Supporting Information

Acylation of oxindoles using methyl/phenyl esters via mixed Claisen condensation – An access to 3-alkylideneoxindoles

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Table of Contents

1. General experimental methods and materials.

Unless otherwise mentioned all the reactions were carried out in screw capped reaction tubes (10 mL) or Schlenk tube (15 ml). Anhydrous CH_3CN, DMF and DMSO were purchased from commercial sources and used without further purification. Solvents like THF, 1,4-Dioxane and Toluene were dried prior to use. Chemicals were purchased from Sigma-Aldrich, Alfa Aesar and AVRA. Thin layer chromatography was carried out on 250 mm diameter aluminium supported silica gel TLC plates (MERCK TLC Plates) and with narrow tip capillary. The products were purified by flash column chromatography using 100-200 mesh silica gel. ^{1}H NMR spectra were recorded on Bruker spectrometer (400 MHz) and reported in units *ppm* (parts per million) relative to the signals for residual chloroform (7.26 *ppm*) in the deuterated solvent. ^{13}C NMR spectra were recorded on Bruker spectrometer (100 MHz) and are reported in *ppm* relative to deuterated chloroform (77.23 *ppm*) with tetramethyl silane as an internal standard. Coupling constants (*J*) are reported in Hz; splitting patterns are assigned *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *dd* = doublet of doublet, *td*= triplet of doublet, *br* = broad signal. High-resolution mass spectra (HRMS) were performed on TOF-Q analyser.

1.1 X-ray crystallography of compounds 5 and 23.

Single crystal X-ray structural data of the compounds **5** and **23** were collected on a CMOS based Bruker D8 Venture PHOTON 100 diffractometer equipped with a INCOATEC microfocus source with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) operating at 50 kV and 30mA. The SAINT[1] program was used for the integration of diffraction profiles and absorption correction was applied with the SADABS[2] program. Both the structures were initially solved by SIR 92[3] and refined by the full matrix least squares method using SHELXL-2013[4] WinGX system, Ver2013.3.[5] The non-hydrogen atoms in all the structures were located using the difference Fourier map and refined anisotropically. The hydrogen atoms were fixed by HFIX and placed in ideal positions and included in the refinement process using a riding model with isotropic thermal parameters. All the crystallographic and structure refinement data of the compounds are summarized in section 5.

2. General procedure for synthesis of N-substituted oxindoles.

N-substituted oxindoles were synthesized using reported procedure.[6]

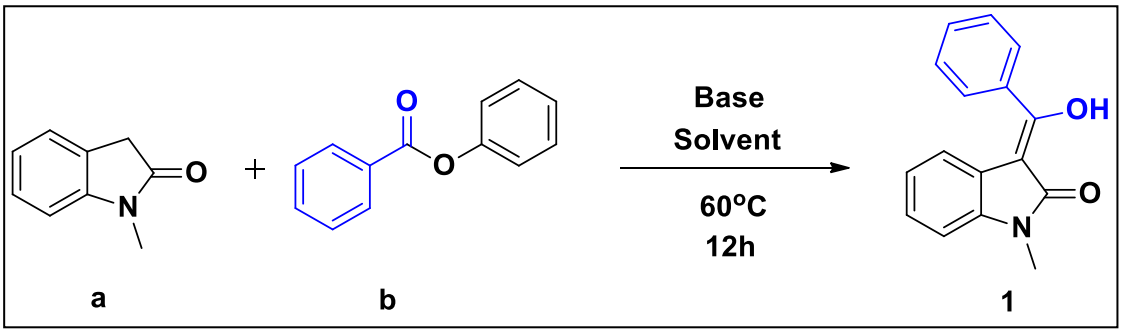
2.1. Synthesis of N-alkyl isatin derivatives:

Isatin derivatives (1.0 equiv), K_2CO_3 (2.0 equiv), DMF (3 mL) were added to a oven dried sealed tube and then alkyl halide (1.5 equiv) was then added dropwise over 10 min. The reaction mass was then heated to 80 °C for 12 h. After the completion of reaction, the mass was then quenched by adding into cold water and the solids were then extracted with ethyl acetate. The organic layer was washed with water, dried over sodium sulphate and the solvent was concentrated over reduced pressure. The crude product was used without further purification.

2.2. Synthesis of N-alkyloxindoles:

Crude isatin and hydrazine hydrate was charged to a reaction tube and then placed over a preheated oil bath maintaining 100 °C temperature. The reaction was continued until TLC shows completion. The mass was then cooled to room temperature, poured into cold water and diluted with ethyl acetate. The aqueous layer was repeatedly washed with ethyl acetate and the combined organic layers were washed with water, dried over sodium sulphate and solvent was concentrated under reduced pressure. The crude was then purified by column chromatography on silica gel using 85% hexane/ 15% ethyl acetate.

3. Optimization table for phenyl esters:



Entry	Base	Solvent	Yield of 1 (%)
1	Et_3N	THF	ND
2	K_2CO_3	THF	ND
3	Cs_2CO_3	THF	ND
4	KOH	THF	52
5	**KO*t*Bu**	**THF**	**81**
6	KO*t*Bu	DMF	62
7	KO*t*Bu	Toluene	41
8	KO*t*Bu	DCE	23
9	KO*t*Bu	1,4-Dioxane	67
10	KO*t*Bu	CH_3CN	54

[a] Unless and otherwise mentioned all the reactions are carried out using **a** (0.34 mmol), **b** (0.68 mmol), base (0.85 mmol) and solvent (2 mL) at 60^{o}C for 12 h. [b] Isolated yields.

4.1 General procedure for acylation of oxindoles using methyl/phenyl esters via mixed Claisen condensation

(a) An oven-dried vial equipped with a stir bar was charged with N-alkyloxindole (0.34 mmol) and the corresponding phenyl esters (0.68 mmol) and KO*t*Bu (0.85 mmol) and 1 mL of dry THF was added and placed under a positive pressure of nitrogen and subjected to two evacuation/backfilling cycles. Then the reaction mixture was placed in a preheated oil bath at 60 °C, and stirred for 12 h. (b) In the case of methyl esters, 10 ml schlenk tube equipped with a stir bar was charged with N-alkyloxindole (0.34 mmol) and the corresponding methyl esters (0.68 mmol) and 1M LiHMDS in THF (1 mmol) was added in presence of nitrogen under glove-box free condition in fume hood (No external solvent added, only the reagent containing LiHMDS in THF is utilized). The reaction mixture was placed under a positive pressure of nitrogen and subjected to two evacuation/backfilling cycles. Then the reaction mixture was placed in a preheated oil bath at 60 °C, and stirred for 12 h. After the indicated time, the reaction mixture was diluted with 1M HCl (25 mL), extracted with DCM (25 mL) and concentrated. The crude material was purified by column chromatography on silica gel using n-hexane – diethyl ether as eluent, to yield the title compound as pale yellow solid.

5. Crystallographic data for 5 and 23

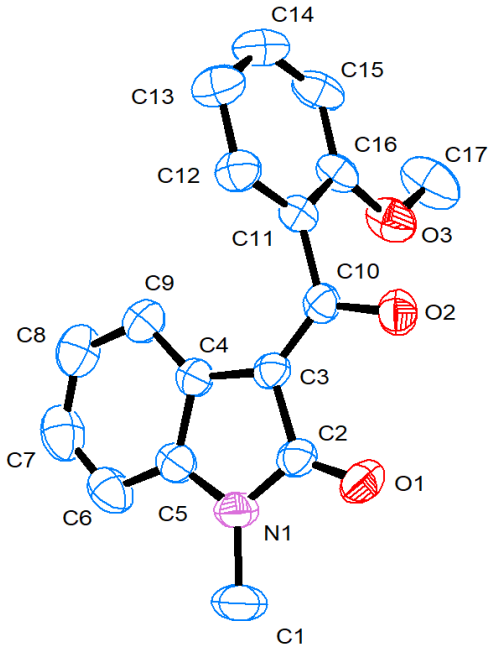


Fig S1. Perspective view of the X-ray structure of **5**. Hydrogen atoms are omitted for clarity.

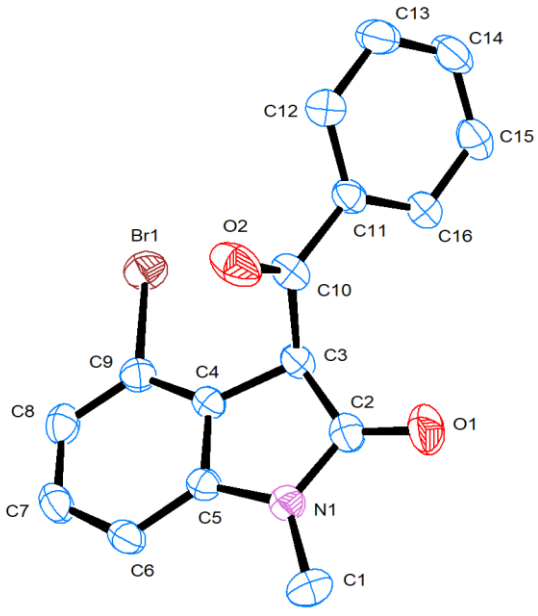


Fig S2. Perspective view of the X-ray structure of **23**. Hydrogen atoms are omitted for clarity.

Compound	**5**	**23**
CCDC No.	1960147	1960146
Empirical formula	$C_{17}H_{14}NO_3$	$C_{16}H_{11}BrNO_2$
Formula weight	280.29	329.17
Temperature/K	273	273
Crystal system	Monoclinic	Triclinic
Wavelength	0.71073 Å	0.71073 Å
Space group	P 21/C	P -1
a/Å	11.1312(4)	8.3268(14)
b/Å	8.2115(4)	9.2126(13)
c/Å	16.7219(7)	9.6765(16)
α /°	90	83.964(5)
β/°	109.1920(10)	73.197(5)
γ/°	90	73.333(5)
Volume	1443.50(11)	680.55(19)
Z	4	2
Calculated density g/cm^3	1.290	1.606
Absorption coefficient (μ/mm^{-1})	0.089	3.020
F(000)	588	330
Index ranges	-13<h<13 -10<k<10 -18<l<20	-10<h<10 -11<k<11 -12<l<12
Reflections collected	14276	12915
Independent reflections	2941	2770
Data/restraint/parameters	2941/0/190	2770/0/181
Goodness of fit on F^2	1.058	1.062
Final R indices[I>2σ(I)]	R_1=0.0607 wR_2=0.0607	R_1=0.0370 wR_2=0.1054
Final R indices [all data]	R_1=0.0686 wR_2=0.1766	R_1=0.0404 wR_2=0.1032

5.1. Bond distances of 5

Atom	Atom	Distance Å	Atom	Atom	Distance Å
O2	C10	1.341(3)	C12	H12	0.93
O3	C16	1.364(2)	C12	C13	1.384(3)
O3	C17	1.420(3)	C6	H6	0.93
O1	C2	1.239(3)	C6	C7	1.378(5)
N1	C5	1.404(3)	C8	H8	0.93
N1	C2	1.364(3)	C8	C7	1.378(4)
N1	C1	1.456(3)	C15	H15	0.93
C4	C5	1.402(2)	C15	C14	1.368(4)
C4	C3	1.455(3)	C7	H7	0.93
C4	C9	1.390(3)	C14	H14	0.93
C10	C11	1.485(3)	C14	C13	1.377(4)
C10	C3	1.352(2)	C13	H13	0.93
C5	C6	1.371(3)	C1	H1A	0.96
C11	C16	1.392(2)	C1	H1B	0.96
C11	C12	1.372(3)	C1	H1C	0.96
C3	C2	1.461(3)	C17	H17A	0.96
C16	C15	1.391(3)	C17	H17B	0.959
C9	H9	0.93	C17	H17C	0.96
C9	C8	1.388(3)	C12	H12	0.93
O2	C10	1.341(3)			

5.2. Bond angles of 5

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
C16	O3	C17	118.2(2)	C11	C16	C15	119.3(2)
C5	N1	C2	110.6(2)	O1	C2	N1	125.4(2)
C5	N1	C1	125.3(2)	O1	C2	C3	127.6(2)
C2	N1	C1	124.0(2)	N1	C2	C3	107.0(2)
C5	C4	C3	106.4(2)	C4	C9	H9	120.6
C5	C4	C9	118.9(2)	C4	C9	C8	118.8(2)
C3	C4	C9	134.7(2)	H9	C9	C8	120.5
O2	C10	C11	113.9(2)	C11	C12	H12	119.3
O2	C10	C3	122.0(2)	C11	C12	C13	121.3(2)
C11	C10	C3	124.0(2)	H12	C12	C13	119.4
N1	C5	C4	109.1(2)	C5	C6	H6	121
N1	C5	C6	128.7(2)	C5	C6	C7	118.0(2)
C4	C5	C6	122.2(2)	H6	C6	C7	121
C10	C11	C16	120.6(2)	C9	C8	H8	119.6
C10	C11	C12	119.9(2)	C9	C8	C7	120.8(2)
C16	C11	C12	119.5(2)	H8	C8	C7	119.6
C4	C3	C10	132.4(2)	C16	C15	H15	120
C4	C3	C2	106.9(2)	C16	C15	C14	120.0(2)
C10	C3	C2	120.6(2)	H15	C15	C14	120
O3	C16	C11	115.2(2)	C6	C7	C8	121.2(3)
O3	C16	C15	125.5(2)	C6	C7	H7	119.4

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
C8	C7	H7	119.3	H1A	C1	H1B	109.4
C15	C14	H14	119.4	H1A	C1	H1C	109.4
C15	C14	C13	121.2(2)	H1B	C1	H1C	109.5
H14	C14	C13	119.4	O3	C17	H17A	109.5
C12	C13	C14	118.6(2)	O3	C17	H17B	109.5
C12	C13	H13	120.7	O3	C17	H17C	109.5
C14	C13	H13	120.7	H17A	C17	H17B	109.4
N1	C1	H1A	109.5	H17A	C17	H17C	109.4
N1	C1	H1B	109.5	H17B	C17	H17C	109.6
N1	C1	H1C	109.5				

5.3. Bond distances of 23

Atom	Atom	Distance Å	Atom	Atom	Distance Å
Br1	C9	1.893(3)	C8	H8	0.931
C1	H1A	0.96	C8	C9	1.391(4)
C1	H1B	0.96	C8	C7	1.374(4)
C1	H1C	0.96	C11	C10	1.489(4)
C1	N1	1.446(4)	C11	C12	1.395(4)
C2	N1	1.371(3)	C11	C16	1.380(3)
C2	O1	1.212(4)	C4	C5	1.391(4)
C2	C3	1.533(5)	C4	C9	1.376(4)
N1	C5	1.402(4)	C4	C3	1.496(4)
O2	C10	1.200(3)	C5	C6	1.385(4)

Atom	Atom	Distance Å	Atom	Atom	Distance Å
C3	C10	1.543(3)	C14	H14	0.93
C12	H12	0.93	C14	C13	1.371(4)
C12	C13	1.377(4)	C14	C15	1.369(4)
C6	H6	0.93	C13	H13	0.93
C6	C7	1.390(4)	C7	H7	0.93
C16	H16	0.931	C15	H15	0.93
C16	C15	1.388(4)			

5.4. Bond angles of 23

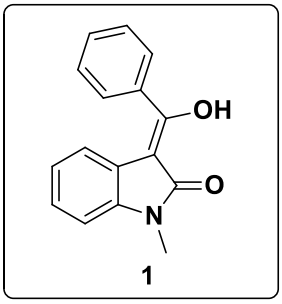
Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
H1A	C1	H1B	109.4	H8	C8	C7	120.3
H1A	C1	H1C	109.5	C9	C8	C7	119.4(3)
H1A	C1	N1	109.5	C10	C11	C12	117.7(2)
H1B	C1	H1C	109.5	C10	C11	C16	122.8(3)
H1B	C1	N1	109.4	C12	C11	C16	119.5(3)
H1C	C1	N1	109.5	C5	C4	C9	118.7(2)
N1	C2	O1	125.3(3)	C5	C4	C3	109.1(2)
N1	C2	C3	107.9(2)	C9	C4	C3	132.1(3)
O1	C2	C3	126.7(3)	N1	C5	C4	109.5(2)
C1	N1	C2	123.9(2)	N1	C5	C6	128.2(2)
C1	N1	C5	125.0(2)	C4	C5	C6	122.3(2)
C2	N1	C5	111.1(2)	Br1	C9	C8	120.8(2)
H8	C8	C9	120.3	Br1	C9	C4	118.7(2)

Atom	Atom	Atom	Angle [˚]	Atom	Atom	Atom	Angle [˚]
C8	C9	C4	120.5(3)	C11	C16	C15	119.6(3)
C2	C3	C4	102.3(2)	H16	C16	C15	120.2
C2	C3	C10	109.2(2)	H14	C14	C13	119.6
C4	C3	C10	111.0(2)	H14	C14	C15	119.6
O2	C10	C11	121.6(3)	C13	C14	C15	120.8(3)
O2	C10	C3	119.3(3)	C12	C13	C14	119.7(3)
C11	C10	C3	119.1(2)	C12	C13	H13	120.1
C11	C12	H12	119.9	C14	C13	H13	120.2
C11	C12	C13	120.2(3)	C8	C7	C6	122.0(3)
H12	C12	C13	119.9	C8	C7	H7	119
C5	C6	H6	121.5	C6	C7	H7	119
C5	C6	C7	117.1(2)	C16	C15	C14	120.2(3)
H6	C6	C7	121.4	C16	C15	H15	119.9
C11	C16	H16	120.2	C14	C15	H15	119.9

6. Charaterization Data:

(Z)-3-(hydroxyl(phenyl)methylene)-1-methylindolin-2-one (1)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 95/5)



1

Yield: A: 67 mg, 79% **B:** 69 mg, 81%, pale yellow colored solid

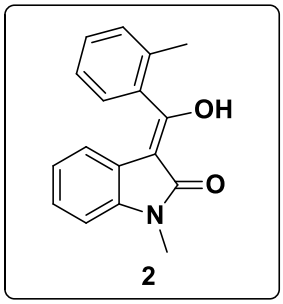
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 6.4 Hz, 2H), 7.52-7.44 (m, 3H), 7.14-7.10 (m, 2H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 3.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 171.0, 139.1, 134.1, 131.3, 128.6, 128.4, 125.9, 121.9, 121.6, 119.7, 108.4, 101.5, 25.9.

Spectral data match those previously reported.[7]

(Z)-3-(hydroxyl(*o*-tolyl)methylene)-1-methylindolin-2-one (2)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 96/4)



2

Yield: A: 10 mg, 11% **B:** 40 mg, 44%, pale yellow colored solid

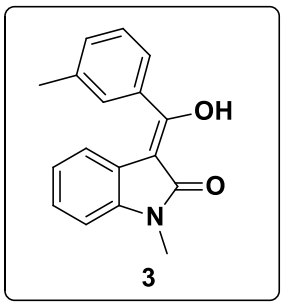
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38-7.34 (m, 2H), 7.29-7.23 (m, 2H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.37 (d, *J* = 7.6 Hz, 1H), 3.32 (s, 3H), 2.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.5, 170.9, 139.2, 136.2, 133.4, 130.9, 130.5, 128.3, 126.1, 125.9, 122.1, 121.7, 119.5, 108.2, 102.9, 25.8, 19.2.

HR-MS: $[M+H]^+$ calculated for $C_{17}H_{16}NO_2$, 266.1176; found, 266.1156

(Z)-3-(hydroxyl(*m*-tolyl)methylene)-1-methylindolin-2-one (3)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 96/4)



3

Yield: A: 60 mg, 67% **B:** 66 mg, 73%, pale yellow colored solid

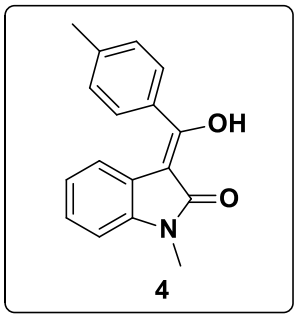
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52-7.50 (m, 2H), 7.37-7.29 (m, 2H), 7.14-7.10 (m, 2H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 3.33 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 171.3, 139.1, 138.5, 134.1, 132.1, 128.8, 128.5, 125.8, 125.5, 121.9, 121.7, 119.7, 108.3, 101.4, 25.9, 21.4.

Spectral data match those previously reported.[7]

(Z)-3-(hydroxy(p-tolyl)methylene)-1-methylindolin-2-one (4)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 96/4)



4

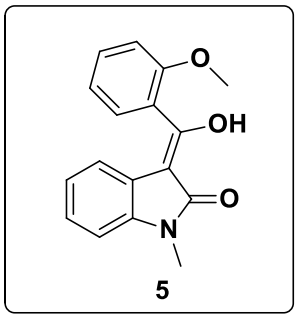
Yield: A: 71 mg, 79% **B:** 72 mg, 80%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (d, *J* = 8 Hz, 2H), 7.27 (d, *J* = 8 Hz, 2H), 7.18-7.16 (m, 1H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.8 Hz, 1H), 3.33 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 171.4, 141.9, 139.0, 131.3, 129.3, 128.4, 125.7, 121.8, 121.8, 119.7, 108.3, 101.1, 25.9, 21.7. Spectral data match those previously reported.[7]

(Z)-3-(hydroxy(2-methoxyphenyl)methylene)-1-methylindolin-2-one (5)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



5

Yield: A: 61 mg, 64% **B:** 60 mg, 63%, white colored solid

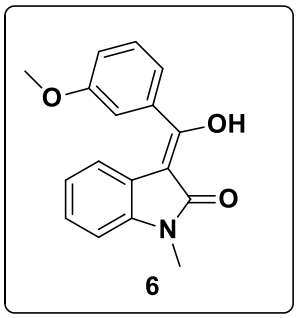
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55 (t, *J* = 8 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.14-7.08 (m, 2H), 6.95 (d, *J* = 8 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 3.82 (s, 3H), 3.41 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.6, 168.4, 156.9, 139.2, 132.2, 130.0, 125.6, 123.1, 121.9, 120.8, 119.7, 111.6, 108.1, 103.4, 55.8, 25.8.

HR-MS: $[M+H]^+$ calculated for $C_{17}H_{16}NO_3$, 282.1125; found, 282.1123

(Z)-3-(hydroxy(3-methoxyphenyl)methylene)-1-methylindolin-2-one (6)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



6

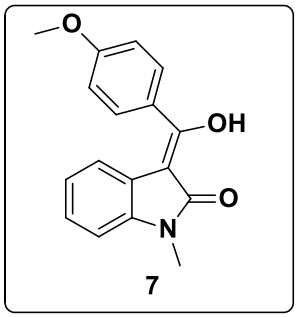
Yield: A: 61 mg, 64% **B:** 65 mg, 68%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.22 (s, 1H), 7.16-7.10 (m, 2H), 7.04-7.01 (m, 1H), 6.88-6.82 (m, 2H), 3.78 (s, 3H), 3.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 170.8, 159.7, 139.2, 135.4, 129.8, 125.9, 121.9, 121.6, 120.8, 119.9, 117.6, 113.2, 108.4, 101.5, 55.5, 25.9.

HR-MS: $[M+H]^+$ calculated for $C_{17}H_{16}NO_3$, 282.1125; found, 282.1122

(Z)-3-(hydroxy(4-methoxyphenyl)methylene)-1-methylindolin-2-one (7)
Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



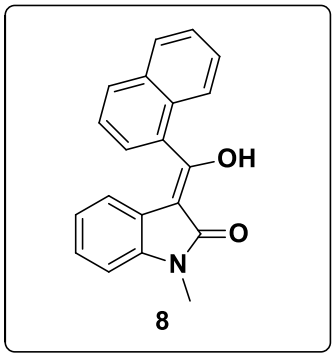
Yield: A: 66 mg, 69% **B:** 68 mg, 71%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 6.89-6.83 (m, 2H), 3.84 (s, 3H), 3.33 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 171.1, 162.1, 138.9, 130.3, 126.4, 125.6, 121.9, 121.8 119.6, 114.0, 108.3, 100.7, 55.5, 25.9.

Spectral data match those previously reported.[7]

(Z)-3-(hydroxy(naphthalen-1-yl)methylene)-1-methylindolin-2-one (8)
Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)

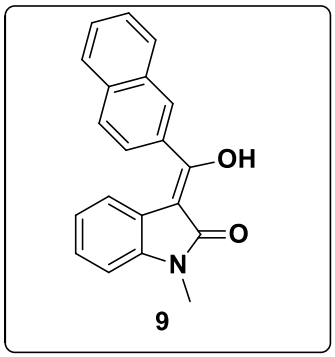


Yield: A: 62 mg, 61% **B:** 63 mg, 62%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.97 (t, *J* = 8.2 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.67 (d, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 6.85 (d, *J* = 8 Hz, 1H), 6.60 (t, *J* = 7.8 Hz, 1H), 6.17 (d, *J* = 7.6 Hz, 1H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.7, 170.0, 139.3, 133.7, 131.3, 131.07, 130.0, 128.5, 127.3, 127.0, 126.6, 125.9, 125.2, 125.2, 122.0, 121.4, 120.1, 108.3, 103.9, 25.9.
HR-MS: $[M+H]^+$ calculated for $C_{20}H_{16}NO_2$, 302.1176; found, 302.1179

(Z)-3-(hydroxy(naphthalen-2-yl)methylene)-1-methylindolin-2-one (9)
Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)

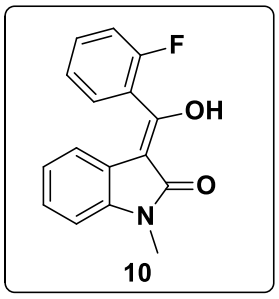


Yield: A: 64 mg, 63% **B:** 68 mg, 67%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.26 (s, 1H), 7.94 (d, *J* = 8.4 Hz, 1H), 7.88 (d, *J* = 8 Hz, 2H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.57-7.49 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 7.6 Hz, 1H), 3.36 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 171.0, 139.2, 134.7, 132.7, 131.4, 129.0, 128.8, 128.5, 128.0, 127.8, 126.9, 129.0, 124.9, 121.9, 121.7, 119.8, 108.4, 101.7, 25.9.
HR-MS: $[M+H]^+$ calculated for $C_{20}H_{16}NO_2$, 302.1176; found, 302.1174

(Z)-3-((2-fluorophenyl)(hydroxy)methylene)-1-methylindolin-2-one (10)
Purified by column chromatography on silica gel using (hexane/diethyl ether = 91/9)

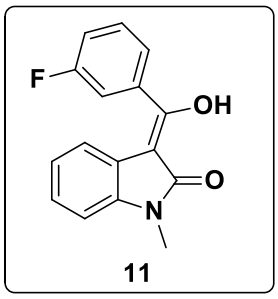


Yield: A: 50 mg, 55% **B:** 48 mg, 53%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (t, *J* = 7.2 Hz, 1H), 7.47-7.43 (m, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 9 Hz, 1H), 7.09 (t, *J* = 7.8 Hz, 1H), 6.84-6.78 (m, 2H), 6.67 (d, *J* = 7.6 Hz, 1H), 3.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.5, 164.7, 159.5 (d, *J* = 252 Hz), 139.4, 132.8 (d, *J* = 8 Hz), 130.3 (d, *J* = 2 Hz), 126.2, 124.6 (d, *J* = 4Hz), 122.3, 122.1, 121.1, 119.7 (d, *J* = 2 Hz), 116.6 (d, *J* = 21 Hz) 108.4, 103.9, 25.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ: -112.
HR-MS: $[M+H]^+$ calculated for $C_{16}H_{13}FNO_2$, 270.0925; found, 270.0858

(Z)-3-((3-fluorophenyl)(hydroxy)methylene)-1-methylindolin-2-one (11)
Purified by column chromatography on silica gel using (hexane/diethyl ether = 91/9)

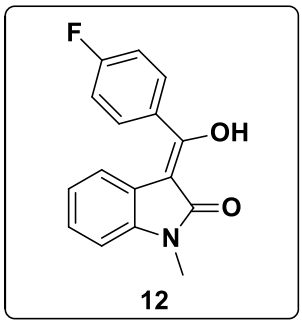


Yield: A: 69 mg, 76% **B:** 72 mg, 79%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.52 (d, *J* = 8 Hz, 1H), 7.46-7.39 (m, 2H), 7.21-7.09 (m, 3H), 6.89-6.83 (m, 2H), 3.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 169.0, 162.7 (d, *J* = 246 Hz), 139.3, 136.2 (d, *J* = 7 Hz), 130.4 (d, *J* = 8 Hz), 126.3, 124.3 (d, *J* = 4 Hz), 122.1, 121.2, 119.7, 118.3 (d, *J* = 21 Hz), 115.5 (d, *J* = 23 Hz), 108.5, 101.9, 25.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ: -111.6
HR-MS: $[M+H]^+$ calculated for $C_{16}H_{13}FNO_2$, 270.0925; found, 270.0923

(Z)-3-((4-fluorophenyl)(hydroxy)methylene)-1-methylindolin-2-one (12)
Purified by column chromatography on silica gel using (hexane/diethyl ether = 91/9)



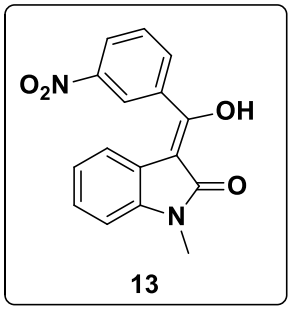
Yield: A: 73 mg, 80% **B:** 77 mg, 85%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74-7.71 (m, 2H), 7.18-7.08 (m, 4H), 6.89-6.82 (m, 2H), 3.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 169.8, 164.5 (d, *J* = 251 Hz), 139.2, 130.8 (d, *J* = 9 Hz), 130.3 (d, *J* = 3 Hz), 126.0, 121.9, 121.4, 119.5, 115.9 (d, *J* = 22 Hz), 108.5, 101.5, 25.9.
^{19}F NMR (376 MHz, $CDCl_3$) δ: -107.6
Spectral data match those previously reported.[7]

(Z)-3-(hydroxy(3-nitrophenyl)methylene)-1-methylindolin-2-one (13)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 80/20)



13

Yield: A: ND **B:** 43 mg, 43%, pale yellow colored solid

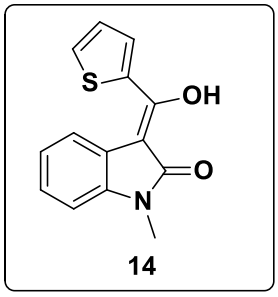
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.61 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 7.6 Hz, 1H), 7.68 (t, *J* = 7.8 Hz, 1H), 7.19-7.15 (m, 1H), 7.02 (d, *J* = 8 Hz, 1H), 6.92 (d, *J* = 8 Hz, 1H), 6.86 (t, *J* = 7.6 Hz, 1H), 3.35 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.8, 167.2, 148.4, 139.5, 135.8, 134.4, 130.0, 126.8, 125.8, 123.7, 122.3, 120.6, 119.4, 108.9, 102.6, 26.0.

HR-MS: $[M+H]^+$ calculated for $C_{16}H_{13}N_2O_4$, 297.0870; found, 297.0869

(Z)-3-(hydroxy(thiophen-2-yl)methylene)-1-methylindolin-2-one (14)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 88/12)



14

Yield: A: 40 mg, 46% **B:** 42 mg, 48%, pale yellow colored solid

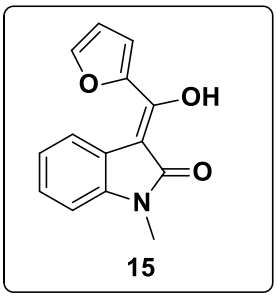
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.80 (d, *J* = 3.6 Hz, 1H), 7.62 (d, *J* = 8 Hz, 1H), 7.58 (d, *J* = 5.2 Hz, 1H), 7.18-7.13 (m, 2H), 6.92 (t, *J* = 7.8 Hz, 1H), 6.90 (d, *J* = 8 Hz, 1H), 3.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 164.1, 139.0, 136.5, 130.8, 130.8, 127.5, 126.0, 122.0, 121.4, 119.7, 108.5, 101.0, 26.0.

Spectral data match those previously reported.[7]

(Z)-3-(furan-2-yl(hydroxy)methylene)-1-methylindolin-2-one (15)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



15

Yield: A: 50 mg, 61% **B:** 53 mg, 65%, pale yellow colored solid

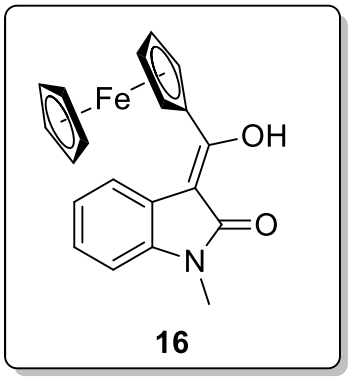
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.22 (d, *J* = 8 Hz, 1H), 7.73 (s, 1H), 7.25 (d, *J* = 3.2 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8 Hz, 1H), 6.61-6.60 (m, 1H), 3.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.8, 158.3, 148.9, 145.6, 139.0, 125.9, 122.3, 122.2, 121.3, 116.9, 112.6, 108.2, 99.5, 26.0.

Spectral data match those previously reported.[8]

(Z)-3-(ferrocene-2-yl(hydroxy)methylene)-1-methylindolin-2-one (16)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 85/15)



16

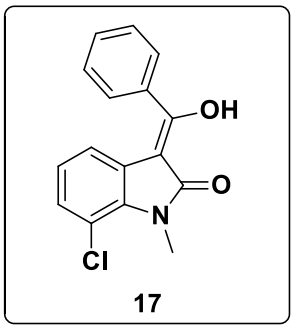
Yield: A: 23 mg, 19%, reddish-brown colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.55-7.52 (m, 2H), 7.06 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 8 Hz, 1H), 4.79 (s, 2H), 4.40 (s, 2H), 4.19 (s, 5H), 3.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 183.4, 177.7, 158.3, 151.5, 138.4, 125.3, 123.9, 117.5, 109.9, 72.0, 70.6, 70.1, 69.7, 26.3.
HR-MS: $[M+Na]^+$ calculated for $C_{20}H_{17}FeNO_2Na$, 382.0501; found, 382.1554

(Z)-7-chloro-3-(hydroxy(phenyl)methylene)-1-methylindolin-2-one (17)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



17

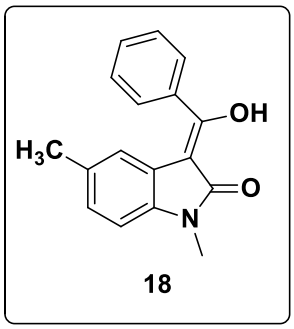
Yield: A: 36 mg, 46% **B:** 40 mg, 51%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.67 (d, *J* = 8 Hz, 2H), 7.53-7.44 (m, 3H), 7.03 (d, *J* = 8 Hz, 1H), 6.96 (d, *J* = 8 Hz, 1H), 6.69 (t, *J* = 8 Hz, 1H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.5, 172.2, 134.6, 133.8, 131.6, 128.8, 128.4, 127.8, 124.5, 122.4, 118.0, 116.2, 100.8, 29.3.
HR-MS: $[M+Na]^+$ calculated for $C_{16}H_{12}ClNO_2Na$, 308.0449; found, 308.0423

(Z)-3-(hydroxy(phenyl)methylene)-1,5-dimethylindolin-2-one (18)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)



18

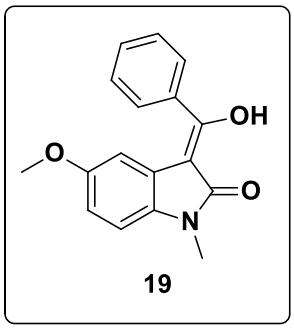
Yield: A: 66 mg, 80% **B:** 68 mg, 83%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 6.4 Hz, 2H), 7.52-7.44 (m, 3H), 6.93-6.91 (m, 2H), 6.76 (d, *J* = 8.4 Hz, 1H), 3.29 (s, 3H), 2.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 170.7, 137.1, 134.2, 131.4, 131.3, 128.6, 128.4, 126.5, 121.6, 120.4, 108.1, 101.5, 25.9, 21.4.
HR-MS: $[2M+K]^+$ calculated for $C_{34}H_{30}N_2O_4K$, 569.1837; found, 569.1022

(Z)-3-(hydroxy(phenyl)methylene)-5-methoxy-1-methylindolin-2-one (19)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)



19

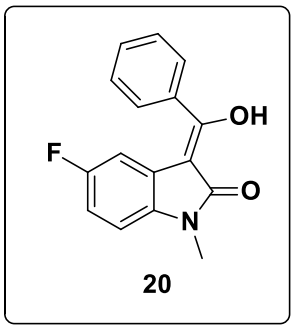
Yield: A: 60 mg, 76% **B:** 63 mg, 79%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8 Hz, 2H), 7.51-7.44 (m, 3H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.70-6.65 (m, 2H), 3.57 (s, 3H), 3.29 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 171.2, 155.4, 134.1, 133.4, 131.4, 128.7, 128.4, 122.6, 111.0, 108.6, 106.6, 101.8, 55.7, 25.9.
Spectral data match those previously reported.[9]

(Z)-5-fluoro-3-(hydroxy(phenyl)methylene)-1-methylindolin-2-one (20)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



20

Yield: A: 41 mg, 51% **B:** 49 mg, 60%, pale yellow colored solid

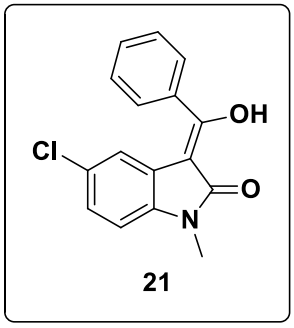
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 7.6 Hz, 2H), 7.54-7.46 (m, 3H), 6.84-6.75 (m, 3H), 3.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 172.0, 158.8 (d, *J* = 236 Hz), 135.1, 133.7, 131.7, 128.5 (d, *J* = 59 Hz), 122.8 (d, *J* = 10 Hz), 112.1 (d, *J* = 25 Hz), 108.6 (d, *J* = 9 Hz), 107.2 (d, *J* = 26 Hz), 26.0.
^{19}F NMR (376 MHz, $CDCl_3$) δ: -121.1

HR-MS: $[M+H]^+$ calculated for $C_{16}H_{13}FNO_2$, 270.0925; found, 270.0922

(Z)-5-chloro-3-(hydroxy(phenyl)methylene)-1-methylindolin-2-one (21)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



21

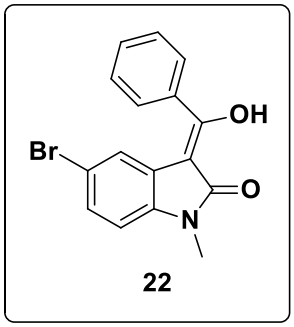
Yield: A: 44 mg, 56% **B:** 46 mg, 58%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8 Hz, 2H), 7.56-7.47 (m, 3H), 7.10-7.07 (m, 2H), 6.80 (d, *J* = 8 Hz, 2H), 3.32 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.4, 171.8, 137.5, 133.7, 131.8, 128.7, 128.3, 127.4, 125.6, 123.0, 119.7, 109.2, 100.9, 26.0.
Spectral data match those previously reported.[9]

(Z)-5-bromo-3-(hydroxy(phenyl)methylene)-1-methylindolin-2-one (22)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



22

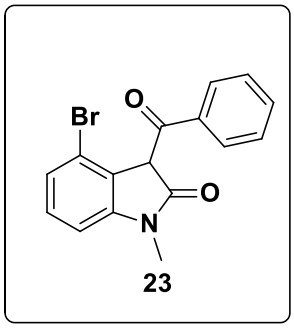
Yield: A: 39 mg, 53% **B:** 48 mg, 66%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 6.4 Hz, 2H), 7.56-7.47 (m, 3H), 7.24-7.22 (m, 2H), 6.75 (d, *J* = 8.4 Hz, 2H), 3.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.4, 171.7, 137.9, 133.7, 131.9, 128.8, 128.4, 128.3, 123.5, 122.5, 114.8, 109.7, 100.7, 26.0.
HR-MS: $[M+H]^+$ calculated for $C_{16}H_{13}BrNO_2$, 330.0124; found, 330.0104

3-benzoyl-4-bromo-1-methylindolin-2-one (23)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 85/15)



23

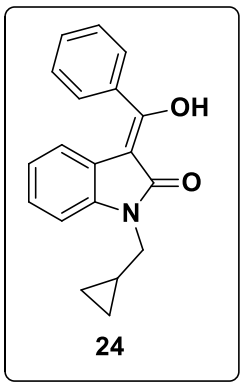
Yield: A: ND **B:** 43 mg, 59%, white colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (d, *J* = 8 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 2H), 7.19-7.13 (m, 2H), 6.76 (d, *J* = 6.8 Hz, 1H), 5.41 (s, 1H), 3.14 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.1, 168.8, 145.3, 135.5, 132.8, 129.5, 128.7, 127.7, 125.6, 125.0, 118.6, 106.2, 55.5, 25.9.
HR-MS: $[M+H]^+$ calculated for $C_{16}H_{13}BrNO_2$, 330.0124; found, 330.0124

(Z)-1-(cyclopropylmethyl)-3-(hydroxy(phenyl)methylene)indolin-2-one (24)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)



24

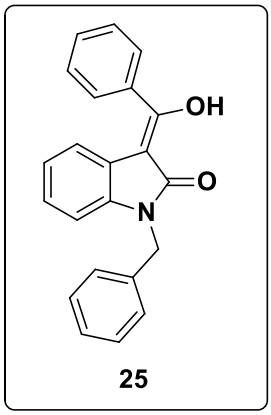
Yield: A: 45 mg, 58% **B:** 49 mg, 63%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 7.6 Hz, 2H), 7.51-7.44 (m, 3H), 7.10 (t, *J* = 6.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 3.72 (d, *J* = 6.8 Hz, 1H), 1.13-1.16 (m, 1H), 0.50 (q, *J* = 6.2 Hz, 2H), 0.39 (q, *J* = 5.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 171.1, 138.7, 134.3, 131.3, 128.7, 128.4, 125.8, 121.7, 121.7, 119.8, 108.8, 101.5, 44.1, 10.0, 4.0.
HR-MS: $[M+Na]^+$ calculated for $C_{19}H_{17}NO_2Na$, 314.1151; found, 314.1155

(Z)-1-benzyl-3-(hydroxy(phenyl)methylene)indolin-2-one (25)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 88/12)



25

Yield: A: 46 mg, 63% **B:** 51 mg, 70%, pale yellow colored solid

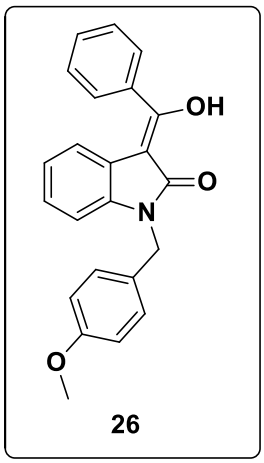
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.74 (d, *J* = 7.2 Hz, 2H), 7.52-7.45 (m, 3H), 7.26-7.19 (m, 5H), 7.11 (d, *J* = 8 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 2H), 5.03 (s, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.1, 171.3, 138.3, 136.0, 134.1, 131.4, 128.8, 128.7, 128.4, 127.7, 127.3, 125.9, 121.9, 121.7, 119.8, 109.3, 101.4, 43.5.

HR-MS: $[M+H]^+$ calculated for $C_{22}H_{18}NO_2$, 328.1332; found, 328.1321

(Z)-3-(hydroxy(phenyl)methylene)-1-(4-methoxybenzyl)indolin-2-one (26)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)



26

Yield: A: 43 mg, 62% **B:** 52 mg, 74%, pale yellow colored solid

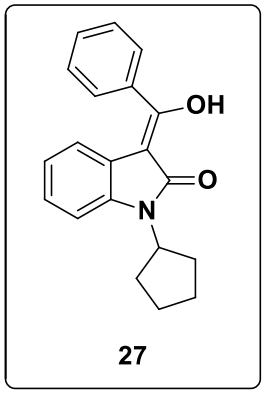
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (d, *J* = 6.4 Hz, 2H), 7.52-7.44 (m, 3H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.82-6.76 (m, 4H), 4.96 (s, 2H), 3.70 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 171.2, 159.1, 138.3, 134.2, 131.4, 128.7, 128.7, 128.4, 128.1, 125.8, 121.8, 121.7, 119.8, 114.2, 109.3, 101.4, 55.3, 43.0.

HR-MS: $[M+Na]^+$ calculated for $C_{23}H_{19}NO_3Na$, 380.1257; found, 380.1268

(Z)-1-cyclopentyl-3-(hydroxy(phenyl)methylene)indolin-2-one (27)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)



27

Yield: A: 44 mg, 58% **B:** 46 mg, 61%, pale yellow colored solid

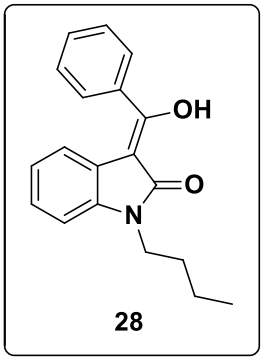
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (dd, *J* = 3 Hz, 2H), 7.51-7.43 (m, 3H), 7.10-7.05 (m, 2H), 6.97 (d, *J* = 8 Hz, 1H), 6.79 (td, *J* = 3.2 Hz, 1H), 4.90-4.81 (m, 1H), 2.18-2.08 (m, 2H), 1.95-1.90 (m, 4H), 1.70-1.66 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.0, 171.3, 137.5, 134.4, 131.2, 128.7, 128.4, 125.4, 122.1, 121.4, 119.9, 110.0, 101.5, 52.3, 28.3, 25.2.

HR-MS: $[M+Na]^+$ calculated for $C_{20}H_{19}NO_2Na$, 328.1308; found, 328.1322

(Z)-1-butyl-3-(hydroxy(phenyl)methylene)indolin-2-one (28)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 92/8)



28

Yield: A: 55 mg, 71% **B:** 61 mg, 79%, yellow colored oil

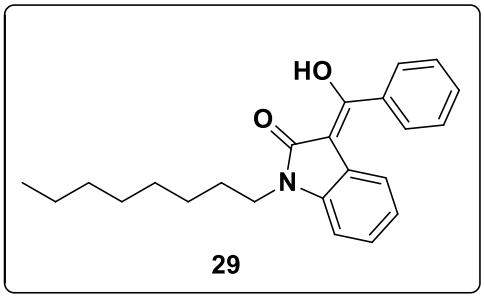
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (dd, *J* = 3.2 Hz, 2H), 7.50-7.42 (m, 3H), 7.10-7.06 (m, 2H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 3.81 (t, *J* = 7.4 Hz, 2H), 1.70-1.62 (m, 2H), 1.40-1.30 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 171.1, 138.5, 134.3, 131.3, 128.7, 128.4, 125.8, 121.8, 121.7, 119.8, 108.7, 101.4, 39.6, 30.0, 20.3, 13.8.

HR-MS: $[M+H]^+$ calculated for $C_{19}H_{20}NO_2$, 294.1489; found, 294.1485

(Z)-3-(hydroxy(phenyl)methylene)-1-octylindolin-2-one (29)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 85/15)



29

Yield: A: 43 mg, 61% **B:** 49 mg, 69%, yellow colored solid

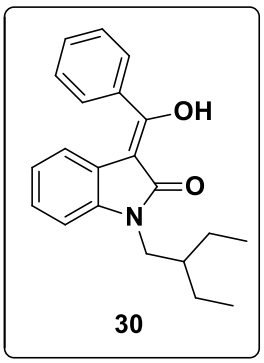
^{1}H NMR (400 MHz, $CDCl_3$) δ: 14.04 (br s, 1H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.82 (d, *J* = 7.2 Hz, 1H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8 Hz, 1H), 3.70 (t, *J* = 7.4 Hz, 2H), 1.69-1.62 (m, 2H), 1.33-1.19 (m, 10H), 0.80 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.8, 142.9, 132.8, 132.2, 131.5, 130.2, 129.0, 128.5, 127.9, 123.5, 122.2, 119.8, 109.3, 40.0, 31.7, 29.2, 29.1, 27.6, 27.0, 22.6, 14.1.

HR-MS: $[2M+2K+H]^{3+}$ calculated for $C_{46}H_{55}N_2O_4K_2$, 777.3420; found, 777.4086

(Z)-1-(2-ethylbutyl)-3-(hydroxy(phenyl)methylene)indolin-2-one (30)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)



30

Yield: A: 42 mg, 57% **B:** 47 mg, 64%, yellow colored oil

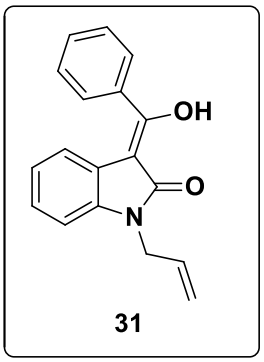
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (dd, *J* = 3 Hz, 2H), 7.50-7.44 (m, 3H), 7.11-7.07 (m, 2H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 1H), 3.72 (d, *J* = 7.6 Hz, 2H), 1.83-1.76 (m, 1H), 1.38-1.31 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 172.3, 171.2, 138.8, 134.3, 131.3, 128.6, 128.4, 125.7, 121.8, 121.6, 119.7, 108.9, 101.3, 43.7, 39.3, 23.5, 10.7.

HR-MS: $[M+Na]^+$ calculated for $C_{21}H_{23}NO_2Na$, 344.1621; found, 344.1617

(Z)-1-allyl-3-(hydroxy(phenyl)methylene)indolin-2-one (31)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 88/12)



31

Yield: A: 44 mg, 55% **B:** 51 mg, 64%, pale yellow colored solid

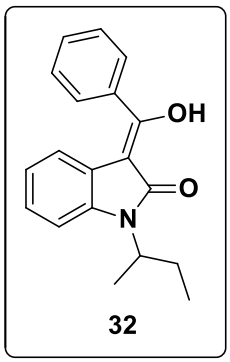
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.71 (d, *J* = 8 Hz, 2H), 7.50-7.42 (m, 3H), 7.11-7.04 (m, 2H), 6.86 (d, *J* = 8 Hz, 1H), 6.79 (t, *J* = 7.6 Hz, 1H), 5.87-5.78 (m, 1H), 5.17 (d, *J* = 1.2 Hz, 1H), 5.14 (d, *J* = 4.8 Hz, 1H), 4.44 (d, *J* = 5.2 Hz, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.7, 171.2, 138.3, 134.2, 131.6, 131.4, 128.7, 128.4, 125.9, 121.9, 121.7, 119.8, 117.6, 109.2, 101.4, 42.1.

HR-MS: $[M+H]^+$ calculated for $C_{18}H_{16}NO_2$, 278.1176; found, 278.1158

(Z)-1-(sec-butyl)-3-(hydroxy(phenyl)methylene)indolin-2-one (32)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 90/10)



32

Yield: A: 42 mg, 54% **B:** 48 mg, 62%, yellow colored oil

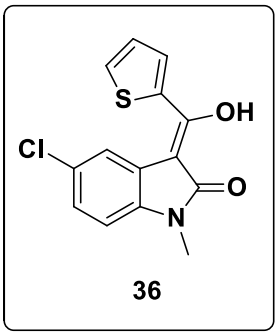
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8 Hz, 2H), 7.50-7.42 (m, 3H), 7.09-6.99 (m, 3H), 6.77 (t, *J* = 7.4 Hz, 1H), 4.48-4.39 (m, 1H), 2.11-1.99 (m, 1H), 1.84-1.74 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.0, 170.4, 136.8, 133.4, 130.2, 127.6, 127.3, 124.4, 121.0, 120.3, 118.8, 109.1, 100.3, 49.0, 25.8, 17.1, 10.4.

HR-MS: $[M+H]^+$ calculated for $C_{19}H_{20}NO_2$, 294.1489; found, 294.1487

(Z)-5-chloro-3-(hydroxy(thiophen-2-yl)methylene)-1-methylindolin-2-one (36)

Purified by column chromatography on silica gel using (hexane/diethyl ether = 88/12)



36

Yield: A: 32 mg, 40% **B:** 41 mg, 51%, pale yellow colored solid

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.79 (d, *J* = 3.6 Hz, 1H), 7.63 (d, *J* = 4.8 Hz, 1H), 7.58 (s, 1H), 7.20-7.18 (m, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 1H), 3.31 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 171.9, 165.5, 137.3, 136.0, 131.4, 131.0, 127.8, 127.5, 125.6, 122.9, 119.7, 109.3, 100.2, 26.1.

HR-MS: $[M+H]^+$ calculated for $C_{14}H_{11}ClNO_2S$, 292.0194; found, 292.0188

7. References

[1] SMART (V 5.628), SAINT (V 6.45a), XPREP, SHELXTL; Bruker AXS Inc., Madison, Wisconsin, USA, **2004**.

[2] G. M. Sheldrick, Siemens Area Detector Absorption Correction Program. University of Göttingen, Göttingen, Germany **2004**.

[3] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993,** *26*, 343.

[4] G. M. Sheldrick, SHELXL-2014, Program for Crystal Structure Solution and Refinement; University of Göttingen, Göttingen, Germany, **2014.**

[5] L. J. Farrugia, WinGX-A Windows Program for Crystal Structure Analysis, *J. Appl. Crystallogr.* **2012,** *45*, 849.

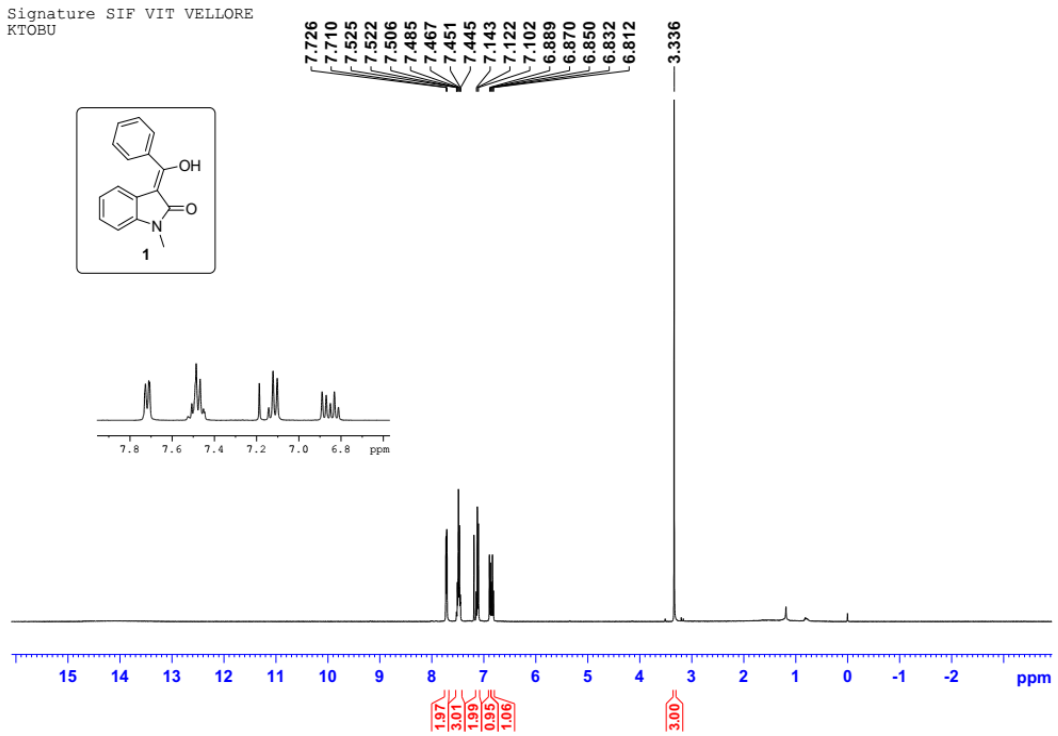
[6] P. K. Reddy Panyam, B. Ugale, T. Gandhi, *J. Org. Chem.* **2018,** *83*, 7622-7632.

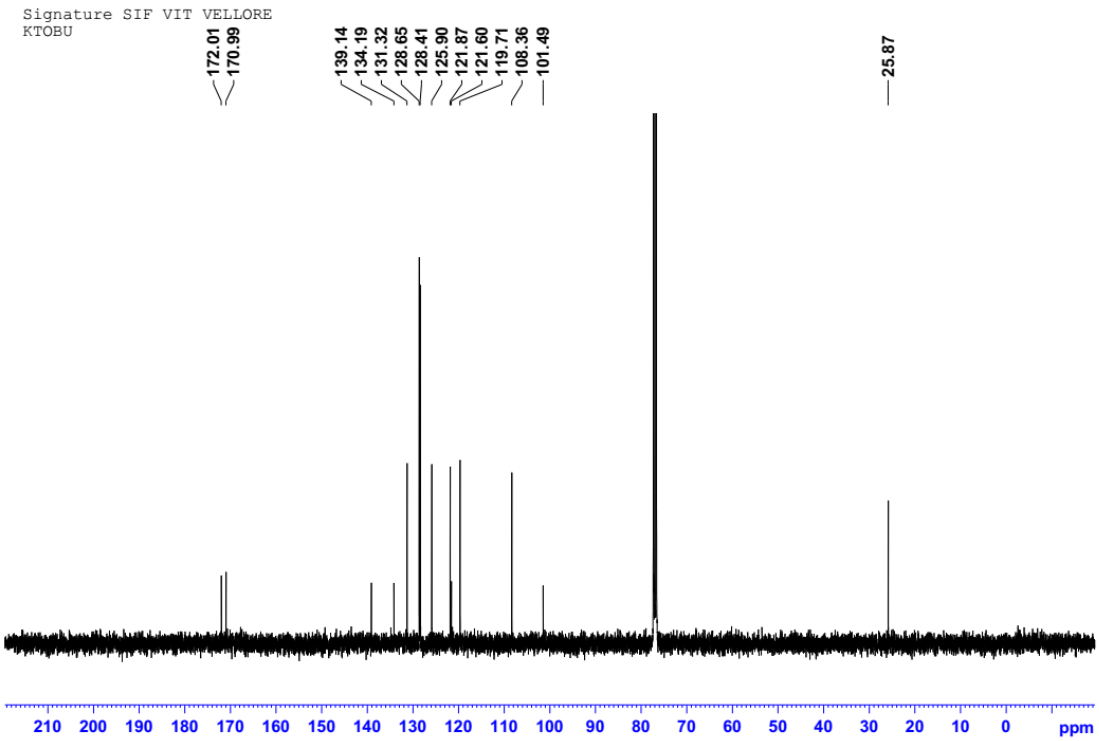
[7] Z. Lian, S. D. Friis, T. Skrydstrup, *Angew. Chem. Int. Ed.* **2014**, *53*, 9582-9586.

[8] X. D. Xia, L. Q. Lu, W. Q. Liu, D. Z. Chen, Y. H. Zheng, L. Z. Wu, W. J. Xiao, *Chem. Eur. J.* **2016,** *22*, 8432-8437.

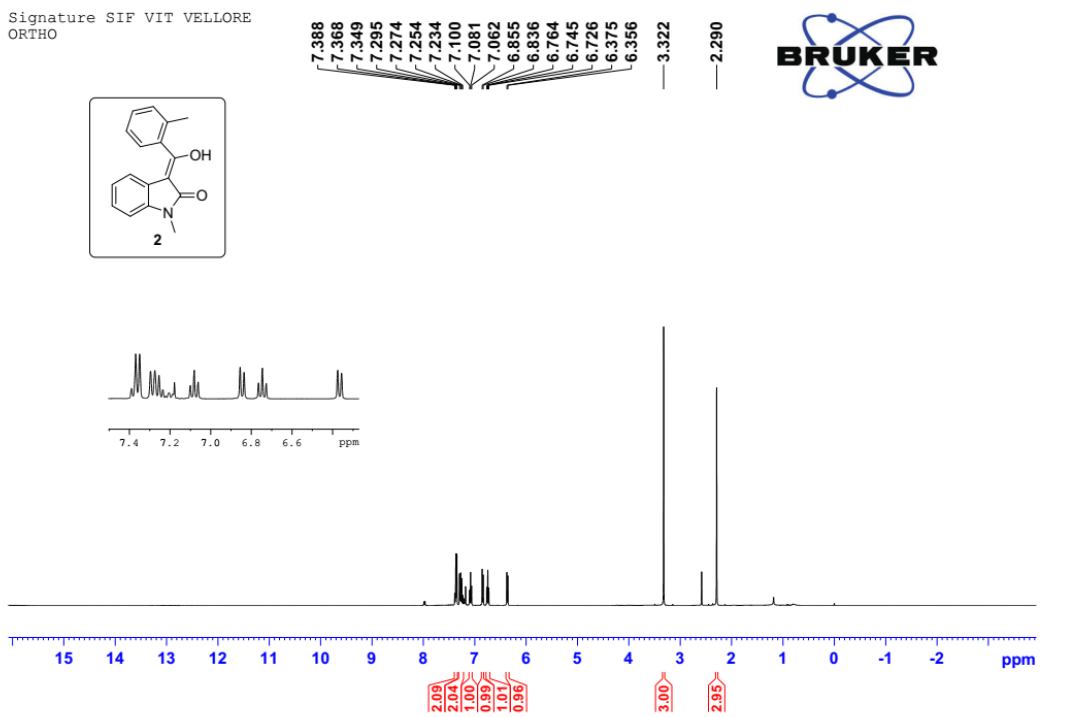
[9] W.-W. Chan, T.-L. Kwong, W.-Y. Yu, *Org. Biomol. Chem.* **2012**, *10*, 3749-3755.

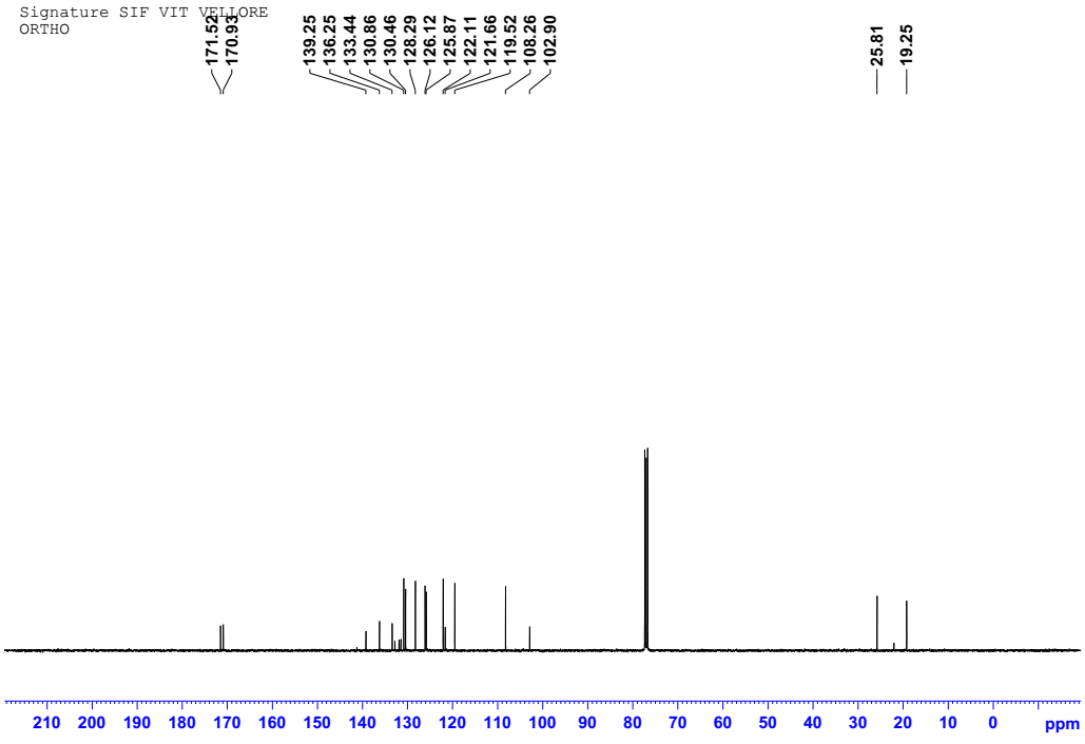
^{1}H and ^{13}C NMR spectrum of **1**



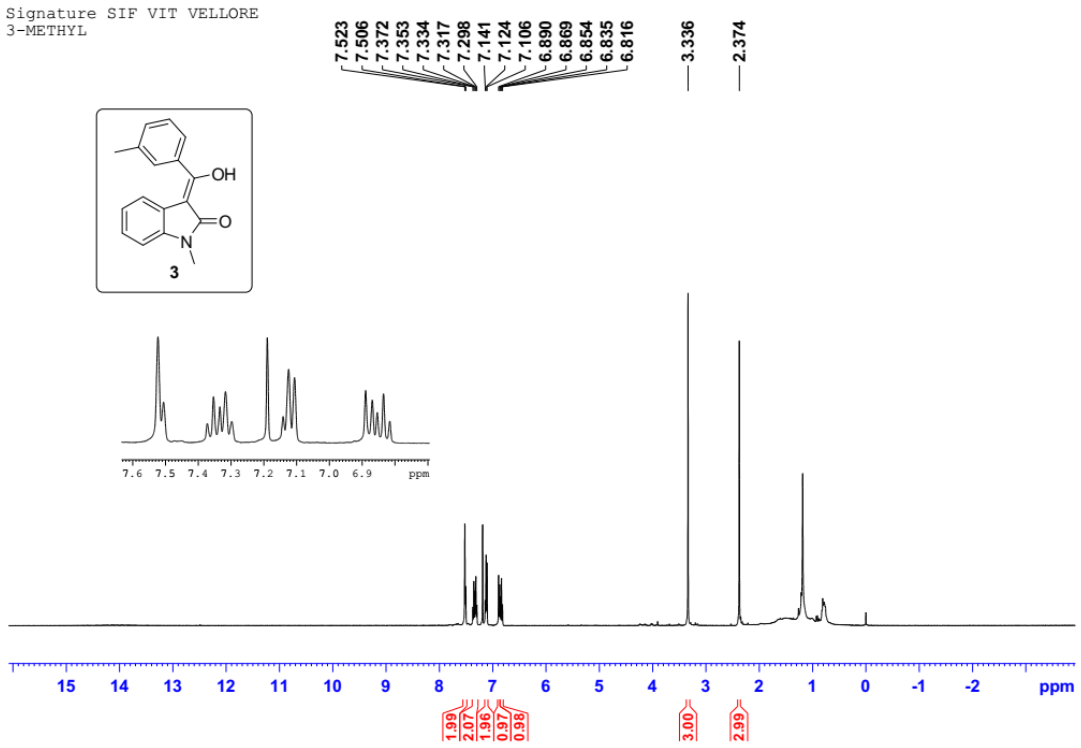


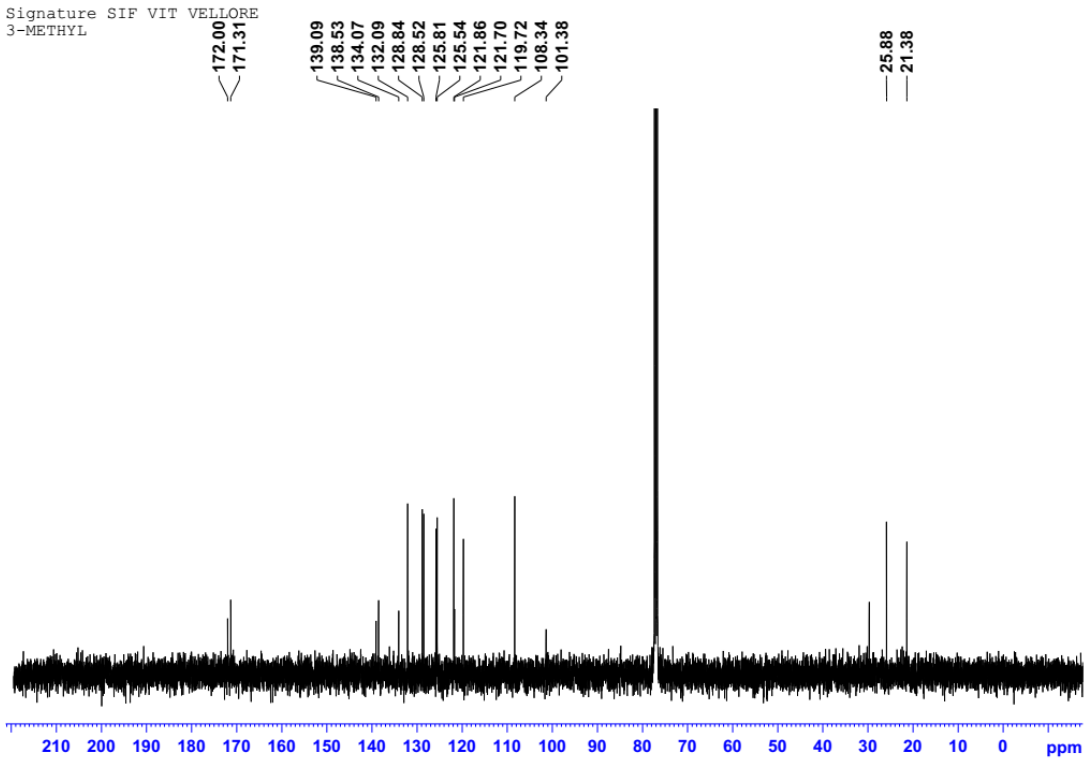
^{1}H and ^{13}C NMR spectrum of **2**



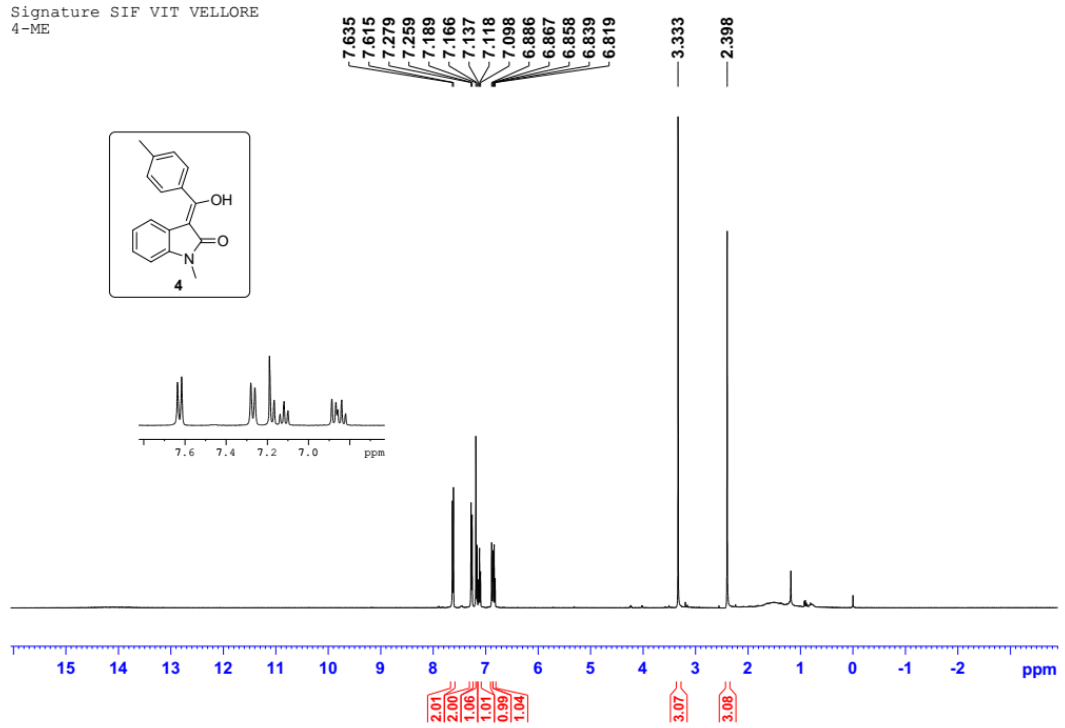


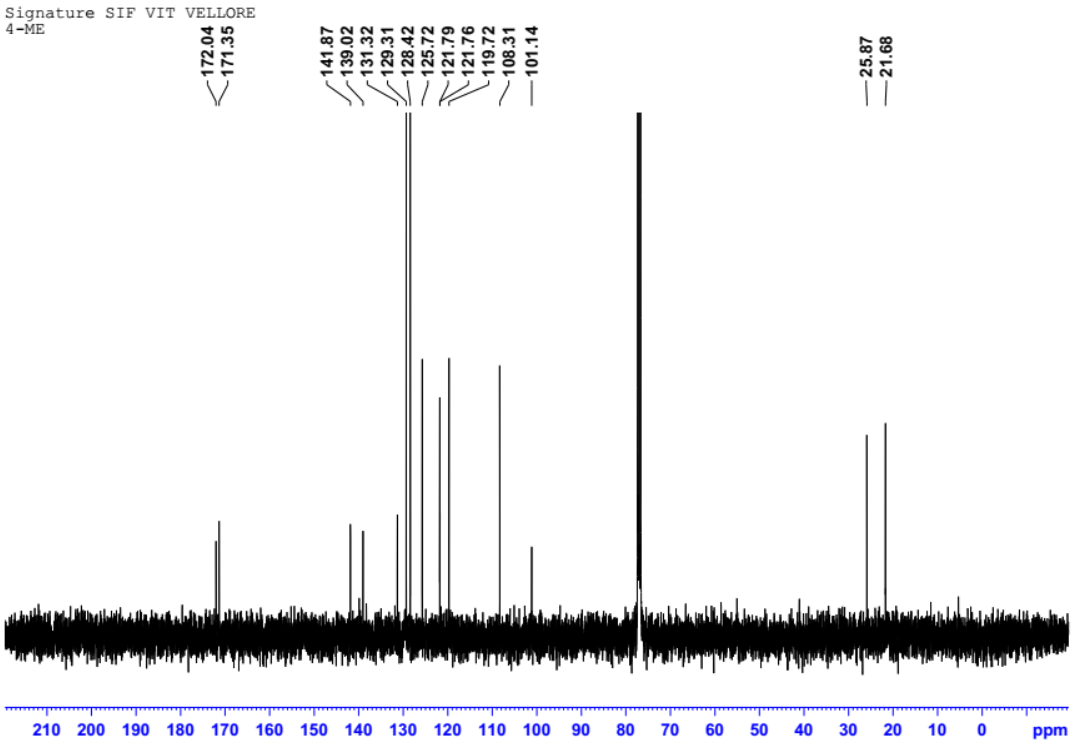
^{1}H and ^{13}C NMR spectrum of **3**



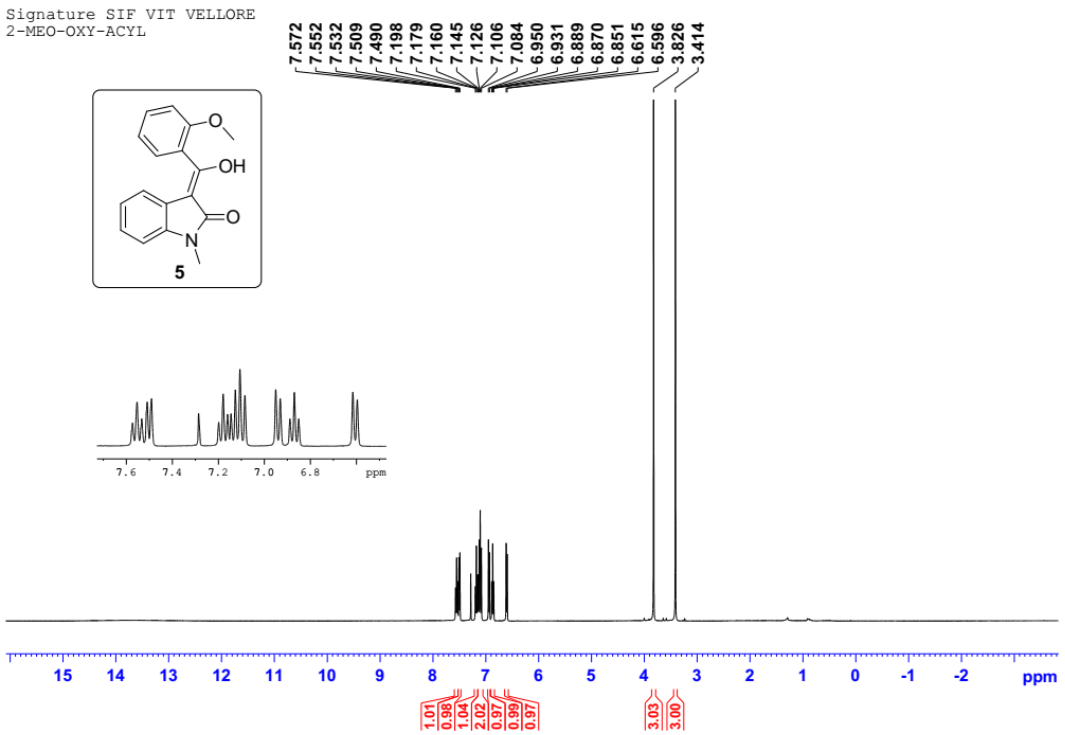


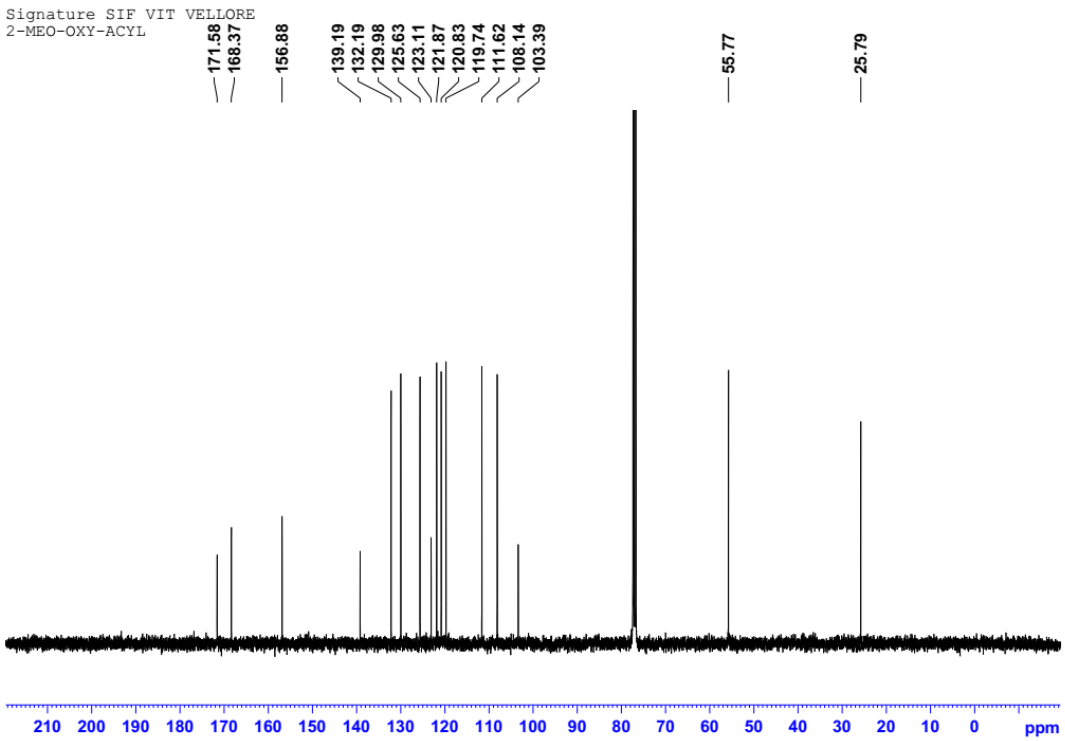
^{1}H and ^{13}C NMR spectrum of **4**



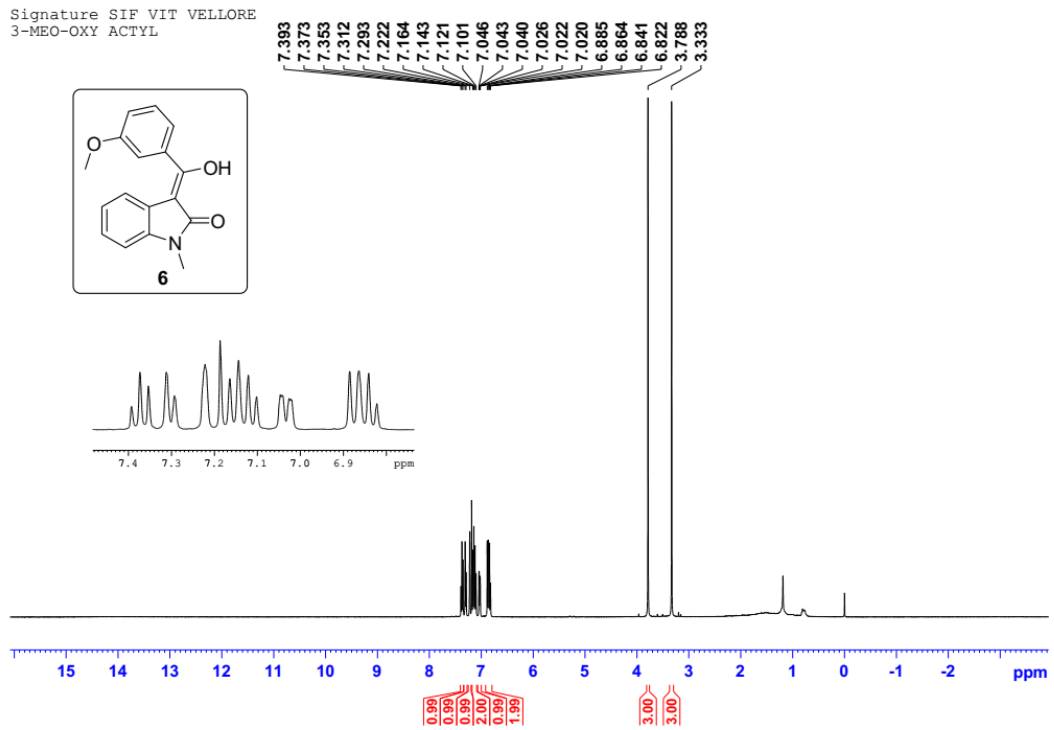


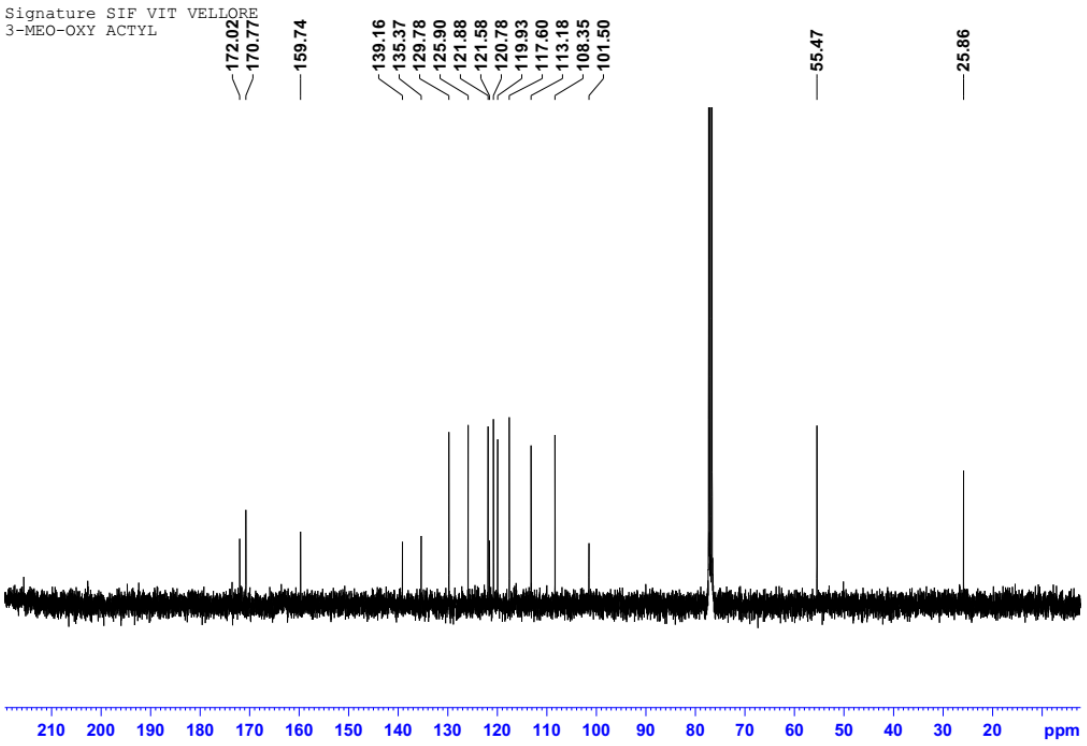
^{1}H and ^{13}C NMR spectrum of **5**



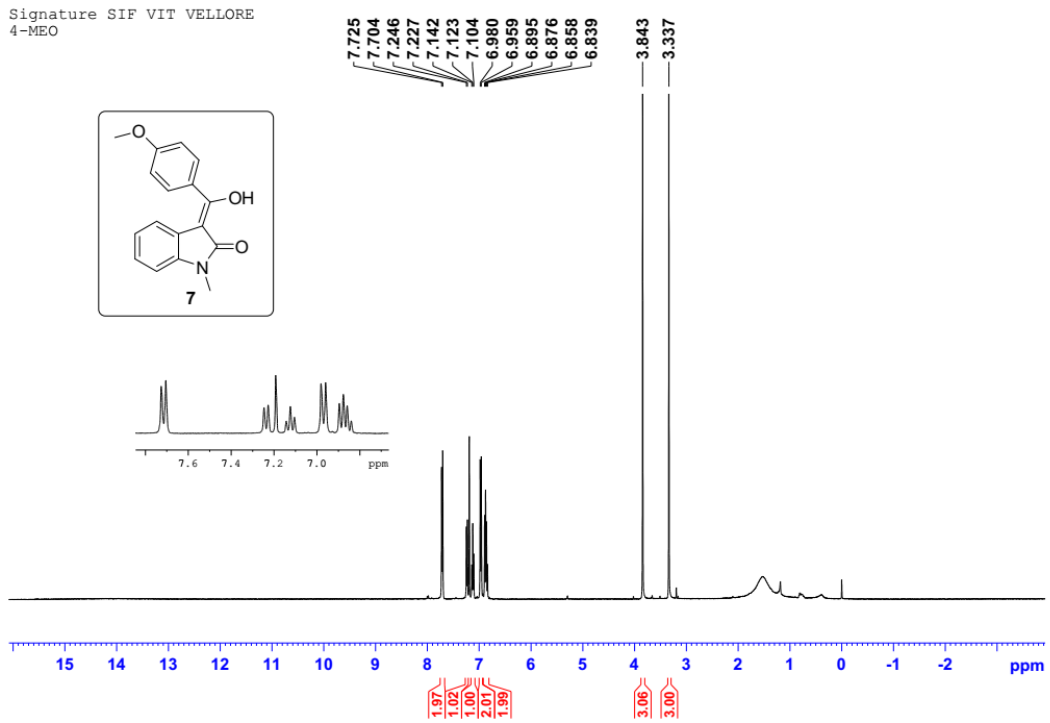


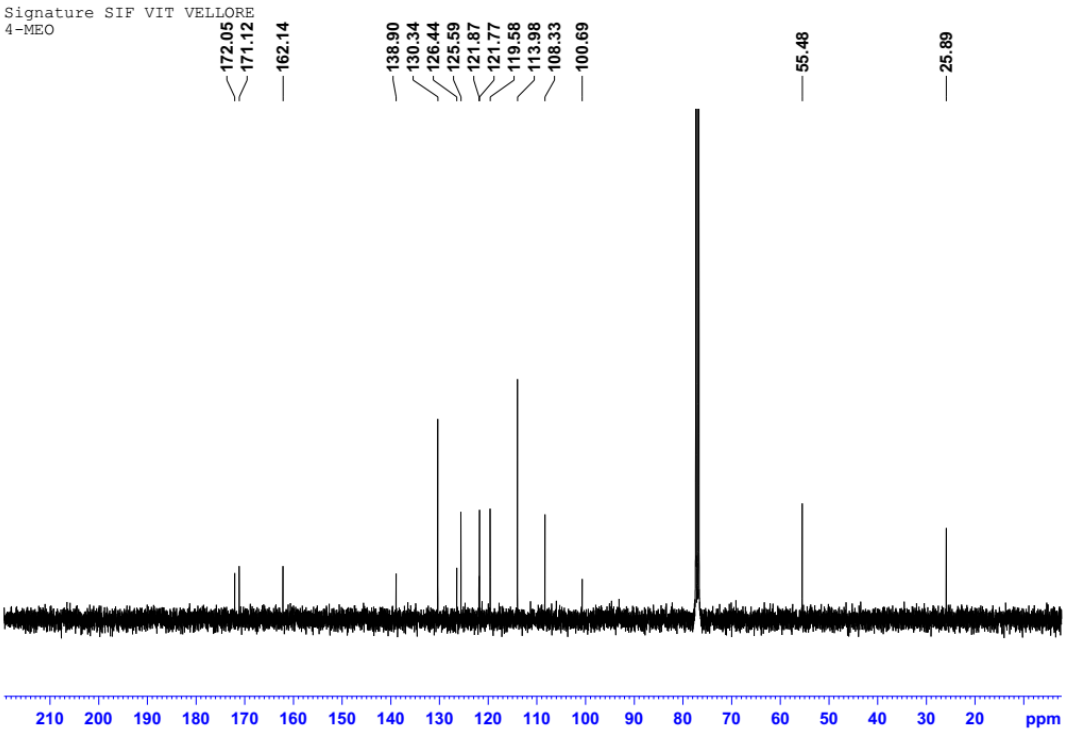
^{1}H and ^{13}C NMR spectrum of **6**



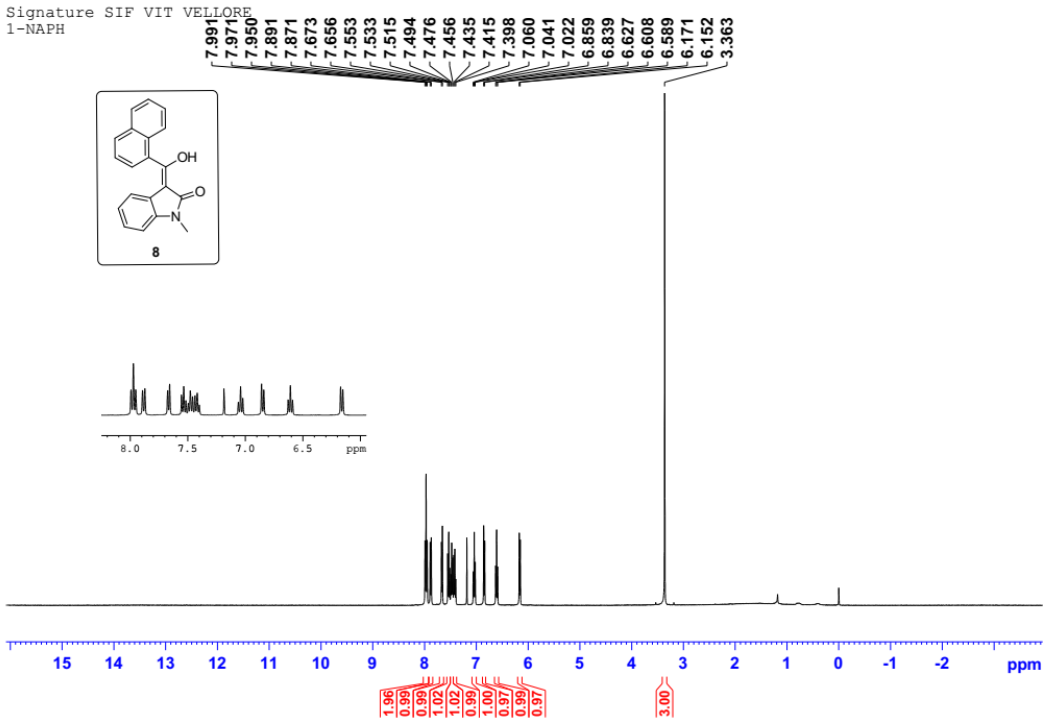


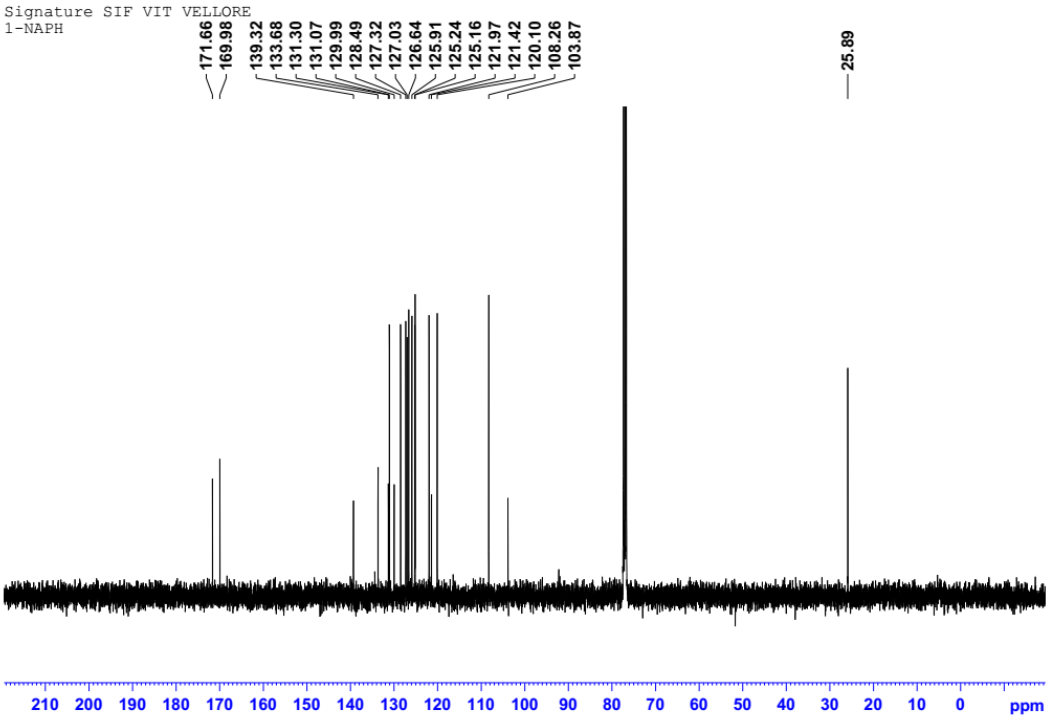
^{1}H and ^{13}C NMR spectrum of **7**



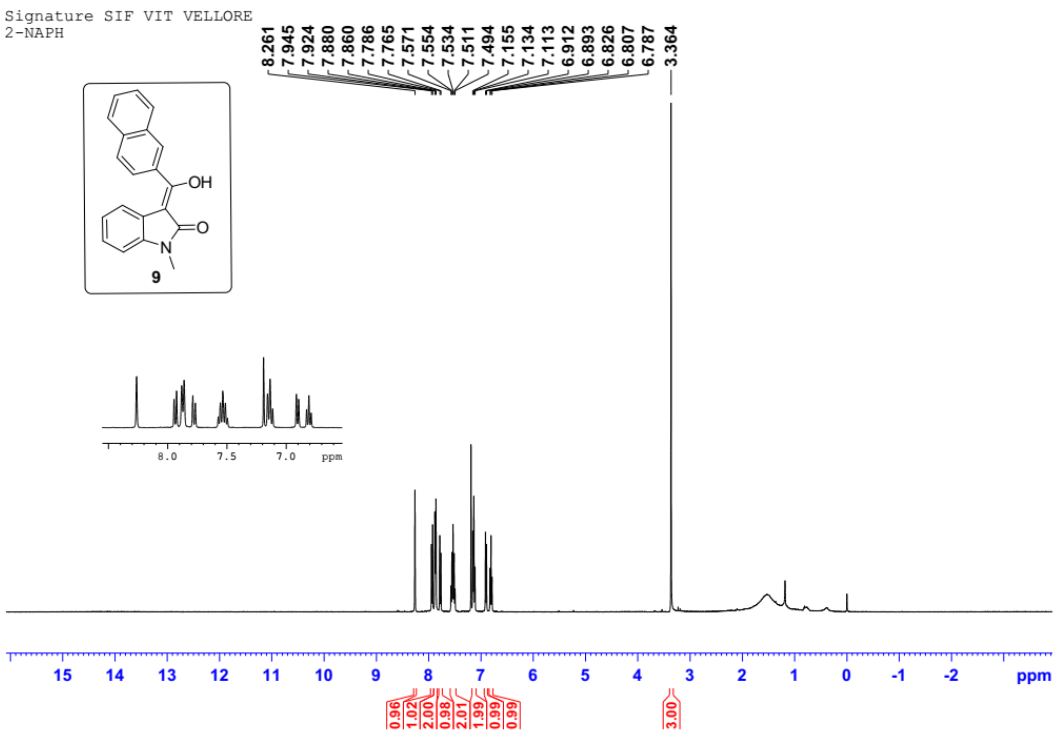


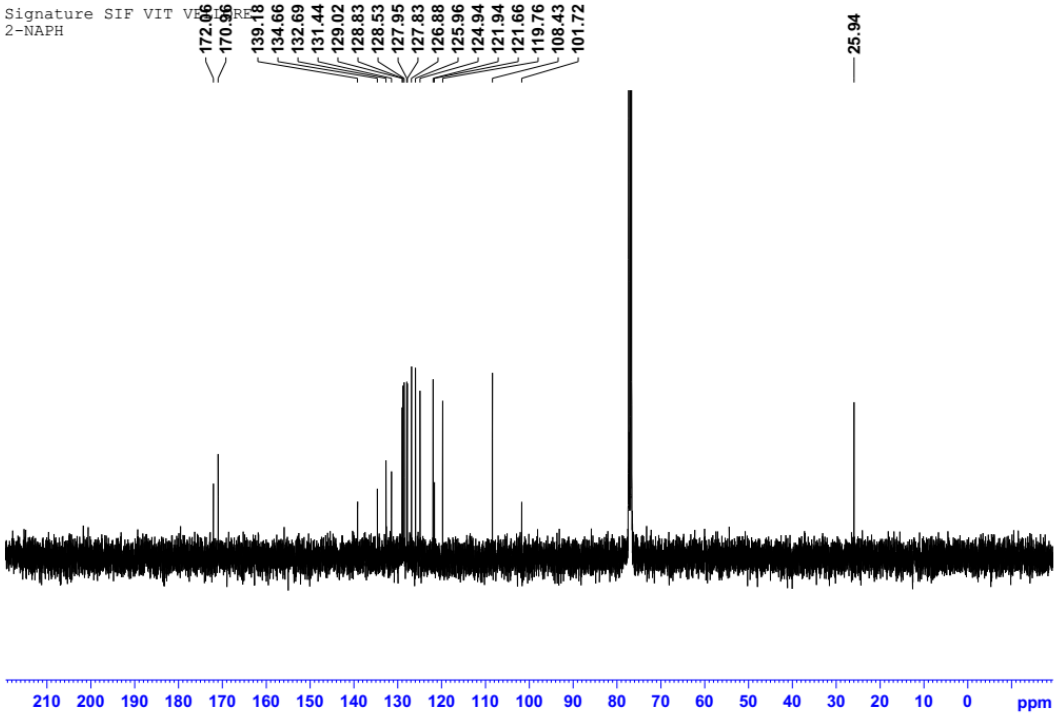
^{1}H and ^{13}C NMR spectrum of **8**



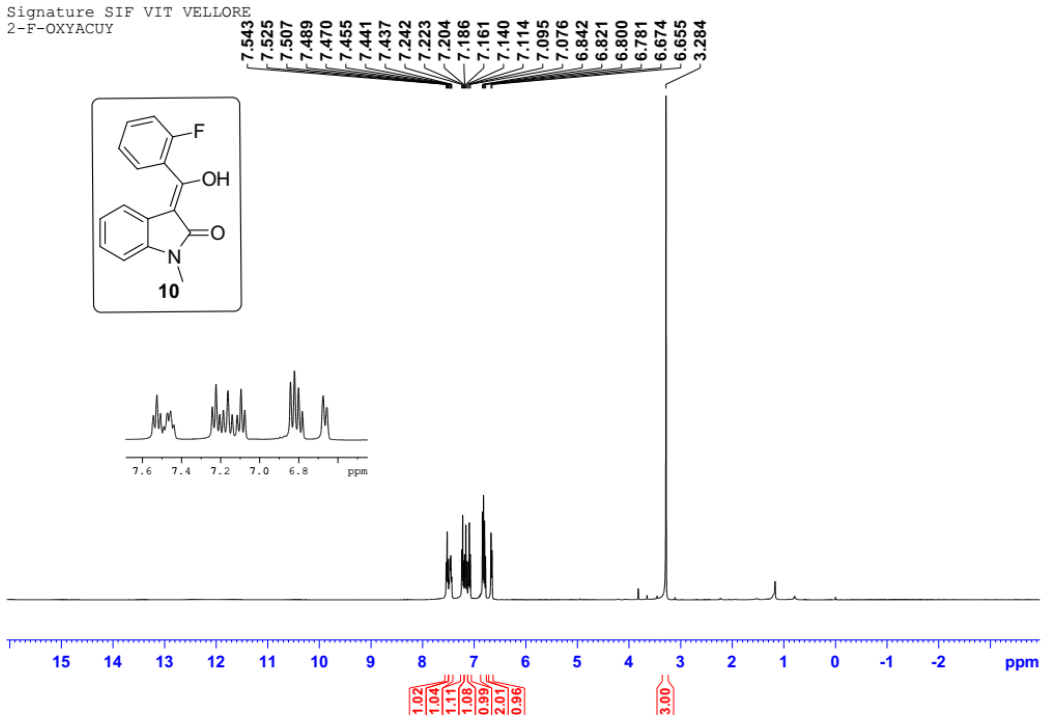


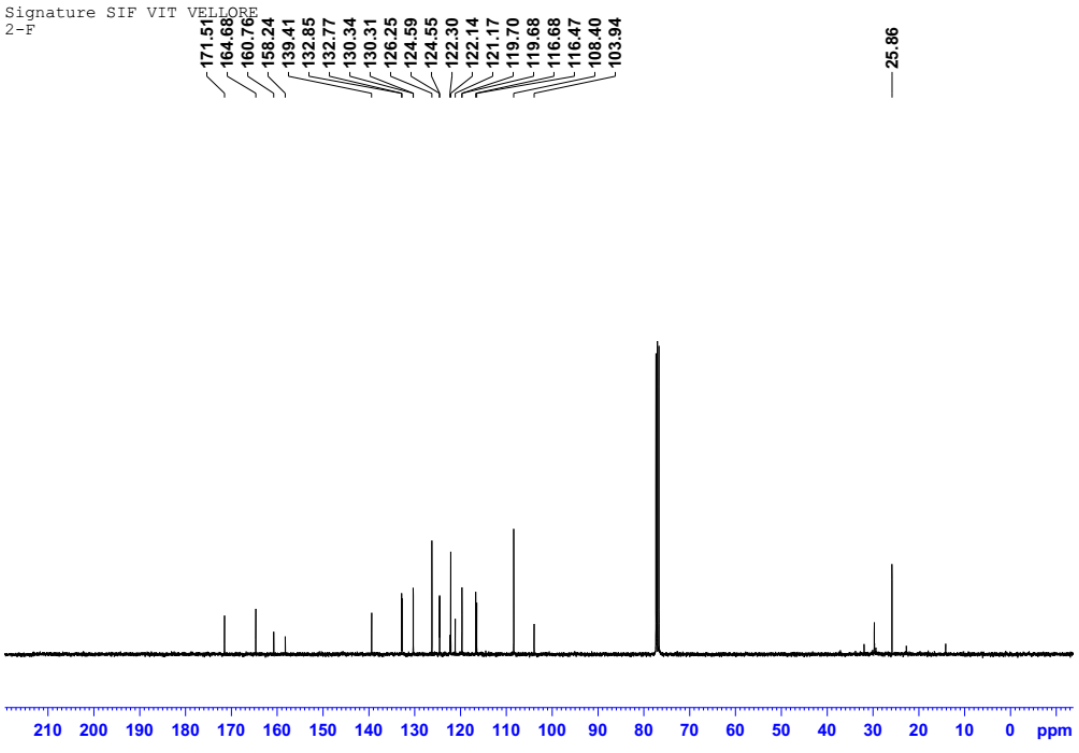
^{1}H and ^{13}C NMR spectrum of **9**

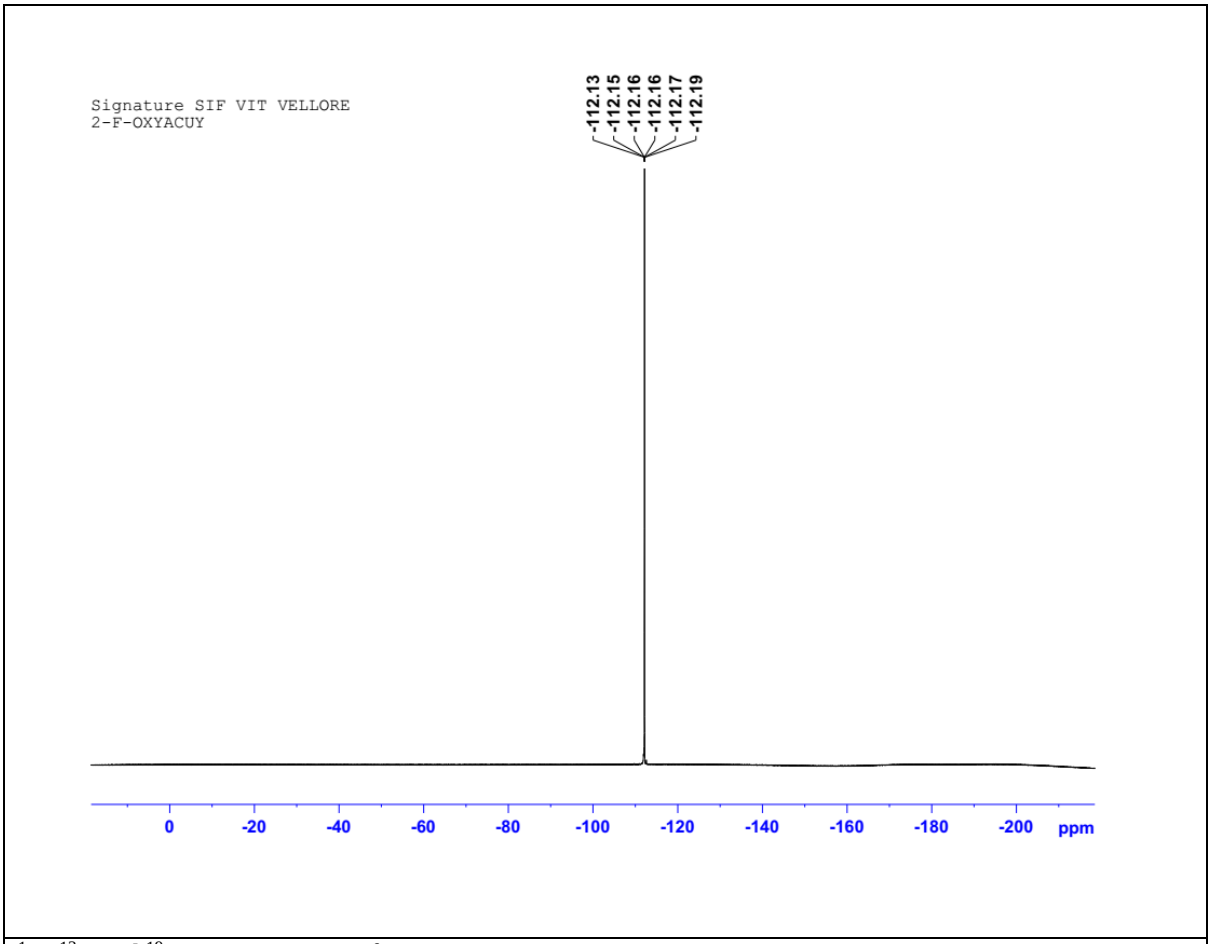




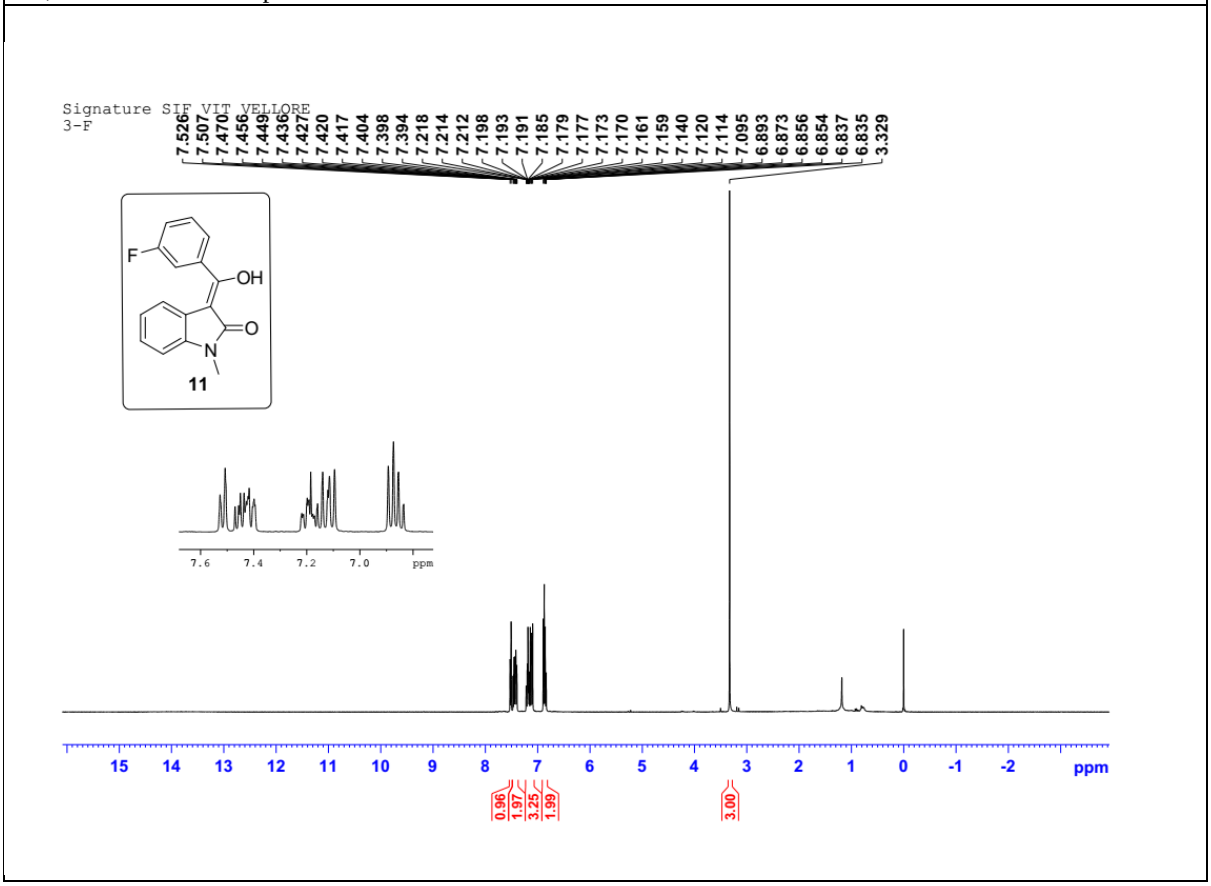
^{1}H, ^{13}C and ^{19}F NMR spectrum of **10**

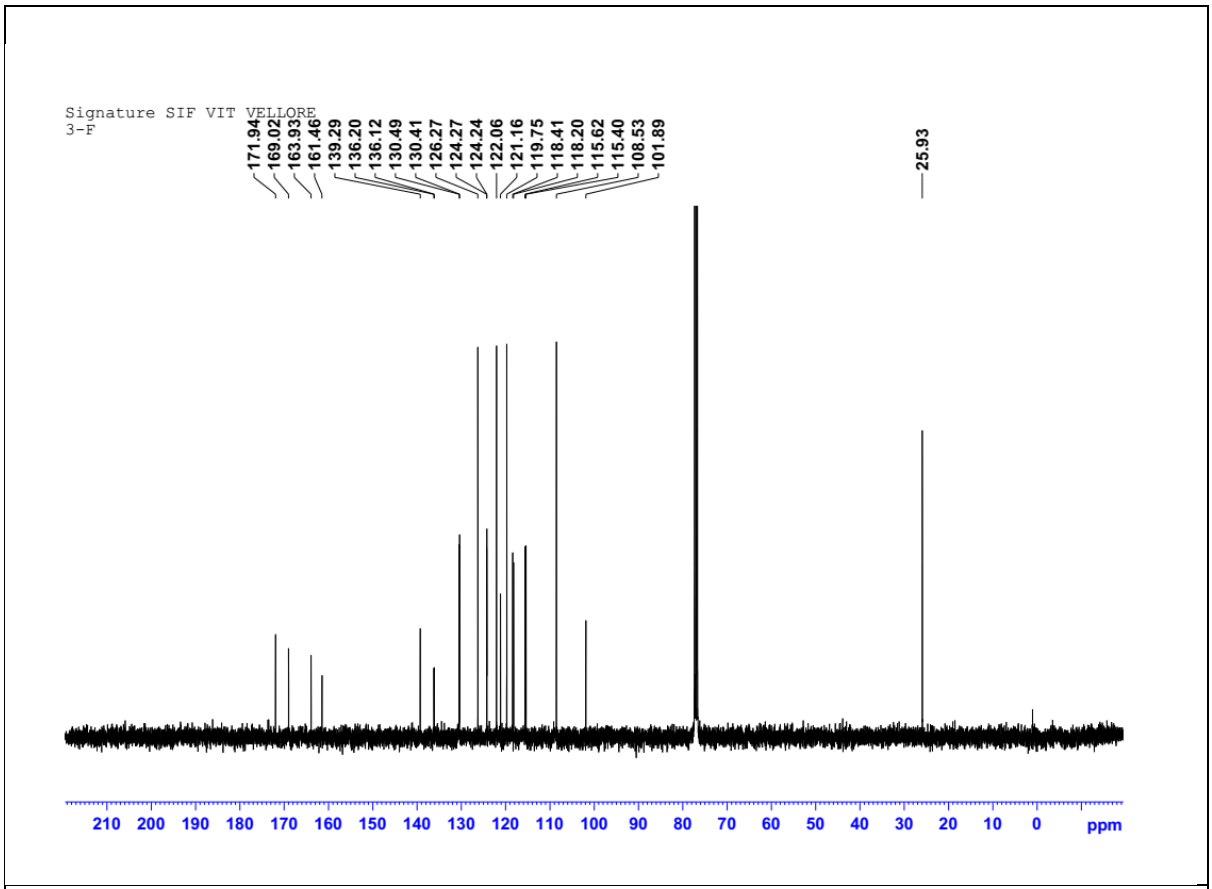






^{1}H, ^{13}C and ^{19}F NMR spectrum of **11**




Signature SIF VIT VELLORE
3-F
171.94
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126.27
124.27
124.24
122.06
121.16
119.75
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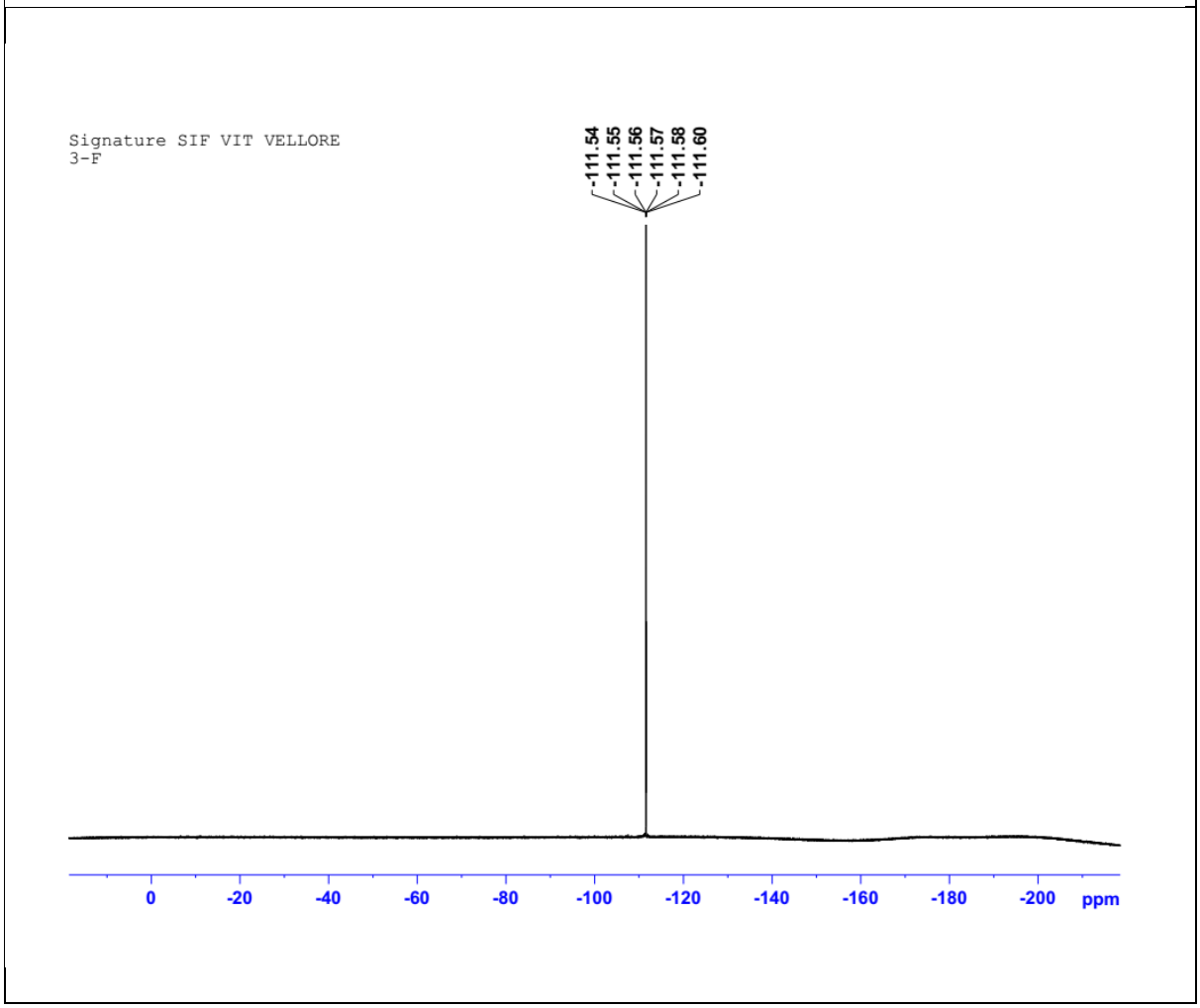
101.89
25.93
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Signature SIF VIT VELLORE
3-F
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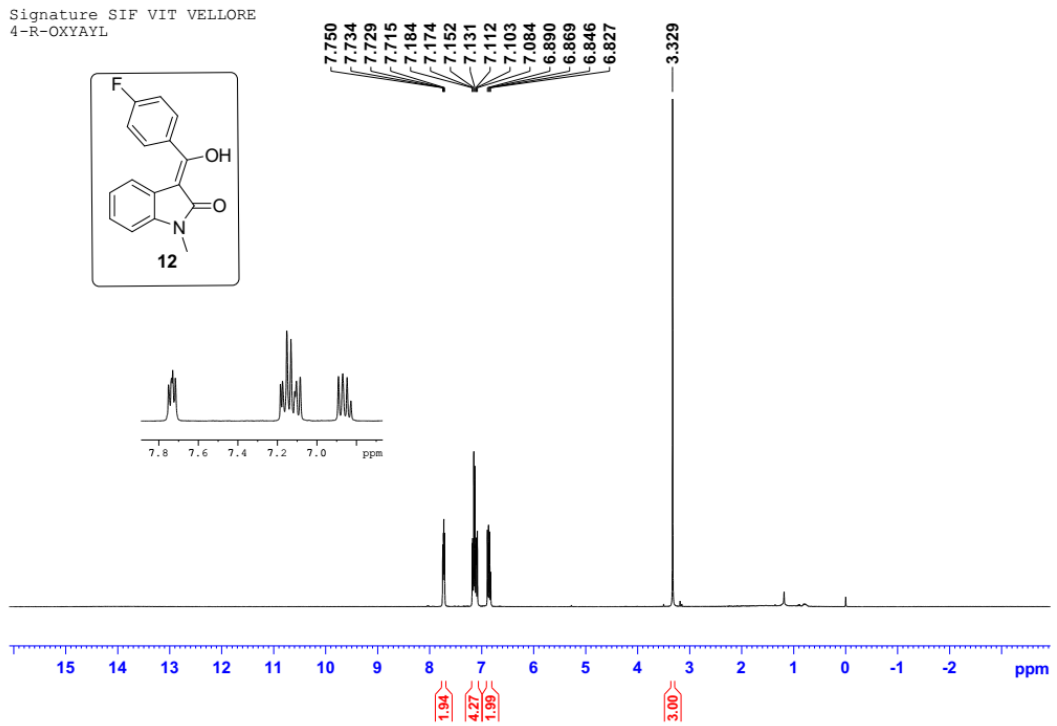
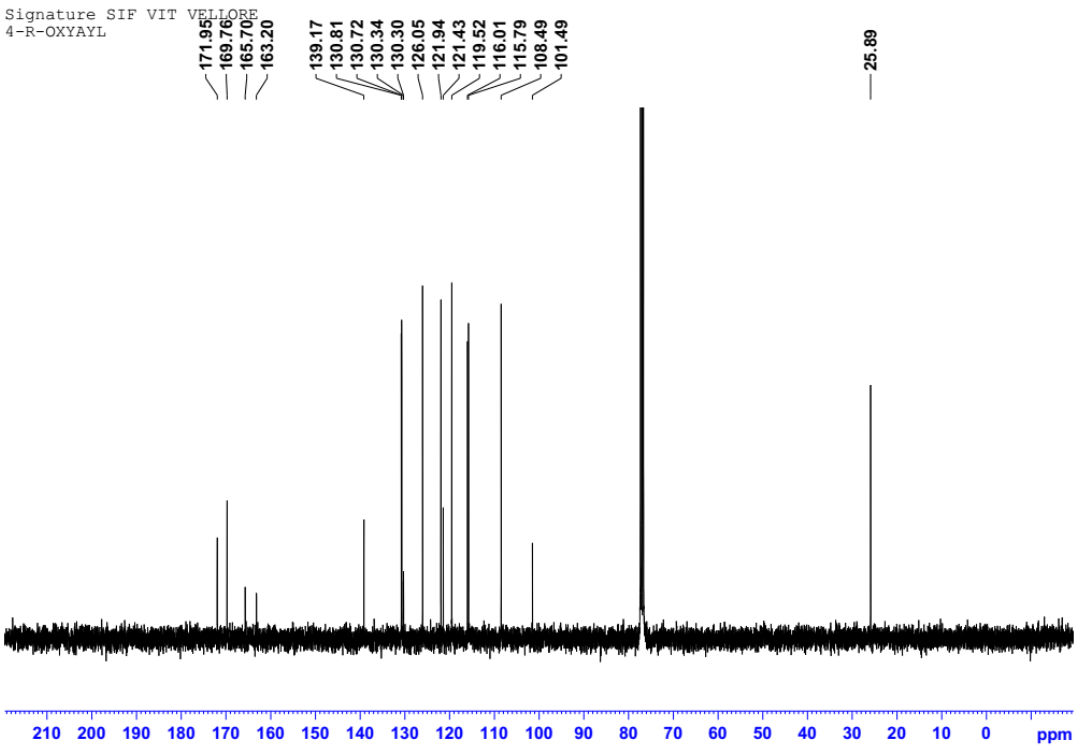
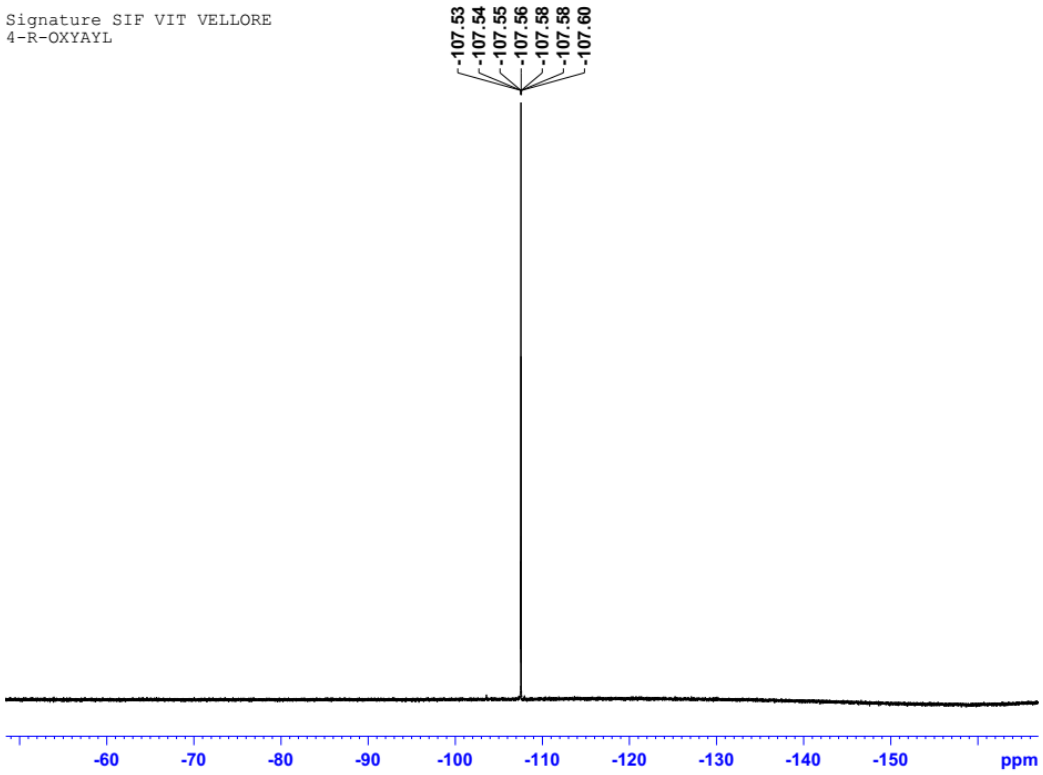
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

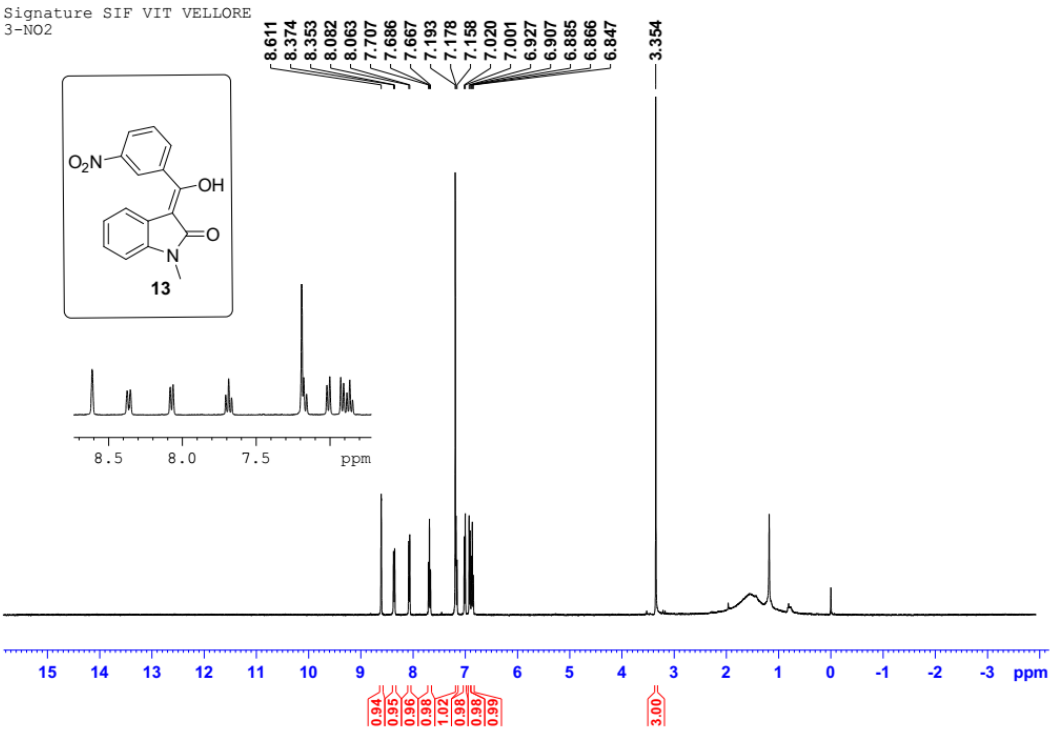
^{1}H, ^{13}C and ^{19}F NMR spectrum of **12**

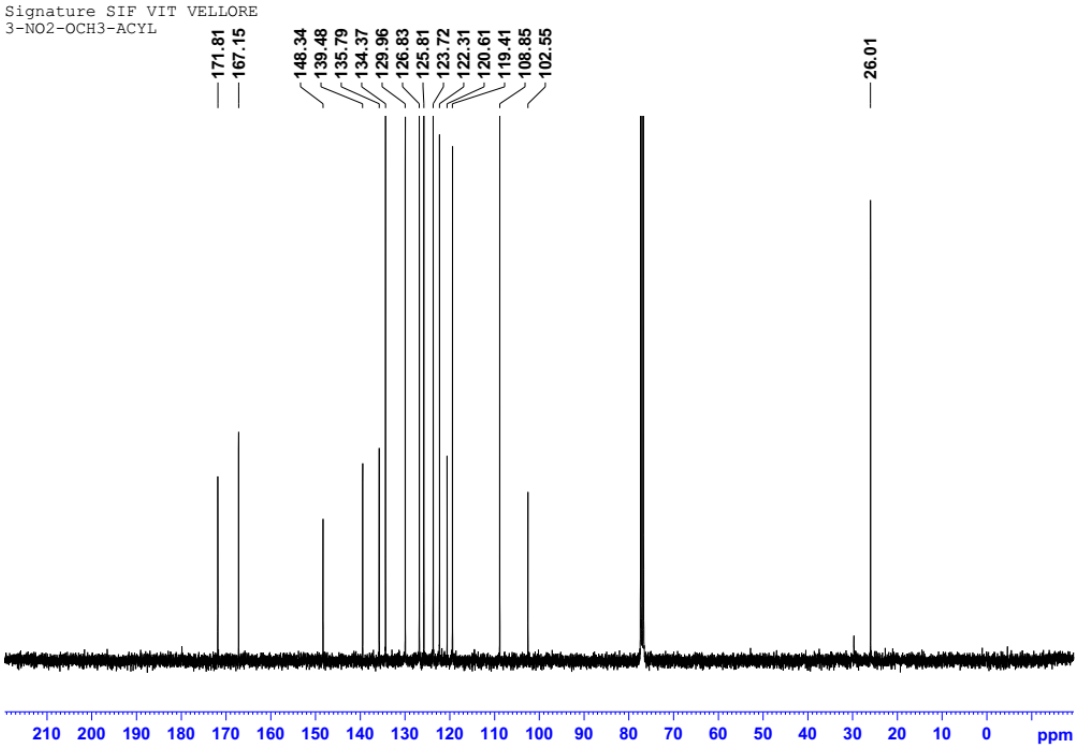




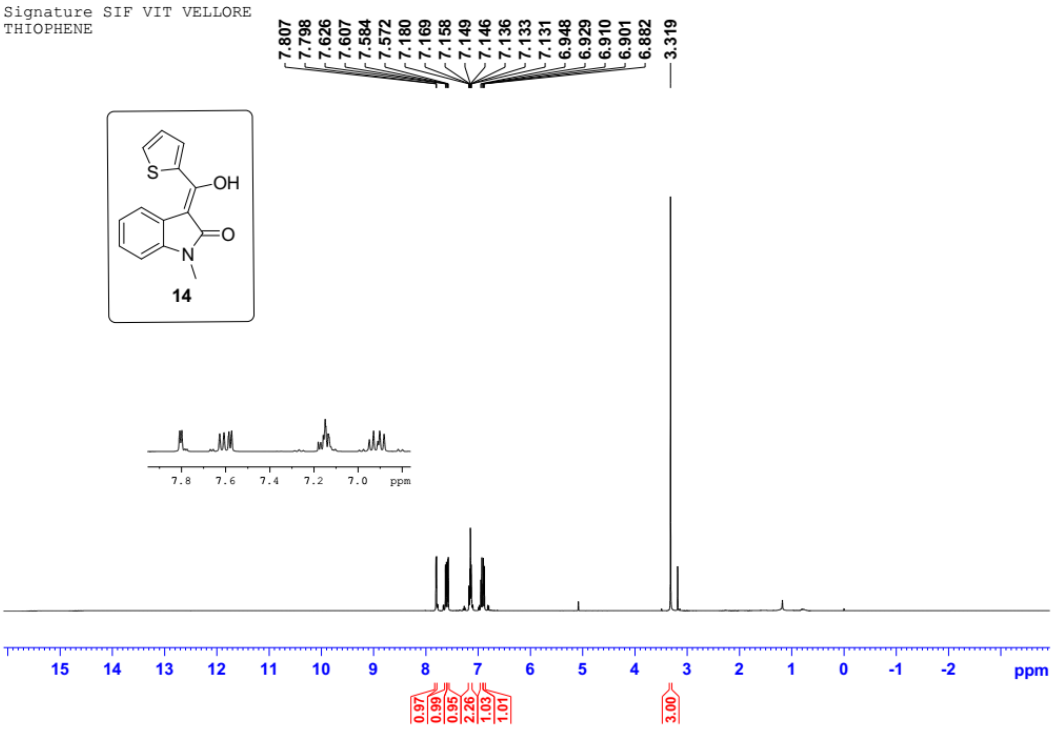


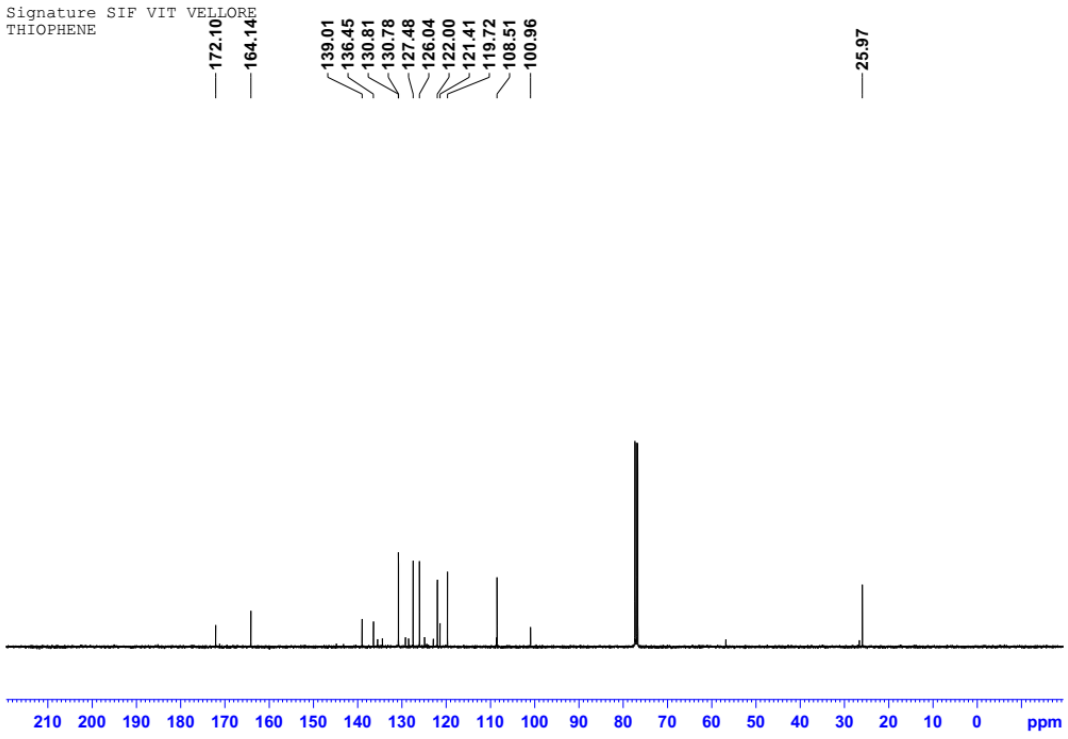
^{1}H and ^{13}C NMR spectrum of **13**



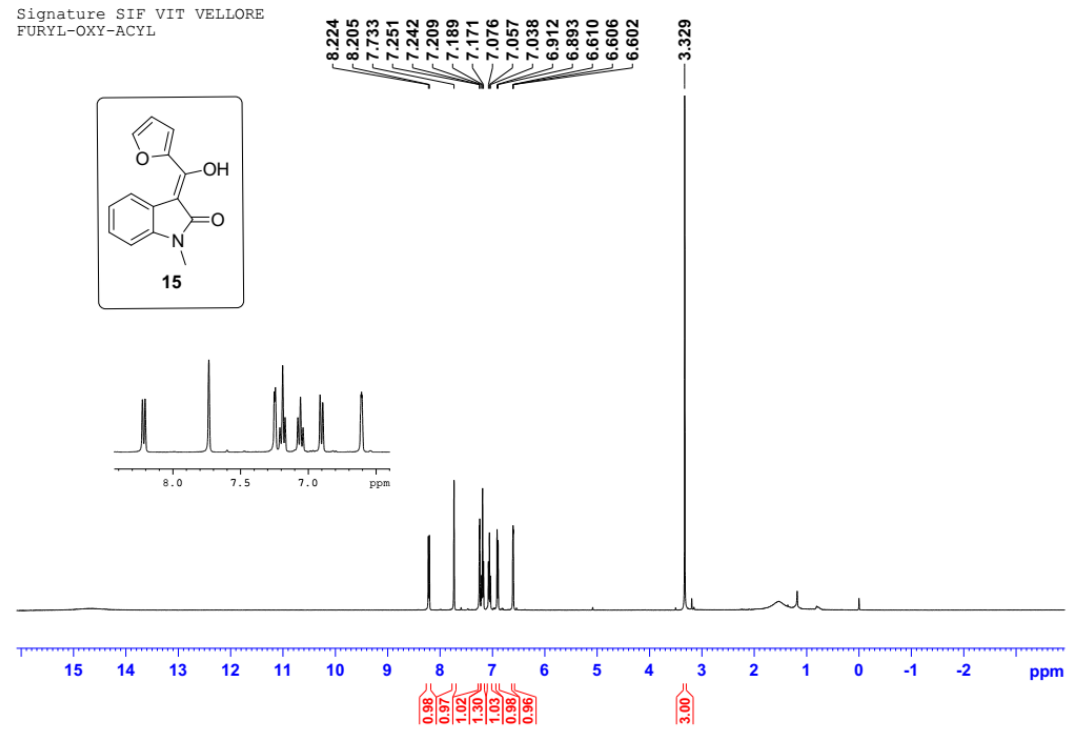


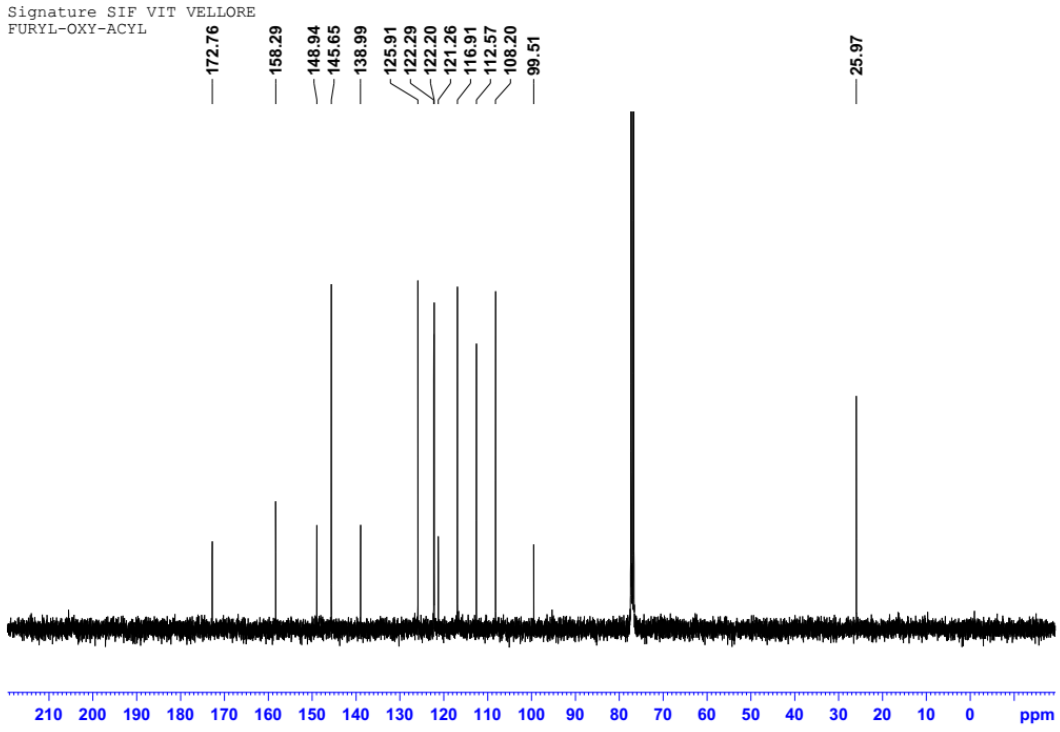
^{1}H and ^{13}C NMR spectrum of **14**



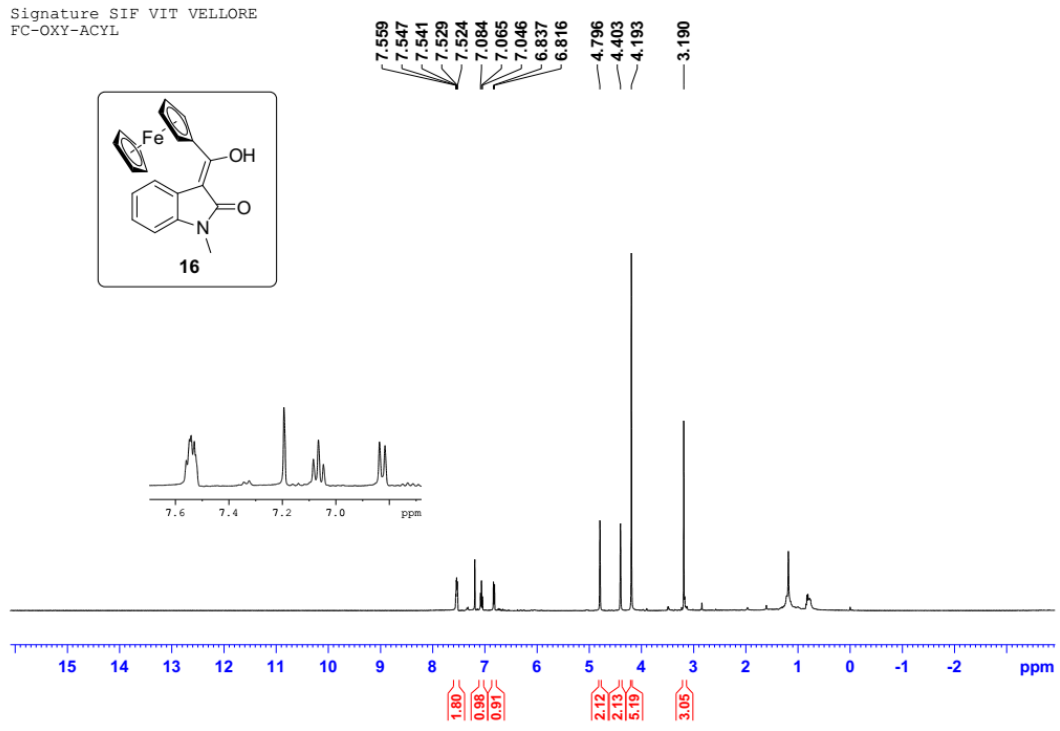


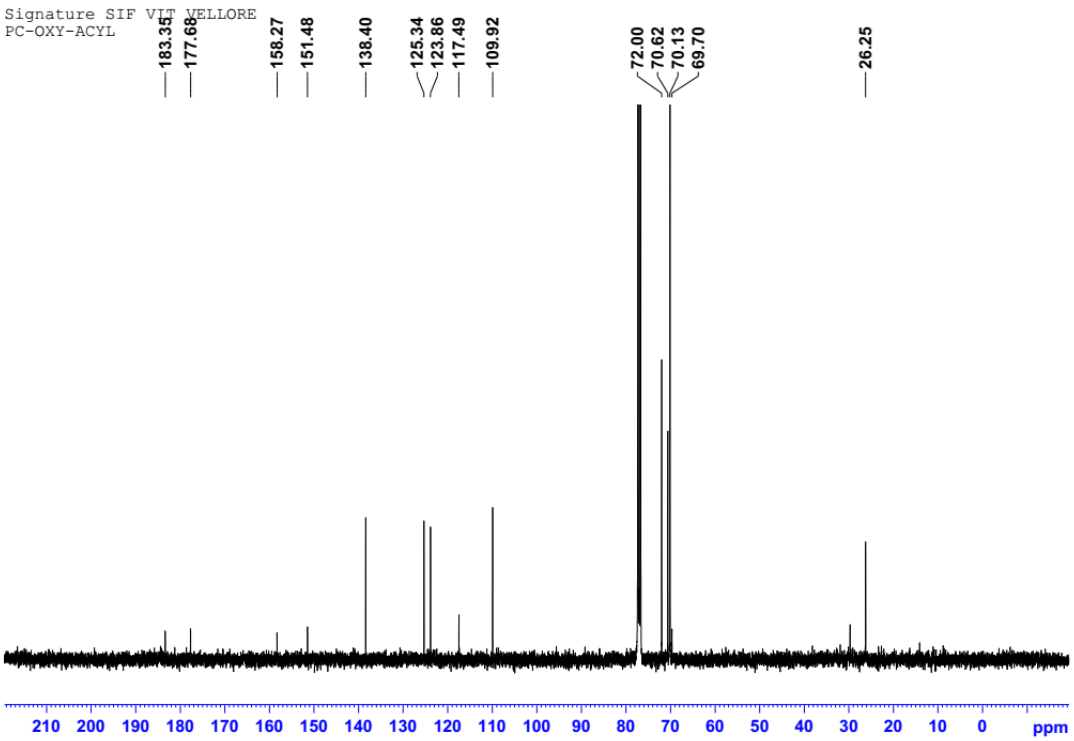
^{1}H and ^{13}C NMR spectrum of **15**



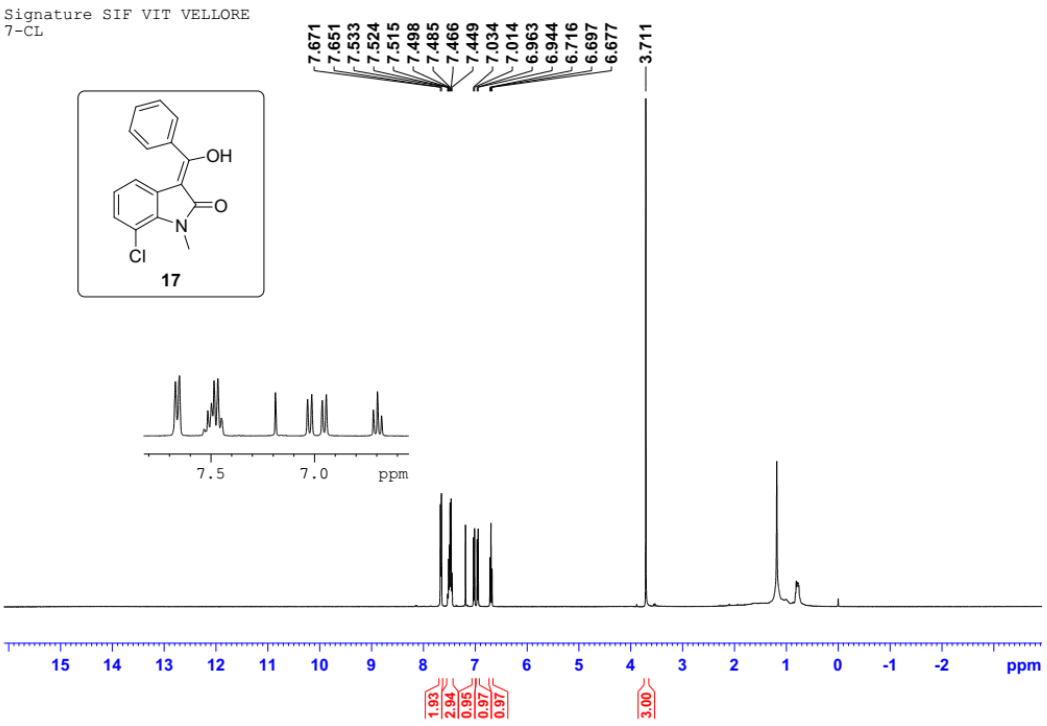


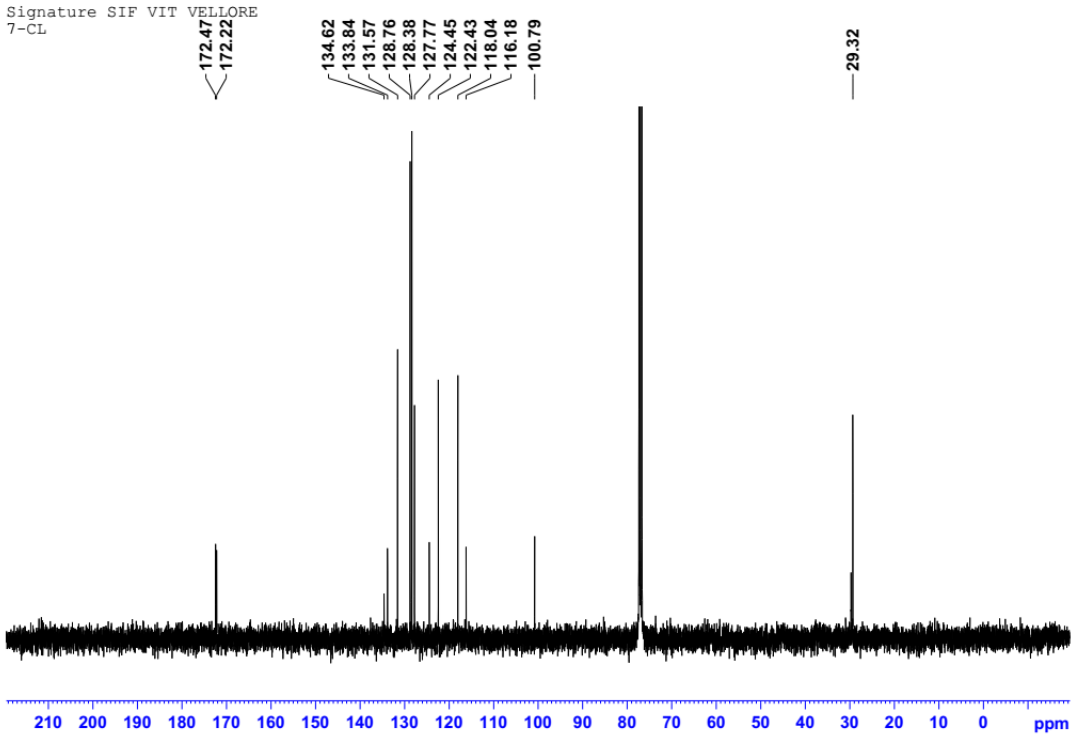
^{1}H and ^{13}C NMR spectrum of **16**



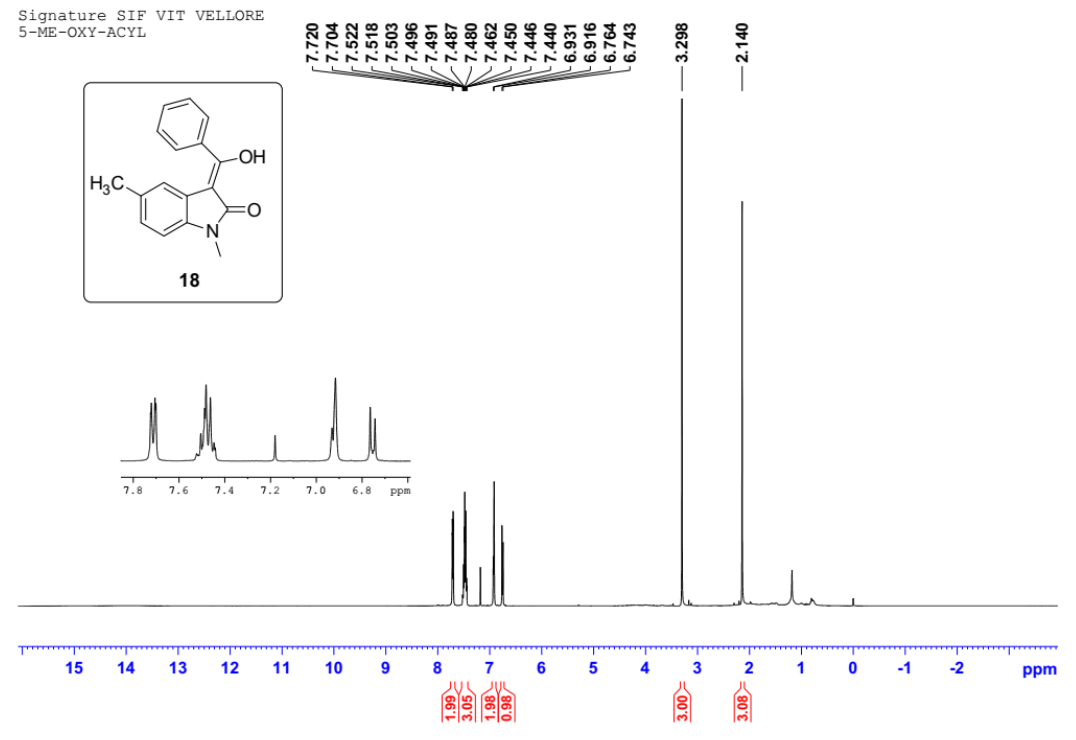


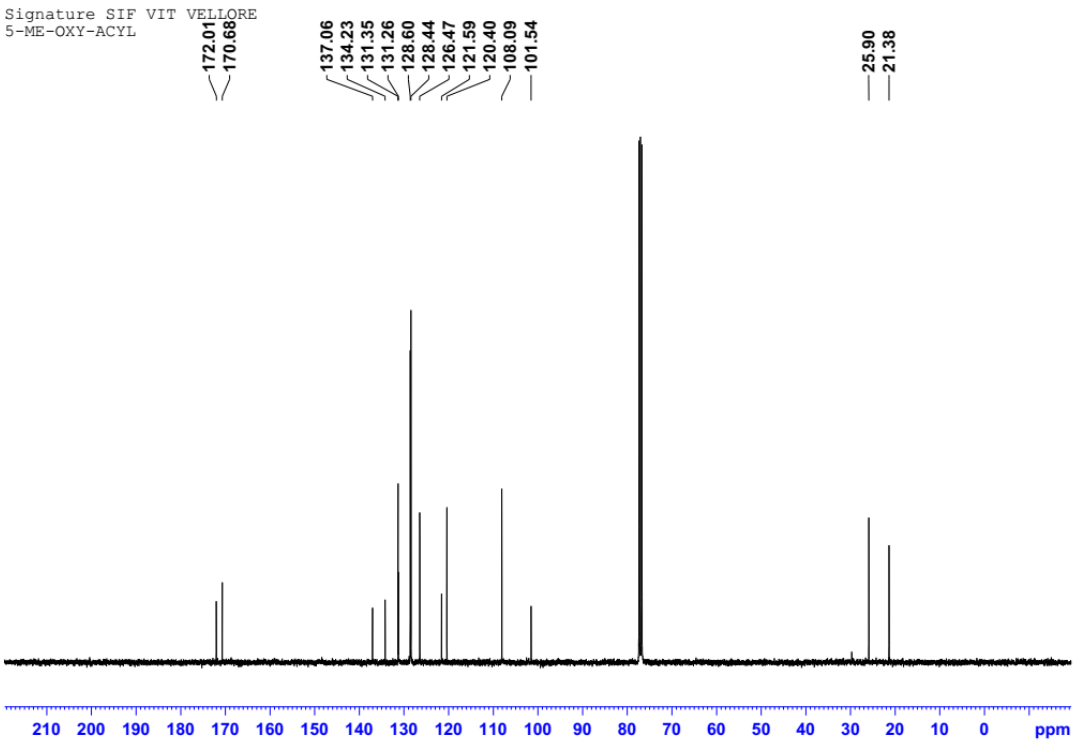
^{1}H and ^{13}C NMR spectrum of **17**



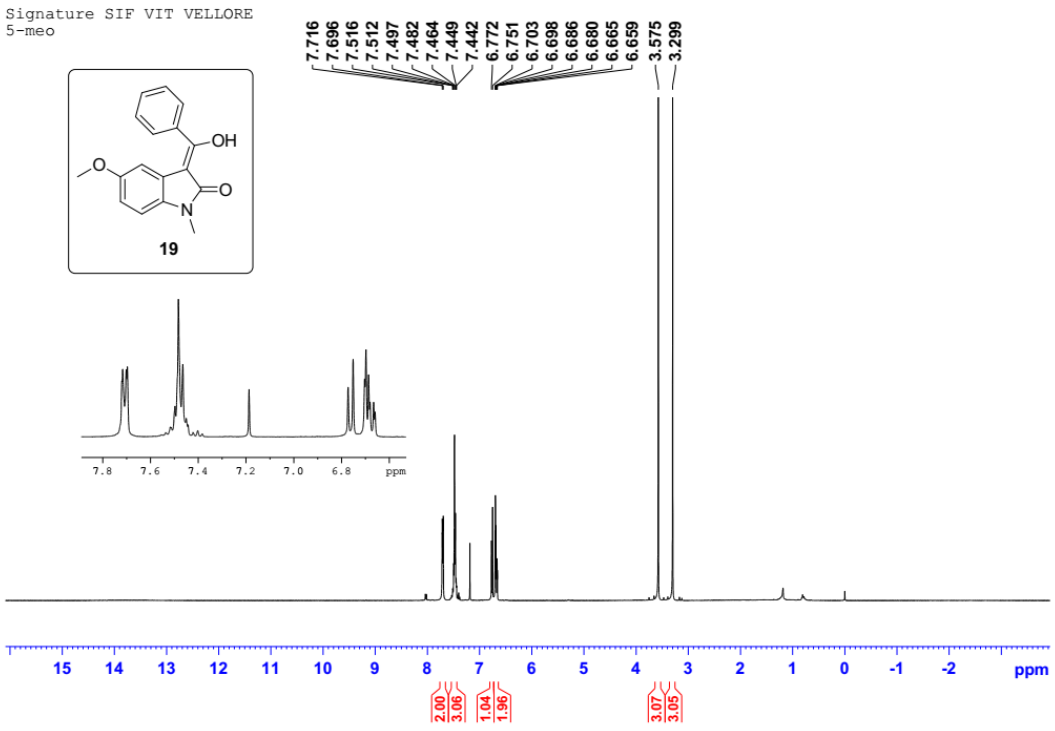


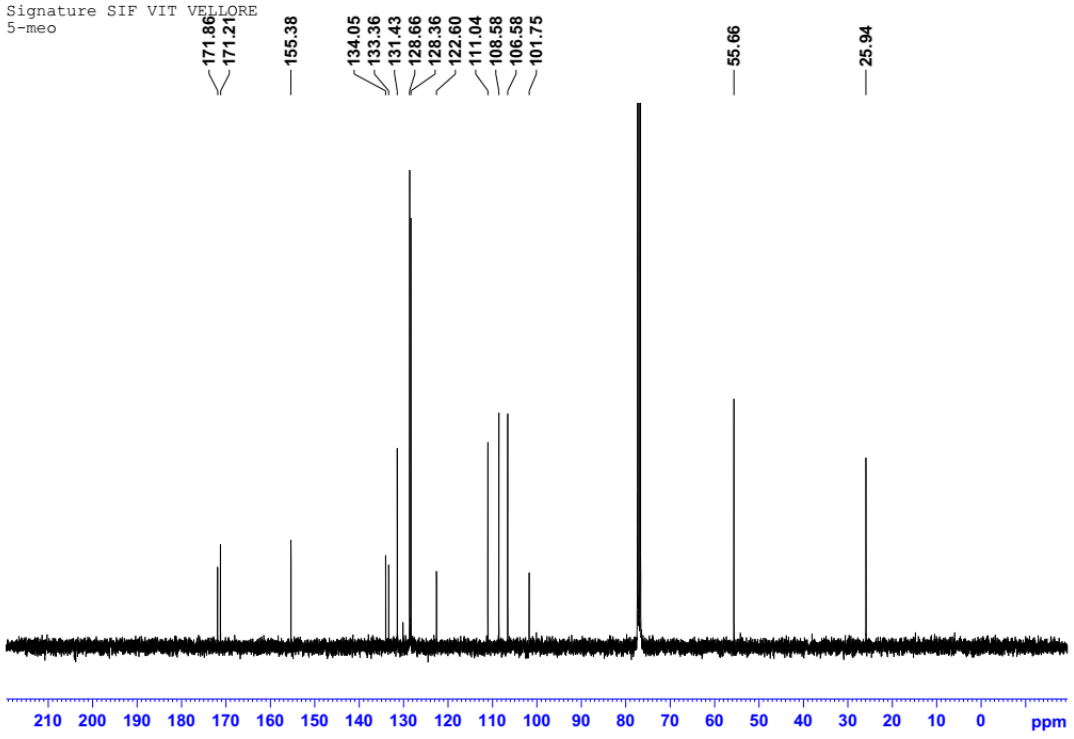
^{1}H and ^{13}C NMR spectrum of **18**



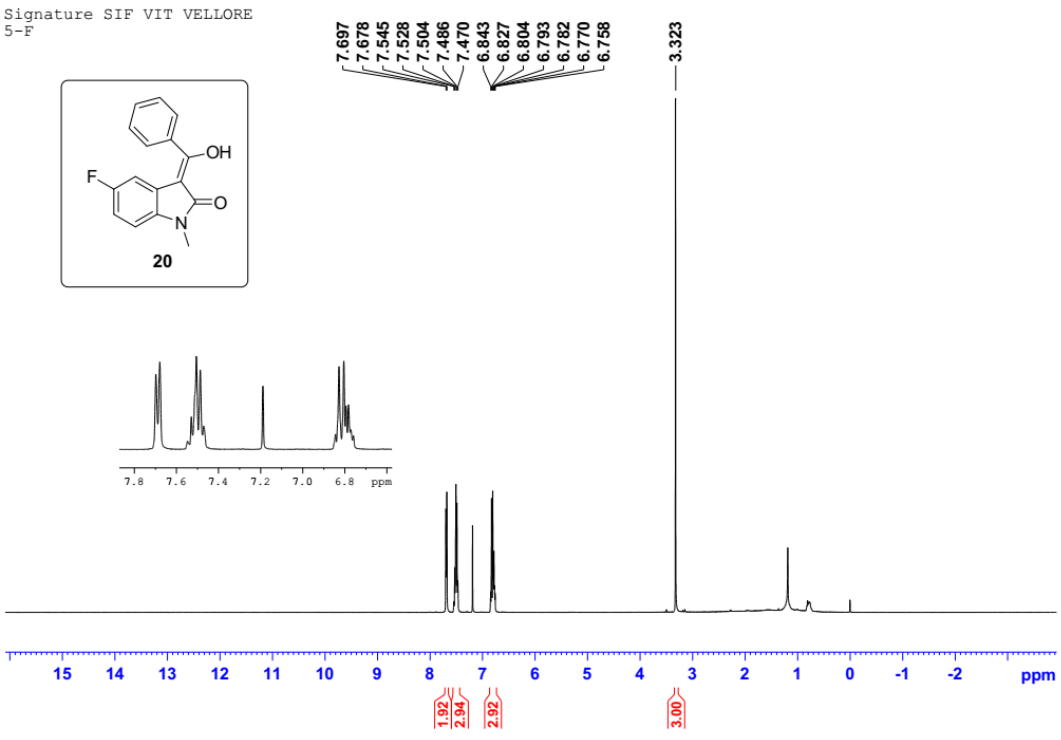


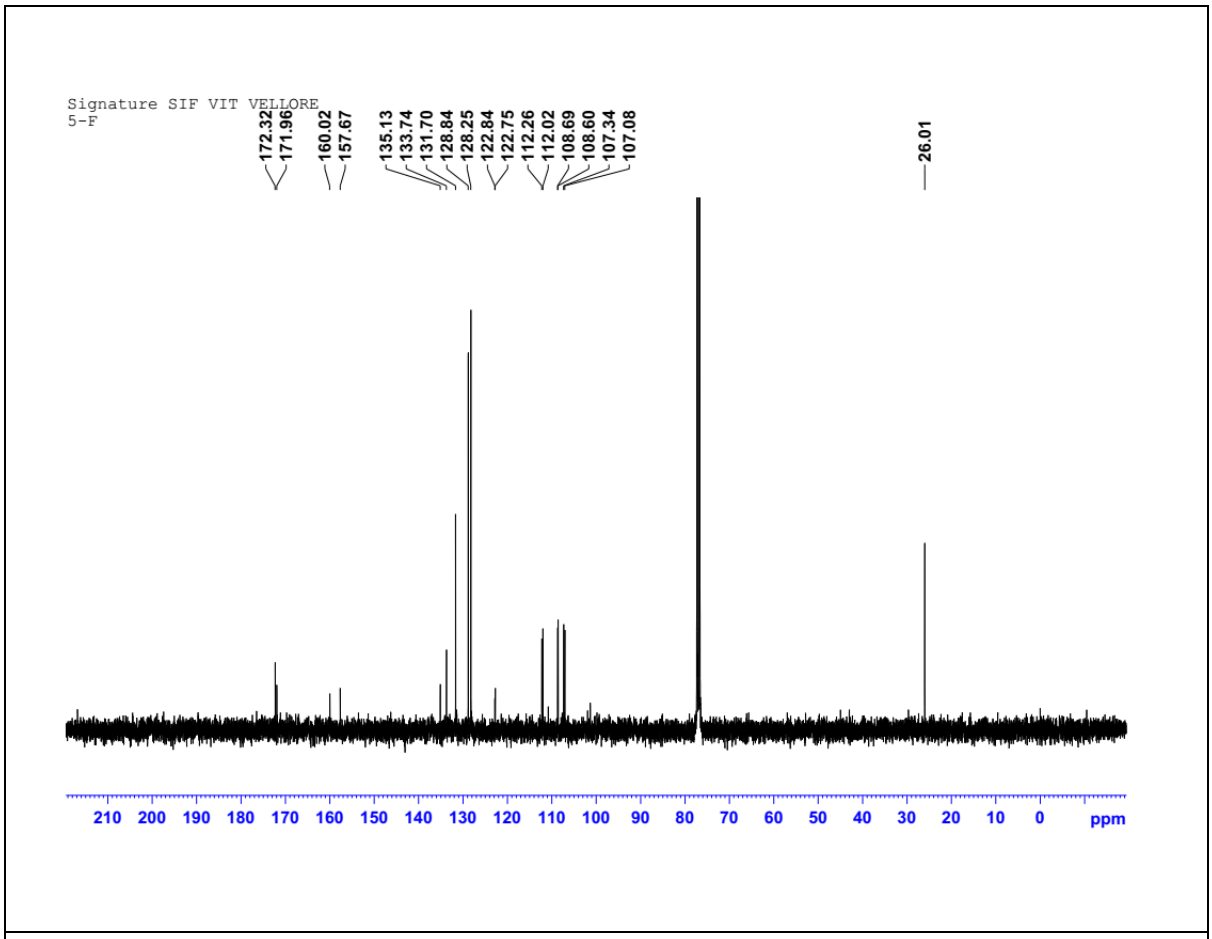
^{1}H and ^{13}C NMR spectrum of **19**





^{1}H, ^{13}C and ^{19}F NMR spectrum of **20**

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107.34
107.08
26.01
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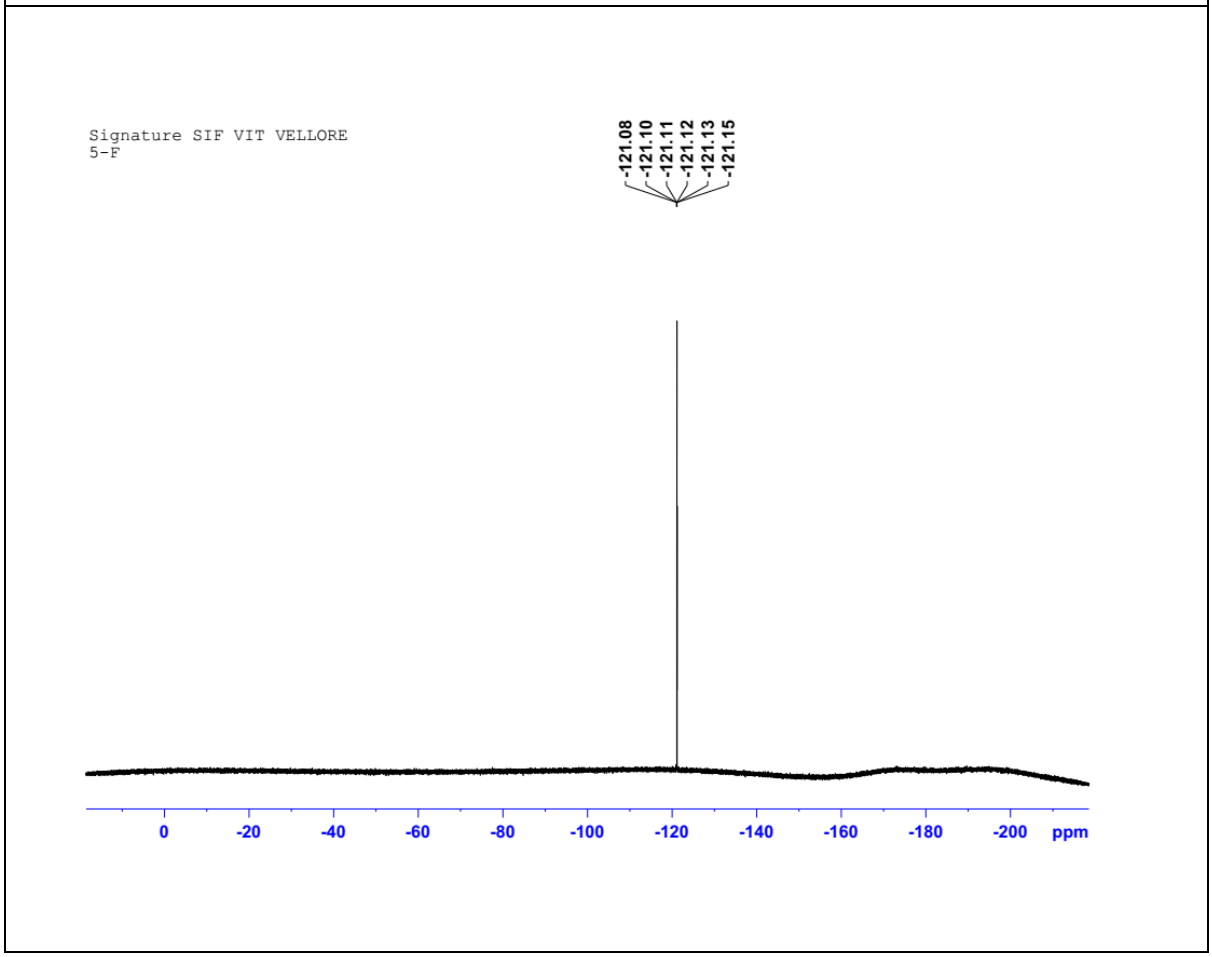
Signature SIF VIT VELLORE
5-F
-121.08
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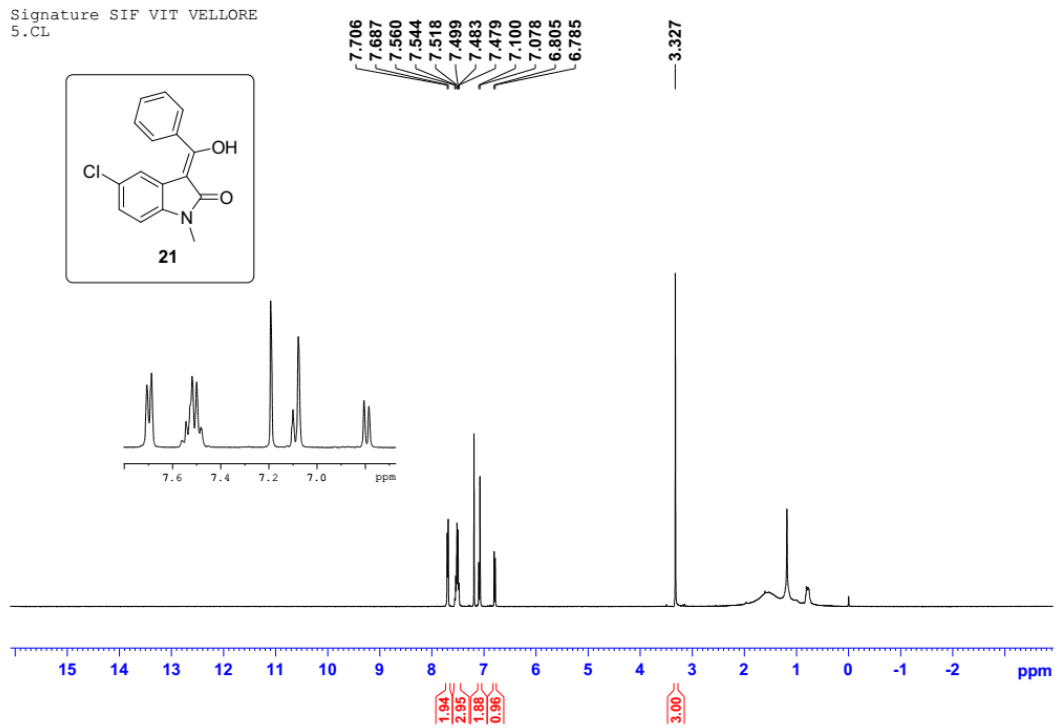
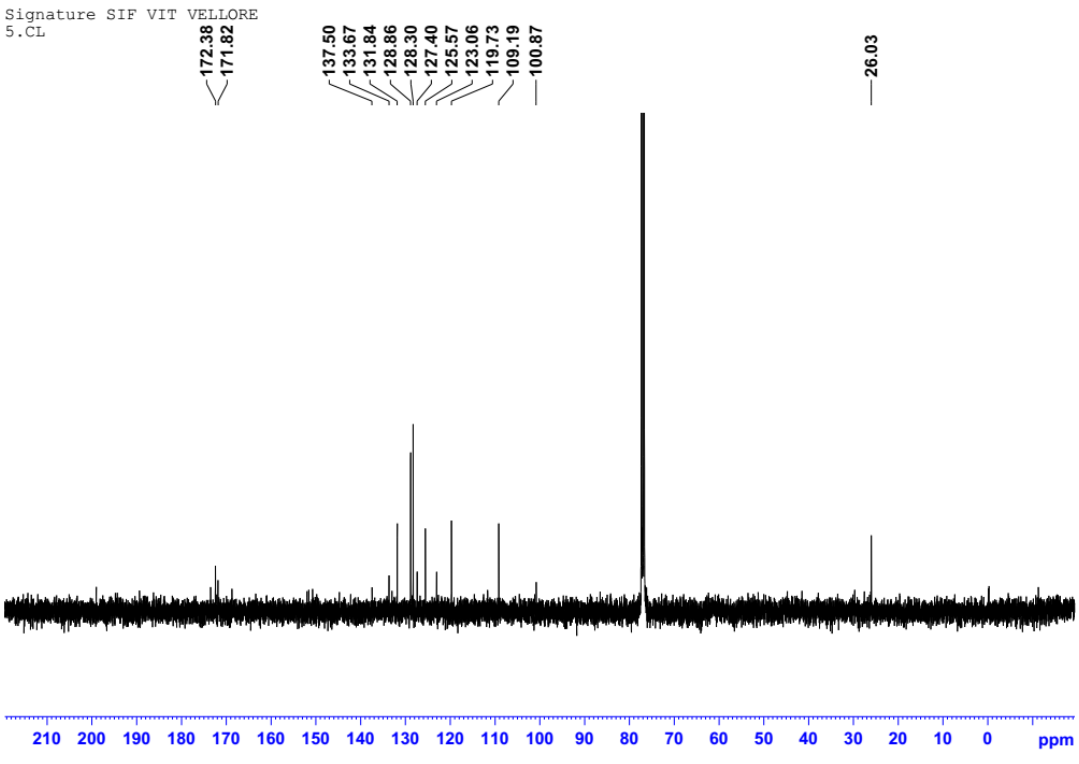
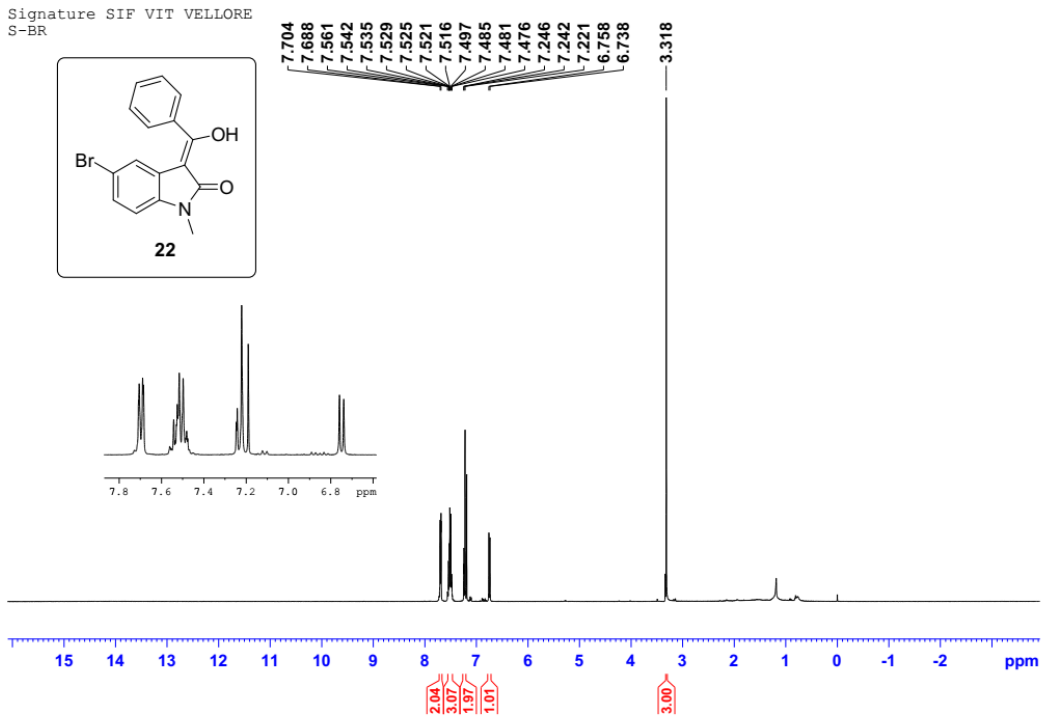
-121.15
0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 ppm

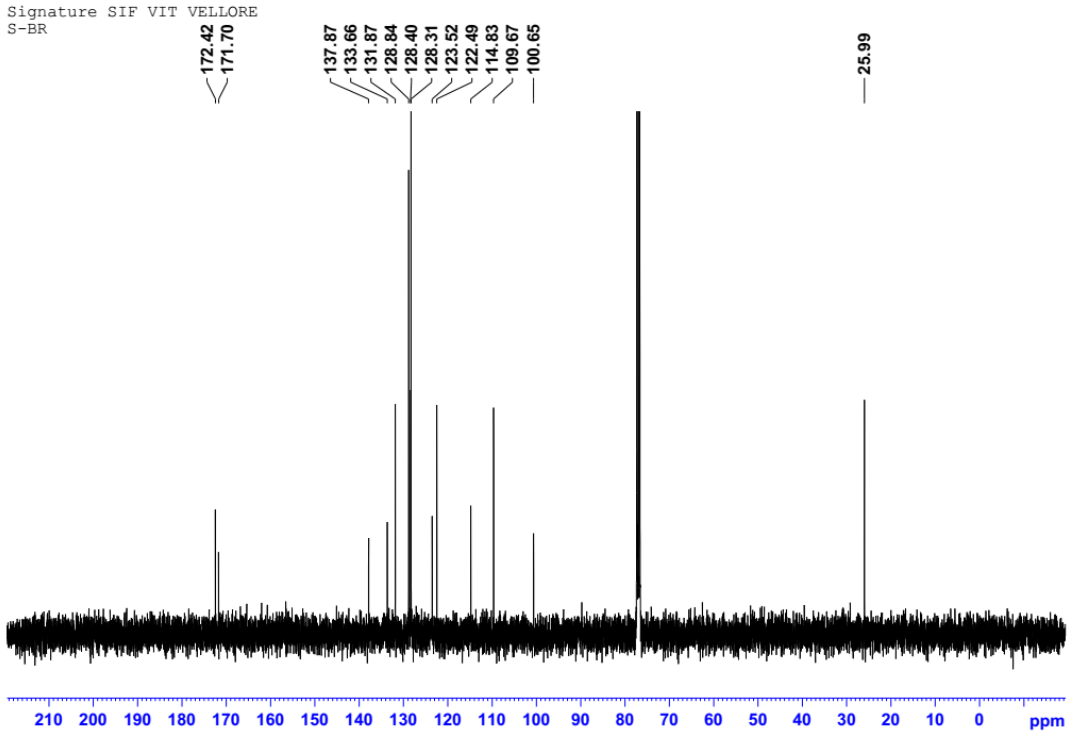
^{1}H and ^{13}C NMR spectrum of **21**



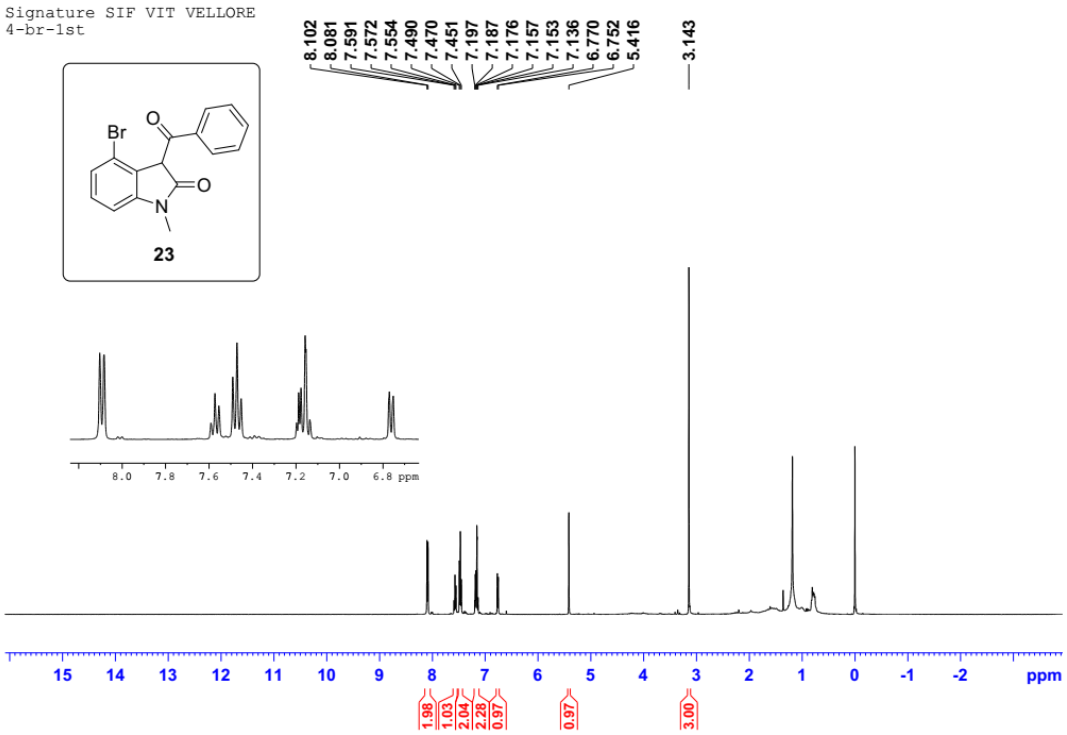


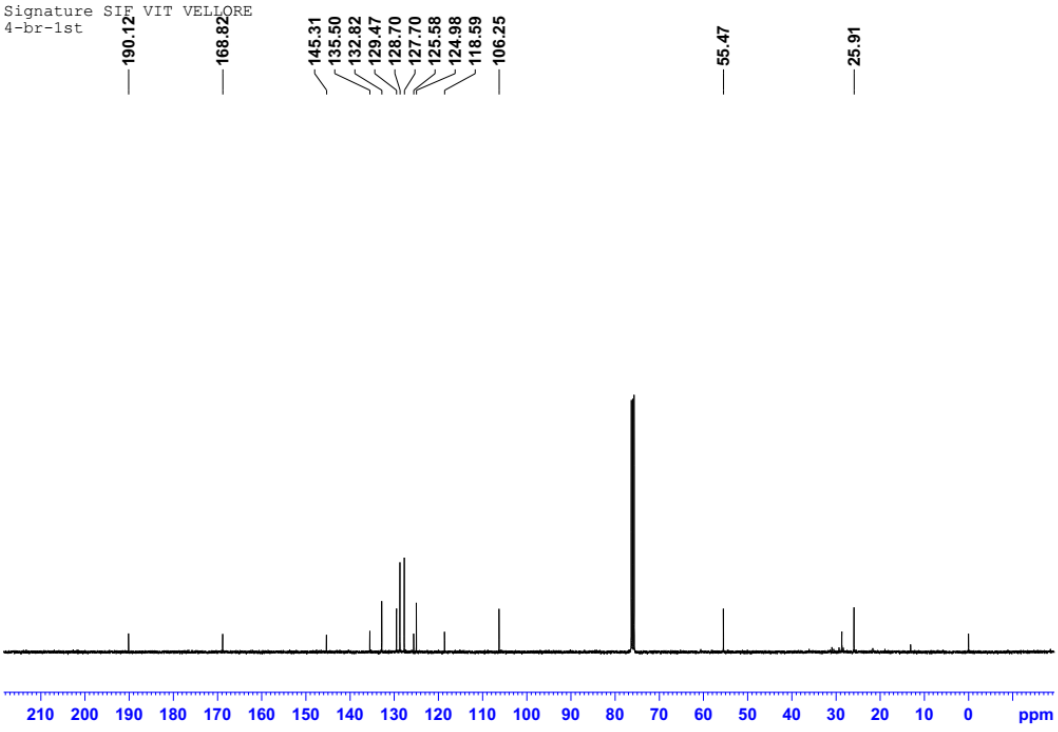
^{1}H and ^{13}C NMR spectrum of **22**



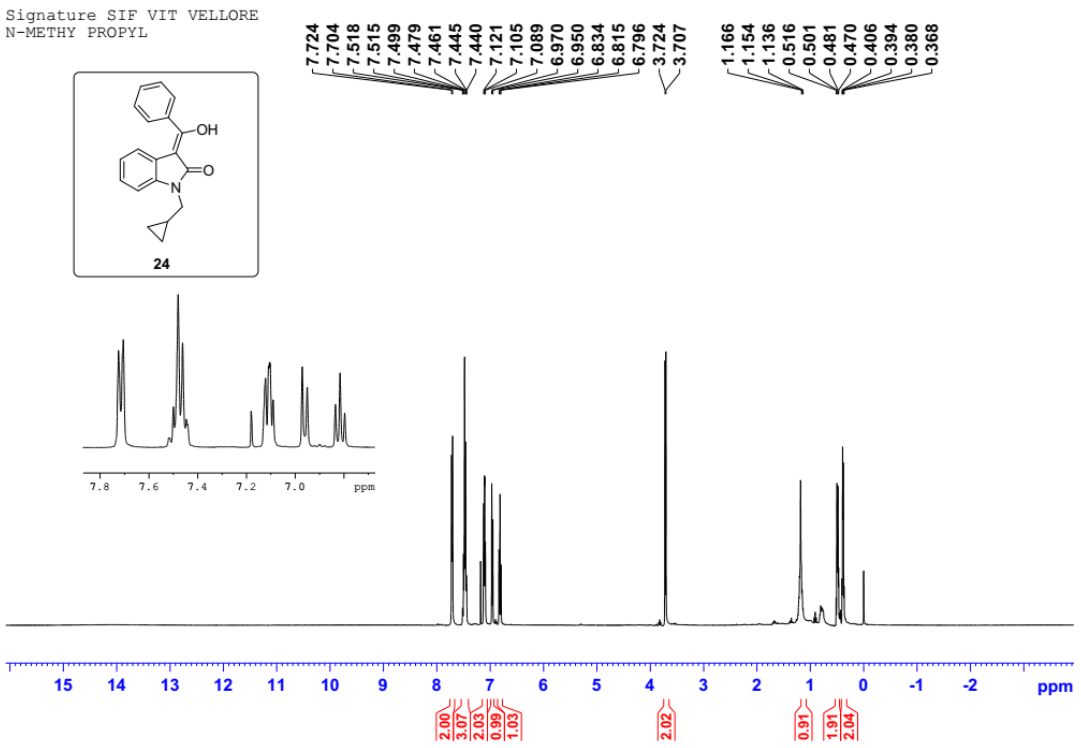


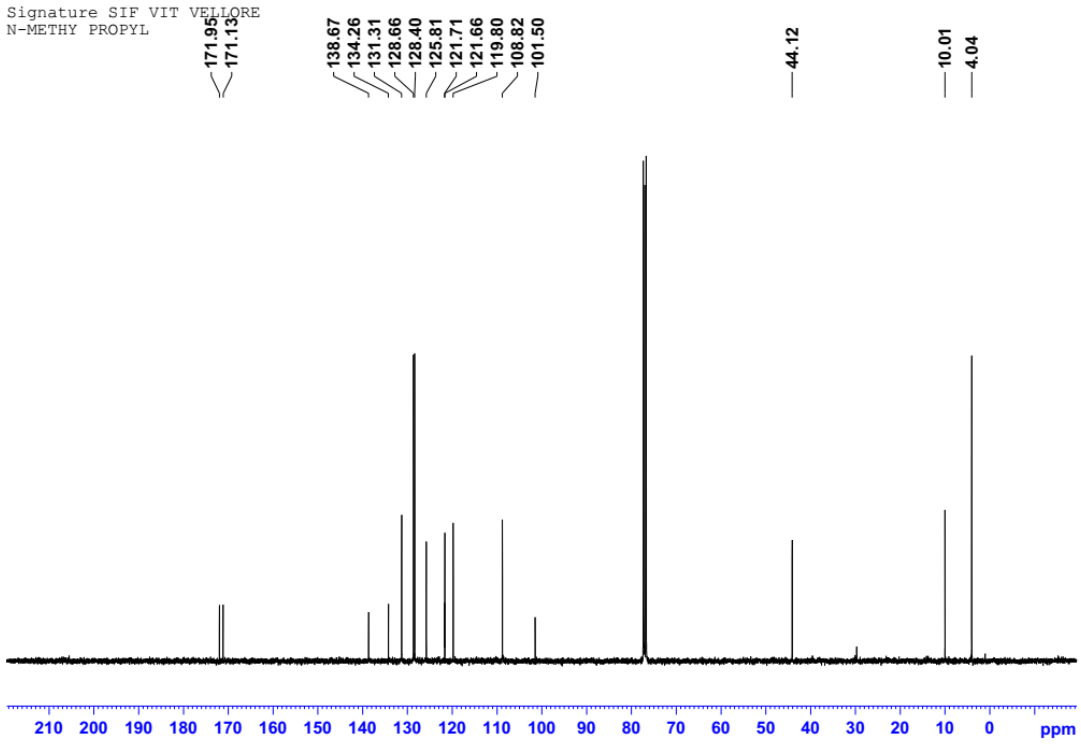
^{1}H and ^{13}C NMR spectrum of **23**



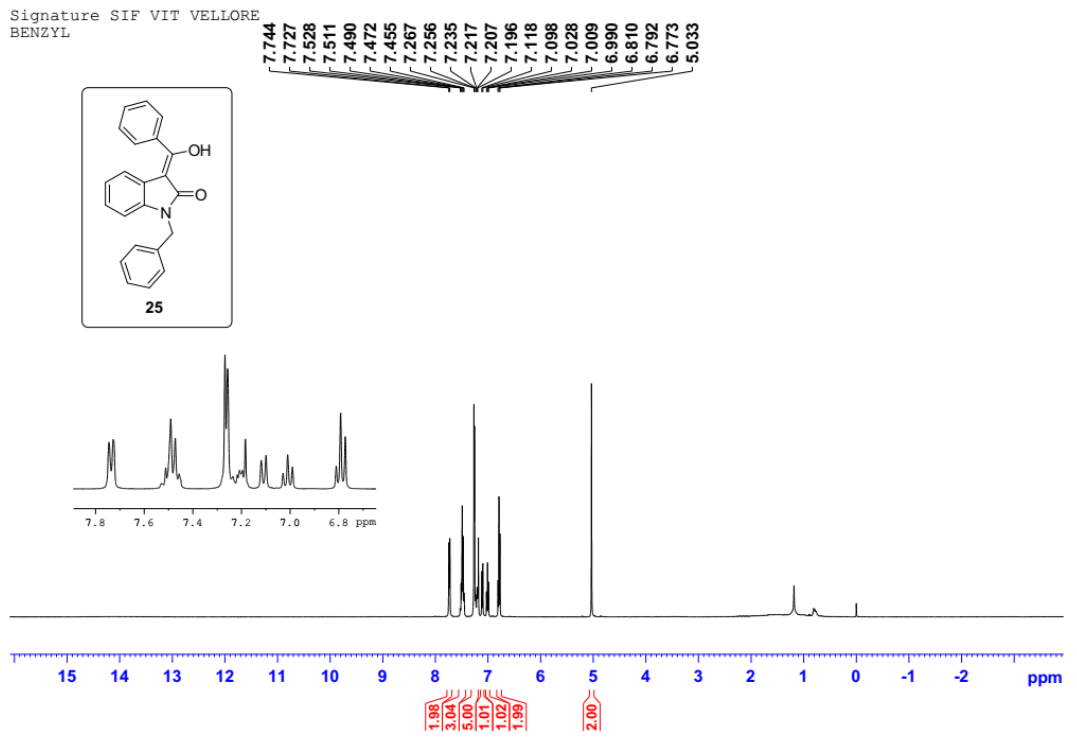


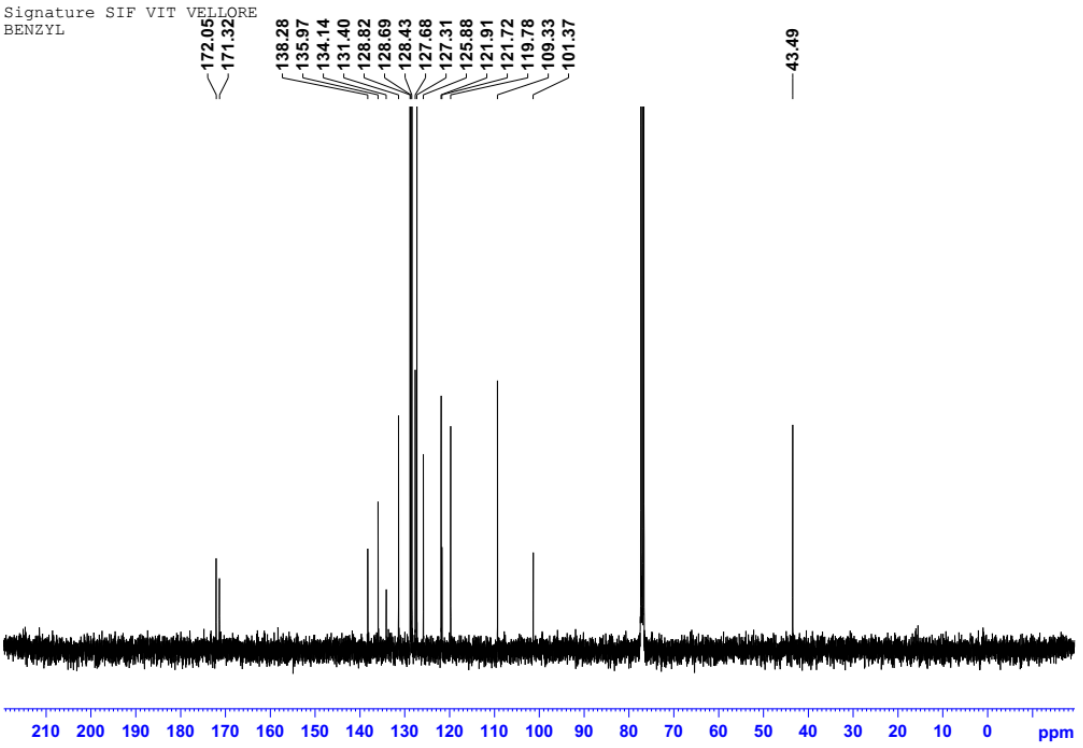
^{1}H and ^{13}C NMR spectrum of **24**



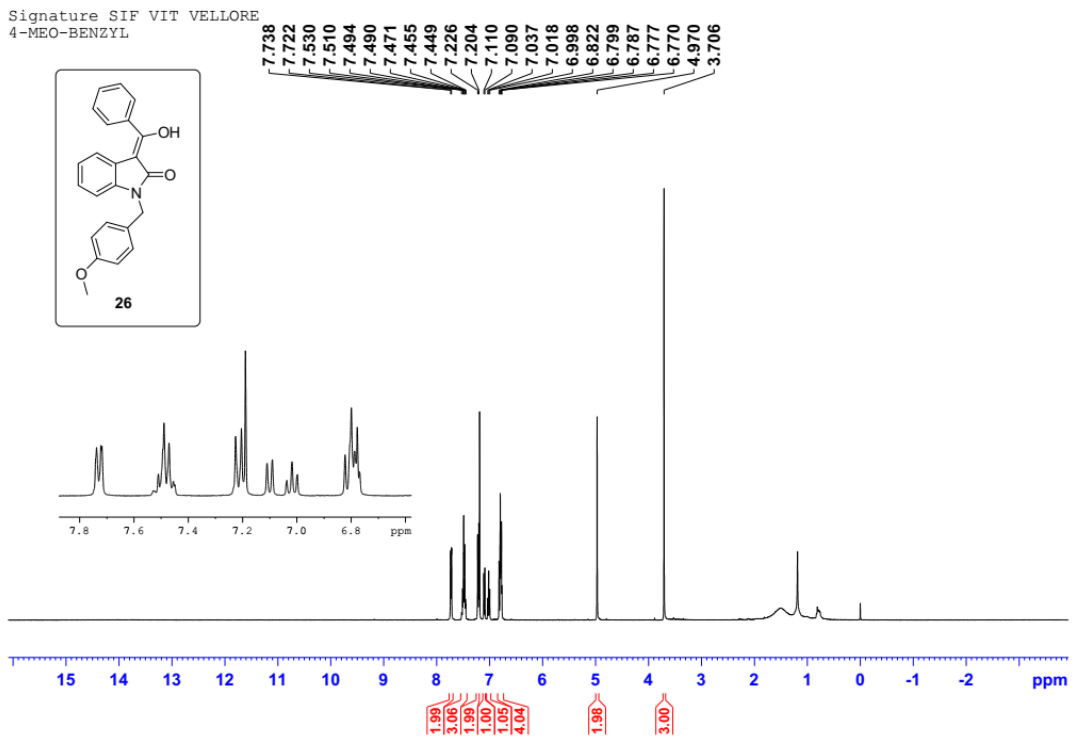


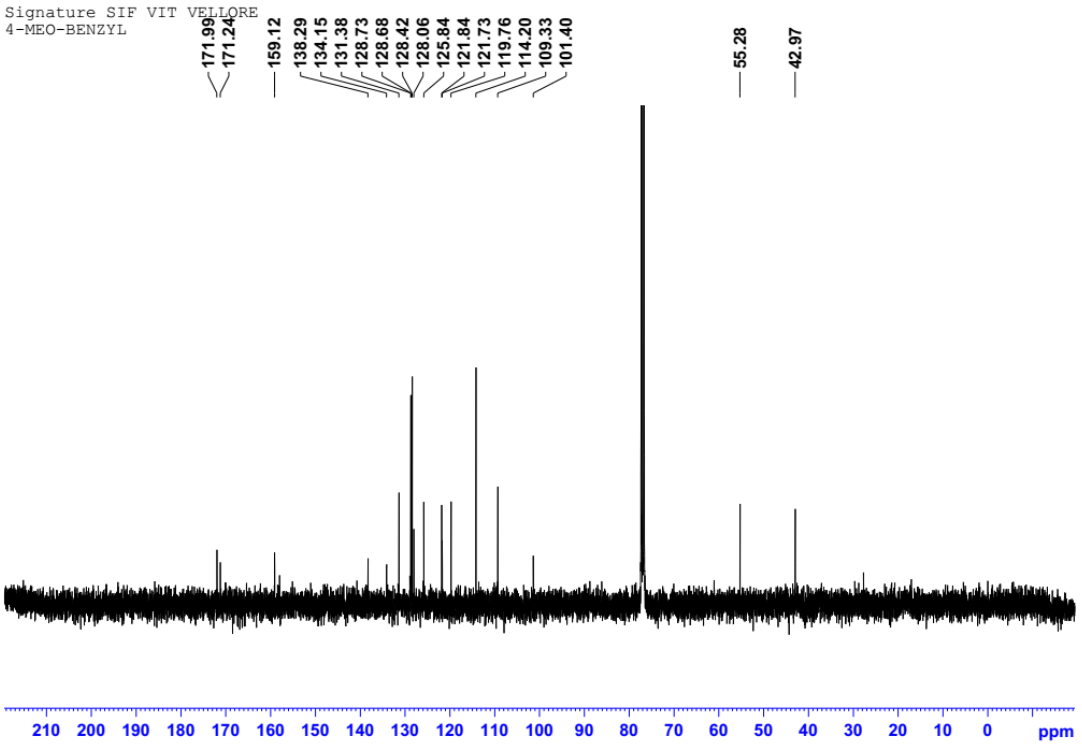
^{1}H and ^{13}C NMR spectrum of **25**



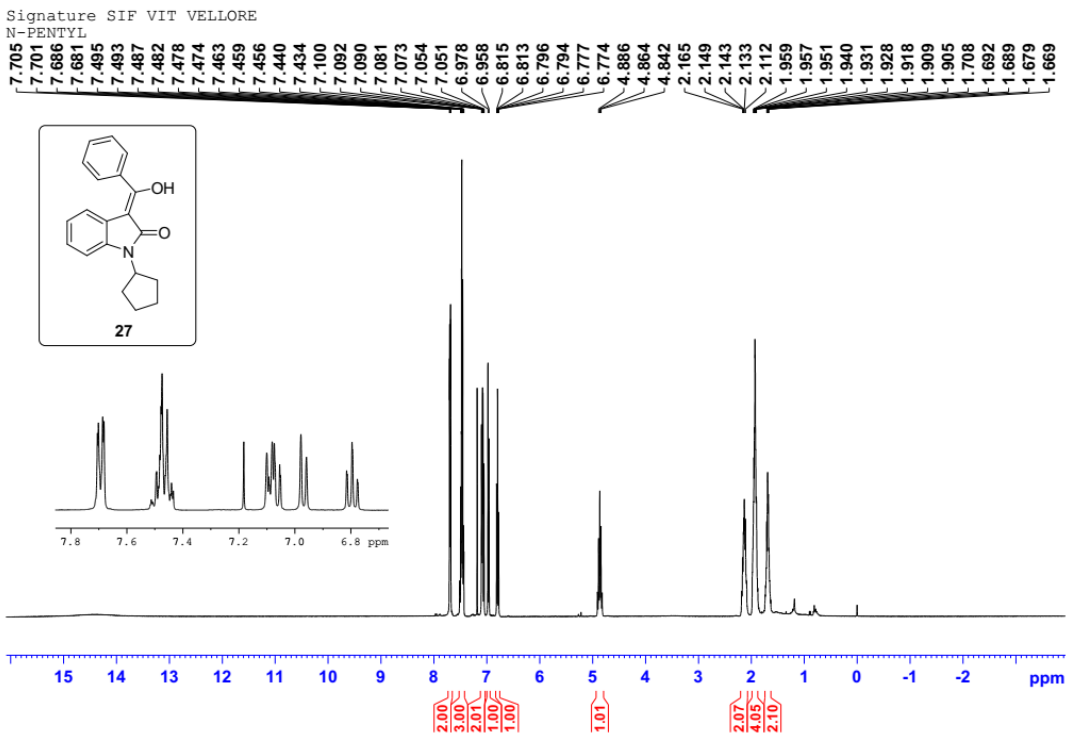


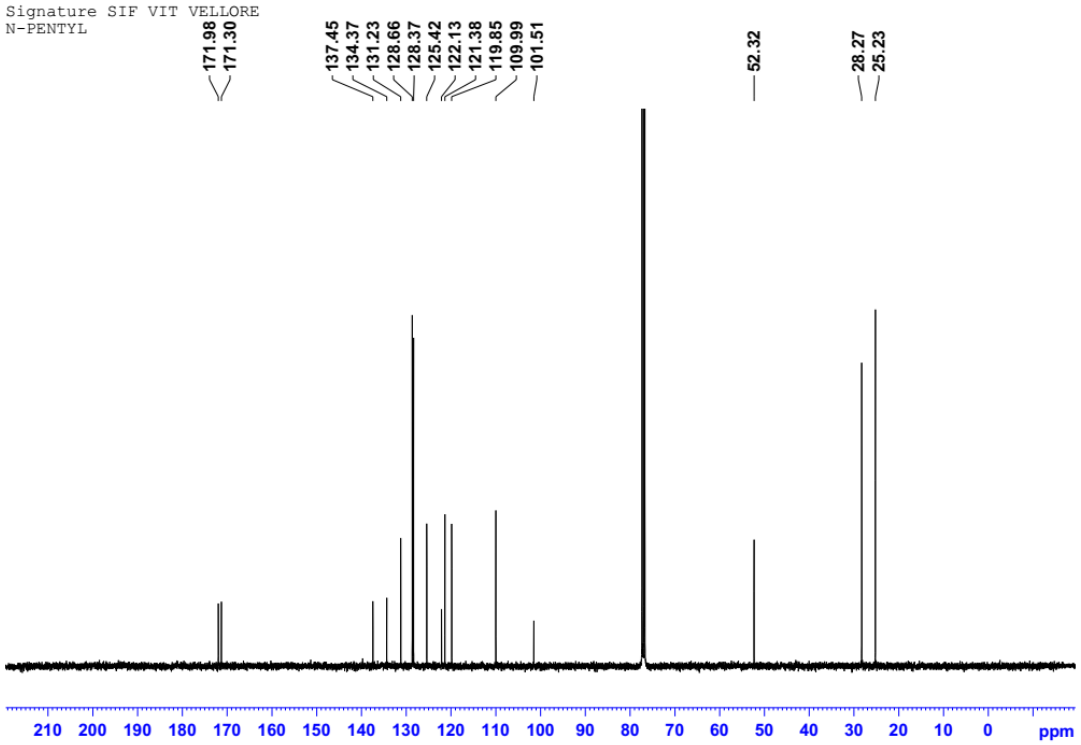
^{1}H and ^{13}C NMR spectrum of **26**



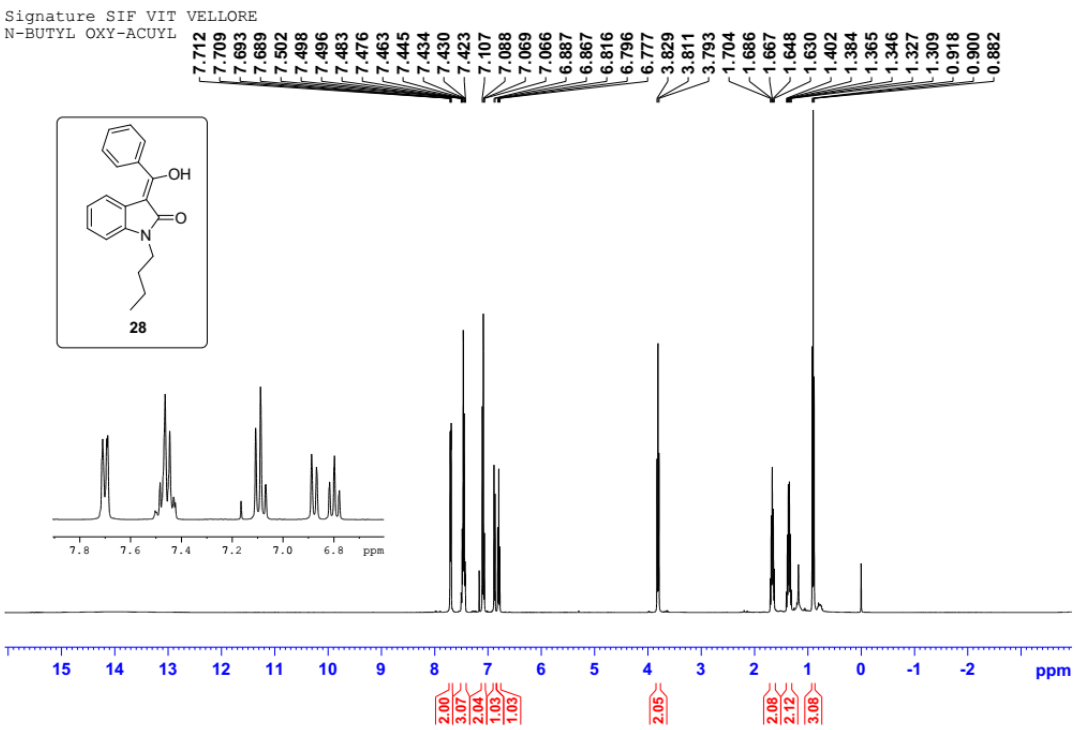


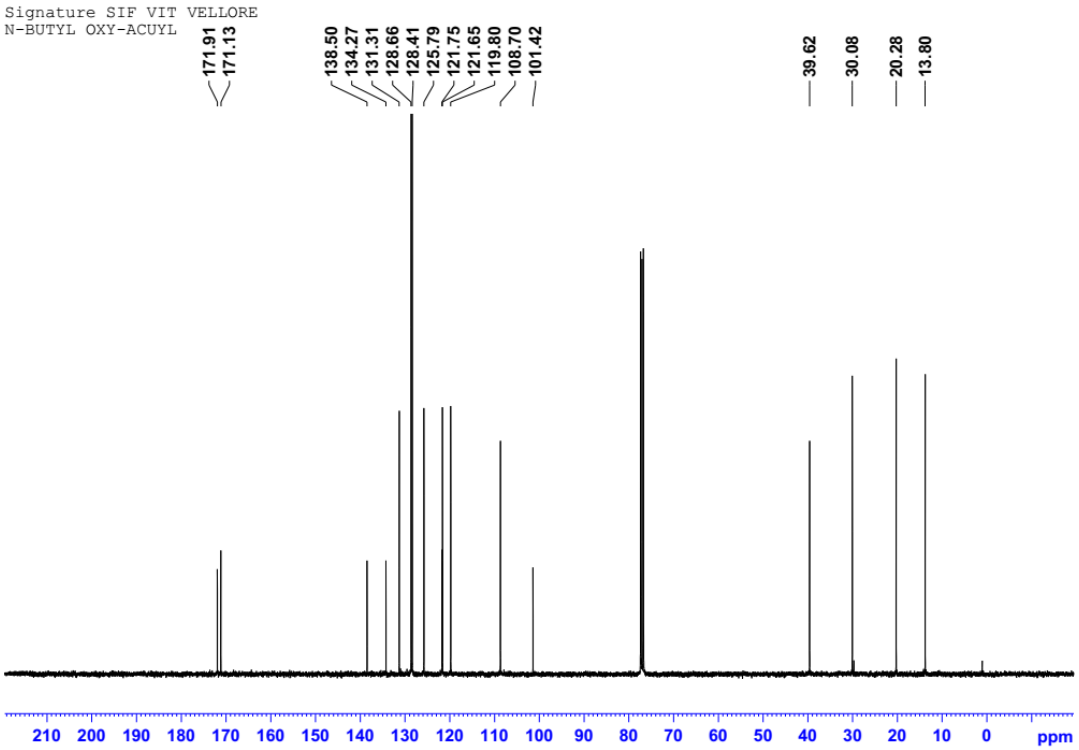
^{1}H and ^{13}C NMR spectrum of **27**



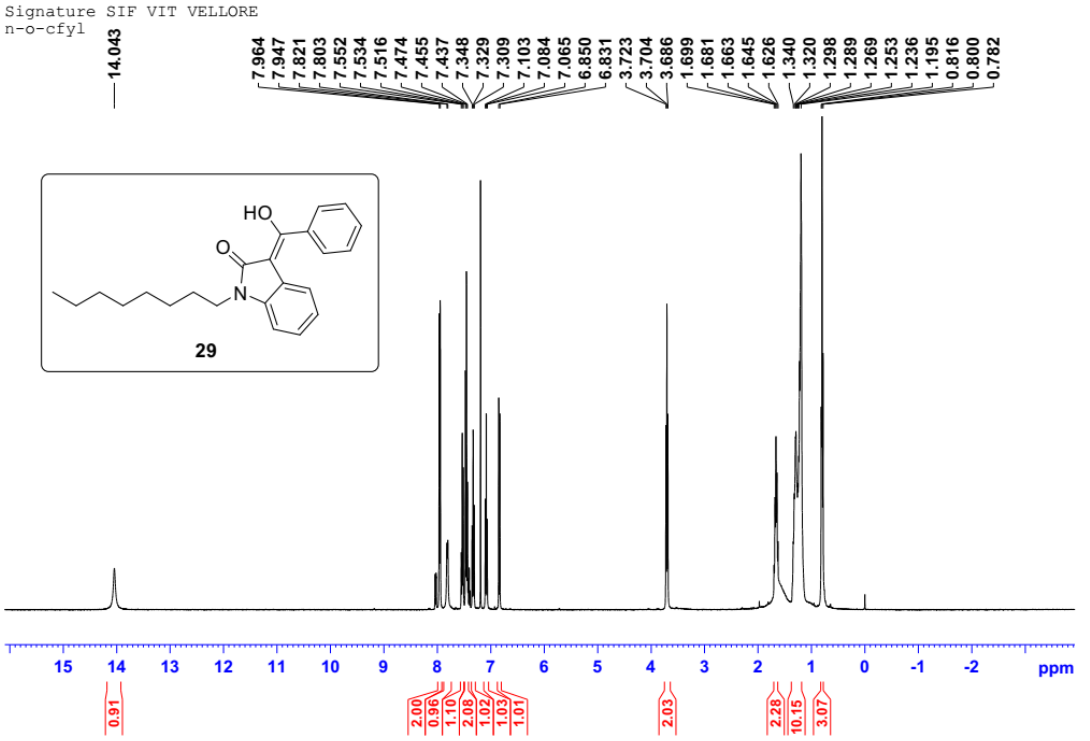


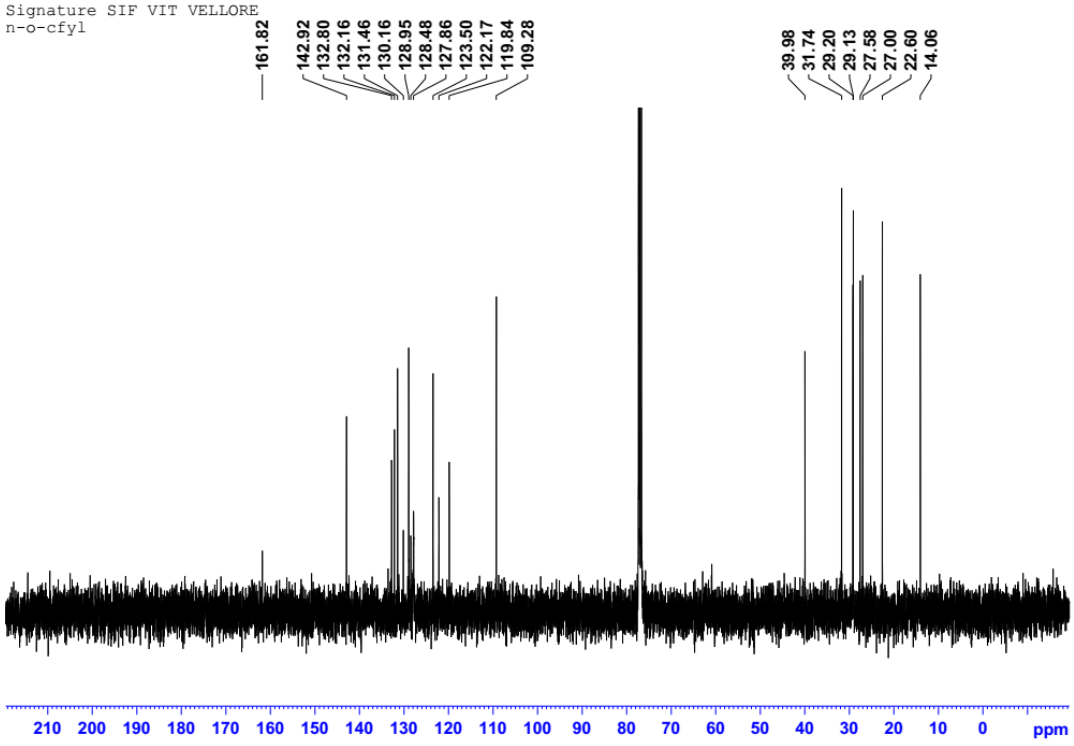
^{1}H and ^{13}C NMR spectrum of **28**



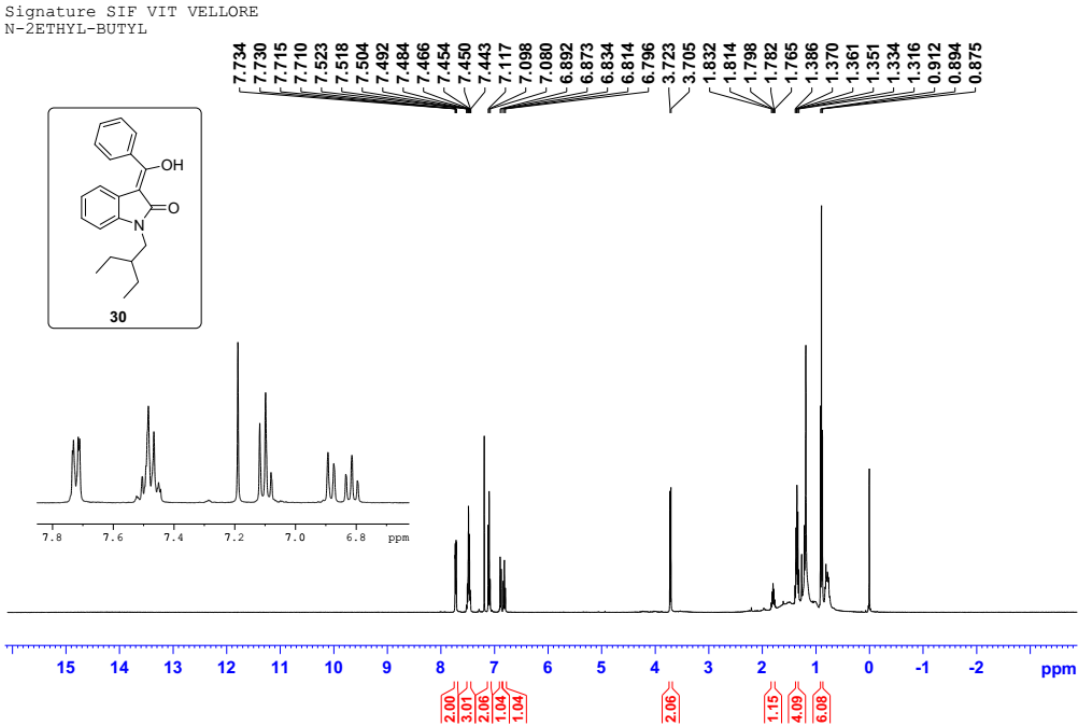


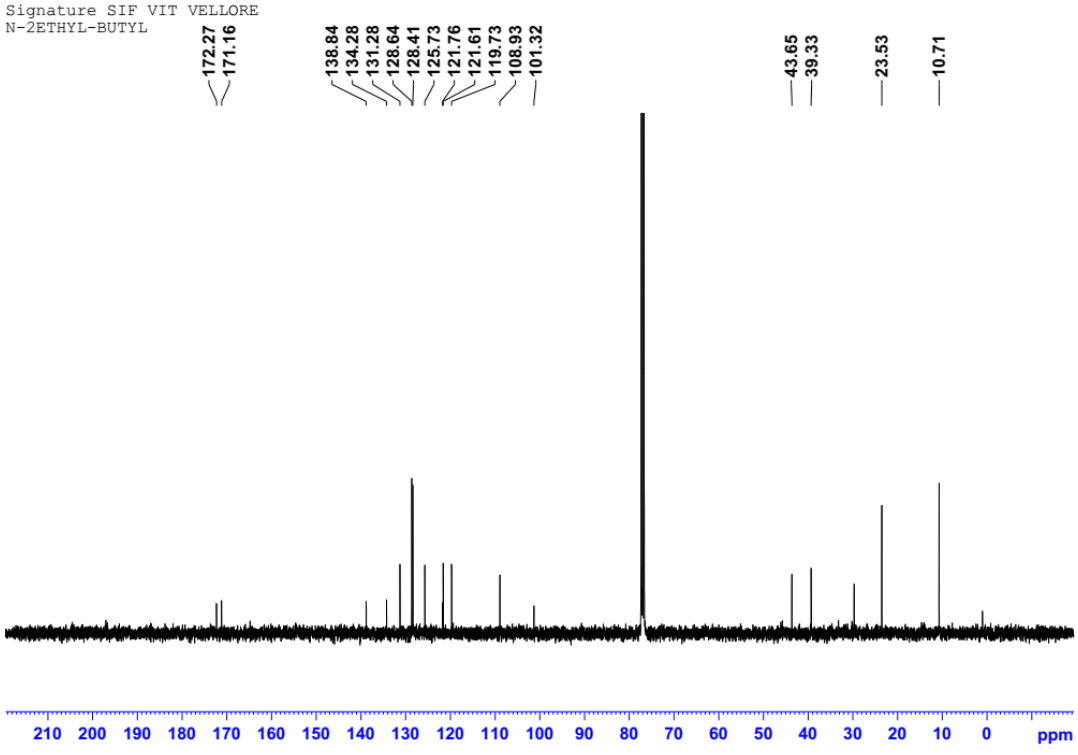
^{1}H and ^{13}C NMR spectrum of **29**



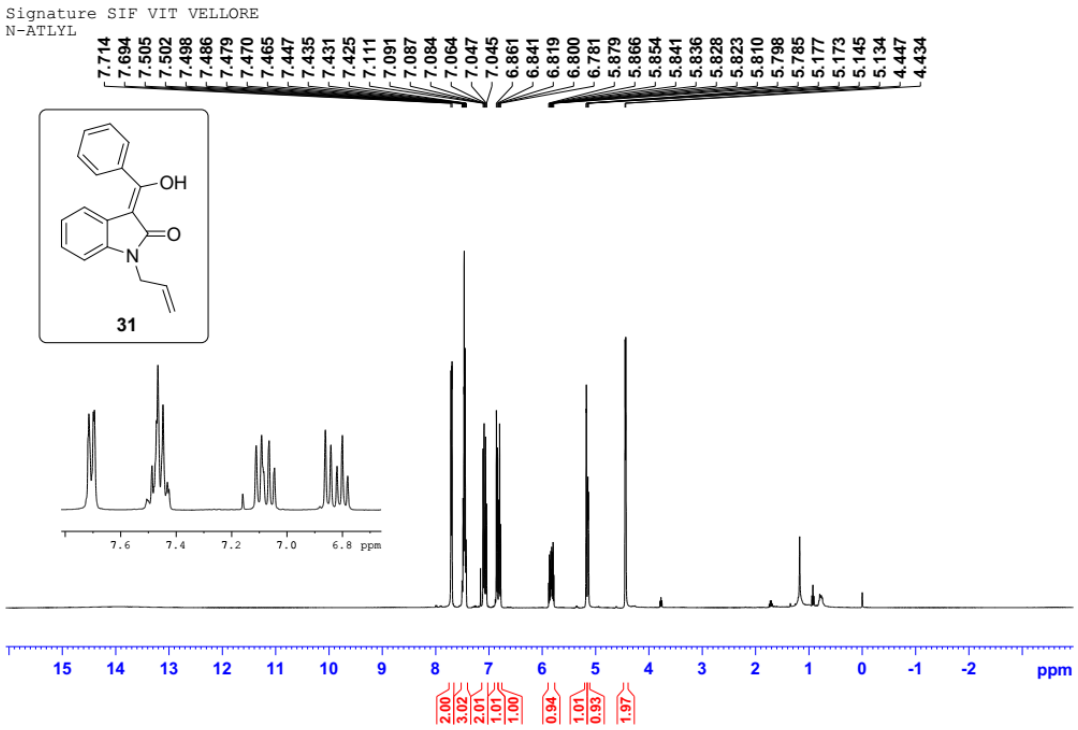


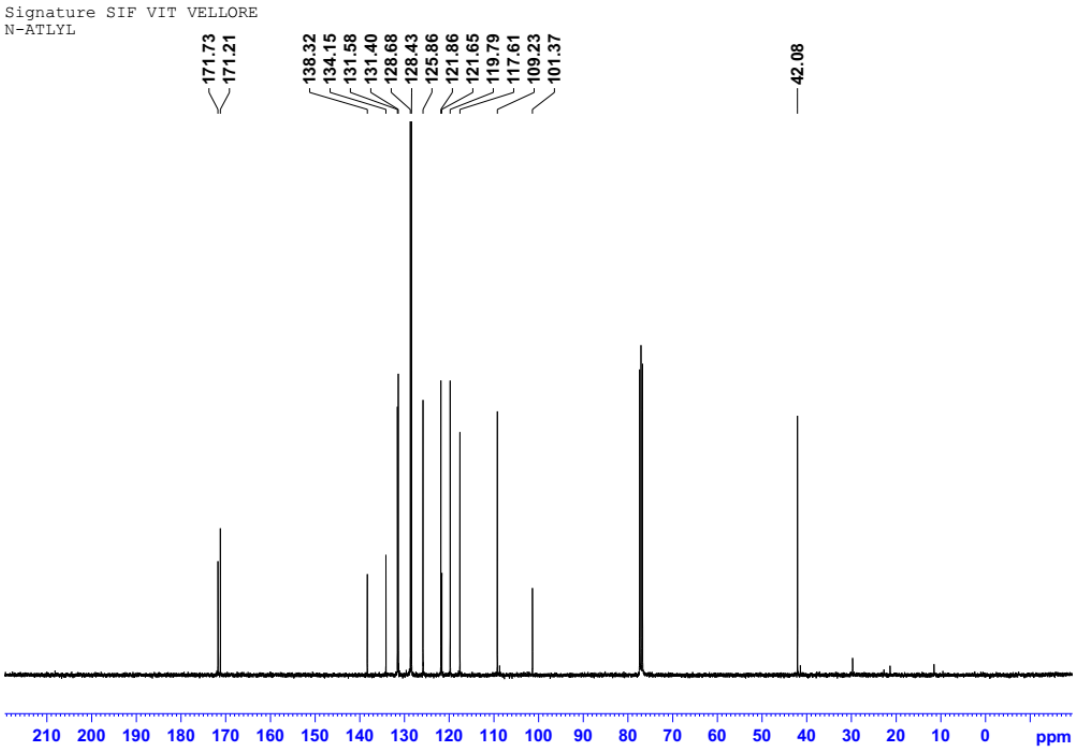
^{1}H and ^{13}C NMR spectrum of **30**



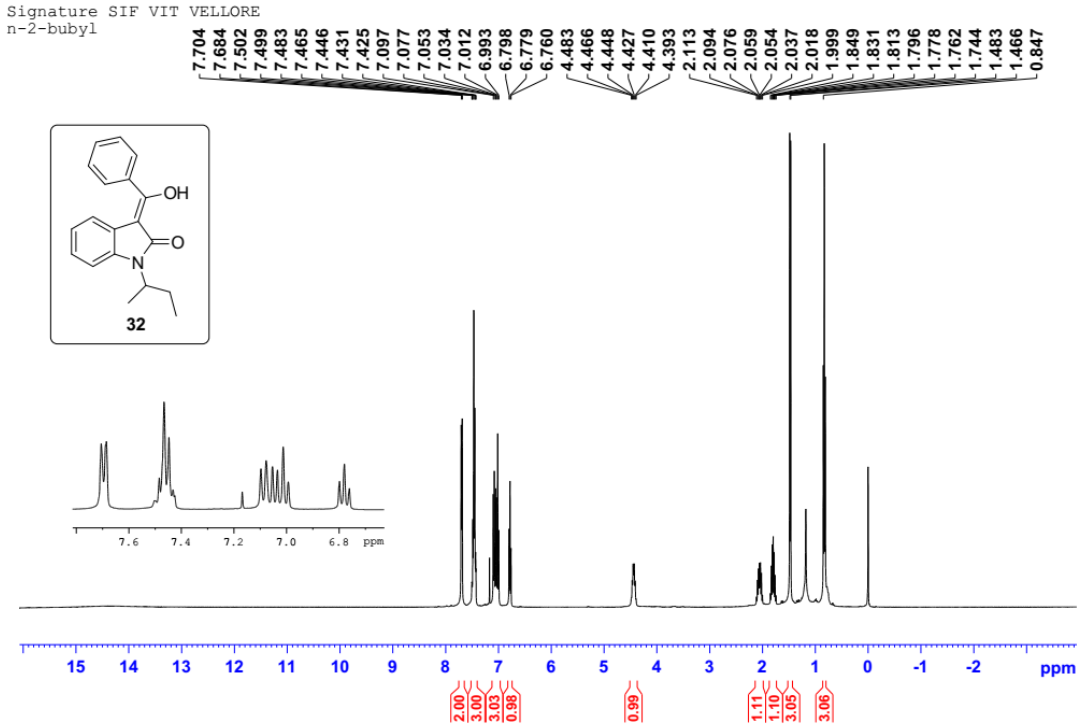


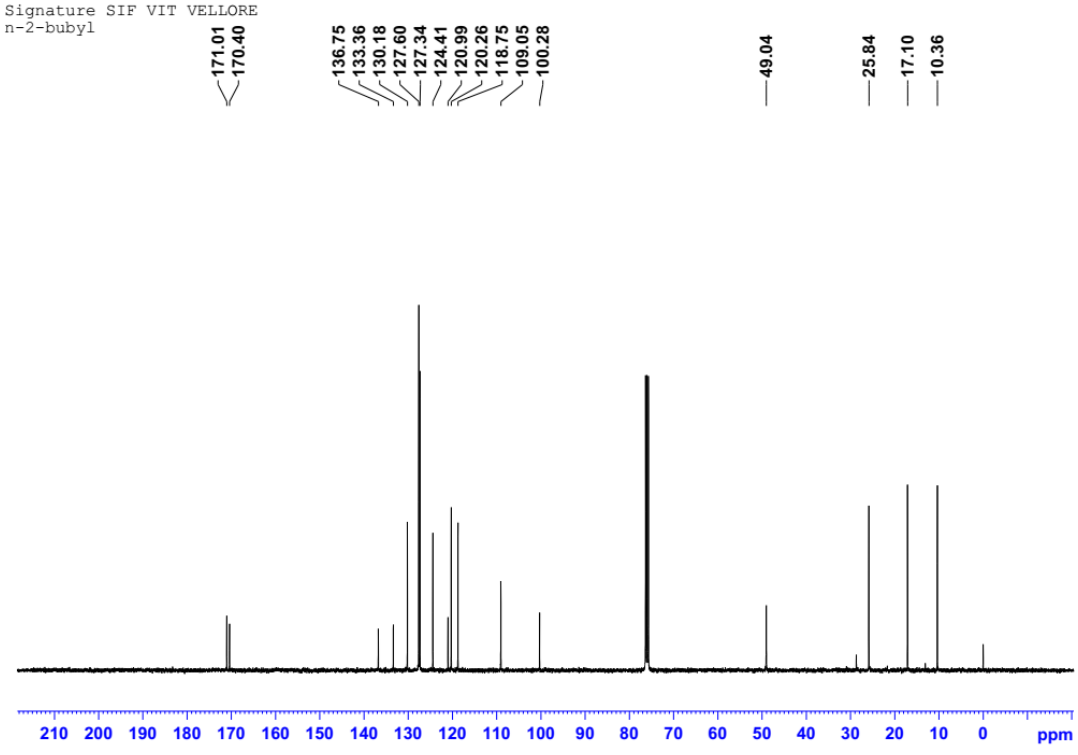
^{1}H and ^{13}C NMR spectrum of **31**





^{1}H and ^{13}C NMR spectrum of **32**





^{1}H and ^{13}C NMR spectrum of **36**