Supplementary Information

Iron-Mediated Annulation between Methylene Ketones and Diethanolamines: A Sustainable and Scalable Procedure toward *N*-(2-Hydroxyethyl) Pyrroles

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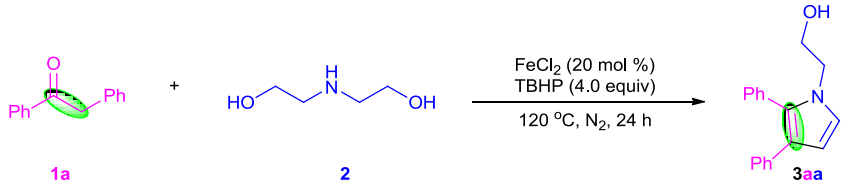
1. Research of Mechanism

1.1 Free Radical Capture Experiments

General Procedure:



Scheme S1 Standard procedure

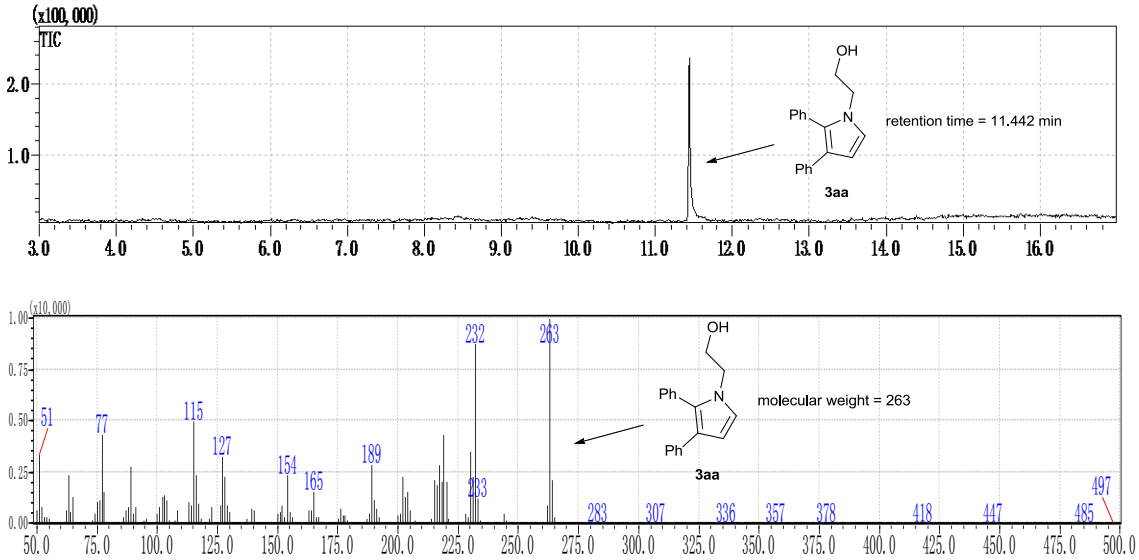
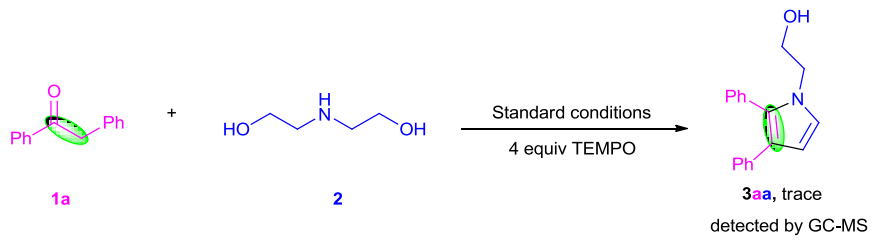


Fig S1 Detection of 3aa by GC-MS

Add 4.0 equiv of radical-trapping reagent TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxyl) to the reaction mixture

Under N_2, a 20 mL of Schlenk tube equipped with a stir bar was charged with 2-phenylacetophenone (0.2 mmol), *tert*-butyl hydroperoxide (0.8 mmol, 4.0 equiv, 70% aqueous), $FeCl_2$ (5.1 mg, 20 mol%), TEMPO (0.8 mmol, 4 equiv, 2,2,6,6-tetramethyl-1-piperidinyloxyl)，diethanolamine (1.0 mL). The tube was sealed with a Teflon lined cap. The reaction mixture was stirred at 120 °C for 24 h in oil bath. The reaction was shut down totally, and the reaction mixture was analyzed using GC-MS spectrometer, as shown in Figure S2.



Scheme S2 Free radical inhibition experiment

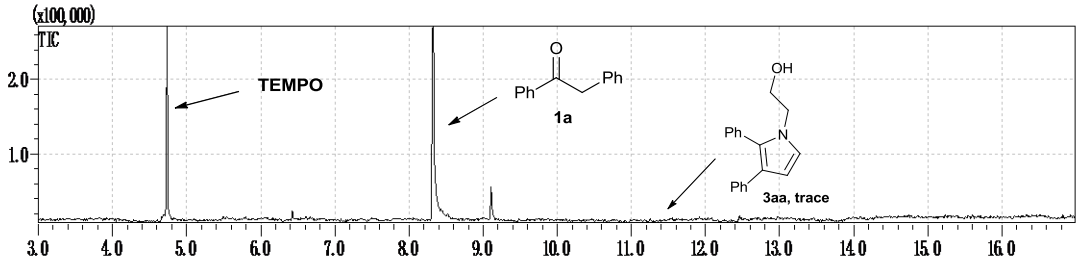


Fig S2 Free radical inhibition experiment

Detecting 2-((2-hydroxyethyl)amino)acetaldehyde by GC-MS

Table S1 Detecting the presumed imtermediate 2-((2-hydroxyethyl)amino)acetaldehyde

Reaction time	Detection result	Reaction time	Detection result
10 min	×	4 h	×
30 min	×	8 h	×
1 h	×	12 h	×
1.5 h	×	16 h	×
2 h	×	20 h	×
3 h	×	24 h	×

"×" means negative result for detecting of 2-((2-hydroxyethyl)amino) acetaldehyde in methanol solvent, whose molecular weight was 103， and 149 for the acetal with methanol.

2. X-ray structure of product 3na

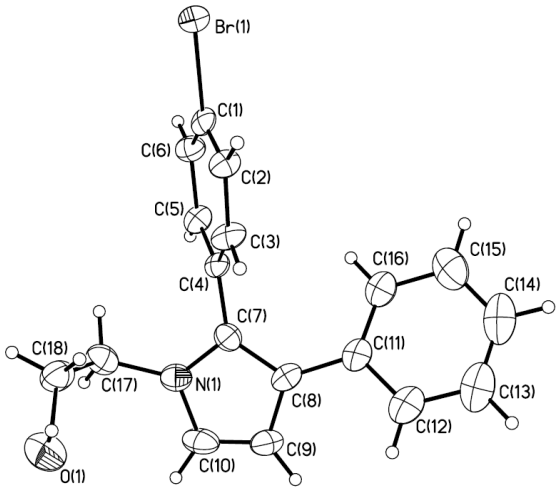


Figure S3. ORTEP diagram of compound 3na showing an atom numbering scheme. Thermal ellipsoids are drawn at the 30% probability level.

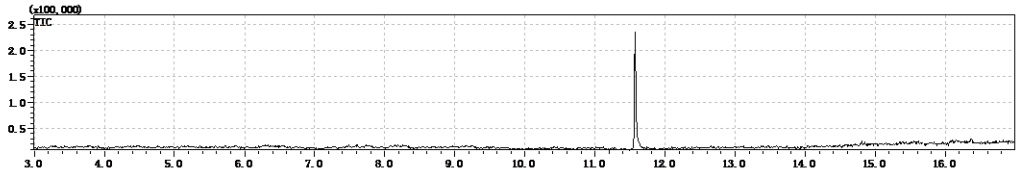
Table S2 Crystallographic data for compound 3na

Compound	**3na**
Formula	$C_{18}H_{16}BrNO$
fw	341.04
T/K	293(2)
Crystal system	Triclinic
Crystal size/mm	0.220 × 0.210 × 0.180
Space group	$P\bar{1}$
a/Å	9.022(4)
b/Å	11.781(6)
c/Å	15.387(8)
α (°)	98.559(13)
β (°)	101.929(13)
γ (°)	90.335(12)
V/Å^3	1581.1(13)
Z	2

D_{calcd}/g cm^{-3}	1.438
μ/mm^{-1}	2.598
F(000)	696
θ_{max}/°	22.023
Collected	5851
Unique reflns	3018
Obsd reflns[$I > 2.0\sigma(I)$]	7140
No. of variables	543
GOF	0.948
R	0.0636
wR	0.1396
R_{int}	0.0637
Largest diff. peak, hole/e Å^{-3}	1.170, -0.813

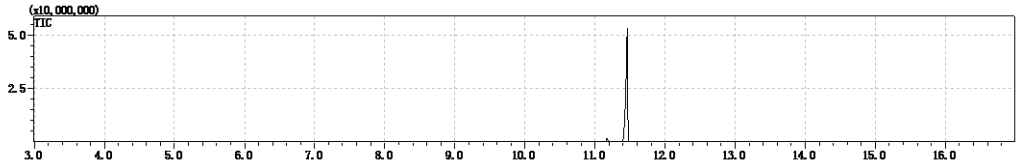
3. GC Analysis of *N*-(2-hydroxyethyl) Pyrrole Analogues

2-(2,3-diphenyl-1*H*-pyrrol-1-yl)ethanol (3aa):



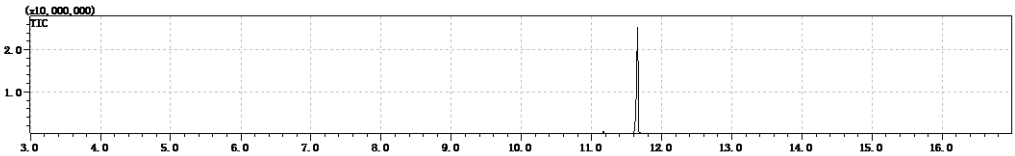
retention time of 3aa is 11.575 min

2-(3-phenyl-2-(*m*-tolyl)-1*H*-pyrrol-1-yl)ethanol (3ba):



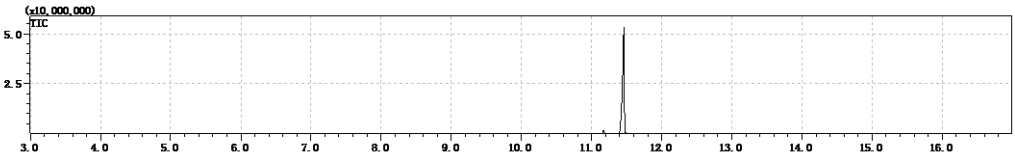
retention time of 3ba is 11.450 min

2-(2-(3,5-dimethylphenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3ca):



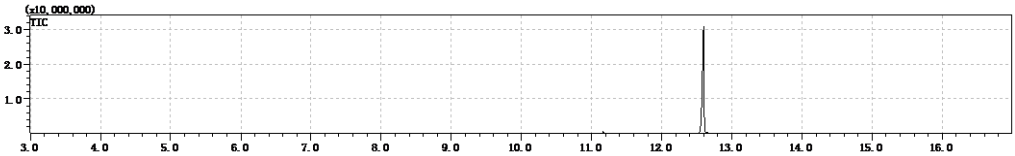
retention time of 3ca is 11.658 min

2-(3-phenyl-2-(*p*-tolyl)-1*H*-pyrrol-1-yl)ethanol (3da):



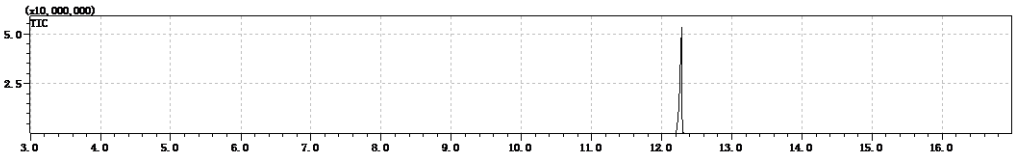
retention time of 3da is 11.455 min

2-(2-(4-(*tert*-butyl)phenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3ea):



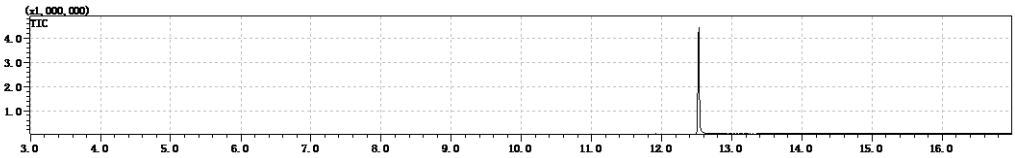
retention time of 3ea is 12.600 min

2-(2-(3-methoxyphenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3fa):



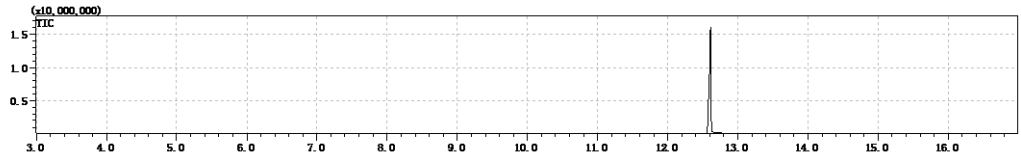
retention time of 3fa is 12.283 min

2-(2-(4-methoxyphenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3ga):



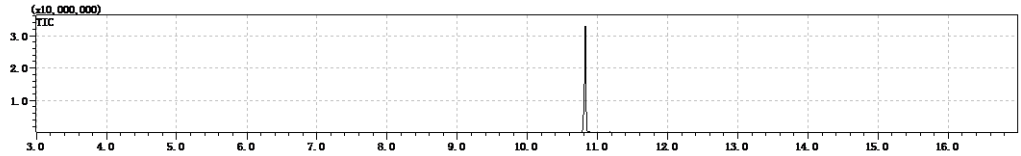
retention time of 3ga is 12.525 min

2-(3-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-1-yl)ethanol (3ha):



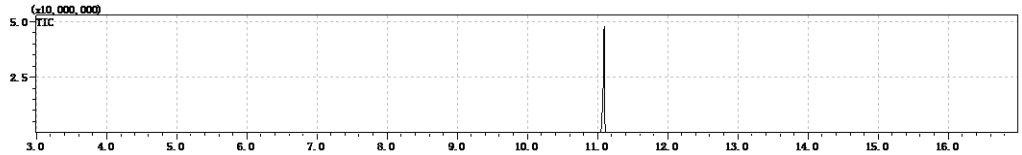
retention time of 3ha is 12.608 min

2-(3-phenyl-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-1-yl)ethanol (3ia)：



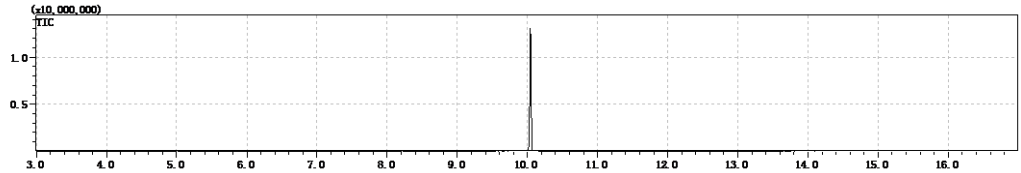
retention time of 3ia is 10.825 min

2-(2-phenyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-1-yl)ethanol (3ja):



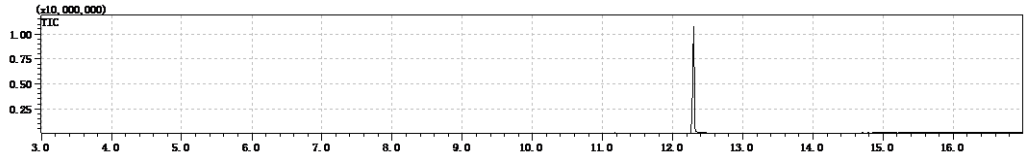
retention time of 3ja is 11.092 min

2-(3-(4-fluorophenyl)-2-phenyl-1*H*-pyrrol-1-yl)ethanol (3ka):



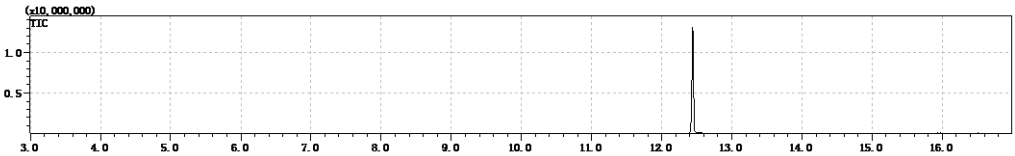
retention time of 3ka is 10.042 min

2-(2-(4-chlorophenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3la):



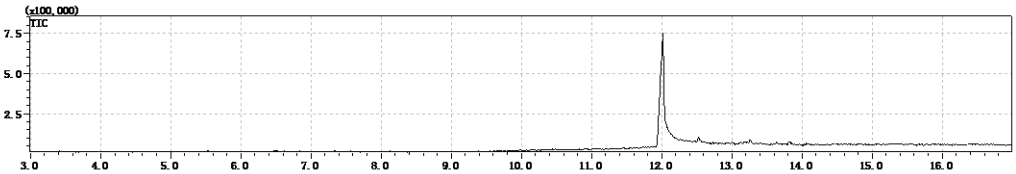
retention time of 3la is 12.300 min

2-(3-(4-chlorophenyl)-2-phenyl-1*H*-pyrrol-1-yl)ethanol (3ma):



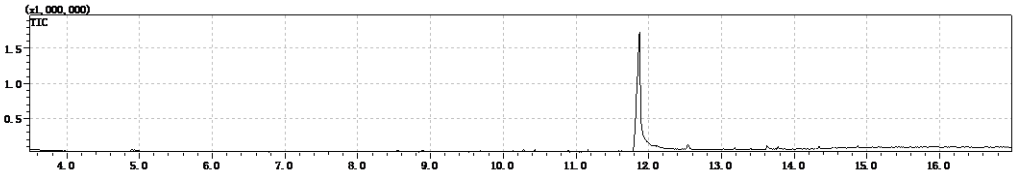
retention time of 3ma is 12.442 min

2-(2-(4-bromophenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3na):



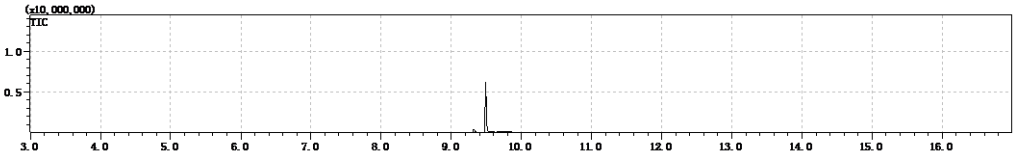
retention time of 3na is 12.008 min

2-(3-(4-bromophenyl)-2-phenyl-1*H*-pyrrol-1-yl)ethanol (3oa):



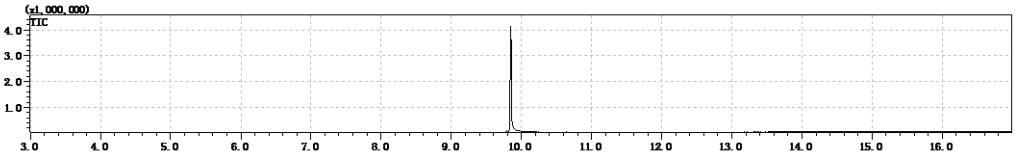
retention time of 3oa is 11.875 min

2-(indeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4aa):



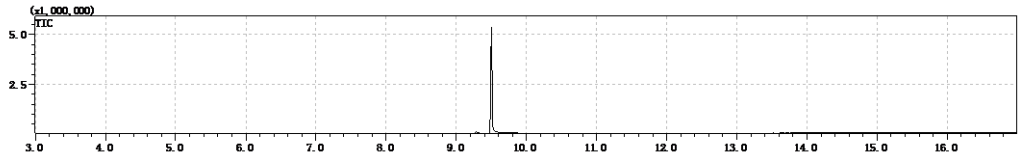
retention time of 4aa is 9.490 min

2-(indeno[2,1-*b*]pyrrol-1(8*H*)-yl)ethanol (4ba):



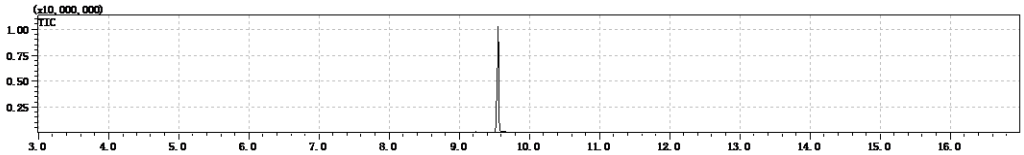
retention time of 4ba is 9.850 min

2-(6-fluoroindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4ca):



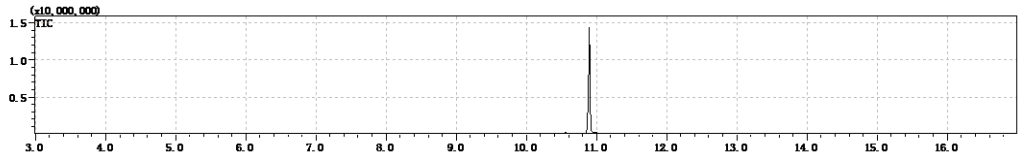
retention time of 4ca is 9.500 min

2-(7-fluoroindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4da):



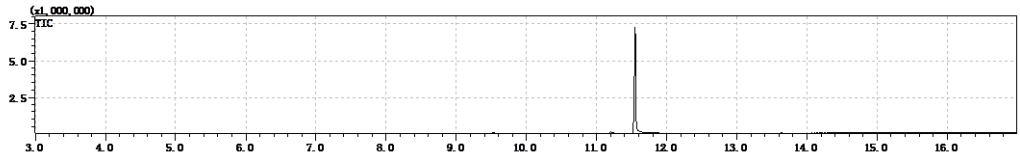
retention time of 4da is 9.558 min

2-(6-chloroindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4ea):



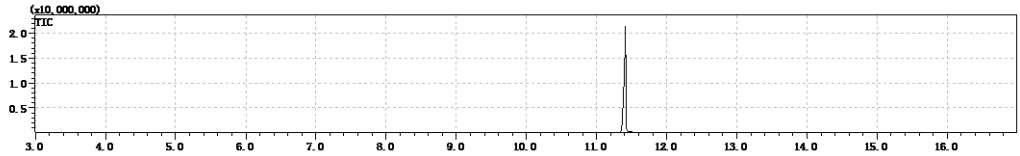
retention time of 4ea is 10.900 min

2-(6-bromoindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4fa):



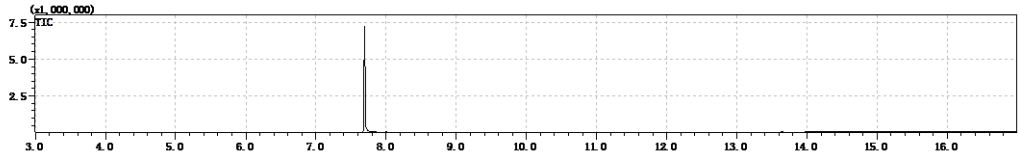
retention time of 4fa is 11.550 min

2-(7-bromoindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4ga):



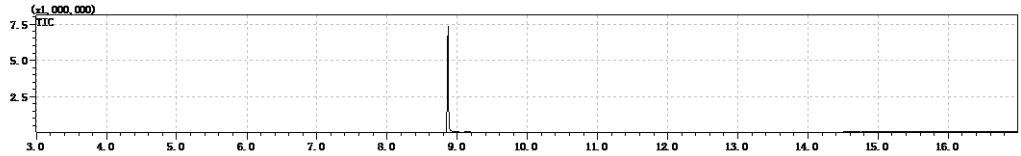
retention time of 4ga is 11.408 min

2-(2-phenyl-1*H*-pyrrol-1-yl)ethanol (5aa):



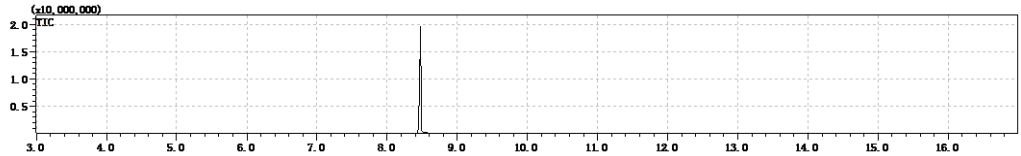
retention time of 5aa is 7.691 min

2-(2-(4-chlorophenyl)-1*H*-pyrrol-1-yl)ethanol (5ba):



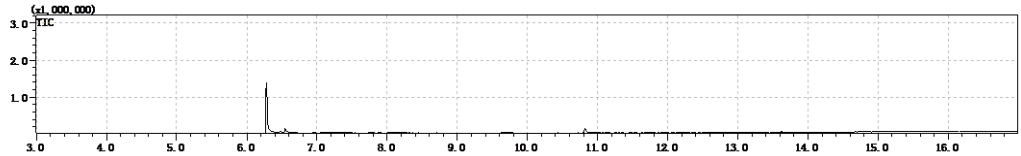
retention time of 5ba is 8.865 min

2-(3-benzyl-1*H*-pyrrol-1-yl)ethanol (5ca):



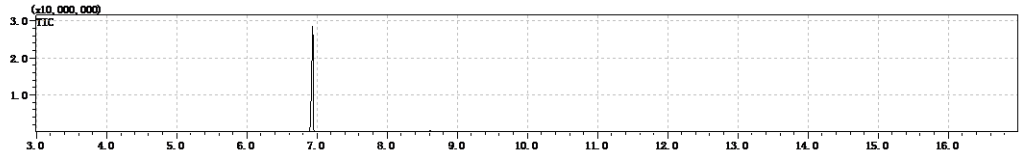
retention time of 5ca is 8.475 min

2-(5,6-dihydrocyclopenta[*b*]pyrrol-1(4*H*)-yl)ethanol (5da):



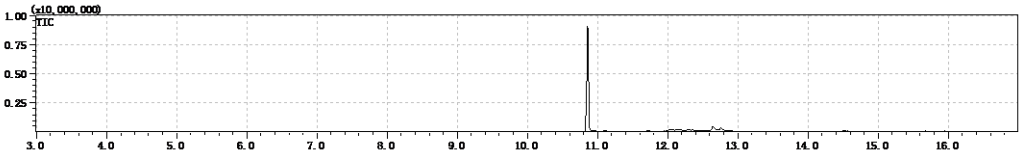
retention time of 5da is 5.283 min

2-(4,5,6,7-tetrahydro-1*H*-indol-1-yl)ethanol (5ea):



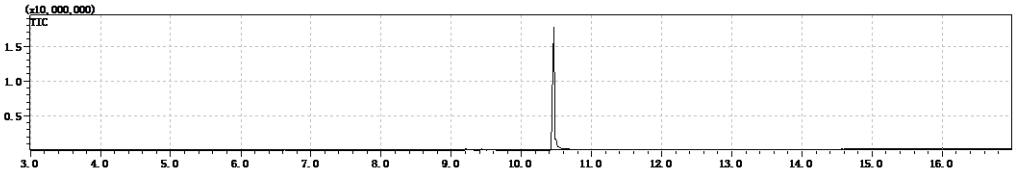
retention time of 5ea is 6.933 min

2-(5-phenyl-4,5,6,7-tetrahydro-1*H*-indol-1-yl)ethanol (5fa):



retention time of 5fa is 10.858 min

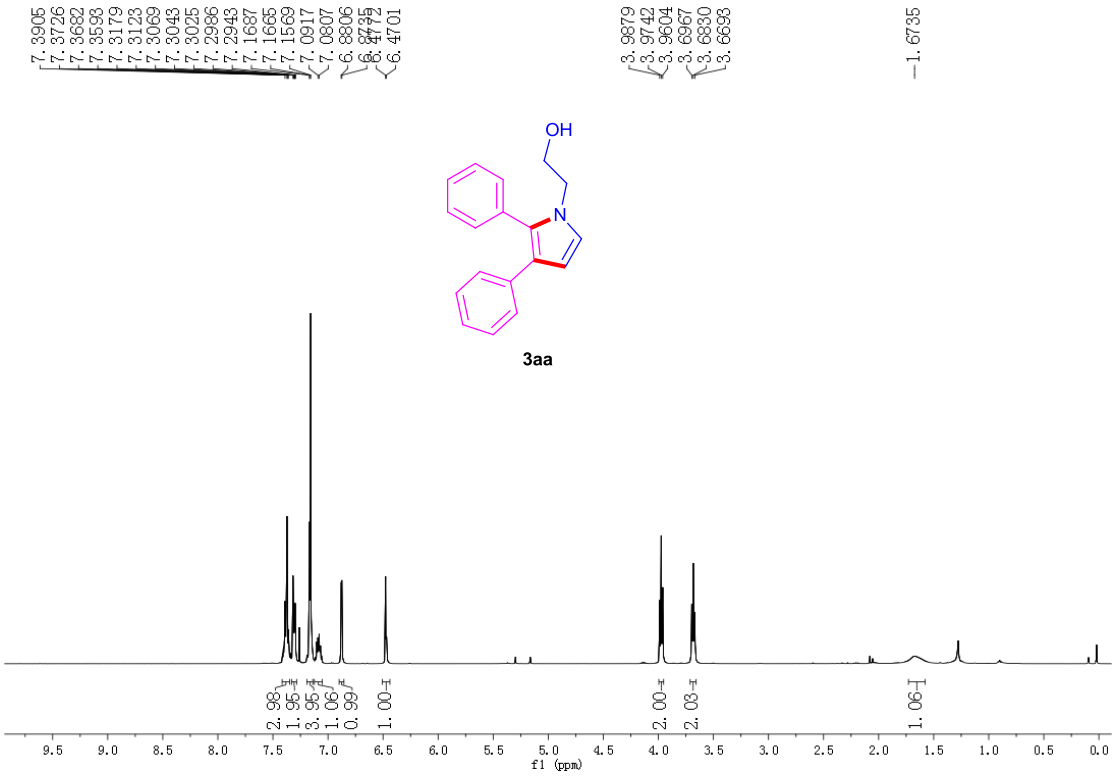
ethyl 1-(2-hydroxyethyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5ga):

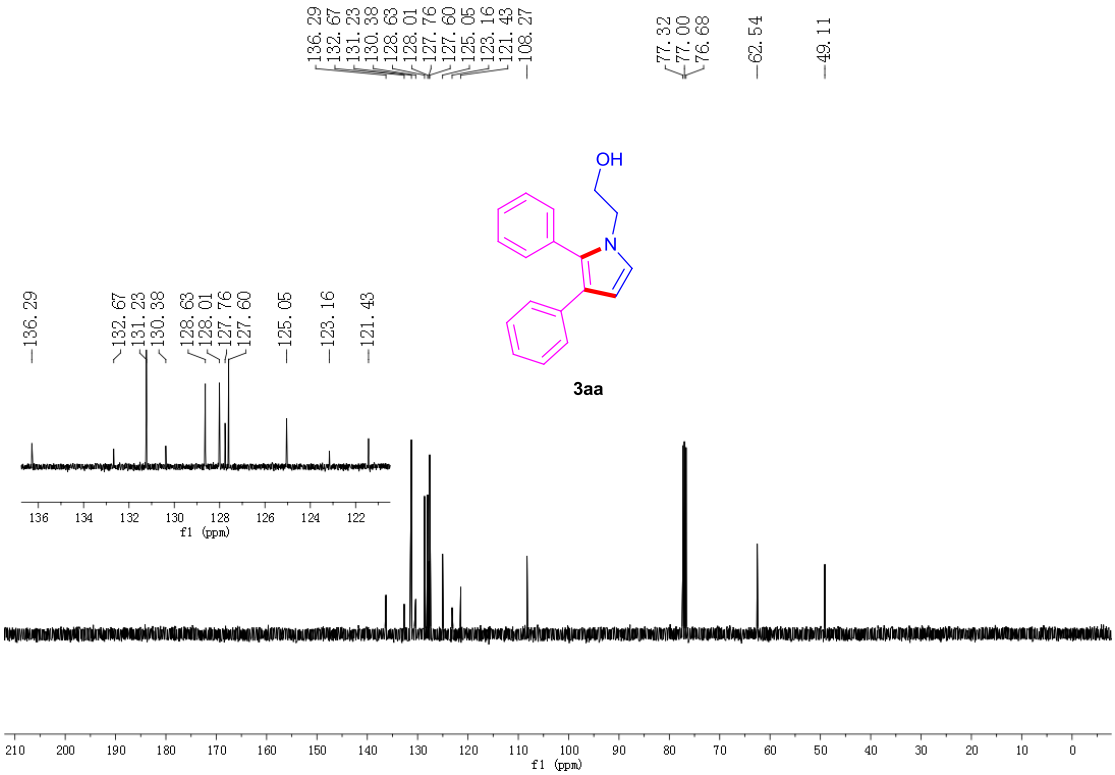


retention time of 5ga is 10.458 min

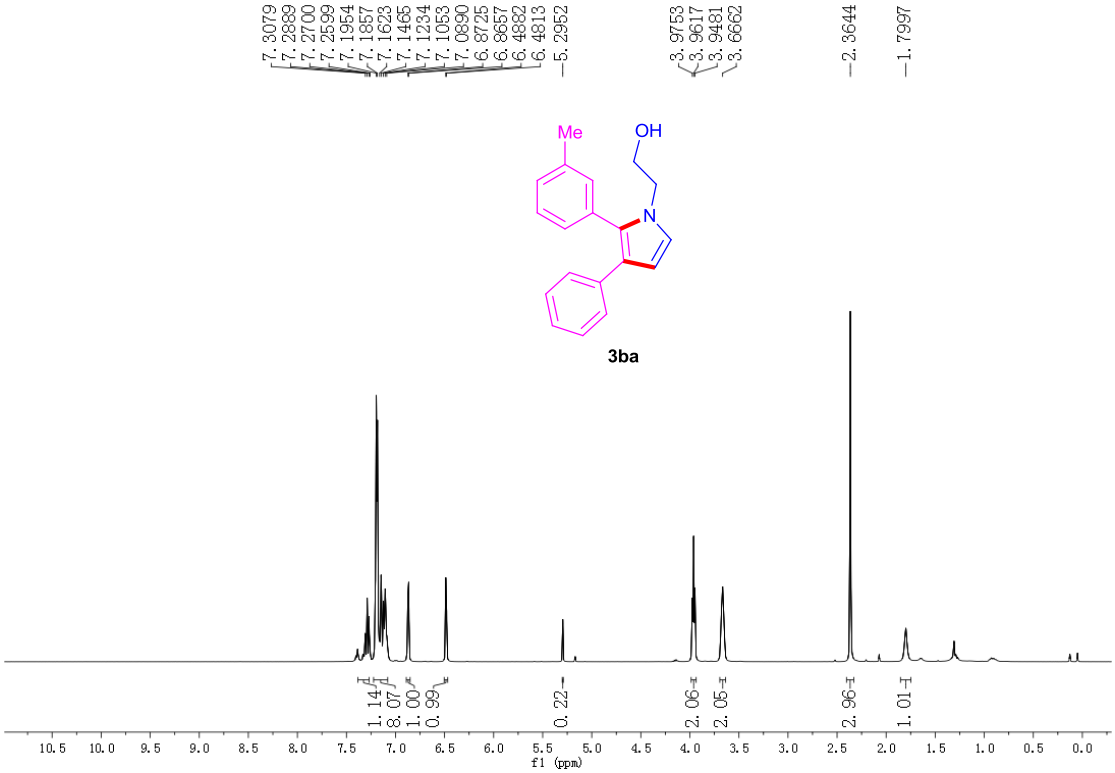
4. Copies of the ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

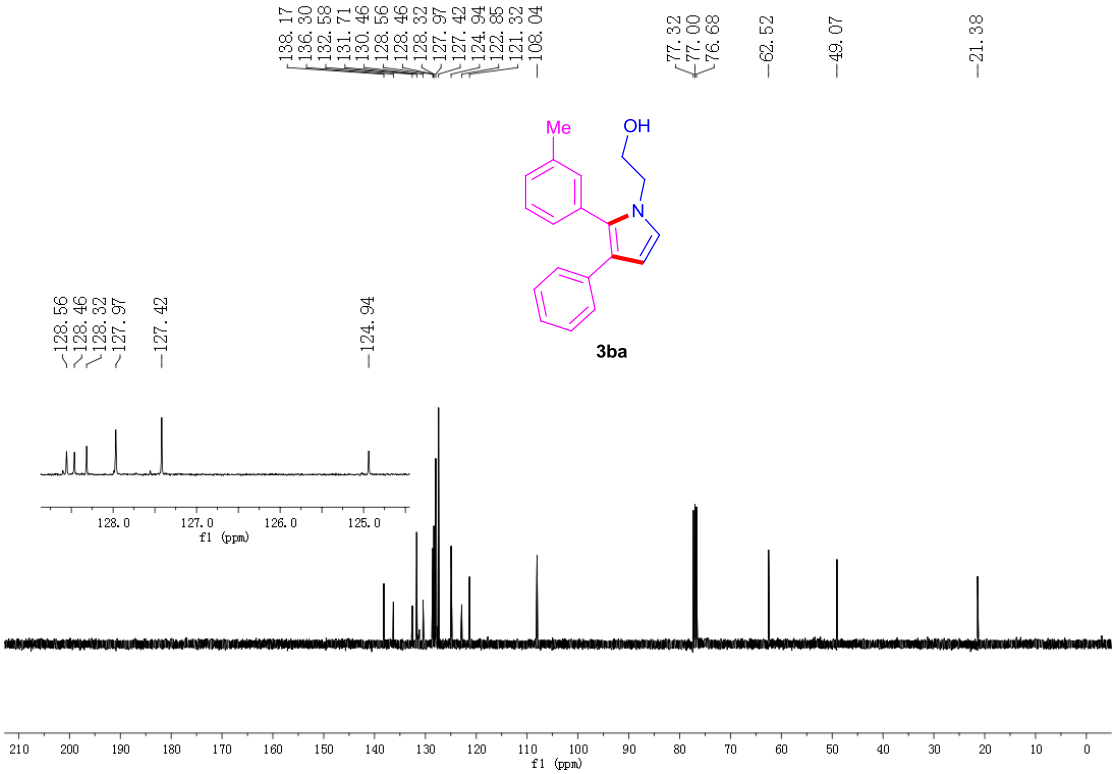
2-(2,3-diphenyl-1*H*-pyrrol-1-yl)ethanol (3aa):



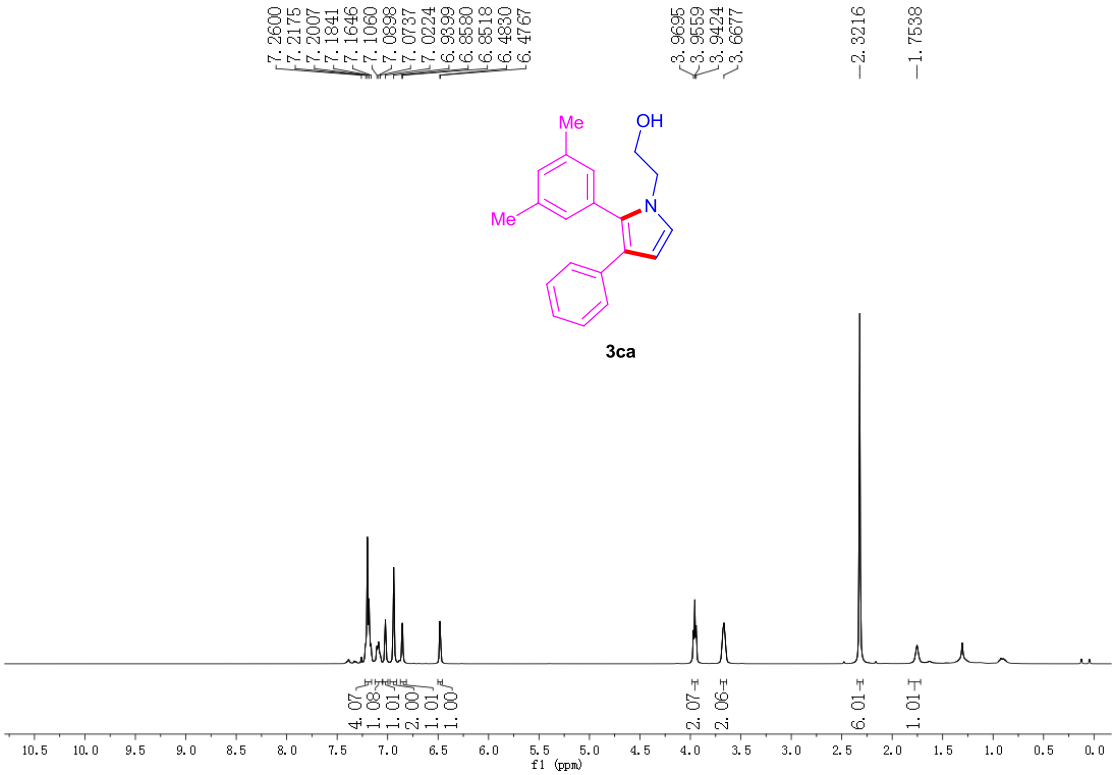


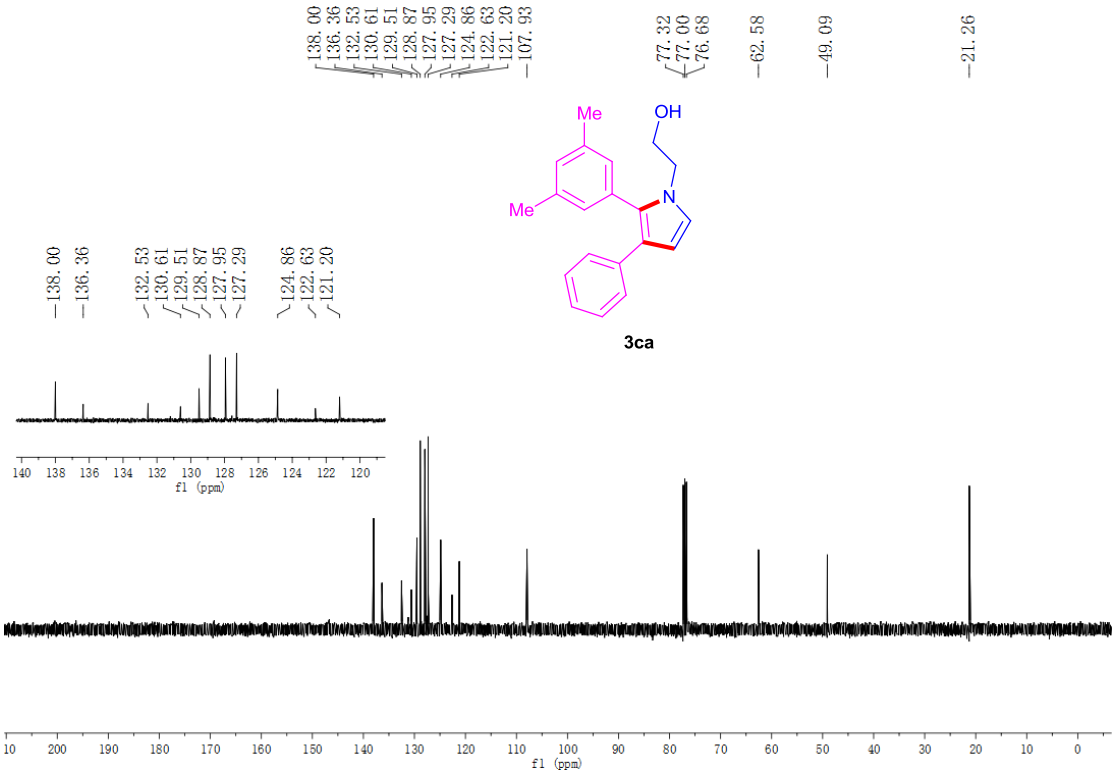
2-(3-phenyl-2-(*m*-tolyl)-1*H*-pyrrol-1-yl)ethanol (3ba):



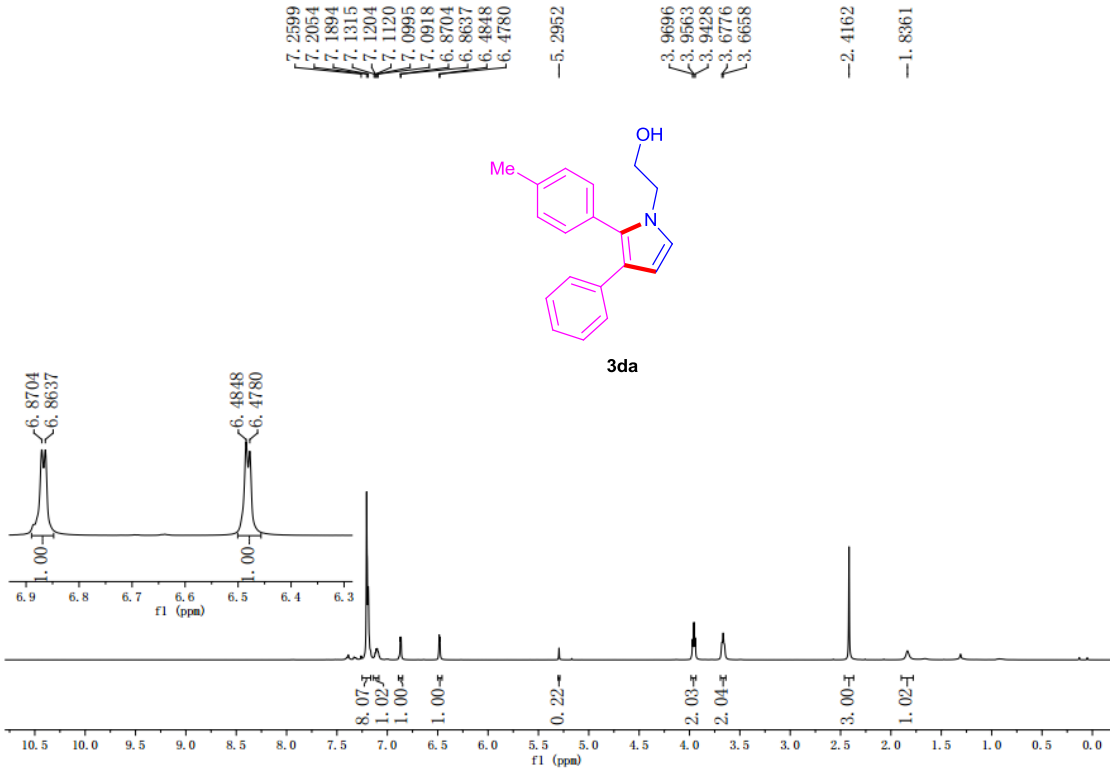


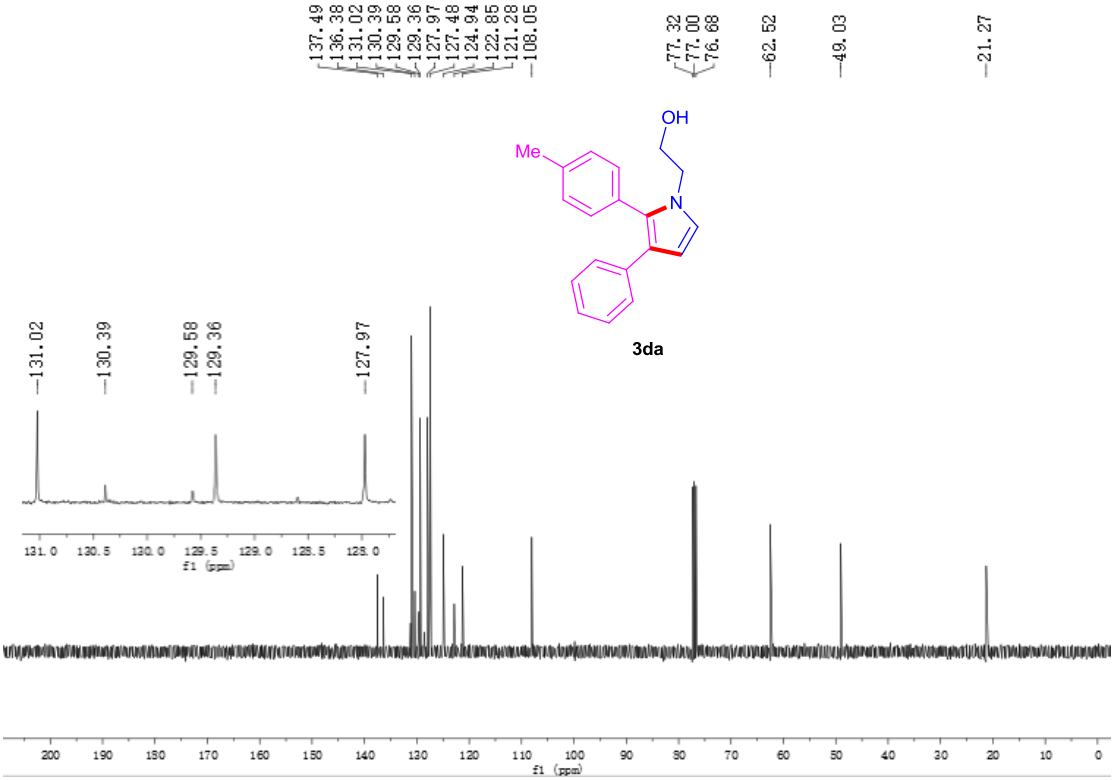
2-(2-(3,5-dimethylphenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3ca):



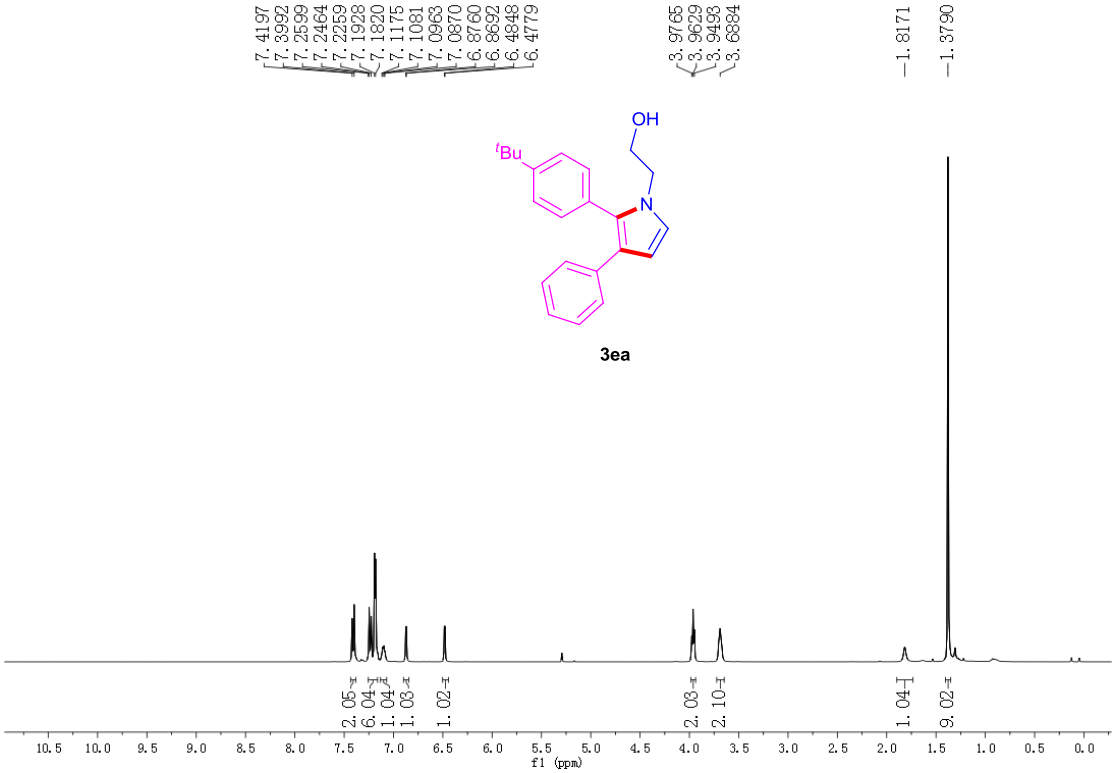


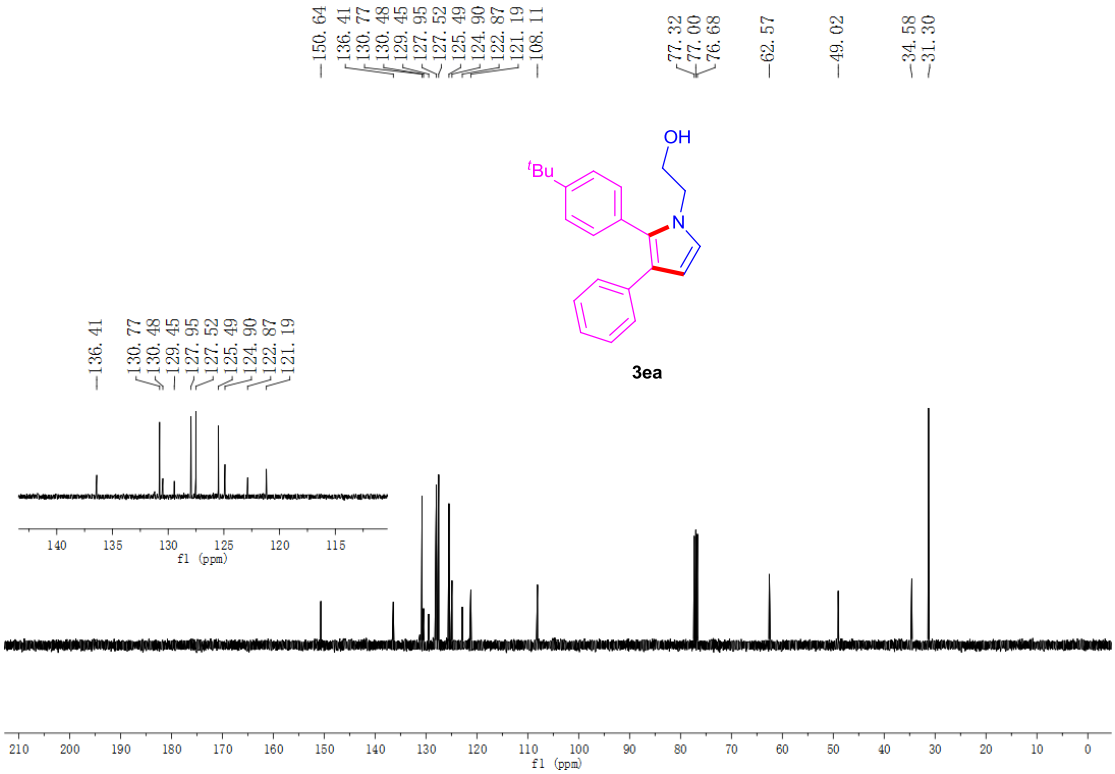
2-(3-phenyl-2-(*p*-tolyl)-1*H*-pyrrol-1-yl)ethanol (3da):



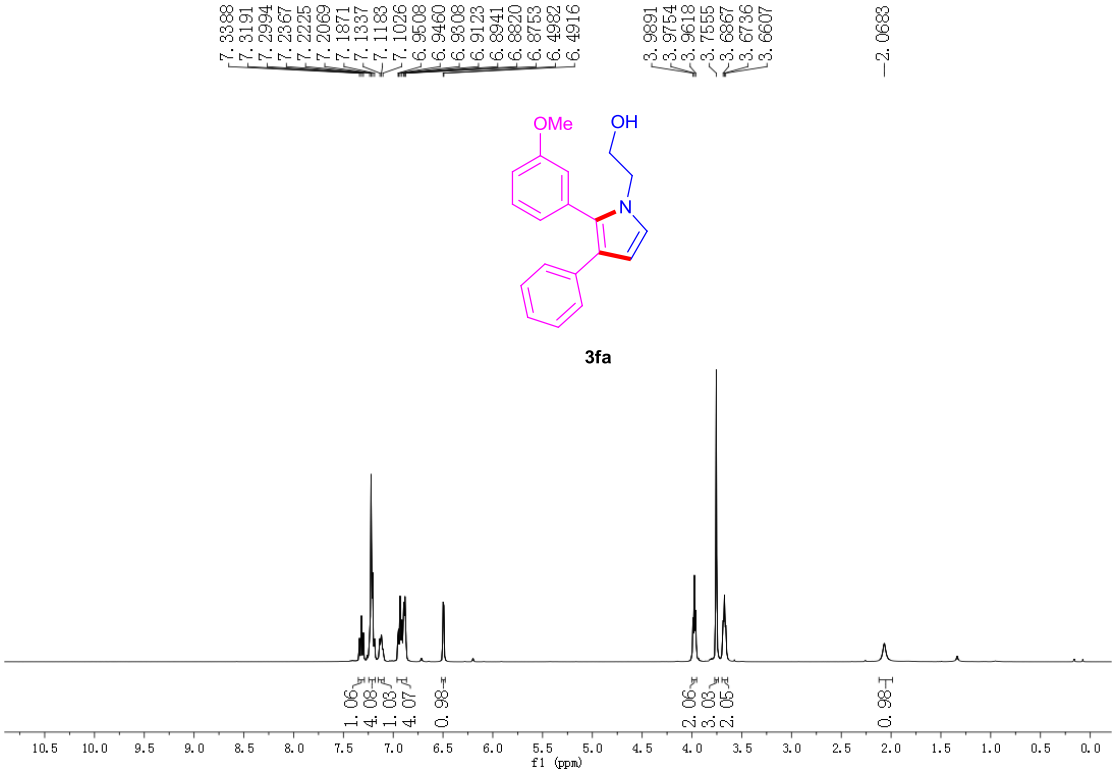


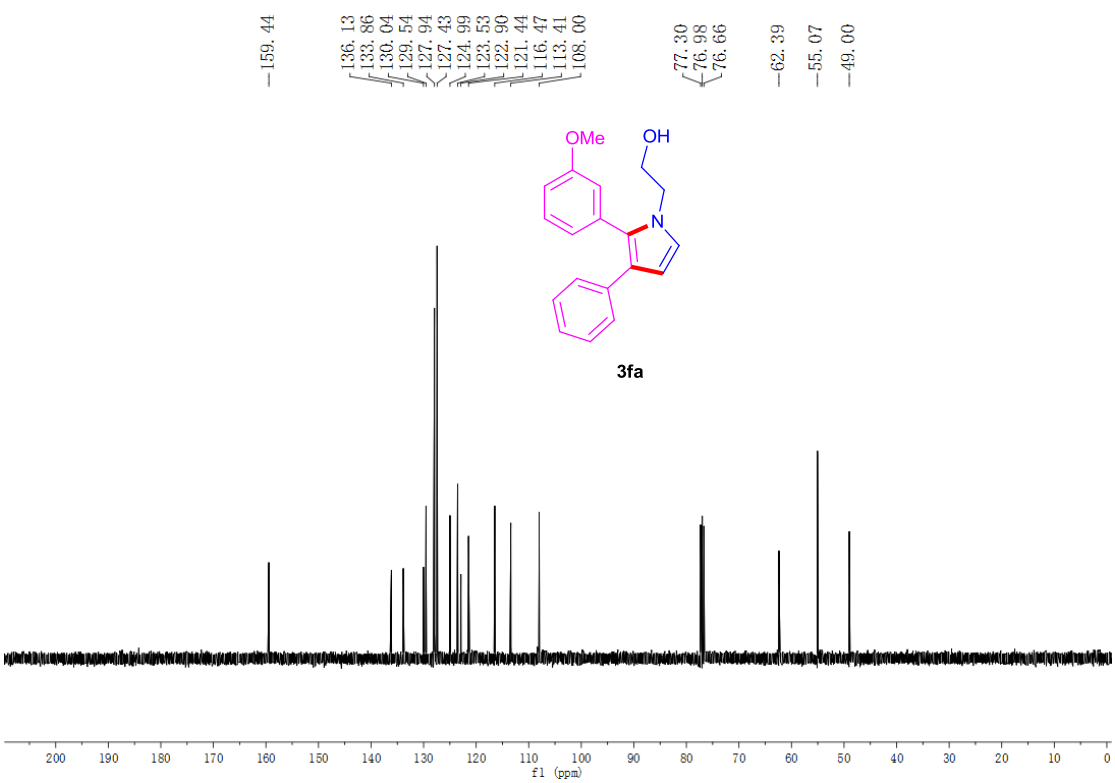
2-(2-(4-(*tert*-butyl)phenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3ea):



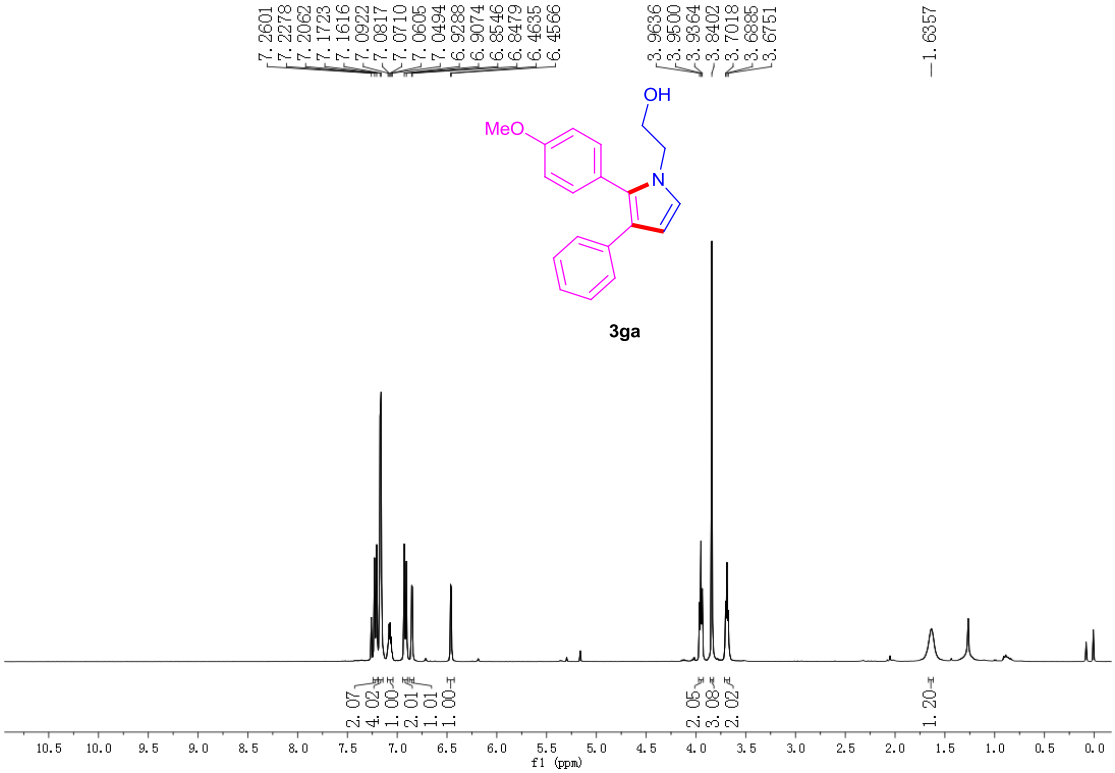


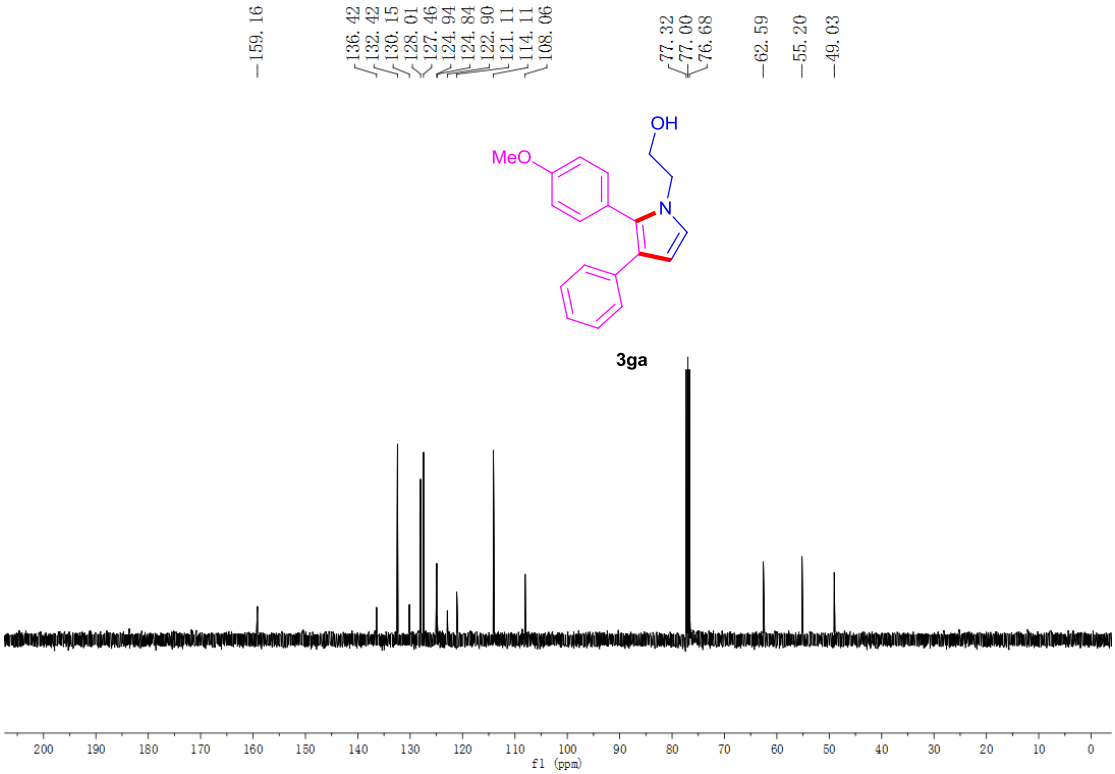
2-(2-(3-methoxyphenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3fa):



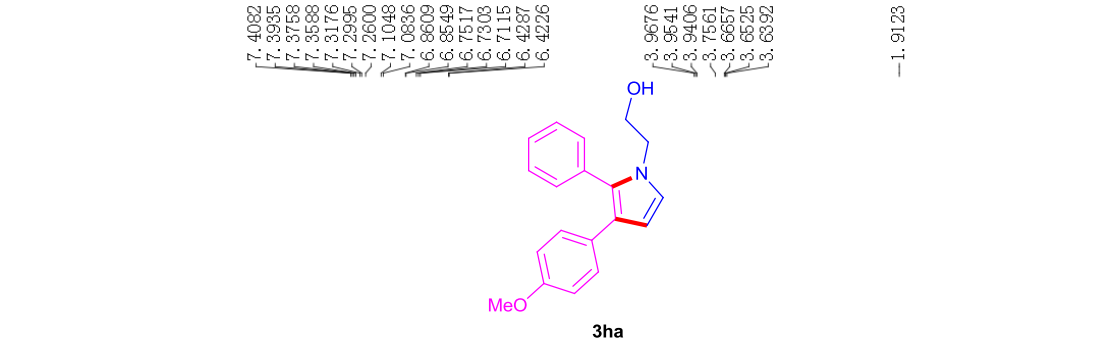


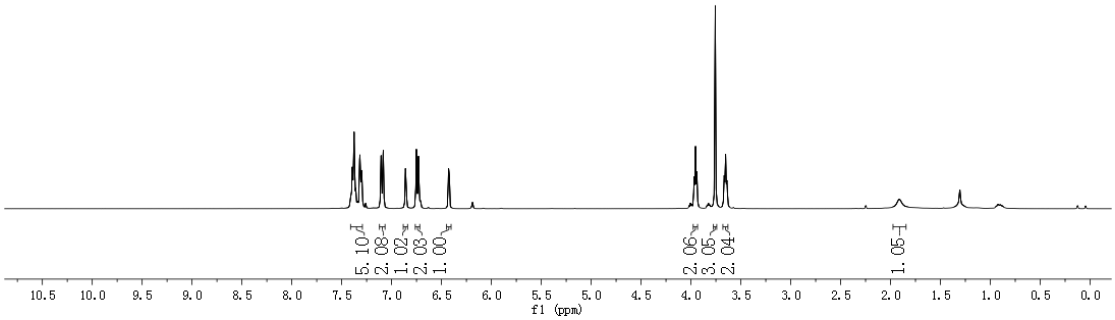
2-(2-(4-methoxyphenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3ga):

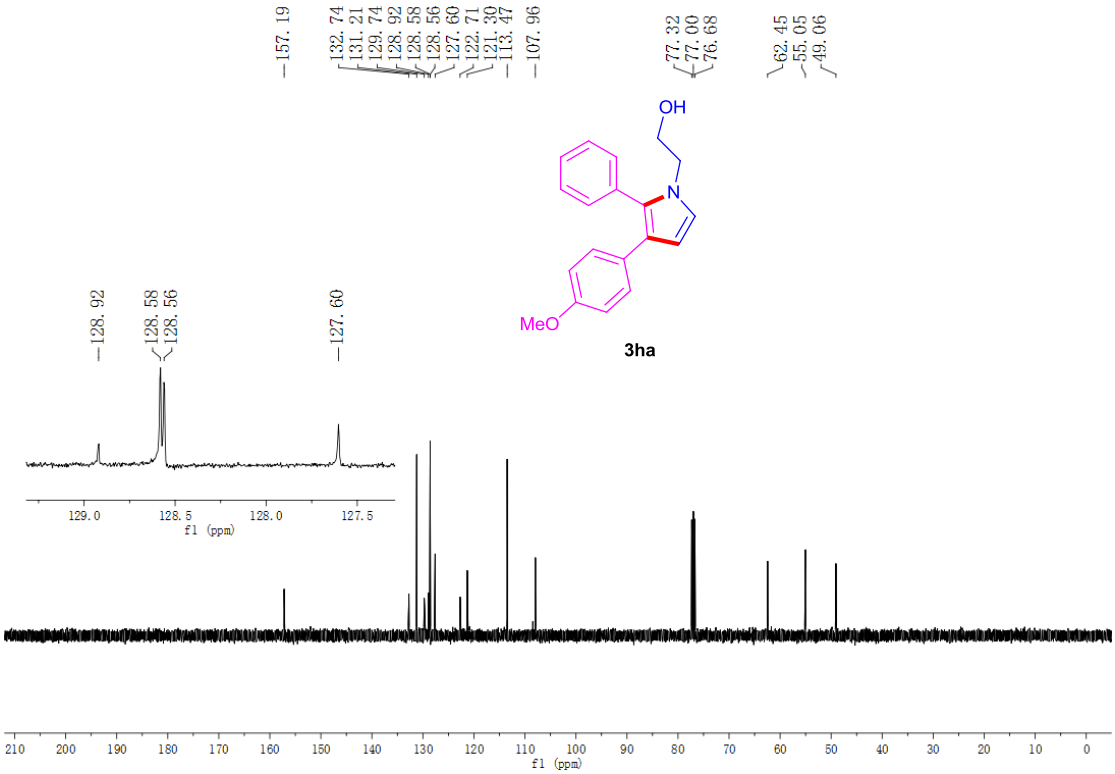




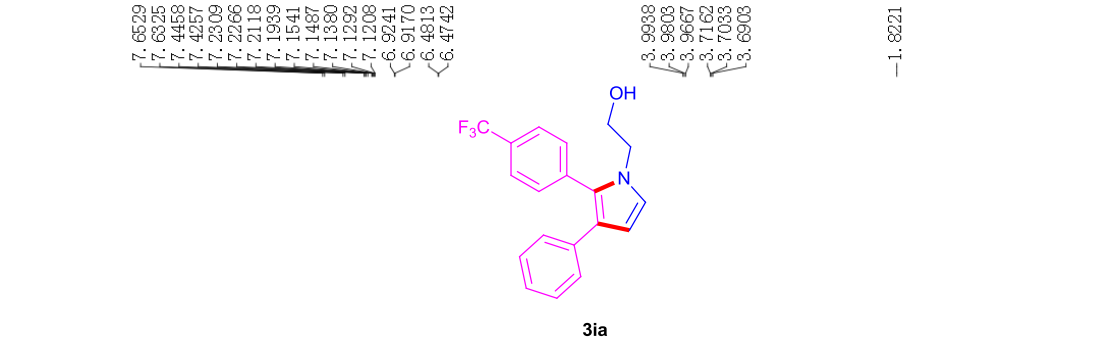
2-(3-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrol-1-yl)ethanol (3ha):

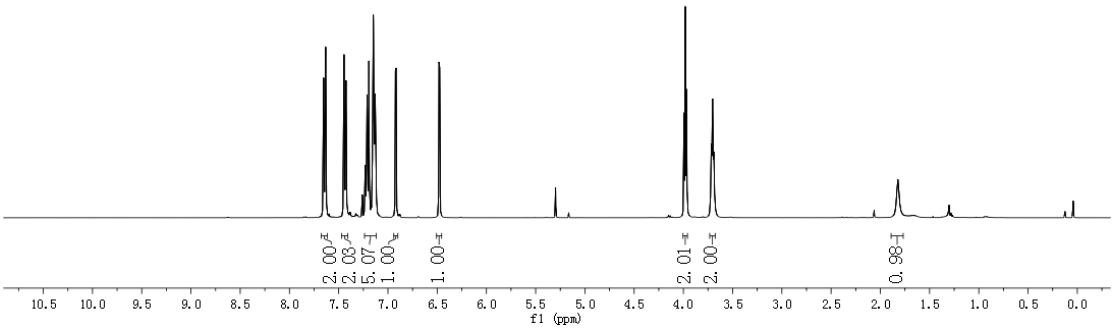


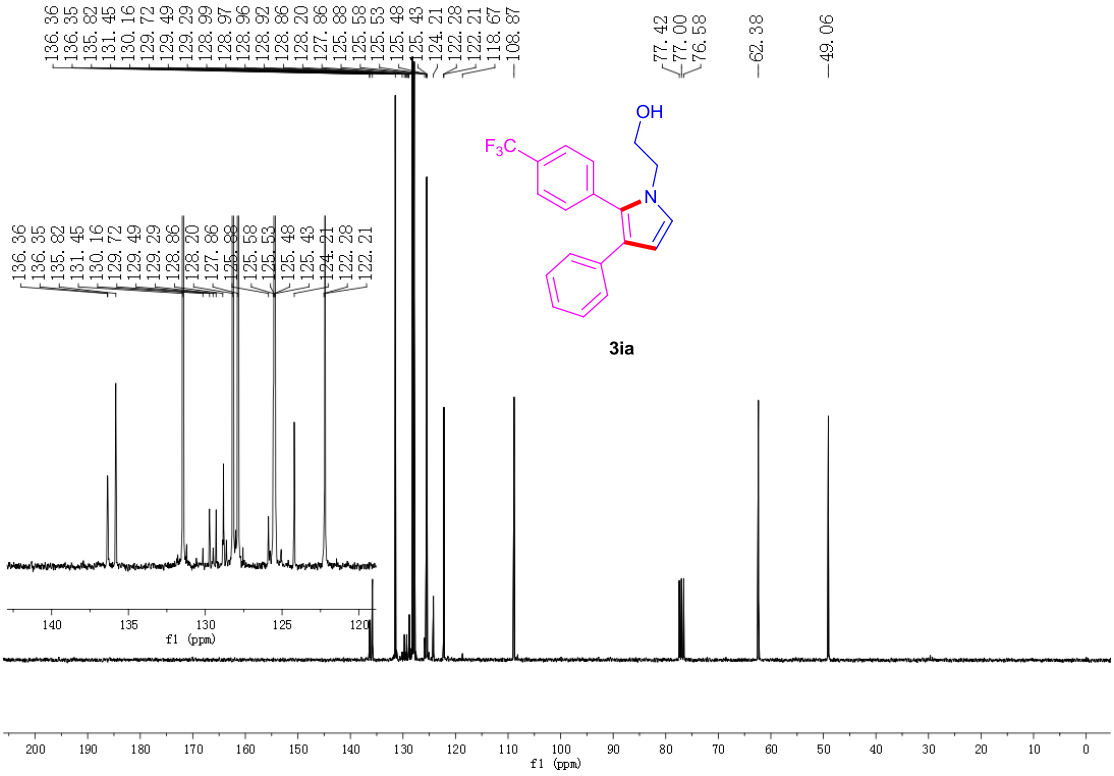




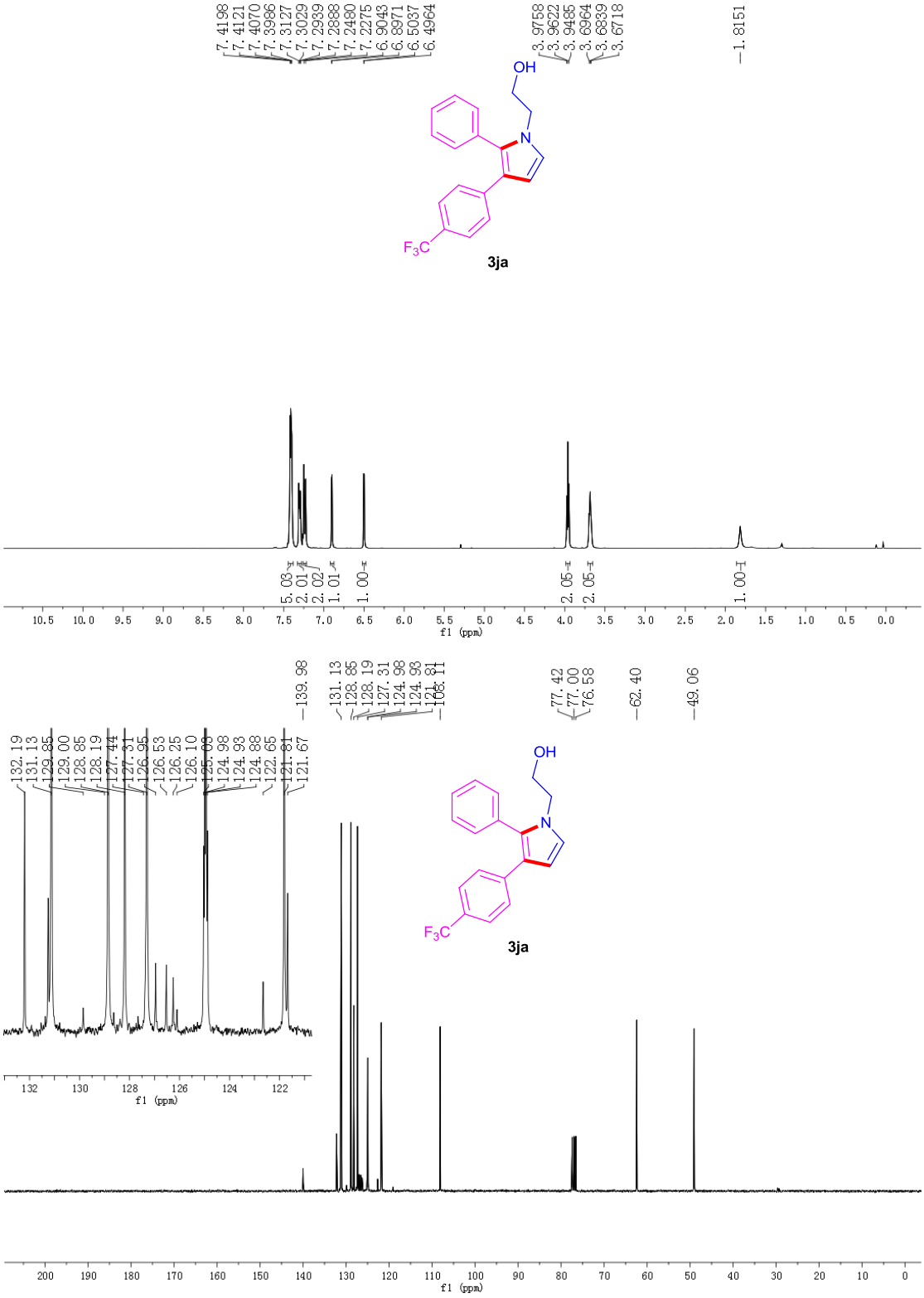
2-(3-phenyl-2-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-1-yl)ethanol (3ia)：



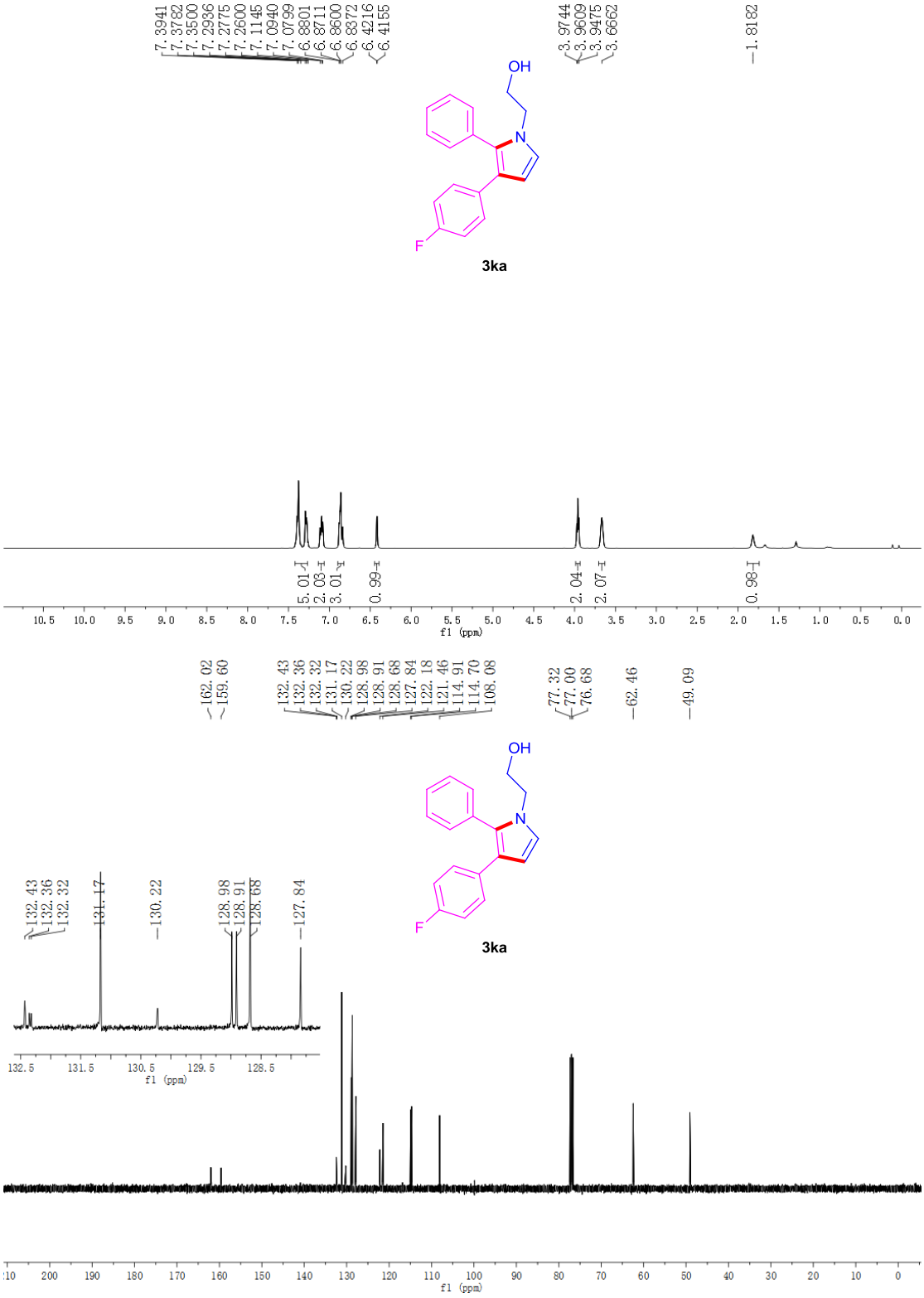




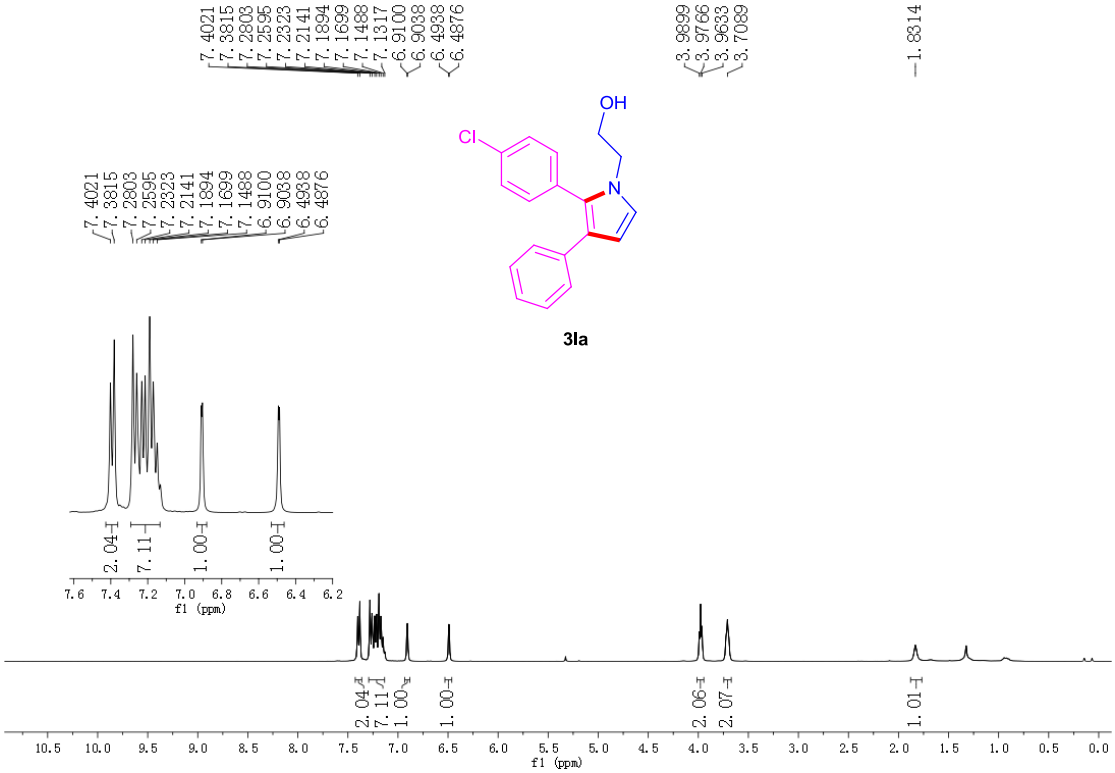
2-(2-phenyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrol-1-yl)ethanol (3ja):

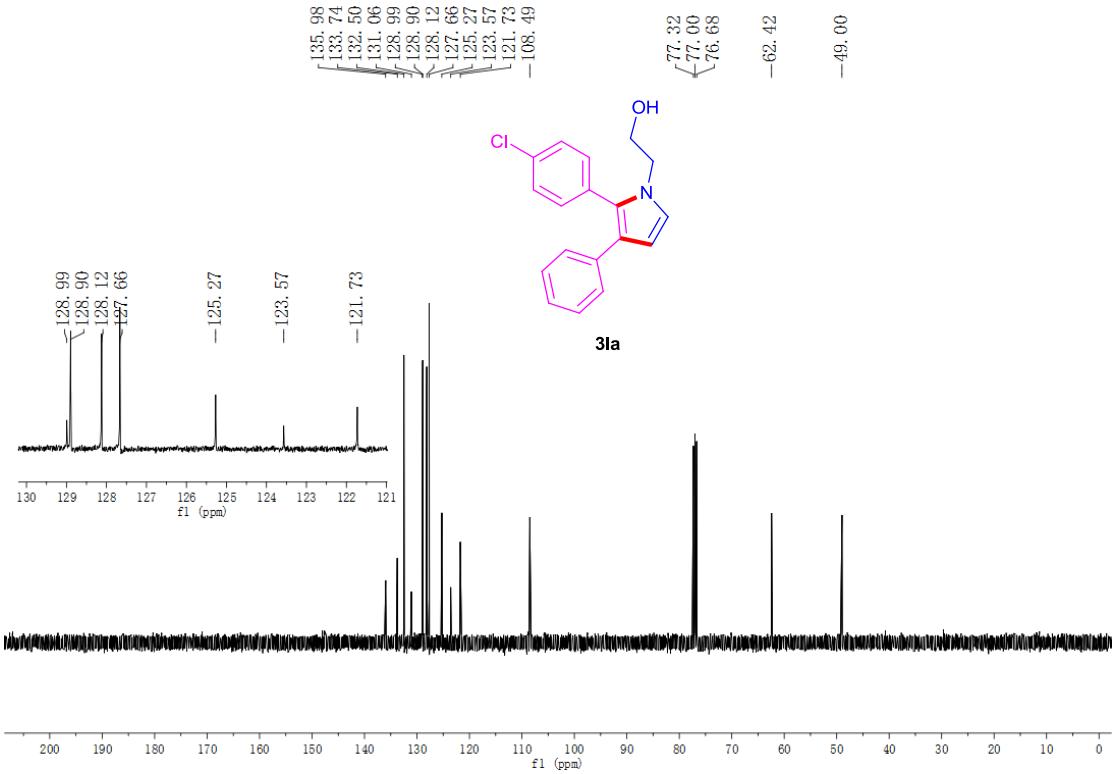


2-(3-(4-fluorophenyl)-2-phenyl-1*H*-pyrrol-1-yl)ethanol (3ka):

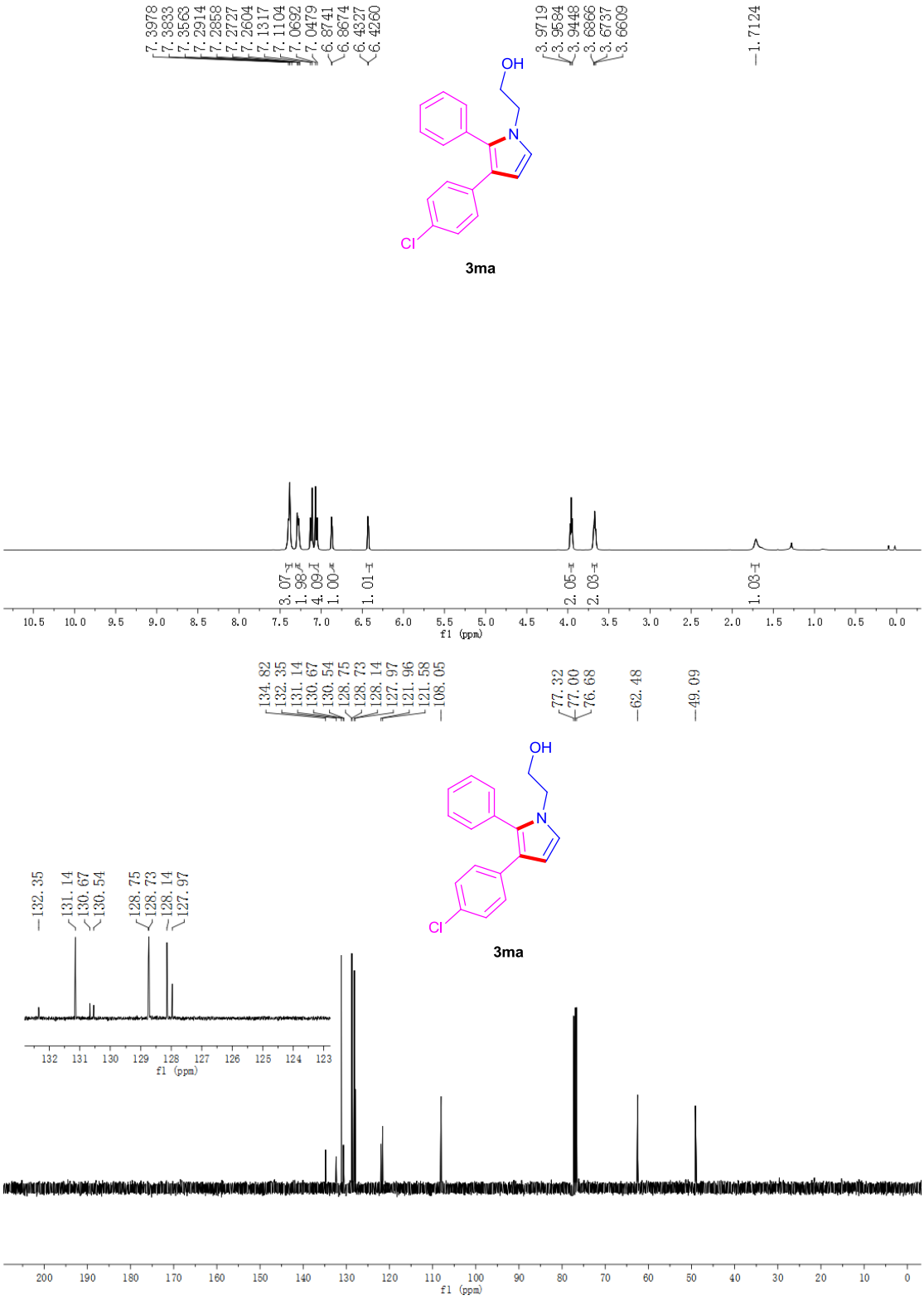


2-(2-(4-chlorophenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3la):

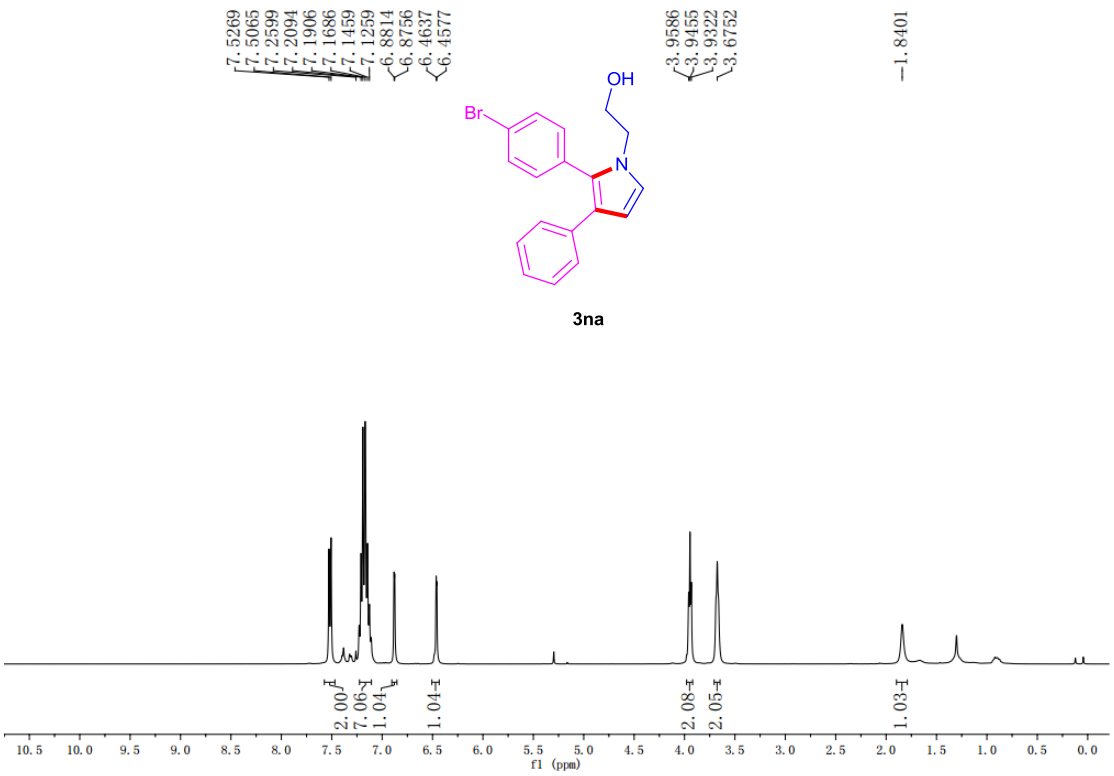


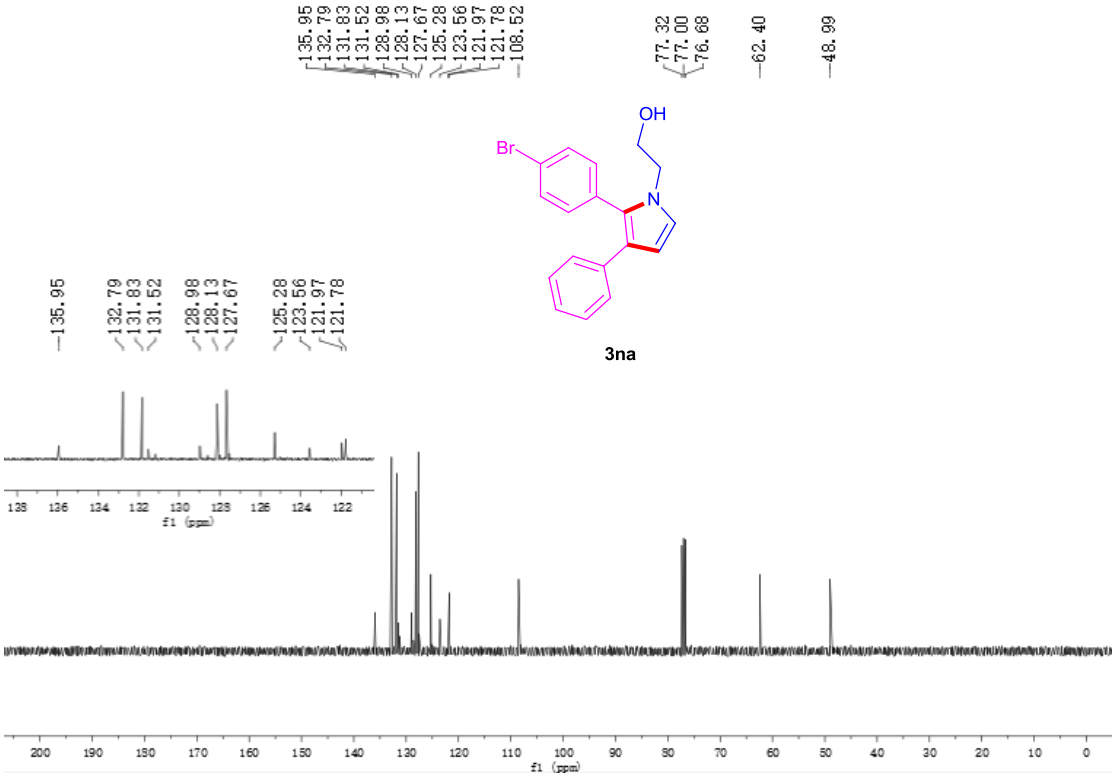


2-(3-(4-chlorophenyl)-2-phenyl-1*H*-pyrrol-1-yl)ethanol (3ma):

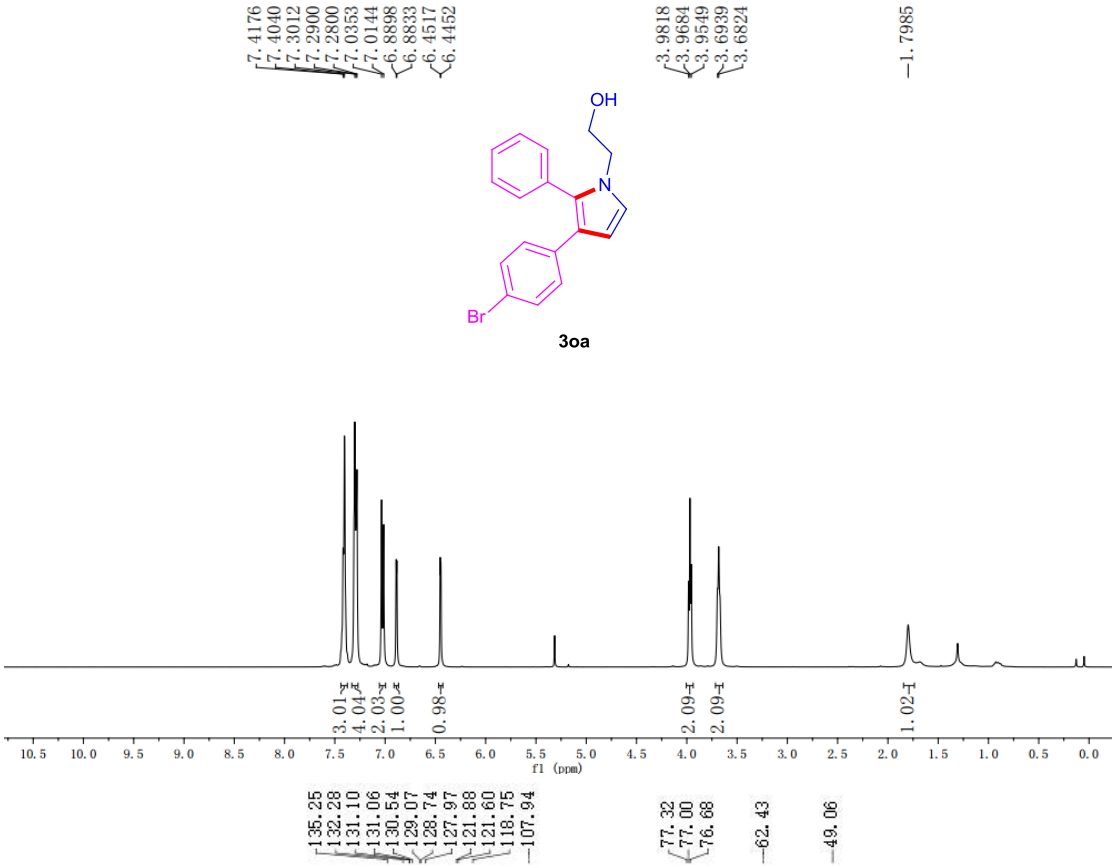


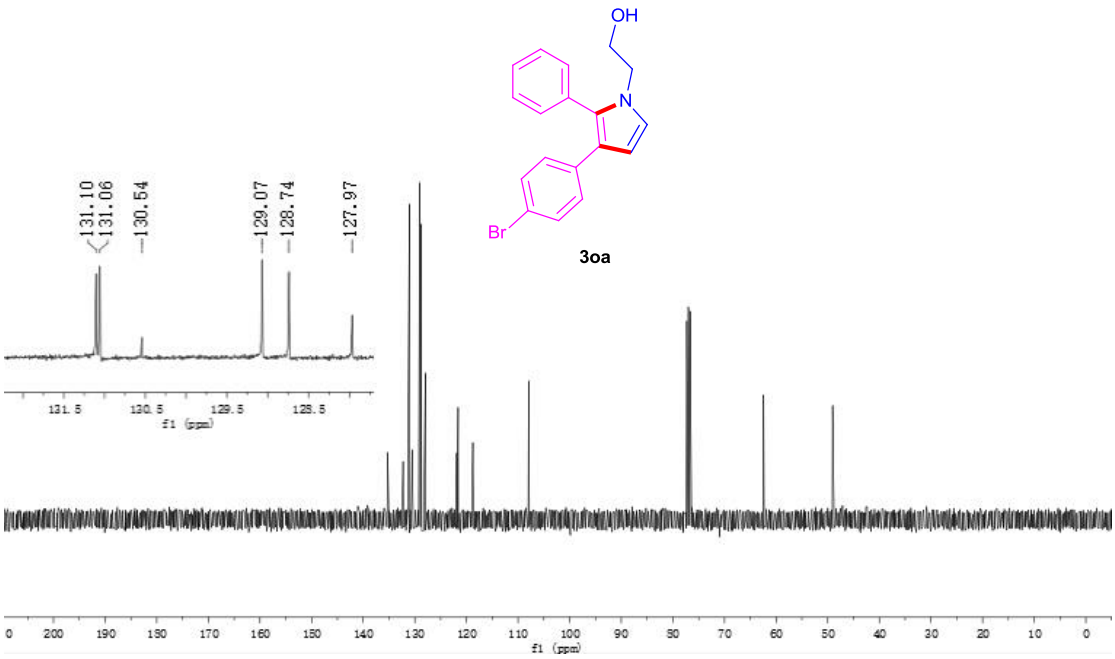
2-(2-(4-bromophenyl)-3-phenyl-1*H*-pyrrol-1-yl)ethanol (3na):



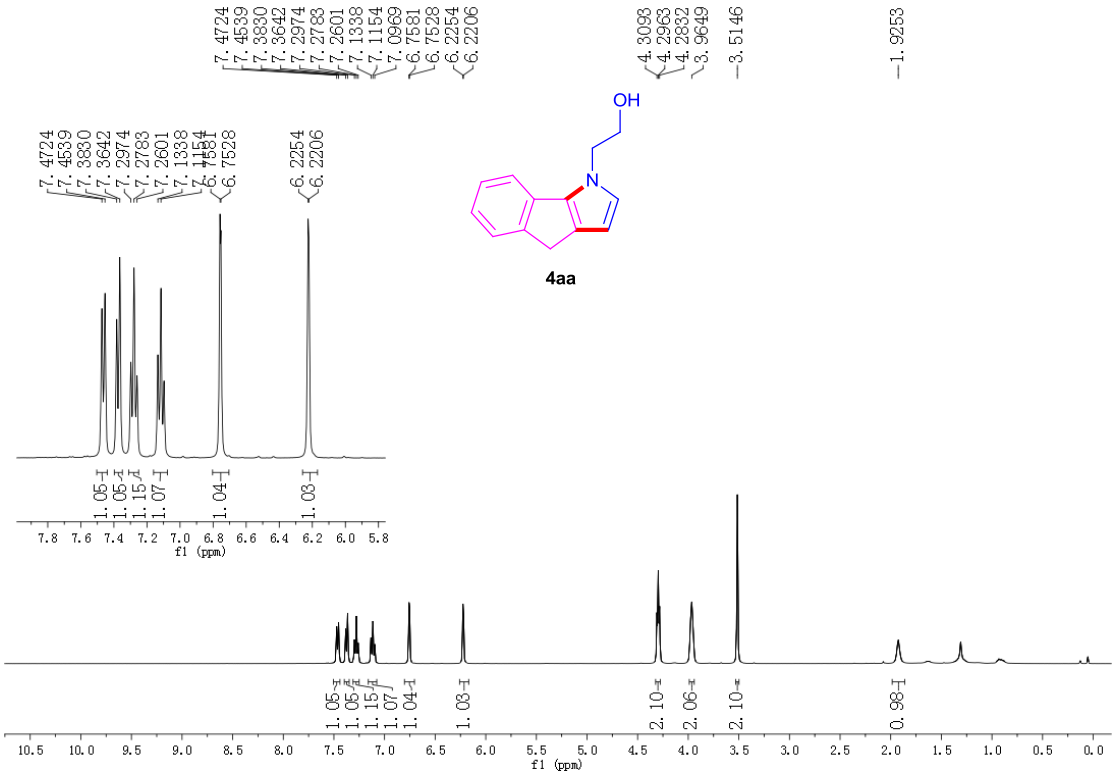


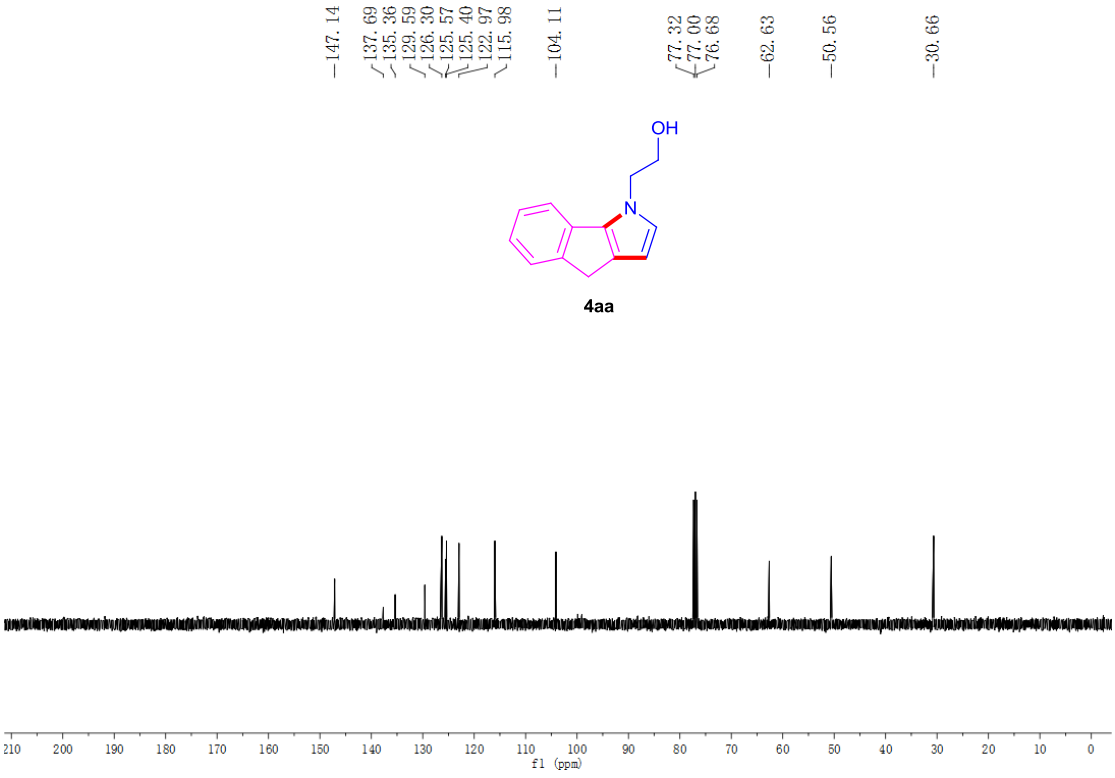
2-(3-(4-bromophenyl)-2-phenyl-1*H*-pyrrol-1-yl)ethanol (3oa):



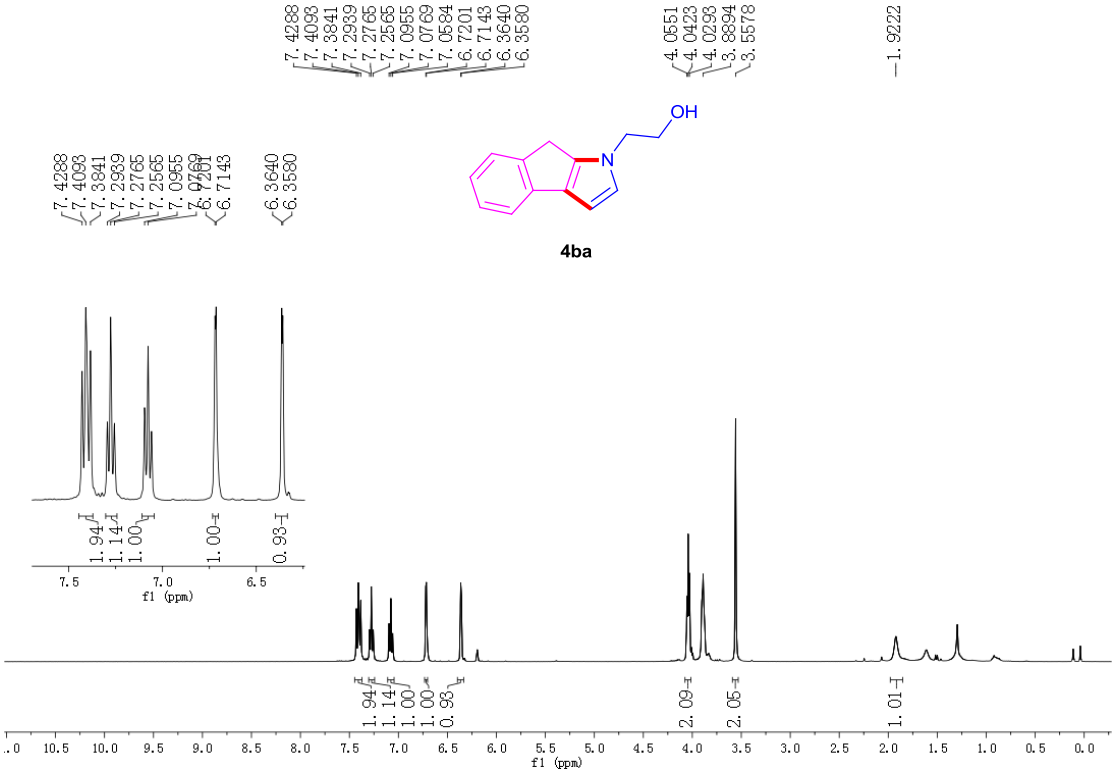


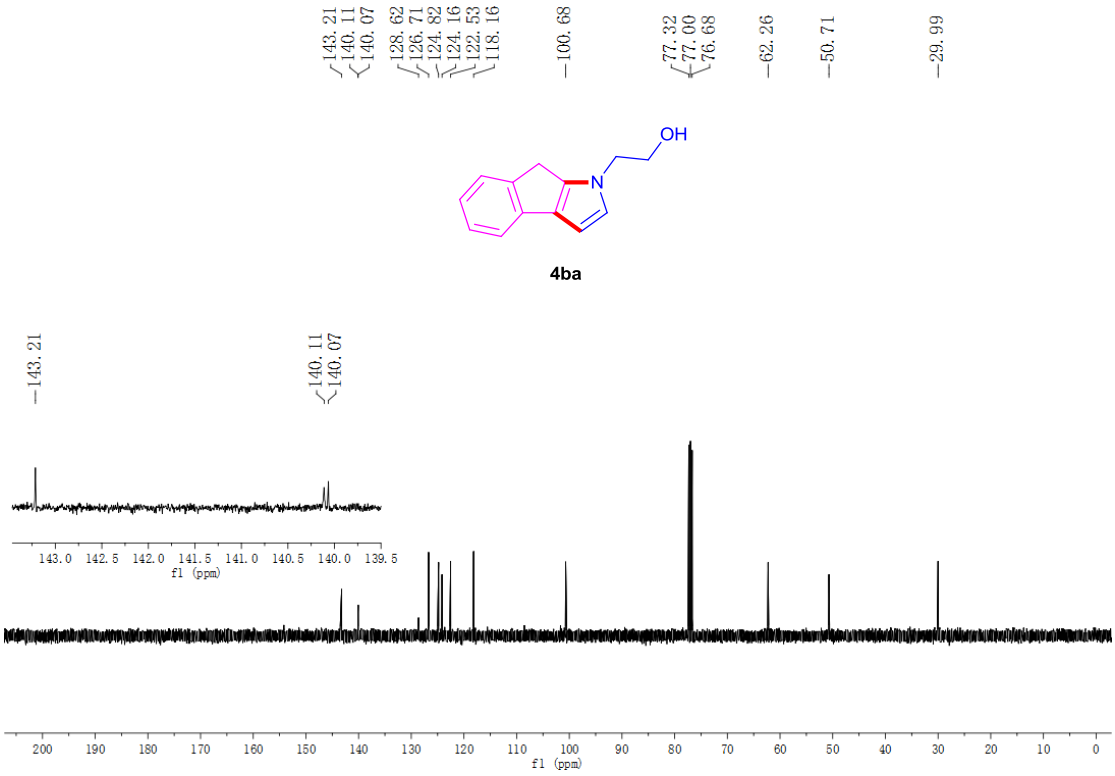
2-(indeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4aa):



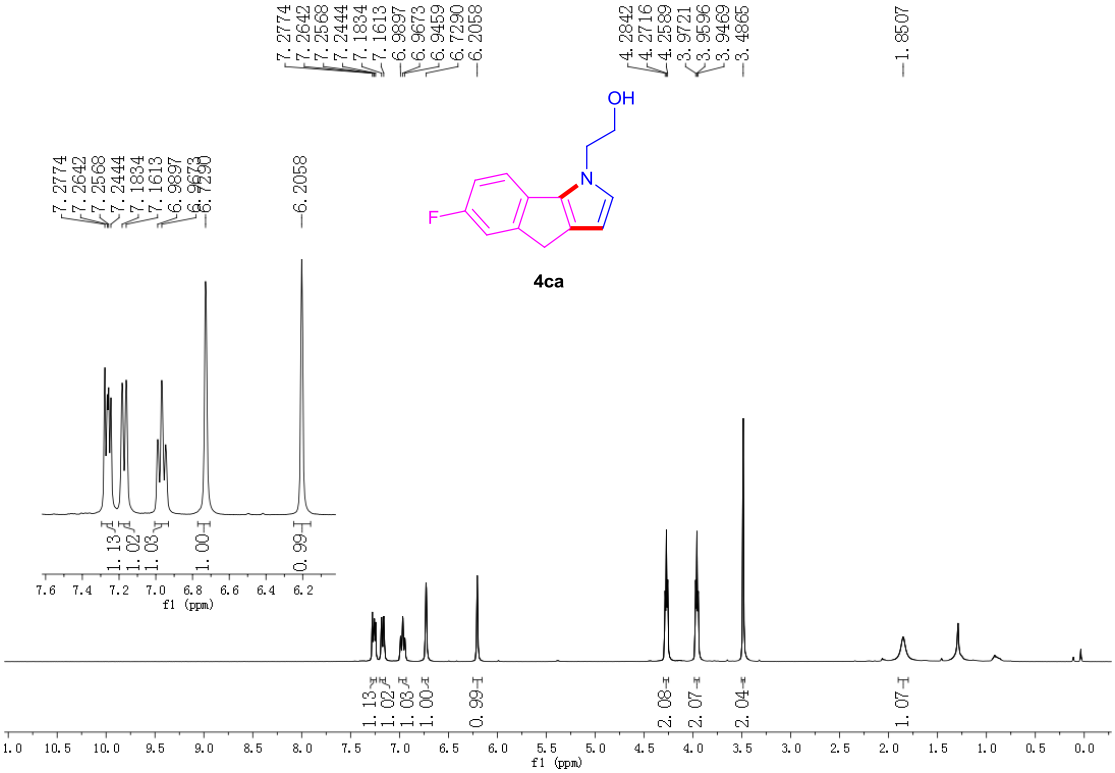


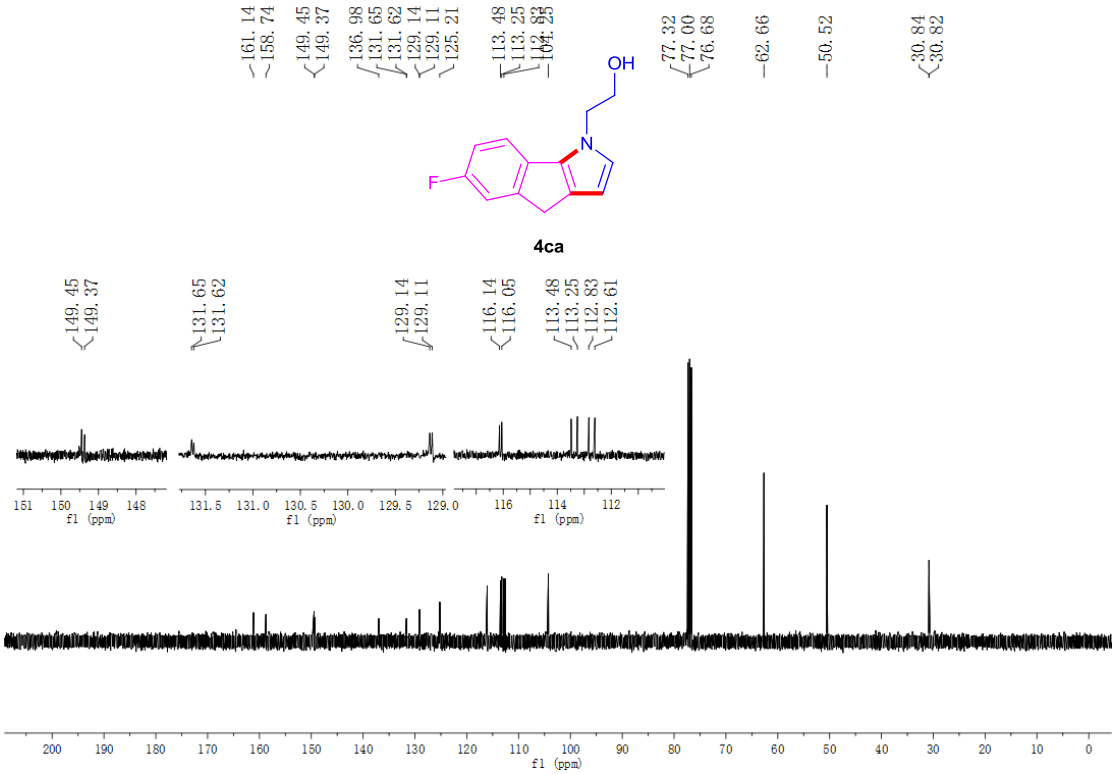
2-(indeno[2,1-*b*]pyrrol-1(8*H*)-yl)ethanol (4ba):



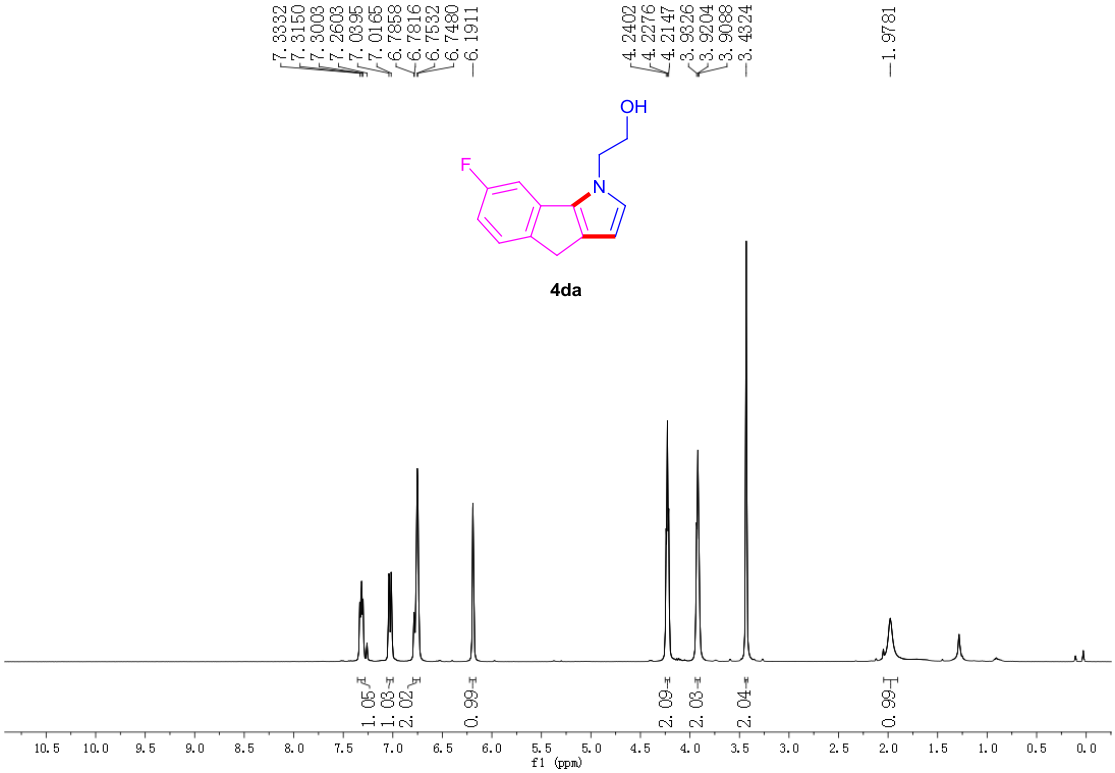


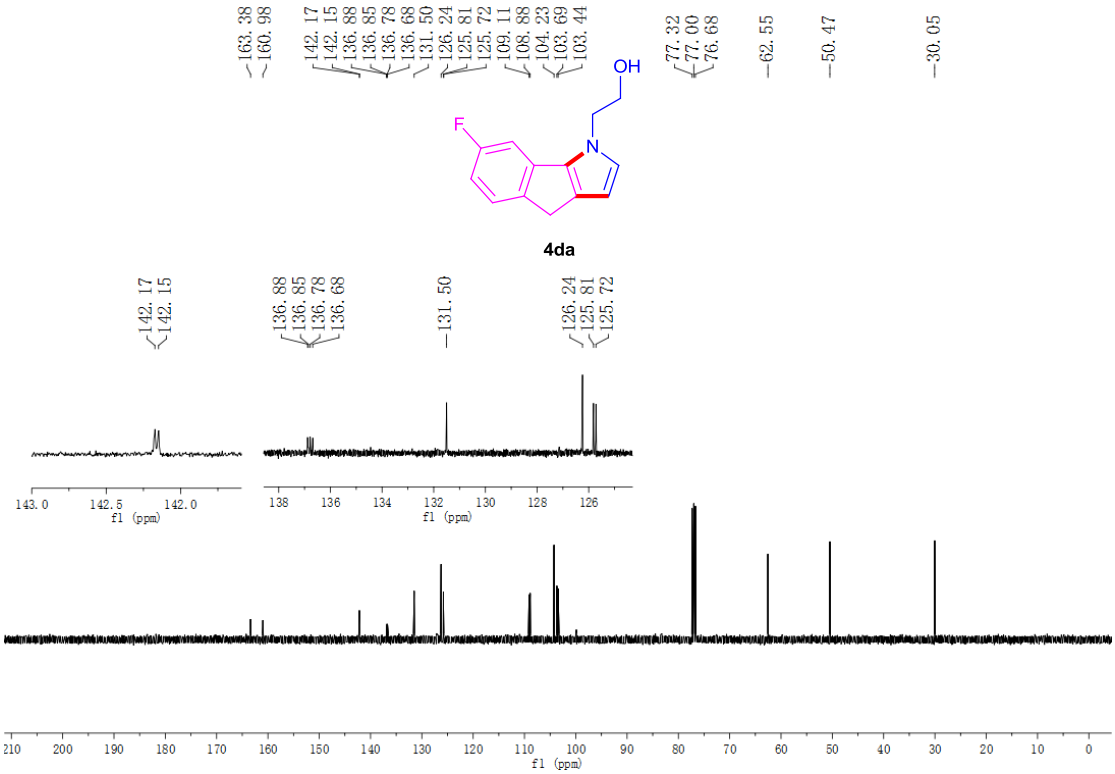
2-(6-fluoroindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4ca):



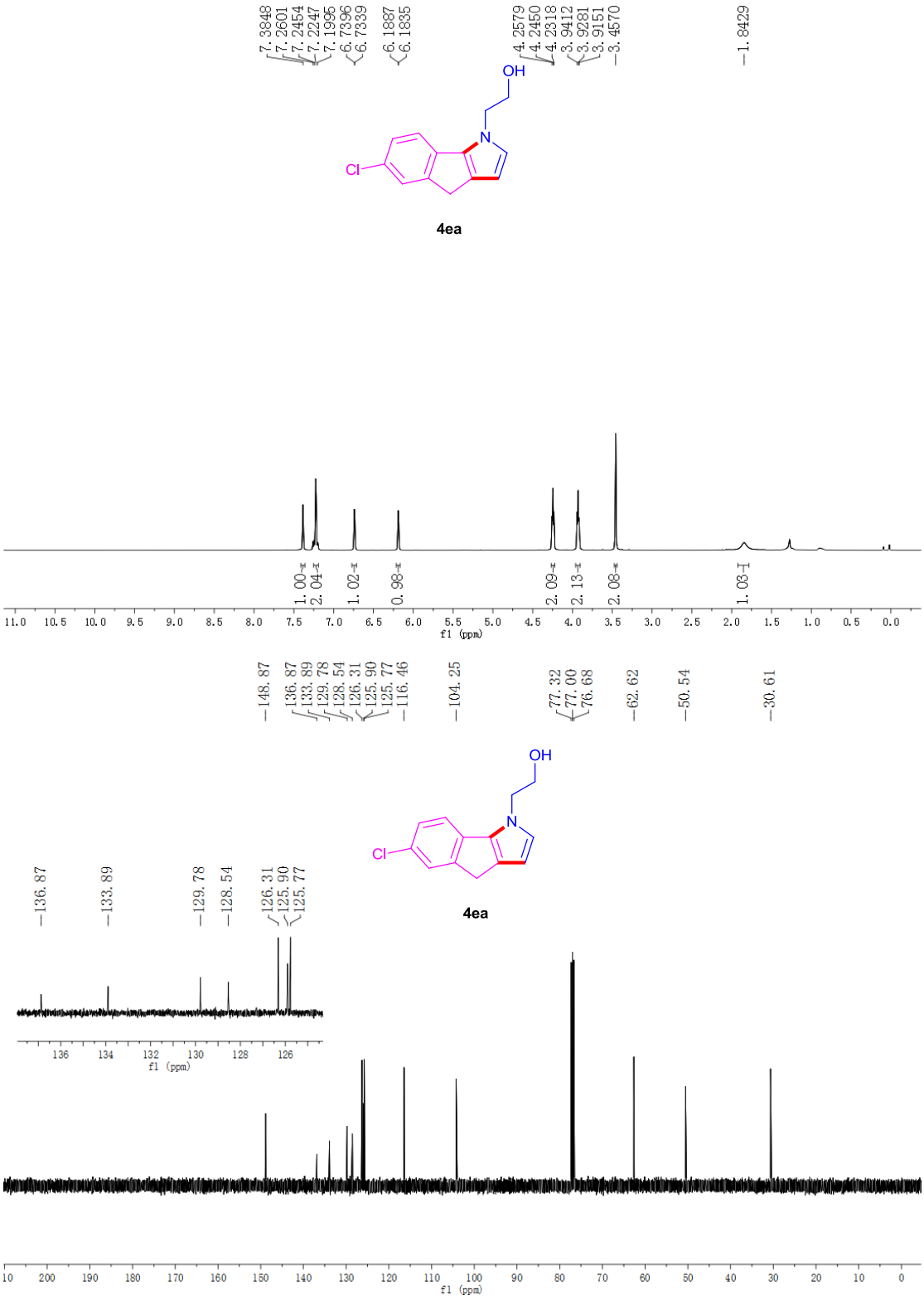


2-(7-fluoroindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4da):

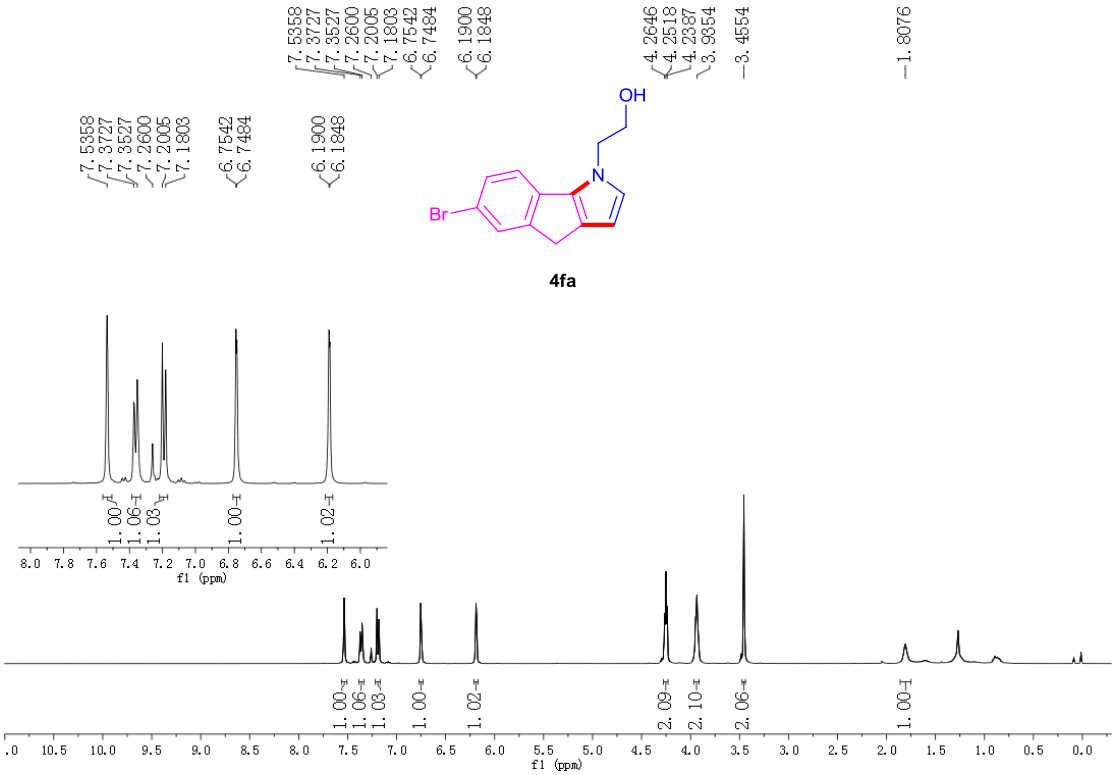


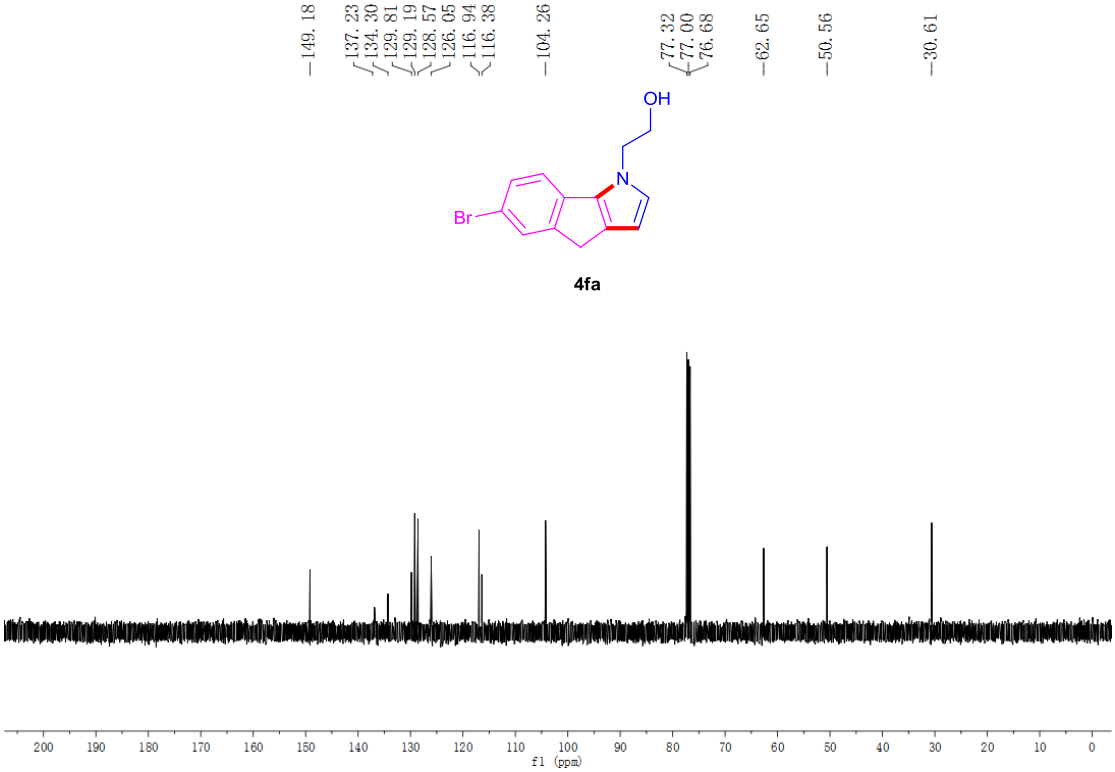


2-(6-chloroindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4ea):

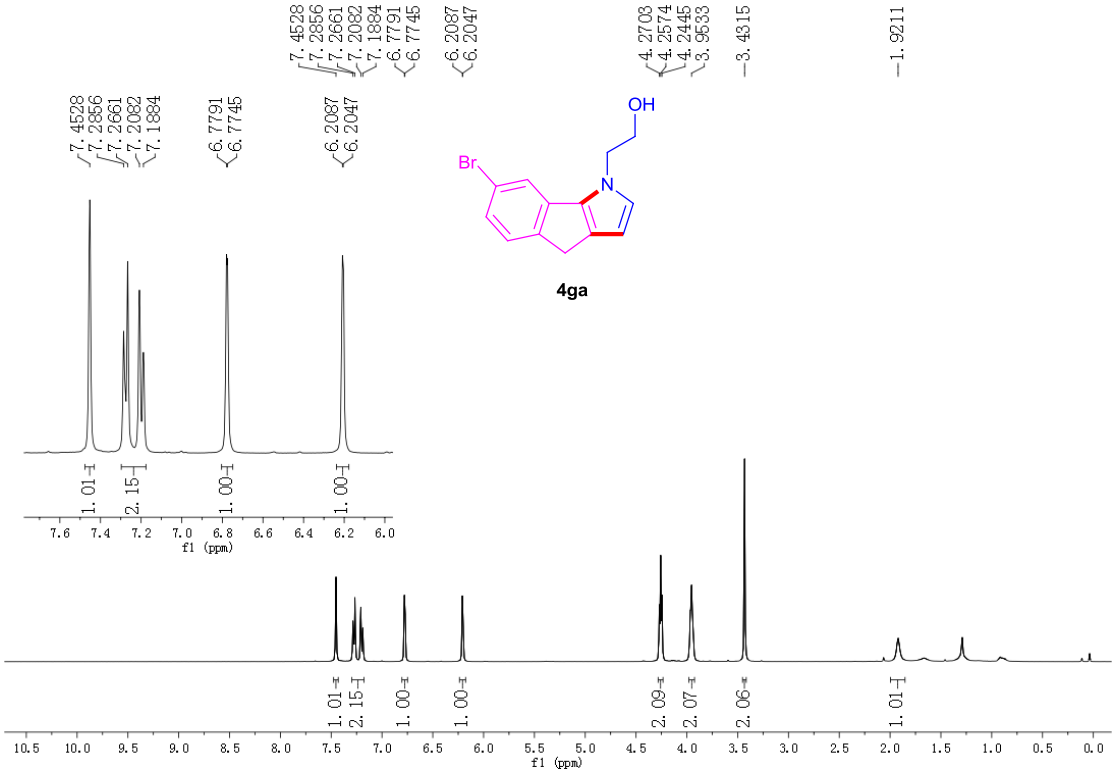


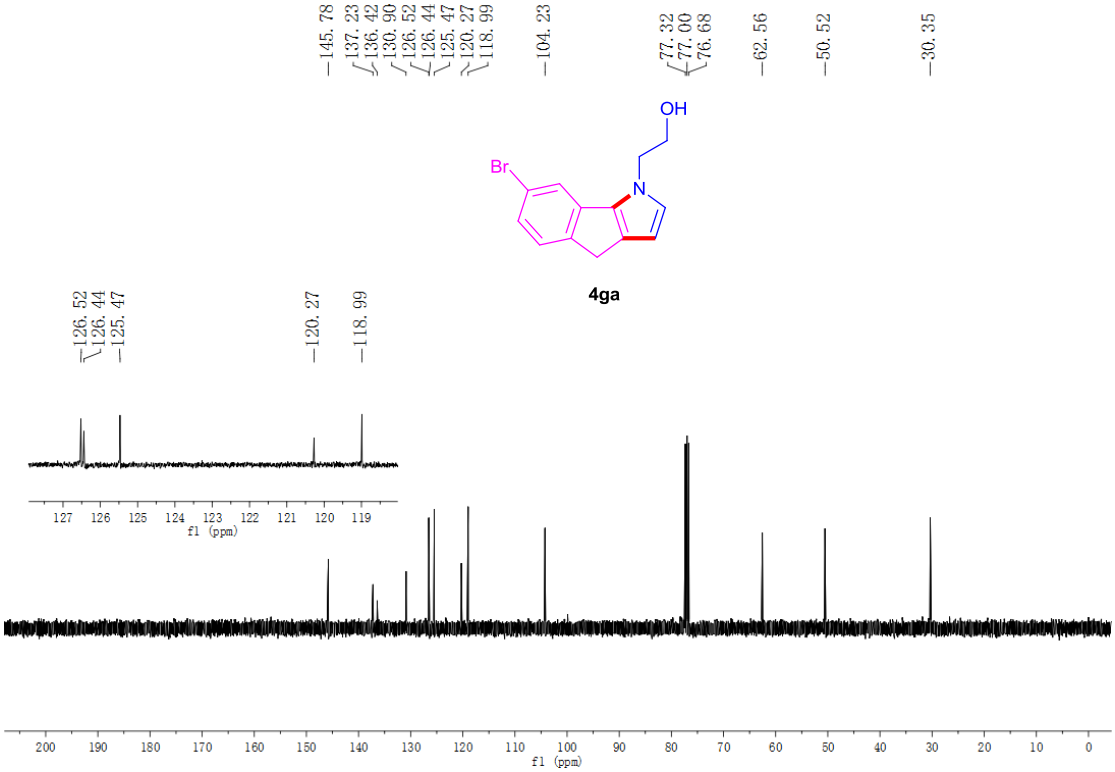
2-(6-bromoindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4fa):



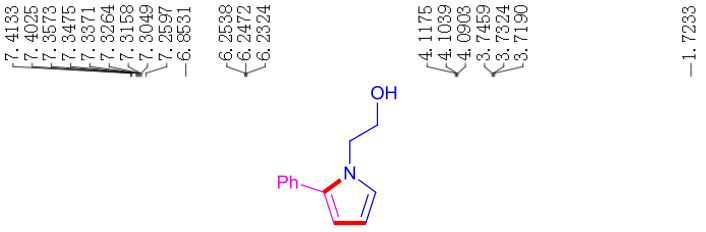


2-(7-bromoindeno[1,2-*b*]pyrrol-1(4*H*)-yl)ethanol (4ga):

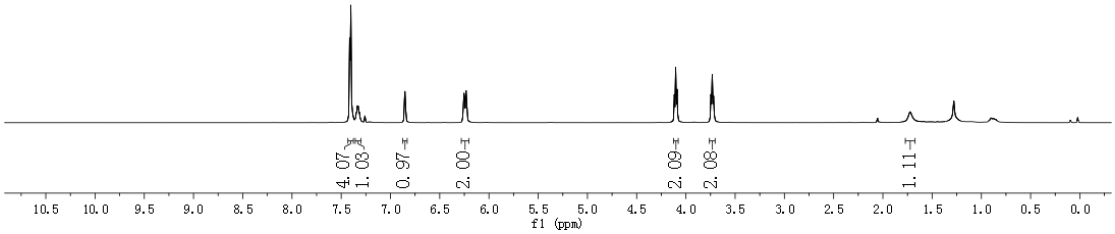


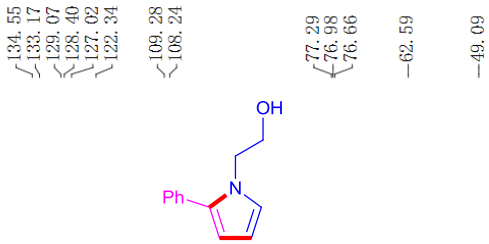


2-(2-phenyl-1*H*-pyrrol-1-yl)ethanol (5aa):

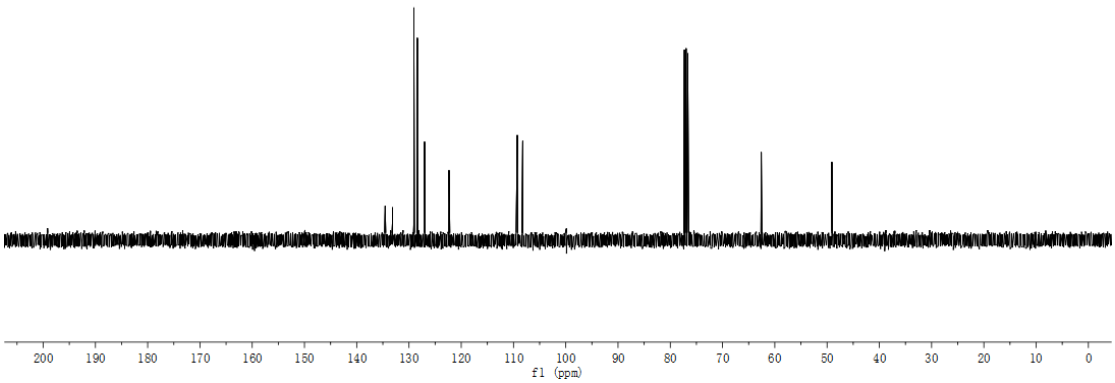


5aa

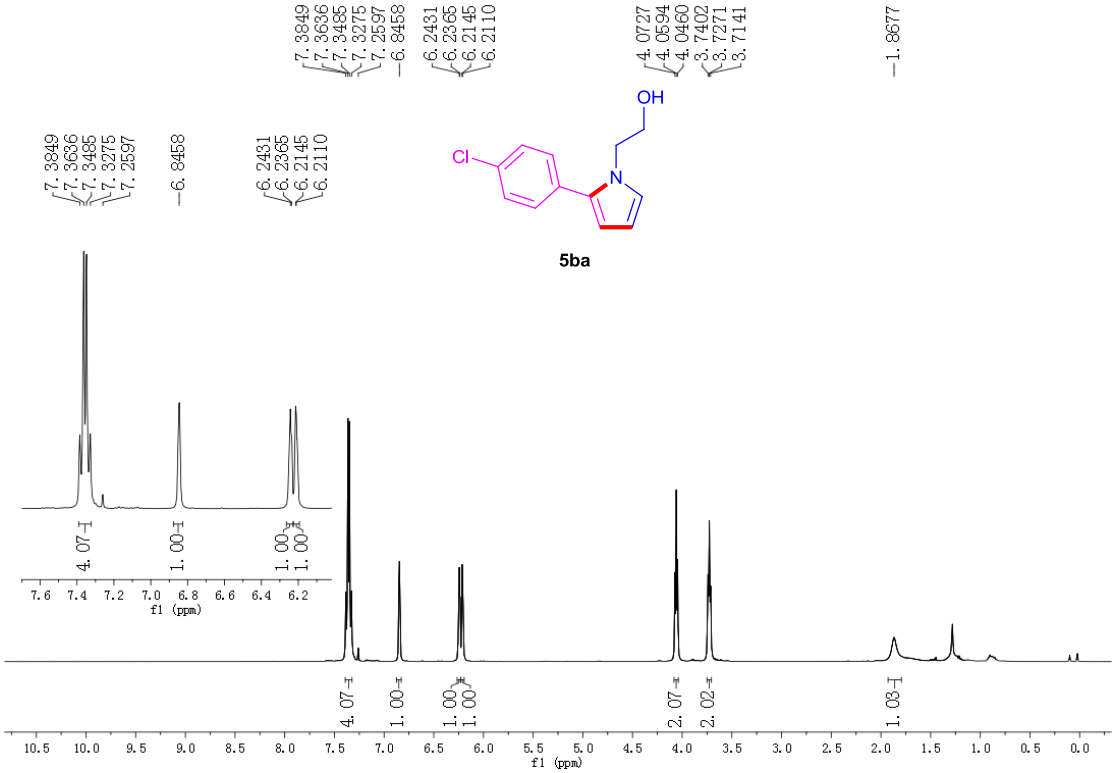


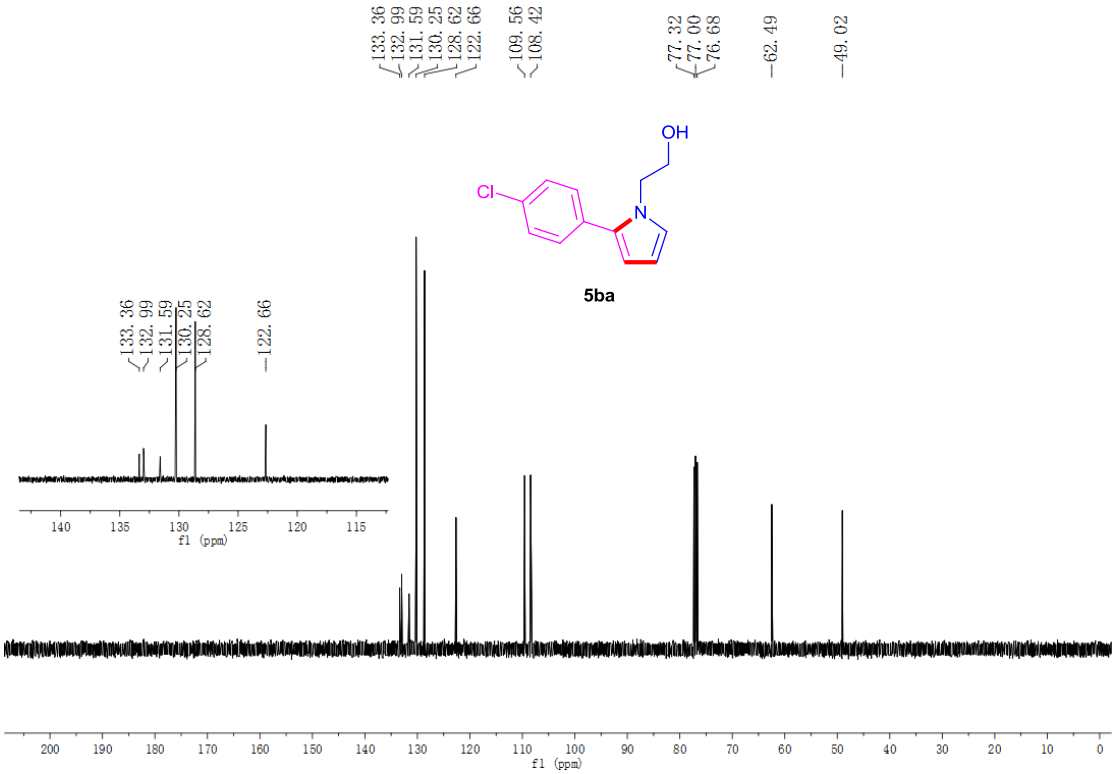


5aa

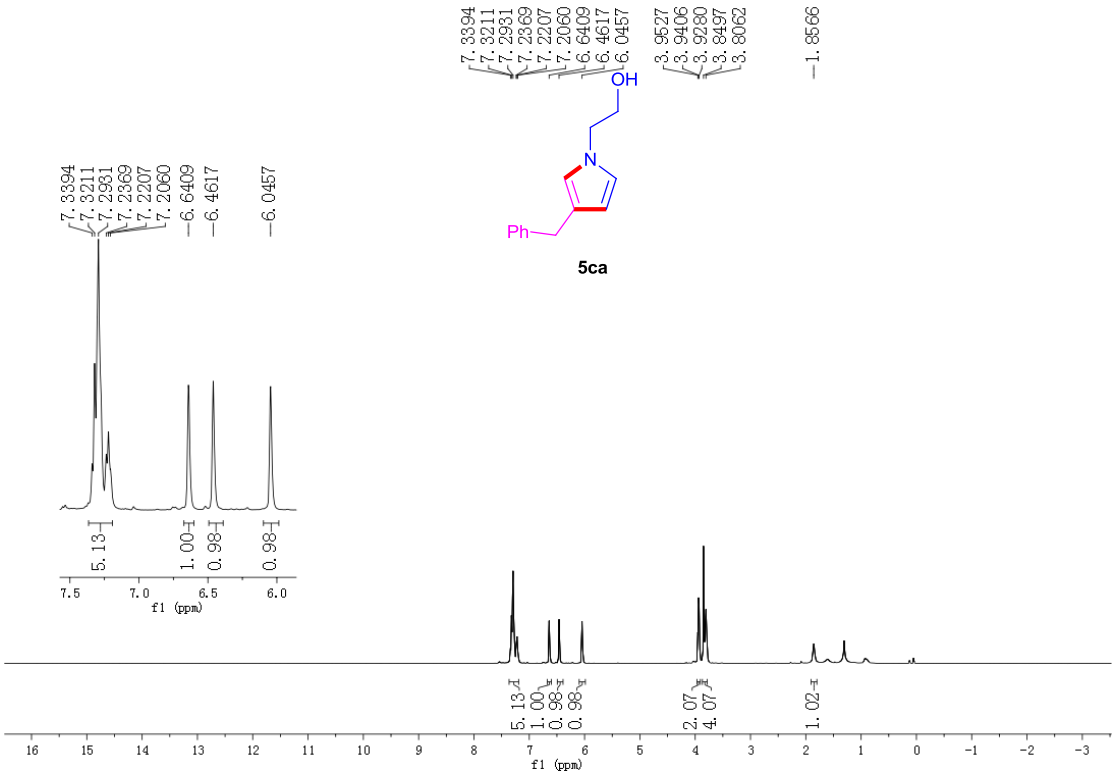


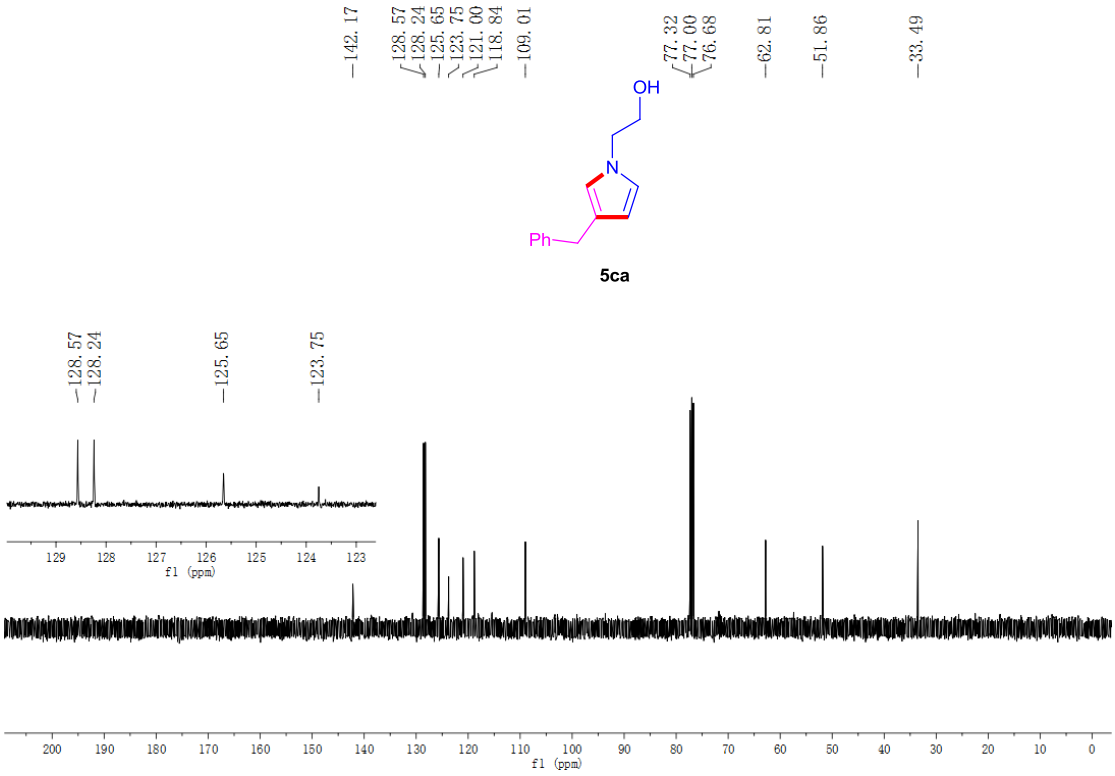
2-(2-(4-chlorophenyl)-1*H*-pyrrol-1-yl)ethanol (5ba):



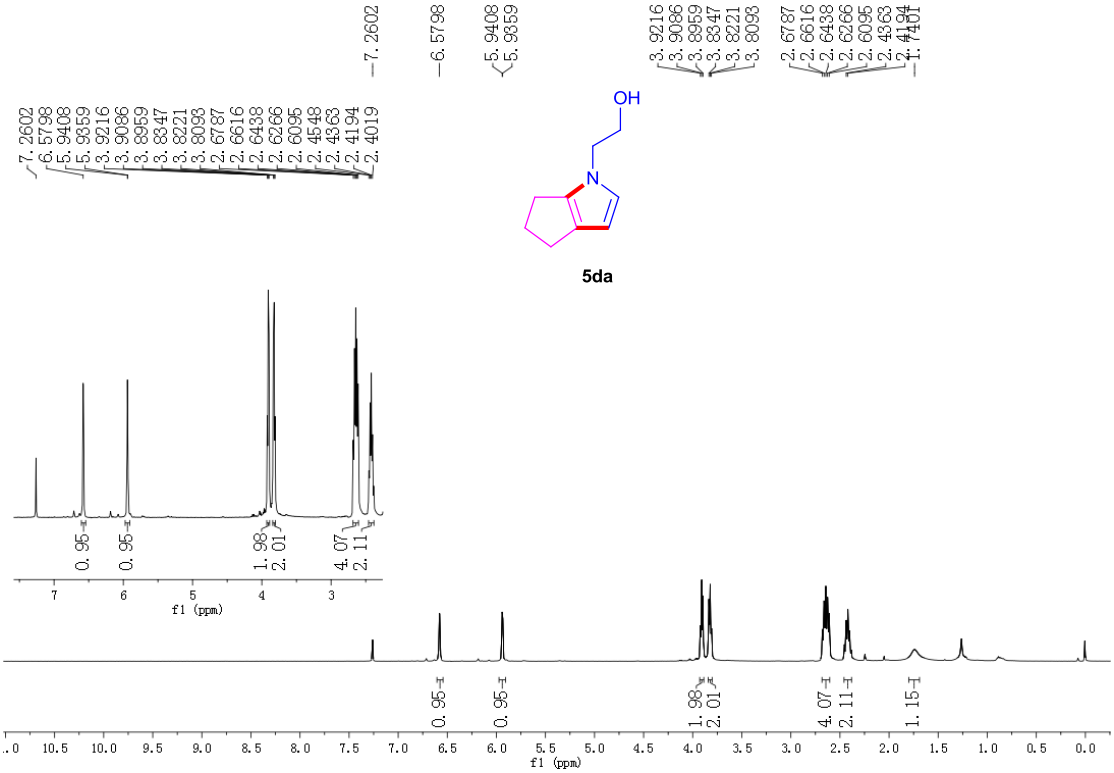


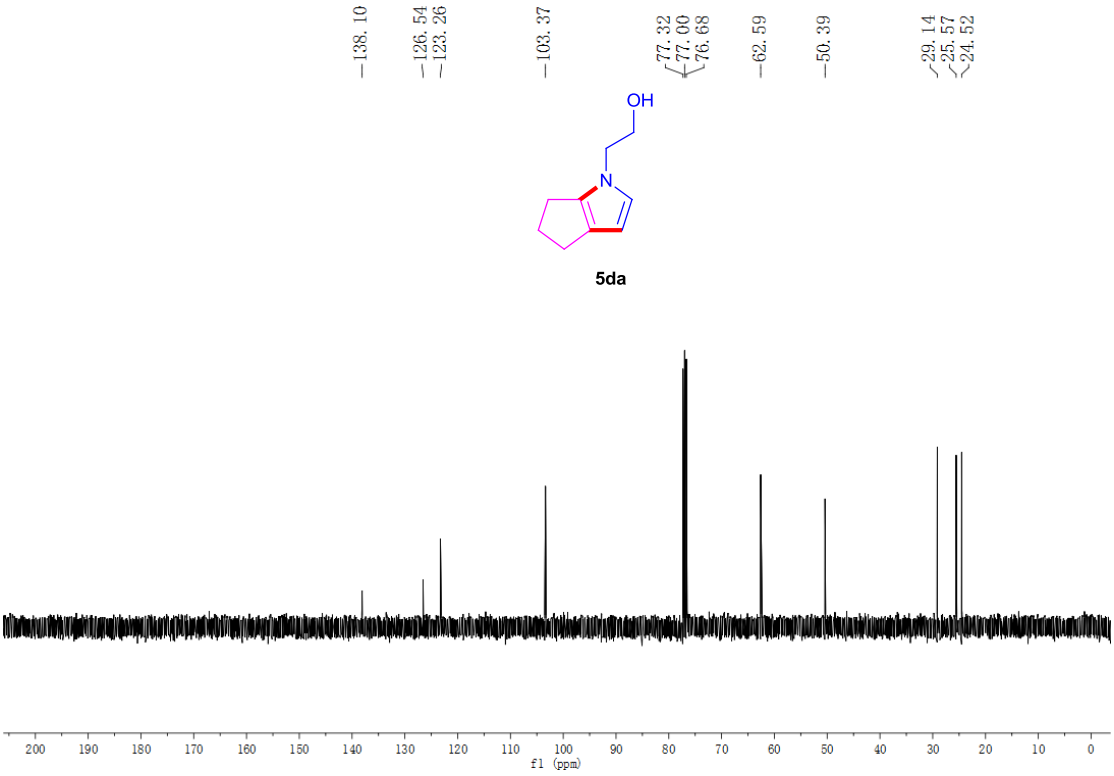
2-(3-benzyl-1*H*-pyrrol-1-yl)ethanol (5ca):



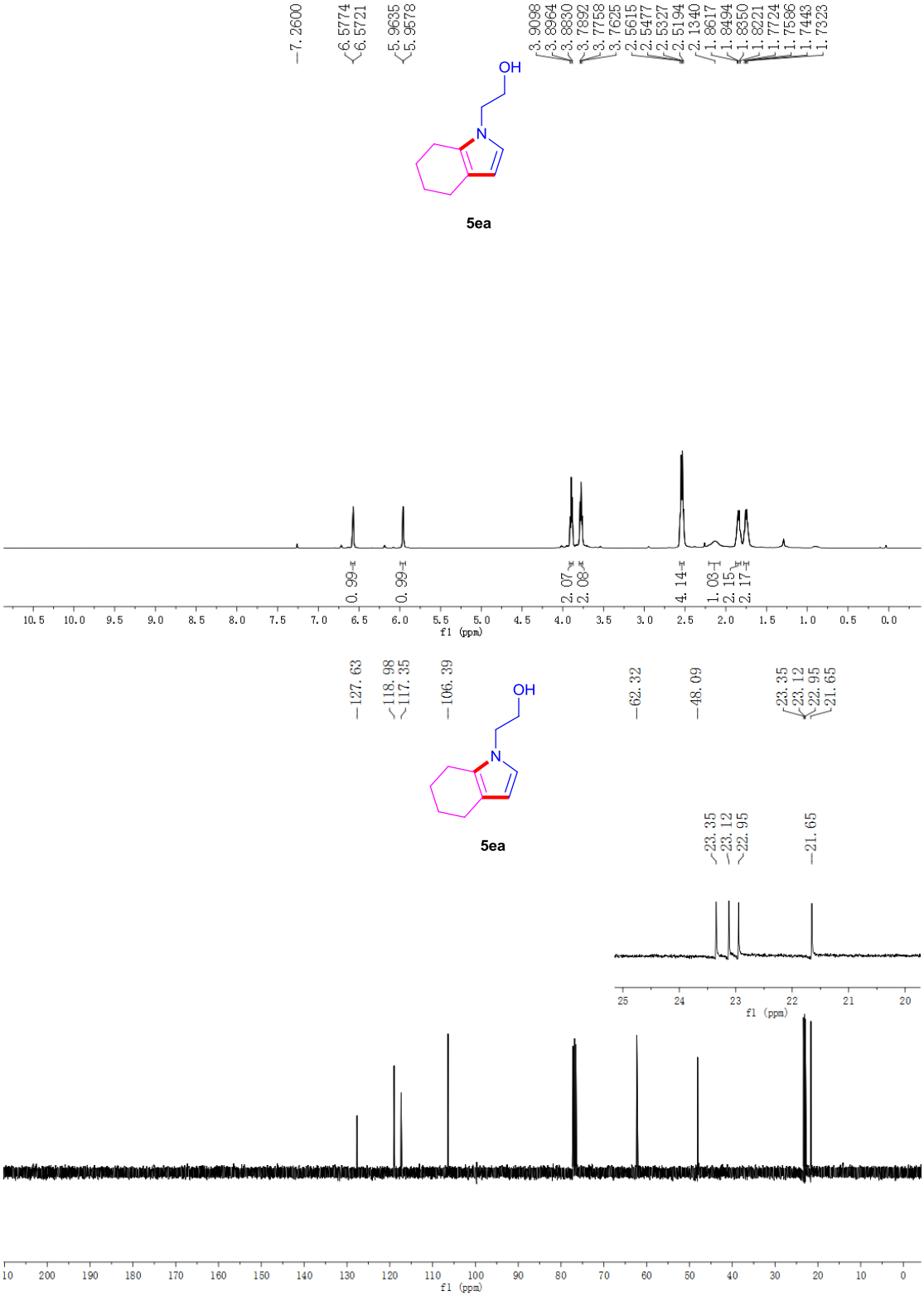


2-(5,6-dihydrocyclopenta[*b*]pyrrol-1(4*H*)-yl)ethanol (5da):

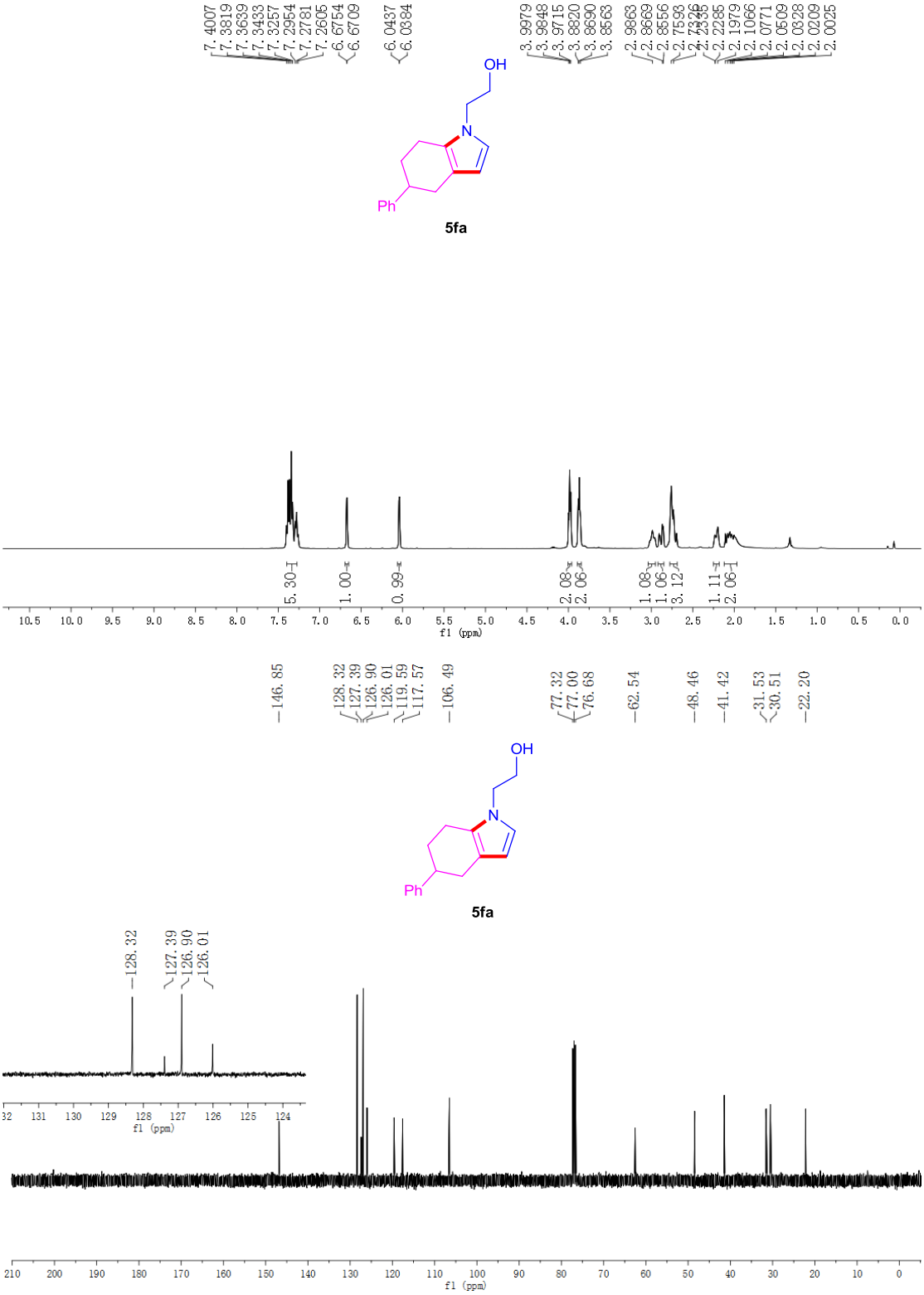




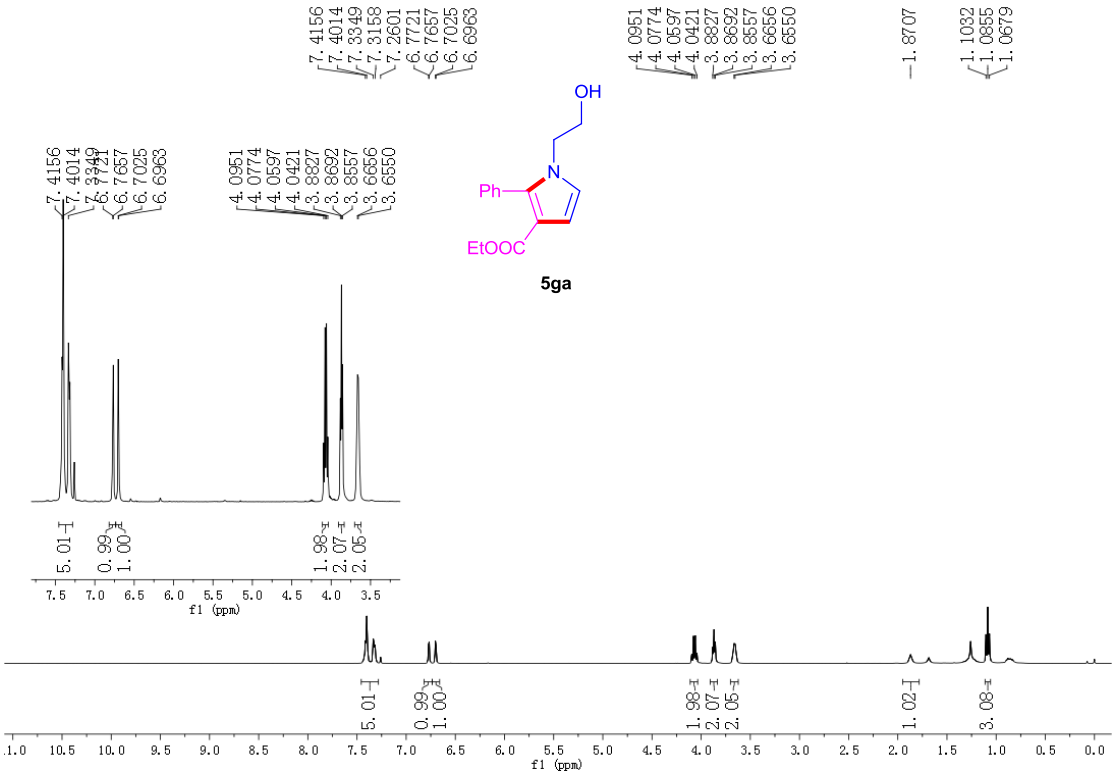
2-(4,5,6,7-tetrahydro-1*H*-indol-1-yl)ethanol (5ea):

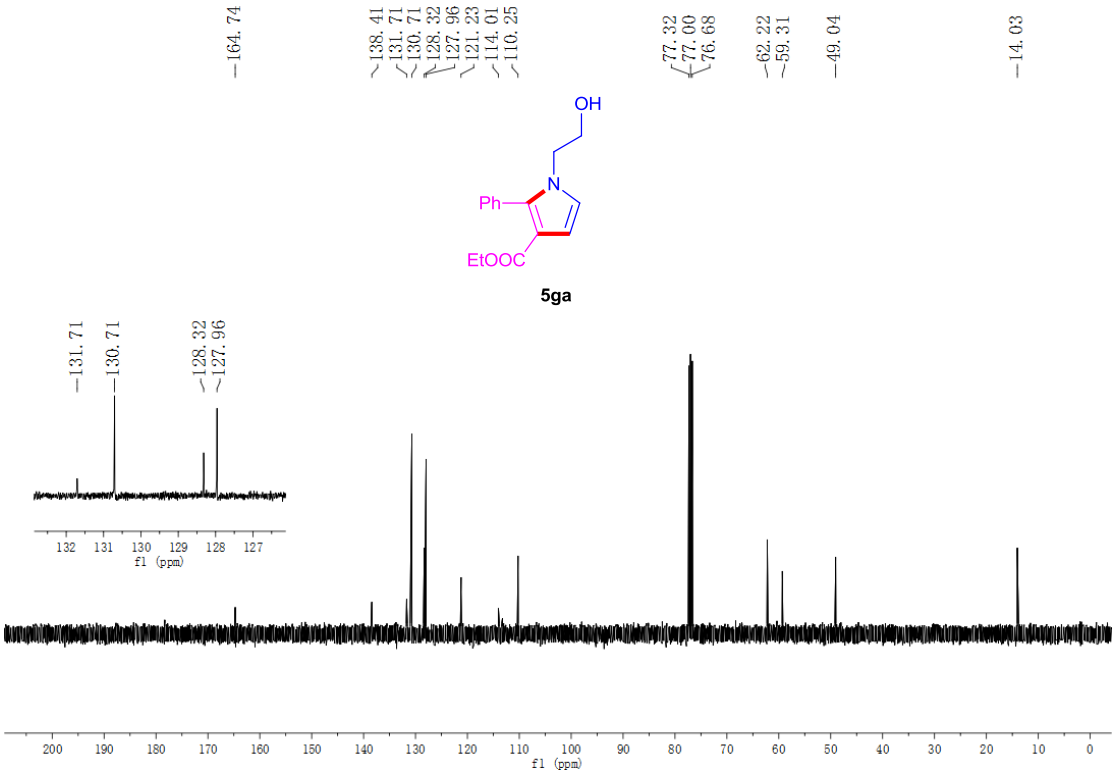


2-(5-phenyl-4,5,6,7-tetrahydro-1*H*-indol-1-yl)ethanol (5fa):

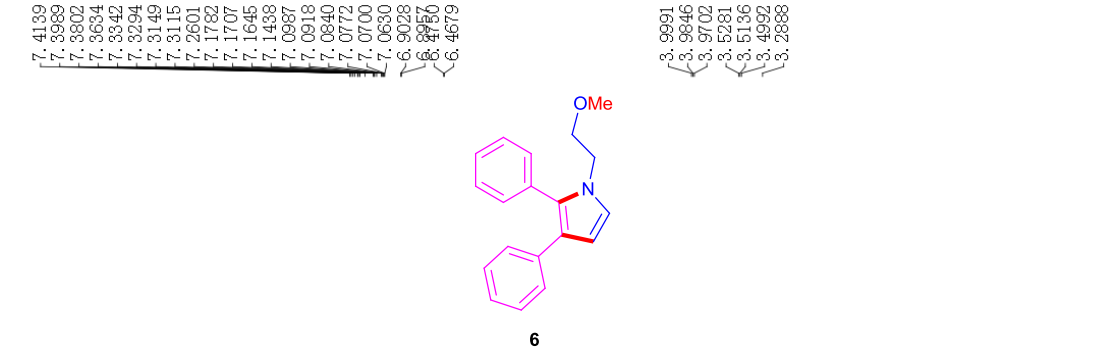


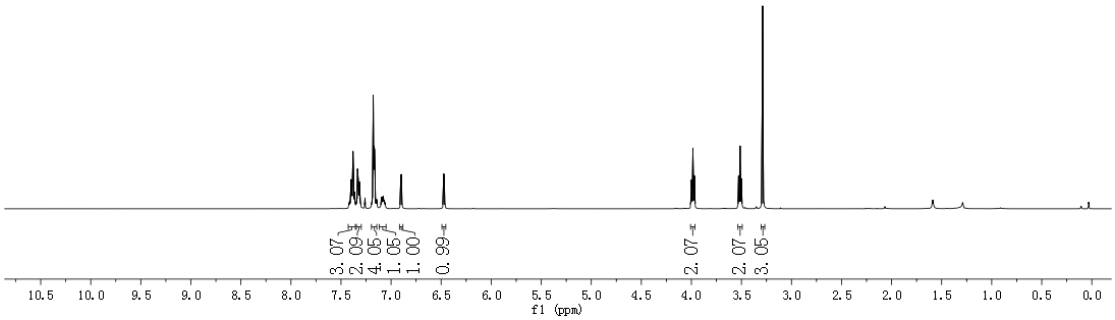
ethyl 1-(2-hydroxyethyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (5ga):

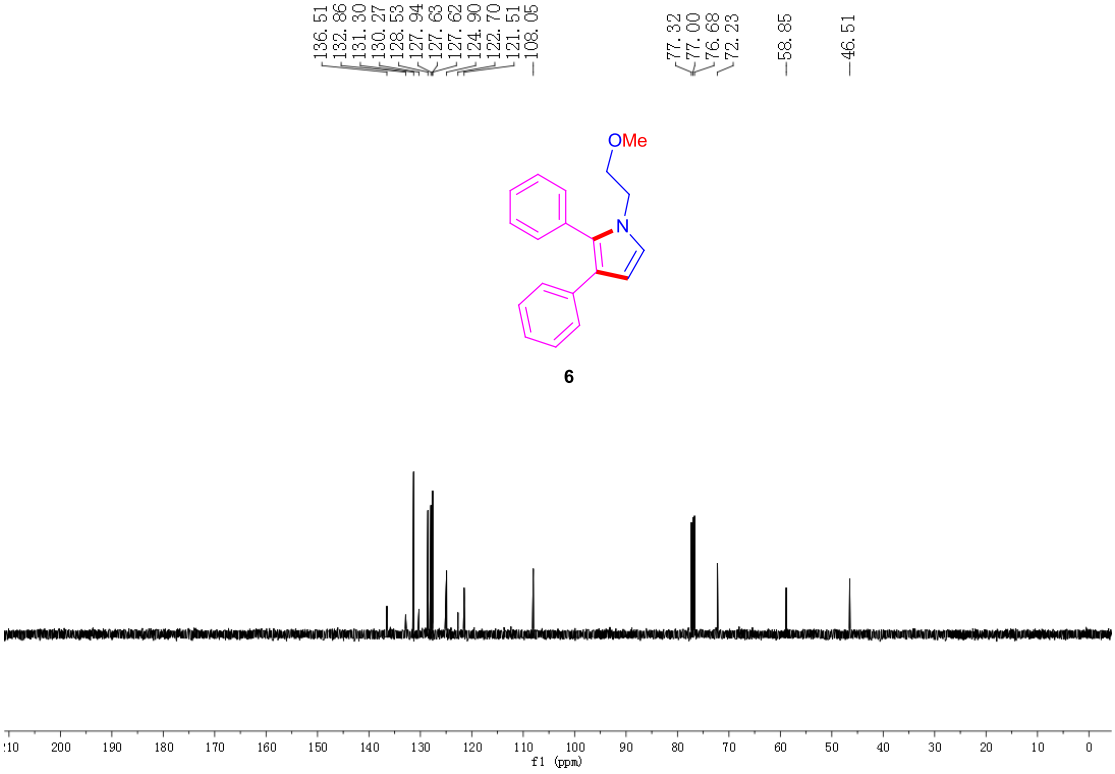




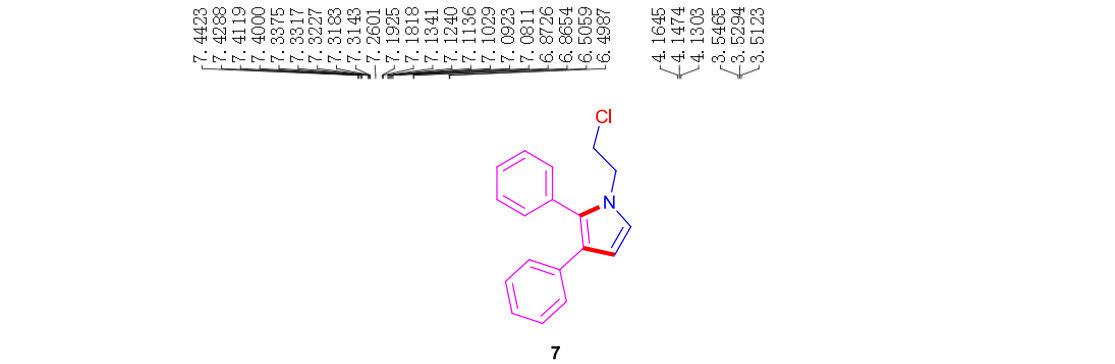
1-(2-methoxyethyl)-2,3-diphenyl-1*H*-pyrrole (6):

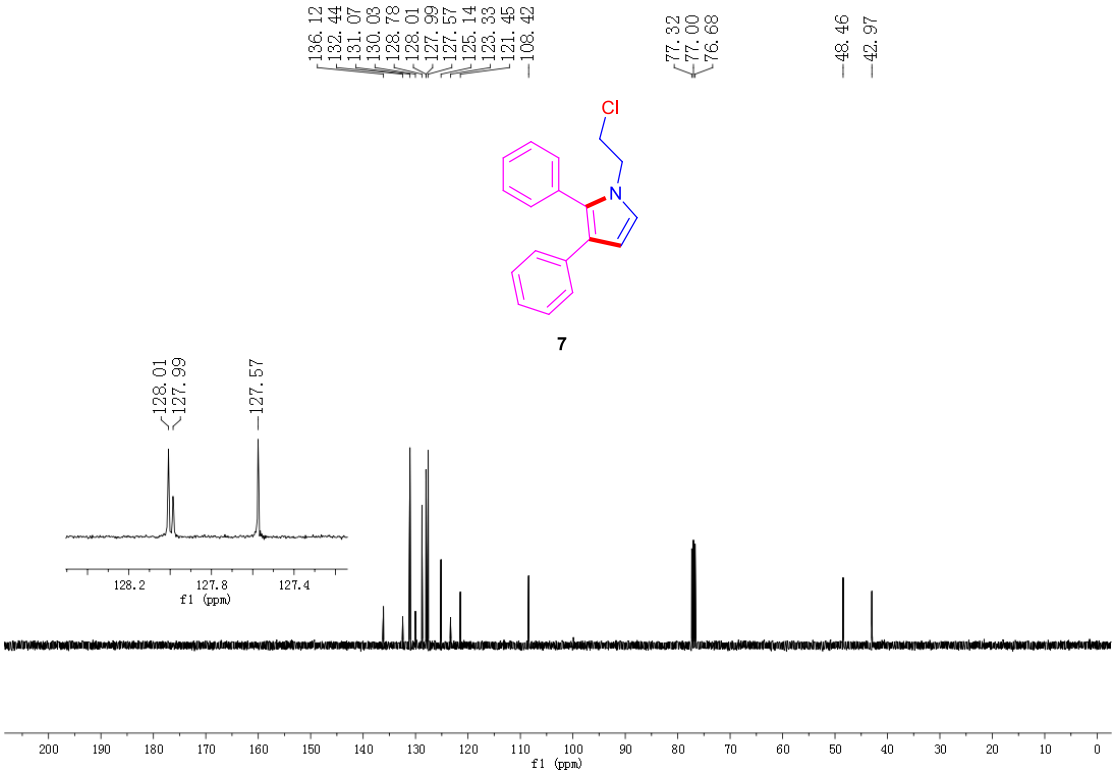
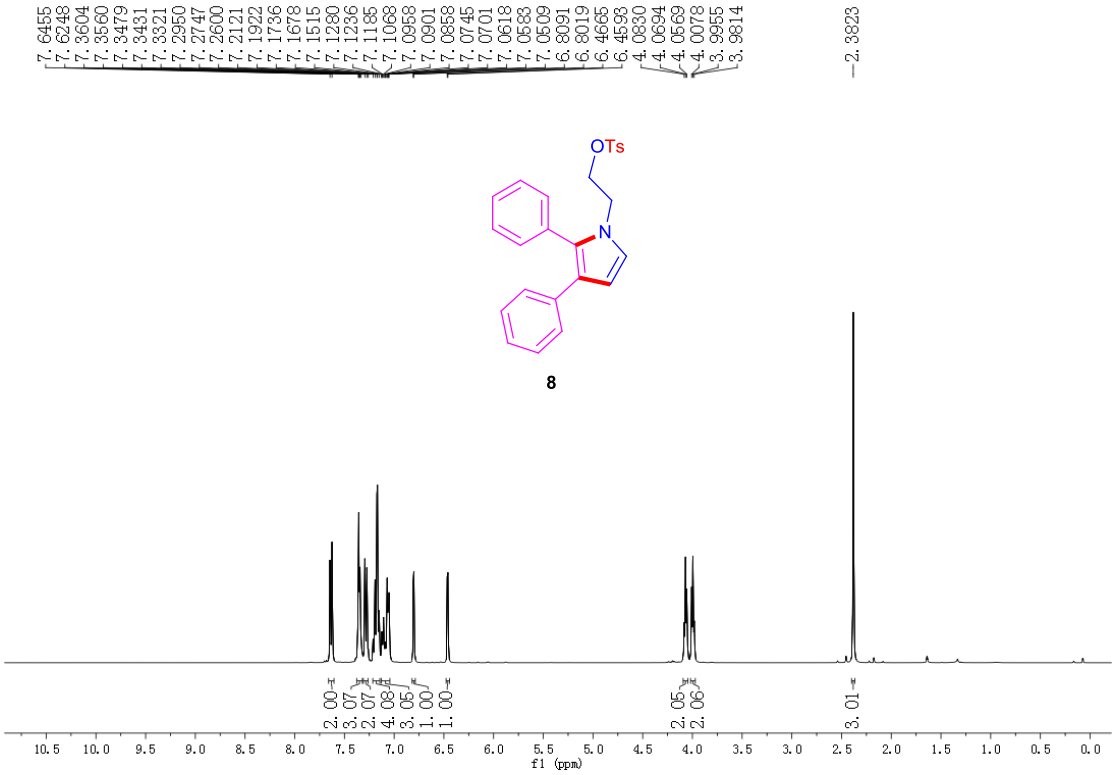
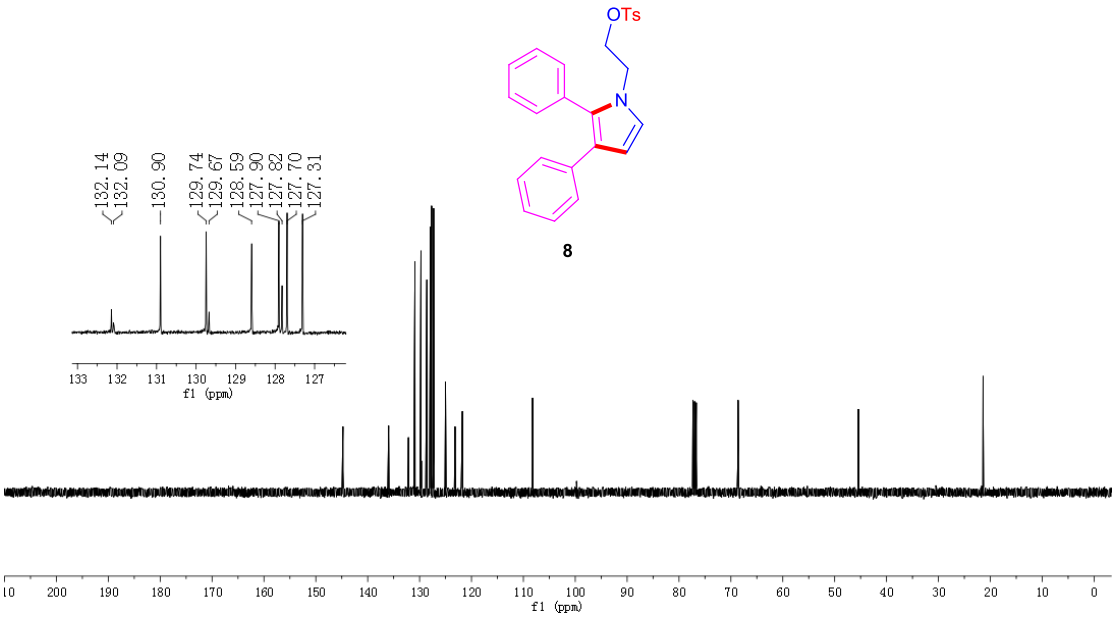






1-(2-chloroethyl)-2,3-diphenyl-1*H*-pyrrole (7):





2-(2,3-diphenyl-1*H*-pyrrol-1-yl)ethyl 4-methylbenzenesulfonate (8):