Supporting Information

Step-wise and one-pot synthesis of highly substituted conjugated trienes from 2-oxobenzo[*h*]chromenes/2*H*-pyran-2-ones

Amr Elagamy,[a] *Ismail Althagafi*[b] *and Ramendra Pratap*[a,]*

[a]Department of Chemistry, University of Delhi, North Campus, Delhi, India-110007
[b]Chemistry Department, Faculty of Science, Umm Al-Qura University, 21955 Makkah, Saudi Arabia

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1. X-ray Crystallographic Data for Compounds 3a and 4f

In a 5 mL glass vial 20-25 mg of (*E*)-3-(piperidin-1-yl)-3-(1-vinyl-3,4-dihydronaphthalen-2-yl)acrylonitrile **3a** and (*E*)-5-methyl-2-oxo-4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-5-(1-(*p*-tolyl)prop-1-en-1-yl)-2,5-dihydrofuran-3-carbonitrile **4f** were dissolved separately in methanol till saturation point, and then the solutions were allowed for slow evaporation at room temperature to provide transparent crystals suitable for X-ray analysis. Single crystal diffraction data for **3a** and **4f** were collected at room temperature with an Oxford XCalibur CCD diffractometer equipped with a graphite monochromatic Mo-Kα radiation (λ = 0.71073 Å). Data reduction was performed with the CrysAllis-Pro. The structure was solved by direct methods using SIR-92 program and refined on F^2 using all data by full matrix least-squares procedures with ShelXL-2016/6 incorporated in WinGX 1.8.05 crystallographic collective package. All calculations were done using the WinGX software package. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were placed at the calculated positions and included in the last cycles of the refinement. Crystallographic data collection and structure solution parameters are summarized in Table S1.

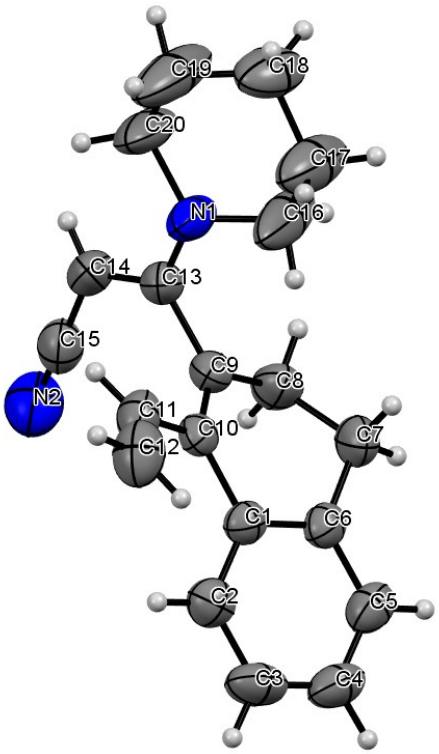


Figure S1. ORTEP diagram of (*E*)-3-(piperidin-1-yl)-3-(1-vinyl-3,4-dihydronaphthalen -2-yl)acrylonitrile **3a**

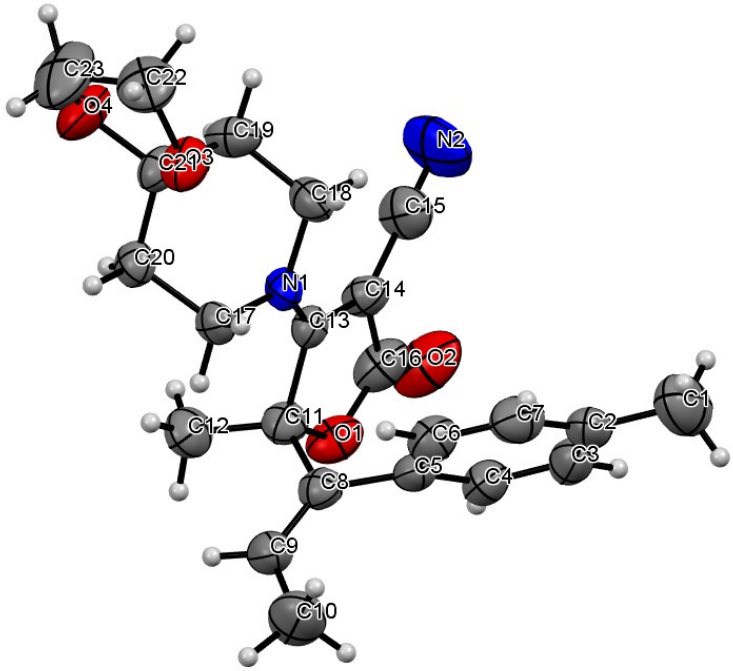


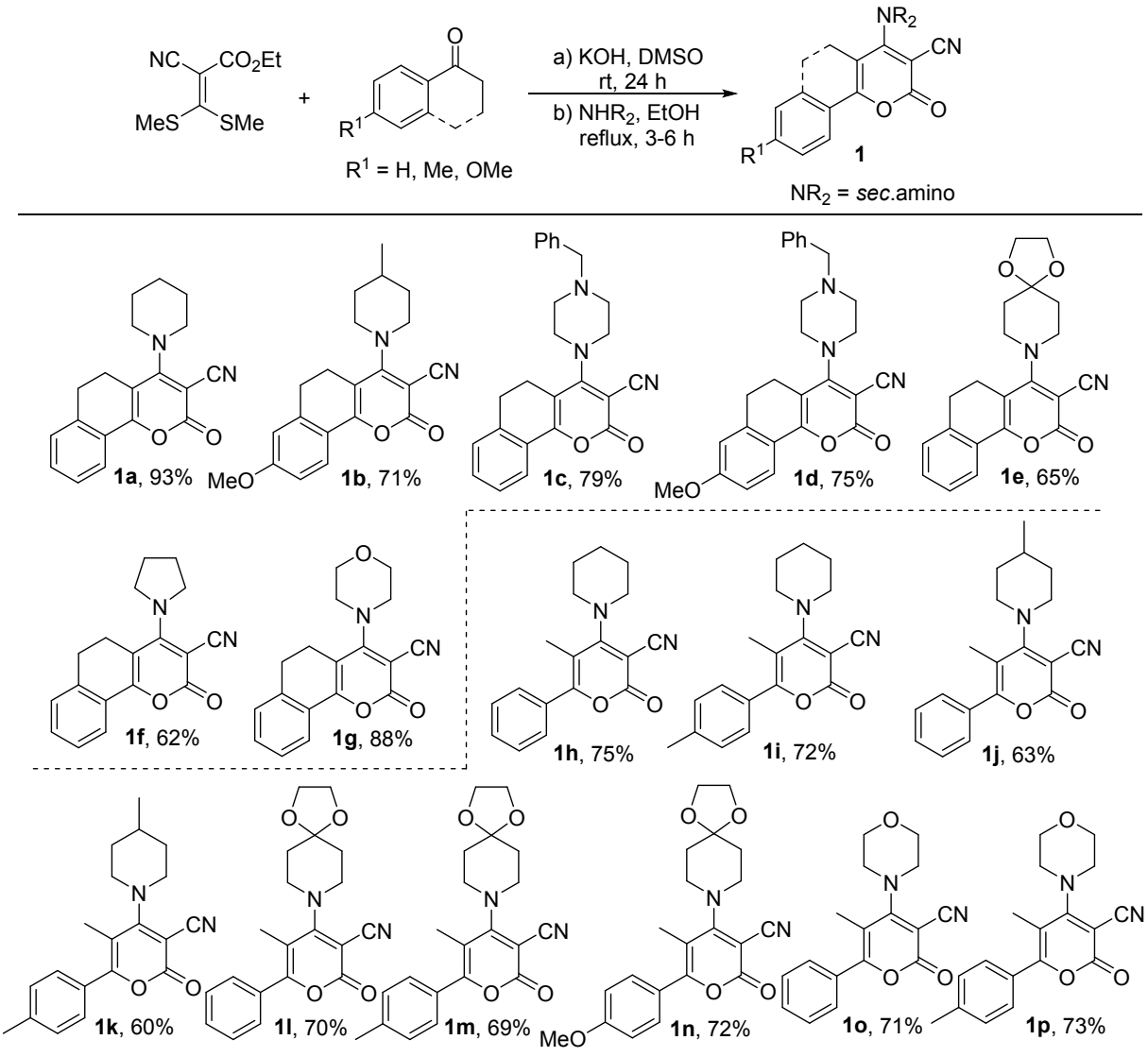
Figure S2. ORTEP diagram of (*E*)-5-methyl-2-oxo-4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-5-(1-(*p*-tolyl)prop-1-en-1-yl)-2,5-dihydrofuran-3-carbonitrile **4f**

Table S1. Crystal data and structure refinement for **3a** and **4f**

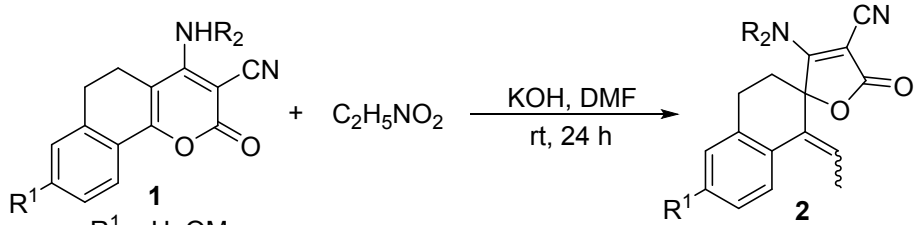
Compound code	**3a**	**4f**
CCDC No.	1969714	1968703
Empirical formula	$C_{20}H_{22}N_2$	$C_{23}H_{26}N_2O_4$
Formula weight	290.39	364.46
Temperature/k	293	293
Crystal system	monoclinic	monoclinic
Space group	Cc	I a
a/Å	6.2510(2)	8.5442(4)
b/Å	18.8202(6)	23.0145(11)
c/Å	14.2270(5)	11.2615(6)
α/°	90	90
β/°	98.706(3)	104.150(5)
γ/°	90	90
Volume/Å^3	1654.45(10)	2147.28(19)
Z	4	4
ρ_{calc}g/cm^3	1.166	1.220
μ/mm^{-1}	0.068	0.084
F(000)	624.0	840
Crystal size/mm^3	0.22 × 0.18 × 0.15	0.21 × 0.18 × 0.15
2Θ range for data collection/°	6.94 to 54.192	7.082 to 59.018
Index ranges	$-8 \le h \le 8$, $-23 \le k \le 24$, $-18 \le l \le 18$	-11<=h<=11, -31<=k<=30, -14<=l<=15
Reflections collected	11420	16049
Independent reflections	3615 [R_{int} = 0.0204, R_{sigma} = 0.0226]	5223 [R_{int} = 0.0376]
Data/restraints/parameters	3615/2/203	5223/2/262
Goodness-of-fit on F^2	1.082	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0761, wR_2 = 0.2068	R_1 = 0.0778, wR_2 = 0.2053
Final R indexes [all data]	R_1 = 0.0836, wR_2 = 0.2139	R_1 = 0.1139, wR_2 = 0.2289
Largest diff. peak/hole / e Å^{-3}	0.39/-0.36	0.32/-0.21

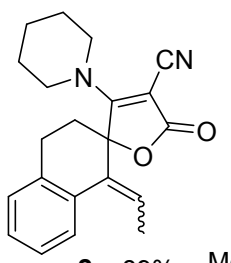
2. Preparation of Precursors

Scheme S1. Synthesis of 2-oxo-4-*sec*.amino-5,6-dihydro-2*H*-benzo[*h*]chromene-3-carbonitriles and 6-aryl-5-methyl-2-oxo-4-*sec*.amino-2*H*-pyran-3-carbonitriles

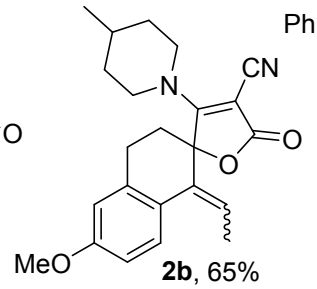


Scheme S2. Synthesis of 1'-ethylidene-5-oxo-3-sec.amino-3',4'-dihydro-1'*H*,5*H*-spiro[furan-2,2'-naphthalene]-4-carbonitriles

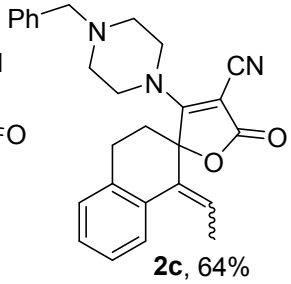




2a, 89%



2b, 65%



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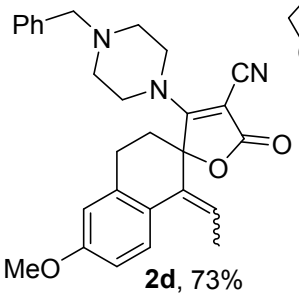
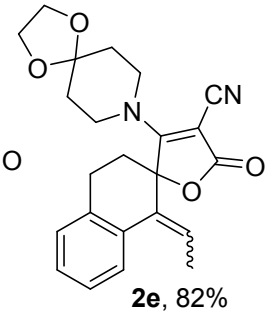
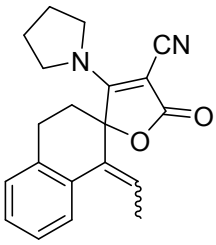


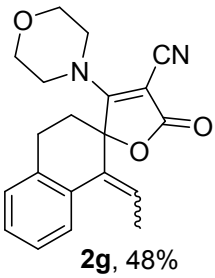
2d, 73%



2e, 82%

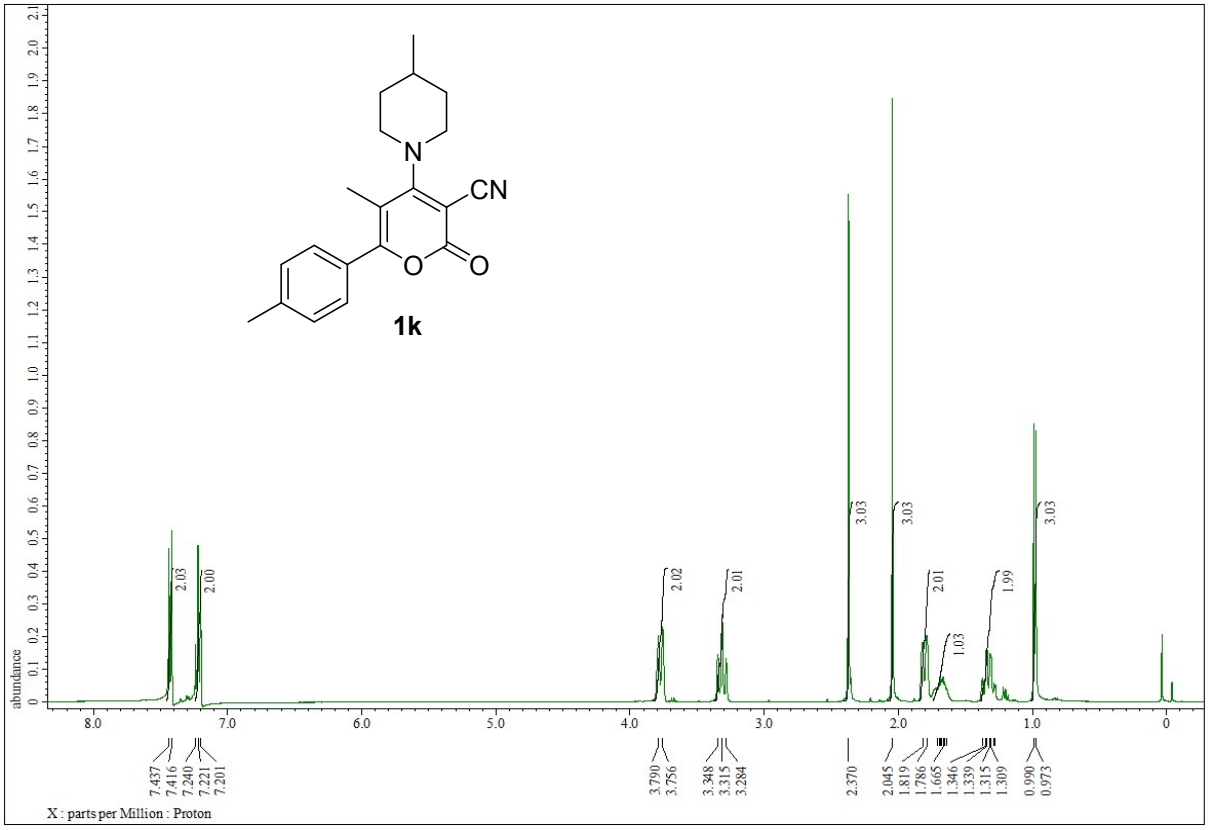


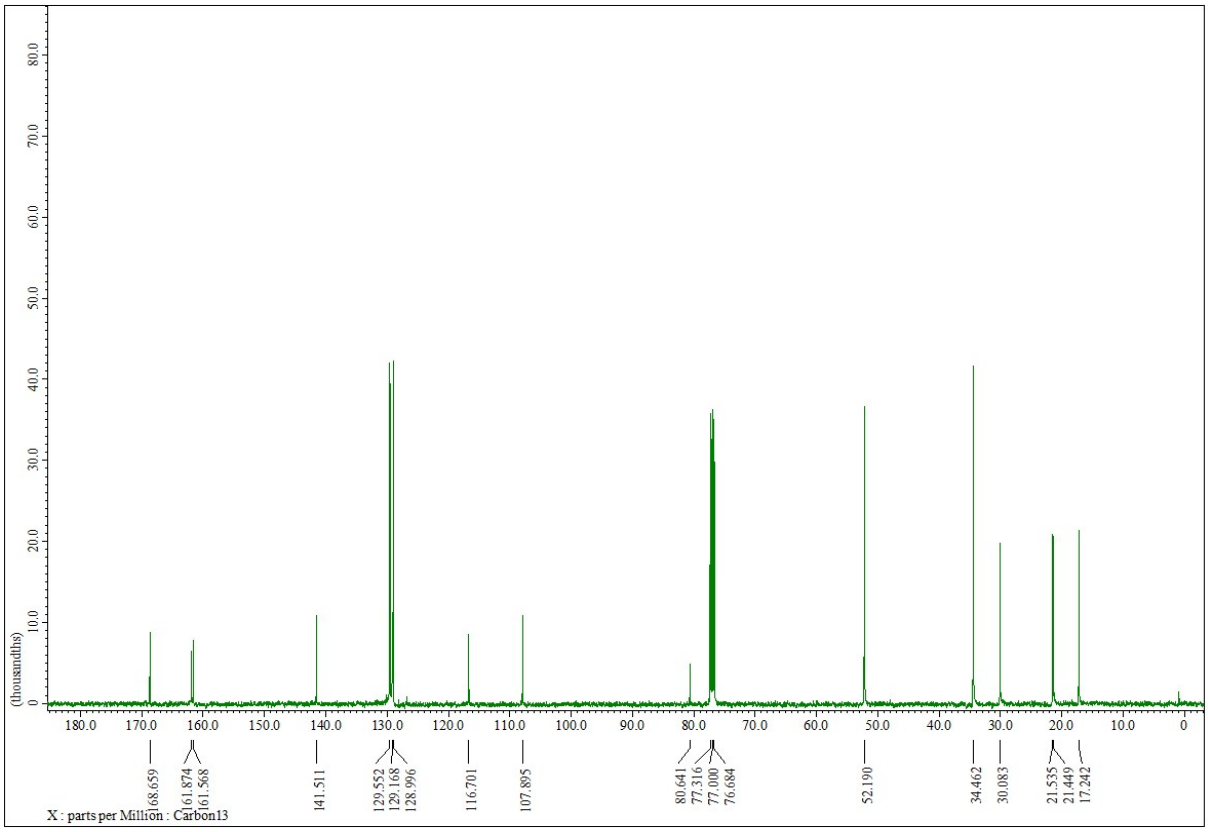
2f, 55%



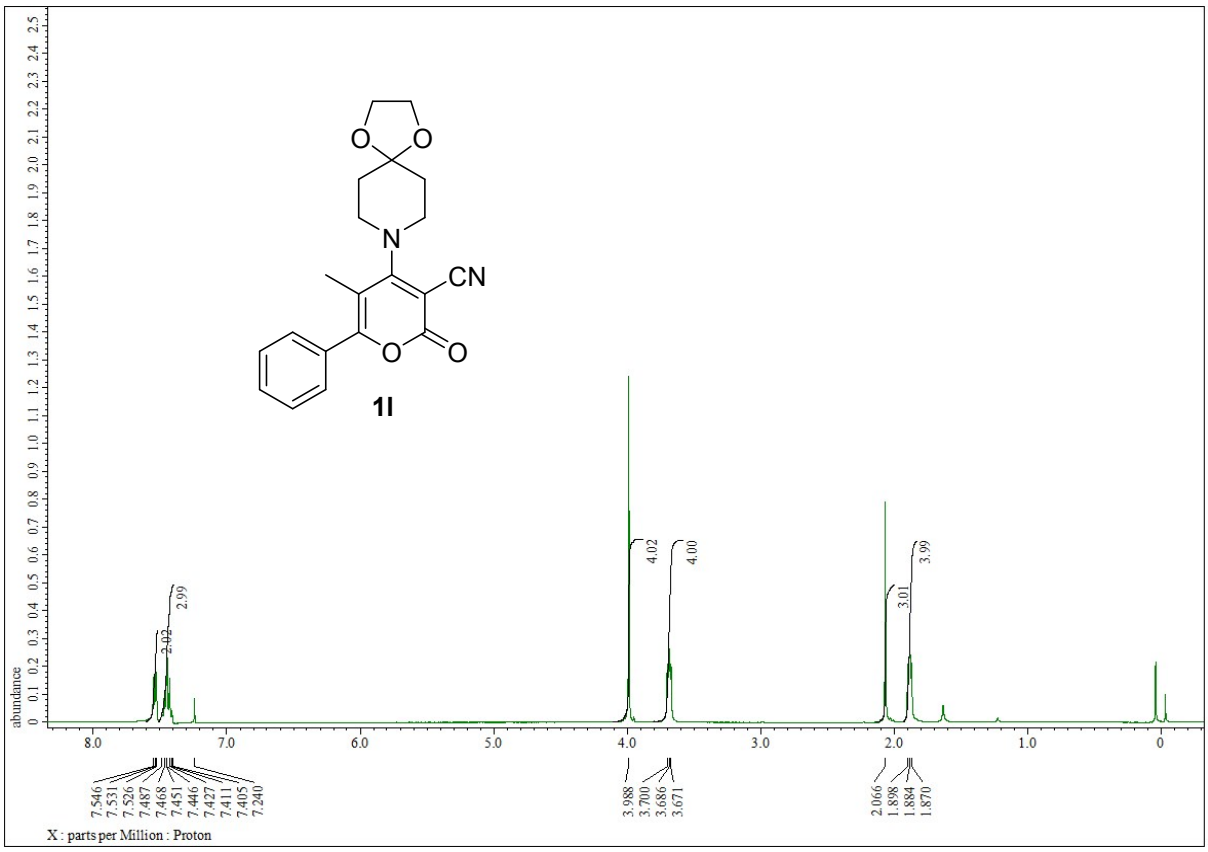
2g, 48%

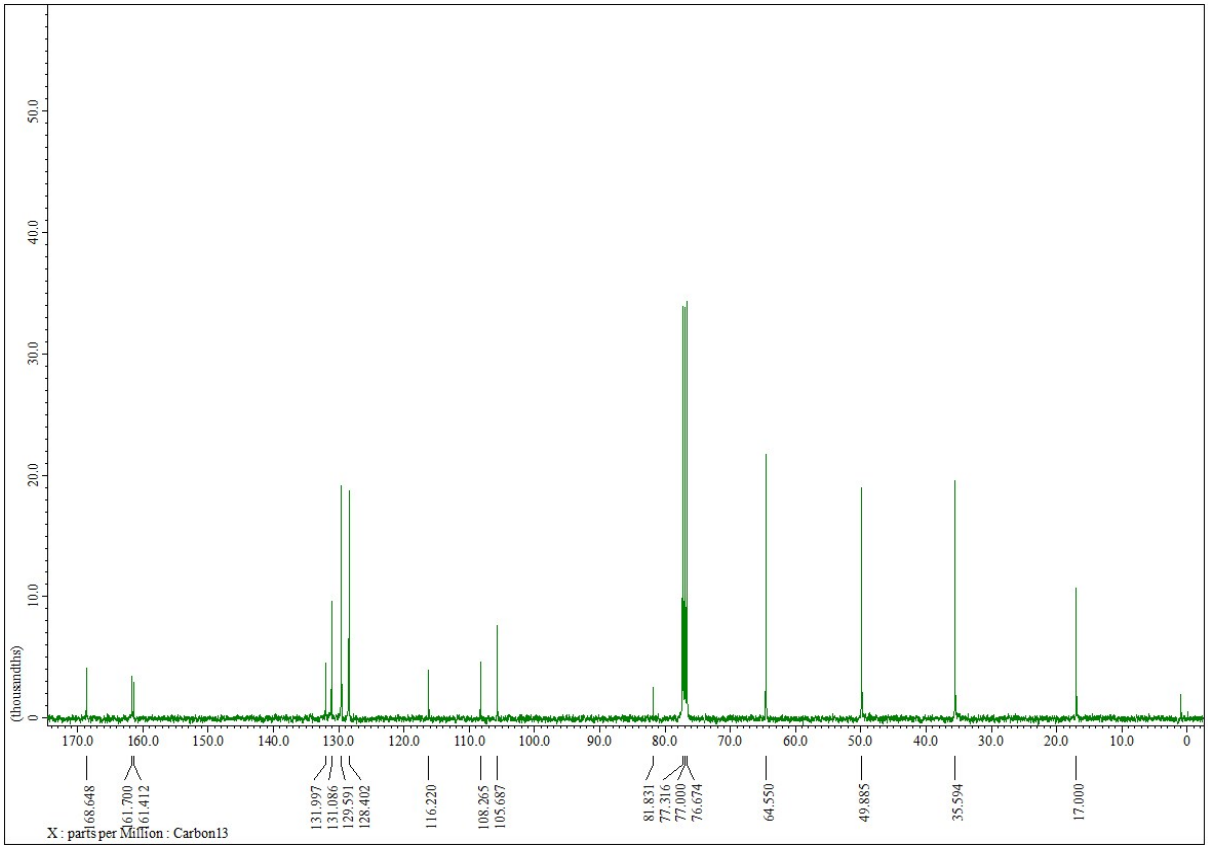
3. ^{1}H NMR and ^{13}C NMR spectra



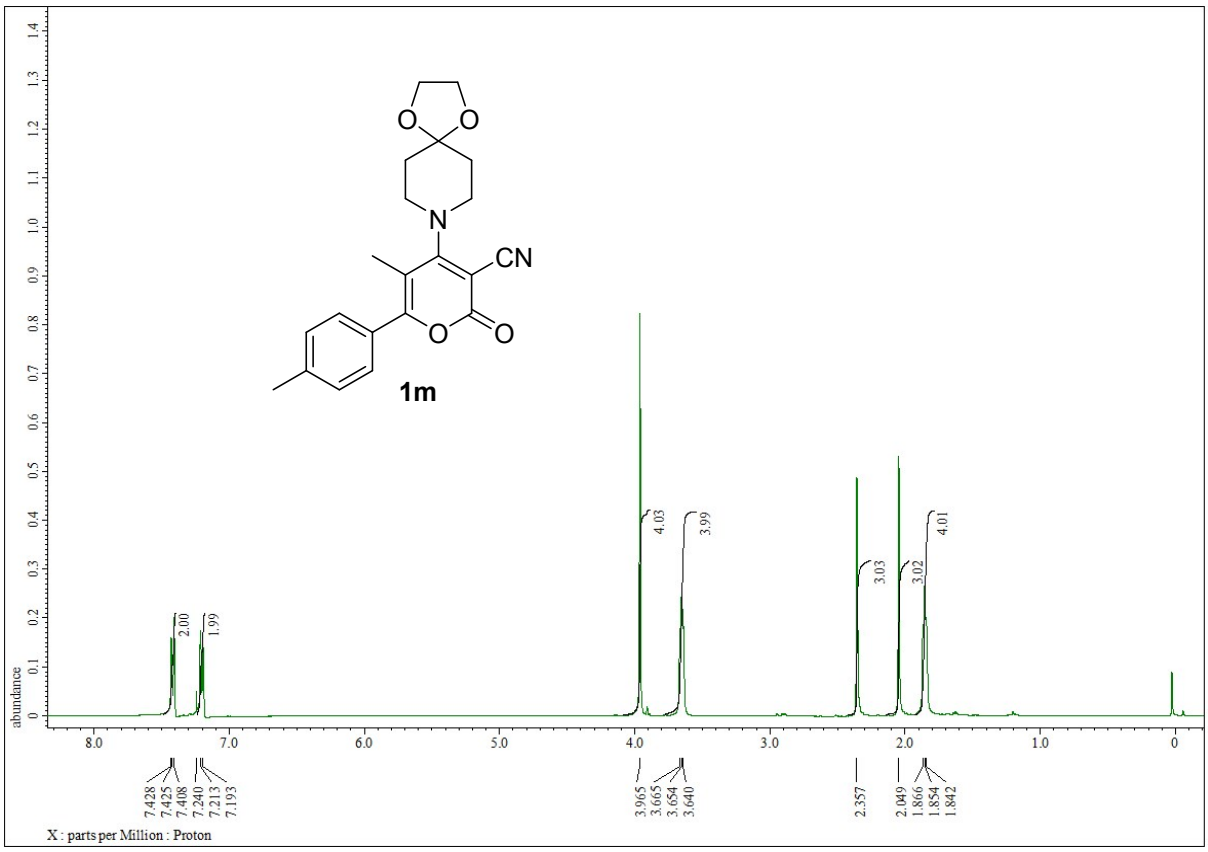


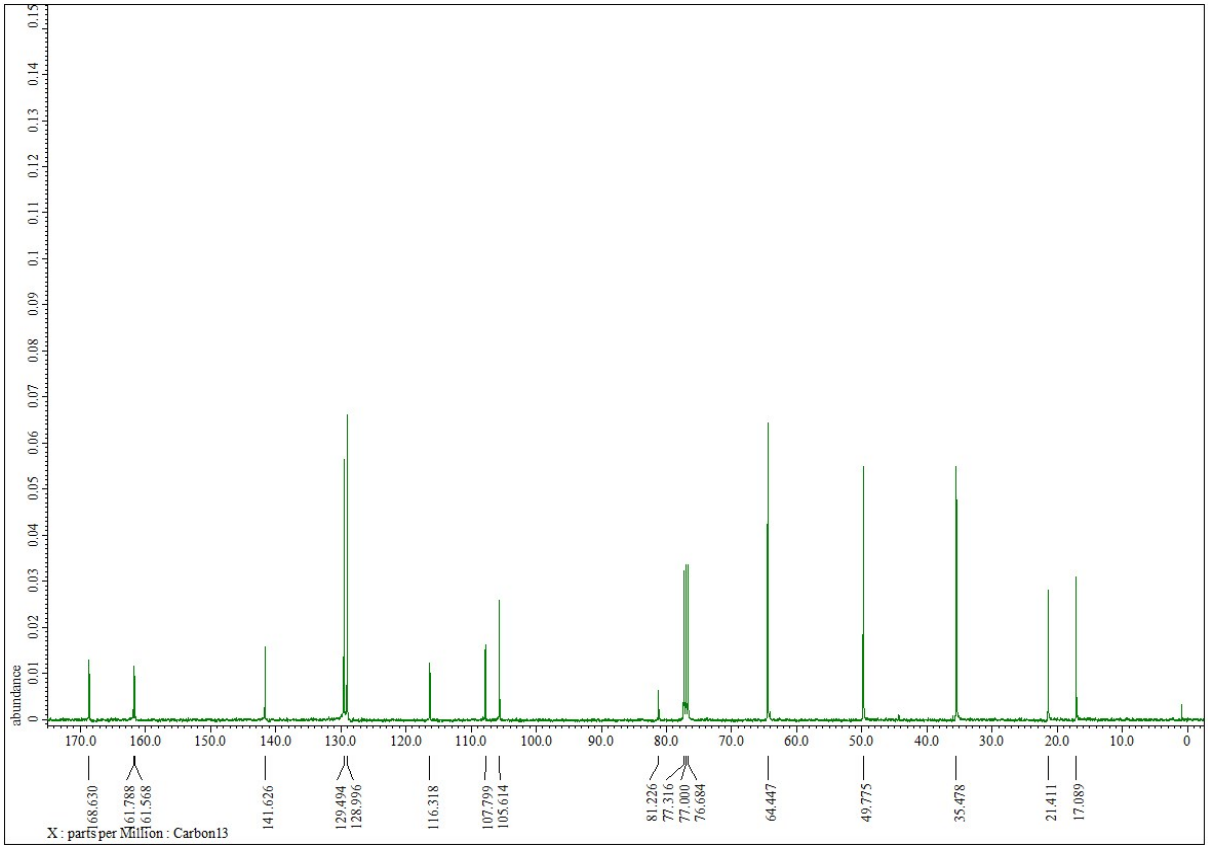
^{1}H and ^{13}C spectra of 5-methyl-4-(4-methylpiperidin-1-yl)-2-oxo-6-(*p*-tolyl)-2*H*-pyran-3-carbonitrile **1k**



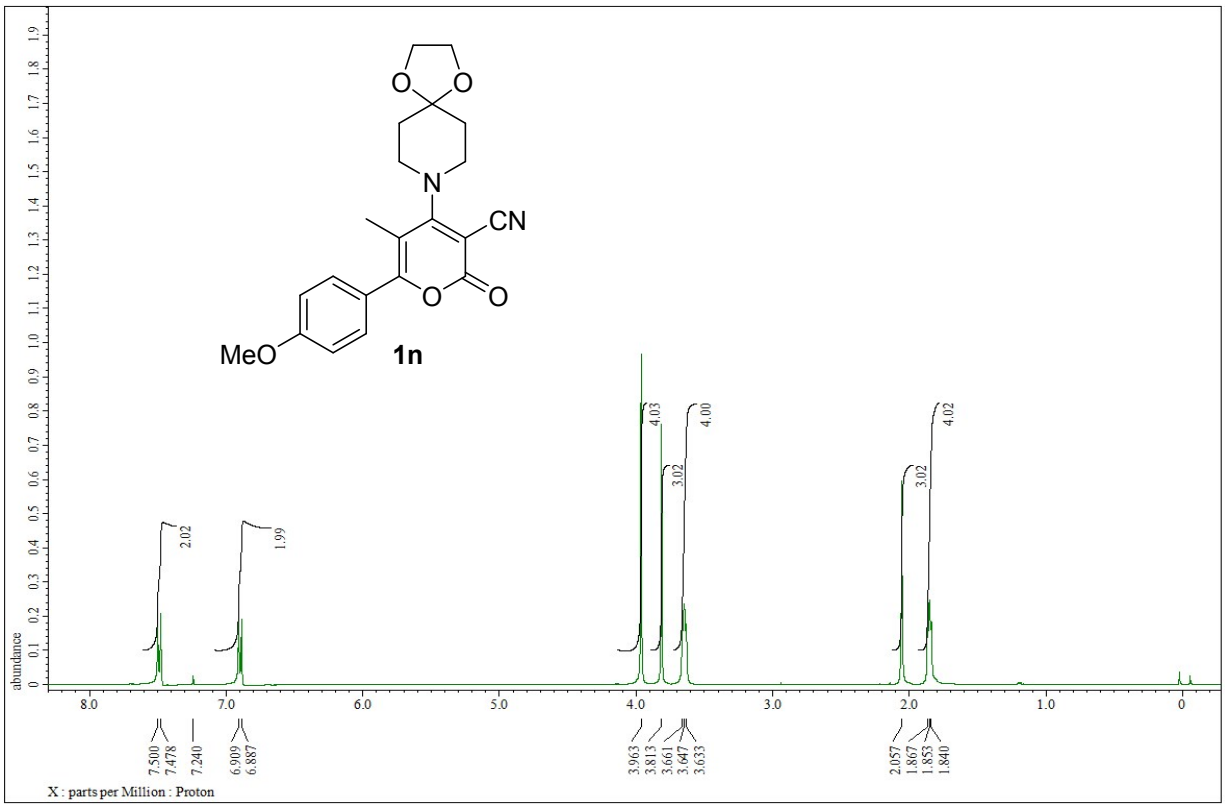


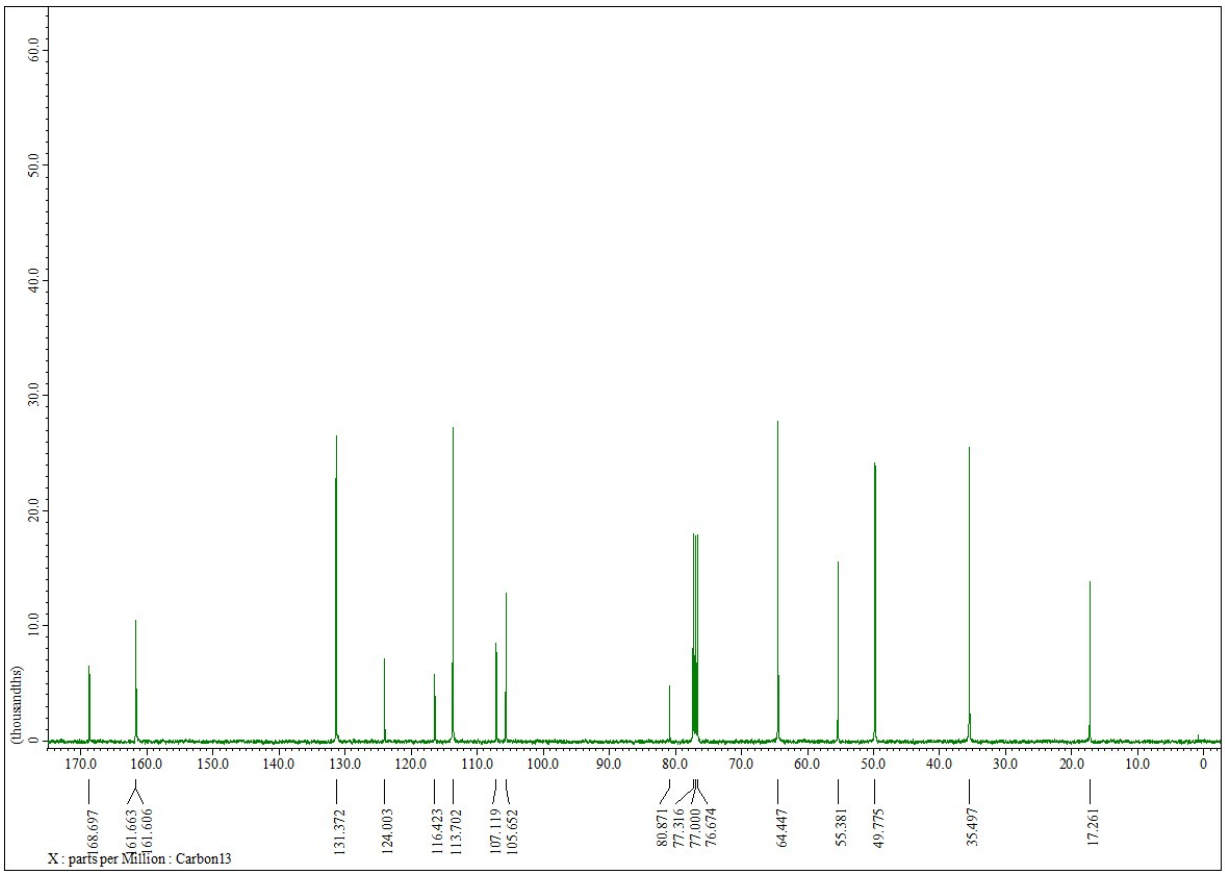
^{1}H and ^{13}C spectra of 5-methyl-2-oxo-6-phenyl-4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-2*H*-pyran-3-carbonitrile **1l**



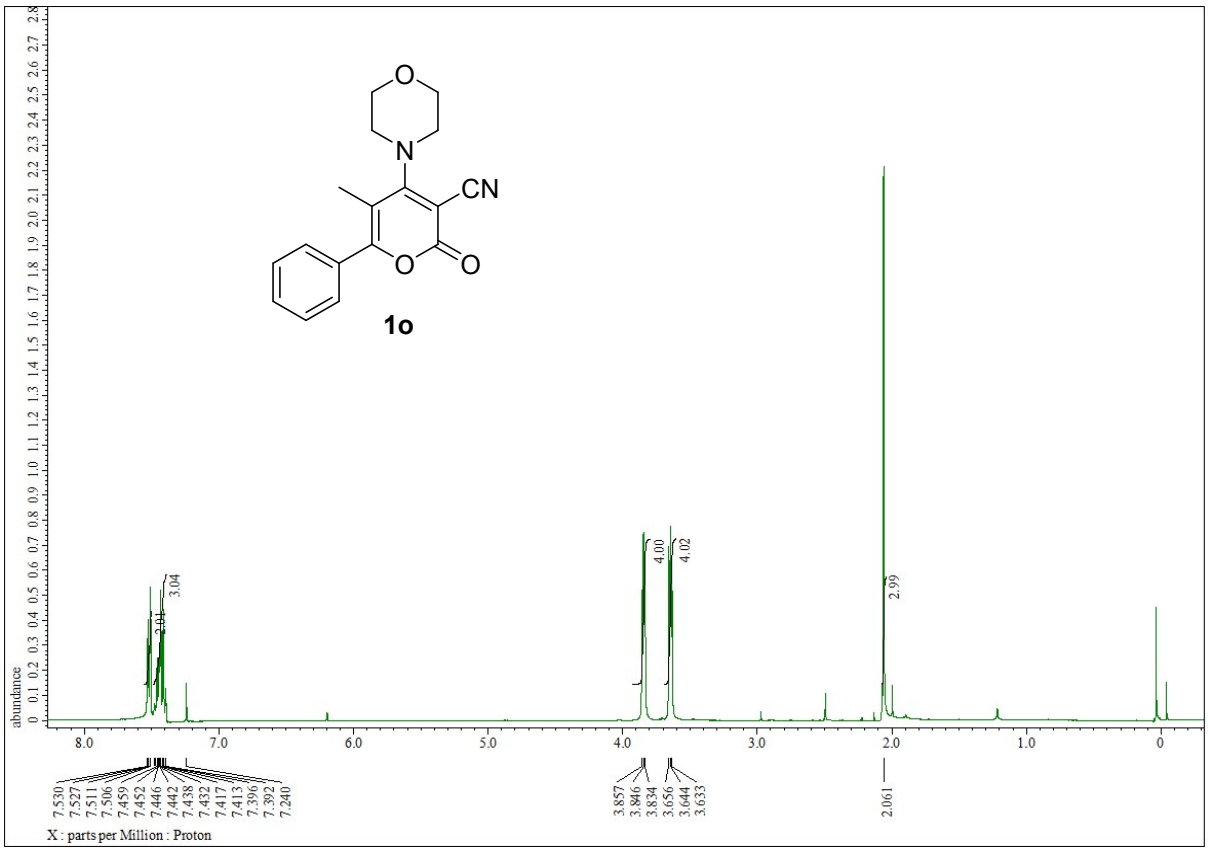


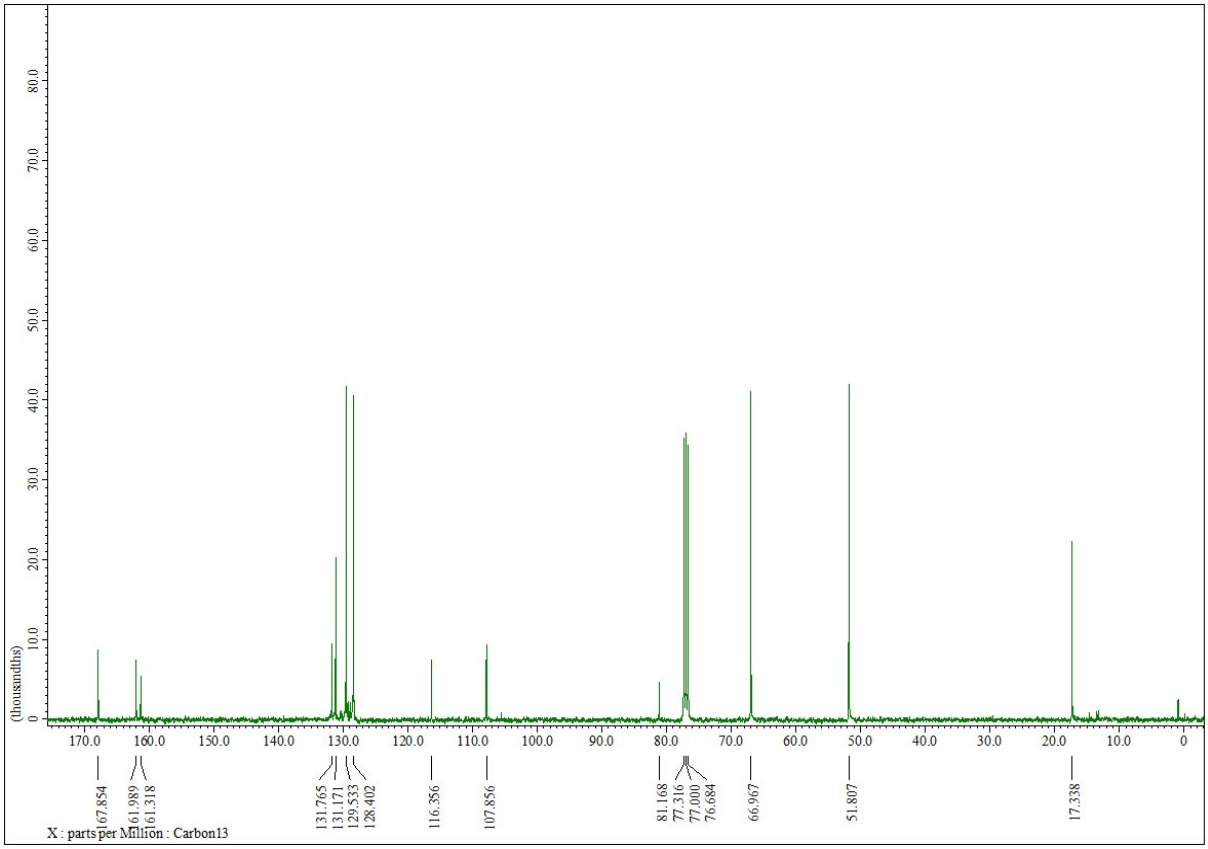
^{1}H and ^{13}C spectra of 5-methyl-2-oxo-4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-6-(*p*-tolyl)-2*H*-pyran-3-carbonitrile **1m**



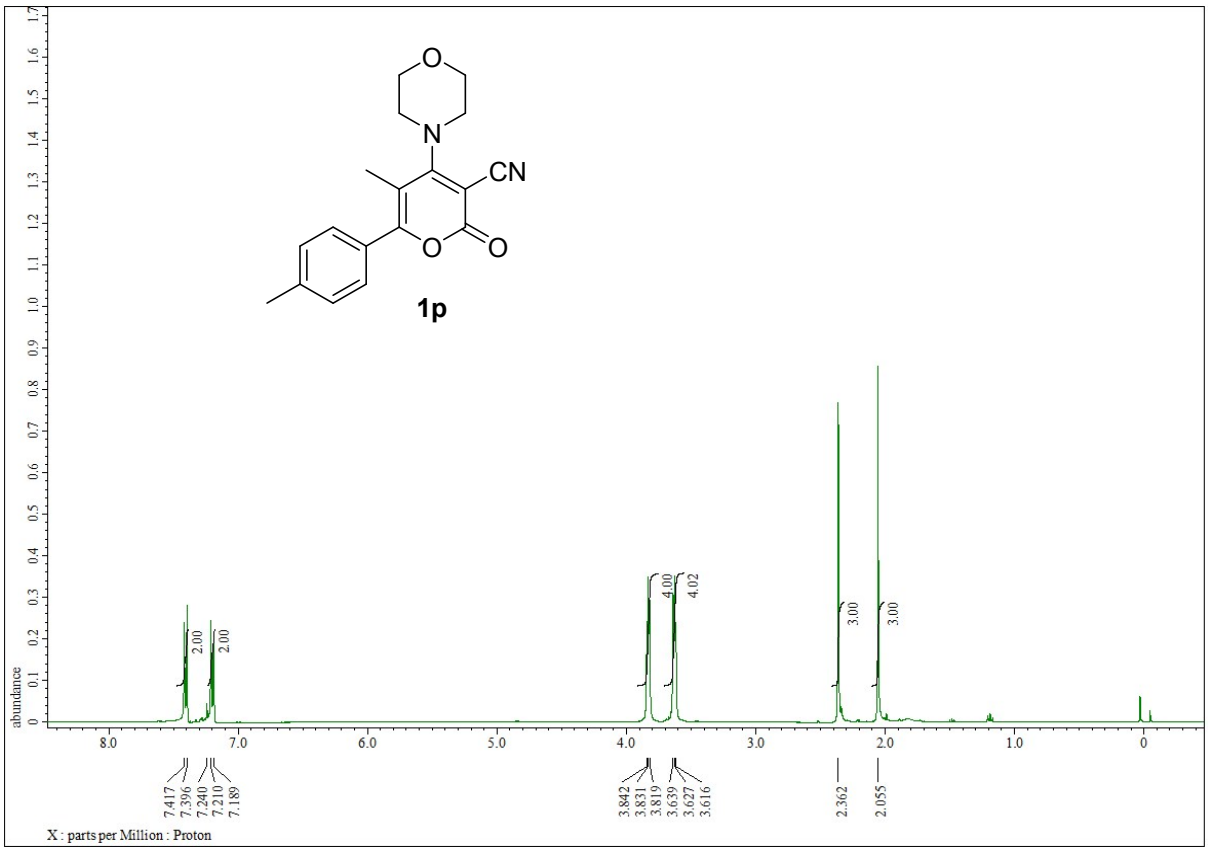


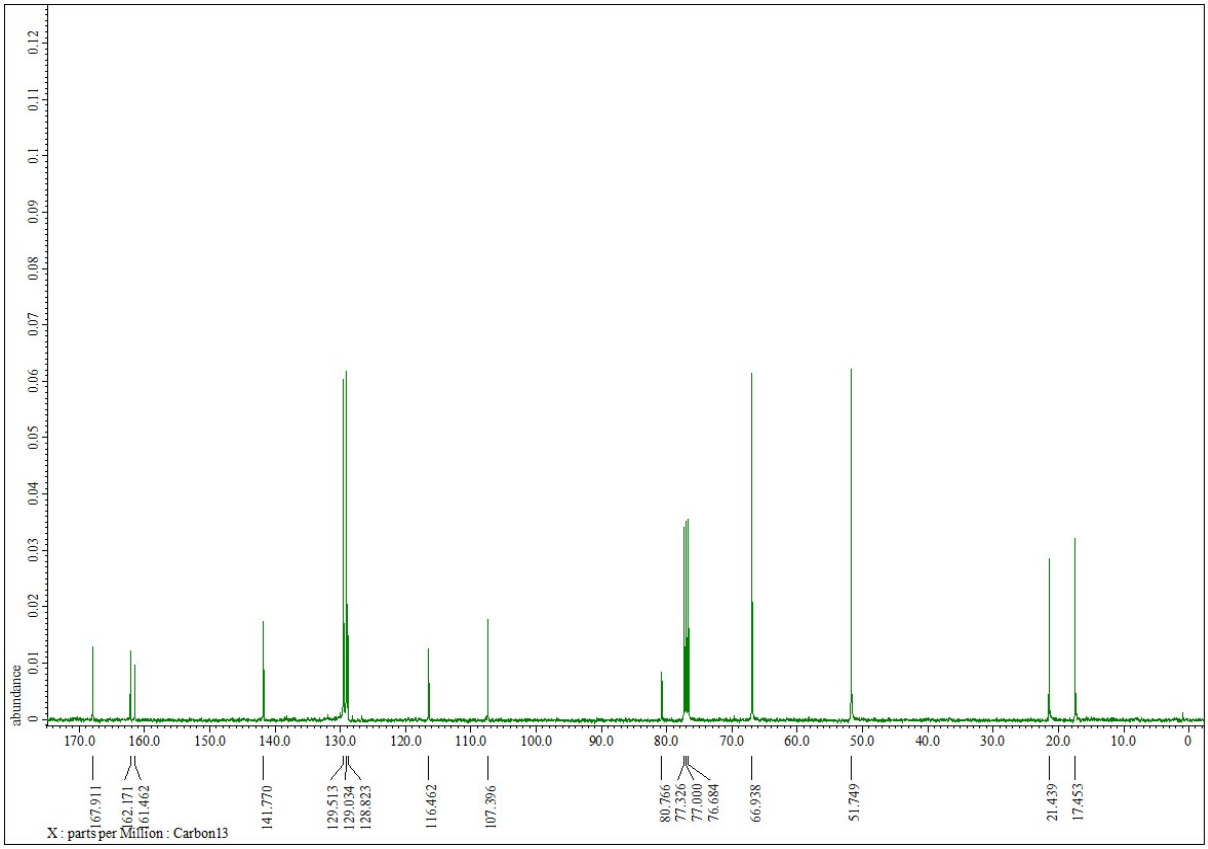
^{1}H and ^{13}C spectra of 6-(4-methoxyphenyl)-5-methyl-2-oxo-4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-2*H*-pyran-3-carbonitrile **1n**



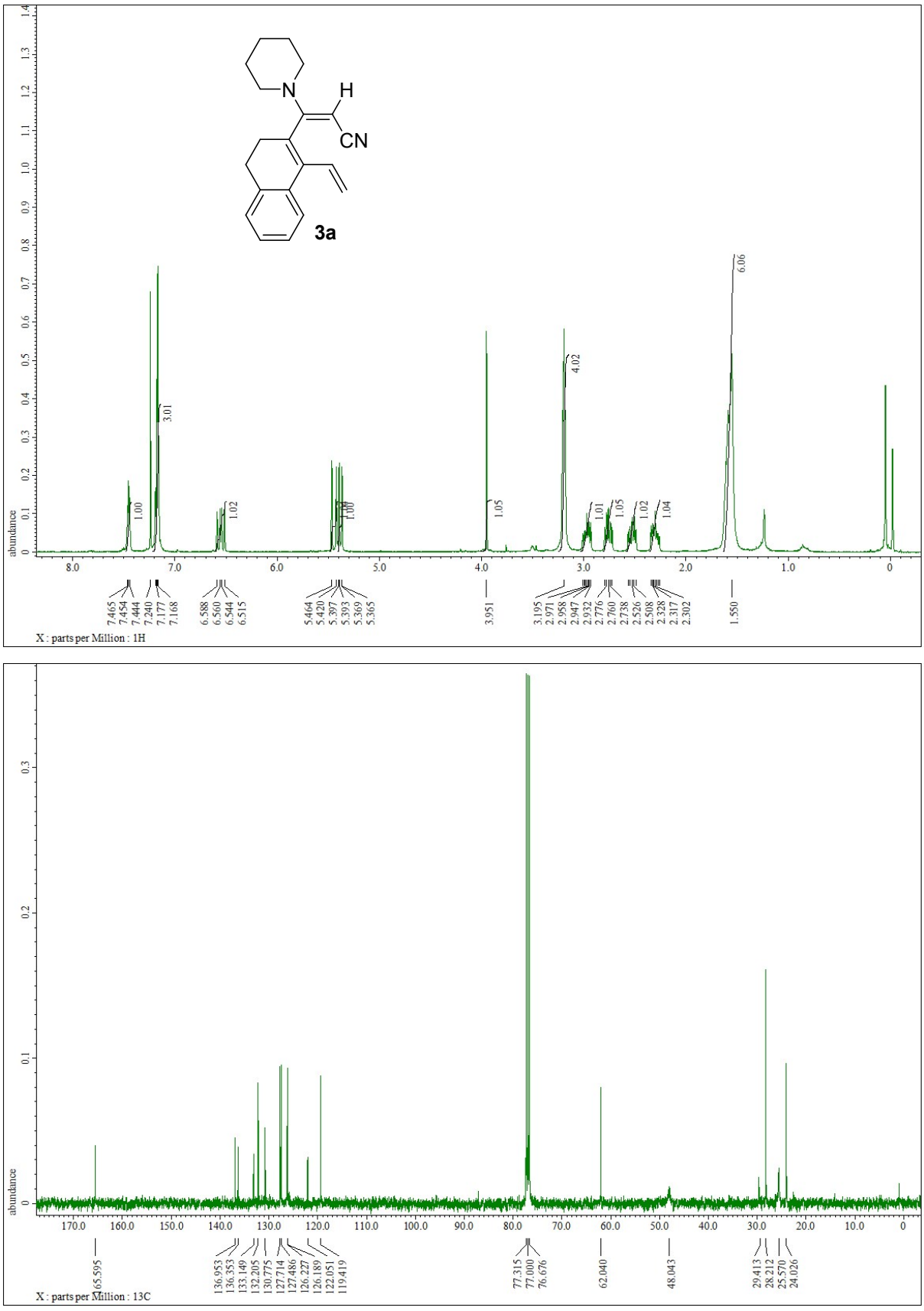


^{1}H and ^{13}C spectra of 5-methyl-4-morpholino-2-oxo-6-phenyl-2*H*-pyran-3-carbonitrile **1o**

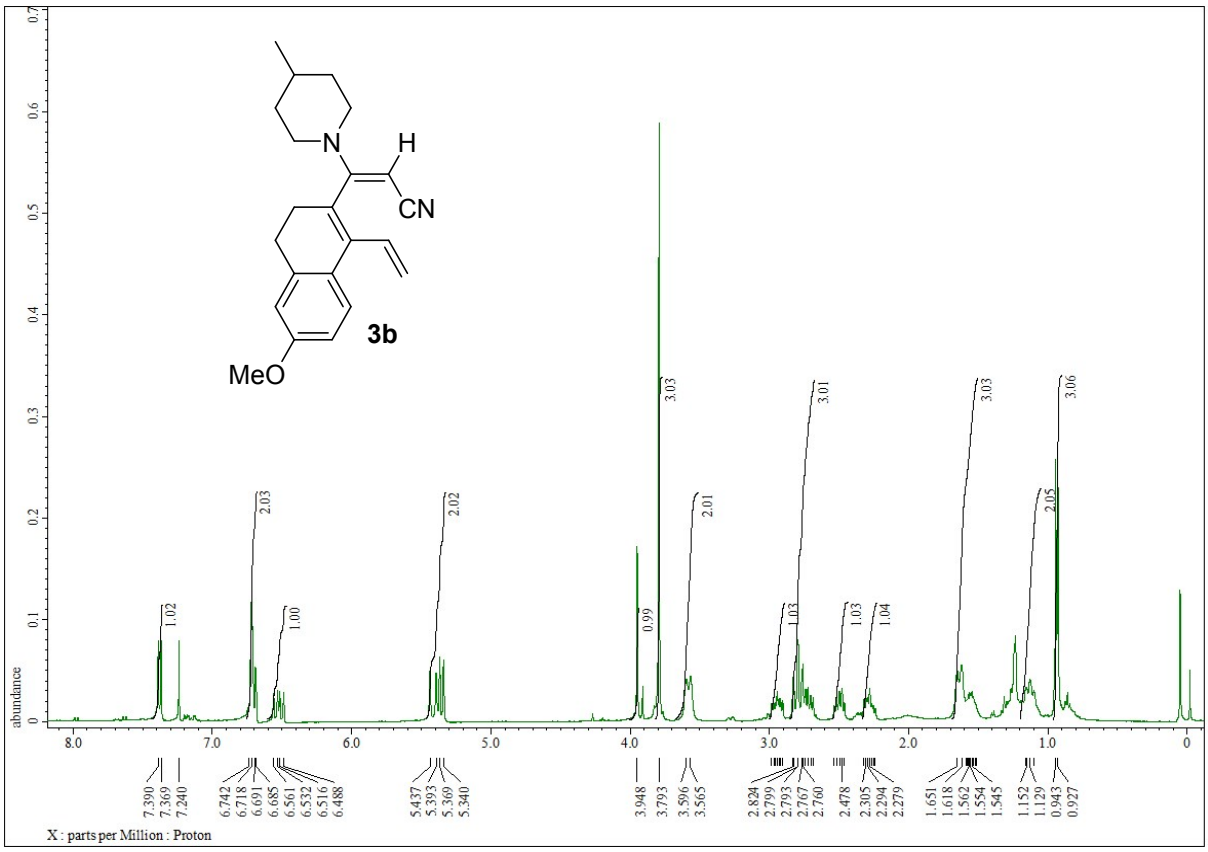


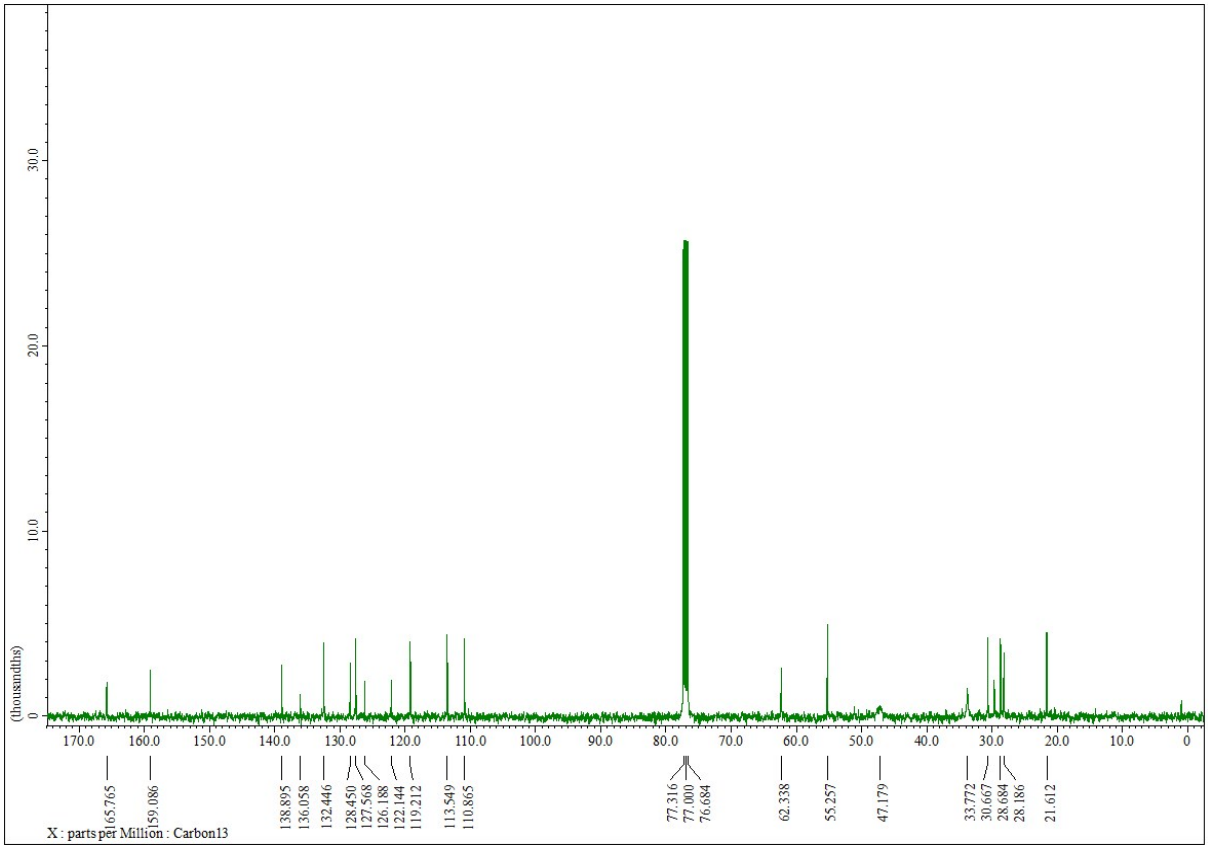


^{1}H and ^{13}C spectra of 5-methyl-4-morpholino-2-oxo-6-(*p*-tolyl)-2*H*-pyran-3-carbonitrile **1p**

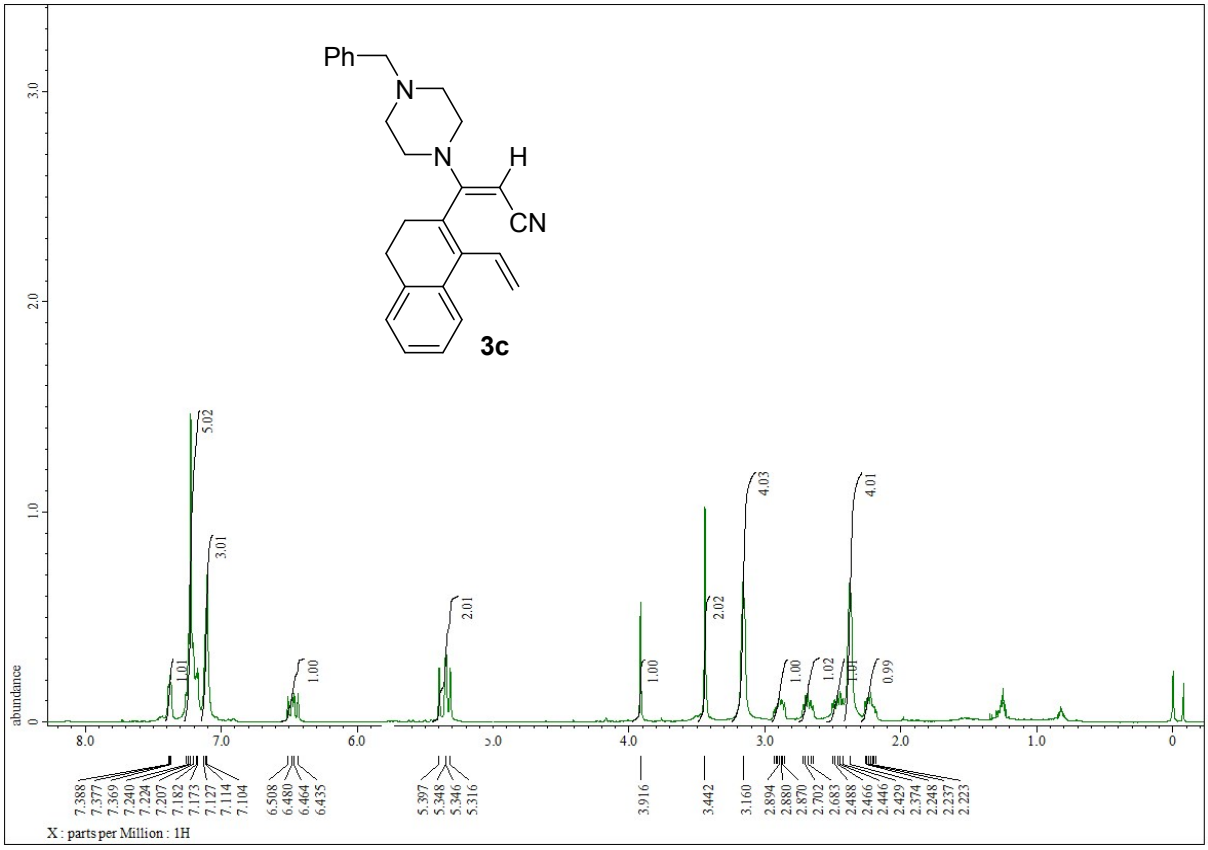


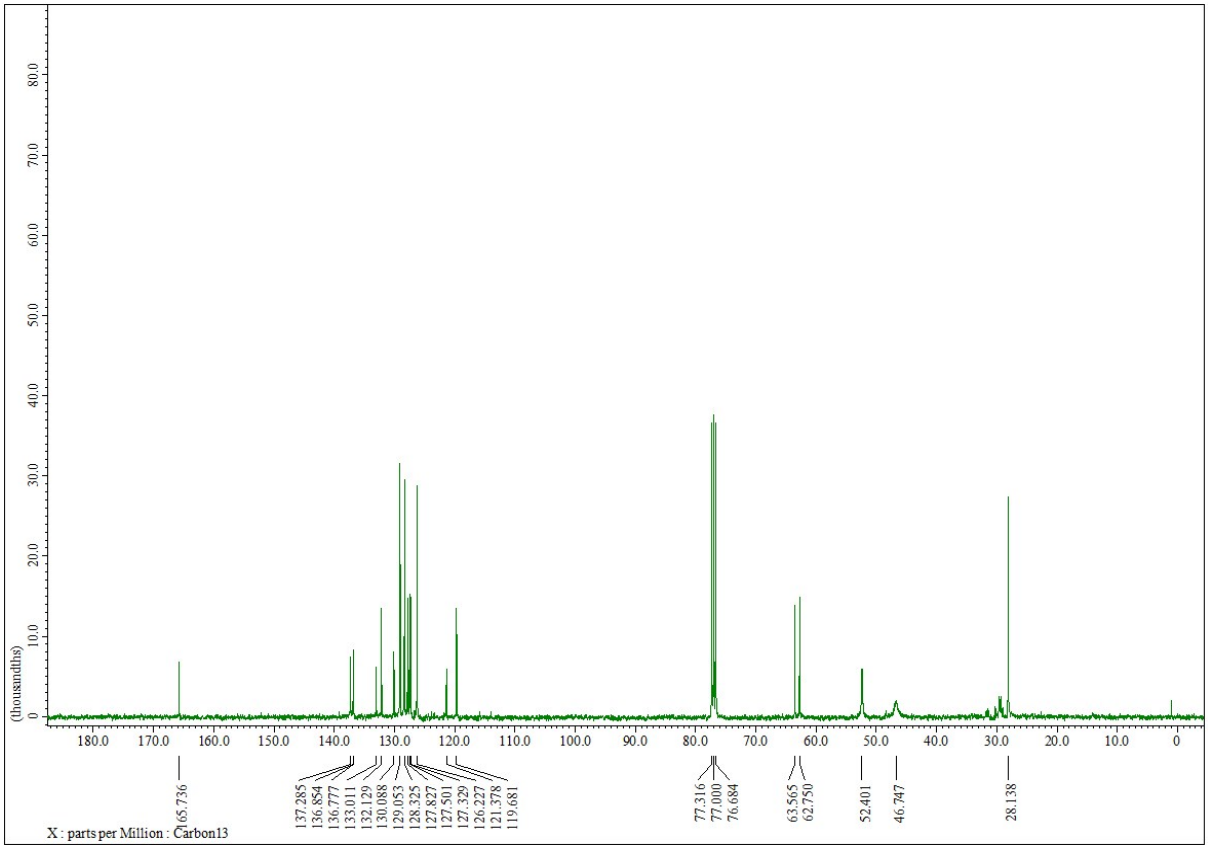
^{1}H and ^{13}C spectra of (*E*)-3-(piperidin-1-yl)-3-(1-vinyl-3,4-dihydronaphthalen-2-yl)acrylonitrile **3a**



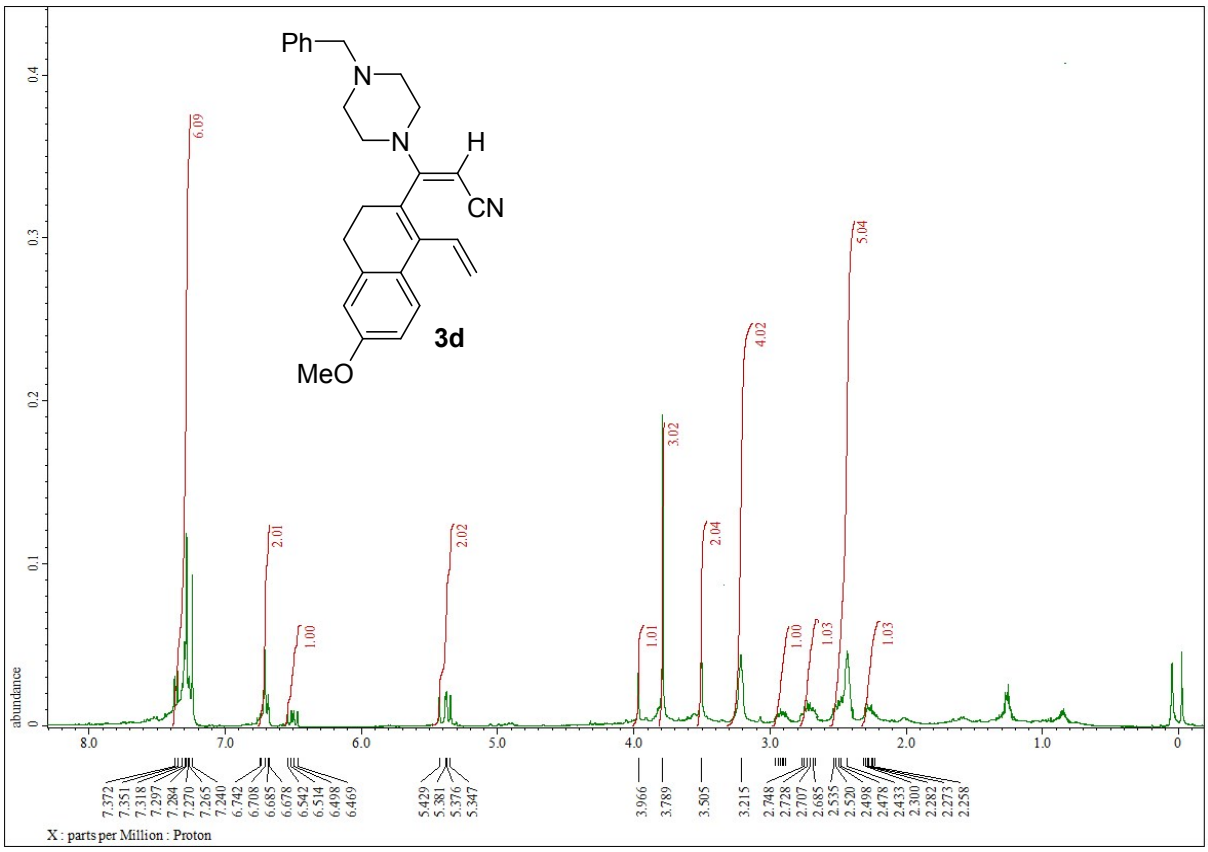


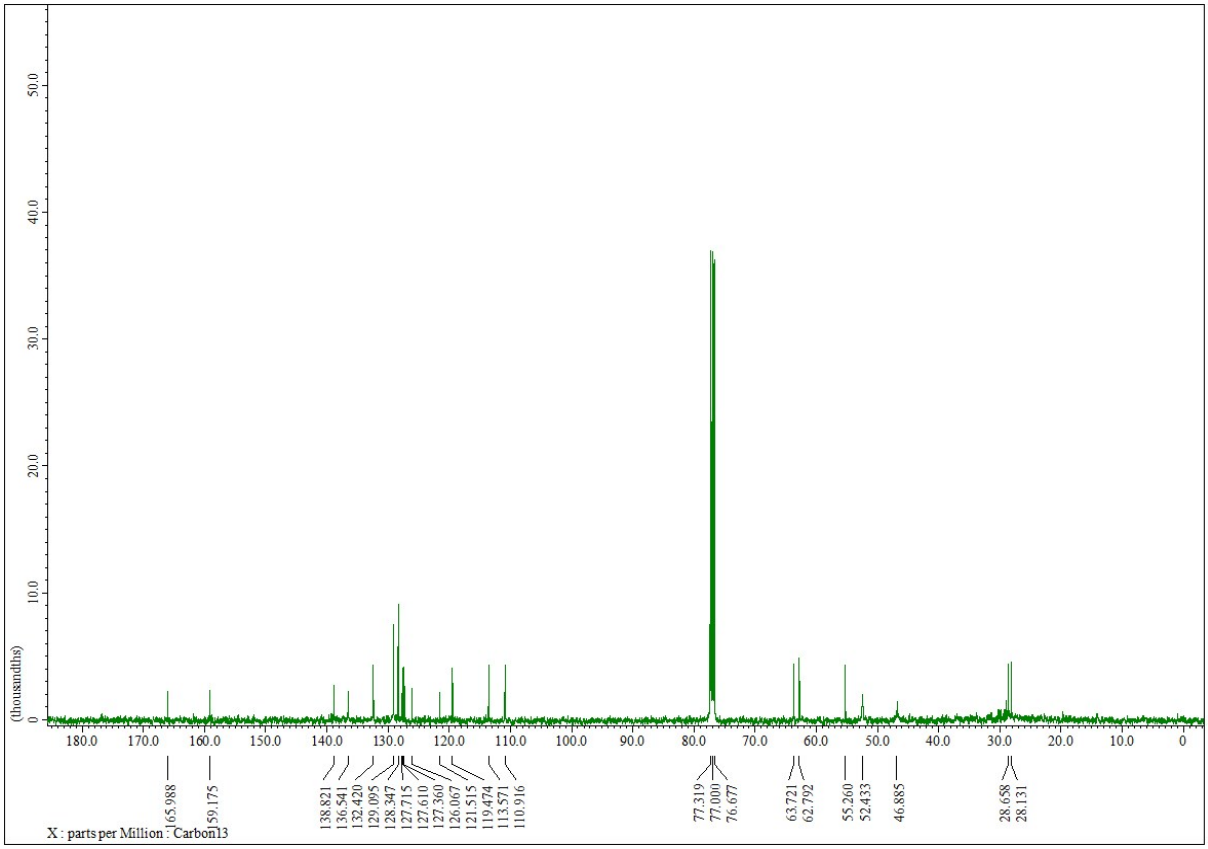
^{1}H and ^{13}C spectra of (*E*)-3-(6-methoxy-1-vinyl-3,4-dihydronaphthalen-2-yl)-3-(4-methylpiperidin-1-yl)acrylonitrile **3b**



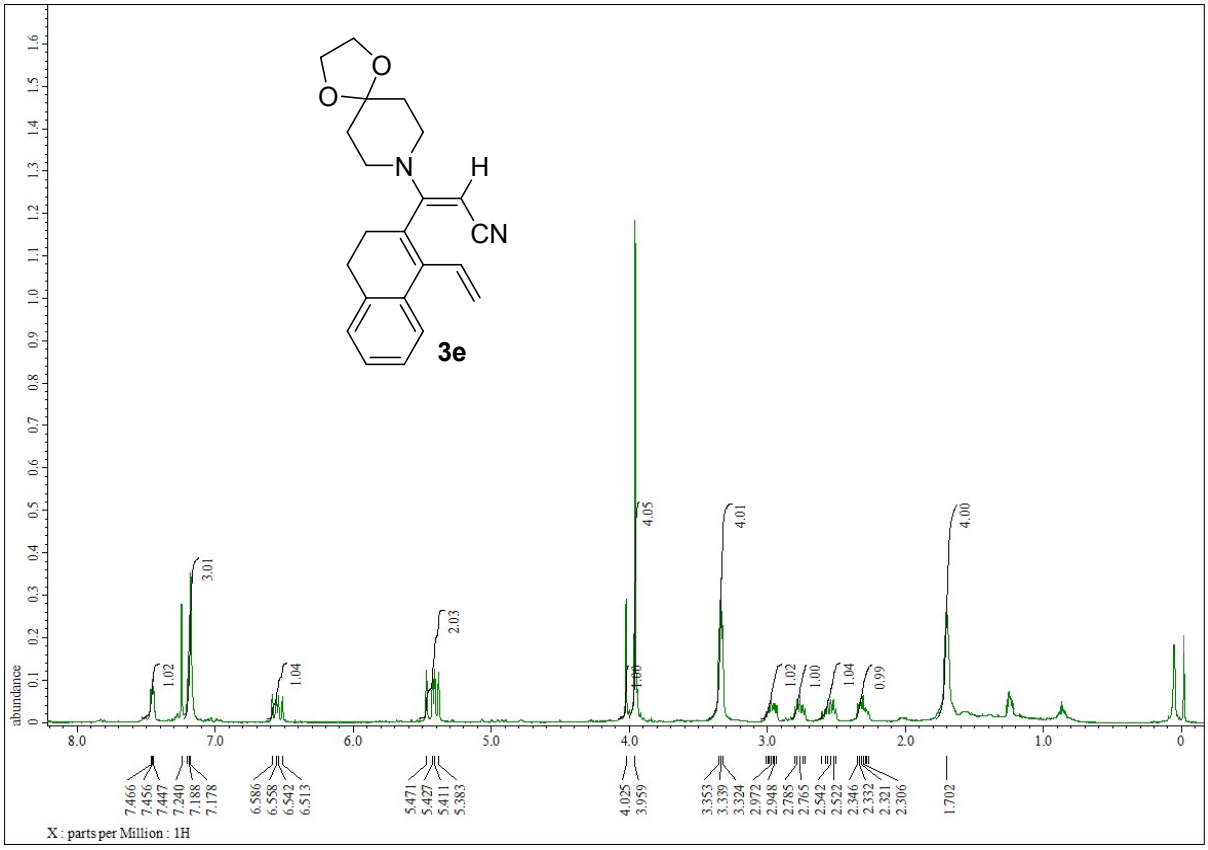


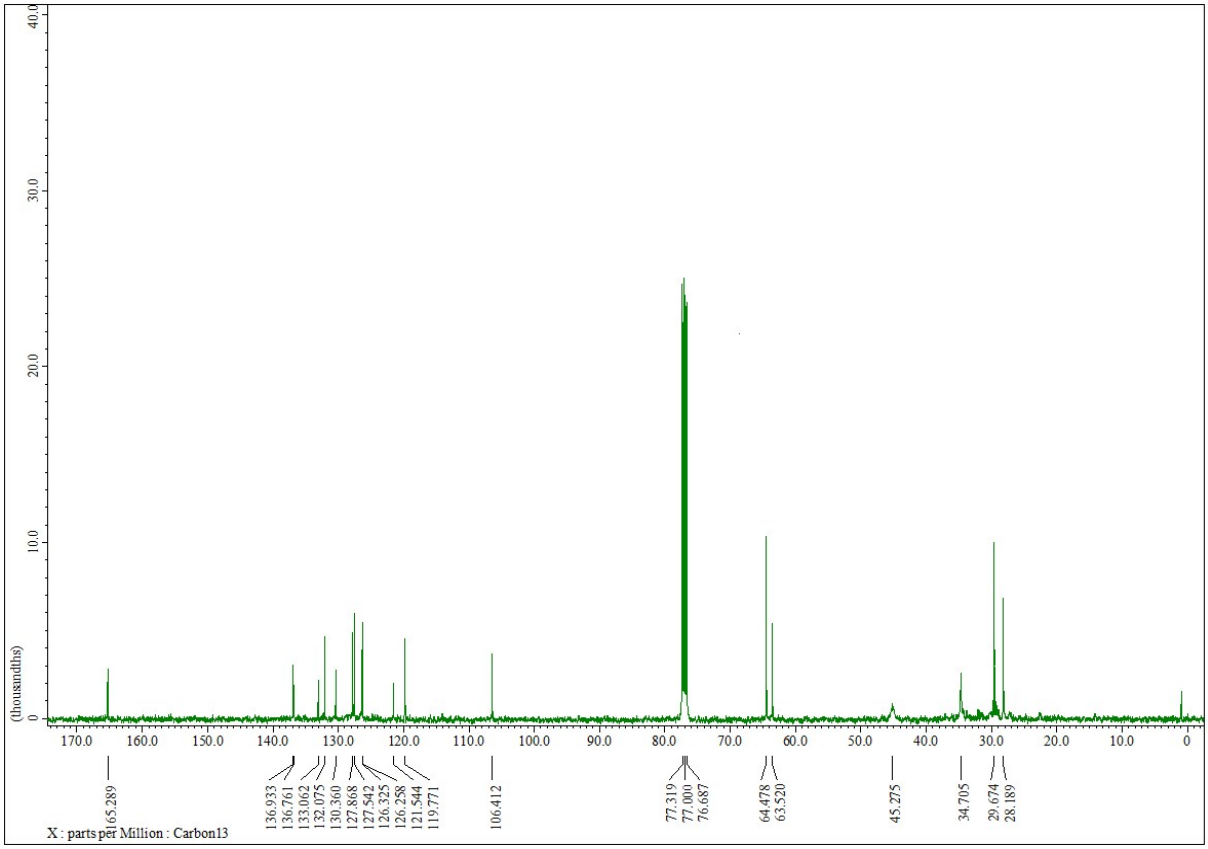
^{1}H and ^{13}C spectra of (*E*)-3-(4-benzylpiperazin-1-yl)-3-(1-vinyl-3,4-dihydronaphthalen-2-yl)acrylonitrile **3c**



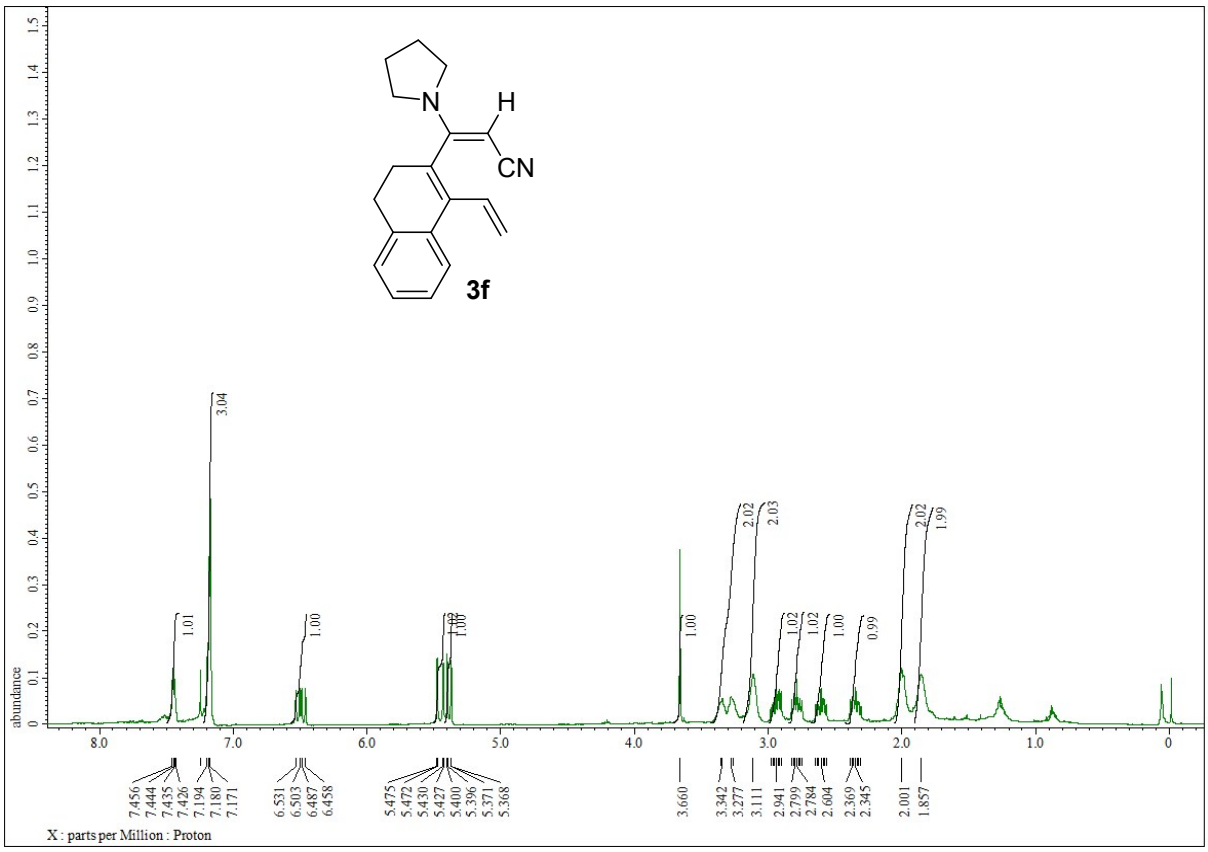


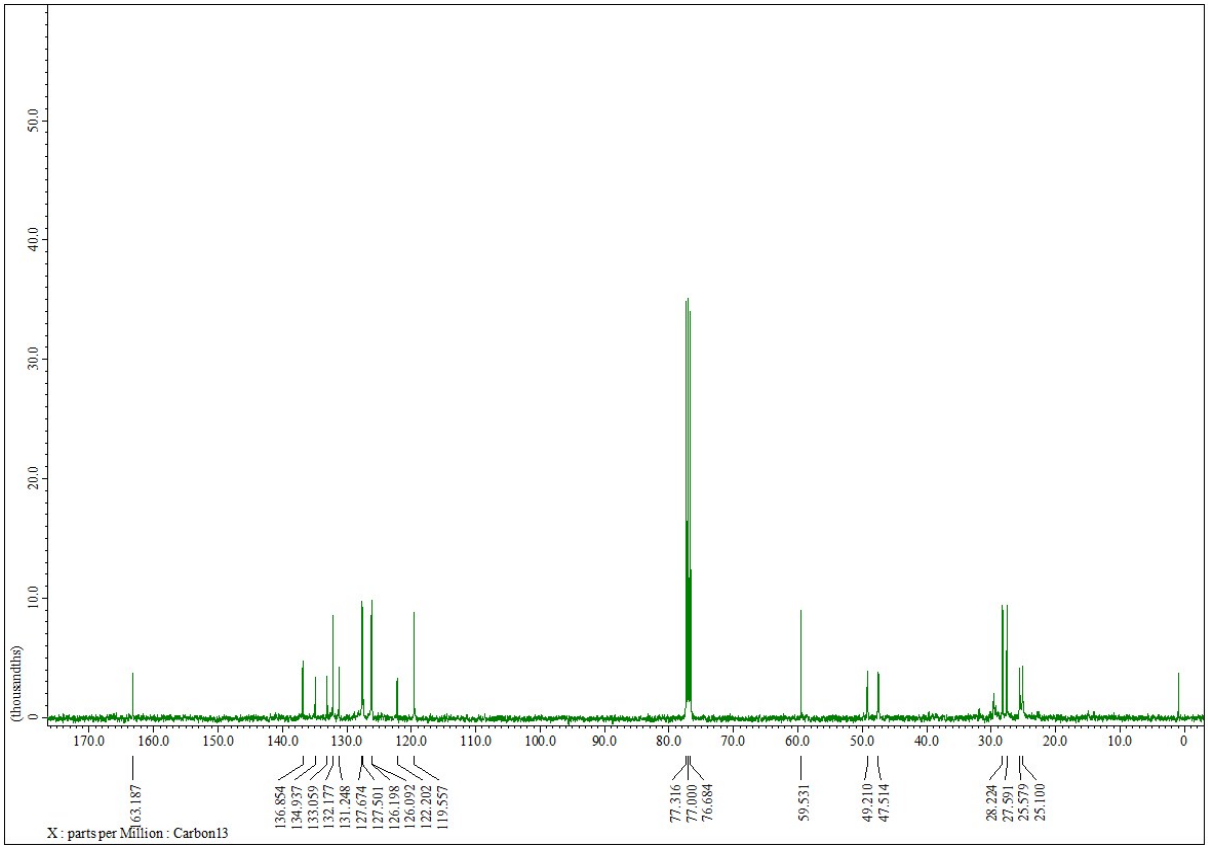
^{1}H and ^{13}C spectra of (*E*)-3-(4-benzylpiperazin-1-yl)-3-(6-methoxy-1-vinyl-3,4-dihydronaphthalen-2-yl)acrylonitrile **3d**



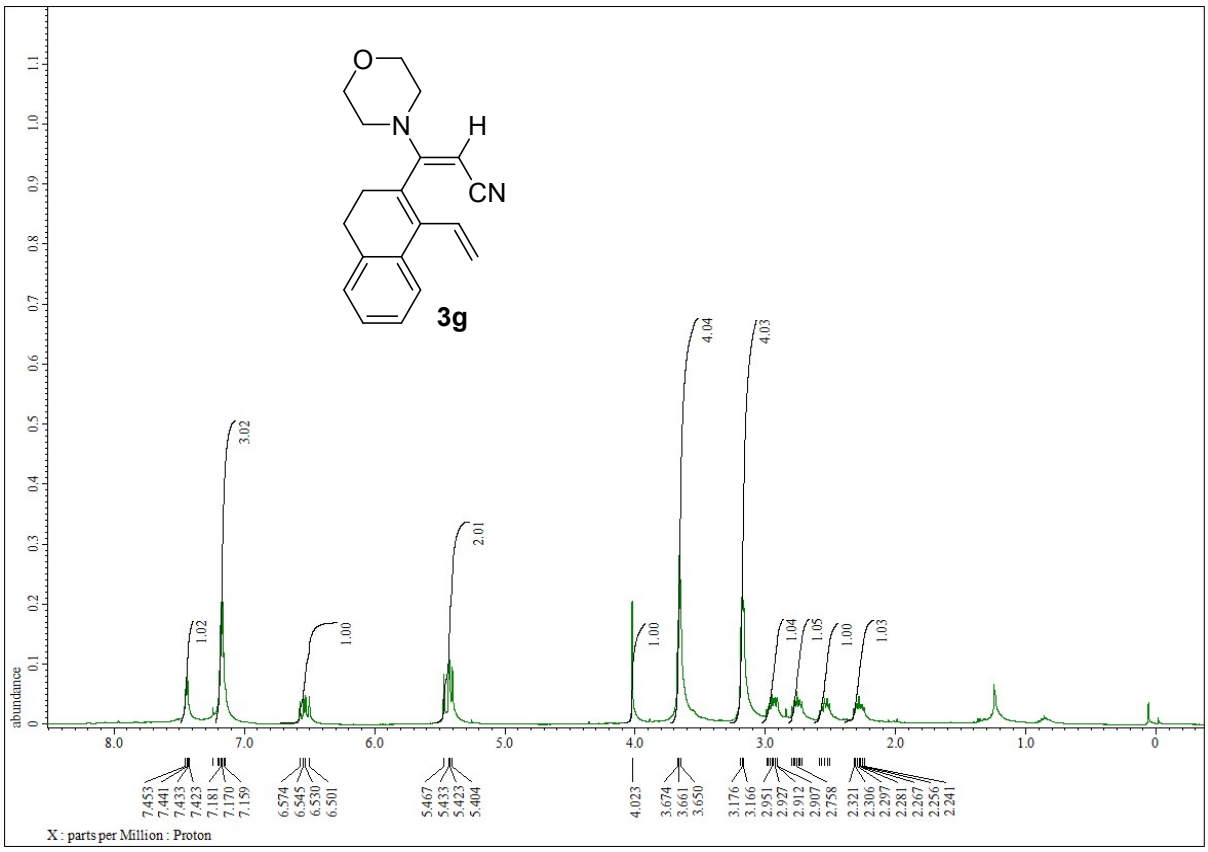


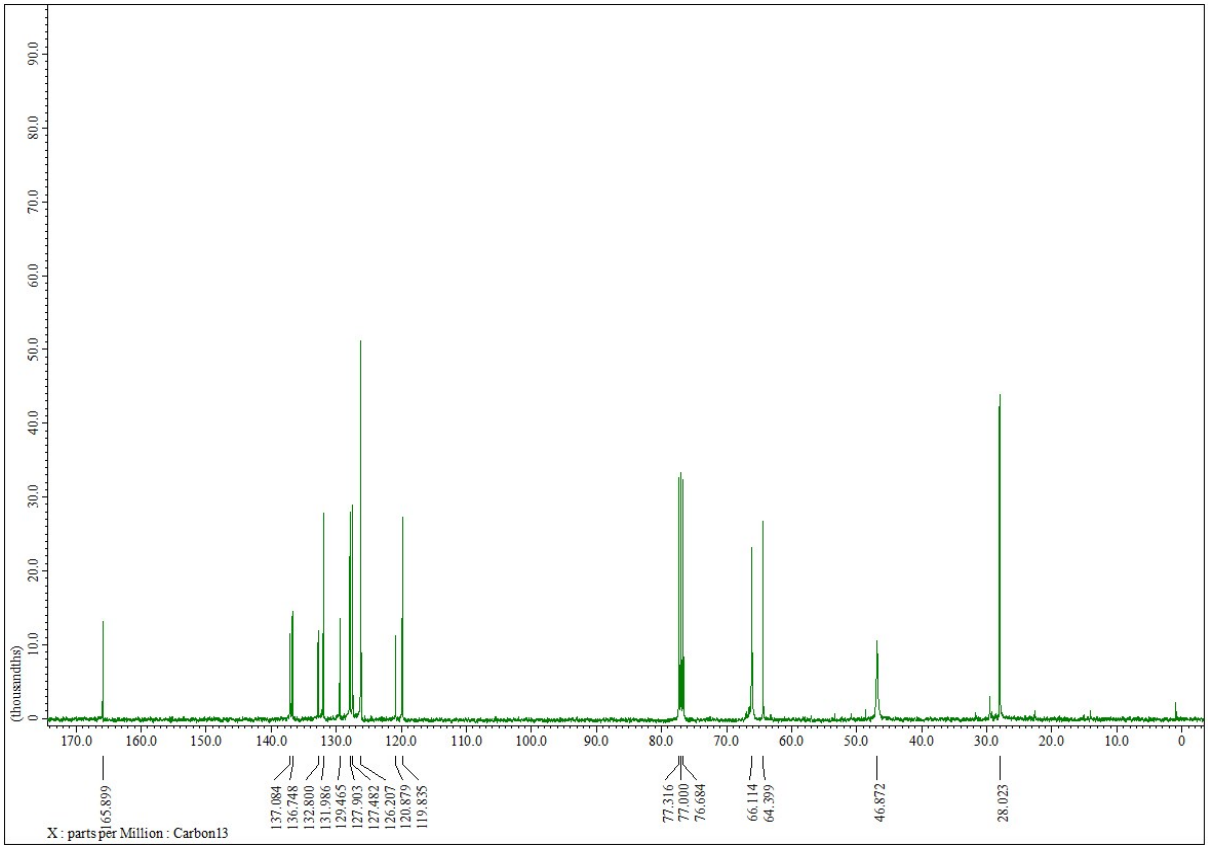
^{1}H and ^{13}C spectra of (*E*)-3-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-3-(1-vinyl-3,4-dihydronaphthalen-2-yl)acrylonitrile **3e**



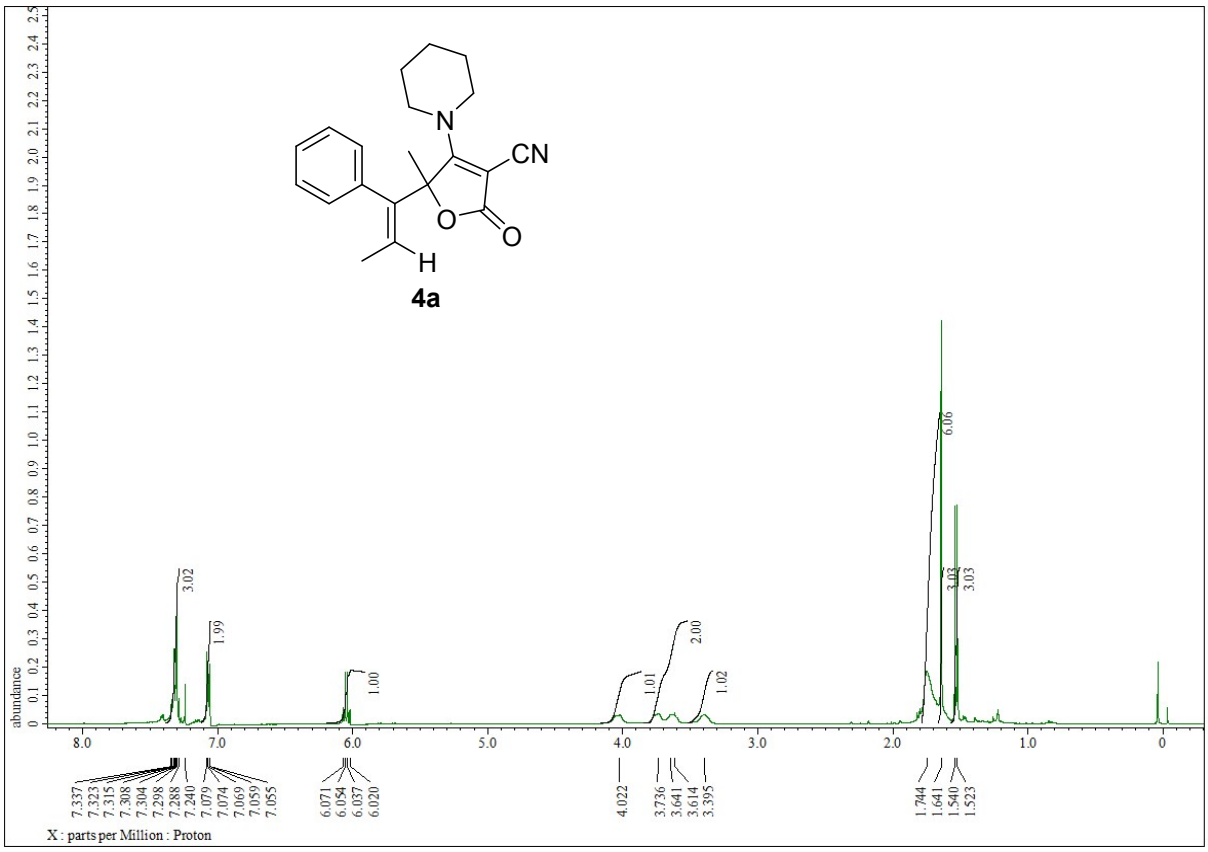


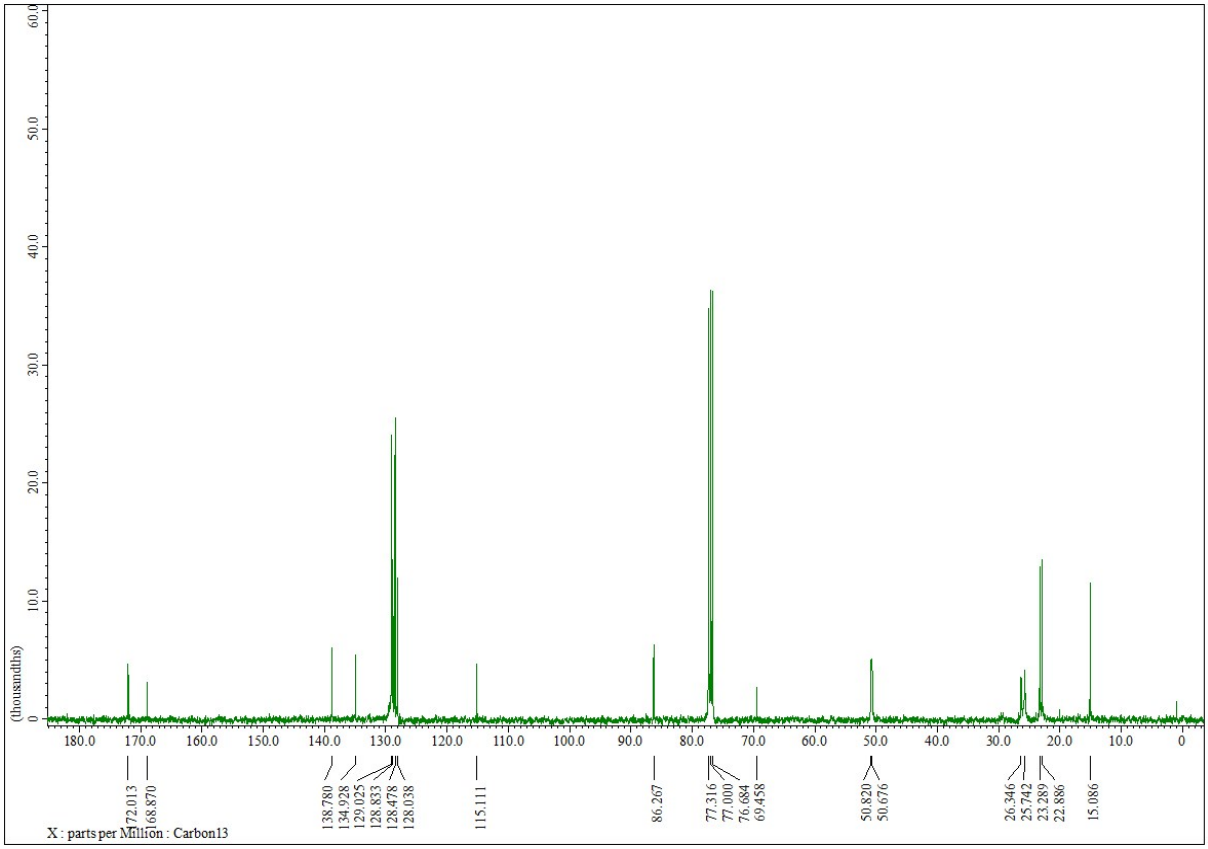
^{1}H and ^{13}C spectra of (*E*)-3-(pyrrolidin-1-yl)-3-(1-vinyl-3,4-dihydronaphthalen-2-yl)acrylonitrile **3f**



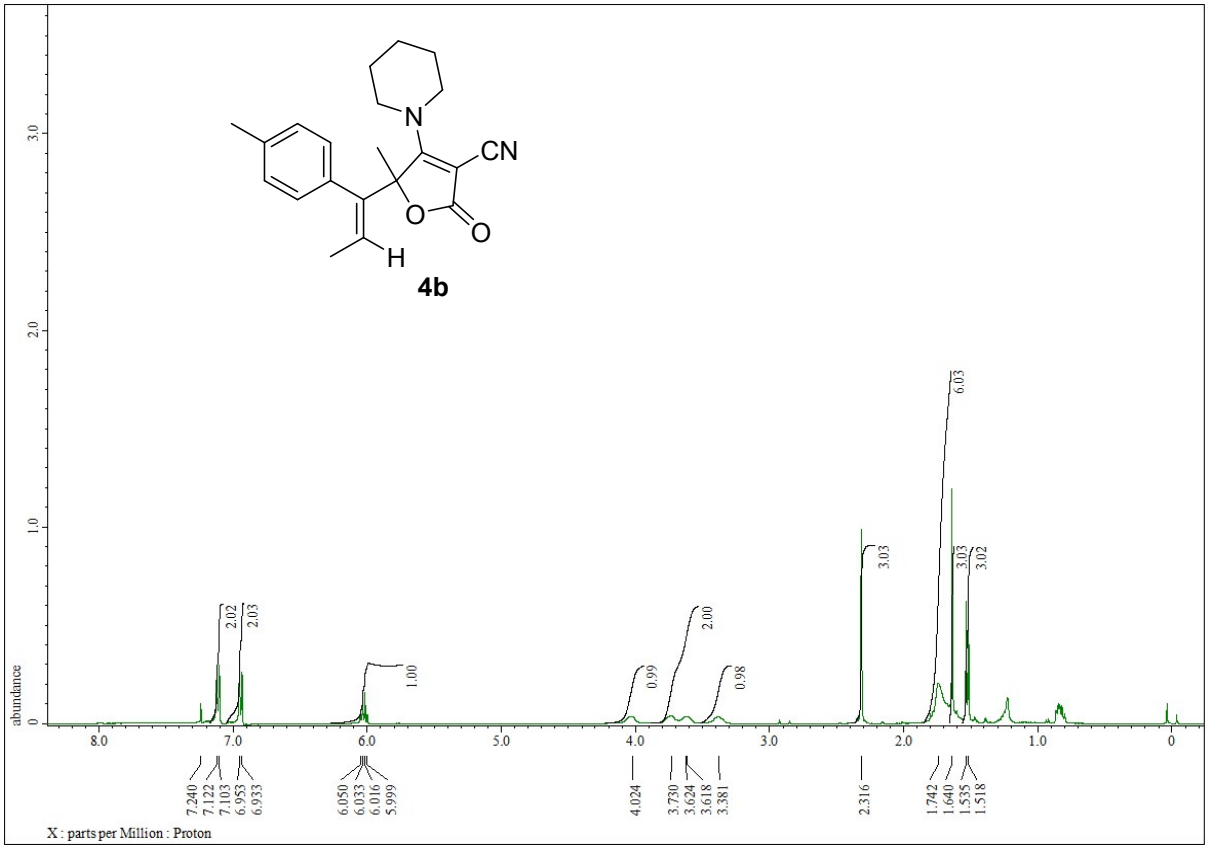


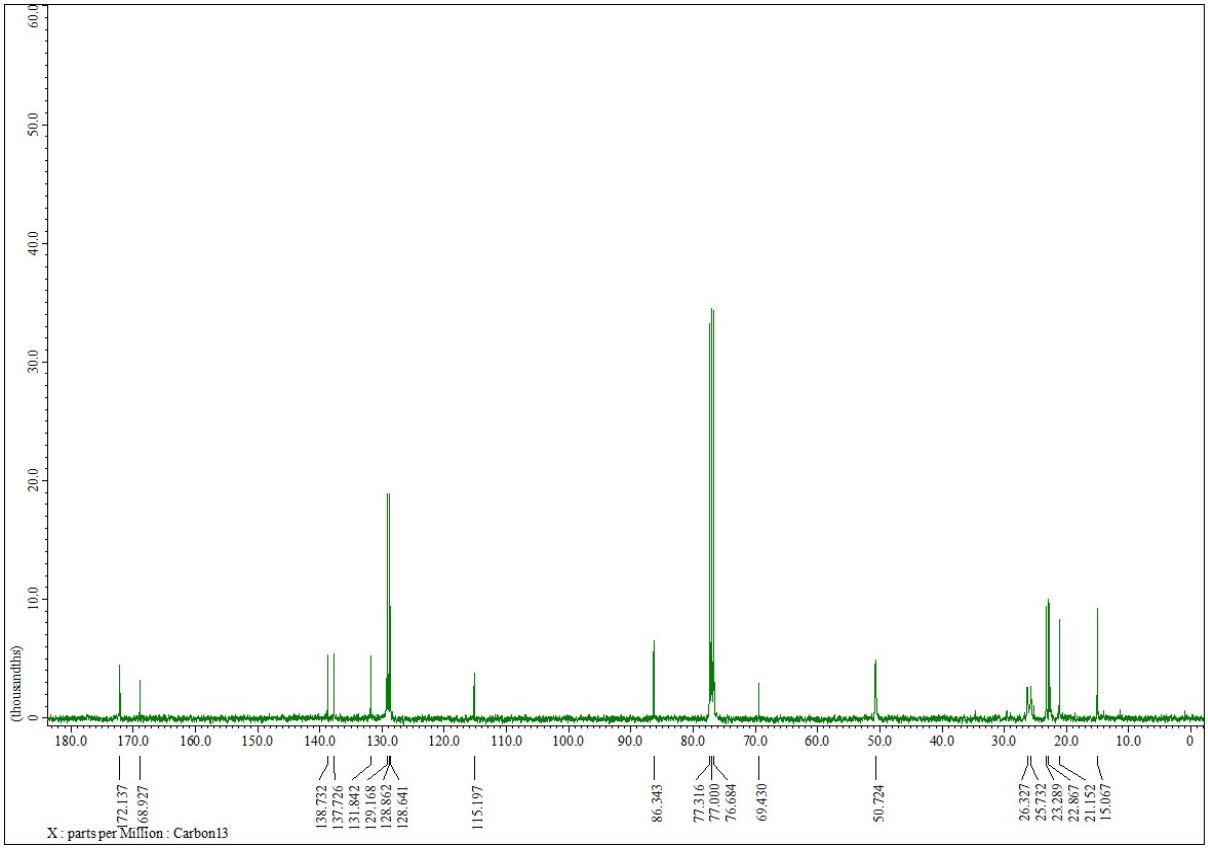
^{1}H and ^{13}C spectra of (*E*)-3-morpholino-3-(1-vinyl-3,4-dihydronaphthalen-2-yl)acrylonitrile **3g**



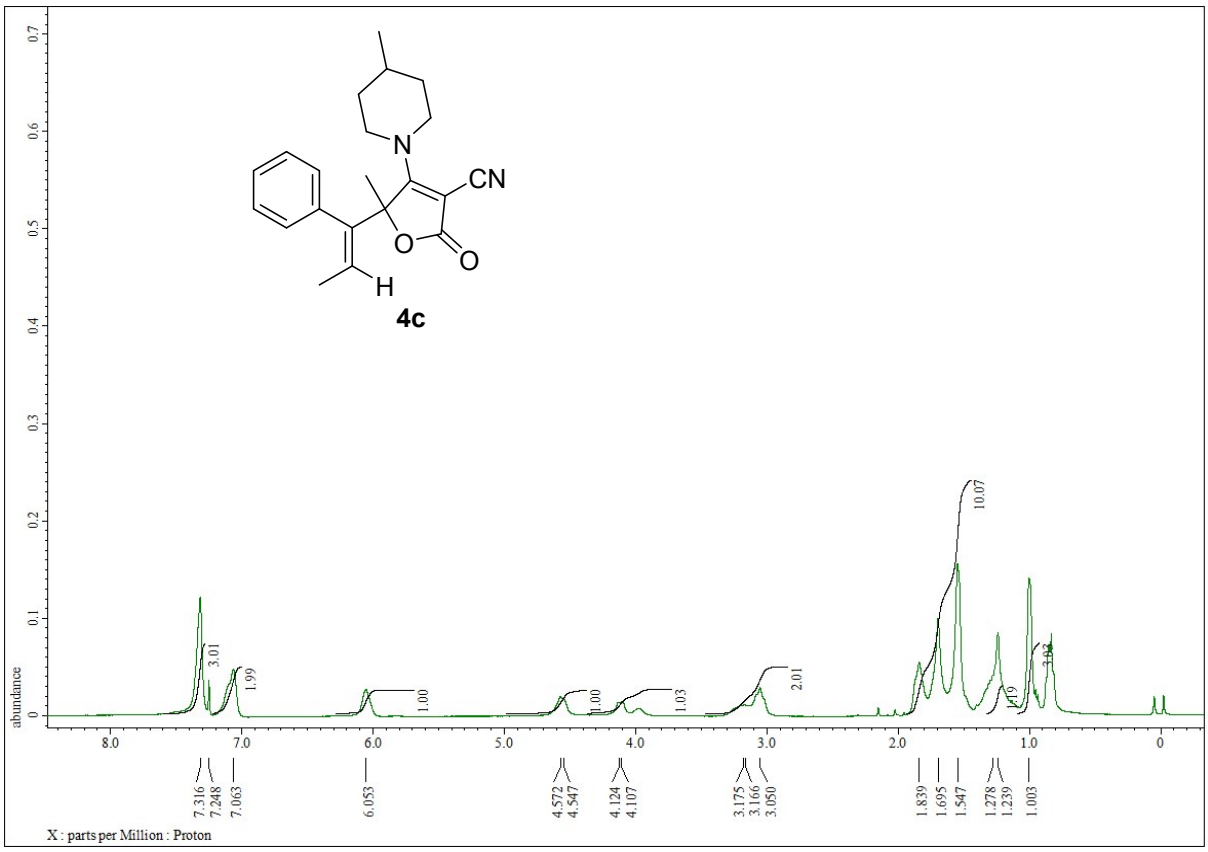


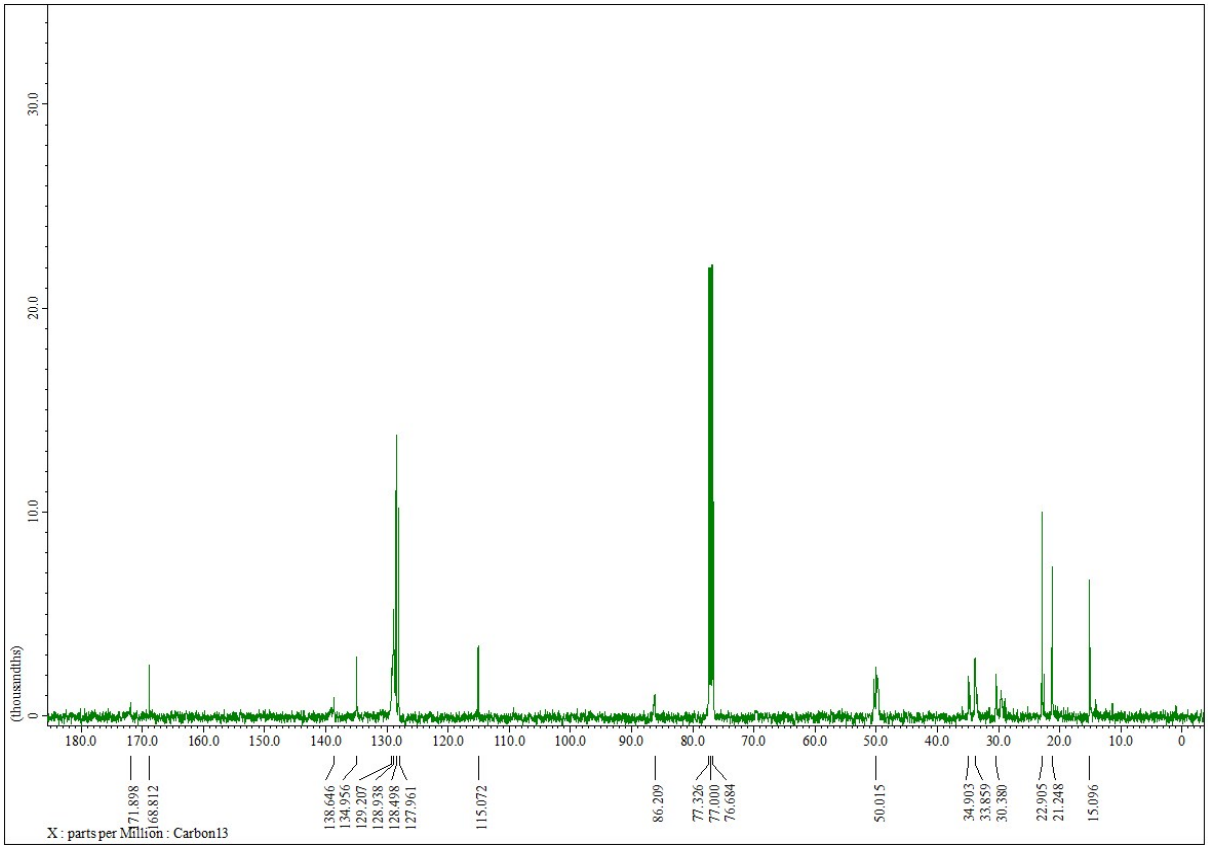
^{1}H and ^{13}C spectra of (*E*)-5-methyl-2-oxo-5-(1-phenylprop-1-en-1-yl)-4-(piperidin-1-yl)-2,5-dihydrofuran-3-carbonitrile **4a**



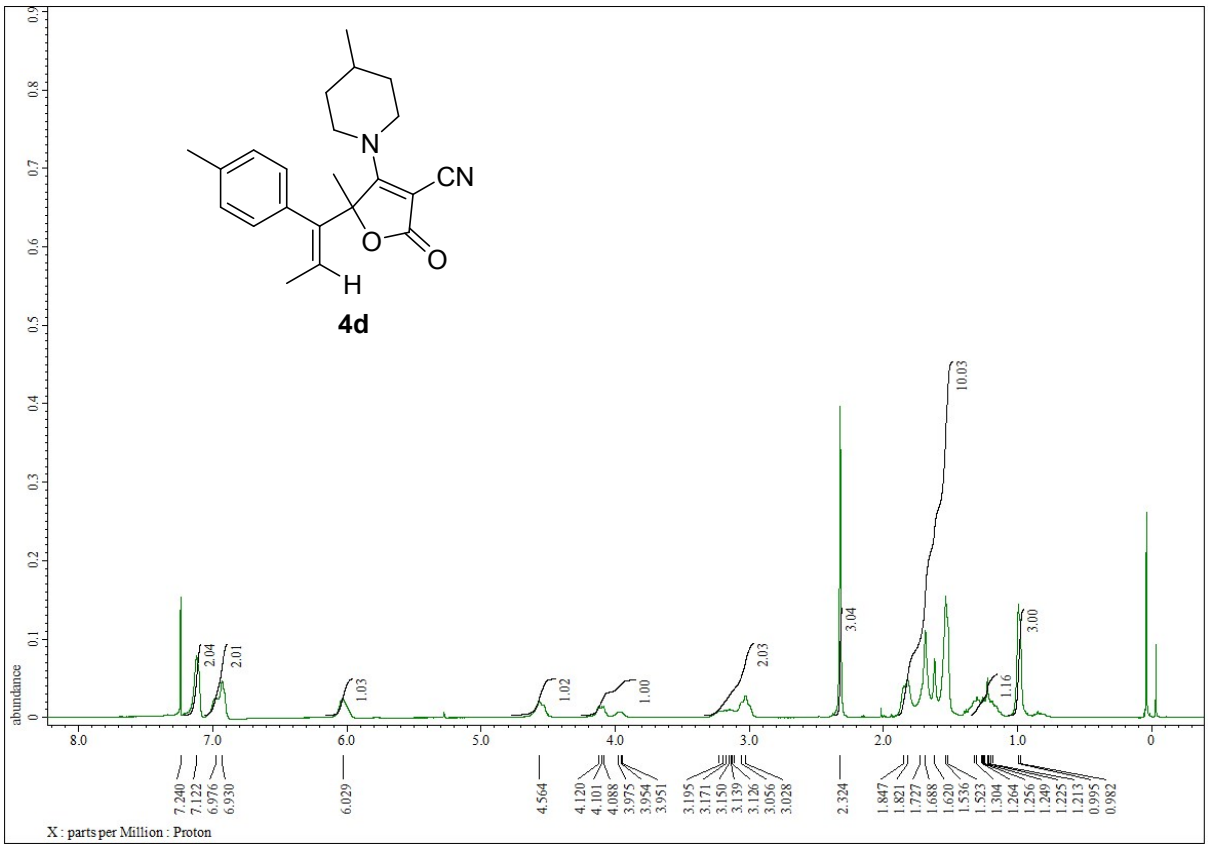


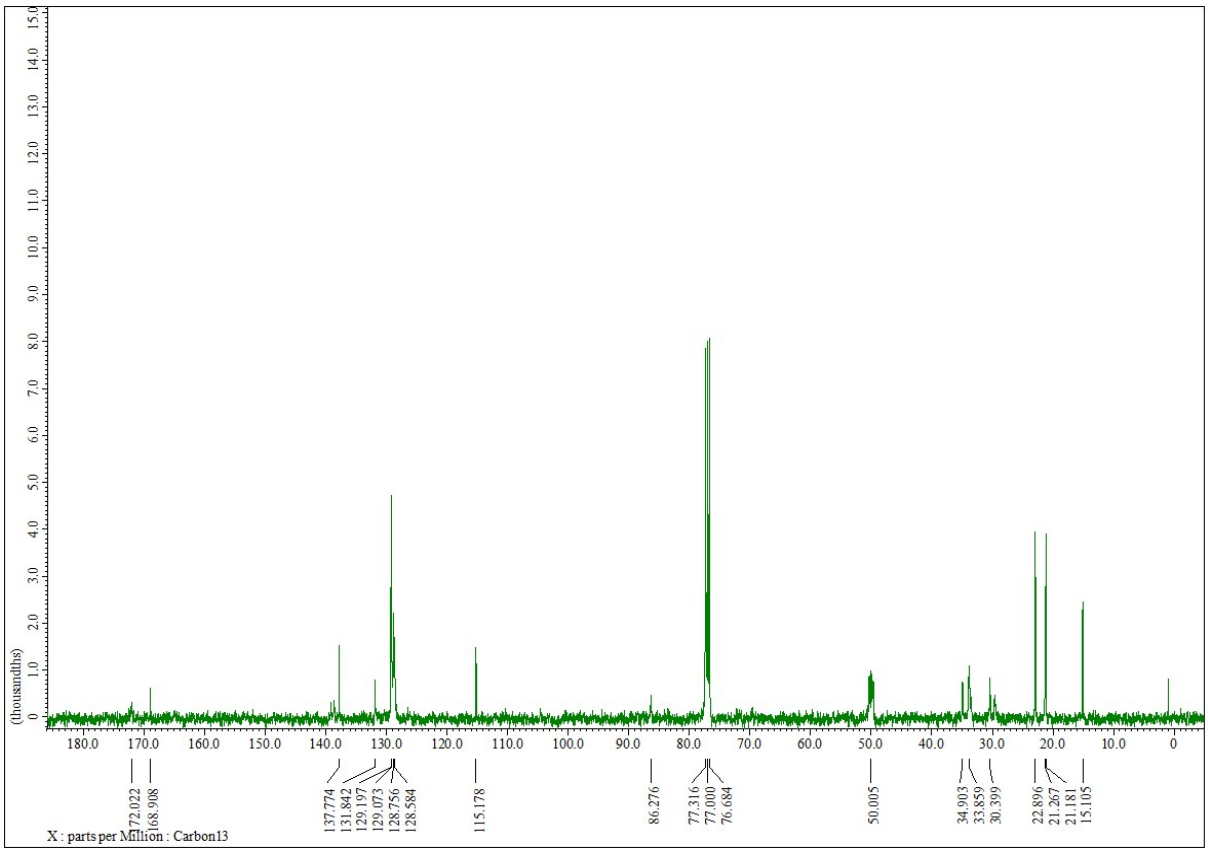
^{1}H and ^{13}C spectra of (*E*)-5-methyl-2-oxo-4-(piperidin-1-yl)-5-(1-(*p*-tolyl)prop-1-en-1-yl)-2,5-dihydrofuran-3-carbonitrile **4b**



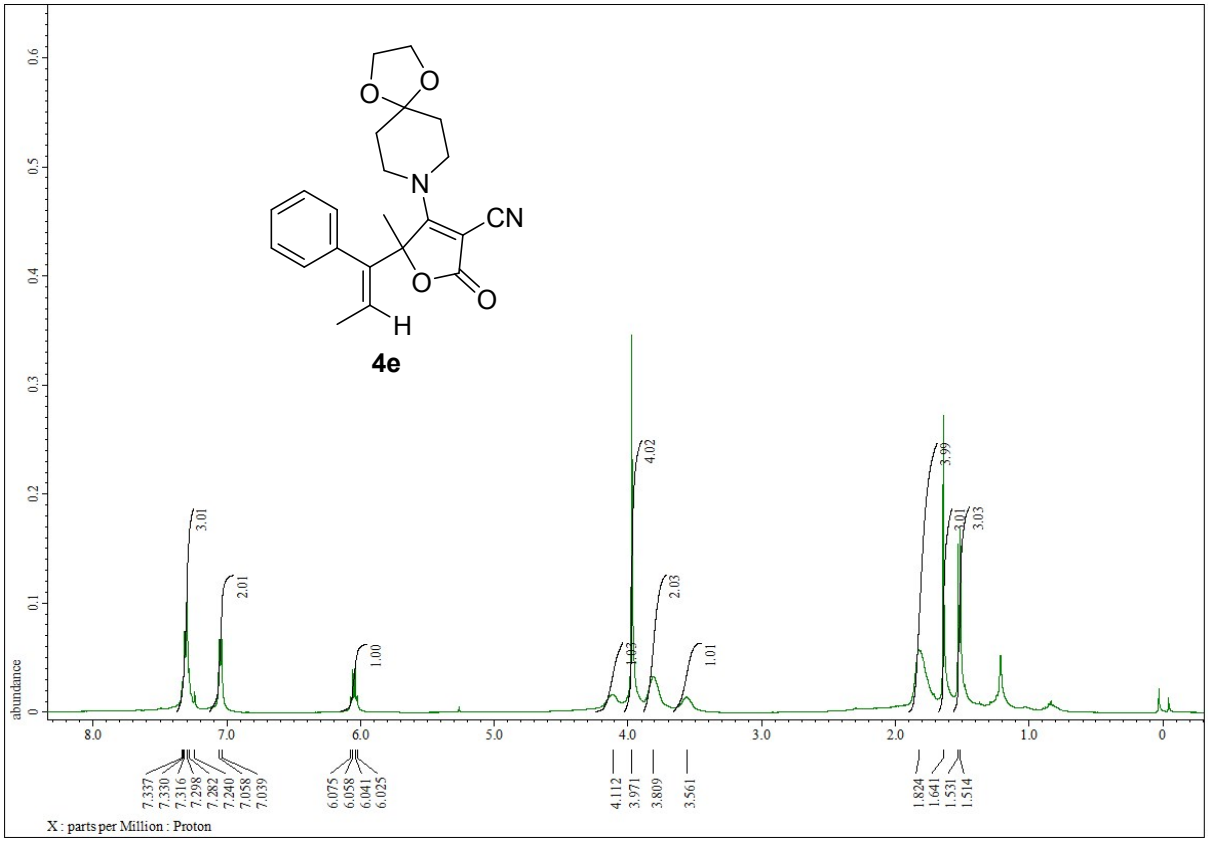


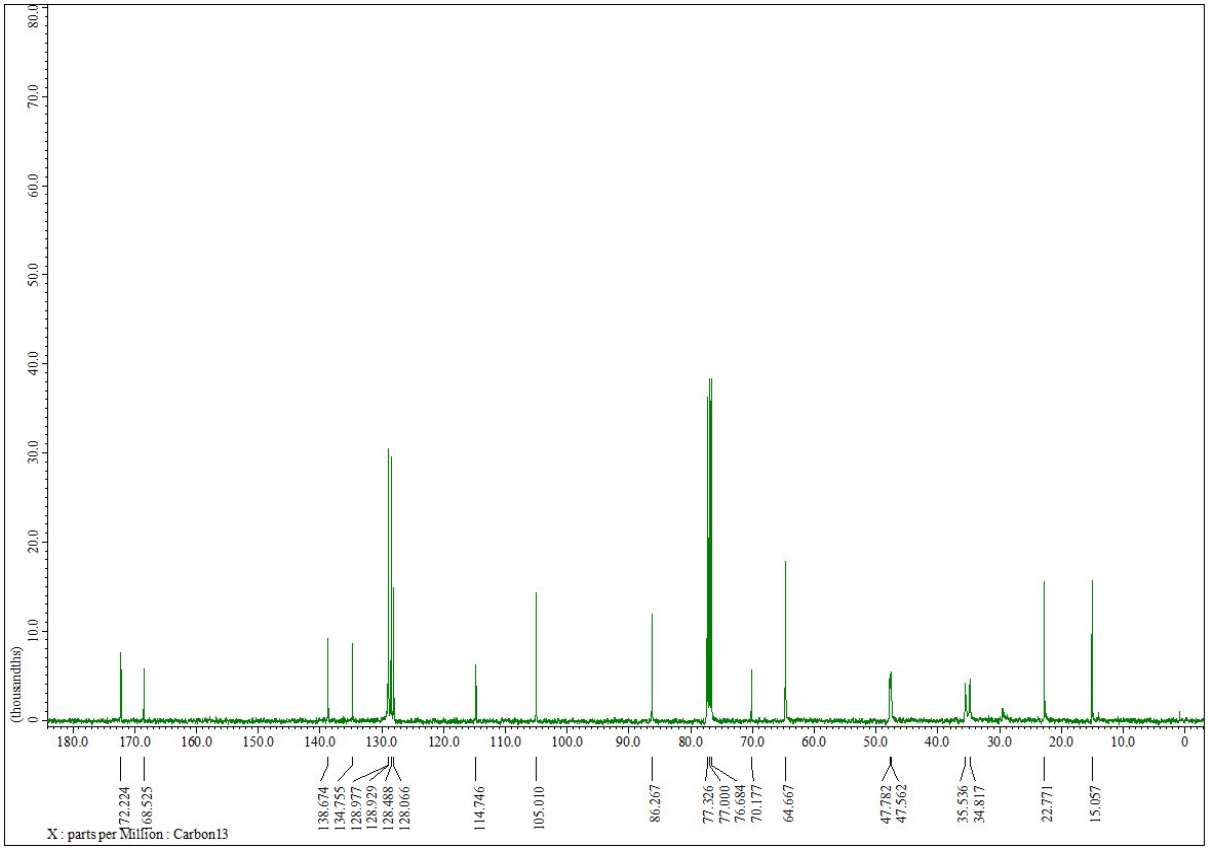
^{1}H and ^{13}C spectra of (*E*)-5-methyl-4-(4-methylpiperidin-1-yl)-2-oxo-5-(1-phenylprop-1-en-1-yl)-2,5-dihydrofuran-3-carbonitrile **4c**



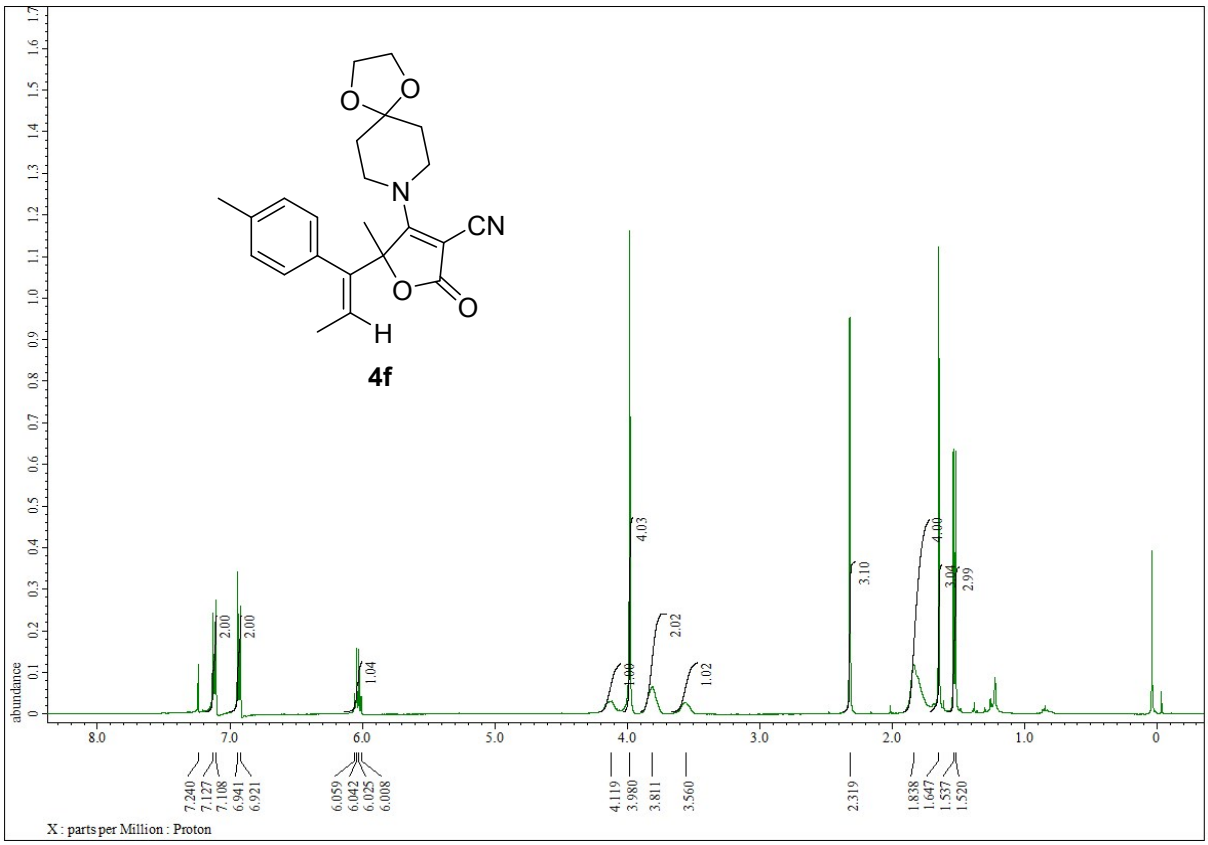


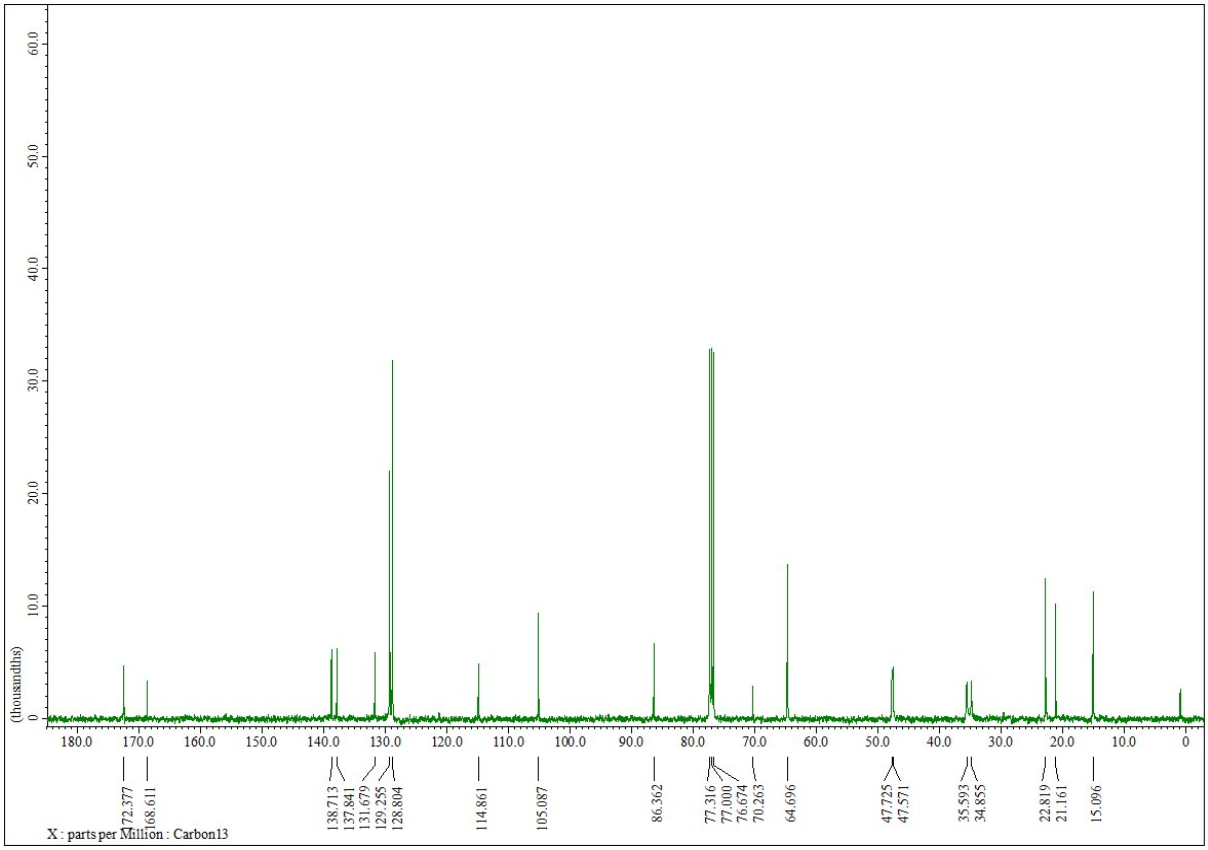
^{1}H and ^{13}C spectra of (*E*)-5-methyl-4-(4-methylpiperidin-1-yl)-2-oxo-5-(1-(*p*-tolyl)prop-1-en-1-yl)-2,5-dihydrofuran-3-carbonitrile **4d**



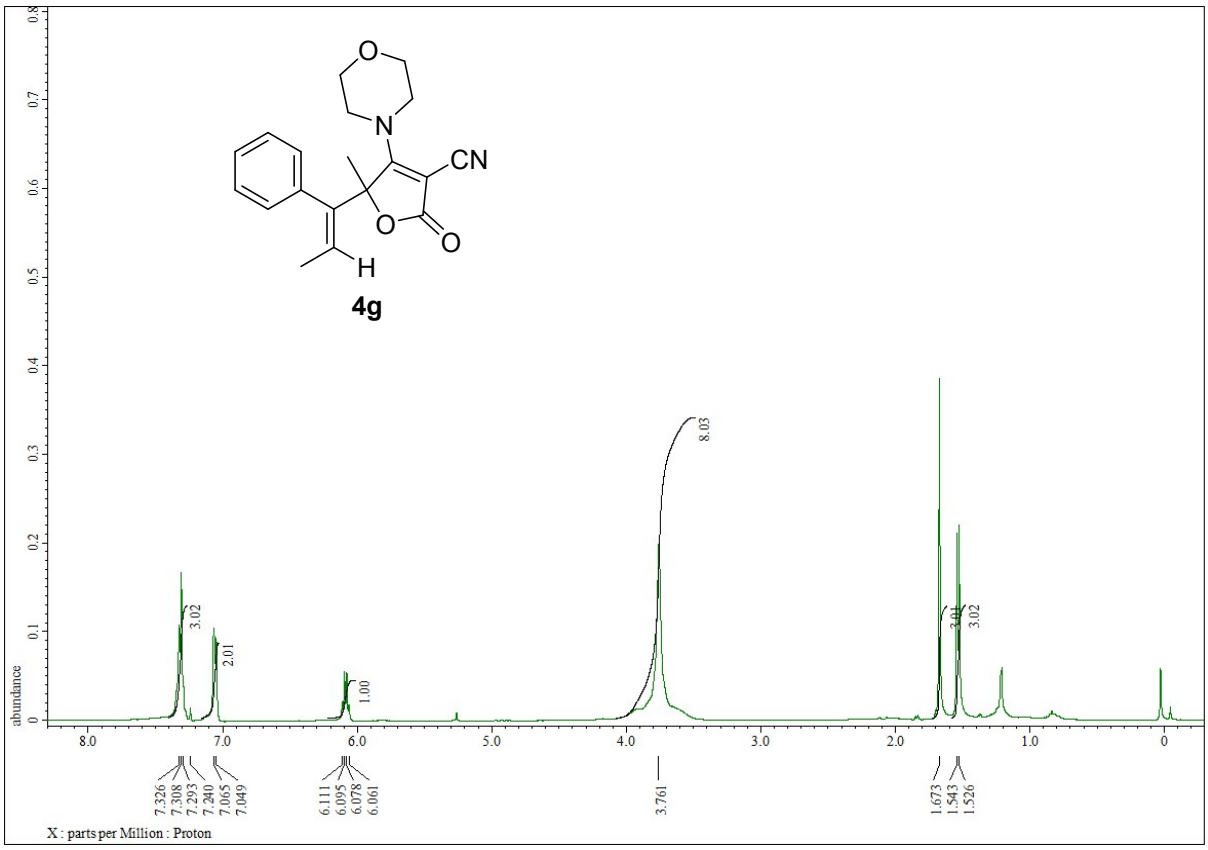


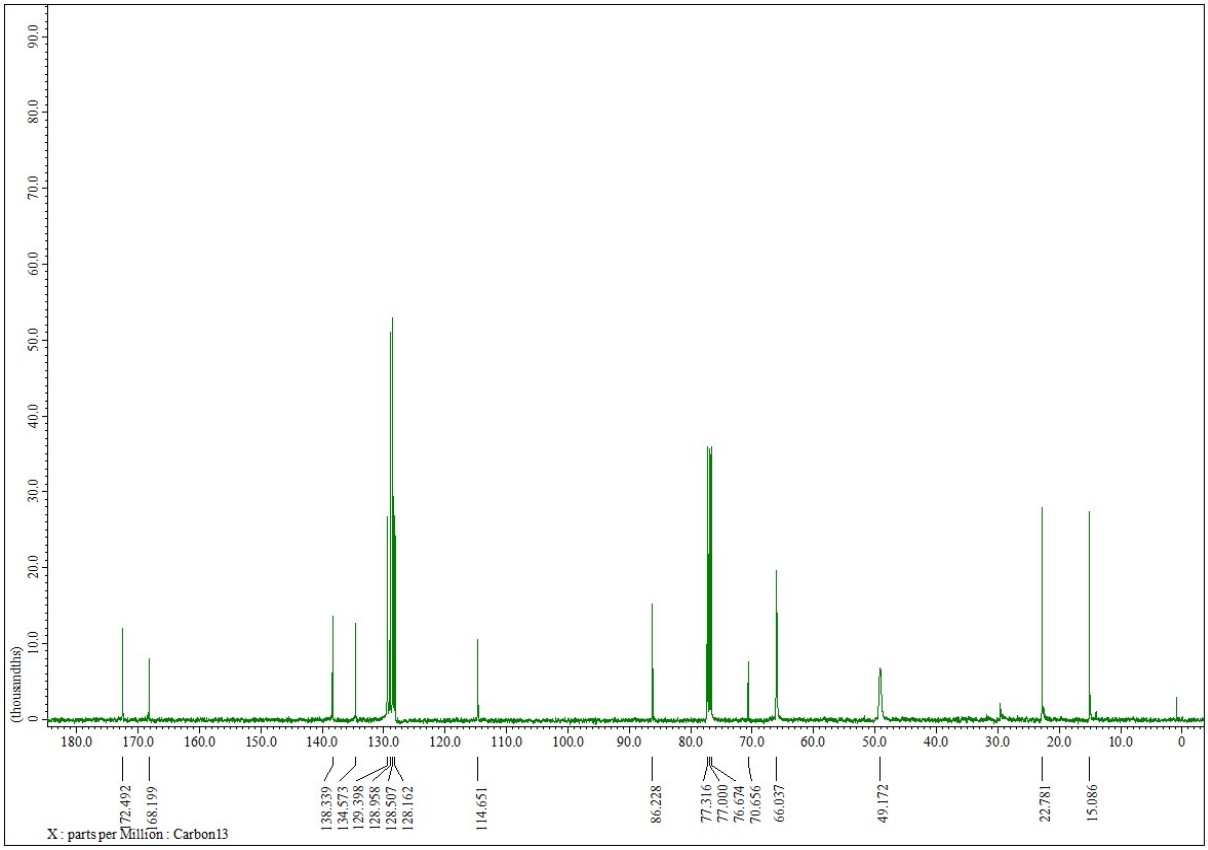
^{1}H and ^{13}C spectra of (*E*)-5-methyl-2-oxo-5-(1-phenylprop-1-en-1-yl)-4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-2,5-dihydrofuran-3-carbonitrile **4e**



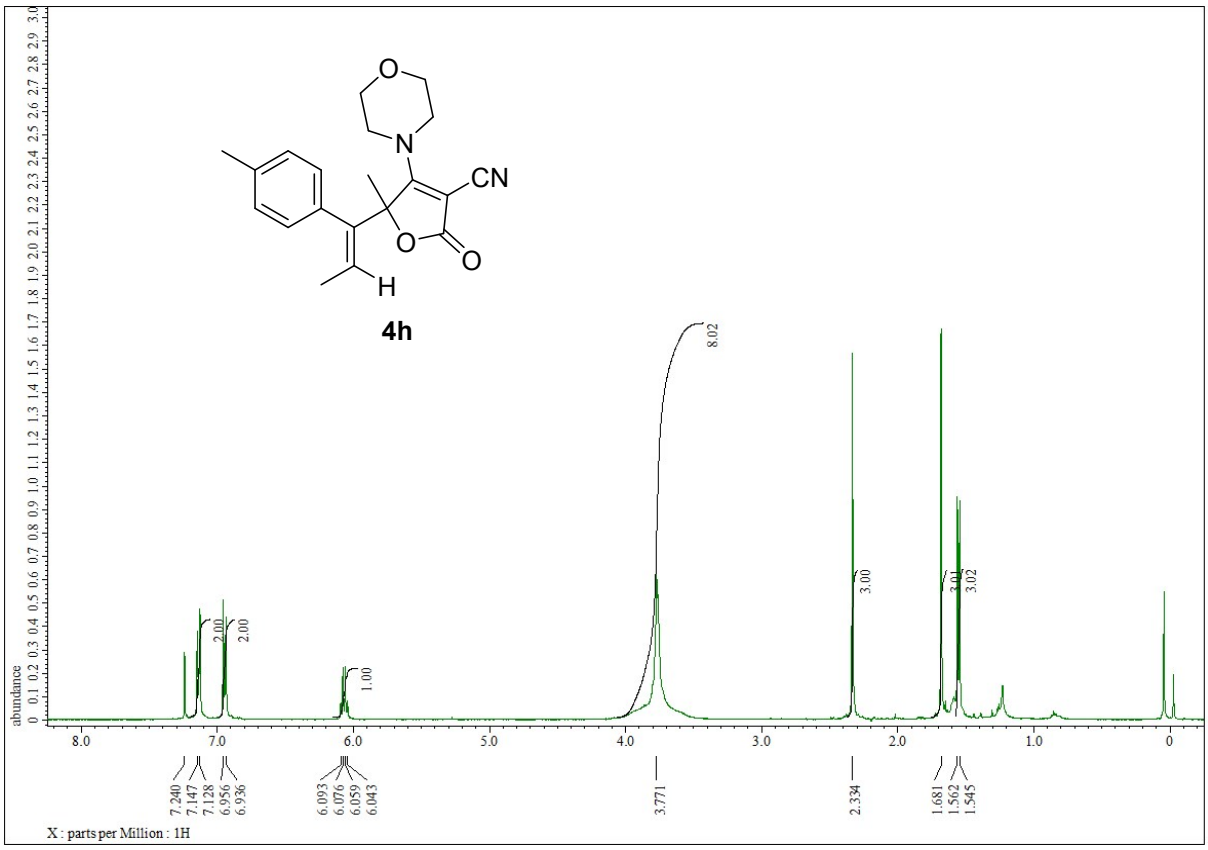


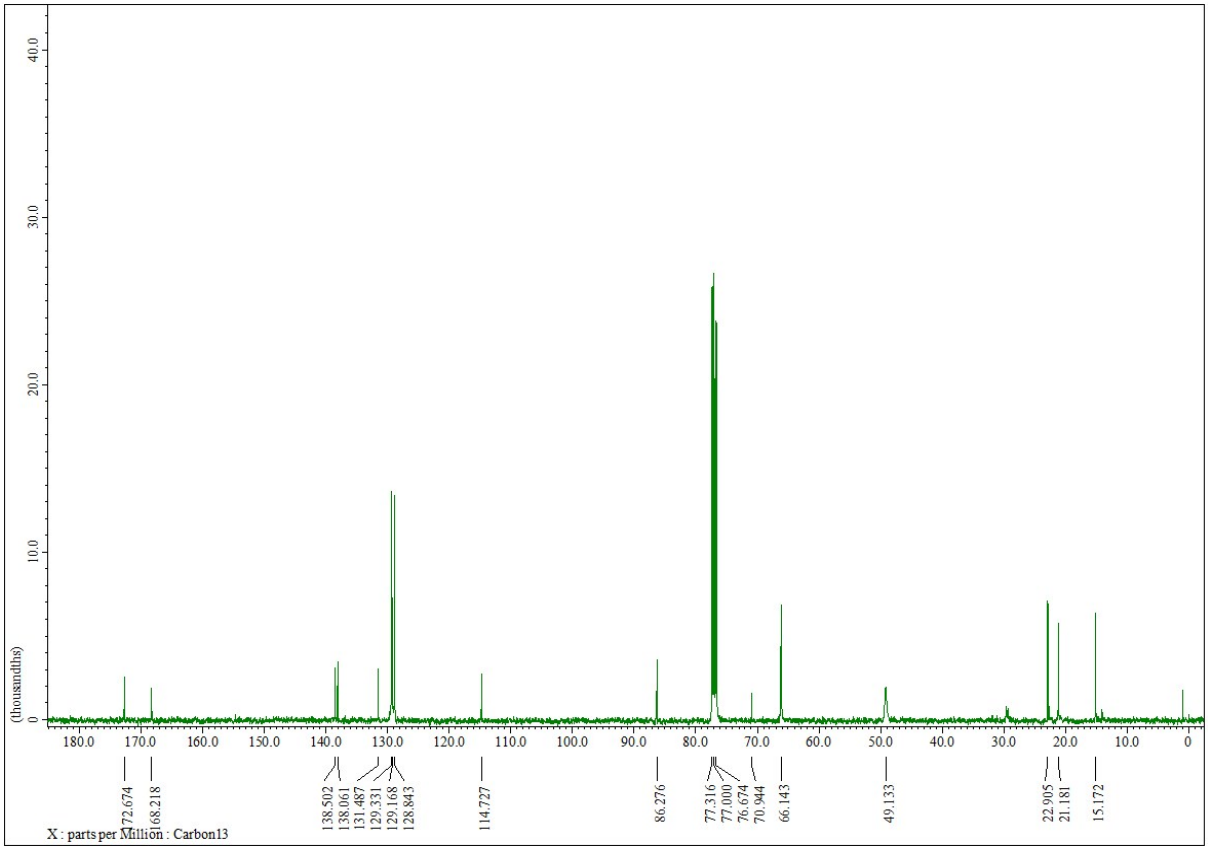
^{1}H and ^{13}C spectra of (*E*)-5-methyl-2-oxo-4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-5-(1-(*p*-tolyl)prop-1-en-1-yl)-2,5-dihydrofuran-3-carbonitrile **4f**



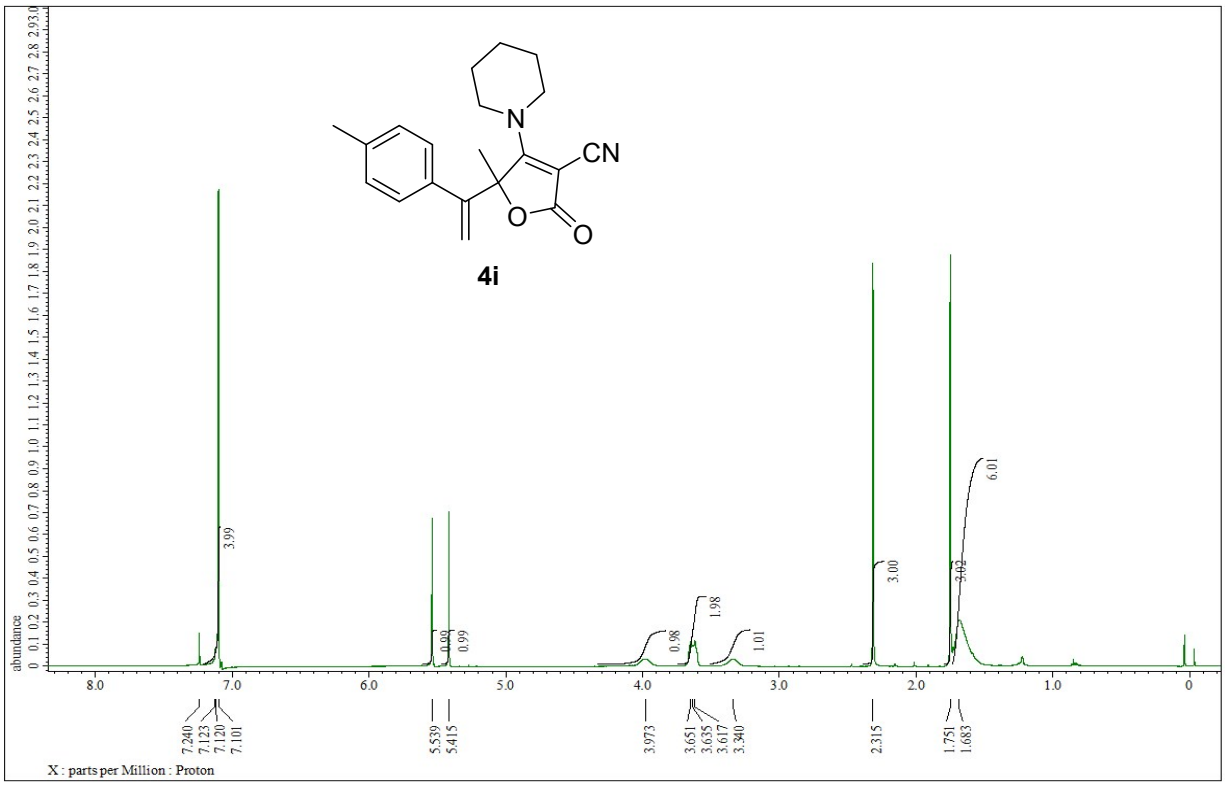


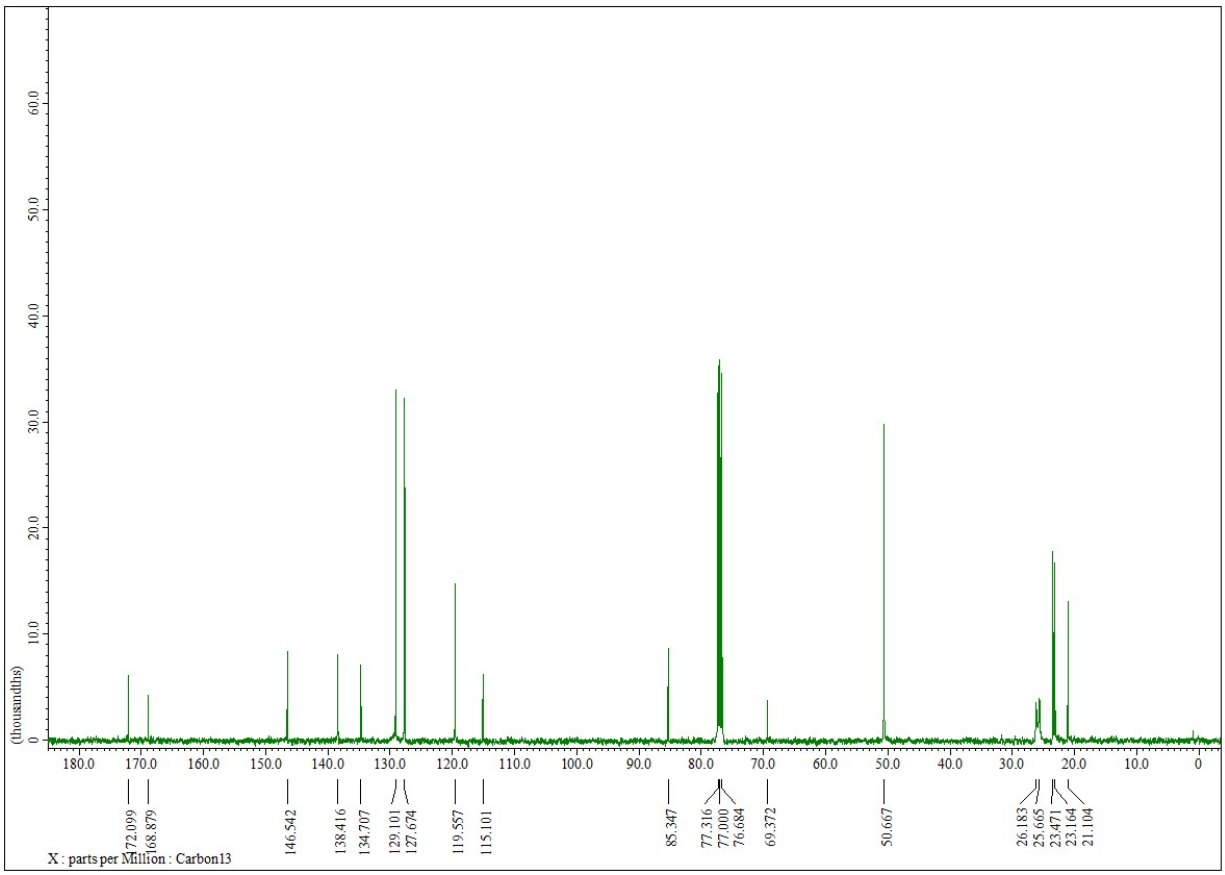
^{1}H and ^{13}C spectra of (*E*)-5-methyl-4-morpholino-2-oxo-5-(1-phenylprop-1-en-1-yl)-2,5-dihydrofuran-3-carbonitrile **4g**



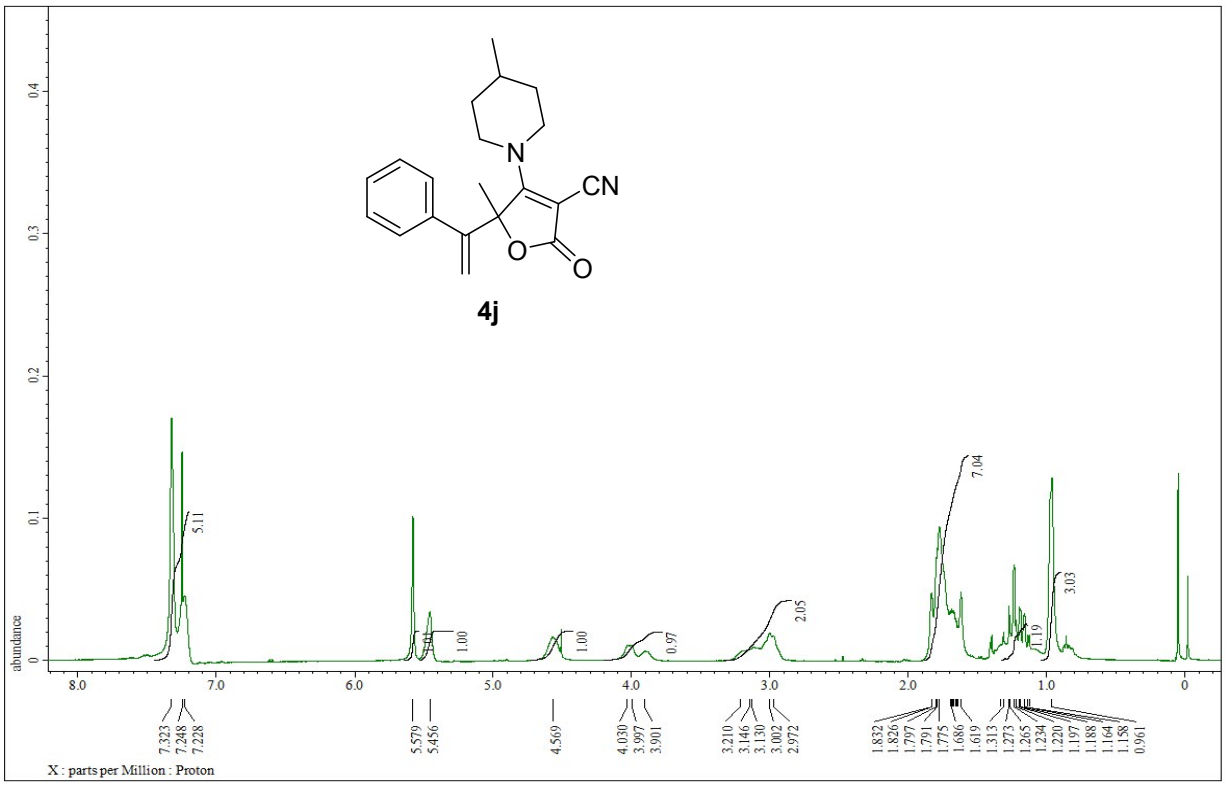


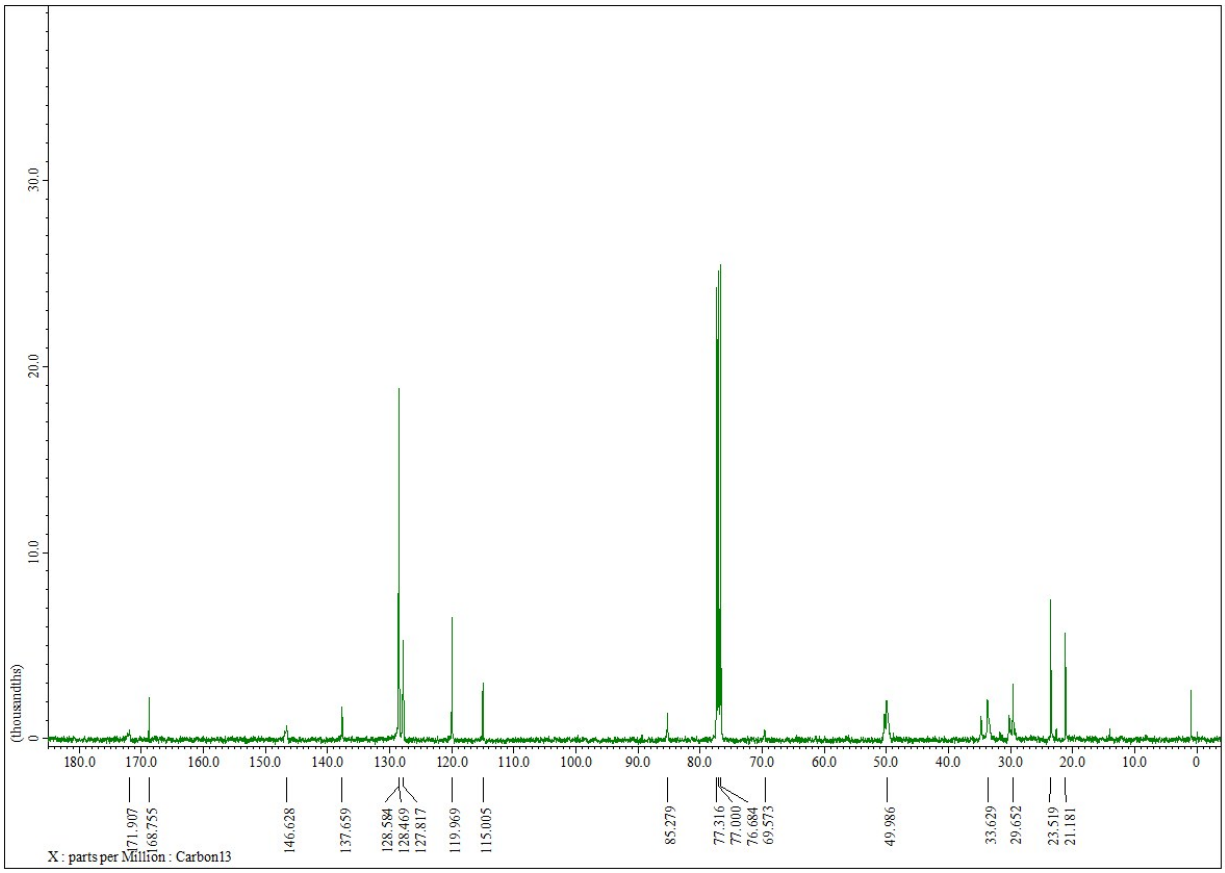
^{1}H and ^{13}C spectra of (*E*)-5-methyl-4-morpholino-2-oxo-5-(1-(*p*-tolyl)prop-1-en-1-yl)-2,5-dihydrofuran-3-carbonitrile **4h**



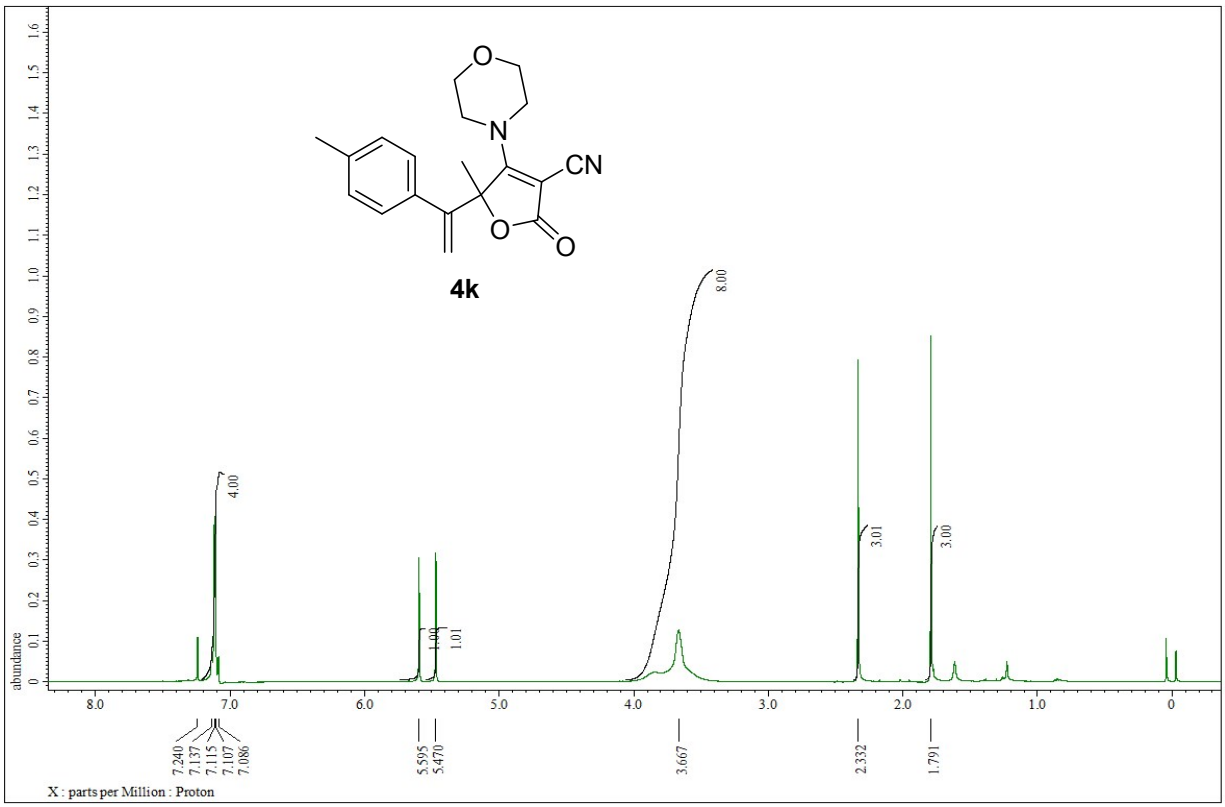


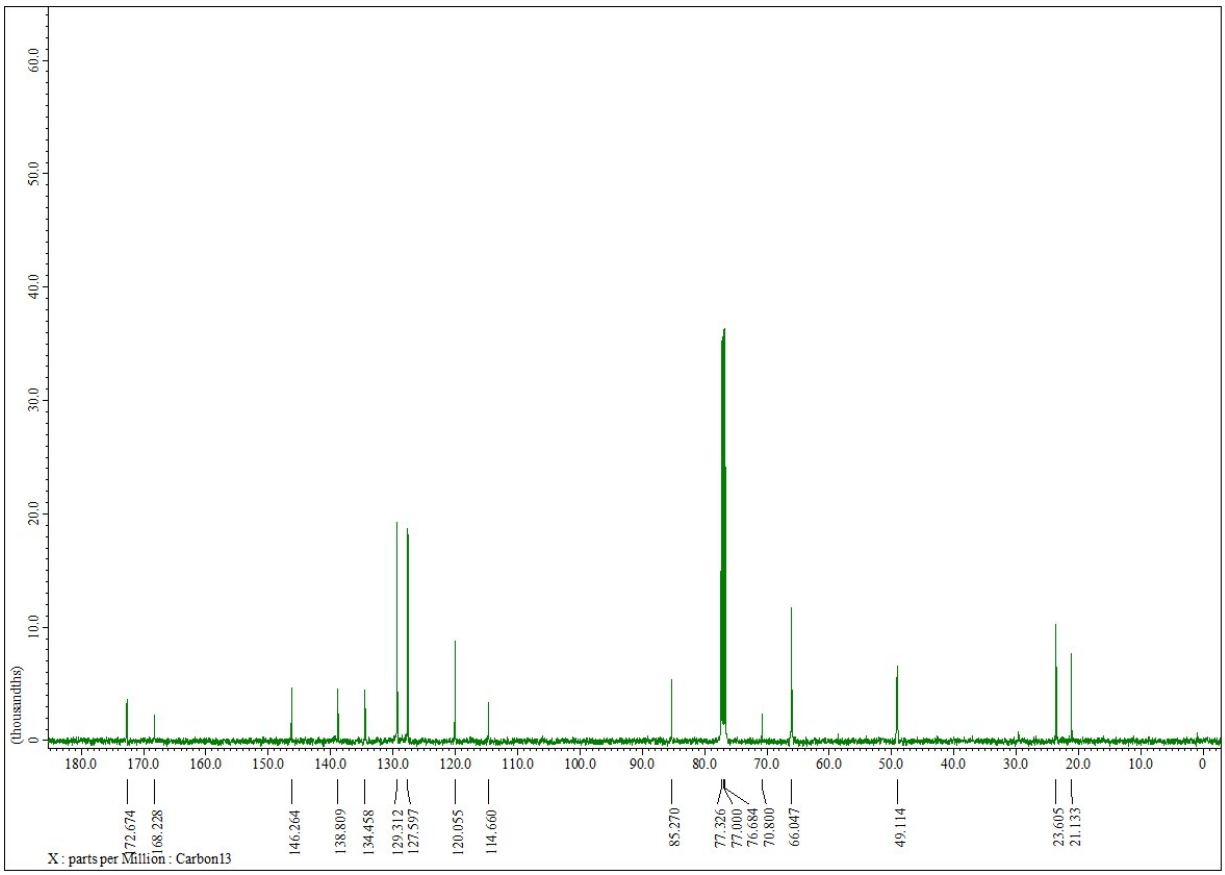
^{1}H and ^{13}C spectra of 5-methyl-2-oxo-4-(piperidin-1-yl)-5-(1-(*p*-tolyl)vinyl)-2,5-dihydrofuran-3-carbonitrile **4i**



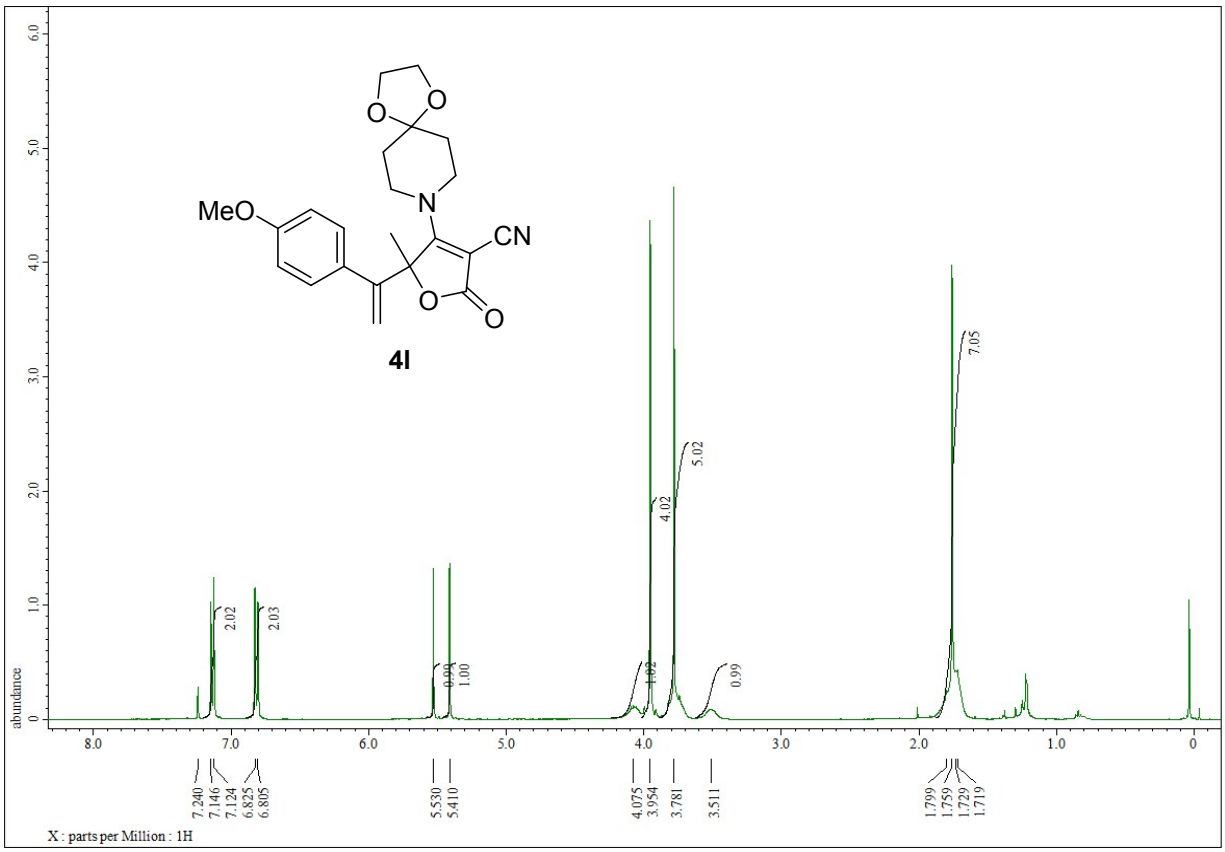


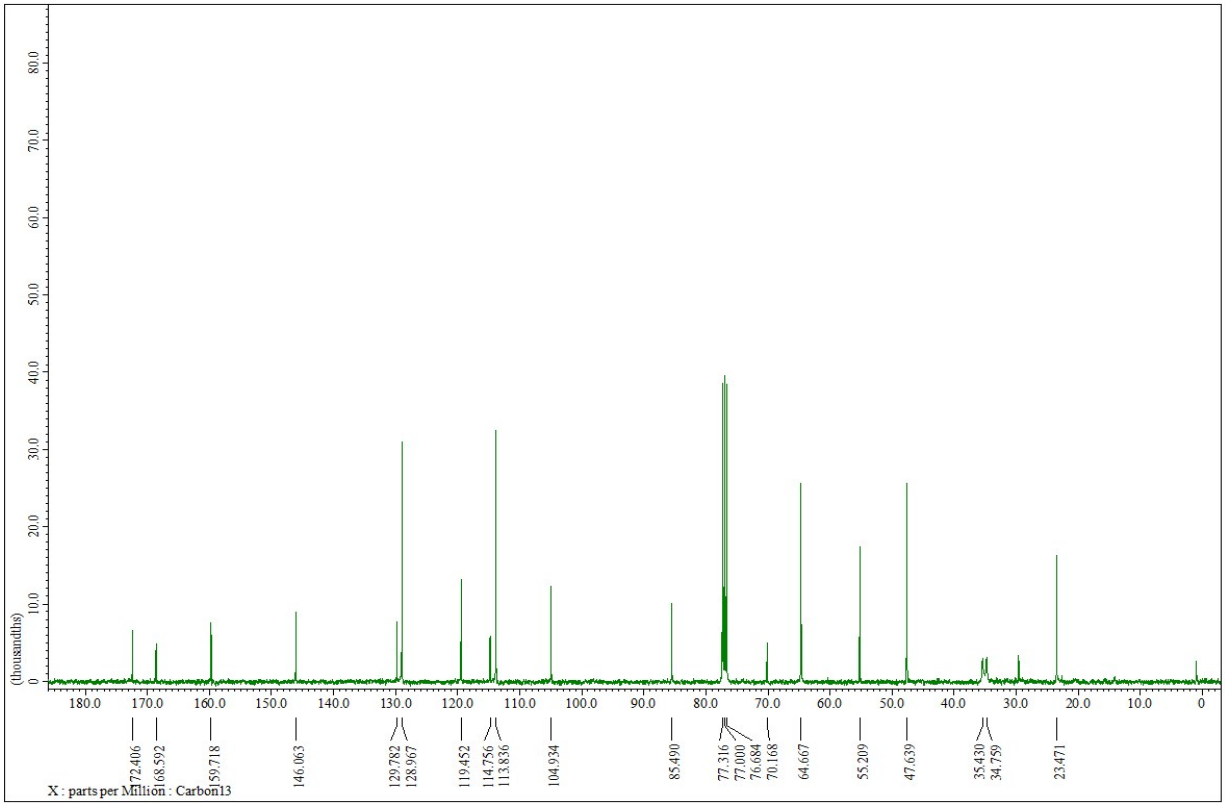
^{1}H and ^{13}C spectra of 5-methyl-4-(4-methylpiperidin-1-yl)-2-oxo-5-(1-phenylvinyl)-2,5-dihydrofuran-3-carbonitrile **4j**



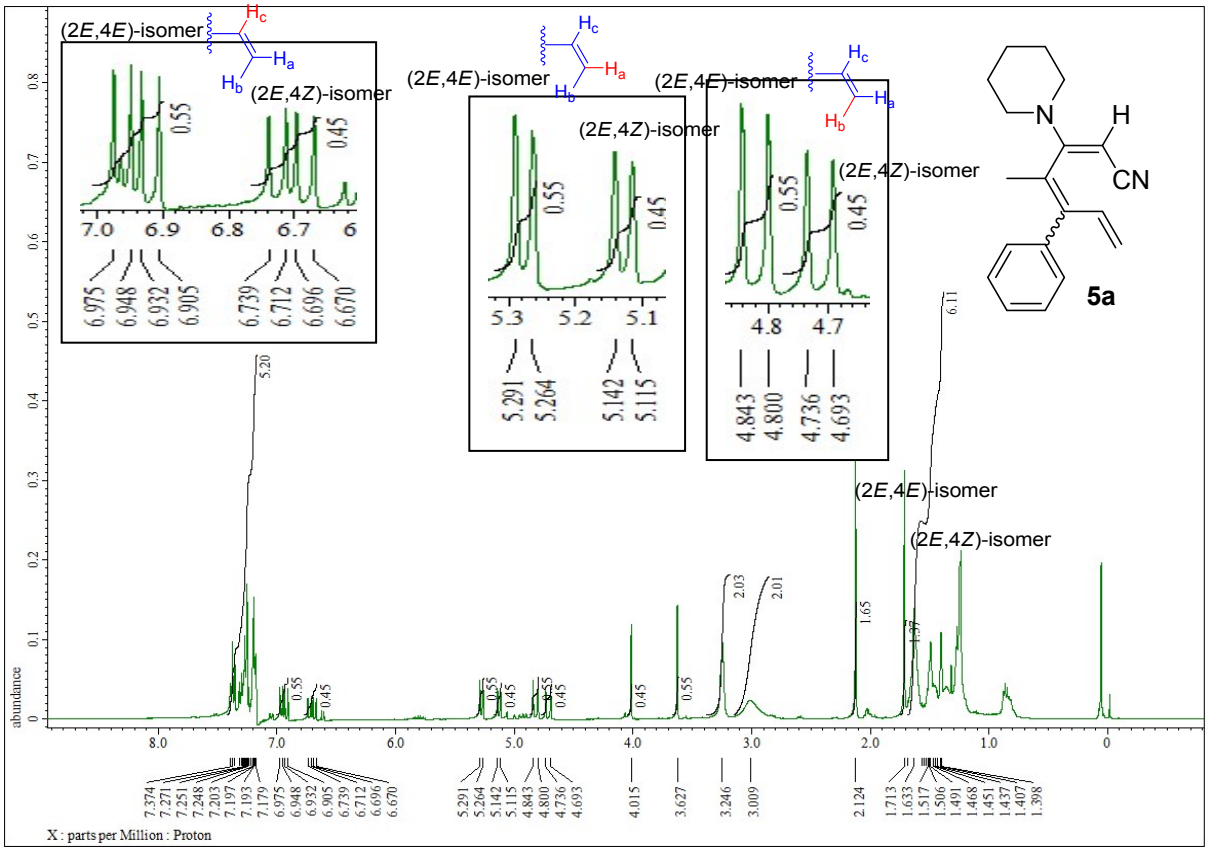


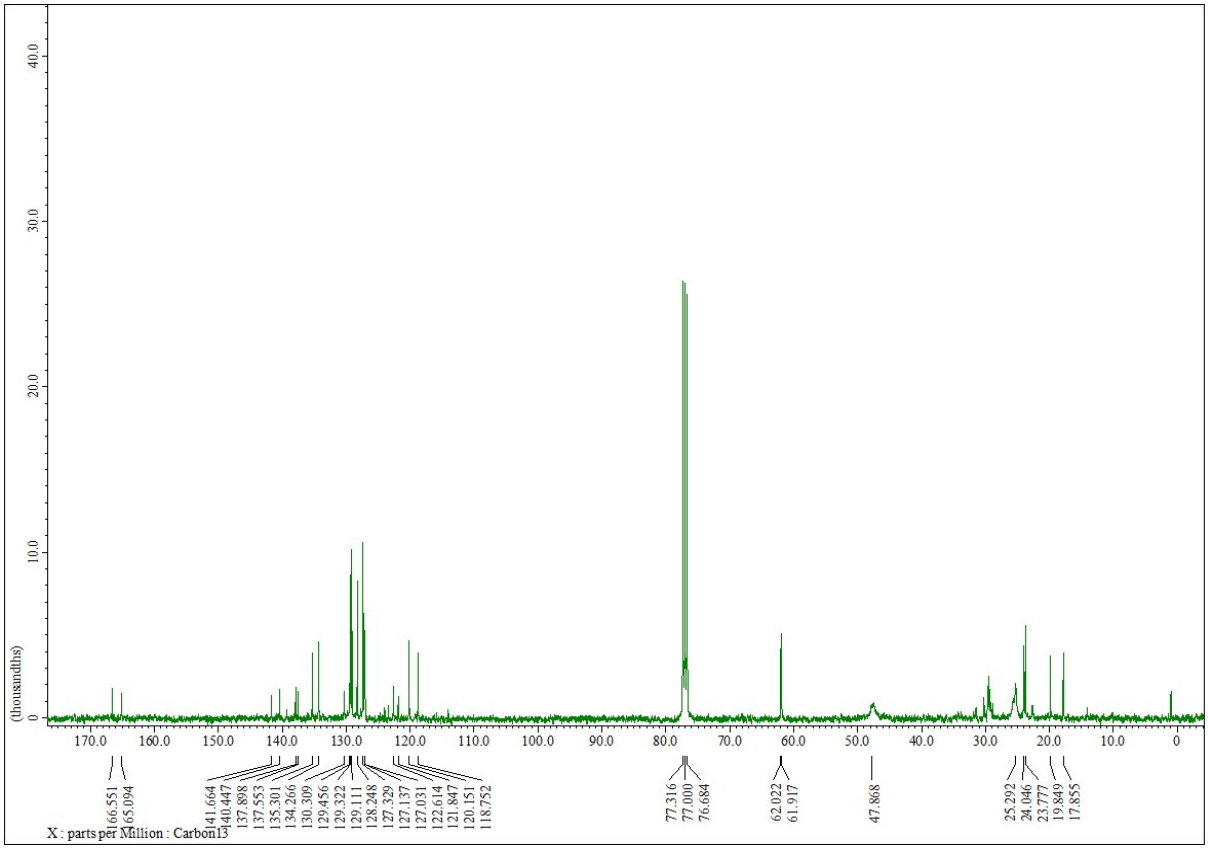
^{1}H and ^{13}C spectra of 5-methyl-4-morpholino-2-oxo-5-(1-(*p*-tolyl)vinyl)-2,5-dihydrofuran-3-carbonitrile **4k**



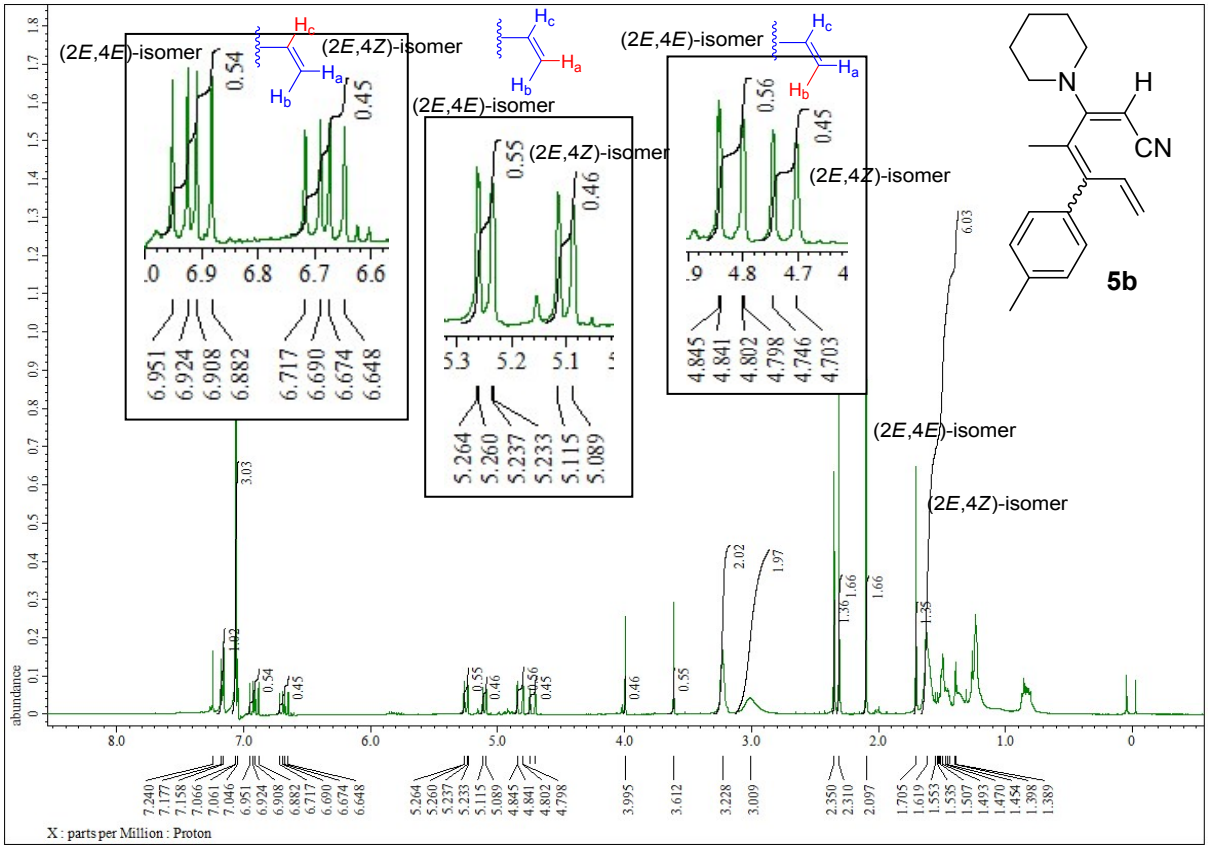


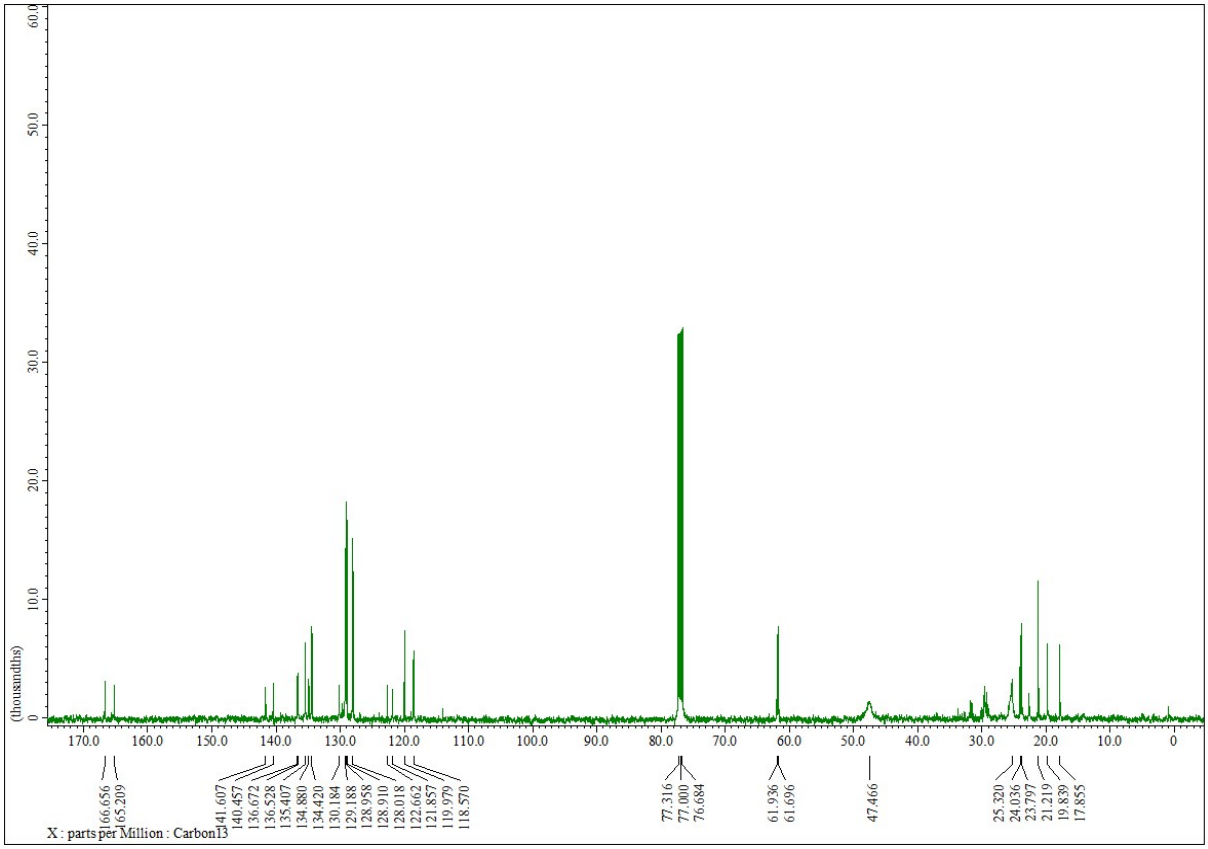
^{1}H and ^{13}C spectra of 5-(1-(4-methoxyphenyl)vinyl)-5-methyl-2-oxo-4-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-2,5-dihydrofuran-3-carbonitrile **4l**



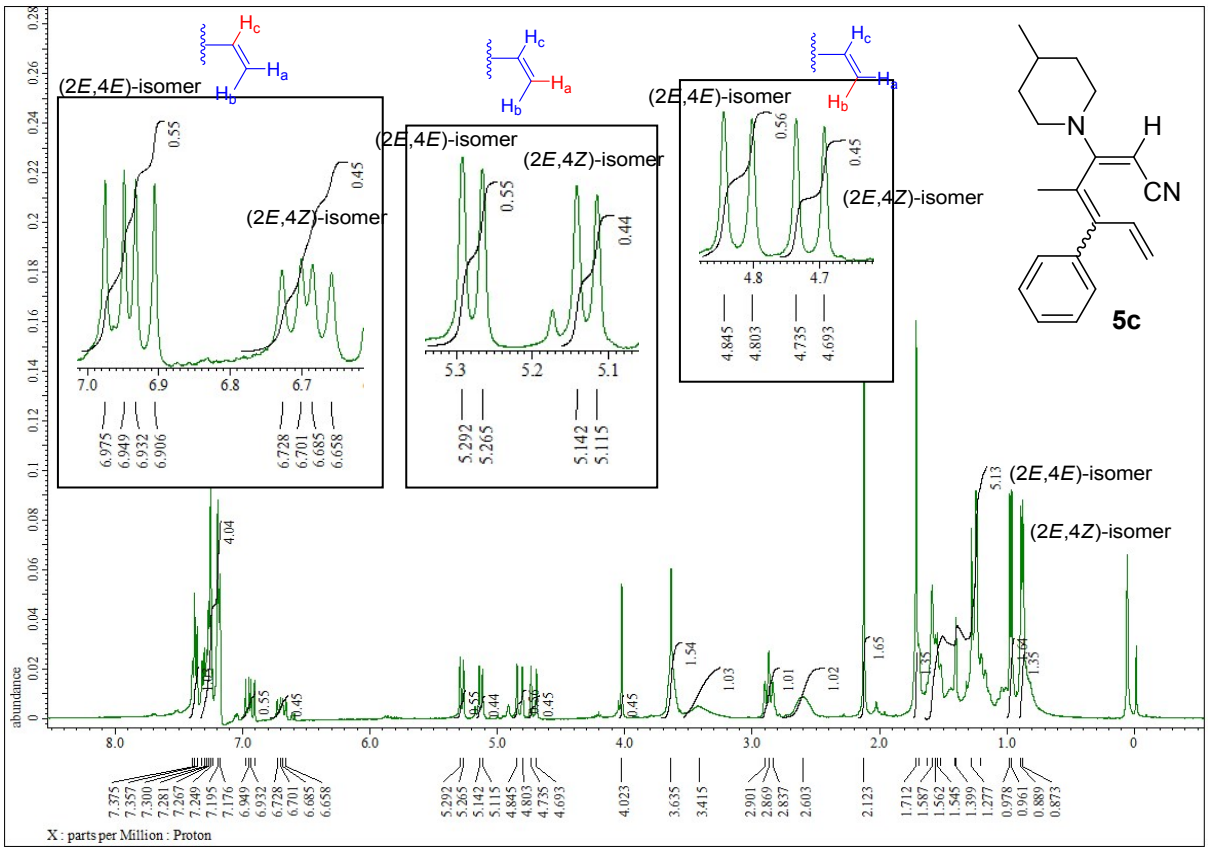


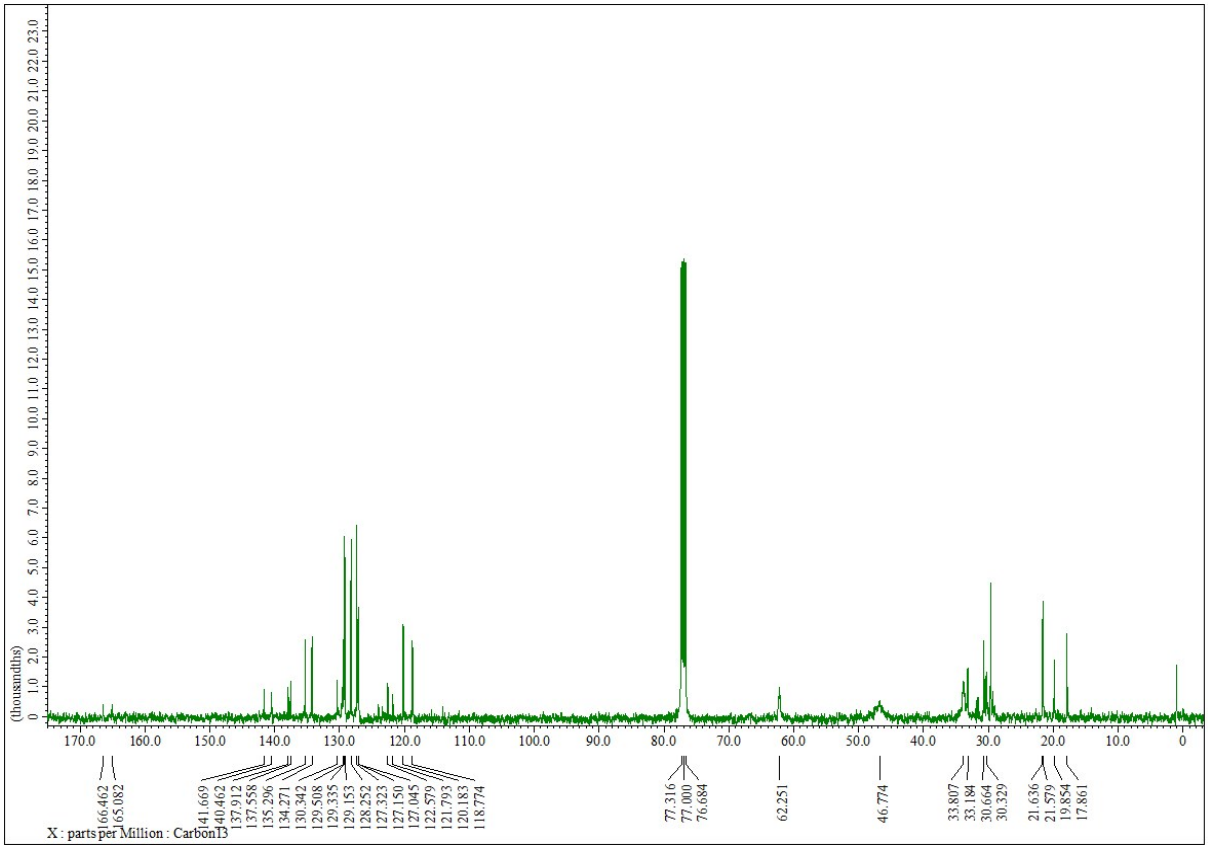
^{1}H and ^{13}C spectra of (2*E*)-4-methyl-5-phenyl-3-(piperidin-1-yl)hepta-2,4,6-trienenitrile **5a**



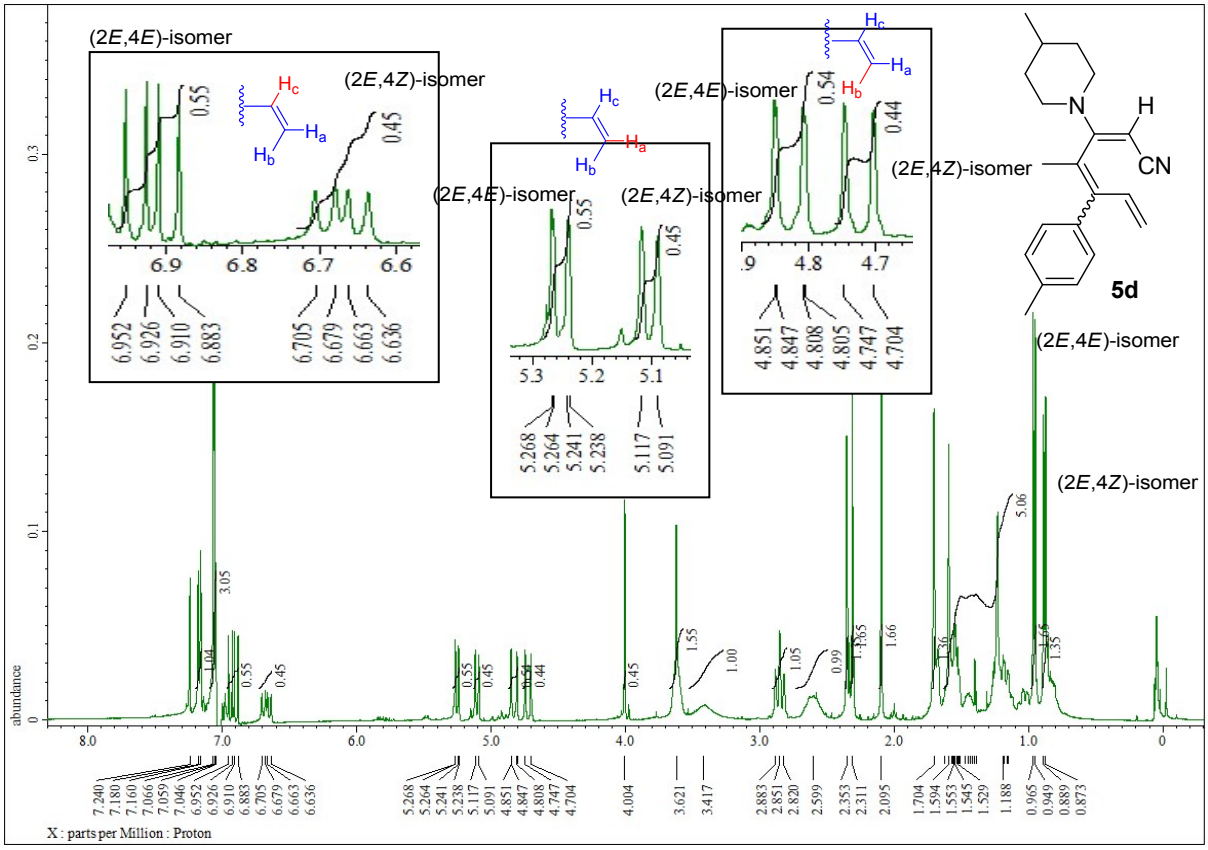


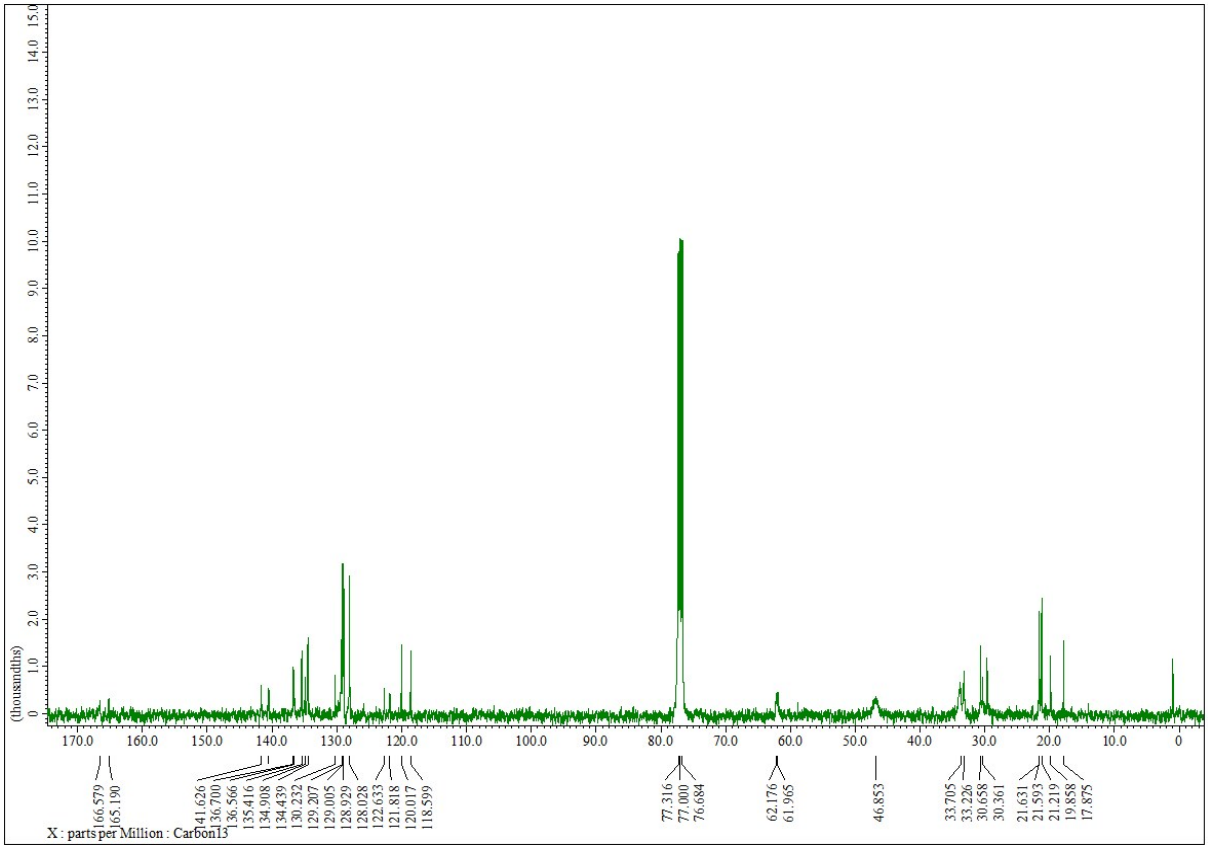
^{1}H and ^{13}C spectra of (2*E*)-4-methyl-3-(piperidin-1-yl)-5-(p-tolyl)hepta-2,4,6-trienenitrile **5b**



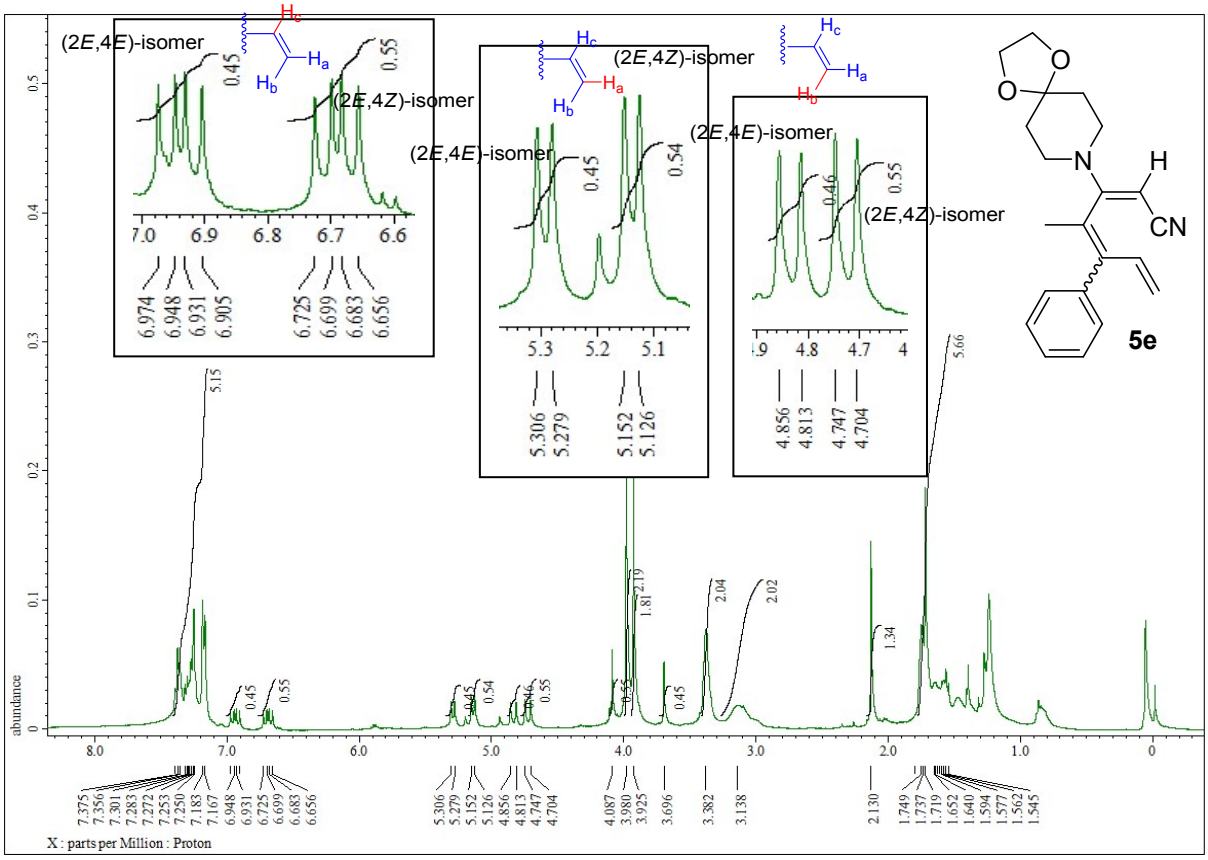


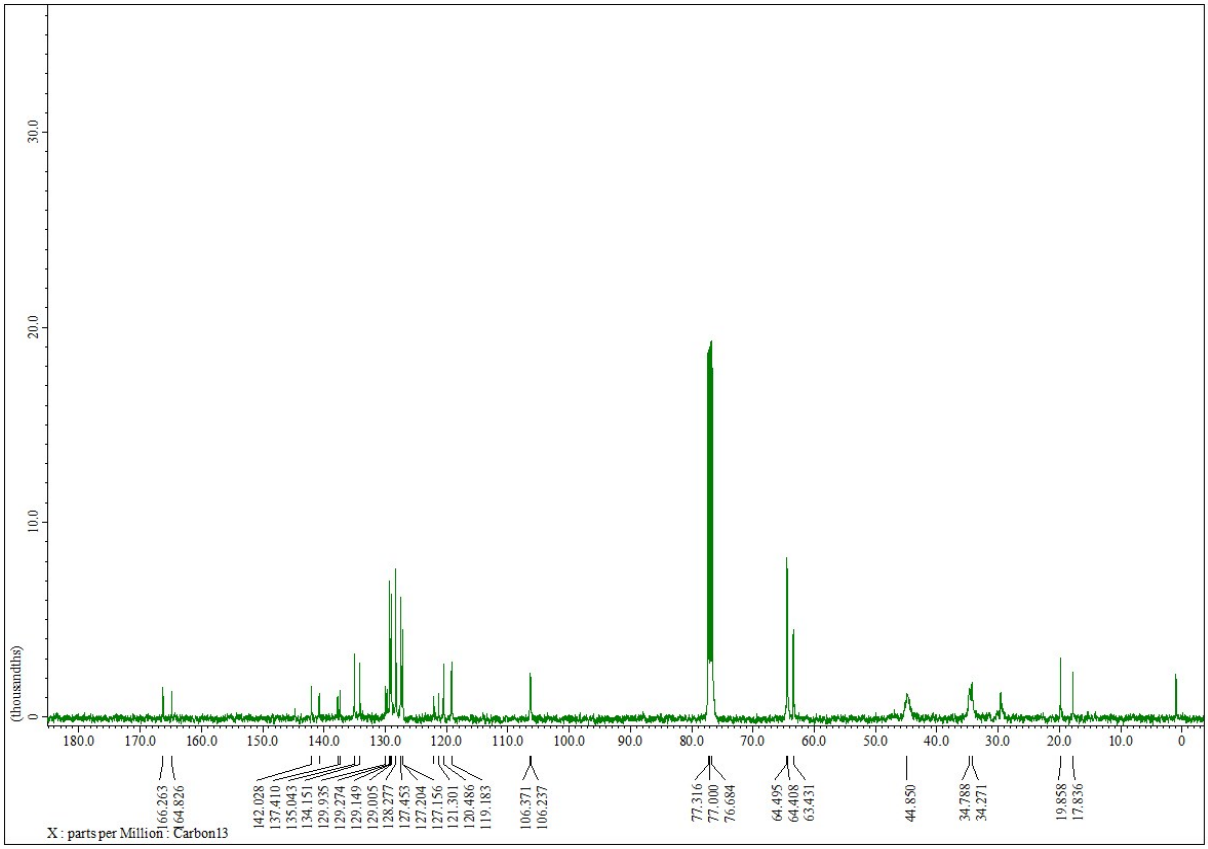
^{1}H and ^{13}C spectra of (2*E*)-4-methyl-3-(4-methylpiperidin-1-yl)-5-phenylhepta-2,4,6-trienenitrile **5c**



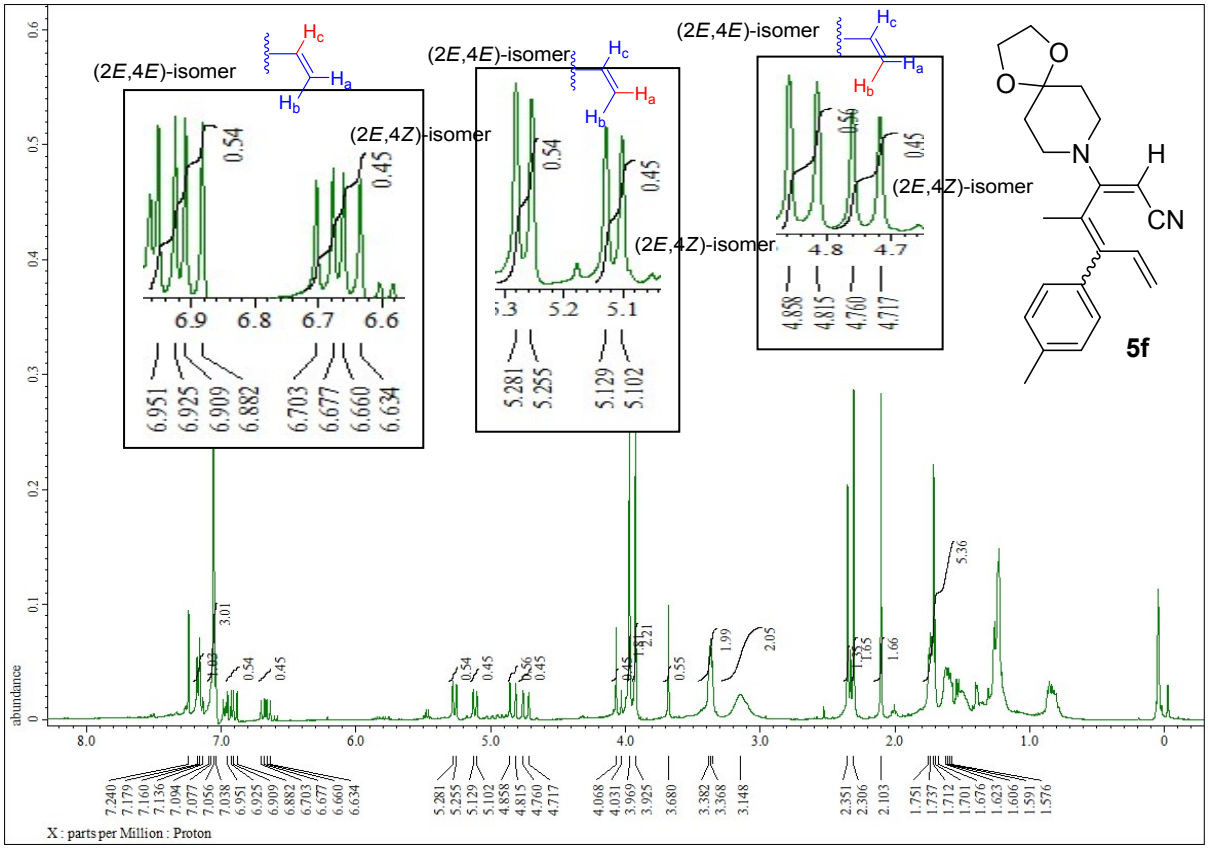


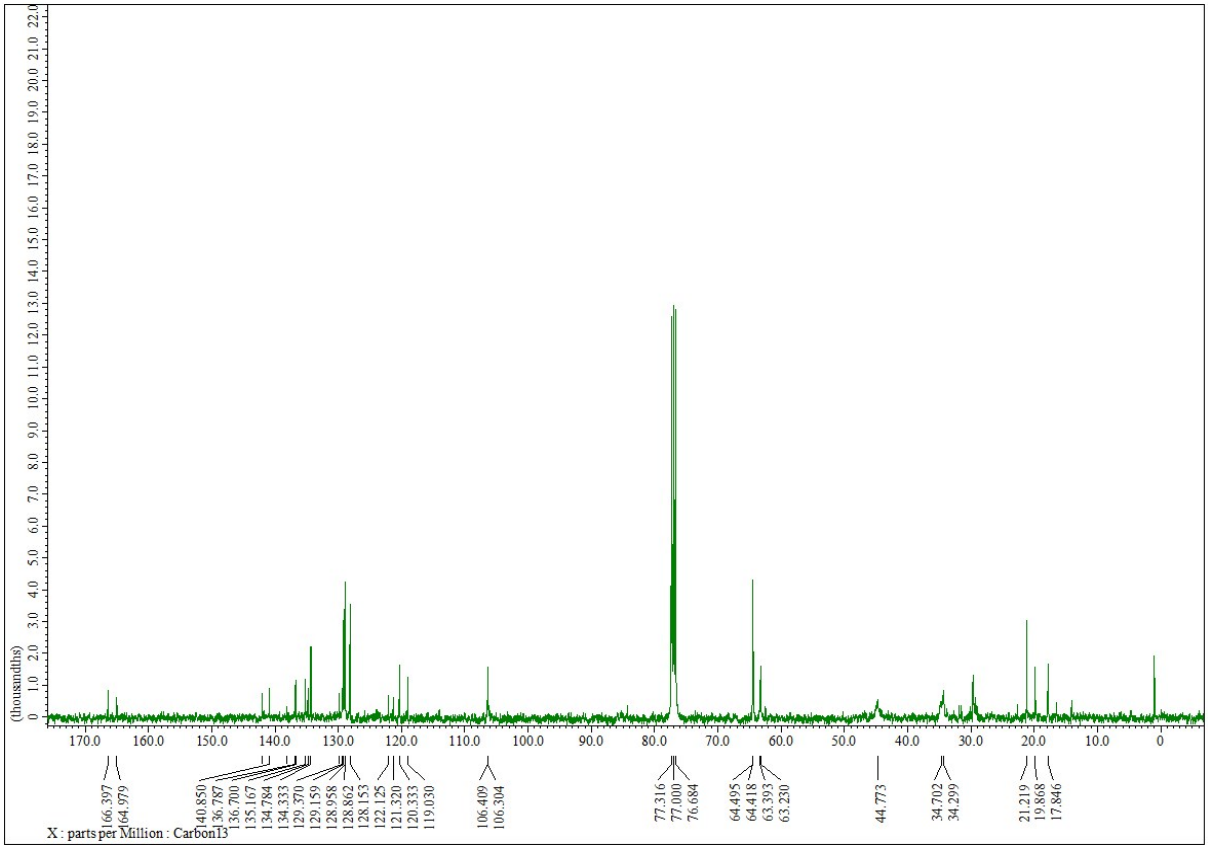
^{1}H and ^{13}C spectra of (2*E*)-4-methyl-3-(4-methylpiperidin-1-yl)-5-(*p*-tolyl)hepta-2,4,6-trienenitrile **5d**



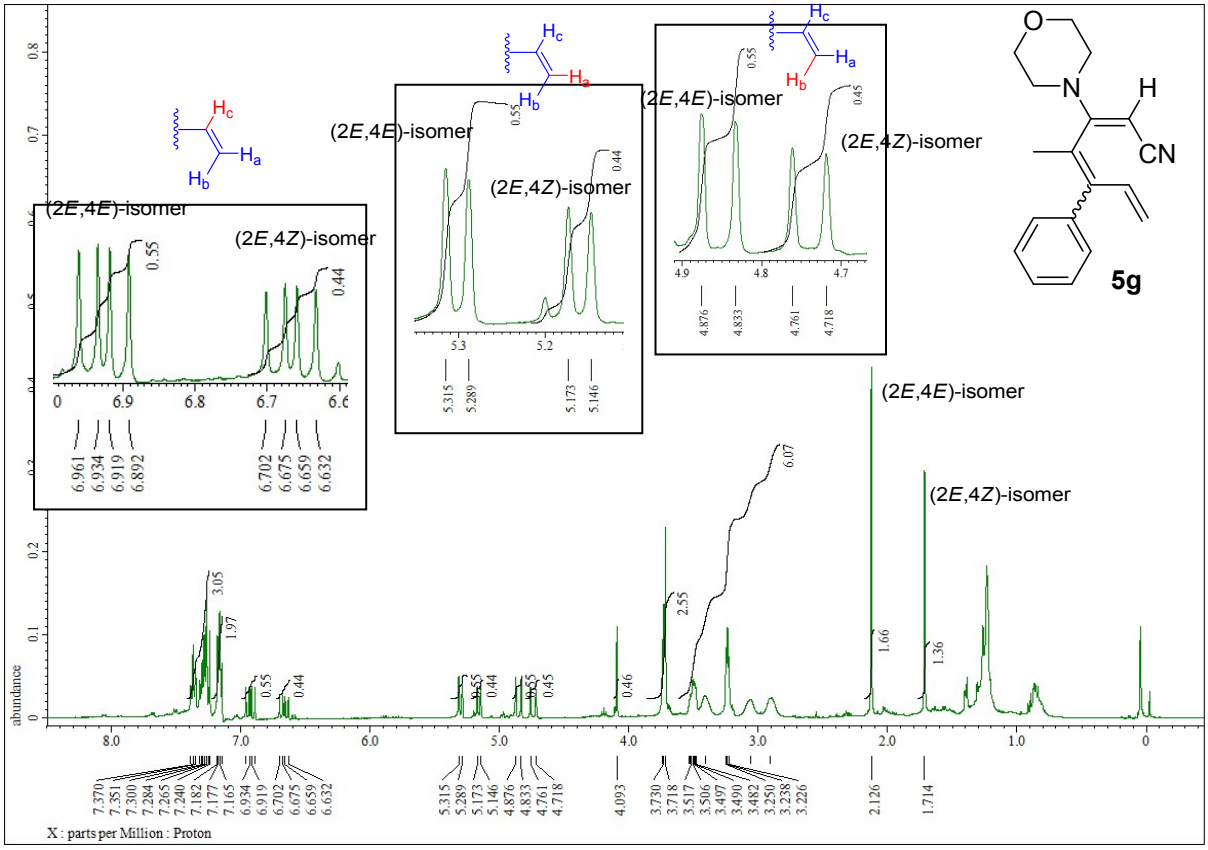


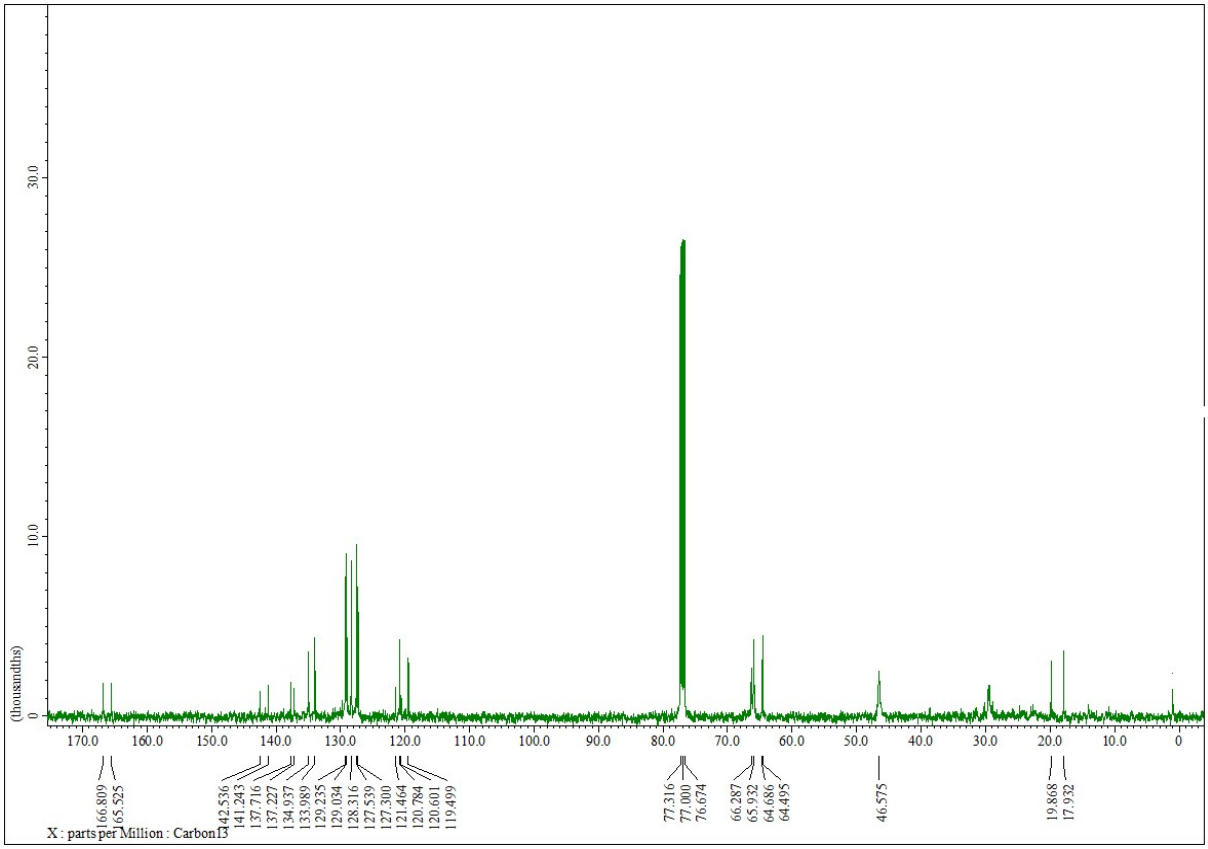
^{1}H and ^{13}C spectra of (2*E*)-4-methyl-5-phenyl-3-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)hepta-2,4,6-trienenitrile **5e**



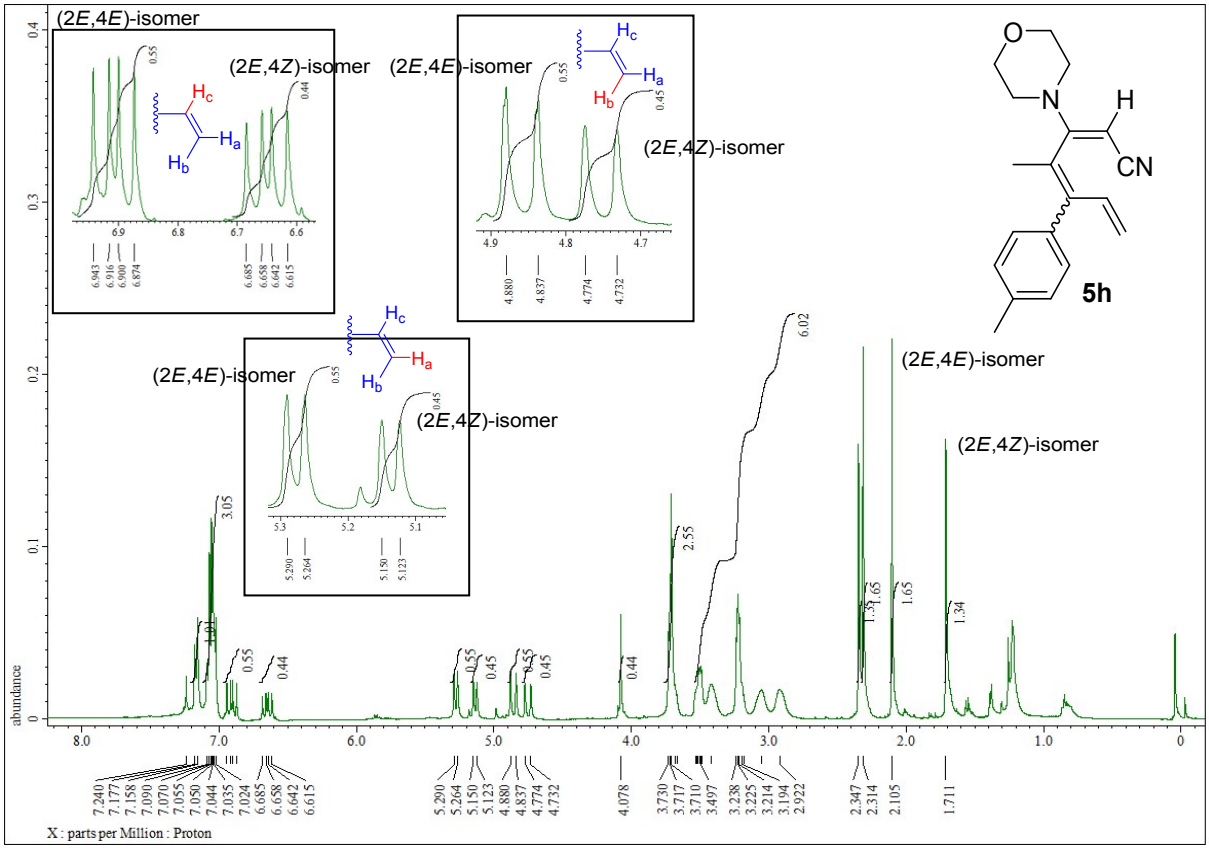


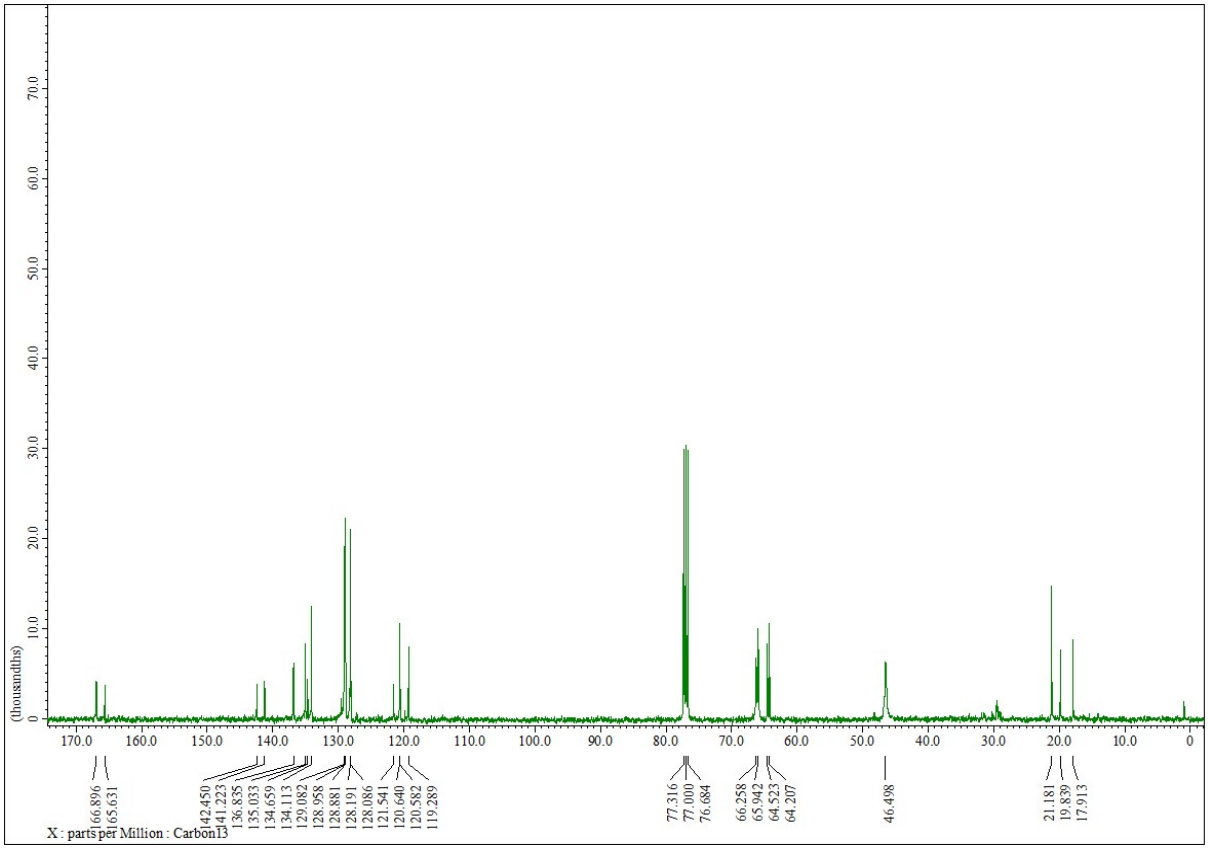
^{1}H and ^{13}C spectra of (2*E*)-4-methyl-3-(1,4-dioxa-8-azaspiro[4.5]decan-8-yl)-5-(*p*-tolyl)hepta-2,4,6-trienenitrile **5f**





^{1}H and ^{13}C spectra of (2*E*)-4-methyl-3-morpholino-5-phenylhepta-2,4,6-trienenitrile **5g**





^{1}H and ^{13}C spectra of (2*E*)-4-methyl-3-morpholino-5-(*p*-tolyl)hepta-2,4,6-trienenitrile **5h**