Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

DMSO-KOH Mediated Stereoselective Synthesis of *Z*-Enamides: An expeditious route to *Z*-Enamide bearing Natural Products

Showkat Ahmad Bhat,[a,b] , Qazi Naveed Ahmed [b,c], Khursheed Ahmad Bhat [a,b*]

[a] Bioorganic Chemistry Division, Indian Institute of Integrative Medicine (CSIR), Srinagar, Jammu & Kashmir-190005, India

[b] Natural Product and Medicinal Chemistry Division, CSIR-Indian Institute of Integrative Medicine, Jammu-180001, India

[c]Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

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1. General Introduction

All the necessary reagents and solvents were purchased from Sigma Aldrich, TCI, and Sdfine respectively. Solvents were purified using standard protocols. All the reactions were carried out in oven-dried glassware. UV lamp (254 nm) was used to analyze developed chromatograms. All the products were purified using silica gel (mesh size 100-200) column chromatography. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ and DMSO-d_6 as per requirement using 400 MHZ spectrometer. Chemical shifts of ^{1}H and ^{13}C NMR were expressed in parts per million (ppm). The representation of the signals includes the following: s = singlet, d = doublet, t = triplet, dd =doublet of doublet, dt = doublet of triplet, q = quartet, dq = doublet of quartet, m = multiplet , br= broad . Solvent peaks: $CDCl_3$, ^{1}H δ 7.26 (s), ^{13}C δ 77.2 (t). DMSO-d_6, ^{1}H δ 2.5 (m) & δ 3.4 (s) corresponding to moisture, ^{13}C δ 39.5 (m)

2. General procedure for the synthesis of 3a-3o, 4a-4i, 6a & 7

In a round bottom flask, a mixture of **1a** (1 mmol), **2a** (1 mmol) and KOH (1 mmol) in 3 mL of DMSO were stirred at 80 ^{o}C for 15 minutes. The progress of the reaction was monitored by TLC. After the reaction was complete, ice cold water was added to the reaction mixture and was extracted with EtOAc (20 mL × 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100-200) and ethyl acetate and hexane as eluents to obtain the desired product.

3. Procedure for synthesis of 6b

In a round bottom flask containing 3 mL of Dry dichloromethane was added **6a** (1 mmol). Thereafter addition of 1 mmol of sodium hydride was done at 0 ^{o}C. After 15 minutes, methyl iodide (1 mmol) was added to the reaction mixture. The reaction was continuously kept on stirring for further 30 minutes to obtain **6b** with 97% yield.

4. Procedure for control experiments

Control experiment 1

In a round bottom flask benzamide (1 mmol), phenylacetylene (1mmol), TEMPO (1 mmol) and KOH (1mmol) in 3 mL of DMSO were heated at 100 ^{o}C for 15 minutes . it was observed that no desired product was formed even after continuing the reaction for 1 hour.

Control experiment 2

In a round bottom flask, a mixture of **1a** (1 mmol), **2a** (1 mmol) and KOH (1 mmol) in 3 mL of DMSO-d_6 were stirred at 80 ^{o}C for 15 minutes. The progress of the reaction was monitored by TLC. After the reaction was complete, ice cold water was added to the reaction mixture and was extracted with EtOAc (20 mL × 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100-200) and ethyl acetate and hexane as eluents to obtain the desired product (**8**).

Control experiment 3

In a round bottom flask, **3a** (1 mmol), was dissolved in 3 mL of DMF. Further, triethylamine (1 mmol) was added to the reaction mixture. The reaction mixture was stirred at 110 ^{o}C for 3 hours.

The progress of the reaction was monitored by TLC. After the reaction was complete, ice cold water was added to the reaction mixture and was extracted with EtOAc (20 mL × 3). The organic layer was dried using sodium sulfate, concentrated over reduced pressure, and purified by using silica gel column chromatography (mesh size 100-200) and ethyl acetate and hexane as eluents to obtain the desired product (**9**).

5. Crystallographic data and molecular structure of 4i

Bond precision:	C-C = 0.0039 A		Wavelength=0.71073
Cell:	a=9.8231(7)	b=9.7118(10)	c=28.545(3)
	alpha=90	beta=90	gamma=90
Temperature: 203 K			
	Calculated		Reported
Volume	2723.2(4)		2723.2(4)
Space group	P b c a		P b c a
Hall group	-P 2ac 2ab		-P 2ac 2ab
Moiety formula	C16 H12 F3 N O		C16 H12 F3 N O
Sum formula	C16 H12 F3 N O		C16 H12 F3 N O
Mr	291.27		291.27
Dx,g cm-3	1.421		1.421
Z	8		8
Mu (mm-1)	0.117		0.117
F000	1200.0		1200.0
F000'	1200.79		
h,k,lmax	13,12,38		12,12,37
Nref	3402		3177
Tmin,Tmax	0.998,0.999		0.580,0.746
Tmin'	0.991		

Correction method= # Reported T Limits: Tmin=0.580 Tmax=0.746 AbsCorr = MULTI-SCAN

Data completeness= 0.934 Theta(max)= 28.353

R(reflections)= 0.0726(2299) wR2(reflections)= 0.1905(3177)

S = 1.071 Npar= 190

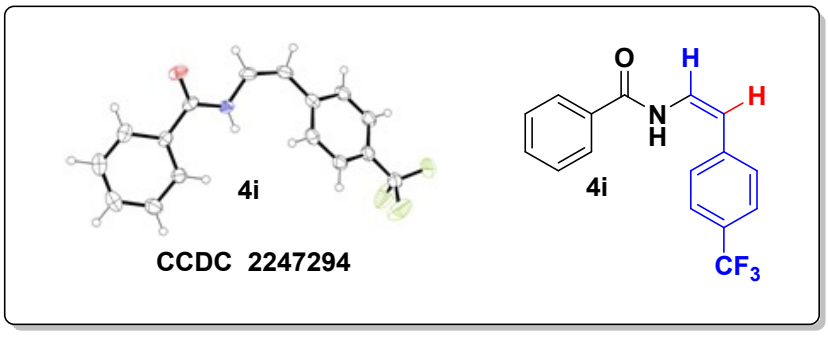
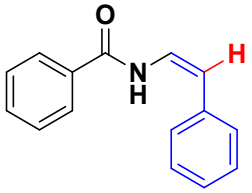


Figure S1. X-ray crystal structure of **4i**, thermal ellipsoids shown at 30% probability level. Sample preparation: 15 mg of **4i** was dissolved in 5 mL ethanol at room temperature and was left for slow evaporation for about 4 days. The crystals were mounted on a glass fiber for diffraction

experiments. 22 Intensity data were collected on a Bruker D8 VENTURE diffractometer with Mo Kα radiation (0.71073 Å) below room temperature. Crystal Data for Compound **4i**: CCDC 2247294 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

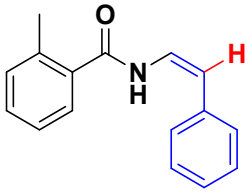
6. ^{1}H and ^{13}C NMR of products

(*Z*)-N-styrylbenzamide (3a)[1]



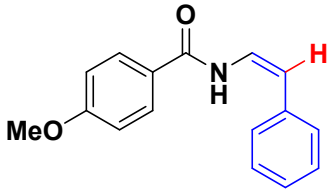
The crude product was purified by column chromatography (Hexane/ EtOAc = 92/8) to afford **3a** as a white Solid, (153.8 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 10.7 Hz, 1H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.8 Hz, 4H), 7.16 (d, *J* = 7.4 Hz, 2H), 7.08 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 10.3 Hz, 1H), 5.68 (d, *J* = 9.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (s), 135.8 (s), 133.3 (s), 132.1 (s), 129.2 (s), 128.8 (s), 127.9 (s), 127.2 (s), 127.1 (s), 122.4 (s), 111.1 (s).

(*Z*)-2-methyl-N-styrylbenzamide (3b)



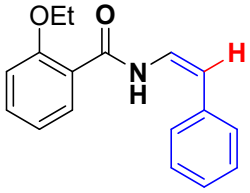
The crude product was purified by column chromatography (Hexane/ EtOAc = 95/5) to afford **3b** as a white Solid, (158.7 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 10.4 Hz, 1H), 7.27 (m,4H), 7.24 – 7.19 (m, 2H), 7.13 (m, 3H), 7.09 – 7.04 (m, 1H), 5.78 (d, *J* = 9.6 Hz, 1H), 2.39 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 166.9 (s), 137.0 (s), 135.6 (s), 134.9 (s), 131.4 (s), 130.6 (s), 129.1 (s), 127.9 (s), 127.0 (s), 126.8 (s), 126.0 (s), 122.2 (s), 110.8 (s), 20.1 (s).

(*Z*)-2-methoxy-N-styrylbenzamide (3c)[1]



The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **3c** as a white Solid, (169.5 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 10.8 Hz, 1H), 7.65 – 7.57 (m, 2H), 7.36 – 7.28 (m, 2H), 7.24 (d, *J* = 7.1 Hz, 2H), 7.16 (m,1H), 7.08 (m,1H), 6.88 – 6.74 (m, 2H), 5.74 (d, *J* = 9.5 Hz, 1H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.9 (s), 162.7 (s), 135.9 (s), 129.2 (s), 129.0 (s), 127.8 (s), 127.0 (s), 125.4 (s), 122.6 (s), 114.0 (s), 110.4 (s), 55.4 (s).

(*Z*)-2-ethoxy-N-styrylbenzamide (3d)

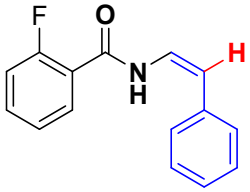


The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **3d** as a white Solid, (176.2 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (d, *J* = 11.0 Hz, 1H), 8.08 (m,1H), 7.23 – 7.13 (m, 5H), 7.13 – 7.00 (m, 2H), 6.87 – 6.78 (m, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 5.59 (d, *J* = 9.6 Hz, 1H), 3.82 (d, *J* = 7.0 Hz, 2H), 0.81 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.0 (s), 156.7 (s), 136.1 (s), 133.5 (s), 132.5 (s), 128.8 (s), 128.0 (s), 126.7 (s), 122.6 (s), 121.1 (s), 120.4 (s), 112.4 (s), 110.5 (s), 64.7 (s), 13.9 (s).

(*Z*)-2,3-dimethoxy-N-styrylbenzamide (3e)

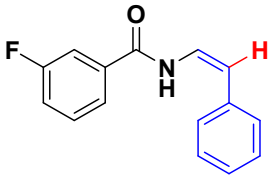
The crude product was purified by column chromatography (Hexane/ EtOAc = 87/13) to afford **3e** as a white Solid, (184 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.56 (d, *J* = 10.8 Hz, 1H), 7.82 (m,1H), 7.48 – 7.38 (m, 4H), 7.33 – 7.23 (m, 2H), 7.19 (t, *J* = 8.1 Hz, 1H), 7.09 (m, 1H), 5.87 (d, *J* = 9.6 Hz, 1H), 3.91 (s, 3H), 3.76 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6 (s), 152.4 (s), 147.6 (s), 136.0 (s), 128.9 (s), 127.9 (s), 126.8 (s), 125.1 (s), 124.5 (s), 123.2 (s), 122.4 (s), 116.0 (s), 110.8 (s), 61.2 (s), 56.0 (s).

(*Z*)-2-fluoro-N-styrylbenzamide (3f)



The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **3f** as a white Solid, (192.8 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (t, *J* = 11.9 Hz, 1H), 8.06 (m,1H), 7.42 – 7.35 (m, 1H), 7.35 – 7.24 (m, 4H), 7.22 – 7.09 (m, 3H), 7.01 (m,1H), 5.79 (d, *J* = 9.6 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.6 (m, *J* = 125.3, 122.1 Hz), 160.6 (d, *J* = 3.1 Hz), 135.5 (s), 134.1 (d, *J* = 9.5 Hz), 132.3 (d, *J* = 1.7 Hz), 129.1 (s), 127.8 (s), 127.1 (s), 125.1 (d, *J* = 3.1 Hz), 121.8 (s), 120.0 (d, *J* = 10.7 Hz), 116.1 (d, *J* = 24.7 Hz), 111.5 (s).

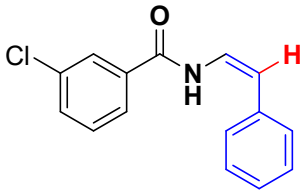
(*Z*)-3-fluoro-N-styrylbenzamide (3g)



The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **3g** as a white Solid, (192.8 mg, 80% yield)^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 10.0 Hz, 1H), 7.45 (m,5H), 7.38 – 7.11 (m, 5H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.1 (s), 162.4 (d, *J* =

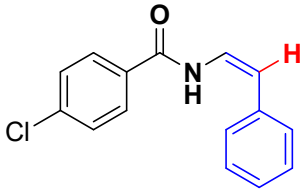
154.6 Hz), 135.5 (s), 130.5 (d, *J* = 7.8 Hz), 129.3 (s), 127.8 (s), 127.2 (s), 122.3 (d, *J* = 3.0 Hz), 122.1 (s), 119.3 (s), 119.1 (s), 114.8 (s), 114.5 (s), 111.6 (s).

(*Z*)-3-chloro-N-styrylbenzamide (3h)



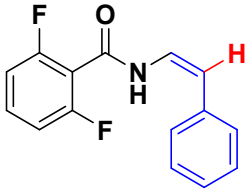
The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **3h** as a white Solid, (187.6 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 10.1 Hz, 1H), 7.69 (t, *J* = 1.7 Hz, 1H), 7.52 – 7.47 (m, 1H), 7.42 (m,1H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.27 (t, *J* = 6.0 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.15 – 7.03 (m, 1H), 5.84 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (s), 135.5 (s), 135.1 (s), 132.2 (s), 130.1 (s), 129.3 (s), 127.8 (s), 127.6 (s), 127.3 (s), 124.9 (s), 122.1 (s).

(*Z*)-4-chloro-N-styrylbenzamide (3i)



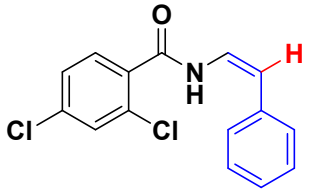
The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **3i** as a white Solid, (187.6 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 10.5 Hz, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 4H), 7.39 – 7.29 (m, 3H), 7.23 – 7.15 (m, 1H), 5.94 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.3 (s), 138.5 (s), 135.6 (s), 131.7 (s), 129.3 (s), 129.1 (s), 128.5 (s), 127.8 (s), 127.2 (s), 122.1 (s), 111.4 (s).

(*Z*)-2,6-difluoro-N-styrylbenzamide (3j)



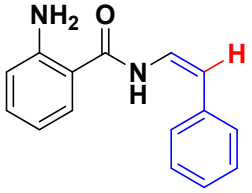
The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **3j** as a white Solid, (220 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.7 Hz, 1H), 7.36 – 7.25 (m, 3H), 7.22 (d, *J* = 7.1 Hz, 2H), 7.15 (m,1H), 7.04 (t, *J* = 10.3 Hz, 1H), 6.86 (t, *J* = 8.4 Hz, 2H), 5.82 (d, *J* = 9.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7 (d, *J* = 6.3 Hz), 159.1 (d, *J* = 6.3 Hz), 157.8 (s), 135.2 (s), 132.6 (t, *J* = 10.6 Hz), 129.1 (s), 127.9 (s), 127.2 (s), 122.1 – 121.4 (m), 112.8 (t, *J* = 17.9 Hz), 112.5 – 112.4 (m), 112.3 – 112.1 (m), 112.0 (s).

(*Z*)-2,4-dichloro-N-styrylbenzamide (3k)



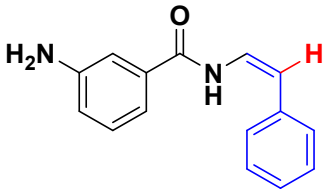
The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **3k** as a white Solid, (227.7 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (d, *J* = 10.3 Hz, 1H), 7.69 (m,1H), 7.29 (m,6H), 7.17 (m,1H), 7.06 (t, *J* = 10.3 Hz, 1H), 5.86 (d, *J* = 9.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.4 (s), 137.7 (s), 135.2 (s), 132.4 (s), 131.7 (s), 131.3 (s), 130.2 (s), 129.0 (s), 128.0 (s), 127.8 (s), 127.3 (s), 121.7 (s), 112.1 (s).

(*Z*)-2-amino-N-styrylbenzamide (3l)



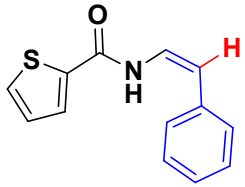
The crude product was purified by column chromatography (Hexane/ EtOAc = 85/15) to afford **3l** as a white Solid, (161.8 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 10.9 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.17 – 7.09 (m, 1H), 7.02 (m,3H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.68 – 6.61 (m, 1H), 5.72 (d, *J* = 9.5 Hz, 1H), 3.78 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8 (s), 147.3 (s), 135.8 (s), 134.4 (s), 129.6 (s), 129.2 (s), 127.9 (s), 127.0 (s), 122.4 (s), 118.6 (s), 116.1 (s), 113.9 (s), 110.9 (s).

(*Z*)-3-amino-N-styrylbenzamide (3m)



The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **3m** as a white Solid, (159.4 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 10.4 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.11 – 6.99 (m, 3H), 6.74 – 6.32 (m, 2H), 5.71 (d, *J* = 9.5 Hz, 1H), 5.55 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2 (s), 149.7 (s), 135.9 (s), 133.1 (s), 129.2 (s), 127.9 (s), 126.99 (d, *J* = 2.2 Hz), 122.2 (s), 117.6 (s), 116.7 (s), 114.2 (s), 110.3 (s).

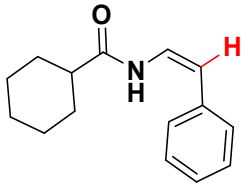
(*Z*)-N-styrylthiophene-2-carboxamide (3n)



The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **3n** as a white Solid, (146.5 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 9.6 Hz,

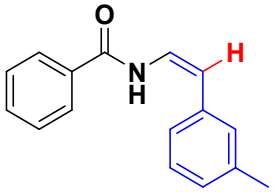
1H), 7.56 (m, 1H), 7.52 – 7.42 (m, 3H), 7.37 (d, J = 7.2 Hz, 2H), 7.31 (t, 1H), 7.22 – 7.08 (m, 2H), 5.90 (d, J = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.91 (s), 137.93 (s), 135.69 (s), 131.23 (s), 129.29 (s), 128.79 (s), 127.96 (s), 127.87 (s), 127.16 (s), 121.95 (s), 110.81 (s).

(*Z*)-N-styrylcyclohexanecarboxamide (3o)



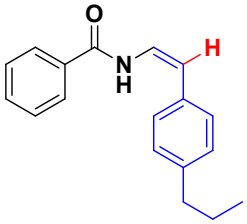
The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **3o** as a white Solid, (144.2 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 10.2 Hz, 1H), 7.33 (t, 2H), 7.20 (m, 3H), 6.91 (m, 1H), 5.66 (d, J = 9.6 Hz, 1H), 2.23 – 1.99 (m, 1H), 1.81 (d, J = 13.2 Hz, 2H), 1.73 (m, 2H), 1.67 – 1.57 (m, 1H), 1.37 (m, 2H), 1.19 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.50 (s), 135.91 (s), 129.14 (s), 127.84 (s), 126.87 (s), 122.21 (s), 109.67 (s), 45.42 (s), 29.39 (s), 25.62 (s), 25.58 (s).

(*Z*)-N-(3-methylstyryl)benzamide (4a)



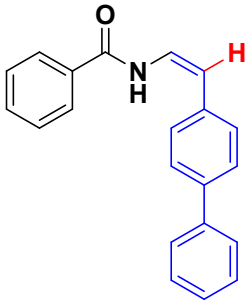
The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4a** as a white Solid, (158.7 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, J = 10.3 Hz, 1H), 7.79 (d, J = 7.3 Hz, 2H), 7.56 (m,1H), 7.48 (t, J = 7.5 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.26 – 7.15 (m, 3H), 7.13 (d, J = 7.5 Hz, 1H), 5.90 (d, J = 9.5 Hz, 3H), 2.42 (s, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (s), 139.0 (s), 135.7 (s), 133.4 (s), 132.1 (s), 129.1 (s), 128.8 (s), 128.8 (s), 127.9 (s), 127.1 (s), 124.7 (s), 122.2 (s), 111.1 (s), 21.5 (s).

(*Z*)-N-(4-propylstyryl)benzamide (4b)



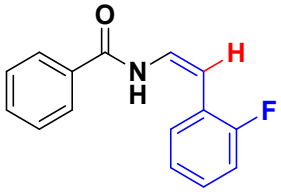
The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4b** as a white Solid, (172.2 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 10.8 Hz, 1H), 7.65 (m, 2H), 7.45 – 7.39 (m, 2H), 7.38 – 7.30 (m, 4H), 7.19 – 7.10 (m, 1H), 7.05 (dd, J = 11.0, 9.6 Hz, 1H), 5.75 (d, J = 9.5 Hz, 1H), 2.77 – 2.28 (m, 2H), 1.71 – 1.42 (m, 2H), 0.86 (t, J = 7.3 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (s), 141.7 (s), 133.4 (s), 133.1 (s), 132.1 (s), 129.3 (s), 128.8 (s), 127.7 (s), 127.1 (s), 121.9 (s), 111.0 (s), 37.7 (s), 24.5 (s), 13.9 (s).

(*Z*)-N-(2-([1,1'-biphenyl]-4-yl)vinyl)benzamide (4c)



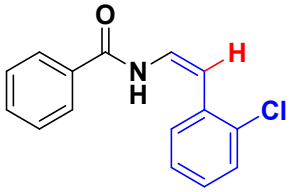
The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4c** as a white Solid, (182.3 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 7.9 Hz, 1H), 7.83 (d, *J* = 6.9 Hz, 2H), 7.68 (m, 4H), 7.61 – 7.37 (m, 8H), 7.29 (d, *J* = 5.7 Hz, 1H), 5.97 (d, *J* = 9.1 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (s), 140.3 (s), 139.8 (s), 134.8 (s), 133.3 (s), 132.2 (s), 128.9 (s), 128.9 (s), 128.3 (s), 127.8 (s), 127.5 (s), 127.14(s), 126.9 (s), 122.6 (s), 110.6 (s).

(*Z*)-N-(2-fluorostyryl)benzamide (4d)



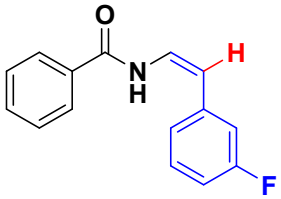
The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4d** as a white Solid, (188 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.79 (d, *J* = 7.4 Hz, 2H), 7.58 – 7.49 (m, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.31 (m, 1H), 7.31 – 7.21 (m, 2H), 7.22 – 7.10 (m, 2H), 5.77 (d, *J* = 9.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3 (s), 159.2 (d, *J* = 245.3 Hz), 133.3 (s), 132.2 (s), 130.2 (d, *J* = 4.5 Hz), 128.9 (d, *J* = 8.7 Hz), 128.8 (s), 127.1 (s), 124.7 (d, *J* = 3.3 Hz), 123.6 (s), 122.9 (d, *J* = 15.5 Hz), 116.3 (d, *J* = 23.0 Hz), 103.7 (s).

(*Z*)-N-(2-chlorostyryl)benzamide (4e)



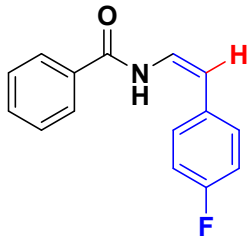
The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4e** as a white Solid, (188 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 10.1 Hz, 1H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 7.40 – 7.31 (m, 4H), 7.27 – 7.18 (m, 2H), 7.19 – 7.12 (m, 1H), 5.87 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1 (s), 135.5 (s), 135.1 (s), 132.2 (s), 130.1 (s), 129.3 (s), 127.8 (s), 127.6 (s), 127.3 (s), 124.9 (s), 122.1 (s).

(*Z*)-N-(3-fluorostyryl)benzamide (4f)



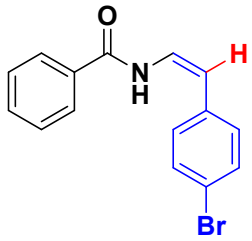
The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4f** as a white Solid, (188 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, *J* = 10.1 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 2H), 7.59 – 7.51 (m, 1H), 7.47 (m, 2H), 7.39 (m,1H), 7.23 (m,1H), 7.13 (d, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 9.9 Hz, 1H), 6.97 (t, *J* = 8.4 Hz, 1H), 5.83 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 (d, *J* = 9.2 Hz), 163.1 – 136.8 (m), 133.1 (s), 132.3 (s), 130.8 (s), 130.8 (s), 128.9 (s), 127.1 (s), 123.73 – 122.93 (m), 114.7 (d, *J* = 21.5 Hz), 114.0 (d, *J* = 21.0 Hz), 109.6 (s).

(*Z*)-N-(4-fluorostyryl)benzamide (4g)



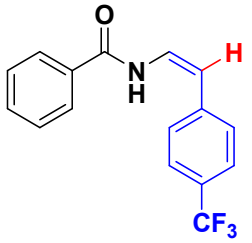
The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4g** as a white Solid, (188 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 10.1 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 2H), 7.39 (m,3H), 7.27 – 7.17 (m, 2H), 7.03 (m,3H), 5.74 (d, *J* = 9.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 (s), 161.5 (d, *J* = 247.3 Hz), 133.2 (s), 132.2 (s), 131.7 (d, *J* = 3.2 Hz), 129.5 (d, *J* = 7.8 Hz), 128.9 (s), 127.1 (s), 122.4 (s), 116.3 (s), 116.1 (s), 110.0 (s).

(*Z*)-N-(4-bromostyryl)benzamide (4h)



The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4g** as a white Solid, (227 mg, 71% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 9.9 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.68 – 7.42 (m, 5H), 7.39 – 7.16 (m, 3H), 5.83 (d, *J* = 9.5 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (s), 134.6 (s), 133.1 (s), 132.3 (s), 129.5 (s), 128.9 (s), 127.1 (s), 123.0 (s), 120.8 (s), 109.7 (s).

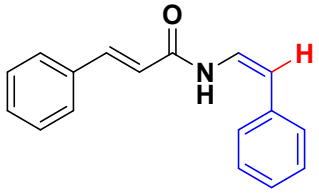
(*Z*)-N-(4-(trifluoromethyl)styryl)benzamide (4i)



The crude product was purified by column chromatography (Hexane/ EtOAc = 80/20) to afford **4i** as a white Solid, (218.2 mg, 75% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 10.5 Hz, 1H), 7.85 – 7.75 (m, 2H), 7.69 (d, *J* = 8.1 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 4H), 7.29 (t, *J* = 10.4 Hz, 1H), 5.90 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5 (s),

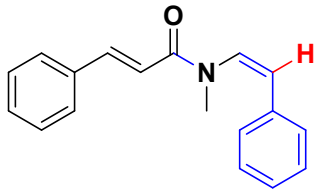
139.5 (s), 133.0 (s), 132.4 (s), 128.9 (s), 128.1 (s), 127.1 (s), 126.1 (q, *J* = 3.8 Hz), 124.0 (s), 109.3 (s).

N-((*Z*)-styryl)cinnamamide (6a)[2]



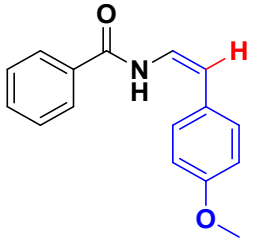
The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **6a** as a yellowish Solid, (157 mg, 63% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 11.5 Hz, 1H), 7.66 (d, *J* = 15.5 Hz, 1H), 7.44 (m,2H), 7.39 – 7.17 (m, 8H), 7.06 (m,1H), 6.31 (d, *J* = 15.5 Hz, 1H), 5.77 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.13 (s), 143.16 (s), 135.7 (s), 134.4 (s), 130.19 (s), 129.19 (s), 128.9 (s), 128.0 (s), 127.9 (s), 127.0 (s), 122.3 (s), 119.4 (s), 110.6 (s).

N-methyl-N-((*Z*)-styryl)cinnamamide (6b)[2]



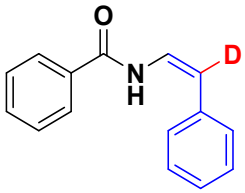
The crude product was purified by column chromatography (Hexane/ EtOAc = 95/05) to afford **6a** as a Clear viscous liquid, (255.4 mg, 97% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 15.5 Hz, 1H), 7.37 (m,2H), 7.30 – 7.21 (m, 7H), 7.18 – 7.12 (m, 1H), 6.86 (d, *J* = 15.5 Hz, 1H), 6.42 (d, *J* = 8.7 Hz, 1H), 6.17 (d, *J* = 8.7 Hz, 1H), 3.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4 (s), 142.7 (s), 135.1 (s), 134.4 (s), 129.7 (s), 128.8 (s), 128.7 (s), 128.6 (s), 128.0 (s), 127.9 (s), 125.0 (s), 118.3 (s), 34.6 (s).

(Z)-N-(4-methoxystyryl)benzamide (7)



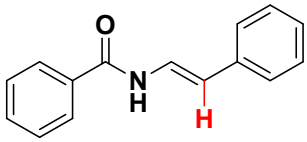
The crude product was purified by column chromatography (Hexane/ EtOAc = 82/18) to afford **6a** as white solid (167 mg, 66% yield). ^{1}H NMR (400 MHz, DMSO-d6) δ 9.96 (d, J = 9.0 Hz, 1H), 7.98 – 7.93 (m, 2H), 7.62 – 7.56 (m, 1H), 7.51 (t, J = 7.4 Hz, 2H), 7.44 (d, J = 8.7 Hz, 2H), 6.98 (t, J = 5.8 Hz, 2H), 6.85 (t, J = 9.4 Hz, 1H), 5.82 (d, J = 9.7 Hz, 1H), 3.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d6) δ 165.72 (s), 158.43 (s), 134.01 (s), 132.23 (s), 130.19 (s), 128.83 (s), 128.73 (s), 128.30 (s), 121.74 (s), 114.47 (s), 113.25 (s), 55.56 (s). HRMS (ESI) for $C_{16}H_{15}NO_2$ [M + H]+ : Calculated 329.1260 Found: 329.1254

(*Z*)-N-(2-phenylvinyl-2-d)benzamide (8)



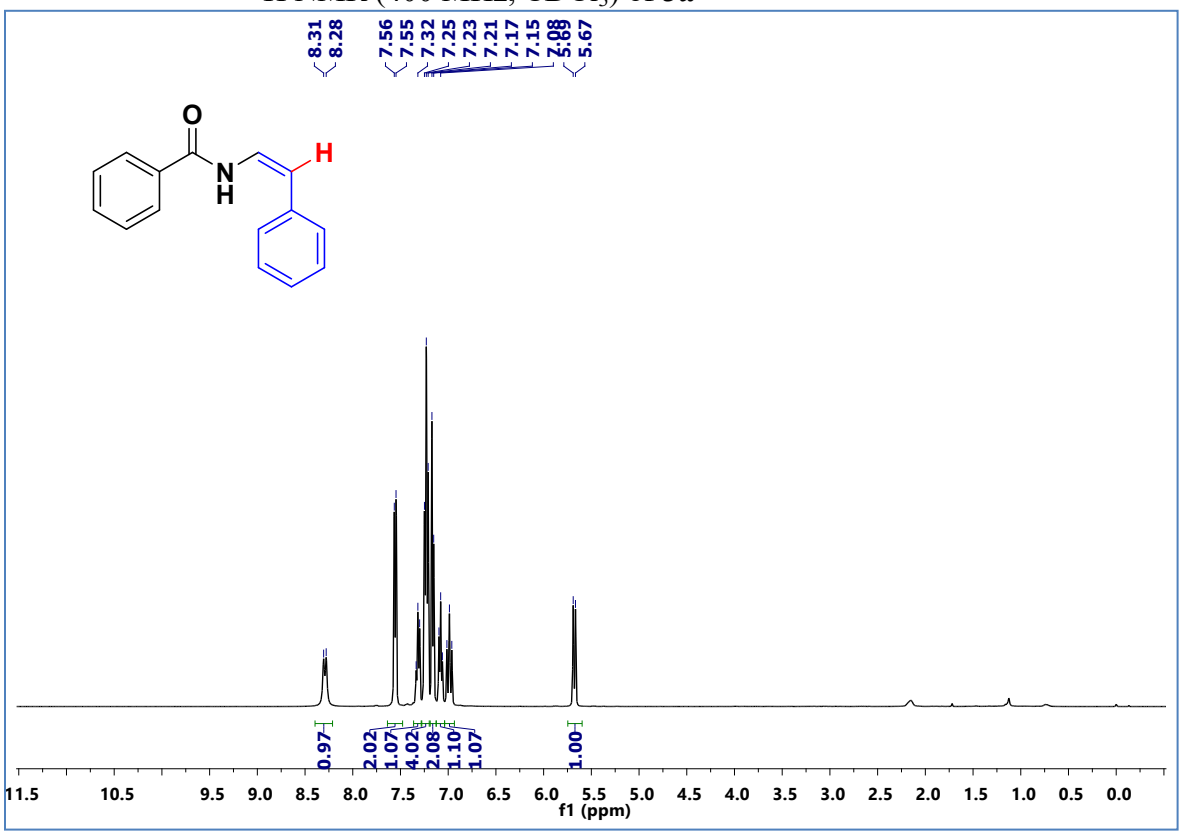
The crude product was purified by column chromatography (Hexane/ EtOAc = 85/15) to afford **6a** as white solid (143.4 mg, 64% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.71 (d, *J* = 7.4 Hz, 2H), 7.56 – 7.18 (m, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.4 (s), 135.7 (s), 133.3 (s), 132.2 (s), 129.2 (s), 128.8 (s), 127.9 (s), 127.1 (s), 127.1 (s).

(*E*)-N-styrylbenzamide (9)[1]

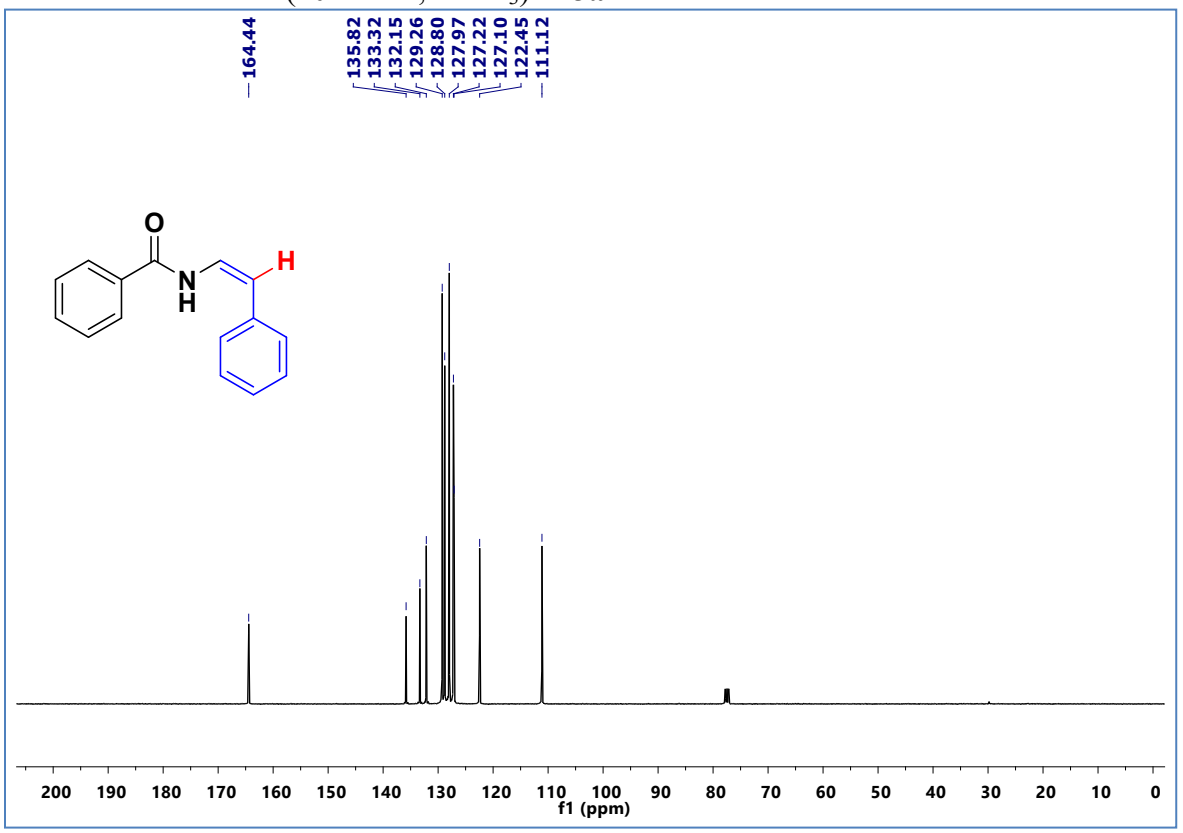


The crude product was purified by column chromatography (Hexane/ EtOAc = 90/10) to afford **6a** as a yellowish Solid, (189.5 mg, 85% yield).^{1}H NMR (400 MHz, DMSO-d_6) δ 10.66 (d, *J* = 9.8 Hz, 1H), 7.98 (d, *J* = 7.4 Hz, 2H), 7.72 – 7.58 (m, 2H), 7.54 (t, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.32 (t, 2H), 7.18 (t, 1H), 6.48 (d, *J* = 14.7 Hz, 1H).

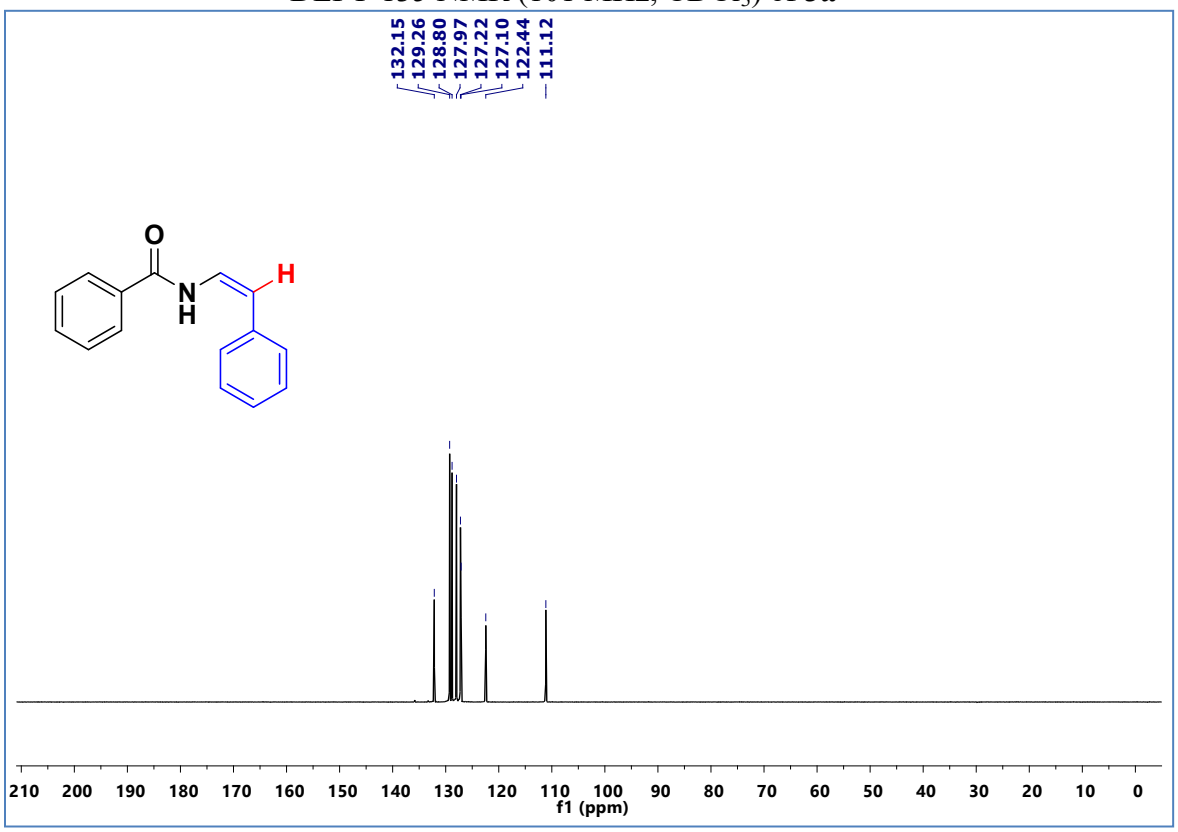
^{1}H NMR (400 MHz, $CDCl_3$) of **3a**



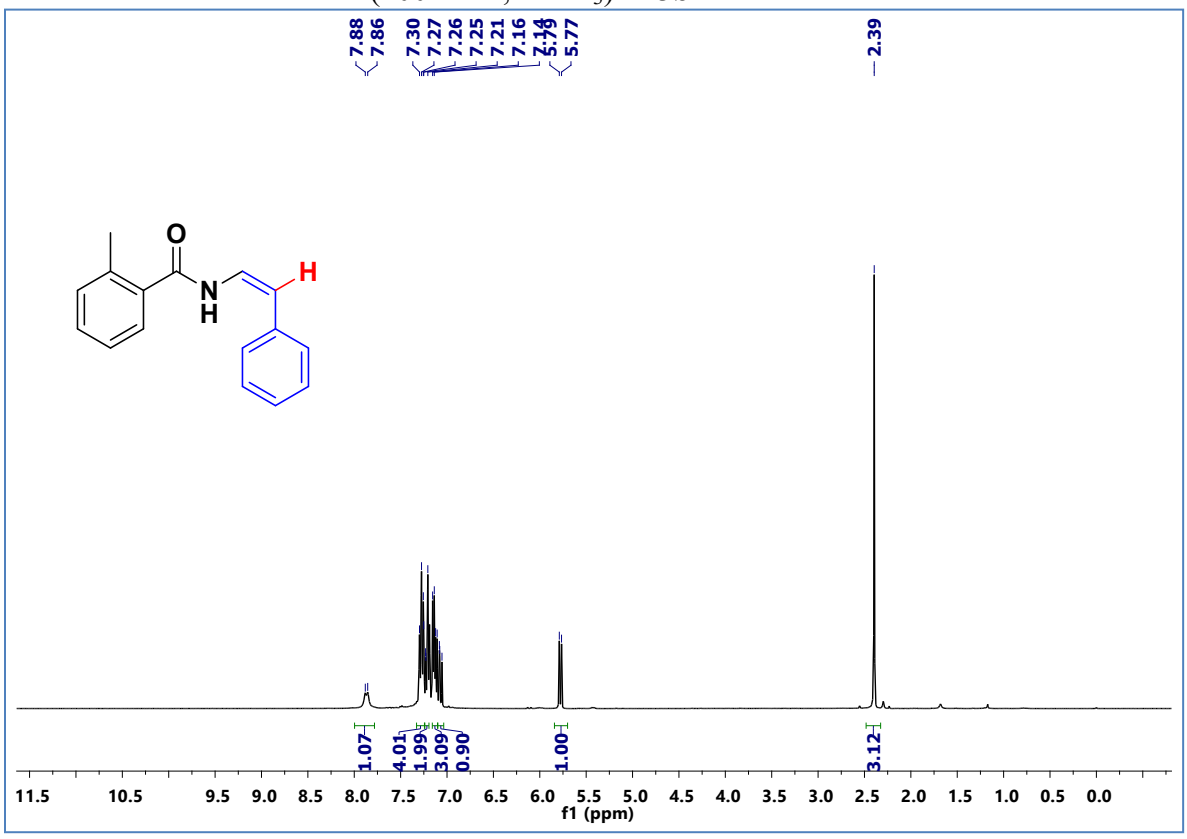
^{13}C NMR (101 MHz, $CDCl_3$) of **3a**



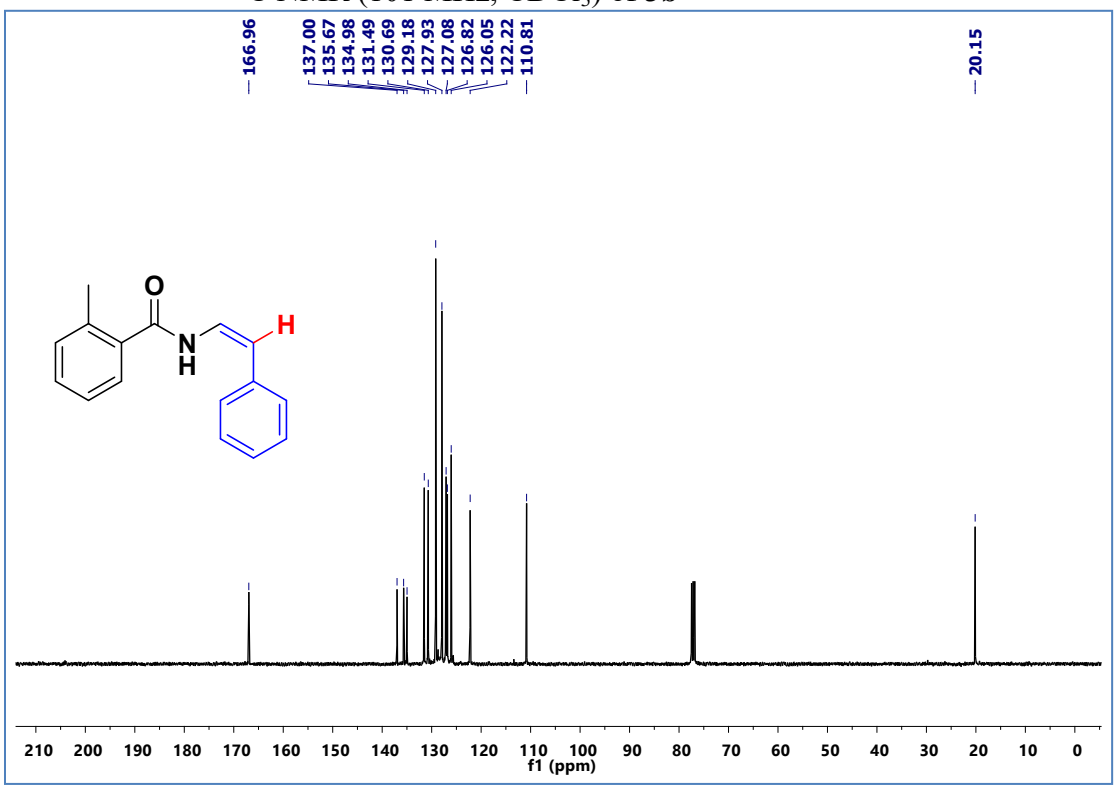
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3a**



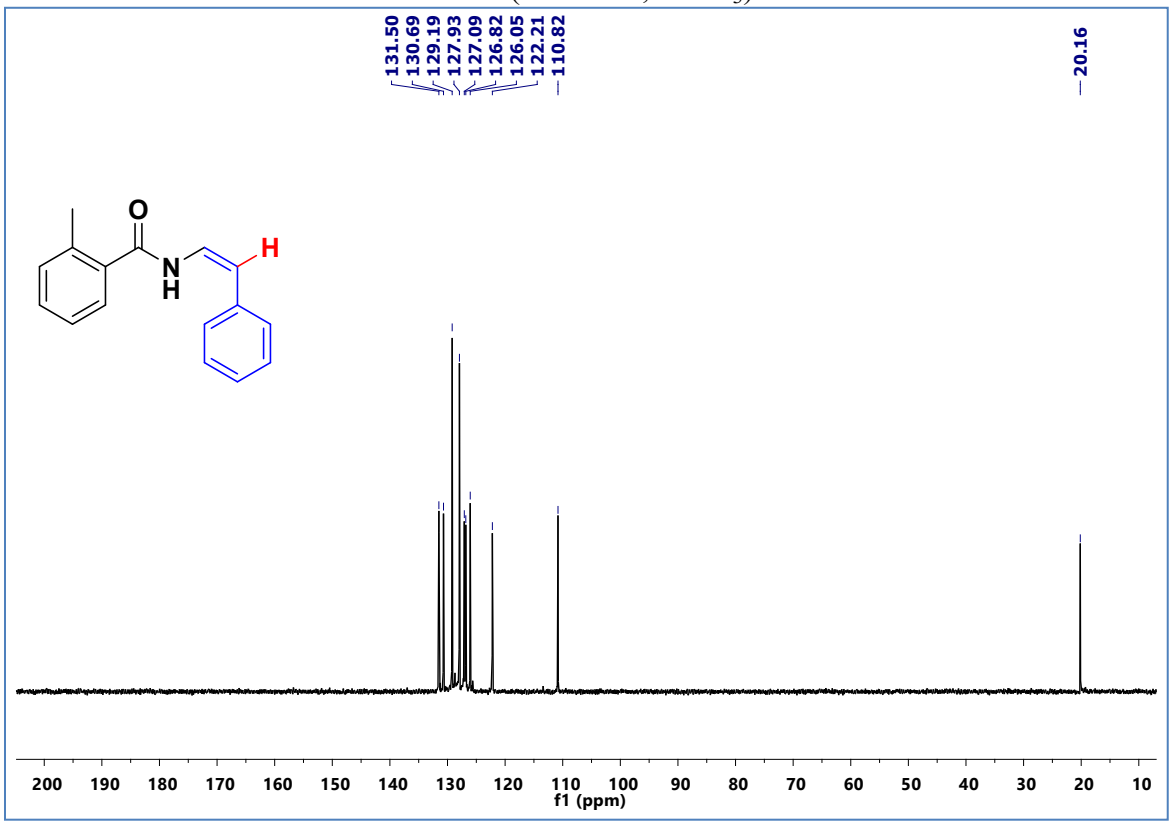
^{1}H NMR (400 MHz, $CDCl_3$) of **3b**



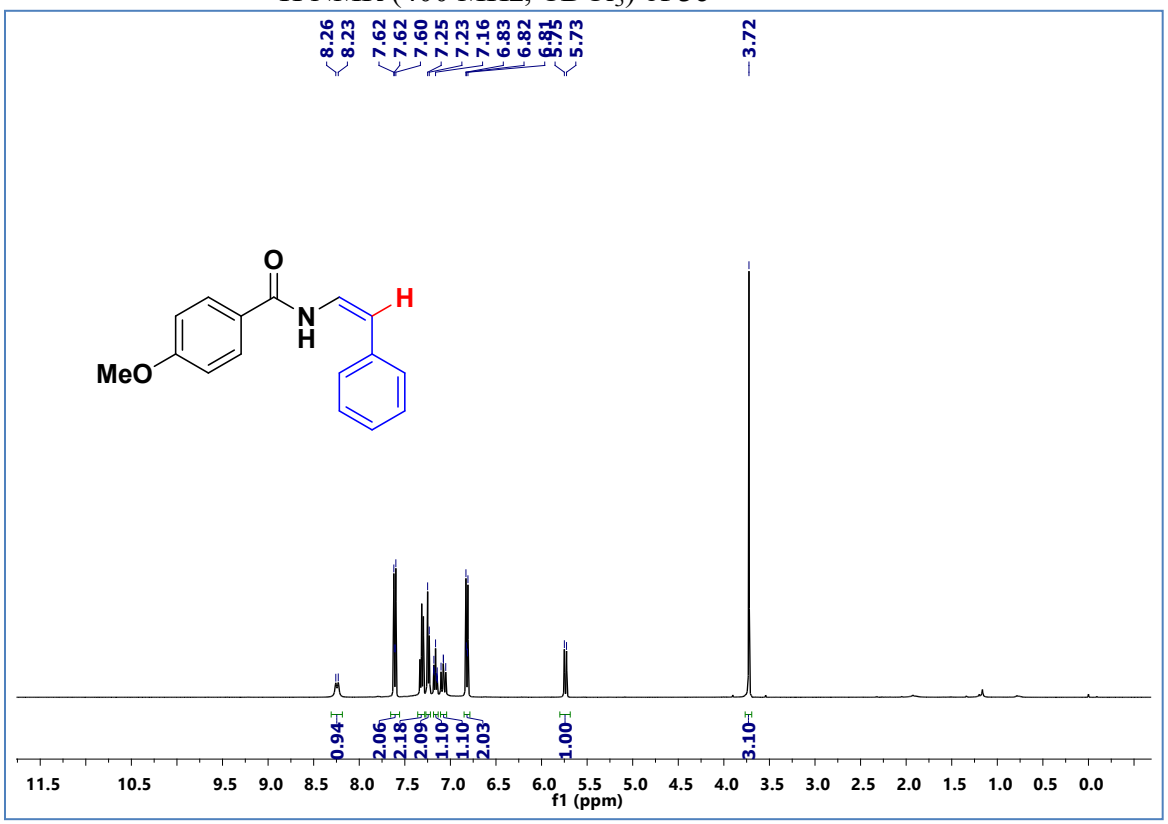
^{13}C NMR (101 MHz, $CDCl_3$) of **3b**



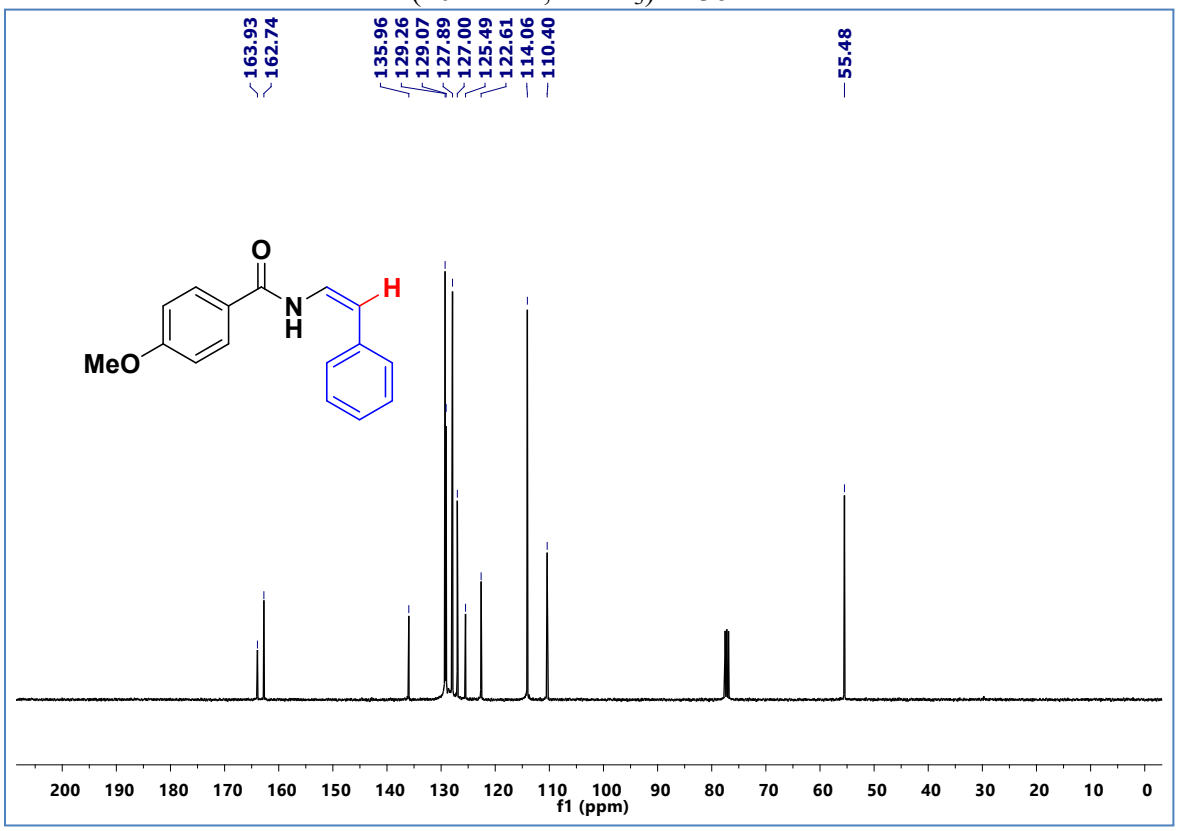
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3b**



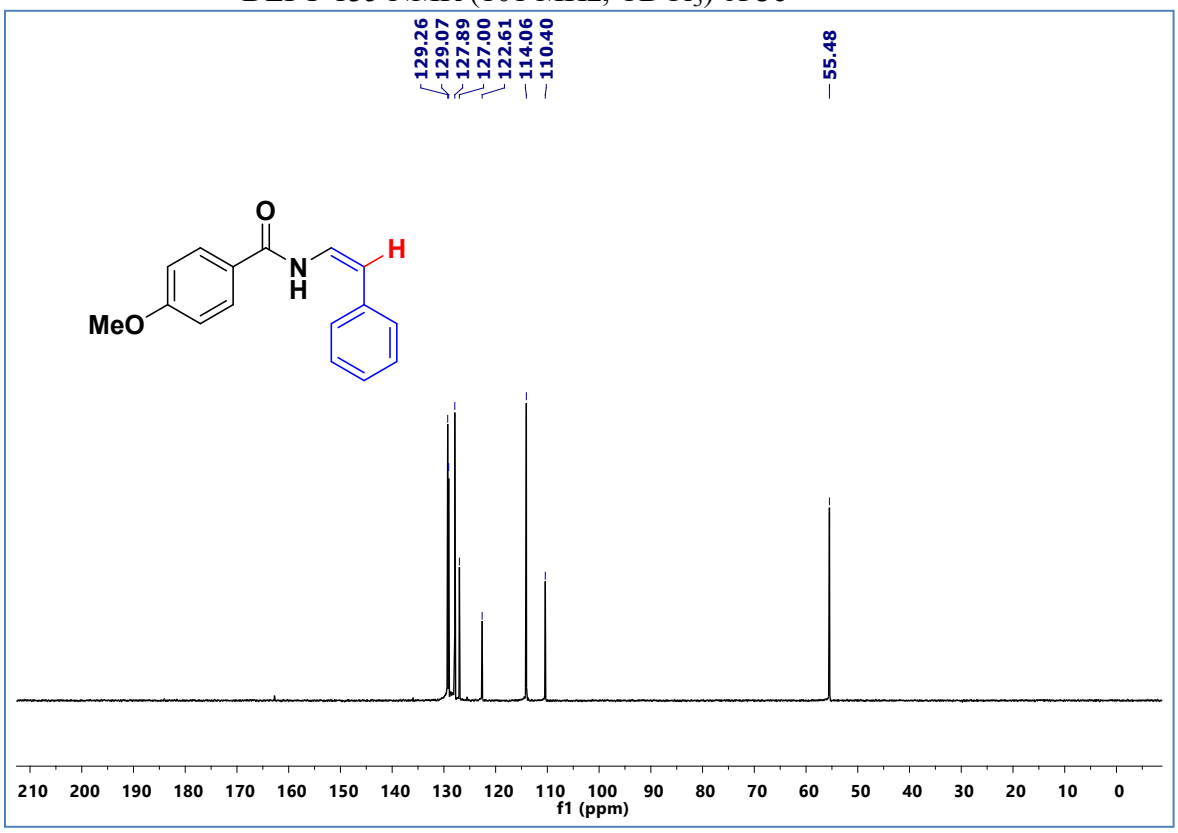
^{1}H NMR (400 MHz, $CDCl_3$) of **3c**



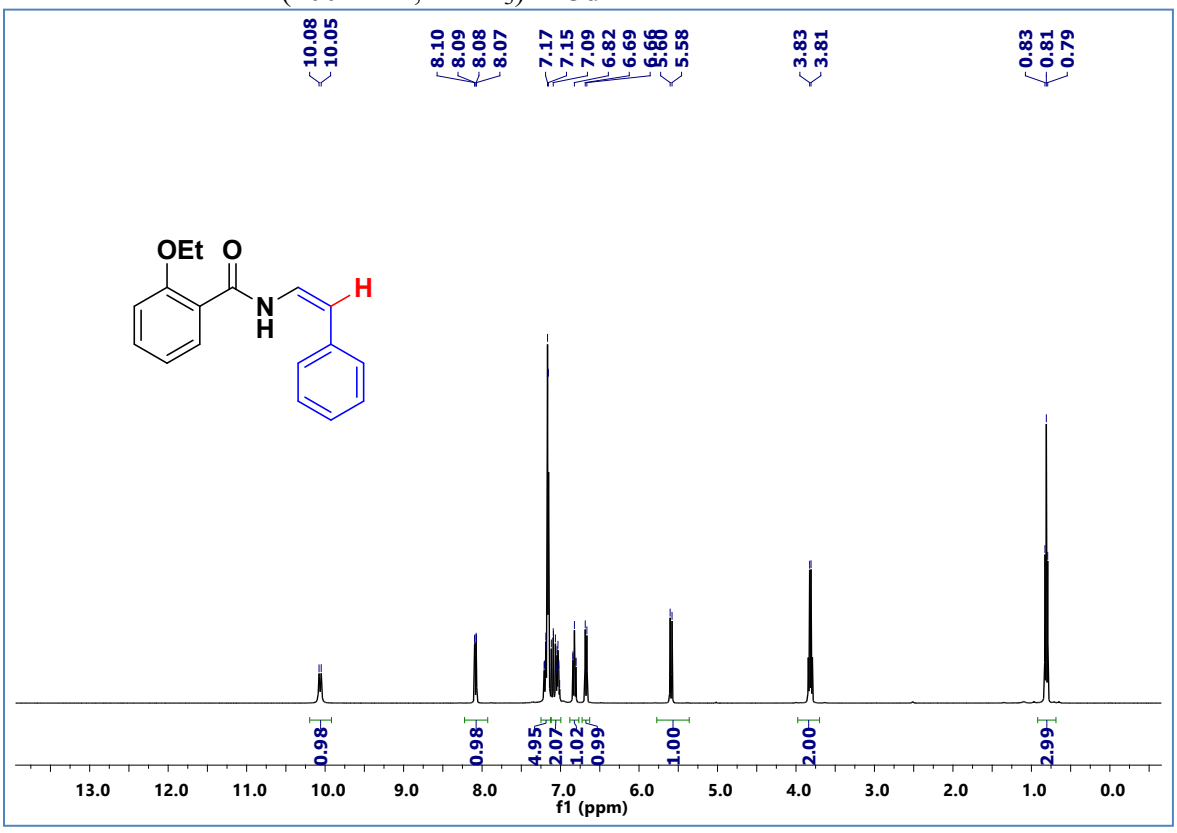
^{13}C NMR (101 MHz, $CDCl_3$) of **3c**



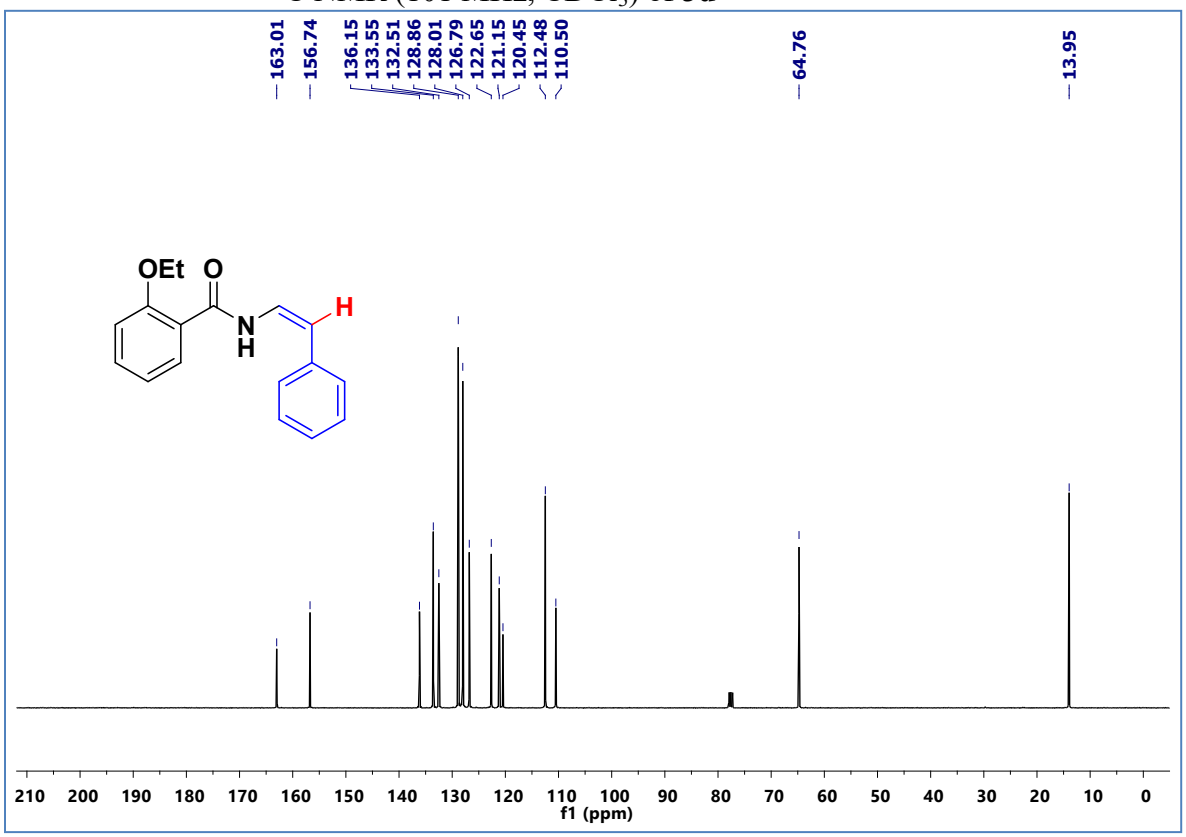
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3c**



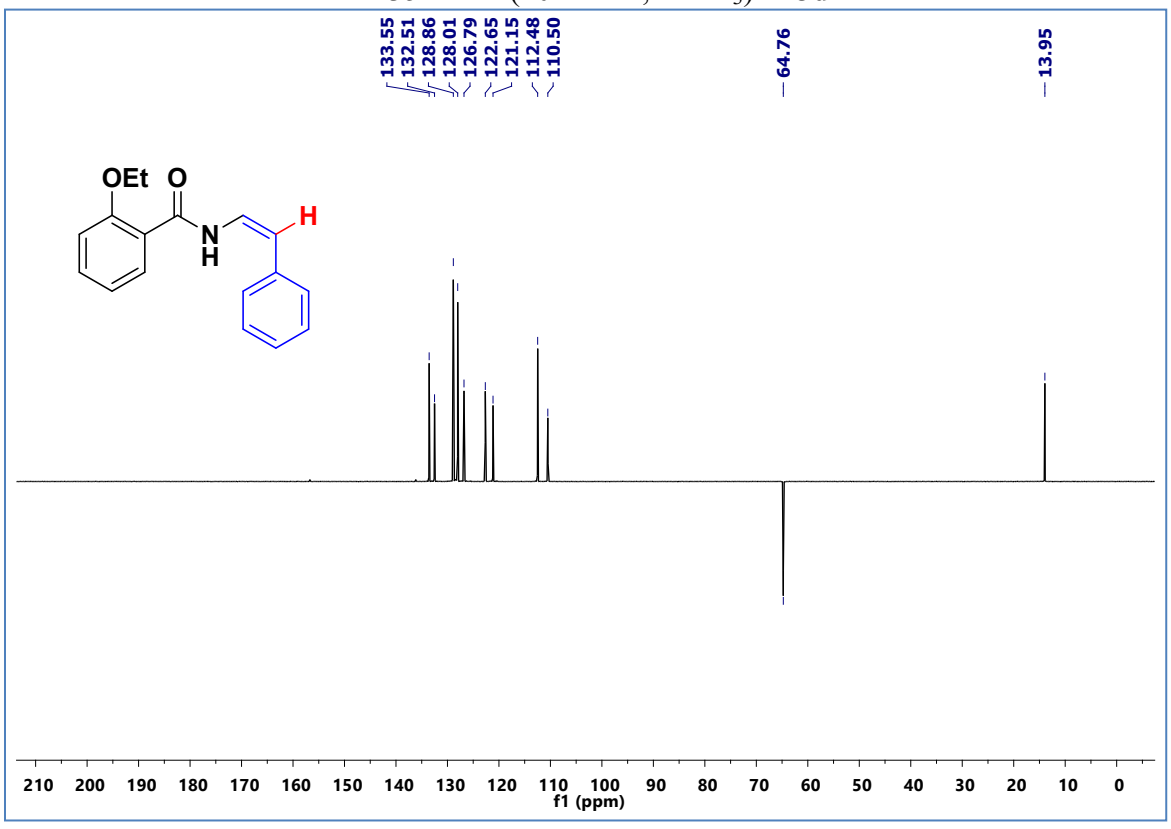
^1H NMR (400 MHz, $CDCl_3$) of **3d**



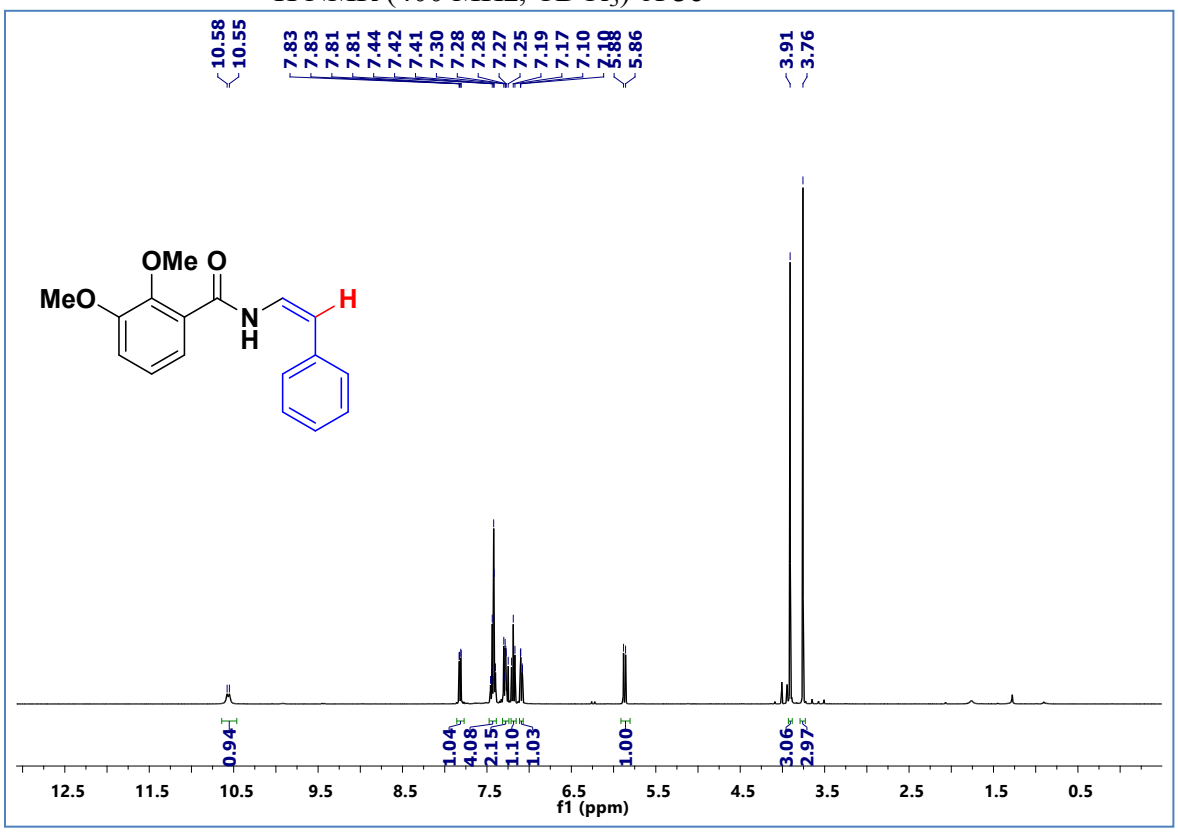
^{13}C NMR (101 MHz, $CDCl_3$) of **3d**



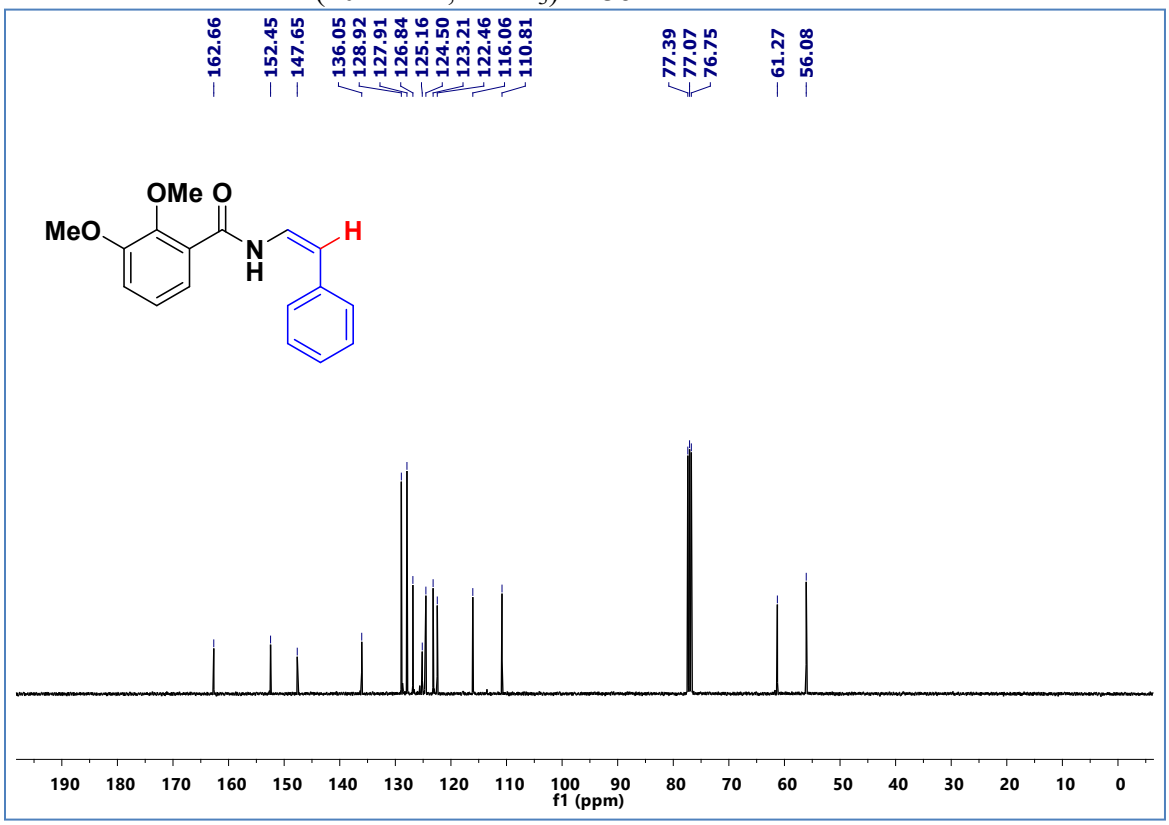
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3d**



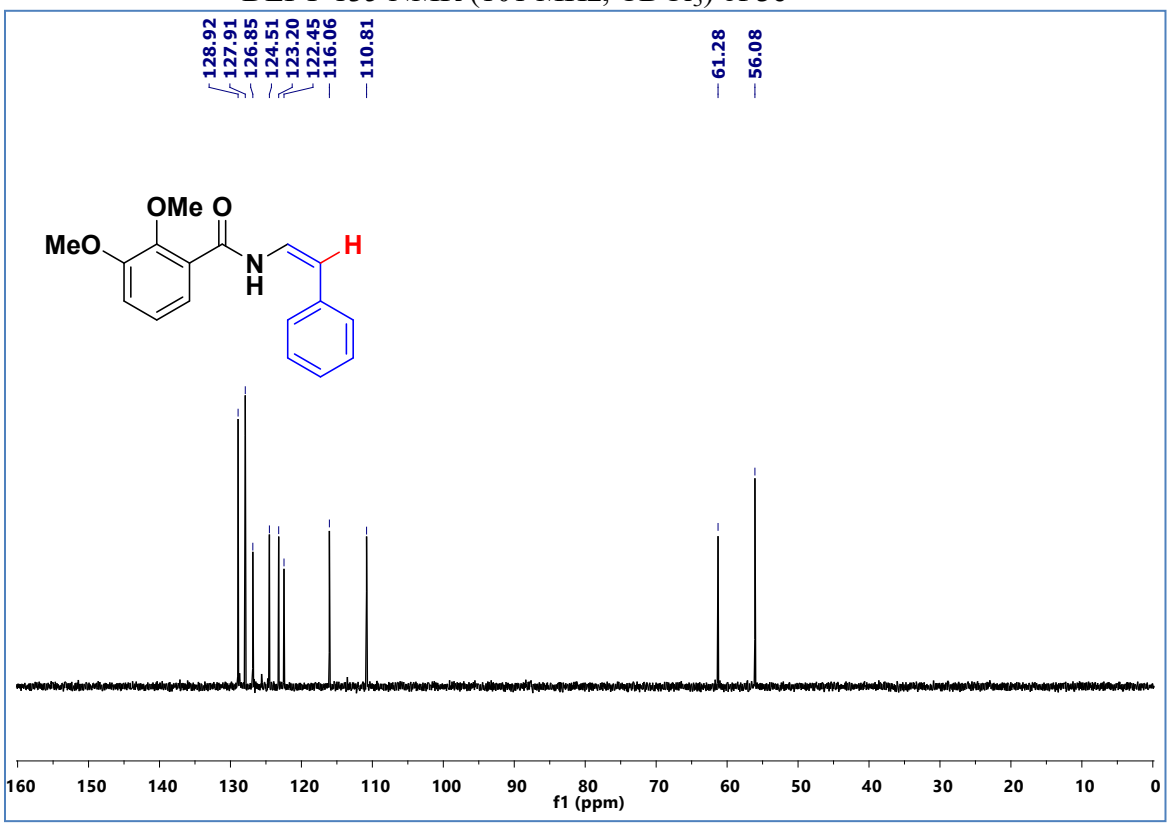
^{1}H NMR (400 MHz, $CDCl_3$) of **3e**



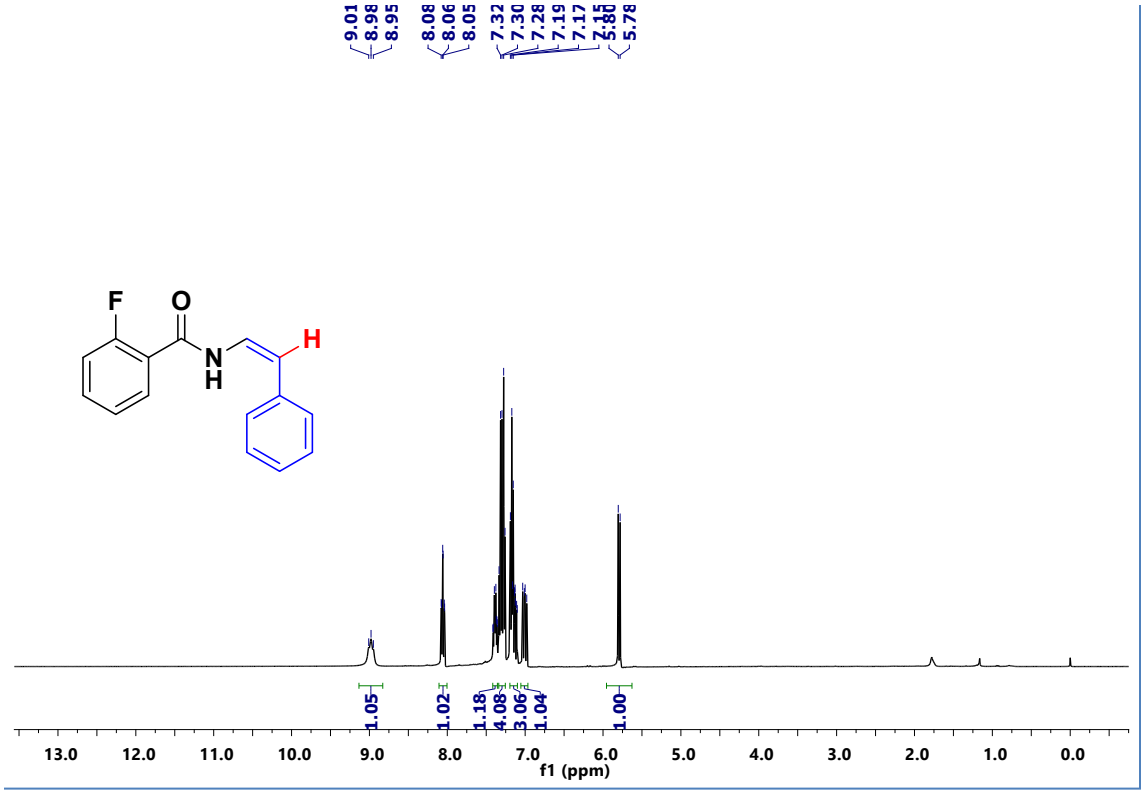
^{13}C NMR (101 MHz, $CDCl_3$) of **3e**



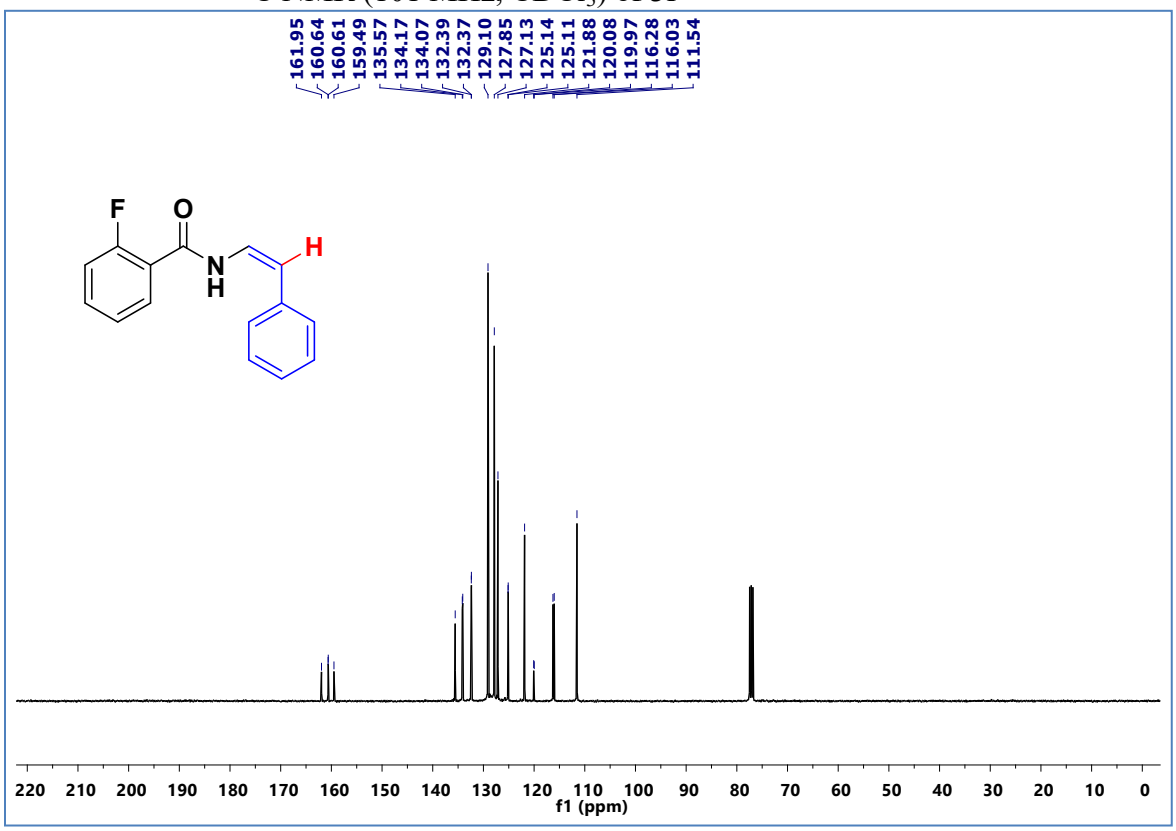
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3e**



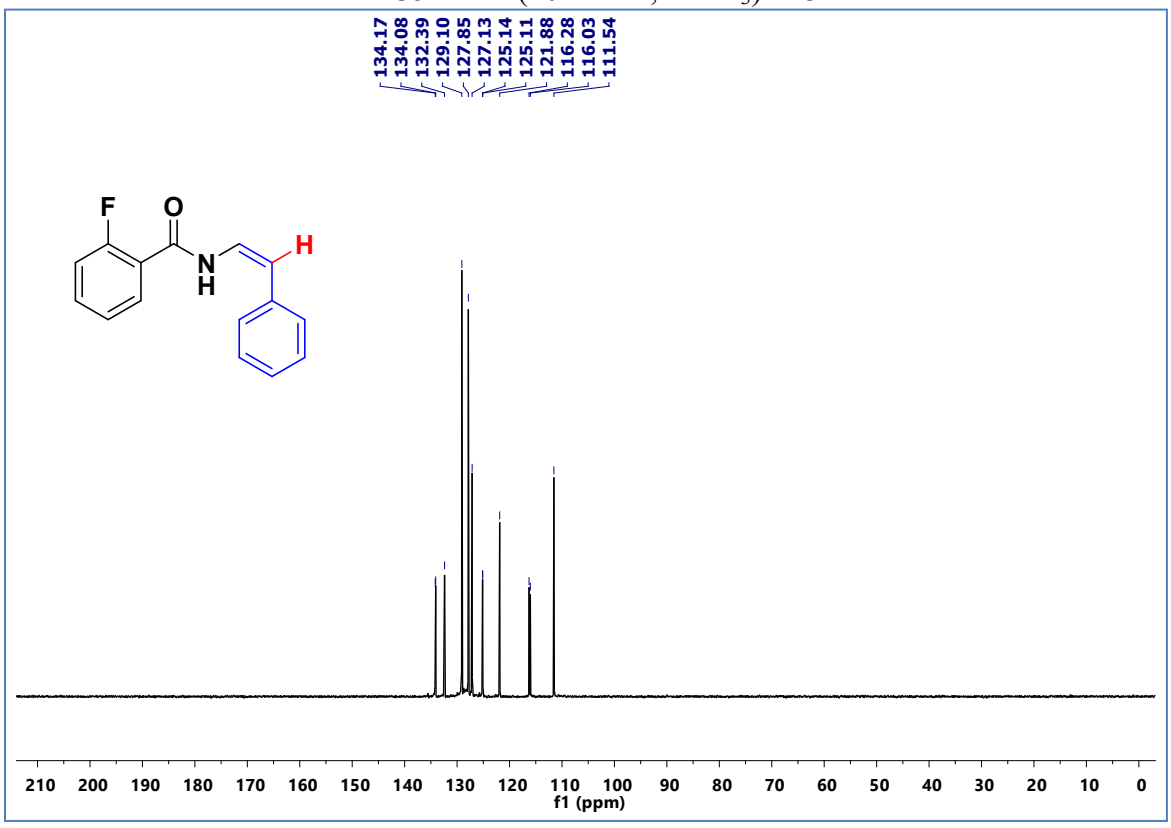
^1H NMR (400 MHz, $CDCl_3$) of **3f**



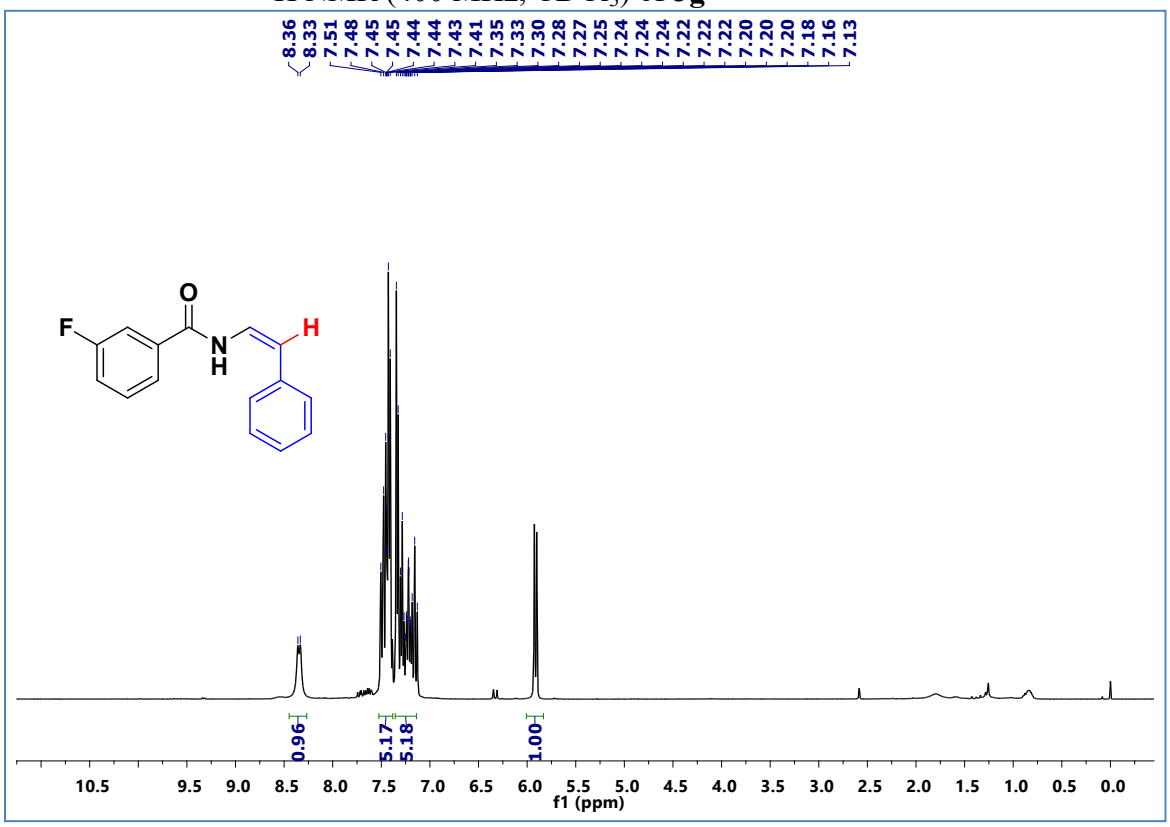
^{13}C NMR (101 MHz, $CDCl_3$) of **3f**



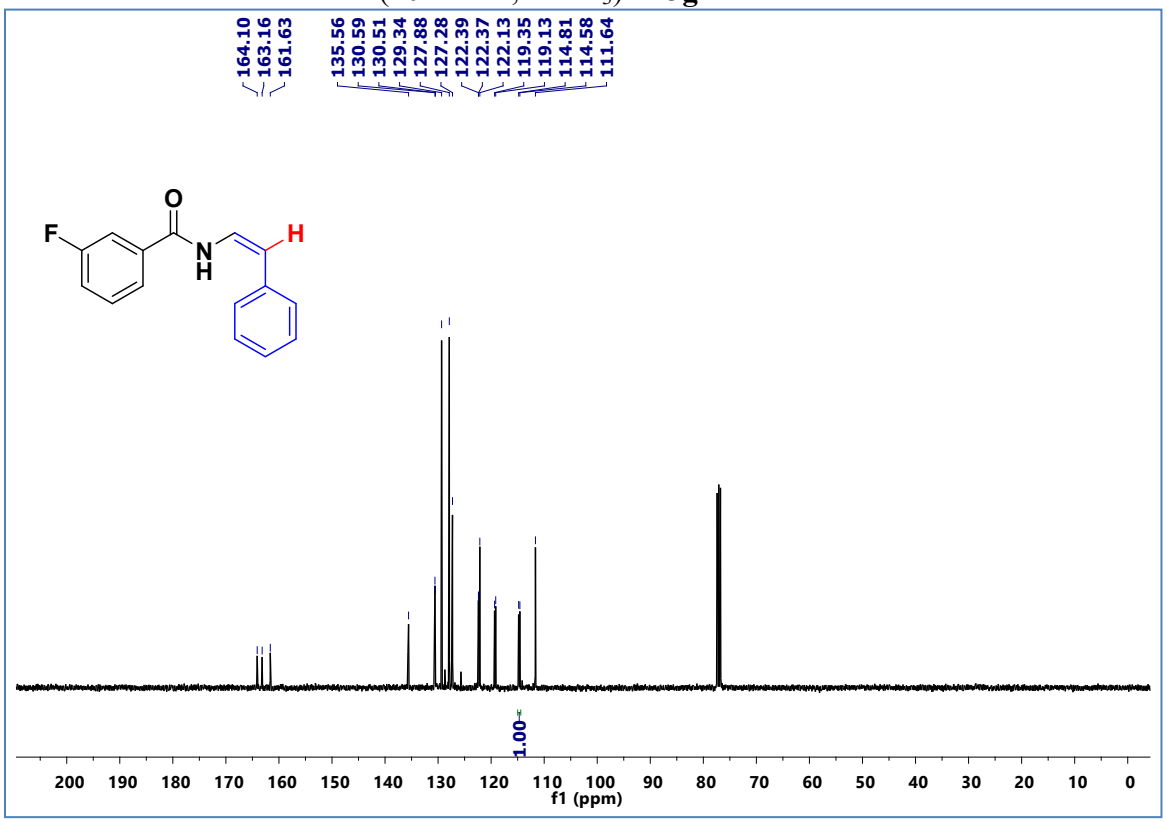
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3f**



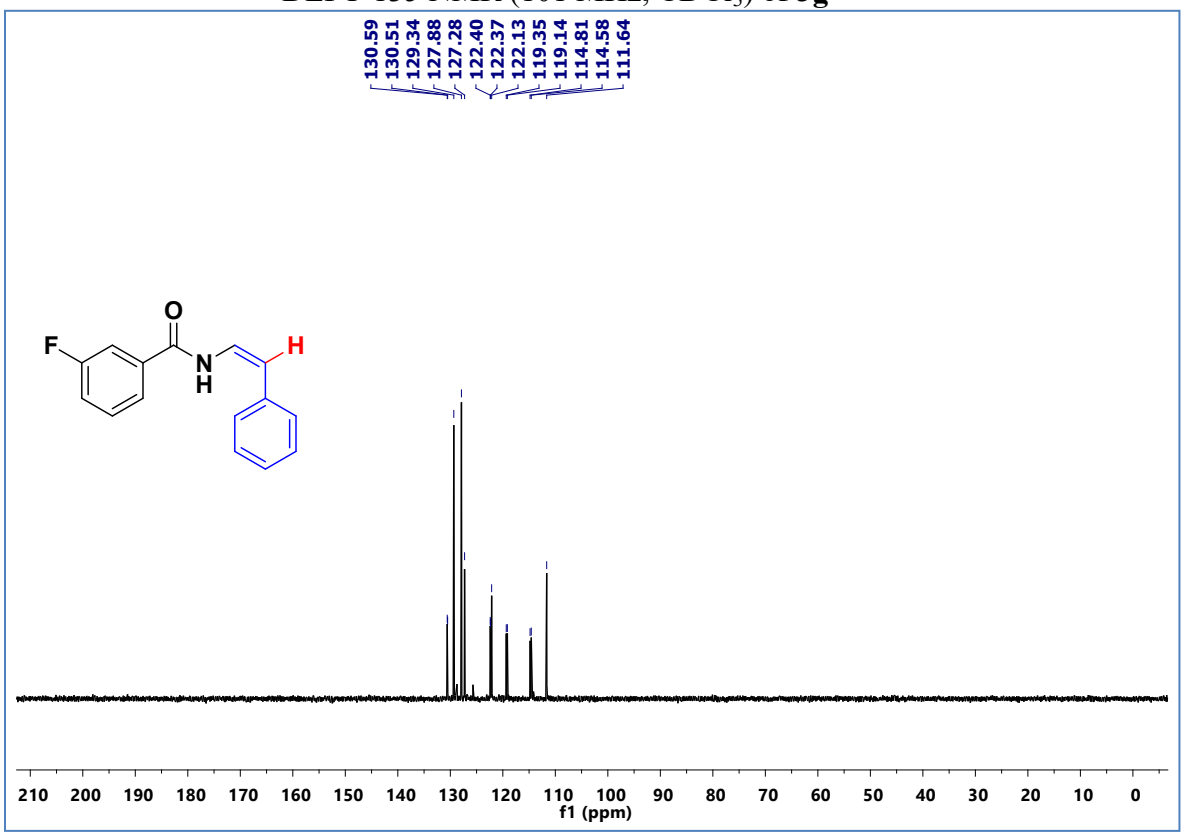
^{1}H NMR (400 MHz, $CDCl_3$) of **3g**



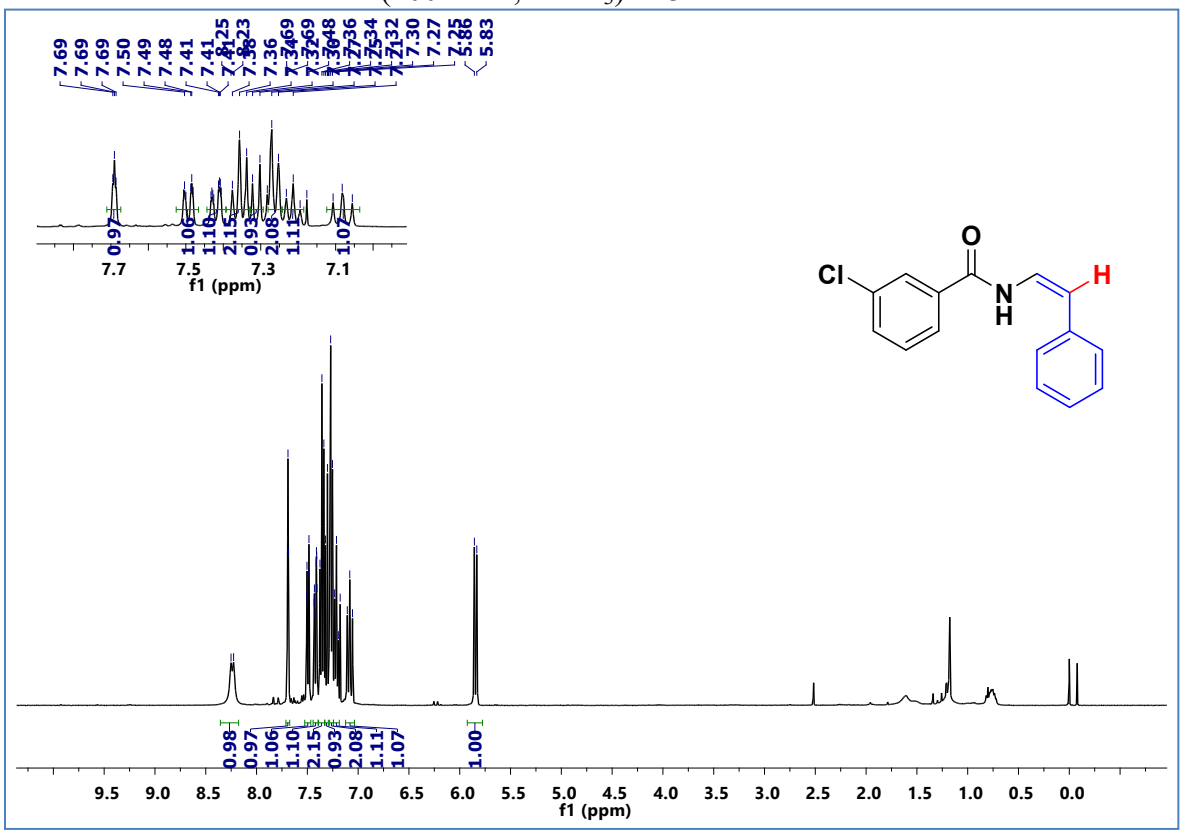
^{13}C NMR (101 MHz, $CDCl_3$) of **3g**



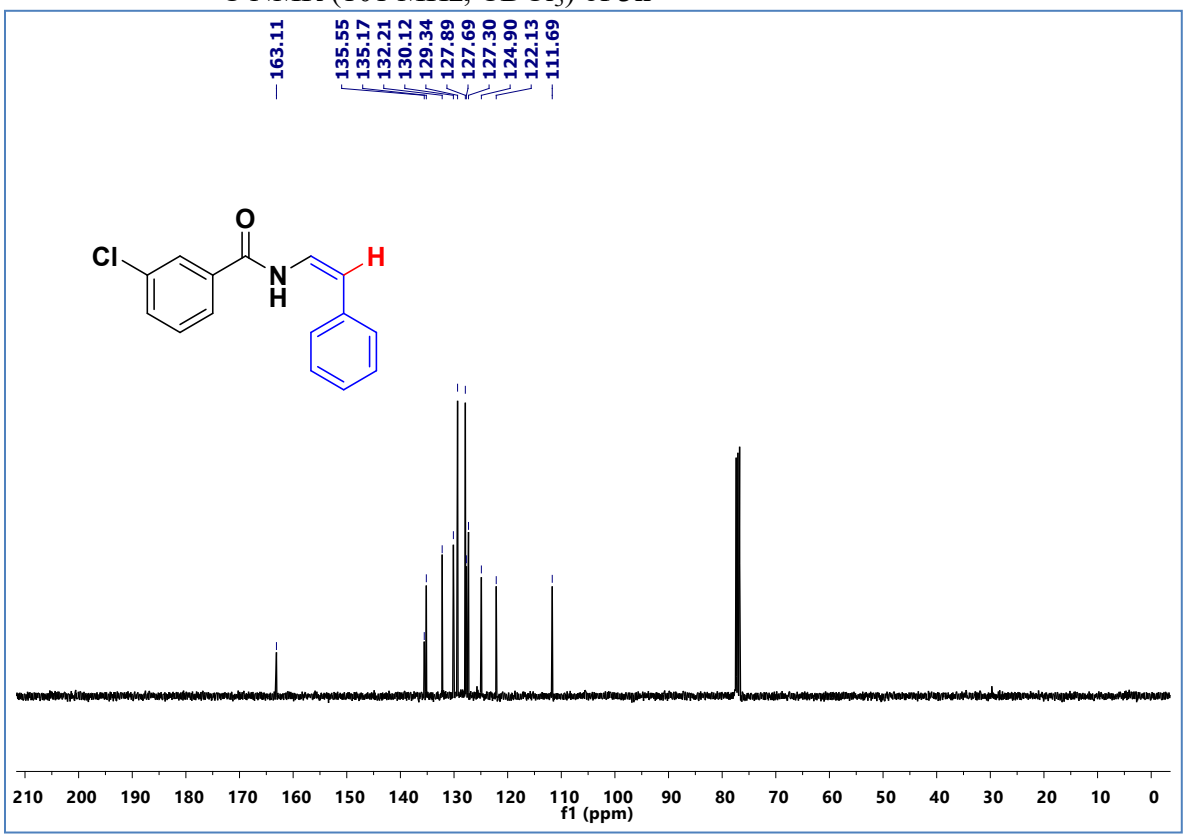
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3g**



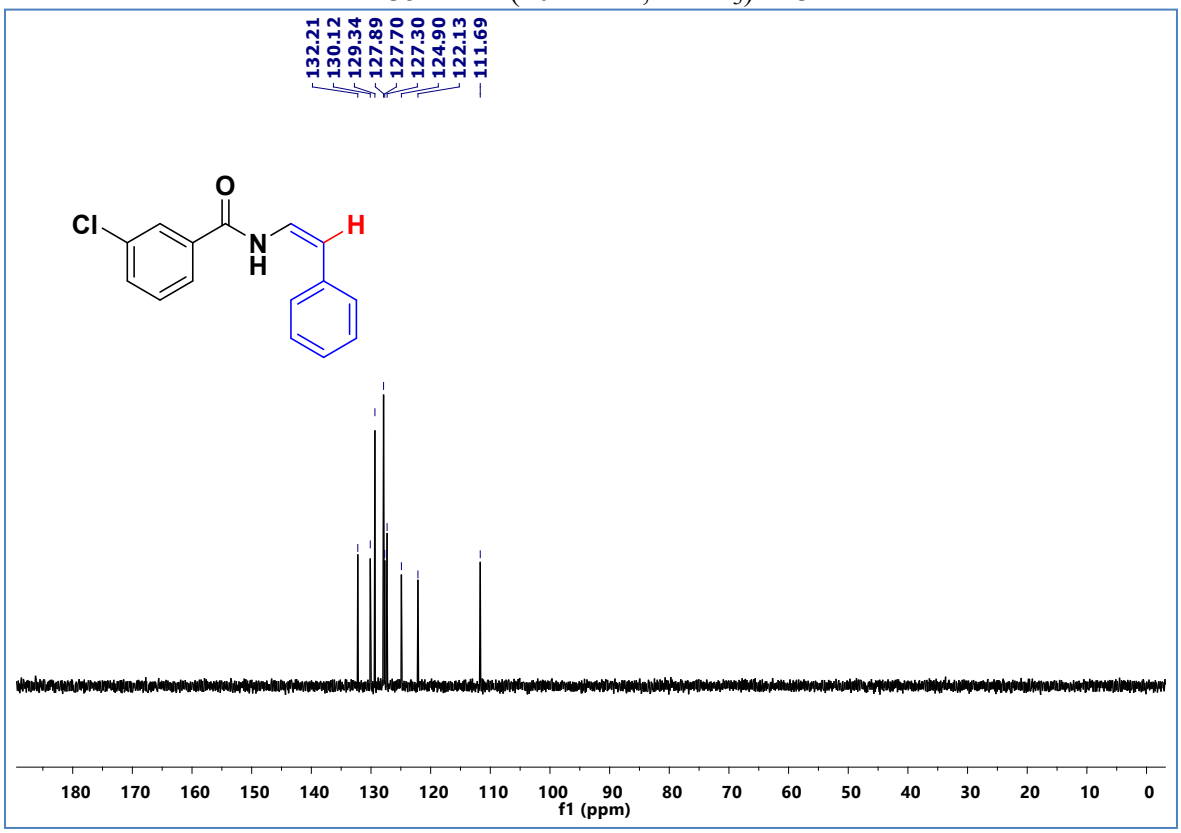
^1H NMR (400 MHz, $CDCl_3$) of **3h**



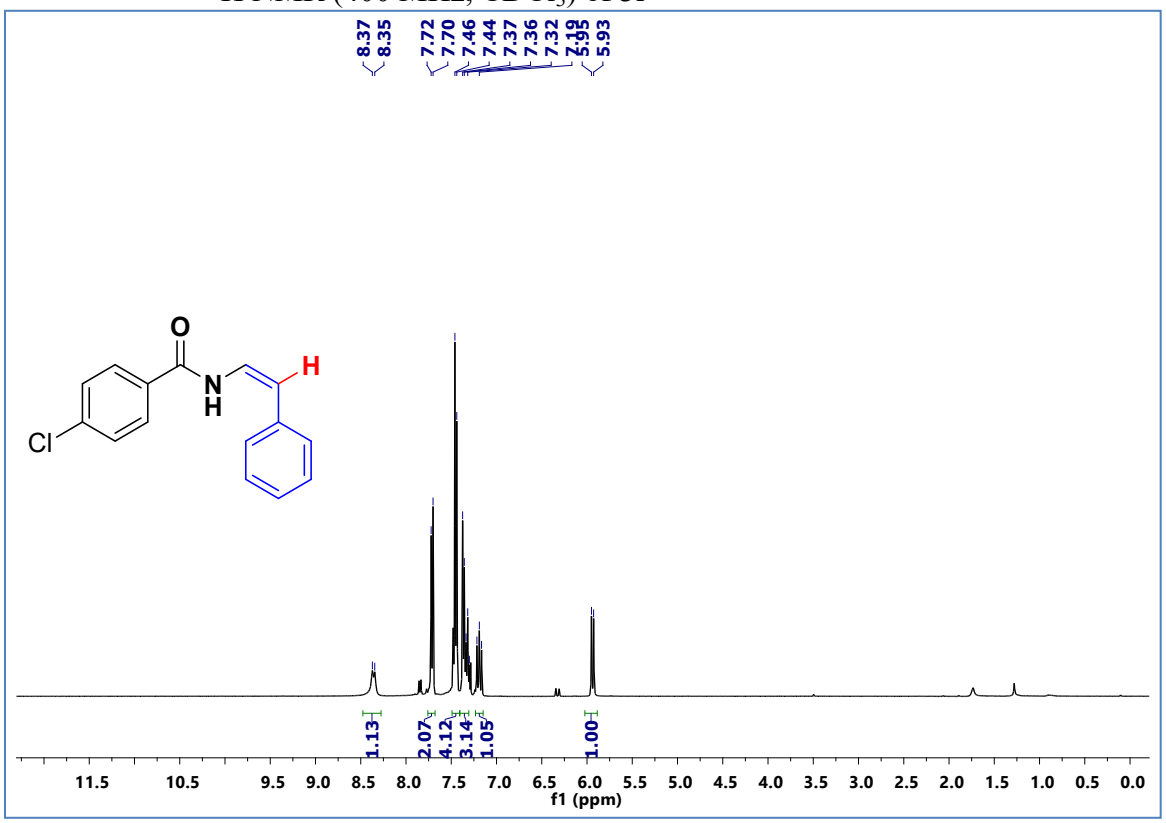
^{13}C NMR (101 MHz, $CDCl_3$) of **3h**



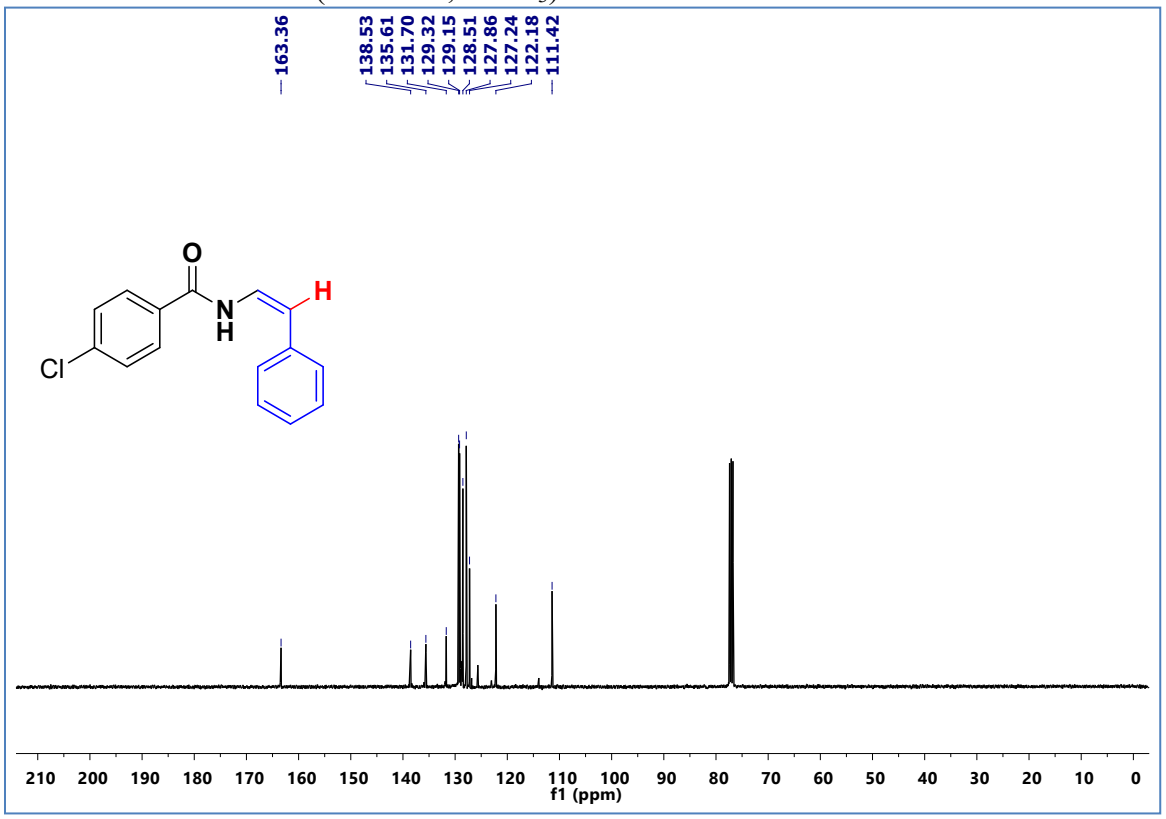
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3h**



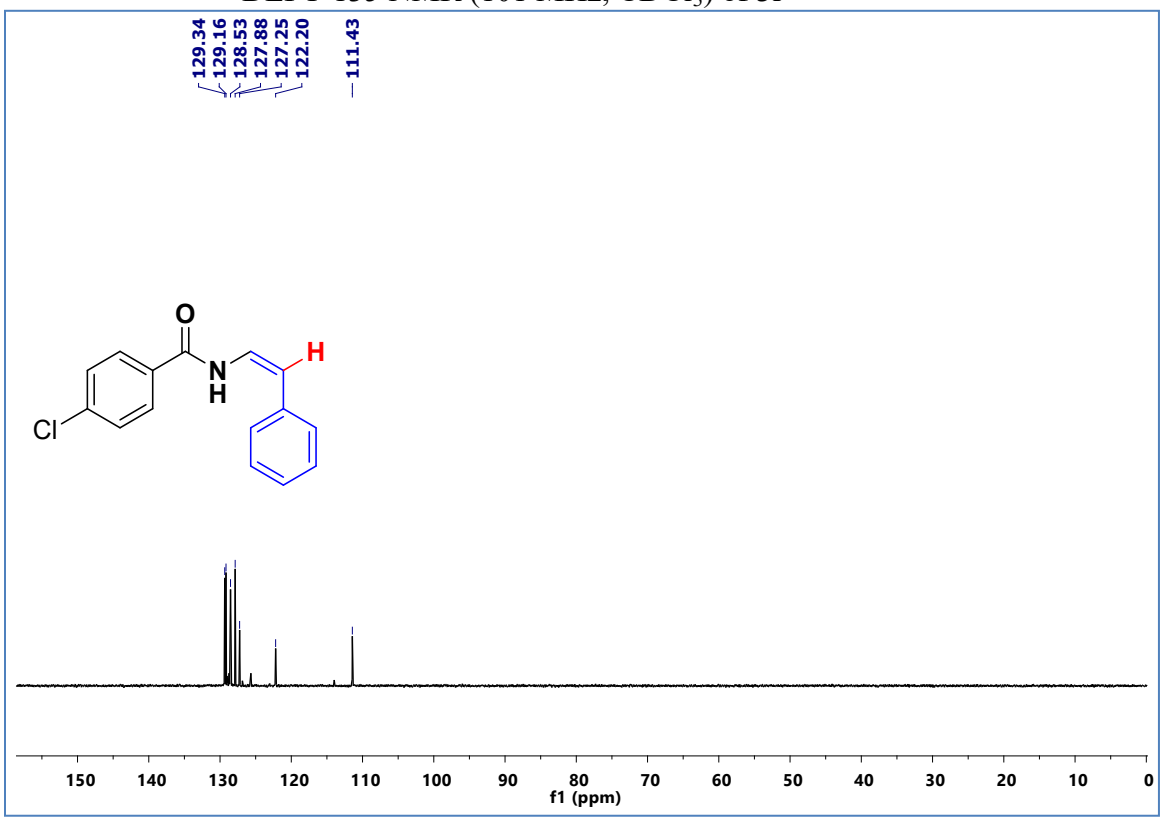
^{1}H NMR (400 MHz, $CDCl_3$) of **3i**



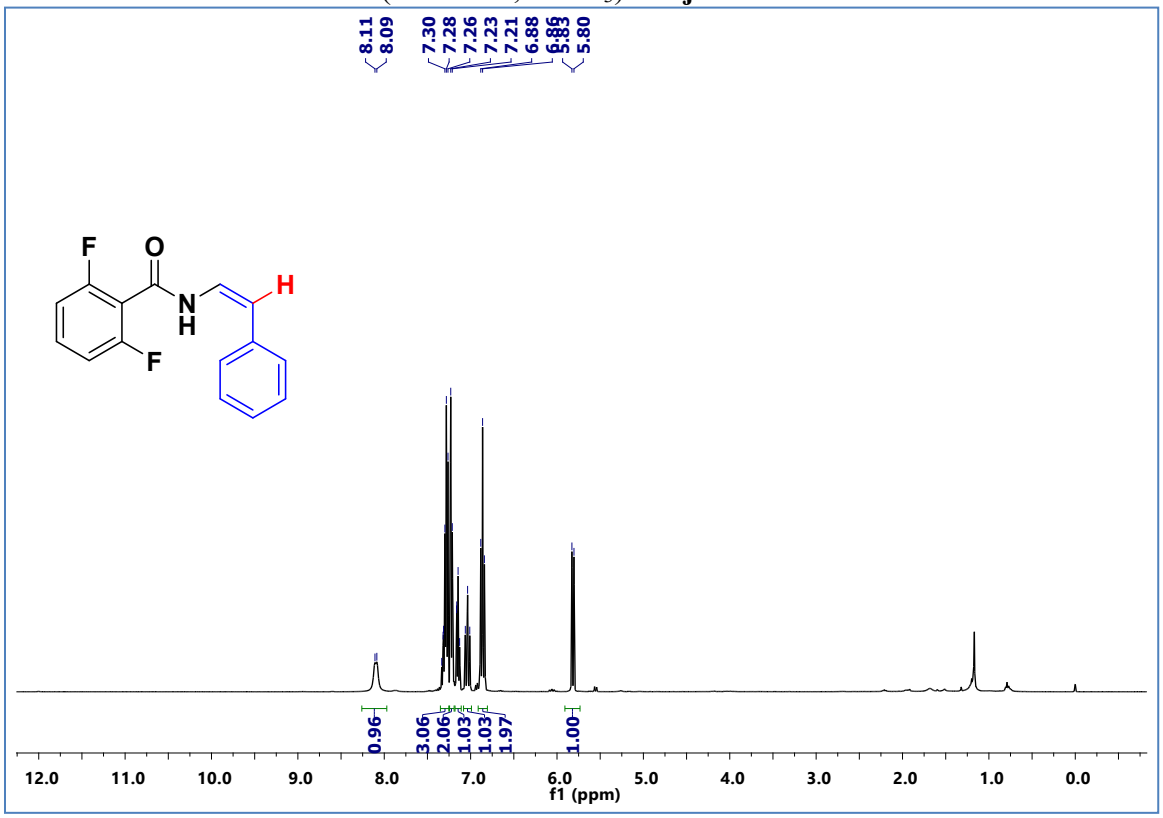
^{13}C NMR (101 MHz, $CDCl_3$) of **3i**



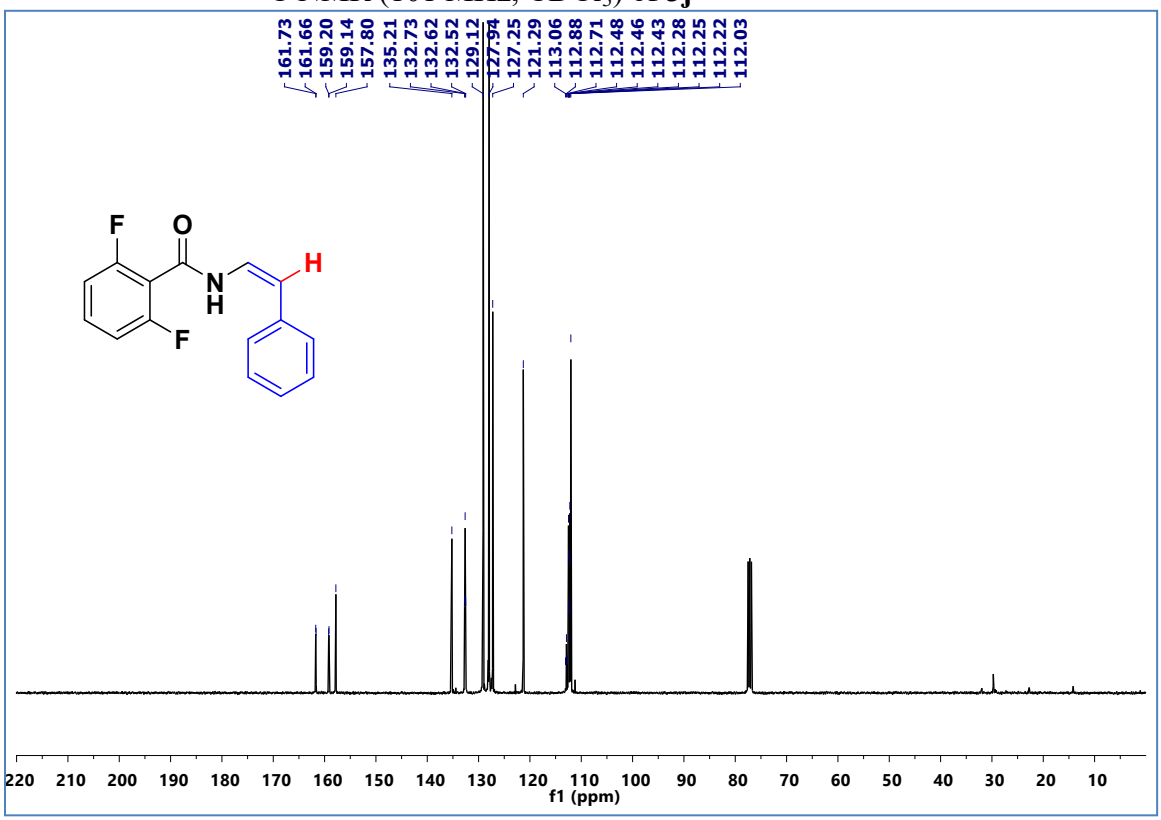
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3i**



^1H NMR (400 MHz, $CDCl_3$) of **3j**



^{13}C NMR (101 MHz, $CDCl_3$) of **3j**



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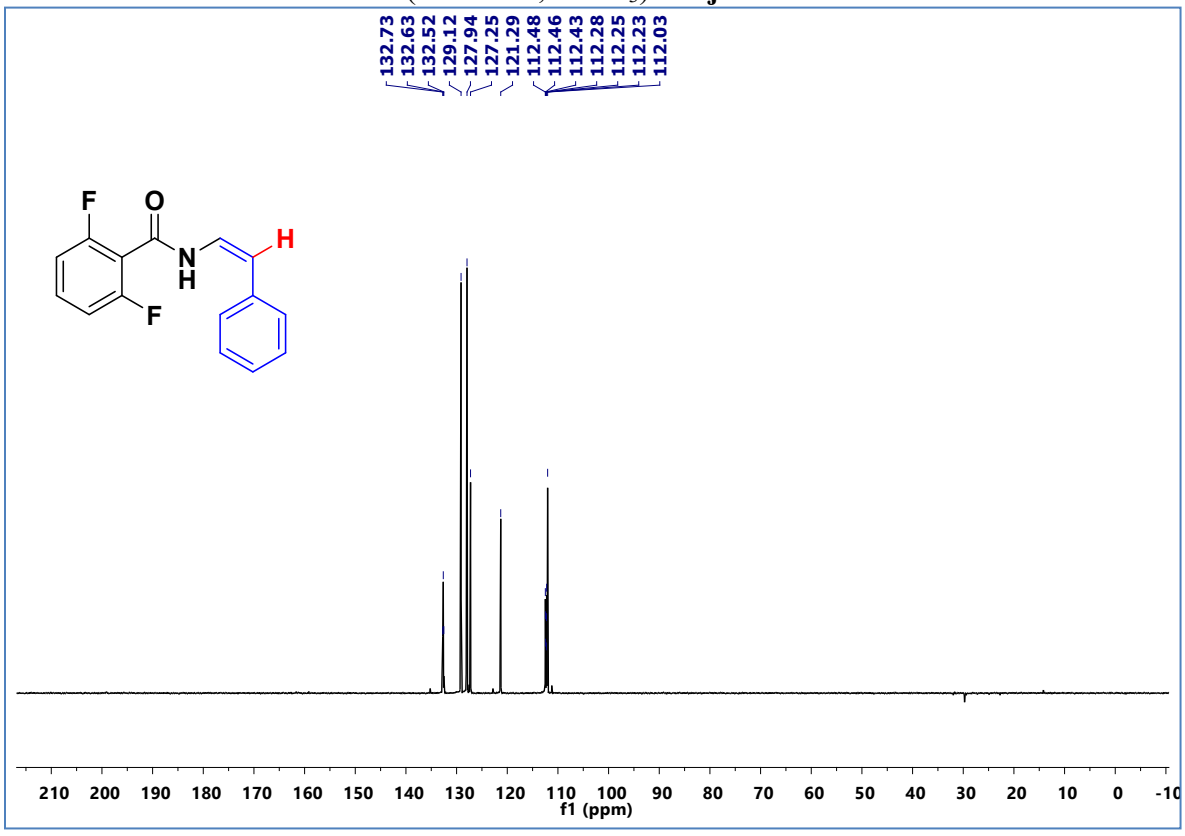
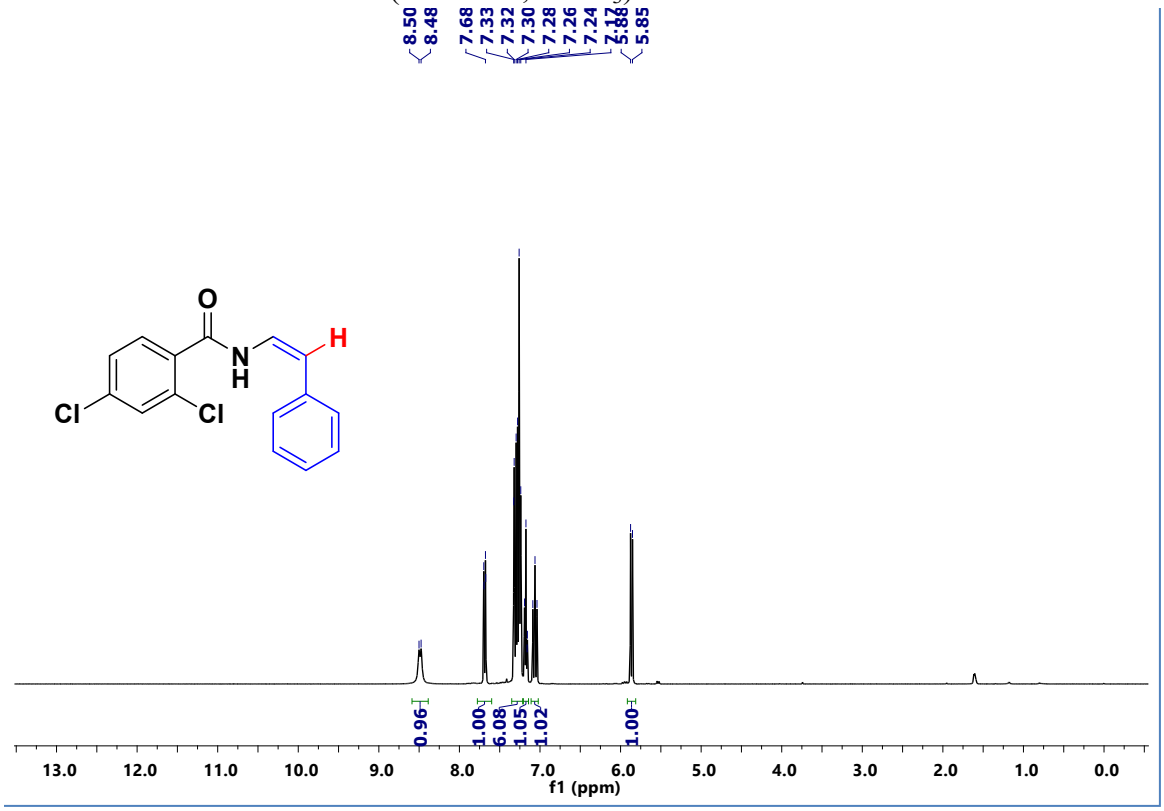
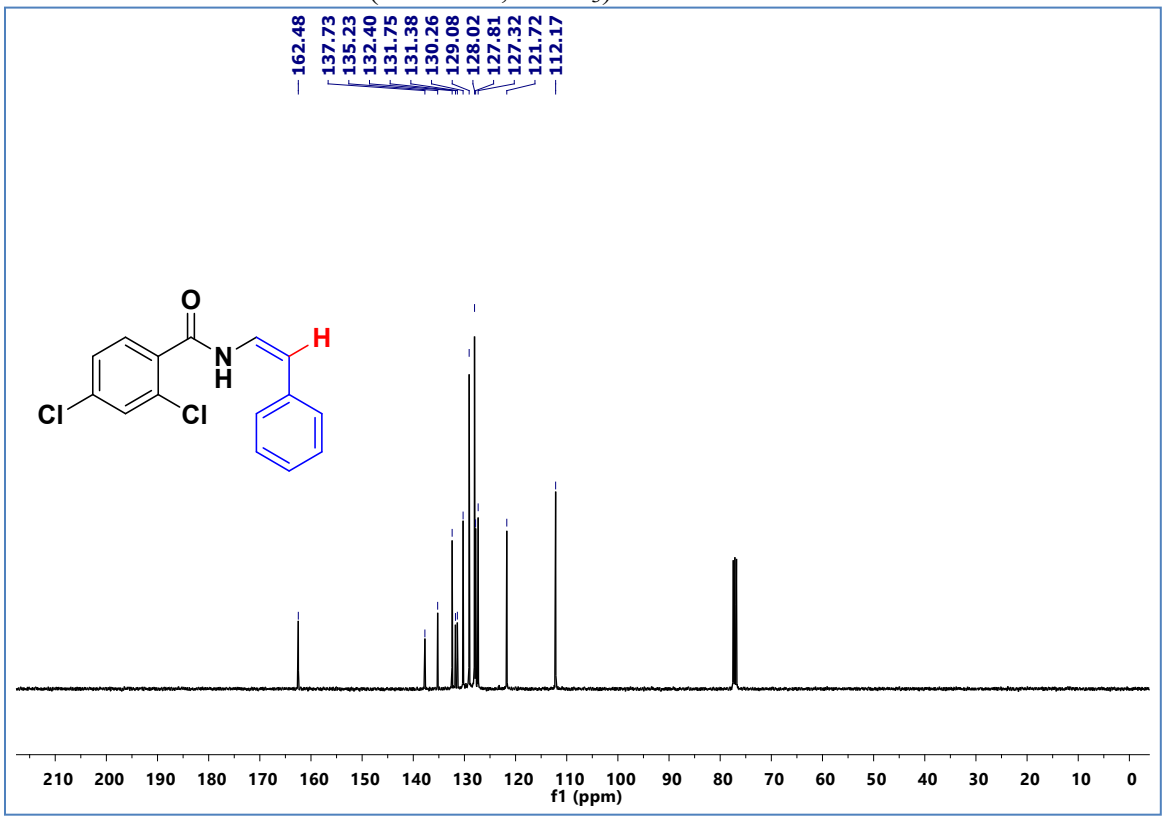


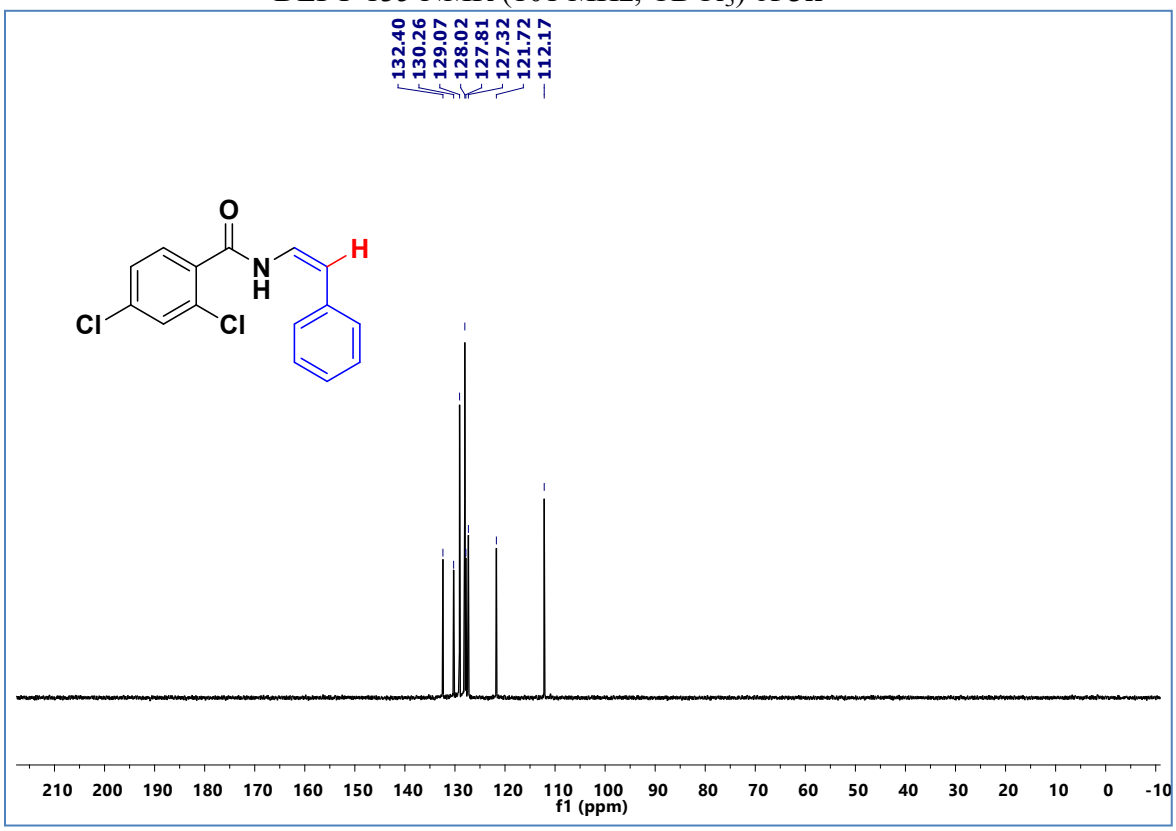
^{1}H NMR (400 MHz, $CDCl_3$) of **3k**



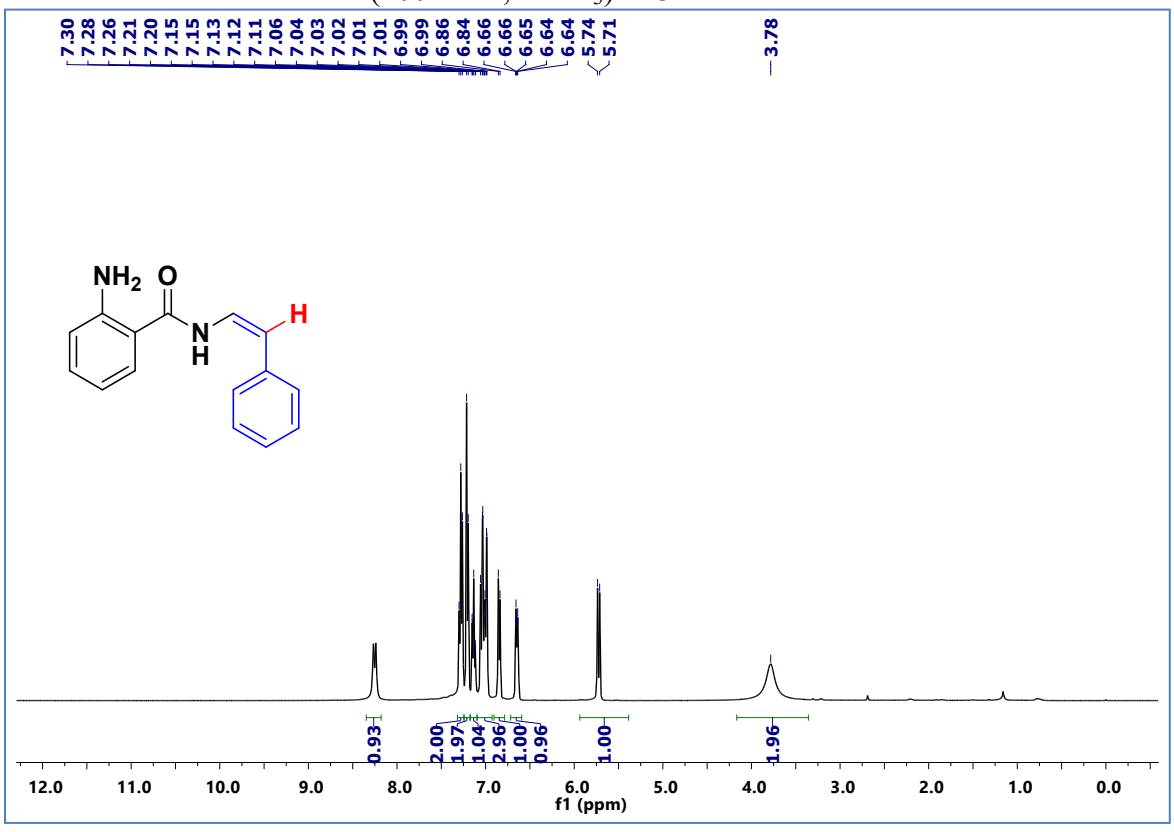
^{13}C NMR (101 MHz, $CDCl_3$) of **3k**



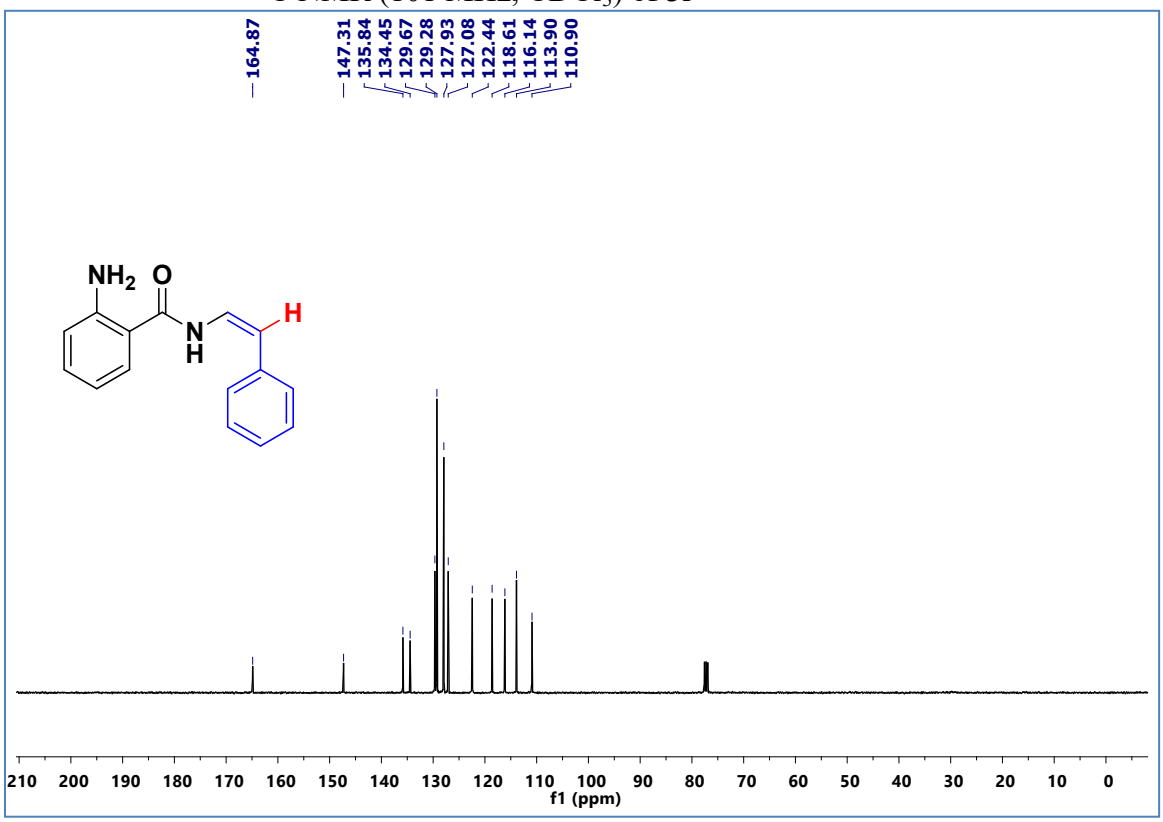
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3k**



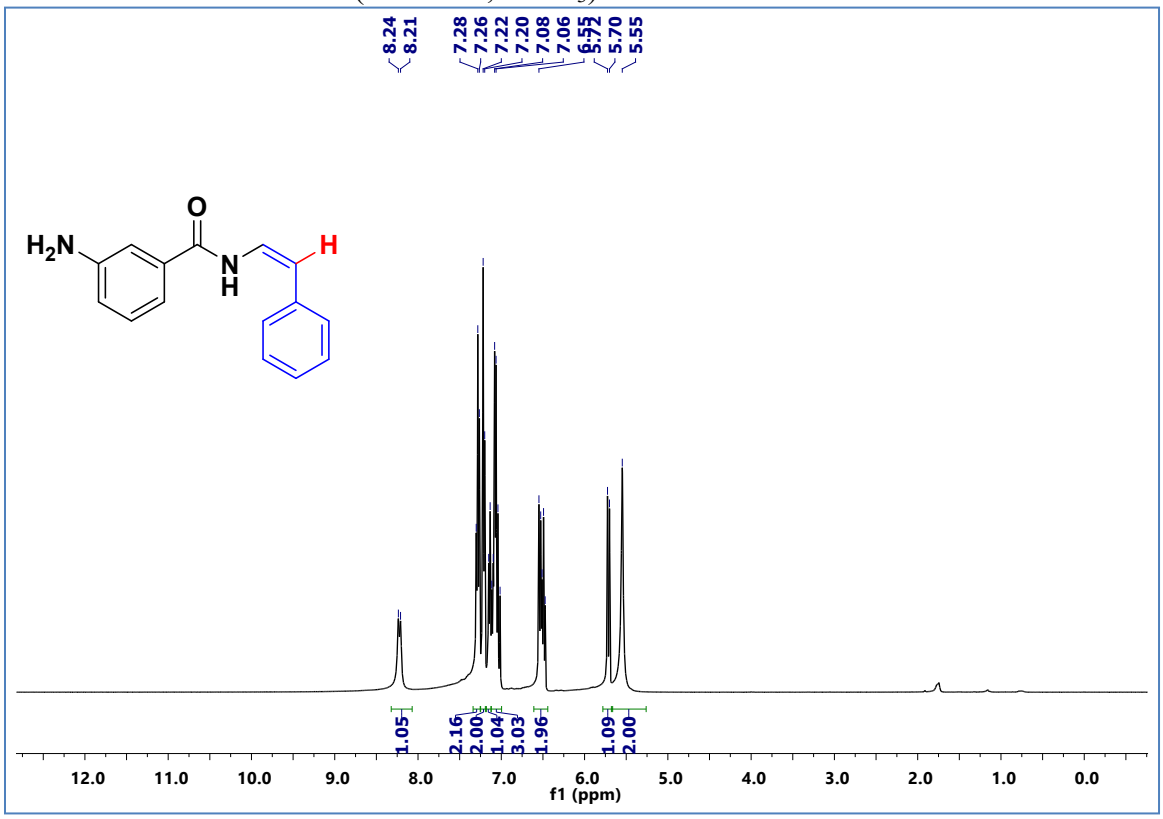
^1H NMR (400 MHz, $CDCl_3$) of **3l**



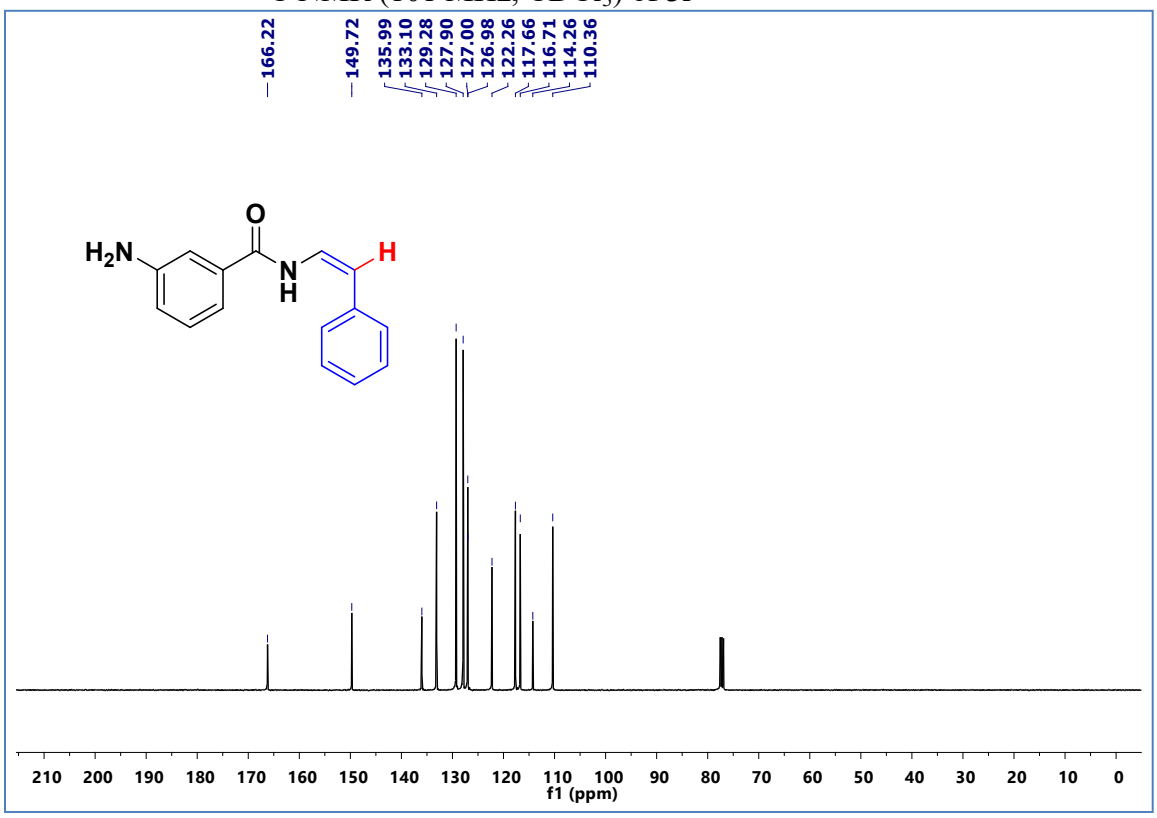
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



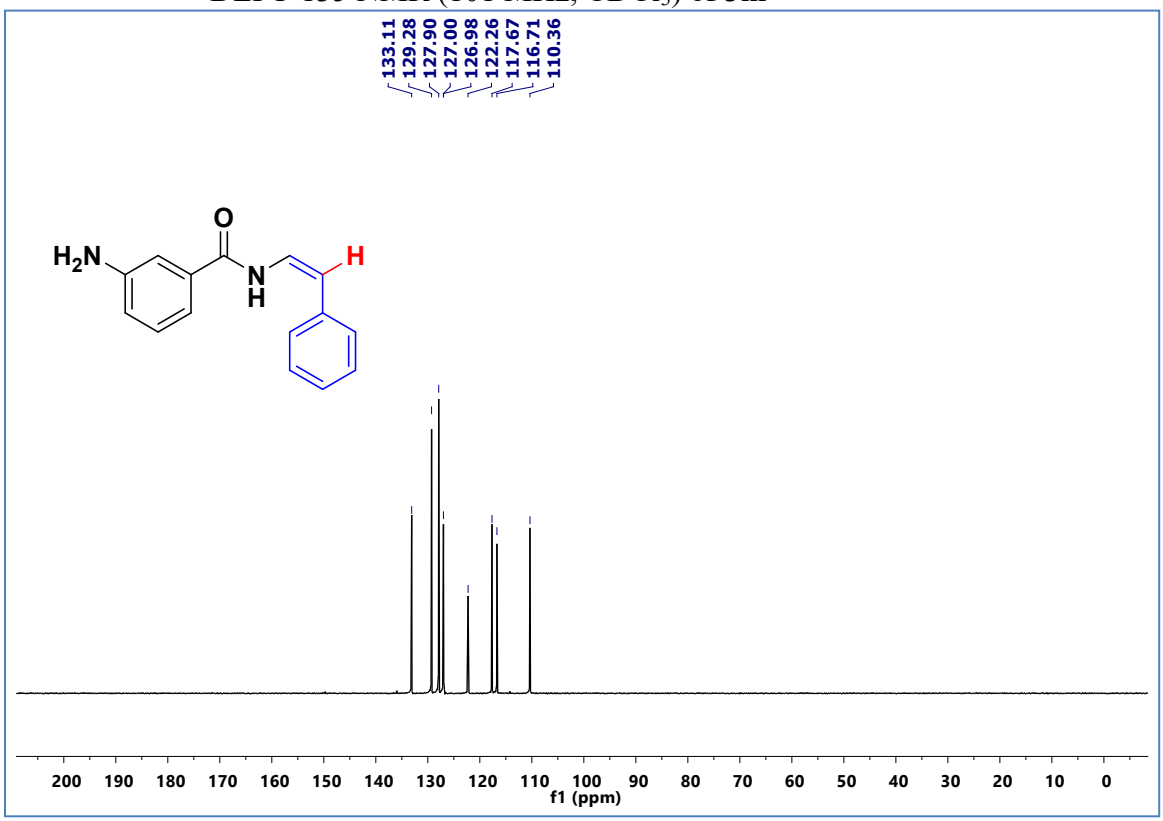
^{1}H NMR (400 MHz, $CDCl_3$) of **3m**



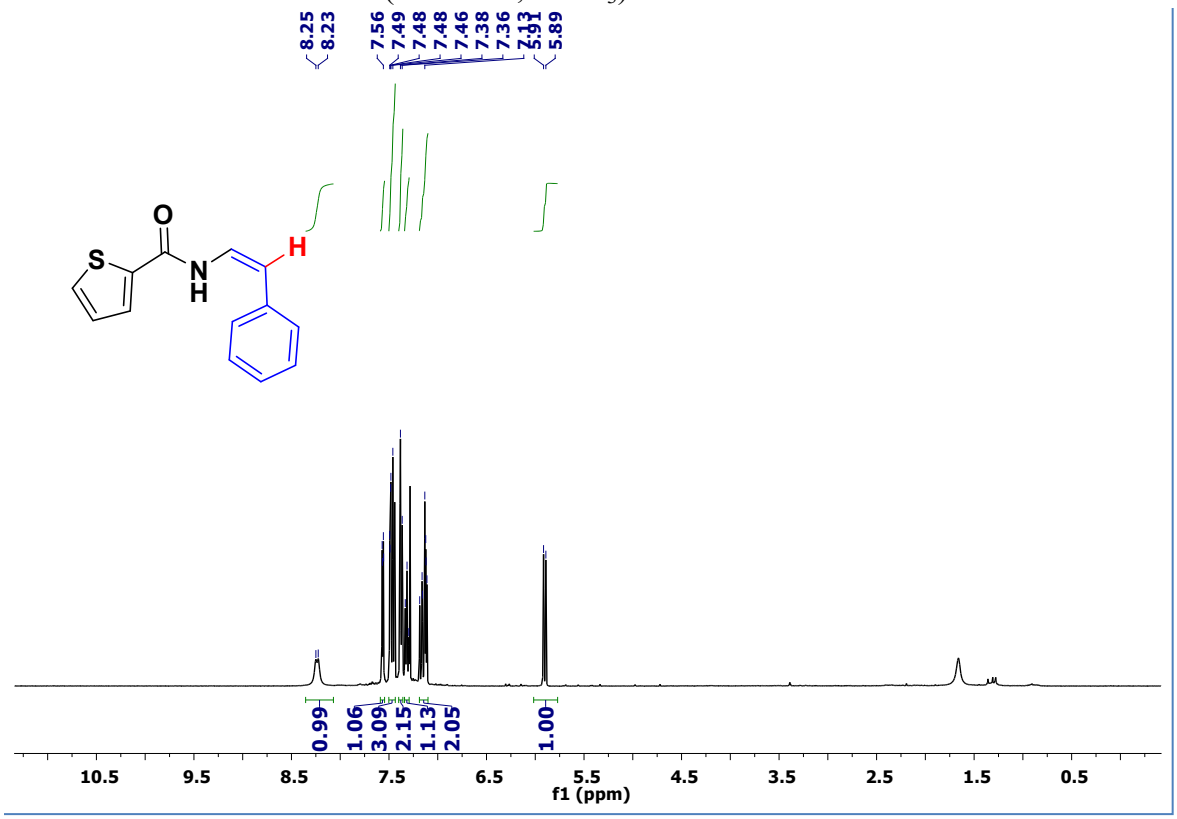
^{13}C NMR (101 MHz, $CDCl_3$) of **3l**



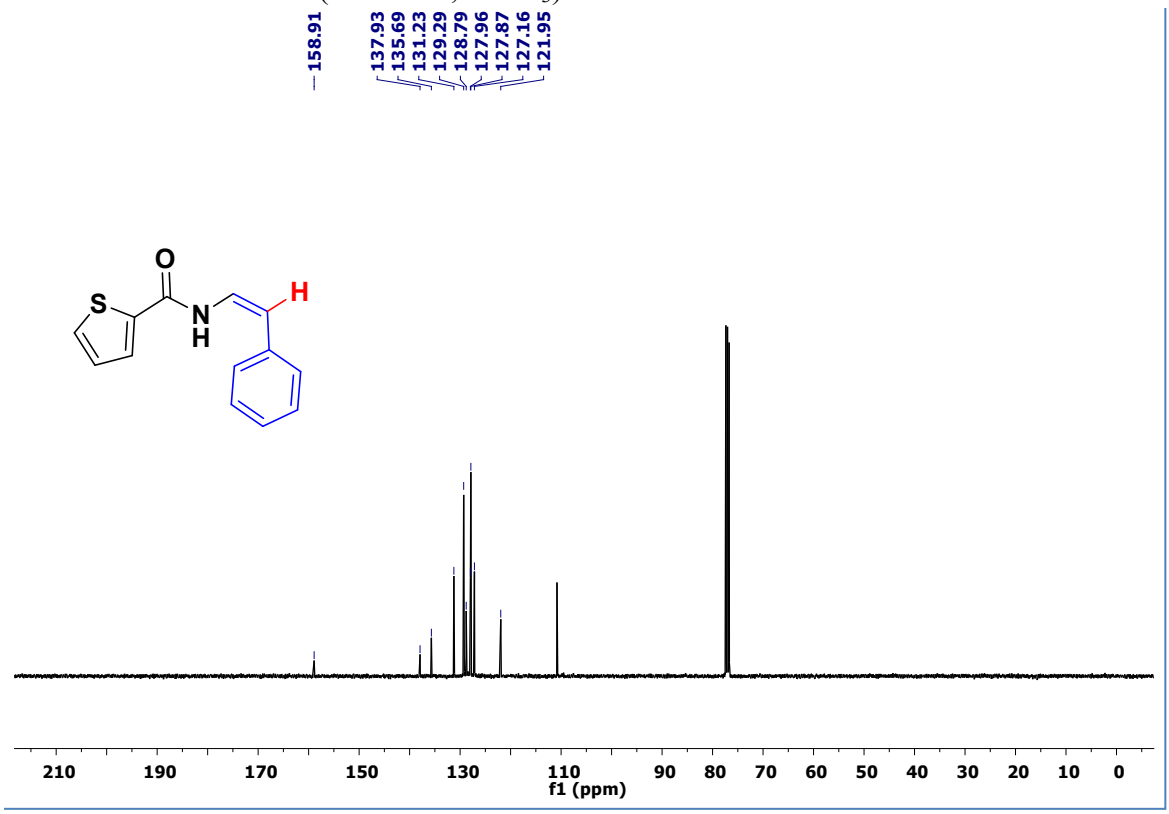
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3m**



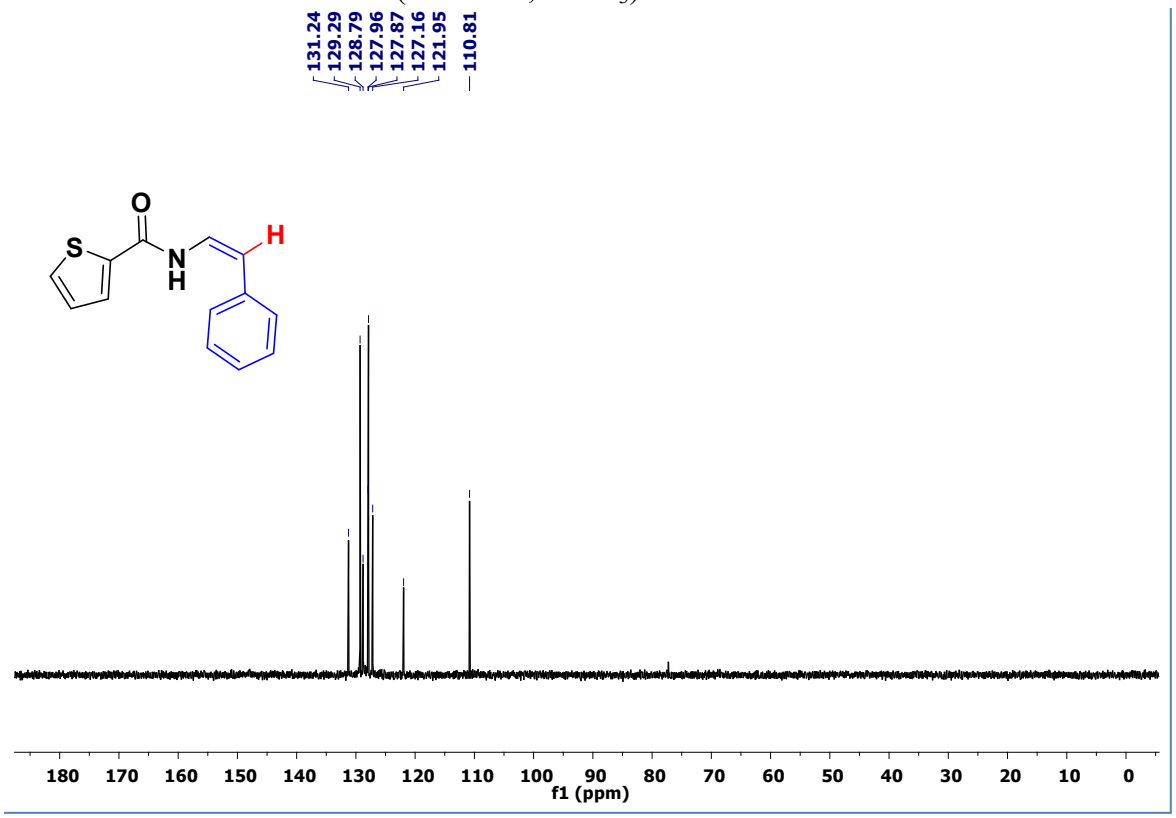
^{1}H NMR (400 MHz, $CDCl_3$) of **3n**



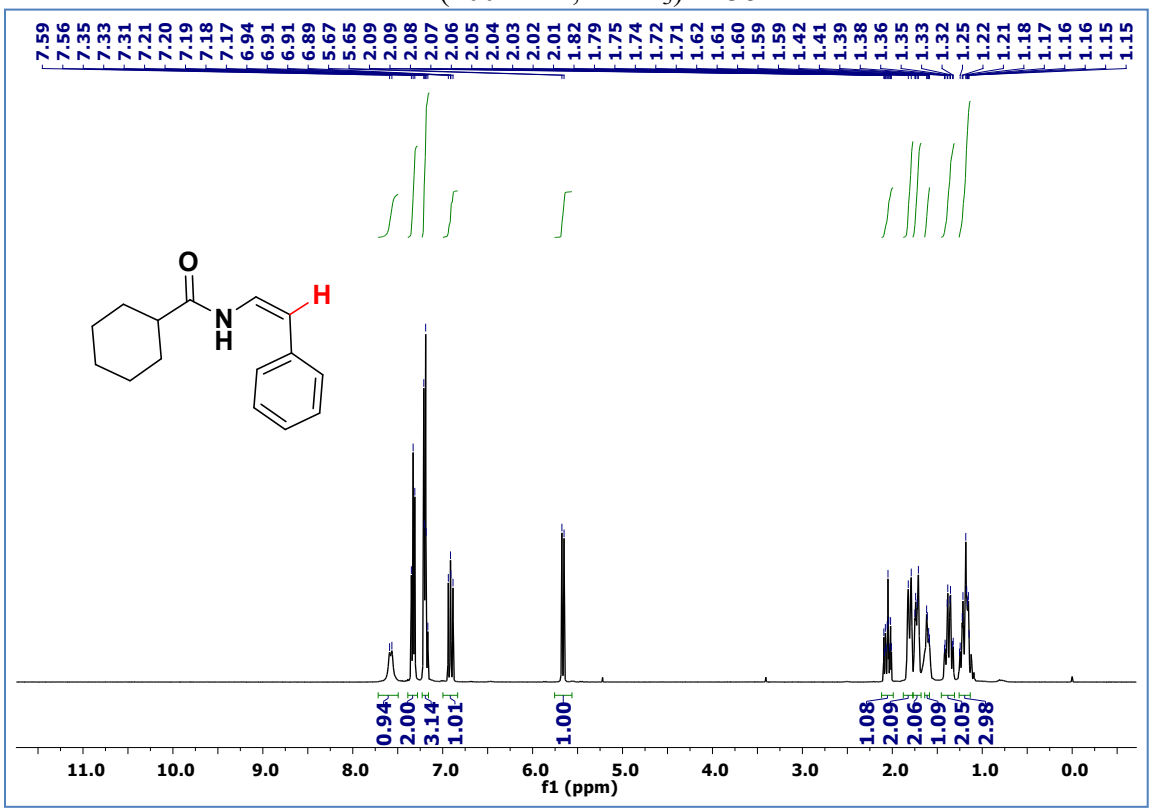
^{13}C NMR (101 MHz, $CDCl_3$) of **3n**



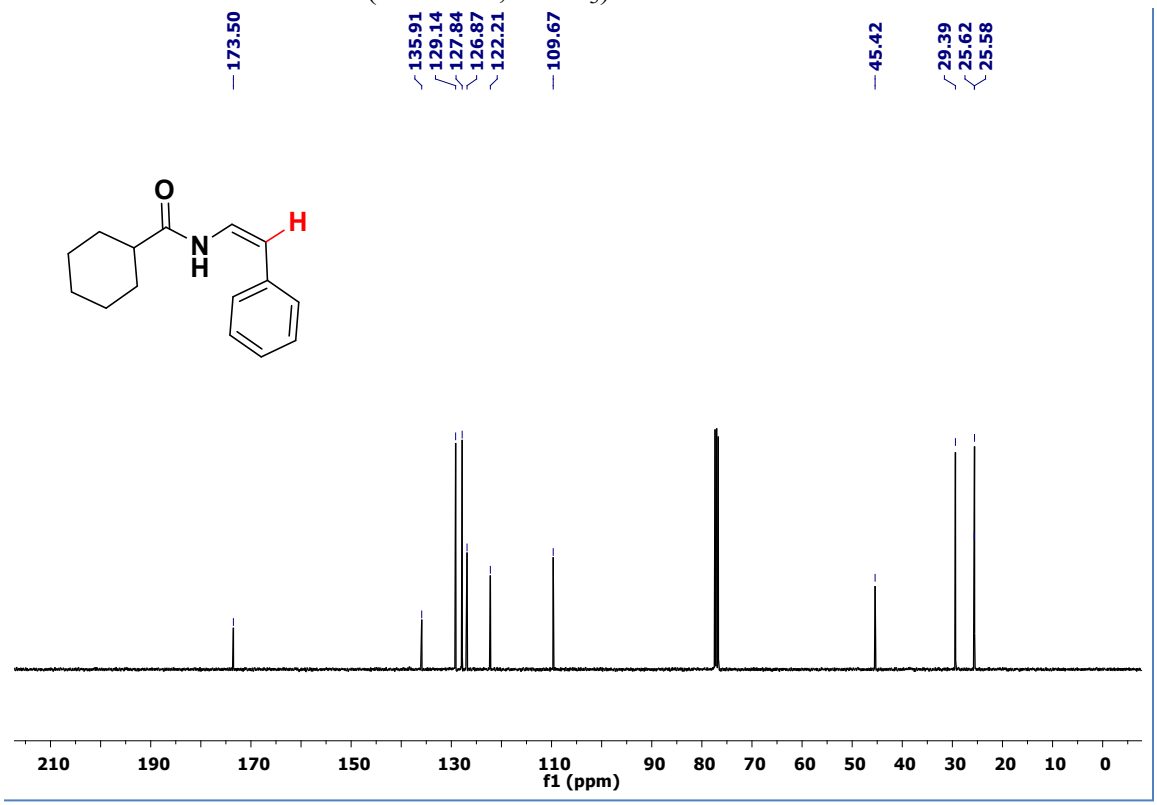
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3n**



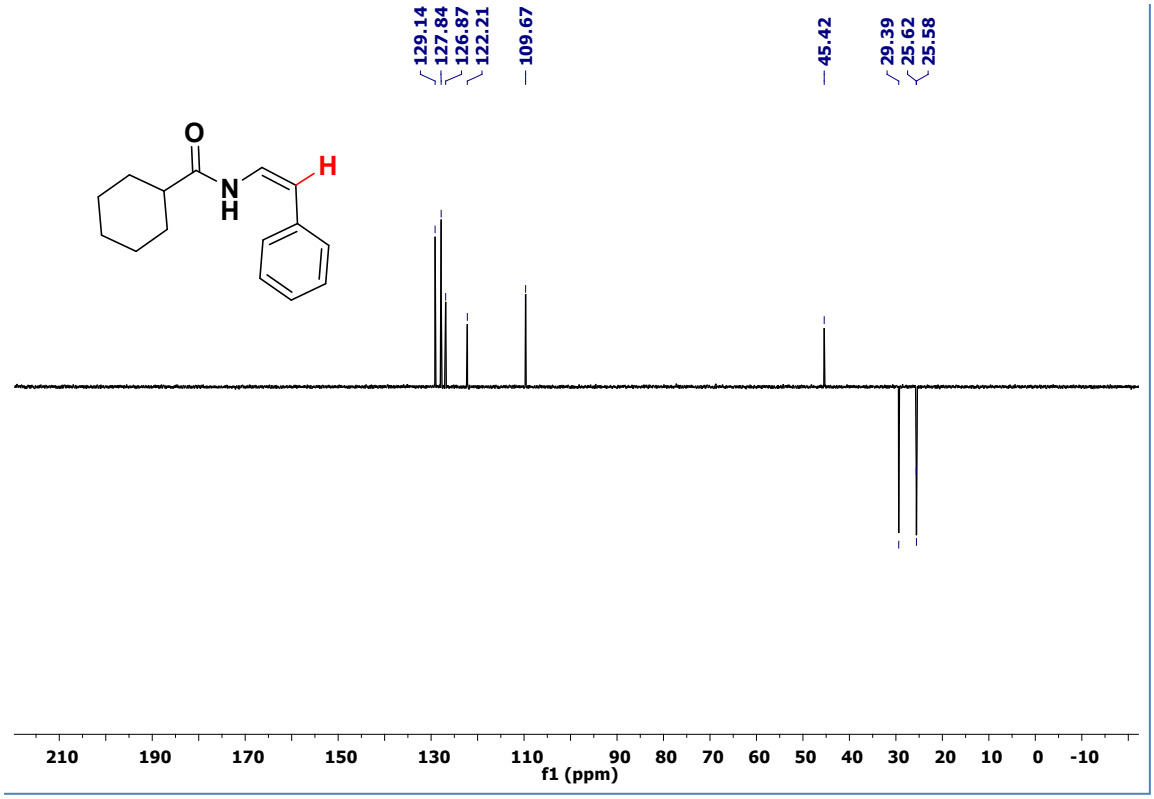
^1H NMR (400 MHz, $CDCl_3$) of **3o**



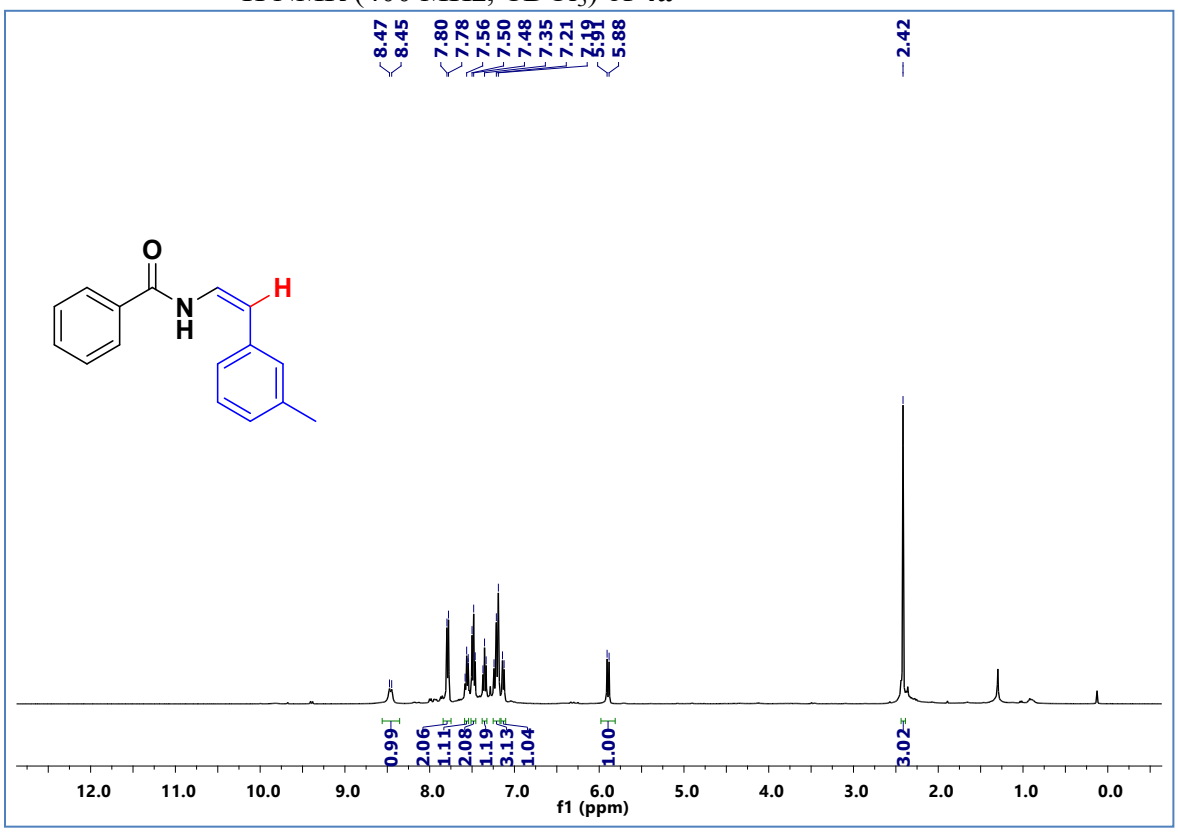
^{13}C NMR (101 MHz, $CDCl_3$) of **3o**



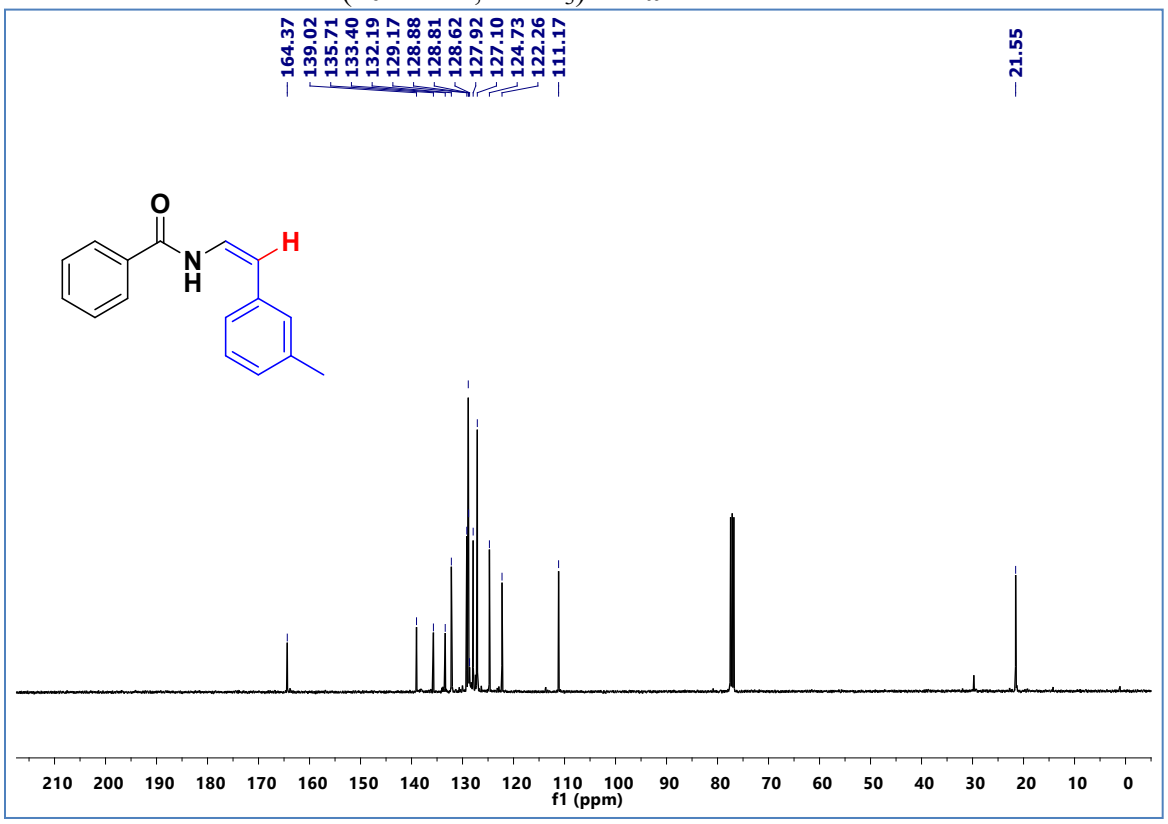
DEPT-135 NMR (101 MHz, $CDCl_3$) of **3o**



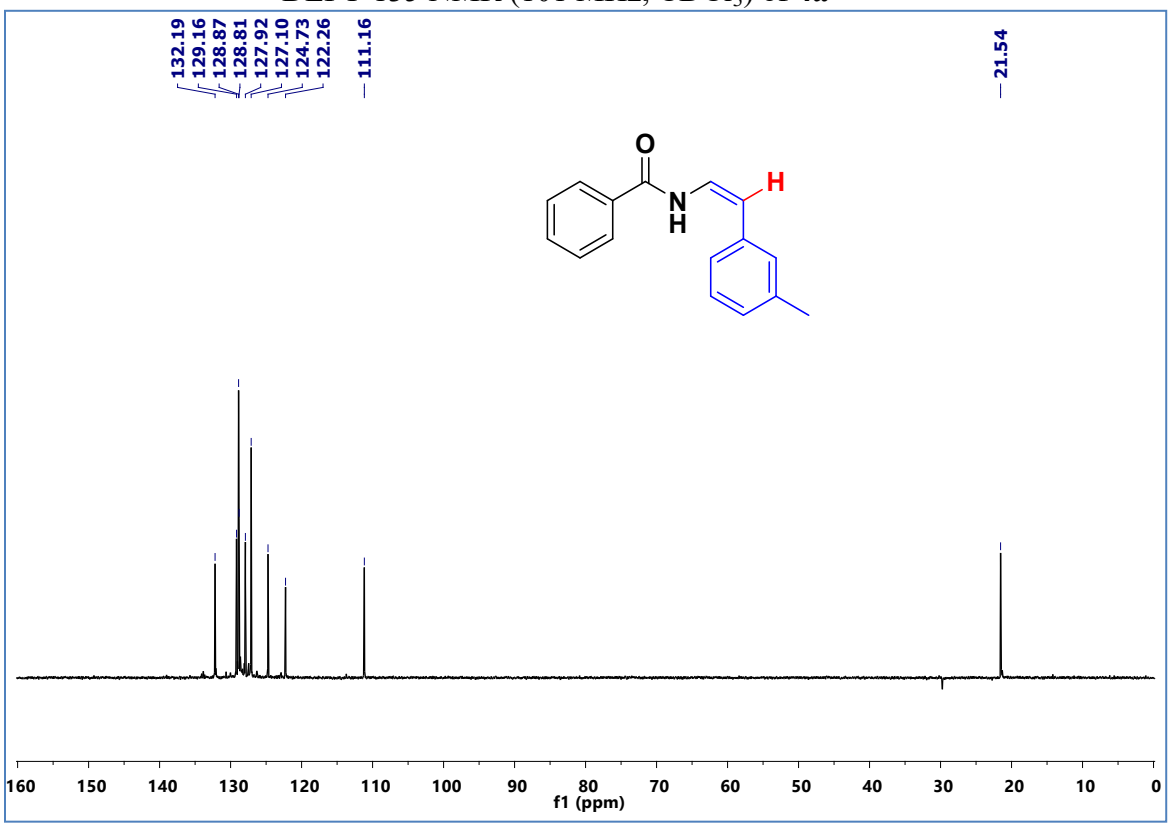
^{1}H NMR (400 MHz, $CDCl_3$) of **4a**



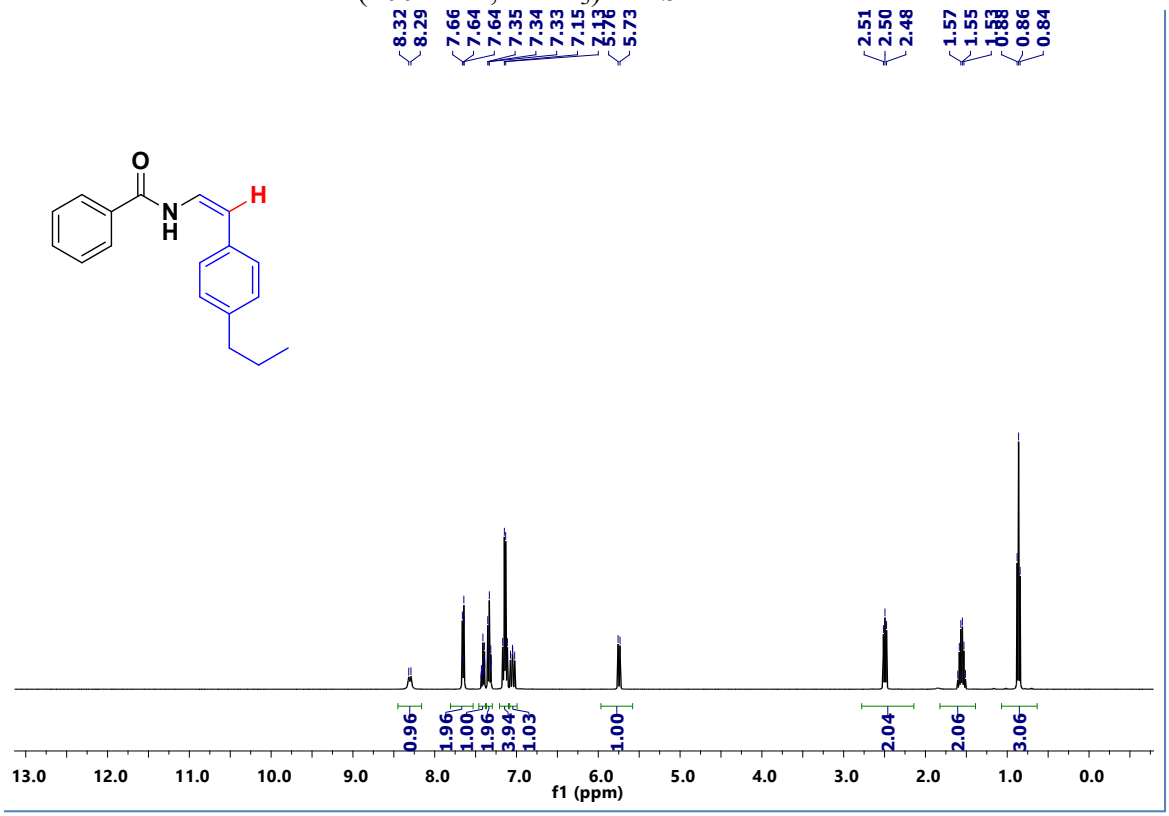
^{13}C NMR (101 MHz, $CDCl_3$) of **4a**



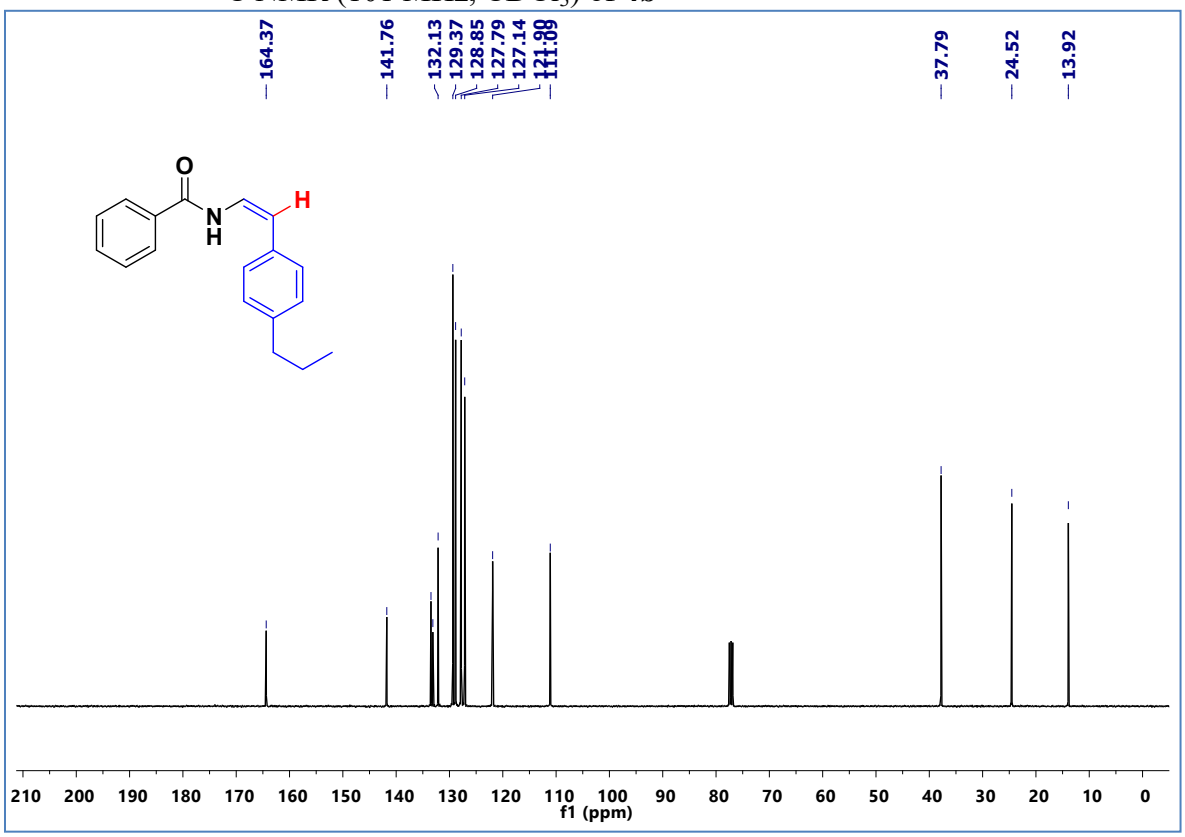
DEPT-135 NMR (101 MHz, $CDCl_3$) of **4a**



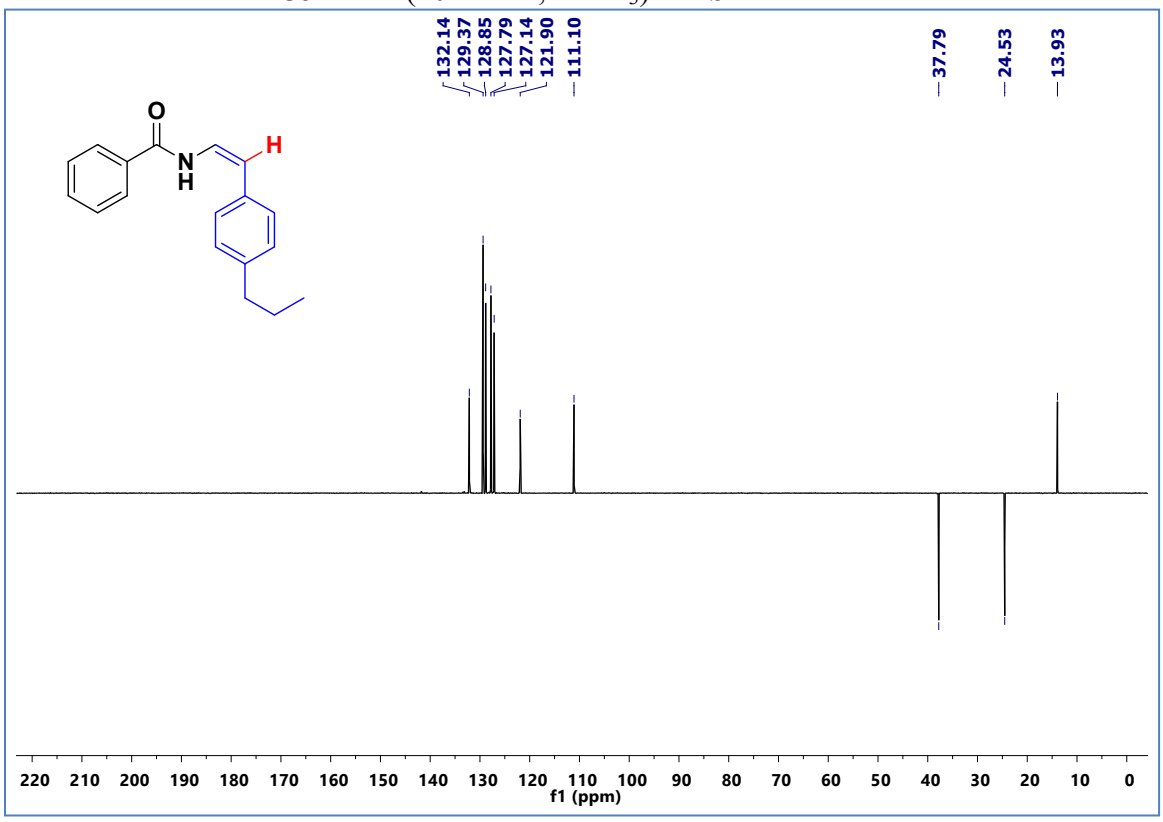
^1H NMR (400 MHz, $CDCl_3$) of **4b**



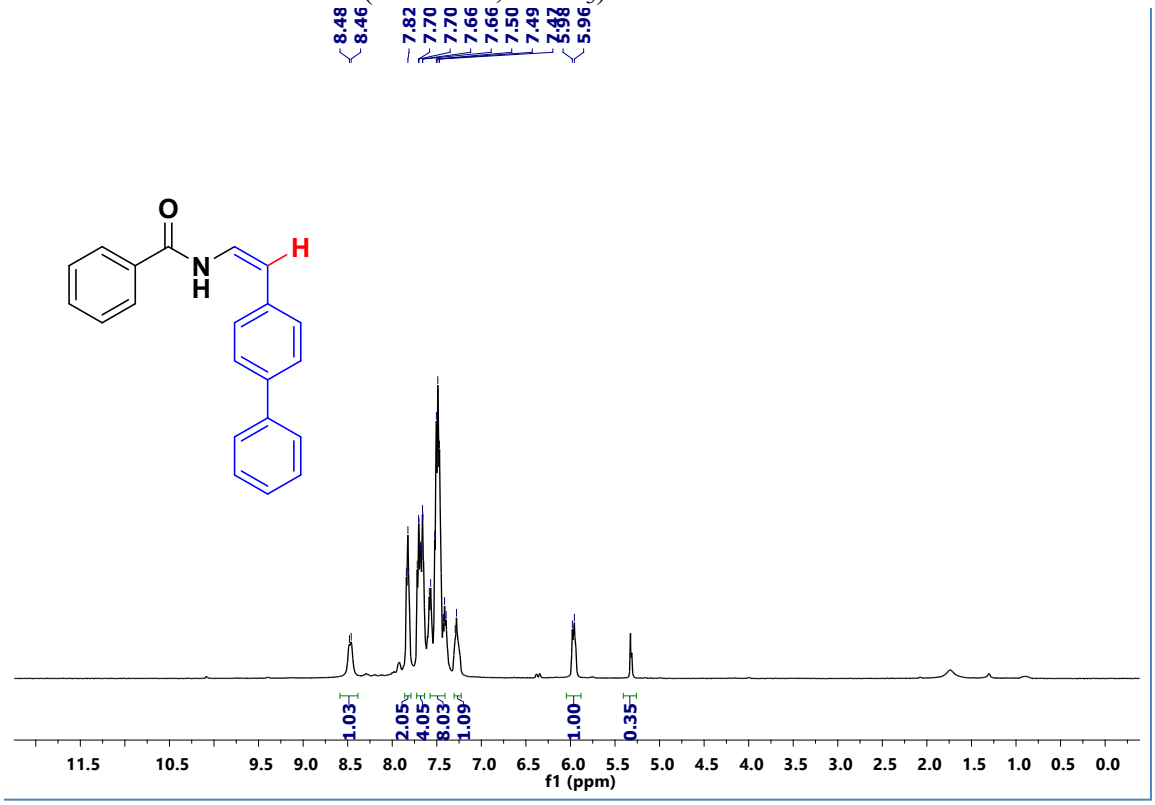
^{13}C NMR (101 MHz, $CDCl_3$) of **4b**



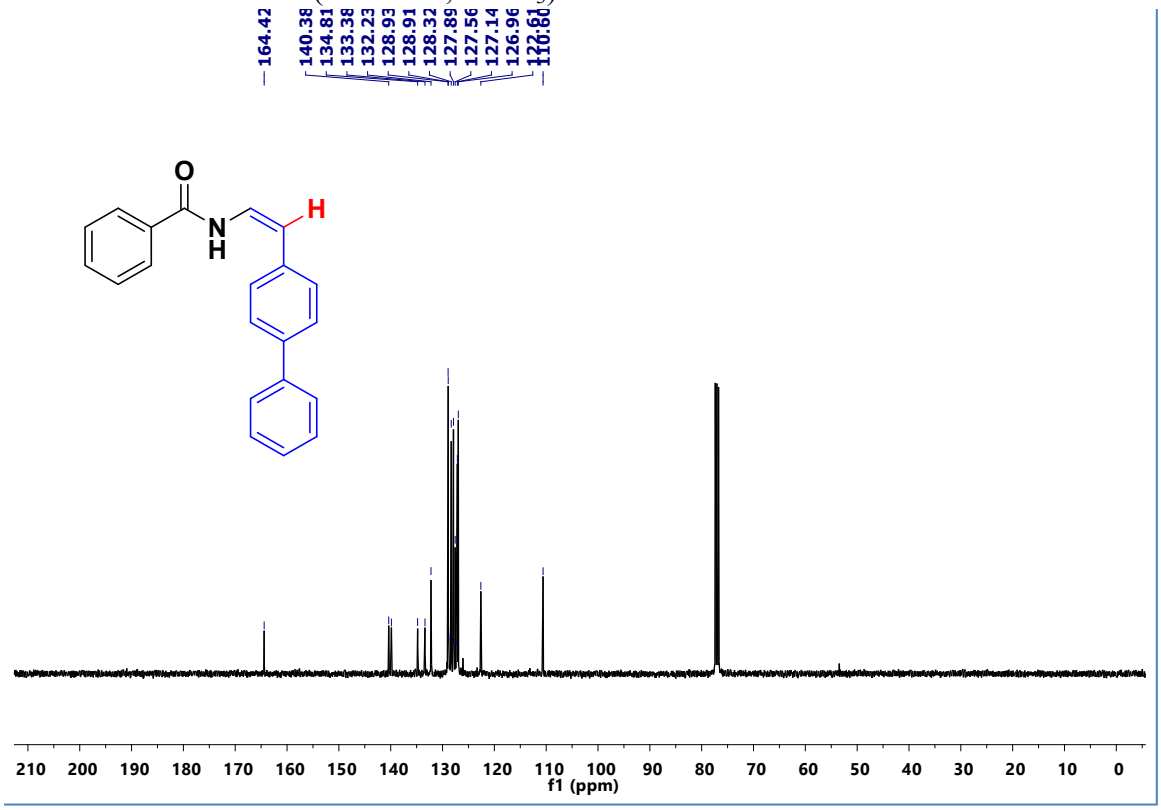
DEPT-135 NMR (101 MHz, $CDCl_3$) of **4b**



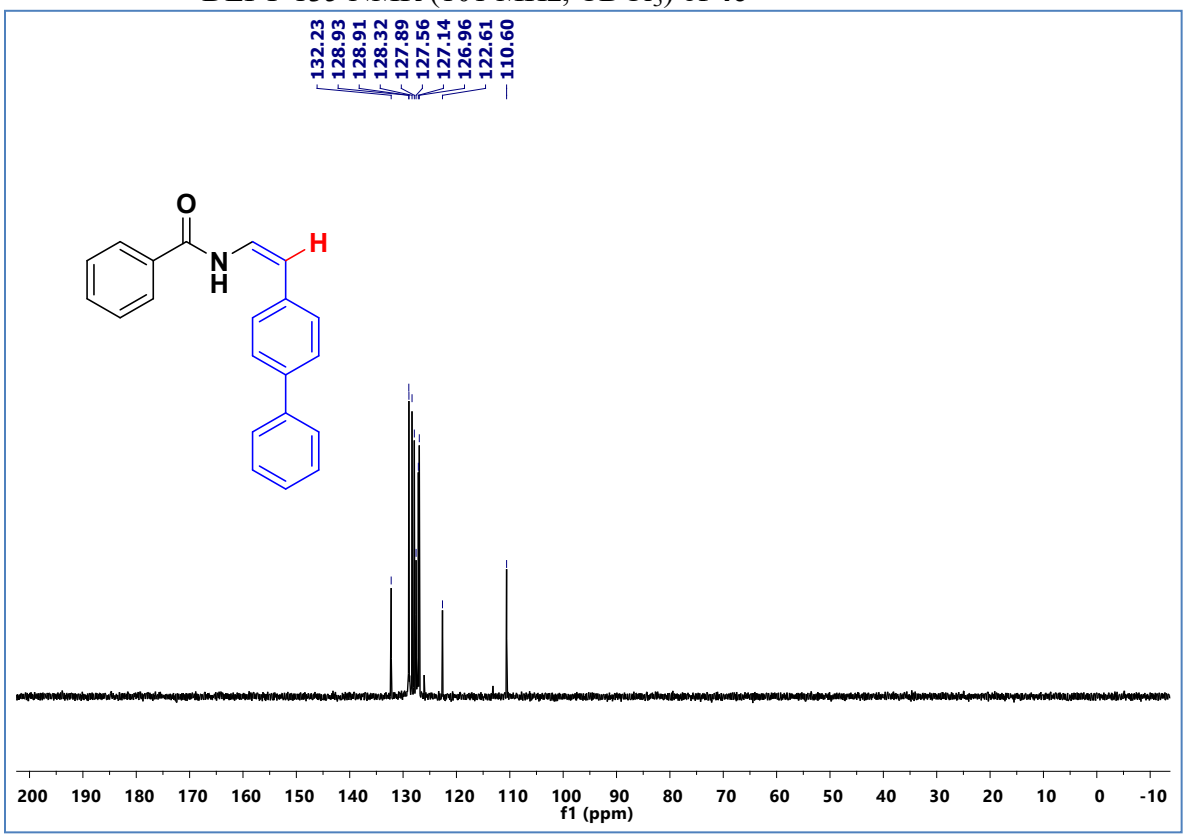
^{1}H NMR (400 MHz, $CDCl_3$) of **4c**



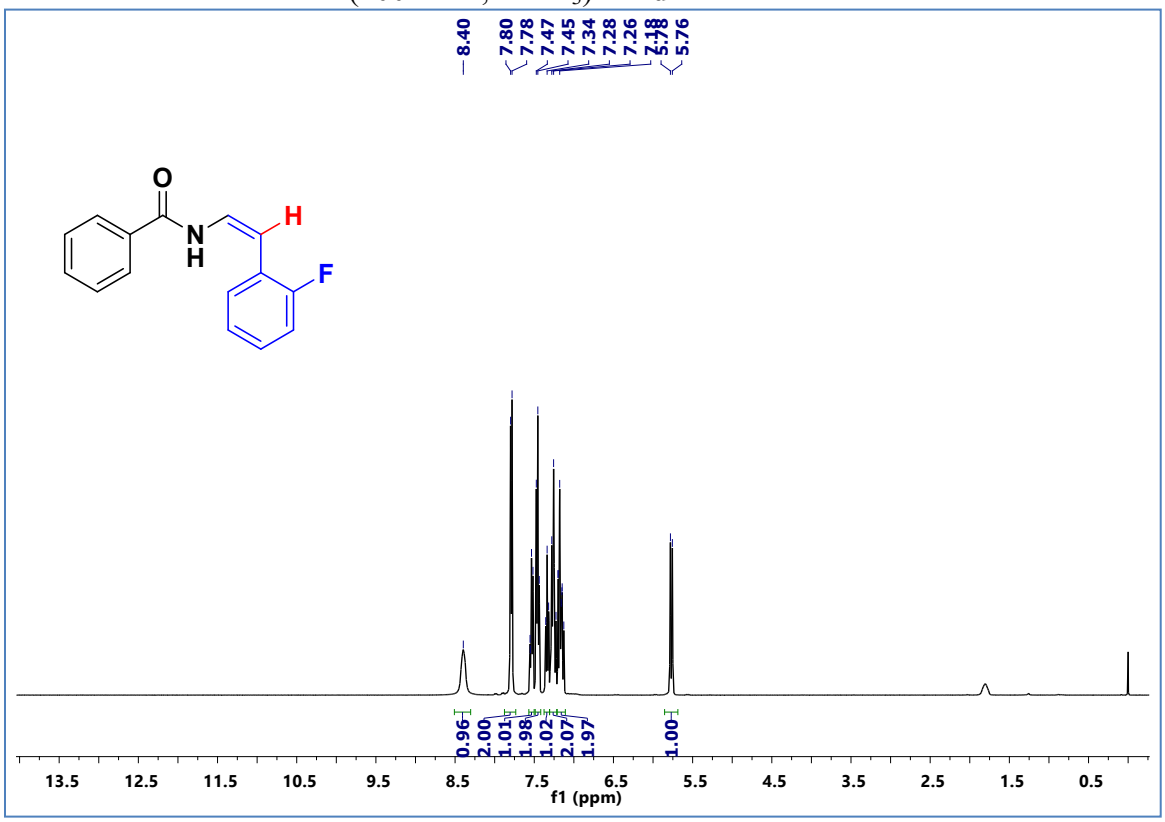
^{13}C NMR (101 MHz, $CDCl_3$) of **4c**



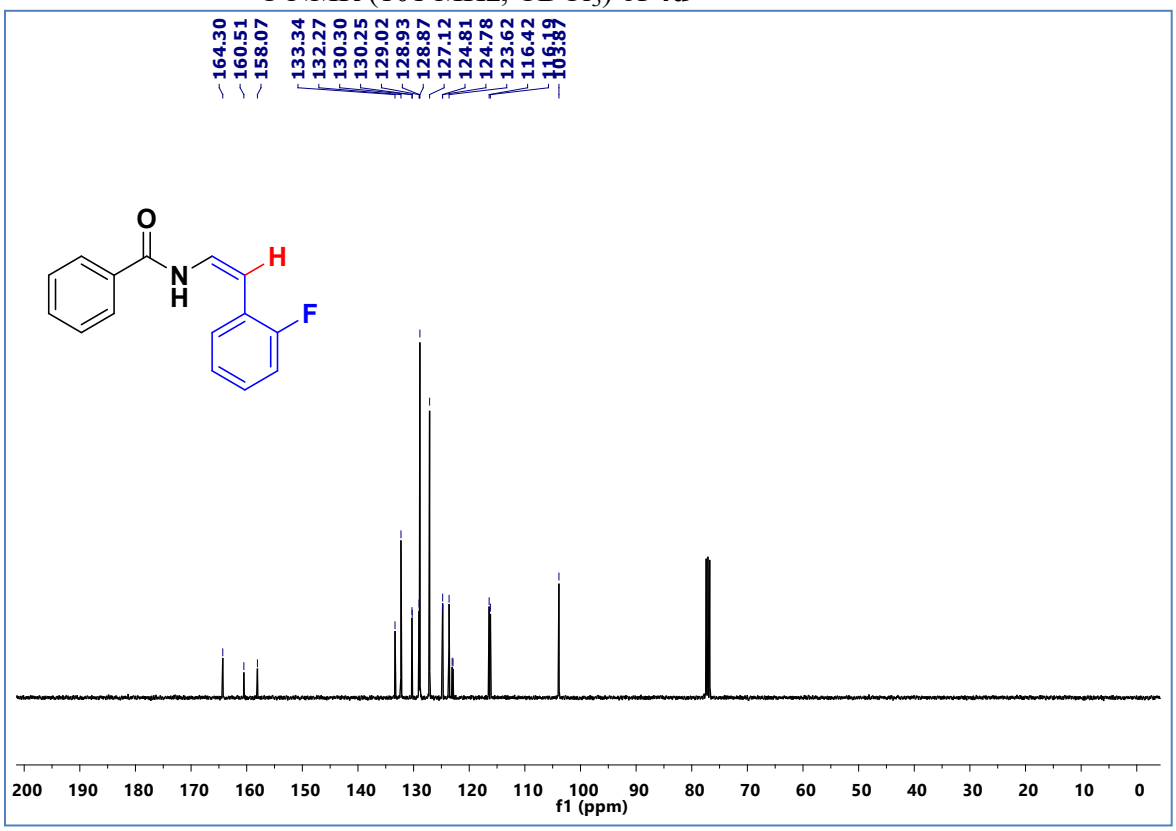
DEPT-135 NMR (101 MHz, $CDCl_3$) of **4c**



^{1}H NMR (400 MHz, $CDCl_3$) of **4d**



^{13}C NMR (101 MHz, $CDCl_3$) of **4d**



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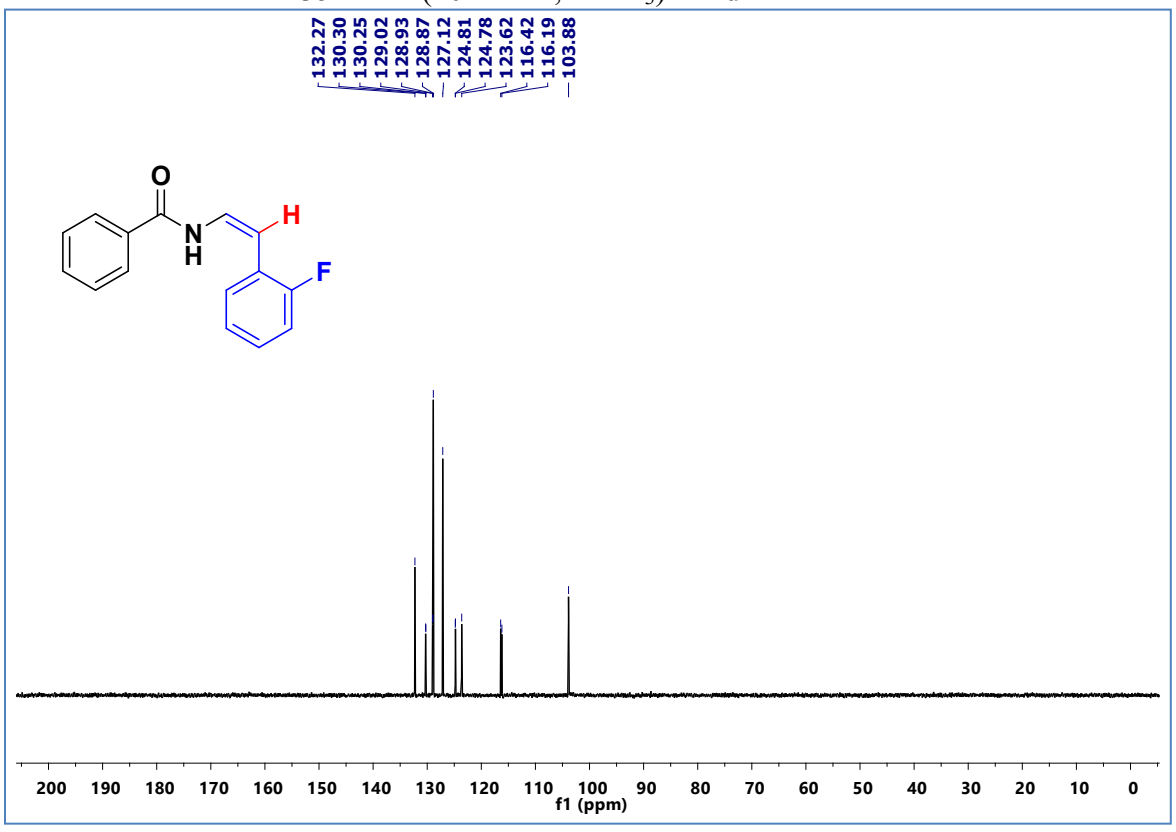

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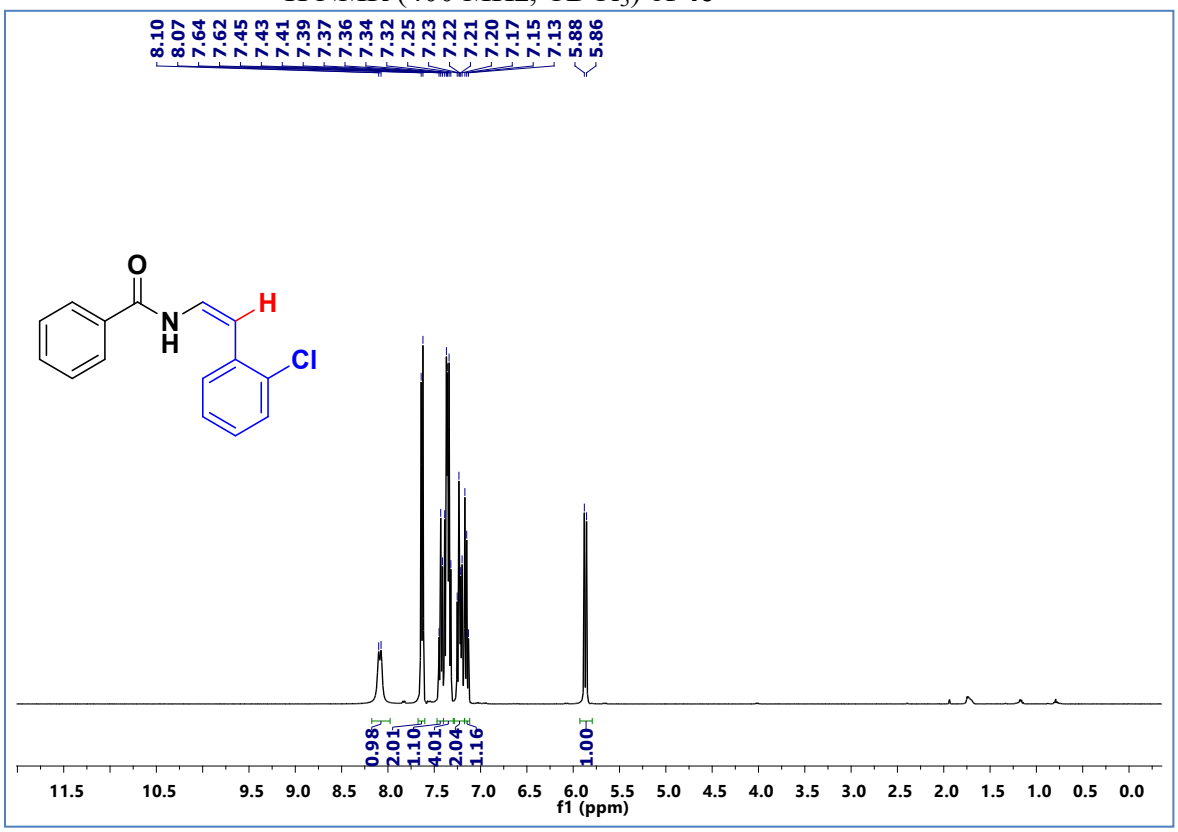
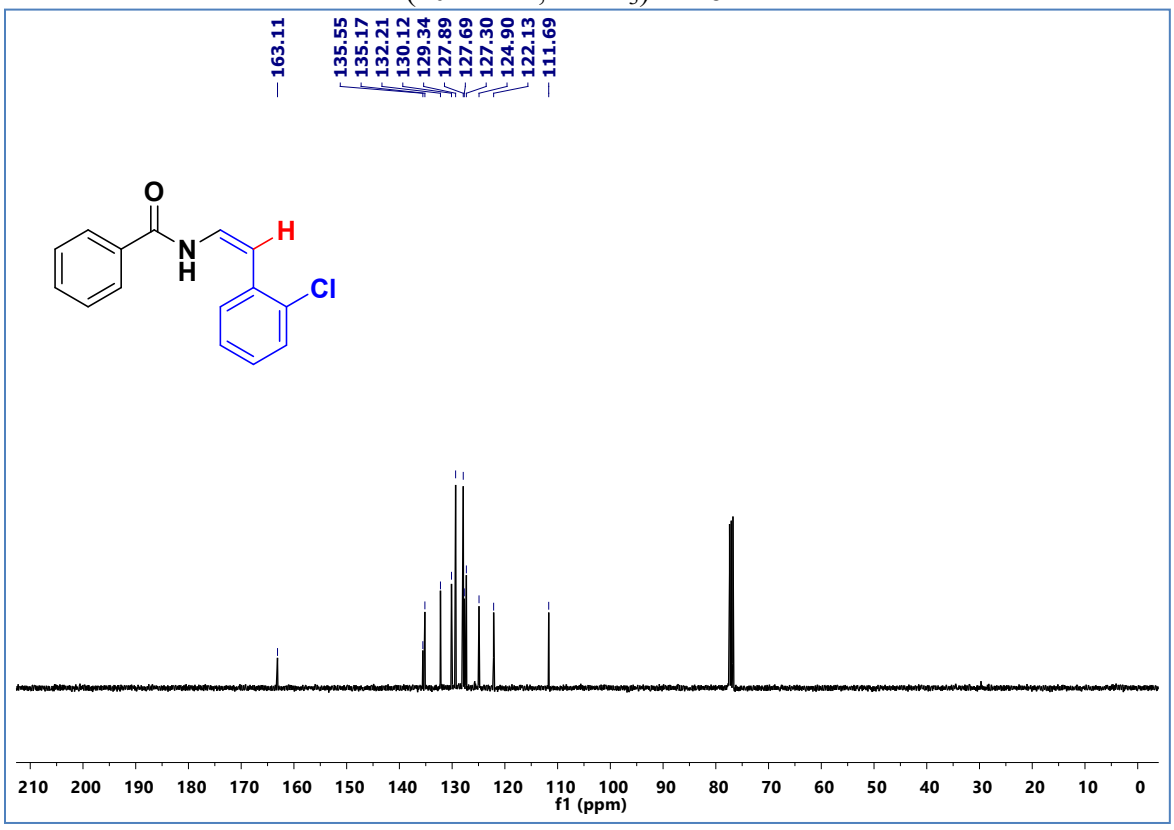
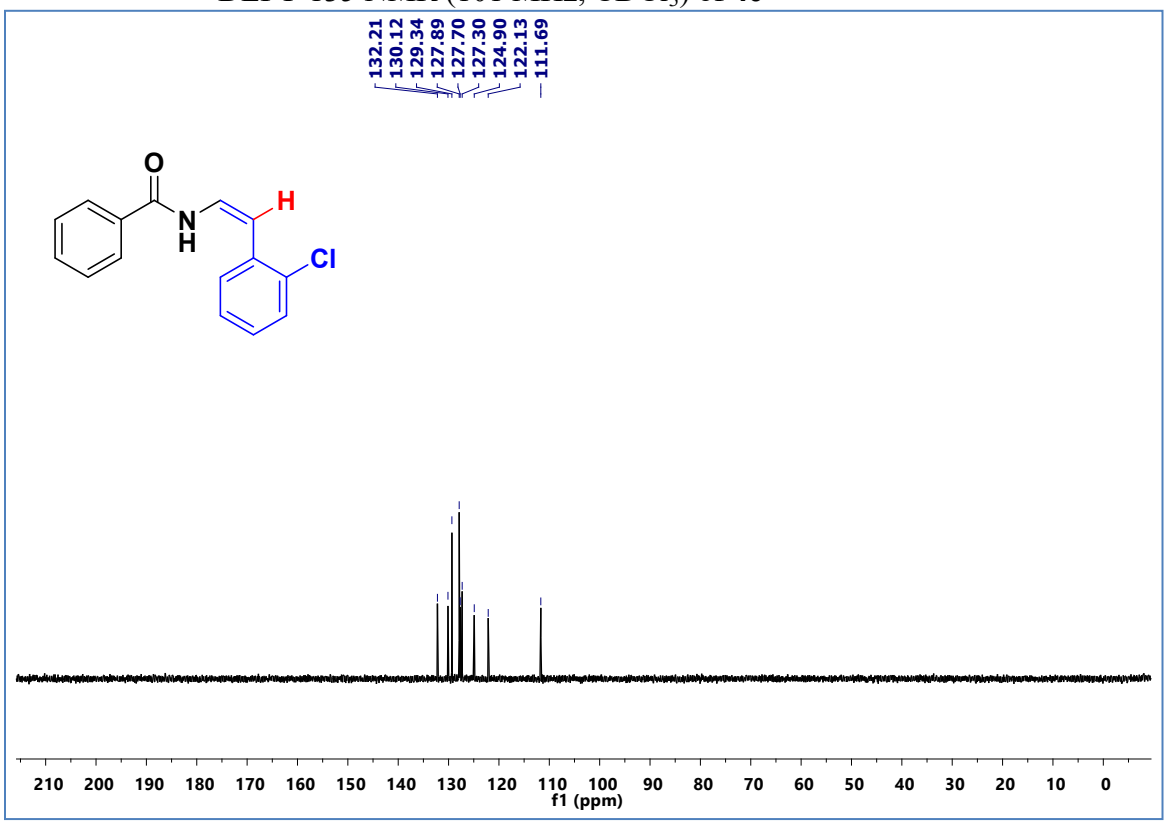


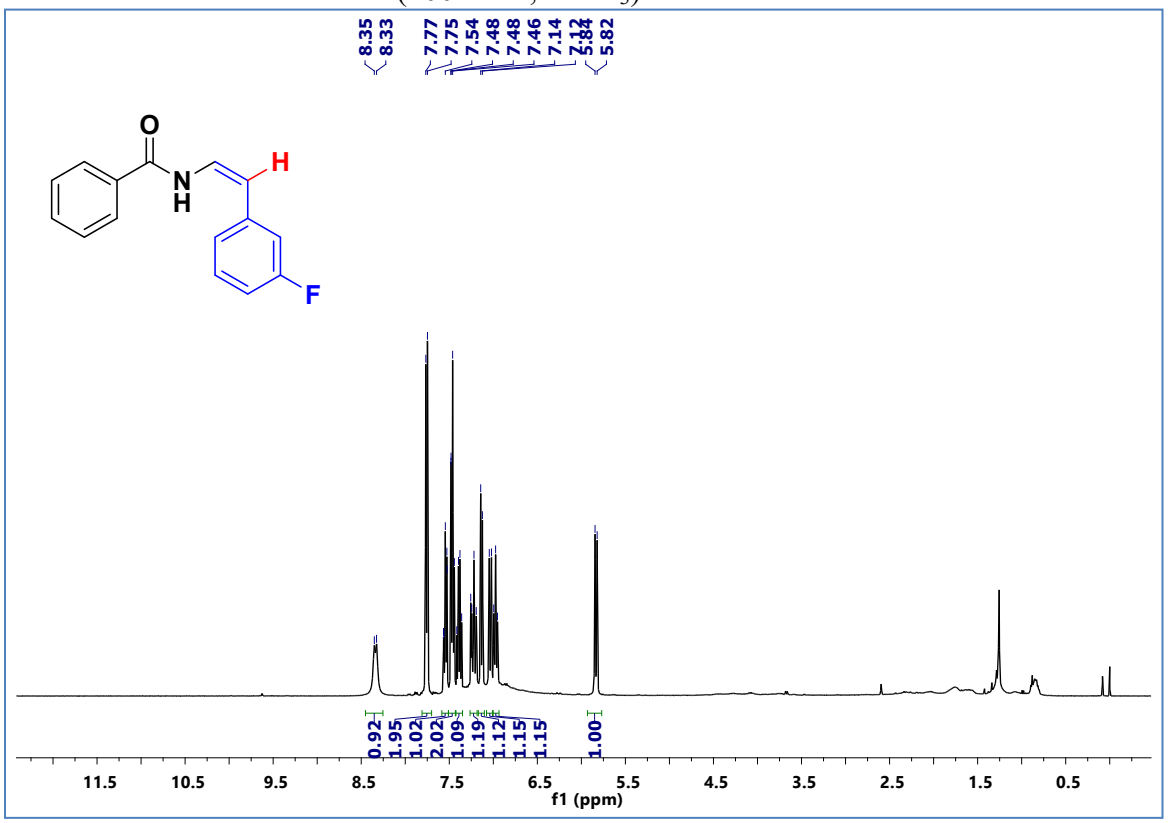
^{13}C NMR (101 MHz, $CDCl_3$) of **4e**



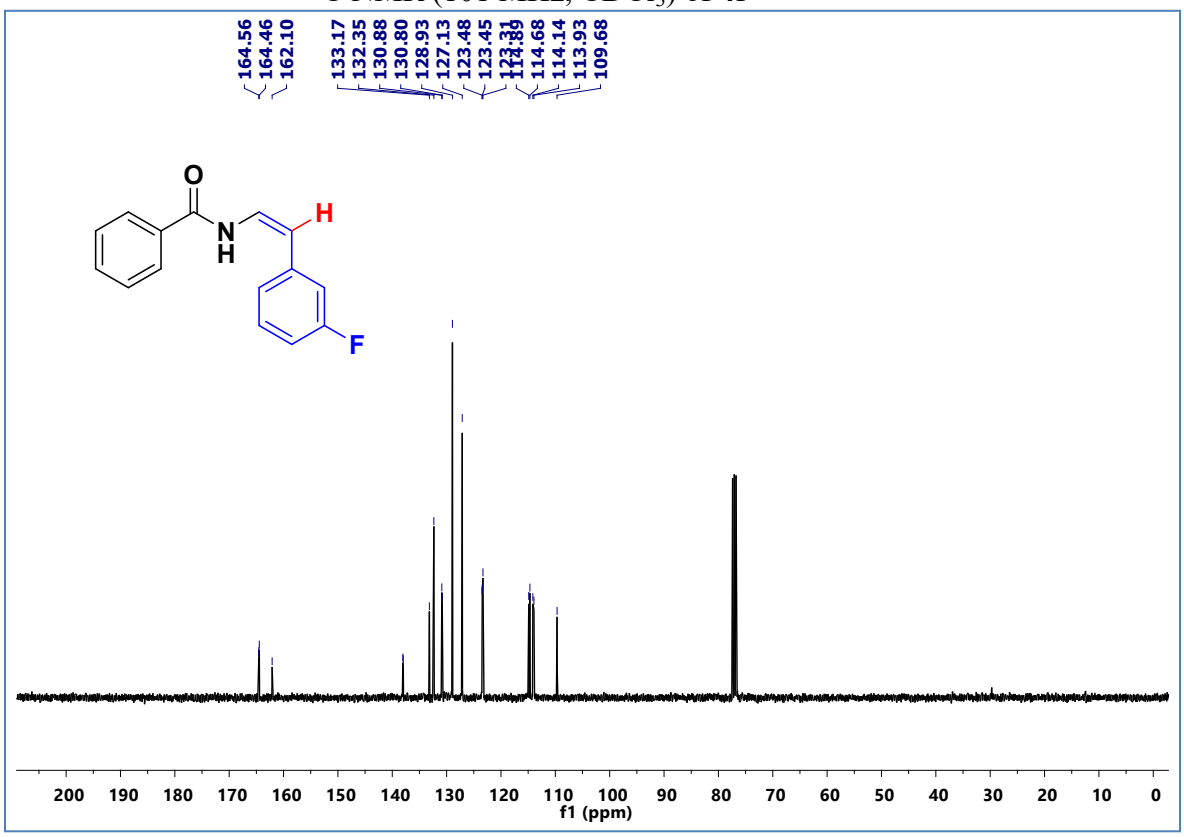
DEPT-135 NMR (101 MHz, $CDCl_3$) of **4e**



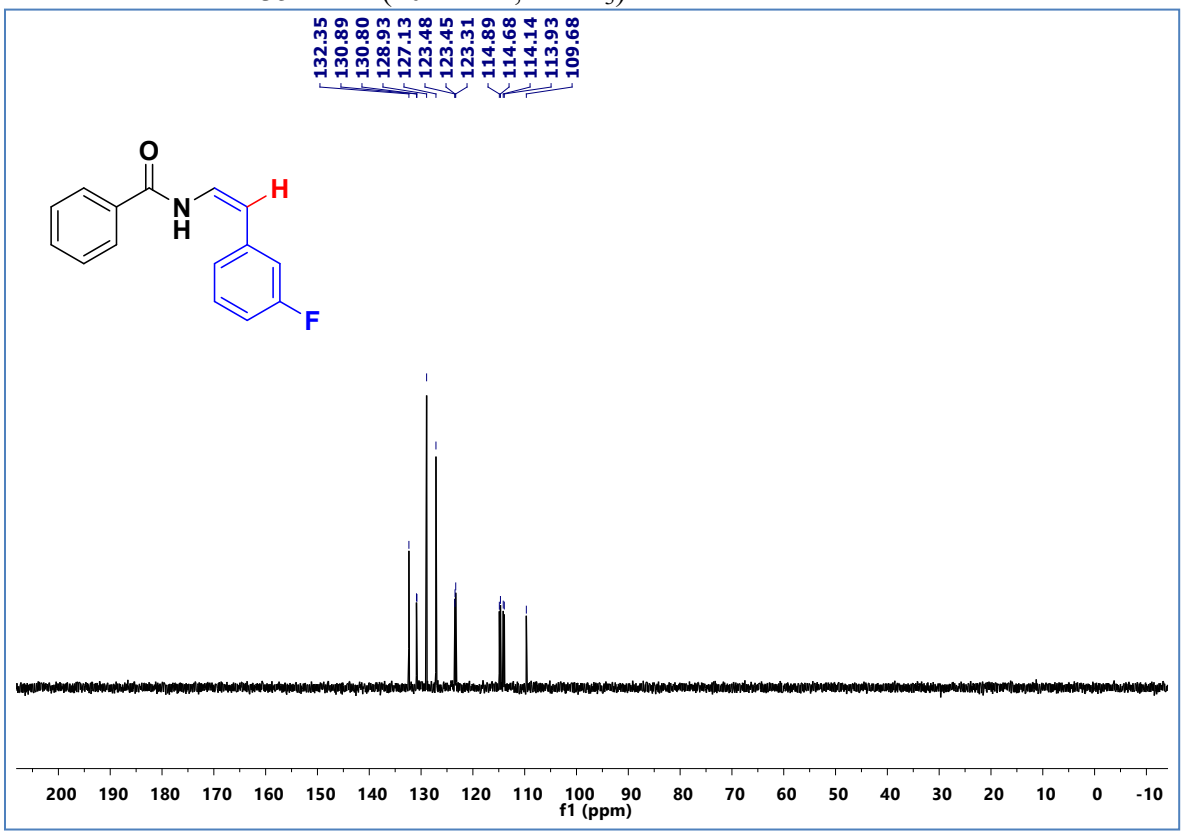
^1H NMR (400 MHz, $CDCl_3$) of **4f**



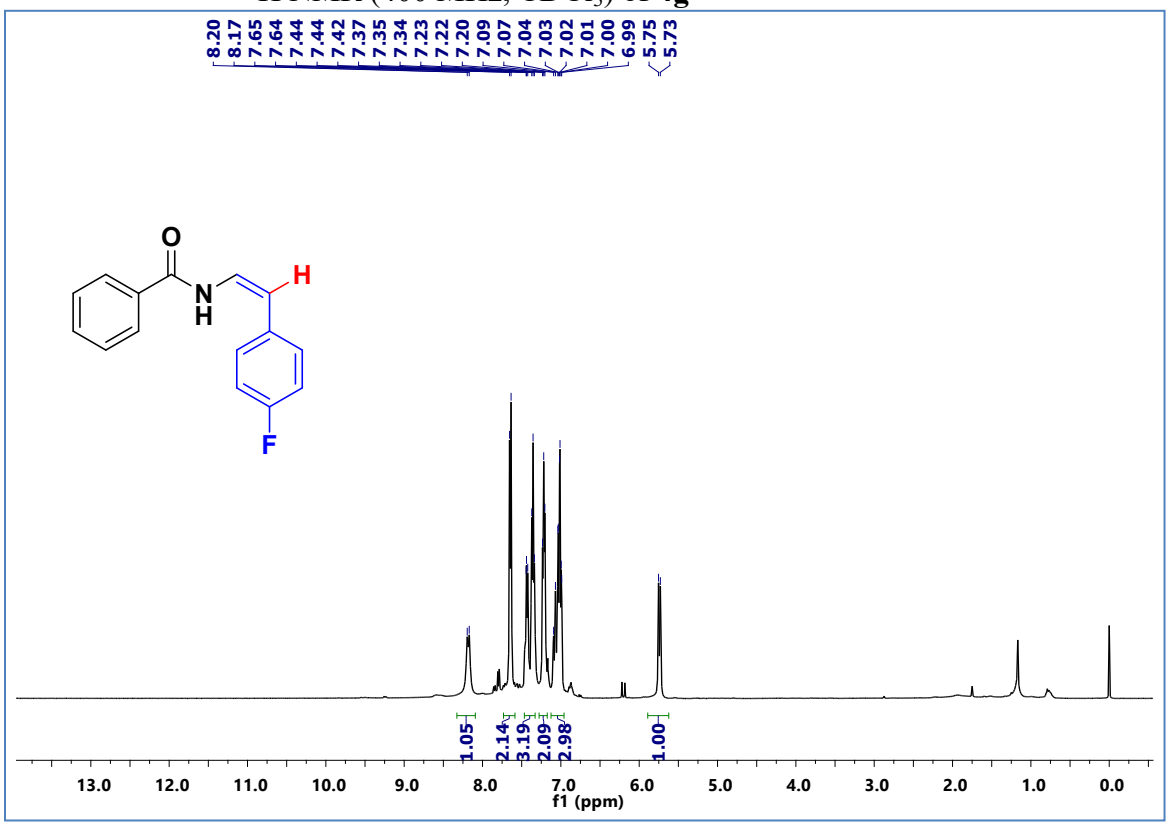
^{13}C NMR (101 MHz, $CDCl_3$) of **4f**



DEPT-135 NMR (101 MHz, $CDCl_3$) of **4f**



^{1}H NMR (400 MHz, $CDCl_3$) of **4g**



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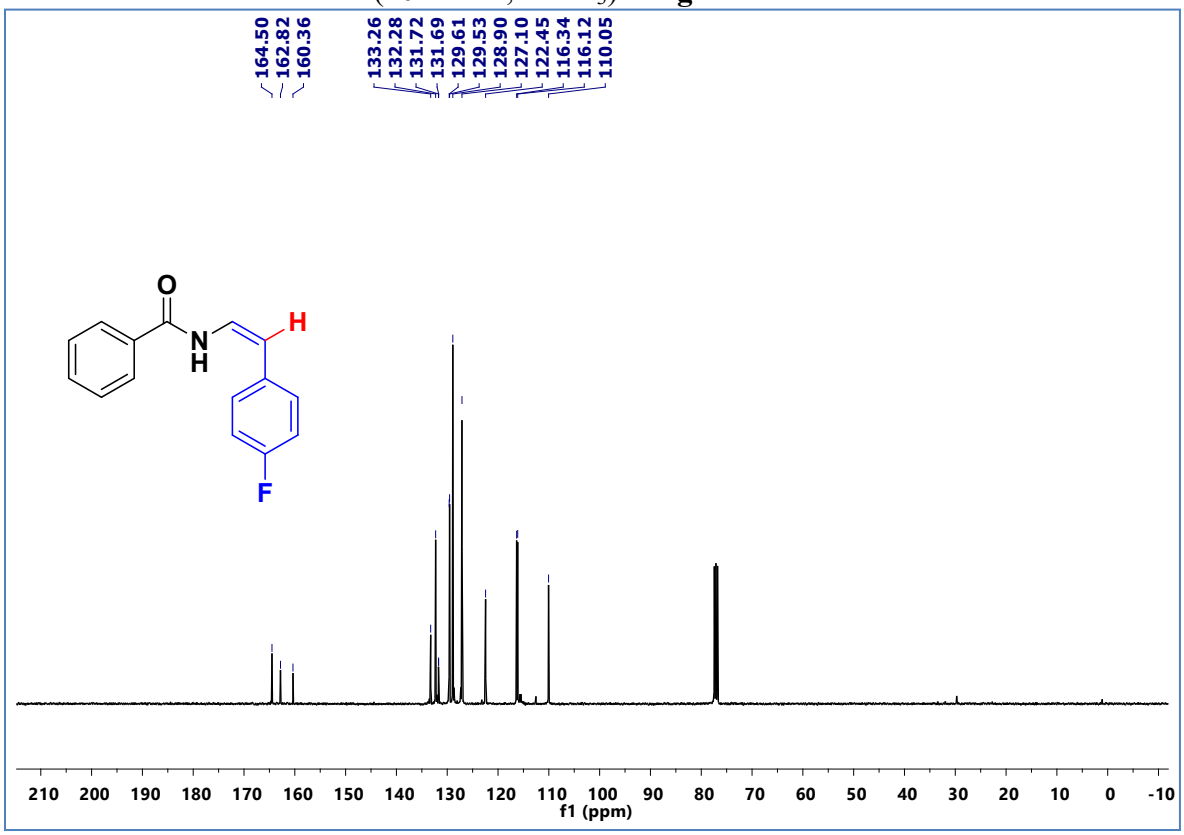
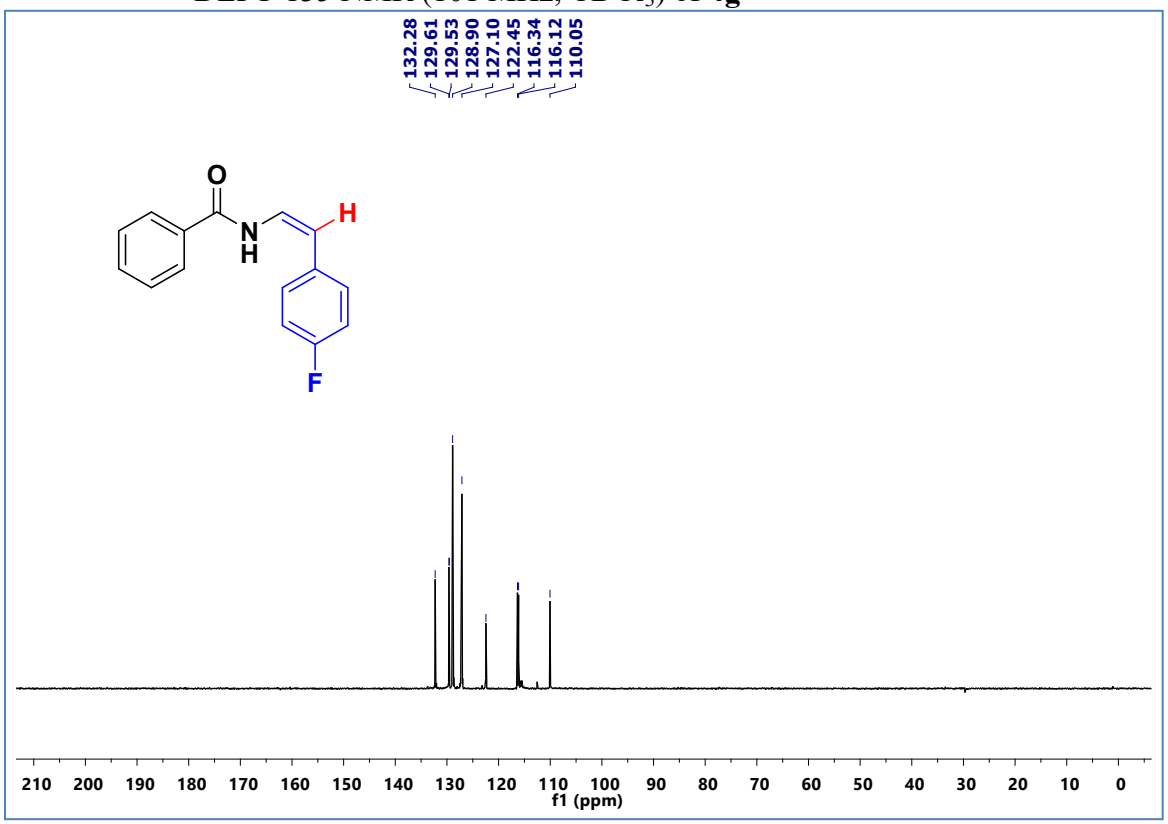
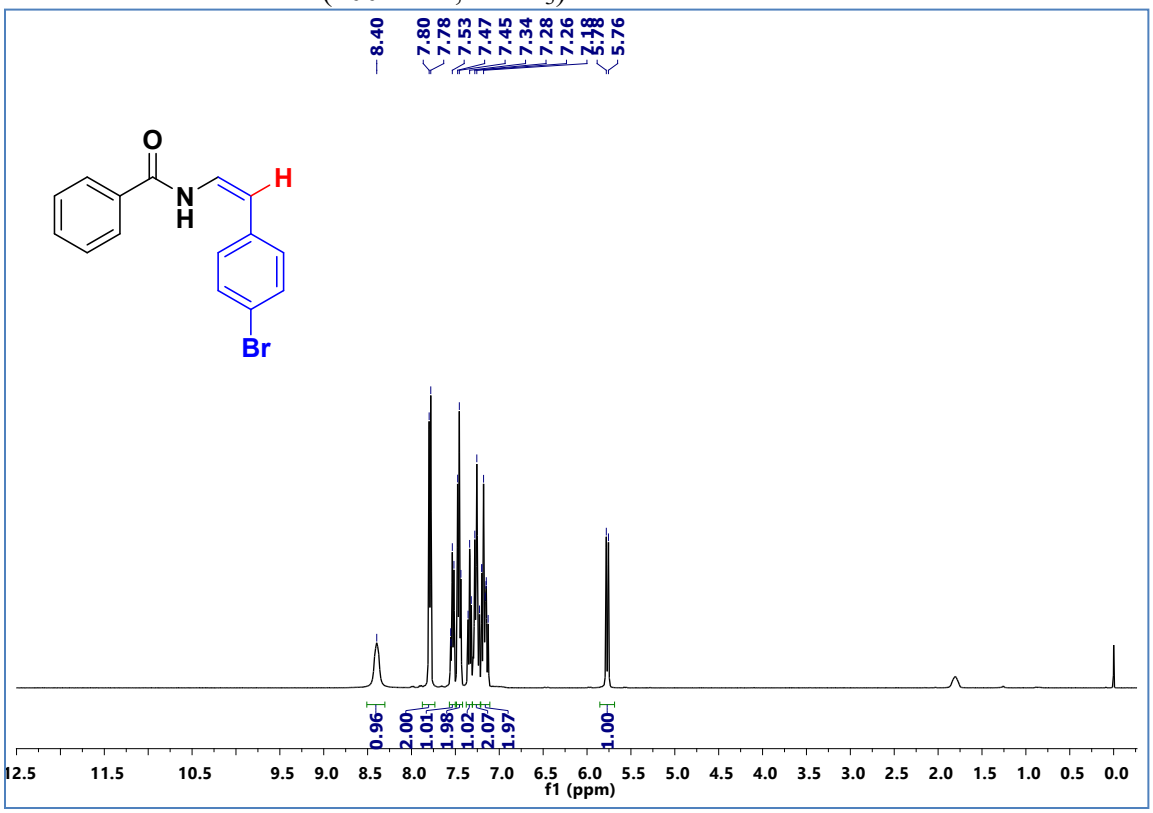


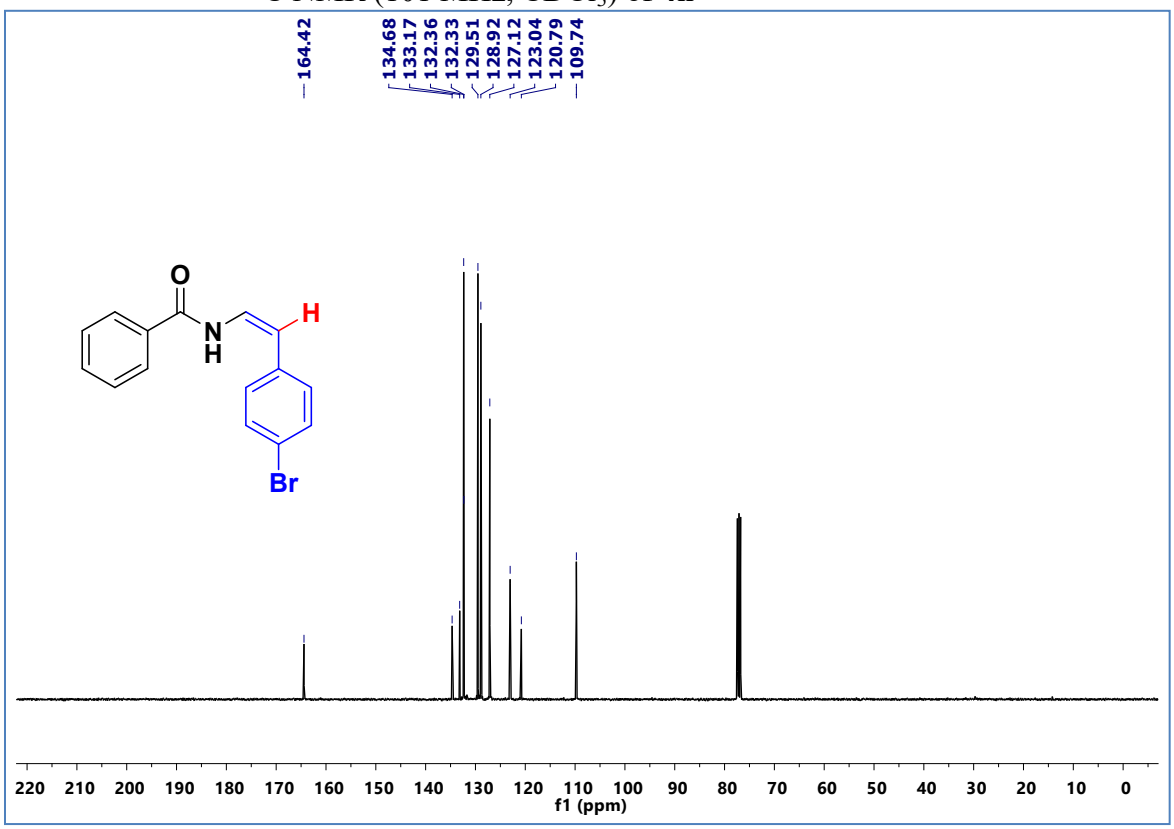
DEPT-135 NMR (101 MHz, $CDCl_3$) of **4g**



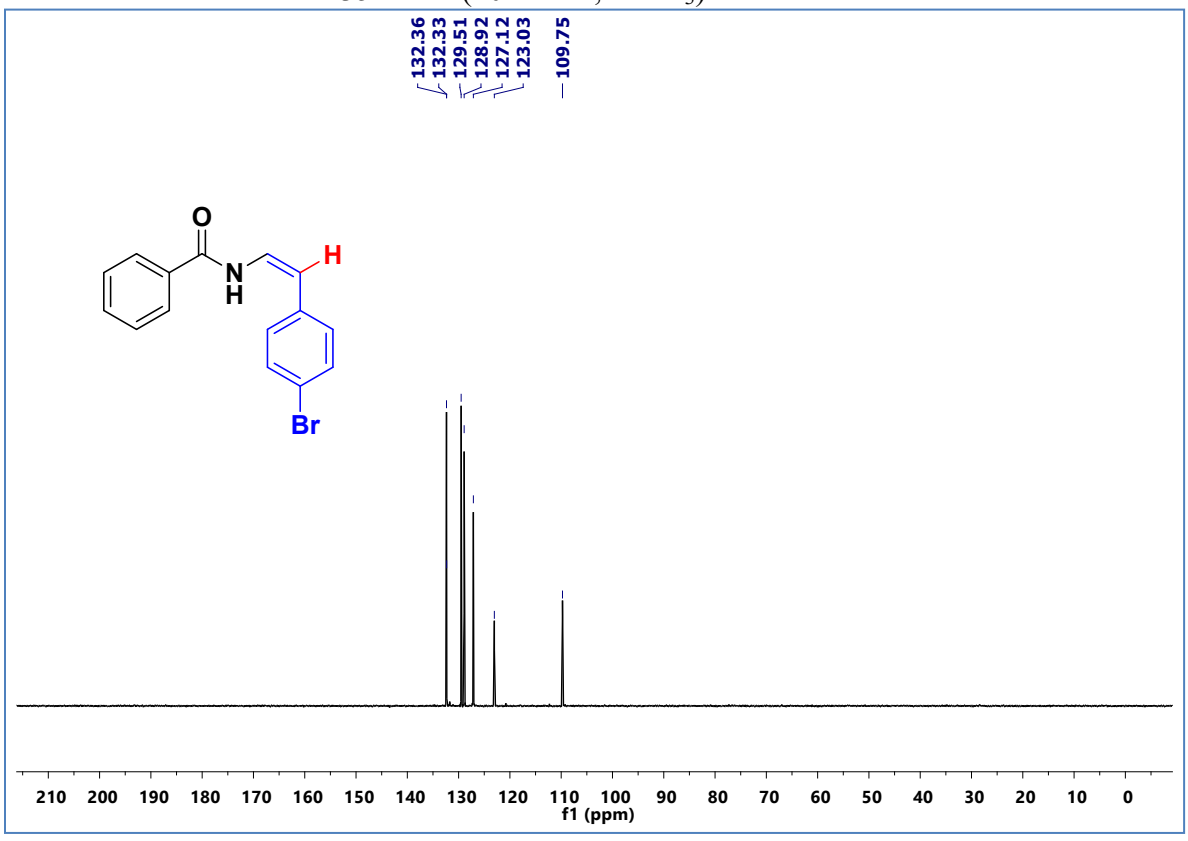
^1H NMR (400 MHz, $CDCl_3$) of **4h**



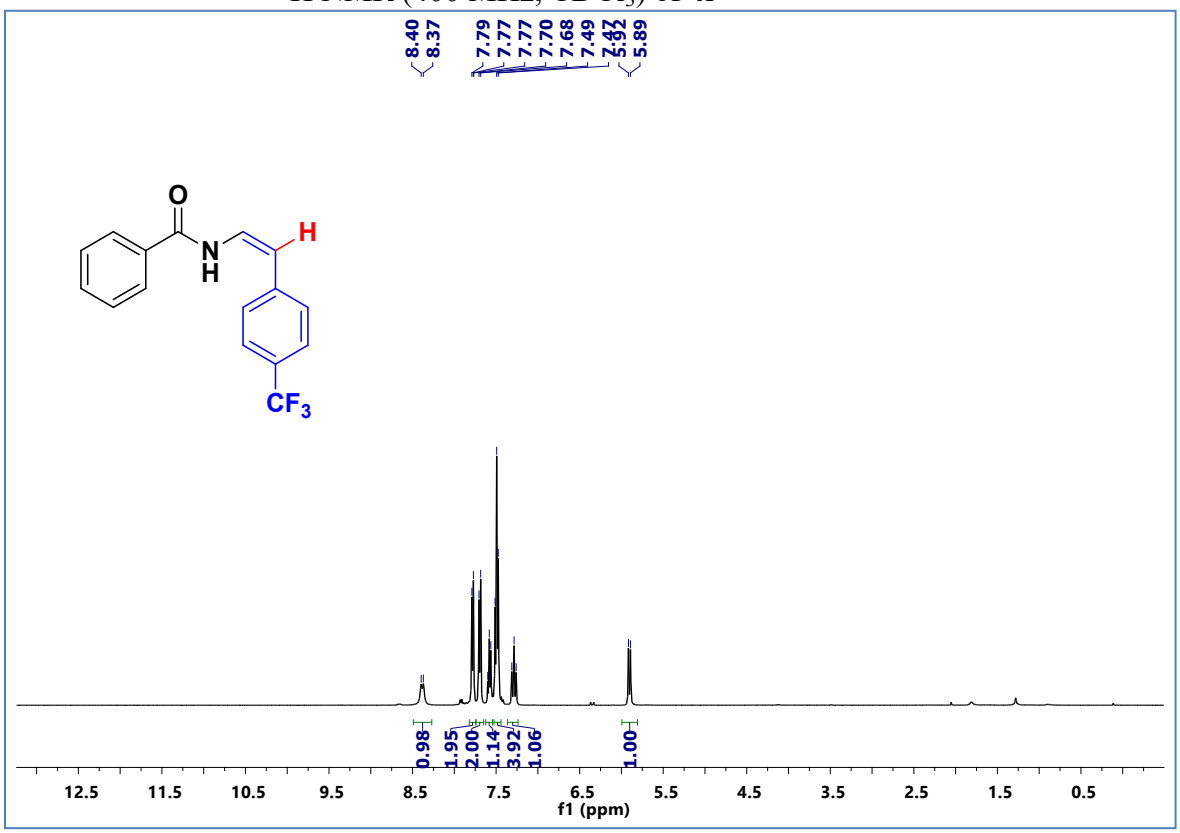
^{13}C NMR (101 MHz, $CDCl_3$) of **4h**



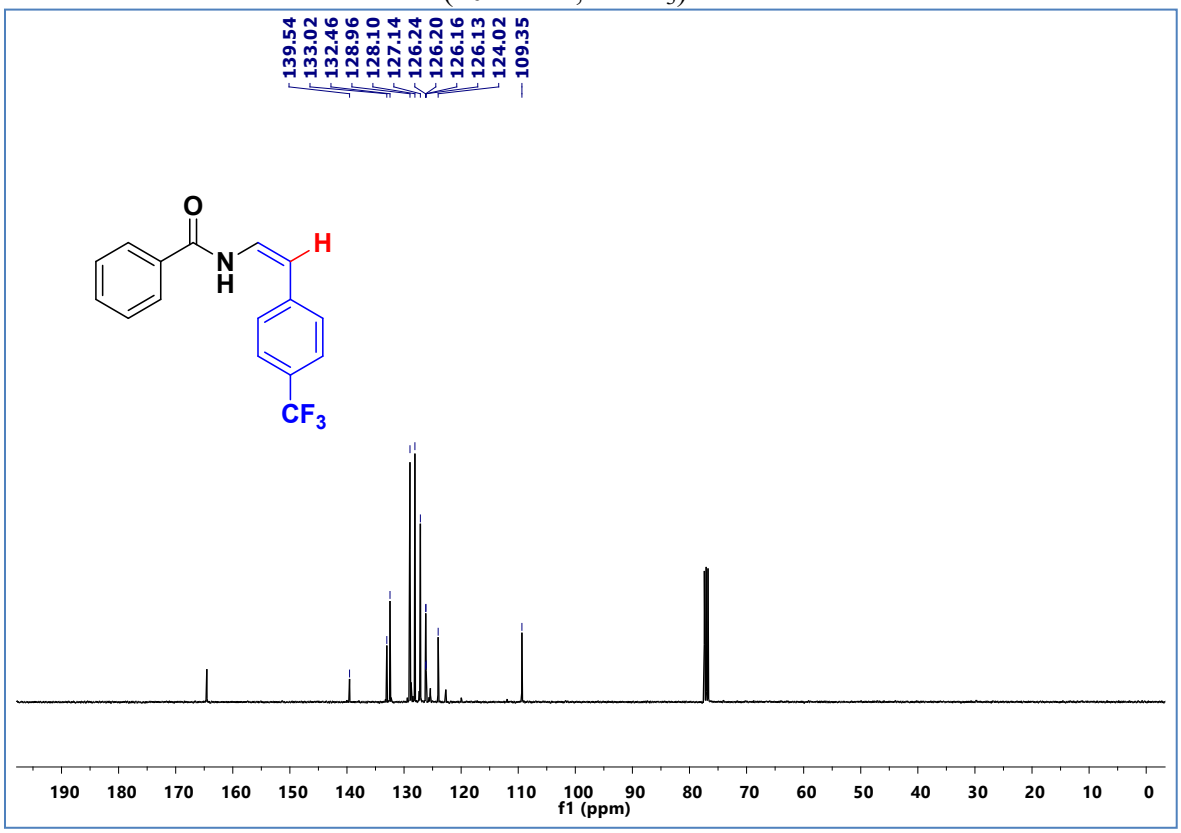
DEPT-135 NMR (101 MHz, $CDCl_3$) of **4h**



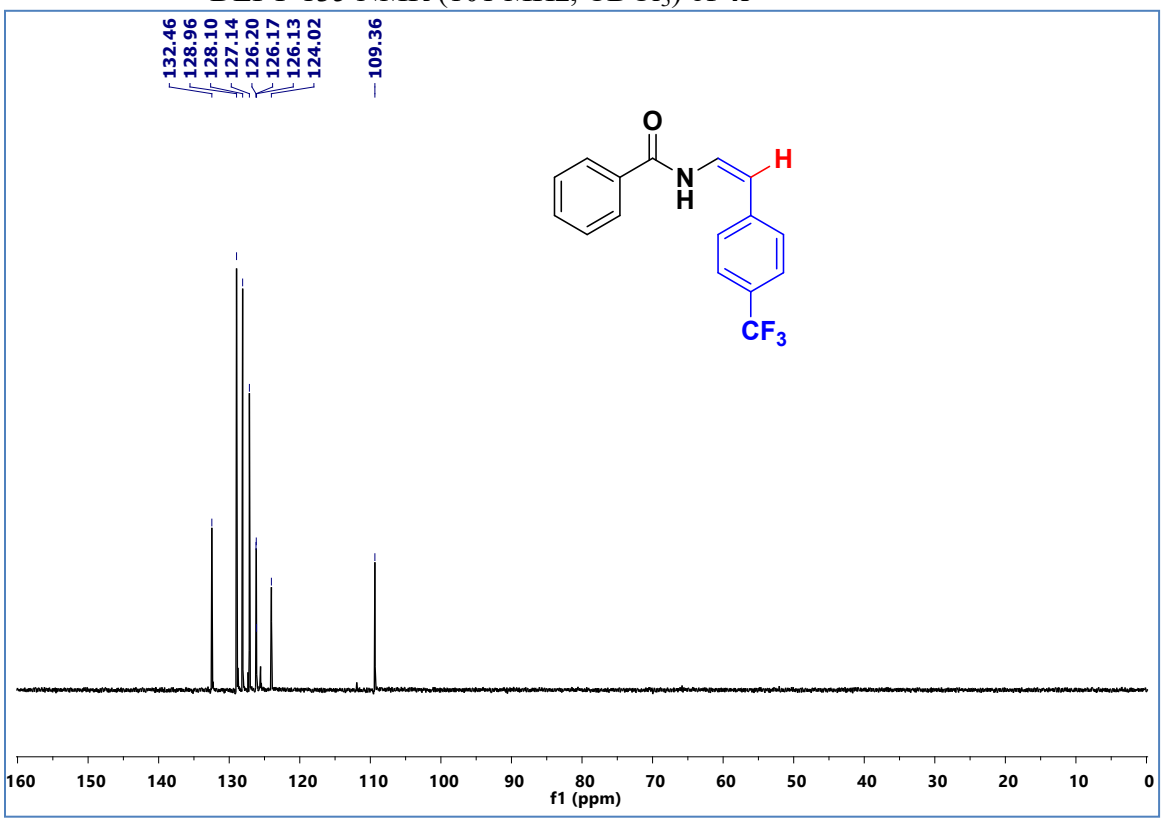
^{1}H NMR (400 MHz, $CDCl_3$) of **4i**



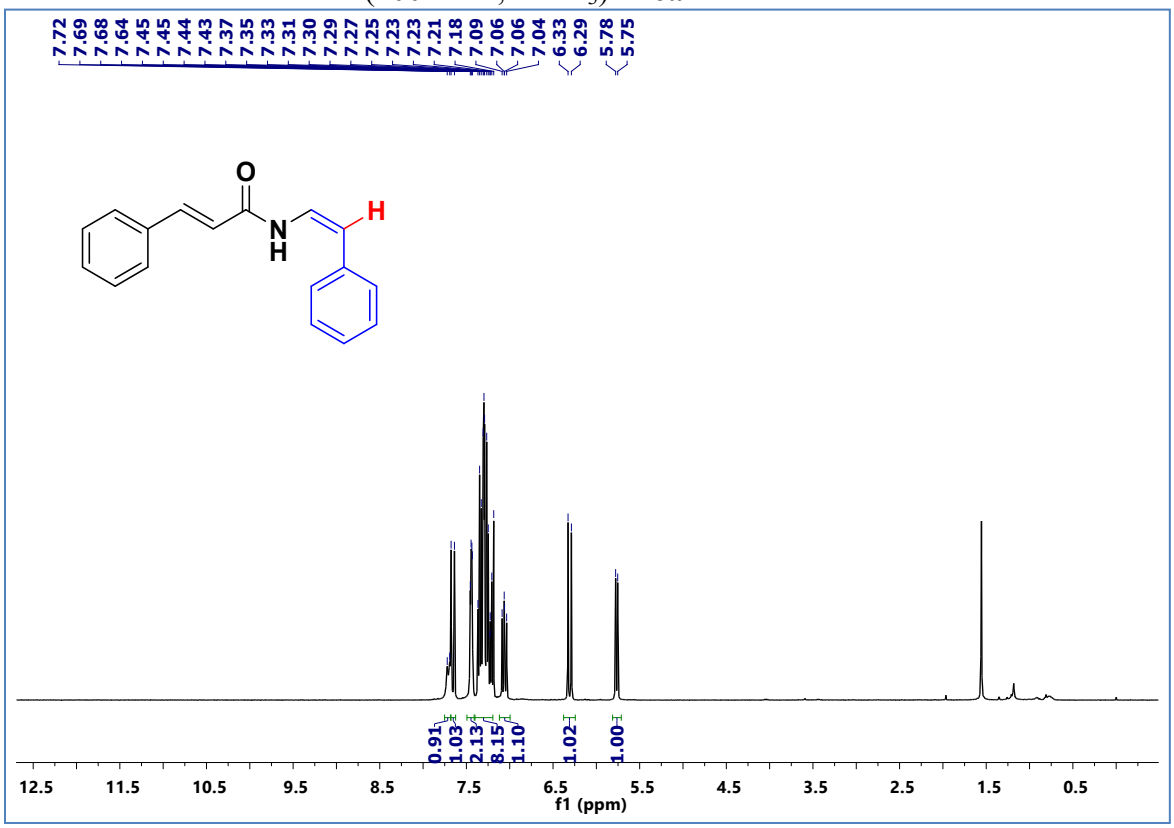
^{13}C NMR (101 MHz, $CDCl_3$) of **4i**



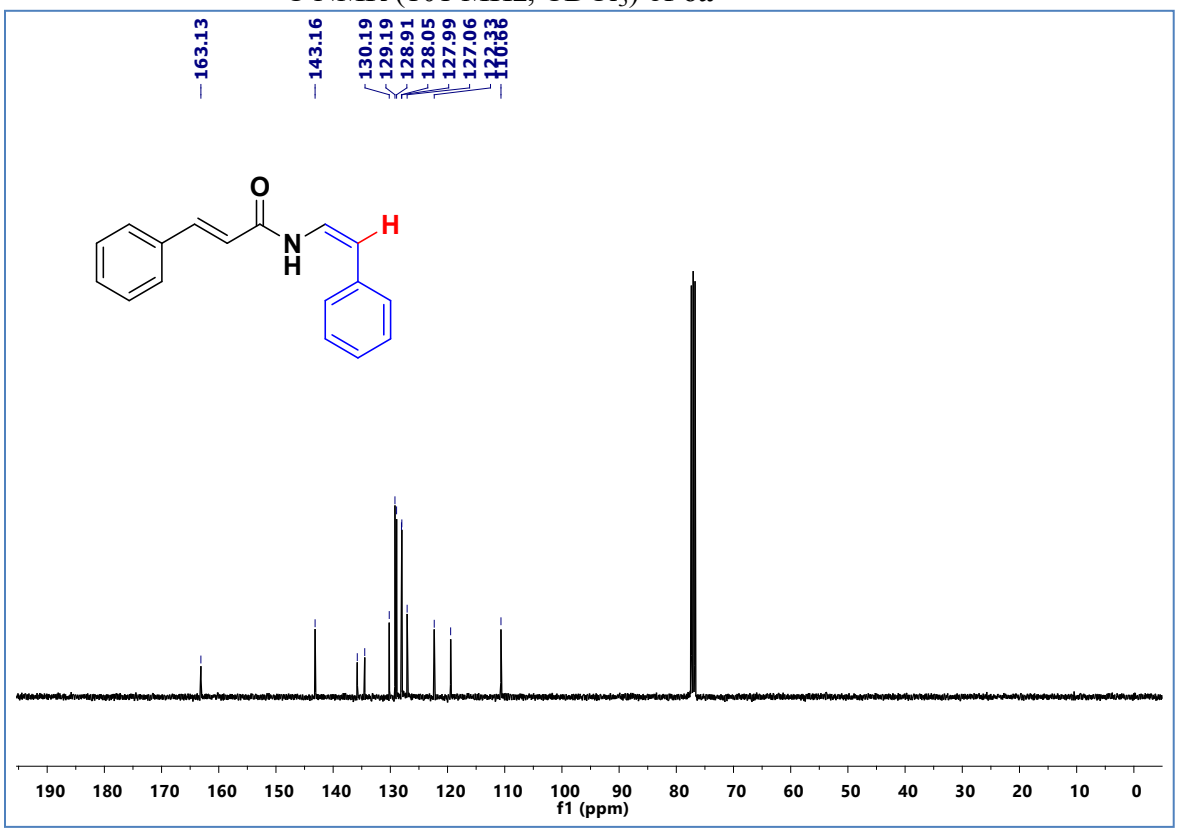
DEPT-135 NMR (101 MHz, $CDCl_3$) of **4i**



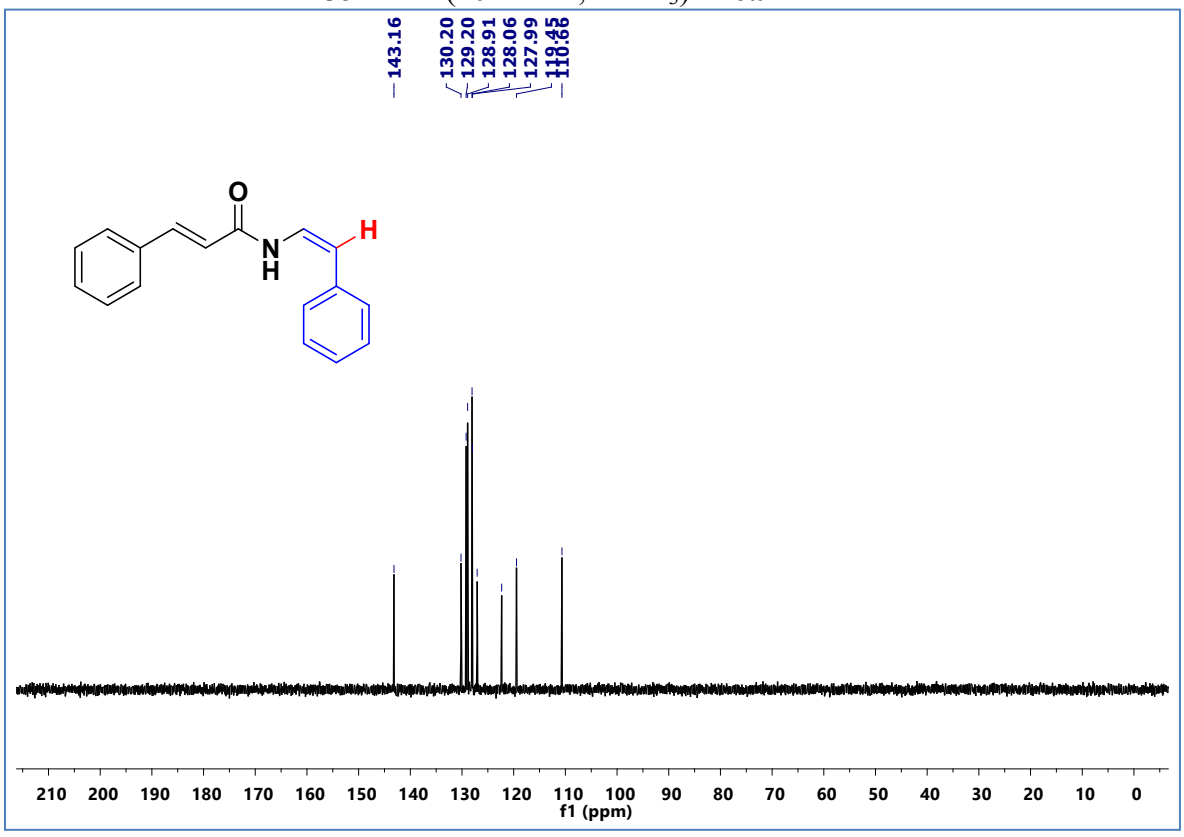
^1H NMR (400 MHz, $CDCl_3$) of **6a**



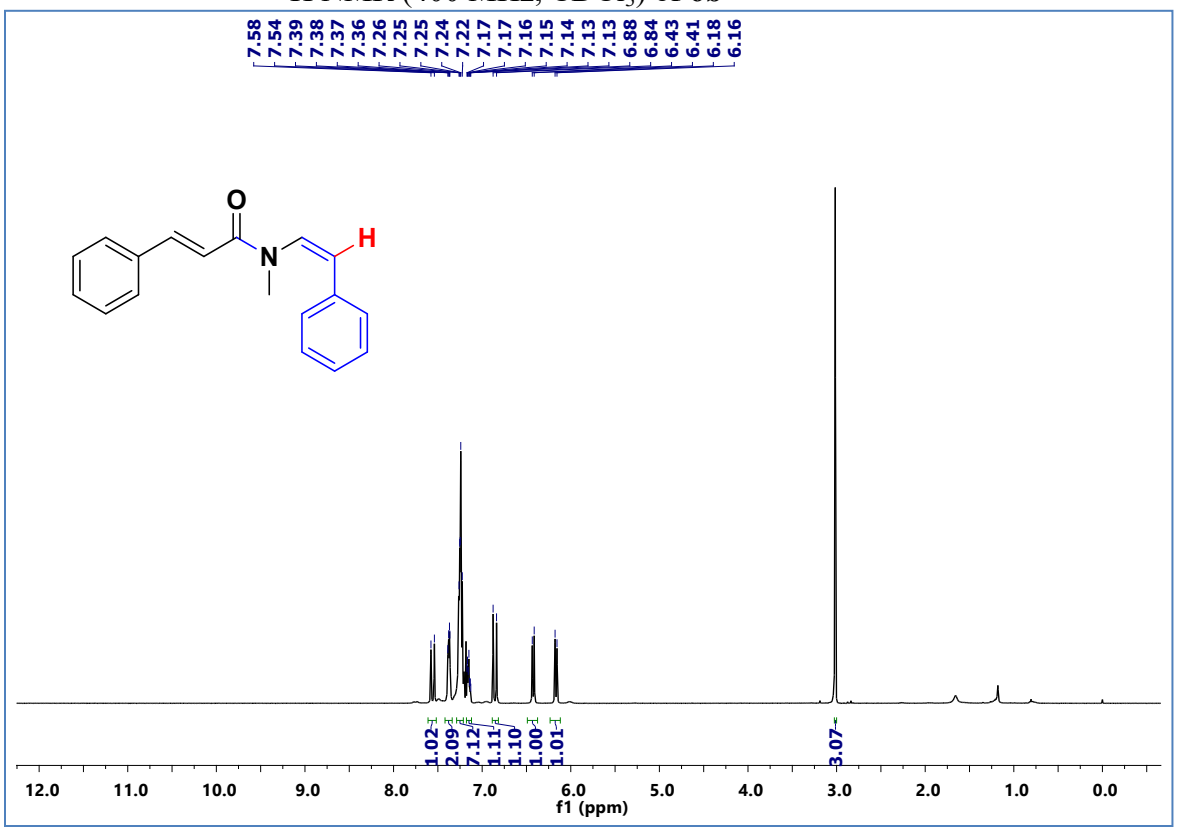
^{13}C NMR (101 MHz, $CDCl_3$) of **6a**



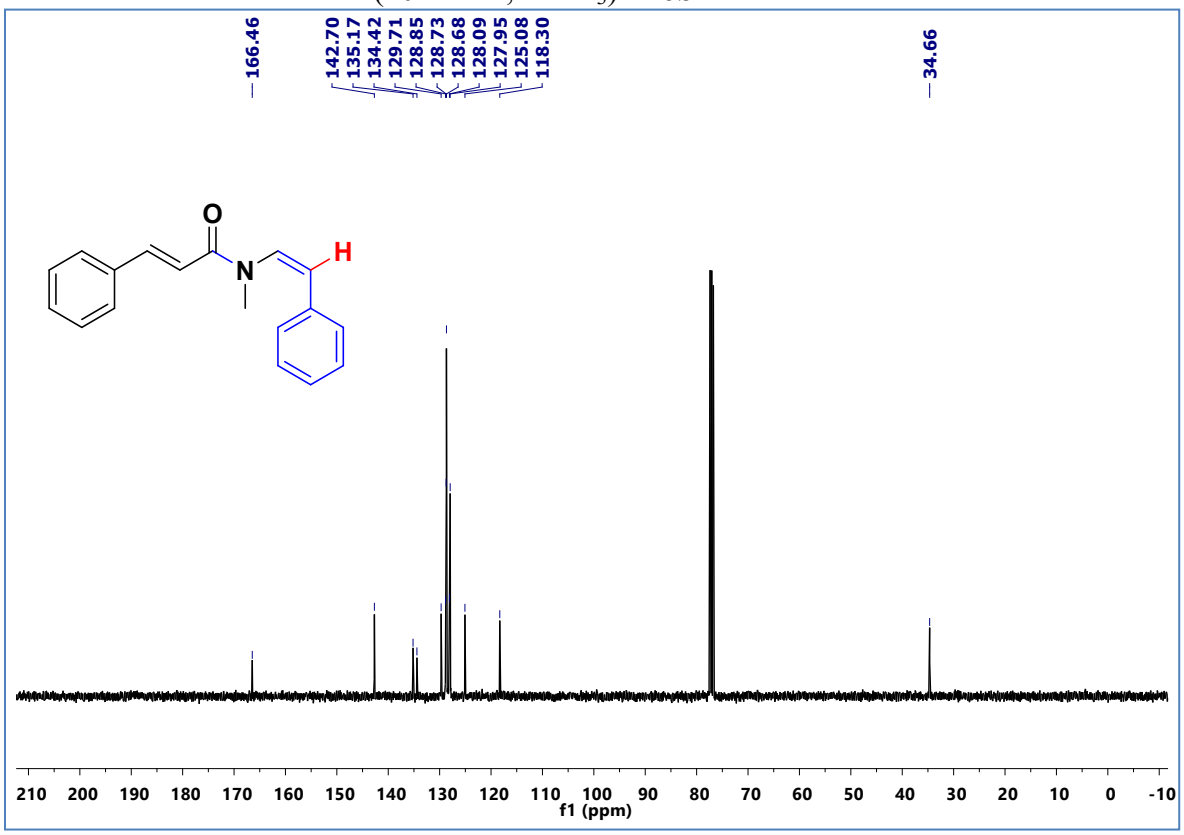
DEPT-135 NMR (101 MHz, $CDCl_3$) of **6a**



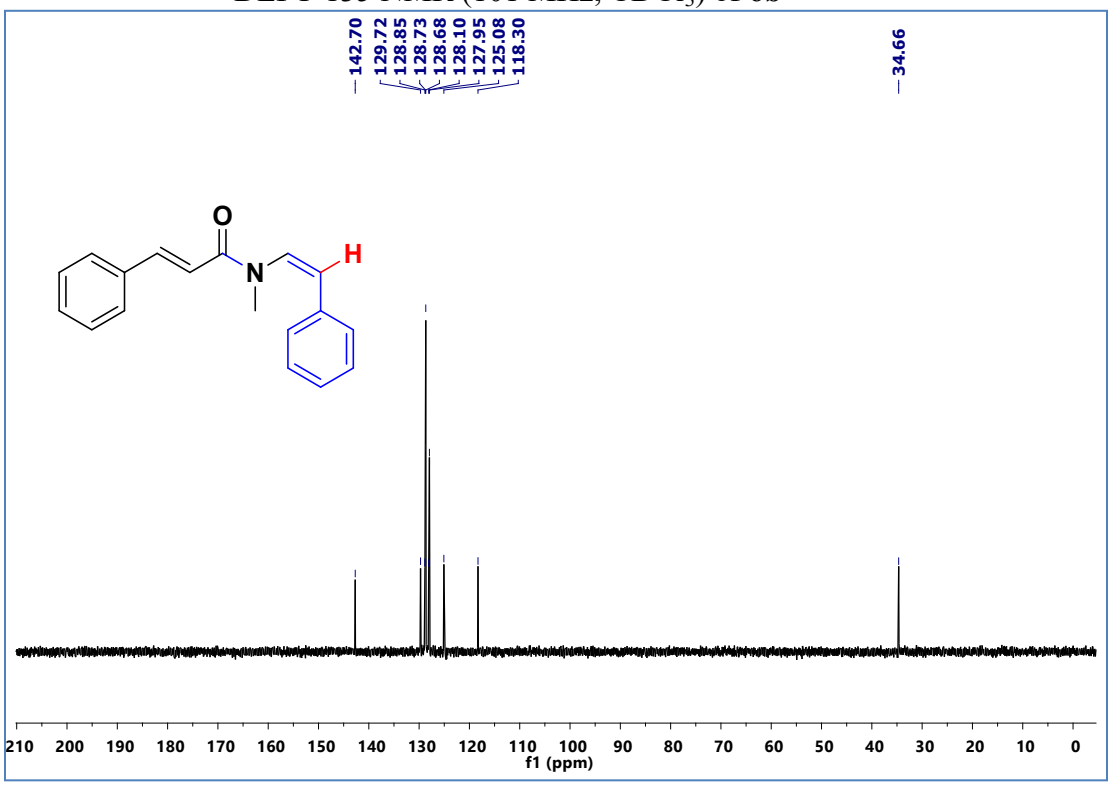
^{1}H NMR (400 MHz, $CDCl_3$) of **6b**



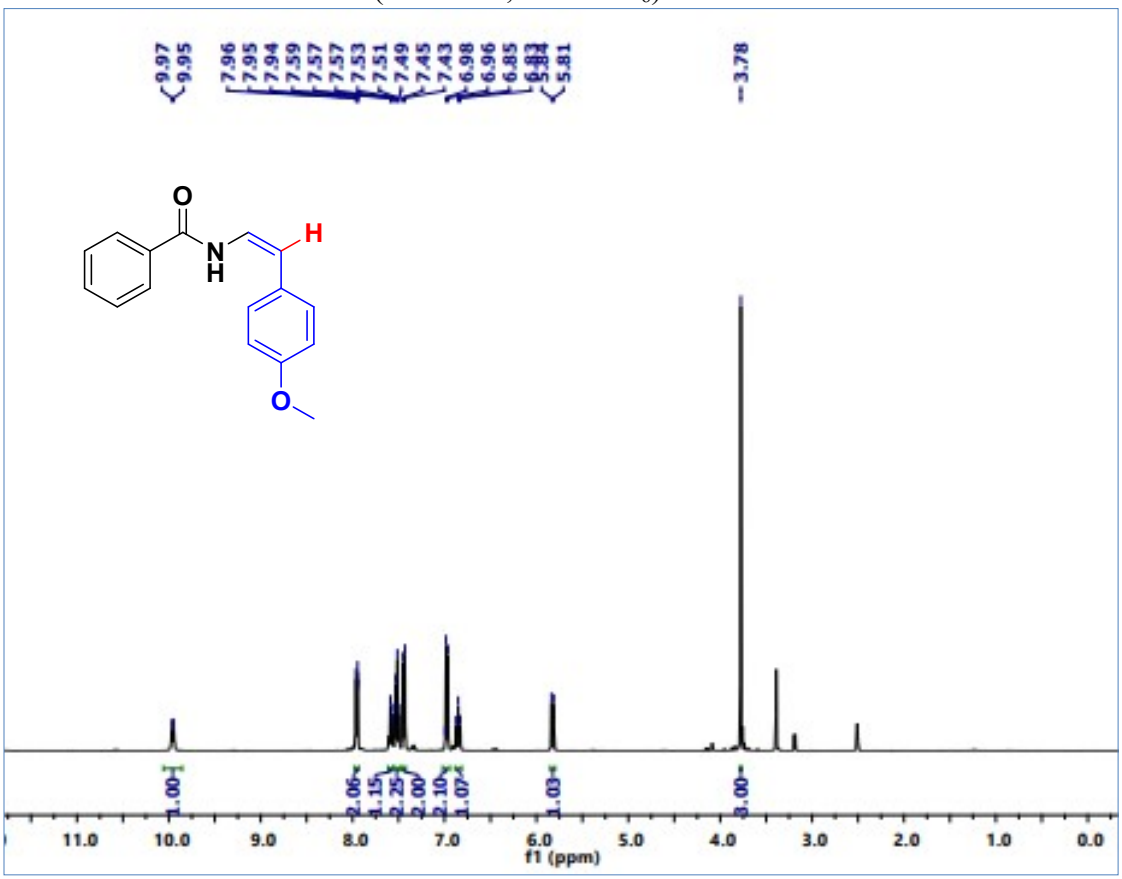
^{13}C NMR (101 MHz, $CDCl_3$) of **6b**



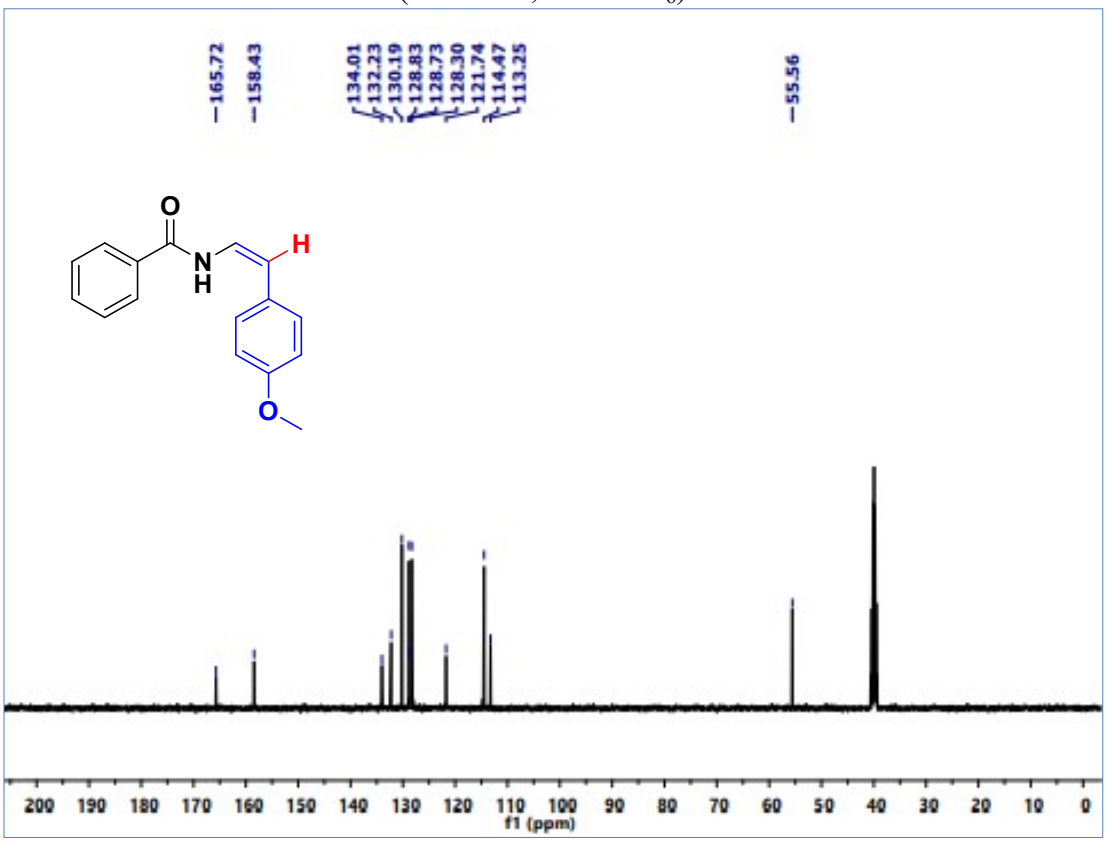
DEPT-135 NMR (101 MHz, $CDCl_3$) of **6b**



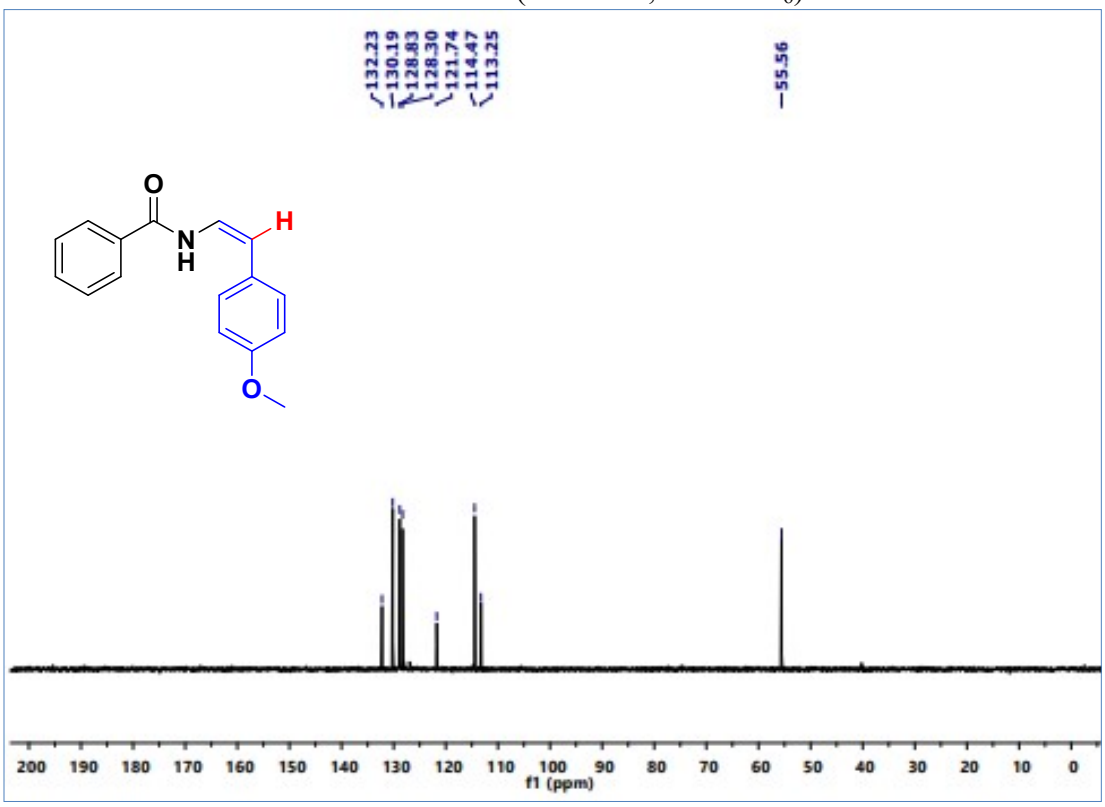
^1H NMR (400 MHz, DMSO-d_6) of **7**



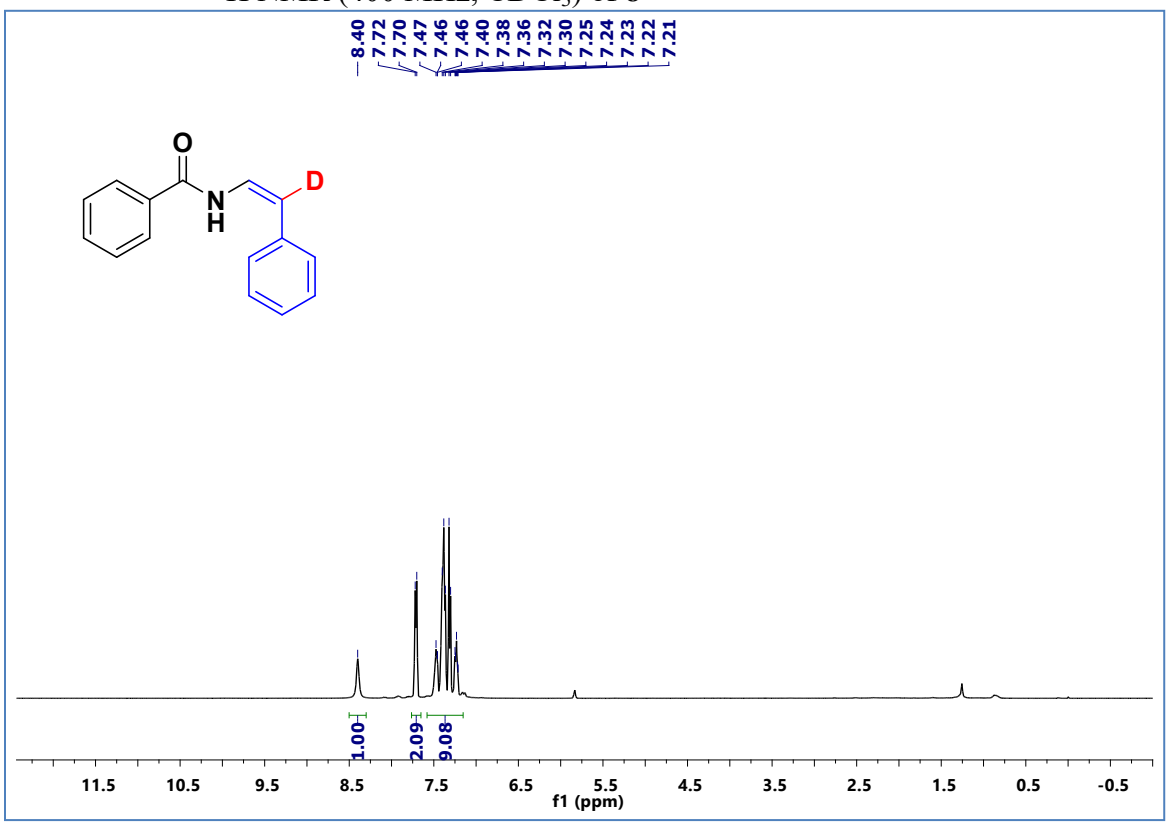
^{13}C NMR (101 MHz, DMSO-d_6) of **7**



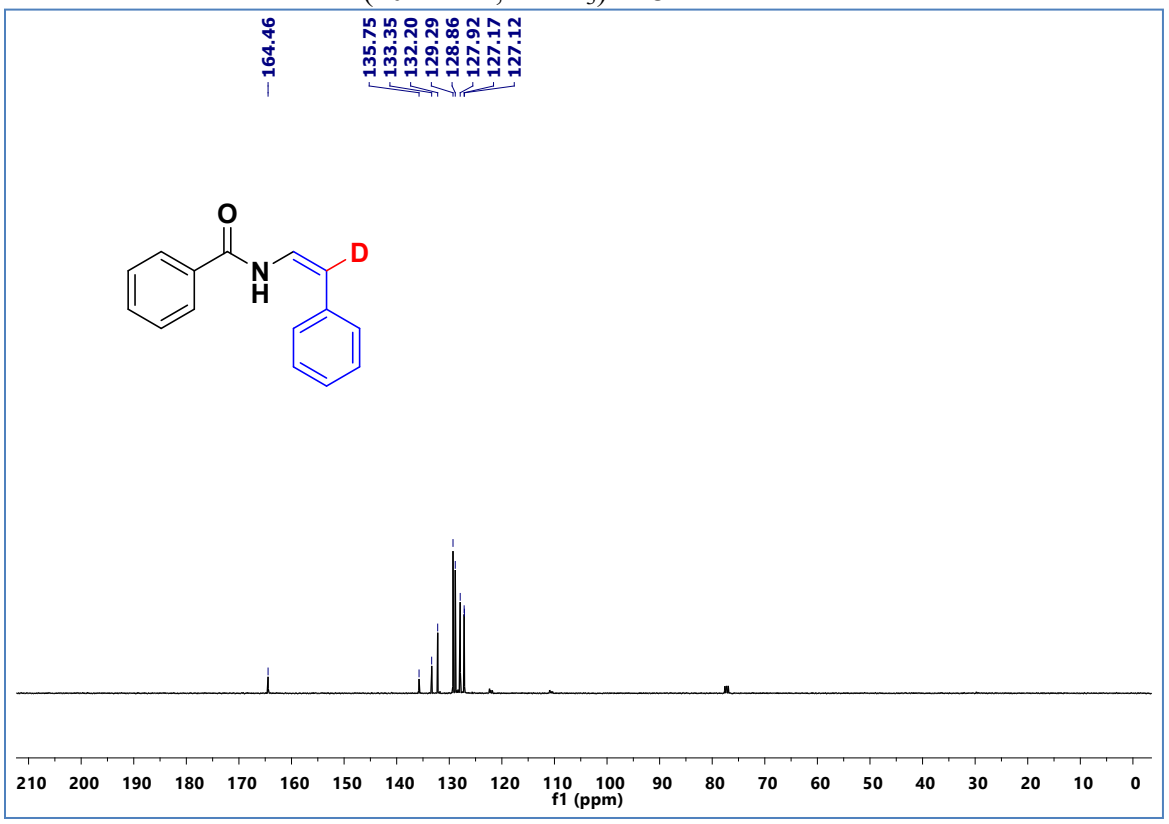
DEPT-135 NMR (101 MHz, DMSO-d_6) of **7**



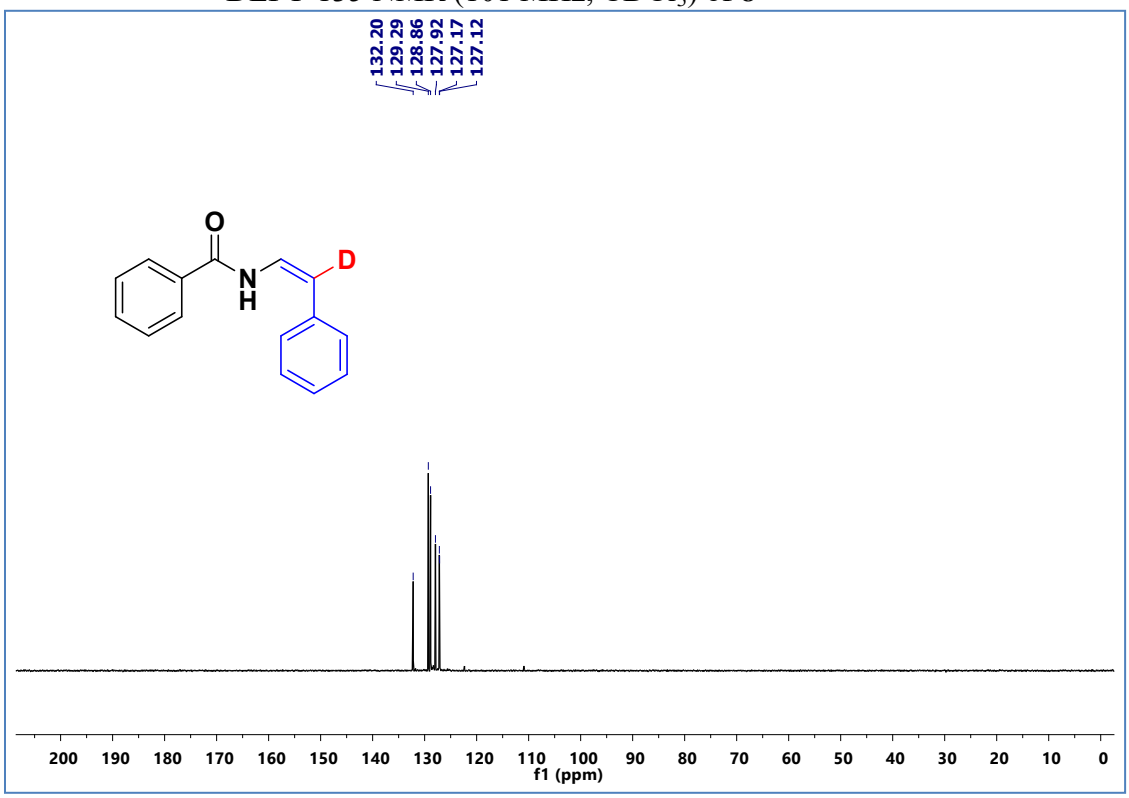
^{1}H NMR (400 MHz, $CDCl_3$) of **8**



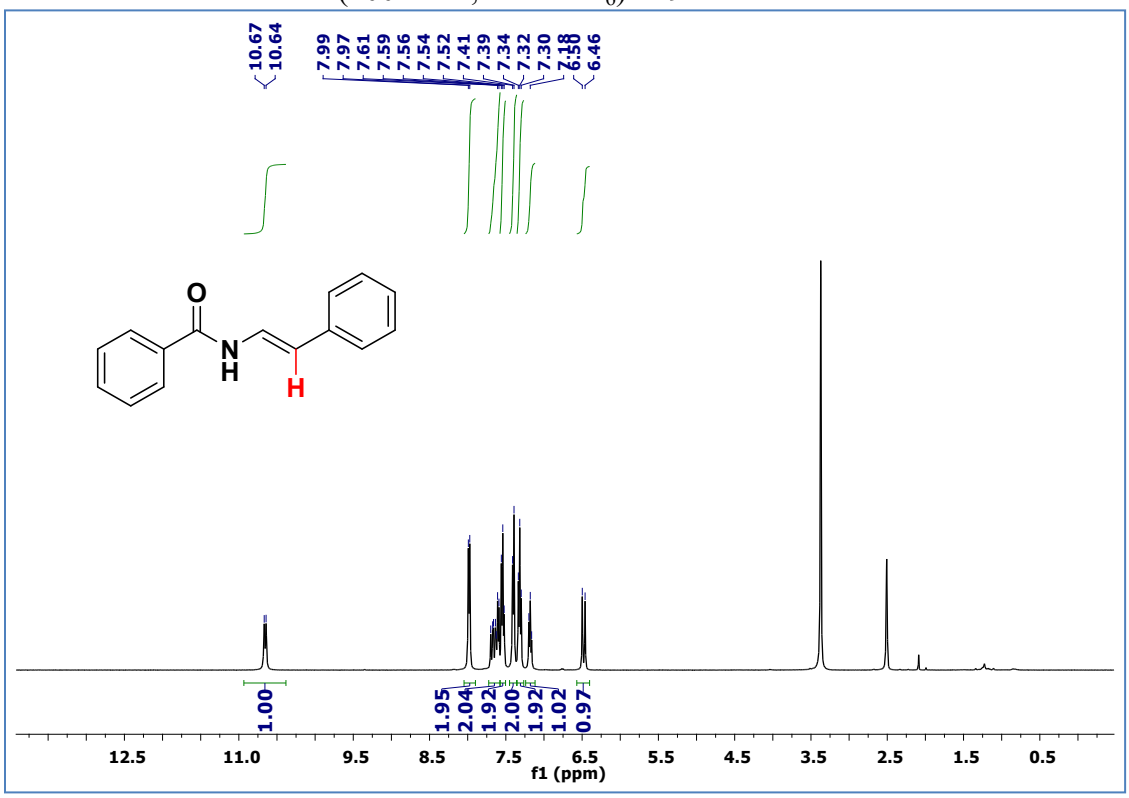
^{13}C NMR (101 MHz, $CDCl_3$) of **8**



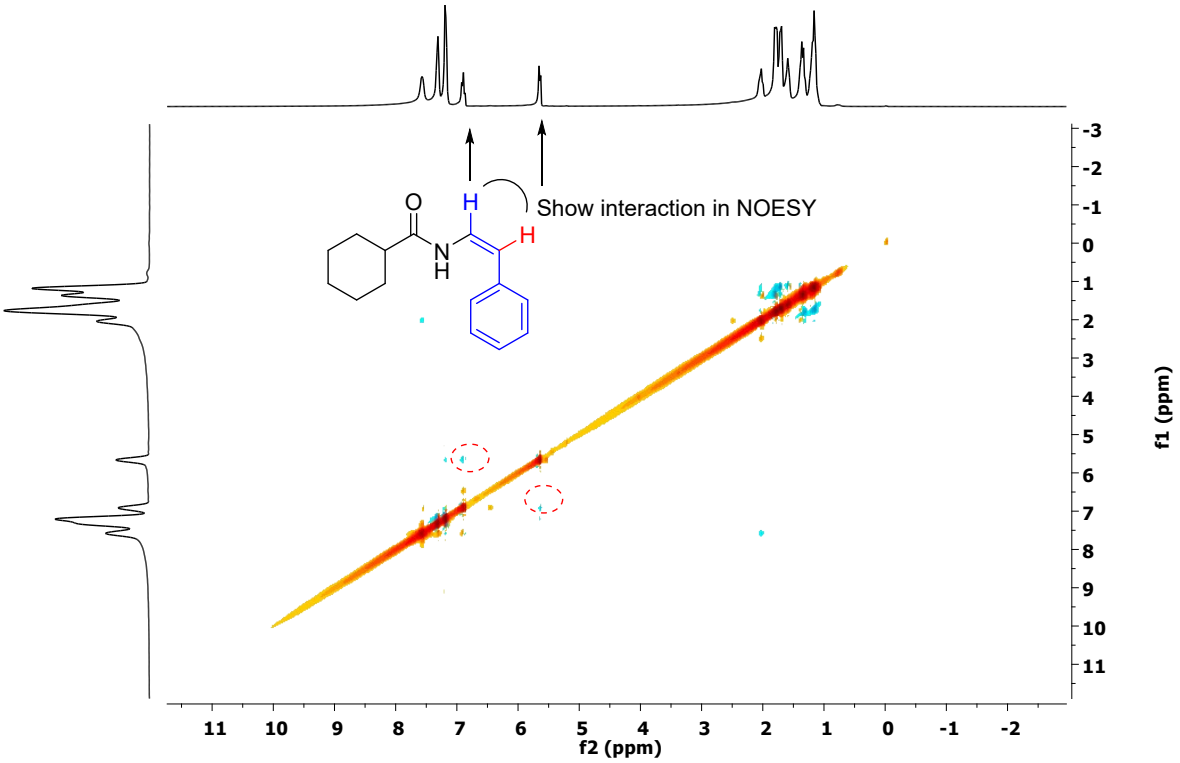
DEPT-135 NMR (101 MHz, $CDCl_3$) of **8**



^{1}H NMR (400 MHz, DMSO-d_6) of **9**



7. [1]NOESY spectrum of compound 3o



8. References

1. L. J. Gooßen, K. S. M. Salih and M. Blanchot, *Angewandte Chemie International Edition*, 2008, **47**, 8492-8495.

2. A. E. Pasqua, F. D. Ferrari, J. J. Crawford and R. Marquez, *Tetrahedron Letters*, 2014, **55**, 6042-6043.