

*Supplementary Information*

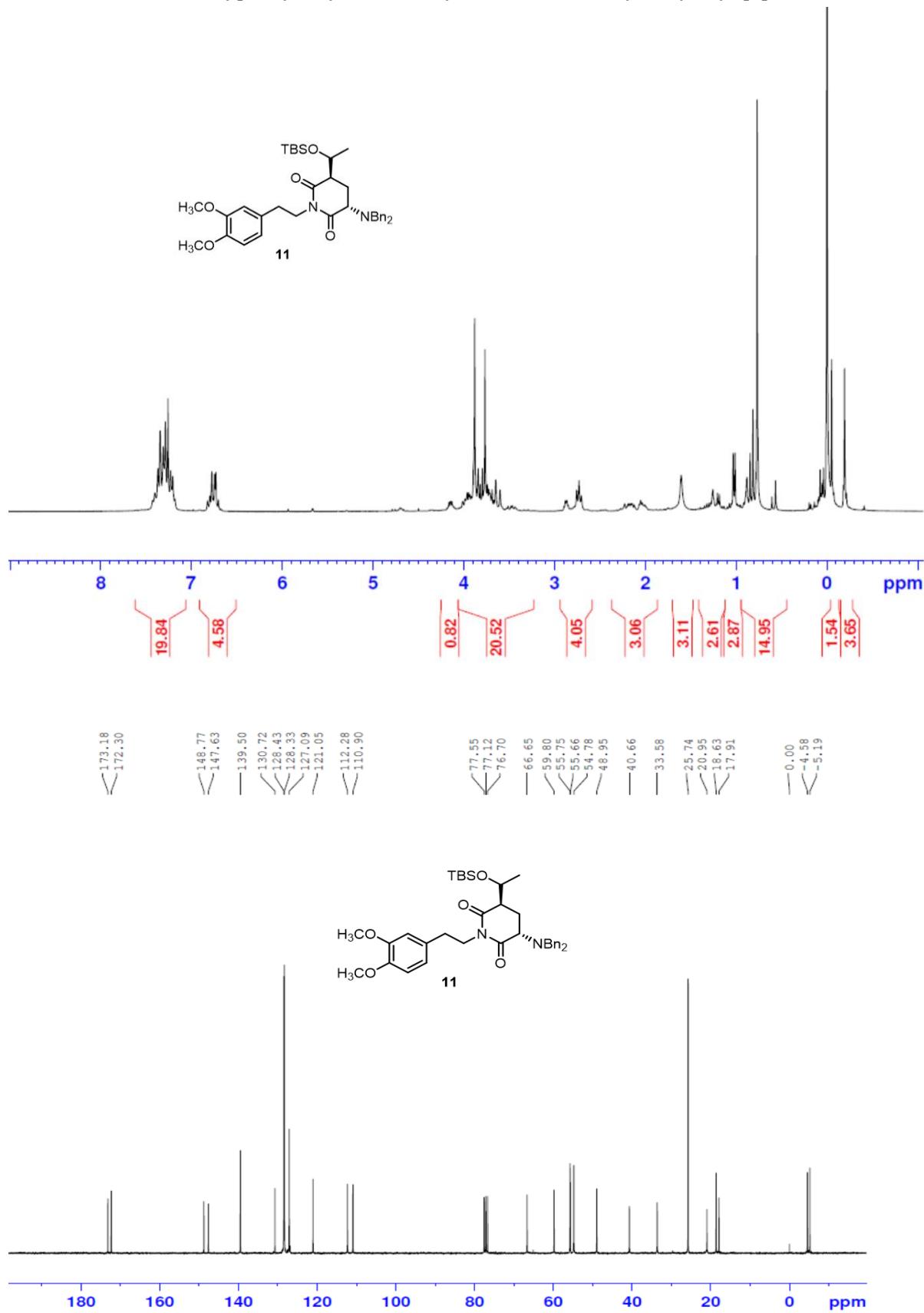
## Enantiodivergent Synthesis of Benzoquinolizidinones from L-glutamic Acid

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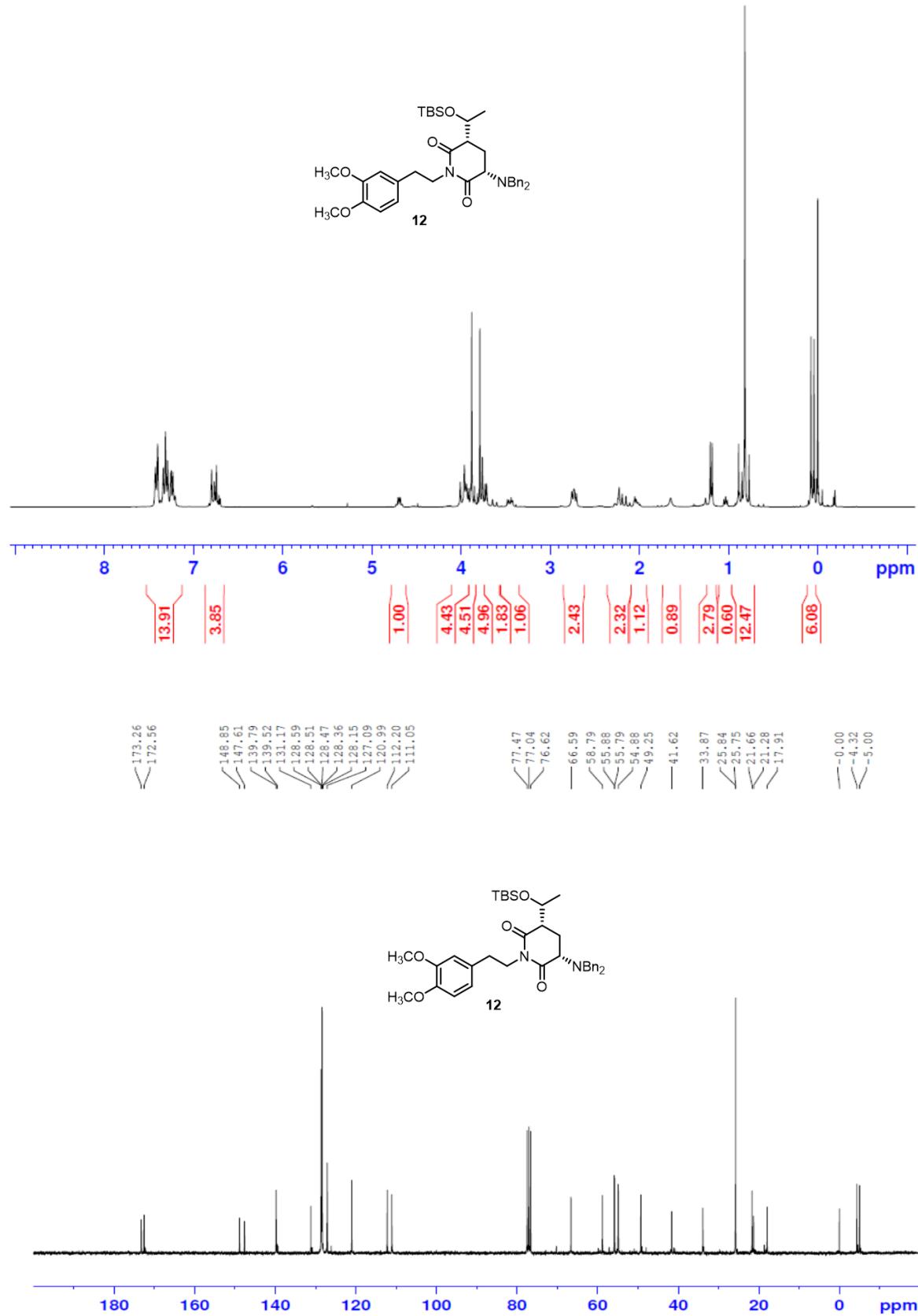
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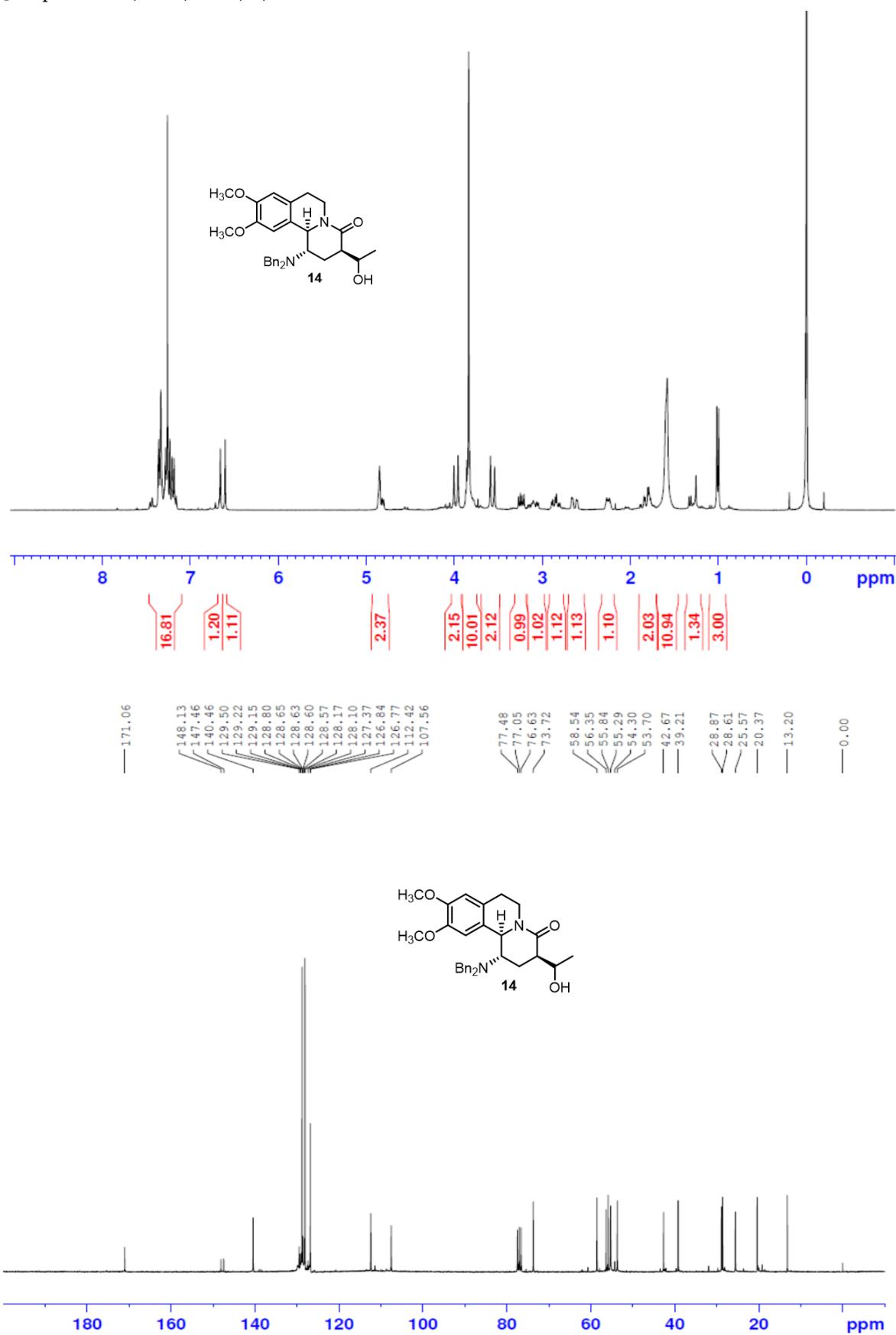
<sup>1</sup>H and <sup>13</sup>C NMR Spectra of Compounds synthesized in this study (**11, 12, 14, 15, 17, ent-15, 18, 19, 21, 22, 24, ent-22, 26 and 28**)

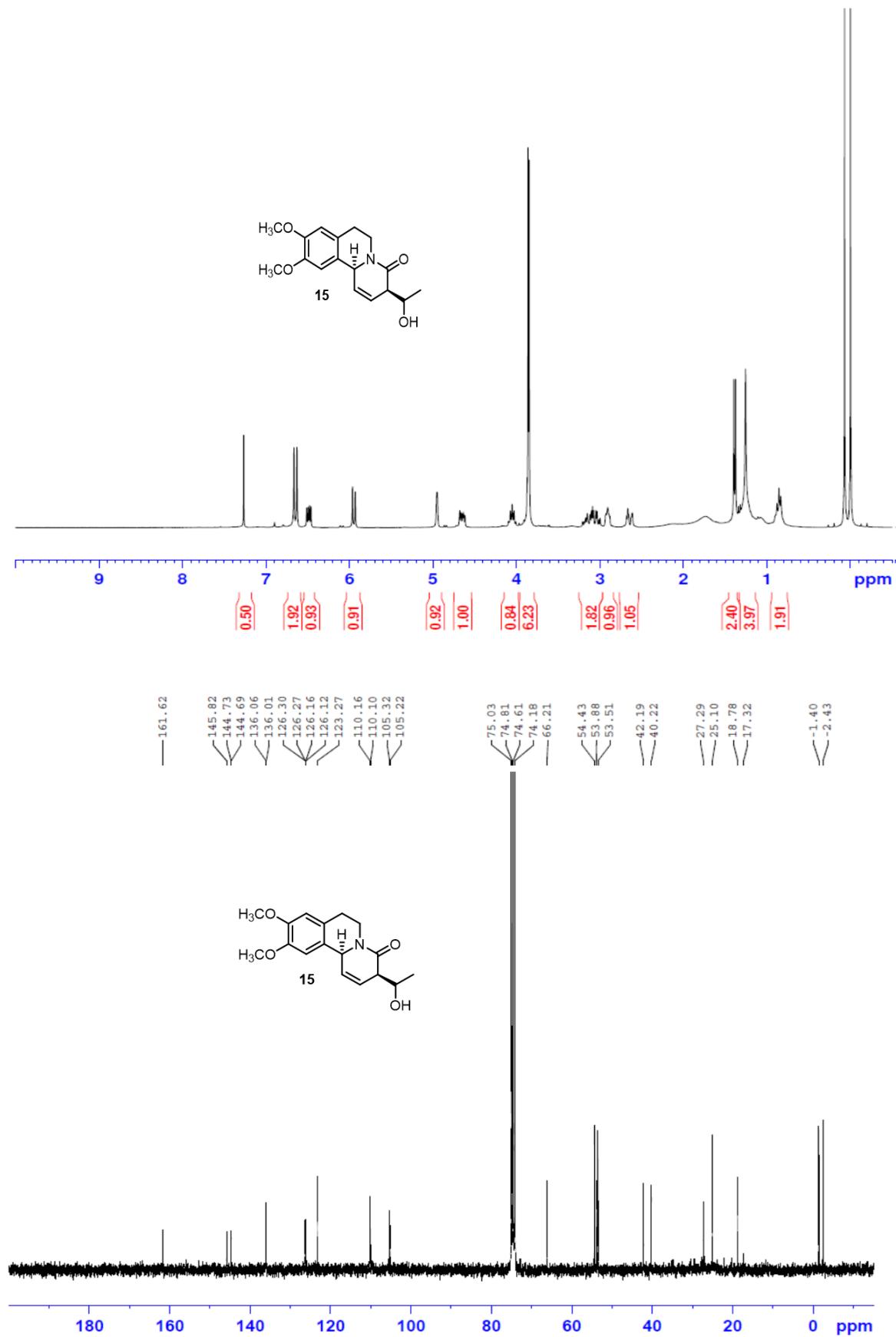
(3*S*,5*R*)-1-(3,4-Dimethoxyphenylethyl)-3-(dibenzylamino)-5-((*R*)-1-hydroxyethyl)piperidine-2,6-dione TBS ether **11**

(3*S*,5*S*)-1-(3,4-Dimethoxyphenylethyl)-3-(dibenzylamino)- 5-((*S*)-1-hydroxyethyl)piperidine-2,6-dione TBS ether **12**

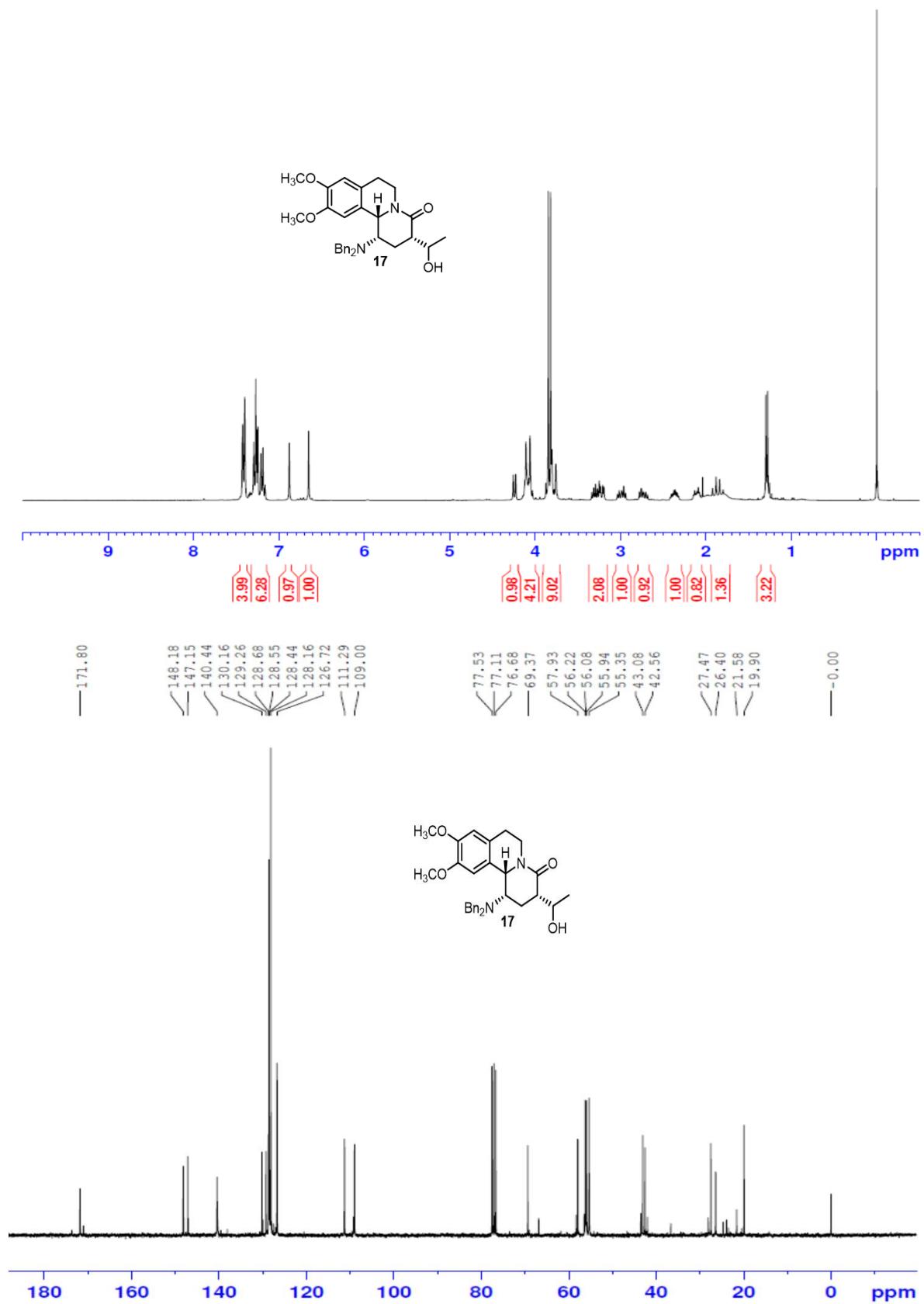


(1*S*,3*R*,11*b**R*)-1-(dibenzylamino)-2,3,6,7-tetrahydro-3-((*S*)-1-hydroxyethyl)-9,10-dimethoxy-1*H*-pyrido[2,1-*a*]isoquinolin-4(11*b**H*)-one (**14**)

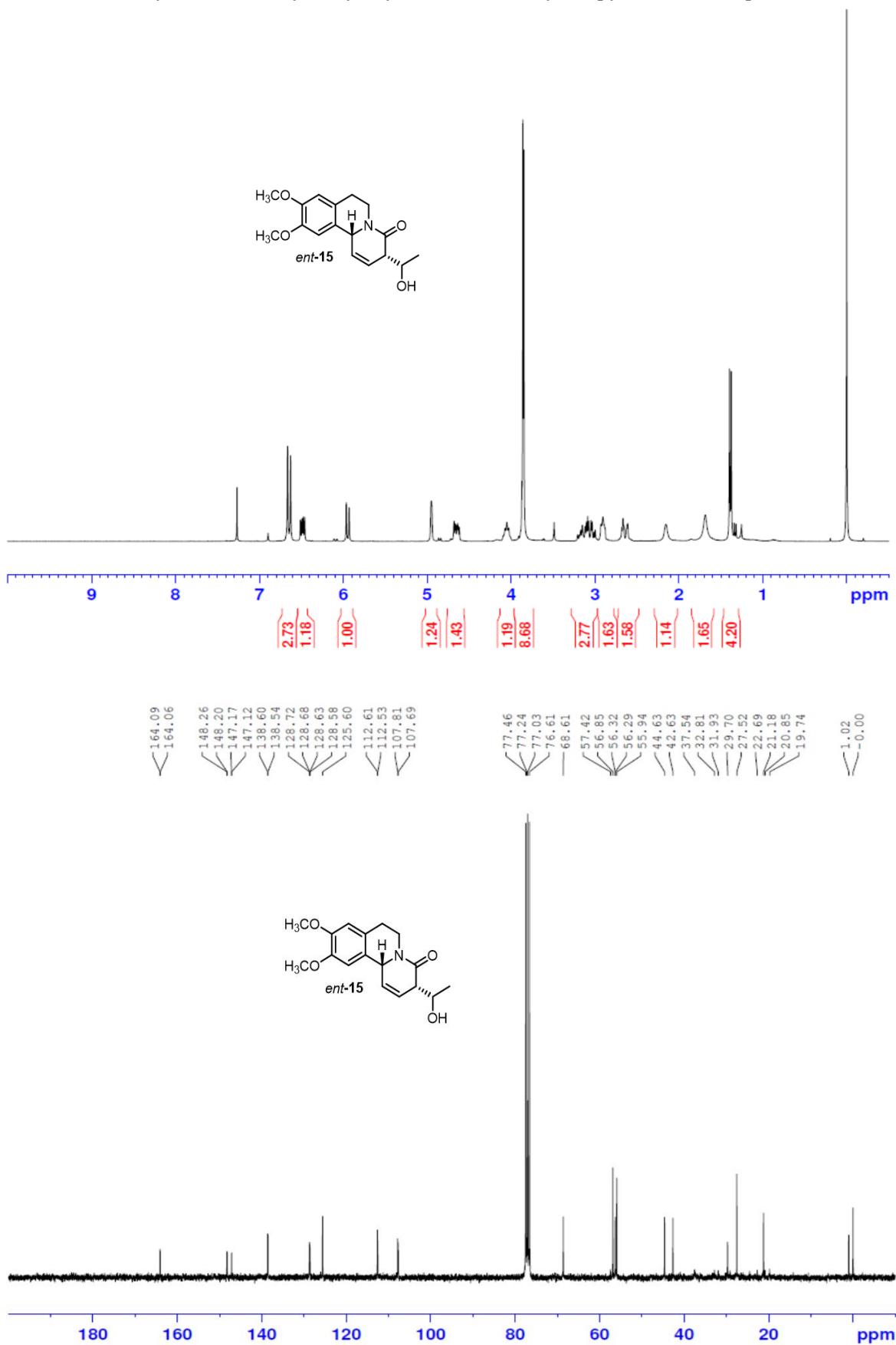


(3*R*,11*b**S*)-6,7-dihydro-3-((*S*)-1-hydroxyethyl)-9,10-dimethoxy-3*H*-pyrido[2,1-*a*]isoquinolin-4(11*b**H*)-one (**15**)

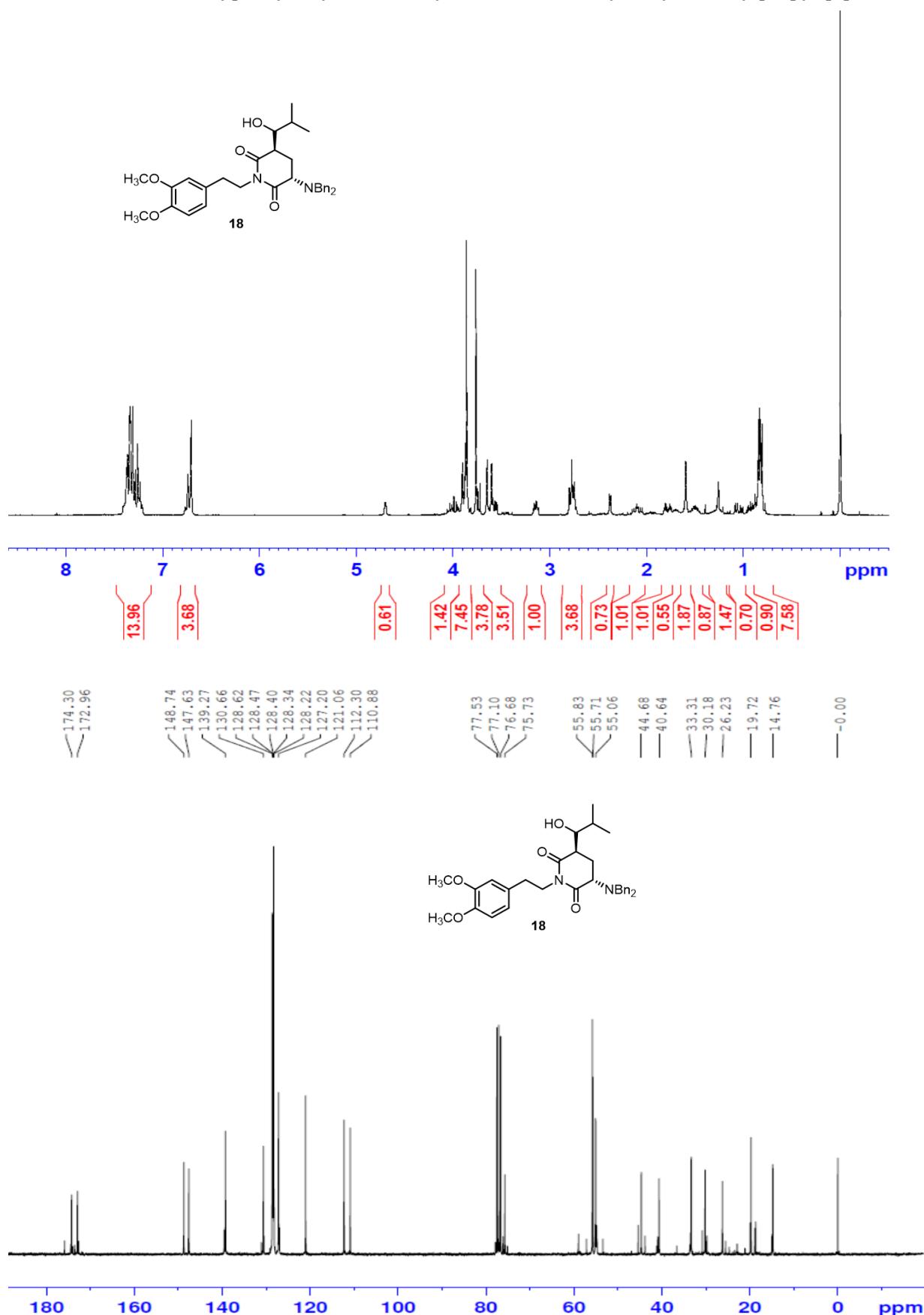
(1*S*,3*S*,11*b**S*)-1-(dibenzylamino)-2,3,6,7-tetrahydro-3-((*S*)-1-hydroxyethyl)-9,10-dimethoxy-1*H*-pyrido[2,1-*a*]isoquinolin-4(11*b**H*)-one (**17**)

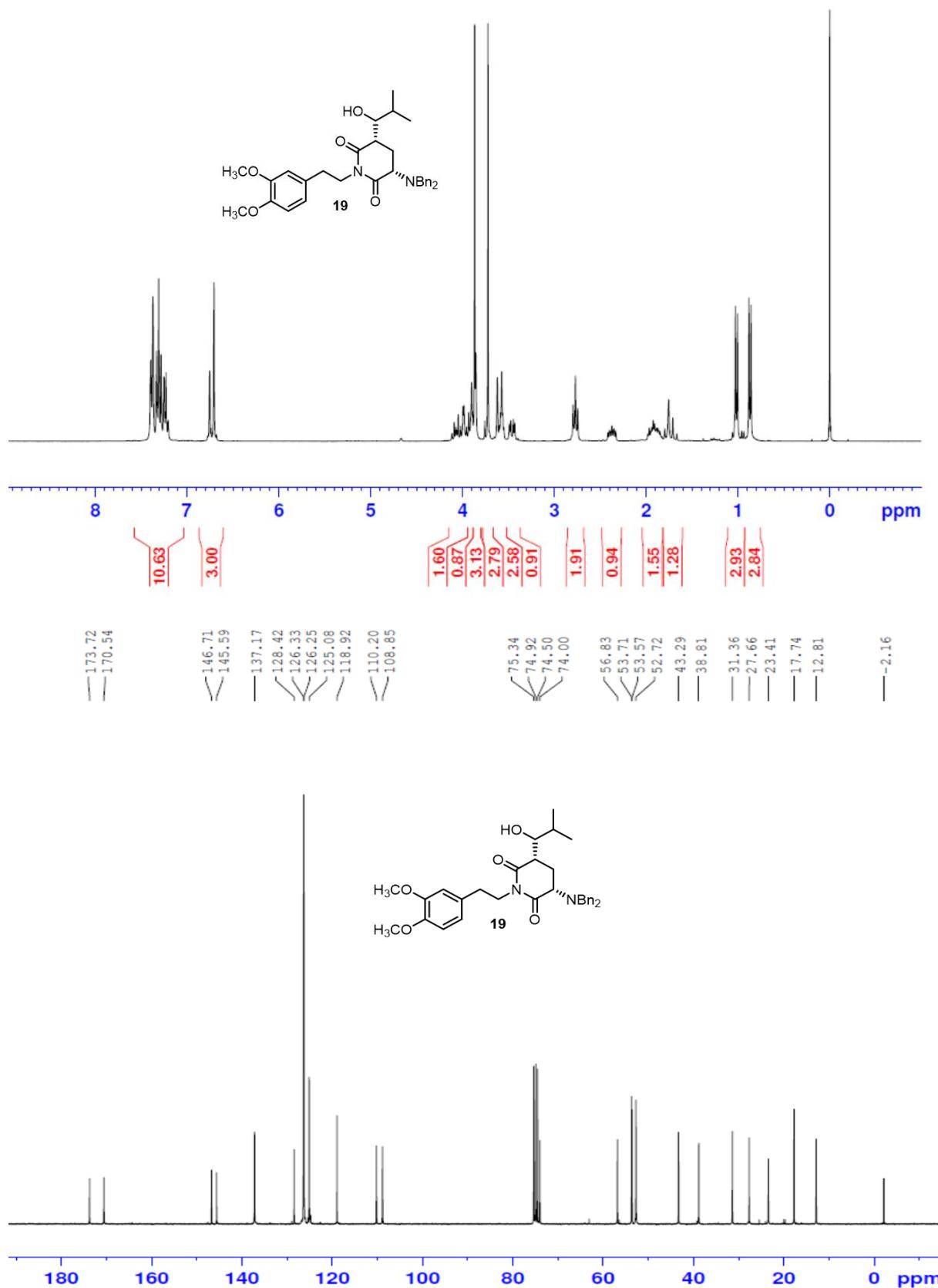


(3S,11bR)-6,7-dihydro-3-((*R*)-1-hydroxyethyl)-9,10-dimethoxy-3*H*-pyrido[2,1-*a*]isoquinolin-4(11b*H*)-one (*ent*-15)

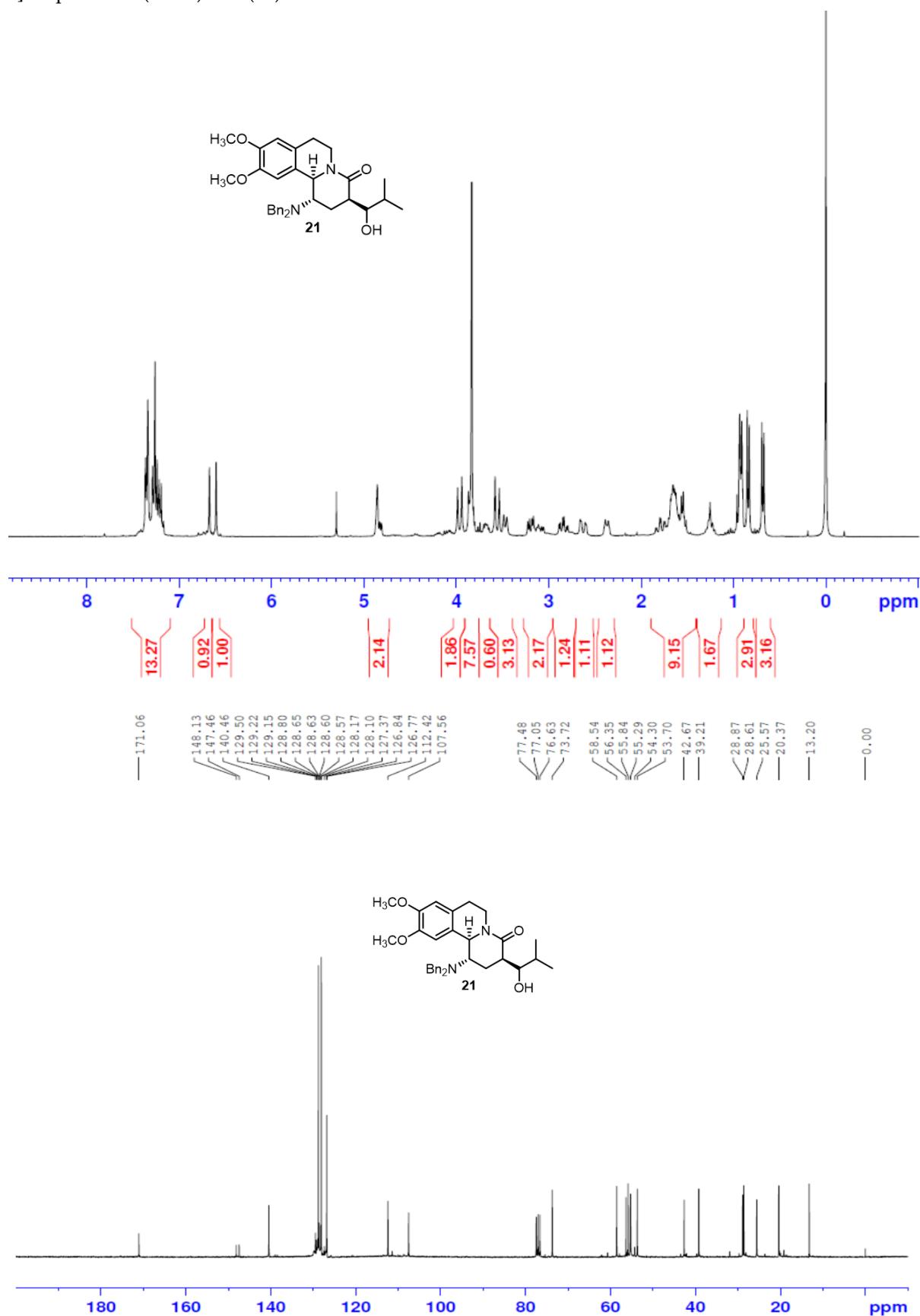


(3*S*,5*R*)-1-(3,4-Dimethoxyphenylethyl)-3-(dibenzylamino)-5-((*S*)-1-hydroxy-2-methylpropyl)piperidine-2,6-dione (**18**)

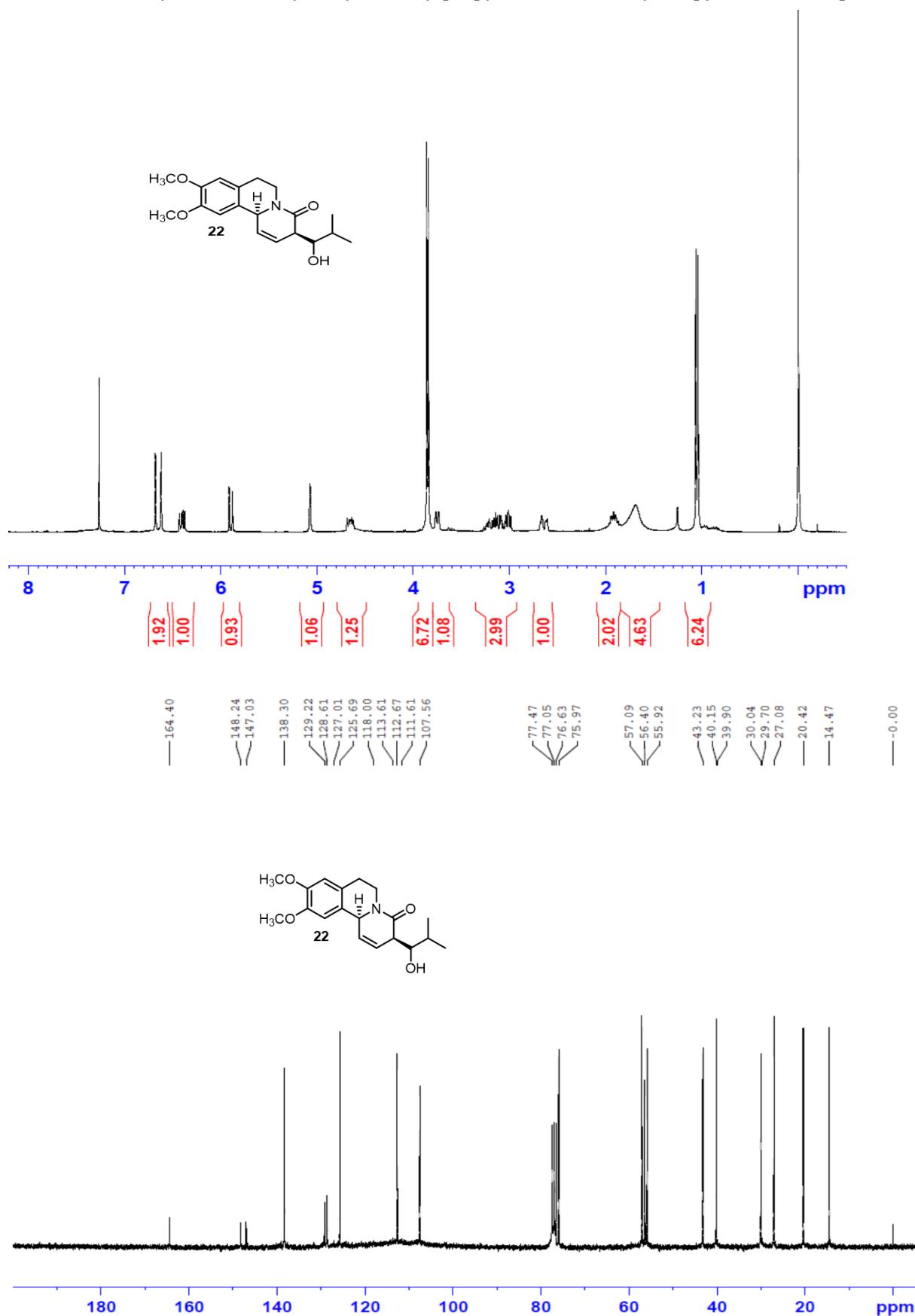


(3*S*, 5*S*)-1-(3,4-Dimethoxyphenylethyl)-3-(dibenzylamino)- 5-((*R*)-1-hydroxy-2-methylpropyl)piperidine-2,6-dione (**19**)

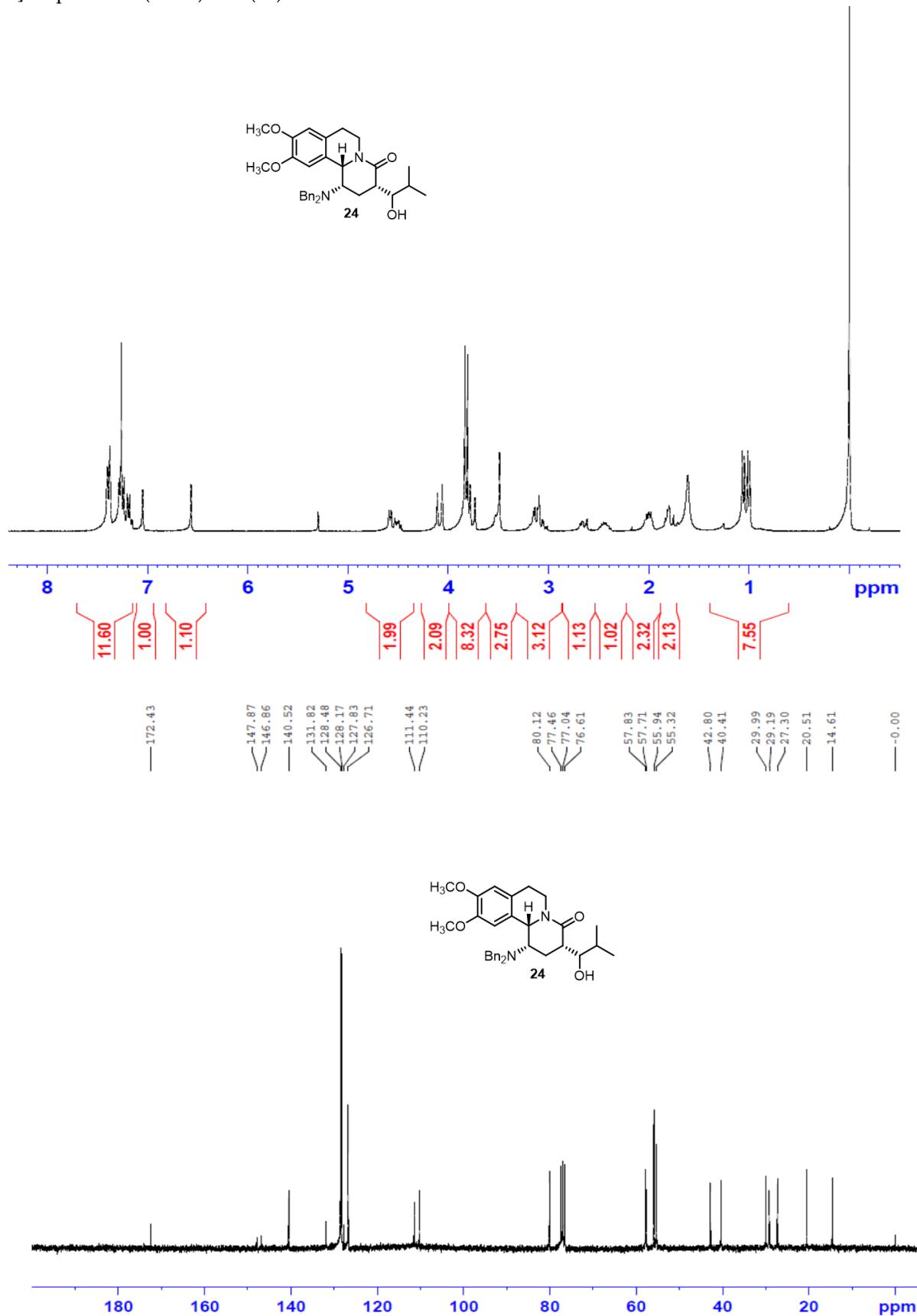
(1*S*,3*R*,11*b**R*)-1-(dibenzylamino)-2,3,6,7-tetrahydro-3-((*S*)-1-hydroxy-2-methylpropyl)-9,10-dimethoxy-1*H*-pyrido[2,1-*a*]isoquinolin-4(11*b**H*)-one (**21**)



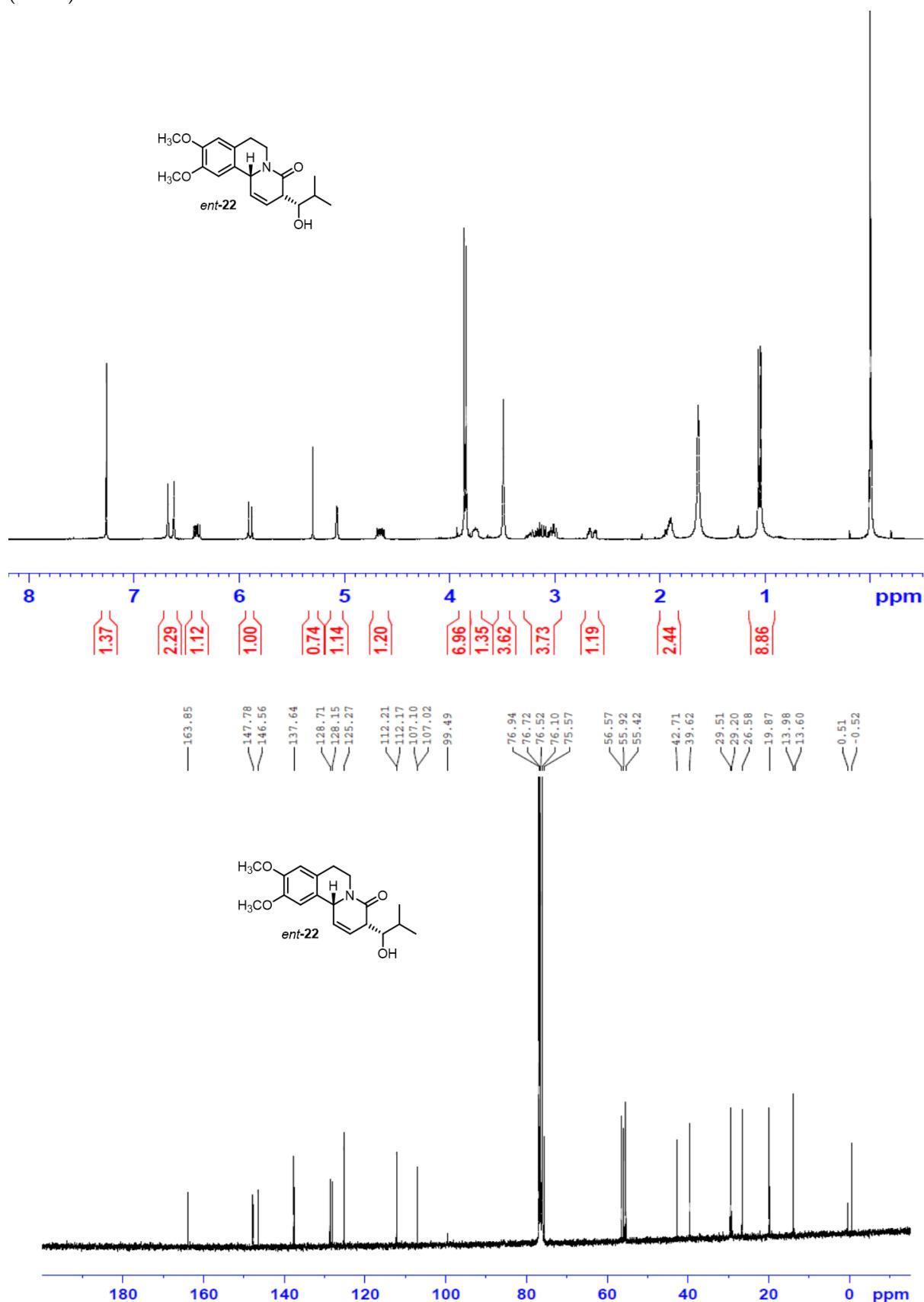
(3*R*,11*b**S*)-6,7-dihydro-3-((*S*)-1-hydroxy-2-methylpropyl)-9,10-dimethoxy-3*H*-pyrido[2,1-*a*]isoquinolin-4(11*b**H*)-one (**22**)

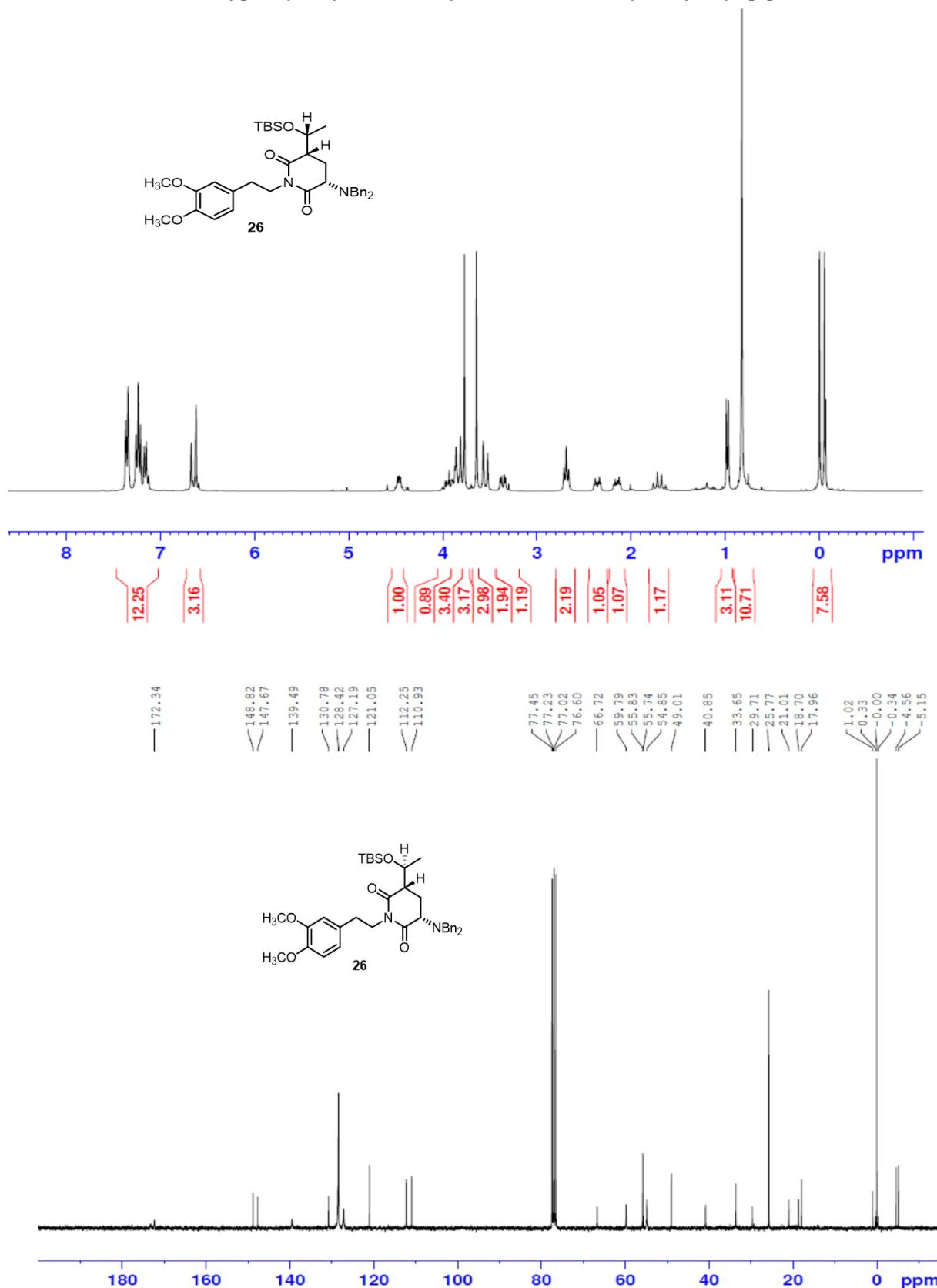


(1*S*,3*S*,11*b**S*)-1-(dibenzylamino)-2,3,6,7-tetrahydro-3-((*R*)-1-hydroxy-2-methylpropyl)-9,10-dimethoxy-1*H*-pyrido[2,1-*a*]isoquinolin-4(11*b**H*)-one (**24**)



(3*S*,11*b**R*)-6,7-dihydro-3-((*R*)-1-hydroxy-2-methylpropyl)-9,10-dimethoxy-3*H*-pyrido[2,1-*a*]isoquinolin-4(11*b**H*)-one (*ent*-22)



(3S, 5S)-1-(3,4-Dimethoxyphenylethyl)-3-(dibenzylamino)- 5-((R)-1-hydroxyethyl)piperidine-2,6-dione TBS ether **26**

(1S,3S,11bS)-1-(dibenzylamino)-2,3,6,7-tetrahydro-3-((R)-1-hydroxyethyl)-9,10-dimethoxy-1*H*-pyrido[2,1-*a*]isoquinolin-4(11b*H*)-one (**28**)

