Supporting Information

Influence of steric hindrance on 1,4- versus 1,6-Michael addition: Synthesis of furans and pentasubsituted benzenes

Shally Rana,[a,c] Ranjay Shaw[b], and Ramendra Pratap*[a]

[a] Dr. S. Rana and Dr. R. Pratap
Department of Chemistry, University of Delhi, North Campus, Delhi, India, Pin-110007
[b] Dr. Ranjay Shaw
Department of Chemistry, GLA University, Mathura, India, 281406
[c] Dr. S. Rana
Department of Chemistry, School of Science Indrashil University, Rajpur, Kadi, Ahmedabad-Mehsana Highway Gujarat, 382740.

Table of Contents:

SN	Content	Page no
1	X-ray crystallography data of 4d and 5b	S2-S4
2	^{1}H NMR and ^{13}C NMR Spectra of 4a-4k	S5-S15
3	^{1}H NMR and ^{13}C NMR Spectra of 5a-5c	S16-S18
4	^{1}H NMR and ^{13}C NMR Spectra of 7a-7k	S19-S29
5	^{1}H NMR and ^{13}C NMR Spectra of 9a-9j	S30-S39
6	^{1}H NMR and ^{13}C NMR Spectra of 11 and 12a-12e	S40-S45

Crystal data for (4d) and (5b): To a 5 ml glass vial 25-30 mg of 2-(bis(methylthio)methyl)-3-(3,4-dimethoxyphenyl)-5-methylfuran **(4d)** or 4-acetyl-3-amino-2'-chloro-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile **(5b)** was completely dissolved in DCM followed by addition of 1-2 drops of hexanes. Further, solution was kept for slow evaporation at room temperature until yellow rod shaped type suitable crystal obtained for X-ray analysis.

A white crystal was mounted on a capillary tube for indexing and intensity data collection at 302 and 293 K respectively on an Oxford Xcalibur Sapphire3 CCD single-crystal diffractometer (MoKα radiation, λ = 0.71073 Å).[1] Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the ABSCALE 3 program [CrysAlis Pro software system, Version 171.34; Oxford Diffraction Ltd., Oxford, U.K., 2011]. Data reduction was performed with the CrysAllis-PRO.[1] The structure was solved by direct methods using SIR-92 program[2] and refined on F2 using all data by full matrix least-squares procedures with SHELXL-2016/6 incorporated in WINGX 1.8.05 crystallographic collective package.[3] The hydrogen atoms were placed at the calculated positions and included in the last cycles of the refinement. All calculations were done using the WinGX software package.[4-5] Crystallographic data collection and structure solution parameters are summarized in **Table S1**. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

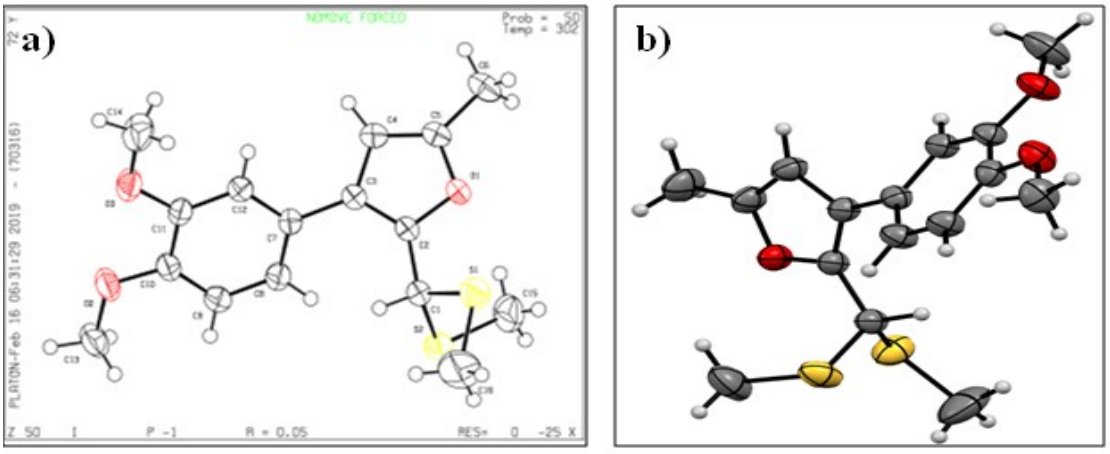


Figure S1. ORTEP diagram of **4d**; thermal ellipsoids are drown at the 50% probability level

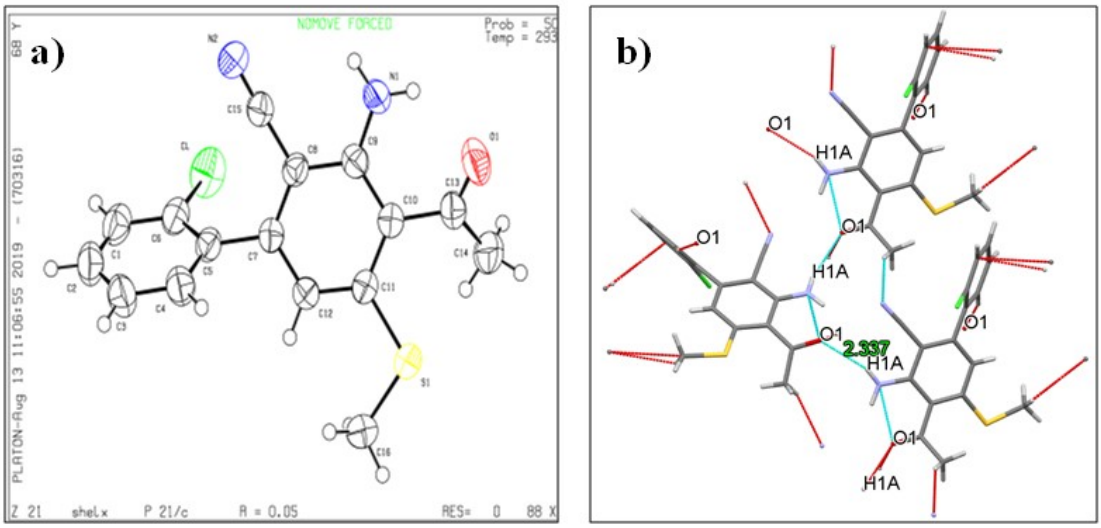


Figure S2: (a) ORTEP diagram of **5b**; thermal ellipsoids are drowned at the 50% probability level. (**b**) **5b** showing intermolecular C-H···N≡C interaction.

TableS1: Crystal data and structure refinement for **4d** and **5b**

	4d	**5b**
CCDC No.	**1974747**	**1974746**
Empirical formula	$C_{16}H_{20}O_3S_2$	$C_{16}H_{13}ClN_2OS$
Formula weight	324.44	316.79
Temperature/k	302	293
Crystal system	Triclinic	Monoclinic
Space group	P -1	P21/c
a/Å	7.4509(5)	10.9847(6) Å
b/Å	8.5535(6)	9.3266(4) Å
c/Å	13.4726(9)	15.3230(8) Å
α/°	87.055(2)	90°.
β/°	83.603(2)	107.140(6)°
γ/°	79.582(2)	90°.
Volume/Å^3	838.79(10)	1500.12(14)
Z	2	4
ρ_{calc}g/cm^3	1.285	1.403
μ/mm^{-1}	0.324	0.393
F(000)	344	656
Crystal size/mm^3	0.43 x 0.28 x 0.12	0.22 x 0.20 x 0.18

2Θ range for data collection/°	2.422 to 28.302	3.474 to 25.000°
Index ranges	-9<=h<=9, -11<=k<=11, -17<=l<=17	-13<=h<=13, -11<=k<=11, -18<=l<=18
Reflections collected	11608	18167
Independent reflections	4093 [R(int) = 0.0868]	2626 [R(int) = 0.0420]
Data/restraints/parameters	4093 /0/195	2626 / 0 / 190
Goodness-of-fit on F^2	1.125	1.004
Final R indexes [I>=2σ (I)]	R_1 = 0. 0458, wR_2 = 0. 1361	R1 = 0.0454, wR2 = 0.1035
Final R indexes [all data]	R_1 =0.0514, wR_2 = 0.1407	R1 = 0.0614, wR2 = 0.1109
Largest diff. peak/hole / e $Å^{-3}$	0.251 and -0.284 e.$Å^{-3}$	0.187 and -0.239e.$Å^{-3}$

References

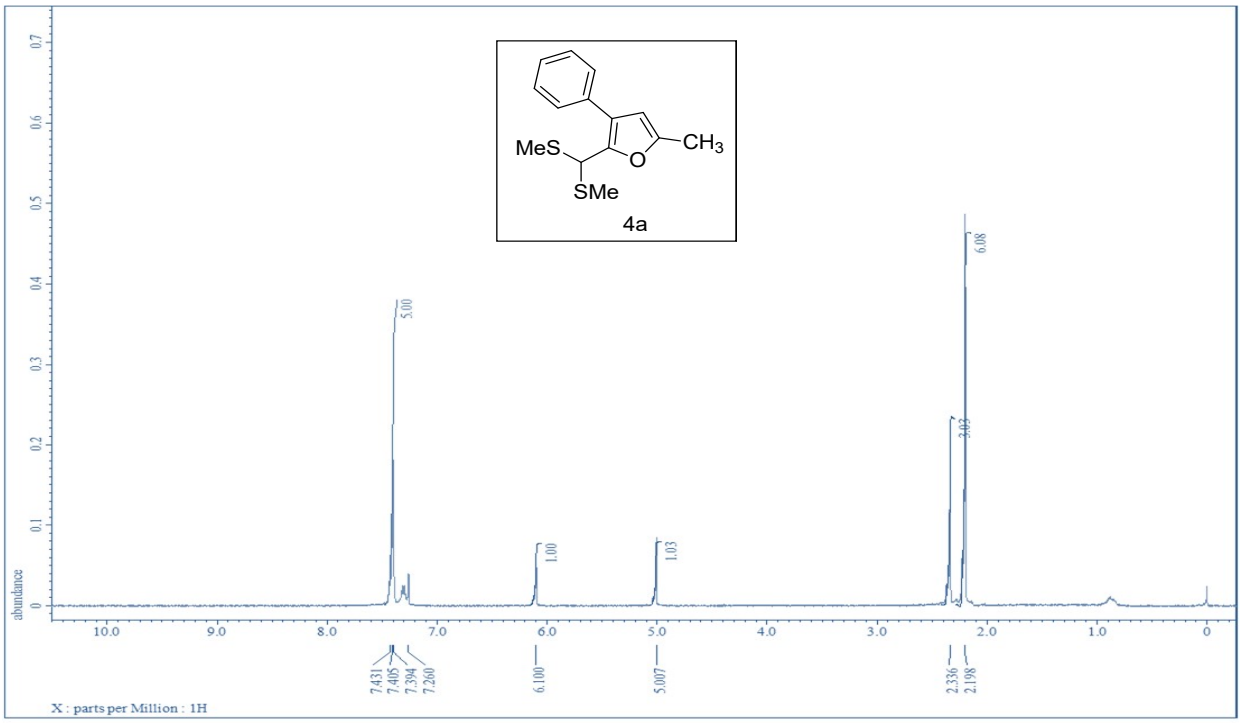
(1) CrysAlisPro, v. 1.171.33.49b, Oxford Diffraction Ltd., **2009**.

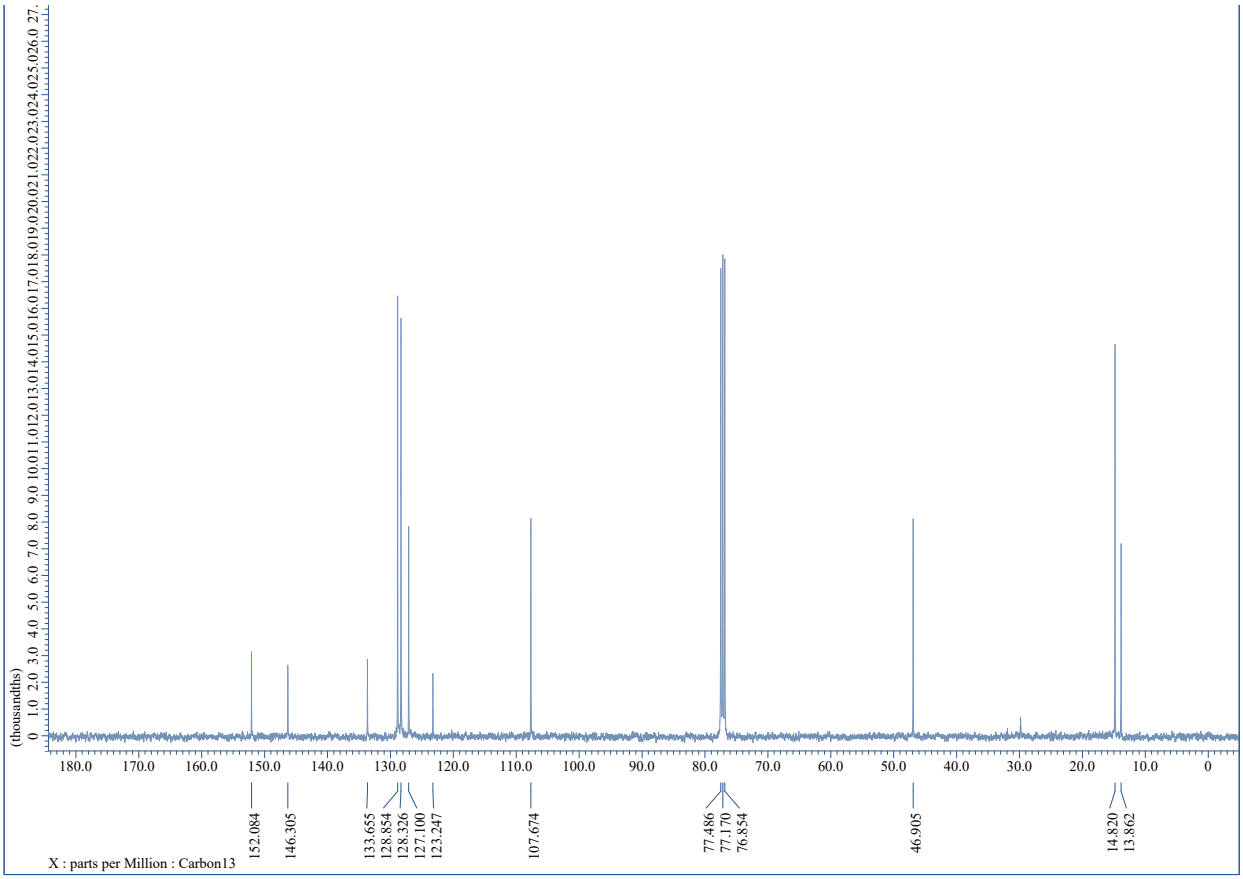
(2) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst*. **1993**, 26, 343.

(3) Sheldrick, G. M. SHELXL-2014/7: Program for the solution of crystal structures, University of Gottingen, Gottingen, Germany, **2014**.

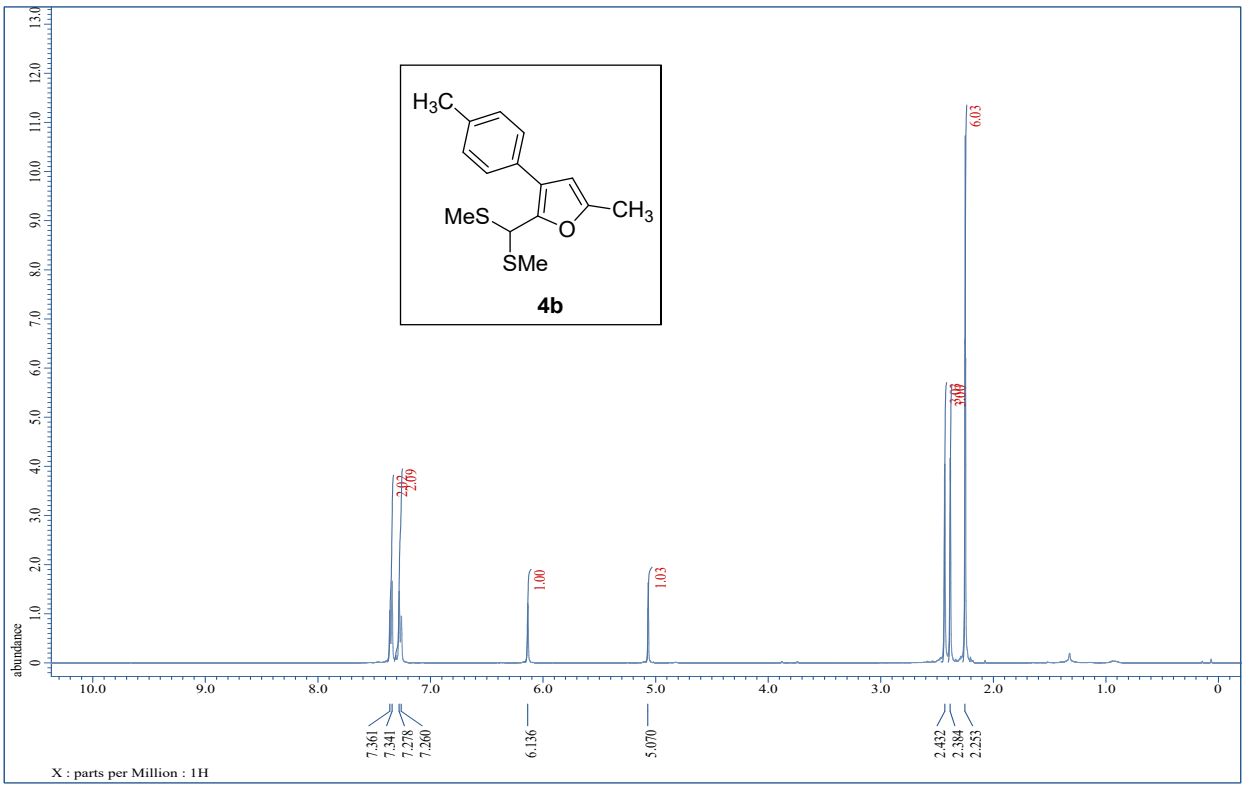
(4) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr., **2008**, 64, 112.

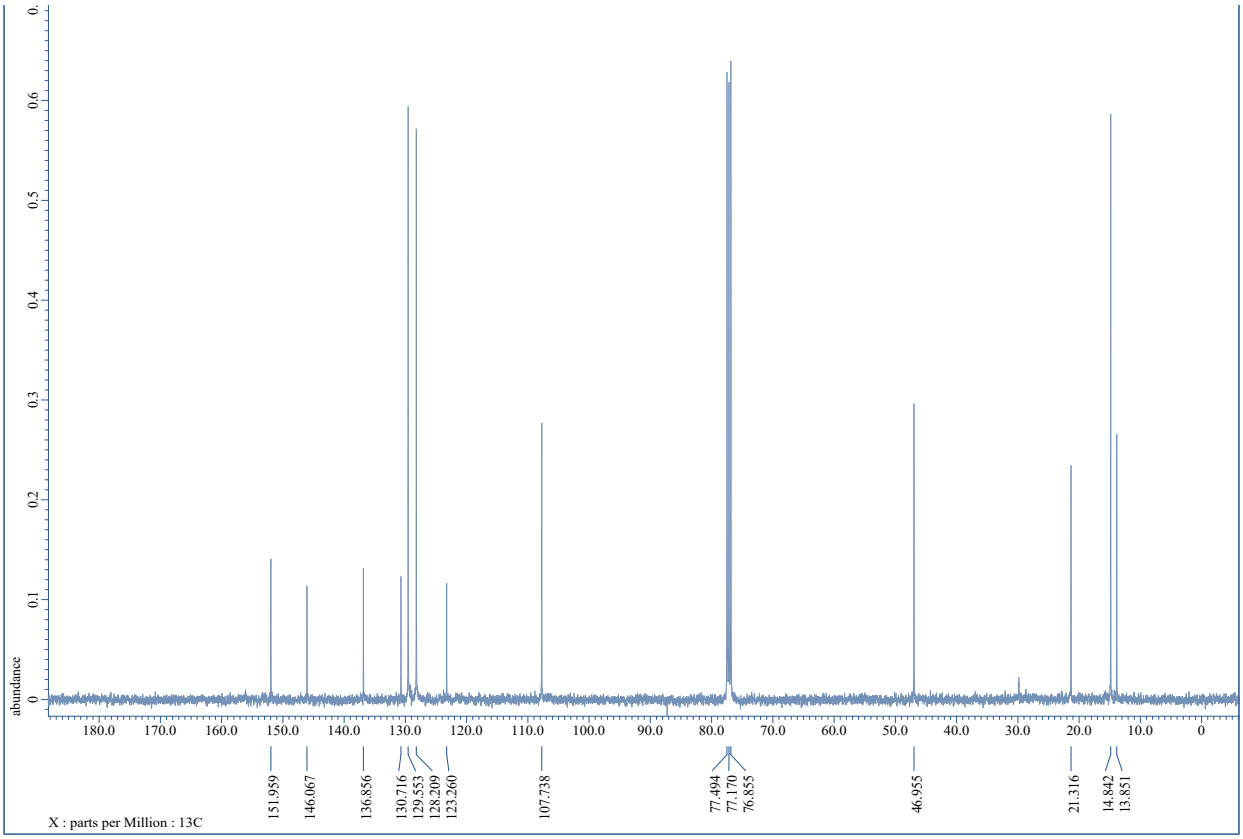
(5) Farrugia, L. J. WinGX, v. 1.70, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-ray Diffraction Data, Department of Chemistry, University of Glasgow, **2003**.



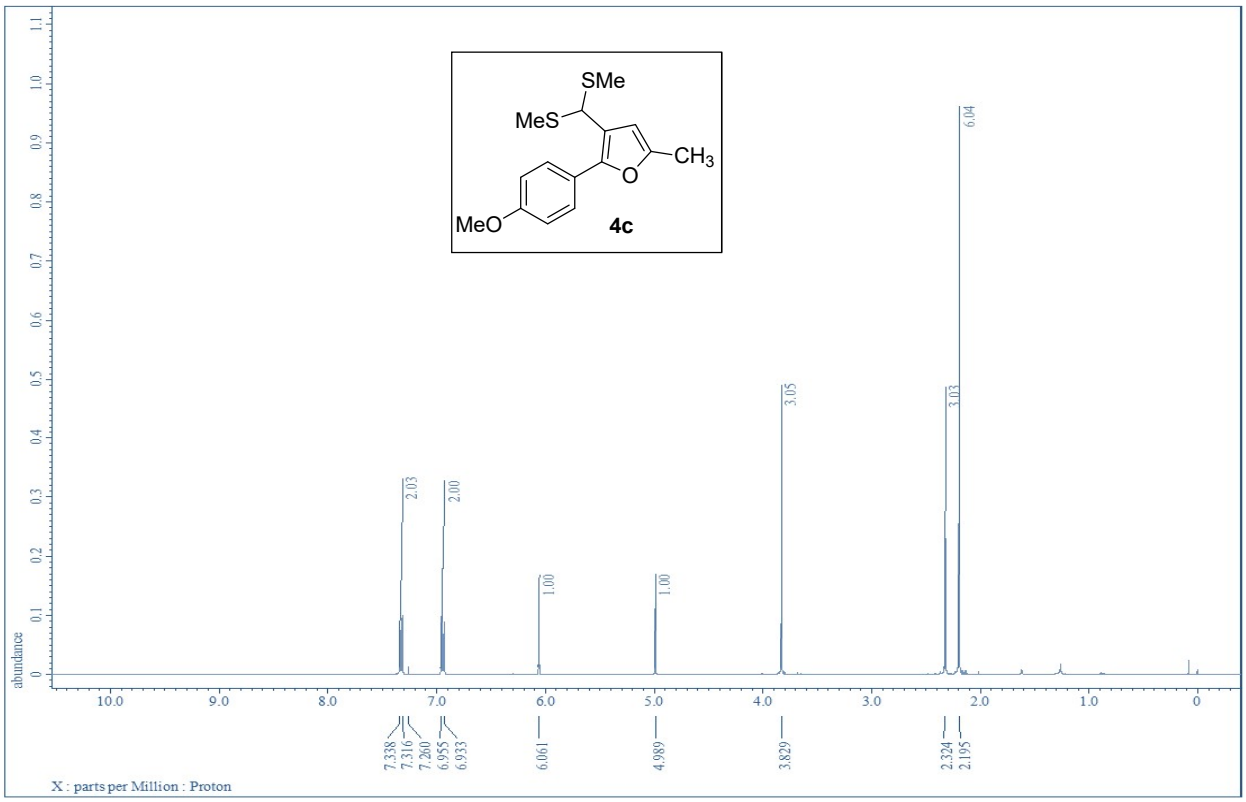


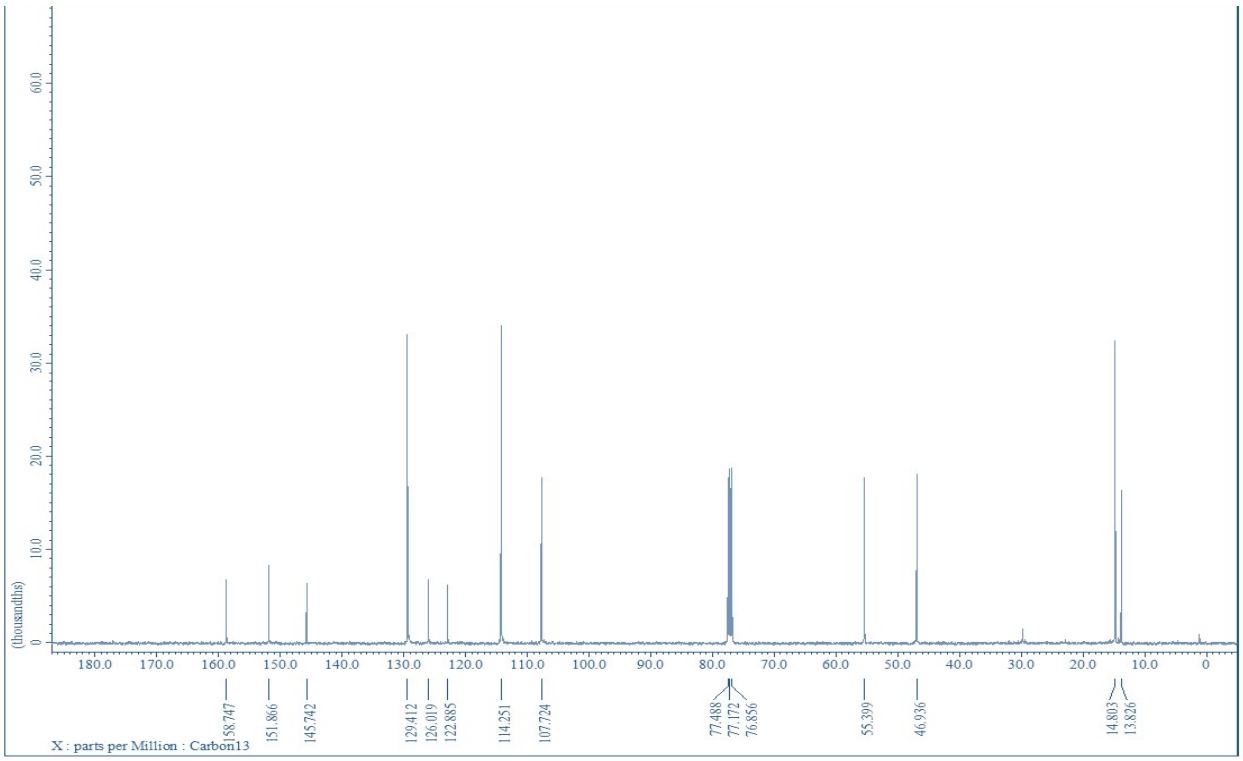
^{1}H NMR and ^{13}C NMR spectra of 2-(bis(methylthio)methyl)-5-methyl-3-phenylfuran (4a)



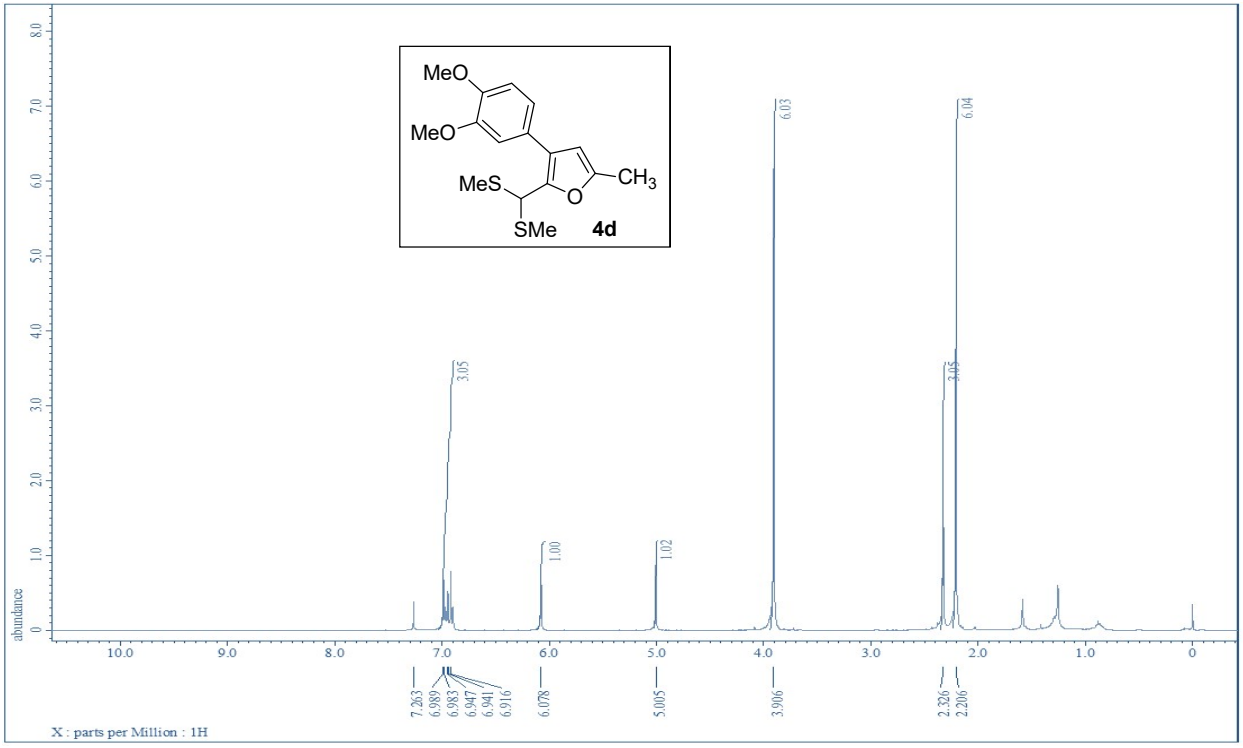


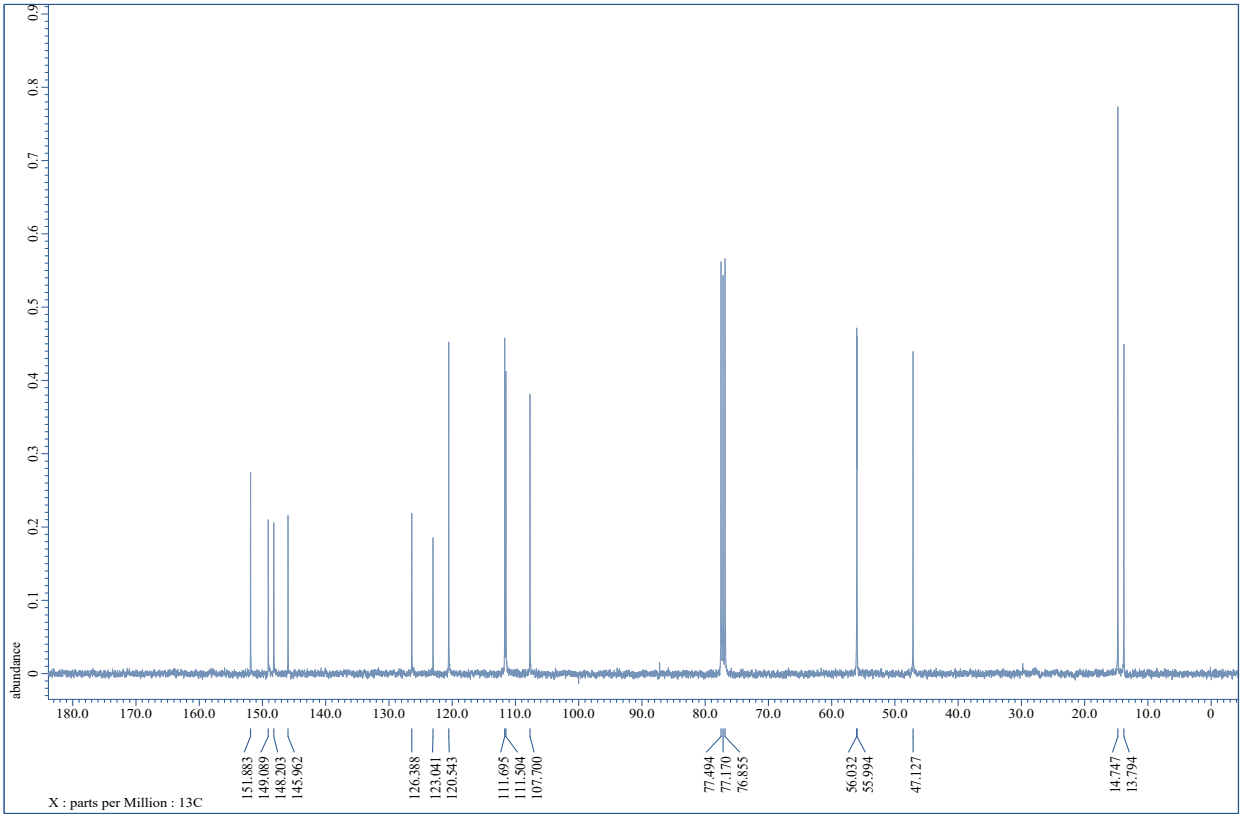
^{1}H NMR and ^{13}C NMR Spectra of 2-(bis(methylthio)mehyl)-5-methyl-3-(*p*-tolyl)furan (4b)



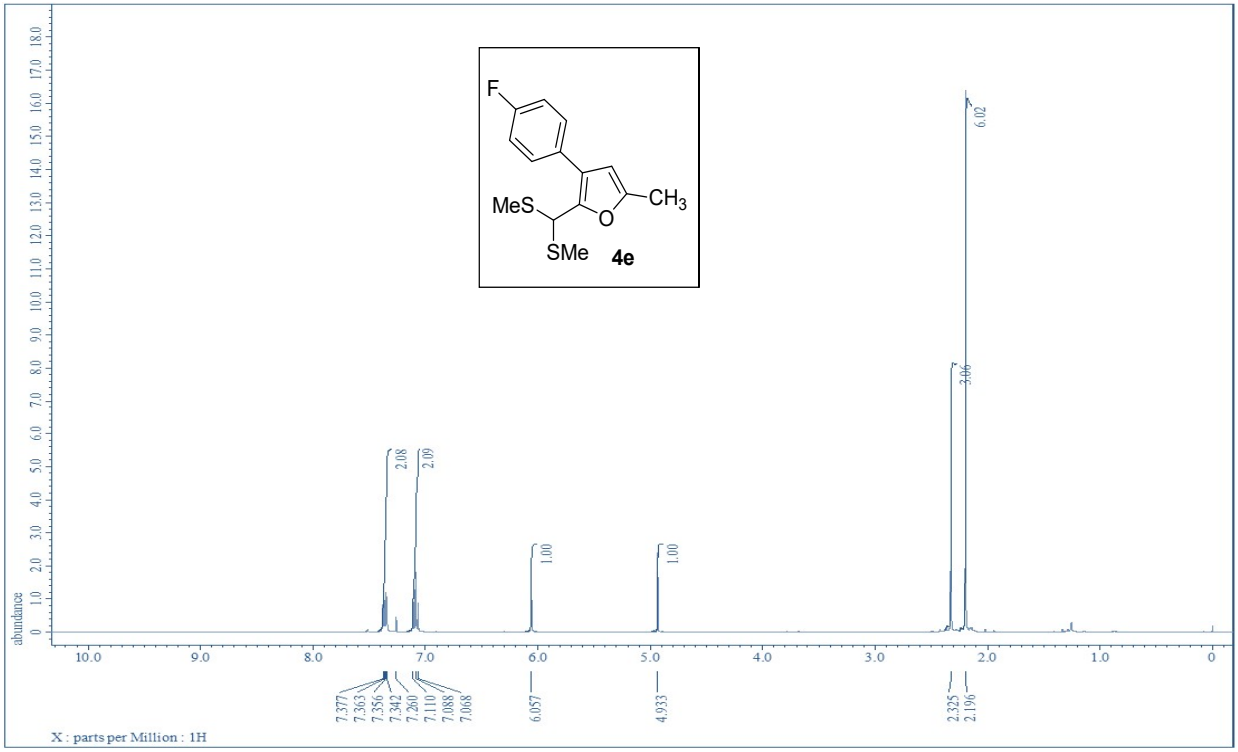


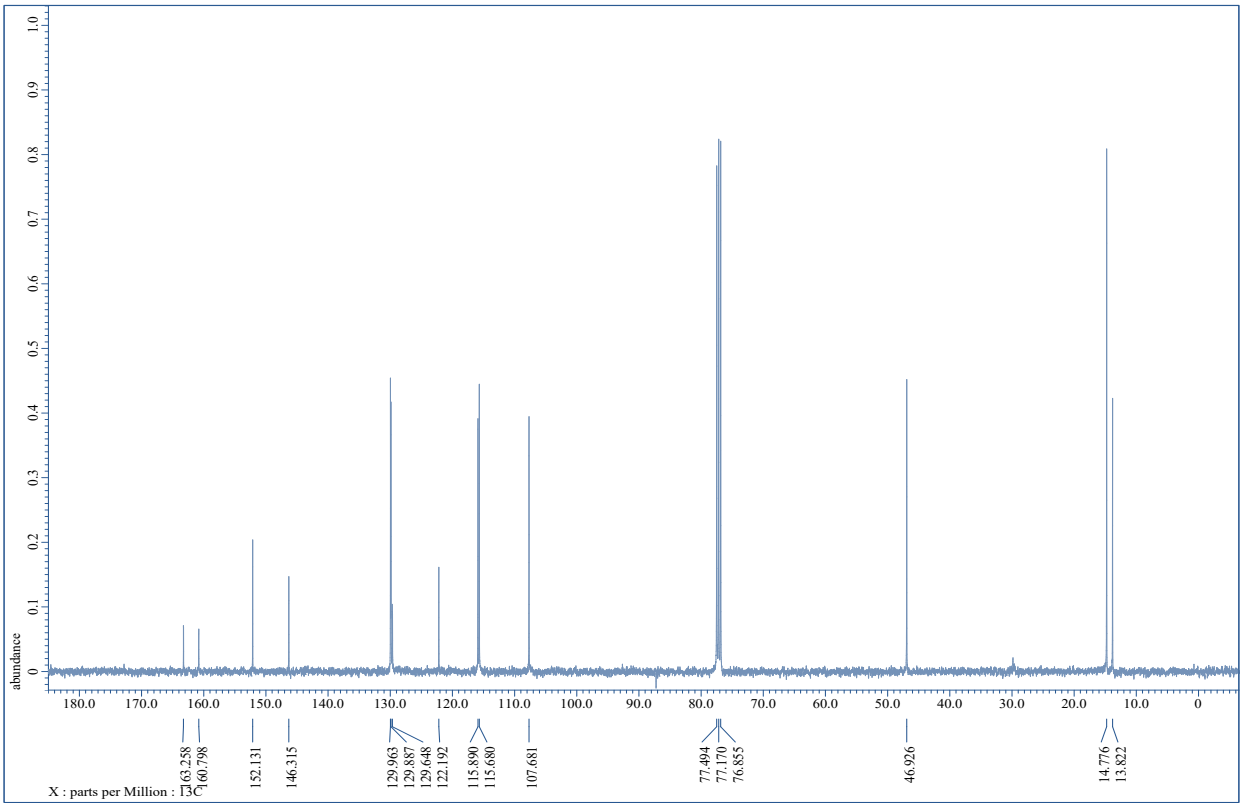
^{1}H NMR and ^{13}C NMR spectra of 3-(bis(methylthio)methyl)-2-(4-methoxyphenyl)-5-methylfuran(4c)



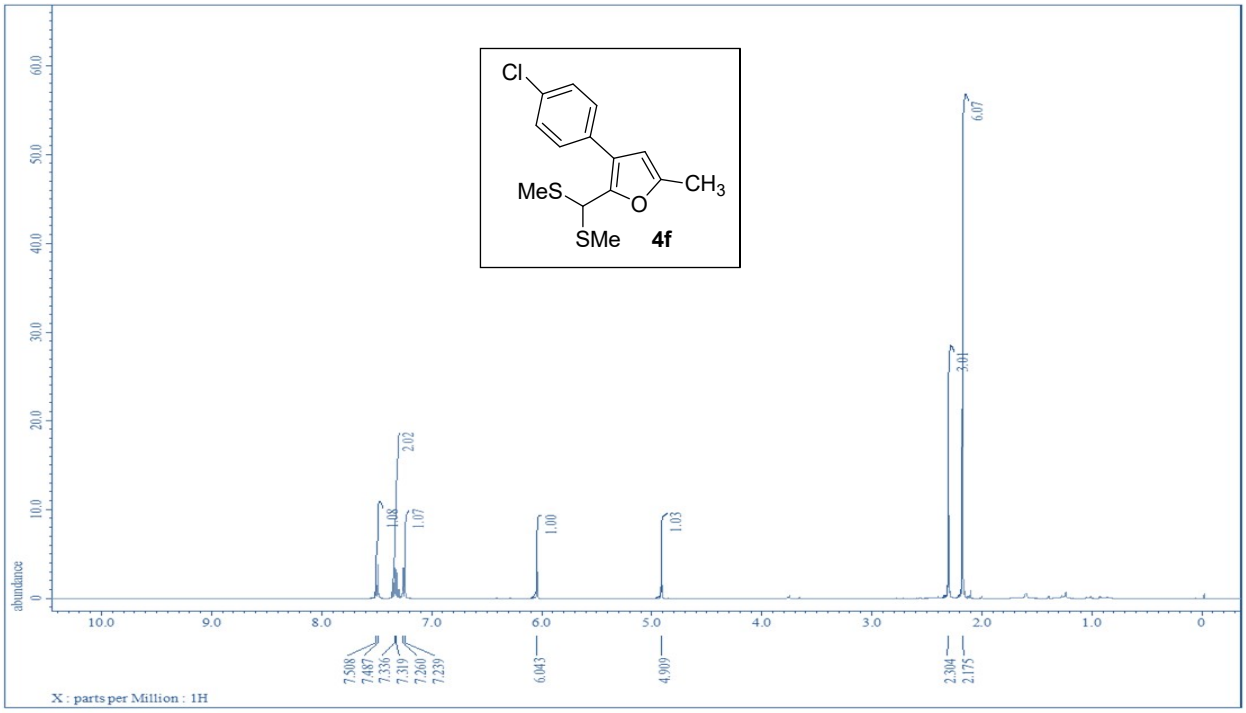


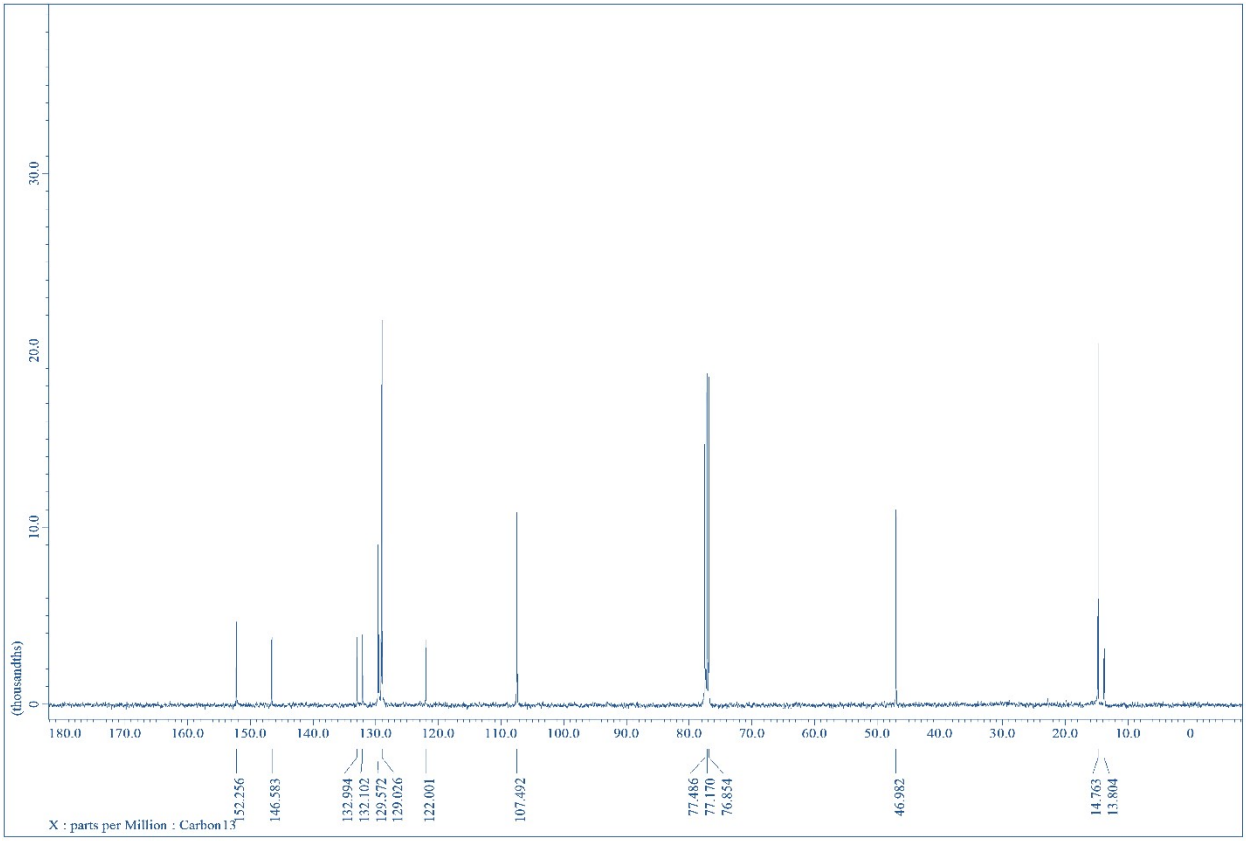
^{1}H NMR and ^{13}C NMR spectra of 2-(bis(methylthio)methyl)-3-(3,4-dimethoxyphenyl)-5-methylfuran (4d)



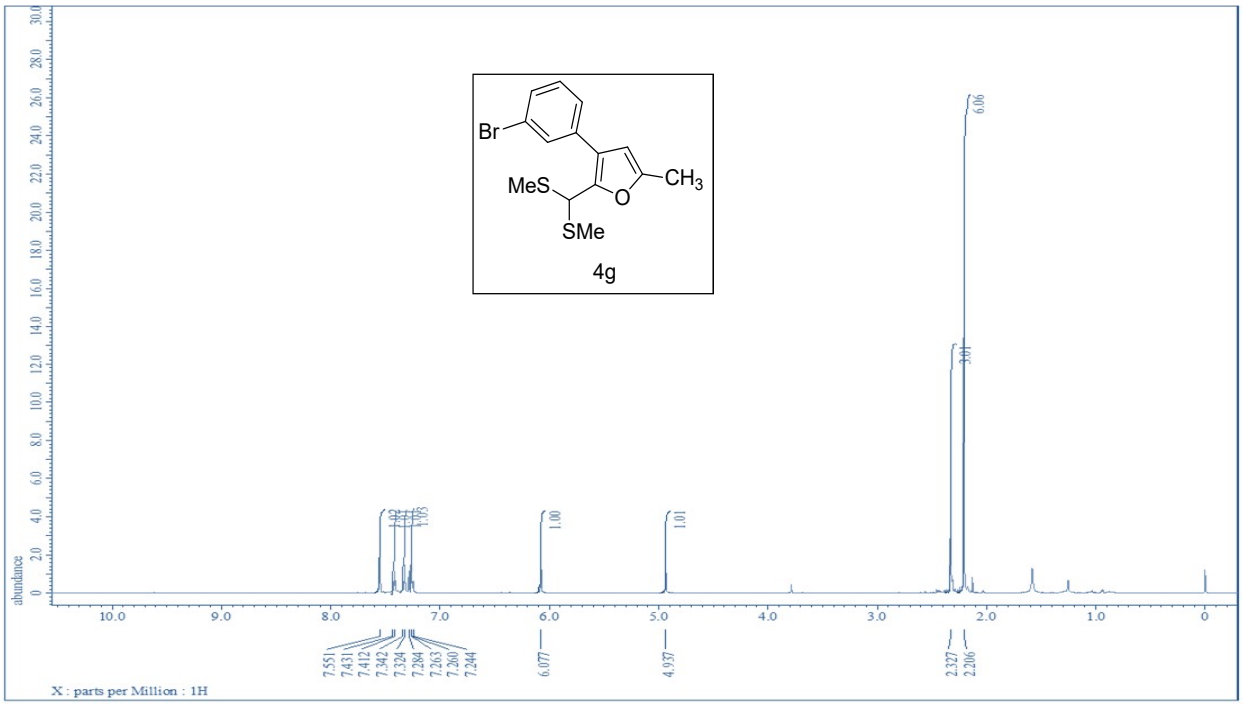


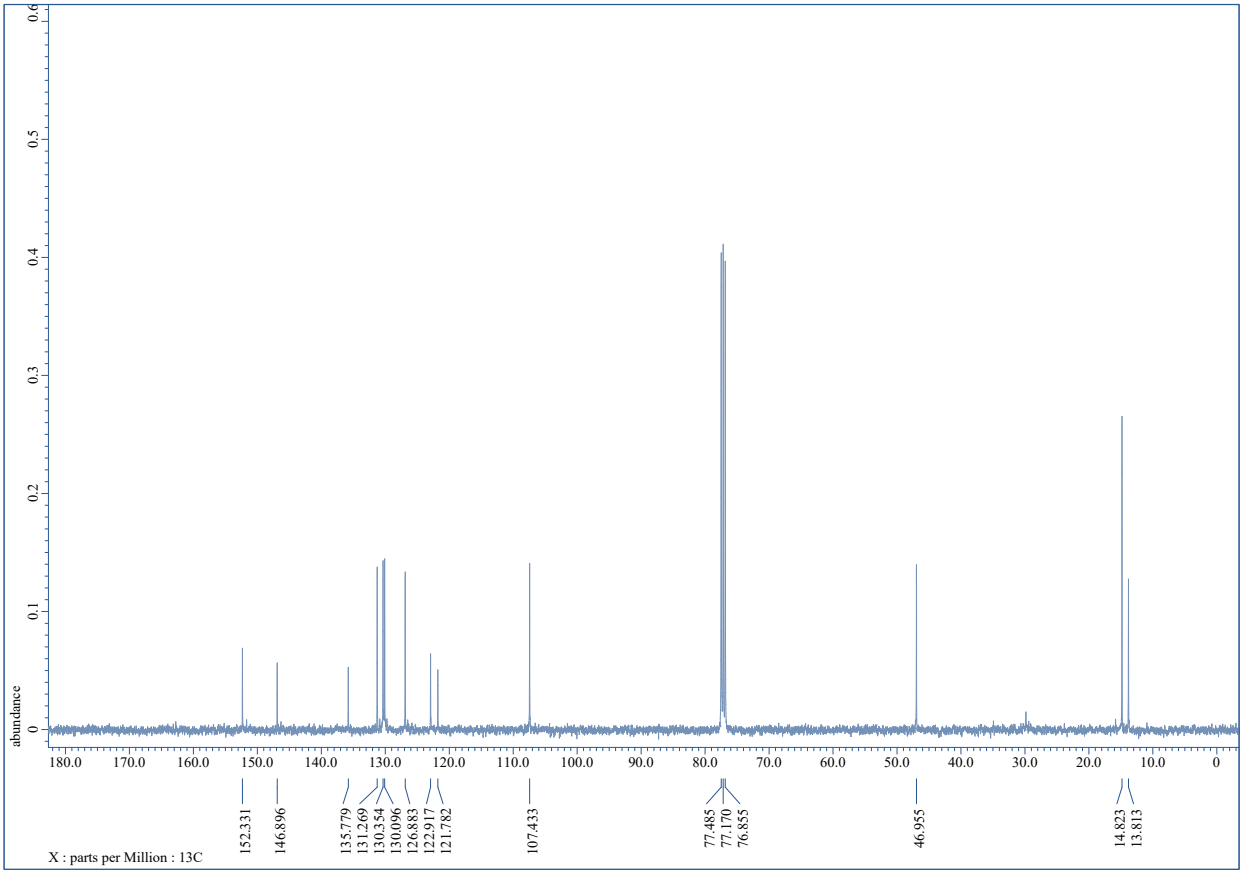
^{1}H NMR and ^{13}C NMR spectra of 2-(bis(methylthio)methyl)-3-(4-fluorophenyl)-5-methylfuran (4e)



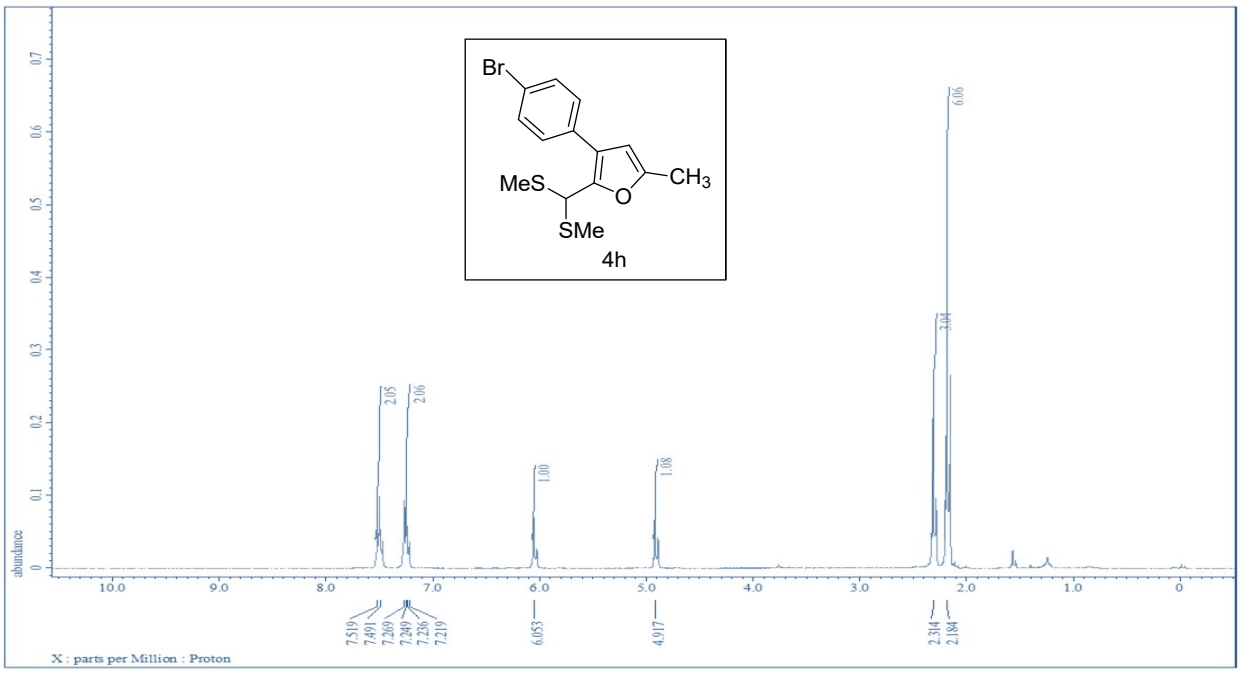


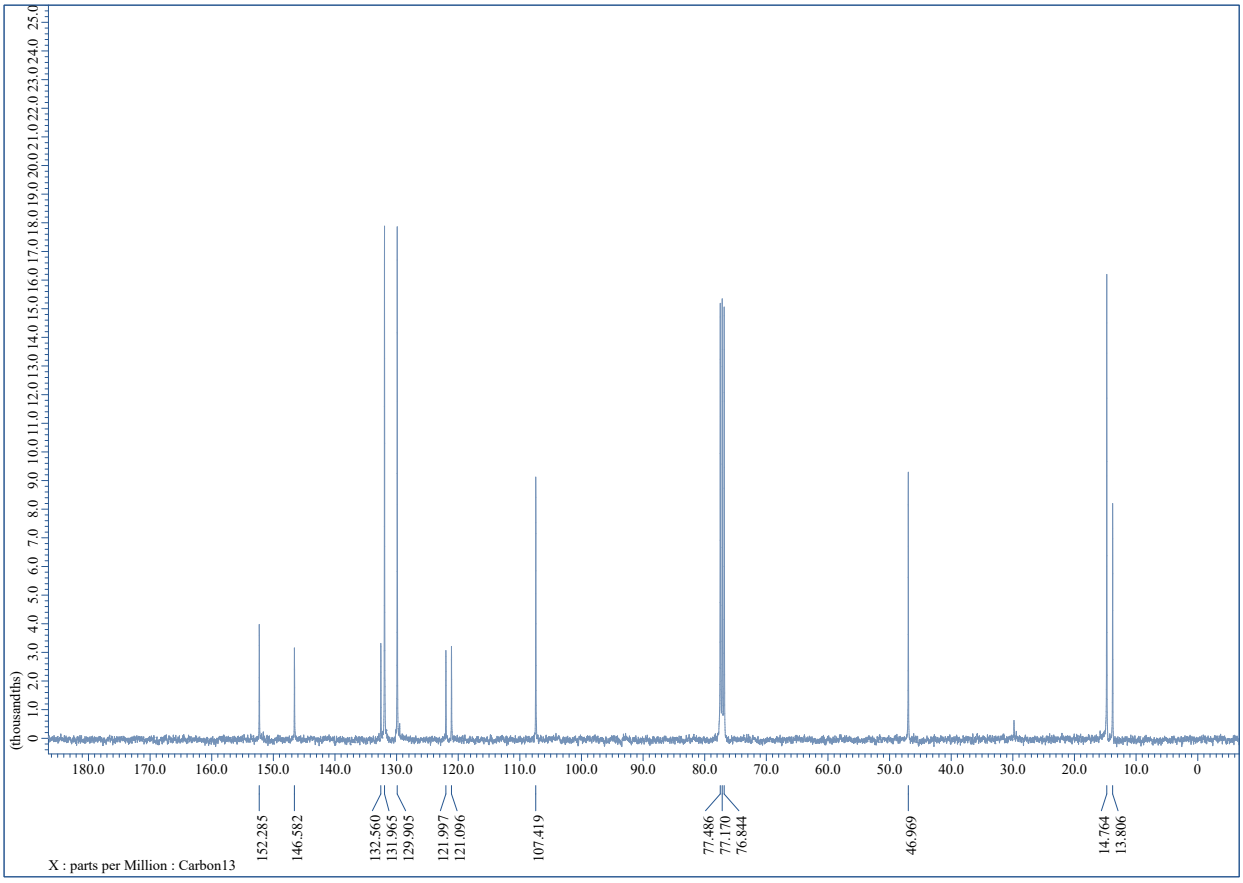
^{1}H NMR and ^{13}C NMR spectra of 3-(bis(methylthio)methyl)-2-(4-chlorophenyl)-5-methylfuran (4f)



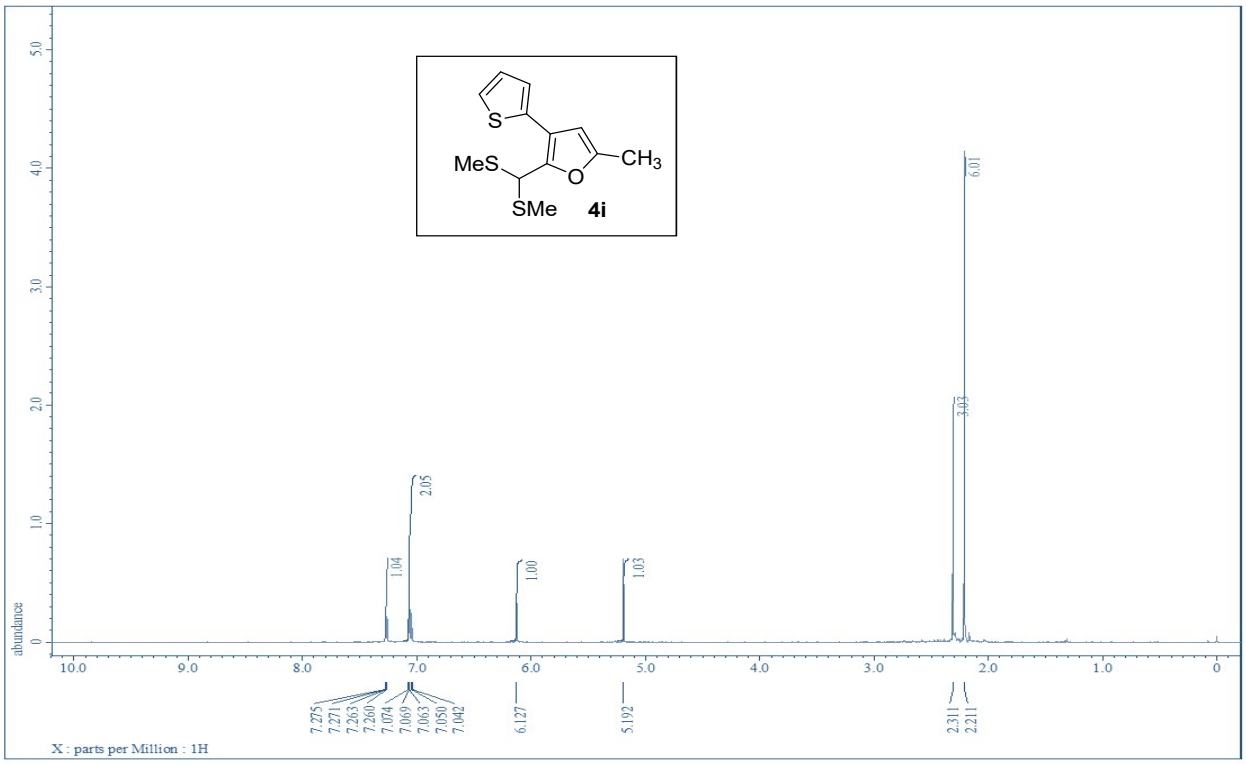


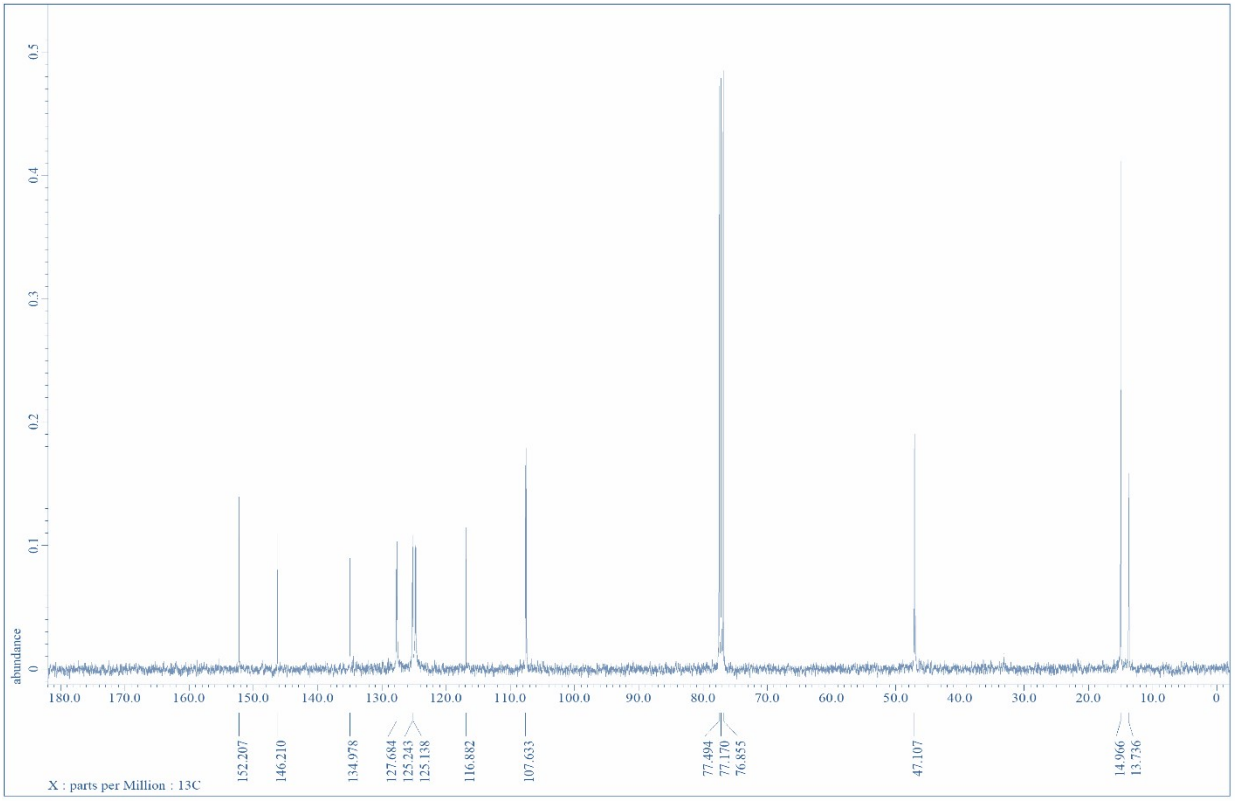
^{1}H NMR and ^{13}C NMR spectra of 2-(bis(methylthio)methyl)-3-(3-bromophenyl)-5-methylfuran (4g)



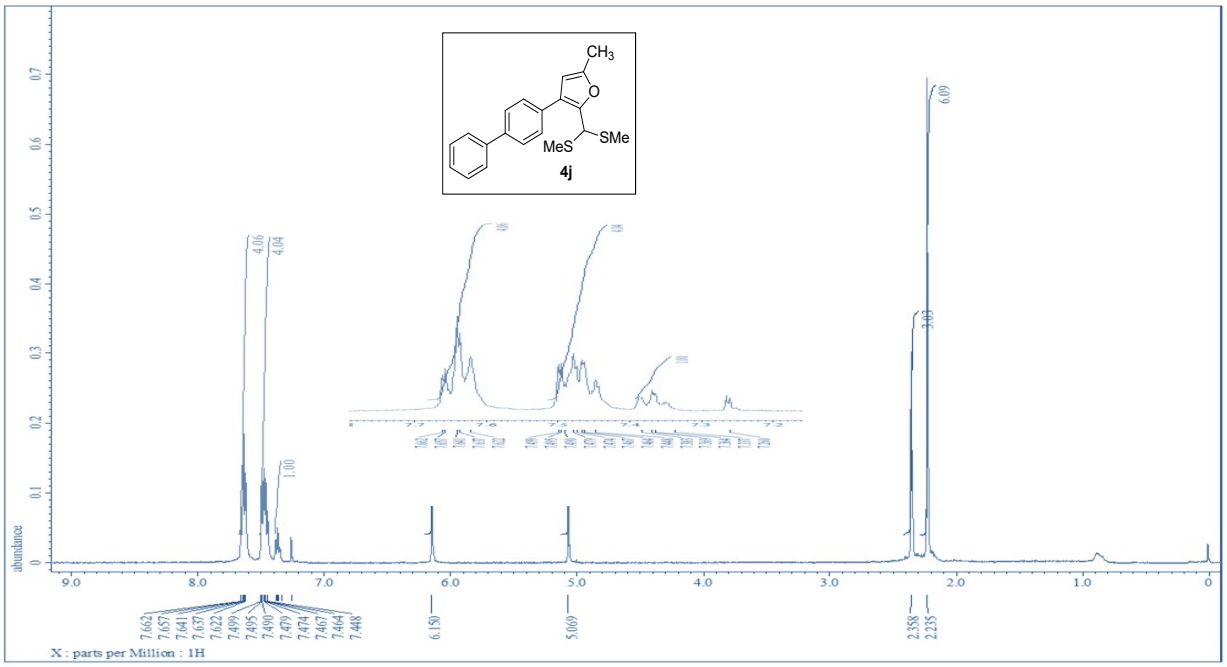


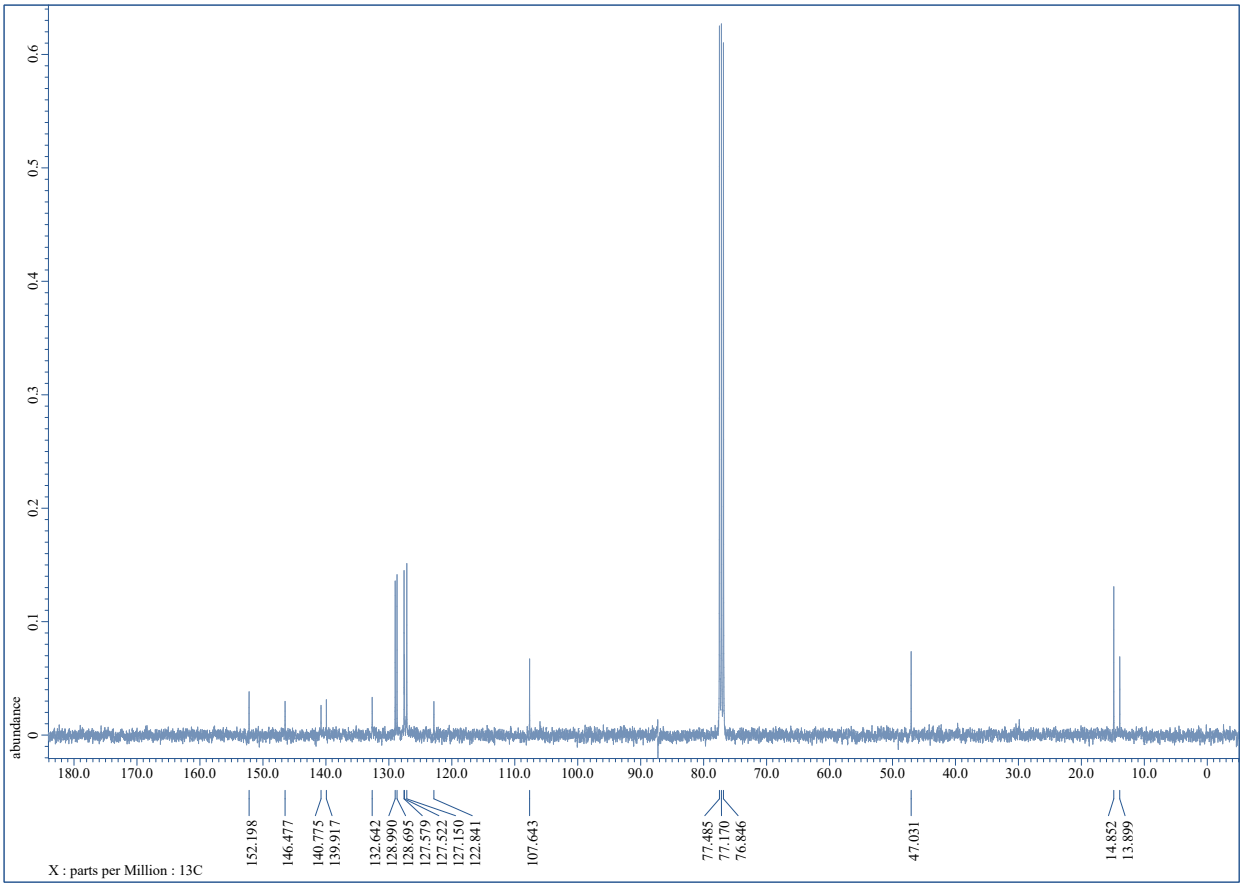
^{1}H NMR and ^{13}C NMR spectra of 2-(bis(methylthio)methyl)-3-(4-bromophenyl)-5-methylfuran (4h)



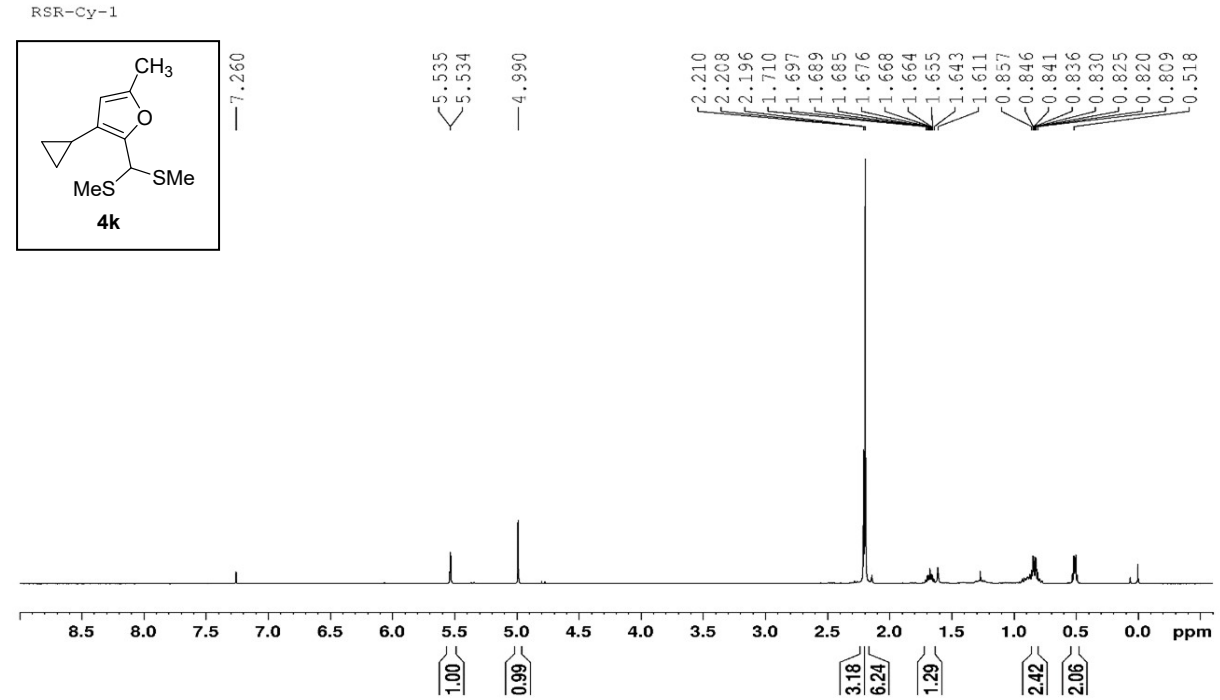


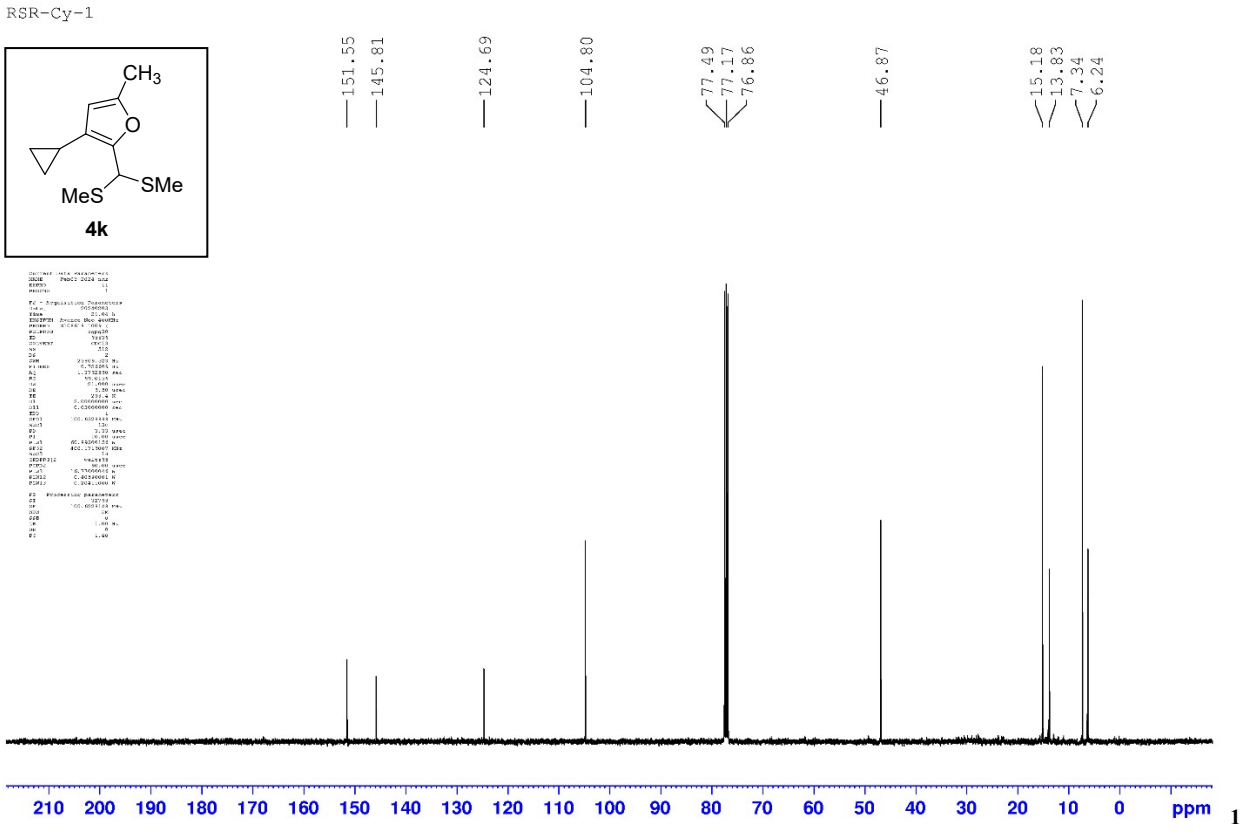
^{1}H NMR and ^{13}C NMR spectra of 3-(bis(methylthio)methyl)-5-methyl-2-(thiophen-2-yl)furan (4i)



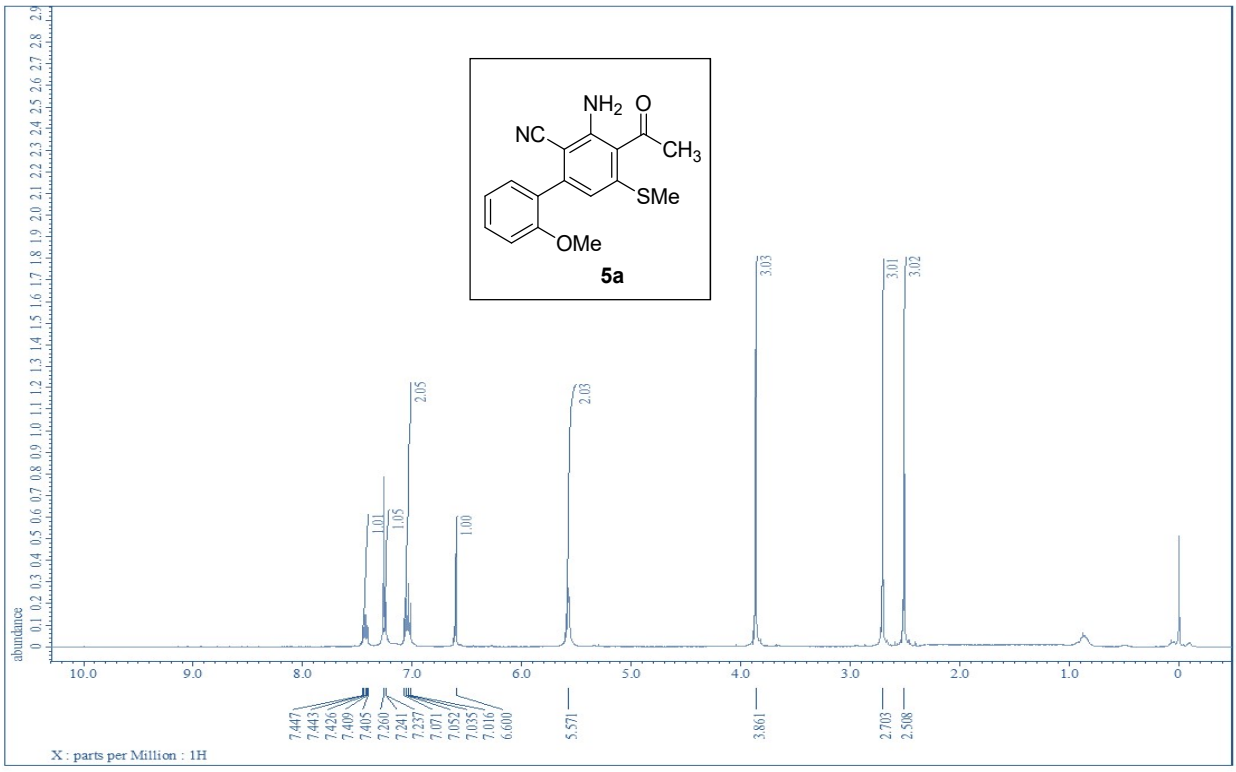


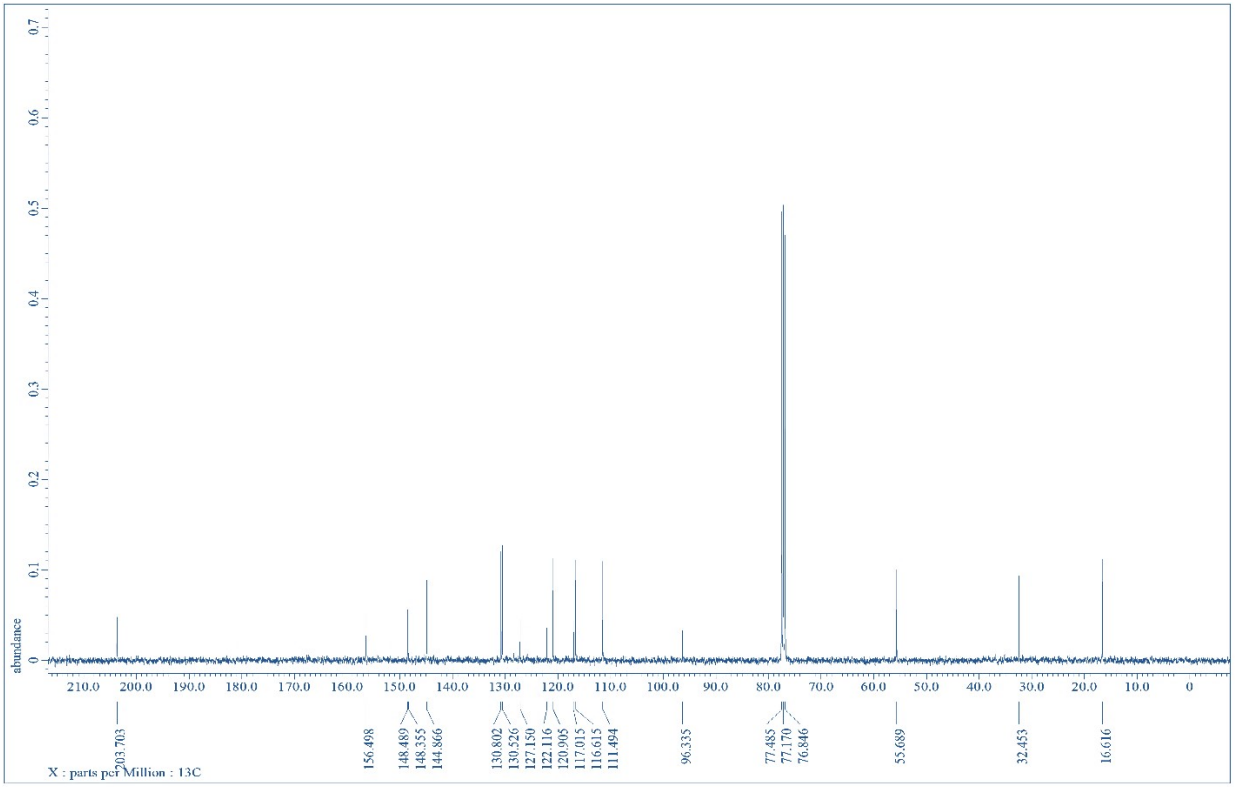
^{1}H NMR and ^{13}C NMR spectra of 2-([1,1'-biphenyl]-4-yl)-3-(bis(methylthio)methyl)-5-methylfuran (4j)



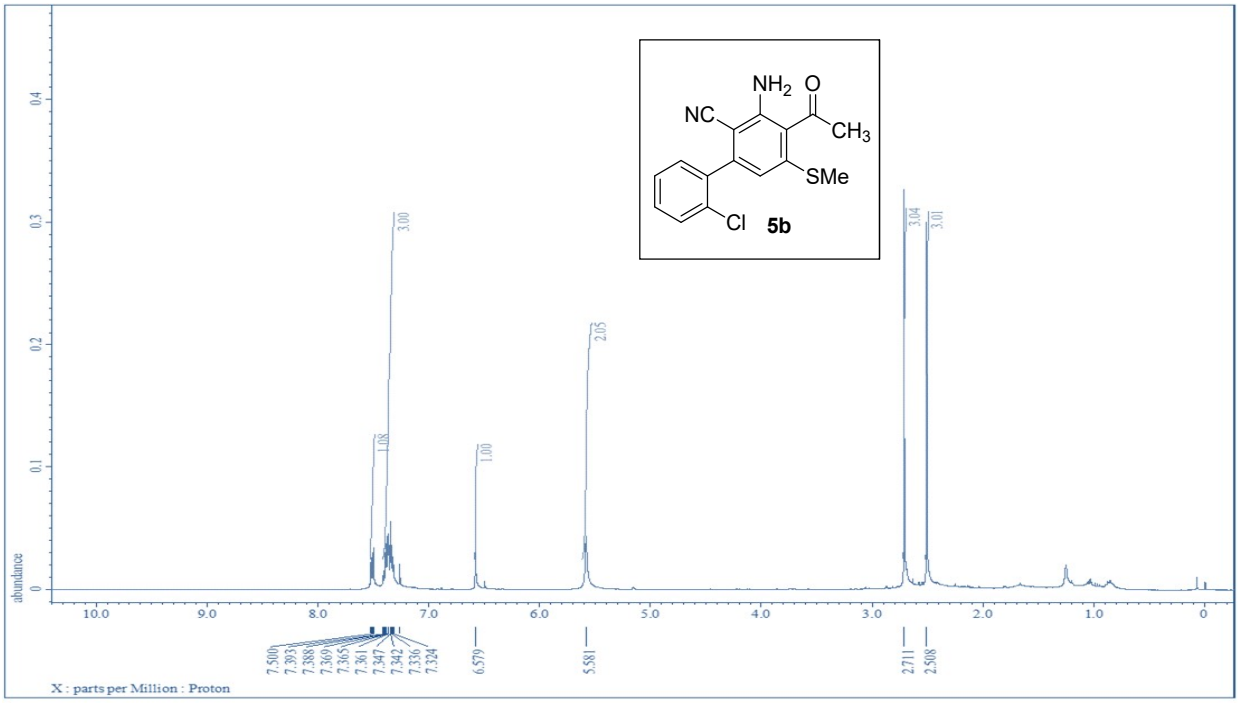


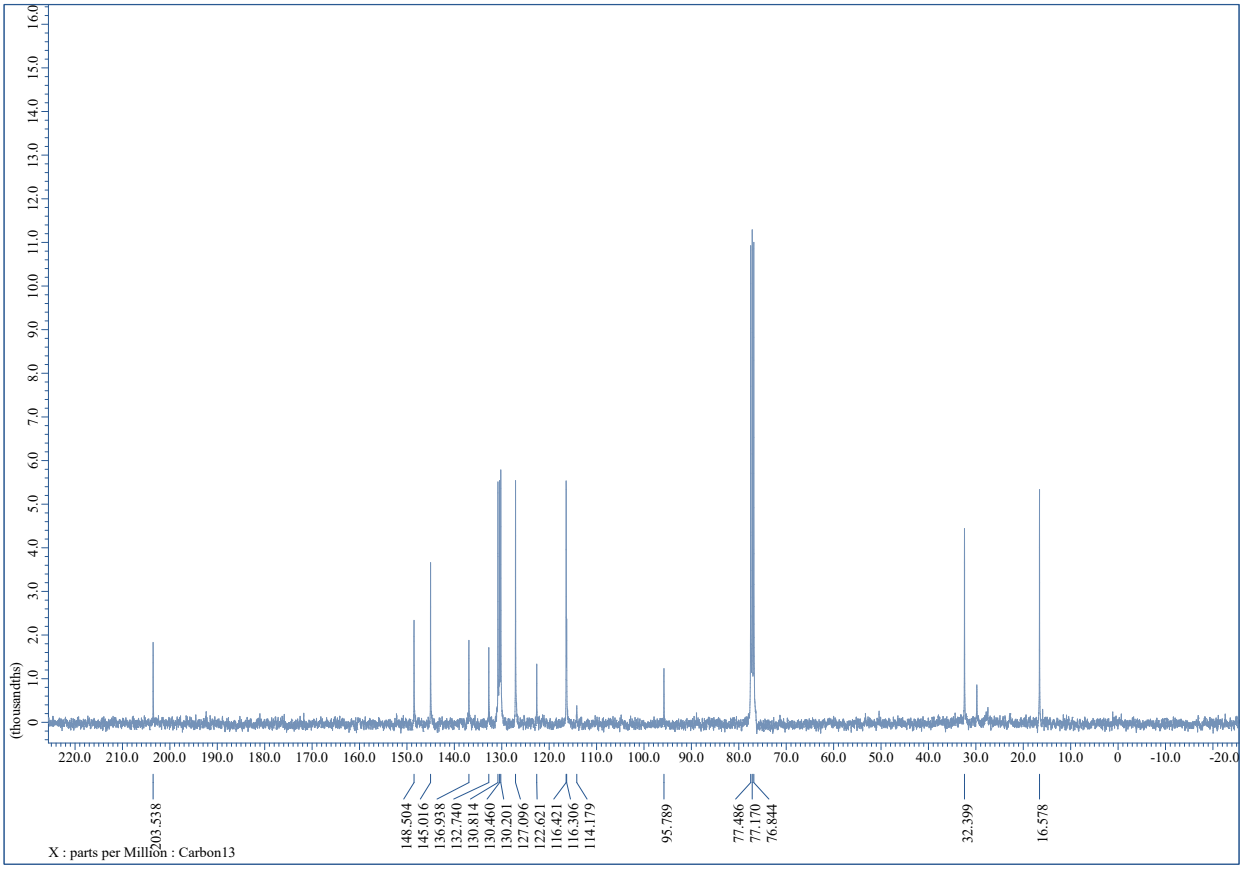
H NMR and ^{13}C NMR spectra of 2-(bis(methylthio)methyl)-3-cyclopropyl-5-methylfuran (4k)



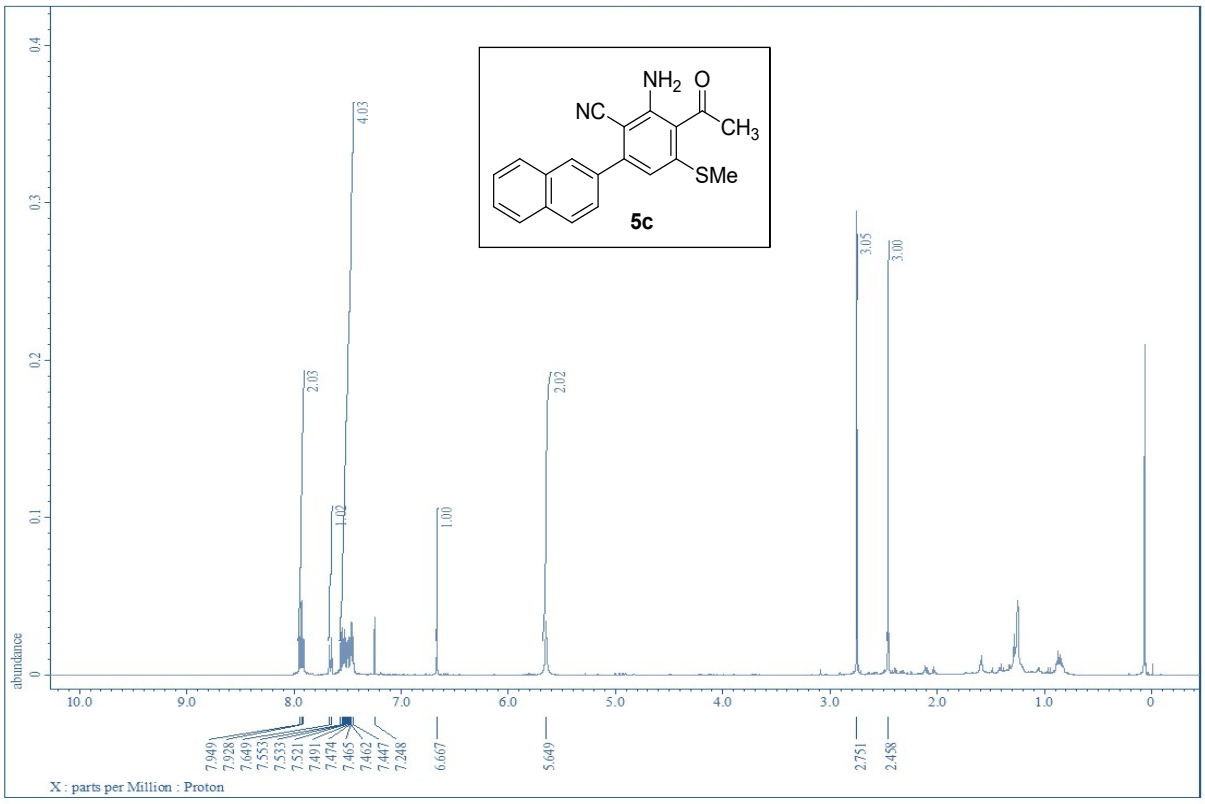


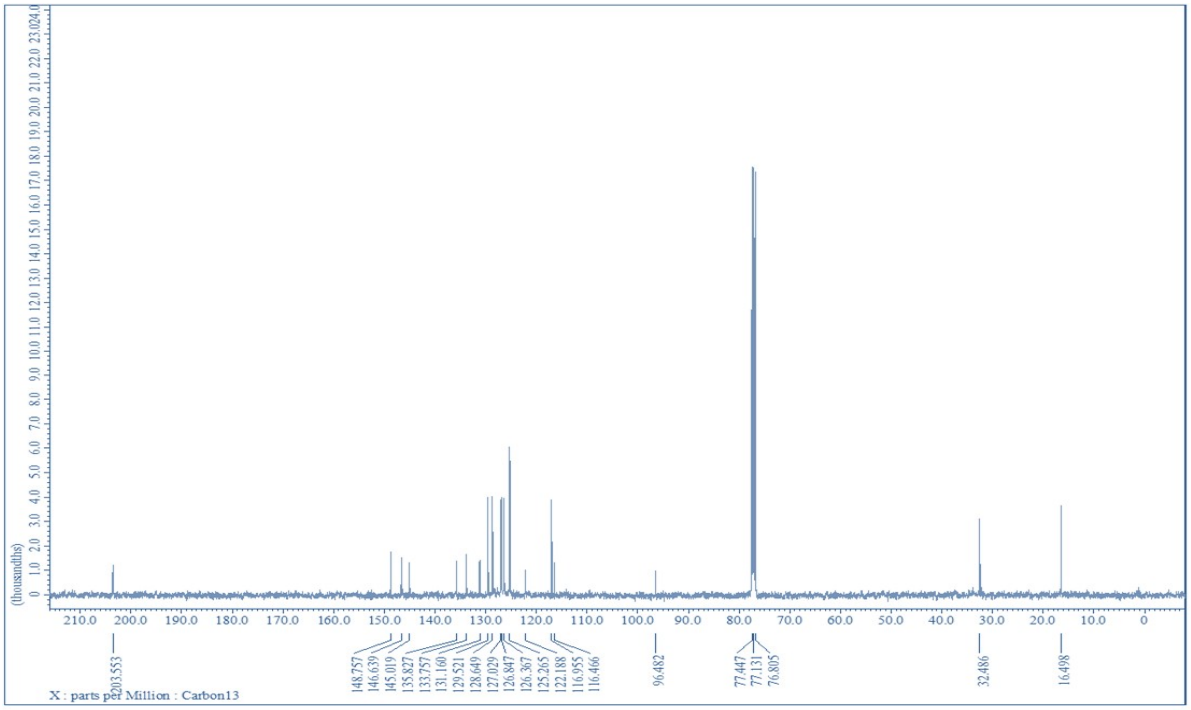
^{1}H NMR and ^{13}C NMR spectrum of 4-acetyl-3-amino-2'-methoxy-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (5a)



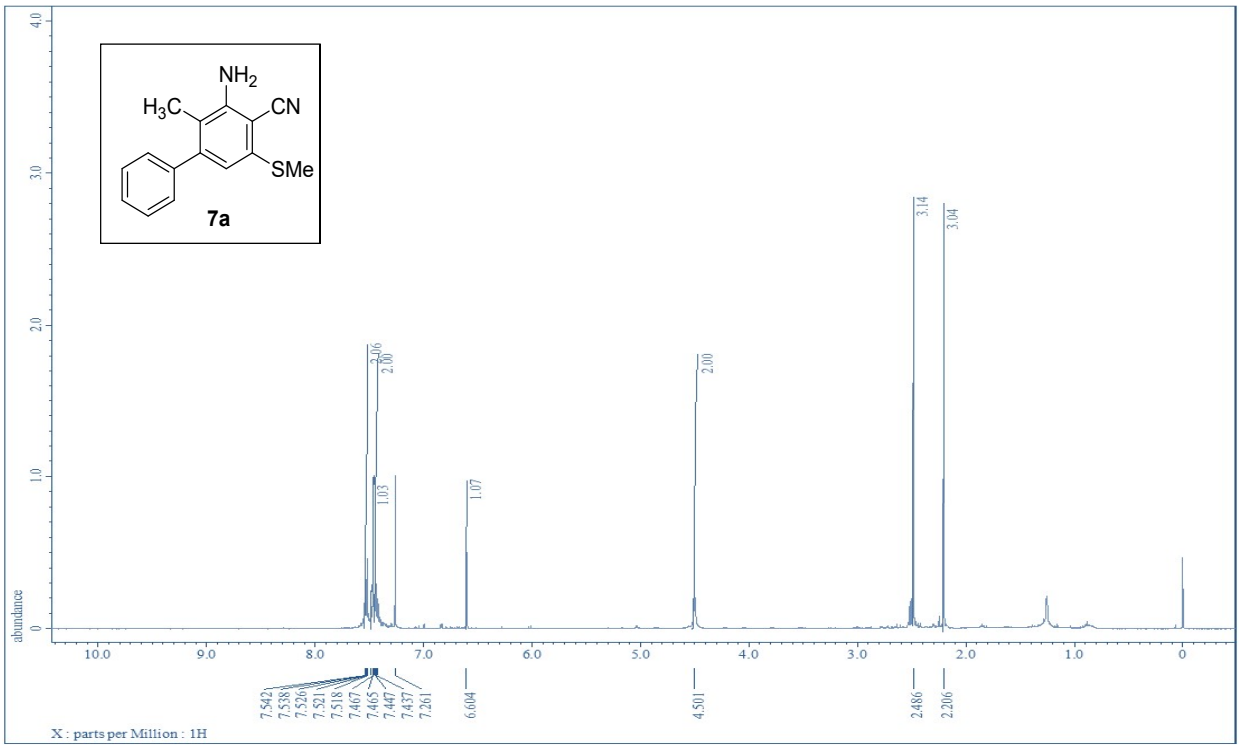


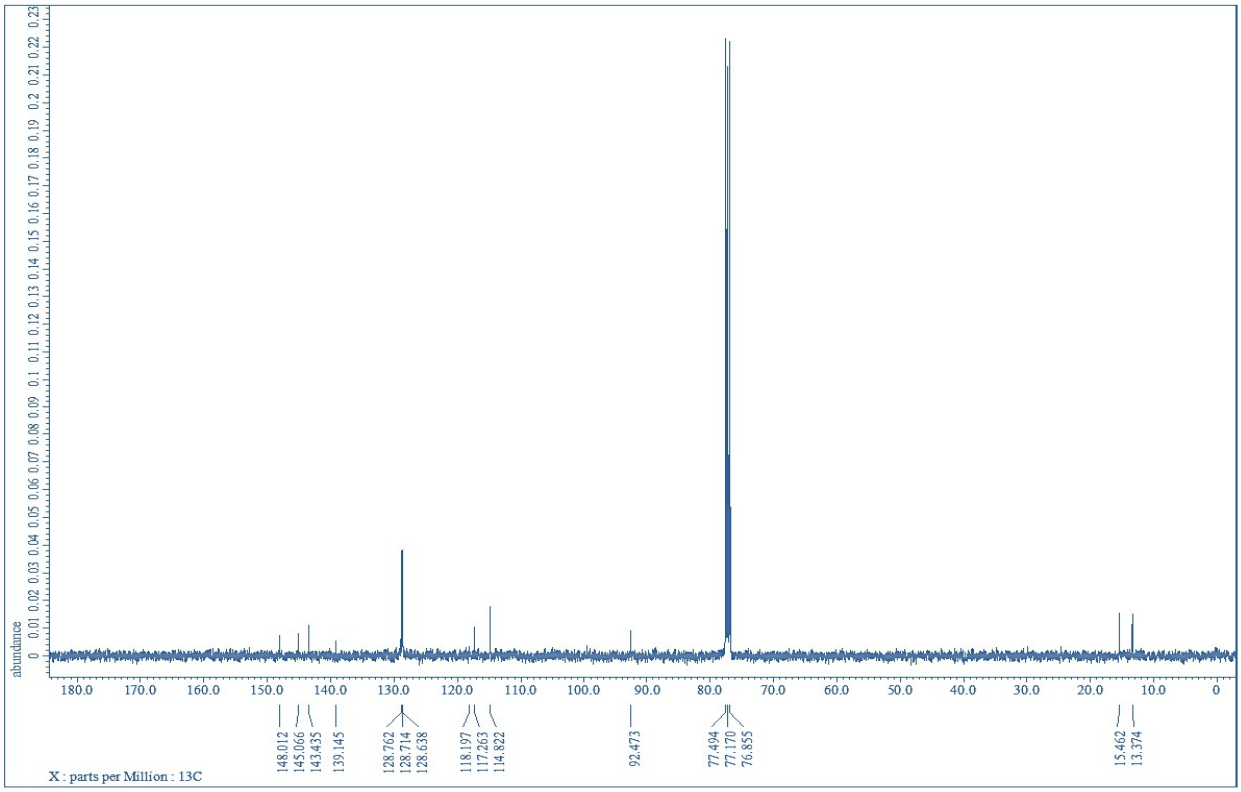
^{1}H NMR and ^{13}C NMR spectrum of 4-acetyl-3-amino-2'-chloro-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (5b)



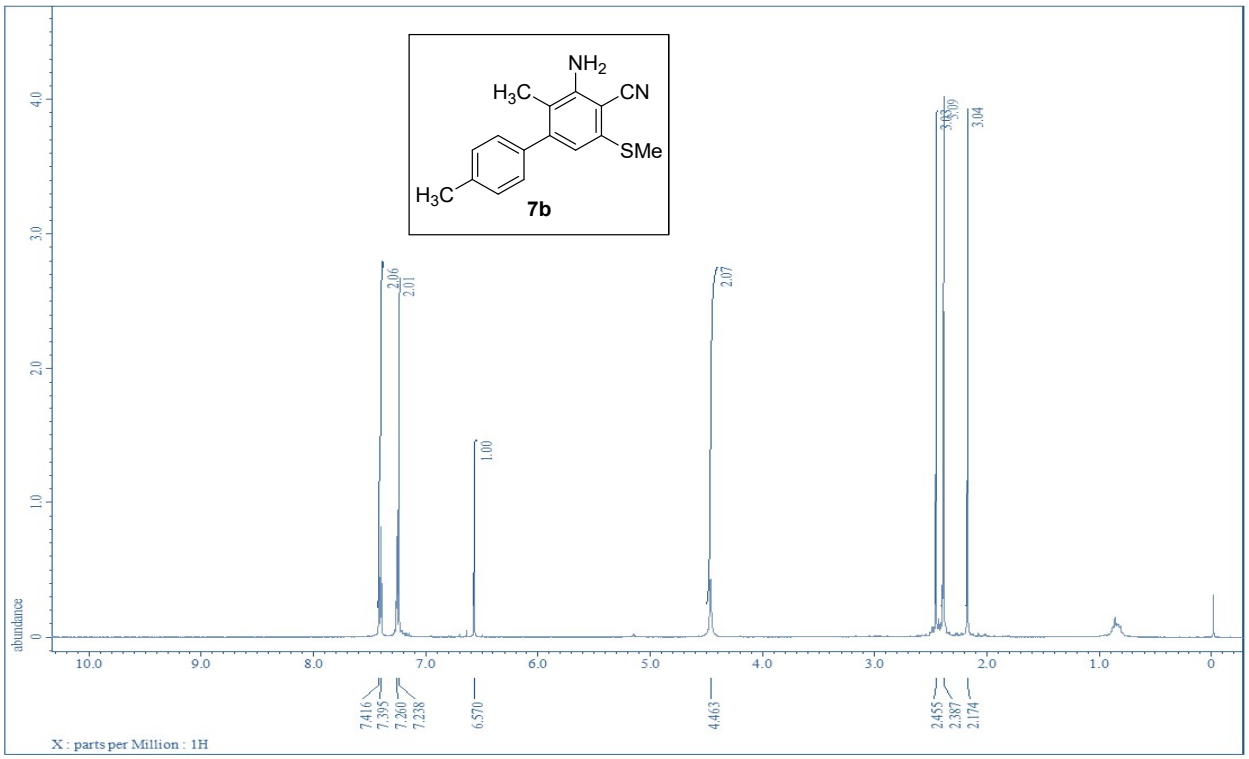


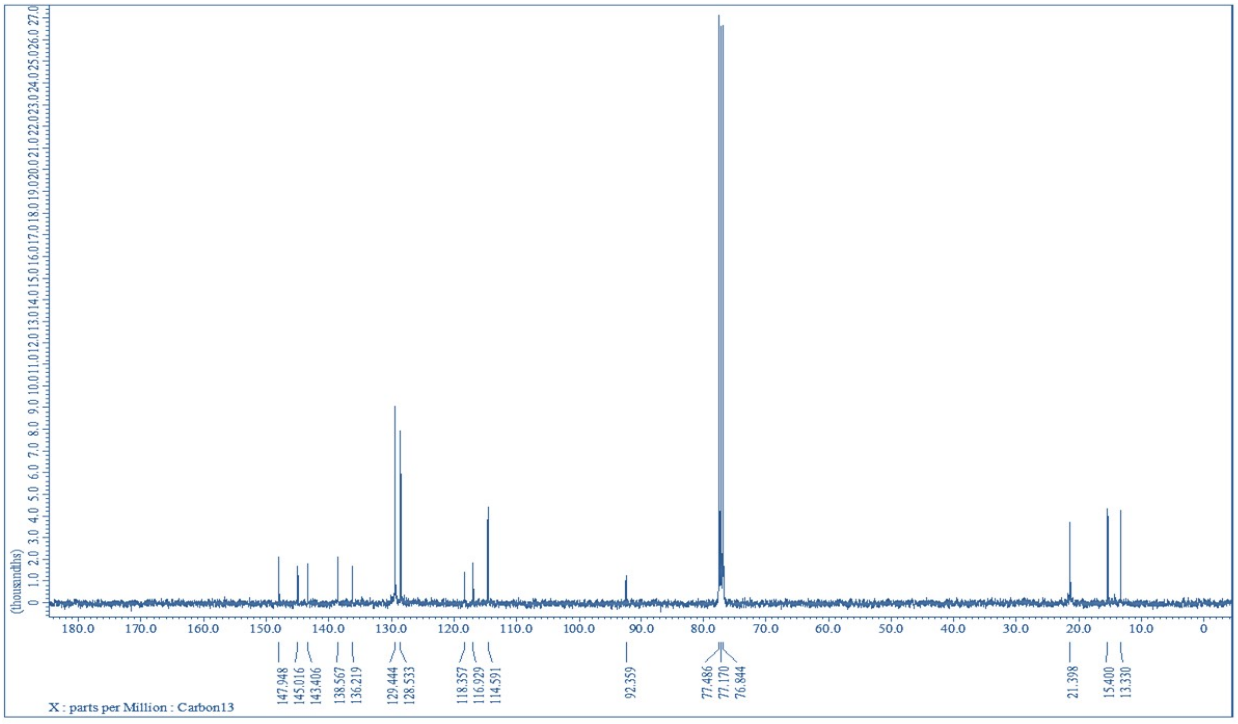
^{1}H NMR and ^{13}C NMR spectrum of 3-acetyl-2-amino-4-(methylthio)-6-(naphthalen-2-yl)benzonitrile (5c)



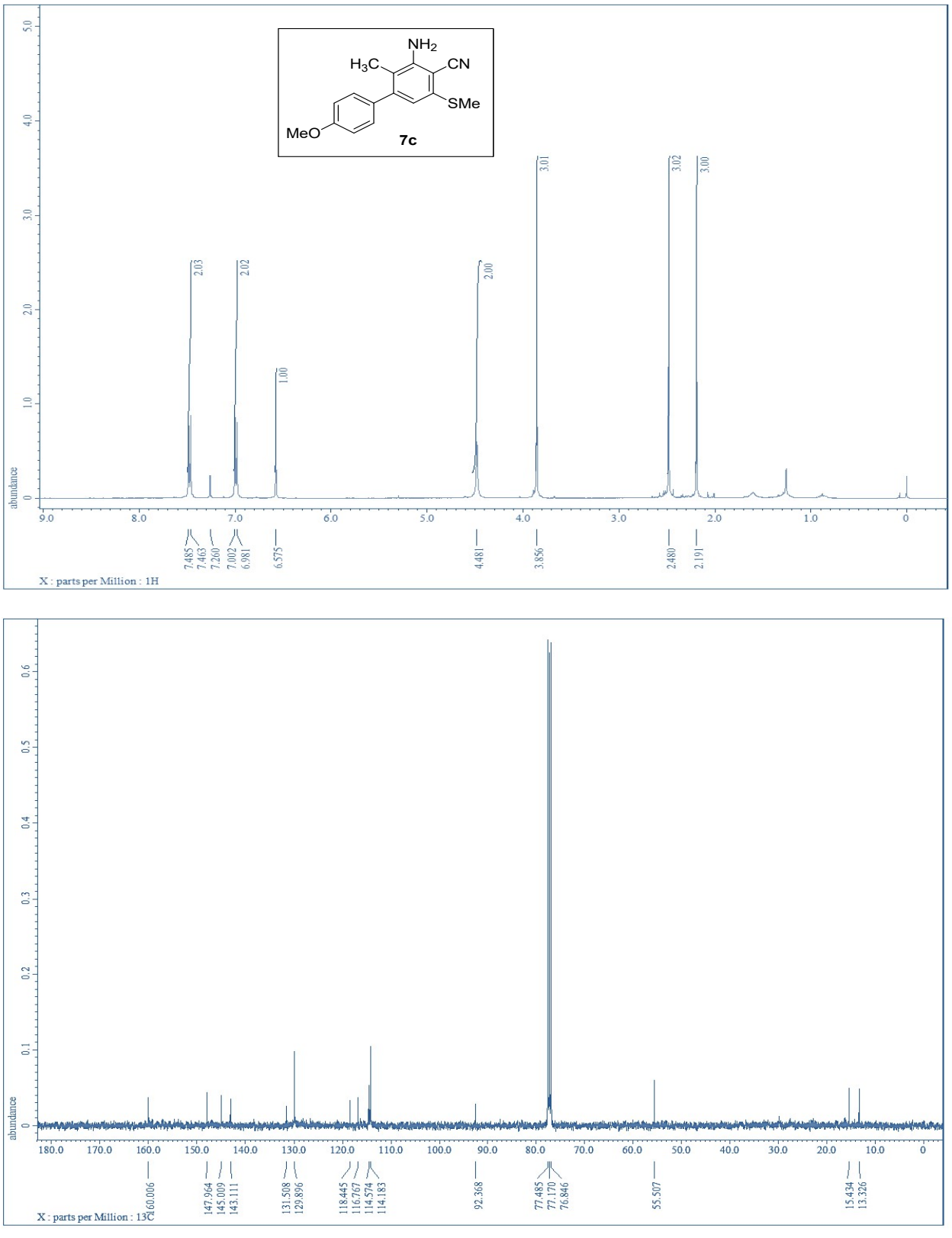


^{1}H NMR and ^{13}C NMR spectra of 3-amino-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7a)

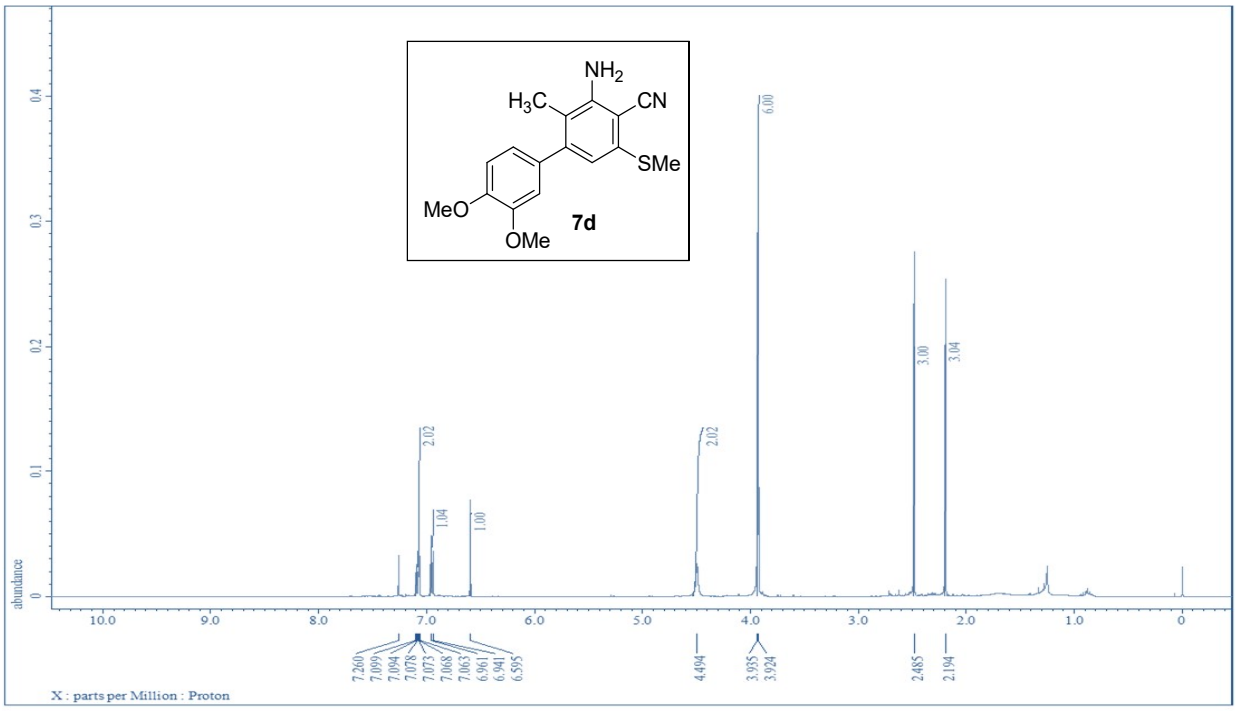


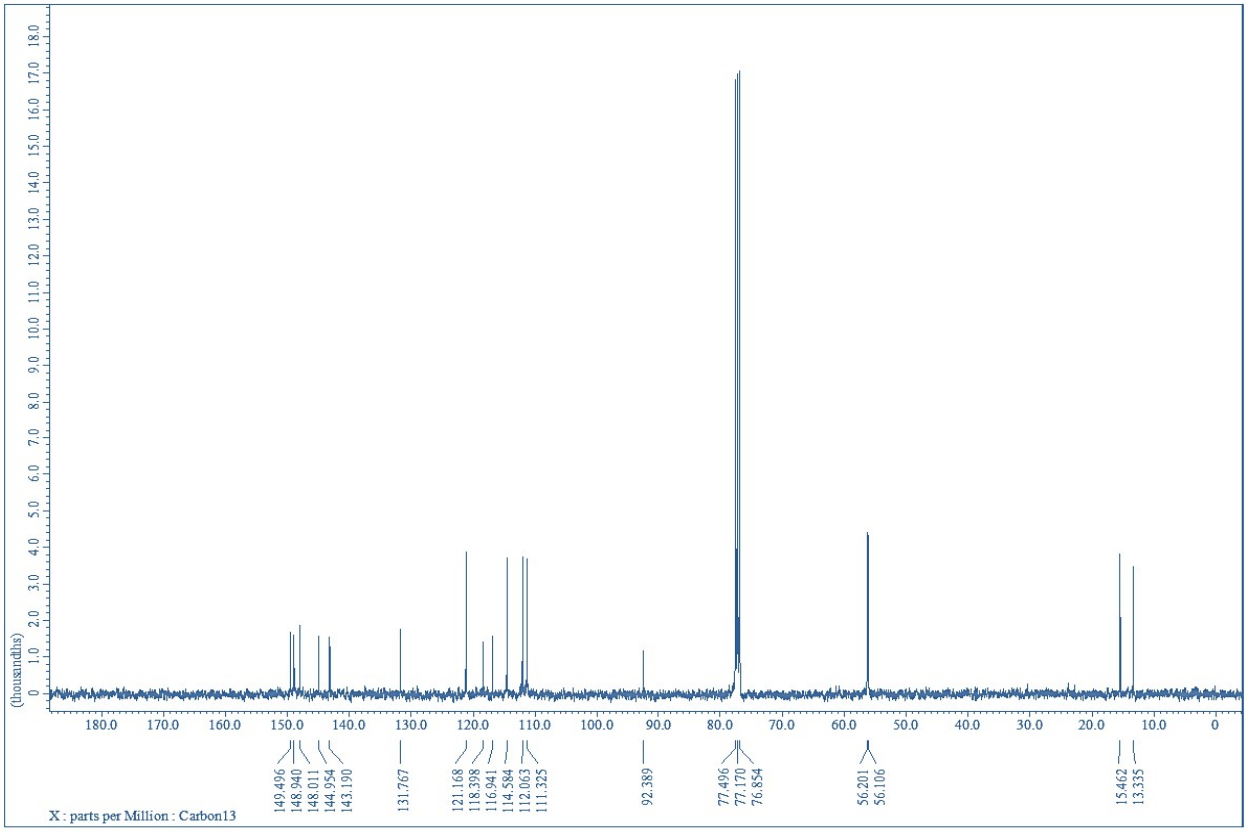


^{1}H NMR and ^{13}C NMR spectrum of 3-amino-2,4'-dimethyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7b)

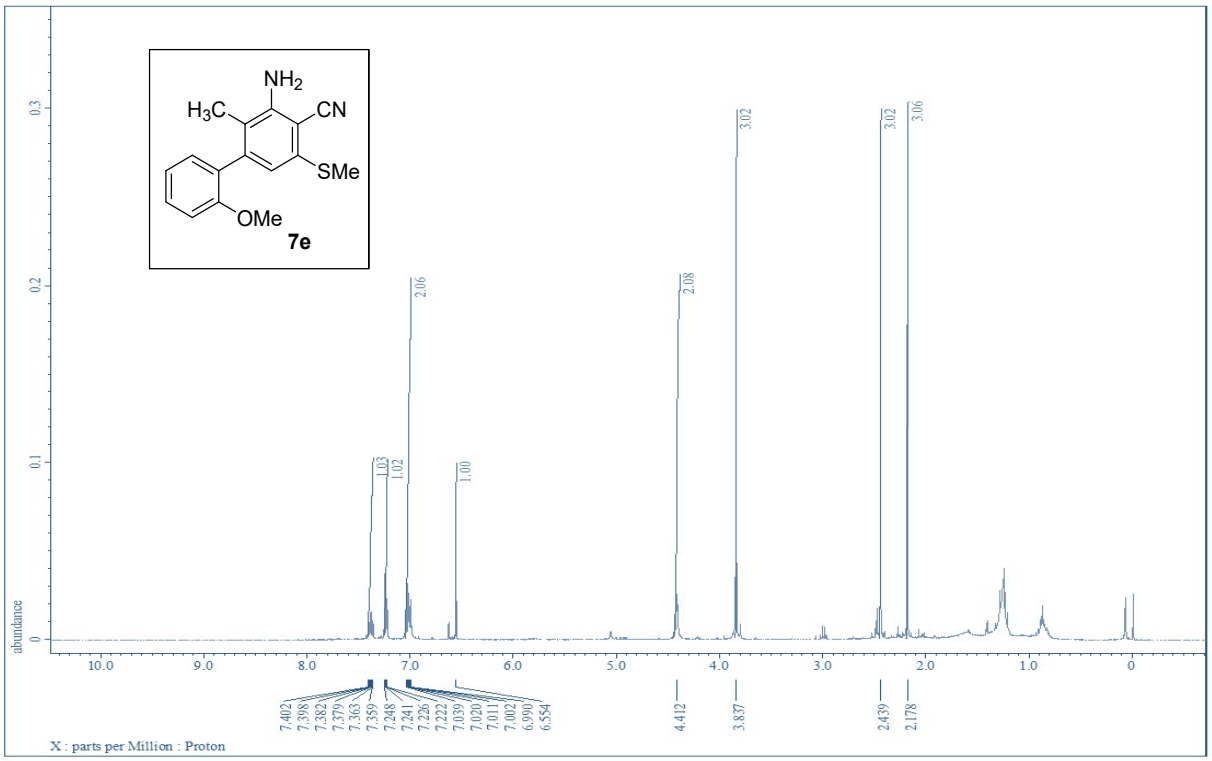


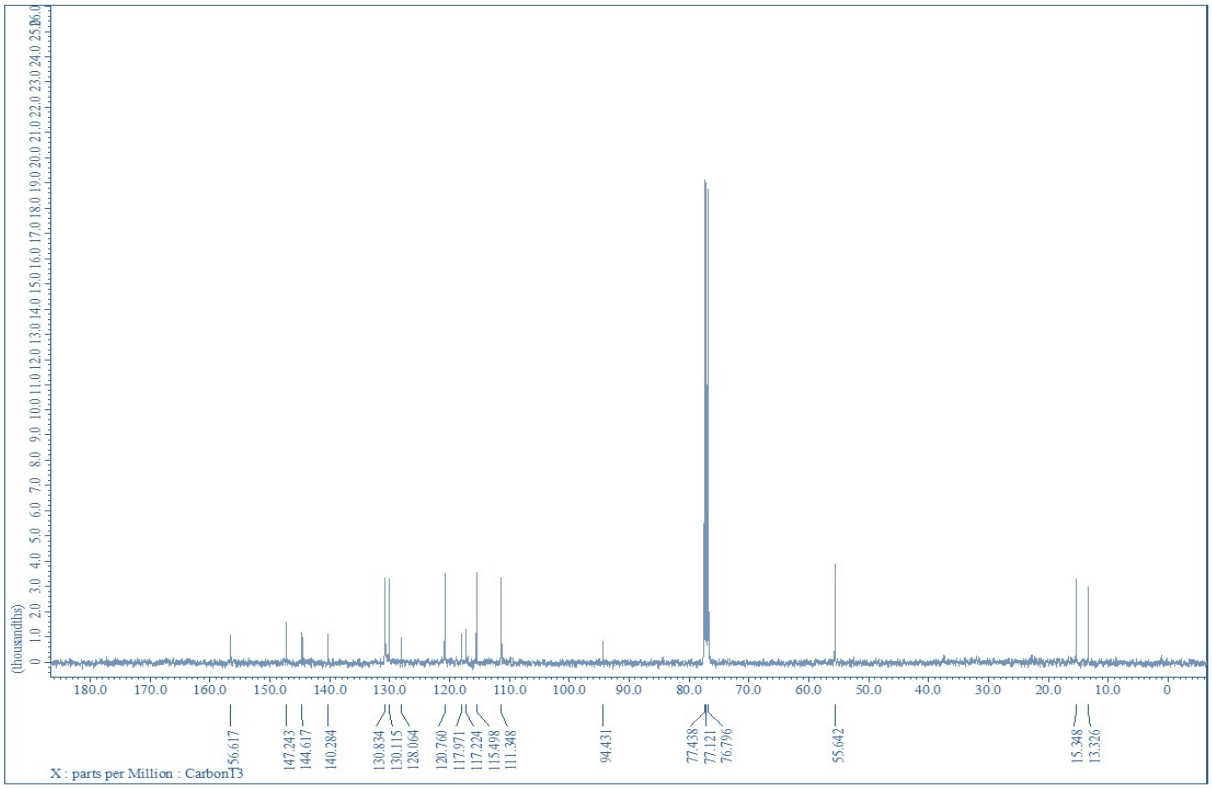
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-4'-methoxy-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7c)



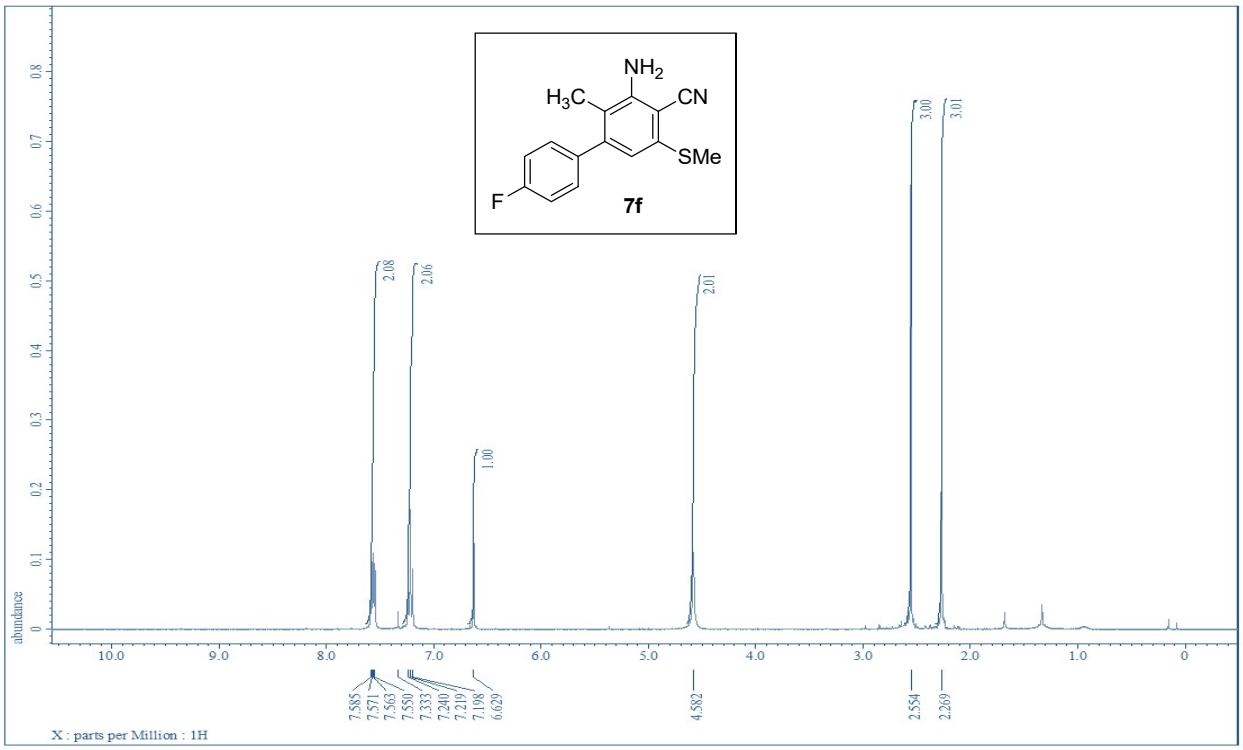


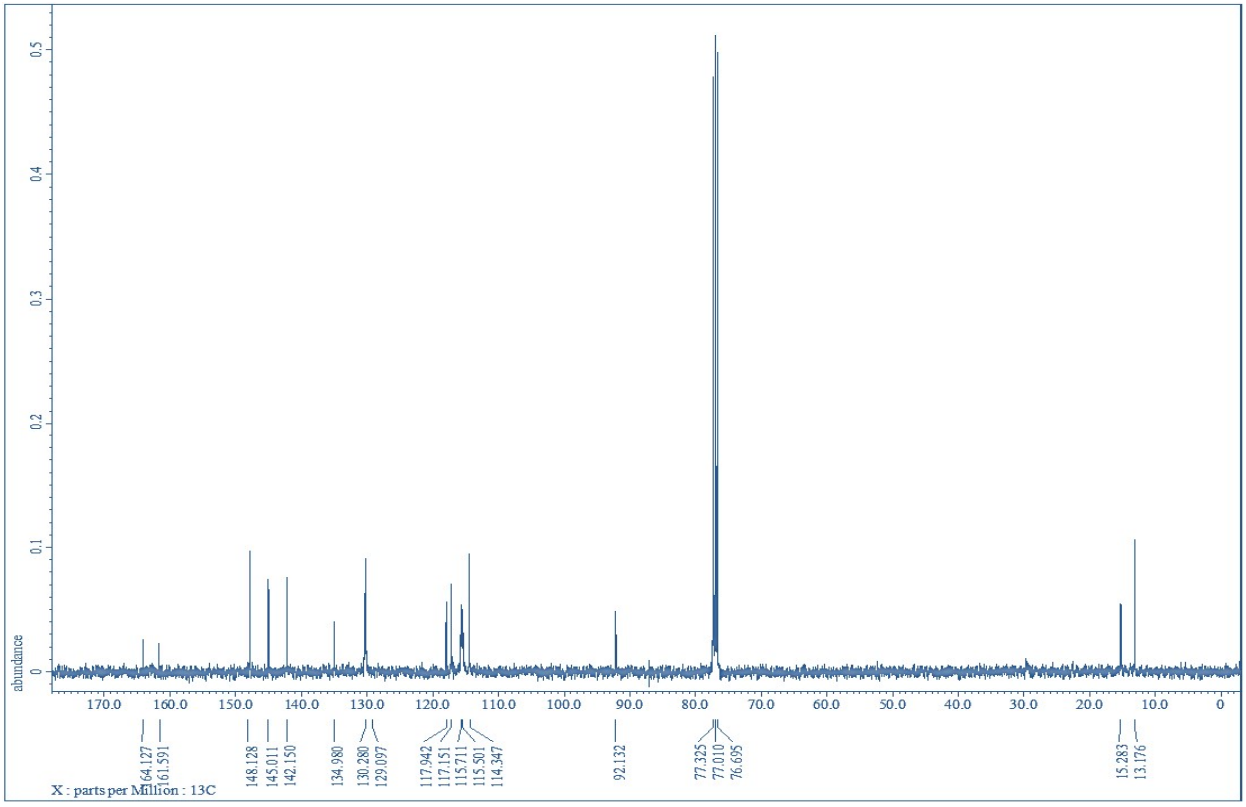
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-3',4'-dimethoxy-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7d)



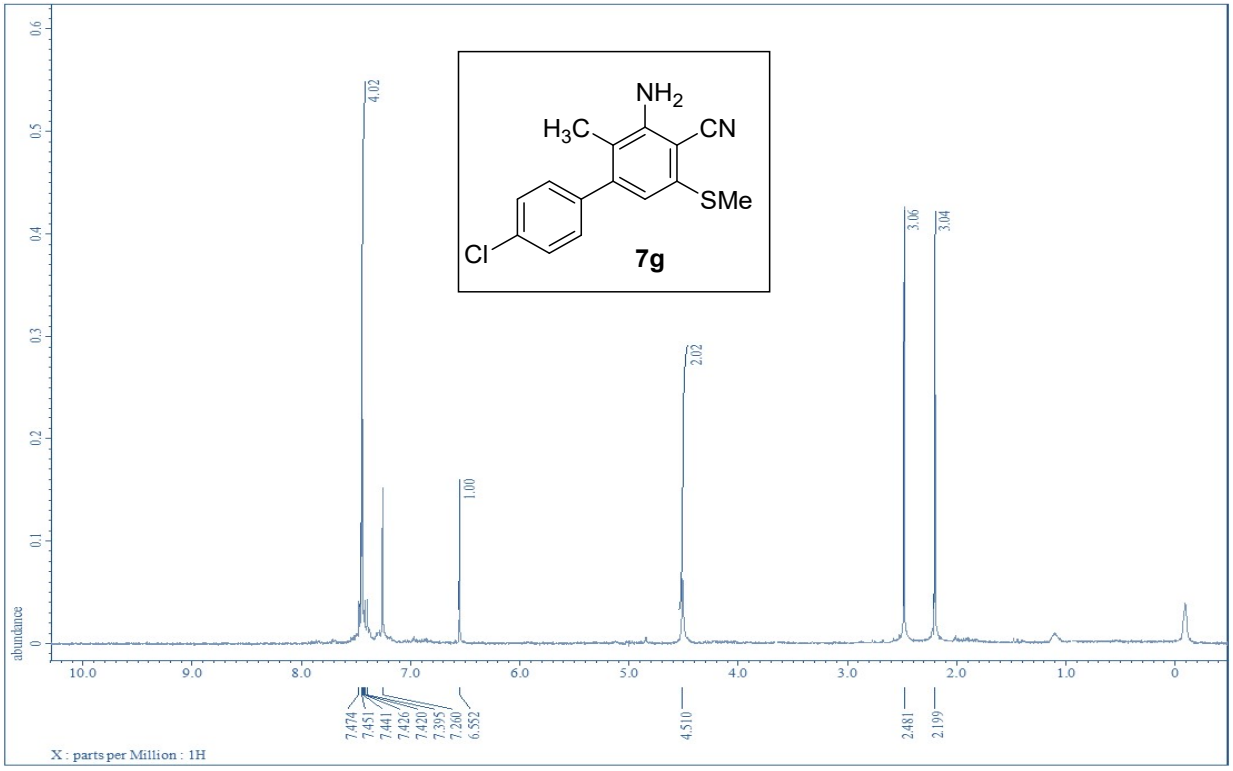


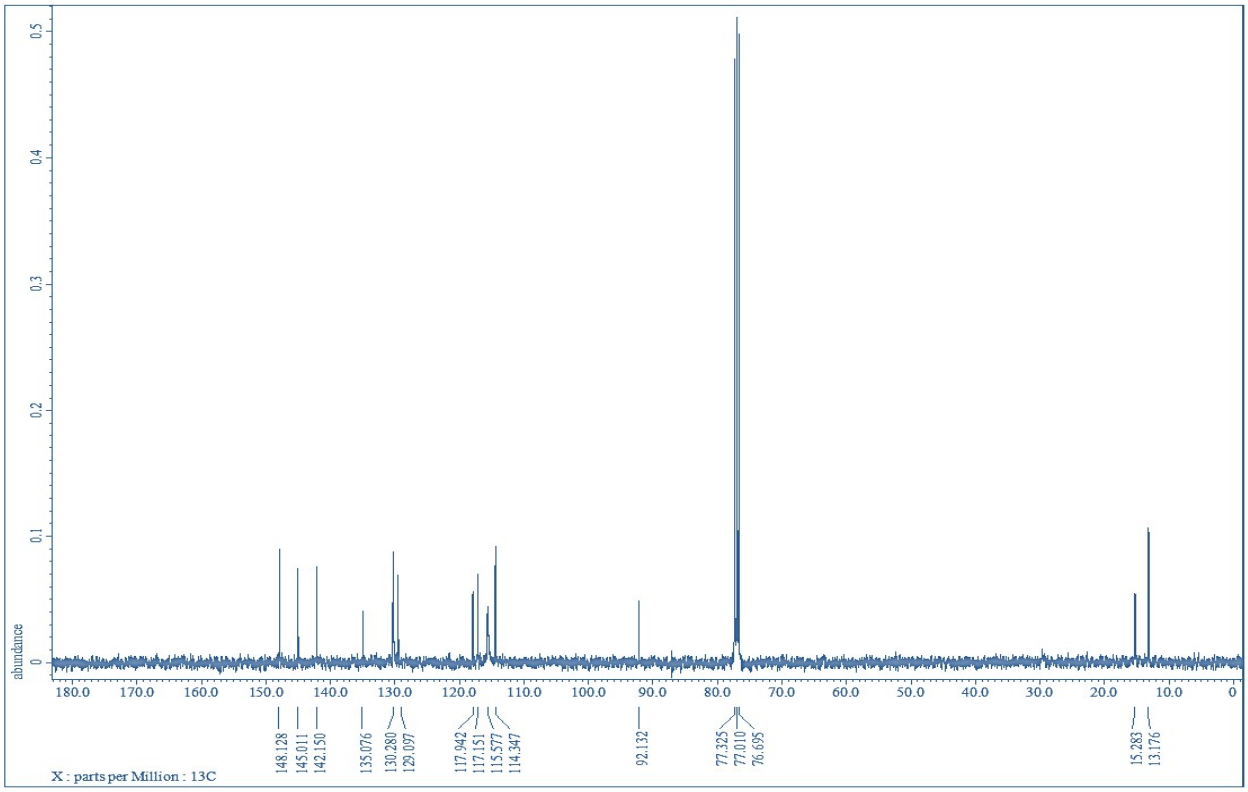
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-2'-methoxy-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7e)



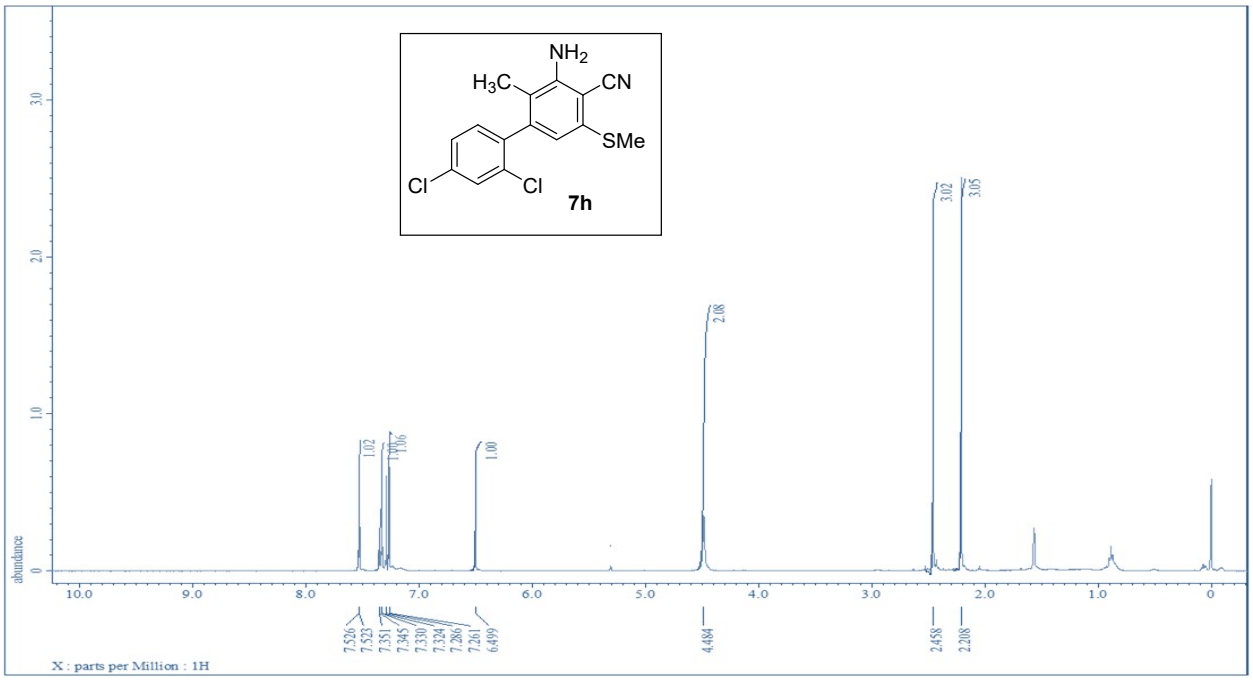


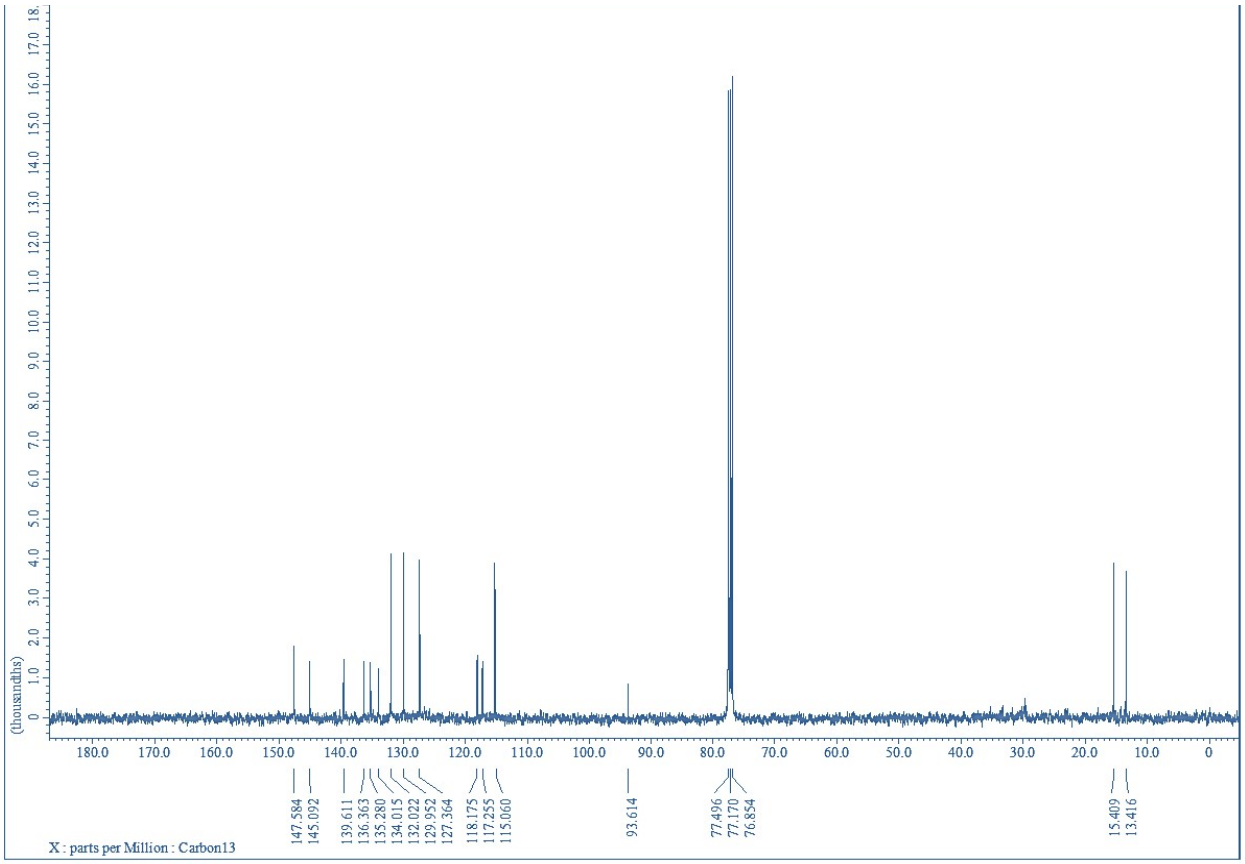
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-4'-fluoro-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7f)



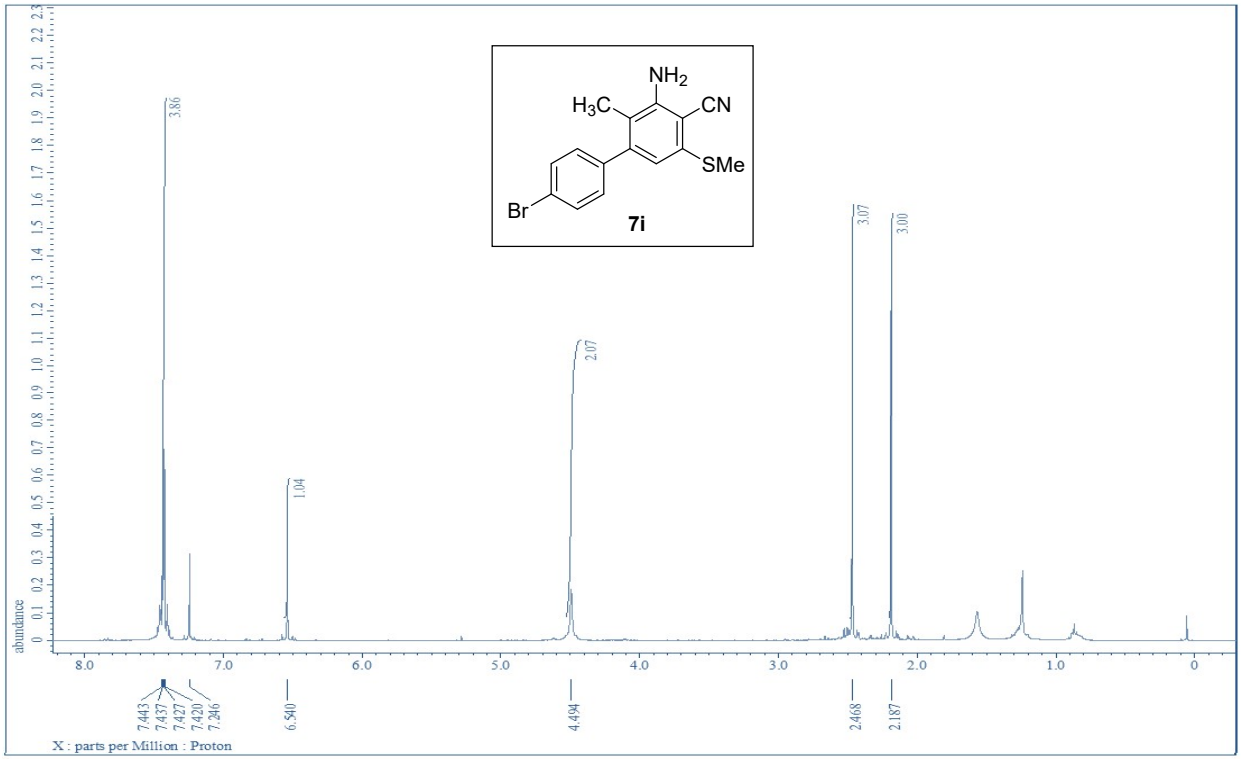


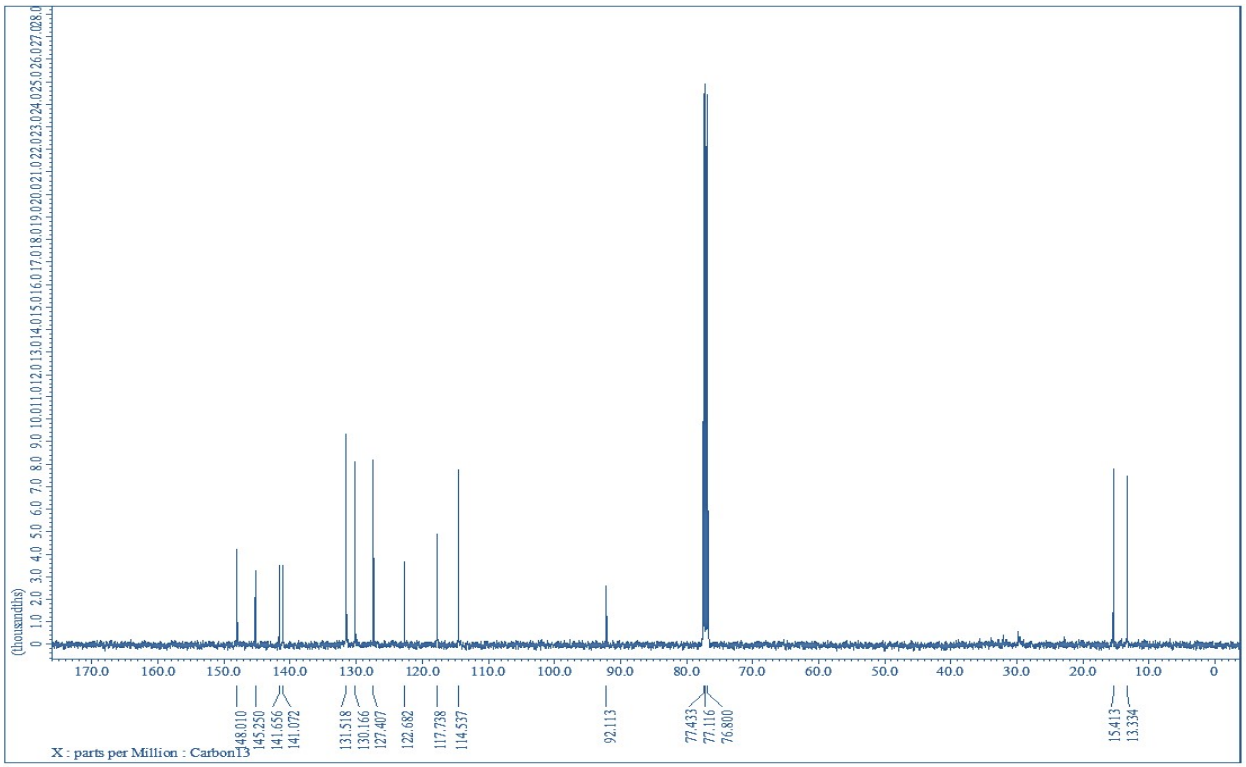
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-4'-chloro-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7g)



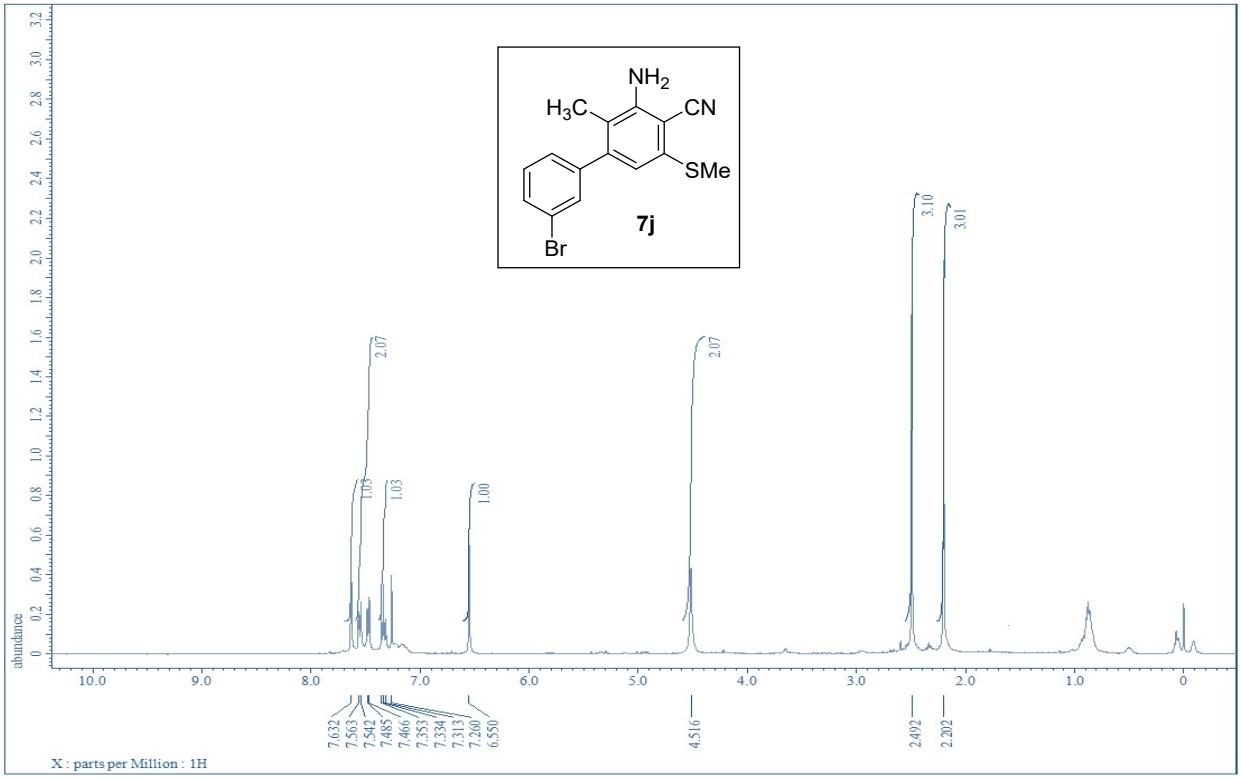


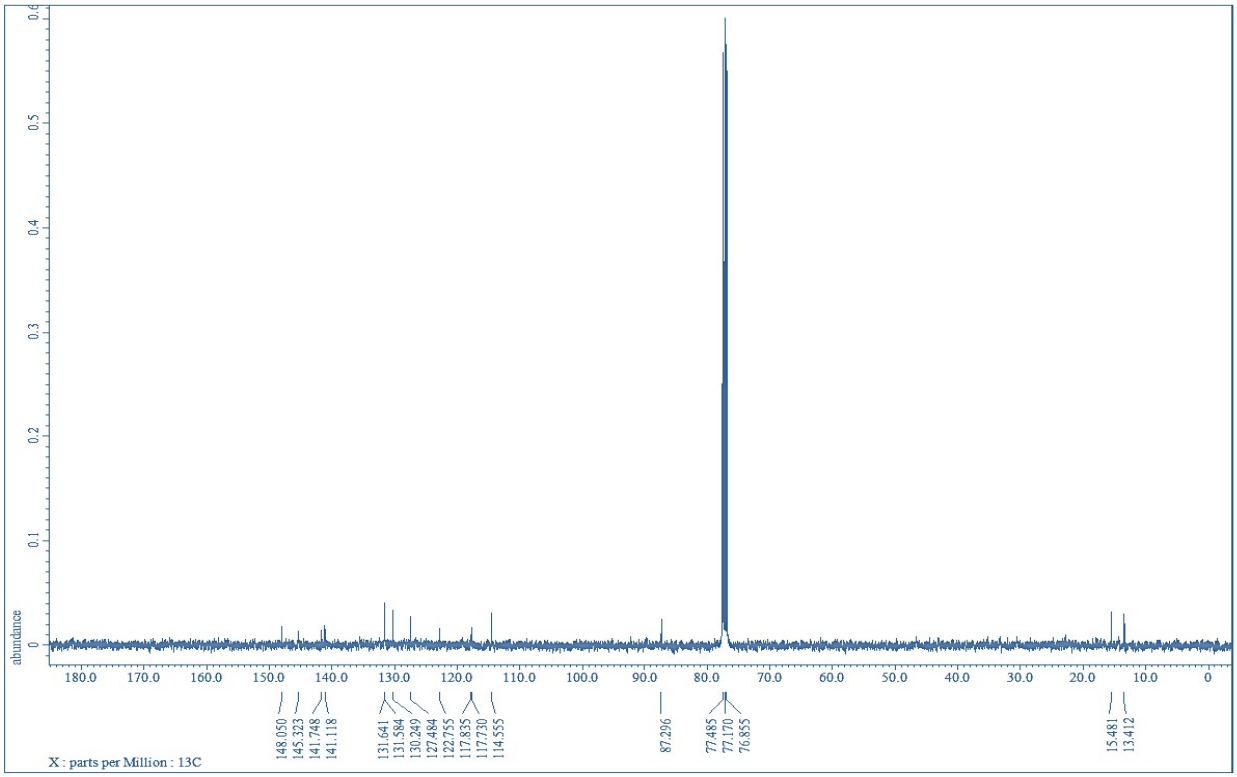
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-2',4'-dichloro-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7h)



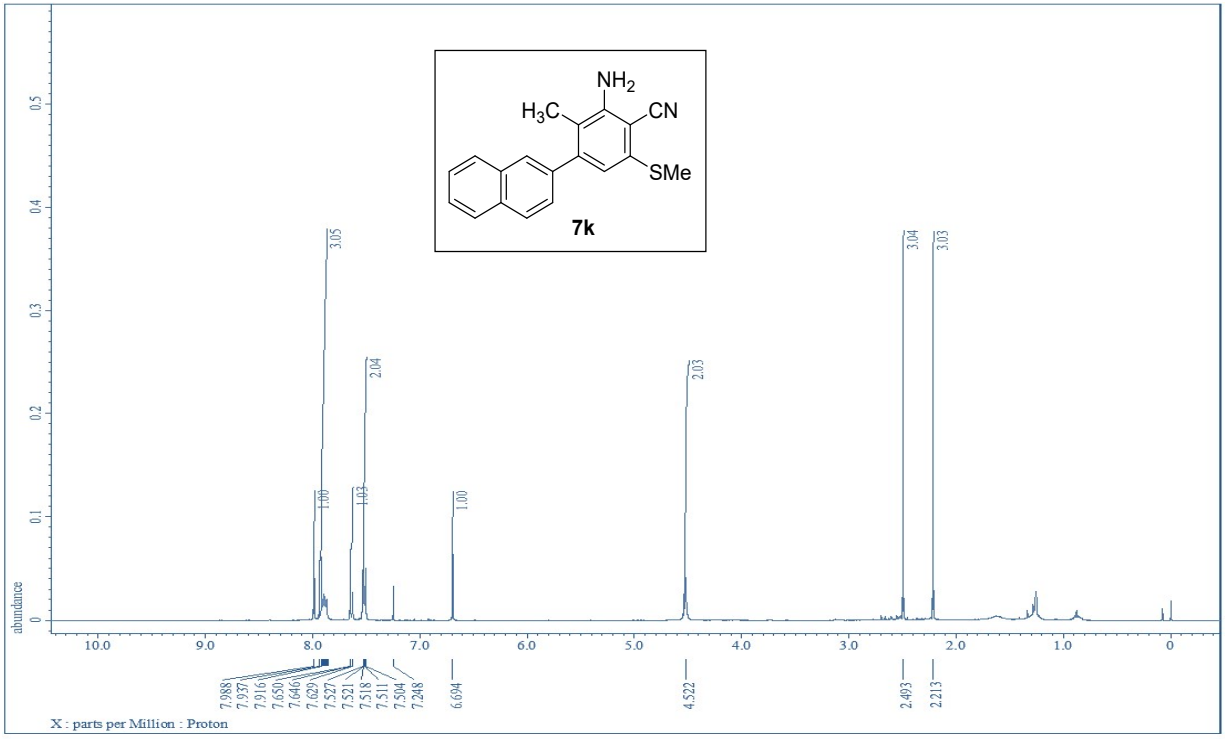


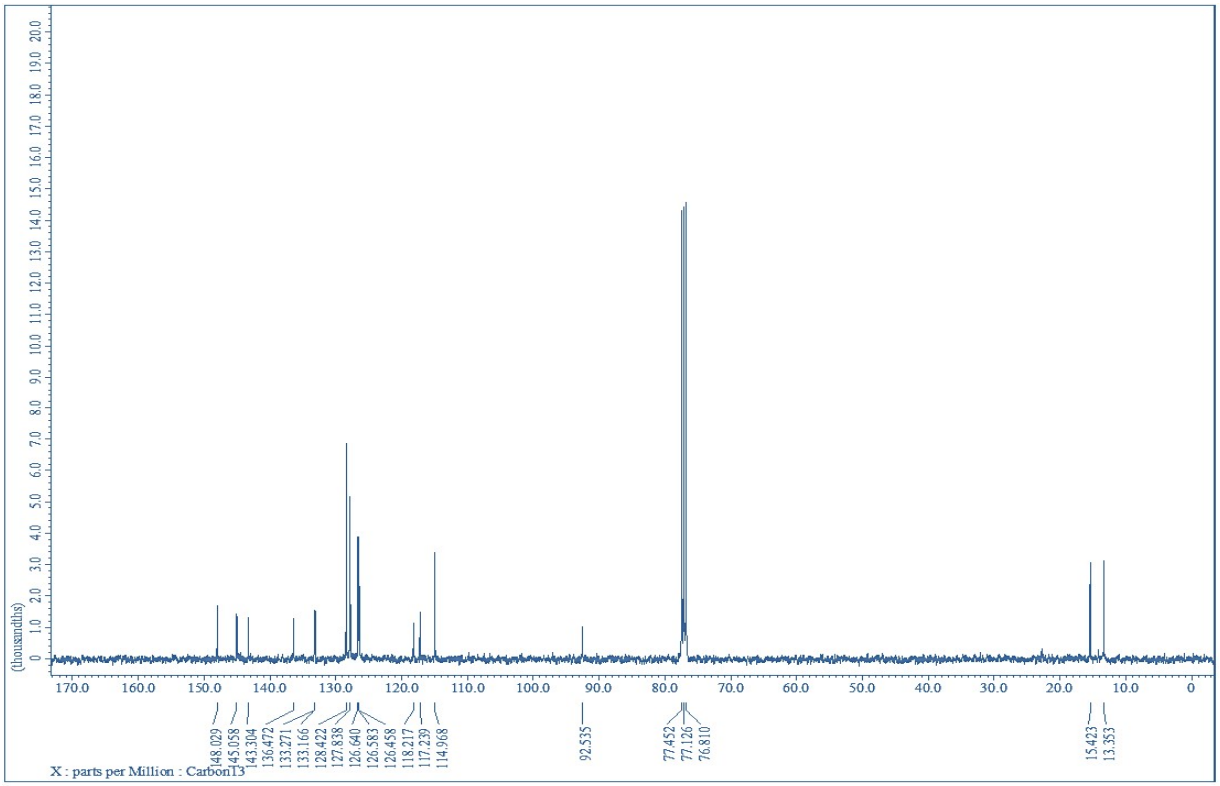
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-4'-bromo-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7i)



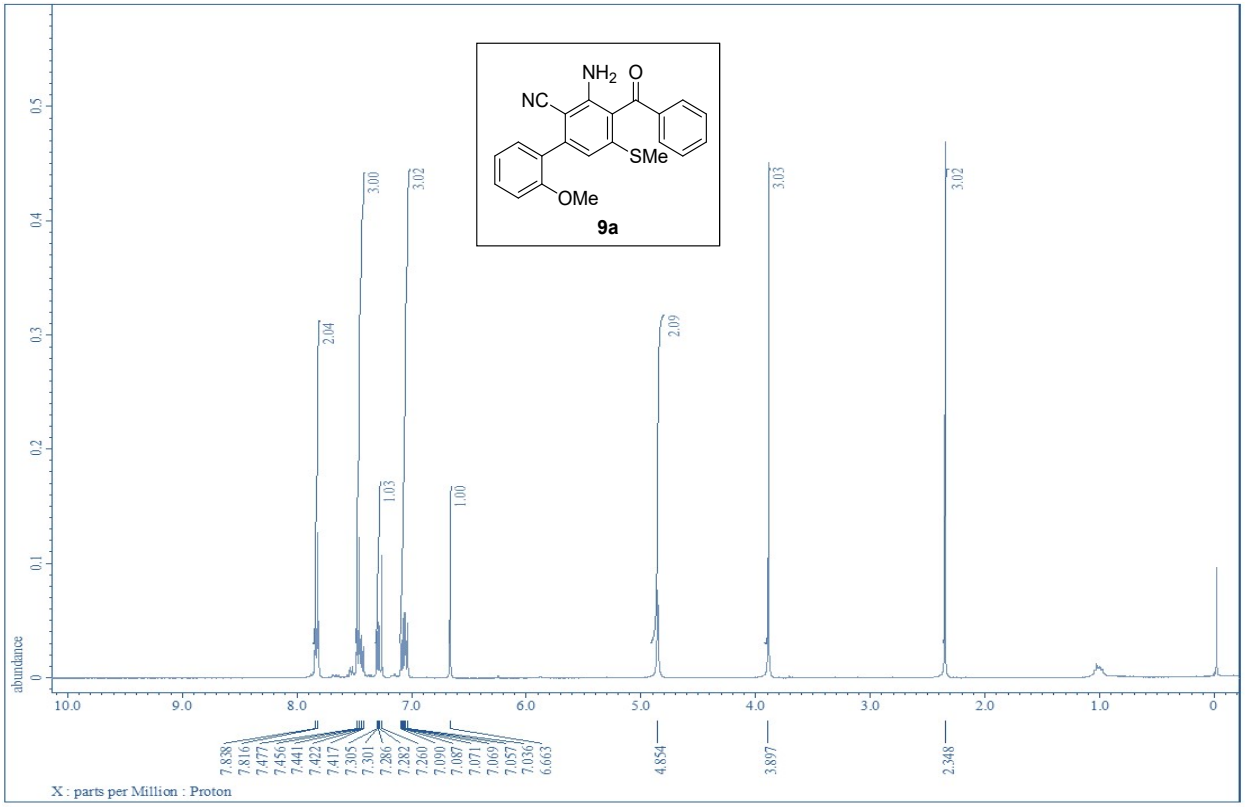


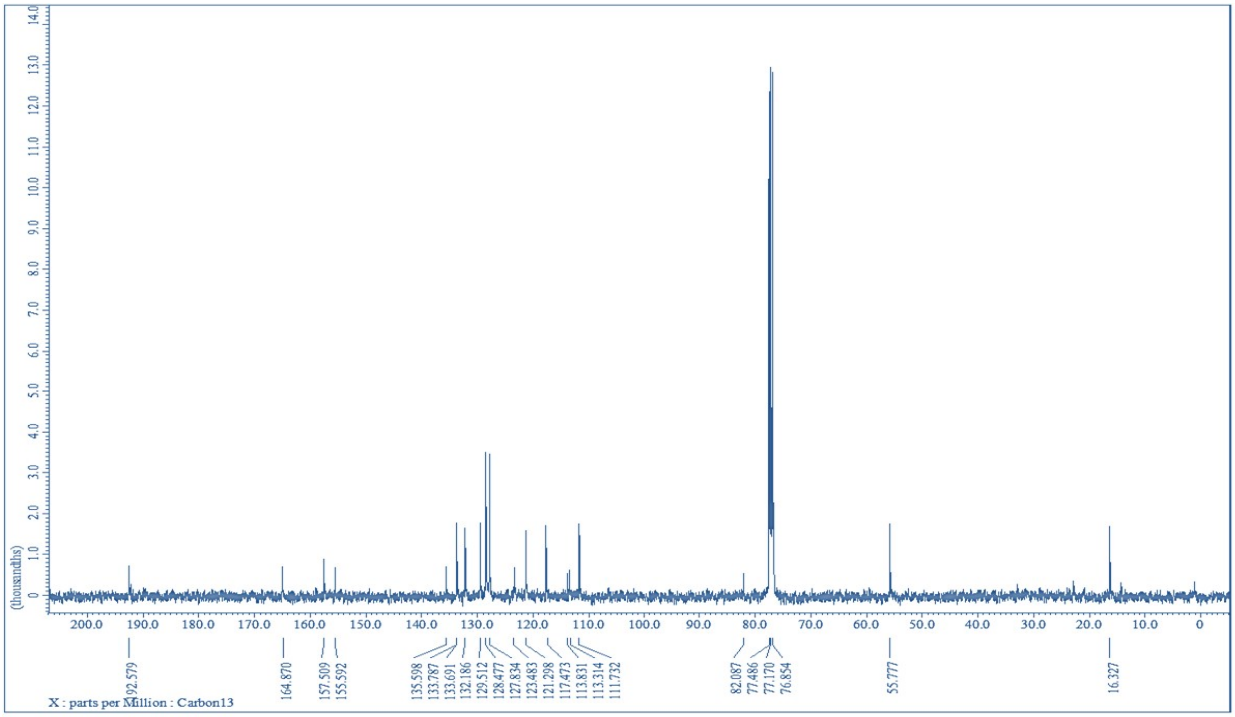
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-3'-bromo-2-methyl-5-(methylthio)-[1,1'-biphenyl]-4-carbonitrile (7j)



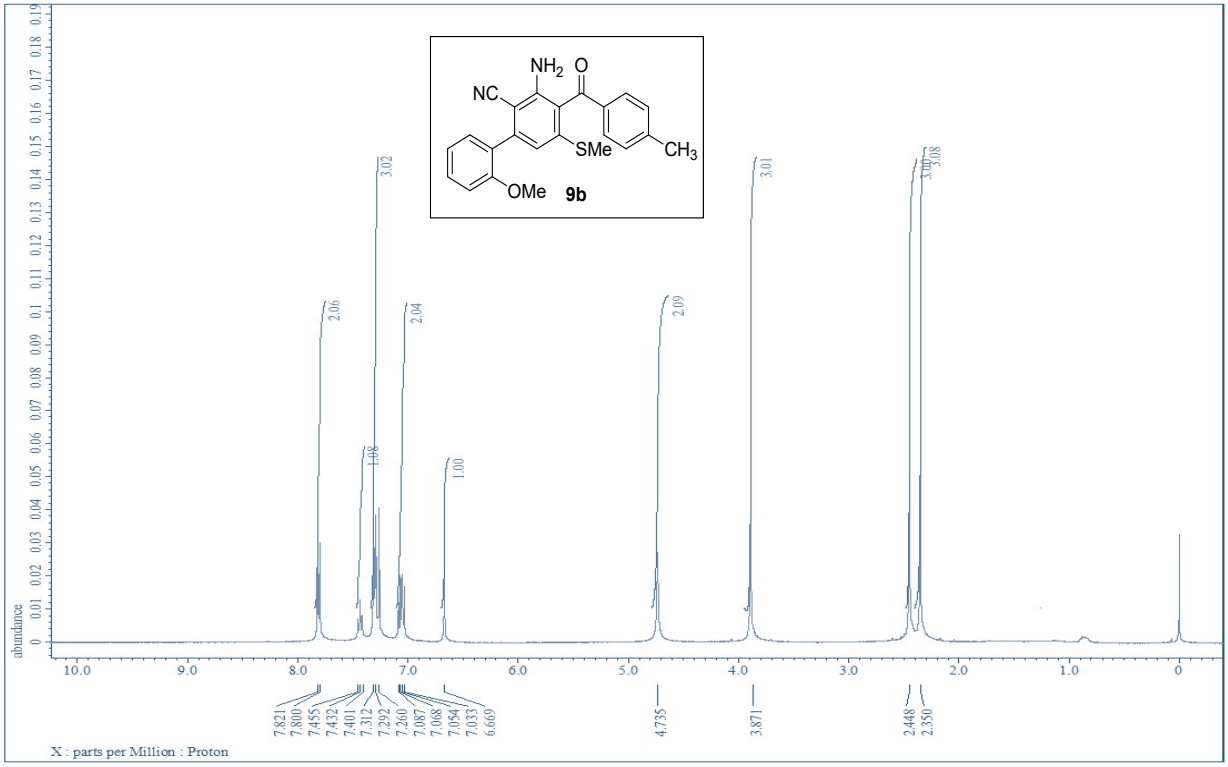


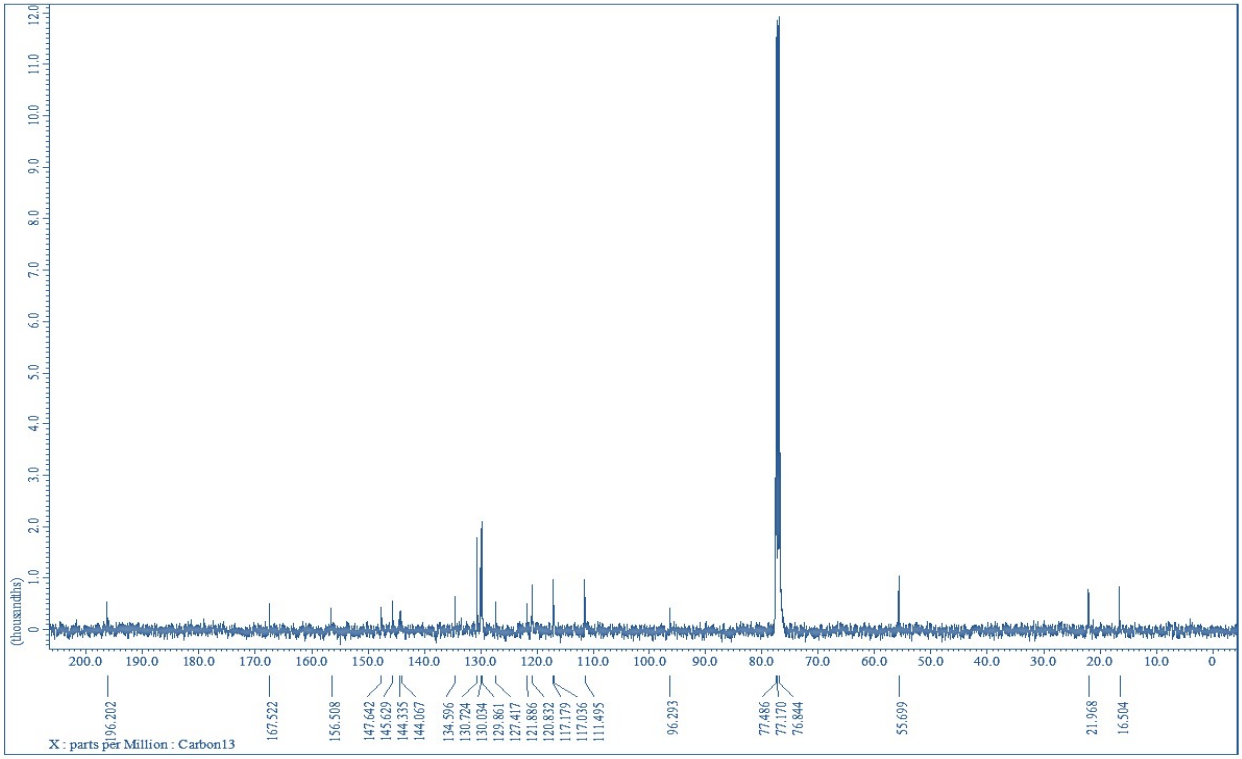
^{1}H NMR and ^{13}C NMR spectrum of 2-amino-3-methyl-6-(methylthio)-4-(naphthalen-2-yl)benzonitrile (7k)



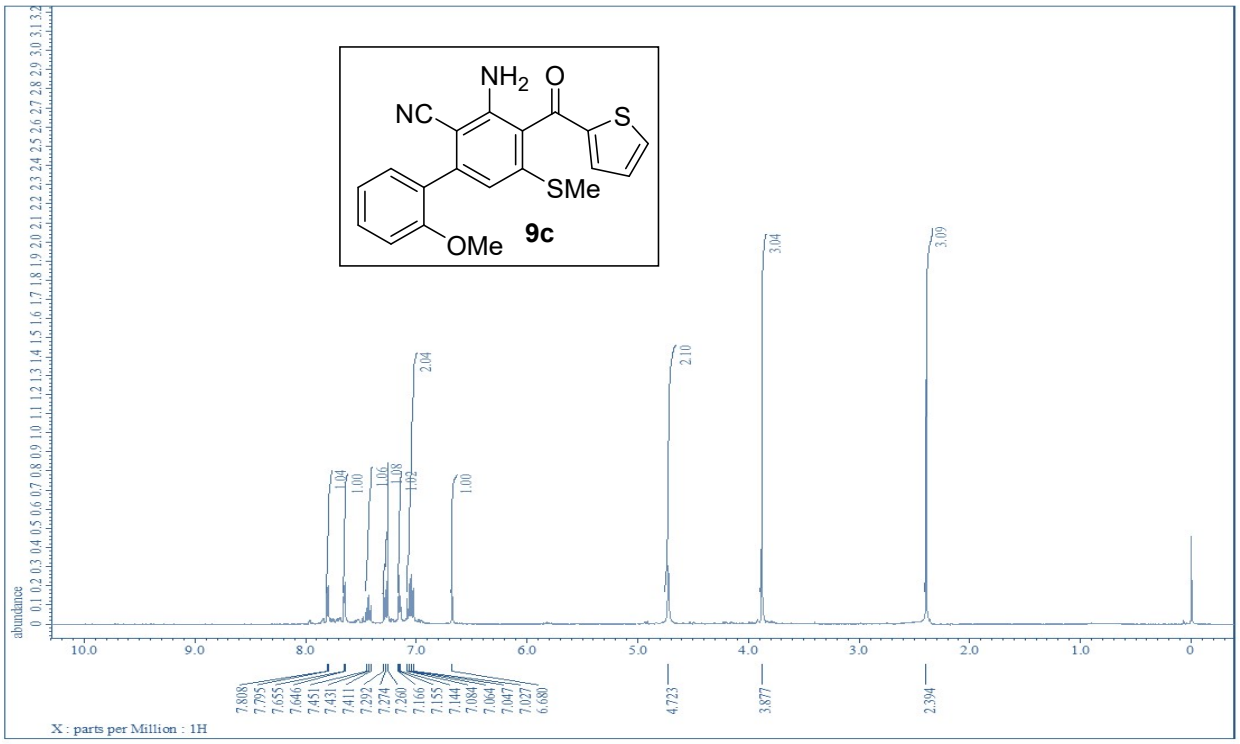


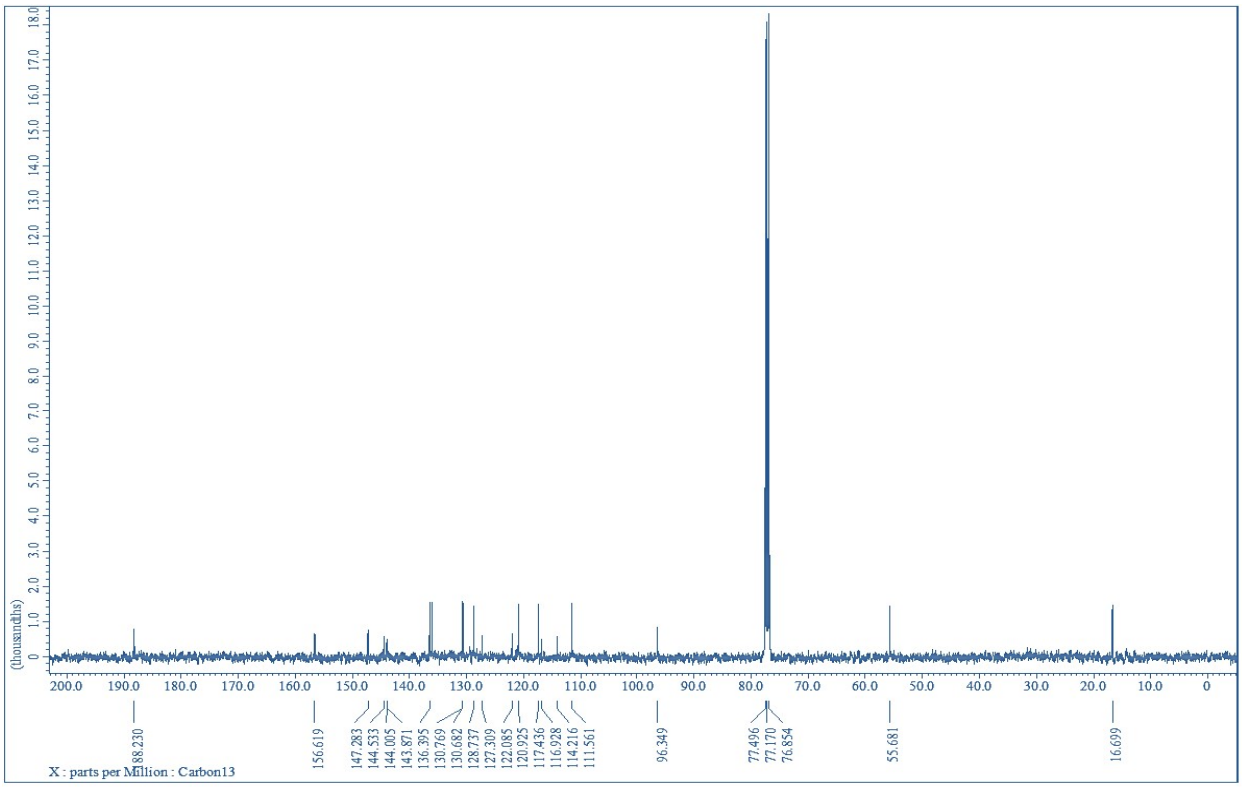
^{1}H NMR and ^{13}C NMR spectrum of 3-Amino-4-benzoyl-2'-methoxy-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (9a)



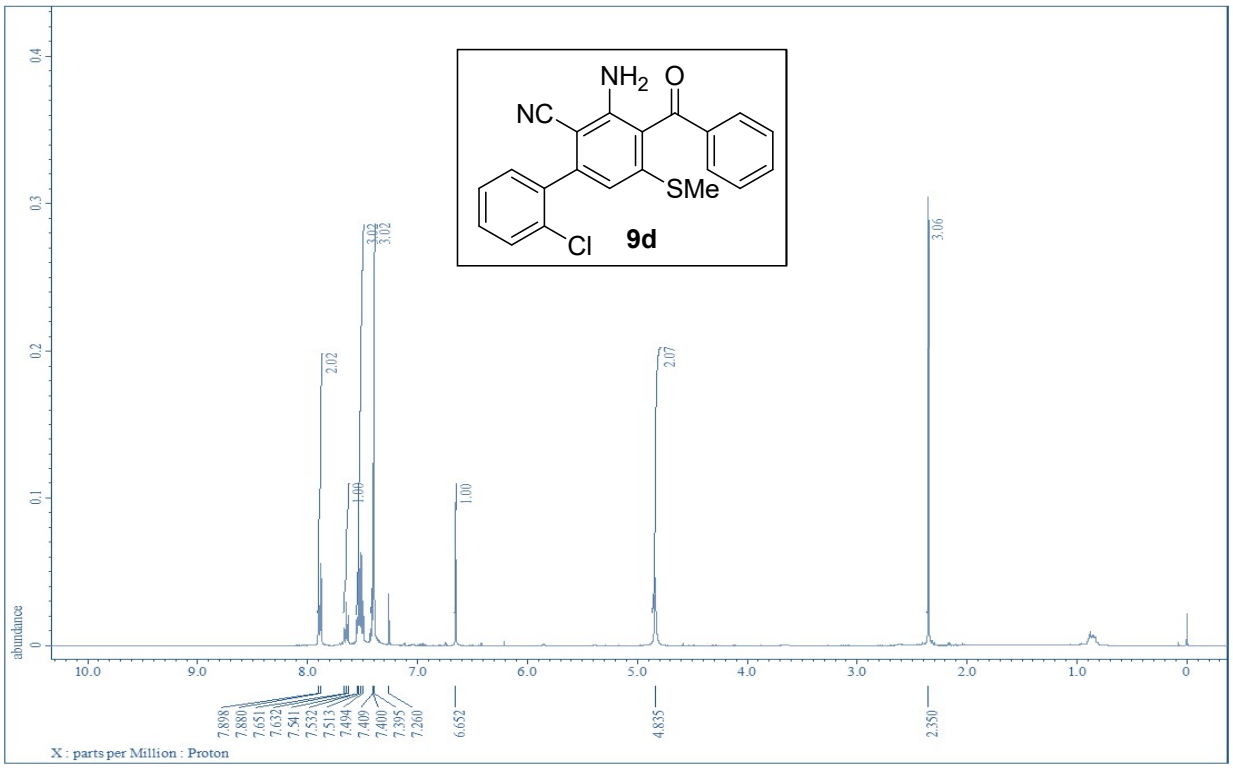


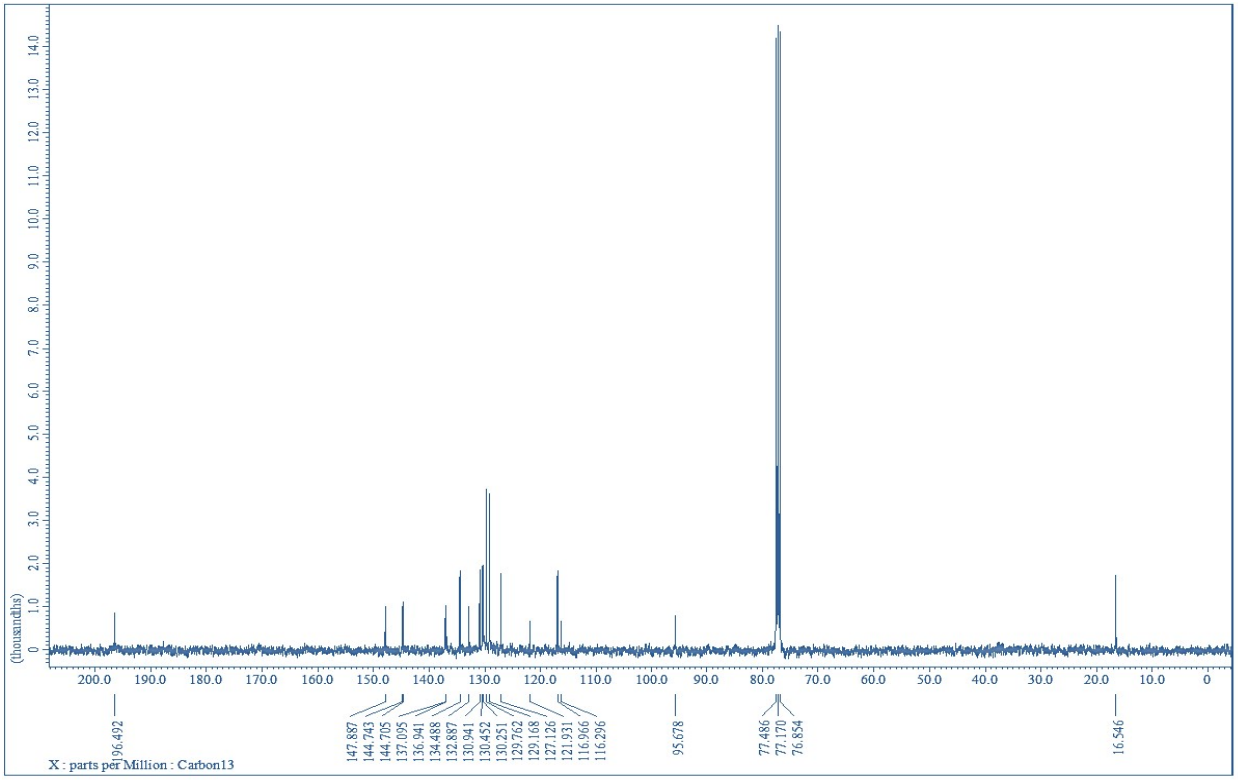
^{1}H NMR and ^{13}C NMR spectrum of 3-Amino-2'-methoxy-4-(4-methylbenzoyl)-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (9b)



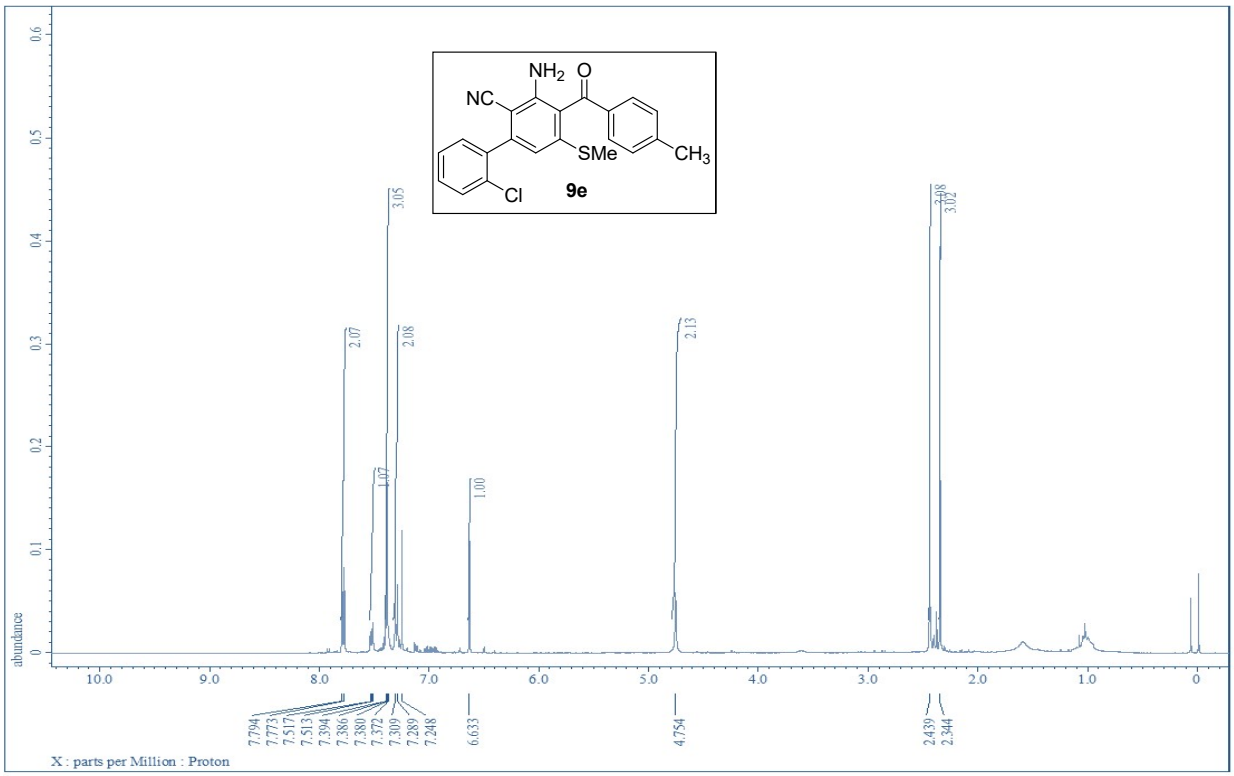


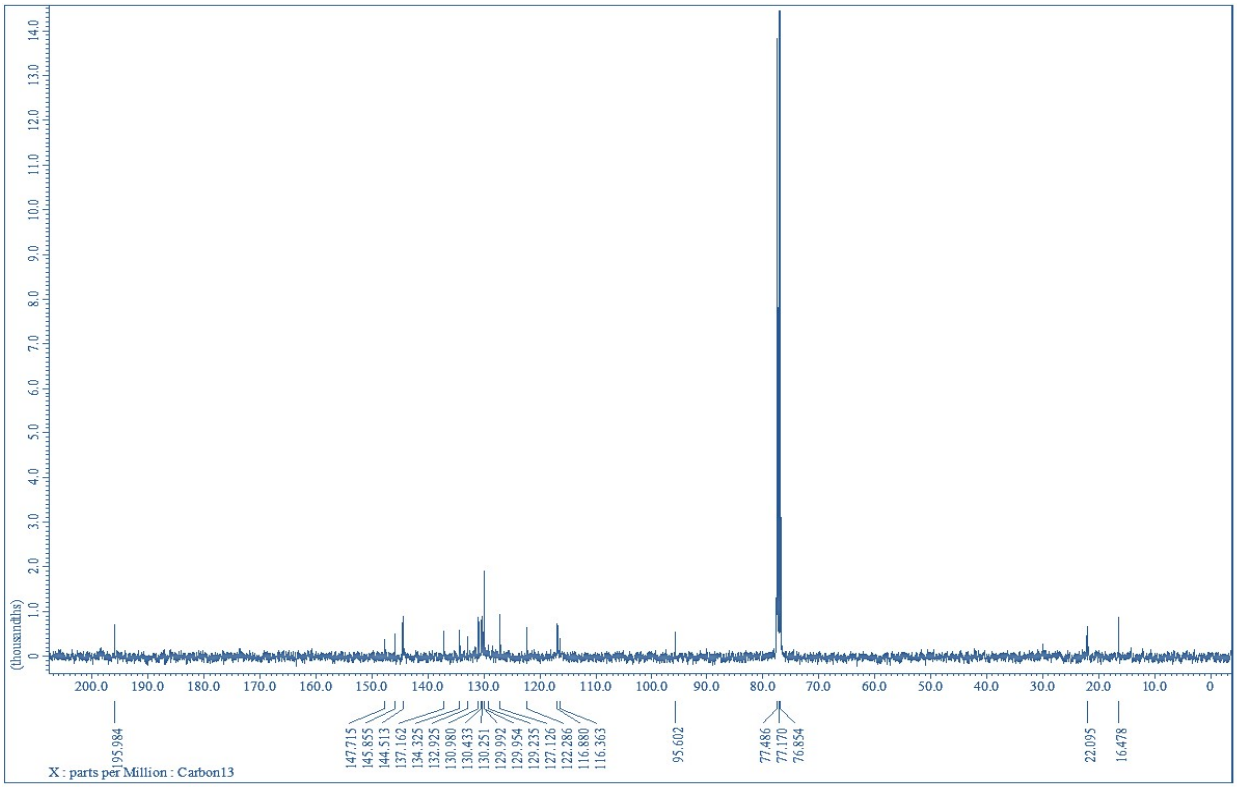
^{1}H NMR and ^{13}C NMR spectrum of 3-Amino-2'-methoxy-5-(methylthio)-4-(thiophene-2-carbonyl)-[1,1'-biphenyl]-2-carbonitrile (9c)



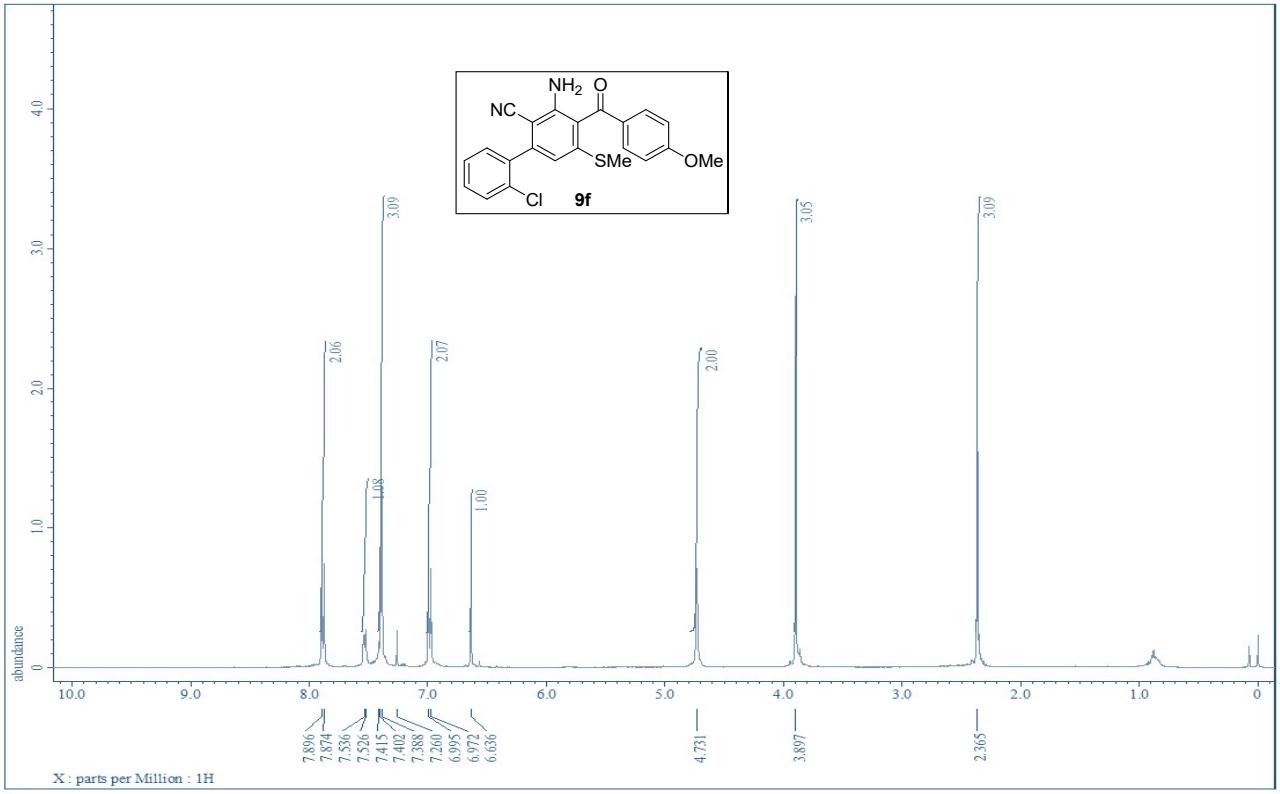


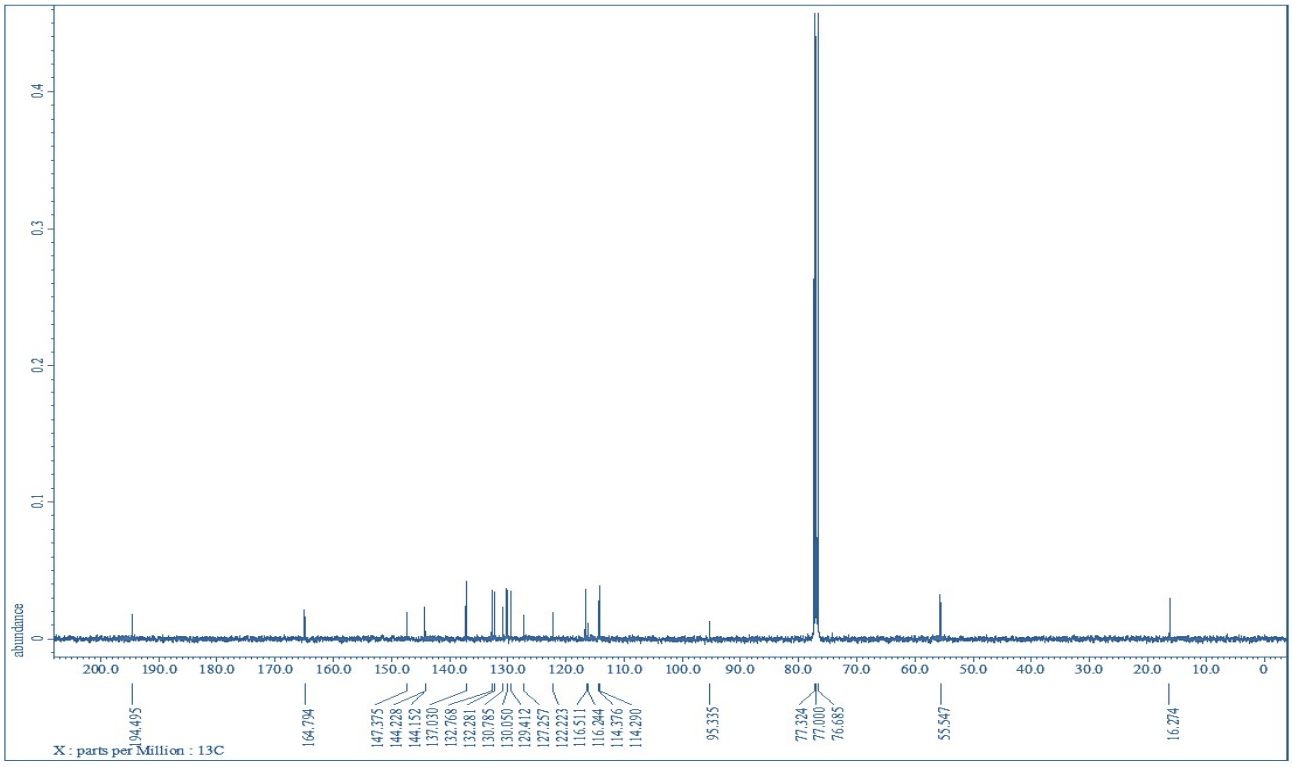
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-4-benzoyl-2'-chloro-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (9d)



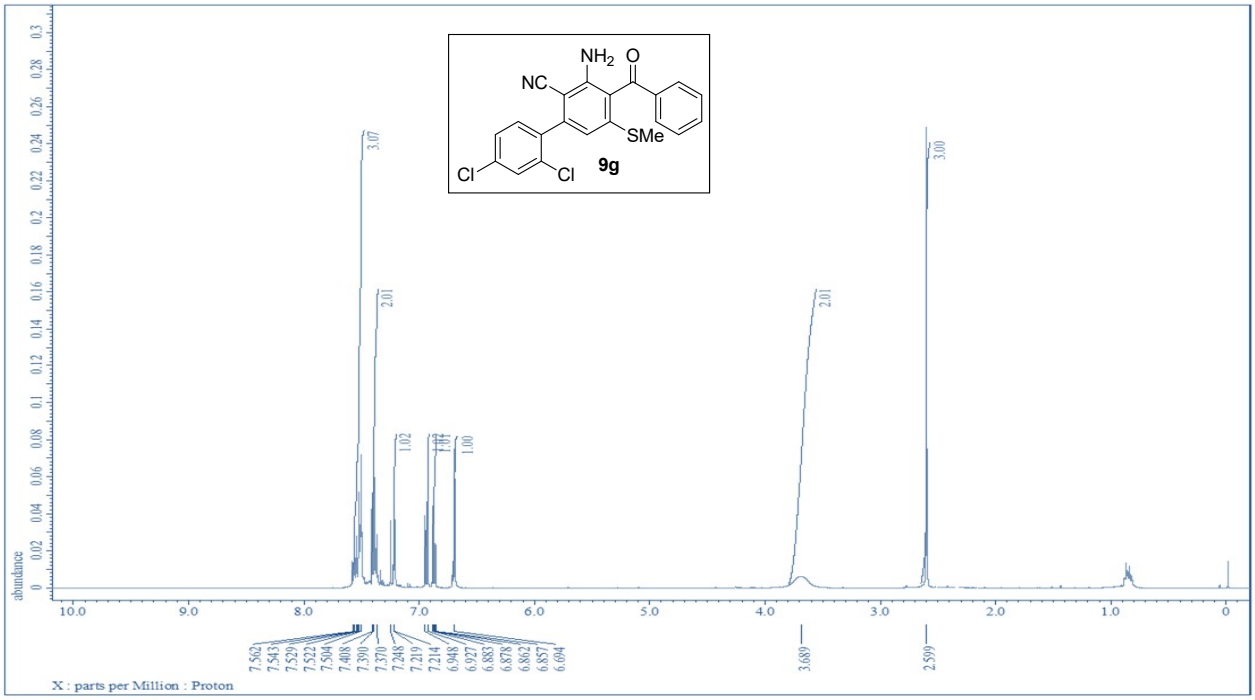


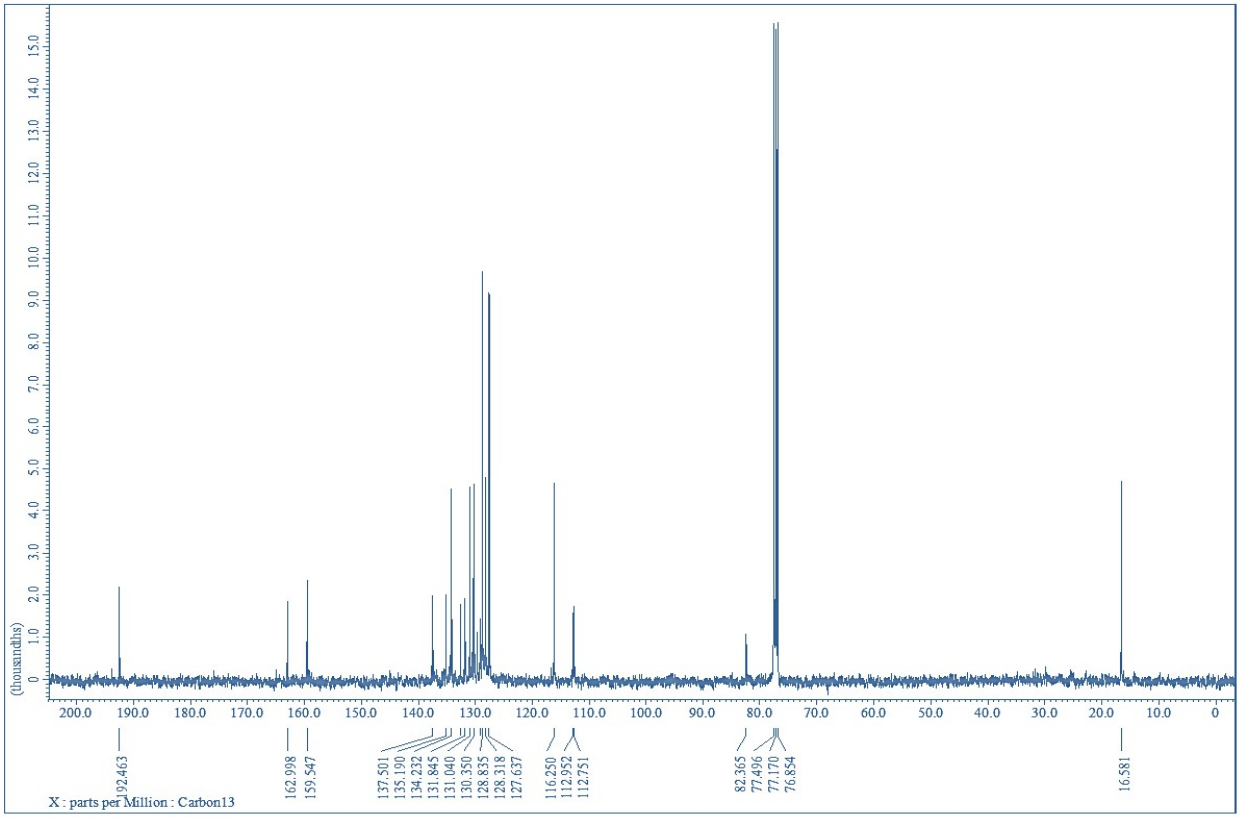
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-2'-chloro-4-(4-methylbenzoyl)-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (9e)



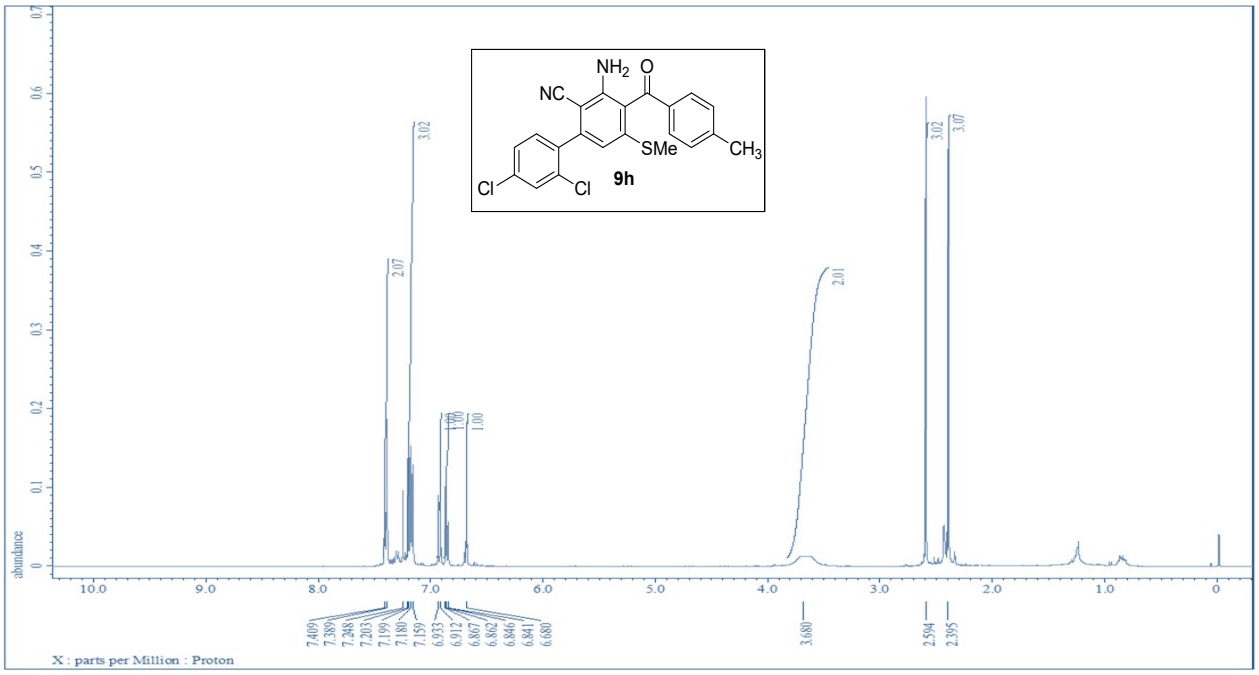


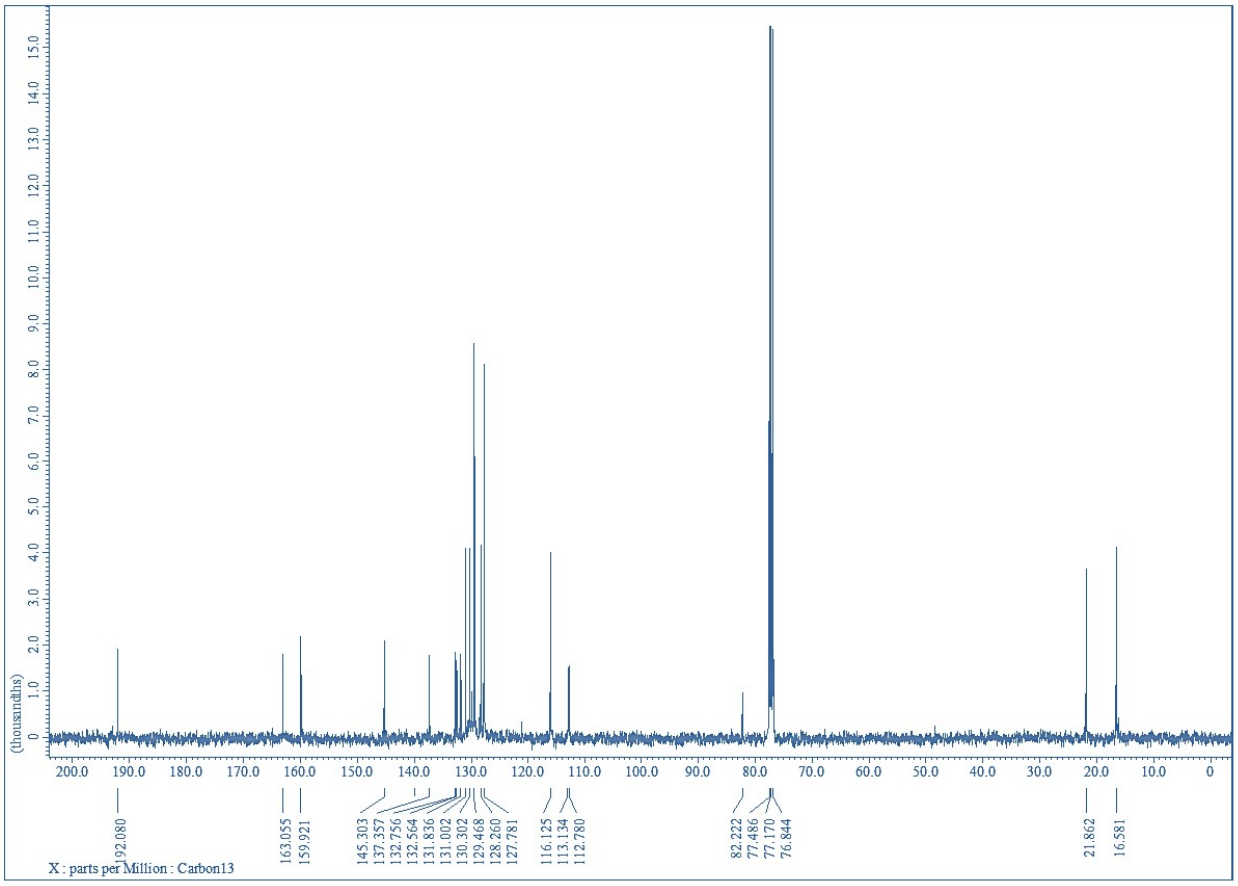
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-2'-chloro-4-(4-methoxybenzoyl)-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (9f)



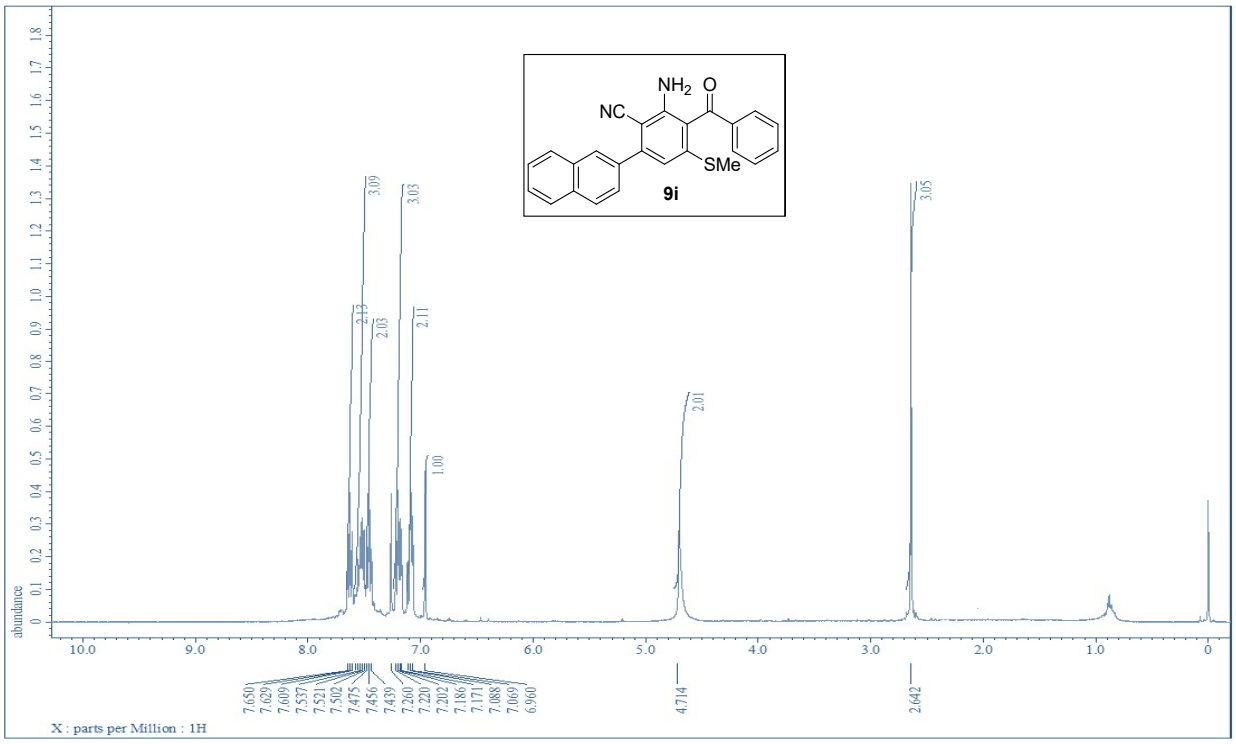


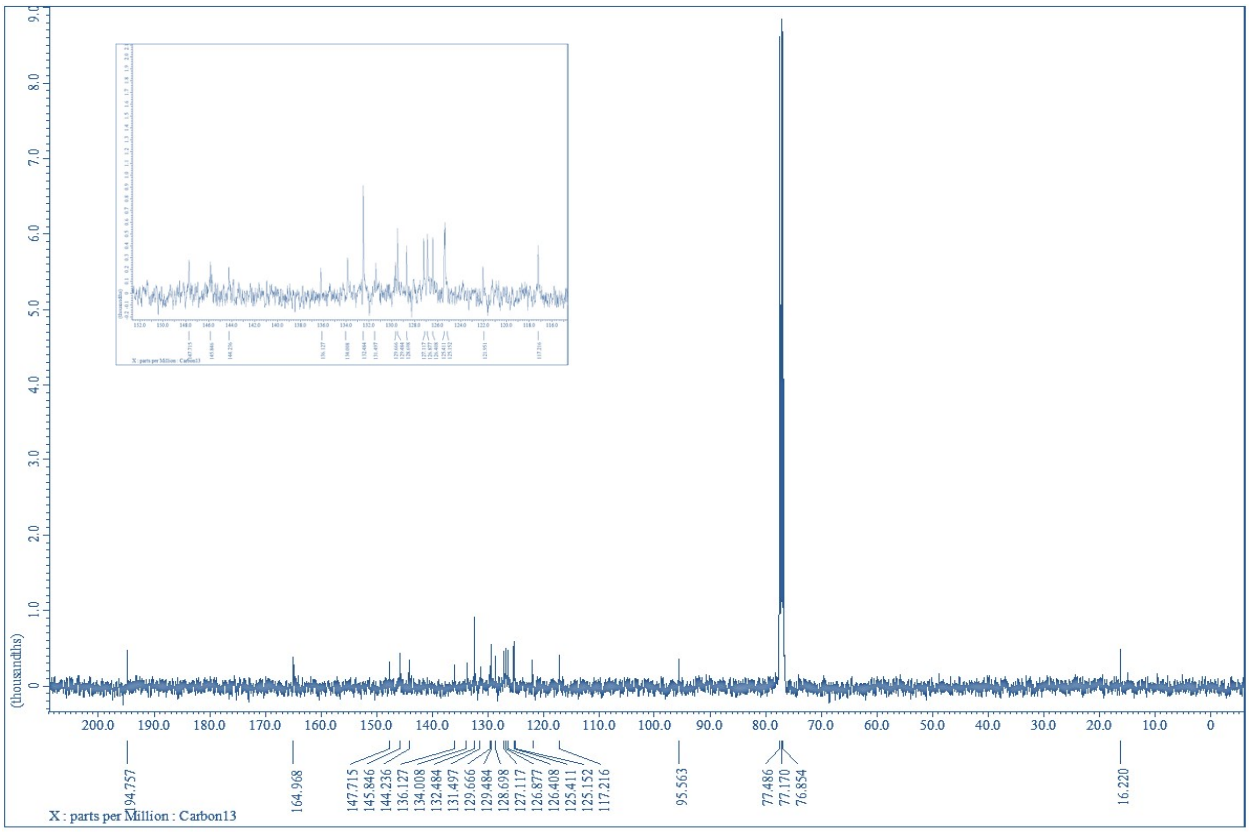
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-4-benzoyl-2',4'-dichloro-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (9g)



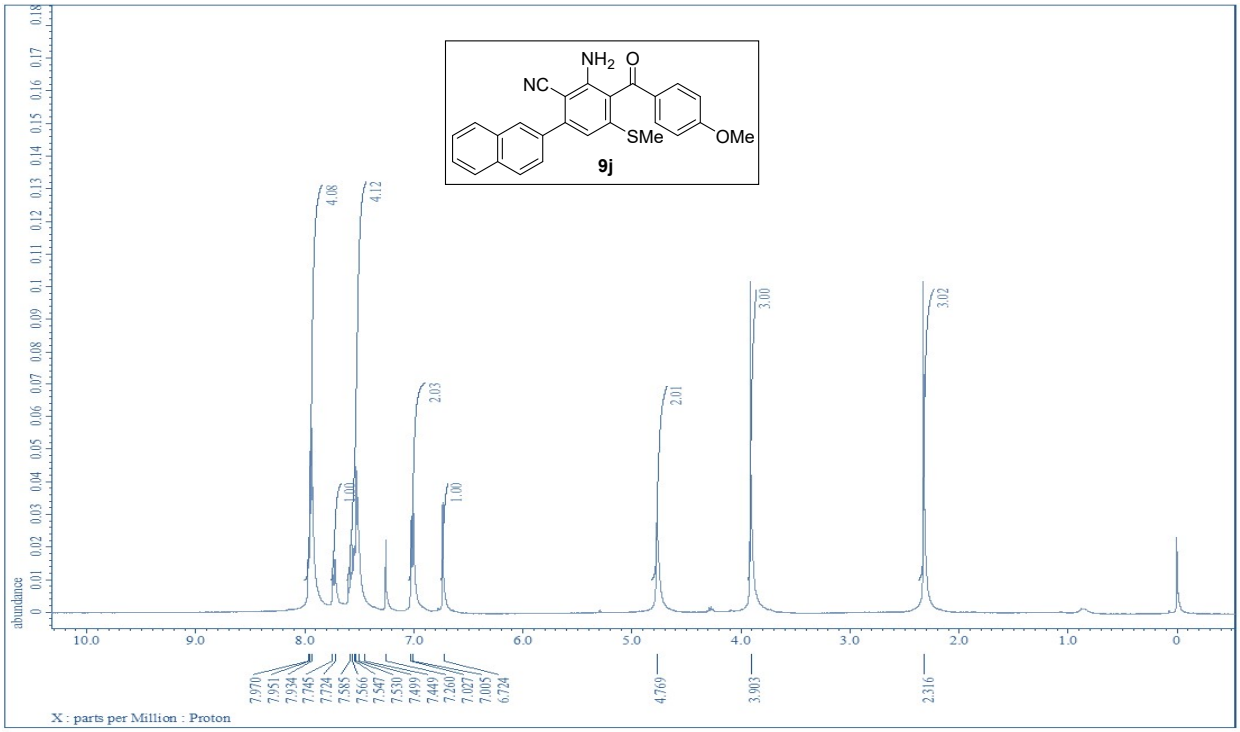


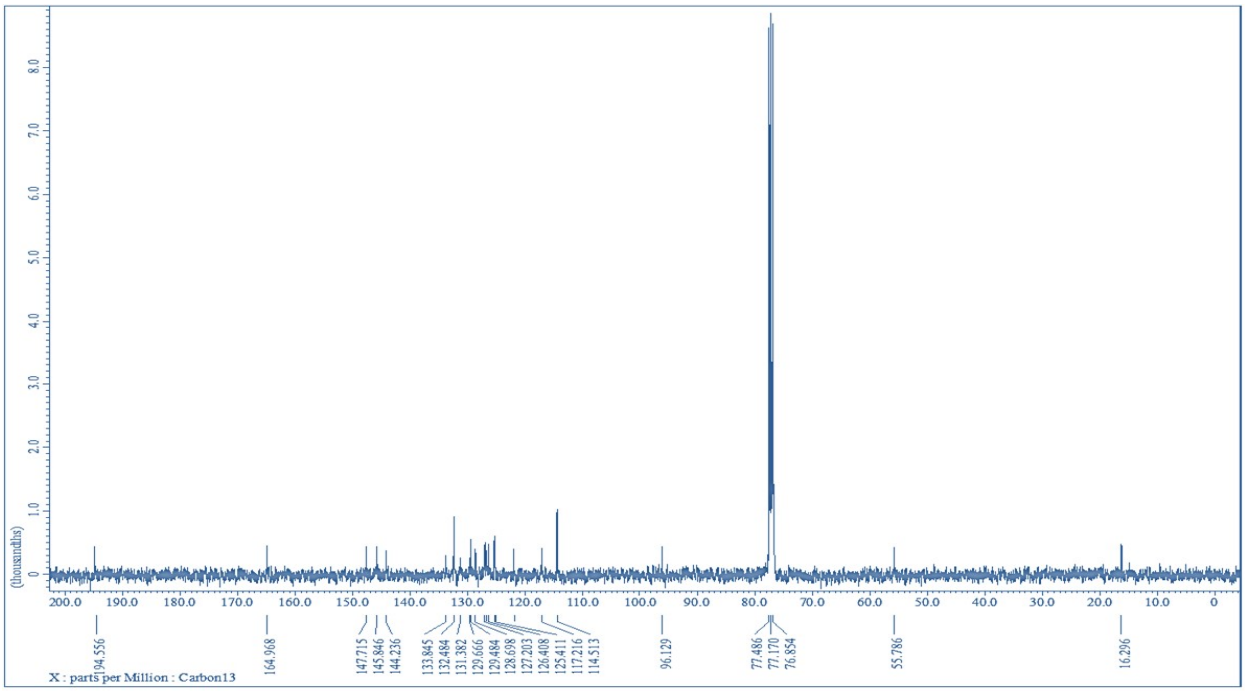
^{1}H NMR and ^{13}C NMR spectrum of 3-amino-2',4'-dichloro-4-(4-methylbenzoyl)-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile (9h)



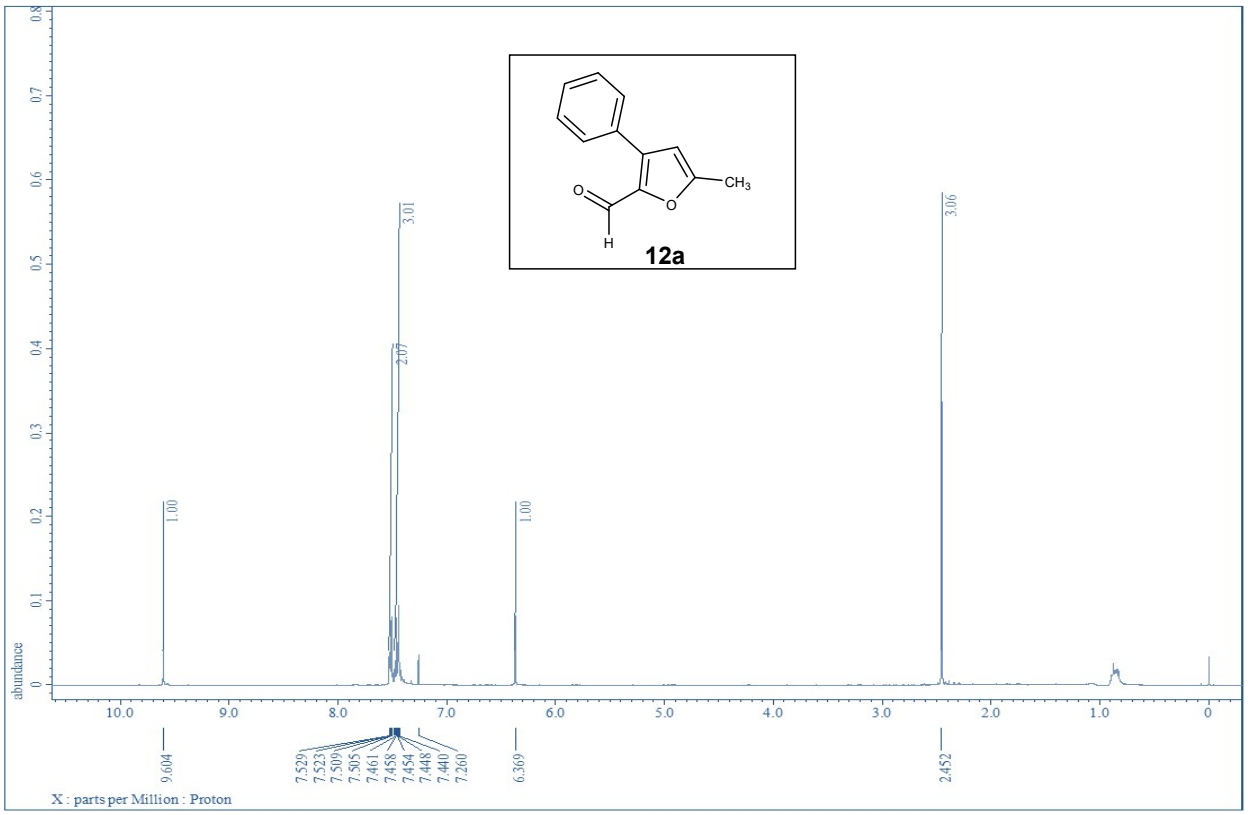


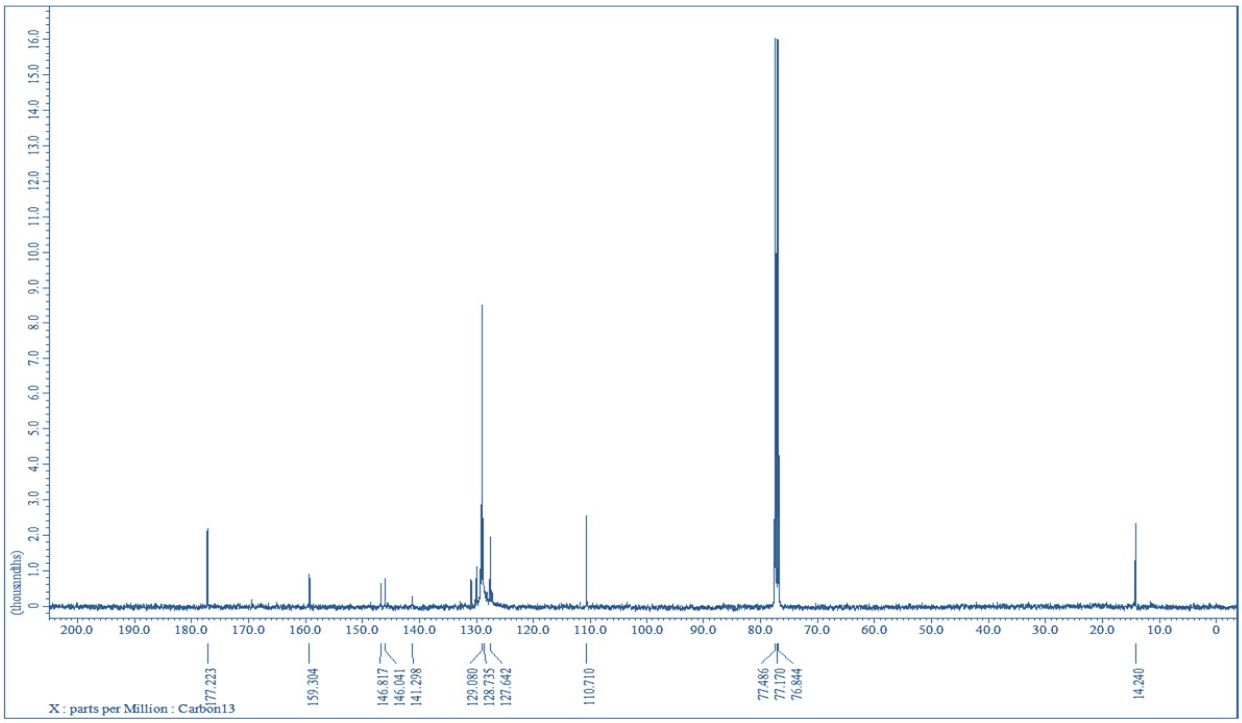
^{1}H NMR and ^{13}C NMR spectrum of 2-amino-3-(4-methoxybenzoyl)-4-(methylthio)-6-(naphthalen-2-yl)benzonitrile (9i)



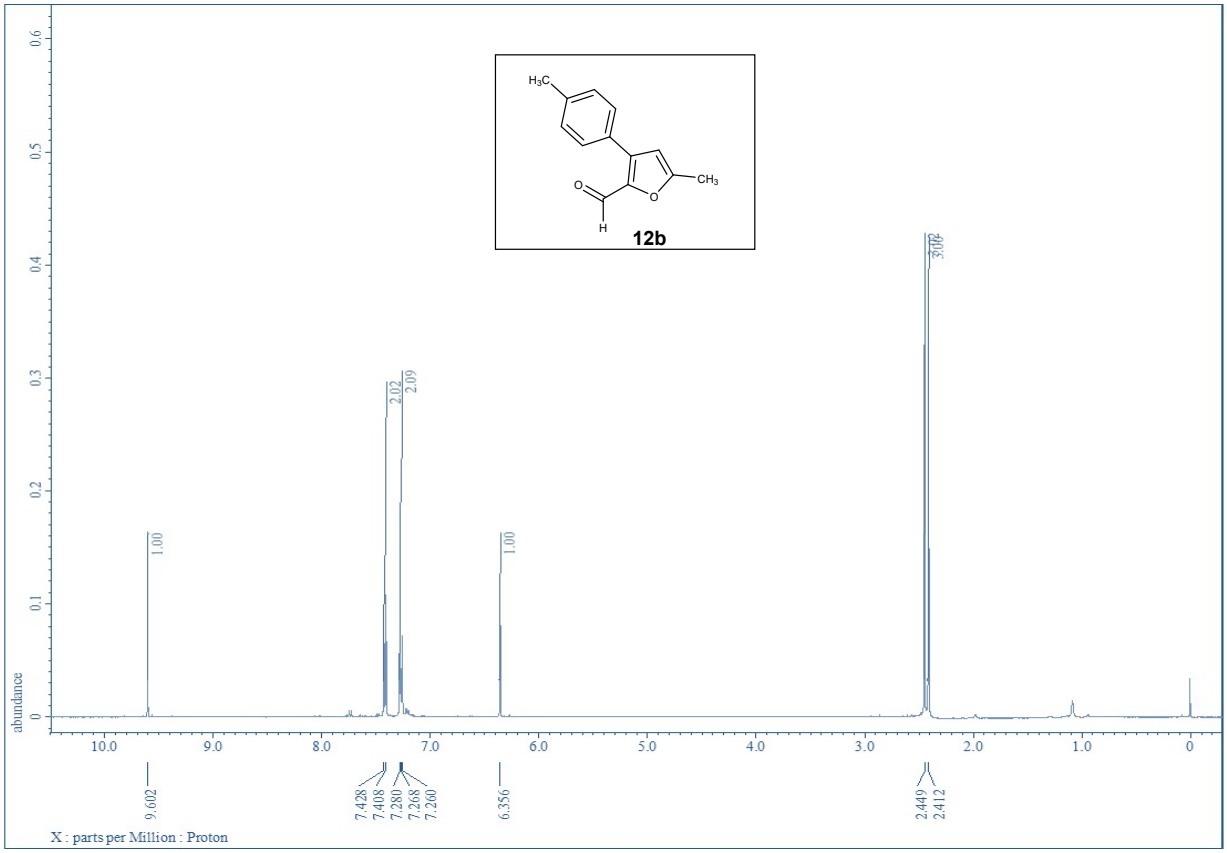


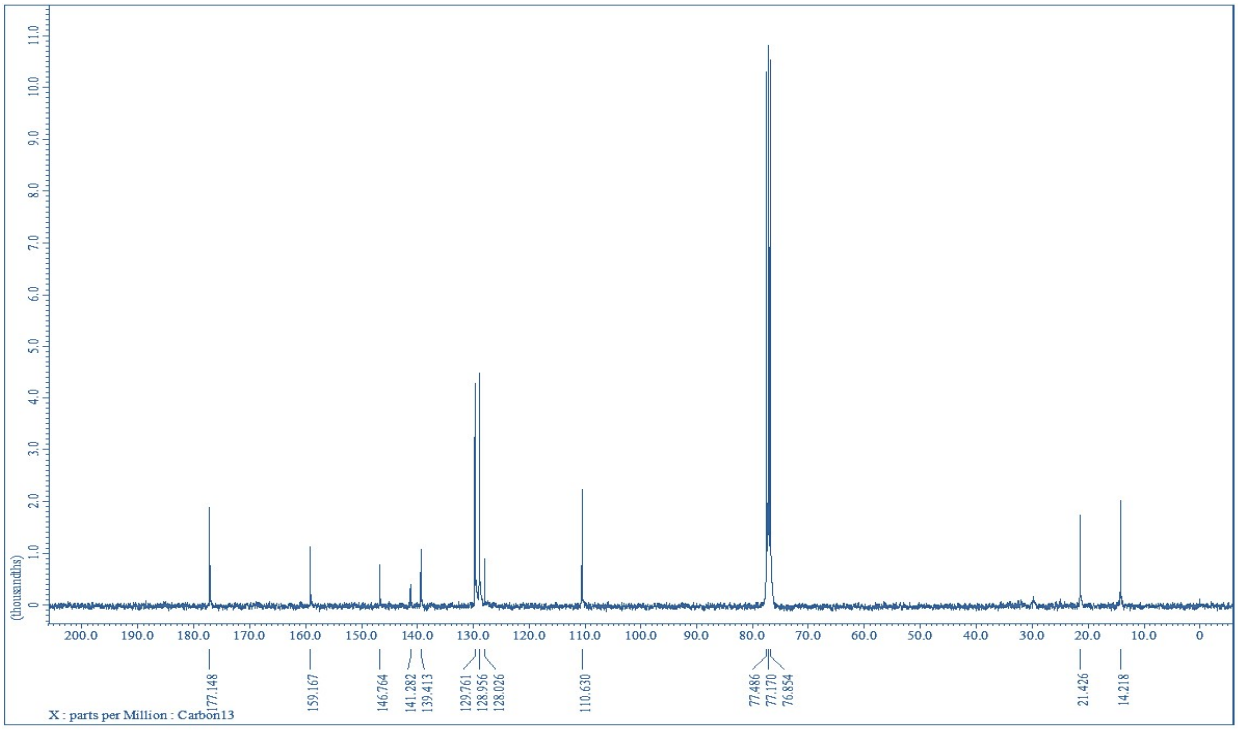
^{1}H NMR and ^{13}C NMR spectrum of 2-amino-3-(4-methoxybenzoyl)-4-(methylthio)-6-(naphthalen-2-yl)benzonitrile (9j)



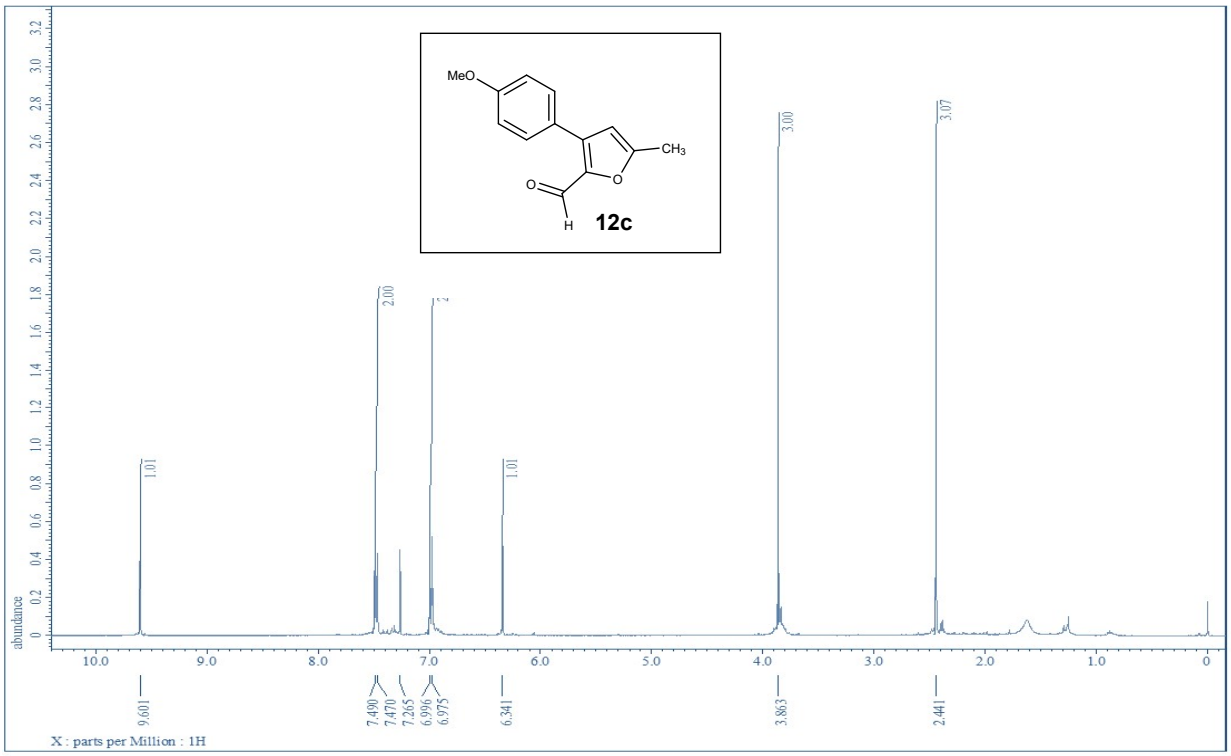


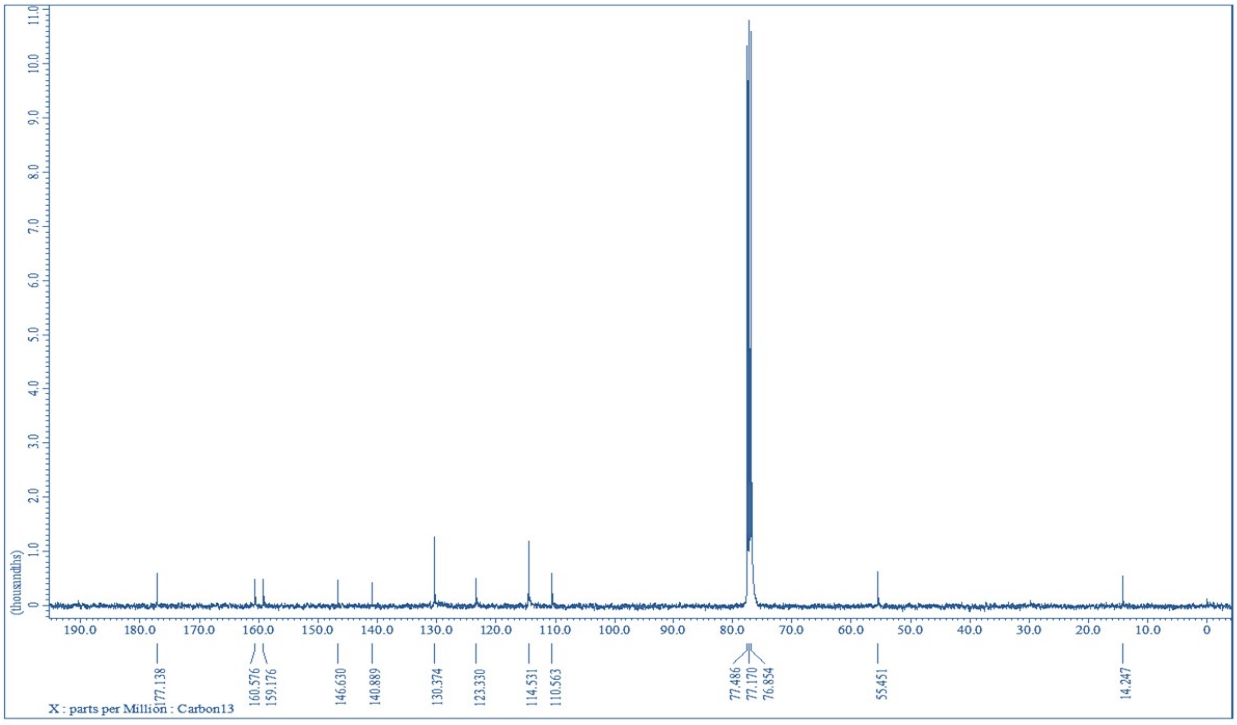
^{1}H NMR and ^{13}C NMR spectrum of 5-methyl-3-phenylfuran-2-carbaldehyde (12a)



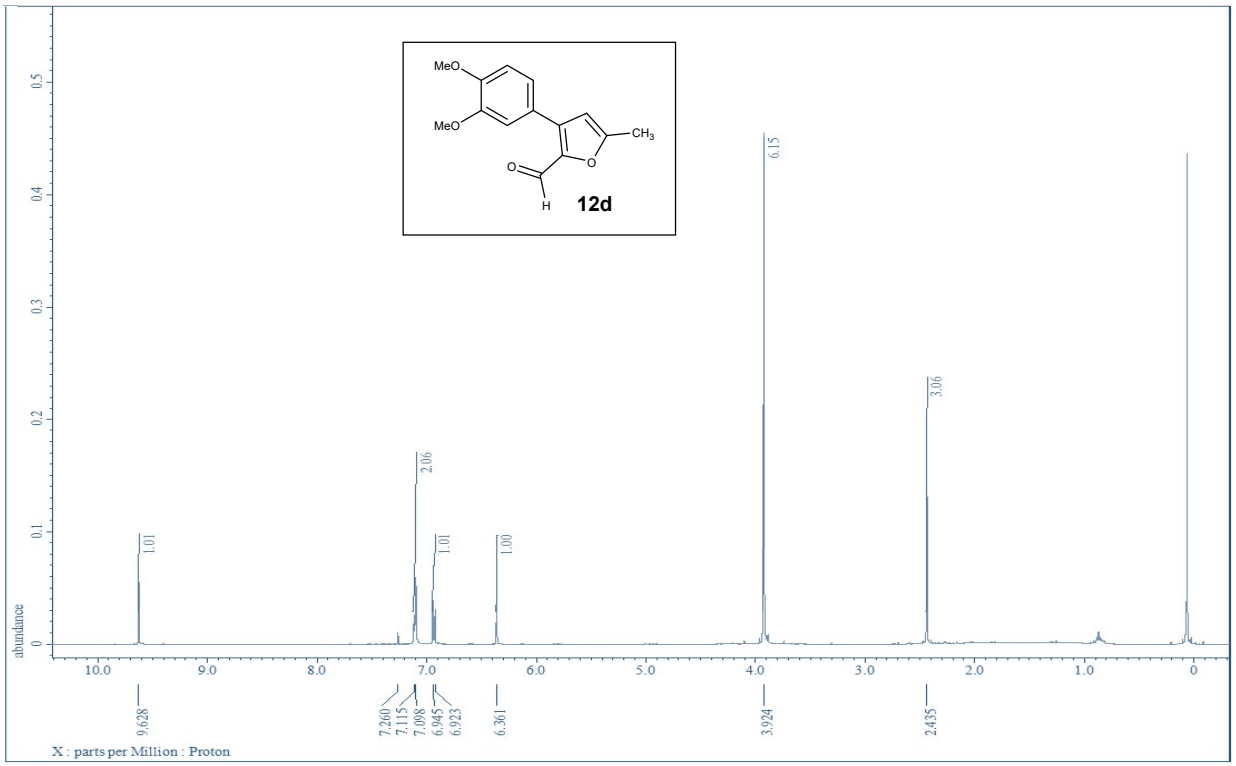


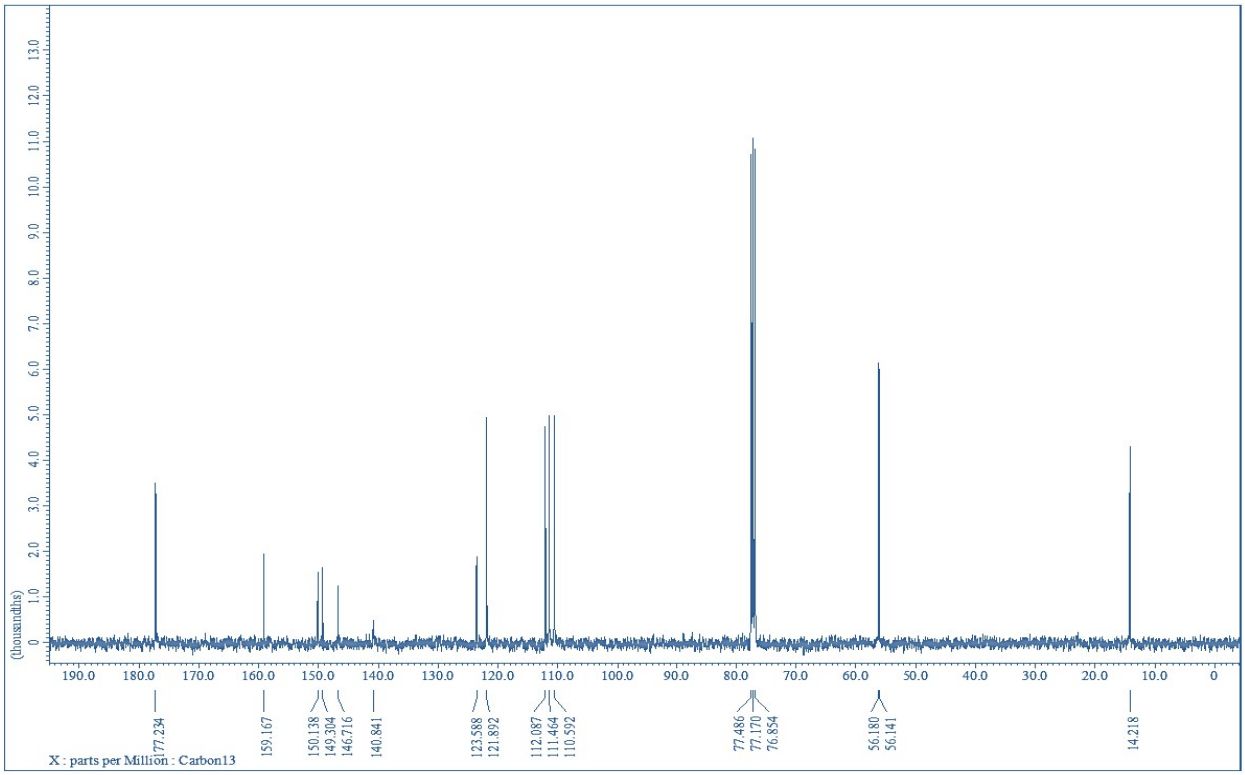
^{1}H NMR and ^{13}C NMR spectrum of 5-methyl-3-(*p*-tolyl)furan-2-carbaldehyde (12b)



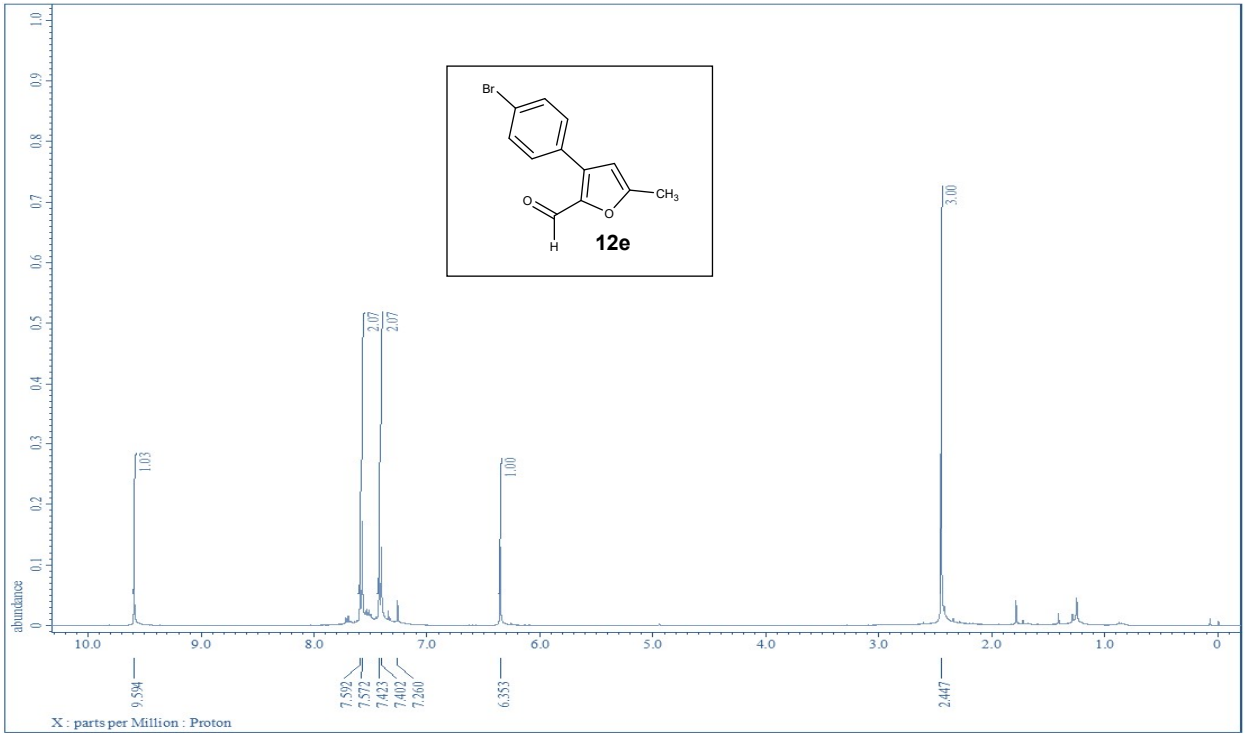


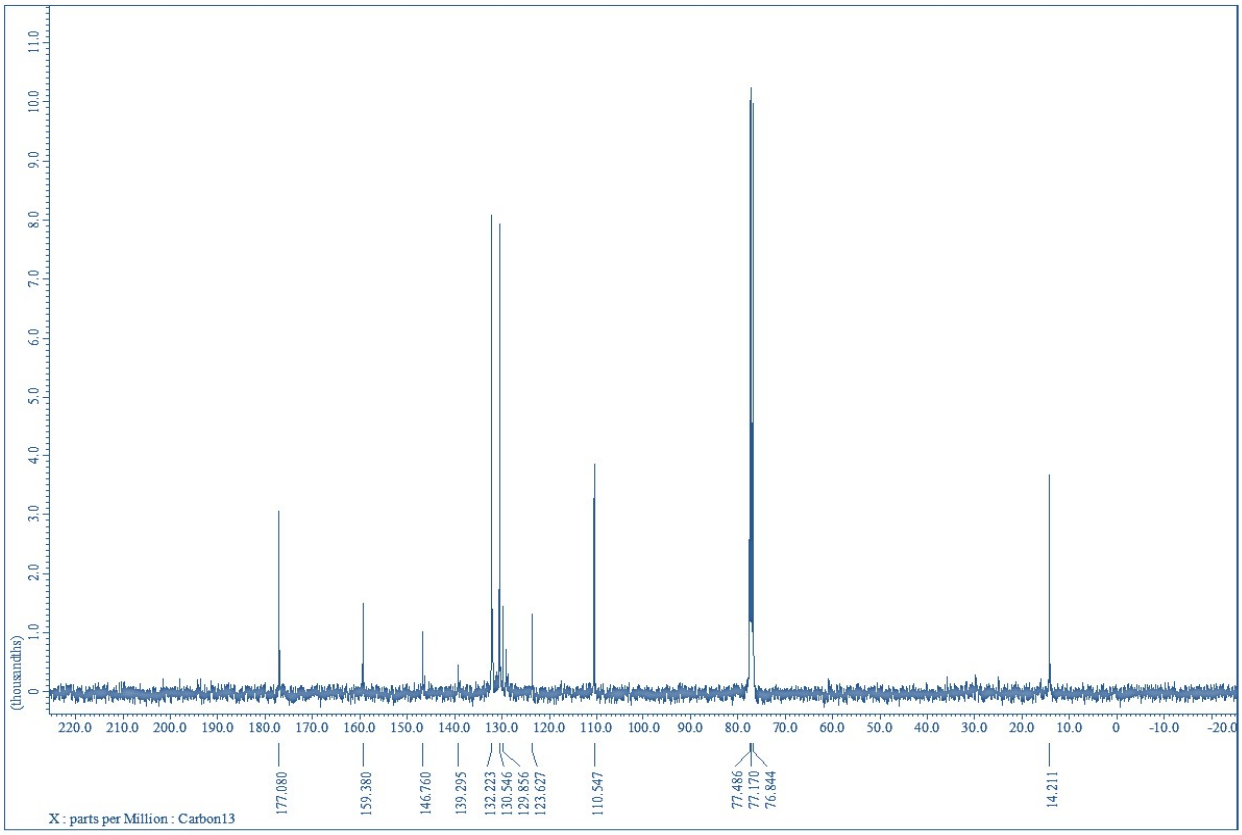
^{1}H NMR and ^{13}C NMR spectrum of 3-(4-methoxyphenyl)-5-methylfuran-2-carbaldehyde (12c)



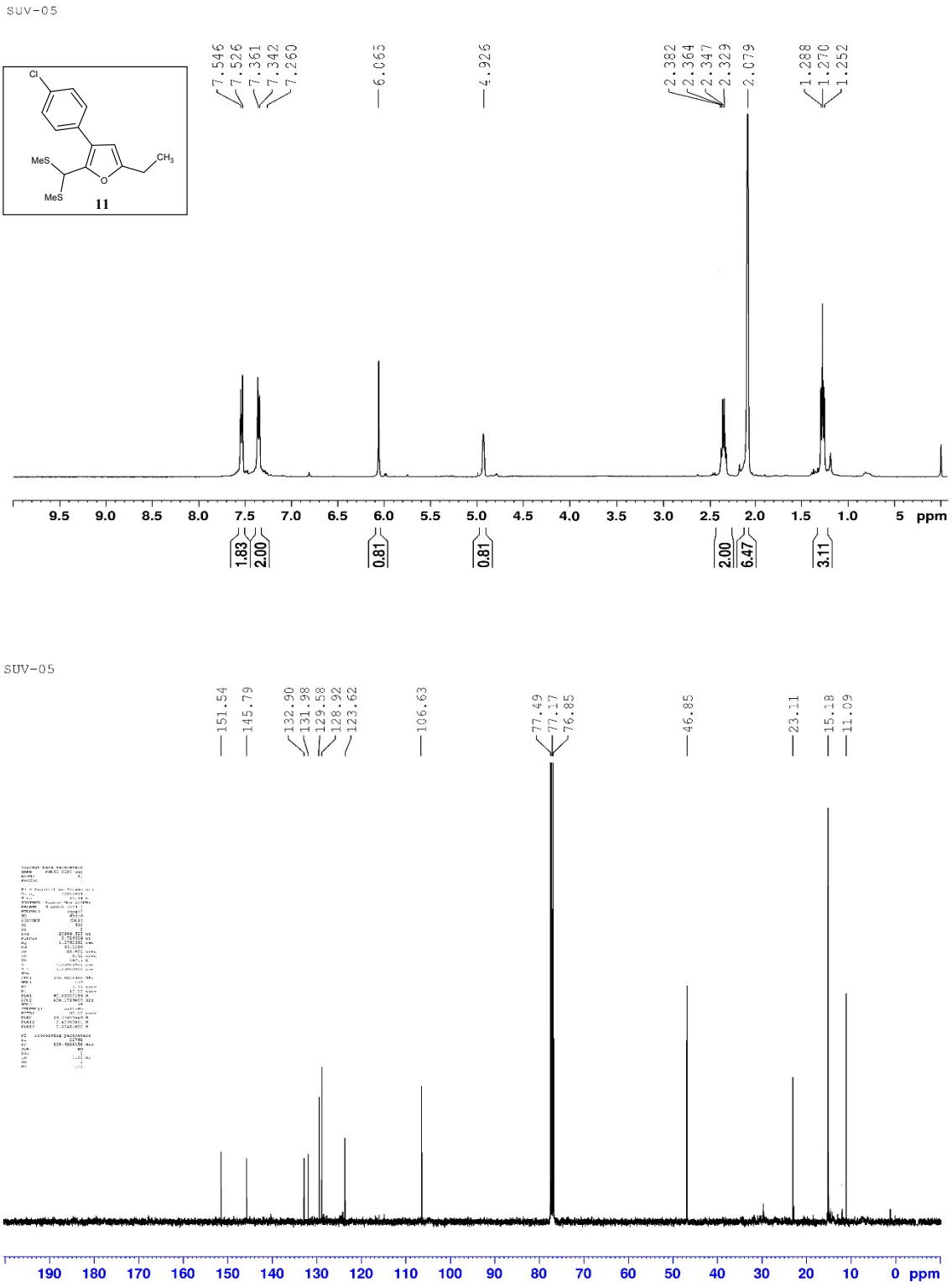


^{1}H NMR and ^{13}C NMR spectrum of 2-(3,4-dimethoxyphenyl)-5-methylfuran-3-carbaldehyde (12d)





^{1}H NMR and ^{13}C NMR spectrum of 3-(4-bromophenyl)-5-methylfuran-2-carbaldehyde (12e)



^{1}H NMR and ^{13}C NMR spectrum of 2-(bis(methylthio)methyl)-3-(4-chlorophenyl)-5-ethylfuran (11)