Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Eco-friendly reactions in PEG-400: highly efficient and green approach for stereoselective access to multisubstituted 3,4-dihydro-2(1*H*)-quinazolines using 2-aminobenzylamines

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X-ray Crystallographic Studies

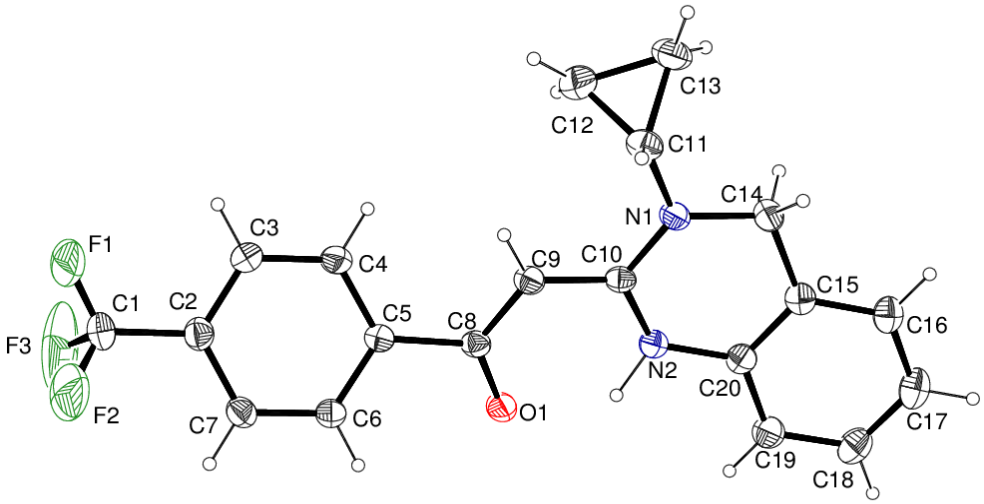


Figure 1. ORTEP Structure of compound 4o

The intensity data for 4o was collected on an Oxford CCD diffractometer with an Xcalibur sapphire diffraction measurement Mo-Kα radiation (λ = 0.71073 Å) at 293(2) K[1]. A multi-scan correction was applied. The structure was solved by the direct methods using SIR-92 and refined by full-matrix least-squares refinement techniques on F^2 using SHELXL97[2]. The hydrogen atoms were placed into the calculated positions and included in the last cycles of the refinement. All calculations were done using Wingx software package[3].

Table1. Crystal data collection and structure refinement parameters for **4o**

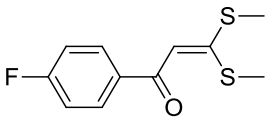
Empirical formula	$C_{20}H_{17}F_3N_2O$
Formula weight	358.36
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	*P* -1
a	7.2030(7) Å
b	10.0784(8) Å
c	13.335(2) Å
α	108.279(9)°
β	92.593(10)°
γ	107.656(8)°
Volume	865.30(17) $Å^3$
Z	2
Density (calculated)	1.375 Mg/m^3
Absorption coefficient	0.108 mm^{-1}
F(000)	372
Crystal size	0.22 x 0.19 x 0.18 mm^3
Theta range for data collection	3.10 to 25.00°
Index ranges	$-8 \leq h \leq 6$, $-11 \leq k \leq 11$, $-15 \leq l \leq 15$
Reflections collected	5952
Independent reflections	3048 [*R*(int) = 0.0143]
Completeness to theta = 25.00°	99.9 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9808 and 0.9767
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3048 / 0 / 236
Goodness-of-fit on F^2	1.051
Final *R* indices [I>2sigma(I)][a, b]	R_1 = 0.0852, wR_2 = 0.2504
R indices (all data)	R_1 = 0.1057, wR_2 = 0.2691
Extinction coefficient	0.034(9)
Largest diff. peak and hole	0.826 and -0.576 $e.Å^{-3}$

[a] $R = \sum(\|Fo| - |Fc\|)/\sum|Fo|$; [b] $wR = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^1$

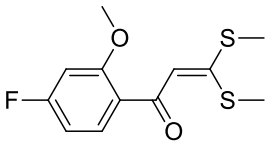
General procedure for the synthesis of α-oxoketene dithioacetals (3a-c)

The procedure for the synthesis of α-oxoketene dithioacetals is previously reported.[4] Compounds **2a-c** are previously reported.[4] The structure and purity of known starting material was confirmed by comparison of physical and spectral data (^{1}H NMR, ^{13}C NMR) with those reported in literature.

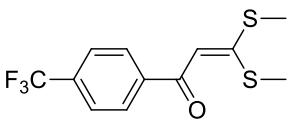
Analytical data of α-oxoketene dithioacetals



1-(4-Fluoro-phenyl)-3,3-bis-methylsulfanyl-propenone (3a) The compound was obtained as a yellow crystalline solid, mp 83-85°C: IR (ν_{max}cm^{-1}) ($CHCl_3$): 2919, 1597, 1470; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.92-7.88 (m, 2H), 7.08 (t, *J* = 8.79Hz, 2H), 6.68 (s, 1H, vinylic CH), 2.51 (s, 6H, 2 x SCH_3); **^{13}C NMR** (100 MHz,$CDCl_3$) δ: 184.05, 166.9, 166.1, 163.6, 135.3, 129.8, 115.3, 108.9 (vinylic CH), 17.3 (-SCH_3), 15.0 (-SCH_3) ; **HRMS** (ESI) $(M+H)^+$ Calcd for $C_{11}H_{11}FOS_2$: 243.0313, found 243.0306.



1-(4-Fluoro-2-methoxy-phenyl)-3,3-bis-methylsulfanyl-propenone (3b)
The compound was obtained as a pale yellow solid, mp 96-98°C: **IR** (ν_{max}cm^{-1}) ($CHCl_3$): 2920, 1592, 1471 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.77 (dd, *J* = 8.79, 7.32 Hz, 1H), 6.84 (s, 1H, vinylic CH), 6.68 (td, *J* = 8.79, 8.05 Hz, 2.2, 1H), 6.62 (dd, *J* = 10.98, 2.2 Hz, 1H), 3.8 (s, 3H, Ar-OCH_3), 2.48 (s, 3H, (-SCH_3), 2.47 (s, 3H, -SCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 184.3, 166.5, 164.0, 158.8, 132.6, 125.7, 114.4, 107.7(vinylic CH), 99.4, 55.7 (Ar-OCH_3), 17.2(-SCH_3), 15.0(-SCH_3).



3,3-Bis-methylsulfanyl-1-(4-trifluoromethyl-phenyl)-propenone (3c)
The compound was obtained as a dark yellow solid, mp 84-86°C: **IR** (ν_{max}cm^{-1}) ($CHCl_3$): 2992, 1480, 1323 ; **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 7.98 (d, *J* = 8.05 Hz, 2H), 7.67 (d, *J* = 8.05 Hz, 2H), 6.7 (s, 1H,vinylic CH), 2.56 (s, 3H, -SCH_3), 2.53 (s, 3H, -SCH_3); **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 184.1, 168.8, 142.0, 127.9, 125.4, 108.6 (vinylic CH), 17.3(-SCH_3), 15.0(-SCH_3) ; **HRMS** (ESI) $(M+H)^+$ Calcd for $C_{12}H_{11}F_3OS_2$: 293.0281, found 293.0273.

References:

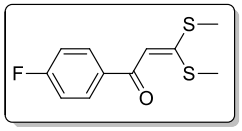
1. *CrysAlisPro*, v. 1.171.33.49b, Oxford Diffraction Ltd., Abingdon, UK, **2009**.

2. G. M. Sheldrick, *Acta Cryst.*, **2008**, A64, 112-122.

3. L. J. Farrugia, WinGX Version 1.80.05, *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 (**1997-2009**).

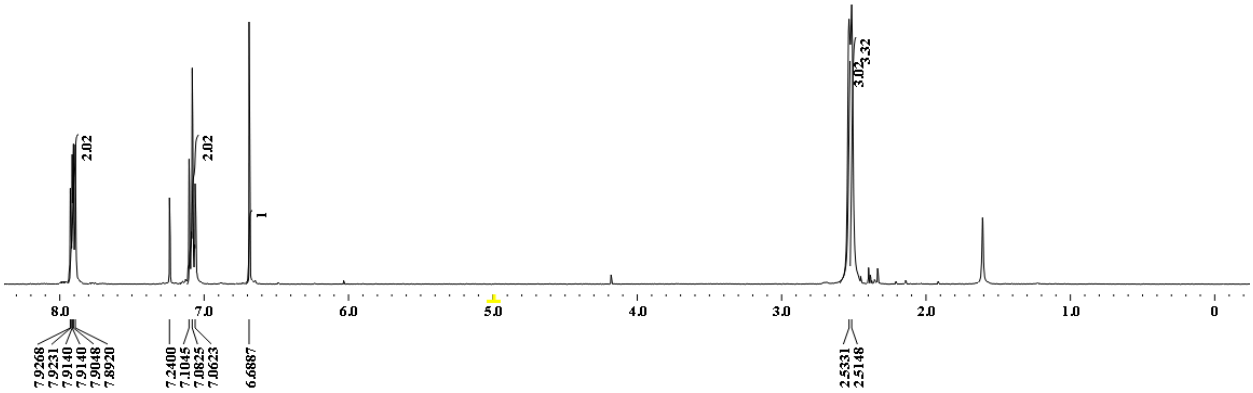
4. N. Sharma, T.S. Chundawat, S. C. Mahopatra, S. Bhagat, *RSC Advances*, **2013**, 3, 16336-16339.

COPIES OF ^{1}HNMR & ^{13}CNMR DATA

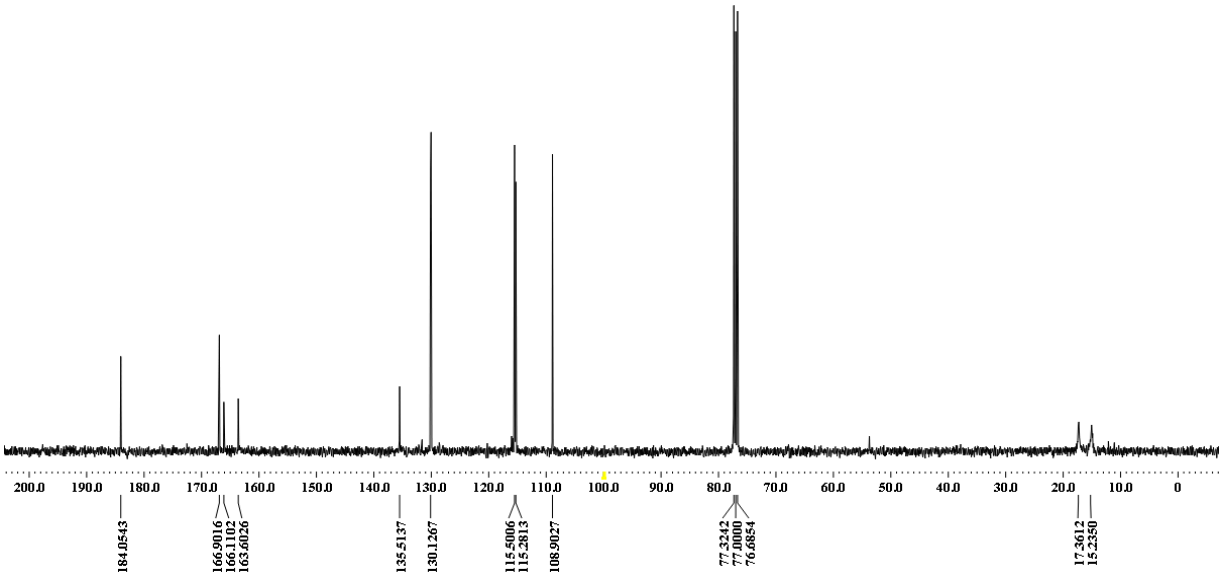


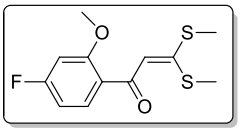
3a

^{1}H-NMR in $CDCl_3$ (400MHz)



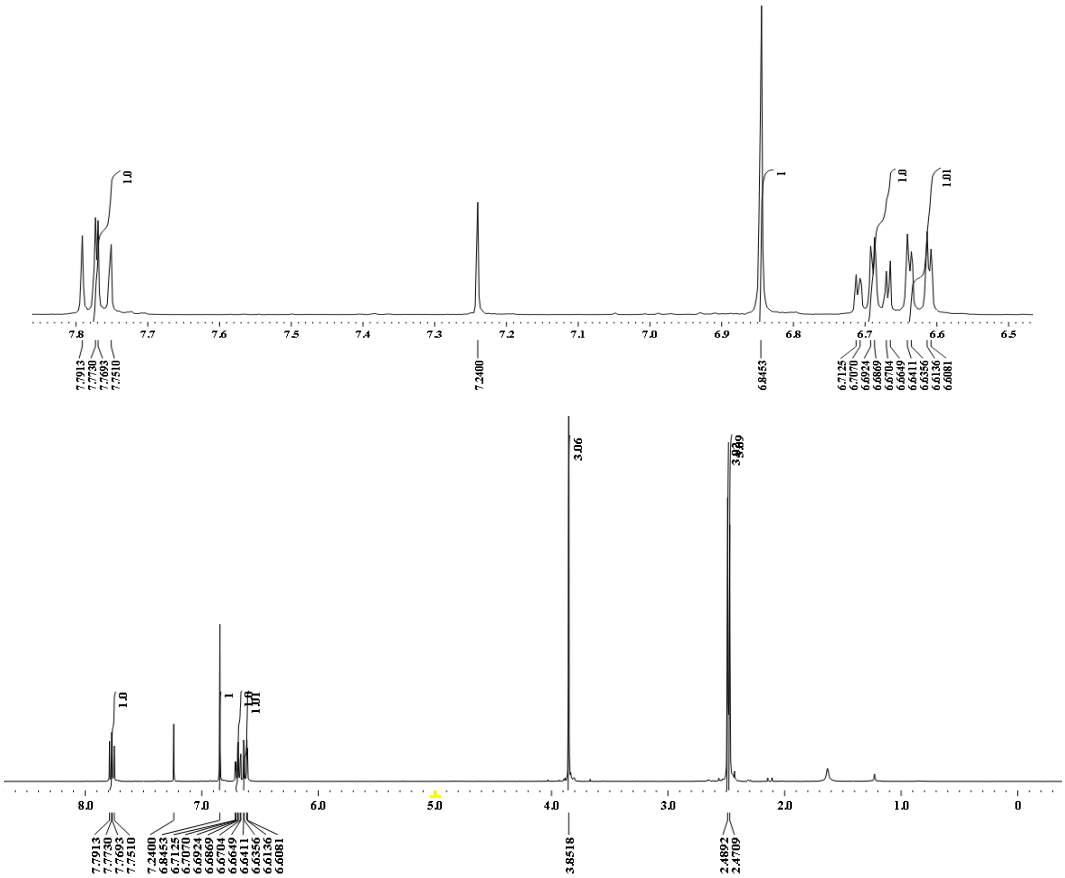
^{13}C NMR in $CDCl_3$ (100MHz)





3b

^{1}H-NMR in $CDCl_3$ (400MHz)



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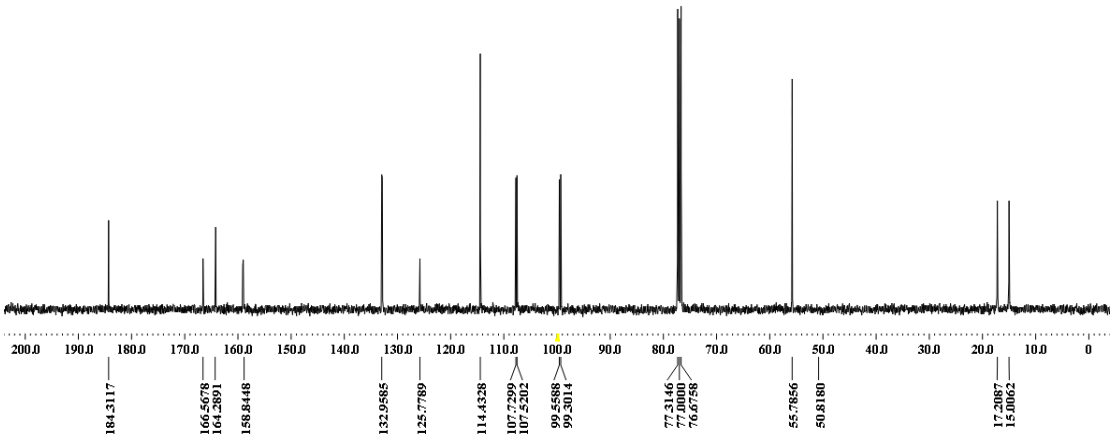
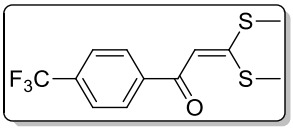
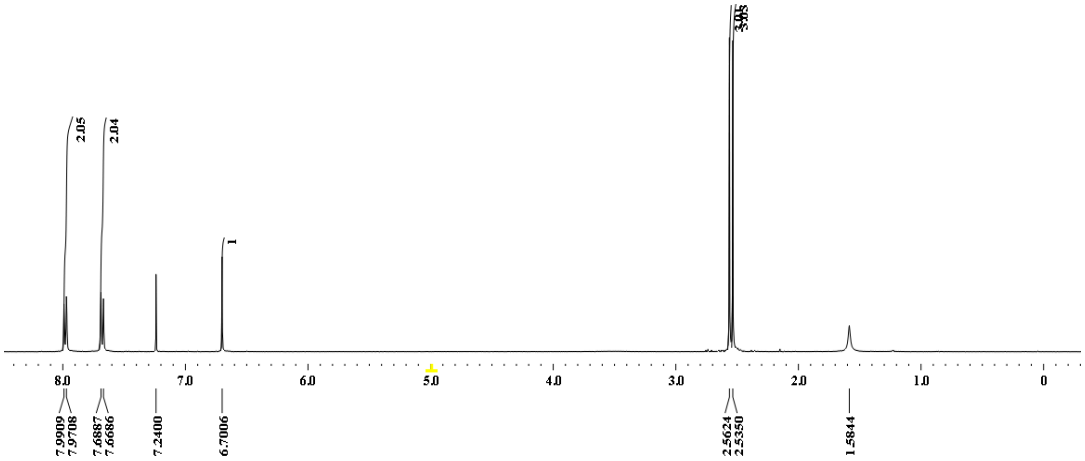




3c

^{1}H-NMR in $CDCl_3$ (400MHz)



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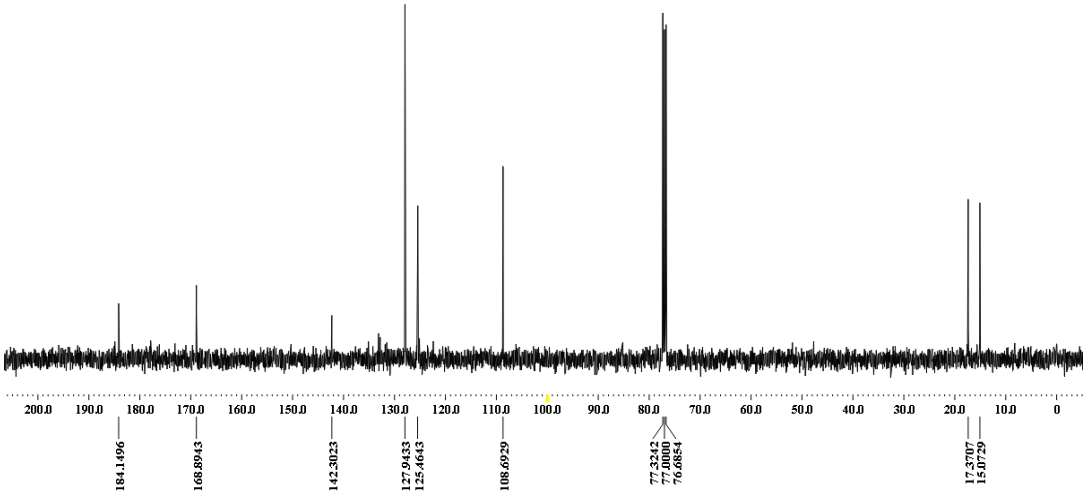
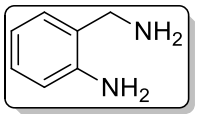
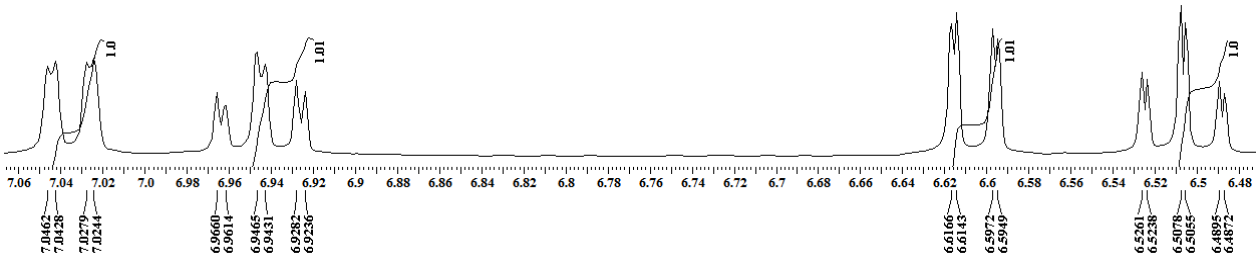
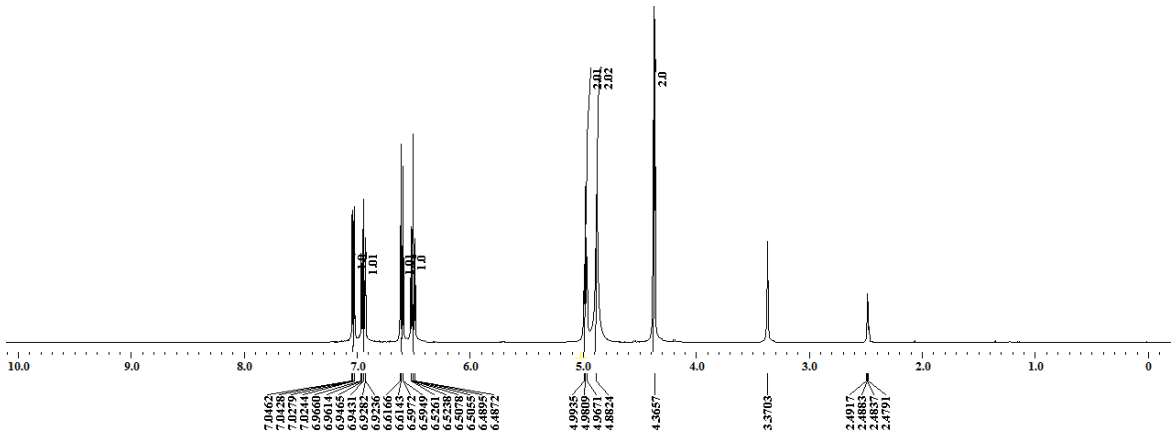




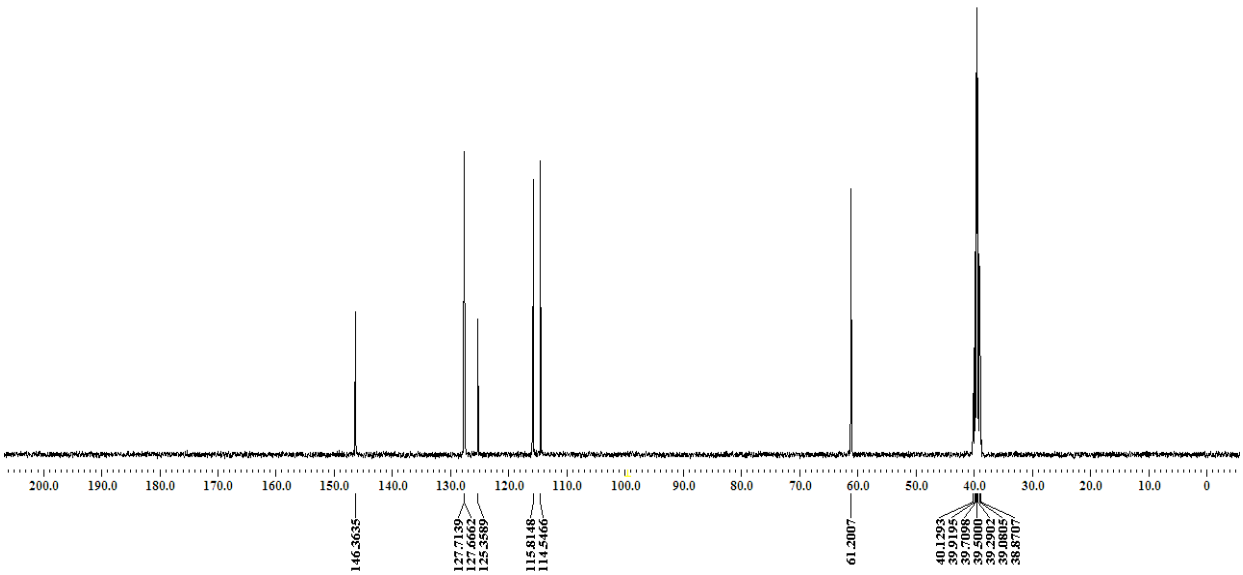
2a

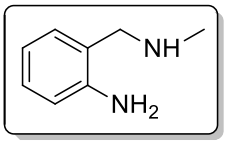
^{1}H NMR in DMSO-d$_6$ (400Mz)





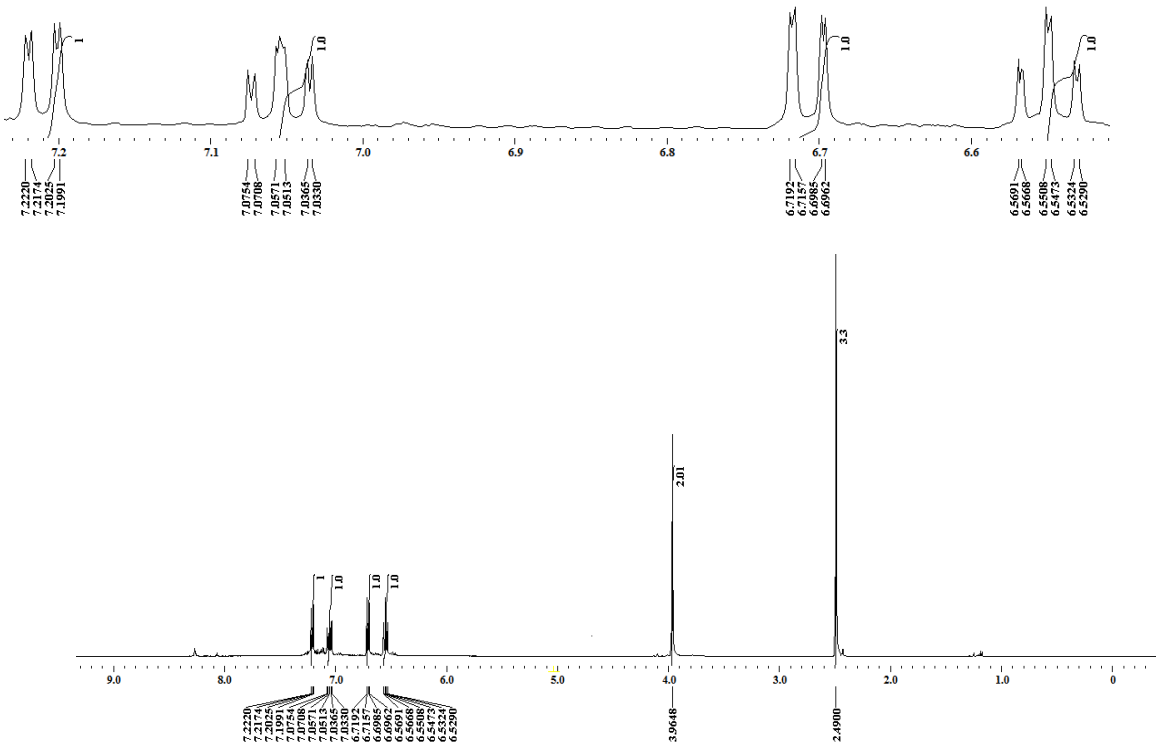
^{13}C-NMR in DMSO-d$_6$ (100MHz)



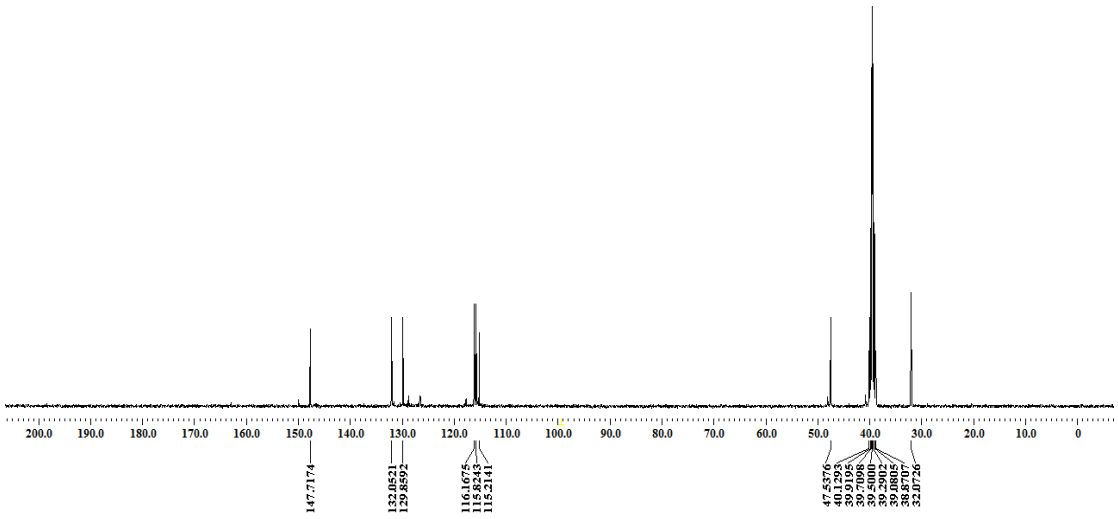


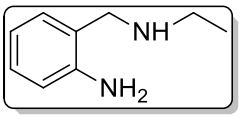
2b

^{1}H NMR in DMSO-d$_6$ (400Mz)



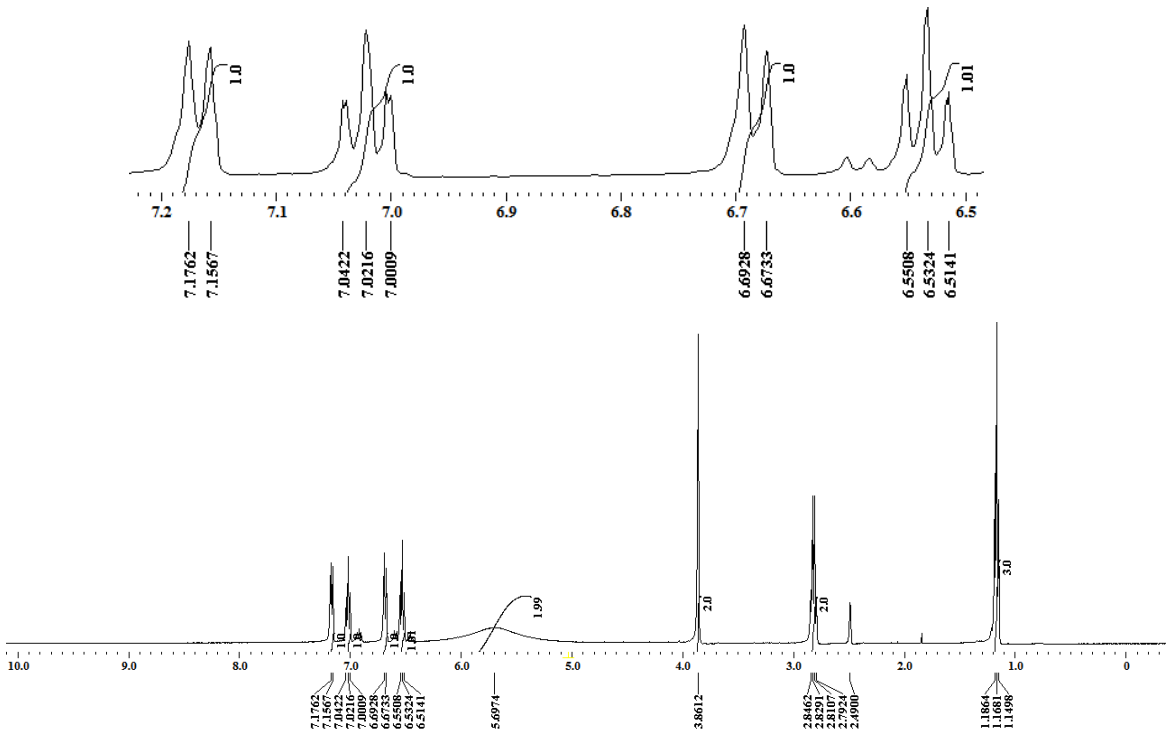
^{13}C-NMR in DMSO-d$_6$ (100MHz)



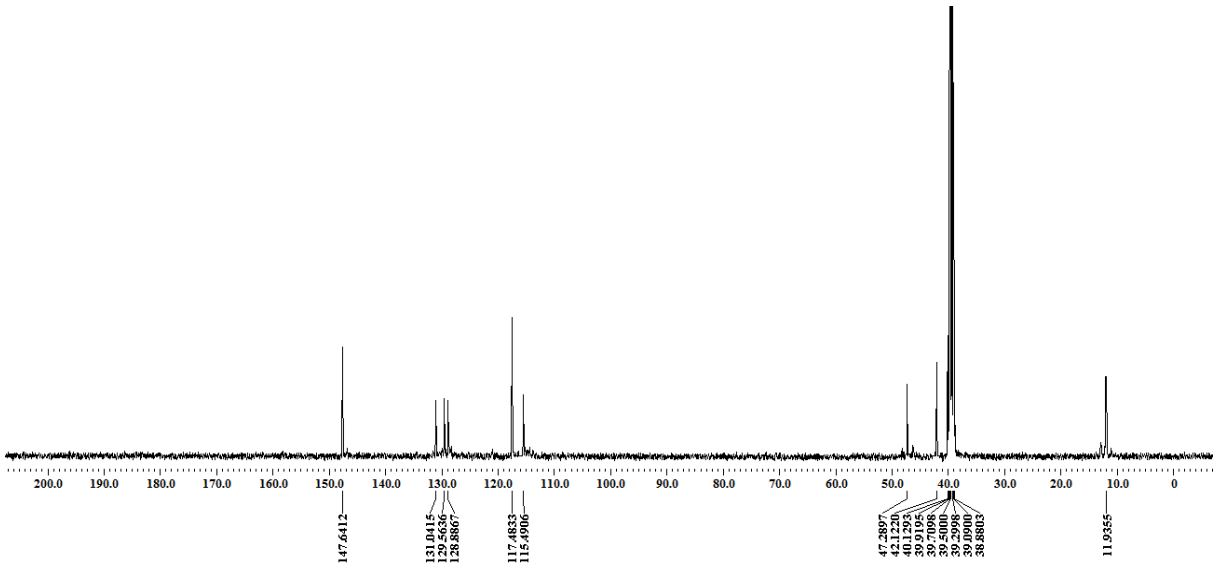


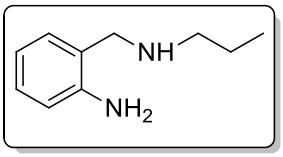
2c

^{1}H NMR in DMSO-d$_6$ (400Mz)



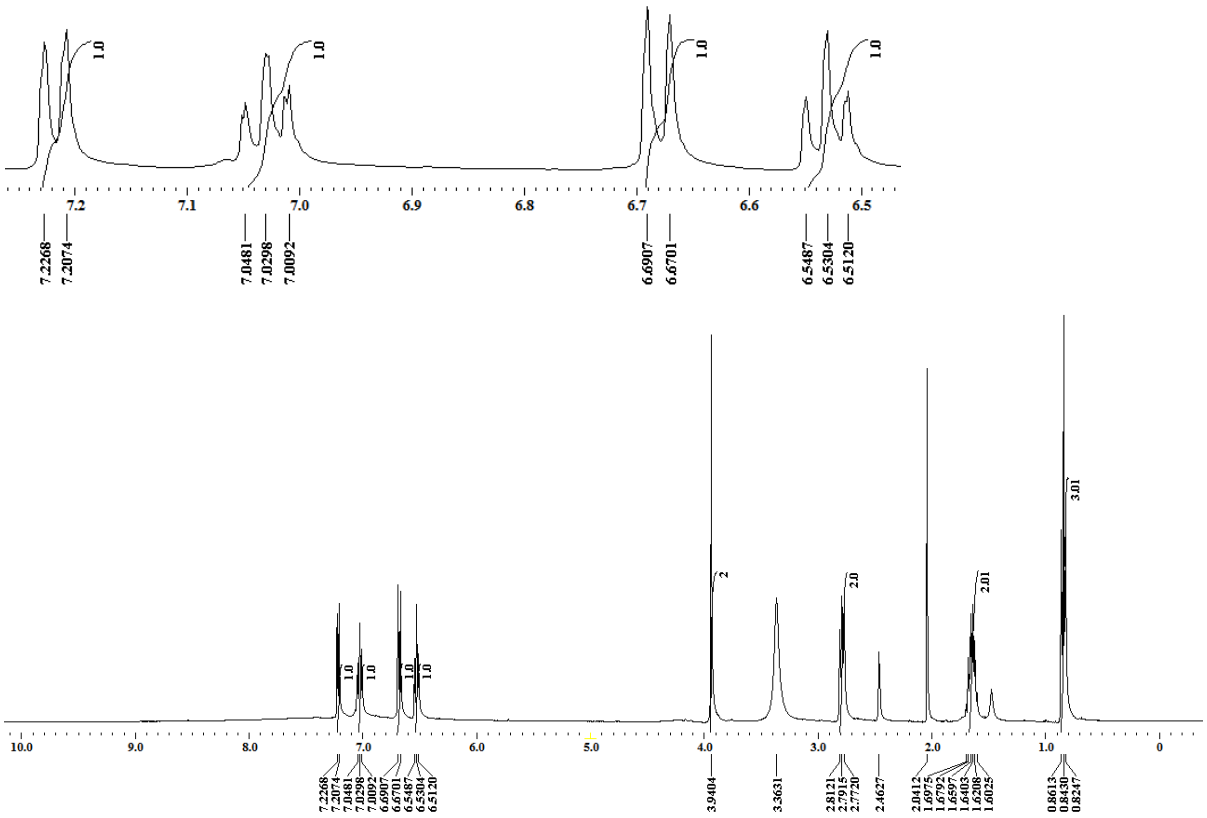
^{13}C-NMR in DMSO-d$_6$ (100MHz)



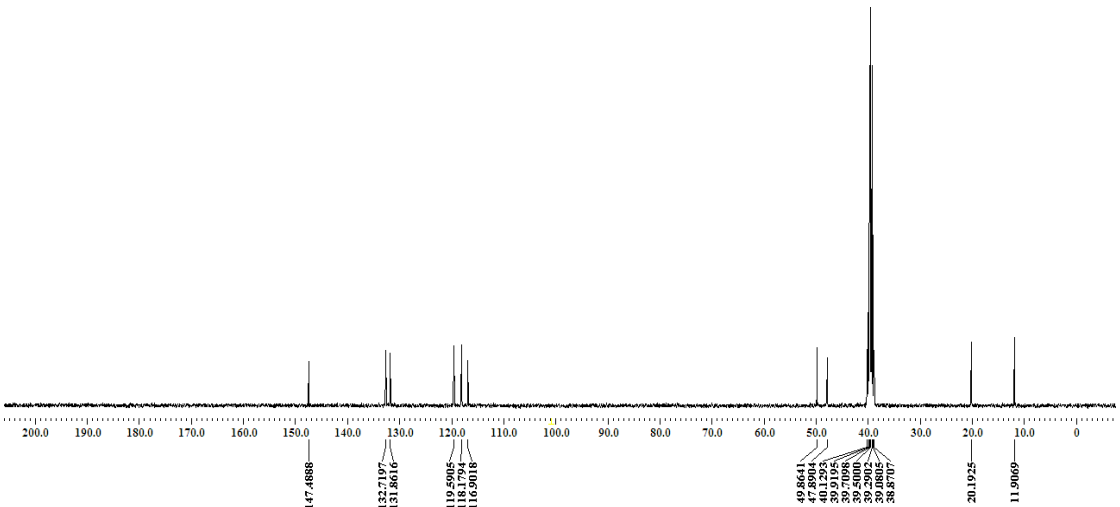


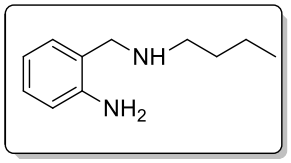
2d

^{1}H NMR in DMSO-d_6 (400Mz)



^{13}C-NMR in DMSO-d_6 (100MHz)





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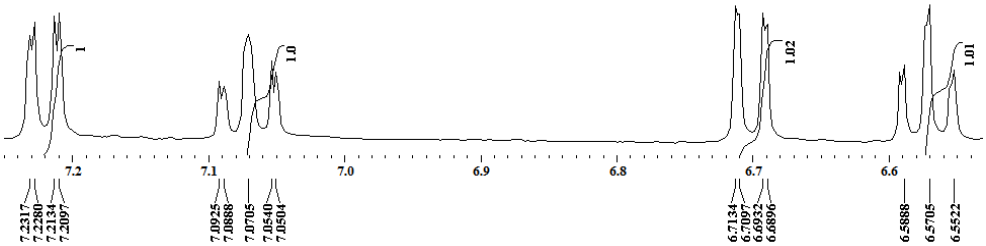
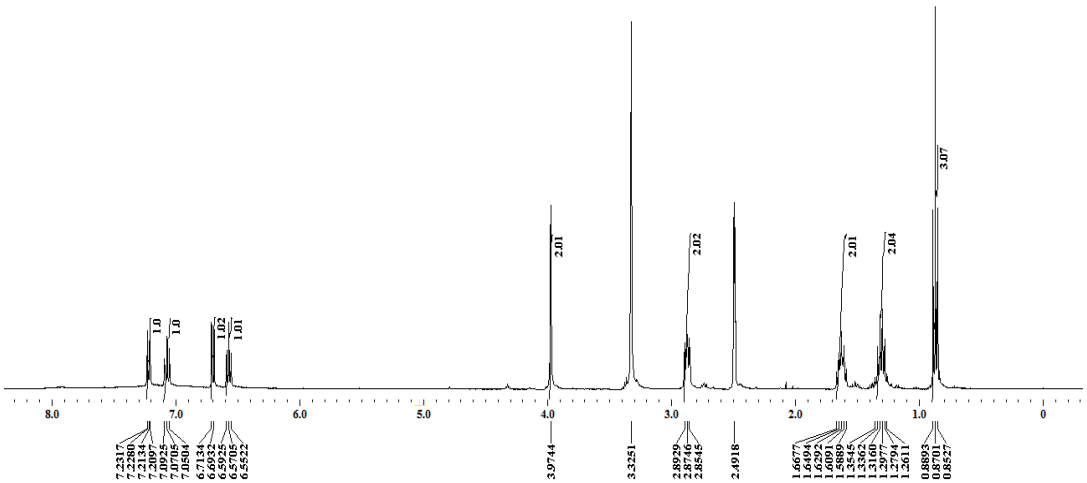
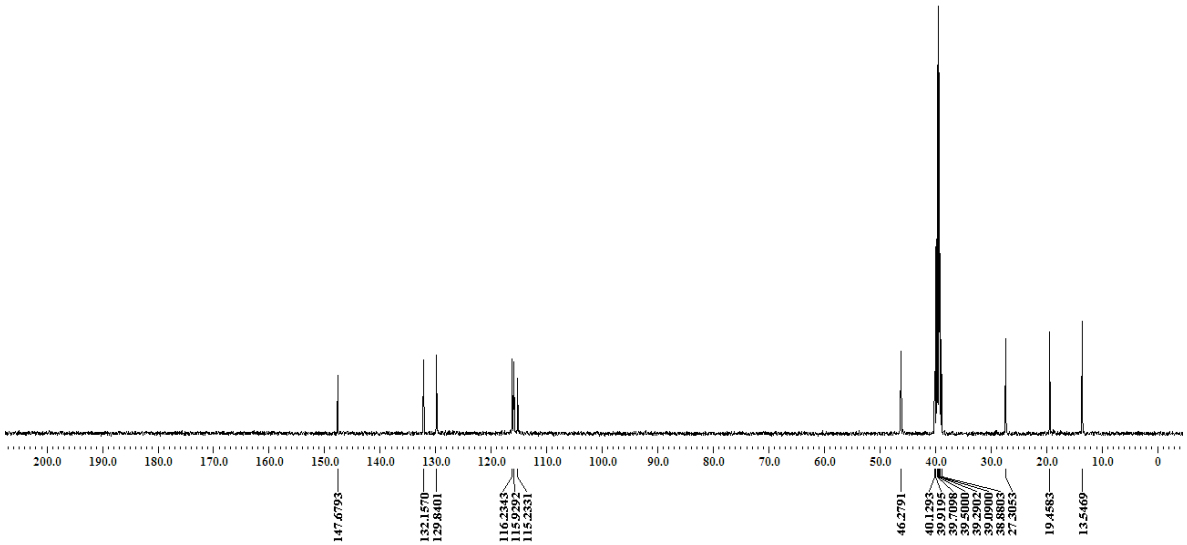
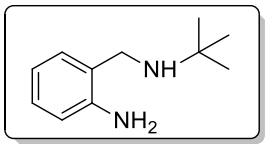
^{1}H NMR in DMSO-d$_6$ (400Mz)





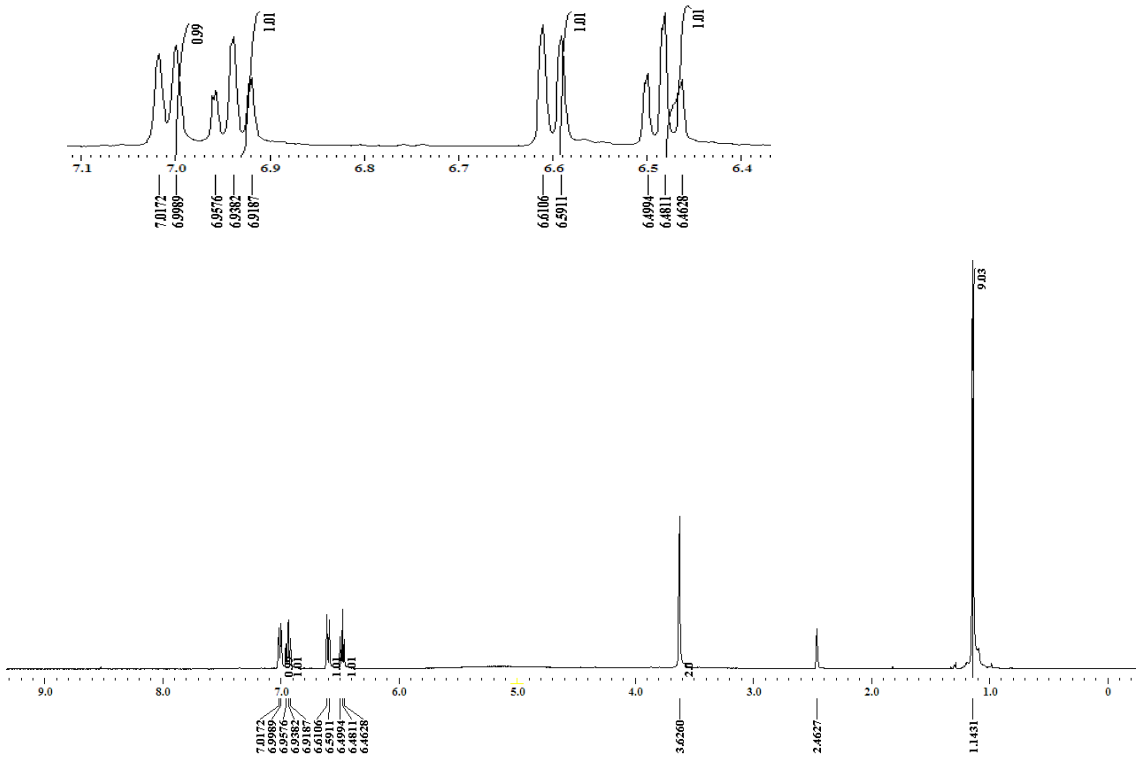
^{13}C NMR in DMSO-d$_6$ (100Mz)



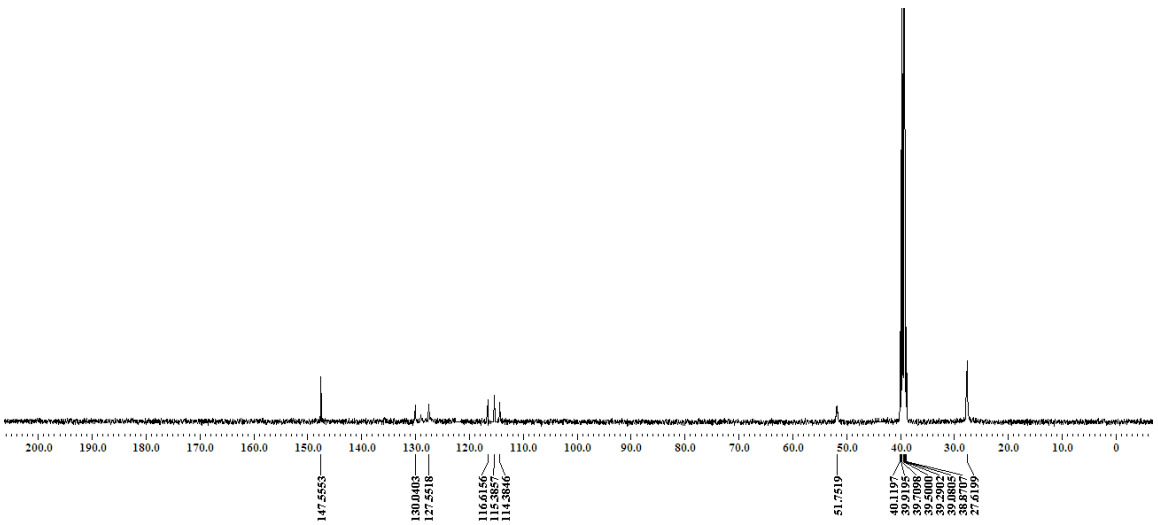


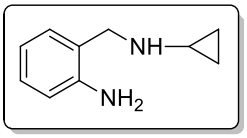
2g

^{1}H NMR in DMSO-d$_6$ (400Mz)



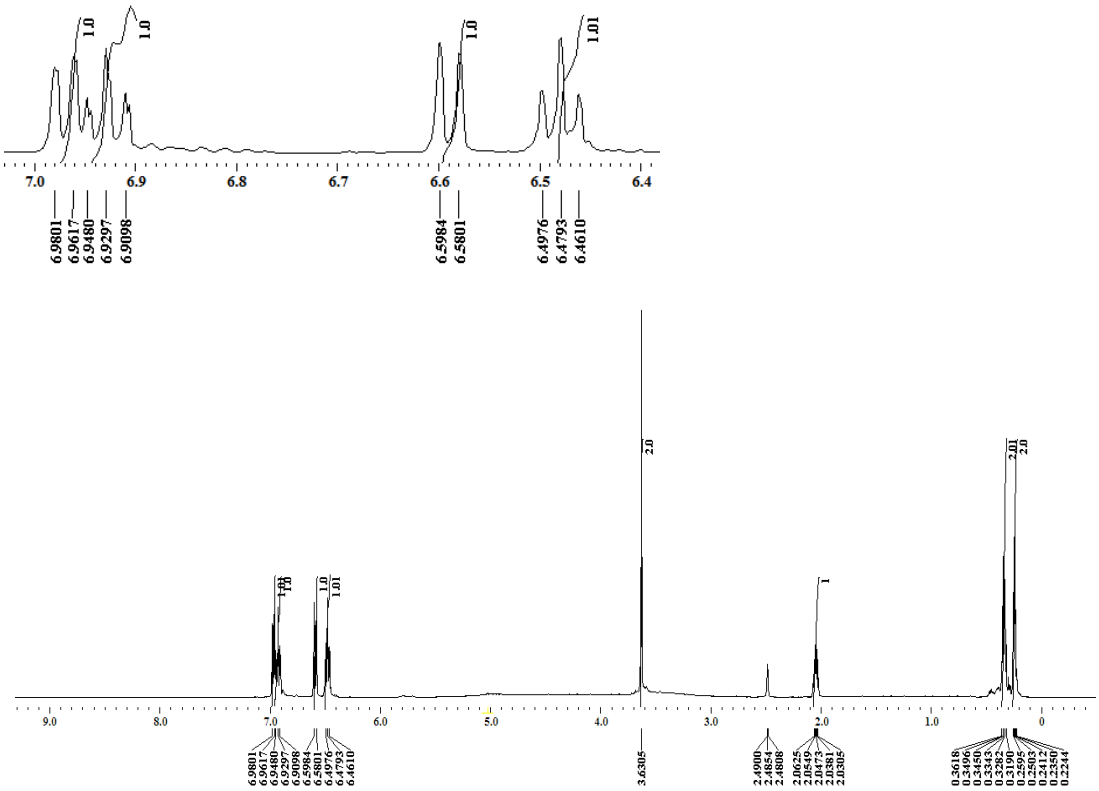
^{13}C NMR in DMSO-d$_6$ (100Mz)



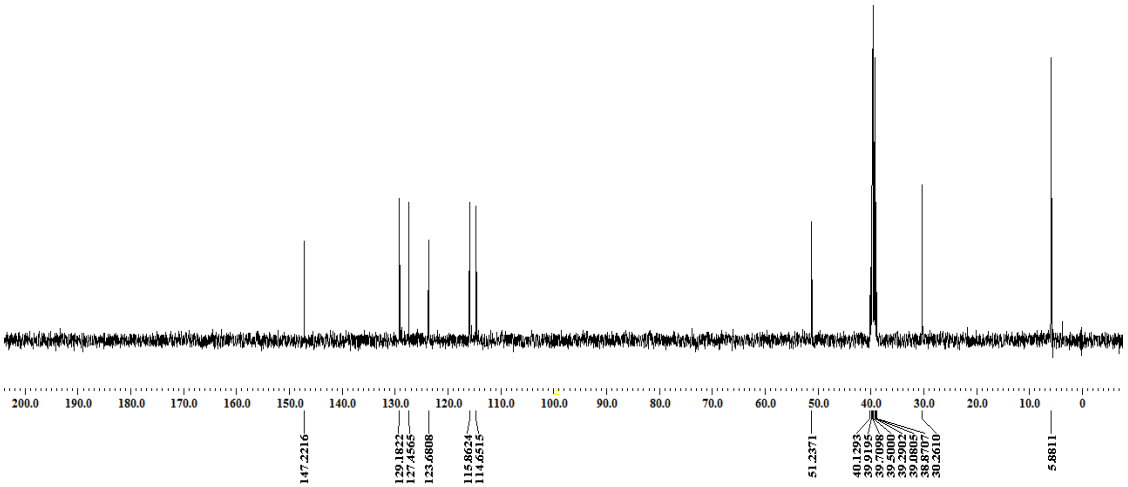


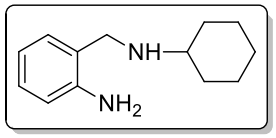
2h

^{1}H NMR in DMSO-d$_6$ (400Mz)



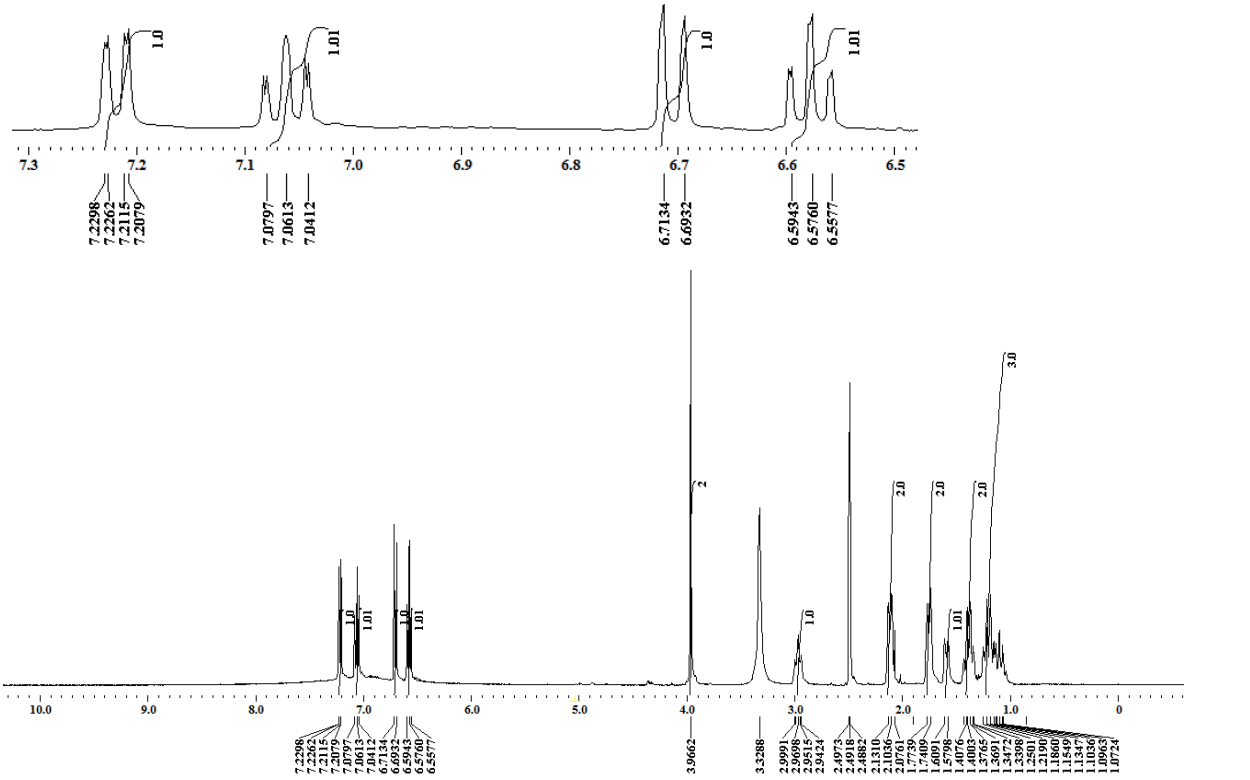
^{13}C NMR in DMSO-d$_6$ (100Mz)



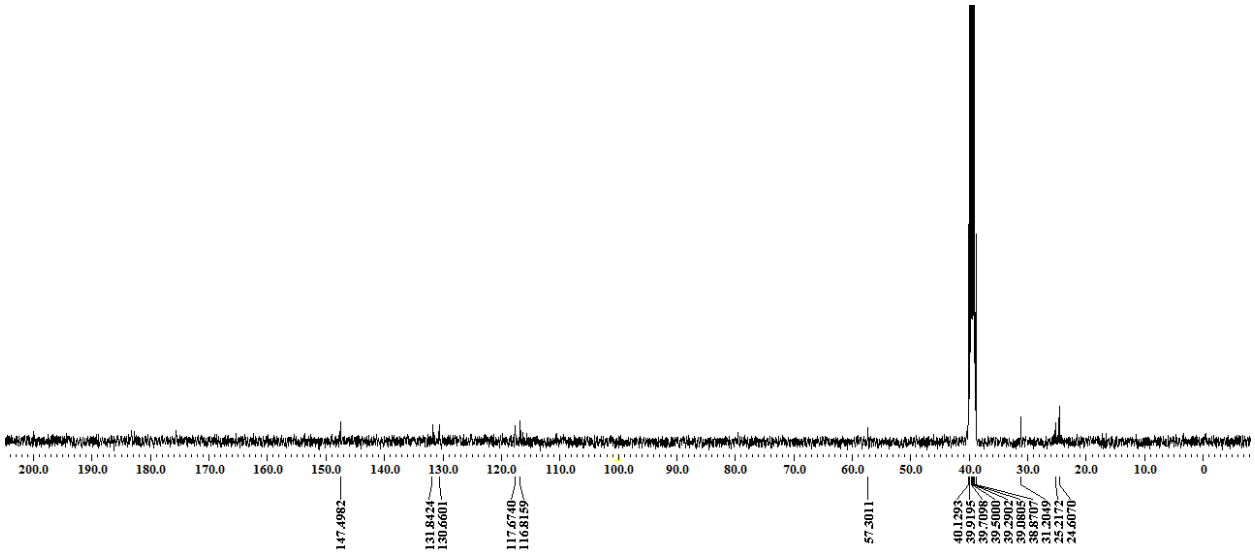


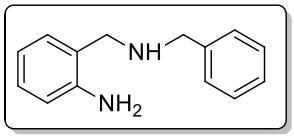
2i

^{1}H NMR in DMSO-d$_6$ (400Mz)



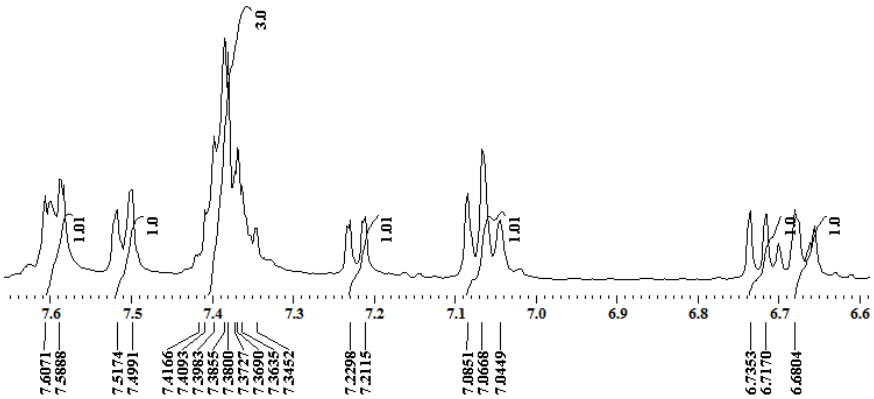
^{13}C NMR in DMSO-d$_6$ (100Mz)

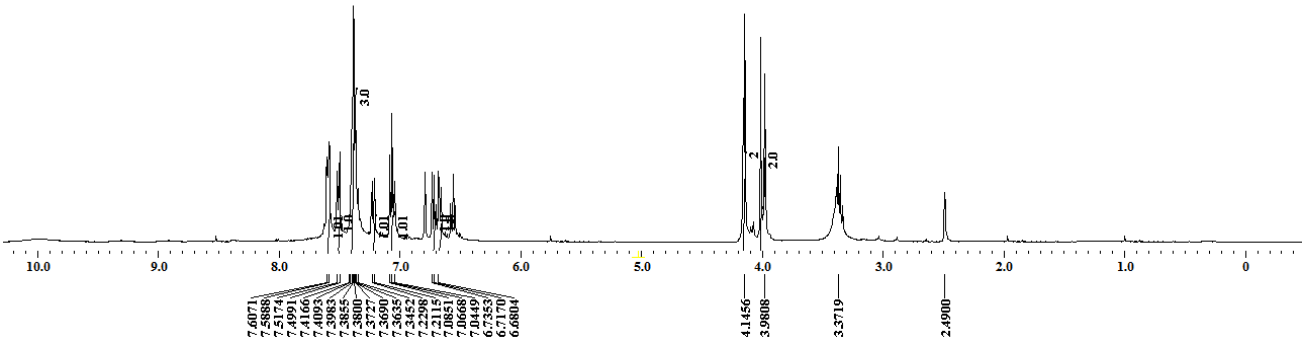


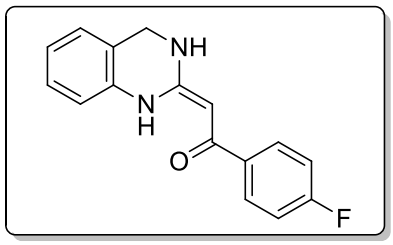


2j

^{1}H NMR in DMSO-d$_6$ (400Mz)

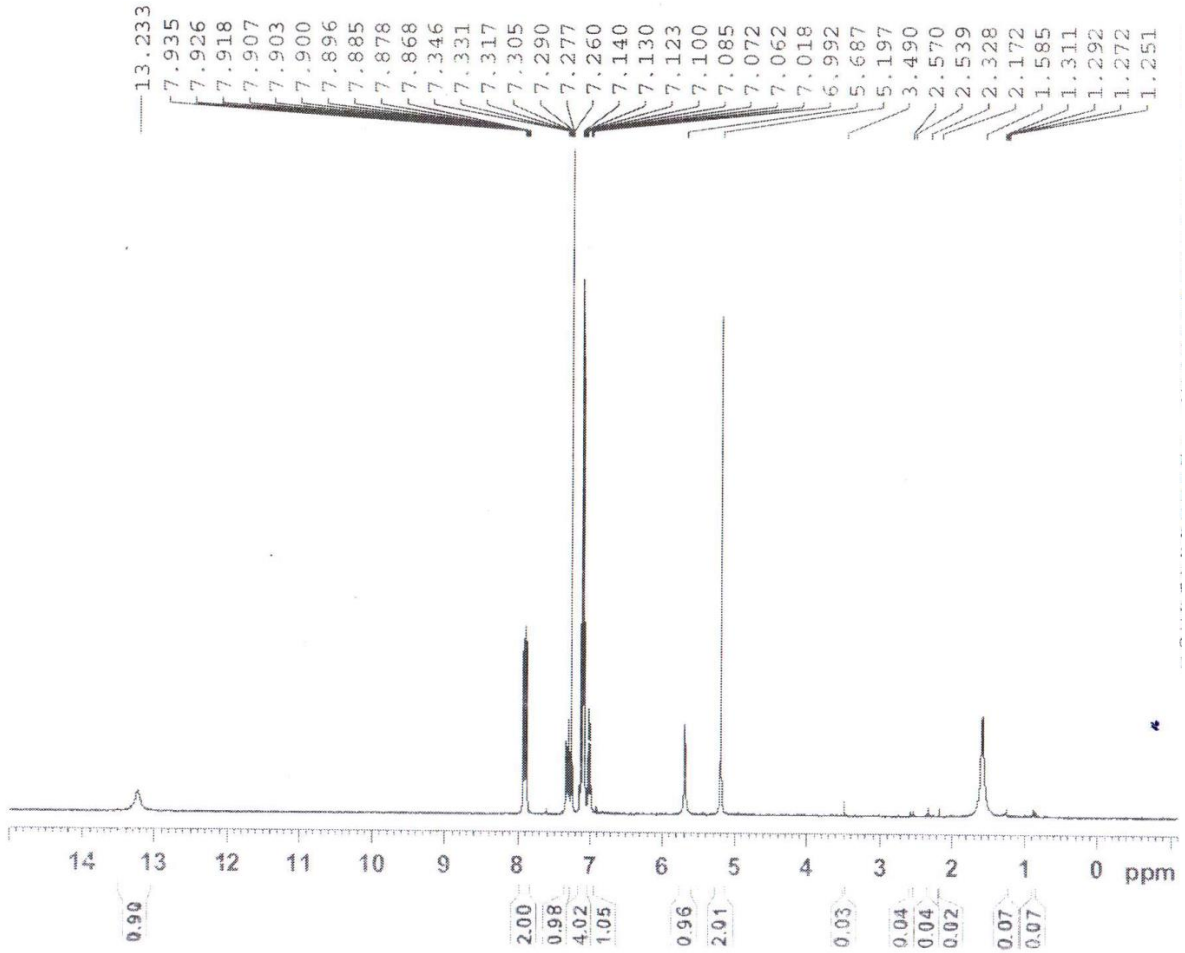


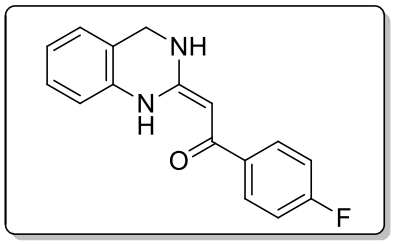




4a

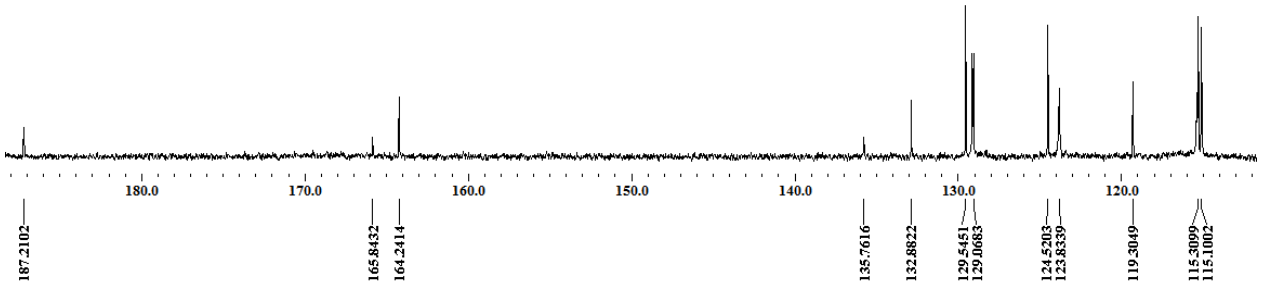
^{1}H-NMR in $CDCl_3$ (400MHz)

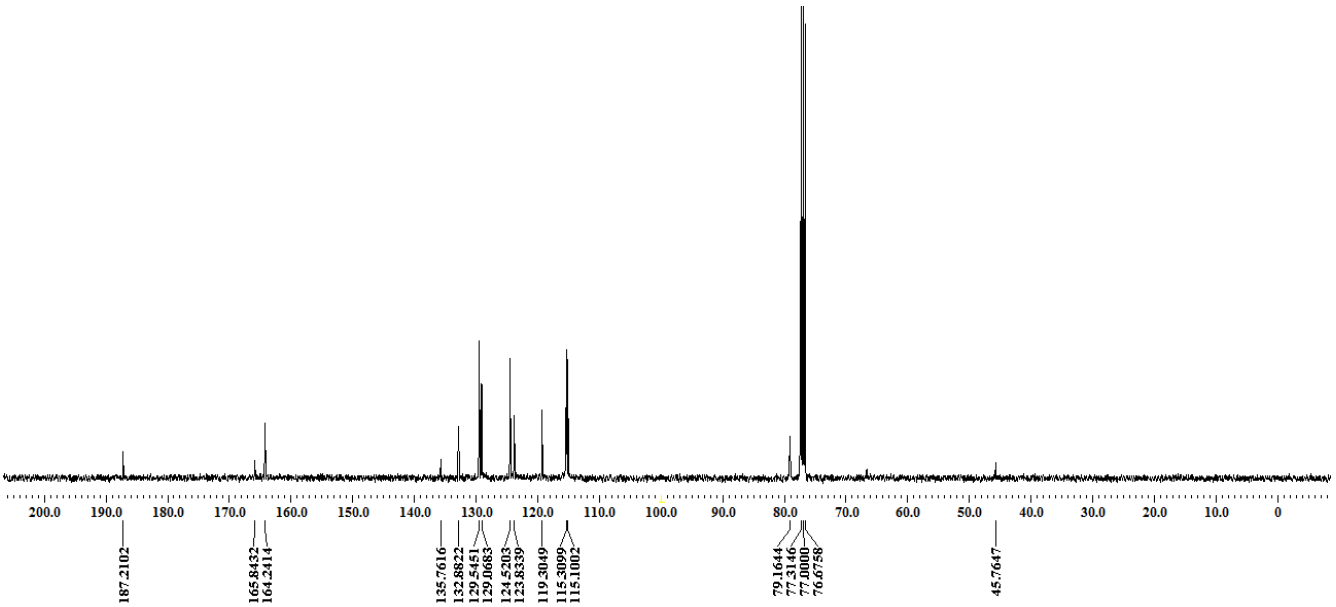


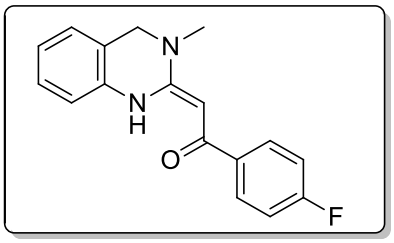


4a

^{13}C NMR in $CDCl_3$ (100MHz)

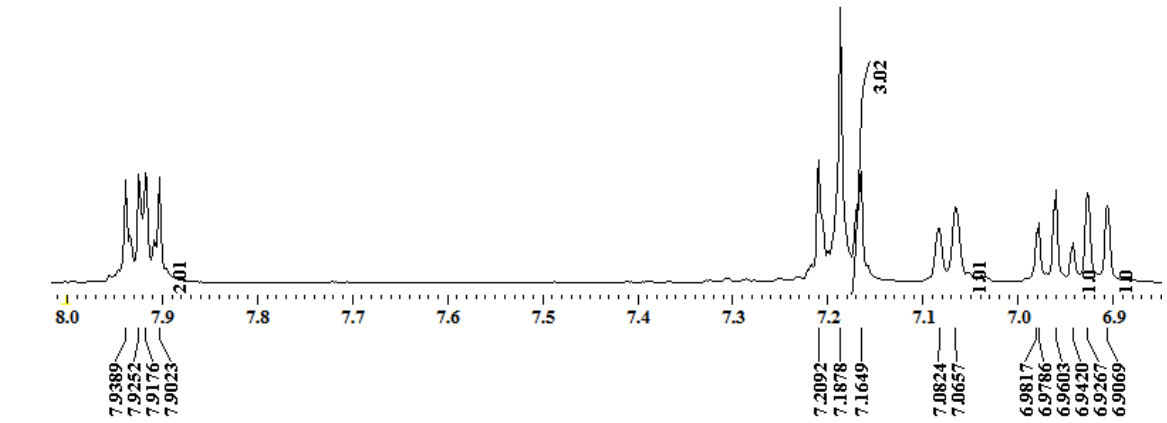


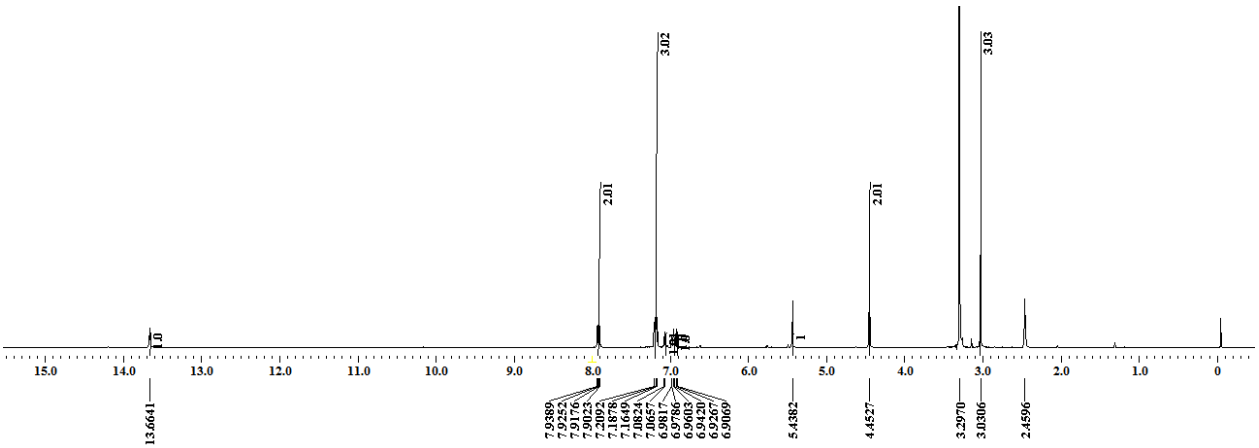


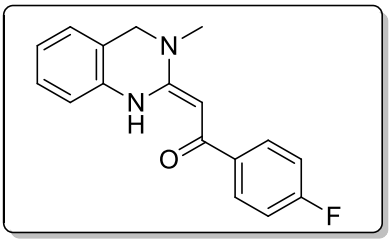


4b

^{1}H-NMR in DMSO-d_6 (400MHz)

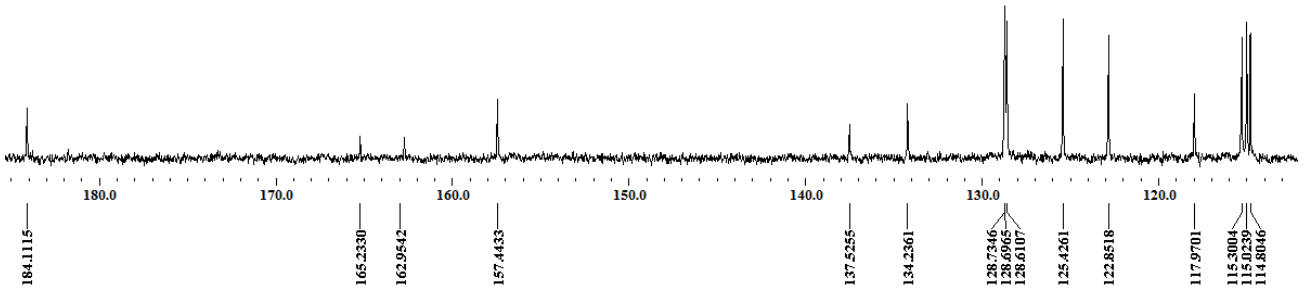


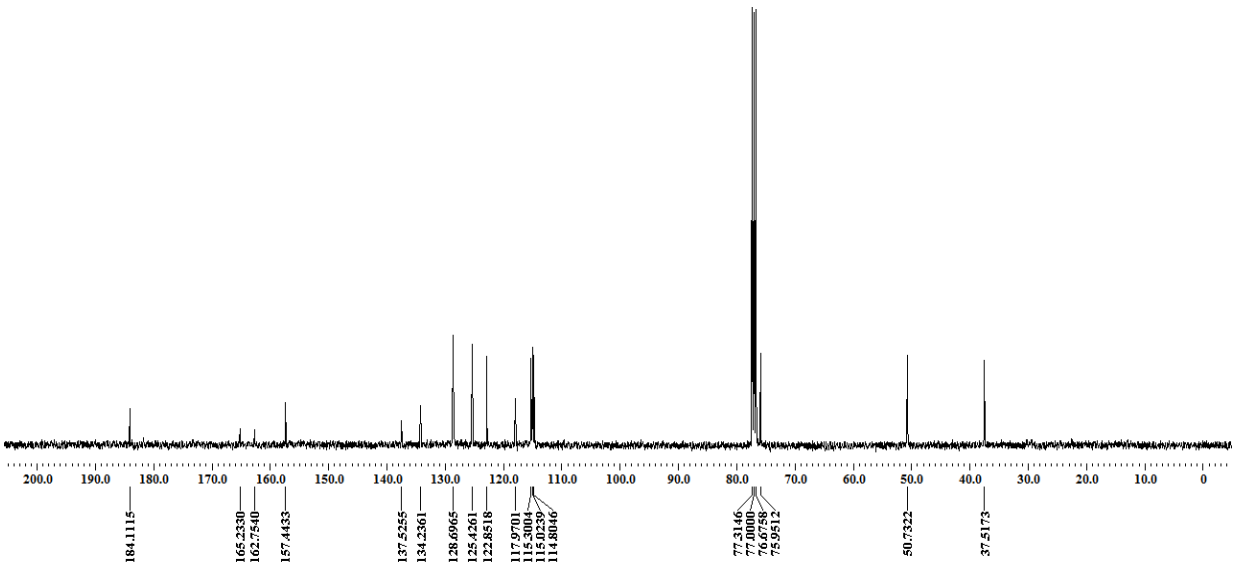


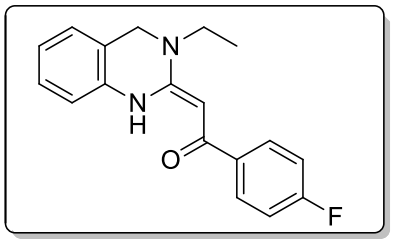


4b

^{13}C NMR in $CDCl_3$ (100MHz)

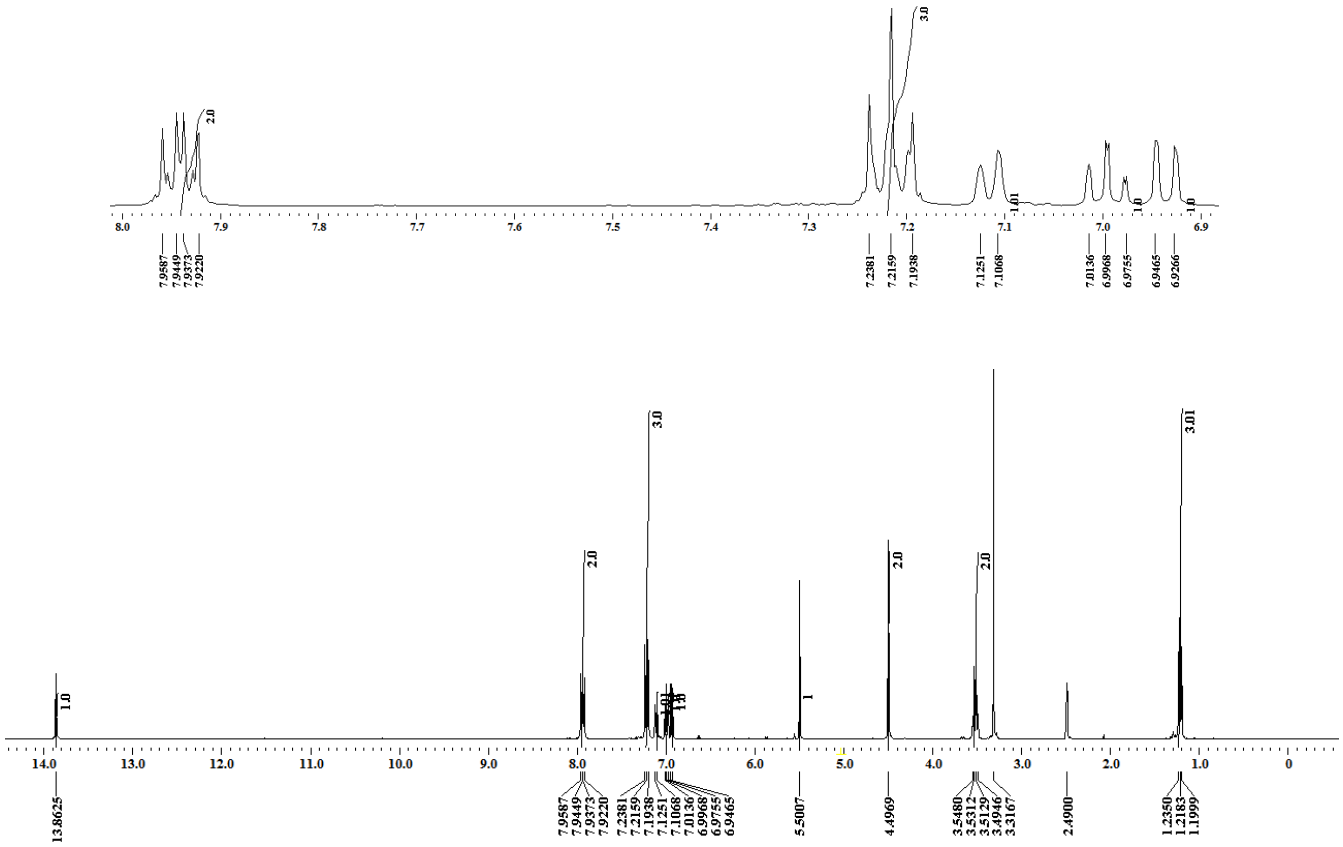


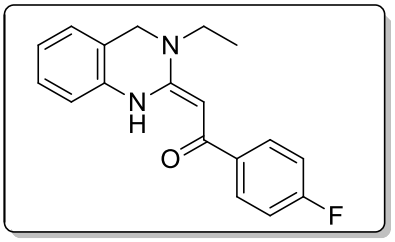




4c

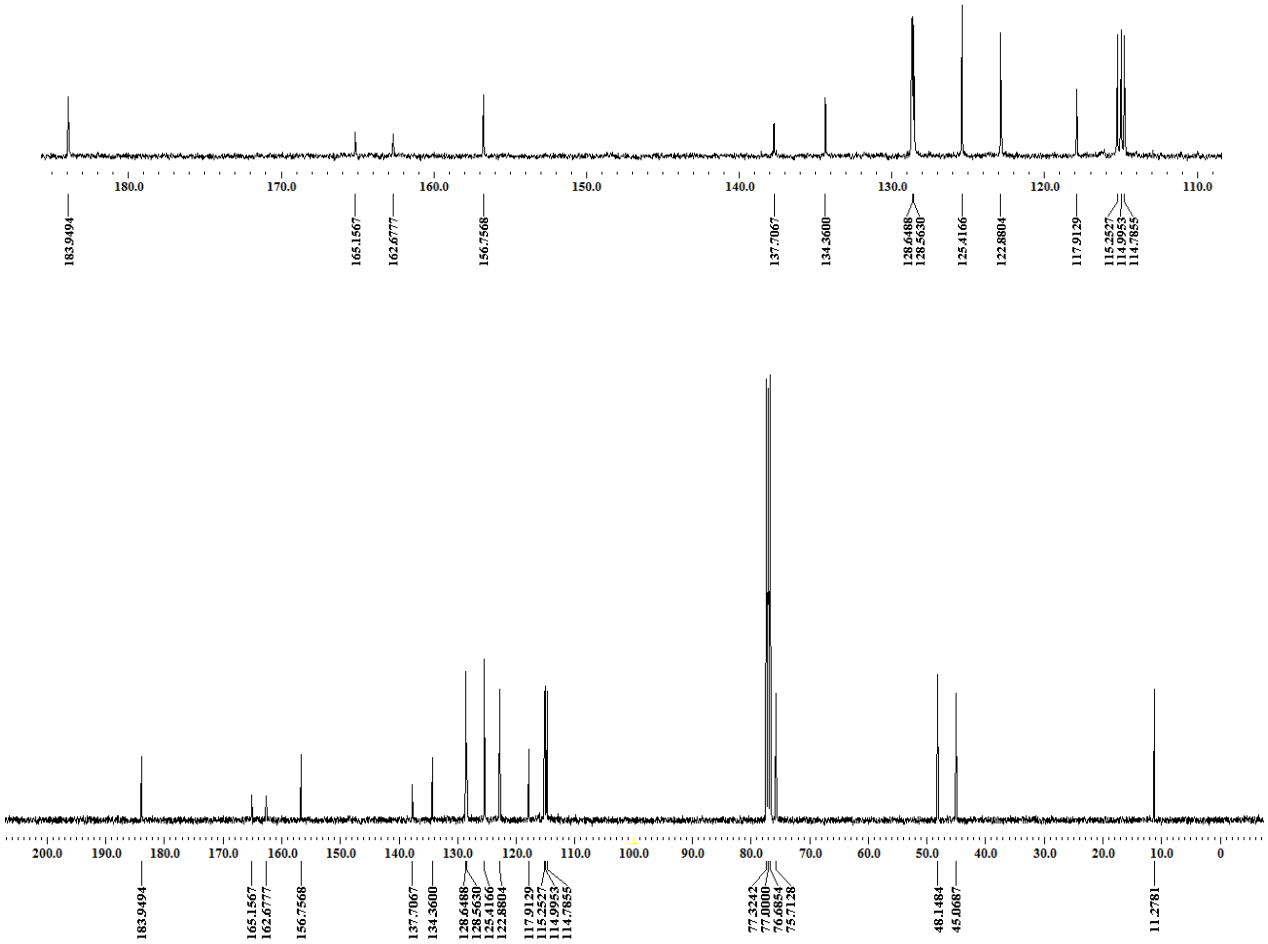
^{1}H-NMR in $CDCl_3$ (400MHz)

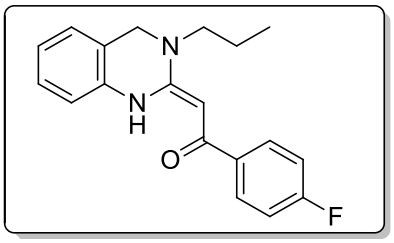




4c

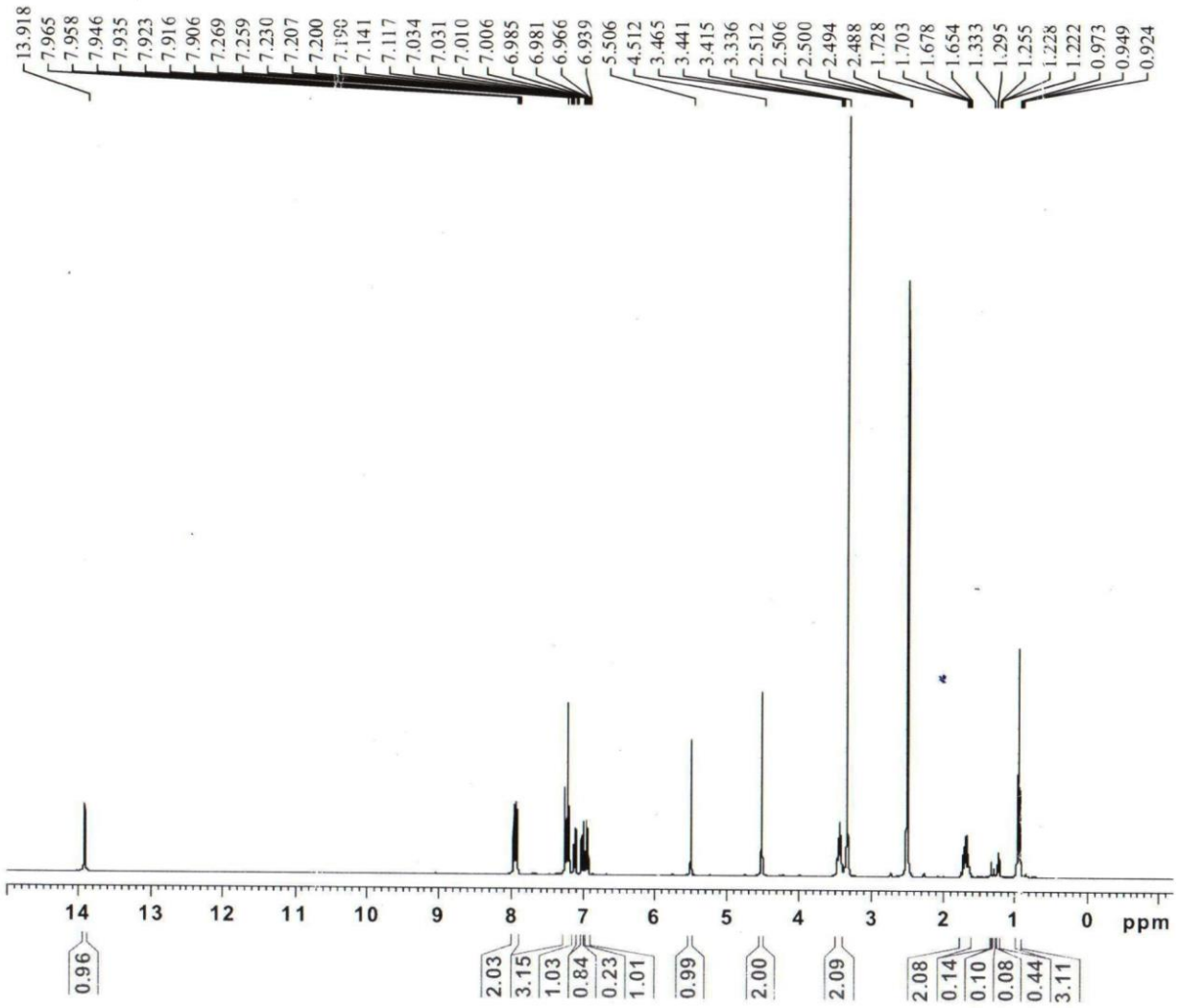
^{13}C-NMR in $CDCl_3$ (100MHz)

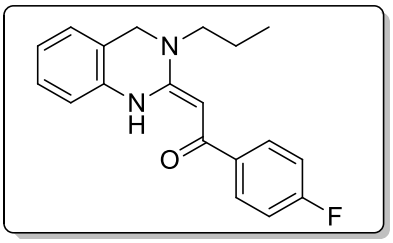




4d

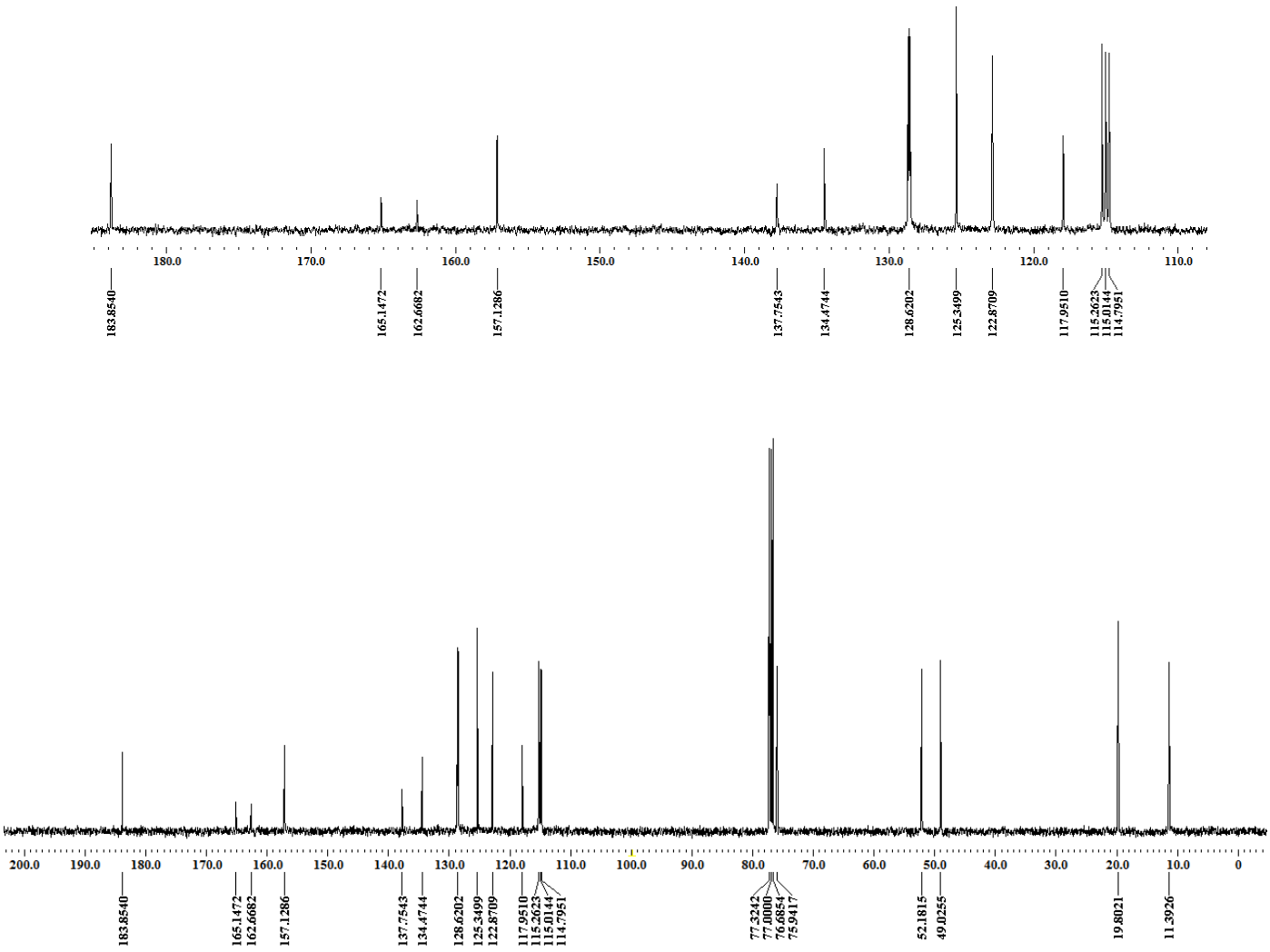
^{1}H-NMR in $CDCl_3$ (400MHz)

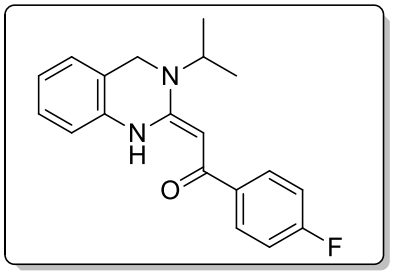




4d

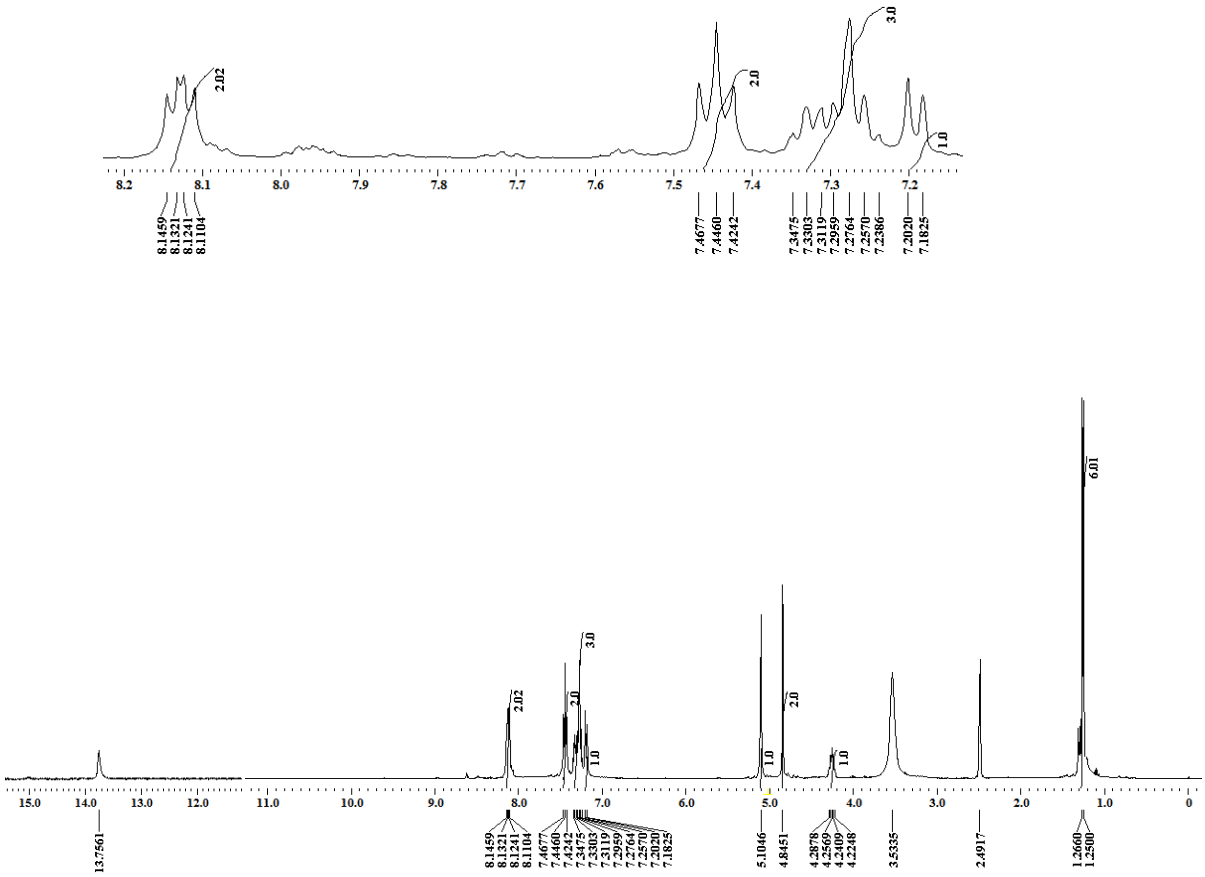
^{13}C-NMR in $CDCl_3$ (100MHz)

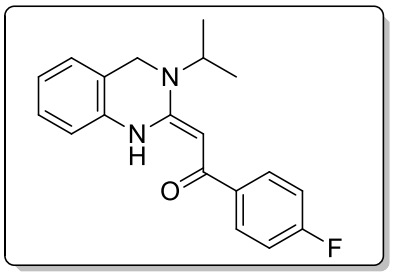




4e

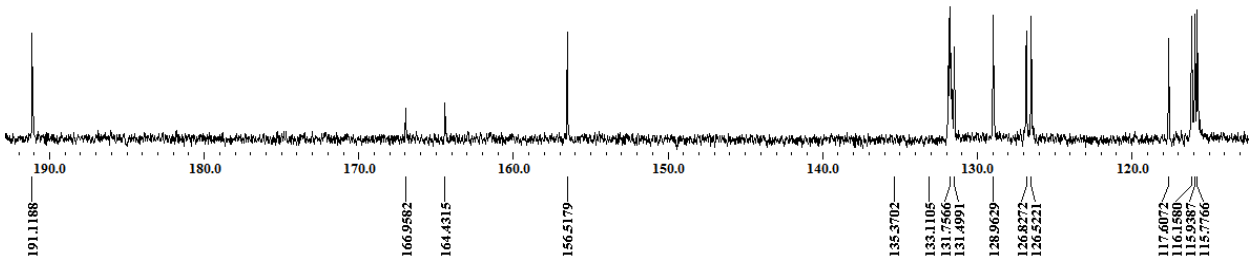
^{1}H-NMR in $CDCl_3$ (400MHz)

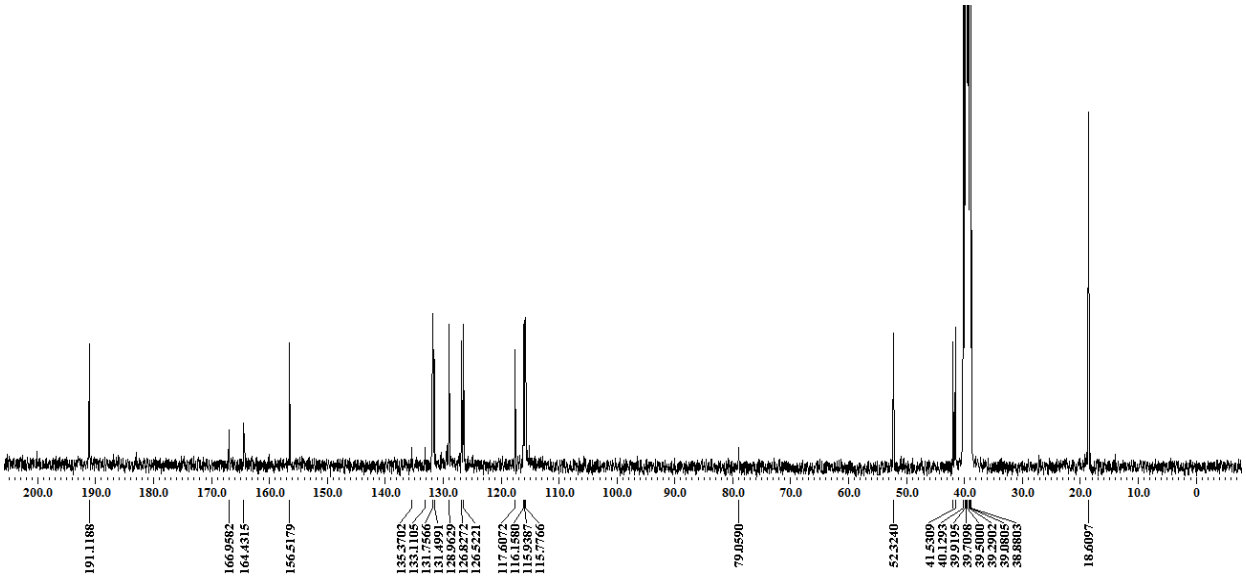


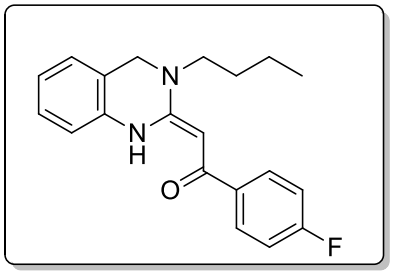


4e

^{13}C-NMR in $CDCl_3$ (100MHz)

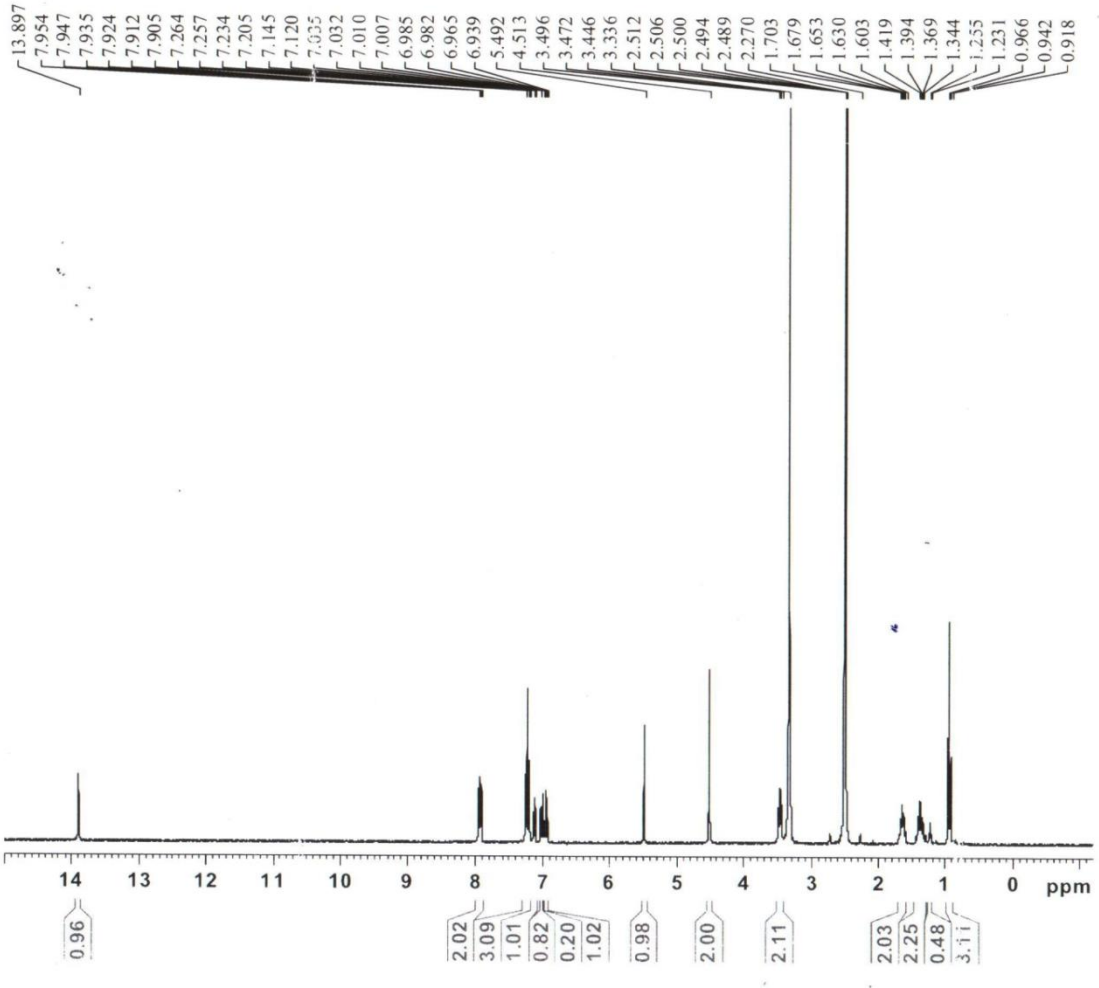


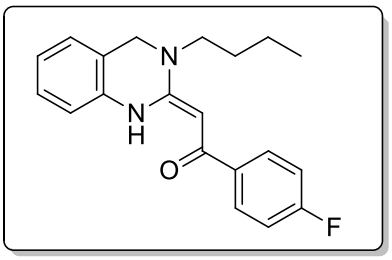




4f

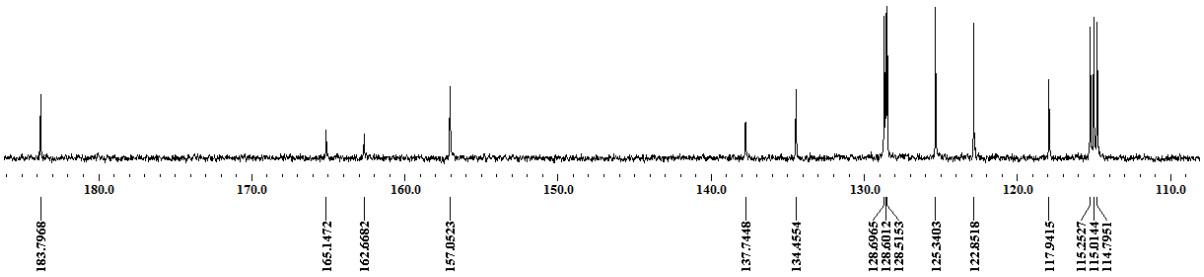
^{1}H-NMR in DMSO-d_6 (400MHz)

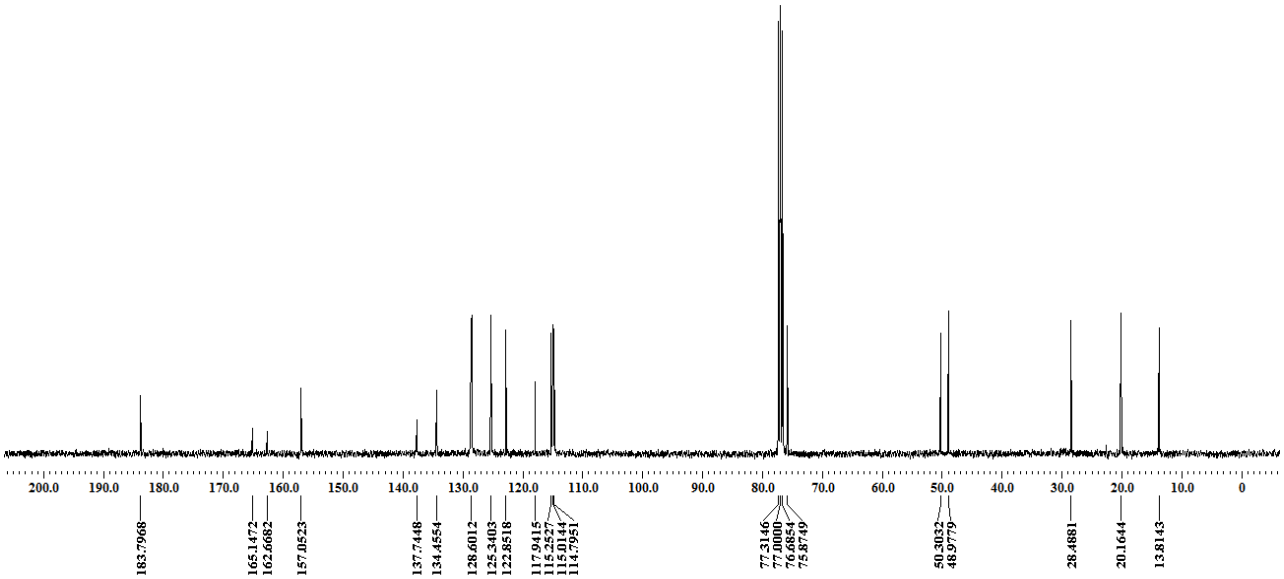


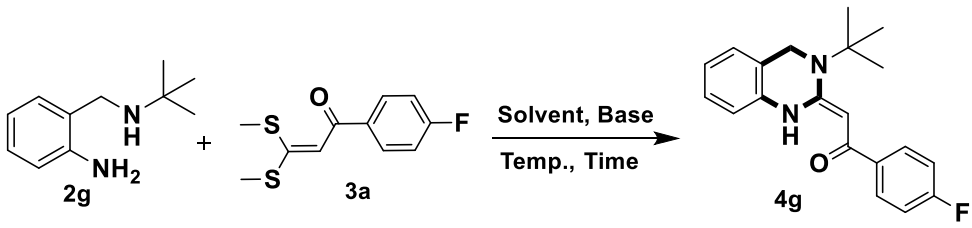


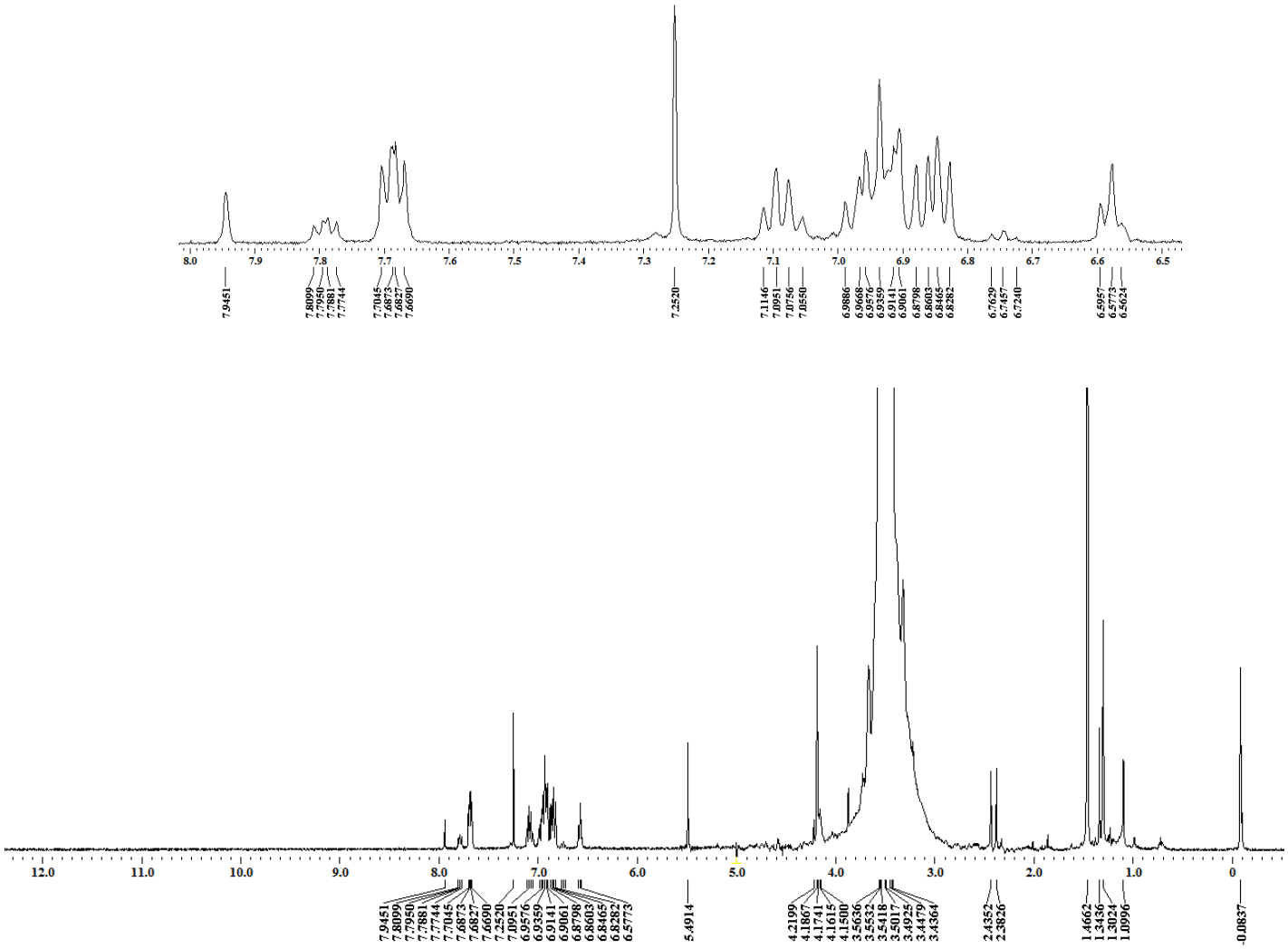
4f

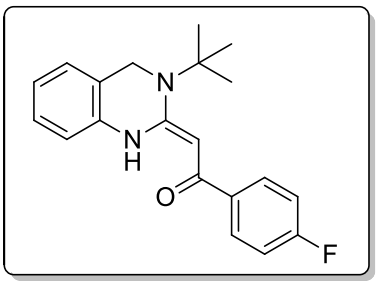
^{13}C-NMR in $CDCl_3$ (100MHz)





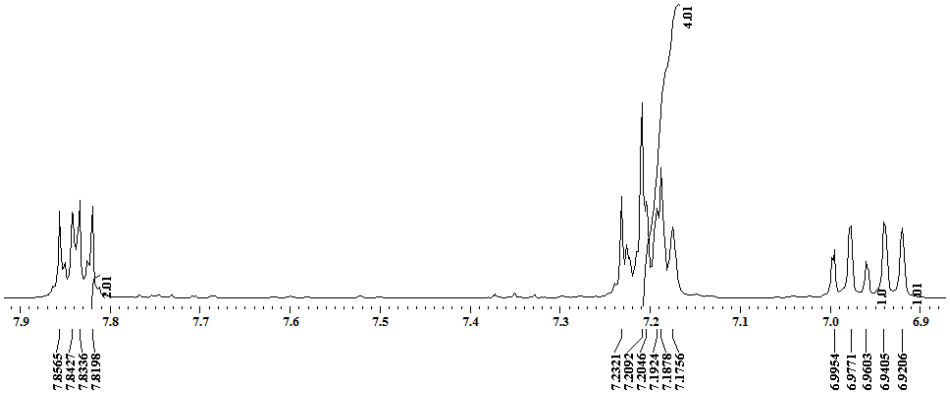

Solvent, Base
Temp., Time
2g
3a
4g

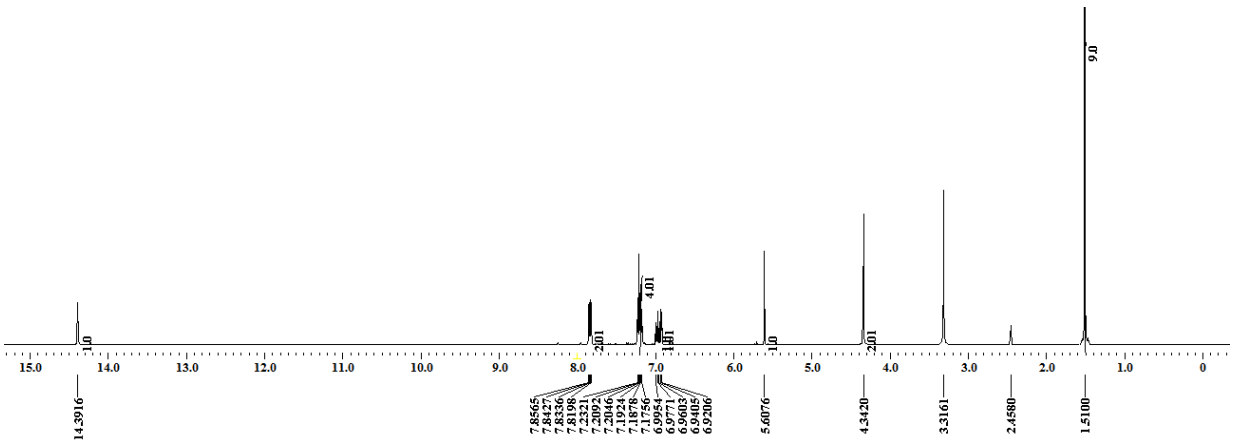


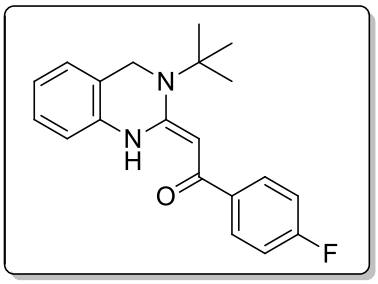


4g

^{1}H-NMR in $CDCl_3$ (400MHz)

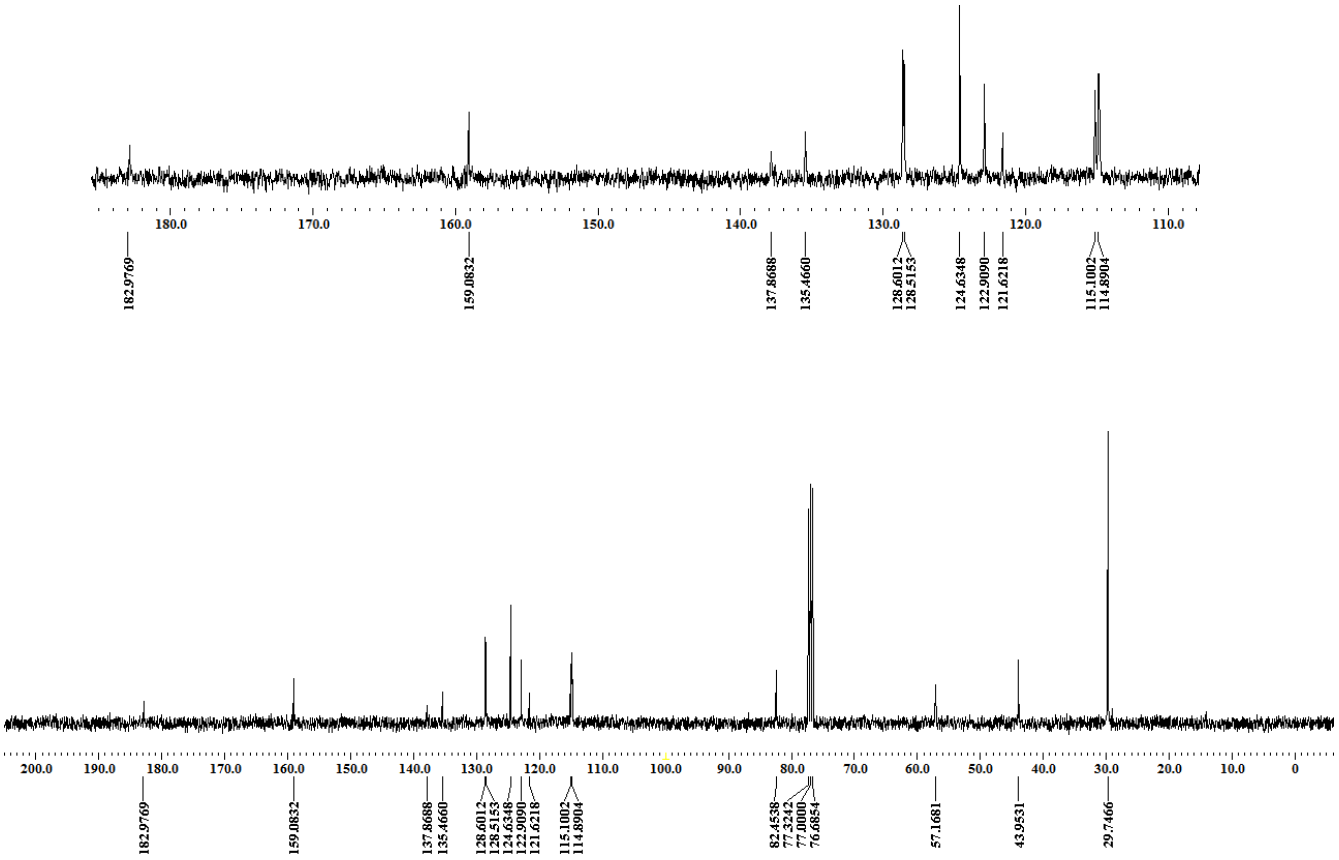


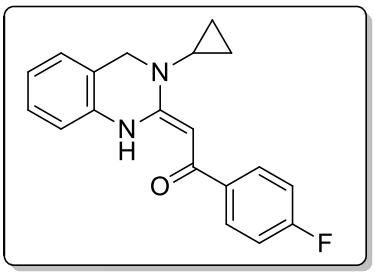




4g

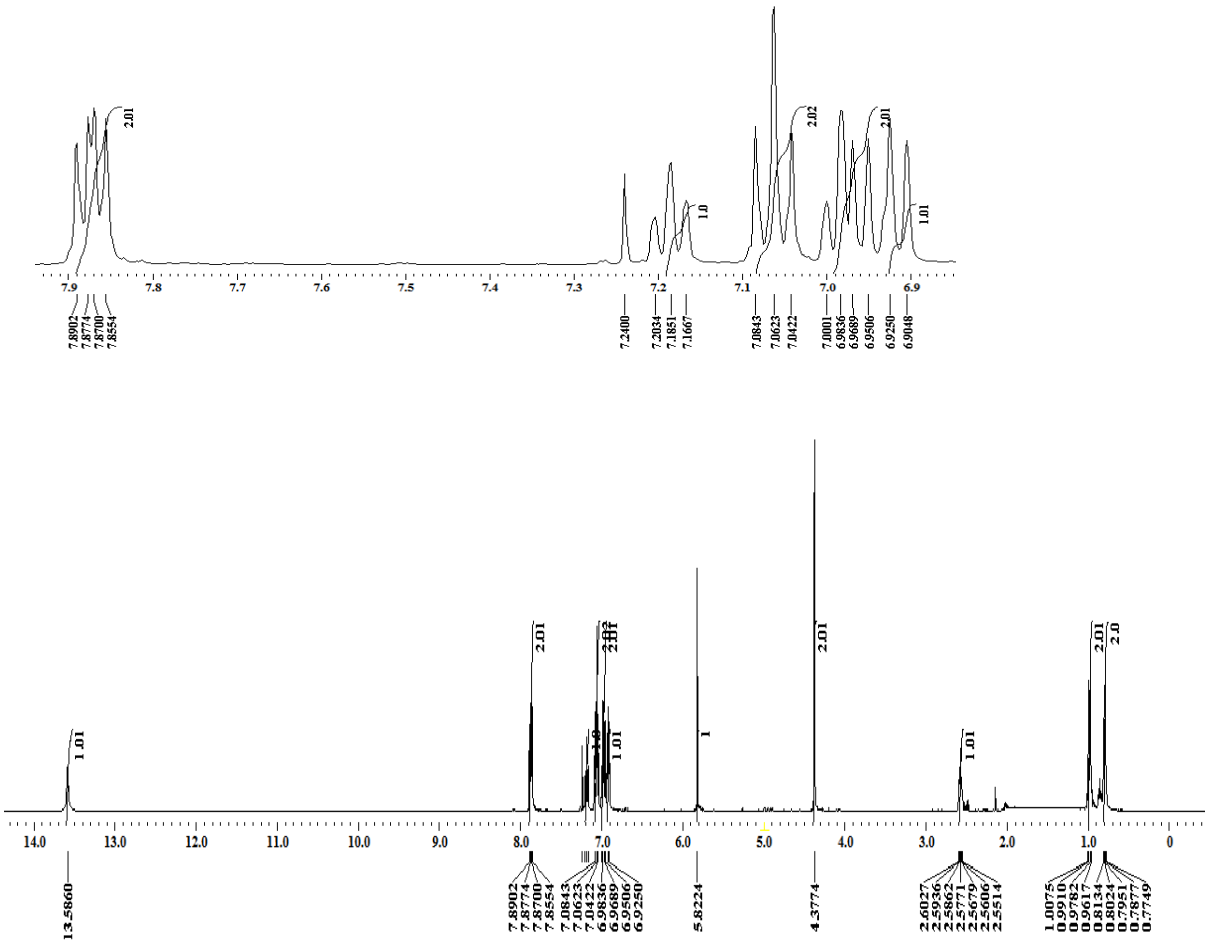
^{13}C-NMR in $CDCl_3$ (100MHz)

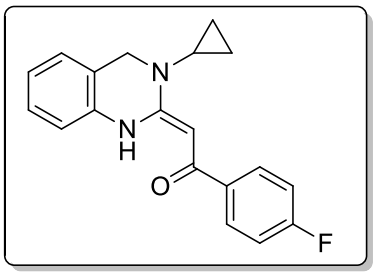




4h

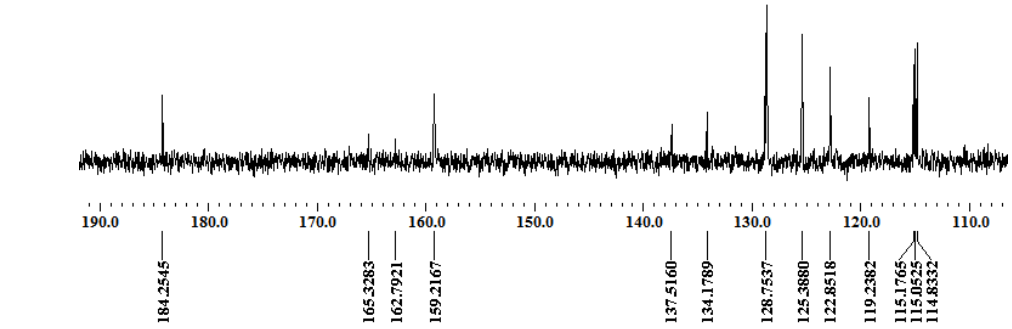
^{1}H-NMR in DMSO-d$_6$ (400MHz)

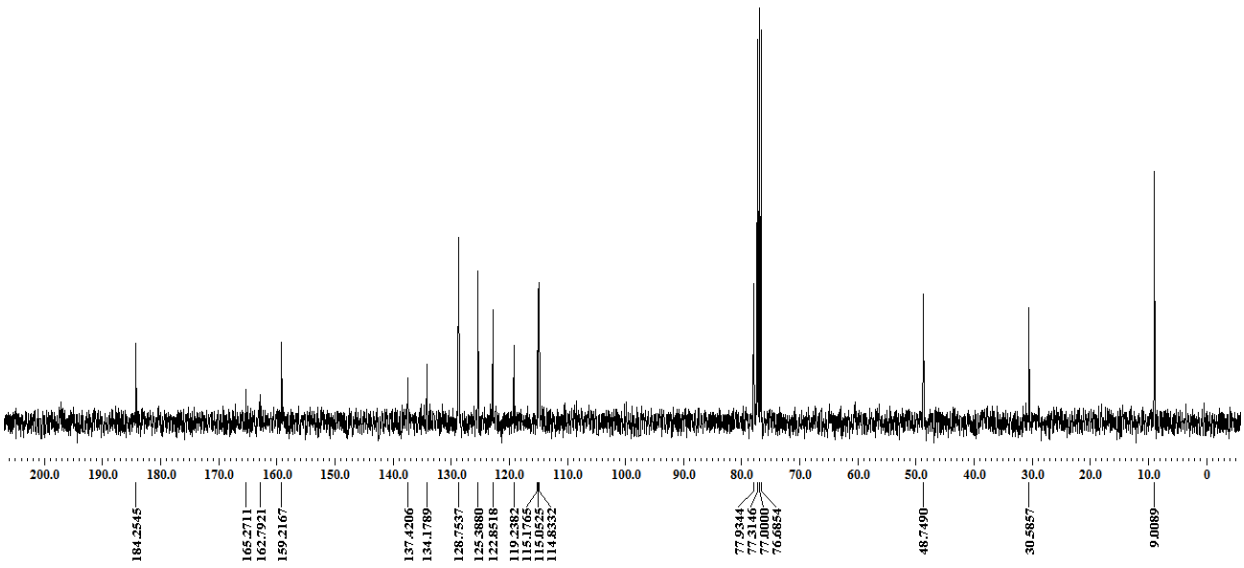


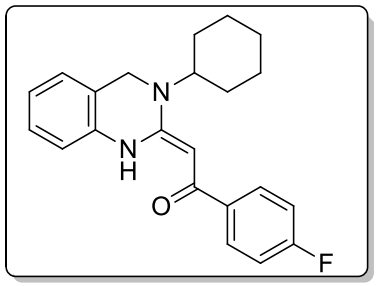


4h

^{13}C-NMR in $CDCl_3$ (100MHz)

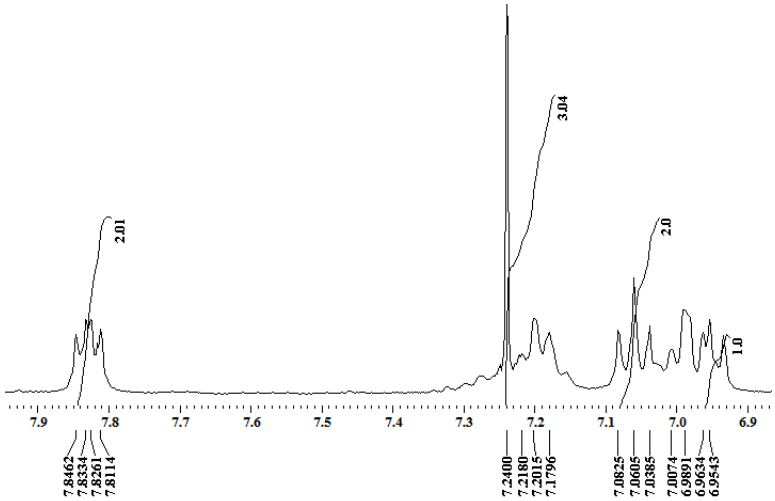


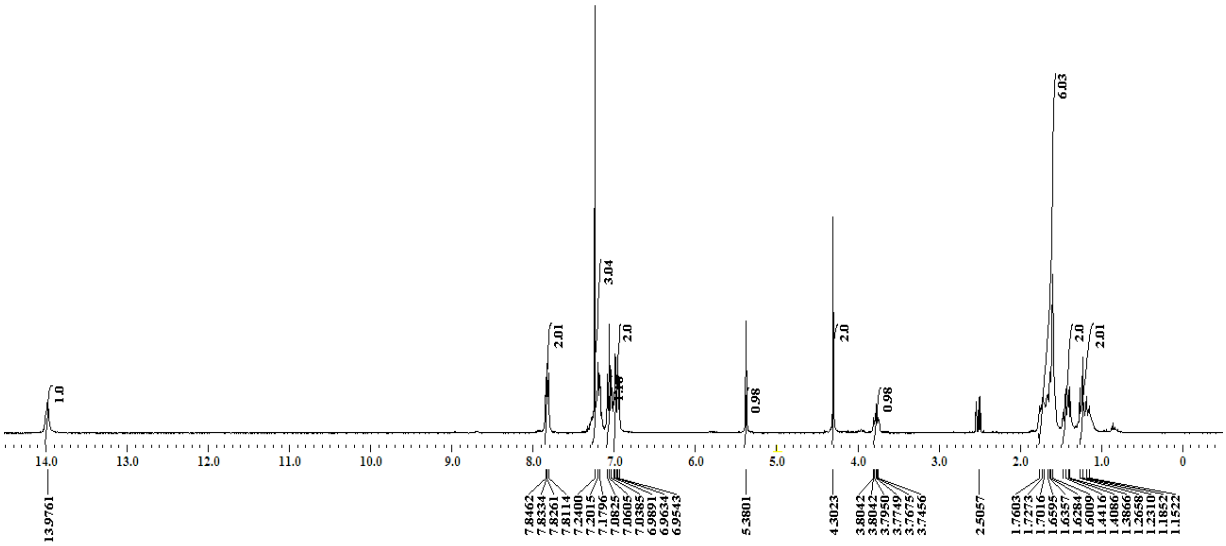


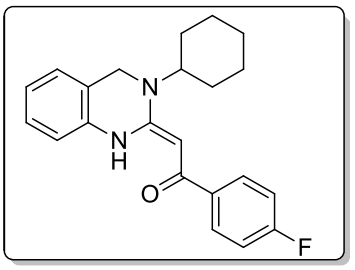


4i

^{1}H-NMR in $CDCl_3$ (400MHz)

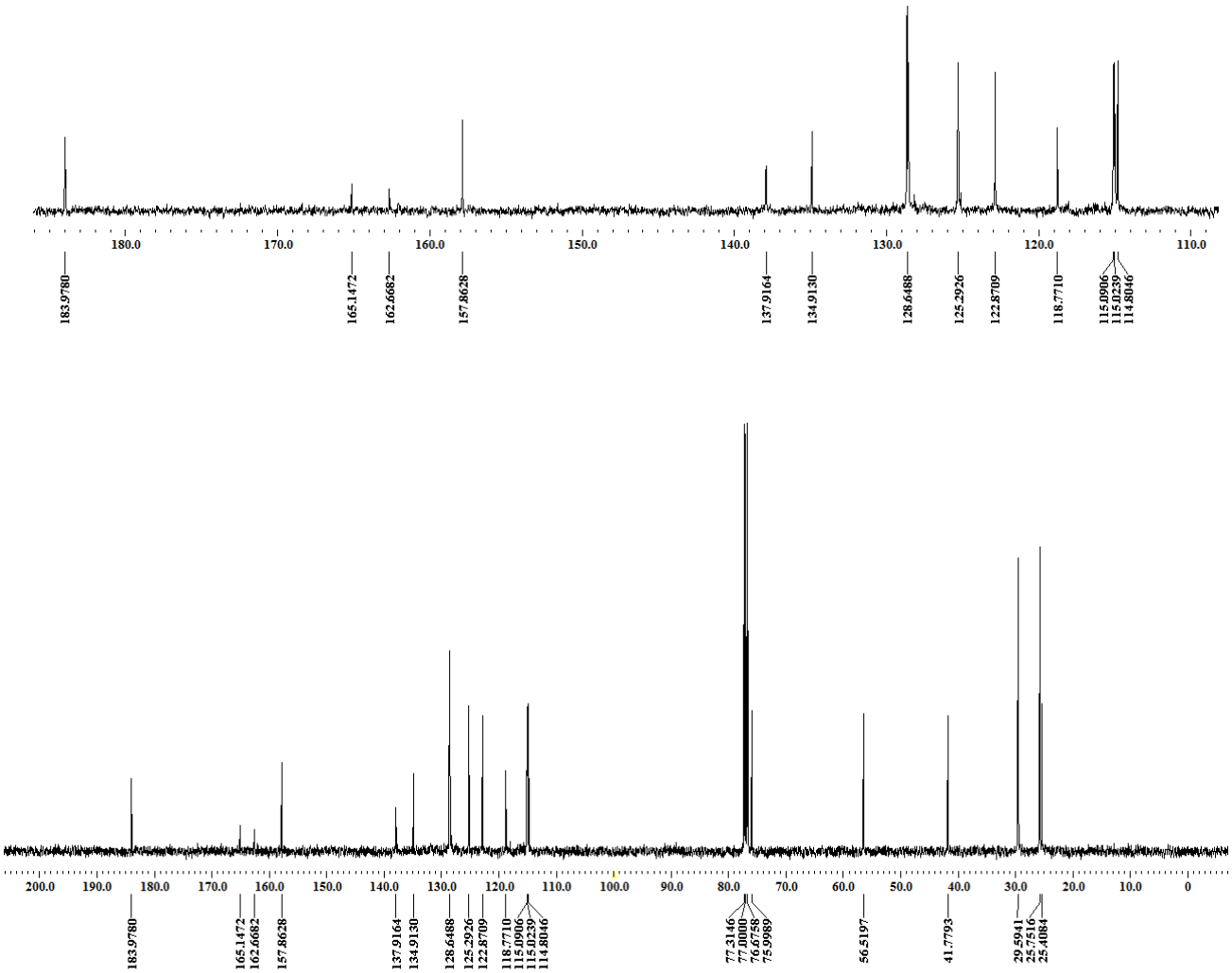


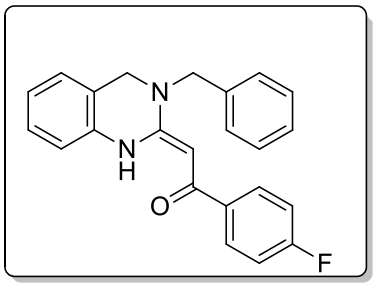




4i

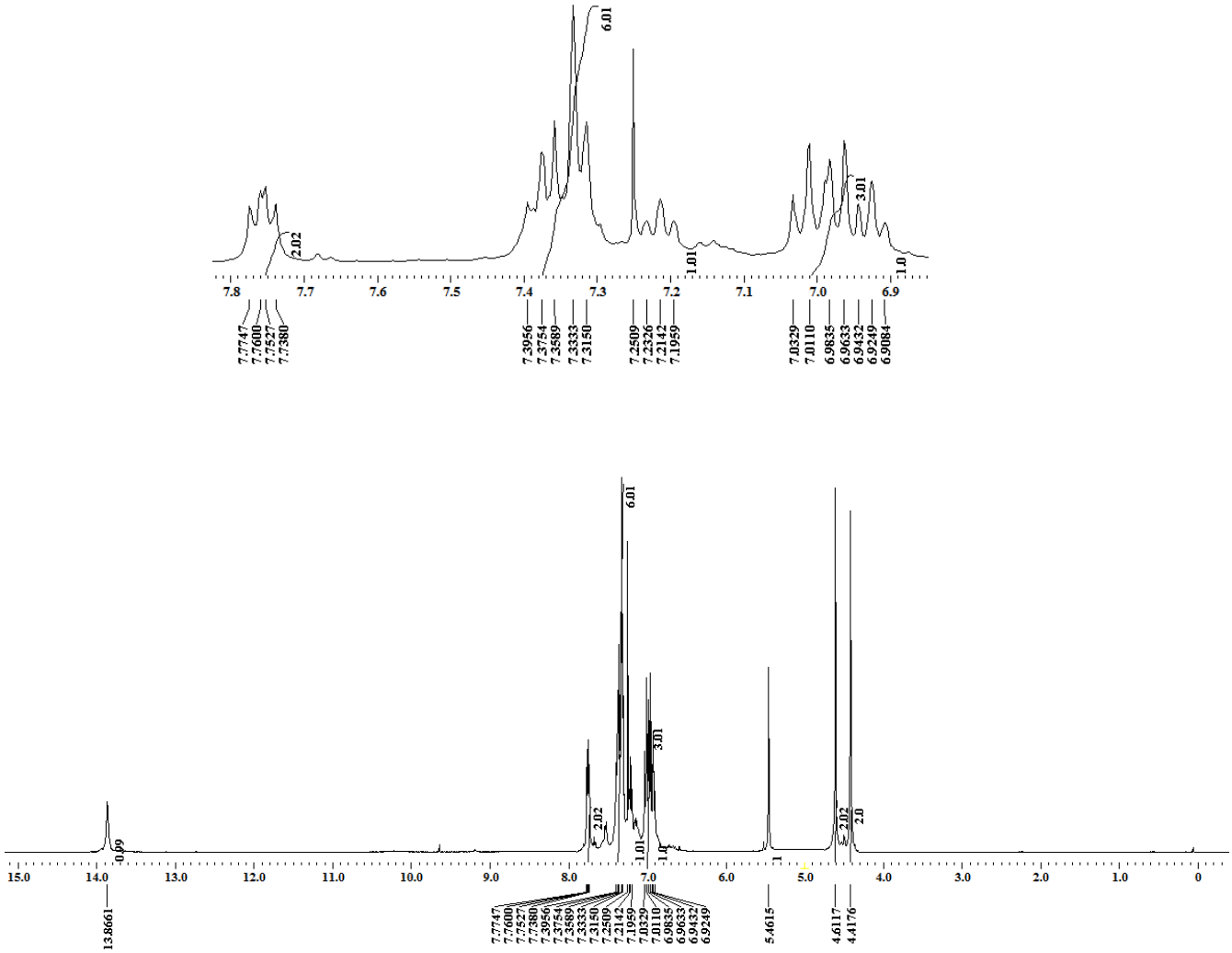
^{13}C-NMR in $CDCl_3$ (100MHz)

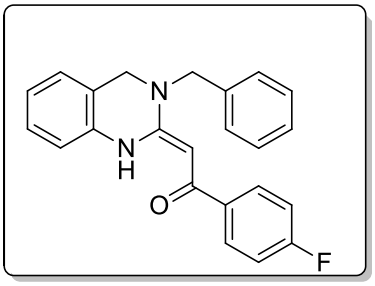




4j

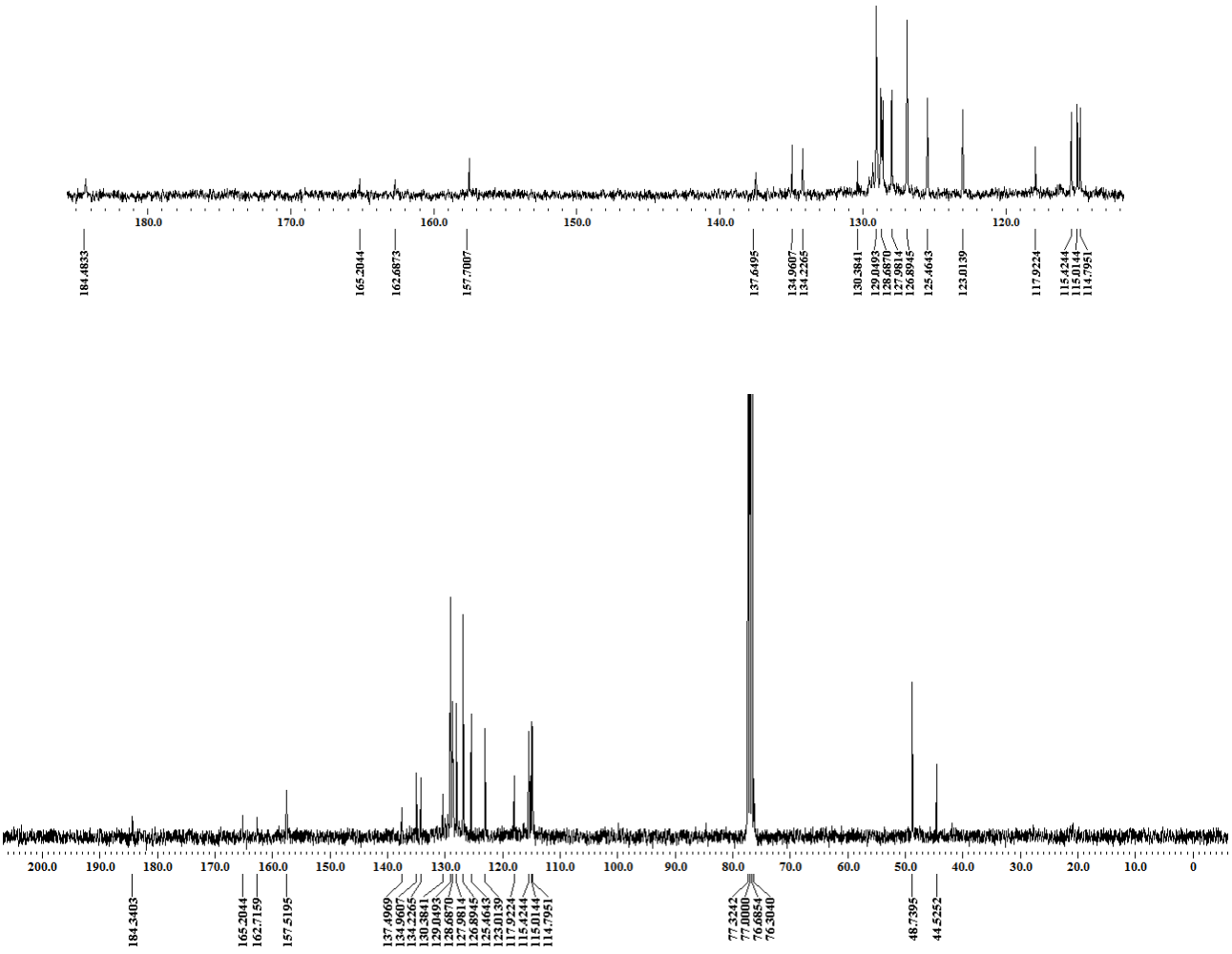
^{1}H-NMR in $CDCl_3$ (400MHz)

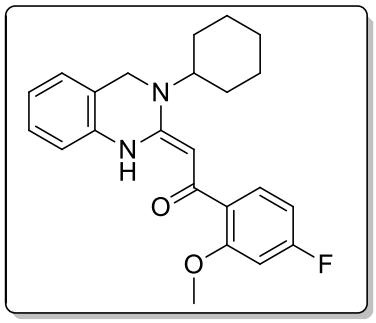




4j

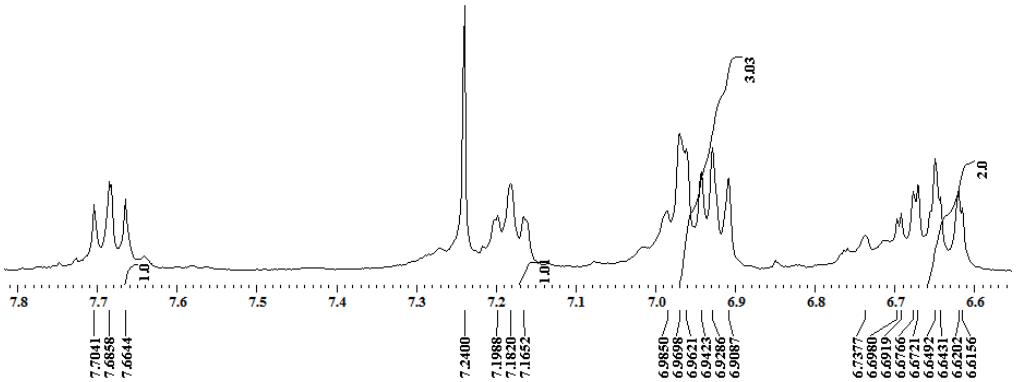
^{13}C-NMR in $CDCl_3$ (100MHz)

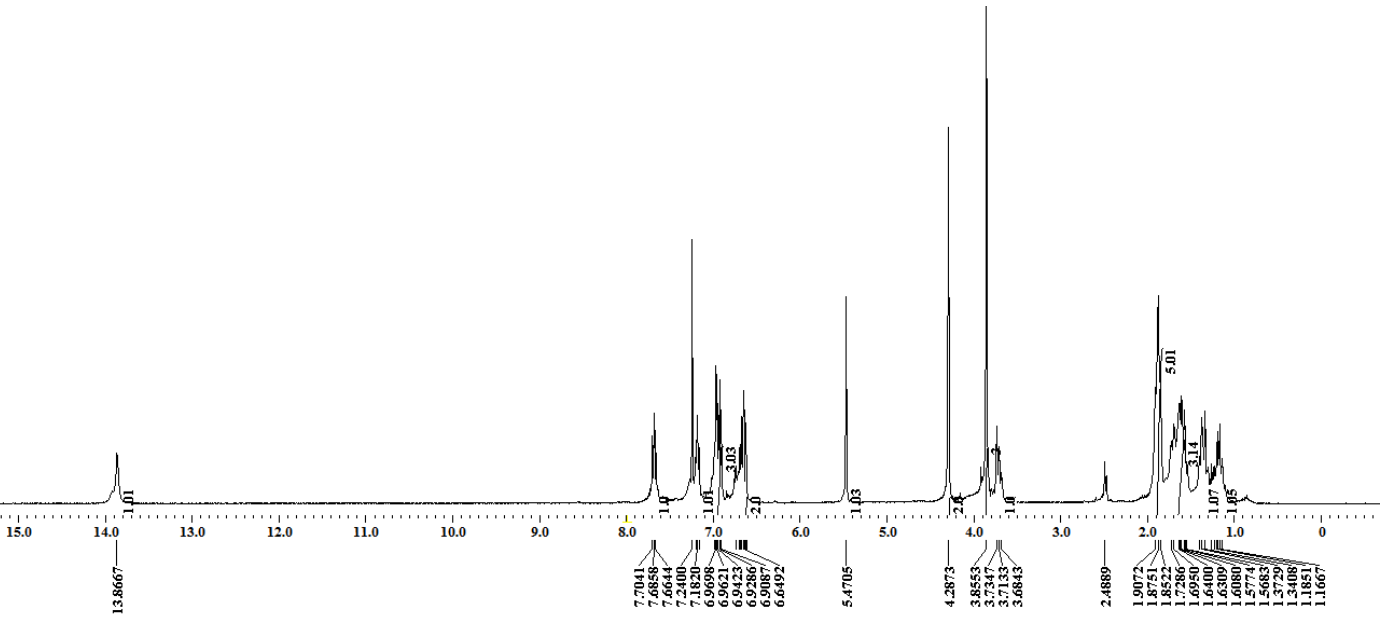


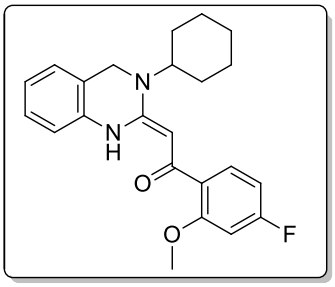


4k

^{1}H-NMR in $CDCl_3$ (400MHz)

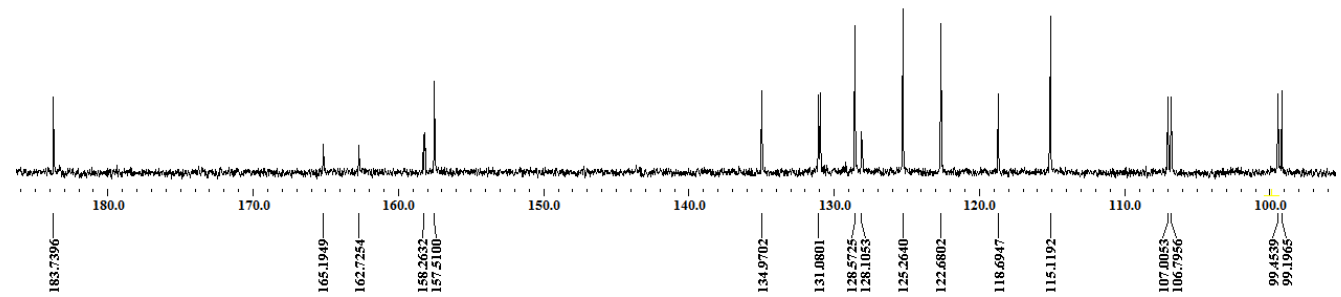


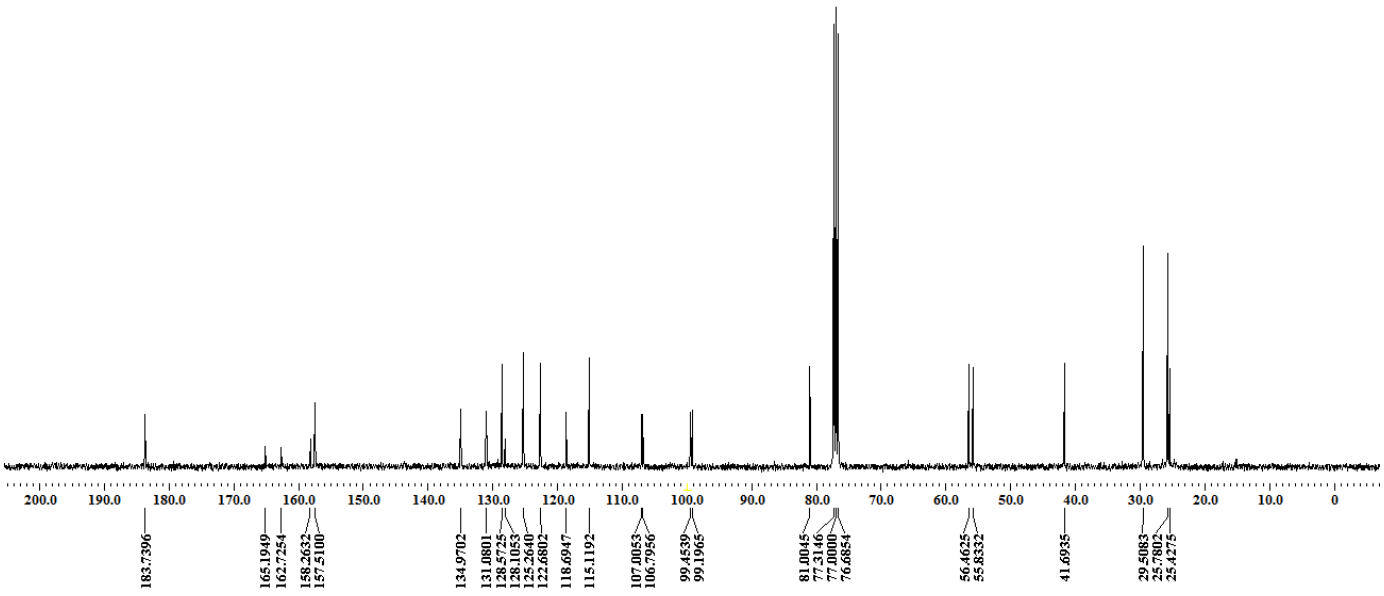


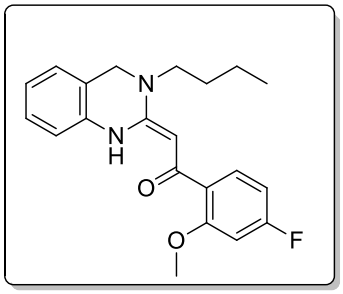


4k

^{13}C-NMR in $CDCl_3$ (100MHz)

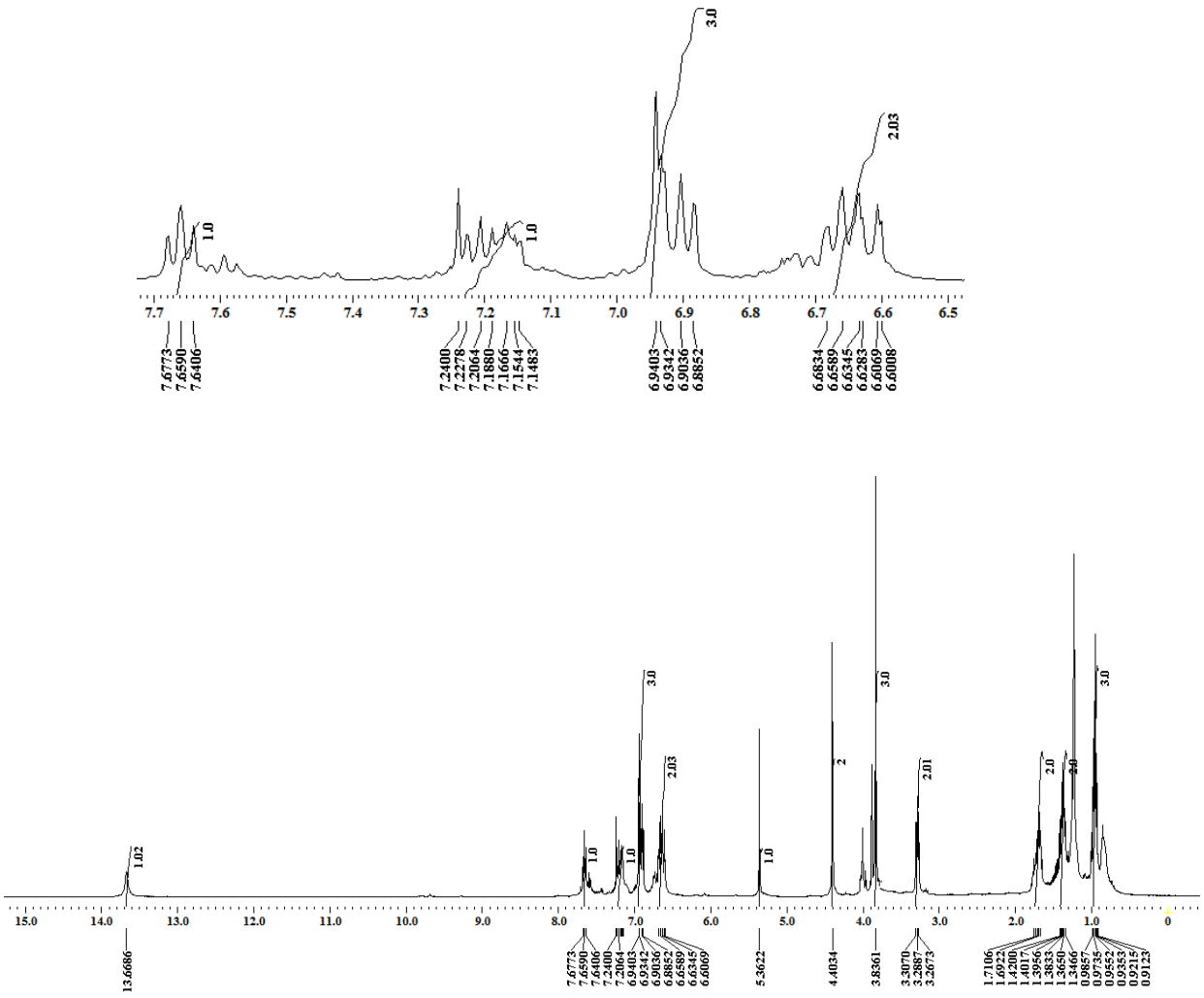


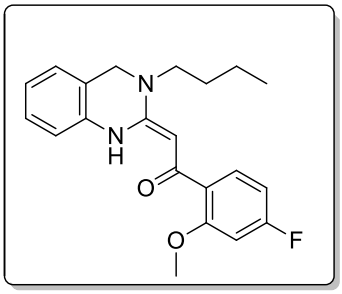




4l

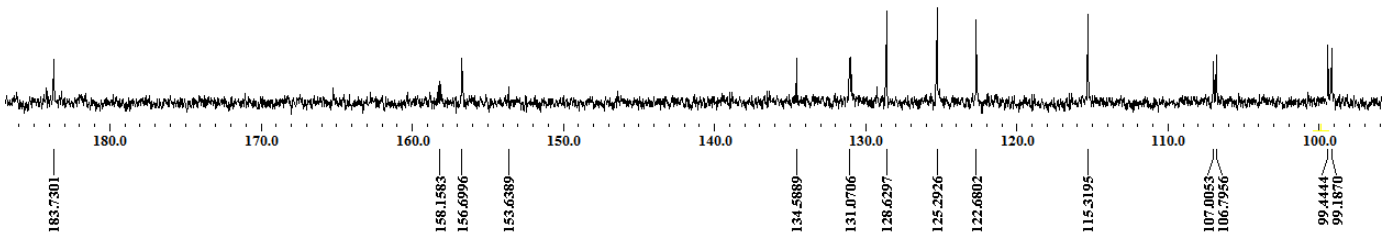
^{1}H-NMR in $CDCl_3$ (400MHz)

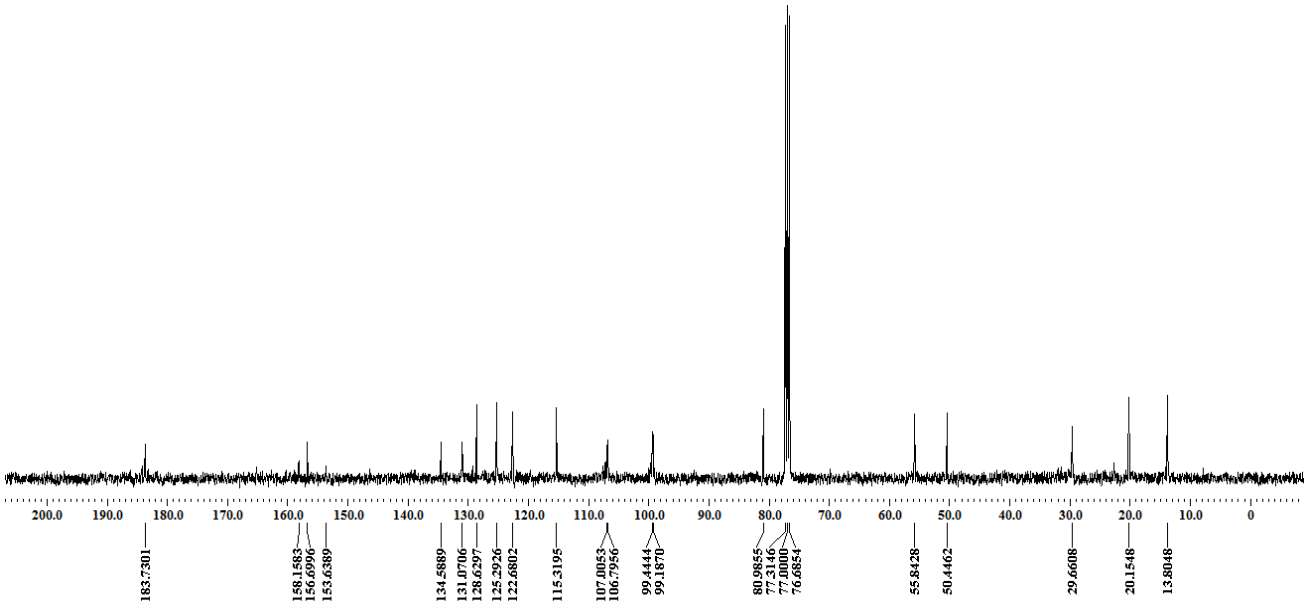


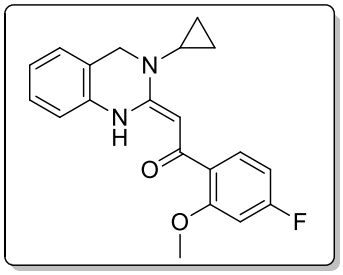


4l

^{13}C-NMR in $CDCl_3$ (100MHz)

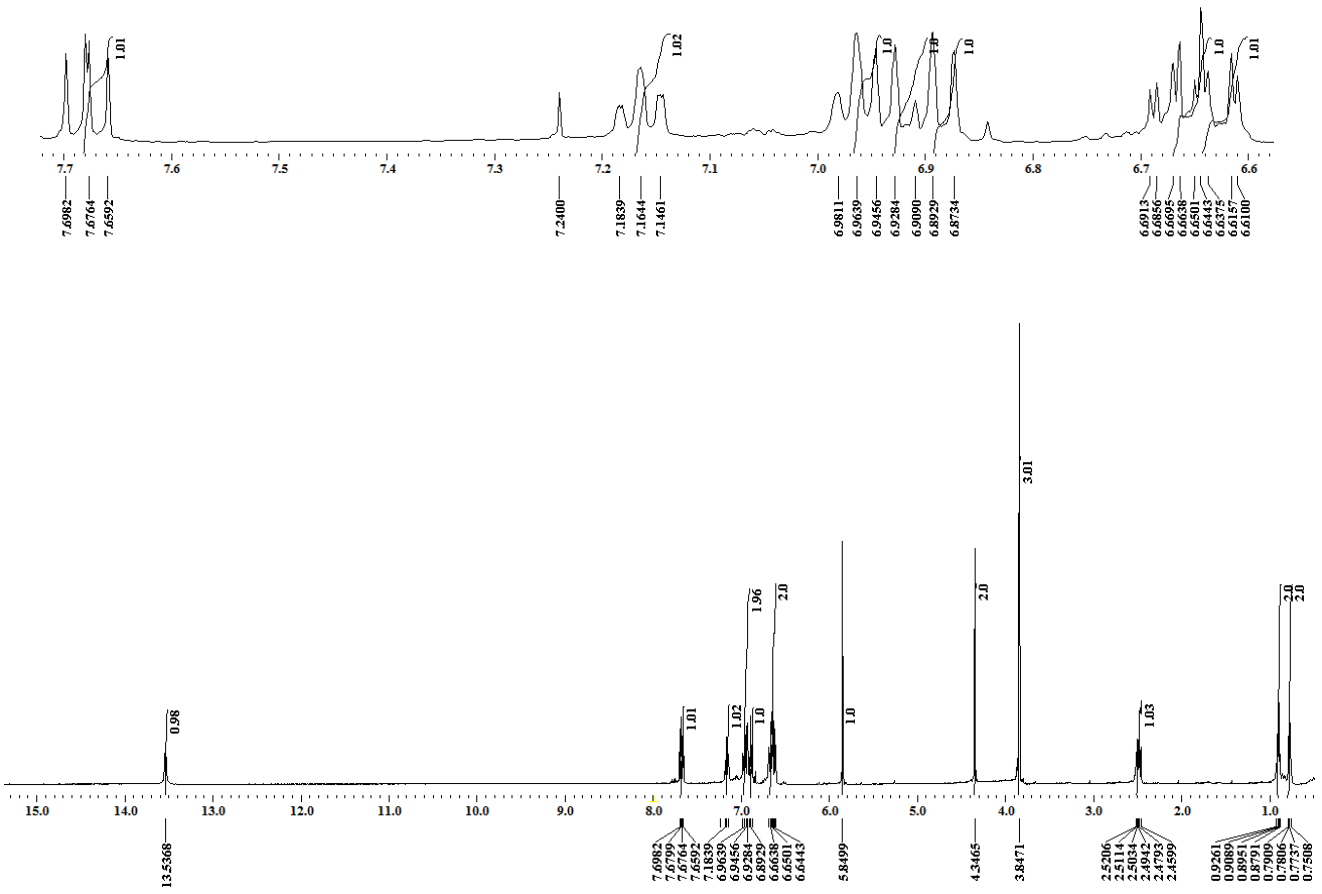


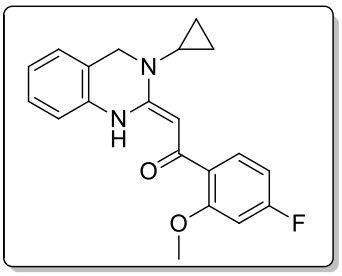




4m

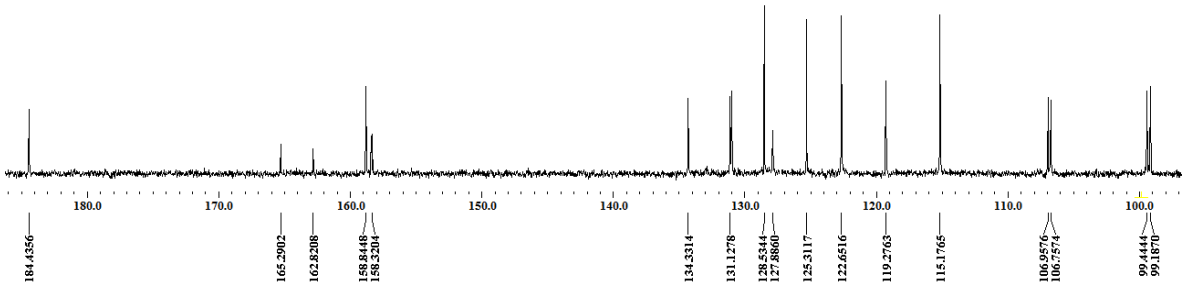
^{1}H-NMR in $CDCl_3$ (400MHz)

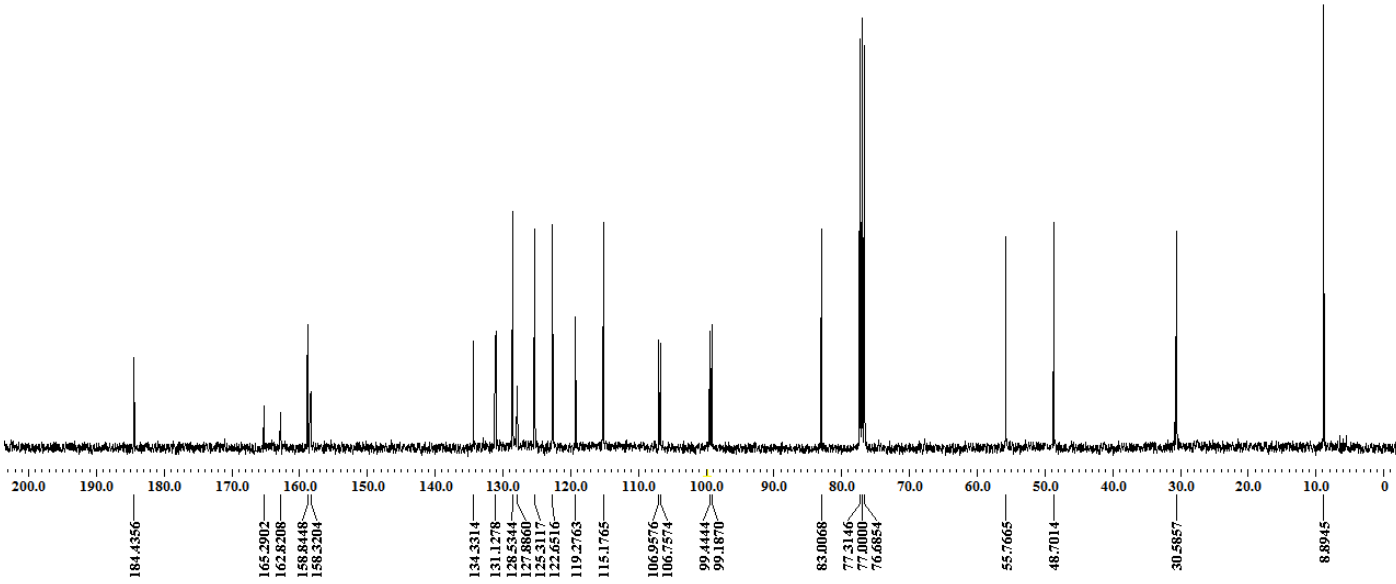


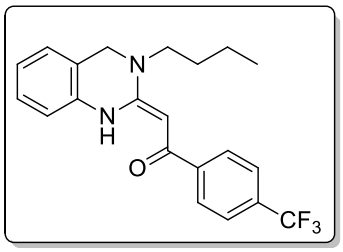


4m

^{13}C-NMR in $CDCl_3$ (100MHz)

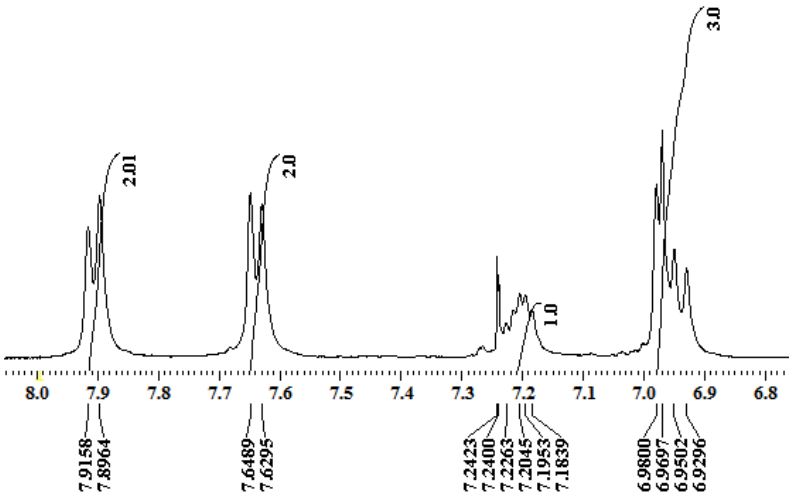


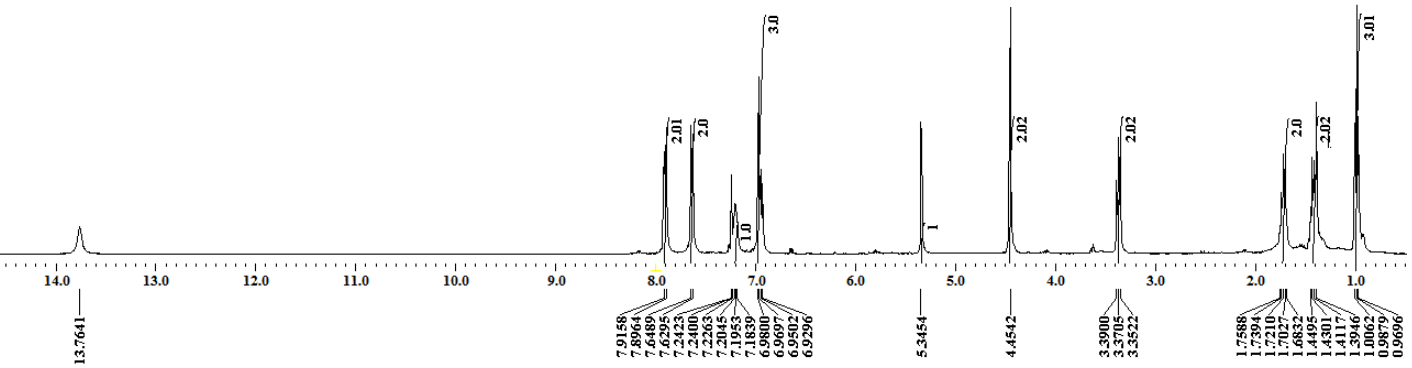


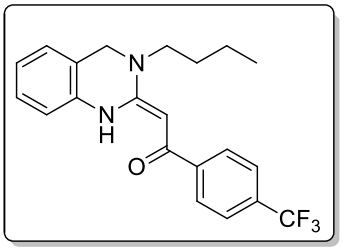


4n

^{1}H-NMR in $CDCl_3$ (400MHz)

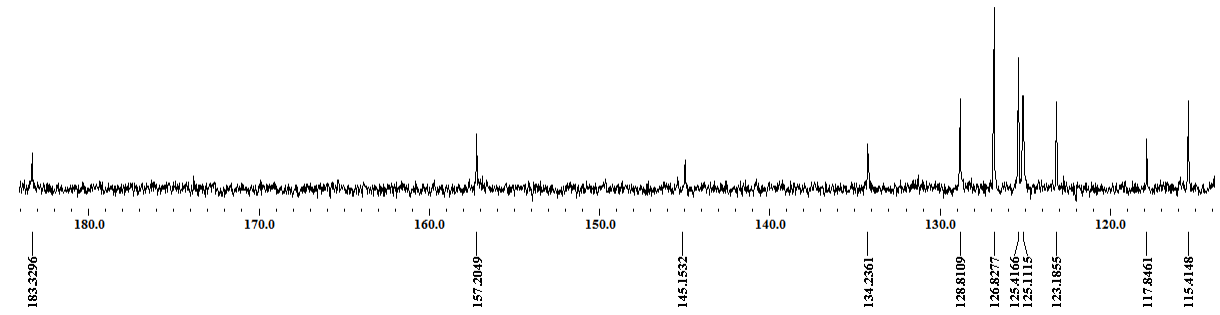


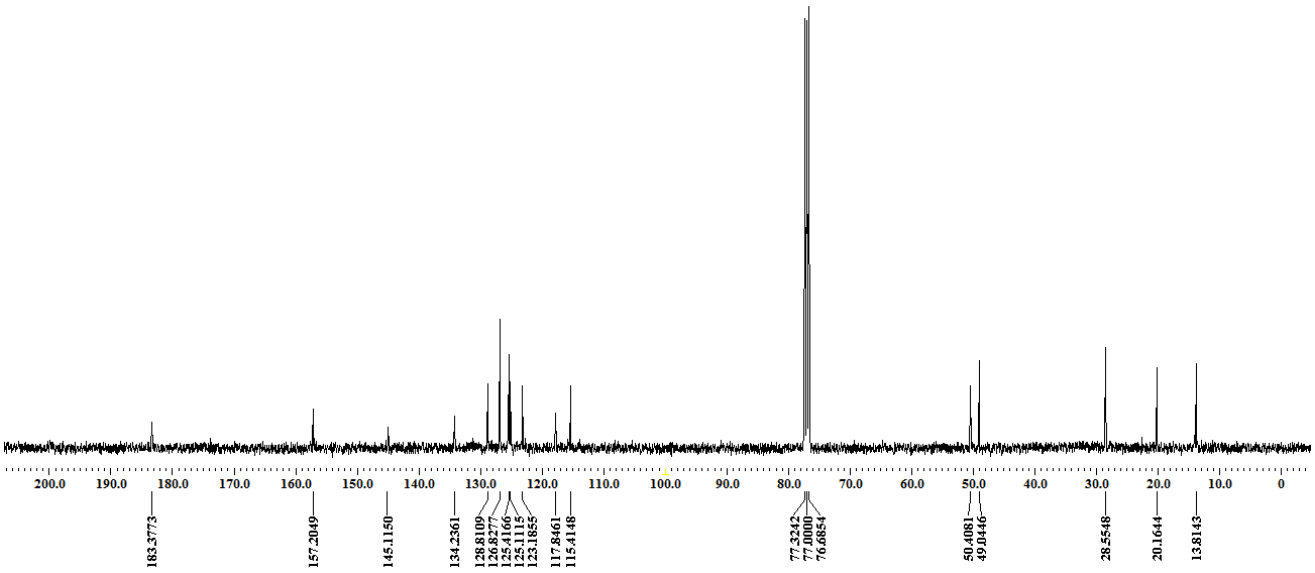


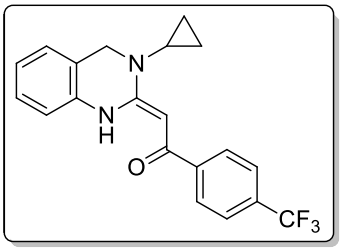


4n

^{13}C-NMR in $CDCl_3$ (100MHz)

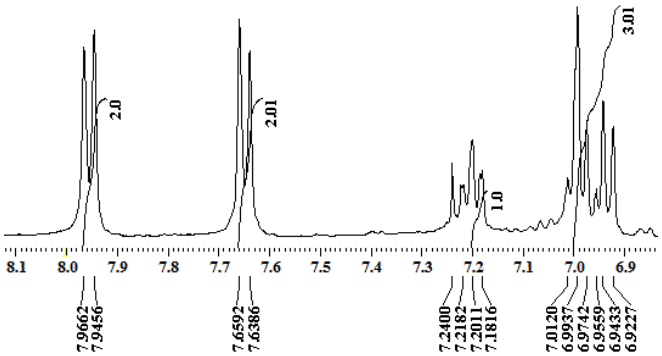


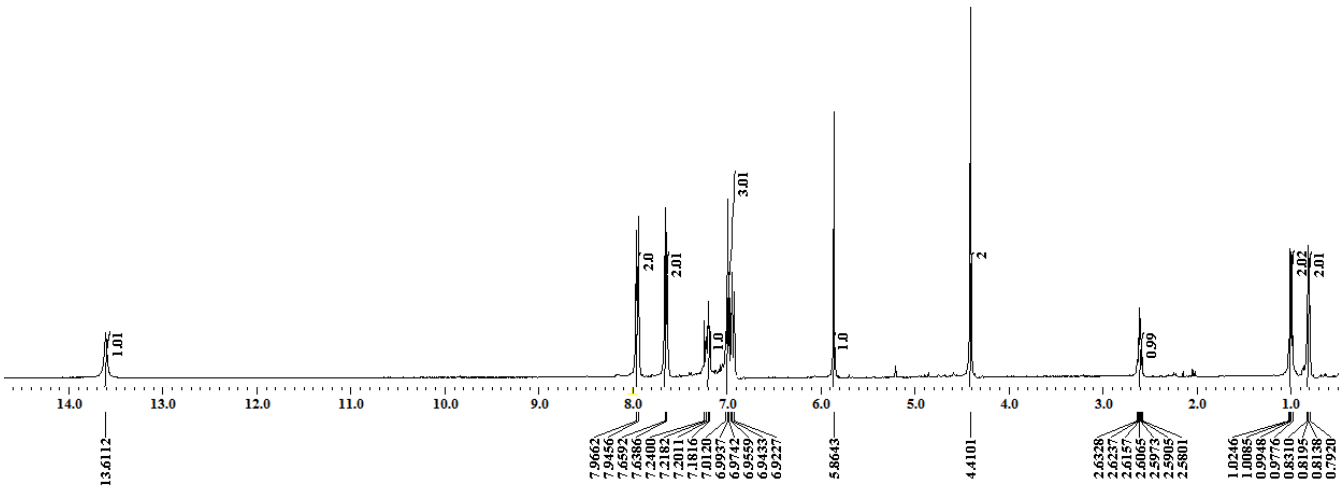


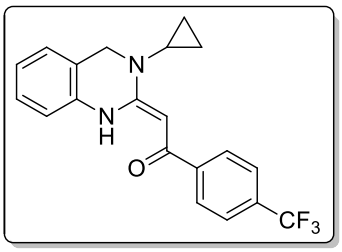


4o

^{1}H-NMR in $CDCl_3$ (400MHz)

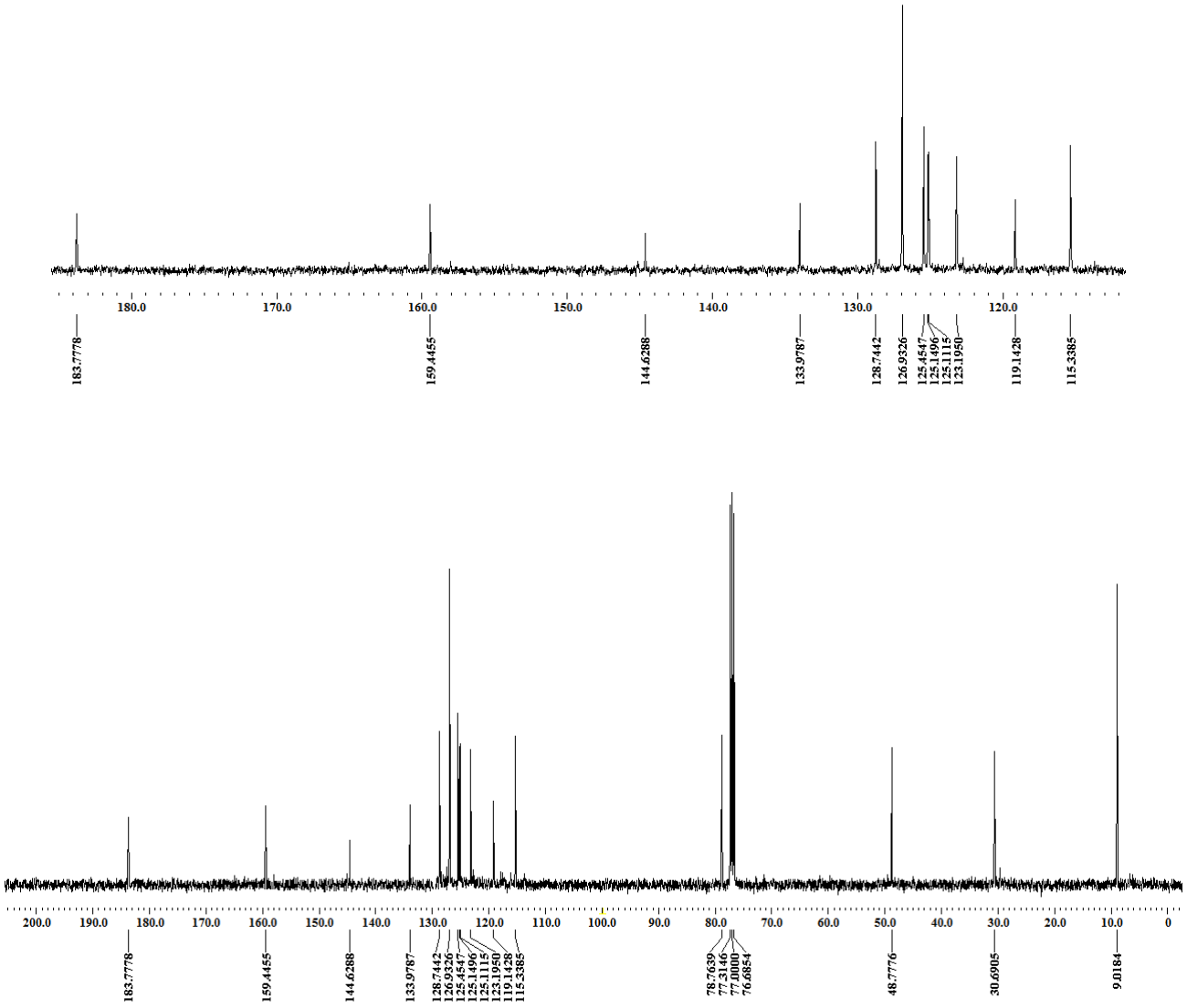


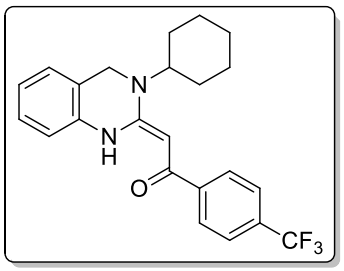




4o

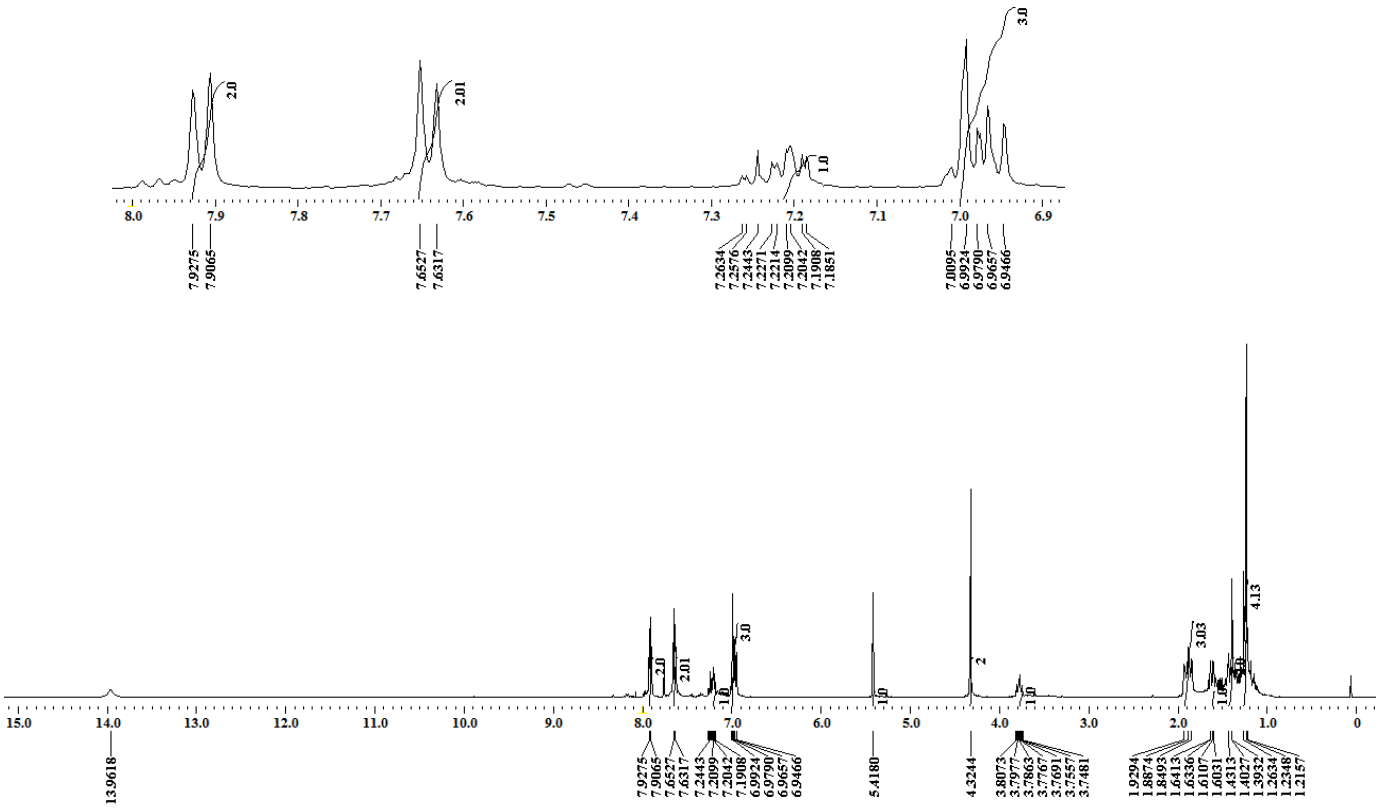
^{13}C-NMR in $CDCl_3$ (100MHz)

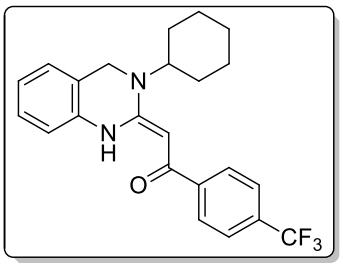




4p

^{1}H-NMR in $CDCl_3$ (400MHz)





4p

^{13}C-NMR in $CDCl_3$ (100MHz)