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The reaction of 2-amino-*N′*-arylbenzamidines with tetracyanoethene reinvestigated: Routes to imidazoles, quinazolines and quinolino[2',3':4,5]imidazo[1,2-*c*]quinazoline-8-carbonitrile

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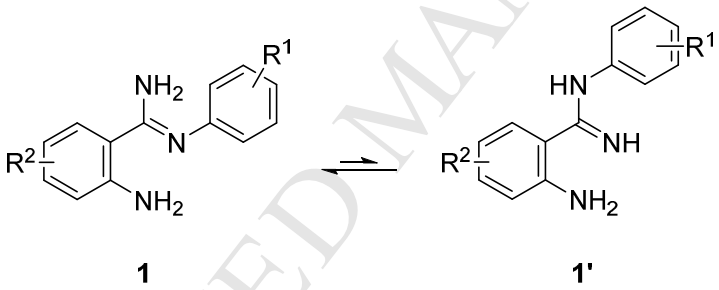
2-Amino-*N′*-phenylbenzamidine (**1a**) reacts with tetracyanoethene (TCNE) to give 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**11a**), 4-(phenylamino)quinazoline-2-carbonitrile (**5a**) and 4-imino-3-phenyl-3,4-dihydroquinazoline-2-carbonitrile (**9a**). By optimizing the reaction conditions each of the compounds can be isolated as the main product and seven examples of these reactions are described. The [1*H*-imidazol-4(5*H*)-ylidene]malononitrile **11a** was also independently synthesized in three steps from 2-amino-*N′*-(2-nitrophenyl)benz-amidine (**25**) and TCNE in an overall yield of 56%. Dimroth rearrangement of either 2-aminophenyl- or 2-nitrophenyl-substituted [1*H*-imidazol-4(5*H*)-ylidene]malono-nitriles **11a** or **27** with DBU in hot DCM gave the 2-[2-(2-aminophenyl)- and 2-[2-(2-nitrophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitriles **28** (71%) and **34** (59%), respectively. Treatment of the [3*H*-imidazol-4(5*H*)-ylidene]malono-nitrile **28** with ethyl orthoformate in DMA at 165 ^{o}C gave (*Z*)-2-[3-(phenylimino)-imidazo[1,2-*c*]quinazolin-2(3*H*)-ylidene]malononitrile (**36**) (70%), thermolysis of which gave quinolino[3',2':4,5]imidazo[1,2-*c*]quinazoline-13-carbonitrile (**30**) (97%).

Keywords: Heterocycles; quinazolines; imidazoles; tetracyanoethylene; amidines; cyclization reactions.

1. Introduction

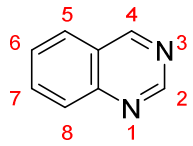
2-Amino-*N'*-arylbenzamidines **1**, which exist in equilibrium with several proto- and rota-tautomeric forms such as 2-amino-*N*-arylbenzamidine **1'** (Scheme 1), are synthetically useful building blocks and selected analogues target tyrosine kinases which are important in cancer drug discovery and development.[1] The benzamidines **1** can be readily prepared from: a) anthranilonitriles and anilines in the presence of $AlCl_3$;[2] b) reduction of *N*-aryl-2-nitrobenzamidines using $SnCl_2$ in concd. HCl;[3] c) reductive cleavage of 1,2,3-benzotriazines with hydrazine and Raney nickel;[4] or from d) HCl mediated hydrolytic cleavage of *N*-aryl-2,2-dimethyl-1,2-dihydroquinazolin-4-amines.[1b,1c]



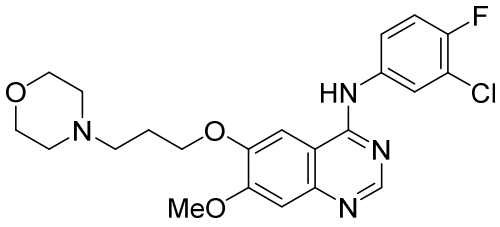
1 **1'**

Scheme 1. Structures of 2-amino-*N'*-arylbenzamidine **1** (lowest energy conformer) and the isomeric prototautomer 2-amino-*N*-arylbenzamidine **1'** (next lowest energy conformer $\Delta E_{\mathbf{1\text{-}1'}}$ -2.7 kcal mol^{-1}).[5]

2-Amino-*N'*-arylbenzamidines **1** are particularly useful for the synthesis of 4-(arylamino)quinazolines, a subclass of quinazolines,[6] that also act as kinase inhibitors.[7] Several derivatives, *e.g.*, Gefitnib (Iressa®),[8] have been approved and marketed for the treatment of cancer.

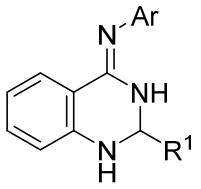


Quinazoline

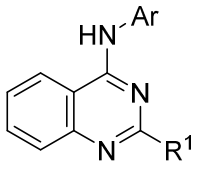


Gefitnib (Iressa®)

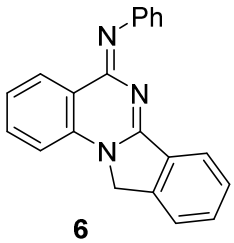
Treatment of 2-amino-*N'*-arylbenzamidines **1** with formic acid gives the 4-(aryl-amino)quinazolines **3**.[9] While reaction of 2-amino-*N'*-arylbenzamidines **1** with alkyl- or aryl-aldehydes with or without iodine affords 2-(alkyl/aryl)-*N*-aryl-2,3-dihydro-quinazolin-4(1*H*)-imines **2**,[2c,10] which can be oxidized to the aromatic 2-(alkyl/aryl)-4-anilinoquinazolines **4**.[2c,10] Treating amidines **1** with tetracyanoethene (TCNE) gave 4-(arylamino)quinazoline-2-carbonitriles **5** as the sole products.[2b] Interestingly, treating 2-amino-*N'*-phenylbenzamidine (**1a**) with phthalaldehyde afforded the poly-cyclic (*Z*)-*N*-phenylisoindolo[2,1-*a*]quinazolin-5(11*H*)-imine (**6**),[11] while treatment with tetracyanoquinodimethane (TCNQ) gave (Z)-2-{4-[4-(phenylimino)-3,4-dihydroquinazolin-2(1*H*)-ylidene]cyclohexa-2,5-dien-1-ylidene}malononitrile (**7**);[12] a similar substitution of both geminal nitriles was also observed with 2-(1,3-dioxo-1,3-dihydro-2*H*-inden-2-ylidene)malononitrile.[13]



2 (R^1 = Ar/Alk)



3 (R^1 = H)
4 (R^1 = Ar/Alk)
5 (R^1 = CN)



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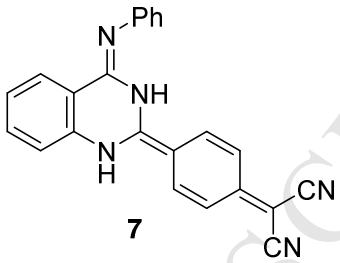
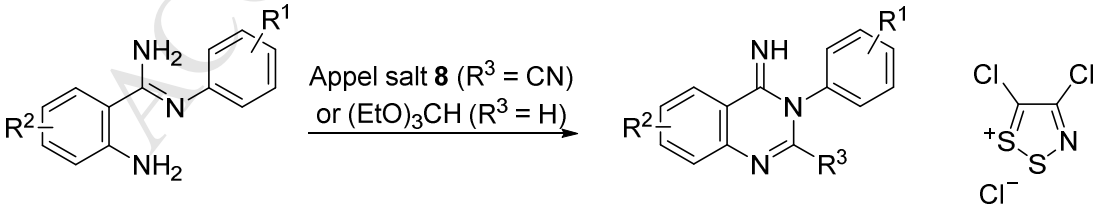


7

Recently, we reported the reaction of 2-amino-*N*′-arylbenzamidines **1** with 4,5-dichloro-1,2,3-dithiazolium chloride (**8**) (Appel salt) to give 3-aryl-4-imino-3,4-dihydroquinazoline-2-carbonitriles **9** (Scheme 2).[14] Since then, Szczepankiewicz *et al.*,[15] developed a solvent free synthesis of 3-arylquinazolin-4(3*H*)-imines **10** from 2-amino-*N*′-arylbenzamidines **1** and triethyl orthoformate (Scheme 2). The same group also proposed the intermediacy of 3-arylquinazolin-4(3*H*)-imines in the reaction of butane-2,3-diones with 2-amino-*N*′-arylbenzamidines to give 2-acetyl-3-aryl-2-methyl-2,3-dihydroquinazolin-4(1*H*)-ones and suggested that the formation of the quinazolin-4(3*H*)-imine was kinetically controlled.[16]



1

9 (R^3 = CN)
10 (R^3 = H)

8

Scheme 2. Reactions of 2-amino-*N*′-arylbenzamidines **1** with Appel salt **8** or triethyl orthoformate to give 3-aryl-quinazolin-4(3*H*)-imines **9** and **10**, respectively.

The transformation of 2-amino-*N′*-arylbenzamidines **1** into quinazolin-4(3*H*)-imines is important since this heterocycle features in biologically active compounds that behave as cholinesterase inhibitors,[17] cMET kinase inhibitors,[18] modulators of chemokine CCR3 activity,[19] or exhibit antiproliferative[20] or cardiotonic activities.[21] An understanding of the cyclization modes of 2-amino-*N′*-arylbenzamidines **1** can help the development of improved syntheses of these and other heterocycles.

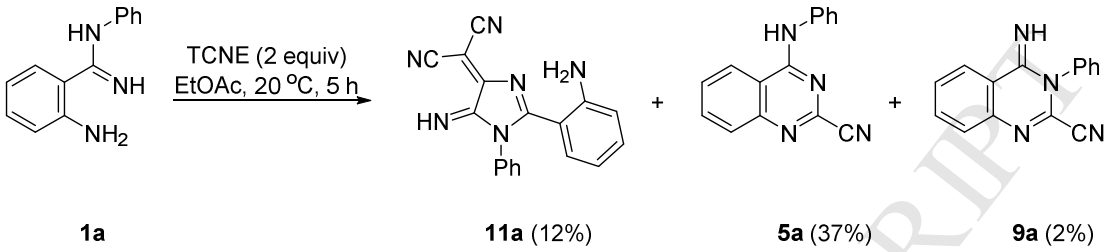
The recent results from the Szczepankiewicz team[15,16] prompted us to report our latest study: a reinvestigation of the reaction of 2-amino-*N′*-phenylbenzamidine (**1a**) with TCNE. In our hands, the reaction mixture was complex, affording not one but three products that can be isolated by column chromatography (Scheme 3). Reaction conditions were developed that enabled each of the compounds to be isolated as the major product. The results support Szczepankiewicz's kinetic ring closure arguments.[16] Finally, some cyclization chemistry of the obtained products are reported.

2. Results and discussion

2.1. Reinvestigating the reaction of TCNE and 2-amino-*N′*-phenyl-benzamidine (1a)

In our hands, repeating the literature reaction,[2b] *i.e.* adding a solution of 2-amino-*N′*-phenylbenzamidine (**1a**) (1 equiv) to a stirred solution of TCNE (2 equiv) in dry EtOAc, at *ca.* 20 ^{o}C failed after 5 h to give the expected precipitation of 4-(phenyl-amino)quinazoline-2-carbonitrile (**5a**) in the reported 71% isolated yield. TLC analysis of the reaction mixture supported the presence of three products that were isolated by chromatography and identified as 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**11a**) (12%), 4-(phenylamino)-quinazoline-2-carbonitrile (**5a**) (37%) and 4-imino-3-phenyl-3,4-dihydroquinazoline-

2-carbonitrile (**9a**) (2%) (Scheme 3). The isolated yields of products **5a**, **9a** and **11a** were reproducible on both 0.1 and 1.0 mmol reaction scales and the possibility that the products readily interconverted under the reaction conditions was excluded.



Scheme 3. The reaction of 2-amino-*N'*-phenylbenzamidine (**1a**) with TCNE according to the reported procedure.

The structure of the 4,5-dihydroimidazole **11a** was elucidated by single crystal X-ray crystallography (Figure 1), while the structures of the quinazolines **5a** and **9a** were supported by comparison of their known spectroscopic data. Nevertheless, owing to a mismatch in the reported melting point data of the quinazoline **5a** (mp 84-85 ^{o}C)[2b] and that obtained from our sample (mp 211.5-212.5 ^{o}C) we also solved its structure by single crystal X-ray crystallography (Figure 2).

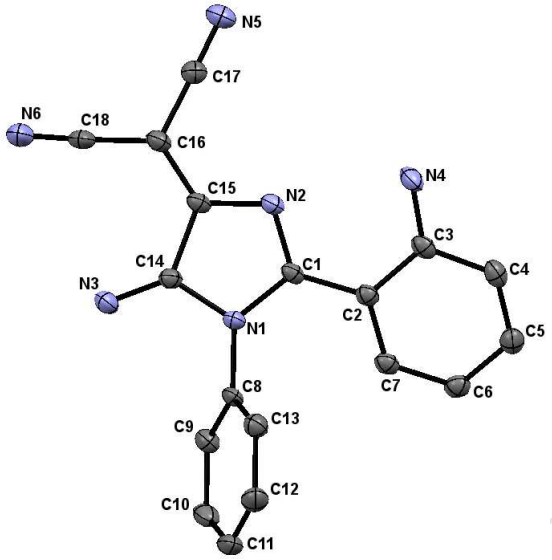


Fig. 1. The crystal structure of 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**11a**) (50% probability ellipsoids and hydrogen atoms omitted for clarity). An intramolecular N···H-N hydrogen bond (N···N 2.69 Å) holds the 2-(2-aminophenyl) substituent in an almost coplanar conformation (18.8°) with the imidazole ring.

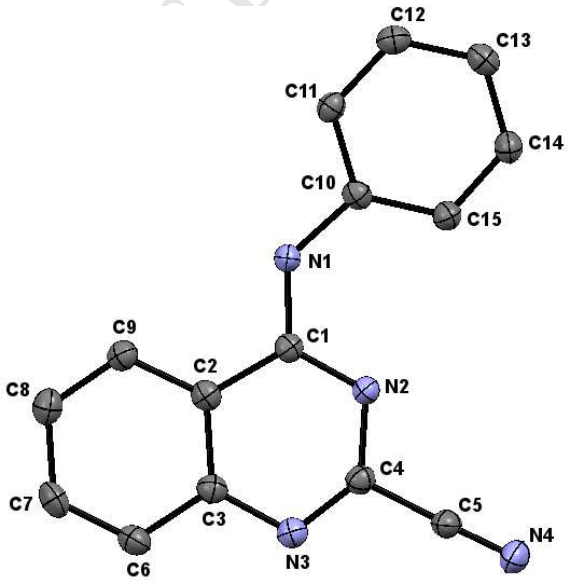


Fig. 2. The crystal structure of 4-(phenylamino)quinazoline-2-carbonitrile (**5a**) (50% probability ellipsoids and hydrogen atoms omitted for clarity).

In light of our interest in the chemistry of benzamidines and TCNE[22] we reoptimized this reaction by examining the mode of addition, reagent equivalents, choice of solvent, reaction temperature and use of acid or base additives.

Reversing the mode of addition, *i.e.* adding a solution of TCNE to a solution of benzamidine **1a** led to higher yields of the 4-(phenylamino)quinazoline **5a**. To clarify the need of excess TCNE we ran both modes of additions using equimolar ratios of benzamidine **1a**/TCNE (1:1) and obtained the products in very similar yields to the respective reactions run with benzamidine **1a**/TCNE ratio of 1:2. Investigating further, we added EtOAc solutions of TCNE (1 equiv) to EtOAc solutions of the benzamidine **1a** (1 equiv) cooled to 0-5 ^{o}C and also heated to 77 ^{o}C. At 0-5 ^{o}C the reaction after 3 days gave only two products, the quinazolines **5a** and **9a** in 92 and 1% yields, respectively but at 77 ^{o}C all three products formed and notably the yield of the imidazole **11a** was relatively high (25%). While the low temperature reaction gave a surprisingly good yield of the phenylaminoquinazoline **5a** (92%) it was difficult to maintain the temperature of the reaction mixture at *ca.* 5 ^{o}C for 3 days, as such, we investigated the effect of additives (acids and bases) in the hope that these could improve the reaction conditions or affect a change in the product distributions. Regardless of the mode of addition, when a 1:1 ratio of benzamidine **1a** to TCNE was reacted in EtOAc at 20 ^{o}C, the introduction of strong bases (0.25-1.5 equiv) such as NaOH, DBU or *i*-Pr_2NEt led to very low product yields and predominantly formation of intractable precipitates, while the addition of weaker bases such as pyridine or NaOAc gave product distributions and yields similar to reactions that were run without additives. The introduction of strong acids such as concd. HCl, TsOH·H_2O, H_2SO_4 and TFA, led to the formation of benzamidine salts, which precipitated from the reaction mixture, and very little reaction was observed with the TCNE even after

heating the reaction mixtures at reflux. The addition of milder acids, however, significantly affected the yields and product distributions. When TCNE (1 equiv) was added to a mixture of benzamidine **1a** (1 equiv) and glacial acetic acid (AcOH) (pK_a 4.76) (0.5 to 2.0 equiv) in EtOAc at 20 ^oC then the yields of the phenylamino-quinazoline **5a** improved; the highest yield (87%) was obtained using AcOH (1.5 equiv). Replacing AcOH with either formic acid (pK_a 3.77) or *t*-BuCO_2H (pK_a 5.02) gave lower overall yields. Interestingly, when the mode of addition was reversed and benzamidine **1a** (1 equiv) was added to a mixture of TCNE (1 equiv) and AcOH (0.5-1.0 equiv) a very different product distribution was obtained, with the imidazole **11a** (32%) and the phenylaminoquinazoline **5a** (33%) forming in near equal amounts. In this case, replacing the AcOH with formic acid led to the imidazole **11a** becoming the major product (up to 43% using 0.5 equiv of HCO_2H), while products **5a** and **9a** were observed as traces. The use of formic acid (0.5 equiv) to improve the yield of the imidazole **11a** was not applicable when the reaction solvent was replaced by THF, DCM, acetone or acetonitrile (MeCN). Our best reaction conditions for preparing the 4,5-dihydroimidazole **11a** were when a solution of the benzamidine **1a** (1 equiv) in EtOAc was added dropwise to a hot (77 ^oC) solution of TCNE (1 equiv) and formic acid (0.5 equiv) in EtOAc followed by heating at 77 ^oC for 2 h (*Conditions A*) which gave the imidazole **11a** in 45% yield. Using these conditions several analogues **11a-g** were prepared in 41-51% yields (Table 1, entries 1-7).

Since the addition of TCNE (1 equiv) to a mixture of benzamidine **1a** (1 equiv) and AcOH (1.5 equiv) in EtOAc at 20 ^oC led to phenylaminoquinazoline **5a** in 87% yield, we then examined replacement of the solvent in the hope that this reaction could be improved further. When the solvent was replaced by either THF, $MeNO_2$ or DCM the phenylaminoquinazoline **5a** was isolated in good yields (64-80%) while in EtOH and

PhH the yields were very low (8-17%). When MeCN used as the solvent the yield of the phenylaminoquinazoline **5a** (89%) was similar to that obtained with EtOAc (87%) but, there was no trace of the imidazole **11a**.

Table 1. Reactions of 2-amino-*N'*-arylbenzamidines **1** with TCNE under Conditions A, B and C, respectively.[a]

entry	Ar	conditions[a]	yields **11** (%)	yields **5** (%)	yields **9a** (%)
1	Ph	A	**11a** (45)	**5a** (6)	**9a** (trace)
2	4-Tol	A	**11b** (41)	**5b** (6)	**9b** (trace)
3	4-$MeOC_6H_4$	A	**11c** (48)	**5c** (7)	**9c** (trace)
4	4-FC_6H_4	A	**11d** (51)	**5d** (6)	**9d** (trace)
5	4-ClC_6H_4	A	**11e** (43)	**5e** (7)	**9e** (trace)
6	4-BrC_6H_4	A	**11f** (42)	**5f** (5)	**9f** (trace)
7	3,4-$(MeO)_2C_6H_3$	A	**11h** (44)	**5g** (6)	**9g** (trace)
8	Ph	B	0	**5a** (97)	**9a** (1)
9	4-Tol	B	0	**5b** (98)	**9b** (1)
10	4-$MeOC_6H_4$	B	0	**5c** (97)	**9c** (1)
11	4-FC_6H_4	B	0	**5d** (98)	**9d** (1)
12	4-ClC_6H_4	B	0	**5e** (95)	**9e** (2)
13	4-BrC_6H_4	B	0	**5f** (97)	**9f** (1)
14	3,4-$(MeO)_2C_6H_3$	B	0	**5g** (93)	**9g** (1)
15	Ph	C	0	**5a** (29)	**9a** (69)
16	4-Tol	C	0	**5b** (30)	**9b** (62)
17	4-$MeOC_6H_4$	C	0	**5c** (29)	**9c** (62)
18	4-FC_6H_4	C	0	**5d** (30)	**9d** (65)
19	4-ClC_6H_4	C	0	**5e** (31)	**9e** (69)
20	4-BrC_6H_4	C	0	**5f** (27)	**9f** (65)
21	3,4-$(MeO)_2C_6H_3$	C	0	**5g** (28)	**9g** (64)

[a] **Conditions A**: a solution of the benzamidine **1** (1 equiv) in EtOAc was added dropwise to a hot (77 ^oC) solution of TCNE (1 equiv) and formic acid (0.5 equiv) in EtOAc followed by heating at 77 ^oC for 2 h; **Conditions B**: a solution of TCNE (1 equiv) in MeCN was added to a solution of the benzamidine **1** (1 equiv) and AcOH (1 equiv) in MeCN at 20 ^oC and left to stir for 7-8 h; **Conditions C**: a solution of the benzamidine **1** (1 equiv) in MeCN was added dropwise to a solution of TCNE (2 equiv) in MeCN at -20 ^oC and left to stir at this temperature for 1 d.

As such, the reaction in MeCN was investigated further and when the quantity of AcOH added was reduced from 1.5 to 1 equiv the phenylaminoquinazoline **5a** yield improved to 97% and identified our best conditions (*Conditions B*) for the preparation of the 4-arylaminoquinazolines **5**. Interestingly, removal of the AcOH also led to high yields (94%) of the quinazoline **5a** but under these conditions the yields dropped for benzamidine analogues that hosted electron withdrawing halogen substituents on the aniline moiety. In these cases introducing the AcOH (1 equiv) additive to the reaction mixtures helped return product yields to greater than 93% (Table 1, entries 8-14).

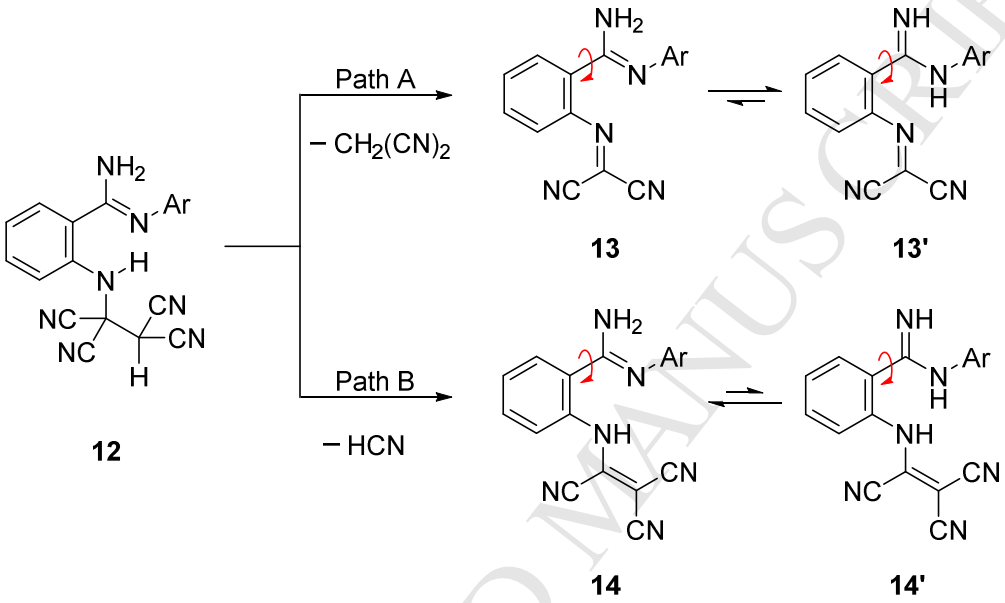
During an initial screen of reaction temperature we also noted that lower reaction temperatures (-20 ^{o}C) led to higher yields of both the imidazole **11a** (34%) and the iminoquinazoline **9a** (14%). A subsequent solvent screen identified that in DMF, DCM, $MeNO_2$ and MeCN no imidazole **11a** formed and that in MeCN the yield of the iminoquinazoline **9a** reached 69%. In MeCN the equivalents of TCNE could be reduced from 2 to 1 without a significant loss in product yield (69 to 64%) but these reactions required at least 4 days to consume all the starting benzamidine **1a**. Under these partially optimized conditions reversing the mode of addition *i.e.* adding TCNE (1 equiv) to a -20 ^{o}C cooled MeCN solution of the benzamidine **1a** (1 equiv) led to a ~50/50 mixture of both quinazolines, but interestingly the same mode of addition using EtOAc led to a good yield of the phenylaminoquinazoline **5a** (77%) and only a trace (1%) of the iminoquinazoline **9a**. In light of the lengthy reaction times (4 days) when a 1:1 ratio of reagents we chose our best conditions for the formation of the iminoquinazoline **9a** as the addition of the benzamidine **1a** (1 equiv) to a -20 ^{o}C cooled MeCN solution of TCNE (2 equiv) (*Conditions C*). Using these conditions we prepared several analogues **9a-g** in 62-69% yields (Table 1, entries 15-21).

2.2. Mechanistic rationale for the formation of products 5, 9 and 11

*2.2.1. Formation of 4-arylaminoquinazoline-2-carbonitriles **5** and 3-aryl-4-imino-3,4-dihydroquinazoline-2-carbonitriles **9***

2-Amino-*N'*-phenylbenzamidine (**1a**) contains three different nitrogen atoms: the primary amine of the aniline, which is the more nucleophilic, and two amidine nitrogens which are more basic, preferentially protonating on the imine nitrogen (C=N-Ph) to give the more delocalized cation.[23] Since primary anilines can react with TCNE to give *N*-aryltricyanovinylamines in good yields,[24] and in rare cases

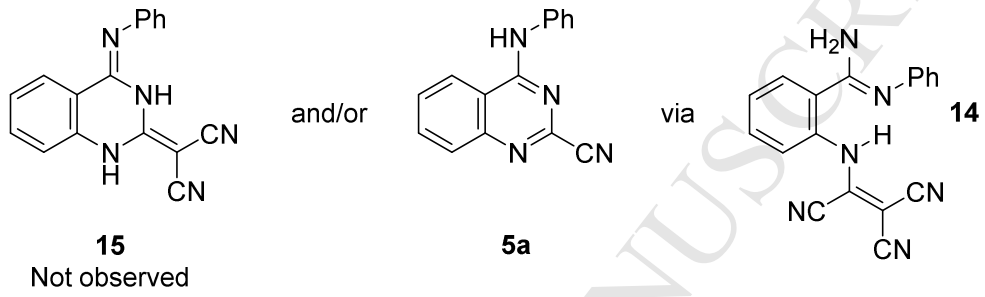
carbonimidoyl dicyanides,[25] we assume that the reaction between the 2-amino-*N'*-arylbenzamidines and TCNE yields an adduct **12** that converts to either the dicyanide **13** *via* loss of malononitrile (Path A) or the tricyanovinylamine **14** *via* loss of HCN (Path B) both of which can exist in equilibrium with various proto- and rota-tautomeric isomers (*e.g.*, isomers, **13'** and **14'**, respectively) (Scheme 4).



Scheme 4. Tentative formation of the dicyanide **13** and/or tricyanovinylamine **14**.

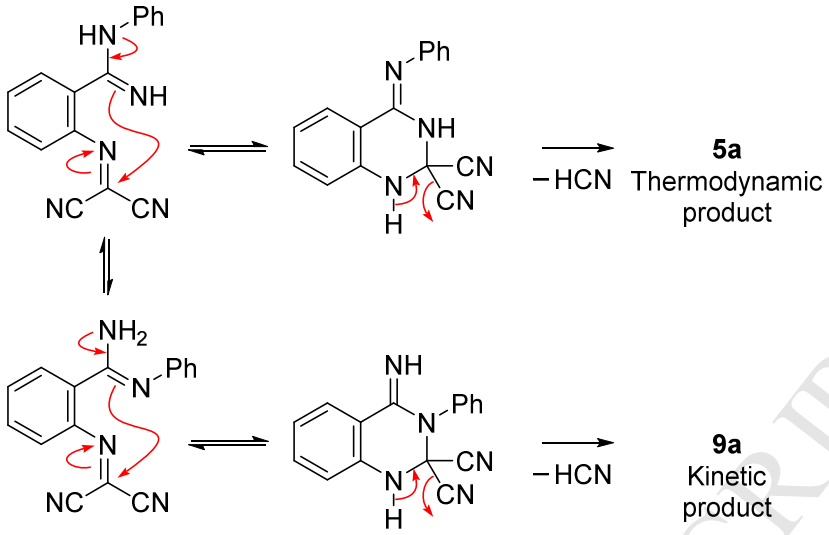
Disappointingly, none of these possible intermediates were observed in the reaction mixtures, presumably owing to a subsequent rapid intramolecular cyclization onto the neighboring amidine moiety to give the observed quinazolines **5** and **9**. There was some tentative support, however, that the intermediate was the carbonimidoyl dicyanide **13** rather than the tricyanovinylamine **14**: Firstly, the initial TCNE adduct **12** was expected to have the aniline NH group H-bonded to the amidine enhancing its acidity and therefore more likely to facilitate the subsequent elimination of malononitrile; secondly, had the tricyanovinylamine **14** been the intermediate then this could have reacted in a similar manner to TCNQ and led to the formation of the

ylidenemalononitrile **15** (Scheme 5) (*c.f.* compound **7**); thirdly, the carbonimidoyl dicyanide **13** was expected to be the more reactive (electrophilic) of the two and thus could explain why the subsequent cyclizations occurred so quickly that intermediates were not isolable. The above suppositions are intuitively derived and a clear picture can only come from further studies, nevertheless, for the purpose of the subsequent discussions we assume the carbonimidoyl dicyanide **13** to be the intermediate.



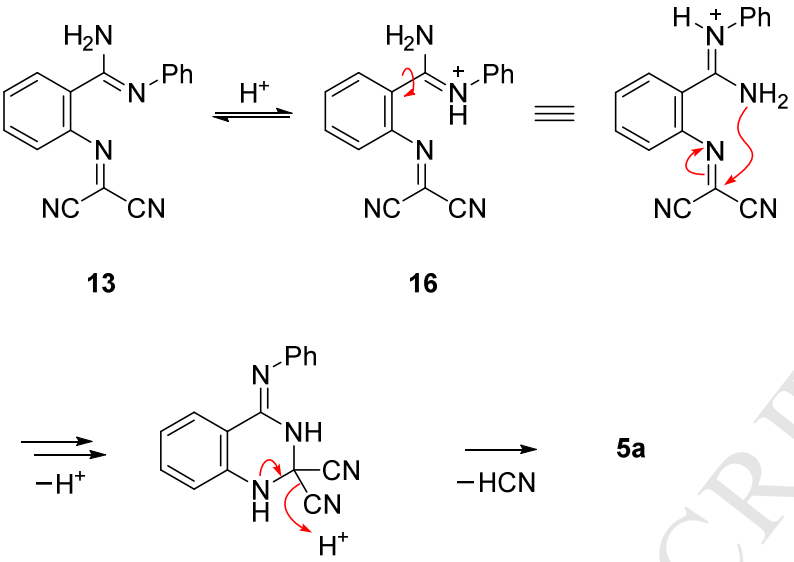
Scheme 5. Possible cyclization products derivable from the tricyanovinylamine **14**.

Computational studies by Szczepankiewicz *et al.*,[16] on the reaction of 2-amino-*N'*-phenylbenzamidine (**1a**) with butane-2,3-dione suggested that in our case the 4-imino-3-phenylquinazoline **9a** was the kinetic product and the phenylaminoquinazoline **5a** the thermodynamic product. Fortunately, when benzamidine **1a** and TCNE reacted in MeCN the relative formation of quinazolines **5a** and **9a** was satisfactorily controlled by moderating the reaction temperature and mode of addition. In the absence of additives the reaction mechanism presumably follows that shown in Scheme 6.



Scheme 6. Unassisted intramolecular cyclizations of the possible dicyanide **13** intermediate to give the observed quinazolines **5a** (thermodynamic product) and **9a** (kinetic product).

When preparing the arylaminoquinazolines **5**, it was noted that electron withdrawing halogens on the aniline moiety led to lower yields, necessitating the addition of AcOH (1 equiv) to the benzamidine solution. We assume that the role of the weak acid is to protonate the more basic amidine imine nitrogen (C=N-Ph) making it less nucleophilic, to afford the intermediate **16** that then undergoes a subsequent cyclization *via* the amidine amide-like nitrogen (=C-NH_2) (Scheme 7).



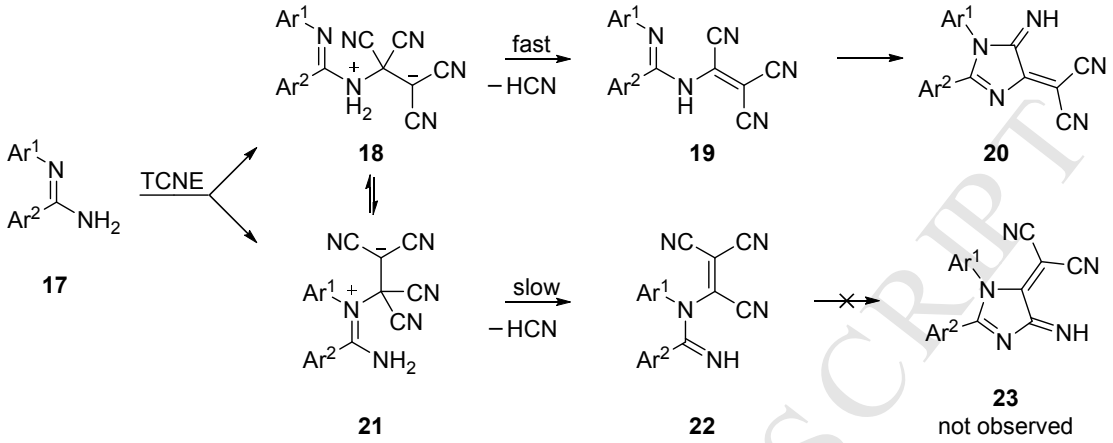
Scheme 7. Acid catalysed intramolecular cyclization of the possible dicyanide **13** intermediate to give the phenylaminoquinazoline **5a**.

Worthy of note is that most of the reported cyclizations of 2-amino-*N*′-phenyl-benzamidine (**1a**) that lead to the formation of 4-anilino or 4-arylimino quinazolines have been performed with heating and thus the isolation in these cases of the thermodynamic and not the kinetic product is unsurprising.

*2.2.2. Formation of 2-[2-(2-aminophenyl)-1-aryl-5-imino-1*H*-imidazol-4(5*H*)-ylidene]malononitriles **11**.*

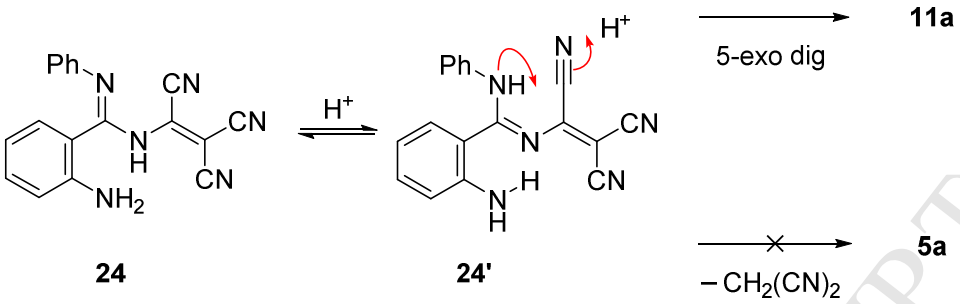
The mechanistic rationale for the formation of the red colored [1*H*-imidazol-4(5*H*)-ylidene]malononitriles **11** was more complex. From our earlier work, we know that 2-[2-aryl-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitriles **20** can be prepared from the reaction of *N*′-arylbenzamidines **17** with TCNE.[22] This addition of TCNE to the amidine amide-like nitrogen (=C-NH_2) (pK_a 8.2)[26] was unexpected. Presumably, the initial TCNE adducts **18** or **21** are in equilibrium but adduct **18**

proceeds more rapidly to the isolable tricyanovinylamidine **19** that then undergoes the *5-exo dig* cycloaddition to the observed imidazole **20** (Scheme 8).



Scheme 8. The reaction of *N'*-arylbenzamidine **17** with TCNE to give 2-[2-aryl-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitriles **20**.

In the reaction between TCNE and 2-amino-*N'*-phenylbenzamidine (**1a**), which contains a more nucleophilic phenylamine, the formation of the imidazole **11a** was surprising. Tentatively, the formic acid in the reaction mixture assists the formation of the imidazole **11a** in two distinct ways: firstly, by protonating the more basic amidine imine nitrogen (C=N-Ph) which enables TCNE to react with the remaining amide-like nitrogen (=C-NH_2), and secondly, by facilitating an acid-catalyzed *5-exo dig* cycloaddition[27] (Scheme 9).



24 **24'**

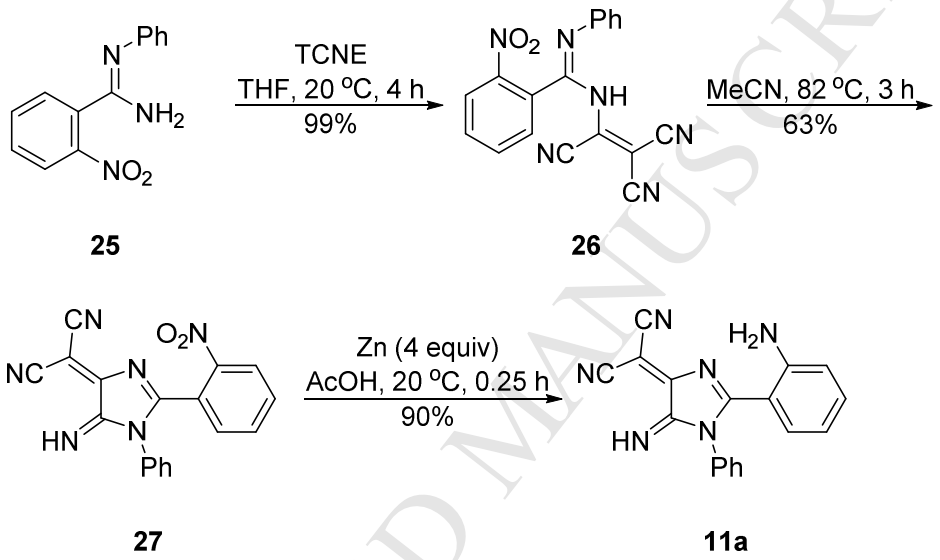
Scheme 9. Tentative reaction sequence for the conversion of the benzamidine **1a** into imidazole **11a** *via* the tricyanovinylamidine intermediate **24**.

Furthermore, this formic acid-catalyzed cyclization must be sufficiently fast to limit the alternative cyclization involving the tricyanovinylamidine **24** to give again the quinazoline **5a**. Worthy of note was that a highly probable internal H-bond in the tricyanovinylamidine **24** would hinder the latter cyclization. That the yield for the imidazole **11a** could not be improved above 45% suggests that the reaction is more complex that we describe. At least half of the reaction products remain as intractable polar materials and further work is needed to clarify the reactions mechanisms. We note that 2-amino-*N'*-arylbenzamidines **1** in neat 85% formic acid heated at 95 ^{o}C for 2 h afford the 4-arylaminoquinazolines **3** in 70-92% yields,[9] however, no trace of these products were observed in the reaction with TCNE.

2.3. Independent synthesis and chemistry of 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (11a)

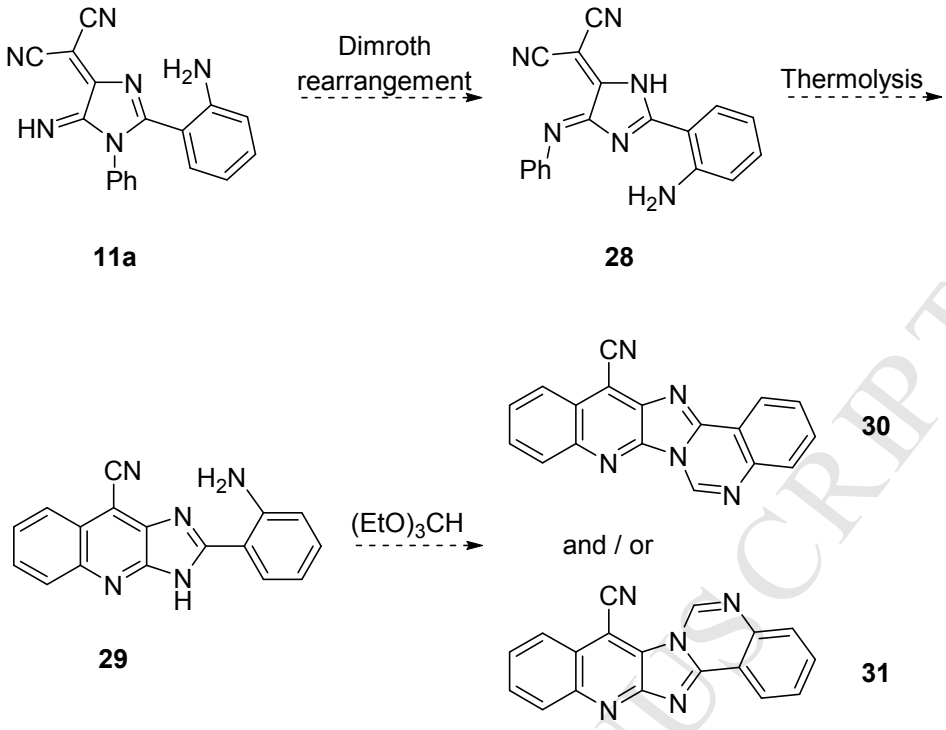
Previously, we reported an efficient route to [1*H*-imidazol-4(5*H*)-ylidene]malononitriles **20** *via* the reaction of TCNE with *N'*-arylbenzamidines **17** (Scheme 8).[22] In a similar manner the [1*H*-imidazol-4-ylidene]malononitrile **11a** can be independently

prepared by reacting TCNE with (*Z*)-2-nitro-*N'*-phenylbenzamidine (**25**) to give (*Z*)-2-nitro-*N'*-phenyl-*N*-(1,2,2-tricyanovinyl)benzamidine (**26**) which on warming in MeCN gave 2-[5-imino-2-(2-nitro-phenyl)-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]-malononitrile (**27**), mild reduction of which using Zn powder in AcOH gave the desired (imidazolylidene)malononitrile **11a** in four steps with a 43% overall yield (Scheme 10).



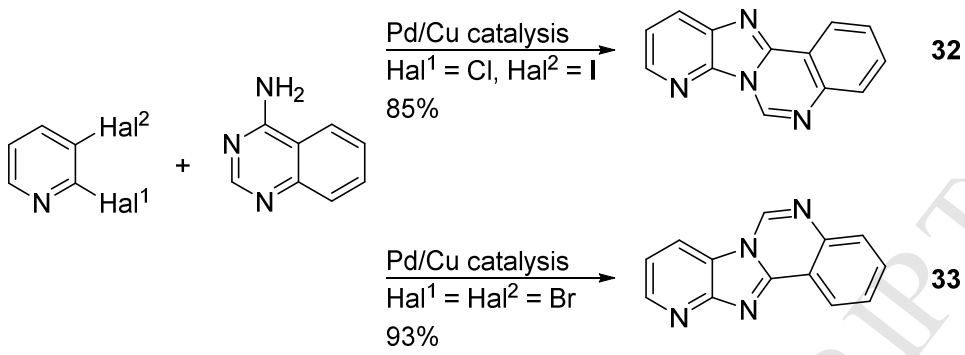
Scheme 10. Independent synthesis of the [4*H*-imidazol-4-ylidene]malononitrile **11a**.

Furthermore, [1*H*-imidazol-4(5*H*)-ylidene]malononitriles **20** can undergo a Dimroth rearrangement in either DCM/DBU or in MeOH/NaOH to give 2-(2-phenyl-5-aryl-3,5-dihydro-4*H*-imidazol-4-ylidene)malononitriles, thermolysis of which afforded imidazolo[4,5-*b*]quinolines.[22] The analogous Dimroth rearrangement of the [4*H*-imidazol-4-ylidene]malononitrile **11a**, and subsequent thermolysis of the obtained isomer **28**, could give 2-(2-aminophenyl)-1*H*-imidazo[4,5-*b*]quinoline-9-carbonitrile (**29**), which on treatment with triethyl orthoformate should give either quinolino-[3',2':4,5]imidazo[1,2-*c*]quinazoline-13-carbonitrile (**30**) or quinolino[2',3':4,5]-imidazo[1,2-*c*]quinazoline-8-carbonitrile (**31**) or both (Scheme 11).



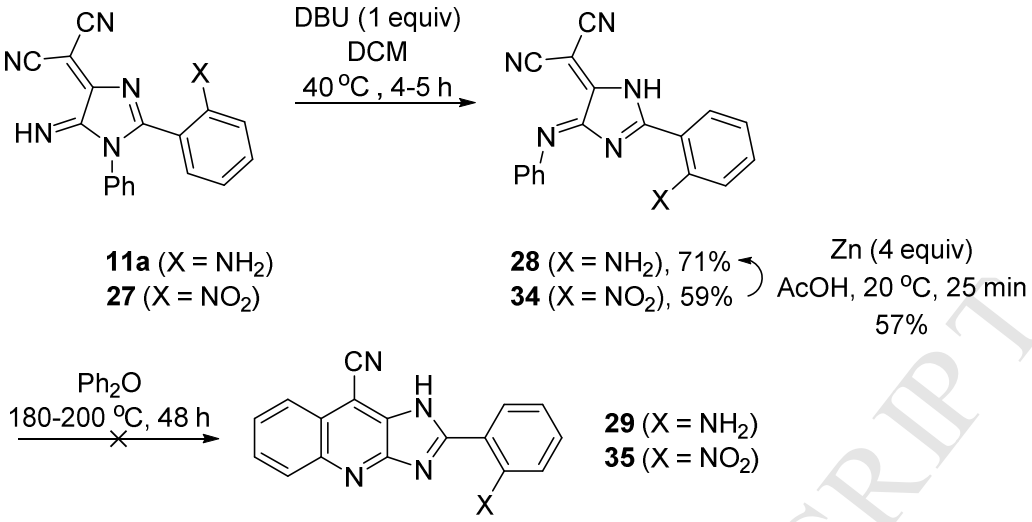
Scheme 11. Proposed route to quinolino[3',2':4,5]imidazo[1,2-*c*]quinazoline-13-carbonitrile (**30**) and quinolino[2',3':4,5]imidazo[1,2-*c*]quinazoline-8-carbonitrile (**31**).

Accessing either of these two pentacyclic heteroarenes looked attractive owing to their potential biological and/or material properties. Interestingly the closely related pyrido[3',2':4,5]imidazo[1,2-*c*]quinazoline (**32**) and pyrido[2',3'-4,5]imidazo[1,2-*c*]-quinazoline (**33**) have been prepared by Maes using an altogether different transition metal-catalyzed synthesis (Scheme 12).[28]



Scheme 12. Maes synthesis of pyrido[3',2':4,5]imidazo[1,2-*c*]quinazoline (**32**) and pyrido[2',3'-4,5]imidazo[1,2-*c*]quinazoline (**33**).[28]

As such, treating the 4,5-dihydroimidazole **11a** with DBU (1 equiv) in DCM at 40 ^{o}C for 3 h gave the Dimroth rearrangement product 2-[2-(2-aminophenyl)-5-(phenyl-imino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**28**) in 71% yield; interestingly, in MeOH/NaOH the Dimroth reaction failed. Unfortunately, thermolysis of the imidazole **28** in diphenyl ether at *ca.* 180 ^{o}C led to a complex reaction mixture with no major product (Scheme 13).

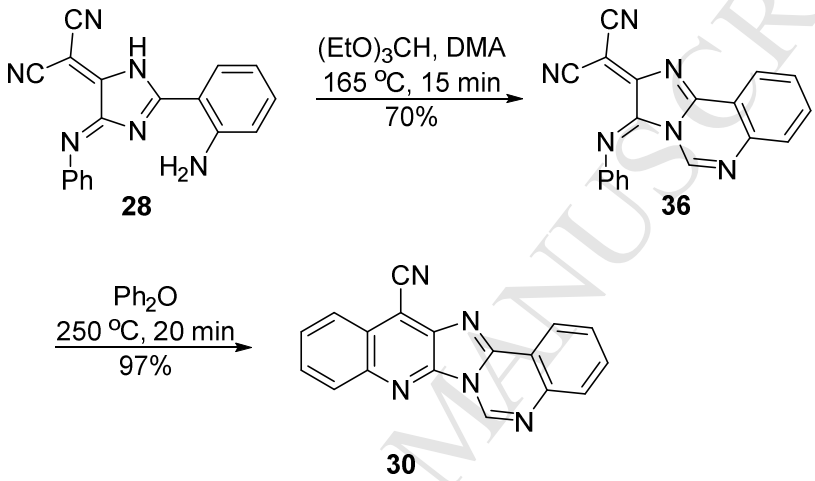


Scheme 13. Dimroth rearrangement of the imidazoles **11a** and **27** and attempted thermal conversion to 1*H*-imidazo[4,5-*b*]quinoline-9-carbonitriles **29** and **35**, respectively.

In light of this, a semi-independent synthesis of the desired imidazo[4,5-*b*]quinoline **29** was attempted: the Dimroth rearrangement of the available 2-nitrophenyl-substituted imidazole **27** using DBU/DCM gave the isomeric 2-nitrophenylimidazole **34** in 59% yield; similar to the amino analogue above, the attempted rearrangement in MeOH/MeONa failed. Furthermore, the thermolysis of the 2-nitrophenylimidazole **34** in diphenyl ether at *ca.* 200 °C time 48 h, led to a complex reaction mixture and intractable solids. Any doubts regarding the structure of the 2-nitrophenyl Dimroth product **34** was probed by reduction of the nitro group in the presence of Zn powder (4 equiv) in AcOH, to give the amino analogue **28** in 57% yield identical to that described above (Scheme 13).

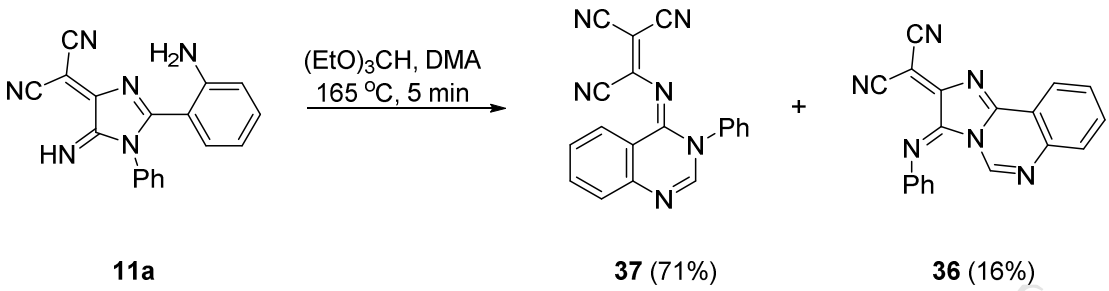
To overcome the above, the [3*H*-imidazol-4(5*H*)-ylidene]malononitrile **28** was treated with triethyl orthoformate in *N*,*N*-dimethylacetamide (DMA) at 165 °C for 15 min to give the orange colored (*Z*)-2-[3-(phenylimino)imidazo[1,2-*c*]quinazolin-2(3*H*)-ylid-

ene]malononitrile (**36**) in 70% yield, the structure of which was supported by single crystal X-ray crystallography (Figure 3). Differential scanning calorimetry (DSC) studies of the imidazoquinazoline **36** indicated a decomposition onset point at 234.6 ^{o}C and gratifyingly, heating the compound in diphenyl ether at 250 ^{o}C for 20 min gave the desired quinolino[3',2':4,5]imidazo[1,2-*c*]quinazoline-13-carbonitrile (**30**) in 97% yield (Scheme 14).



Scheme 14. Synthesis of quinolino[3',2':4,5]imidazo[1,2-*c*]quinazoline-13-carbonitrile (**30**).

Interestingly, attempts to prepare the other isomer, by treating the [1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**11a**) with ethyl orthoformate gave two unexpected products, the yellow colored 2-[(3-phenylquinazolin-4(3*H*)-ylidene)amino]ethene-1,1,2-tricarbonitrile (**37**) in 71% and the imidazo[1,2-*c*]quinazoline **36** (Scheme 15) in 16% yield. The structure of the tricarbonitrile **37** was supported by single crystal X-ray crystallography (Figure 4).



11a **37** (71%) **36** (16%)

Scheme 15. Reaction of the [1*H*-imidazol-4(5*H*)-ylidene]malononitrile **11a** with ethyl orthoformate to give the ethene-1,1,2-tricarbonitrile **37** and the imidazo[1,2-*c*]-quinazoline **36**

2-[(3-Phenylquinazolin-4(3*H*)-ylidene)amino]ethene-1,1,2-tricarbonitrile (**37**) showed a decomposition with an onset temperature at 278.7 °C and a peak max. at 300.4 °C (by DSC); however, **37** was thermally stable after heating in diphenyl ether at *ca*. 300 °C for 24 h, indicating that it was not an intermediate to the formation of the imidazoquinazoline **36**. Presumably, under the reaction conditions the (imidazol-ylidene)malononitrile **11a** can ring open in two distinctly different ways, the first to regenerate a tricyanovinyl intermediate (either before or after the quinazoline is formed) that leads to the formation of the major product **37** and the second must be a Dimroth related ring opening that leads to the formation of the minor product **36**.

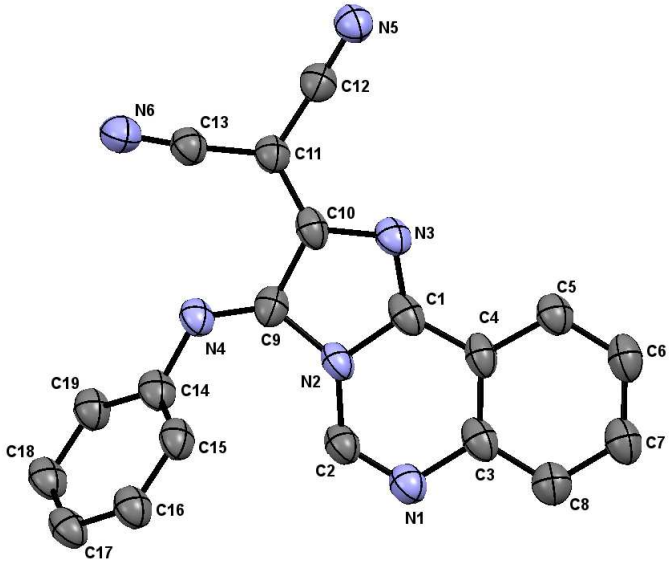


Fig. 3. The crystal structure of (*Z*)-2-[3-(phenylimino)imidazo[1,2-*c*]quinazolin-2(3*H*)-ylidene]malononitrile (**36**) (50% probability ellipsoids and hydrogen atoms omitted for clarity).

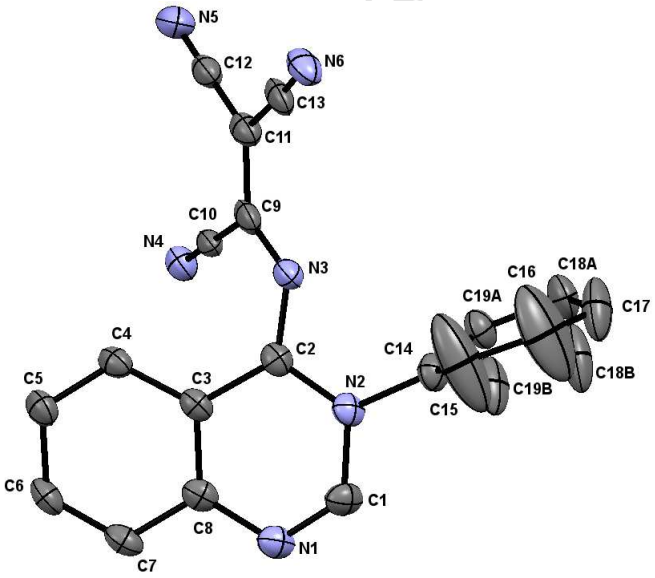


Fig. 4. The crystal structure of 2-[(3-phenylquinazolin-4(3*H*)-ylidene)amino]ethene-1,1,2-tricarbonitrile (**37**) (50% probability ellipsoids and hydrogen atoms omitted for clarity).

3. Conclusions

The reaction of 2-amino-*N'*-arylbenzamidines **1** and TCNE is more complex than originally reported affording three products **5**, **9** and **11** which, depending on the reaction conditions can be isolated as the main reaction products. By adding the benzamidines **1a-g** to a hot EtOAc solution of TCNE in the presence of HCO_2H the [1*H*-imidazol-4(5*H*)-ylidene]malononitriles **11a-g** can be prepared in 41-51% yields. By adding TCNE to a solution of the benzamidines **1a-g** and AcOH in MeCN at 20 ^oC the 4-(arylamino)quinazoline-2-carbonitriles **5a-g** can be prepared in 93-98% yields. While adding the benzamidines **1a-g** to a cooled (-20 ^oC) MeCN solution of TCNE afforded the isomeric 3-aryl-4-iminoquinazoline-2-carbonitriles **9a-g** in 62-69% yields. Mechanistic rationale suggests that the latter quinazolines **9** are the kinetic products and the 4-(arylamino)quinazolines **5** the thermodynamic products. Furthermore, the use of mild acids such as AcOH and HCO_2H was beneficial in enhancing the yields of the 4-(arylamino)quinazolines **5** and the [1*H*-imidazol-4(5*H*)-ylidene]malononitriles **11**. The imidazole **5a**, which undergoes a Dimroth rearrangement in the presence of DBU was also a useful precursor to a new pentacyclic system quinolino[3',2':4,5]imidazo[1,2-*c*]quinazoline-13-carbonitrile (**30**). The mechanistic rationale provided for the above transformations remains tentative pending further studies, nevertheless we believe the chemistry demonstrates that 2-amino-*N'*-arylbenzamidines **1** are valuable building blocks for heterocyclic synthesis and warrant further study.

4. Experimental Section

4.1. General procedures

Reactions were protected from atmospheric moisture by $CaCl_2$ drying tubes. Anhydrous Na_2SO_4 was used for drying organic extracts and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by TLC using commercial glass backed thin layer chromatography (TLC) plates (Merck Kieselgel 60 F_{254}). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography[29] was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm). Melting points were determined using a Koefler−Hotstage microscope apparatus or a DSC with samples hermetically sealed in aluminum pans under an argon atmosphere, using heating rates of 5 ^{o}C/min. Solvents used for recrystallization are indicated after the melting point. UV spectra were obtained using a Perkin-Elmer Lambda-25 UV/vis spectrophotometer and inflections are identified by the abbreviation “inf”. IR spectra were recorded on a Shimadzu FTIR-NIR Prestige-21 spectrometer with a Pike *Miracle* Ge ATR accessory and strong, medium and weak peaks are represented by s, m and w, respectively. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance 300 machine (at 300 and 75 MHz, respectively) or on a 500 machine (at 500 and 125 MHz, respectively). Deuterated solvents were used for homonuclear lock, and the signals are referenced to the deuterated solvent peaks. APT NMR studies identified quaternary, tertiary, secondary, and primary carbons, which are indicated by (s), (d), (t), and (q) notations, respectively. Low resolution (EI) mass spectra were recorded on a Shimadzu Q2010 GCMS with direct inlet probe. MALDI TOF mass spectra were recorded on a Bruker Autoflex III Smartbeam instrument. 2-

Amino-*N'*-aryl-benzamidines **1a-f**[2a] and tetracyanoethylene (TCNE)[30] were prepared according to literature procedures.

4.2. Preparation of new 2-amino-*N'*-arylbenzamidines

*4.2.1. 2-Amino-N'-(3,4-dimethoxyphenyl)benzamidine (**1g**).* To stirred anthranilonitrile (550 μL, 5.36 mmol) at *ca.* 20 ^{o}C was added in one portion powdered anhydrous $AlCl_3$ (706 mg, 5.36 mmol). The reaction mixture was then heated (*ca.* 100 ^{o}C) until a homogenous melt formed. To this hot melt was then added 3,4-dimethoxyaniline (489 μL, 5.36 mmol) and the mixture was heated (*ca.* 100 ^{o}C) for 12 h and then allowed to cool to *ca.* 20 ^{o}C. The resultant solid mass was then crushed and slurried in 10% NaOH (40 mL), extracted with DCM (5 × 50 mL), washed with H_2O (1 × 40 mL) and the organic phase dried (Na_2SO_4), adsorbed onto silica and chromatographed (*t*-BuOMe/EtOH, 95:05) to give the *title compound* **1g** (873 mg, 60%) as colorless needles, mp (hotstage) 144-145 ^{o}C (*c*-hexane/DCM, 9:1); R_f 0.45 (*t*-BuOMe/EtOH, 95:05); (found: C, 66.45; H, 6.45; N, 15.41. $C_{15}H_{17}N_3O_2$ requires C, 66.40; H, 6.32; N, 15.49%); λ_{max}(DCM)/nm 251 inf (log ε 4.20), 297 (3.91), 328 (3.91); ν_{max}/cm^{-1} 3493w, 3431w, 3366w and 3204w (NH_2), 3007w (Ar CH), 2968w and 2959w (Alk CH), 1626s, 1582m, 1574w, 1537w, 1504s, 1464w, 1451w, 1439w, 1410w, 1375w, 1325w, 1279w, 1260w, 1231s, 1198m, 1161w, 1152w, 1132m, 1026m, 941m, 868w, 842w, 818w, 773m, 762m, 748s, 719w; δ_H(500 MHz; $CDCl_3$) 7.42 (1H, d, *J* 7.5, Ar *H*), 7.19 (1H, ddd, *J* 7.5, 7.5, 1.0, Ar *H*), 6.87 (1H, d, *J* 8.5, Ar *H*), 6.74-6.68 (2H, m, Ar *H*), 6.58 (1H, d, *J* 2.0, Ar *H*), 6.54 (1H, dd, *J* 8.3, 2.3, Ar *H*), 6.00 (2H, br s, N*H*$_2$), 4.85 (2H, br s, N*H*$_2$), 3.87 (3H, s, OC*H*$_3$), 3.86 (3H, s, OC*H*$_3$); δ_C(75 MHz; $CDCl_3$) 156.6 (s), 149.9 (s), 147.8 (s), 145.1 (s), 142.1 (s), 131.1 (d),

127.3 (d), 117.2 (d), 116.7 (d), 116.5 (s), 112.8 (d), 112.2 (d), 106.2 (d), 56.2 (q, O*C*H$_3$), 55.8 (q, O*C*H$_3$); *m*/*z* (MALDI-TOF) 273 (MH$^+$+1, 5%), 272 (MH$^+$, 100).

4.3. The reaction of TCNE with 2-amino-*N'*-phenylbenzamidine (1a) according to the reported literature[2b]

To a stirred solution of TCNE (256 mg, 2.00 mmol) in dry EtOAc (10 mL) at *ca*. 20 ^{o}C was added a solution of 2-amino-*N'*-phenylbenzamidine (**1a**) (211 mg, 1.00 mmol) in dry EtOAc (10 mL) and left to stir for 5 h at *ca*. 20 ^{o}C. The reaction mixture was then adsorbed onto silica and chromatographed (DCM/*t*-BuOMe, 90:05) to give *2-[2-(2-aminophenyl)-5-imino-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile **(11a)*** (38.2 mg, 12%) as red needles, mp (DSC) decomp. onset 197.9 ^{o}C, peak max. 201.2 ^{o}C (from *n*-pentane/THF, 90:10); R_f 0.47 (DCM/Et$_2$O, 98:02); (found: C, 69.20; H, 3.72; N, 26.83. $C_{18}H_{12}N_6$ requires C, 69.22; H, 3.87; N, 26.91%); λ_{max}(DCM)/nm 256 inf (log ε 4.36), 296 inf (4.21), 336 (4.34), 407 (4.37), 431 (4.49), 510 (4.48); ν_{max}/cm^{-1} 3404w (NH_2), 3327w, 3285w and 3231w (NH), 2226w and 2207w (C≡N), 1622m, 1578w, 1551w, 1495s, 1477s, 1422s, 1396s, 1341m, 1318m, 1267m, 1248s, 1229m, 1198w, 1169m, 1113w, 1077w, 1067w, 1026w, 989w, 943w, 877w, 847w, 833w, 812w, 785w, 774w, 744s, 721w; δ_H(500 MHz; DMSO-d_6) 9.93 (1H, s, N*H*), 7.75 (2H, br s, N*H*$_2$), 7.61-7.59 (3H, m, Ar *H*), 7.40 (2H, d, *J* 6.5, Ar *H*), 7.18 (1H, dd, *J* 7.8, 7.8, Ar *H*), 6.81 (1H, d, *J* 9.0, Ar *H*), 6.59 (1H, d, *J* 8.5, Ar *H*), 6.17 (1H, dd, *J* 8.3, 8.3, Ar *H*); δ_C(125 MHz; DMSO-d_6) one C (d) resonance missing, 169.1 (s), 166.7 (s), 155.2 (s), 154.5 (s), 135.6 (d), 134.0 (s), 130.7 (d), 130.1 (d), 128.8 (d), 117.7 (d), 115.0 (d), 114.3 (s, *C*≡N), 113.4 (s, *C*≡N), 104.2 (s), 63.2 [s, *C*(CN)$_2$]; *m/z* (EI) 312 (M$^+$, 100%), 284 (7), 245 (8), 220 (11), 194 (22), 167 (8), 118 (35), 104 (22), 92 (14), 77 (46), 65 (10), 51 (18). Further elution (DCM/*t*-BuOMe, 90:20) gave

4-(phenylamino)quinazoline-2-carbonitrile (**5a**) (92.6 mg, 37%) as colorless needles, mp (hotstage) 210-211 °C (from $CHCl_3$), mp (DSC) onset 211.7 °C, peak max. 212.5 °C (lit.[2b] 84-85 °C) (from $CHCl_3$); R_f 0.58 (DCM/*t*-BuOMe, 95:05); (found: C, 73.29; H, 3.97; N, 22.60. $C_{15}H_{10}N_4$ requires C, 73.16; H, 4.09; N, 22.75%); λ_{max}(DCM)/nm 245 (log ε 3.66), 259 (4.75), 280 (3.28), 336 (4.27); ν_{max}/cm^{-1} 3402w, 3373w and 3346w (NH), 3061w and 3011w (Ar CH), 2247w (C≡N), 1614m, 1607m, 1568s, 1530m, 1522m, 1495s, 1487s, 1449m, 1422m, 1412m, 1369m, 1361m, 1317m, 1304w, 1292w, 1258w, 1217w, 1175w, 1161w, 1125w, 1107w, 1094w, 1078w, 1032w, 993w, 903w, 864w, 795w, 789w; δ_H(500 MHz; $CDCl_3$) 7.99 (1H, d, *J* 8.0, Ar *H*), 7.94 (1H, d, *J* 8.0, Ar *H*), 7.91 (1H, d, *J* 7.5, Ar *H*), 7.78 (2H, d, *J* 8.0, Ar *H*), 7.73 (1H, dd, *J* 7.8, 7.8 Ar *H*), 7.63 (1H, br s, N*H*), 7.46 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.24 (1H, dd, *J* 7.5, 7.5, Ar *H*); δ_H(500 MHz; DMSO-d_6) 10.31 (1H, br s, N*H*), 8.62 (1H, d, *J* 8.0, Ar *H*), 7.98 (1H, dd, *J* 8.0, 8.0, Ar *H*), 7.88 (1H, d, *J* 8.0, Ar *H*), 7.81 (1H, ddd, *J* 7.8, 7.8, 1.0, Ar *H*), 7.75 (2H, d, *J* 7.3, Ar *H*), 7.46 (2H, dd, *J* 8.0, 8.0, Ar *H*), 7.23 (1H, dd, *J* 7.5, 7.5, Ar *H*); δ_C(75 MHz; DMSO-d_6) 158.5 (s), 149.0 (s), 140.1 (s), 138.1 (s), 134.5 (d), 129.1 (d), 128.8 (d), 128.2 (d), 125.2 (d), 123.45 (d), 123.4 (d), 117.0 (s), 115.6 (s); *m/z* (EI) 246 (M^+, 42%), 245 (M^+-1, 100), 219 (2), 192 (4), 169 (8), 123 (6), 102 (10), 97 (7), 77 (14). Further elution (DCM/*t*-BuOMe, 90:20) gave 4-imino-3-phenyl-3,4-dihydroquinazoline-2-carbonitrile (**9a**) (4.7 mg, 2%) as colorless needles, mp (hotstage) 141-142 °C (lit.[14] 141-142 °C) (from *c*-hexane), mp (DSC) onset 143.9 °C, peak max. 146.2 °C (from *c*-hexane); R_f 0.48 (DCM/*t*-BuOMe, 90:10); λ_{max}(DCM)/nm 237 inf (log ε 4.25), 245 inf (4.18), 255 (4.13), 265 (4.19), 274 (4.11), 298 inf (3.77), 311 (3.94), 324 (3.99), 340 inf (3.85); ν_{max}/cm^{-1} 3341w, 3308w (NH), 3071w (Ar CH), 2239w (C≡N), 1643m, 1605w, 1574w, 1560m, 1491w, 1472w, 1462m, 1348m, 1302m, 1283m, 1227w, 1217w, 1167m, 1138m, 1030w,

1007w, 997w, 876w, 827w, 800w, 760s; δ_H(300 MHz; $CDCl_3$) 8.25 (1H, d, *J* 6.9, Ar *H*), 7.69-7.63 (5H, m, Ar *H*), 7.54 (1H, ddd, *J* 7.4, 7.4, 1.8, Ar *H*), 7.44-7.40 (2H, m, Ar *H*), 6.71 (1H, br s, N*H*); δ_C(125 MHz; $CDCl_3$) 153.4 (s), 143.2 (s), 135.0 (s), 133.4 (d), 131.3 (d), 131.2 (s), 131.0 (d), 129.9 (d), 129.0 (d), 128.4 (d), 125.6 (d), 122.5 (s), 111.3 (s, *C*≡N); *m/z* (EI) 246 (M^+, 34%), 245 (M^+-H, 100), 236 (7), 219 (17), 192 (11), 160 (8), 141 (7), 129 (7), 118 (12), 113 (11), 111 (12), 102 (25), 97 (17), 91 (20), 85 (19), 83 (17), 77 (64), identical to an authentic sample.

4.4. Preparation of 2-[2-(2-aminophenyl)-1-aryl-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitriles 11a-g (see Table 1, entries 1-7, Conditions A)

*4.4.1. 2-[2-(2-Aminophenyl)-5-imino-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylid-ene]malononitrile (**11a**) (typical procedure).* To a stirred solution of TCNE (128 mg, 1.00 mmol) in dry EtOAc (10 mL) at *ca*. 20 °C was added 85% formic acid (18.9 μL, 0.5 equiv) and the mixture was then heated to *ca*. 77 °C. To this mixture, a solution of 2-amino-*N'*-phenylbenzamidine (**1a**) (211 mg, 1.00 mmol) in dry EtOAc (10 mL) was added dropwise (10 min) and left to stir for 2 h at *ca*. 77 °C. On cooling to *ca.* 20 °C, the reaction mixture was adsorbed onto silca and chromatographed (DCM/*t*-BuOMe, 90:05) to give the title compound **11a** (141.2 mg, 45%) as red needles, mp (DSC) decomp. onset 197.9 °C, peak max. 201.2 °C (from *n*-pentane/THF, 90:10); R_f 0.47 (DCM/Et_2O, 98:02); identical to that described above. Further elution (DCM/*t*-BuOMe, 95:05) gave 4-(phenylamino)quinazoline-2-carbonitrile (**5a**) (14.2 mg, 6%) as colorless needles, mp (hotstage) 210-211 °C (lit.[2b] 84-85 °C) (from $CHCl_3$); R_f 0.58 (DCM/*t*-BuOMe, 95:05), identical to that described above. Further elution (DCM/*t*-BuOMe, 95:10) gave a trace of 4-imino-3-phenyl-3,4-dihydroquinazoline-2-

carbonitrile (**9a**) as colorless needles, mp (hotstage) 141-142 °C (lit.[14] 141-142 °C) (from *c*-hexane); R_f 0.48 (DCM/*t*-BuOMe, 90:10), identical to that described above.

*4.4.2. 2-[2-(2-Aminophenyl)-5-imino-1-(*p*-tolyl)-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11b**)* (134.2 mg, 41%) as red needles, mp (DSC) decomp. onset 175.3 °C, peak max. 188.6 °C (from *n*-pentane/THF, 90:10); R_f 0.53 (DCM/Et_2O, 98:02); (found: C, 69.87; H, 4.43; N, 25.68. $C_{19}H_{14}N_6$ requires C, 69.92; H, 4.32; N, 25.75%); λ_{max}(DCM)/nm 255 inf (log ε 4.34), 297 (4.23), 335 (4.23), 406 inf (4.27), 432 (4.40), 507 (4.40); ν_{max}/cm^{-1} 3433w (NH_2), 3364w, 3314w and 3265w (NH), 2220 (C≡N), 1656w, 1630m, 1609w, 1578w, 1574w, 1551w, 1510w, 1493s, 1477s, 1425m, 1396s, 1354m, 1317m, 1310m, 1273m, 1254s, 1234m, 1201w, 1169m, 1153w, 1120w, 1070w, 1018w, 993w, 982w, 943w, 934w, 860m, 835w, 826m, 764m, 719s; δ_H(500 MHz; DMSO-d_6) 9.87 (1H, br s, N*H*), 7.74 (2H, br s, NH_2), 7.40 (2H, d, *J* 7.5, Ar *H*), 7.27 (2H, d, *J* 8.0, Ar *H*), 7.19 (1H, dd, *J* 7.8, 7.8, Ar *H*), 6.81 (1H, d, *J* 8.5, Ar *H*), 6.66 (1H, d, *J* 8.5, Ar *H*), 6.20 (1H, dd, *J* 7.5, 7.5, Ar *H*), 2.40 (3H, s, CH_3); δ_C(125 MHz; DMSO-d_6) 169.2 (s), 166.7 (s), 155.4 (s), 154.5 (s), 139.8 (s), 135.6 (d), 131.3 (s), 131.2 (d), 130.1 (d), 128.5 (d), 117.7 (d), 115.0 (d), 114.3 (s, *C*≡N), 113.5 (s, *C*≡N), 104.3 (s), 63.1 [s, *C*$(CN)_2$], 20.9 (q, *C*H_3); *m*/*z* (MALDI-TOF) 328 (MH^++1, 100%), 274 (23), 261 (30), 242 (60), 209 (28), 153 (6), 130 (7).

*4.4.3. 2-[2-(2-Aminophenyl)-5-imino-1-(4-methoxyphenyl)-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11c**)* (163.2 mg, 48%) as red needles, mp (DSC) decomp. onset 207.0 °C, peak max. 208.6 °C (from *n*-pentane/THF, 90:10); R_f 0.50 (DCM/Et_2O, 98:02); (found: C, 66.65; H, 4.04; N, 24.48. $C_{19}H_{14}N_6O$ requires C, 66.66; H, 4.12; N, 24.55%); λ_{max}(DCM)/nm 256 inf (log ε 4.22), 275 inf (4.10), 283 (4.10), 302 (4.10), 326 inf (4.04), 379 inf (3.96), 408 inf (4.07), 433 (4.19), 509 (4.21); ν_{max}/cm^{-1} 3424w (NH_2), 3281w and 3262w (NH), 2228w (C≡N), 1659w,

1622w, 1605w, 1582w, 1549w, 1512m, 1493s, 1479s, 1441w, 1422m, 1418m, 1391s, 1350s, 1315m, 1300m, 1273s, 1254s, 1221s, 1204w, 1190w, 1175w, 1165m, 1109w, 1105w, 1069w, 1015w, 937w, 881m, 843m, 833w, 825w, 804w, 777w, 768w, 750s; δ_H(500 MHz; DMSO-d_6) 9.87 (1H, br s, N*H*), 7.77 (2H, br s, NH_2), 7.34 (2H, d, *J* 8.5, Ar *H*), 7.19 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.14 (2H, d, *J* 8.5, Ar *H*), 6.81 (1H, d, *J* 8.5, Ar *H*), 6.69 (1H, d, *J* 8.5, Ar *H*), 6.22 (1H, dd, *J* 6.5, 6.5, Ar *H*), 3.83 (3H, s, OCH_3); δ_C(125 MHz; DMSO-d_6) 169.1 (s), 166.7 (s), 160.1 (s), 155.7 (s), 154.6 (s), 135.6 (d), 130.15 (d), 130.1 (d), 126.2 (s), 117.7 (d), 115.8 (d), 115.1 (d), 114.4 (s, *C*≡N), 113.5 (s, *C*≡N), 104.3 (s), 62.9 [s, *C*$(CN)_2$], 55.6 (q, O*C*H_3); *m*/*z* (MALDI-TOF) 344 (MH^++1, 18%), 343 (MH^+, 100), 342 (M^+, 7), 226 (5), 225 (65).

*4.4.4. 2-[2-(2-Aminophenyl)-1-(4-fluorophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11d**)* (168.7 mg, 51%) as red needles, mp (DSC) decomp. onset 195.7 °C, peak max. 201.2 °C (from *n*-pentane/THF, 90:10); R_f 0.56 (DCM/Et_2O, 98:02); (found: C, 65.32; H, 3.25; N, 25.29. $C_{18}H_{11}FN_6$ requires C, 65.45; H, 3.36; N, 25.44%); λ_{max}(DCM)/nm 256 inf (log ε 4.02), 302 inf (3.93), 336 (4.07), 404 inf (4.10), 429 (4.23), 510 (4.22); ν_{max}/cm^{-1} 3428w (NH_2), 3246w (NH), 3034w (Ar CH), 2224w (C≡N), 1661w, 1622w, 1607w, 1599w, 1574w, 1549w, 1506m, 1489s, 1481s, 1422m, 1393s, 1350s, 1319w, 1273m, 1253w, 1236w, 1219s, 1200m, 1171m, 1157w, 1096w, 1069w, 984w, 889m, 847m, 833w, 824w, 812w, 771w, 745s, 729w; δ_H(500 MHz; DMSO-d_6) 10.1 (1H, br s, N*H*), 7.71 (2H, br s, NH_2), 7.50-7.43 (4H, m, Ar *H*), 7.20 (1H, ddd, *J* 7.8, 7.8, 1.0, Ar *H*), 6.81 (1H, d, *J* 8.5, Ar *H*), 6.63 (1H, d, *J* 8.0, Ar *H*), 6.24 (1H, dd, *J* 7.8, 7.8, Ar *H*); δ_C(125 MHz; DMSO-d_6) 169.1 (s), 166.8 (s), 162.5 (d, $^1J_{CF}$ 245.9 Hz), 155.0 (s), 154.4 (s), 135.6 (d), 131.4 (d, $^3J_{CF}$ 9.0 Hz), 130.3 (s), 130.0 (d), 117.7 (d), 117.5 (d, $^2J_{CF}$ 23.0 Hz),

115.1 (d), 114.3 (s, *C*≡N), 113.4 (s, *C*≡N), 104.3 (s), 63.1 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 332 (MH^++1, 38%), 331 (MH^+, 100), 330 (M^+, 7), 242 (5), 214 (2), 213 (30).

*4.4.5. 2-[2-(2-Aminophenyl)-1-(4-chlorophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11e**)* (149.0 mg, 43%) as red needles, mp (DSC) decomp. onset 171.1 °C, peak max. 183.5 °C (from *n*-pentane/THF, 90:10); R_f 0.44 (DCM/Et_2O, 98:02); (found: C, 62.44; H, 3.18; N, 24.16. $C_{18}H_{11}ClN_6$ requires C, 62.34; H, 3.20; N, 24.24%); λ_{max}(DCM)/nm 259 inf (log ε 4.08), 301 inf (4.96), 337 (4.07), 405 inf (4.02), 429 (4.13), 510 (4.12); ν_{max}/cm^{-1} 3406w (NH_2), 3310w and 3281w (NH), 2224w and 2208w (C≡N), 1643w, 1624m, 1574w, 1553w, 1493s, 1477s, 1421s, 1396s, 1341m, 1317m, 1265m, 1248s, 1204w, 1169m, 1117w, 1092m, 1065m, 1018w, 993w, 986w, 937w, 849w, 831m, 766w, 747s, 718m; δ_H(500 MHz; DMSO-d_6) 10.19 (1H, br s, N*H*), 7.66 (2H, d, *J* 8.5, Ar *H*), 7.64 (2H, br s, NH_2), 7.44 (2H, d, *J* 8.5, Ar *H*), 7.20 (1H, dd, *J* 7.5, 7.5 Ar *H*), 6.80 (1H, d, *J* 8.5, Ar *H*), 6.63 (1H, d, *J* 8.0, Ar *H*), 6.26 (1H, dd, *J* 7.5, 7.5 Ar *H*); δ_C(125 MHz; DMSO-d_6) 169.1 (s), 166.8 (s), 154.7 (s), 154.2 (s), 135.5 (d), 134.6 (s), 133.0 (s), 130.8 (d), 130.1 (d), 128.7 (d), 117.7 (d), 115.1 (d), 114.3 (s, *C*≡N), 113.4 (s, *C*≡N), 104.4 (s), 63.3 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 349 (MH^++2, 25%), 348 (MH^++1, 20), 347 (MH^+, 100), 281 (45), 229 (46).

*4.4.6. 2-[2-(2-Aminophenyl)-1-(4-bromophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11f**)* (165.1 mg, 42%) as red needles, mp (DSC) decomp. onset 184.7 °C, peak max. 190.4 °C (from *n*-pentane/THF, 90:10); R_f 0.50 (DCM/Et_2O, 98:02); (found: C, 55.36; H, 2.83; N, 21.36. $C_{18}H_{11}BrN_6$ requires C, 55.26; H, 2.83; N, 21.48%); λ_{max}(DCM)/nm 263 inf (log ε 4.11), 301 inf (4.00), 338 (4.13), 405 inf (3.99), 430 (4.10), 512 (4.07); ν_{max}/cm^{-1} 3389w (NH_2), 3302w and 3269w (NH), 2229w and 2212w (C≡N), 1639w, 1624m, 1612w, 1574w, 1549w,

1491s, 1477s, 1418s, 1396s, 1368w, 1342m, 1315w, 1277m, 1252s, 1209w, 1171w, 1119w, 1070m, 1063m, 1016w, 988w, 937m, 847m, 829m, 766m, 752s, 716m; δ_H(500 MHz; DMSO-d_6) 10.20 (1H, br s, N*H*), 7.66 (1H, d, *J* 8.5, Ar *H*), 7.64 (2H, br s, NH_2), 7.37 (2H, d, *J* 8.5, Ar *H*), 7.21 (1H, dd, *J* 7.5, 7.5, Ar *H*), 6.81 (1H, d, *J* 8.5, Ar *H*), 6.64 (1H, d, *J* 9.0, Ar *H*), 6.27 (1H, dd, *J* 7.8, 7.8, Ar *H*); δ_C(125 MHz; DMSO-d_6) 169.1 (s), 166.8 (s), 158.3 (s), 154.6 (s), 154.1 (s), 135.5 (d), 133.4 (s), 131.0 (d), 130.1 (d), 129.2 (d), 117.7 (d), 115.1 (d), 114.3 (s, *C*≡N), 113.4 (s, *C*≡N), 104.4 (s), 63.3 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 394 (MH^++2, 13%), 392 (MH^++1, 30), 391 (MH^+, 71), 327 (29), 325 (13), 275 (68), 273 (55), 257 (100), 138 (21), 134 (19).

*4.4.7. 2-[2-(2-Aminophenyl)-1-(3,4-dimethoxyphenyl)-5-imino-1,5-dihydro-4*H-*imidazol-4-ylidene]malononitrile (**11g**)* (158.0 mg, 44%) as maroon needles, mp (DSC) decomp. onset 153.9 °C, peak max. 156.7 °C (from *n*-pentane/THF, 90:10); R_f 0.41 (DCM/Et_2O, 95:05); (found: C, 64.39; H, 4.25; N, 22.48. $C_{20}H_{16}N_6O_2$ requires C, 64.51; H, 4.33; N, 22.57%); λ_{max}(DCM)/nm 247 (log ε 4.30), 282 inf (4.09), 290 inf (4.13), 305 inf (4.17), 328 (4.21), 405 inf (4.17), 432 (4.20), 509 (4.23); ν_{max}/cm^{-1} 3435w and 3391w (NH_2), 3239w and 3198w (NH), 3086w (Ar CH), 2932w and 2837w (Alk CH), 2220w (C≡N), 1624m, 1605w, 1578w, 1574w, 1553w, 1512s, 1493s, 1482s, 1425m, 1422m, 1414s, 1396s, 1344m, 1315w, 1290w, 1267s, 1252s, 1233s, 1167m, 1136w, 1090w, 1024w, 999w, 951w, 887w, 868w, 856w, 831w, 812w, 768m, 760m, 750w; δ_H(500 MHz; DMSO-d_6) 9.94 (1H, br s, N*H*), 7.84 (2H, br s, NH_2), 7.20 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.12 (1H, d, *J* 8.5, Ar *H*), 7.09 (1H, d, *J* 1.5, Ar *H*), 6.91 (1H, dd, *J* 8.3, 2.3, Ar *H*), 6.81 (1H, d, *J* 8.5, Ar *H*), 6.76 (1H, d, *J* 8.5, Ar *H*), 6.24 (1H, dd, *J* 7.8, 7.8 Ar *H*), 3.83 (3H, s, OCH_3). 3.72 (3H, s, OCH_3); δ_C(125 MHz; DMSO-d_6) 168.9 (s), 166.7 (s), 155.6 (s), 154.8 (s), 149.9 (s), 149.8 (s), 135.7

(d), 130.1 (d), 126.2 (s), 121.1 (d), 117.8 (d), 115.1 (d), 114.4 (s, *C*≡N), 113.5 (s, *C*≡N), 112.5 (d), 112.2 (d), 104.2 (s), 62.7 [s, *C*$(CN)_2$], 55.8 (q, O*C*H_3), 55.7 (q, O*C*H_3); *m*/*z* (MALDI-TOF) 373 (MH^+, 16%), 372 (M^+, 100), 242 (9).

4.5. Preparation of 4-(arylamino)quinazoline-2-carbonitriles 5a-g (see Table 1, entries 8-14, Conditions B)

*4.5.1. 4-(Phenylamino)quinazoline-2-carbonitrile (**5a**) (typical procedure).* To a stirred solution of 2-amino-*N'*-phenylbenzamidine (**1a**) (211 mg, 1.00 mmol) in MeCN (10 mL) at *ca*. 20 °C was added glacial AcOH (57.0 μL, 1.00 mmol). To that mixture, was added dropwise a solution of TCNE (128 mg, 1.00 mmol) in MeCN (10 mL) at *ca*. 20 °C and left to stir for 7 h. The reaction mixture was then adsorbed onto silca and chromatographed (DCM/*t*-BuOMe, 95:05) to give the title compound **5a** (238.1 mg, 97%) as colorless needles, mp (hotstage) 210-211 °C (lit.[2b] 84-85 °C) (from $CHCl_3$); R_f 0.58 (DCM/*t*-BuOMe, 95:05), identical to that described above. Further elution (DCM/*t*-BuOMe, 95:10) gave 4-imino-3-phenyl-3,4-dihydro-quinazoline-2-carbonitrile (**9a**) (2.1 mg, 1%) as colorless needles, mp 141-142 °C (lit.[14] 141-142 °C) (from *c*-hexane), R_f 0.48 (DCM/*t*-BuOMe, 90:10), identical to that described above.

*4.5.2. 4-(p-Tolylamino)quinazoline-2-carbonitrile (**5b**)* (255.0 mg, 98%) as colorless needles, mp (hotstage) 208-209 °C (lit.[2b] 130-131 °C) (from $CHCl_3$), mp (DSC) onset 208.8 °C, peak max. 209.3 °C (from $CHCl_3$); R_f 0.78 (DCM/*t*-BuOMe, 95:05); ν_{max}/cm^{-1} 3389w (NH), 3048w (Ar CH), 2953w, 2918w and 2855w (Alk CH), 2243w (C≡N), 1618s, 1607s, 1574s, 1566s, 1530s, 1495s, 1454w, 1423m, 1369s, 1319w, 1304w, 1267w, 1258w, 1234w, 1223w, 1217w, 1134w, 1090w, 997w, 864w, 810m, 799m, 790m, 768s; δ_H(500 MHz; DMSO-d_6) 10.25 (1H, br s, N*H*), 8.60 (1H, d,

J 8.0, Ar *H*), 7.97 (1H, ddd, *J* 7.8, 7.8, 1.0, Ar *H*), 7.86 (1H, d, *J* 8.0, Ar *H*), 7.79 (1H, ddd, *J* 7.5, 7.5, 1.0, Ar *H*), 7.60 (2H, d, *J* 8.5, Ar *H*), 7.25 (2H, d, *J* 8.5, Ar *H*), 2.33 (3H, s, C*H*$_3$); δ_C(75 MHz; DMSO-d_6) 158.6 (s), 148.9 (s), 140.2 (s), 135.4 (s), 134.5 (s), 134.4 (d), 129.0 (d), 128.2 (d), 128.0 (d) 123.6 (d), 123.5 (d), 117.0 (s), 115.6 (s), 20.6 (q, *C*H$_3$); *m*/*z* (MALDI-TOF) 262 (MH^++1, 19%), 261 (MH^+, 100), 236 (2).

*4.5.3. 4-[(4-Methoxyphenyl)amino]quinazoline-2-carbonitrile (**5c**)* (268.4 mg, 97%) as pale yellow needles, mp (hotstage) 198-199 °C (lit.[2b] 90-91 °C) (from $CHCl_3$); mp (DSC) onset 197.4 °C, peak max. 199.1 °C (from $CHCl_3$); R_f 0.62 (DCM/*t*-BuOMe, 95:05); ν_{max}/cm^{-1} 3350m (NH), 3075w and 3049w (Ar CH), 2953w (Alk CH), 2249w (C≡N), 1612w, 1600m, 1582s, 1564w, 1558w, 1514s, 1489m, 1456w, 1429w, 1408w, 1373m, 1358w, 1314m, 1296m, 1261m, 1253m, 1236m, 1225w, 1186w, 1171m, 1128w, 1111w, 1094w, 1038m, 995w, 868w, 860w, 820w, 799w, 787w, 768s, 758m; δ_H(500 MHz; DMSO-d_6) 10.25 (1H, br s, N*H*), 8.57 (1H, d, *J* 8.5, Ar *H*), 7.96 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.86 (1H, d, *J* 8.0, Ar *H*), 7.78 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.61 (2H, d, *J* 7.8, Ar *H*), 7.03 (2H, d, *J* 7.5, Ar *H*), 3.79 (3H, s, OC*H*$_3$); δ_C(125 MHz; DMSO-d_6) 158.6 (s), 156.9 (s), 148.8 (s), 140.3 (s), 134.4 (d), 130.7 (s), 129.0 (d), 128.1 (d), 125.3 (d), 123.4 (d), 117.1 (s), 115.6 (s), 114.0 (d), 55.4 (q, O*C*H$_3$); *m/z* (EI) 278 (MH^++1, 17%), 277 (MH^+, 100), 252 (2), 215 (1).

*4.5.4. 4-[(4-Fluorophenyl)amino]quinazoline-2-carbonitrile (**5d**)* (258.8 mg, 98%) as pale yellow needles, mp (hotstage) 209-211 °C (from $CHCl_3$), mp (DSC) onset 210.8 °C, peak max. 212.2 °C (from $CHCl_3$); R_f 0.77 (DCM/*t*-BuOMe, 95:05); (found: C, 68.30; H, 3.30; N, 21.12. $C_{15}H_9FN_4$ requires C, 68.18; H, 3.43; N, 21.20%); λ_{max}(DCM)/nm 258 inf (log ε 4.22), 268 inf (4.20), 282 inf (4.15), 332 (4.35); ν_{max}/cm^{-1} 3385w (NH), 3059w and 3034w (Ar CH), 2247w (C≡N), 1616m, 1607m, 1570s, 1558m, 1533m, 1506w, 1495s, 1456w, 1449w, 1425w, 1369m, 1321w, 1256w,

1246w, 1234w, 1217w, 1161w, 1130w, 1105w, 1034w, 976w, 955w, 897w, 864w, 831w, 795w, 789w, 766s, 745s; δ_H(500 MHz; DMSO-d_6) 10.34 (1H, br s, N*H*), 8.59 (1H, d, *J* 8.5, Ar *H*), 7.99 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.89 (1H, d, *J* 8.5, Ar *H*), 7.81 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.79-7.74 (2H, m, Ar *H*), 7.33-7.28 (2H, m, Ar *H*); δ_C(125 MHz; DMSO-d_6) 159.3 (d, $^1J_{CF}$ 241.3), 158.5 (s), 148.8 (s), 140.0 (s), 134.4 (d), 134.2 (s), 129.0 (d), 128.1 (d), 125.4 (d, $^3J_{CF}$ 8.3), 123.4 (d), 116.9 (s), 115.41 (d, $^2J_{CF}$ 22.3), 115.44 (s); *m/z* (EI) 265 (MH^+, 15%), 248 (55), 247 (100), 236 (7).

*4.5.5. 4-[(4-Chlorophenyl)amino]quinazoline-2-carbonitrile (**5e**)* (264.8 mg, 95%) as colorless needles, mp 230-231 °C (lit.[2b] 208-201 °C) (from $CHCl_3$); mp (DSC) onset 230.1 °C, peak max. 230.7 °C (from $CHCl_3$); R_f 0.73 (DCM/*t*-BuOMe, 95:05); ν_{max}/cm^{-1} 3348w (NH), 3063w (Ar CH), 2251w (C≡N), 1614m, 1601m, 1574s, 1564m, 1526s, 1497m, 1487s, 1456w, 1425m, 1400w, 1368m, 1359w, 1314w, 1258w, 1223w, 1179w, 1126w, 1098w, 1092w, 1016w, 993w, 864w, 854w, 816m, 787m, 766s, 752w; δ_H(500 MHz; DMSO-d_6) 10.37 (1H, br s, N*H*), 8.60 (1H, d, *J* 8.0, Ar *H*), 7.99 (1H, ddd, *J* 7.8, 7.8, 1.0, Ar *H*), 7.89 (1H, d, *J* 8.0, Ar *H*), 7.84-7.79 (3H, m, Ar *H*), 7.51 (2H, d, *J* 7.5, Ar H); δ_C(125 MHz; DMSO-d_6) 158.4 (s), 149.0 (s), 139.9 (s), 137.2 (s), 134.6 (d), 129.2 (d), 128.8 (s), 128.7 (d), 128.2 (d), 124.9 (d), 123.5 (d), 117.0 (s), 115.7 (s); *m/z* (MALDI-TOF) 283 (MH^++2, 25%), 282 (MH^++1, 9), 281 (MH^+, 100), 153 (7), 130 (3).

*4.5.6. 4-[(4-Bromophenyl)amino]quinazoline-2-carbonitrile (**5f**)* (314.7 mg, 97%) as pale yellow needles, mp 234.5-235 °C (lit.[2b] 176-177 °C) (from $CHCl_3$), mp (DSC) onset 233.0 °C, peak max. 233.6 °C, (from $CHCl_3$); R_f 0.77 (DCM/*t*-BuOMe, 95:05); ν_{max}/cm^{-1} 3352w (NH), 3063w (Ar CH), 2255w (C≡N), 1616m, 1603m, 1570s, 1562m, 1522s, 1487s, 1456w, 1422m, 1398w, 1368m, 1354w, 1315m, 1296w, 1258w, 1236w, 1217w, 1182w, 1128w, 1076m, 1009w, 993m, 951w, 937w, 870w,

845w, 820s, 791m, 764s; δ_H(500 MHz; DMSO-d_6) 10.35 (1H, br s, Ar *H*), 8.60 (1H, d, *J* 8.0, Ar *H*), 8.00 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.90 (1H, d, *J* 8.5, Ar *H*), 7.82 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.75 (2H, d, *J* 8.5, Ar *H*), 7.64 (2H, d, *J* 7.5, Ar H); δ_C(125 MHz; DMSO-d_6) 158.4 (s), 149.0 (s), 139.9 (s), 137.6 (s), 134.6 (d), 131.7 (d), 129.3 (d), 128.3 (d), 125.2 (d), 123.5 (d), 117.0 (s), 115.7 (s); *m*/*z* (MALDI-TOF) 327 (MH^++2, 28%), 325 (MH^+, 33), 309 (4), 308 (19), 307 (100), 282 (3), 153 (30).

*4.5.7. 4-[(3,4-Dimethoxyphenyl)amino]quinazoline-2-carbonitrile (**5g**)* (286.0 mg, 93%) as pale yellow plates, mp (hotstage) 202-203 ^oC (from $CHCl_3$); mp (DSC) onset 202.1 ^oC, peak max. 203.9 ^oC (from $CHCl_3$); R_f 0.34 (DCM/*t*-BuOMe, 95:05); (found: C, 66.71; H, 4.52; N, 18.18. $C_{17}H_{14}N_4O_2$ requires C, 66.66; H, 4.61; N, 18.29%); λ_{max}(DCM)/nm 239 inf (log ε 4.10), 283 inf (3.76), 344 (3.67); ν_{max}/cm^{-1} 3375w (NH), 3017w (Ar CH), 2937w and 2837w (Alk CH), 2247w (C≡N), 1622m, 1609w, 1574s, 1530m, 1518m, 1499s, 1464m, 1429w, 1414w, 1373m, 1323w, 1307w, 1265w, 1279w, 1236w, 1223s, 1202m, 1175w, 1165w, 1144m, 1090w, 1042w, 1028s, 999w, 955w, 870w, 843w, 800m, 792s, 772m, 761s, 746s; δ_H(500 MHz; DMSO-d_6) 10.23 (1H, br s, N*H*), 8.60 (1H, d, *J* 8.0, Ar *H*), 7.97 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.87 (1H, d, *J* 7.5, Ar *H*), 7.80 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.38 (1H, d, *J* 2.5, Ar *H*), 7.31 (1H, dd, *J* 9.0, 2.3, Ar *H*), 7.04 (1H, d, *J* 8.5, Ar *H*), 3.79 (6H, s, 2 × OC*H*$_3$); δ_C(125 MHz; DMSO-d_6) 158.5 (s), 148.9 (s), 148.6 (s), 146.5 (s), 140.2 (s), 134.4 (d), 131.1 (s), 129.0 (d), 128.2 (d), 123.4 (d), 117.0 (s), 115.8 (d), 115.6 (s), 111.8 (d), 108.5 (d), 55.8 (q, O*C*H$_3$), 55.7 (q, O*C*H$_3$); *m*/*z* (MALDI-TOF) 308 (MH^++1, 13%), 307 (MH^+, 100), 306 (M^+, 8).

4.6. Preparation of 3-aryl-4-imino-3,4-dihydroquinazoline-2-carbonitriles 9a-g (see Table 1, entries 15-21, Conditions C)

*4.6.1. 4-Imino-3-phenyl-3,4-dihydroquinazoline-2-carbonitrile (**9a**) (typical procedure).* To a stirred solution of TCNE (256 mg, 2.00 mmol) in dry MeCN (10 mL) cooled to *ca*. -20 °C was added dropwise a solution of 2-amino-*N'*-phenyl-benzamidine (**1a**) (211 mg, 1.00 mmol) in dry MeCN (10 mL). The reaction mixture was then and left to stir at *ca*. -20 °C for 1 d, after which time it was adsorbed onto silica and chromatographed (DCM/*t*-BuOMe, 95:05) to give 4-(phenylamino)-quinazoline-2-carbonitrile (**5a**) (71.0 mg, 29%) as colorless needles, mp (hotstage) 210-211 °C (lit.[2b] 84-85 °C) (from $CHCl_3$); R_f 0.58 (DCM/*t*-BuOMe, 95:05), identical to that described above. Further elution (DCM/*t*-BuOMe, 95:10) gave the title compound **9a** (169.6 mg, 69%) as colorless needles, mp (hotstage) 141-142 °C (lit.[14] 141-142 °C) (from *c*-hexane); R_f 0.48 (DCM/*t*-BuOMe, 90:10); identical to that described above.

*4.6.2. 4-Imino-3-*p*-tolyl-3,4-dihydroquinazoline-2-carbonitrile (**9b**)* (160.3 mg, 62%) as colorless needles, mp (hotstage) 155-156 °C (lit.[14] 155-156 °C) (from *n*-hexane/DCM); R_f 0.60 (DCM/*t*-BuOMe, 90:10); δ_H(300 MHz; $CDCl_3$) 8.26 (1H, d, *J* 8.1, Ar *H*), 7.70–7.60 (2H, m, Ar *H*), 7.52 (1H, ddd, *J* 7.4, 7.4, 1.8, Ar *H*), 7.44 (2H, d, *J* 8.1, Ar *H*), 7.28 (2H, d, *J* 8.4, Ar *H*), 6.34 (1H, br s, N*H*), 2.47 (3H, s, CH_3); δ_C(75 MHz; $CDCl_3$) 153.5 (s), 143.3 (s), 141.7 (s), 133.4 (d), 132.2 (s), 131.7 (d), 131.3 (s), 129.8 (d), 128.6 (d), 128.3 (d), 125.7 (d), 122.4 (s), 111.3 (s, *C*≡N), 21.4 (q, *C*H_3); *m*/*z* (MALDI-TOF) 262 (MH^++1, 19%), 261 (MH^+, 100), 246 (24), 153 (2), identical to an authentic sample.

4.6.3. 4-Imino-3-(4-methoxyphenyl)-3,4-dihydroquinazoline-2-carbonitrile ***(9c)*** (172.0 mg, 62%) as colorless needles, mp (hotstage) 140-141 °C (lit.[14] 140-141 °C) (from *n*-hexane/DCM); R_f 0.42 (DCM/*t*-BuOMe, 90:10); δ_H(300 MHz; $CDCl_3$) 8.27 (1H, d, *J* 7.8, Ar *H*), 7.72–7.62 (2H, m, Ar *H*), 7.52 (1H, ddd, *J* 7.4, 7.4, 1.7, Ar *H*), 7.32 (2H, d, *J* 9.0, Ar *H*), 7.14 (2H, d, *J* 9.0, Ar *H*), 6.89 (1H, br s, N*H*), 3.91 (3H, s, OCH_3); δ_C(75 MHz; $CDCl_3$) 161.3 (s), 153.5 (s), 143.2 (s), 133.3 (d), 131.6 (s), 130.1 (d), 129.7 (d), 128.2 (d), 127.0 (s), 125.6 (d), 122.5 (s), 116.1 (d), 111.4 (s), 55.6 (q); *m*/*z* (MALDI-TOF) 278 (MH^++1, 3%), 277 (MH^+, 100), 153 (2), 130 (13), identical to an authentic sample.

4.6.4. 3-(4-Fluorophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile ***(9d)*** (171.0 mg, 65%) as colorless needles, mp (hotstage) 163-163.5 °C (lit.[14] 163-163.5 °C) (from *n*-hexane/DCM); R_f 0.52 (DCM/*t*-BuOMe, 90:10); δ_H(300 MHz; $CDCl_3$) N*H* deuterium exchanged, 8.21 (1H, d, *J* 7.5, Ar *H*), 7.74-7.64 (2H, m, Ar *H*), 7.55 (1H, ddd, *J* 7.4, 7.4, 1.5, Ar *H*), 7.45-7.32 (4H, m, Ar *H*); δ_C(75 MHz; $CDCl_3$) 165.4 (s), 162.0 (d, $^1J_{CF}$ 252.9), 153.8 (s), 143.0 (s), 133.5 (d), 131.1 (d, $^3J_{CF}$ 9.1), 130.0 (d), 128.5 (d), 125.4 (d), 122.2 (s), 118.2 (d, $^2J_{CF}$ 22.7), 111.2 (s); *m*/*z* (MALDI-TOF) 265 (MH^+, 39%), 167 (32), 153 (100), 130 (9), identical to an authentic sample.

4.6.5. 3-(4-Chlorophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile ***(9e)*** (193.1 mg, 69%) as colorless needles, mp (hotstage) 209-210 °C (lit.[14] 209-210 °C) (from *n*-hexane/DCM); R_f 0.61 (DCM/*t*-BuOMe, 90:10); δ_H(300 MHz; $CDCl_3$) 8.21 (1H, d, *J* 8.1, Ar *H*), 7.71-7.64 (2H, m, Ar *H*), 7.65 (2H, d, *J* 8.4, Ar *H*), 7.56 (1H, ddd, *J* 7.4, 7.4, 1.4, Ar *H*), 7.38 (2H, d, *J* 8.7, Ar *H*), 5.70 (1H, br s, N*H*); δ_C(75 MHz; $CDCl_3$) 153.8 (s), 143.0 (s), 137.5 (s), 133.7 (s), 133.6 (d), 131.3 (d), 130.9 (s), 130.4 (d), 130.1 (d), 128.6 (d), 125.4 (d), 122.1 (s), 111.2 (s); *m*/*z* (MALDI-TOF) 283

(MH^++2, 72%), 282 (MH^++1, 31), 281 (MH^+, 100), 246 (31), 188 (3), 153 (12), 130 (2), 116 (3), 100 (4), identical to an authentic sample.

*4.6.6. 3-(4-Bromophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9f**)* (210 mg, 65%) as colorless needles, mp (hotstage) 191-192 °C (lit.[14] 191-192 °C) (from *n*-hexane/DCM); R_f 0.75 (DCM/*t*-BuOMe, 90:10); δ_H(300 MHz; $CDCl_3$) 8.18 (1H, d, *J* 7.8, Ar *H*), 7.79 (2H, d, *J* 8.7, Ar *H*), 7.70-7.64 (2H, m, Ar *H*), 7.55 (1H, ddd, *J* 7.4, 7.4, 1.8, Ar *H*), 7.31 (2H, d, *J* 8.7, Ar *H*), 6.86 (1H, br s, N*H*); δ_C(125 MHz; $CDCl_3$) 153.7 (s), 143.0 (s), 134.3 (d), 133.6 (d), 130.8 (s), 130.6 (d), 130.1 (d), 128.6 (d), 125.6 (s), 125.3 (d), 122.1 (s), 111.2 (s); *m*/*z* (MALDI-TOF) 328 (MH^++3, 50%), 327 (MH^++2, 100), 326 (MH^++1, 44), 325 (MH^+, 96), 300 (46), 298 (41), 245 (95), 219 (10), 144 (10), identical to an authentic sample.

*4.6.7. 3-(3,4-Dimethoxyphenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9g**)* (194.8 mg, 64%) as colorless needles, mp (hotstage) 192-193 °C (from *c*-hexane/DCM, 9:1); mp (DSC) onset 193.1 °C, peak max. 193.9 °C (from *c*-hexane/DCM, 9:1); R_f 0.35 (DCM/Et_2O, 90:10); (found: C, 66.77; H, 4.49; N, 18.17. $C_{17}H_{14}N_4O_2$ requires C, 66.66; H, 4.61; N, 18.29%); λ_{max}(DCM)/nm 237 (log ε 4.41), 254 inf (4.26), 264 (4.26), 274 (4.22), 298 inf (3.96), 310 (4.05), 323 (4.06), 341 inf (3.92), 362 inf (3.68); ν_{max}/cm^{-1} 3277w (NH), 3044w and 3007w (Ar CH), 2965w (Alk CH), 2239w (C≡N), 1634s, 1603w, 1597w, 1574w, 1562w, 1512s, 1468m, 1441w, 1422w, 1362w, 1335w, 1321m, 1310m, 1262s, 1240s, 1213w, 1180m, 1171s, 1152s, 1146s, 1107w, 1072w, 1036m, 1026m, 1016m, 970w, 905m, 889w, 860s, 826m, 779m, 770s, 746w, 731w; δ_H(500 MHz; $CDCl_3$) 8.28 (1H, br s, Ar *H*), 7.70 (1H, dd, *J* 8.0, 8.0, Ar *H*), 7.64 (1H, d, *J* 8.0, Ar *H*), 7.53 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.07 (1H, d, *J* 8.5, Ar *H*), 7.00 (1H, dd, *J* 8.5, 2.5, Ar *H*), 6.84 (1H, d, *J* 2.5, Ar *H*), 3.98 (3H, s, OCH_3), 3.91 (3H, s, OCH_3); δ_C(125 MHz; $CDCl_3$) 153.4 (s), 151.1

(s), 150.7 (s), 143.3 (s), 133.4 (d), 131.6 (s), 129.9 (d), 128.3 (d), 127.1 (s), 125.7 (d), 122.6 (s), 121.6 (d), 112.1 (d), 111.4 (s, *C*≡N), 111.2 (d), 56.2 (q, O*C*H$_3$), 56.1 (q, O*C*H$_3$); *m/z* (EI) 327 (MH$^+$, 15%), 326 (M$^+$, 100), 307 (11).

4.7. Independent synthesis of 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (11a)

*4.7.1. (*Z*)-2-Nitro*-N'-*phenylbenzamidine (**25**)*. To stirred 2-nitrobenzonitrile (398 mg, 2.68 mmol) at *ca.* 20 °C was added in one portion powdered anhydrous $AlCl_3$ (358 mg, 2.68 mmol). The reaction mixture was then heated (*ca.* 100 °C) until a homogenous melt formed. To this hot melt was then added aniline (245 μL, 2.68 mmol) and the mixture was heated (*ca.* 100 °C) for 8 h and then allowed to cool to *ca.* 20 °C. The resultant solid mass was then crushed and slurried in 10% NaOH (40 mL). extracted with DCM (4 × 40 mL), washed with H_2O (1 × 40 mL) and the organic phase dried (Na_2SO_4), adsorbed onto silica and chromatographed (*t*-BuOMe) to give the *title compound* **25** (465 mg, 72%) as yellow plates, mp (hotstage) 81.5-83 °C (from *c*-hexane), mp (DSC) onset 79.4 °C, peak max. 84.8 °C (from *c*-hexane); R_f 0.38 (DCM/*t*-BuOMe, 90:10); (found: C, 64.70; H, 4.49; N, 17.39. $C_{13}H_{11}N_3O_2$ requires C, 64.72; H, 4.60; N, 17.42%); λ_{max}(DCM)/nm 259 inf (log ε 4.05); ν_{max}/cm^{-1} 3464w and 3333w (NH_2), 3059w (Ar CH), 1616s, 1585m, 1574m, 1522s, 1483m, 1449w, 1383m, 1362s, 1304w, 1275w, 1236w, 1177w, 1157w, 1074w, 1024w, 995w, 962w, 918w, 889w, 856w, 837m, 804w, 783s, 766s; δ_H(500 MHz; DMSO-d_6) 7.96 (1H, d, *J* 8.5, Ar *H*), 7.78-7.75 (2H, m, Ar *H*), 7.66 (1H, dd, *J* 7.3, 7.3, Ar *H*), 7.31 (2H, dd, *J* 7.5, 7.5 Ar *H*), 6.99 (1H, dd, *J* 7.5, 7.5, Ar *H*), 6.82 (1H, d, *J* 8.0, Ar *H*), 6.69 (1H, br s, Ar *H*), 6.49 (2H, br s, N*H*$_2$); δ_C(125 MHz; DMSO-d_6 at 55 °C) 152.5

(s), 149.6 (s), 148.7 (s), 132.6 (s), 132.4 (d), 129.9 (d), 129.7 (d), 129.0 (d), 123.6 (d), 122.0 (d), 121.0 (d); *m*/*z* (MALDI-TOF) 243 (MH^++1, 15%), 242 (MH^+, 100).

4.7.2. 2-Nitro-N'-*phenyl*-N-*(1,2,2-tricyanovinyl)benzamidine (**26**).* To a stirred solution of TCNE (256 mg, 2.00 mmol) in dry THF (5 mL) at *ca.* 20 °C was added in one portion a solution of 2-nitro-*N'*-phenyl-benzamidine (**25**) (241 mg, 1.00 mmol) in dry THF (5 mL). The mixture was then left to stir at *ca*. 20 °C for 4 h, after which time the reaction was complete (by TLC), and the volatiles were removed under reduced pressure (at < 25 °C). The residue was then dissolved in Et_2O (2 mL) and after cooling to 0 °C, *n*-pentane (40 mL) was added and triturated to precipitate the *title compound* **26** (338.2 mg, 99%) as colorless plates, mp (hotstage) 130-131 °C (from *n*-pentane/THF); R_f 0.50 (DCM/Et_2O, 95:05); (found: C, 62.97; H, 2.87; N, 24.63. $C_{18}H_{10}N_6O_2$ requires C, 63.16; H, 2.94; N, 24.55%); λ_{max}(DCM)/nm 258 (log ε 4.18); ν_{max}/cm^{-1} 3244m (NH), 3096w (Ar CH), 2261w and 2228w (C≡N), 1697s, 1630w, 1591s, 1574w, 1537s, 1530s, 1495m, 1456w, 1393m, 1346s, 1325m, 1308m, 1269w, 1221w, 1152w, 1132m, 1074w, 1071m, 1041w, 1032w, 968w, 943w, 939w, 916w, 891w, 854m, 810w, 797m, 770w, 760w; δ_H(500 MHz; $CDCl_3$) 8.10 (1H, d, *J* 8.5 Ar *H*), 8.01 (1H, br s, N*H*), 7.78 (1H, dd, *J* 7.3, 7.3, Ar *H*), 7.71-7.66 (2H, m, Ar *H*), 7.39-7.38 (3H, br s, Ar *H*), 7.05 (2H, br s, Ar *H*); δ_C(125 MHz; $CDCl_3$) 168.2 (s), 160.2 (s), 146.6 (s), 134.5 (d), 132.7 (d), 131.5 (d), 130.73 (d), 130.69 (d), 130.6 (s), 127.8 (d), 125.0 (d), 123.4 (s), 111.7 (s, *C*≡N), 108.3 (s, *C*≡N), 108.1 (s, *C*≡N), 66.9 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 343 (MH^+, 26%), 334 (46), 333 (100), 311 (9), 283 (8), 130 (59), 102 (8), 100 (27).

*4.7.3. 2-[5-Imino-2-(2-nitrophenyl)-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]-malononitrile (**27**).* A stirred solution of 2-nitro-*N'*-phenyl-*N*-(1,2,2-tricyanovinyl)-

benzamidine (**26**) (34.2 mg, 0.10 mmol) in dry MeCN (1 mL) was heated at *ca*. 82 °C for 3 h. On cooling to *ca*. 20 °C the reaction mixture was adsorbed onto silica and chromatographed (DCM) to give the *title compound* **27** (21.5 mg, 63%) as yellow hexagonal plates, mp (DSC) decomp. onset 258.8 °C peak max. 262.4 °C (from *n*-pentane/THF, 90:10); R_f 0.56 (DCM/Et_2O, 95:05); (found: C, 63.03; H, 2.84; N, 24.44. $C_{18}H_{10}N_6O_2$ requires C, 63.16; H, 2.94; N, 24.55%); λ_{max}(DCM)/nm 256 inf (log ε 4.21), 388 (3.72); ν_{max}/cm^{-1} 3304w (NH), 3078 (Ar CH), 2234w (C≡N), 1647w, 1632w, 1593w, 1576w, 1559w, 1530s, 1510s, 1483m, 1456w, 1445w, 1391w, 1364m, 1346s, 1321w, 1260w, 1227w, 1186w, 1157w, 1146w, 1074w, 1065w, 1026w, 1009w, 999w, 966w, 920w, 868w, 855m, 799s, 790m, 768m, 748m; δ_H(300 MHz; CD_3CN) N*H* deuterium exchanged, 8.00 (1H, d, *J* 9.0, Ar *H*), 7.68 (1H, ddd, *J* 7.5, 7.5, 1.0, Ar *H*), 7.59-7.52 (2H, m, Ar *H*), 7.38-7.36 (3H, m, Ar *H*), 7.19 (2H, dd, *J* 6.0, 3.0, Ar *H*); (75 MHz; CD_3CN) four C (s) resonances missing, 152.3 (s), 138.1 (s), 135.5 (d), 132.7 (d), 131.5 (d), 131.4 (d), 129.6 (s), 128.8 (d), 126.3 (d), 125.7 (d), 114.8 (s, *C*≡N), 113.4 (s, *C*≡N); *m*/*z* (MALDI-TOF) 344 (MH^++1, 13%), 343 (MH^+, 100), 242 (3), 100 (5).

*4.7.4. 2-[2-(2-Aminophenyl)-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (**11a**).* To a solution of 2-[5-imino-2-(2-nitrophenyl)-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**27**) (17.1 mg, 0.05 mmol) in glacial AcOH (0.5 mL) at *ca*. 20 °C was added Zn powder (13.0 mg, 0.200 mmol) and left to stir at *ca*. 20 °C for 15 min. After the reaction was complete (by TLC) the mixture was filtered, diluted with Et_2O (5 mL), washed with H_2O (2 × 5 mL) and dried (Na_2SO_4). The organic phase was adsorbed onto silica and chromatographed (DCM/Et_2O, 95:05) to give the title compound **11a** (14.1 mg, 90%) as red needles, mp (DSC) decomp. onset 197.9 °C, peak max. 201.2 °C (from *n*-pentane/THF, 90:10); R_f 0.47 (DCM/Et_2O,

98:02); δ_H(500 MHz; DMSO-d_6) 9.93 (1H, s, N*H*), 7.77 (2H, s, NH_2), 7.61-7.59 (3H, m, Ar *H*), 7.40 (2H, d, *J* 6.5, Ar *H*), 7.18 (1H, dd, *J* 7.8, 7.8, Ar *H*), 6.81 (1H, d, *J* 9.0, Ar *H*), 6.59 (1H, d, *J* 8.5, Ar *H*), 6.17 (1H, dd, *J* 8.3, 8.3, Ar *H*); identical that described above.

4.8. Chemistry of 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1*H*-imidazol-4(5*H*)-ylidene]malononitrile (11a)

*4.8.1. 2-[2-(2-Aminophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**28**).* To a stirred solution of 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11a**) (31.2 mg, 0.100 mmol) in dry DCM (1 mL) at *ca*. 20 °C was added DBU (14.9 μL, 0.100 mmol). The reaction mixture was then heated at *ca*. 40 °C for 4 h, allowed to come to *ca*. 20 °C and then extracted with 5% HCl (1 mL), washed with H_2O (1 × 1 mL) and the organic fraction dried (Na_2SO_4). Removal of the volatiles followed by addition of MeOH (0.5 mL), H_2O (3 mL), and filtration of the precipitate, gave the *title compound* **28** (22.4 mg, 71%) as maroon needles, mp (DSC) decomp. onset 203.5 °C, peak max. 214.8 °C (from *n*-pentane/THF, 50:50); R_f 0.40 (DCM/Et_2O, 98:02); (found: C, 69.13; H, 3.74; N, 26.80. $C_{18}H_{12}N_6$ requires C, 69.22; H, 3.87; N, 26.91%); λ_{max}(DCM)/nm 248 (log ε 4.02), 269 (3.88), 295 (3.88), 329 (3.78), 376 inf (3.80), 397 (3.91), 417 inf (3.90), 463 inf (3.90), 503 (3.98), 566 inf (3.71), 632 inf (3.38); ν_{max}/cm^{-1} 3422w and 3401w (NH_2), 3294w and 3242w (NH), 3063w (Ar CH), 2224w (C≡N), 1643m, 16281m, 1601m, 1574w, 1559w, 1530s, 1501m, 1452m, 1414w, 1383w, 1327w, 1306m, 1260s, 1229m, 1202w, 1171m, 1072w, 1042w, 1024w, 1001w, 972w, 924w, 851w, 835w, 773w, 758m, 743s; δ_H(500 MHz; DMSO-d_6) two H resonances missing owing to prototautomerism, 9.32 (2H, br s, NH_2), 7.91 (1H, br s, Ar *H*), 7.46 (2H, dd, *J* 8.0,

8.0, Ar *H*), 7.35 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.26 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.21 (1H, br s, N*H*), 6.84 (1H, d, *J* 9.0, Ar *H*), 6.60 (1H, dd, *J* 7.0, 7.0, Ar *H*); δ_C(125 MHz; DMSO-d_6) threeC (s) resonances missing owing to prototautomerism, 153.6 (s), 146.5 (s), 135.9 (d), 130.4 (d), 128.9 (d), 125.9 (d), 122.7 (d), 117.0 (d), 115.3 (d), 114.3 (s, *C*≡N), 113.6 (s, *C*≡N), 104.5 (s), 66.8 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 313 (MH^+, 80%), 311 (M^+-1, 97%), 190 (100), 167 (90).

*4.8.2. 2-[2-(2-Nitrophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malono-nitrile (**34**)*. To a stirred solution of 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**27**) (24.1 mg, 0.100 mmol) in dry DCM (1 mL) at *ca*. 20 °C was added DBU (14.9 μL, 0.100 mmol). The reaction mixture was then heated at *ca*. 40 °C for 5 h, allowed to come to *ca.* 20 °C and then extracted with 5% HCl (1 mL), washed with H_2O (1 × 1 mL) and the organic fraction dried (Na_2SO_4). Adsorption of the organic phase on silica and chromatography (DCM/Et_2O, 95:05) gave the *title compound* **34** (14.2 mg, 59%) as maroon needles, mp (DSC) decomp. onset 180.2 °C, peak max. 186.5 °C (from *n*-pentane/THF, 50:50); R_f 0.65 (DCM/Et_2O, 95:05); (found: C, 63.03; H, 2.86; N, 24.40. $C_{18}H_{10}N_6O_2$ requires C, 63.16; H, 2.94; N, 24.55%); λ_{max}(DCM)/nm 256 (log ε 3.90), 294 inf (3.76), 409 (3.70), 440 (3.69), 467 inf (3.69), 561 inf (2.94), 606 (2.84); ν_{max}/cm^{-1} 2210w (C≡N), 1748w, 1734w, 1719w, 1645w, 1634w, 1597w, 1574w, 1530s, 1526s, 1506m, 1497m, 1489w, 1472w, 1456w, 1418w, 1346m, 1315w, 1301w, 1258w, 1191w, 1163w, 1148w, 1123w, 1072w, 1053w, 1026w, 1002w, 966w, 910w, 883w, 854w, 843w, 831w, 820w, 789w, 785w, 756w, 734w; δ_H(500 MHz; CD_3CN) N*H* deuterium exchanged, 8.17 (1H, dd, *J* 7.8, 1.8, Ar *H*), 7.91-7.87 (2H, m, Ar *H*), 7.84 (1H, dd, *J* 6.8, 2.5, Ar *H*), 7.46 (2H, dd, *J* 8.3, 8.3 Ar *H*), 7.32-7.29 (3H, m, Ar *H*); δ_C(125 MHz; CD_3CN) three C (s) resonances missing owing to prototautomerism, 149.2 (s), 147.5

(s), 134.8 (d), 132.3 (d), 130.5 (d), 129.9 (d), 129.7 (d), 128.5 (d), 126.0 (d), 123.3 (s), 114.0 (s, *C*≡N), 113.5 (s, *C*≡N), 66.3 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 344 (MH^+, 21%), 343 (MH^+, 100), 219 (10), 153 (86), 133 (51), 130 (49), 104 (2).

*4.8.3. Zinc reduction of 2-[2-(2-nitrophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**34**).* To a solution of 2-[2-(2-nitrophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**34**) (17.1 mg, 0.050 mmol) in glacial AcOH (0.5 mL) at *ca.* 20 °C was added Zn powder (13.0 mg, 0.200 mmol) and left to stir at *ca.* 20 °C for 15 min. After the reaction was complete (by TLC) the mixture was filtrated, diluted in Et_2O (5 mL), washed with H_2O (2 × 5 mL), dried (Na_2SO_4), adsorbed onto silica and chromatographed (DCM/Et_2O, 95:05) to give 2-[2-(2-aminophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**28**) (8.9 mg, 57%) as maroon needles, mp (DSC) decomp. onset 203.5 °C, peak max. 214.8 °C; R_f 0.40 (DCM/Et_2O, 98:02); identical to that described above.

*4.8.4. (*Z*)-2-[3-(Phenylimino)imidazo[1,2-*c*]quinazolin-2(*3H*)-ylidene]malononitrile (**36**)* To a stirred solution of (*Z*)-2-[2-(2-aminophenyl)-5-(phenylimino)-3,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**28**) (32.2 mg, 0.100 mmol) in DMA (100 μL) at *ca.* 20 °C was added triethyl orthoformate (100 μL) and the reaction mixture was immersed into a preheated (*ca.* 170 °C) Wood's metal bath and left to stir for 15 min, after which time the reaction mixture was removed from the Wood's metal bath, allowed to cool to *ca.* 20 °C, diluted in DCM (5 mL), washed with H_2O (2 × 5 mL), dried (Na_2SO_4), adsorbed onto silica and chromatographed (DCM) to give the title compound **36** (22.4 mg, 70%) as orange needles, mp (hotstage) 234-235 °C (from *c*-hexane/THF, 90:10), mp (DSC) decomp. onset 234.6 °C, peak max. 235.8 °C (from *c*-hexane/THF, 90:10); R_f 0.47 (DCM); (found: C, 70.69; H, 2.94; N, 25.97.

$C_{19}H_{10}N_6$ requires C, 70.80; H, 3.13; N, 26.07%); λ_{max}(DCM)/nm 247 inf (log ε 4.48), 252 (4.49), 281 inf (4.48), 290 (4.56), 310 inf (4.45), 323 inf (4.28), 348 (4.05), 367 (3.99), 451 inf (4.32), 480 (4.48), 513 (4.43); ν_{max}/cm^{-1} 3080w (Ar CH), 2220m (C≡N), 1628m, 1589w, 1574m, 1493s, 1485s, 1471m, 1452s, 1391w, 1346m, 1331m, 1312m, 1275w, 1250w, 1220w, 1190w, 1171w, 1132s, 1101w, 1088m, 1022w, 999w, 986w, 912w, 876w, 847w, 820w, 793w, 775s, 752s, 702m; δ_H(500 MHz; $CDCl_3$) 8.53 (1H, dd, *J* 8.0, 1.0, Ar *H*), 7.94 (1H, ddd, *J* 7.8, 7.8, 1.5, Ar *H*), 7.82 (1H, br s, C*H*), 7.74 (1H, d, *J* 8.0, Ar *H*), 7.69 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.51 (2H, d, *J* 7.8, 7.8, Ar *H*), 7.33 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.06 (2H, d, *J* 7.5, Ar *H*); δ_C(125 MHz; $CDCl_3$) 163.1 (s), 161.5 (s), 146.2 (s), 144.7 (s), 140.5 (s), 138.1 (d), 136.8 (s) 130.4 (d), 130.0 (d), 128.8 (d), 127.6 (d), 127.0 (d), 118.1 (d), 117.0 (s), 112.8 (s, *C*≡N), 112.2 (s, *C*≡N), 71.1 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 324 (MH^++1, 9%), 323 (MH^+, 100), 296 (6), 270 (9), 248 (3), 220 (15), 129 (2), 104 (2).

*4.8.5. Quinolino[3',2':4,5]imidazo[1,2-c]quinazoline-13-carbonitrile (**30**).* A stirred solution of 2-[3-(phenylimino)imidazo[1,2-*c*]quinazolin-2(3*H*)-ylidene]malononitrile (**36**) (32.2 mg, 0.100 mmol) in diphenyl ether (1 mL) was immersed into a preheated (*ca*. 250 ^oC) Wood's metal bath and left to stir for 20 min, after which time the reaction mixture was removed from the Wood's metal bath, allowed to cool to *ca*. 20 ^oC, and triturated with *n*-pentane (4 mL). Filtration gave the *title compound* **30** (28.6 mg, 97%) as yellow fibres, mp (hotstage) 305-306 ^oC (from *c*-hexane/THF, 90:10), mp (DSC) onset 306.3 ^oC, peak max. 306.8 ^oC (from *c*-hexane/THF, 90:10); R_f 0.63 (DCM/Et_2O, 95:15); (found: C, 73.29; H, 2.98; N, 23.61. $C_{18}H_9N_5$ requires C, 73.21; H, 3.07; N, 23.72%); λ_{max}(DCM)/nm 269 inf (log ε 4.46), 279 (4.67), 288 (4.78), 303 (4.55), 325 (3.97), 349 inf (4.18), 368 (4.42), 392 (4.31), 414 (4.33); ν_{max}/cm^{-1} 3061 (Ar CH), 2228w (C≡N), 1632m, 1601m, 1584w, 1520m, 1503w,

1466m, 1450m, 1406w, 1395m, 1379m, 1368w, 1323w, 1306w, 1296w, 1271w, 1252w, 1233m, 1198w, 1140m, 1094w, 1036w, 1020w, 1011w, 963w, 953w, 923w, 889m, 876w, 793w, 777s, 762s, 725s, 702s; δ_H(500 MHz; $CDCl_3$) 9.51 (1H, s, C*H*), 8.83 (1H, d, *J* 8.0, Ar *H*), 8.45 (1H, d, *J* 8.0, Ar *H*), 8.34 (1H, d, *J* 8.5, Ar *H*), 8.07 (1H, d, *J* 8.5, Ar *H*), 7.95 (1H, dd, *J* 7.8, 7.8, Ar *H*), 7.90 (1H, dd, *J* 7.5, 7.5, Ar *H*), 7.84-7.79 (2H, m, Ar *H*); δ_C(125 MHz; $CDCl_3$) 152.4 (s), 144.5 (s), 144.0 (s), 143.9 (s), 137.7 (s), 135.4 (d), 134.5 (d), 129.6 (d), 129.4 (d), 129.35 (d), 129.0 (d), 128.2 (d), 126.4 (s), 125.6 (d), 125.4 (d), 118.3 (s), 114.0 (s, *C*≡N), 105.5 (s); *m*/*z* (MALDI-TOF) 296 (MH^+, 53%), 295 (M^+, 13), 242 (100), 142 (3), 129 (2).

*4.8.6. 2-[(3-Phenylquinazolin-4(3*H*)-ylidene)amino]ethene-1,1,2-tricarbonitrile (**37**).* To a stirred solution of 2-[2-(2-aminophenyl)-5-imino-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11a**) (31.2 mg, 0.100 mmol) in DMA (100 μL) at *ca*. 20 °C was added triethyl orthoformate (100 μL). The reaction mixture was then immersed into a preheated (*ca*. 170 °C) Wood's metal bath and left to stir for 5 min, after which time the reaction mixture was removed from the Wood's metal bath, allowed to cool to *ca*. 20 °C, diluted in DCM (5 mL), washed with H_2O (2 × 5 mL) and dried (Na_2SO_4). Removal of the volatiles and chromatography (DCM) of the residue gave the *title compound* **37** (23.0 mg, 71%) as yellow plates, mp (hotstage) 191-192 °C (from *c*-hexane/THF, 90:10), mp (DSC) onset 191.2 °C, peak max. 192.8 °C, decomp. onset 278.7 °C, peak max. 300.4 °C (from *c*-hexane/THF, 90:10); R_f 0.63 (DCM); (found: C, 70.60; H, 3.01; N, 25.99. $C_{19}H_{10}N_6$ requires C, 70.80; H, 3.13; N, 26.07%); λ_{max}(DCM)/nm 272 inf (log ε 4.10), 318 (3.92), 405 (4.24); ν_{max}/cm^{-1} 3080w (Ar CH), 2212w and 2199w (C≡N), 1607m, 1591m, 1562w, 1520s, 1497s, 1487s, 1464m, 1452s, 1360w, 1331m, 1281m, 1265w, 1227w, 1211w, 1200w, 1167w, 1157w, 1150w, 1111w, 1078w, 1069w, 1032w, 1003w, 986w, 964w, 926w,

914w, 876w, 856w, 804w, 770m, 758w, 711w; δ_H(500 MHz; $CDCl_3$) 8.28 (1H, s, C*H*), 8.13 (1H, d, *J* 8.5, Ar *H*), 8.05 (1H, ddd, *J* 7.8, 7.8, 1.0, Ar *H*), 8.00 (1H, d, *J* 7.5, Ar *H*), 7.79 (1H, ddd, *J* 7.8, 7.8, 1.0, Ar *H*), 7.70-7.64 (3H, m, Ar *H*), 7.47 (2H, d, *J* 8.0 Ar *H*); δ_C(125 MHz; $CDCl_3$) 154.5 (s), 147.5 (s), 144.4 (d), 143.0 (s), 137.2 (s), 137.1 (d), 131.1 (d), 130.7 (d), 130.0 (d), 129.1 (d), 127.8 (d), 127.1 (d), 118.3 (s), 112.3 (s), 111.9 (s, *C*≡N), 111.2 (s, *C*≡N), 71.9 [s, *C*$(CN)_2$]; *m*/*z* (MALDI-TOF) 324 (MH^++1, 24%), 323 (MH^+, 100), 296 (10), 285 (12), 283 (20), 262 (10), 232 (14), 226 (26), 222 (25), 153 (83), 134 (7), 130 (6). Further elution (DCM) gave (*Z*)-2-[3-(phenylimino)imidazo[1,2-c]quinazolin-2(3*H*)-ylidene]malononitrile (**36**) (3.8 mg, 15%) as orange needles, mp (DSC) decomp. onset 234.6 °C, peak max. 235.8 °C (from *c*-hexane/THF, 90:10); R_f 0.47 (DCM); identical to that described above.

4.9. X-ray crystallographic studies

Data were collected on an Oxford-Diffraction Supernova diffractometer, equipped with a CCD area detector utilizing either Cu Kα radiation (λ = 1.5418 Å) for compounds **5a**, **11a** and **36** or Mo Kα radiation (λ = 0.71073 Å) for compound **37**. Suitable crystals were attached to glass fibres using paratone-N oil and transferred to a goniostat where they were cooled for data collection. Unit cell dimensions were determined and refined by using 6948 ($5.71 \leq \theta \leq 72.76°$), 2290 ($3.39 \leq \theta \leq 66.98°$), 3262 ($8.50 \leq \theta \leq 66.87°$) and 2301 ($3.12 \leq \theta \leq 28.88°$) reflections for compounds **5a**, **11a**, **36** and **37**, respectively. Empirical absorption corrections (multi-scan based on symmetryrelated measurements) were applied using CrysAlis RED software.[31] The structures were solved by direct methods using SIR92[32] and refined on F^2 using full-matrix least squares using SHELXL97.[33] Software packages used: CrysAlis CCD[31] for data collection, CrysAlis RED[31] for cell refinement and data reduction, WINGX

for geometric calculations[34] and DIAMOND[35] for molecular graphics. The non-H atoms were treated anisotropically, whereas the hydrogen atoms were placed in calculated, ideal positions and refined as riding on their respective carbon atoms.

4.9.1. *Crystal refinement data for compound **5a**:* $C_{15}H_9N_4$, M = 245.26, Monoclinic, space group *P* $2_1/c$, a = 7.1177(2) Å, b = 21.5777(5) Å, c = 30.8365(7) Å, α = 90°, β = 92.281(2)°, γ = 90°, V = 4732.2(2) Å^3, Z = 16, T = 100(2) K, ρ_{calcd} = 1.377 g cm^{-3}, $2\theta_{max}$ = 67. Refinement of 685 parameters on 8433 independent reflections out of 16808 measured reflections (R_{int} = 0.0249) led to R_1 = 0.0450 [I > 2s(I)], wR_2 = 0.1445 (all data), and S = 1.083 with the largest difference peak and hole of 0.704 and -0.283 e^{-3}, respectively.

*4.9.2. Crystal refinement data for compound **11a**:* $C_{18}H_{12}N_6$, M = 312.34, Monoclinic, space group *P 2/n*, a = 10.3562(5) Å, b = 5.6532(3) Å, c = 26.1430(13) Å, α = 90°, β = 94.754(4)°, γ = 90°, V = 1525.29(13) Å^3, Z = 4, T = 100(2) K, ρ_{calcd} = 1.360 g cm^{-3}, $2\theta_{max}$ = 67. Refinement of 230 parameters on 2705 independent reflections out of 5184 measured reflections (R_{int} = 0.0374) led to R_1 = 0.0509 [I > 2s(I)], wR_2 = 0.1480 (all data), and S = 1.013 with the largest difference peak and hole of 0.294 and -0.328 e^{-3}, respectively.

*4.9.3. Crystal refinement data for compound **36**:* $C_{19}H_{10}N_6$, M = 322.33, Triclinic, space group *P -1*, a = 8.2982(8) Å, b = 12.5334(11) Å, c = 15.6588(15) Å, α = 93.241(8)°, β = 98.358(8)°, γ = 105.279(8)°, V = 1546.7(3) Å^3, Z = 4, T = 100(2) K, ρ_{calcd}= 1.384 g cm^{-3}, $2\theta_{max}$ = 67. Refinement of 452 parameters on 5338 independent reflections out of 9122 measured reflections (R_{int} = 0.0648) led to R_1 = 0.0937 [I > 2s(I)], wR_2 = 0.3269 (all data), and S = 0.817 with the largest difference peak and hole of 0.479 and -0.691 e^{-3}, respectively.

*4.9.4. Crystal refinement data for compound **37**:* $C_{19}H_{10}N_6$, M = 322.33, Monoclinic, space group *P 21/c*, a = 17.5482(9) Å, b = 8.6967(4) Å, c = 10.4977(7) Å, α = 90°, β = 104.070(6)°, γ = 90°, V = 1554.01(15) Å^3, Z = 4, T = 100(2) K, ρ_{calcd} = 1.377 g cm^{-3}, $2\theta_{max}$ = 25. Refinement of 262 parameters on 2737 independent reflections out of 10007 measured reflections (R_{int} = 0.0300) led to R_1 = 0.0740 [I > 2s(I)], wR_2 = 0.1889 (all data), and S = 1.077 with the largest difference peak and hole of 0.943 and -0.891 e^{-3}, respectively.

Crystallographic data for compounds **5a**, **11a**, **36** and **37** have been deposited with the Cambridge Crystallographic Data Centre with deposit numbers CCDC-1402622, CCDC-1061767, CCDC-1061766 and CCDC-1061768, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; or e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information: Copies of 1D ^{1}H and ^{13}C NMR spectra of compounds **1g**, **5a-g**, **9a-g**, **11a-g**, **25-28**, **30**, **34**, **36** and **37**.

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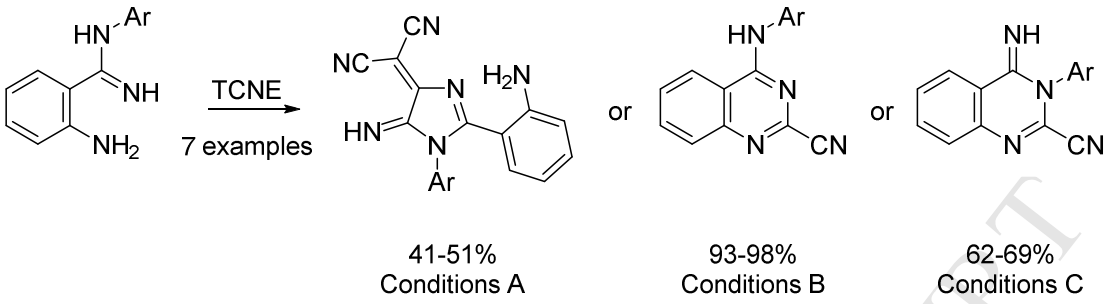
Graphical Abstract



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Conditions A

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Conditions B

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Conditions C

Supporting Information

The reaction of 2-amino-*N'*-arylbenzamidines with tetracyanoethene reinvestigated: Routes to imidazoles, quinazolines and quinolino[2',3':4,5]imidazo[1,2-*c*]quinazoline-8-carbonitrile

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Supporting Information

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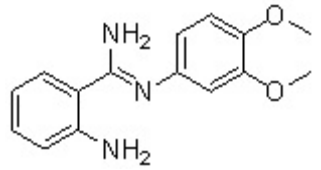
2-Amino-*N*′-(3,4-dimethoxyphenyl)benzamidine (**1g**), DMSO-d_6, ^{1}H-NMR



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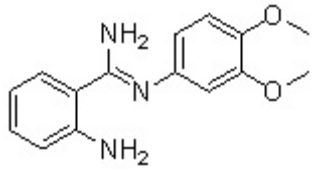

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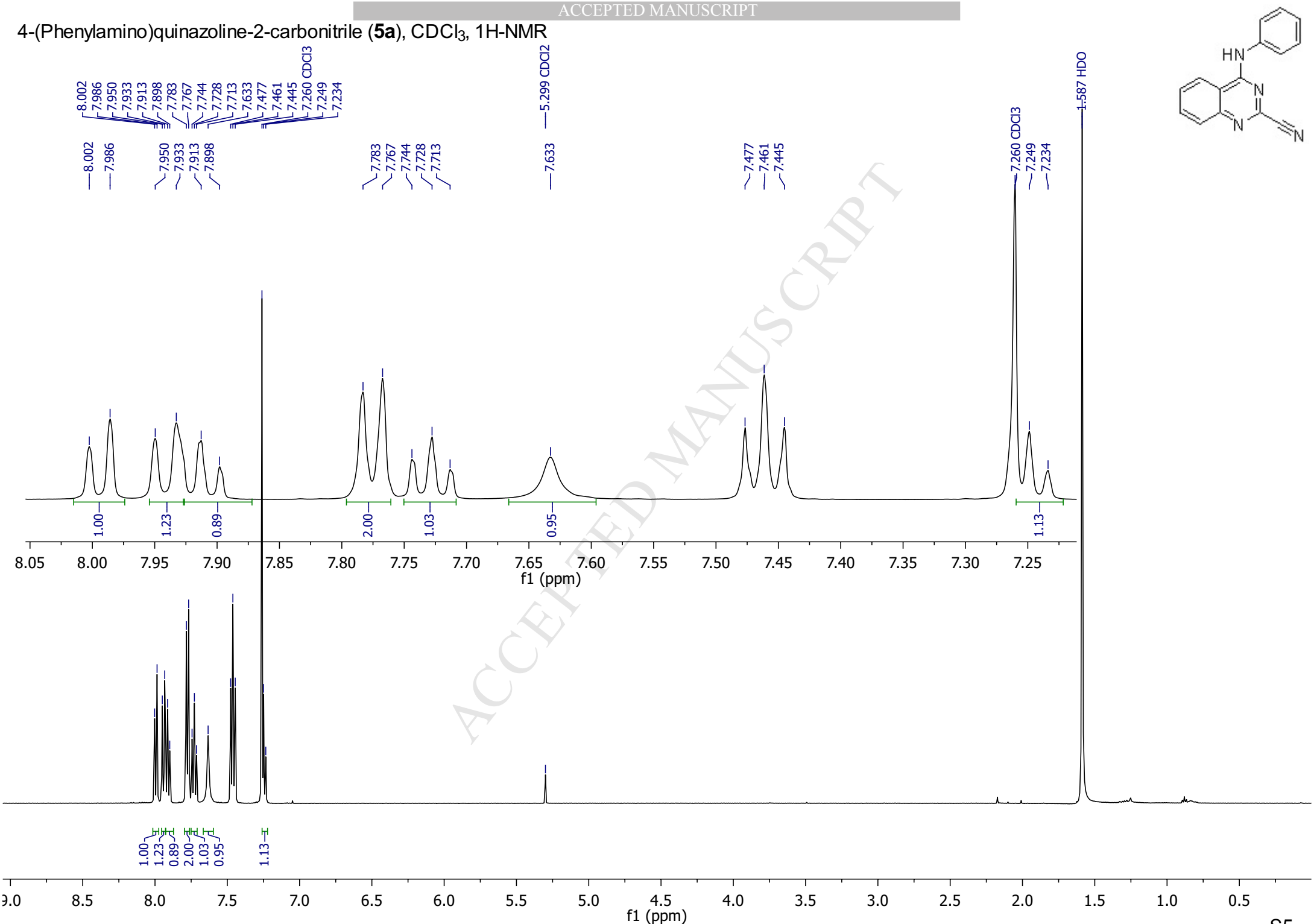

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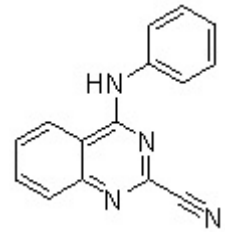

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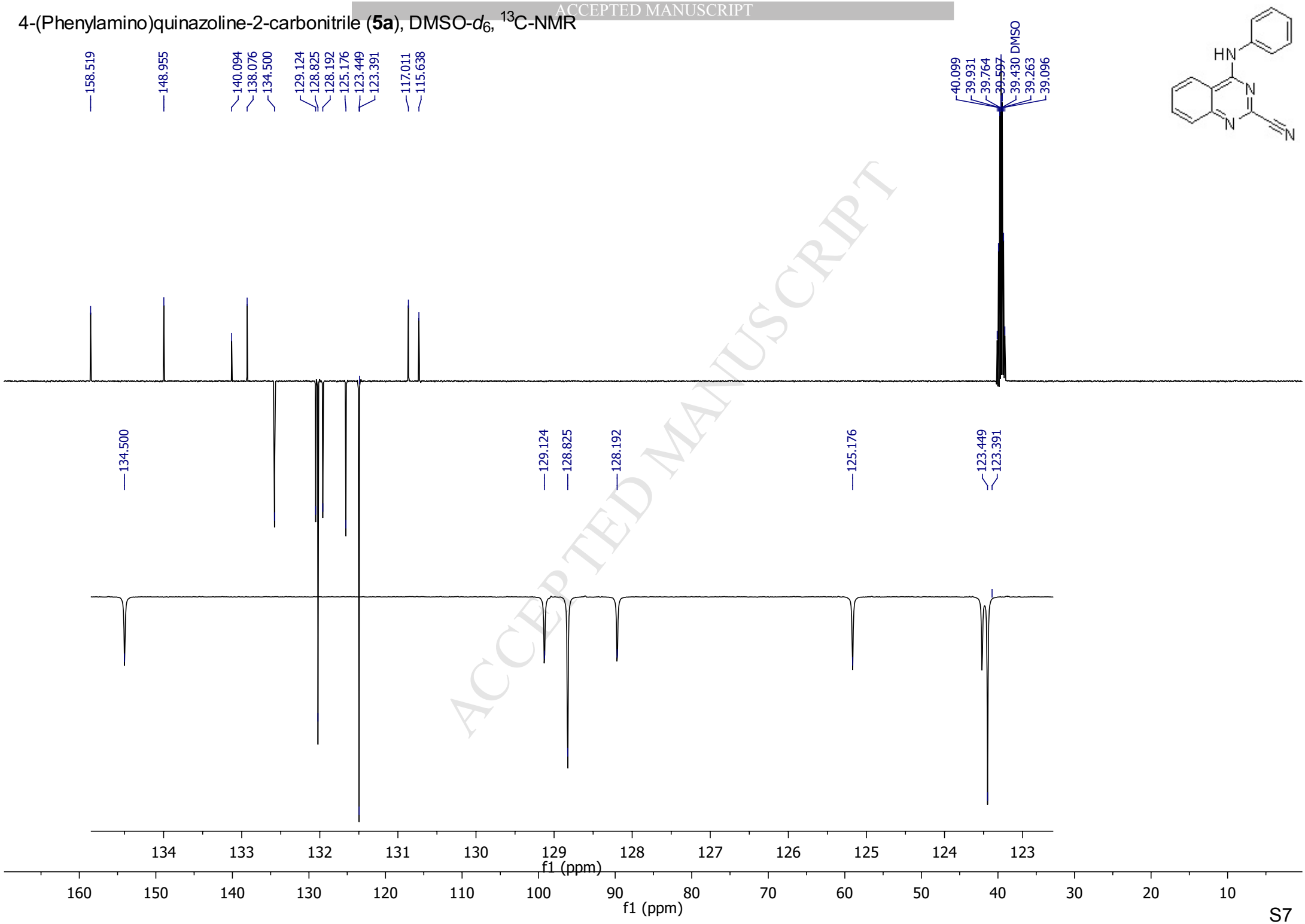

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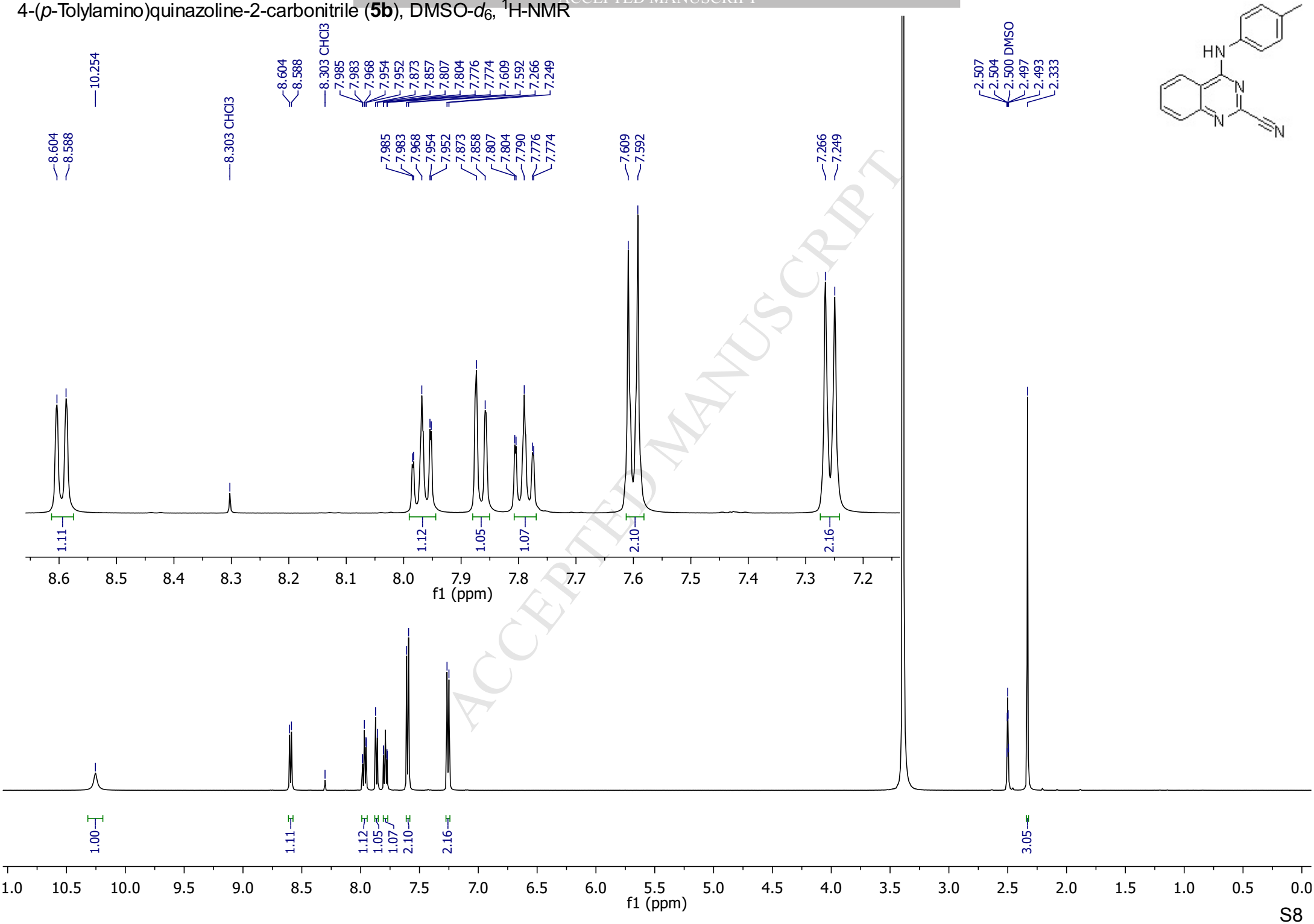

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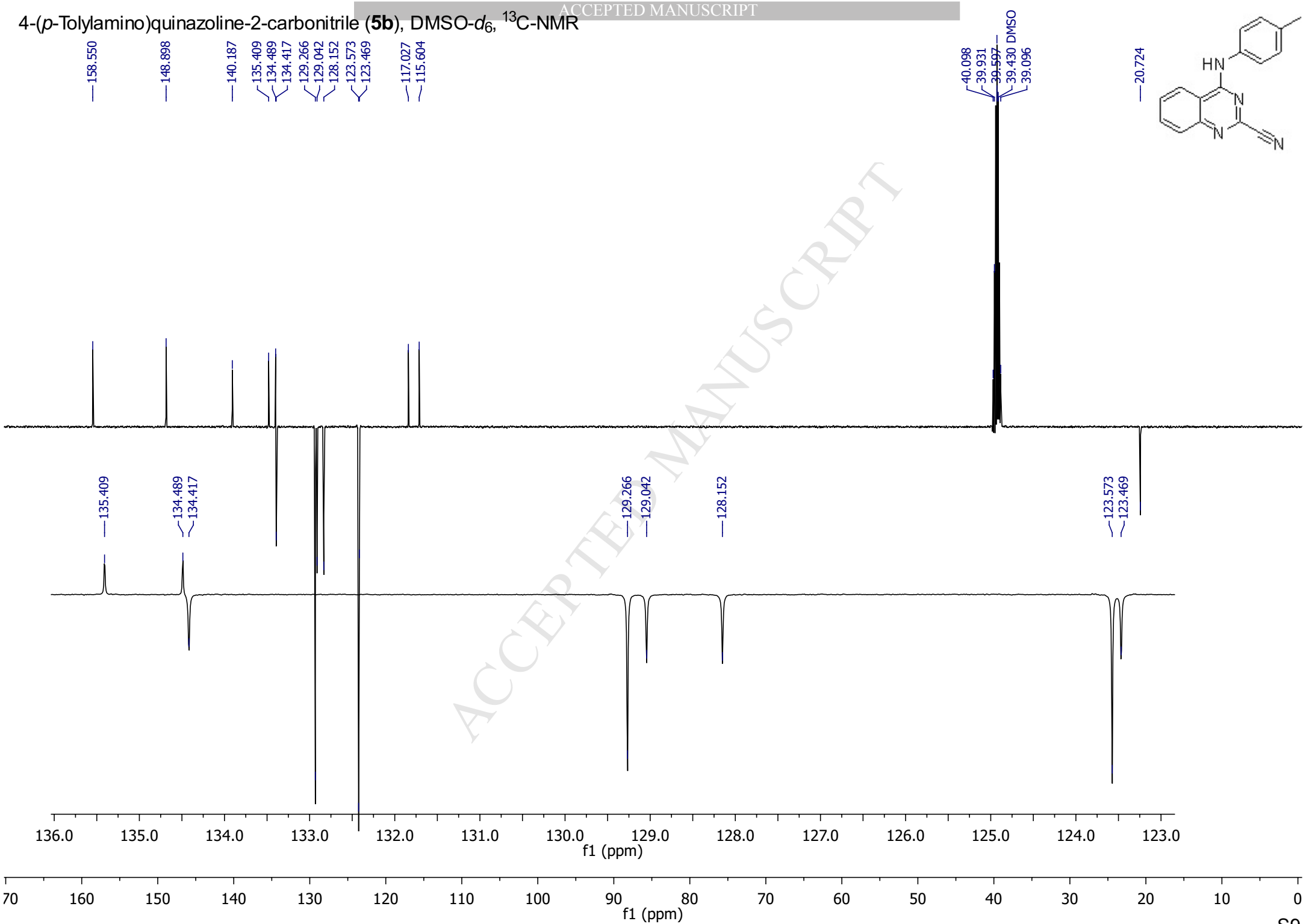

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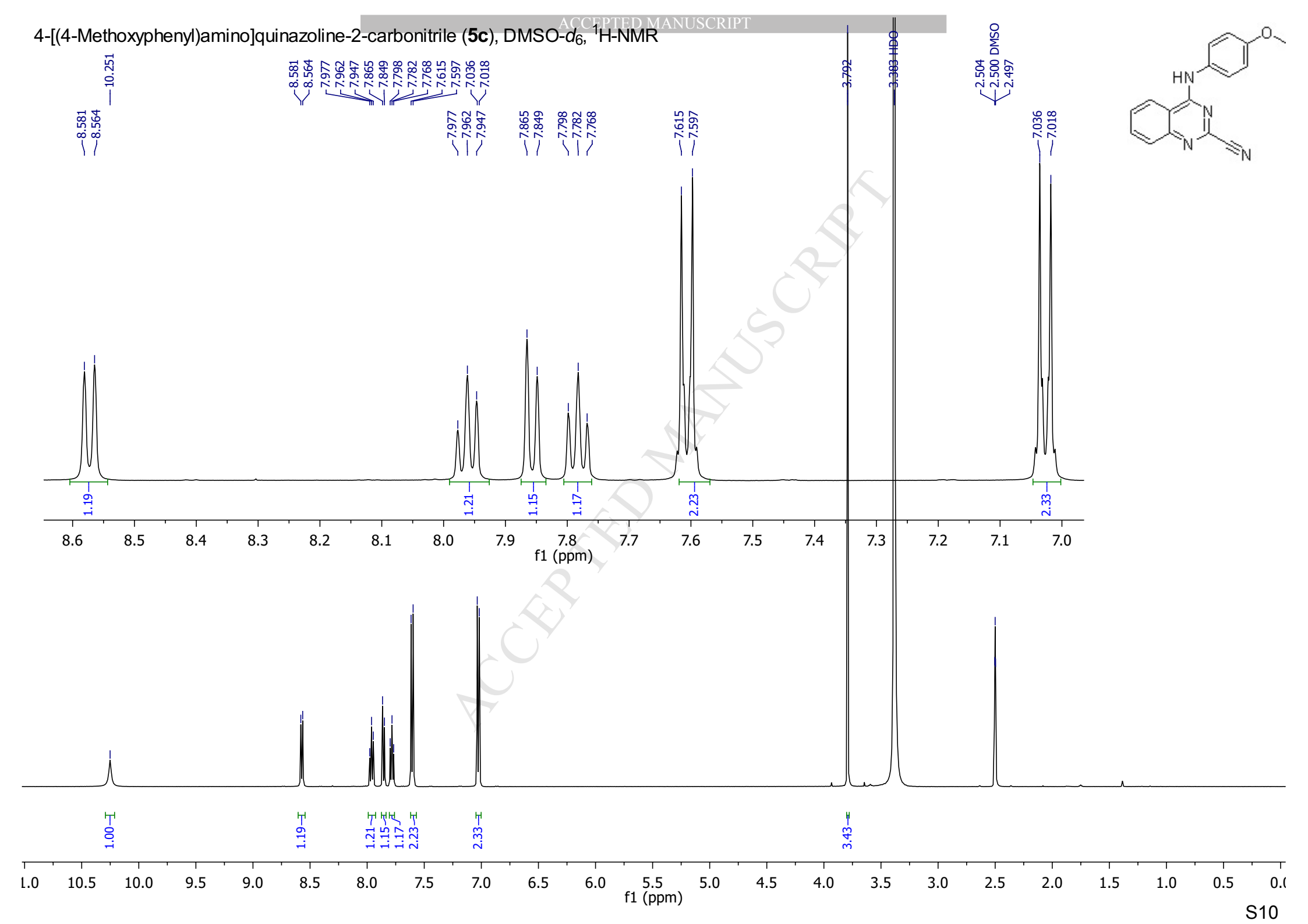

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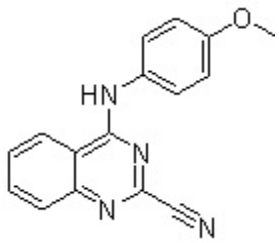

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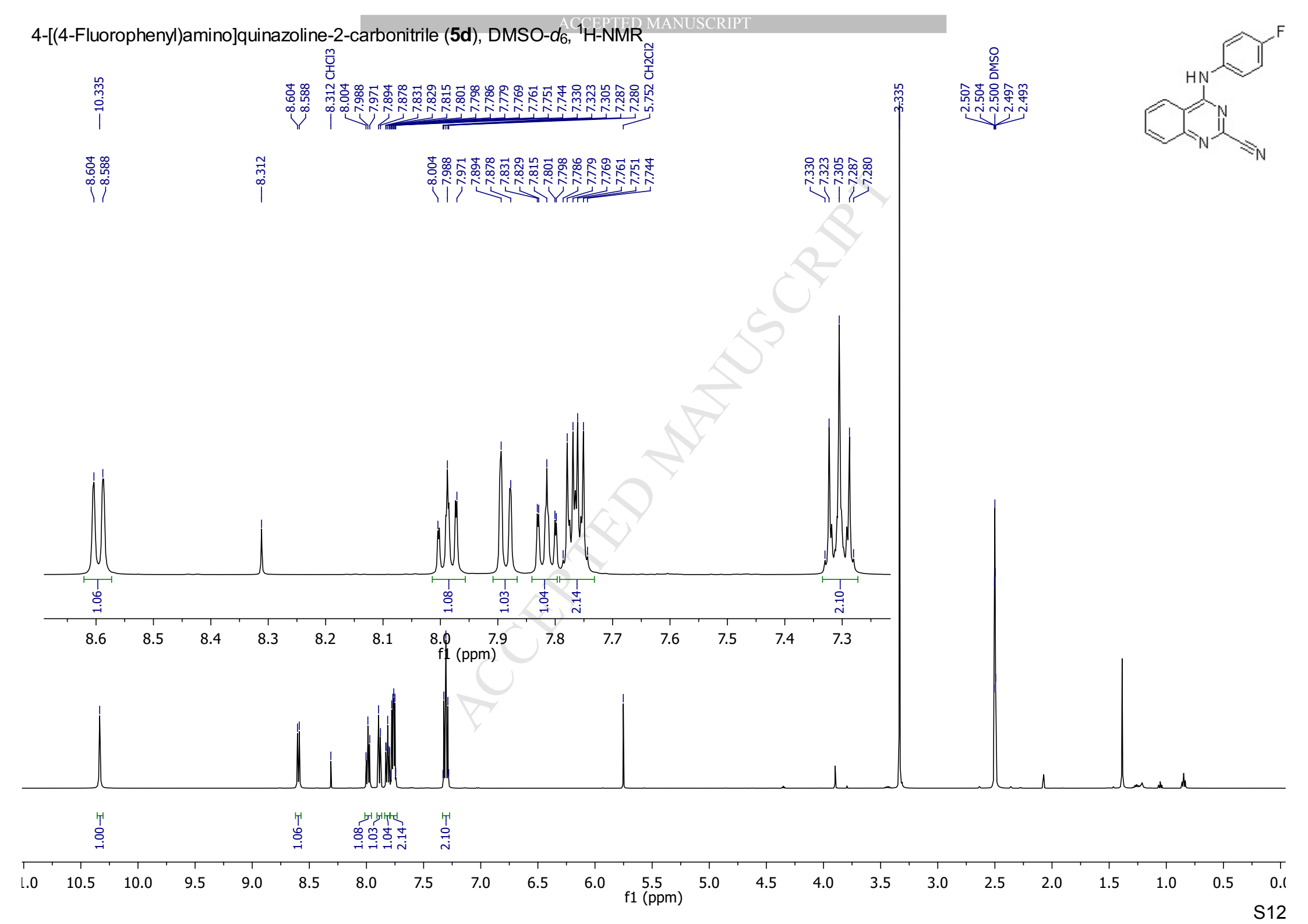

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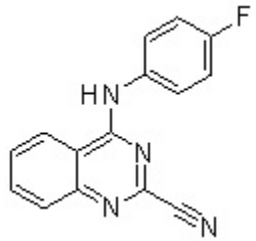

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158.477, 158.320

158.0

f1 (ppm)

134.398, 134.234, 129.017, 128.100, 125.454, 125.389, 123.369, 116.870, 115.495, 115.440, 115.317

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f1 (ppm)

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f1 (ppm)

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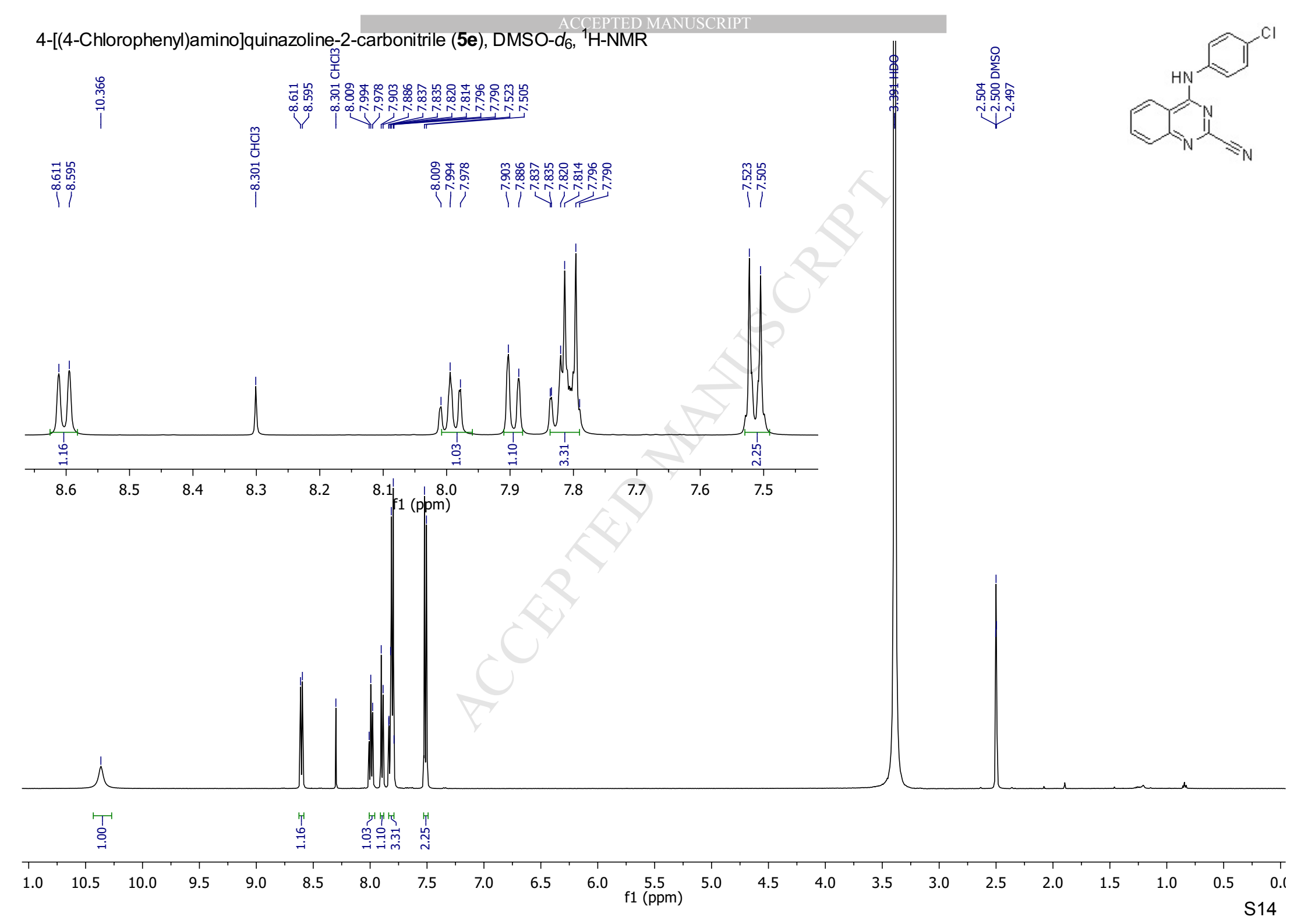

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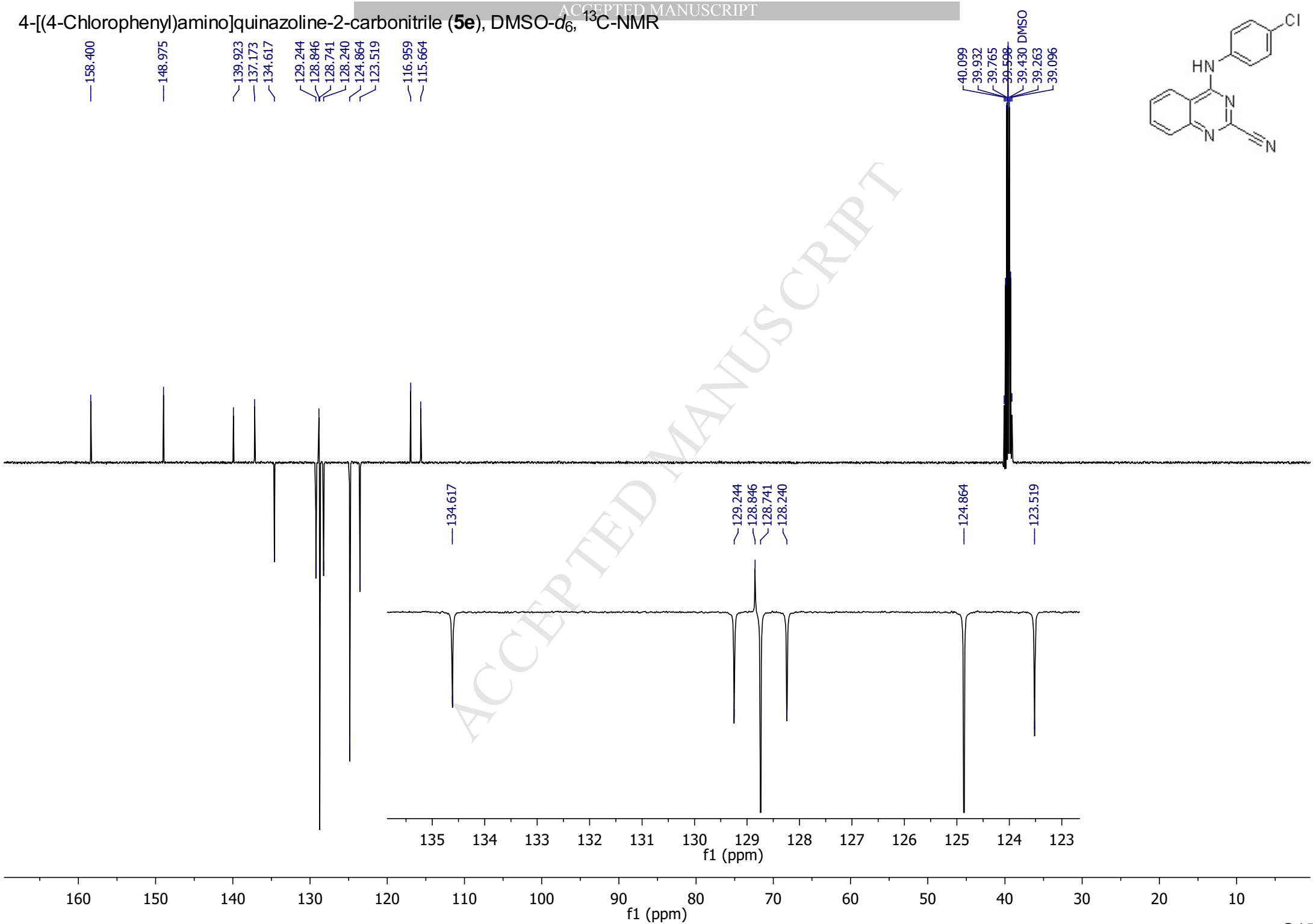

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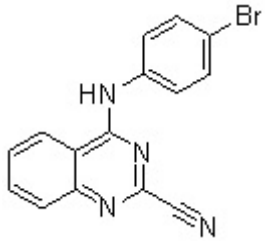

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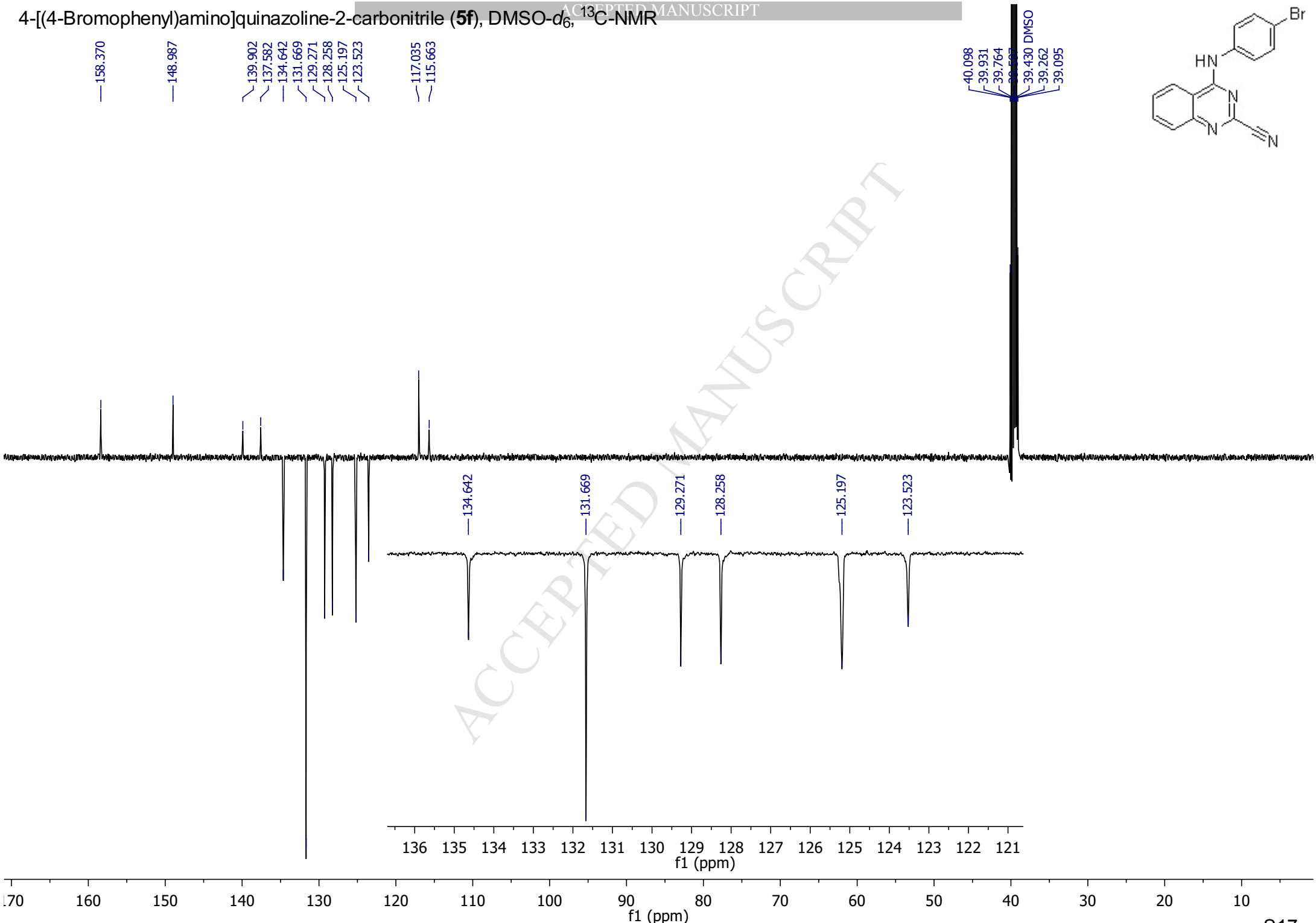

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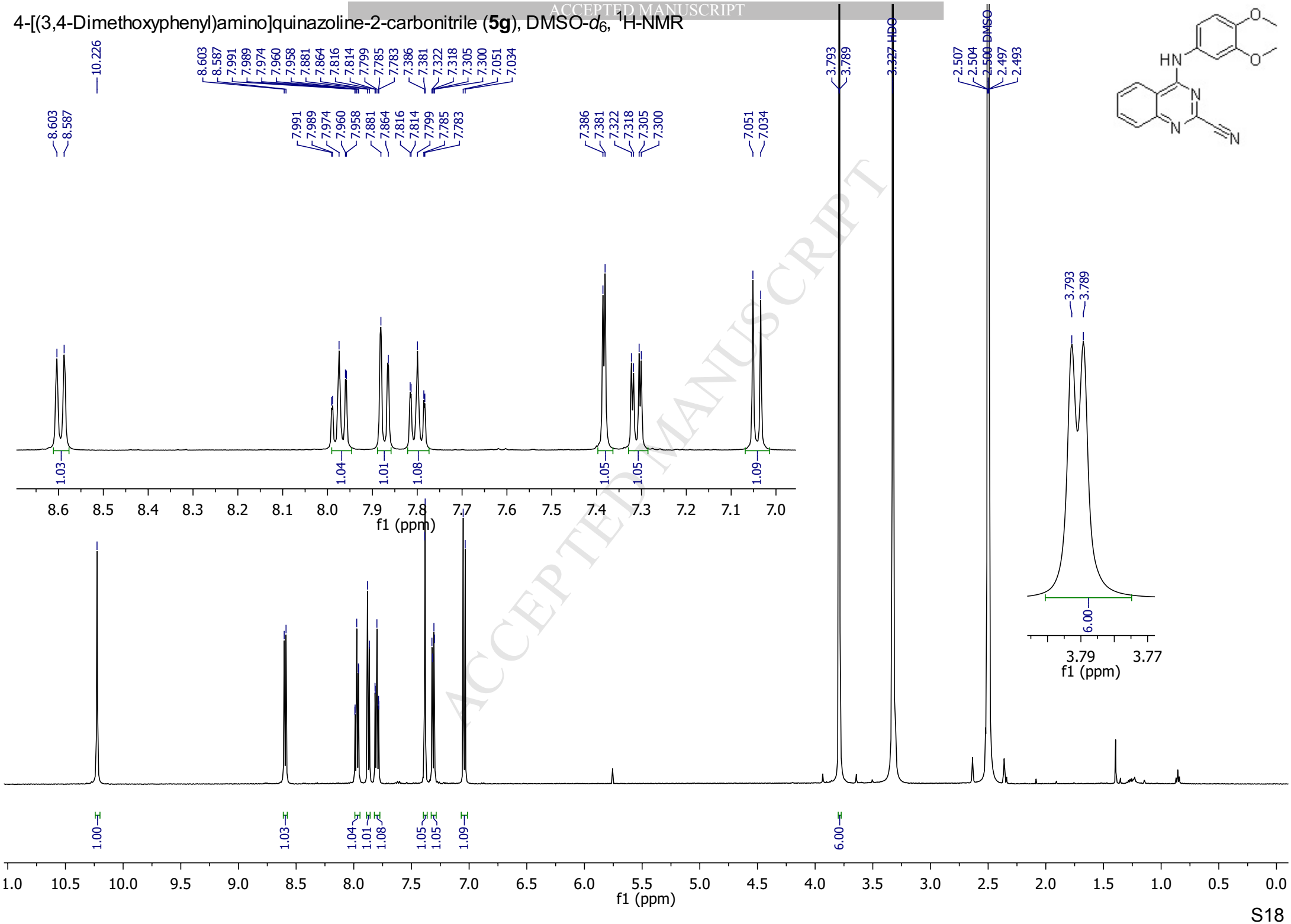
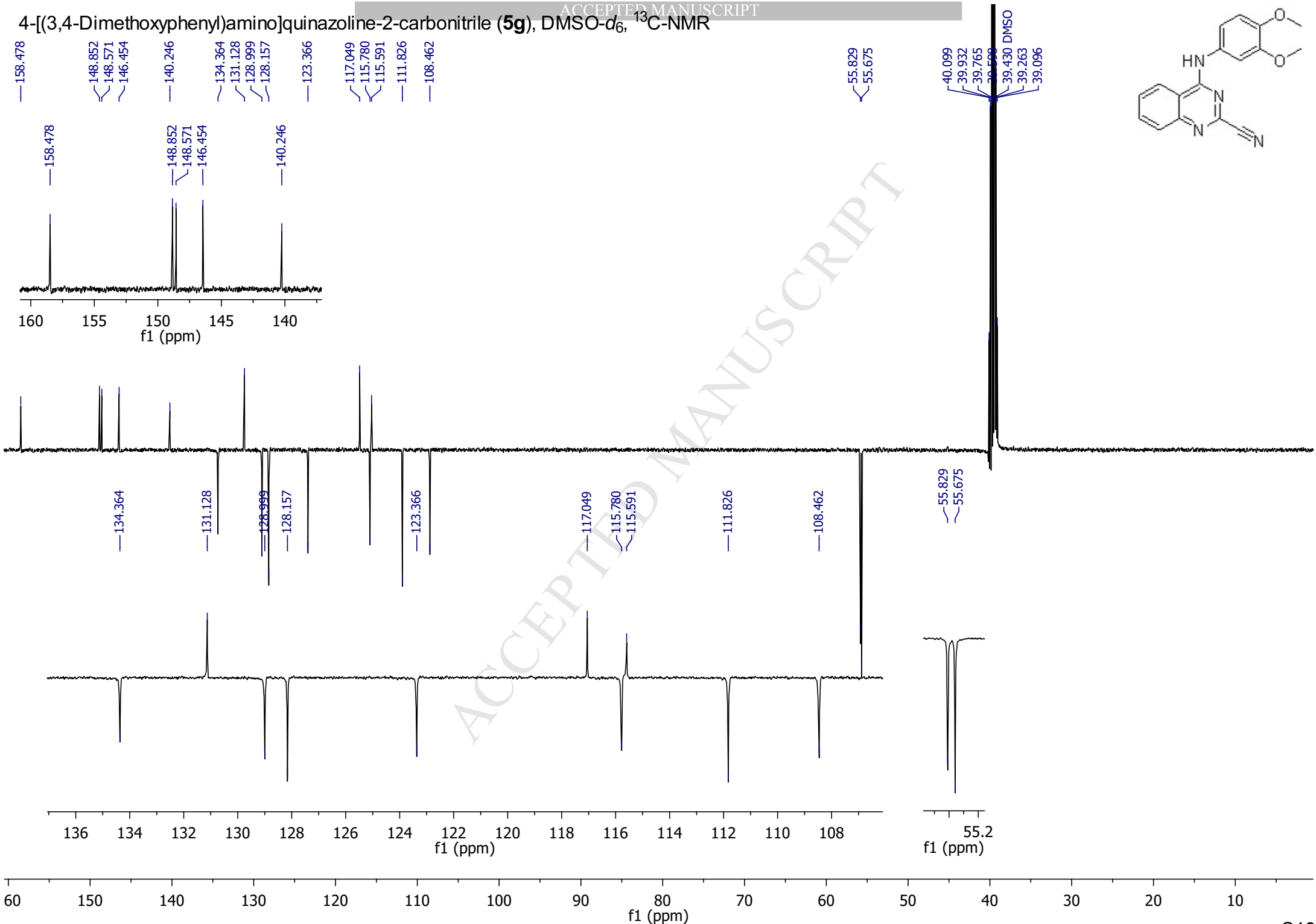
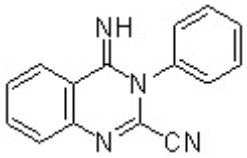
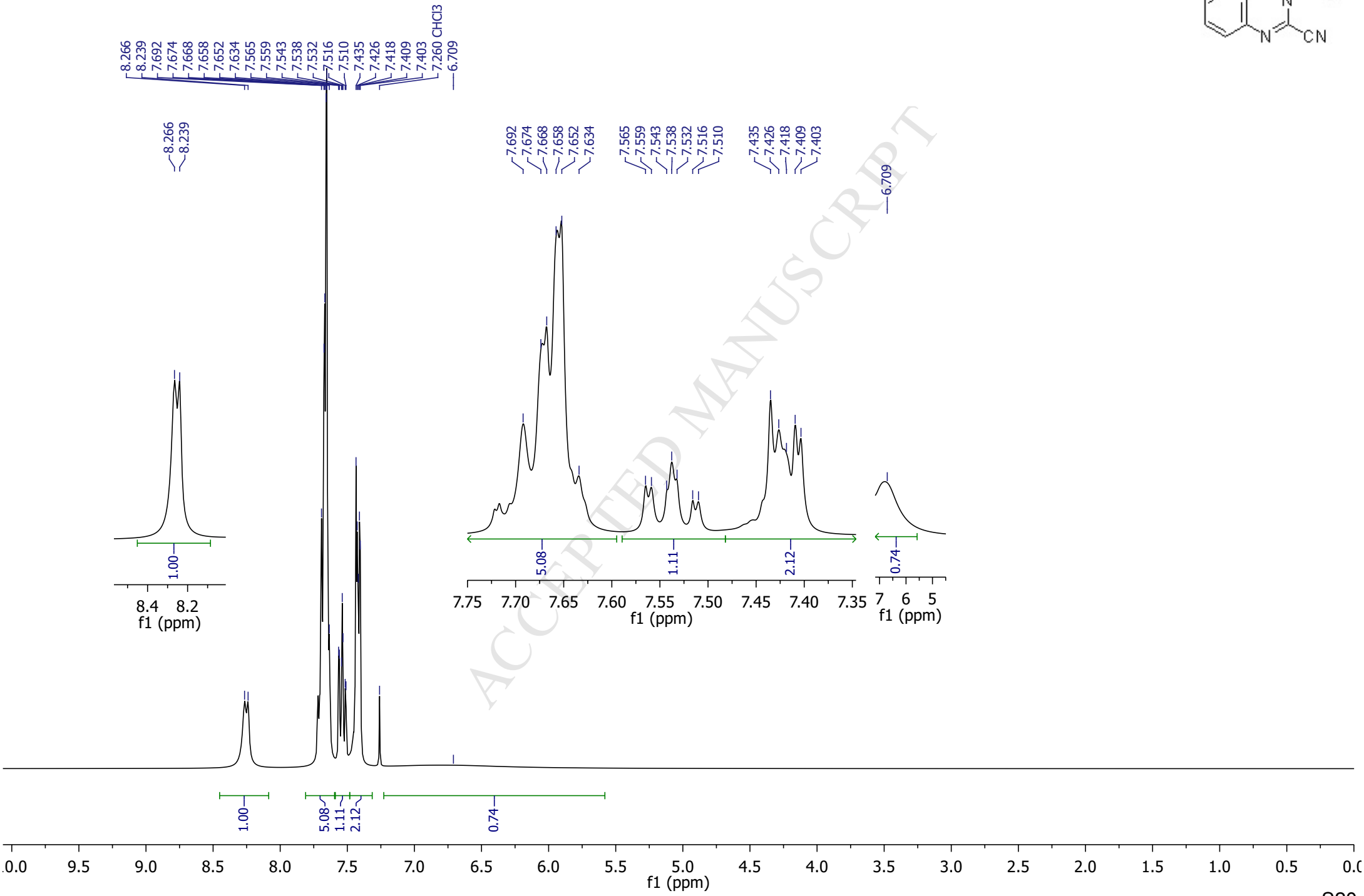


4-[(3,4-Dimethoxyphenyl)amino]quinazoline-2-carbonitrile (**5g**), DMSO-d_6, ^{13}C-NMR

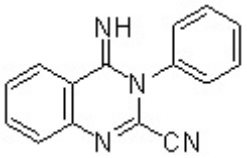


4-Imino-3,4-dihydroquinazoline-2-carbonitrile (**9a**), $CDCl_3$, ^{1}H-NMR

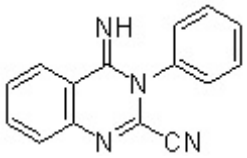




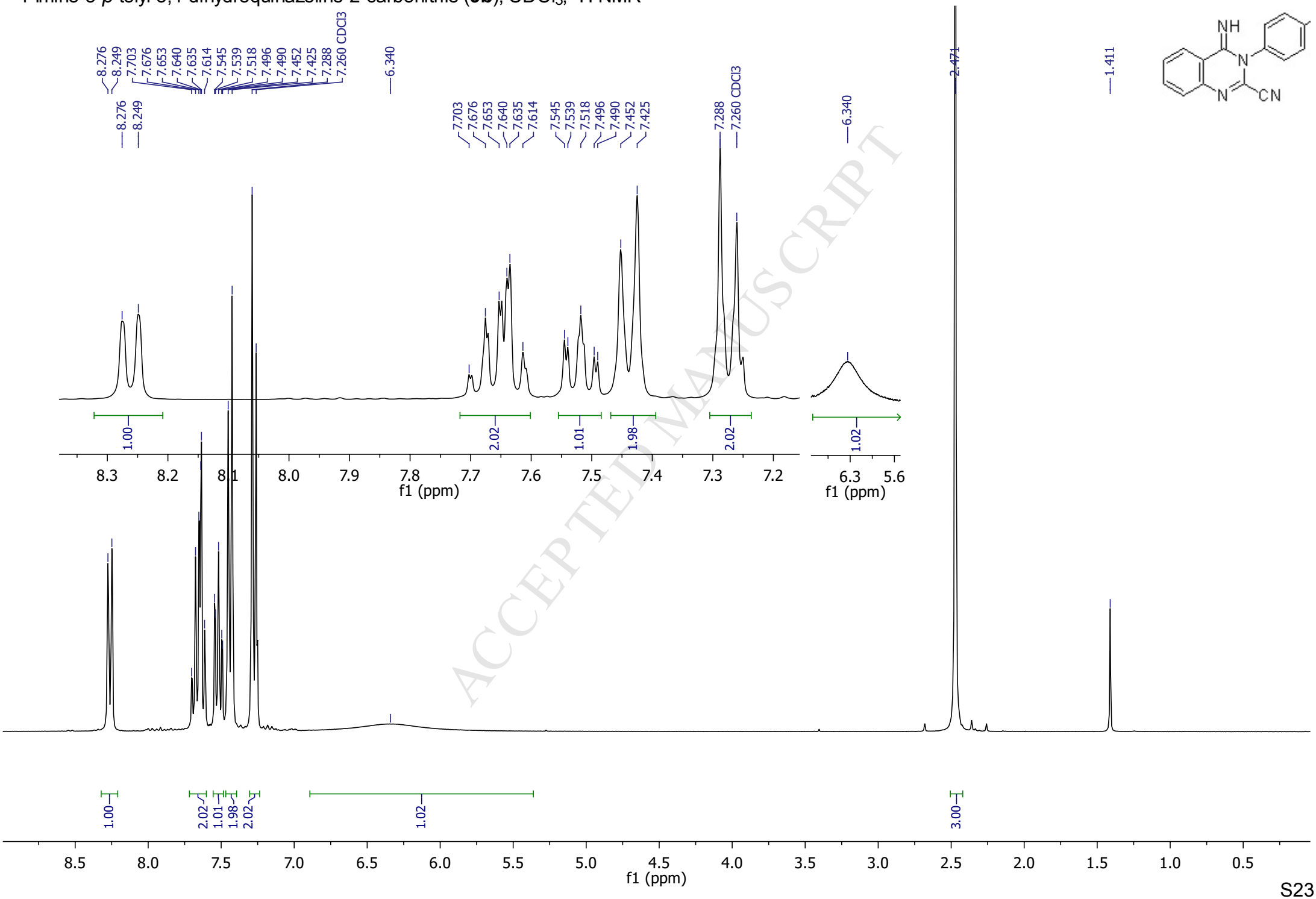
4-Imino-3,4-dihydroquinazoline-2-carbonitrile (**9a**), $CDCl_3$, ^{13}C-NMR



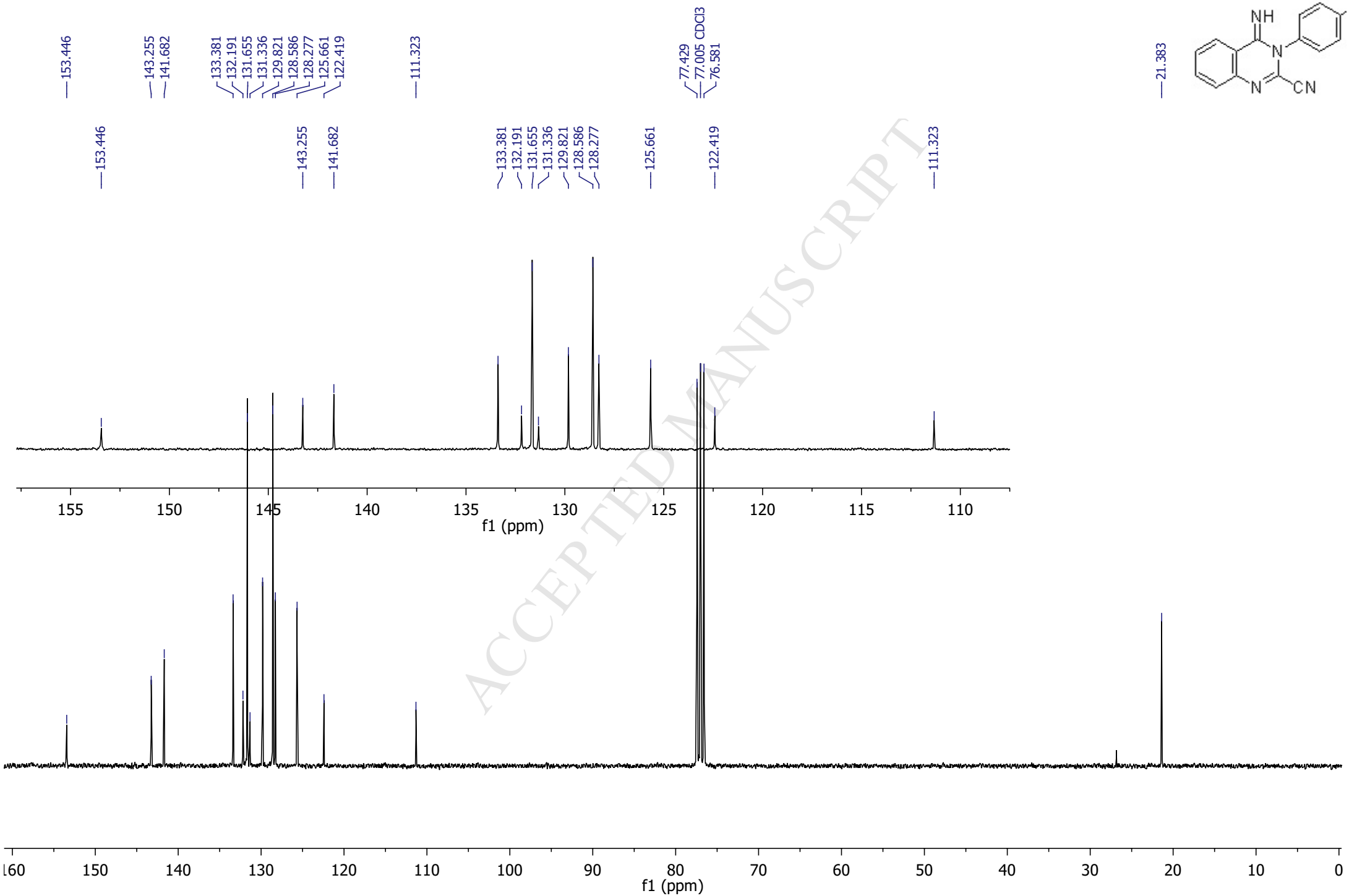
4-Imino-3,4-dihydroquinazoline-2-carbonitrile (**9a**), $CDCl_3$, DEPT135



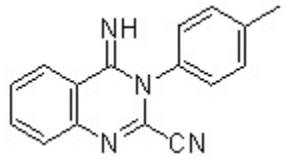
4-Imino-3-*p*-tolyl-3,4-dihydroquinazoline-2-carbonitrile (**9b**), $CDCl_3$, ^{1}H-NMR



4-Imino-3-*p*-tolyl-3,4-dihydroquinazoline-2-carbonitrile (**9b**), $CDCl_3$, ^{13}C-NMR



4-Imino-3-*p*-tolyl-3,4-dihydroquinazoline-2-carbonitrile (**9b**), $CDCl_3$, DEPT135



133.385
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129.825
128.589
128.281
125.663
133.385
131.659
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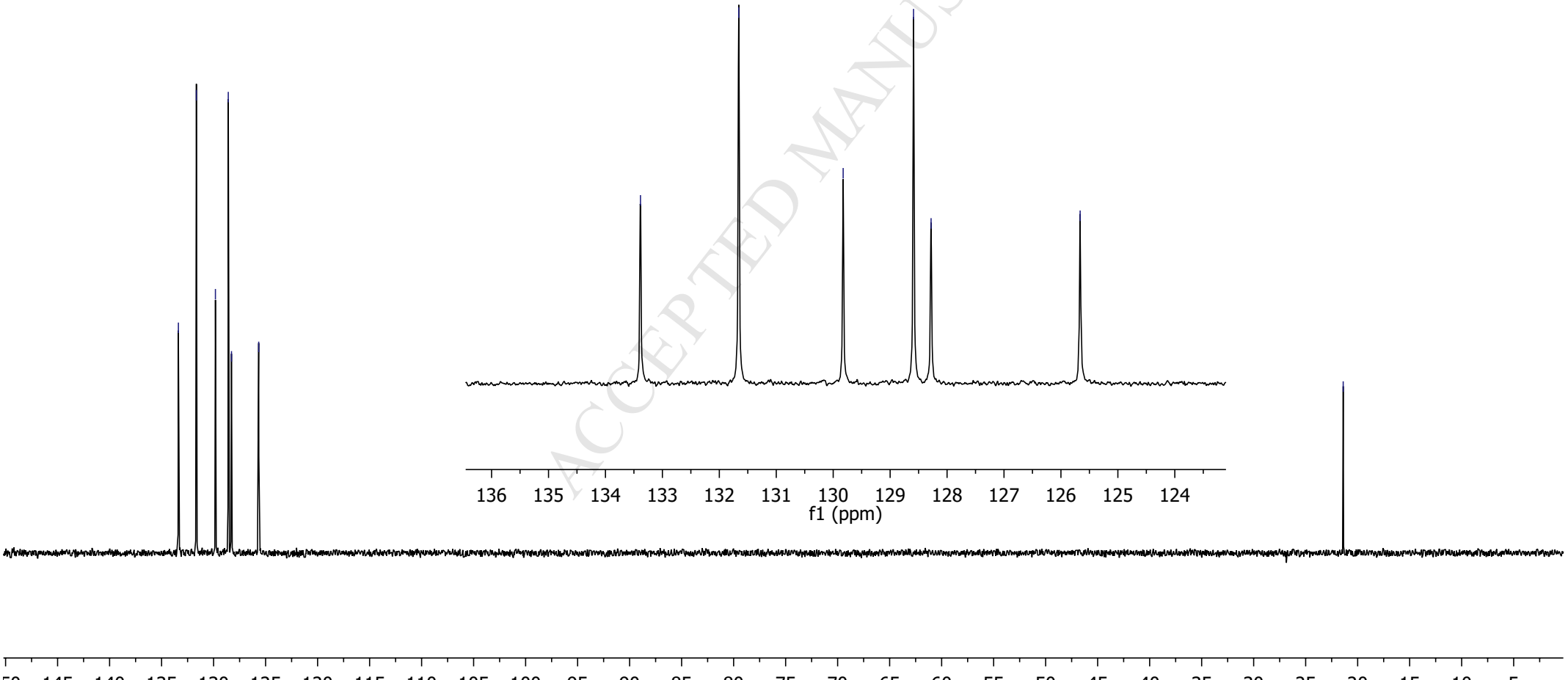
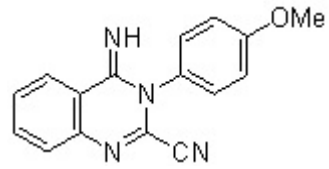
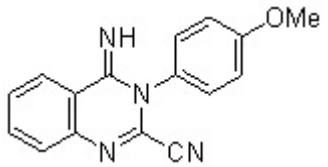
125.663
21.391

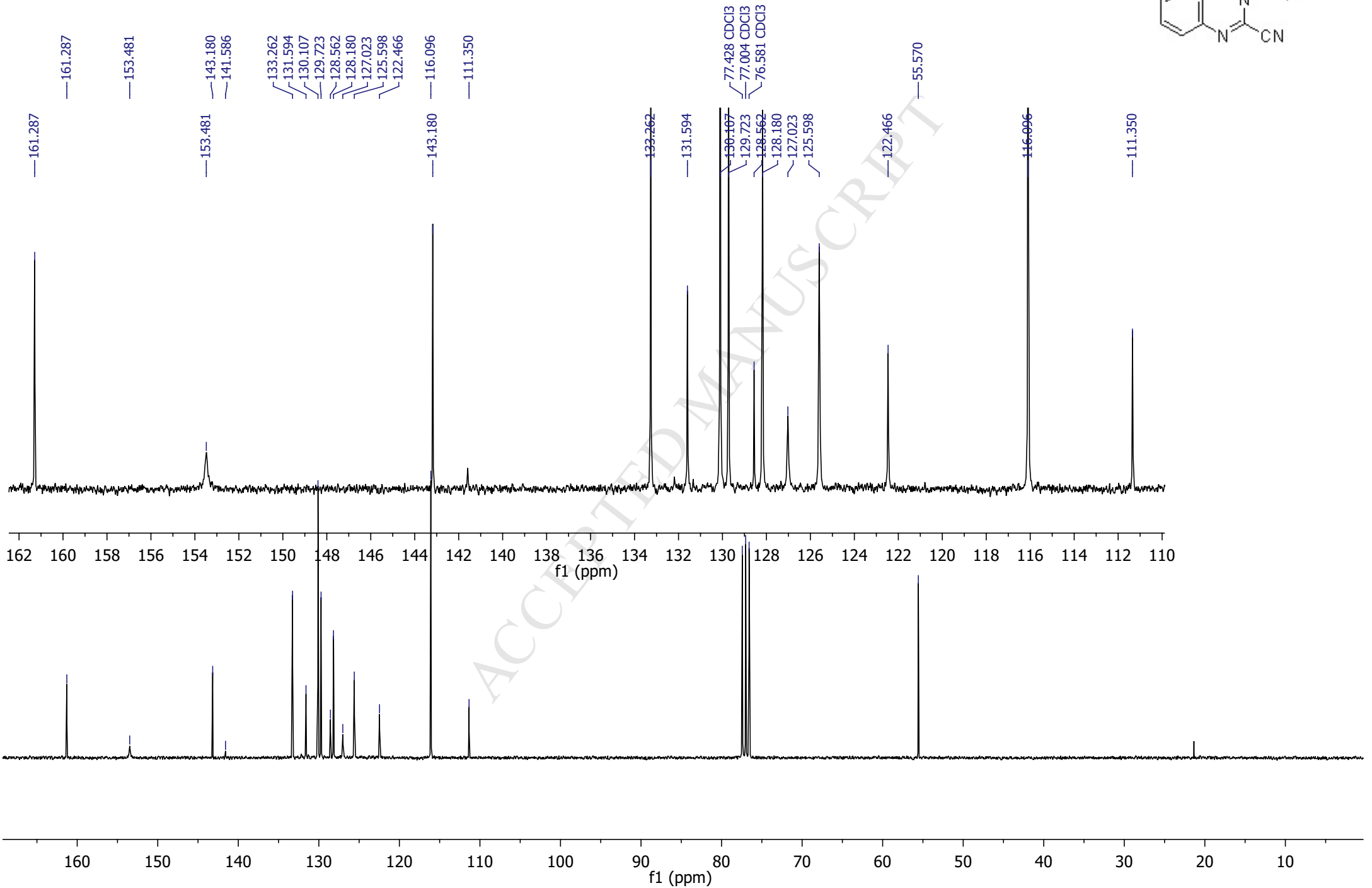


4-Imino-3-(4-methoxyphenyl)-3,4-dihydroquinazoline-2-carbonitrile (**9c**), $CDCl_3$, ^{1}H-NMR

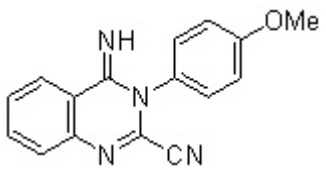


4-Imino-3-(4-methoxyphenyl)-3,4-dihydroquinazoline-2-carbonitrile (**9c**), $CDCl_3$, ^{13}C-NMR

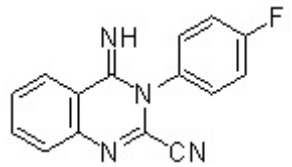


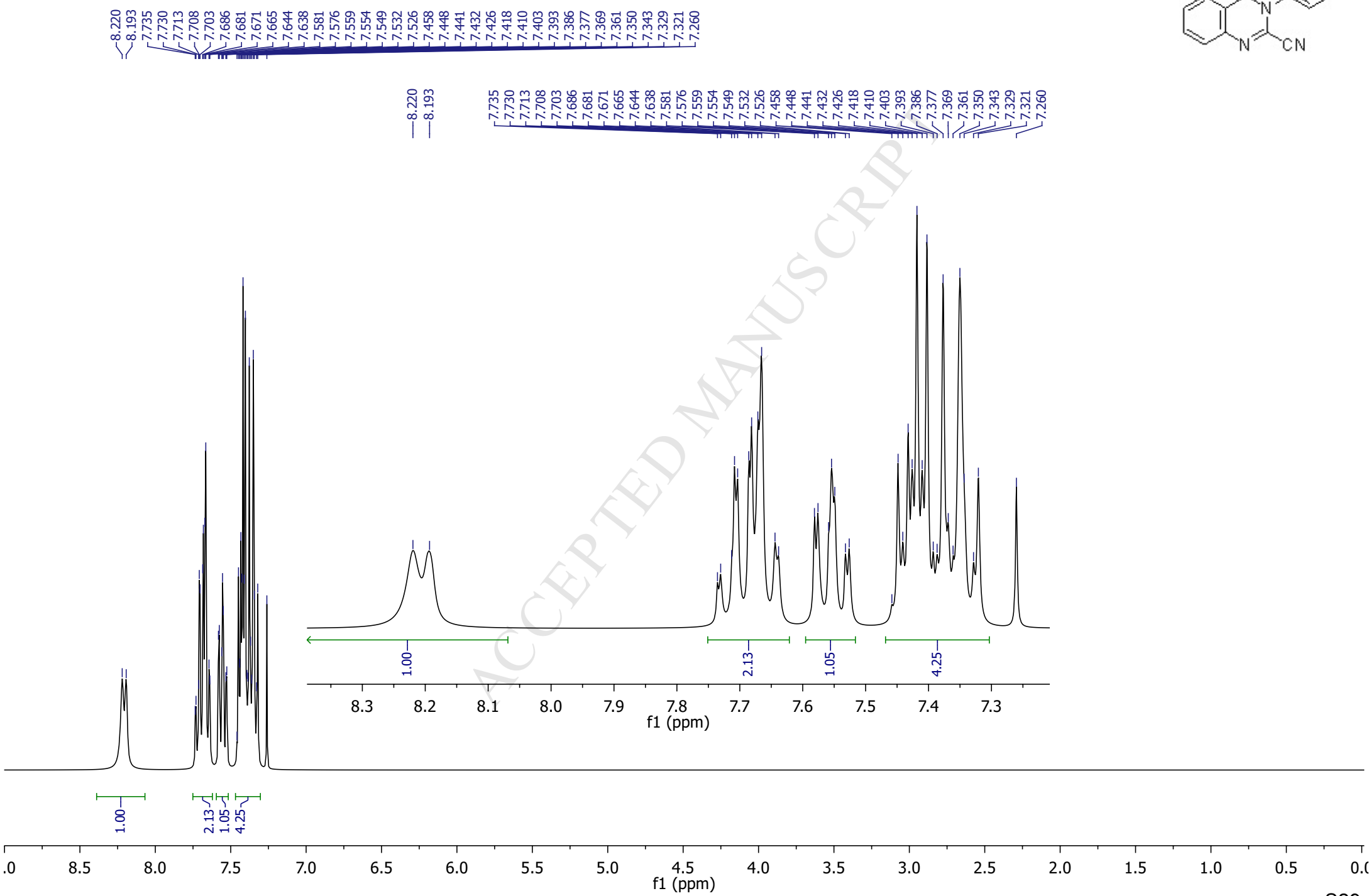


4-Imino-3-(4-methoxyphenyl)-3,4-dihydroquinazoline-2-carbonitrile (**9c**), $CDCl_3$, DEPT135

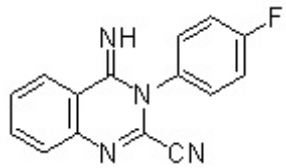


3-(4-Fluorophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9d**), $CDCl_3$, ^{1}H-NMR

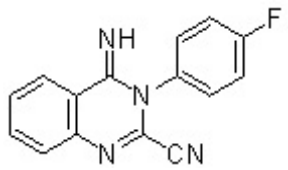


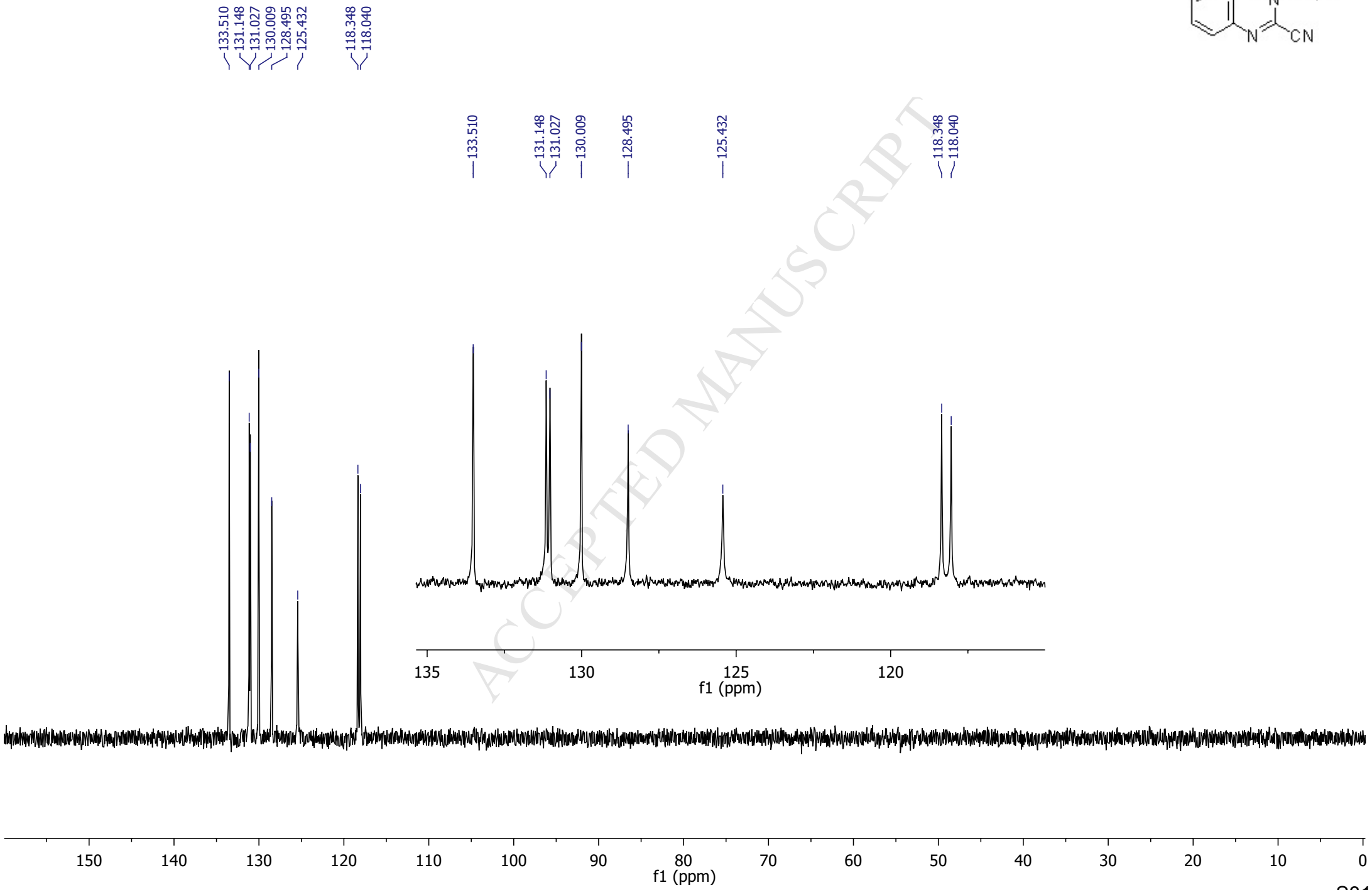


3-(4-Fluorophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9d**), $CDCl_3$, ^{13}C-NMR

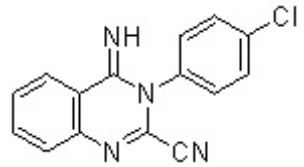


3-(4-Fluorophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9d**), $CDCl_3$, DEPT135

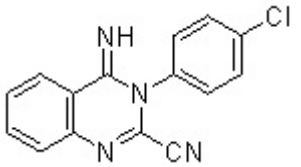




3-(4-Chlorophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9e**), $CDCl_3$, ^{1}H-NMR



3-(4-Chlorophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9e**), $CDCl_3$, ^{13}C-NMR



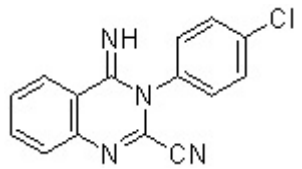
153.806 143.029 137.471 133.727 133.623 131.296 130.859 130.344 130.109 128.605 125.419 122.114 111.180 77.429 CDCl3 77.207 CDCl3 77.005 CDCl3 76.582 CDCl3

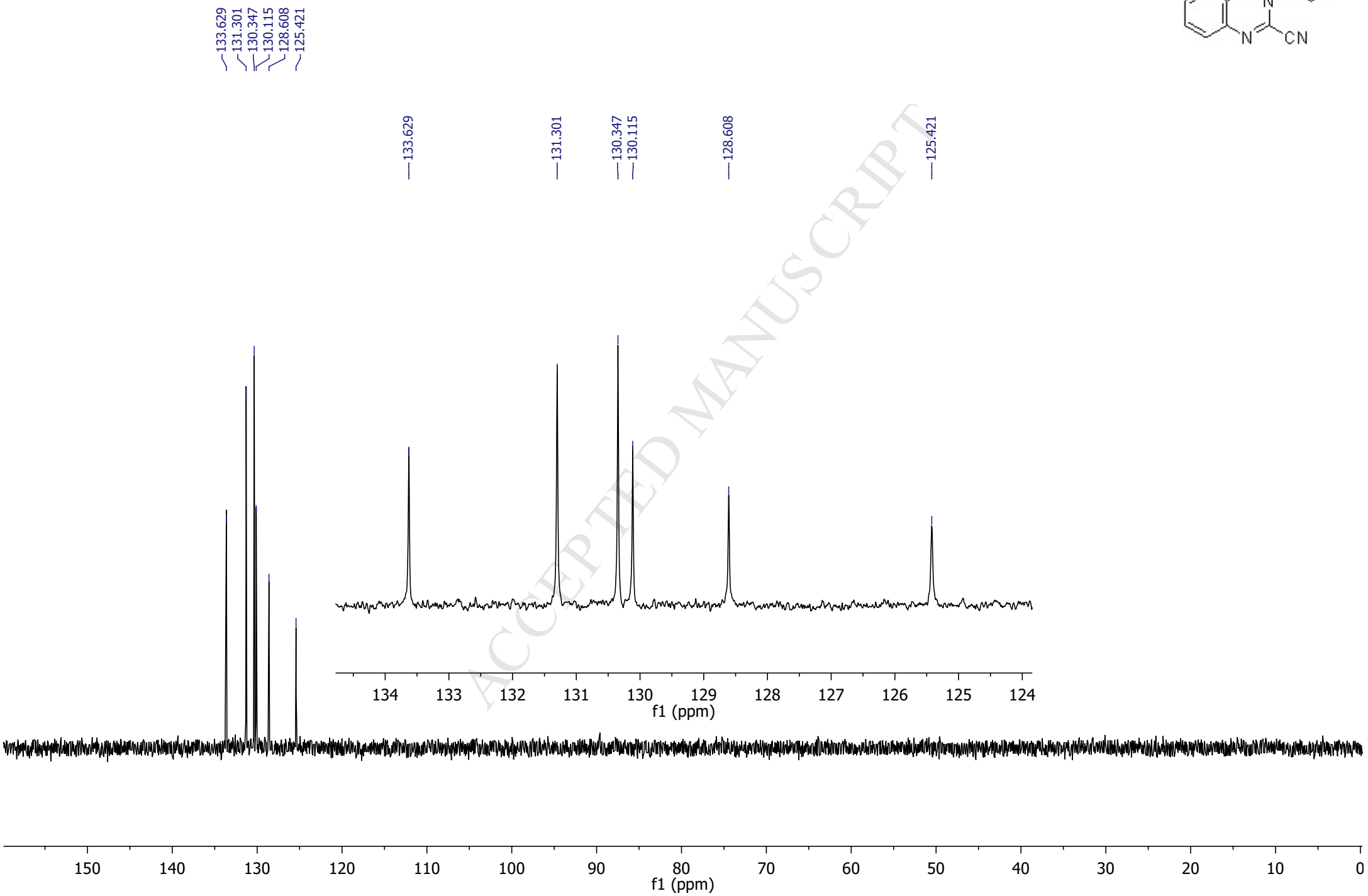
143.029 137.471 133.727 133.623 131.296 130.859 130.344 130.109 128.605 125.419 122.114

143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121
f1 (ppm)

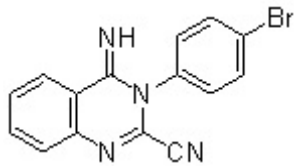
150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3-(4-Chlorophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9e**), $CDCl_3$, DEPT135

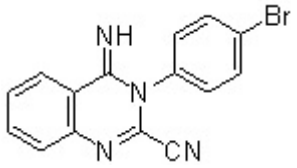




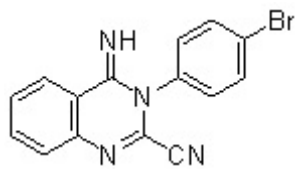
3-(4-Bromophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9f**), $CDCl_3$, ^{1}H-NMR

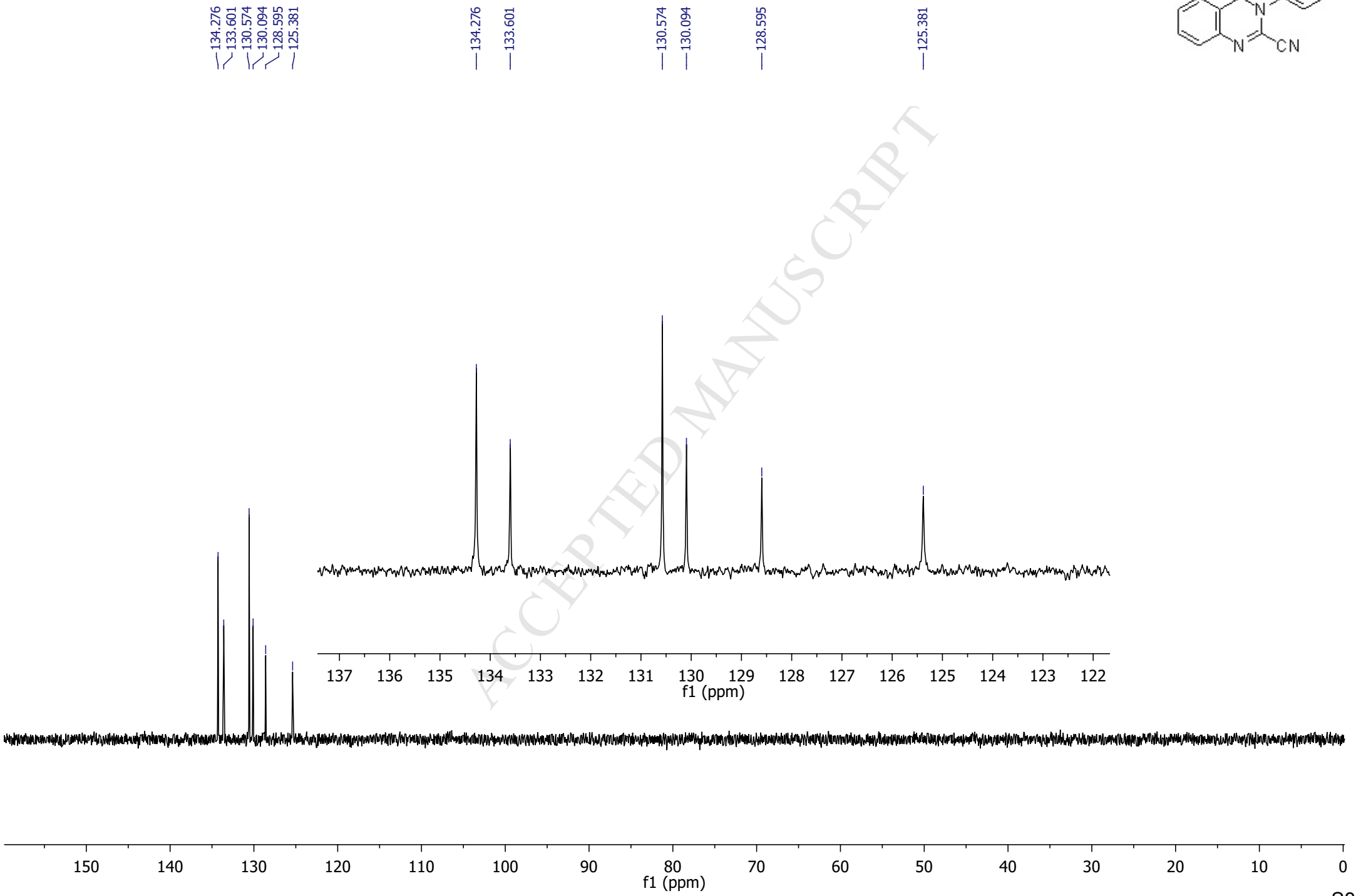


3-(4-Bromophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9f**), $CDCl_3$, ^{13}C-NMR

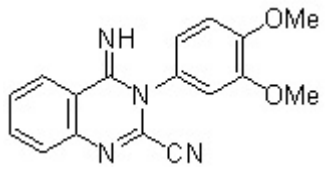


3-(4-Bromophenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9f**), $CDCl_3$, DEPT135

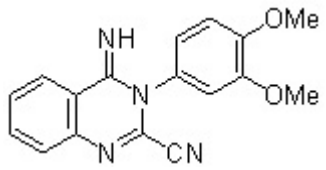


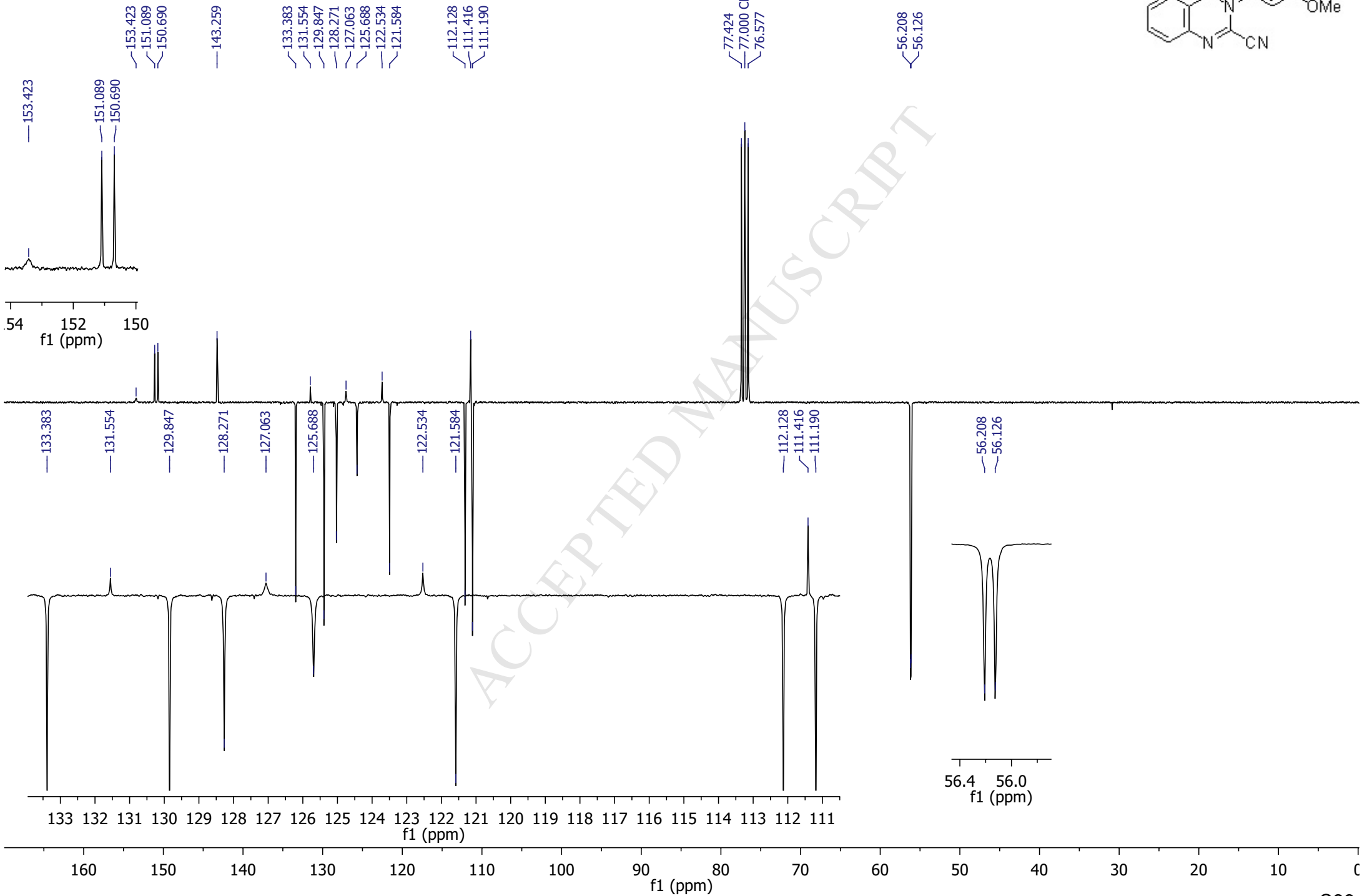


3-(3,4-Dimethoxyphenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9g**), $CDCl_3$, ^{1}H-NMR

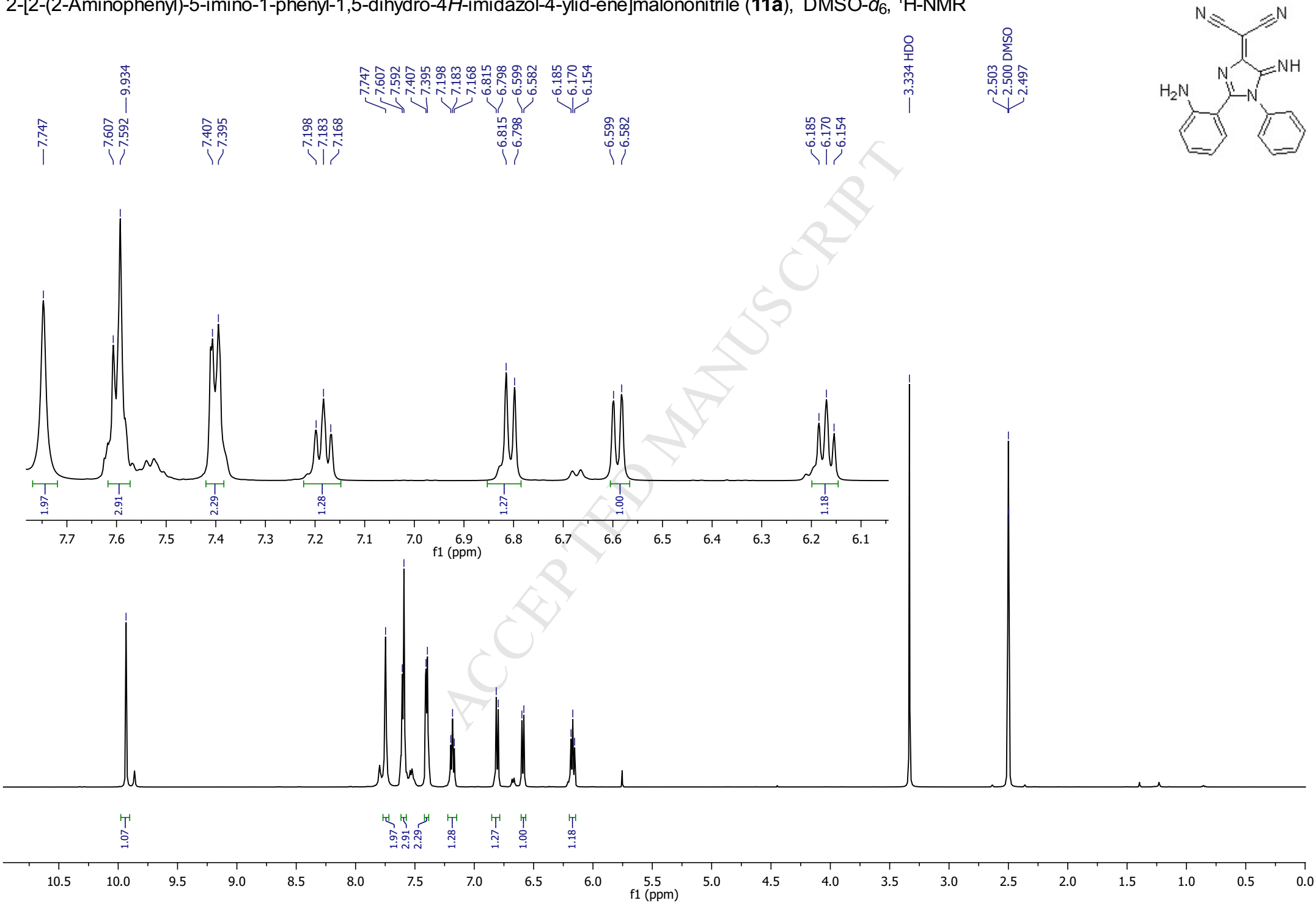


3-(3,4-Dimethoxyphenyl)-4-imino-3,4-dihydroquinazoline-2-carbonitrile (**9g**), $CDCl_3$, ^{13}C-NMR

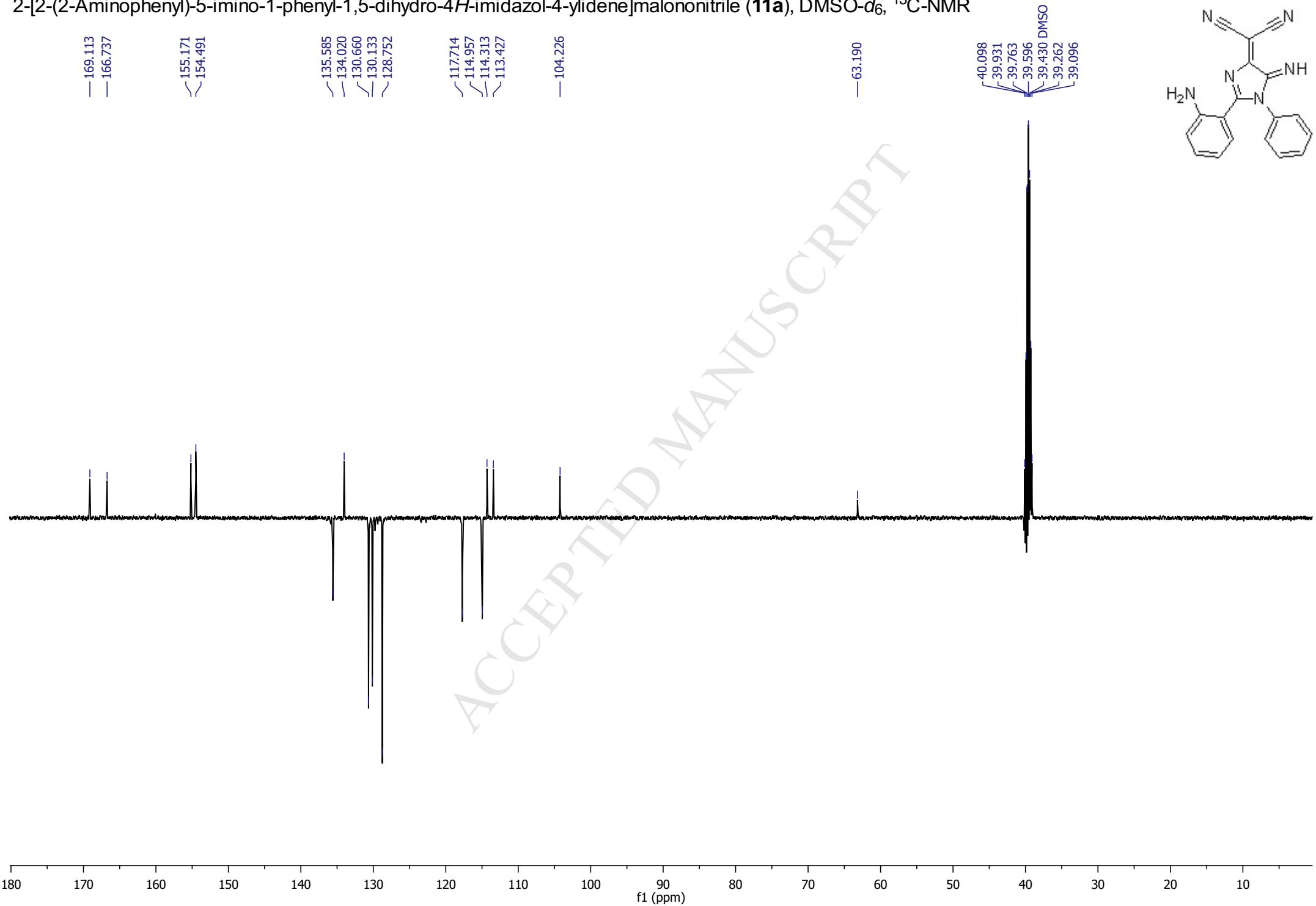




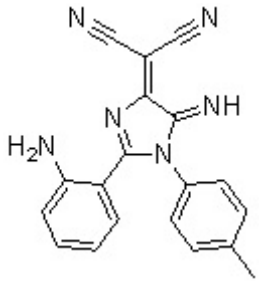
2-[2-(2-Aminophenyl)-5-imino-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylid-ene]malononitrile (**11a**), DMSO-d_6, ^{1}H-NMR



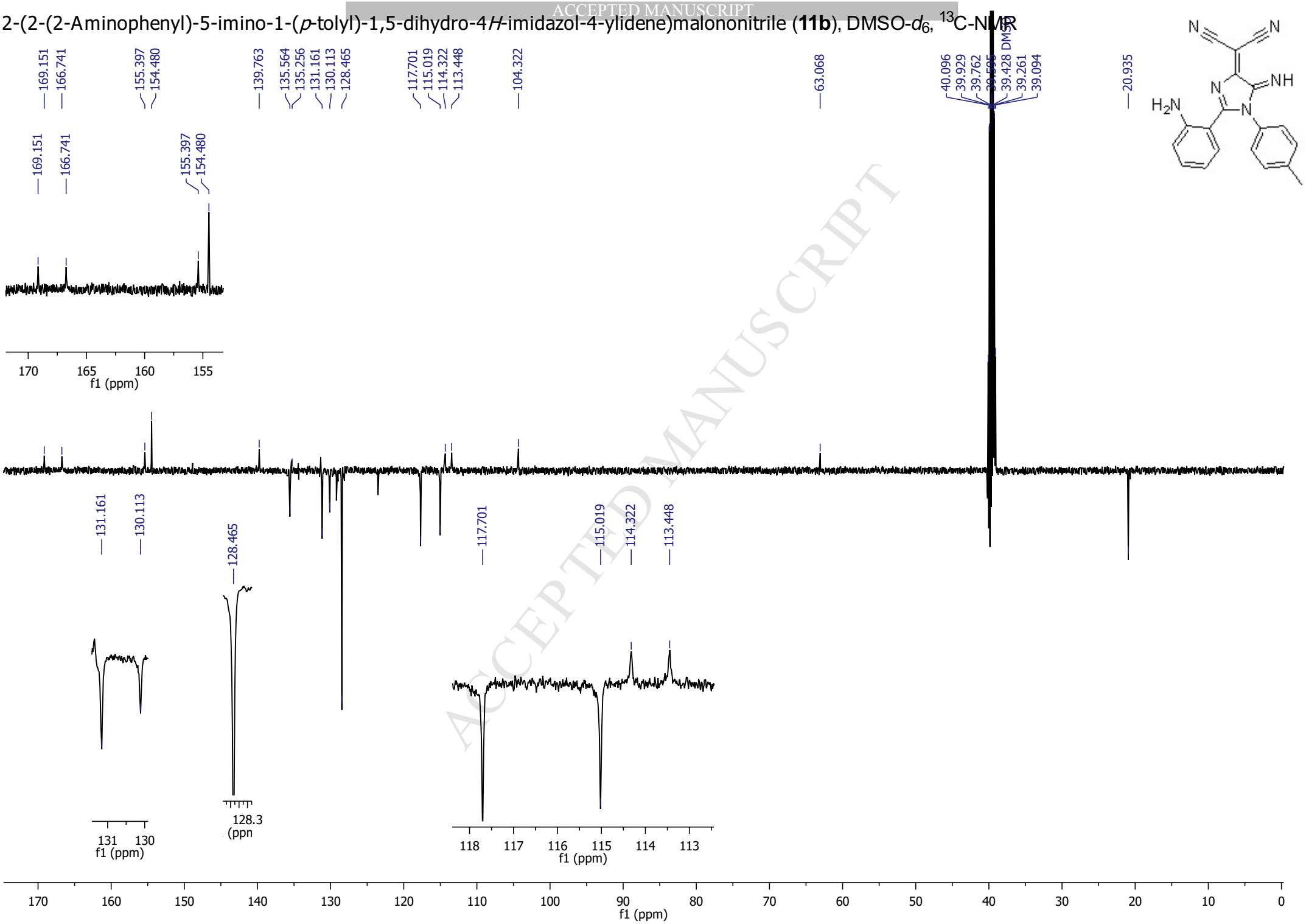
2-[2-(2-Aminophenyl)-5-imino-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11a**), DMSO-d_6, ^{13}C-NMR



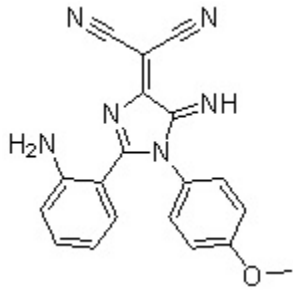
2-(2-(2-Aminophenyl)-5-imino-1-(p-tolyl)-1,5-dihydro-4*H*-imidazol-4-ylidene)malononitrile (**11b**), DMSO-d_6, ^{1}H-NMR



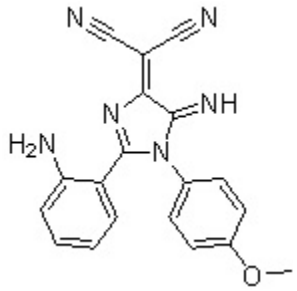
2-(2-(2-Aminophenyl)-5-imino-1-(*p*-tolyl)-1,5-dihydro-4*H*-imidazol-4-ylidene)malononitrile (**11b**), DMSO-d_6, ^{13}C-NMR



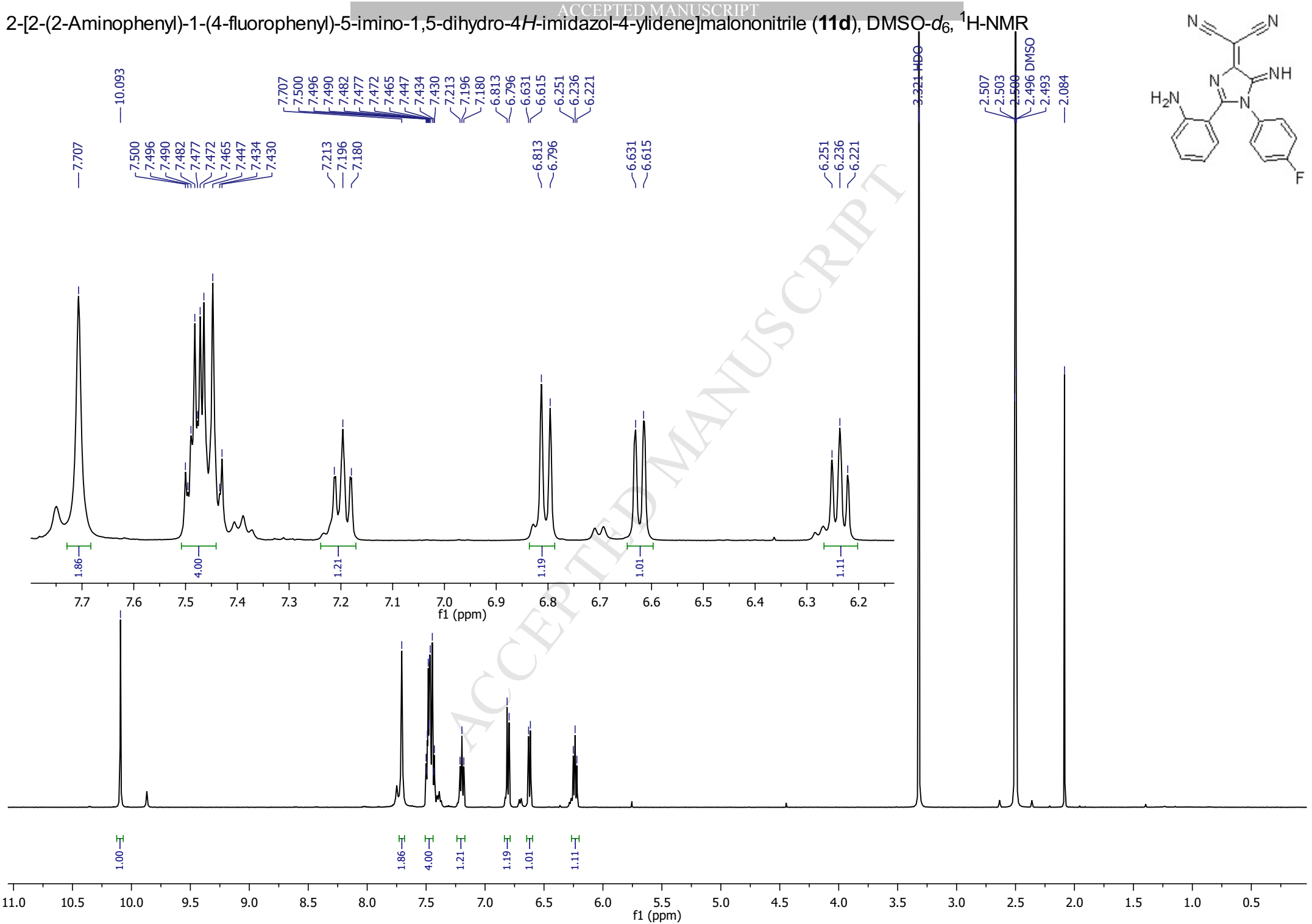
2-[2-(2-Aminophenyl)-5-imino-1-(4-methoxyphenyl)-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11c**), DMSO-d_6, ^{1}H-NMR



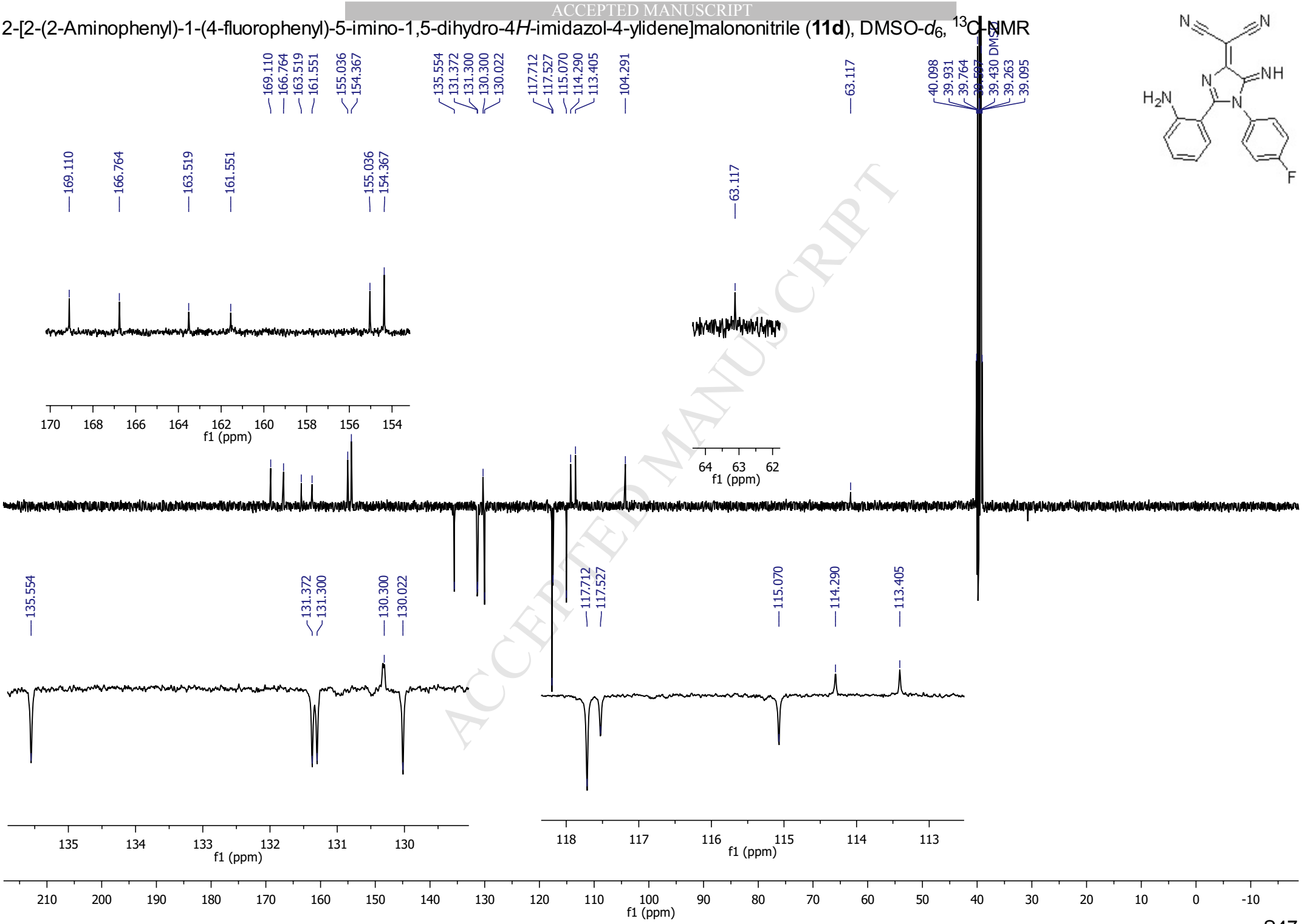
2-[2-(2-Aminophenyl)-5-imino-1-(4-methoxyphenyl)-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11c**), DMSO-d_6, ^{13}C-NMR



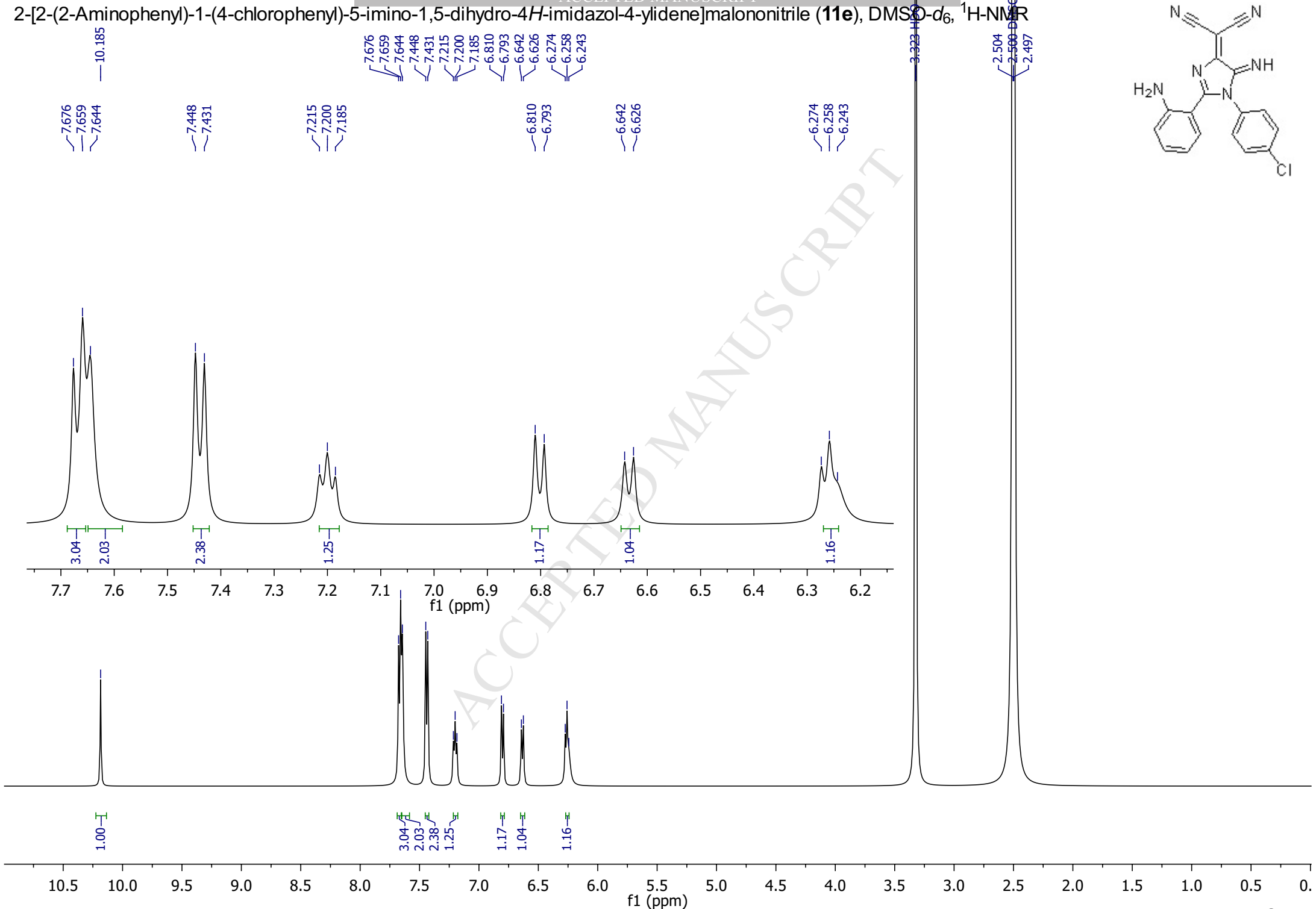
2-[2-(2-Aminophenyl)-1-(4-fluorophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11d**), DMSO-d_6, ^{1}H-NMR



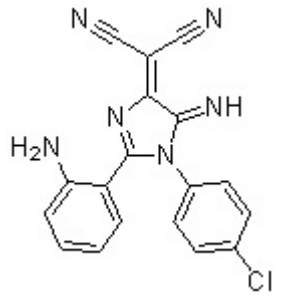
2-[2-(2-Aminophenyl)-1-(4-fluorophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11d**), DMSO-d_6, ^{13}C-NMR



2-[2-(2-Aminophenyl)-1-(4-chlorophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11e**), DMSO-d_6, ^{1}H-NMR



2-[2-(2-Aminophenyl)-1-(4-chlorophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11e**), DMSO-d_6, ^{13}C-NMR

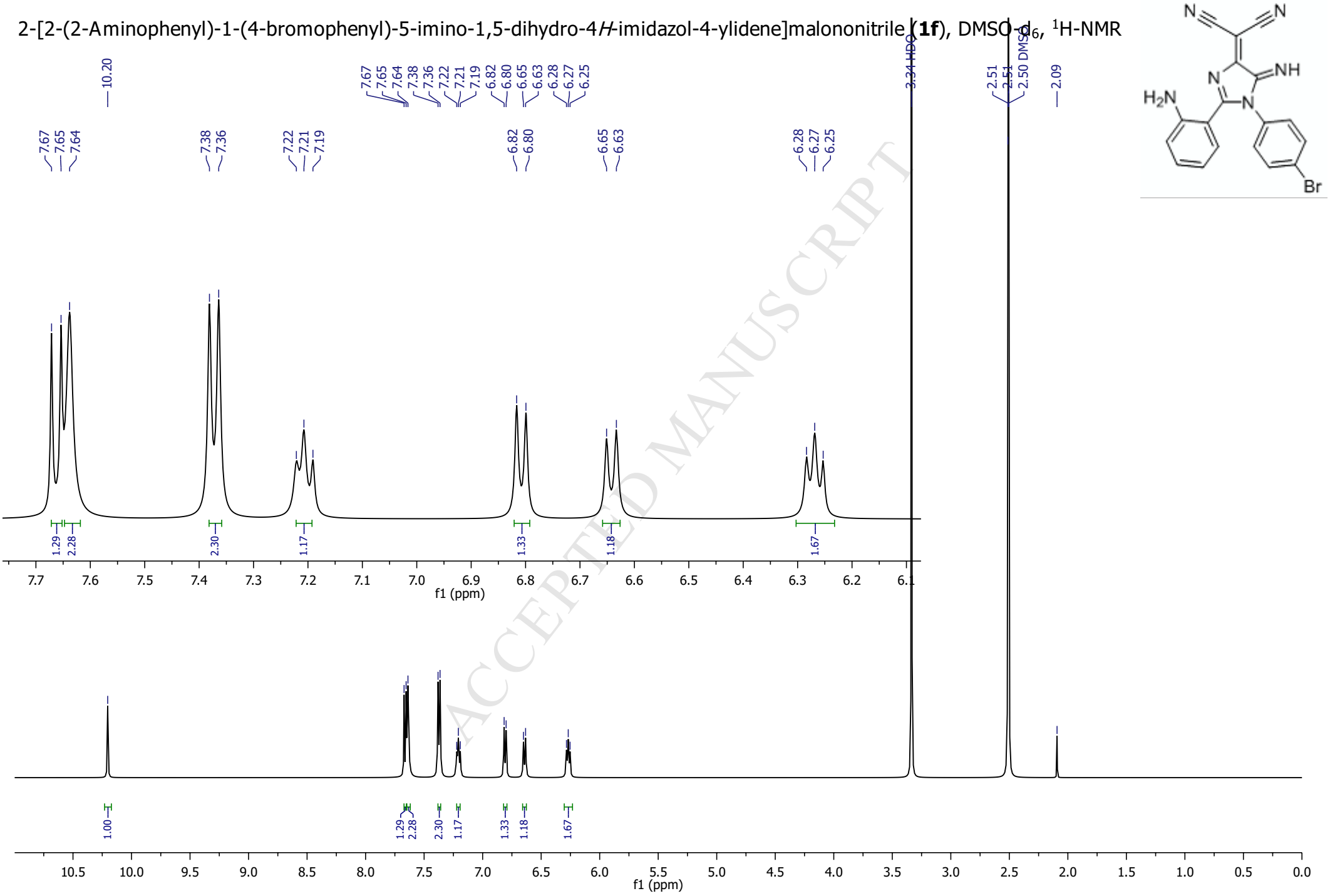


169.125
166.818
154.675
154.175
135.544
134.648
132.982
130.781
130.069
128.706
117.677
115.113
114.267
113.390
104.352
63.278
40.102
39.935
39.768
39.433 DMSO
39.266
39.099

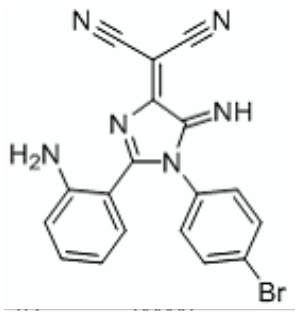
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

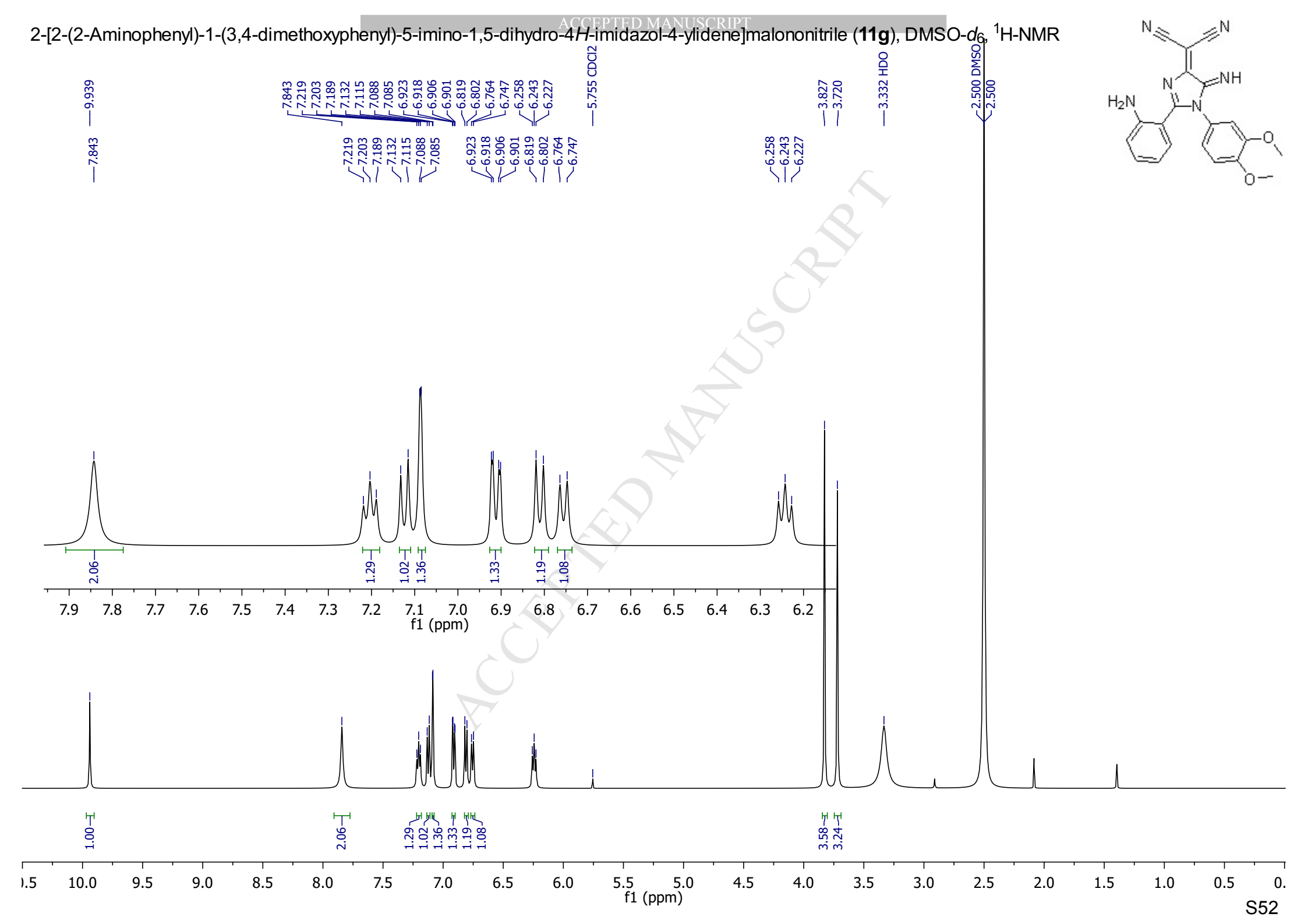
2-[2-(2-Aminophenyl)-1-(4-bromophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**1f**), DMSO-d_6, ^{1}H-NMR



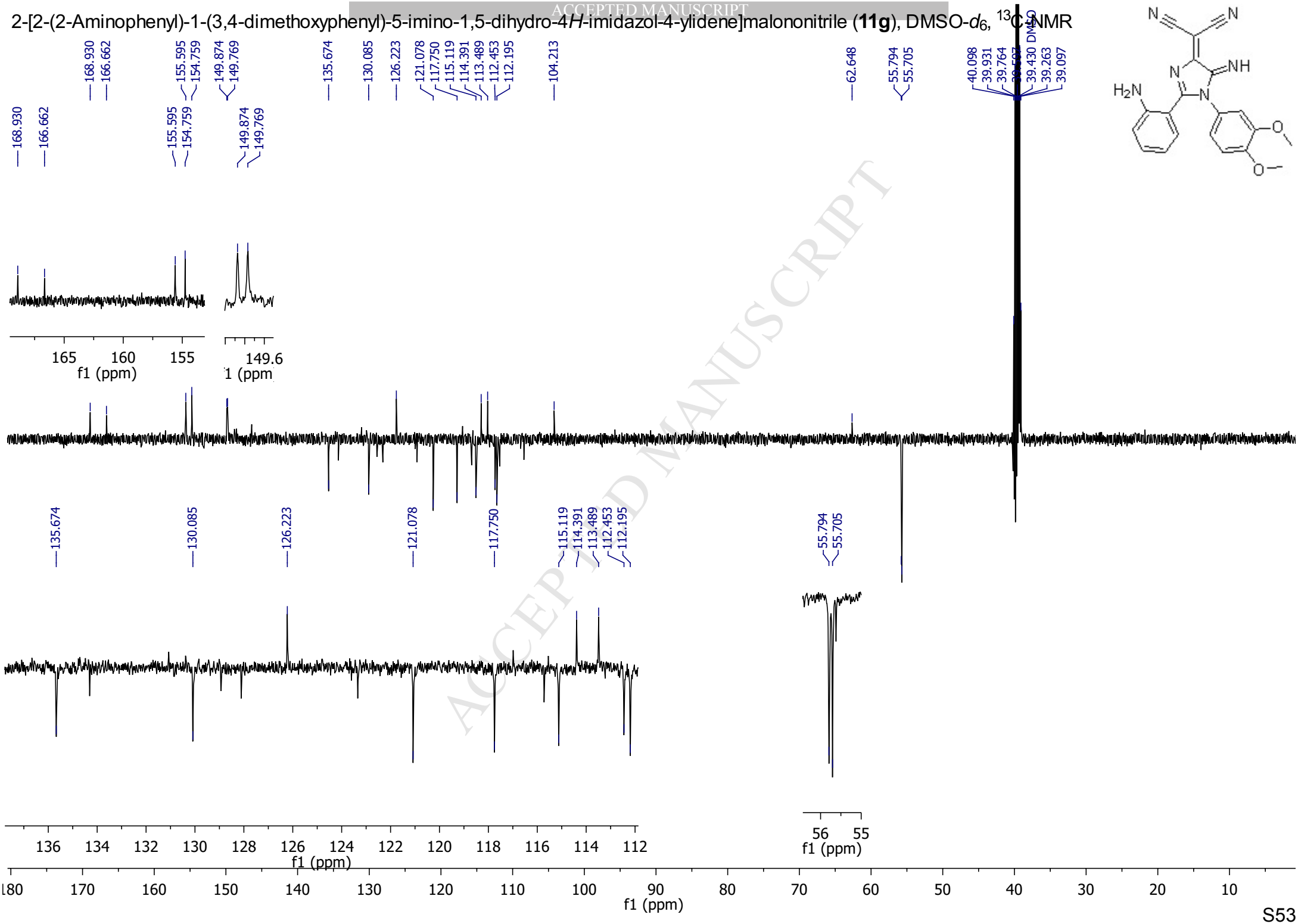
2-[2-(2-Aminophenyl)-1-(4-bromophenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**1f**), DMSO-d_6, ^{13}C-NMR



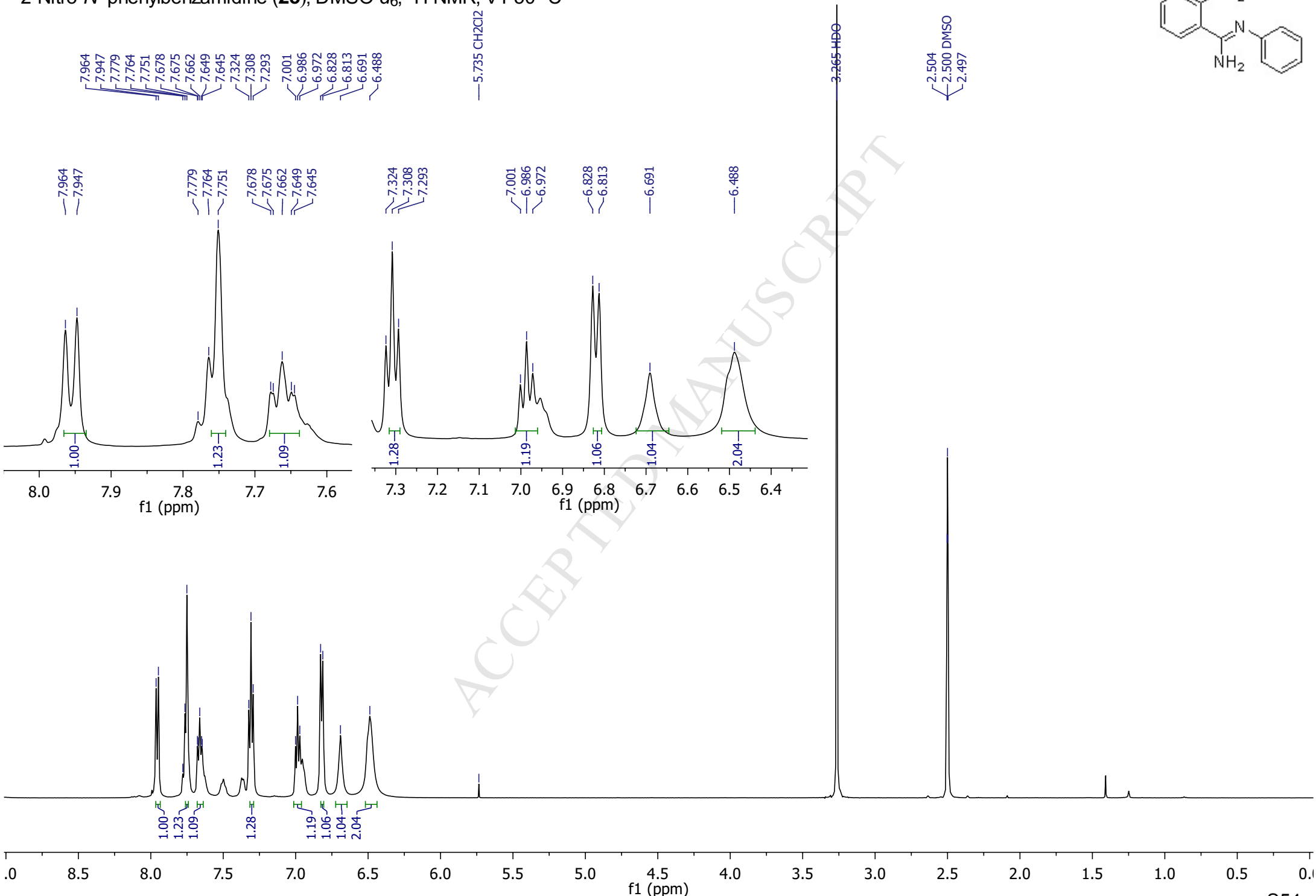
2-[2-(2-Aminophenyl)-1-(3,4-dimethoxyphenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11g**), DMSO-d_6, ^{1}H-NMR



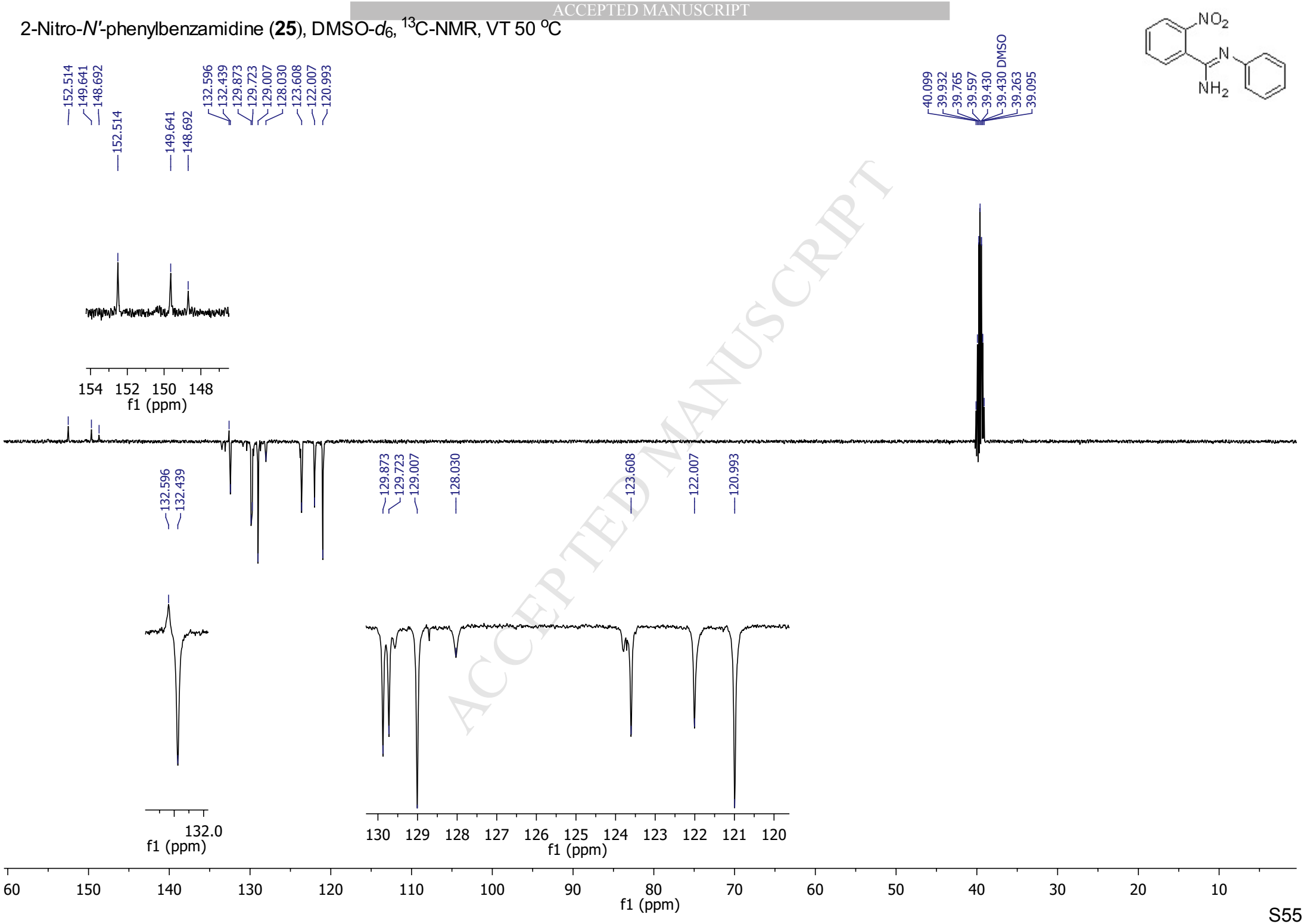
2-[2-(2-Aminophenyl)-1-(3,4-dimethoxyphenyl)-5-imino-1,5-dihydro-4*H*-imidazol-4-ylidene]malononitrile (**11g**), DMSO-d_6, ^{13}C NMR



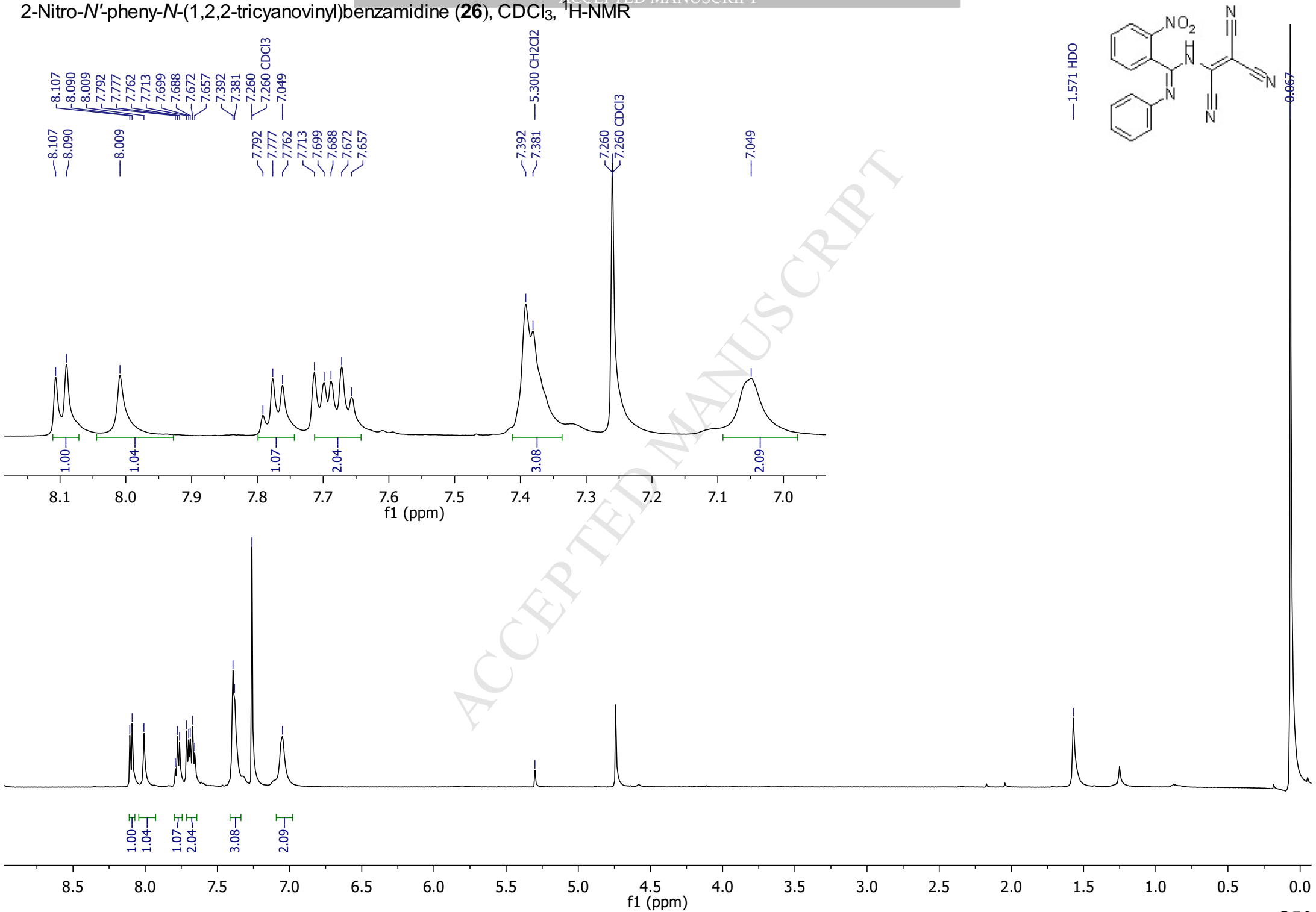
2-Nitro-*N*′-phenylbenzamidine (**25**), DMSO-d_6, ^{1}H-NMR, VT 50 °C



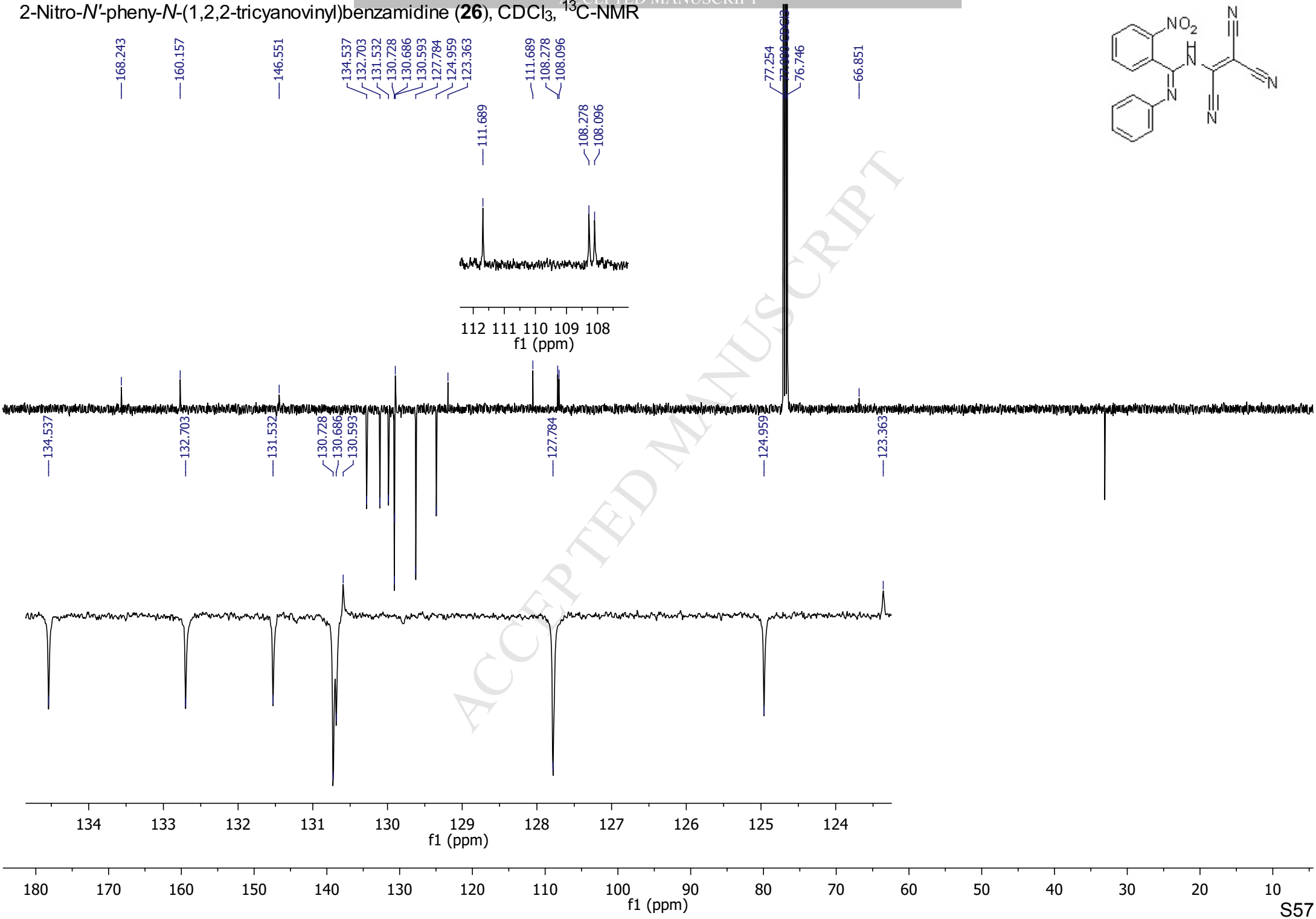
2-Nitro-*N*′-phenylbenzamidine (**25**), DMSO-d_6, ^{13}C-NMR, VT 50 °C



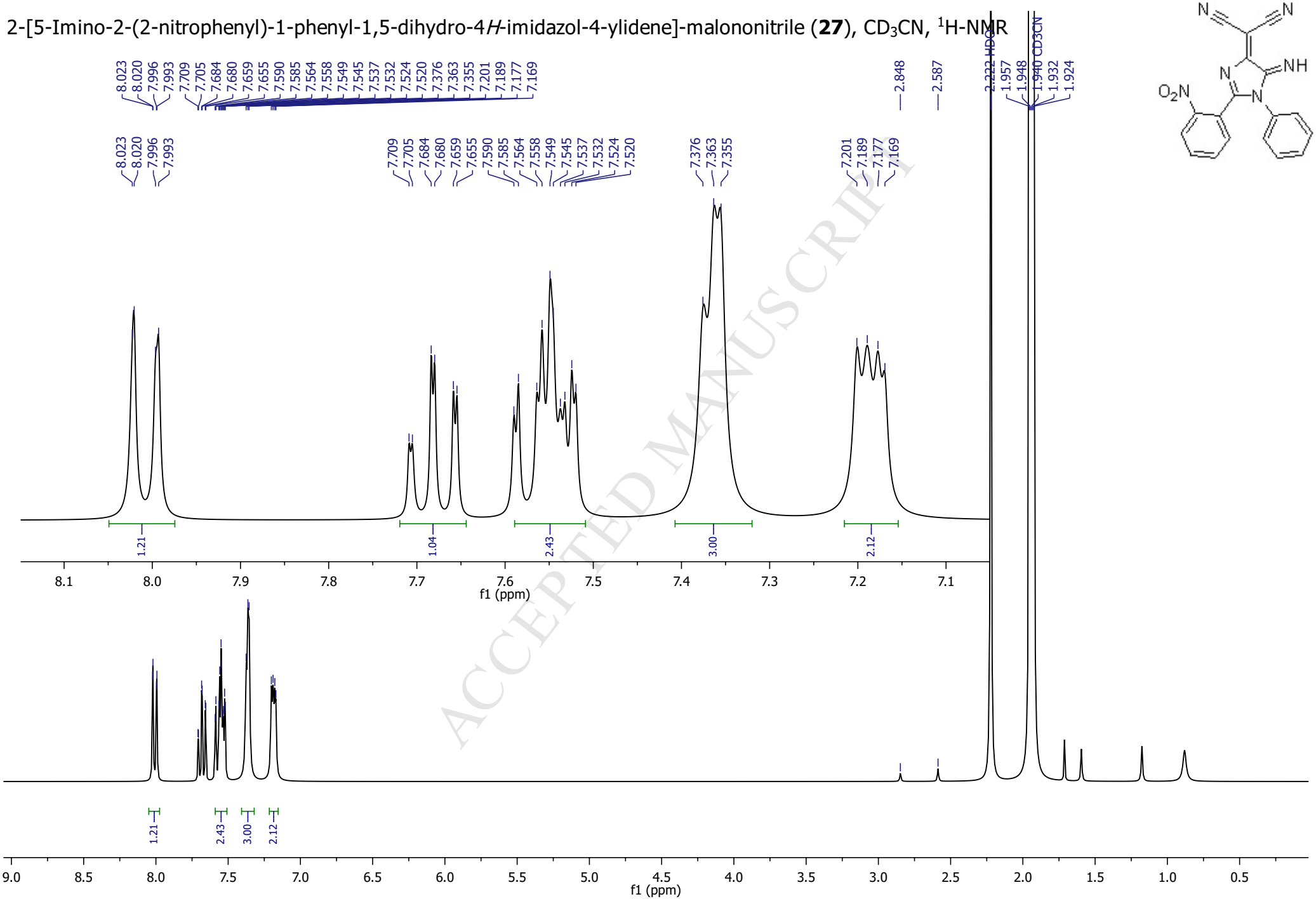
2-Nitro-*N'*-pheny-*N*-(1,2,2-tricyanovinyl)benzamidine (**26**), $CDCl_3$, ^{1}H-NMR



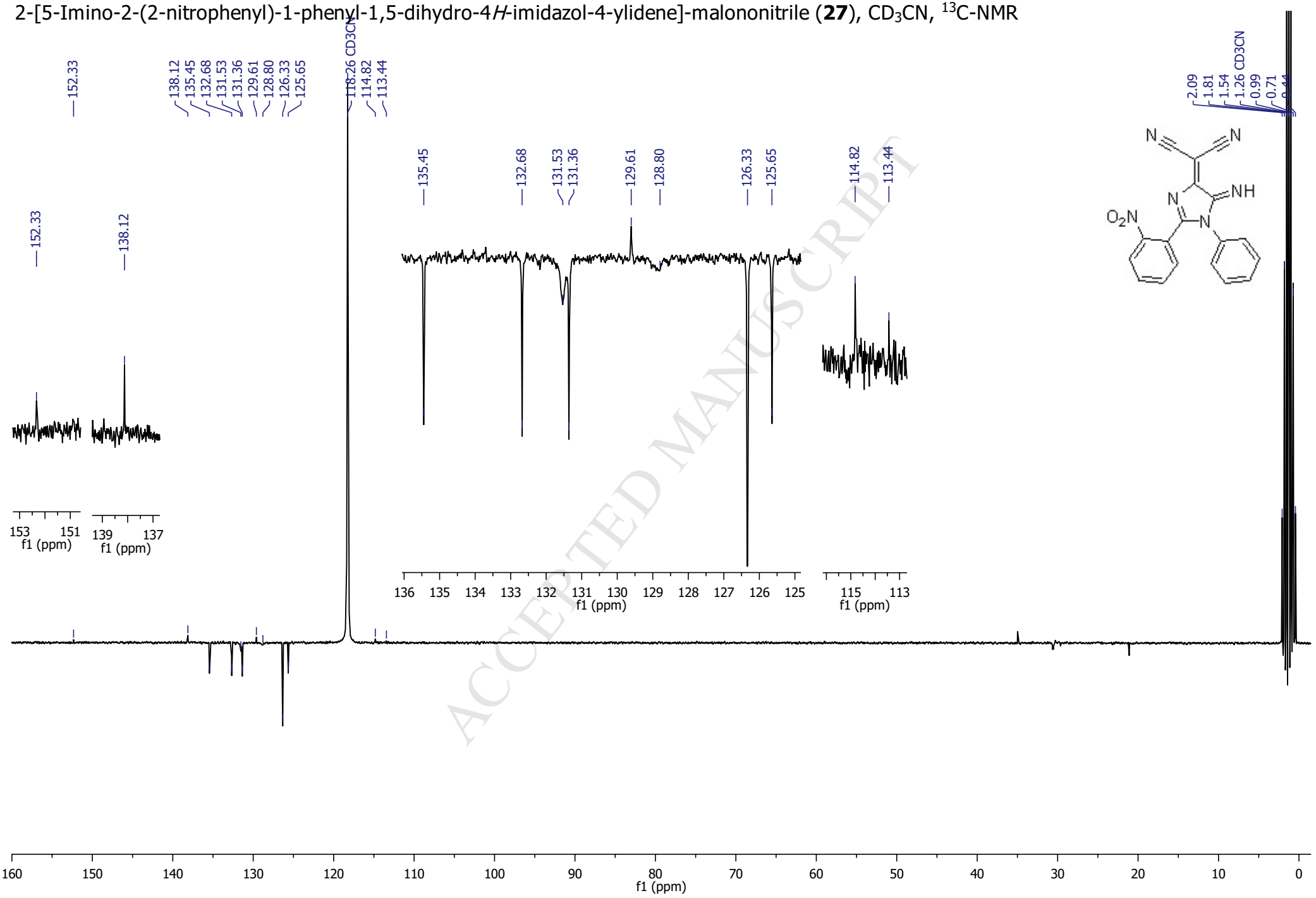
2-Nitro-*N'*-pheny-*N*-(1,2,2-tricyanovinyl)benzamidine (**26**), $CDCl_3$, ^{13}C-NMR



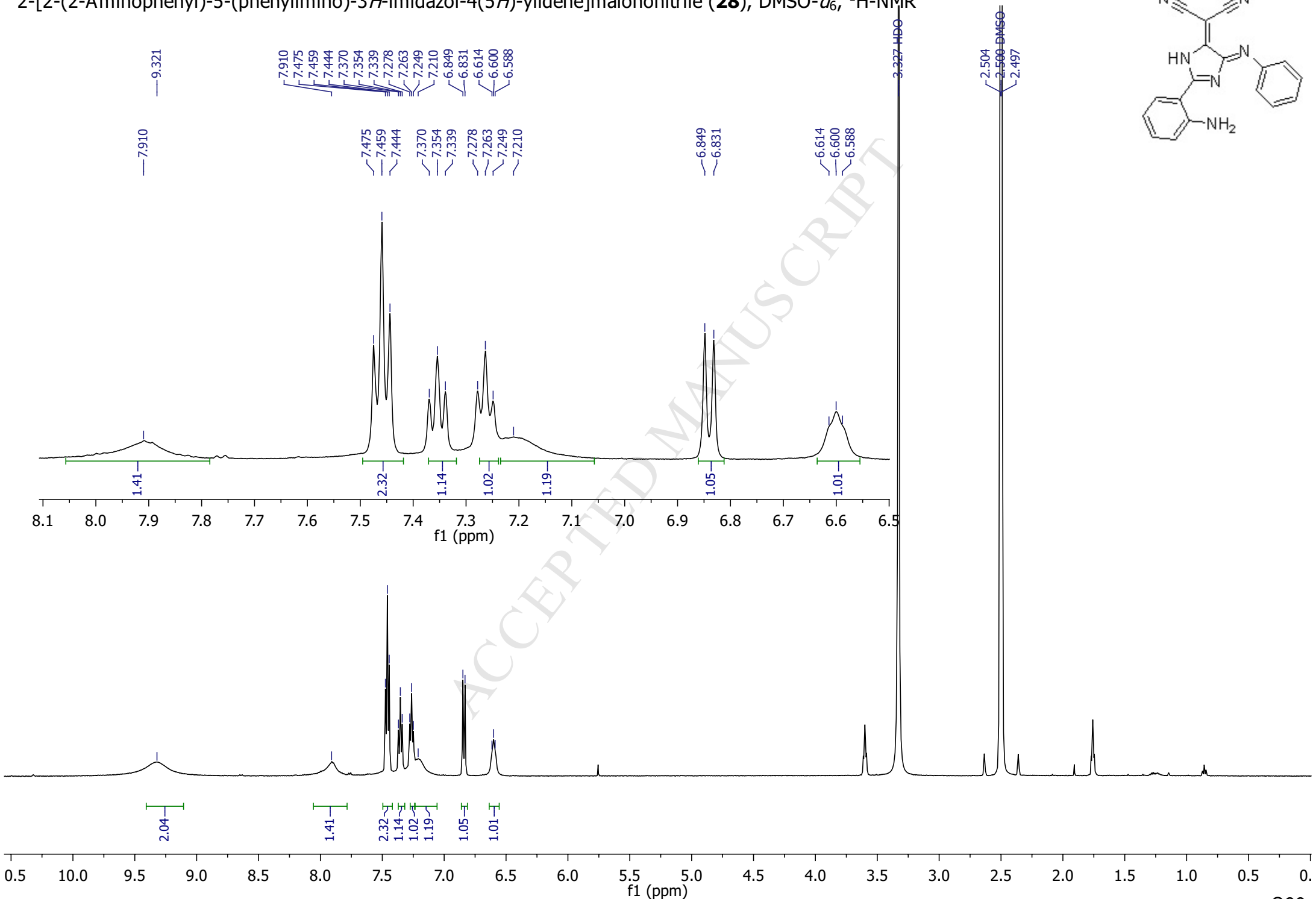
2-[5-Imino-2-(2-nitrophenyl)-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]-malononitrile (**27**), CD_3CN, ^{1}H-NMR



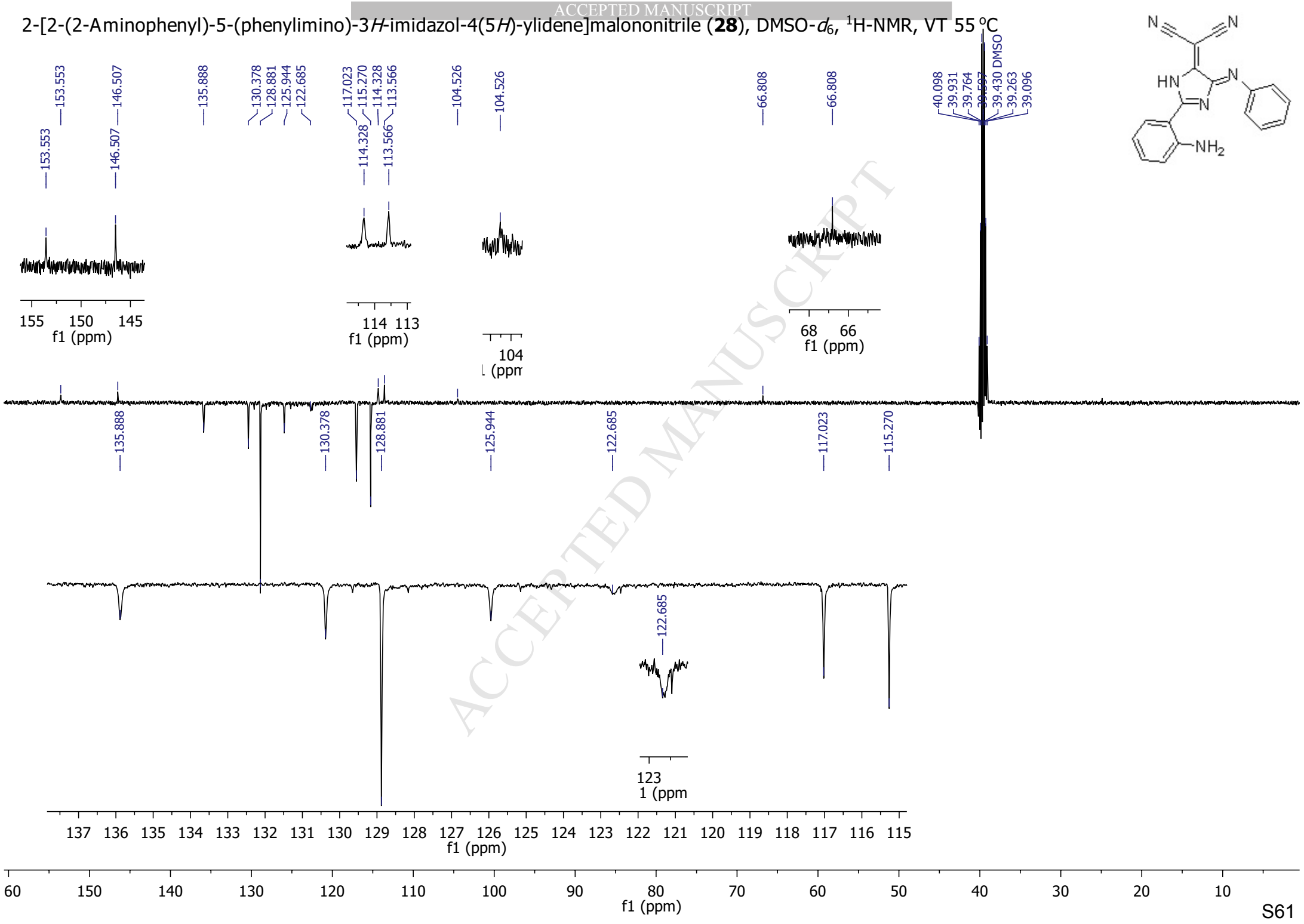
2-[5-Imino-2-(2-nitrophenyl)-1-phenyl-1,5-dihydro-4*H*-imidazol-4-ylidene]-malononitrile (**27**), CD_3CN, ^{13}C-NMR



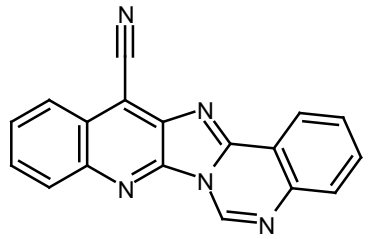
2-[2-(2-Aminophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**28**), DMSO-d_6, ^{1}H-NMR



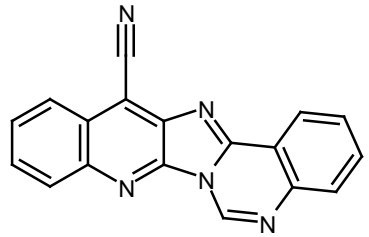
2-[2-(2-Aminophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**28**), DMSO-d_6, ^{1}H-NMR, VT 55 °C



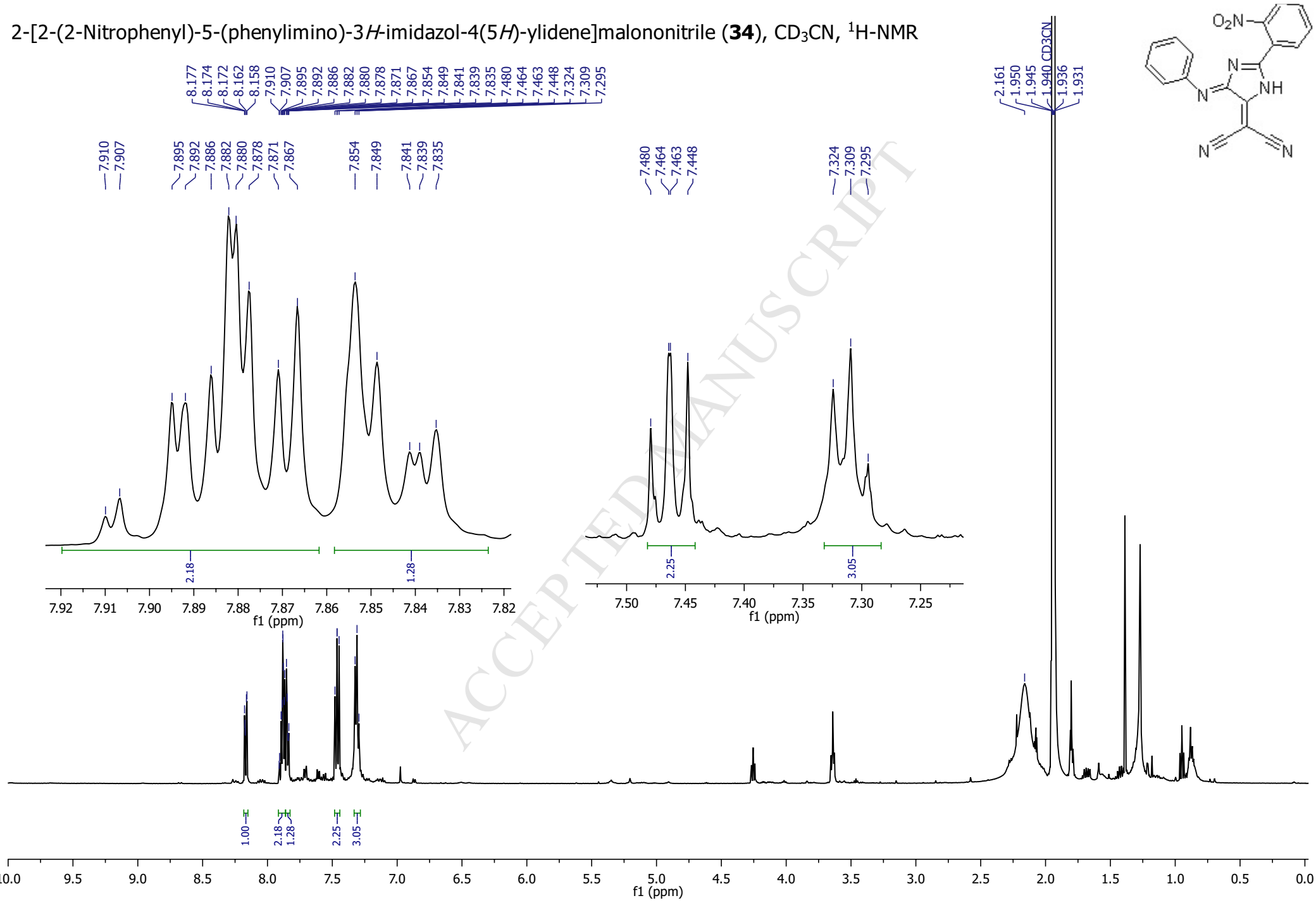
Quinolino[3',2':4,5]imidazo[1,2-c]quinazoline-13-carbonitrile (**30**), $CDCl_3$, ^{1}H-NMR



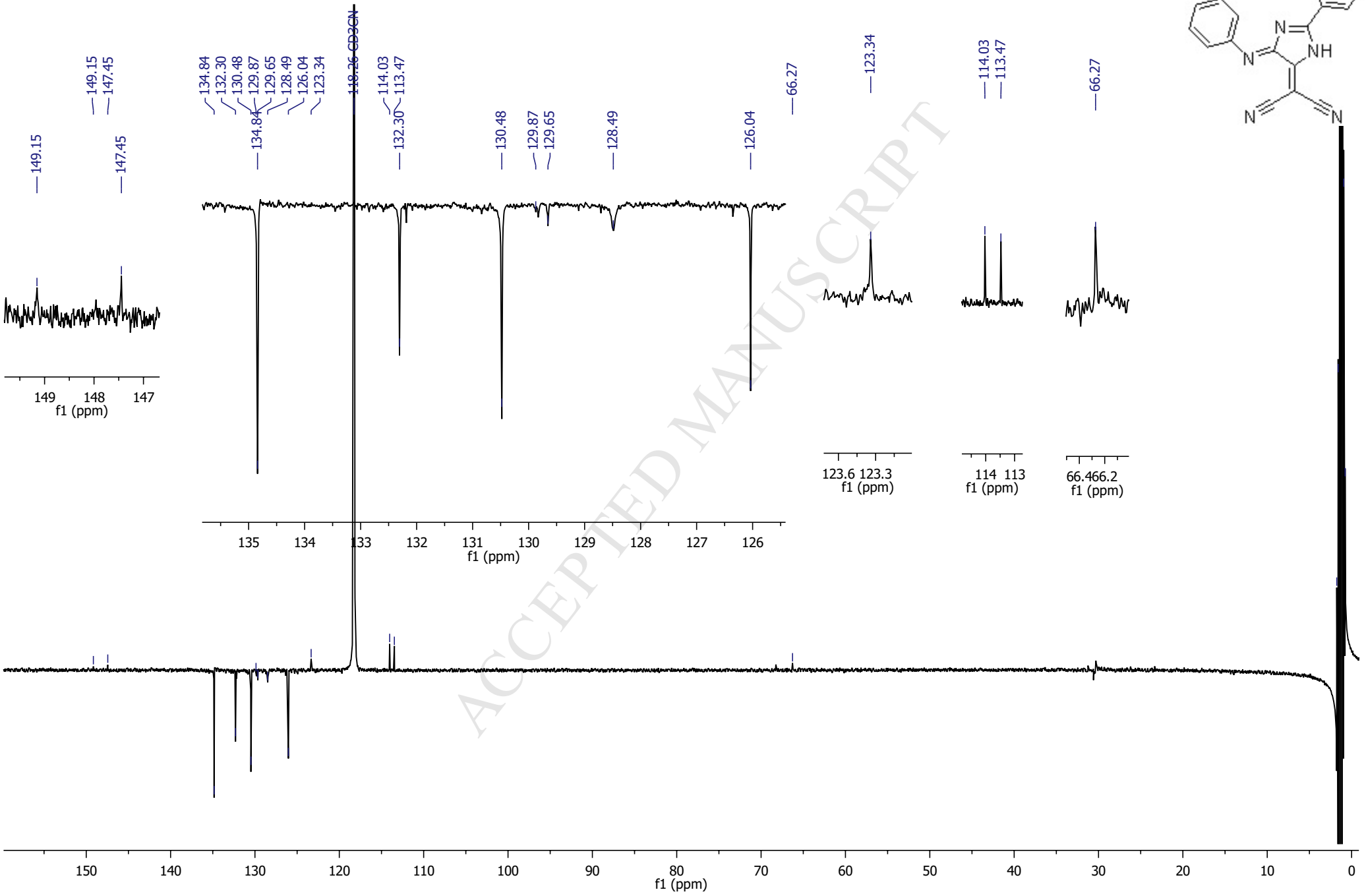
Quinolino[3',2':4,5]imidazo[1,2-*c*]quinazoline-13-carbonitrile (**30**), $CDCl_3$, ^{13}C-NMR



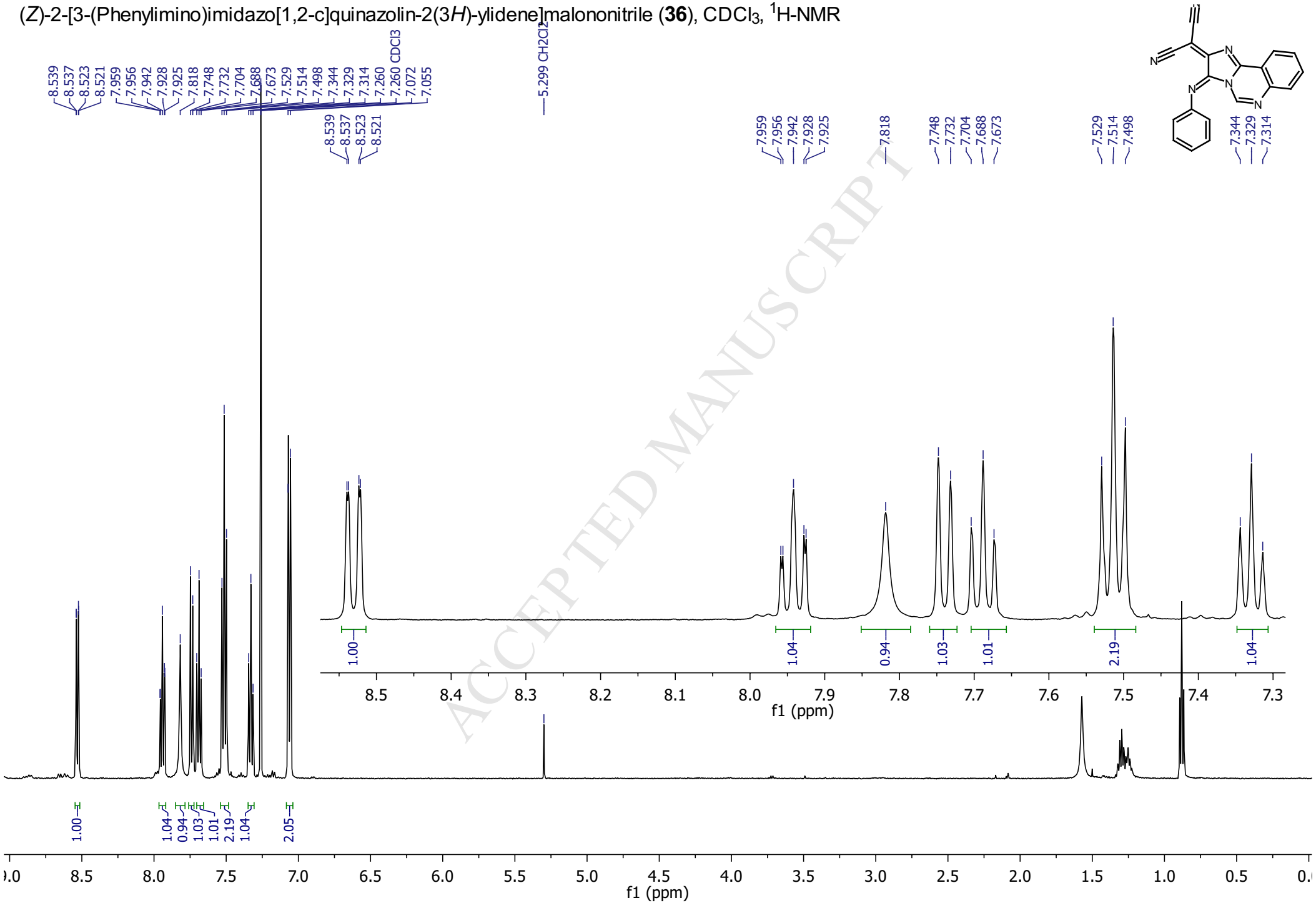
2-[2-(2-Nitrophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**34**), CD_3CN, ^{1}H-NMR



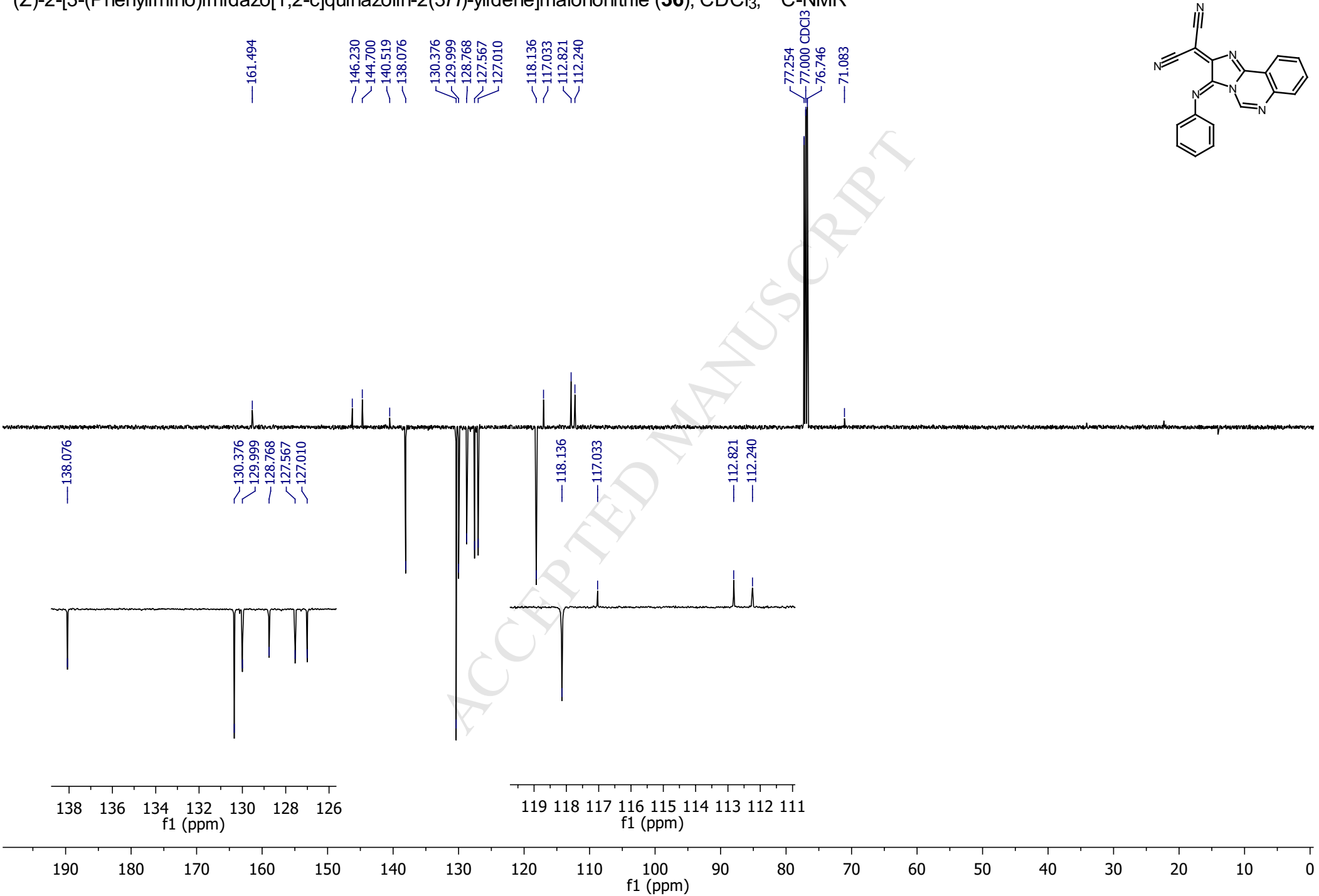
2-[2-(2-Nitrophenyl)-5-(phenylimino)-3*H*-imidazol-4(5*H*)-ylidene]malononitrile (**34**), CD_3CN, ^{13}C-NMR



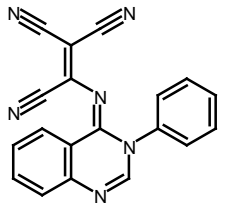
(*Z*)-2-[3-(Phenylimino)imidazo[1,2-c]quinazolin-2(3*H*)-ylidene]malononitrile (**36**), $CDCl_3$, ^{1}H-NMR



(*Z*)-2-[3-(Phenylimino)imidazo[1,2-c]quinazolin-2(3*H*)-ylidene]malononitrile (**36**), $CDCl_3$, ^{13}C-NMR



(*E*)-2-[(3-Phenylquinazolin-4(3*H*)-ylidene)amino]ethene-1,1,2-tricarbonitrile (**37**), $CDCl_3$, ^{1}H-NMR



(*E*)-2-[(3-Phenylquinazolin-4(3*H*)-ylidene)amino]ethene-1,1,2-tricarbonitrile (**37**), $CDCl_3$, ^{13}C-NMR