Supporting Information

Regioselective synthesis of functionalized dihydroisoquinolines from *o*-alkynylarylaldimines via Reformatsky Reaction

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1. X-ray crystal structure

1.1 X-ray crystal structure data of (3a)

The single crystal X-ray data [S1] of the given compound was collected on an Oxford Xcalibur CCD diffractometer using graphite monochromated MoK α-radiation (λ = 0.71073Å) at 293(2) K. The multi-scan correction was applied to it. The structure was solved by the direct method using SIR-92 and refined by full matrix least-square refinement technique on F[1] using SHELXL97.[2] The hydrogen atom were placed into the calculated position and included in the last cycle of the refinement. All the calculations were done using Win GX software package.[3] The main crystallographic data and structural refinement details of **3a** and **3m** are given in Table S1 & S2 respectively. Atomic coordinates, bond lengths, bond angles, and thermal parameters for compound **3a** and **3m** have been deposited at the Cambridge Crystallographic Data Centre (CCDC, deposit no.1062612 and 1420734)

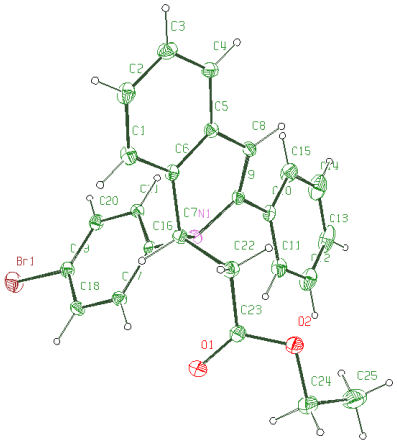


Fig. 1s. X-ray crystallographic ORTEP diagram of compound **3a**

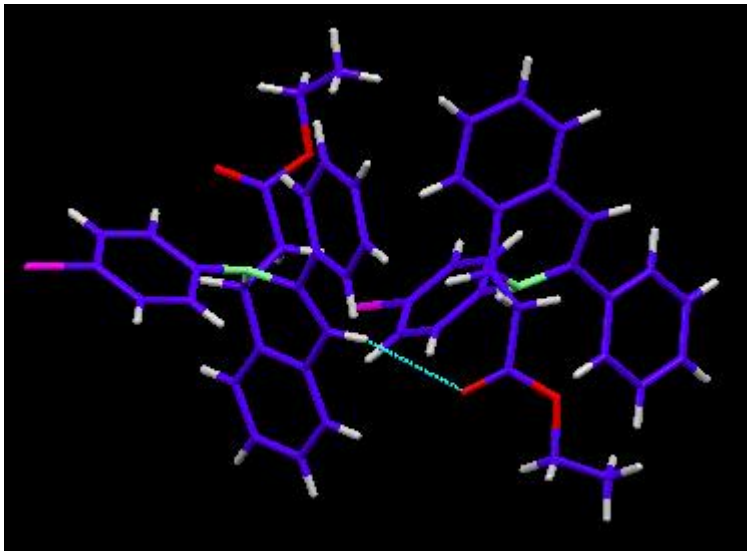


Fig. 2s. Hydrogen bonding in the crystal lattice of **(3a)**.

Table S1. Crystal data and structure refinement for 3a.

Empirical Formula	$C_{25}H_{22}Br_1N_1O_2$
Formula Weight	448.35
Temperature	293(2) K
Wavelength	0.71073Å
Crystal system	Monoclinic
Space group	*I 2/a*
a [Å]	20.6230(12)
b [Å]	11.9083(4)
c [Å]	17.8031(7)
α [°]	90.00
β [°]	97.506
λ [°]	90.00
Volume [$Å^{3]}$	4334.7(3)
Z	8
Density (calculated) [Mg/m^3]	1.374
Absorption coefficient [mm^{-1}]	1.917
F(000)	1840
Crystal size [mm^3]	0.05 x 0.04 x 0.02
Theta range for data collection [°]	2.94 to 25.00
Index ranges	$-24 \leq h \leq 24$, $-14 \leq k \leq 12$, $-21 \leq l \leq 21$
Reflections collected / unique	16314 / 3823

R(int)	0.0584
Completeness of Theta at 25 °C (%)	99.8
Absorption Correction	Semi-empirical from equivalents
Max. and Min. transmission	25.00 and 3.00
Refinement method	Full-matrix least square on F^2
Data/ restraints/ parameters	3823/0/266
Goodness-of-fit on F^2	1.035
Final R indices [I>2sigma (I)][a,b]	R_1 = 0.0669, $^wR_2$ = 0.1346
R indices (all data)	R_1 = 0.1130, $^wR_2$ = 0.1536
Largest diff. peak and hole [$Å^{-3}$]	0.456 and -0.333 e.$Å^{-3}$

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

1.2 X-ray crystal structure data (3m)

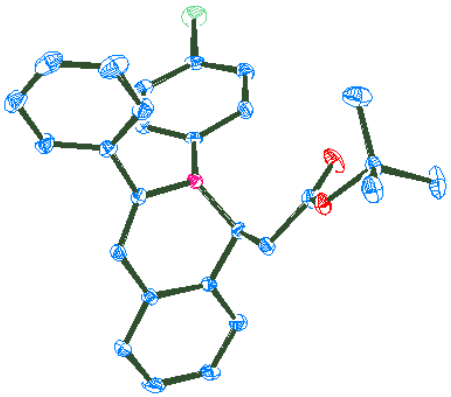


Fig. 3s. X-ray crystallographic ORTEP diagram of compound **3m**

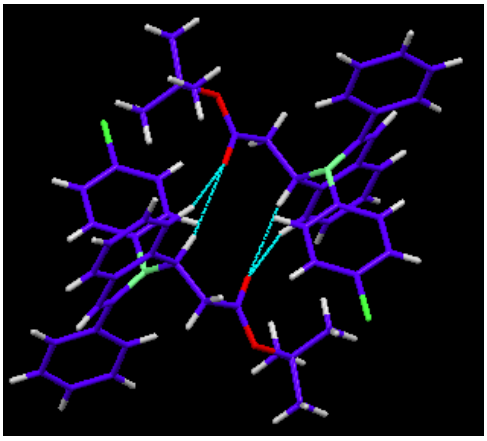


Fig. 4s. Hydrogen bonding in the crystal lattice of **(3m)**.

Table S2. Crystal data and structure refinement for (3m).

Empirical Formula	$C_{27}H_{26}Cl_1N_1O_2$
Formula Weight	431.94
Temperature	293(2) K
Wavelength	0.71073Å
Crystal system	Triclinic
Space group	*P -1*
a [Å]	11.187(5)
b [Å]	19.602(5)
c [Å]	21.429(5)
α [°]	89.988(5)
β [°]	89.828(5)
λ [°]	90.021(5)
Volume [$Å^{3]}$	4699 (3)
Z	8

Density (calculated) [Mg/m^3]	1.221
Absorption coefficient [mm^{-1}]	0.185
F(000)	1824
Crystal size [mm^3]	0.05 x 0.04 x 0.02
Theta range for data collection [°]	3.04 to 25.00
Index ranges	$-13 \leq h \leq 13$, $-23 \leq k \leq 23$, $-16 \leq l \leq 25$
Reflections collected / unique	24698 / 13207
R(int)	0.0252
Completeness of Theta at 25 °C (%)	79.7
Absorption Correction	Semi-empirical from equivalents
Refinement method	Full-matrix least square on F^2
Data/ restraints/ parameters	13207/0/1117
Goodness-of-fit on F^2	0.740
Final R indices [I>2sigma (I)][a,b]	$R_1 = 0.0596$, $^{w}R_2 = 0.1870$
R indices (all data)	$R_1 = 0.0979$, $^{w}R_2 = 0.2280$
Largest diff. peak and hole [$Å^{-3}$]	0.459 and -0.234 $e.Å^{-3}$

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

References:

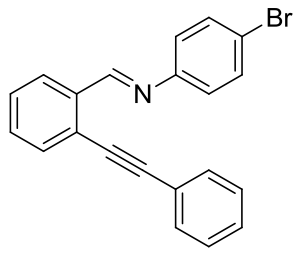
1. G.M. Sheldrick, *ActaCrystallogr., Sect. A*, **1990**,*46*, 467.
2. G.M. Sheldrick, *SHELXL-97, Computer program for crystal structure refinement*University of Göttingen, Germany, **1997**.
3. L. J. Farrugia, WinGX Version 1.80.05, *An integrated system of Windows Programsfor the Solution, Refinement and Analysis of Single Crystal X-Ray Diffraction Data;*Department of Chemistry, University of Glasgow (**1997-2009**).

References

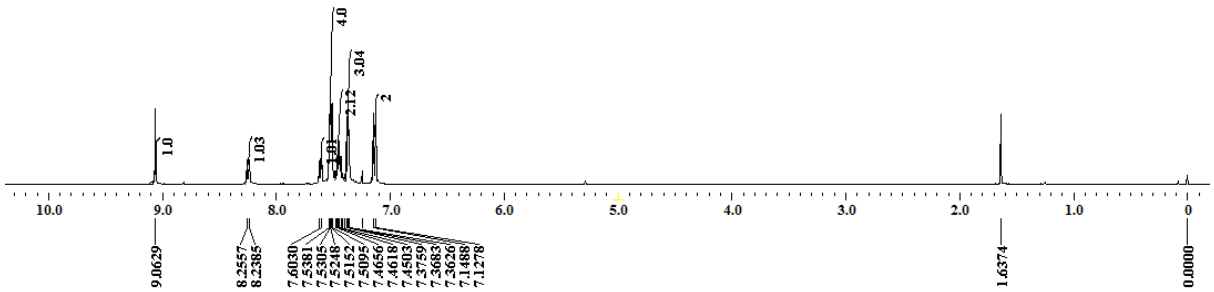
[S1]. CCDC. 1062612 (**3a**) and 1420734 (**3m**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

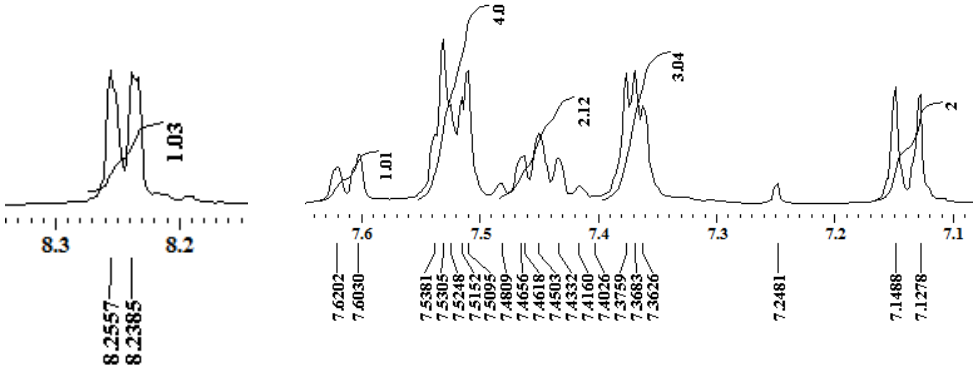
2. ^{1}H, ^{13}C NMR and HRMS spectra of compounds 1a-1n:

^{1}H NMR in $CDCl_3$

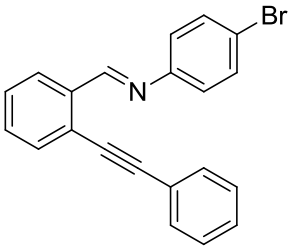


(*E*)-4-Bromo-*N*-(2-(phenylethynyl)benzylidene)aniline (**1a**)

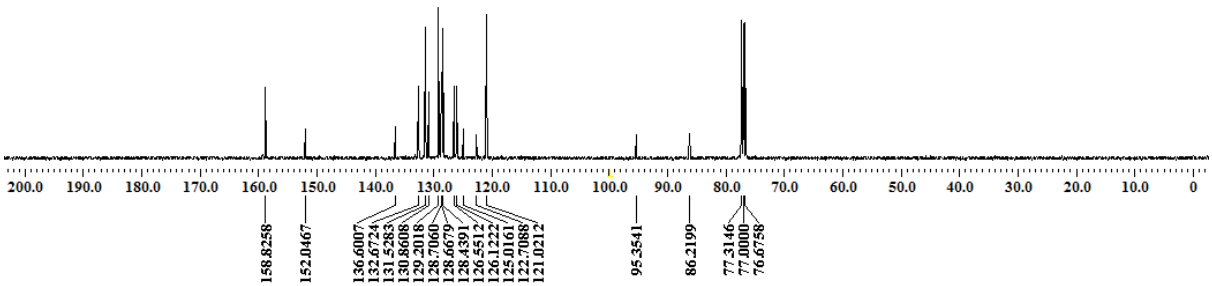


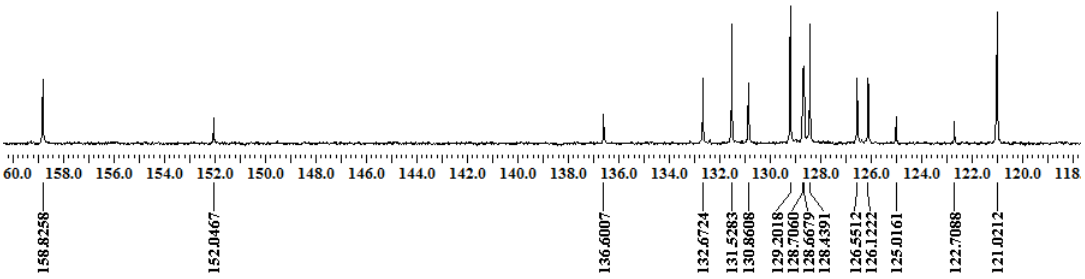


^{13}C NMR in $CDCl_3$

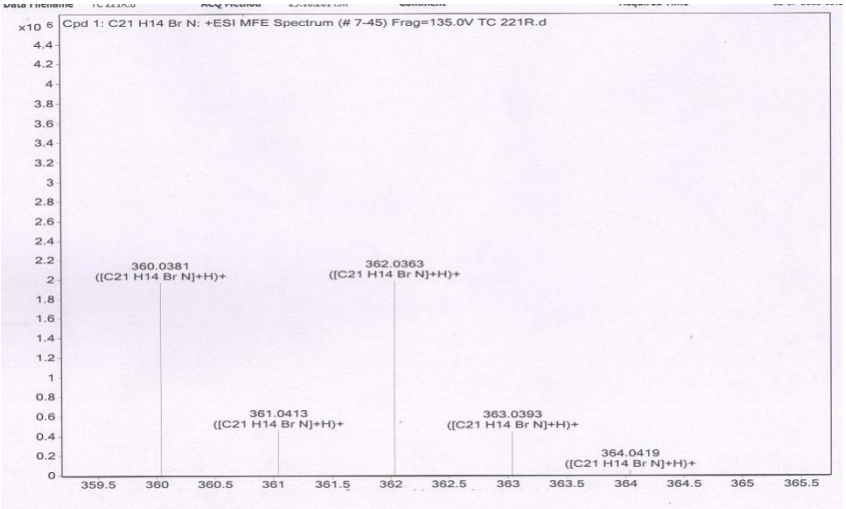


(*E*)-4-Bromo-*N*-(2-(phenylethynyl)benzylidene)aniline (**1a**)

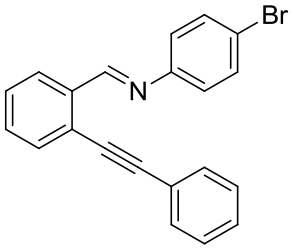




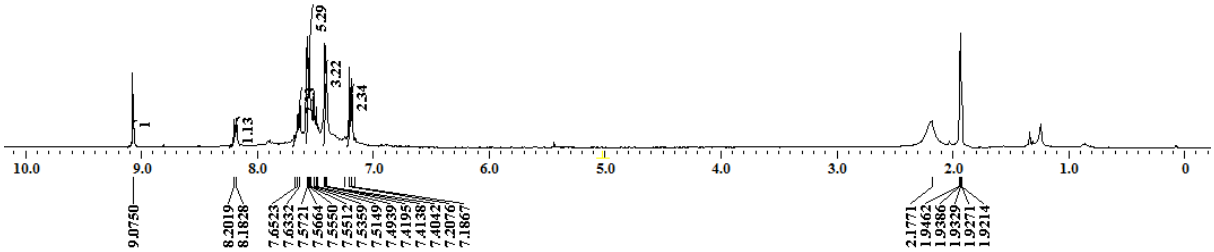
HRMS: (E)-4-Bromo-N-(2-(phenylethynyl)benzylidene)aniline **(1a)**

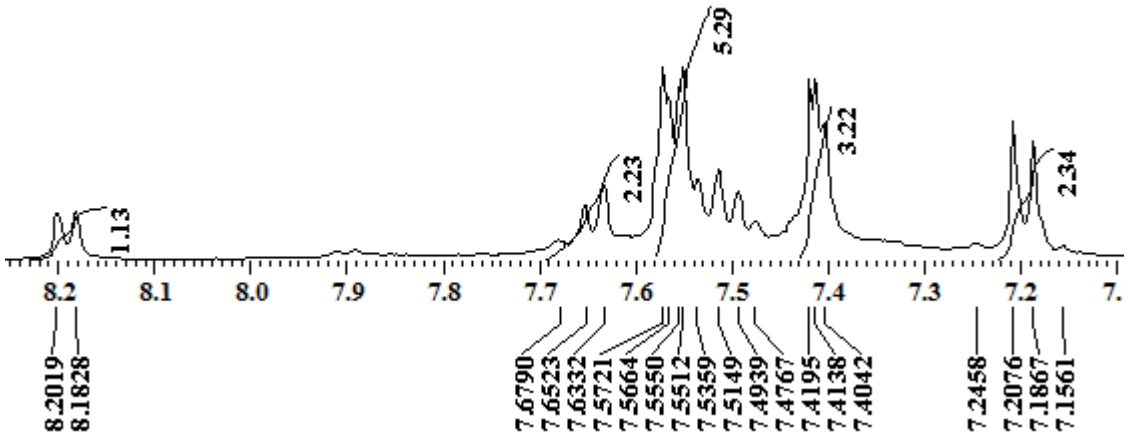


^{1}H NMR in CD_3CN

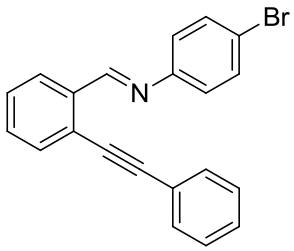


(*E*)-4-bromo-*N*-(2-(phenylethynyl)benzylidene)aniline (**1a**)

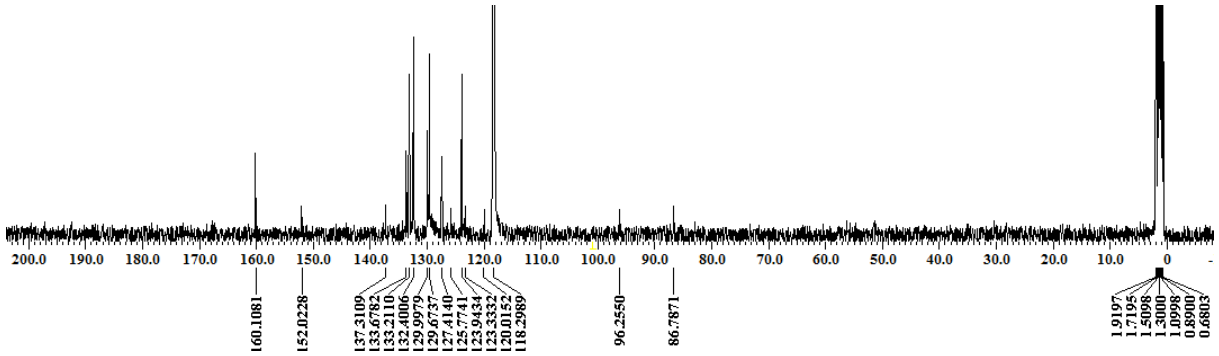


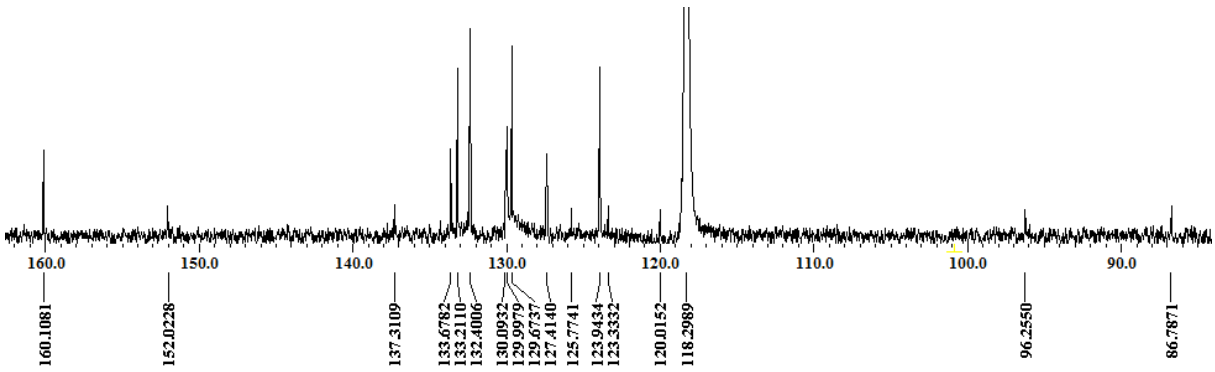


^{13}C NMR in CD_3CN

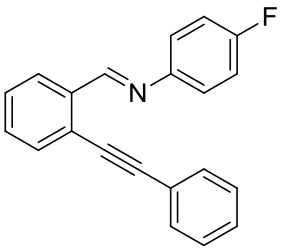


(*E*)-4-bromo-*N*-(2-(phenylethynyl)benzylidene)aniline (**1a**)

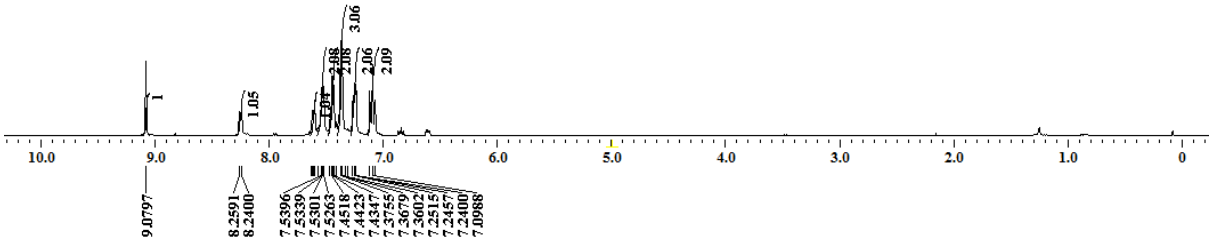


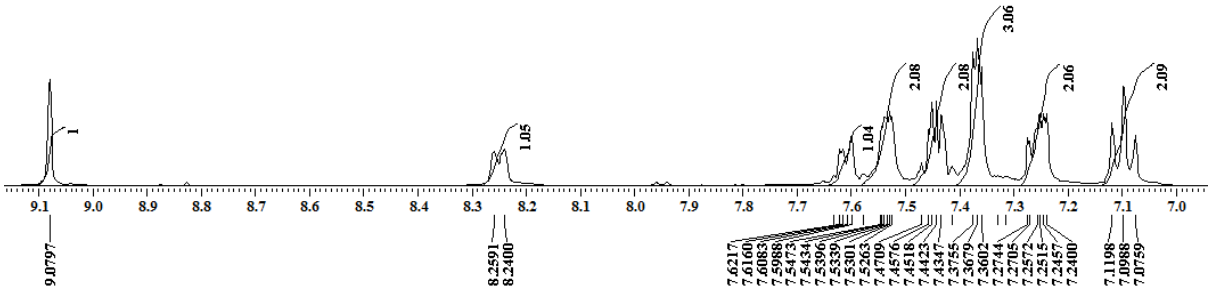


^{1}H NMR in $CDCl_3$

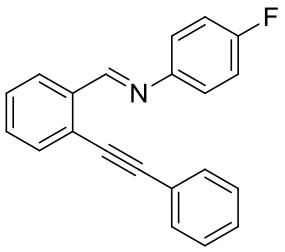


(*E*)-4-Fluoro-*N*-(2-(phenylethynyl)benzylidene)aniline **(1b)**

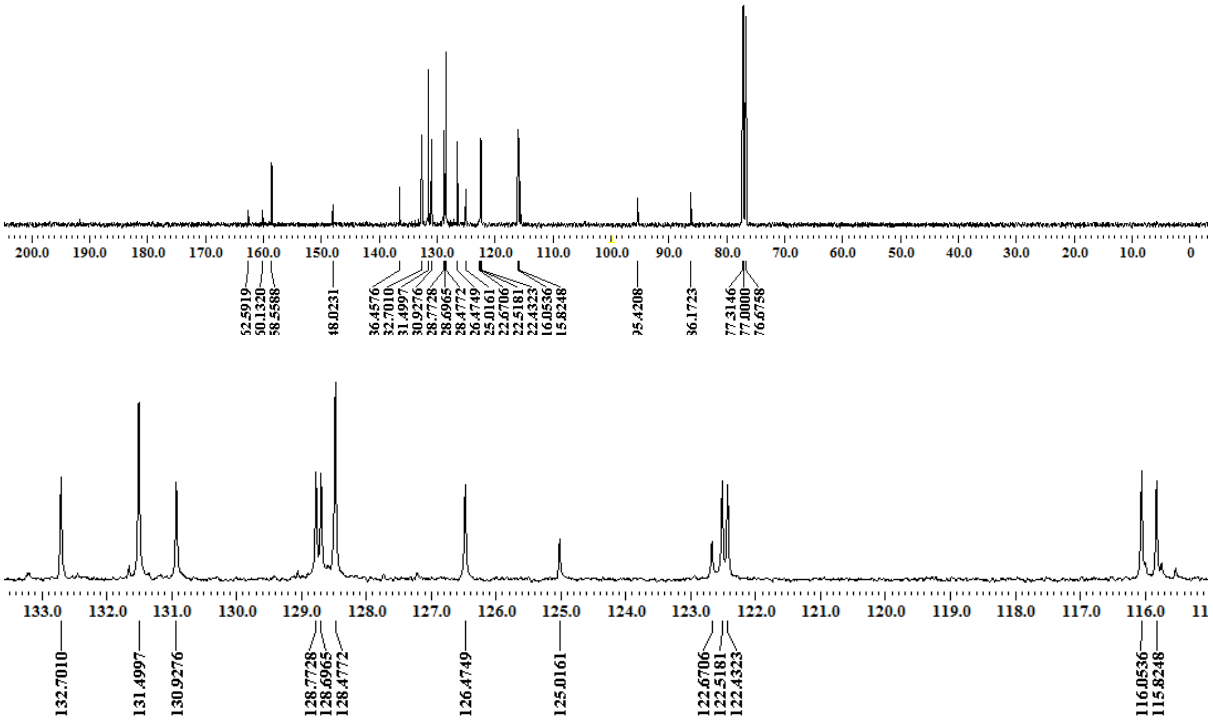




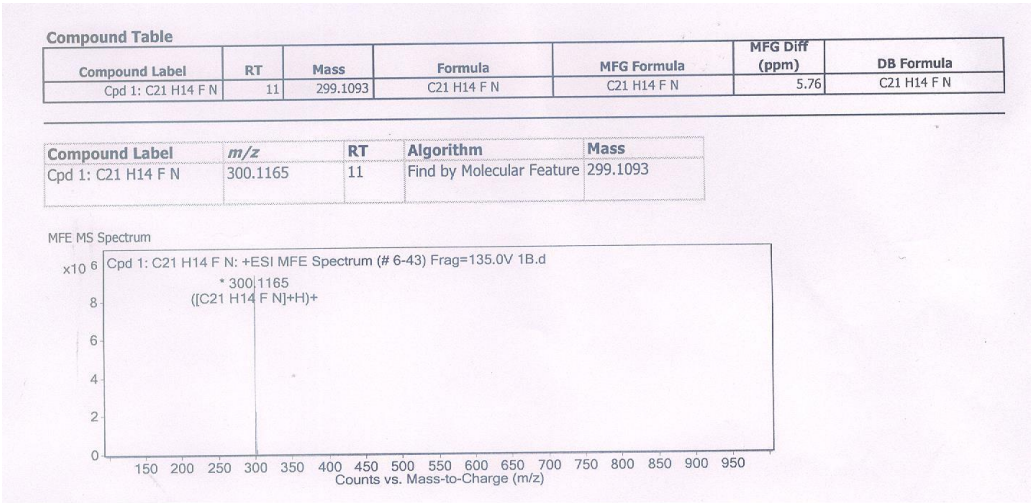
^{13}C NMR in $CDCl_3$



(*E*)-4-Fluoro-*N*-(2-(phenylethynyl)benzylidene)aniline **(1b)**



HRMS: (E)-4-Fluoro-N-(2-(phenylethynyl)benzylidene)aniline **(1b)**



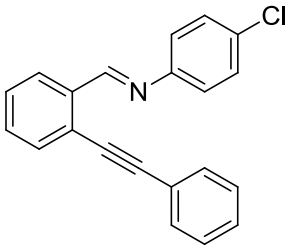
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C21 H14 F N	11	299.1093	C21 H14 F N	C21 H14 F N	5.76	C21 H14 F N

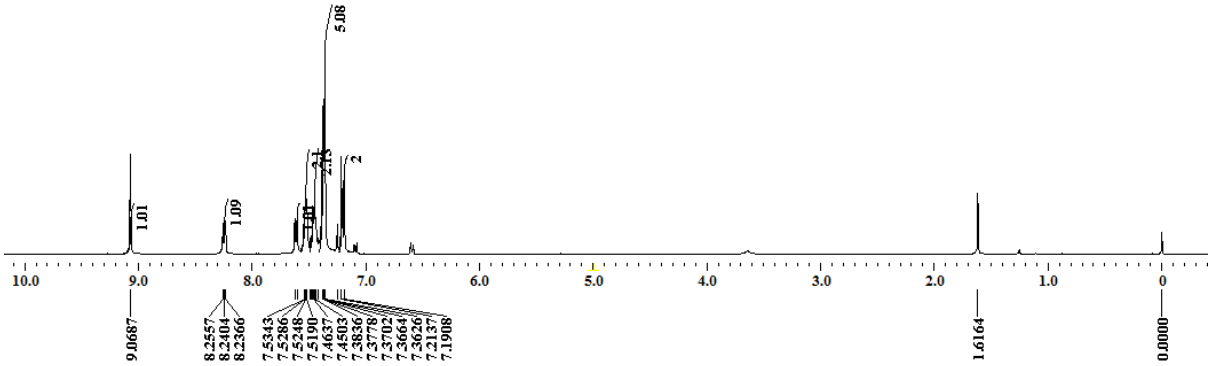
Compound Label	m/z	RT	Algorithm	Mass
Cpd 1: C21 H14 F N	300.1165	11	Find by Molecular Feature	299.1093

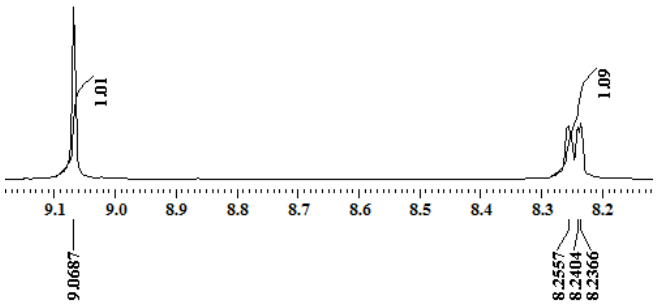
MFE MS Spectrum

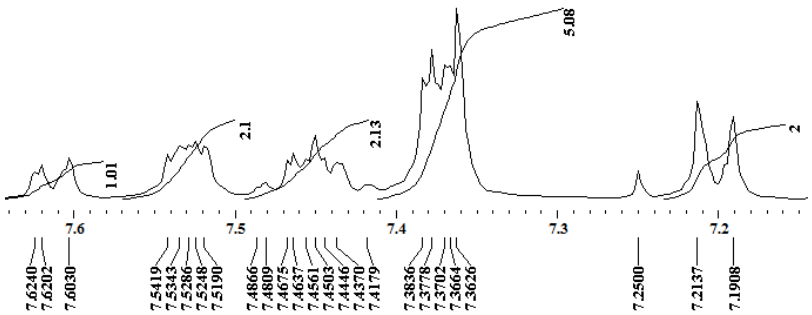
^{1}H NMR in $CDCl_3$



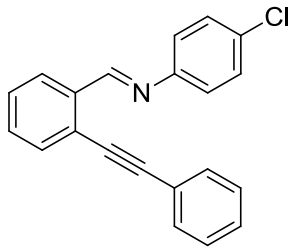
(*E*)-4-Chloro-*N*-(2-(phenylethynyl)benzylidene)aniline **(1c)**



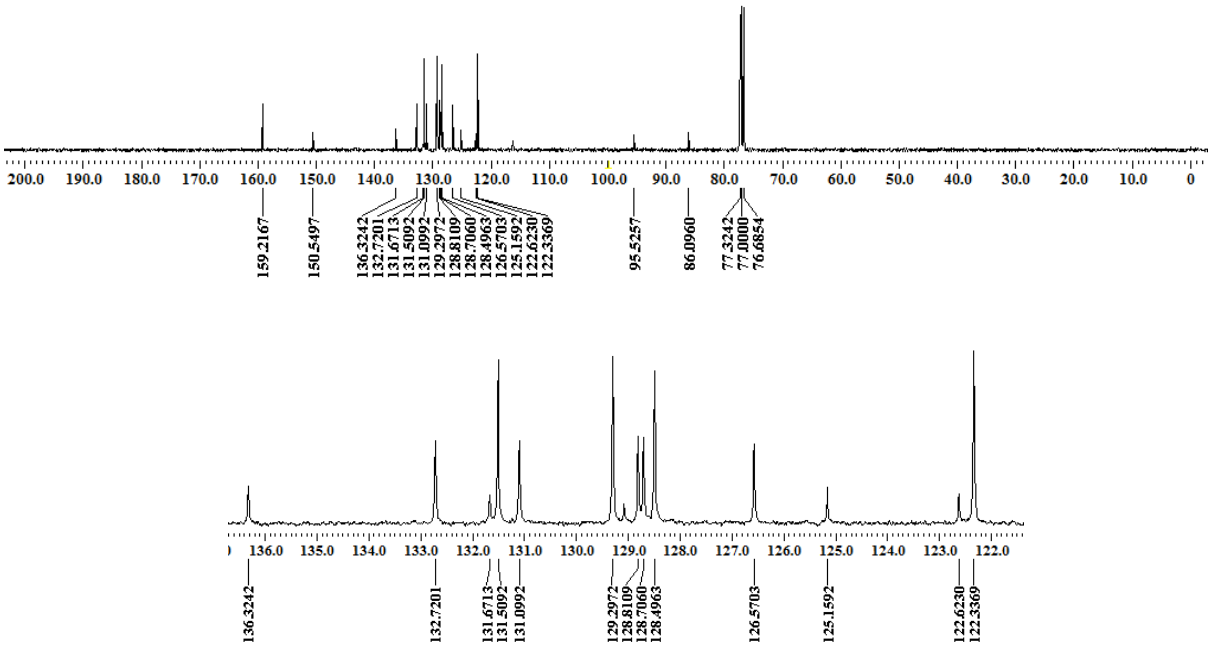




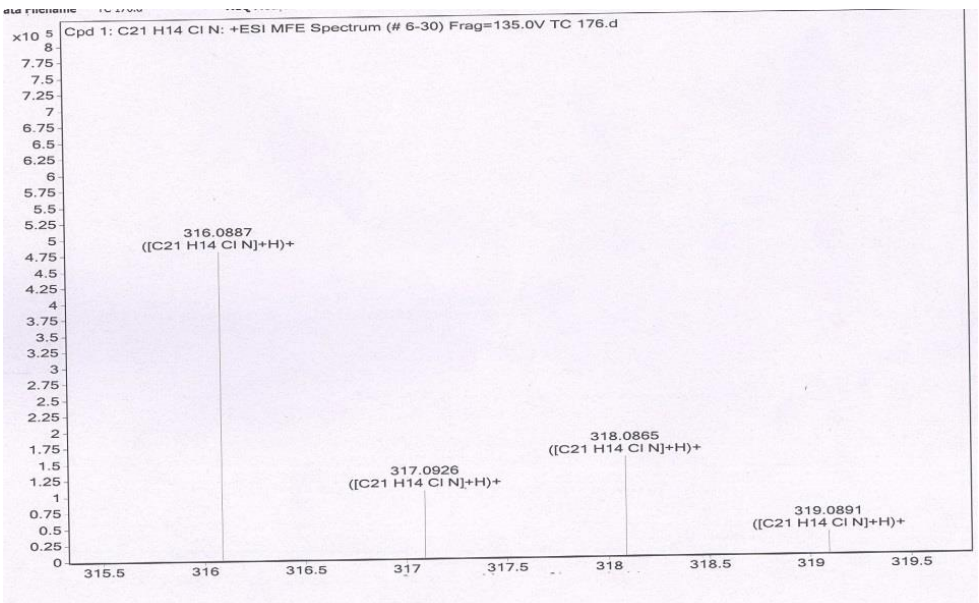
^{13}C NMR in $CDCl_3$



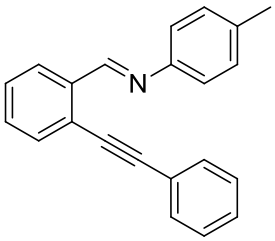
(*E*)-4-Chloro-*N*-(2-(phenylethynyl)benzylidene)aniline **(1c)**



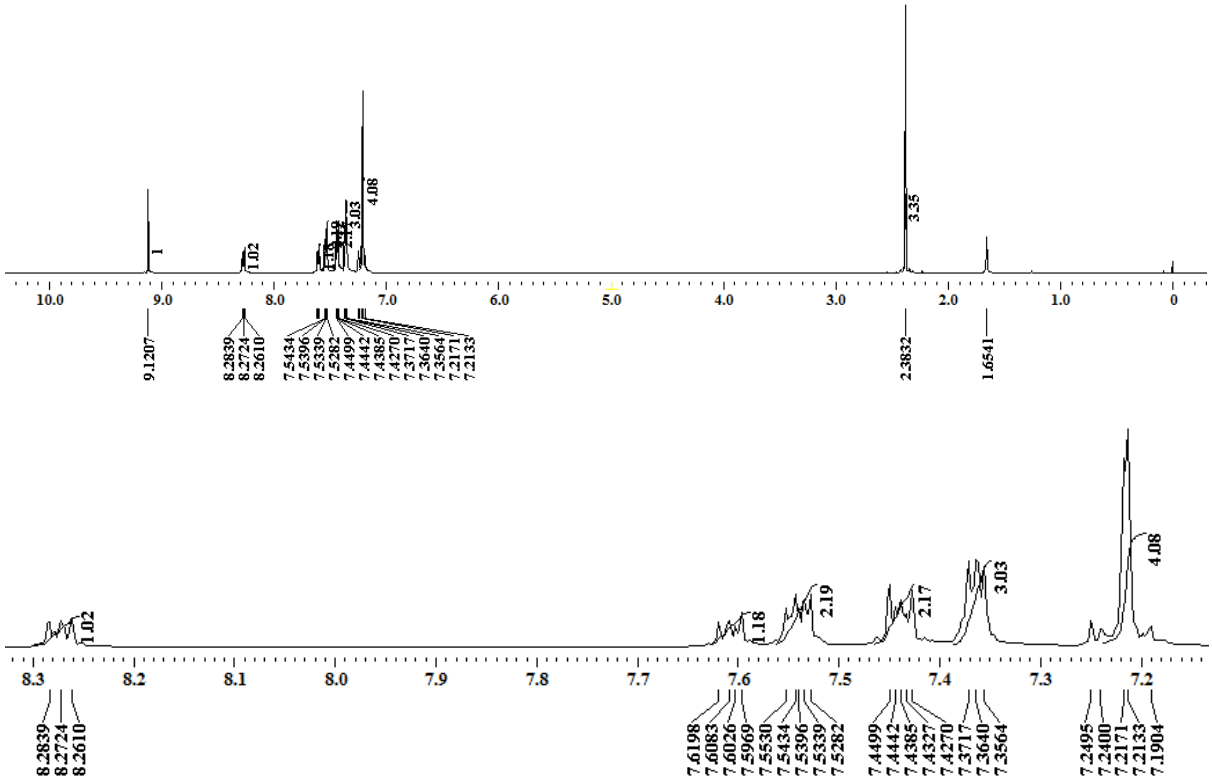
HRMS:(E)-4-Chloro-N-(2-(phenylethynyl)benzylidene)aniline **(1c)**



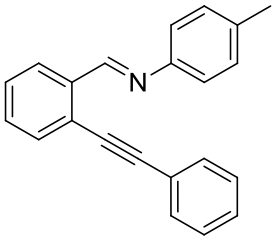
^{1}H NMR in $CDCl_3$



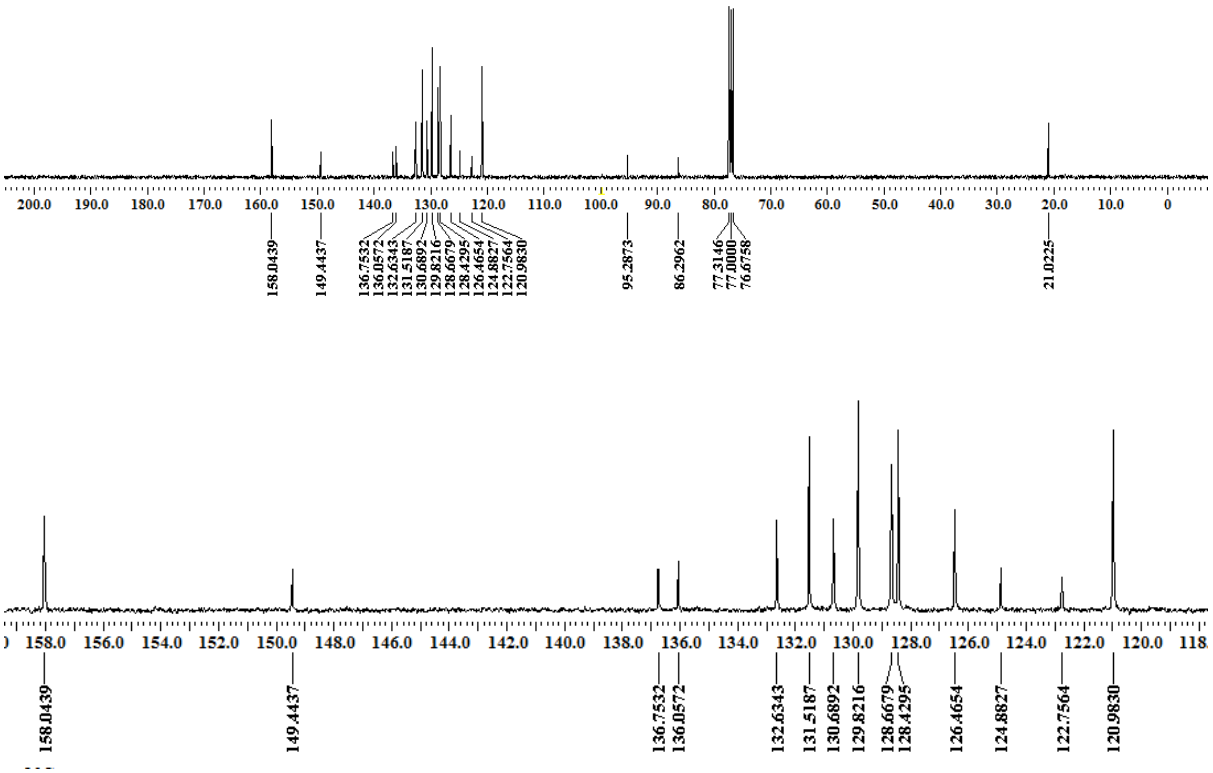
(*E*)-4-Methyl-*N*-(2-(phenylethynyl)benzylidene)aniline **(1d)**



^{13}C NMR in $CDCl_3$



(*E*)-4-Methyl-*N*-(2-(phenylethynyl)benzylidene)aniline **(1d)**



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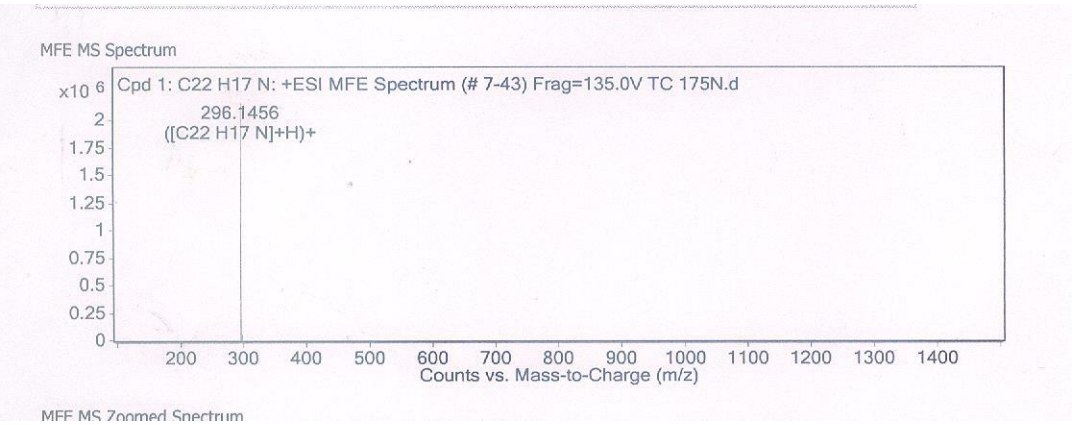

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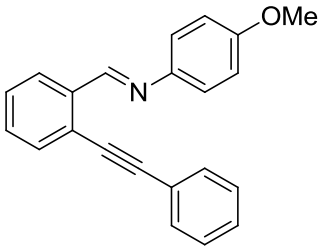
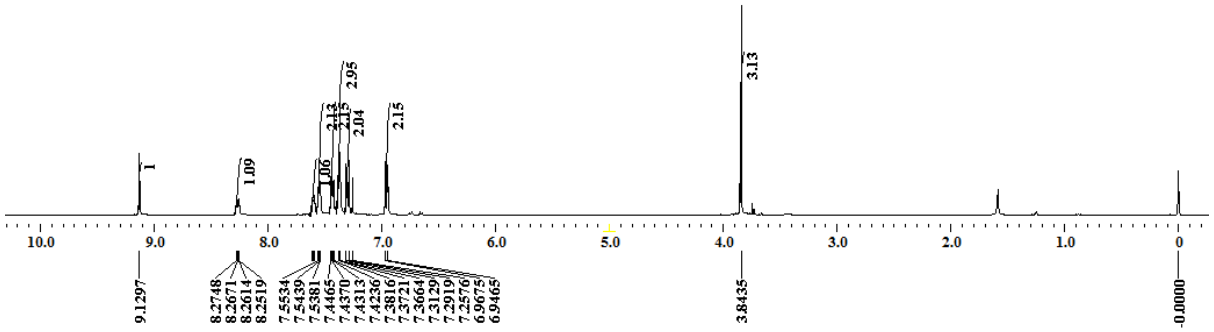
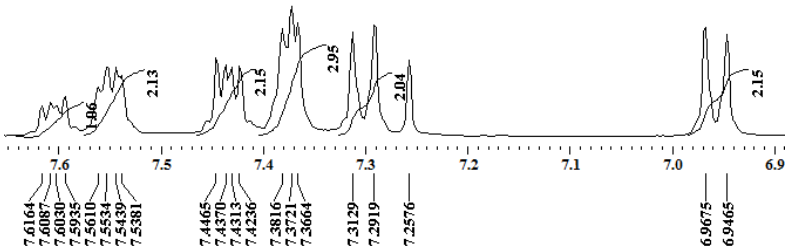
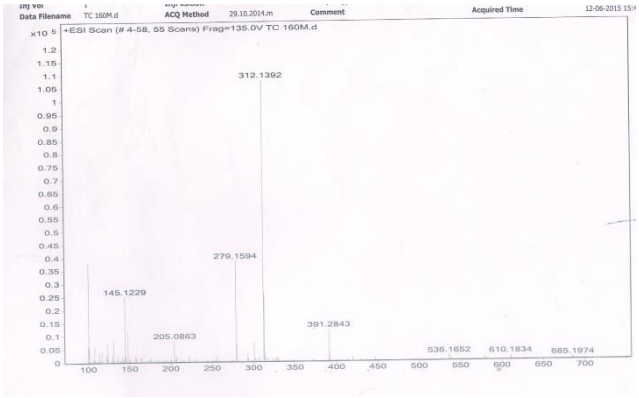


(*E*)-4-Methoxy-*N*-(2-(phenylethynyl)benzylidene)aniline **(1e)**

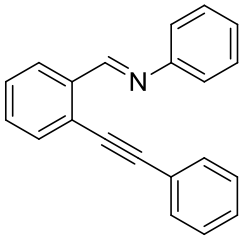




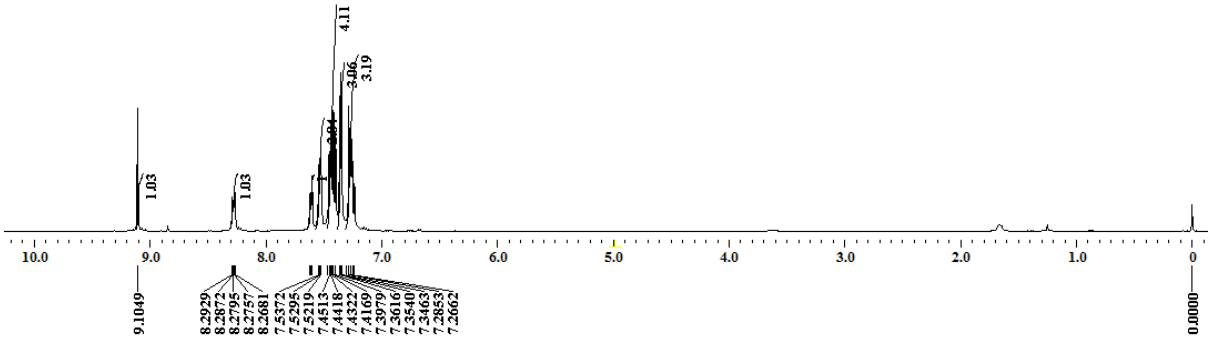
HRMS: (E)-4-Methoxy-N-(2-(phenylethynyl)benzylidene)aniline **(1e)**

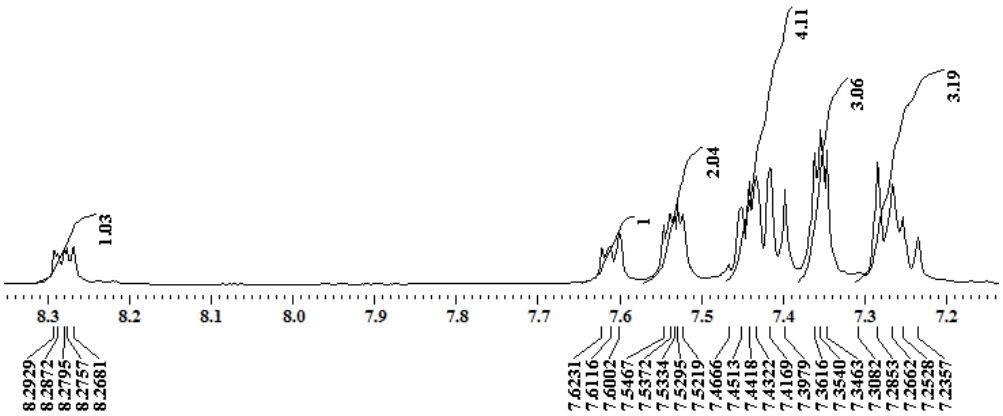


^{1}H NMR in $CDCl_3$

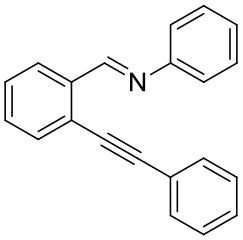


(*E*)-*N*-(2-(phenylethynyl)benzylidene)aniline **(1f)**

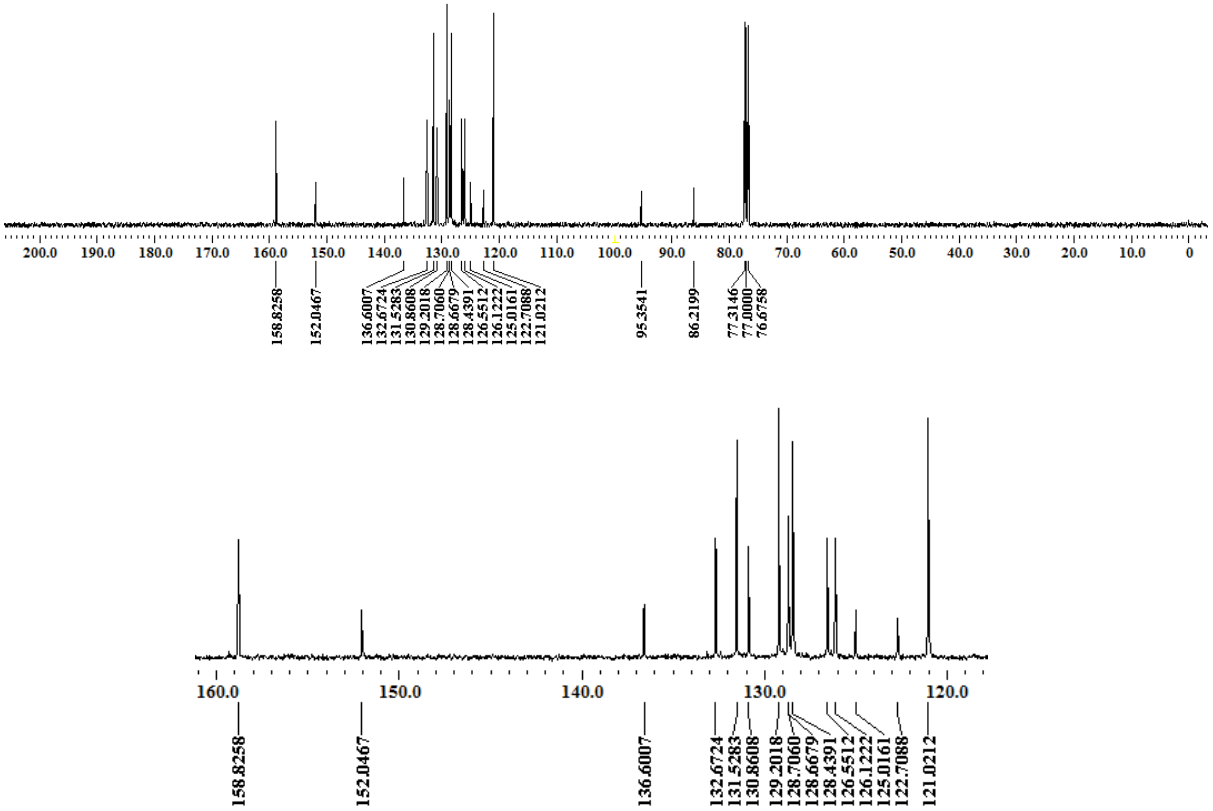




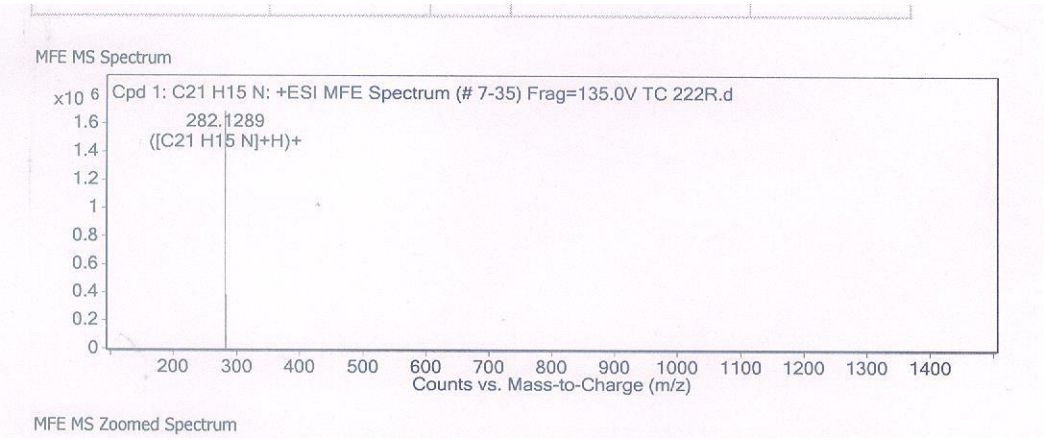
^{13}C NMR in $CDCl_3$



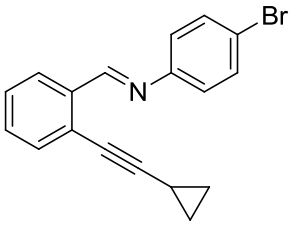
(*E*)-*N*-(2-(phenylethynyl)benzylidene)aniline **(1f)**



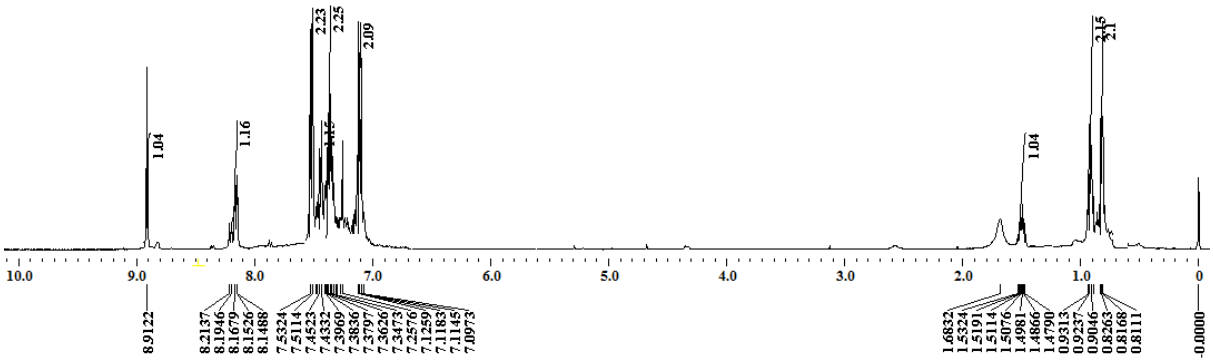
HRMS:(E)-N-(2-(phenylethynyl)benzylidene)aniline (**1f**)

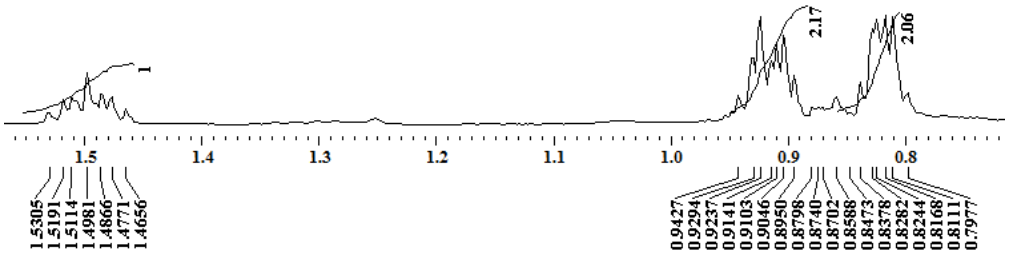


^{1}H NMR in $CDCl_3$

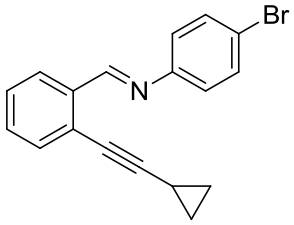


(*E*)-4-bromo-*N*-(2-(cyclopropylethynyl)benzylidene)aniline **(1g)**

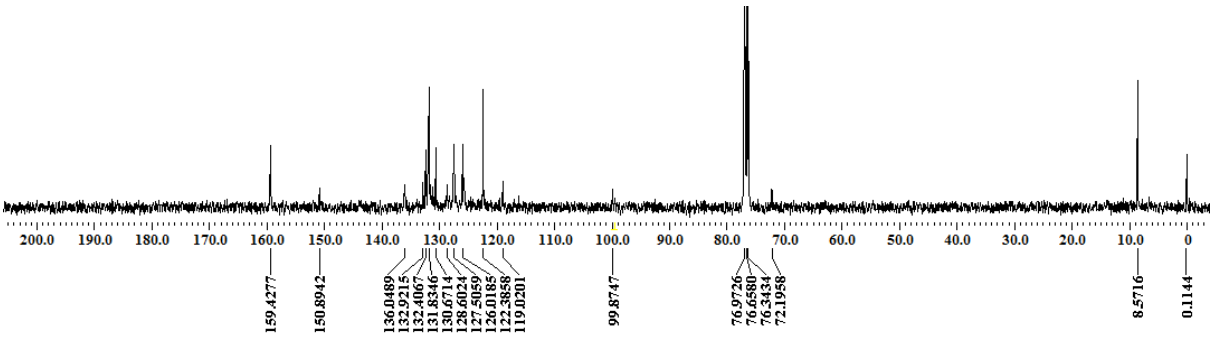




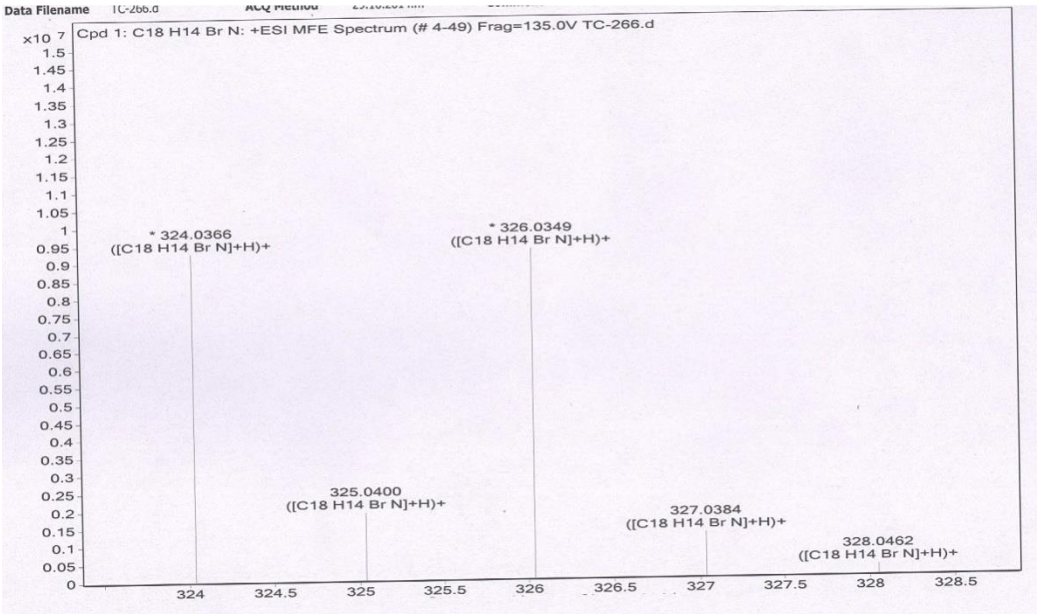
^{13}C NMR in $CDCl_3$



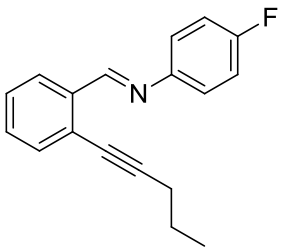
(*E*)-4-Bromo-*N*-(2-(cyclopropylethynyl)benzylidene)aniline **(1g)**



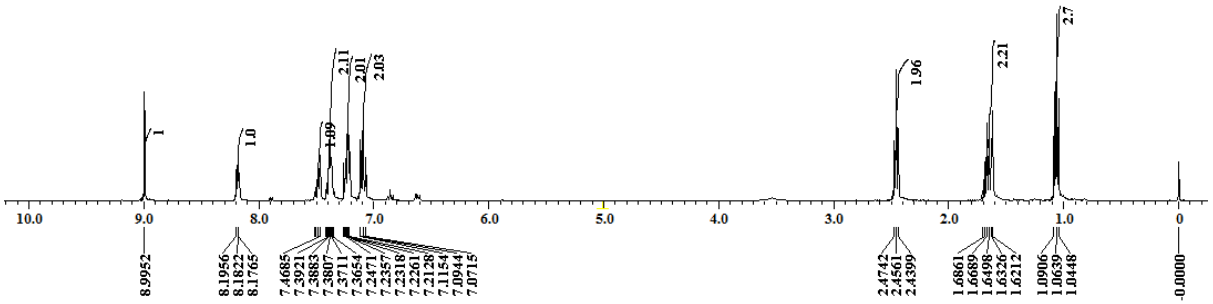
HRMS: (E)-4-Bromo-N-(2-(cyclopropylethynyl)benzylidene)aniline **(1g)**

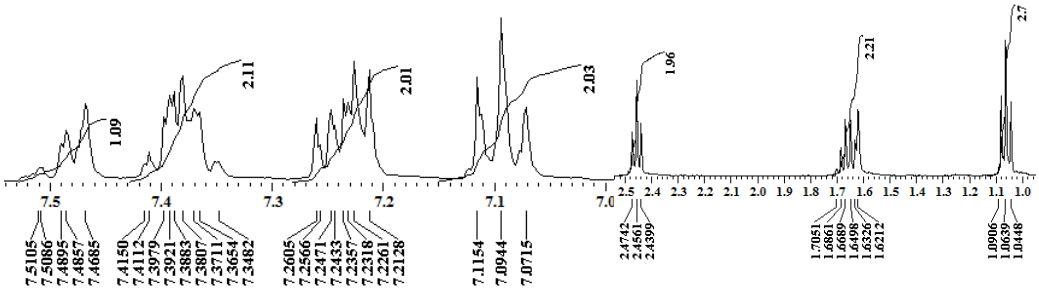


^{1}H NMR in $CDCl_3$

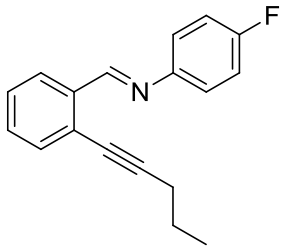


(*E*)-4-Fluoro-*N*-(2-(pent-1-yn-1-yl)benzylidene)aniline **(1h)**

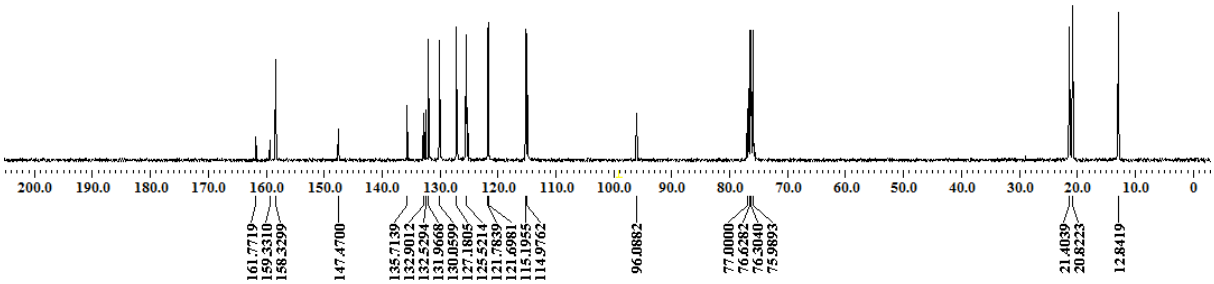




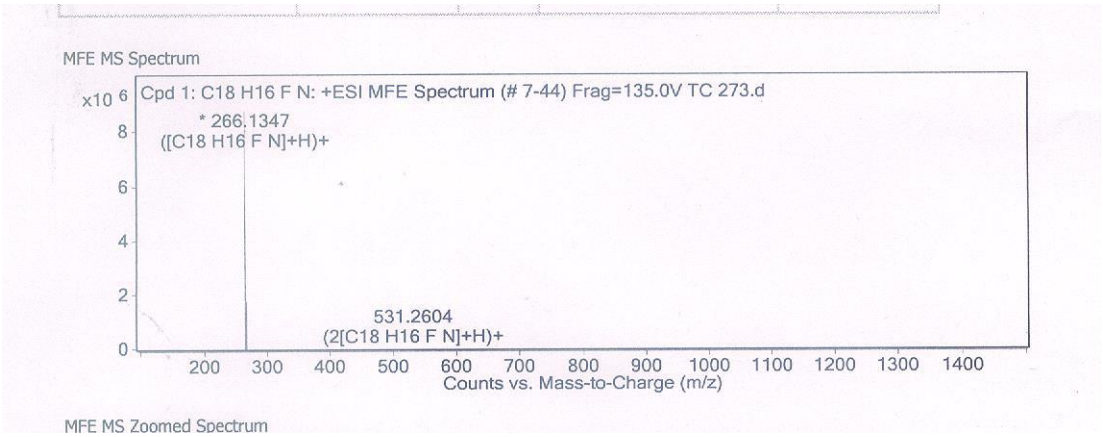
^{13}C NMR in $CDCl_3$



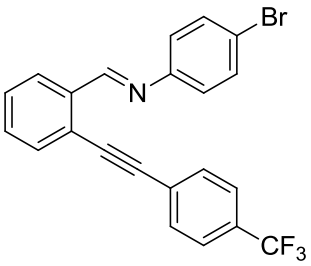
(*E*)-4-Fluoro-*N*-(2-(pent-1-yn-1-yl)benzylidene)aniline **(1h)**



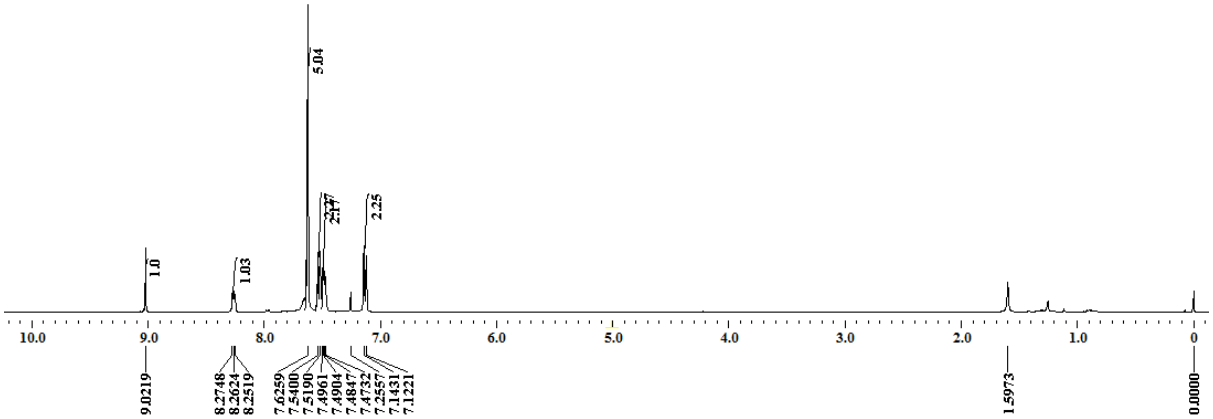
HRMS: (E)-4-fluoro-N-(2-(pent-1-yn-1-yl)benzylidene)aniline **(1h)**

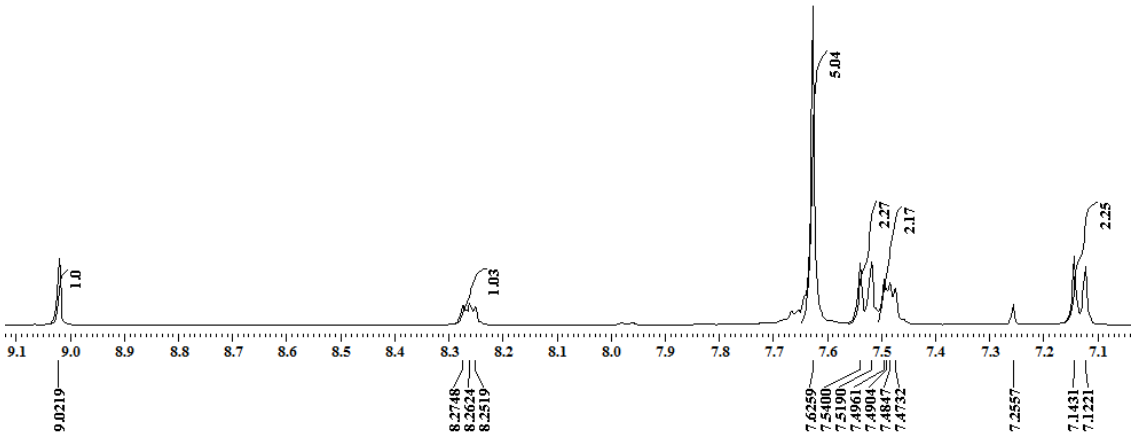


^{1}H NMR in $CDCl_3$

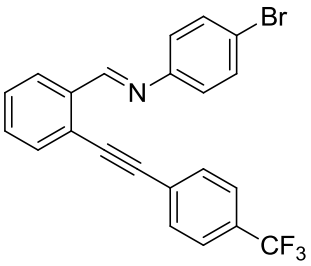


(*E*)-4-bromo-*N*-(2-((4-(trifluoromethyl)phenyl)ethynyl)benzylidene)aniline (**1i**)

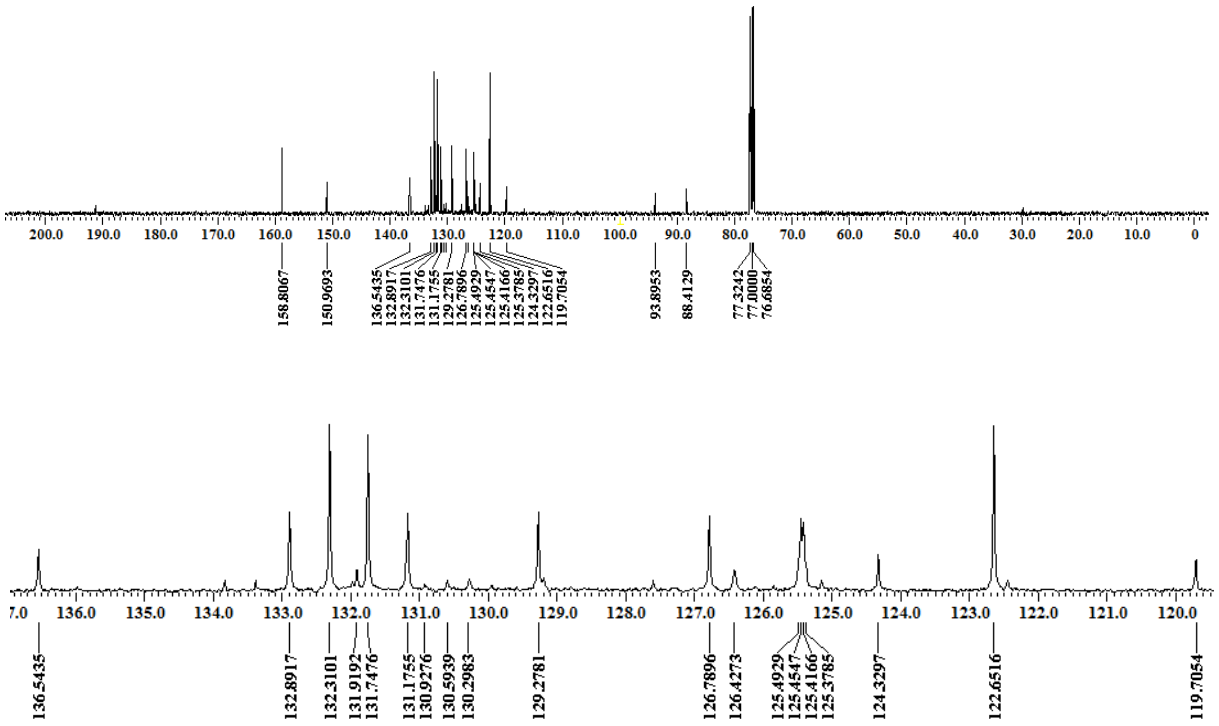




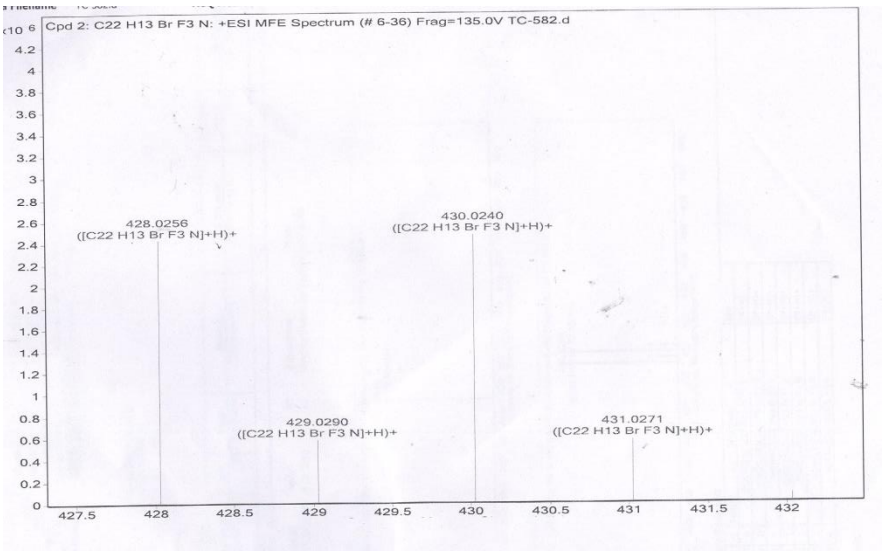
^{13}C NMR in $CDCl_3$



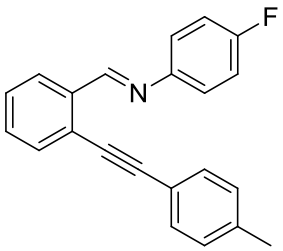
(*E*)-4-bromo-*N*-(2-((4-(trifluoromethyl)phenyl)ethynyl)benzylidene)aniline (**1i**)



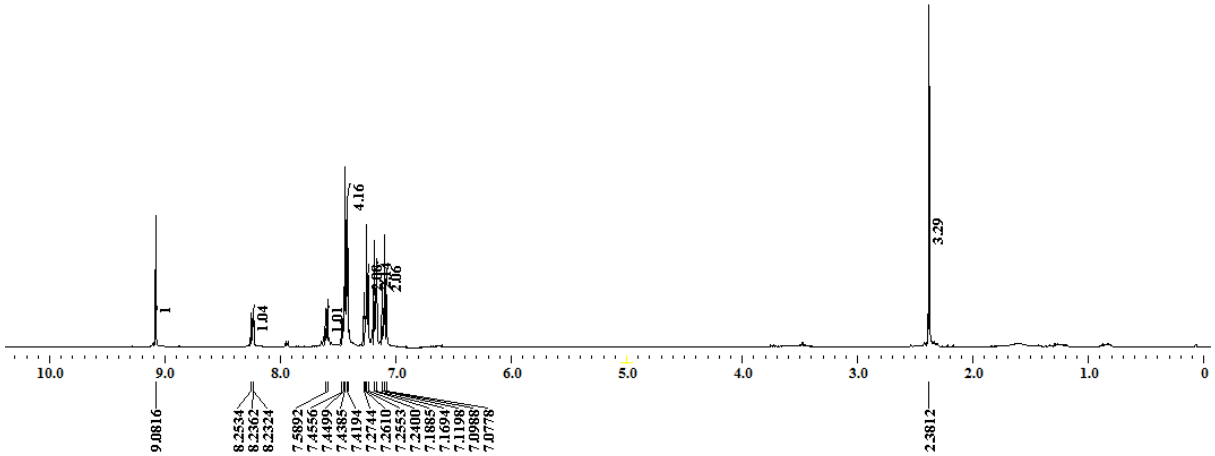
HRMS: (E)-4-bromo-N-(2-((4-(trifluoromethyl)phenyl)ethynyl)benzylidene)aniline (**1i**)

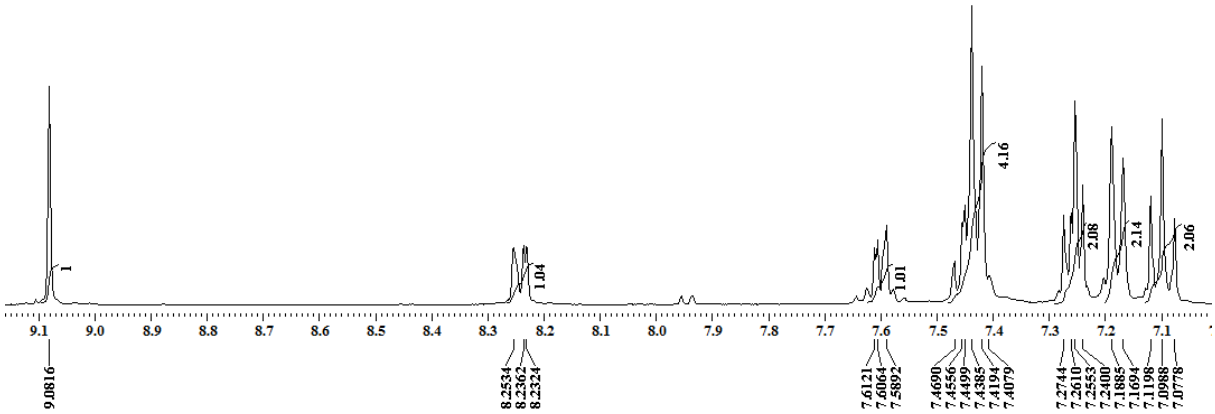


^{1}H NMR in $CDCl_3$

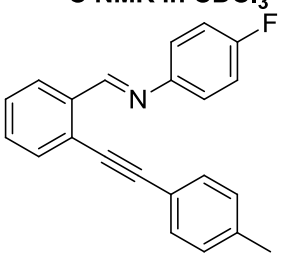


(*E*)-4-Fluoro-*N*-(2-(*p*-tolylethynyl)benzylidene)aniline **(1j)**

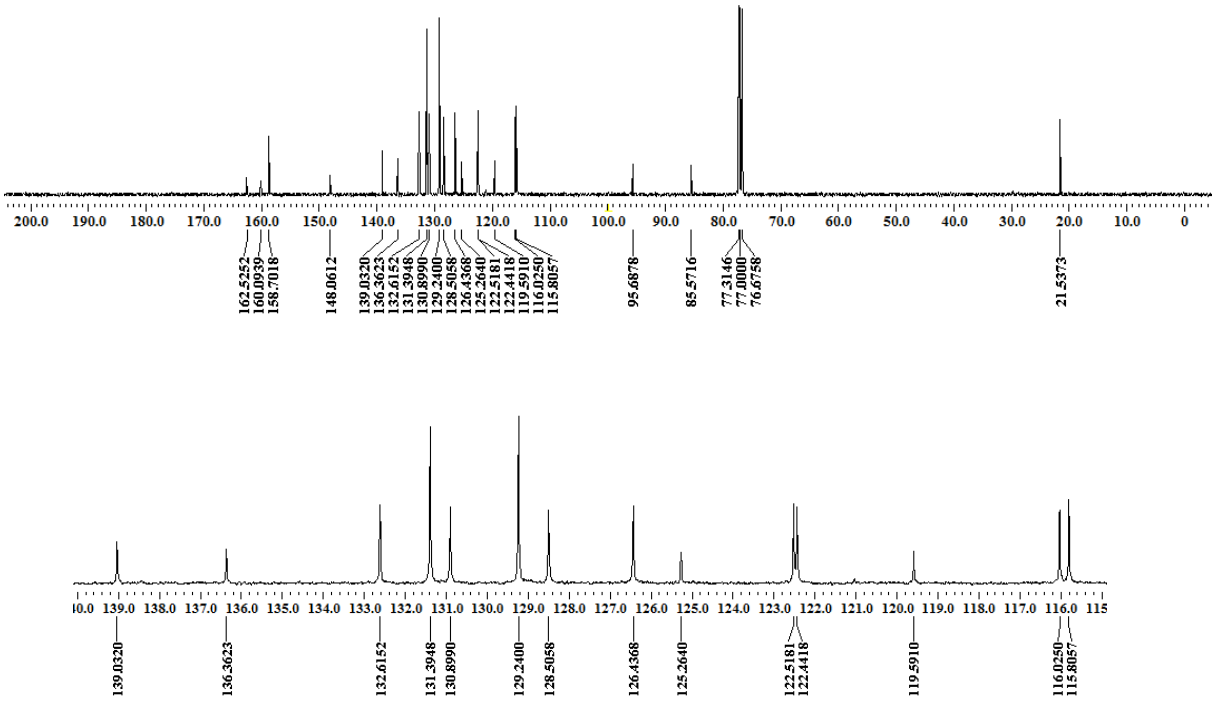




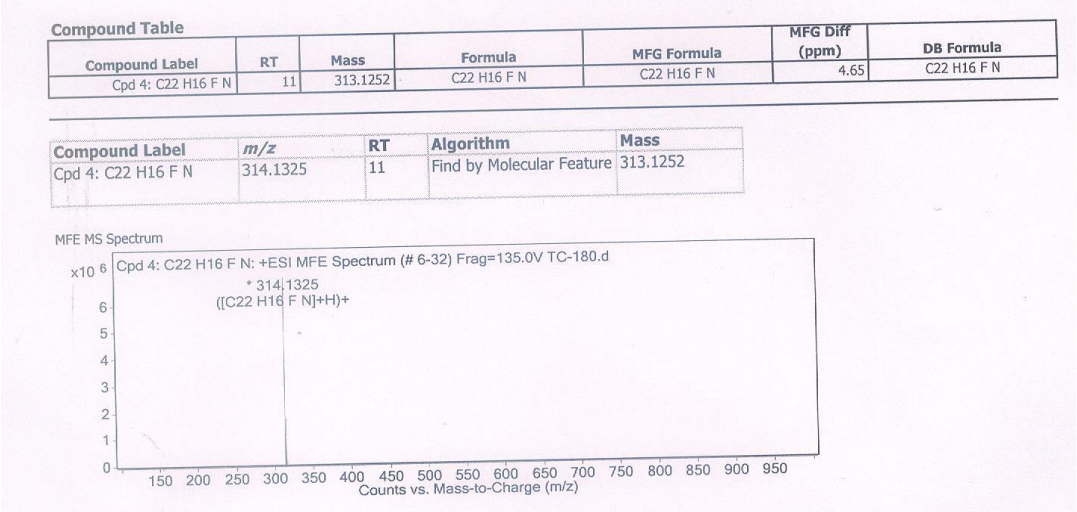
^{13}C NMR in $CDCl_3$



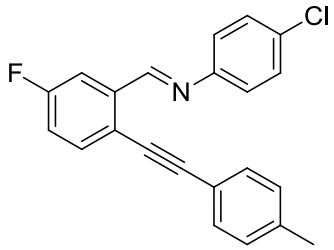
(*E*)-4-Fluoro-*N*-(2-(*p*-tolylethynyl)benzylidene)aniline **(1j)**



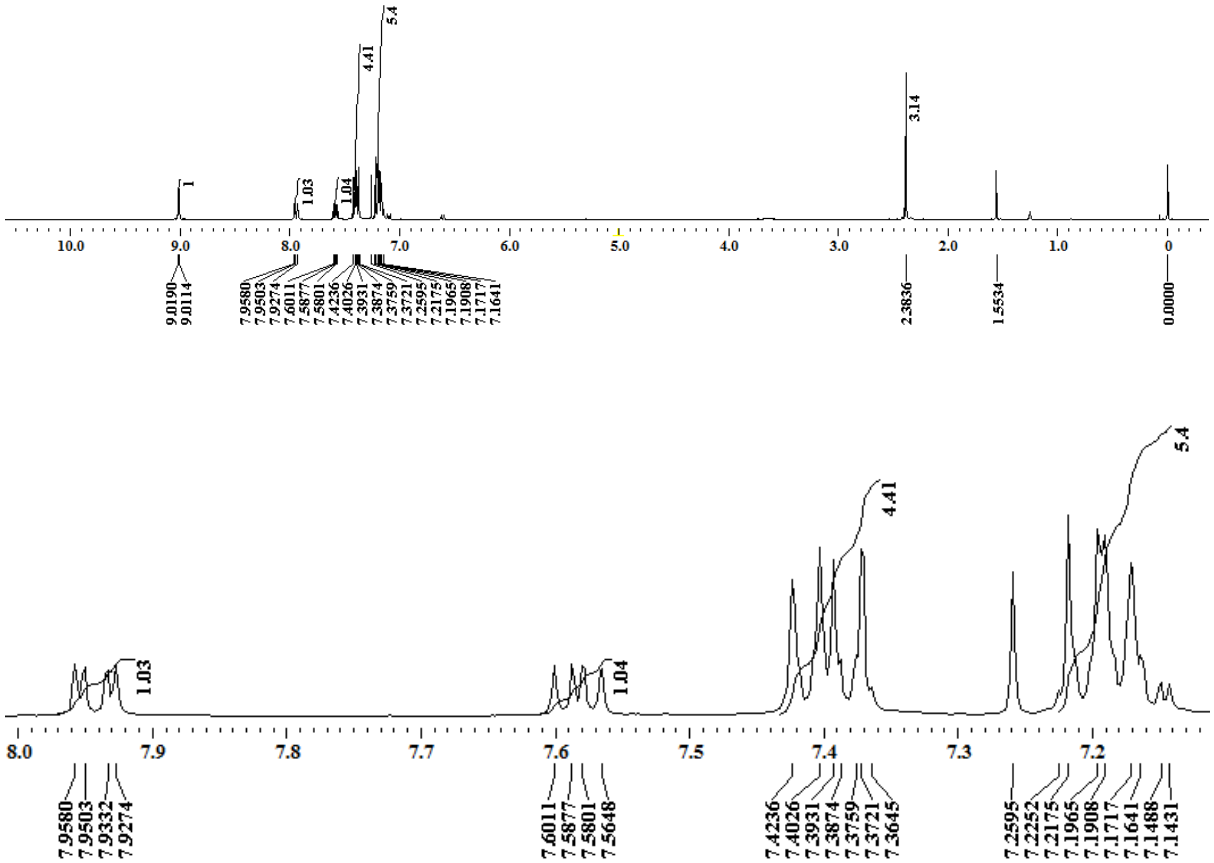
HRMS: (E)-4-Fluoro-N-(2-(p-tolylethynyl)benzylidene)aniline **(1j)**



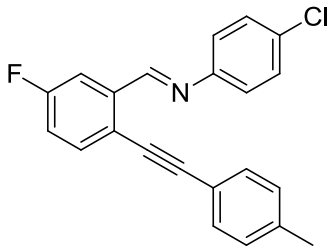
^{1}H NMR in $CDCl_3$



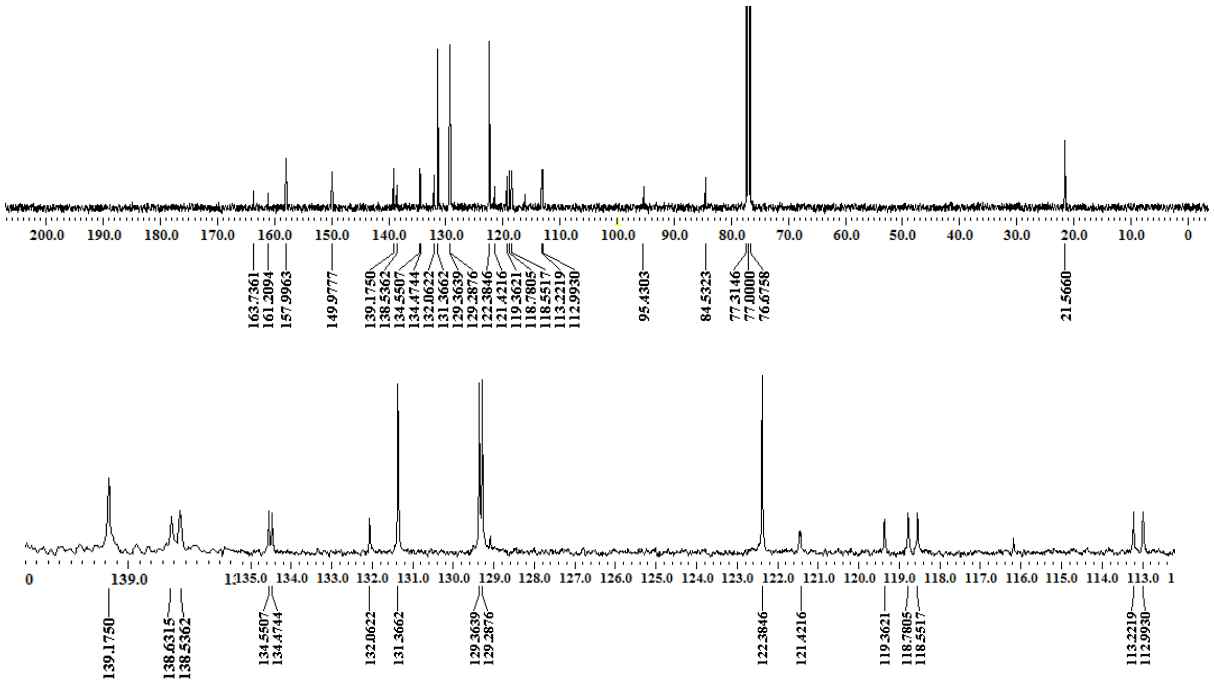
(*E*)-4-chloro-*N*-(5-fluoro-2-(*p*-tolylethynyl)benzylidene)aniline **(1k)**



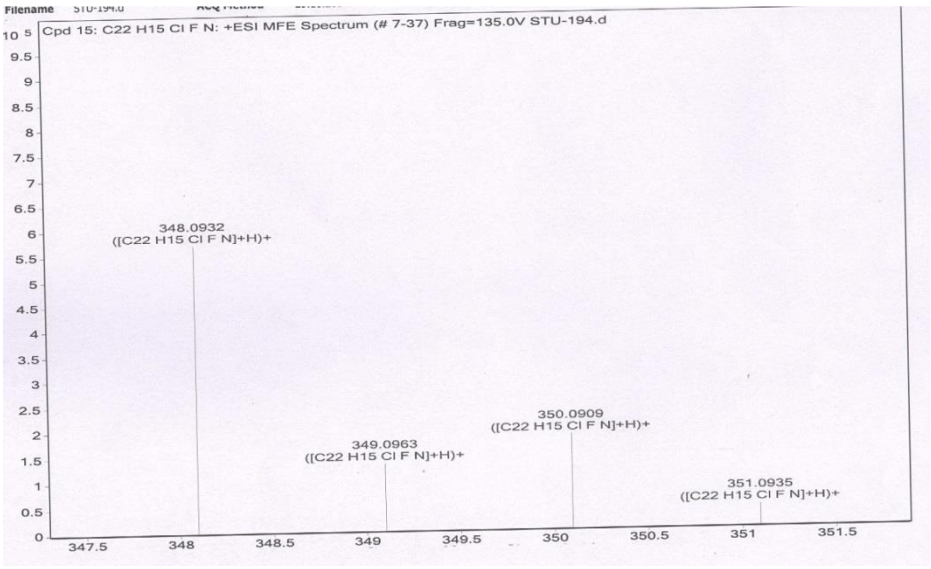
^{13}C NMR in $CDCl_3$



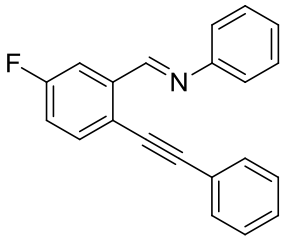
(*E*)-4-Chloro-*N*-(5-fluoro-2-(*p*-tolylethynyl)benzylidene)aniline **(1k)**



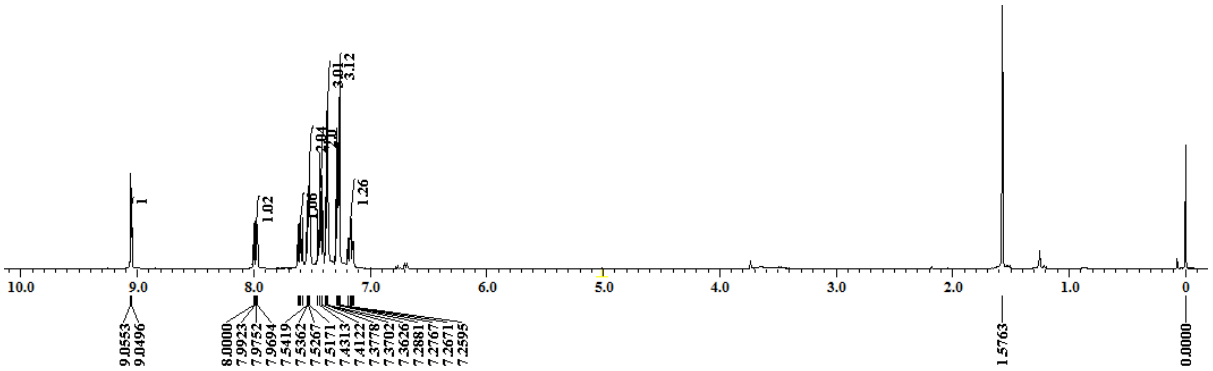
HRMS: (E)-4-Chloro-N-(5-fluoro-2-(p-tolylethynyl)benzylidene)aniline **(1k)**

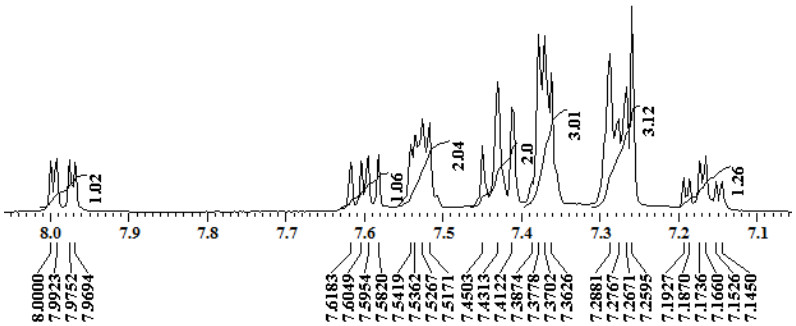


^{1}H NMR in $CDCl_3$

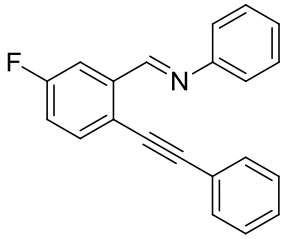


(*E*)-*N*-(5-Fluoro-2-(phenylethynyl)benzylidene)aniline **(1l)**

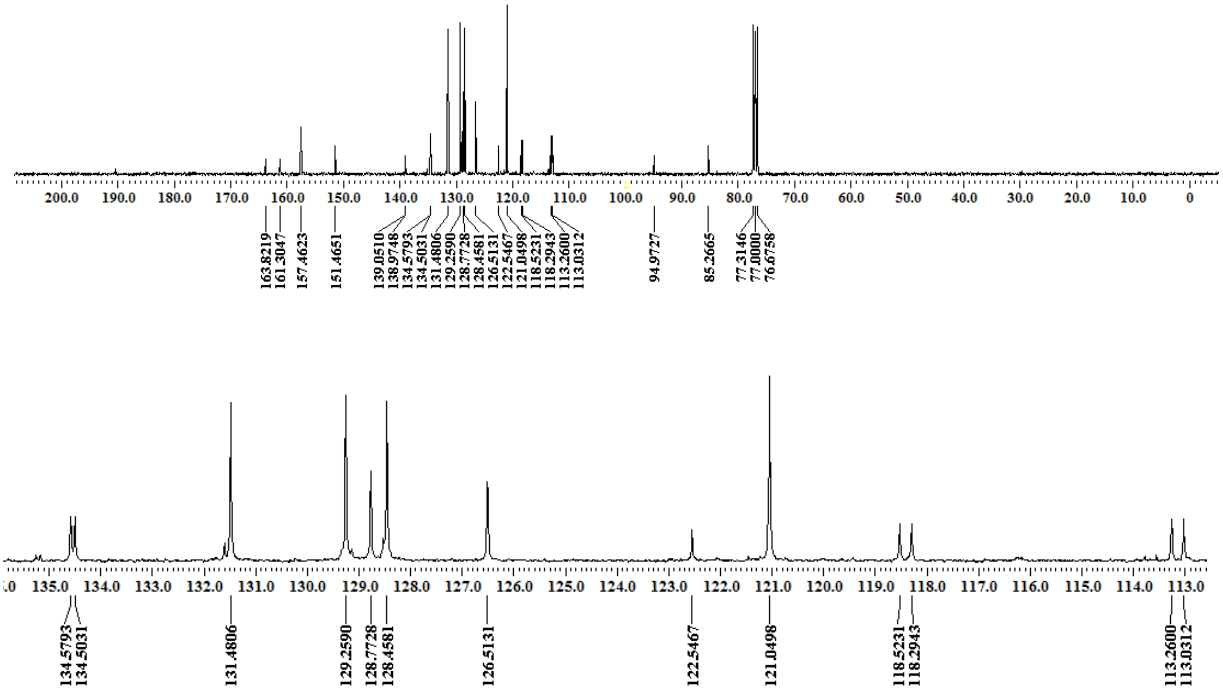




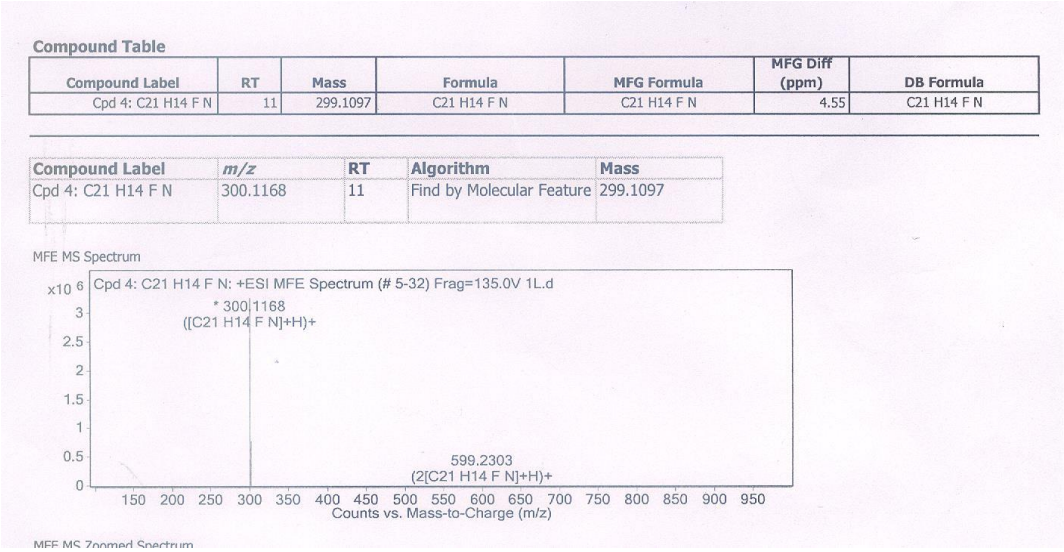
^{13}C NMR in $CDCl_3$



(*E*)-*N*-(5-Fluoro-2-(phenylethynyl)benzylidene)aniline**(1l)**



HRMS: (E)-N-(5-Fluoro-2-(phenylethynyl)benzylidene)aniline**(1l)**



Compound Table

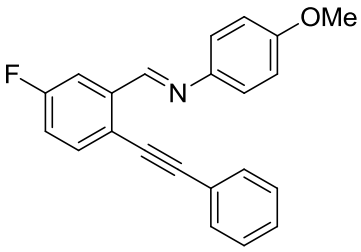
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 4: C21 H14 F N	11	299.1097	C21 H14 F N	C21 H14 F N	4.55	C21 H14 F N

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 4: C21 H14 F N	300.1168	11	Find by Molecular Feature	299.1097

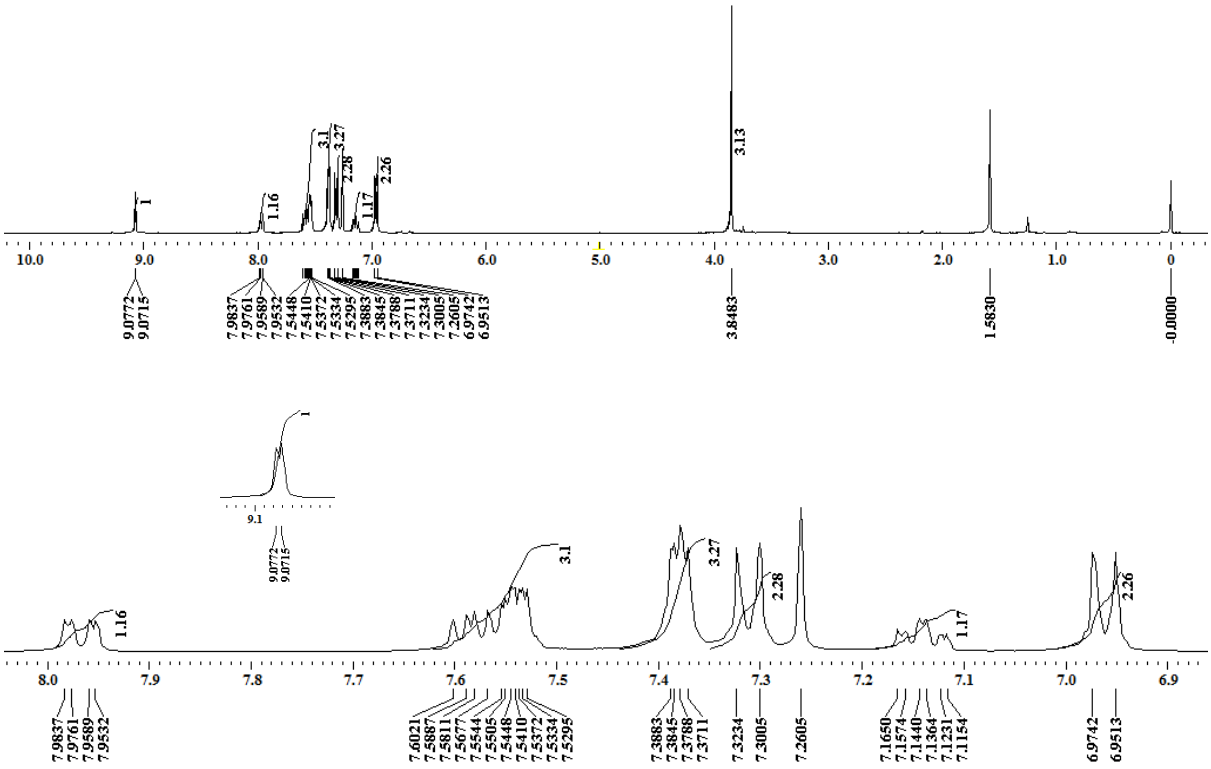
MFE MS Spectrum

MFE MS Zoomed Spectrum

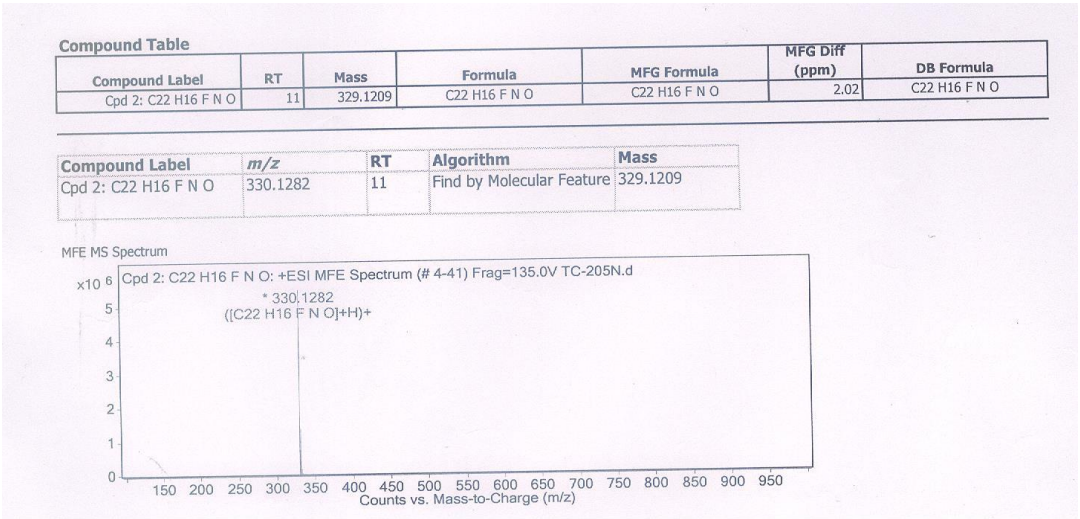
^{1}H NMR in $CDCl_3$



(*E*)-*N*-(5-Fluoro-2-(phenylethynyl)benzylidene)-4-methoxyaniline **(1m)**



HRMS: (E)-N-(5-Fluoro-2-(phenylethynyl)benzylidene)-4-methoxyaniline (**1m**)



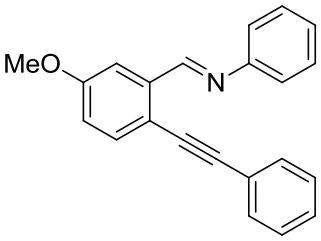
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 2: C22 H16 F N O	11	329.1209	C22 H16 F N O	C22 H16 F N O	2.02	C22 H16 F N O

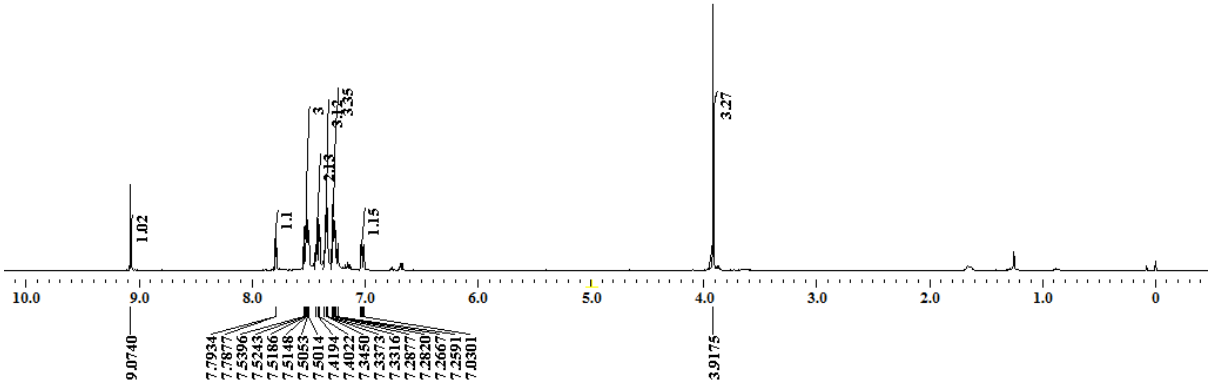
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C22 H16 F N O	330.1282	11	Find by Molecular Feature	329.1209

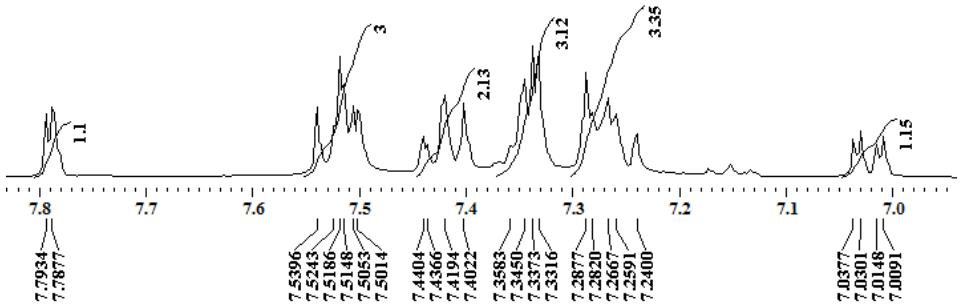
MFE MS Spectrum

^{1}H NMR in $CDCl_3$

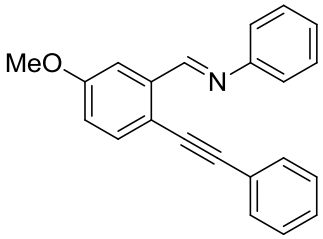


(*E*)-*N*-(5-Methoxy-2-(phenylethynyl)benzylidene)aniline **(1n)**

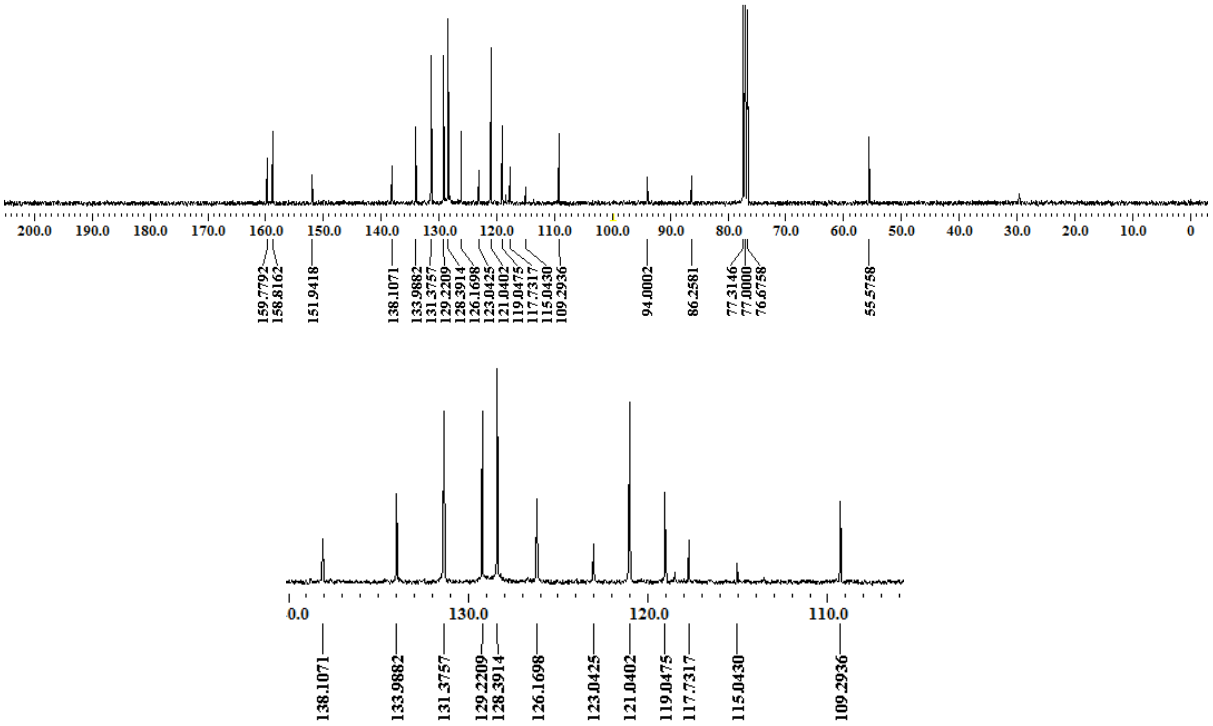




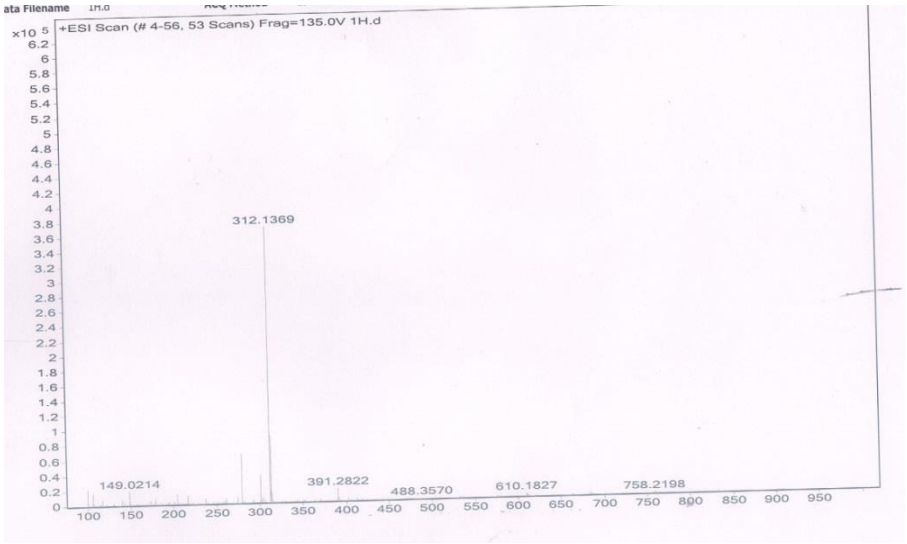
^{13}C NMR in $CDCl_3$



(*E*)-*N*-(5-Methoxy-2-(phenylethynyl)benzylidene)aniline **(1n)**

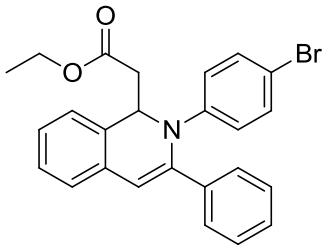


HRMS: (E)-N-(5-Methoxy-2-(phenylethynyl)benzylidene)aniline **(1n)**

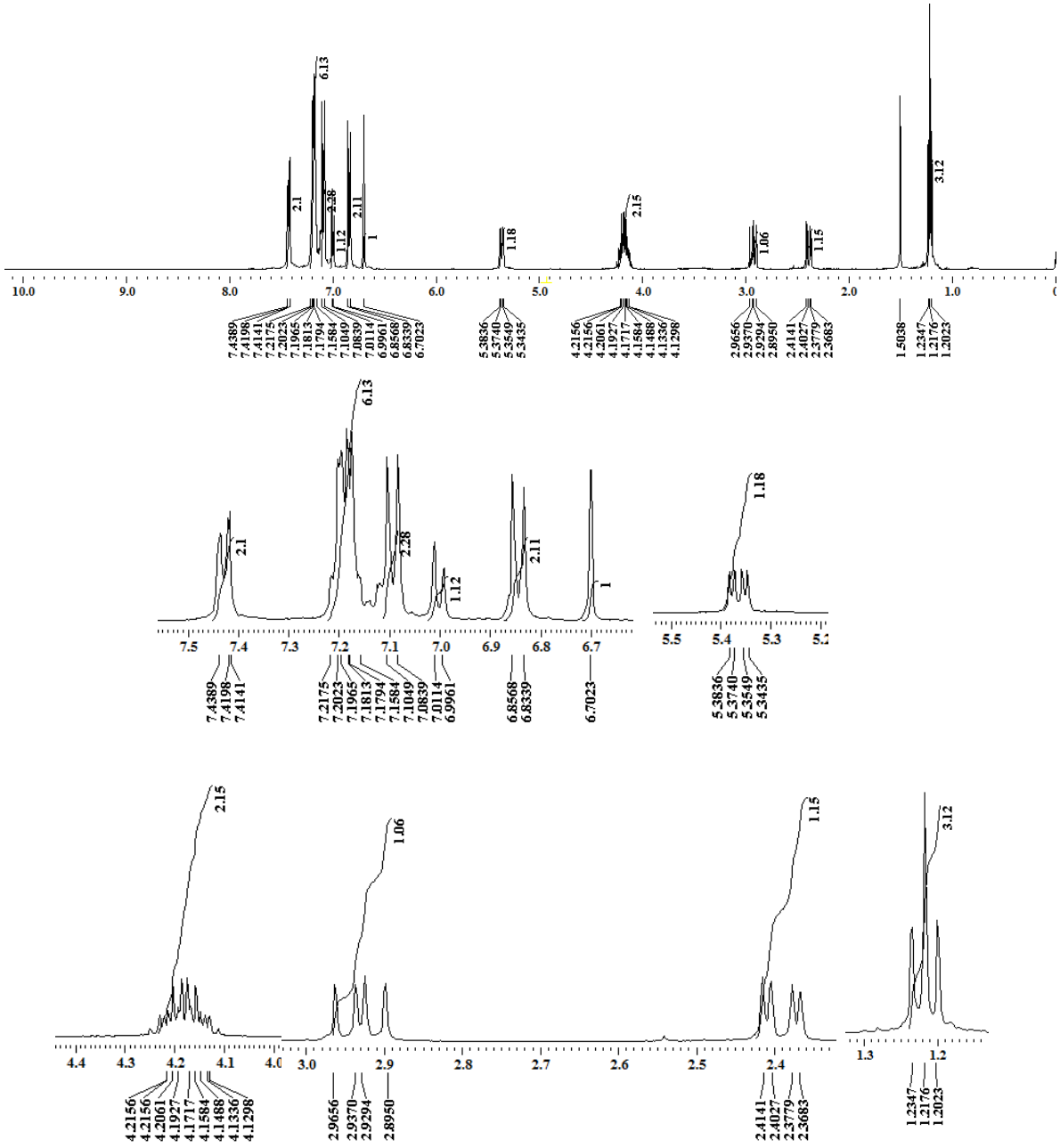


3. ^{1}H, ^{13}C NMR and HRMS Spectra of 3a-3zc, 4a and 5:

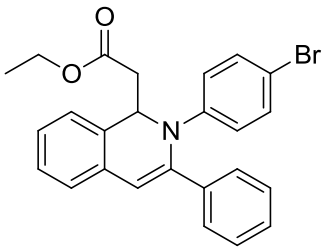
^{1}H NMR in $CDCl_3$



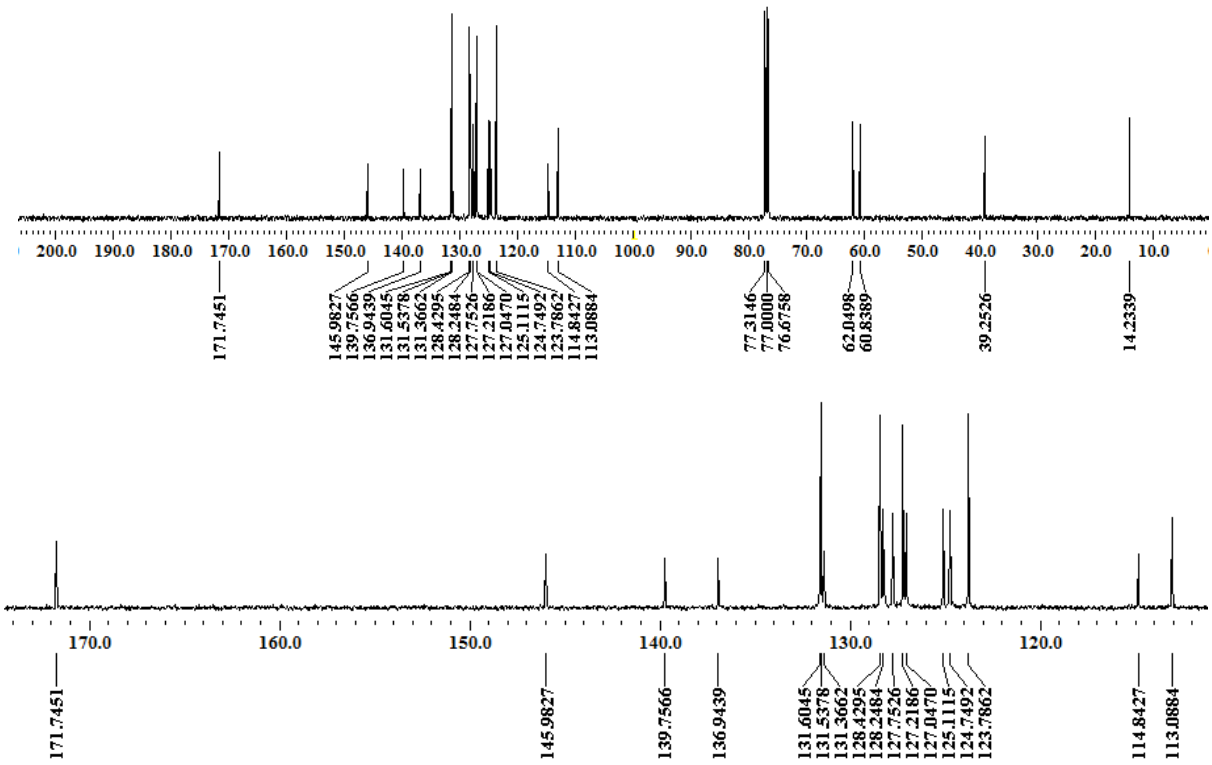
ethyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3a**)



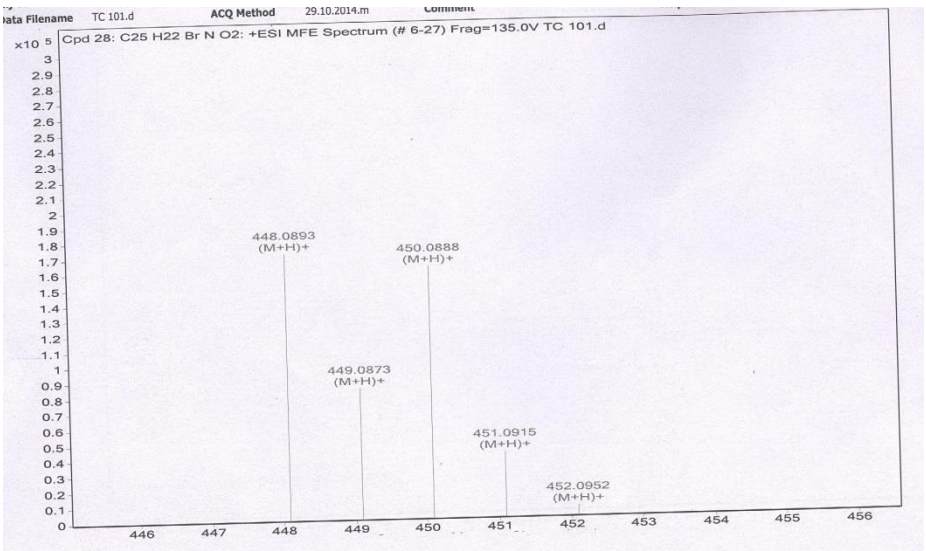
^{13}C NMR in $CDCl_3$



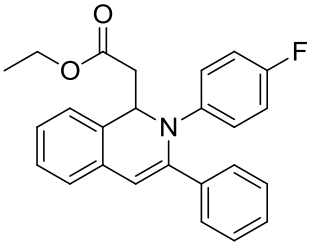
Ethyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3a**)



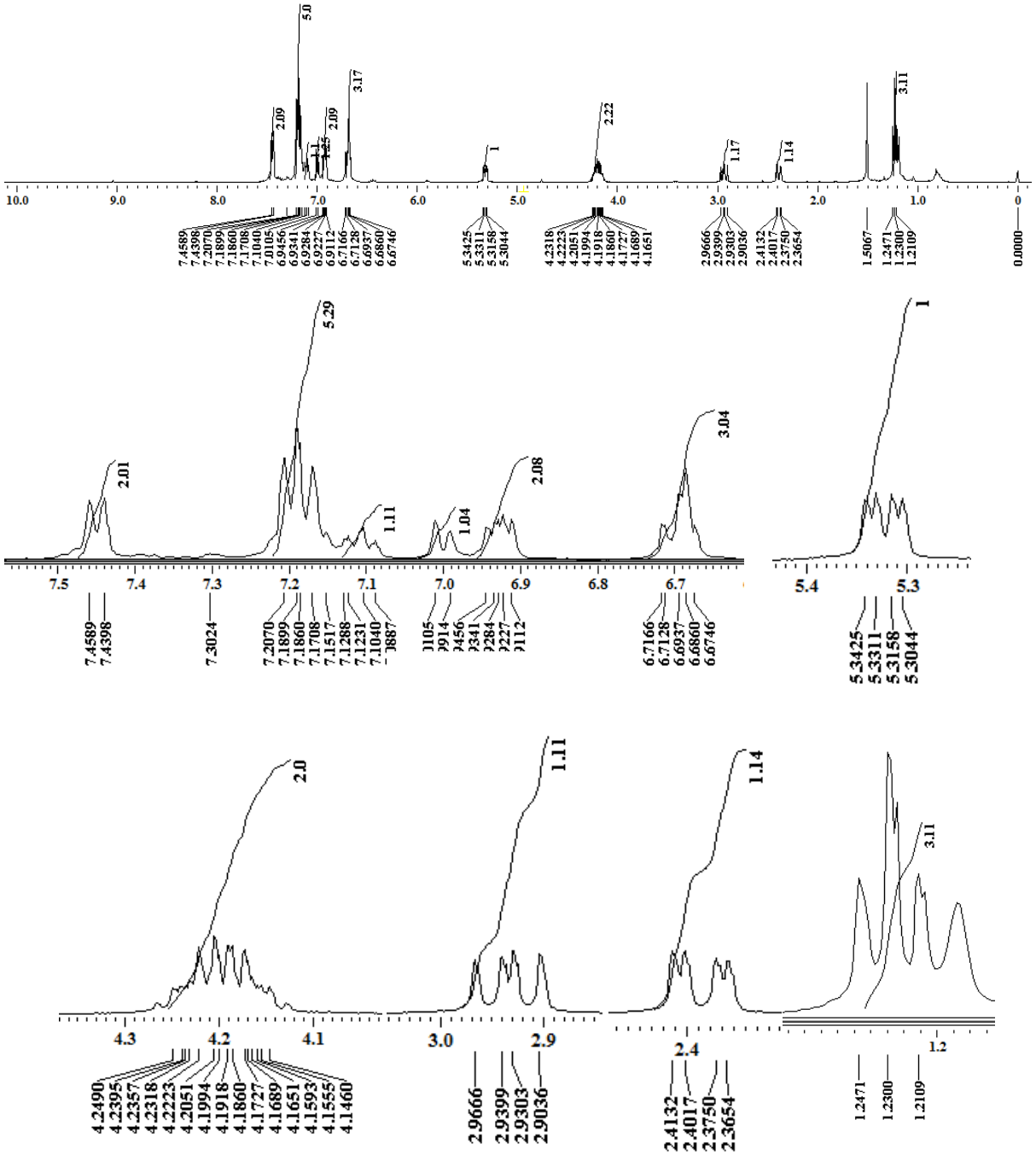
HRMS: Ethyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3a**)



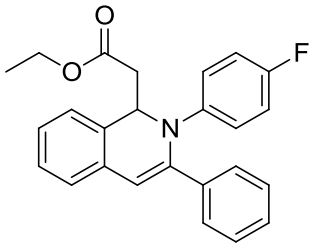
^{1}H NMR IN $CDCl_3$



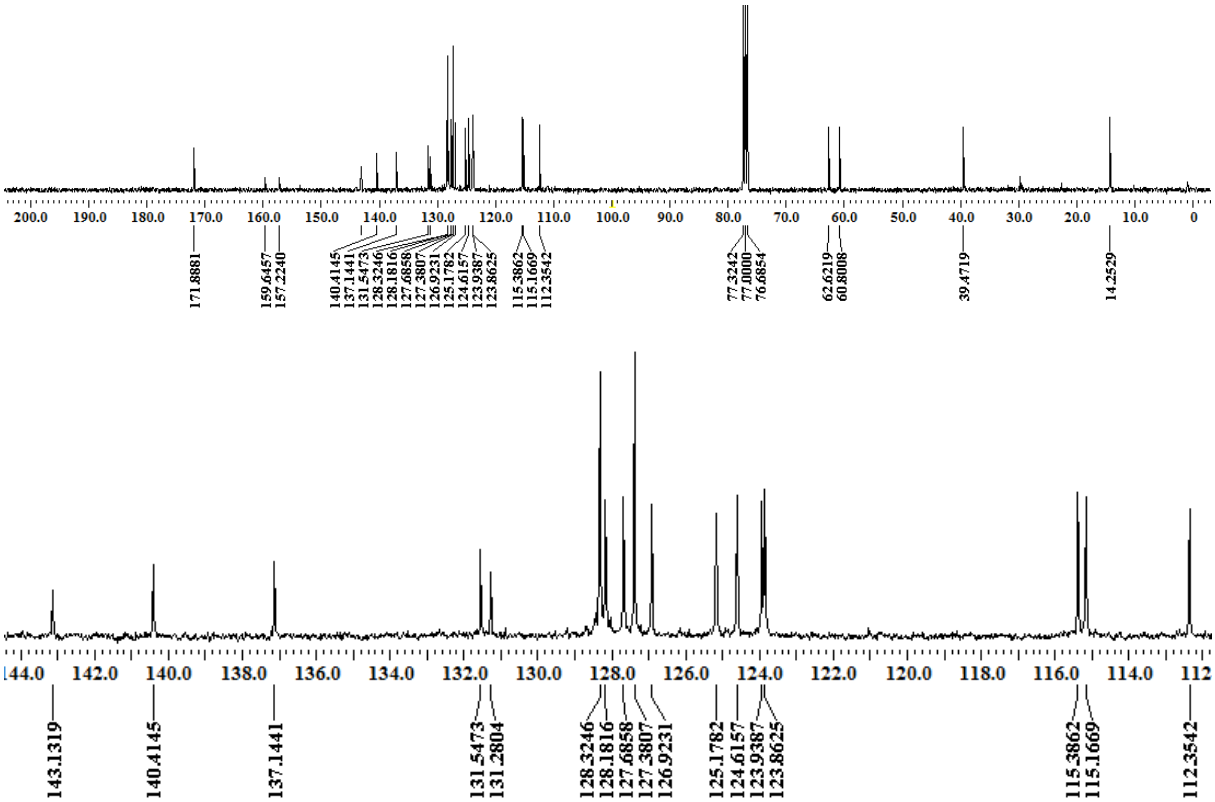
Ethyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3b**)



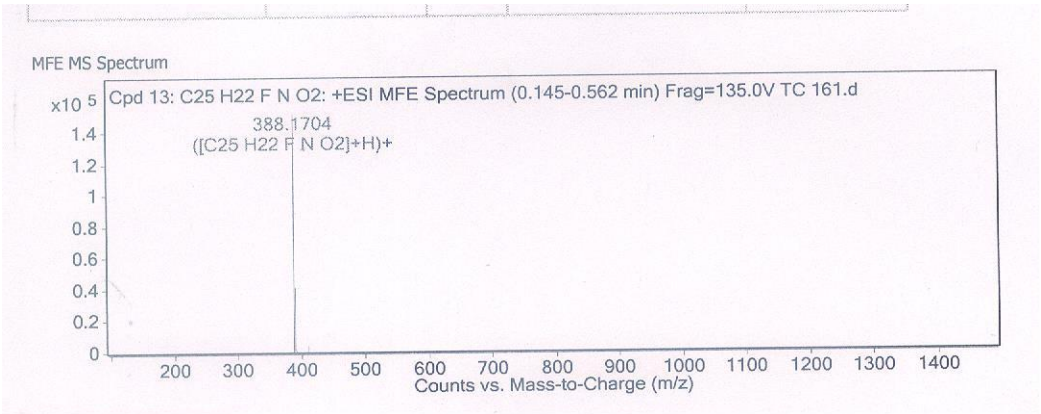
^{13}C NMR IN $CDCl_3$



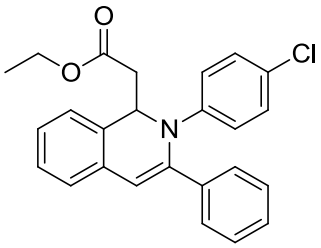
Ethyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3b**)



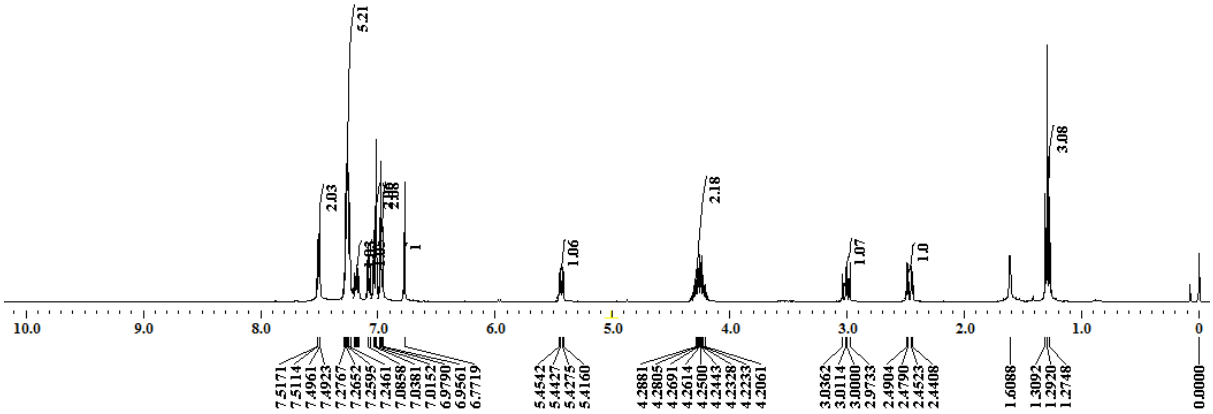
HRMS:ethyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3b**)

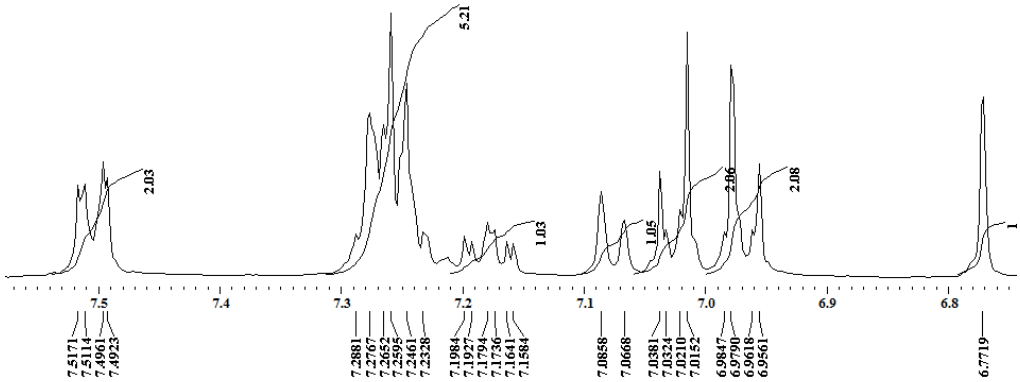


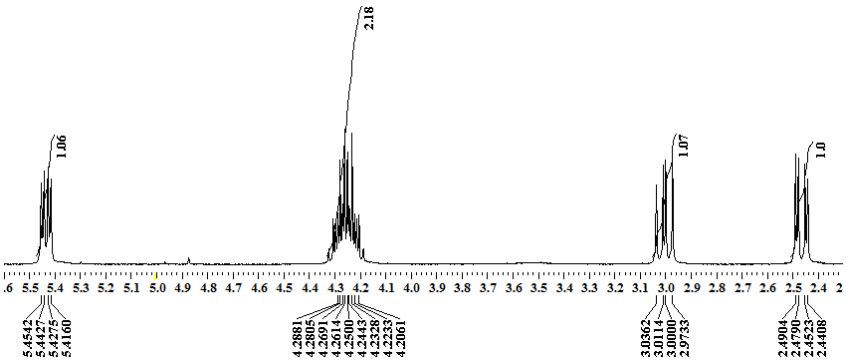
^{1}H NMR in $CDCl_3$



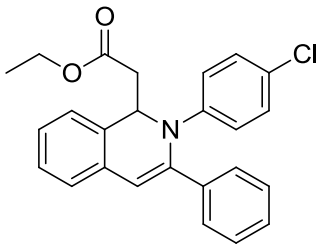
Ethyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3c**)



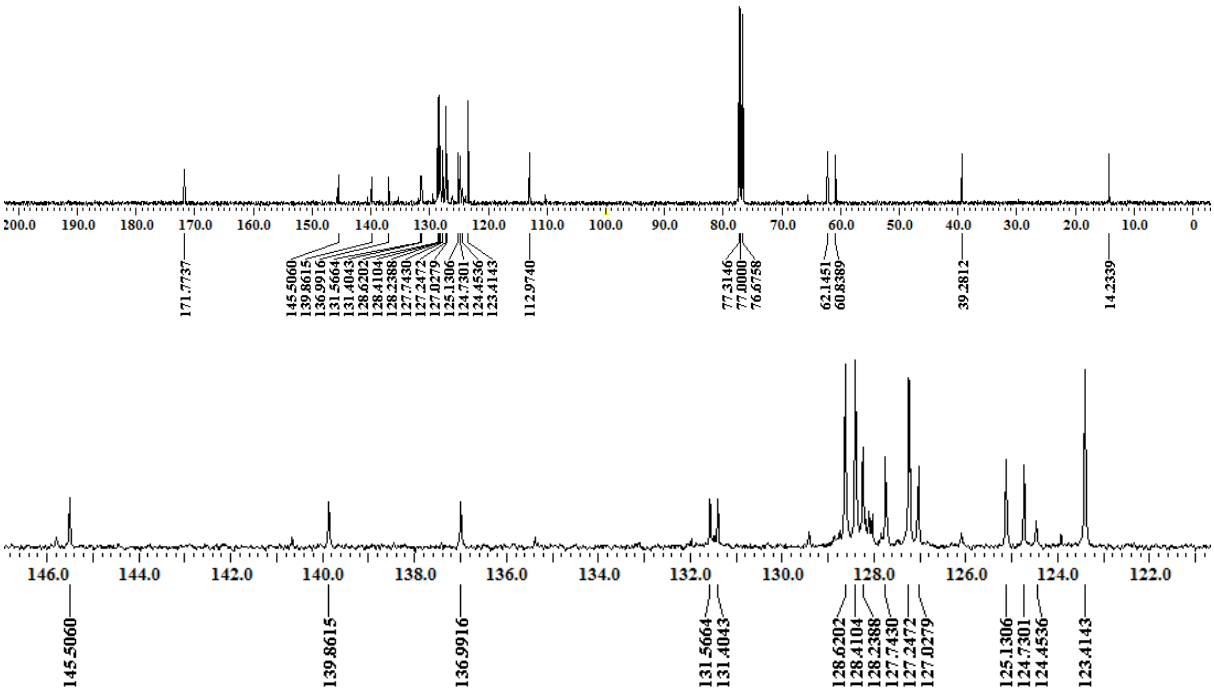




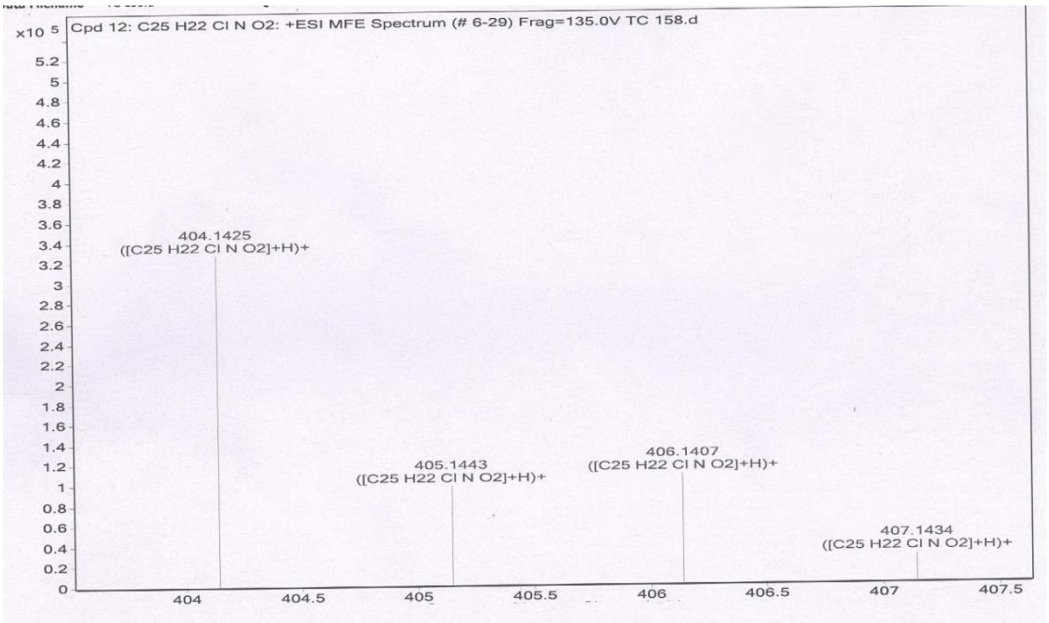
^{13}C NMR in $CDCl_3$



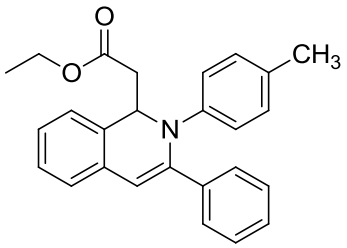
Ethyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3c**)



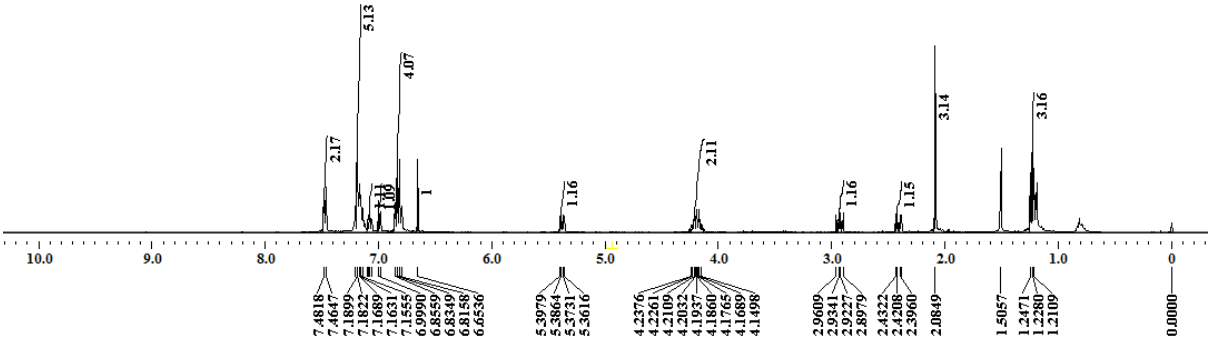
HRMS: Ethyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate(**3c**)

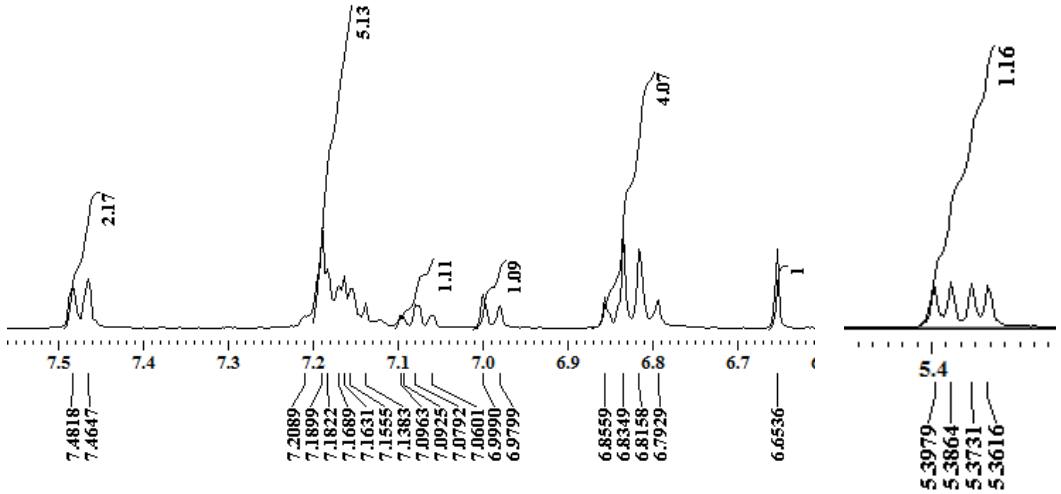


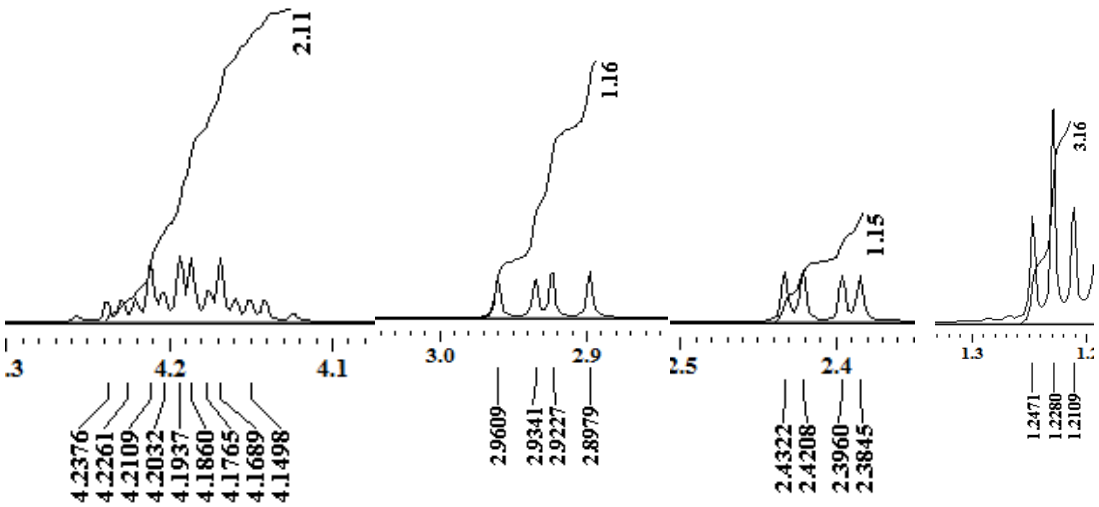
^{1}H NMR in $CDCl_3$



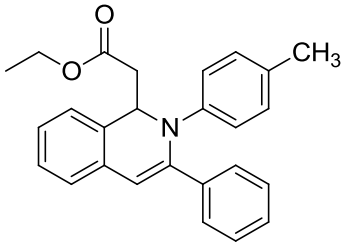
Ethyl 2-(3-phenyl-2-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3d**)



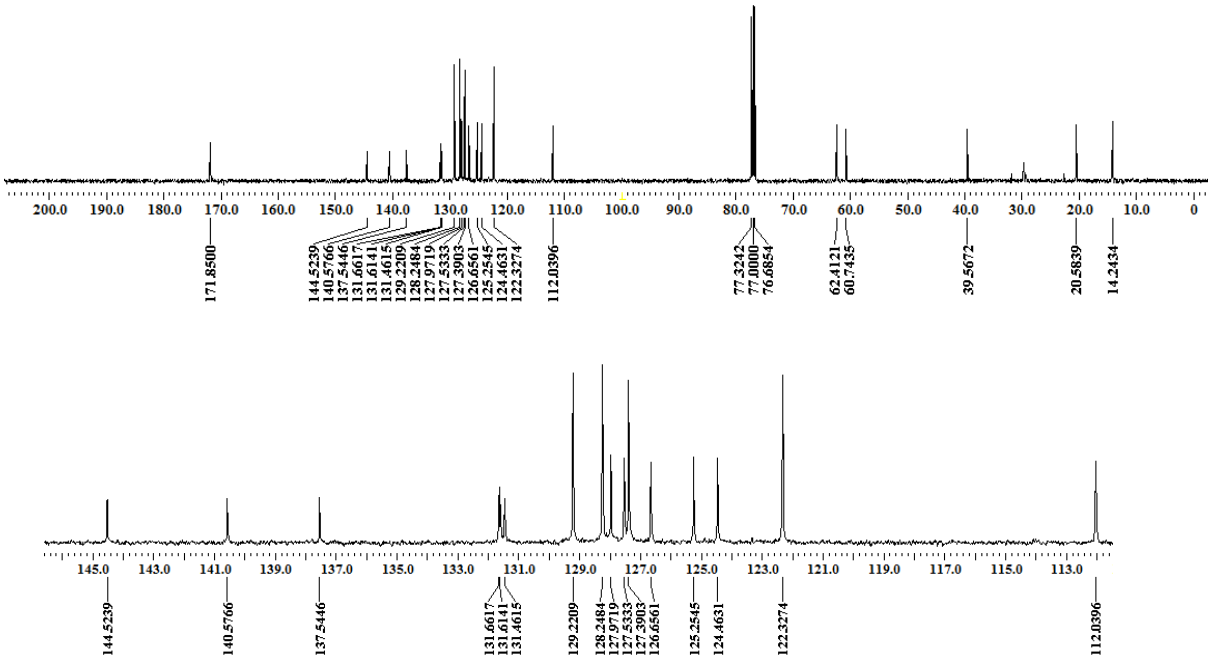




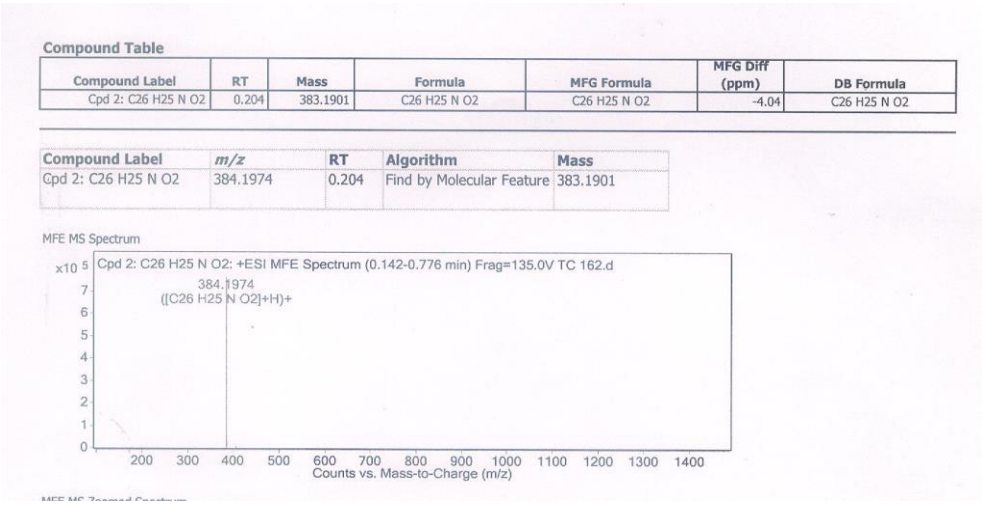
^{13}C NMR in $CDCl_3$



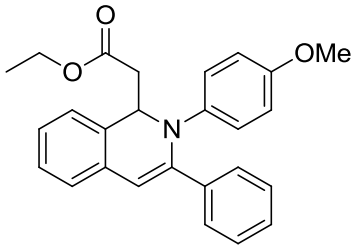
Ethyl 2-(3-phenyl-2-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3d**)



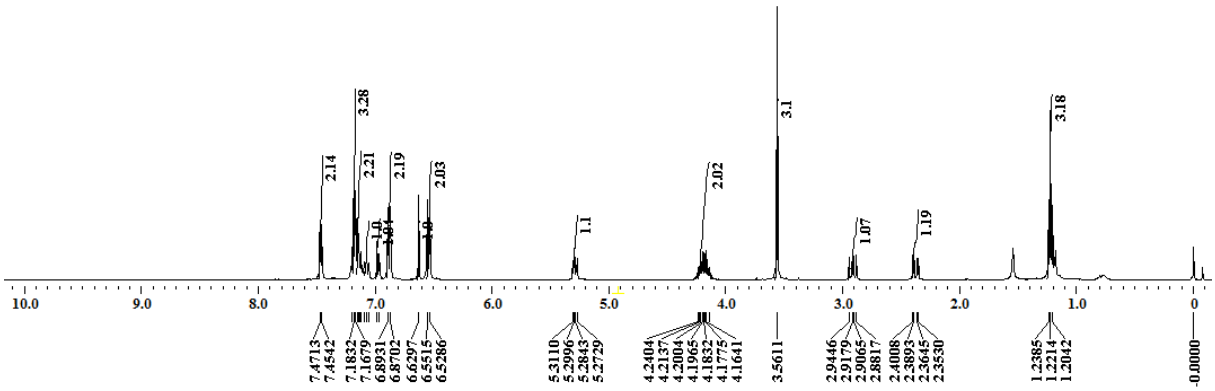
HRMS: Ethyl 2-(3-phenyl-2-(p-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3d**)

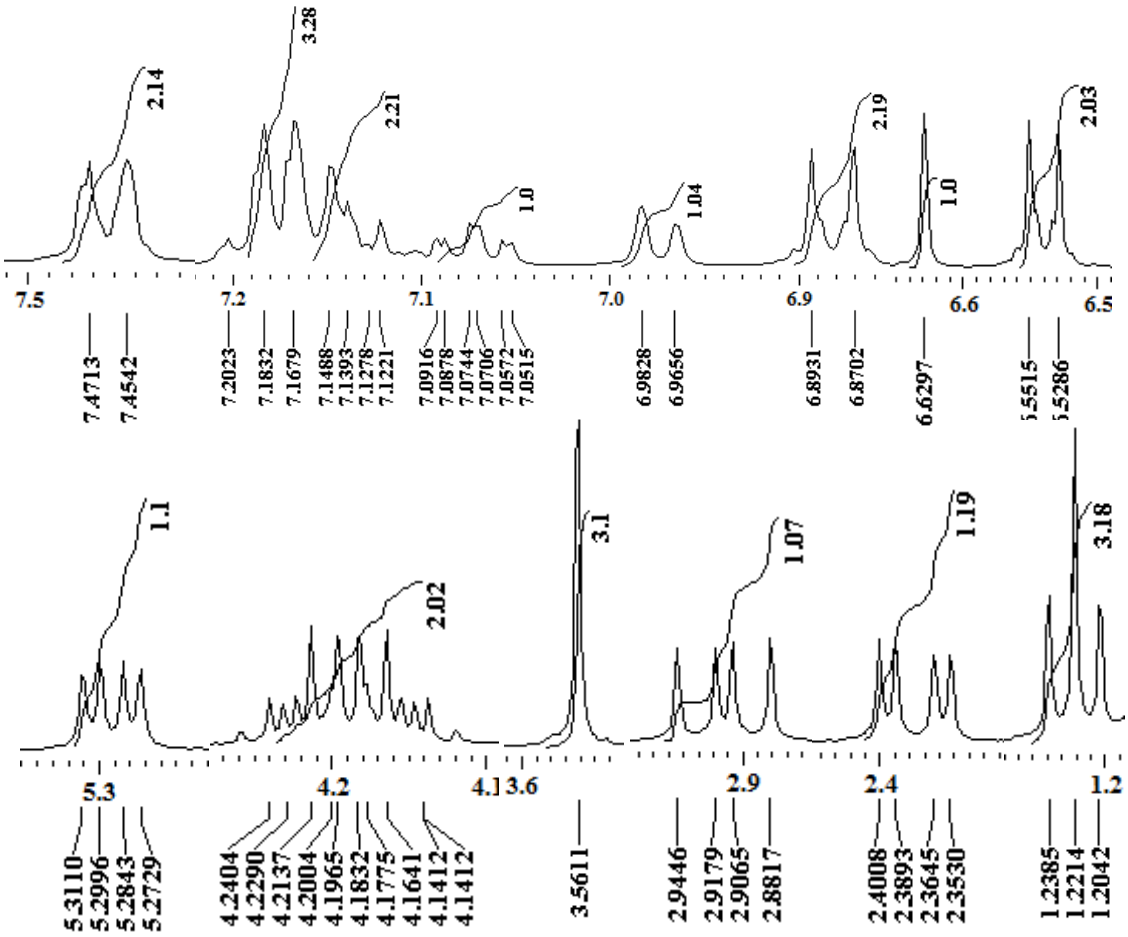


^{1}H NMR in $CDCl_3$

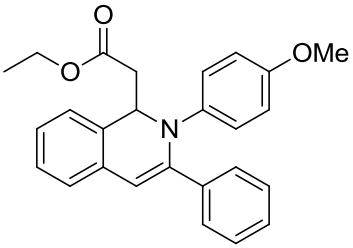


Ethyl 2-(2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3e**)

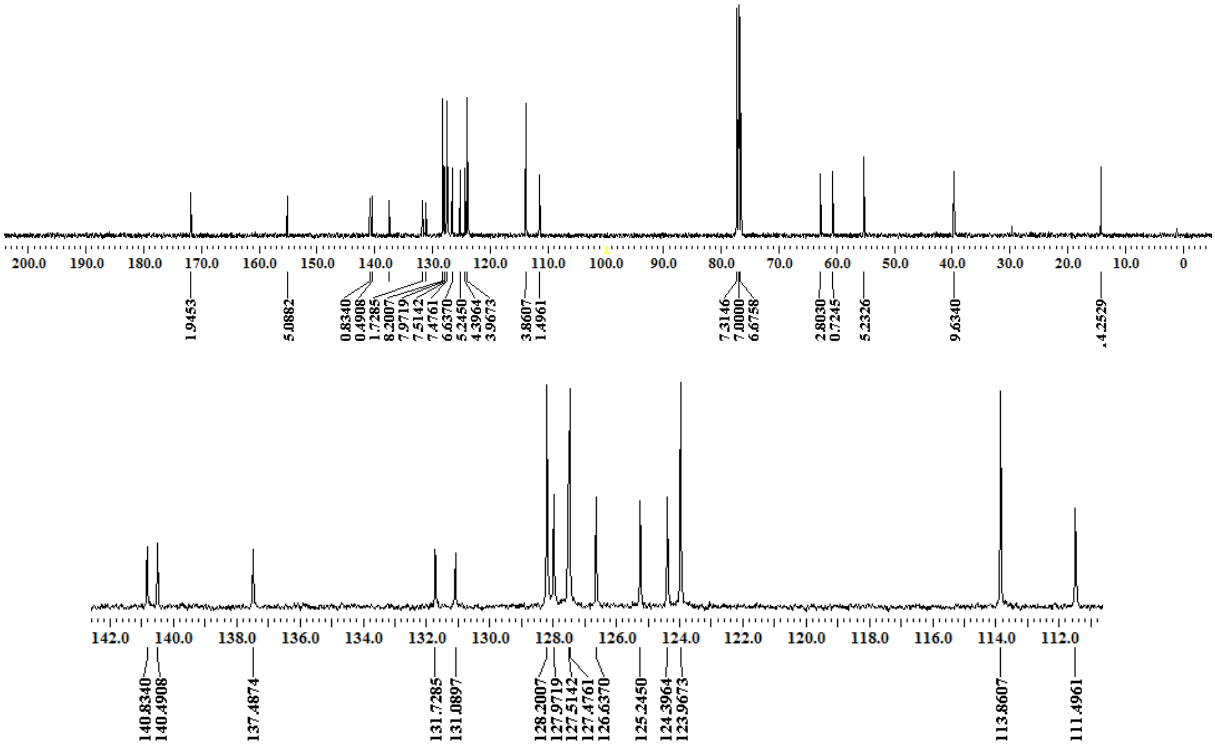




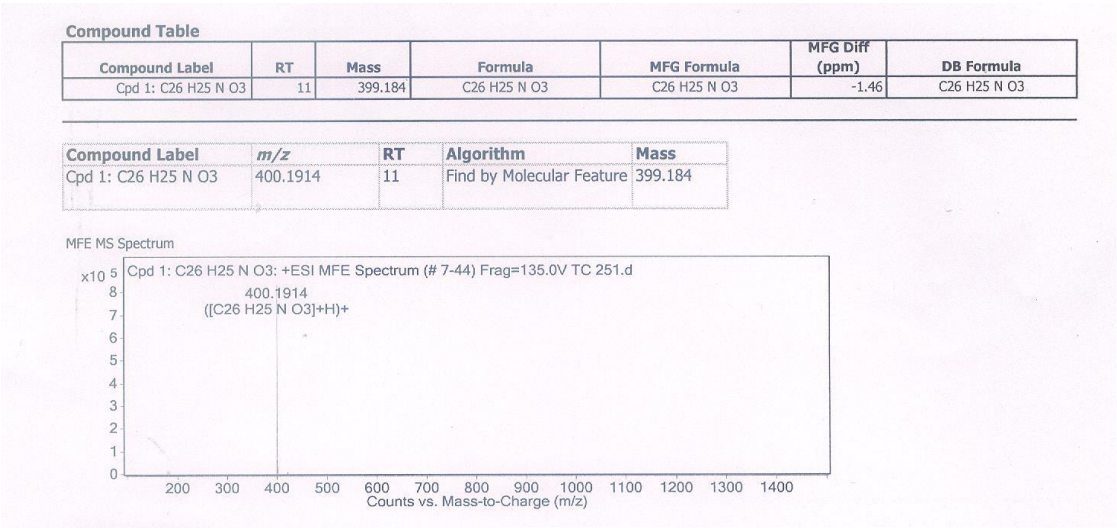
^{13}C NMR in $CDCl_3$



Ethyl 2-(2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3e**)



HRMS: Ethyl 2-(2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3e**)

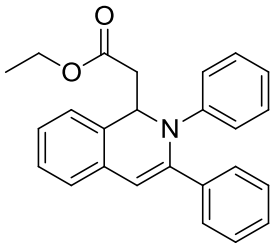


Compound Table

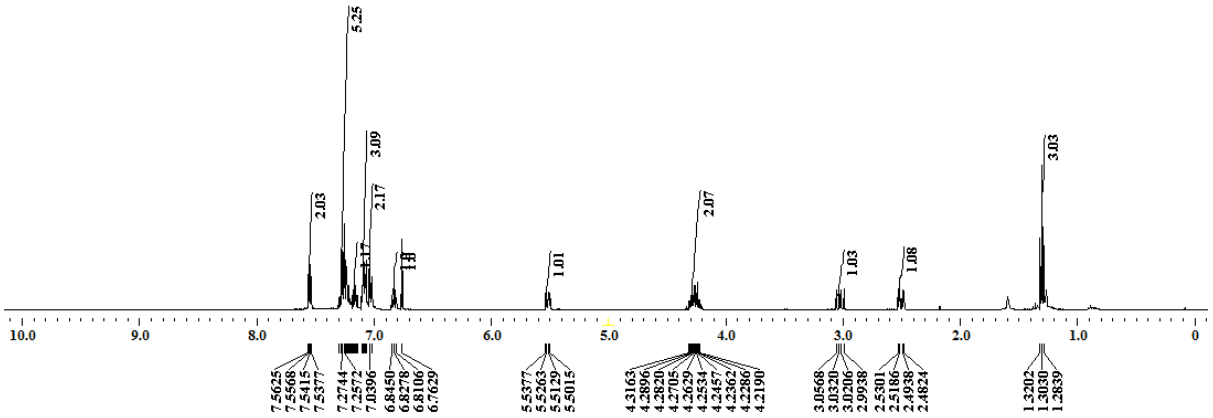
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C26 H25 N O3	11	399.184	C26 H25 N O3	C26 H25 N O3	-1.46	C26 H25 N O3

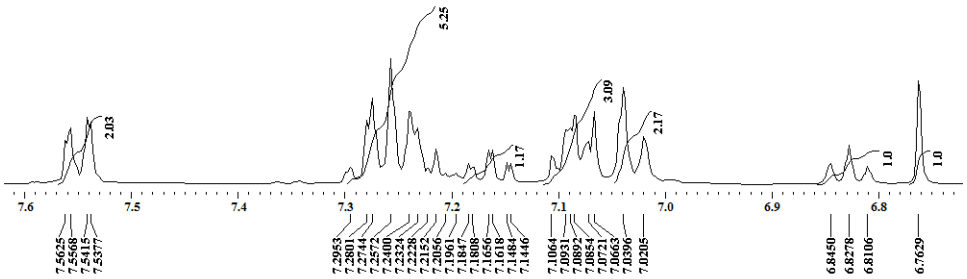
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C26 H25 N O3	400.1914	11	Find by Molecular Feature	399.184

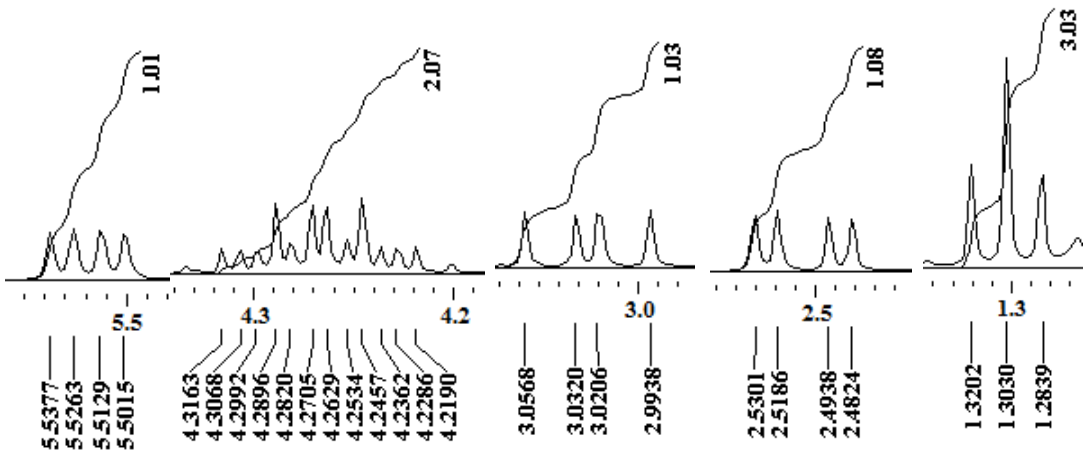
^{1}H NMR in $CDCl_3$



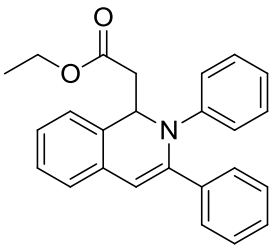
Ethyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3f**)



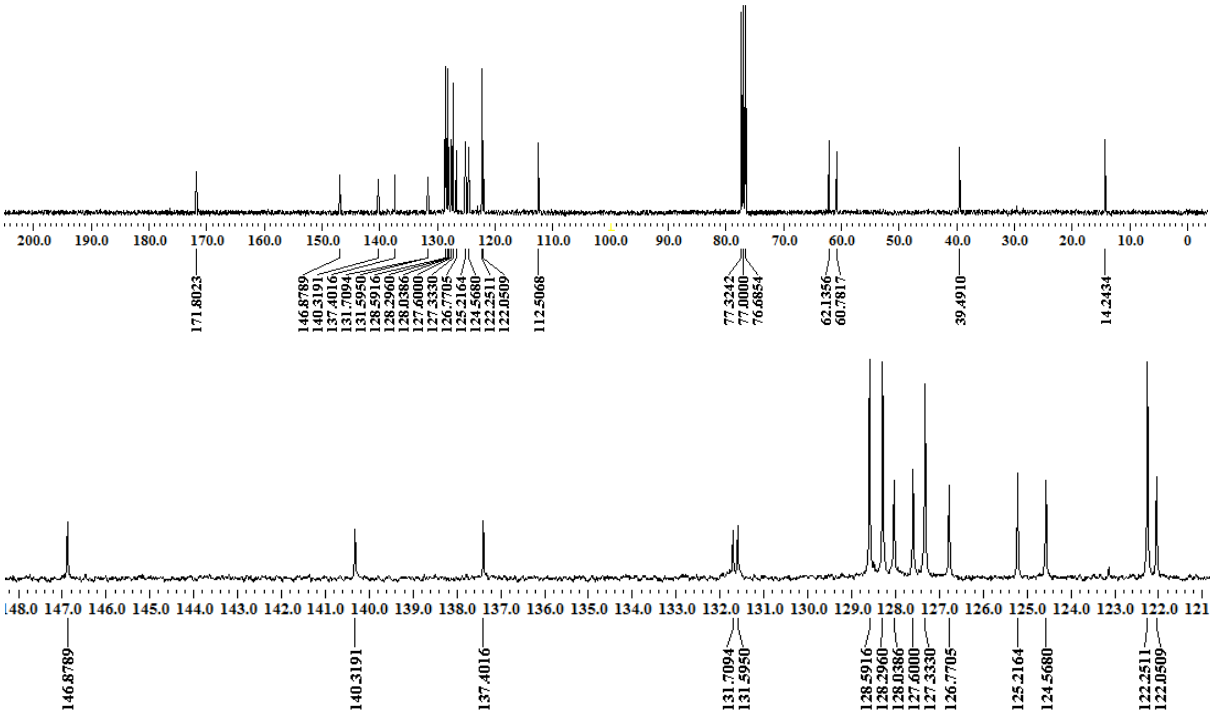




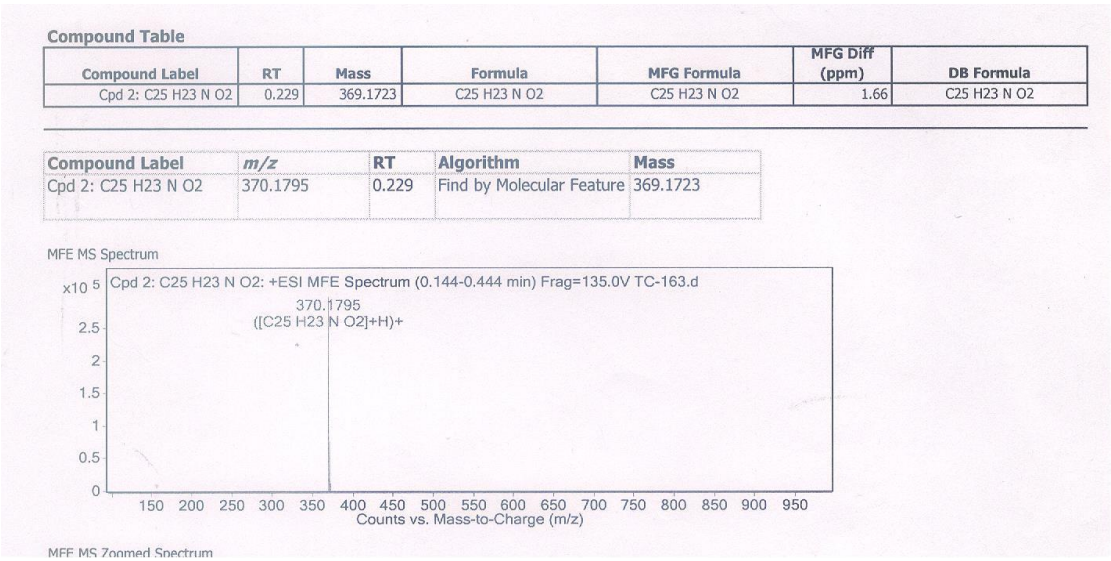
^{13}C NMR in $CDCl_3$



Ethyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3f**)



HRMS: Ethyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3f**)



Compound Table

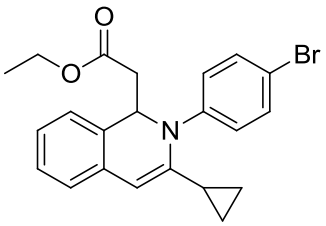
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 2: C25 H23 N O2	0.229	369.1723	C25 H23 N O2	C25 H23 N O2	1.66	C25 H23 N O2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 2: C25 H23 N O2	370.1795	0.229	Find by Molecular Feature	369.1723

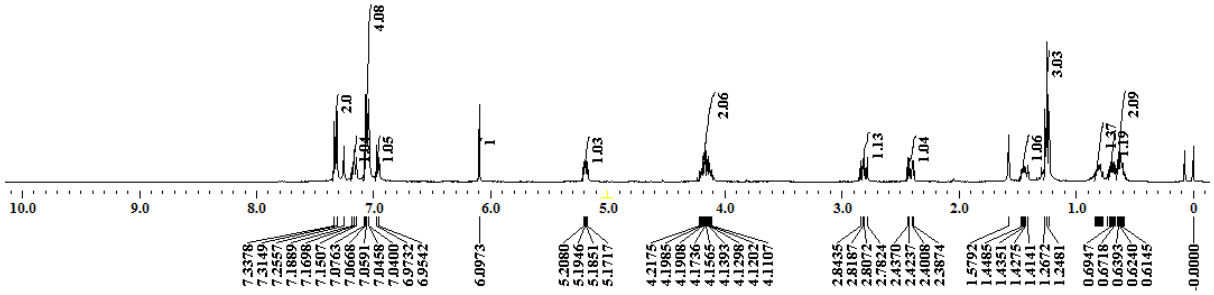
MFE MS Spectrum

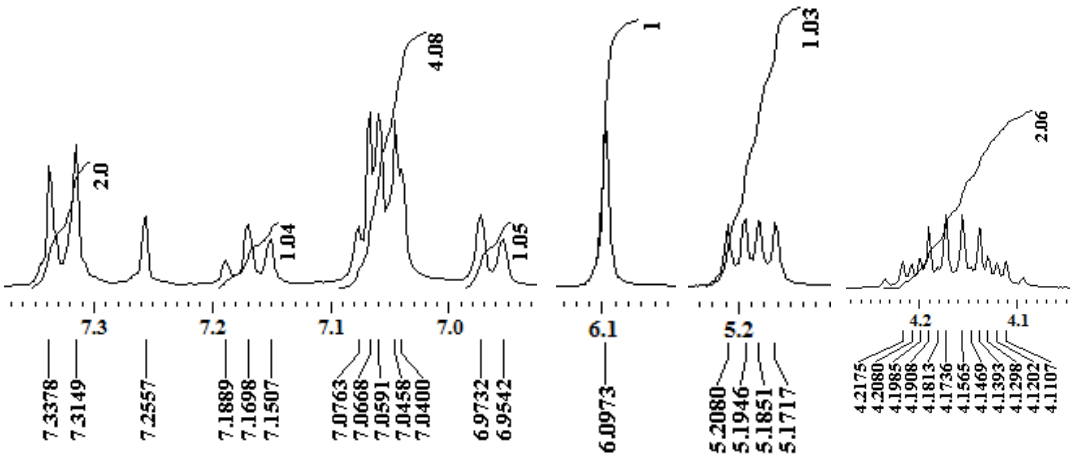
MFE MS Zoomed Spectrum

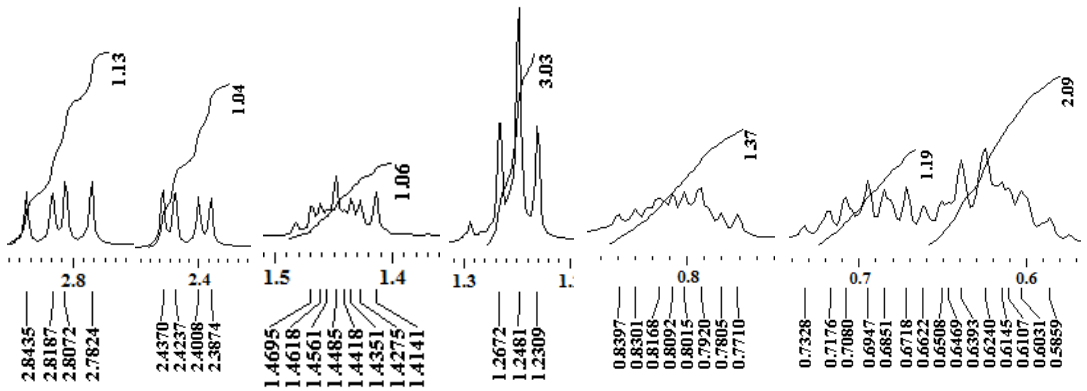
^{1}H NMR in $CDCl_3$



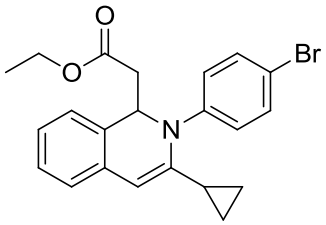
Ethyl 2-(2-(4-bromophenyl)-3-cyclopropyl-1,2-dihydroisoquinolin-1-yl)acetate (**3g**)



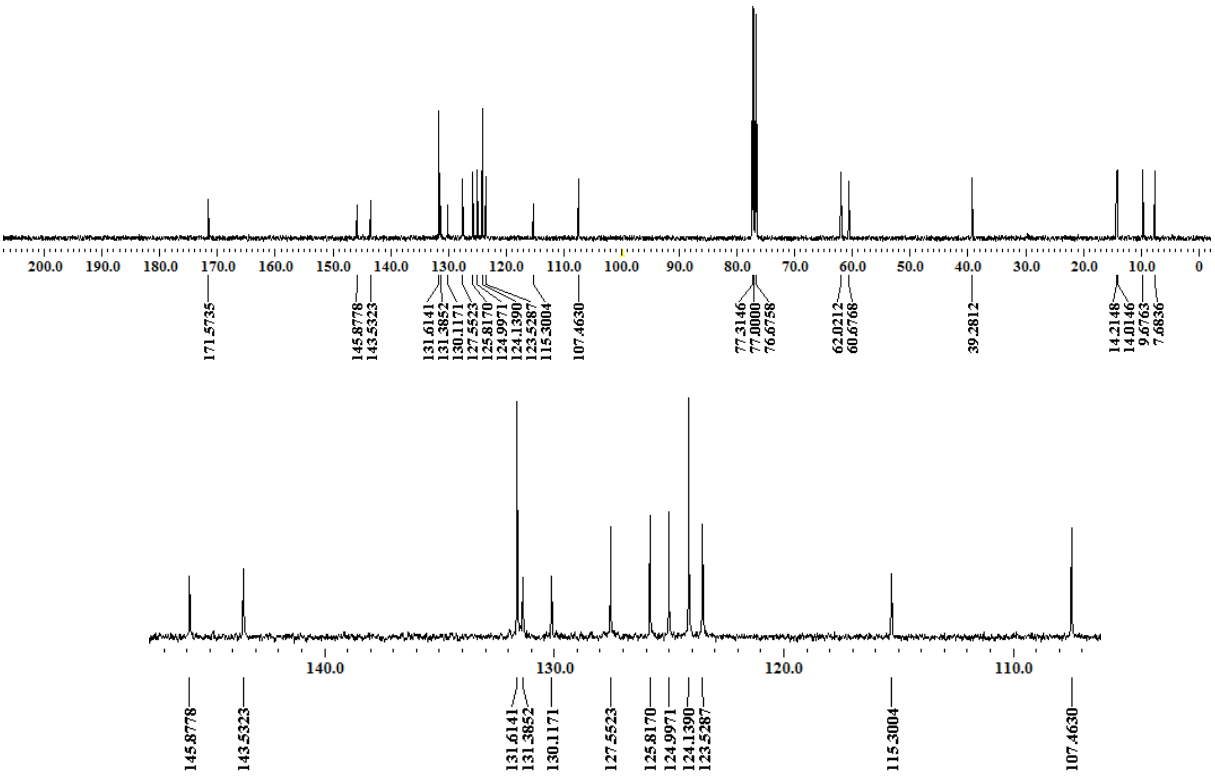




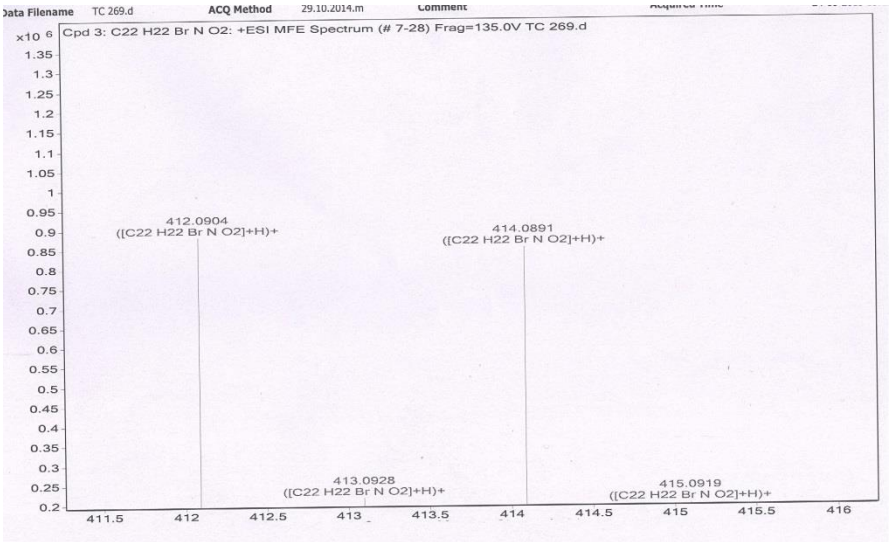
^{13}C NMR in $CDCl_3$



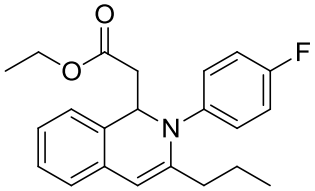
ethyl 2-(2-(4-bromophenyl)-3-cyclopropyl-1,2-dihydroisoquinolin-1-yl)acetate (**3g**)



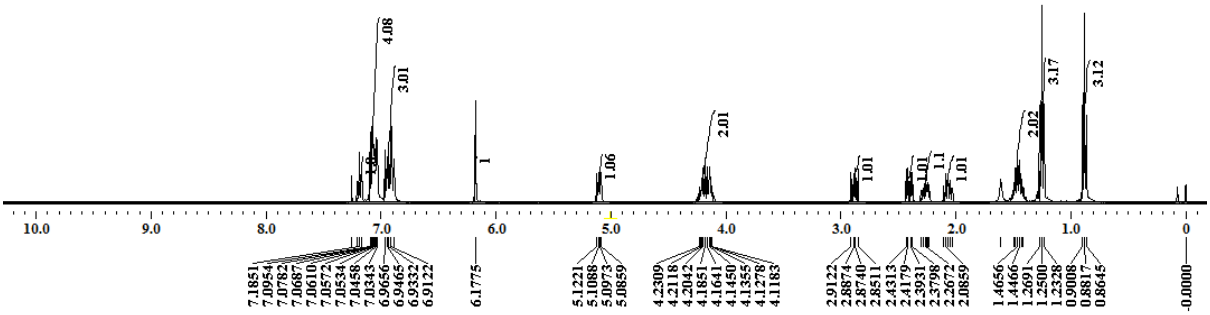
HRMS: Ethyl 2-(2-(4-bromophenyl)-3-cyclopropyl-1,2-dihydroisoquinolin-1-yl)acetate (**3g**)

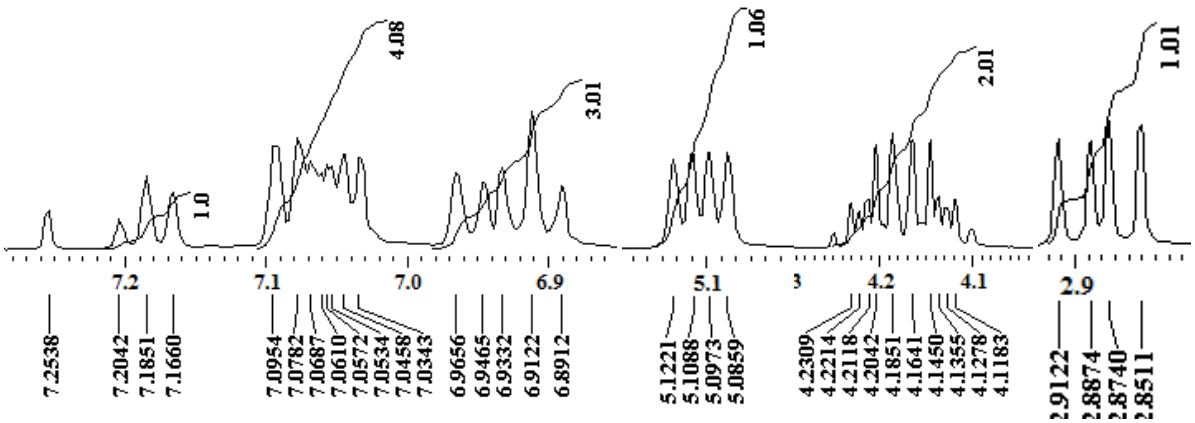


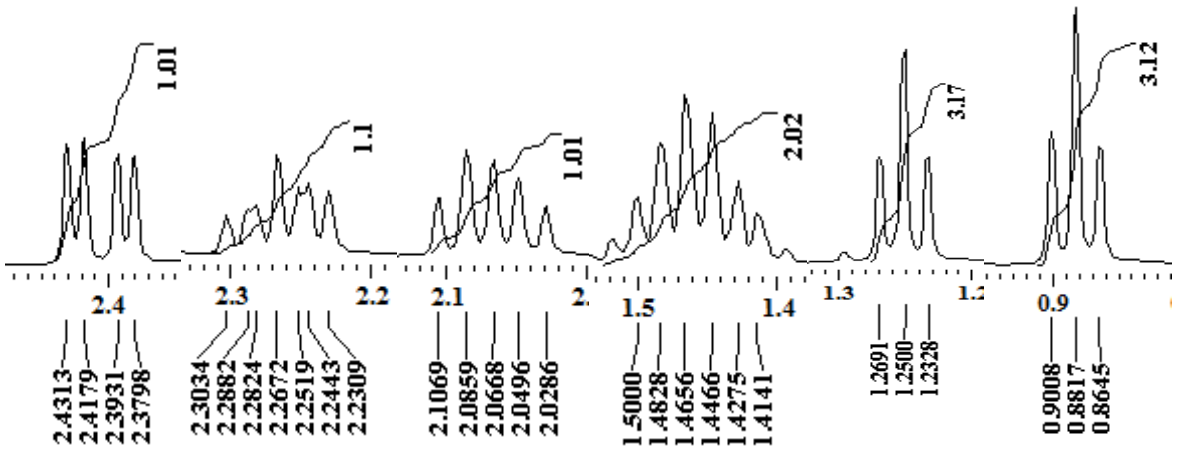
^{13}C NMR in $CDCl_3$



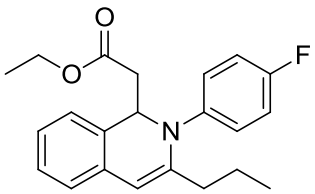
Ethyl 2-(2-(4-fluorophenyl)-3-propyl-1,2-dihydroisoquinolin-1-yl)acetate (**3h**)



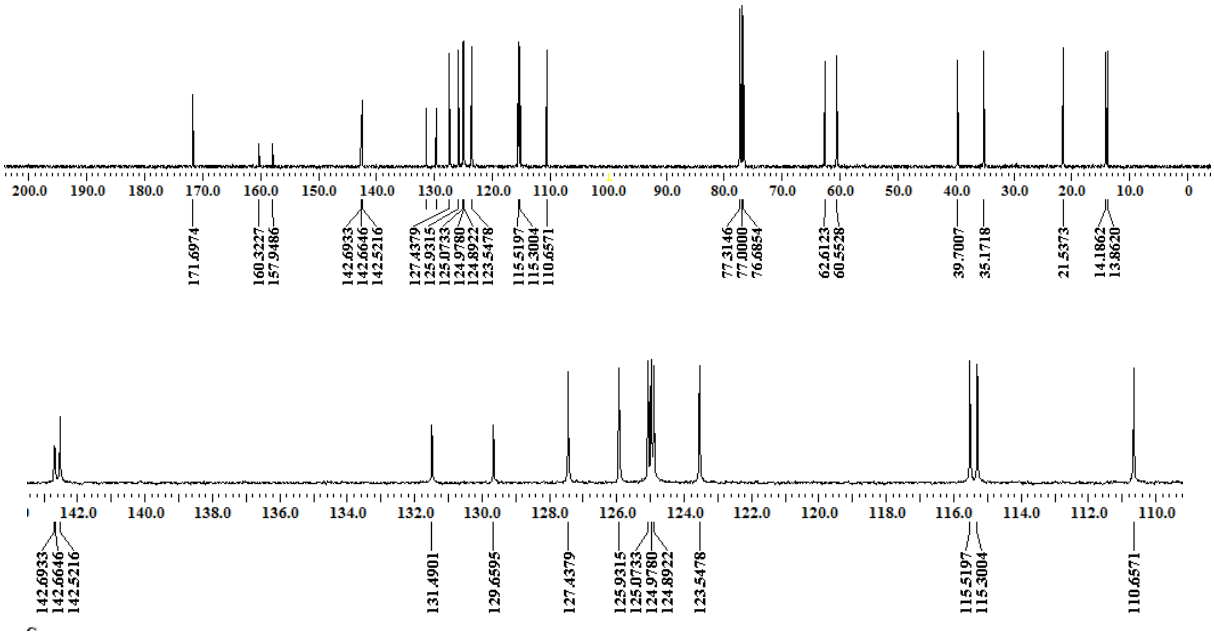




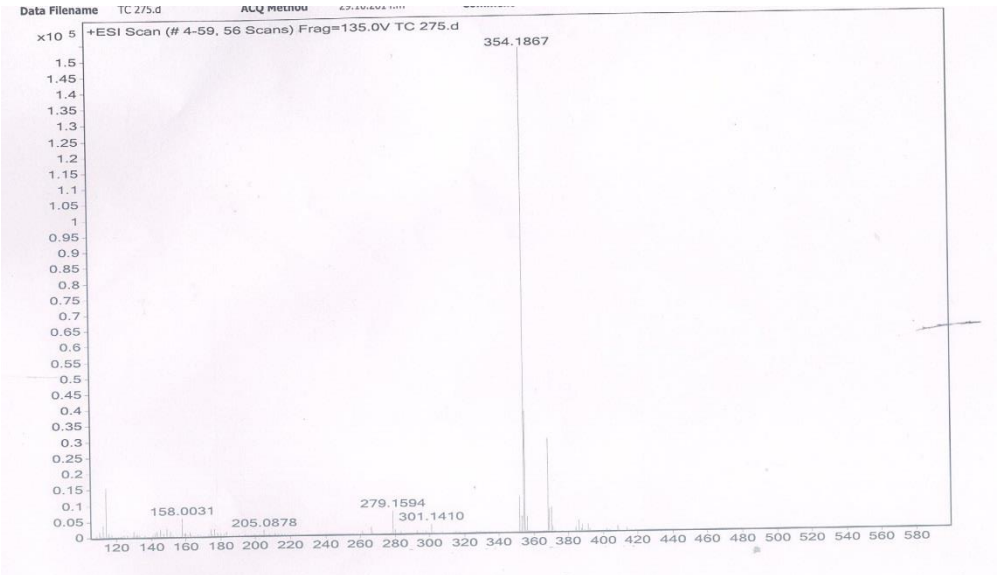
^{13}C NMR in $CDCl_3$



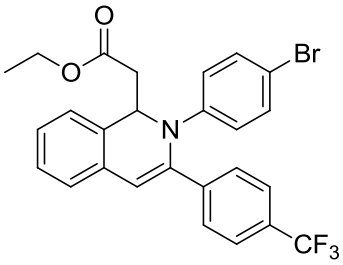
Ethyl 2-(2-(4-fluorophenyl)-3-propyl-1,2-dihydroisoquinolin-1-yl)acetate (**3h**)



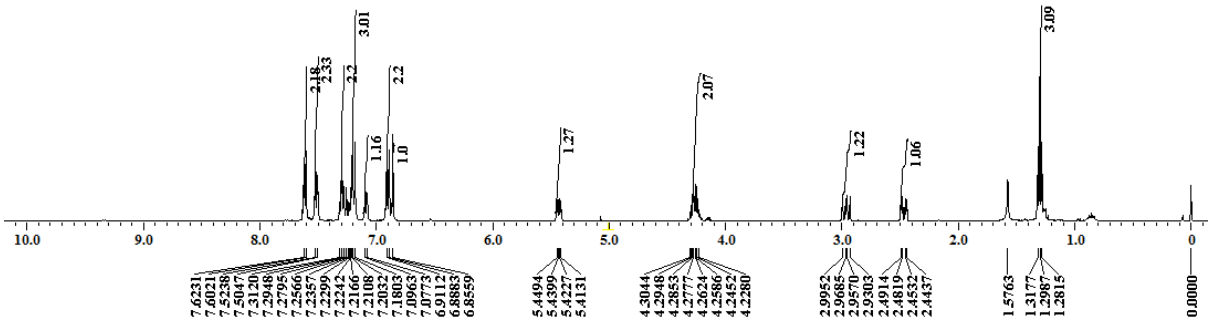
HRMS: Ethyl 2-(2-(4-fluorophenyl)-3-propyl-1,2-dihydroisoquinolin-1-yl)acetate (**3h**)

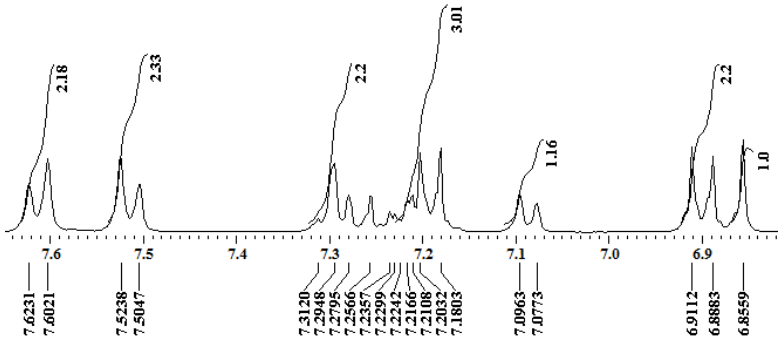


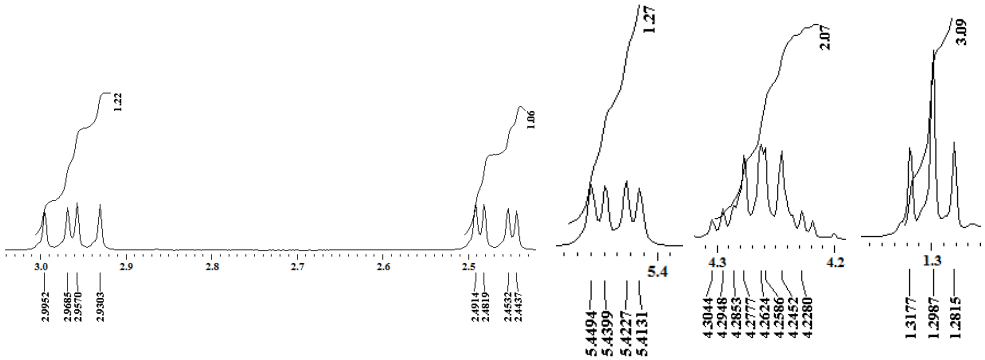
^{1}H NMR in $CDCl_3$



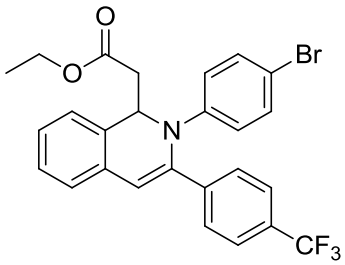
ethyl 2-(2-(4-bromophenyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3i**)



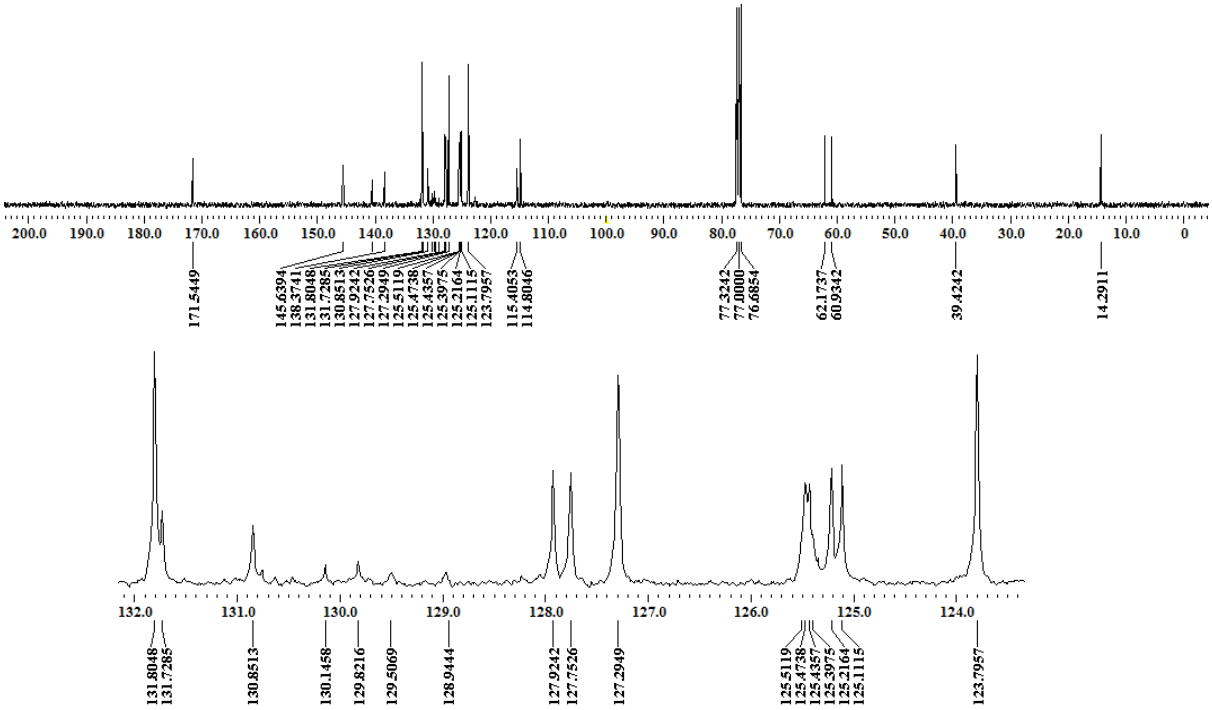




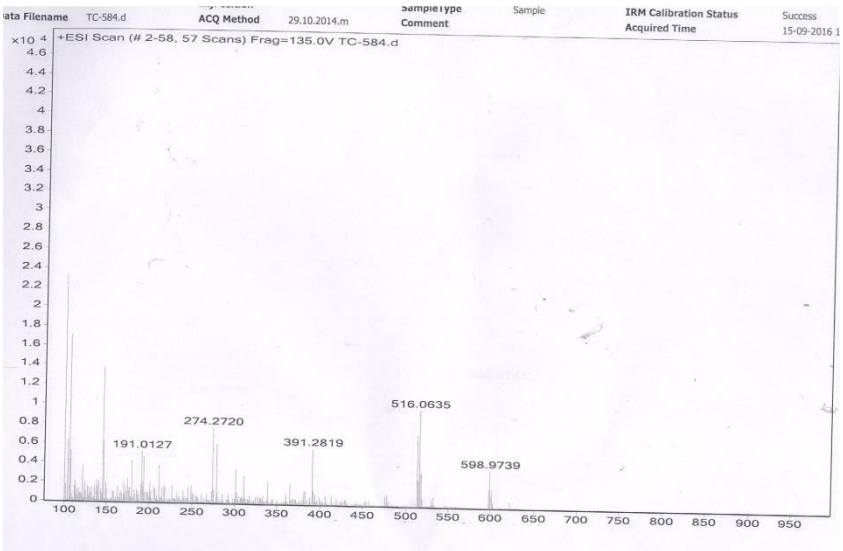
^{13}C NMR in $CDCl_3$



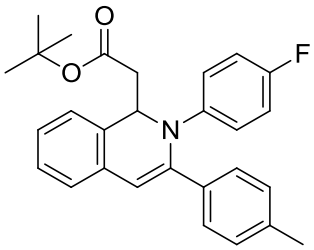
ethyl 2-(2-(4-bromophenyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3i**)



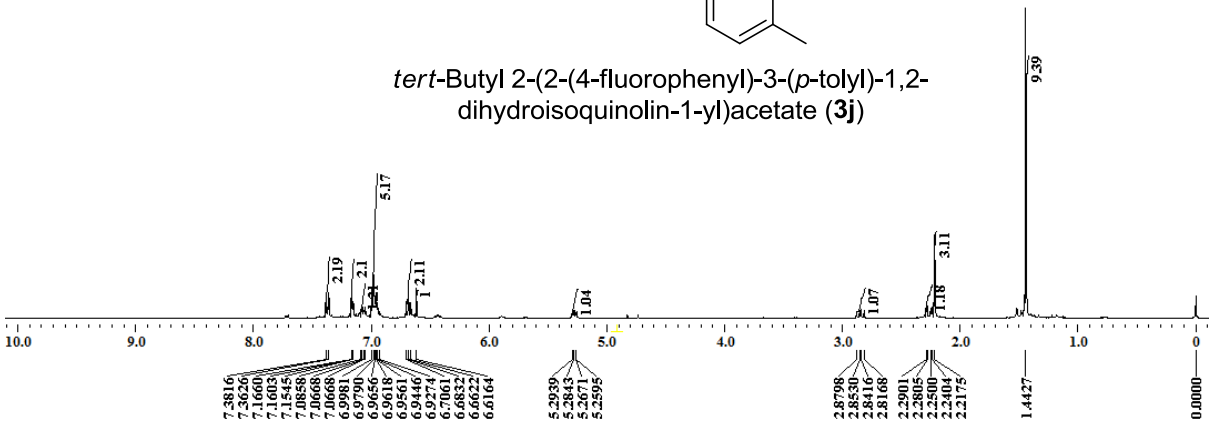
HRMS: Ethyl 2-(2-(4-bromophenyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3i**)

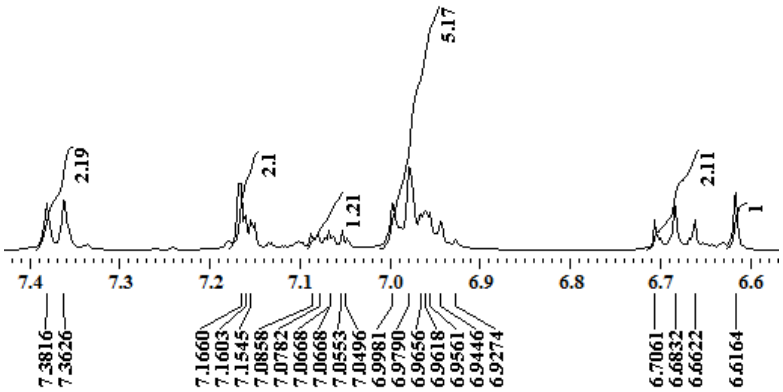


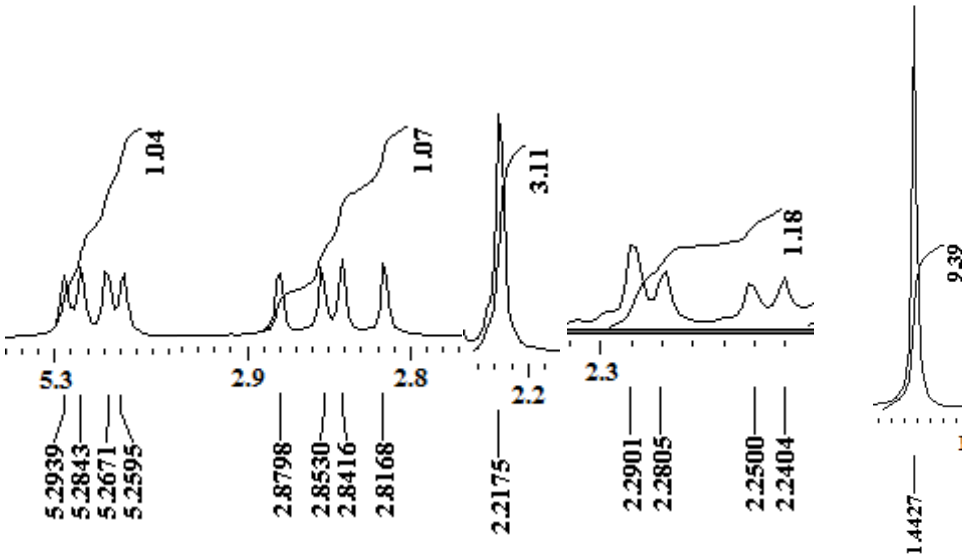
^{1}H NMR in $CDCl_3$



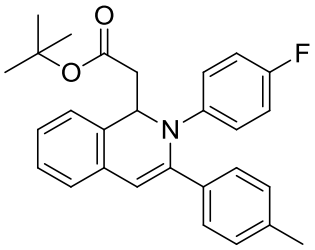
tert-Butyl 2-(2-(4-fluorophenyl)-3-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3j**)



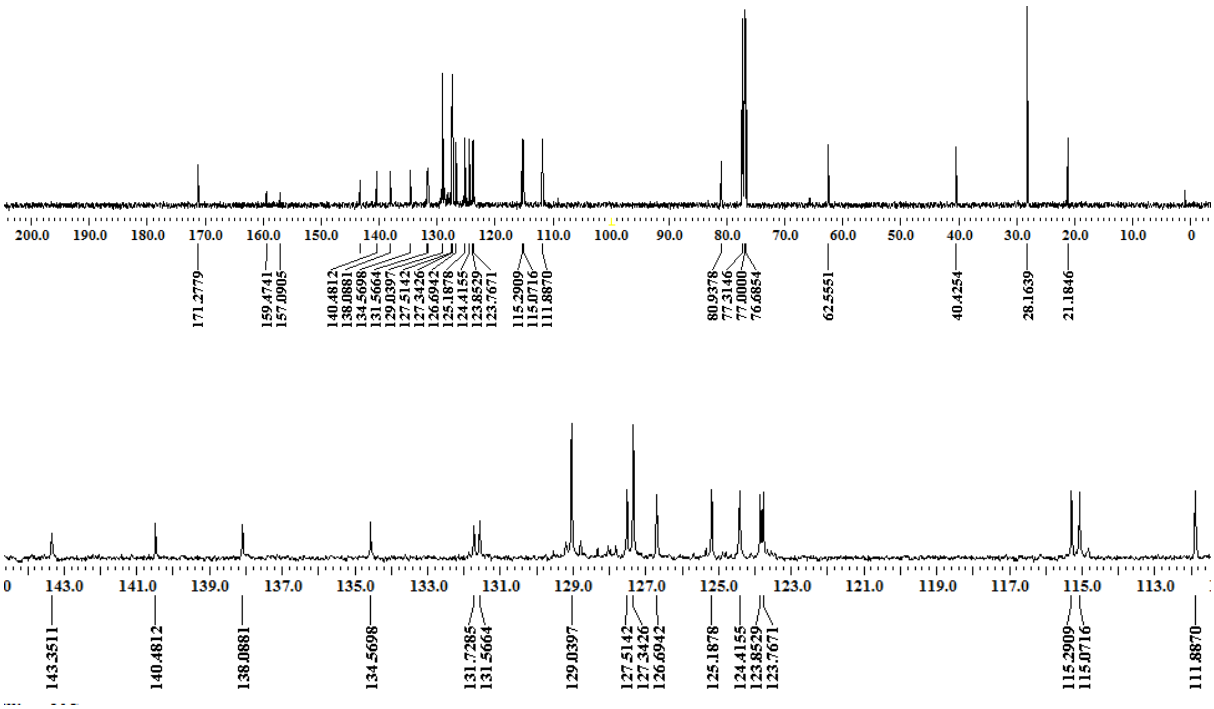




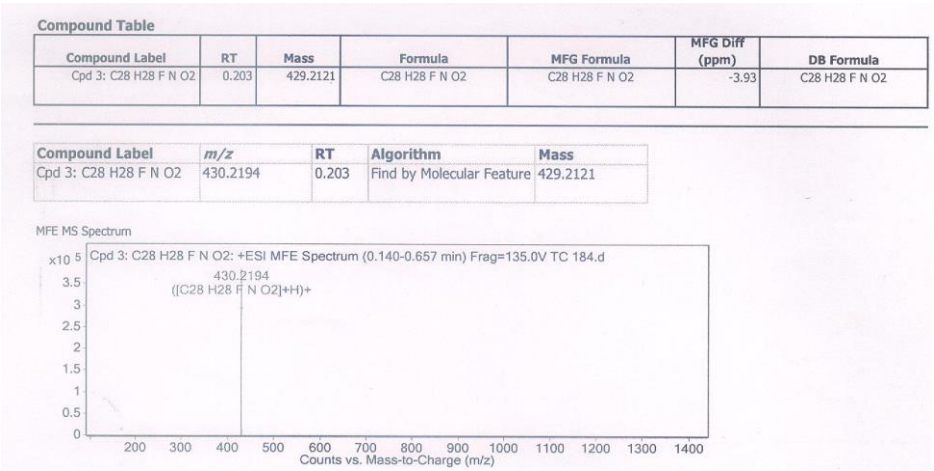
^{13}C NMR in $CDCl_3$



tert-Butyl 2-(2-(4-fluorophenyl)-3-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3j**)



HRMS: *tert*-Butyl 2-(2-(4-fluorophenyl)-3-(p-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3j**)

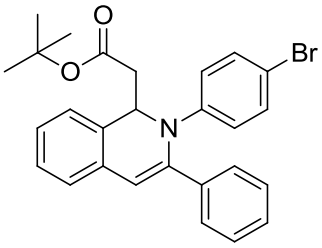


Compound Table

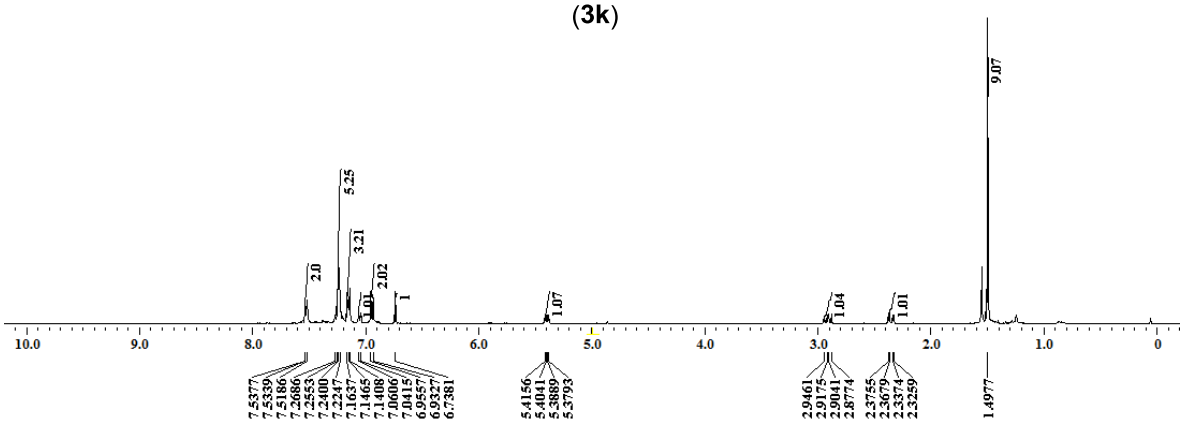
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 3: C28 H28 F N O2	0.203	429.2121	C28 H28 F N O2	C28 H28 F N O2	-3.93	C28 H28 F N O2

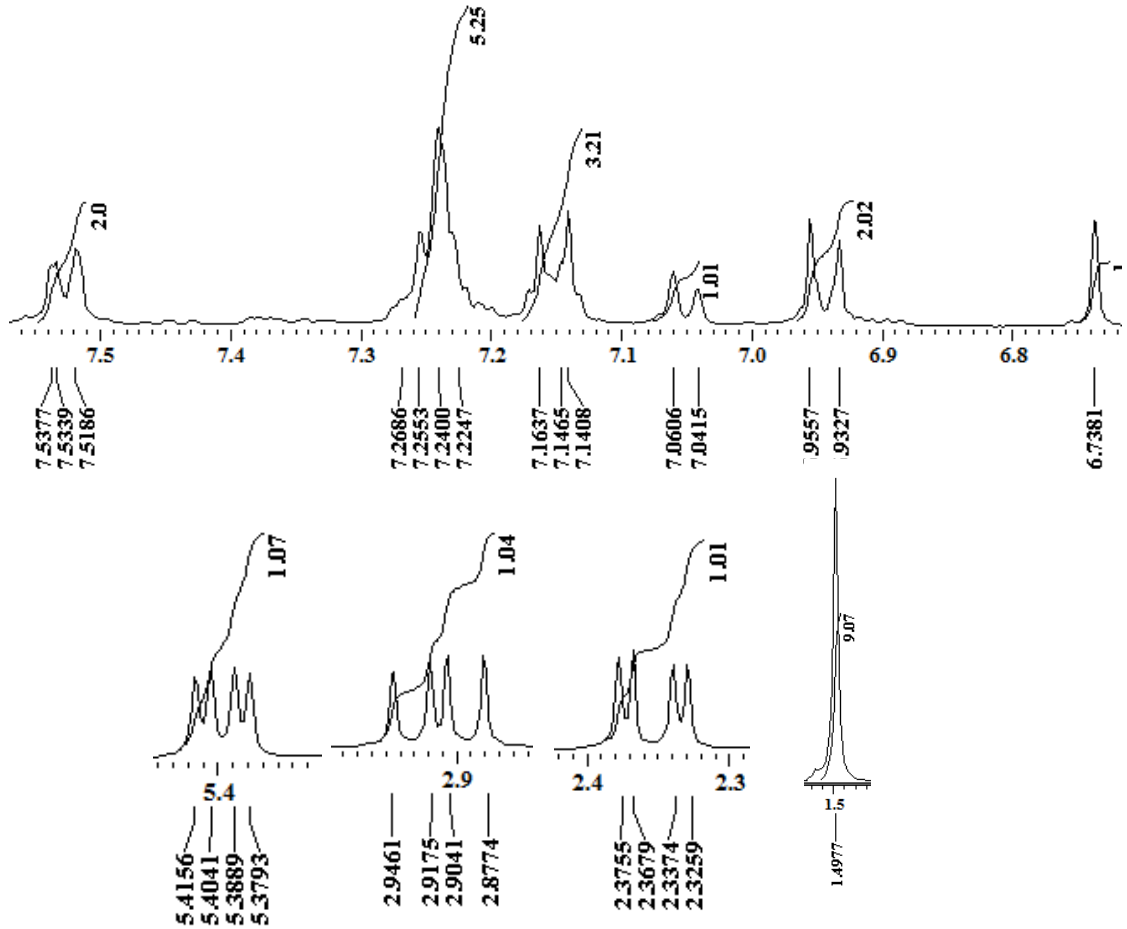
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C28 H28 F N O2	430.2194	0.203	Find by Molecular Feature	429.2121

^{1}H NMR in $CDCl_3$

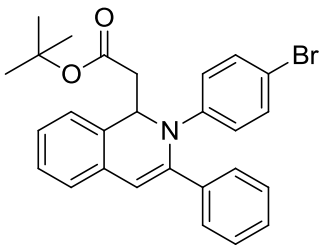


tert-Butyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3k**)

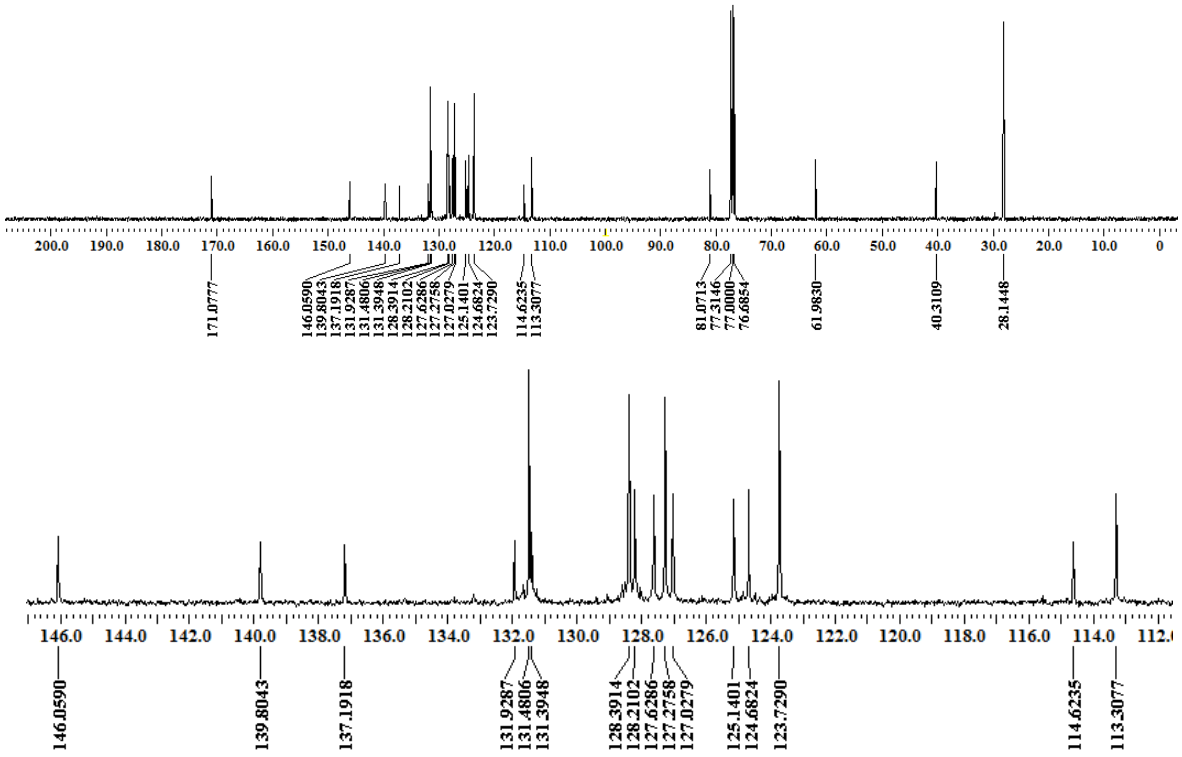




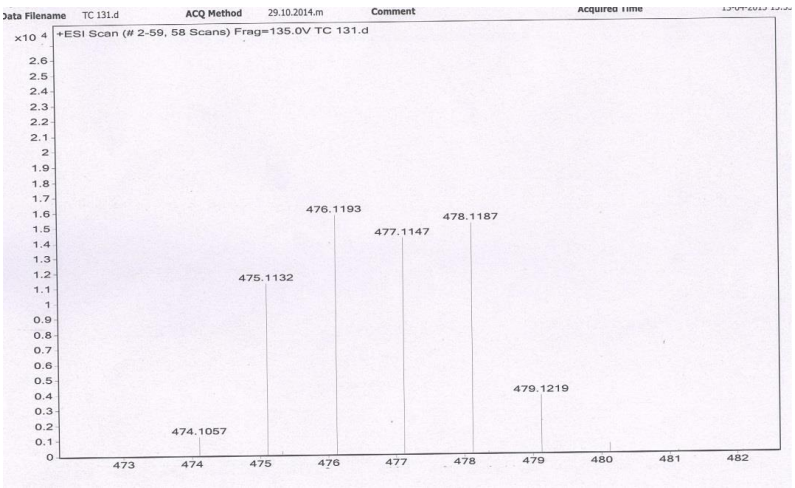
^{13}C NMR in $CDCl_3$



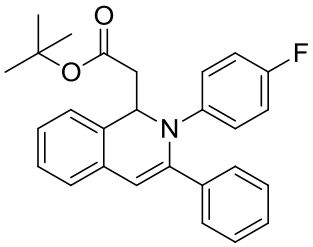
tert-Butyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3k**)



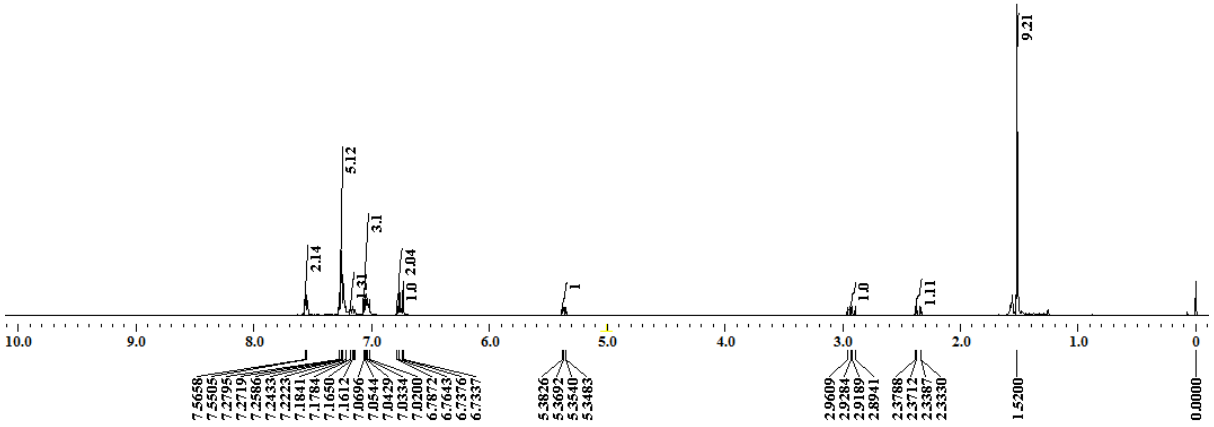
HRMS: tert-Butyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3k**)

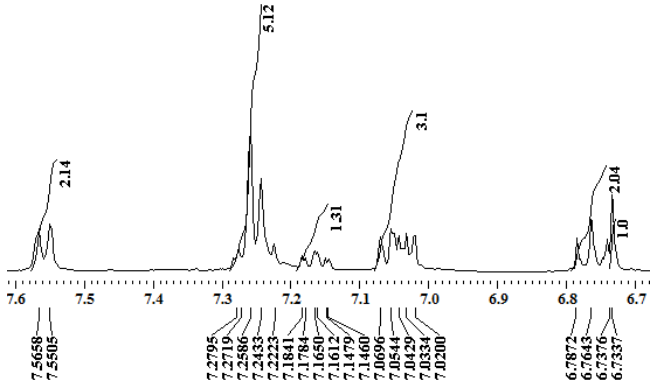


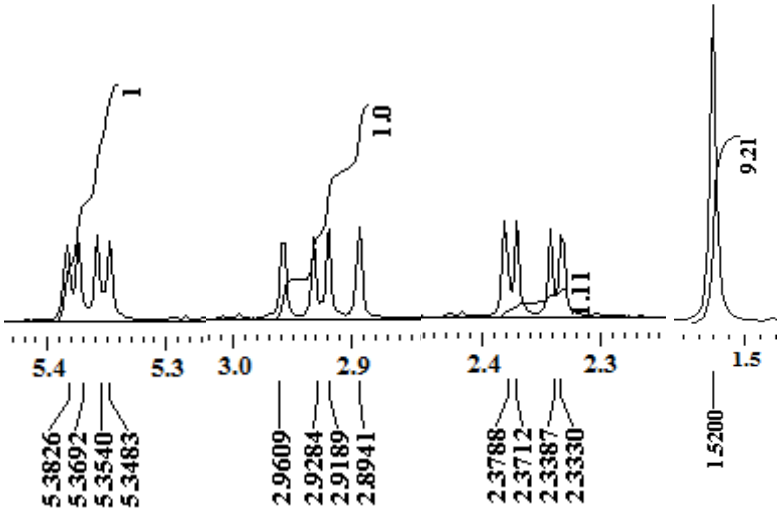
^{1}H NMR in $CDCl_3$



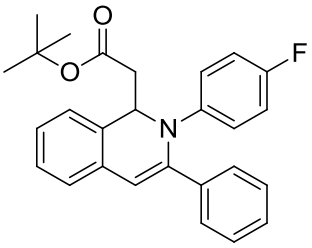
tert-Butyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3l**)



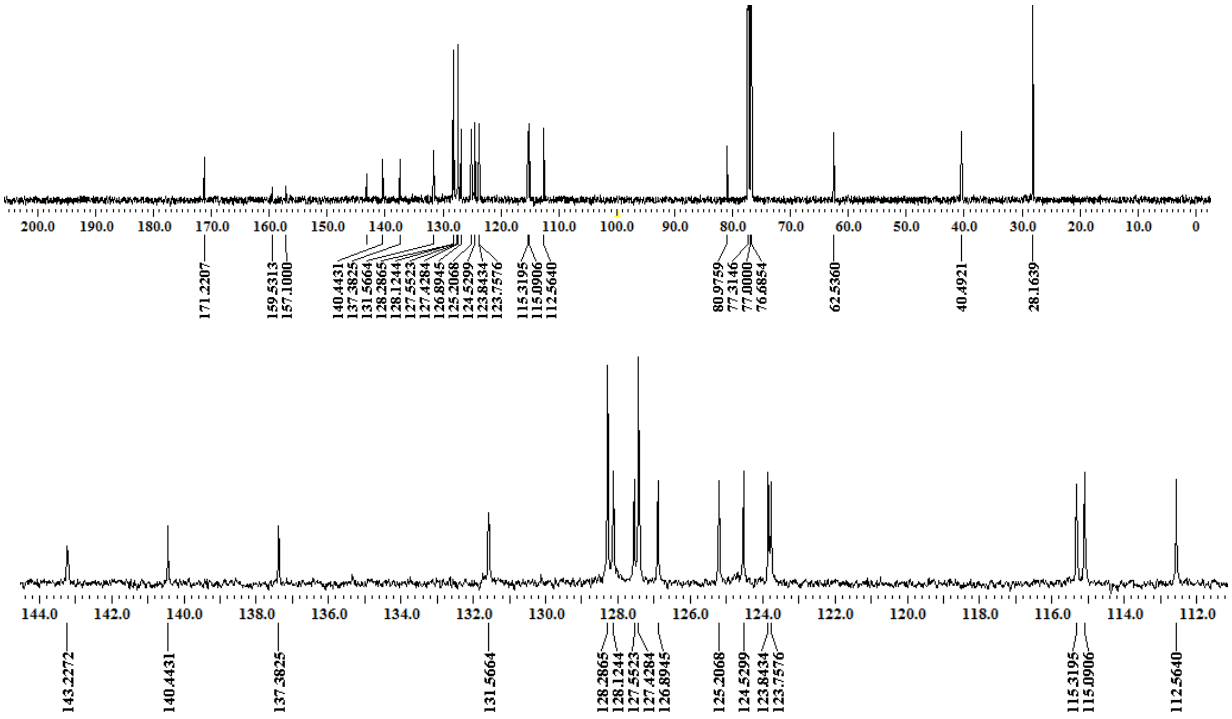




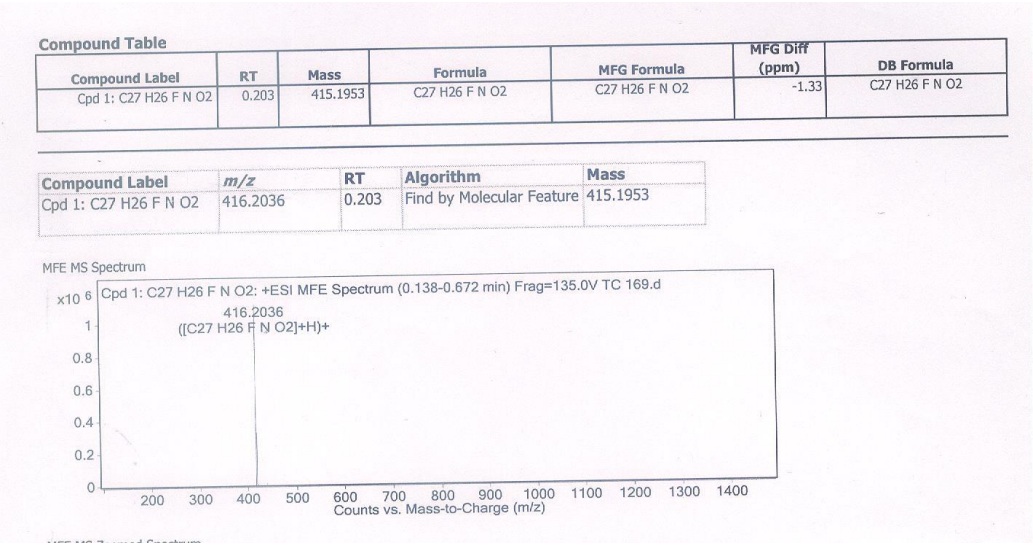
^{13}C NMR in $CDCl_3$



tert-Butyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3l**)



HRMS: tert-Butyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3l**)

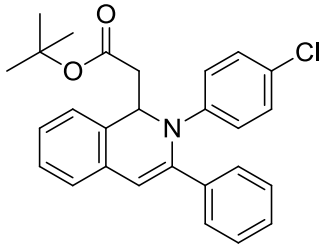


Compound Table

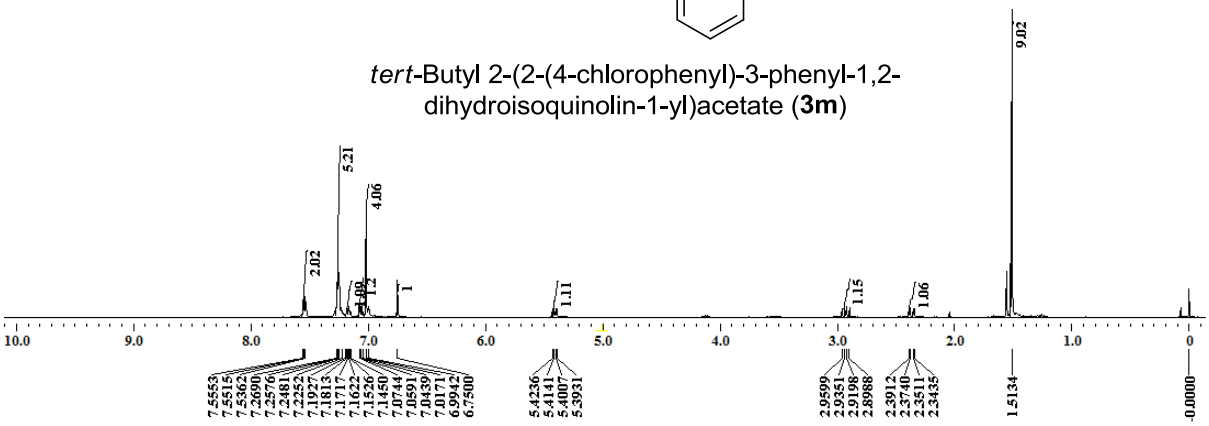
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C27 H26 F N O2	0.203	415.1953	C27 H26 F N O2	C27 H26 F N O2	-1.33	C27 H26 F N O2

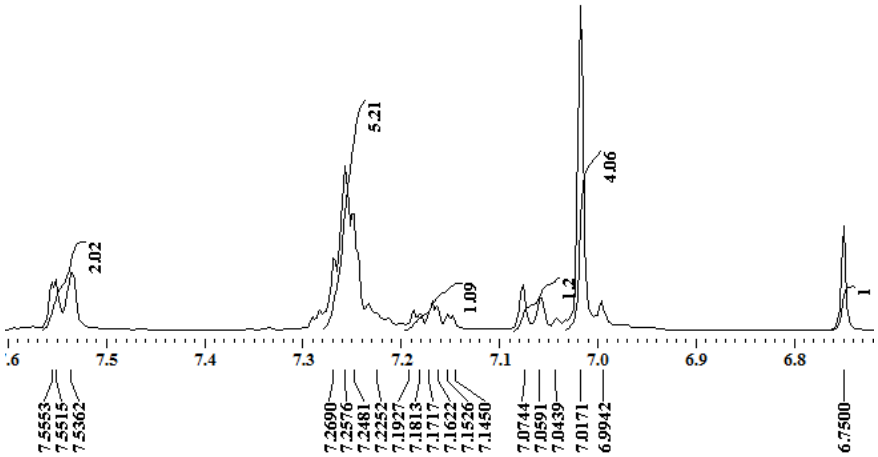
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C27 H26 F N O2	416.2036	0.203	Find by Molecular Feature	415.1953

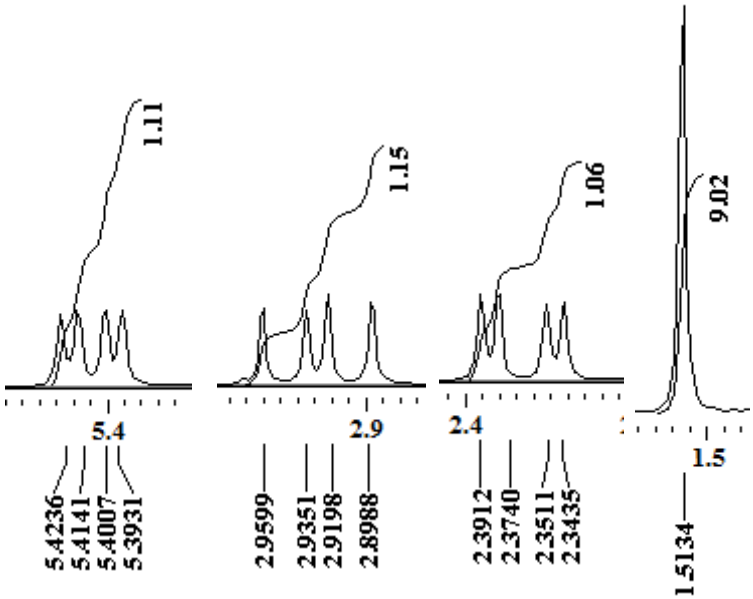
^{1}H NMR in $CDCl_3$



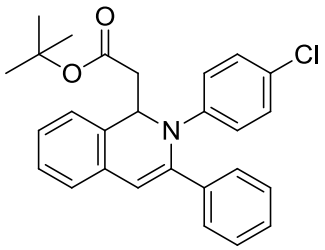
tert-Butyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3m**)



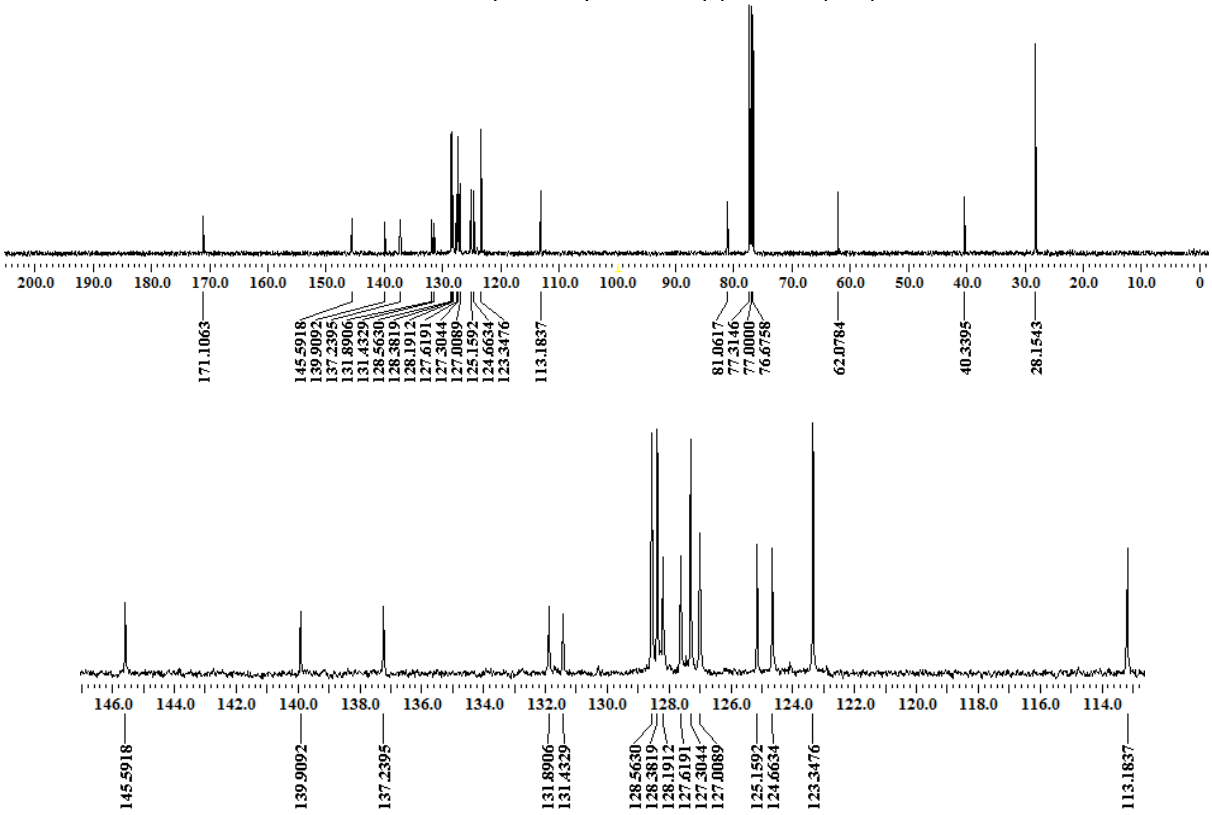




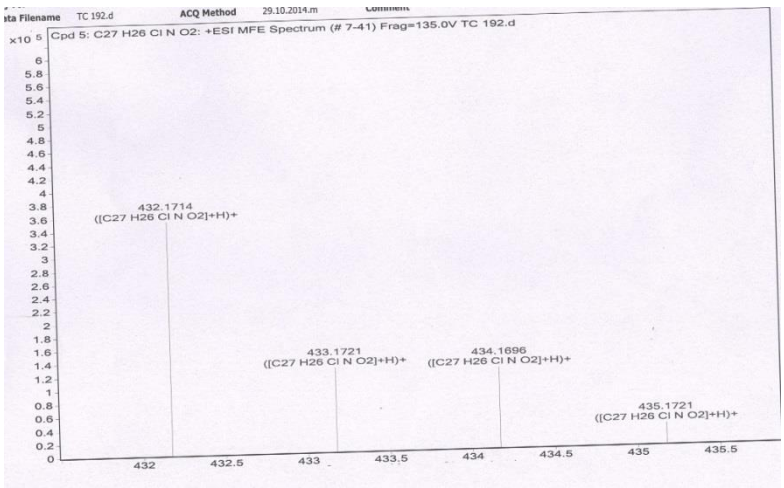
^{13}C NMR in $CDCl_3$



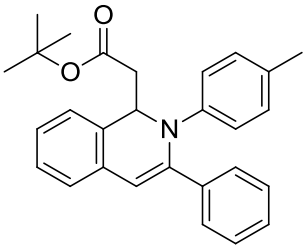
tert-Butyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3m**)



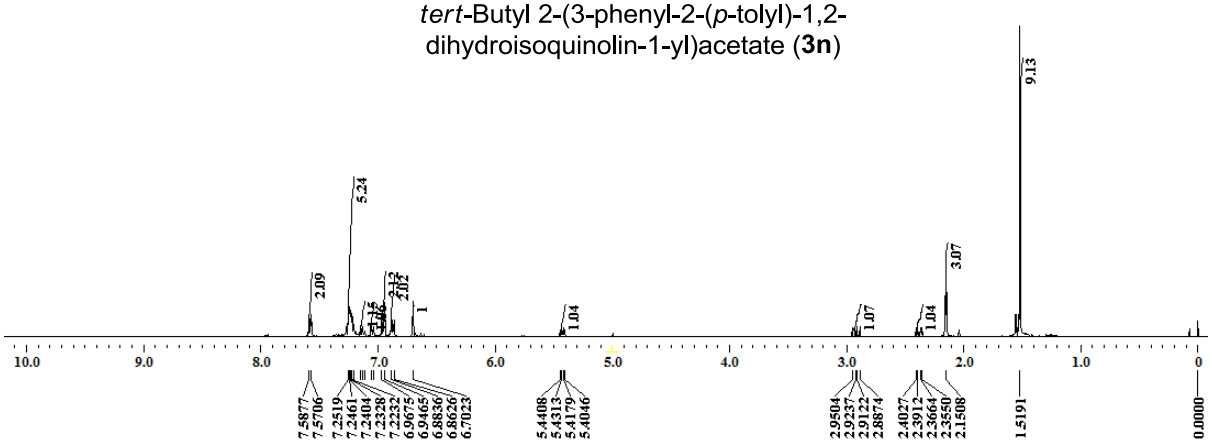
HRMS: tert-Butyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3m**)

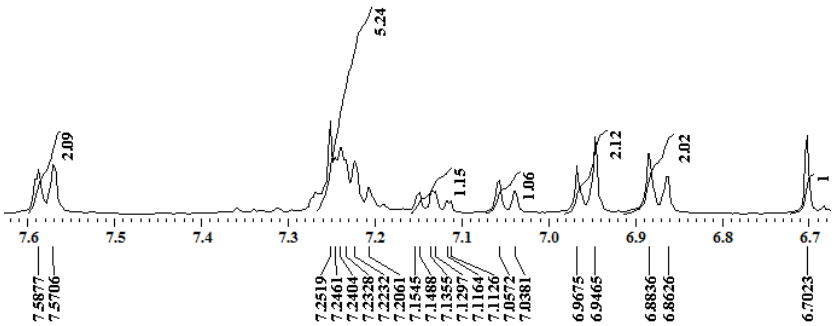


^{1}H NMR in $CDCl_3$



tert-Butyl 2-(3-phenyl-2-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3n**)





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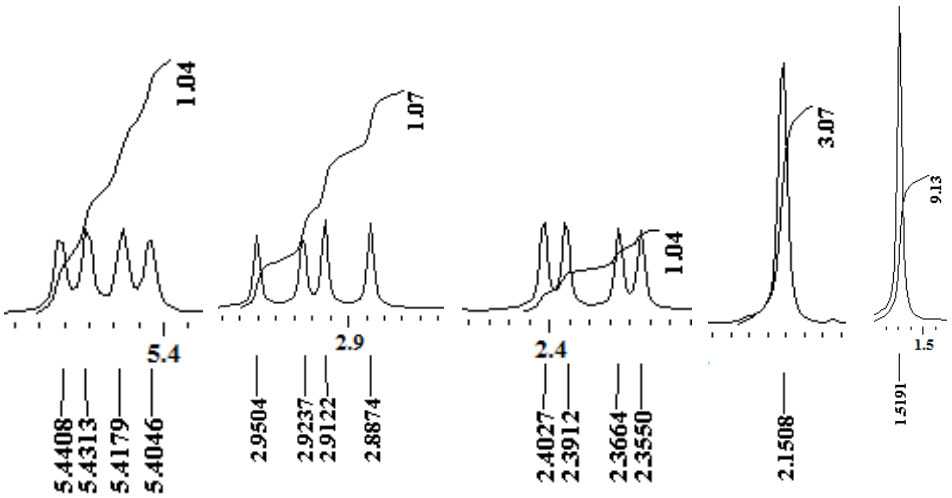
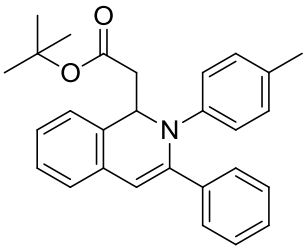
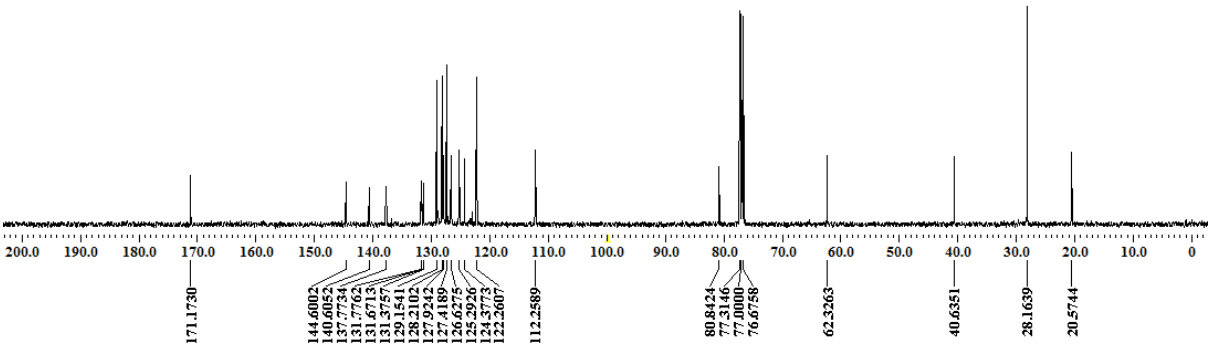
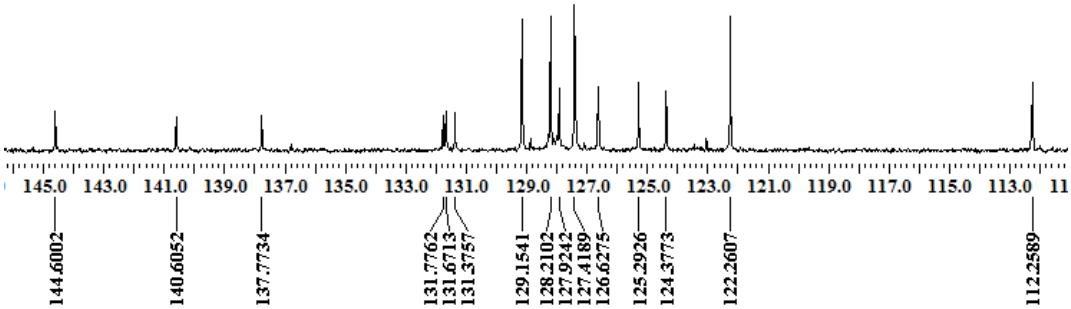


^{13}C NMR in $CDCl_3$

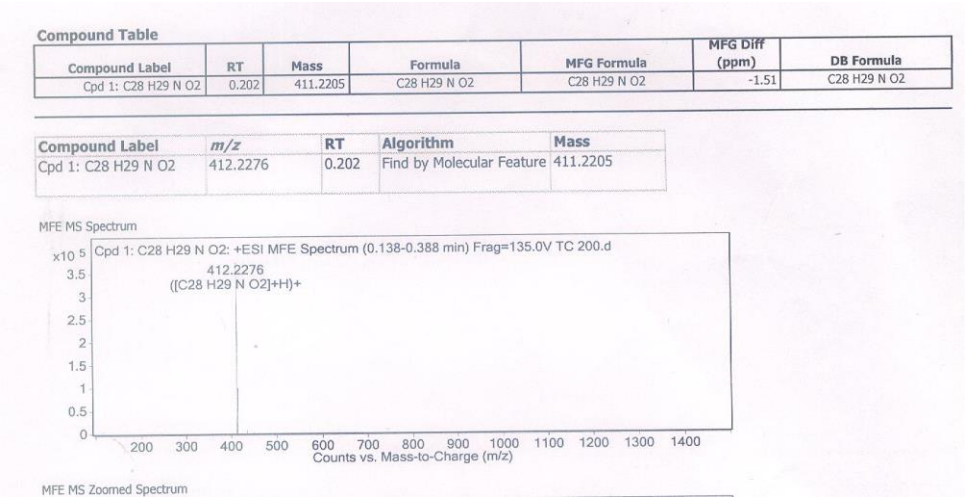


tert-Butyl 2-(3-phenyl-2-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3n**)

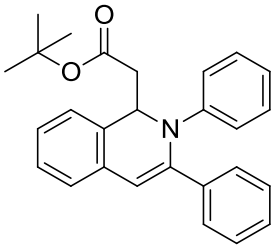




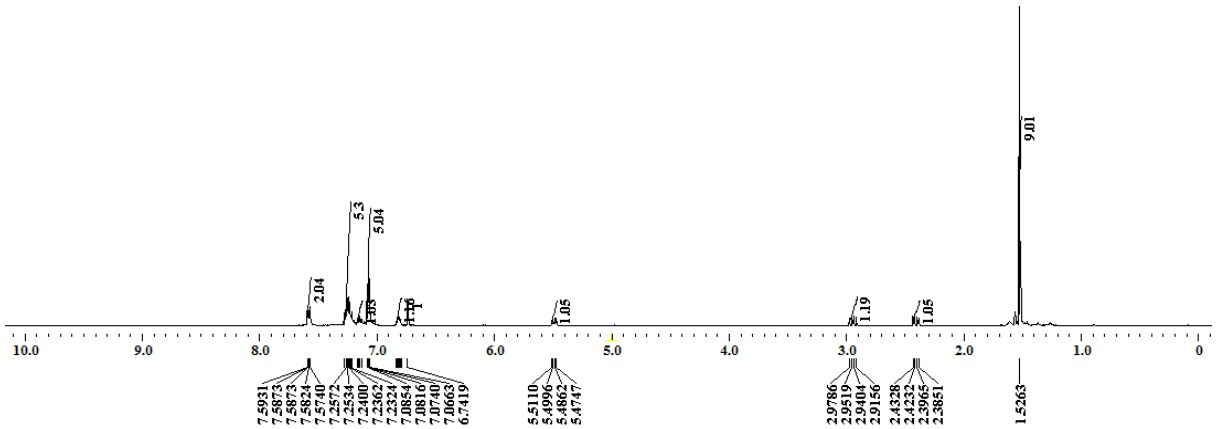
HRMS: tert-Butyl 2-(3-phenyl-2-(p-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3n**)

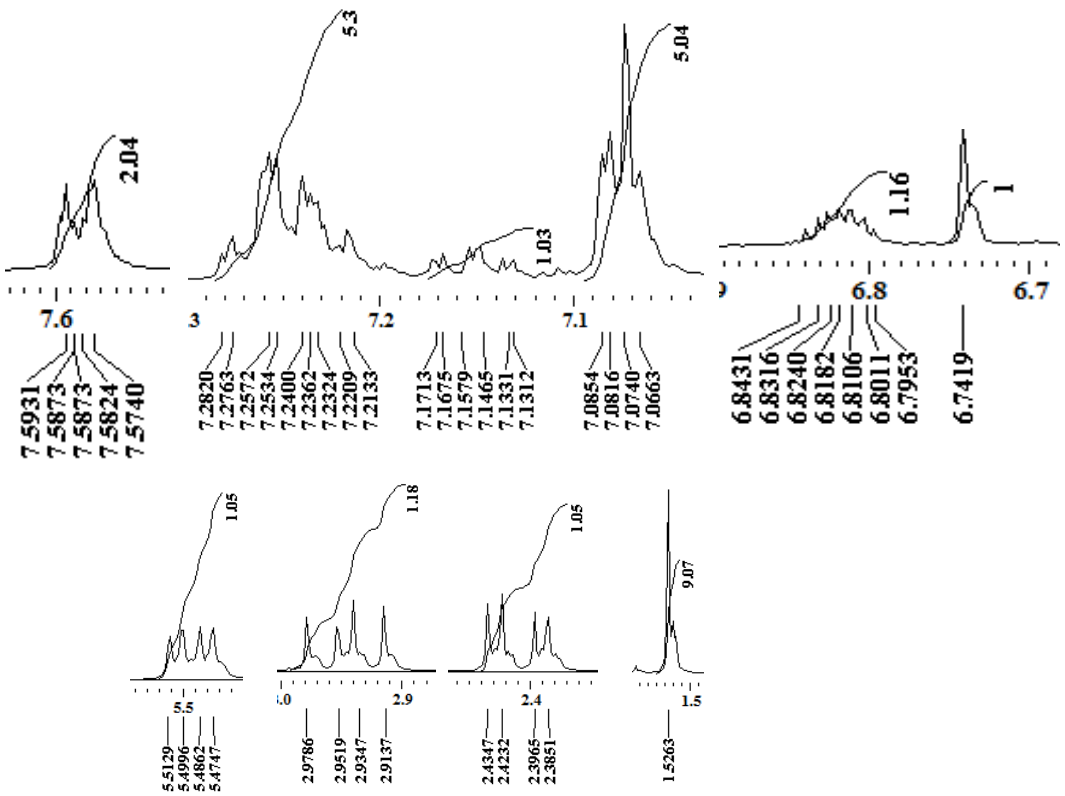


^{1}H NMR in $CDCl_3$

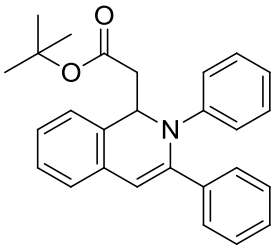


tert-Butyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3o**)

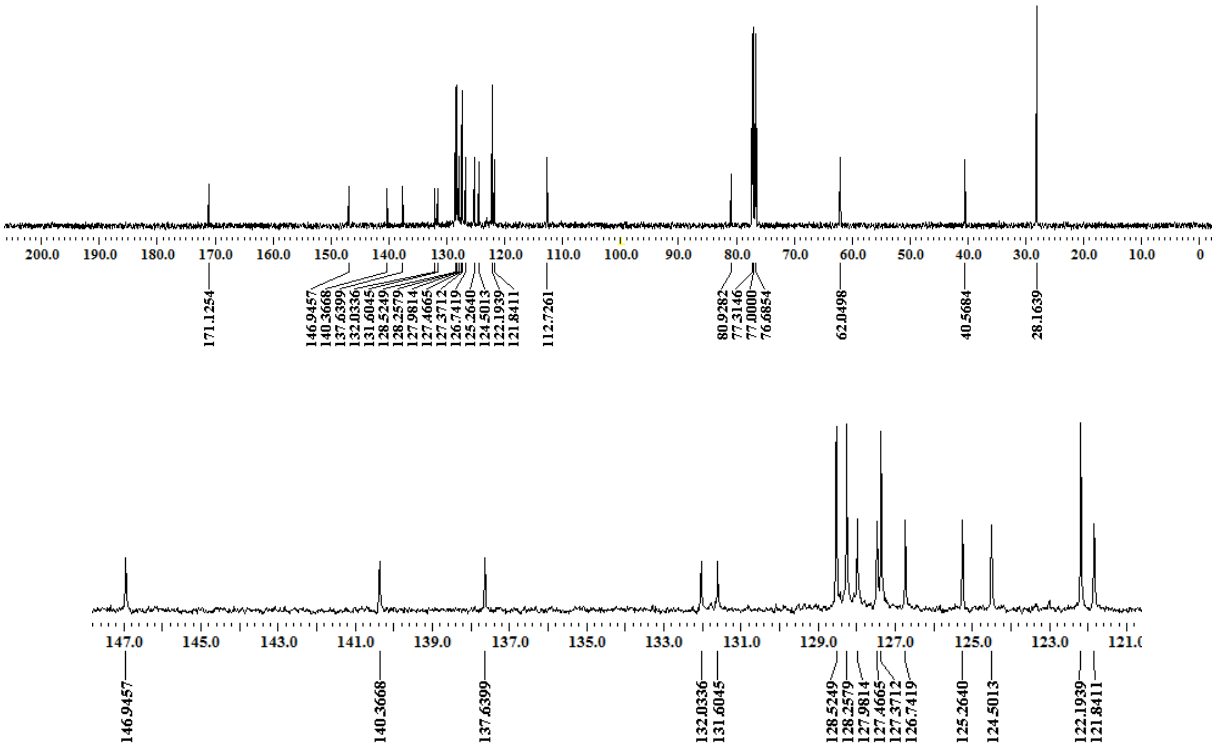




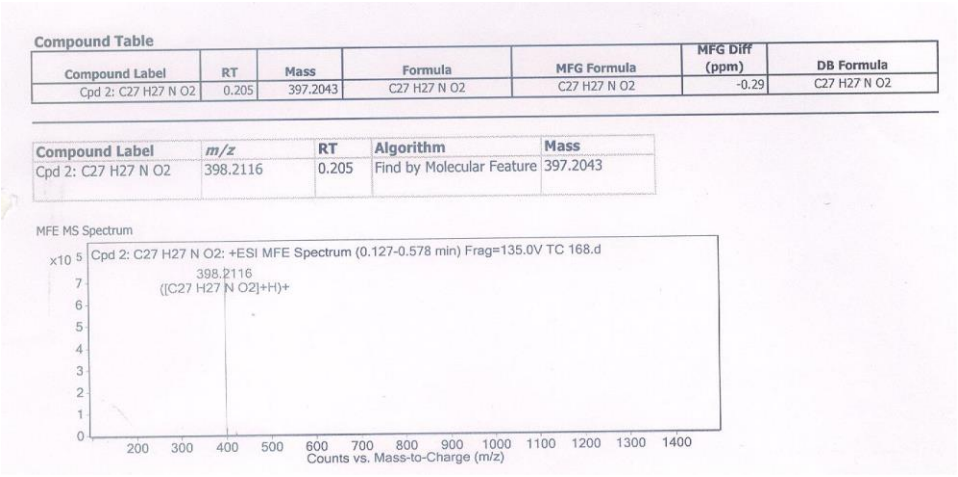
^{13}C NMR in $CDCl_3$



tert-Butyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3o**)



HRMS: tert-Butyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3o**)



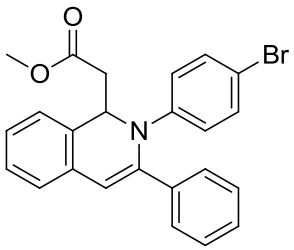
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 2: C27 H27 N O2	0.205	397.2043	C27 H27 N O2	C27 H27 N O2	-0.29	C27 H27 N O2

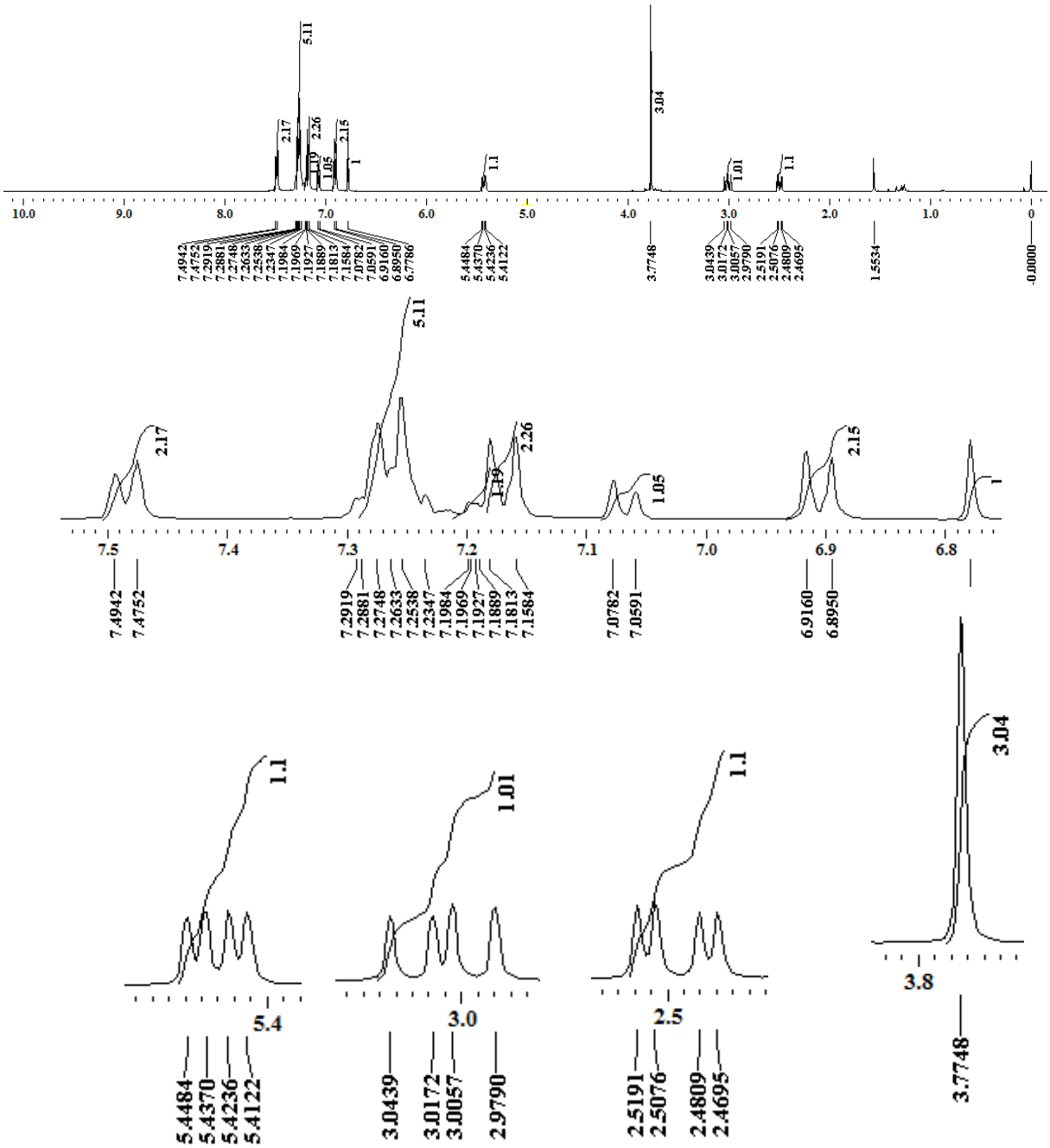
Compound Label	m/z	RT	Algorithm	Mass
Cpd 2: C27 H27 N O2	398.2116	0.205	Find by Molecular Feature	397.2043

MFE MS Spectrum

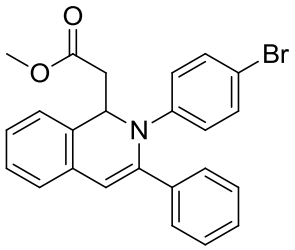
^{1}H NMR in $CDCl_3$



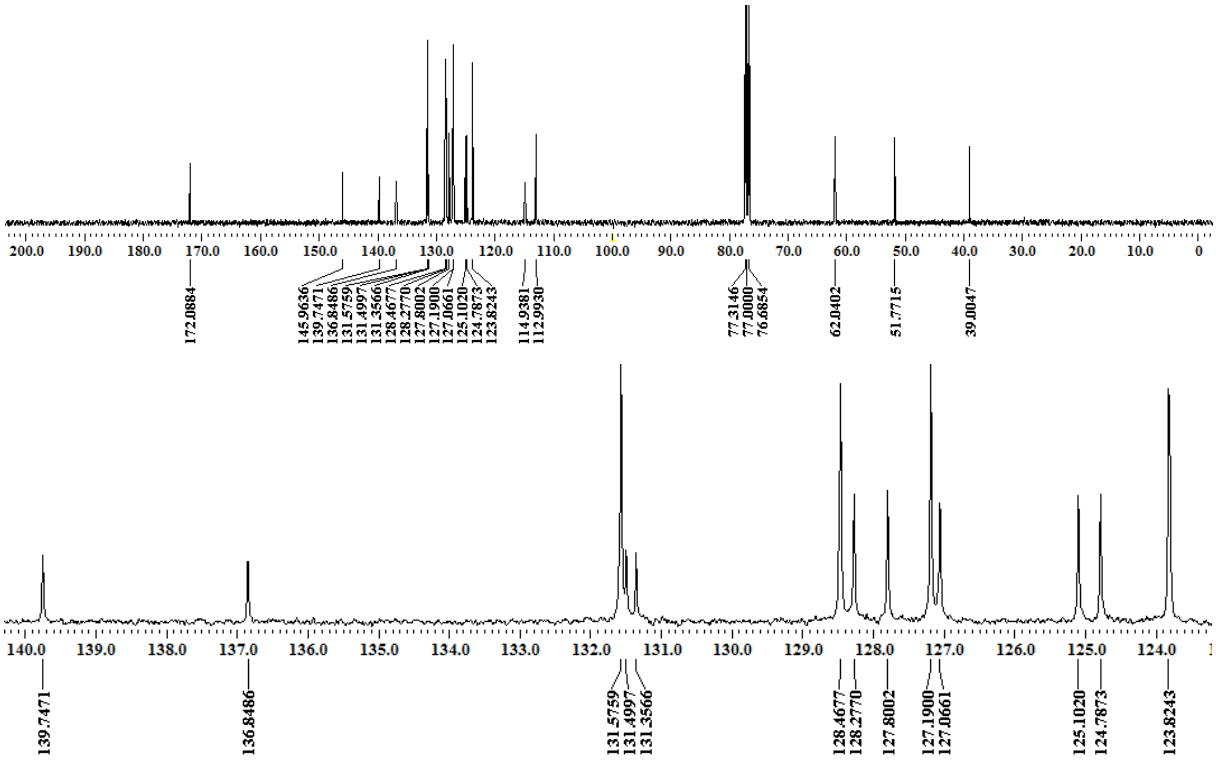
Methyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydro-isoquinolin-1-yl)acetate (**3p**)



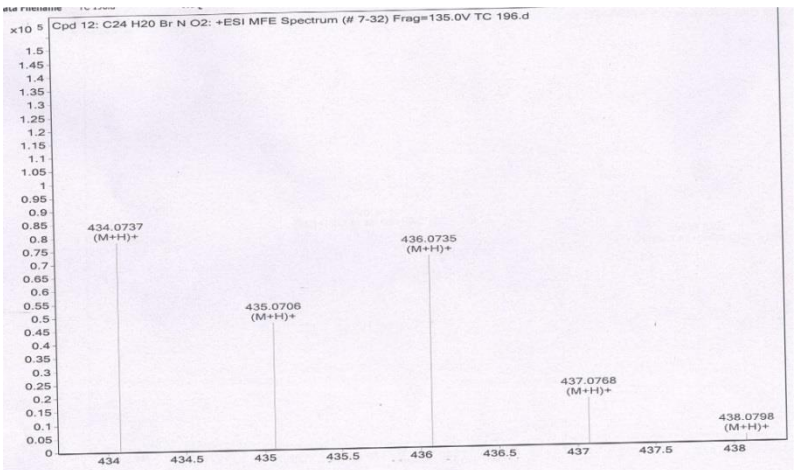
^{13}C NMR in $CDCl_3$



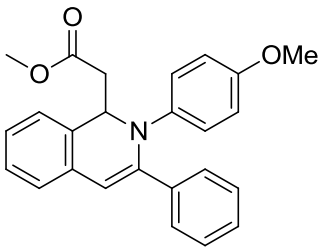
Methyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydro-isoquinolin-1-yl)acetate (**3p**)



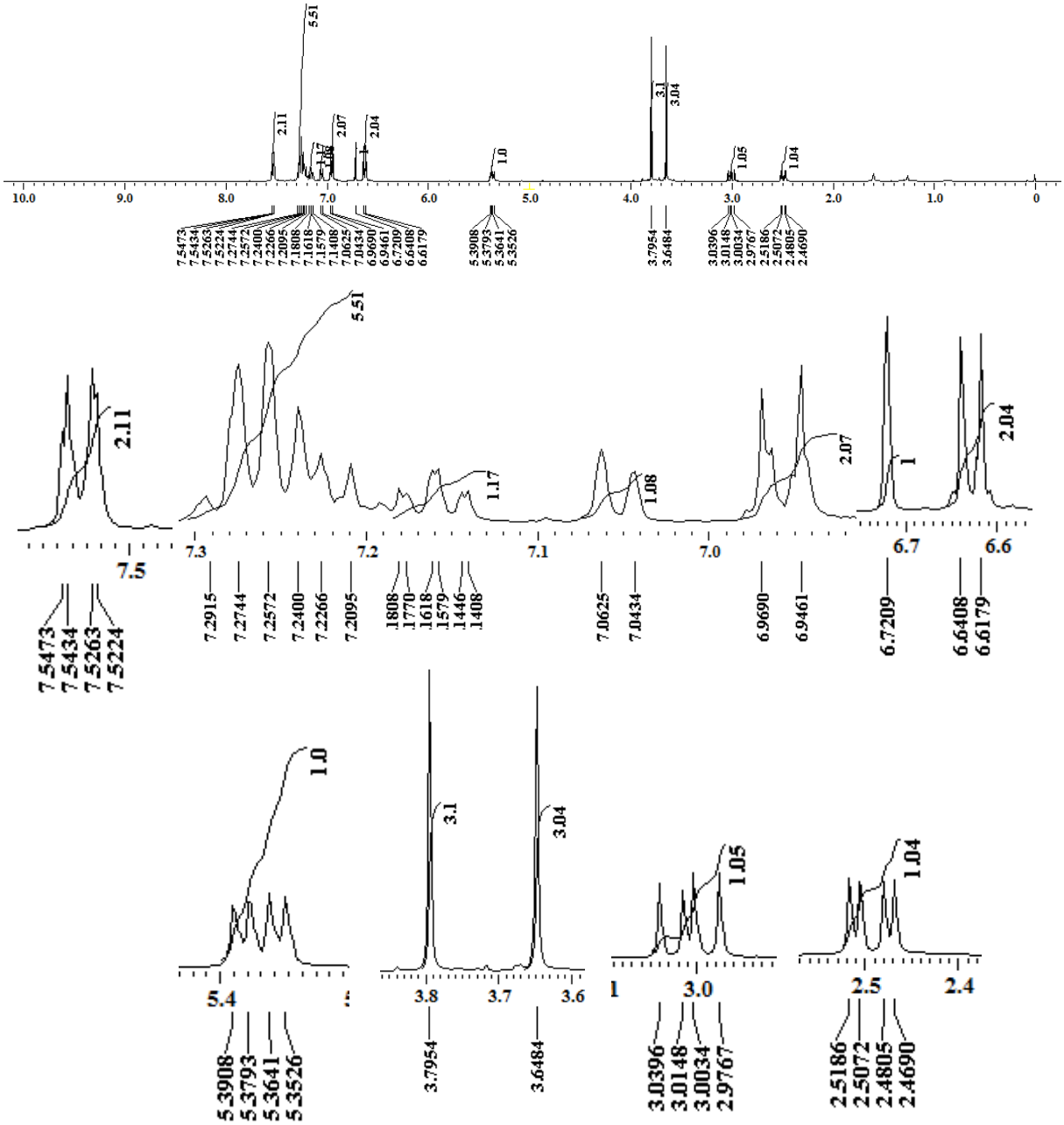
HRMS: Methyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydro-isoquinolin-1-yl)acetate (**3p**)



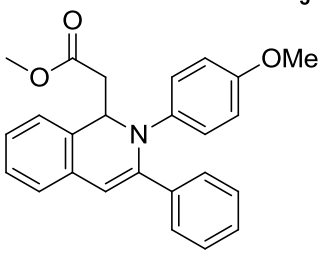
^{1}H NMR in $CDCl_3$



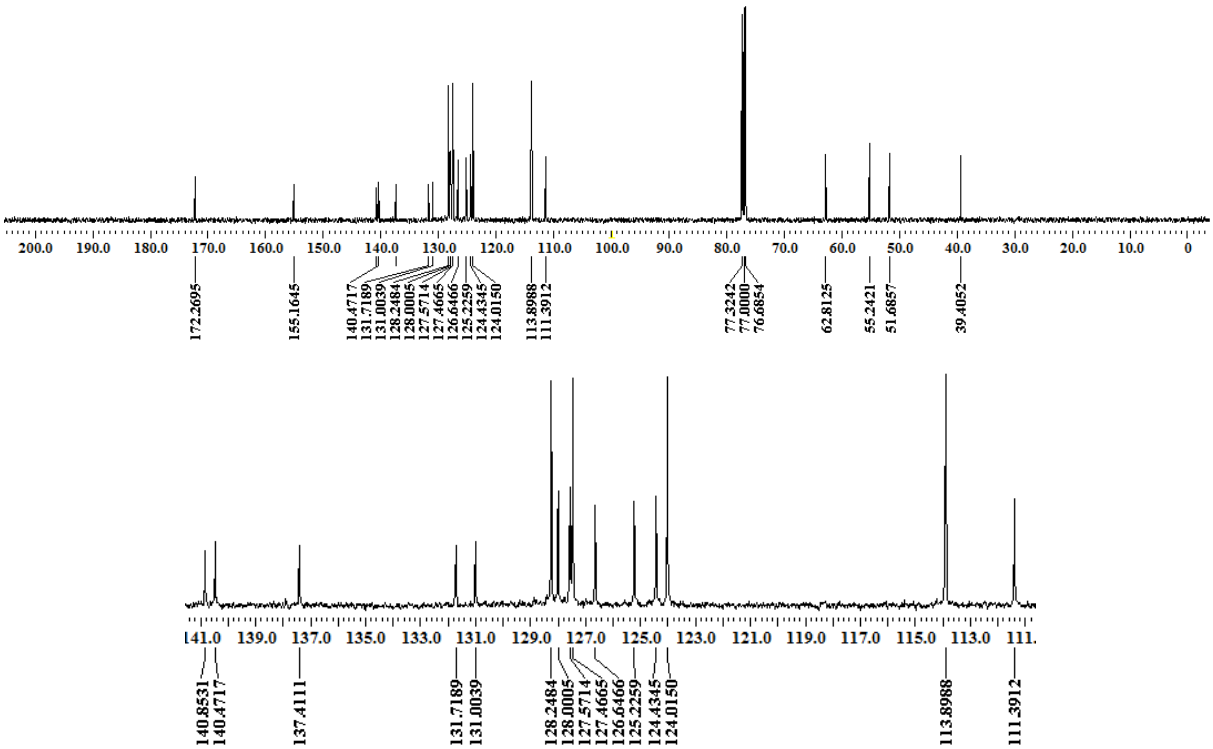
Methyl 2-(2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3q**)



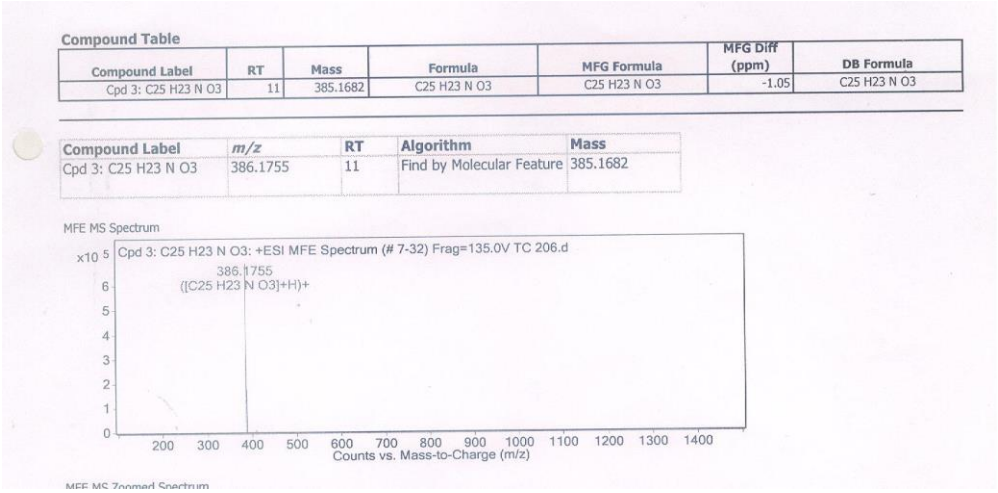
^{13}C NMR in $CDCl_3$



Methyl 2-(2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3q**)



HRMS: Methyl 2-(2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3q**)

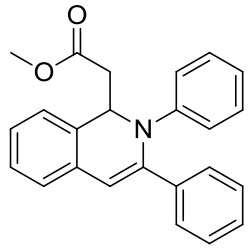


Compound Table

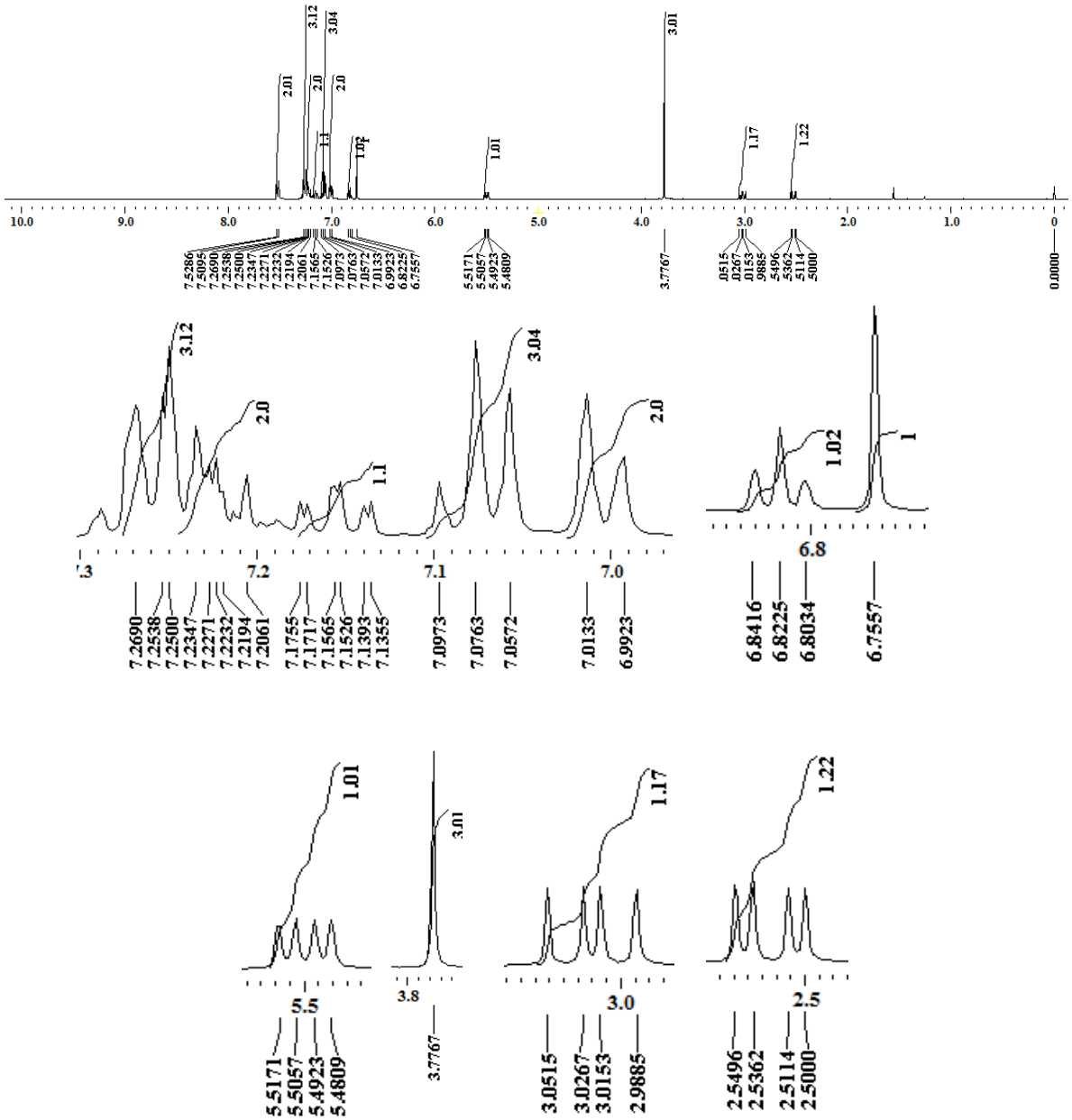
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 3: C25 H23 N O3	11	385.1682	C25 H23 N O3	C25 H23 N O3	-1.05	C25 H23 N O3

Compound Label	m/z	RT	Algorithm	Mass
Cpd 3: C25 H23 N O3	386.1755	11	Find by Molecular Feature	385.1682

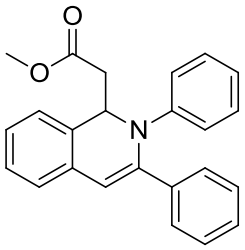
^{1}H NMR in $CDCl_3$



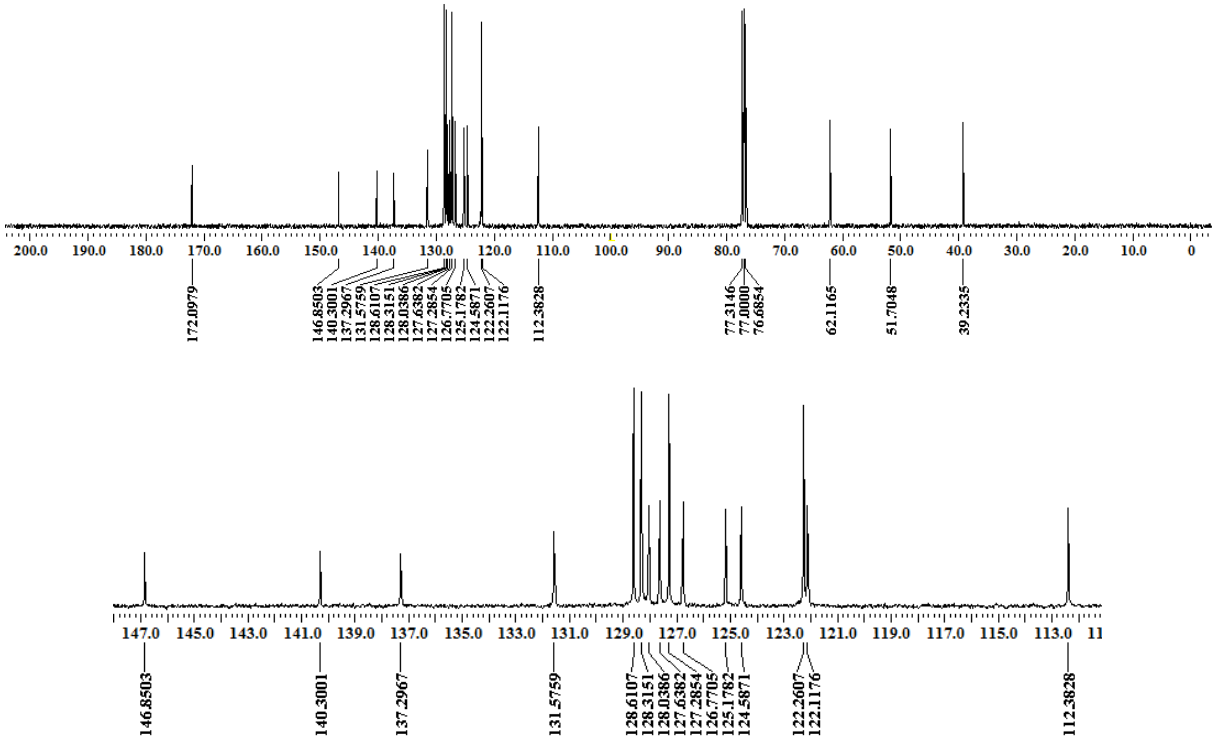
Methyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3r**)



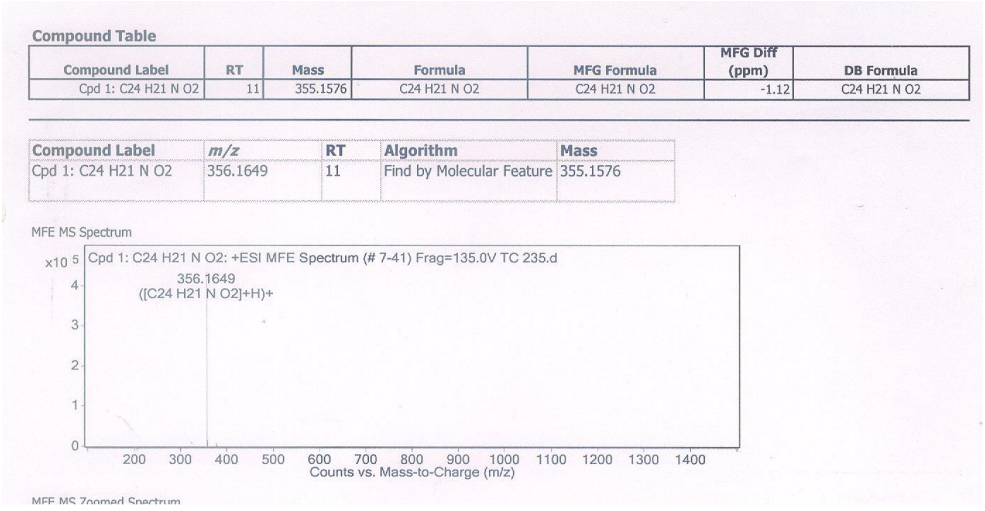
^{13}C NMR in $CDCl_3$



Methyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3r**)



HRMS: Methyl 2-(2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3r**)



Compound Table

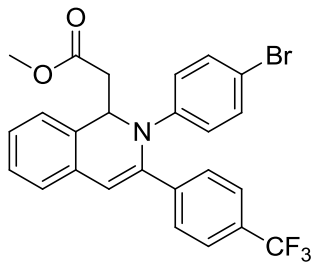
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 1: C24 H21 N O2	11	355.1576	C24 H21 N O2	C24 H21 N O2	-1.12	C24 H21 N O2

Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 1: C24 H21 N O2	356.1649	11	Find by Molecular Feature	355.1576

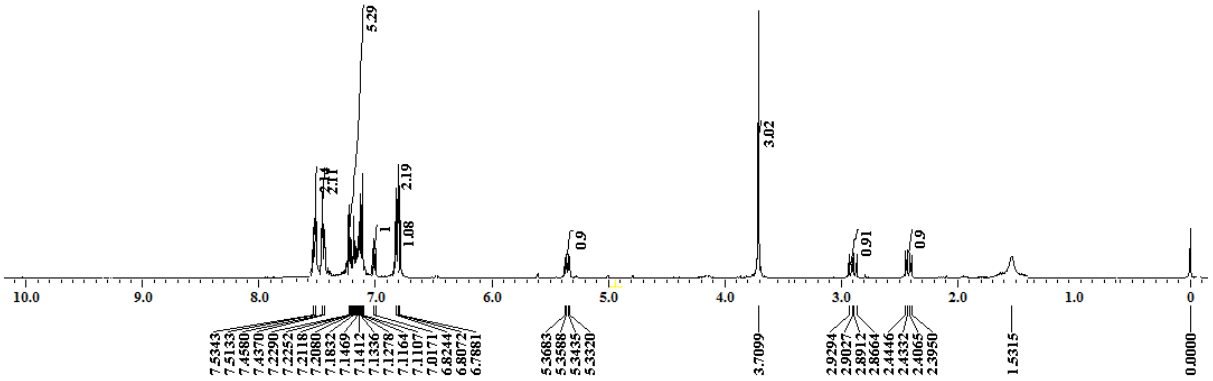
MFE MS Spectrum

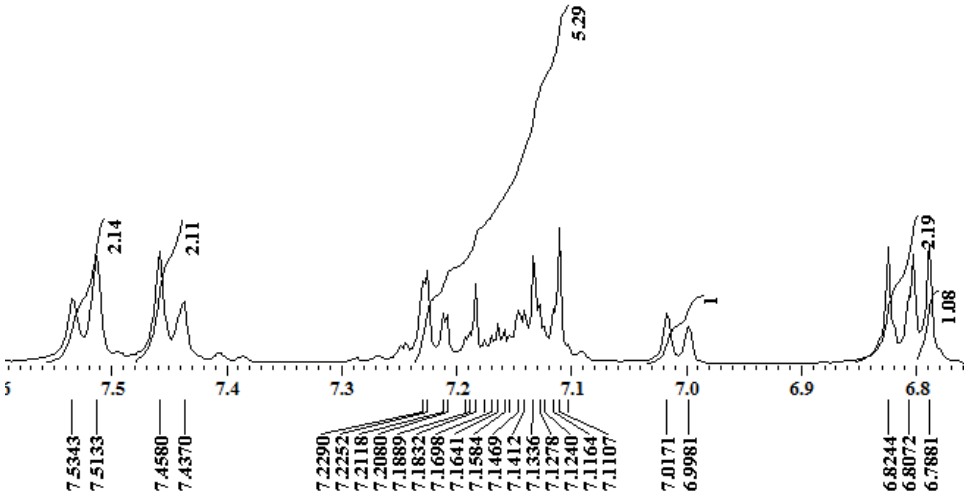
MFE MS Zoomed Spectrum

^{1}H NMR in $CDCl_3$

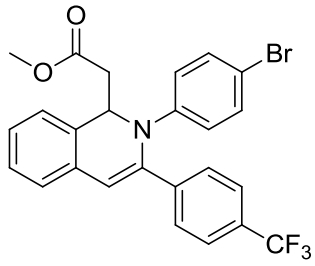


Methyl 2-(2-(4-bromophenyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3s**)

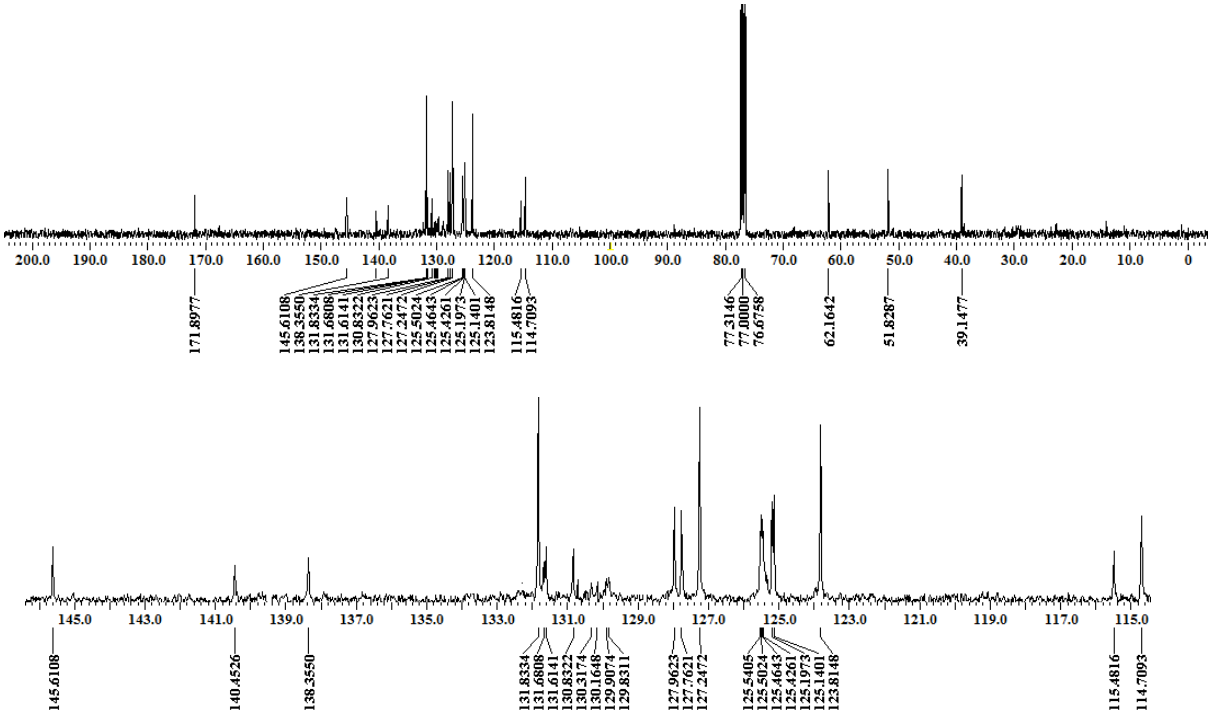




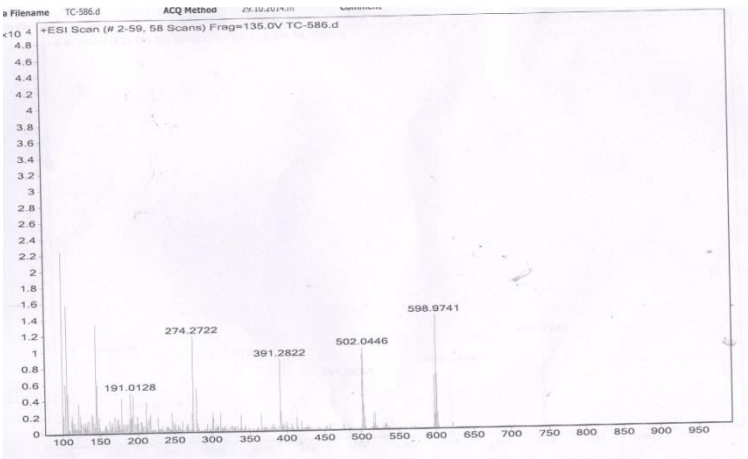
^{13}C NMR in $CDCl_3$



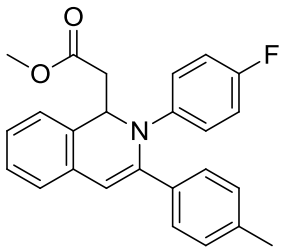
Methyl 2-(2-(4-bromophenyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3s**)



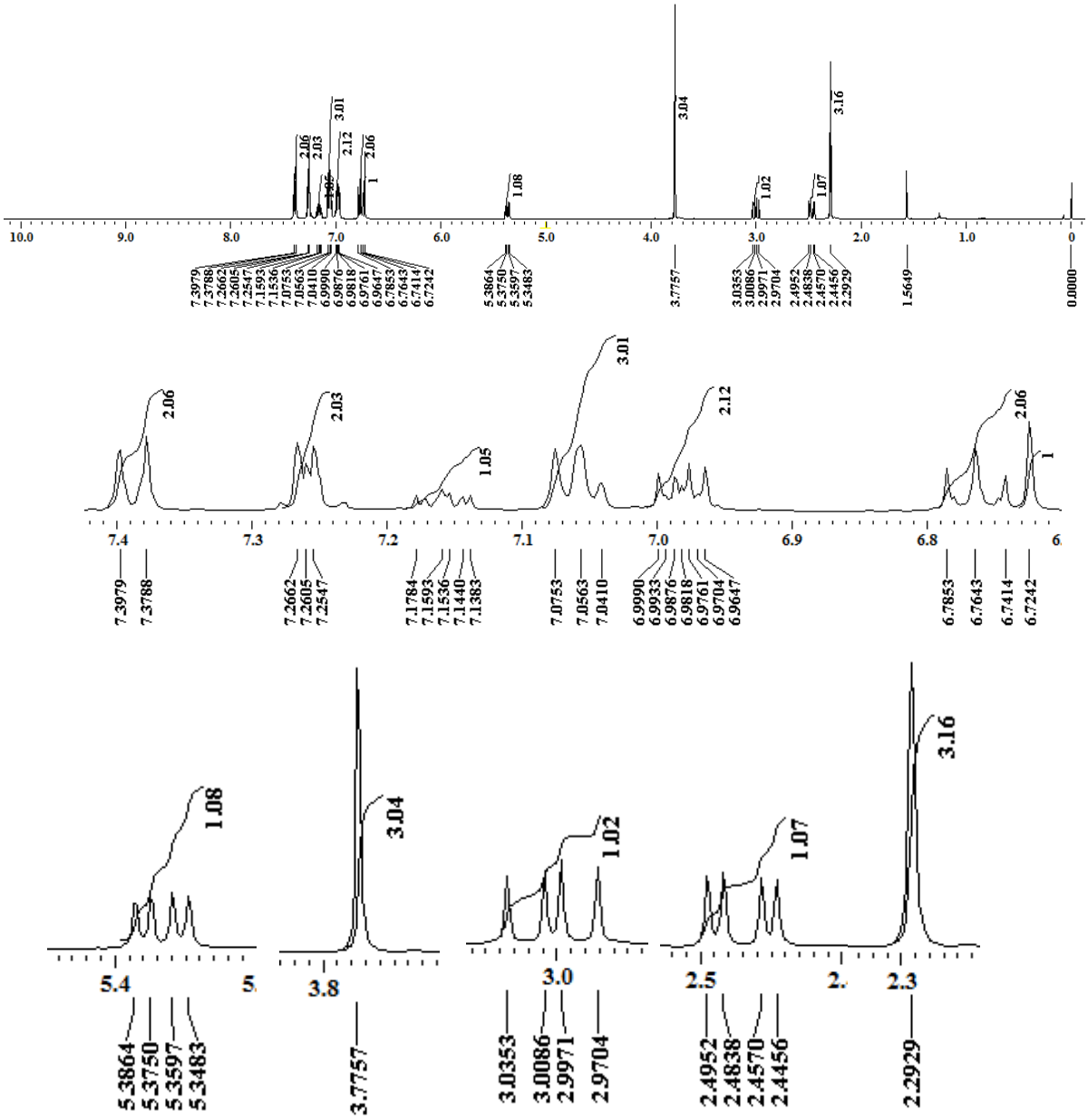
HRMS: Methyl 2-(2-(4-bromophenyl)-3-(4-(trifluoromethyl)phenyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3s**)



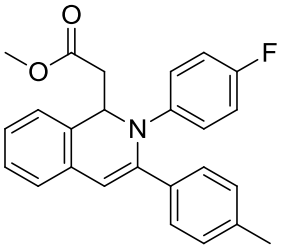
^{1}H NMR in $CDCl_3$



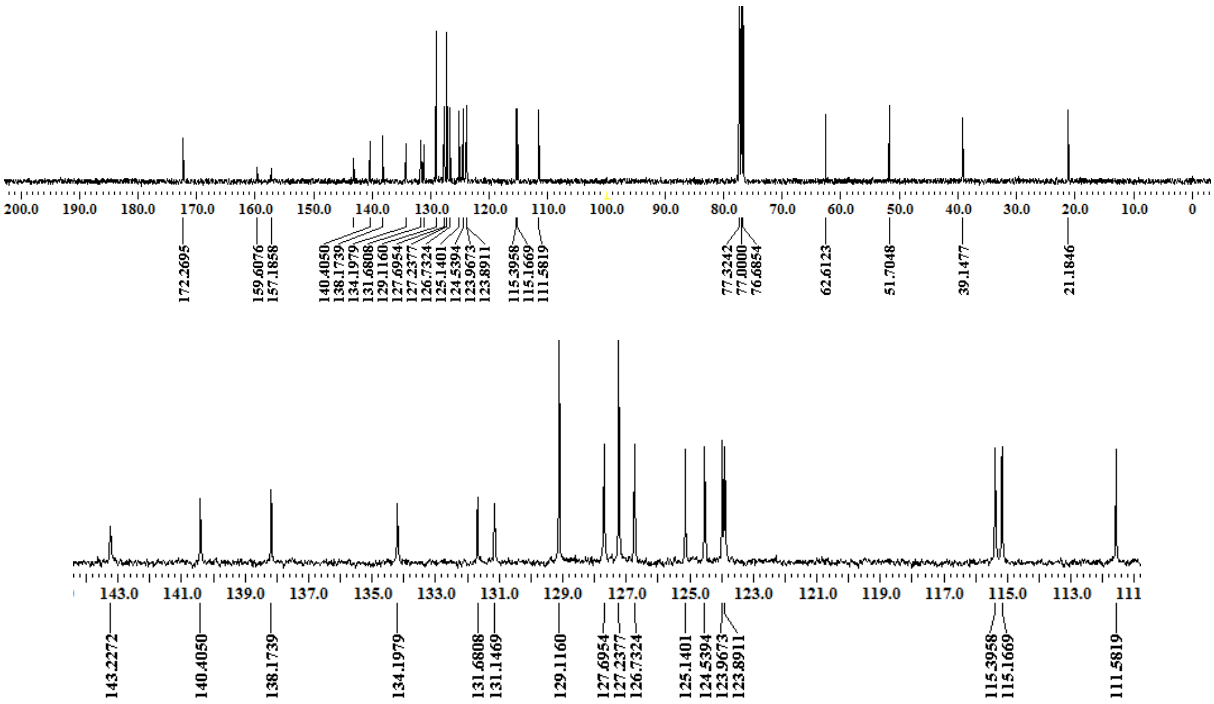
Methyl 2-(2-(4-fluorophenyl)-3-(*p*-tolyl)-1,2-dihydro
-isoquinolin-1-yl)acetate (**3t**)



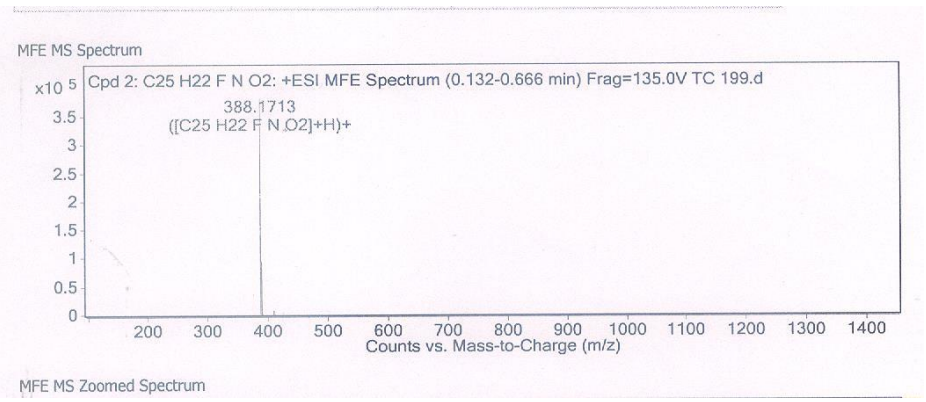
^{13}C NMR in $CDCl_3$



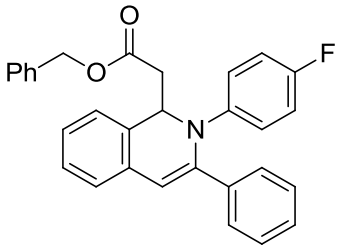
Methyl 2-(2-(4-fluorophenyl)-3-(*p*-tolyl)-1,2-dihydro
-isoquinolin-1-yl)acetate (**3t**)



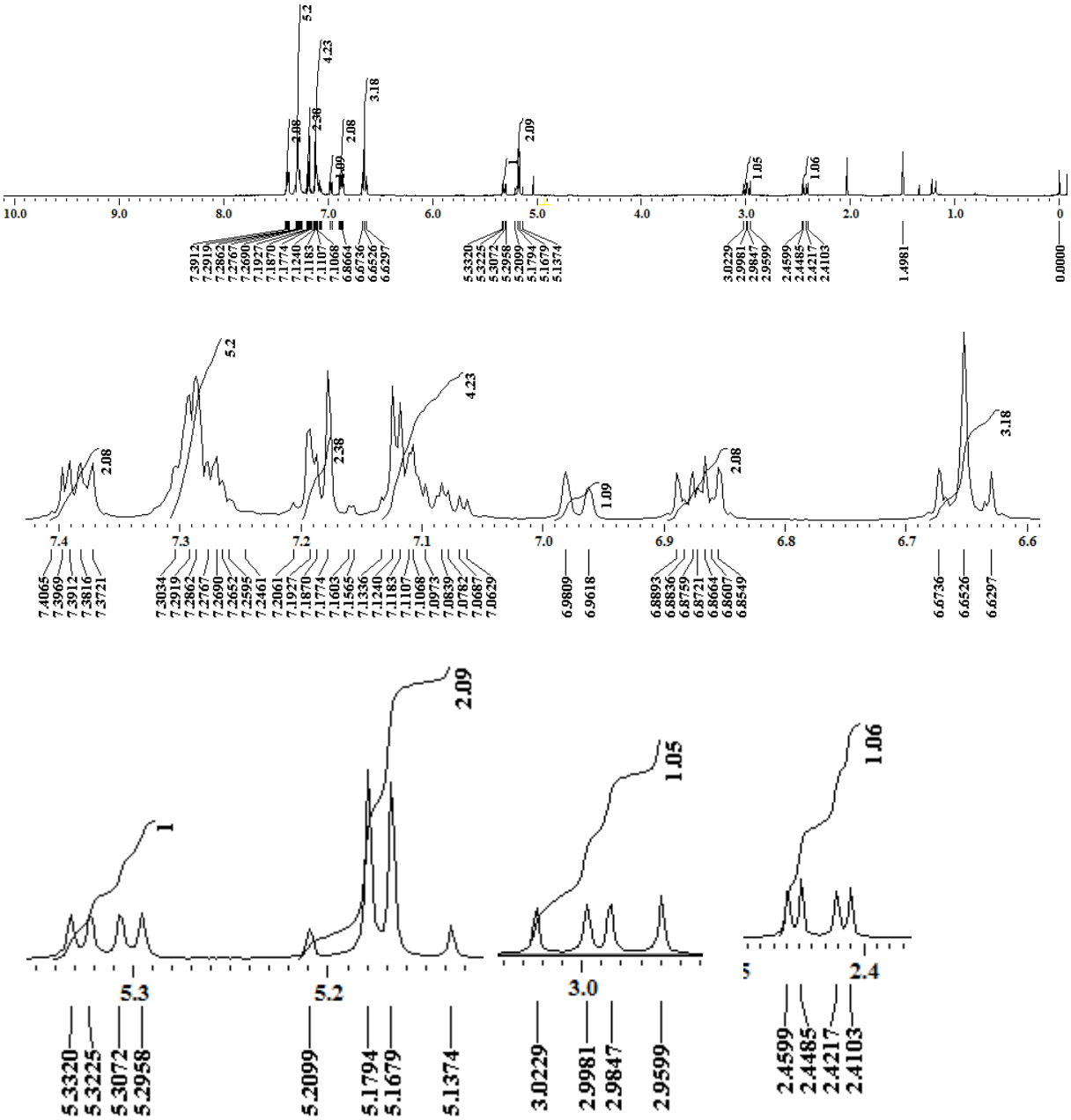
HRMS: Methyl 2-(2-(4-fluorophenyl)-3-(p-tolyl)-1,2-dihydro-isoquinolin-1-yl)acetate (**3t**)



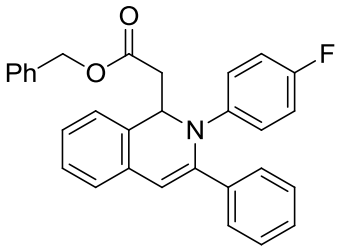
^{1}H NMR in $CDCl_3$



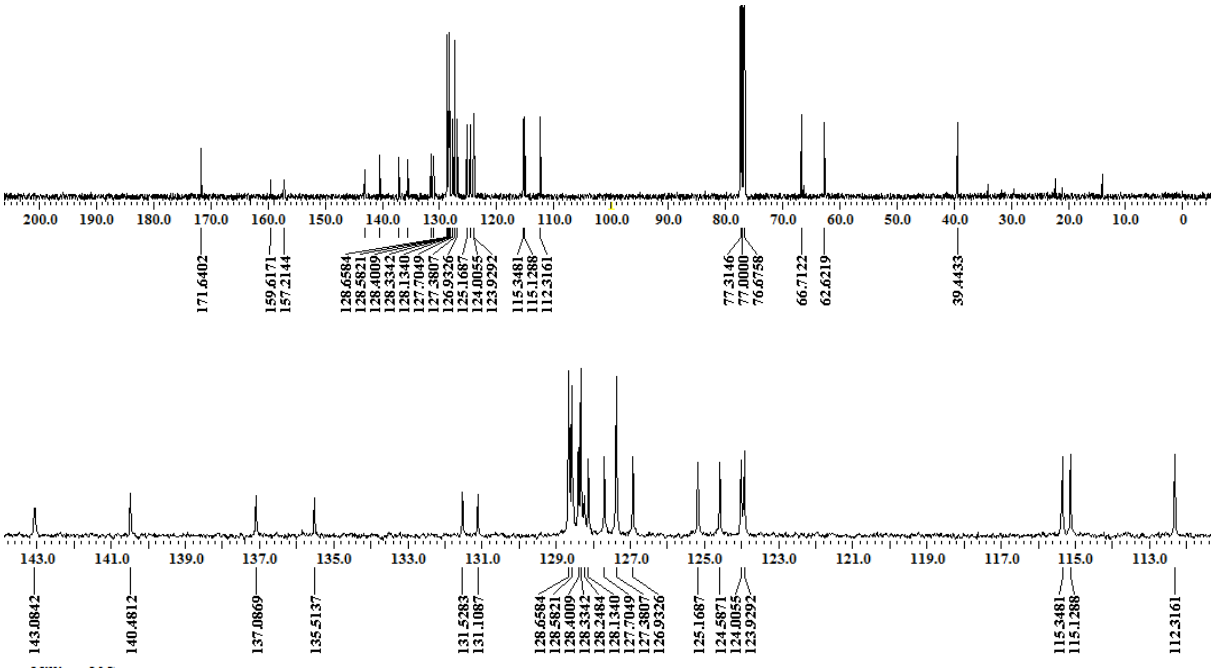
Benzyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3u**)



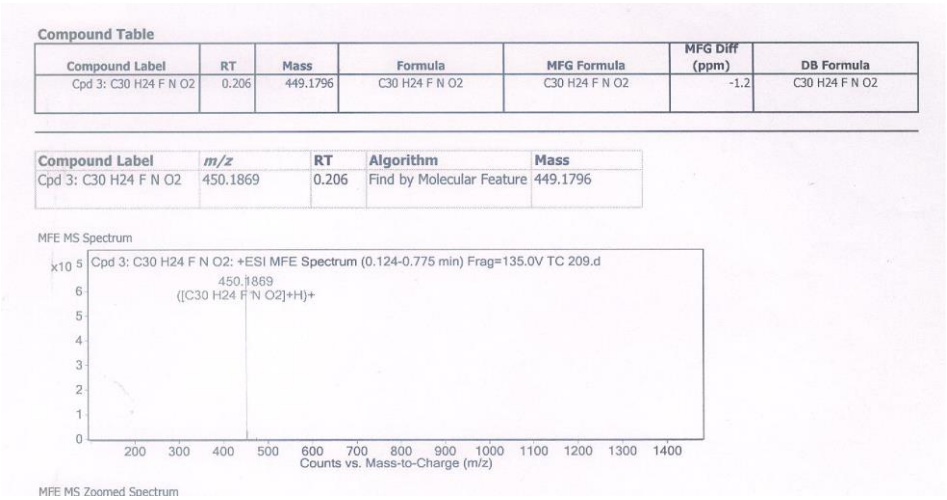
^{13}C NMR in $CDCl_3$



Benzyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3u**)



HRMS: Benzyl 2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3u**)

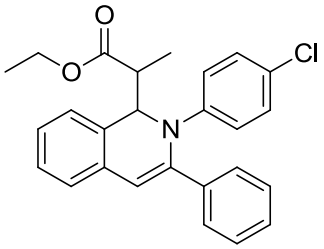


Compound Table

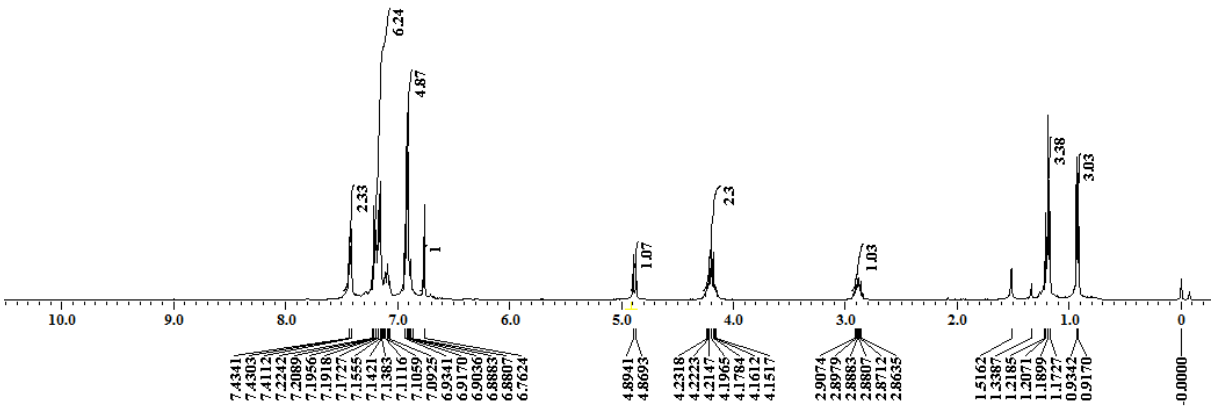
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 3: C30 H24 F N O2	0.206	449.1796	C30 H24 F N O2	C30 H24 F N O2	-1.2	C30 H24 F N O2

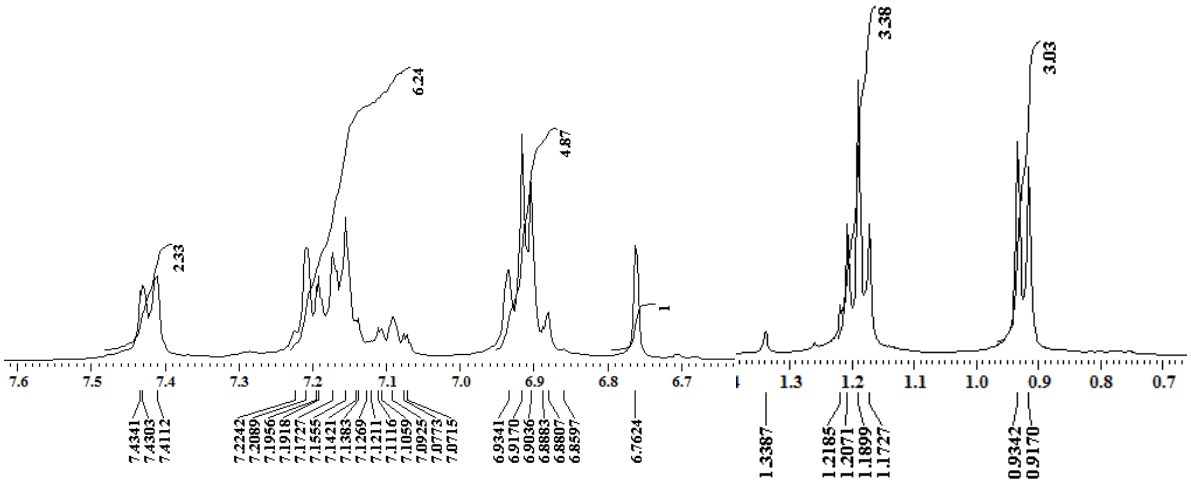
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 3: C30 H24 F N O2	450.1869	0.206	Find by Molecular Feature	449.1796

^{1}H NMR in $CDCl_3$

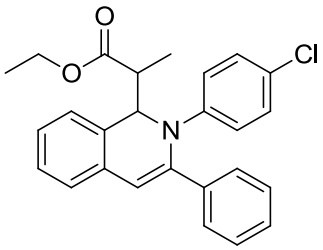


Ethyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)propanoate (**3v**)

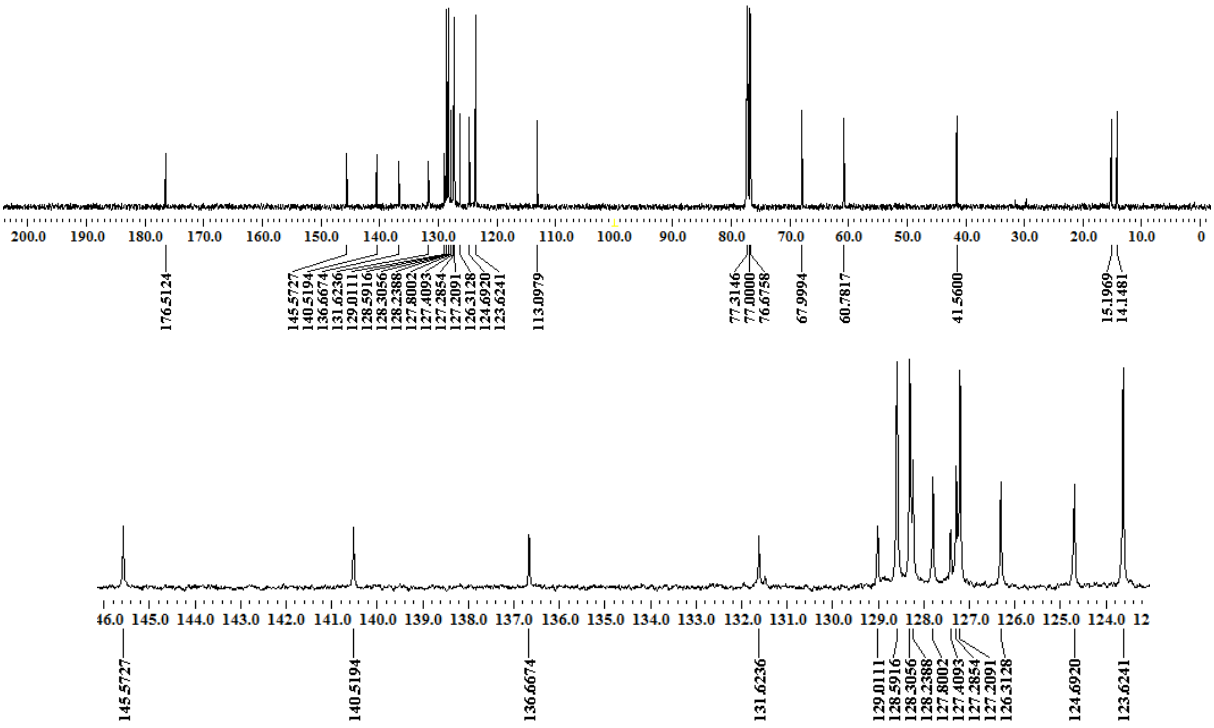




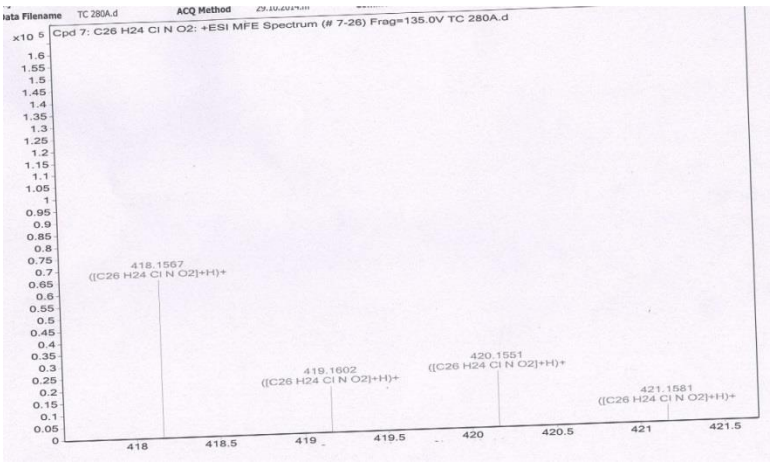
^{13}C NMR in $CDCl_3$



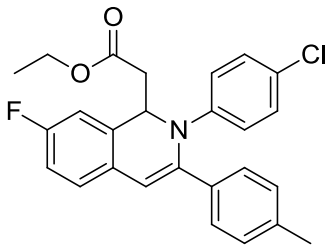
Ethyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)propanoate (**3v**)



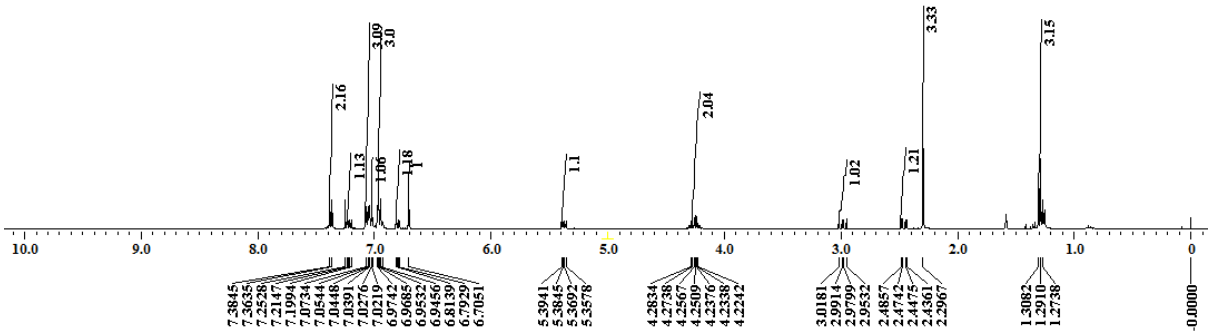
HRMS: Ethyl 2-(2-(4-chlorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)propanoate (**3v**)

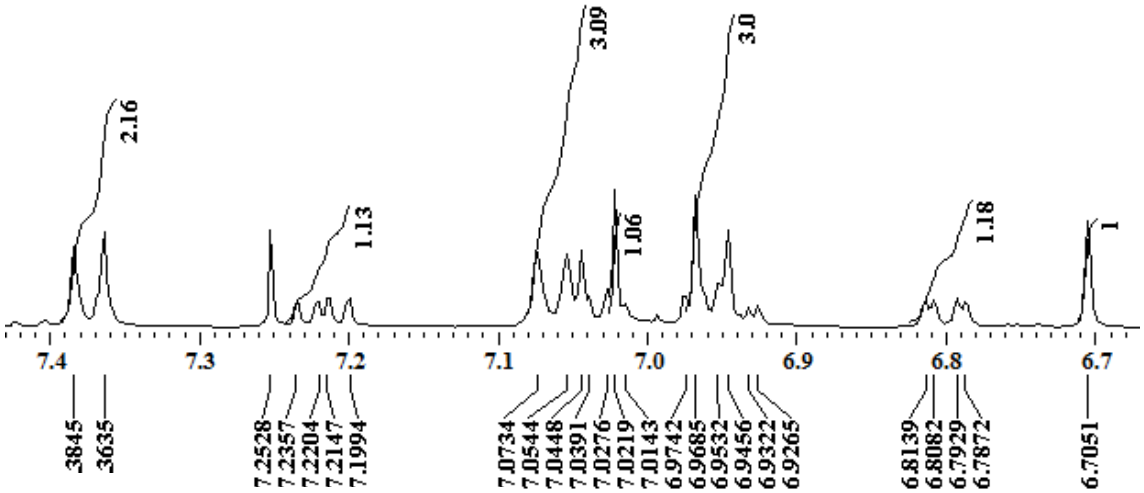


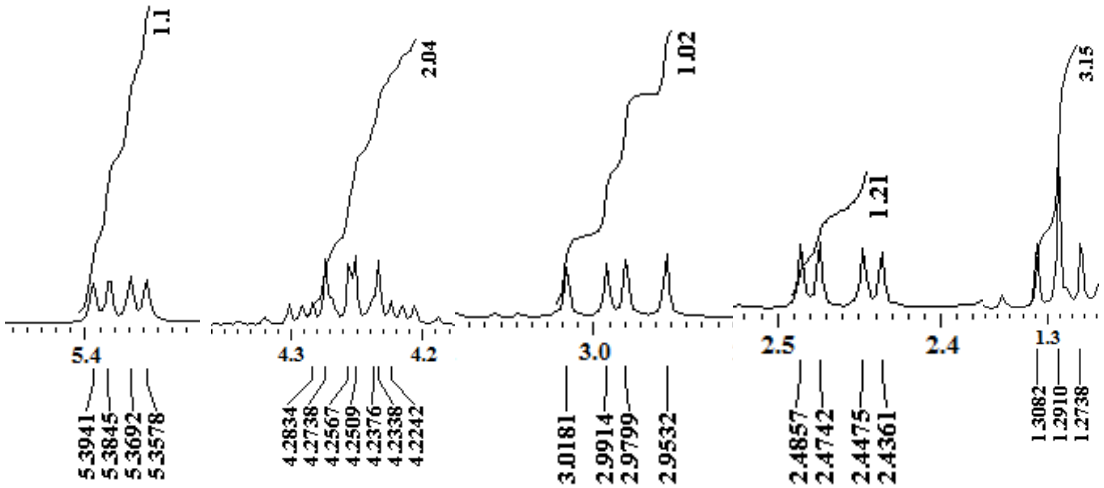
^{1}H NMR in $CDCl_3$



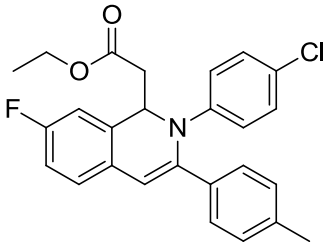
Ethyl 2-(2-(4-chlorophenyl)-7-fluoro-3-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3w**)



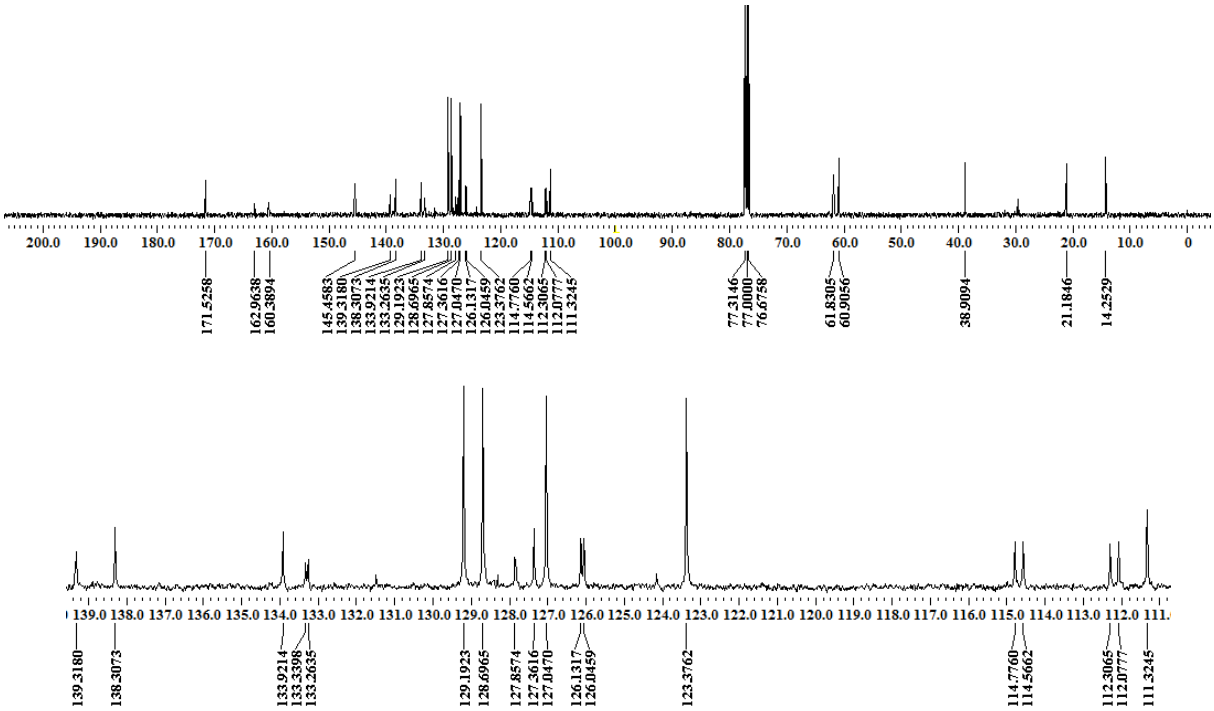




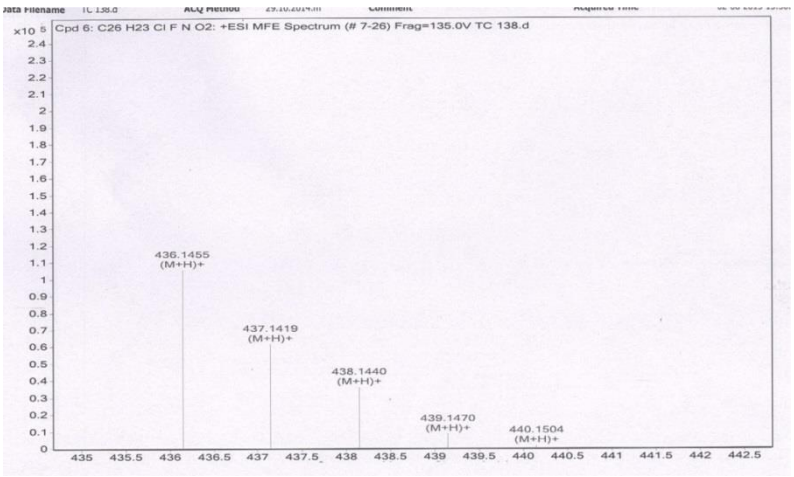
^{13}C NMR in $CDCl_3$



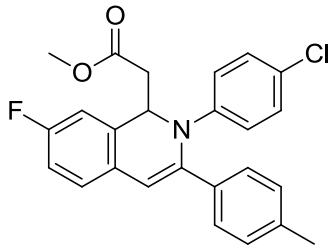
Ethyl 2-(2-(4-chlorophenyl)-7-fluoro-3-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3w**)



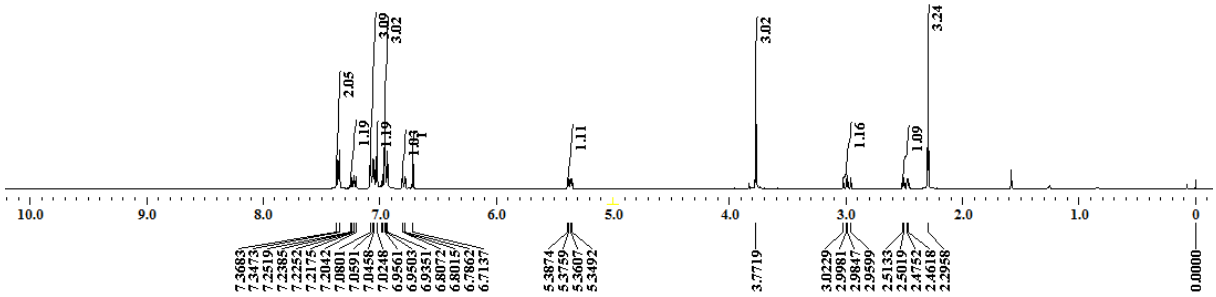
HRMS: Ethyl 2-(2-(4-chlorophenyl)-7-fluoro-3-(p-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3w**)

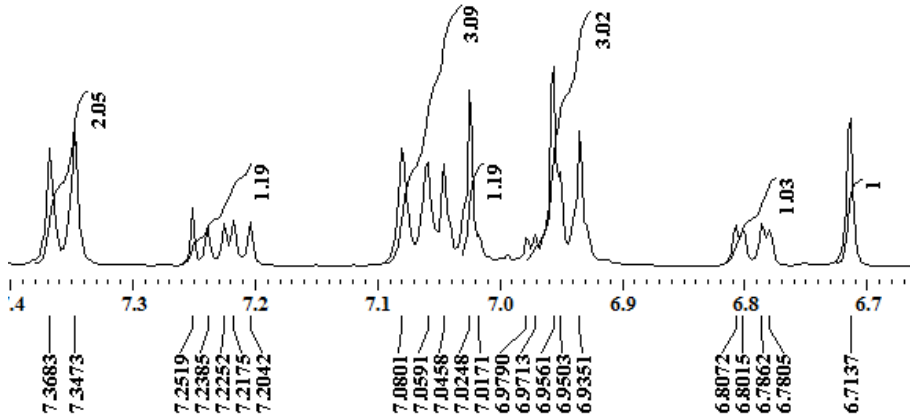


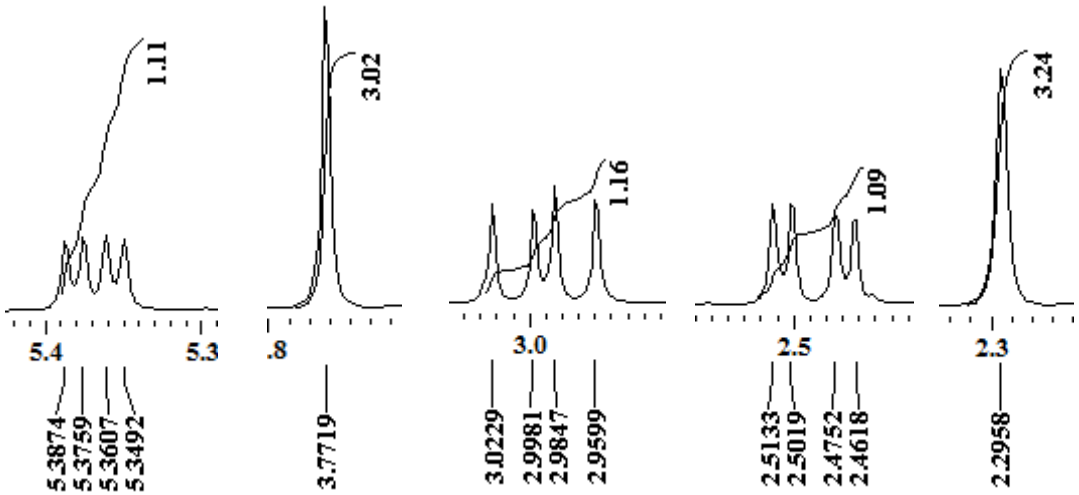
^{1}H NMR in $CDCl_3$



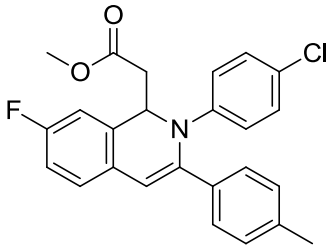
Methyl 2-(2-(4-chlorophenyl)-7-fluoro-3-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3x**)



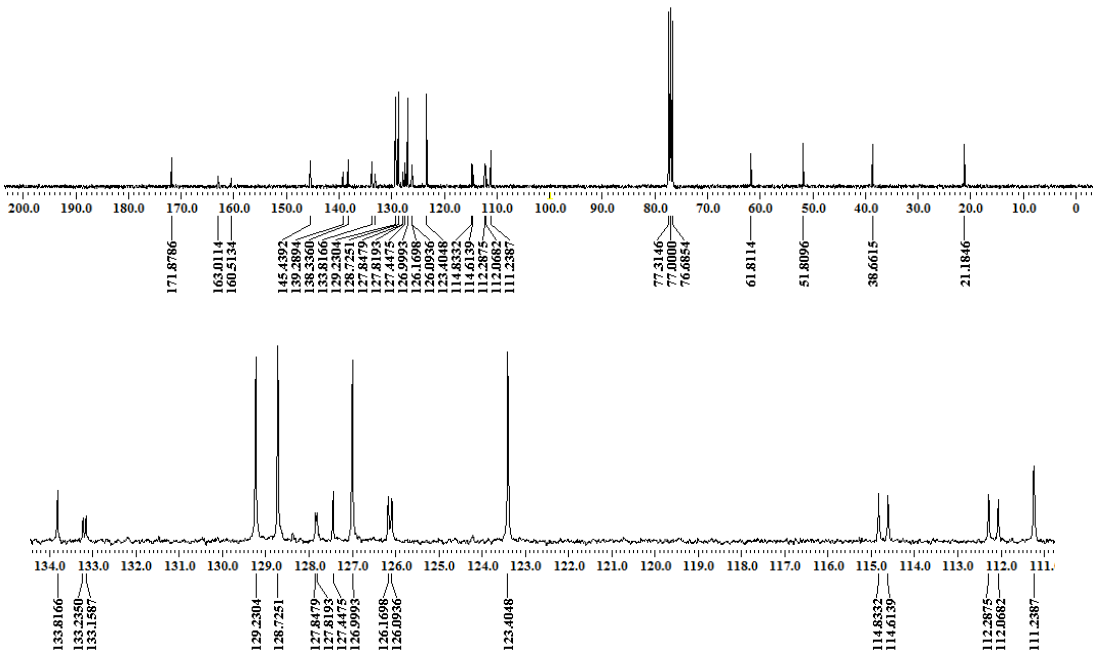




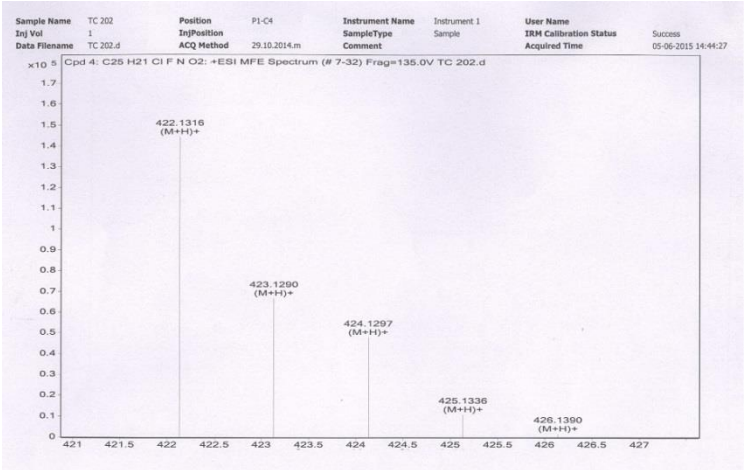
^{13}C NMR in $CDCl_3$



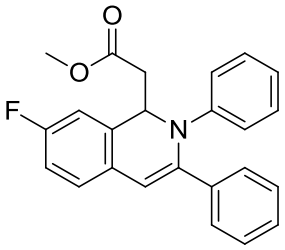
Methyl 2-(2-(4-chlorophenyl)-7-fluoro-3-(*p*-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3x**)



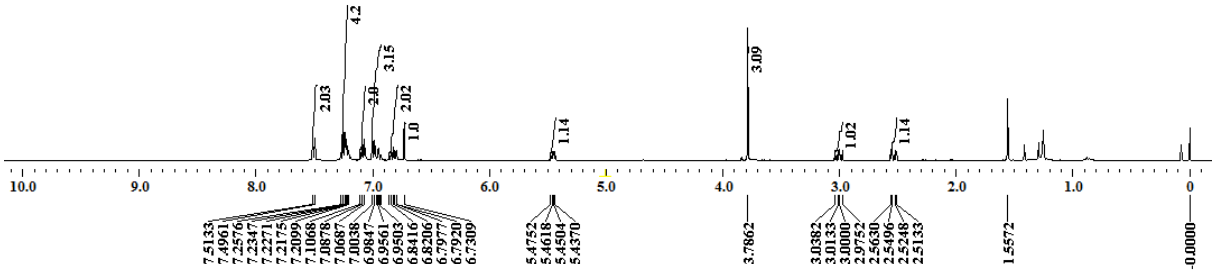
HRMS: Methyl 2-(2-(4-chlorophenyl)-7-fluoro-3-(p-tolyl)-1,2-dihydroisoquinolin-1-yl)acetate (**3x**)

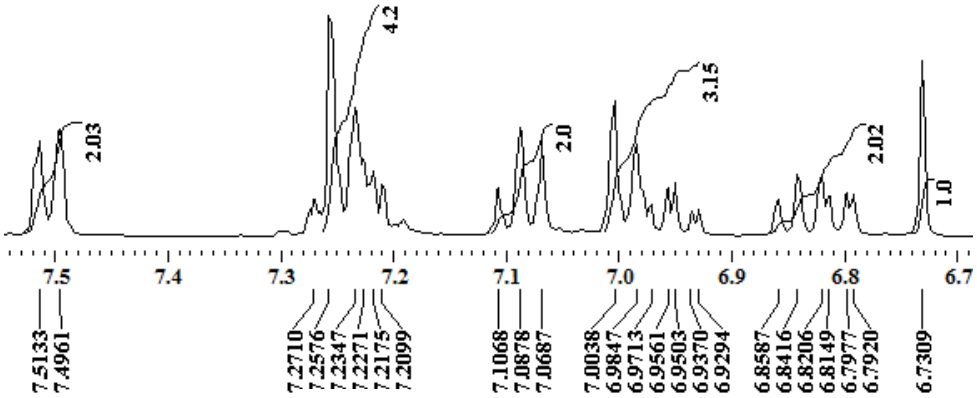


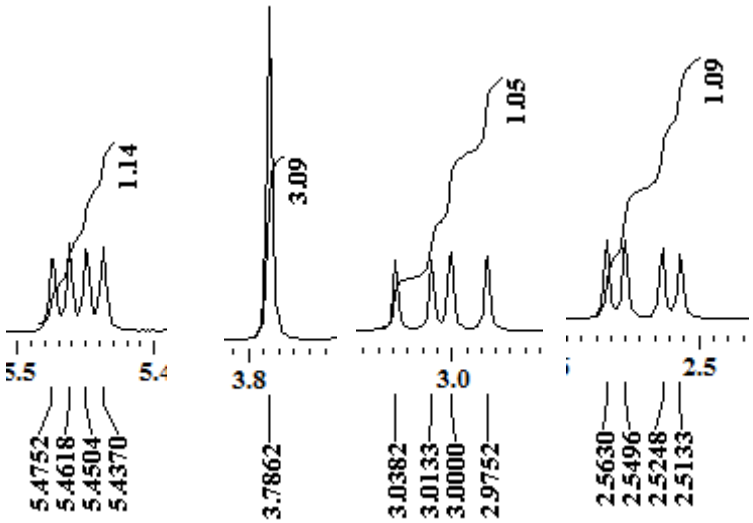
^{1}H NMR in $CDCl_3$



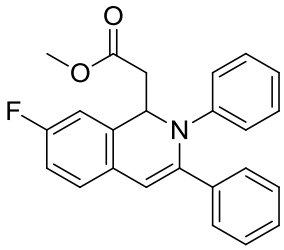
Methyl 2-(7-fluoro-2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3y**)



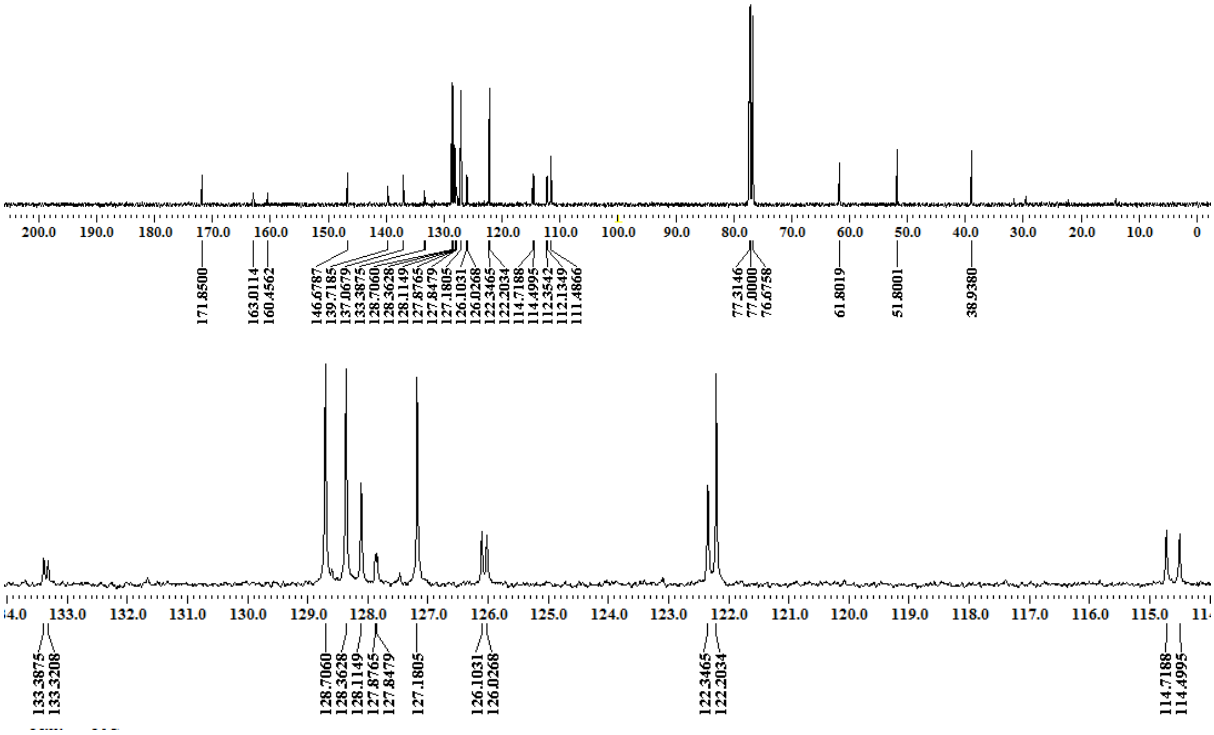




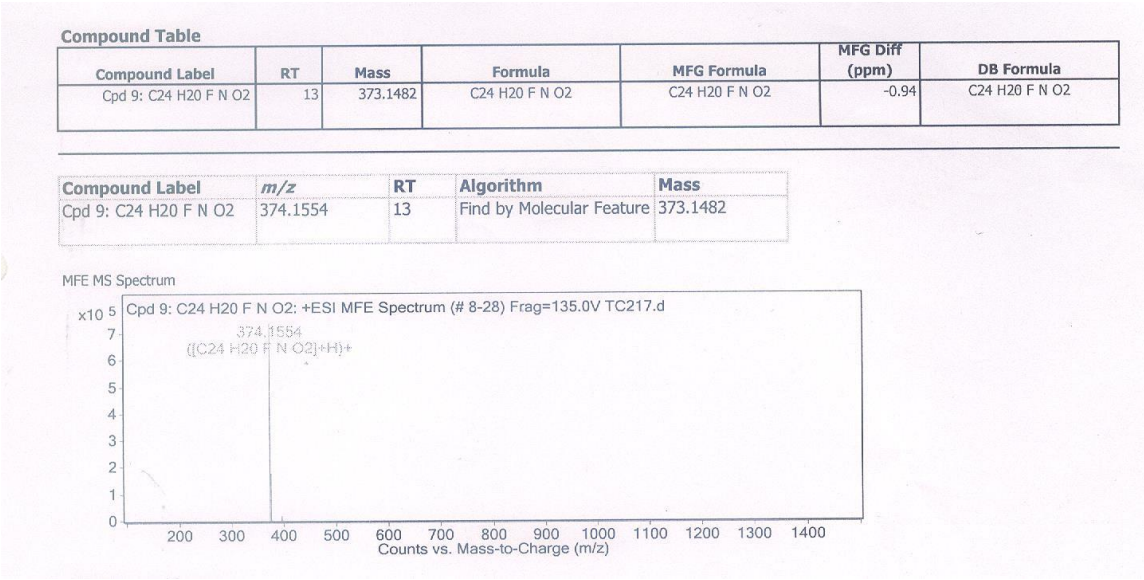
^{13}C NMR in $CDCl_3$



Methyl 2-(7-fluoro-2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3y**)



HRMS: Methyl 2-(7-fluoro-2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3y**)



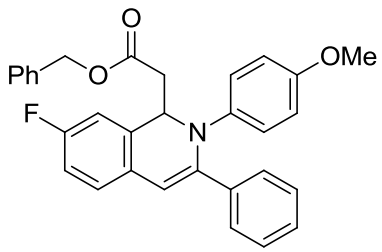
Compound Table

Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 9: C24 H20 F N O2	13	373.1482	C24 H20 F N O2	C24 H20 F N O2	-0.94	C24 H20 F N O2

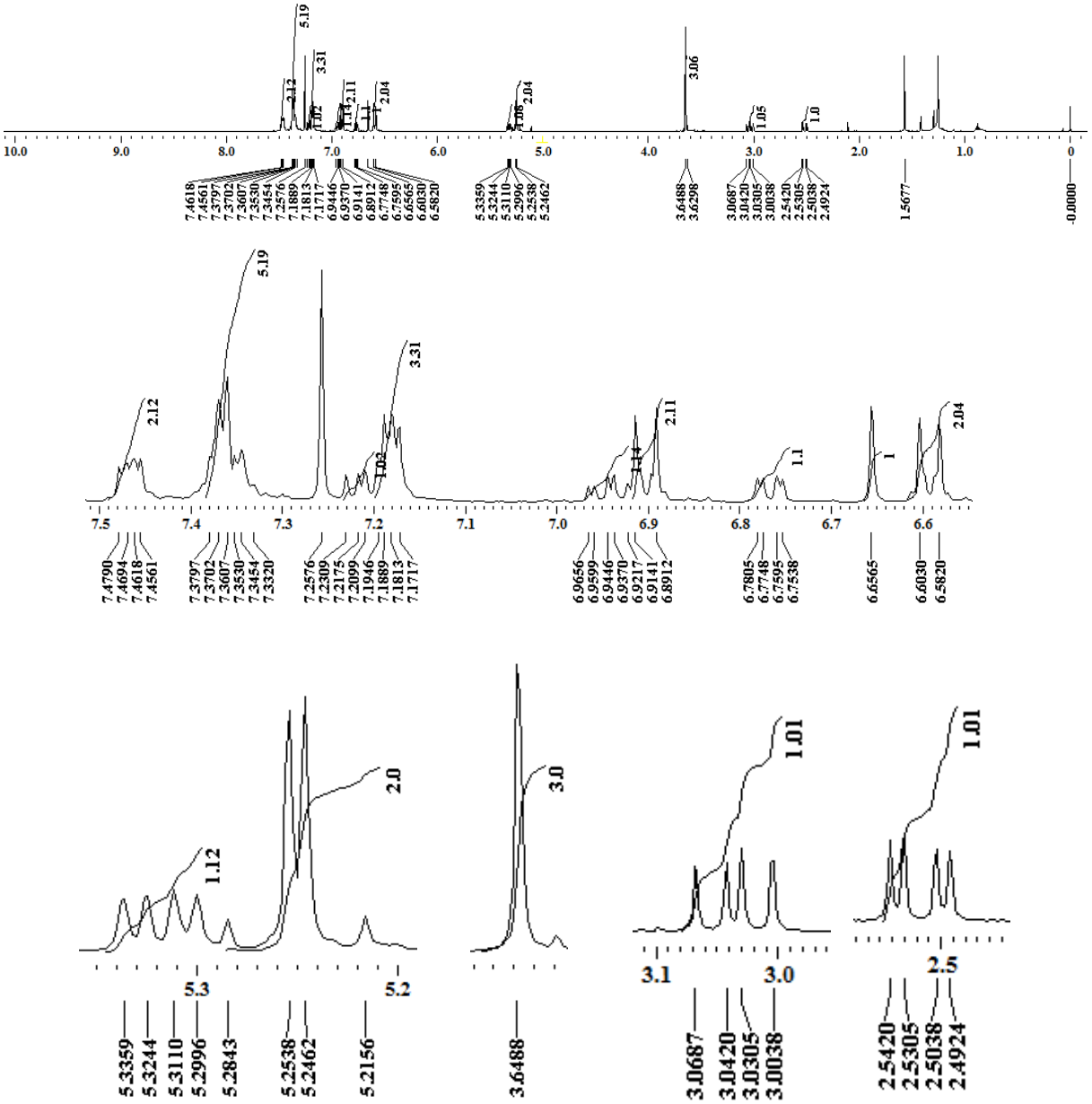
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 9: C24 H20 F N O2	374.1554	13	Find by Molecular Feature	373.1482

MFE MS Spectrum

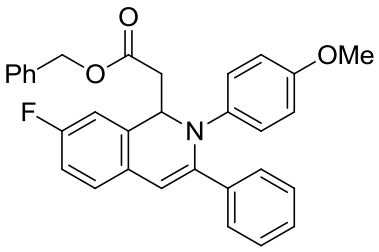
^{1}H NMR in $CDCl_3$



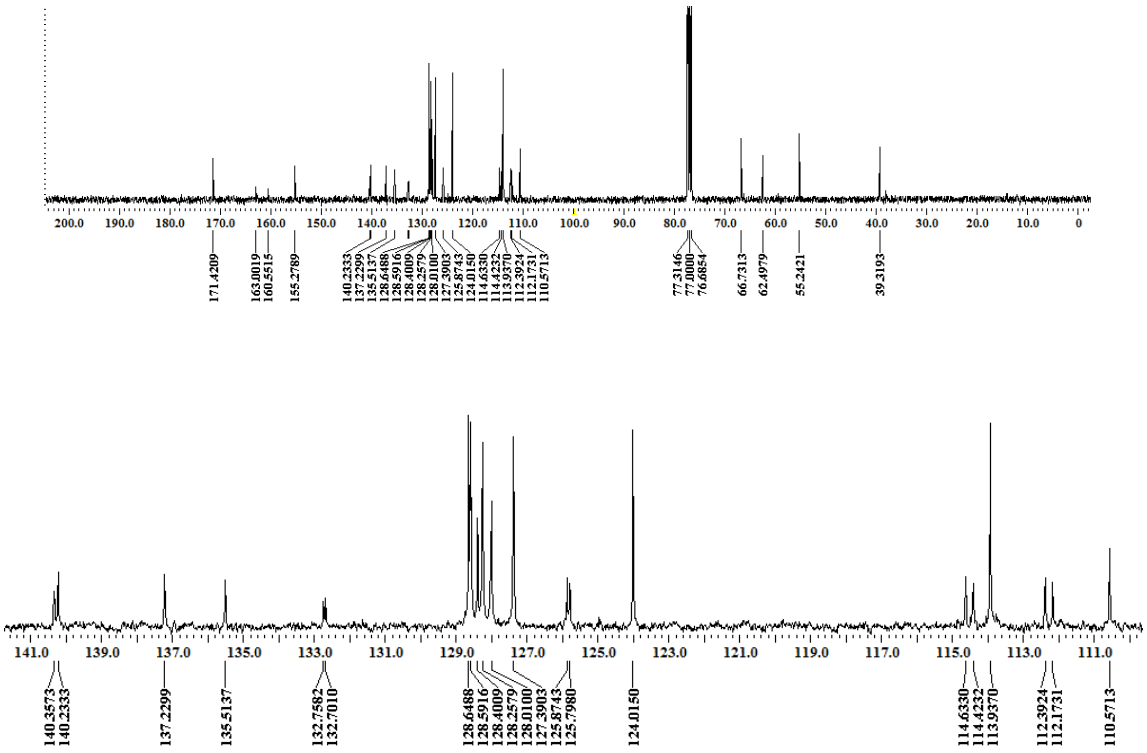
Benzyl 2-(7-fluoro-2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3z**)



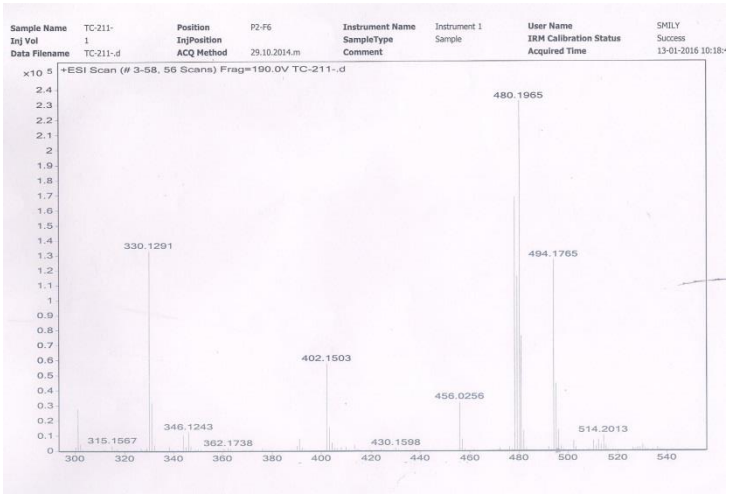
^{13}C NMR in $CDCl_3$



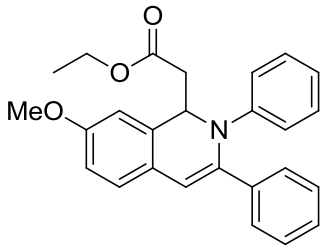
Benzyl 2-(7-fluoro-2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3z**)



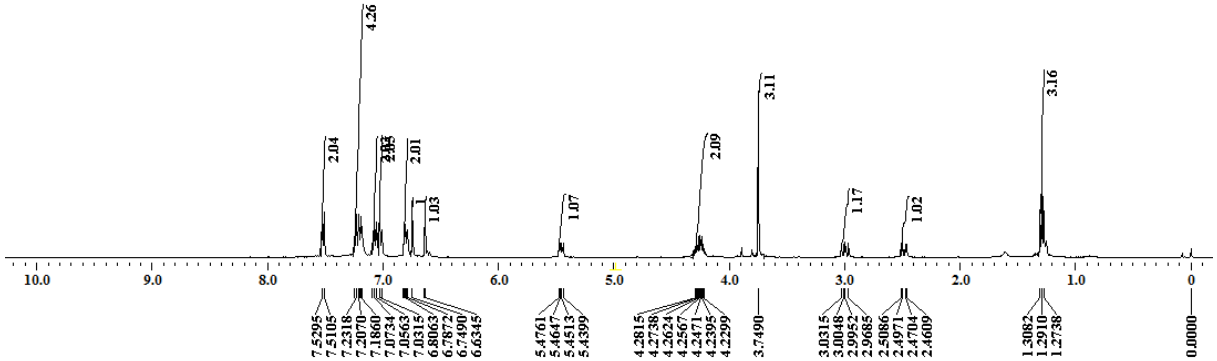
HRMS: Benzyl 2-(7-fluoro-2-(4-methoxyphenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3z**)

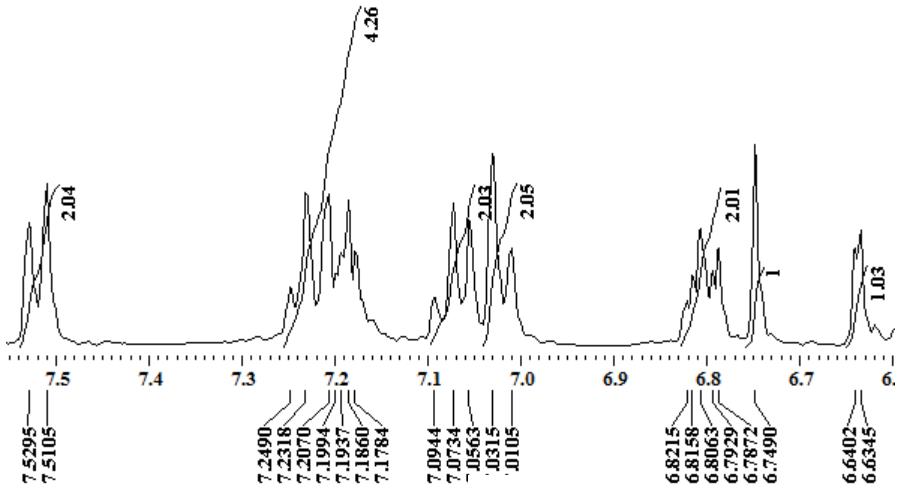


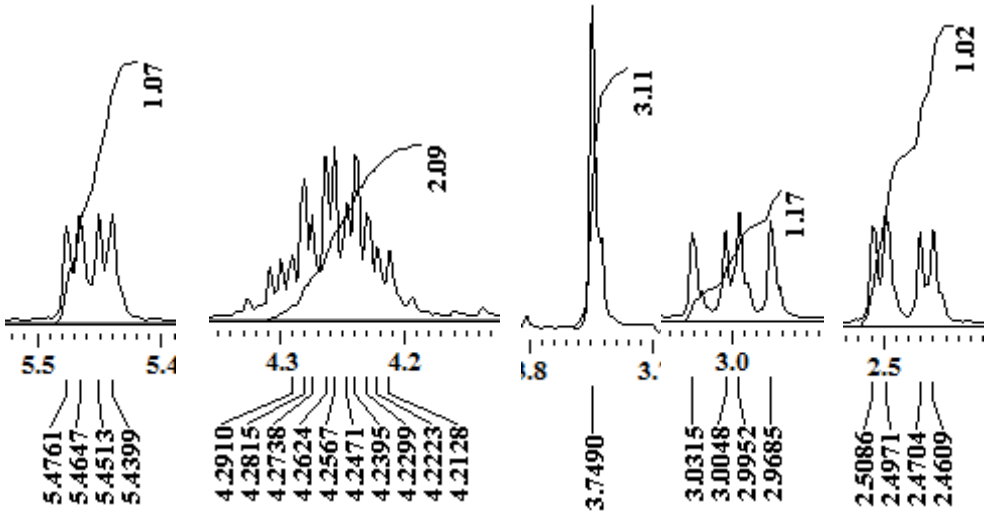
^{1}H NMR in $CDCl_3$



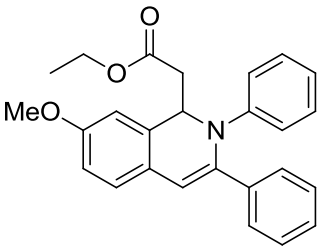
Ethyl 2-(7-methoxy-2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3za**)



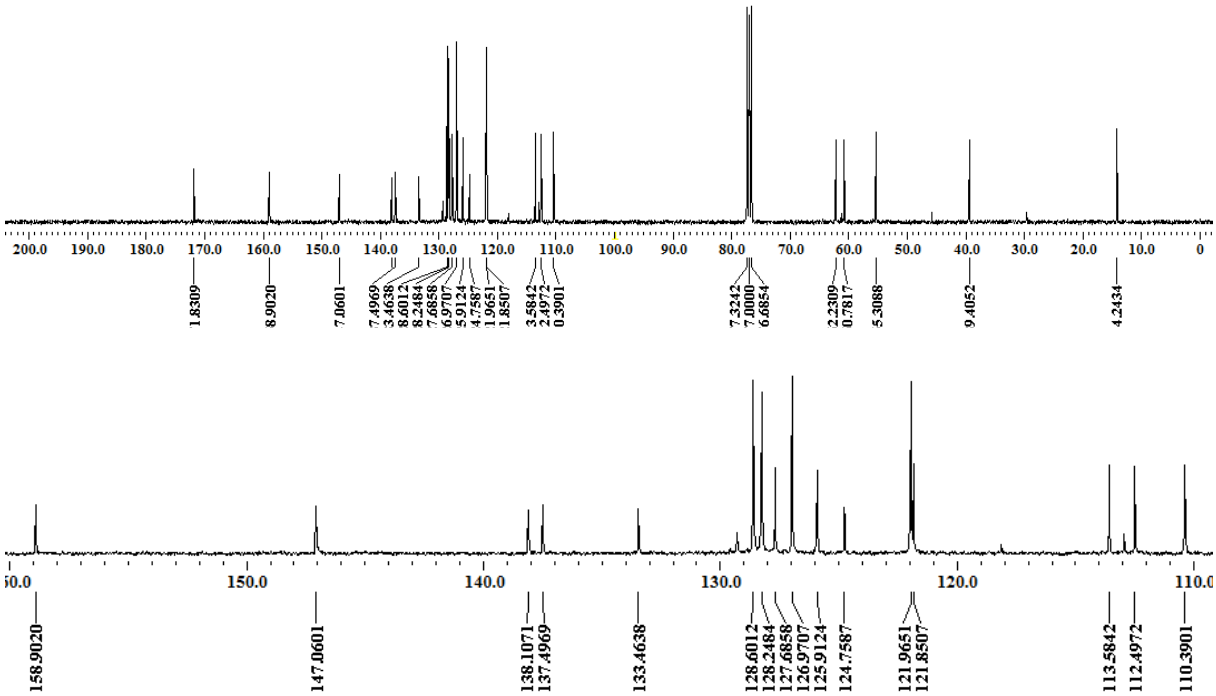




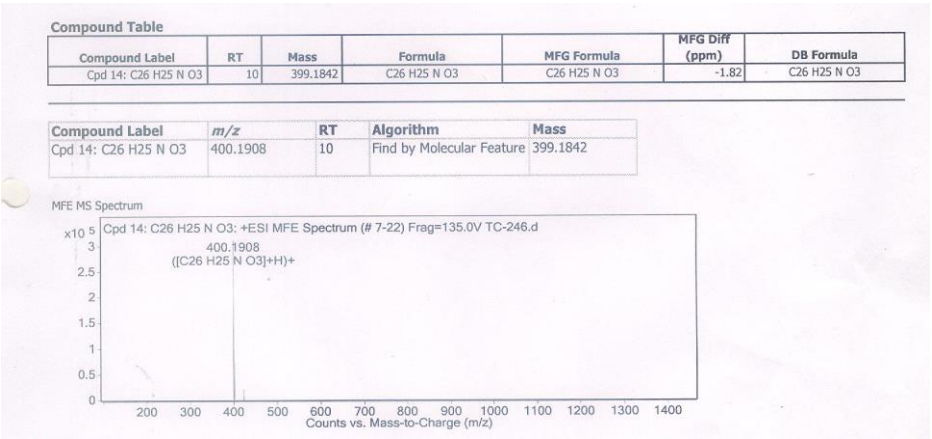
^{13}C NMR in $CDCl_3$



Ethyl 2-(7-methoxy-2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3za**)



HRMS: Ethyl 2-(7-methoxy-2,3-diphenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3za**)

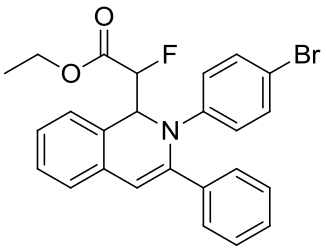


Compound Table

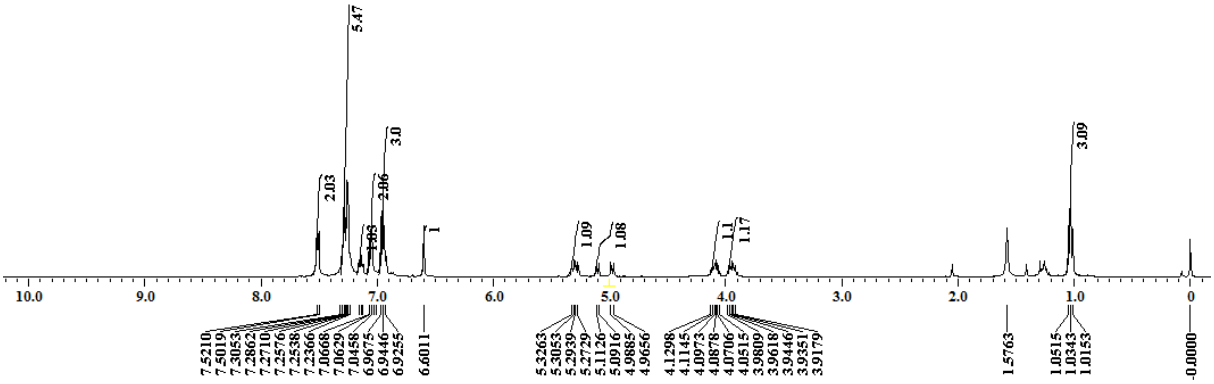
Compound Label	RT	Mass	Formula	MFG Formula	MFG Diff (ppm)	DB Formula
Cpd 14: C26 H25 N O3	10	399.1842	C26 H25 N O3	C26 H25 N O3	-1.82	C26 H25 N O3

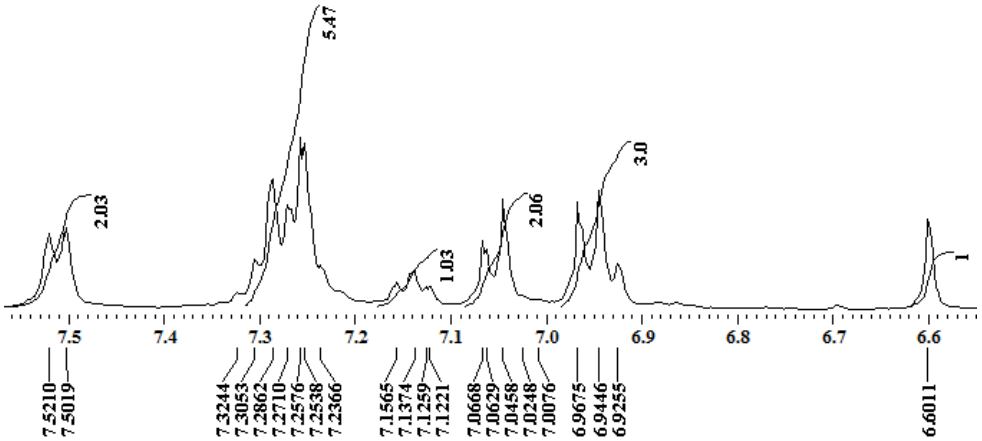
Compound Label	*m/z*	RT	Algorithm	Mass
Cpd 14: C26 H25 N O3	400.1908	10	Find by Molecular Feature	399.1842

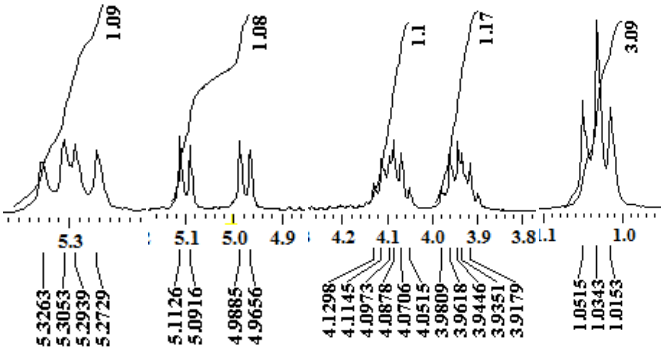
^{1}H NMR in $CDCl_3$



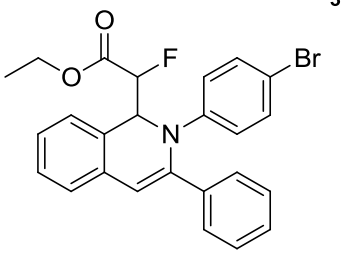
Ethyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)-2-fluoroacetate (**3zb**)



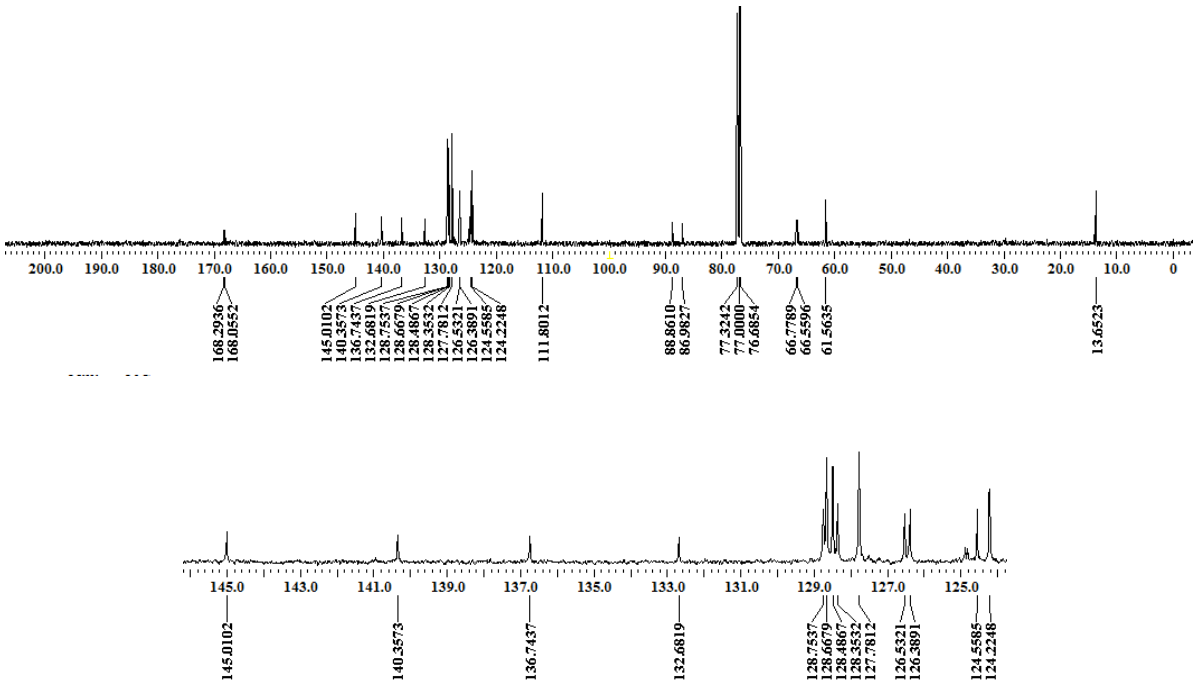




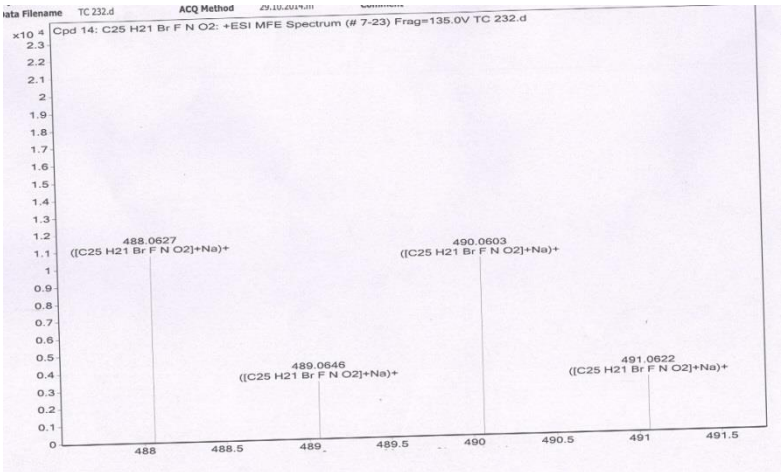
^{13}C NMR in $CDCl_3$



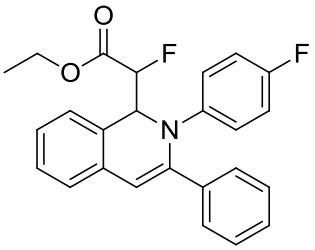
Ethyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)-2-fluoroacetate (**3zb**)



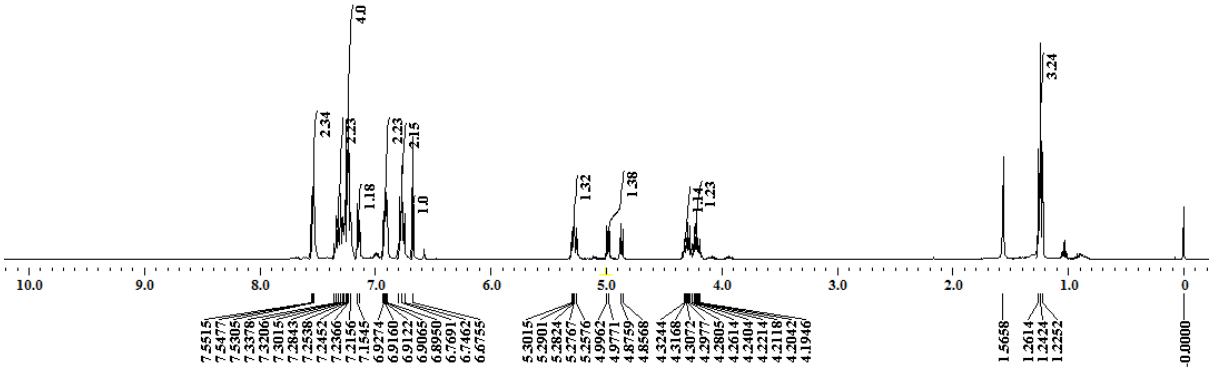
HRMS: Ethyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)-2-fluoroacetate (**3zb**)

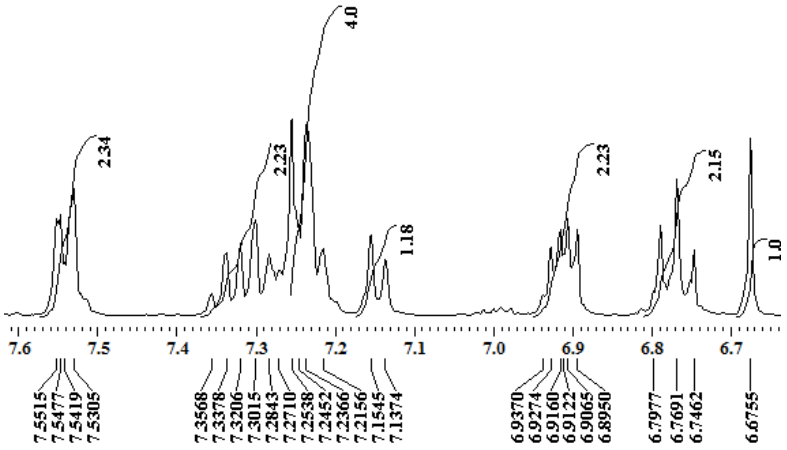


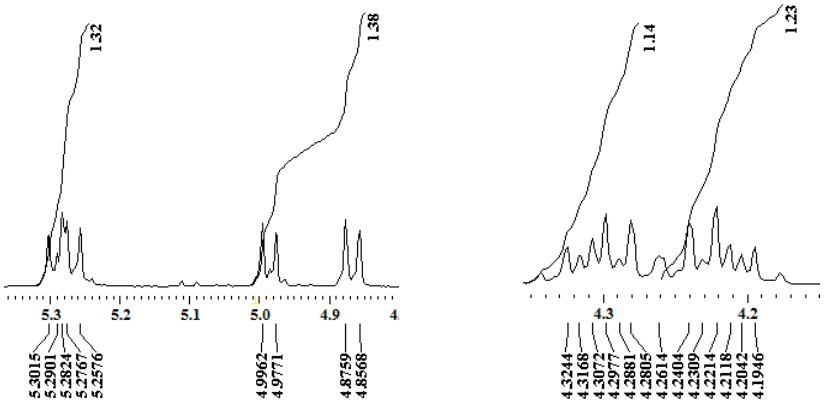
^{1}H NMR in $CDCl_3$



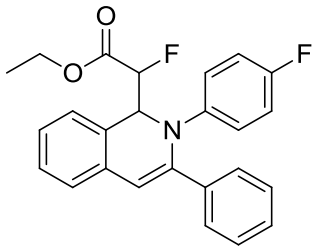
Ethyl 2-fluoro-2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3zc**)



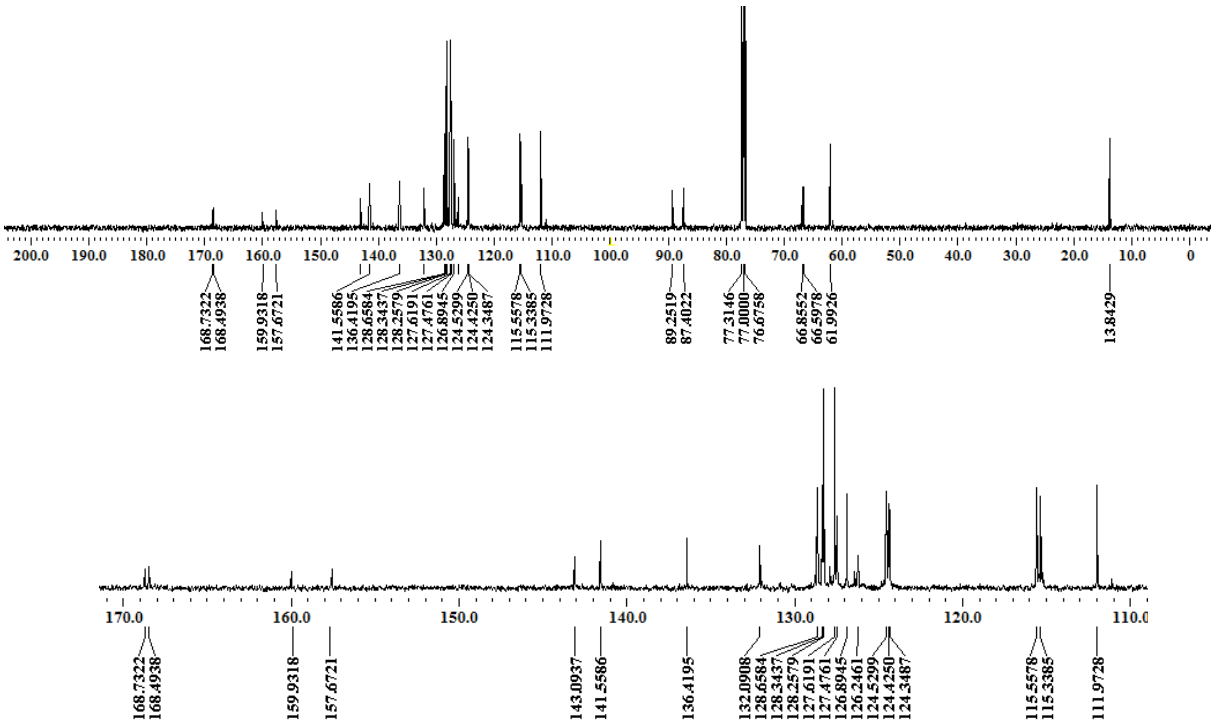




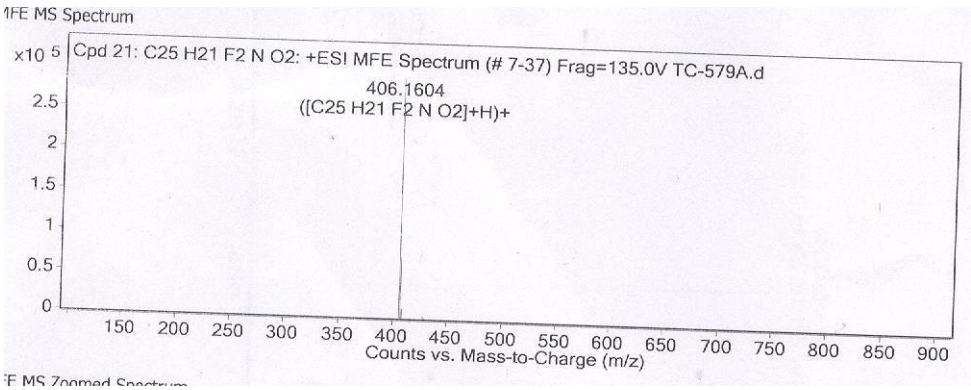
^{13}C NMR in $CDCl_3$



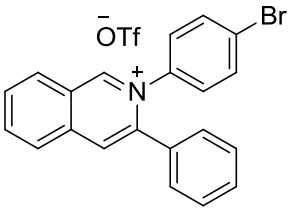
Ethyl 2-fluoro-2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3zc**)



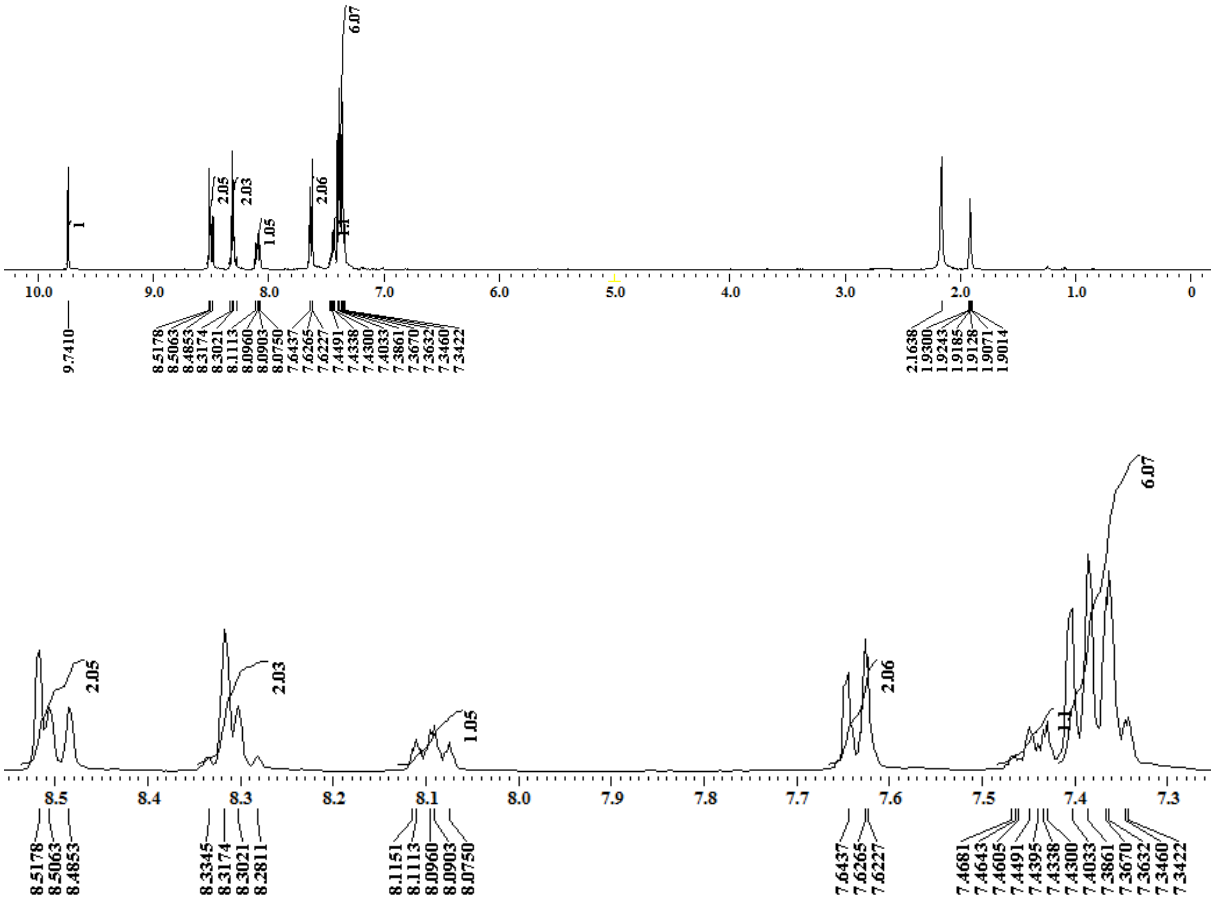
HRMS: Ethyl 2-fluoro-2-(2-(4-fluorophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl)acetate (**3zc**)



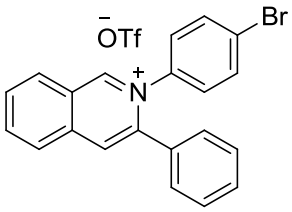
^{1}H NMR in CD_3CN



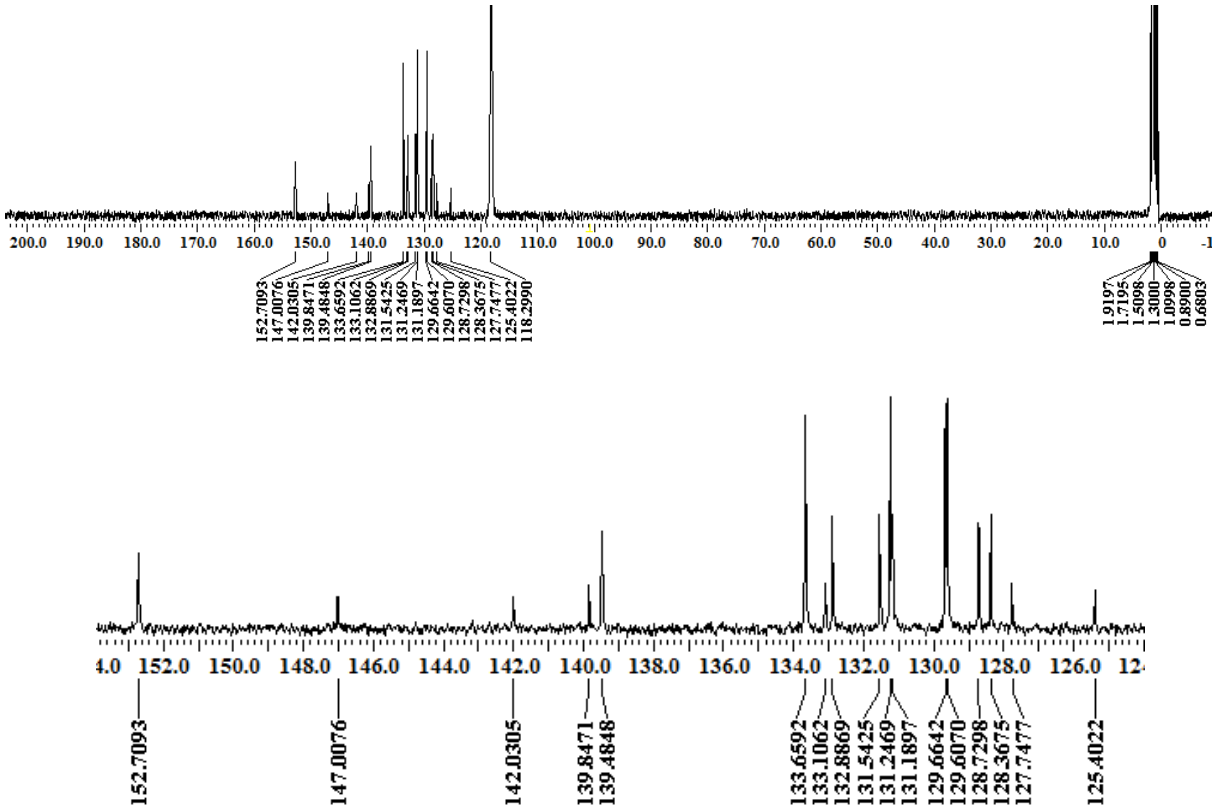
2-(4-Bromophenyl)-3-phenylisoquinolin-2-ium (**4a**)



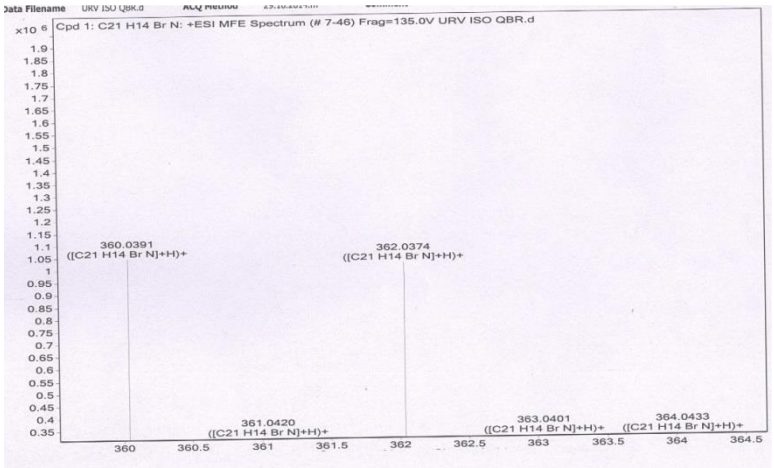
^{13}C NMR in CD_3CN



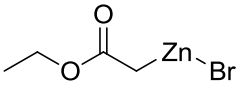
2-(4-Bromophenyl)-3-phenylisoquinolin-2-ium (**4a)**



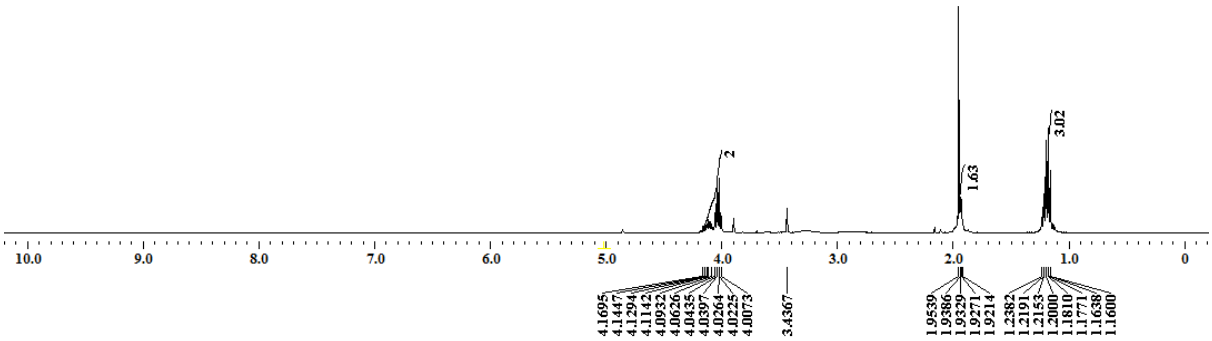
HRMS: 2-(4-Bromophenyl)-3-phenylisoquinolin-2-ium (**4a**)

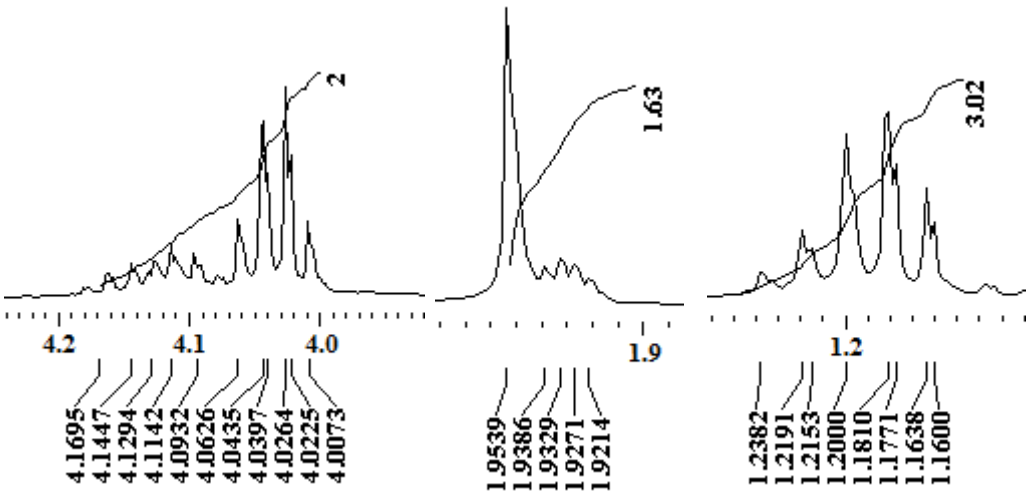


^{1}H NMR in CD_3CN

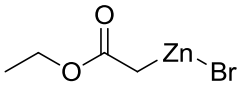


(2-Ethoxy-2-oxoethyl)zinc(II) bromide (**5**)

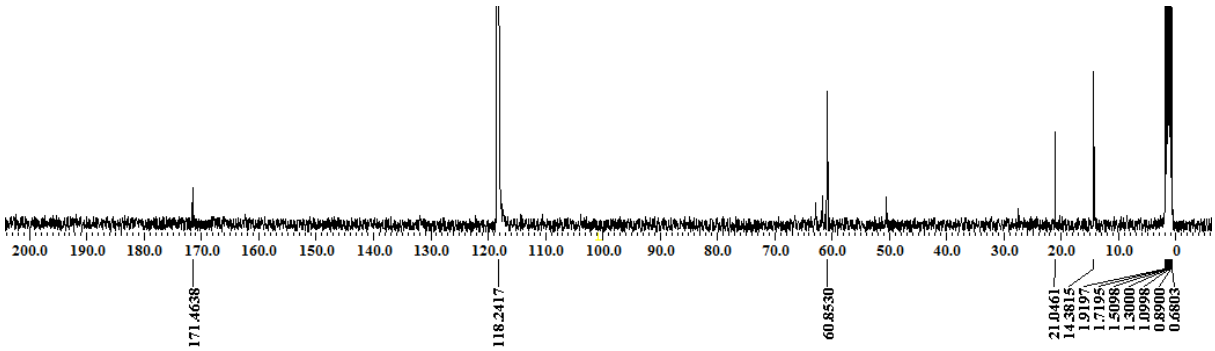


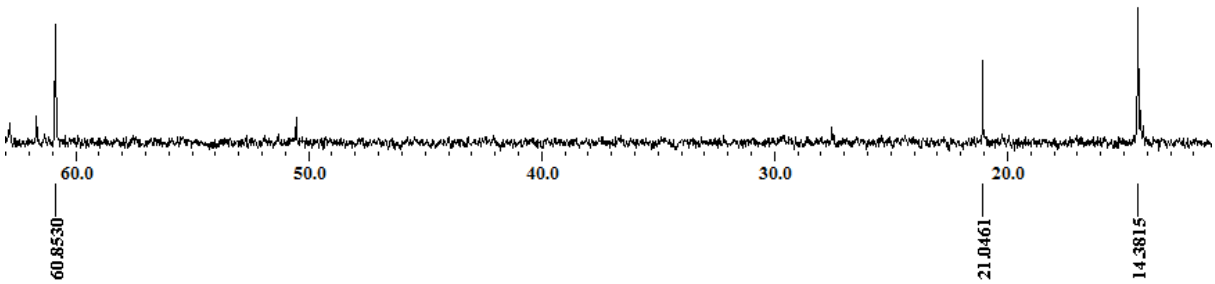


^{13}C NMR in CD_3CN



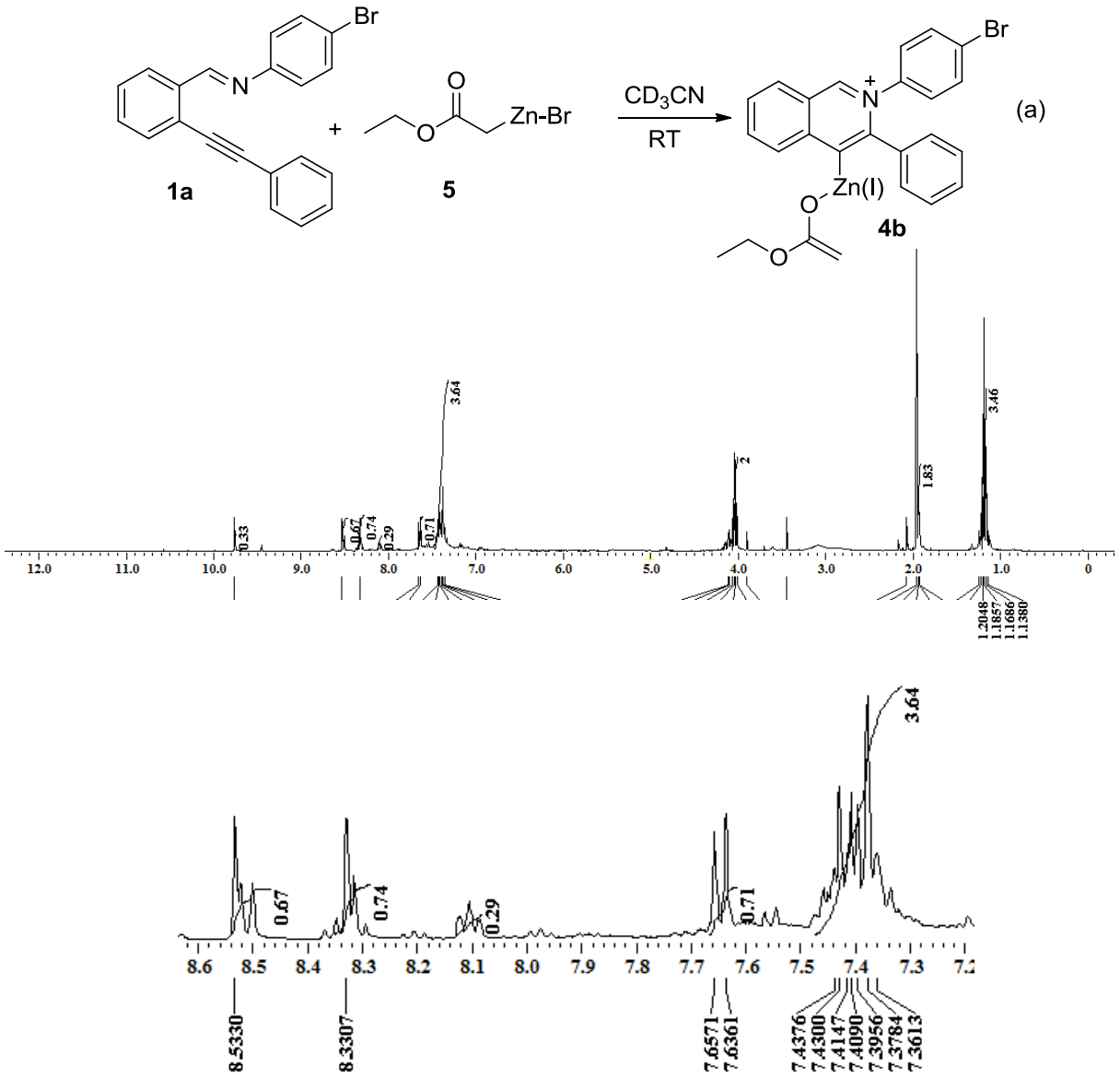
(2-Ethoxy-2-oxoethyl)zinc(II) bromide (**5**)



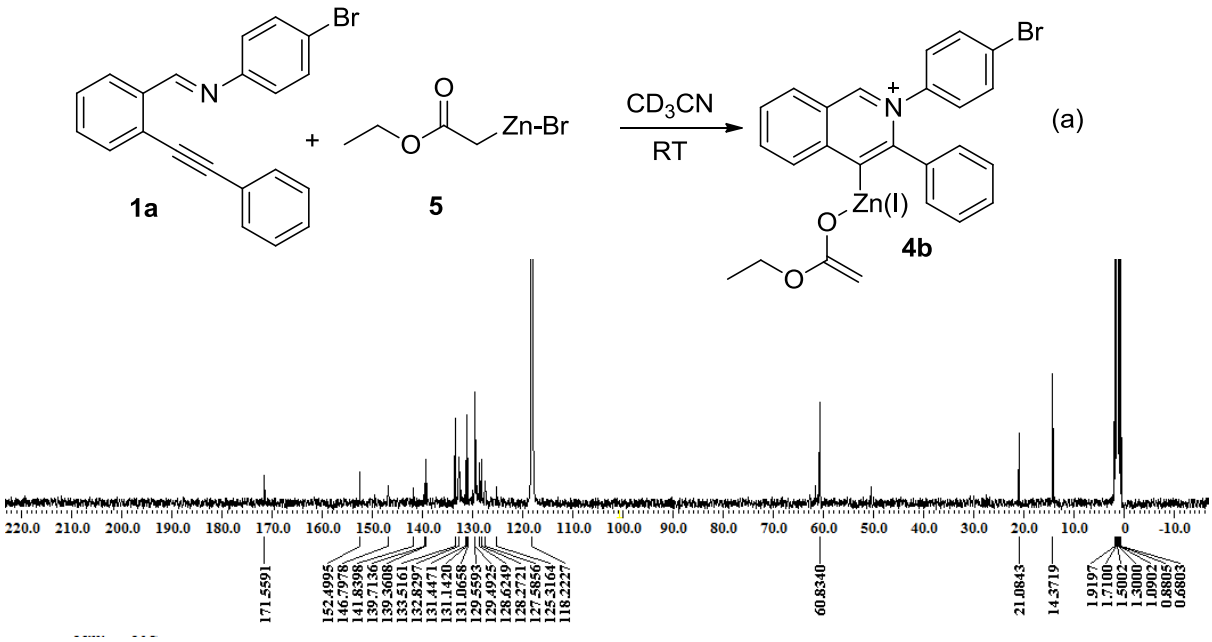


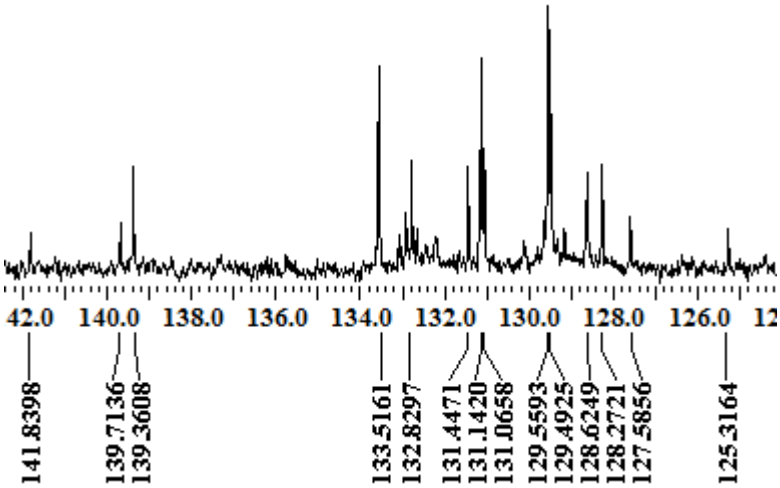
4. Spectra of Mechanistic Experiments

^{1}H NMR (Scheme 4 equation **c):** The NMR given below is a mixture of **5** and **4b**. In this, **1a** was completely converted to isoquinolinium salt (**4b**), but as **5** was used in excess hence, unreacted **5** is in mixture and peak of **5** was also observed in reaction. The NMR was recorded without work up in CD_3CN.

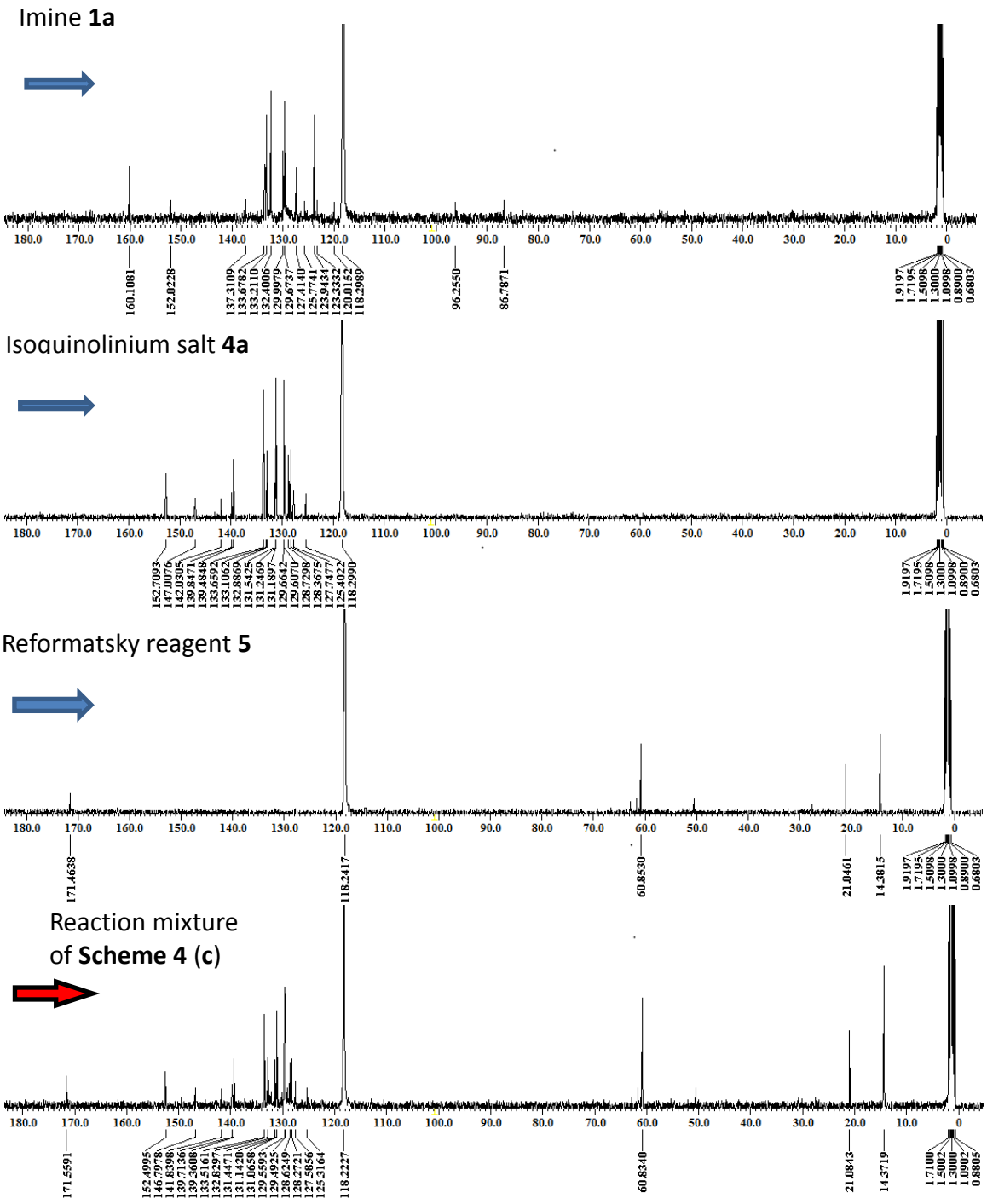


^{13}C NMR of (Scheme 4 equation **c):** The NMR given below is a mixture of **5** and **4b**. **1a** was completely converted to isoquinolinium salt (**4b**), but as **5** was uesd in excess hence, unreacted **5** is in mixture and peak of **5** was also observed in reaction. The NMR was recorded without work up in CD_3CN.



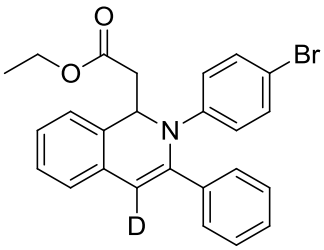


Scheme 4 (eq. c): Comparison of spectra of ^{13}C NMR in CD_3CN of reaction mixture and constituents separately

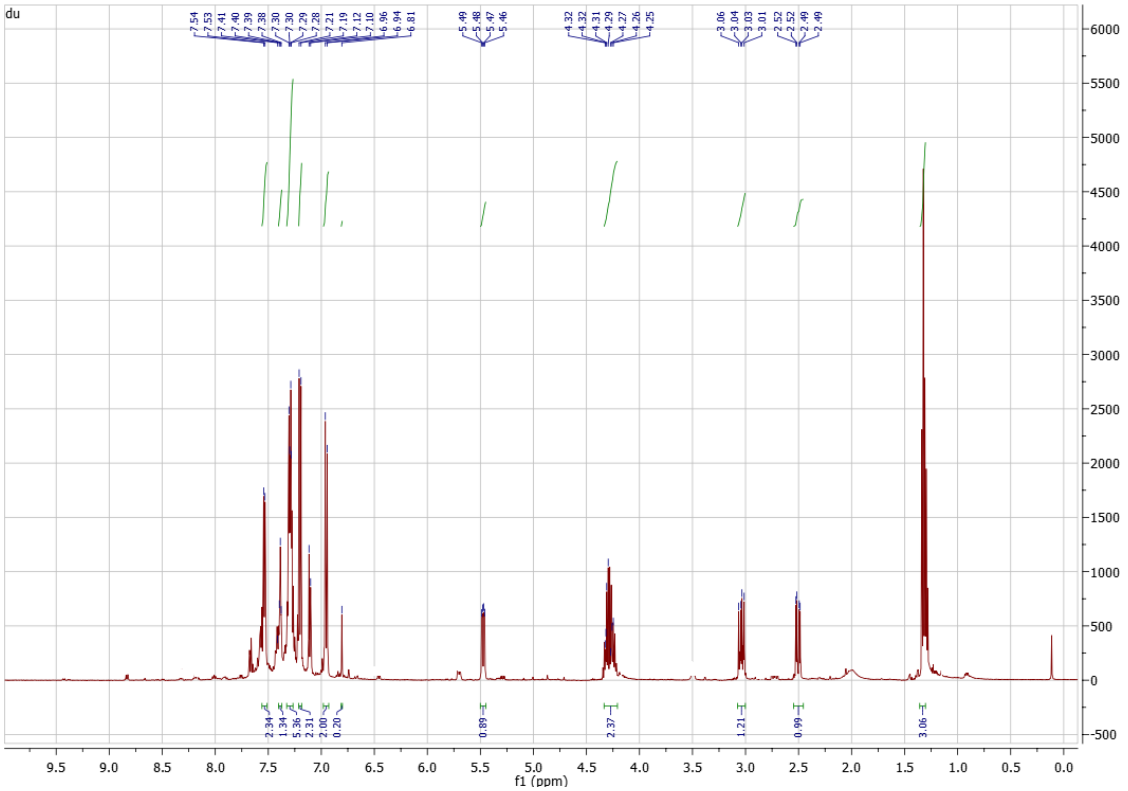


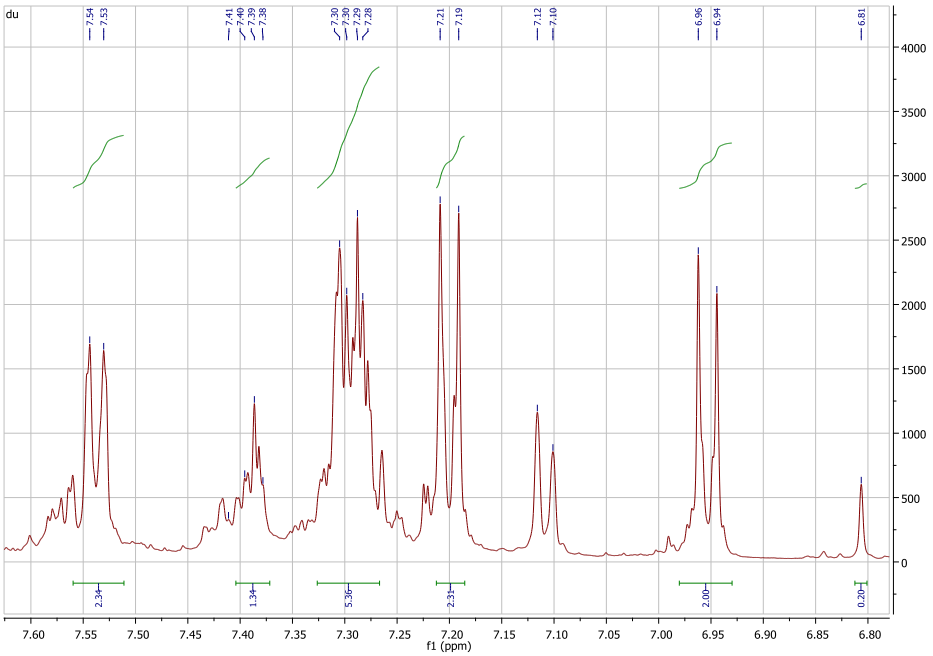
Imine peaks (1a) (ppm)	Isoquinolinium (4a) peaks (ppm)	Reformatsky peaks (5) (ppm)	Reaction Mixture (Scheme 4eq. c) peaks (ppm)
160.108	---	--	---
---	152.709	---	152.4995
152.022	---	---	---
---	147.007	---	146.797
---	142.030	---	141.839
---	139.849	---	139.713
---	139.484	---	139.360
---	133.659	---	133.516
---	132.886	---	132.829
---	131.542	---	131.447
---	131.246	---	131.142
---	131.189	---	131.065
129.997	129.664	---	129.559
129.673	129.607	---	129.492
---	128.729	---	128.624
---	128.367	---	128.272
127.414	127.747	---	127.585
125.774	125.402	---	125.316
123.994	---	---	---
120.015	---	---	---
---	---	171.463	171.559
---	---	60.853	60.834
---	---	21.046	21.0843
---	---	14.381	14.371

^{1}H NMR in $CDCl_3$



Ethyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl-4-*d*) acetate (**3ab**)





HRMS: ethyl 2-(2-(4-bromophenyl)-3-phenyl-1,2-dihydroisoquinolin-1-yl-4-d) acetate (**3ab)**