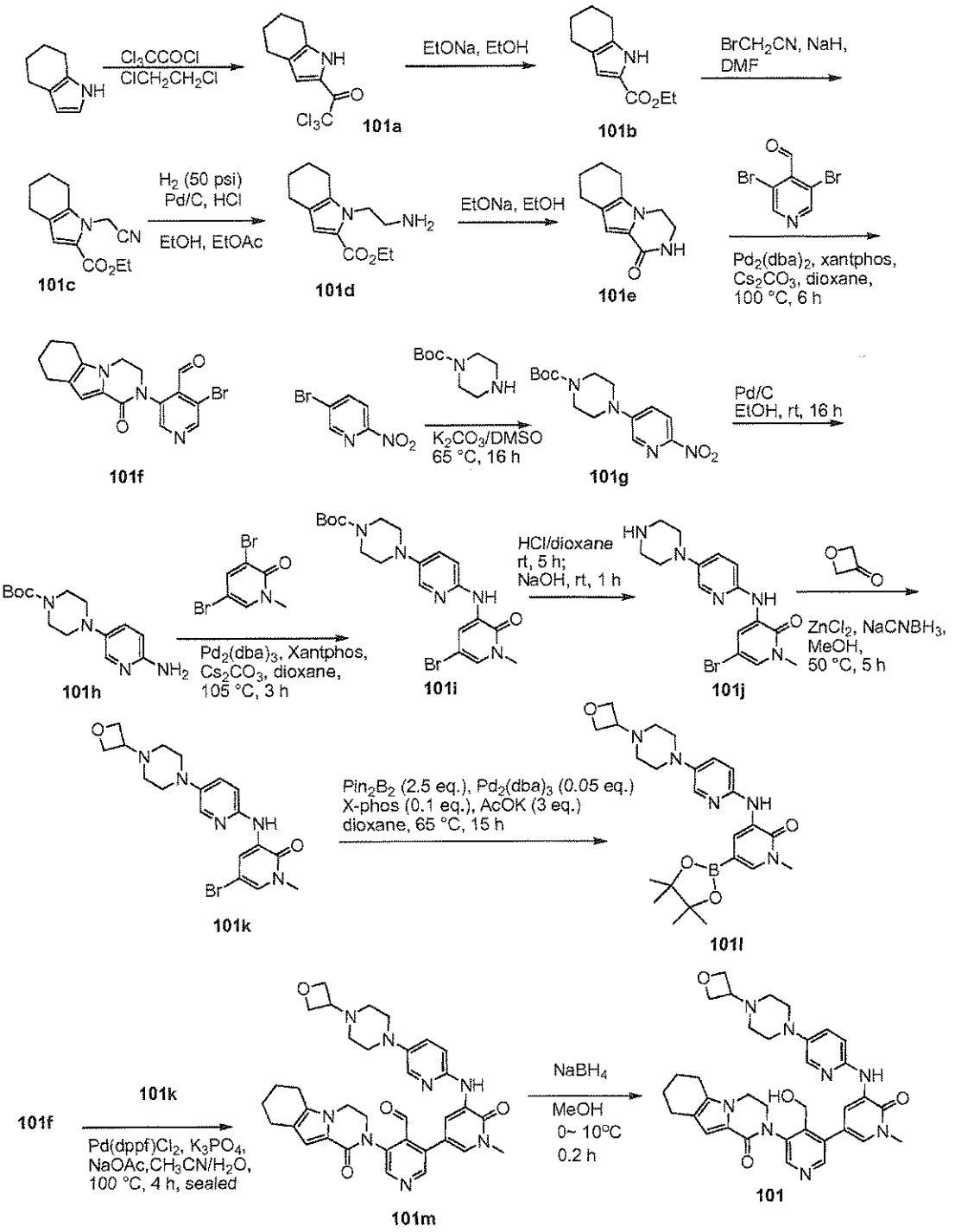

Cl3CCOCl
ClCH2CH2Cl
101a
EtONa, EtOH
101b
BrCH2CN, NaH, DMF
H2 (50 psi)
Pd/C, HCl
EtOH, EtOAc
101c
101d
EtONa, EtOH
101e
Pd2(dba)2, xantphos, Cs2CO3, dioxane, 100 °C, 6 h
101f
K2CO3/DMSO
65 °C, 16 h
101g
Pd/C
EtOH, rt, 16 h
101h
Pd2(dba)3, Xantphos, Cs2CO3, dioxane, 105 °C, 3 h
101i
HCl/dioxane
rt, 5 h;
NaOH, rt, 1 h
101j
ZnCl2, NaCNBH3, MeOH, 50 °C, 5 h
Pin2B2 (2.5 eq.), Pd2(dba)3 (0.05 eq.)
X-phos (0.1 eq.), AcOK (3 eq.)
dioxane, 65 °C, 15 h
101k
101l
101k
101f
Pd(dppf)Cl2, K3PO4, NaOAc,CH3CN/H2O, 100 °C, 4 h, sealed
101m
NaBH4
MeOH
0~ 10°C
0.2 h
101

Figure 1

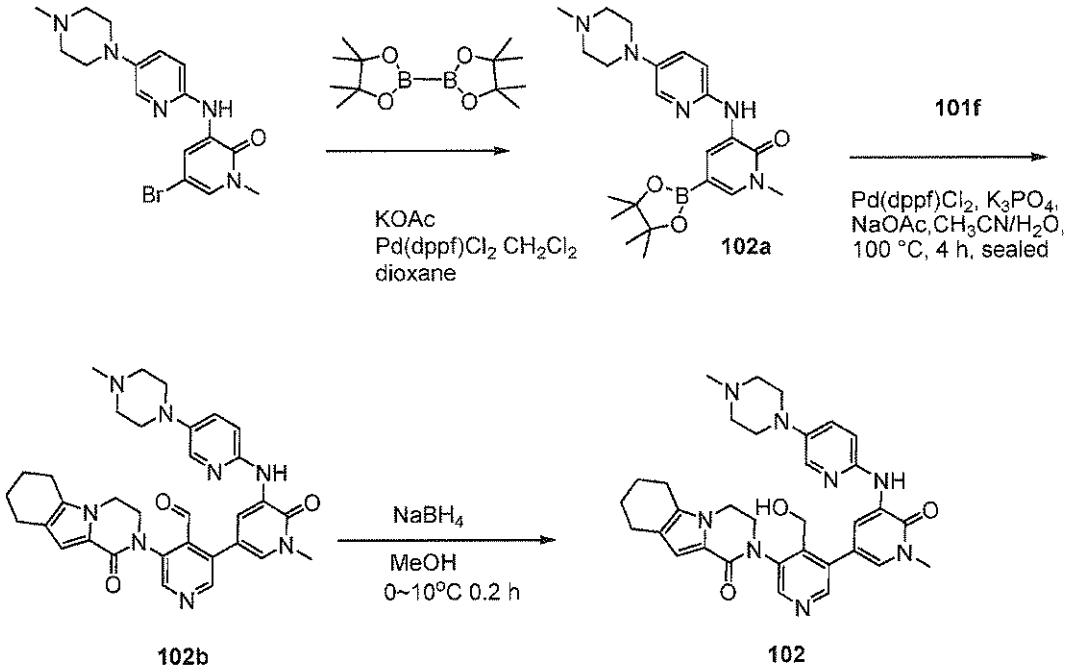


Figure 2

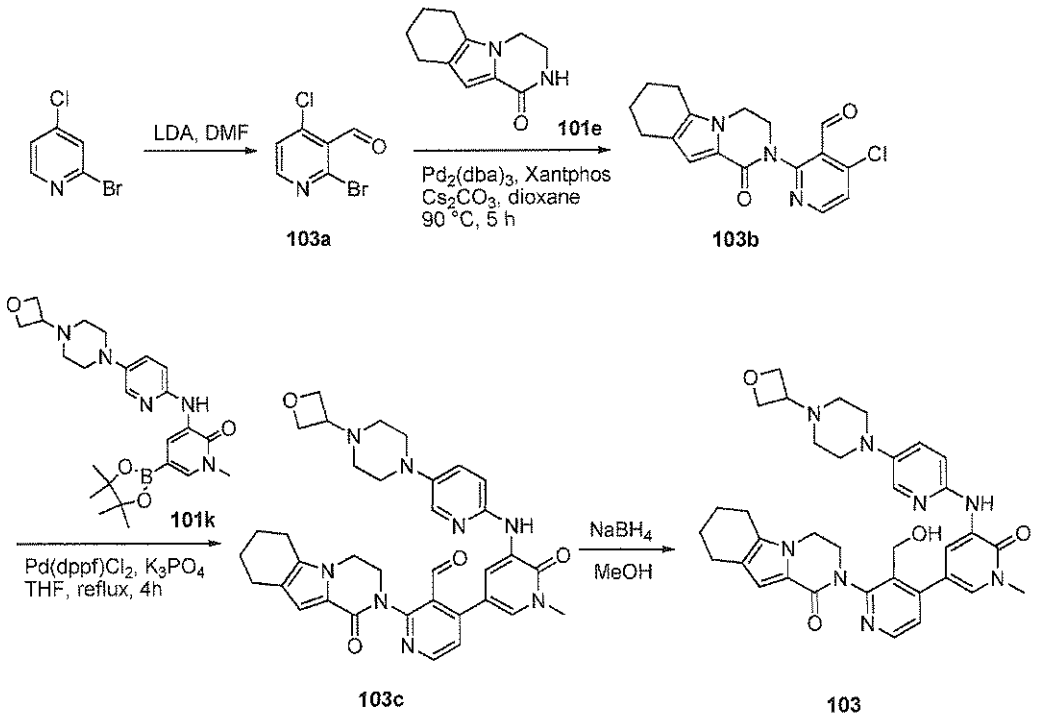


Figure 3

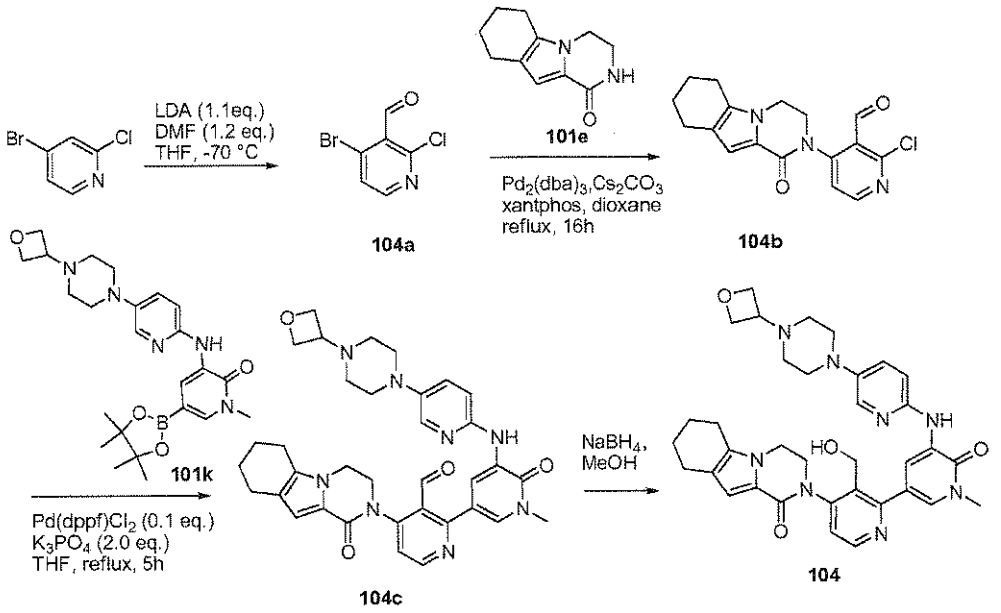


Figure 4

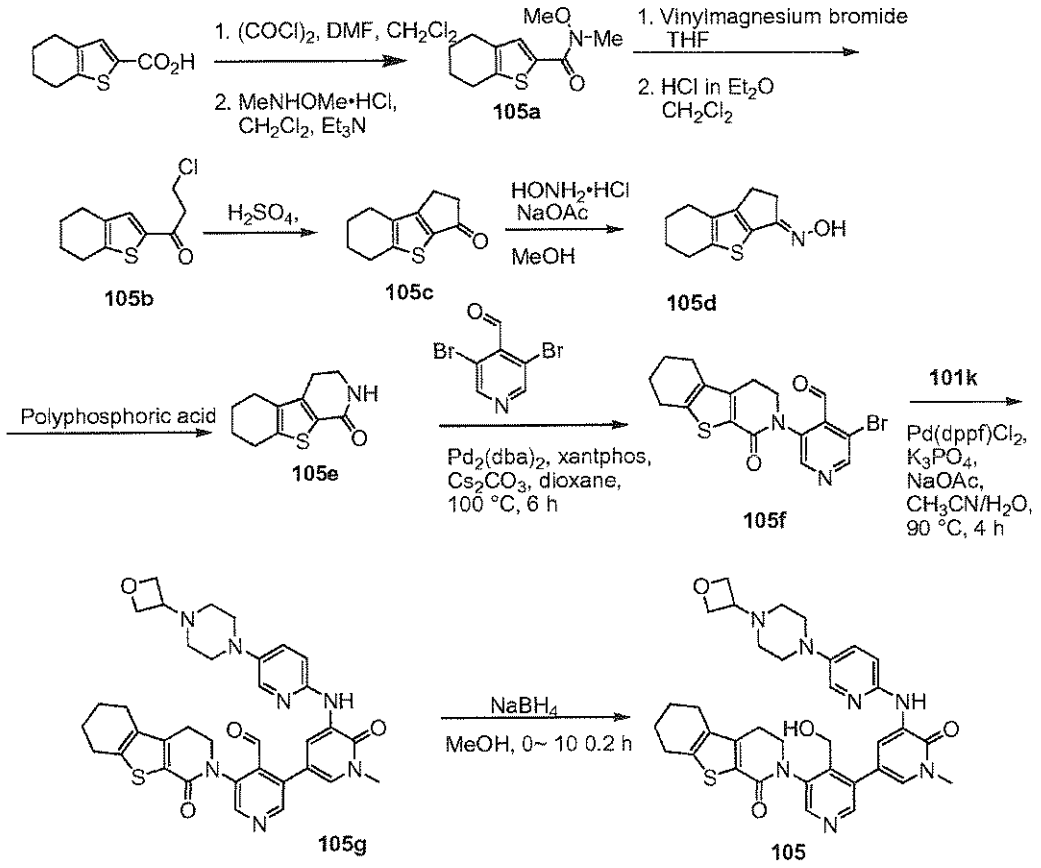


Figure 5

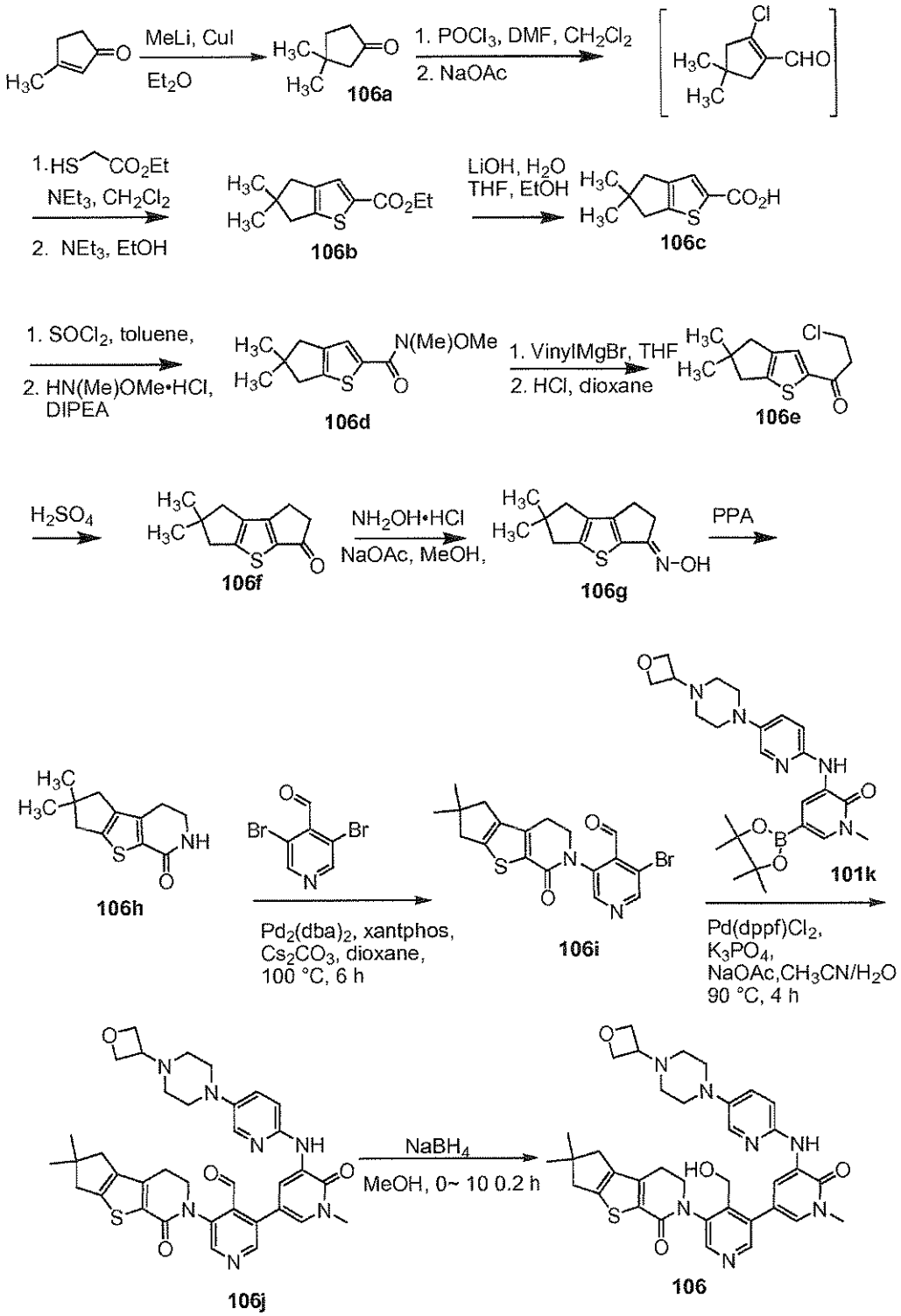
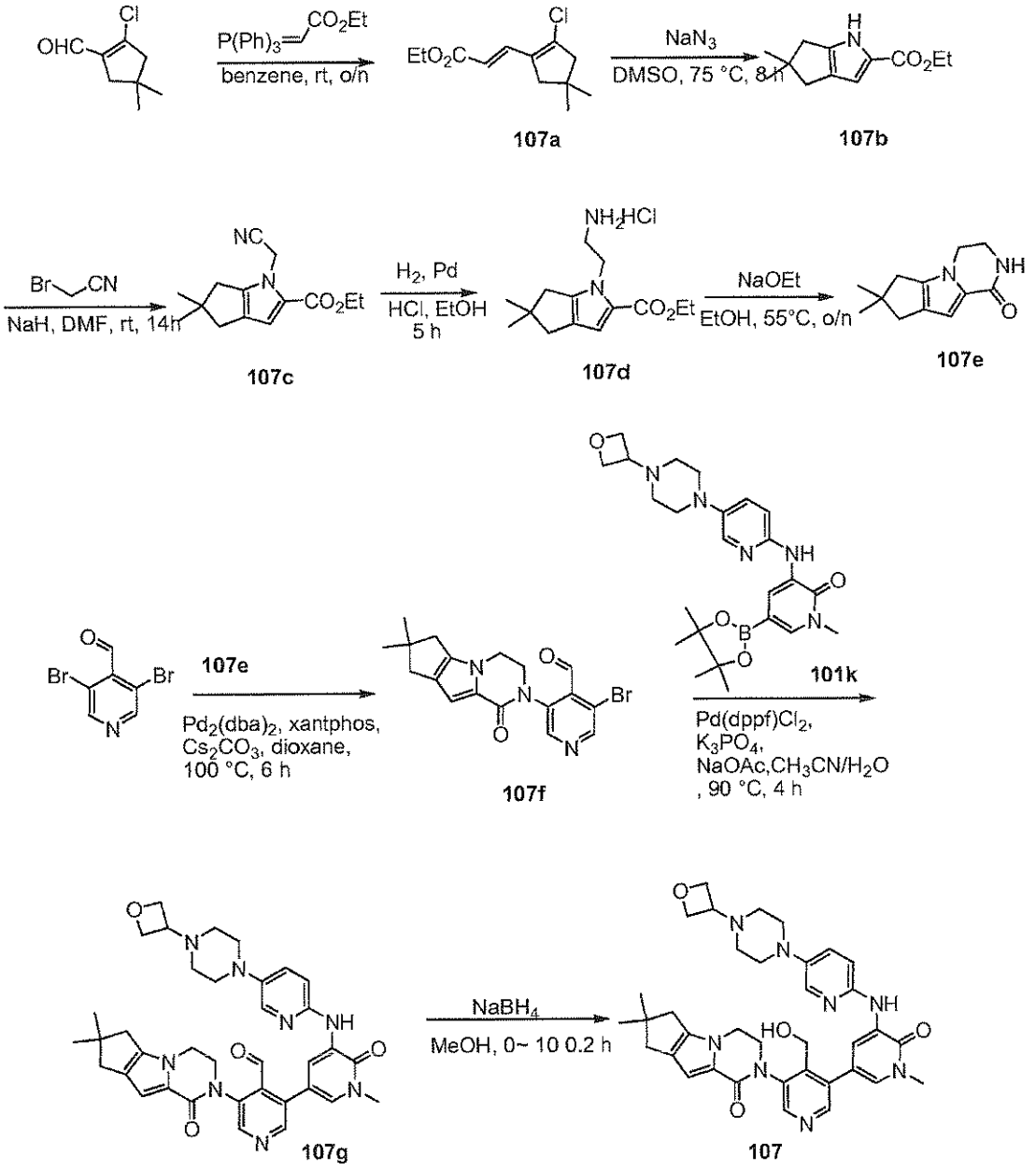

MeLi, CuI
Et2O
106a
1. POCl3, DMF, CH2Cl2
2. NaOAc
1. HS CO2Et
NEt3, CH2Cl2
2. NEt3, EtOH
106b
LiOH, H2O
THF, EtOH
106c
1. SOCl2, toluene,
2. HN(Me)OMe•HCl,
DIPEA
106d
1. VinylMgBr, THF
2. HCl, dioxane
106e
H2SO4
106f
NH2OH•HCl
NaOAc, MeOH,
106g
PPA
106h
Pd2(dba)2, xantphos,
Cs2CO3, dioxane,
100 °C, 6 h
106i
101k
Pd(dppf)Cl2,
K3PO4,
NaOAc,CH3CN/H2O
90 °C, 4 h
NaBH4
MeOH, 0~ 10 0.2 h
106j
106

Figure 6



OHC
Cl
P(Ph)3
CO2Et
benzene, rt, o/n
EtO2C
Cl
107a
NaN3
DMSO, 75 °C, 8 h
H
N
CO2Et
107b
Br
CN
NaH, DMF, rt, 14h
NC
N
CO2Et
107c
H2, Pd
HCl, EtOH
5 h
NH2HCl
N
CO2Et
107d
NaOEt
EtOH, 55°C, o/n
N
NH
O
107e
O
Br
Br
N
107e
Pd2(dba)2, xantphos,
Cs2CO3, dioxane,
100 °C, 6 h
N
N
O
O
Br
N
107f
O
N
N
N
NH
O
O
B
O
N
101k
Pd(dppf)Cl2,
K3PO4,
NaOAc,CH3CN/H2O
, 90 °C, 4 h
O
N
N
N
NH
O
O
N
N
O
N
107g
NaBH4
MeOH, 0~ 10 0.2 h
O
N
N
N
NH
HO
O
N
N
O
N
107

Figure 7

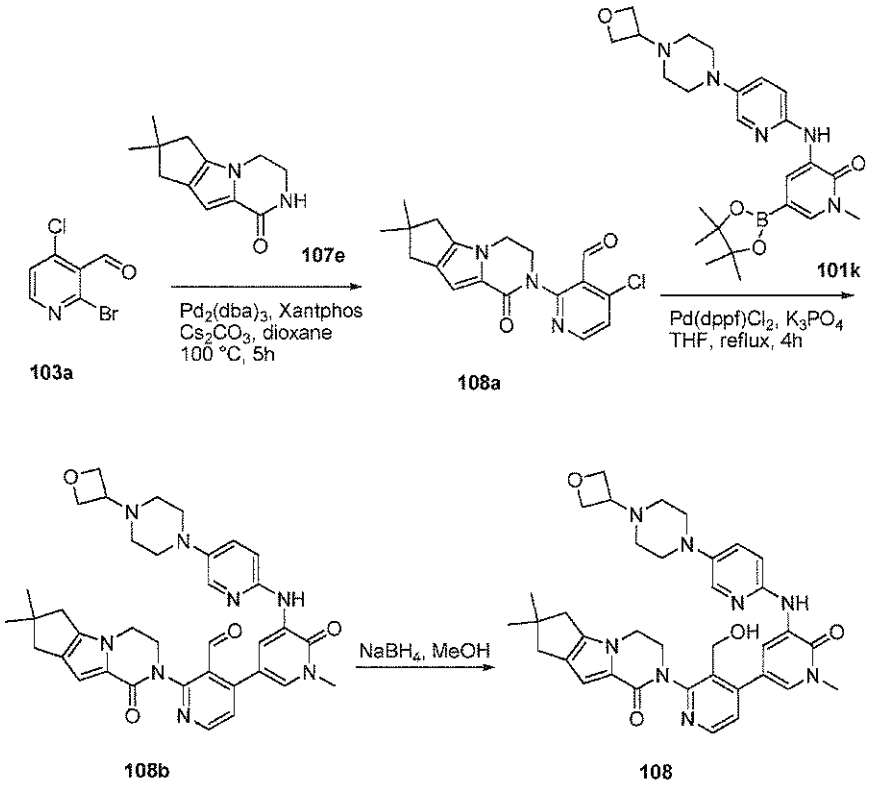


Figure 8

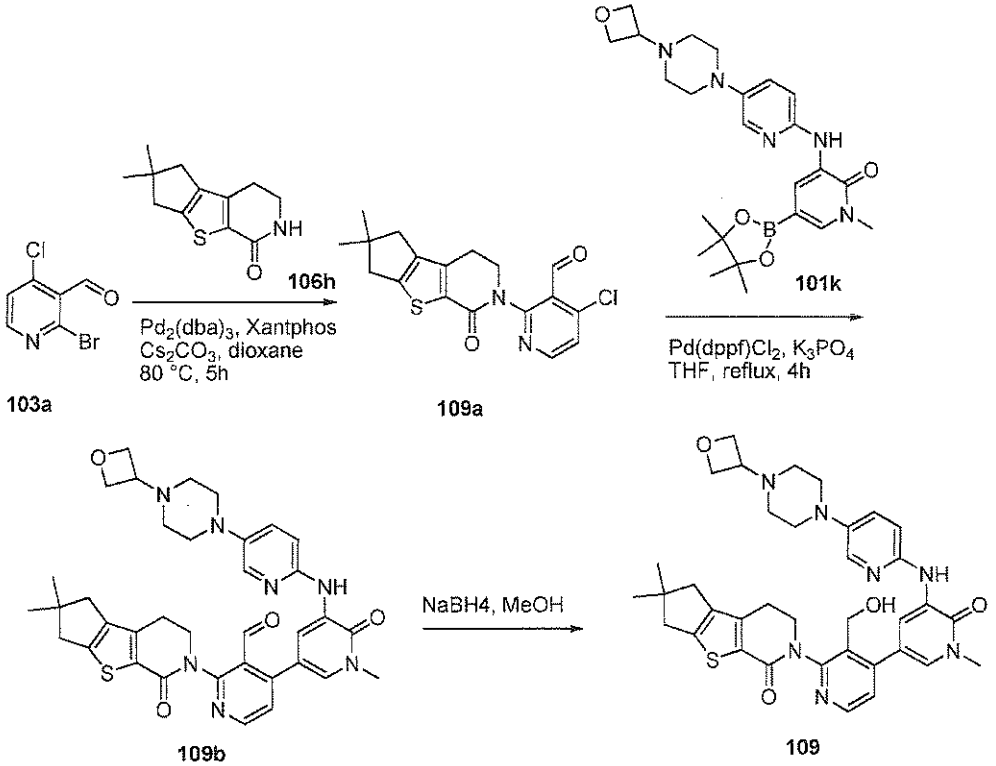


Figure 9

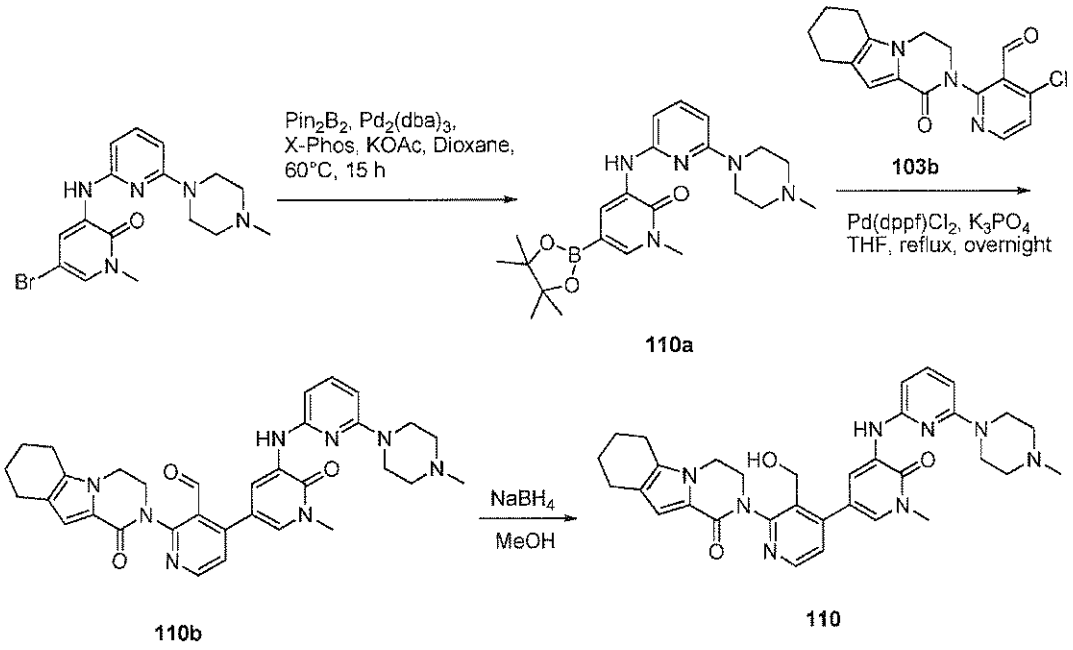


Figure 10

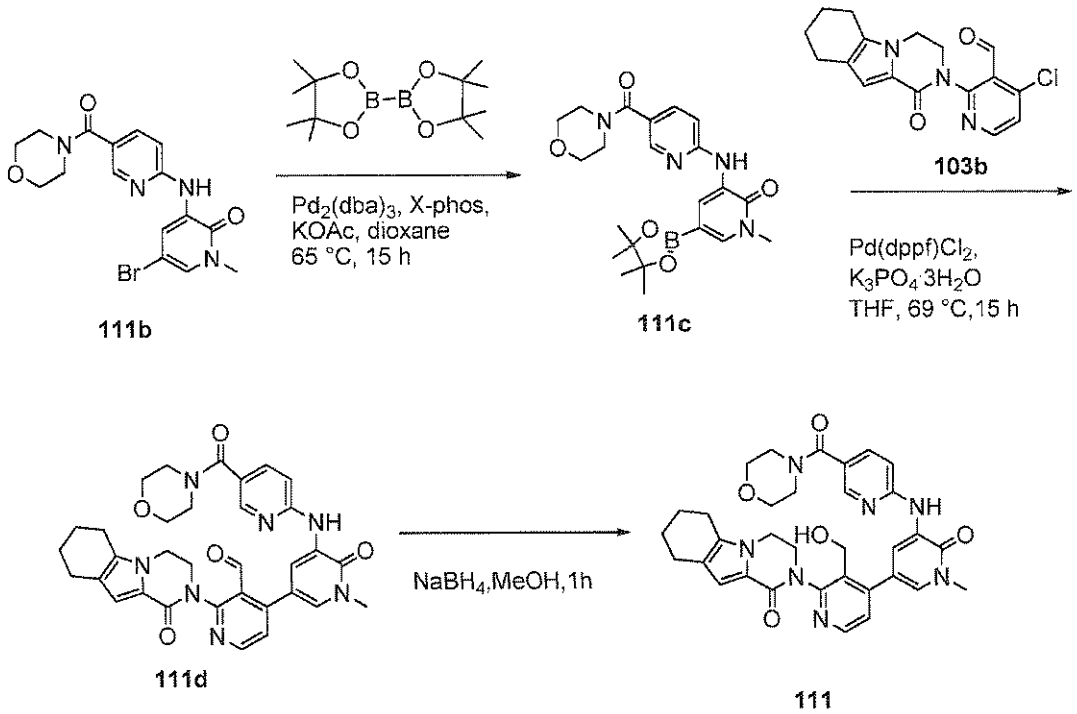


Figure 11

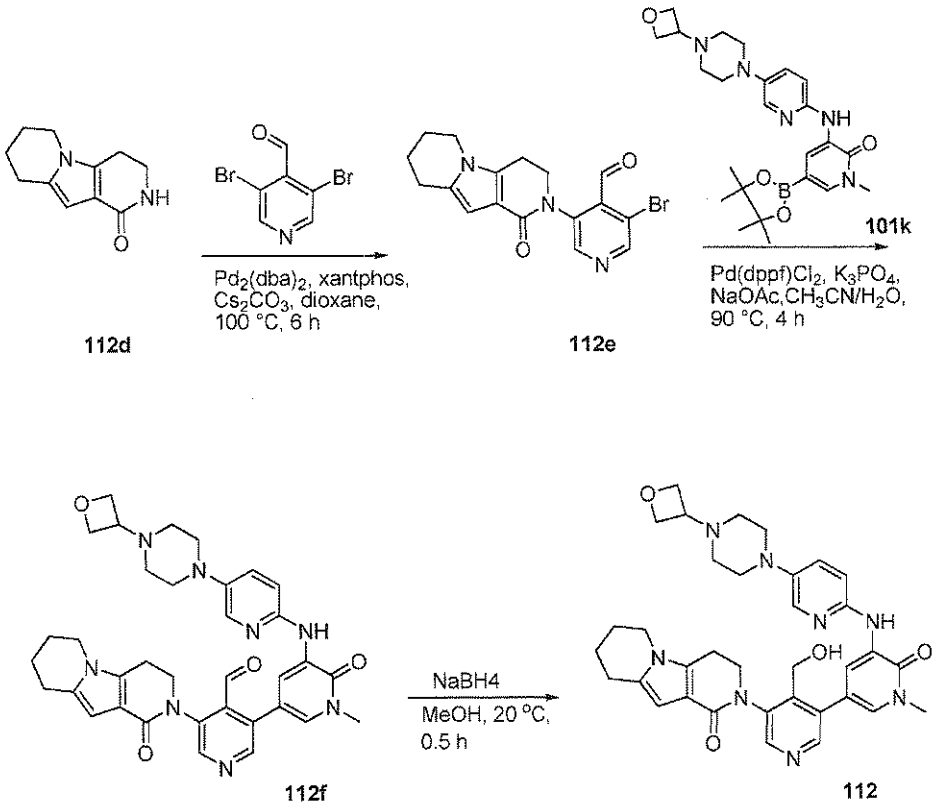

Br
Br
Pd2(dba)3, xantphos,
Cs2CO3, dioxane,
100 °C, 6 h
Pd(dppf)Cl2, K3PO4,
NaOAc,CH3CN/H2O,
90 °C, 4 h
101k
112d
112e
NaBH4
MeOH, 20 °C,
0.5 h
112f
112

Figure 12

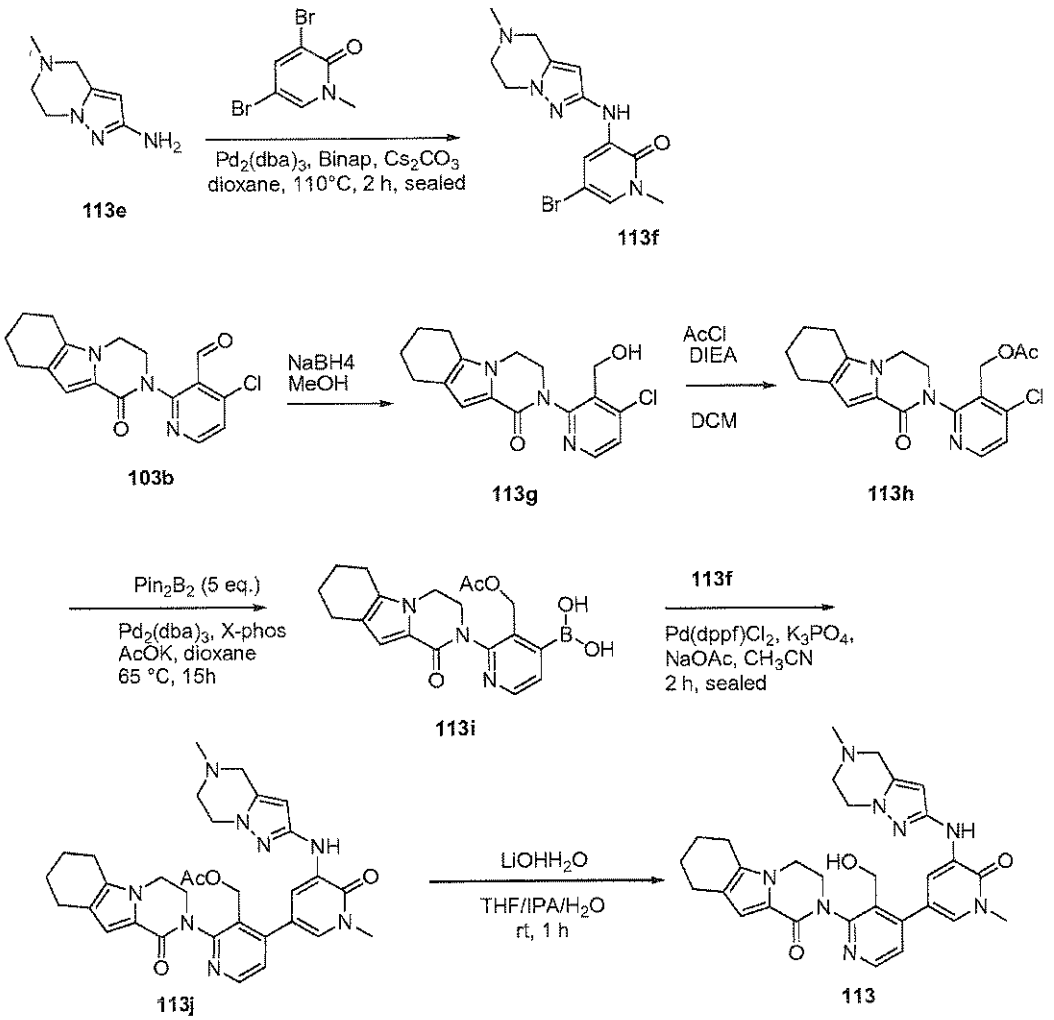

Br
Br
NH2
Pd2(dba)3, Binap, Cs2CO3
dioxane, 110°C, 2 h, sealed
NH
Br
113e
113f
NaBH4
MeOH
AcCl
DIEA
DCM
Cl
OH
OAc
103b
113g
113h
Pin2B2 (5 eq.)
Pd2(dba)3, X-phos
AcOK, dioxane
65 °C, 15h
AcO
OH
B
OH
113f
Pd(dppf)Cl2, K3PO4,
NaOAc, CH3CN
2 h, sealed
113i
LiOHH2O
THF/IPA/H2O
rt, 1 h
HO
113j
113

Figure 13

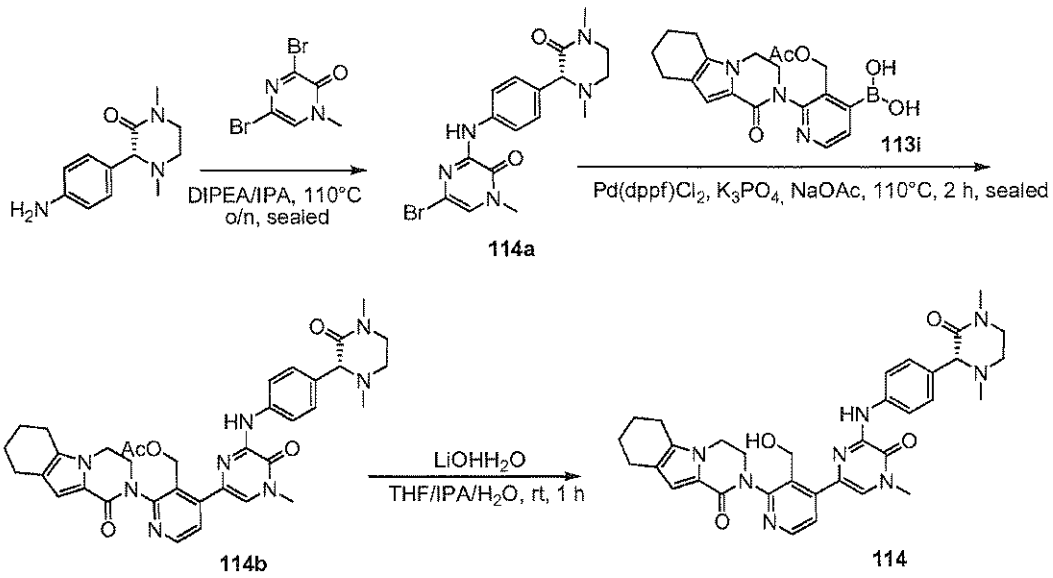


Figure 14

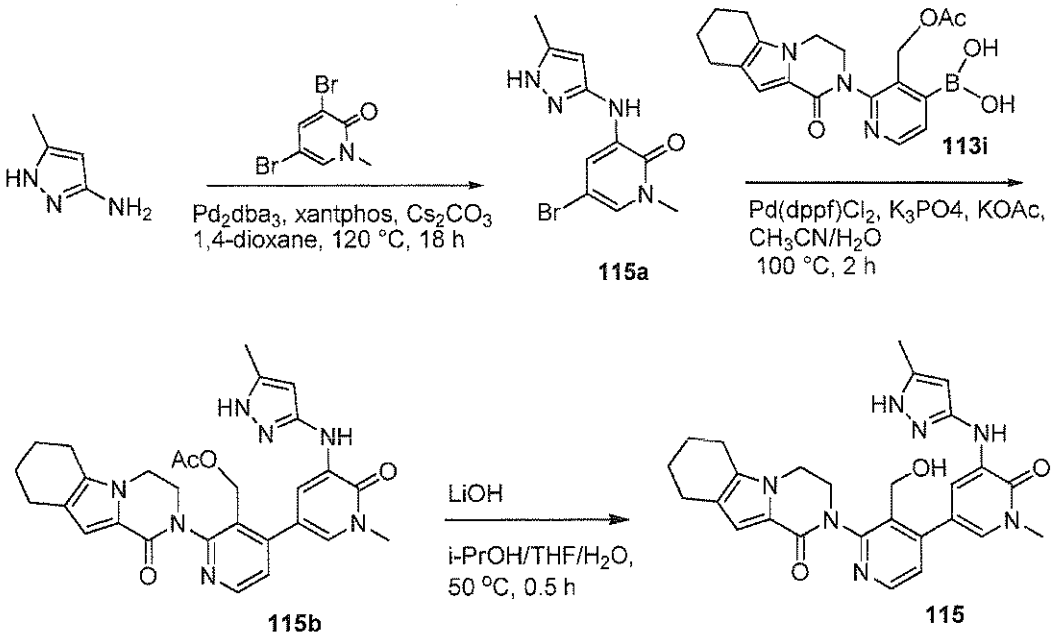
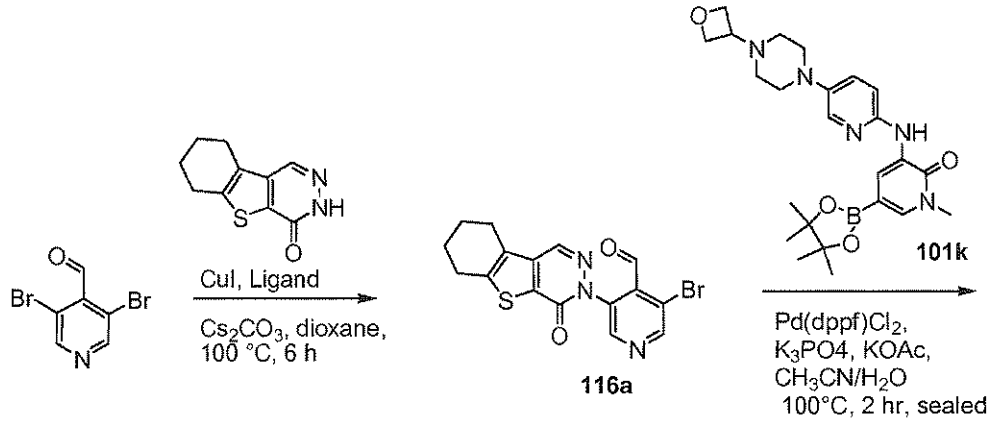


Figure 15


CuI, Ligand
Cs_2CO_3, dioxane,
100 °C, 6 h
116a
101k
$Pd(dppf)Cl_2$,
K_3PO4, KOAc,
CH_3CN/H_2O
100°C, 2 hr, sealed
Ligand =4,7-dimethoxy-1,10-phenanthroline

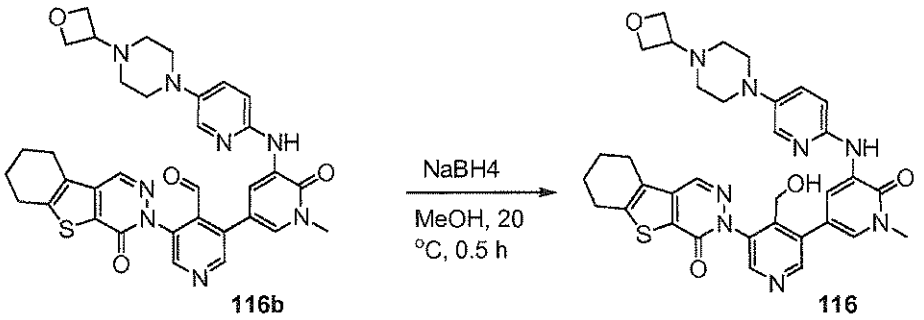

NaBH4
MeOH, 20
°C, 0.5 h
116b
116

Figure 16

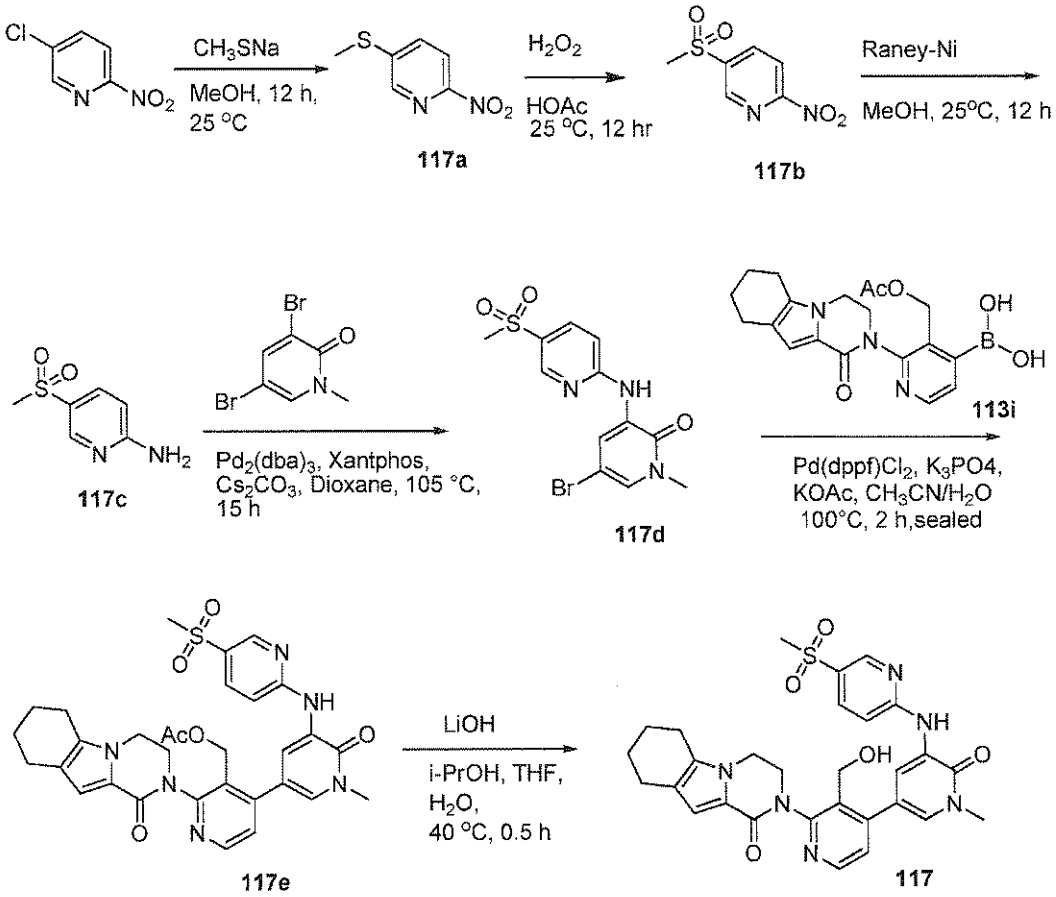

CH3SNa
MeOH, 12 h,
25 °C
H2O2
HOAc
25 °C, 12 hr
Raney-Ni
MeOH, 25°C, 12 h
117a
117b
117c
Pd2(dba)3, Xantphos,
Cs2CO3, Dioxane, 105 °C,
15 h
117d
113i
Pd(dppf)Cl2, K3PO4,
KOAc, CH3CN/H2O
100°C, 2 h,sealed
LiOH
i-PrOH, THF,
H2O,
40 °C, 0.5 h
117e
117

Figure 17

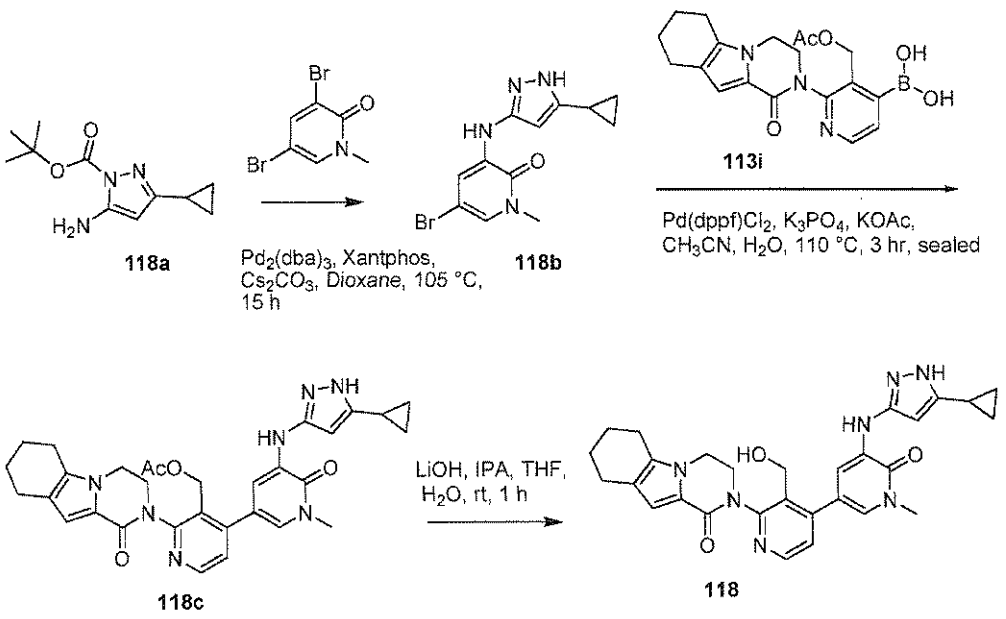


Figure 18

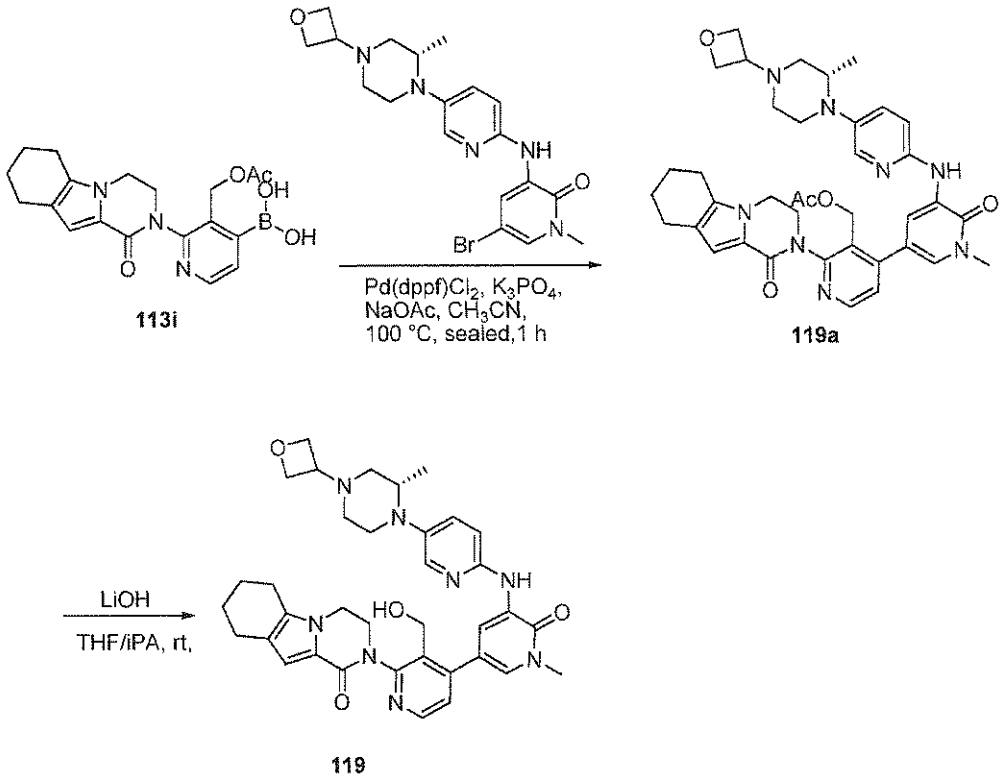


Figure 19

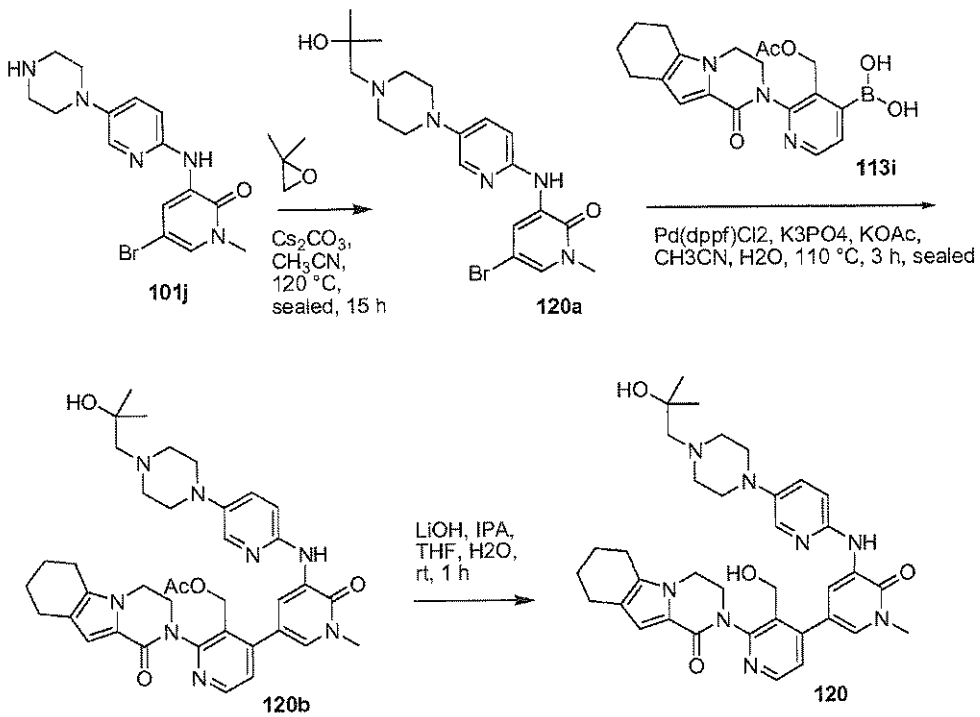


Figure 20

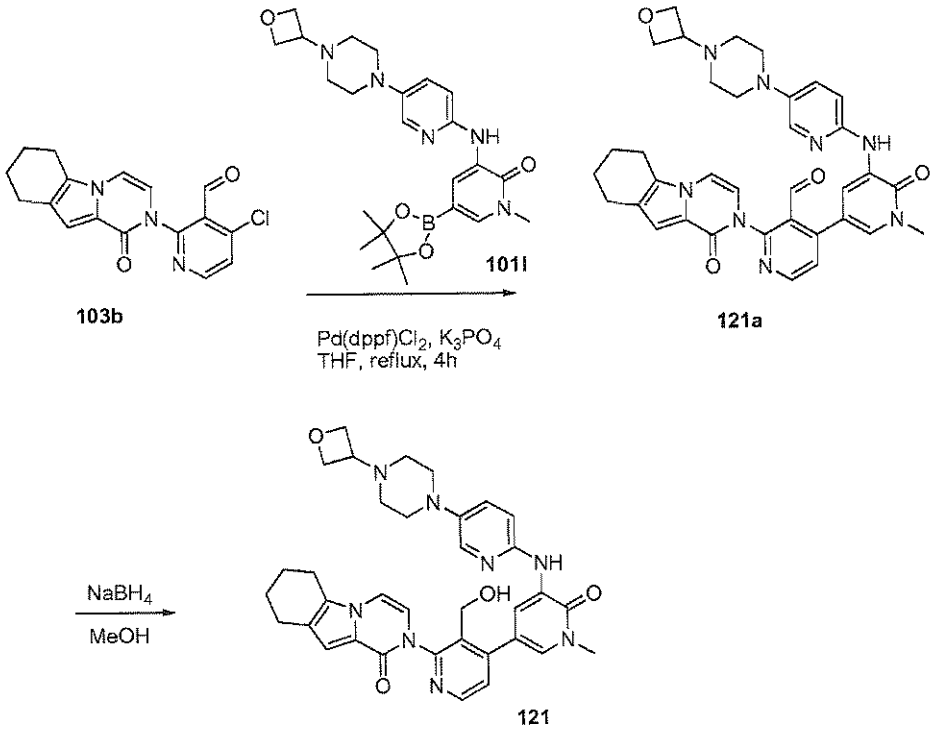


Figure 21

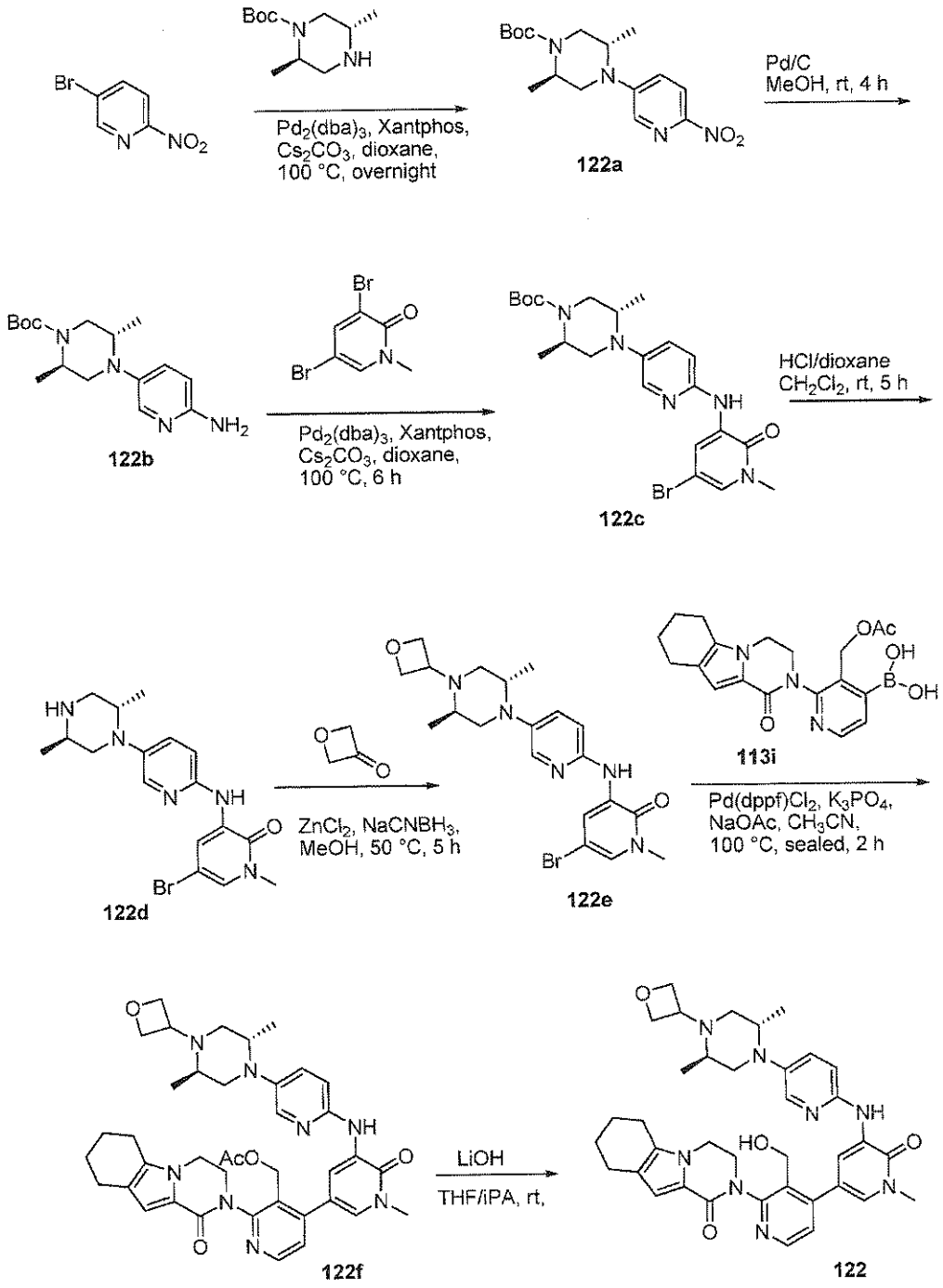

Boc
NH
Br
NO2
Pd2(dba)3, Xantphos,
Cs2CO3, dioxane,
100 °C, overnight
122a
Pd/C
MeOH, rt, 4 h
NH2
122b
Pd2(dba)3, Xantphos,
Cs2CO3, dioxane,
100 °C, 6 h
122c
HCl/dioxane
CH2Cl2, rt, 5 h
HN
122d
ZnCl2, NaCNBH3,
MeOH, 50 °C, 5 h
122e
OAc
OH
B
OH
113i
Pd(dppf)Cl2, K3PO4,
NaOAc, CH3CN,
100 °C, sealed, 2 h
AcO
122f
LiOH
THF/iPA, rt,
HO
122

Figure 22

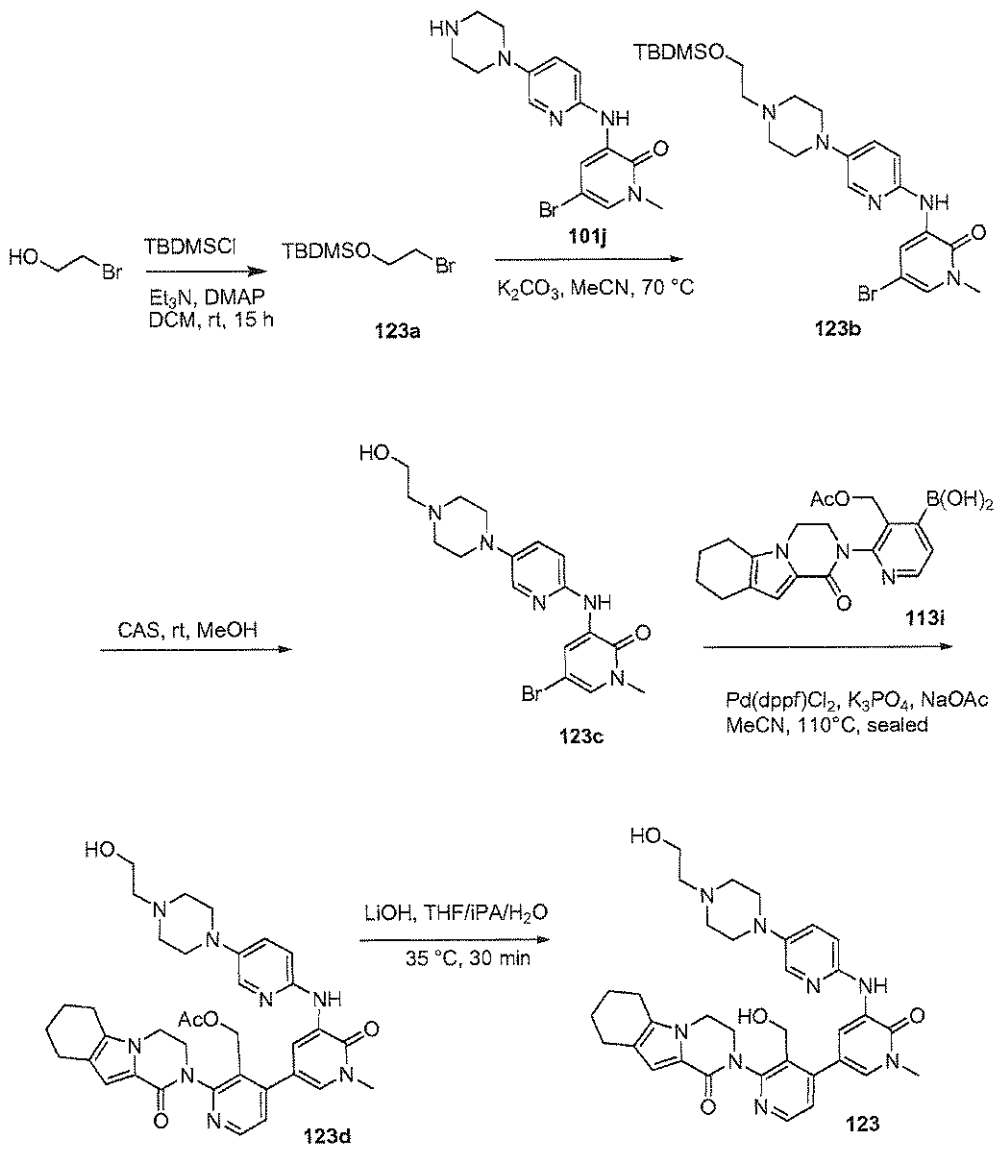

HO
Br
TBDMSCl
Et3N, DMAP
DCM, rt, 15 h
TBDMSO
Br
123a
HN
N
NH
O
Br
101j
K2CO3, MeCN, 70 °C
TBDMSO
123b
CAS, rt, MeOH
AcO
B(OH)2
113i
Pd(dppf)Cl2, K3PO4, NaOAc
MeCN, 110°C, sealed
123c
LiOH, THF/iPA/H2O
35 °C, 30 min
123d
123

Figure 23

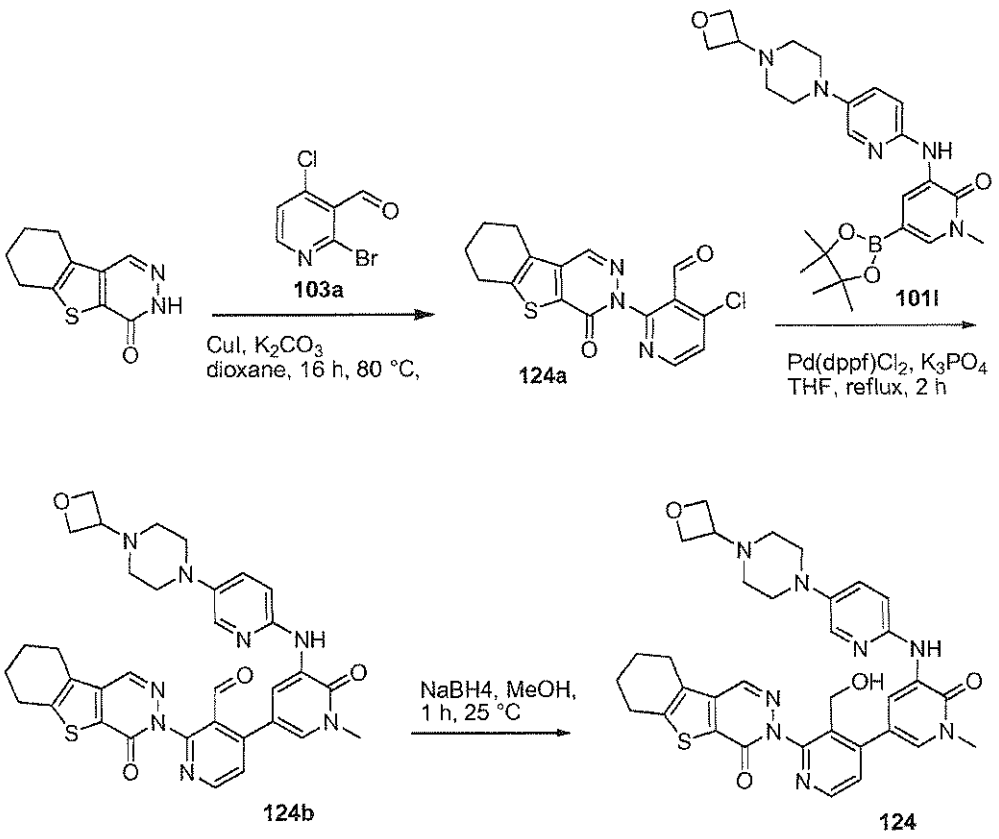

103a
CuI, K2CO3
dioxane, 16 h, 80 °C,
124a
101l
Pd(dppf)Cl2, K3PO4
THF, reflux, 2 h
124b
NaBH4, MeOH,
1 h, 25 °C
124

Figure 24

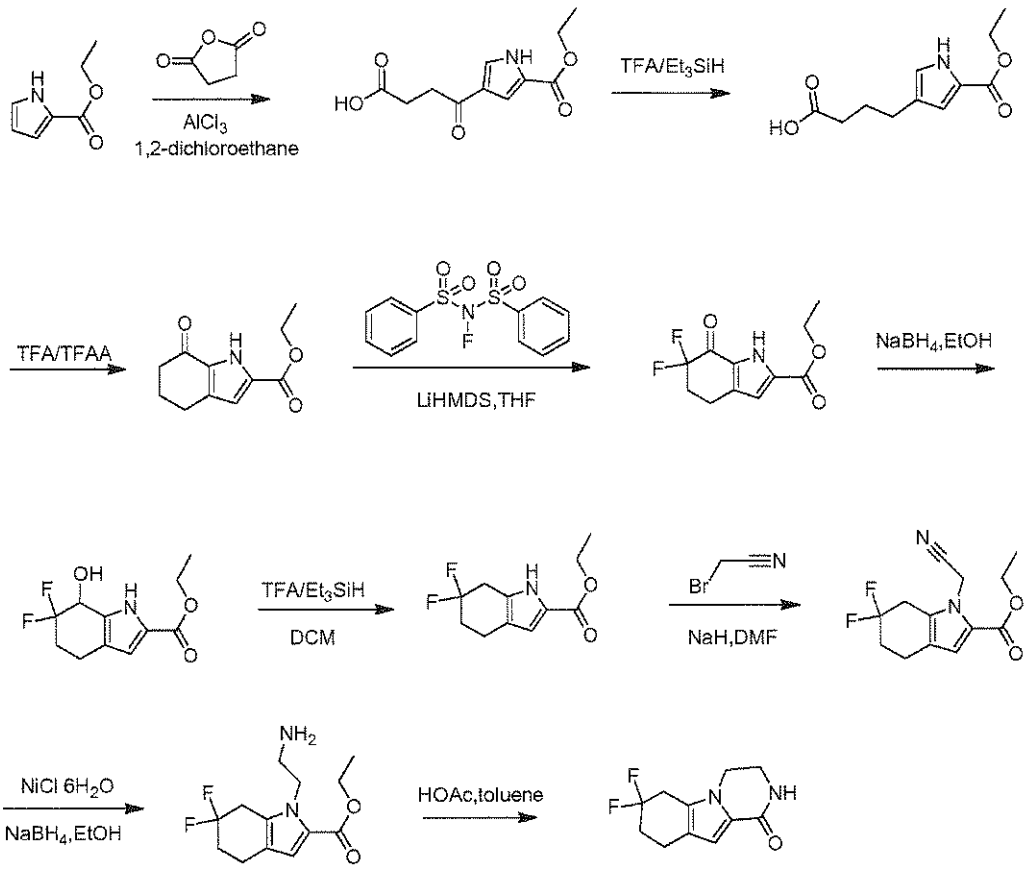

AlCl3
1,2-dichloroethane
TFA/Et3SiH
TFA/TFAA
LiHMDS,THF
NaBH4,EtOH
TFA/Et3SiH
DCM
NaH,DMF
NiCl 6H2O
NaBH4,EtOH
HOAc,toluene

Figure 25

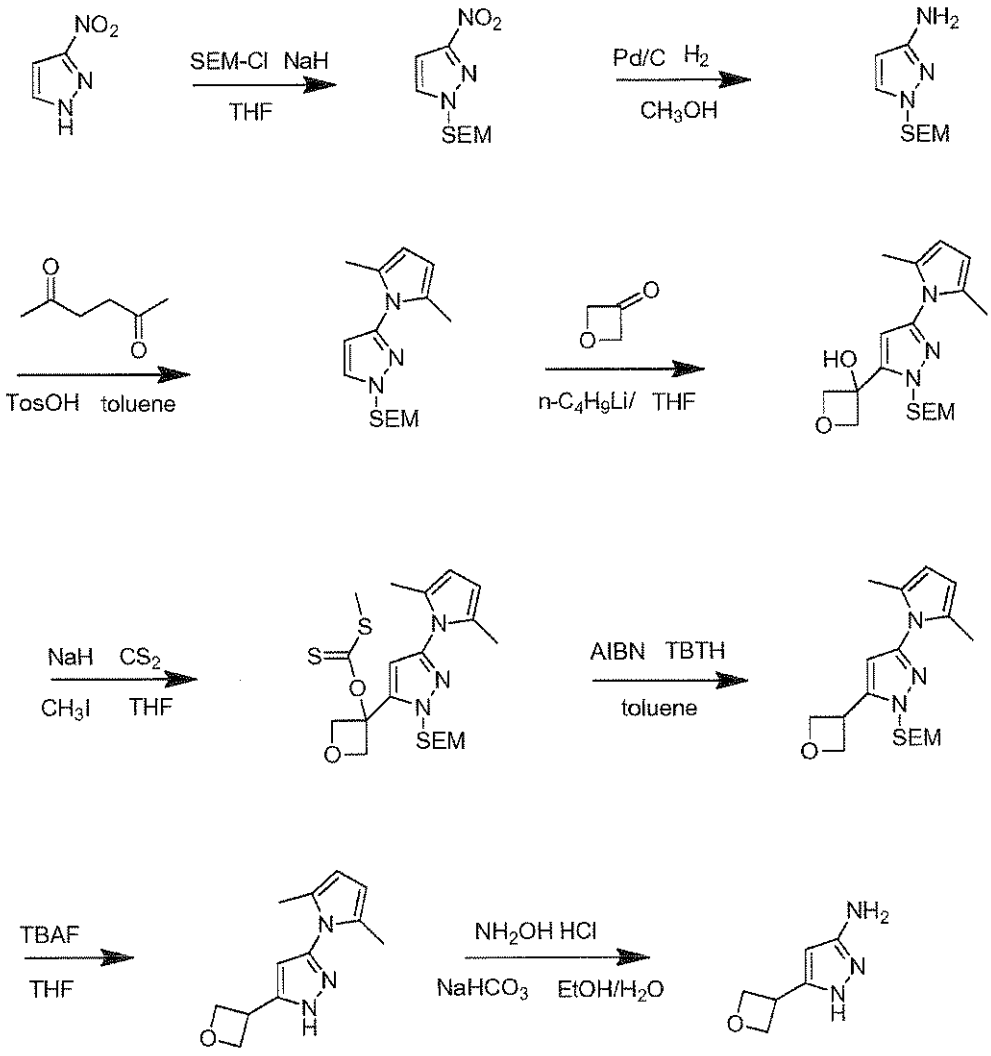

NO2
SEM-Cl NaH
THF
SEM
Pd/C H2
CH3OH
NH2
TosOH toluene
n-C4H9Li/ THF
HO
NaH CS2
CH3I THF
AIBN TBTH
toluene
TBAF
THF
NH2OH HCl
NaHCO3 EtOH/H2O

Figure 26