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Synthetic route to novel asymmetric tetradentate ligands containing both amino and imino groups

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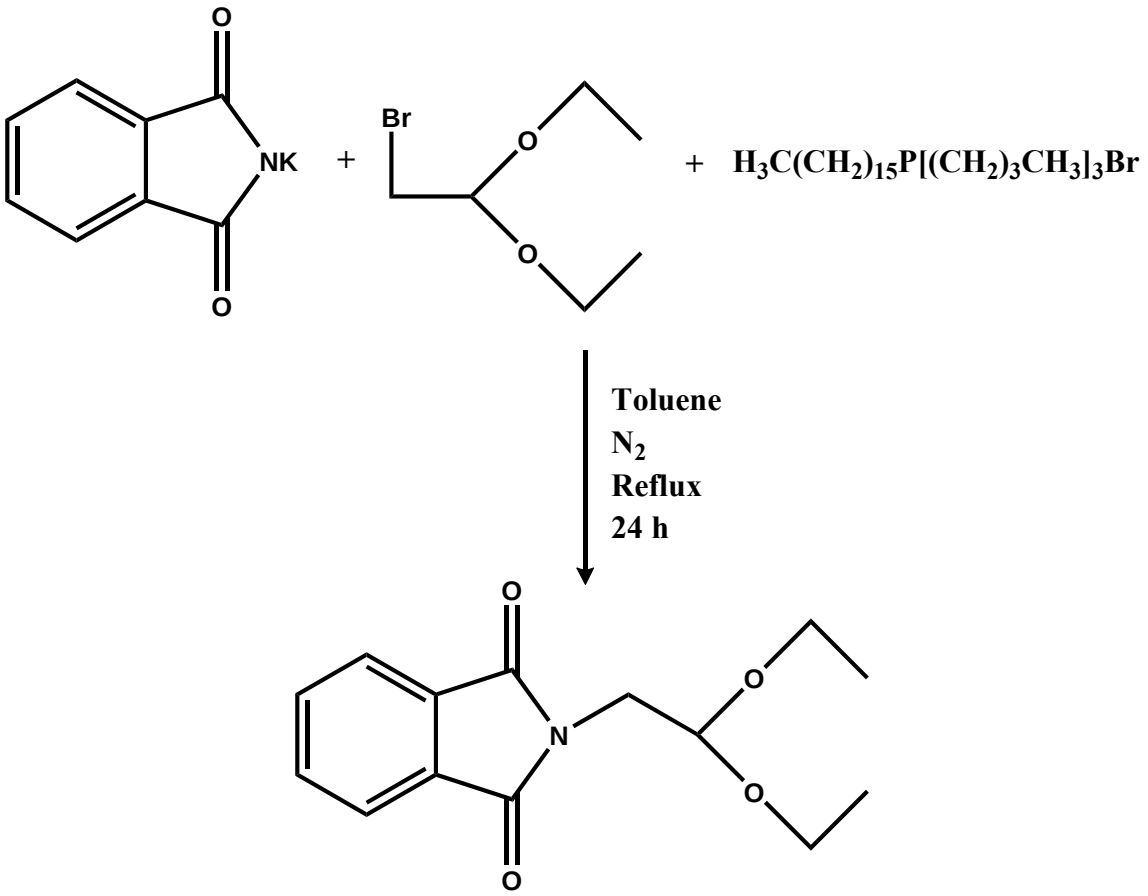
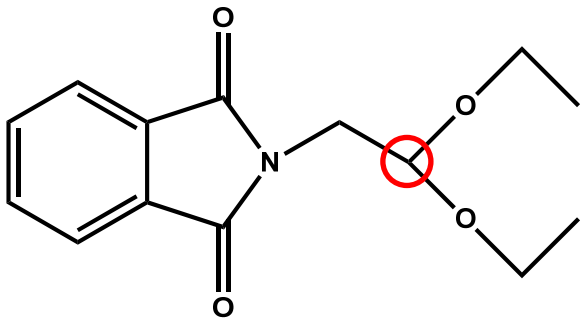
Abstract

The synthesis of the new asymmetric ligand (*E*)-4-bromo-2-(((2-((5-bromo-2-hydroxybenzyl)(methyl)amino)ethyl)imino)methyl)phenol, which was conceived to model the asymmetry in the active site of peroxidase/catalase mimics, is reported. The new synthetic route involves seven steps: 1) Obtention of the phthalimido-acetal; 2) Acetal deprotection; 3) Synthesis of the salicylamine; 4) Obtention of the benzoxacine; 5) Reduction of the benzoxacine with $NaBH_3CN$; 6) Reduction with hydrazine to form salycilamine; 7) Synthesis of the final ligand by condensation of salicylamine with salycilaldehyde. All organic products were characterised by microanalysis, ^1H NMR, IR and mass spectroscopies.

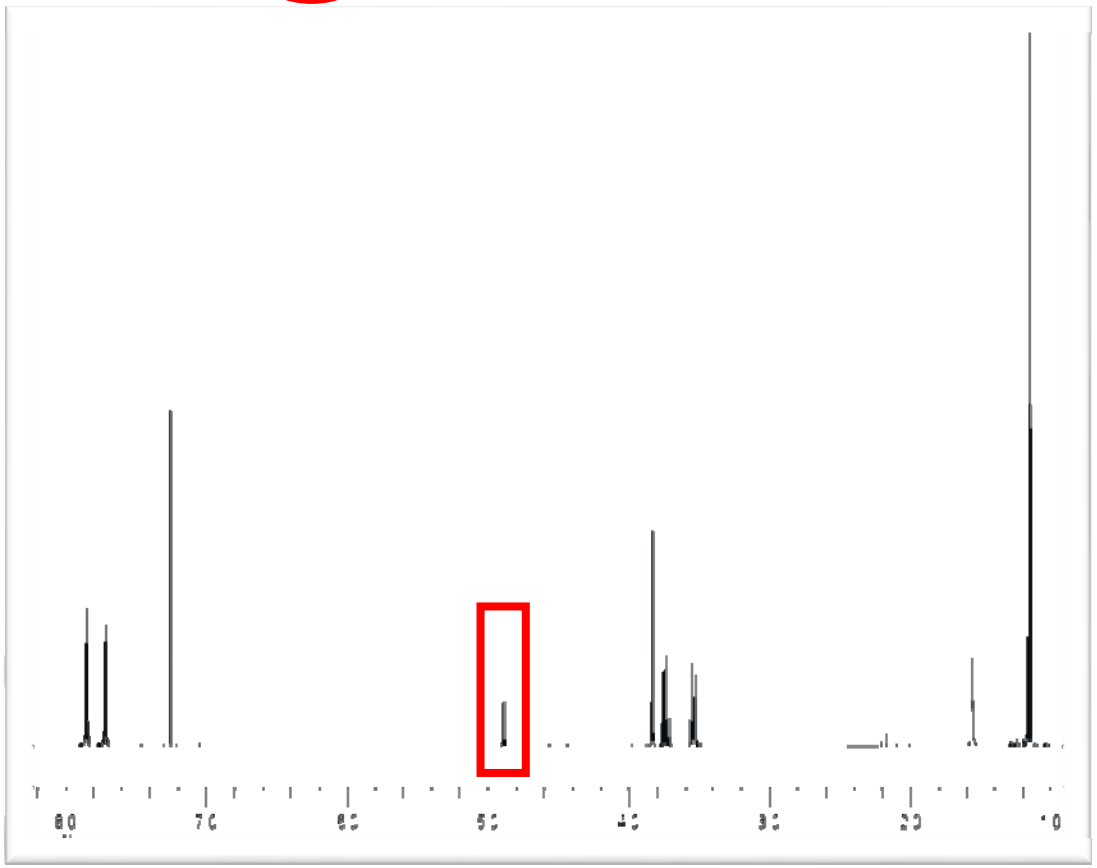
1) Obtention of phthalimido-acetal



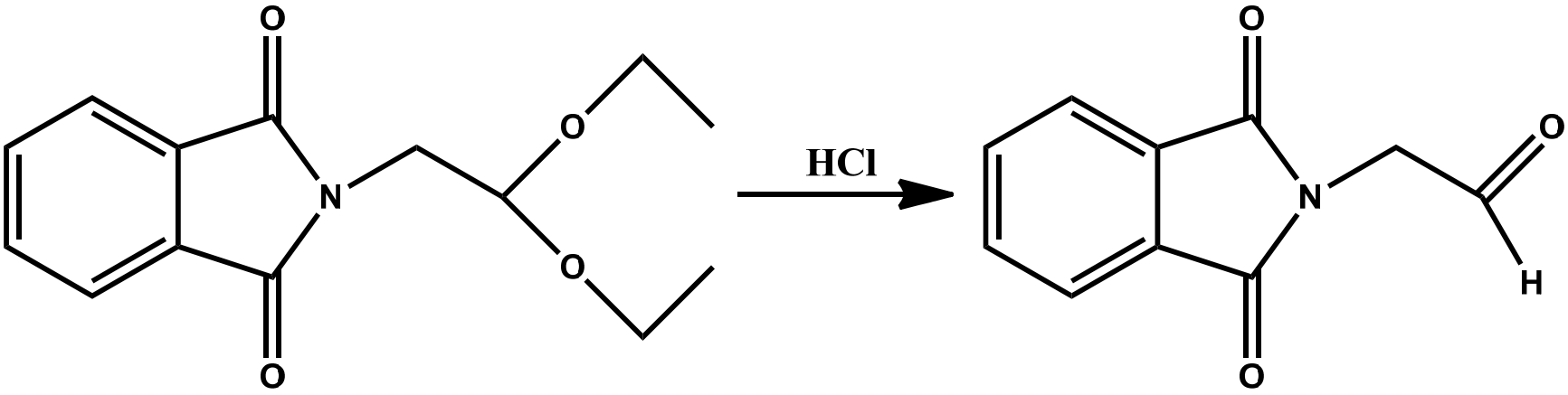


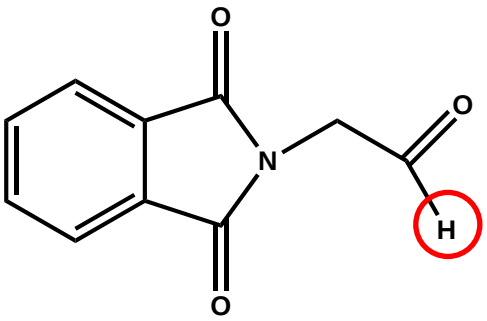
RMN

δ(Harom)*$_{(1)}$	δ(-H)*$_{(3)}$	δ(-CH_2)$_{(2)}$	δ(-CH_2)$_{(4),(5)}$	δ(-CH_3)$_{(6),(7)}$
7,8-7,6	4,79	3,75	3,62-3,42	1,06

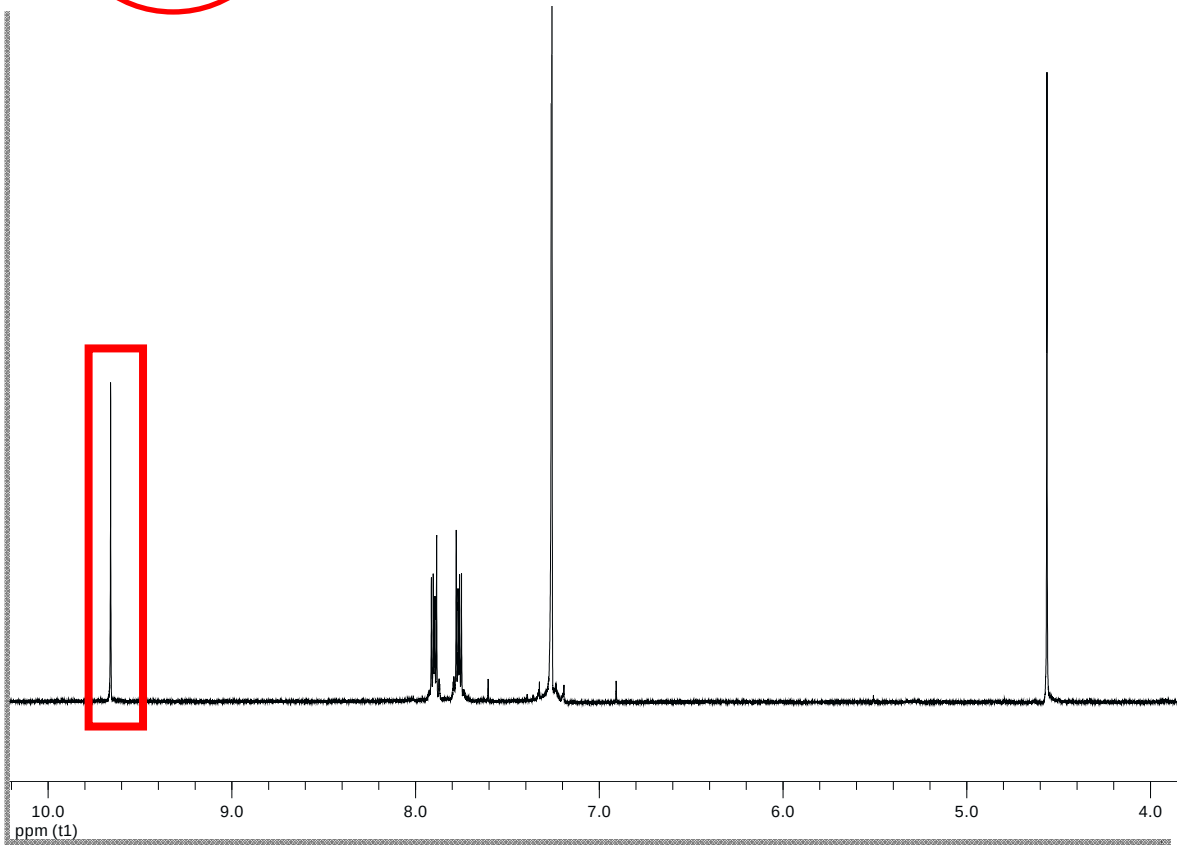


2) Acetal deprotection

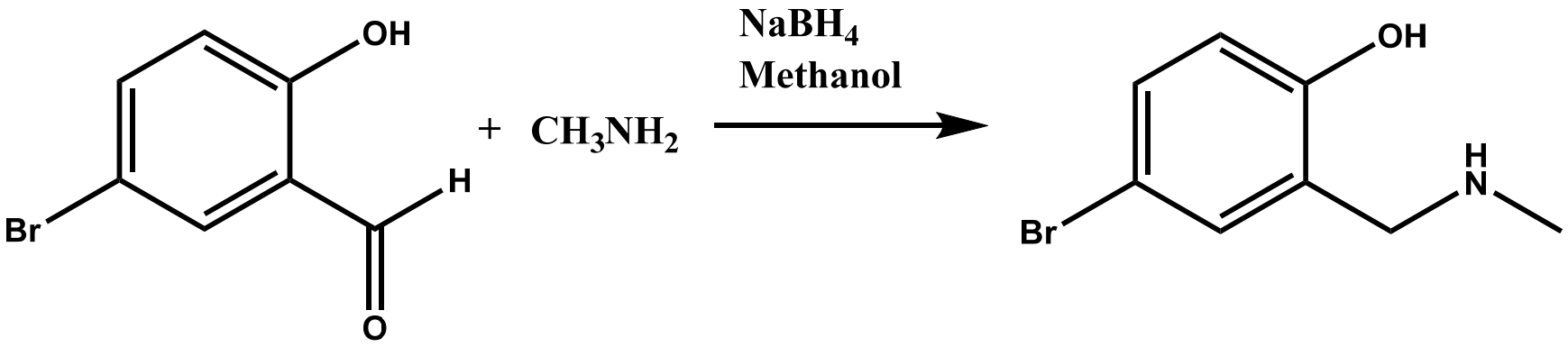




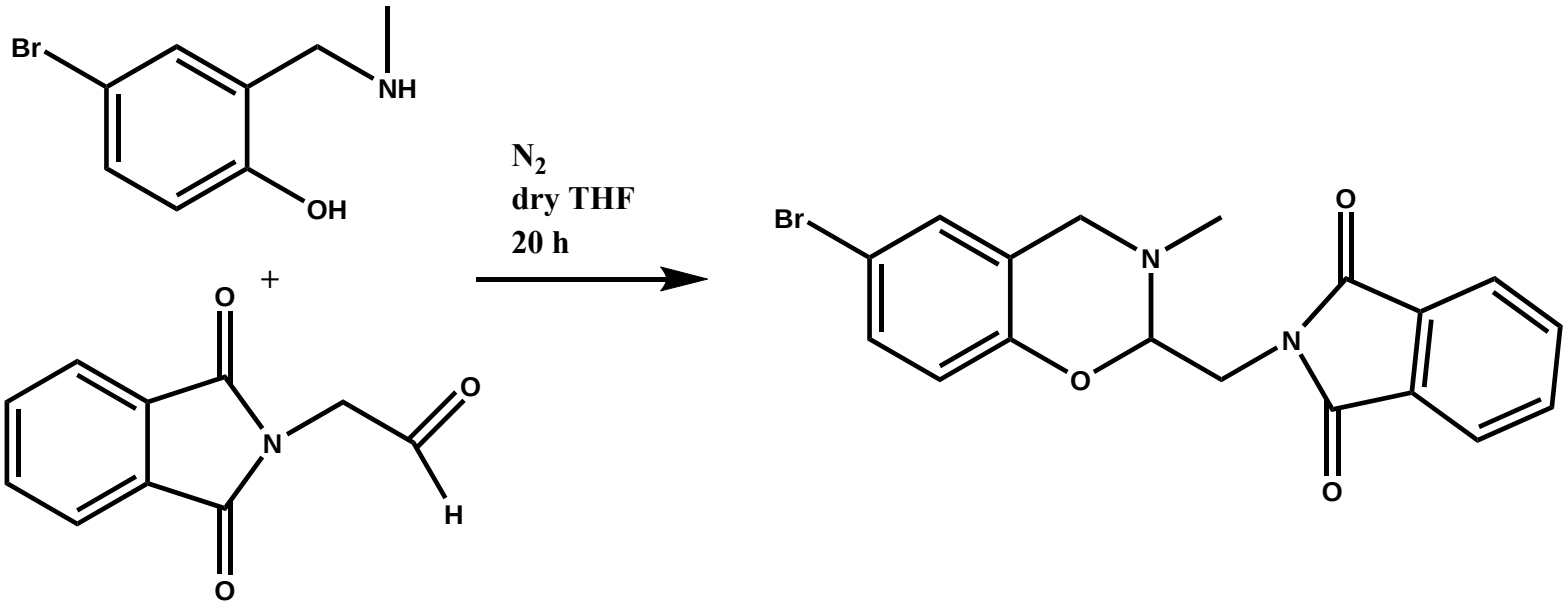
$\delta(\text{-H})^*_{(3)}$	$\delta(\text{Harom})_{(1)}$	$\delta(\text{-CH}_2)_{(2)}$
9,66	7,88-7,65	4,55



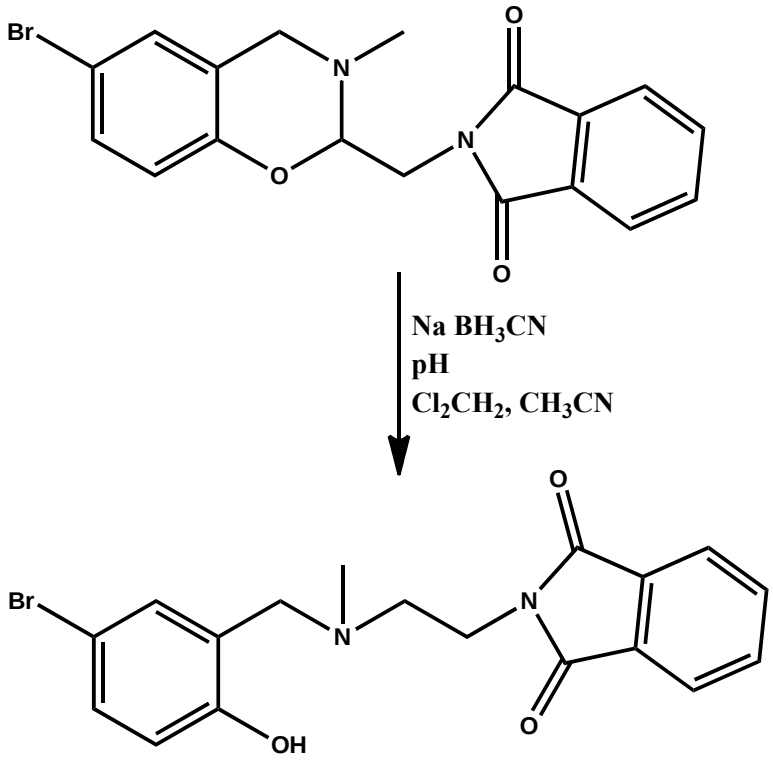
3) Synthesis of the salycilamine



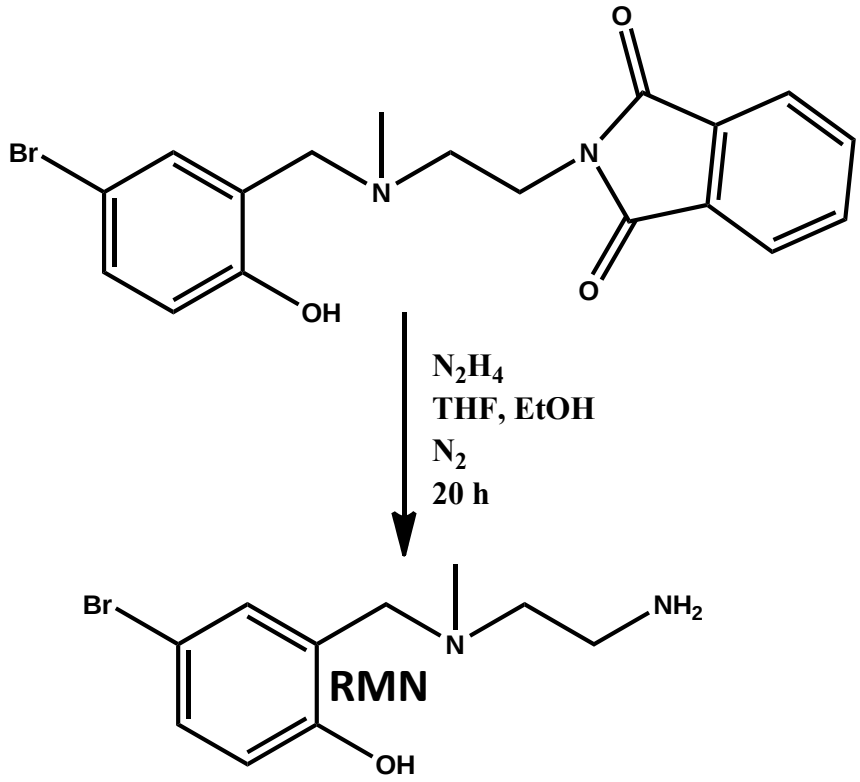
4) Obtention of benzoxacine



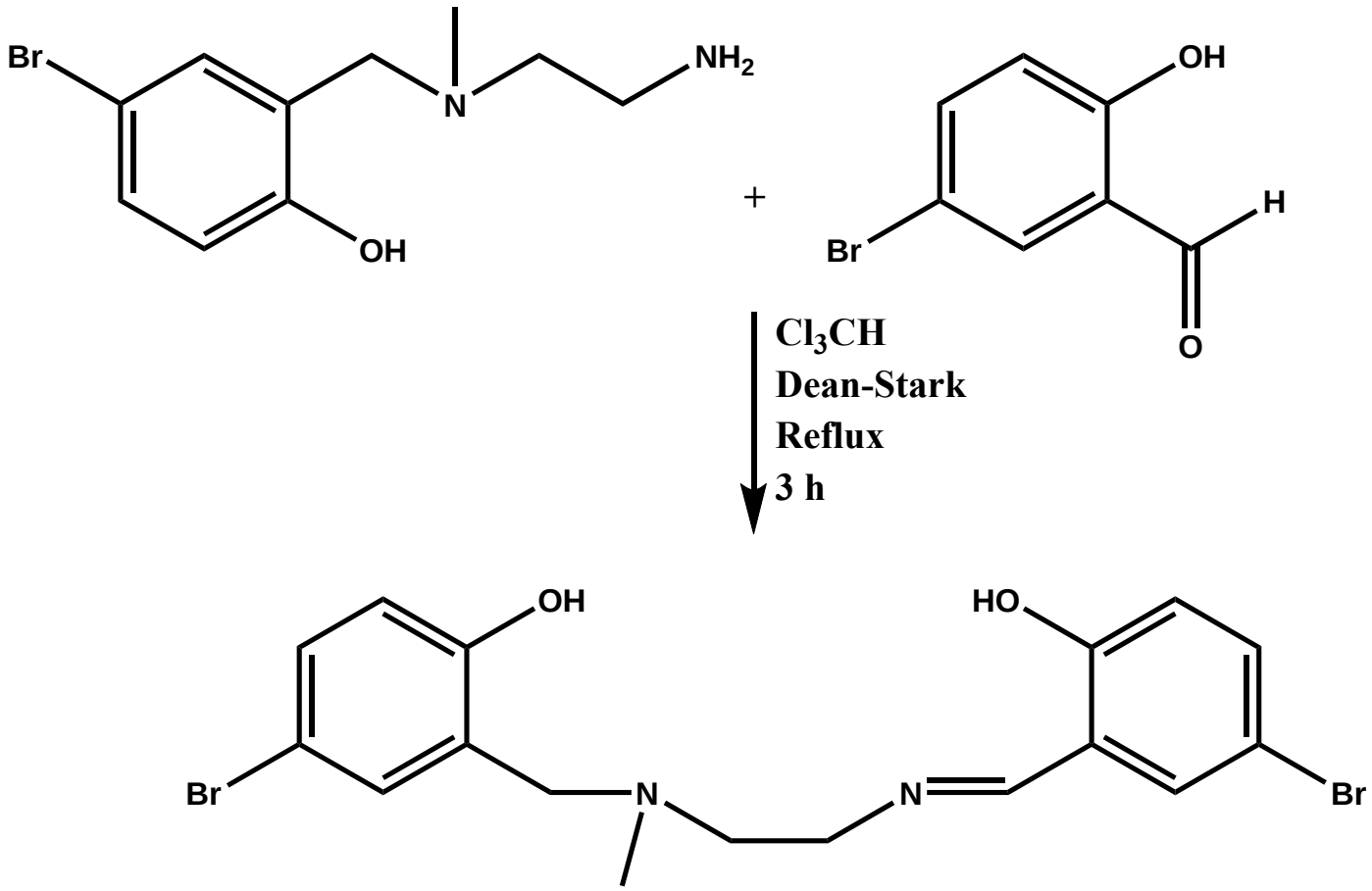
5) Reduction of the benzoxacine



6) Obtention of the salycilamine



7) Synthesis of the final ligand



RMN

$\delta(-H)_{(7)}$	$\delta(Harom)_{(2),(8)}$	$\delta(-CH_2-)_{(6)}$	$\delta(-CH_2-)_{(3)}$	$\delta(-CH_2-)_{(5)}$	$\delta(-CH_3)_{(4)}$
8,22	7,34-6,60	3,81	3,72	2,86	2,86