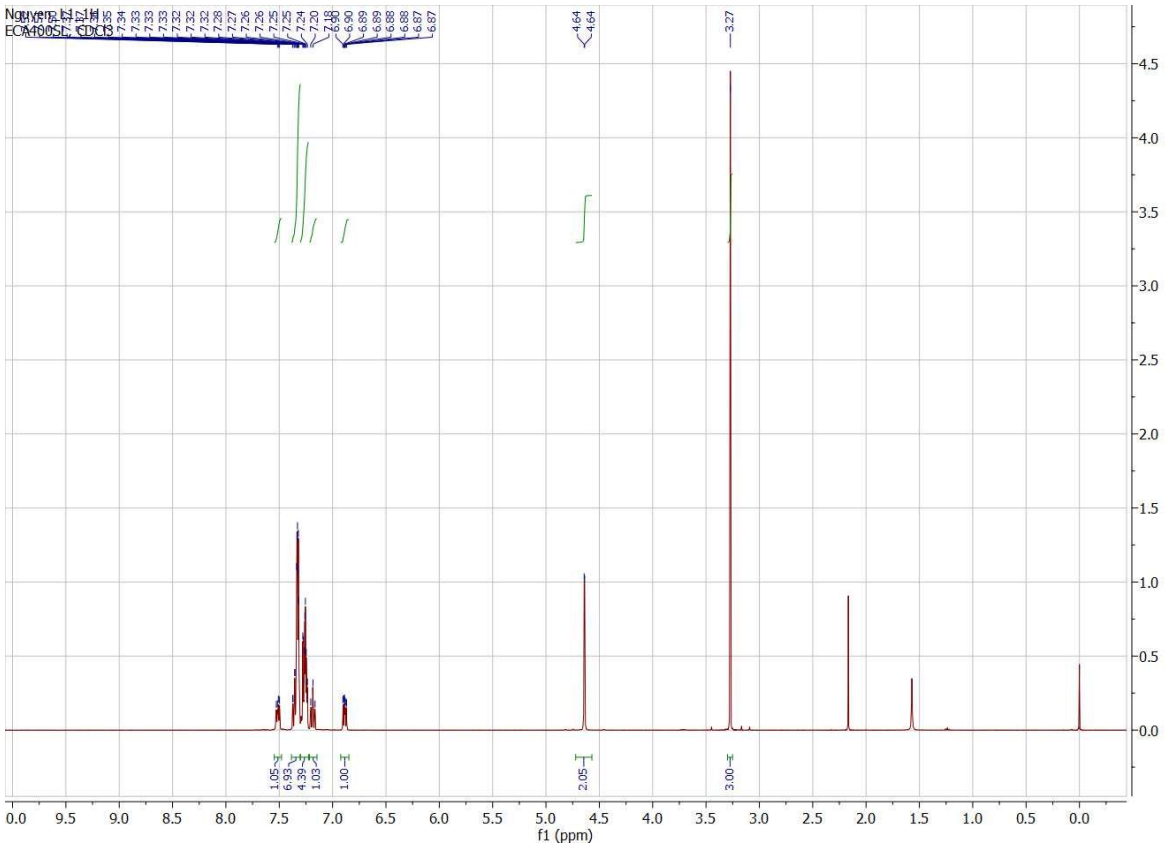
Stereocontrol in the synthesis of cyclic amino acids: a new ligand for directed hydrogenation through hydrogen bonding

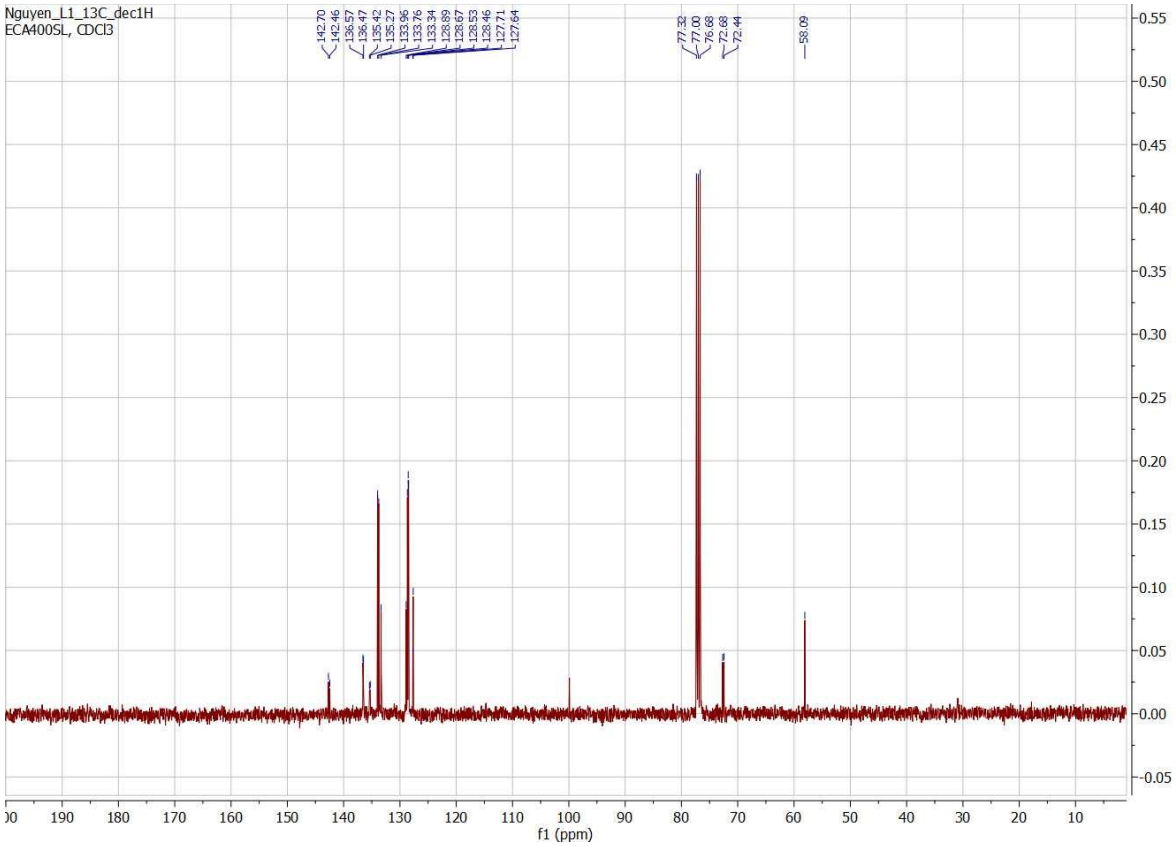
Vasudeva Rao Gandi, Bao Nguyen Do Doan,
Sivarajan Kasinathan, Roderick W. Bates*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences,
Nanyang Technological University, 21 Nanyang Link, Singapore 637371
FAX +65 6791 1961 e-mail: roderick@ntu.edu.sg

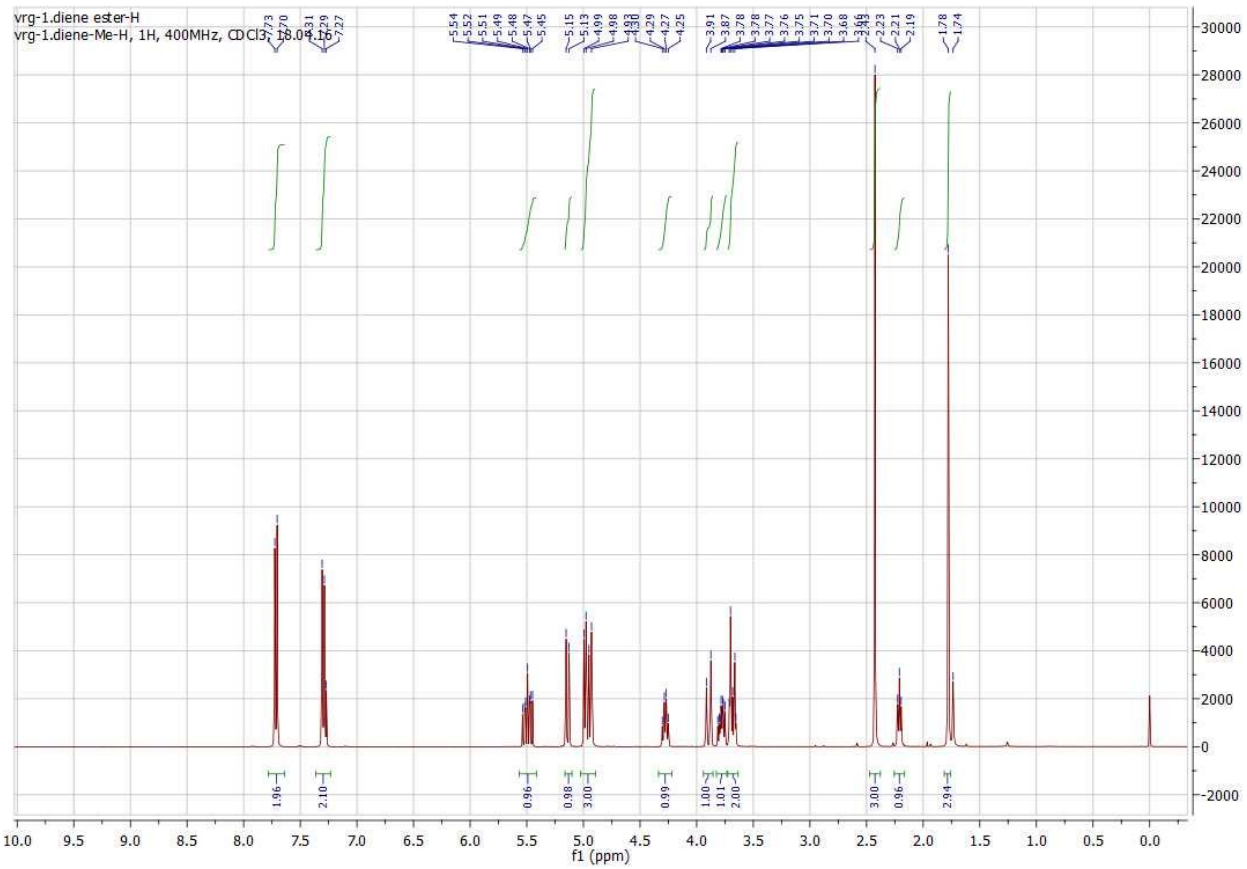
^{1}H and ^{13}C{1H} NMR spectra

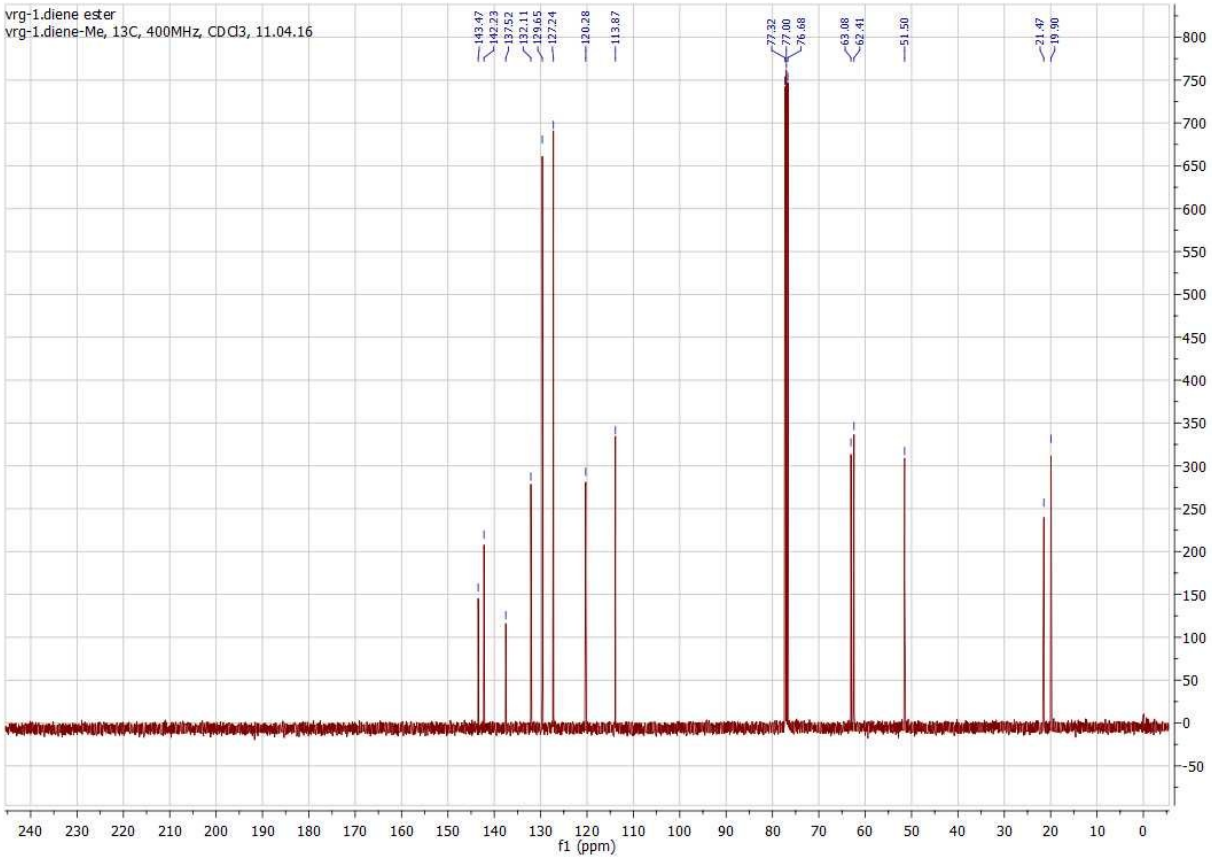
X-ray structures and data



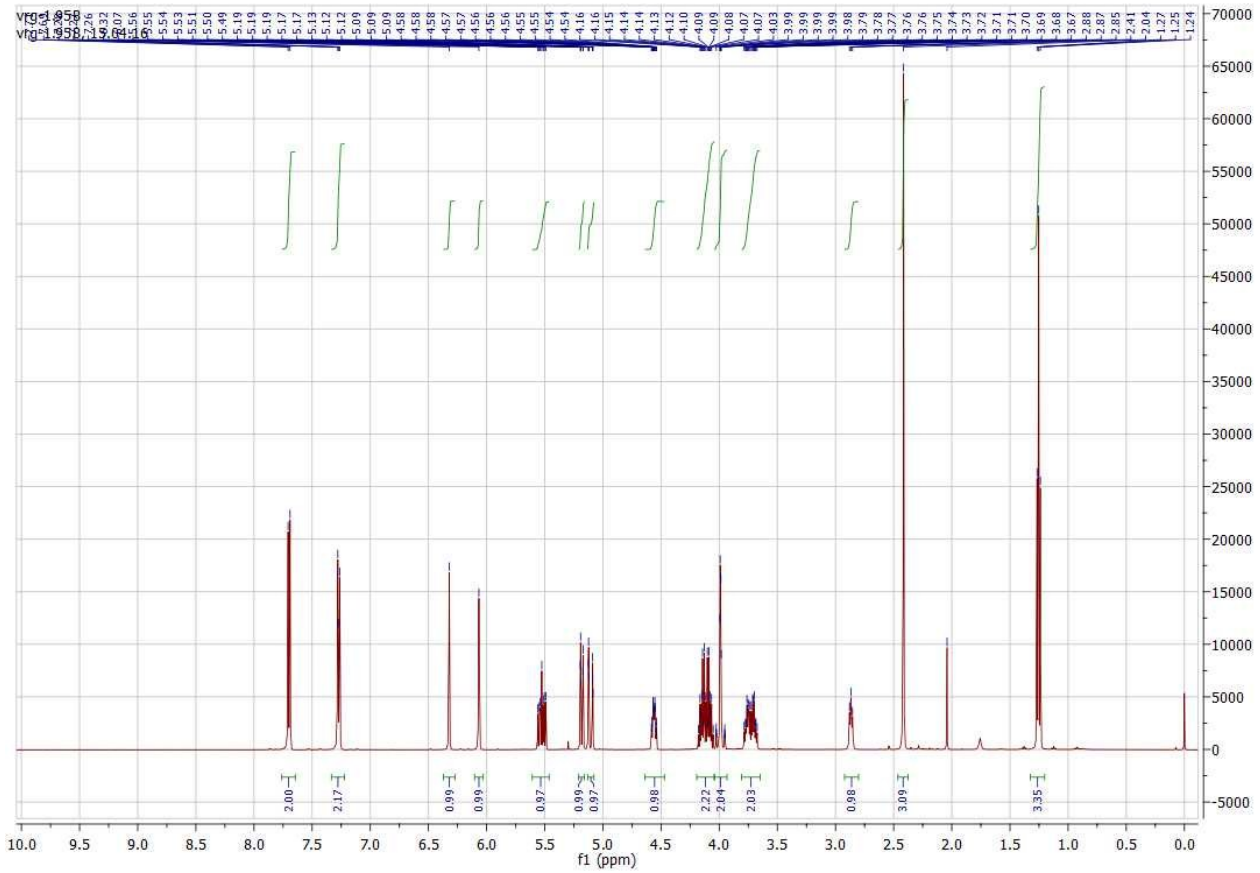


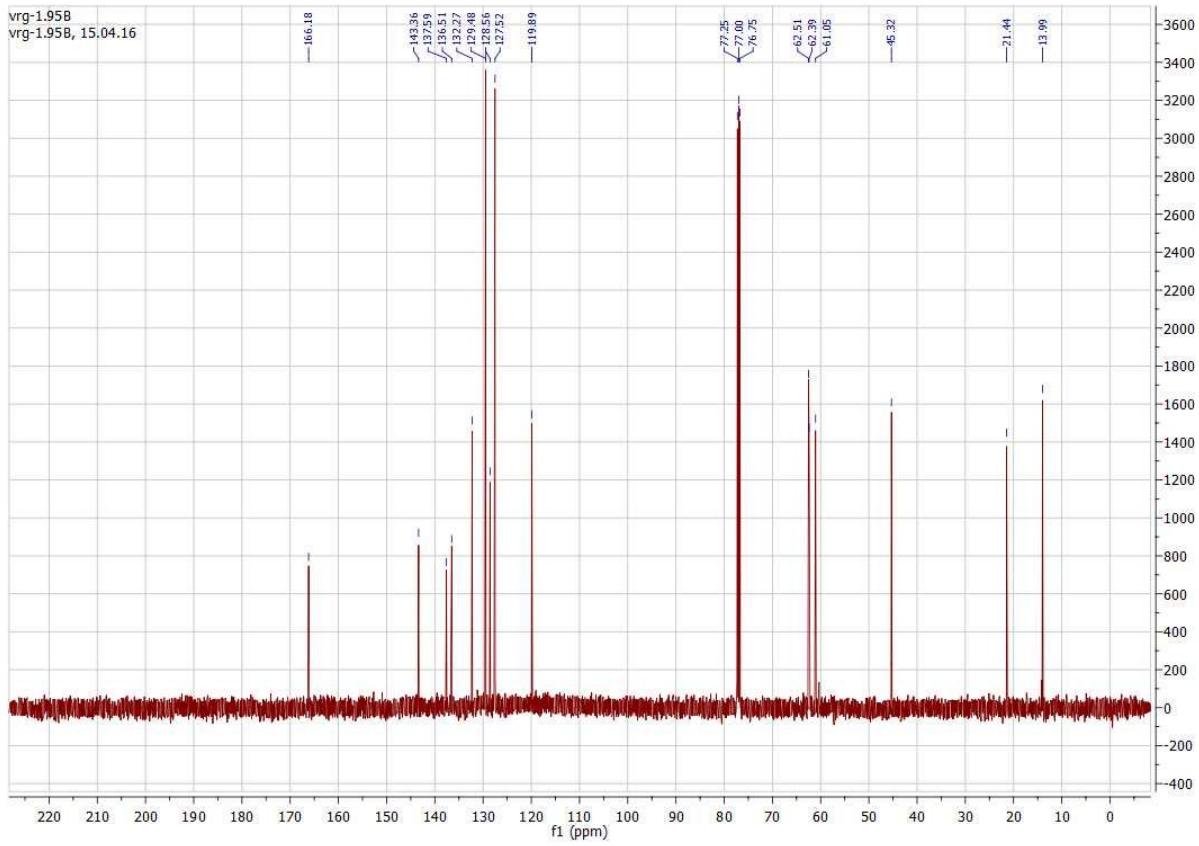
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of ligand **6**



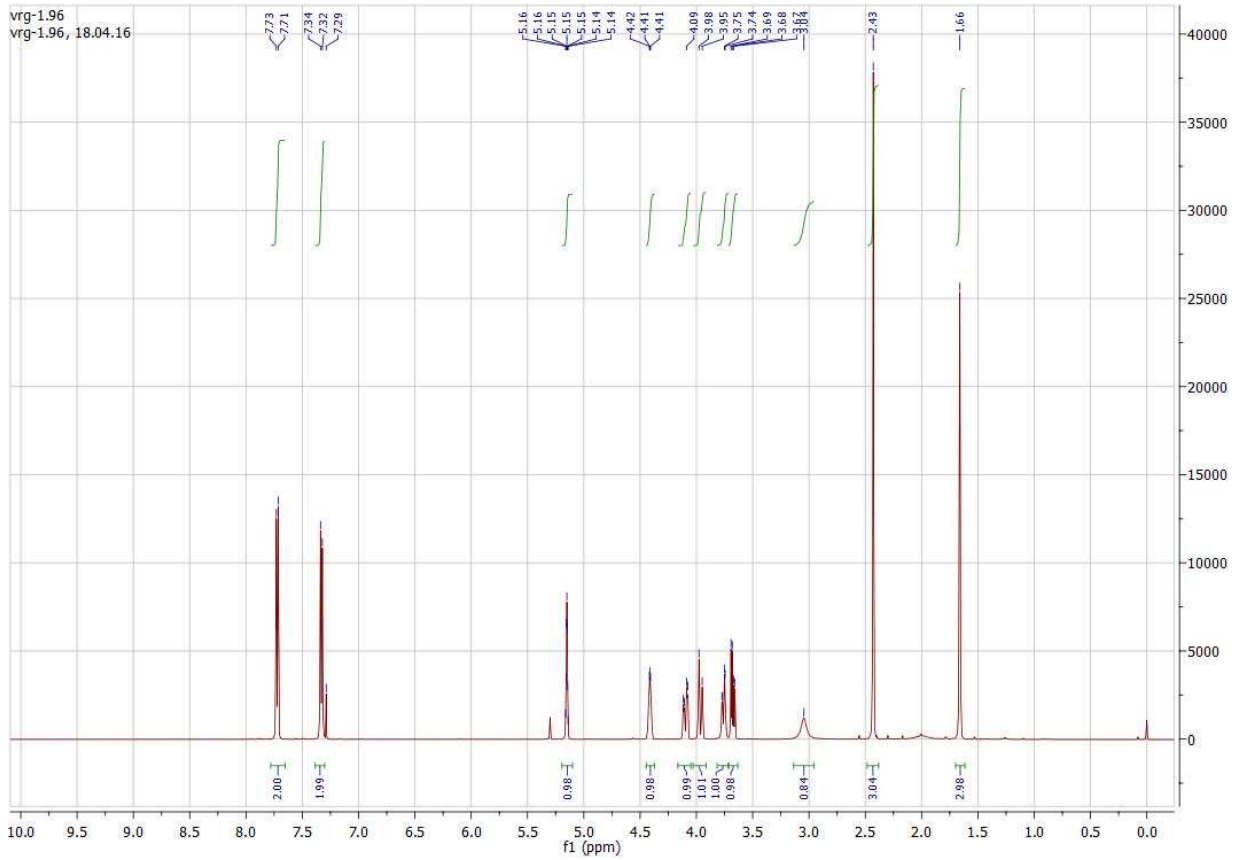


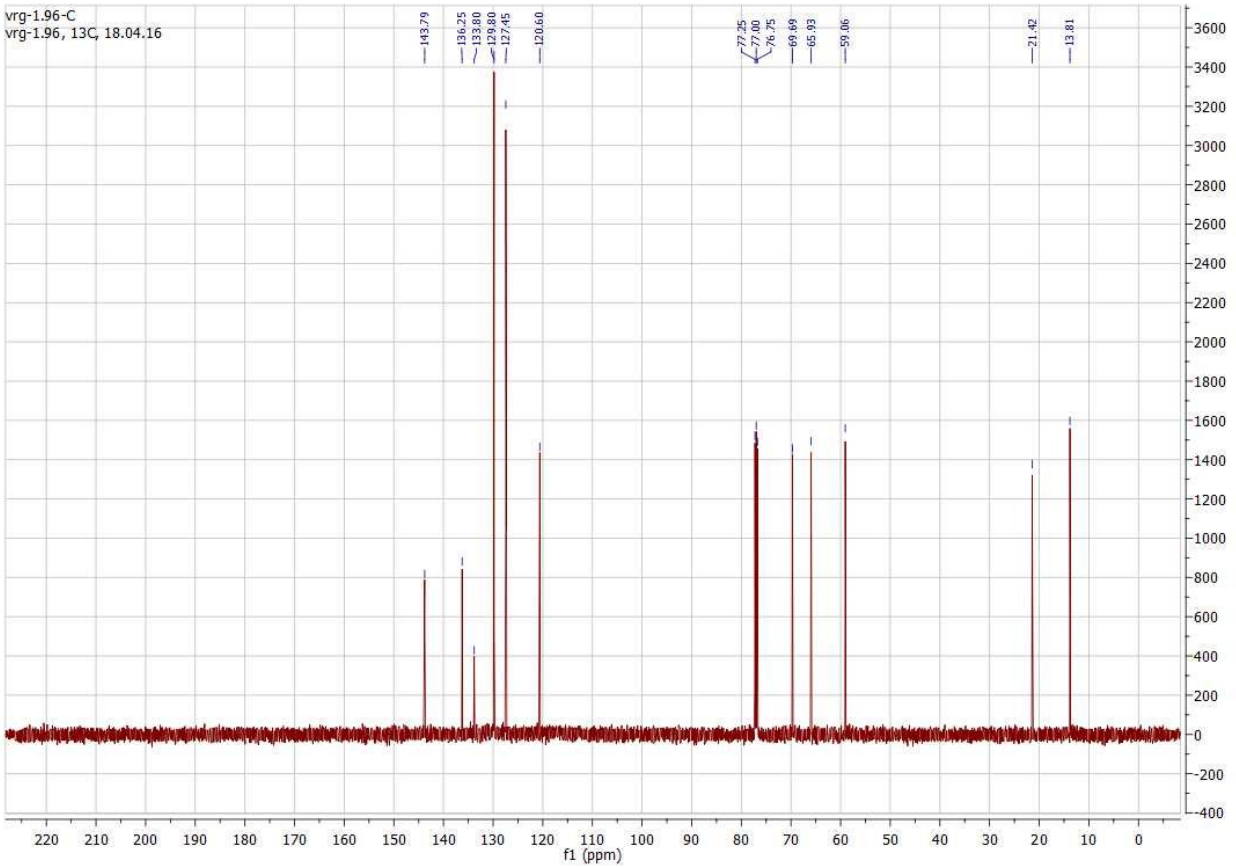
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **9a**



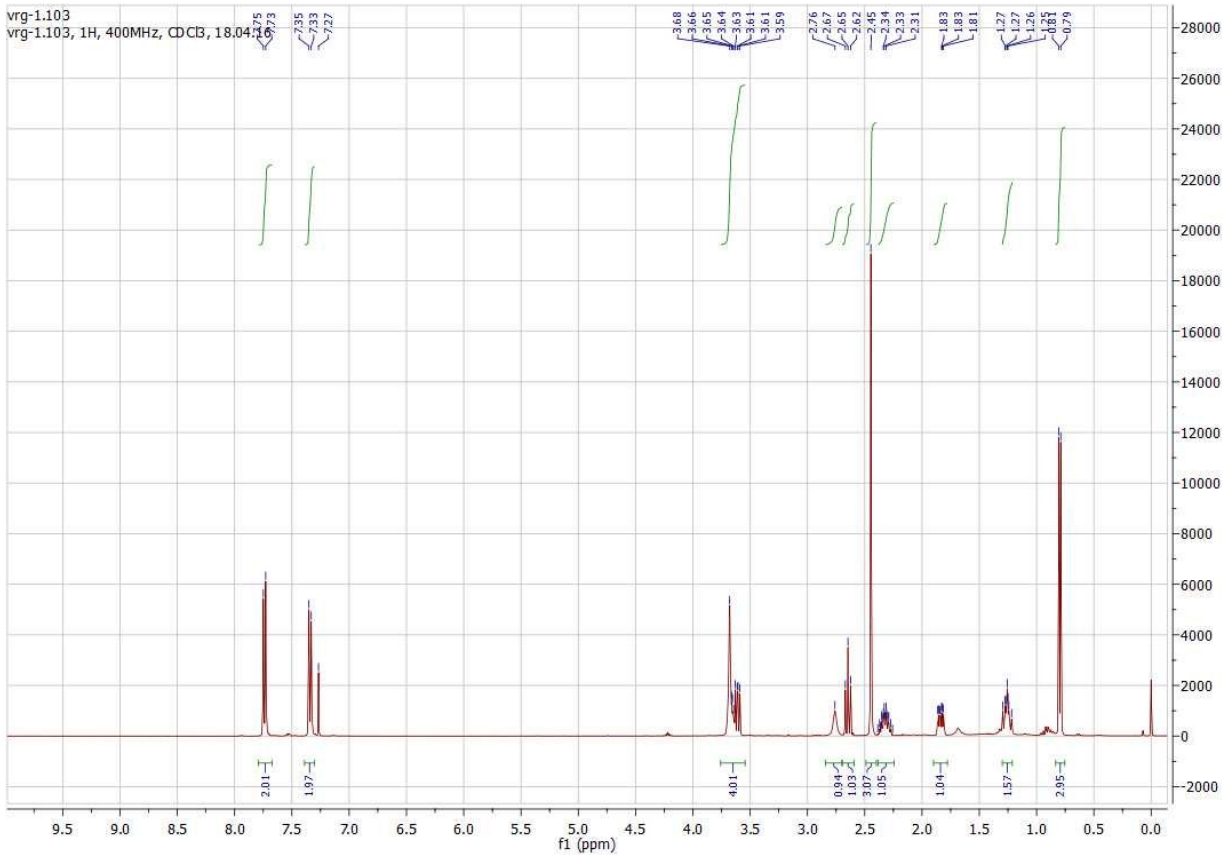


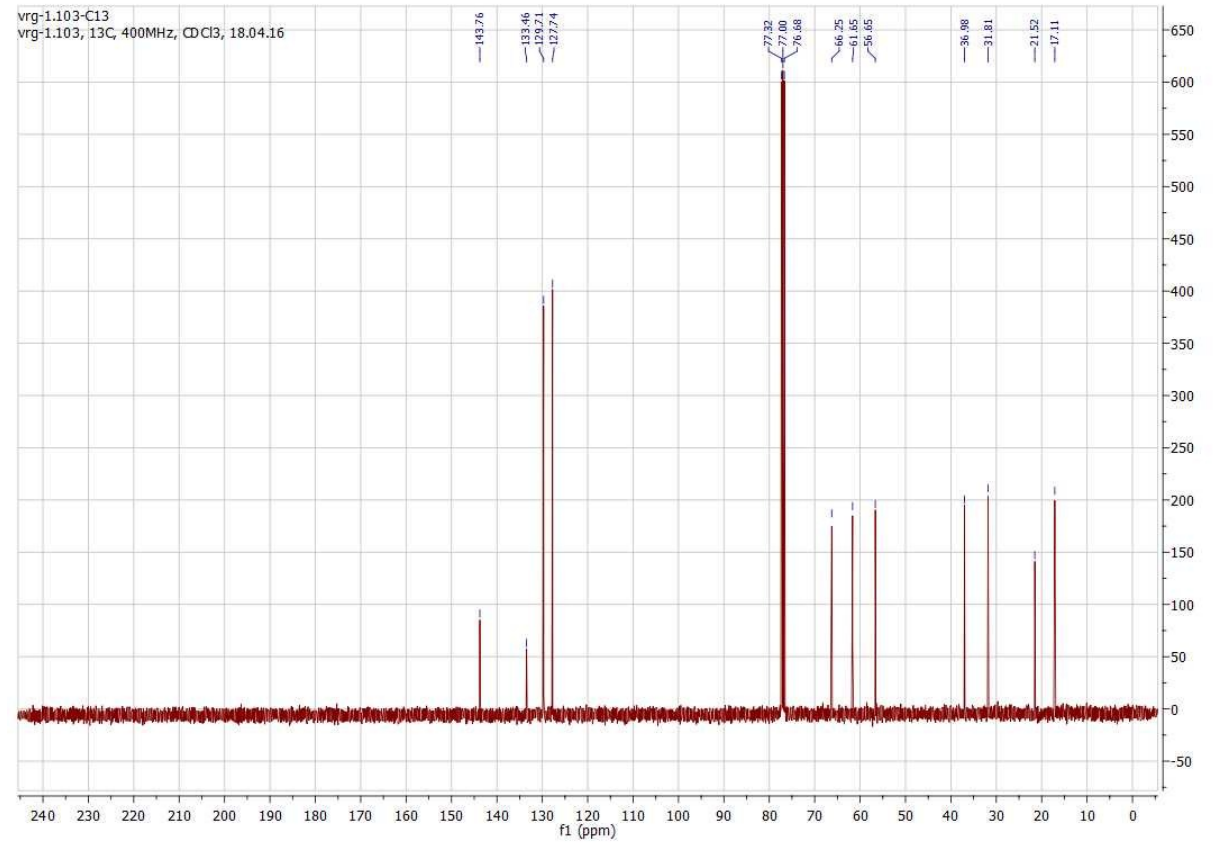
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **9b**



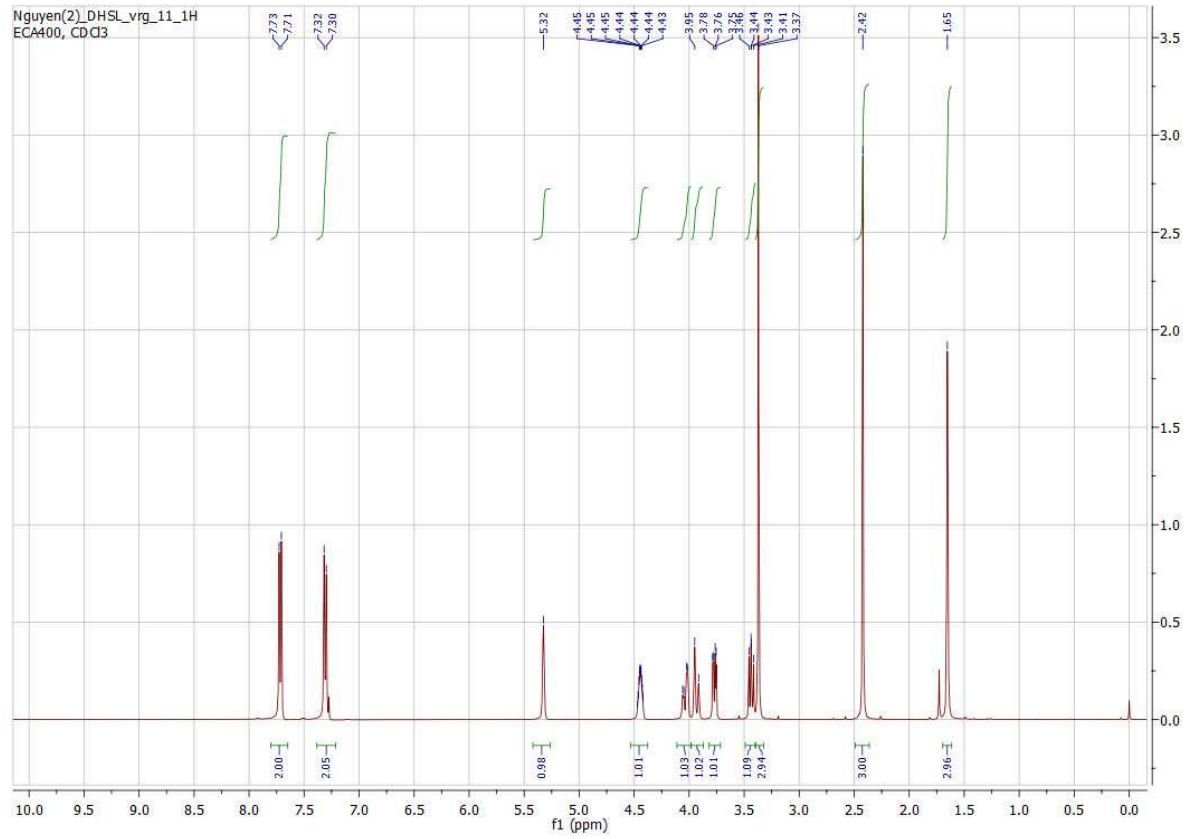


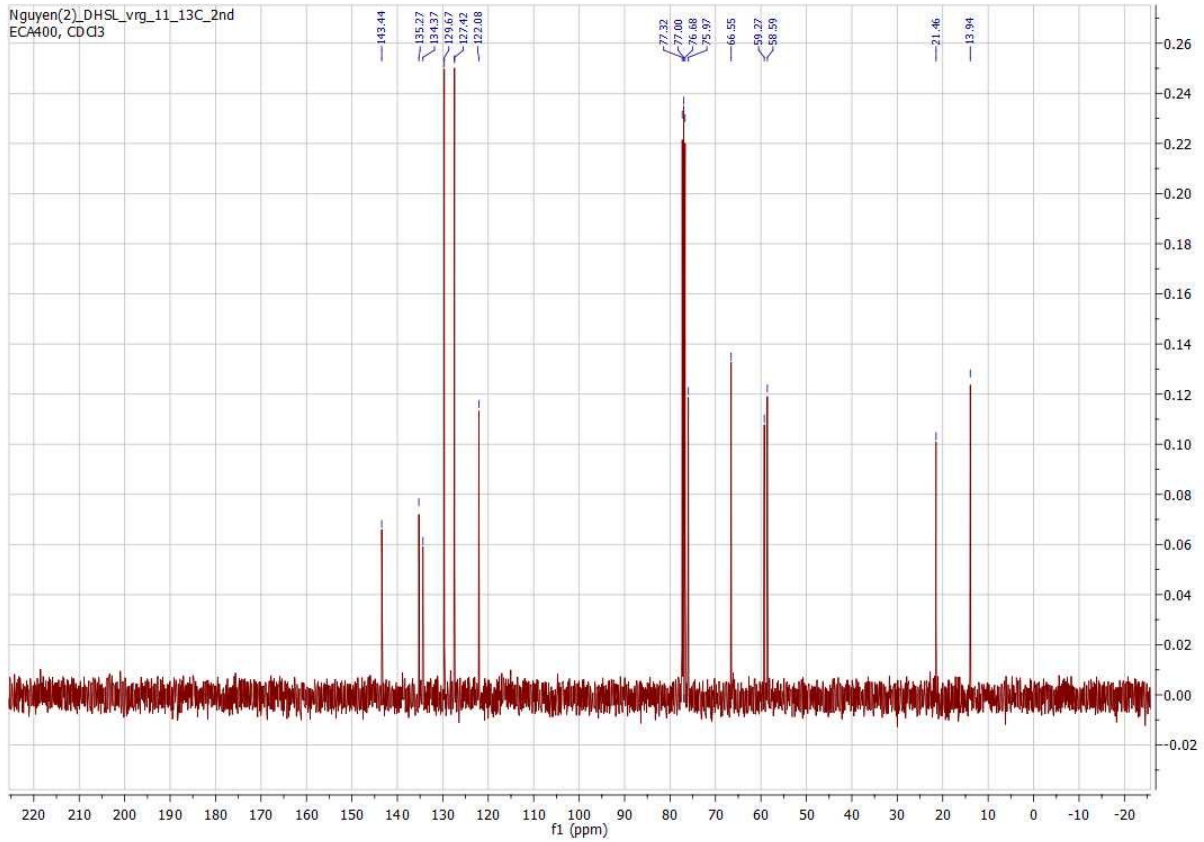
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **10a**



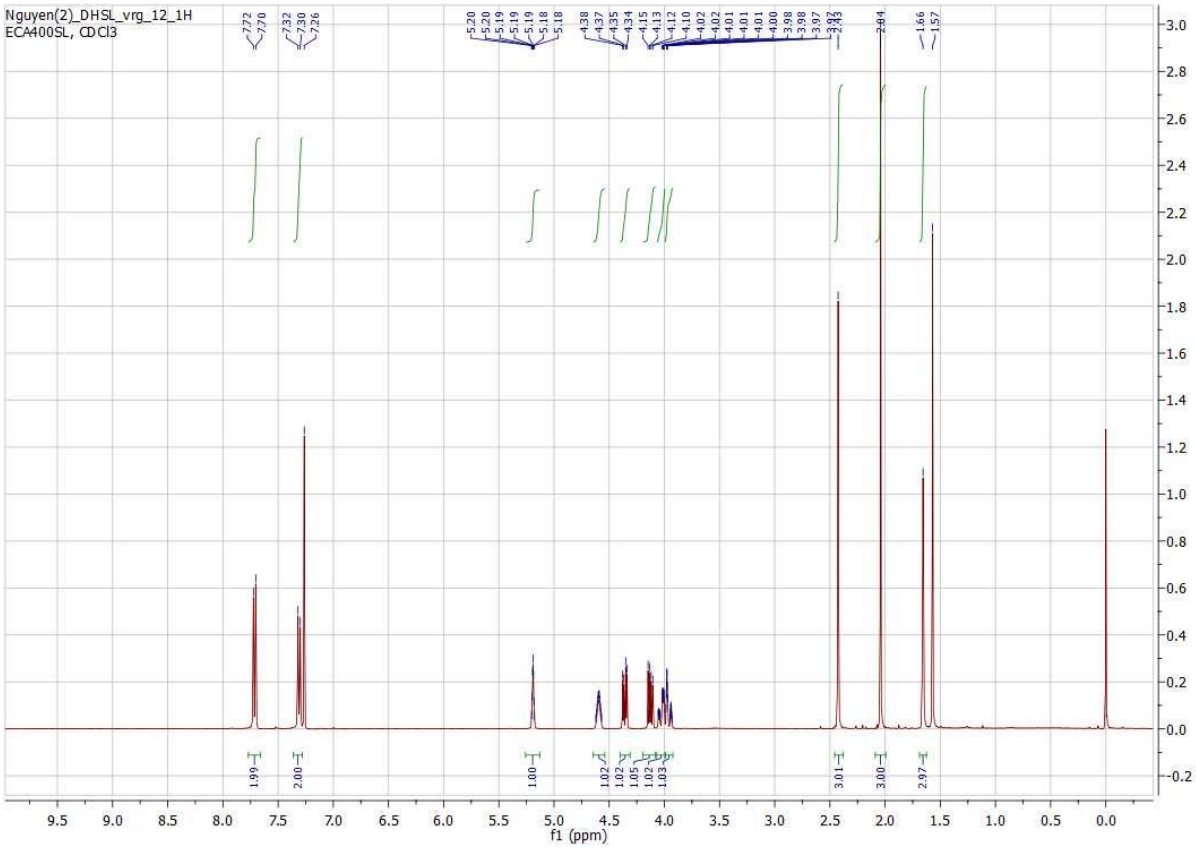


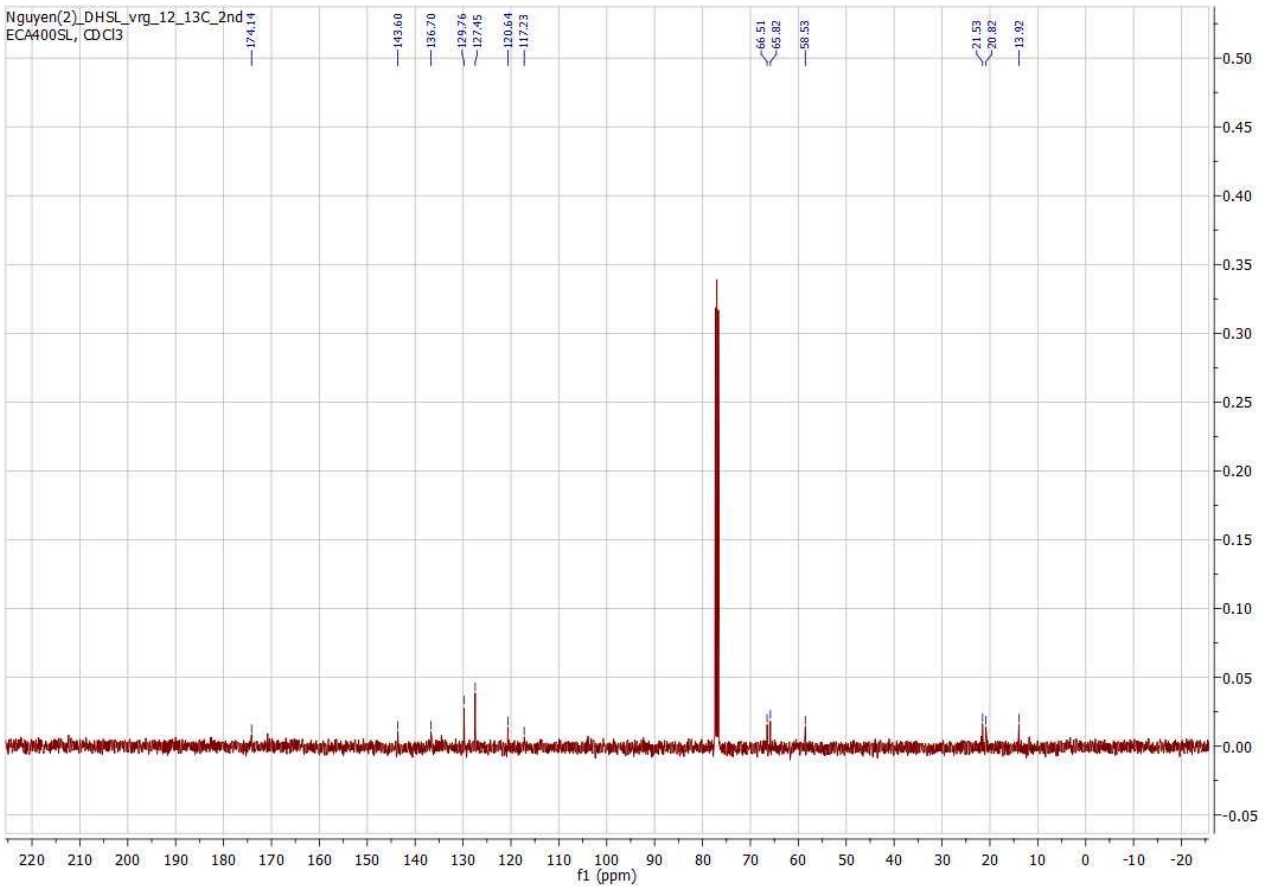
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **11a**



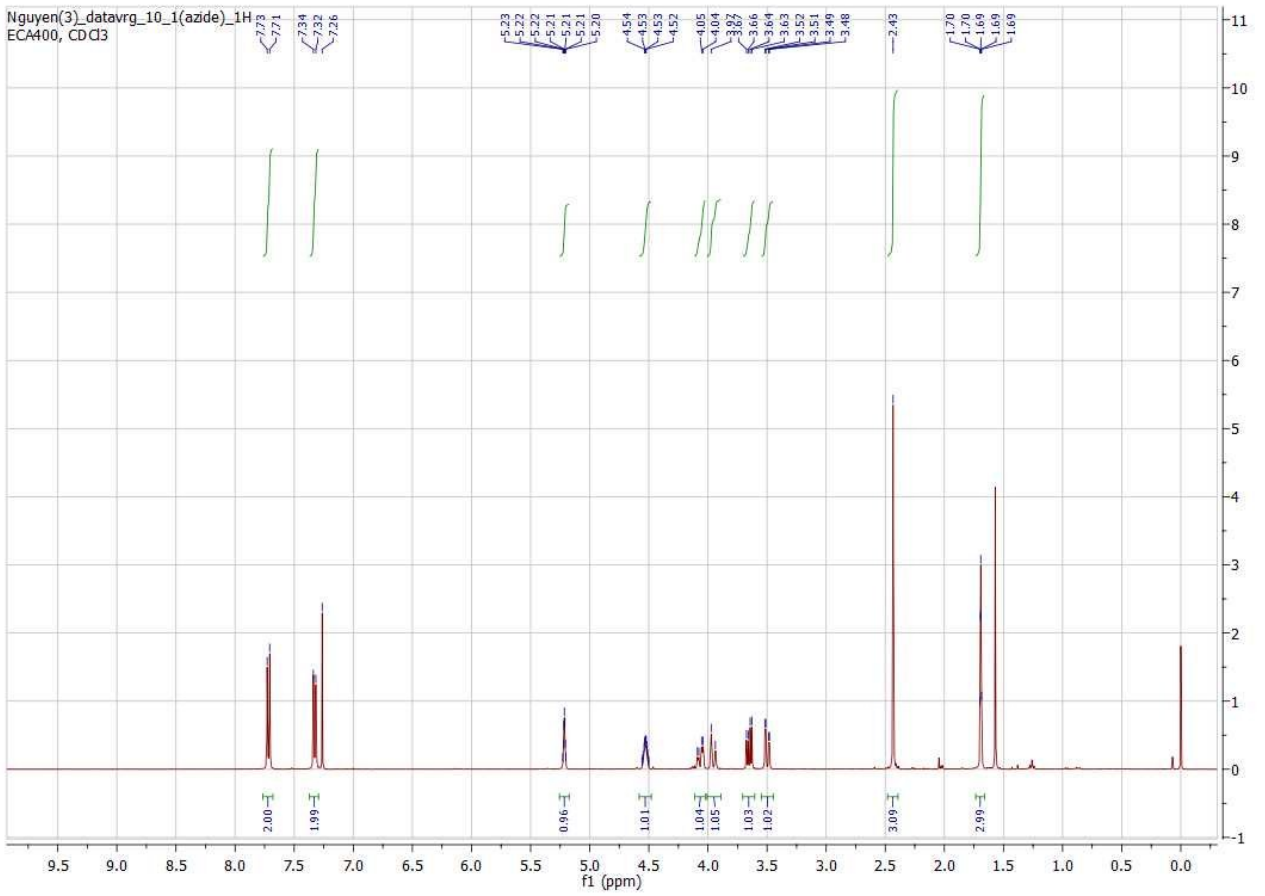


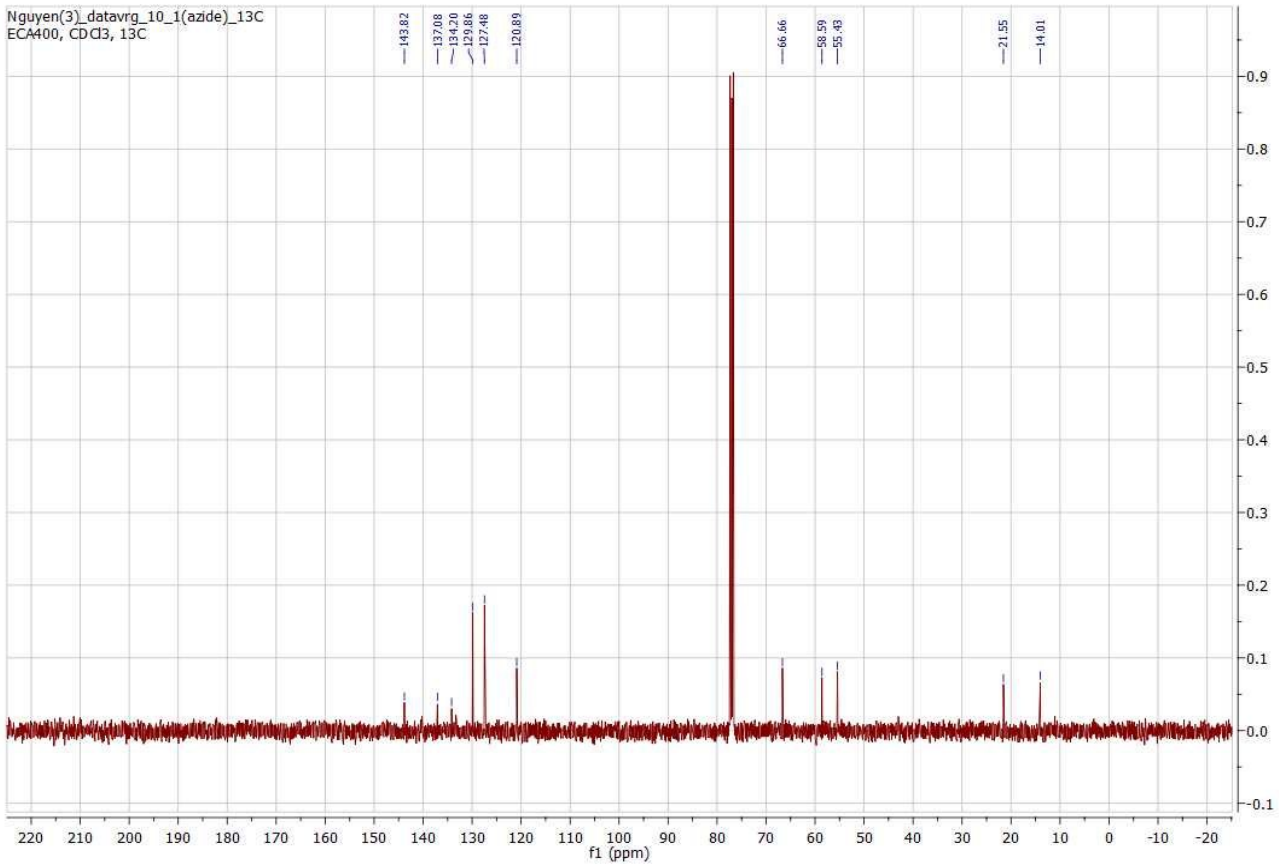
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **10b**


Nguyen(2)_DHSL_vrg_12_1H
ECA400SL, CDCl3
f1 (ppm)

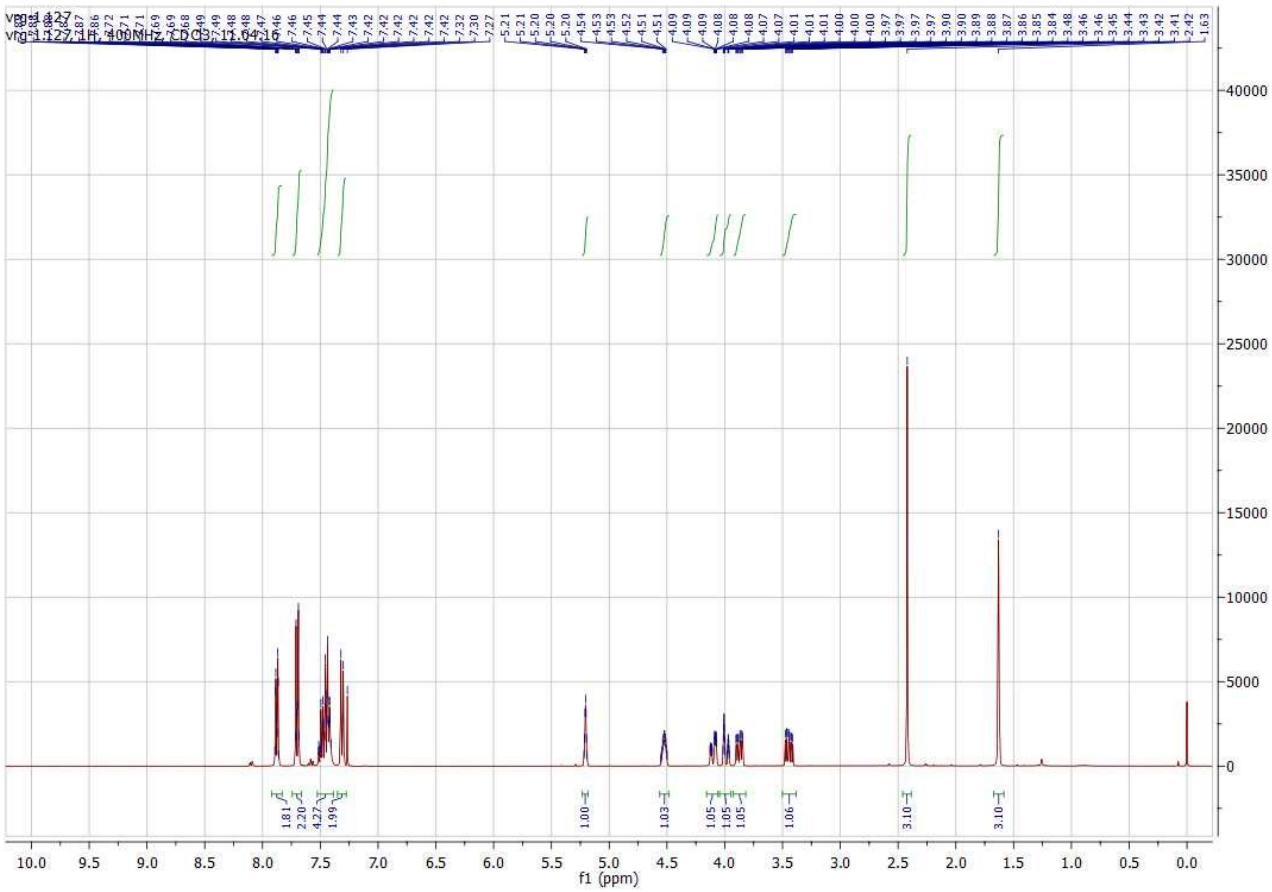


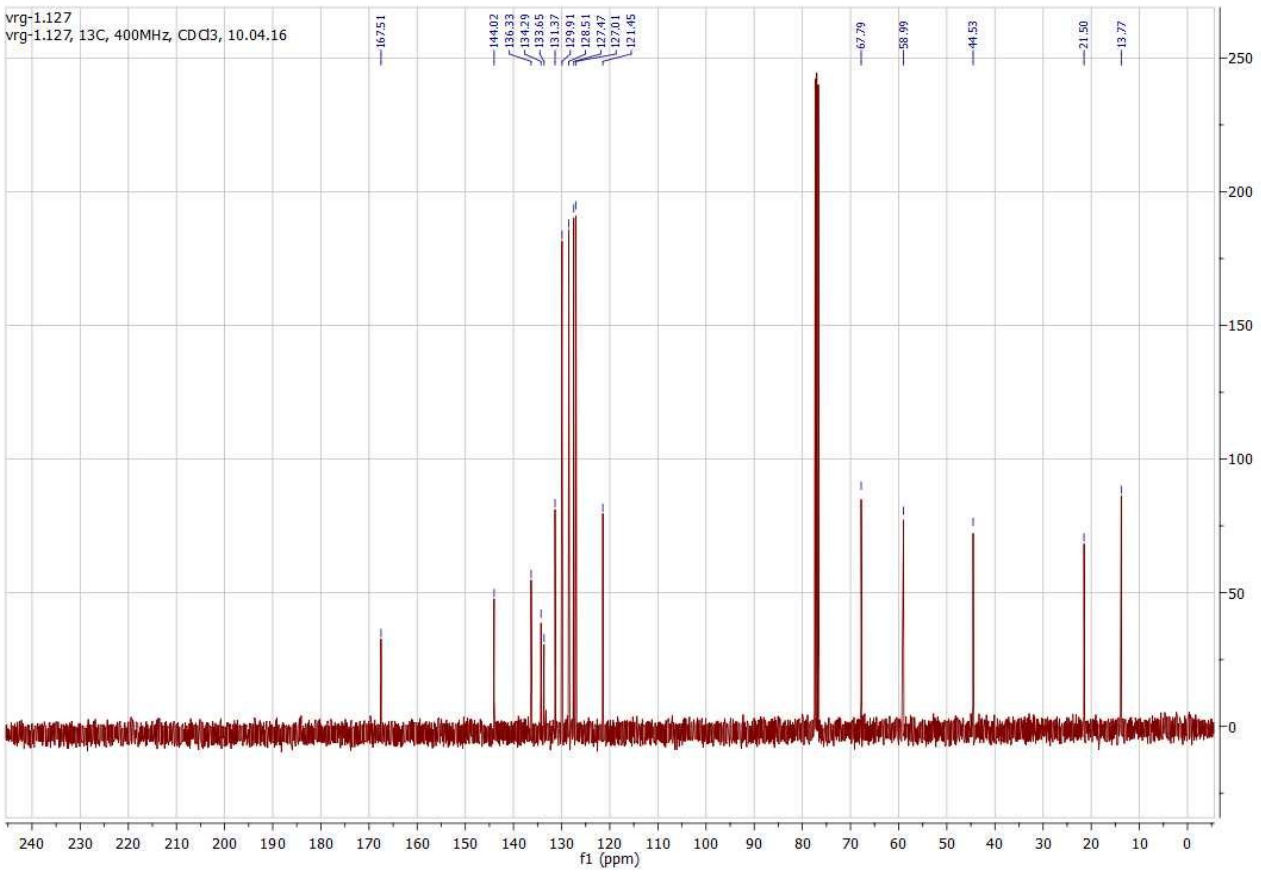
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **10c**


Nguyen(3)_datavrg_10_1(azide)_1H
ECA400, CDCl3
7.73
7.71
7.34
7.32
7.26
5.23
5.22
5.22
5.21
5.21
5.21
5.20
4.54
4.53
4.53
4.52
4.05
4.04
3.67
3.66
3.64
3.63
3.52
3.51
3.49
3.48
2.43
1.70
1.70
1.69
1.69
1.69
2.00
1.99
0.96
1.01
1.04
1.05
1.03
1.02
3.09
2.99
f1 (ppm)

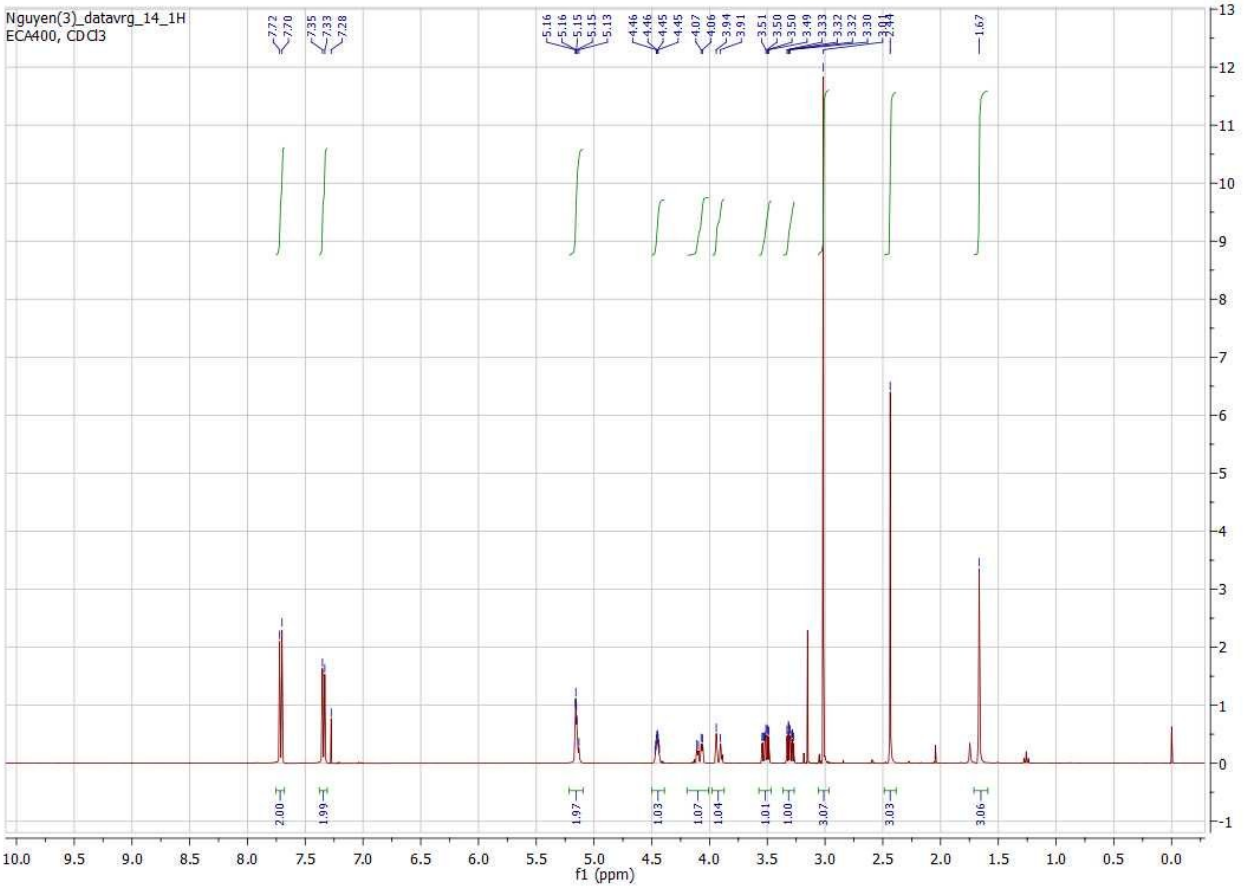

Nguyen(3)_datavrg_10_1(azide)_13C
ECA400, CDCl3, 13C
143.82
137.08
134.20
129.86
127.48
120.89
66.66
58.59
55.43
21.55
14.01
f1 (ppm)

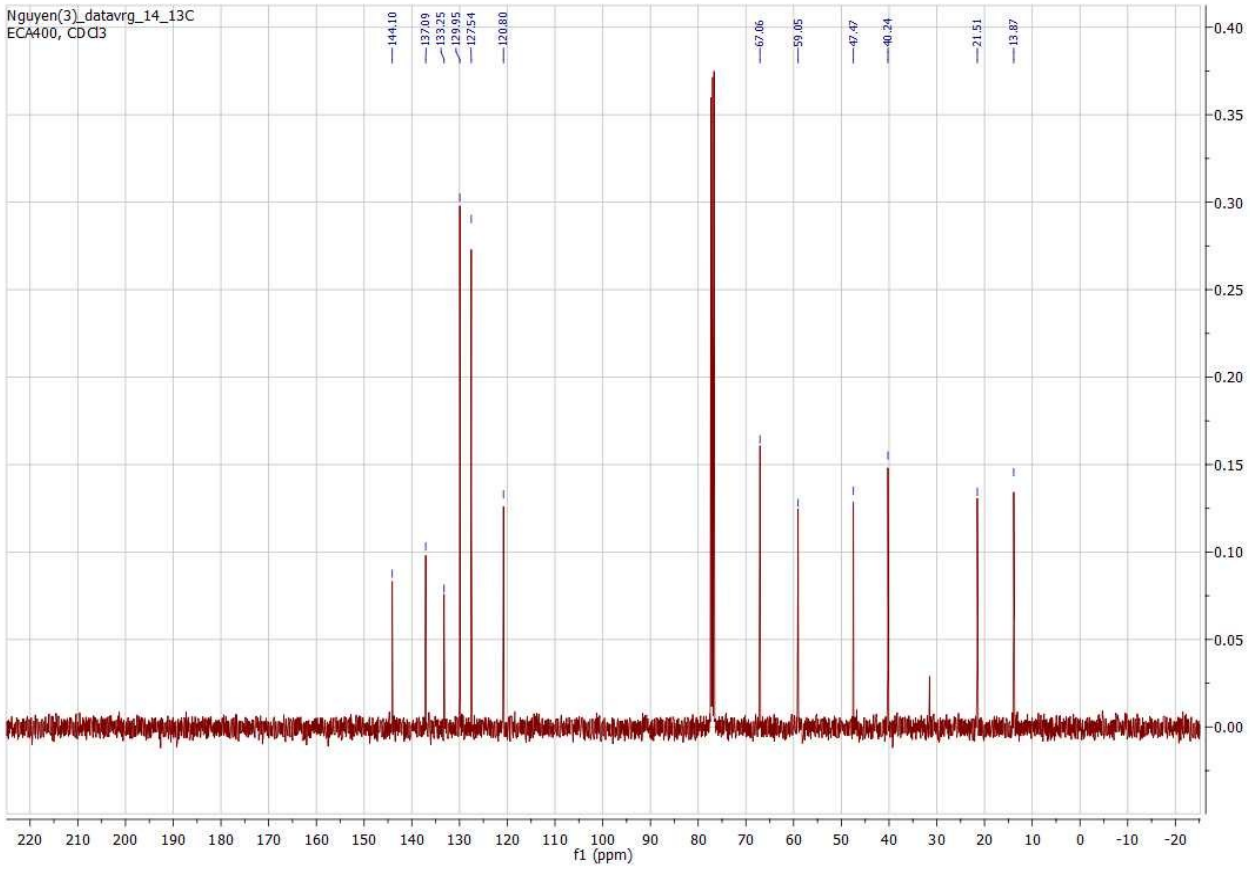
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **10e**



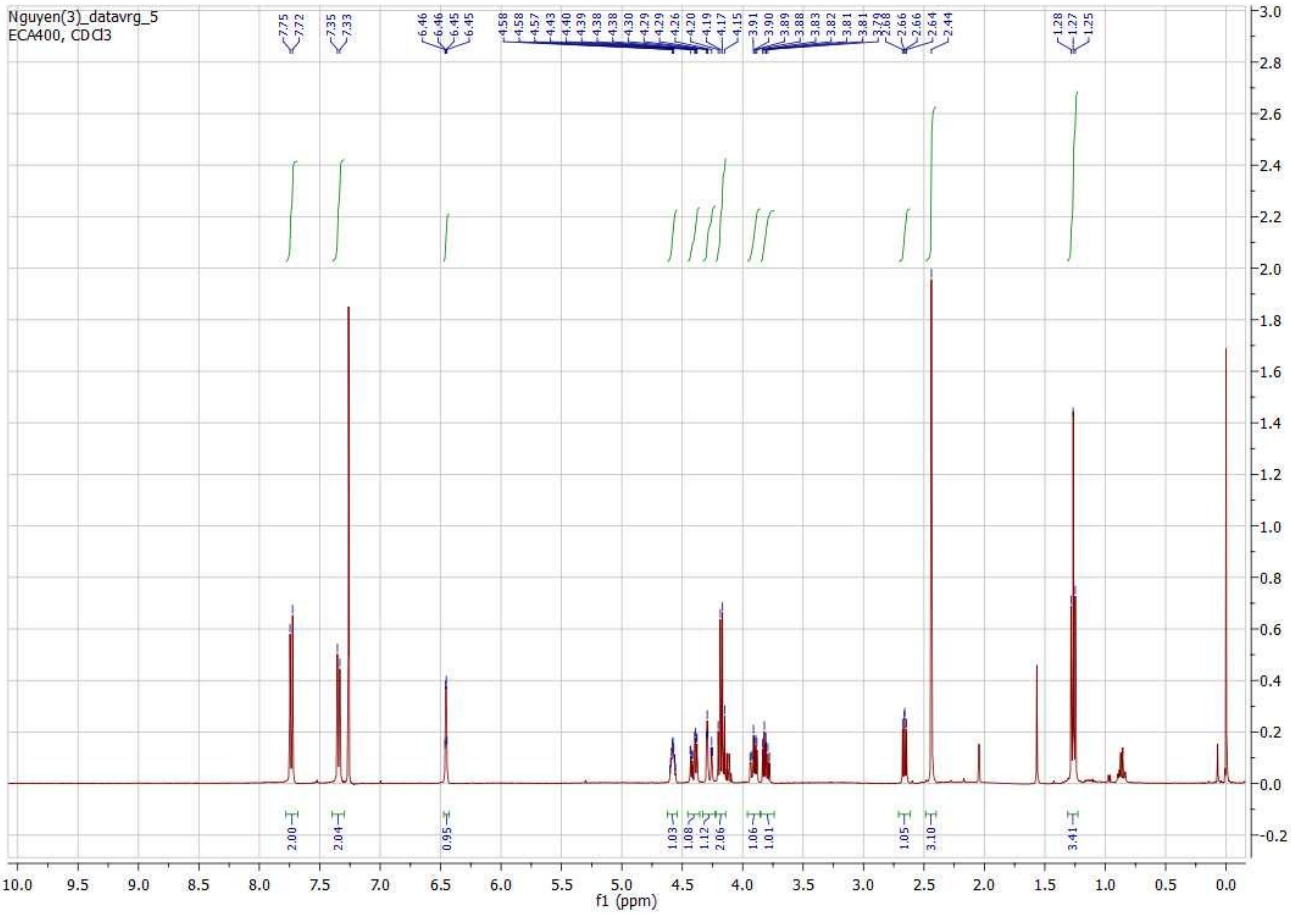


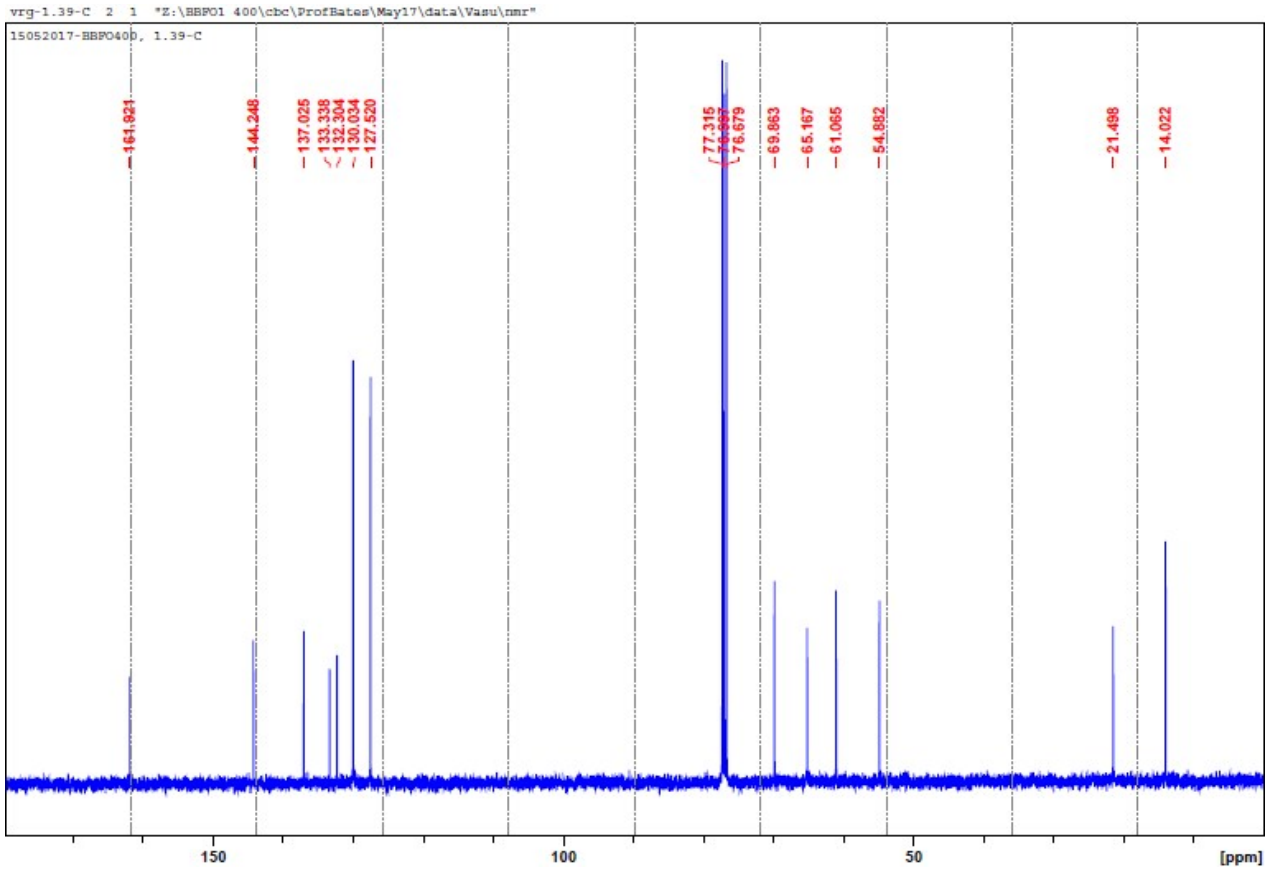
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **10f**


Nguyen(3)_datavrg_14_1H
ECA400, CDCl3
f1 (ppm)

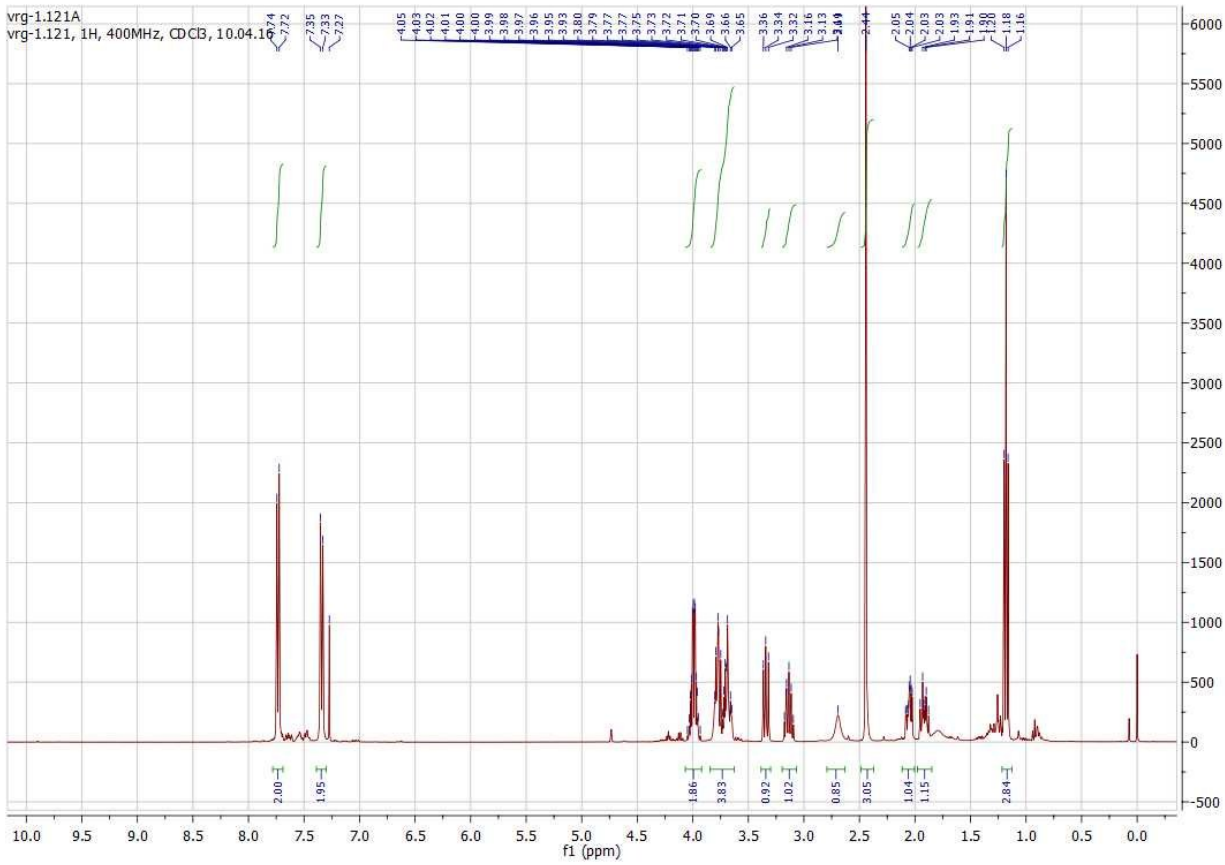

Nguyen(3)_datavrg_14_13C
ECA400, CDCl3
144.10
137.09
133.25
129.95
127.54
120.80
67.06
59.05
47.47
40.24
21.51
13.87
f1 (ppm)

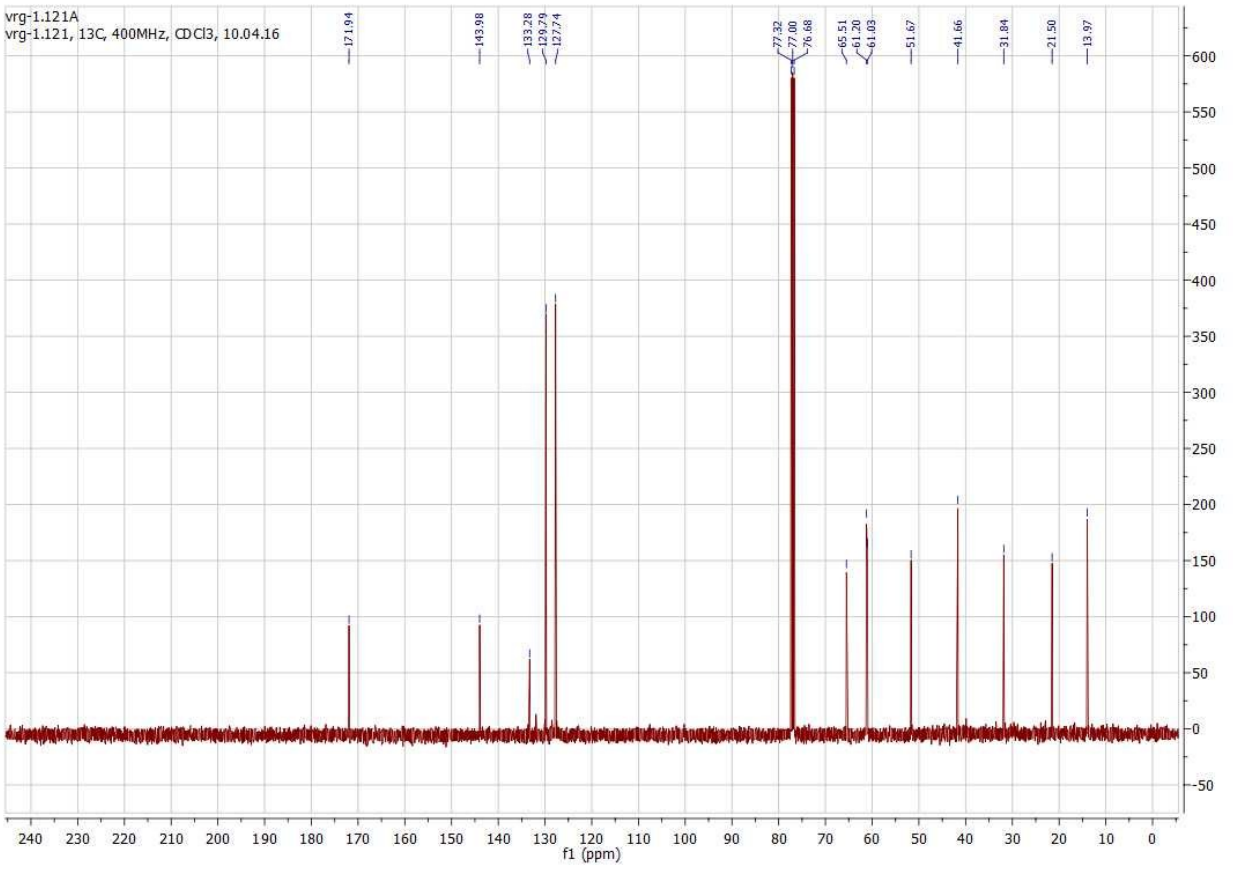
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **10g**



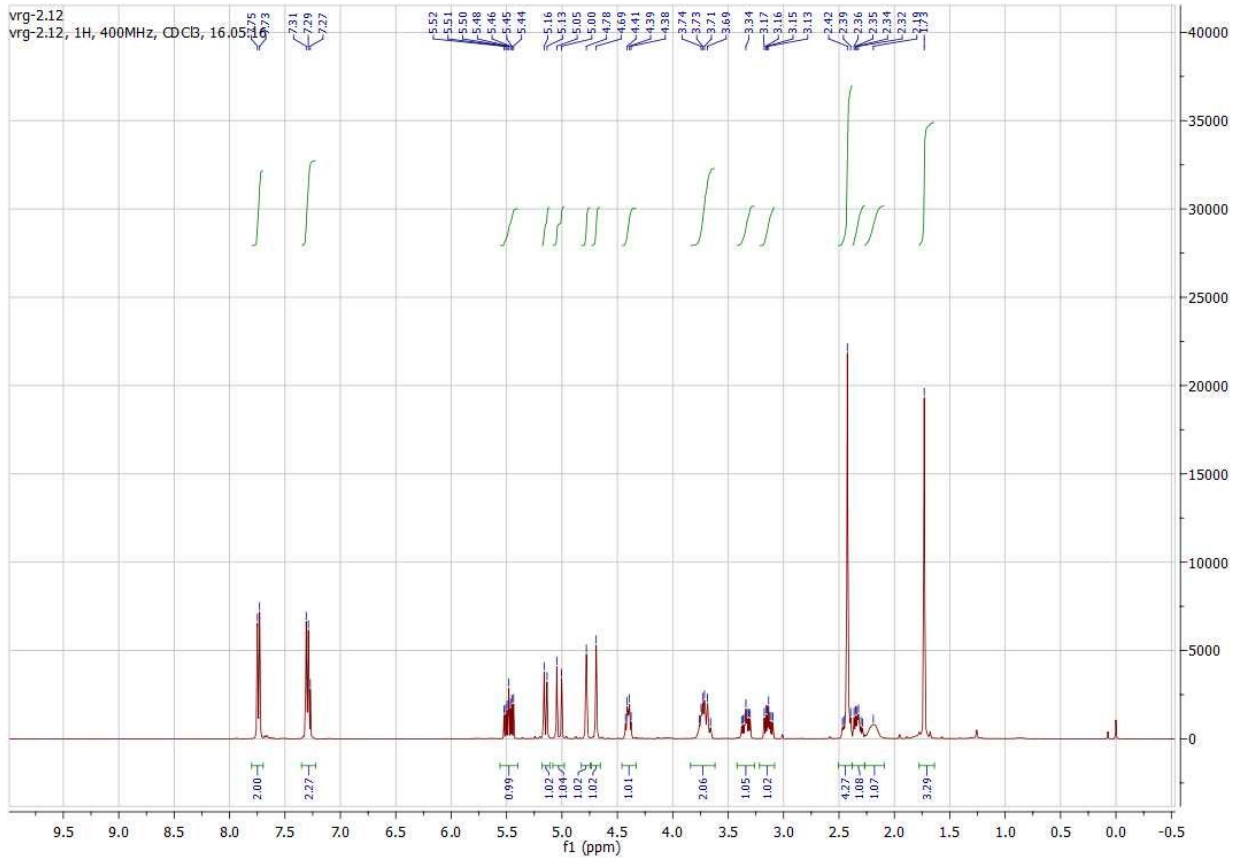


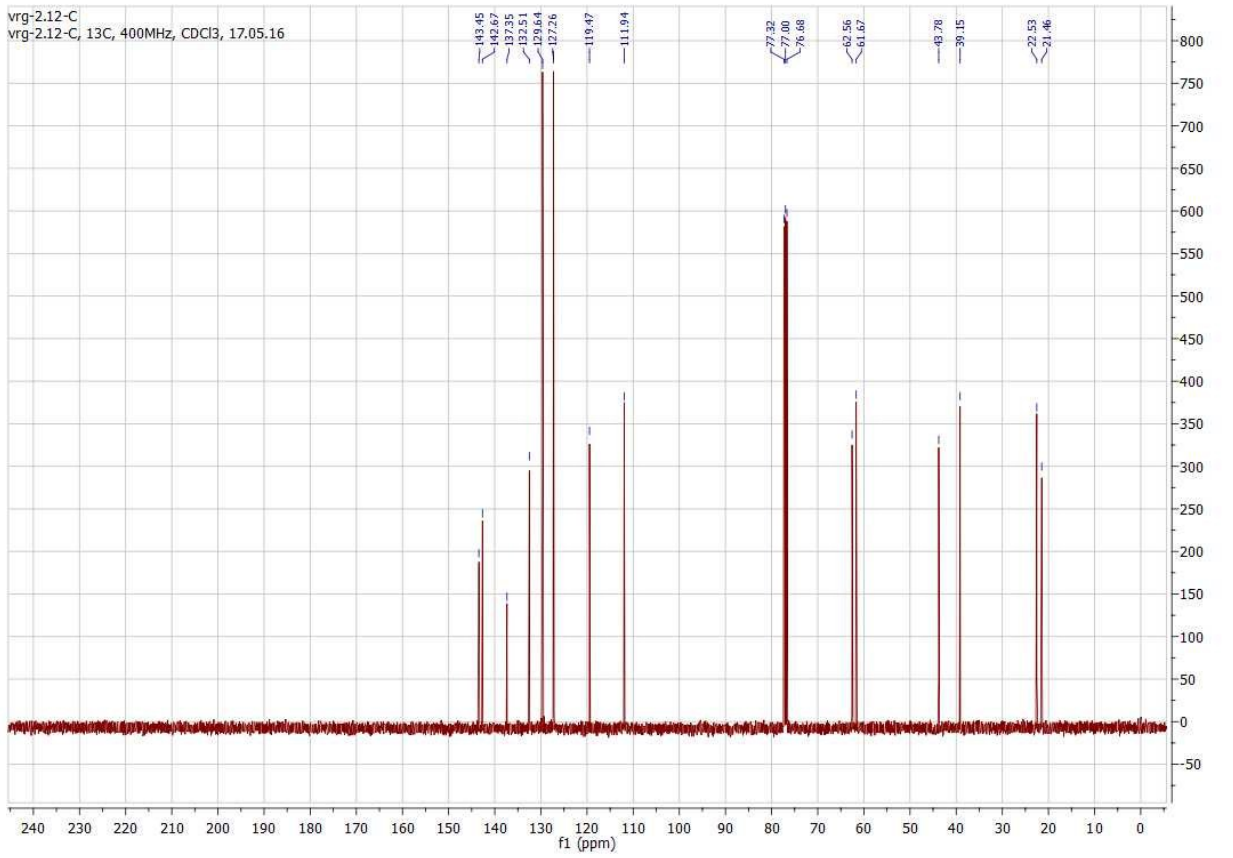
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **12**



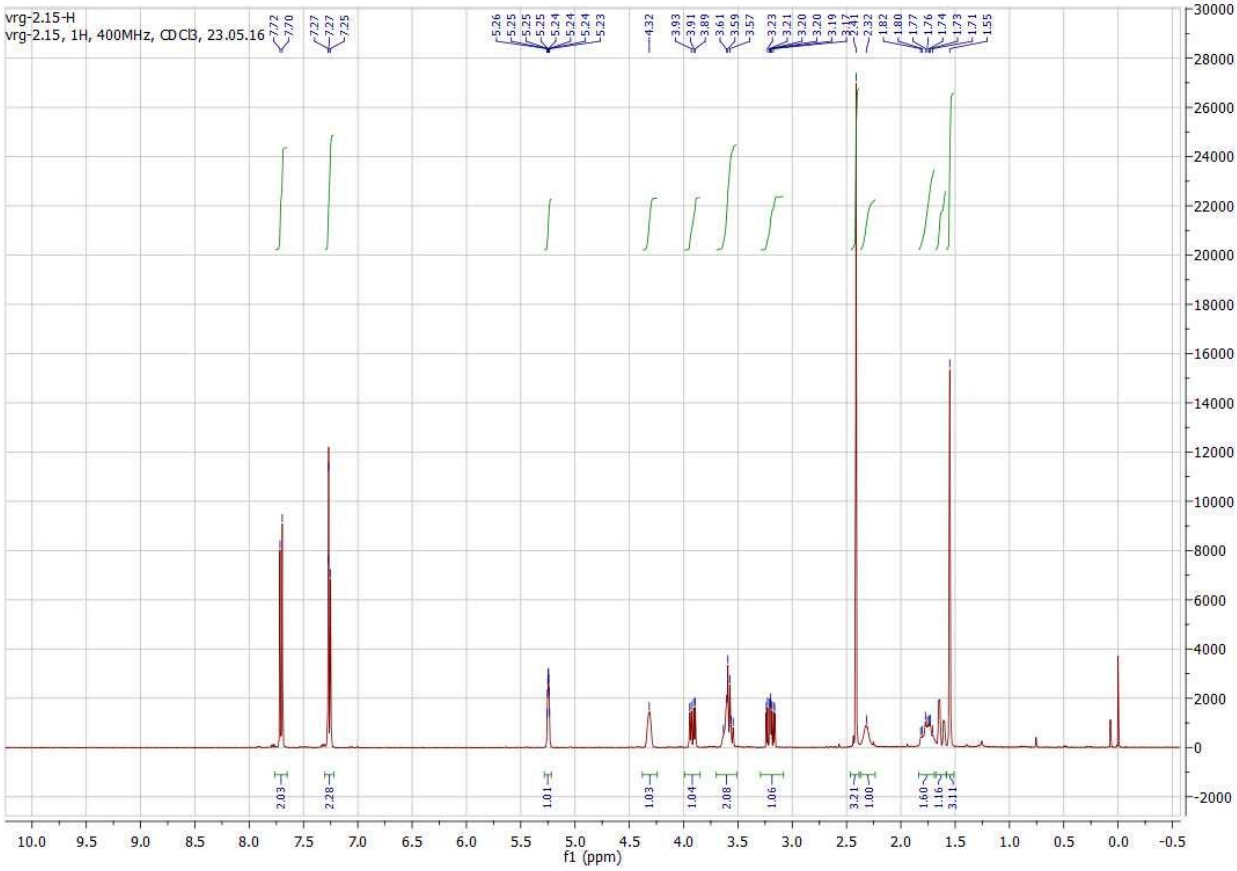


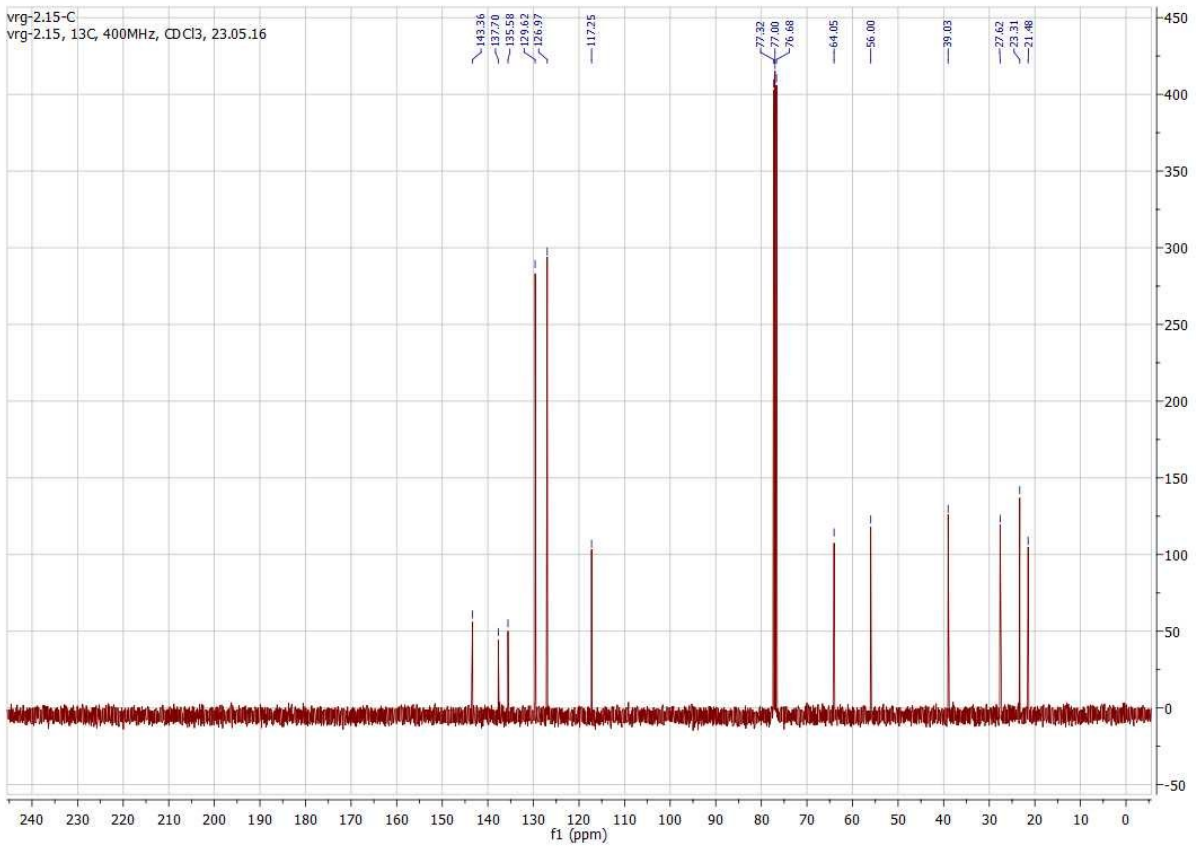
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **13**



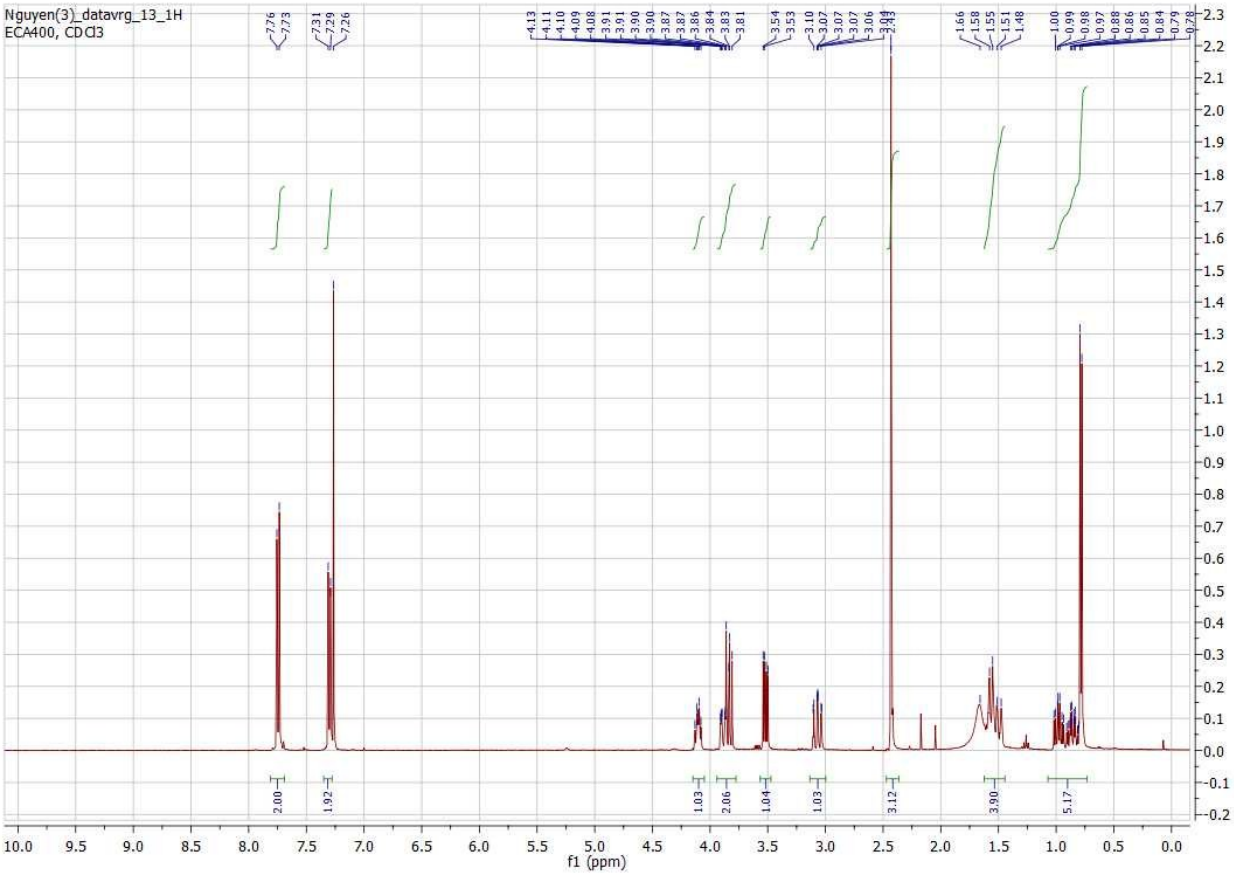


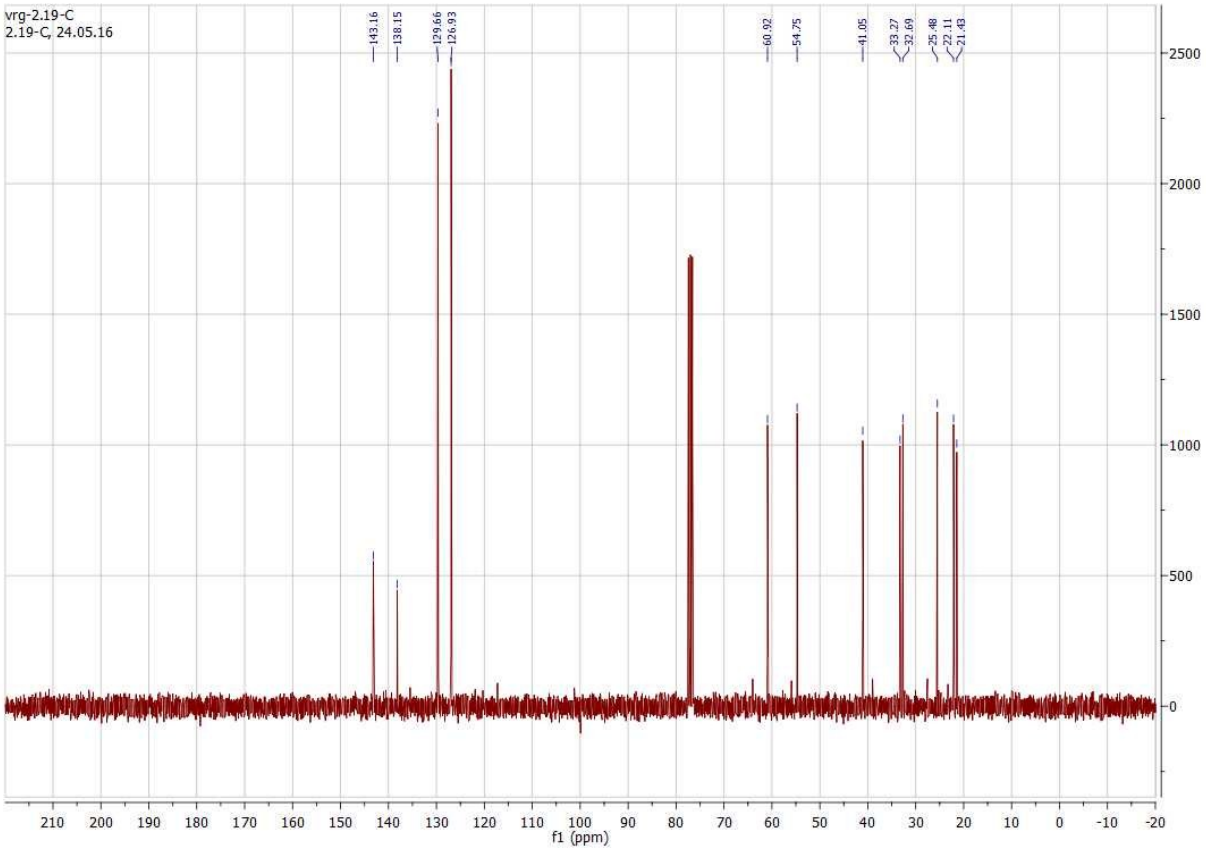
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **17**



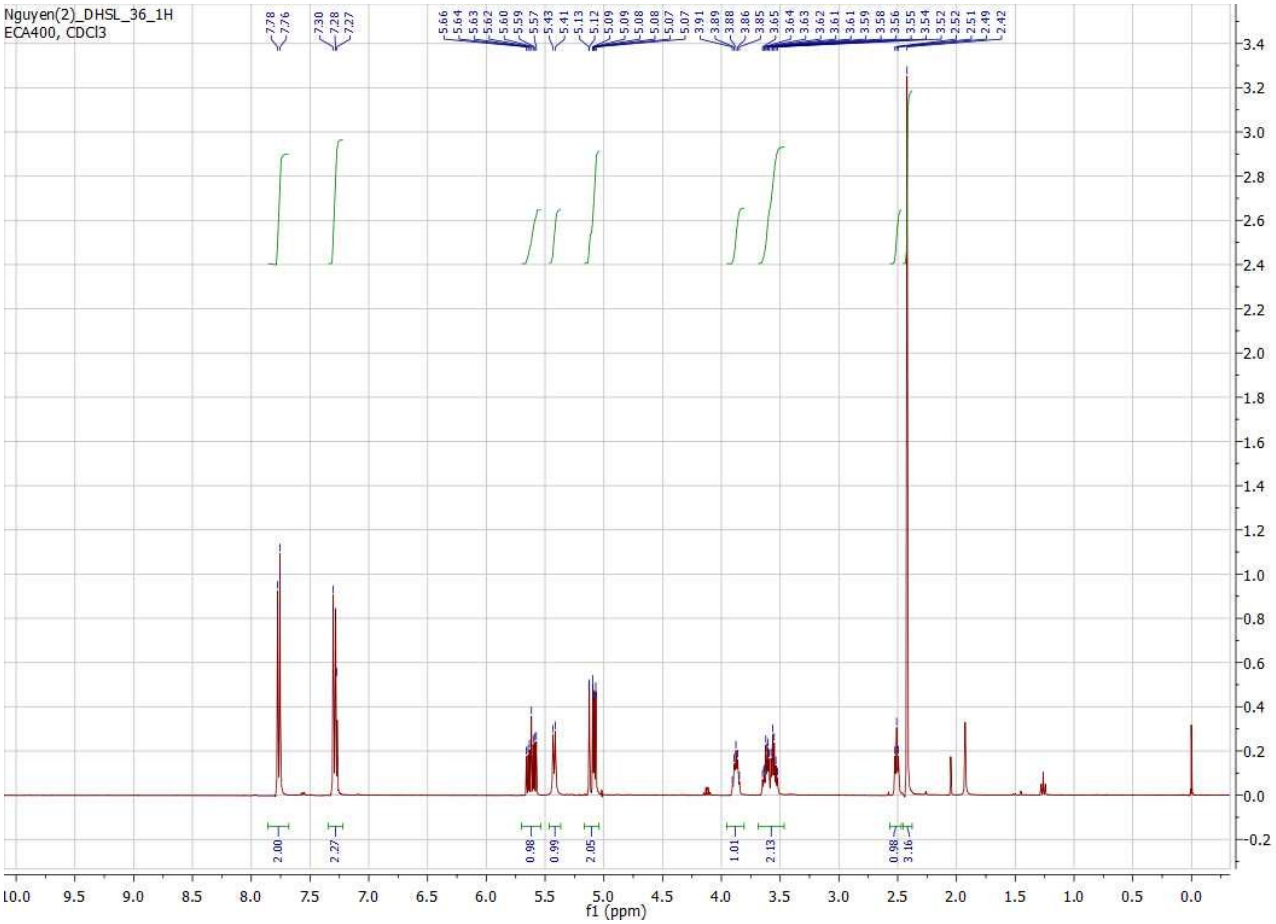


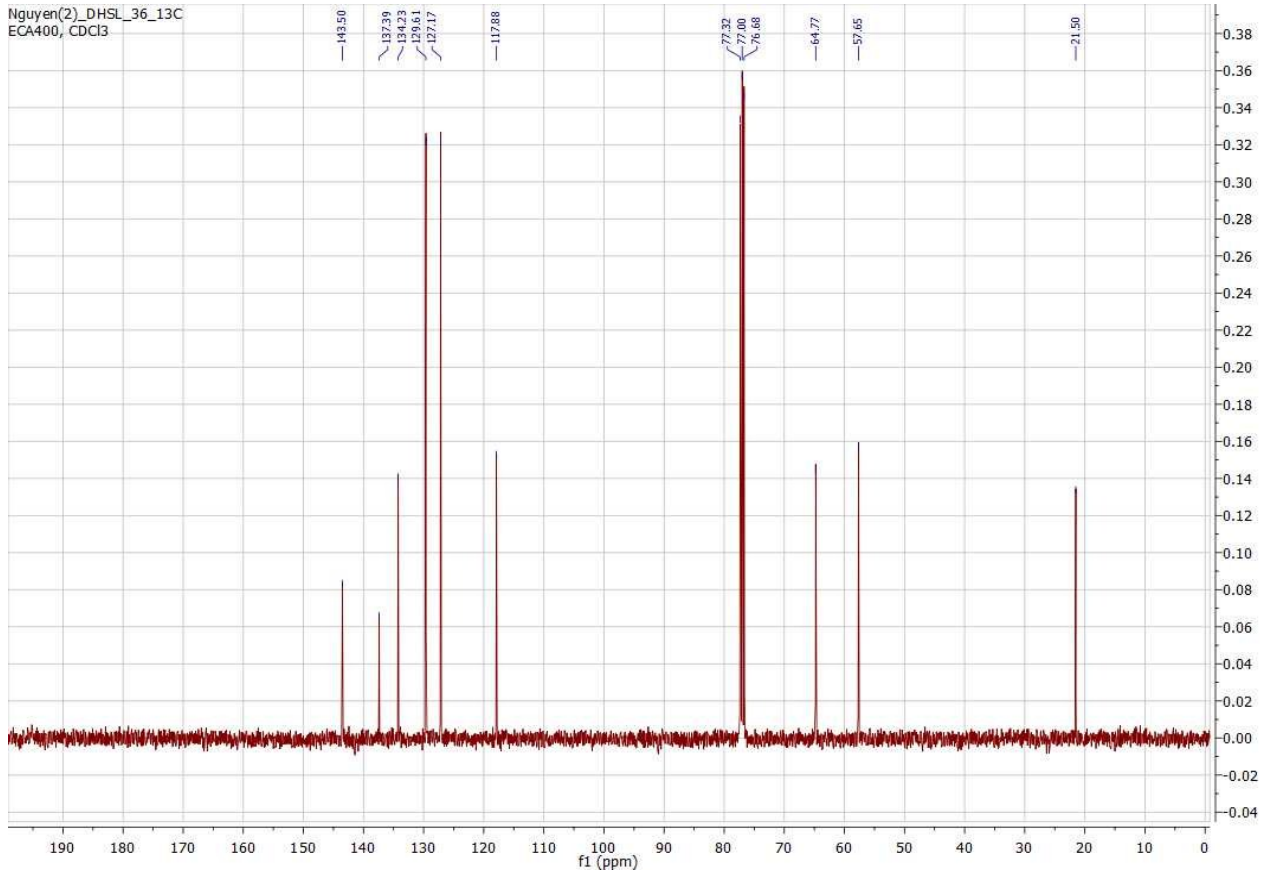
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **18**





^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **19**


Nguyen(2)_DHSL_36_1H
ECA400, CDCl3
f1 (ppm)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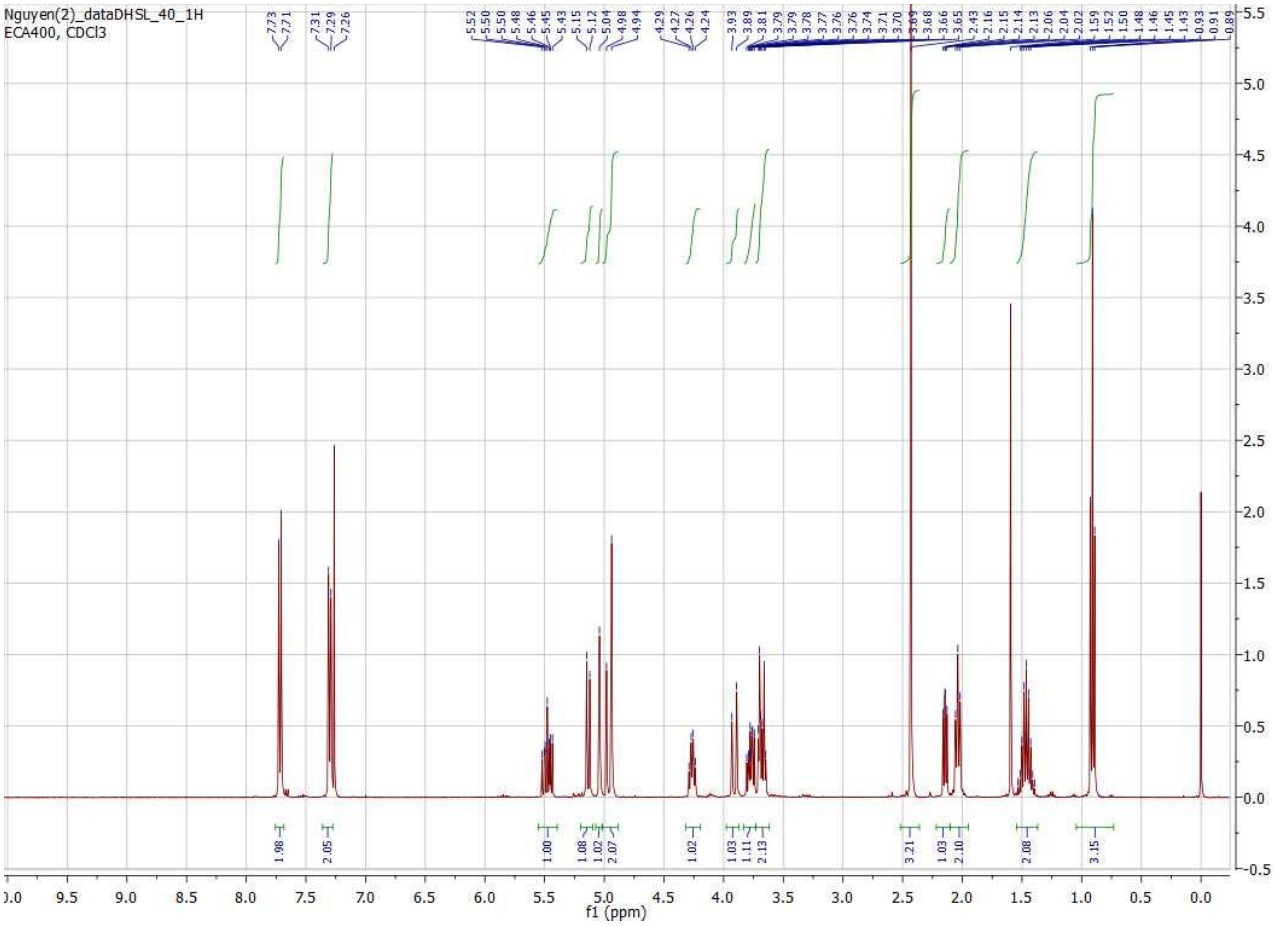
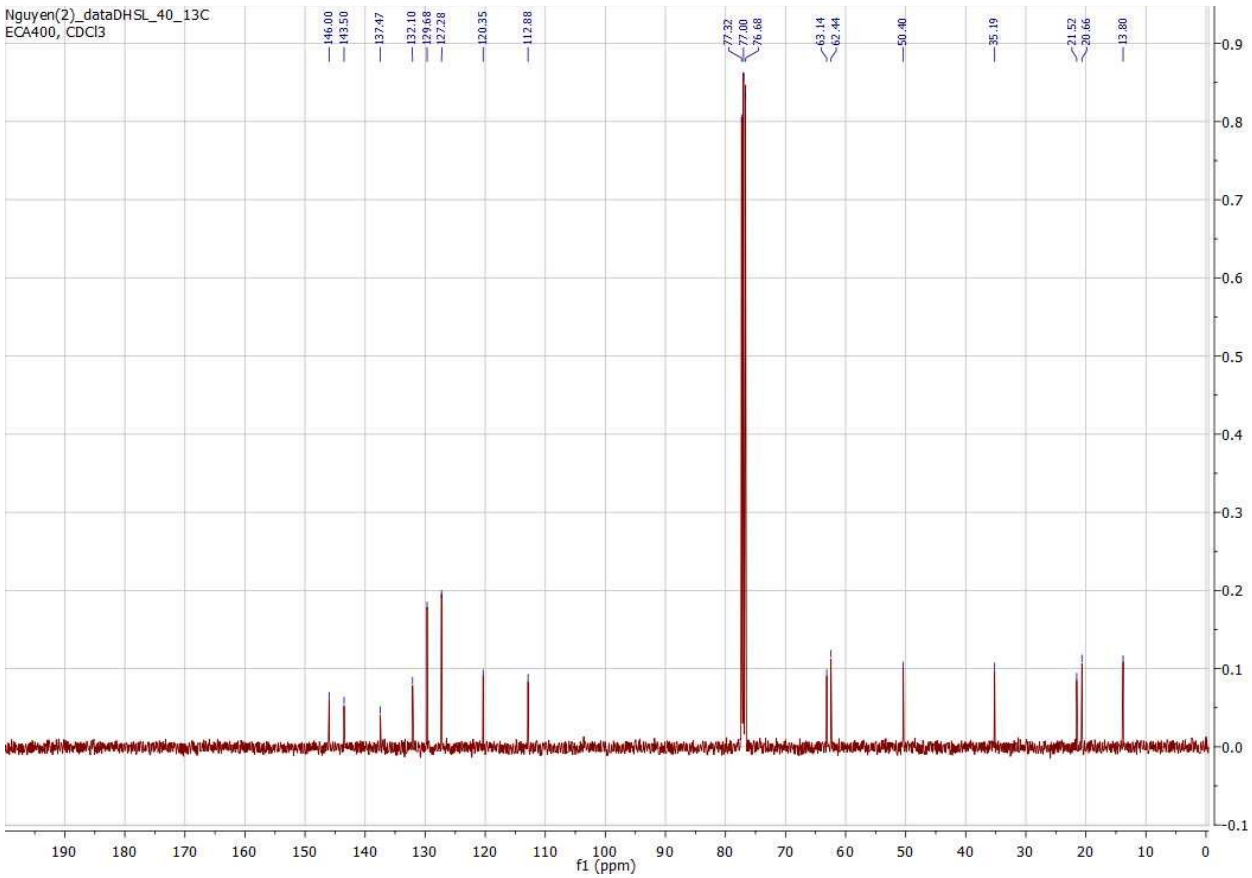
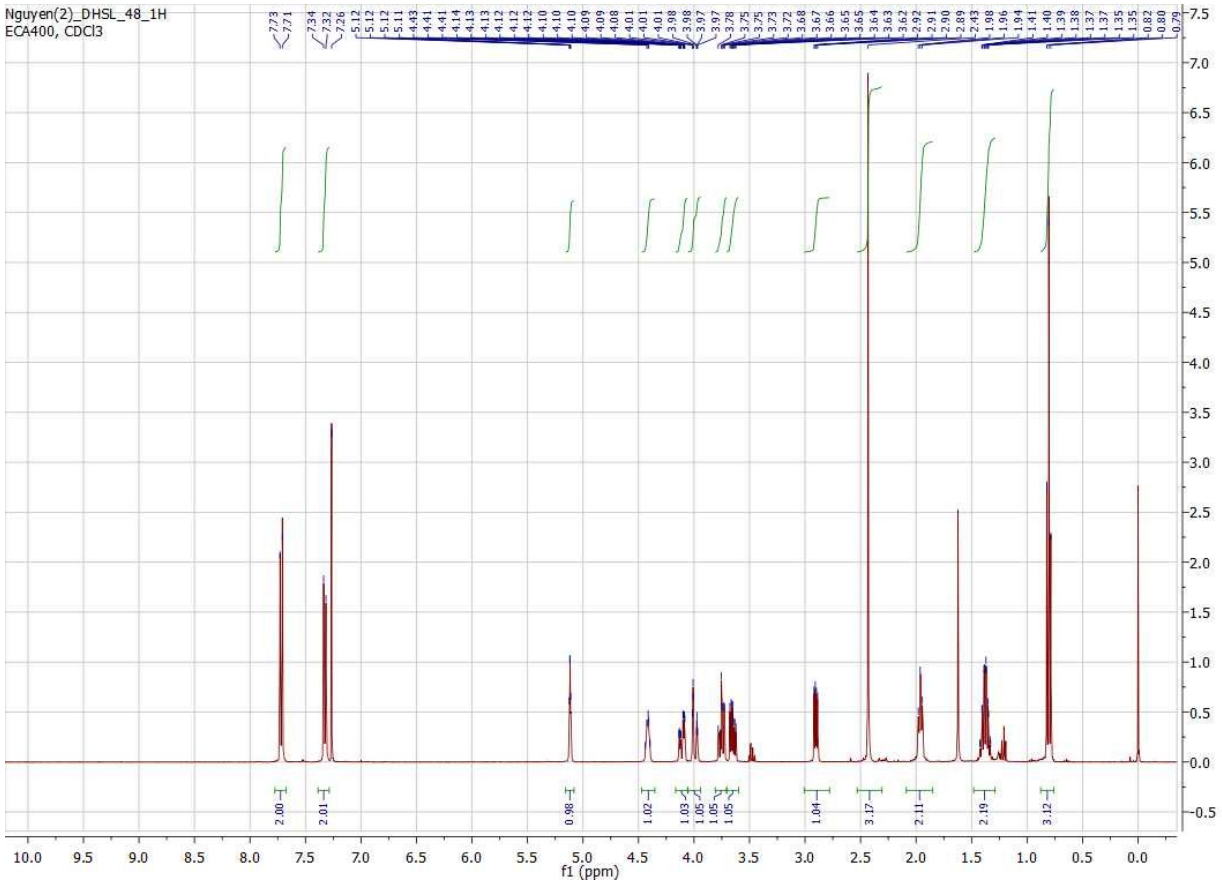
ECA400, CDCl3
f1 (ppm)

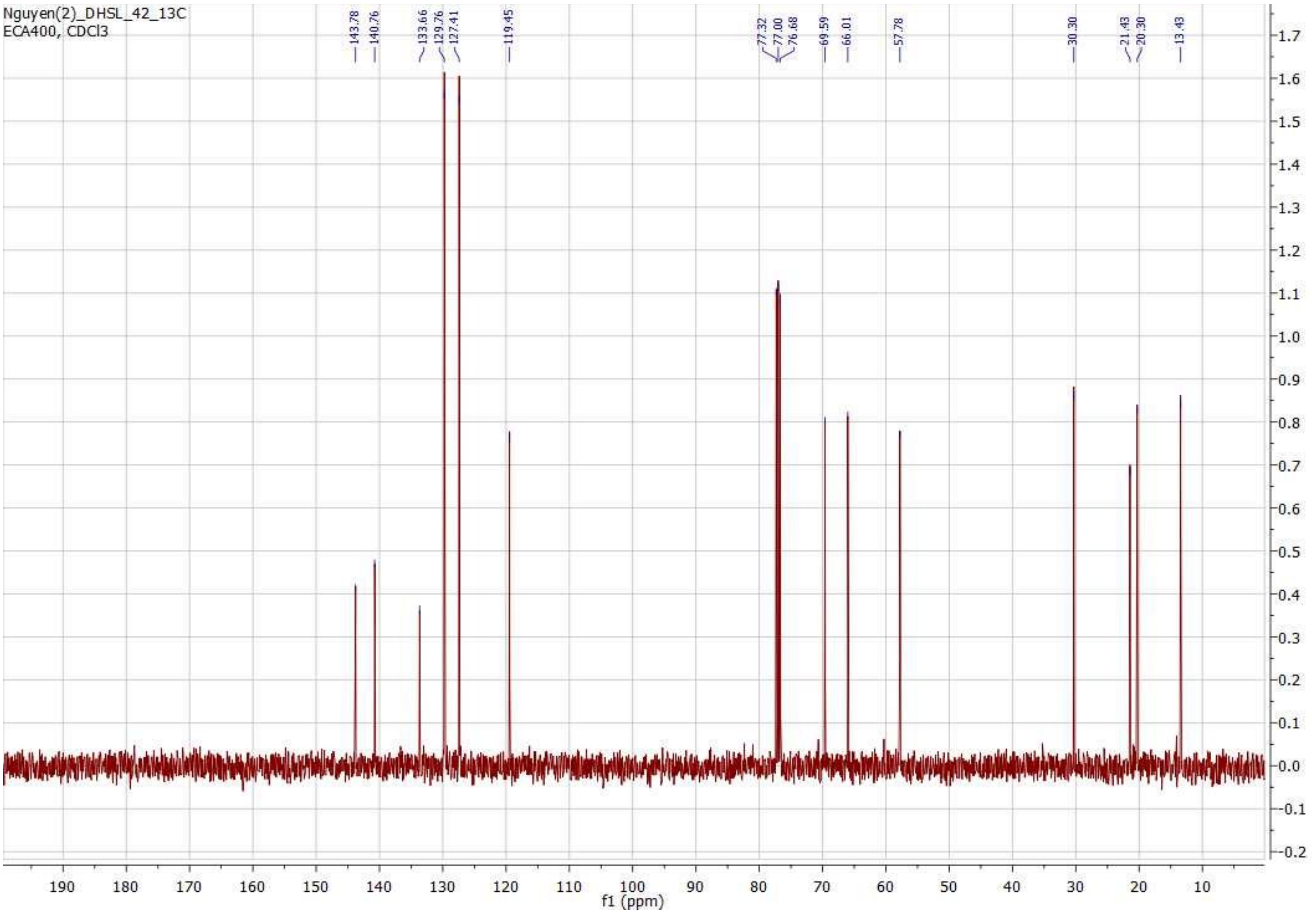
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **7**



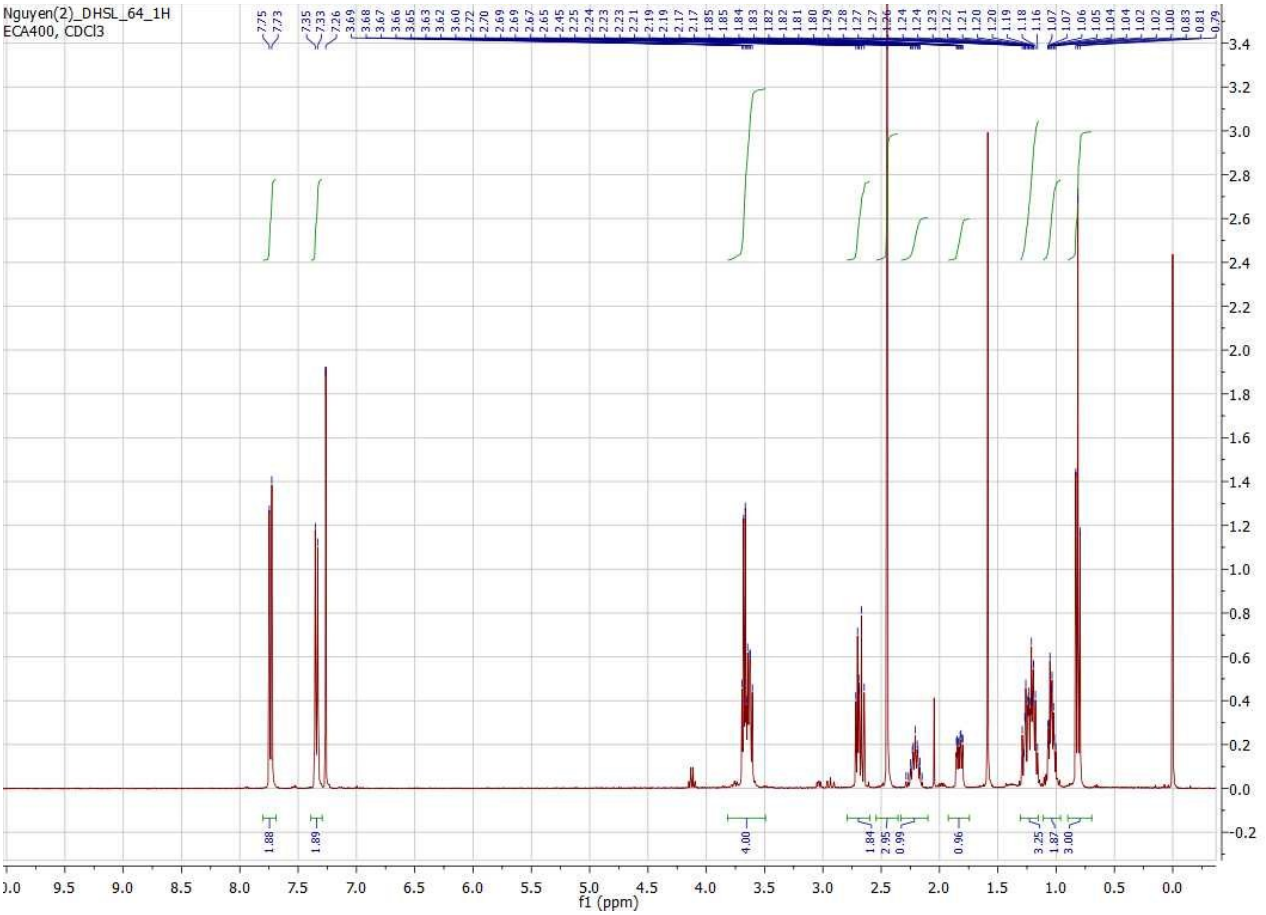


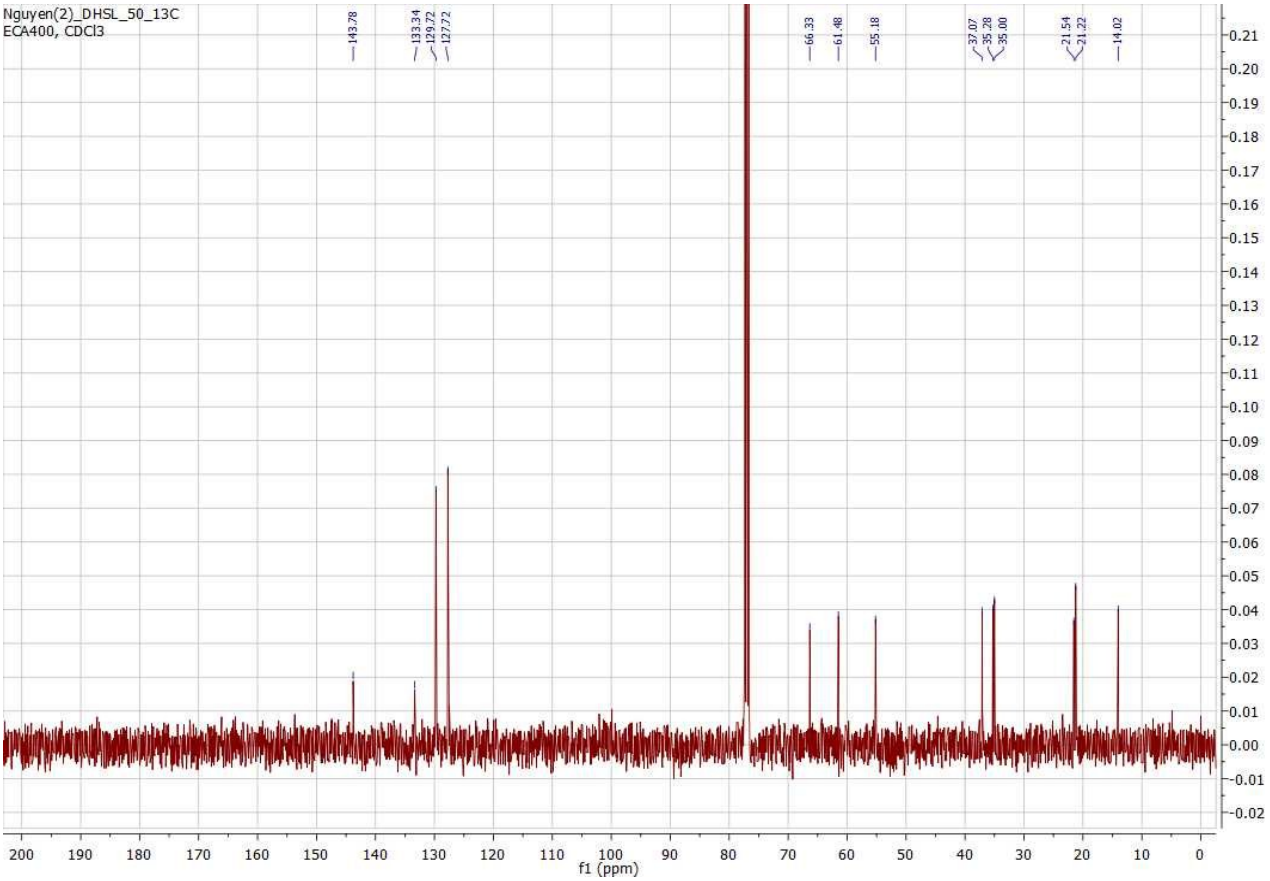
^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra of **9c**



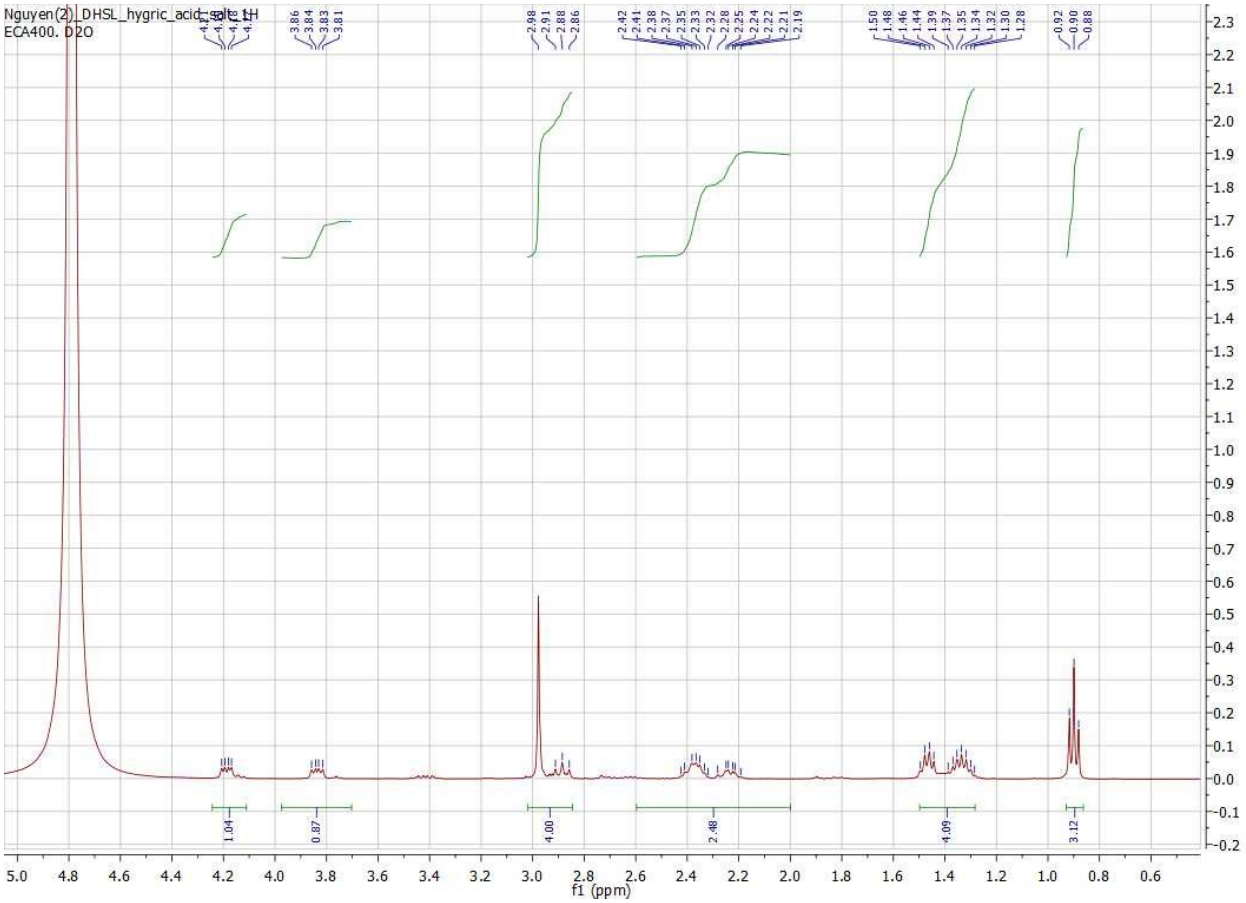


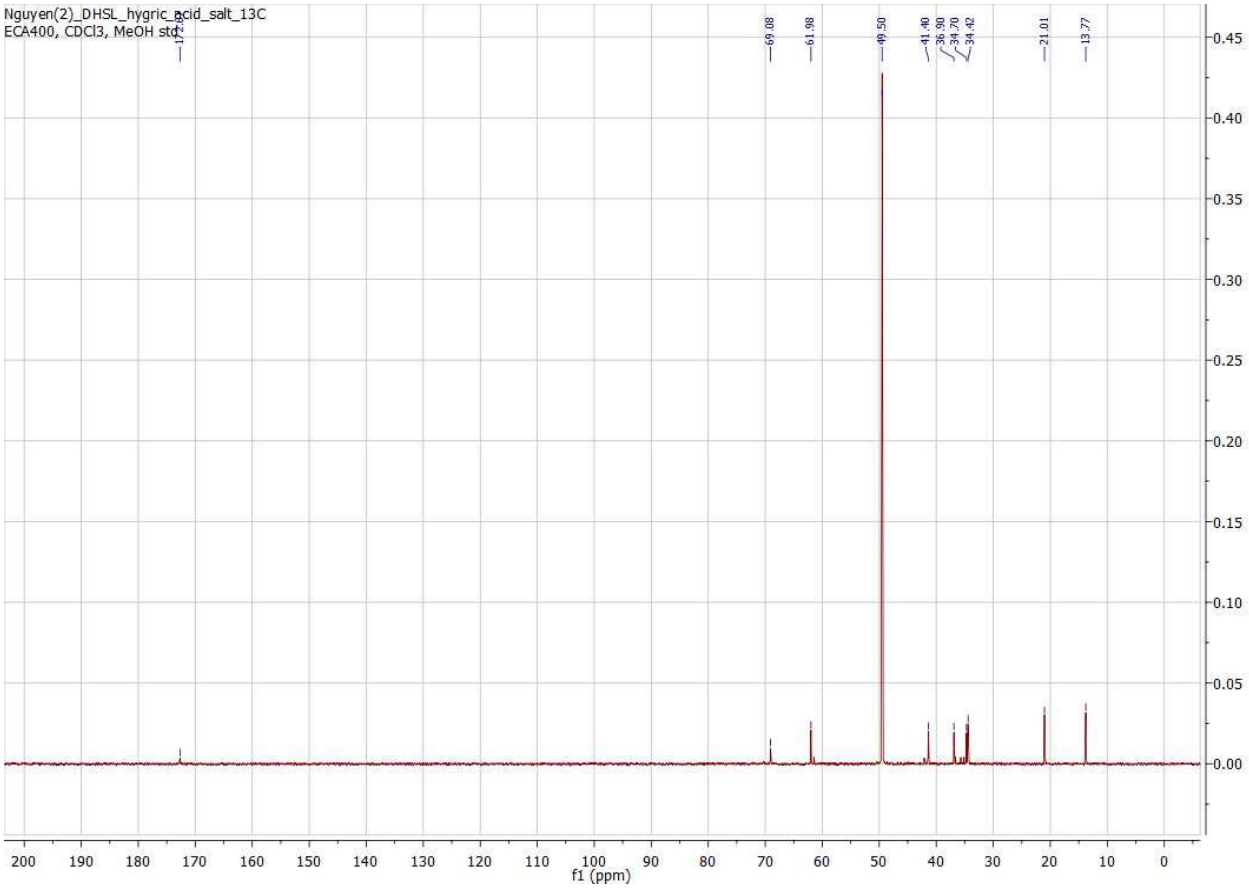
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **14**


Nguyen(2)_DHSL_64_1H
ECA400, CDCl3
f1 (ppm)

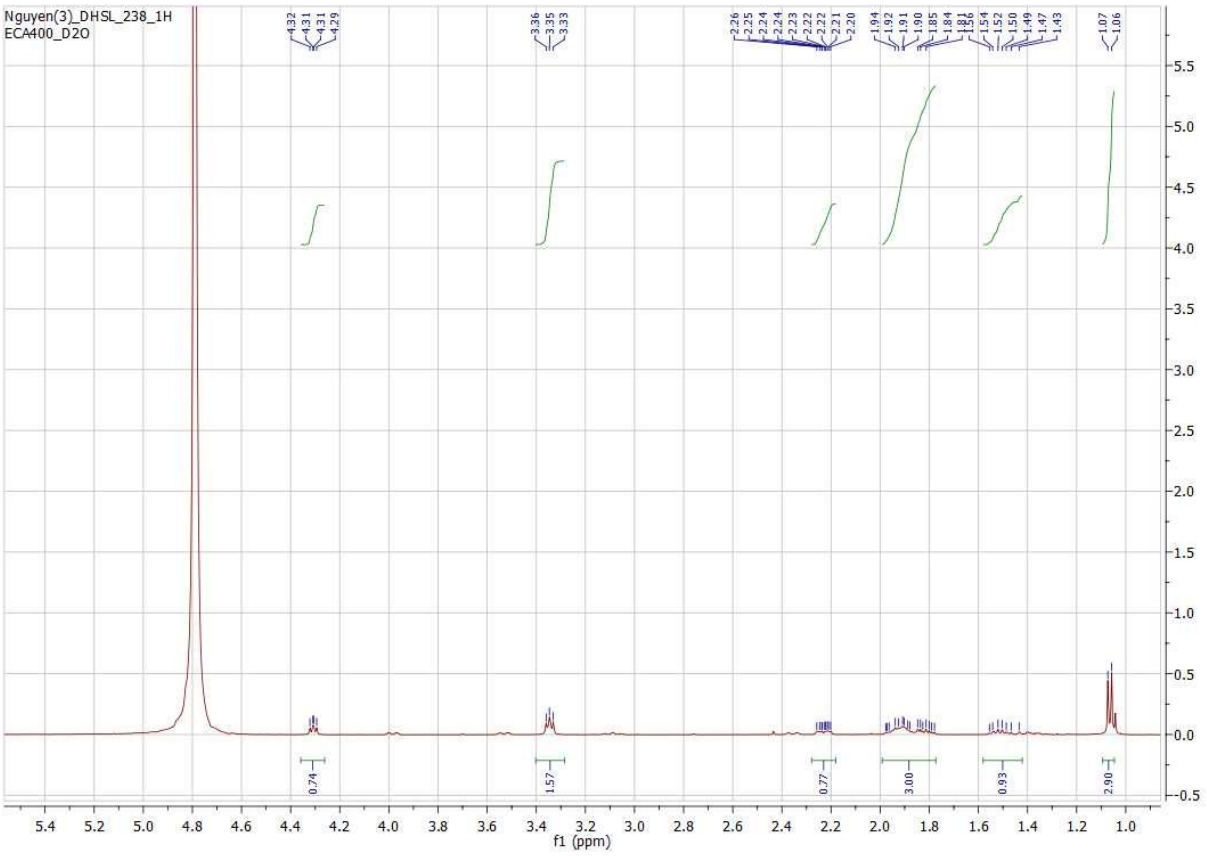

Nguyen(2)_DHSL_50_13C
ECA400, CDCl3
143.78
133.34
129.72
127.72
66.33
61.48
55.18
37.07
35.28
35.00
21.54
21.22
14.02
f1 (ppm)

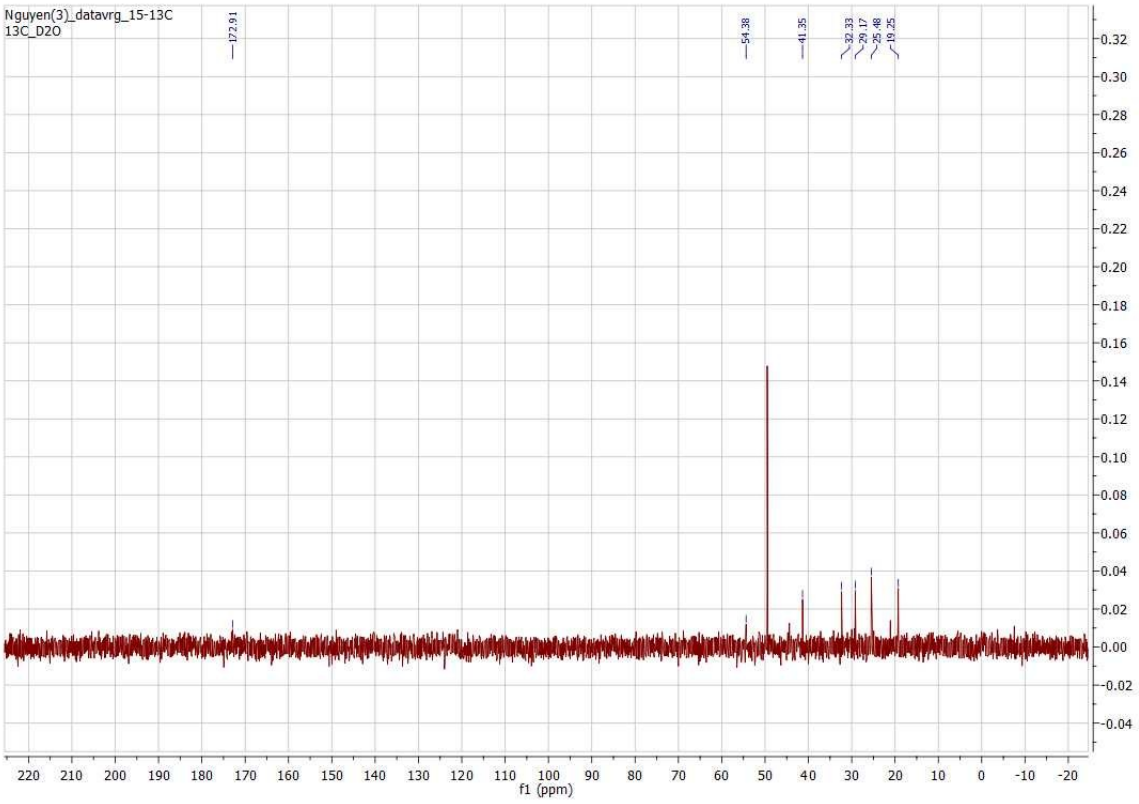
^{1}H NMR and ^{13}C{^{1}H} NMR spectra of **15**



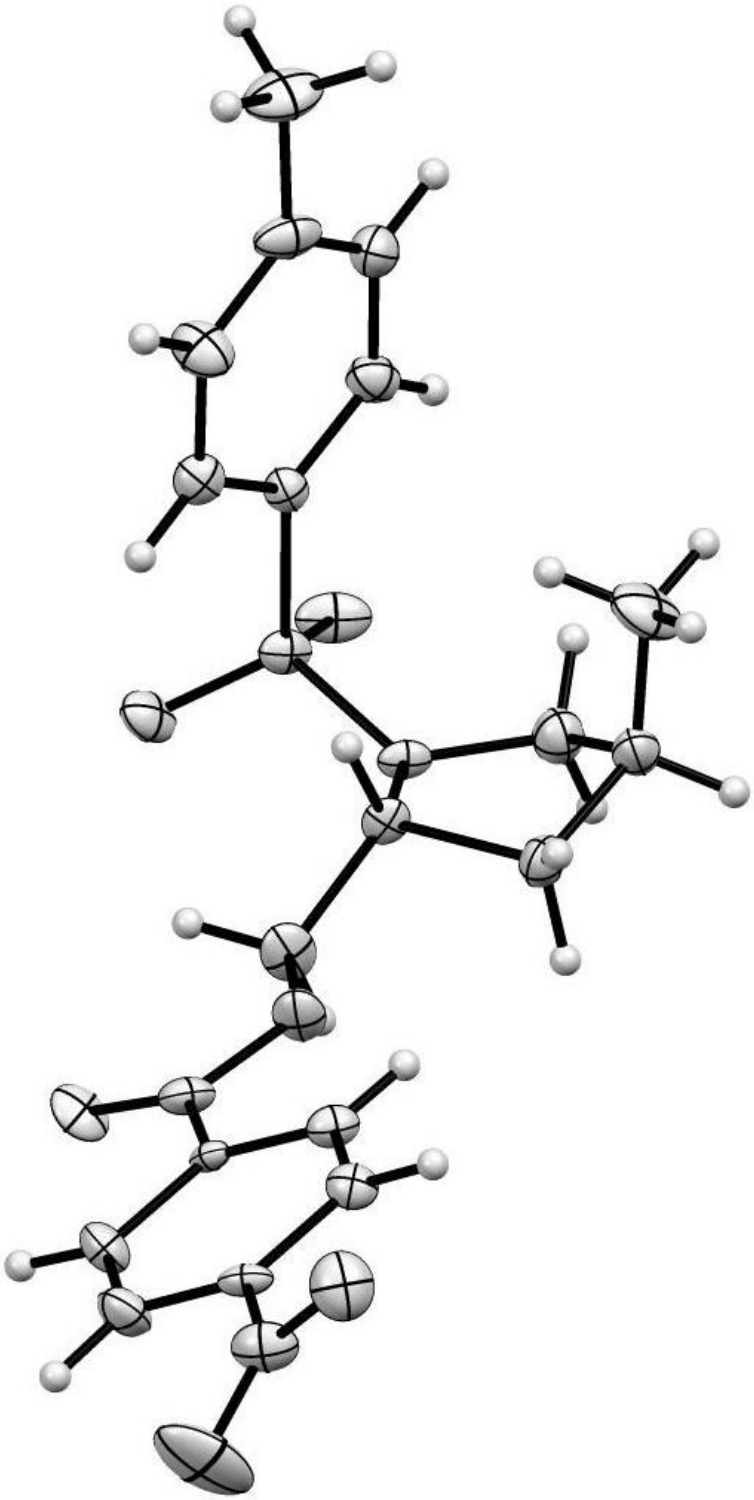


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of hygric acid **1**



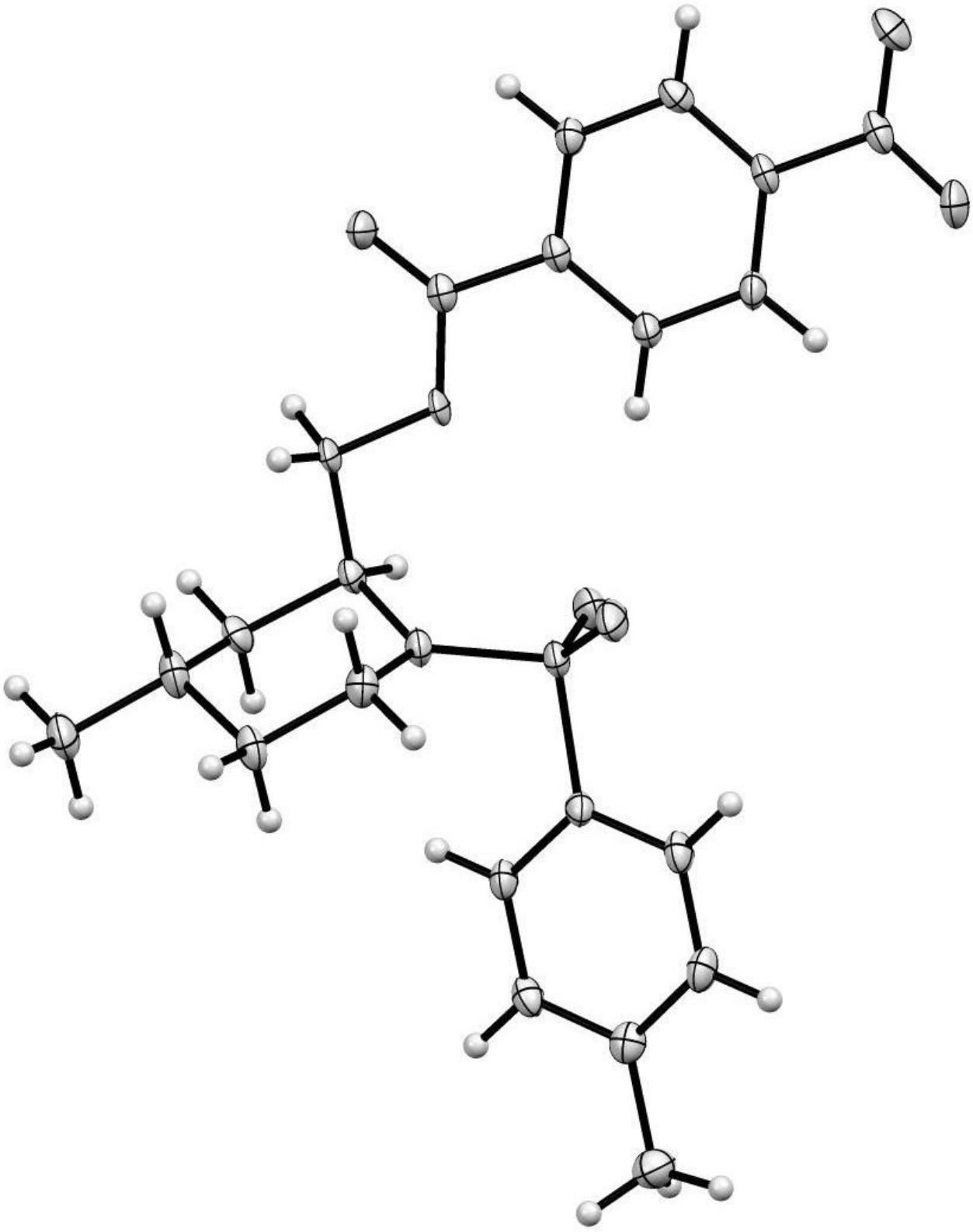


^{1}H NMR and ^{13}C{^{1}H} NMR spectra of pipecolic acid **3**



X-ray structure of pyrrolidine **11a** (*p*-nitrobenzoate ester)

ORTEP, 50% probability



X-ray structure of piperidine **19** (*p*-nitrobenzoate ester)

ORTEP, 50% probability

Sample and crystal data for pyrrolidine 11a.

Chemical formula	$C_{20}H_{22}N_2O_6S$	
Grown from	CH_2Cl_2:hexane 1:4	
Formula weight	418.45 g/mol	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal size	0.100 x 0.140 x 0.200 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.613(3) Å	α = 77.323(5)°
	b = 15.188(5) Å	β = 84.333(4)°
	c = 17.464(6) Å	γ = 89.849(5)°
Volume	1960.1(11) $Å^3$	
Z	4	
Density (calculated)	1.418 g/cm^3	
Absorption coefficient	0.206 mm^{-1}	
F(000)	880	

Data collection and structure refinement for pyrrolidine 11a.

Theta range for data collection	1.20 to 25.49°	
Index ranges	-9<=h<=9, -17<=k<=18, -21<=l<=21	
Reflections collected	7228	
Independent reflections	7228 [R(int) = 0.0602]	
Coverage of independent reflections	99.2%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9800 and 0.9600	
Structure solution technique	direct methods	
Structure solution program	XS, VERSION 2013/1	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	7228 / 60 / 528	
Goodness-of-fit on F^2	1.151	
Final R indices	5504 data; I>2σ(I)	R1 = 0.0954, wR2 = 0.2547
	all data	R1 = 0.1190, wR2 = 0.2687
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1047P)^2+7.7136P]$	
Absolute structure parameter	0.0(6)	
Largest diff. peak and hole	0.788 and -0.803 $eÅ^{-3}$	
R.M.S. deviation from mean	0.151 $eÅ^{-3}$	

Sample and crystal data for piperidine 19 (*p*-nitrobenzoate ester).

Chemical formula	$C_{21}H_{24}N_2O_6S$	
Grown from	CH_2Cl_2:hexane 1:4	
Formula weight	432.48 g/mol	
Temperature	223(2) K	
Wavelength	0.71073 Å	
Crystal size	0.200 x 0.240 x 0.300 mm	
Crystal habit	colorless block	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.5182(15) Å	α = 89.926(4)°
	b = 9.9604(15) Å	β = 89.896(4)°
	c = 10.7803(17) Å	γ = 89.878(4)°
Volume	1022.0(3) $Å^3$	
Z	2	
Density (calculated)	1.405 g/cm^3	
Absorption coefficient	0.200 mm^{-1}	
F(000)	456	

Data collection and structure refinement for piperidine 19 (*p*-nitrobenzoate ester).

Theta range for data collection	1.89 to 29.43°
Index ranges	-13<=h<=13, -13<=k<=13, -14<=l<=14
Reflections collected	49336
Independent reflections	5546 [R(int) = 0.1142]
Coverage of independent reflections	99.0%
Absorption correction	Multi-Scan
Max. and min. transmission	0.9610 and 0.9420
Structure solution technique	direct methods
Structure solution program	XS, VERSION 2013/1
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2014/7 (Sheldrick, 2014)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5546 / 0 / 274
Goodness-of-fit on F^2	0.947
Final R indices	4827 data; I>2σ(I) R1 = 0.0624, wR2 = 0.1522
	all data R1 = 0.0761, wR2 = 0.1637
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.1000P)^2+1.2595P]$
Largest diff. peak and hole	0.529 and -0.566 $eÅ^{-3}$
R.M.S. deviation from mean	0.084 $eÅ^{-3}$