

## A divergent approach to benzyloquinoline-type and oxoaporphine alkaloids via regioselective direct ring metalation of alkoxy isoquinolines

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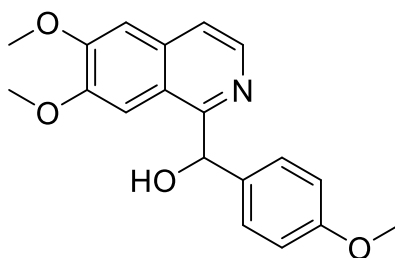
\*Corresponding author. Email: [Franz.Bracher@cup.uni-muenchen.de](mailto:Franz.Bracher@cup.uni-muenchen.de), Phone: +49-89-2180-77301, Fax: +49-89-2180-77802

### Supporting Information

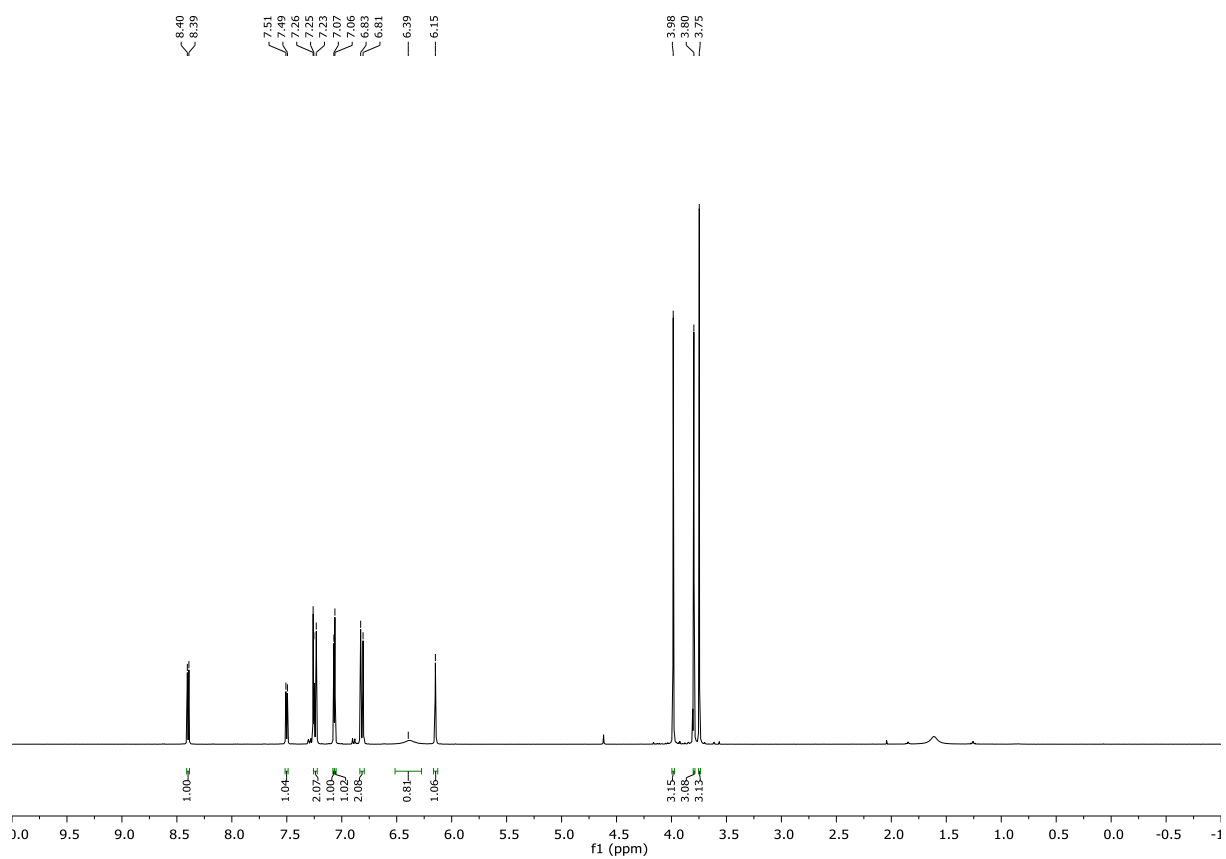
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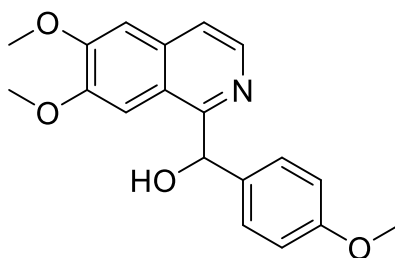
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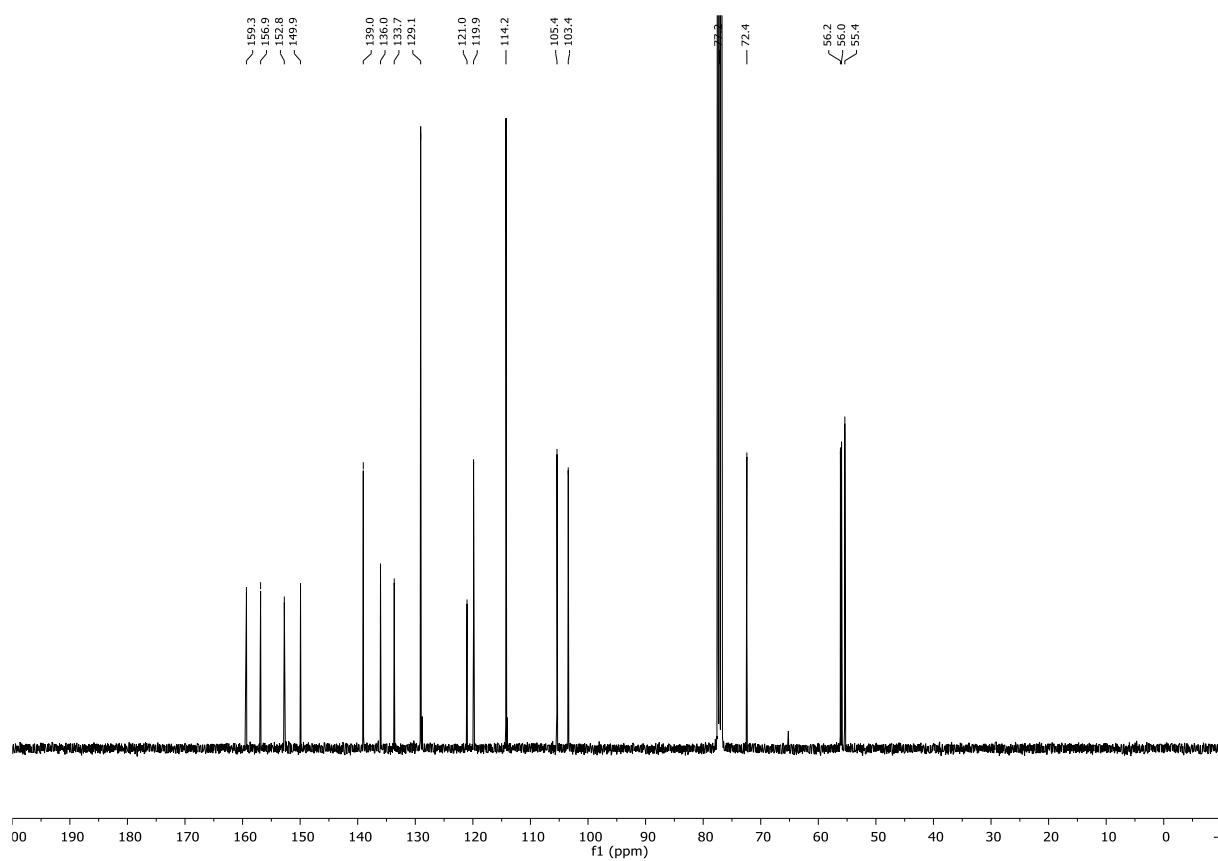
**$^1\text{H}$  NMR spectrum of ( $\pm$ )-(6,7-dimethoxyisoquinolin-1-yl)(4-methoxyphenyl)methanol****(3a)**

Frequency: 400 MHz

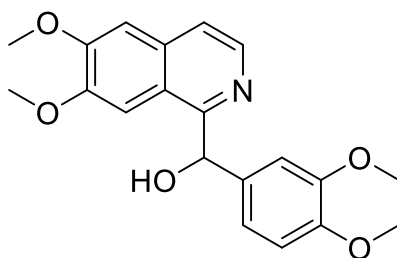
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**<sup>13</sup>C NMR spectrum of (±)-(6,7-dimethoxyisoquinolin-1-yl)(4-methoxyphenyl)methanol****(3a)**

Frequency: 101 MHz

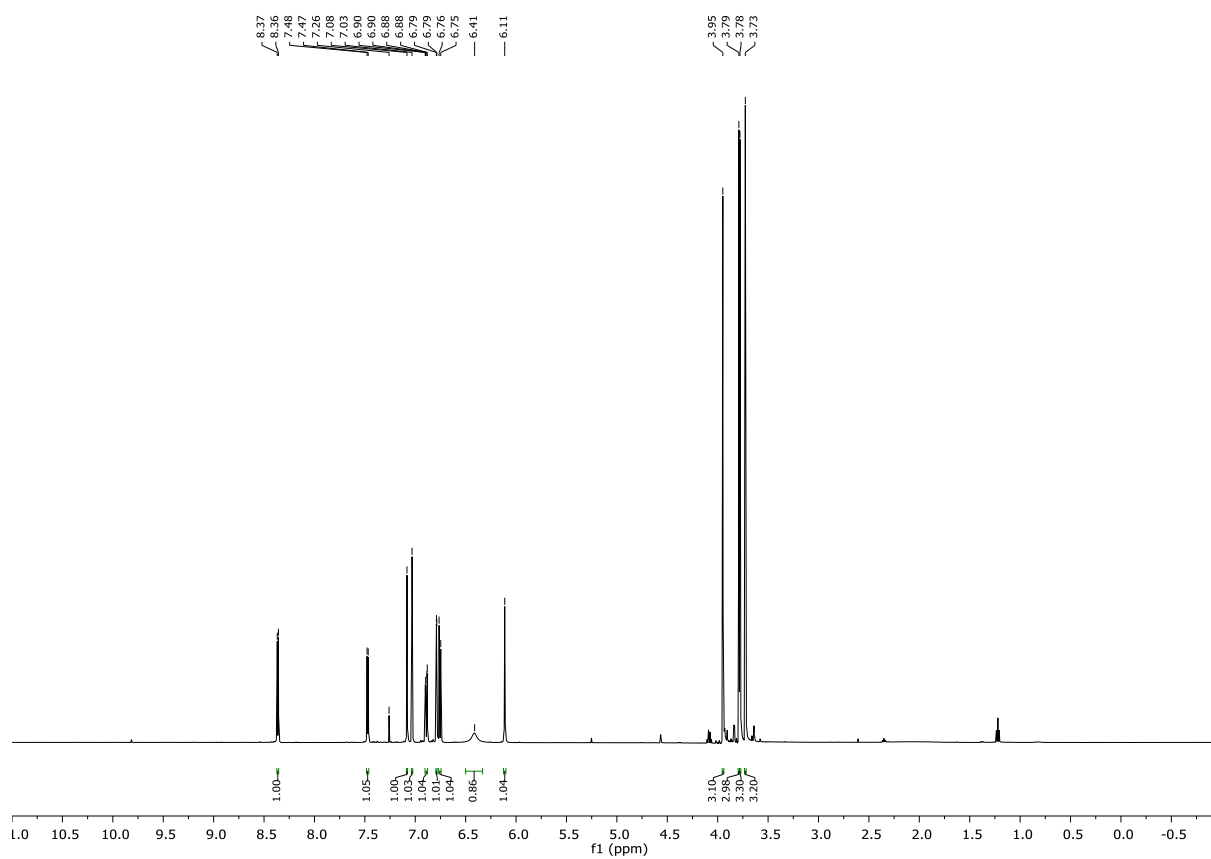
Solvent: CDCl<sub>3</sub>

**<sup>1</sup>H NMR spectrum of (±)-(6,7-dimethoxyisoquinolin-1-yl)(3,4-dimethoxyphenyl)methanol (3b), racemic Papaverinol**

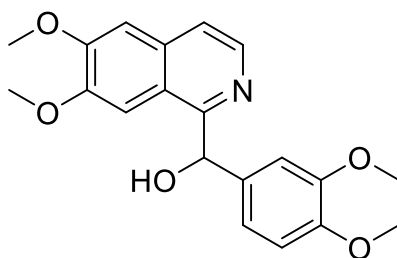


Frequency: 500 MHz

Solvent: CDCl<sub>3</sub>

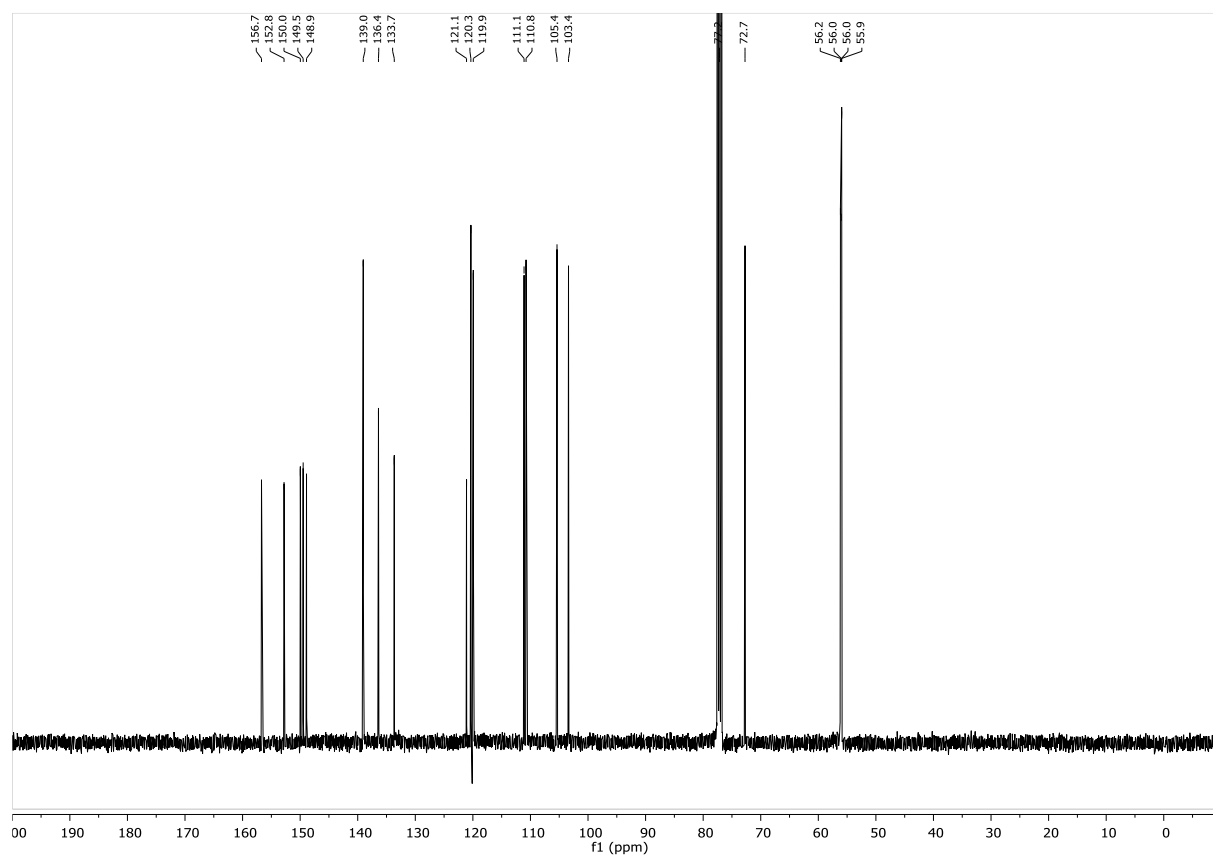


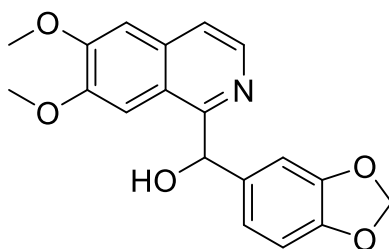
**<sup>13</sup>C NMR spectrum of (±)- (6,7-dimethoxyisoquinolin-1-yl)(3,4-dimethoxyphenyl)methanol (3b), racemic Papaverinol**



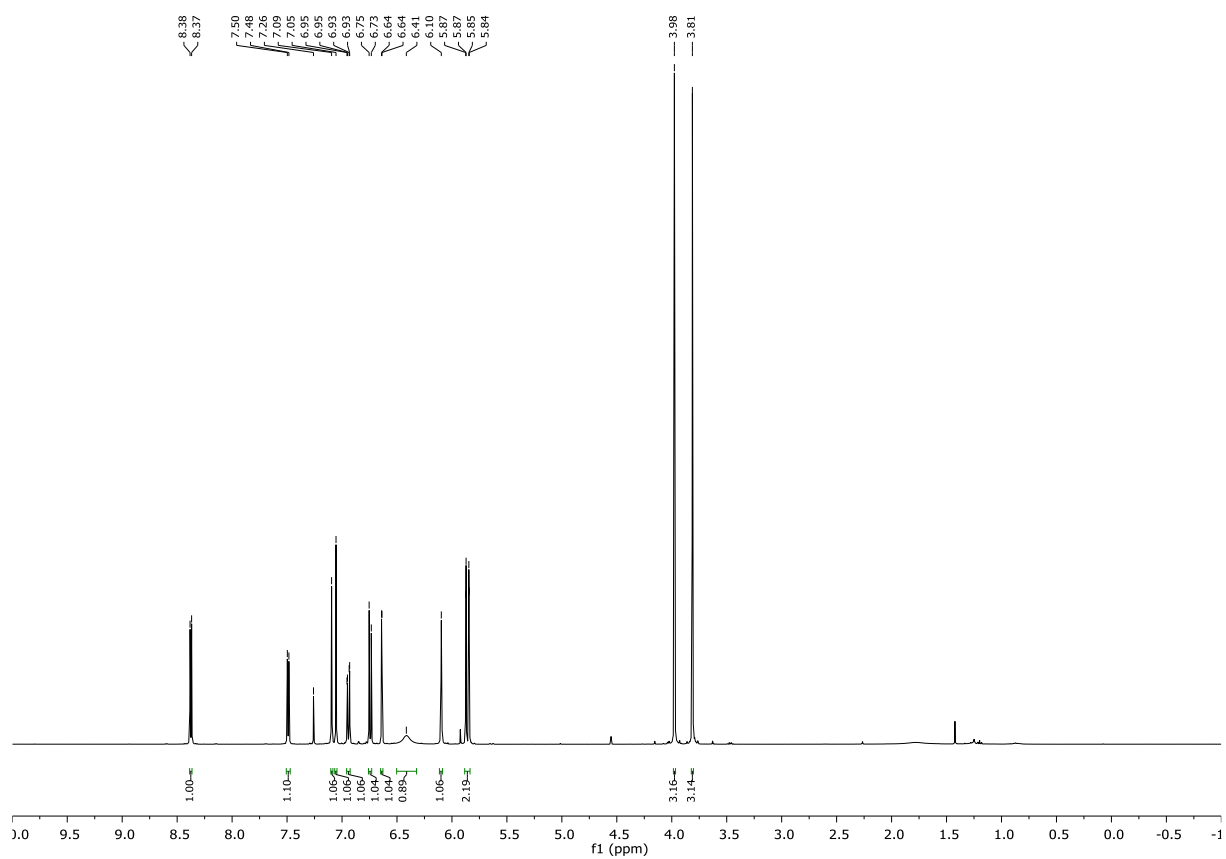
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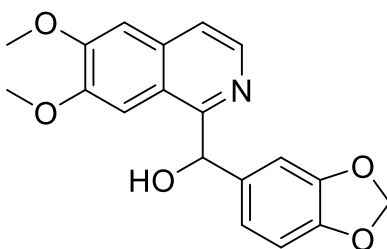


**$^1\text{H}$  NMR spectrum ( $\pm$ )-benzo[d][1,3]dioxol-5-yl(6,7-dimethoxyisoquinolin-1-yl)methanol****(3c)**

Frequency: 400 MHz

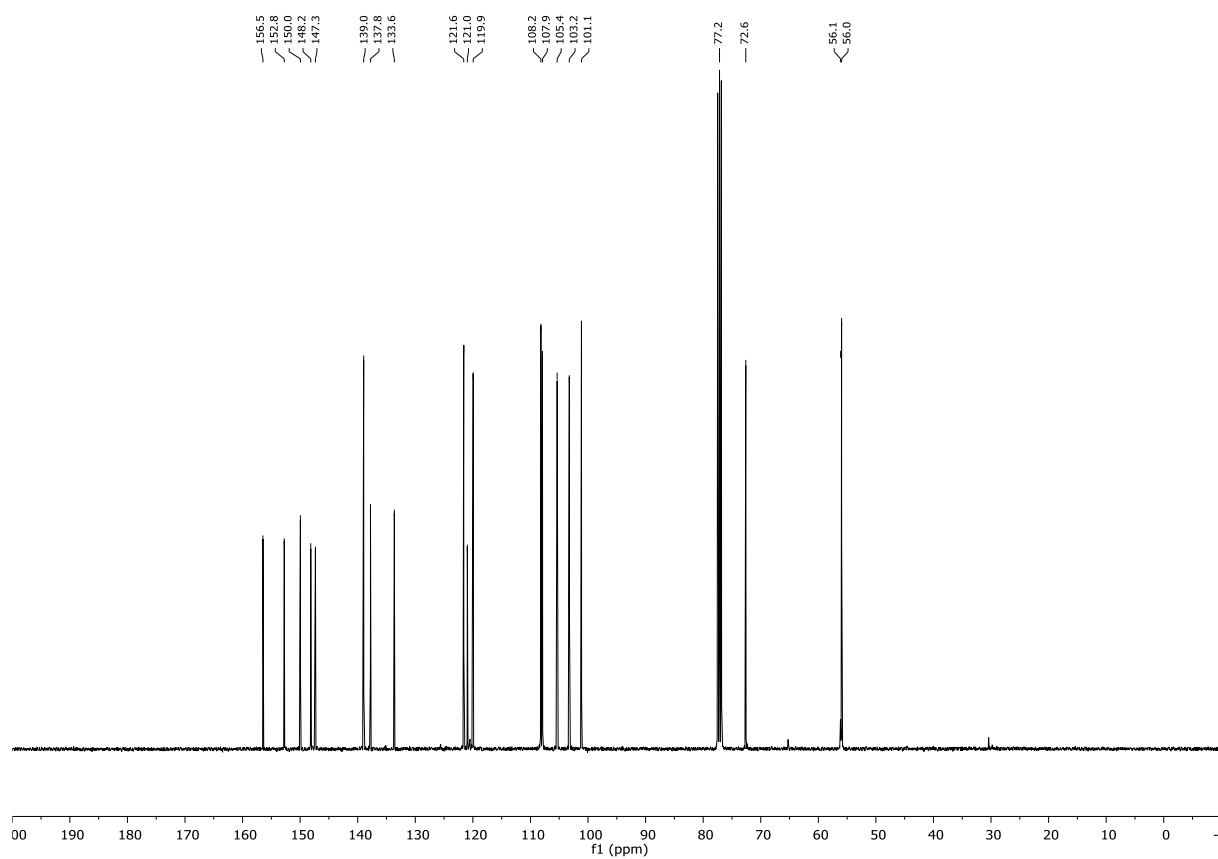
Solvent:  $\text{CDCl}_3$ 

**$^{13}\text{C}$  NMR spectrum of ( $\pm$ )-benzo[d][1,3]dioxol-5-yl(6,7-dimethoxyisoquinolin-1-yl)methanol (3c)**



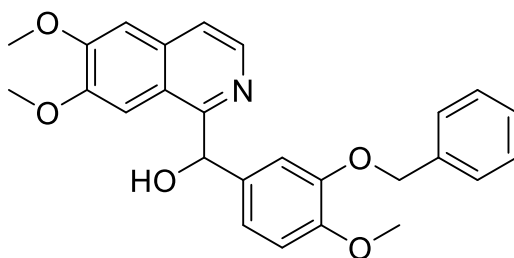
Frequency: 101 MHz

Solvent:  $\text{CDCl}_3$



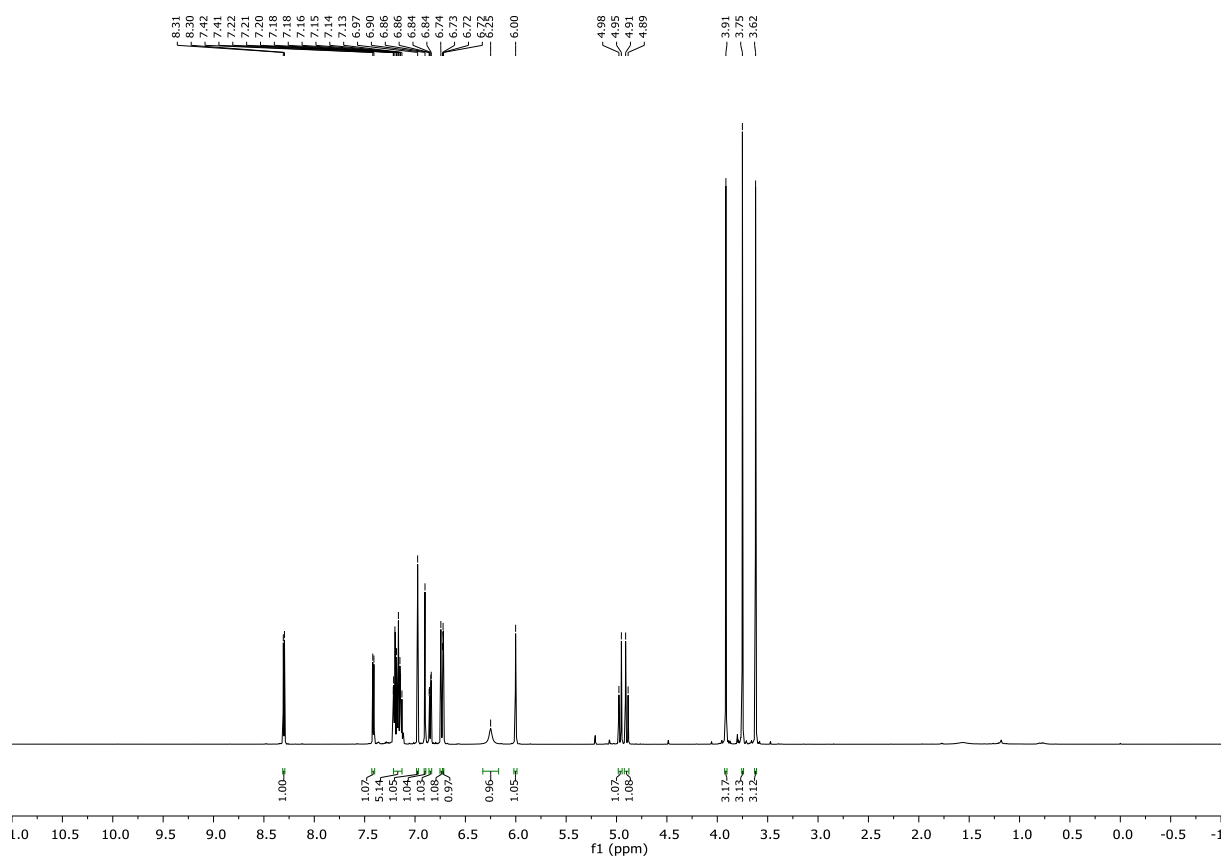


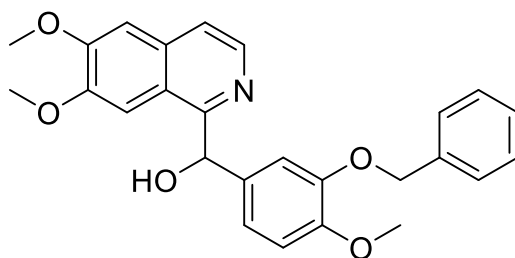
**$^1\text{H}$  NMR spectrum of ( $\pm$ )-(3-(benzyloxy)-4-methoxyphenyl)(6,7-dimethoxyisoquinolin-1-yl)methanol (3d)**



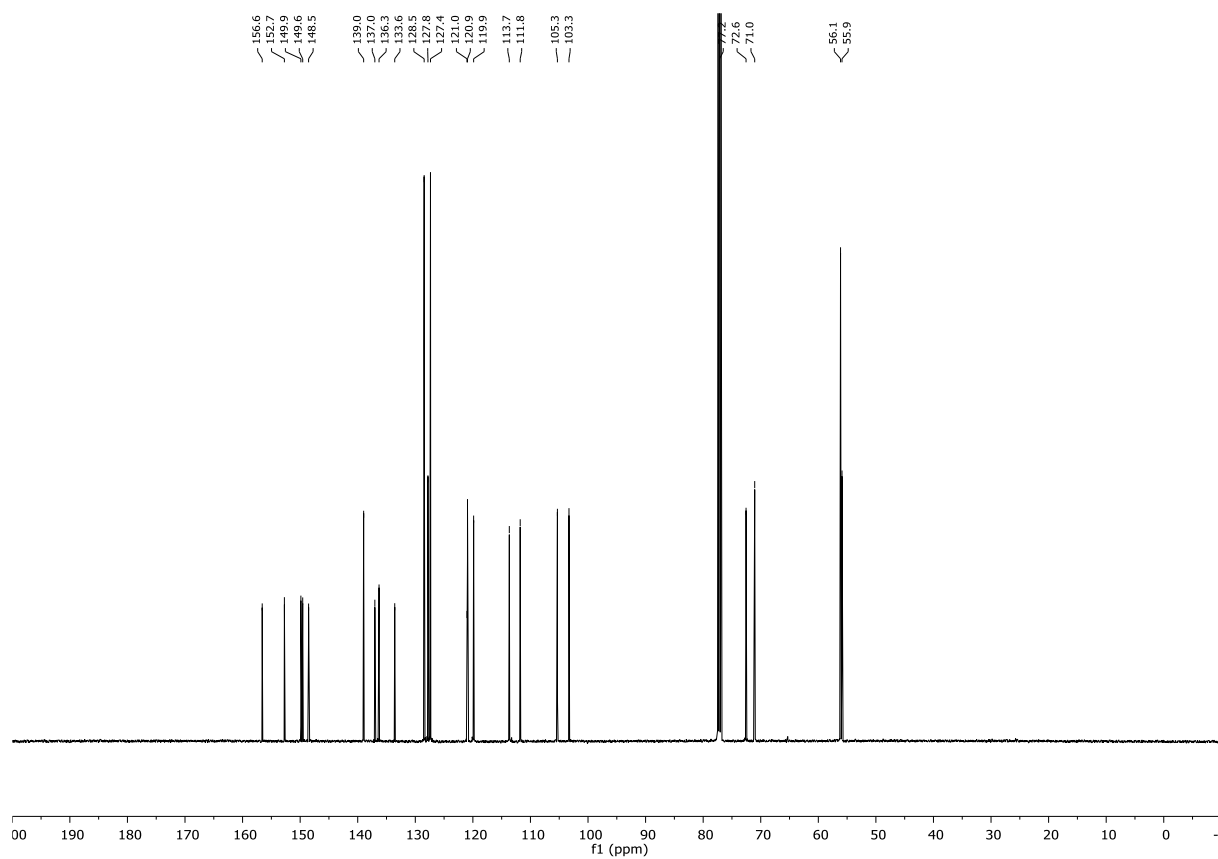
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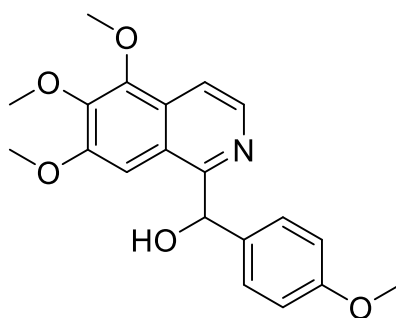
Solvent:  $\text{CDCl}_3$



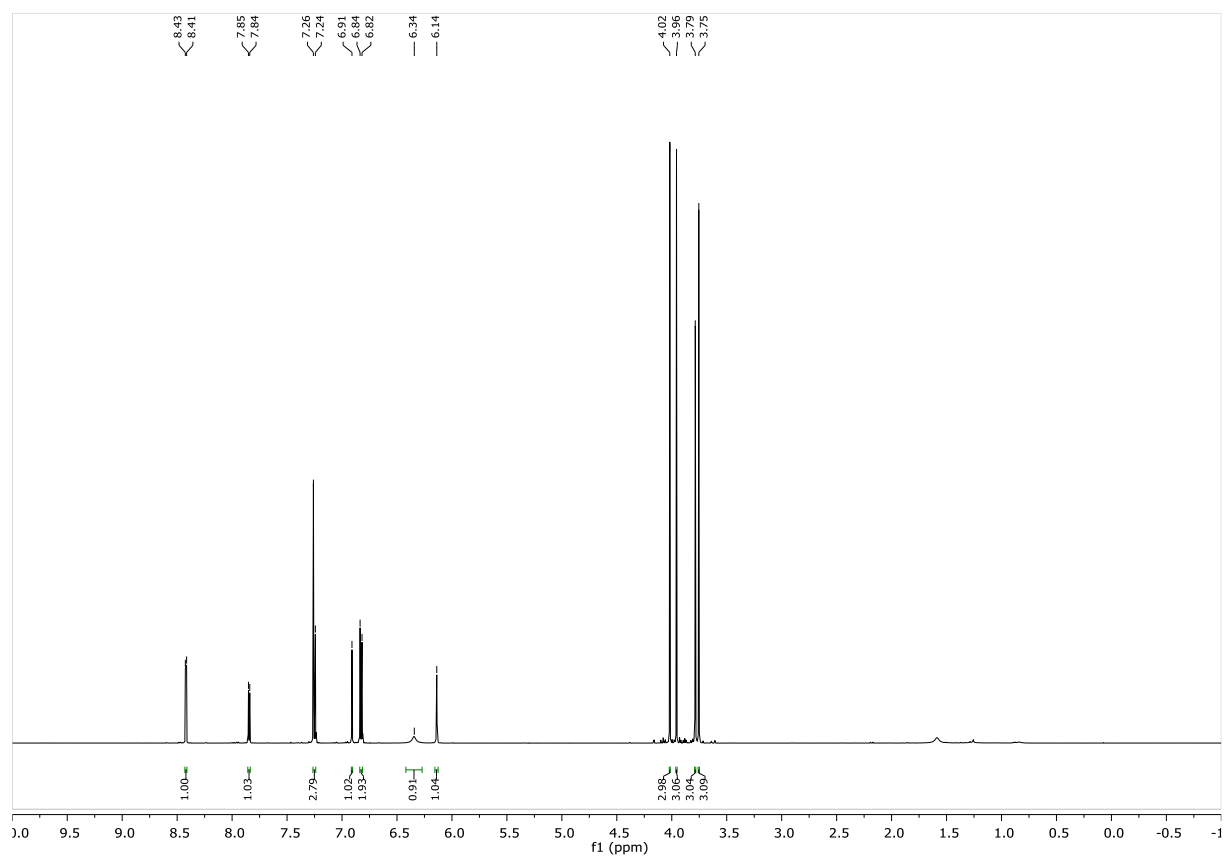
**<sup>13</sup>C NMR spectrum of (±)-(3-(benzyloxy)-4-methoxyphenyl)(6,7-dimethoxyisoquinolin-1-yl)methanol (3d)**

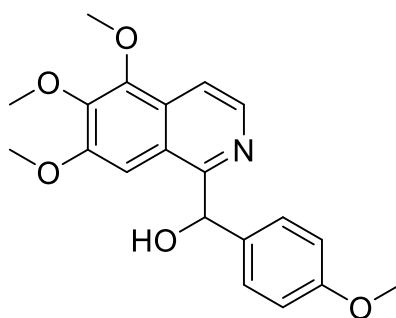
Frequency: 126 MHz

Solvent: CDCl<sub>3</sub>

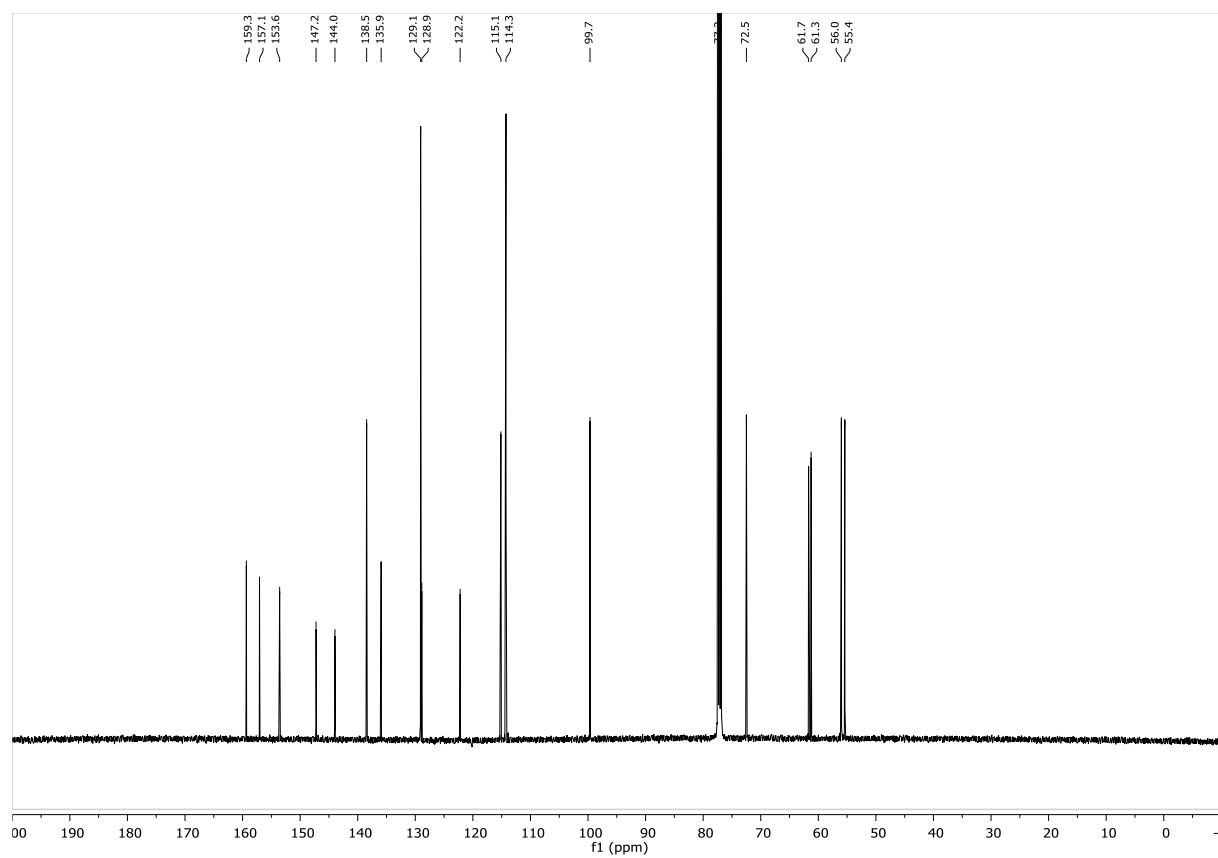
**<sup>1</sup>H NMR spectrum of (±)-(4-methoxyphenyl)(5,6,7-trimethoxyisoquinolin-1-yl)methanol****(3e)**

Frequency: 500 MHz

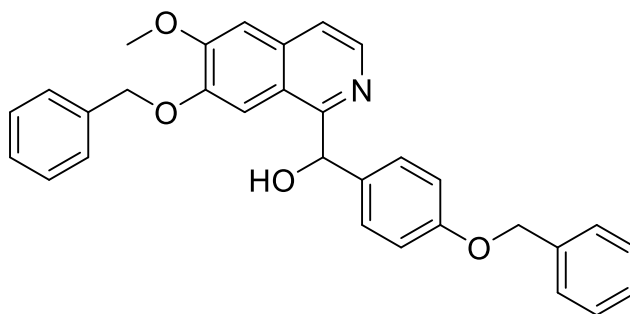
Solvent: CDCl<sub>3</sub>

**$^{13}\text{C}$  NMR spectrum of ( $\pm$ )-(4-methoxyphenyl)(5,6,7-trimethoxyisoquinolin-1-yl)methanol****(3e)**

Frequency: 126 MHz

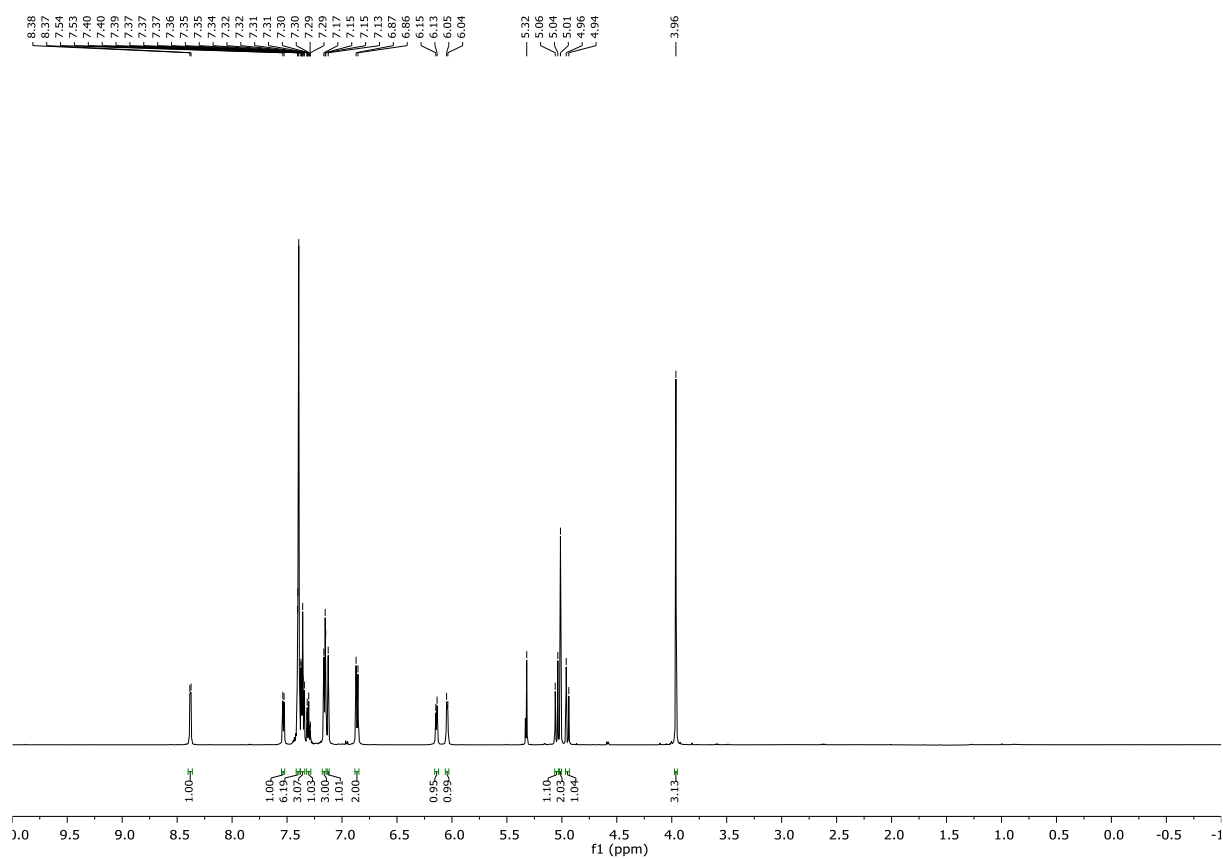
Solvent:  $\text{CDCl}_3$ 

**<sup>1</sup>H NMR spectrum of (±)-(7-(benzyloxy)-6-methoxyisoquinolin-1-yl)(4-(benzyloxy)phenyl)methanol (3f)**

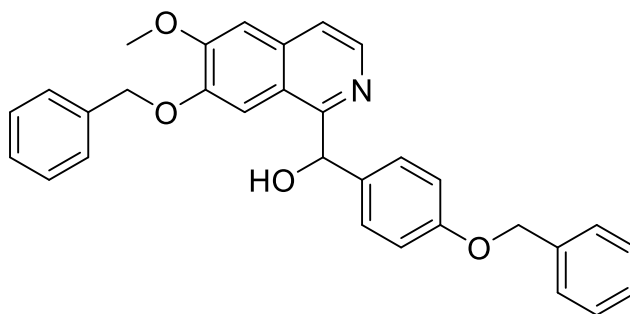


Frequency: 500 MHz

Solvent: CD<sub>2</sub>Cl<sub>2</sub>

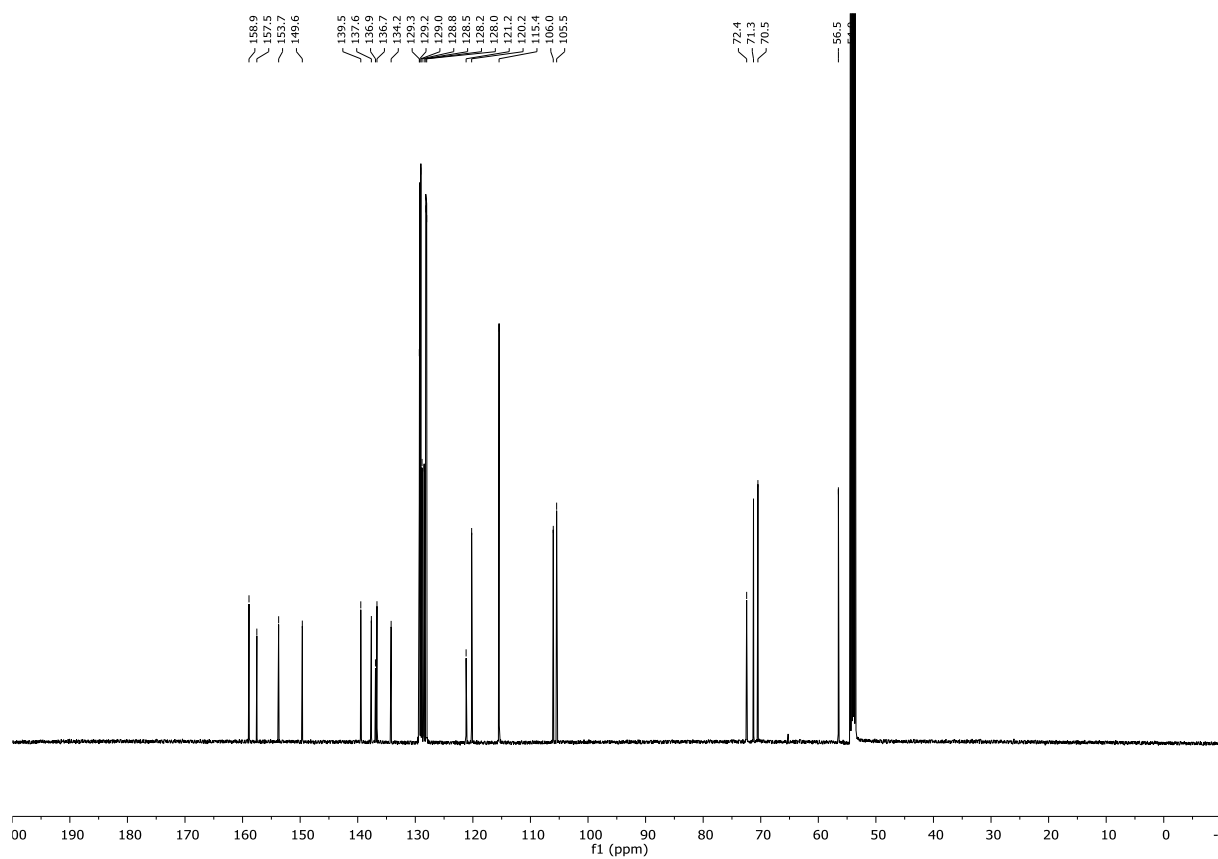


**$^{13}\text{C}$  NMR spectrum of ( $\pm$ )-(7-(benzyloxy)-6-methoxyisoquinolin-1-yl)(4-(benzyloxy)phenyl)methanol (3f)**

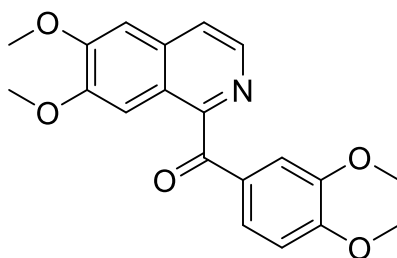


Frequency: 126 MHz

Solvent:  $\text{CD}_2\text{Cl}_2$

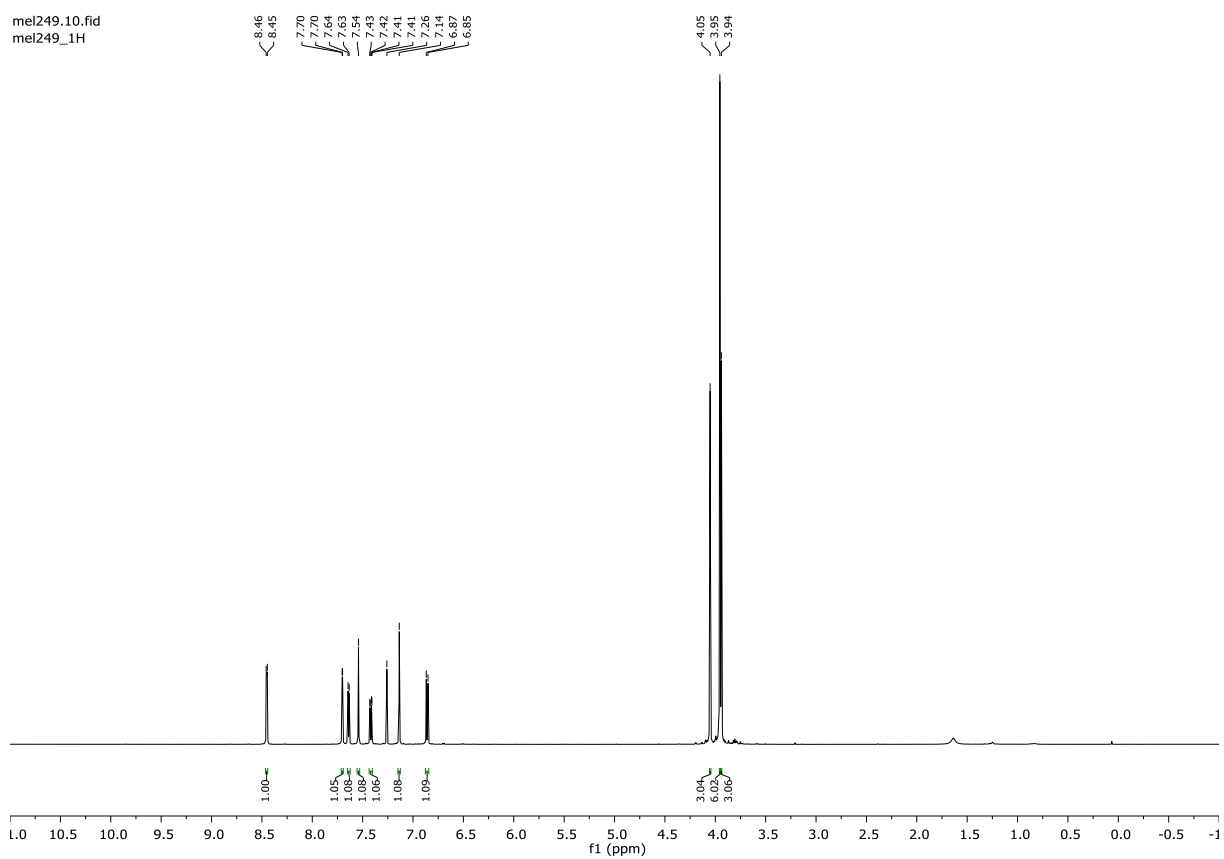


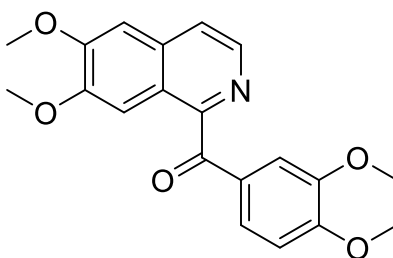
**<sup>1</sup>H NMR spectrum of (6,7-dimethoxyisoquinolin-1-yl)(3,4-dimethoxyphenyl)methanone  
(4), Papaveraldine**



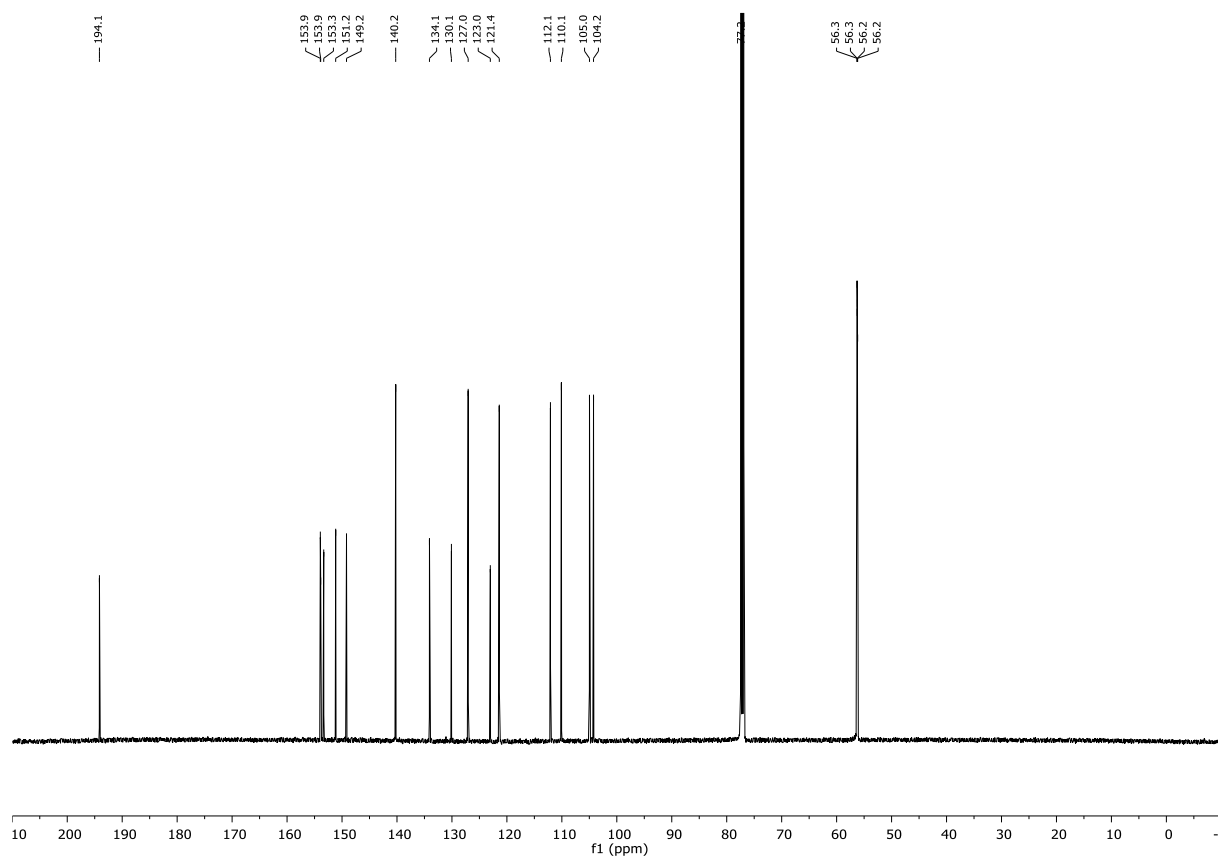
Frequency: 500 MHz

Solvent: CDCl<sub>3</sub>



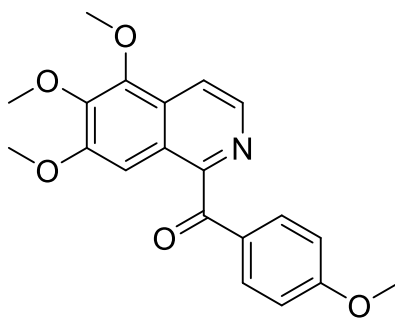
**<sup>13</sup>C NMR spectrum of (6,7-dimethoxyisoquinolin-1-yl)(3,4-dimethoxyphenyl)methanone****(4), Papaveraldine**

Frequency: 126 MHz

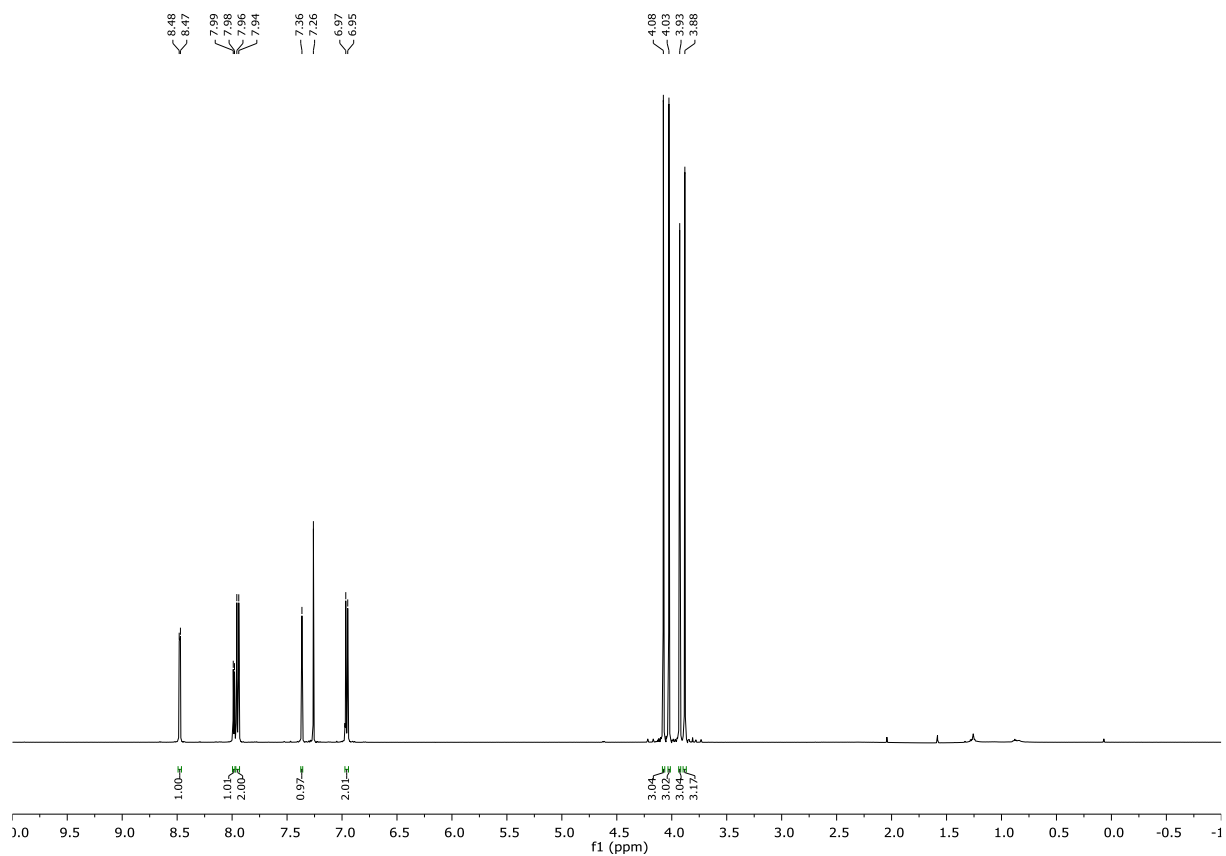
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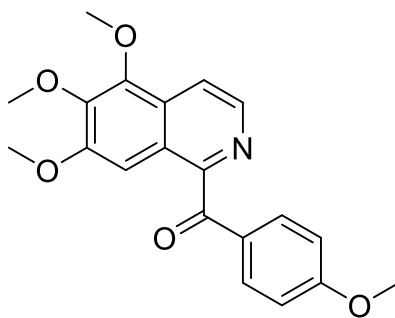


**<sup>1</sup>H NMR spectrum of (4-methoxyphenyl)(5,6,7-trimethoxyisoquinolin-1-yl)methanone  
(5), Thalimicrinone**

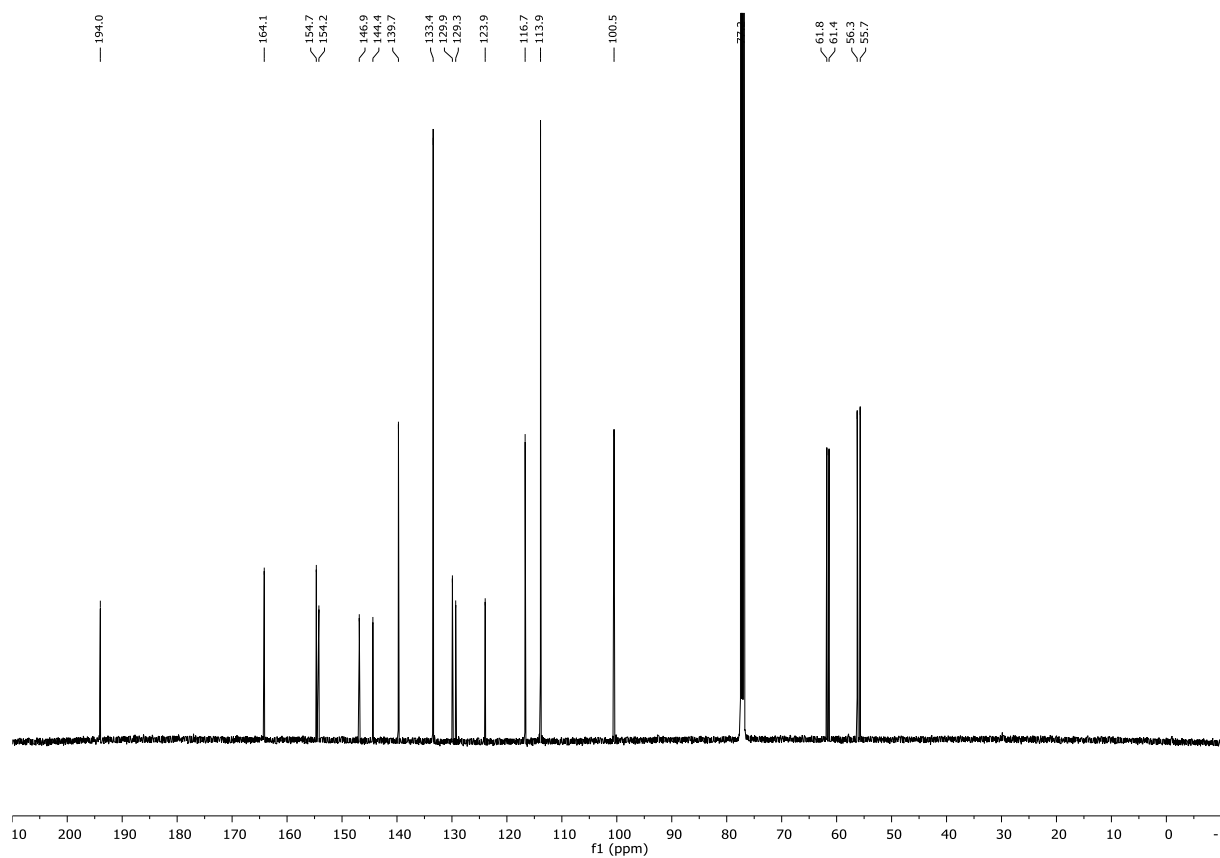


Frequency: 500 MHz

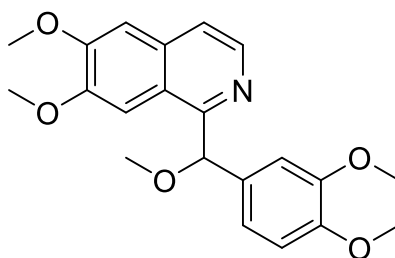
Solvent: CDCl<sub>3</sub>

**<sup>13</sup>C NMR spectrum of (4-methoxyphenyl)(5,6,7-trimethoxyisoquinolin-1-yl)methanone****(5), Thalimicrinone**

Frequency: 126 MHz

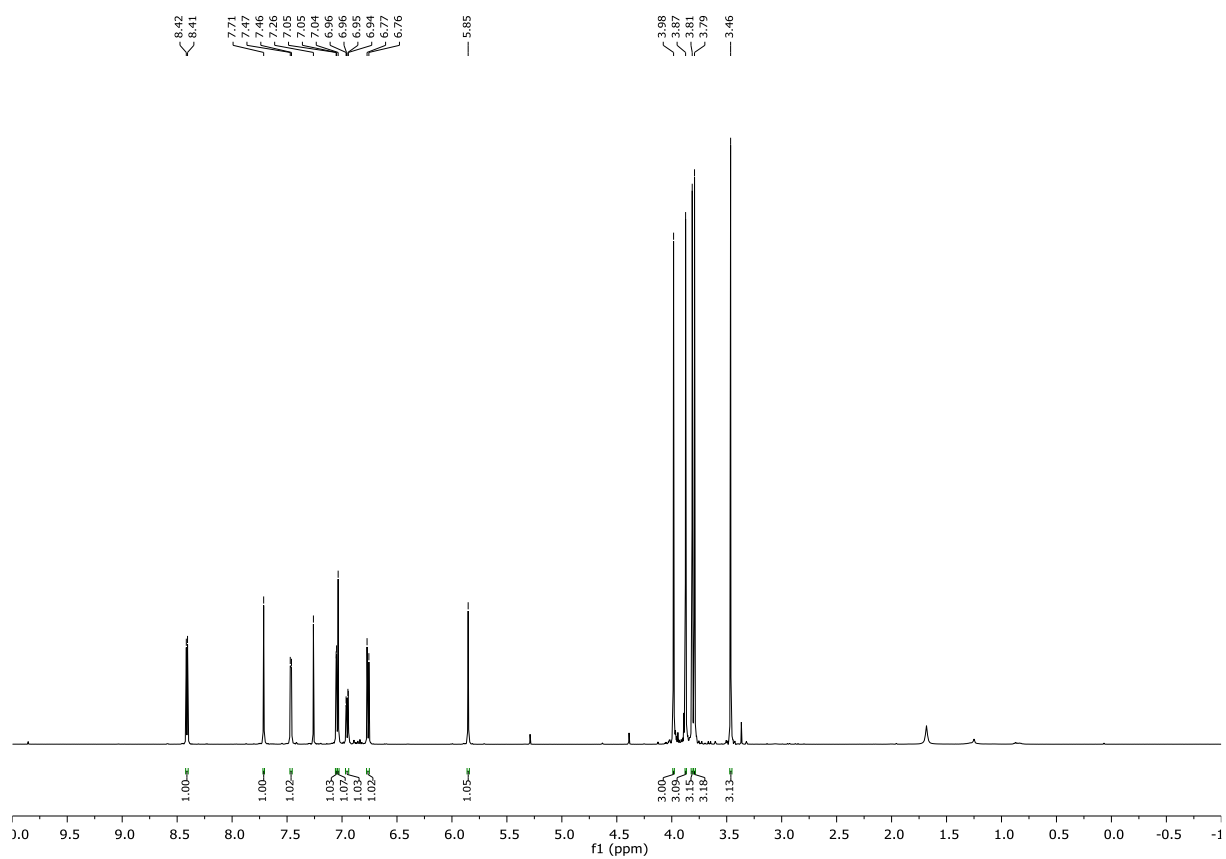
Solvent: CDCl<sub>3</sub>

**<sup>1</sup>H NMR spectrum of (±)-1-((3,4-dimethoxyphenyl)(methoxy)methyl)-6,7-dimethoxyisoquinoline (6a), Setigerine**

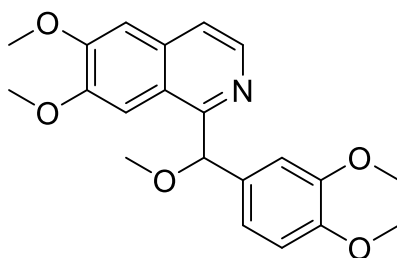


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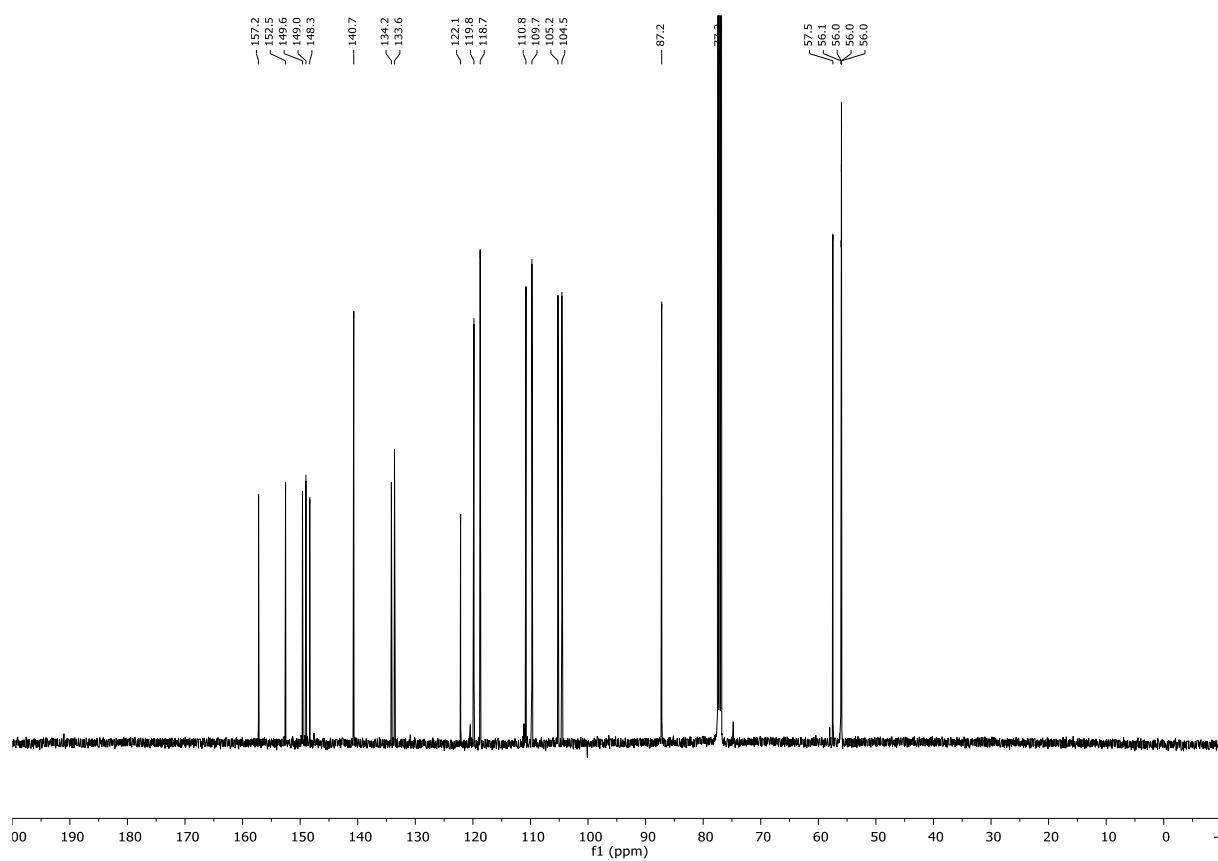


**$^{13}\text{C}$  NMR spectrum of ( $\pm$ )-1-((3,4-dimethoxyphenyl)(methoxy)methyl)-6,7-dimethoxyisoquinoline (6a), Setigerine**

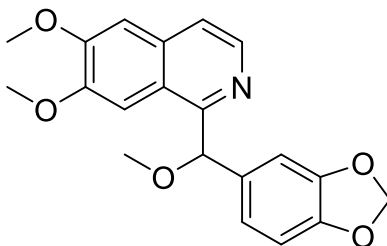


Frequency: 126 MHz

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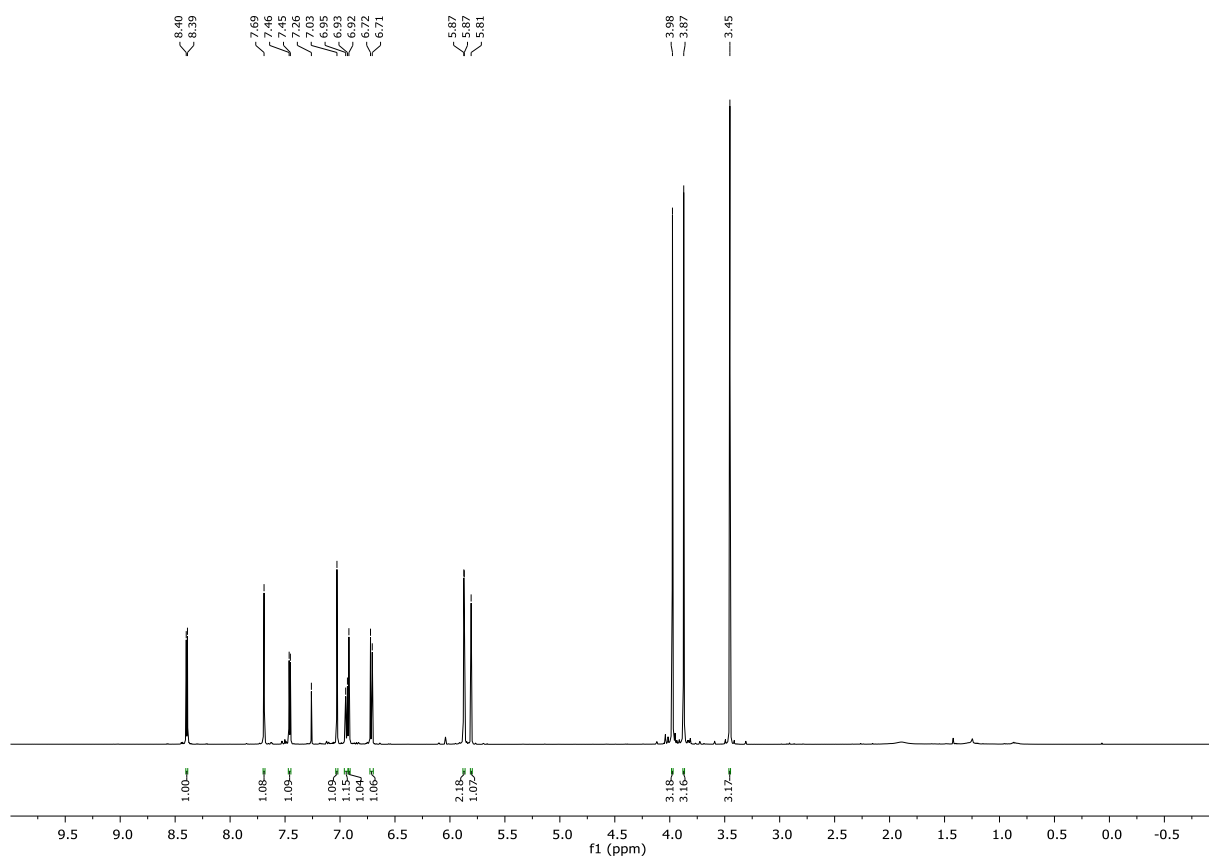


**<sup>1</sup>H NMR spectrum of (±)-1-(benzo[d][1,3]dioxol-5-yl(methoxy)methyl)-6,7-dimethoxyisoquinoline (6b), Setigeridine**

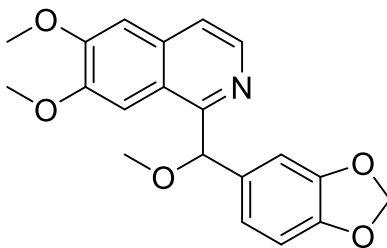


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Solvent: CDCl<sub>3</sub>

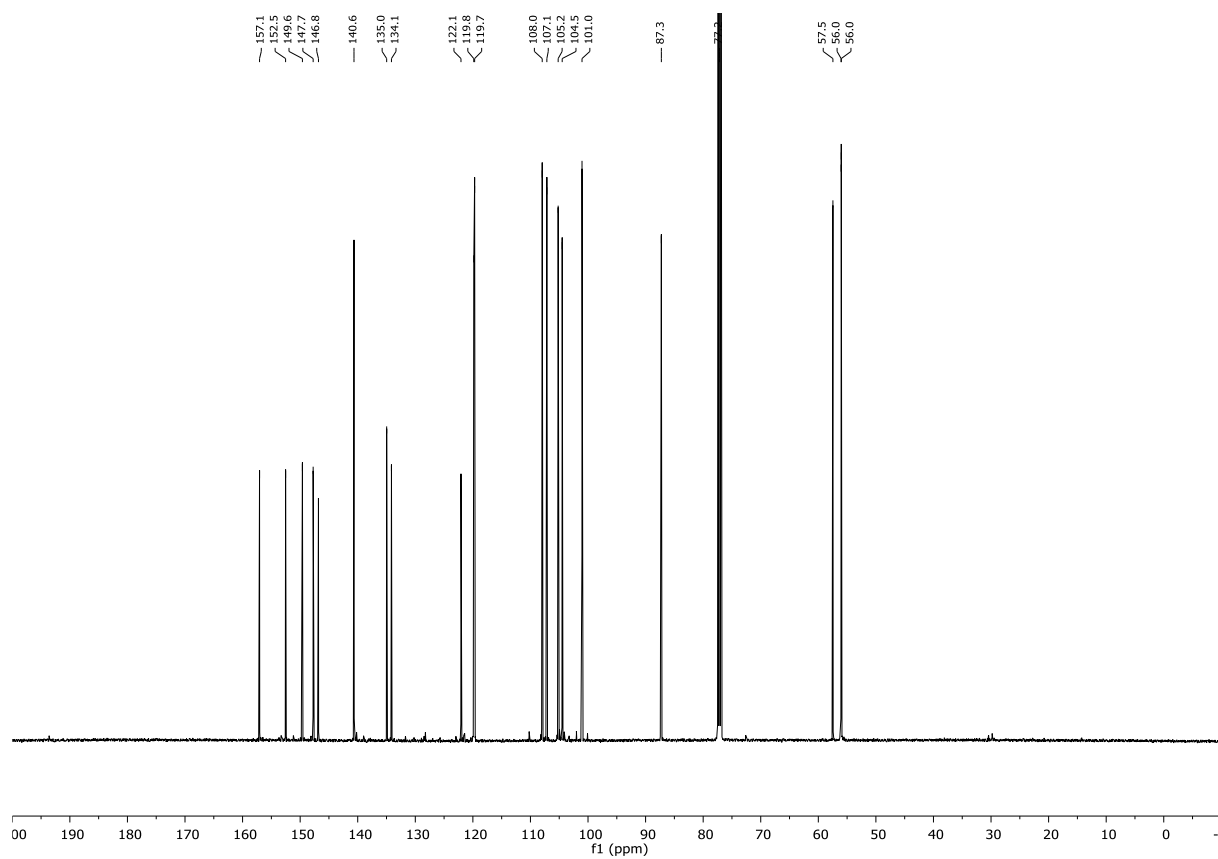


**$^{13}\text{C}$  NMR spectrum ( $\pm$ )-1-(benzo[d][1,3]dioxol-5-yl(methoxy)methyl)-6,7-dimethoxyisoquinoline (6b), Setigeridine**

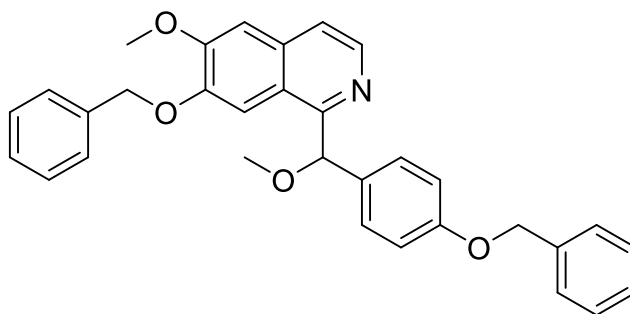


Frequency: 126 MHz

Solvent: CDCl<sub>3</sub>

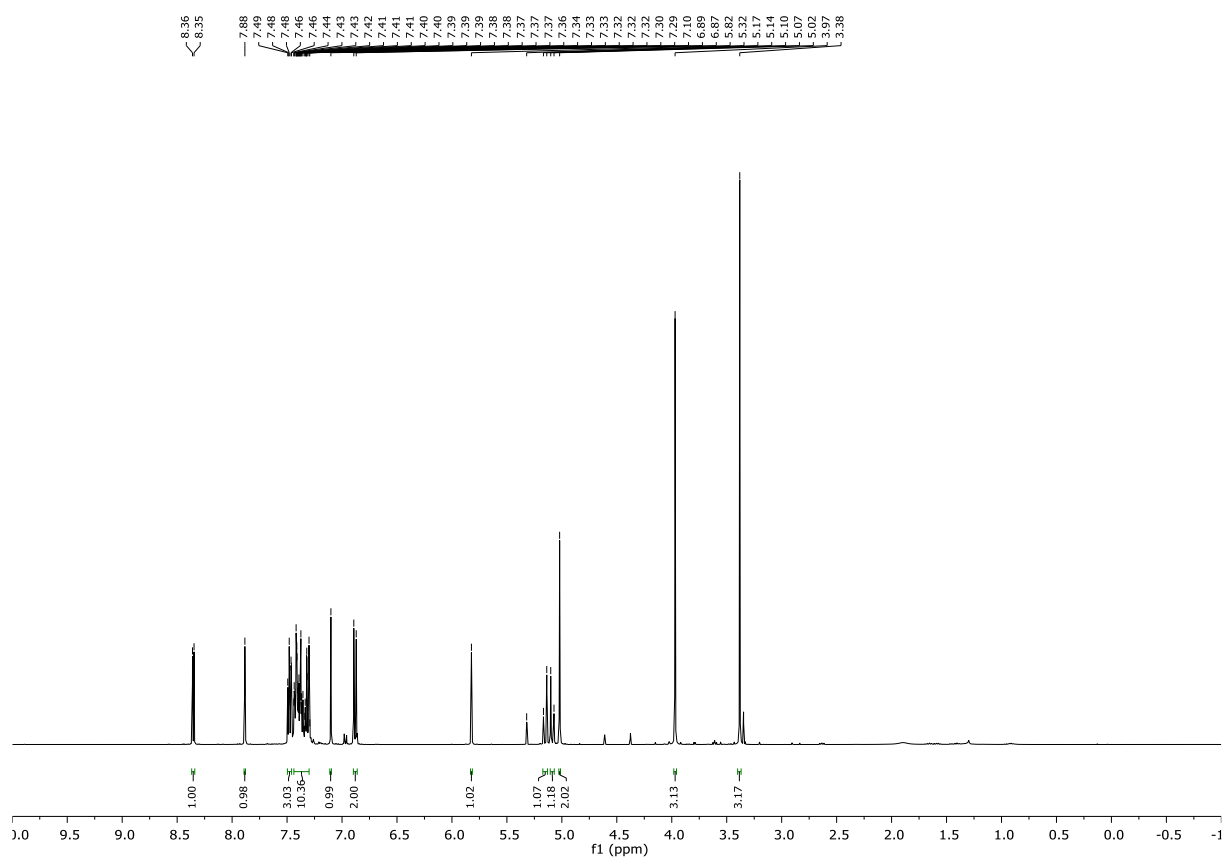


**<sup>1</sup>H NMR spectrum of (±)-7-(benzyloxy)-1-((4-(benzyloxy)phenyl)(methoxy)methyl)-6-methoxyisoquinoline (6c)**

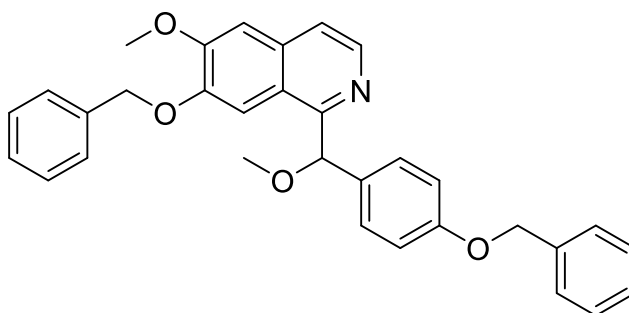


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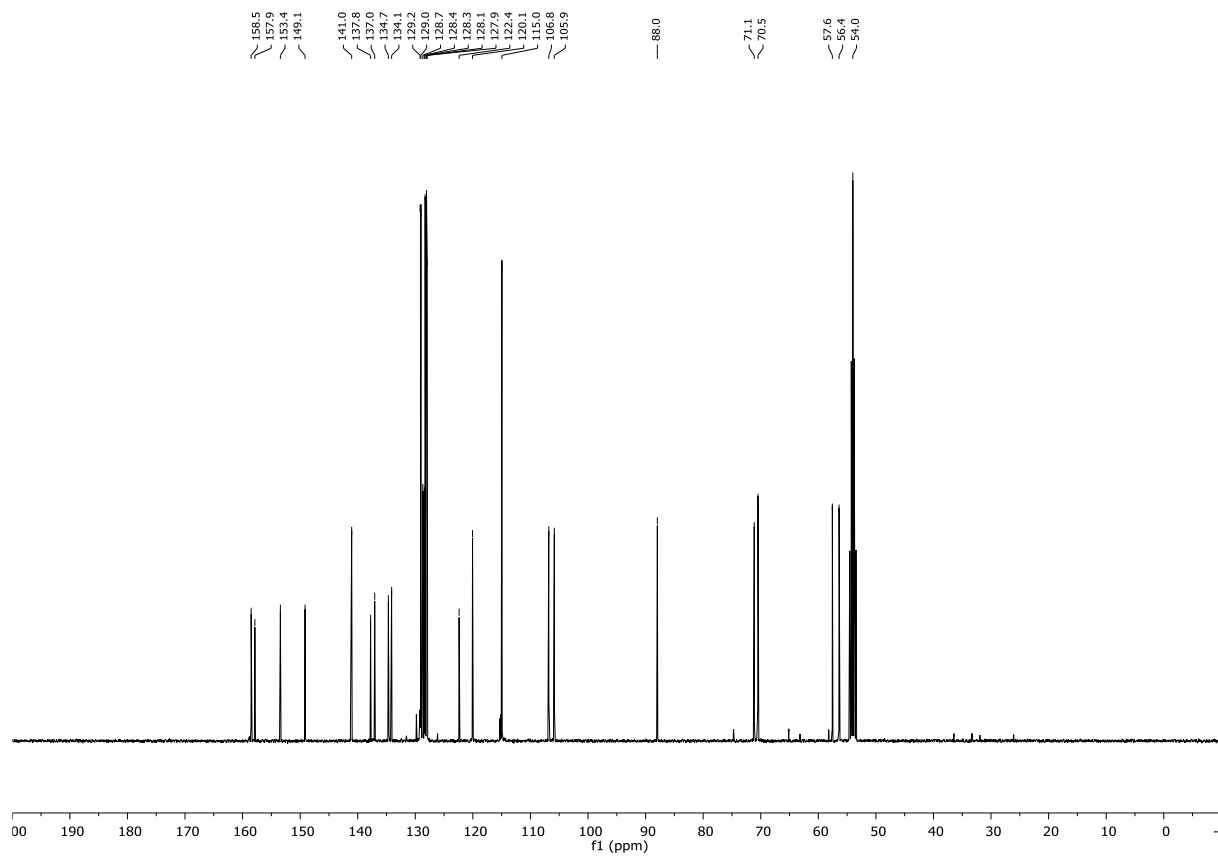


**<sup>13</sup>C NMR spectrum of (±)-7-(benzyloxy)-1-((4-(benzyloxy)phenyl)(methoxy)methyl)-6-methoxyisoquinoline (6c)**



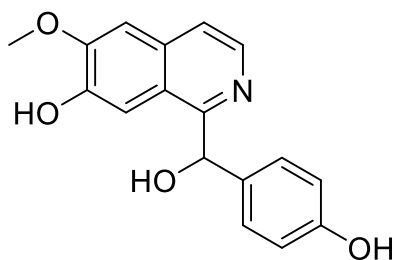
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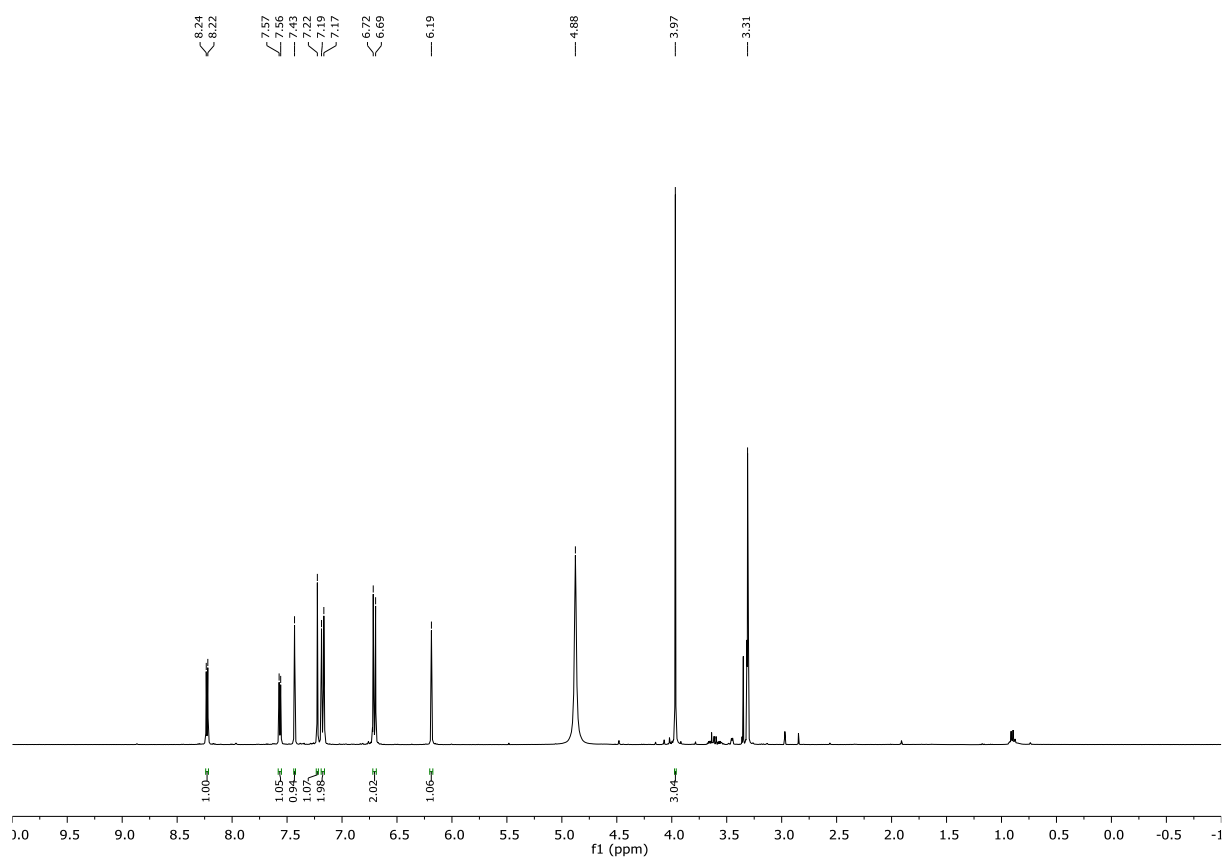


**<sup>1</sup>H NMR spectrum of (±)-1-(hydroxy(4-hydroxyphenyl)methyl)-6-methoxyisoquinolin-7-ol (7), racemic Annocherin A**

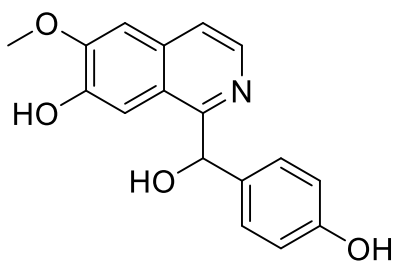


Frequency: 400 MHz

Solvent: MeOD

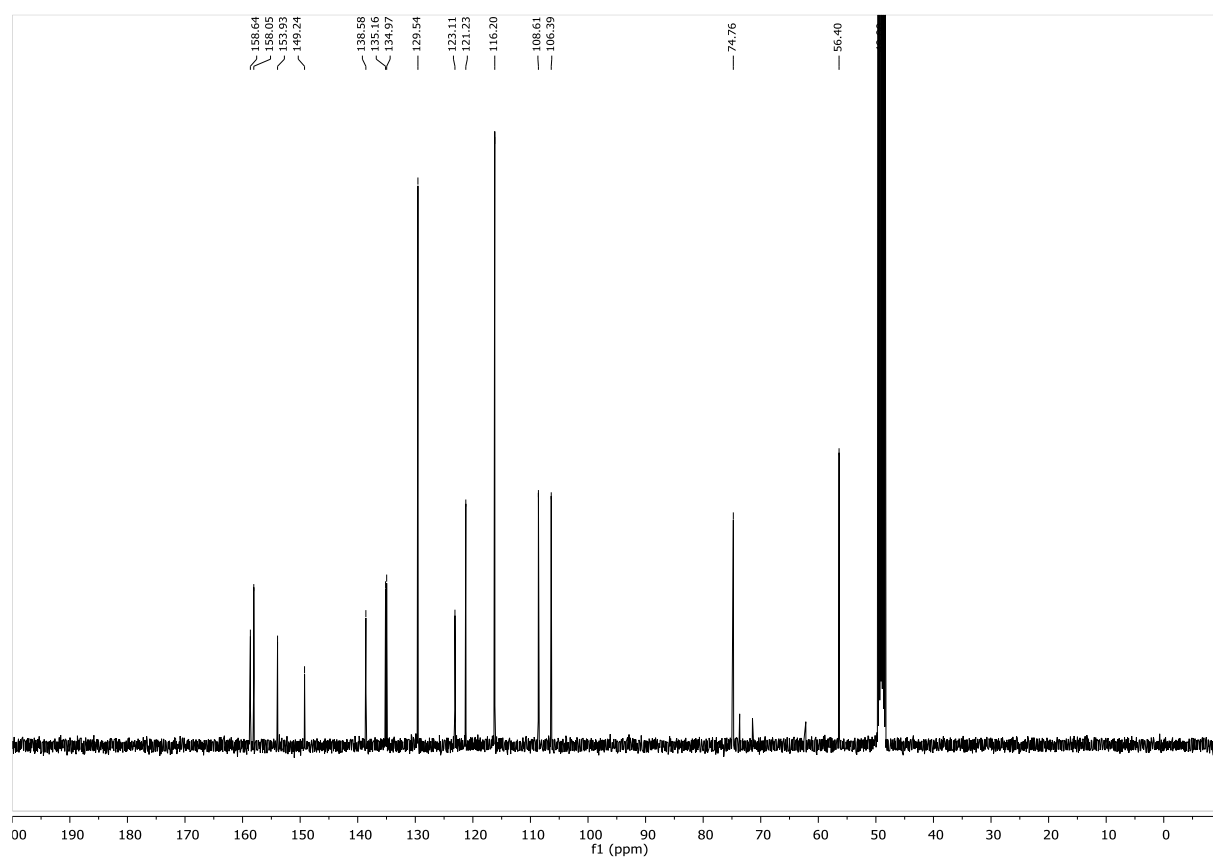


**<sup>13</sup>C NMR spectrum of (±)-1-(hydroxy(4-hydroxyphenyl)methyl)-6-methoxyisoquinolin-7-ol (7), racemic Annocherin A**

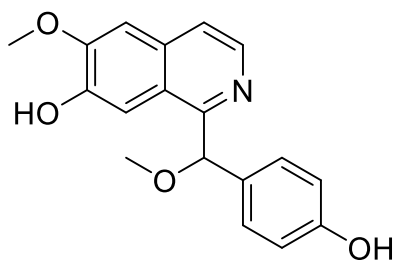


Frequency: 101 MHz

Solvent: MeOD

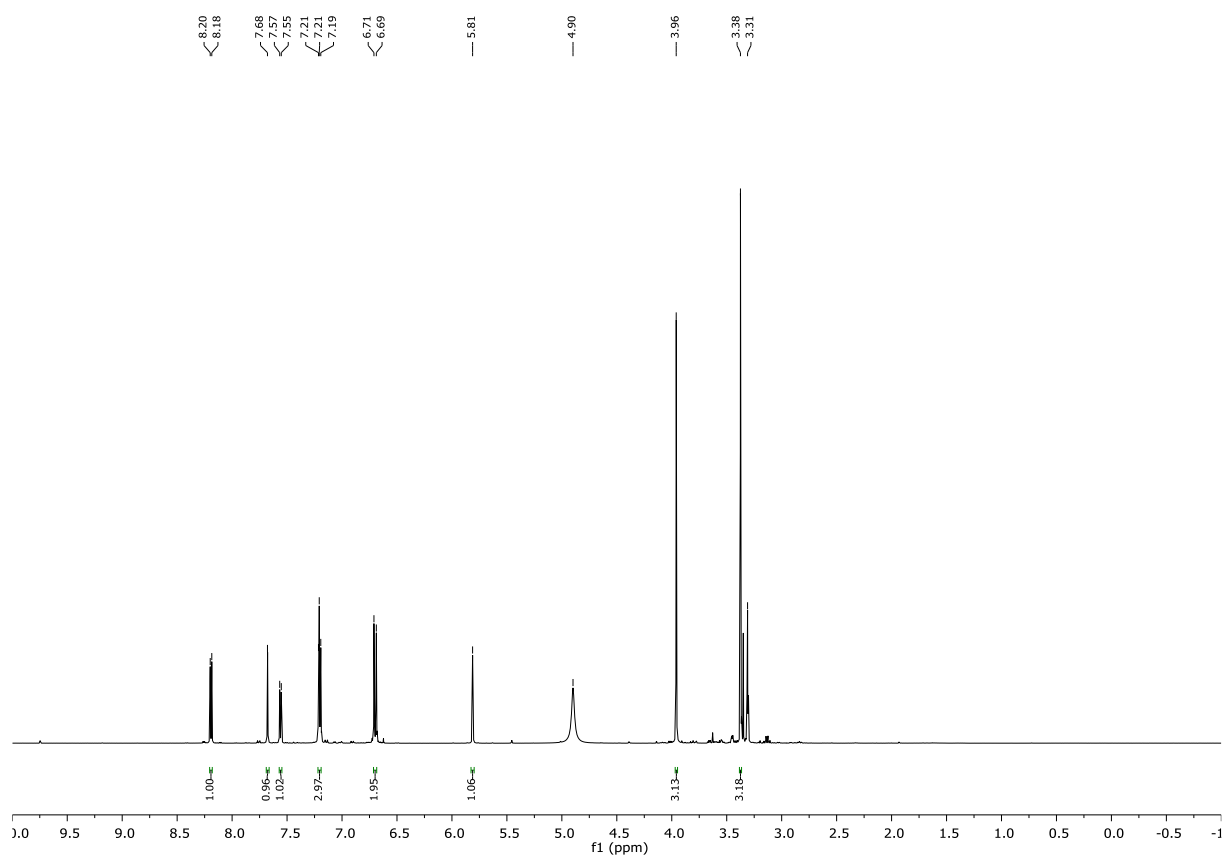


**$^1\text{H}$  NMR spectrum of ( $\pm$ )-1-((4-hydroxyphenyl)(methoxy)methyl)-6-methoxyisoquinolin-7-ol (8), racemic Annocherin B**

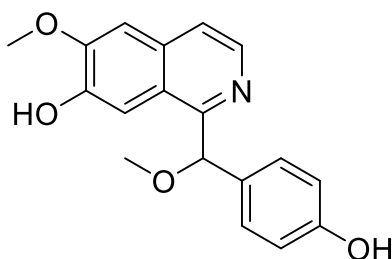


Frequency: 400 MHz

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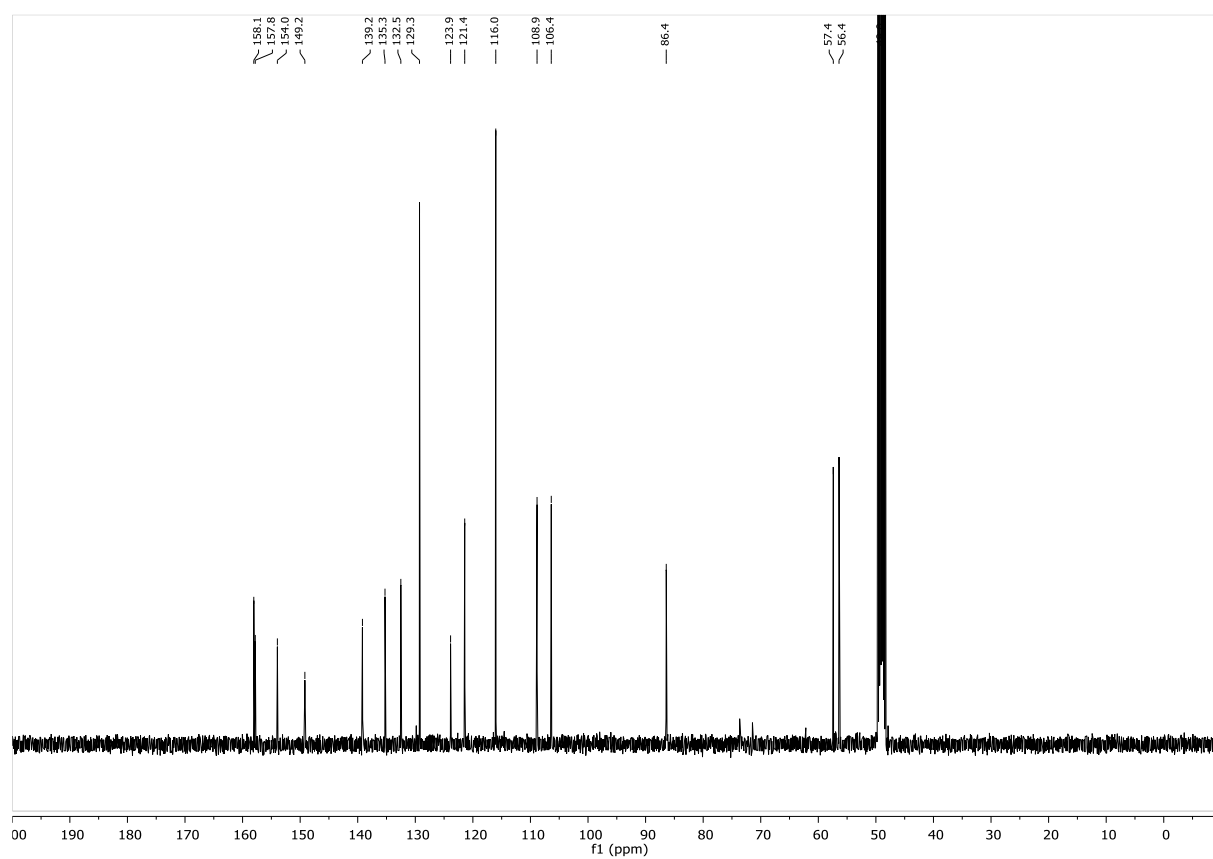


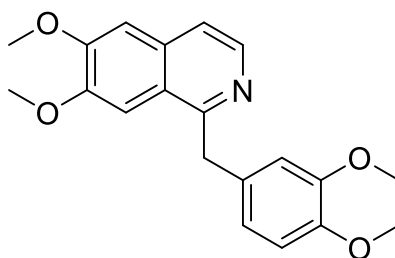
**<sup>13</sup>C NMR spectrum of (±)-1-((4-hydroxyphenyl)(methoxy)methyl)-6-methoxyisoquinolin-7-ol (8), racemic Annocherin B**



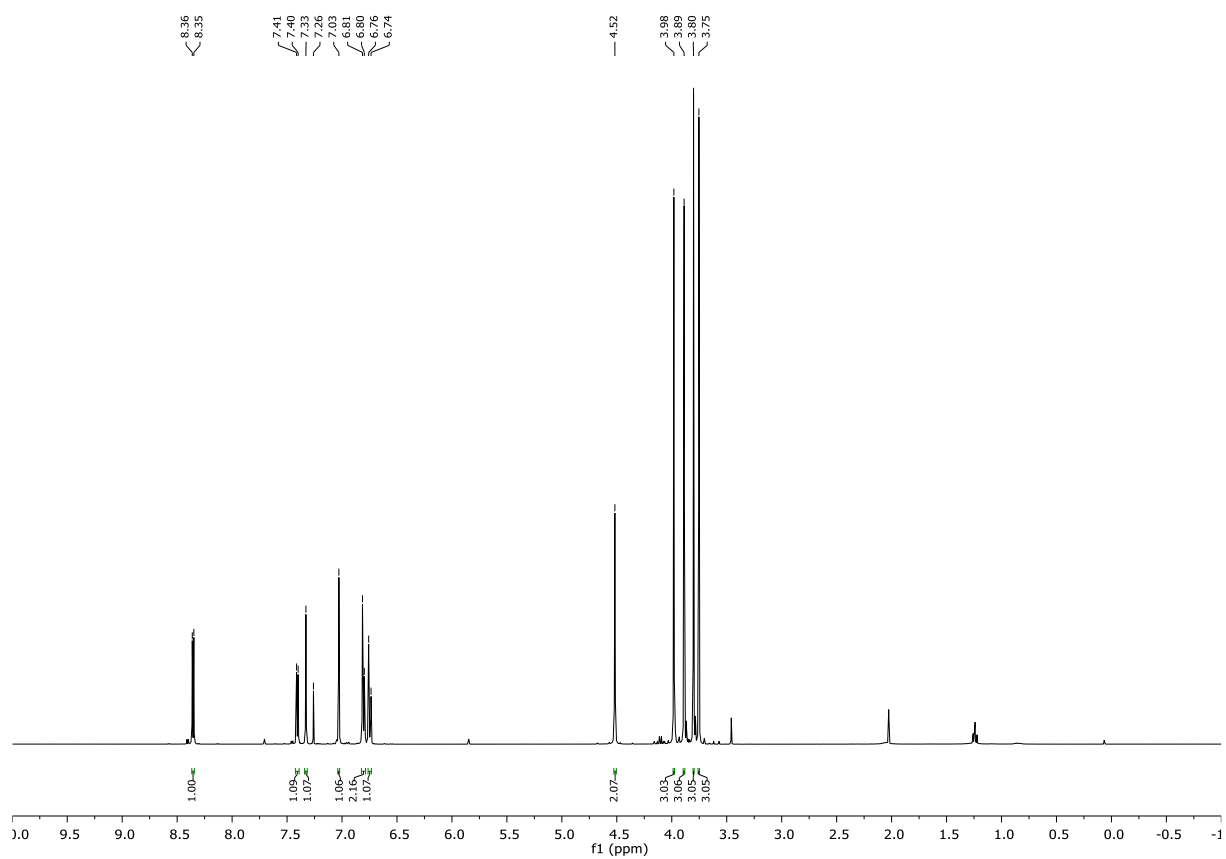
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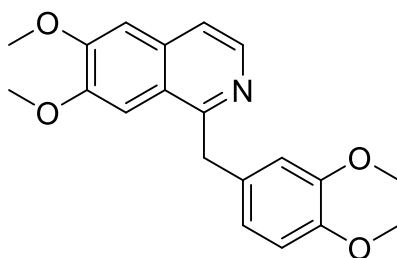
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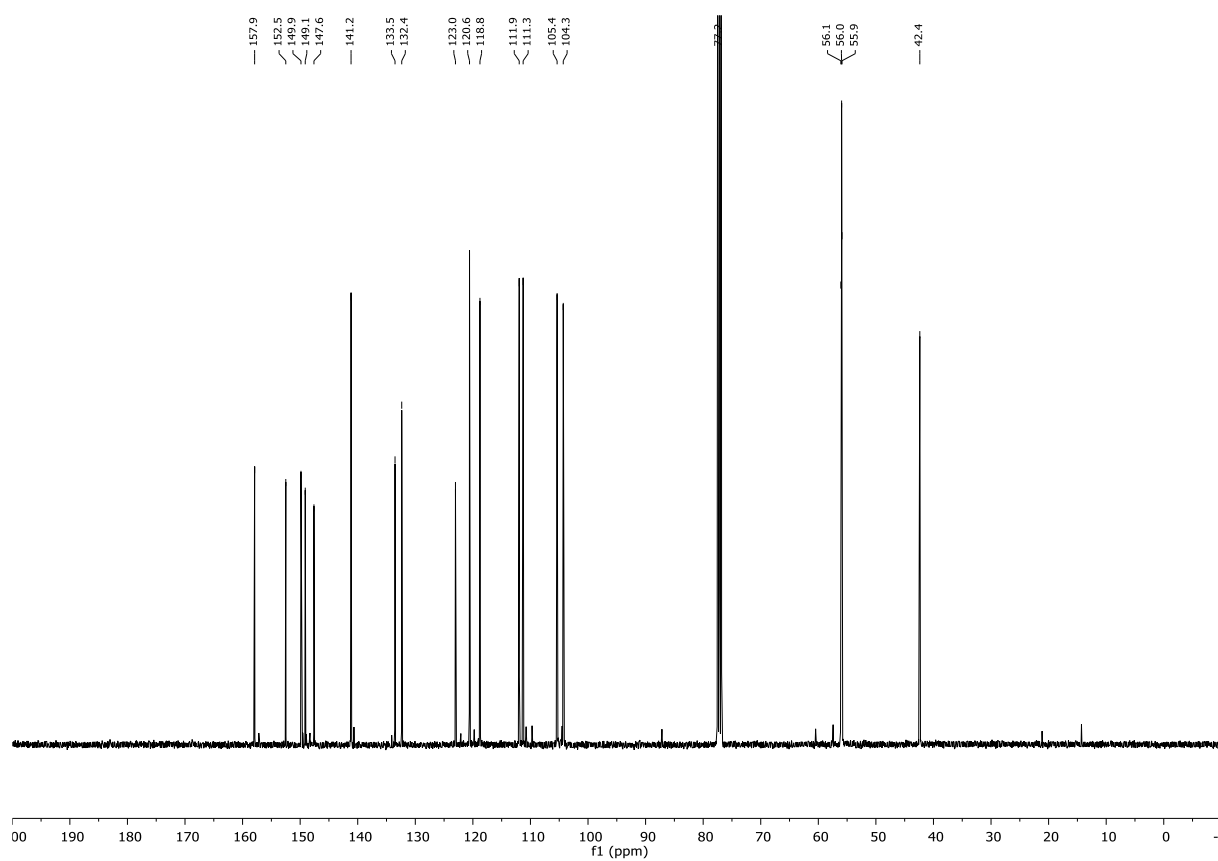
**<sup>1</sup>H NMR spectrum of 1-(3,4-dimethoxybenzyl)-6,7-dimethoxyisoquinoline (9),****Papaverine**

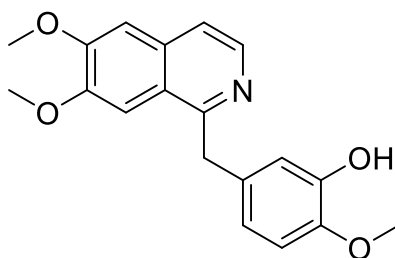
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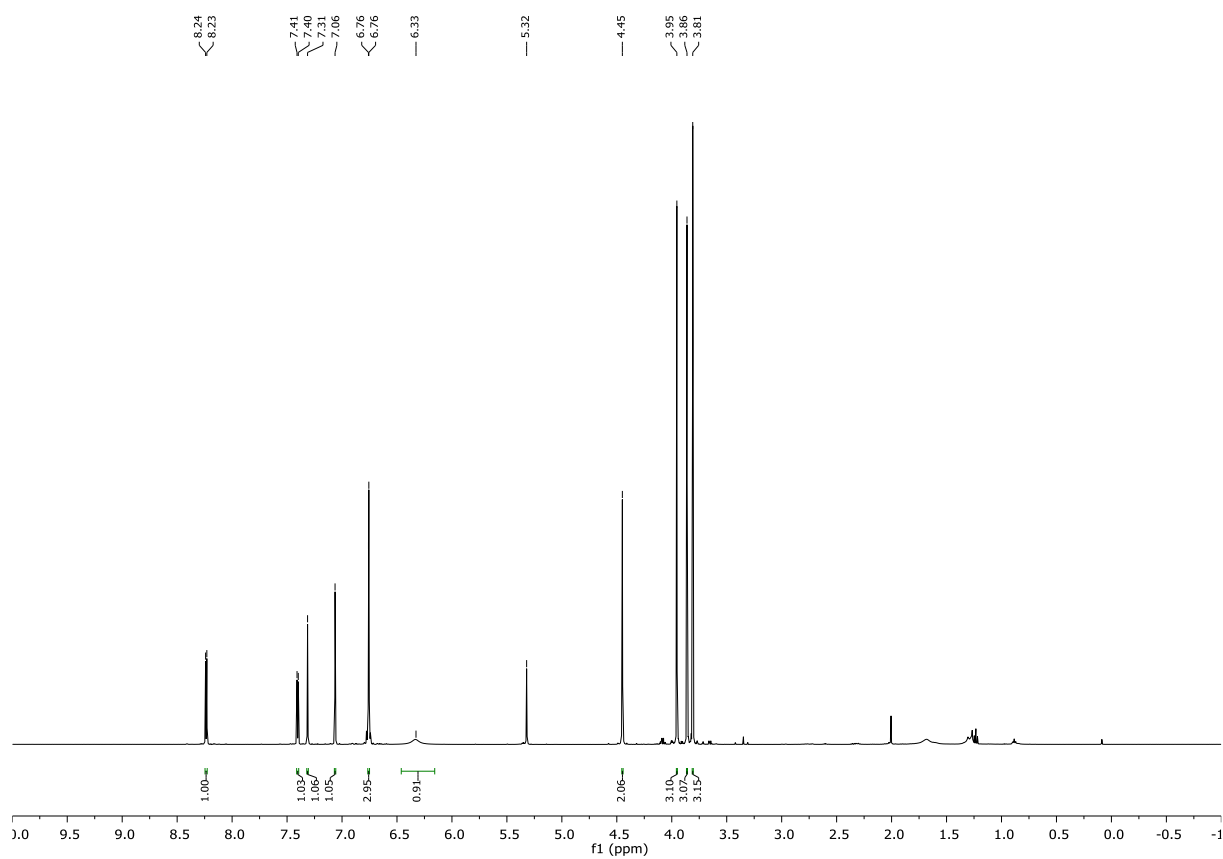
**$^{13}\text{C}$  NMR spectrum of 1-(3,4-dimethoxybenzyl)-6,7-dimethoxyisoquinoline (9),****Papaverine**

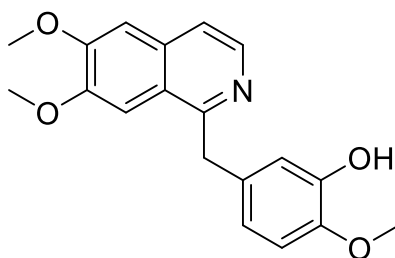
Frequency: 101 MHz

Solvent:  $\text{CDCl}_3$ 

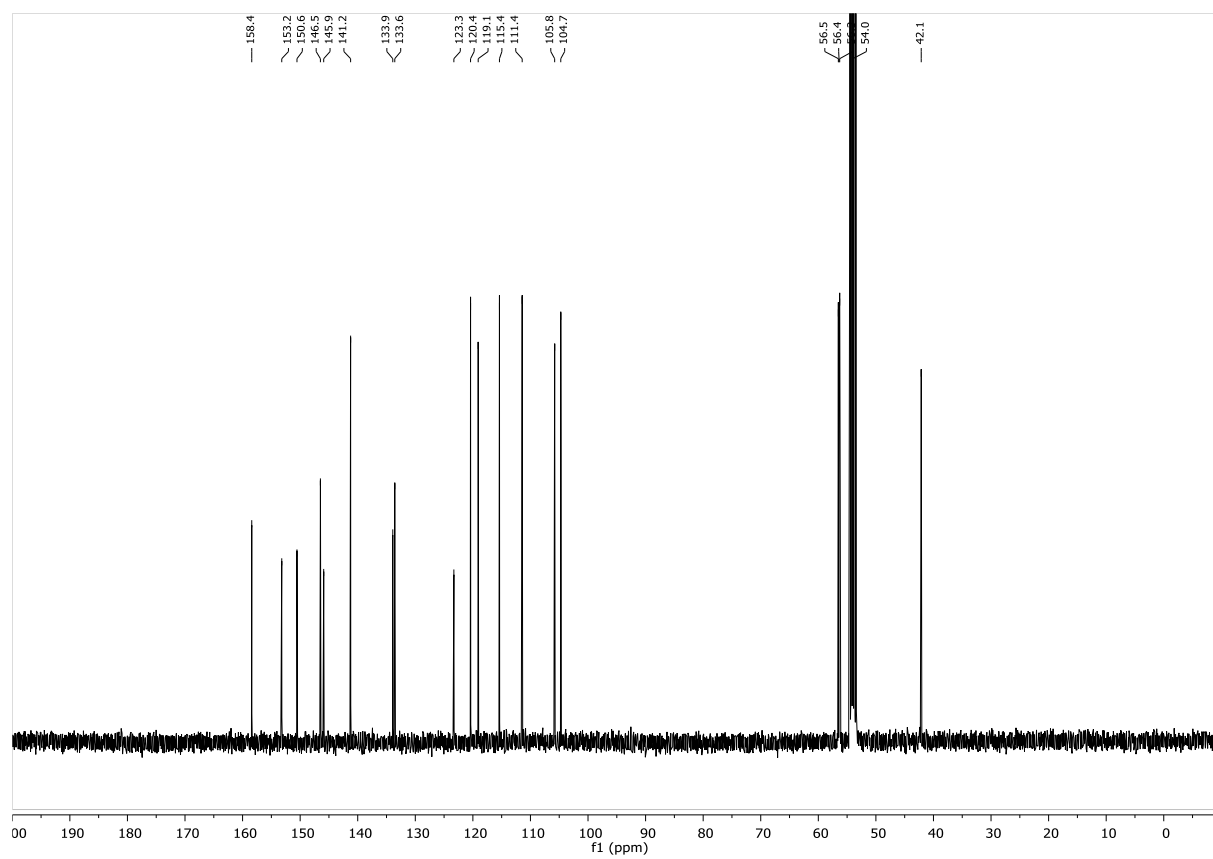
**<sup>1</sup>H NMR spectrum of 1-(3-hydroxy-4-methoxybenzyl)-6,7-dimethoxyisoquinoline (10),****Palaudine**

Frequency: 400 MHz

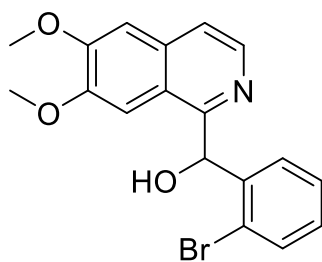
Solvent: CD<sub>2</sub>Cl<sub>2</sub>

**<sup>13</sup>C NMR spectrum of 1-(3-hydroxy-4-methoxybenzyl)-6,7-dimethoxyisoquinoline (10),****Palaudine**

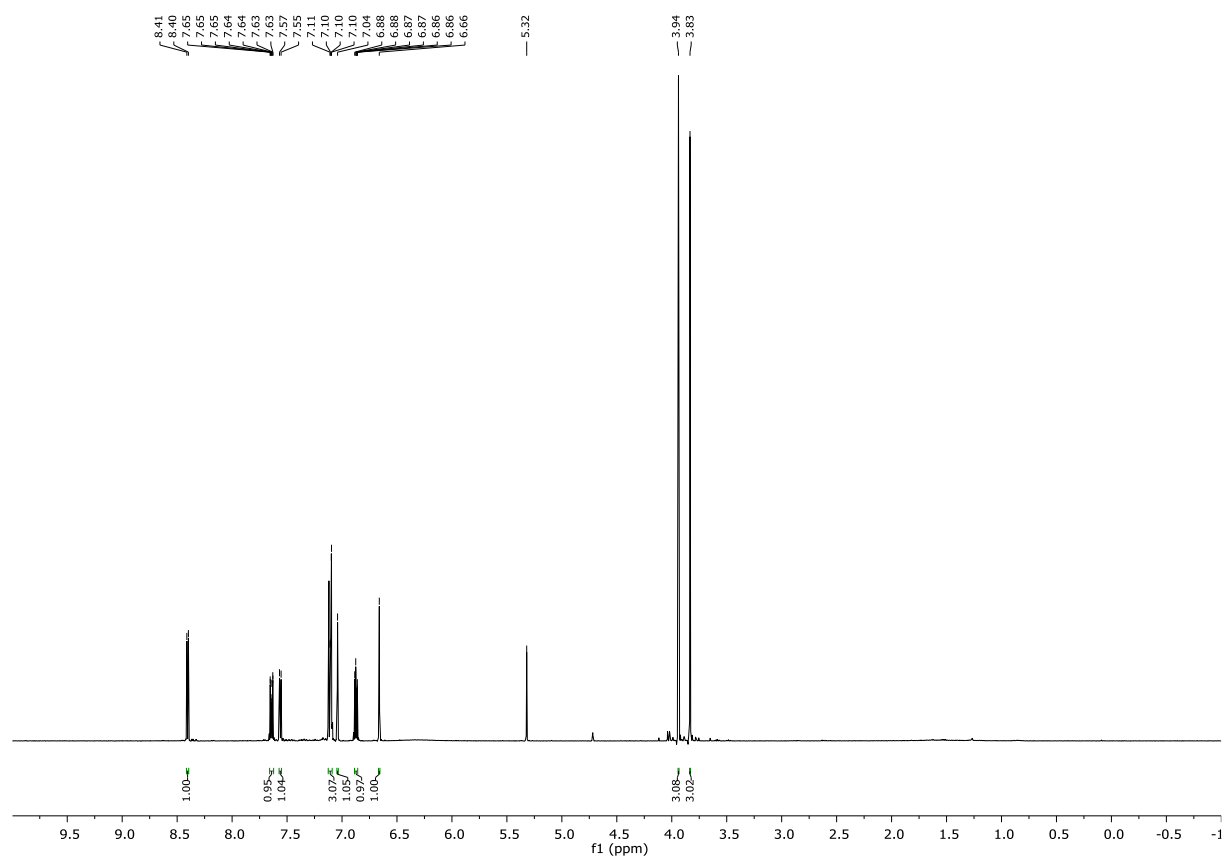
Frequency: 101 MHz

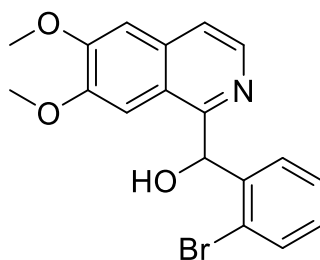
Solvent: CD<sub>2</sub>Cl<sub>2</sub>



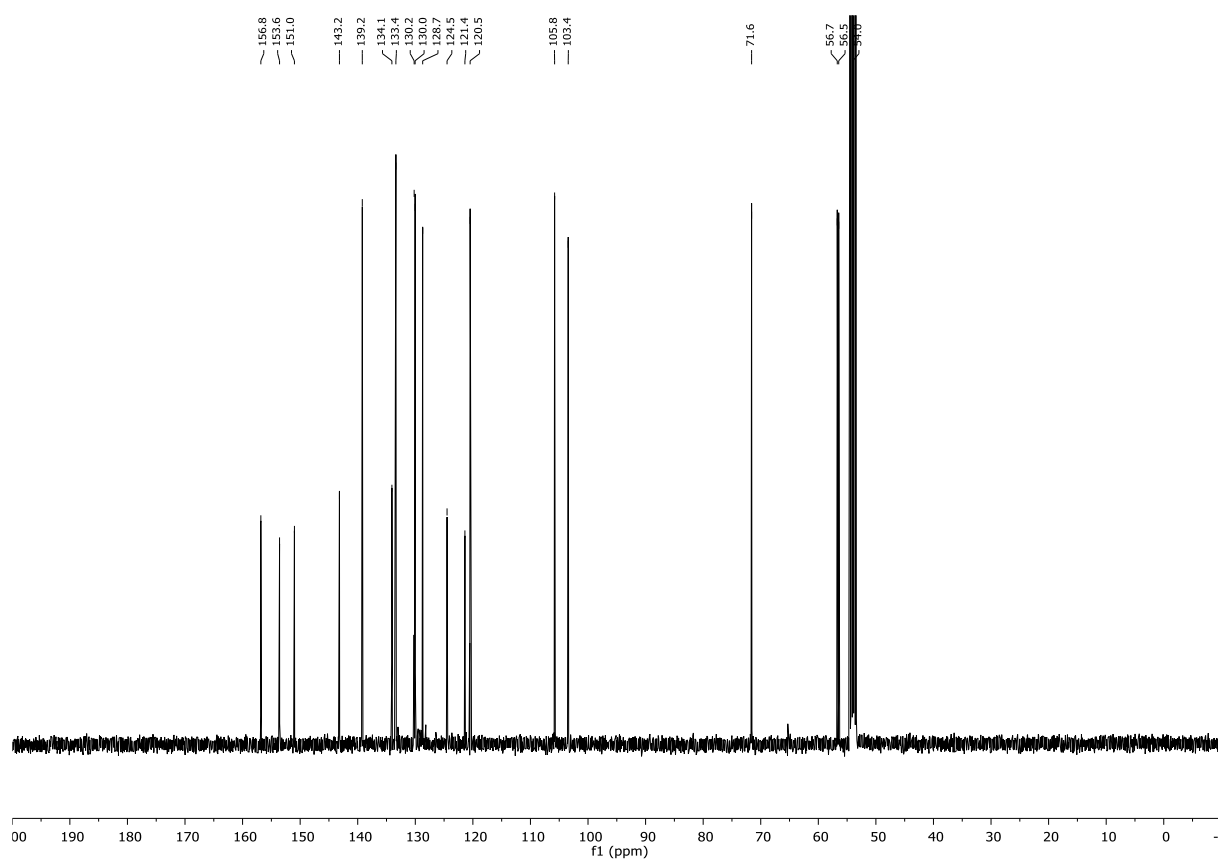
**$^1\text{H}$  NMR spectrum of ( $\pm$ )-(2-bromophenyl)(6,7-dimethoxyisoquinolin-1-yl)methanol (12a)**

Frequency: 400 MHz

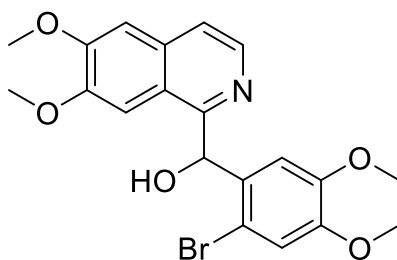
Solvent:  $\text{CD}_2\text{Cl}_2$ 

**$^{13}\text{C}$  NMR spectrum of ( $\pm$ )-(2-bromophenyl)(6,7-dimethoxyisoquinolin-1-yl)methanol****(12a)**

Frequency: 101 MHz

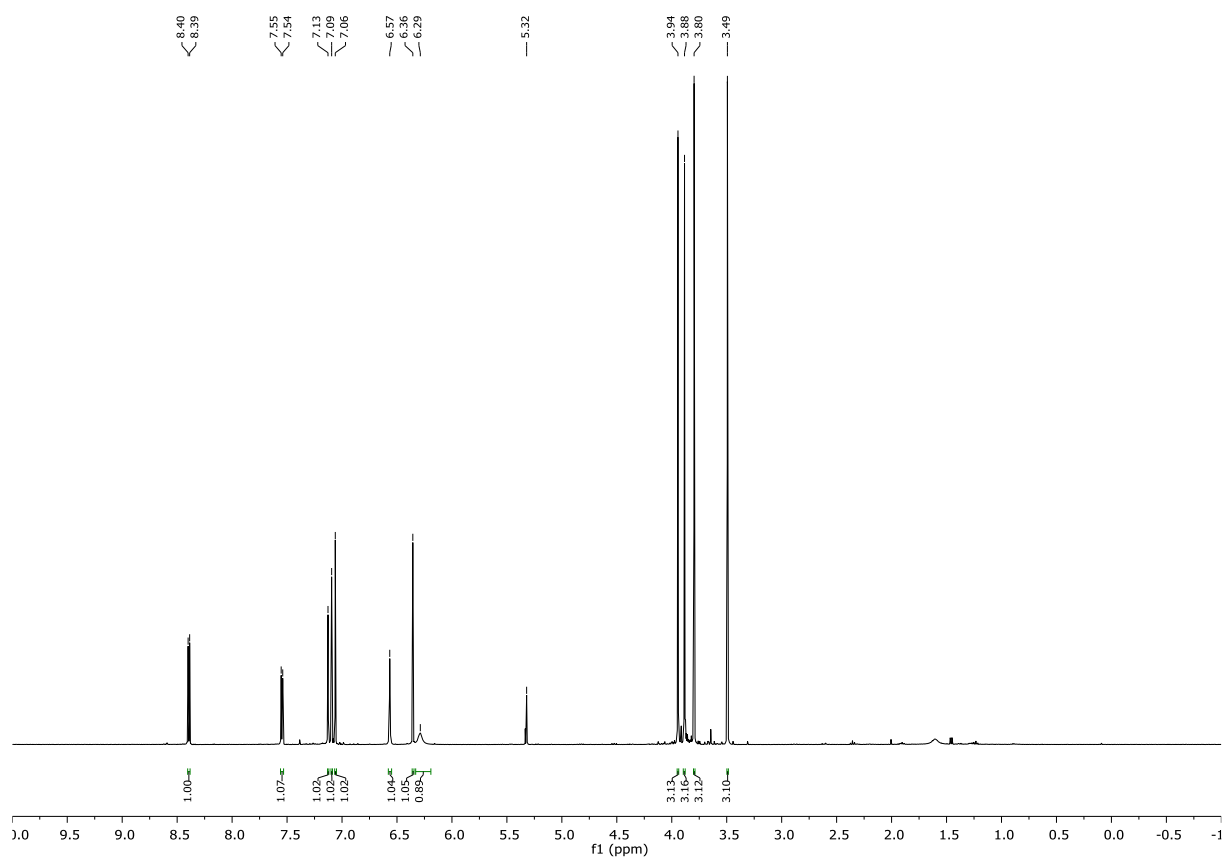
Solvent:  $\text{CD}_2\text{Cl}_2$ 

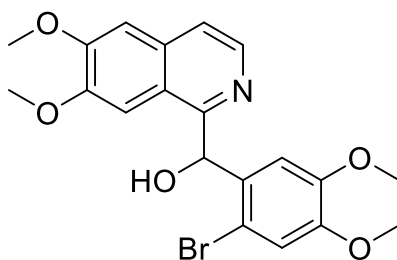
**<sup>1</sup>H NMR spectrum of (±)-(2-bromo-4,5-dimethoxyphenyl)(6,7-dimethoxyisoquinolin-1-yl)methanol (12b)**



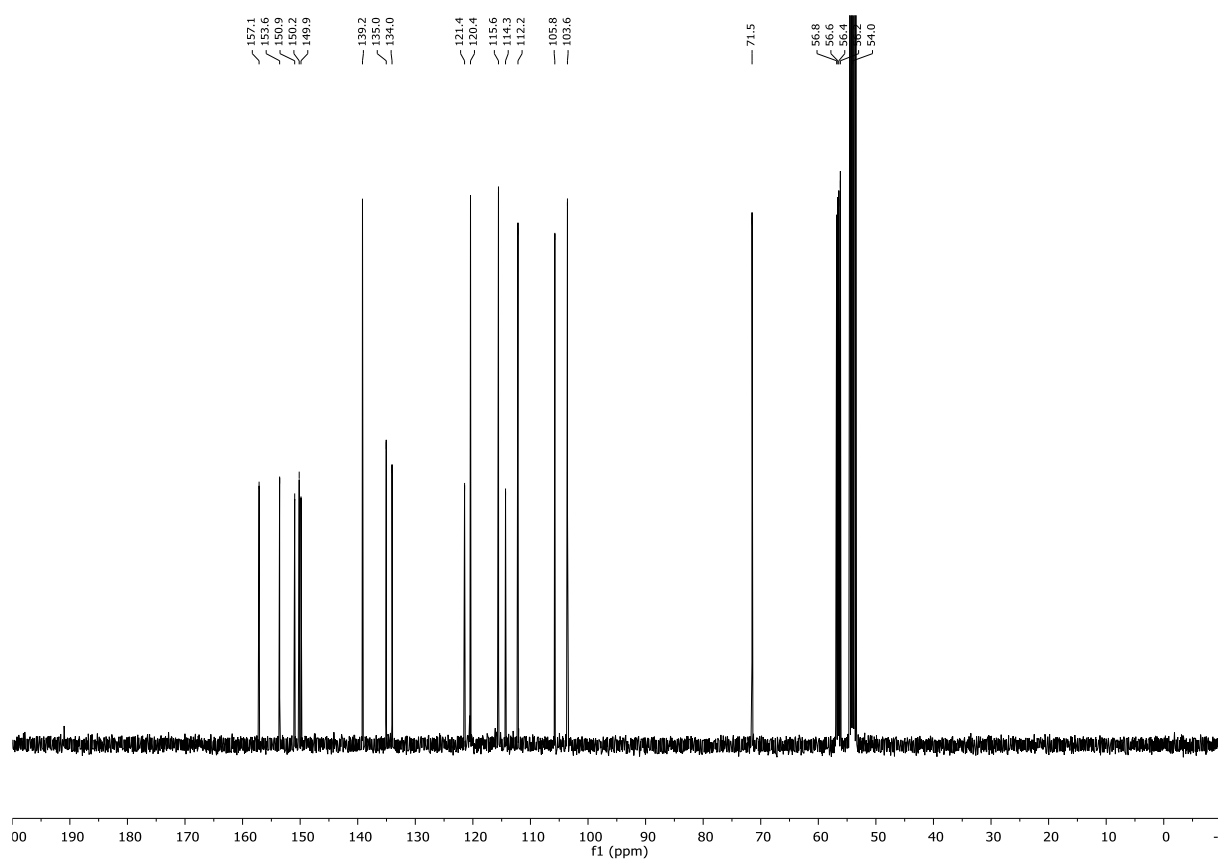
Frequency: 400 MHz

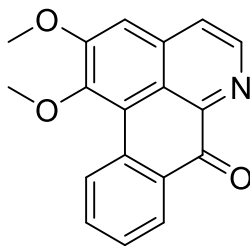
Solvent: CD<sub>2</sub>Cl<sub>2</sub>



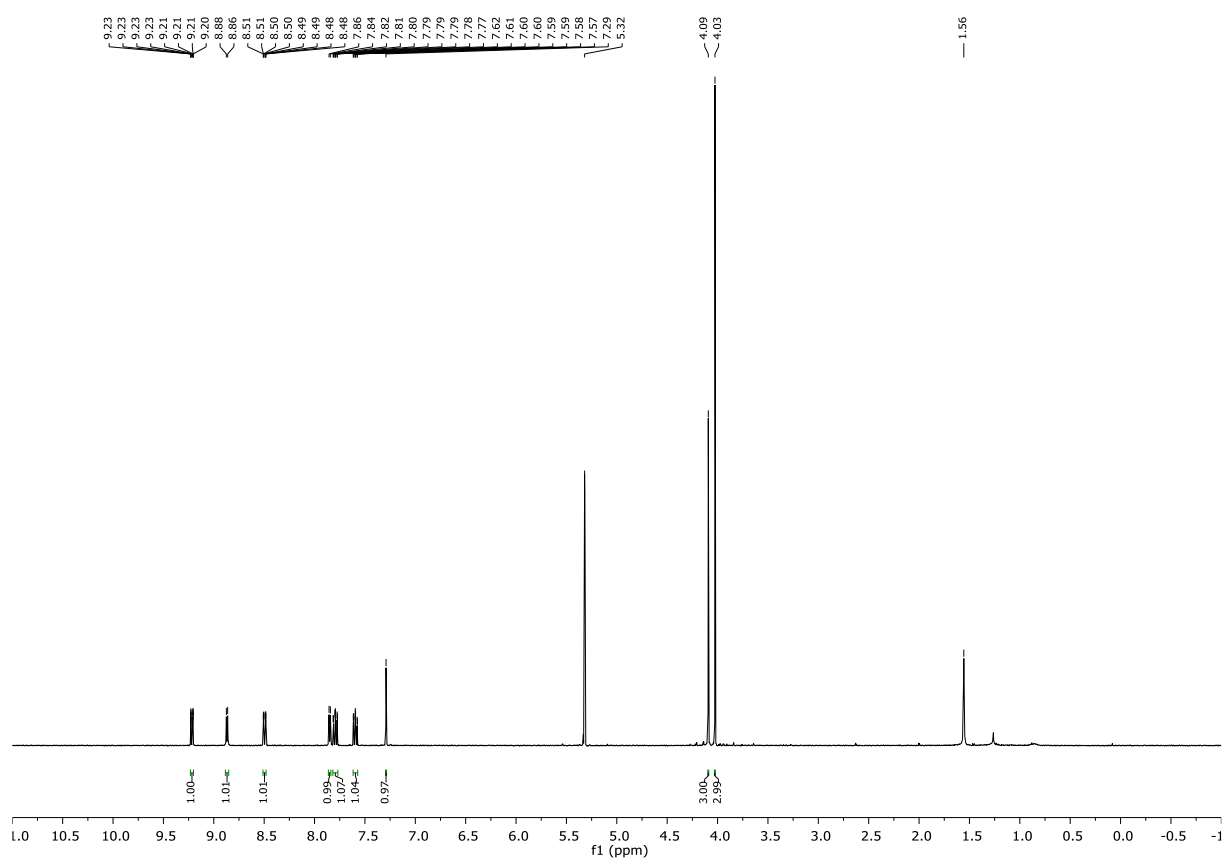
**$^{13}\text{C}$  NMR spectrum of ( $\pm$ )-(2-bromo-4,5-dimethoxyphenyl)(6,7-dimethoxyisoquinolin-1-yl)methanol (12b)**

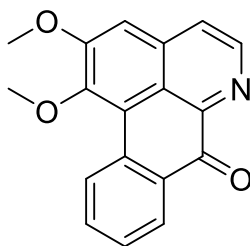
Frequency: 101 MHz

Solvent:  $\text{CD}_2\text{Cl}_2$ 

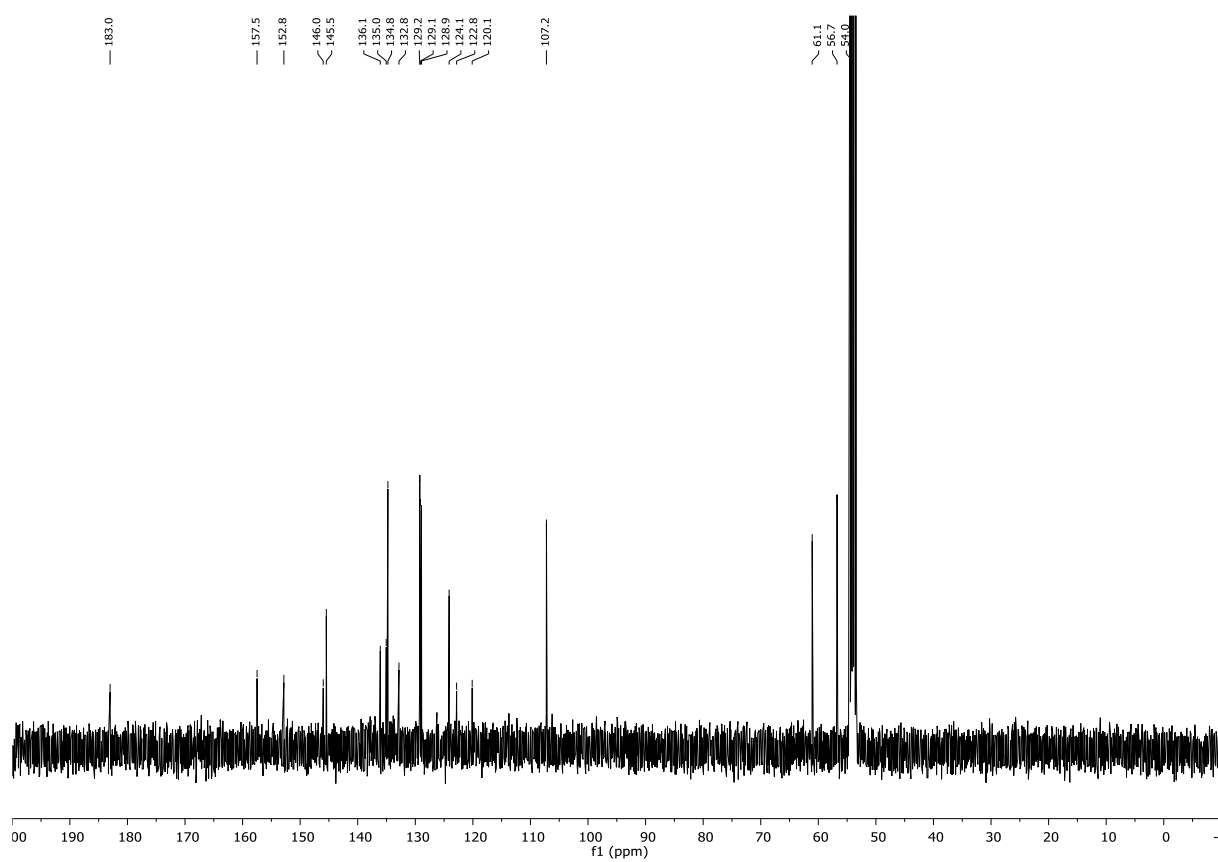
**<sup>1</sup>H NMR spectrum of 1,2-dimethoxy-7*H*-dibenzo[*de,g*]quinolin-7-one (13), Lysicamine**

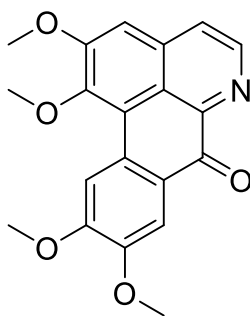
Frequency: 400 MHz

Solvent: CD<sub>2</sub>Cl<sub>2</sub>

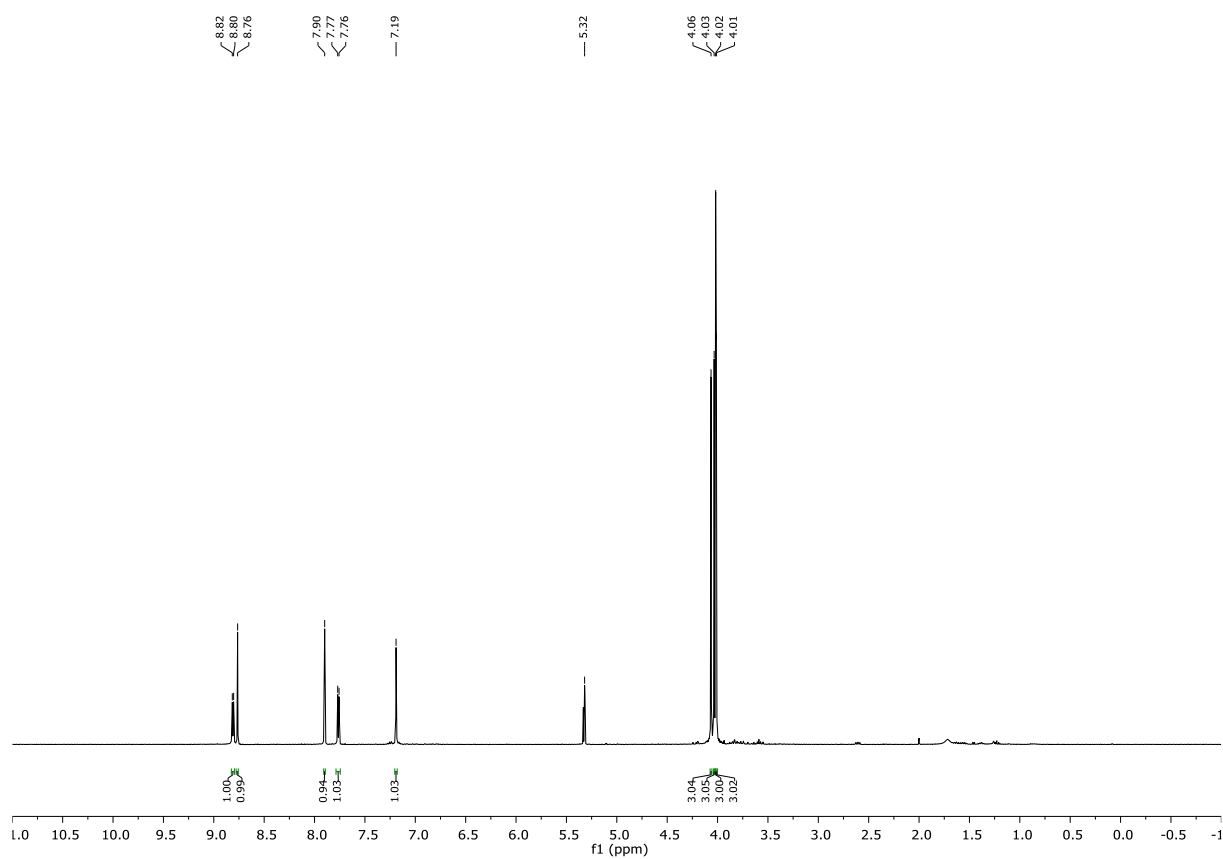
**<sup>13</sup>C NMR spectrum of 1,2-dimethoxy-7*H*-dibenzo[*de,g*]quinolin-7-one (13), Lysicamine**

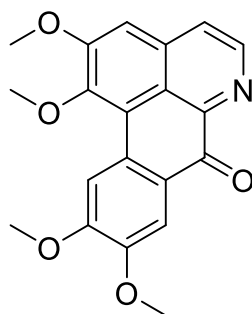
Frequency: 101 MHz

Solvent: CD<sub>2</sub>Cl<sub>2</sub>

**<sup>1</sup>H NMR spectrum of 1,2,9,10-tetramethoxy-7*H*-dibenzo[*de,g*]quinolin-7-one (14),****Oxoglaucine**

Frequency: 400 MHz

Solvent: CD<sub>2</sub>Cl<sub>2</sub>

**<sup>13</sup>C NMR spectrum of 1,2,9,10-tetramethoxy-7*H*-dibenzo[*de,g*]quinolin-7-one (14),****Oxoglaucine**

Frequency: 101 MHz

Solvent: CD<sub>2</sub>Cl<sub>2</sub>