%)
1			**2.1**	81
2			**2.2**	72
3			**2.3**	72
4			**2.4**	92
5			**2.5**	68
6			**2.6**	63
7			**2.7**	67
8			**2.9**	52
9			**2.11**	61
10			**2.16**	74
11			**2.17**	76
12			**2.18**	98
13			**2.19**	75
14			**2.20**	78
15			**2.21**	92
16			**2.22**	84
17			**2.23**	69
18			**2.24**	73
19			**2.25**	98
20			**2.26**	91
21			**2.27**	81
22			**2.28**	68
23			**2.29**	97
24			**2.30**	92
25			**2.31**	68
26			**2.32**	79
27			**2.33**	72
28			**2.34**	91

Continued…….

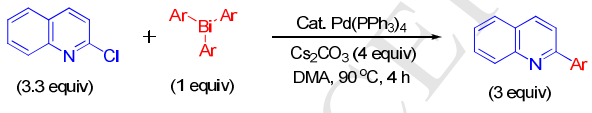
Entry	2-Chloropyridine	2-Arylpyridine		Yield (%)
29			**2.35**	97
30			**2.36**	92
31			**2.37**	89
32			**2.38**	91
33			**2.39**	97
34			**2.40**	92
35			**2.41**	90

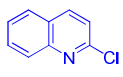
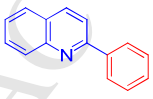
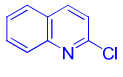
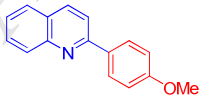
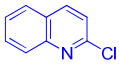
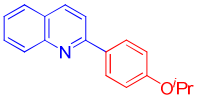
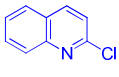
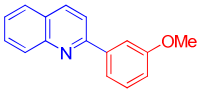
Entry	2-Chloropyridine	2-Arylpyridine		Yield (%)
36			**2.42**	45
37			**2.43**	81
38			**2.44**	71
39			**2.45**	74
40			**2.46**	78[d]
41			**2.47**	82[d]
42			**2.48**	75[d]

[a] Conditions: Chloropyridine (0.825 mmol, 3.3 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), Cs_2CO_3 (1 mmol, 4 equiv), $Pd(PPh_3)_4$ (0.0225 mmol, 9 mol%), DMA, 90 °C, 4 h. [b] Isolated yields based on three aryl couplings from $BiAr_3$. [c] Biaryls formed up to 10%. [d] With 2,6-dichloropyridine (0.412 mmol, 1.65 mmol).

The compatibility of the coupling conditions established for 2-chloropyridine was checked in reactions with 2-chloroquinoline (Table 9). These couplings with different triarylbismuth reagents were proved to be equally efficient with the formation of 2-arylquinolines (Table 9, 6.1-6.4).

Table 9. Coupling of 2-chloroquinoline [a,b,c]



Entry	2-Chloroquinoline	2-Arylquinoline		Yield (%)
1			**6.1**	83
2			**6.2**	75
3			**6.3**	89
4			**6.4**	96

[a] Conditions: 2-Chloroquinoline (0.825 mmol, 3.3 equiv), $BiAr_3$ (0.25 mmol, 1 equiv), Cs_2CO_3 (1 mmol, 4 equiv), $Pd(PPh_3)_4$ (0.0225 mmol, 9 mol%), DMA, 90 °C, 4 h. [b] Isolated yields based on three aryl couplings from $BiAr_3$. [c] Biaryls formed up to 10%.

3. Conclusion

In this study, we have established the viable coupling reactivity of triarylbismuths as atom-economic threefold coupling reagents in reactions with iodo- and chloropyridines under palladium protocol conditions. Additionally, the study of 2-chloroquinoline also demonstrated the facile reactivity with triarylbismuth reagents. This evaluation thus proved to be productive in furnishing good to high coupling yields with broad applicability of triarylbismuth reagents in coupling reactions.

4.Experimental section

4.1. General

Standard methods have been used for purification and drying of the solvents employed. Coupling reactions have been performed in oven-dried Schlenk tubes. Triarylbismuths have been obtained following literature methods.[5a-b] 2-Chloropyridine, 2,4-dichloropyridine, 2,3-dichloropyridine, 2,5-dichloropyridine and 2,6-dichloropyridine were purchased from Avra chemicals. 2-Iodopyridine,[18] 3-iodopyridine,[19] 2-iodo-5-bromopyridine,[20] 4-iodo-2-chloropyridine,[20] 5-iodo-2-bromopyridine,[21] and 2-chloroquinoline[22] have been prepared. Column chromatography was performed on 100-200 mesh silica gel using hexane:ethyl acetate as eluent. ^1H NMR and ^{13}C NMR spectra were recorded on a JEOL-Lambda (500

MHz) spectrometer using $CDCl_3$ as solvent. HRMS spectra were measured on Waters CAB155 GCT Premier analyzer.

4.2. Representative coupling procedures:

4.2.1. Reaction of 3-iodopyridine with $BiPh_3$ reagent (for Table 1):

An oven dried Schlenk tube was purged with nitrogen and charged with 3-iodopyridine (0.875 mmol, 179.3 mg), $BiPh_3$ (0.25 mmol, 110 mg), K_3PO_4 (1.5 mmol, 318 mg), $Pd(OAc)_2$ (0.025 mmol, 5.6 mg), PPh_3 (0.1 mmol, 26.2 mg) followed by dry DMF (3 mL) under nitrogen atmosphere. The reaction mixture was stirred in an oil bath at 90 ^oC for 1 h. It was brought to rt, treated with water (10 mL) and extracted with ethyl acetate (2 X 20 mL). The organic extract was treated with brine, dried over anhydrous $MgSO_4$ and concentrated using rotary evaporator under the reduced pressure. The crude was subjected to silica gel column chromatography (5% EtOAc/hexane) to obtain 3-phenylpyridine (**1.1**) as colorless oil (115 mg, 98%).

4.2.2 Reaction of 2-iodopyridine with Bi(*p*-anisyl)$_3$ reagent (for Tables 3 and 4):

The coupling reaction was performed following the procedure given in **4.2.1** with conditions; 2-iodopyridine (0.875 mmol, 179.3 mg), Bi(*p*-anisyl)$_3$ (0.25 mmol, 132.6 mg), KOAc (1.5 mmol, 147.3 mg), TBAI (0.25 mmol, 92.3 mg), $Pd(OAc)_2$ (0.0125 mmol, 2.8 mg), PPh_3 (0.05 mmol, 13.1 mg), NMP (3 mL), 110 ^oC, 2 h. The product **2.1** was obtained as colorless oil (123 mg, 86%).

4.2.3 Reaction of 5-iodo-2-bromopyridine and $BiPh_3$ reagent (for Table 5):

The coupling reaction was performed following the procedure given in **4.2.1** with conditions; 5-iodo-2-bromopyridine (0.875 mmol, 248.4 mg), $BiPh_3$ (0.25 mmol, 110 mg), K_3PO_4 (1.5 mmol, 318 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), PPh_3 (0.08 mmol, 20.9 mg), DMF (3 mL), 90 ^oC, 1 h. The product **4.1** was obtained as white solid (154 mg, 88%).

4.2.4 One-pot bis-couplings of 2-bromo-5-iodopyridine (for Table 6):

An oven dried Schlenk tube was purged with nitrogen and charged with 2-bromo-5-iodopyridine (0.875 mmol, 248.4 mg), Bi(*p*-anisyl)$_3$ (0.25 mmol, 132.6 mg), K_3PO_4 (1.5 mmol, 318 mg), $Pd(OAc)_2$ (0.02 mmol, 4.5 mg), PPh_3 (0.08 mmol, 20.9 mg), and DMF (3 mL) under nitrogen atmosphere. The reaction mixture was stirred in an oil bath at 90 ^oC for 1 h. For the second coupling, tri(*p*-tolyl)bismuth (0.25 mmol, 120.5 mg), K_3PO_4 (1 mmol, 212.3 mg) and DMF (3mL) were added to the Schlenk tube under nitrogen and the stirring was continued at 90 ^oC for 2 h. It was worked up following the procedure given in **4.2.1**. After column chromatography separation, compounds **4.2** (160 mg, 81%) and **5.1** (25 mg, 12%) were obtained as white solids.

4.2.5 Reaction of 2-chloropyridine with Bi(*p*-anisyl)$_3$ reagent (for Tables 8 and 9):

The coupling reaction was performed following the procedure given in **4.2.1** with the conditions; 2-chloropyridine (0.825 mmol, 93.65 mg), Bi(*p*-anisyl)$_3$ (0.25 mmol, 132.6 mg), Cs_2CO_3 (1.0 mmol, 325.8 mg), $Pd(PPh_3)_4$ (0.0225 mmol, 26 mg), DMA (3 mL), 90 ^oC, 4 h. The product **2.1** was obtained as colorless oil (112 mg, 81%).

4.3.Characterization data:

All products were identified by ^1H and ^{13}C NMR, IR, HRMS spectroscopic analysis. Spectral data for **1.1-1.10**, **1.12**, **2.1-2.17**, **2.19**, **2.20**, **2.25**, **2.27**, **2.38-2.42**, **2.46-2.48**, **5.1** and **6.1-6.3** products is available in ref. 7. Data of other products is given here.

*4.3.1. 3-(3-Chlorophenyl)pyridine (**1.11**)*: Brown liquid, (128 mg, 89%), R_f (17.5% EtOAc/Hexane) 0.37; ^1H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 1H, Ar-H), 8.61 (d, J = 4.3 Hz, 1H, Ar-H), 7.83 (d, J = 7.95 Hz 1H, Ar-H), 7.55 (s, 1H, Ar-H), 7.45-7.35 (m, 4H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.99, 148.16, 139.61, 135.33, 134.98, 134.36, 130.31, 128.13, 127.24, 125.28, 123.63 ppm. IR (neat, cm^{-1}): 3054, 3033, 1577, 1431, 1393, 1333, 1060, 1027, 998, 780. HRMS (ES^+): calcd. for $C_{11}H_8NCl$ $[M]^+$ 189.0345; found 189.0343.

*4.3.2. 3-(3-(trifluoromethyl)phenyl)pyridine (**1.13**):* Brown liquid, (124 mg, 74%), R_f (17.5% EtOAc/Hexane) 0.26; ^1H NMR (500 MHz, $CDCl_3$): δ 8.85 (d, J = 2.4 Hz, 1H, Ar-H), 8.64 (dd, J = 4.9 Hz, 0.95 Hz, 1H, Ar-H), 7.89 (d, J = 7.65 Hz, 1H, Ar-H), 7.81 (s, 1H, Ar-H), 7.76 (d, J = 7.3 Hz, 1H, Ar-H), 7.66 (d, J = 7.95 Hz, 1H, Ar-H), 7.60 (t, J = 7.47 Hz, 1H, Ar-H), 7.40 (dd, J = 7.95 Hz, 4.85 Hz, 1H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 149.19, 148.22, 138.66, 135.22, 134.49, 131.65, 131.40, 130.42, 129.61, 124.82, 124.79, 123.97, 123.94, 123.70 ppm. IR (neat, cm^{-1}): 3037, 2926, 1591, 1571, 1473, 1336, 1267, 1167, 1125, 1061. HRMS (EI^+): calcd. for $C_{12}H_8F_3N$ $[M]^+$ 223.0609; found 223.0603.

*4.3.3. 2-Chloro-4-phenylpyridine (**3.1**)*: White solid (136 mg, 96%), mp 58-60 ^oC, R_f (20% EtOAc/Hexane) 0.45; ^1H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, J = 5.15 Hz, 1H, Ar-H), 7.62-7.60 (m, 2H, Ar-H), 7.54 (s, 1H, Ar-H), 7.51-7.47 (m, 3H, Ar-H), 7.43 (dd, J = 5.15 Hz, 1.7 Hz, 1H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.15, 151.53, 149.97, 136.79, 129.65, 129.23, 127.01, 122.02, 120.47 ppm. IR (KBr, cm^{-1}): 3060, 3024, 1605, 1589, 1535, 1459, 1445, 1377, 1300, 1265, 1227, 1089. HRMS (ES^+): calcd. for $C_{11}H_9ClN$ $[M+H]^+$ 190.0424; found 190.0422.

*4.3.4. 2-Chloro-4-(4-methoxyphenyl)pyridine (**3.2**)*: Off white solid (160 mg, 97%), mp 53-54 ^oC, R_f (20% EtOAc/Hexane) 0.29; ^1H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, J = 5.15 Hz, 1H, Ar-H), 7.57 (d, J = 8.55 Hz, 2H, Ar-H), 7.50 (s, 1H, Ar-H), 7.39-7.38 (m, 1H, Ar-H), 7.01 (d, J = 9.2 Hz, 2H, Ar-H), 3.86 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.95, 152.13, 150.99, 149.86, 128.95, 128.24, 121.27, 119.83, 114.63, 55.41 ppm. IR (KBr, cm^{-1}): 3019, 2935, 2836, 1611, 1591, 1518, 1462, 1379, 1293, 1277, 1251, 1185, 1132, 1088, 1048. HRMS (ES^+): calcd. for $C_{12}H_{11}ClNO$ $[M+H]^+$ 220.0529; found 220.0526.

*4.3.5. 2-Chloro-4-(4-fluorophenyl)pyridine (**3.3**)*: Off white solid (145 mg, 93%), mp 123-124 ^oC, R_f (20% EtOAc/Hexane) 0.42; ^1H NMR (500 MHz, $CDCl_3$): δ 8.43 (d, J = 5.15 Hz, 1H, Ar-H), 7.61-7.58 (m, 2H, Ar-H), 7.50 (s, 1H, Ar-H), 7.39 (dd, J = 5.15 Hz, 1.7 Hz, 1H, Ar-H), 7.19 (t, J = 8.55 Hz, 2H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.71 (d, $J_{C\text{-}F}$ = 149.57 Hz), 152.25, 150.43, 150.05, 132.91, 128.88 (d, $J_{C\text{-}F}$ = 8.4 Hz), 121.86, 120.28, 116.35 (d, $J_{C\text{-}F}$ = 21.6 Hz) ppm. IR (KBr, cm^{-1}): 3055, 1593, 1534, 1514, 1460, 1375, 1225, 1161, 1133, 1087. HRMS (ES^+): calcd. for $C_{11}H_8ClFN$ $[M+H]^+$ 208.0329; found 208.0320.

*4.3.6. 2-Chloro-4-(m-tolyl)pyridine (**3.4**)*: Off white solid (136 mg, 89%), mp 53-54 ^oC, R_f (20% EtOAc/Hexane) 0.40; ^1H NMR (500 MHz, $CDCl_3$): δ 8.41 (d, J = 5.15 Hz, 1H, Ar-H), 7.53 (s, 1H, Ar-H), 7.42-7.36 (m, 4H, Ar-H), 7.28 (d, J = 7.45 Hz, 1H, Ar-H), 2.43 (s, 3H, Me) ppm.^{13}C NMR (125 MHz,

$CDCl_3$): δ 152.09, 151.68, 149.89, 138.99, 136.76, 130.39, 129.12, 127.70, 124.12, 122.01, 120.49, 21.46 ppm. IR (KBr, cm^{-1}): 3026, 2922, 1587, 1536, 1490, 1462, 1370, 1126, 1081, 1038. HRMS (ES^+): calcd. for $C_{12}H_{11}ClN$ $[M+H]^+$ 204.0580; found 204.0583.

4.3.7. 2-Bromo-5-phenylpyridine ***(4.1)***[23]: White solid, (154 mg, 88%), mp 72-74 ^oC, R_f (10% EtOAc/Hexane) 0.58; ^1H NMR (500 MHz, $CDCl_3$): δ 8.58 (d, J = 2.1 Hz, 1H, Ar-H), 7.73 (dd, J = 2.45 Hz, 8.25 Hz, 1H, Ar-H), 7.55-7.53 (m, 3H, Ar-H), 7.49-7.46 (m, 2H, Ar-H), 7.43-7.40 (m, 1H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.46, 140.86, 136.95, 136.45, 135.99, 129.21, 128.49, 127.99, 126.99 ppm. IR (KBr, cm^{-1}): 3038, 1575, 1551, 1446, 1365, 1091, 1001, 993, 837, 760. HRMS (ES^+): calcd. for $C_{11}H_8BrN$ $[M]^+$ 232.9840; found 232.9848.

4.3.8. 2-Bromo-5-(4-methoxyphenyl)pyridine ***(4.2)***[16b]: White solid, (178 mg, 89%), mp 140-142 ^oC, R_f (10% EtOAc/ Hexane) 0.48; ^1H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, J = 2.4 Hz, 1H, Ar-H), 7.68 (dd, J = 2.45 Hz, 8.25 Hz, 1H, Ar-H), 7.50 (d, J = 8.25 Hz, 1H, Ar-H), 7.47 (d, J = 8.6 Hz, 2H, Ar-H), 7.00 (d, J = 8.55 Hz, 2H, Ar-H), 3.85 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.00, 148.00, 140.00, 136.52, 135.63, 128.74, 128.11, 127.93, 114.64, 55.39 ppm. IR (KBr, cm^{-1}): 3012, 2962, 2934, 2837, 1606, 1579, 1550, 1518, 1456, 1322, 1288, 1185. HRMS (ES^+): calcd. for $C_{12}H_{11}BrNO$ $[M+H]^+$ 264.0024; found 264.0023.

4.3.9. 2-Bromo-5-(4-methylphenyl)pyridine ***(4.3)***: White solid, (176 mg, 94%), mp 112-113 ^oC, R_f (10% EtOAc/Hexane) 0.59; ^1H NMR (500 MHz, $CDCl_3$): δ 8.56 (d, J = 2.75 Hz, 1H, Ar-H), 7.70 (dd, J = 2.45 Hz, 8.25 Hz, 1H, Ar-H), 7.52 (d, J = 8.25 Hz, 1H, Ar-H), 7.43 (d, J = 8.25 Hz, 2H, Ar-H), 7.28 (d, J = 8.25 Hz, 2H, Ar-H), 2.40 (s, 3H, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.28, 140.47, 138.53, 136.74, 135.91, 133.50, 129.91, 127.93, 126.80, 21.16 ppm. IR (KBr, cm^{-1}): 2911, 1574, 1452, 1361, 1086, 993, 809. HRMS (ES^+): calcd. for $C_{12}H_{10}BrN$ $[M]^+$ 246.9997; found 246.9996.

4.3.10. 2-Bromo-5-(4-ethoxyphenyl)pyridine ***(4.4)***: White solid, (173 mg, 83%), mp 119-120 ^oC, R_f (10% EtOAc/ Hexane) 0.47; ^1H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, J = 2.55 Hz, 1H, Ar-H), 7.68 (dd, J = 2.55 Hz, 8.30 Hz, 1H, Ar-H), 7.50 (d, J = 8.30 Hz, 1H, Ar-H), 7.46 (d, J = 8.85 Hz, 2H, Ar-H), 6.98 (d, J = 8.55 Hz, 2H, Ar-H), 4.08 (q, J = 7.15 Hz, 2H, OEt), 1.44 (t, J = 6.95 Hz, 3H, OEt) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.42, 147.98, 139.94, 136.50, 135.70, 128.56, 128.09, 127.92, 115.19, 63.60, 14.78 ppm. IR (KBr, cm^{-1}): 3029, 2977, 2932, 2893, 1577, 1546, 1517, 1478, 1419, 1396, 1317, 1292. HRMS (ES^+): calcd. for $C_{13}H_{12}BrNO$ $[M]^+$ 277.0102; found 277.0108.

4.3.11. 2-Bromo-5-(4-isopropoxyphenyl)pyridine ***(4.5)***: White solid, (185 mg, 85%), mp 82-85 ^oC, R_f (10% EtOAc/Hexane) 0.48; ^1H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, J = 2.55 Hz, 1H, Ar-H), 7.69 (dd, J = 2.60 Hz, 8.35 Hz, 1H, Ar-H), 7.50 (d, J = 8.30 Hz, 1H, Ar-H), 7.45 (d, J = 8.30 Hz, 2H, Ar-H), 6.97 (d, J = 8.60 Hz, 2H, Ar-H), 4.62-4.57 (m, 1H, O^{i}Pr), 1.36 (d, J = 6.00 Hz, 6H, O^{i}Pr) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.38, 147.97, 139.90, 136.48, 135.71, 128.41, 128.11, 127.91, 116.39, 69.99, 21.97 ppm. IR (KBr, cm^{-1}): 2976, 2928, 1606, 1513, 1452, 1286, 1250, 1185, 1121, 1091, 953, 828. HRMS (ES^+): calcd. for $C_{14}H_{15}BrNO$ $[M+H]^+$ 292.0337; found 292.0334.

4.3.12. 2-Bromo-5-(3-methoxyphenyl)pyridine ***(4.6)***: White solid, (157 mg, 79%), mp 58-60 ^oC, R_f (10% EtOAc/Hexane) 0.45; ^1H NMR (500 MHz, $CDCl_3$): δ 8.56 (d, J = 2.30 Hz, 1H, Ar-H), 7.71 (dd, J = 2.55 Hz, 8.30 Hz, 1H, Ar-H), 7.53 (d, J = 8.30 Hz, 1H, Ar-H), 7.38 (t, J = 8.0 Hz, 1H, Ar-H), 7.11 (d, J = 8.30 Hz, 1H, Ar-H), 7.06-7.04 (m, 1H, Ar-H), 6.95 (dd, J = 2.60 Hz, 8.30 Hz, 1H), 3.86 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.16, 148.48, 140.96, 137.87, 136.98, 135.85, 130.29, 127.96, 119.38, 113.62, 112.88, 55.36 ppm. IR (KBr, cm^{-1}): 2963, 2935, 2839, 1608, 1581, 1458, 1443, 1294, 1174, 1134, 1087, 1054, 1036. HRMS (ES^+): calcd. for $C_{12}H_{11}BrNO$ $[M+H]^+$ 264.0024; found 264.0023.

4.3.13. 2-Bromo-5-(4-vinylphenyl)pyridine ***(4.7)***: White solid, (141 mg, 72%), mp 107-109 ^oC, R_f (10% EtOAc/Hexane) 0.61; ^1H NMR (500 MHz, $CDCl_3$): δ 8.58 (d, J = 2.45 Hz, 1H, Ar-H), 7.73-7.71 (m, 1H, Ar-H), 7.53 (d, J = 8.25 Hz, 1H, Ar-H), 7.51-7.50 (m, 4H, Ar-H), 6.75 (dd, J = 10.7 Hz, 17.4 Hz, 1H, Ar-H), 5.82 (d, J = 17.75 Hz, 1H, Ar-H), 5.31 (d, J = 11 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.27, 140.85, 137.84, 136.68, 135.97, 135.68, 135.54, 128.01, 127.08, 127.02, 114.90 ppm. IR (KBr, cm^{-1}): 3042, 2923, 1572, 1453, 1360, 1091, 991, 912, 825. HRMS (ES^+): calcd. for $C_{13}H_{11}BrN$ $[M+H]^+$ 260.0075; found 260.0078.

4.3.14. 2-Bromo-5-(4-fluorophenyl)pyridine ***(4.8)***: White solid, (125 mg, 66%), mp 116-119 ^oC, R_f (10% EtOAc/Hexane) 0.59; ^1H NMR (500 MHz, $CDCl_3$): δ 8.53 (d, J = 2.45 Hz, 1H, Ar-H), 7.68 (dd, J = 2.45 Hz, 8.25 Hz, 1H, Ar-H), 7.54-7.48 (m, 3H, Ar-H), 7.16 (t, J = 8.55, 2H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0 (d, $^1J_{C\text{-}F}$ = 266.36 Hz), 148.28, 140.91, 136.79, 13507, 132.61, 128.35 (d, $^3J_{C\text{-}F}$ = 8.38 Hz), 128.04, 116.26 (d, $^2J_{C\text{-}F}$ = 21.58 Hz) ppm. IR (KBr, cm^{-1}): 3054, 1656, 1600, 1578, 1453, 1411, 1163, 1140, 1088, 966, 812. HRMS (ES^+): calcd. for $C_{11}H_8BrFN$ $[M+H]^+$ 251.9824; found 251.9824.

4.3.15. 2-Bromo-5-(4-chlorophenyl)pyridine ***(4.9)****:* White solid, (151 mg, 75%), mp 112-114 ^oC, R_f (10% EtOAc/ Hexane) 0.55; ^1H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, J = 2.45 Hz, 1H, Ar-H), 7.69 (dd, J = 2.75 Hz, 8.30 Hz, 1H, Ar-H), 7.55 (d, J = 8.25 Hz, 1H, Ar-H), 7.48-7.43 (m, 4H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.24, 141.21, 136.73, 134.88, 134.83, 134.81, 129.43, 128.22, 128.10 ppm. IR (KBr, cm^{-1}): 3049, 1574, 1546, 1454, 1405, 1353, 1092, 997. HRMS (ES^+): calcd. for $C_{11}H_7BrClN$ $[M]^+$ 266.9450; found 266.9450.

4.3.16. 2-(4-Methoxyphenyl)-5-phenylpyridine ***(5.2)***[24]: White solid, (70 mg, 35%), mp 168-170 ^oC, R_f (25% EtOAc/Hexane) 0.29; ^1H NMR (500 MHz, $CDCl_3$): δ 8.90 (d, J = 1.8 Hz, 1H, Ar-H), 8.05-8.01 (m, 2H, Ar-H), 7.96 (d, J = 8.55 Hz, 1H, Ar-H), 7.76 (d, J = 7.9 Hz, 1H, Ar-H), 7.52-7.47 (m, 3H, Ar-H), 7.42-7.39 (m, 1H, Ar-H), 7.01 (d, J = 9.2 Hz, 2H, Ar-H), 3.87 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.70, 147.63, 147.20, 135.62, 135.29, 129.11, 128.23, 128.06, 127.05, 126.87, 120.98, 119.87, 114.24, 55.36 ppm. IR (KBr, cm^{-1}): 2958, 1590, 1515, 1445, 1369, 1248, 1180, 1111, 1003. HRMS (ES^+): calcd. for $C_{18}H_{16}NO$ $[M+H]^+$ 262.1232; found 262.1237.

4.3.17. 5-(4-Chlorophenyl)-2-(4-methoxyphenyl)pyridine ***(5.3)***: White solid, (115 mg, 52%), mp 180-182 ^oC, R_f (25% EtOAc/ Hexane) 0.26; ^1H NMR (500 MHz, $CDCl_3$): δ 8.87 (d, J = 2.45 Hz, 1H, Ar-H), 8.03 (d, J = 9.15 Hz, 2H, Ar-H), 7.97 (d, J = 7.95 Hz, 1H, Ar-H), 7.79 (d, J = 7.95 Hz, 1H, Ar-H), 7.55 (d, J = 8.55 Hz, 2H, Ar-H), 7.46 (d, J = 8.55 Hz, 2H, Ar-H), 7.01 (d, J = 8.55 Hz, 2H, Ar-H), 3.87 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.06, 146.32, 136.07, 135.41, 134.51, 133.41, 129.39, 128.44, 128.30, 128.10, 120.25, 114.63, 114.40, 55.42 ppm. IR (KBr, cm^{-1}): 2959, 1605, 1515, 1471,

1419, 1370, 1252, 1179, 1111, 1033, 1019. HRMS (ES$^+$): calcd. for $C_{18}H_{15}ClNO$ $[M+H]^+$ 296.0842; found 296.0845.

4.3.18. 2-(4-Methoxyphenyl)-5-nitropyridine (***2.18***): Yellow solid, (169 mg, 98%), mp 118-120 ^oC, R_f (10% EtOAc/ Hexane) 0.27; ^1H NMR (500 MHz, $CDCl_3$): δ 9.44 (d, J = 2.75 Hz, 1H, Ar-H), 8.46 (dd, J = 8.85 Hz, 2.75 Hz, 1H, Ar-H), 8.06 (d, J = 8.85 Hz, 2H, Ar-H), 7.82 (d, J = 8.85 Hz, 1H, Ar-H), 7.02 (d, J = 9.15 Hz, 2H, Ar-H), 3.88 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.04, 162.0, 145.26, 142.23, 131.81, 129.54, 129.28, 118.94, 114.51, 55.47 ppm. IR (KBr, cm^{-1}): 3074, 2962, 2840, 1597, 1518, 1437, 1288, 1176, 1050. HRMS (ES$^+$): calcd. for $C_{12}H_{10}N_2O_3$ $[M]^+$ 230.0691; found 230.0699.

4.3.19. 2-(4-Ethoxyphenyl)-5-nitropyridine (***2.21***): Yellow solid, (168 mg, 92%), mp 124-127 ^oC, R_f (10% EtOAc/ Hexane) 0.25; ^1H NMR (500 MHz, $CDCl_3$): δ 9.44 (d, J = 2.45 Hz, 1H, Ar-H), 8.47 (dd, J = 8.55 Hz, 2.45 Hz, 1H, Ar-H), 8.05 (d, J = 8.85 Hz, 2H, Ar-H), 7.82 (d, J = 8.85 Hz, 1H, Ar-H), 7.01 (d, J = 9.15 Hz, 2H, Ar-H), 4.11 (q, J = 7.05 Hz, 2H, CH_2), 1.45 (t, J = 6.75 Hz, 3H, CH_3) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.06, 161.45, 145.26, 142.19, 131.79, 129.34, 129.27, 118.90, 114.98, 63.70, 14.72 ppm. IR (KBr, cm^{-1}): 2977, 1598, 1572, 1504, 1458, 1423, 1391, 1342, 1307, 1255, 1181, 1152, 1116, 1152, 1116, 1050. HRMS (ES$^+$): calcd. for $C_{13}H_{12}N_2O_3$ $[M]^+$ 244.0848; found 244.0842.

4.3.20. 2-(3-Methoxyphenyl)-5-nitropyridine (***2.22***)[25]: Yellow solid, (145 mg, 84%), mp 96-99 ^oC, R_f (10% EtOAc/Hexane) 0.29; ^1H NMR (500 MHz, $CDCl_3$): δ 9.48 (d, J = 2.55 Hz, 1H, Ar-H), 8.51 (dd, J = 8.85 Hz, 2.85 Hz, 1H, Ar-H), 7.89 (d, J = 8.9 Hz, 1H, Ar-H), 7.67 (s, 1H, Ar-H), 7.62 (d, J = 7.7 Hz, 1H, Ar-H), 7.43 (t, J = 8.0 Hz, 1H, Ar-H), 7.06 (dd, J = 8.3 Hz, 2.0 Hz, 1H, Ar-H), 3.90 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.19, 160.23, 145.16, 142.89, 138.41, 131.89, 130.10, 120.20, 119.95, 116.88, 112.79, 55.45 ppm. IR (KBr, cm^{-1}): 3075, 2967, 2841, 1597, 1581, 1518, 1461, 1450, 1437, 1351, 1289, 1176. HRMS (ES$^+$): calcd. for $C_{12}H_{10}N_2O_3$ $[M]^+$ 230.0691; found 230.0697.

4.3.21. 2-(4-Chlorophenyl)-5-nitropyridine (***2.23***)[26]: Yellow solid, (121 mg, 69%), mp 153-155 ^oC, R_f (10% EtOAc/Hexane) 0.42; ^1H NMR (500 MHz, $CDCl_3$): δ 9.47 (d, J = 2.75 Hz, 1H, Ar-H), 8.52 (dd, J = 8.85 Hz, 2.75 Hz, 1H, Ar-H), 8.04 (d, J = 8.55 Hz, 2H, Ar-H), 7.88 (d, J = 8.85 Hz, 1H, Ar-H), 7.49 (d, J = 8.85 Hz, 2H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.14, 145.30, 142.94, 137.31, 135.40, 132.07, 129.37, 128.92, 119.81 ppm. IR (KBr, cm^{-1}): 3094, 1598, 1511, 1578, 1459, 1410, 1343, 1289, 1261, 1093. HRMS (ES$^+$): calcd. for $C_{11}H_7ClN_2O_2$ $[M]^+$ 234.0196; found 234.0194.

4.3.22. 2-(4-Fluorophenyl)-5-nitropyridine (***2.24***): Yellow solid, (119 mg, 73%), mp 124-127 ^oC, R_f (10% EtOAc/ Hexane) 0.40; ^1H NMR (500 MHz, $CDCl_3$): δ 9.47 (d, J = 2.6 Hz, 1H, Ar-H), 8.52 (dd, J = 8.85 Hz, 2.55 Hz, 1H, Ar-H), 8.11-8.08 (m, 2H, Ar-H), 7.86 (d, J = 8.55 Hz, 1H, Ar-H), 7.22-7.19 (m, 2H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 164.59 (d, $^1J_{C\text{-}F}$ = 149.56 Hz), 161.28, 145.26, 142.76, 133.19, 132.02, 129.24 (d, $^3J_{C\text{-}F}$ = 8.4 Hz), 119.65, 116.21 (d, $^2J_{C\text{-}F}$ = 22.78 Hz) ppm. IR (KBr, cm^{-1}): 3060, 1904, 1603, 1576, 1588, 1510, 1467, 1347, 1230. HRMS (ES$^+$): calcd. for $C_{11}H_7FN_2O_2$ $[M]^+$ 218.0492; found 218.0494.

4.3.23. 2-(3-Methylphenyl)-3-cyanopyridine (***2.26***): Yellow solid, (132 mg, 91%), mp 78-80 ^oC, R_f (10% EtOAc/Hexane) 0.36; ^1H NMR (500 MHz, $CDCl_3$): δ 8.87 (d, J = 4.6 Hz, 1H, Ar-H), 8.61 (d, J = 4.9 Hz, 1H, Ar-H), 8.07 (d, J = 6.1 Hz, 1H, Ar-H), 8.0 (d, J = 8.25 Hz, 1H, Ar-H), 7.72 (d, J = 5.15 Hz, 2H, Ar-H), 7.32 (d, J = 7.65 Hz, 1H, Ar-H), 2.45 (s, 3H, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.23, 152.82, 152.54, 142.53, 141.84, 138.53, 137.01, 131.04, 129.45, 128.57, 125.95, 122.16, 121.46, 21.44 ppm. IR (KBr, cm^{-1}): 3058, 2994, 2225, 1954, 1578, 1557, 1436, 1400, 1230. HRMS (ES$^+$): calcd. for $C_{13}H_{11}N_2$ $[M+H]^+$ 195.0922; found 195.0920.

4.3.24. 2-(4-Methoxyphenyl)-5-methylpyridine (***2.28***)[27]: Yellow solid, (101 mg, 68%), mp 46-47 ^oC, R_f (10% EtOAc/Hexane) 0.28; ^1H NMR (500 MHz, $CDCl_3$): δ 8.47 (s, 1H, Ar-H), 7.91 (d, J = 8.85 Hz, 2H, Ar-H), 7.56 (d, J = 7.9 Hz, 1H, Ar-H), 7.52-7.50 (m, 1H, Ar-H), 6.98 (d, J = 8.85 Hz, 2H, Ar-H), 3.85 (s, 3H, OMe), 2.34 (s, 3H, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.18, 154.36, 149.70, 137.42, 131.78, 130.85, 127.91, 119.37, 114.06, 55.33, 18.10 ppm. IR (KBr, cm^{-1}): 2921, 1608, 1514, 1477, 1306, 1273, 1173, 1025, 1046, 820. HRMS (ES$^+$): calcd. for $C_{13}H_{14}NO$ $[M+H]^+$ 200.1075; found 200.1072.

4.3.25. 3-Chloro-2-(4-methylphenyl)pyridine (***2.29***): Colorless liquid, (149 mg, 97%), R_f (10% EtOAc/Hexane) 0.28; ^1H NMR (500 MHz, $CDCl_3$): δ 8.58 (dd, J = 4.6 Hz, 1.25 Hz, 1H, Ar-H), 7.78 (dd, J = 8.25 Hz, 1.5 Hz, 1H, Ar-H), 7.63 (d, J = 8.25 Hz, 2H, Ar-H), 7.27 (d, J = 7.95 Hz, 2H, Ar-H), 7.19 (dd, J = 8.25 Hz, 4.55 Hz, 1H, Ar-H), 2.41 (s, 3H, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.55, 147.50, 138.78, 138.04, 135.30, 130.07, 129.21, 128.73, 122.77, 21.36 ppm. IR (neat, cm^{-1}): 3039, 2921, 2863, 1907, 1615, 1571, 1553, 1423, 1130, 1028, 1016. HRMS (ES$^+$): calcd. for $C_{12}H_{11}ClN$ $[M+H]^+$ 204.0580; found 204.0583.

4.3.26. 3-Chloro-2-(4-methoxyphenyl)pyridine (***2.30***)[28]: White solid, (152 mg, 92%), mp 45-47 ^oC, R_f (10% EtOAc/Hexane) 0.22; ^1H NMR (500 MHz, $CDCl_3$): δ 8.56 (dd, J = 4.55 Hz, 1.4 Hz, 1H, Ar-H), 7.76 (dd, J = 8.0 Hz, 1.45 Hz, 1H, Ar-H), 7.71 (d, J = 8.9 Hz, 2H, Ar-H), 7.17 (dd, J = 8.05 Hz, 4.6 Hz, 1H, Ar-H), 6.99 (d, J = 8.85 Hz, 2H, Ar-H), 3.86 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.05, 156.11, 147.49, 138.11, 130.80, 130.62, 129.91, 122.54, 113.42, 55.31 ppm. IR (KBr, cm^{-1}): 3061, 2936, 2841, 1609, 1570, 1514, 1461, 1431, 1305, 1181, 1028, 1111. HRMS (ES$^+$): calcd. for $C_{12}H_{11}ClNO$ $[M+H]^+$ 220.0529; found 220.0525.

4.3.27. 3-Chloro-2-(3-methoxyphenyl)pyridine (***2.31***)[28]: Colorless liquid, (112 mg, 68%), R_f (10% EtOAc/Hexane) 0.27; ^1H NMR (500 MHz, $CDCl_3$): δ 8.59 (d, J = 4.9 Hz, 1H, Ar-H), 7.79 (d, J = 7.95 Hz, 1H, Ar-H), 7.37 (t, J = 7.90 Hz, 1H, Ar-H), 7.30 (d, J = 7.6 Hz, 1H, Ar-H), 7.24-7.21 (m, 2H, Ar-H), 6.99-6.97 (m, 1H), 3.85 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.26, 156.40, 147.48, 139.42, 138.12, 130.18, 129.07, 123.12, 121.76, 114.85, 114.58, 55.33 ppm. IR (*neat*, cm^{-1}): 3046, 2937, 2834, 1601, 1582, 1570, 1455, 1432, 1320, 1300, 1235, 1179, 1028. HRMS (ES$^+$): calcd. for $C_{12}H_{11}ClNO$ $[M+H]^+$ 220.0529; found 220.0528.

4.3.28. 3-Chloro-2-(3,4-dimethoxyphenyl)pyridine (***2.32***): White solid, (149 mg, 79%), mp 84-85 ^oC, R_f (10% EtOAc/Hexane) 0.12; ^1H NMR (500 MHz, $CDCl_3$): δ 8.57 (d, J = 4.6 Hz, 1H, Ar-H), 7.78 (d, J = 7.9 Hz, 1H, Ar-H), 7.37 (d, J = 8.55 Hz, 1H, Ar-H), 7.30 (s, 1H, Ar-H), 7.19 (dd, J = 8.25 Hz, 4.9 Hz, 1H, Ar-H), 6.95 (d, J = 8.25 Hz, 1H, Ar-H), 3.93 (s, 6H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.0, 149.6, 148.5, 147.38, 143.85, 138.27, 130.62, 129.97, 122.64, 122.32, 112.57, 110.40, 55.92 ppm. IR (KBr, cm^{-1}): 2999, 2934, 2835, 1604, 1570, 1519, 1463, 1428, 1270, 1227, 1173, 1027. HRMS (ES$^+$): calcd. for $C_{13}H_{13}ClNO_2$ $[M+H]^+$ 250.0635; found 250.0638.

*4.3.29. 3-Chloro-2-(4-fluorophenyl)pyridine (**2.33**)*[28]: White solid, (113 mg, 72%), mp 76-78 °C, R_f (10% EtOAc/Hexane) 0.45; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.58 (dd, J = 4.6 Hz, 1.2 Hz, 1H, Ar-H), 7.79 (dd, J = 8.25 Hz, 1.5 Hz, 1H, Ar-H), 7.74-7.71 (m, 2H, Ar-H), 7.22 (dd, J = 7.95 Hz, 4.55 Hz, 1H, Ar-H), 7.16-7.13 (m, 2H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.07 (d, J_{C-F} = 251.96 Hz), 155.42, 147.56, 138.22, 134.22, 131.34 (d, J_{C-F} = 8.4 Hz), 130.07, 123.14, 115.05 (d, J_{C-F} = 21.6 Hz) ppm. IR (KBr, cm^{-1}): 3044, 1911, 1605, 1572, 1514, 1432, 1402, 1297, 1217, 1161, 1130. HRMS (ES$^+$): calcd. for $C_{11}H_8ClFN$ $[M+H]^+$ 208.0329; found 208.0321.

*4.3.30. 4-Chloro-2-phenylpyridine (**2.34**)*[29]: Colorless liquid, (130 mg, 91%), R_f (20% EtOAc/Hexane) 0.31; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.59 (d, J = 5.7 Hz, 1H, Ar-H), 7.97 (d, J = 6.9 Hz, 2H, Ar-H), 7.73 (d, J = 1.7 Hz, 1H, Ar-H), 7.50-7.44 (m, 3H, Ar-H), 7.25-7.24 (m, 1H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.95, 150.43, 144.77, 138.04, 129.61, 128.85, 126.97, 122.28, 120.88 ppm. IR (neat, cm^{-1}): 2926, 1572, 1550, 1462, 1443, 1382, 1072. HRMS (ES$^+$): calcd. for $C_{11}H_9ClN$ $[M+H]^+$ 190.0424; found 190.0422.

*4.3.31. 4-Chloro-2-(4-methoxyphenyl)pyridine (**2.35**)*: Colorless liquid, (160 mg, 97%), R_f (20% EtOAc/Hexane) 0.25; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (d, J = 5.15 Hz, 1H, Ar-H), 7.93 (d, J = 8.6 Hz, 2H, Ar-H), 7.67 (s, 1H, Ar-H), 7.19 (d, J = 4.55 Hz, 1H, Ar-H), 6.99 (d, J = 9.15 Hz, 2H, Ar-H), 3.86 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.05, 156.11, 147.49, 138.11, 130.80, 130.62, 129.91, 122.54, 113.42, 55.31 ppm. IR (neat, cm^{-1}): 3048, 3003, 2933, 2836, 1608, 1574, 1549, 1514, 1458, 1441, 1421, 1381, 1267, 1249, 1176, 1056, 1029. HRMS (ES$^+$): calcd. for $C_{12}H_{11}ClNO$ $[M+H]^+$ 220.0529; found 220.0526.

*4.3.32. 4-Chloro-2-(m-tolyl)pyridine (**2.36**)*: Colorless liquid, (140 mg, 92%), R_f (20% EtOAc/Hexane) 0.35; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (d, J = 5.7 Hz, 1H, Ar-H), 7.80 (s, 1H, Ar-H), 7.73-7.71 (m, 2H, Ar-H), 7.36 (t, J = 7.40 Hz, 1H, Ar-H), 7.25-7.22 (m, 2H, Ar-H), 2.43 (s, 3H, Me) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.11, 150.36, 144.71, 138.58, 138.0, 130.37, 128.74, 127.67, 124.05, 122.20, 120.92, 21.48 ppm. IR (neat, cm^{-1}): 3042, 1919, 1571, 1550, 1457, 1384, 1370, 1227, 1109, 1063. HRMS (ES$^+$): calcd. for $C_{12}H_{11}ClN$ $[M+H]^+$ 204.0580; found 204.0583.

*4.3.33. 4-Chloro-2-(4-fluorophenyl)pyridine (**2.37**)*[28]: White solid, (139 mg, 89%), mp 58-60 °C, R_f (20% EtOAc/Hexane) 0.38; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56 (d, J = 5.15 Hz, 1H, Ar-H), 7.98-7.94 (m, 2H, Ar-H), 7.67 (d, J = 1.7 Hz, 1H, Ar-H), 7.24-7.22 (m, 1H, Ar-H), 7.17-7.14 (m, 2H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.82 (d, $^1J_{C-F}$ = 148.37 Hz), 157.86, 150.43, 144.83, 134.19, 128.83 (d, $^3J_{C-F}$ = 8.38 Hz), 122.21, 120.52, 115.80 (d, $^2J_{C-F}$ = 21.6 Hz) ppm. IR (KBr, cm^{-1}): 3040, 2924, 1602, 1574, 1555, 1509, 1460, 1416, 1384, 1297, 1219, 1158, 1101, 1013. HRMS (ES$^+$): calcd. for $C_{11}H_8ClFN$ $[M+H]^+$ 208.0329; found 208.0320.

*4.3.34. 2-Chloro-6-phenylpyridine (**2.43**)*[30]: Colorless liquid, (115 mg, 81%), R_f (10% EtOAc/Hexane) 0.78; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.99 (d, J = 6.75 Hz, 1H, Ar-H), 7.72-7.70 (m, 1H, Ar-H), 7.68-7.59 (m, 1H, Ar-H), 7.52-7.42 (m, 2H, Ar-H), 7.27-7.26 (m, 3H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.66, 139.27, 137.66, 129.59, 128.80, 126.98, 122.86, 122.51, 118.65 ppm. IR (neat, cm^{-1}): 3061, 2924, 1577, 1556, 1434, 1395, 1161, 1137, 1058. HRMS (ES$^+$): calcd. for $C_{11}H_9ClN$ $[M+H]^+$ 190.0424; found 190.0422.

*4.3.35. 2-Chloro-6-(4-methoxyphenyl)pyridine (**2.44**)*[31]: White solid, (117 mg, 71%), mp 80-82 °C, R_f (10% EtOAc/Hexane) 0.49; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.95 (d, J = 8.9 Hz, 2H, Ar-H), 7.65 (t, J = 7.75 Hz, 1H, Ar-H), 7.57 (d, J = 7.7 Hz, 1H, Ar-H), 7.19 (d, J = 7.75 Hz, 1H, Ar-H), 6.97 (d, J = 8.85 Hz, 2H, Ar-H), 3.85 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.93, 157.78, 151.21, 139.17, 130.32, 128.34, 121.65, 117.78, 114.14, 55.37 ppm. IR (KBr, cm^{-1}): 2961, 2840, 1607, 1582, 1554, 1514, 1434, 1308, 1287, 1253, 1180, 1167, 1026. HRMS (ES$^+$): calcd. for $C_{12}H_{11}ClNO$ $[M+H]^+$ 220.0529; found 220.0520.

*4.3.36. 2-Chloro-6-(3-methoxyphenyl)pyridine **(2.45)***: Colorless liquid, (122 mg, 74%), R_f (10% EtOAc/Hexane) 0.55; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.70-7.67 (m, 1H, Ar-H), 7.63 (d, J = 7.65 Hz, 1H, Ar-H), 7.56-7.53 (m, 2H, Ar-H), 7.38-7.35 (m, 1H, Ar-H), 7.27-7.24 (m, 1H, Ar-H), 6.98-6.96 (m, 1H, Ar-H), 3.88 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.02, 157.86, 151.26, 139.24, 139.17, 129.77, 122.64, 119.34, 118.82, 115.51, 112.20, 55.39 ppm. IR (neat, cm^{-1}): 2961, 2840, 1607, 1582, 1554, 1514, 1434, 1308, 1287, 1253, 1180, 1167, 1026. HRMS (ES$^+$): calcd. for $C_{12}H_{11}ClNO$ $[M+H]^+$ 220.0529; found 220.0520.

*4.3.37. 2-(3-Methoxyphenyl)quinoline (**6.4**)*[32]: White solid, (169 mg, 96%), mp 40-42 °C, R_f (10% EtOAc/Hexane) 0.36; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.21 (d, J = 8.55 Hz, 1H, Ar-H), 8.17 (d, J = 8.55 Hz, 1H, Ar-H), 7.86 (d, J = 8.55, 1H, Ar-H), 7.83 (d, J = 7.95 Hz, 1H, Ar-H), 7.76 (s, 1H, Ar-H), 7.74-7.69 (m, 2H, Ar-H), 7.54-7.51 (m, 1H, Ar-H), 7.43 (t, J = 7.90 Hz, 1H, Ar-H), 7.02-7.0 (m, 1H, Ar-H), 3.93 (s, 3H, OMe) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.10, 157.12, 148.16, 141.11, 136.77, 131.32, 129.70, 129.65, 127.43, 127.24, 126.32, 120.0, 119.10, 115.37, 112.66, 55.41 ppm. IR (KBr, cm^{-1}): 3058, 3000, 2935, 2833, 1617, 1598, 1556, 1489, 1463, 1315, 1247.HRMS (ES$^+$): calcd. for $C_{16}H_{13}NO$ $[M]^+$ 235.0997; found 235.0998.

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Supplementary data

The data for unknown products was given in the supporting information. The ^{1}H, ^{13}C NMR and HRMS spectra for all products are available.

References and notes

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Supporting Information

Cross-coupling study of iodo/chloropyridines and 2-chloroquinoline with atom-economic triarylbismuth reagents under Pd-catalysis

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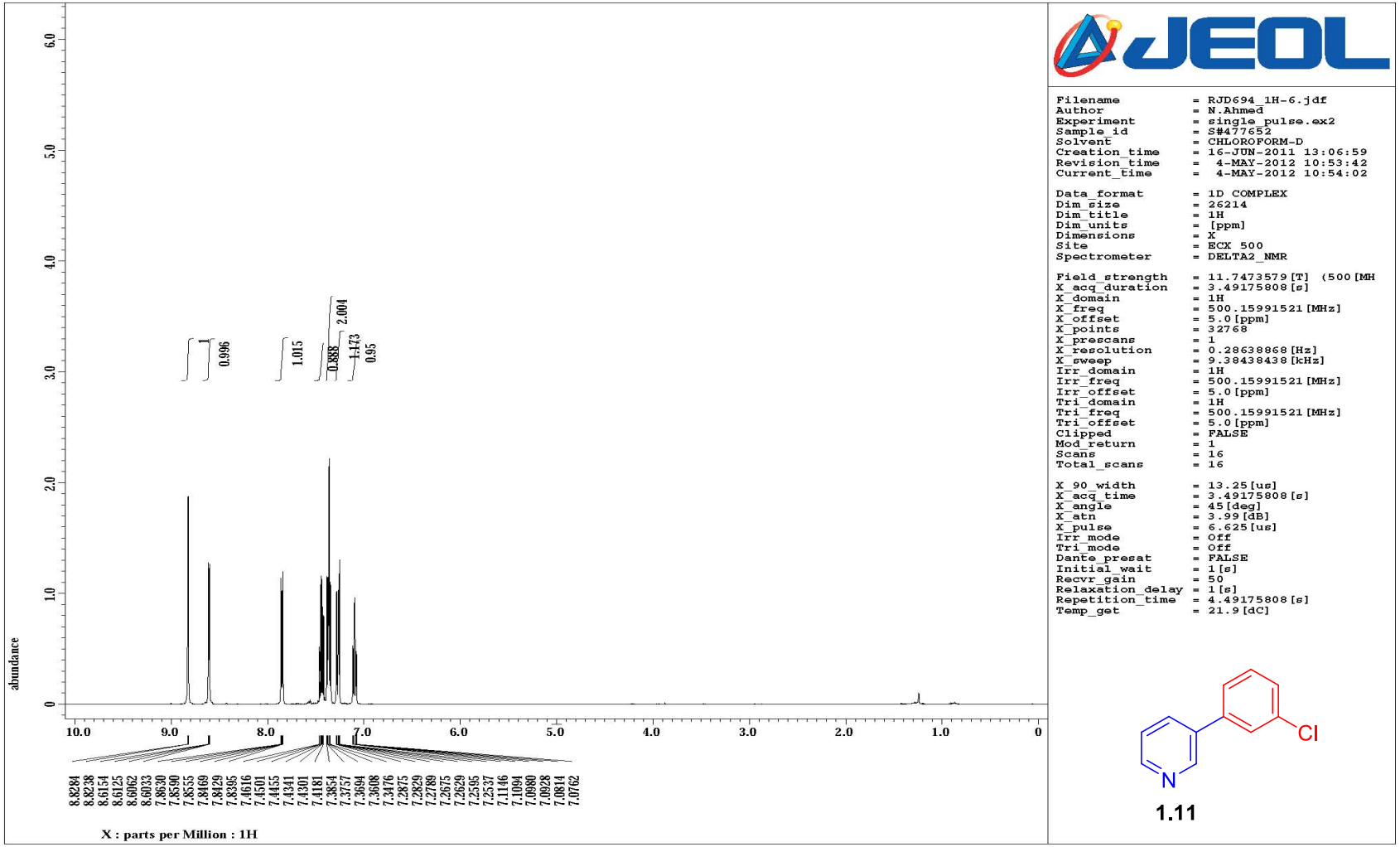
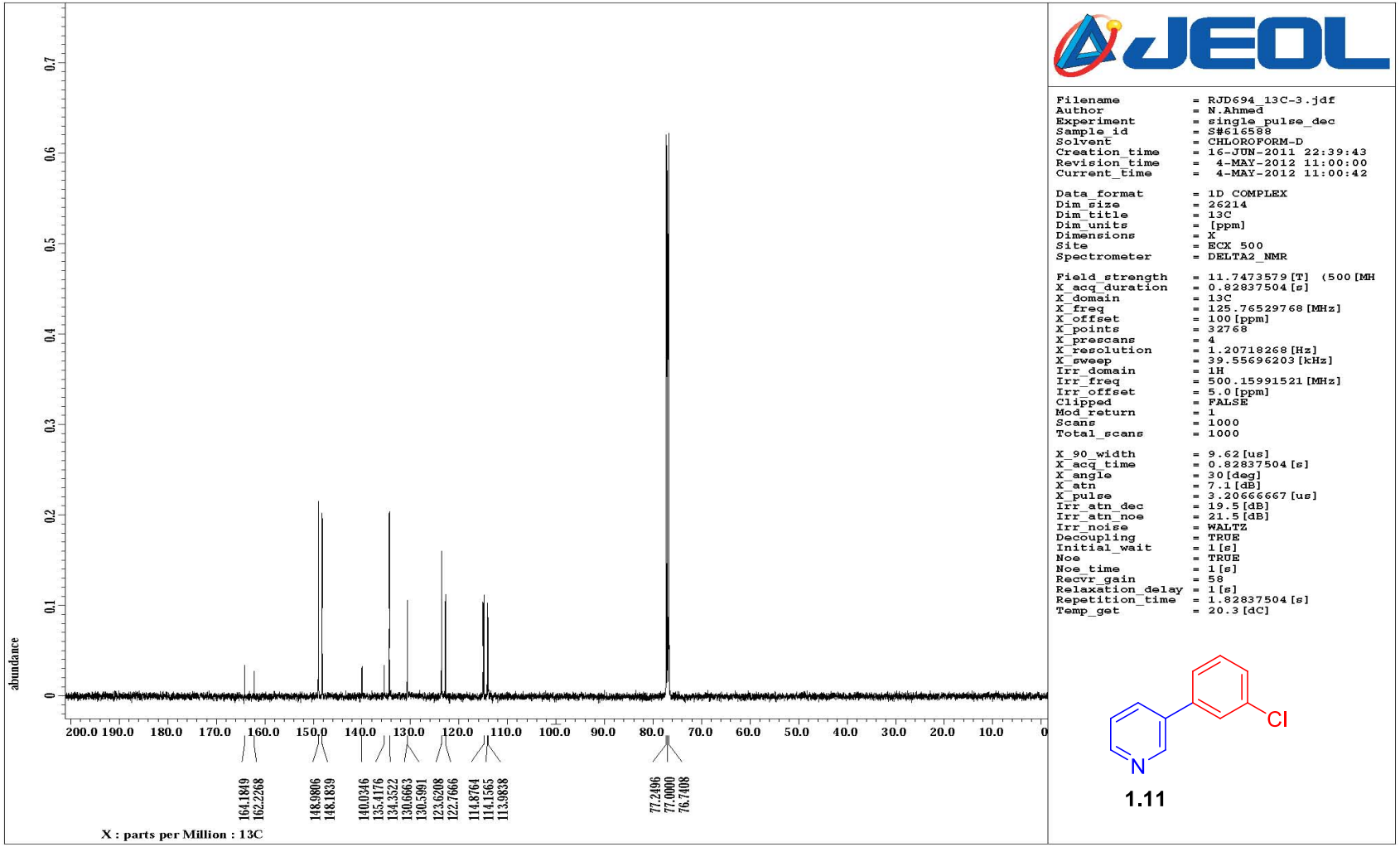
Contents



^{1}H NMR spectrum of 3-(3-chlorophenyl)pyridine (**1.11**)



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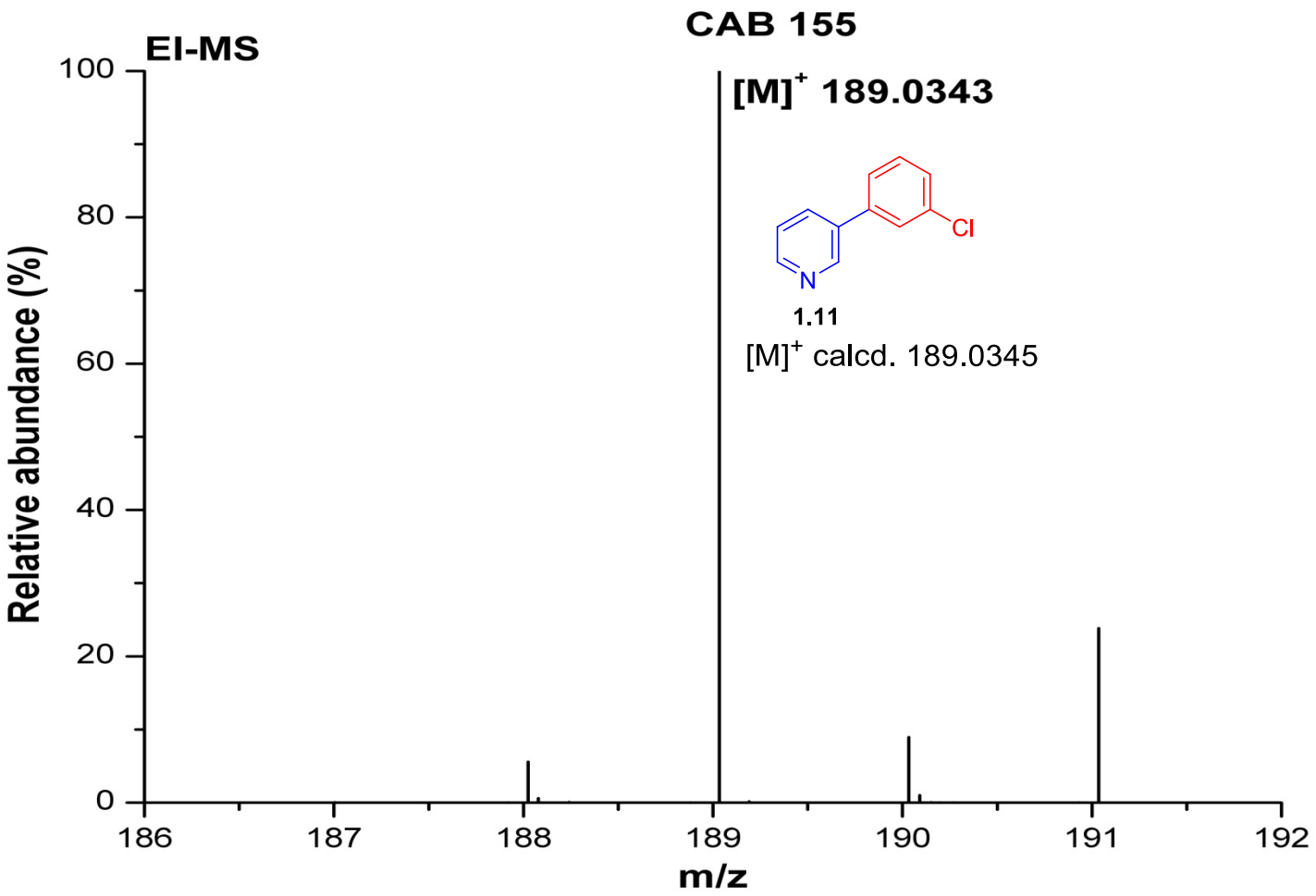
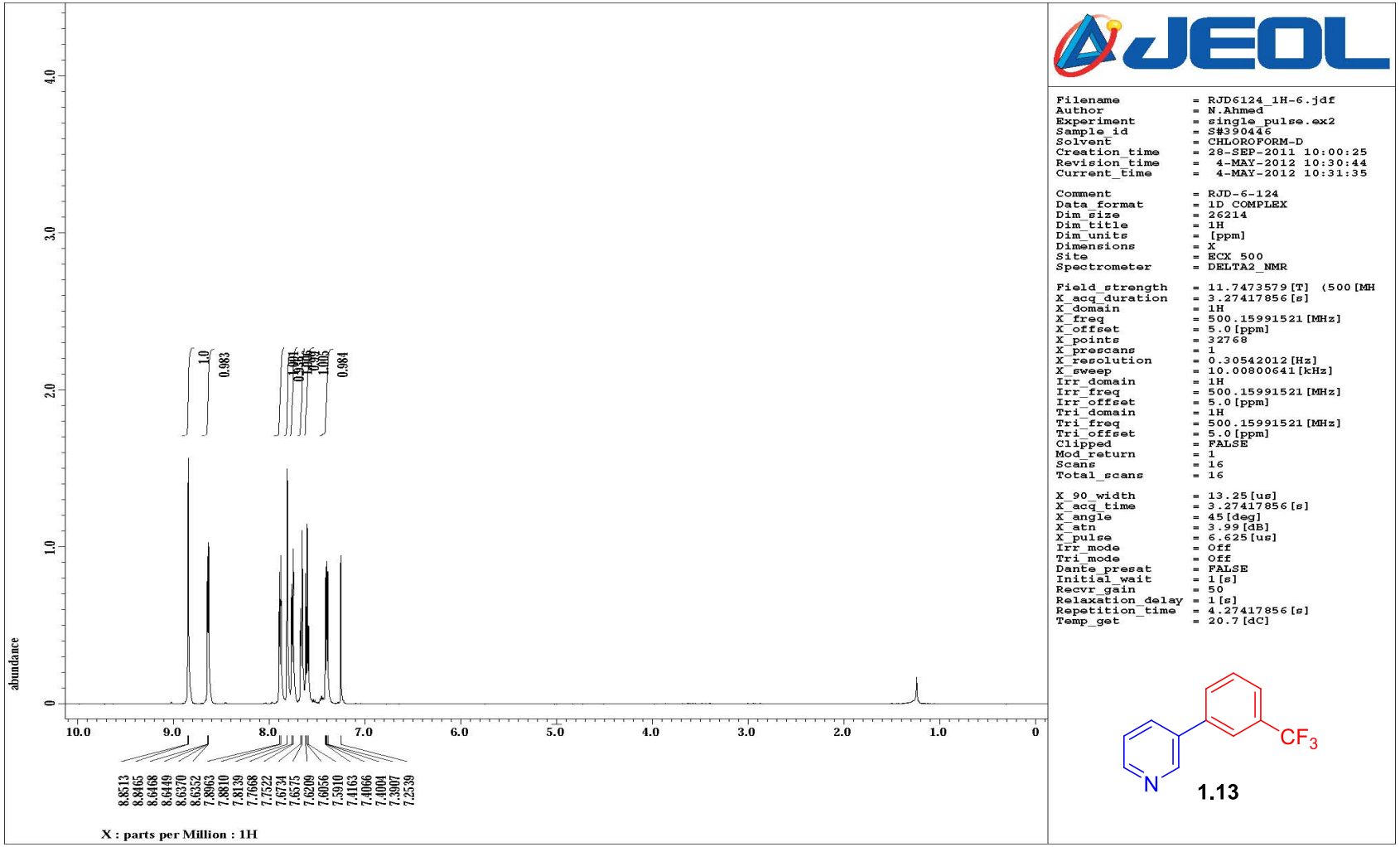
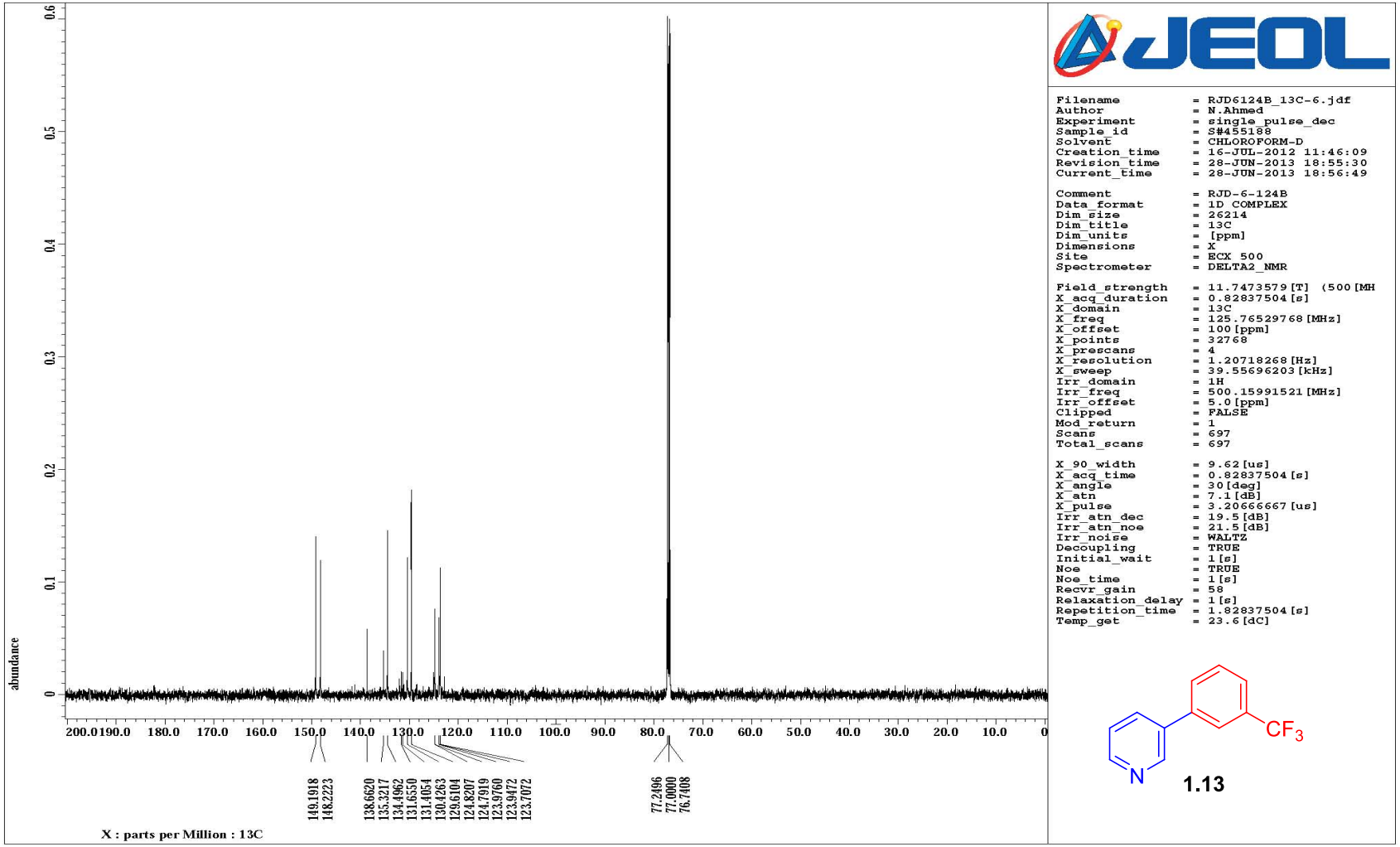


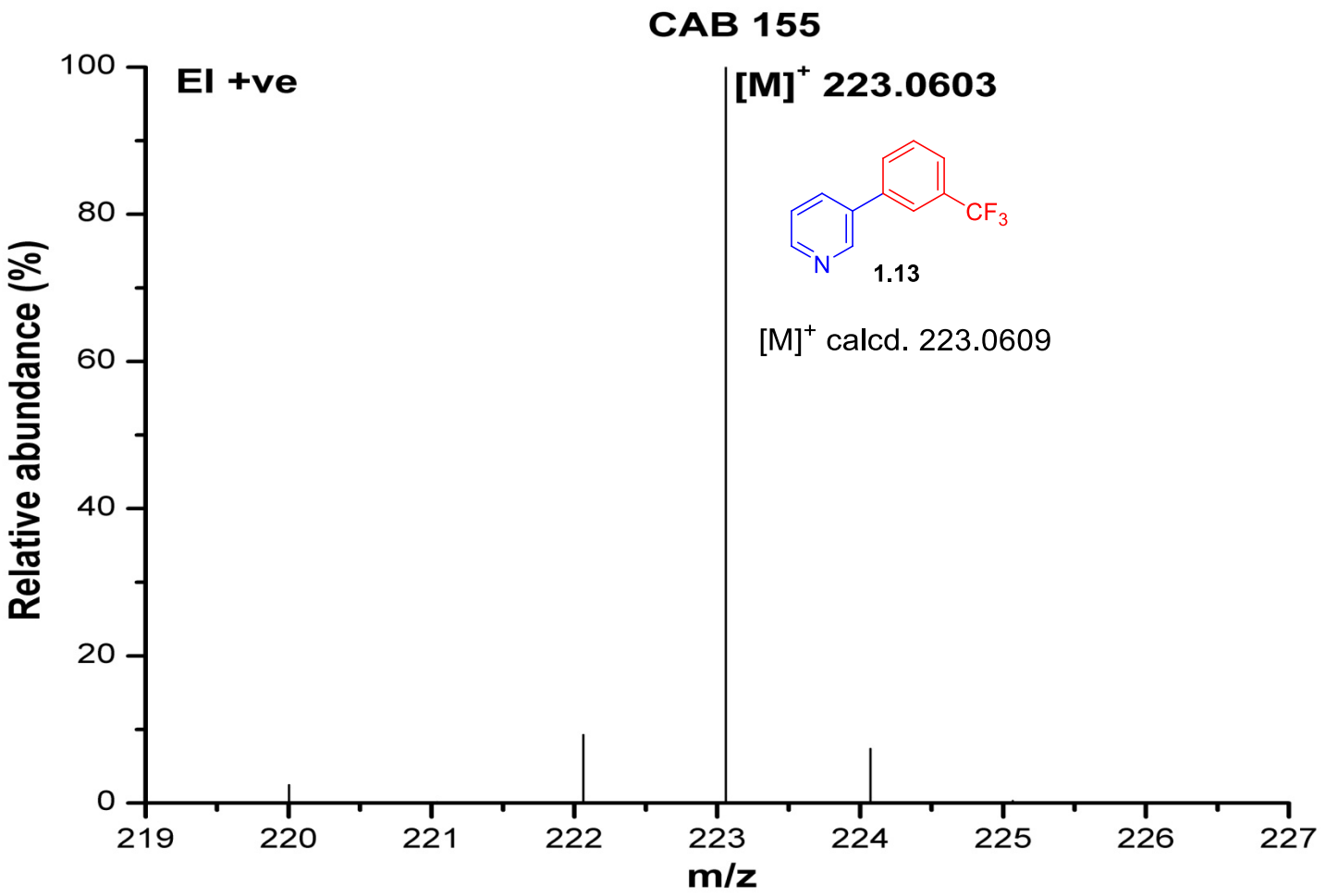
HRMS spectrum of 3-(3-chlorophenyl)pyridine (**1.11**)



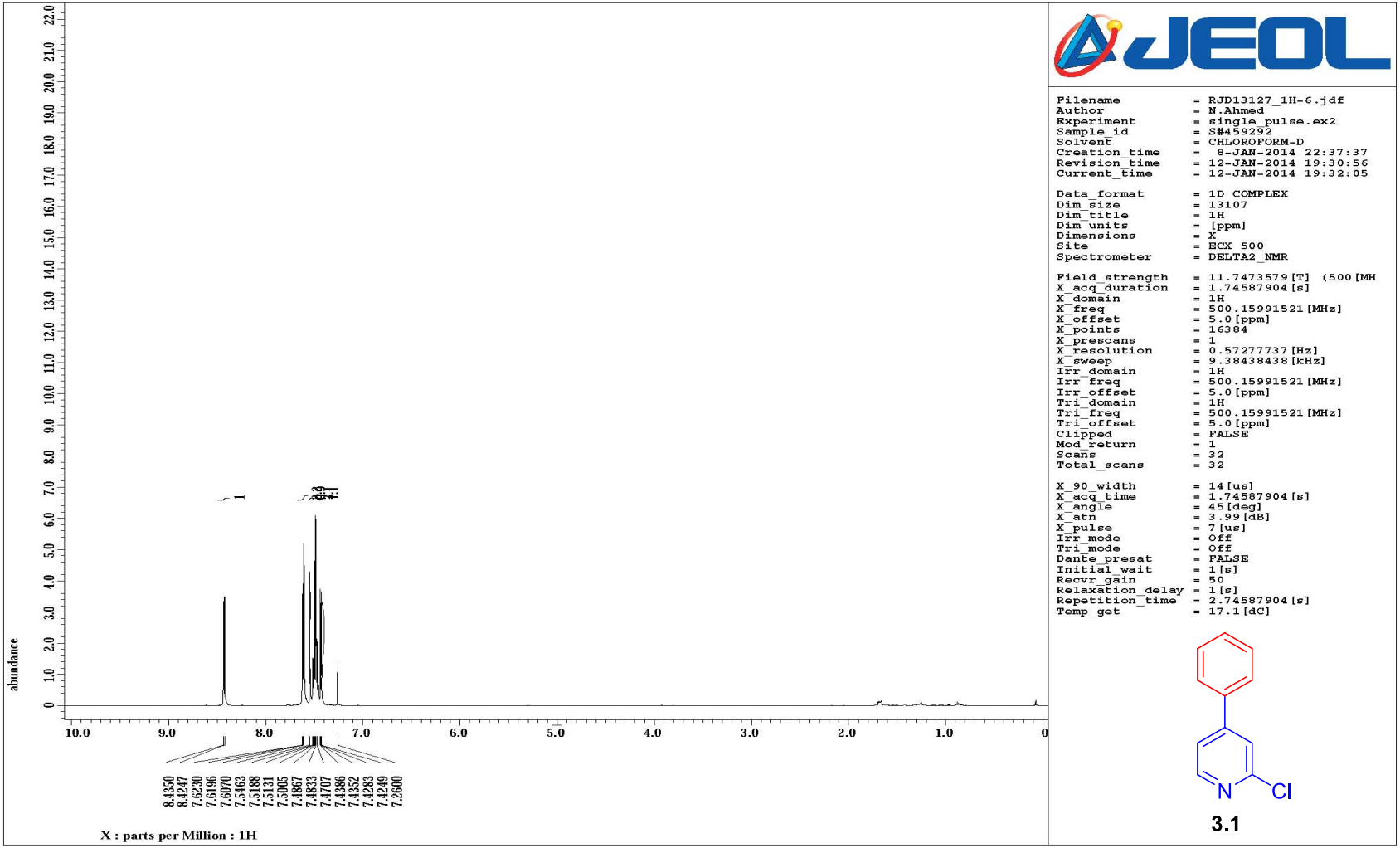
^{1}H NMR spectrum of 3-(3-trifluoromethylphenyl)pyridine (**1.13**)



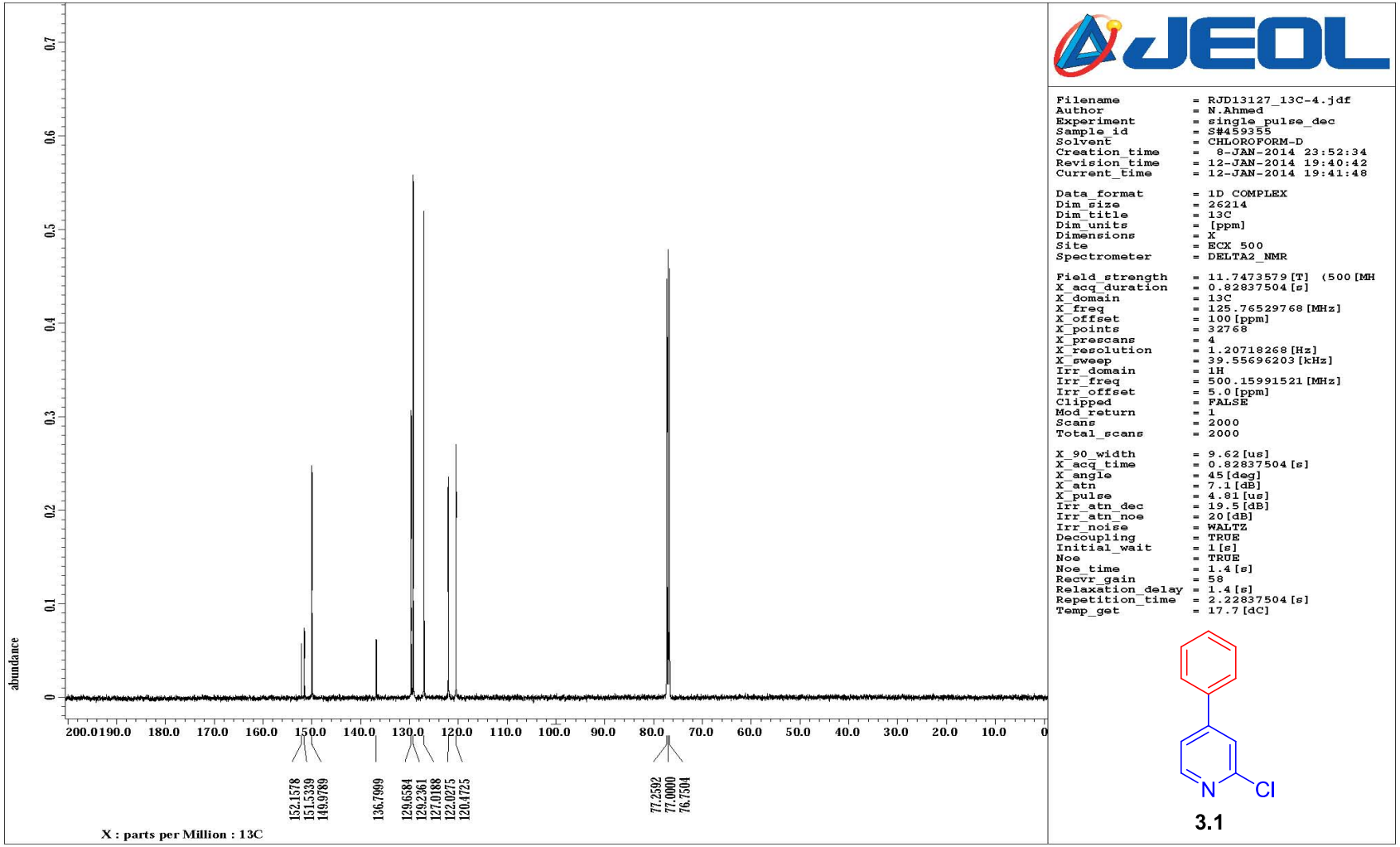
^{13}C NMR spectrum of 3-(3-trifluoromethylphenyl)pyridine (**1.13**)



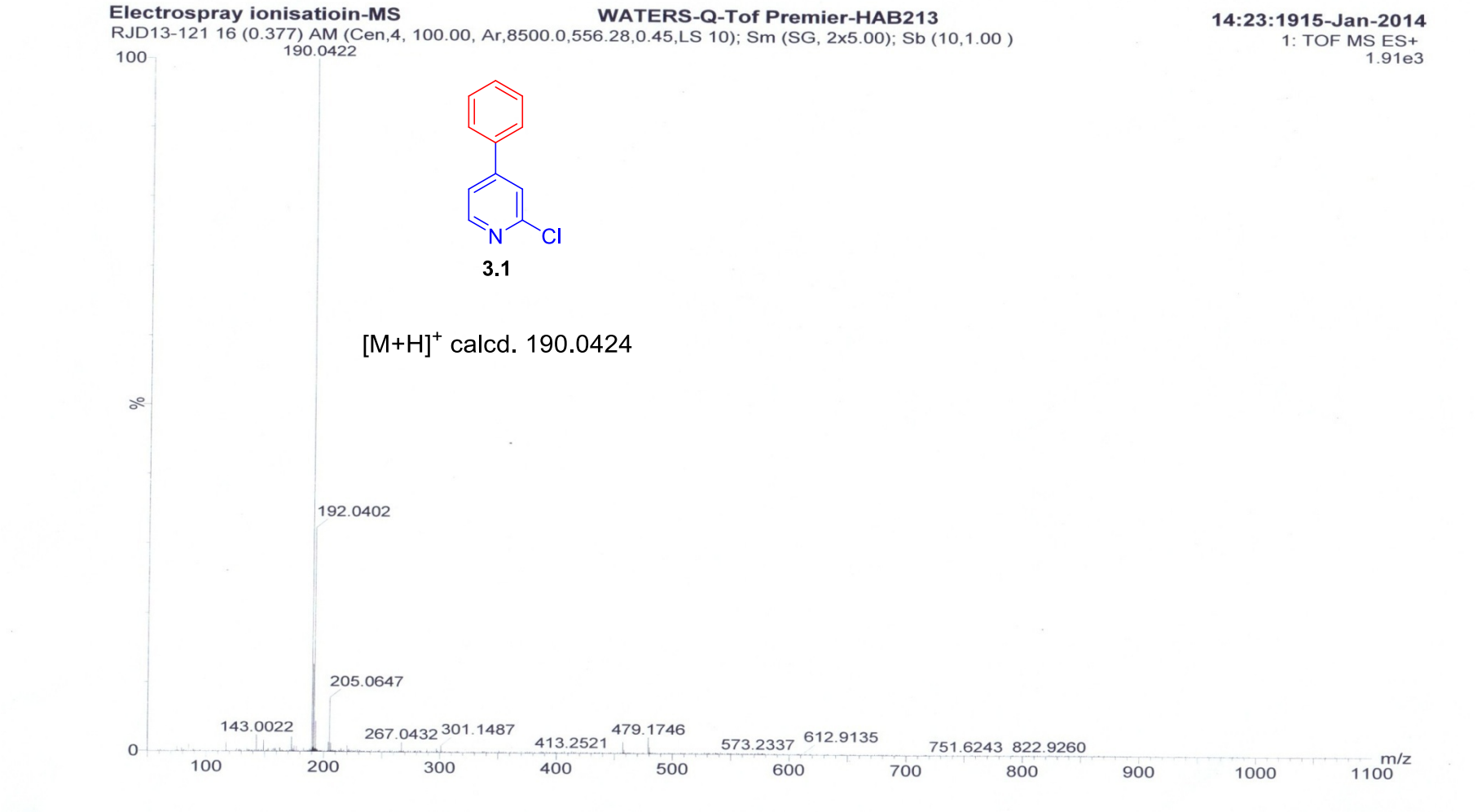
HRMS spectrum of 3-(3-trifluoromethylphenyl)pyridine (**1.13**)



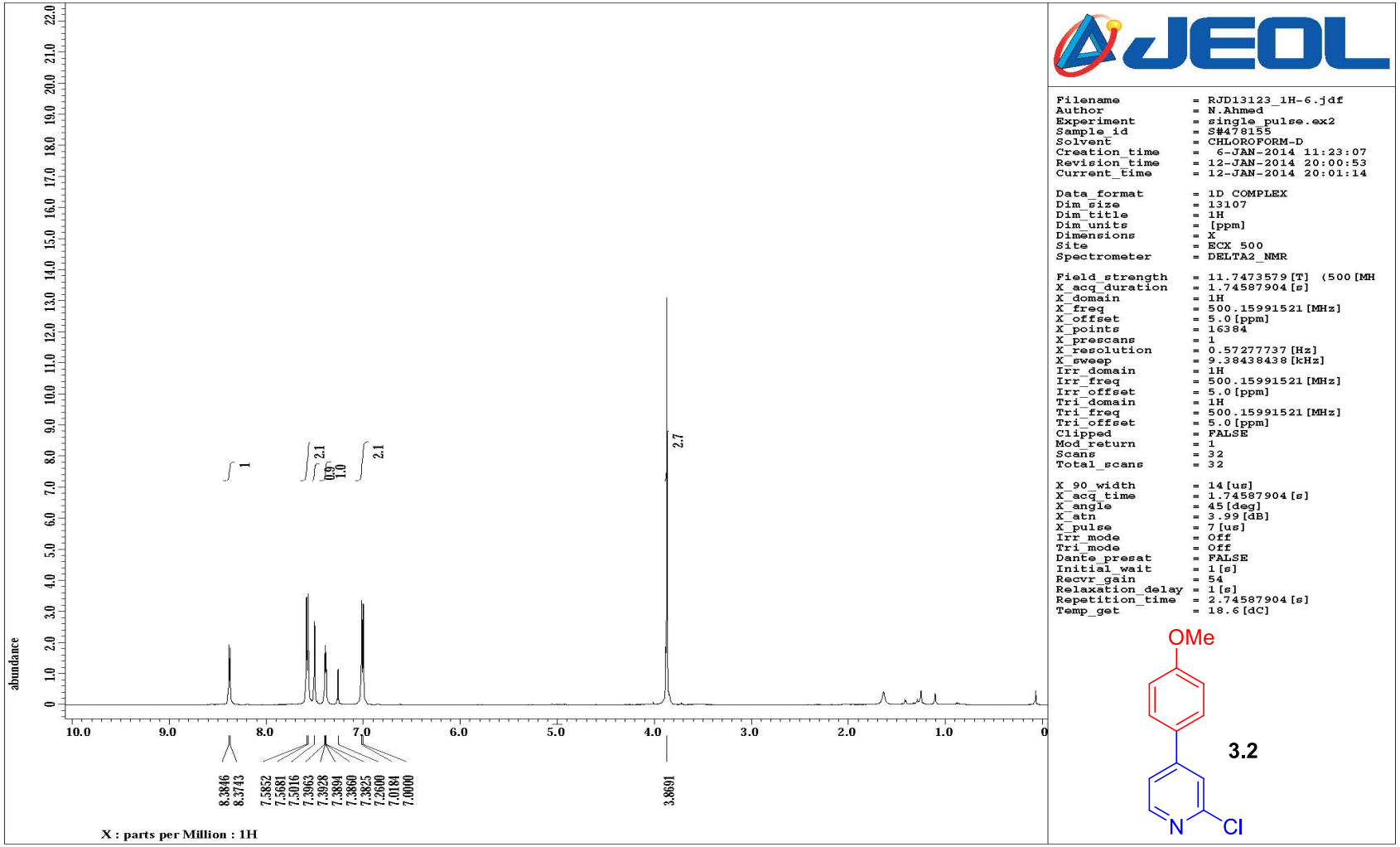
^{1}H NMR spectrum of 2-chloro-4-phenylpyridine (**3.1**)



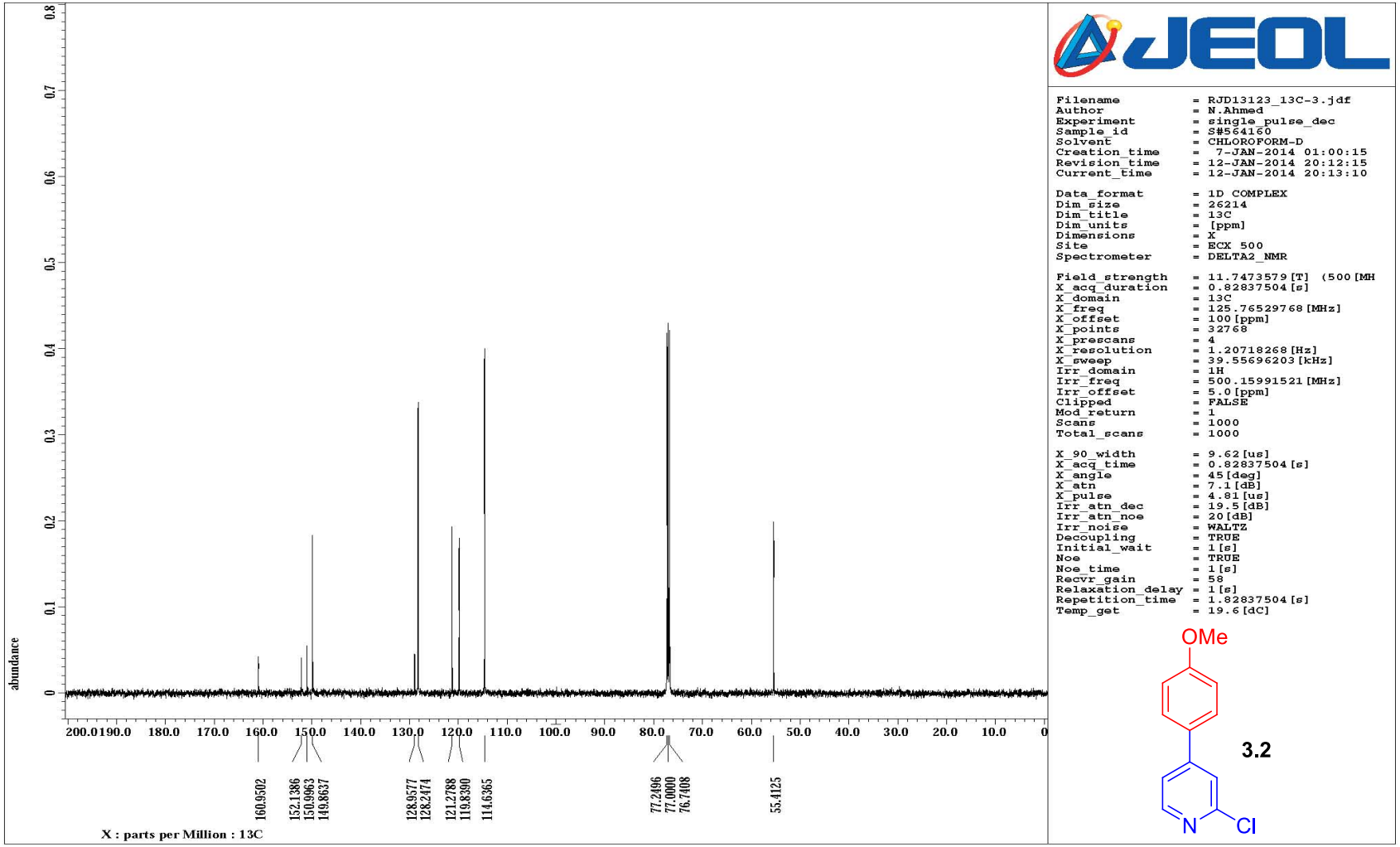
^{13}C NMR spectrum of 2-chloro-4-phenylpyridine (**3.1**)



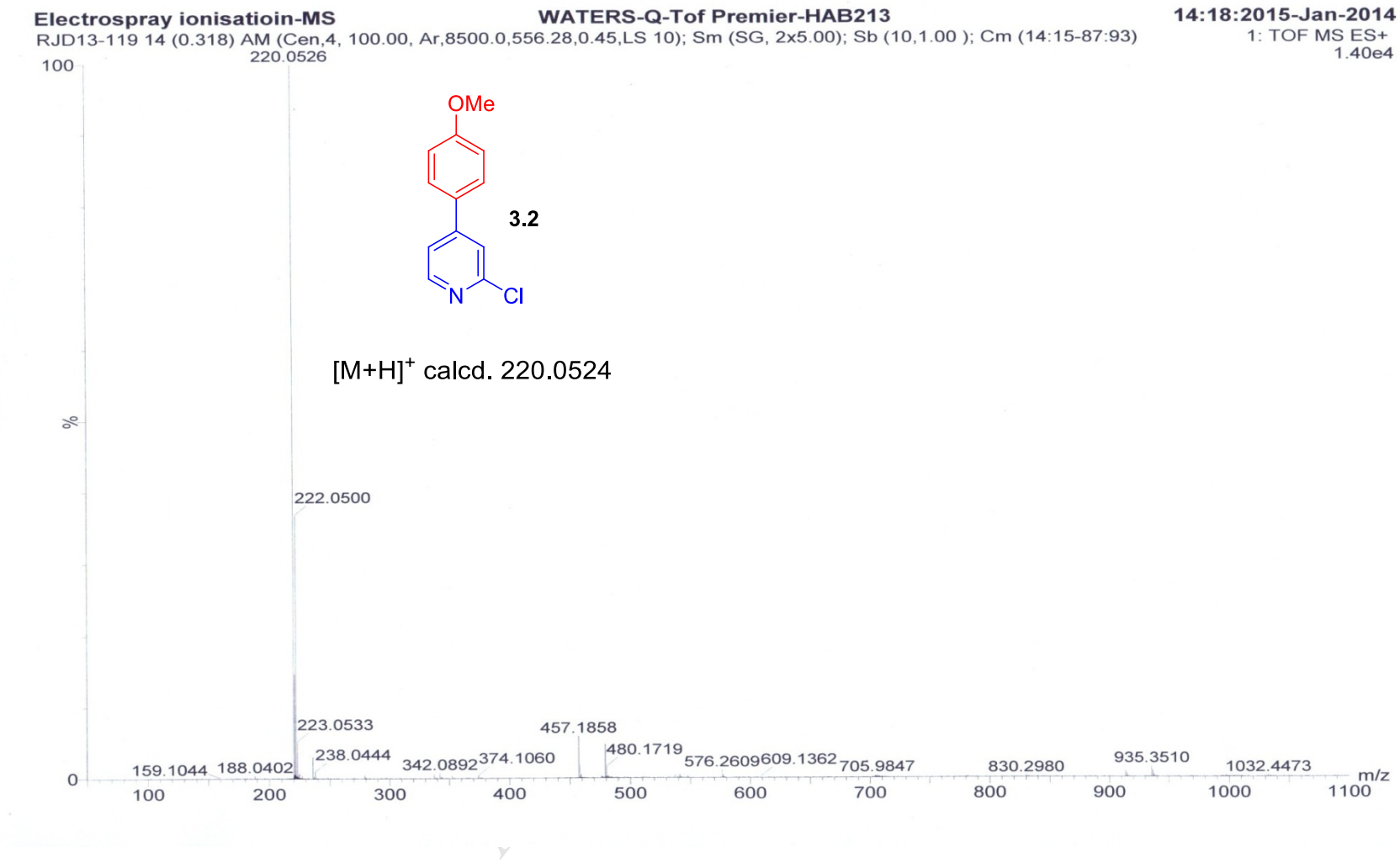
HRMS spectrum of 2-chloro-4-phenylpyridine (**3.1**)



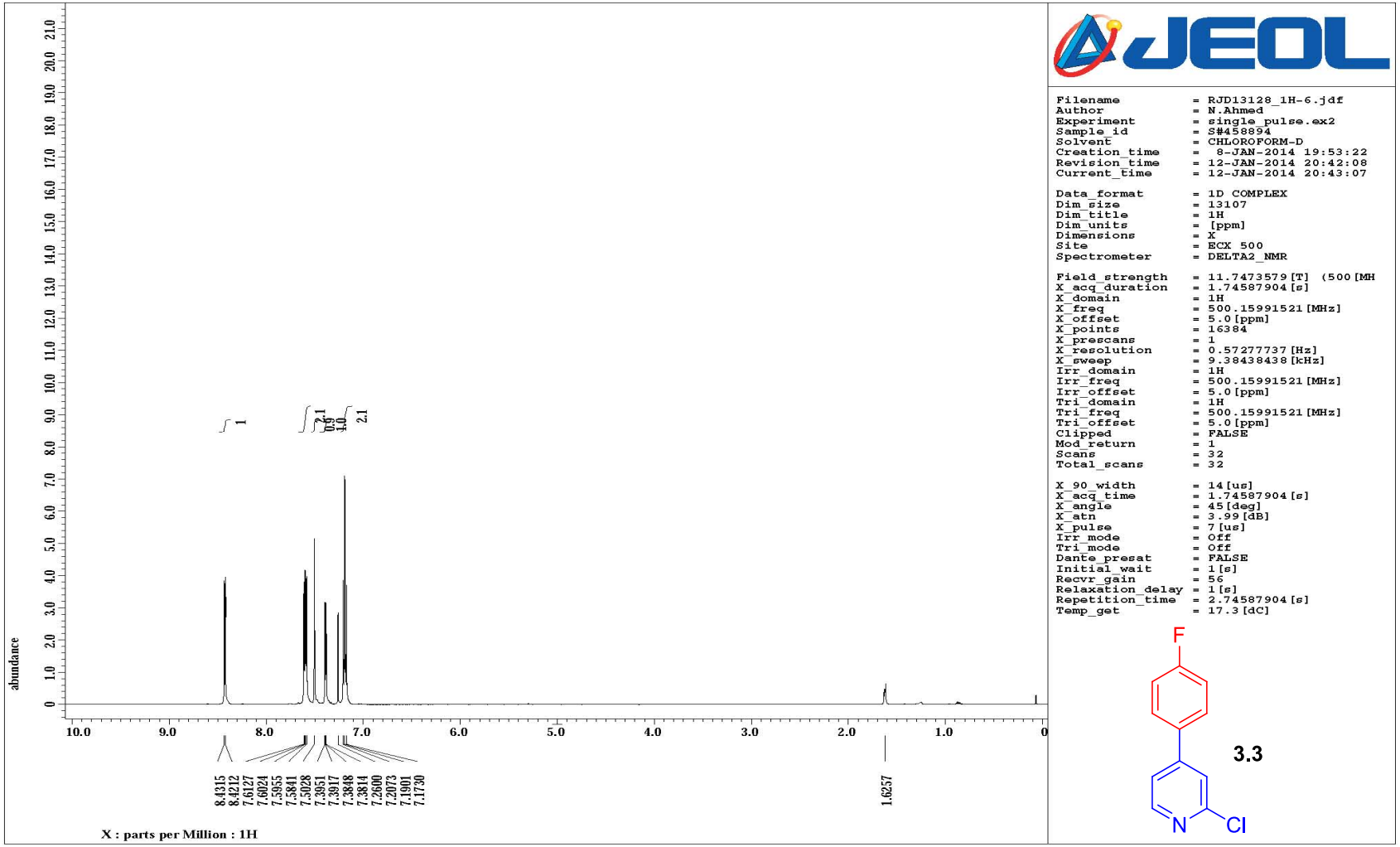
^{1}H NMR spectrum of 2-chloro-4-(4-methoxyphenyl)pyridine (**3.2**)



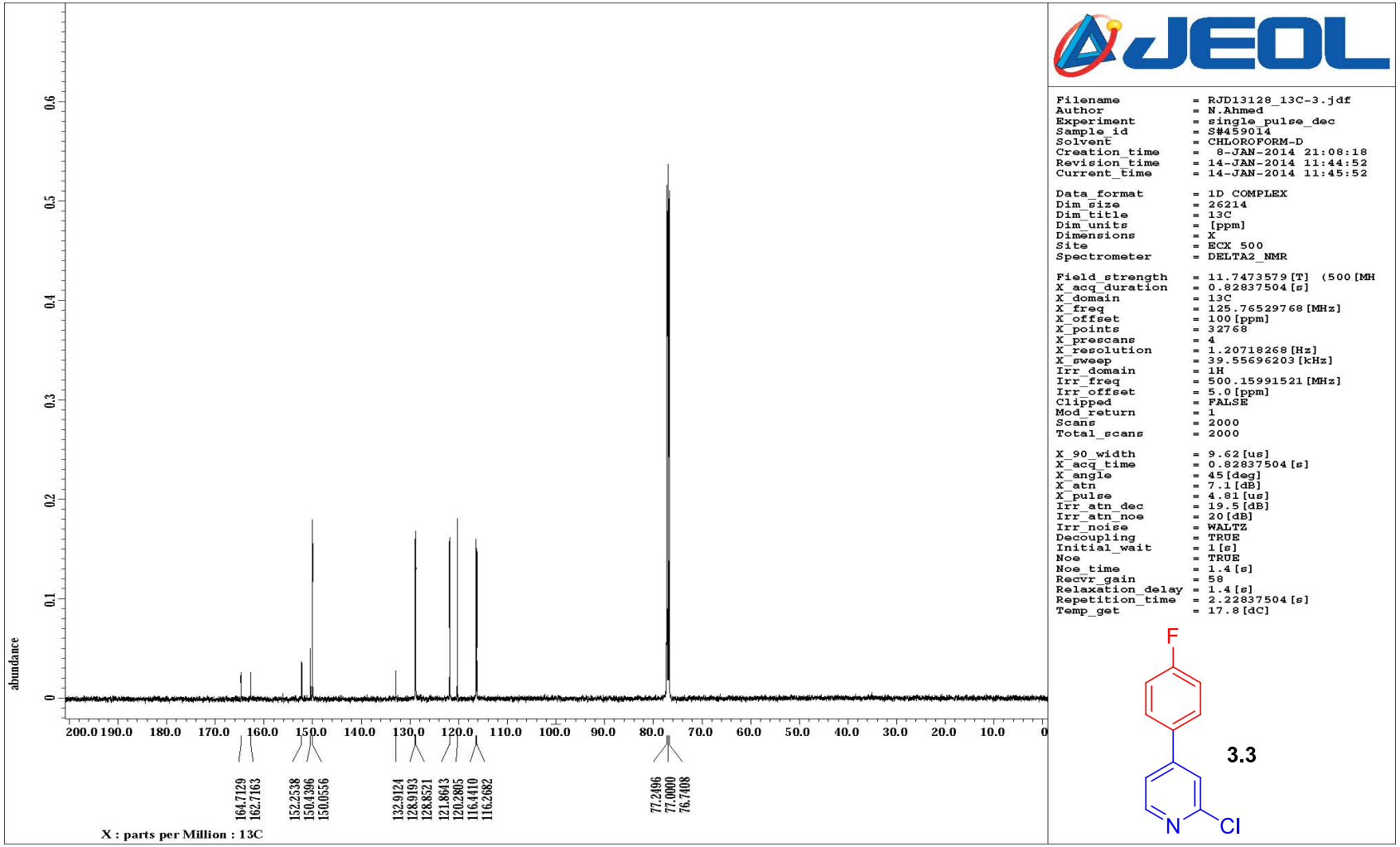
^{13}C NMR spectrum of 2-chloro-4-(4-methoxyphenyl)pyridine (**3.2**)



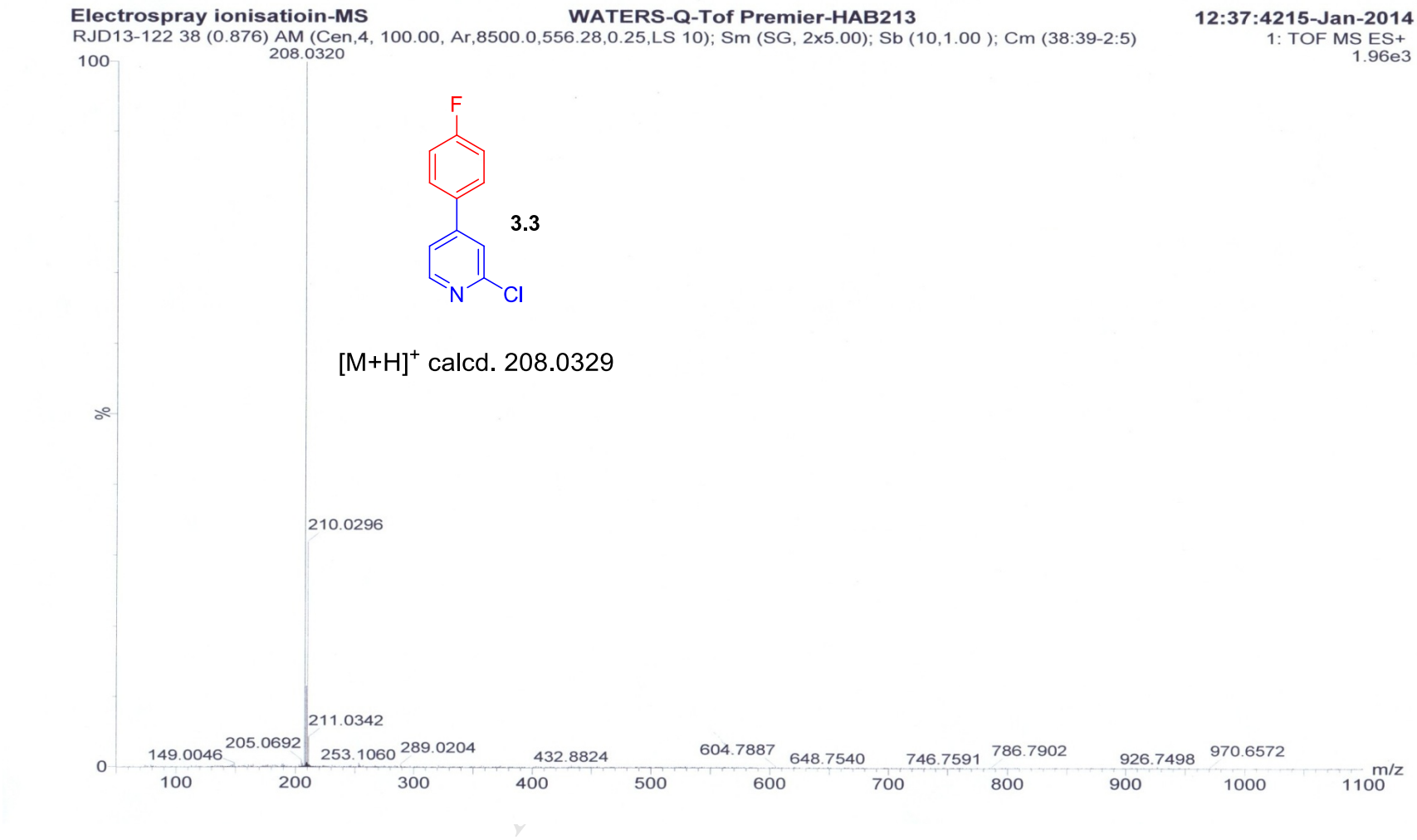
HRMS spectrum of 2-chloro-4-(4-methoxyphenyl)pyridine (**3.2**)



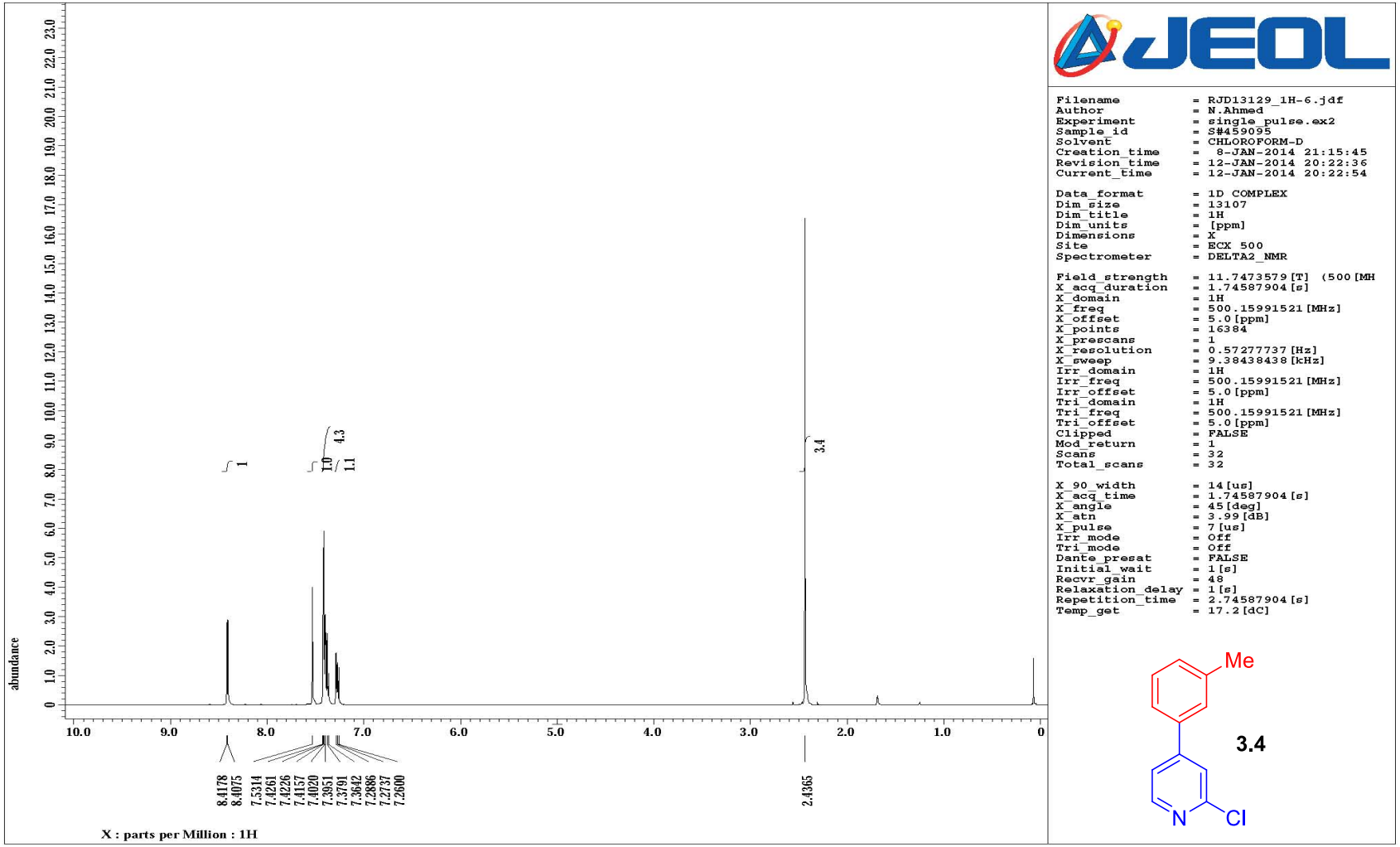
^{1}H NMR spectrum of 2-chloro-4-(4-fluorophenyl)pyridine (**3.3**)



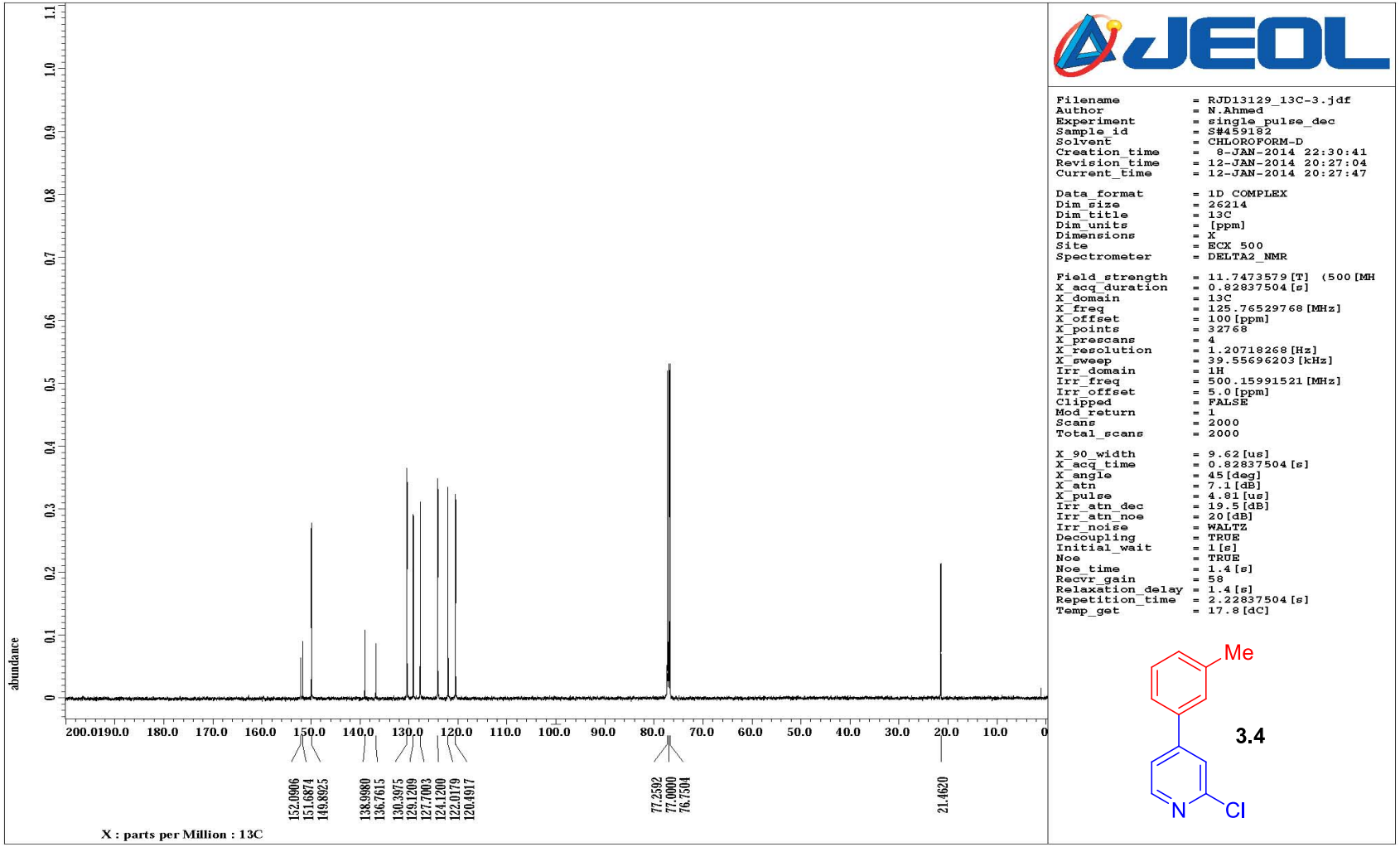
^{13}C NMR spectrum of 2-chloro-4-(4-fluorophenyl)pyridine (**3.3**)



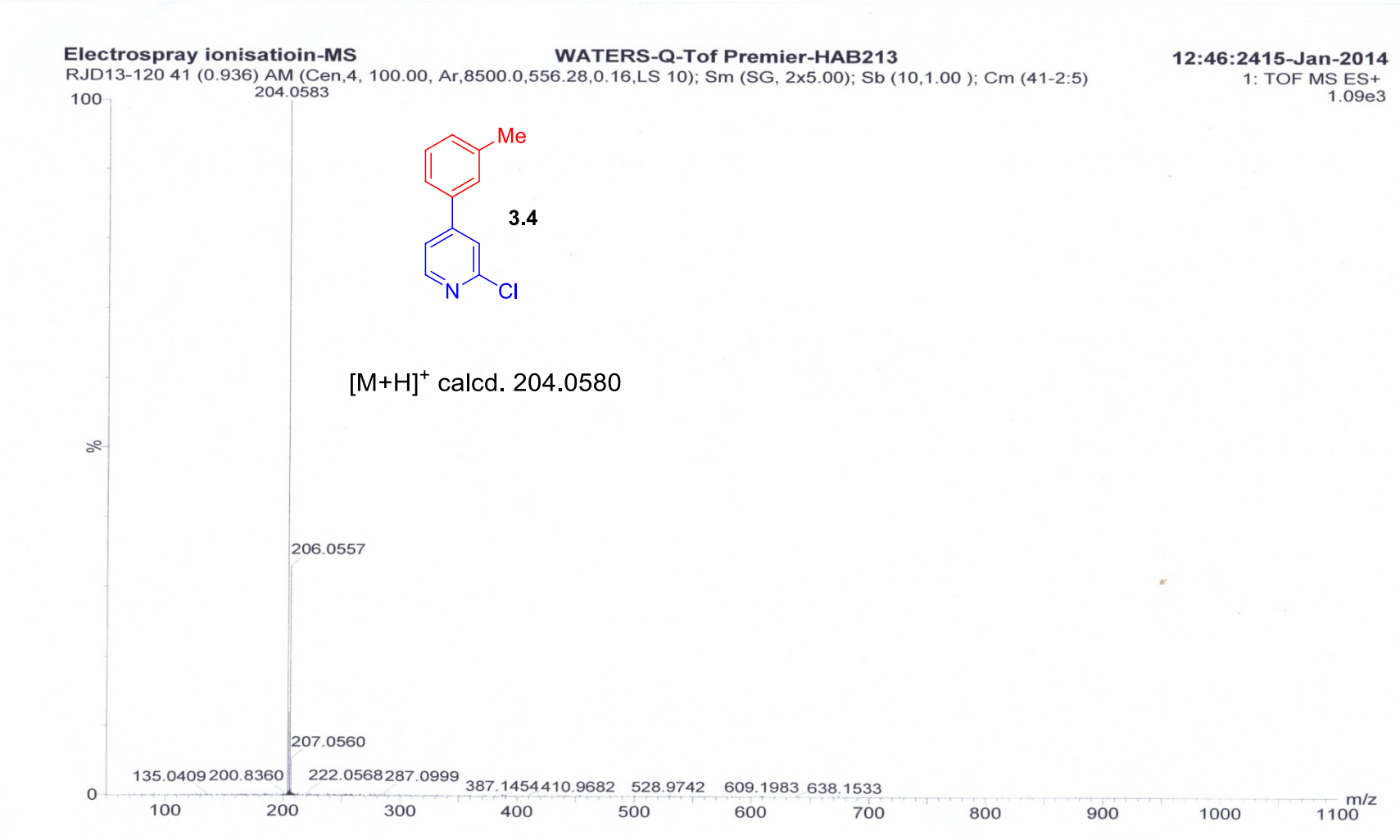
HRMS spectrum of 2-chloro-4-(4-fluorophenyl)pyridine (**3.3**)



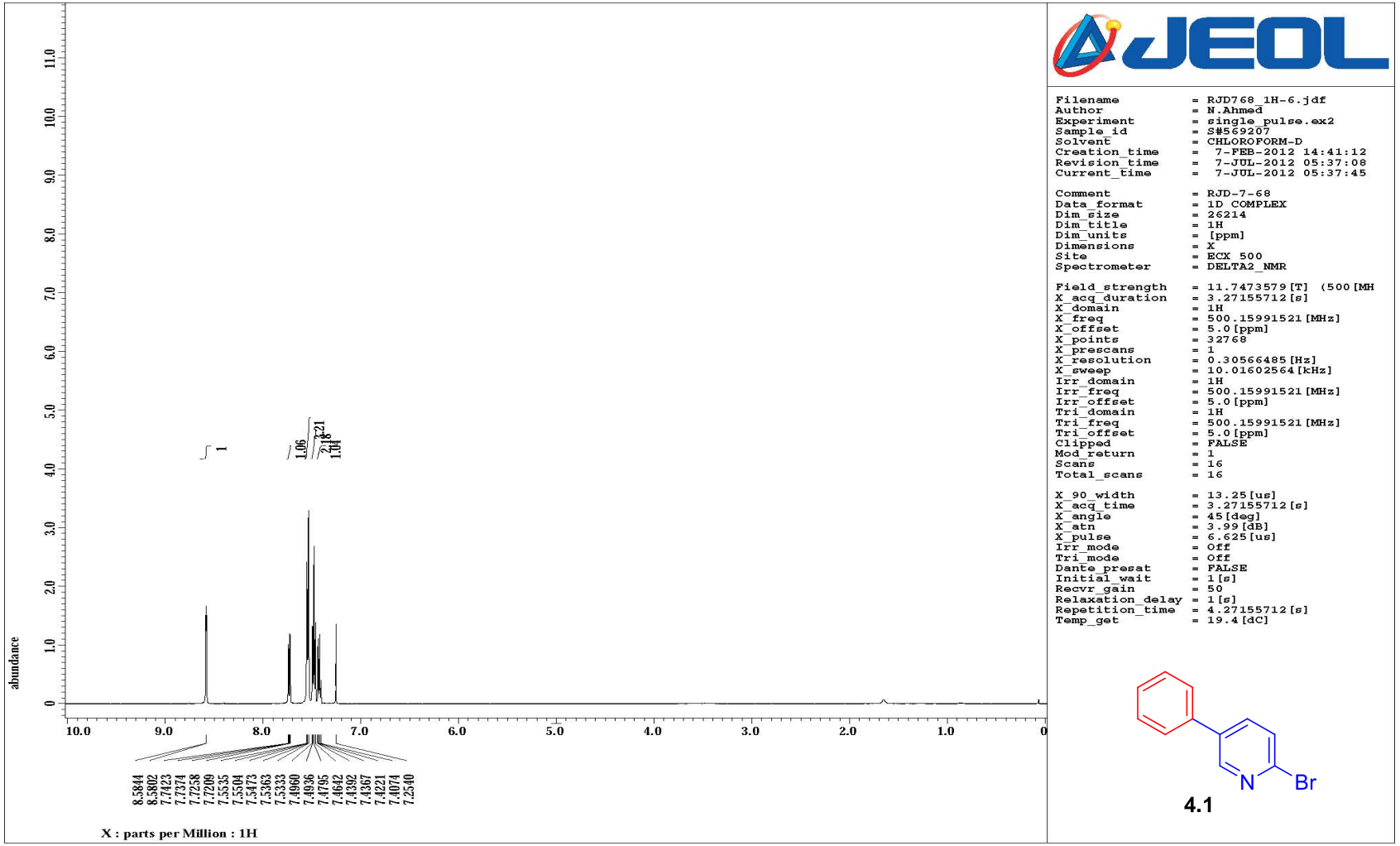
^{1}H NMR spectrum of 2-chloro-4-(*m*-tolyl)pyridine (**3.4**)



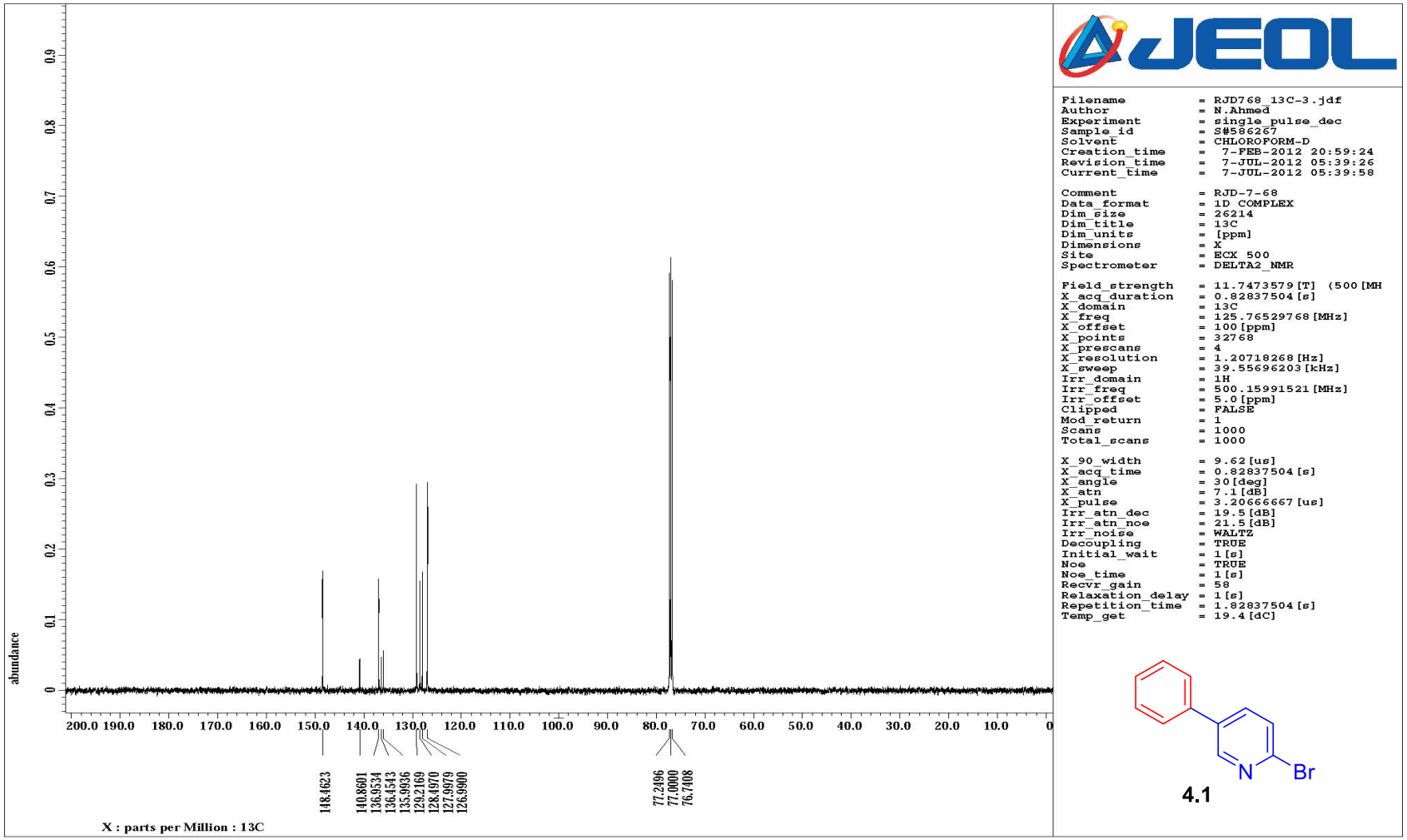
^{13}C NMR spectrum of 2-chloro-4-(*m*-tolyl)pyridine (**3.4**)



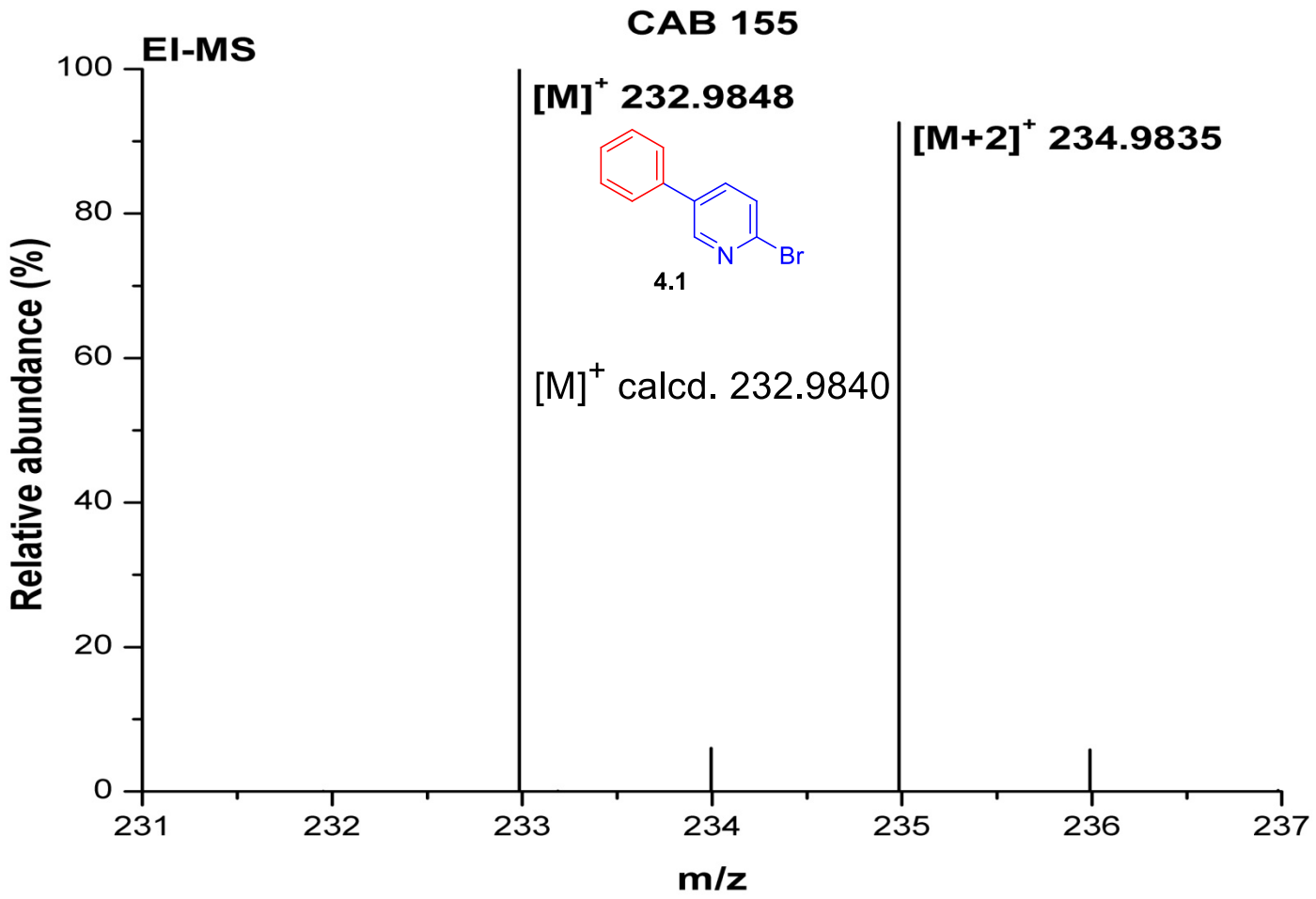
HRMS spectrum of 2-chloro-4-(*m*-tolyl)pyridine (**3.4**)



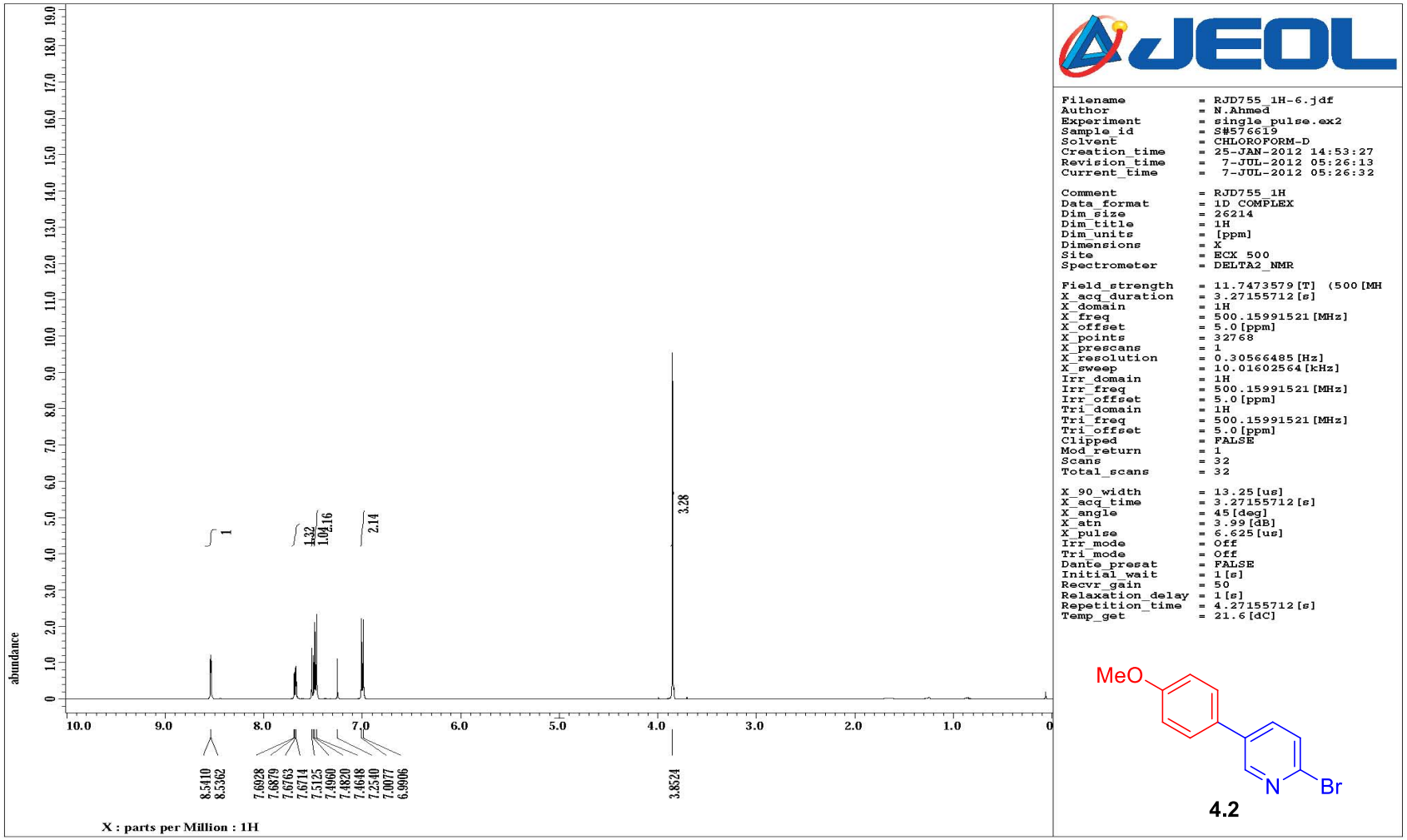
^{1}H NMR spectrum of 2-bromo-5-phenylpyridine (**4.1**)



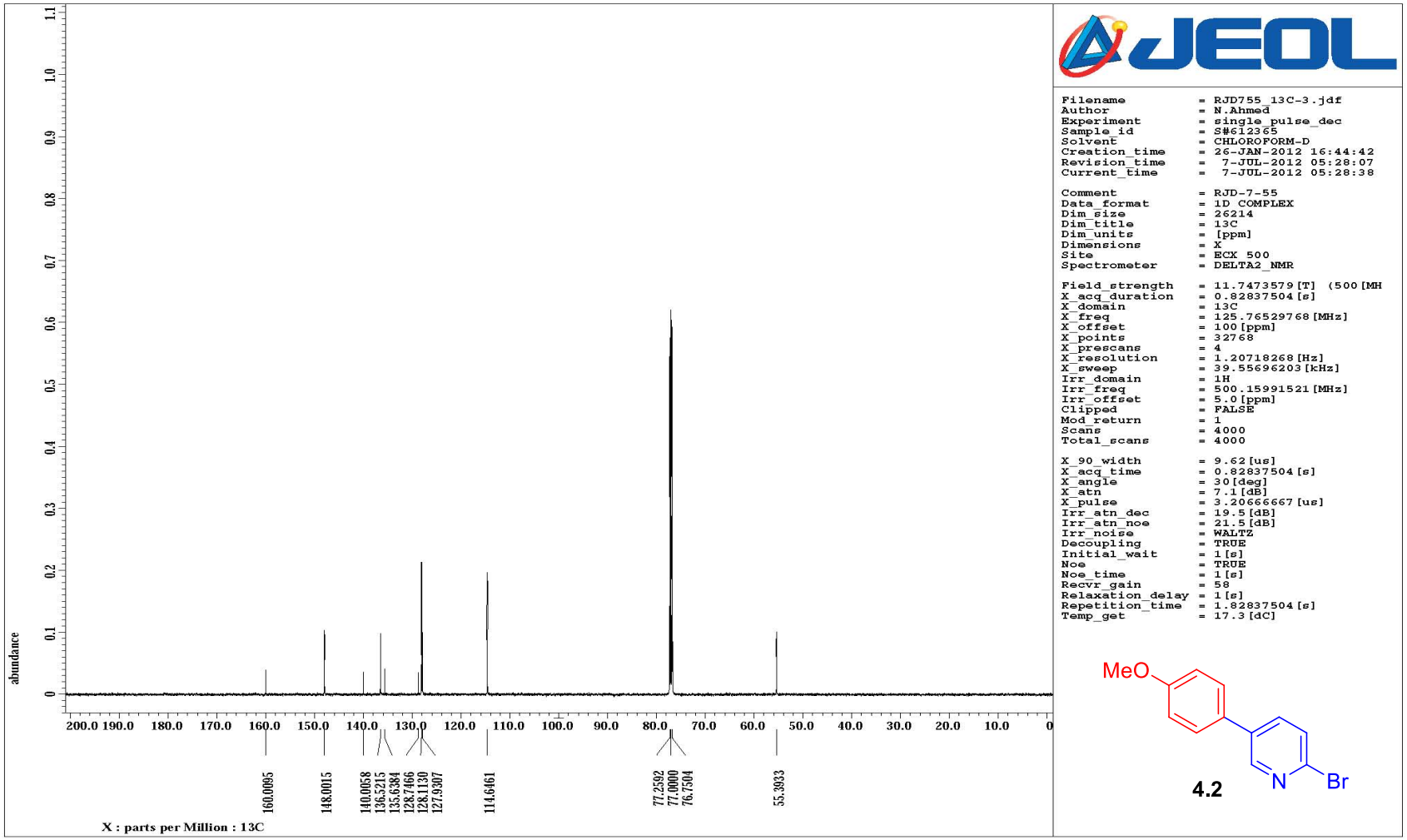
^{13}C NMR spectrum of 2-bromo-5-phenylpyridine (**4.1**)



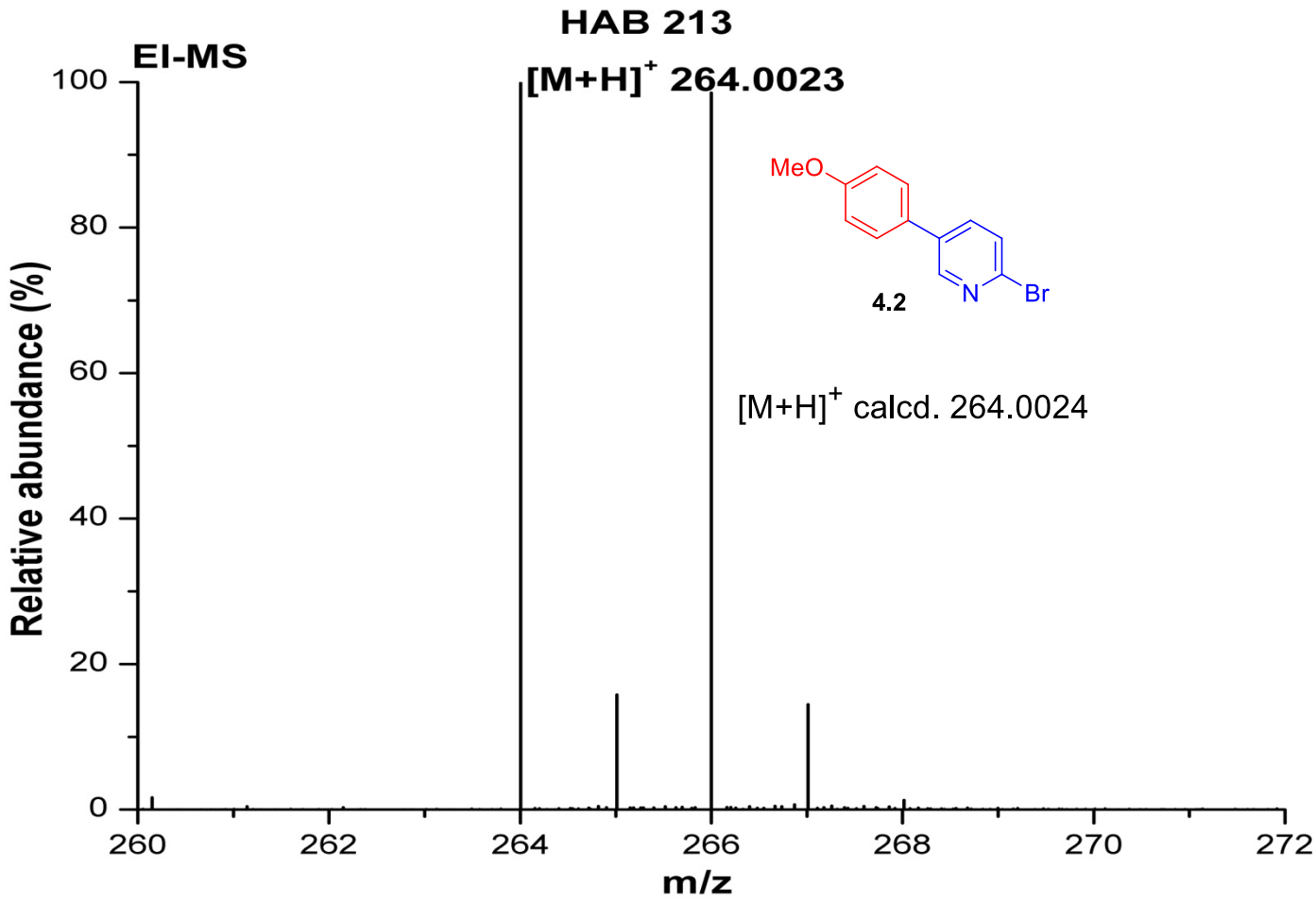
HRMS spectrum of 2-bromo-5-phenylpyridine (**4.1**)



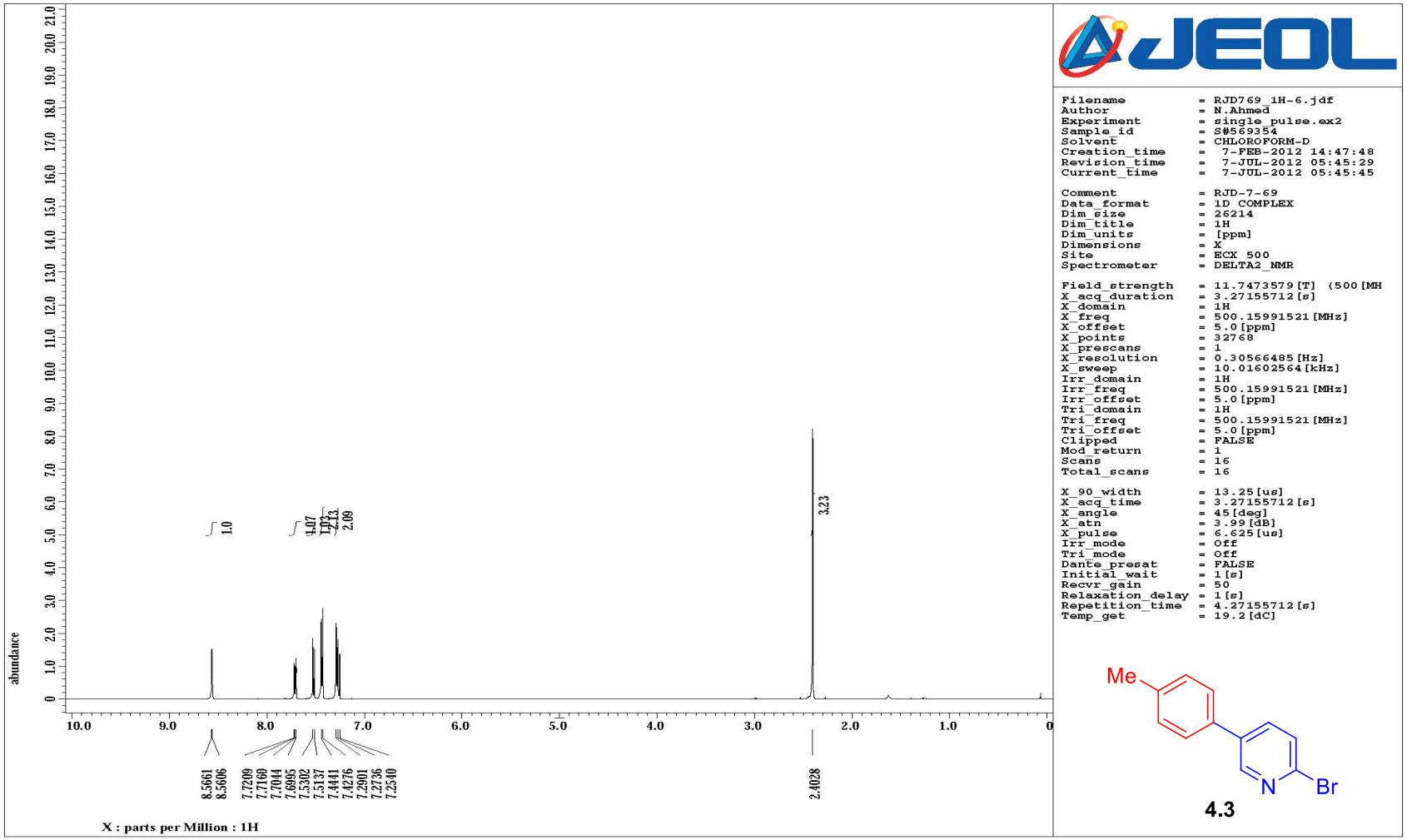
^{1}H NMR spectrum of 2-bromo-5-(4-methoxyphenyl)pyridine (**4.2**)



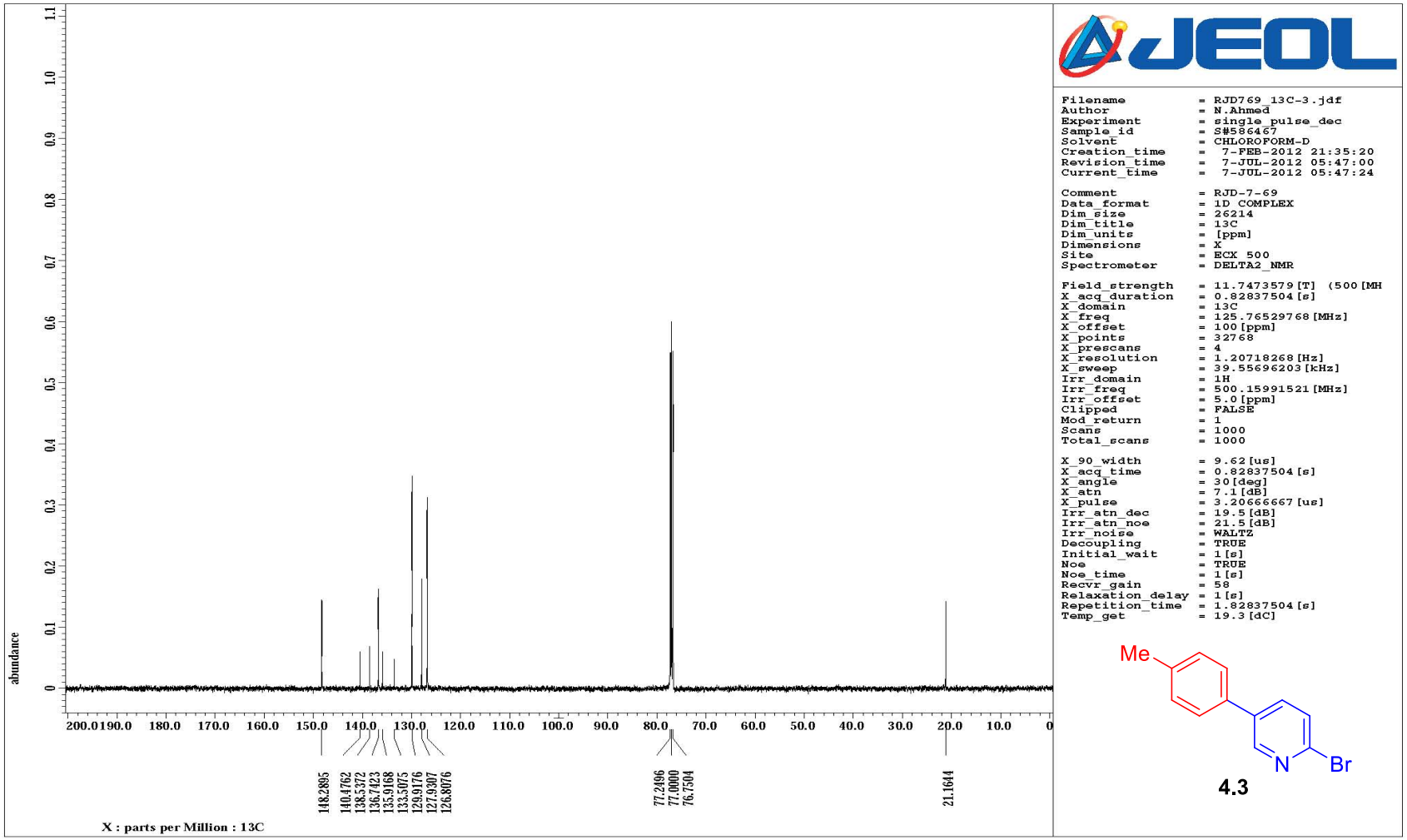
^{13}H NMR spectrum of 2-bromo-5-(4-methoxyphenyl)pyridine (**4.2**)



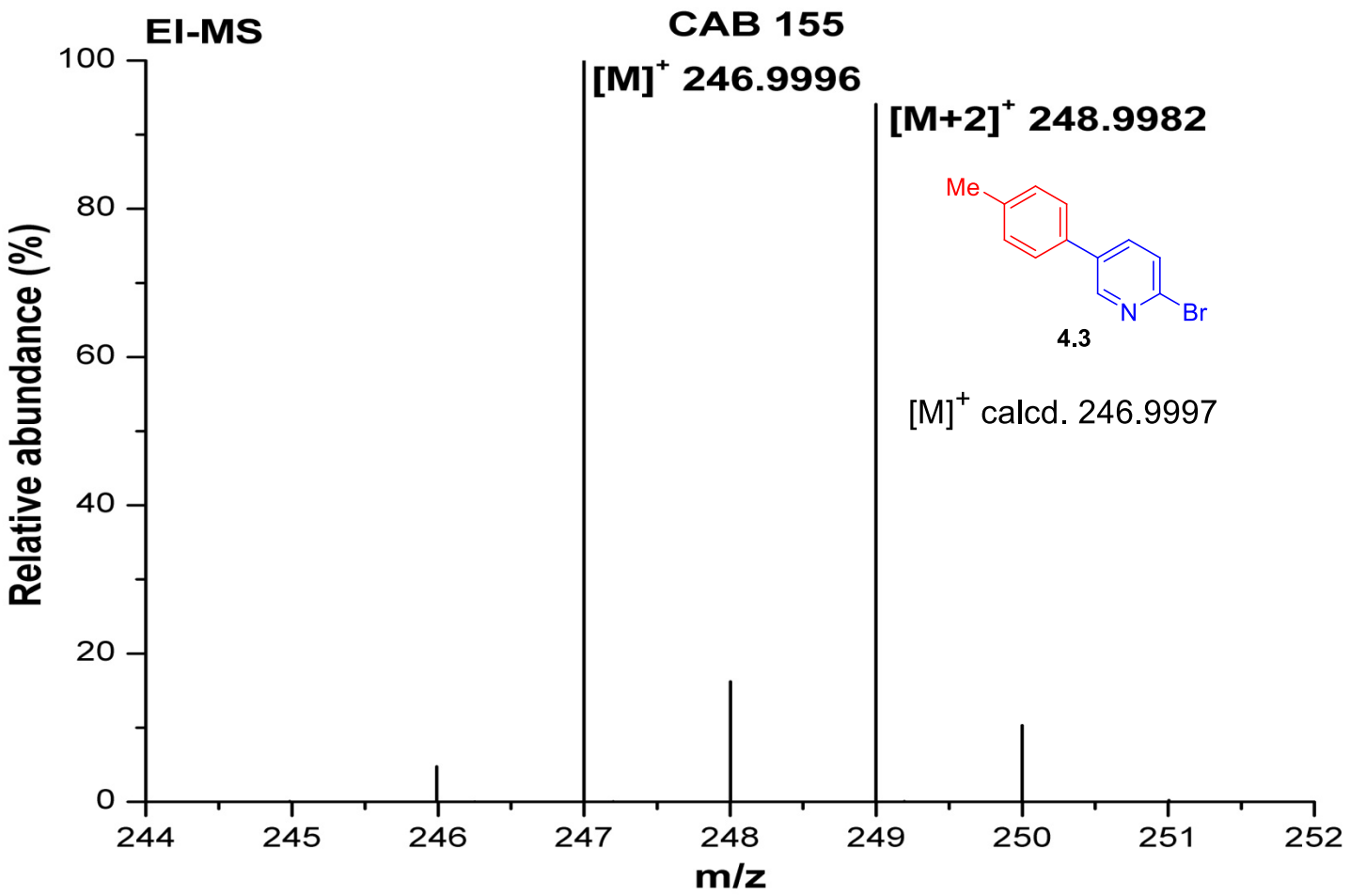
HRMS spectrum of 2-bromo-5-(4-methoxyphenyl)pyridine (**4.2**)



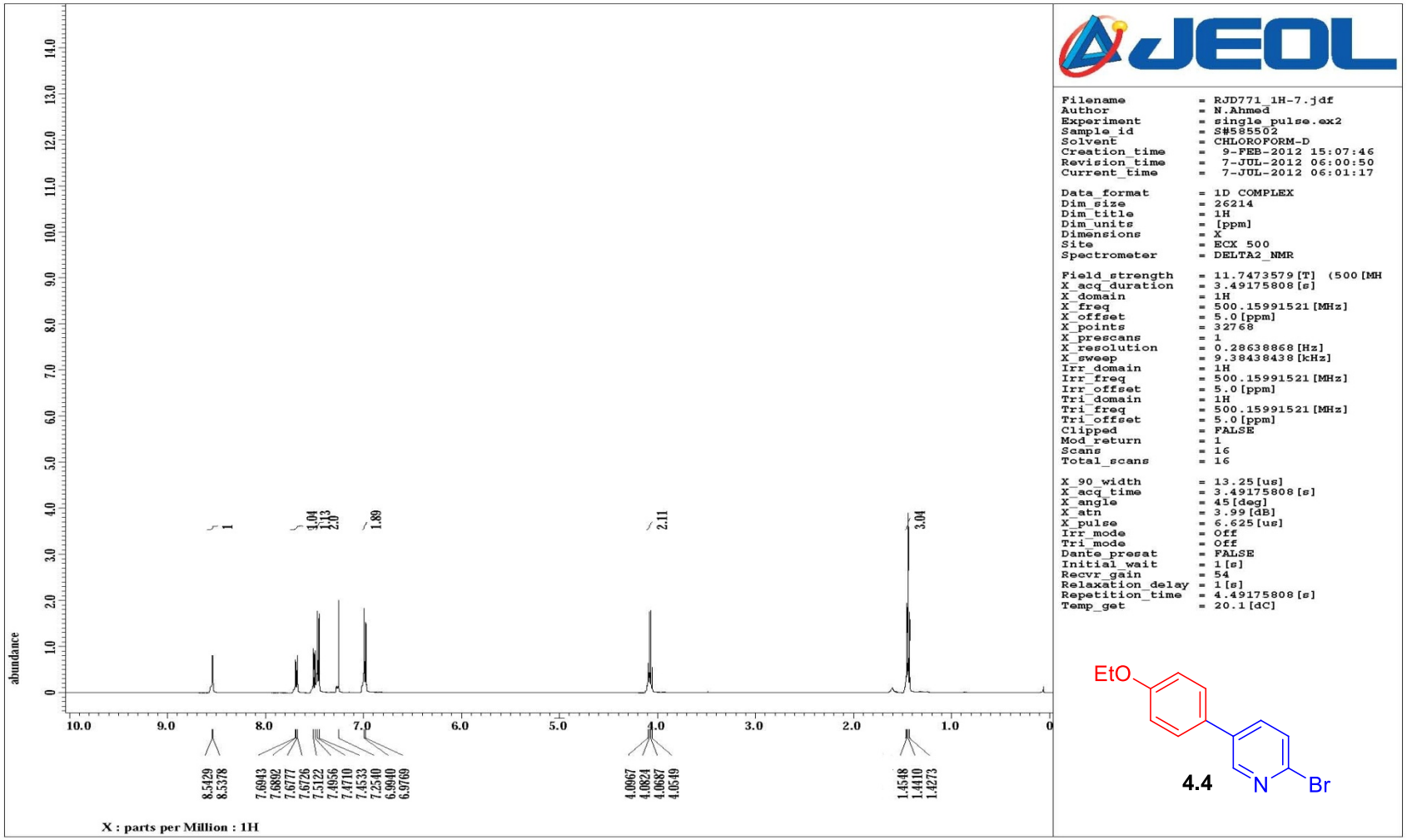
^{1}H NMR spectrum of 2-bromo-5-(4-methylphenyl)pyridine (**4.3**)



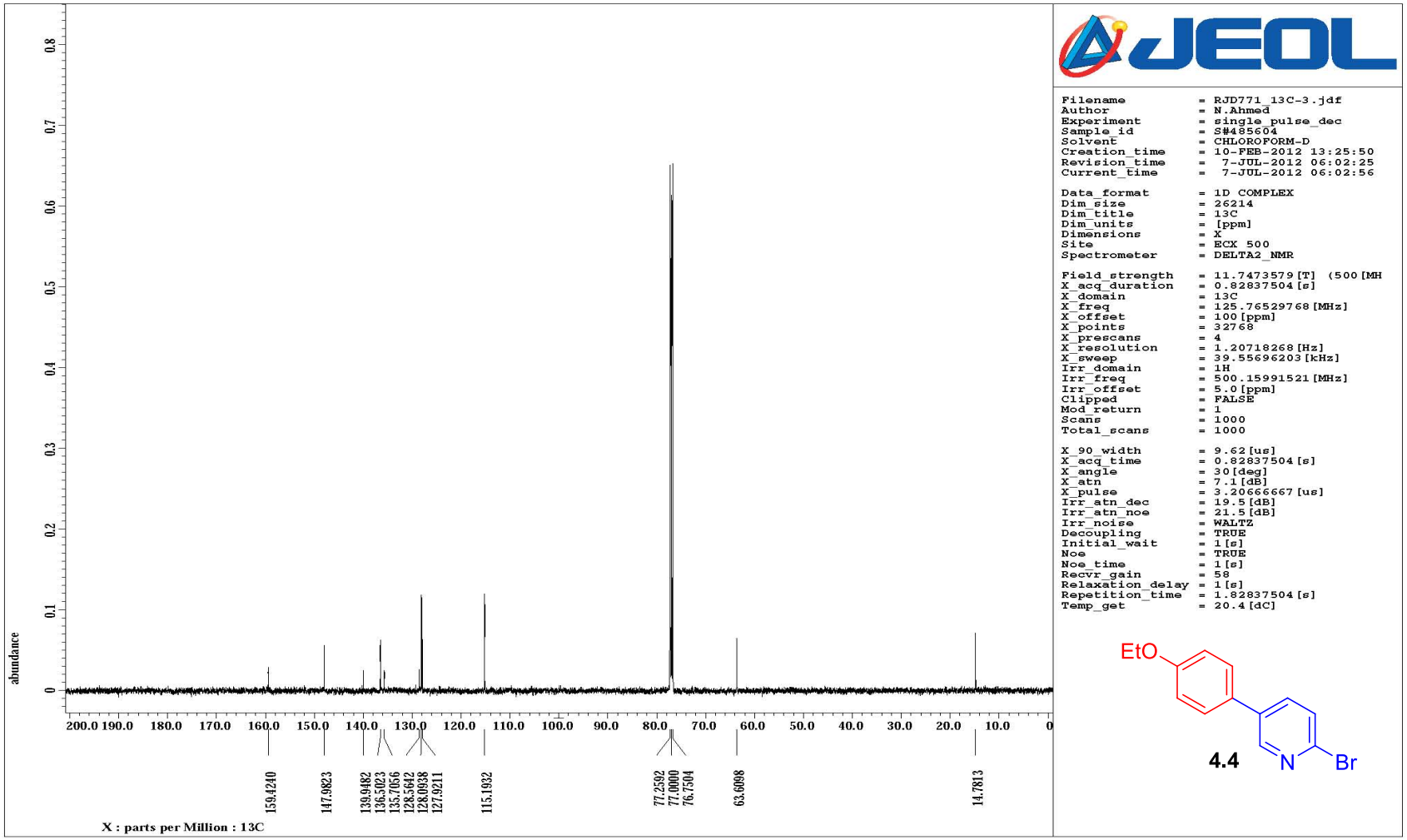
^{13}C NMR spectrum of 2-bromo-5-(4-methylphenyl)pyridine (**4.3**)



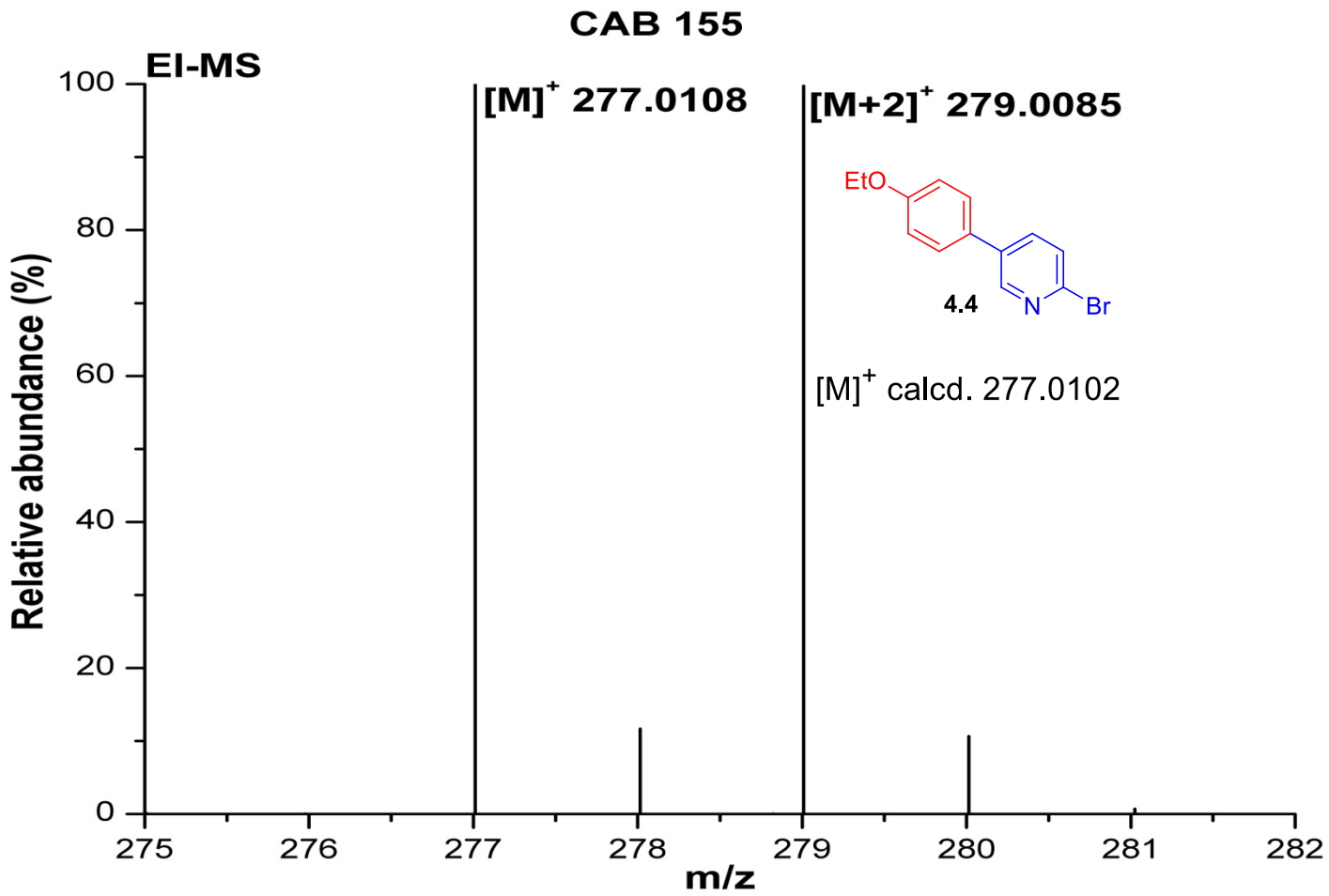
HRMS spectrum of 2-bromo-5-(4-methylphenyl)pyridine (**4.3**)



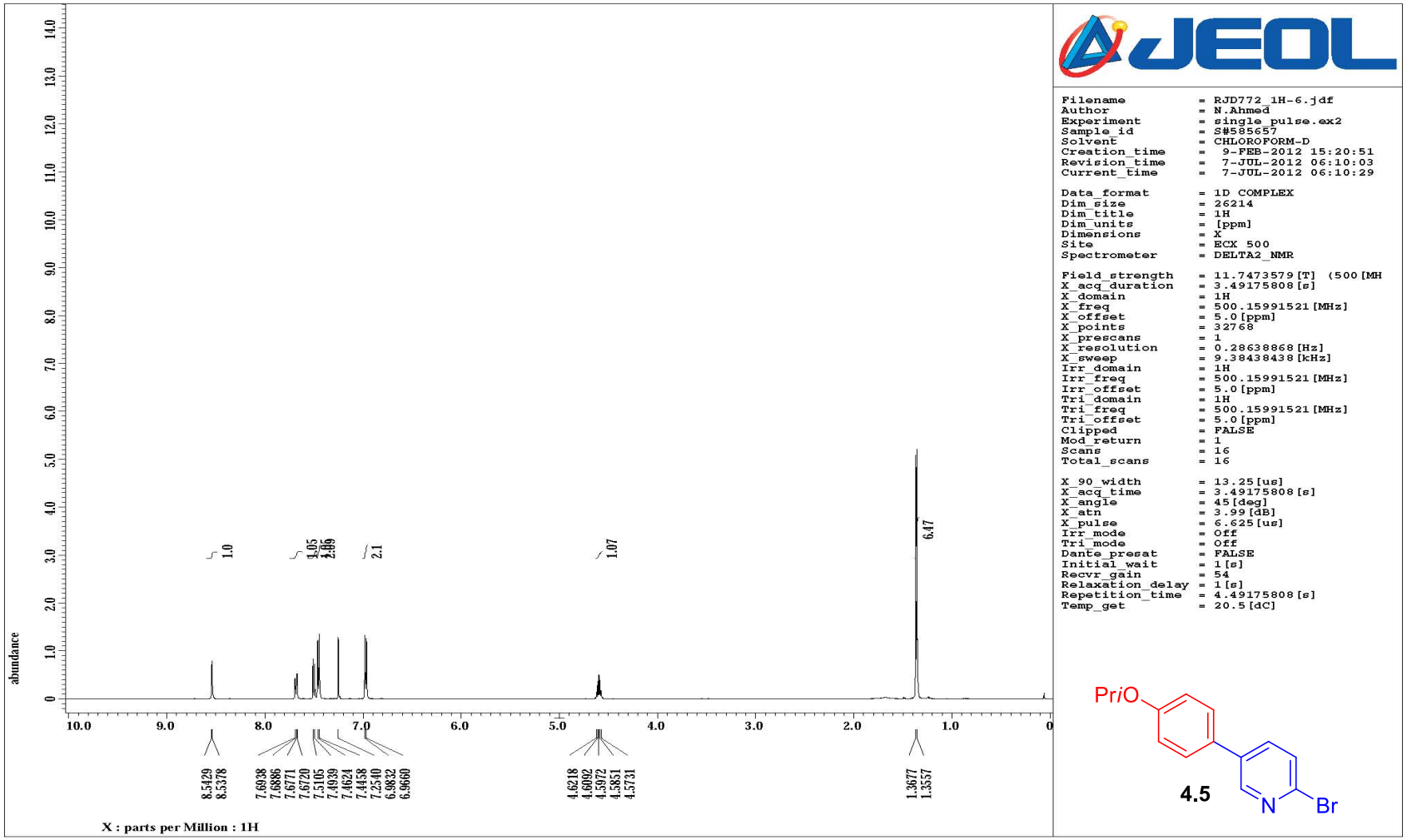
^{1}H NMR spectrum of 2-bromo-5-(4-ethoxyphenyl)pyridine (**4.4**)



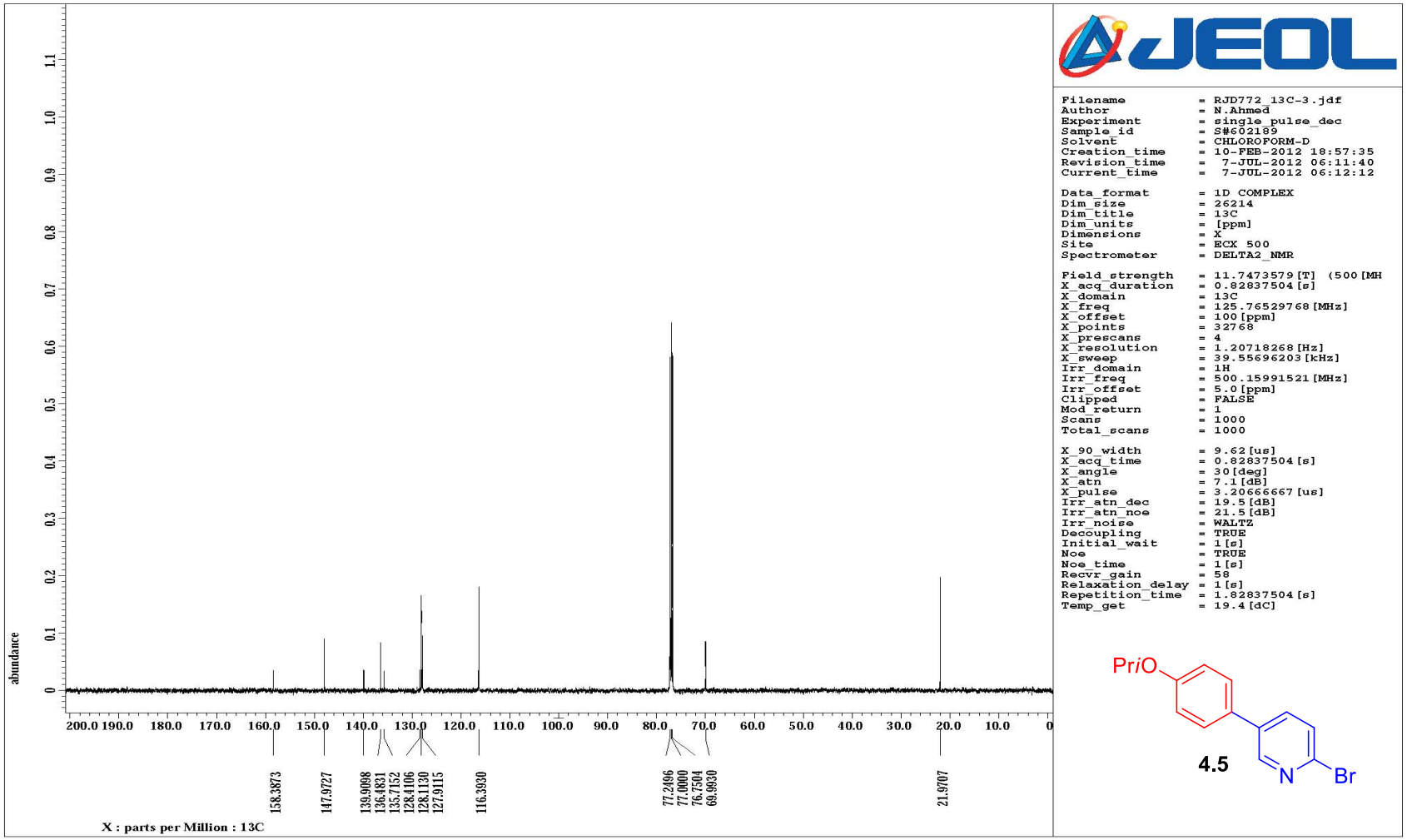
^{13}C NMR spectrum of 2-bromo-5-(4-ethoxyphenyl)pyridine (**4.4**)



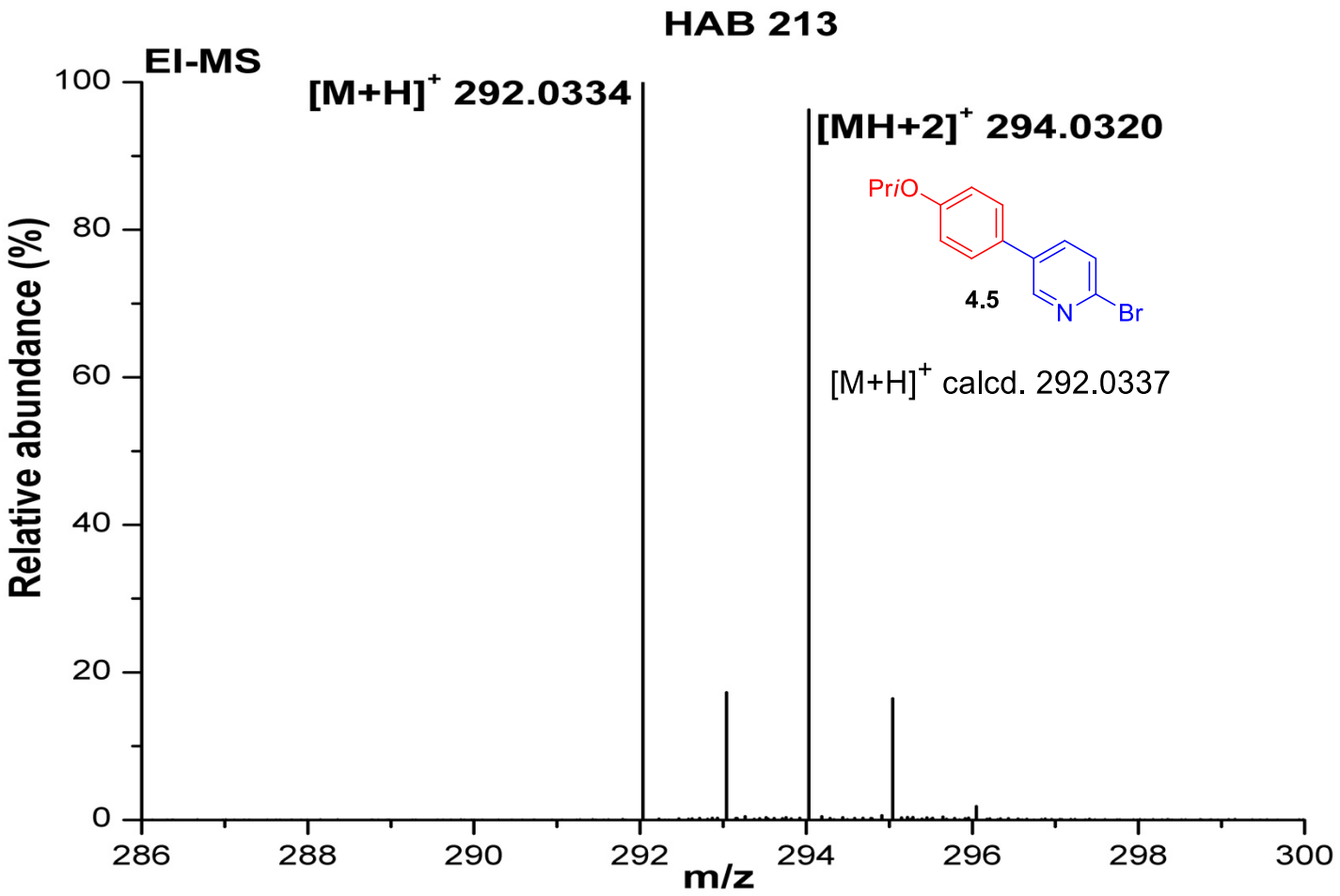
HRMS spectrum of 2-bromo-5-(4-ethoxyphenyl)pyridine (**4.4**)



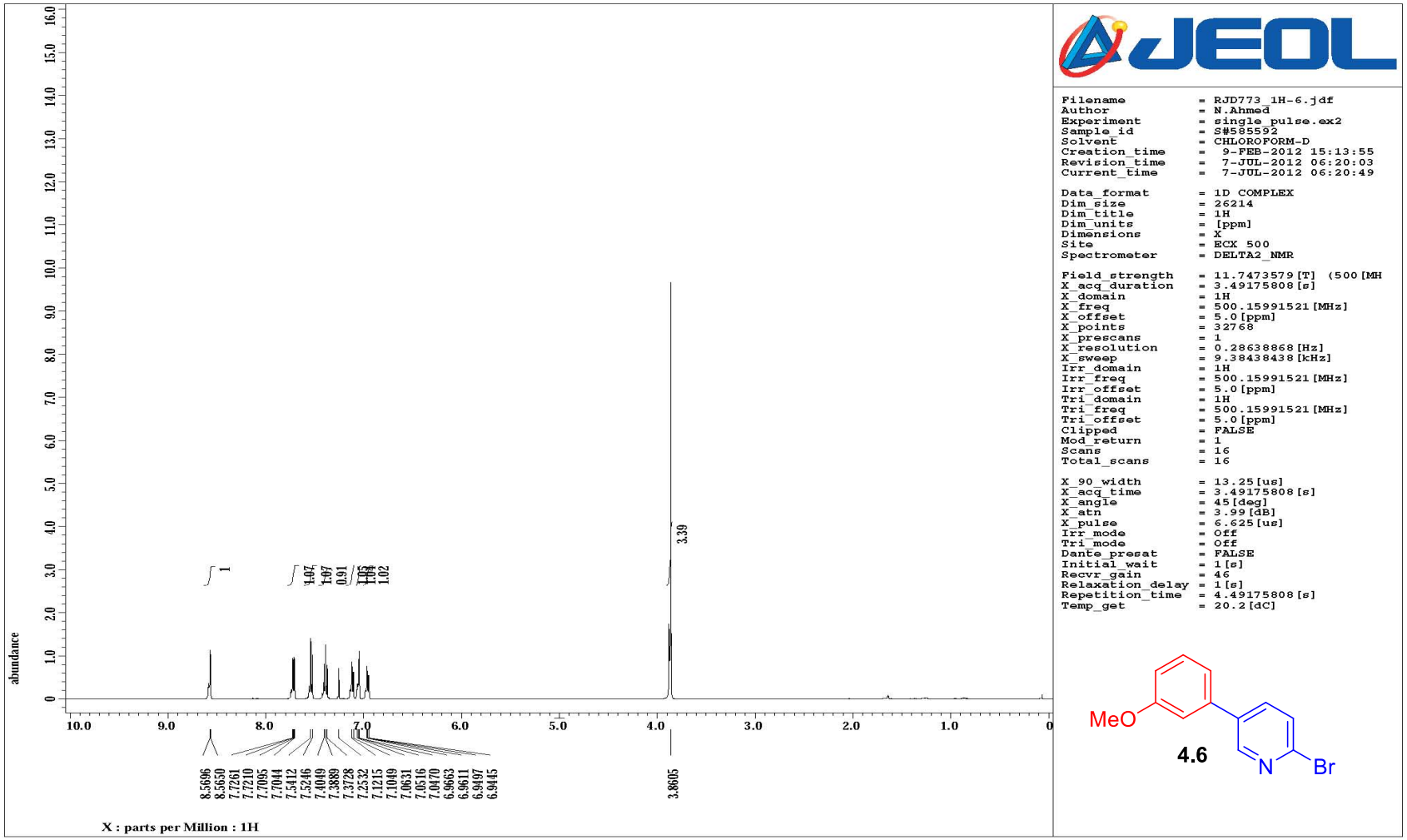
^{1}H NMR spectrum of 2-bromo-5-(4-isopropoxyphenyl)pyridine (**4.5**)



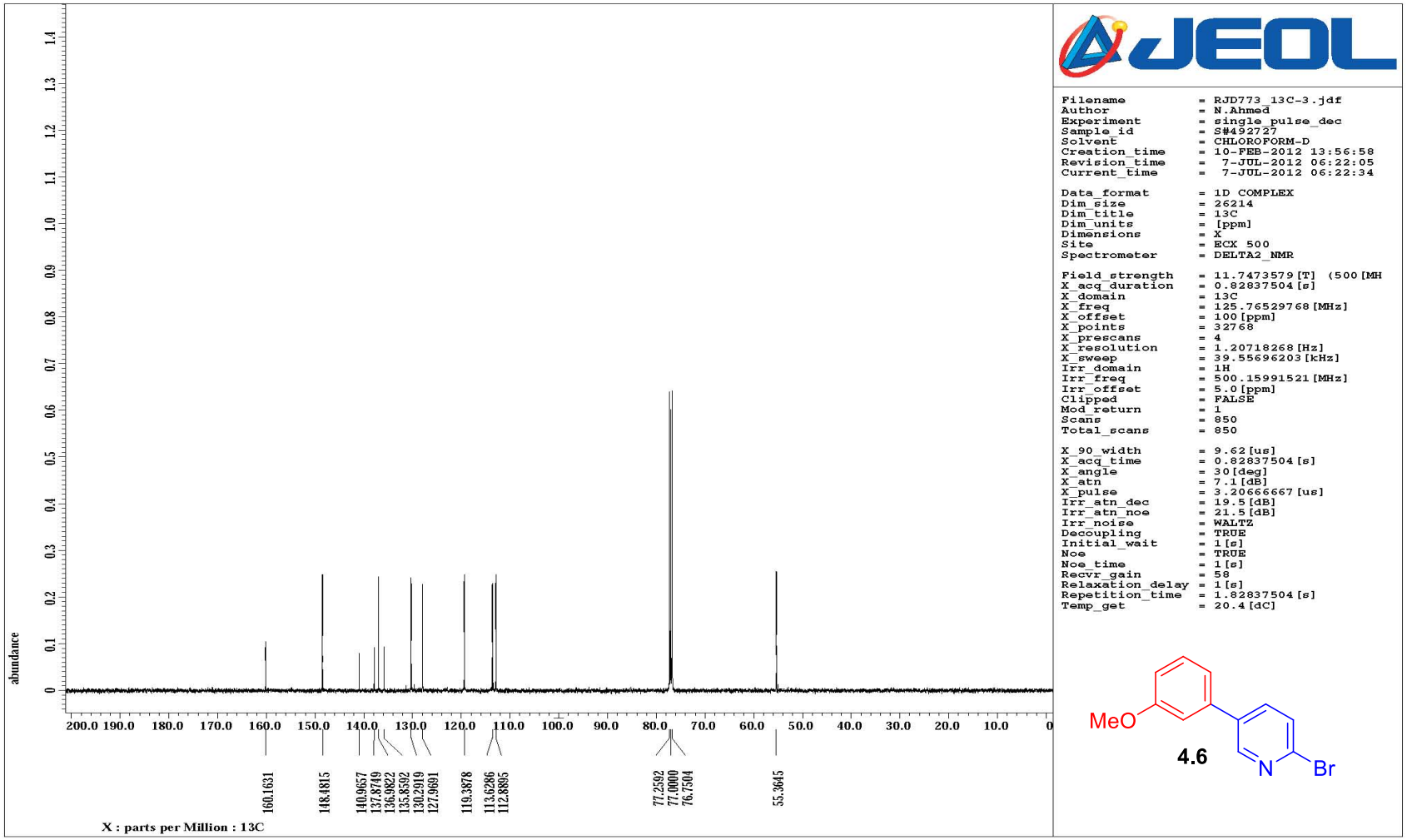
^{13}C NMR spectrum of 2-bromo-5-(4-isopropoxyphenyl)pyridine (**4.5**)



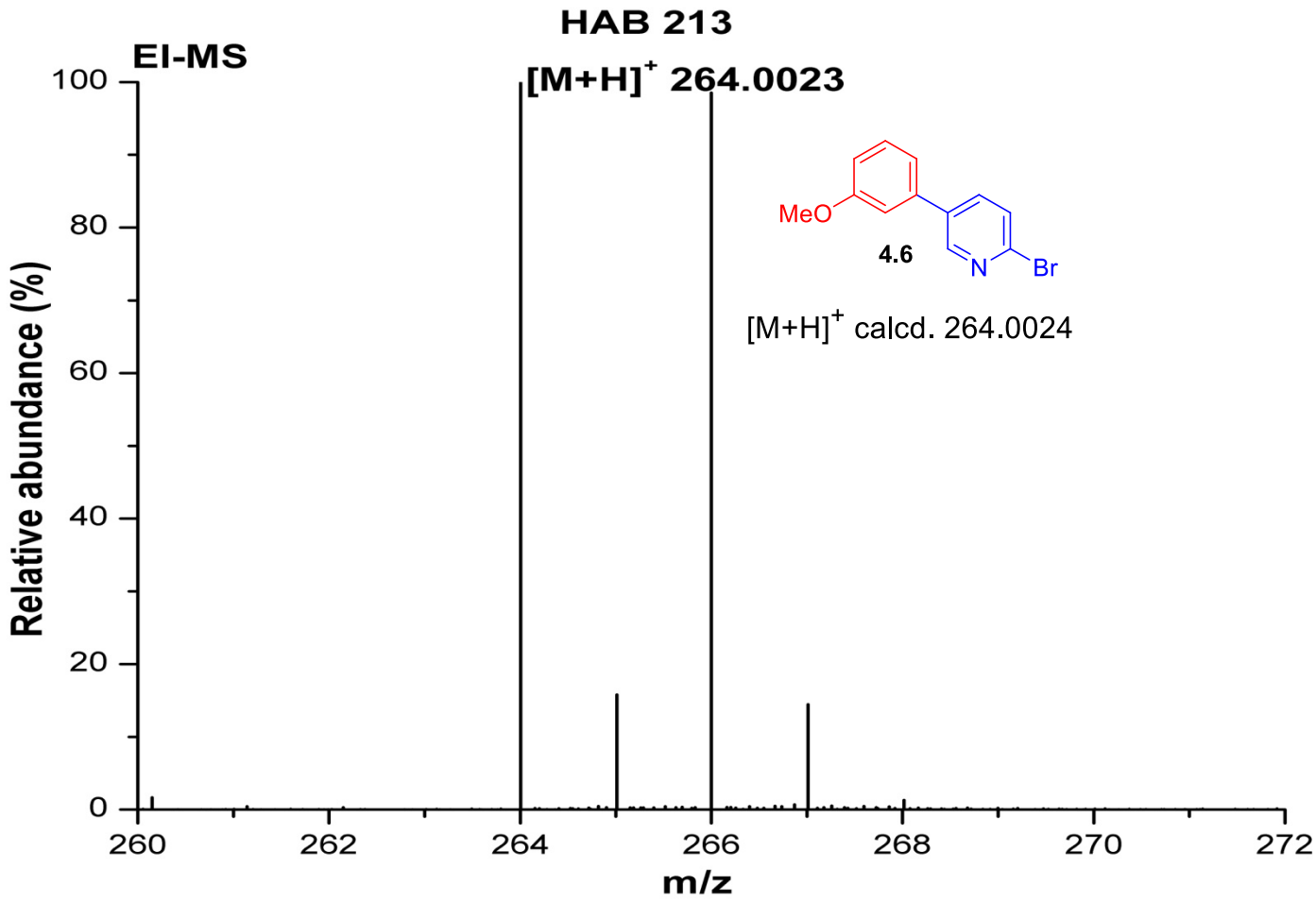
HRMS spectrum of 2-bromo-5-(4-isopropoxyphenyl)pyridine (**4.5**)



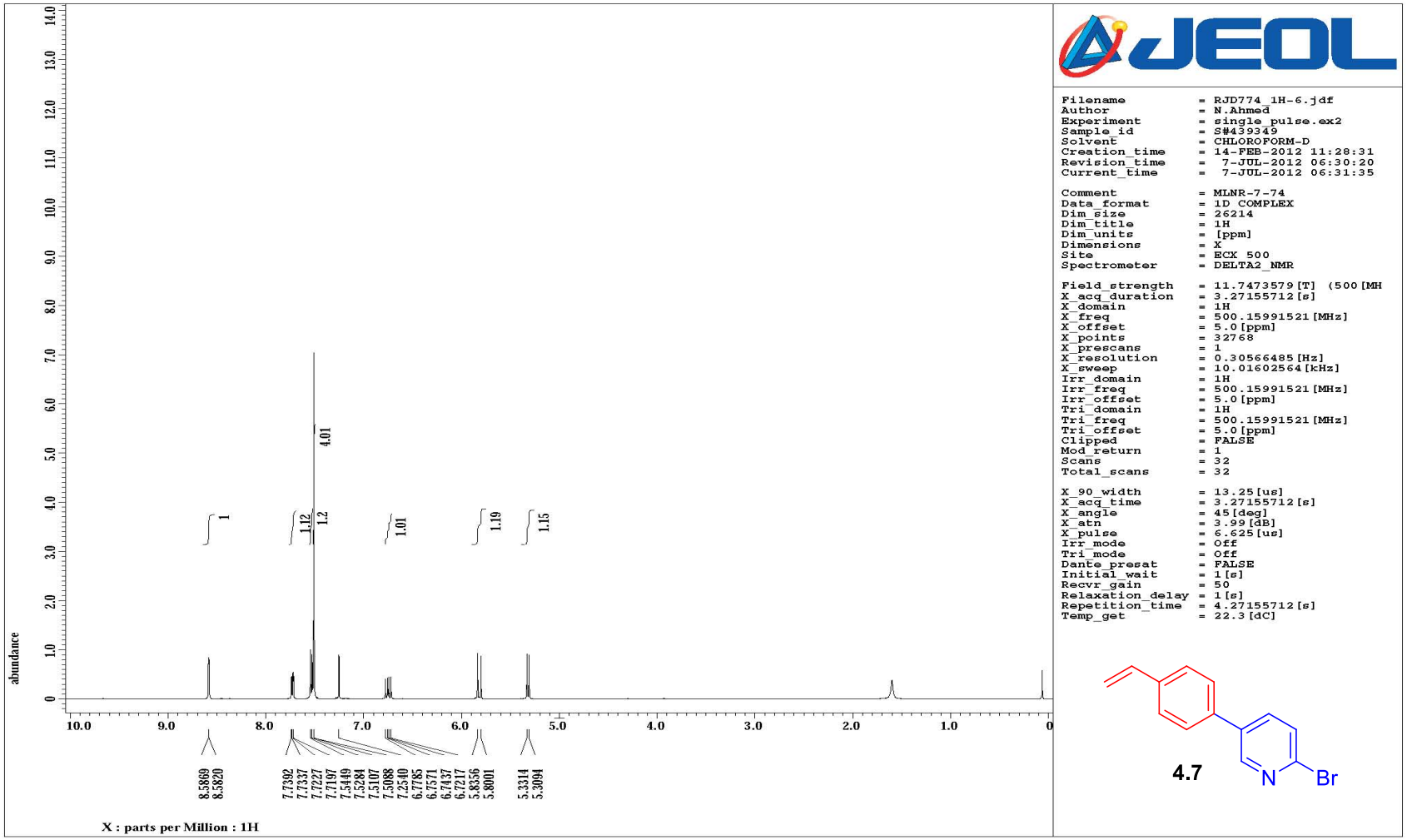
^{1}H NMR spectrum of 2-bromo-5-(3-methoxyphenyl)pyridine (**4.6**)



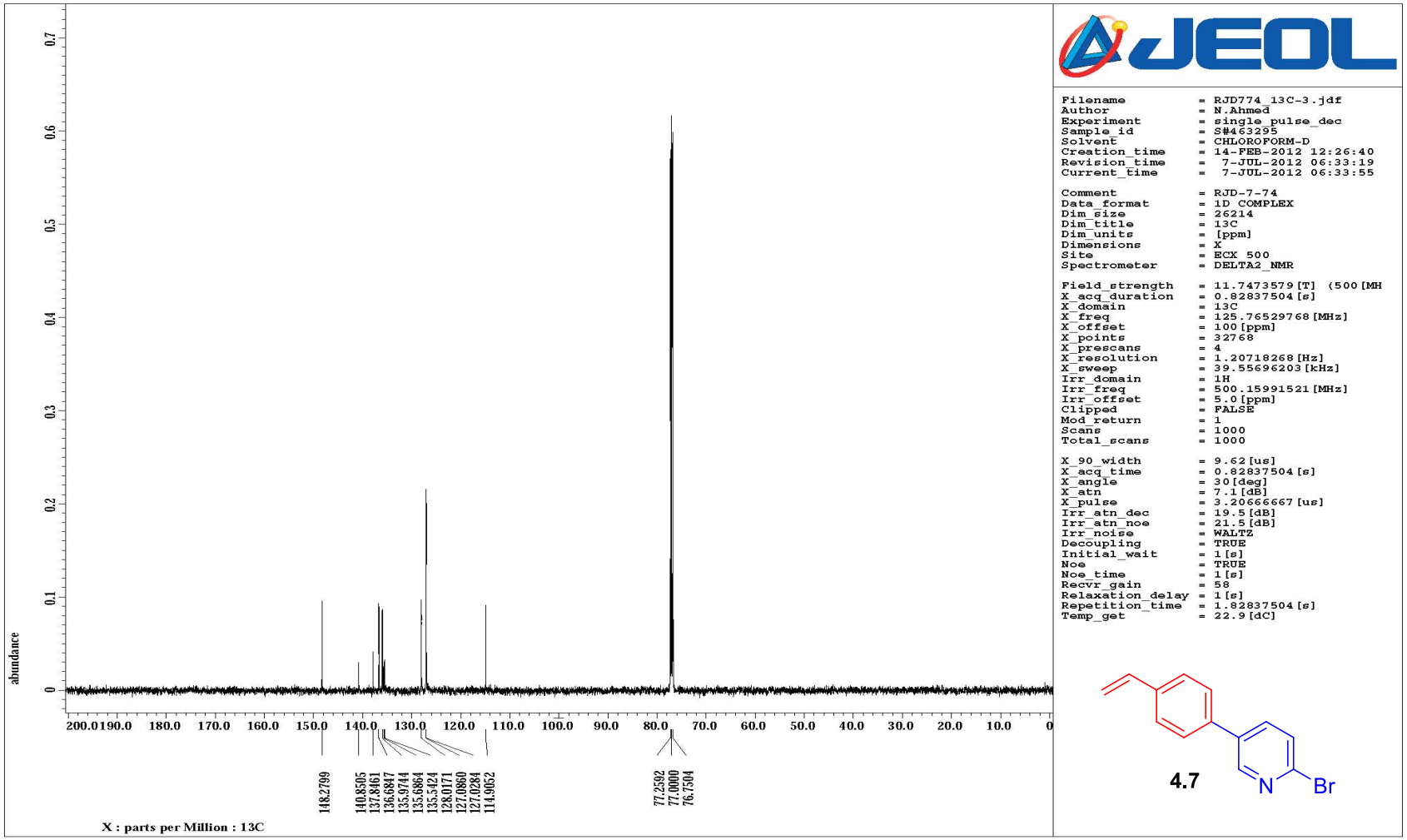
^{13}C NMR spectrum of 2-bromo-5-(3-methoxyphenyl)pyridine (**4.6**)



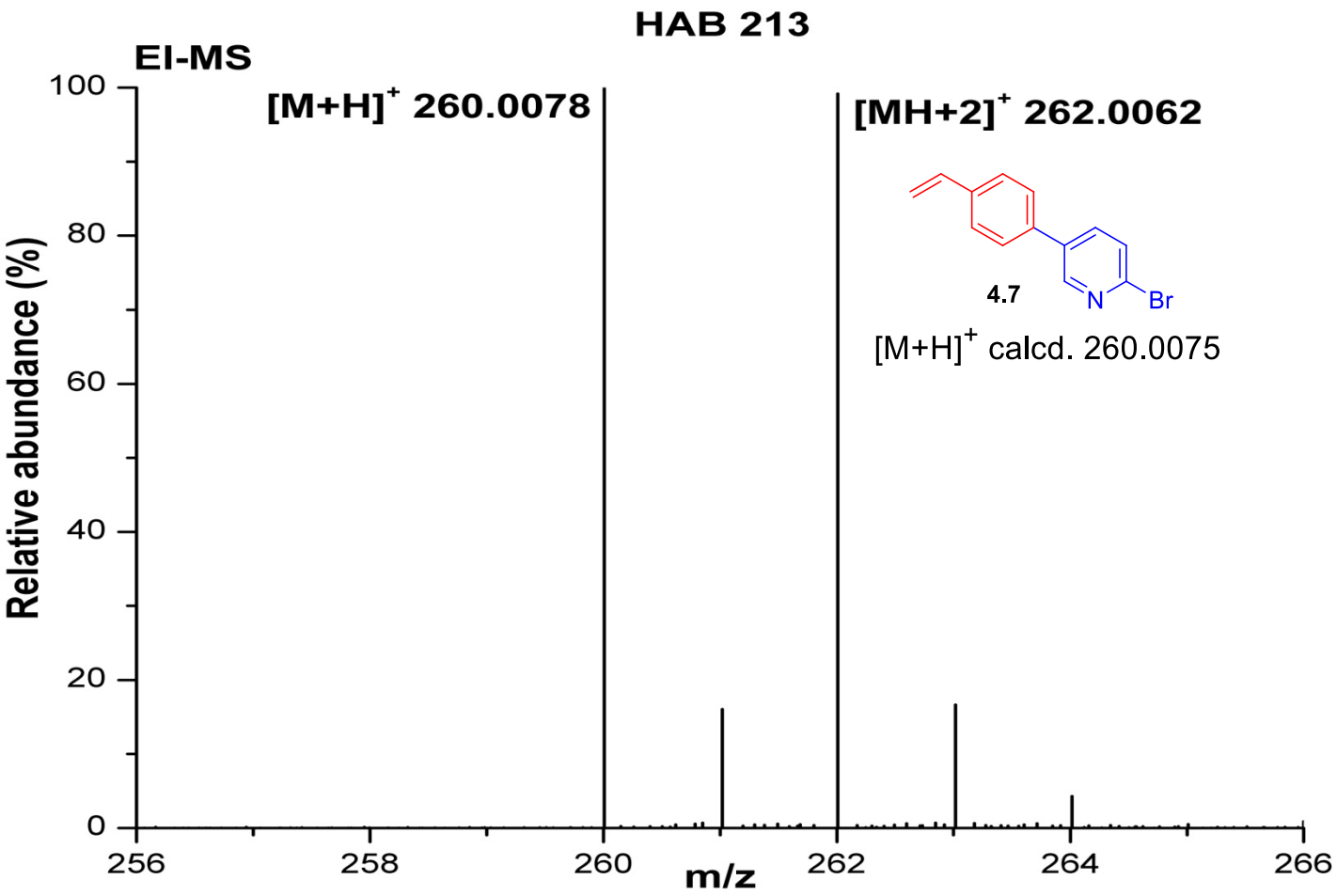
HRMS spectrum of 2-bromo-5-(3-methoxyphenyl)pyridine (**4.6**)



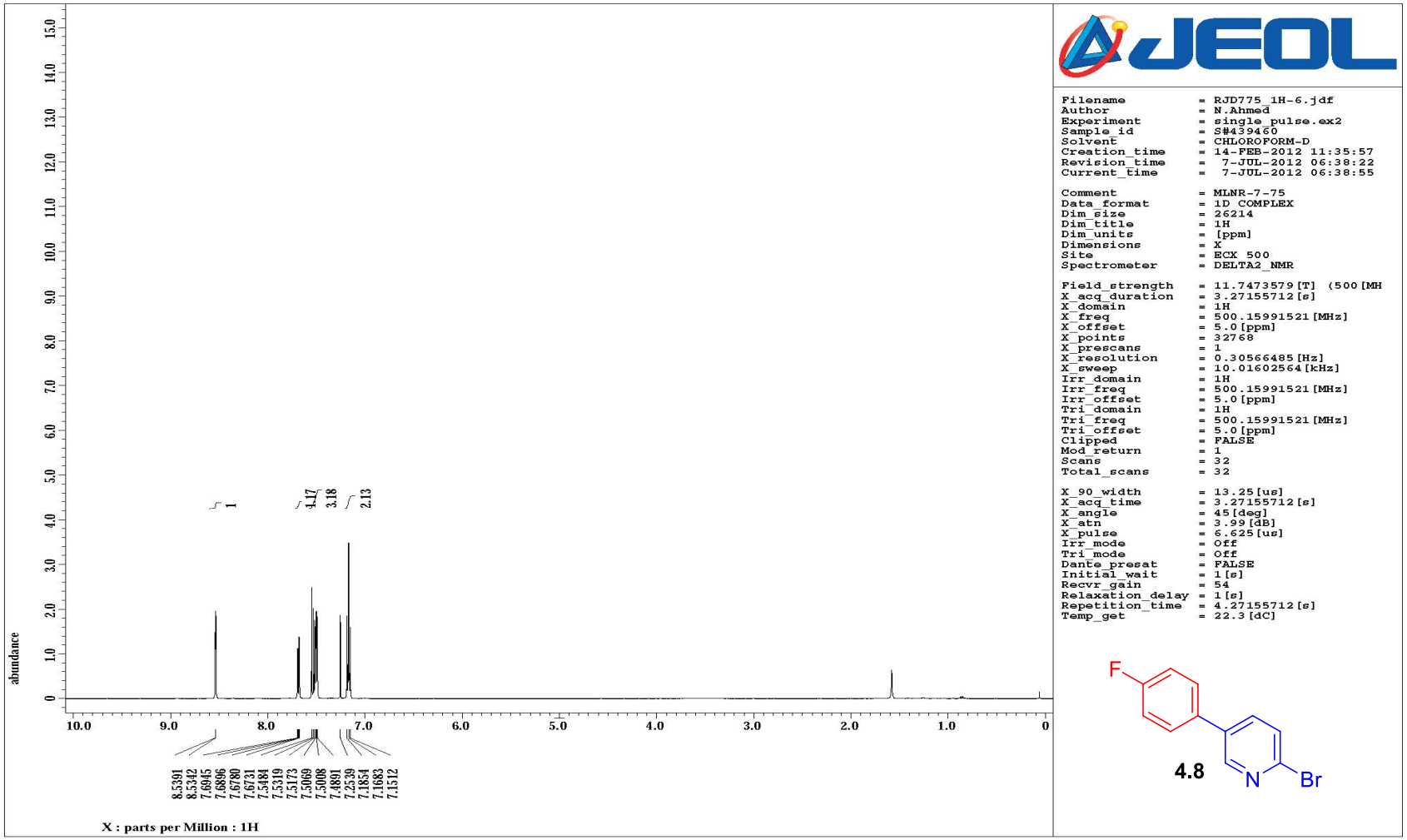
^{1}H NMR spectrum of 2-bromo-5-(4-vinylphenyl)pyridine (**4.7**)



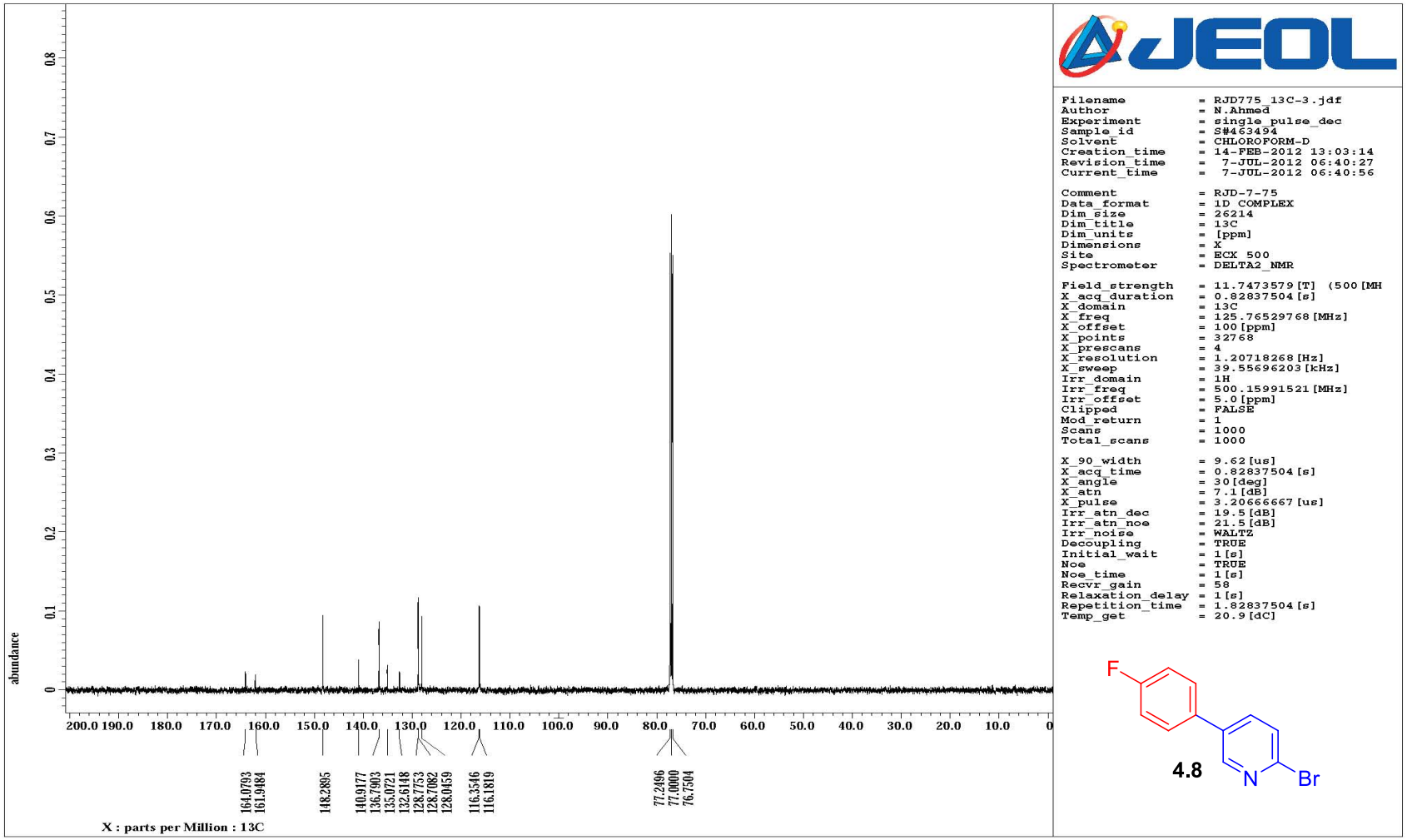
^{13}C NMR spectrum of 2-bromo-5-(4-vinylphenyl)pyridine (**4.7**)



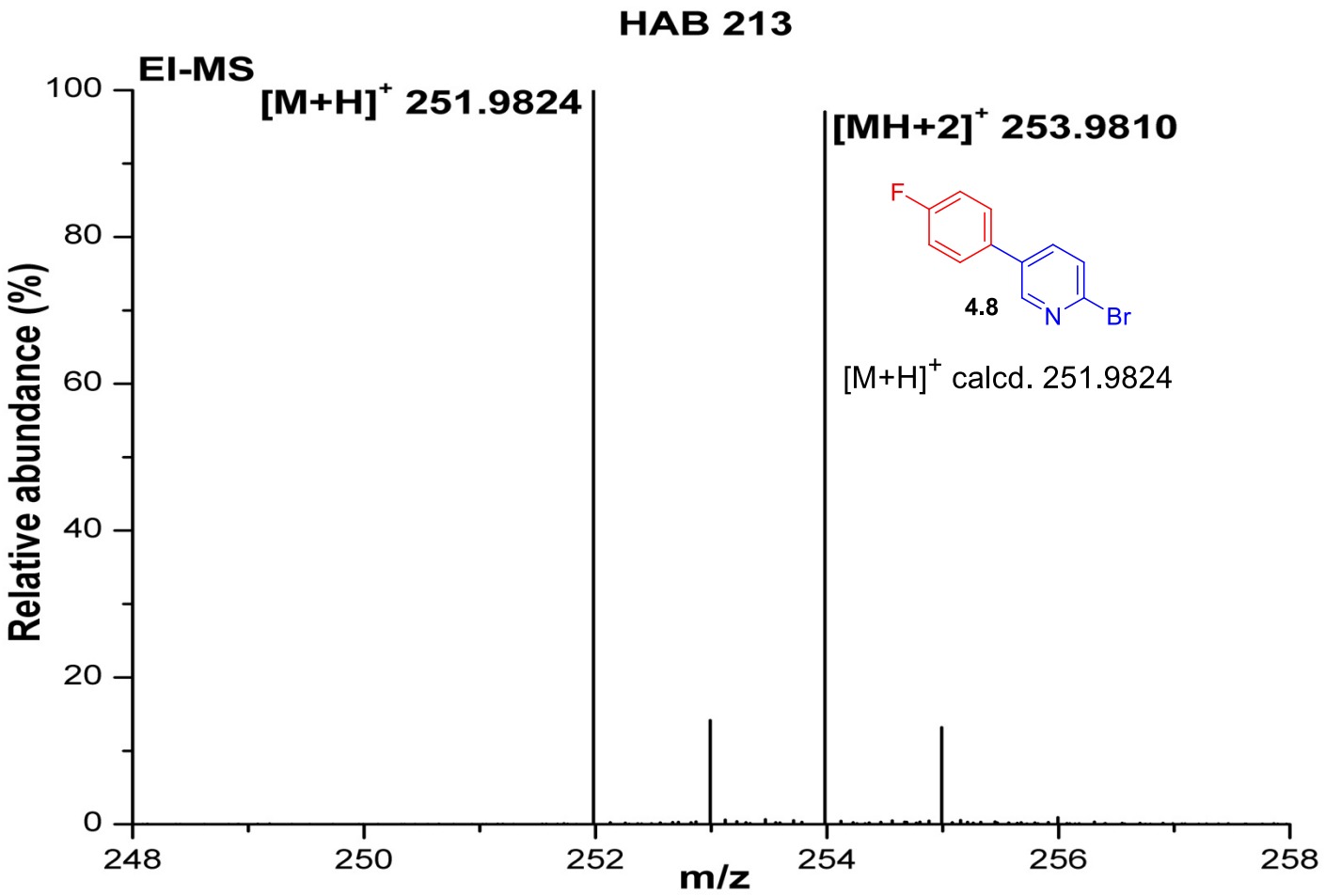
HRMS spectrum of 2-bromo-5-(4-vinylphenyl)pyridine (**4.7**)



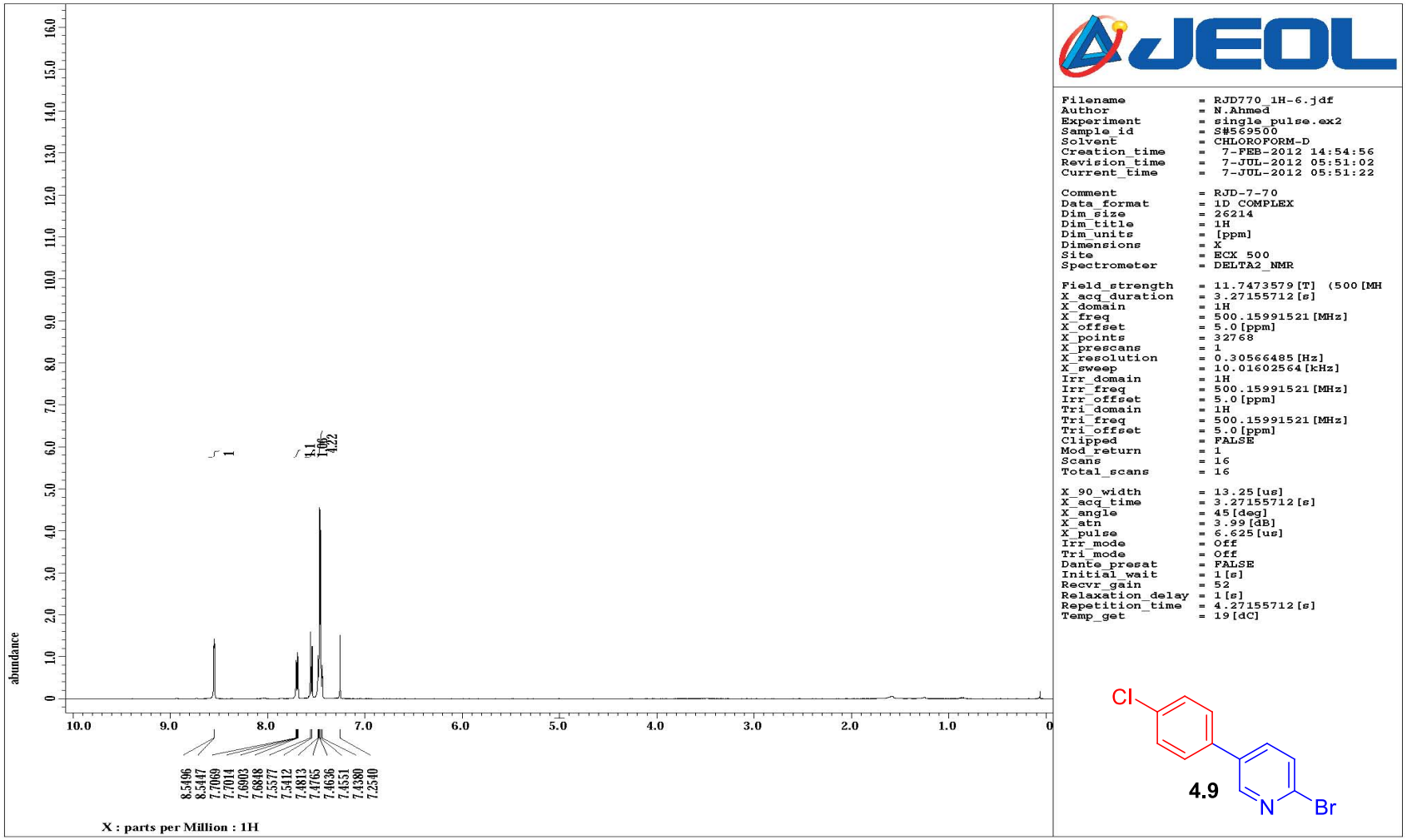
^{1}H NMR spectrum of 2-bromo-5-(4-fluorophenyl)pyridine (**4.8**)



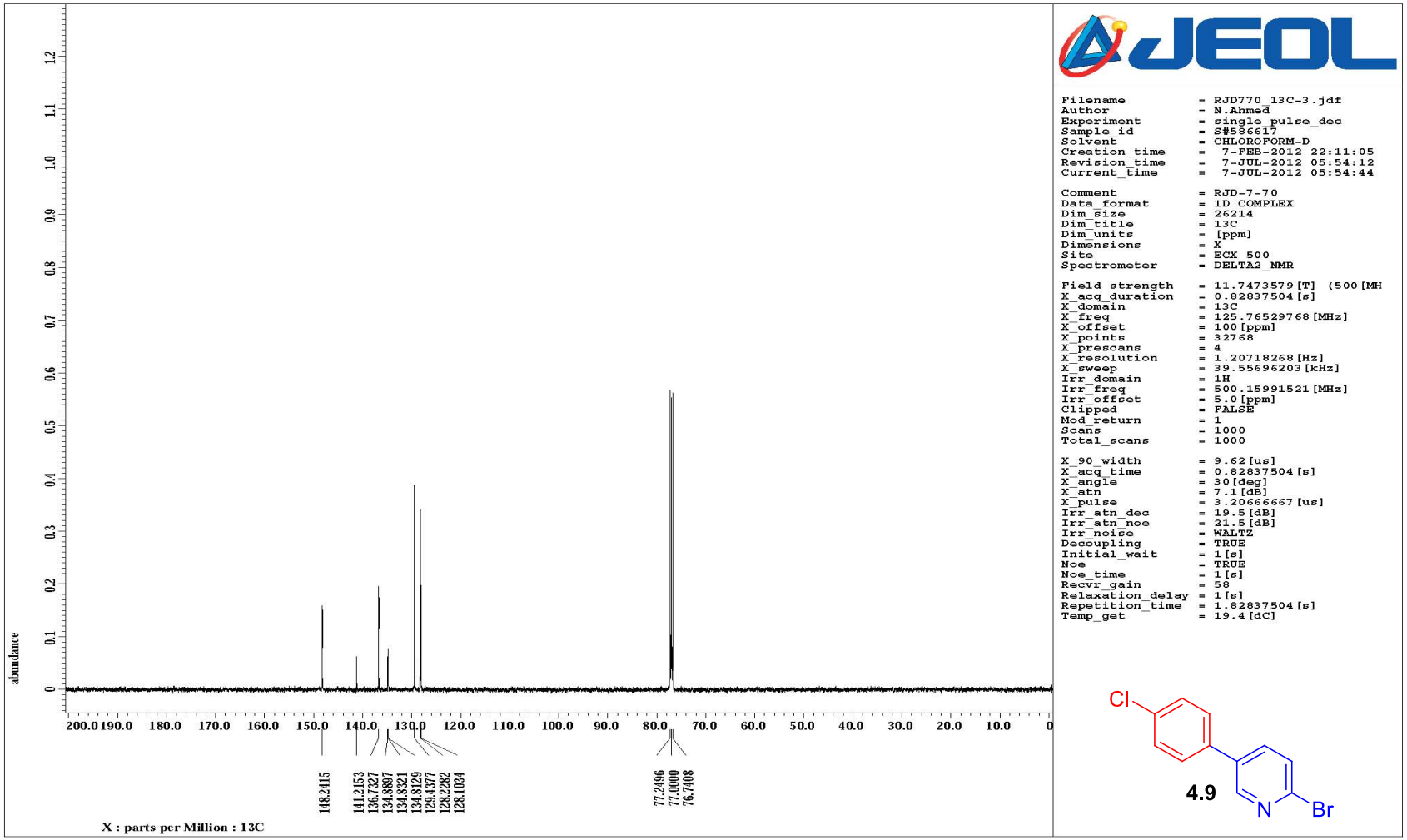
^{13}C NMR spectrum of 2-bromo-5-(4-fluorophenyl)pyridine (**4.8**)



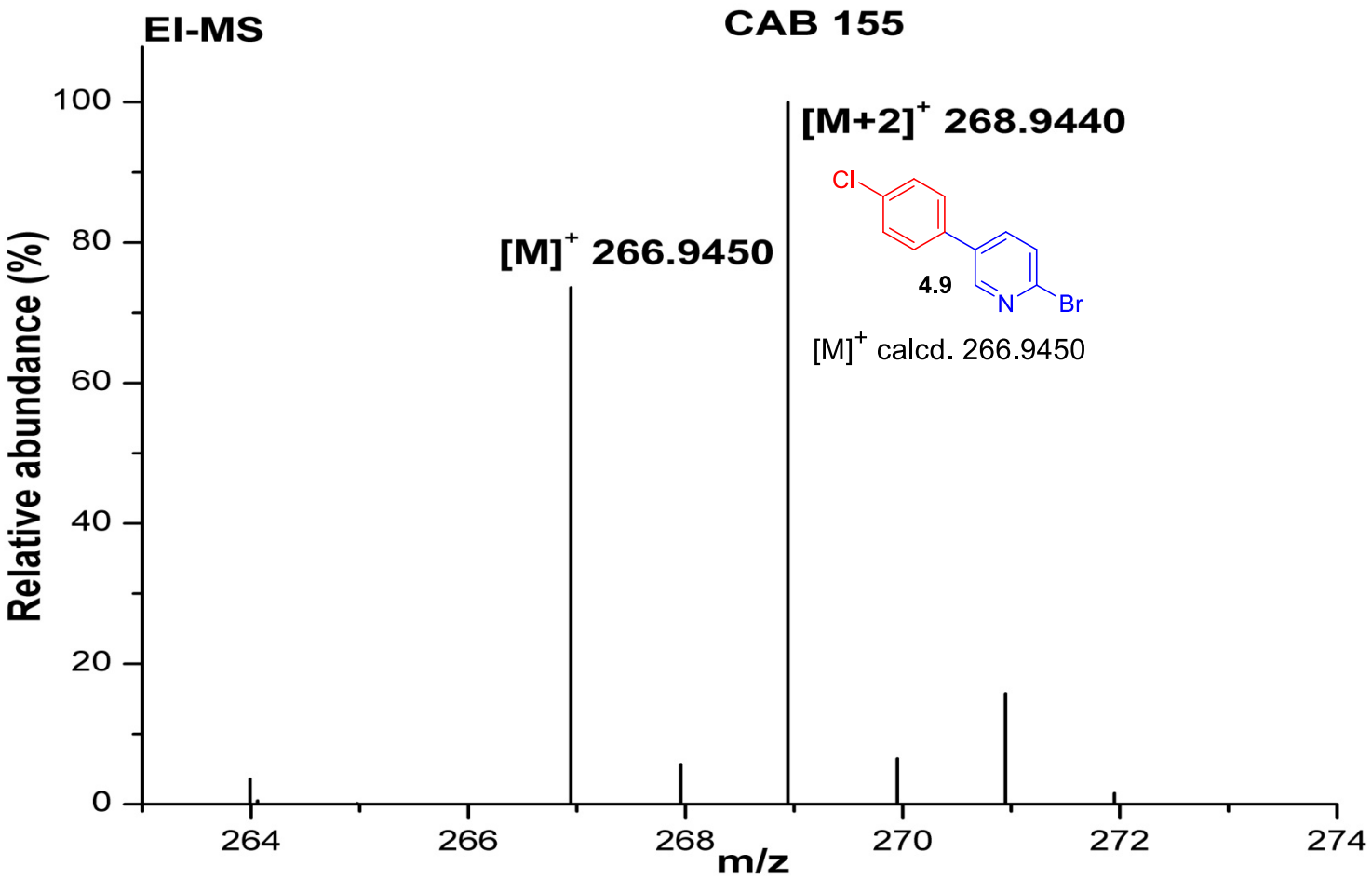
HRMS spectrum of 2-bromo-5-(4-fluorophenyl)pyridine (**4.8**)



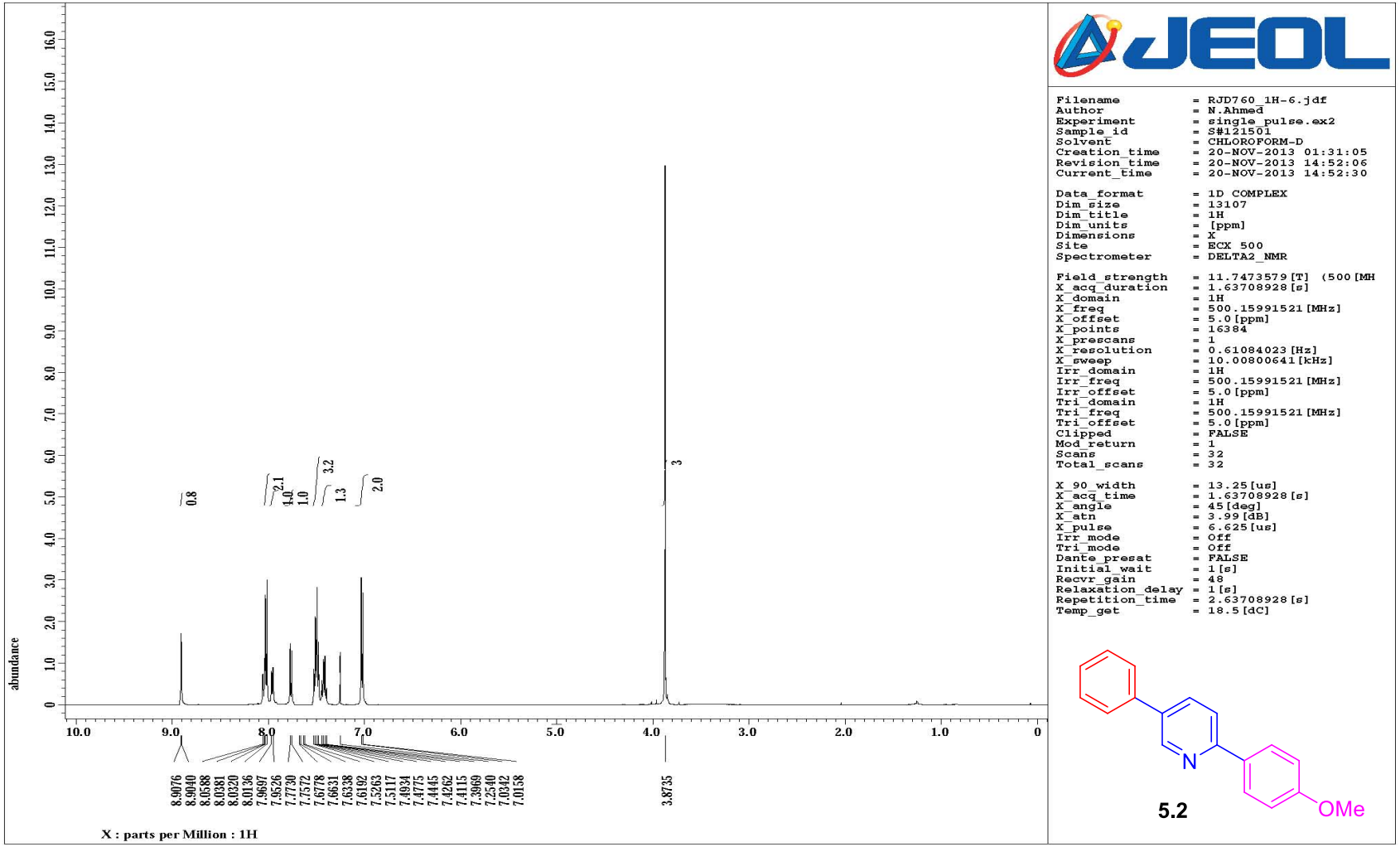
^{1}H NMR spectrum of 2-bromo-5-(4-chlorophenyl)pyridine (**4.9**)



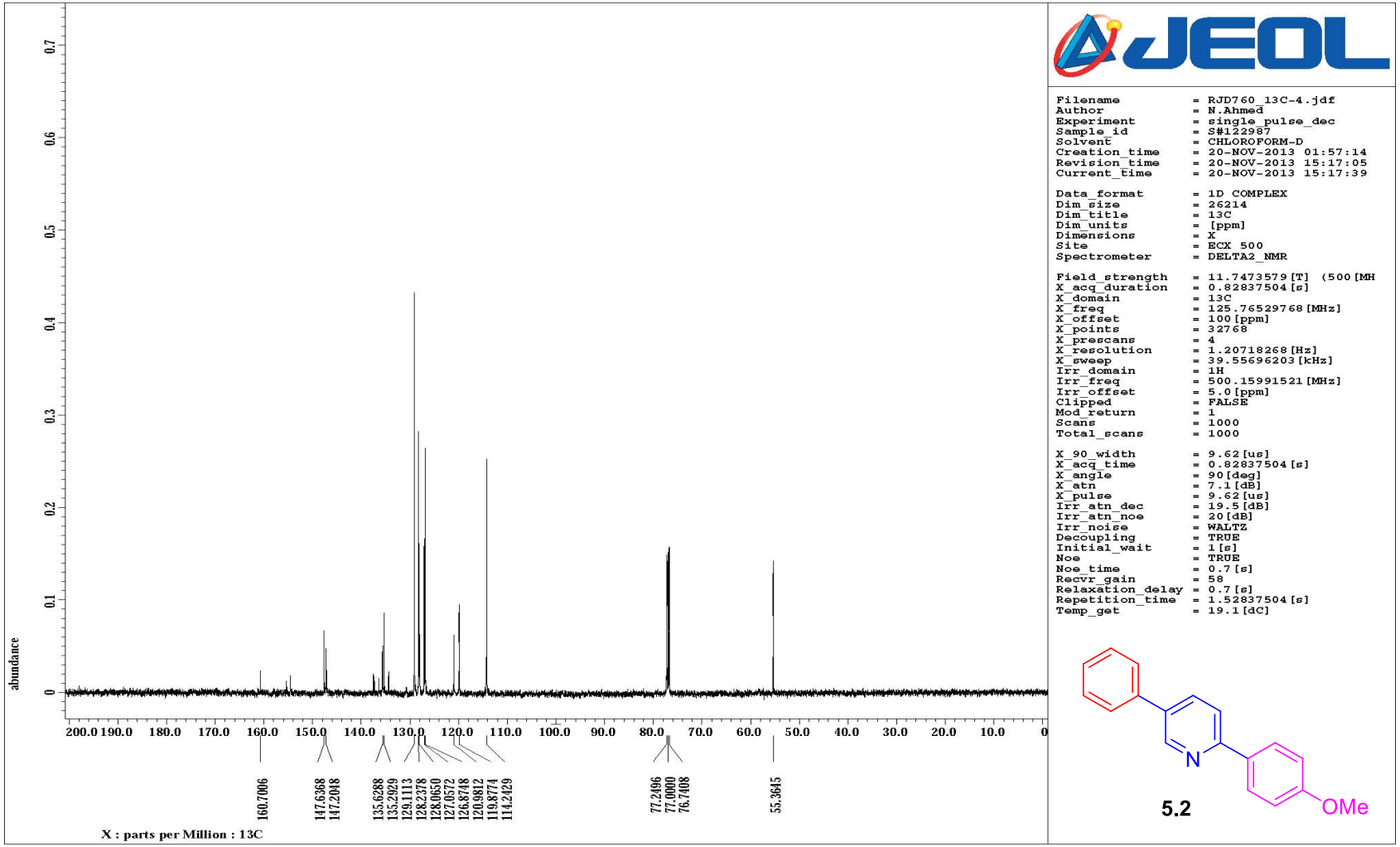
^{13}C NMR spectrum of 2-bromo-5-(4-chlorophenyl)pyridine (**4.9**)



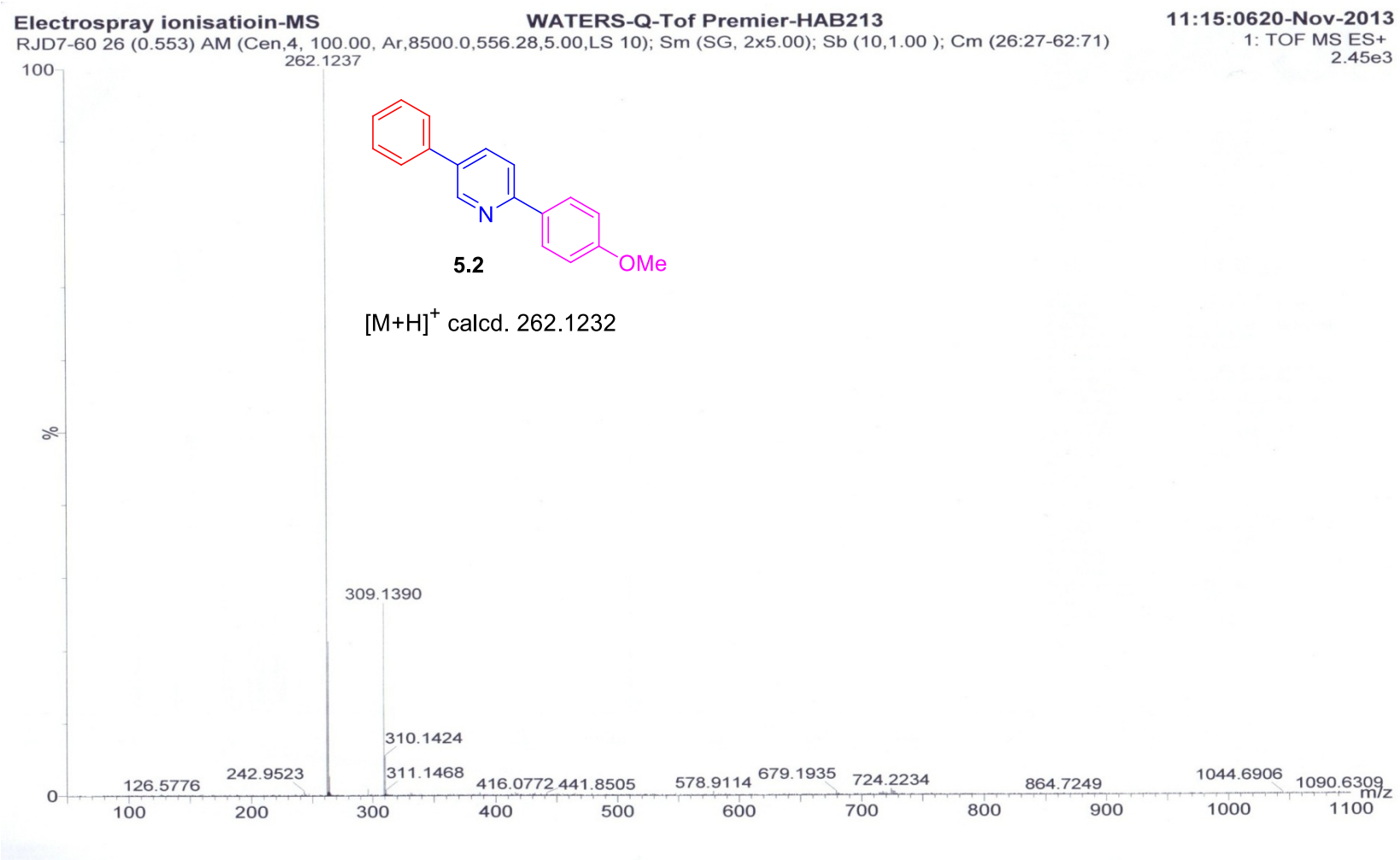
HRMS spectrum of 2-bromo-5-(4-chlorophenyl)pyridine (**4.9**)



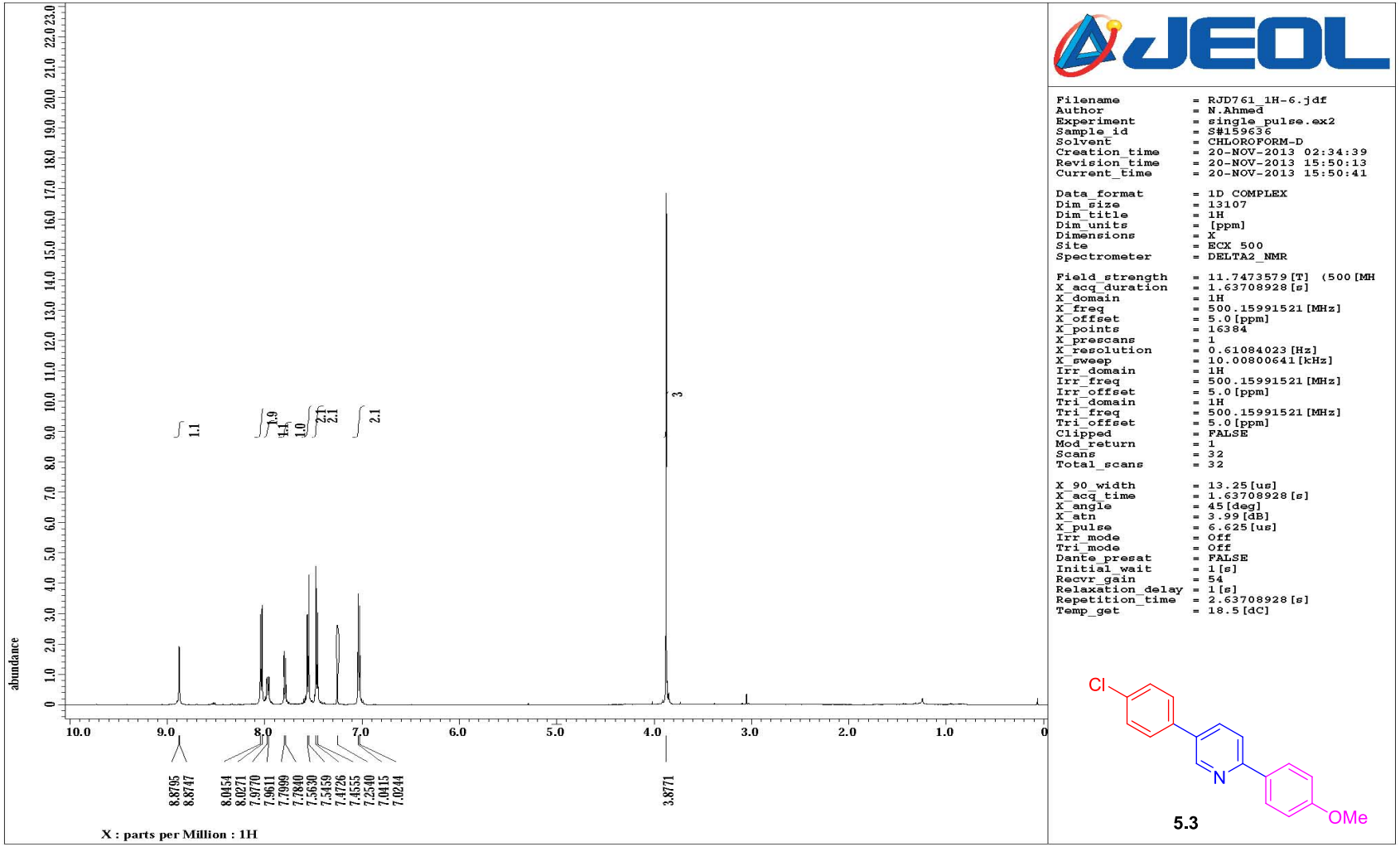
^{1}H NMR spectrum of 2-(4-methoxyphenyl)-5-phenylpyridine (**5.2**)



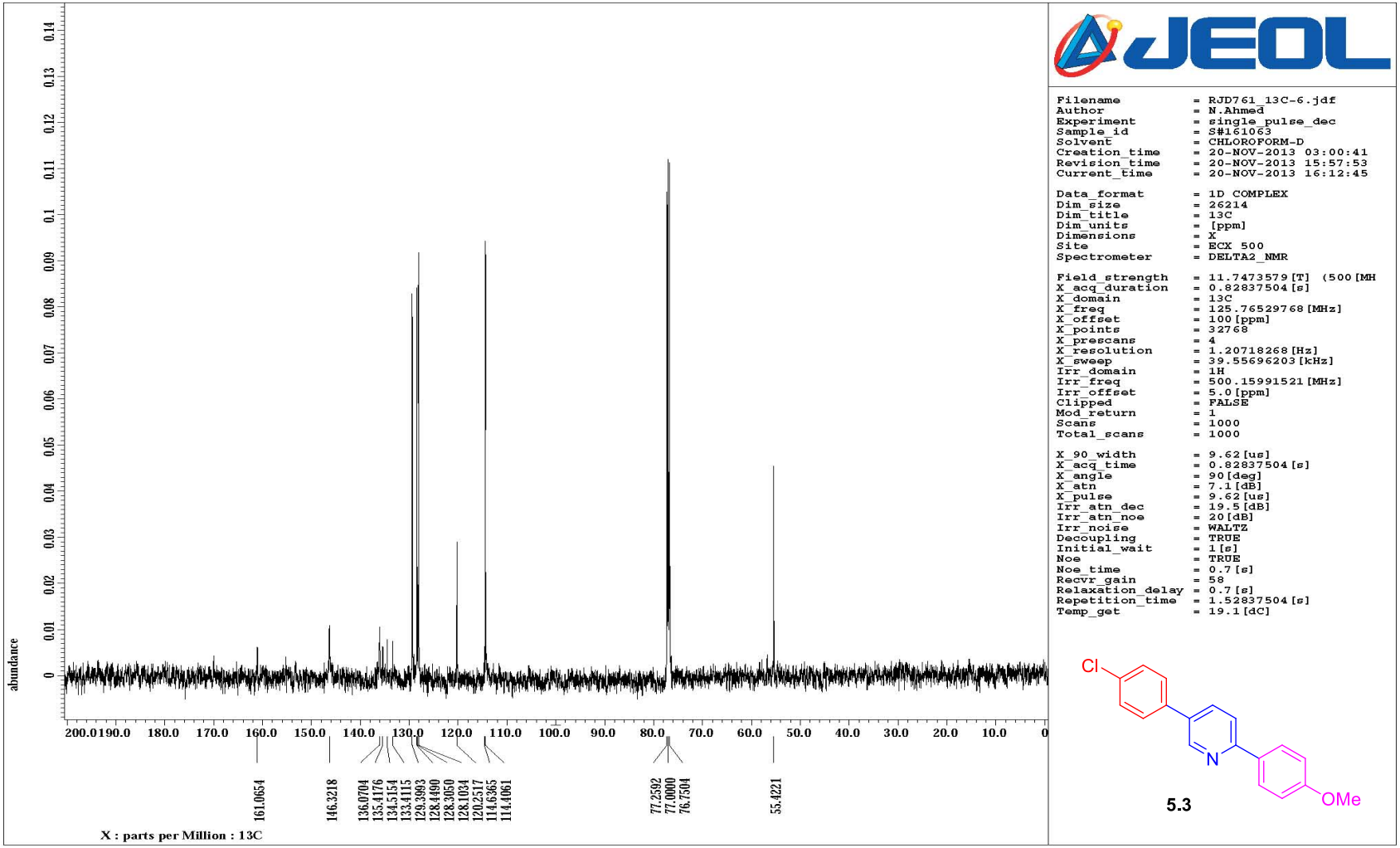
^{13}C NMR spectrum of 2-(4-methoxyphenyl)-5-phenylpyridine (**5.2**)



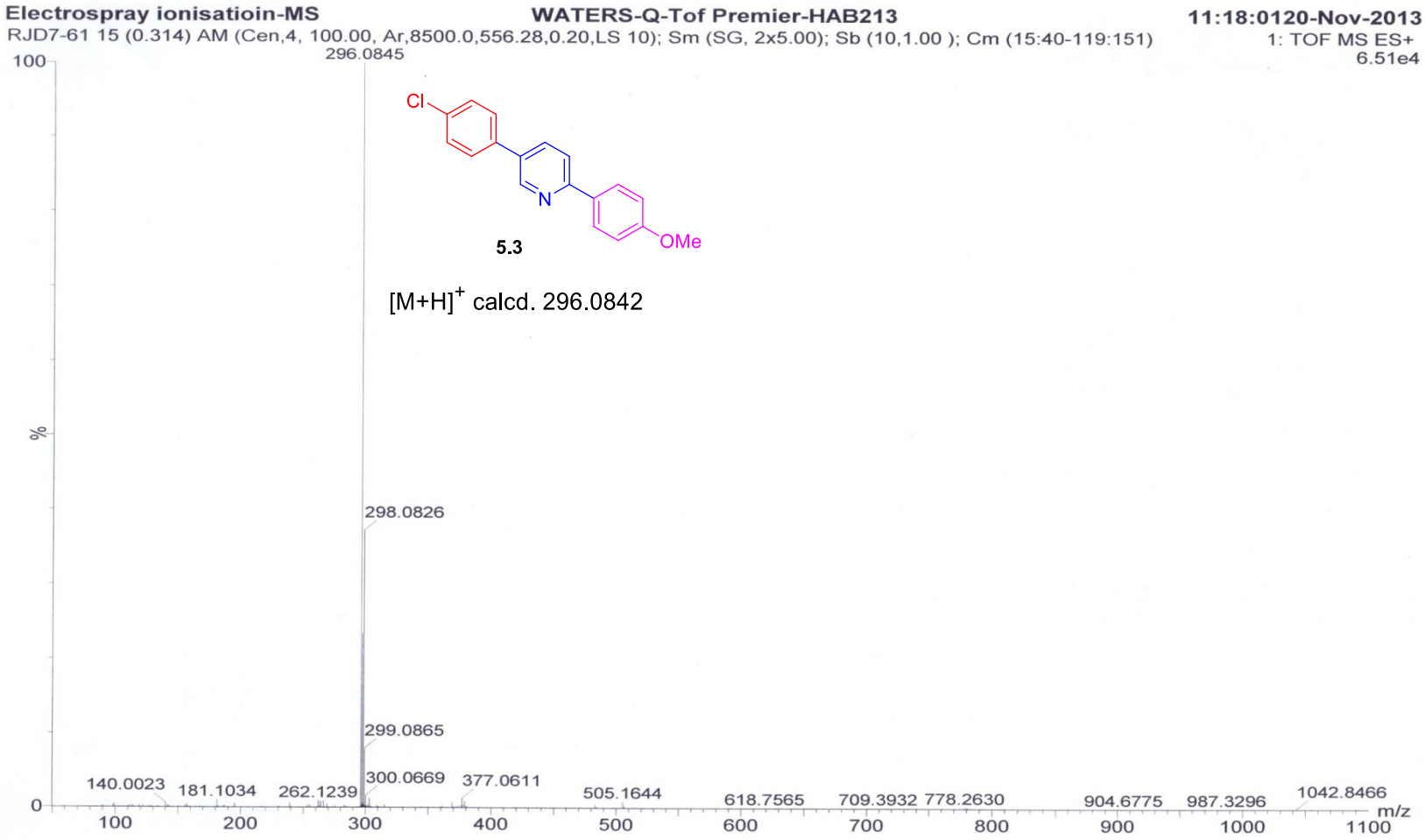
HRMS spectrum of 2-(4-methoxyphenyl)-5-phenylpyridine (**5.2**)



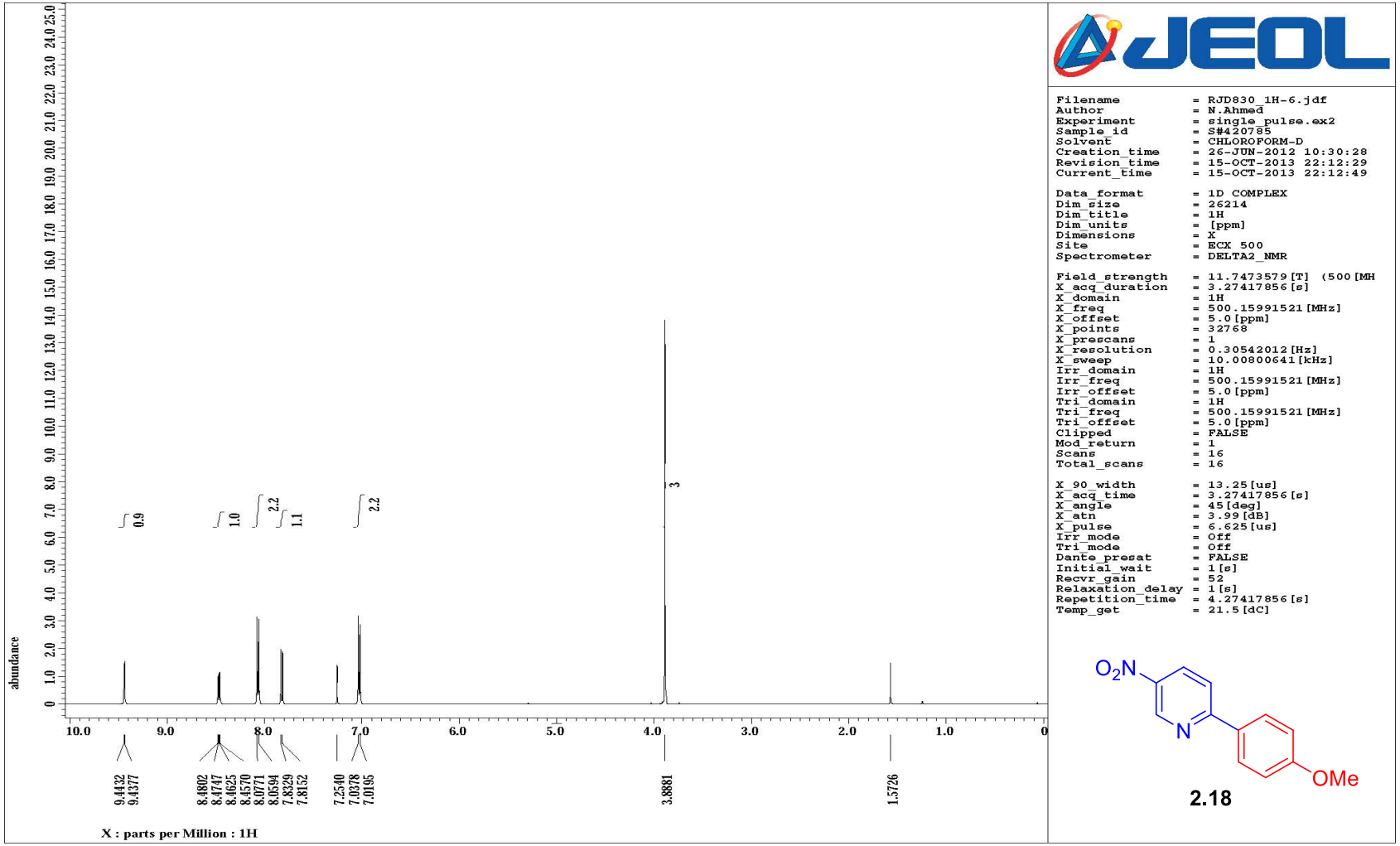
^{1}H NMR spectrum of 5-(4-chlorophenyl)-2-(4-methoxyphenyl)pyridine (**5.3**)



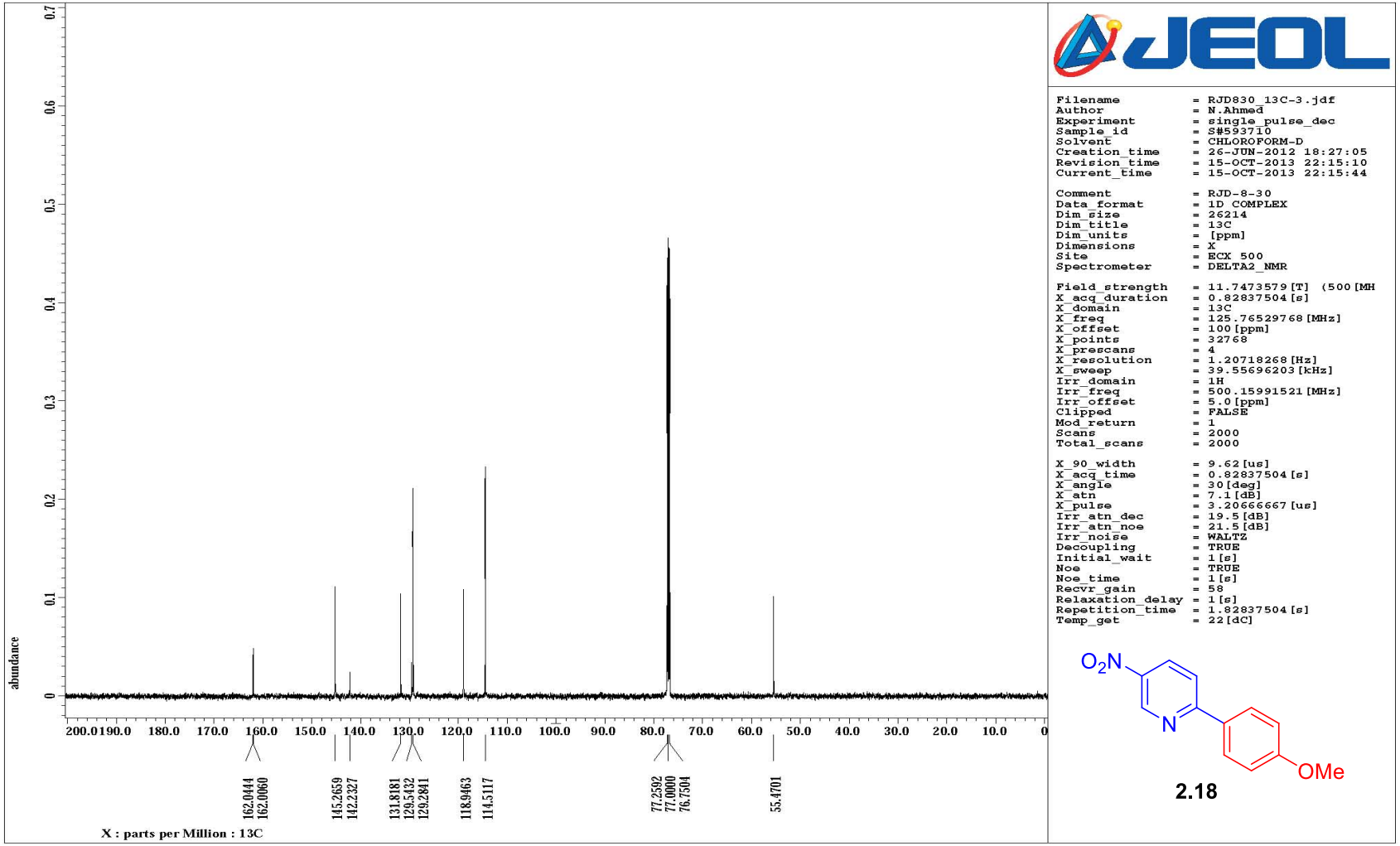
^{13}C NMR spectrum of 5-(4-chlorophenyl)-2-(4-methoxyphenyl)pyridine (**5.3**)



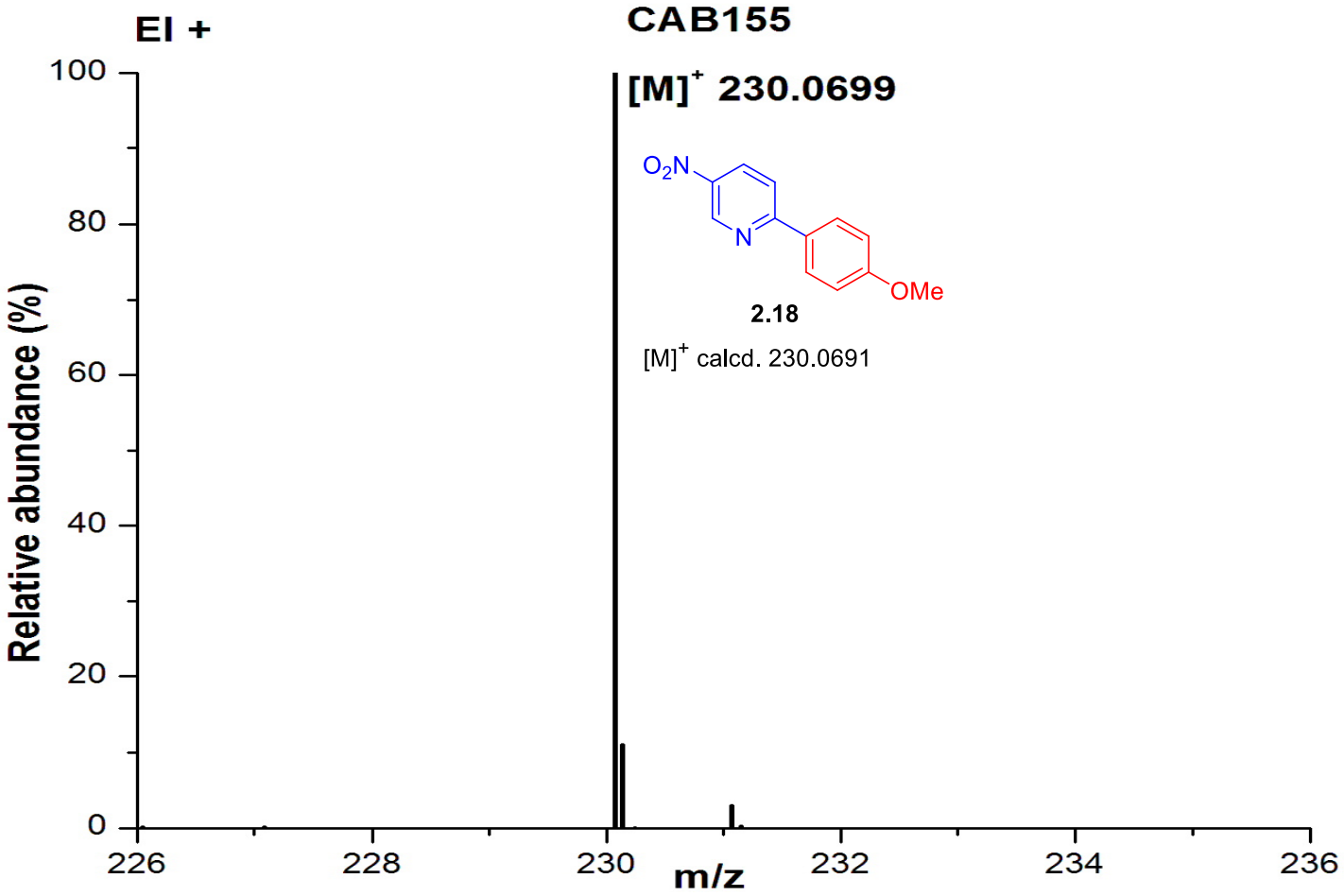
HRMS spectrum of 5-(4-chlorophenyl)-2-(4-methoxyphenyl)pyridine (**5.3**)



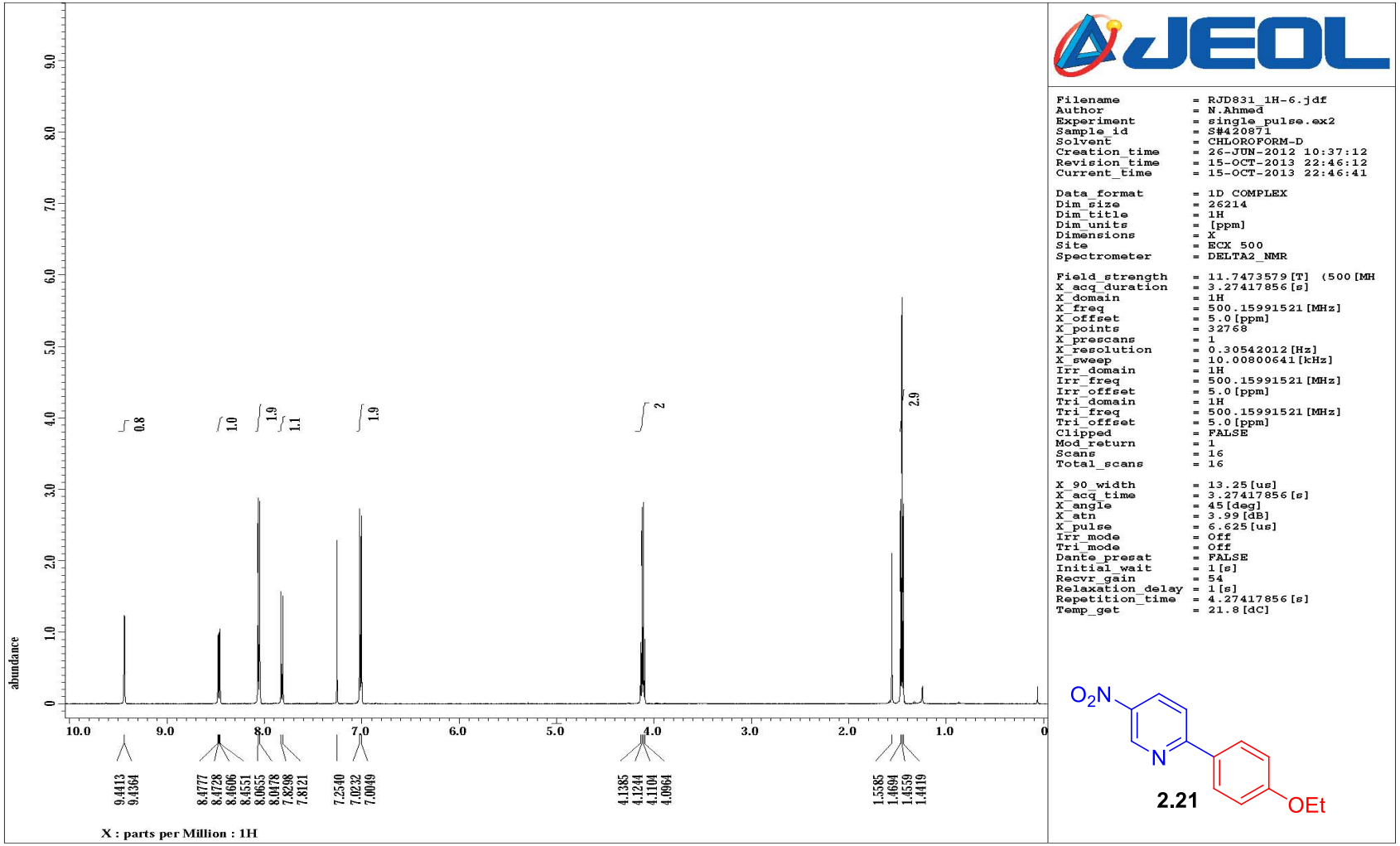
^{1}H NMR spectrum of 2-(4-methoxyphenyl)-5-nitropyridine (**2.18**)



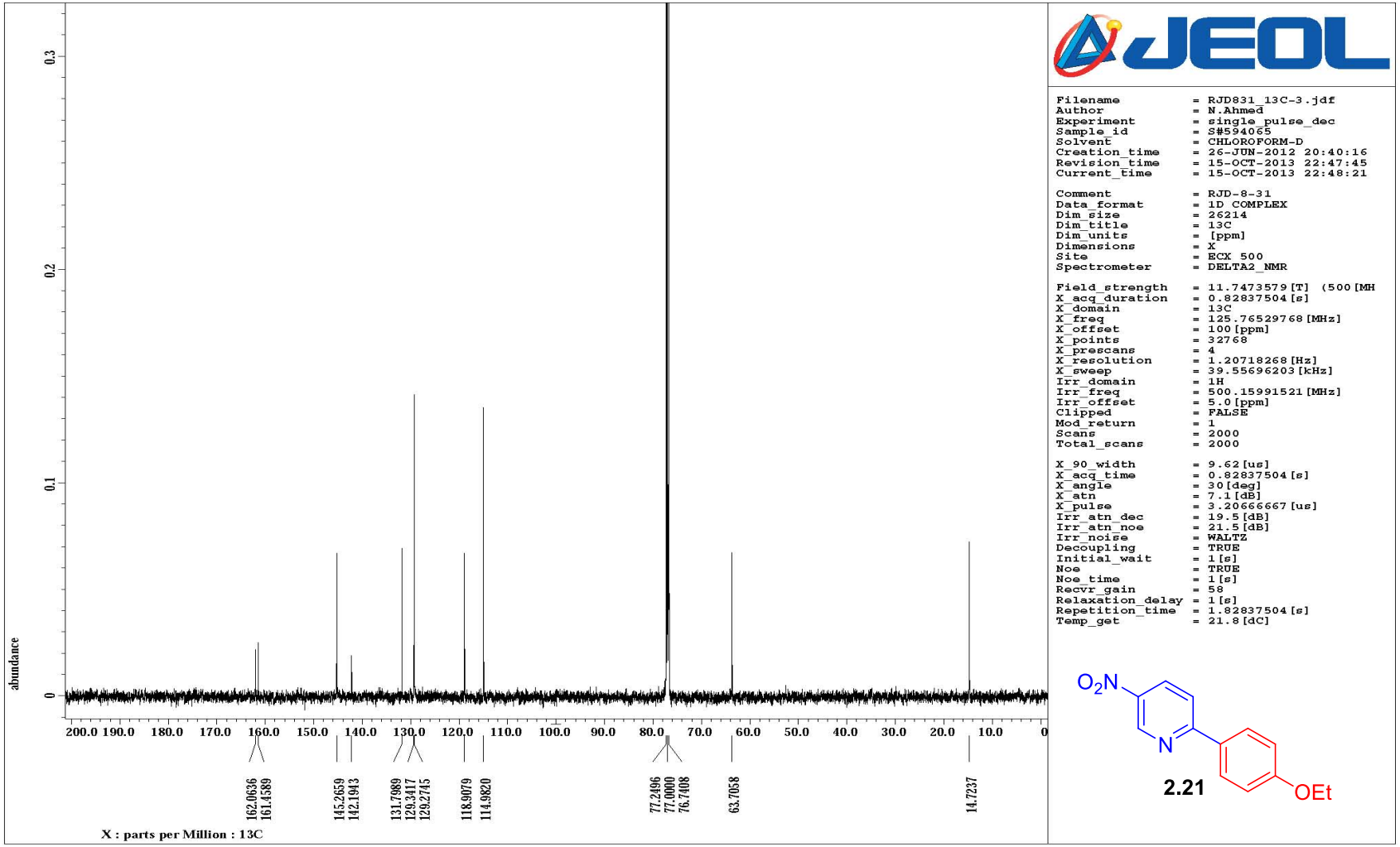
^{13}C NMR spectrum of 2-(4-methoxyphenyl)-5-nitropyridine (**2.18**)



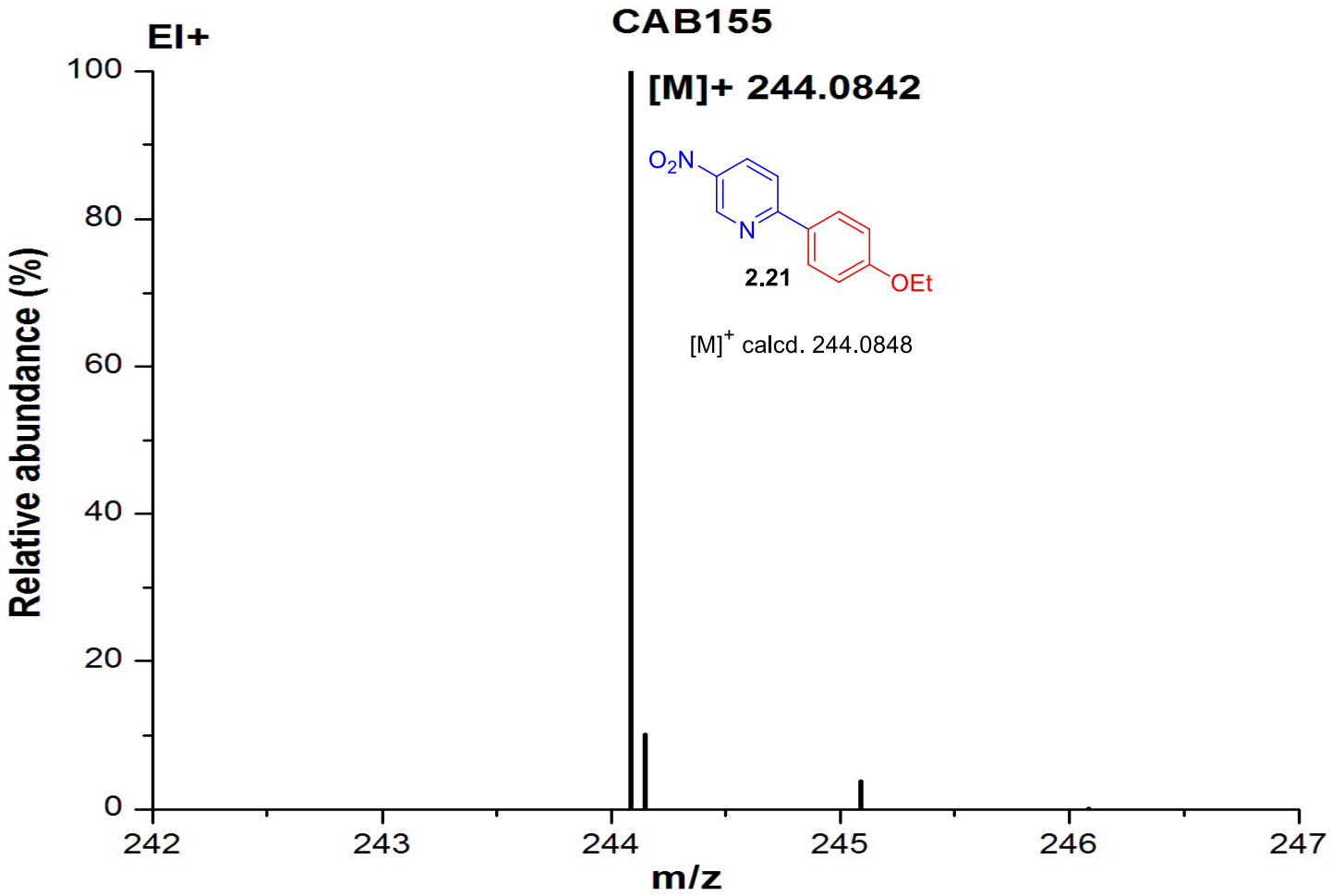
HRMS spectrum of 2-(4-methoxyphenyl)-5-nitropyridine (**2.18**)



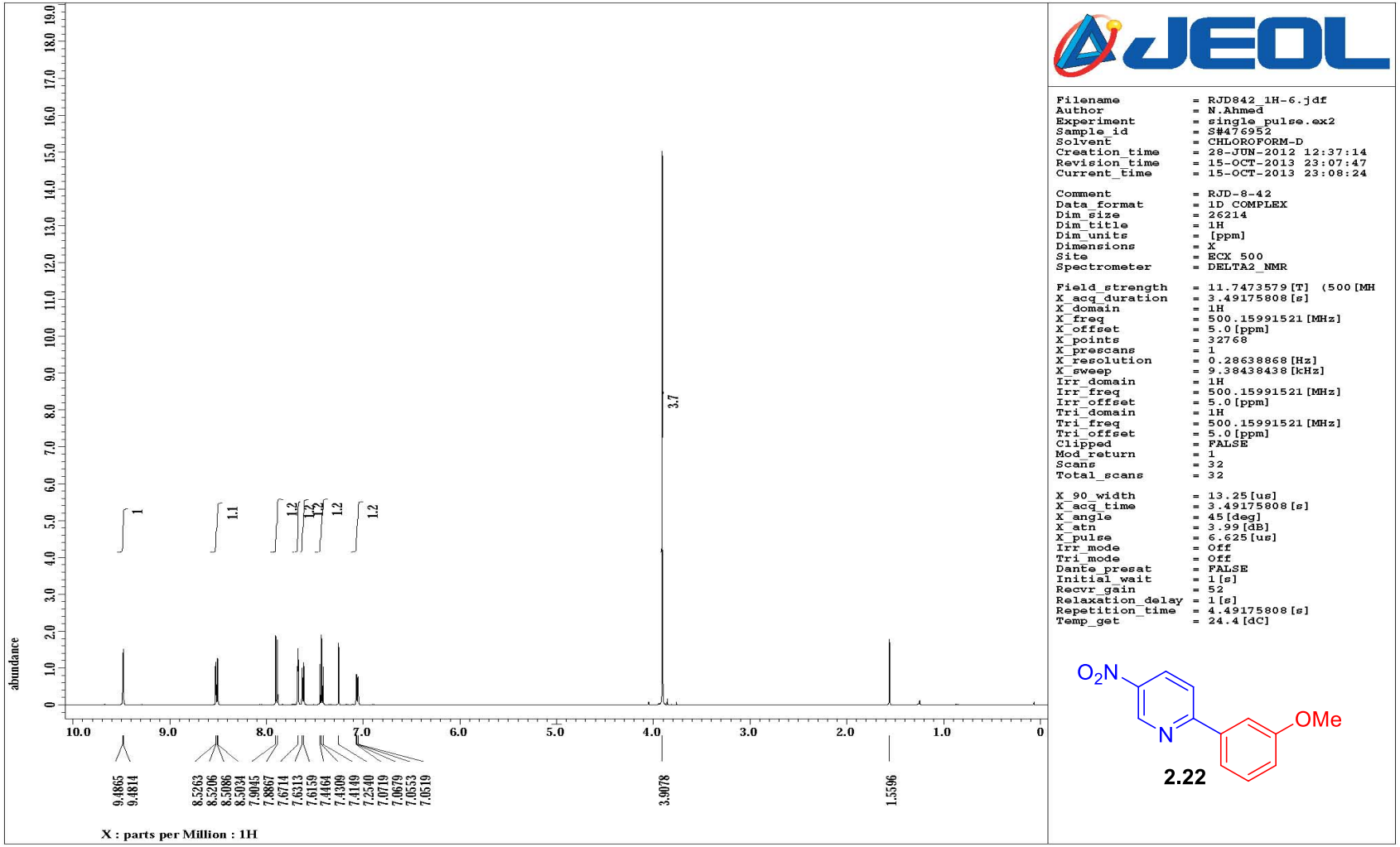
^{1}H NMR spectrum of 2-(4-ethoxyphenyl)-5-nitropyridine (**2.21**)



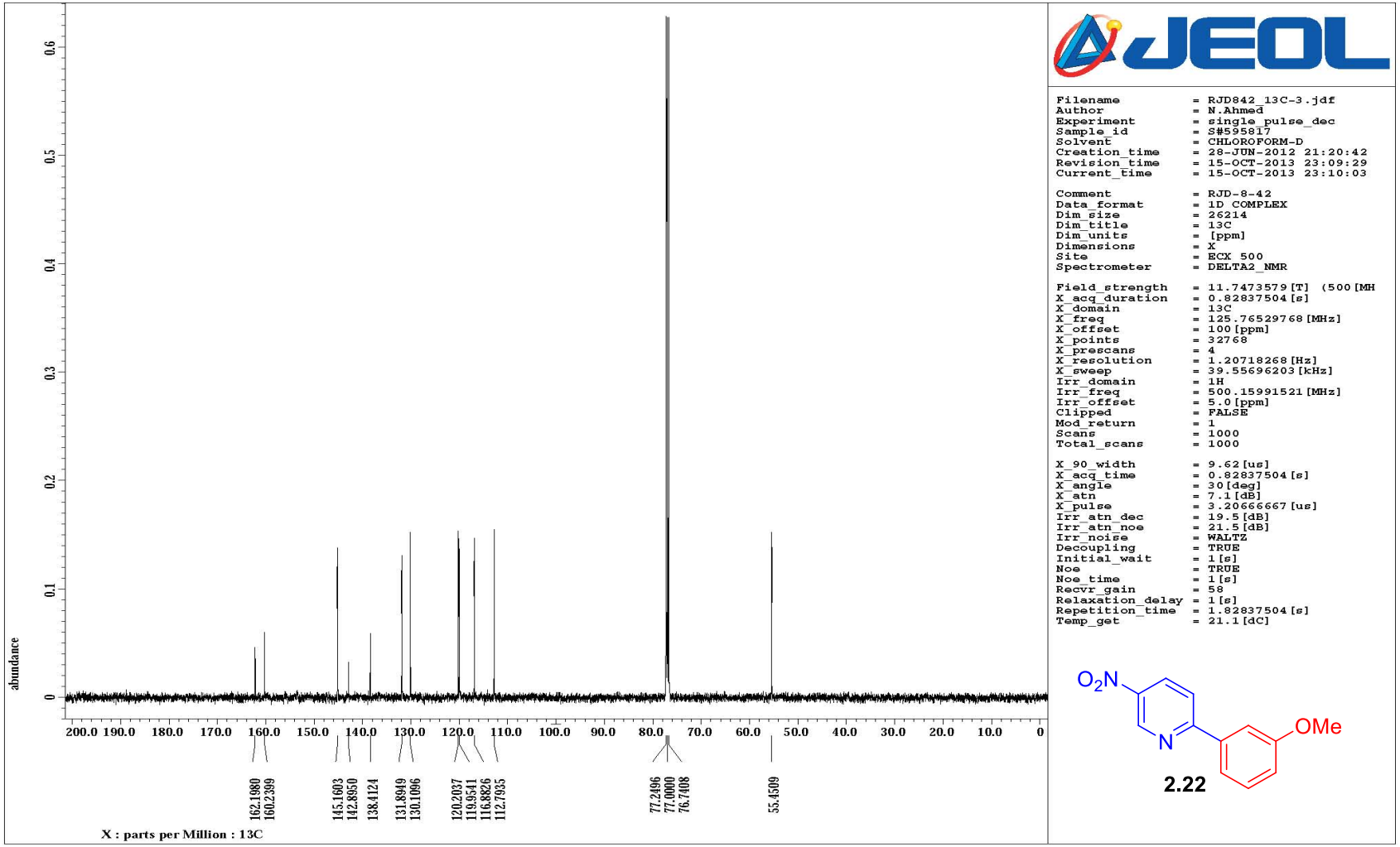
^{13}C NMR spectrum of 2-(4-ethoxyphenyl)-5-nitropyridine (**2.21**)



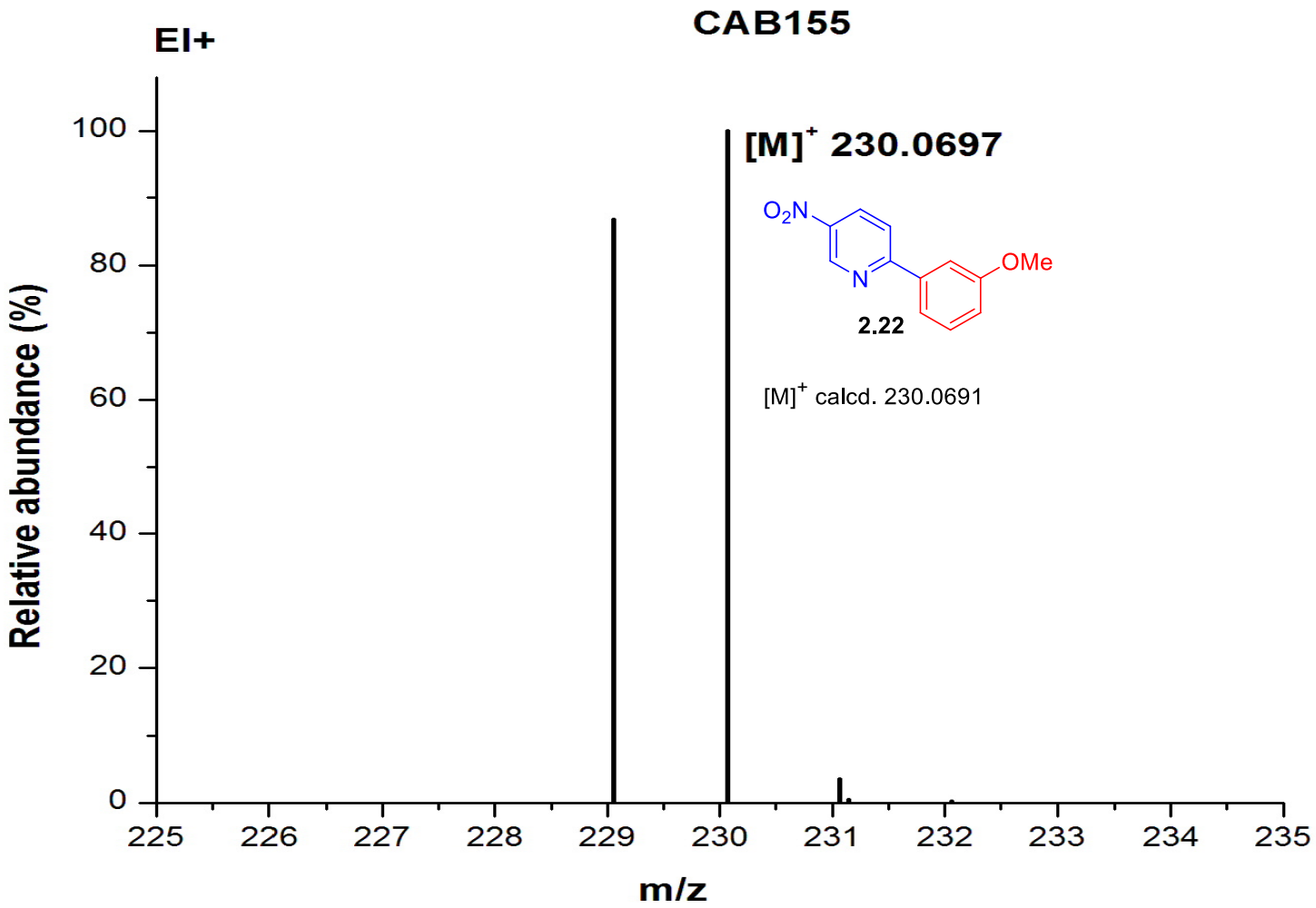
HRMS spectrum of 2-(4-ethoxyphenyl)-5-nitropyridine (**2.21**)



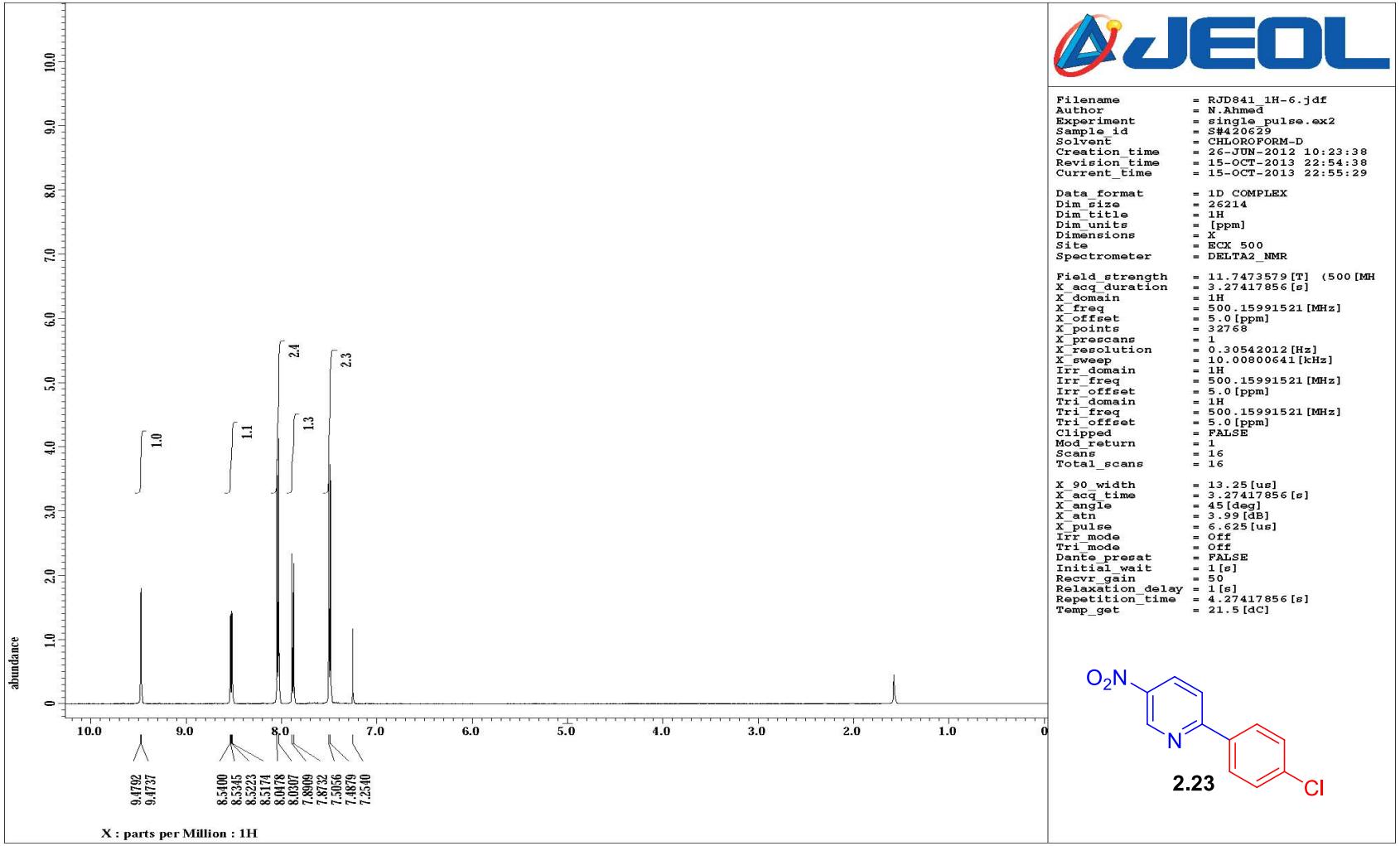
^{1}H NMR spectrum of 2-(3-methoxyphenyl)-5-nitropyridine (**2.22**)



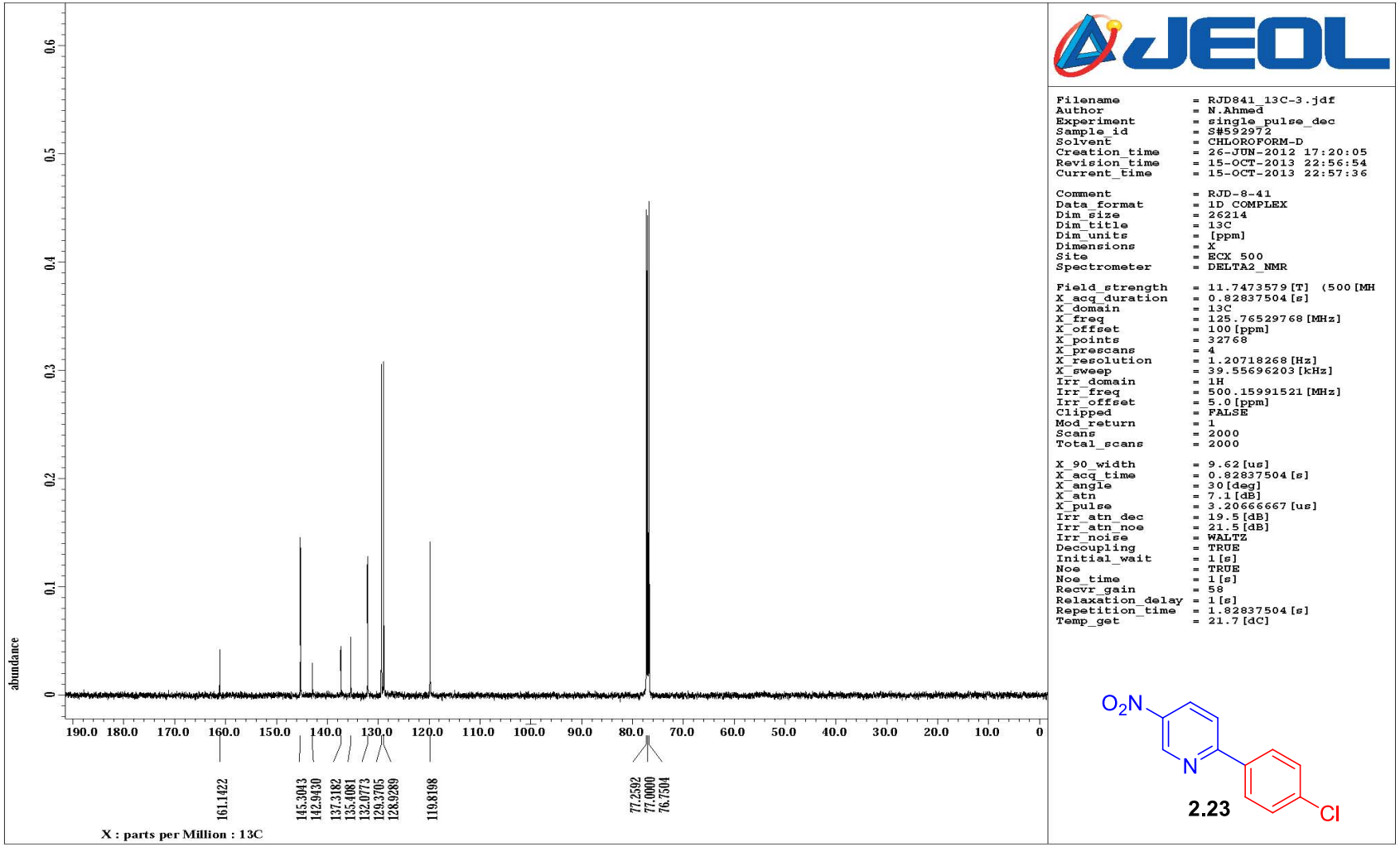
^{13}C NMR spectrum of 2-(3-methoxyphenyl)-5-nitropyridine (**2.22**)



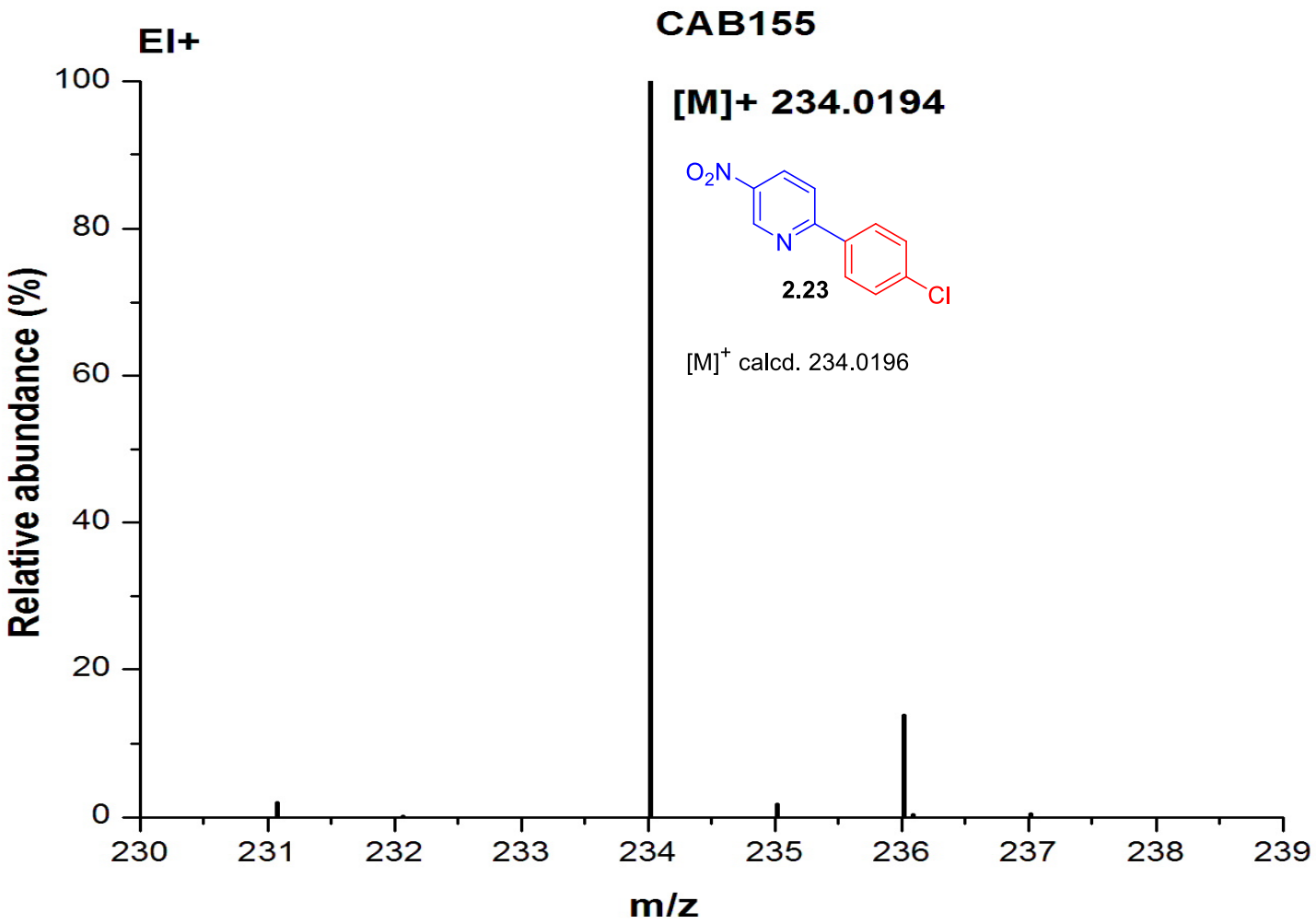
HRMS spectrum of 2-(3-methoxyphenyl)-5-nitropyridine (**2.22**)



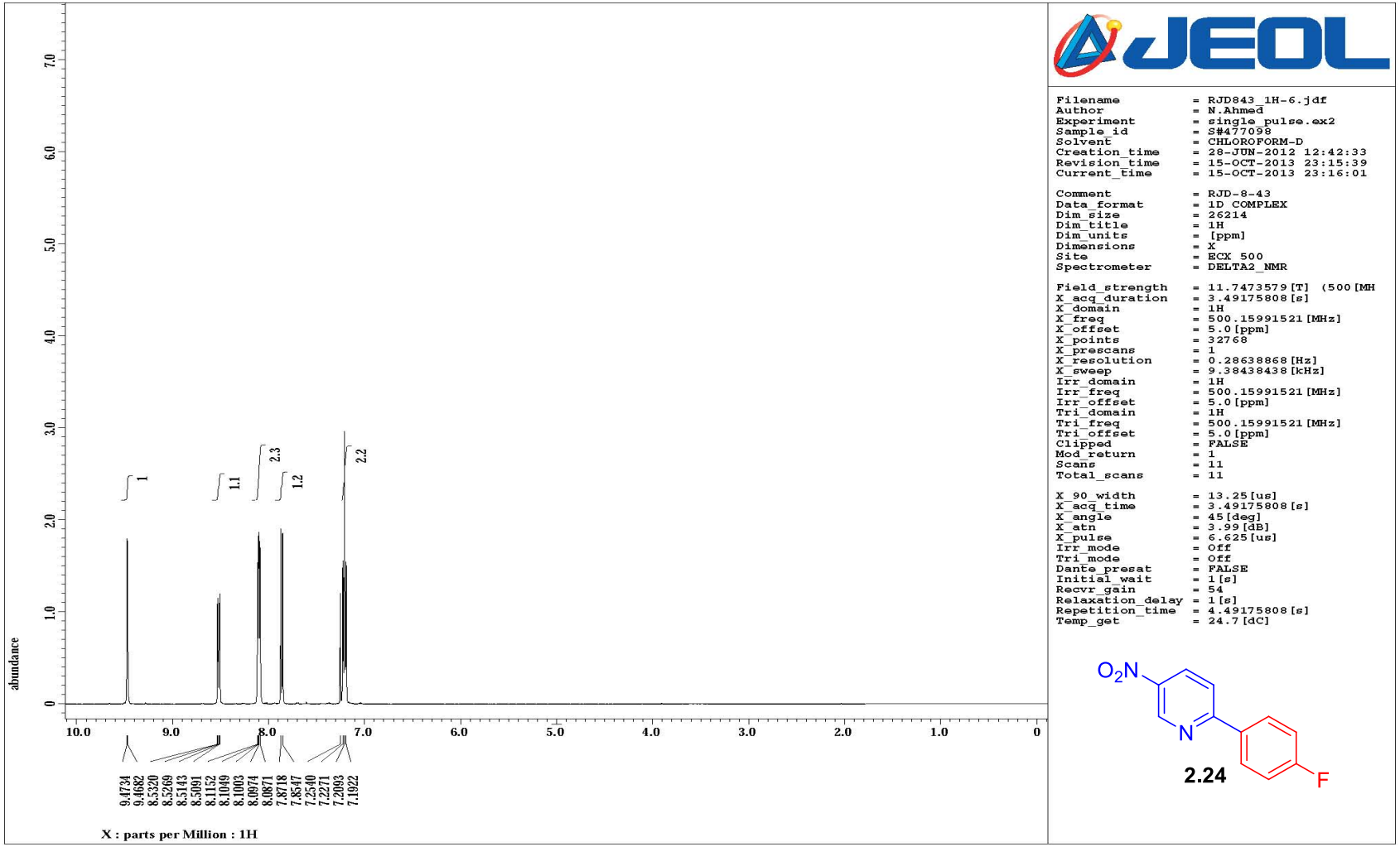
^{1}H NMR spectrum of 2-(4-chlorophenyl)-5-nitropyridine (**2.23**)



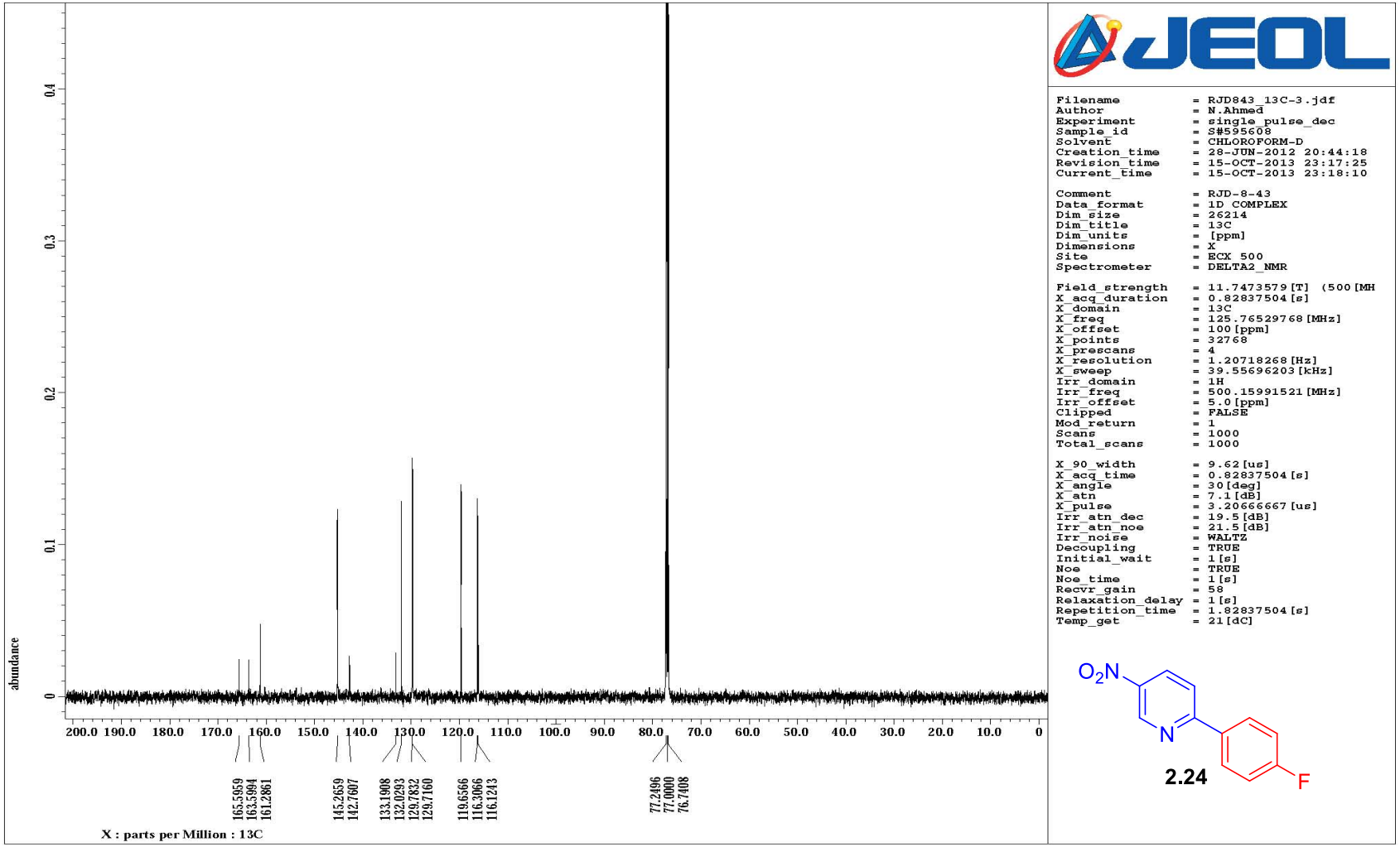
^{13}C NMR spectrum of 2-(4-chlorophenyl)-5-nitropyridine (**2.23**)



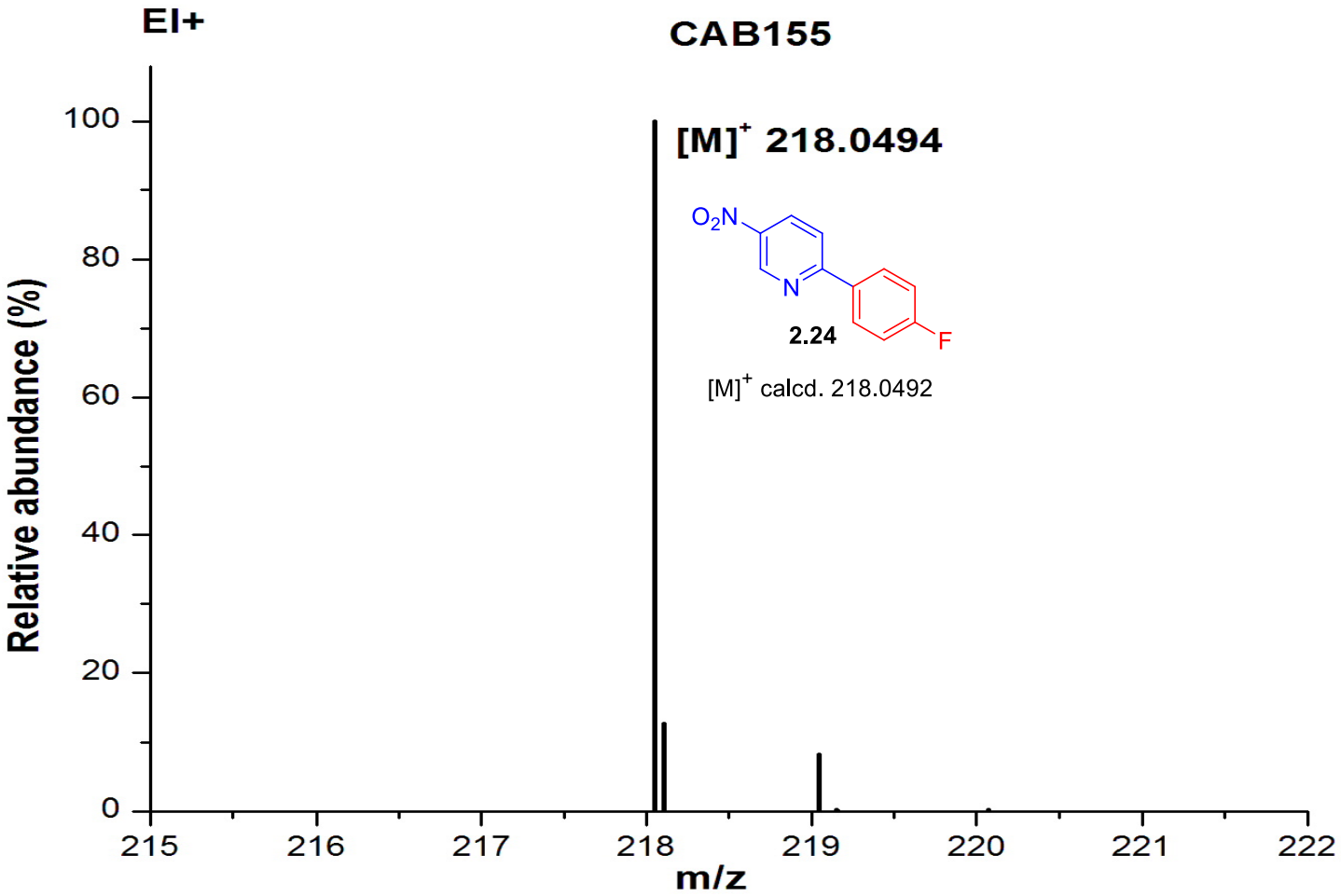
HRMS spectrum of 2-(4-chlorophenyl)-5-nitropyridine (**2.23**)



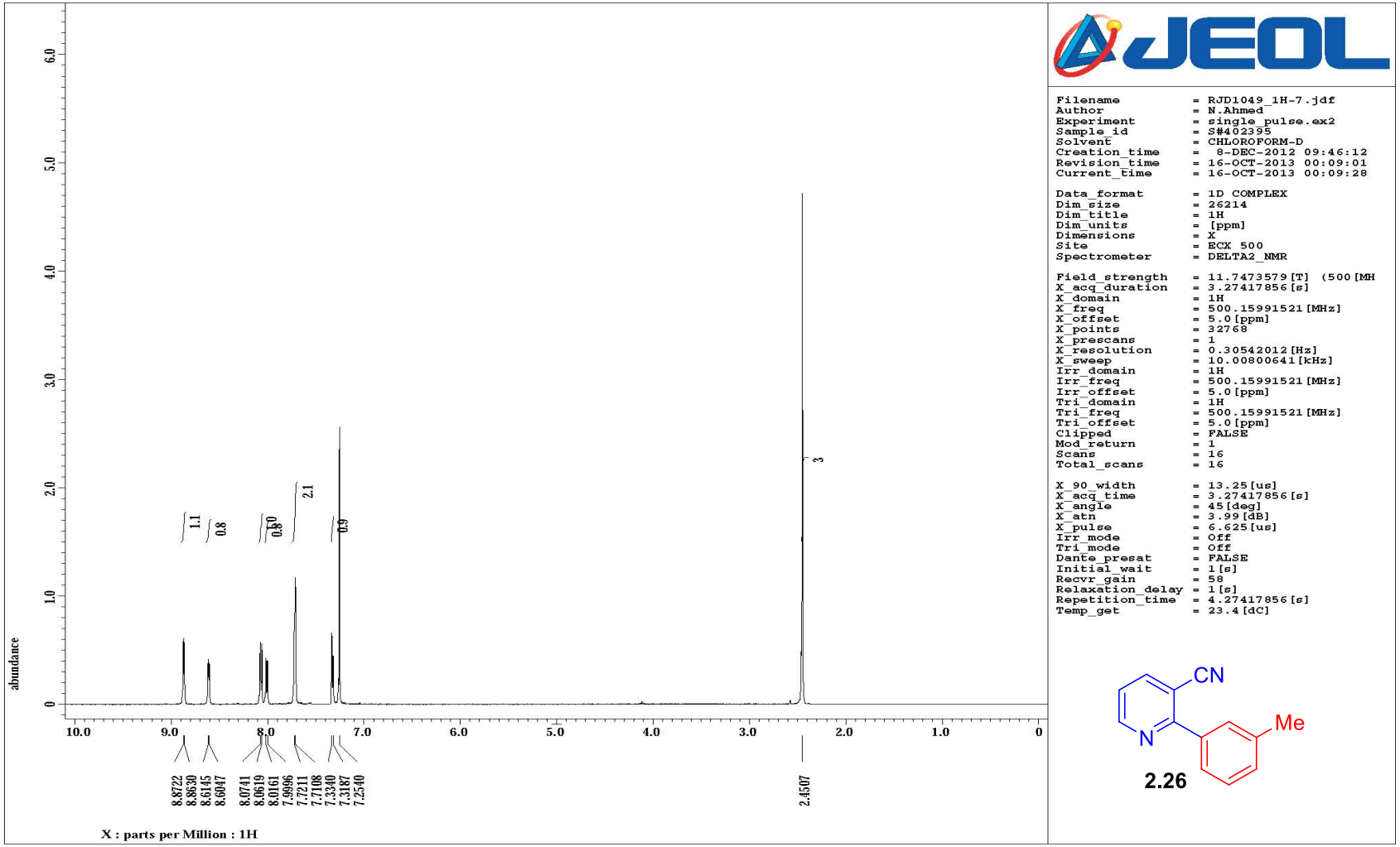
^{1}H NMR spectrum of 2-(4-fluorophenyl)-5-nitropyridine (**2.24**)



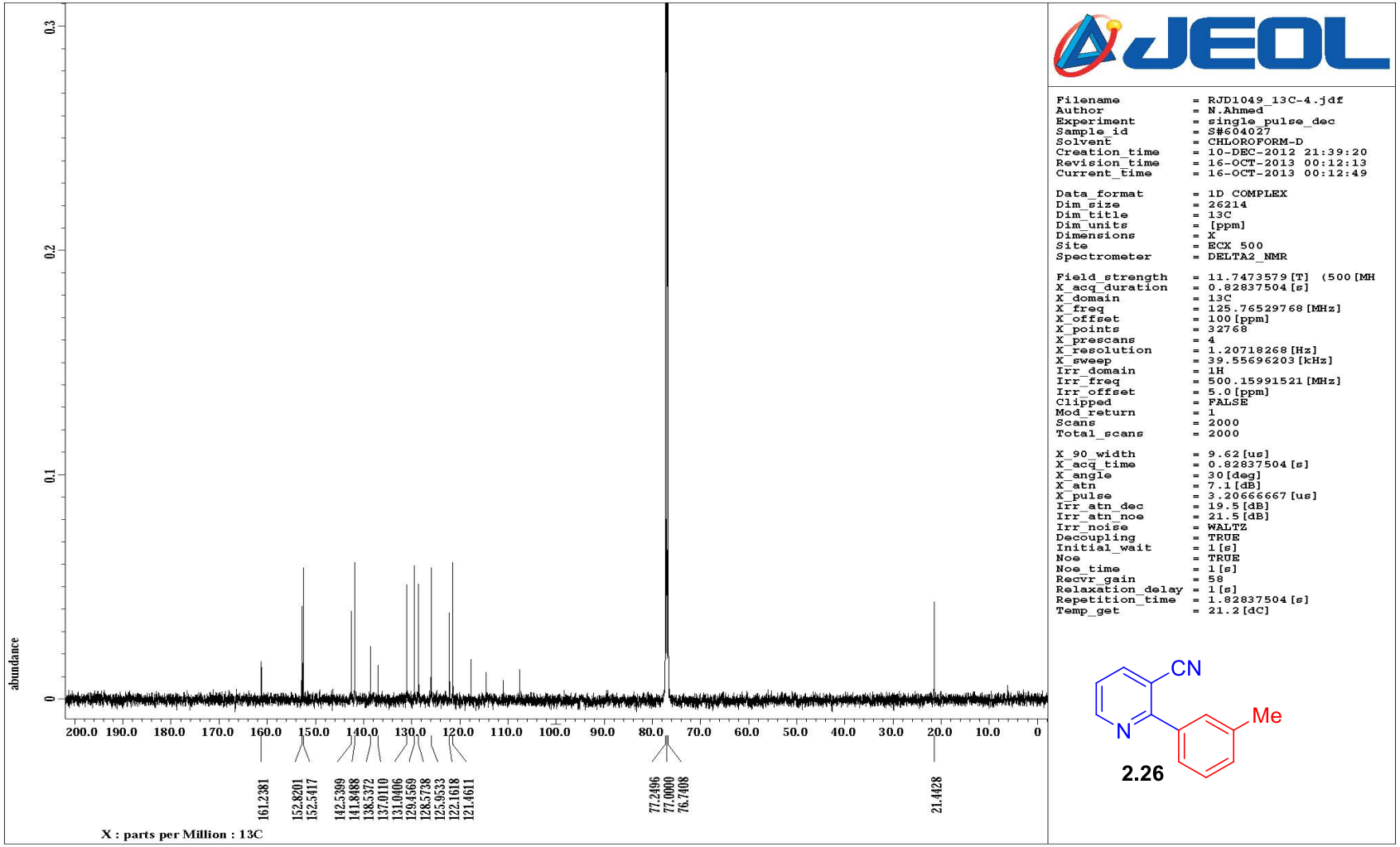
^{13}C NMR spectrum of 2-(4-fluorophenyl)-5-nitropyridine (**2.24**)



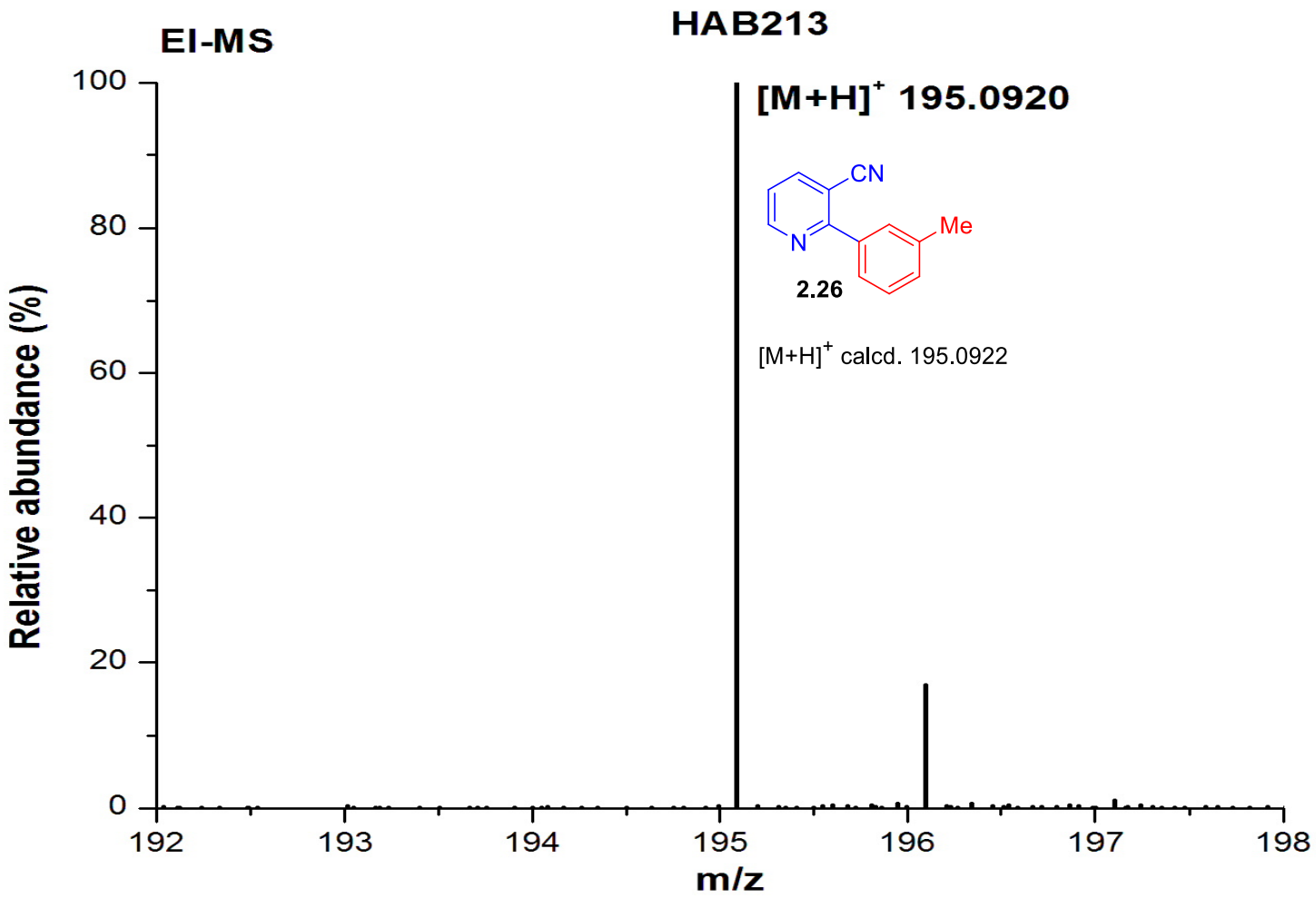
HRMS spectrum of 2-(4-fluorophenyl)-5-nitropyridine (**2.24**)



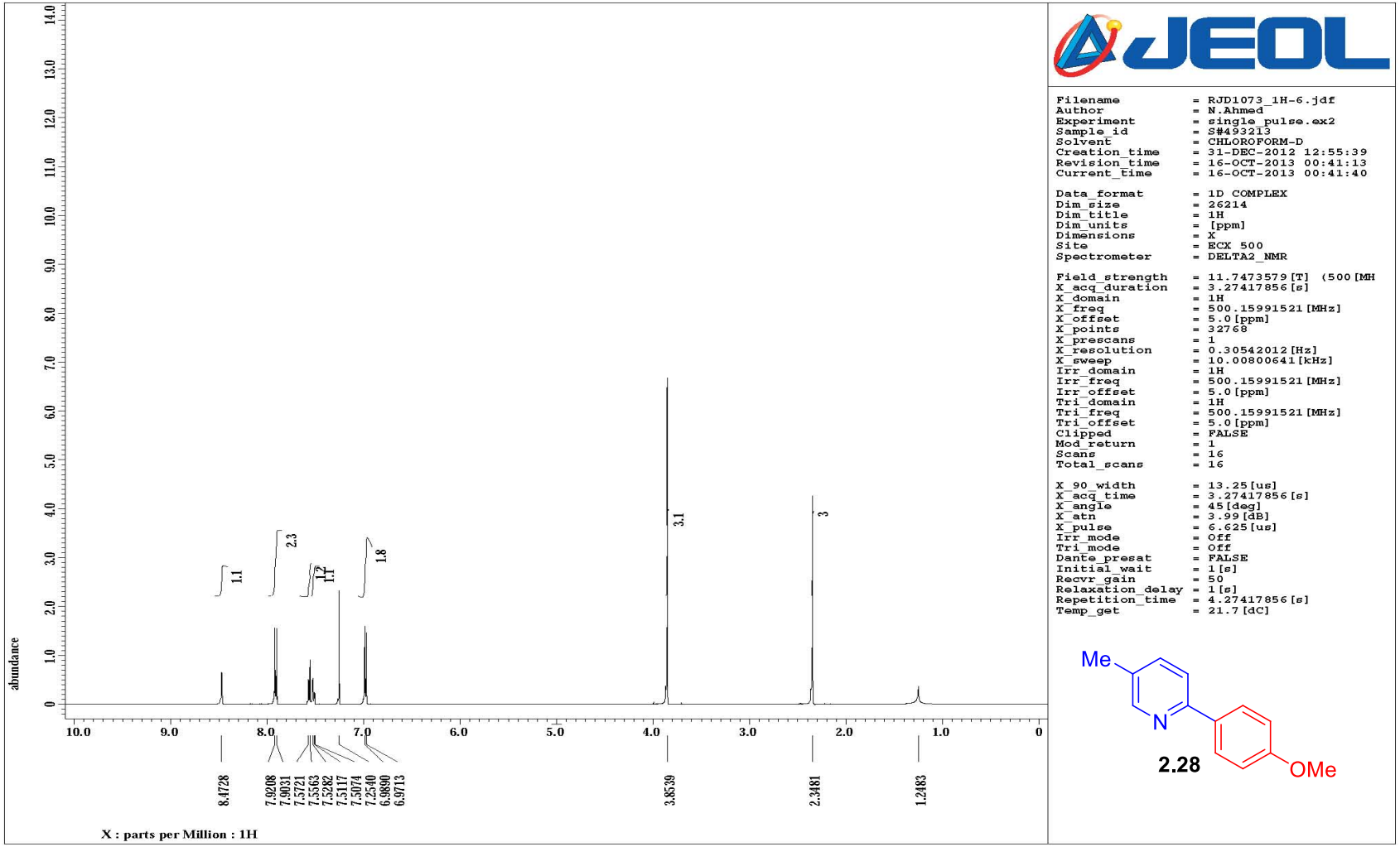
^{1}H NMR spectrum of 2-(3-methylphenyl)-3-cyanopyridine (**2.26**)



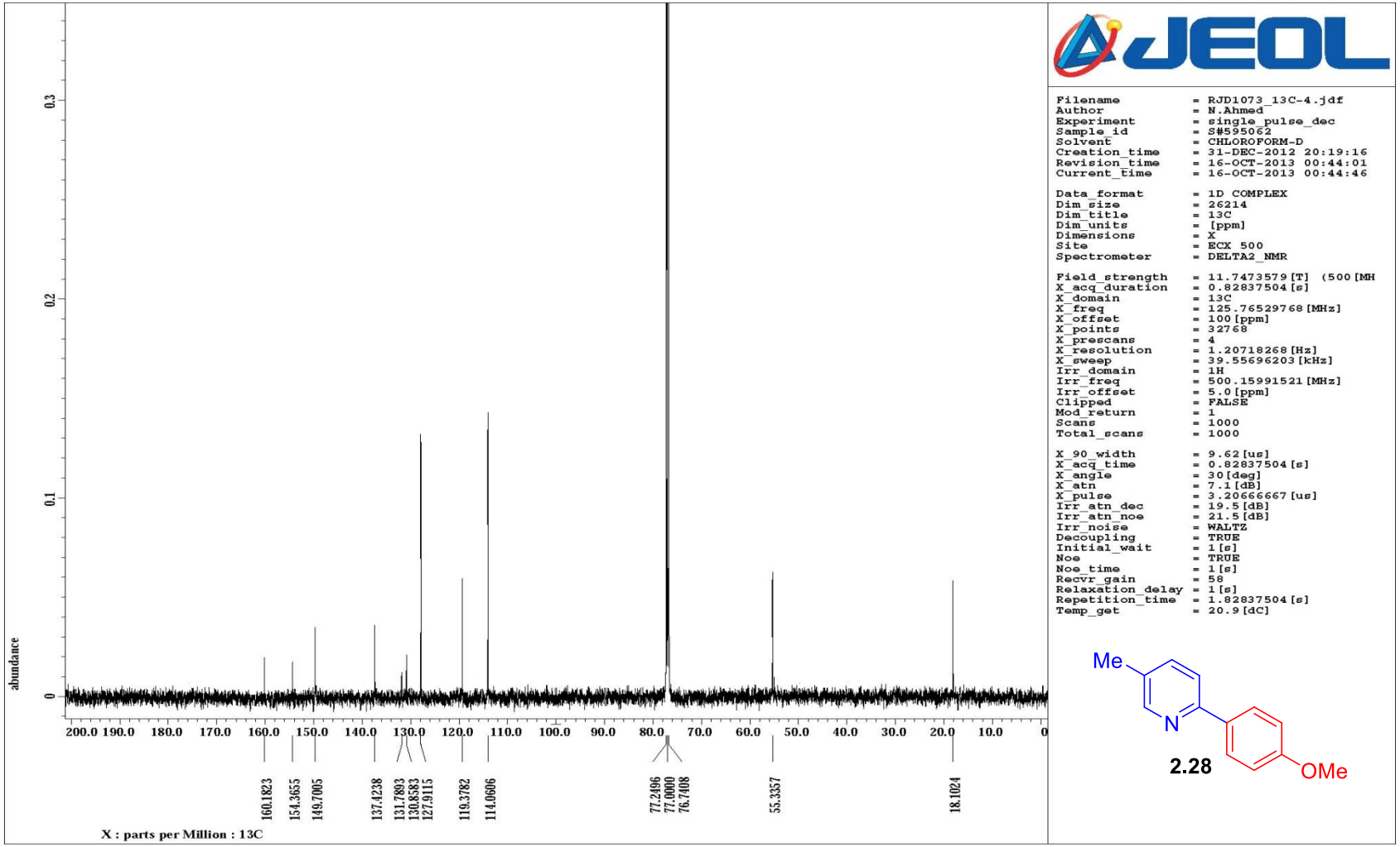
^{13}C NMR spectrum of 2-(3-methylphenyl)-3-cyanopyridine (**2.26**)



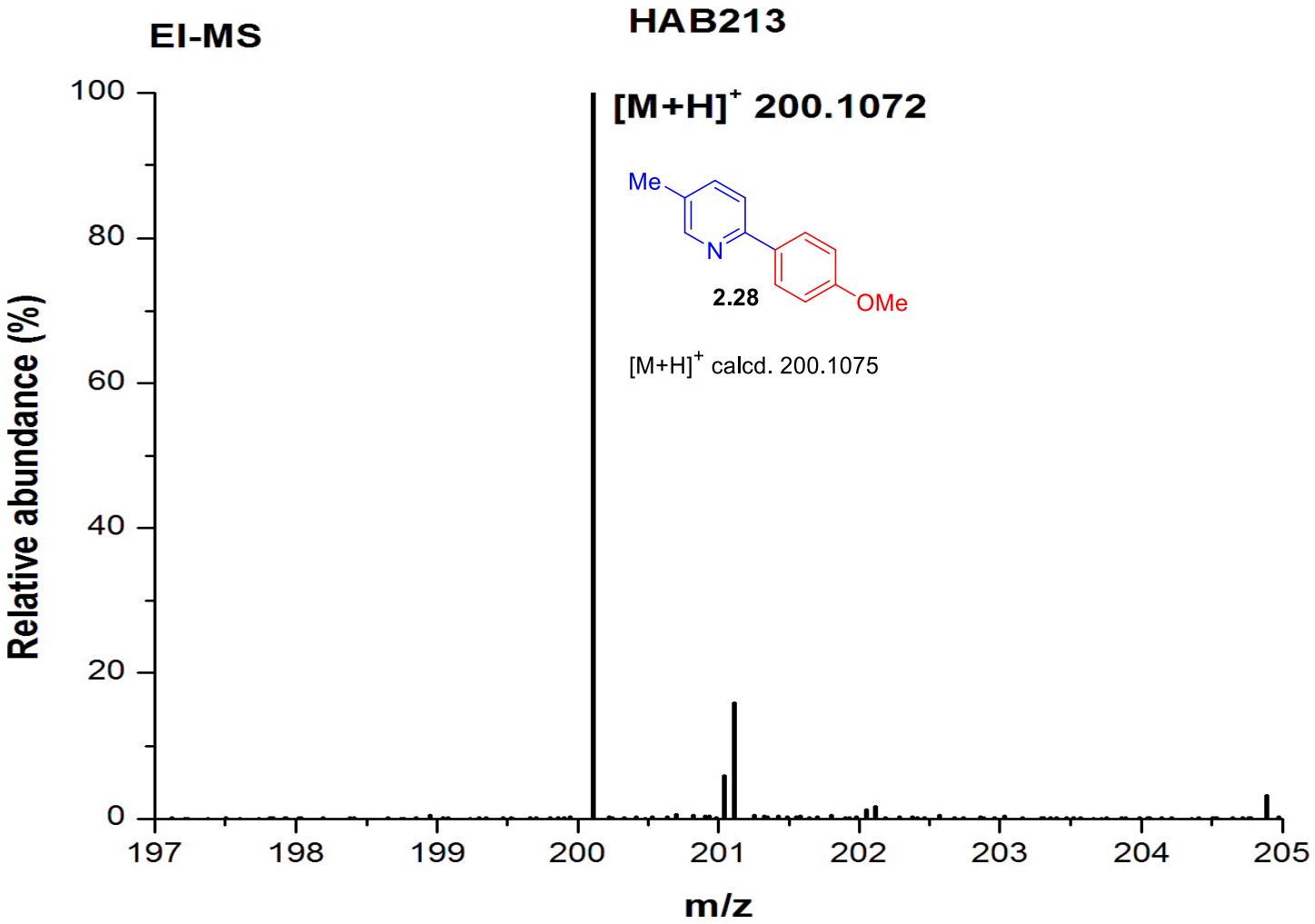
HRMS spectrum of 2-(3-methylphenyl)-3-cyanopyridine (**2.26**)



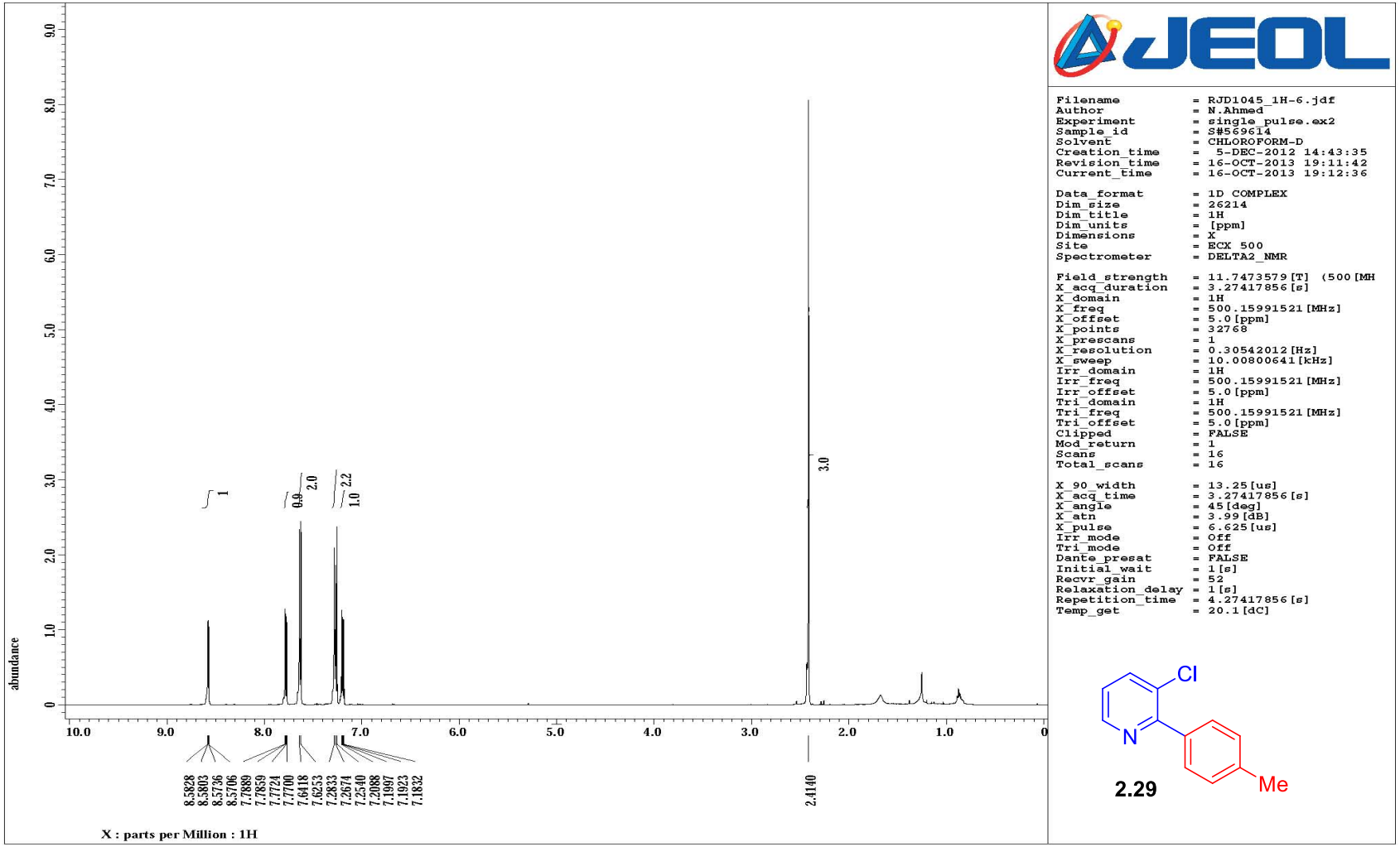
^{1}H NMR spectrum of 2-(4-methoxyphenyl)-5-methylpyridine (**2.28**)



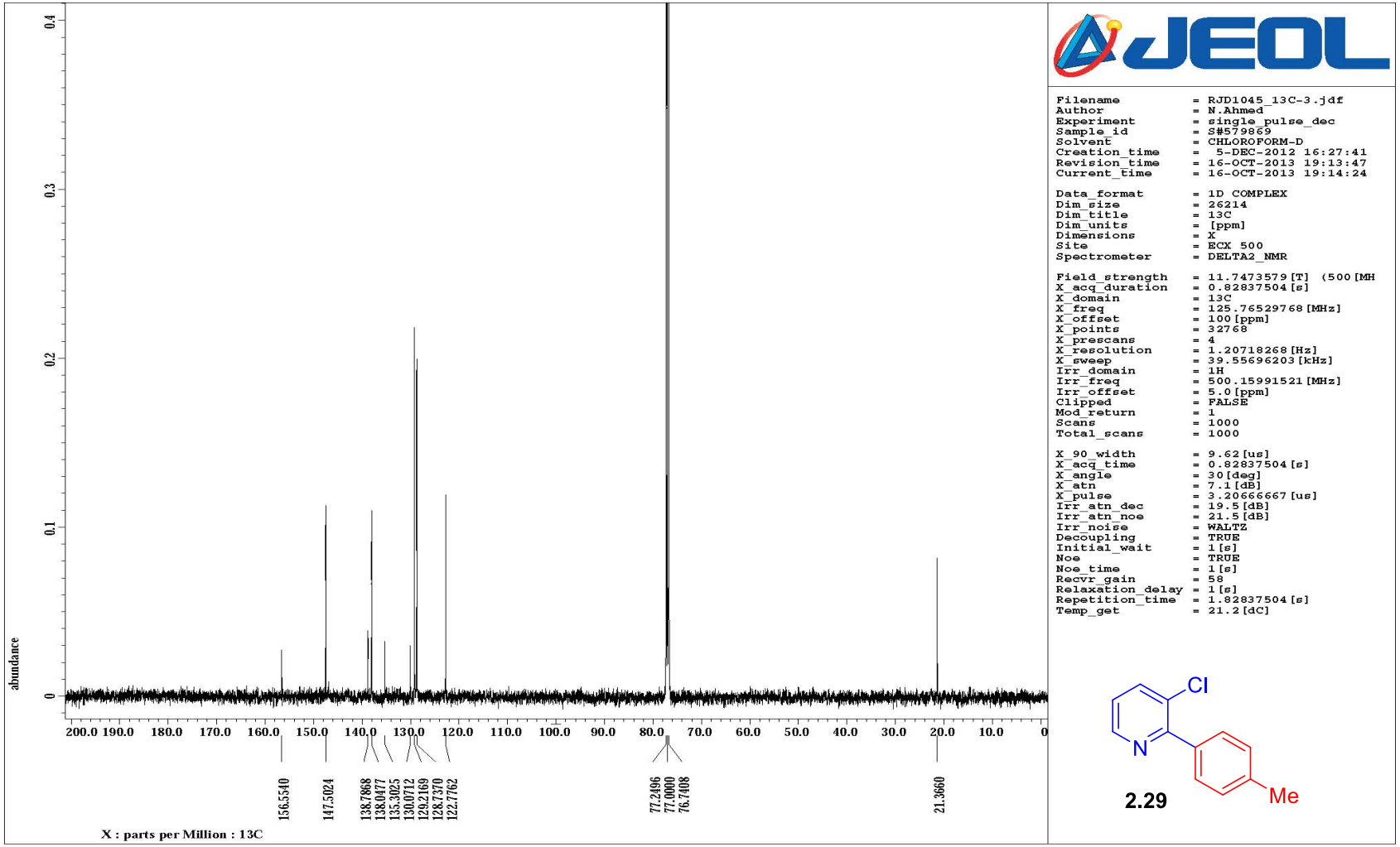
^{13}C NMR spectrum of 2-(4-methoxyphenyl)-5-methylpyridine (**2.28**)



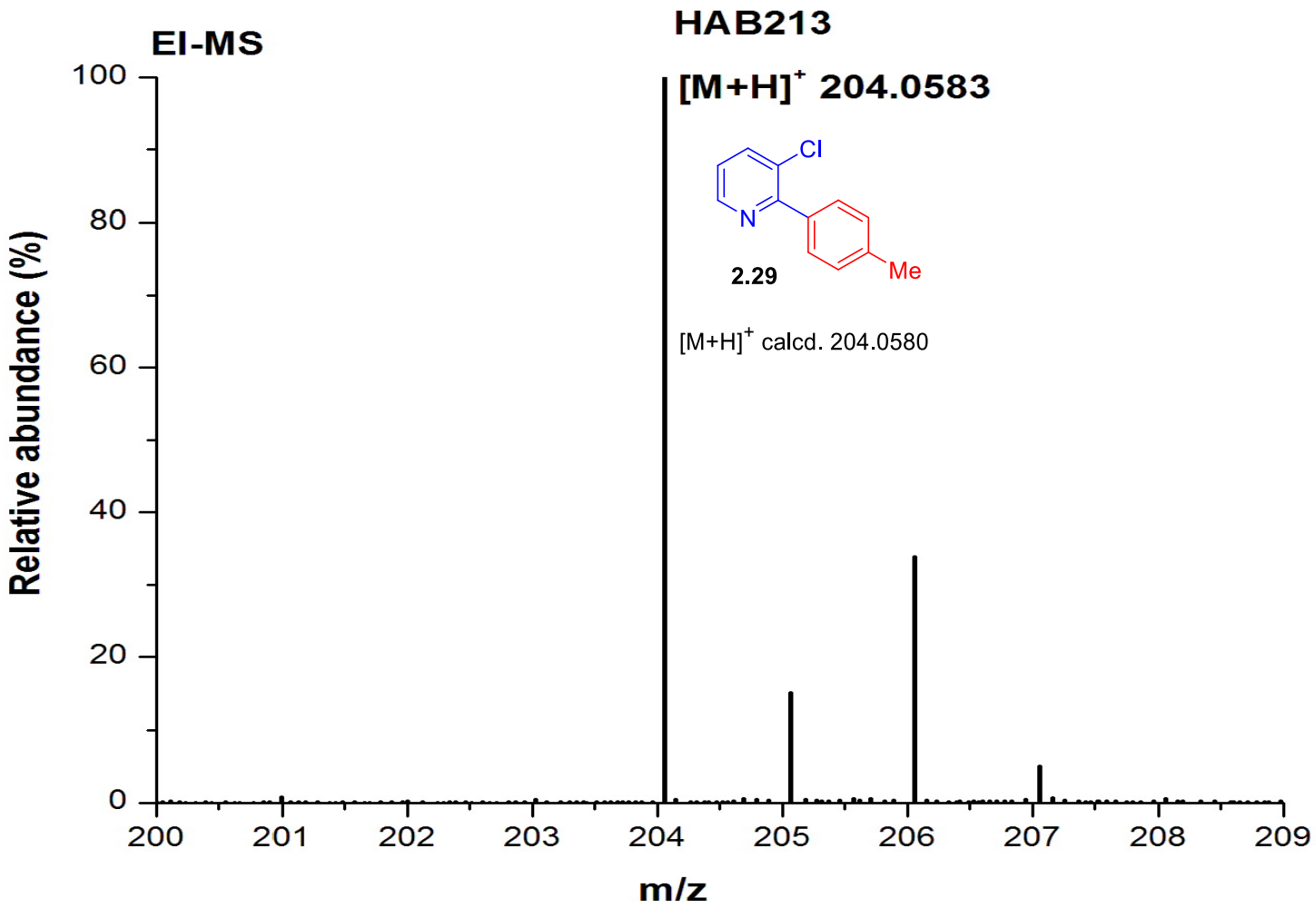
HRMS spectrum of 2-(4-methoxyphenyl)-5-methylpyridine (**2.28**)



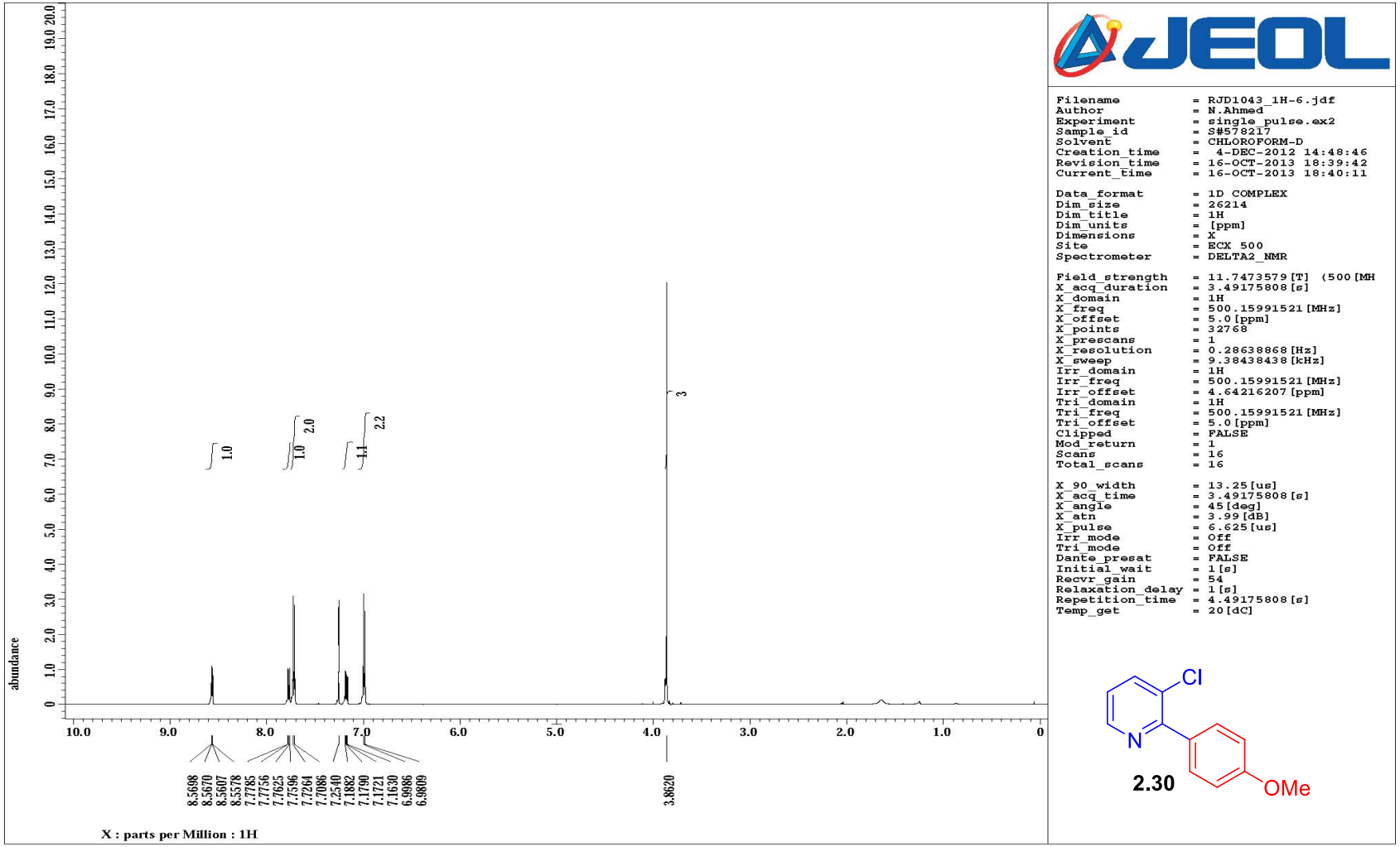
^{1}H NMR spectrum of 3-chloro-2-(4-methylphenyl)pyridine (**2.29**)



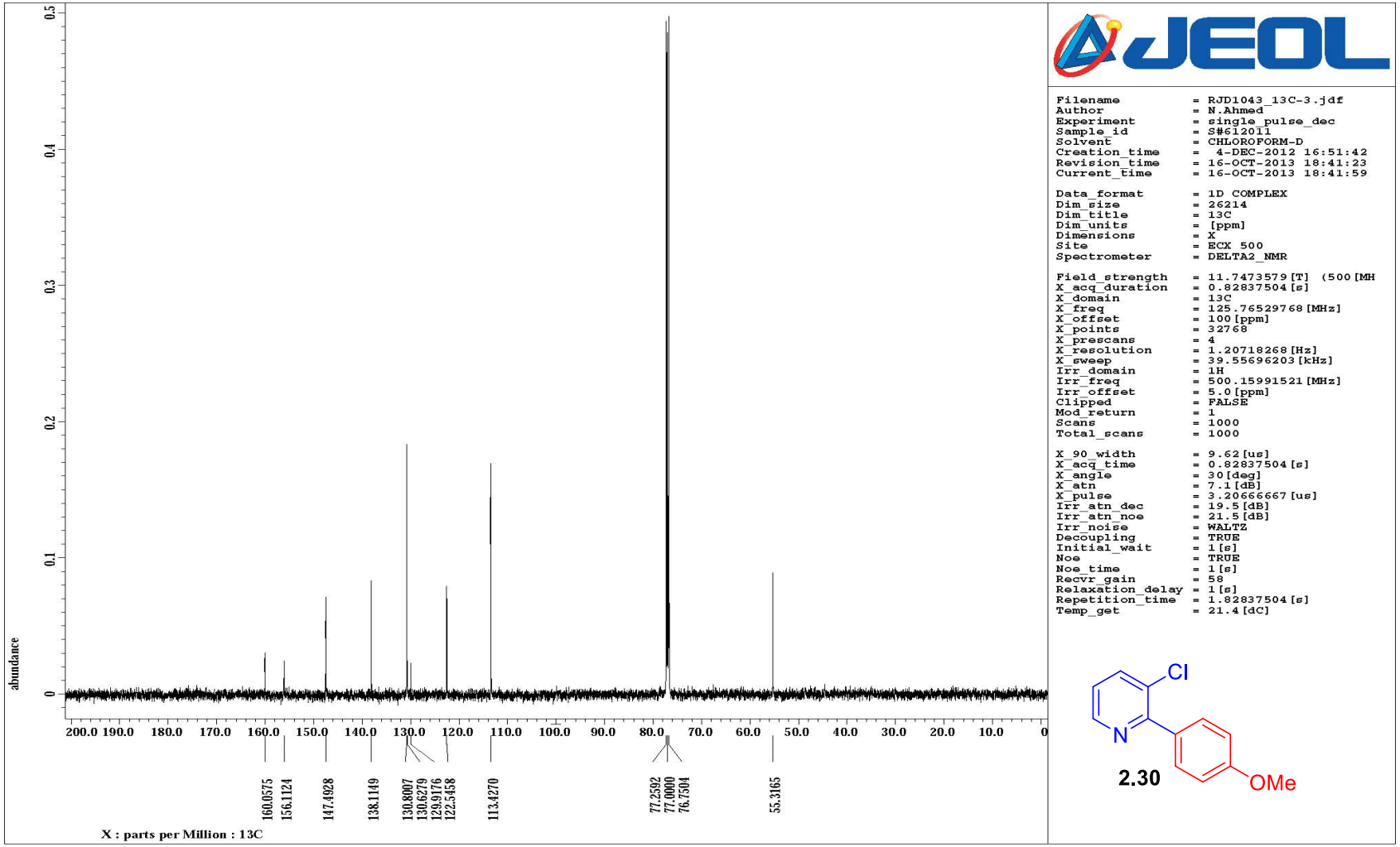
^{13}C NMR spectrum of 3-chloro-2-(4-methylphenyl)pyridine (**2.29**)



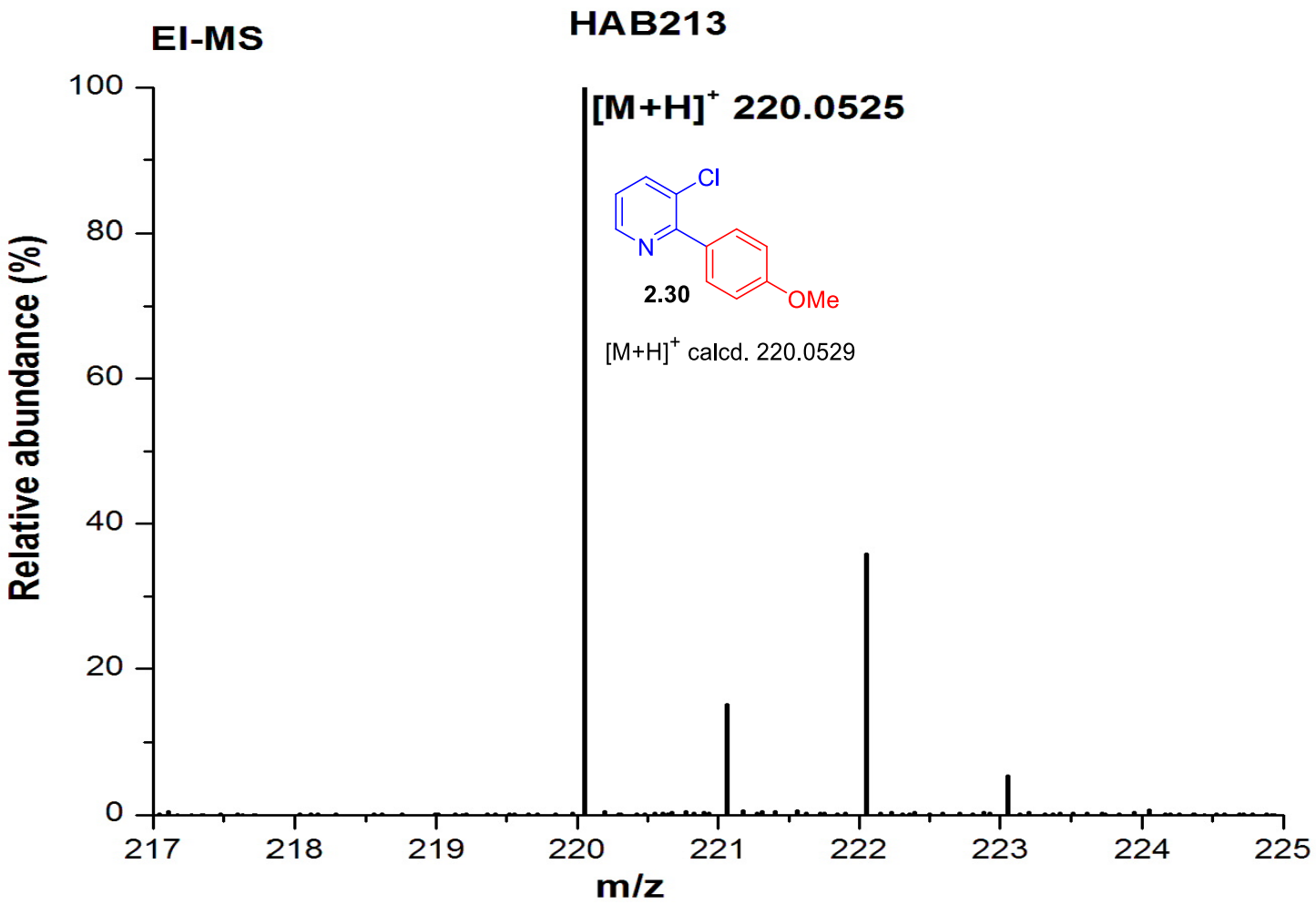
HRMS spectrum of 3-chloro-2-(4-methylphenyl)pyridine (**2.29**)



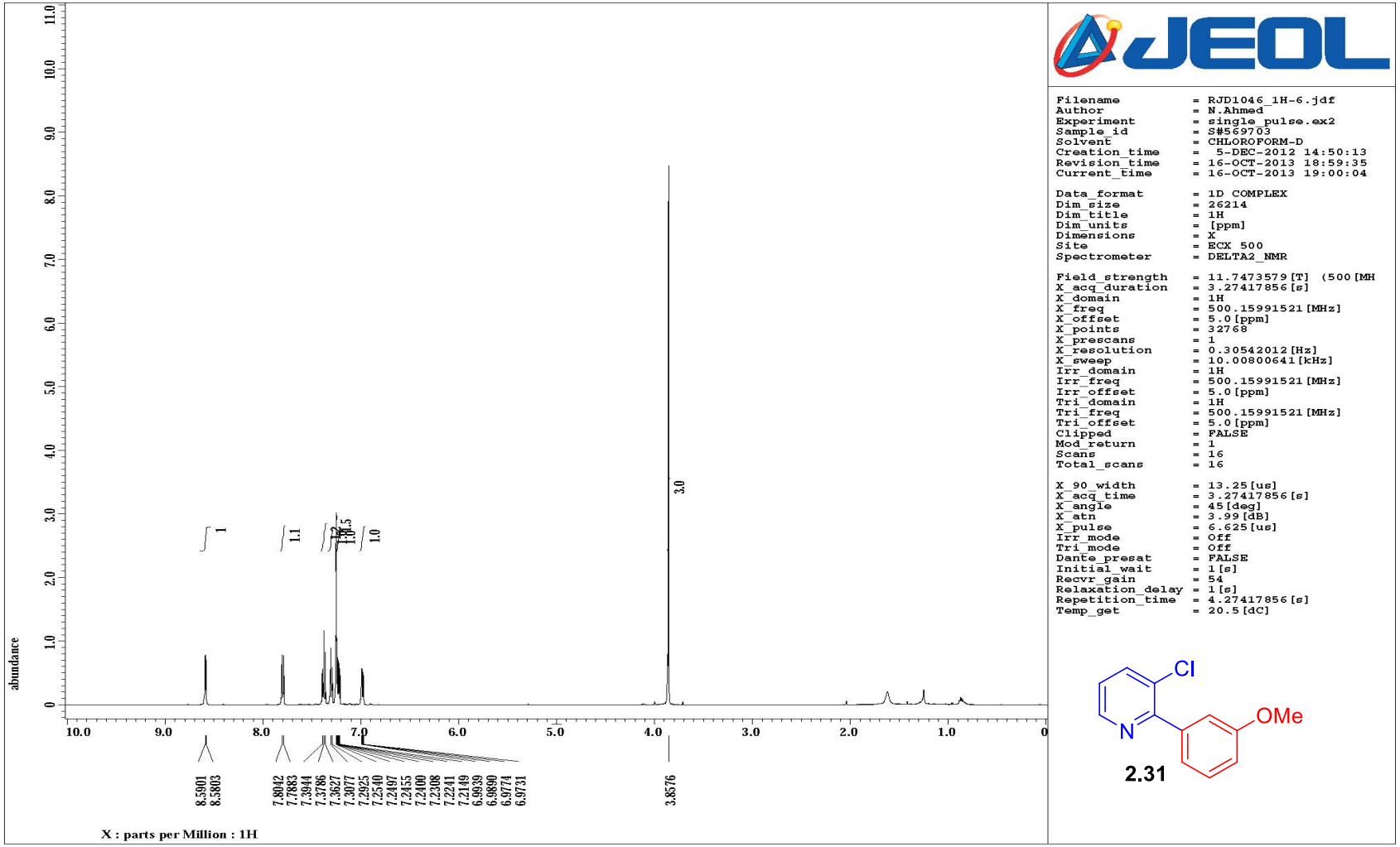
^{1}H NMR spectrum of 3-chloro-2-(4-methoxyphenyl)pyridine (**2.30**)



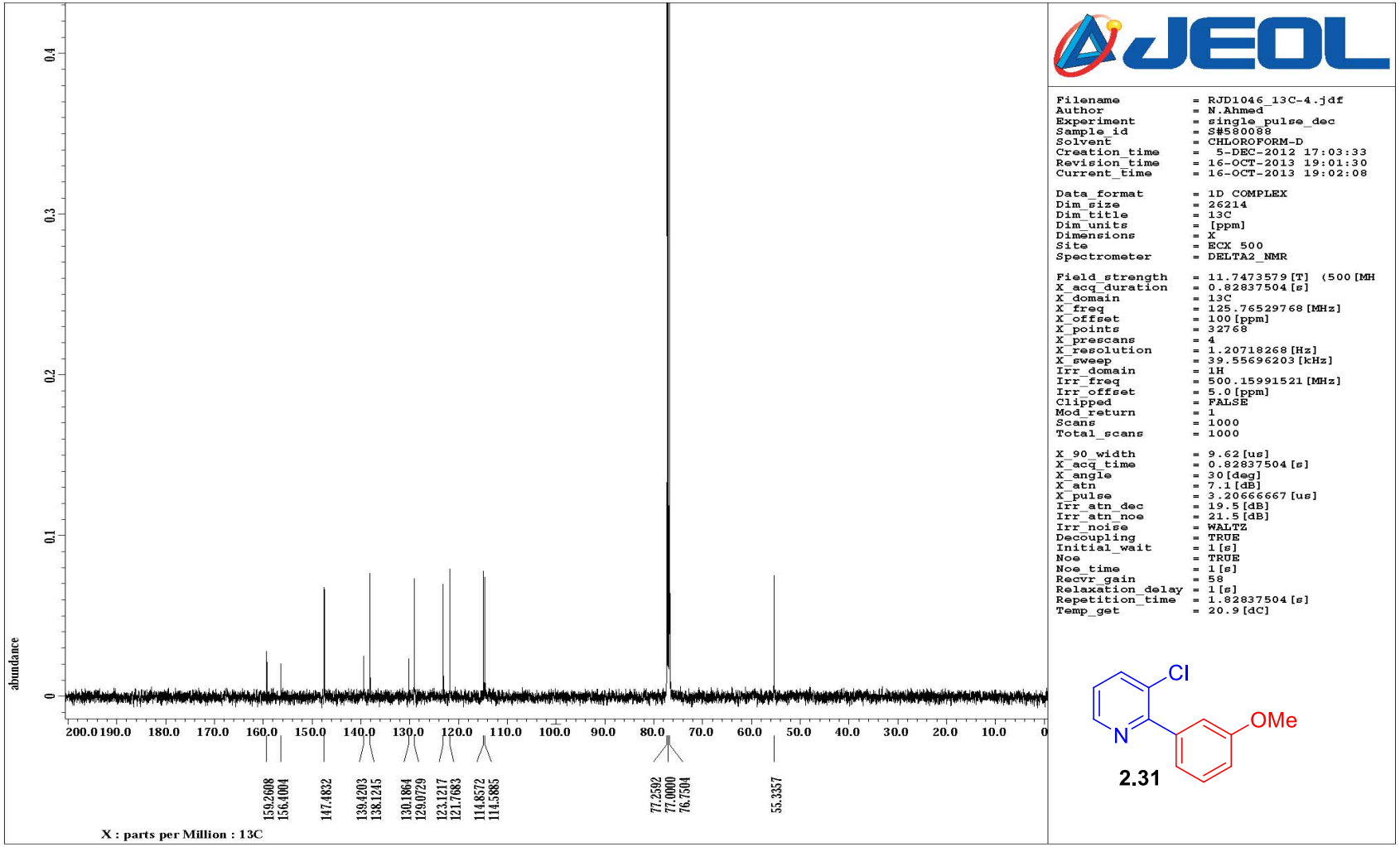
^{13}C NMR spectrum of 3-chloro-2-(4-methoxyphenyl)pyridine (**2.30**)



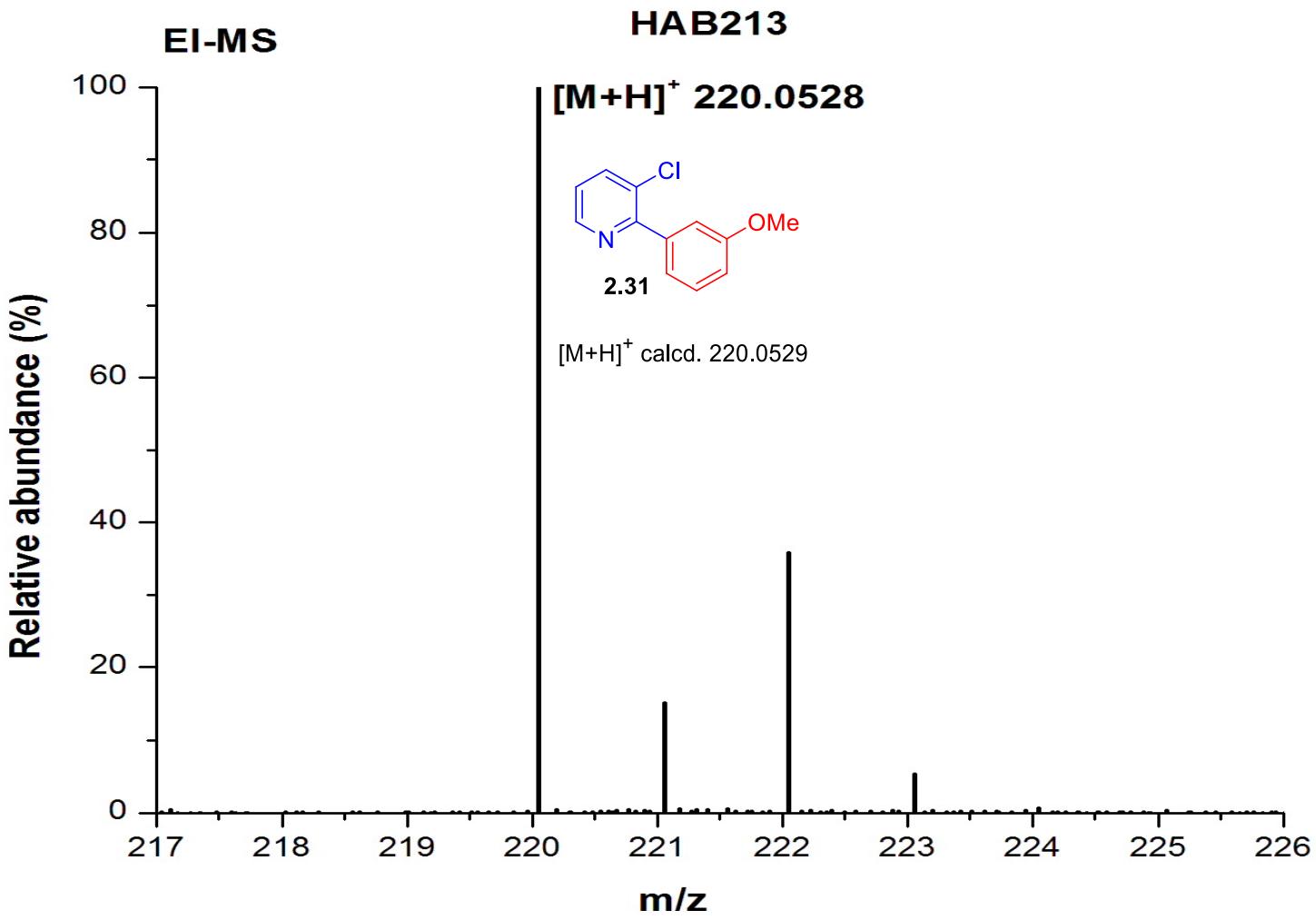
HRMS spectrum of 3-chloro-2-(4-methoxyphenyl)pyridine (**2.30**)



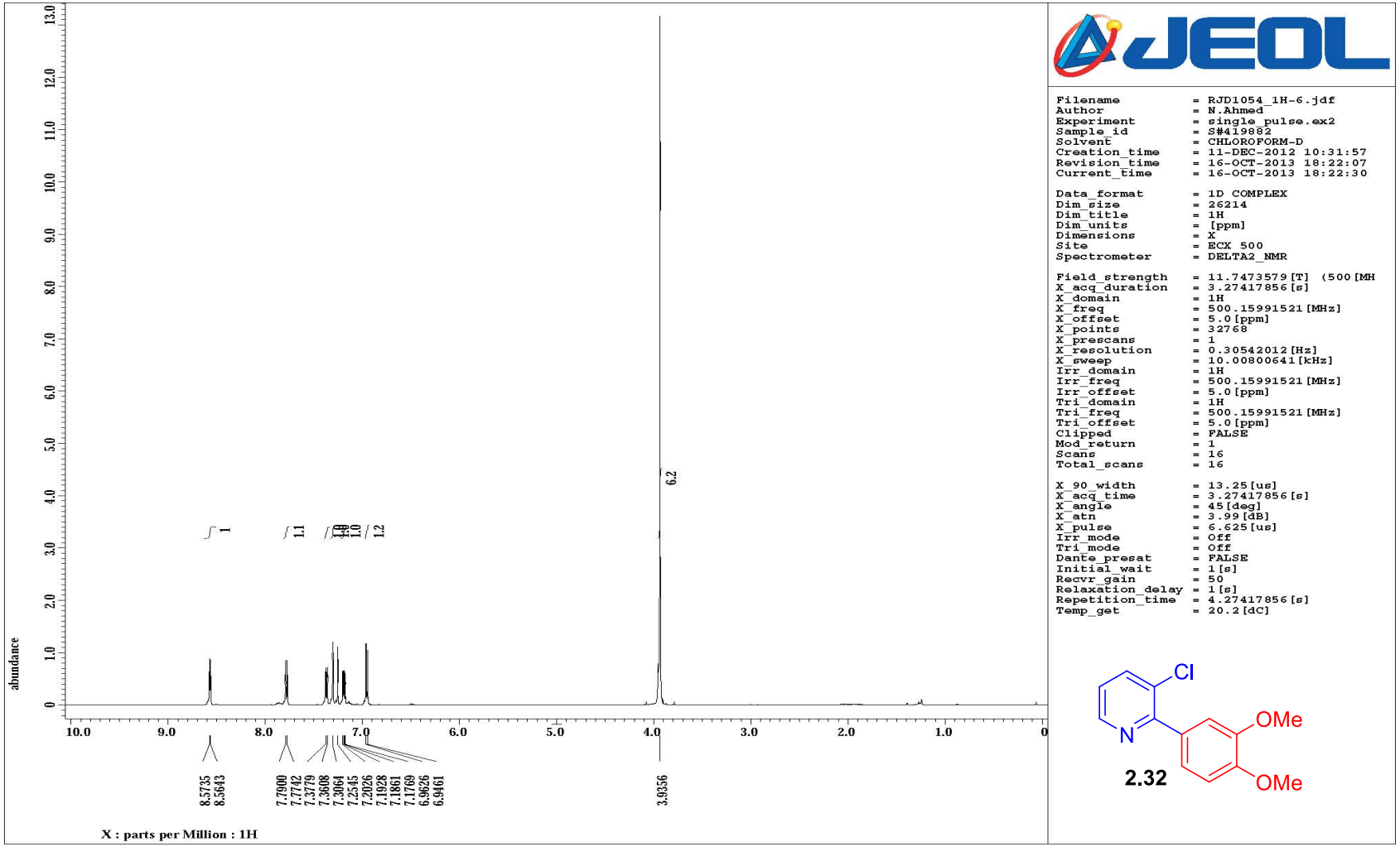
^{1}H NMR spectrum of 3-chloro-2-(3-methoxyphenyl)pyridine (**2.31**)



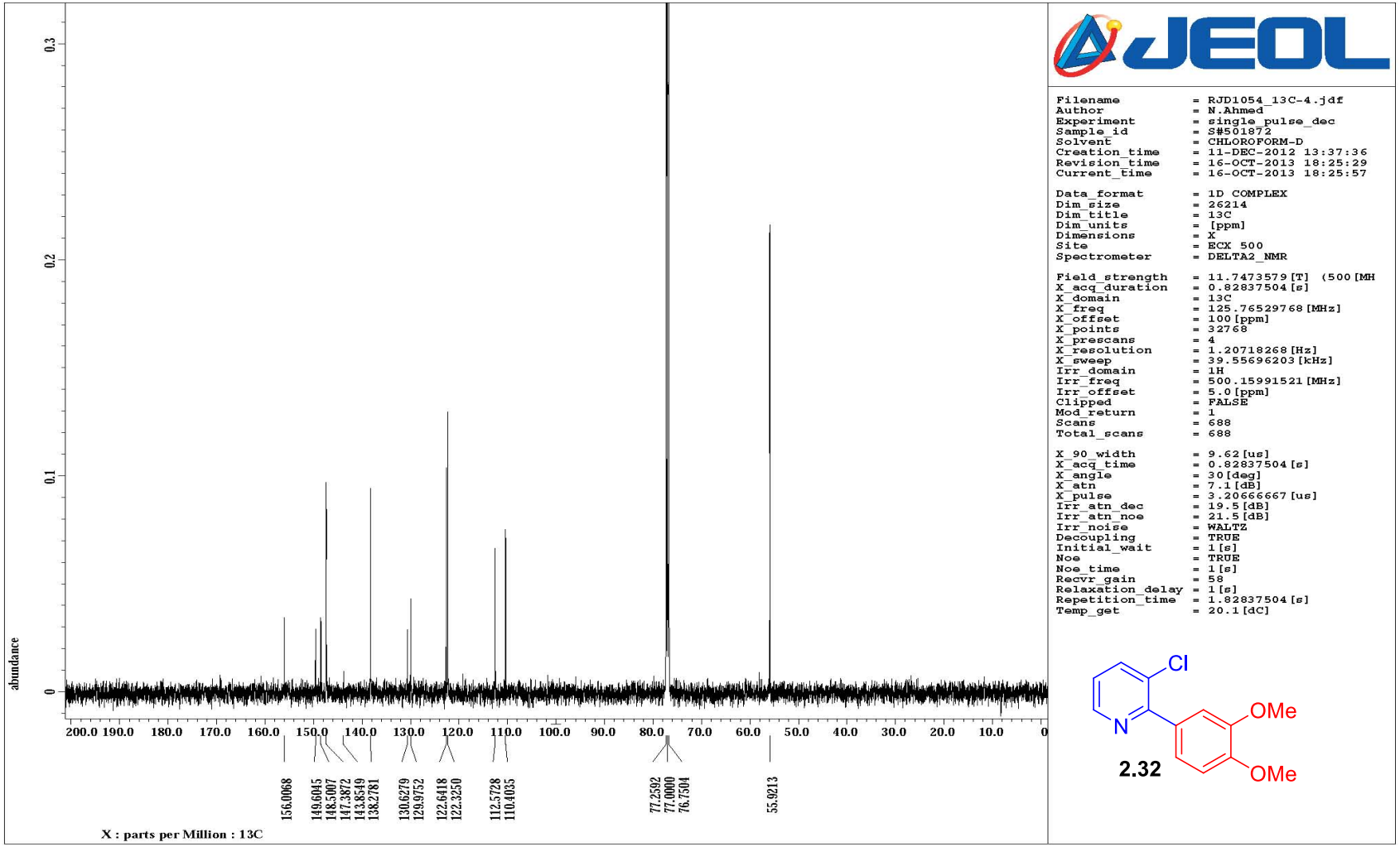
^{13}C NMR spectrum of 3-chloro-2-(3-methoxyphenyl)pyridine (**2.31**)



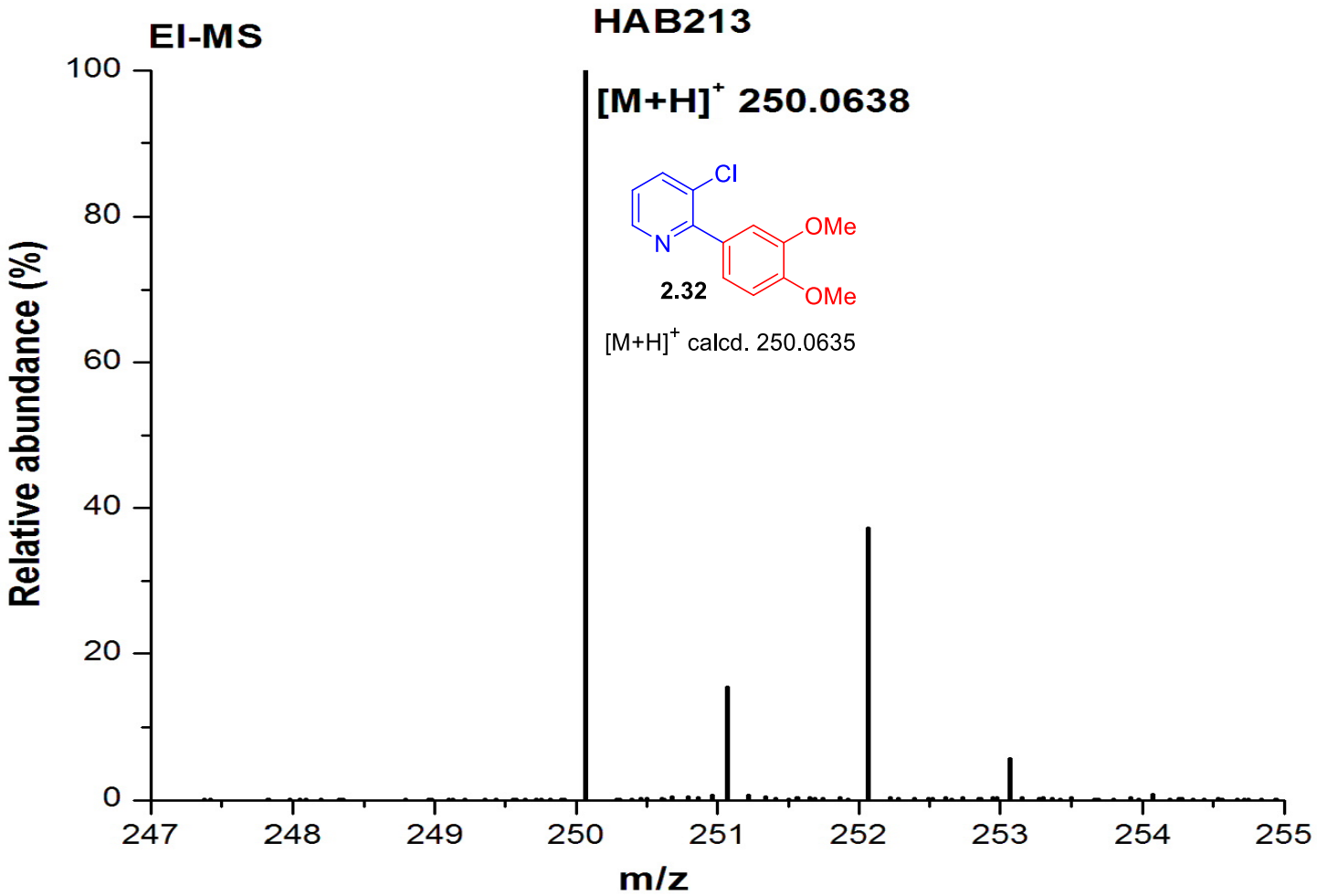
HRMS spectrum of 3-chloro-2-(3-methoxyphenyl)pyridine (**2.31**)



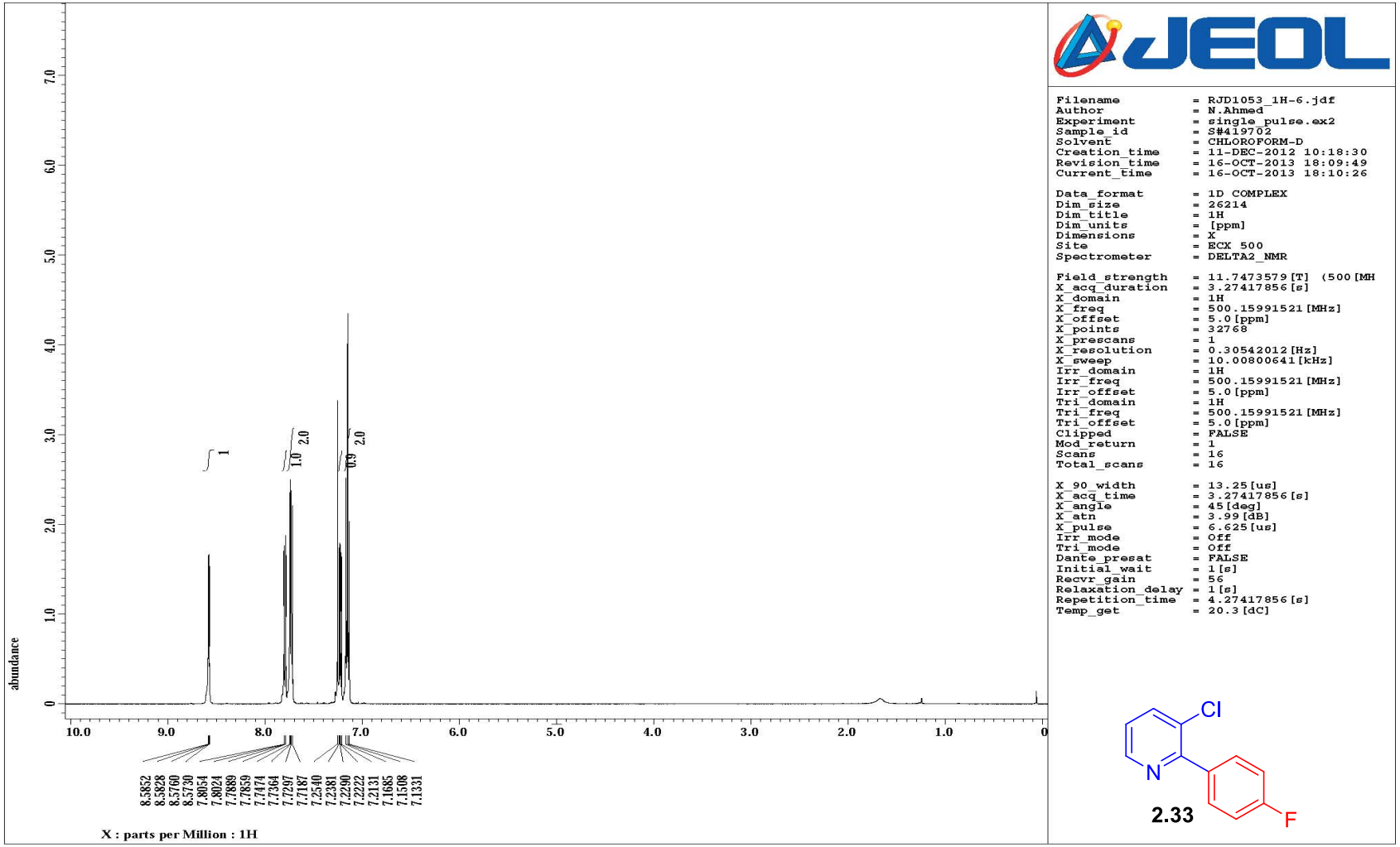
^{1}H NMR spectrum of 3-chloro-2-(3,4-dimethoxyphenyl)pyridine (**2.32**)



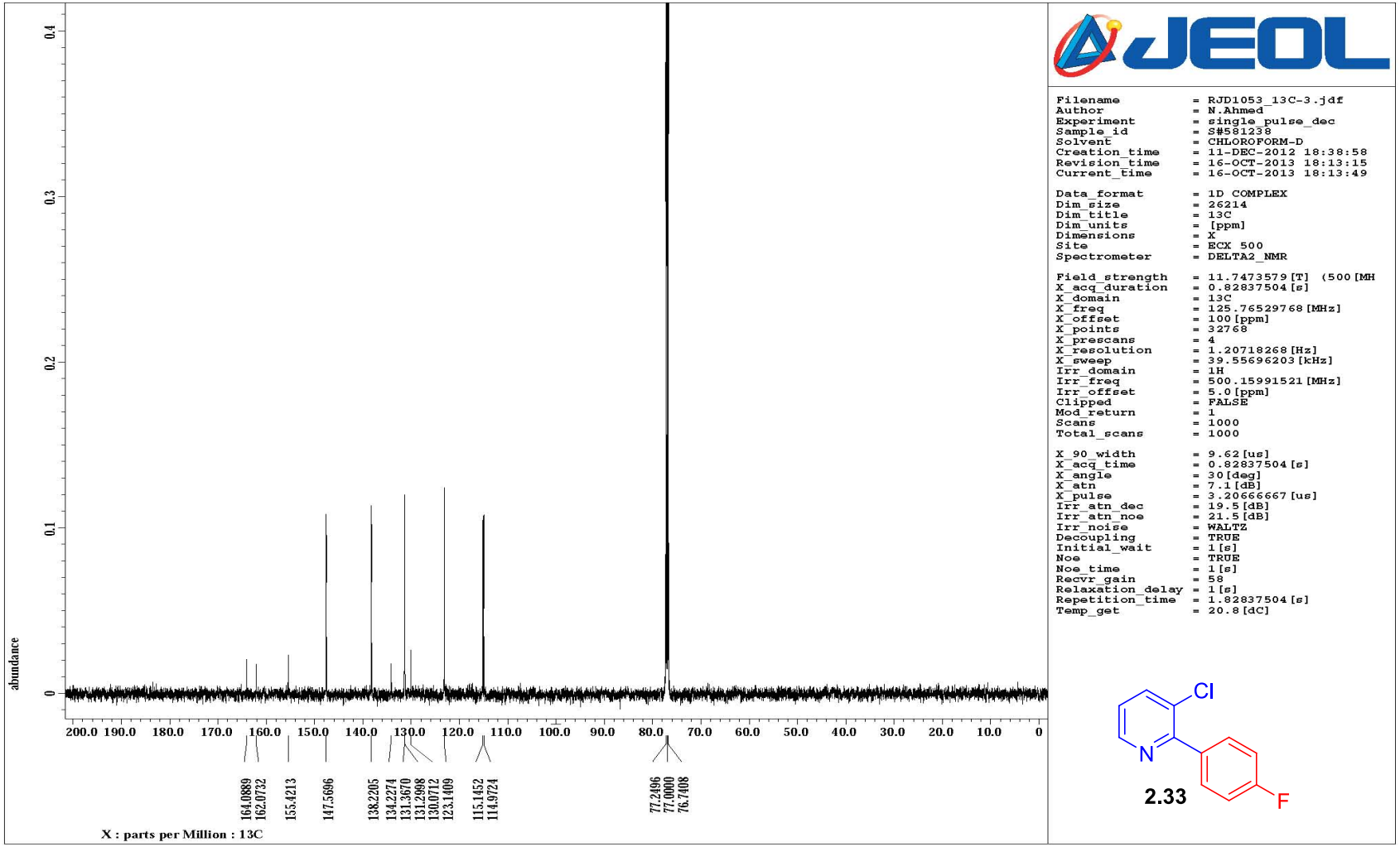
^{13}C NMR spectrum of 3-chloro-2-(3,4-dimethoxyphenyl)pyridine (**2.32**)



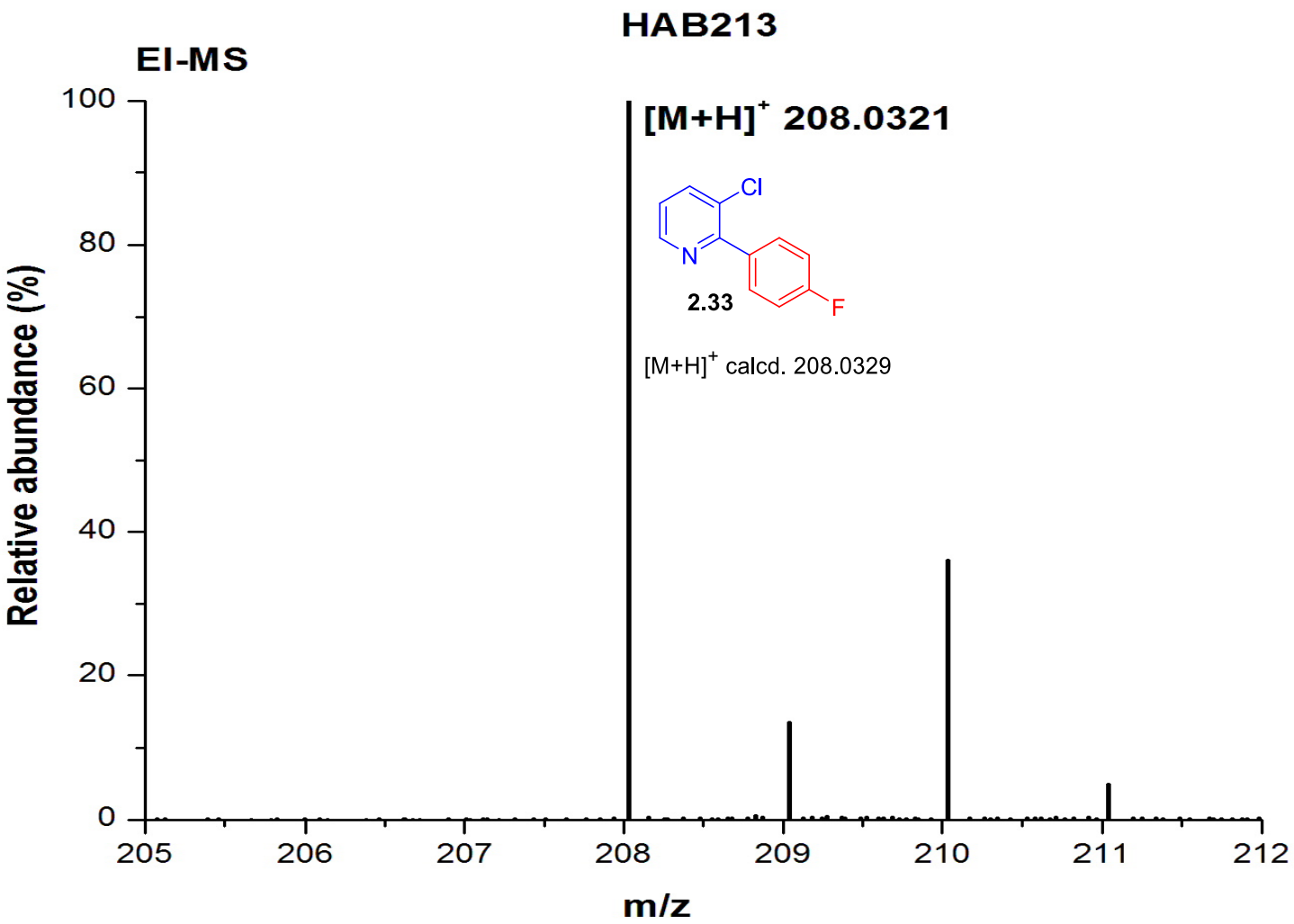
HRMS spectrum of 3-chloro-2-(3,4-dimethoxyphenyl)pyridine (**2.32**)



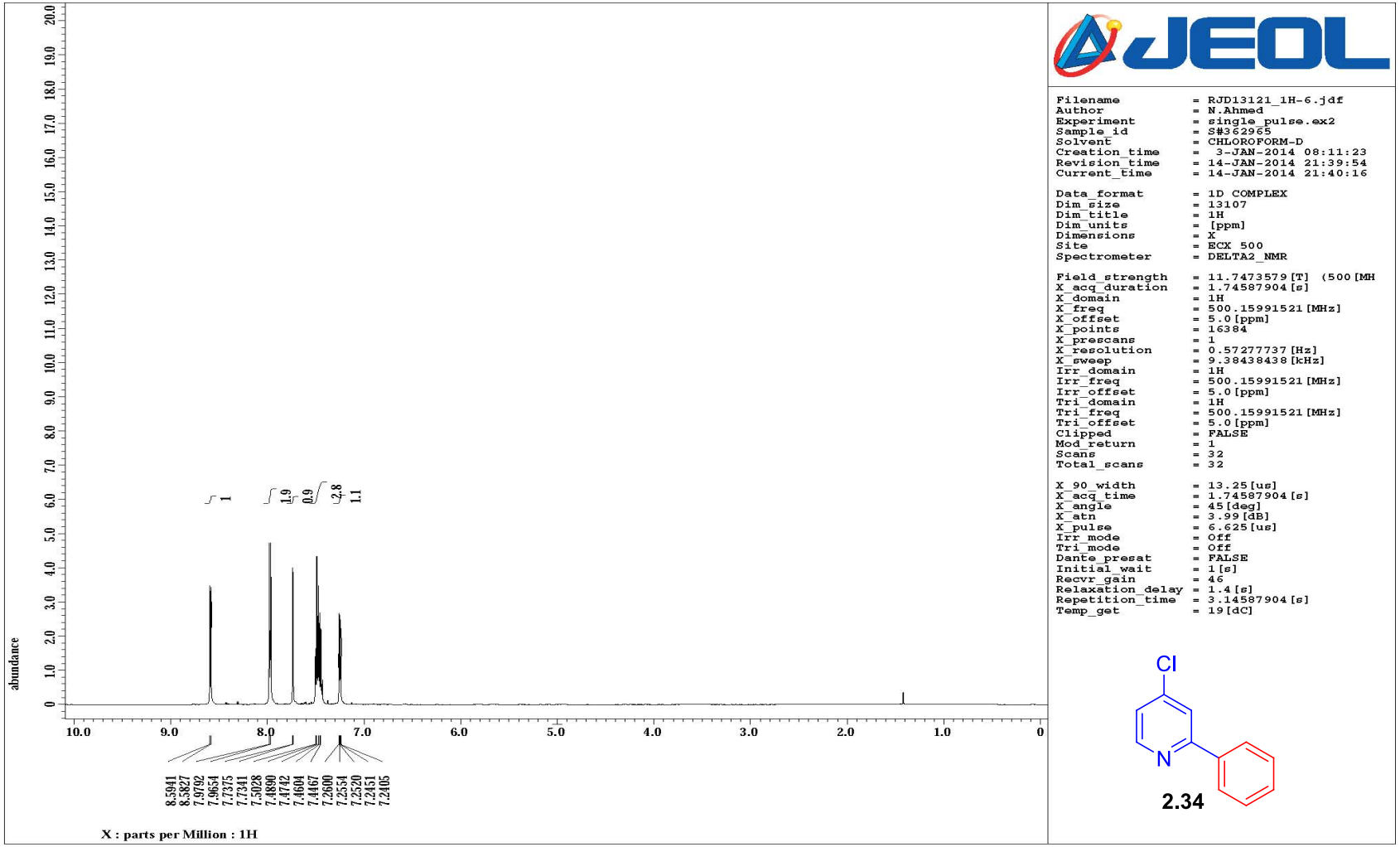
^{1}H NMR spectrum of 3-chloro-2-(4-fluorophenyl)pyridine (**2.33**)



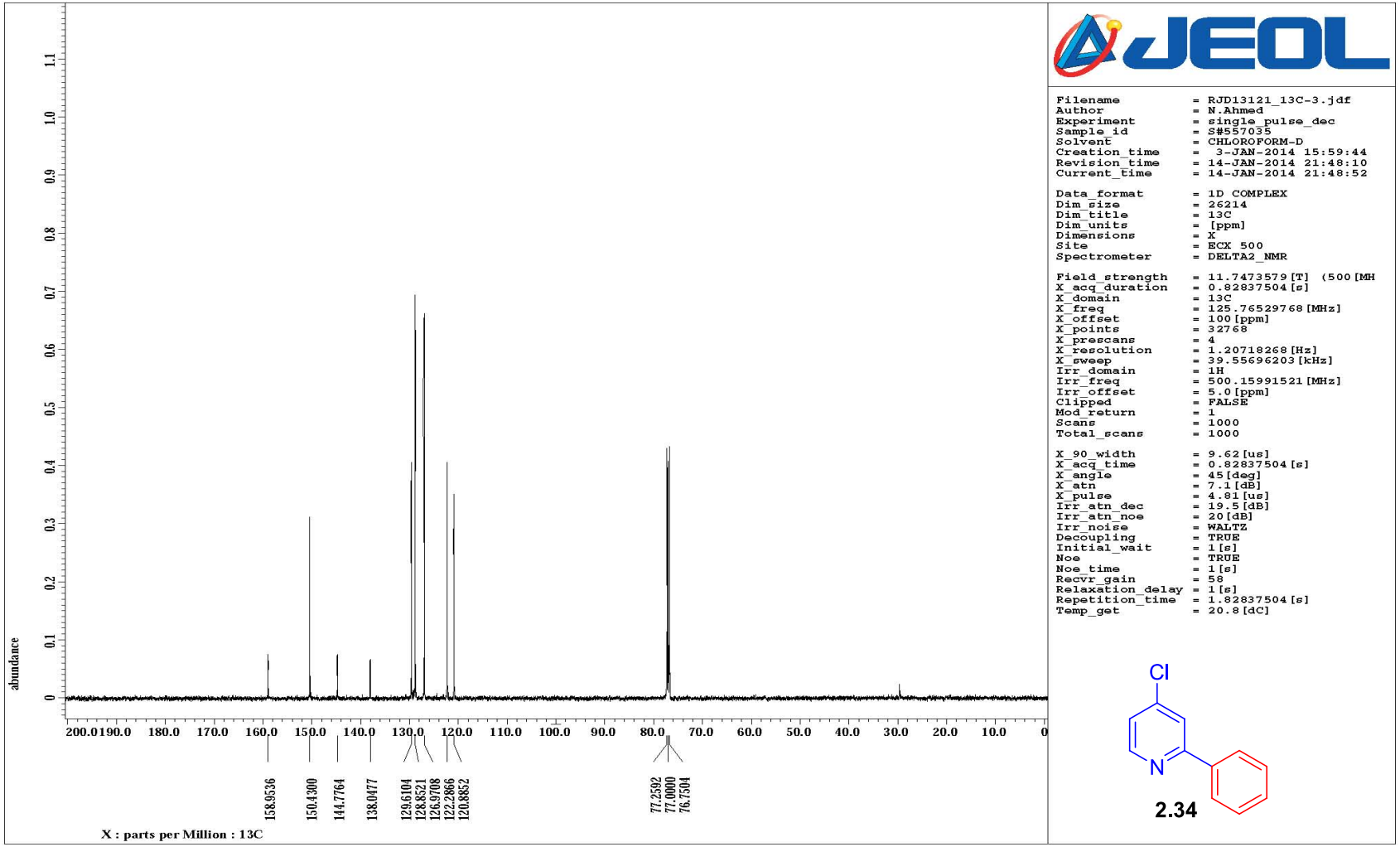
^{13}C NMR spectrum of 3-chloro-2-(4-fluorophenyl)pyridine (**2.33**)



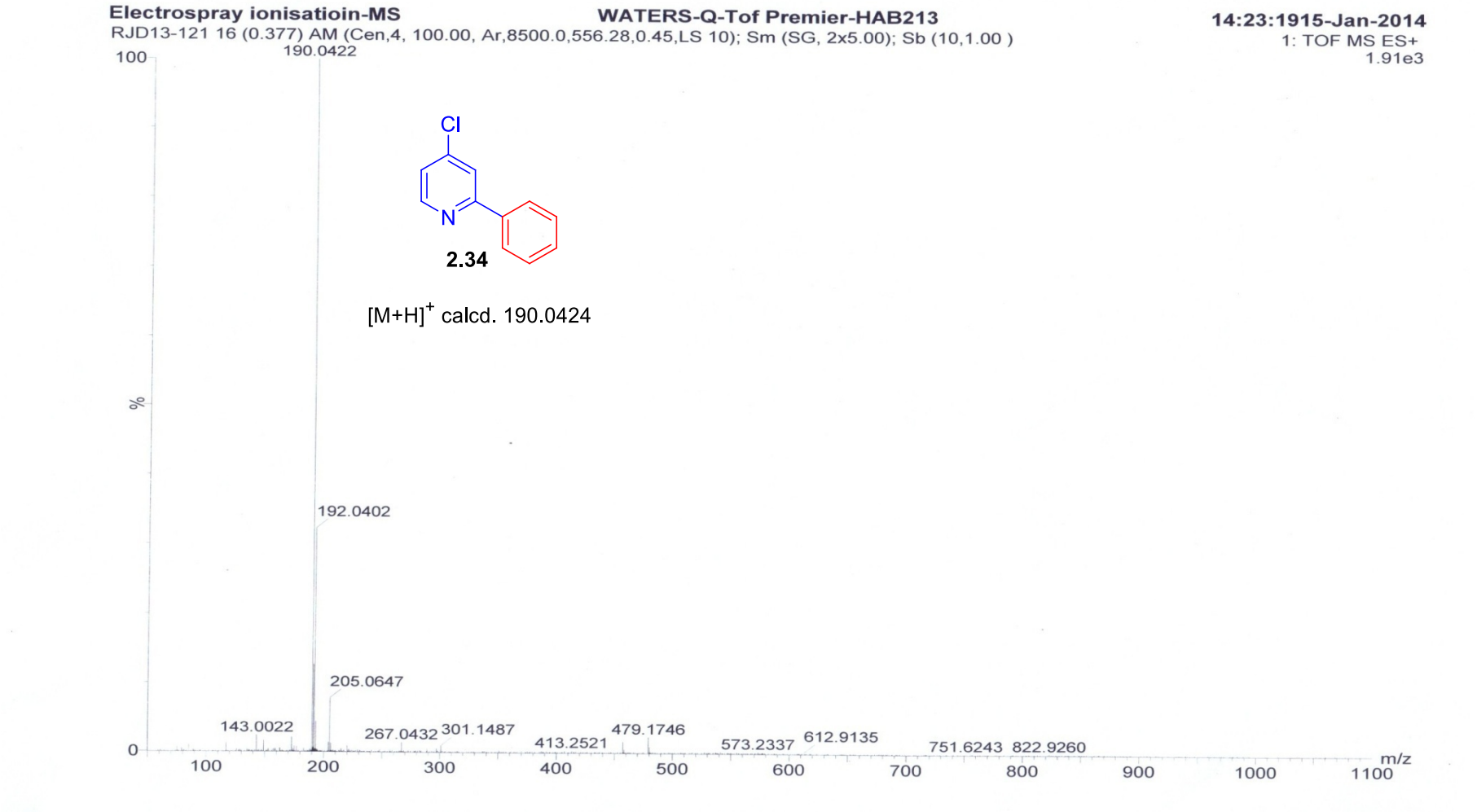
HRMS spectrum of 3-chloro-2-(4-fluorophenyl)pyridine (**2.33**)



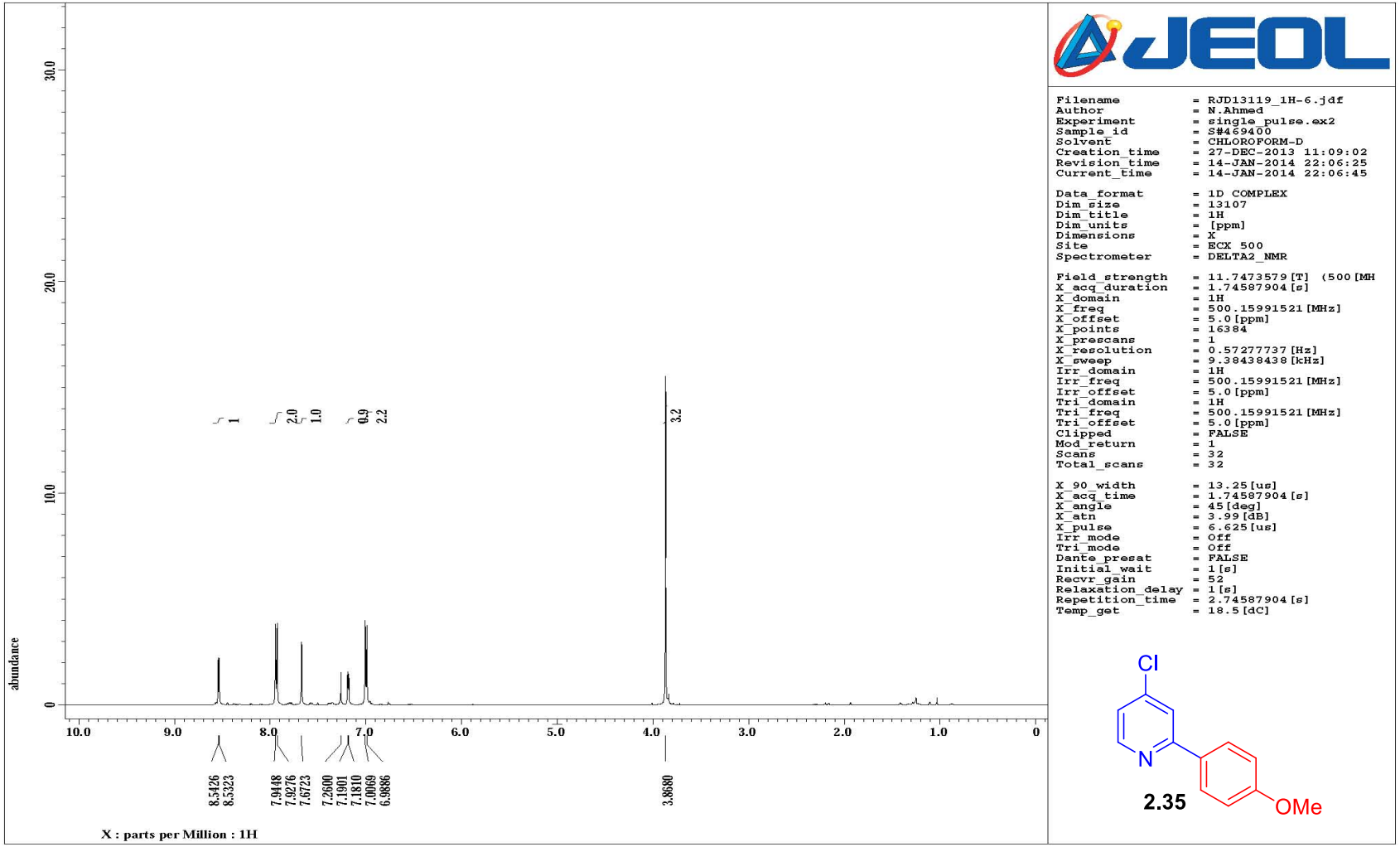
^{1}H NMR spectrum of 4-chloro-2-phenylpyridine (**2.34**)



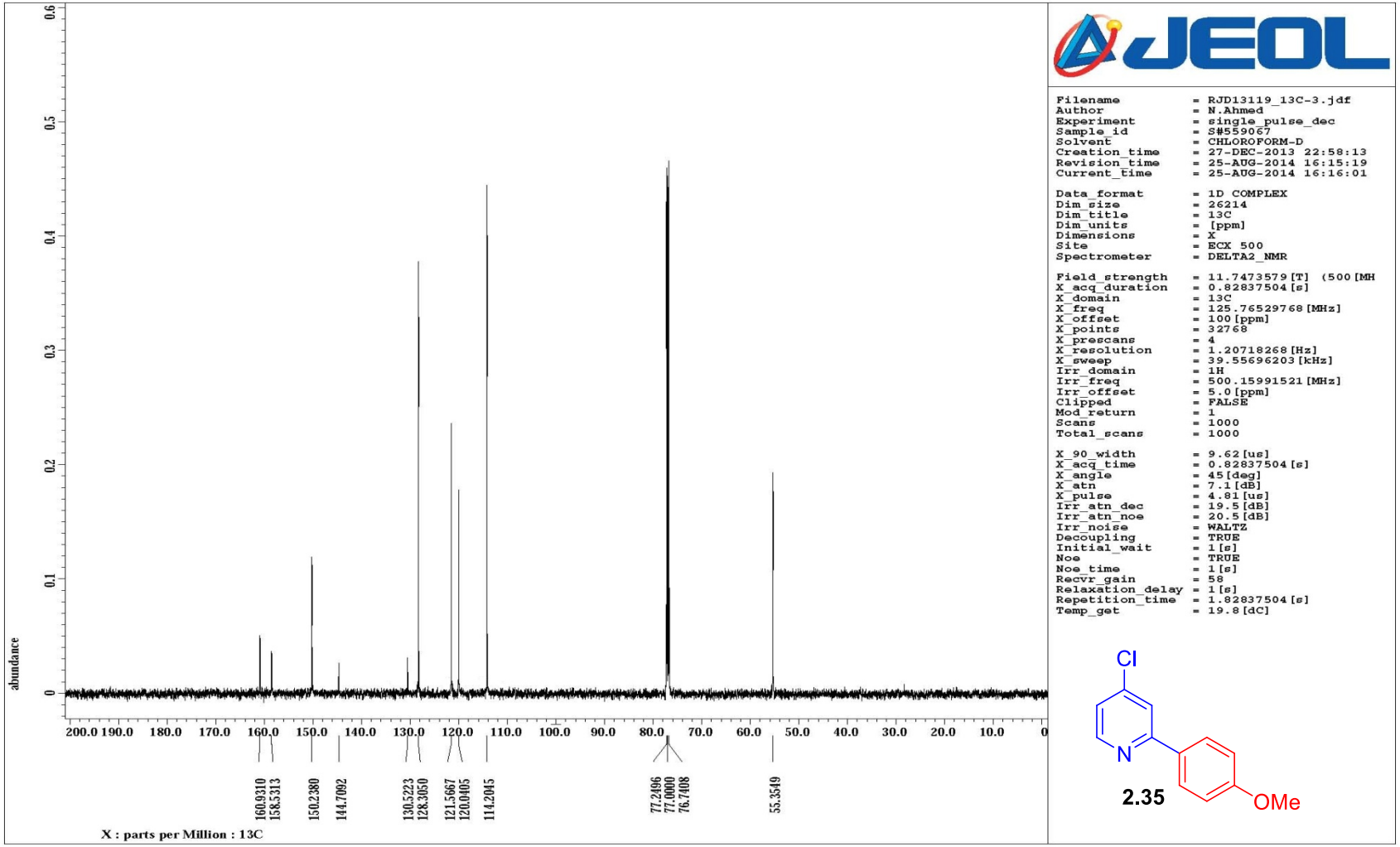
^{13}C NMR spectrum of 4-chloro-2-phenylpyridine (**2.34**)



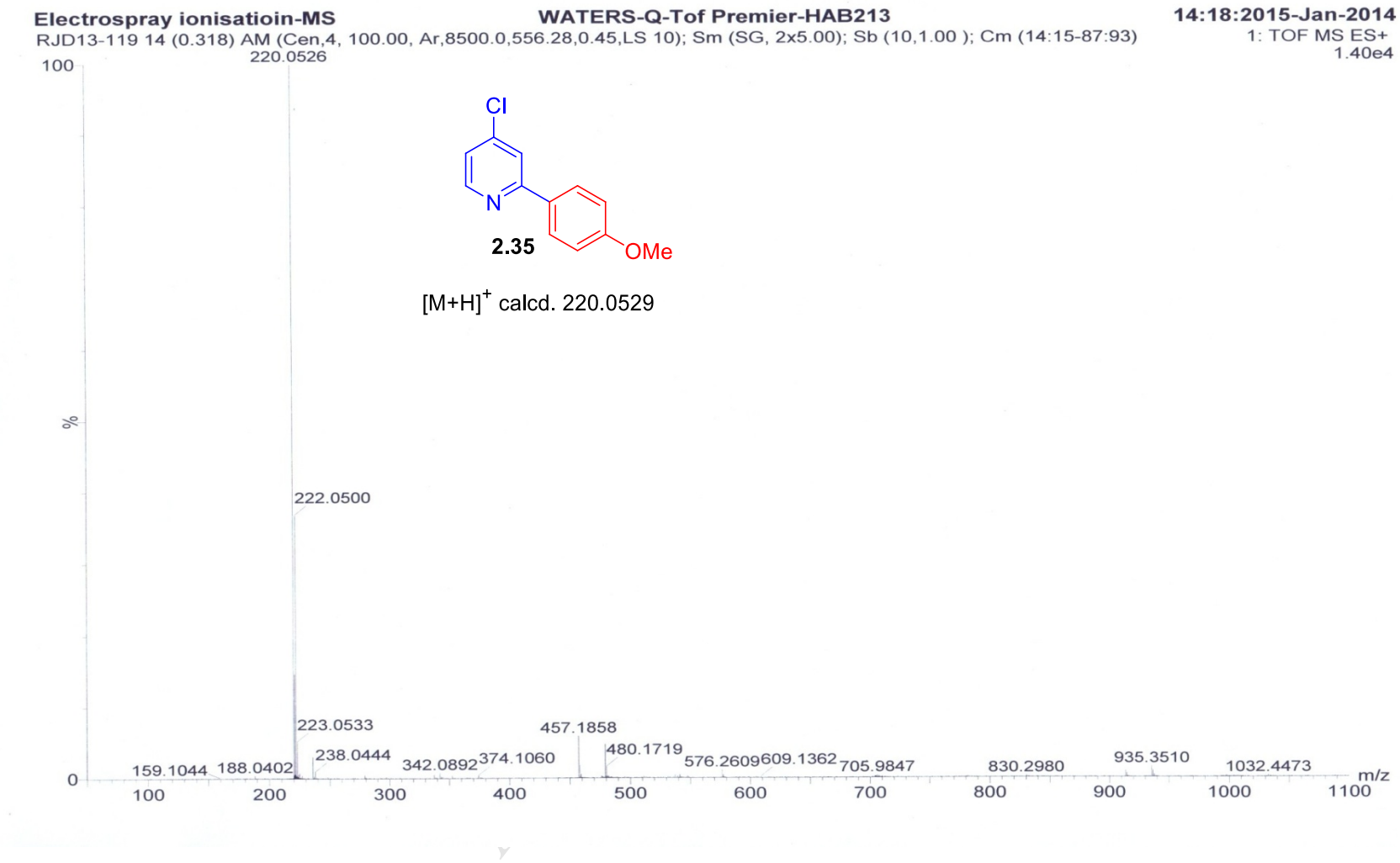
HRMS spectrum of 4-chloro-2-phenylpyridine (**2.34**)



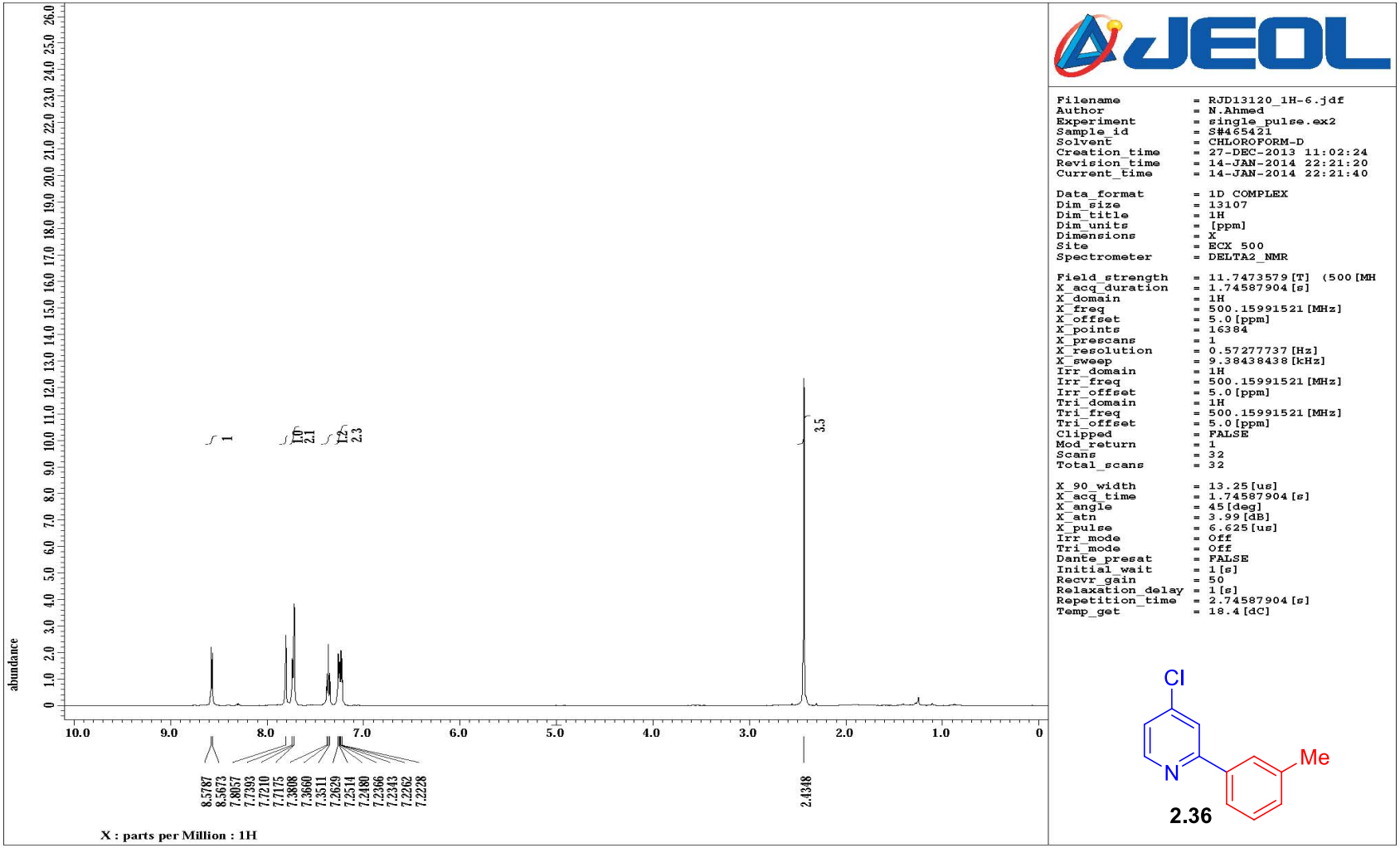
^{1}H NMR spectrum of 4-chloro-2-(4-methoxyphenyl)pyridine (**2.35**)



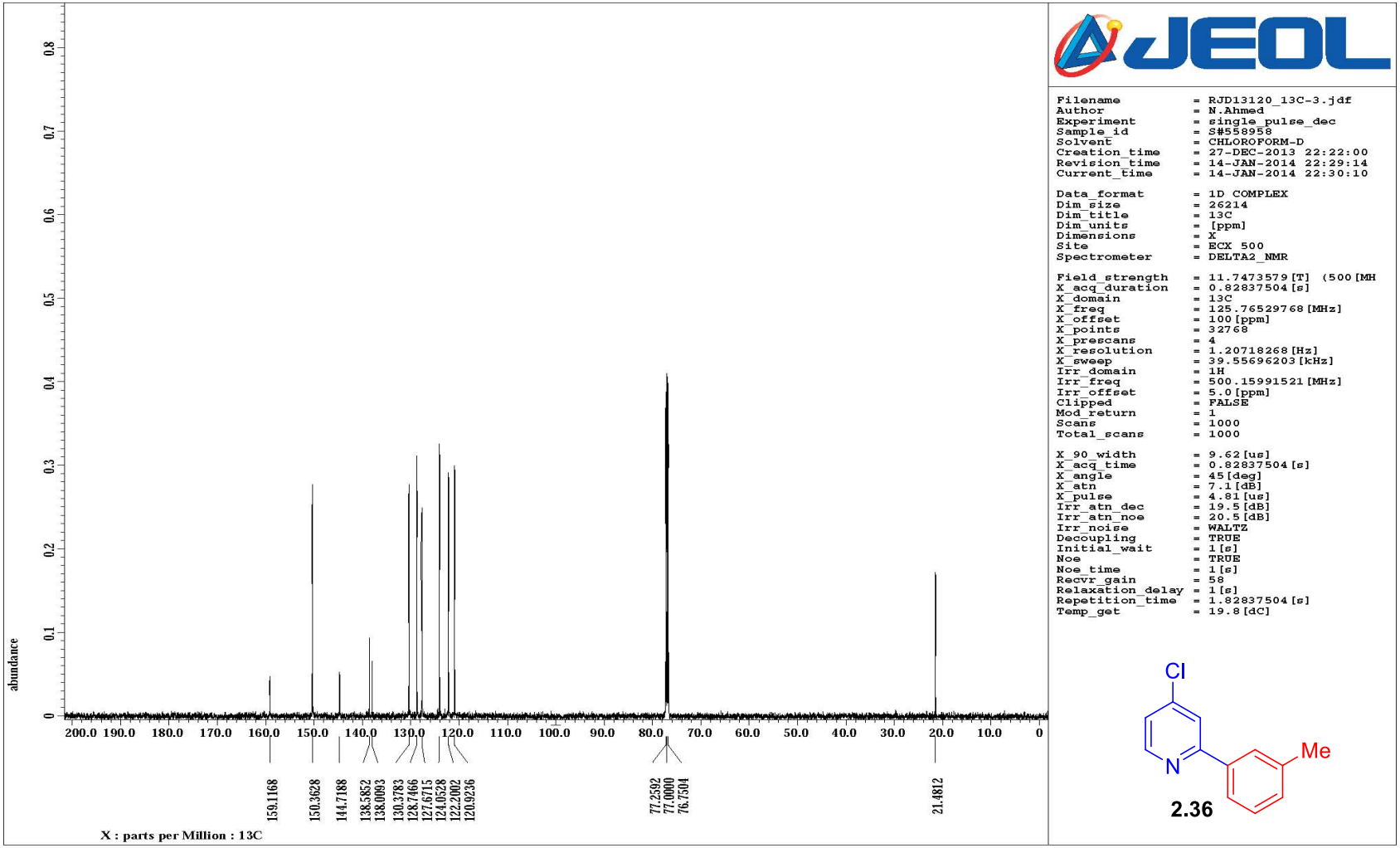
^{13}C NMR spectrum of 4-chloro-2-(4-methoxyphenyl)pyridine (**2.35**)



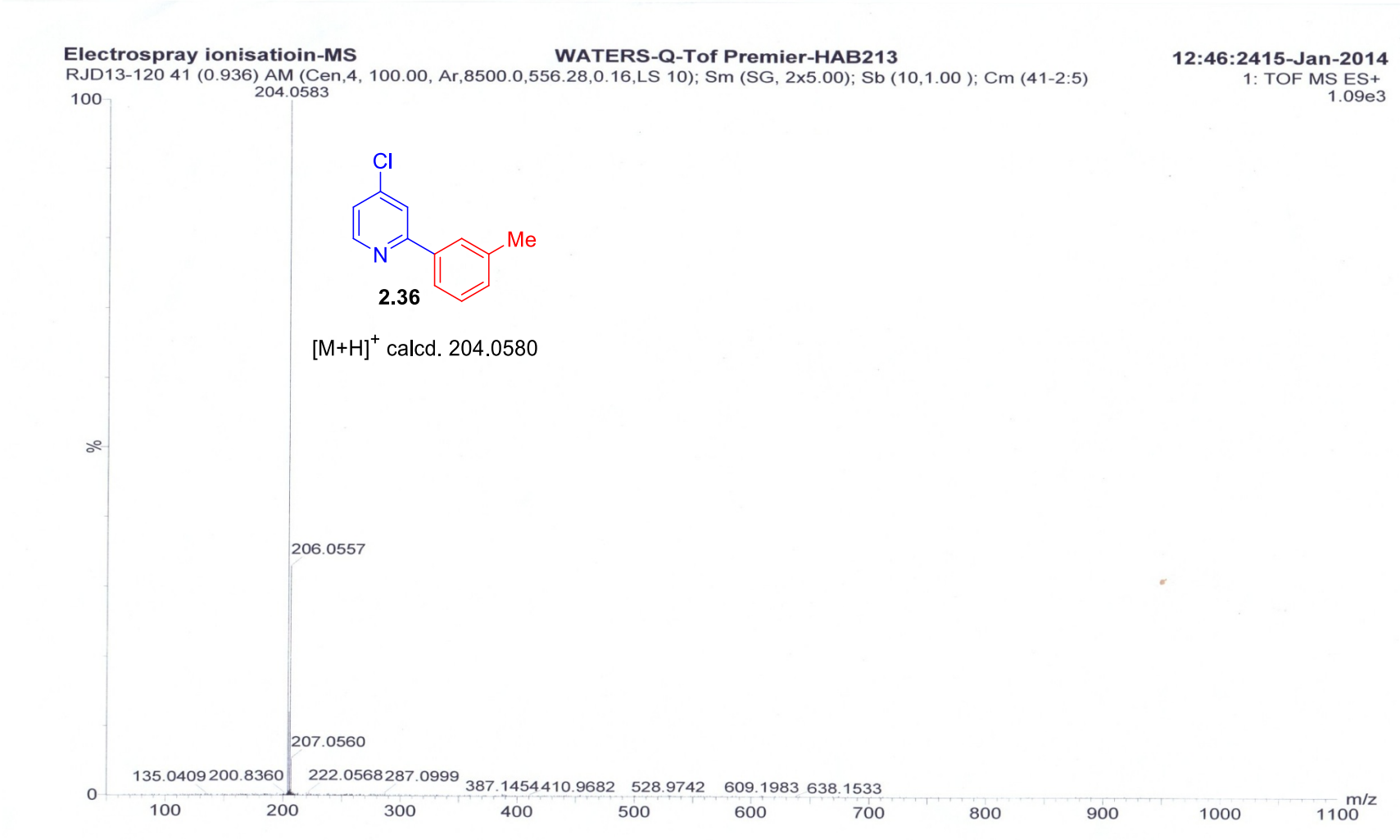
HRMS spectrum of 4-chloro-2-(4-methoxyphenyl)pyridine (**2.35**)



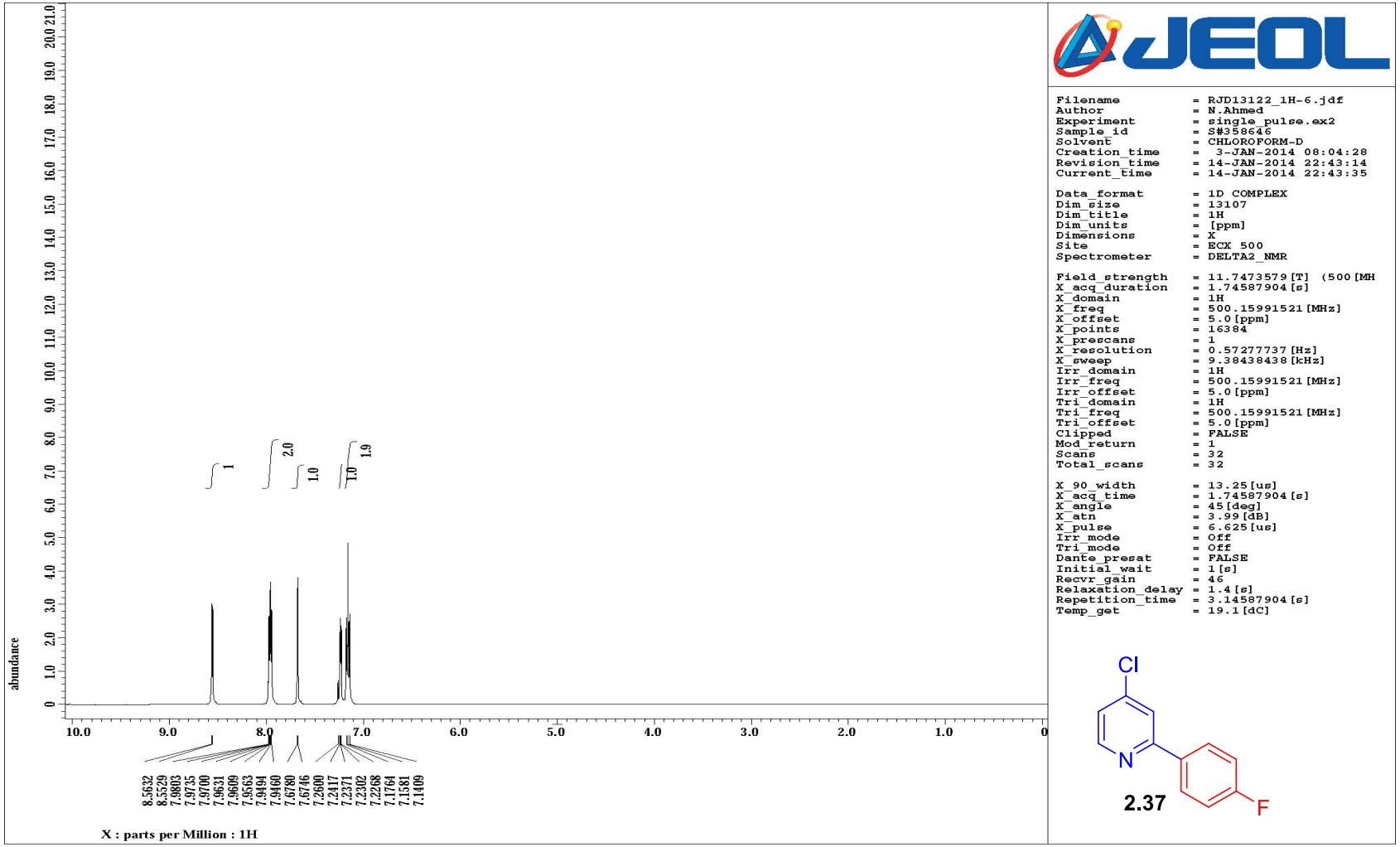
^{1}H NMR spectrum of 4-chloro-2-(3-methylphenyl)pyridine (**2.36**)



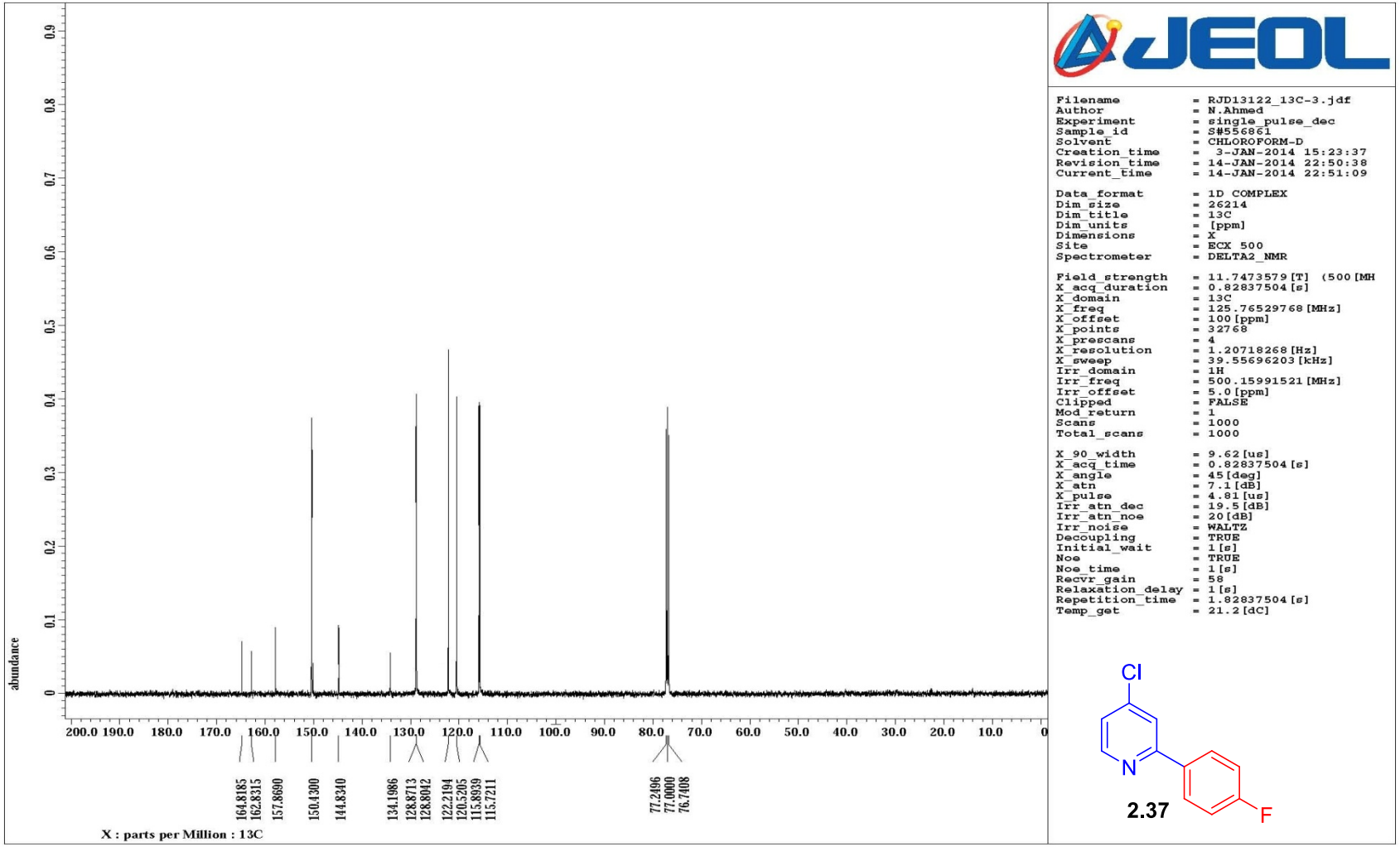
^{13}C NMR spectrum of 4-chloro-2-(3-methylphenyl)pyridine (**2.36**)



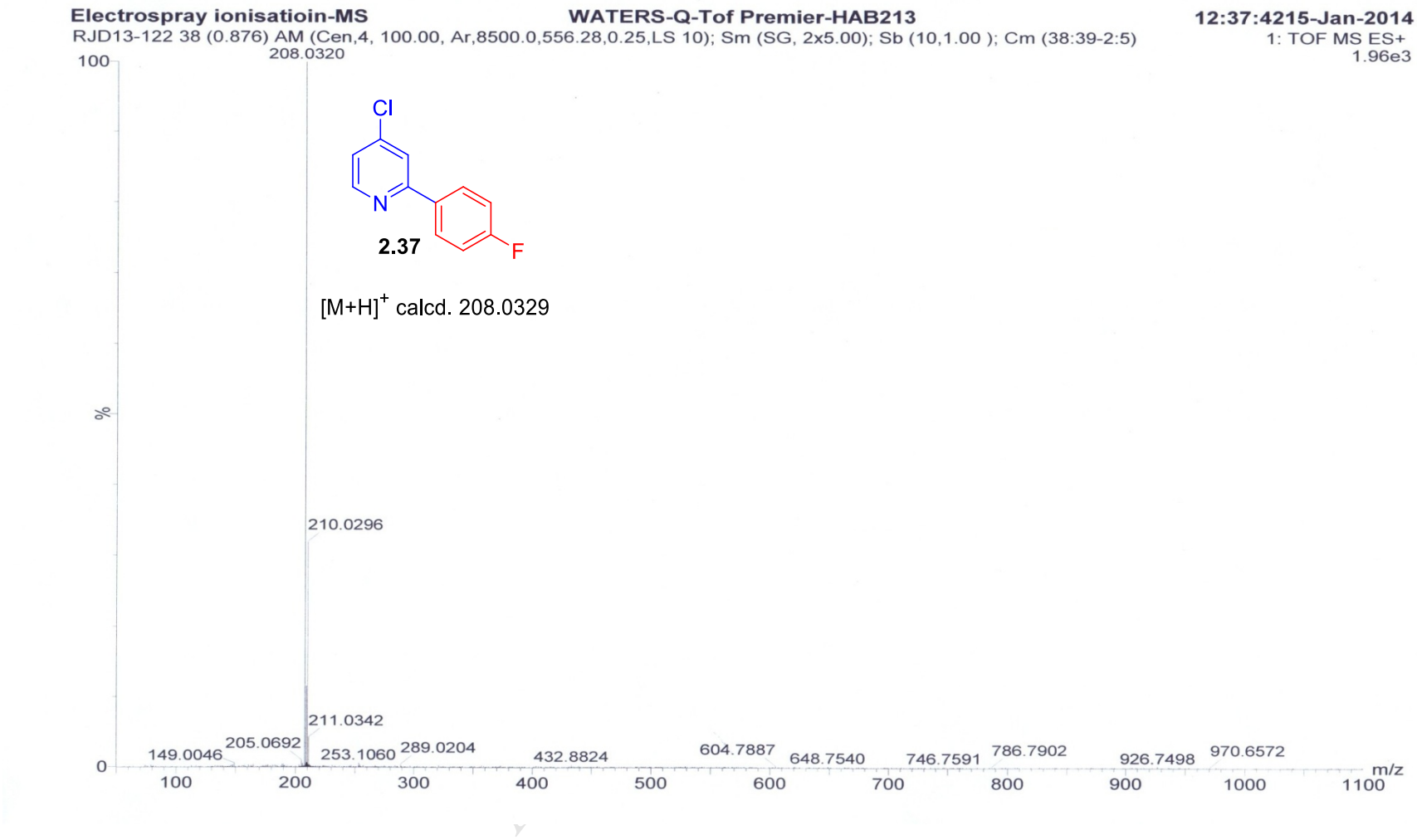
HRMS spectrum of 4-chloro-2-(3-methylphenyl)pyridine (**2.36**)



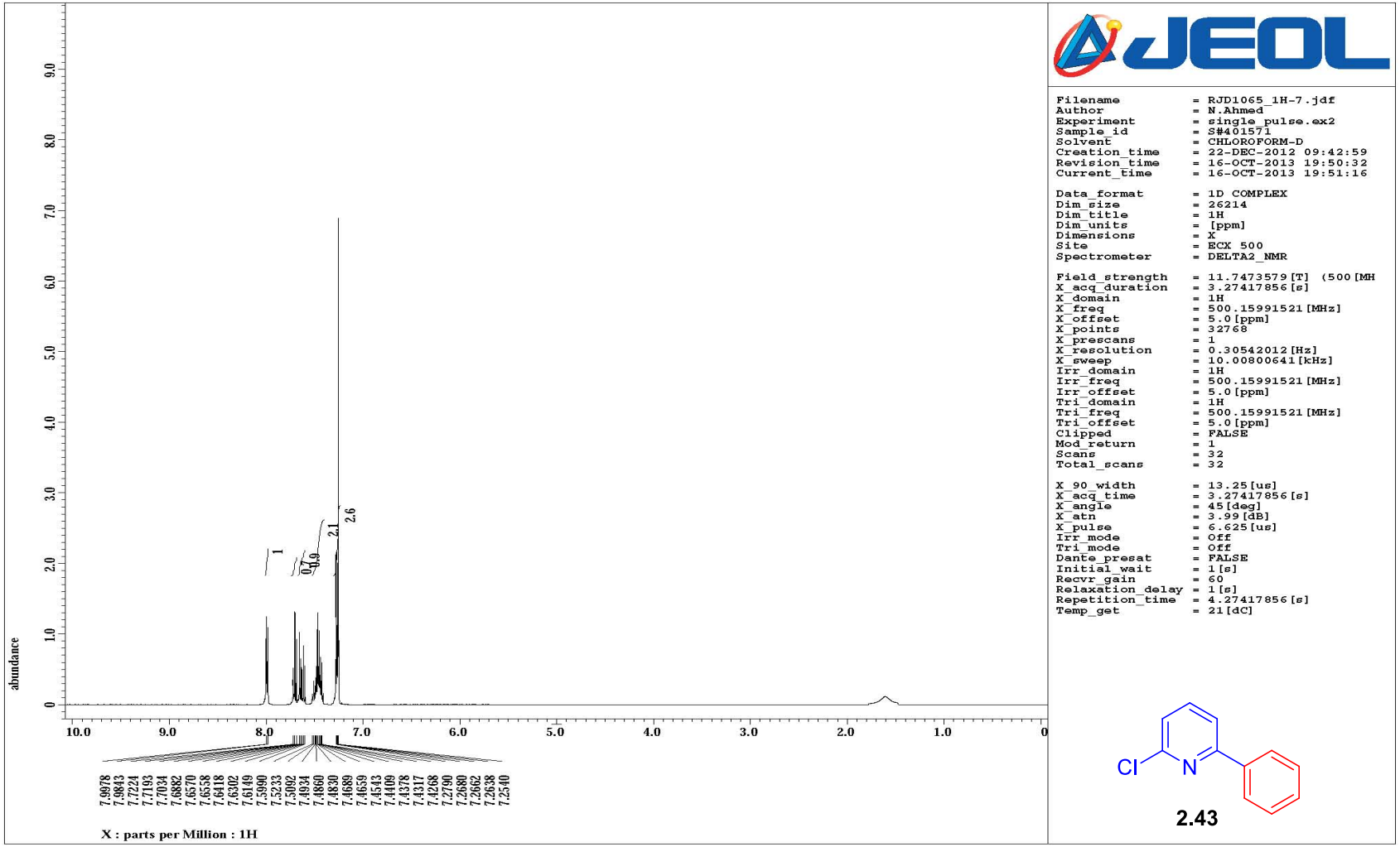
^{1}H NMR spectrum of 4-chloro-2-(4-fluorophenyl)pyridine (**2.37**)



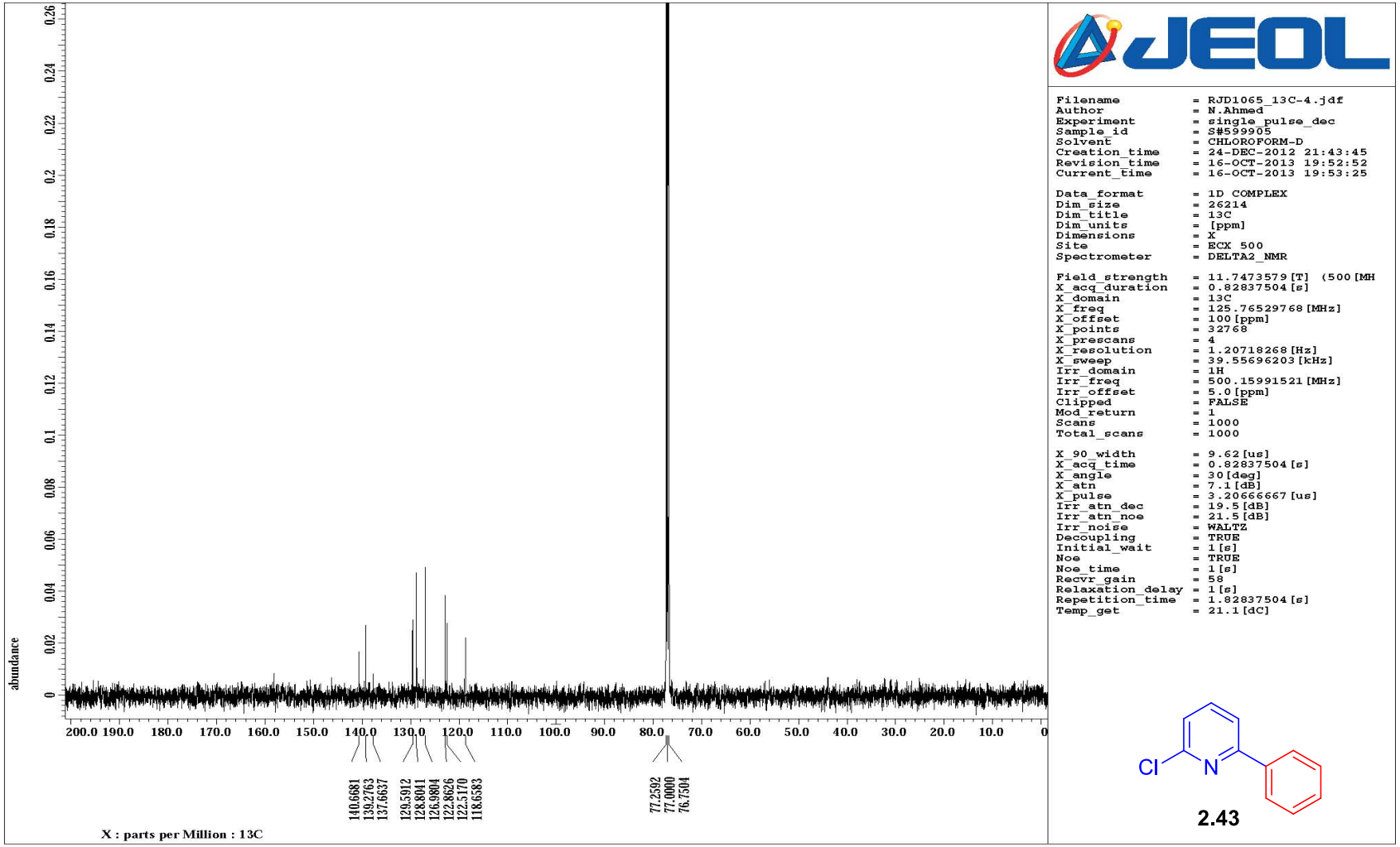
^{13}C NMR spectrum of 4-chloro-2-(4-fluorophenyl)pyridine (**2.37**)



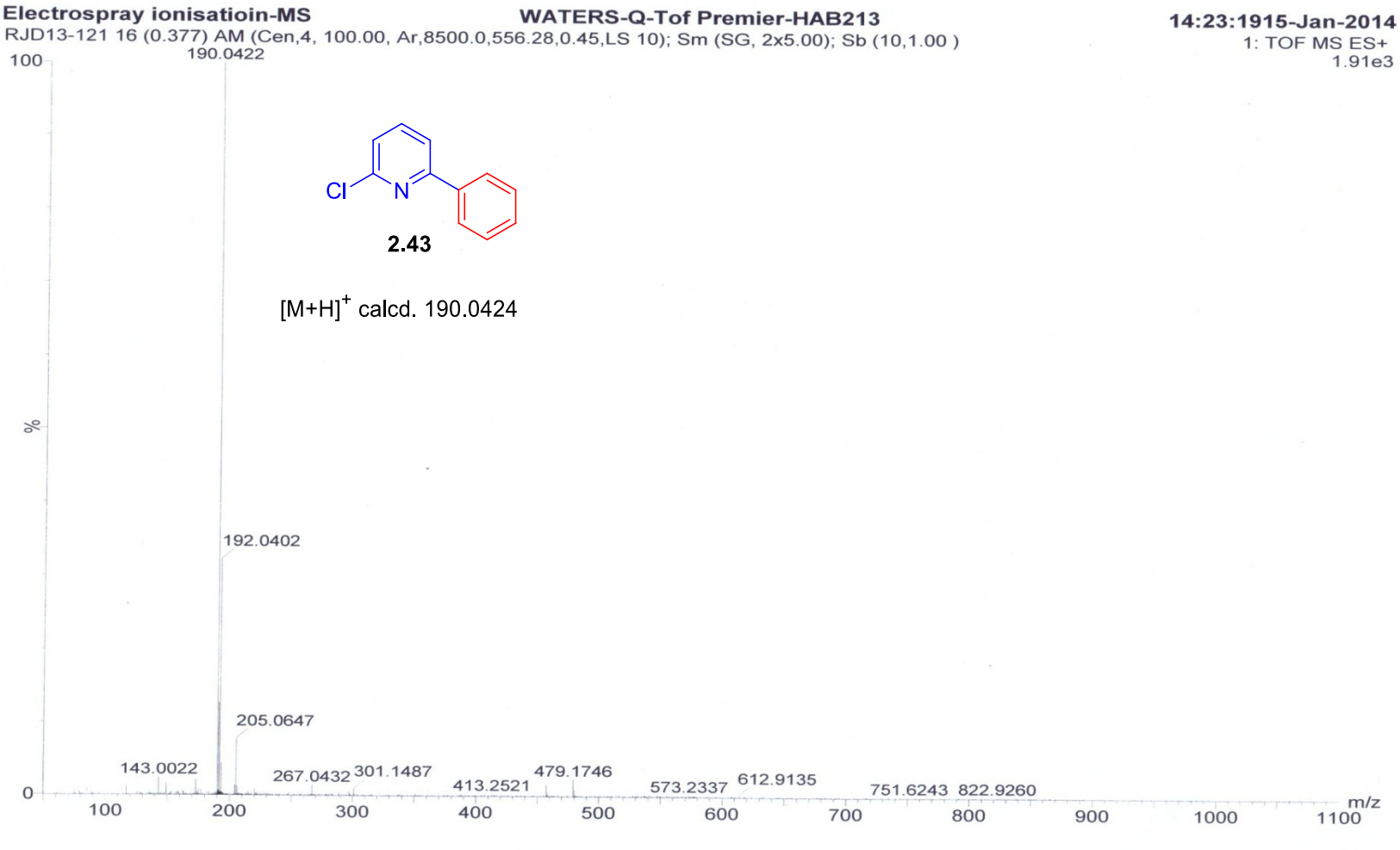
HRMS spectrum of 4-chloro-2-(4-fluorophenyl)pyridine (**2.37**)



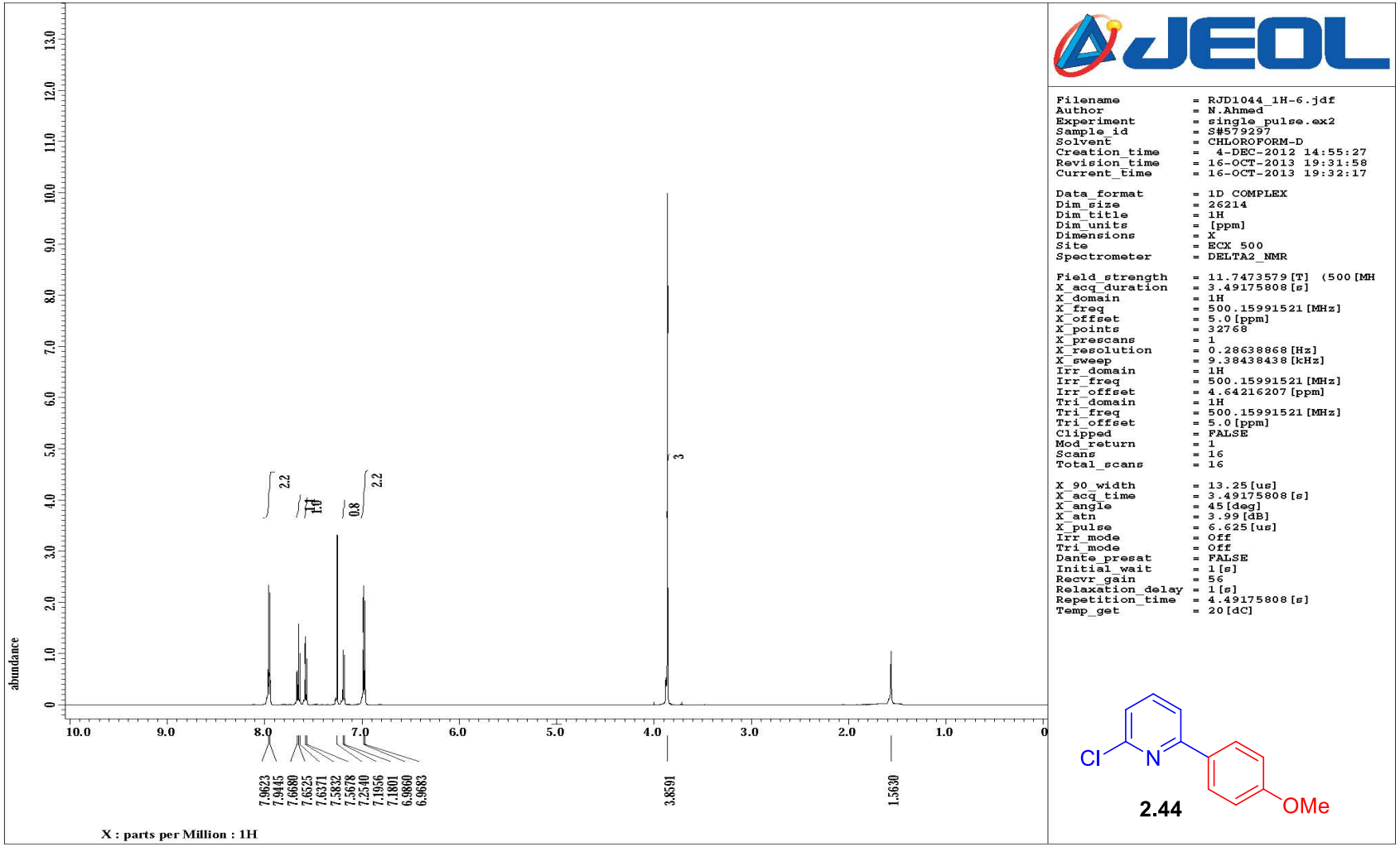
^{1}H NMR spectrum of 6-chloro-2-phenylpyridine (**2.43**)



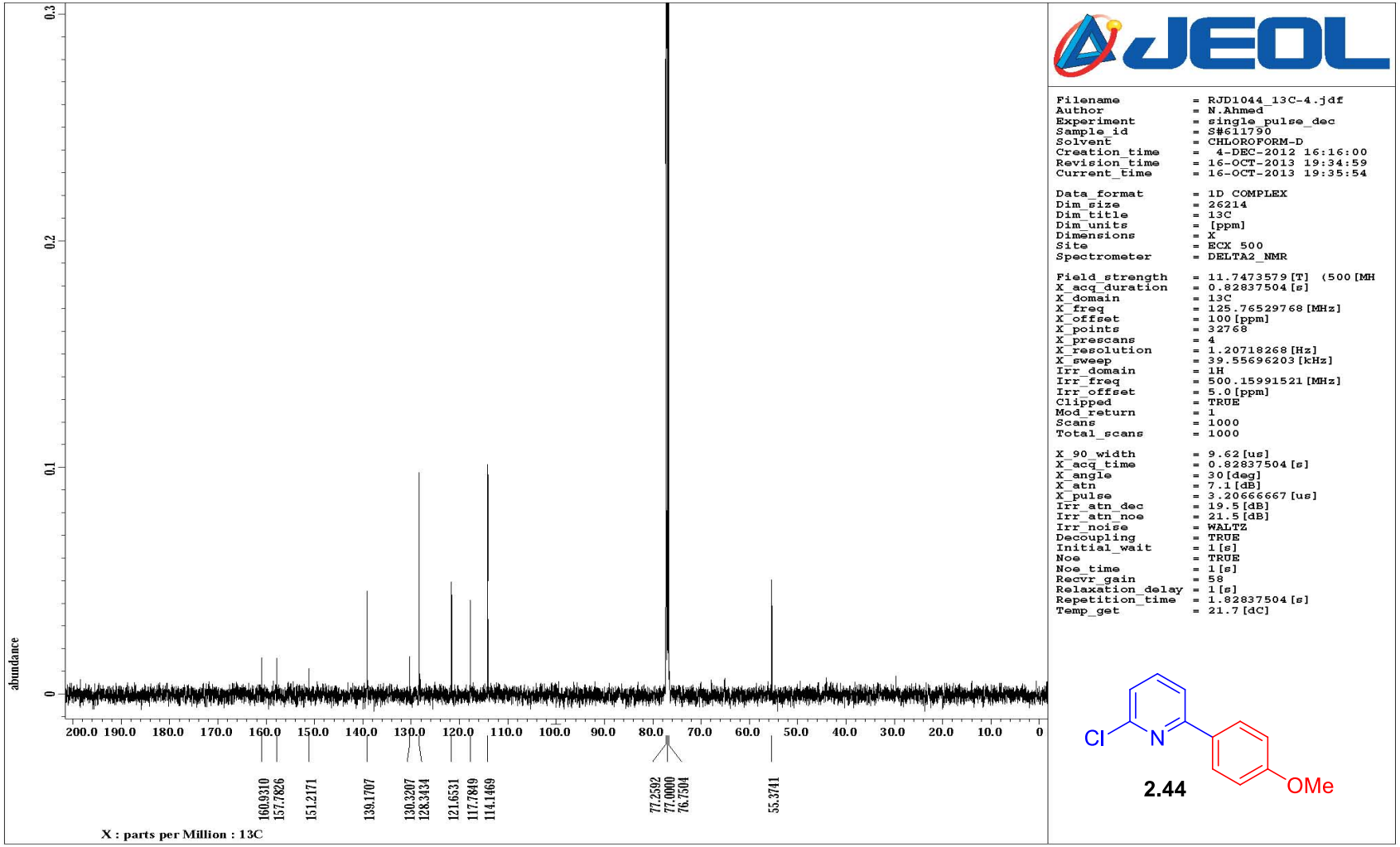
^{13}C NMR spectrum of 6-chloro-2-phenylpyridine (**2.43**)



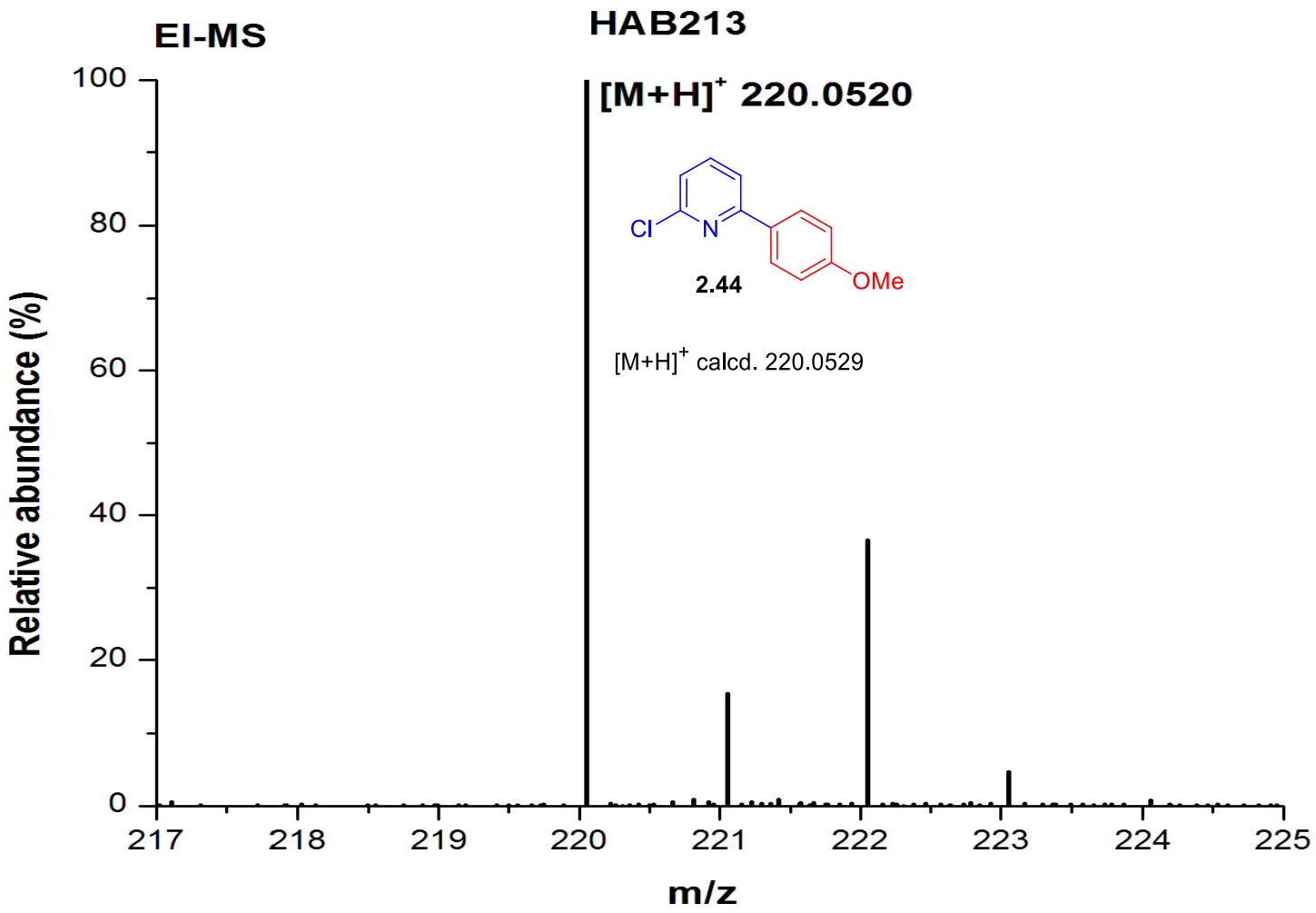
HRMS spectrum of 6-chloro-2-phenylpyridine (**2.43**)



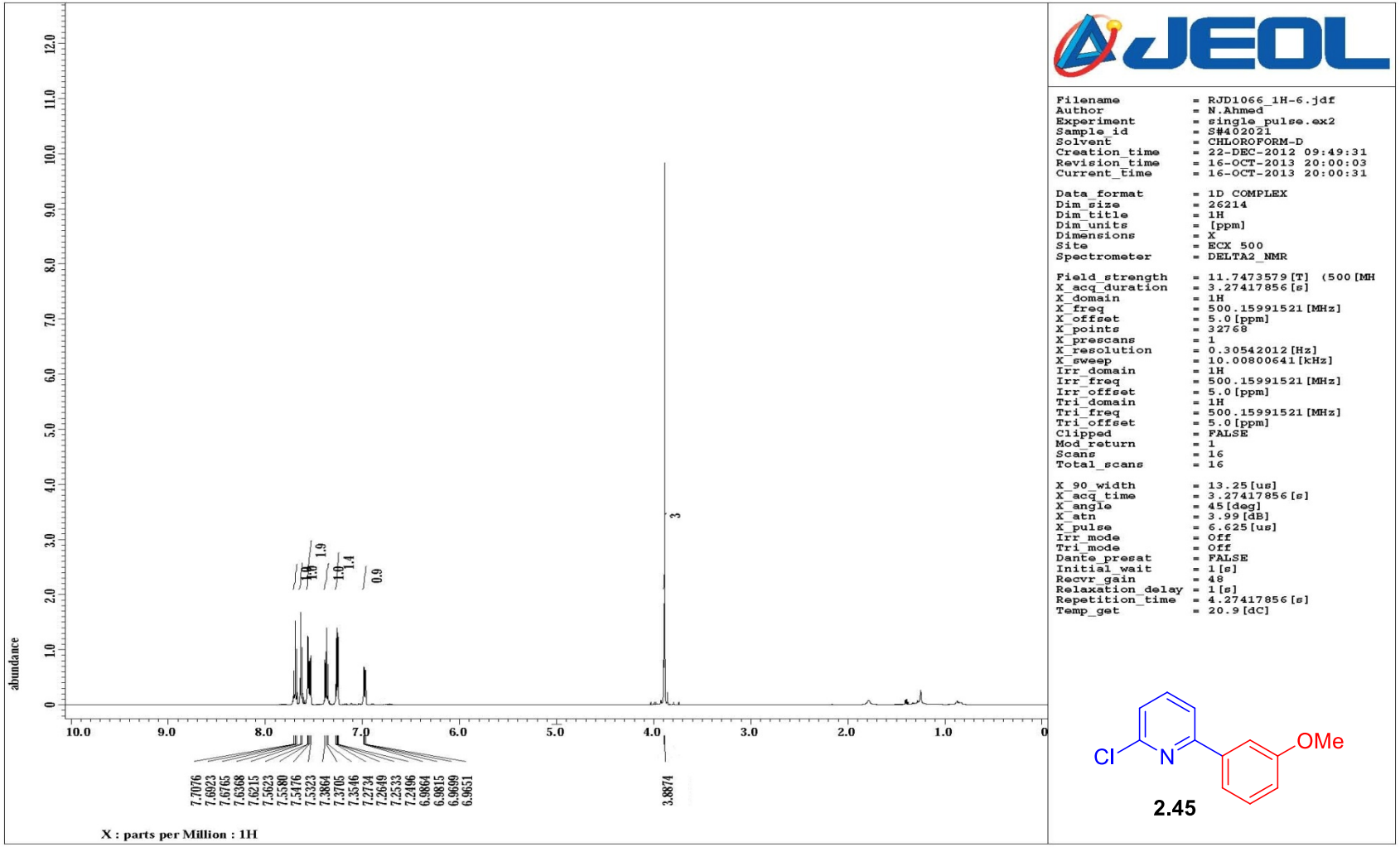
^{1}H NMR spectrum of 6-chloro-2-(4-methoxyphenyl)pyridine (**2.44**)



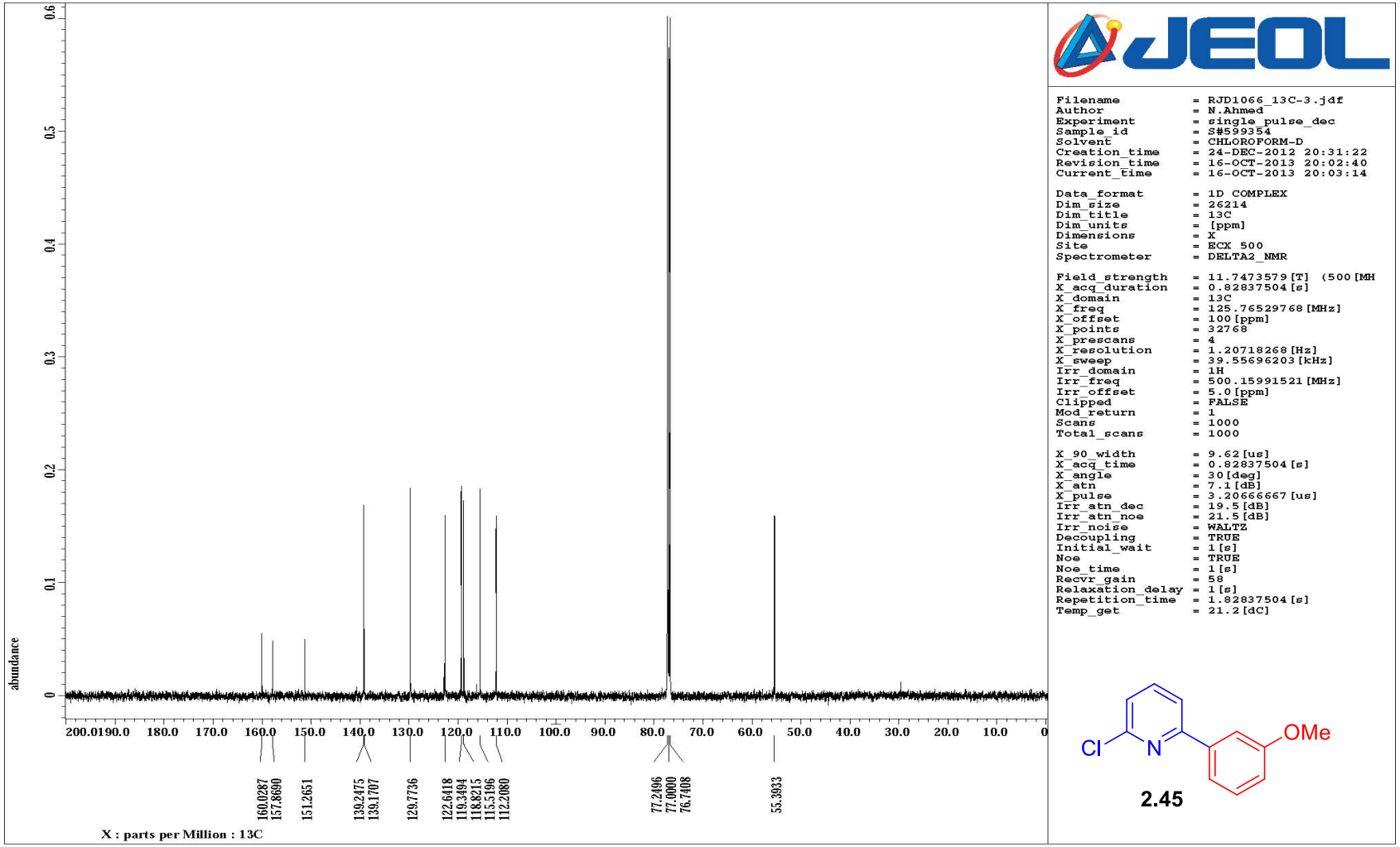
^{13}C NMR spectrum of 6-chloro-2-(4-methoxyphenyl)pyridine (**2.44**)



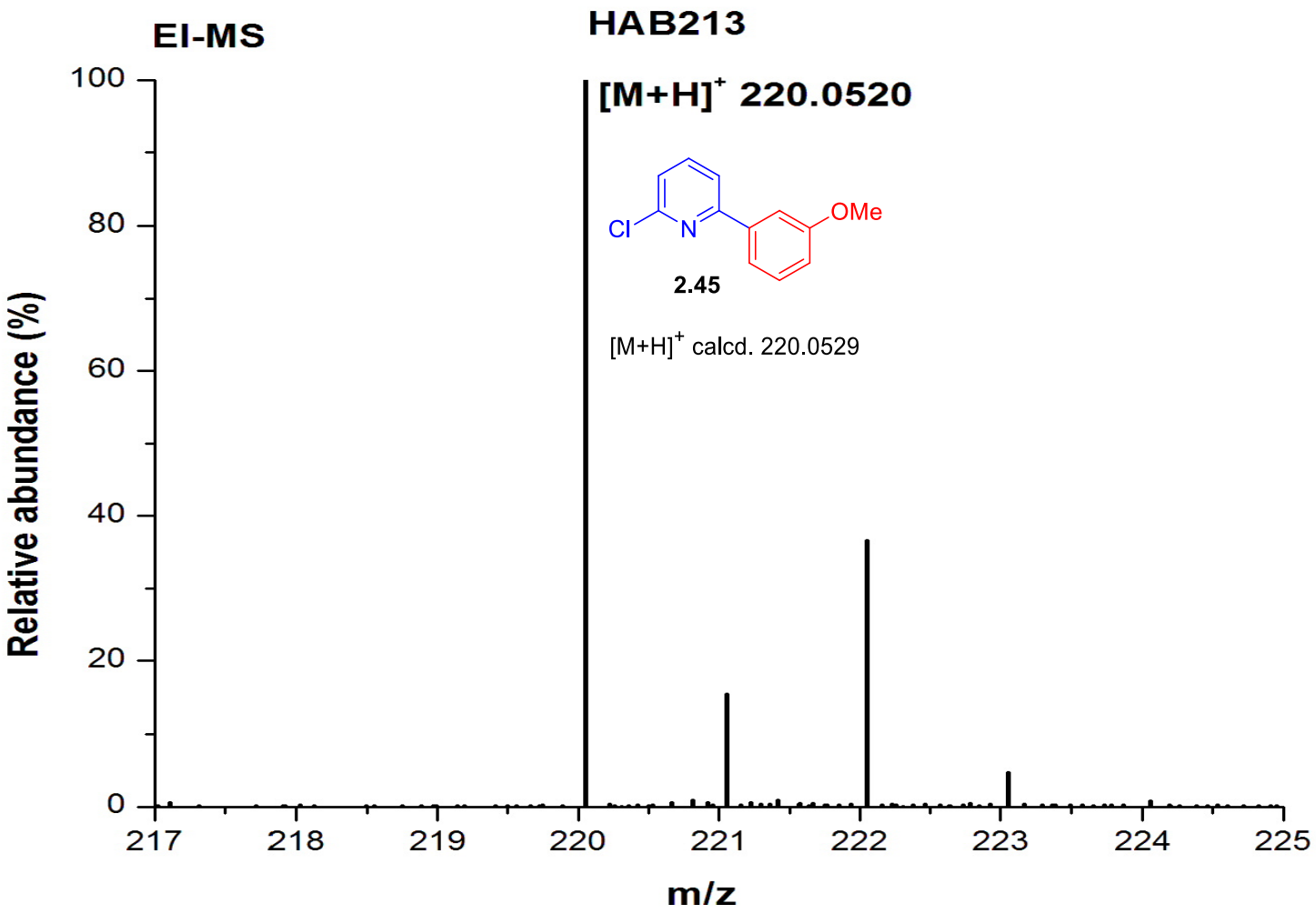
HRMS spectrum of 6-chloro-2-(4-methoxyphenyl)pyridine (**2.44**)



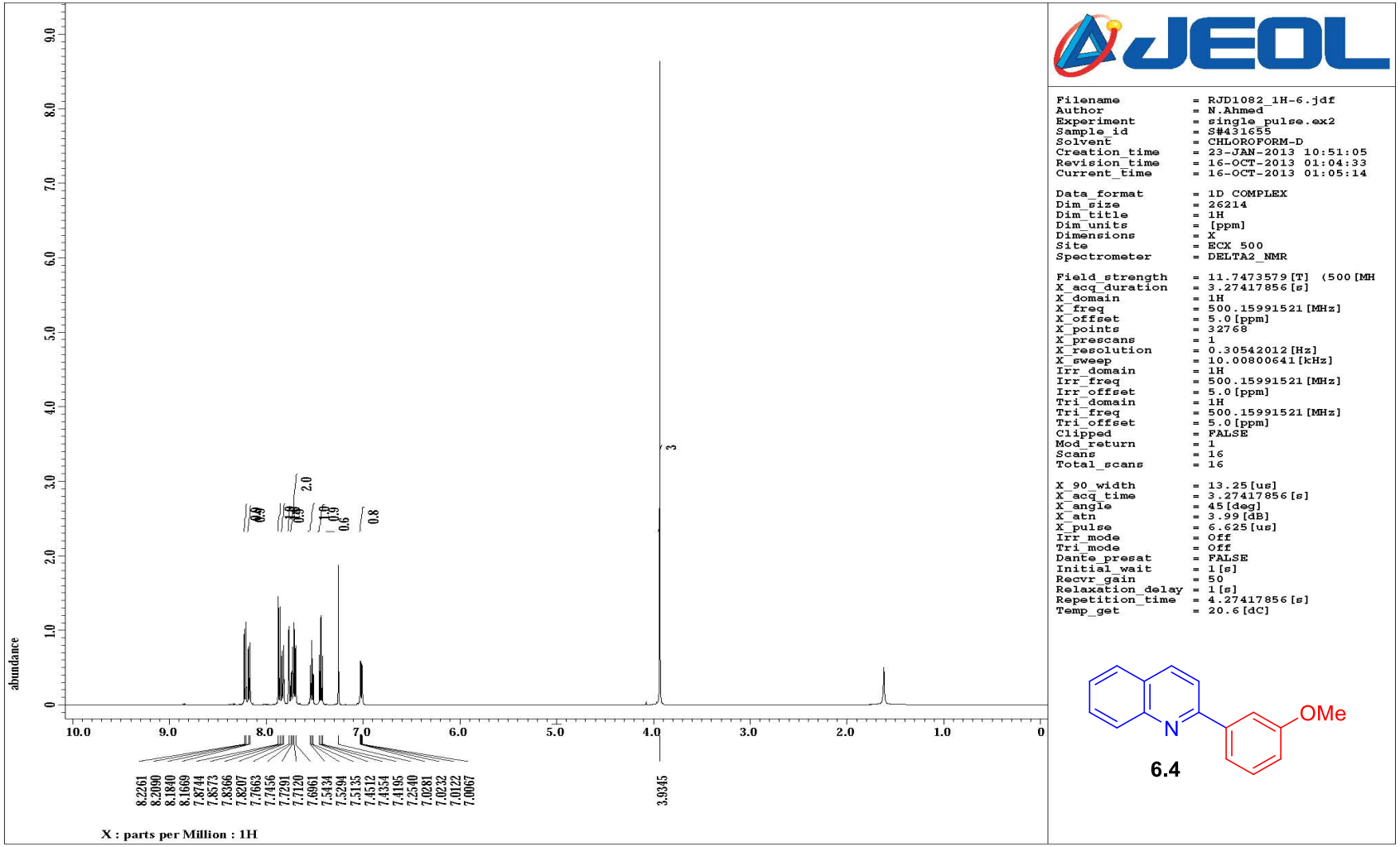
^{1}H NMR spectrum of 6-chloro-2-(3-methoxyphenyl)pyridine (**2.45**)



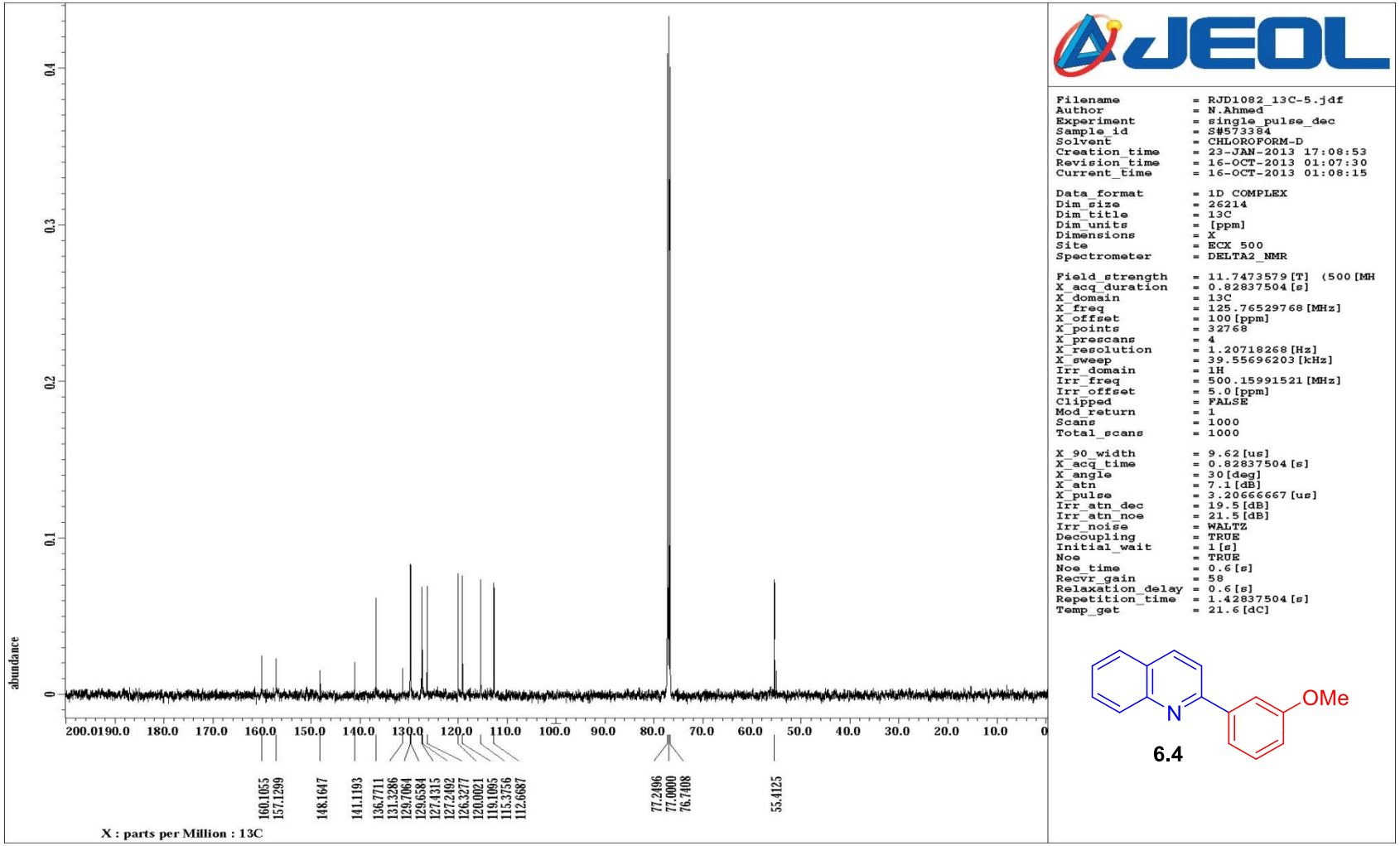
^{13}C NMR spectrum of 6-chloro-2-(3-methoxyphenyl)pyridine (**2.45**)



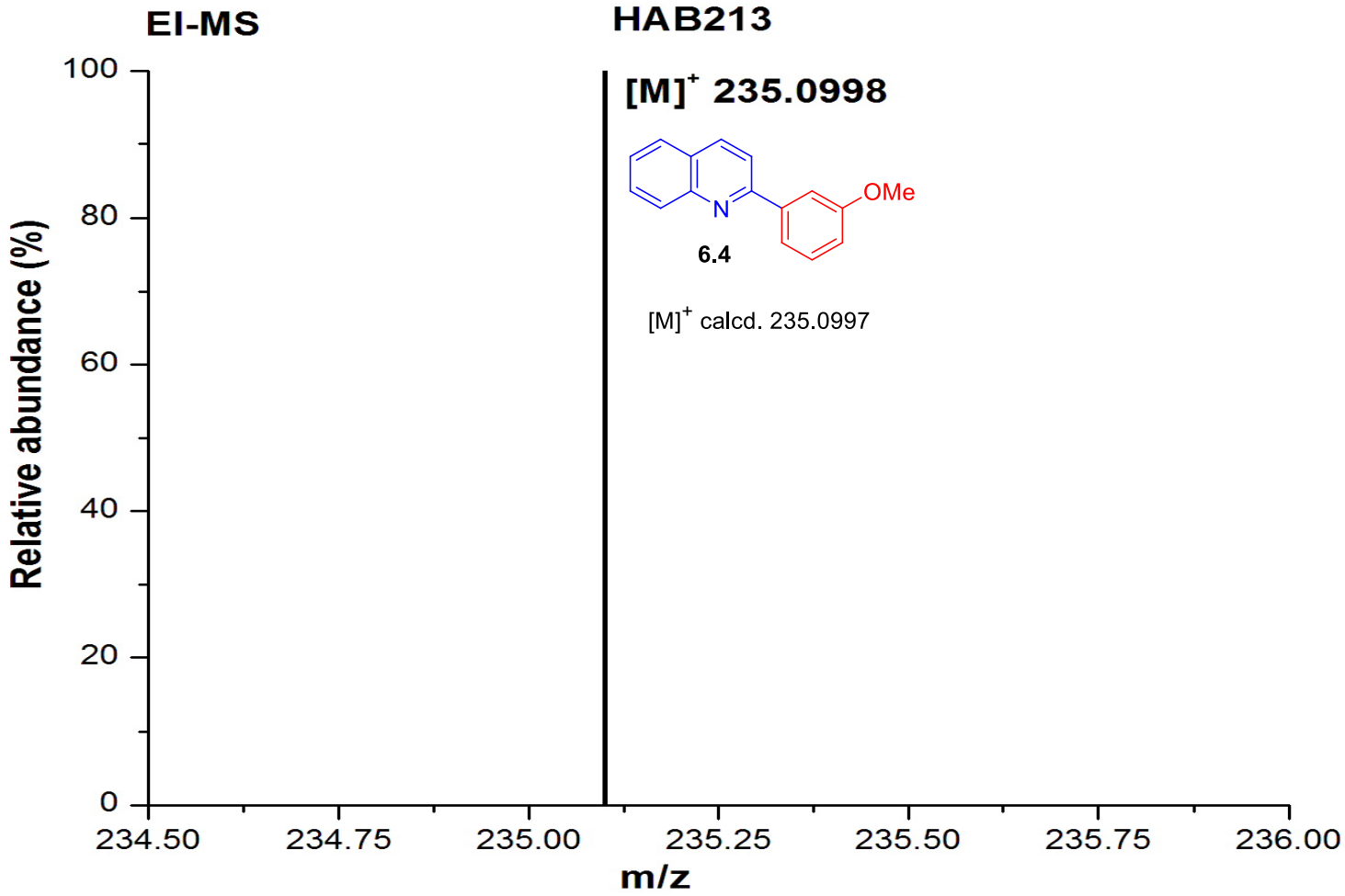
HRMS spectrum of 6-chloro-2-(3-methoxyphenyl)pyridine (**2.45**)



^{1}H NMR spectrum of 2-(3-methoxyphenyl)quinoline (**6.4**)



^{13}C NMR spectrum of 2-(3-methoxyphenyl)quinoline (**6.4**)



HRMS spectrum of 2-(3-methoxyphenyl)quinoline (**6.4**)