Supporting Information

[5+1] Annulation strategy for the synthesis of multifunctional biaryls and *p*-teraryls from 1,6-Michael acceptor ketene dithioacetals

Shally,[a] Ismail Althagafi,[b] Ranjay Shaw,[a] Amr Elagamy,[a] Abhinav Kumar,[c] and Ramendra Pratap[a,*]

[a]*Department of Chemistry, University of Delhi, North Campus, Delhi-110007 India.E-mail: rpratap@chemistry.du.ac.in; ramendrapratap@gmail.com; Tel: +91 1127666646*

[b]*Department of Chemistry, Umm Al-Qura University, Makkah, Saudi Arabia*

[c]*Department of Chemistry, University of Lucknow, Lucknow, Uttar Pradesh-226009 India*

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Optimization of reaction condition for the synthesis of 2

For screening of reaction conditions, We have chosen the 2-(1-aryylethylidene)malononitrile **1** as model substrate. We have started our screening using KOH/NaH and DMF at 0-5^{o}C but no product formation was observed (Table 1, entries 1-2). Now we have been switching the solvent DMF with THF by using KOH, $NaNH_2$, and Cs_2CO_3 at 0-5^{o}C but we failed the formation of product (Table 1, entries 3, 5-6). We have tried reaction with NaH/KO^{t}Bu in THF and surprisingly we get desired produtct in both condition 98&45% product was obtained (Table 1 entries 4&7). As it is confirmed from the table 2, Reaction was going smoothly in THF and NaH with excellent yields.

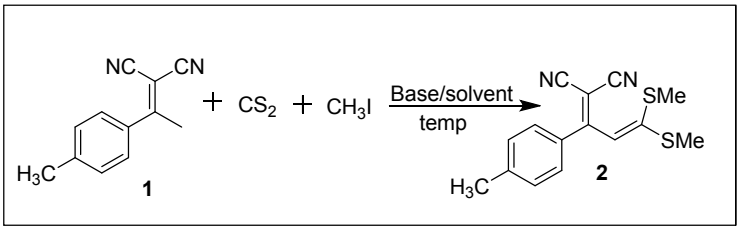


Table 1. Optimization of reaction condition for the synthesis of 2[a]

Entry	Base	Solvent	Temp(^{o}C)	Time(h)	Yield (%) [2]
1	KOH	DMF	0-5	24	S.M
2	NaH	DMF	0-5	24	S.M
3	KOH	THF	0-5	24	S.M
4	NaH	THF	0-5	6	98 (gram scale synthesis)
5	$NaNH_2$	THF	0-5	24	S.M
6	Cs_2CO_3	THF	0-5	7	S.M
7	KO^{t}Bu	THF	0-5	24	45

a) All reaction were performed by **1** (5.0 mmol) and CS_2 (5.5 mmol, 1.1equiv), methyl iodide (11.0 mmol, 2.2 equiv.), base (10 mmol, 2 equiv.) in (50 ml) solvent. (b) Room temperature was ranging from 0-5^{O}C, (c) Isolated yield after purification by washing by ethanol and filter, (d) S.M, starting material left (1).

Optimization of reaction condition for the synthesis of 6

In order to optimized the reaction conditions, a reaction of 2-(3,3-bis(methylthio)-1-arylallylidene)malononitrile (**2**) (0.5 mmol), nitroethane (**5**) (0.5 mmol) was selected as a model substrate. Initially, we performed the reaction using NaOH as a base in DMF and DMSO at 45 ^{o}C and we got our expected product in 43-45 % yield (Table 2 entries 1&2). Further we tested KOH as a base separately in DMSO and DMF at 45 ^{o}C and we got 67-72 % yield of desired product (Table 2, entries 3-4). By increasing the temperature 45-90 ^{o}C the product yield was led to 58 to 35 % (table 2, entries 5&6). Resulting using NaH, KO*t*BU, $NaNH_2$ in DMF at 45 ^{o}C led to 41, 65, 62 % yield of biaryl product (table 2, entries 7-9). From these results, we found that KOH as a base in DMF solvent gave best result of the product.

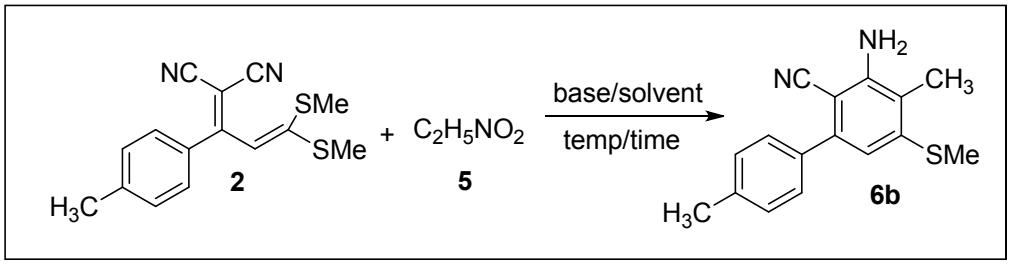


Table 2. Optimization of reaction condition for the synthesis of 6[a]

Entry	Base	Solvent	Temp.(^{o}C)	Time (h)	Yield (%)[b]
1	NaOH	DMSO	45	3	43
2	NaOH	DMF	45	3	45
3	KOH	DMSO	45	1	67
4	**KOH**	**DMF**	**45**	**1**	**72**
5	KOH	DMF	60	1	58
6	KOH	DMF	90	2	35
7	NaH	DMF	45	1	41
8	KO*t*Bu	DMF	45	3	65
9	$NaNH_2$	DMF	45	4	62

[a]All reaction were performed by stirring 2-(3,3-bis(methylthio)-1-arylallylidene)malononitrile (**2**) (0.5 mmol), nitroethane (**5**) (0.5 mmol) and base (1 mmol) in solvent (4 mL) at room temperature and high temperature. (b) Room temperature was ranging between 40-45 ^{o}C and high temperature 60-90 ^{o}C.

X-ray crystallographic data of 2d and 4h

To a 5 ml glass vial 25-30 mg of 2-(1-(4-methoxyphenyl)-3,3-bis(methylthio)allylidene) malononitrile (**2d**) and 3'-amino-4-bromo-5'-(methylthio)-4"-nitro-[1,1': 4',1"-terphenyl]-2'-carbonitrile (**4h**) were dissolved in DCM solvent until saturation point after add 1-2 drops ofhexanes were added. Then sample solution was kept for slow evaporation at room temprature until yellow rod shaped type suitable crystal obtained for X-ray analysis.

The structure of 2-(1-(4-methoxyphenyl)-3,3-bis(methylthio)allylidene)malononitrile (**2d**) was confirmed by single crystal X-ray analysis (**Figure 1**). The compound crystallizes in P21/n space group having four molecules in the monoclinic unit cell. There is no major interaction in this molecule.

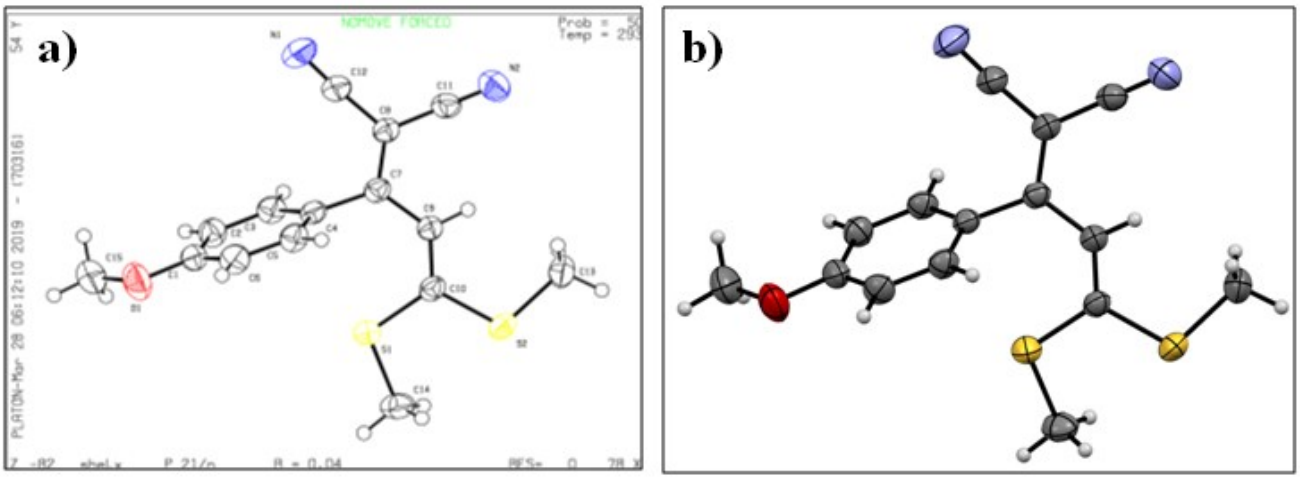


Figure 1: **(a)** ORTEP diagram of **2d**; thermal ellipsoids are drowned at the 50% probability level; (b) The perspective view of **2d**

The structure and geometry of the synthesized compounds was confirmed by single crystal X-raycrystallography of 3'-amino-4-bromo-5'-(methylthio)-4"-nitro-[1,1':4',1"-terphenyl]-2'-carbonitrile (**4h**). The compound crystallizes in P-1 space group having two molecules in the triclinic unit cell (**Figure 2**). The central benzene ring contains SMe, amino, nitrile and two aryl groups. The central benzene ring, SMe, amino and nitro group are in the same plane. The three aryl rings of teraryl are planer and present in different planes.

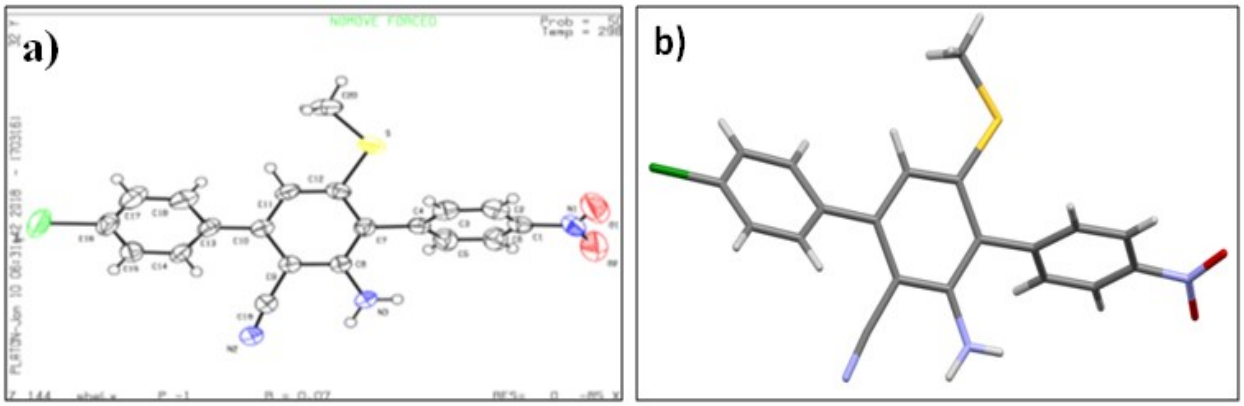


Figure 2: **(a)** ORTEP diagram of **4h**; thermal ellipsoids are drowned at the 50% probability level; (b) The perspective view of **4h**

Crystal data of 2d and **4h:** A white crystal was mounted on a capillary tube forindexing and intensity data collection at 293 and 298K 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].[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]and all data collection and parameter are given in **table 3**.

Table 3: Crystal data and structure refinement for **2d** and **4h**

	2d	**4h**
CCDC No.	**1974744**	**1974745**
Empirical formula	$C_{15}\ H_{14}\ N_2\ O\ S_2$	$C_{20}\ H_{14}\ Br\ N_3\ O_2\ S$
Formula weight	302.40	440.30
Temperature/k	293K	298K
Crystal system	Monoclinic	Triclinic
Space group	P 21/n	P -1
a/Å	9.0969(8)	8.4509(8)
b/Å	11.7978(8)	10.7362(9)
c/Å	14.1107(11)	11.5735(9

α/°	90	108.414(7)
β/°	97.790(8)	104.992(7)
γ/°	14.1107(11)	100.036(7)
Volume/Å^3	1500.4(2)	924.09(15)
Z	4	2
ρ_{calc}g/cm^3	1.339	1.582
μ/mm^{-1}	0.351	2.358
F(000)	632.0	444
Crystal size/mm^3	0.200 x 0.180 x 0.160	0.200 x 0.180 x 0.160
2Θ range for data collection/°	3.053 to 29.355	3.366 to 24.999
Index ranges	-12<=h<=12, -16<=k<=16, -19<=l<=19	-10<=h<=10,12<=k<=12, -13<=l<=13
Data/restraints/parameters	3815 / 0 / 181	248 / 0 / 244
Goodness-of-fit on F^2	0.425	0.864
Final R indexes [I>=2σ (I)]	R1 = 0.0425, wR2 = 0.1326	R1 = 0.0661, wR2 = 0.2086
Final R indexes [all data]	R1 = 0.0551, wR2 = 0.1070	R1 = 0.1028, wR2 = 0.2492
Largest diff. peak/hole / eÅ^3	0.278 and -0.510 e Å^{-3}	0.660 and -0.909 e. Å^{-3}

References

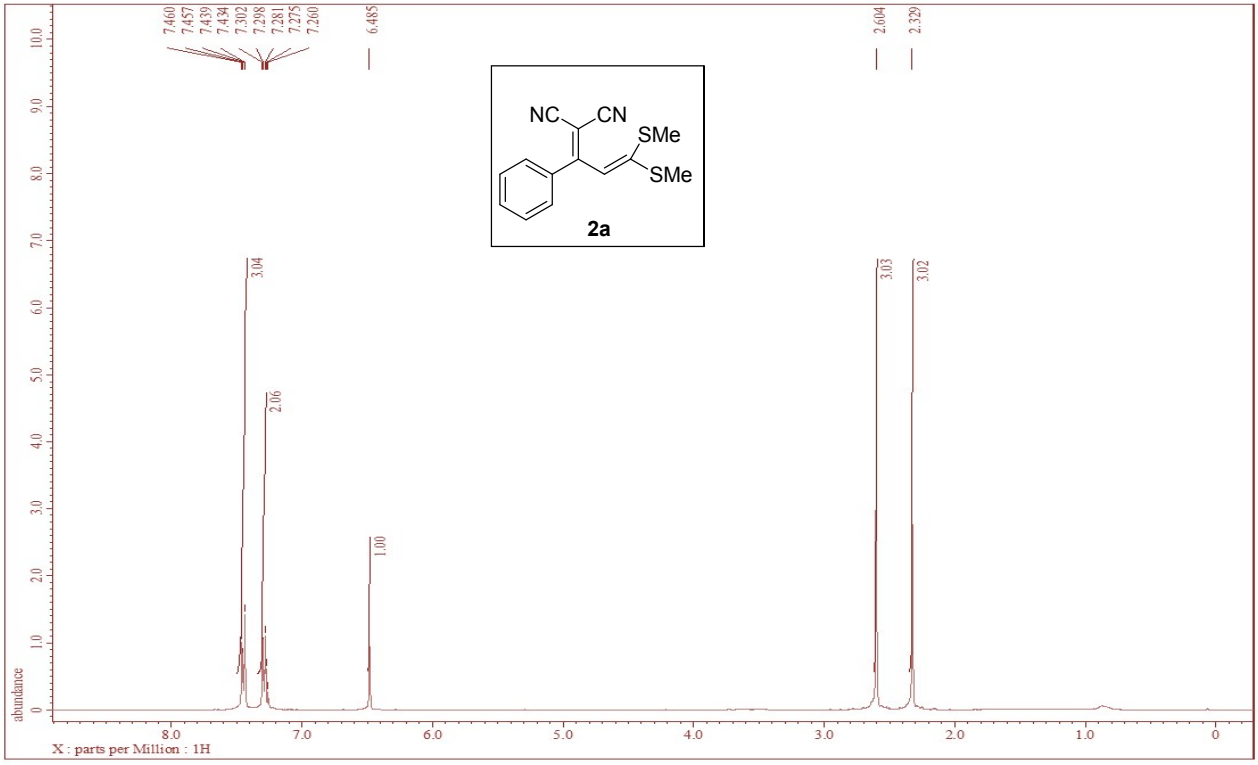
(1) CrysAlisPro, v. 1.171.33.49b, Oxford Diffraction Ltd., **2009**.

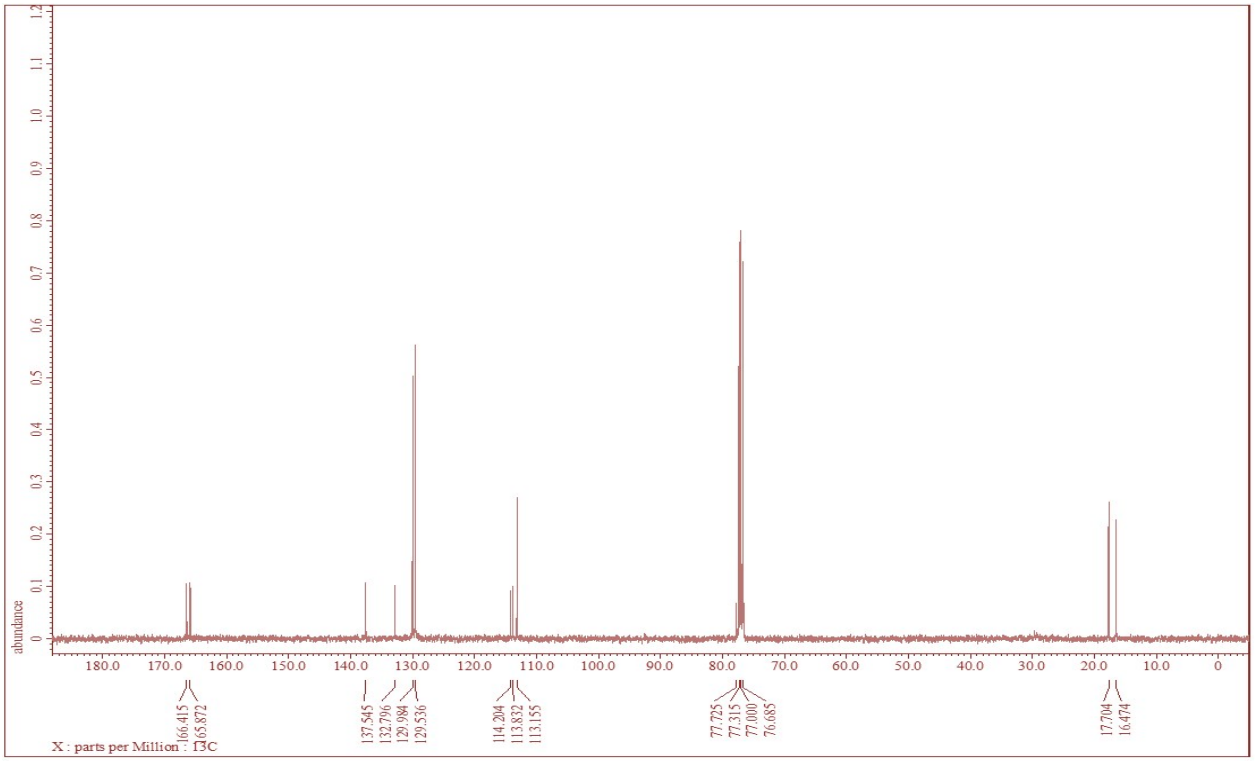
(2) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Cryst*. **1993**, 26, 343.

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

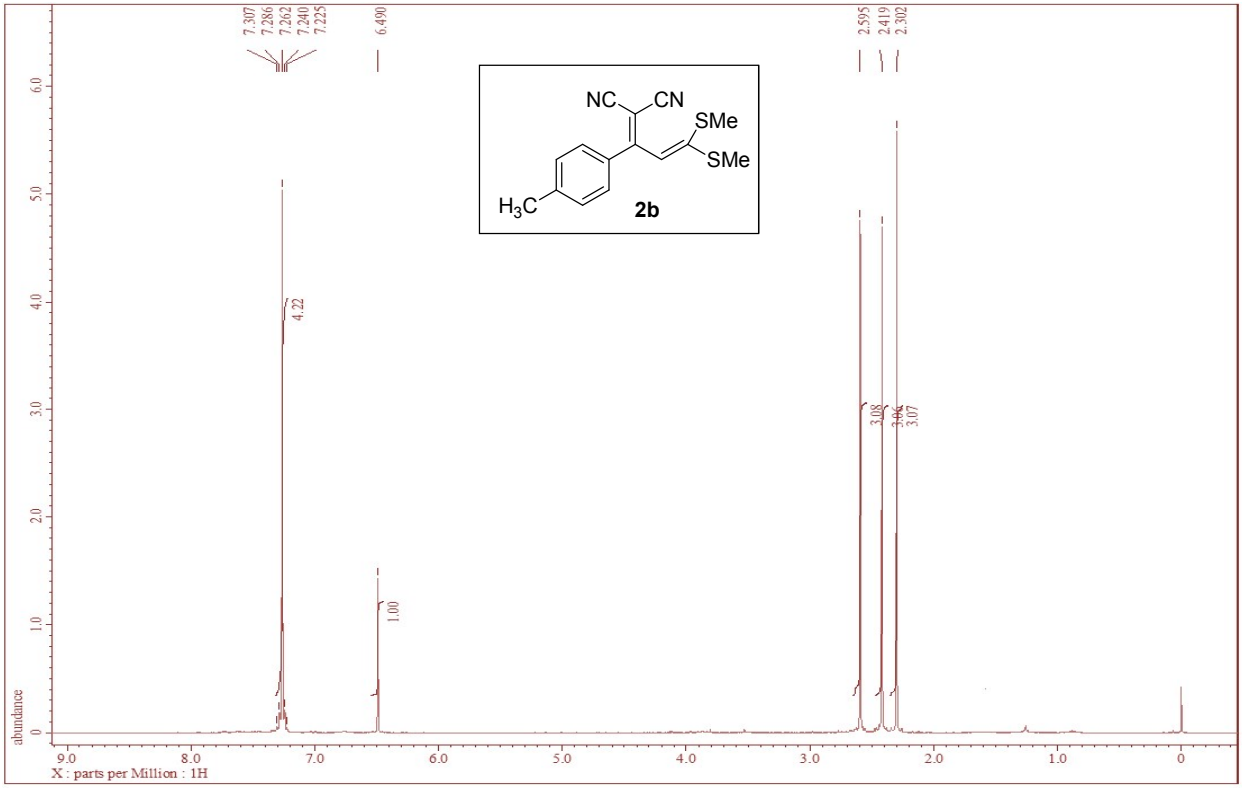
(4) Sheldrick, G. M. Acta Crystallogr., Sect. A: Found. Crystallogr., **2008**, 64, 112.

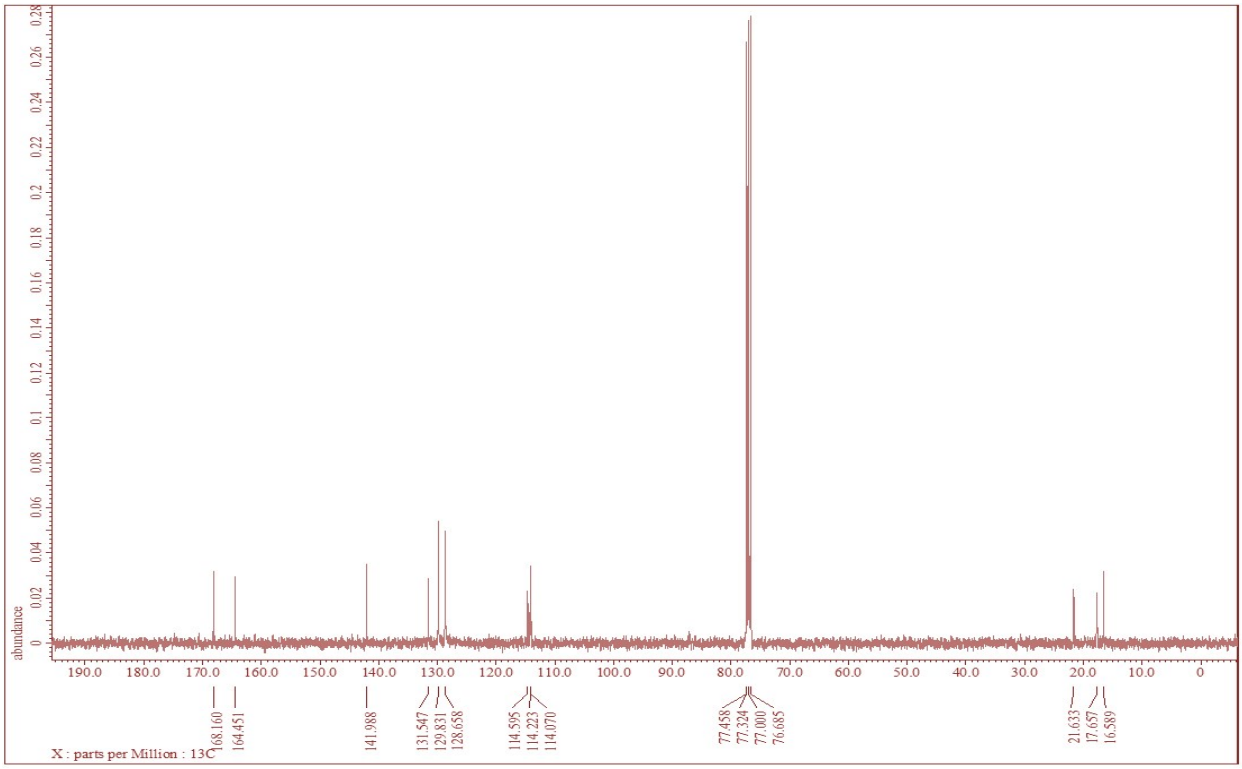
(5) Farrugia, L. J. WinGX, v. 1.70, An Integrated System of Windows Programs for the Solution, Refinement and Analysis of Single-Crystal X-ray Diffraction Data, Department of Chemistry, University of Glasgow, **2003**.





^{1}HNMR and ^{13}C NMR spectrum of2-(3,3-bis(methylthio)-1-phenylallylidene)malononitrile





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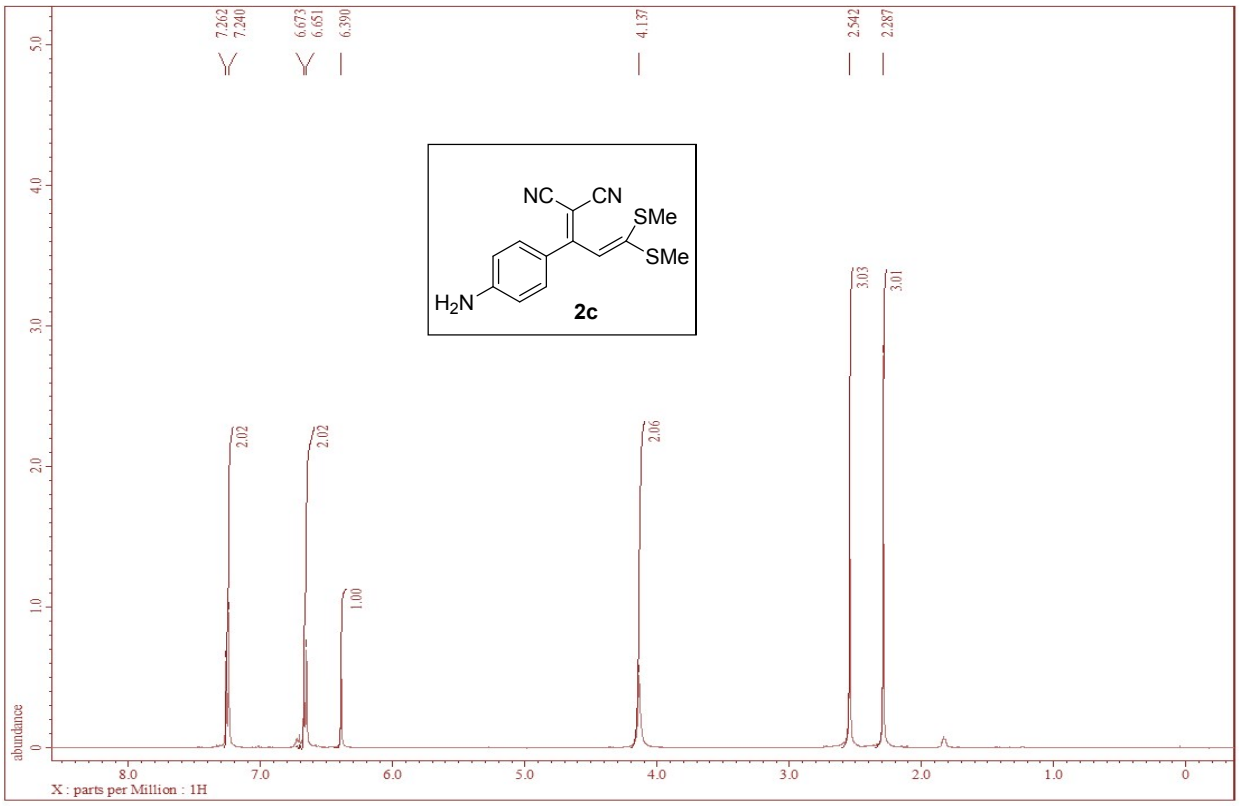

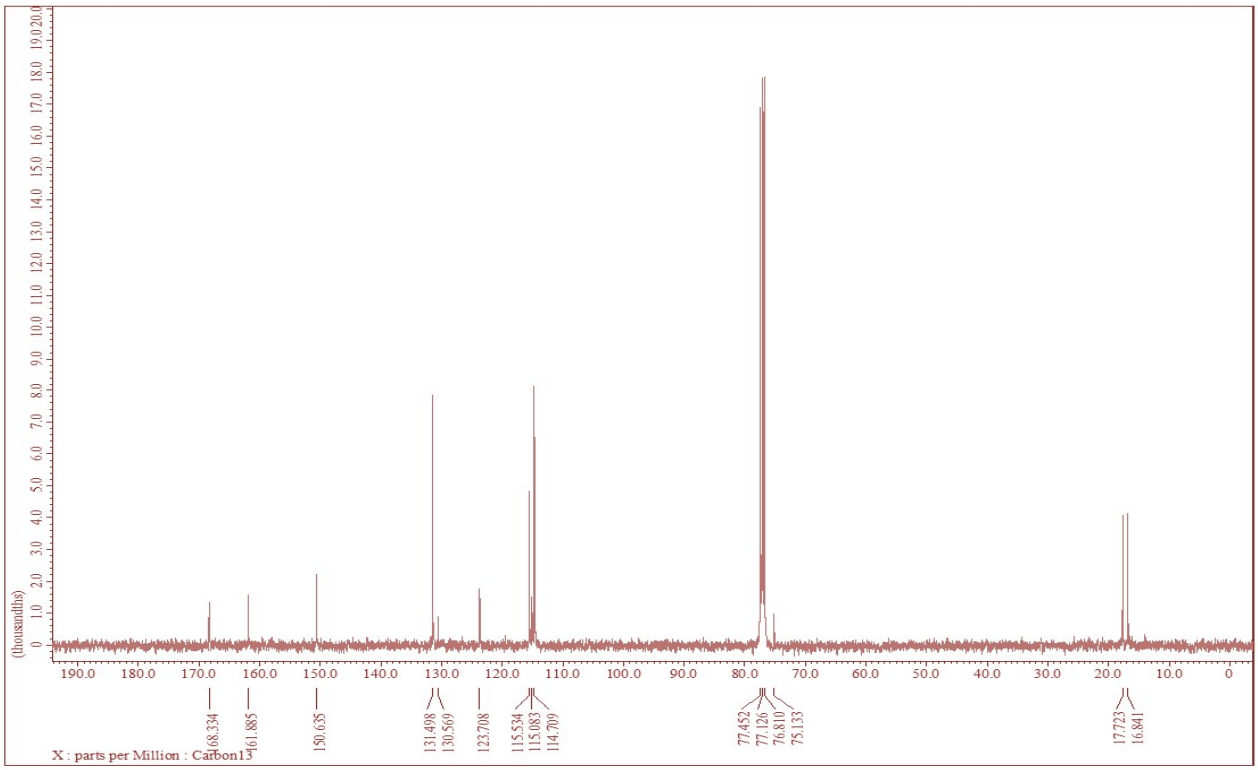

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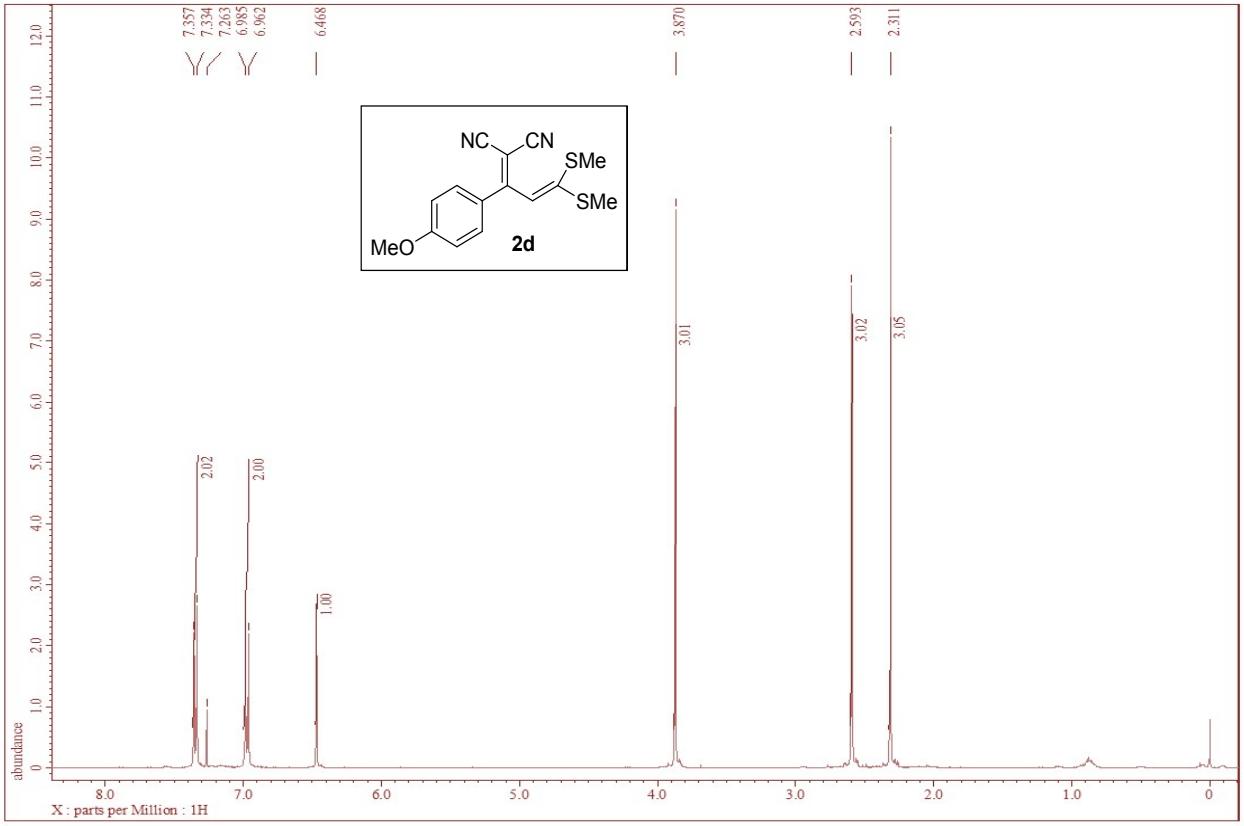

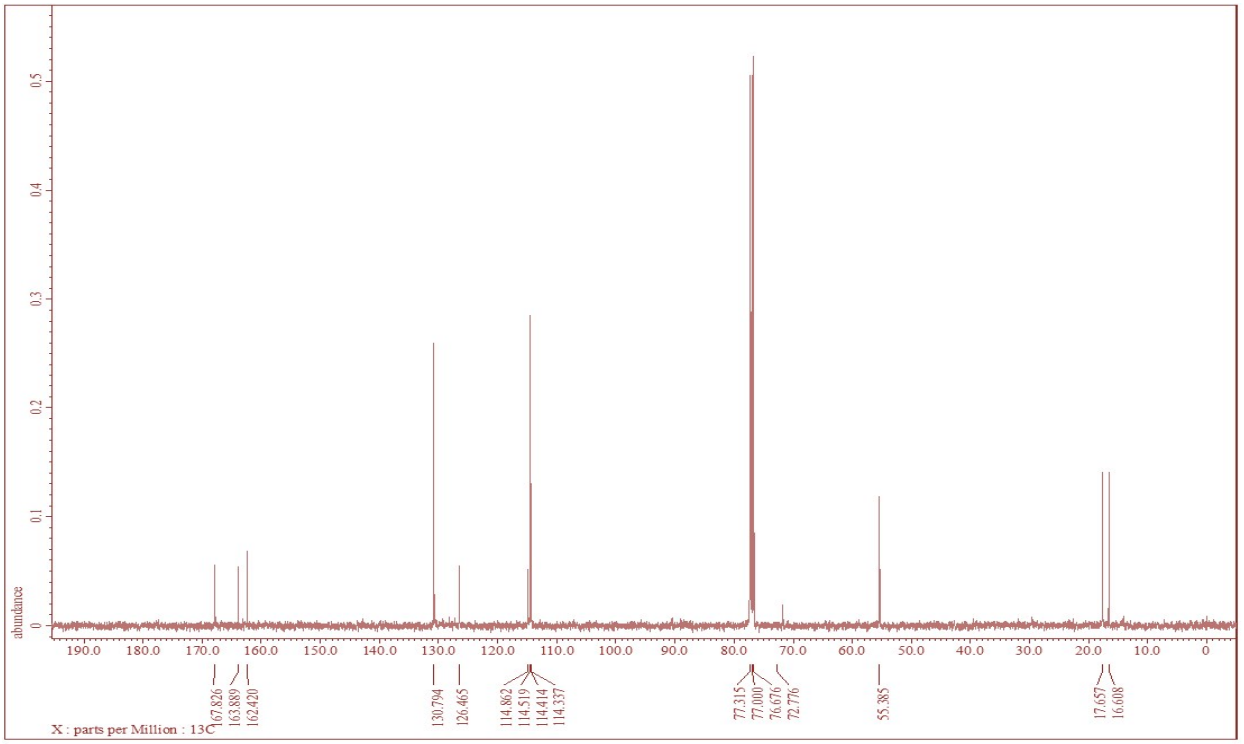

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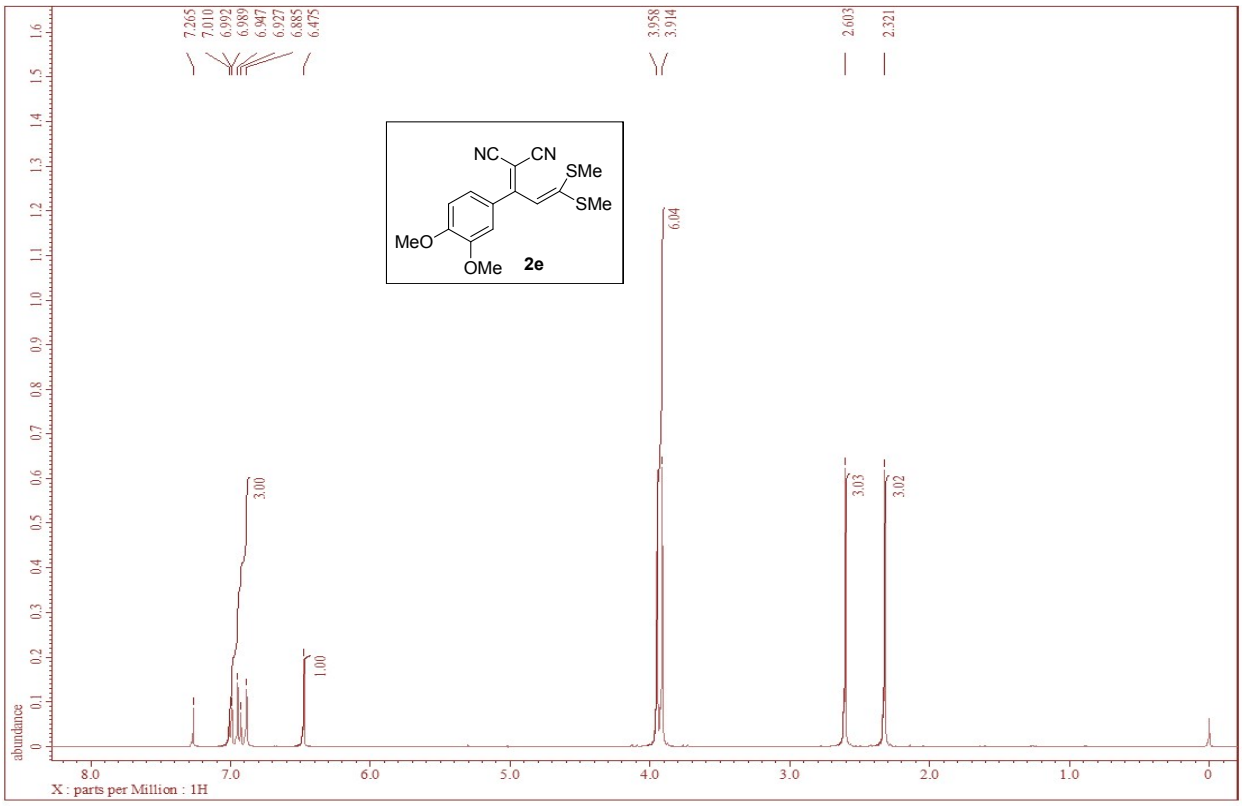

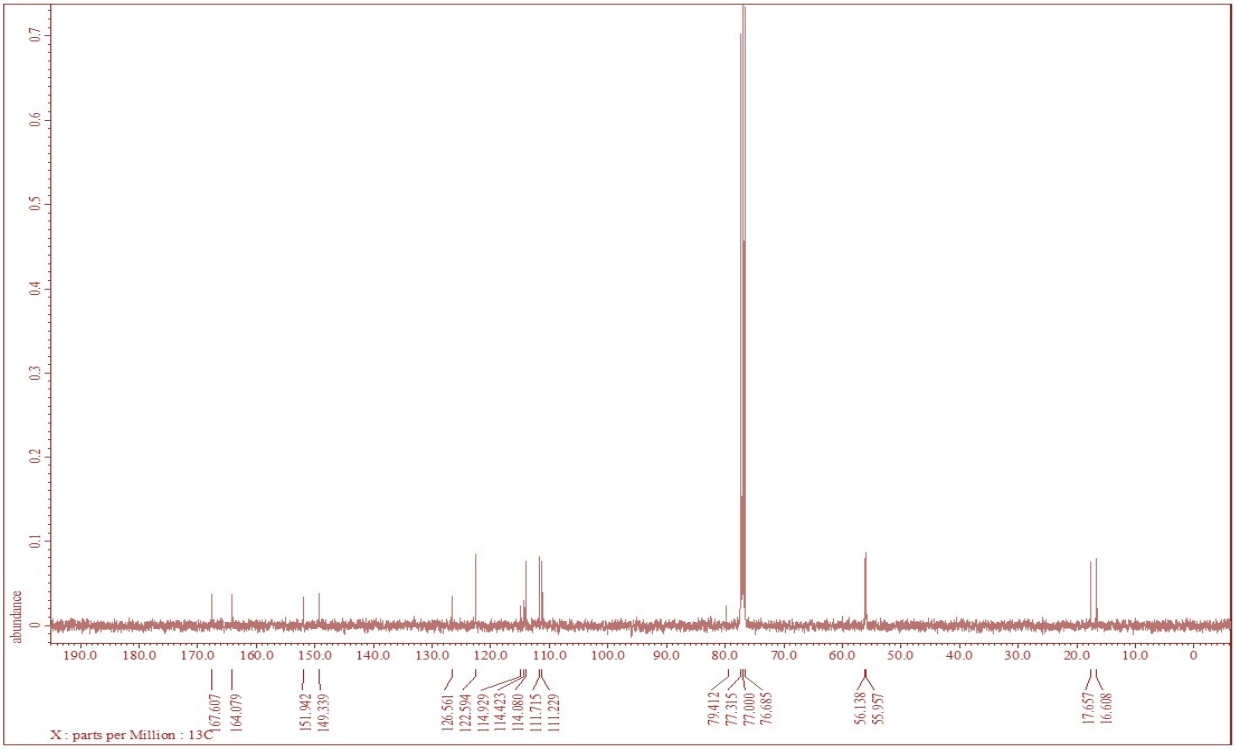

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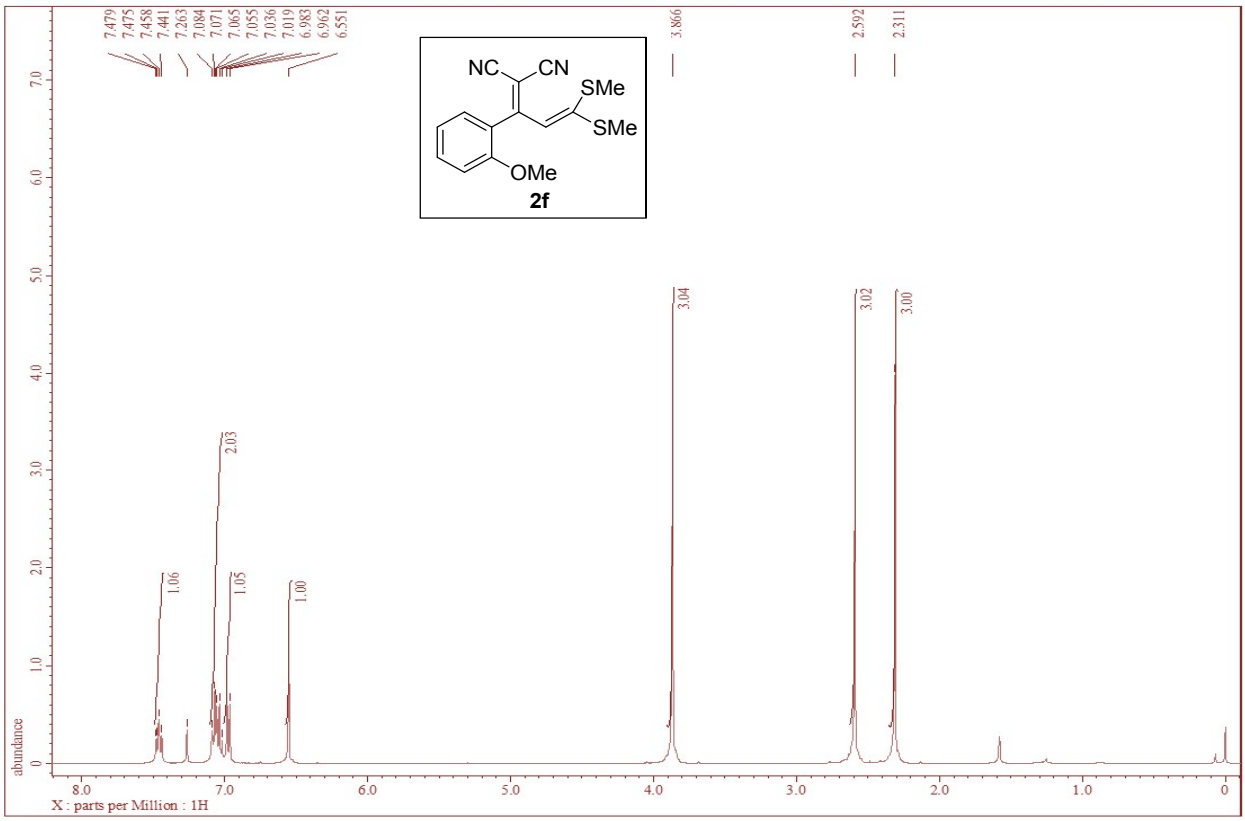

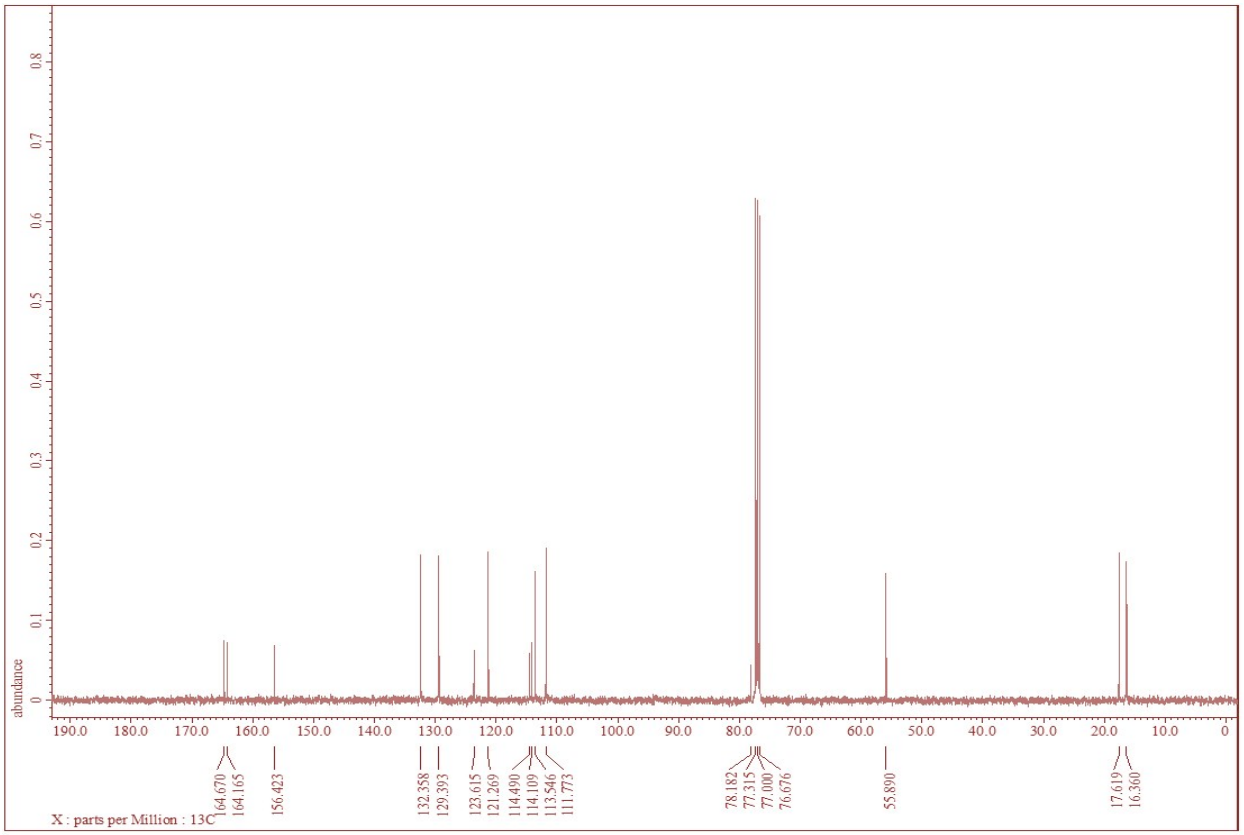

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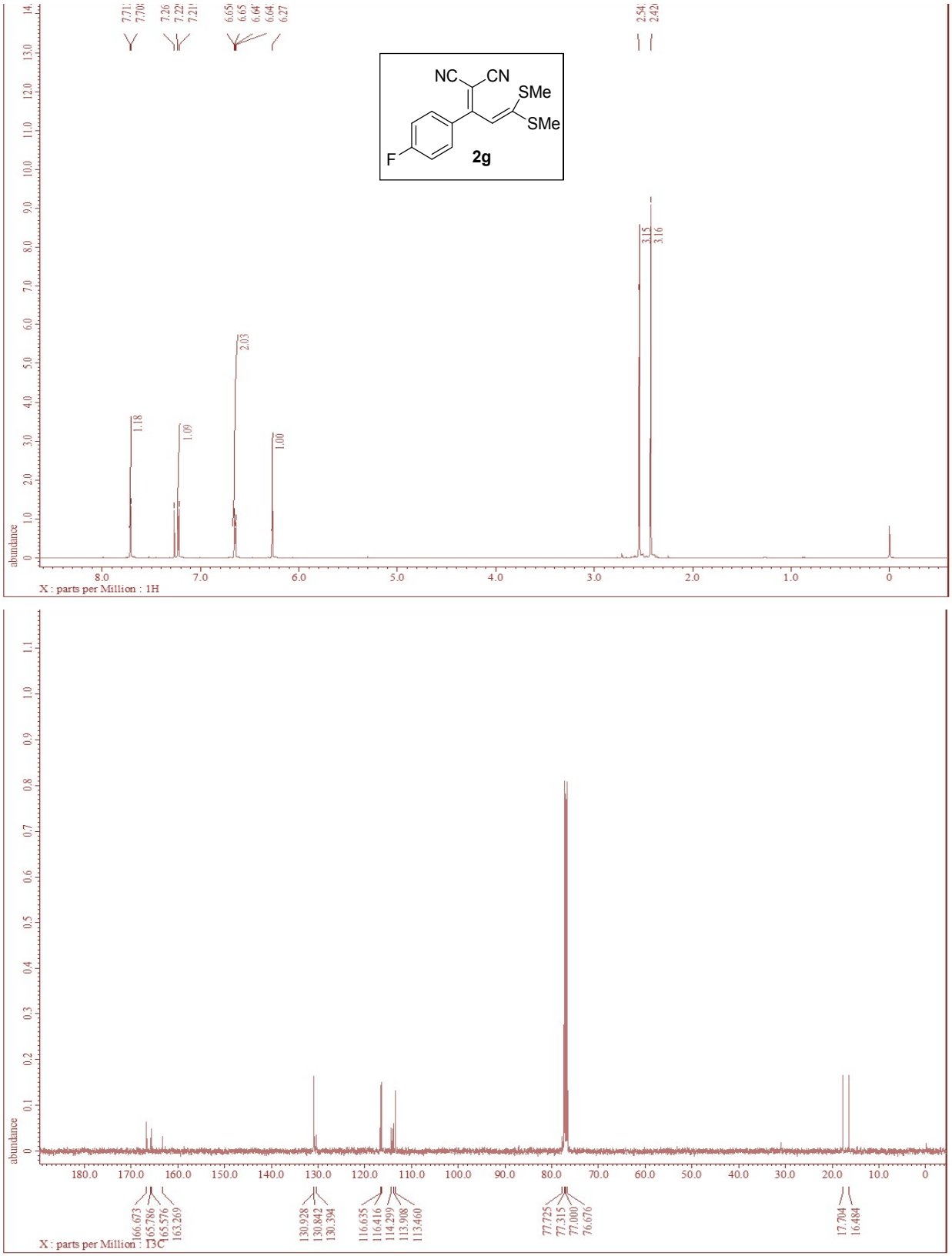

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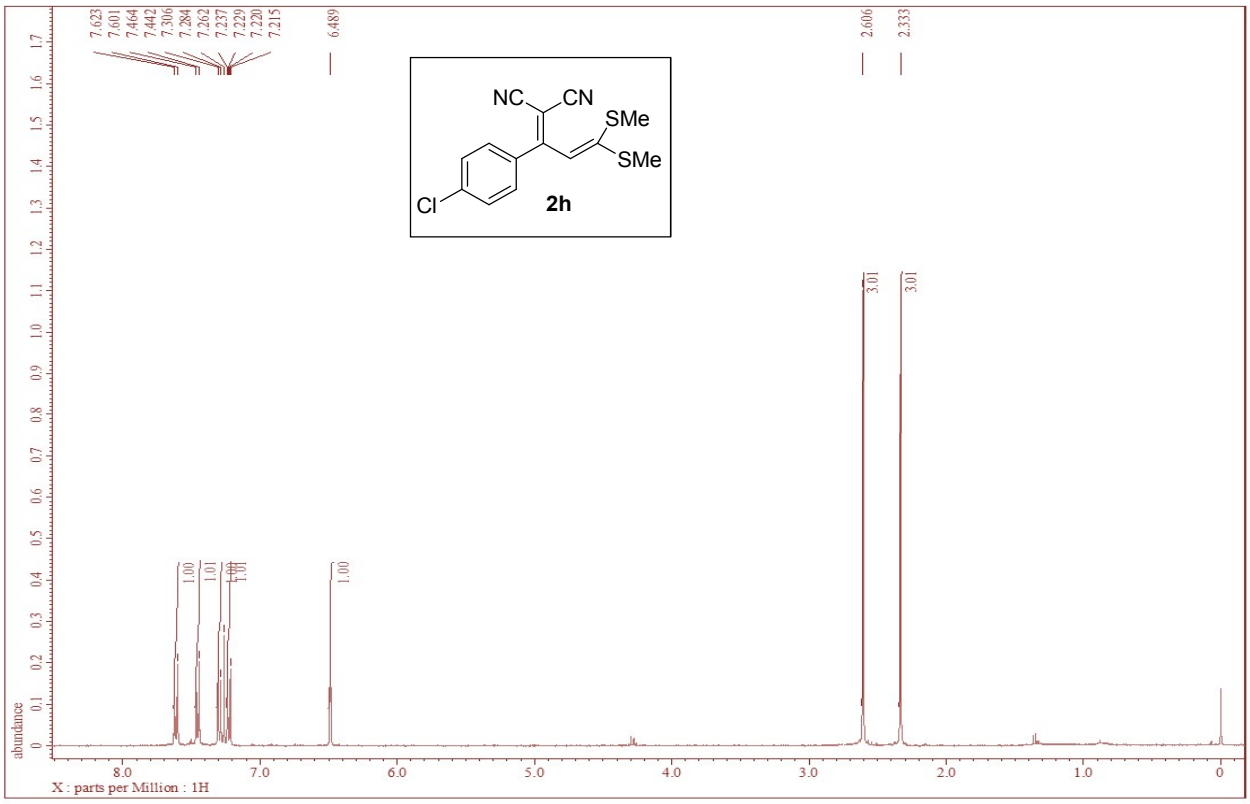

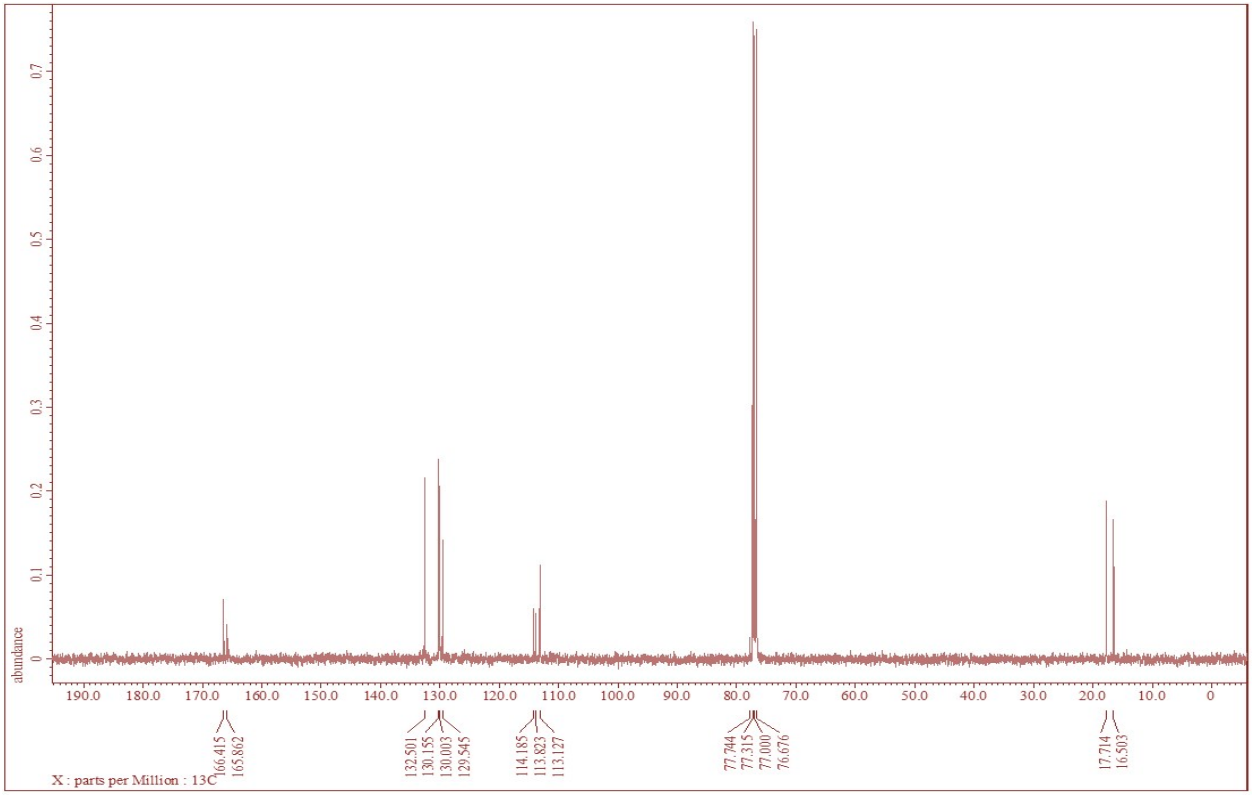

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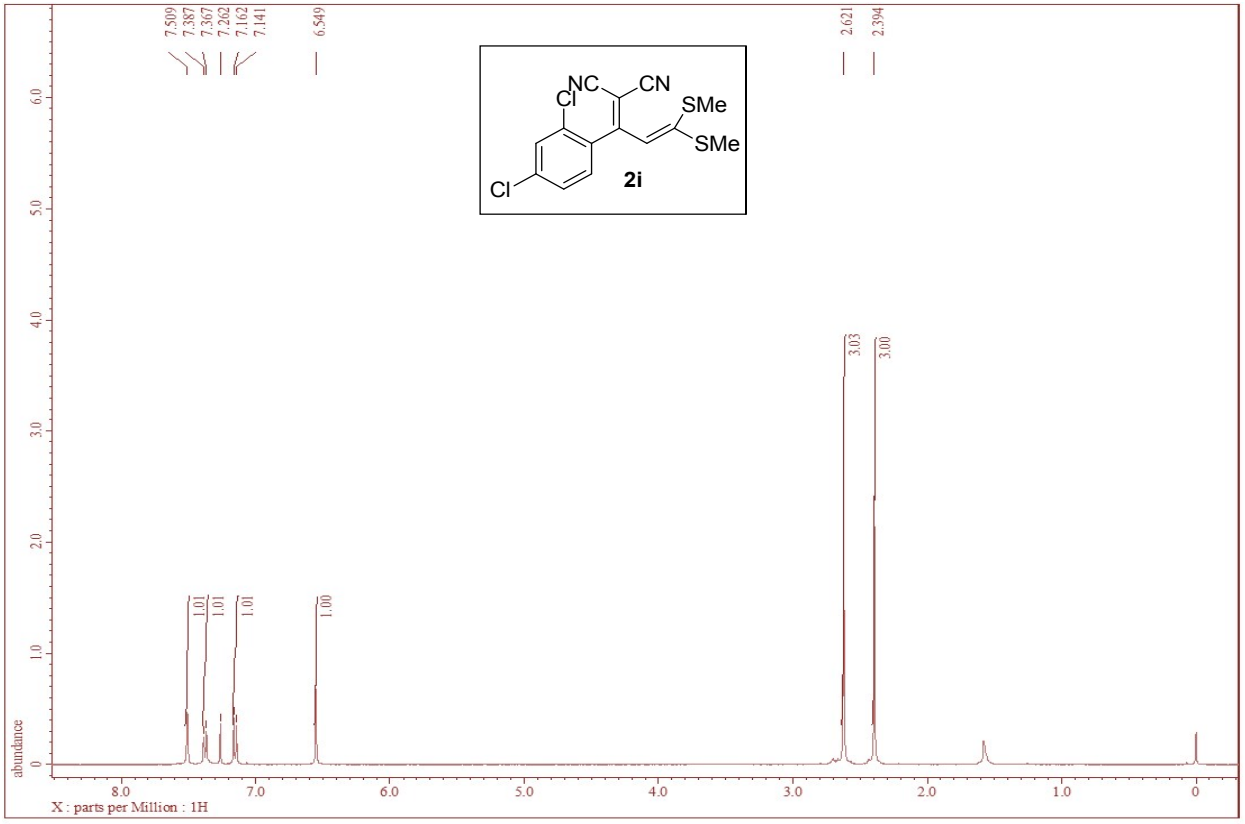

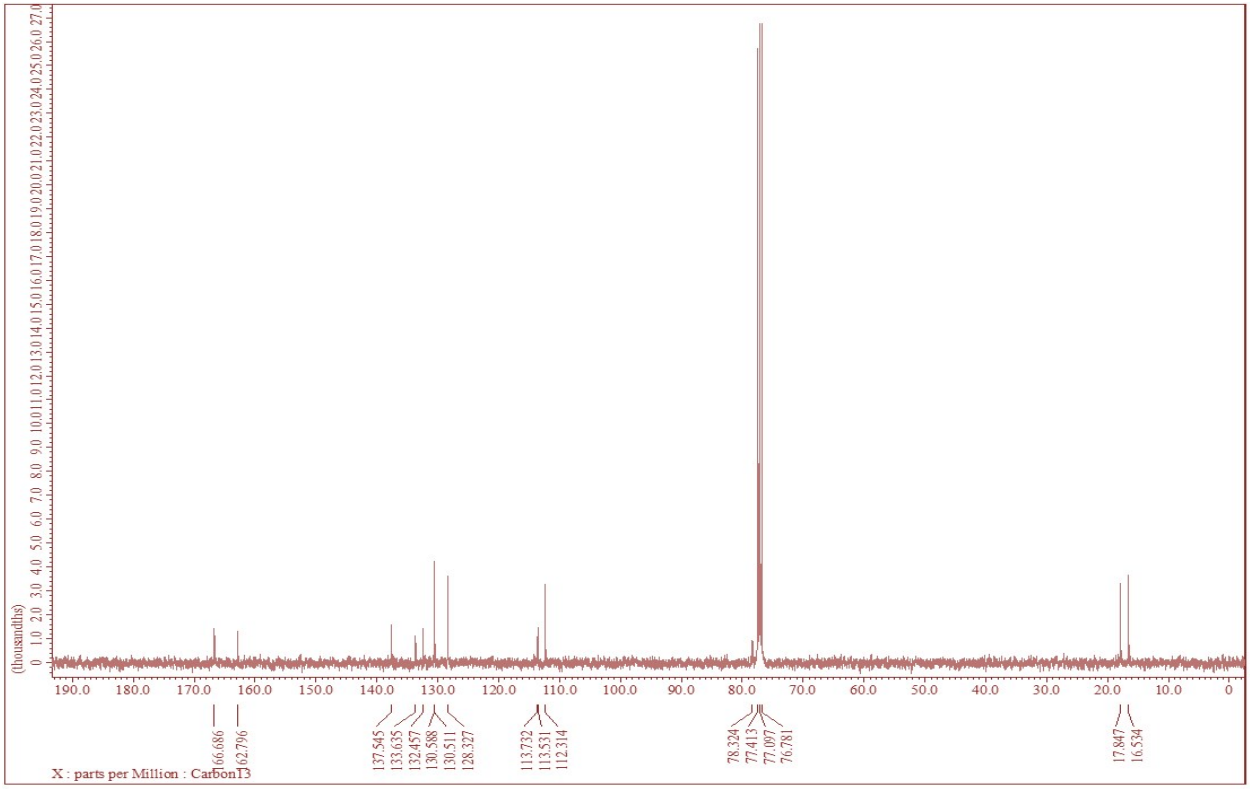

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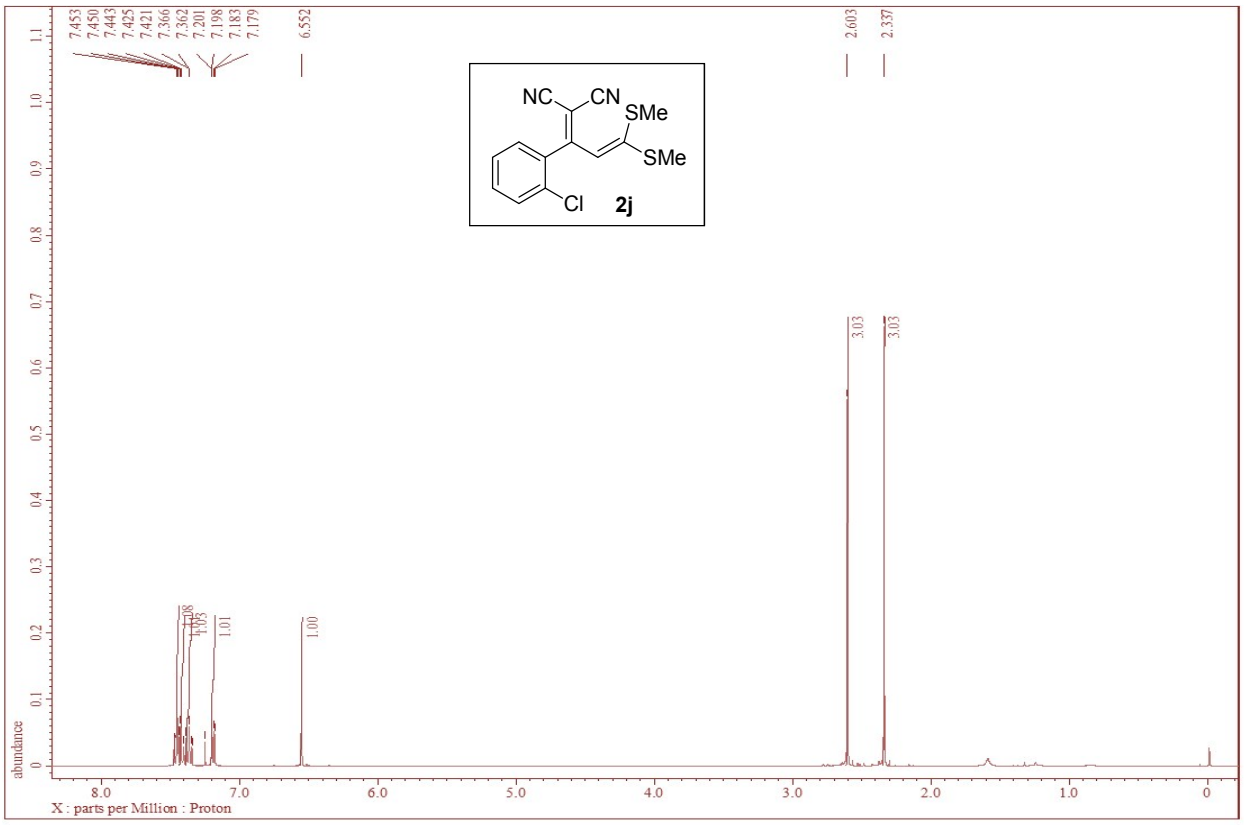

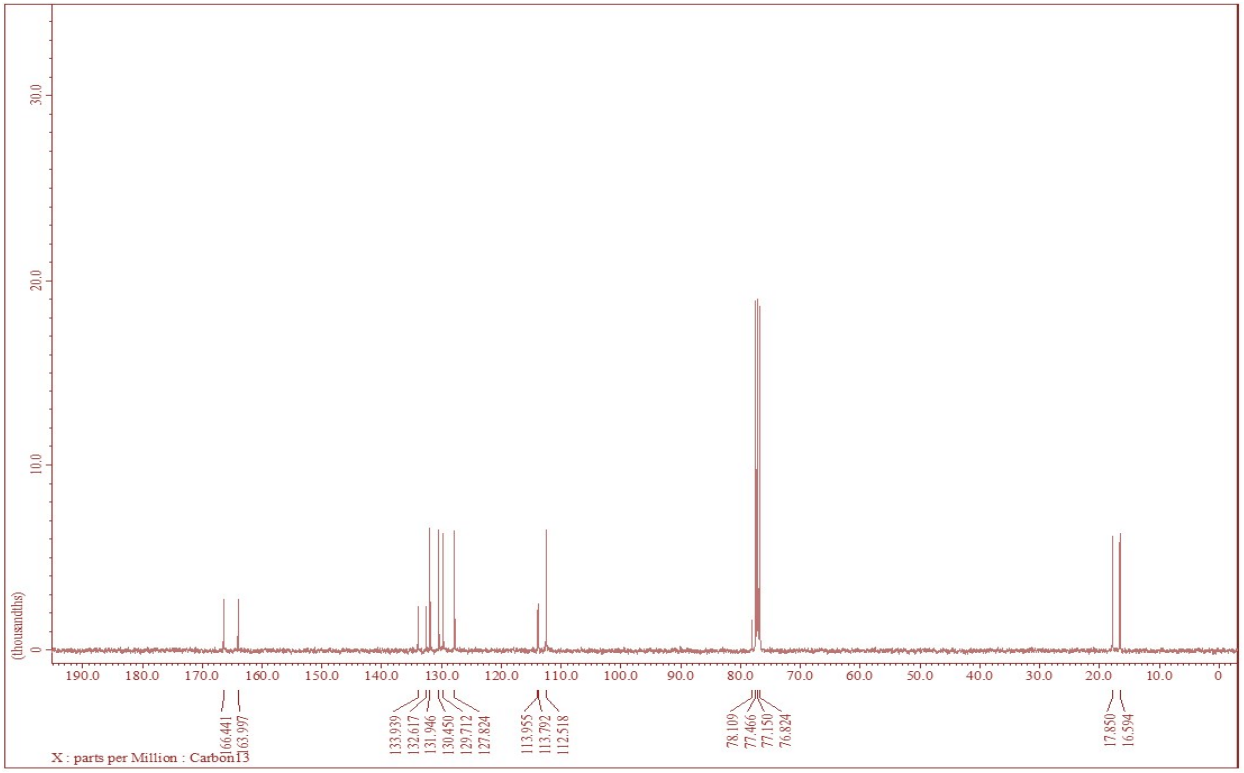

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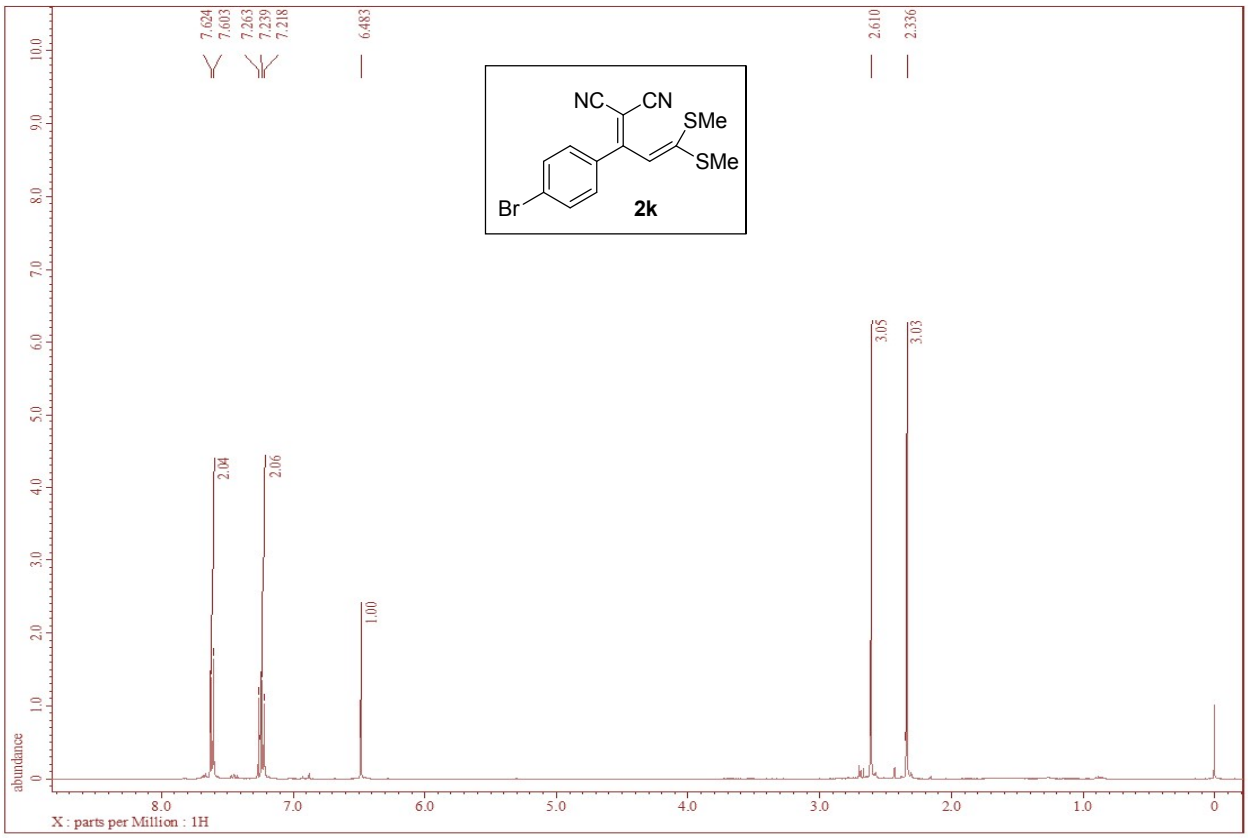

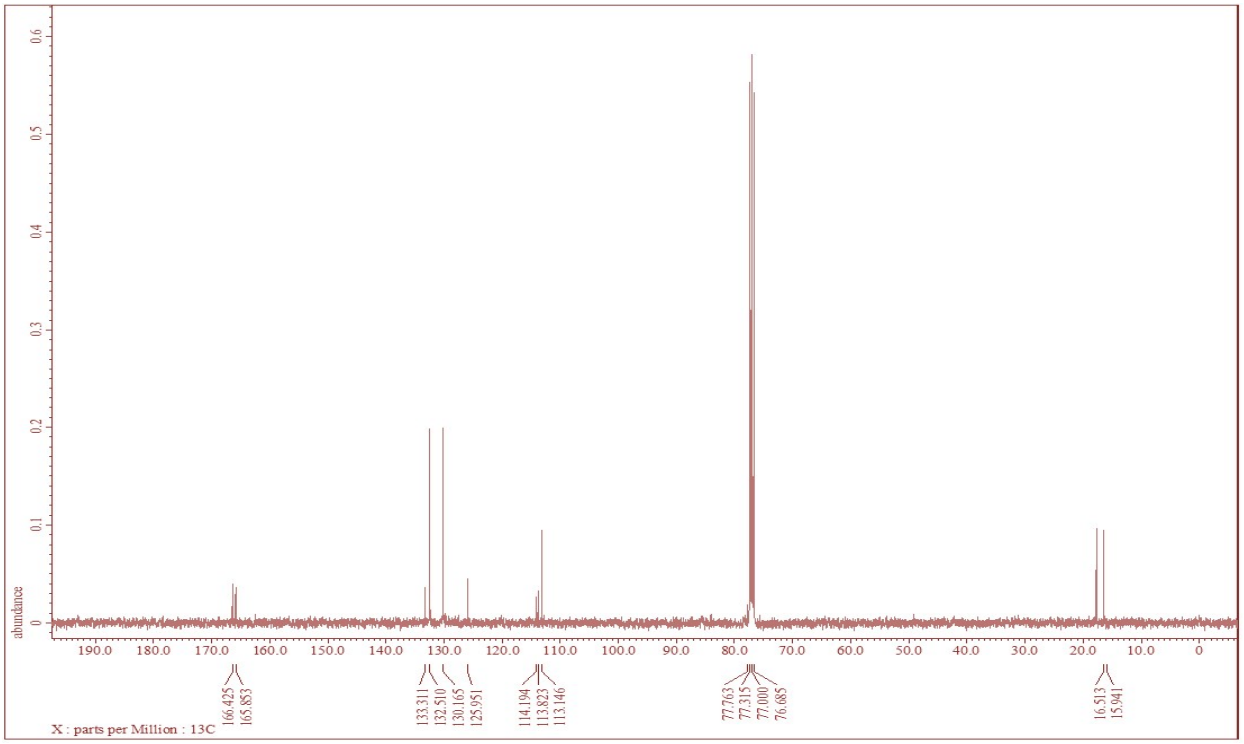

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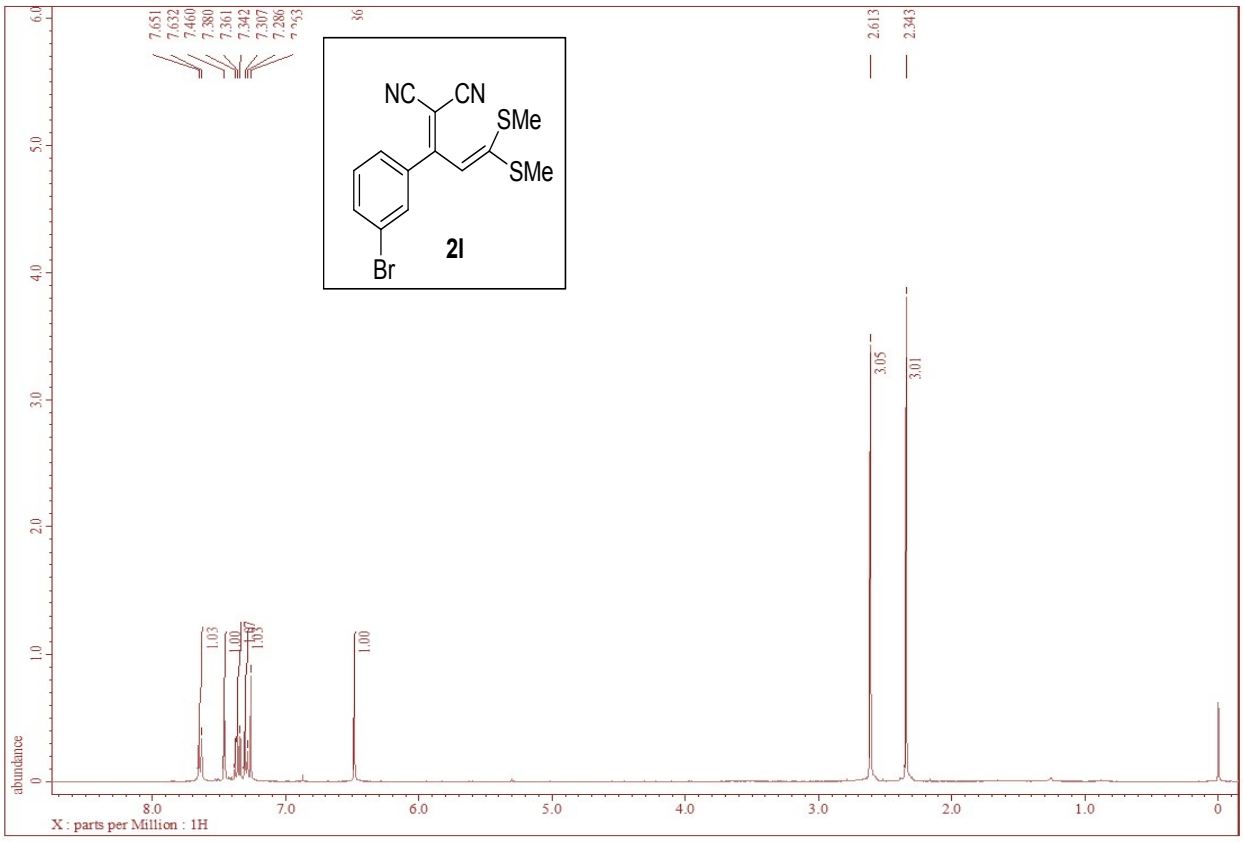

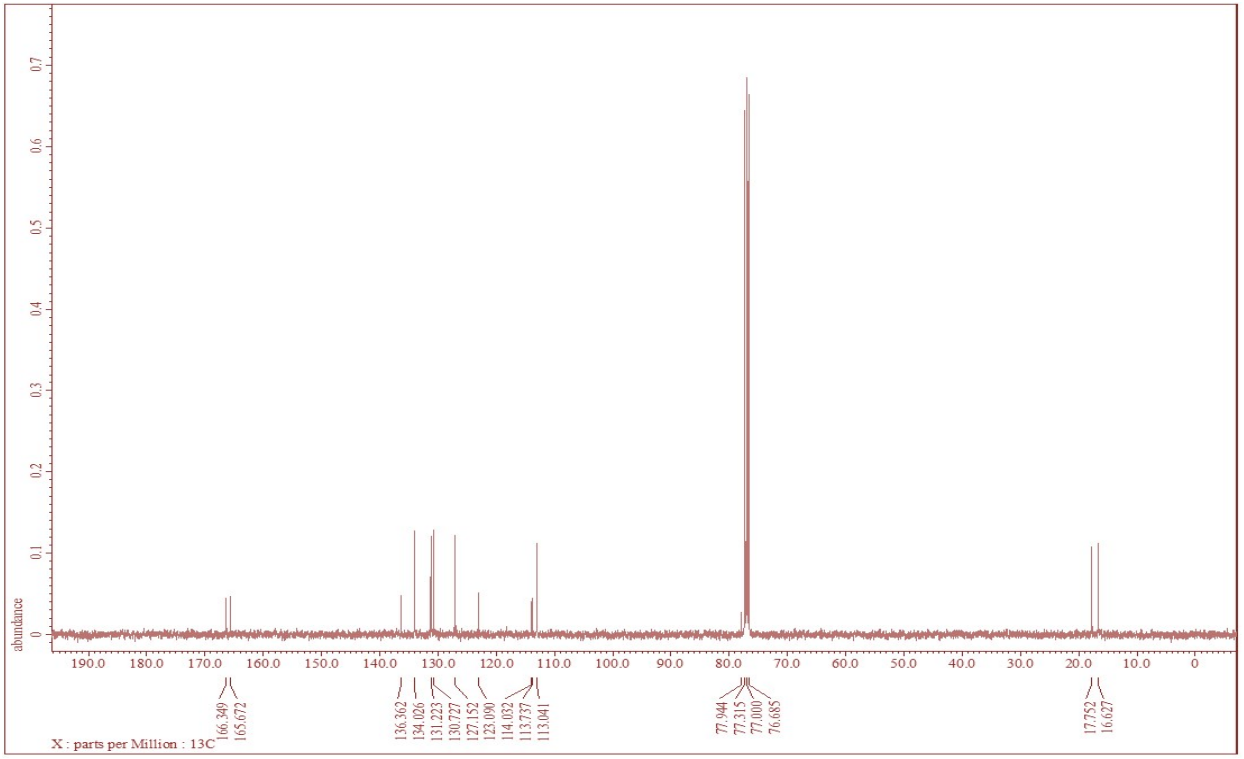

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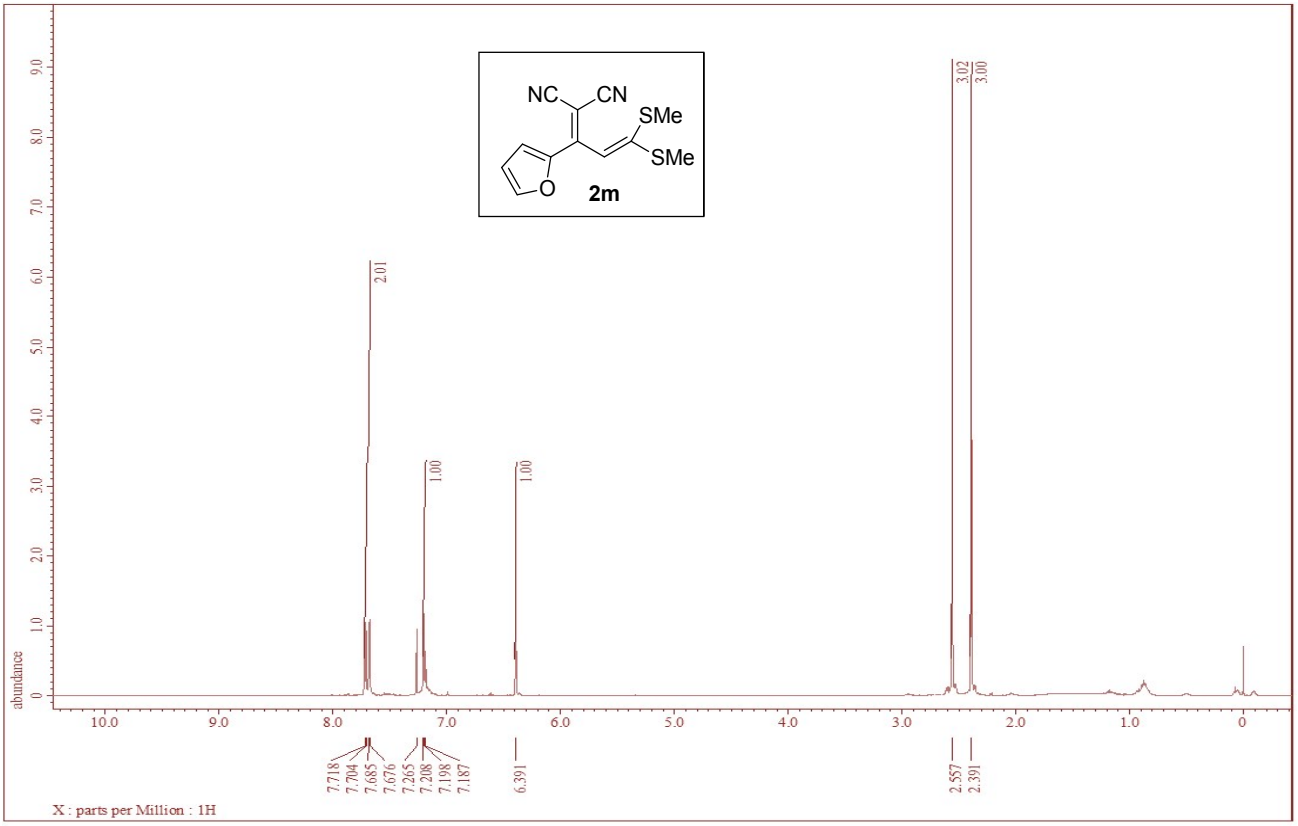

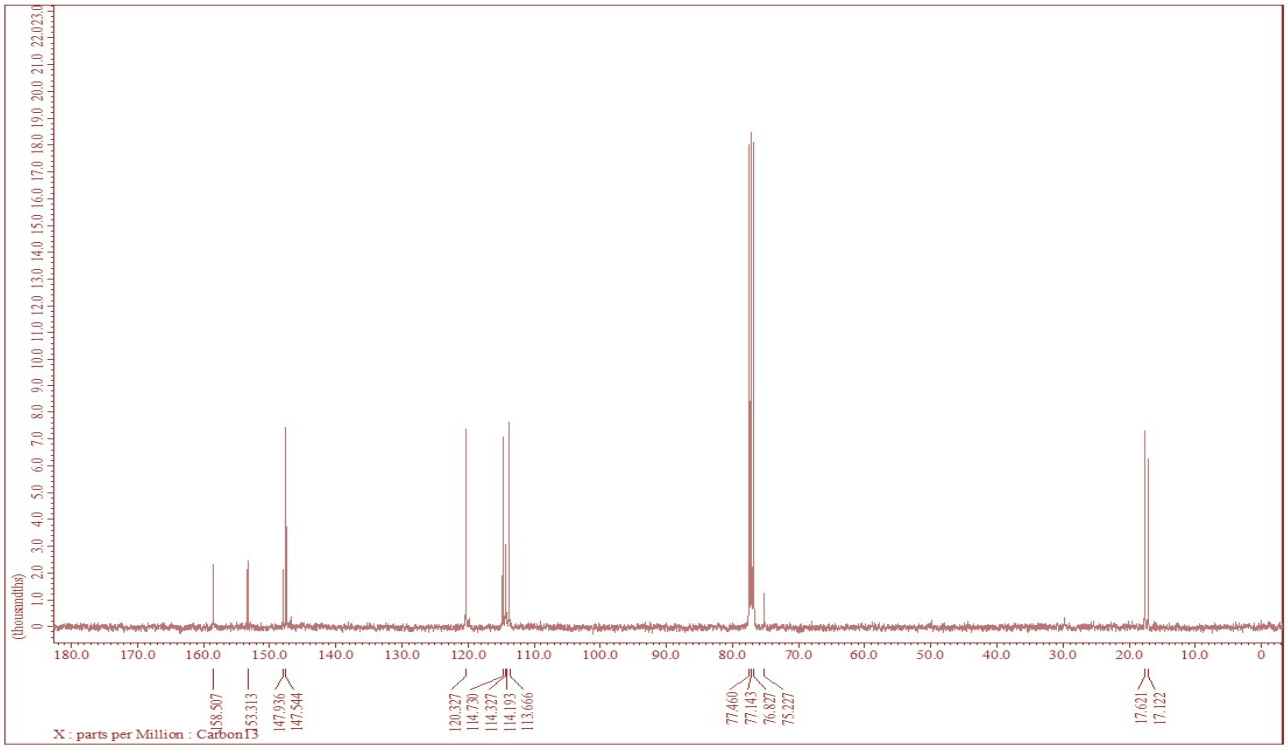

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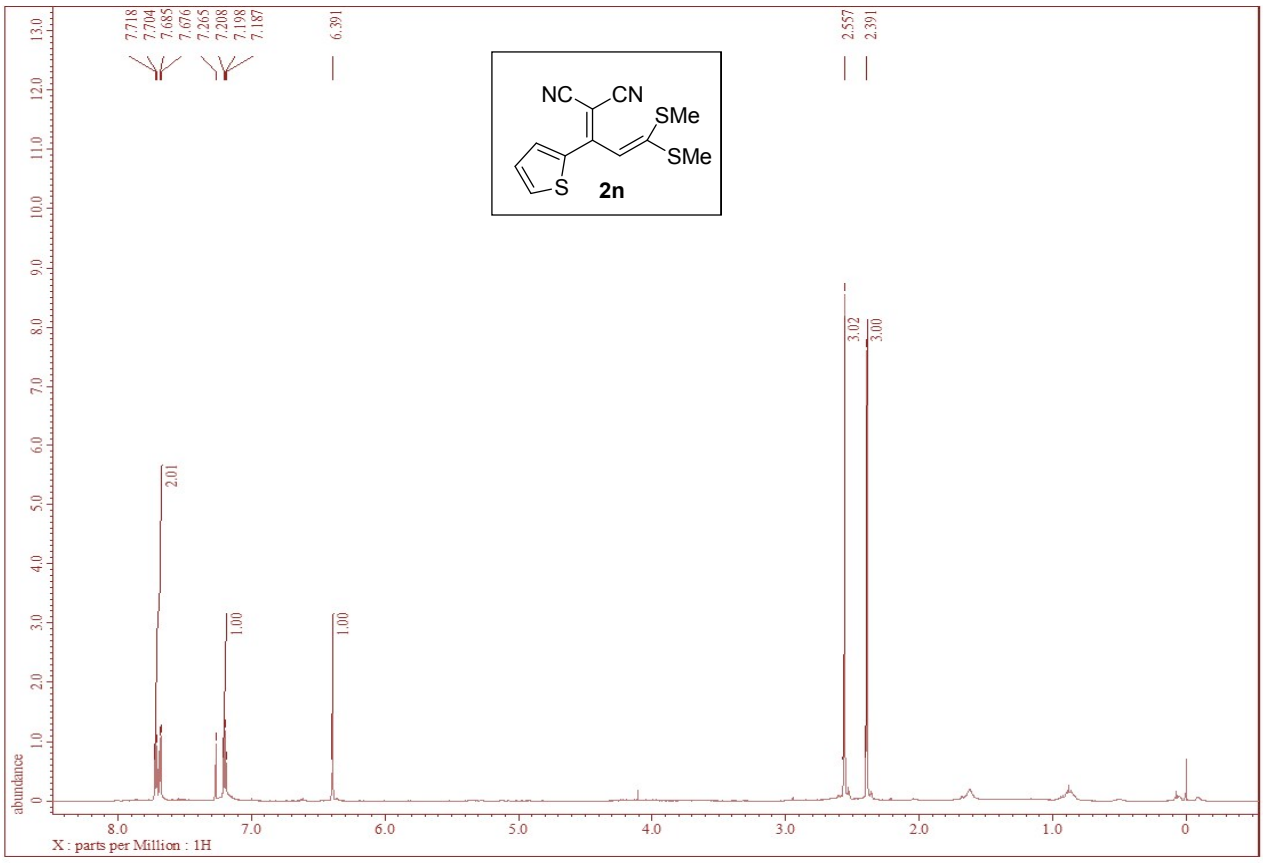

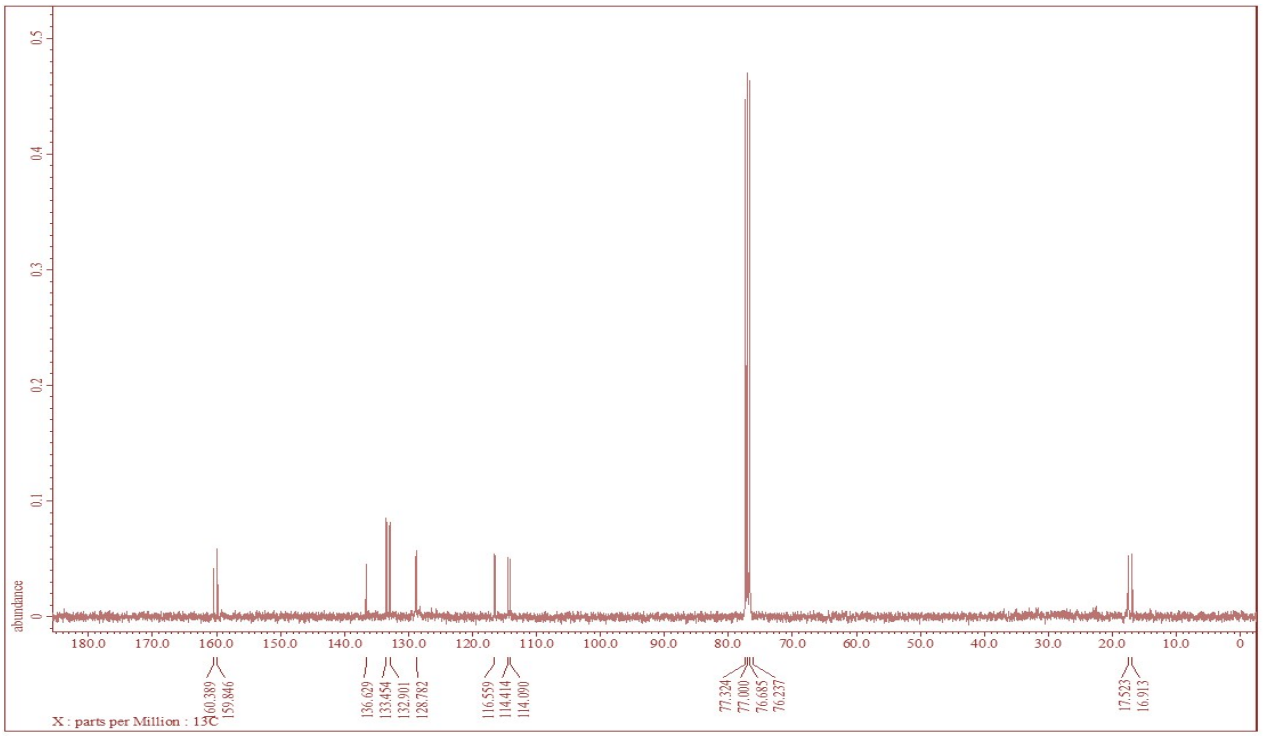

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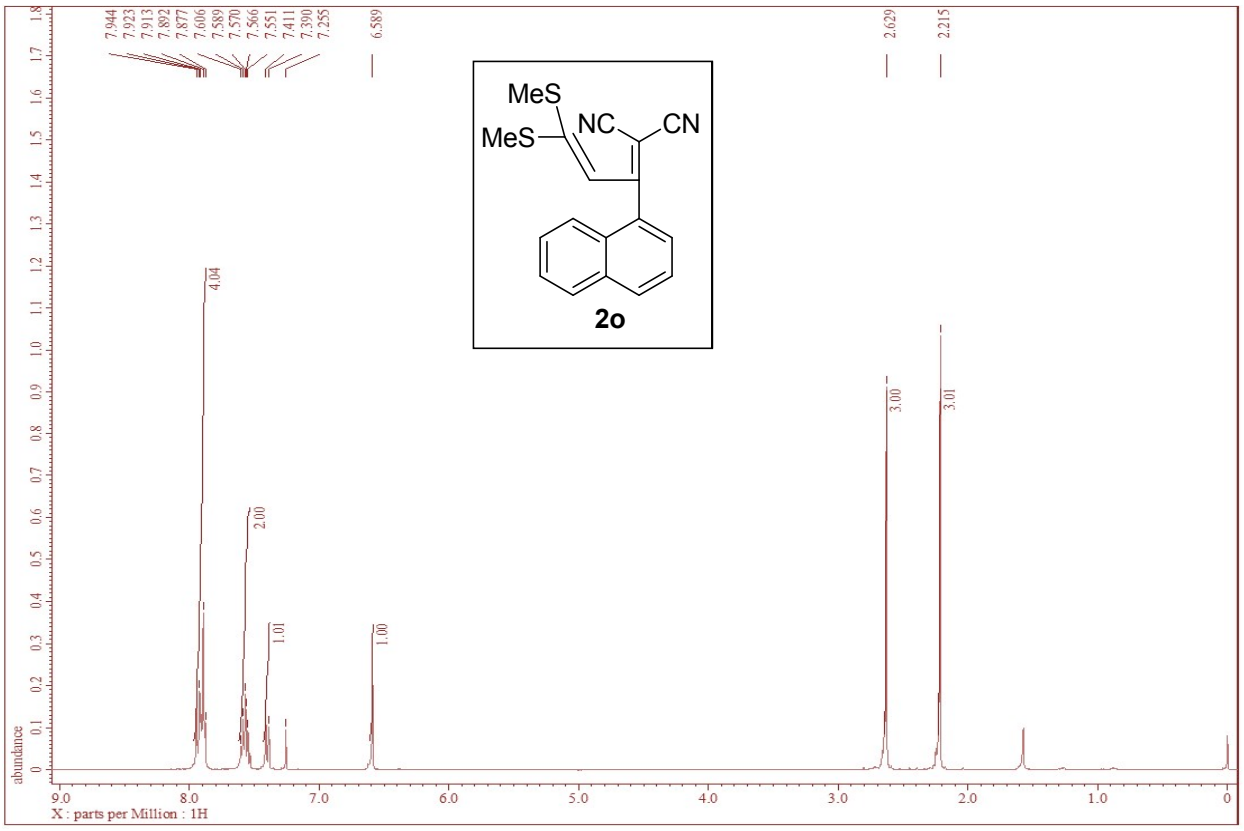

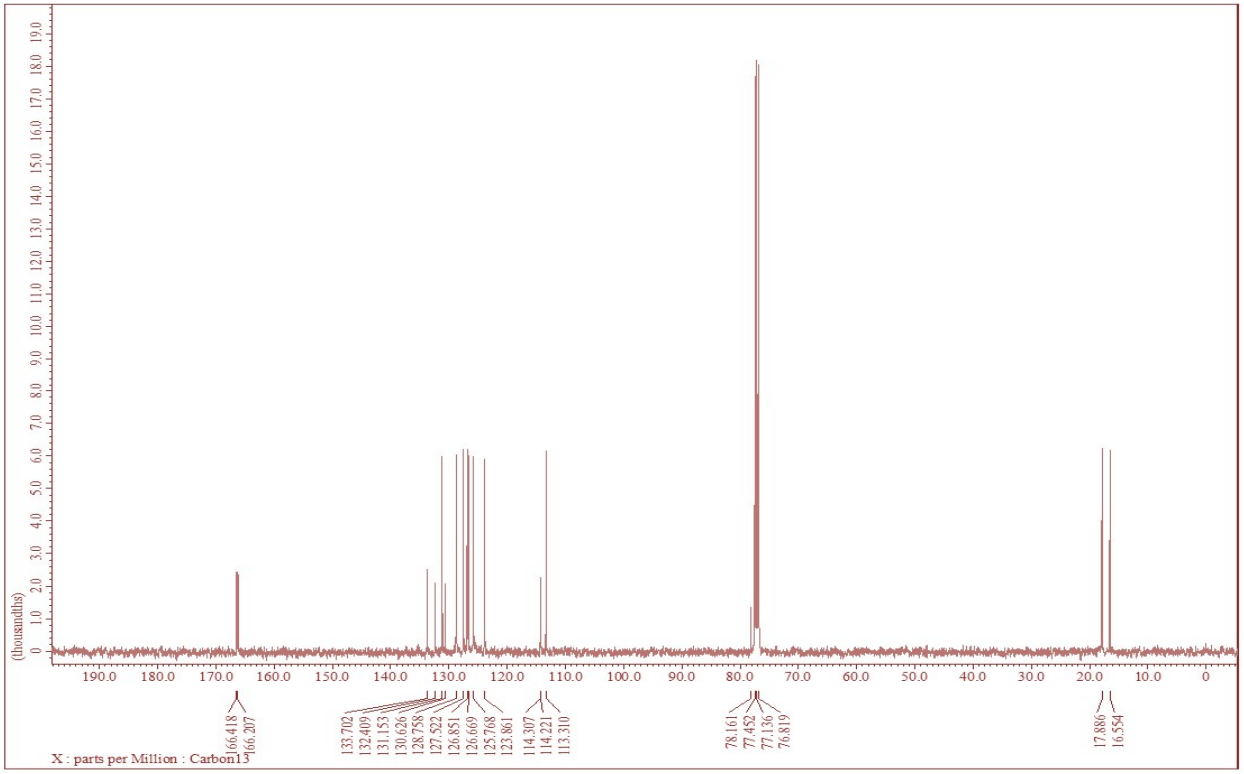

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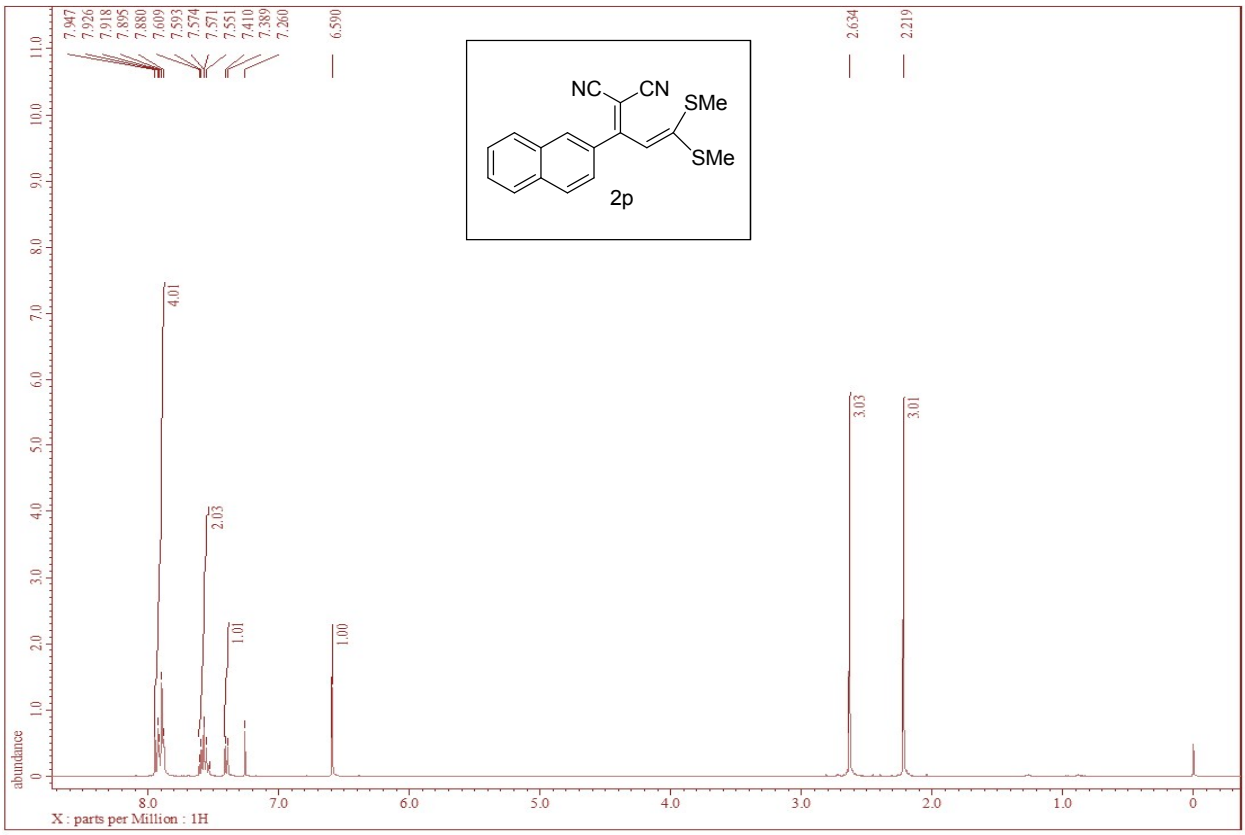
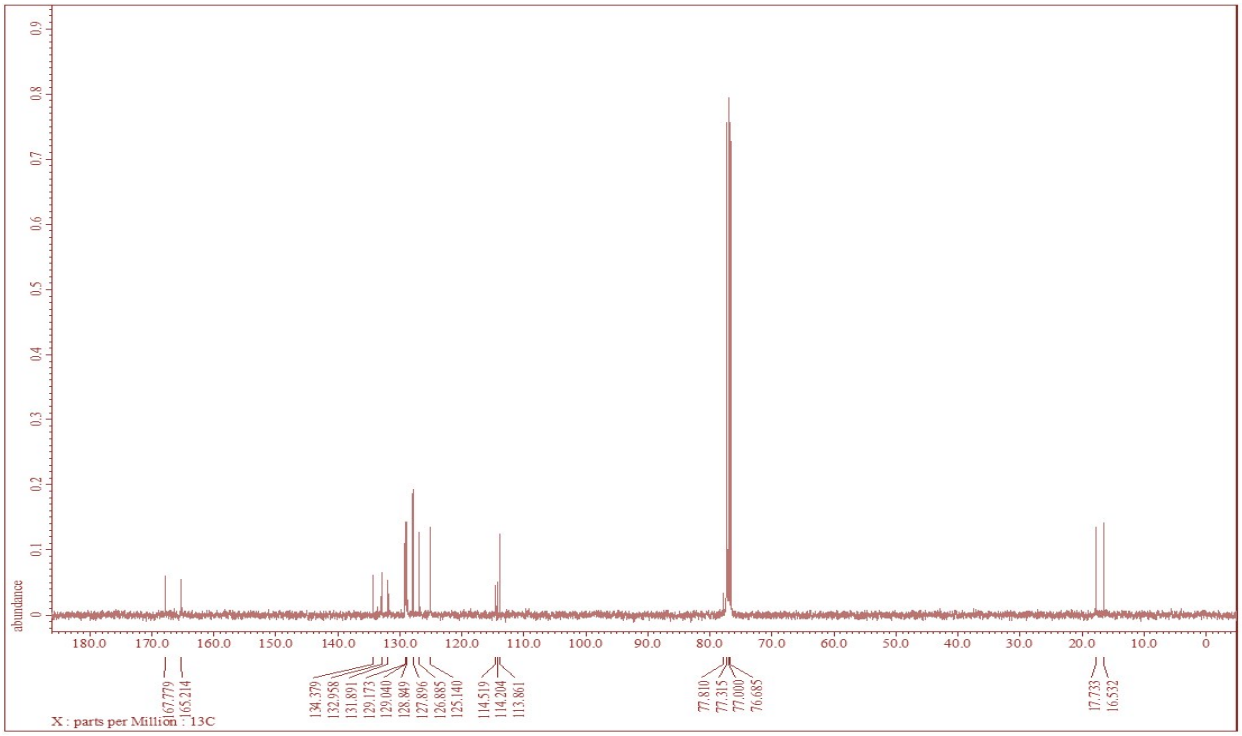
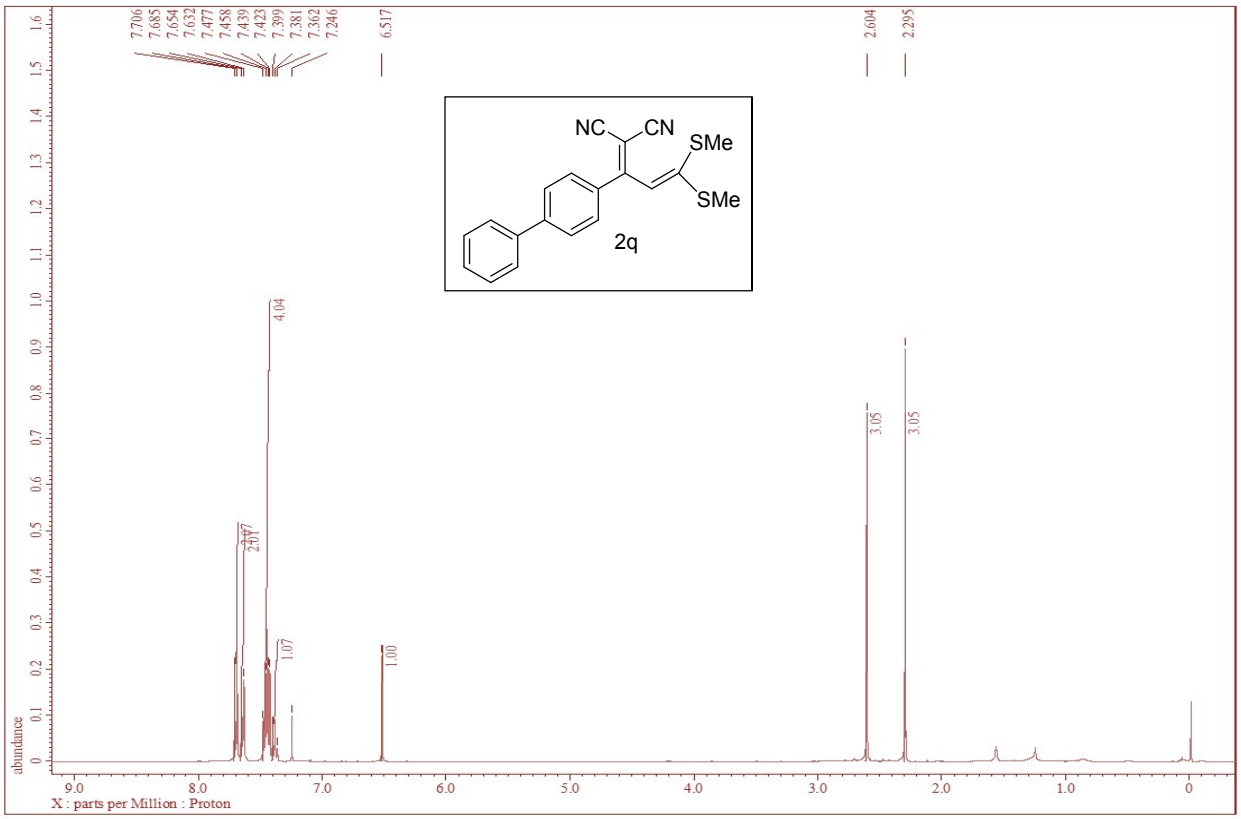
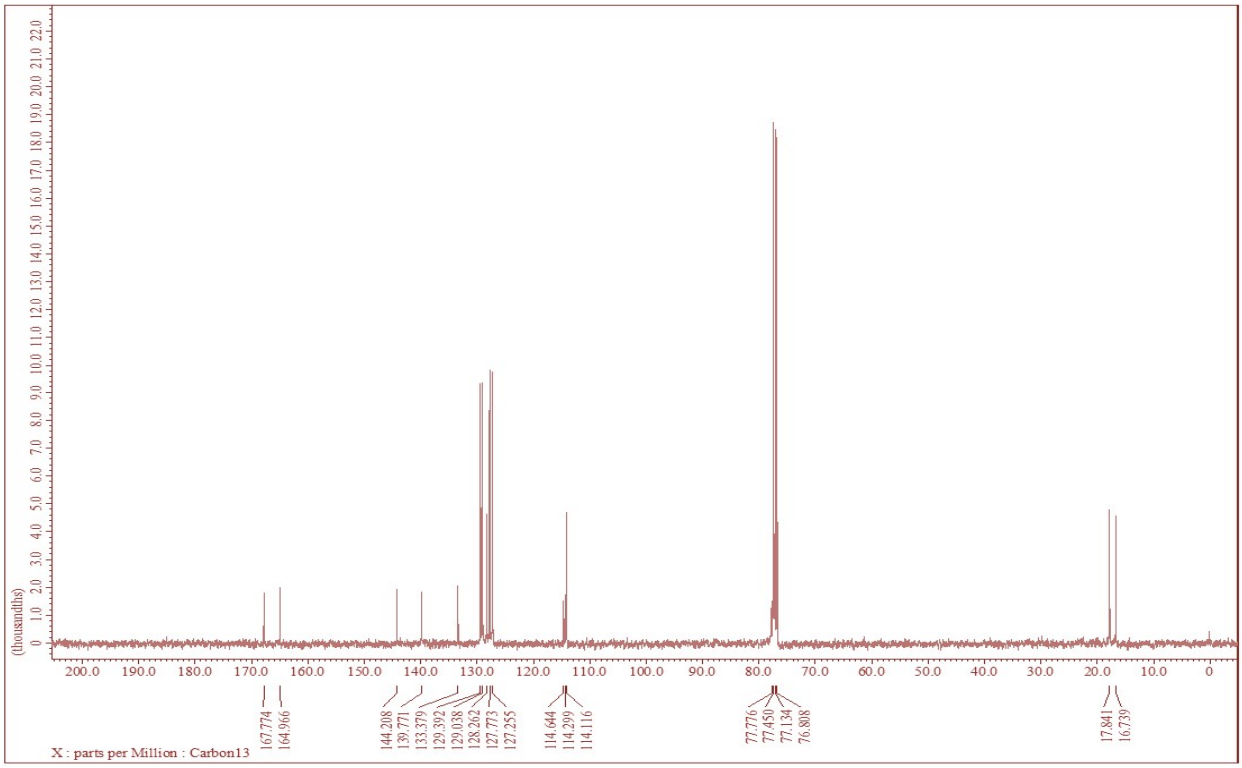


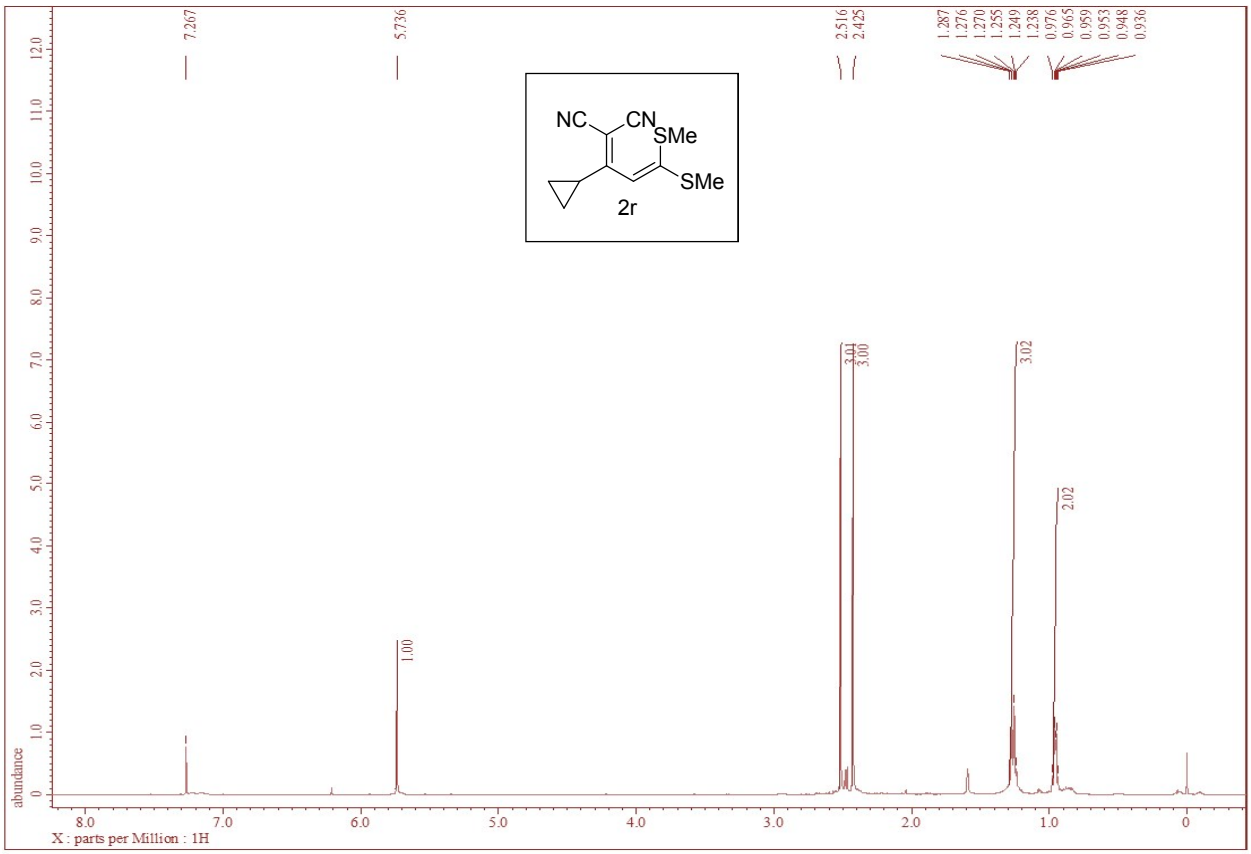


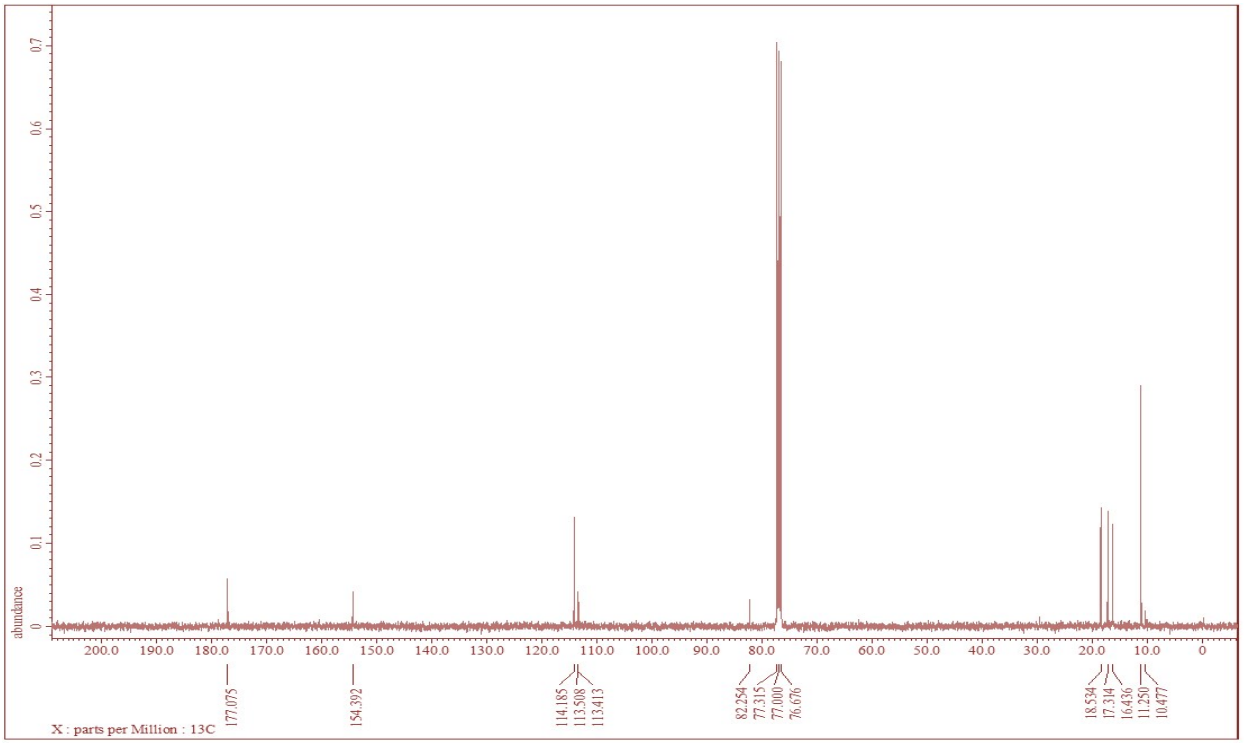
^{1}H NMR and ^{13}C NMR spectrum of2-(3,3-bis(methylthio)-1-(naphthalen-2-yl)allylidene)malononitrile



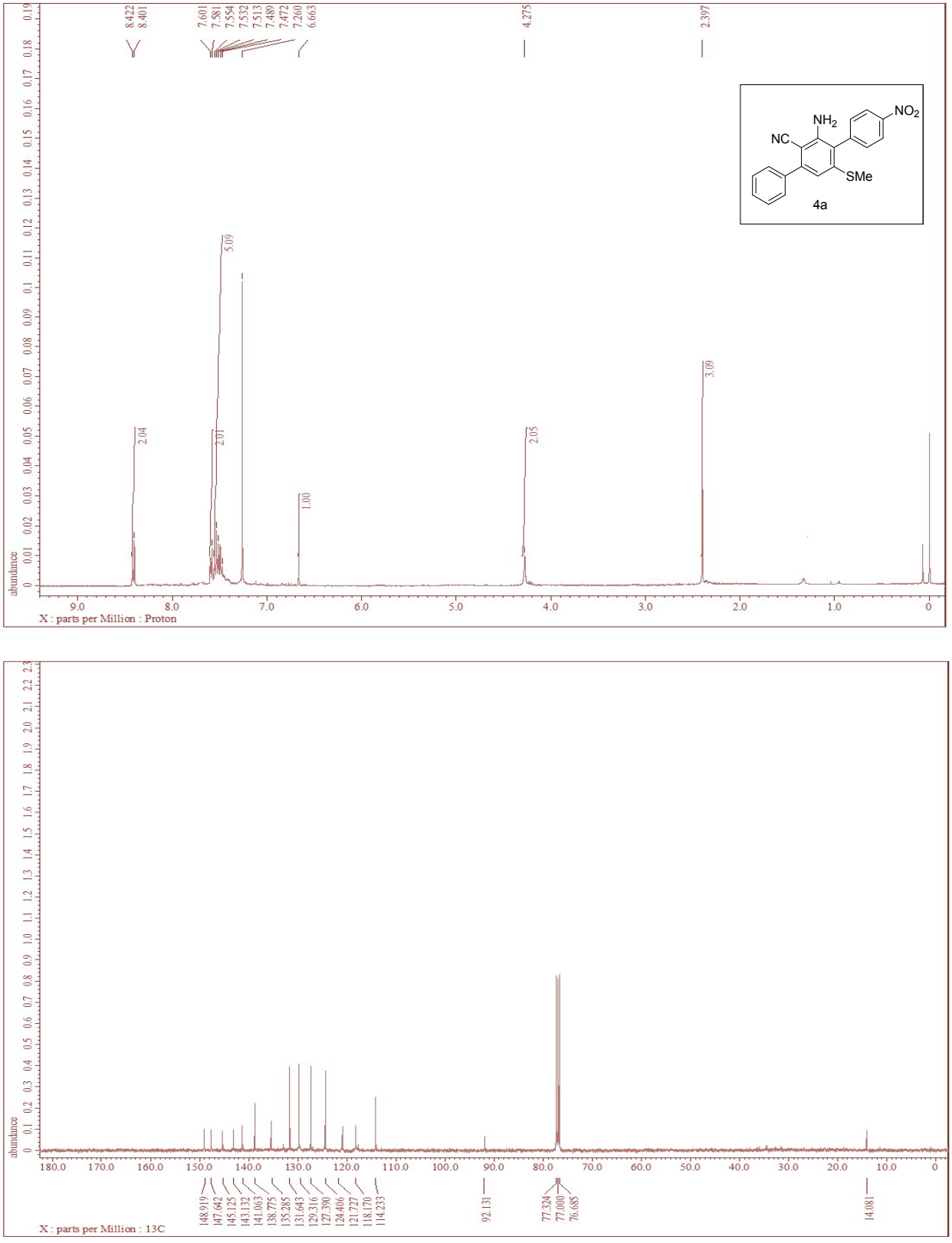


^{1}H NMR and ^{13}C NMR spectrum of 2-(1-([1,1'-biphenyl]-4-yl)-3,3-bis(methylthio)allylidene)malononitrile

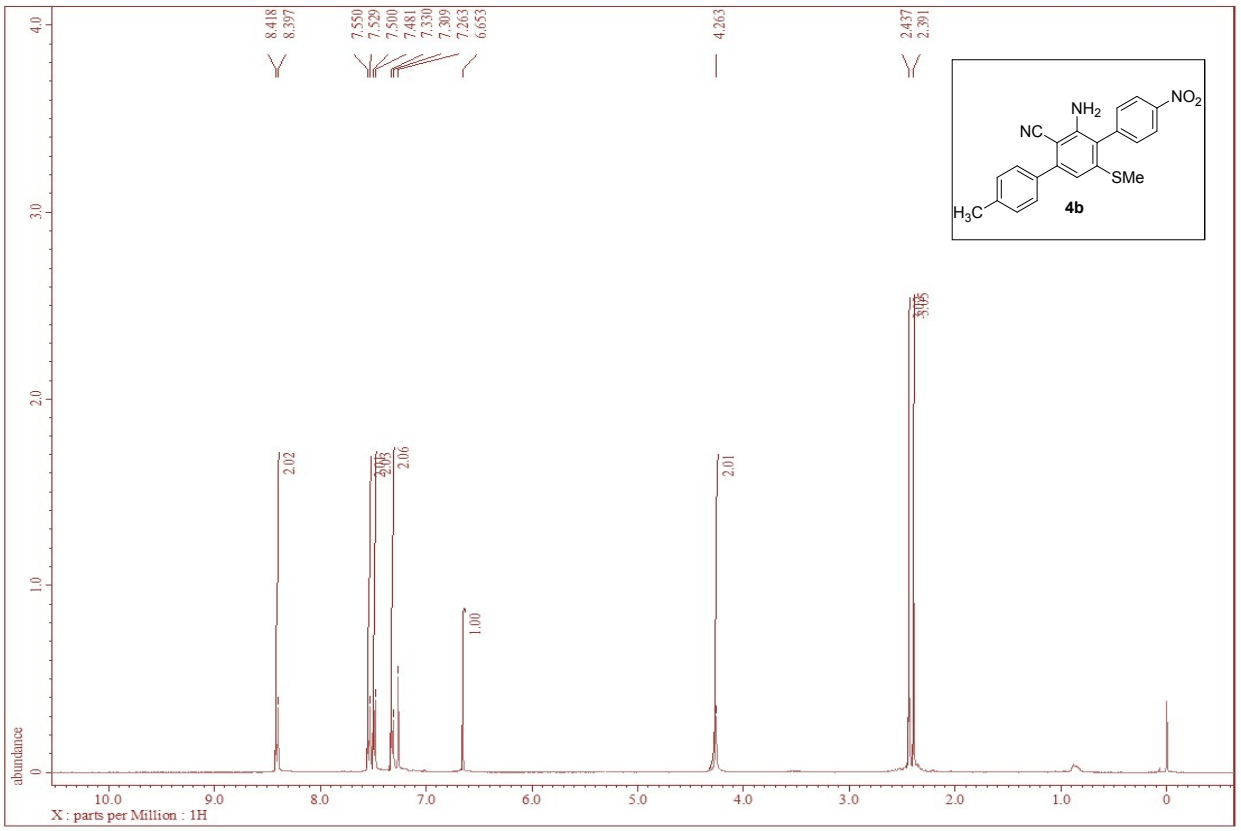


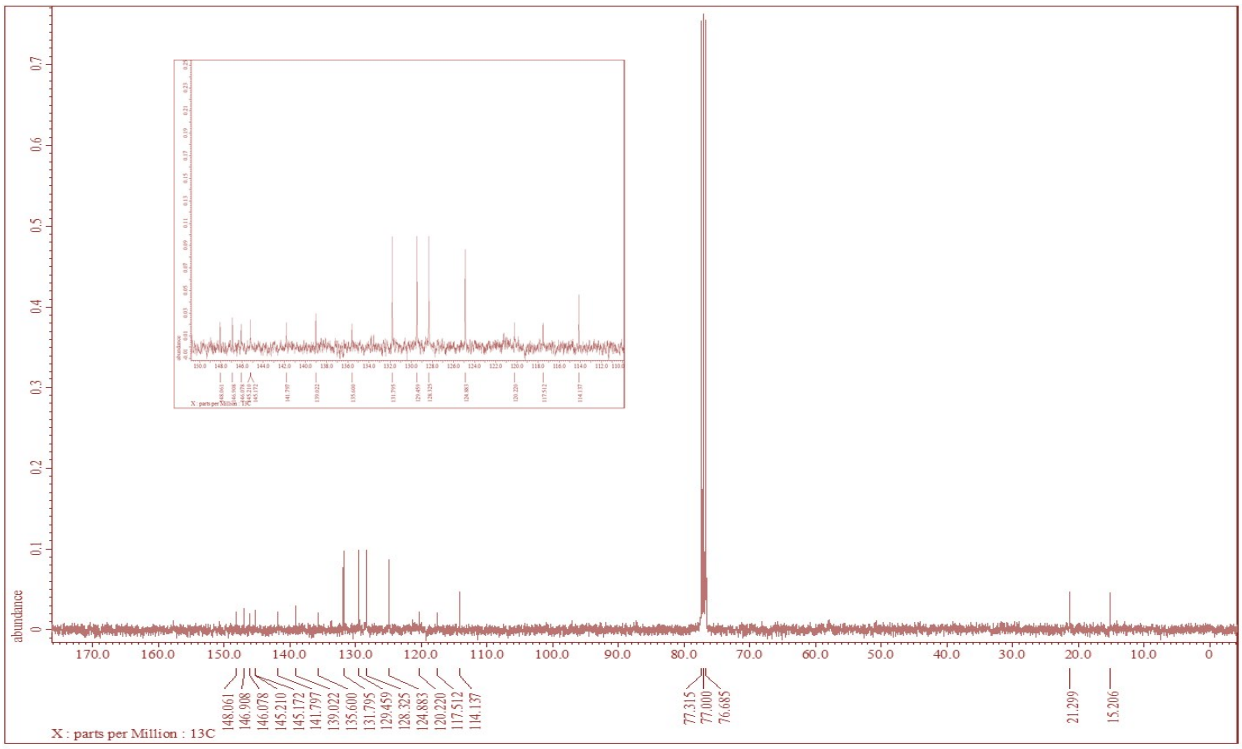


^{1}H NMR and ^{13}C NMR spectrum of 2-(1-cyclopropyl-3,3-bis(methylthio)allylidene)malononitrile

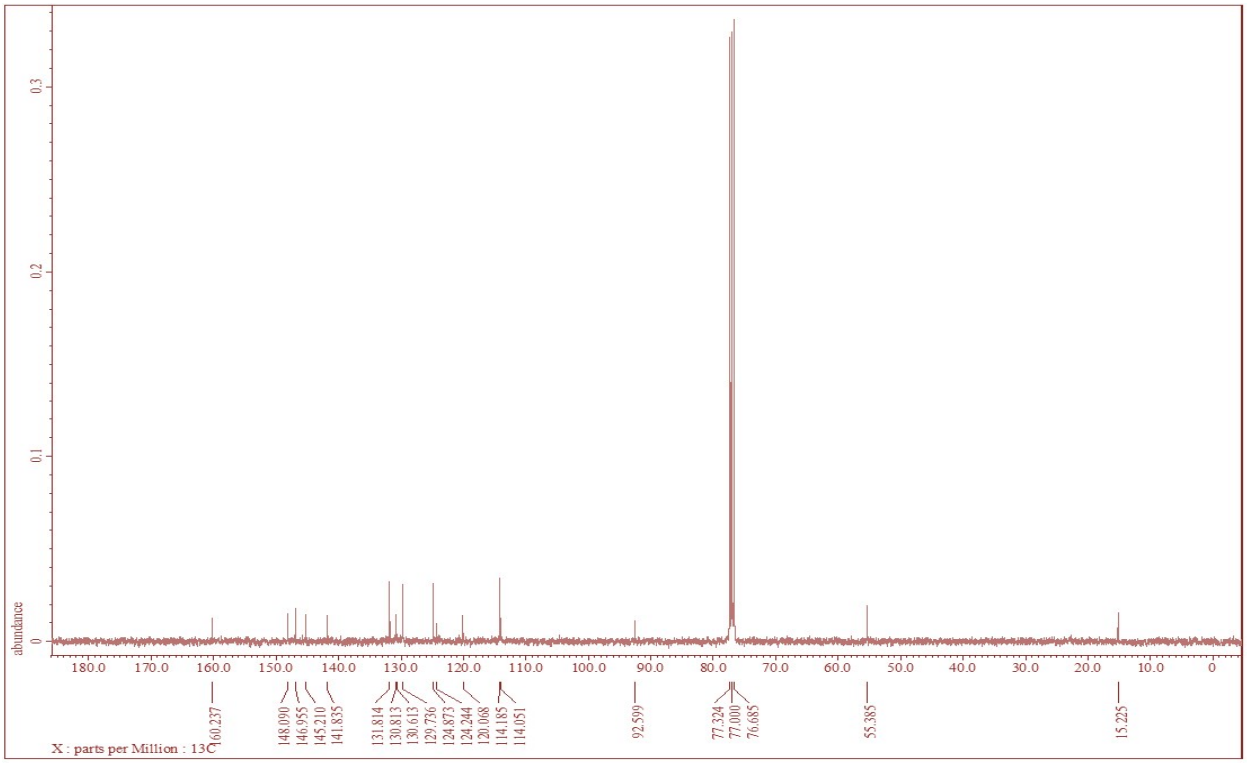


^{1}H NMR and ^{13}C NMR spectrum of 3'-amino-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile

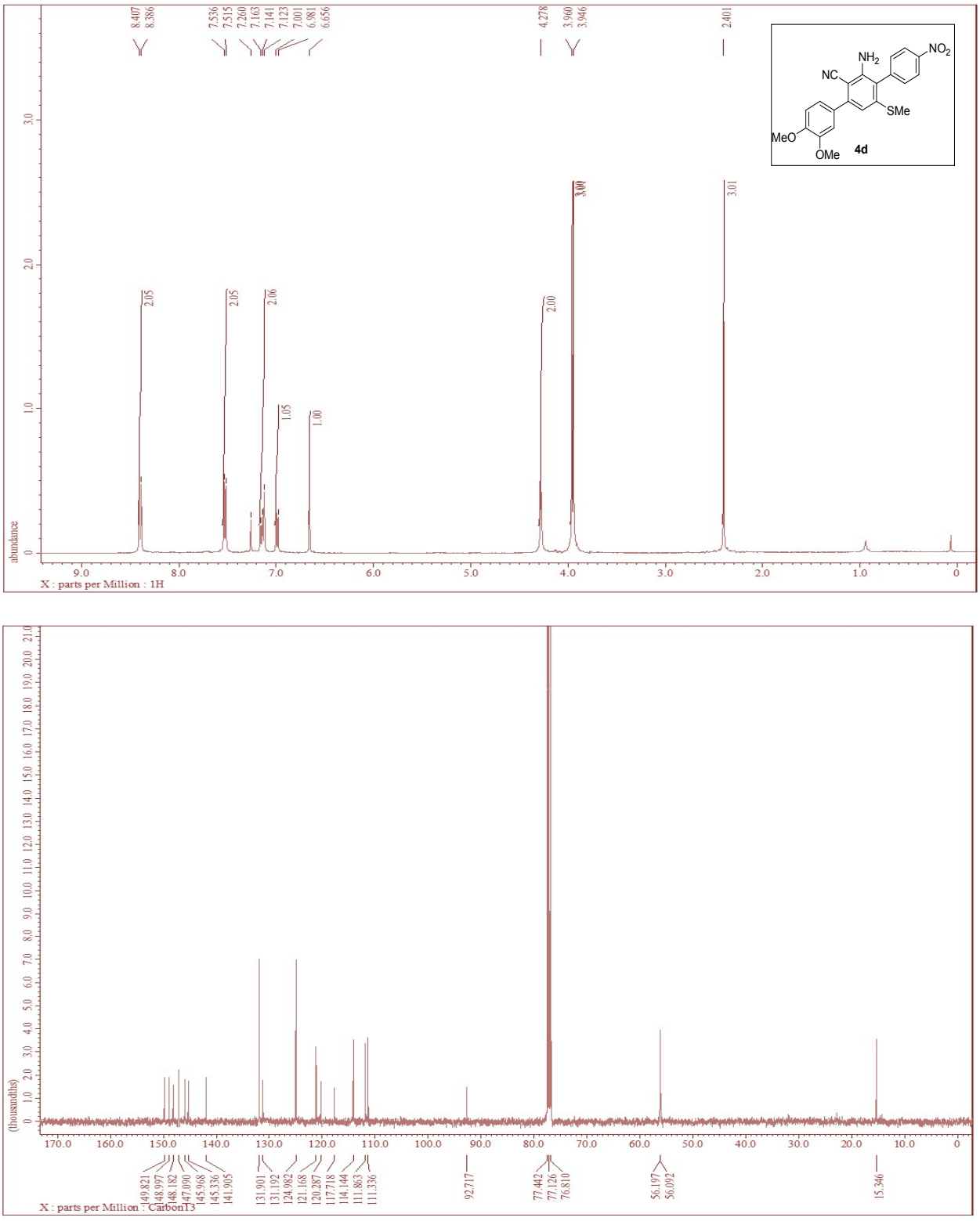




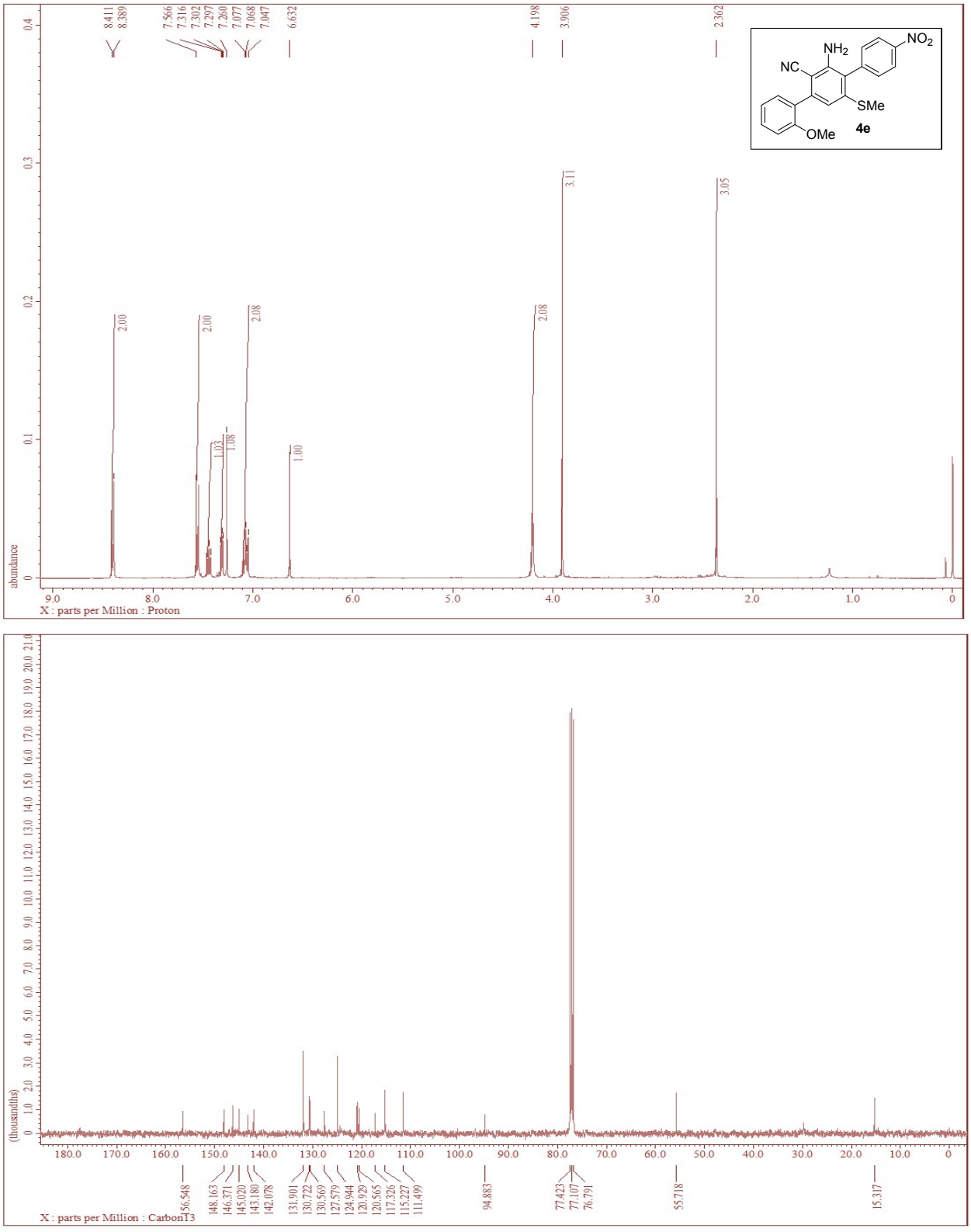
^{1}H NMR and ^{13}C NMR spectrum of3'-amino-4-methyl-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile



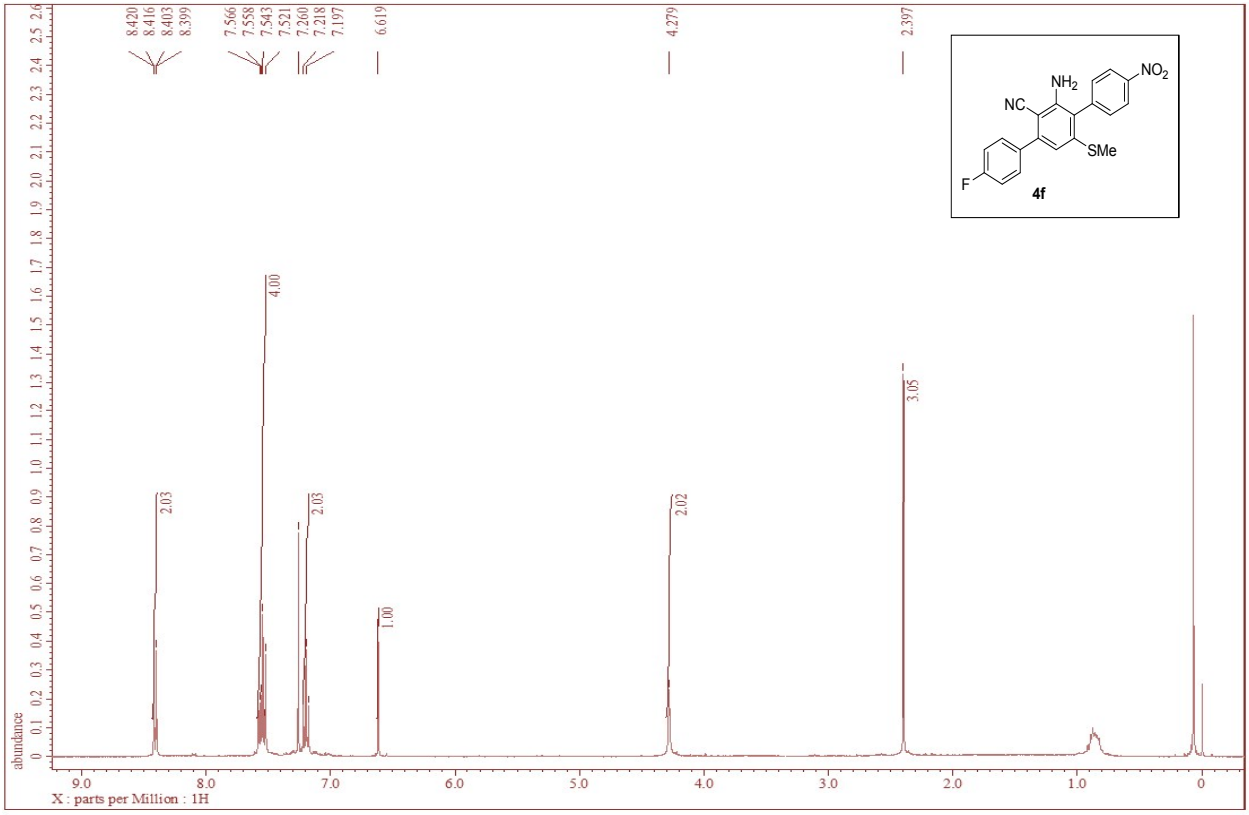
^{1}H NMR and ^{13}C NMR spectrum of3'-amino-4-methoxy-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile

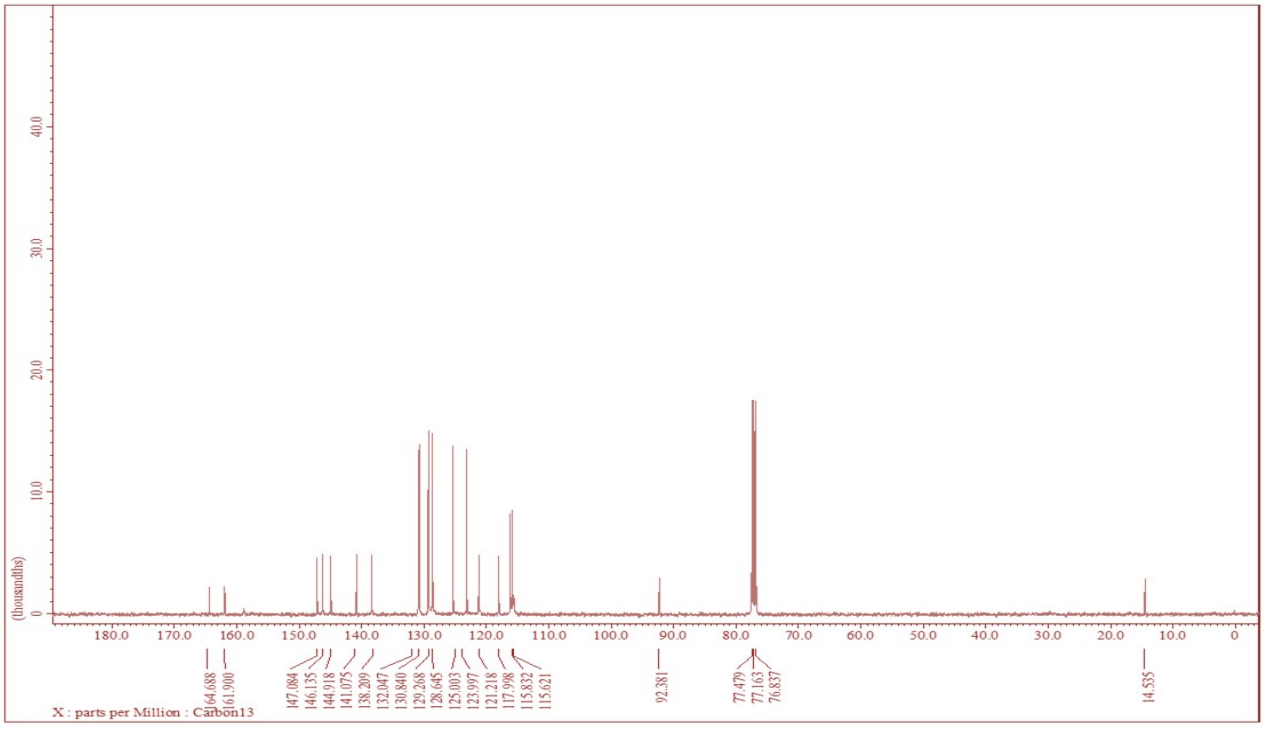


^{1}H NMR and ^{13}C NMR spectrum of 3'-amino-3,4-dimethoxy-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile

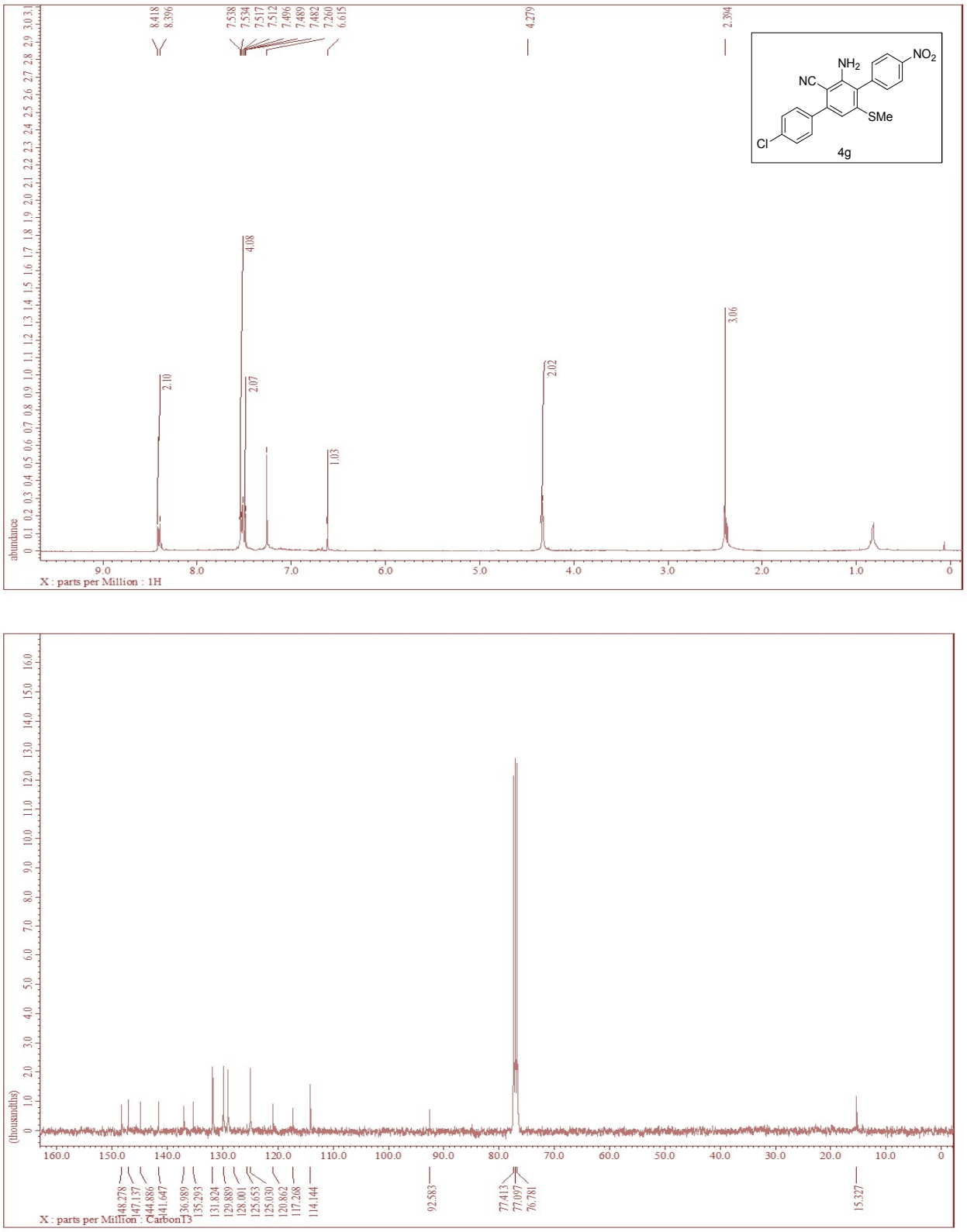


^{1}H NMR and ^{13}C NMR spectrum of 3'-amino-2-methoxy-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile

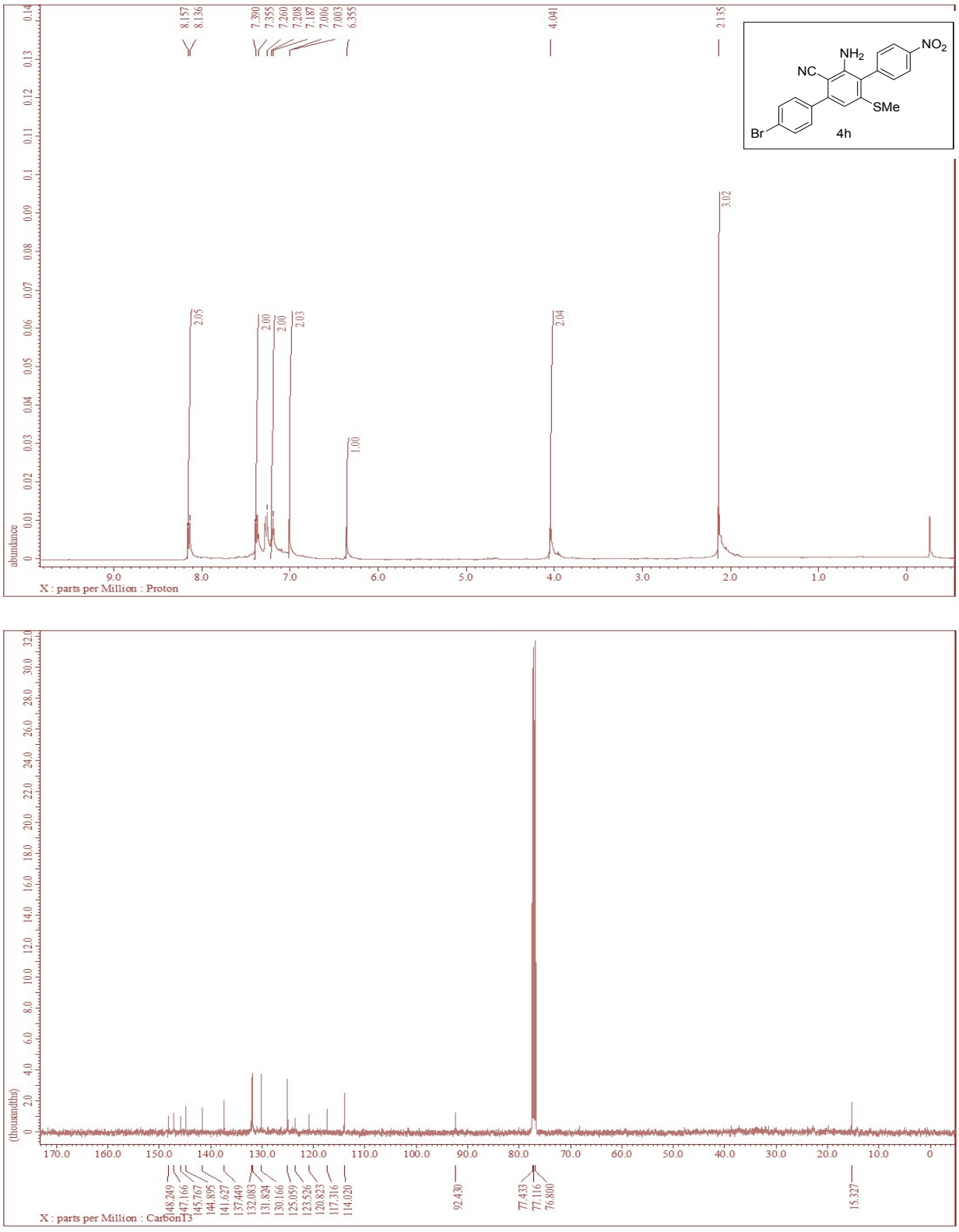




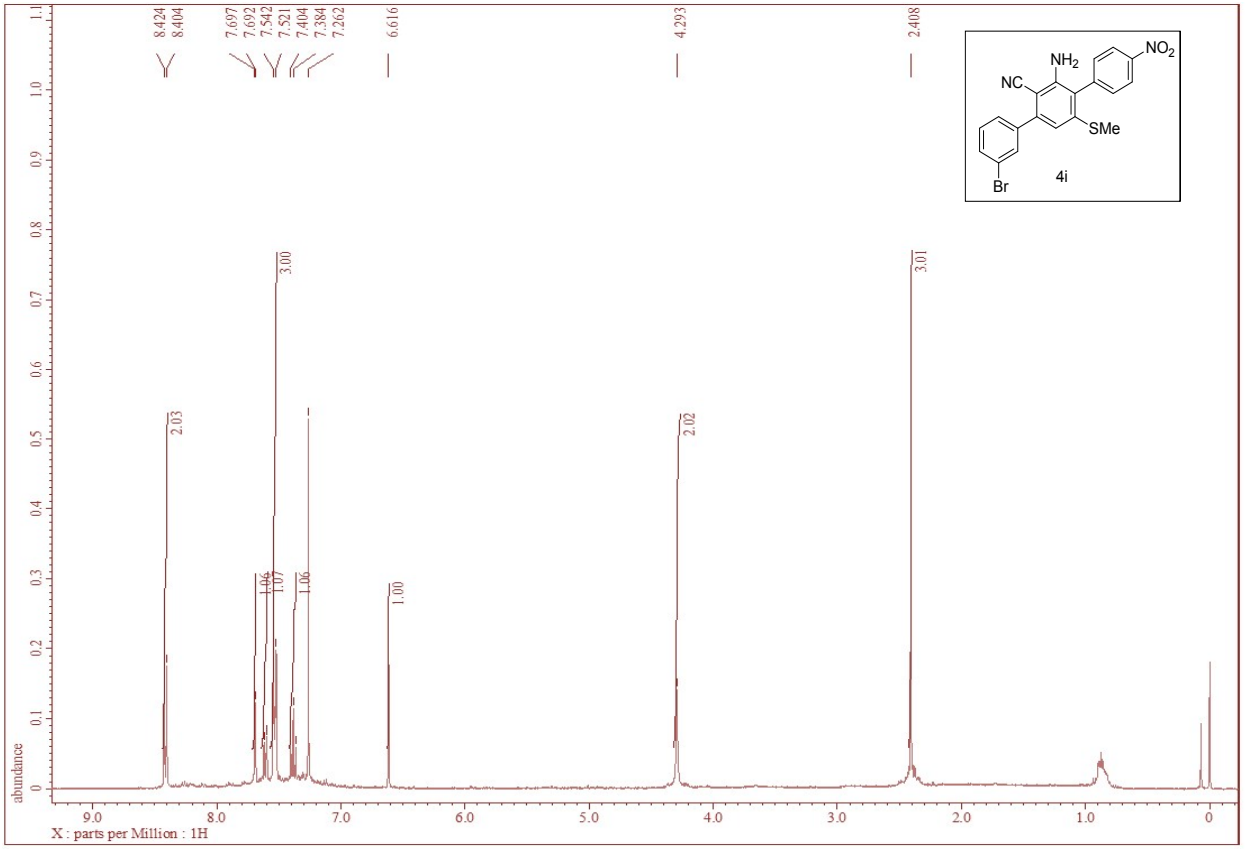
^{1}H NMR and ^{13}C NMR spectrum of 3'-amino-4-fluoro-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile

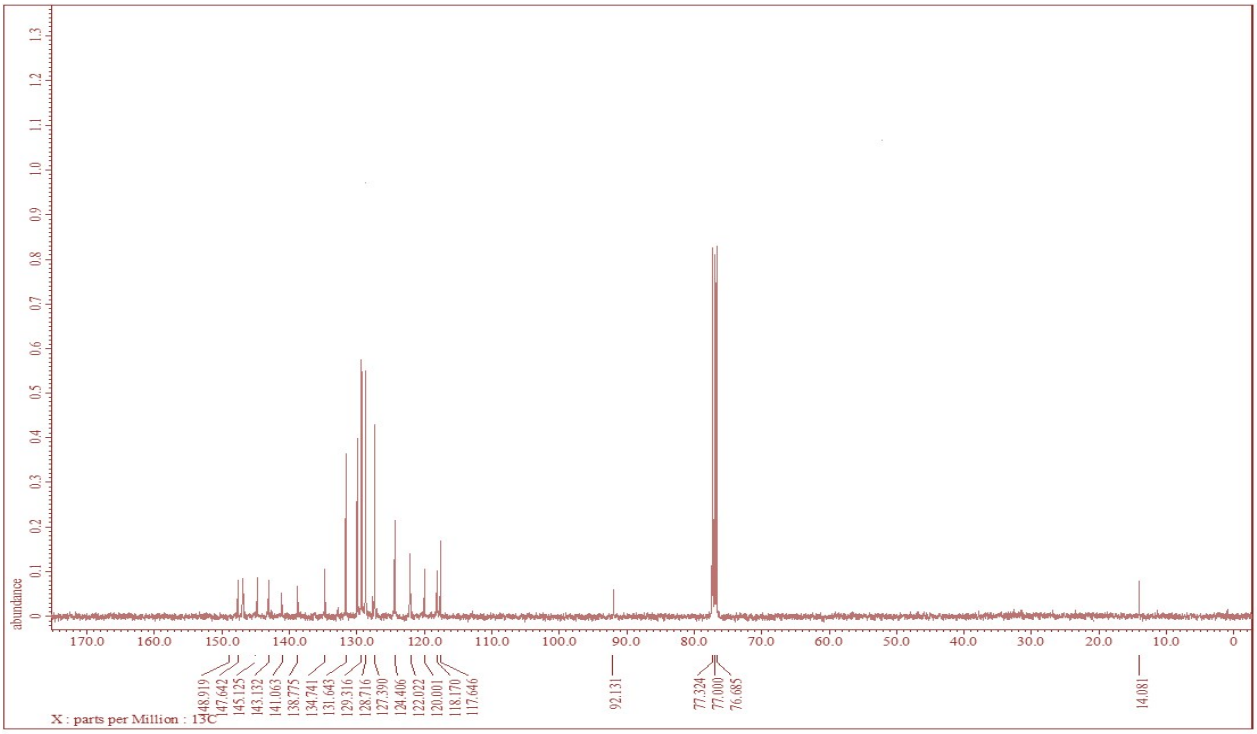


^{1}H NMR and ^{13}C NMR spectrum of 3'-amino-4-chloro-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile

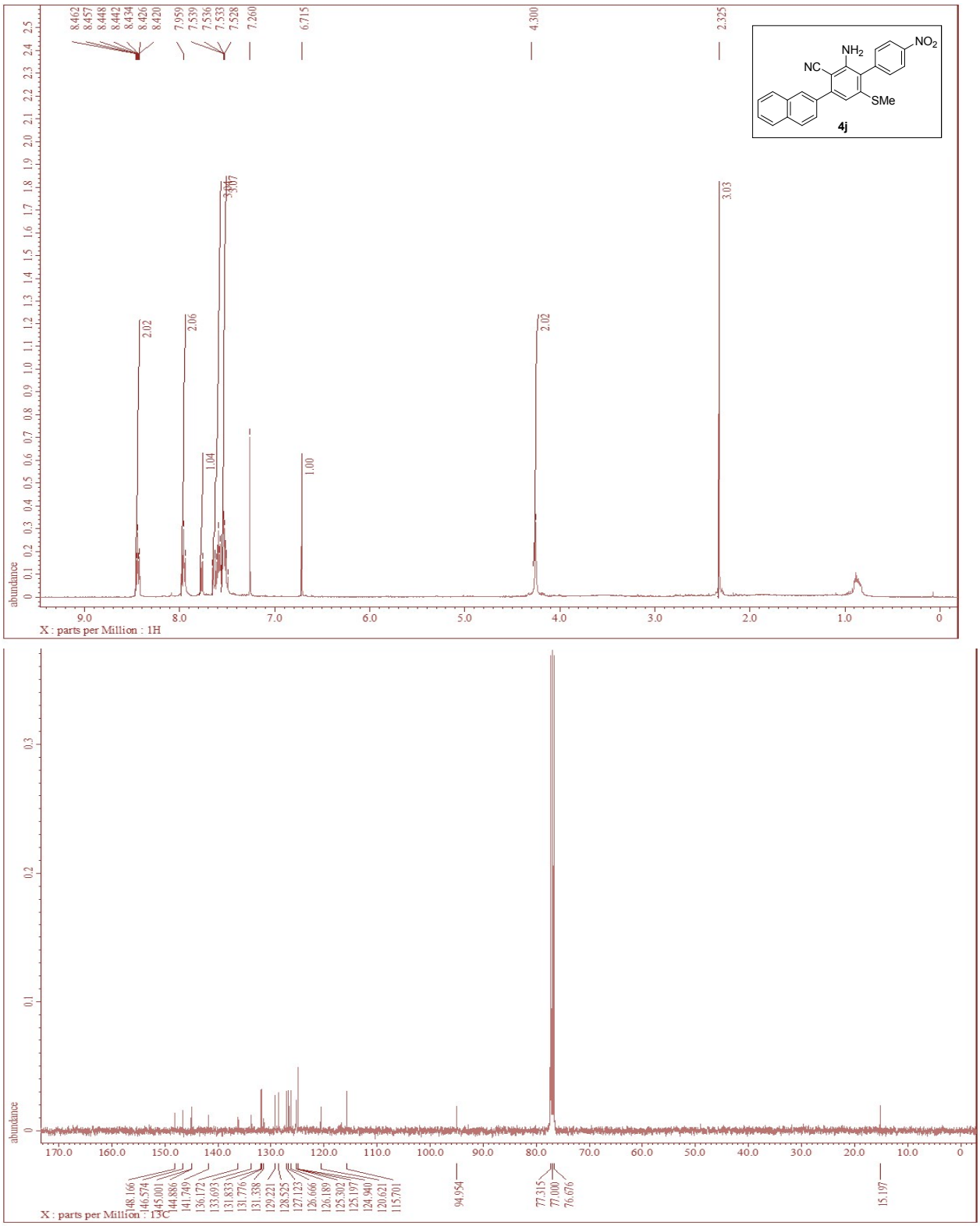


^{1}H NMR and ^{13}C NMR spectrum of3'-amino-4-bromo-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile

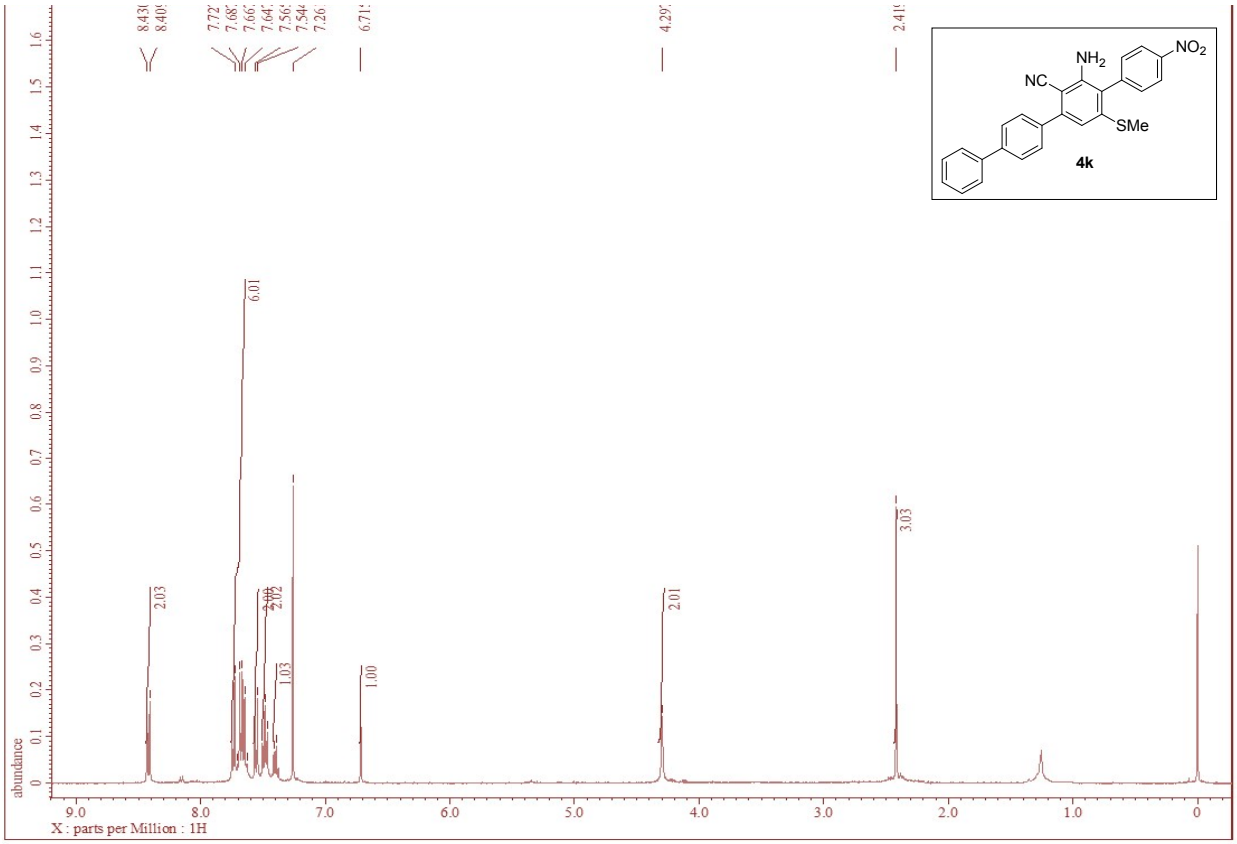


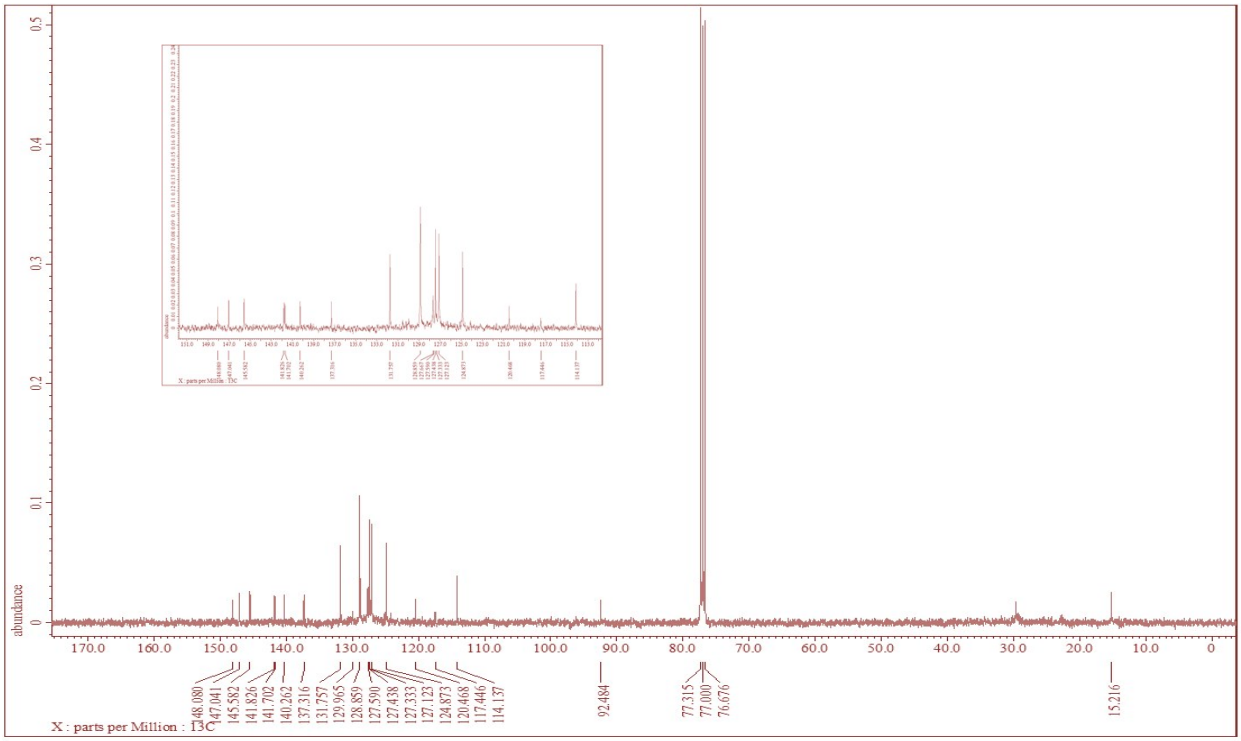


^{1}H NMR and ^{13}C NMR spectrum of3'-amino-3-bromo-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile



^{1}H NMR and ^{13}C NMR spectrum of2-amino-6-(methylthio)-4-(naphthalen-2-yl)-4'-nitro-[1,1'-biphenyl]-3-carbonitrile





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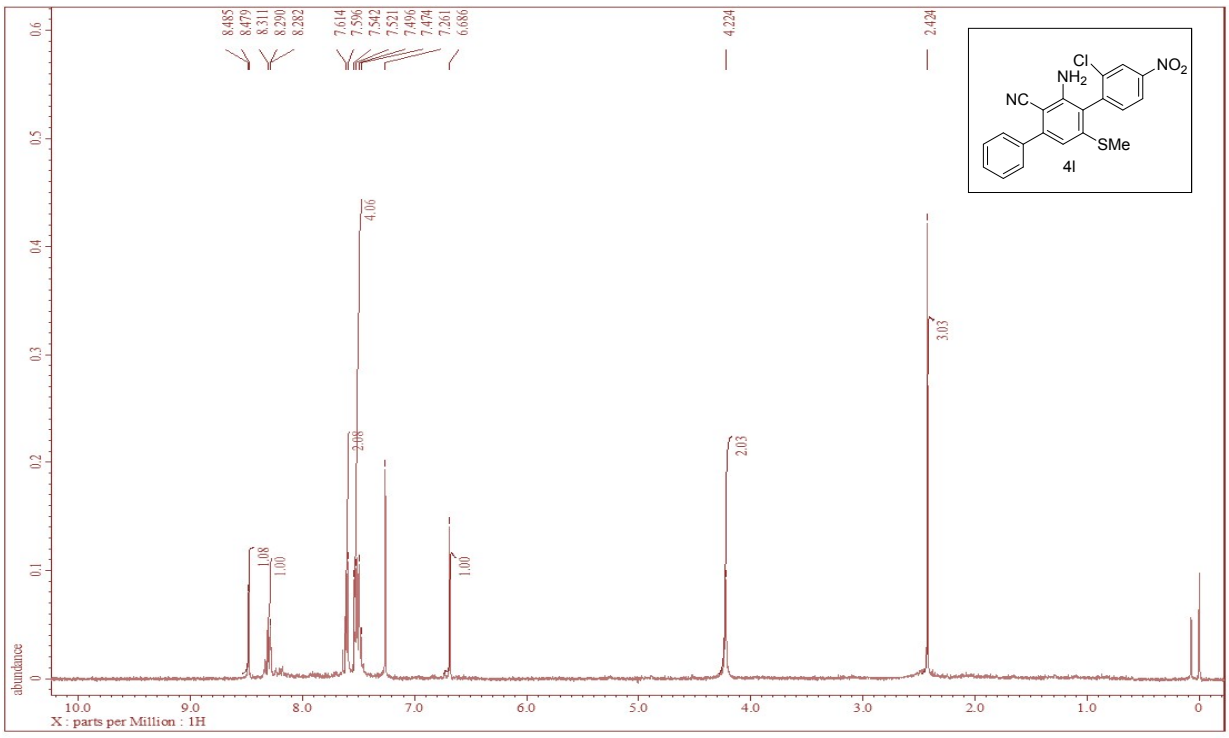
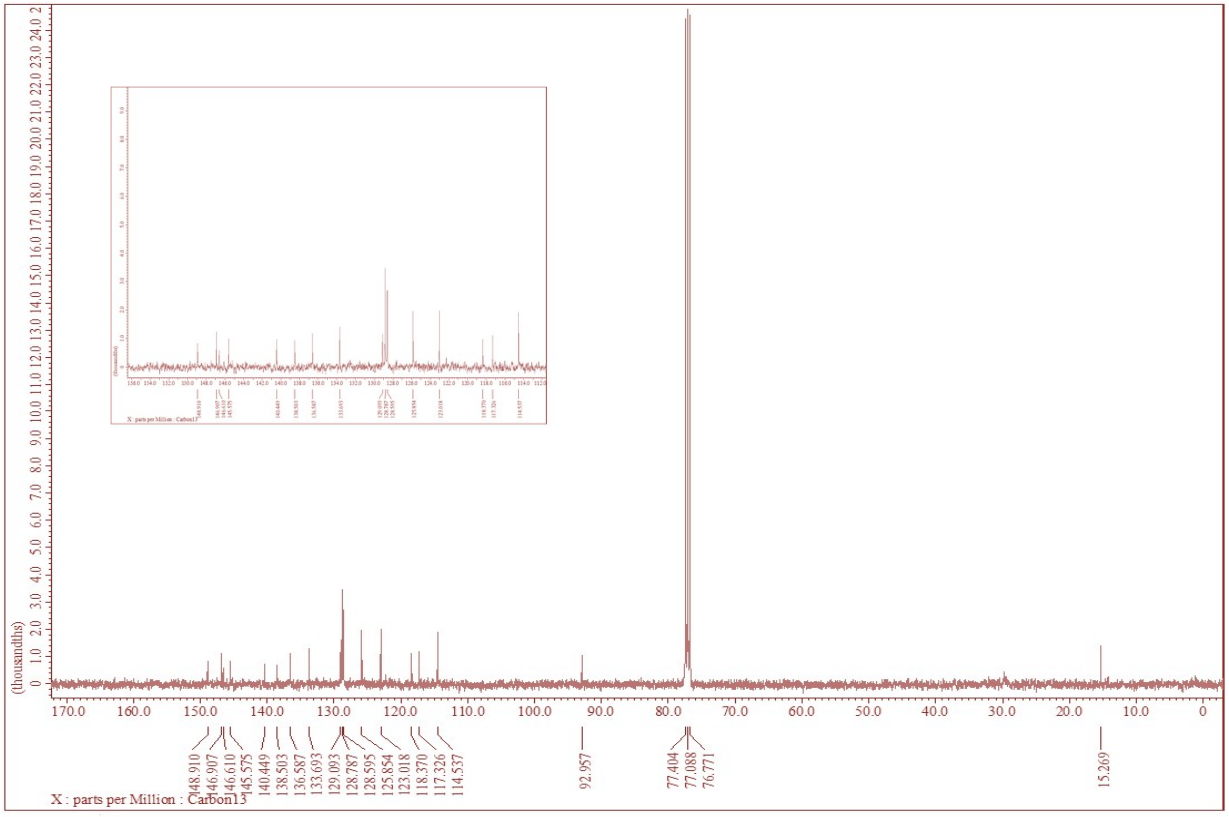
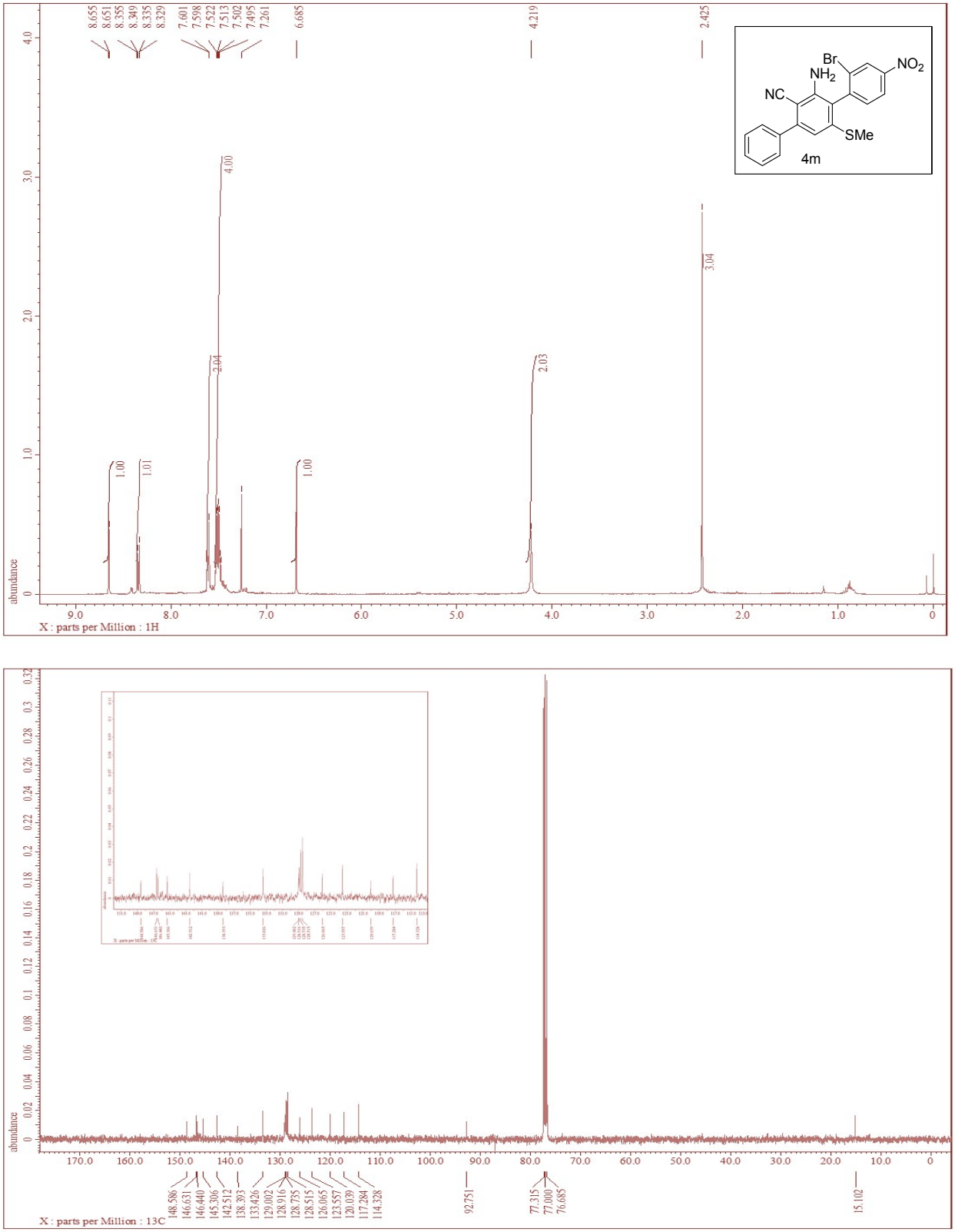
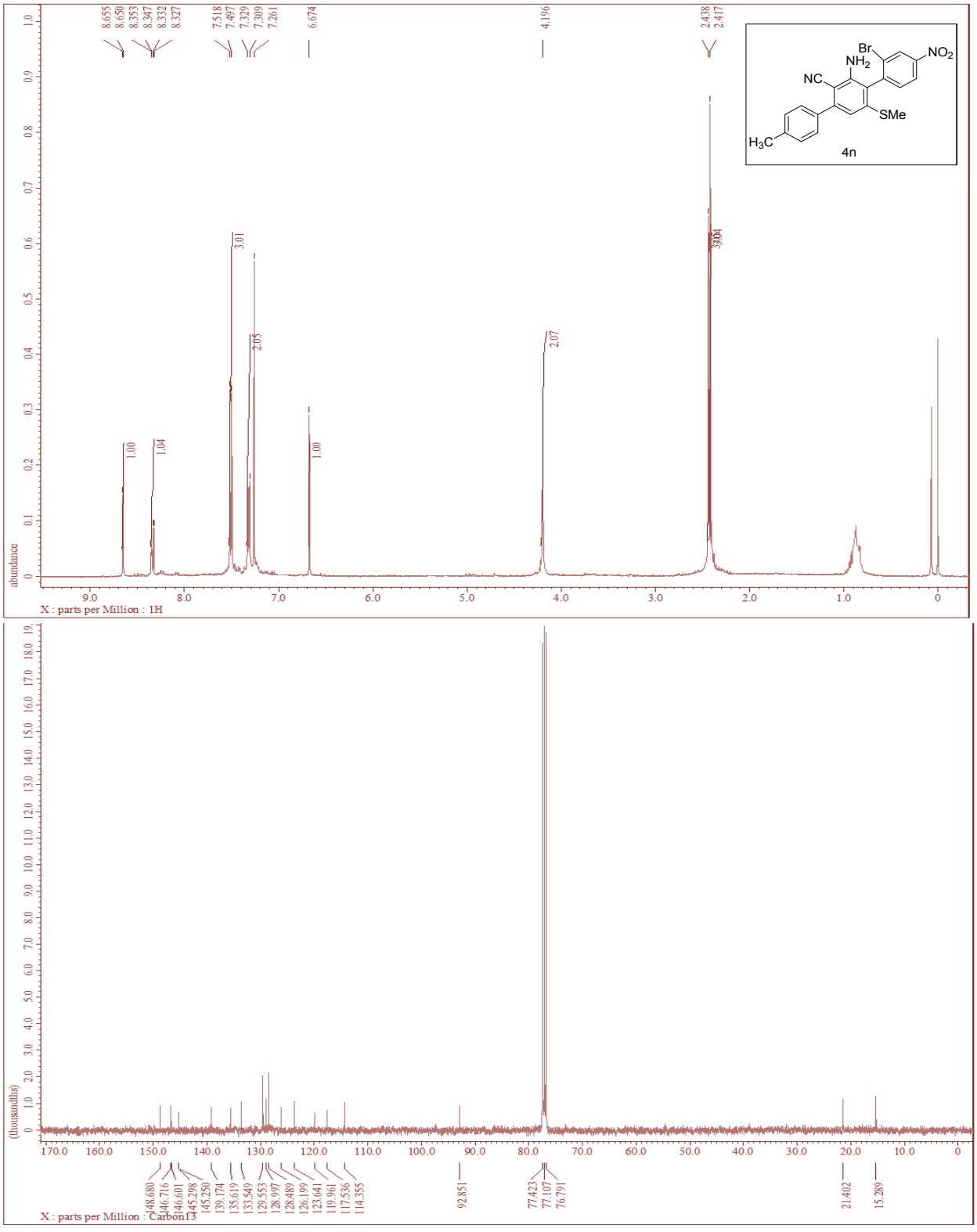




^{1}H NMR and ^{13}C NMR spectrum of 3'-amino-2''-chloro-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile



^{1}H NMR and ^{13}C NMR spectrum of 3'-amino-2''-bromo-5'-(methylthio)-4''-nitro-[1,1':4',1''-terphenyl]-2'-carbonitrile



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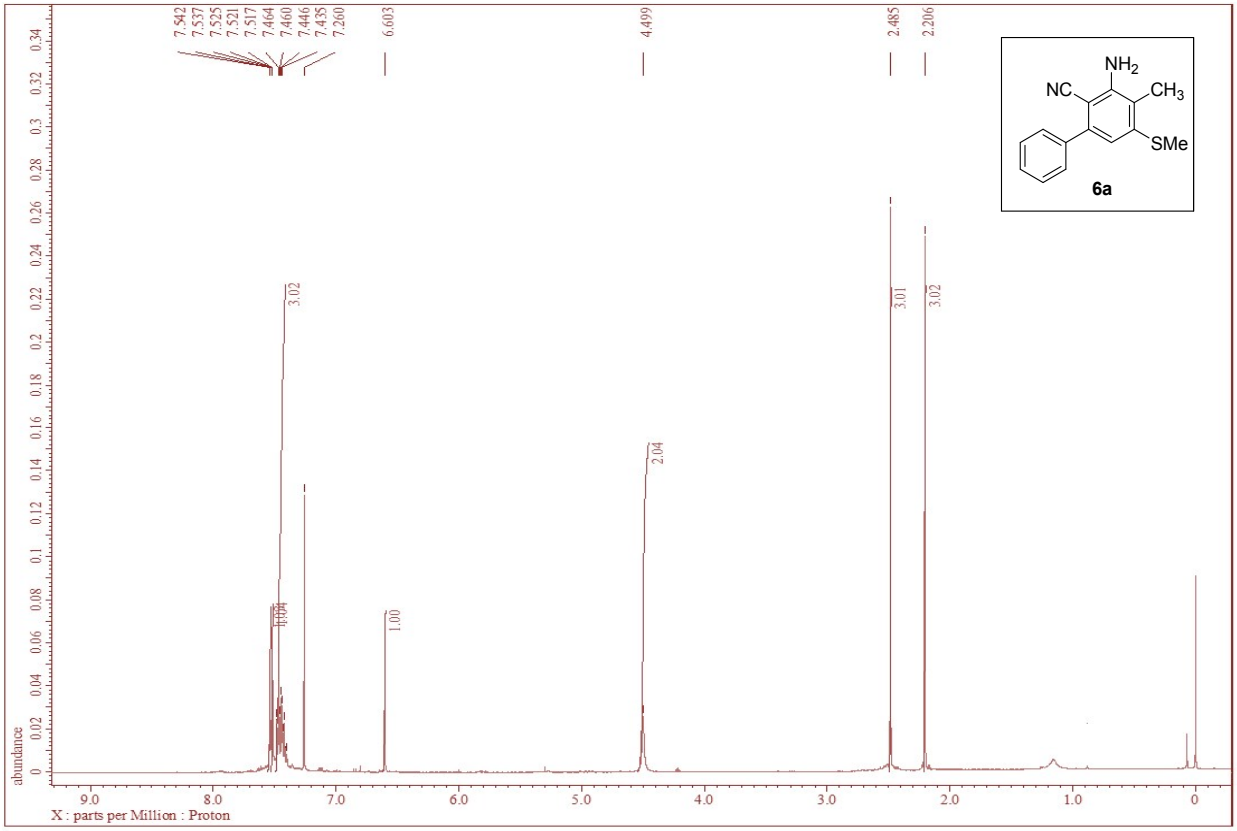

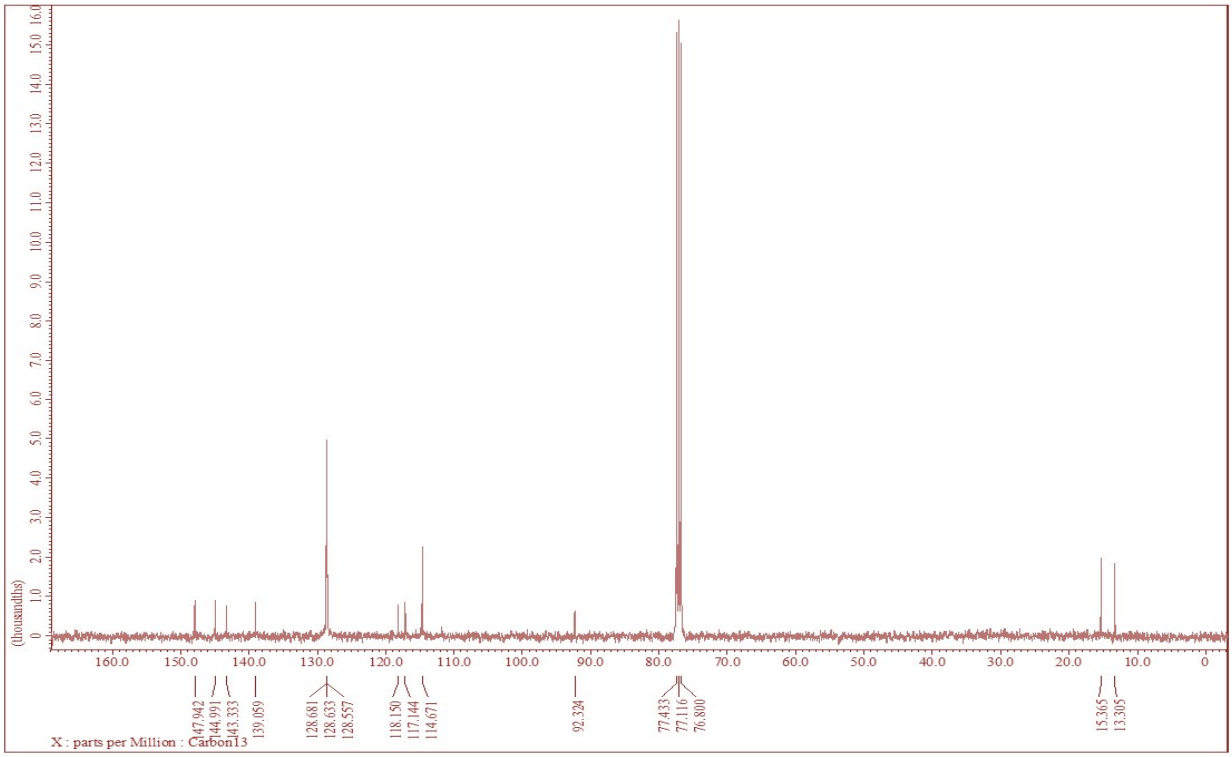

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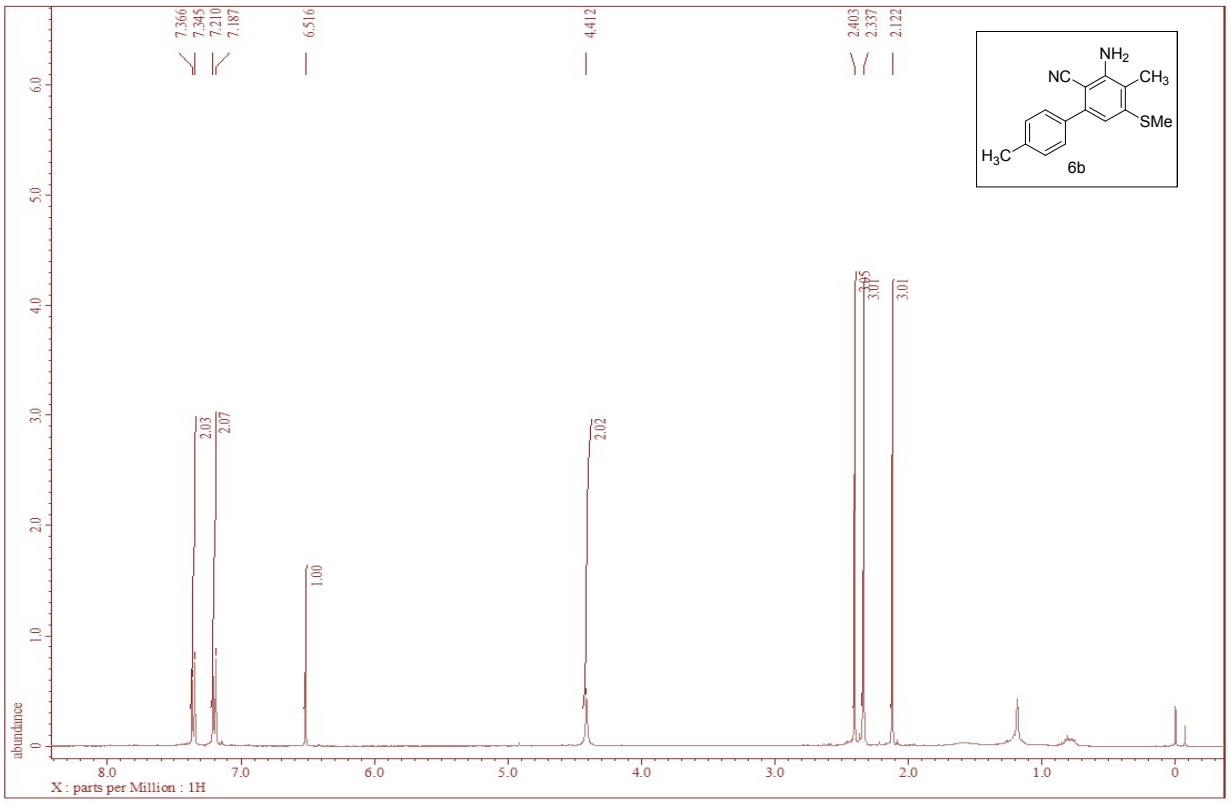

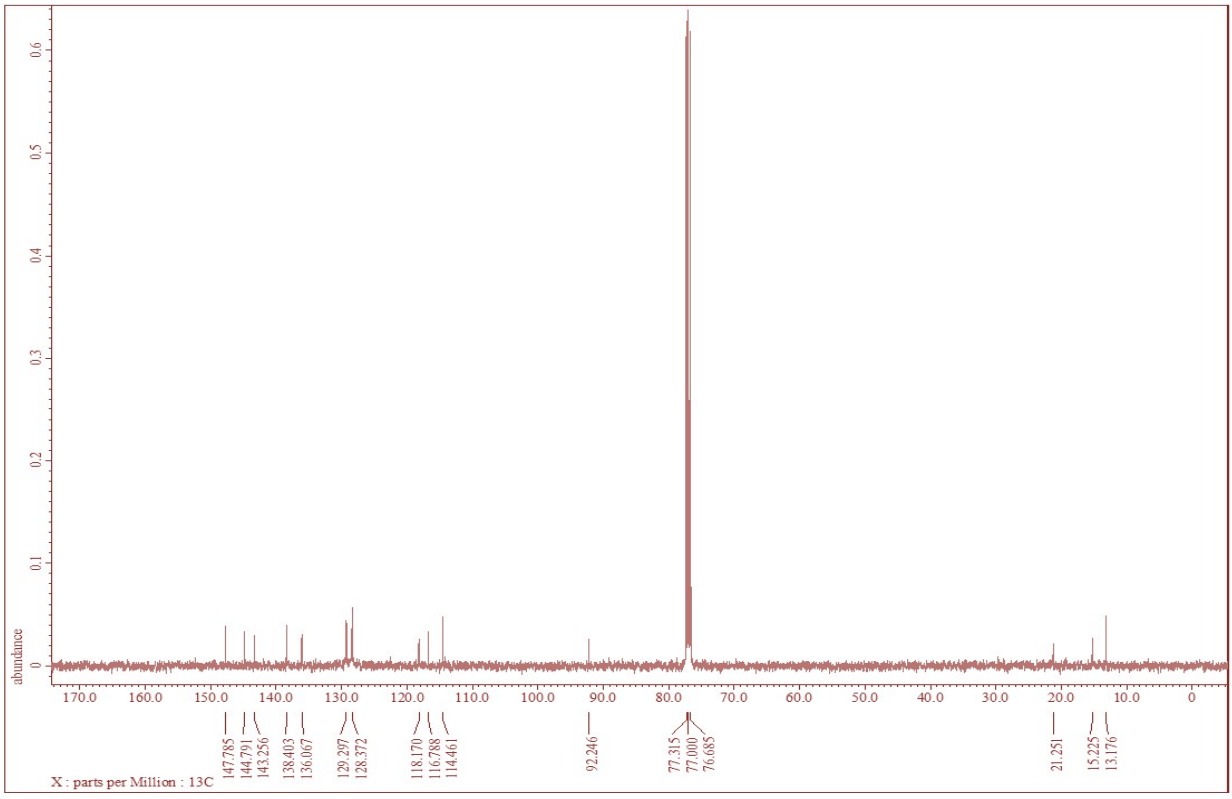

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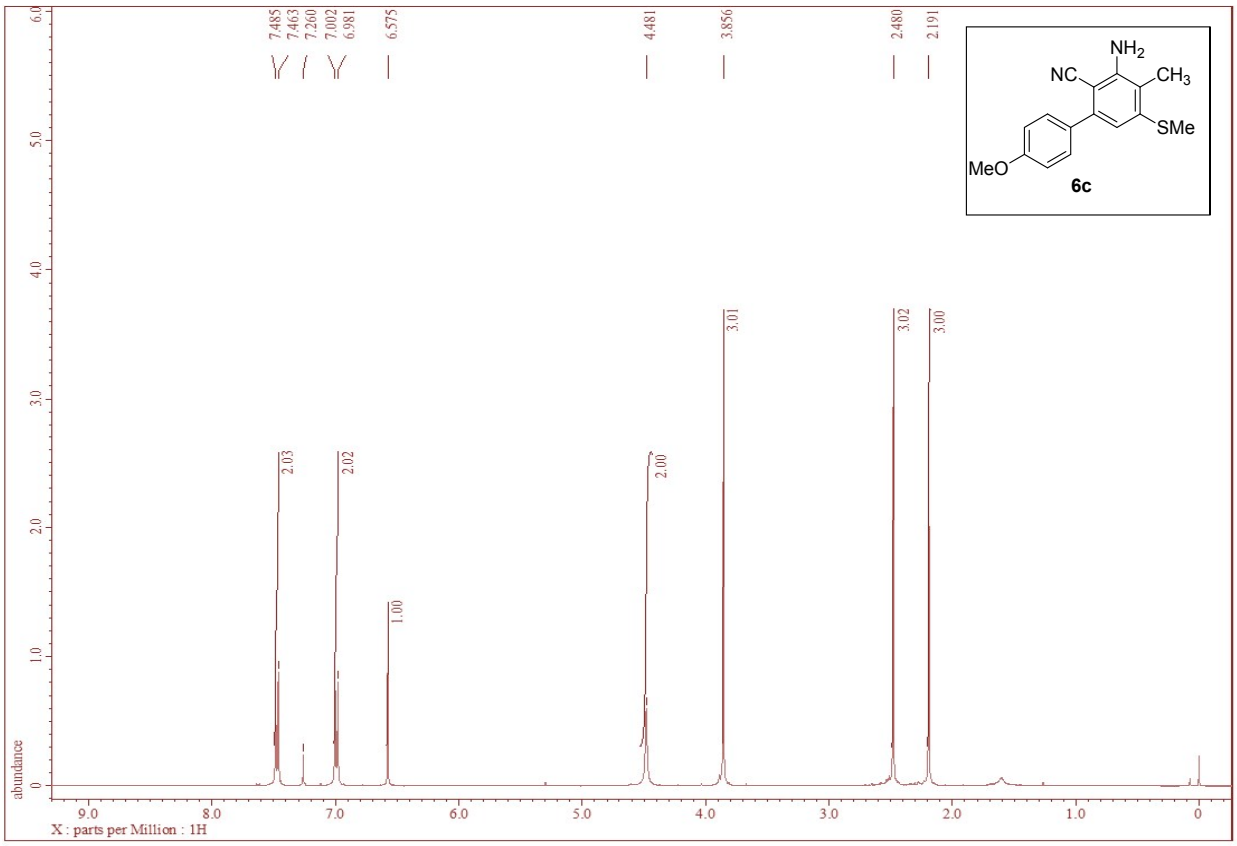

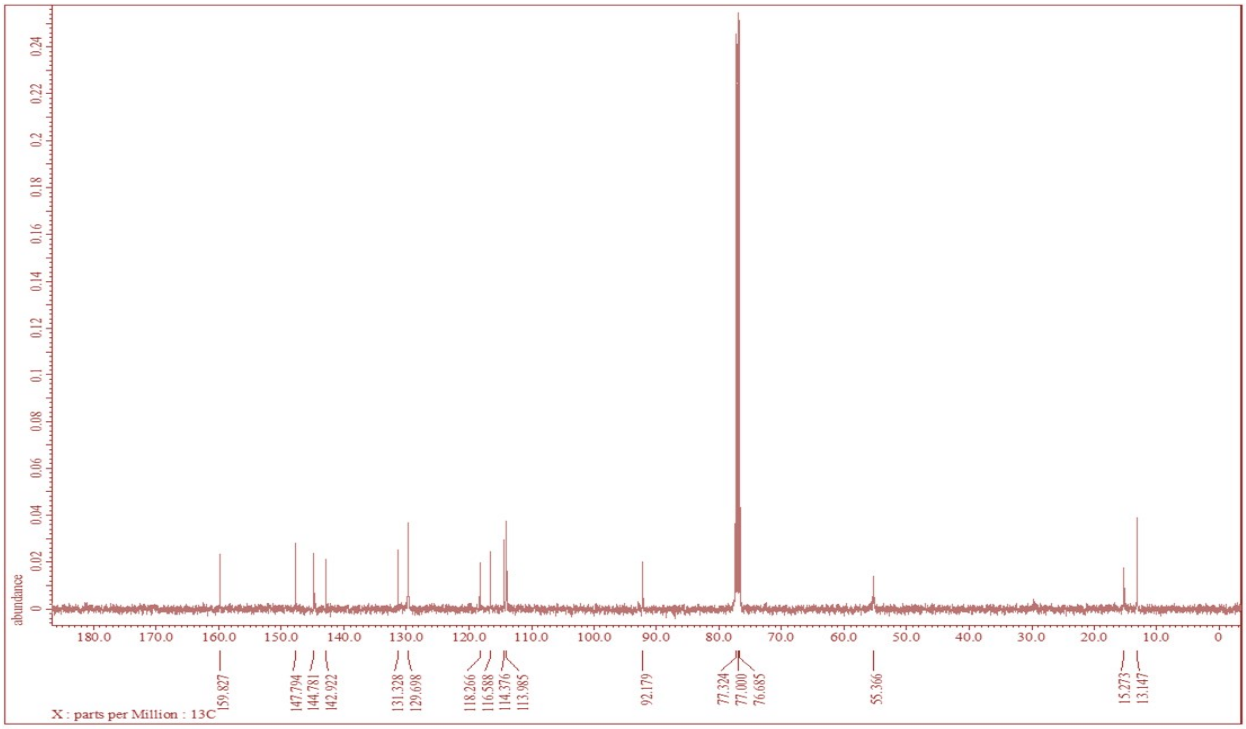

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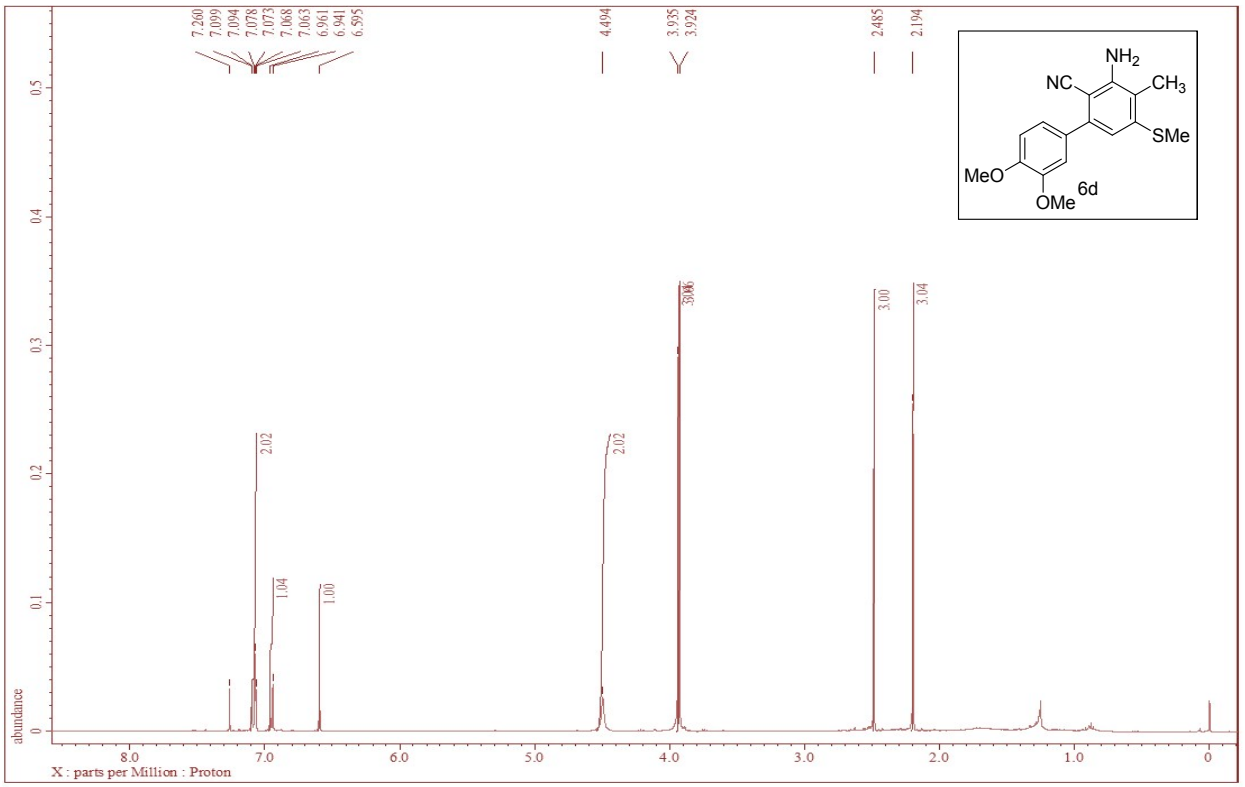
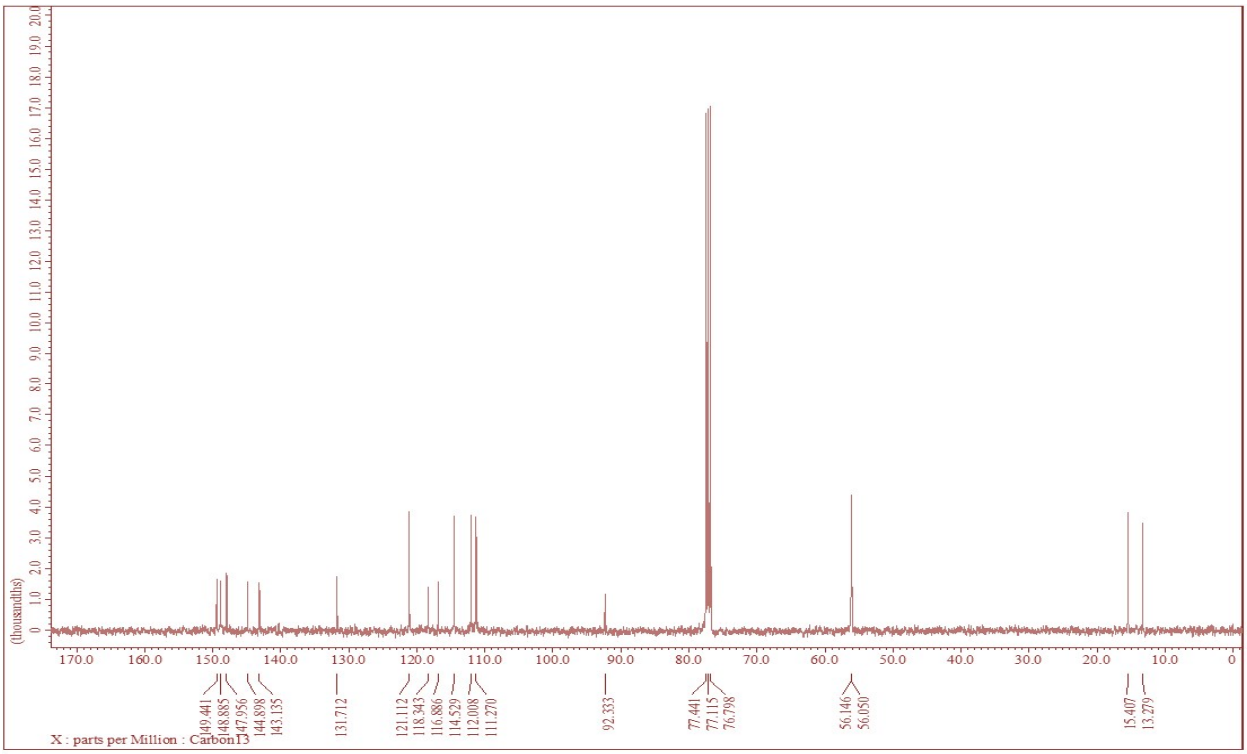
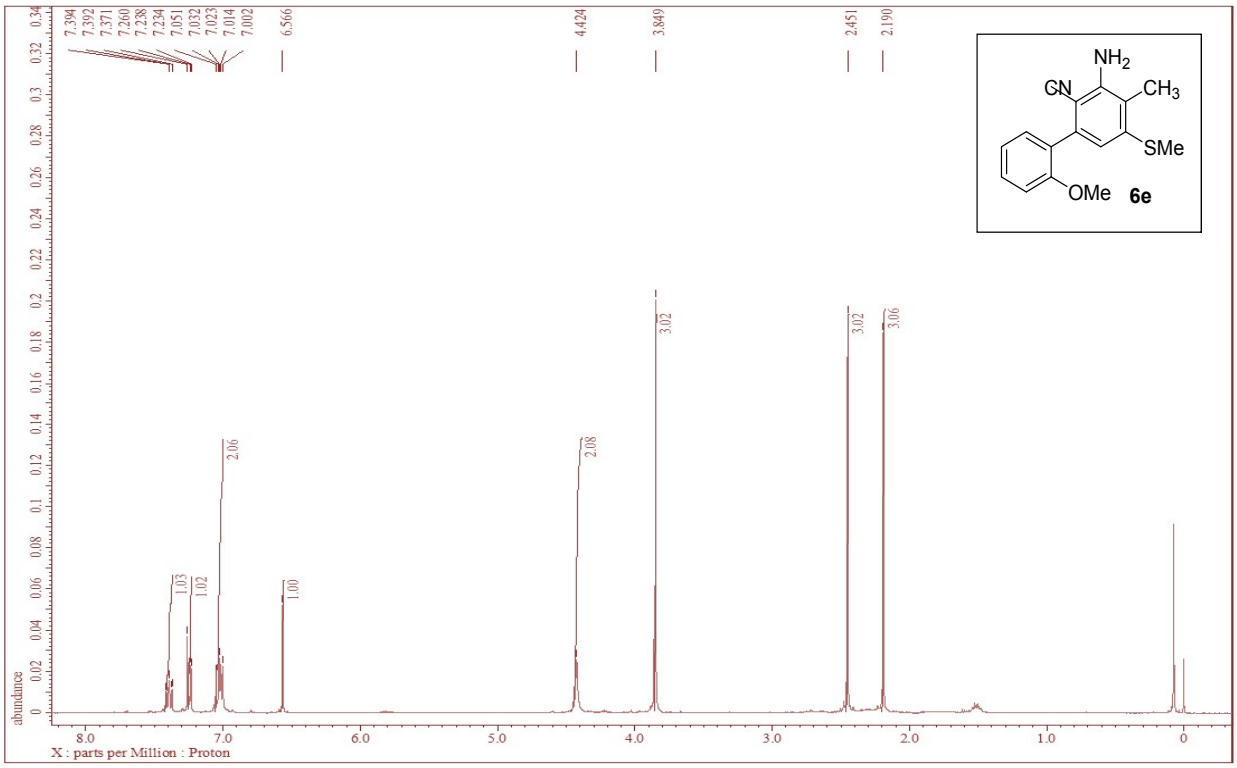
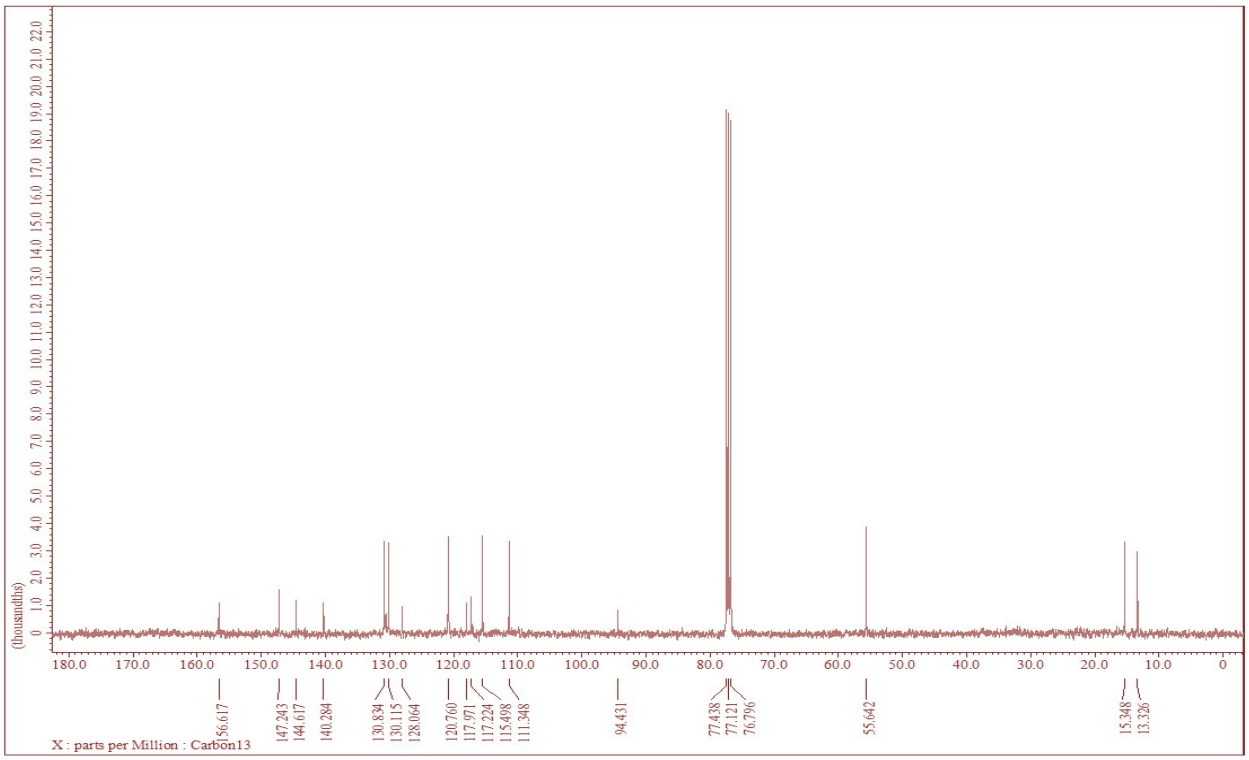


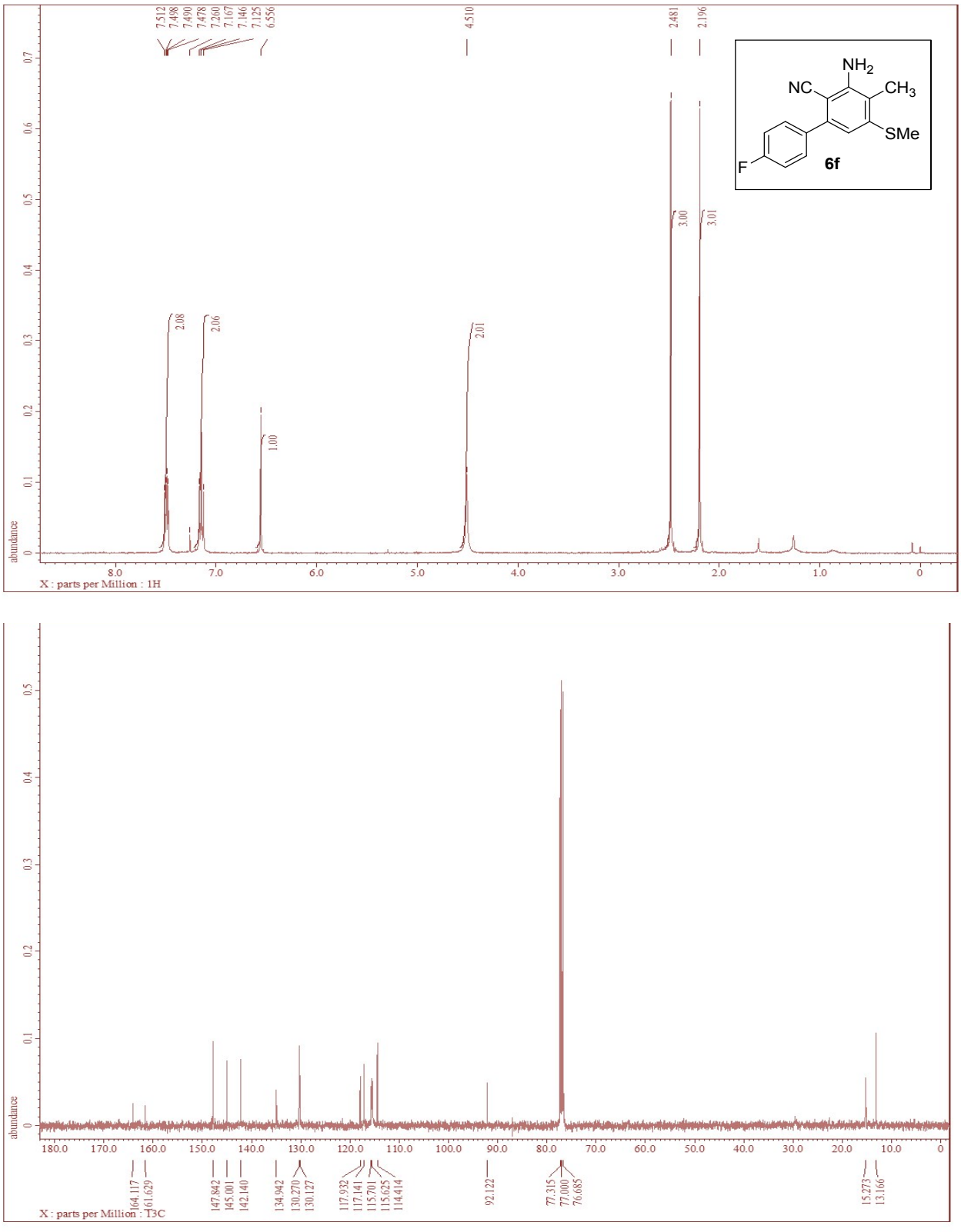


^{1}H NMR and ^{13}C NMR spectrum of3-amino-3',4'-dimethoxy-4-methyl-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile

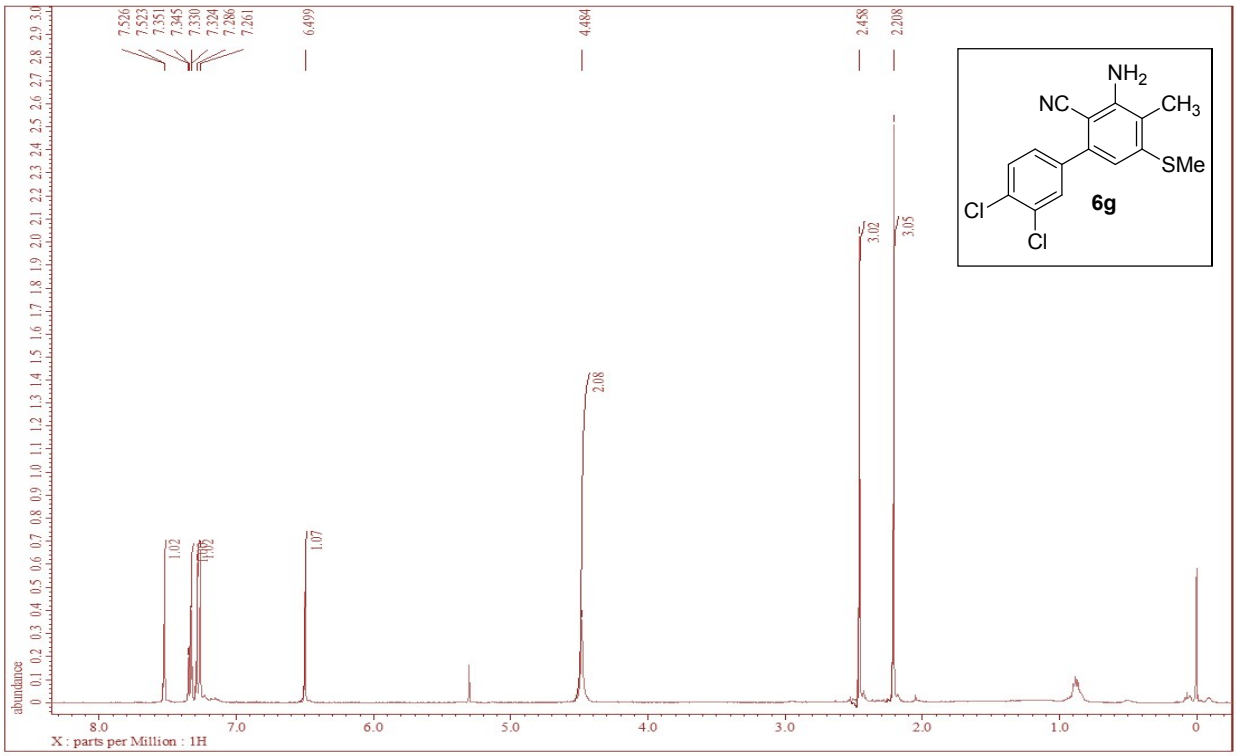


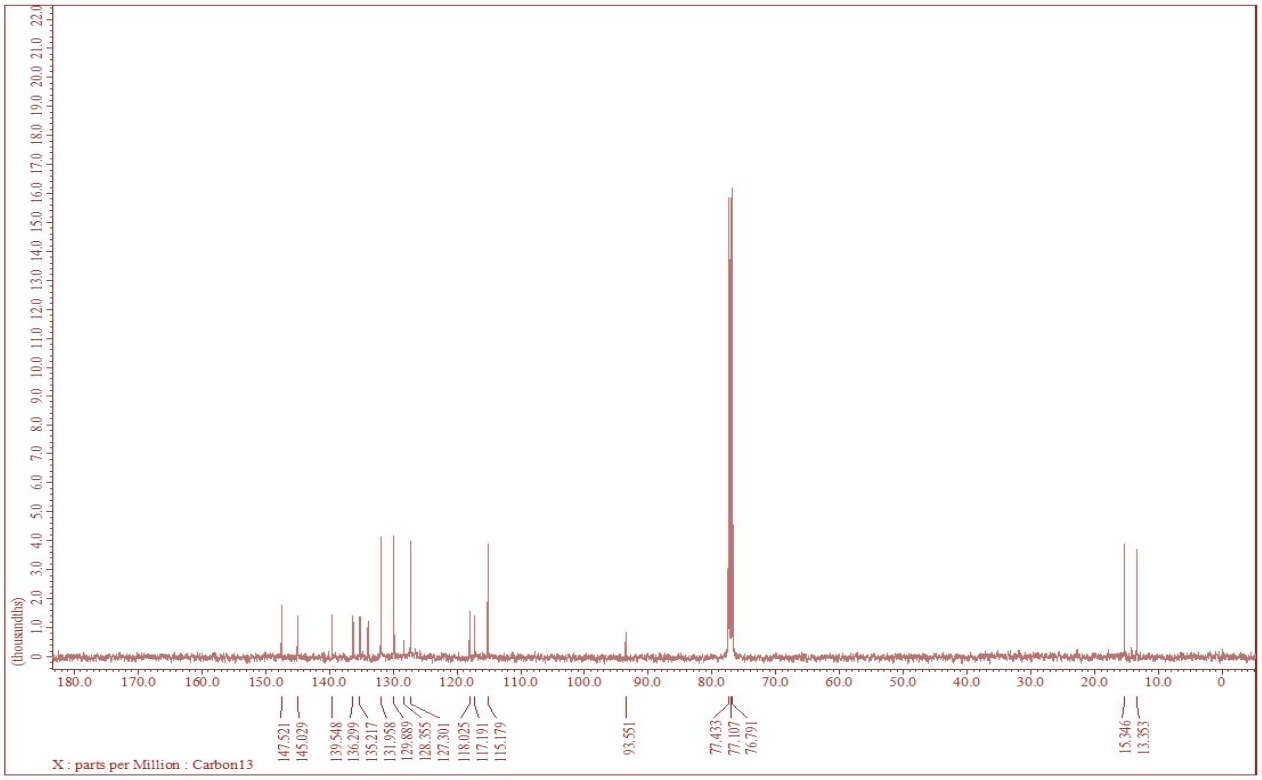


^{1}H NMR and ^{13}C NMR spectrum of 3-amino-2'-methoxy-4-methyl-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile

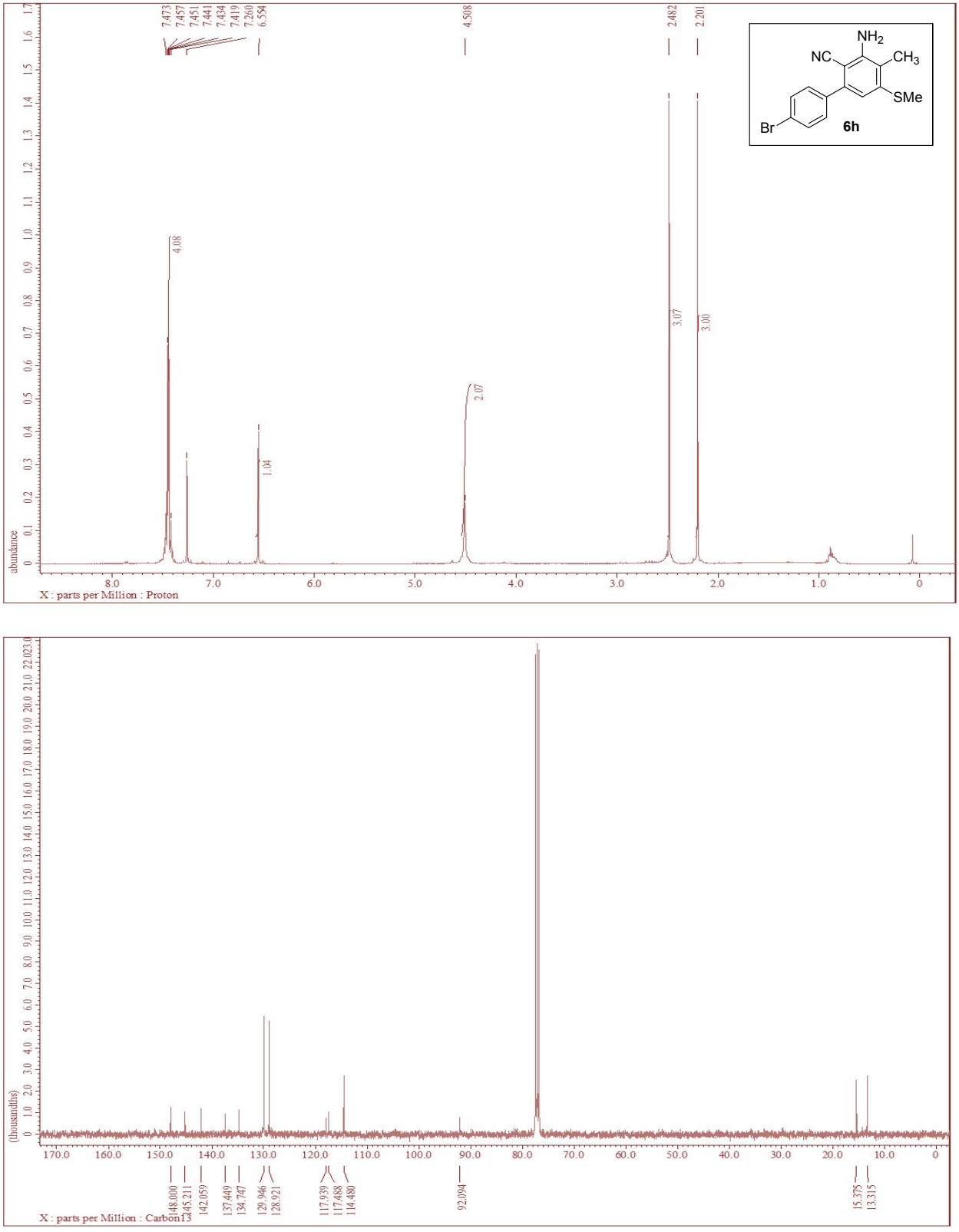


^{1}H NMR and ^{13}C NMR spectrum of 3-amino-4'-fluoro-4-methyl-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile

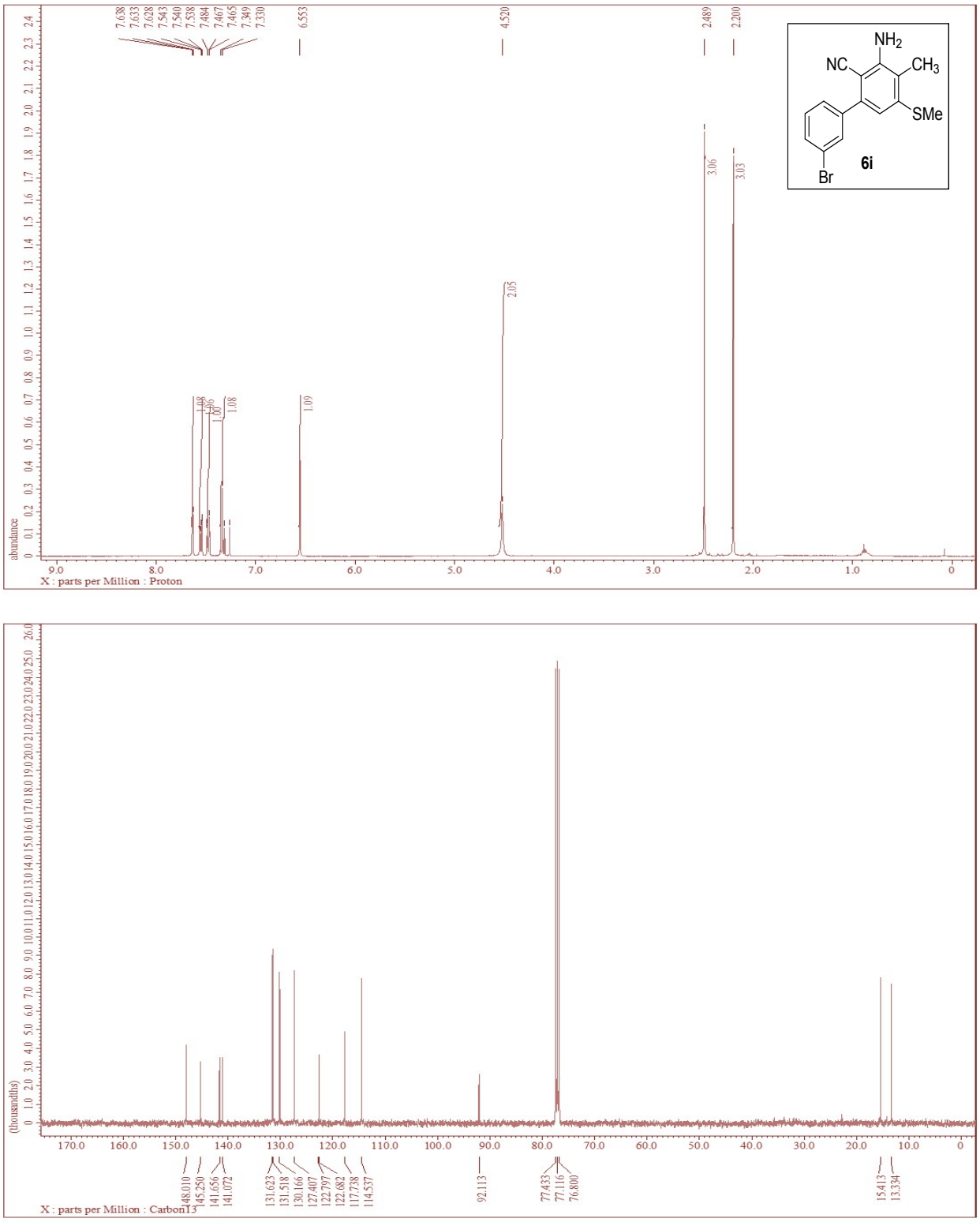




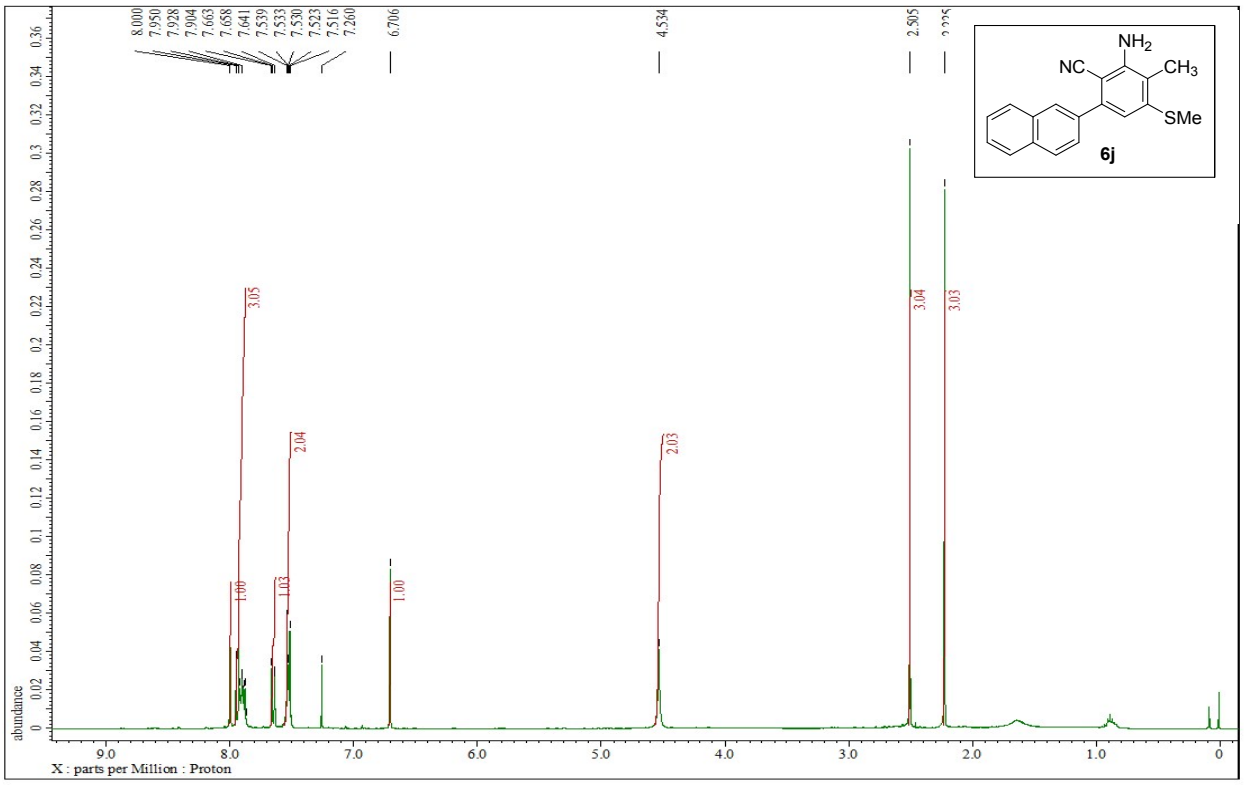
^{1}H NMR and ^{13}C NMR spectrum of 3-Amino-2',4'-dichloro-4-methyl-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile

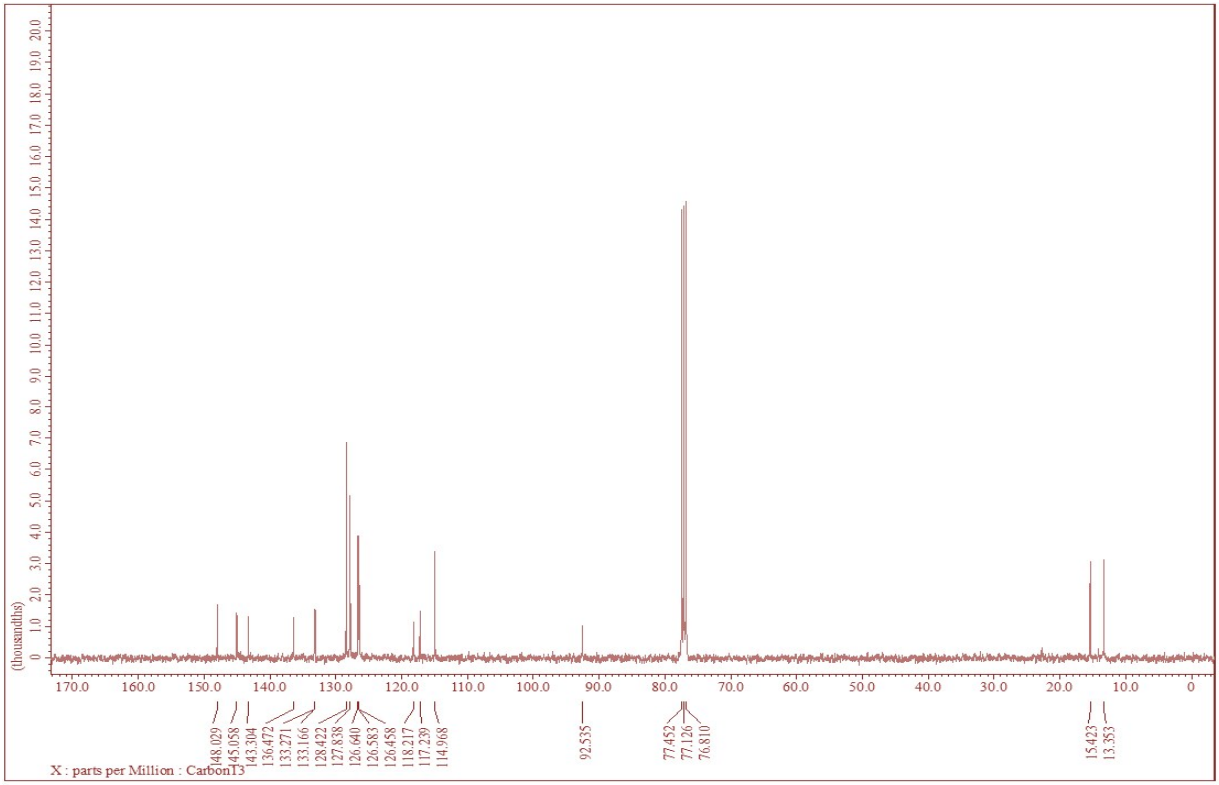


^{1}H NMR and ^{13}C NMR spectrum of 3-amino-4'-bromo-4-methyl-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile

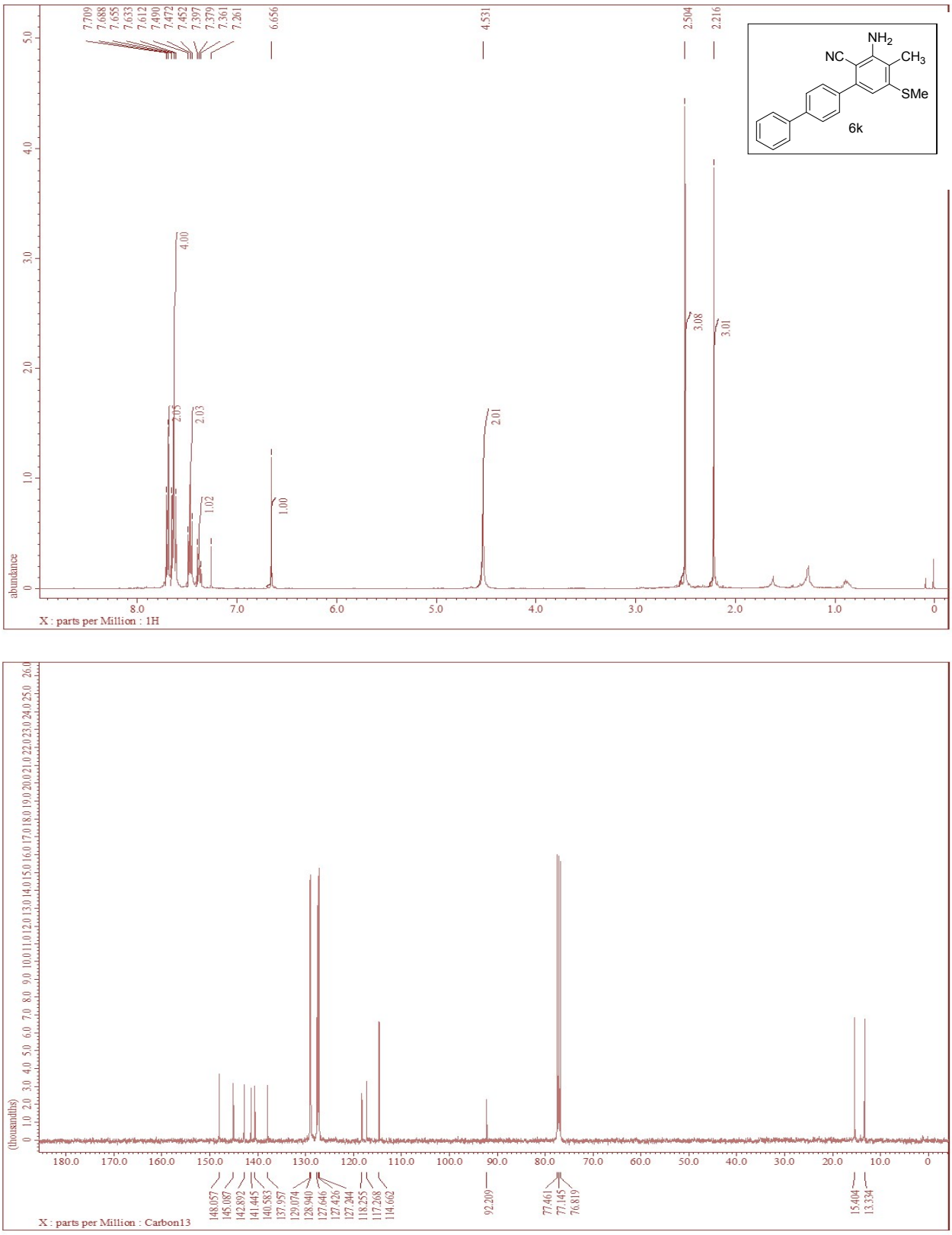


^{1}H NMR and ^{13}C NMR spectrum of3-amino-3'-bromo-4-methyl-5-(methylthio)-[1,1'-biphenyl]-2-carbonitrile





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



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