Supporting Information for

Organocatalytic C3-Functionalization of Indolizines: Synthesis of Biologically Important Indolizine Derivatives

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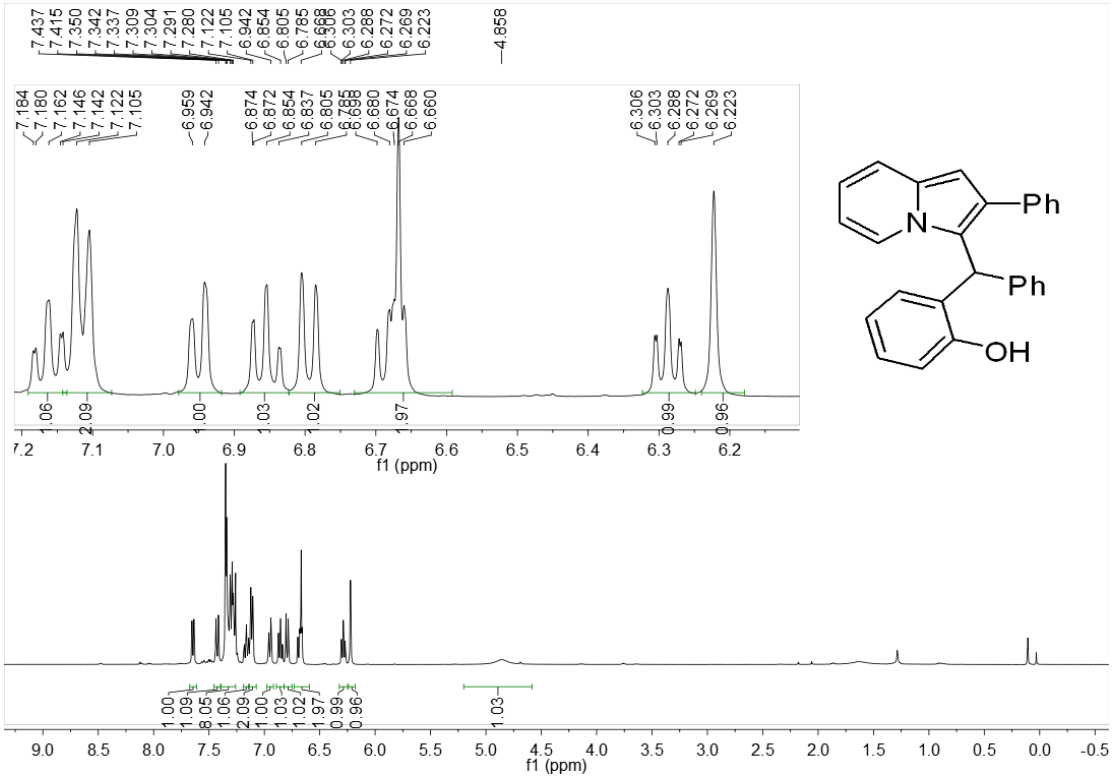
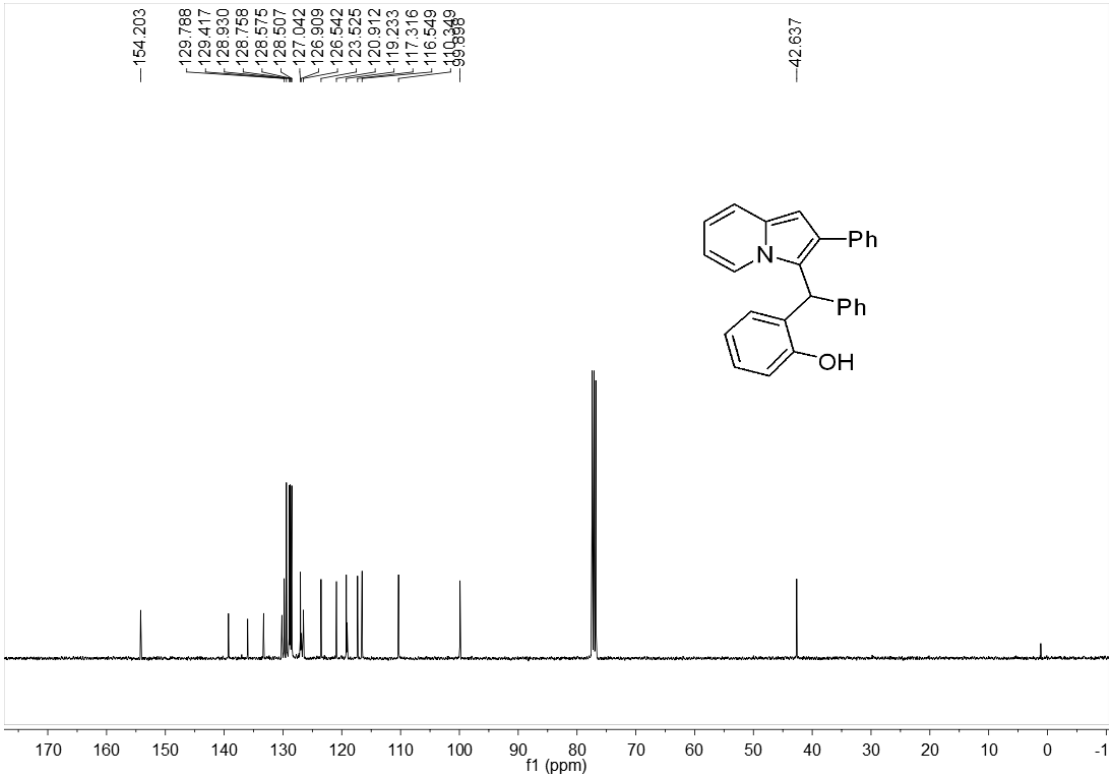
Contents:

1. NMR spectra of products 3, 5, 7, 9, 11 and 13

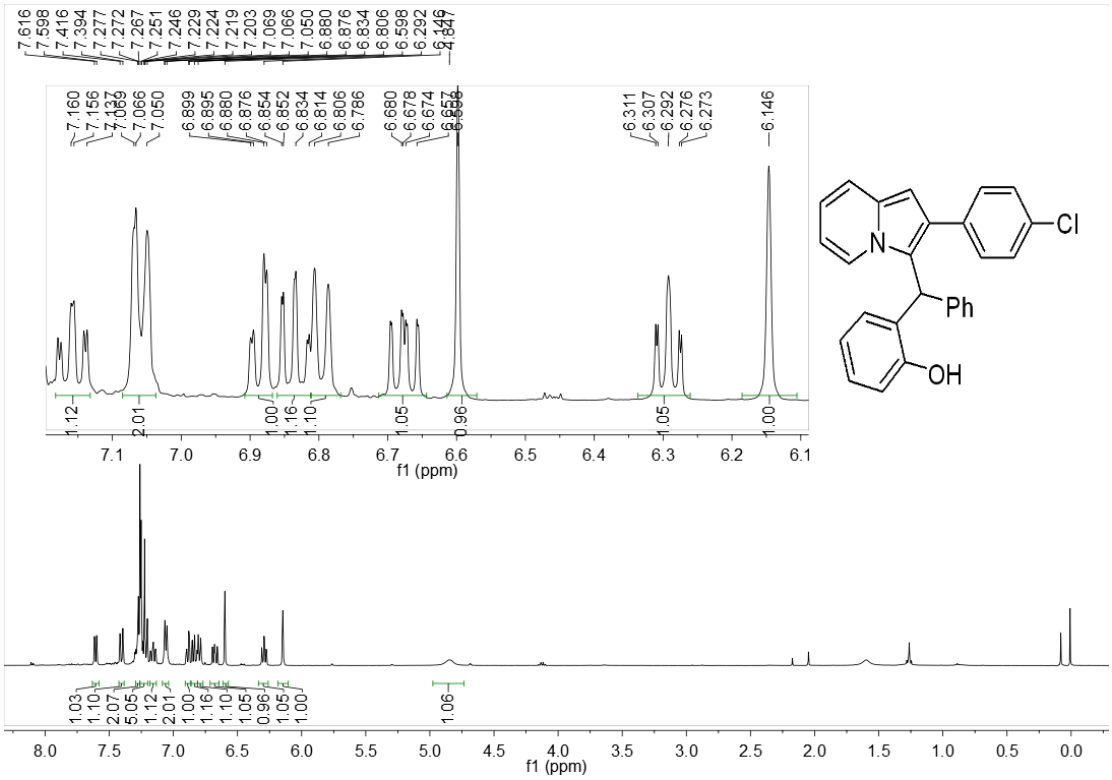
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3aa**



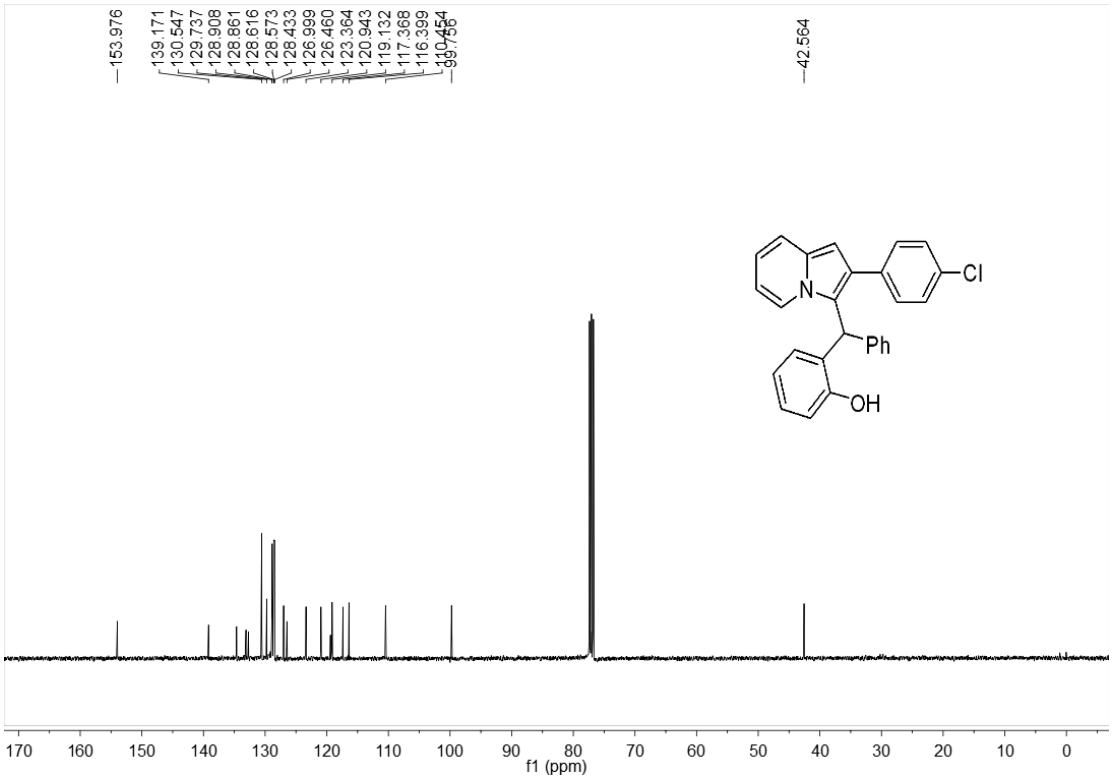
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3aa**



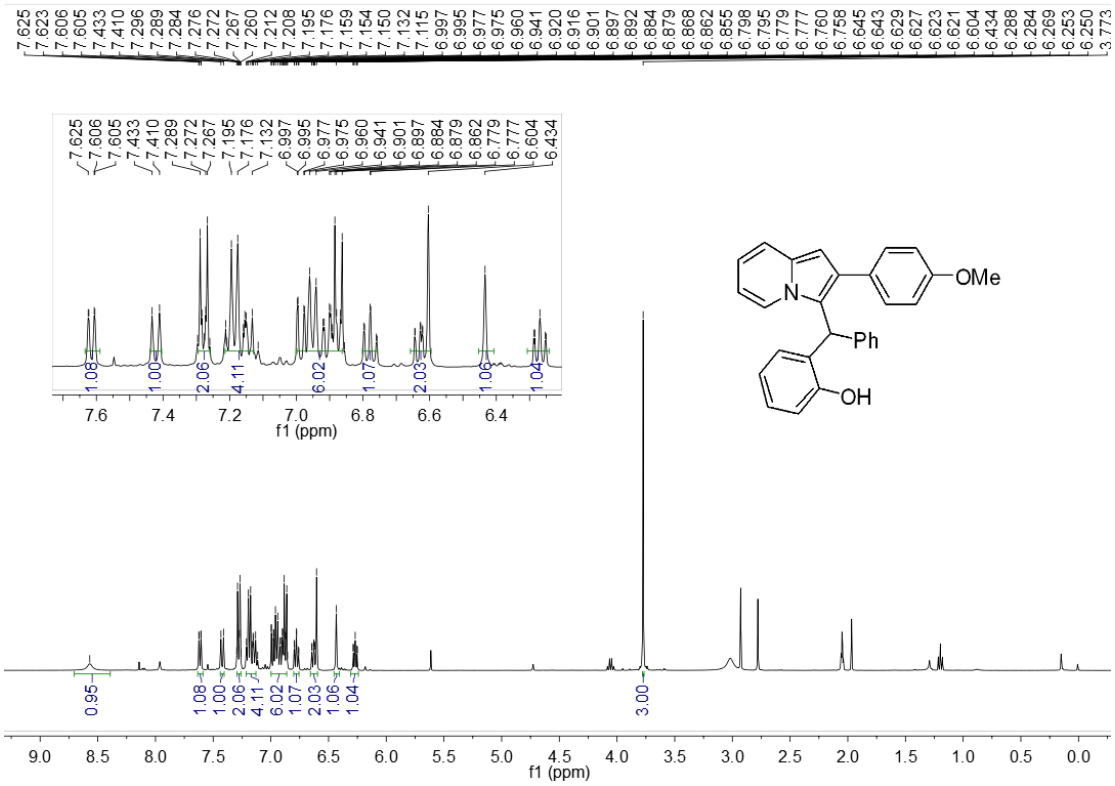
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3ba**



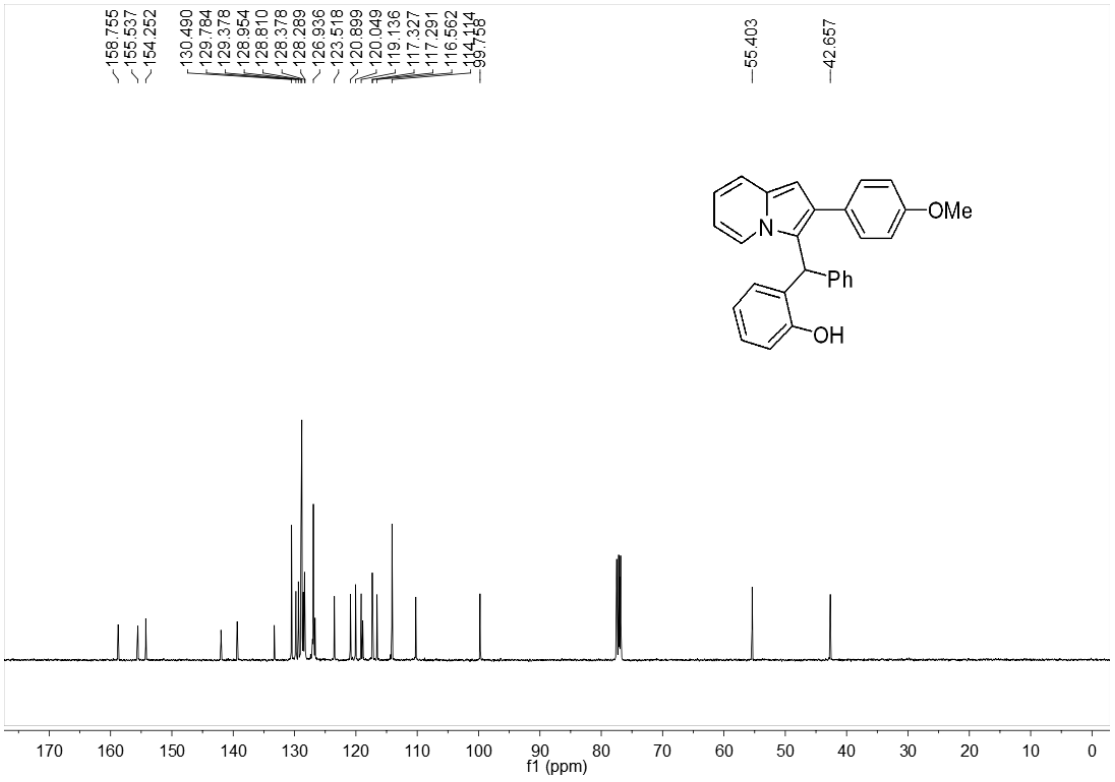
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ba**



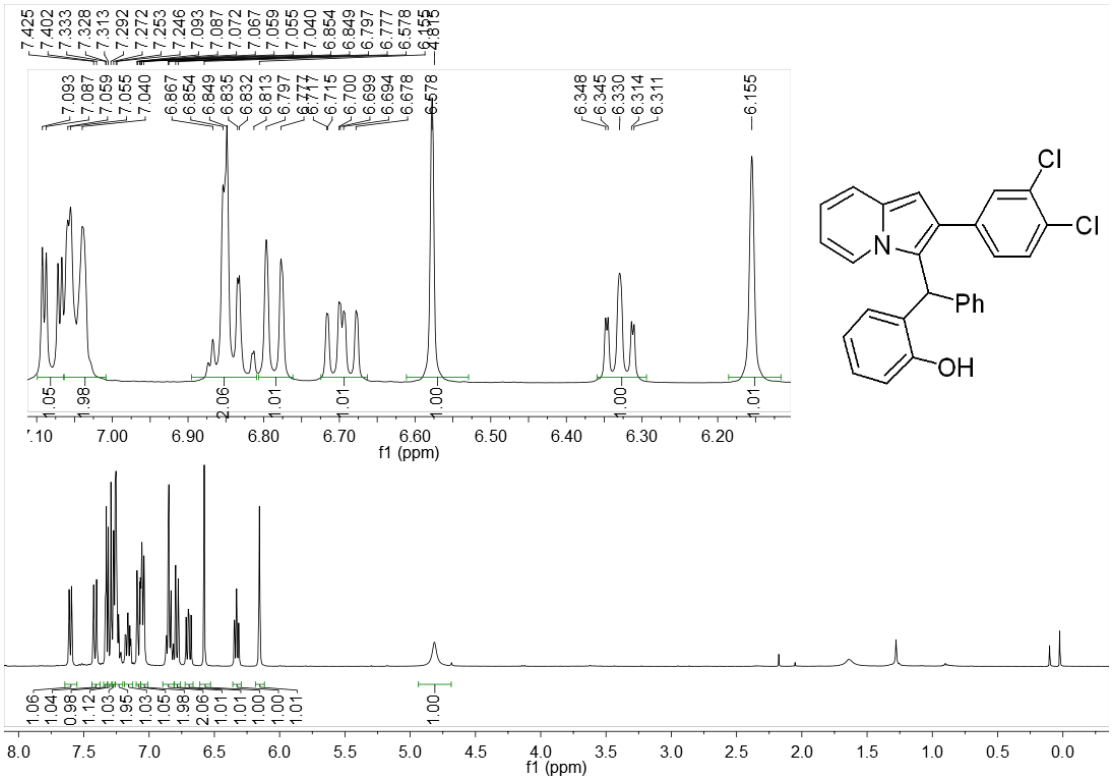
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ca**



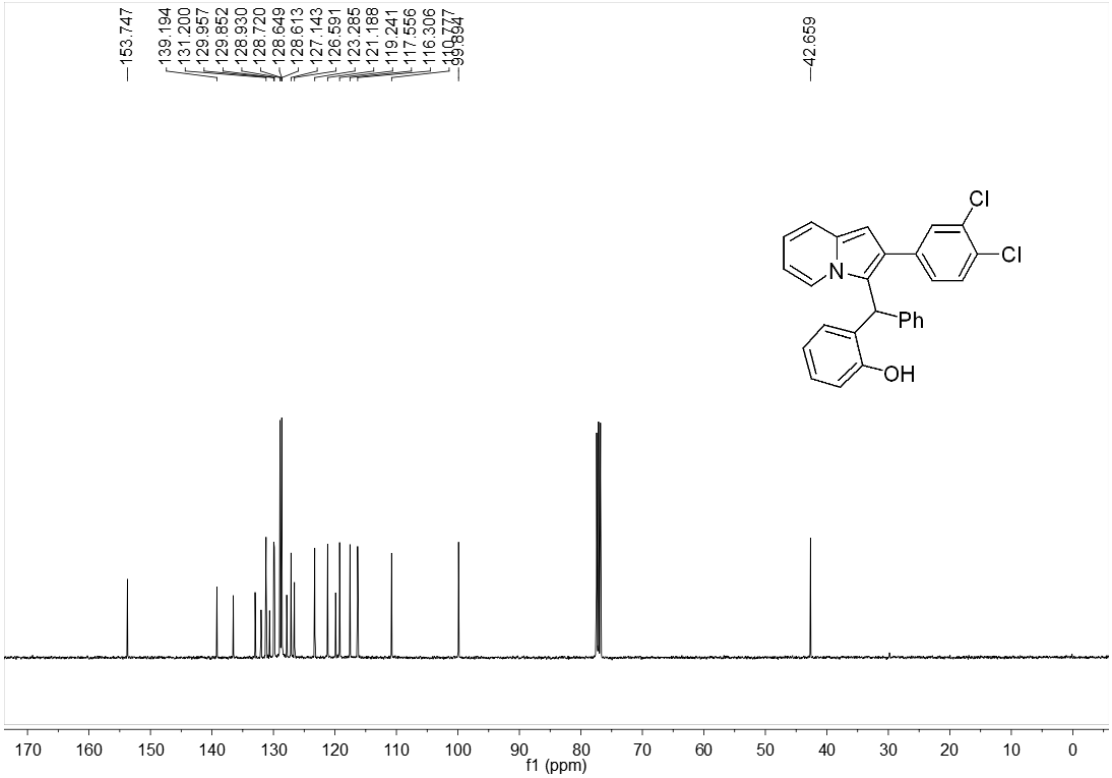
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ca**



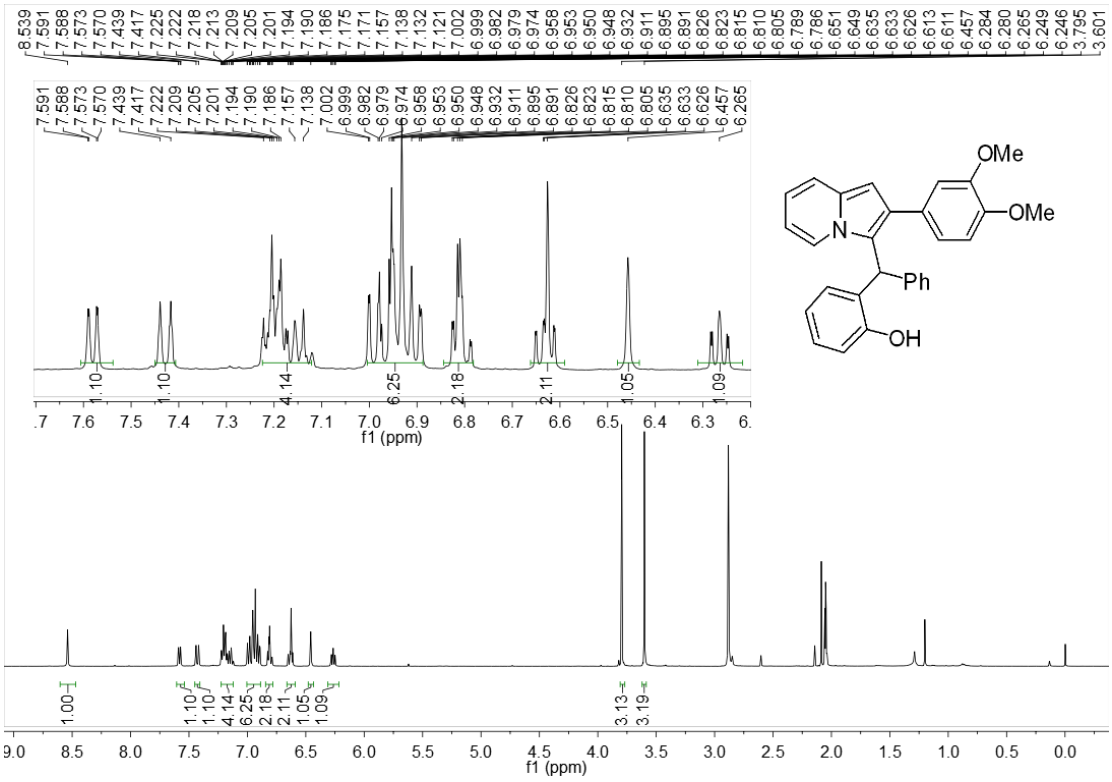
^{1}H NMR (400 MHz, $CDCl_3$) of compound **3da**



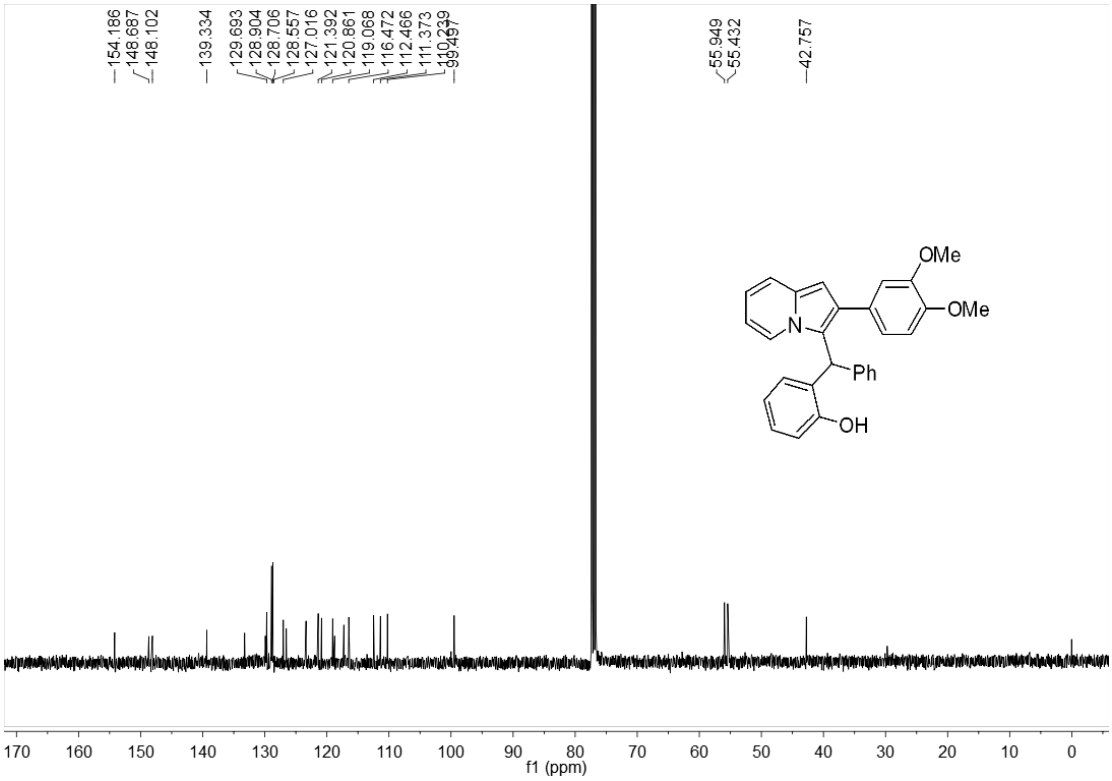
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3da**



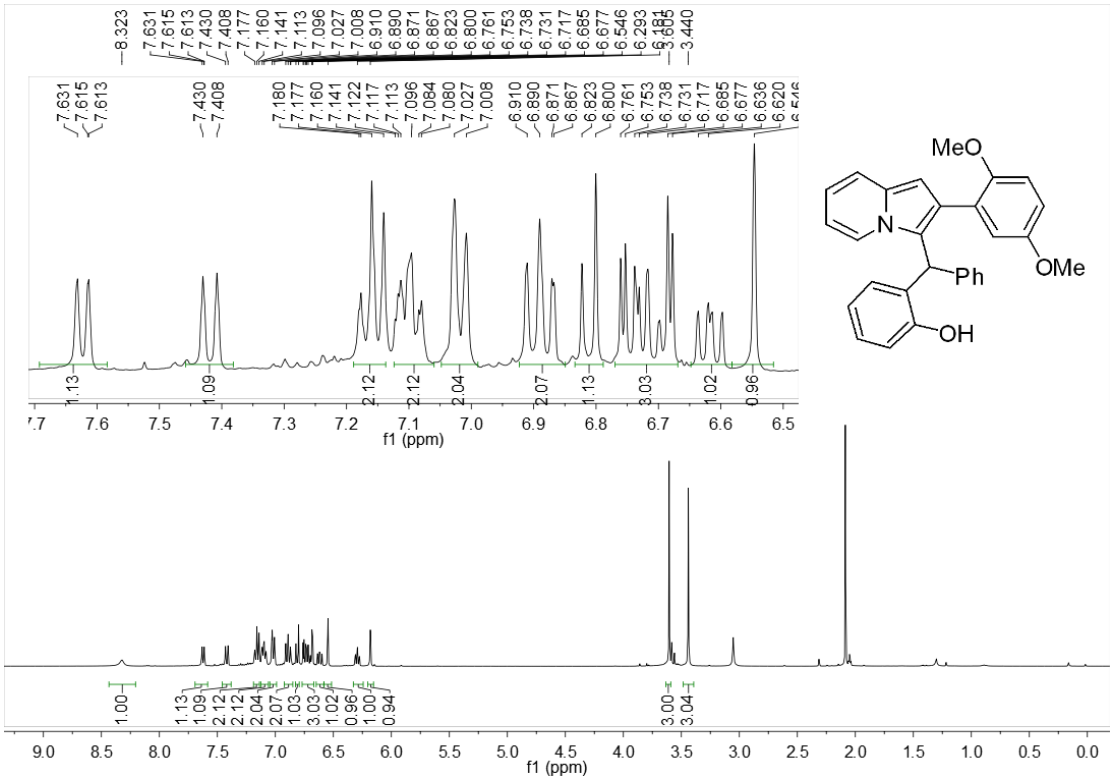
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ea**



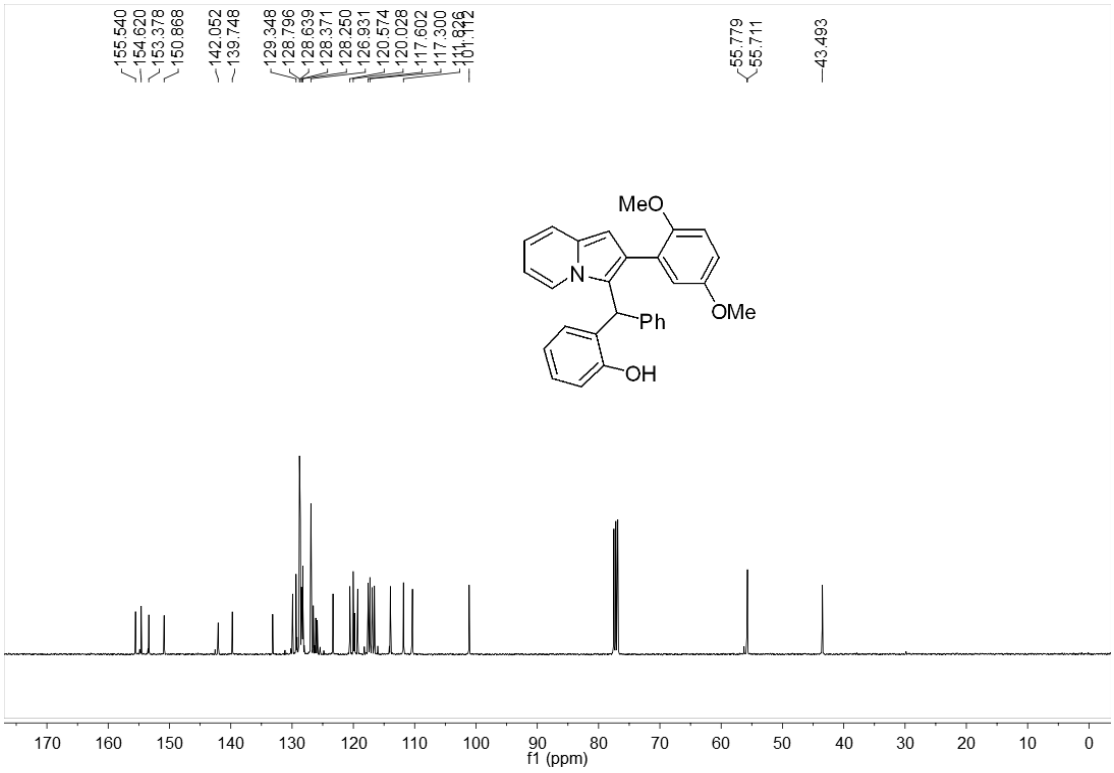
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ea**



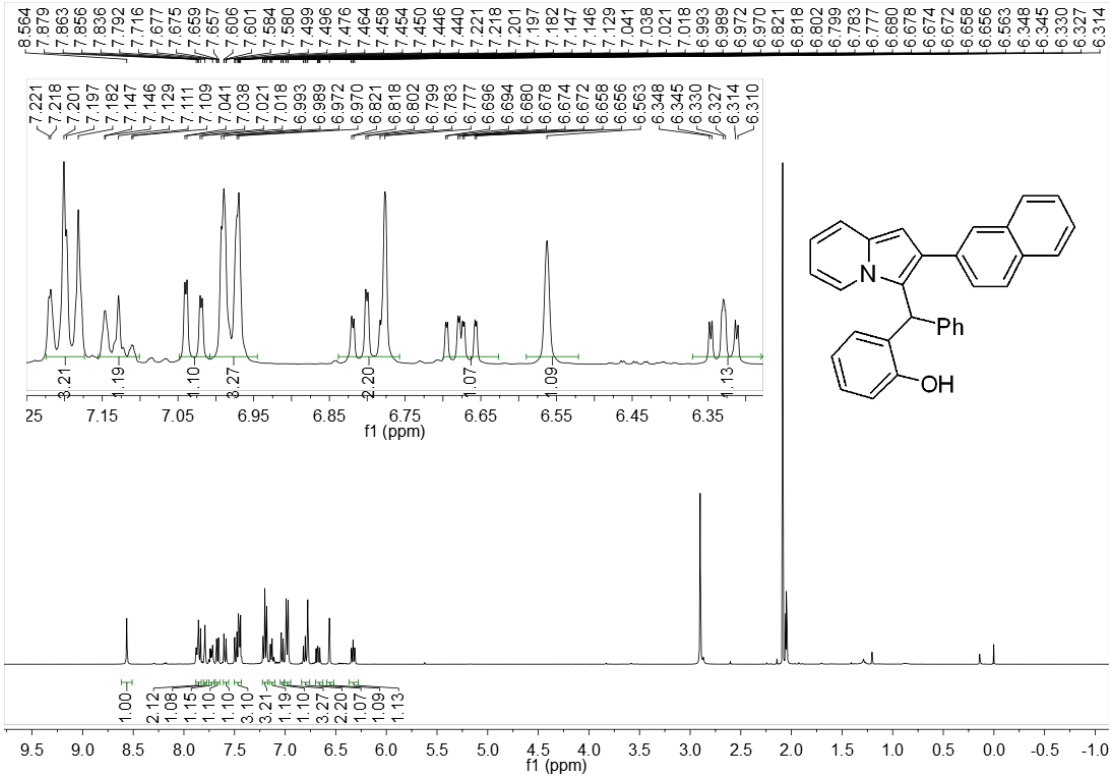
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3fa**



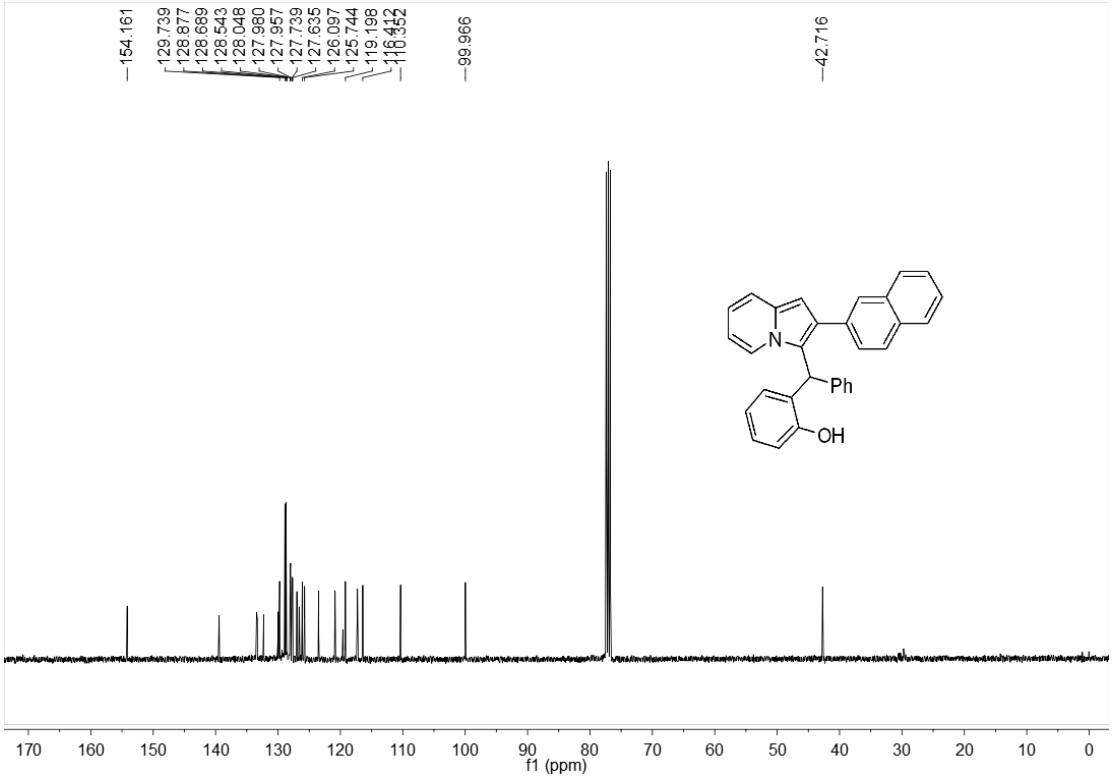
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3fa**



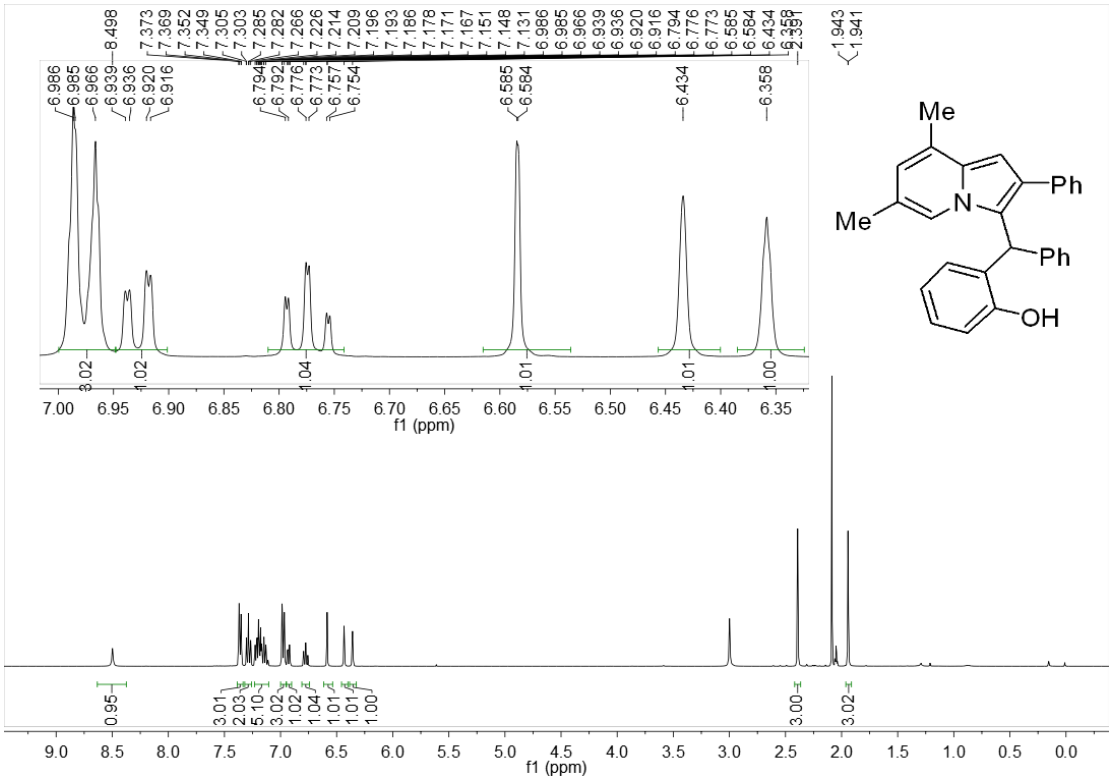
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ga**



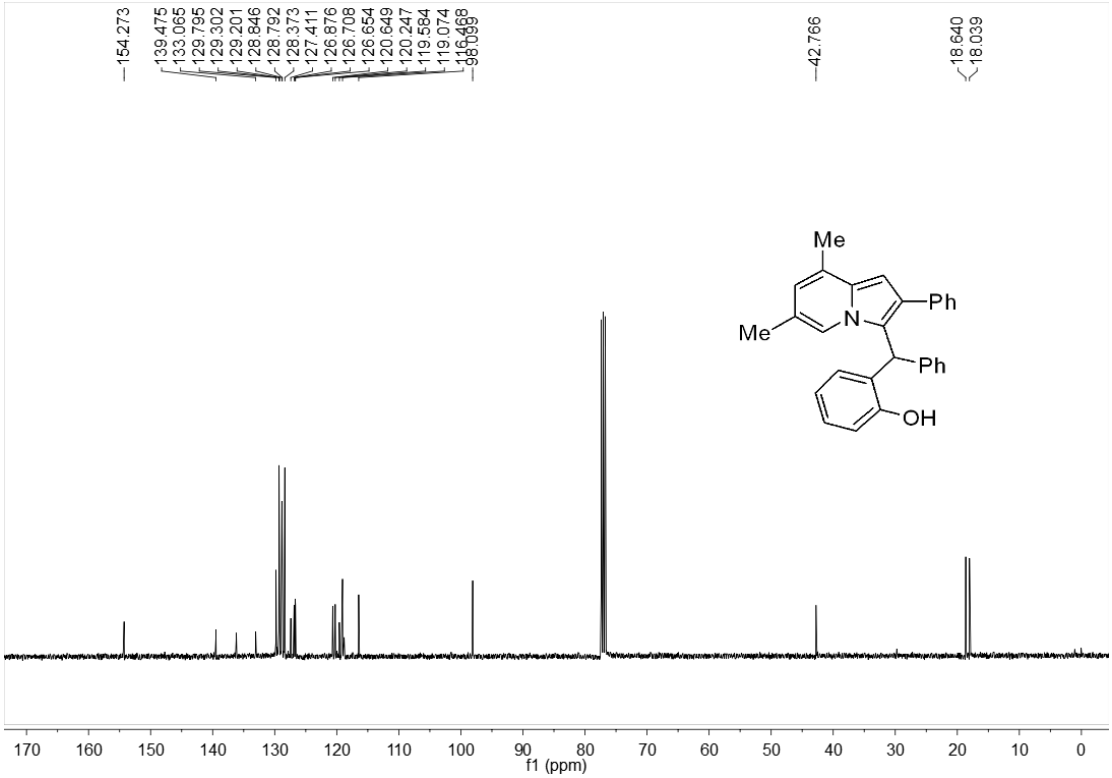
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ga**



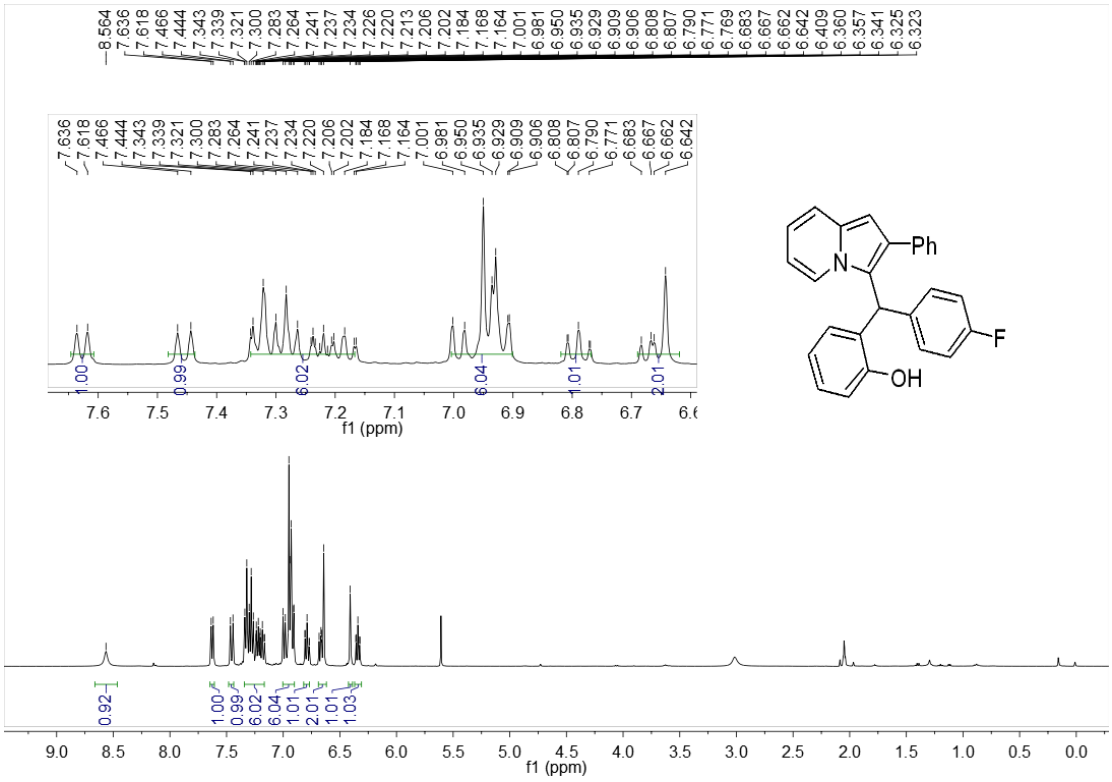
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ha**



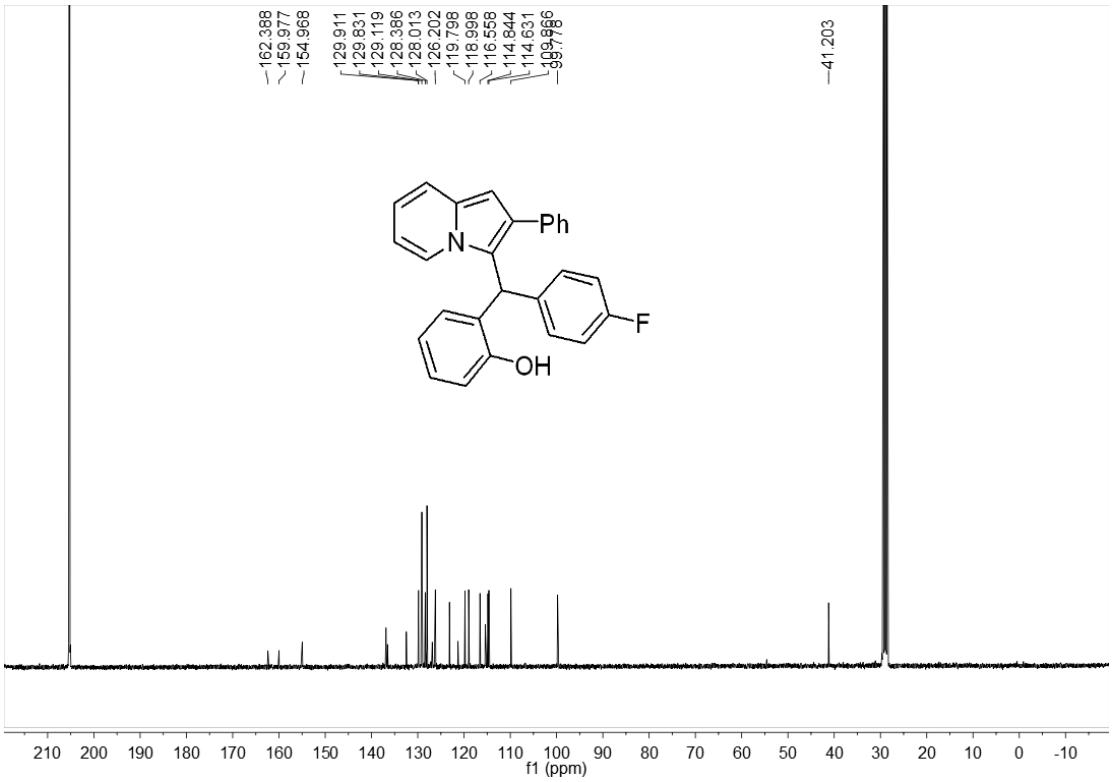
^{13}C NMR (100 MHz, $CDCl_3$) of compound **3ha**



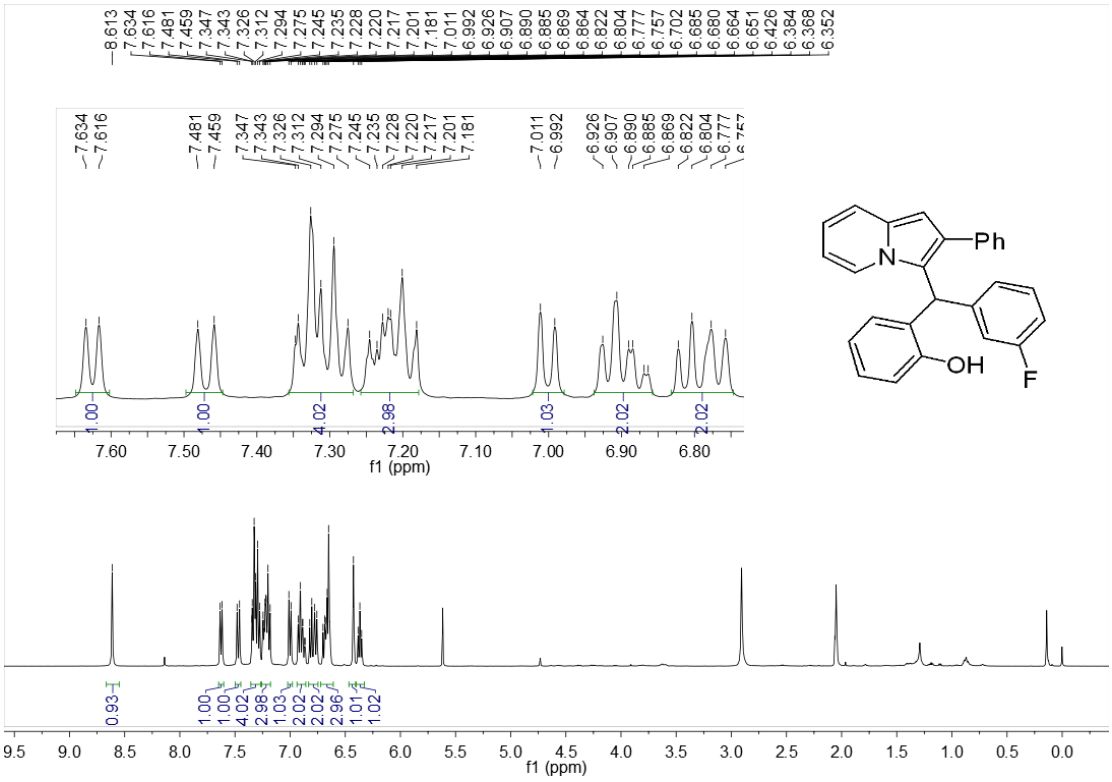
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ab**



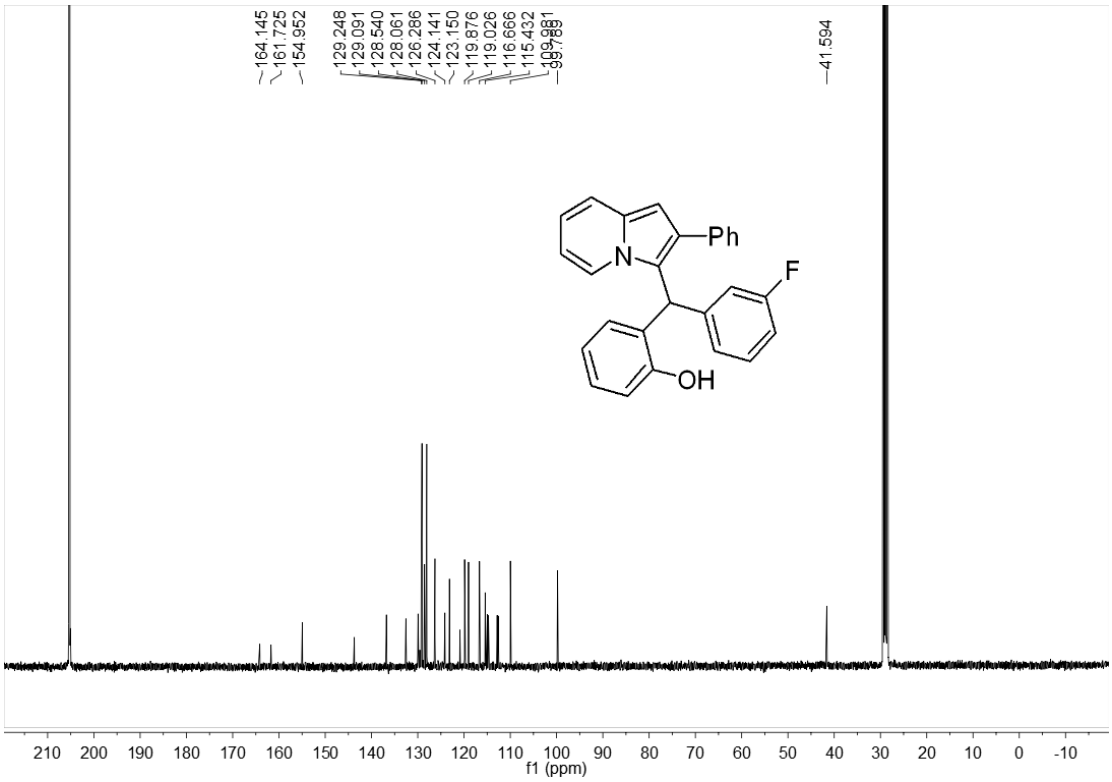
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **3ab**



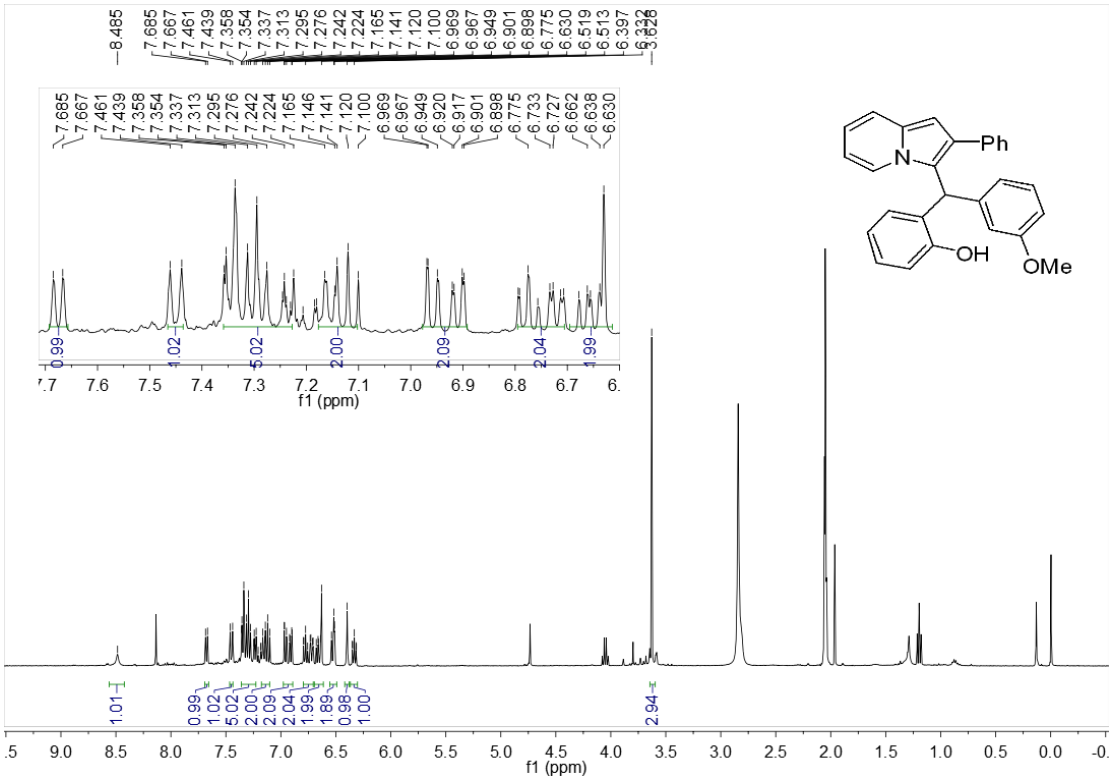
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ac**



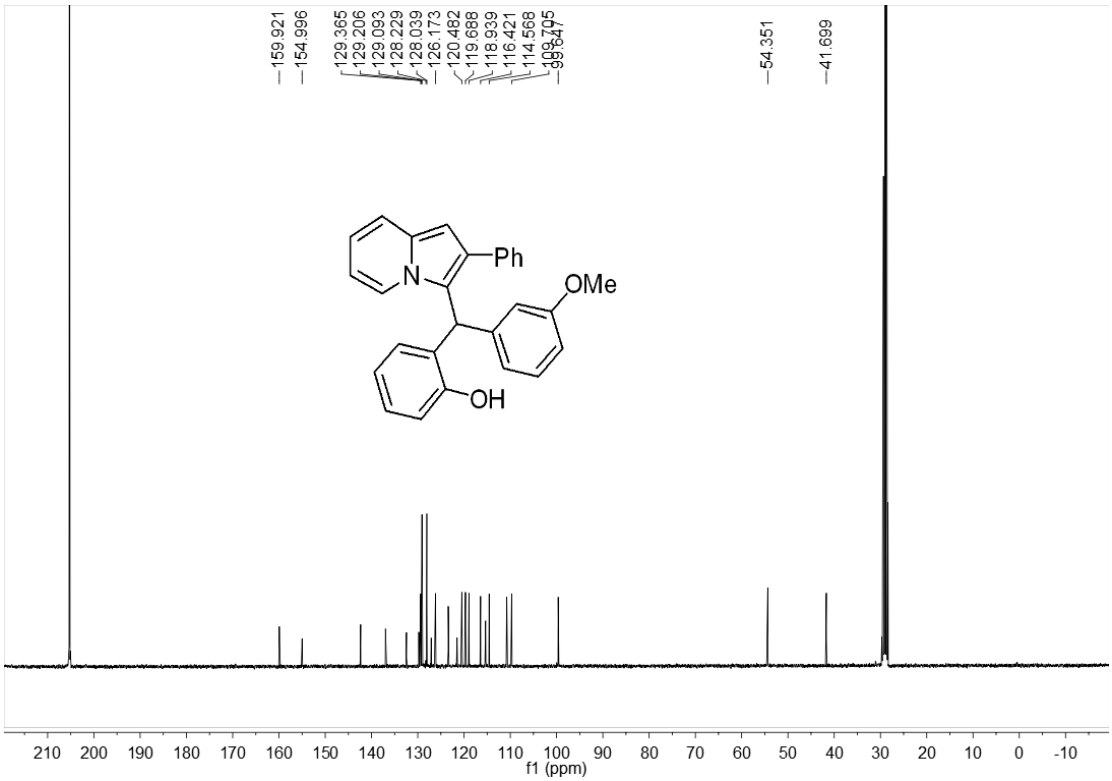
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **3ac**



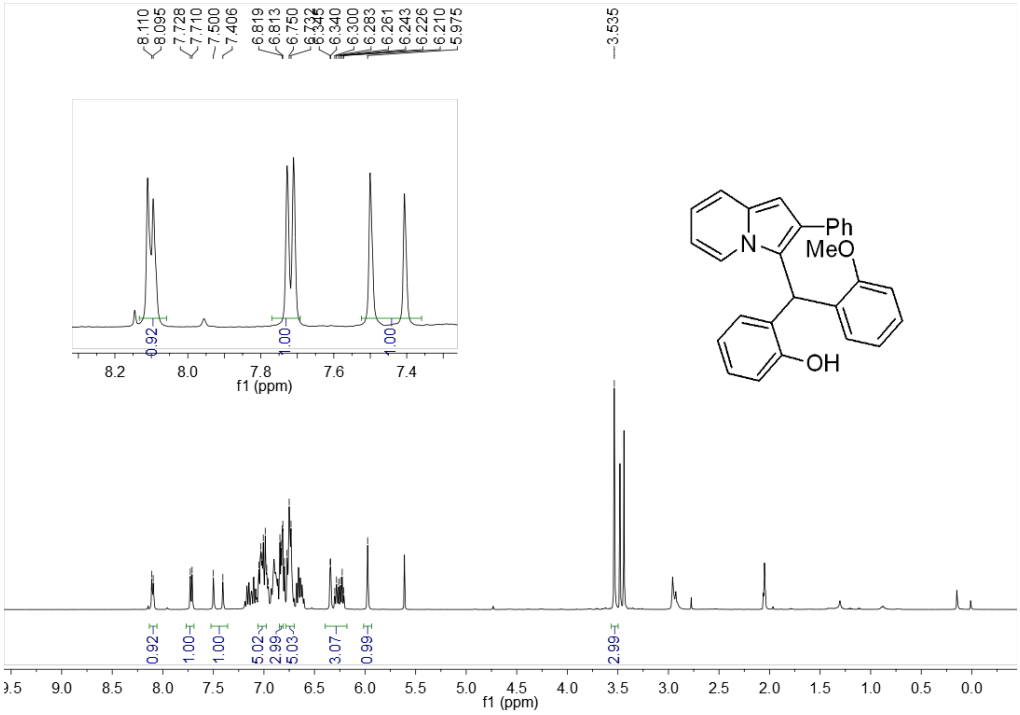
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ad**



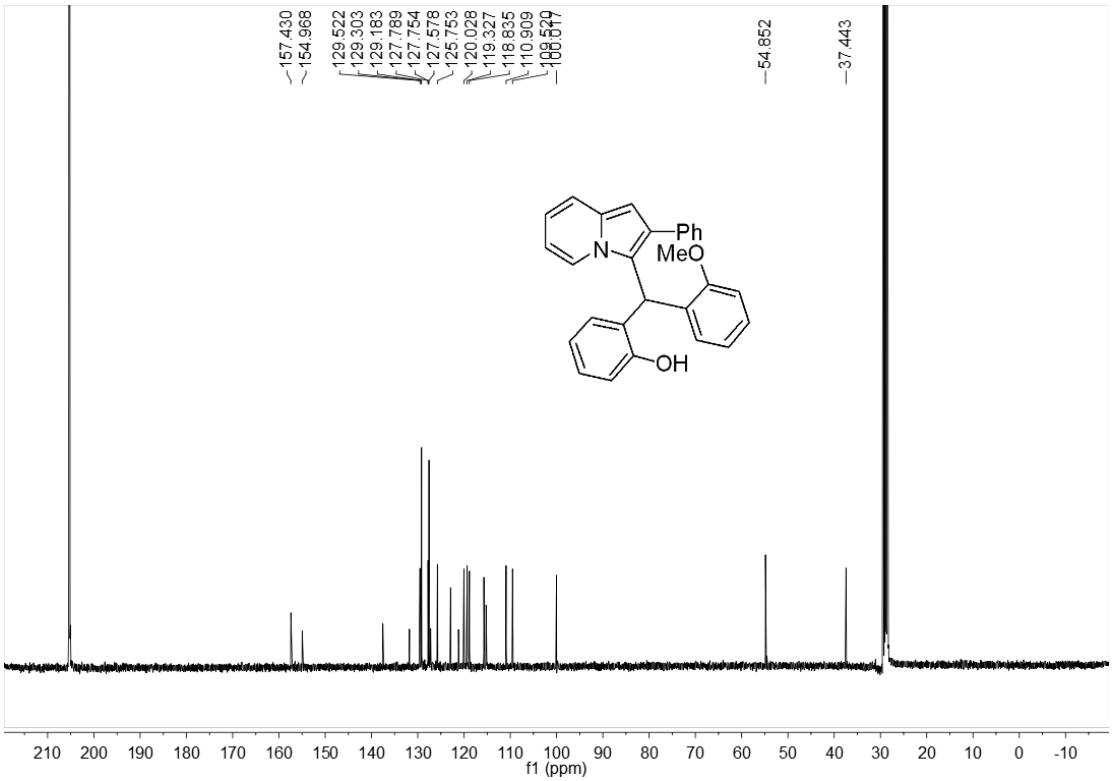
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **3ad**



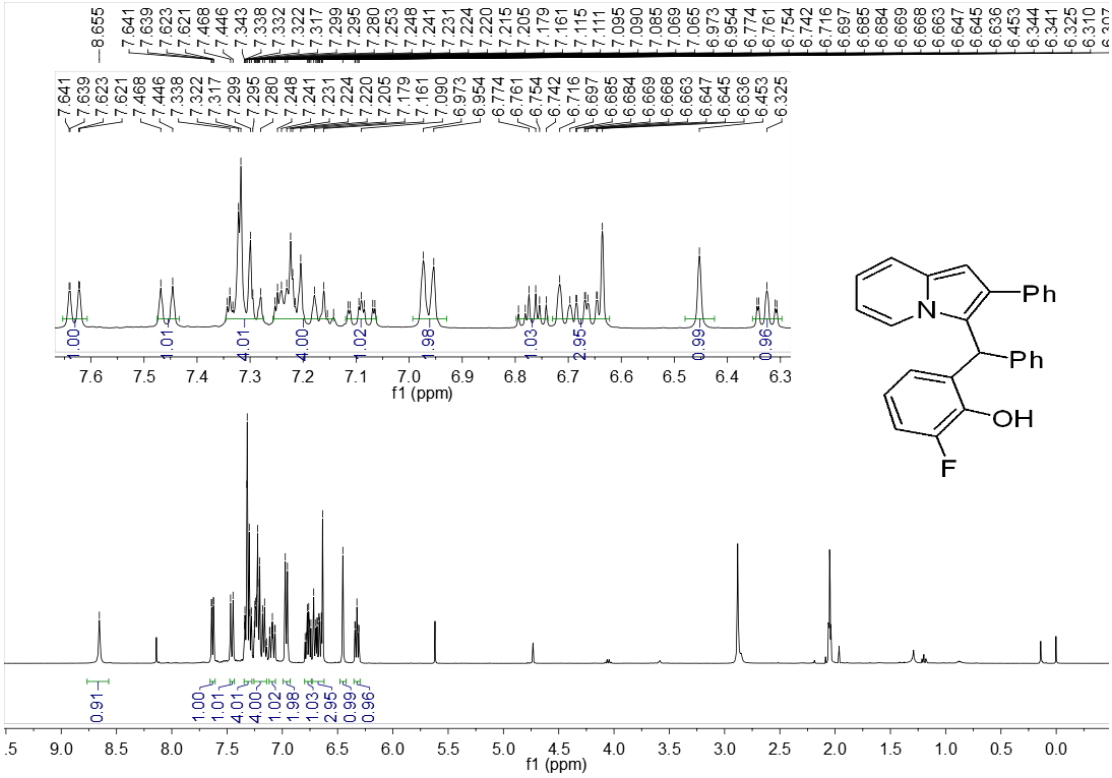
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ae**



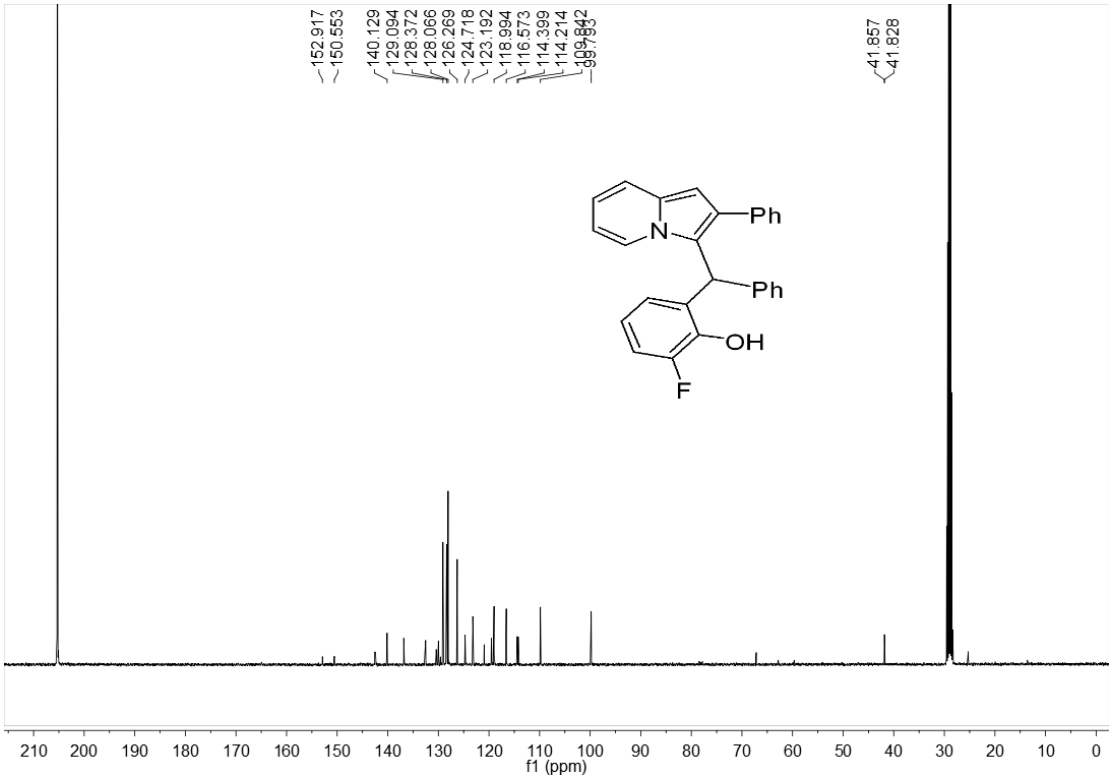
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **3ae**



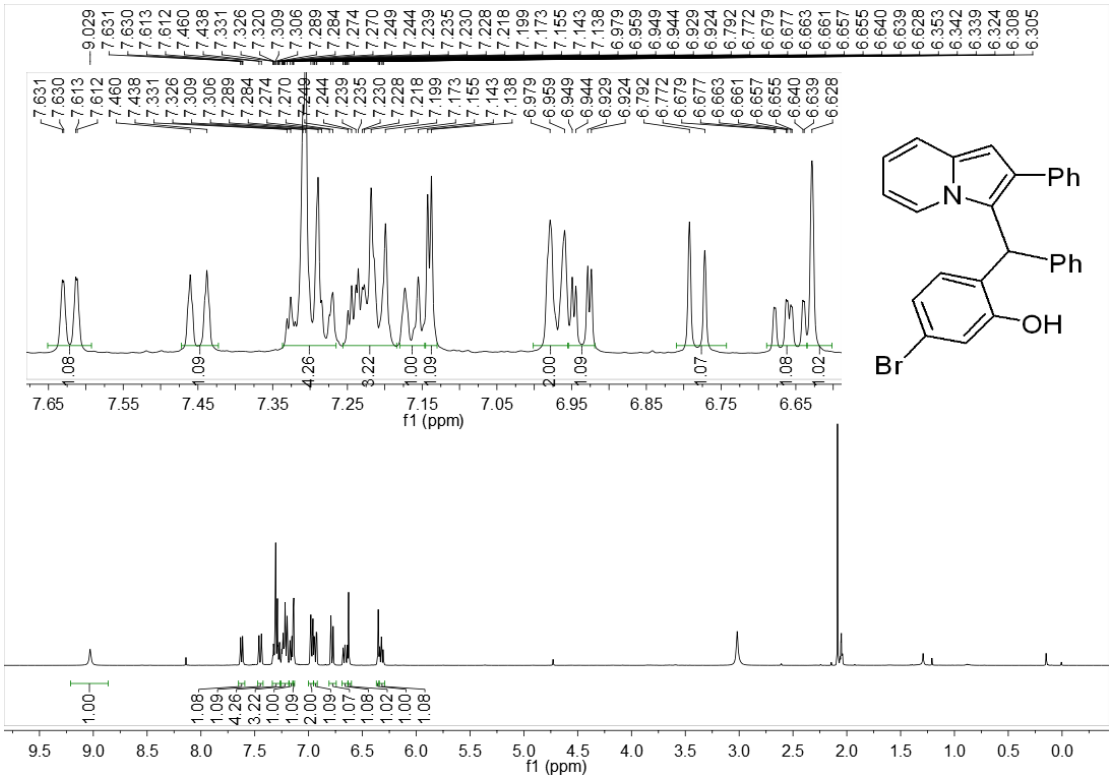
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3af**



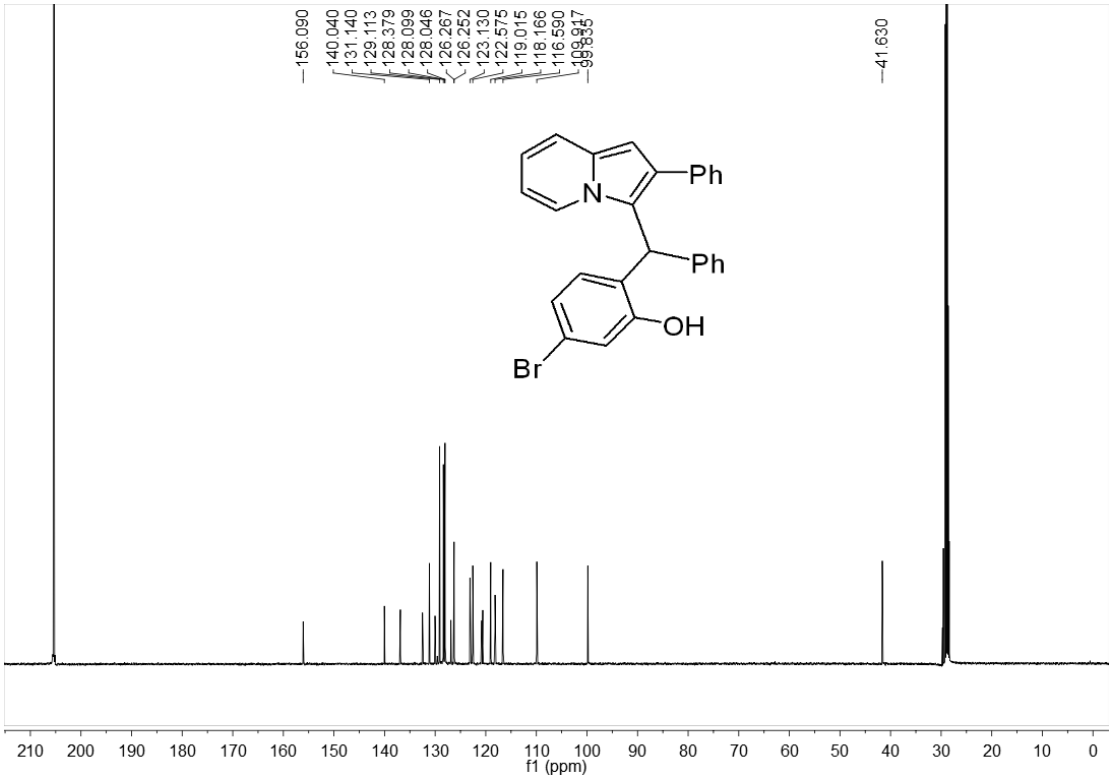
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **3af**



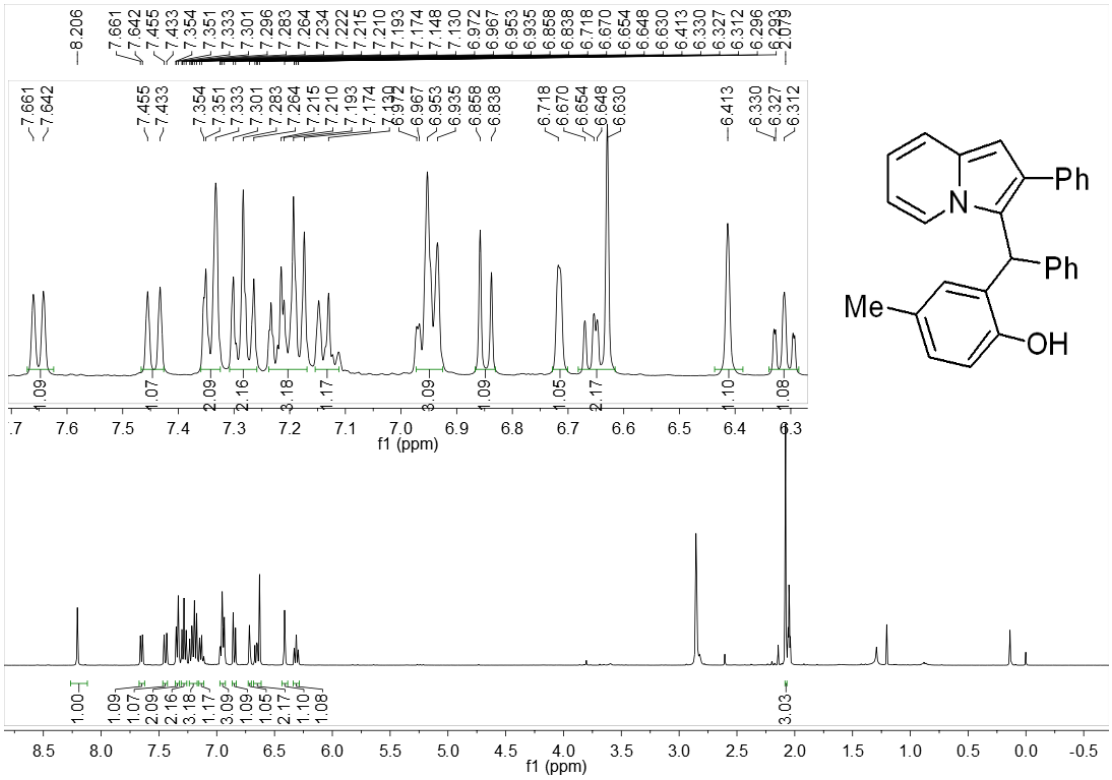
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ag**



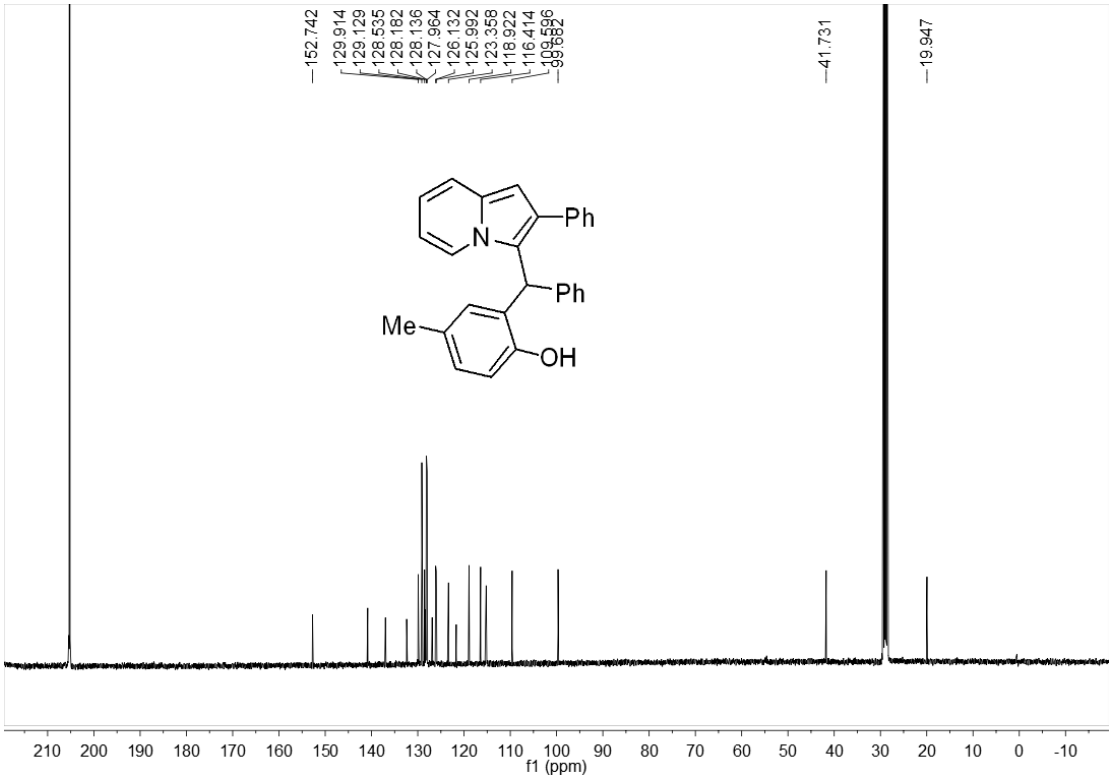
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **3ag**



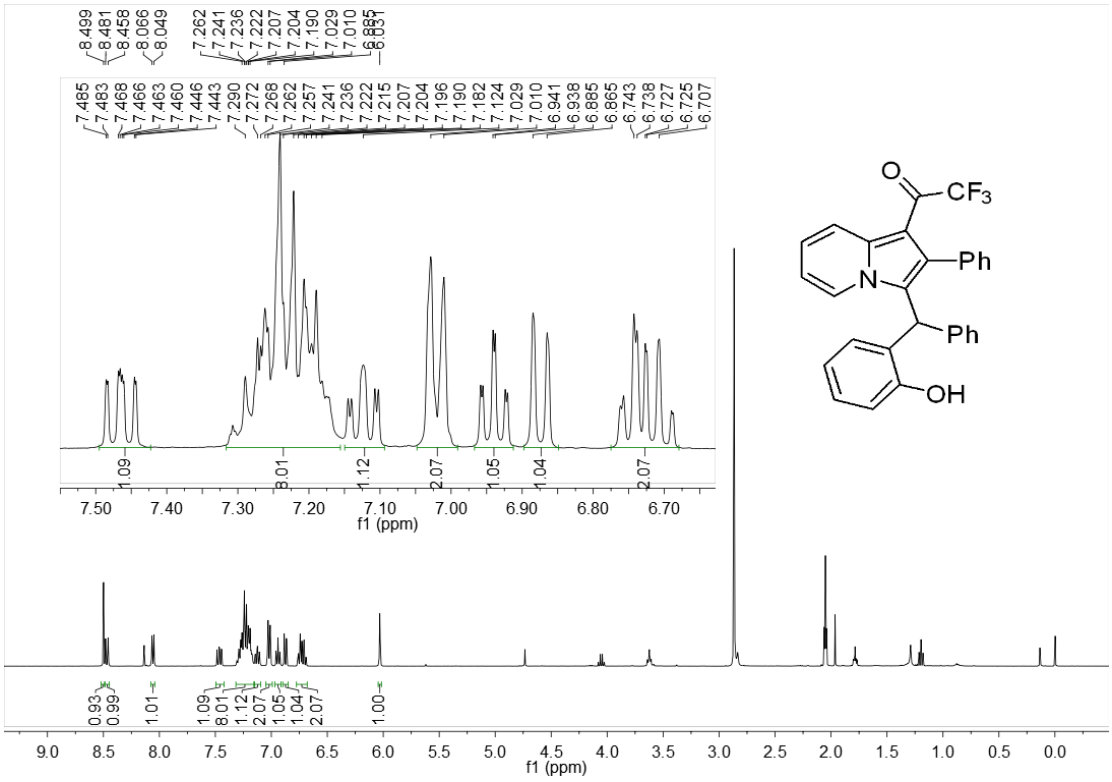
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **3ah**



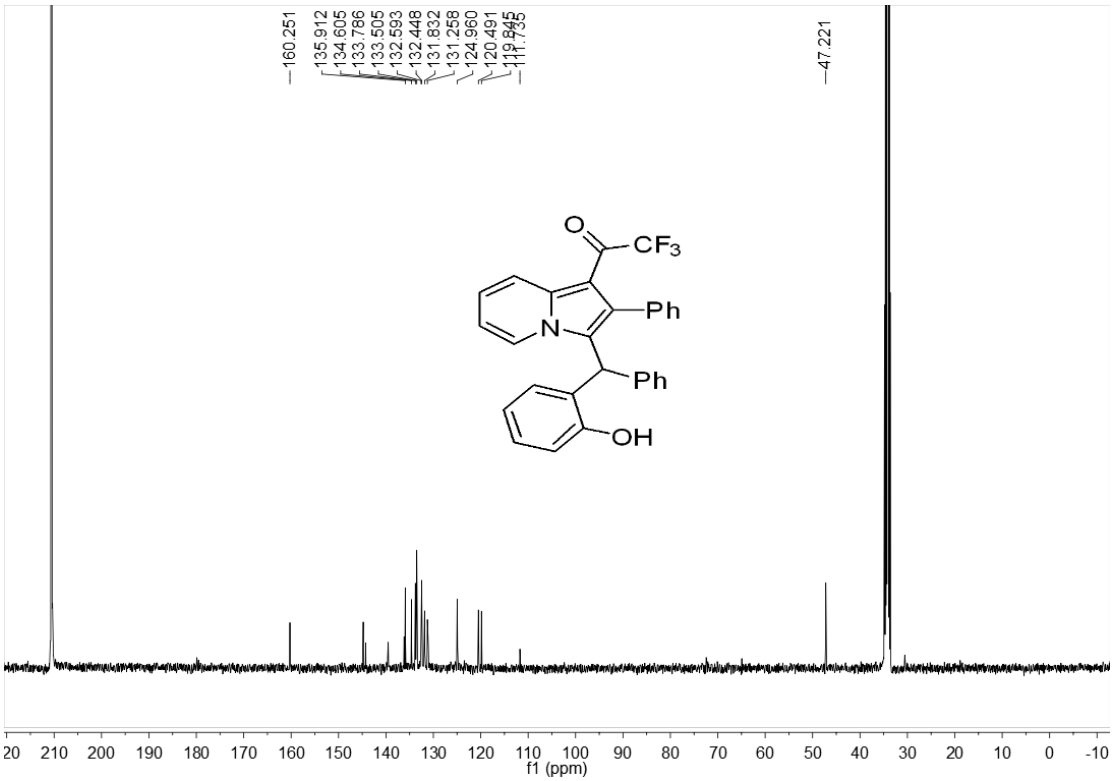
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **3ah**



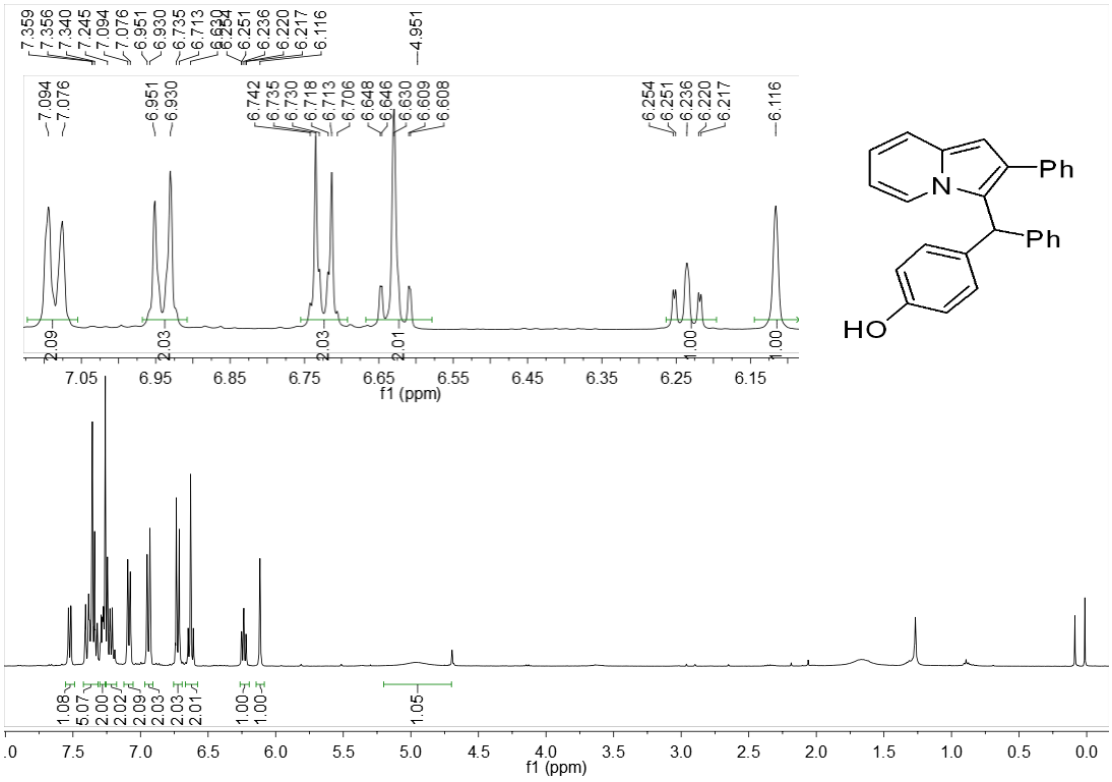
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **5**



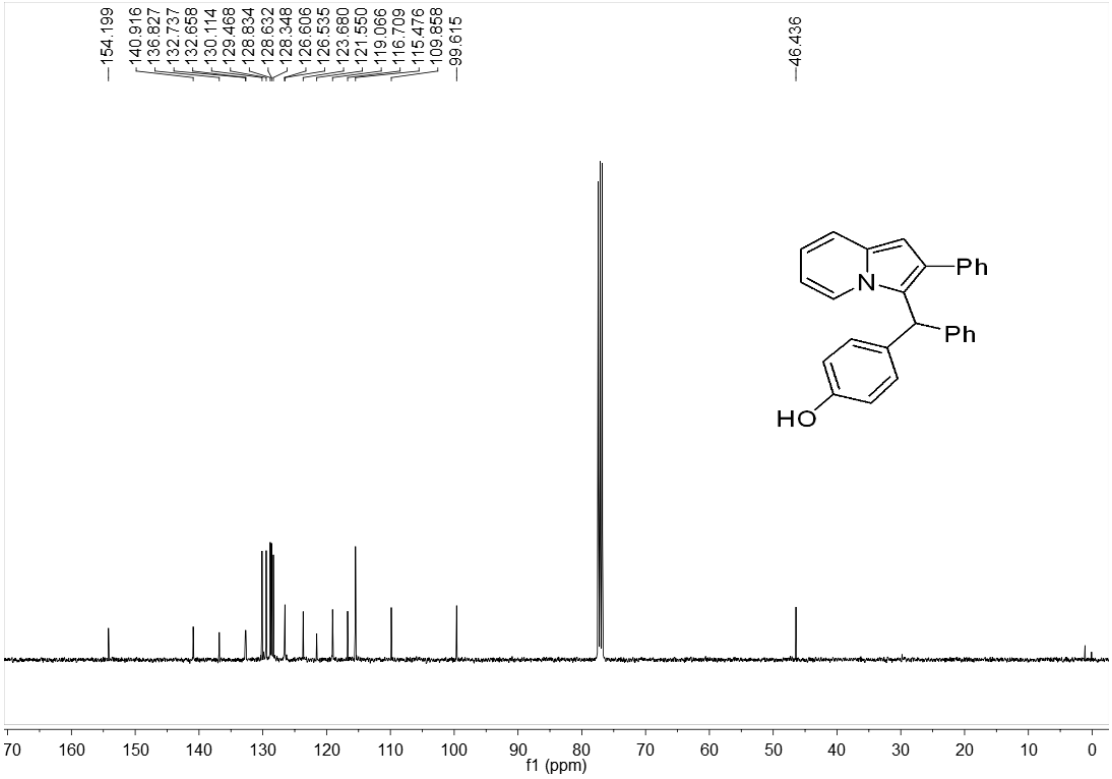
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **5**



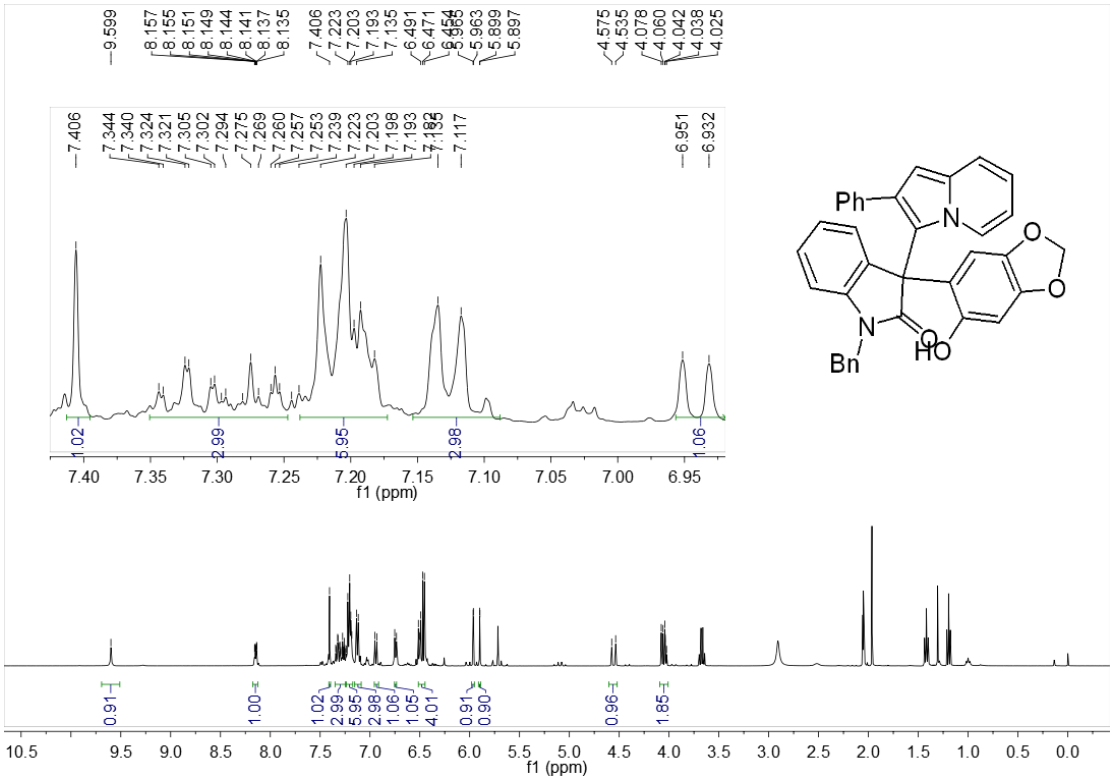
^{1}H NMR (400 MHz, $CDCl_3$) of compound **7**



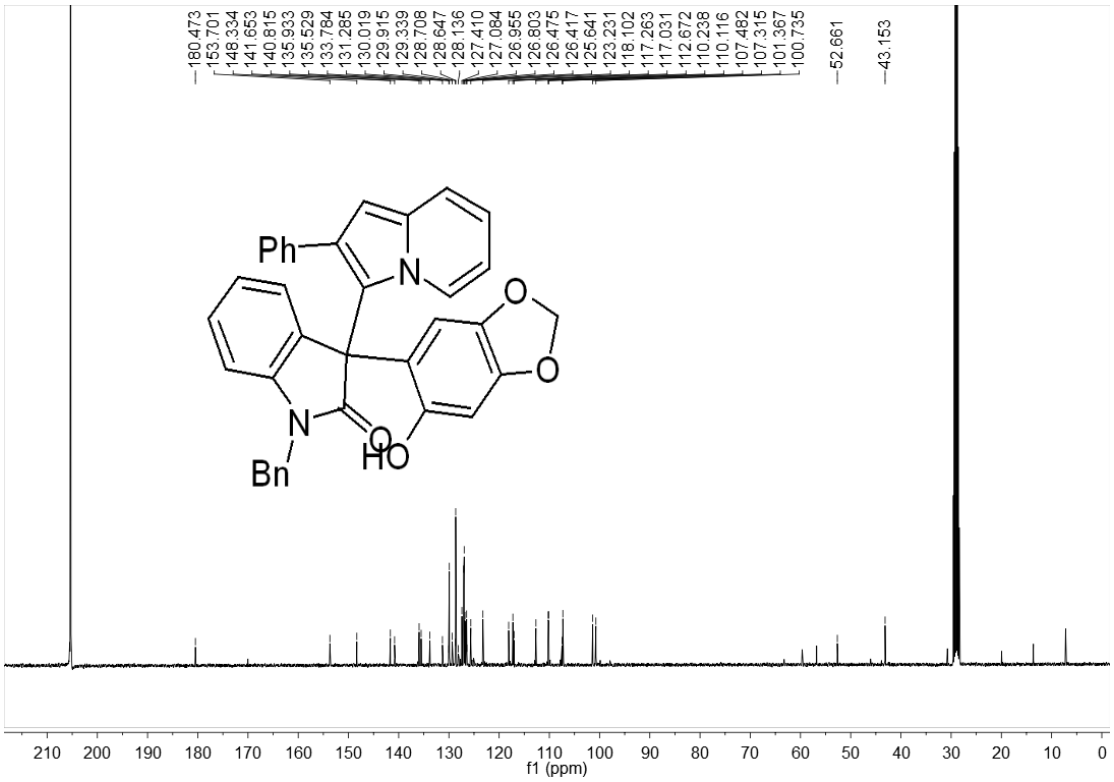
^{13}C NMR (100 MHz, $CDCl_3$) of compound **7**



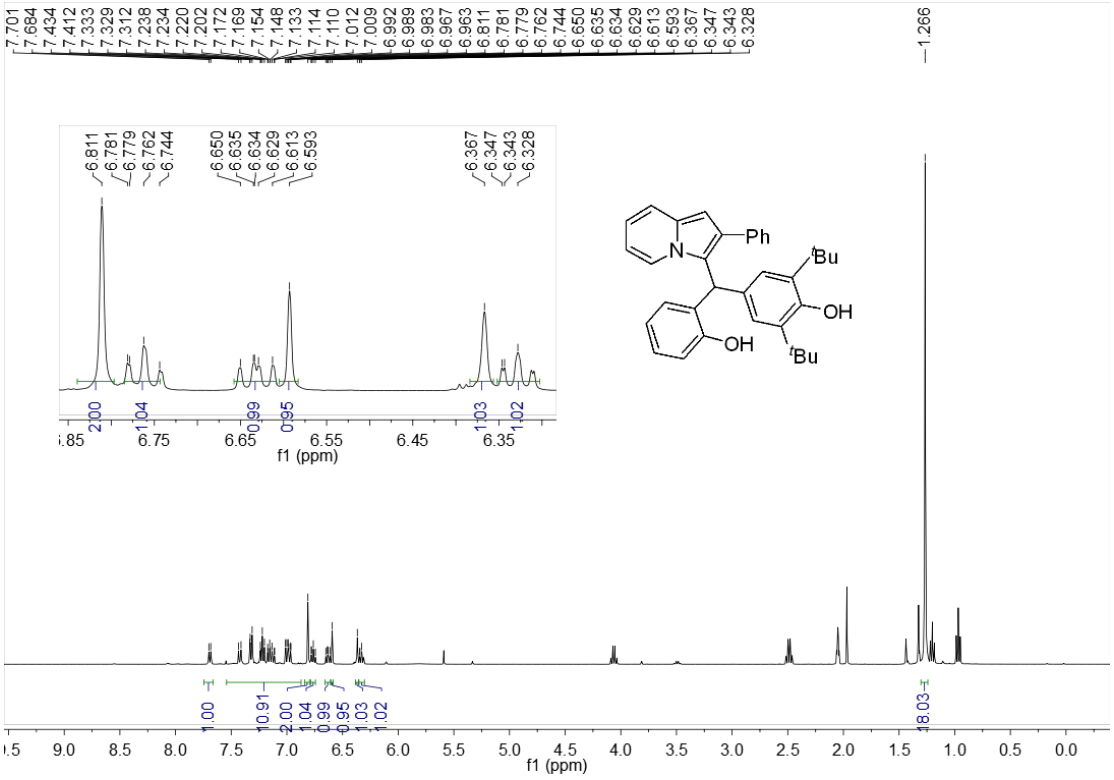
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **9**



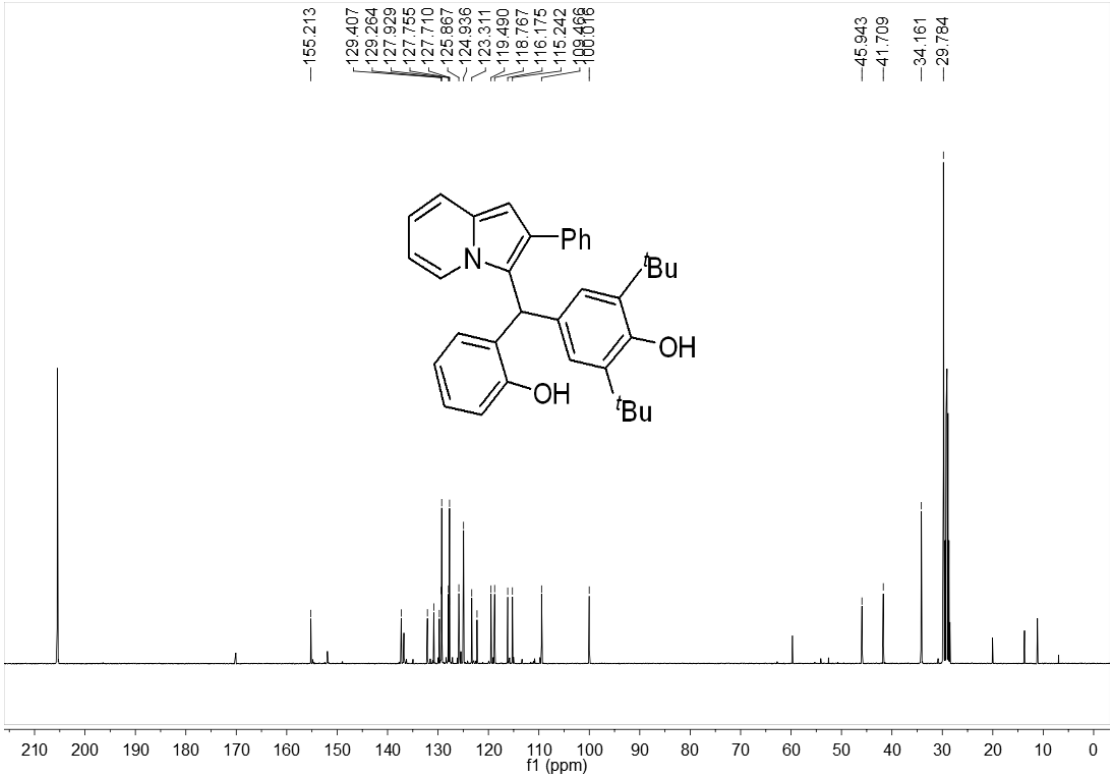
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **9**



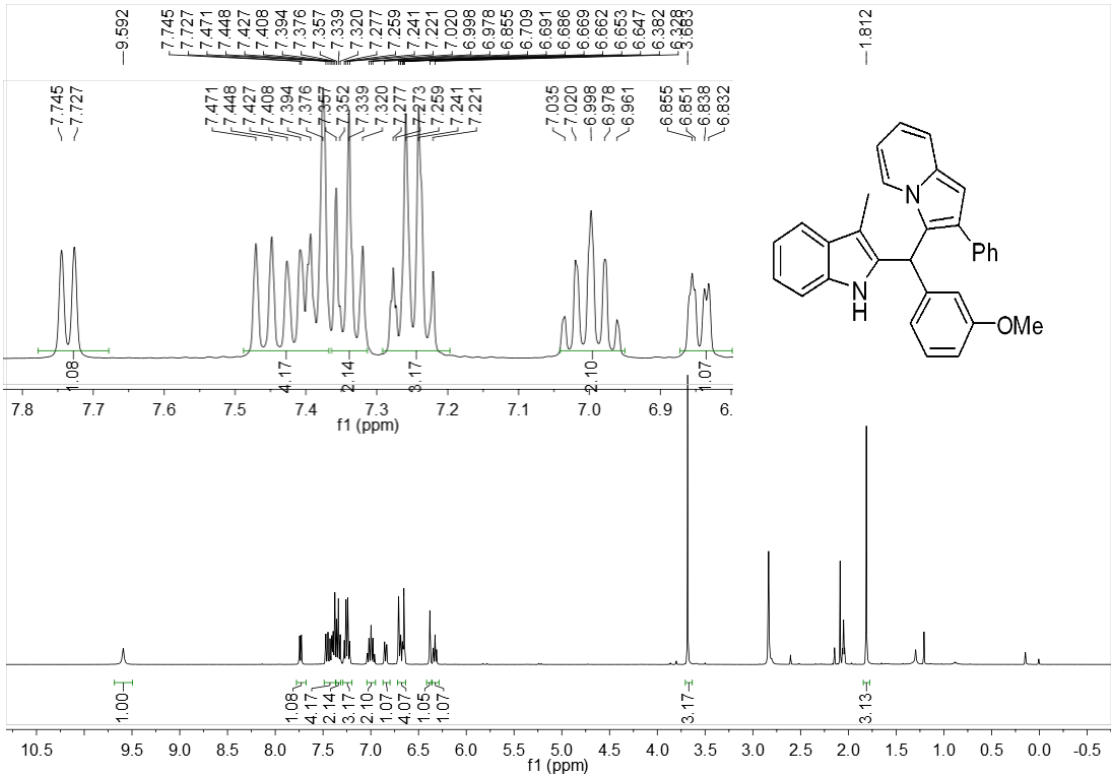
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **11**



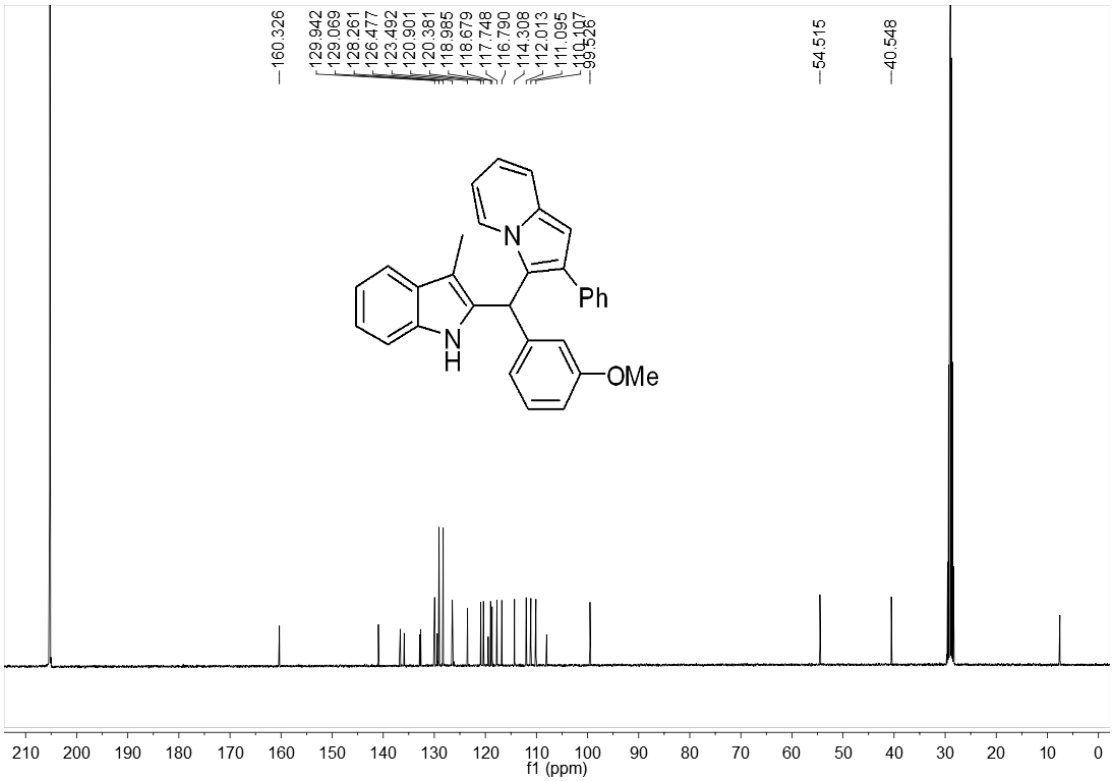
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **11**



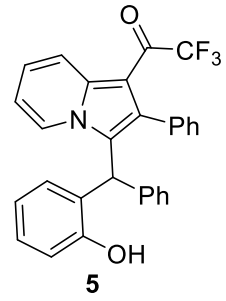
^{1}H NMR (400 MHz, *acetone-d_6*) of compound **13**



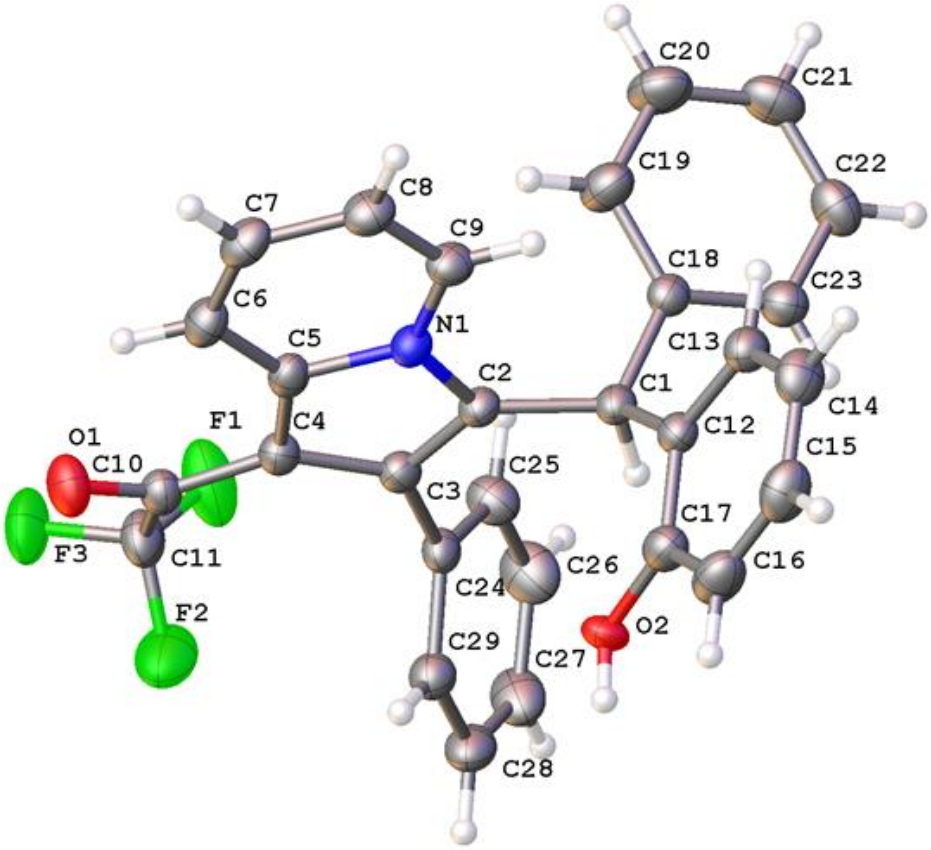
^{13}C NMR (100 MHz, *acetone-d_6*) of compound **13**



2. X-ray single crystal data for compound 5



5



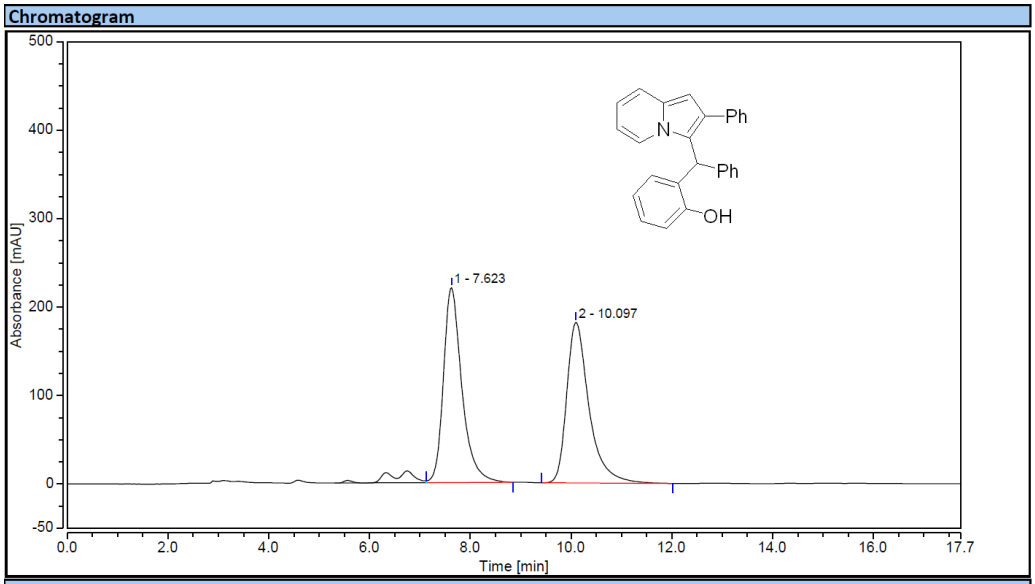
The thermal ellipsoid was drawn at the 30% probability level.

Identification code	sf20190530a_0m	
Empirical formula	C29 H20 F3 N O2	
Formula weight	471.46	
Temperature	296.15 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.333(4) Å	α= 88.838(5) °.
	b = 10.460(4) Å	β= 68.455(5) °.
	c = 11.583(5) Å	γ = 79.684(6) °.

Volume	1144.2(8) $Å^3$
Z	2
Density (calculated)	1.368 Mg/m^3
Absorption coefficient	0.102 mm^{-1}
F(000)	488
Theta range for data collection	2.672 to 25.678 °.
Index ranges	-12<=h<=9, -12<=k<=12, -14<=l<=13
Reflections collected	6041
Independent reflections	4240 [R(int) = 0.0168]
Completeness to theta = 25.242 °	98.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7455 and 0.6815
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4240 / 0 / 327
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0555, wR2 = 0.1420
R indices (all data)	R1 = 0.0887, wR2 = 0.1617
Extinction coefficient	n/a
Largest diff. peak and hole	0.193 and -0.280 $e.Å^{-3}$

3. HPLC copies of 3aa

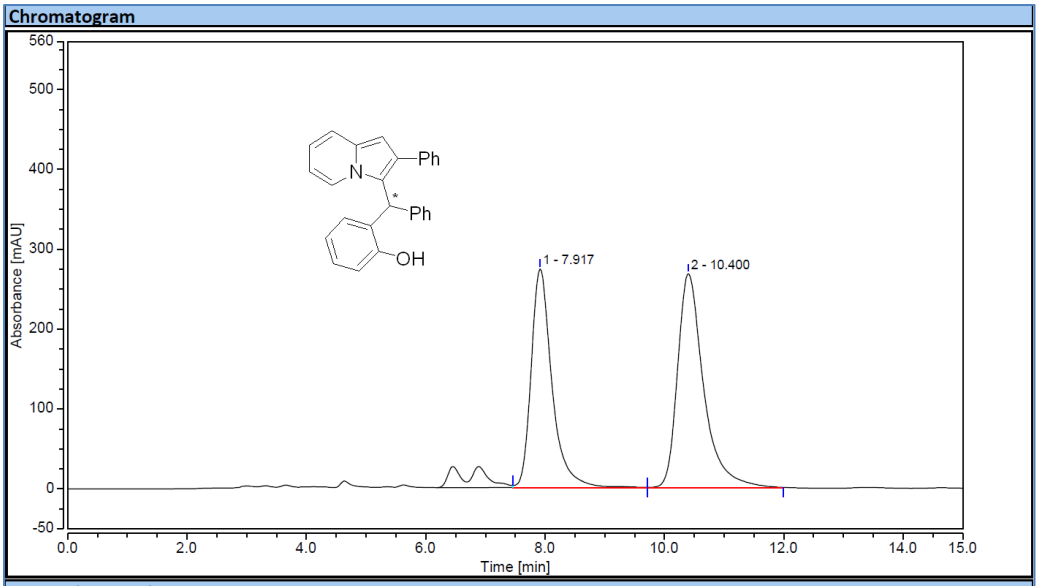
Racemic:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.623	93.571	220.612	50.11	54.83	n.a.
2		10.097	93.178	181.749	49.89	45.17	n.a.
Total:			**186.749**	**402.360**	**100.00**	**100.00**	

Enantioselective:



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.917	110.698	273.832	45.06	50.56	n.a.
2		10.400	134.993	267.776	54.94	49.44	n.a.
Total:			**245.691**	**541.608**	**100.00**	**100.00**	

The enantiomeric excess: 10%, determined by HPLC (Daicel Chiralpak IA, hexane/2-propanol = 90/ 10, flow rate 1.0 mL/min, T = 30 ^{o}C, 254 nm): t_R = 7.917 (minor), t_R = 10.400 (major).