Electronic Supplementary Information

Part I: Experimental studies

Stereochemistry and mechanistic insights in the [$2^t + 2^i + 2^i$] annulations of thioketenes and imines

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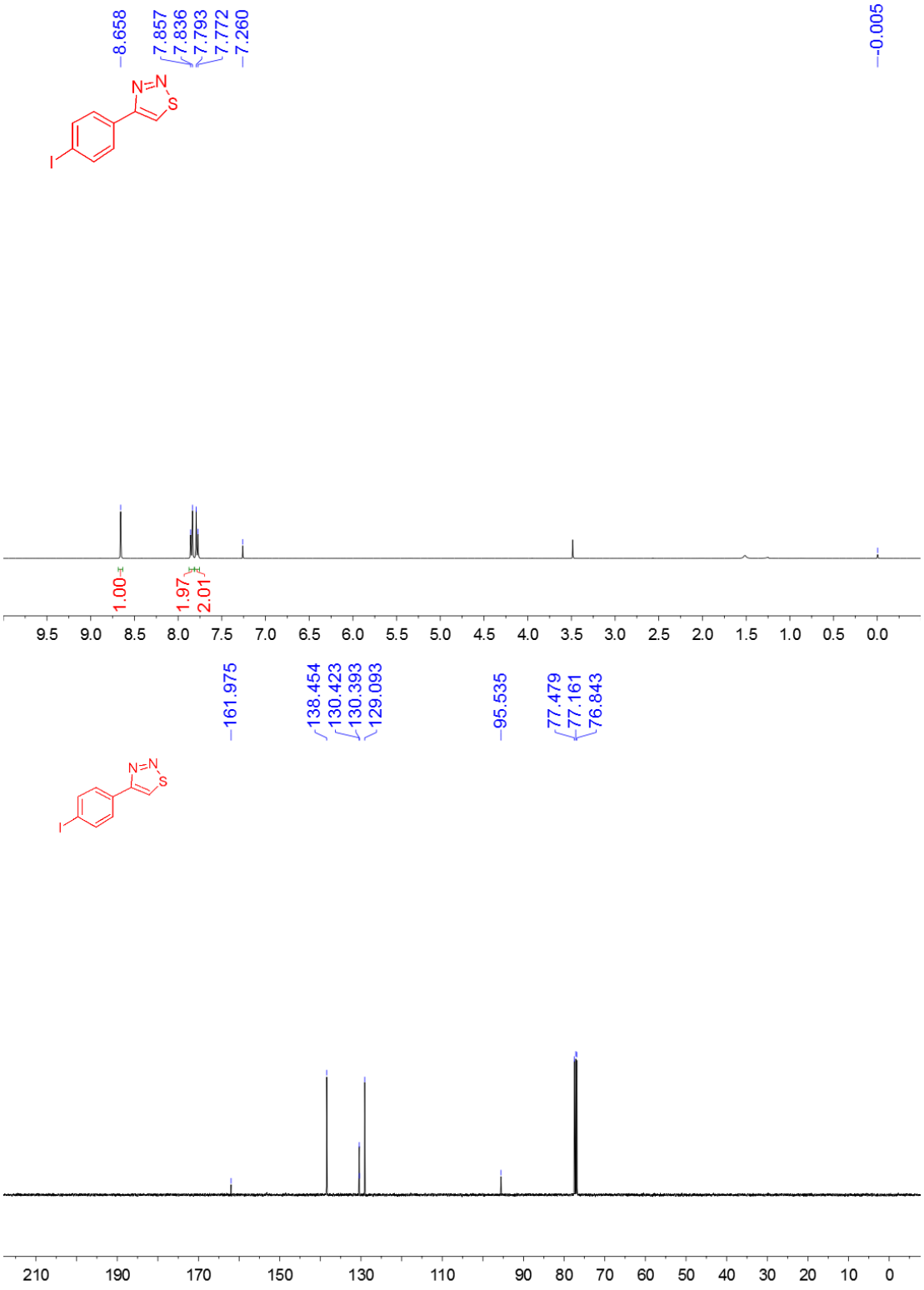
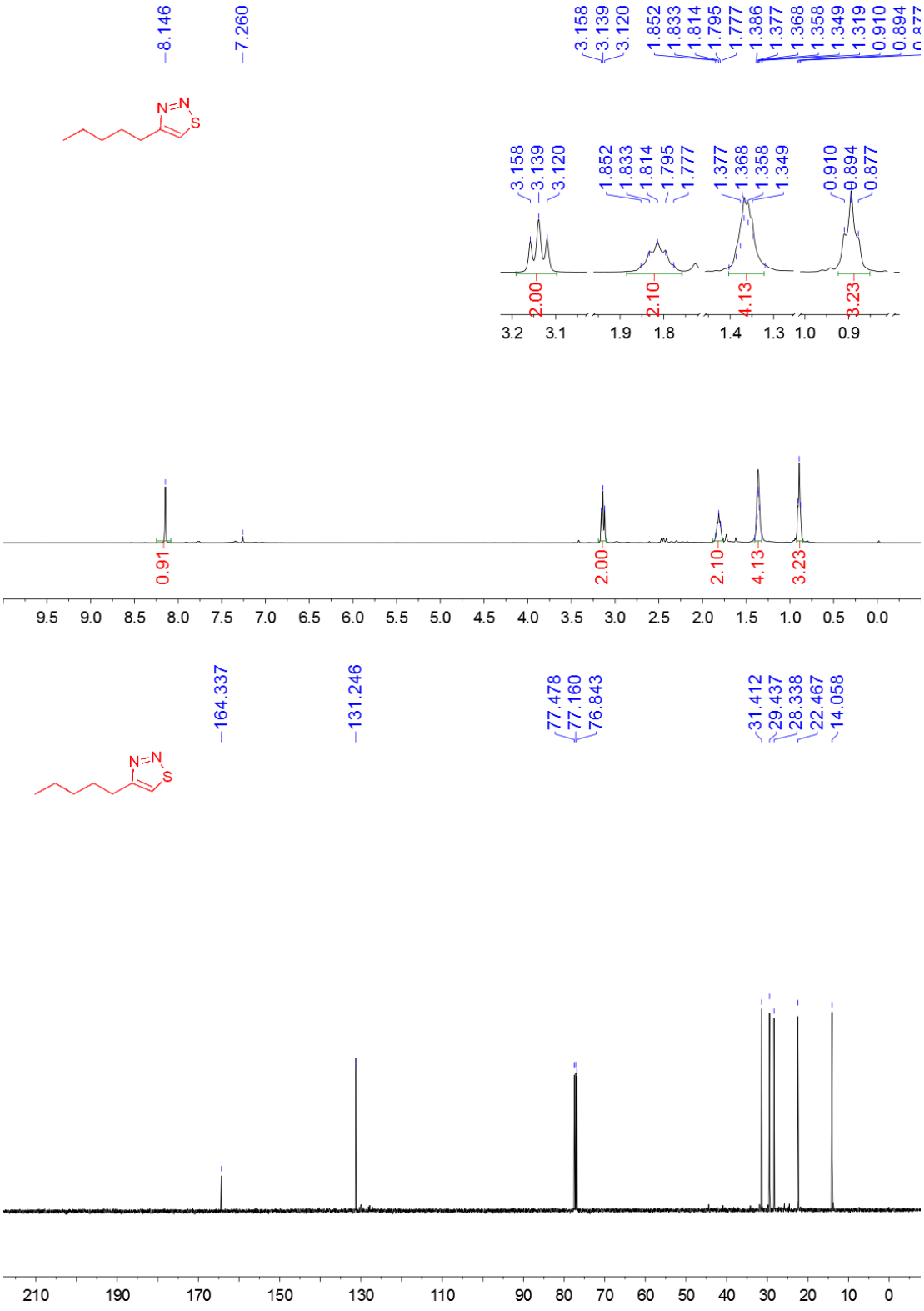
Contents

1. ^{1}H and ^{13}C NMR Spectra of Unknown Compounds

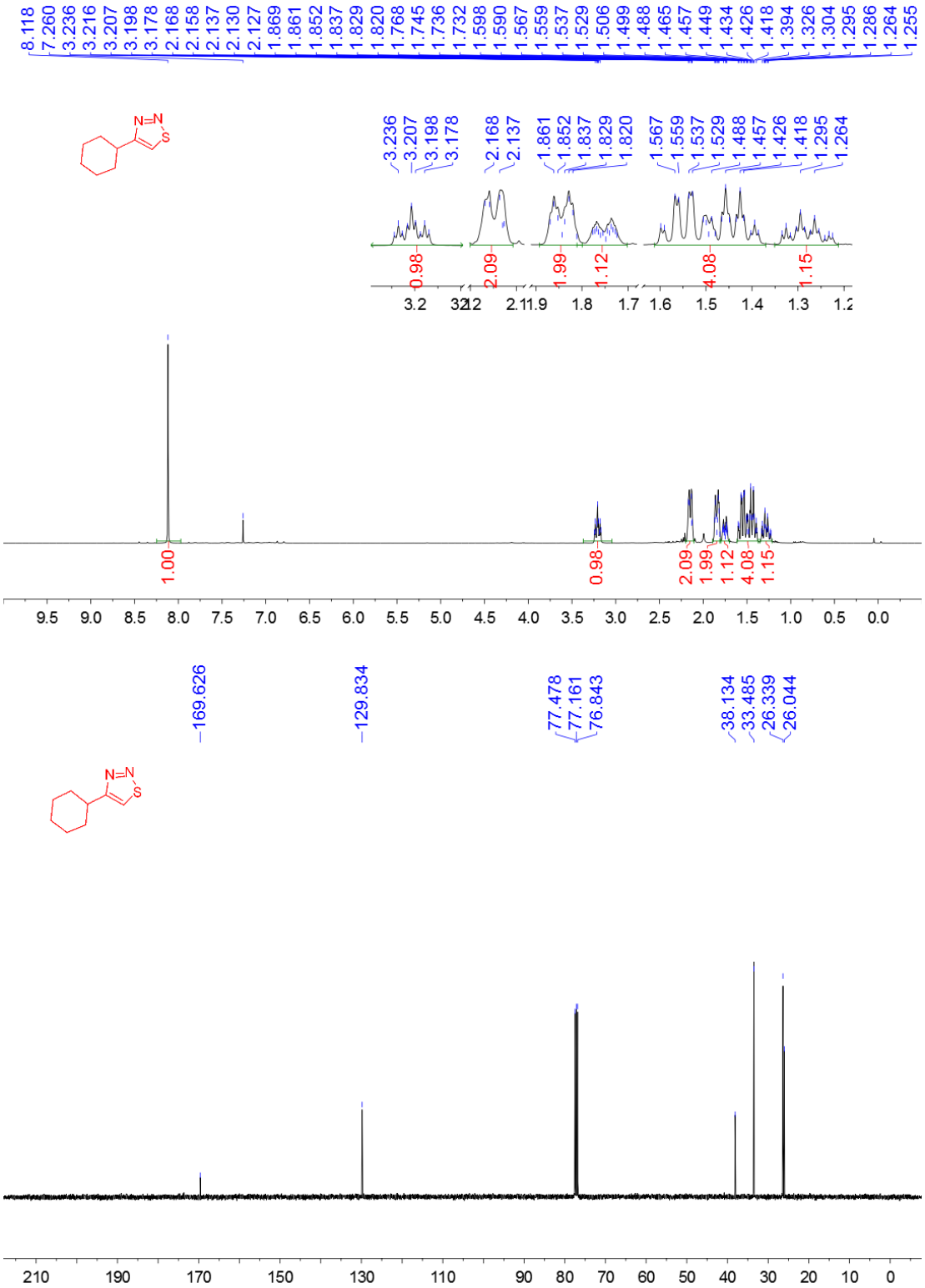
4-(4-Iodophenyl)-1,2,3-thiadiazole (6d)



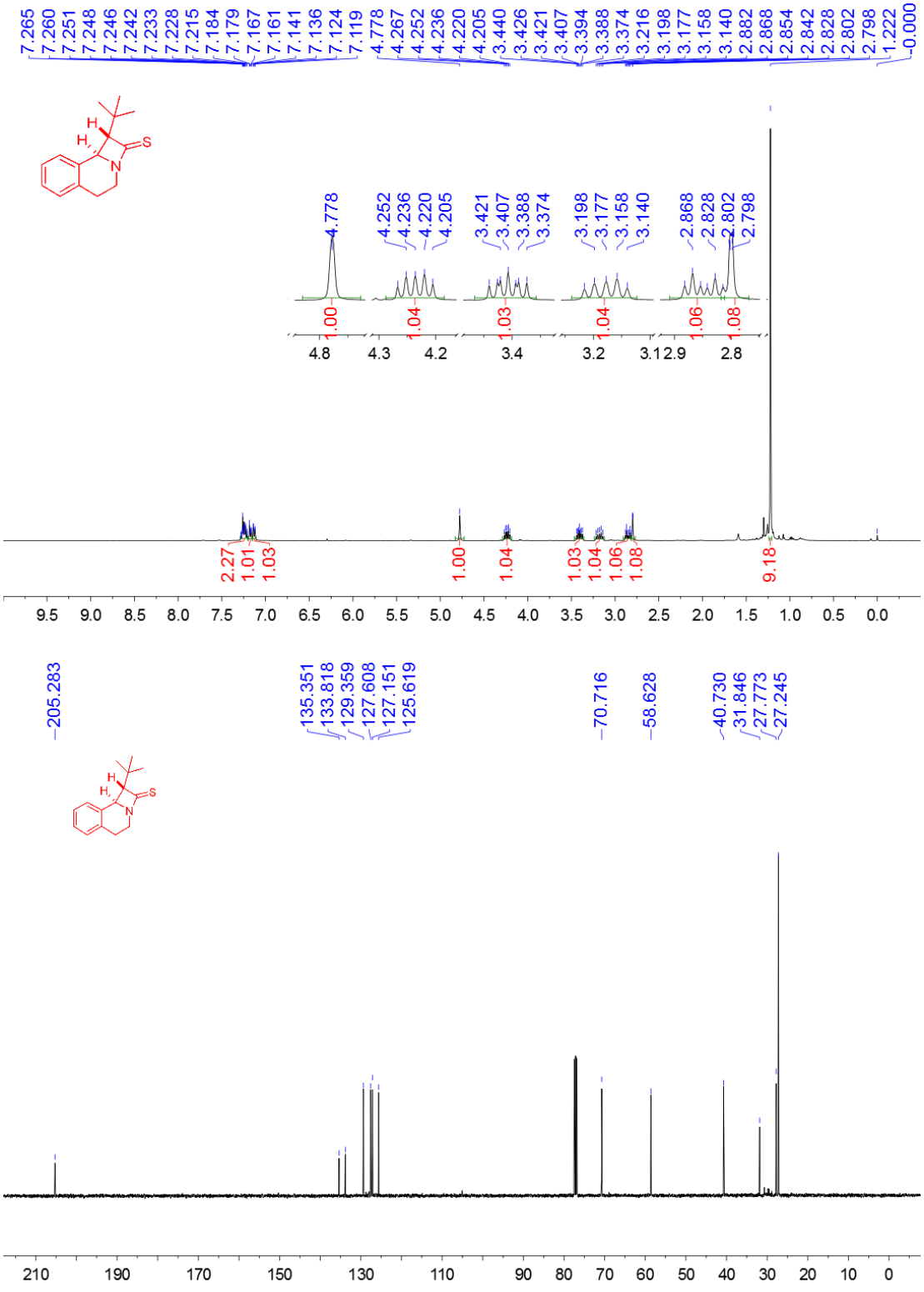
4-Pentyl-1,2,3-thiadiazole (6j)



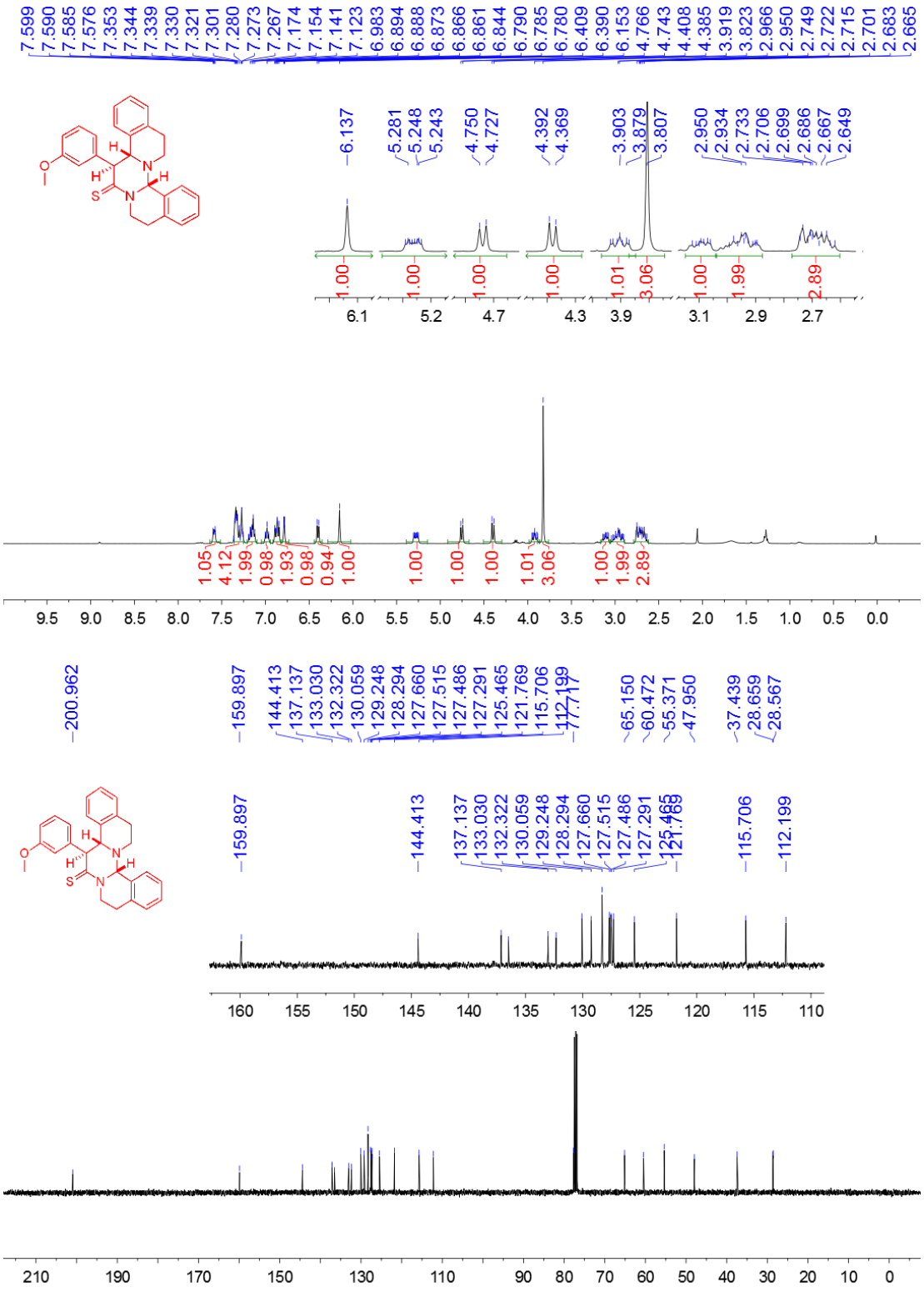
4-Cyclohexyl-1,2,3-thiadiazole (6l)



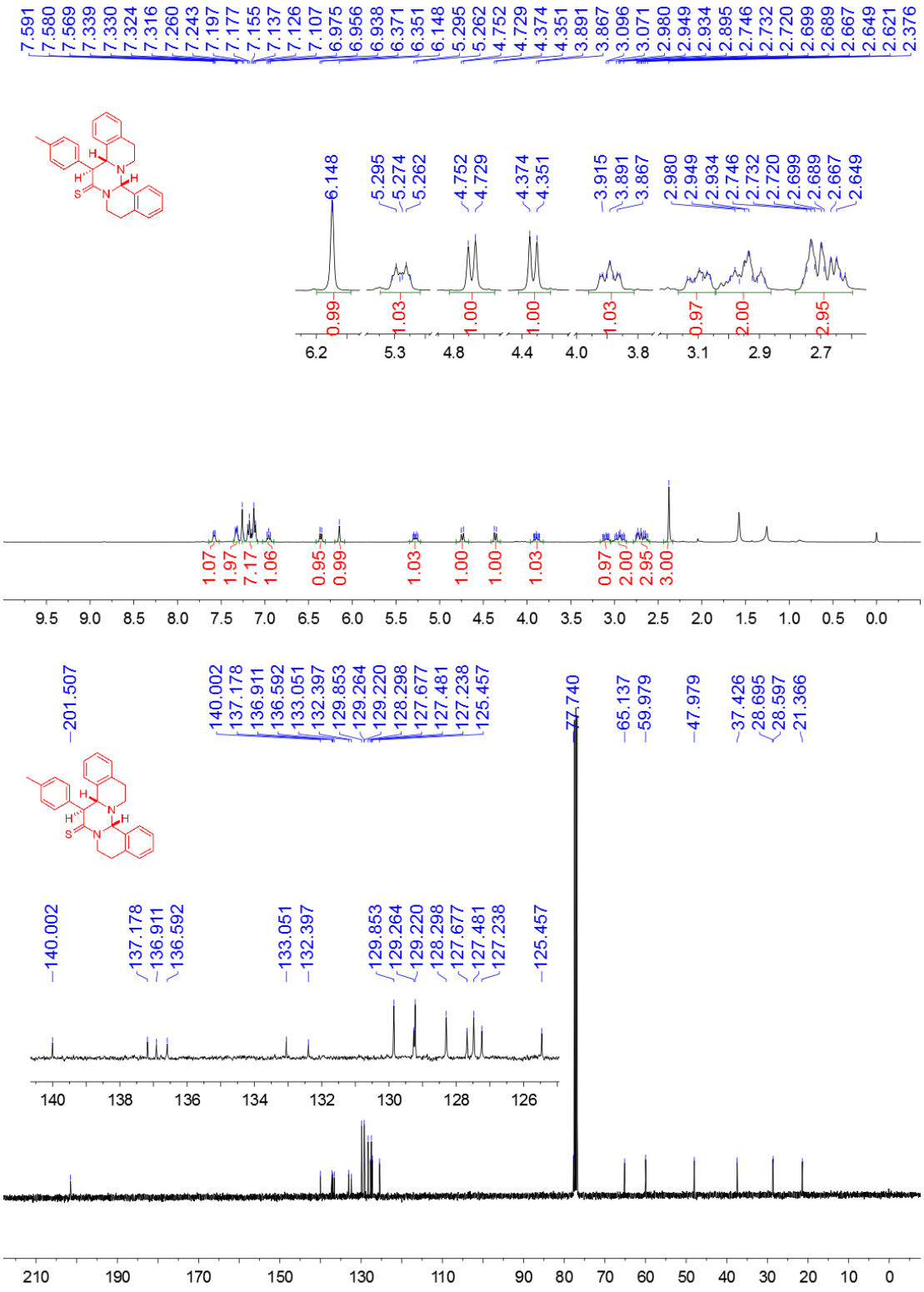
***rel*(1*S*,9b*R*)-1-(*tert*-Butyl)-1,4,5,9b-tetrahydro-2*H*-azeto[2,1-*a*]isoquinoline-2-thione (3n)**



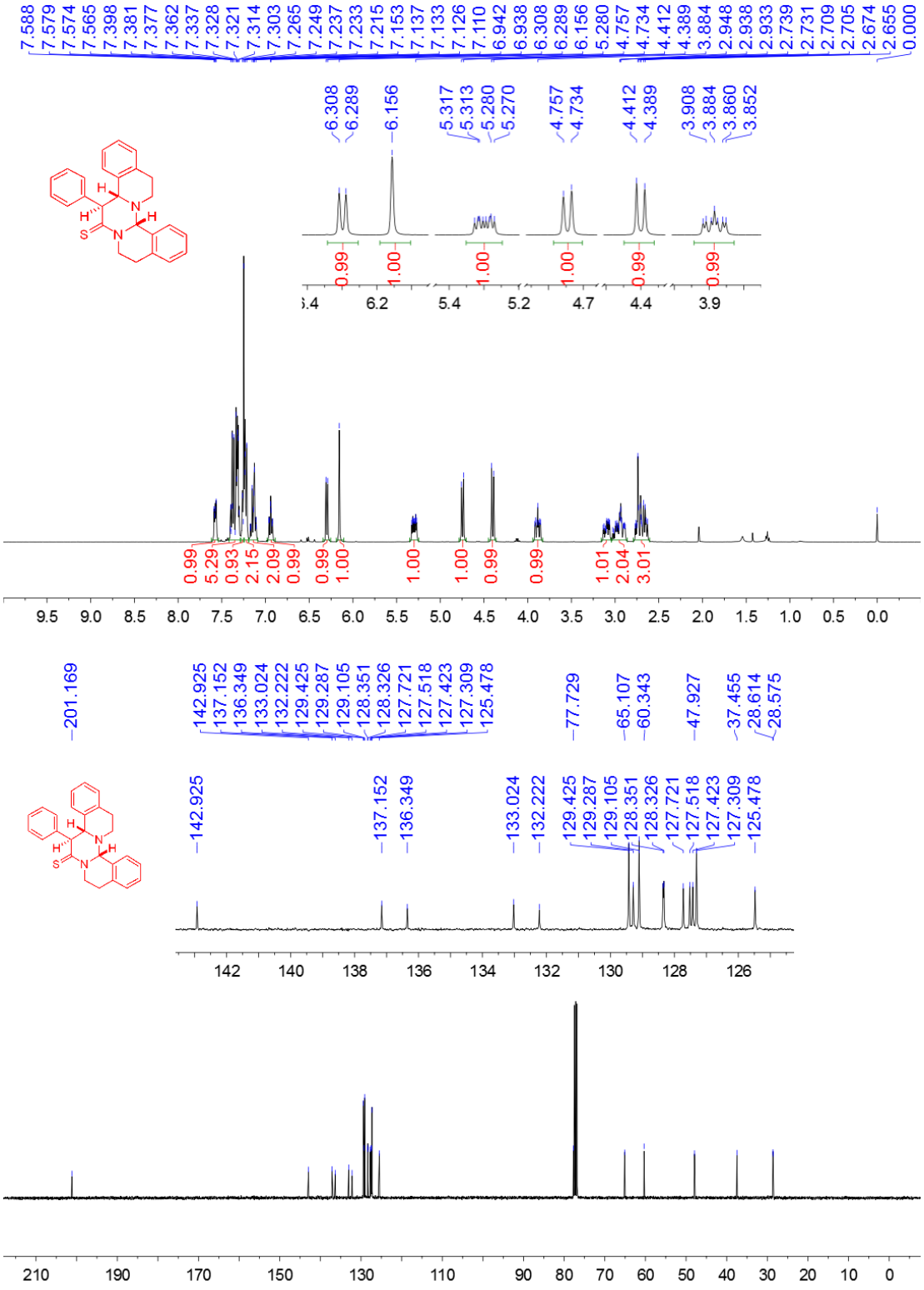
***rel*(4b*R*,5*S*,13b*S*)-5-(3-Methoxyphenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4a)**



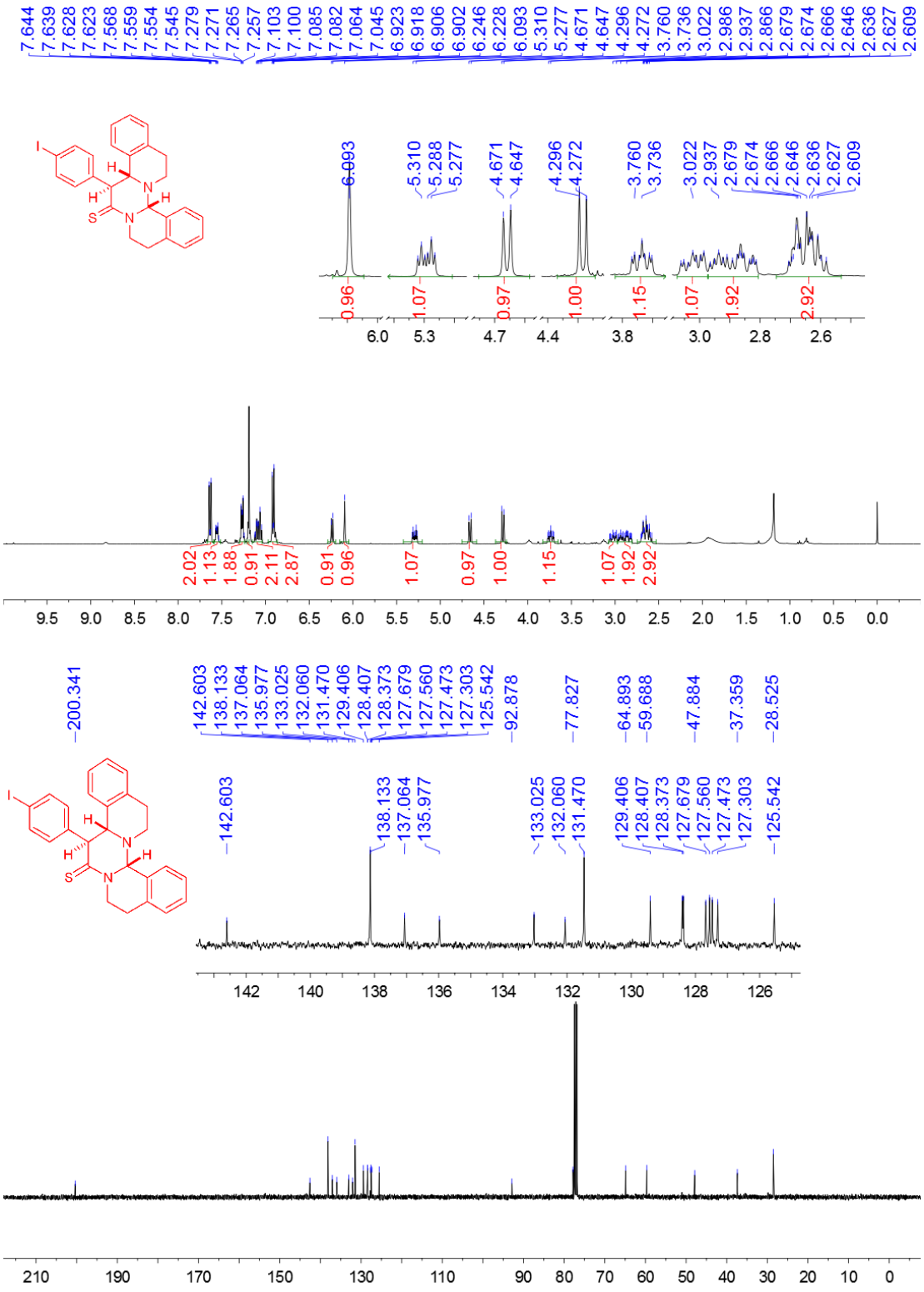
***rel*(4b*R*,5*S*,13b*S*)-5-(4-Methylphenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*] diisoquinoline-6-thione (4b)**



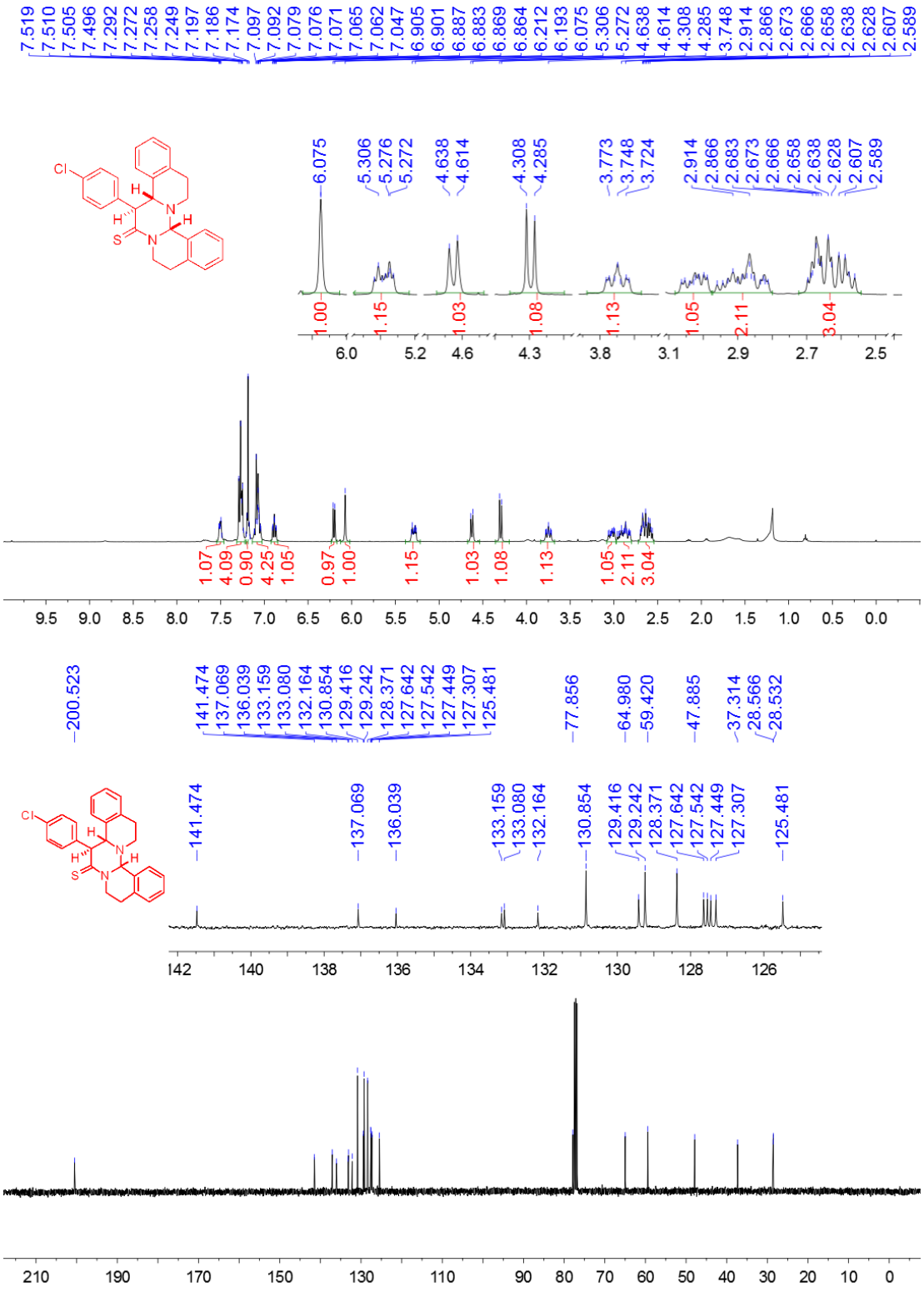
***rel*(4b*R*,5*S*,13b*S*)-5-Phenyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4c)**



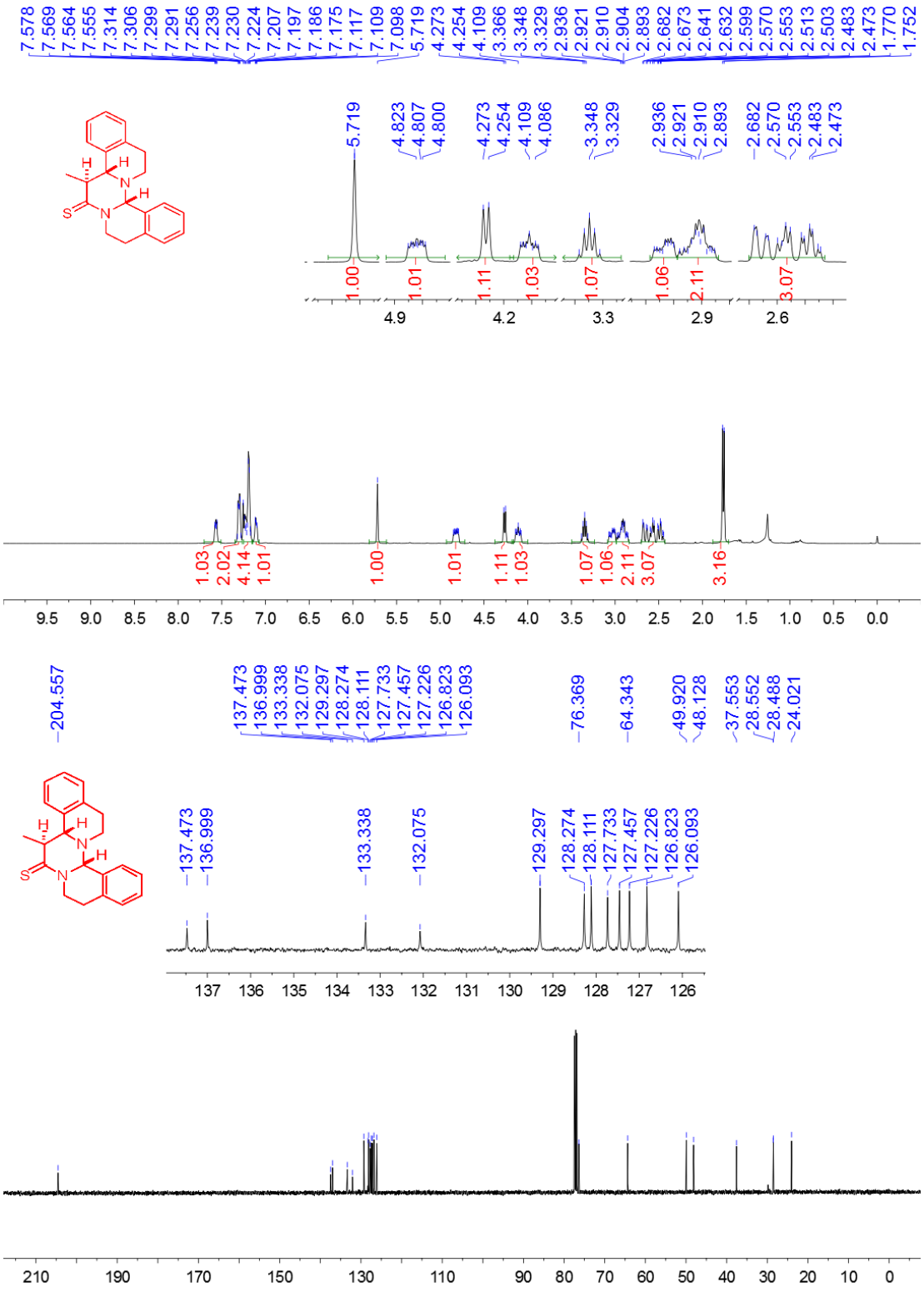
***rel*(4b*R*,5*S*,13b*S*)-5-(4-Iodophenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4d)**



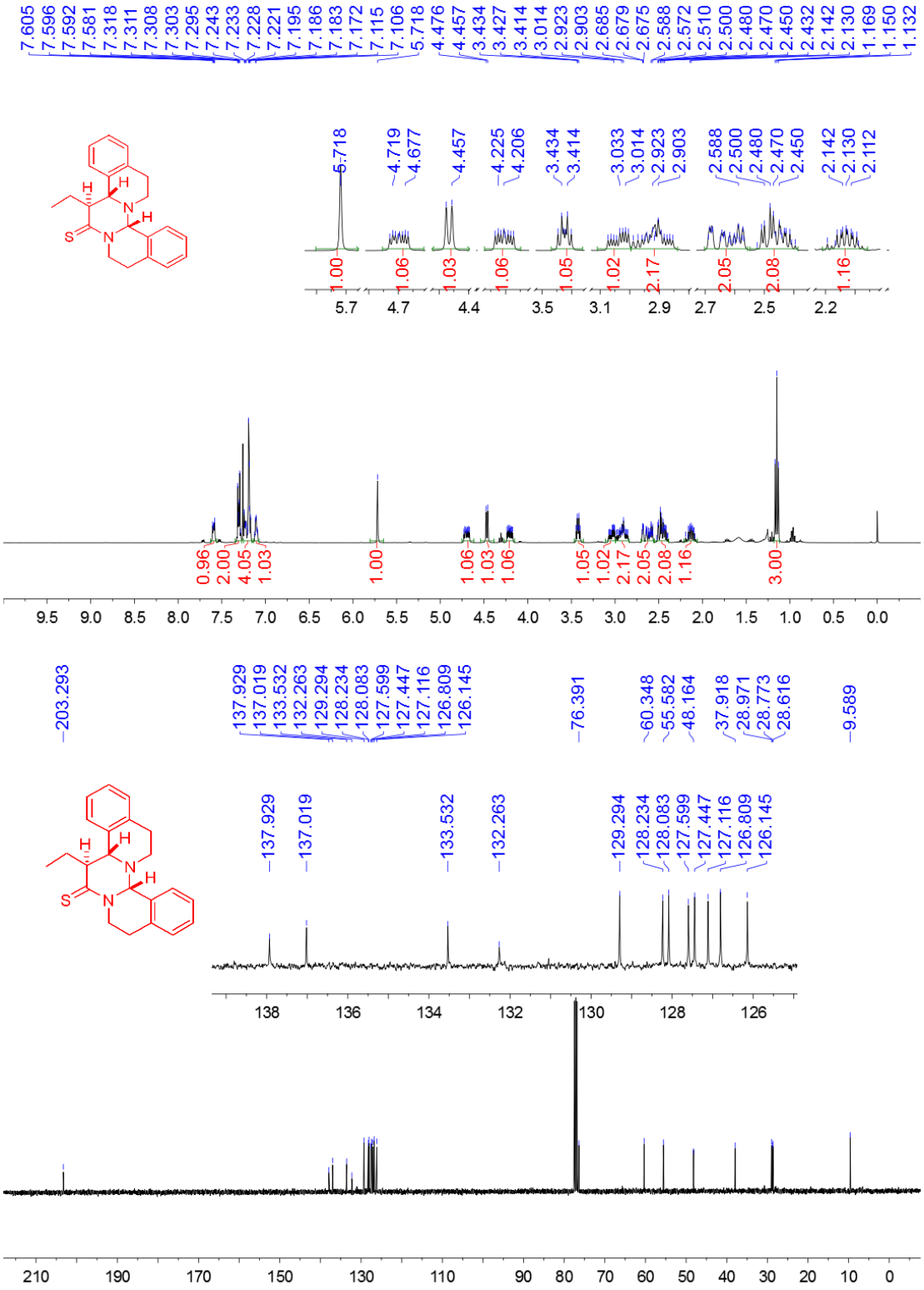
***rel*(4b*R*,5*S*,13b*S*)-5-(4-Chlorophenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4e)**



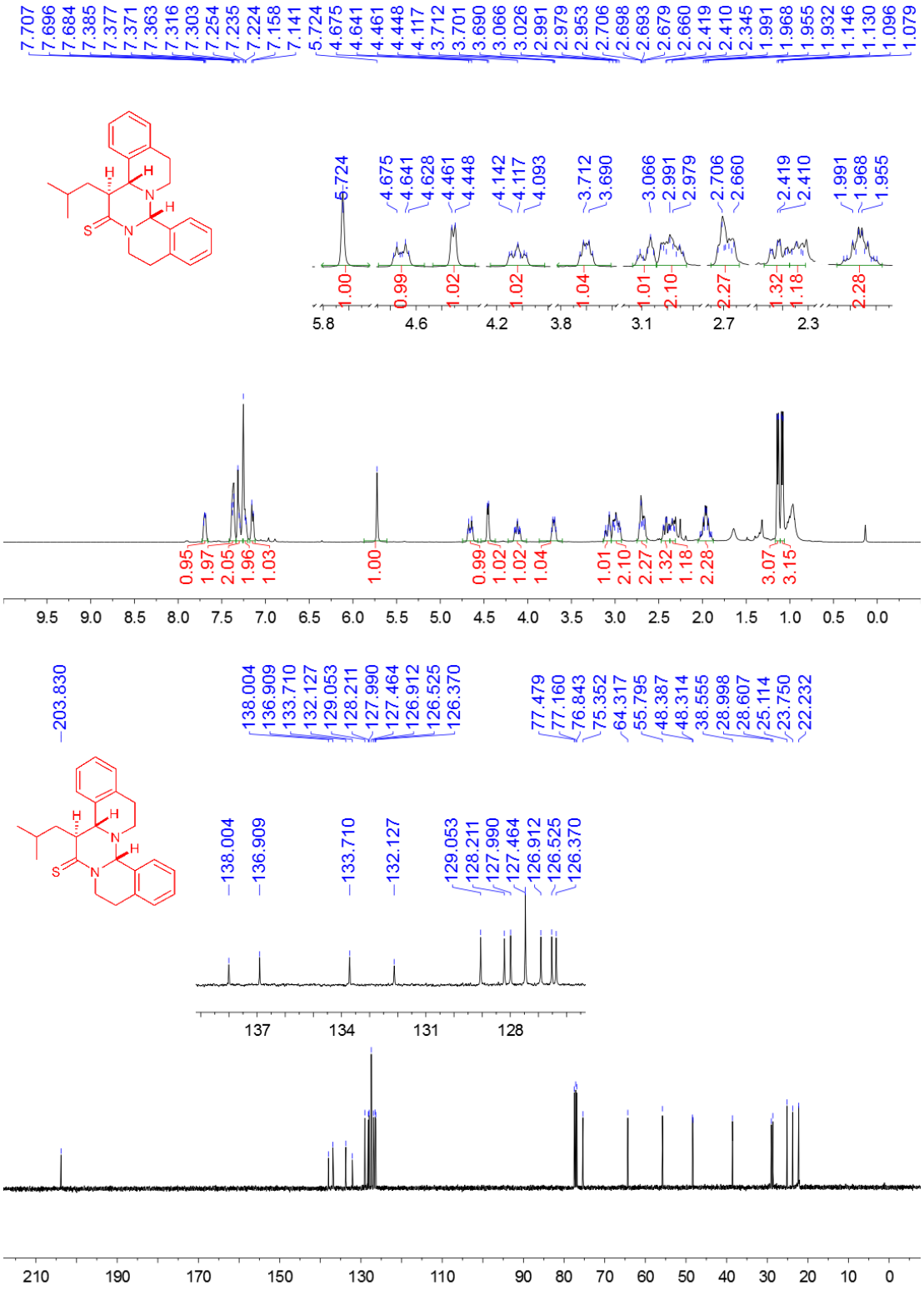
rel(4b*R*,5*S*,13b*S*)-5-Methyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4g)



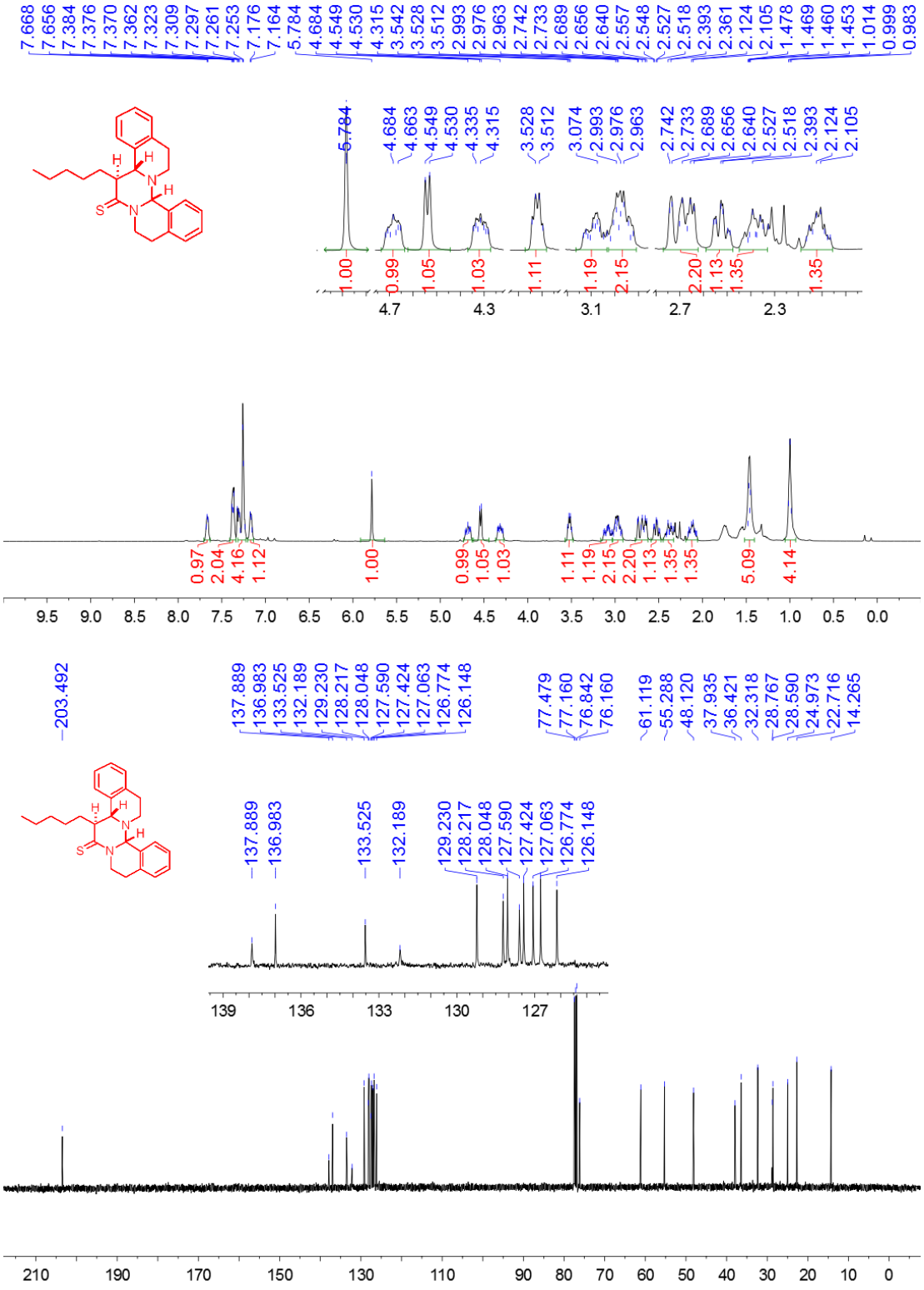
***rel*(4b*R*,5*S*,13b*S*)-5-Ethyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4h)**



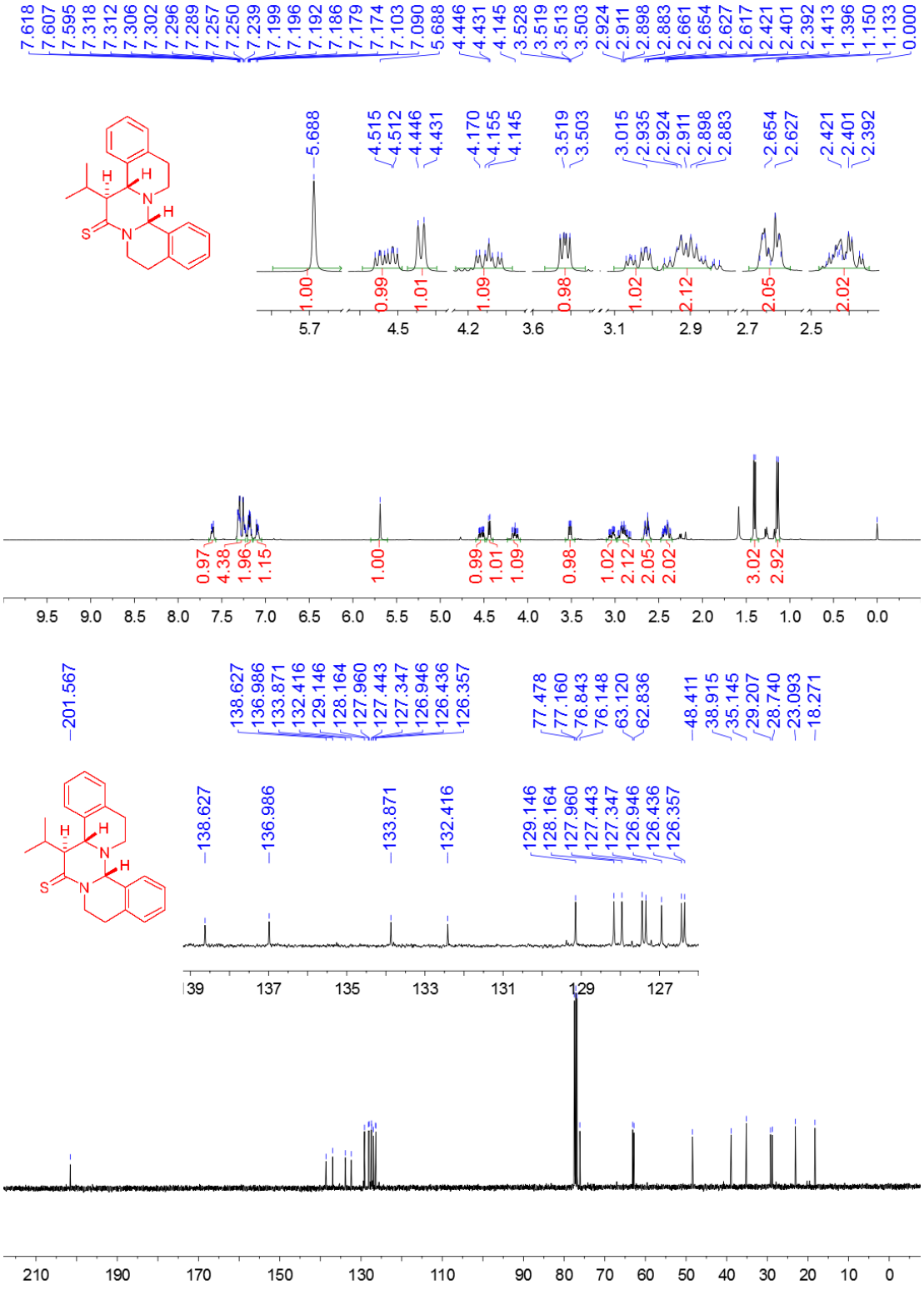
***rel*(4b*R*,5*S*13b*S*)-5-Isobutyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4i)**



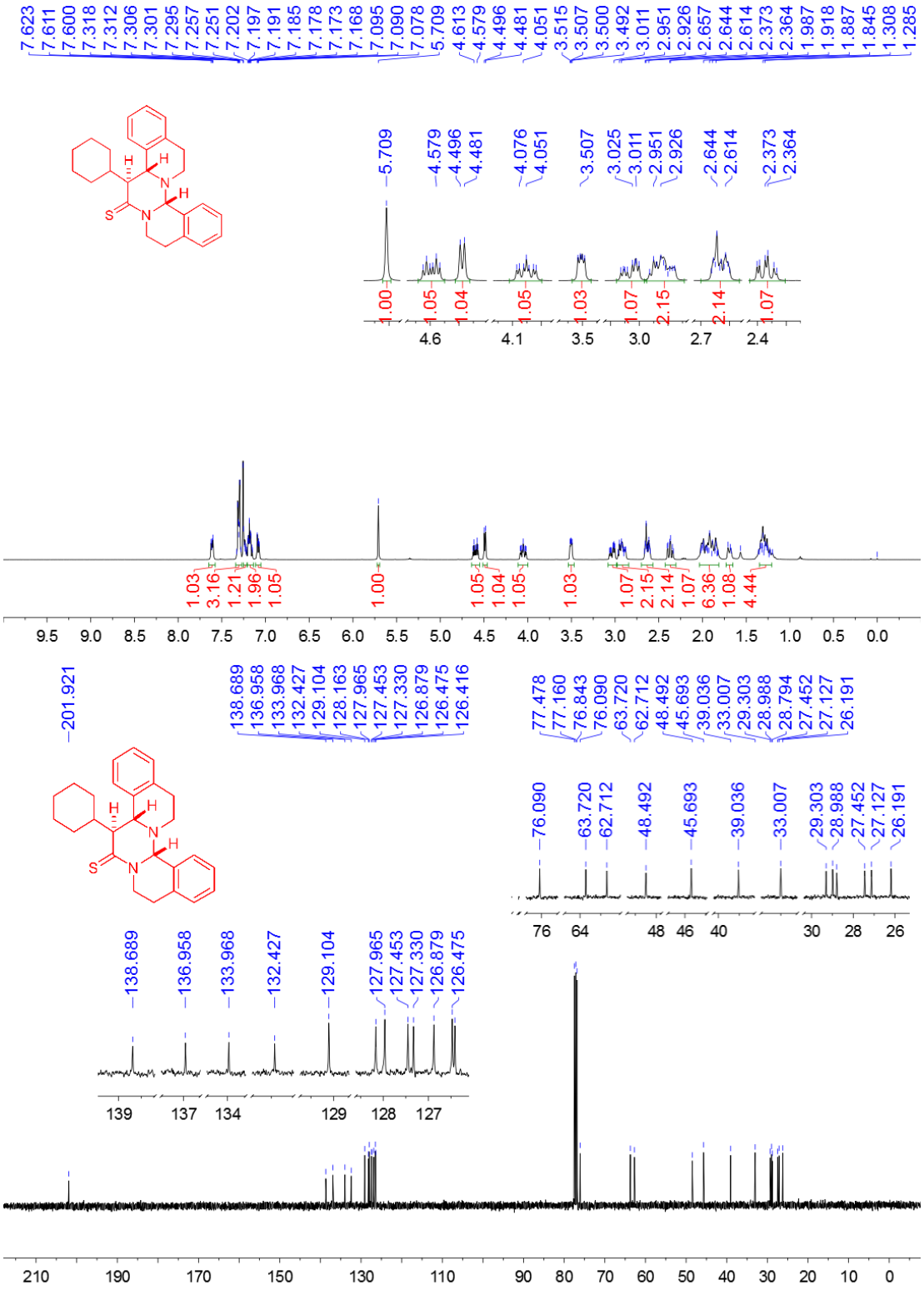
rel(4b*R*,5*S*,13b*S*)-5-Pentyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4j)



rel(4b_R_,5_S_,13b_S_)-5-Isopropyl-4b,5,9,13b,15,16-hexahydro-6_H_,8_H_-pyrimido[2,1-_a_:4,3-_a_']diisoquinoline-6-thione (4k)

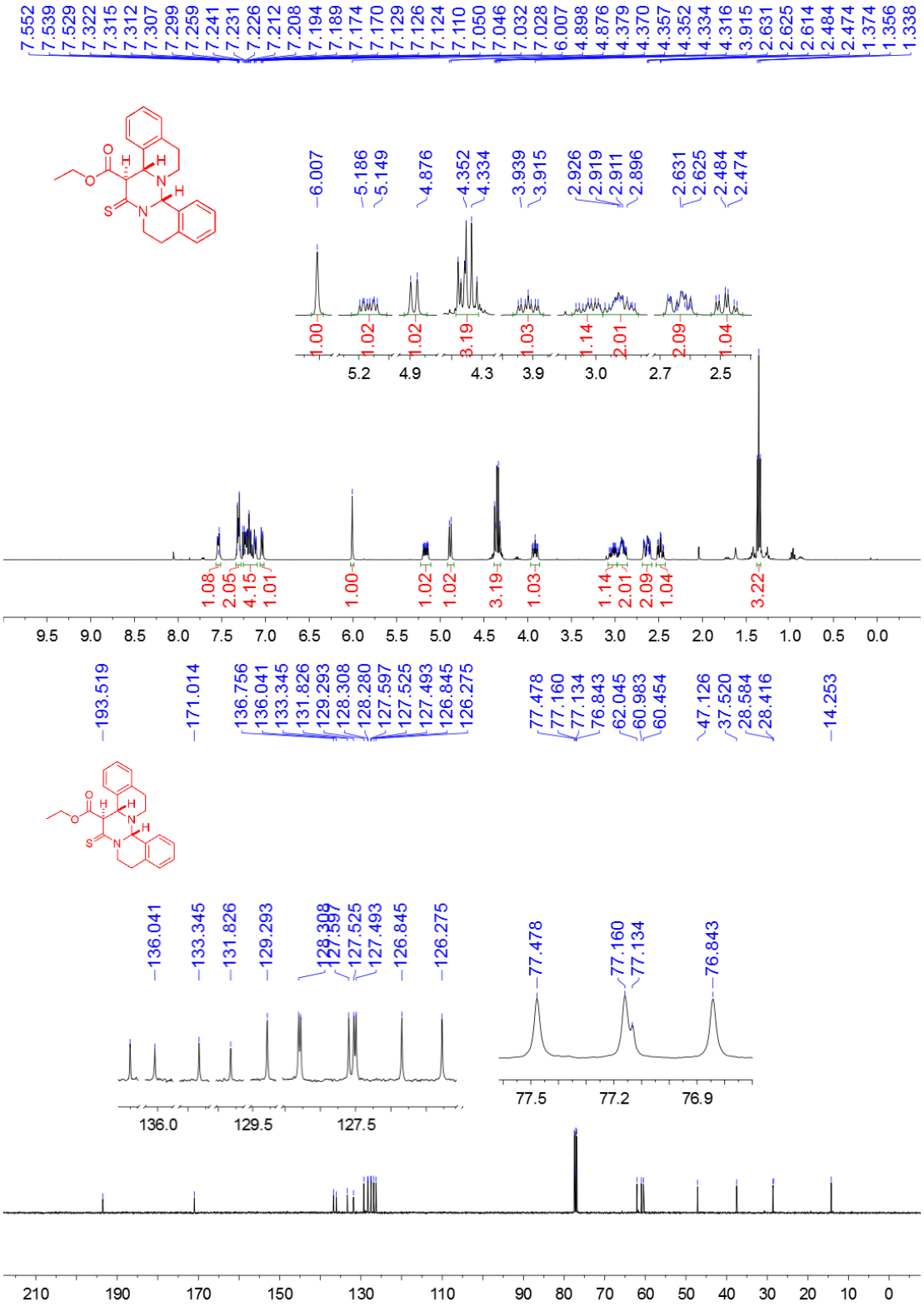


***rel*(4b*R*,5*S*,13b*S*)-5-Cyclohexyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4l)**



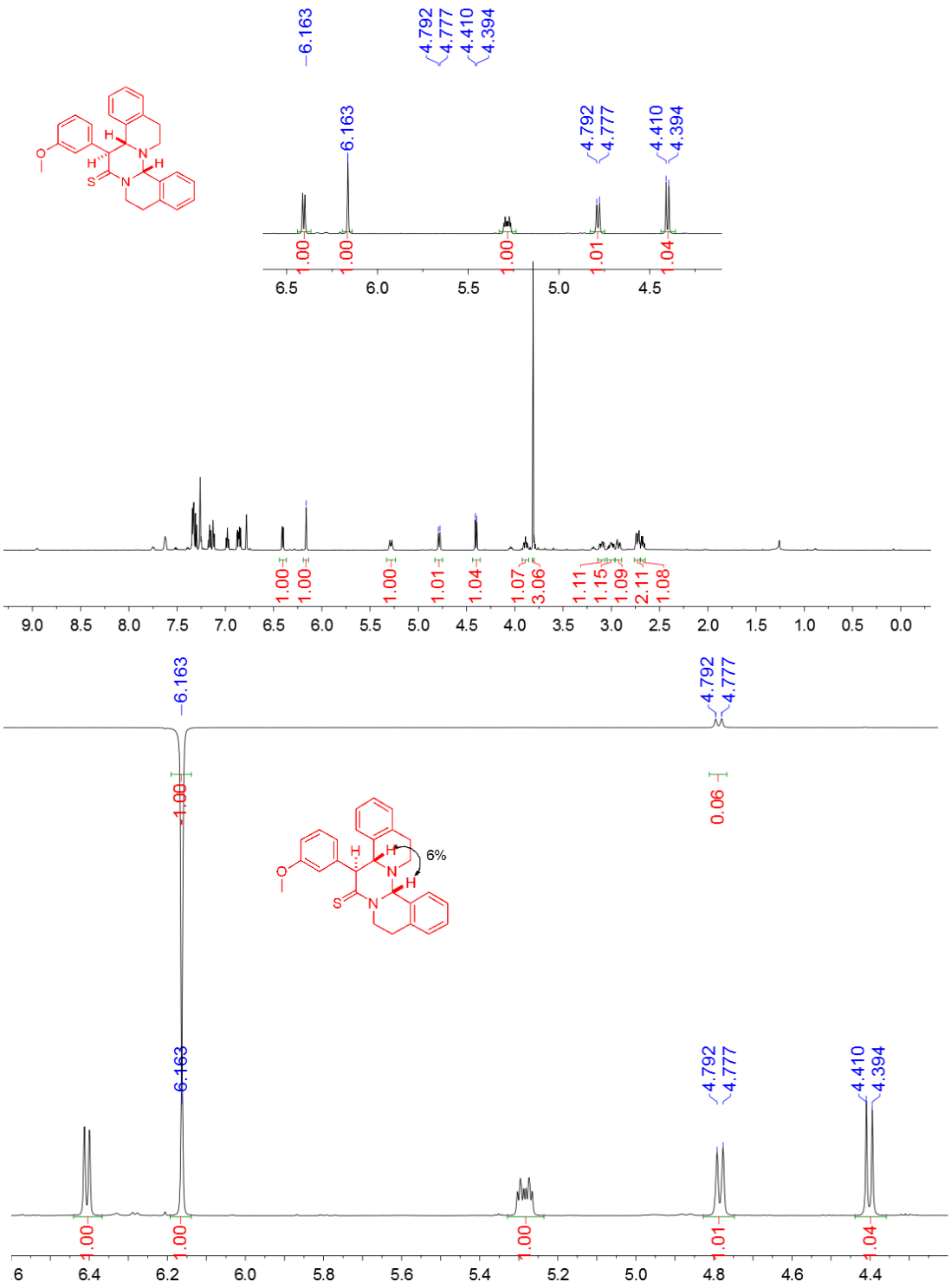
Ethyl

***rel*(4b*R*,5*R*,13b*S*)-6-thioxo-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-5-carboxylate (4m)**

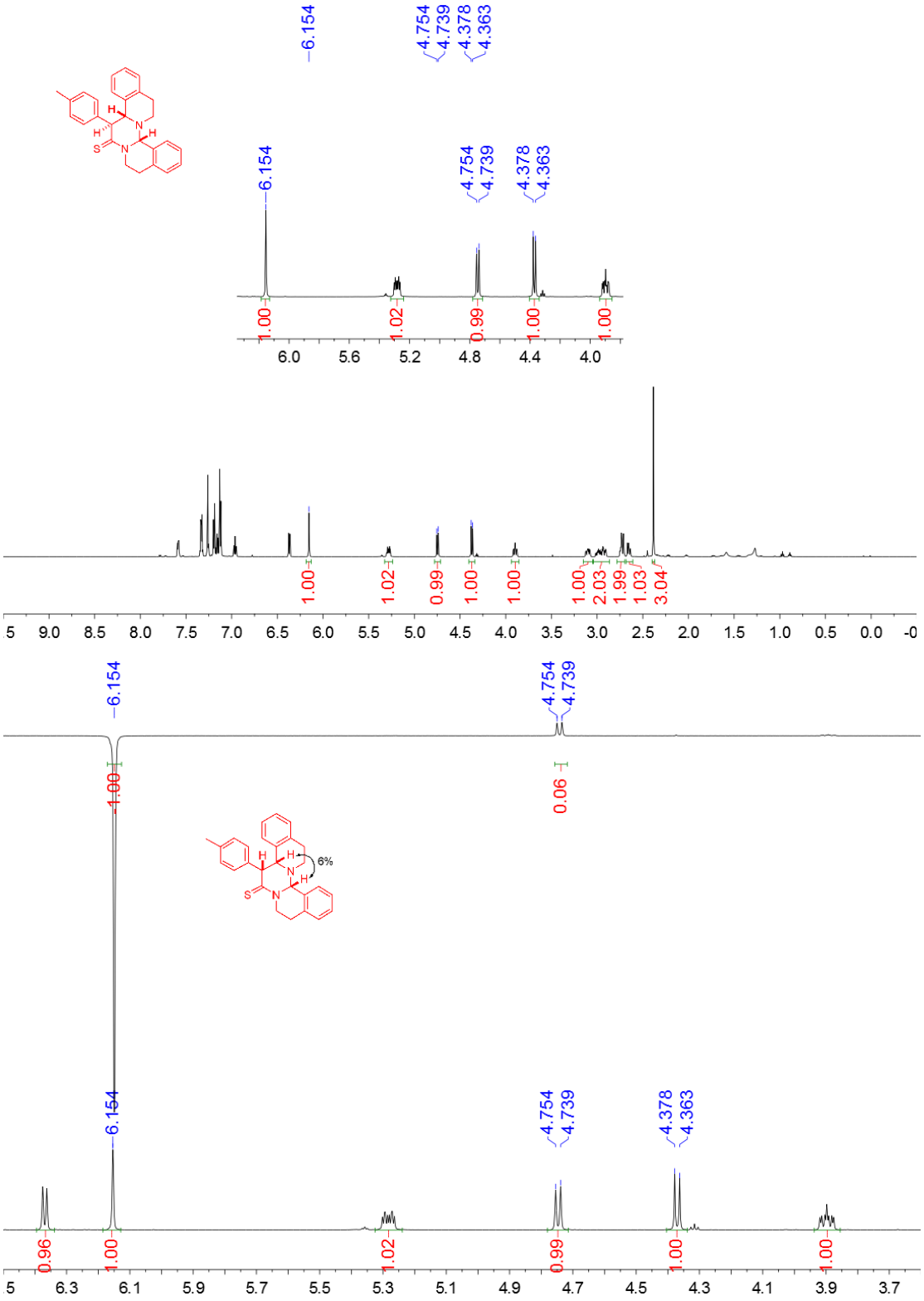


2. One-dimention NOE Spectra of [2^t + 2^i +2^i] Annuladducts (600 MHz)

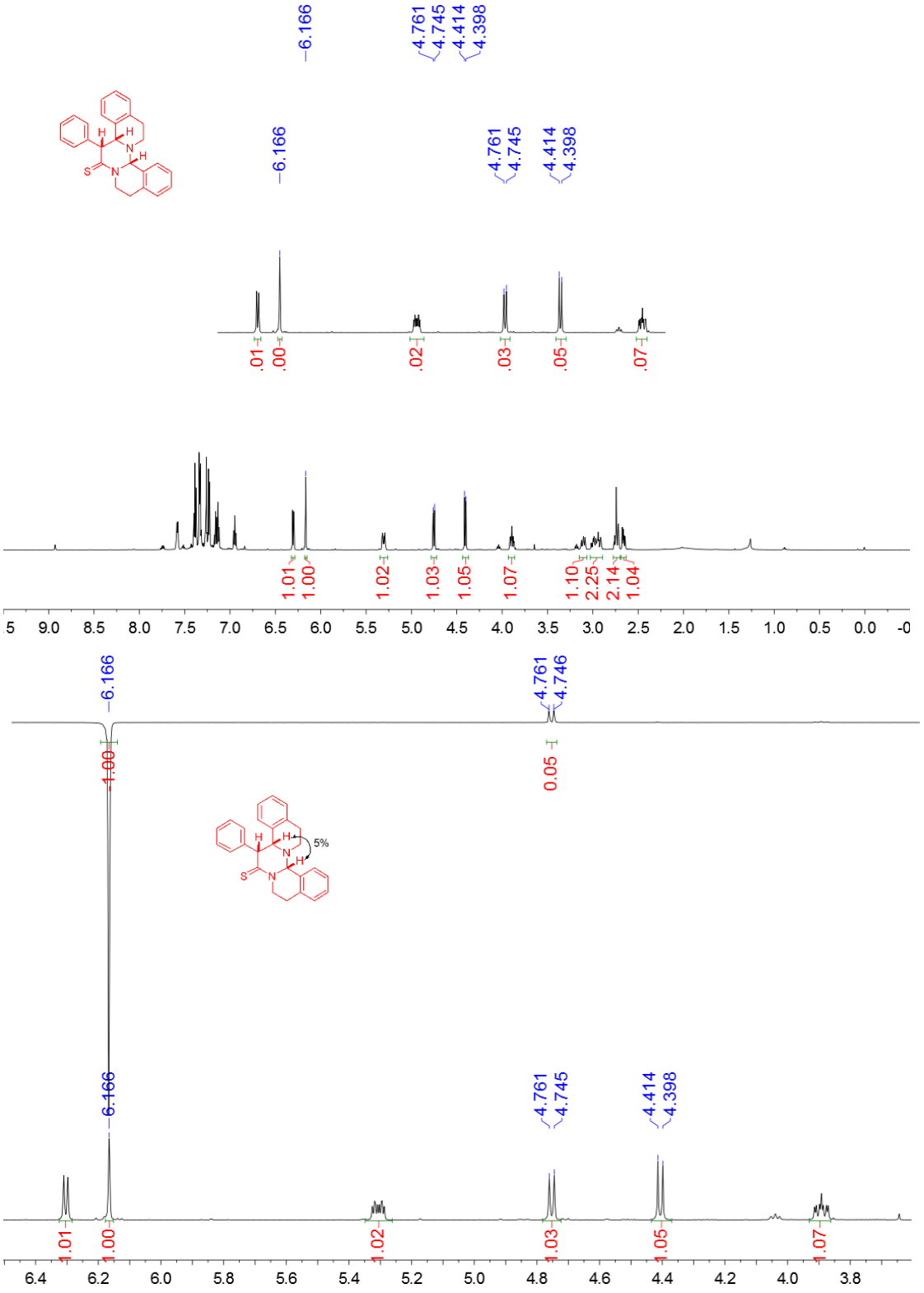
***rel*(4b*R*,5*S*,13b*S*)-5-(3-Methoxyphenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4a):**



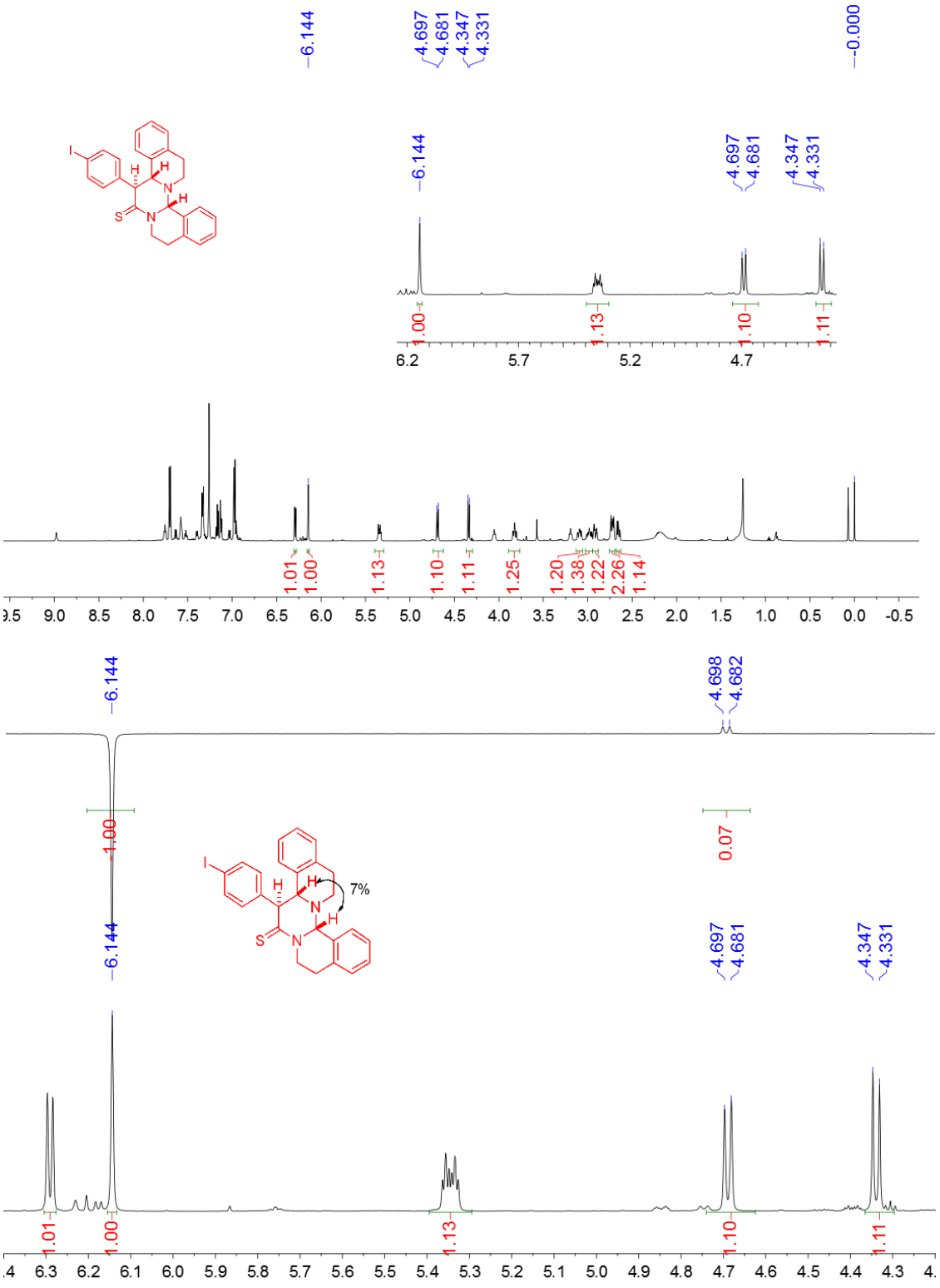
***rel*(4b*R*,5*S*,13b*S*)-5-(4-Methylphenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4b):**



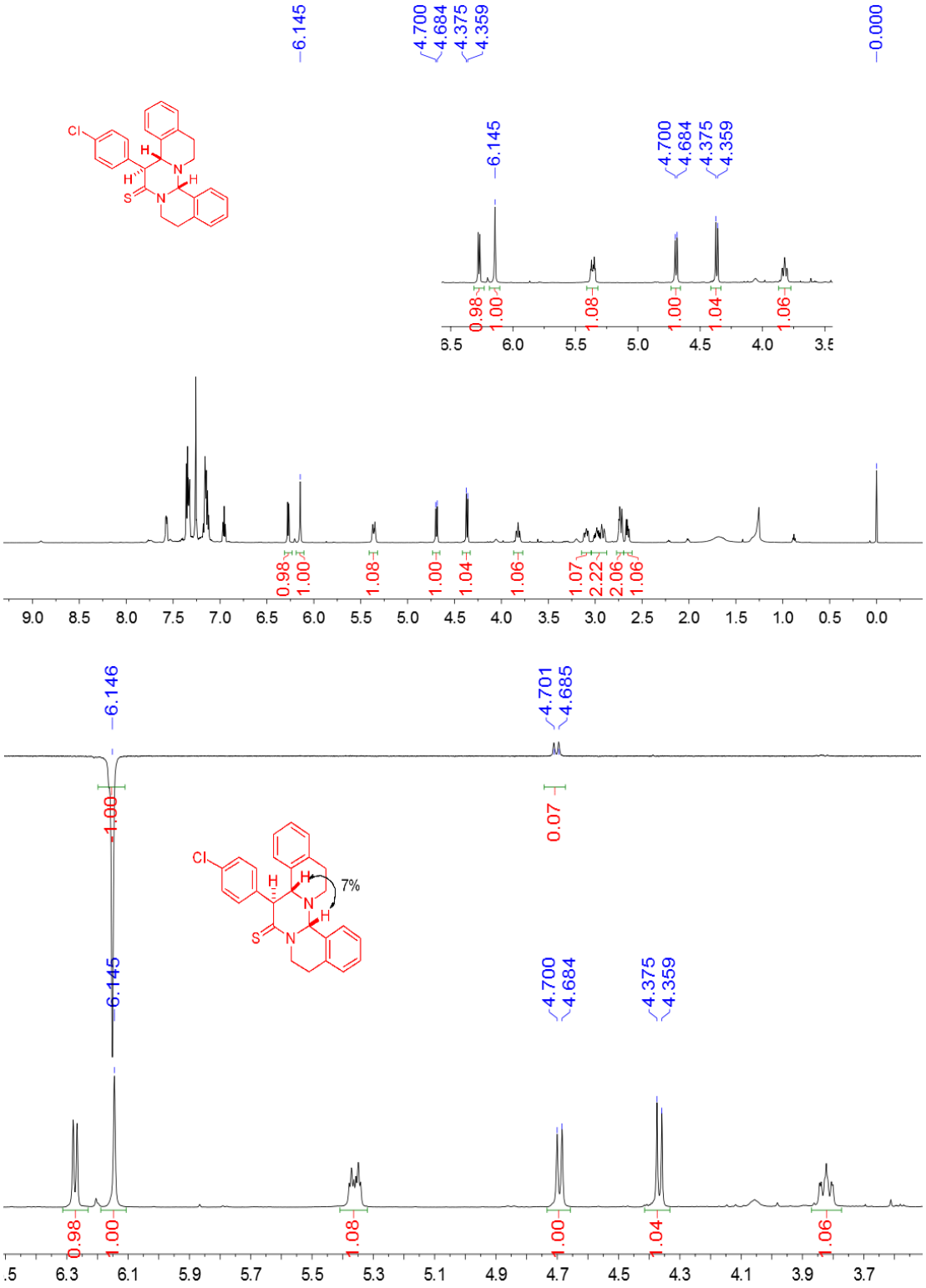
***rel*(4b*R*,5*S*,13b*S*)-5-Phenyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4c):**



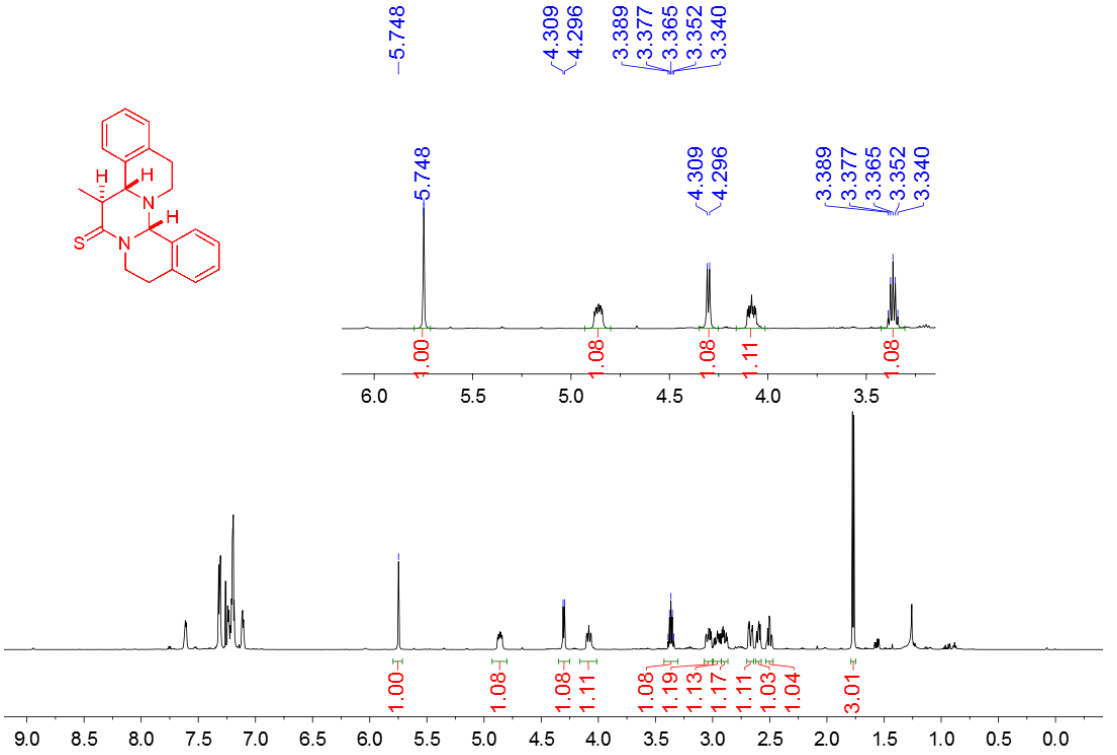
***rel*(4b*R*,5*S*,13b*S*)-5-(4-Iodophenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4d):**

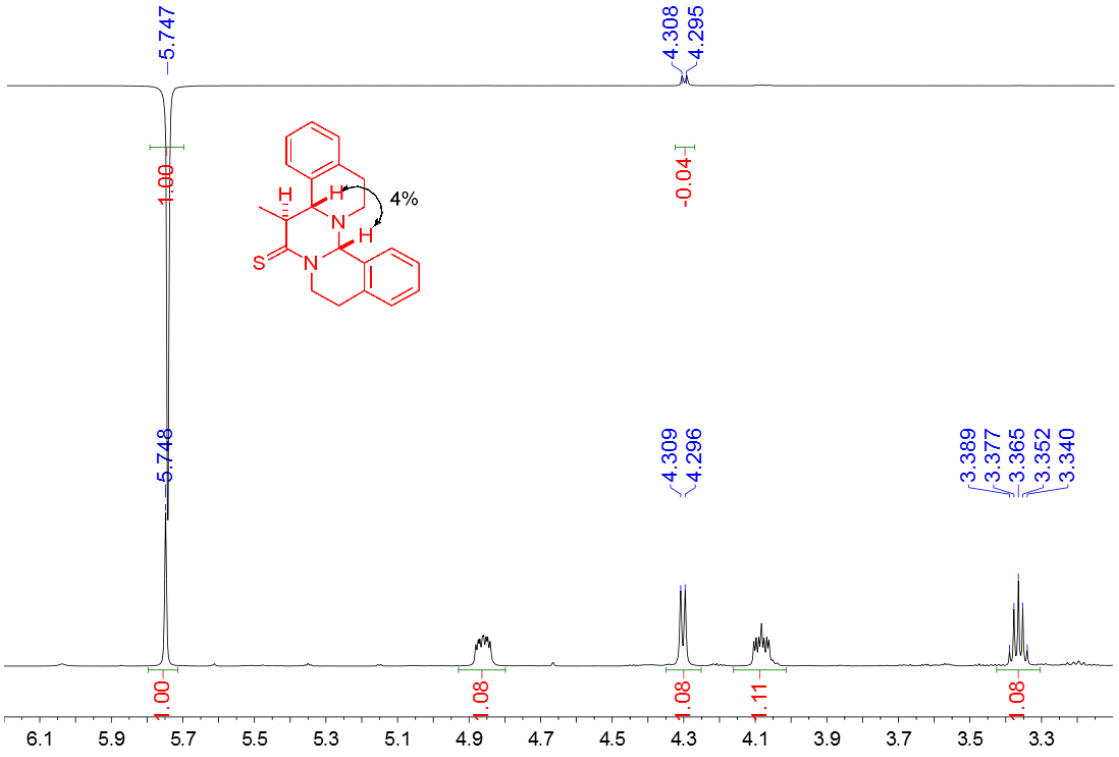


***rel*(4b*R*,5*S*,13b*S*)-5-(4-Chlorophenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4e):**

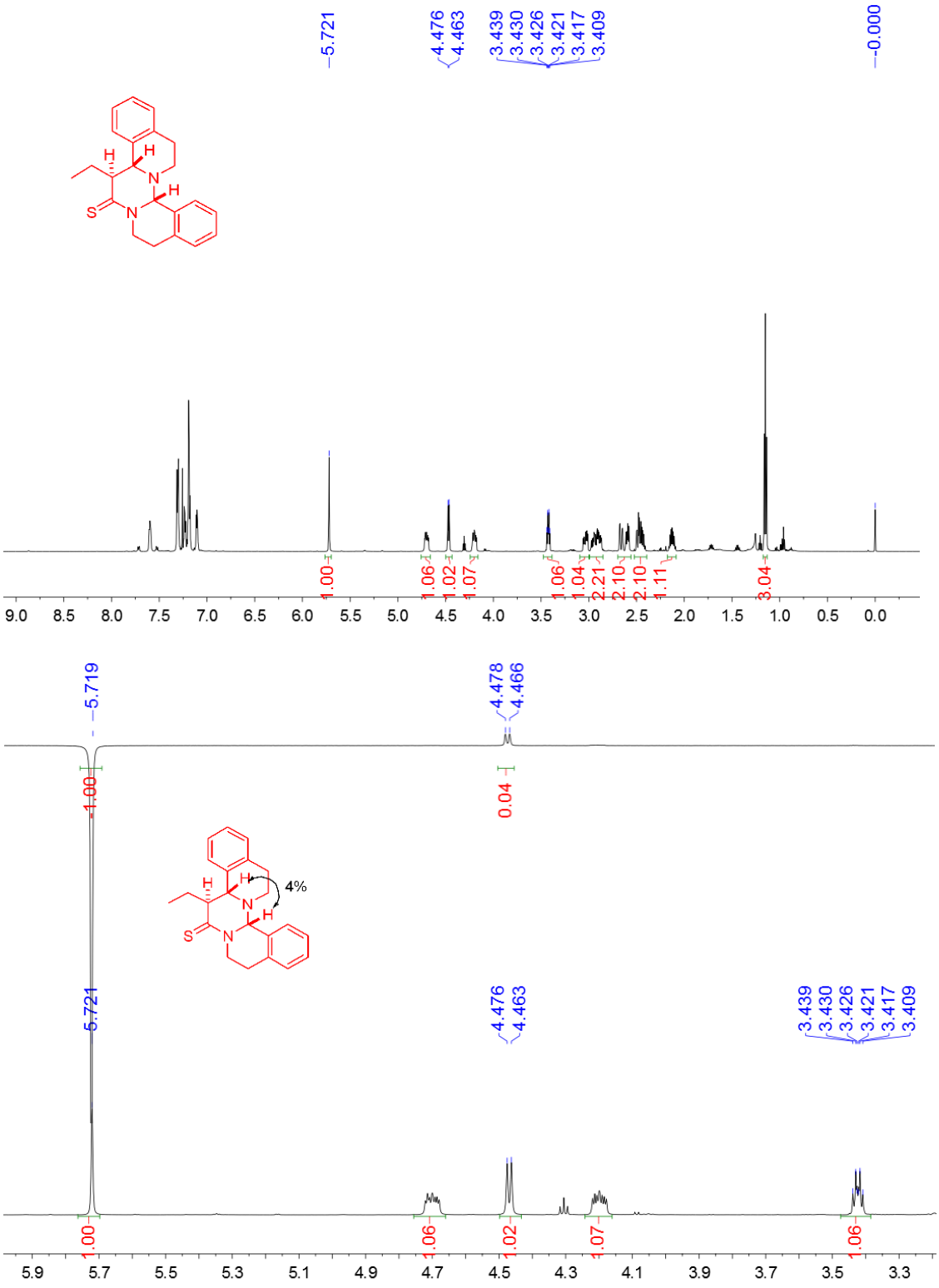


***rel*(4b*R*,5*S*,13b*S*)-5-Methyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4g):**

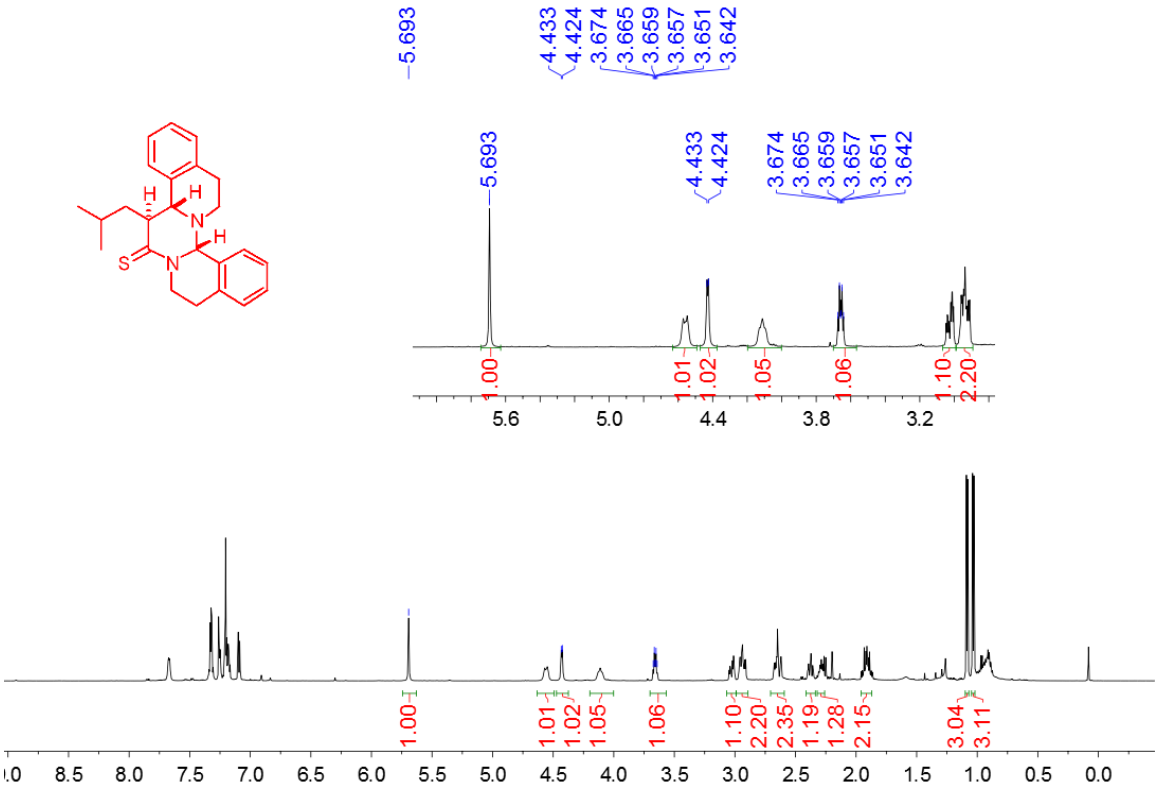


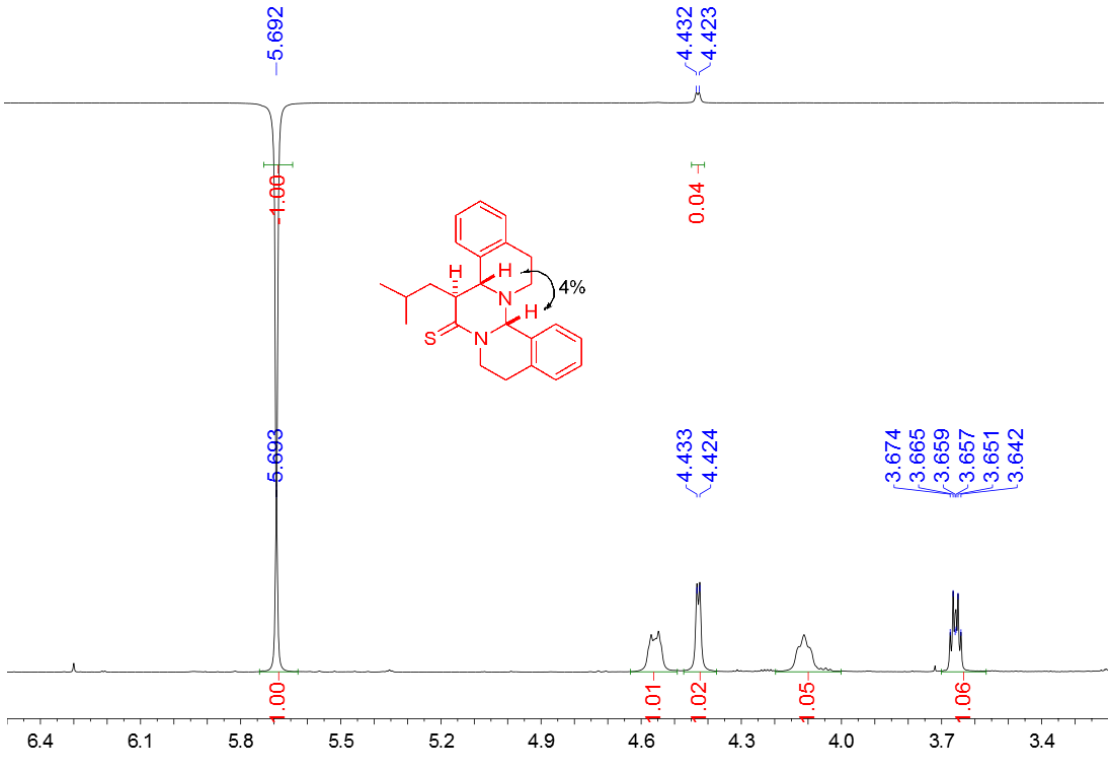


***rel*(4b*R*,5*S*,13b*S*)-5-Ethyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4h):**

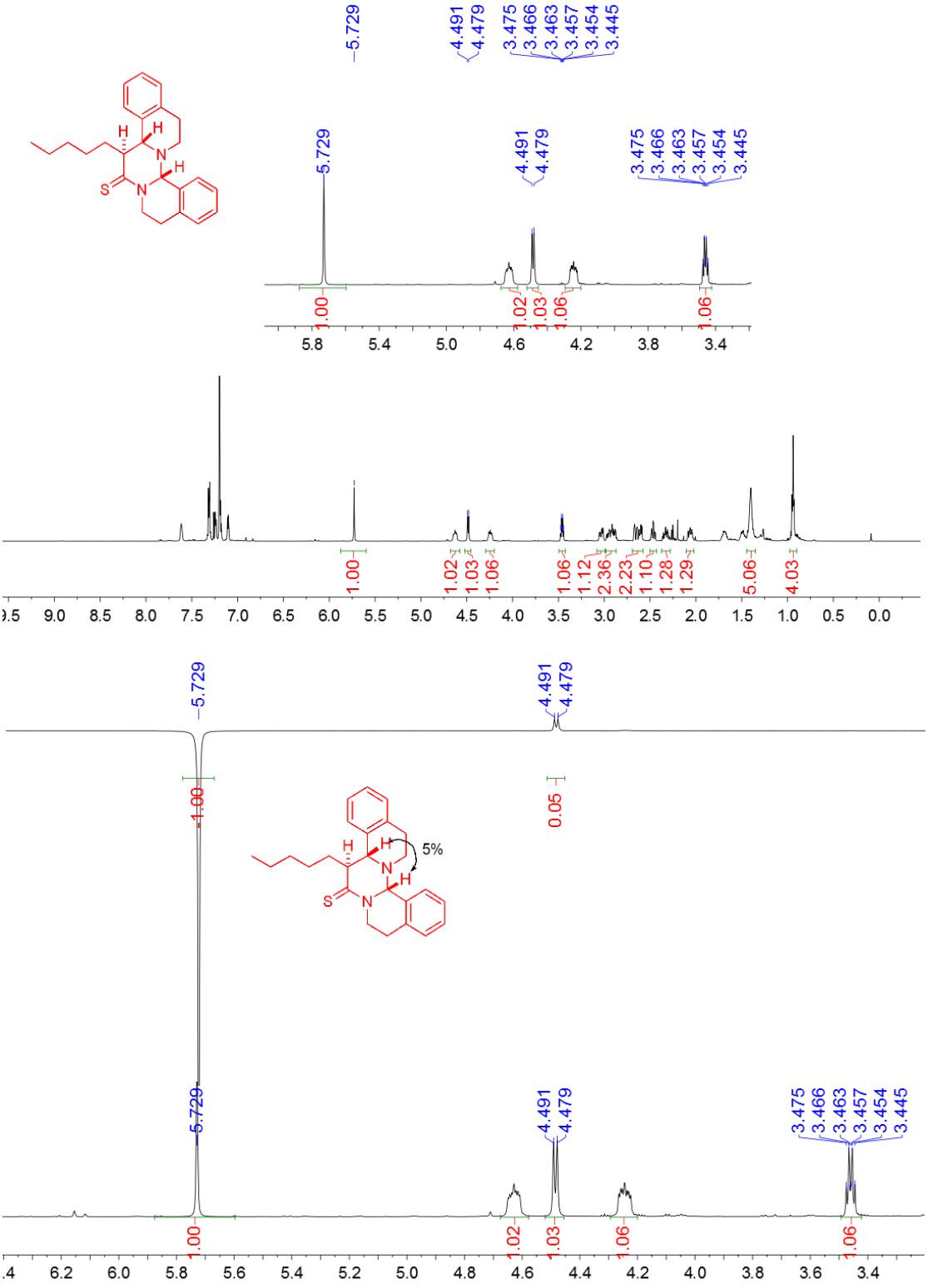


***rel*(4b*R*,5*S*13b*S*)-5-Isobutyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4i):**

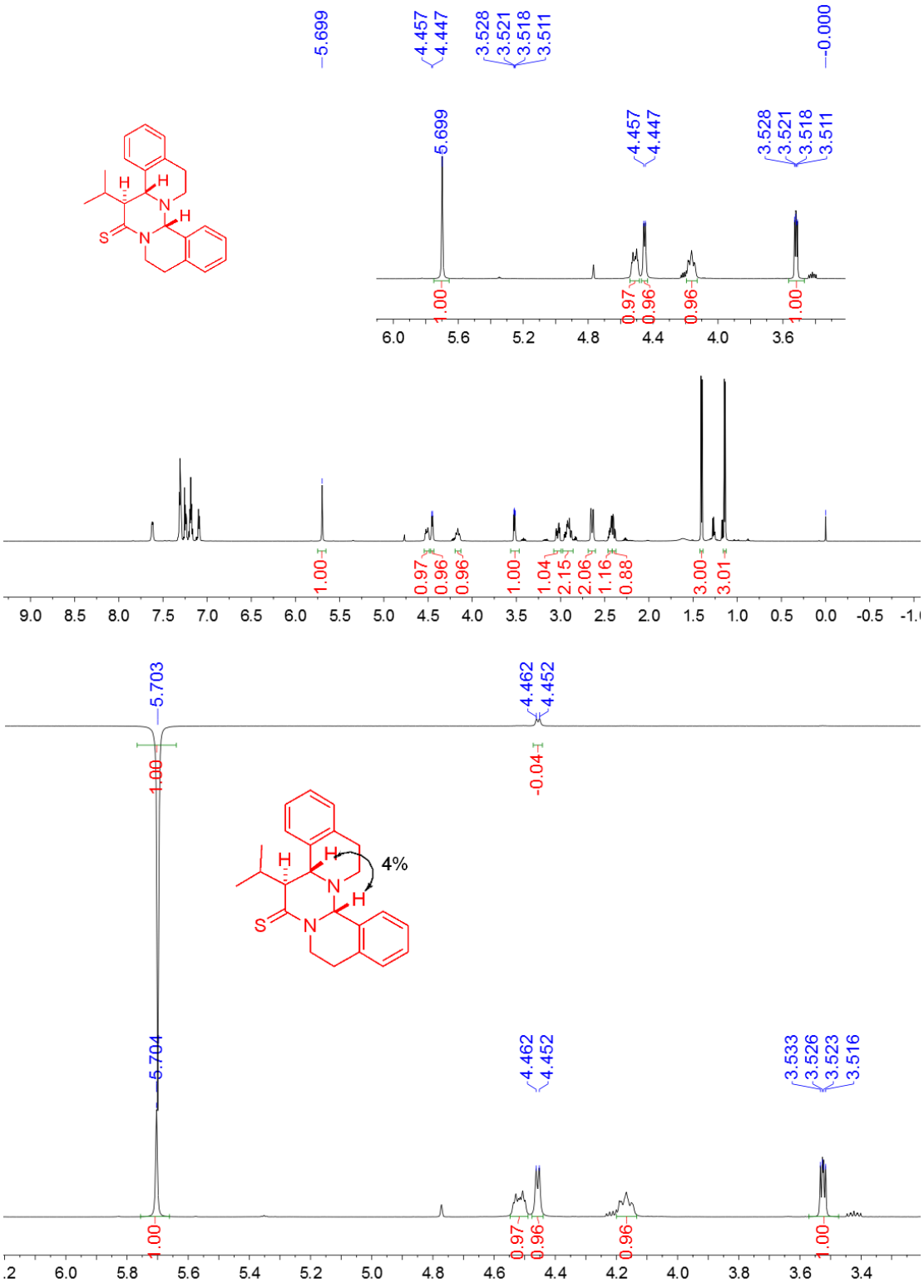




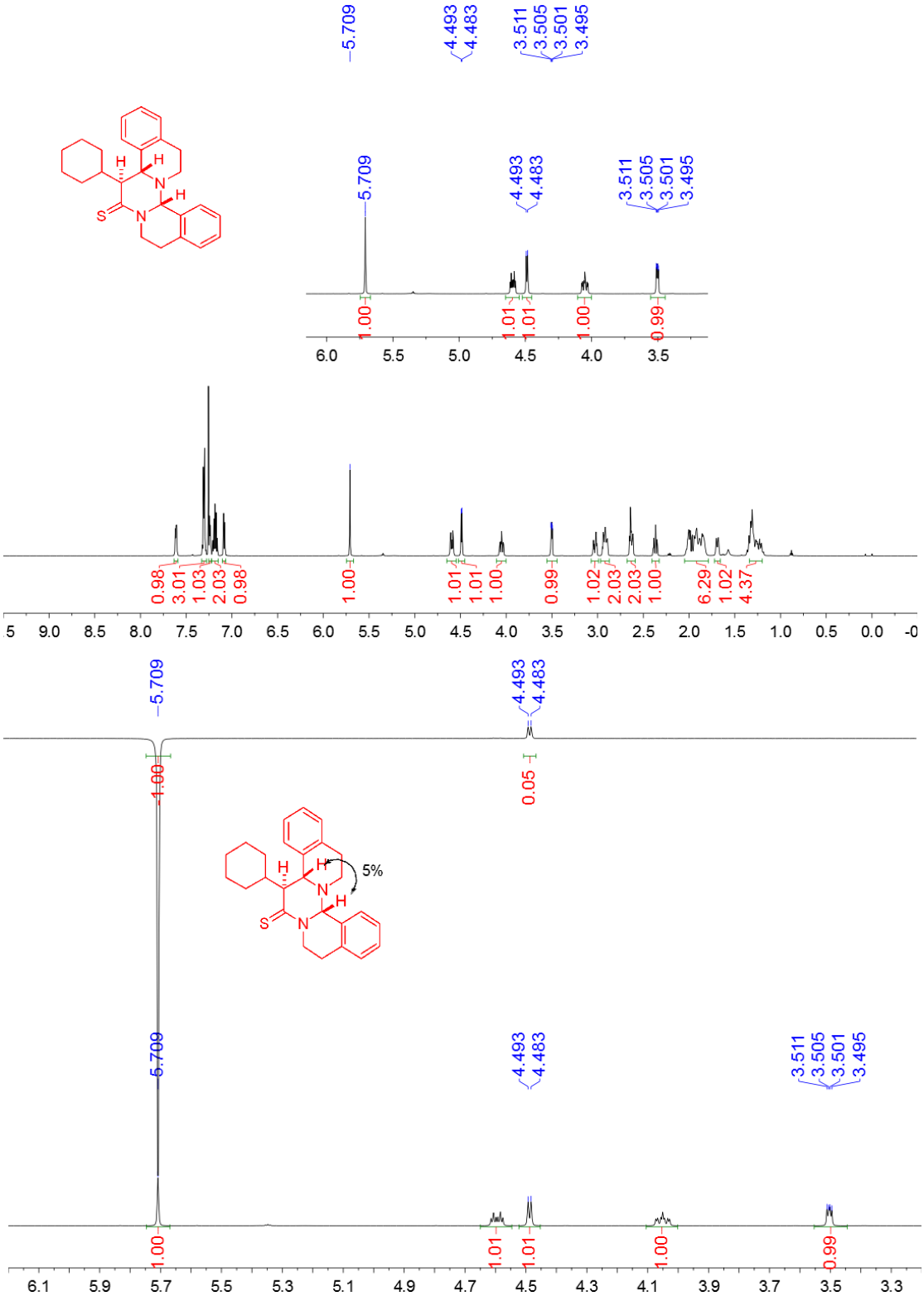
***rel*(4b*R*,5*S*,13b*S*)-5-Pentyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4j):**



***rel*(4b*R*,5*S*,13b*S*)-5-Isopropyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4k):**



***rel*(4b*R*,5*S*,13b*S*)-5-Cyclohexyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-6-thione (4l):**



Ethyl *rel*(4b*R*,5*R*,13b*S*)-6-thioxo-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a*']diisoquinoline-5-carboxylate (4m):