

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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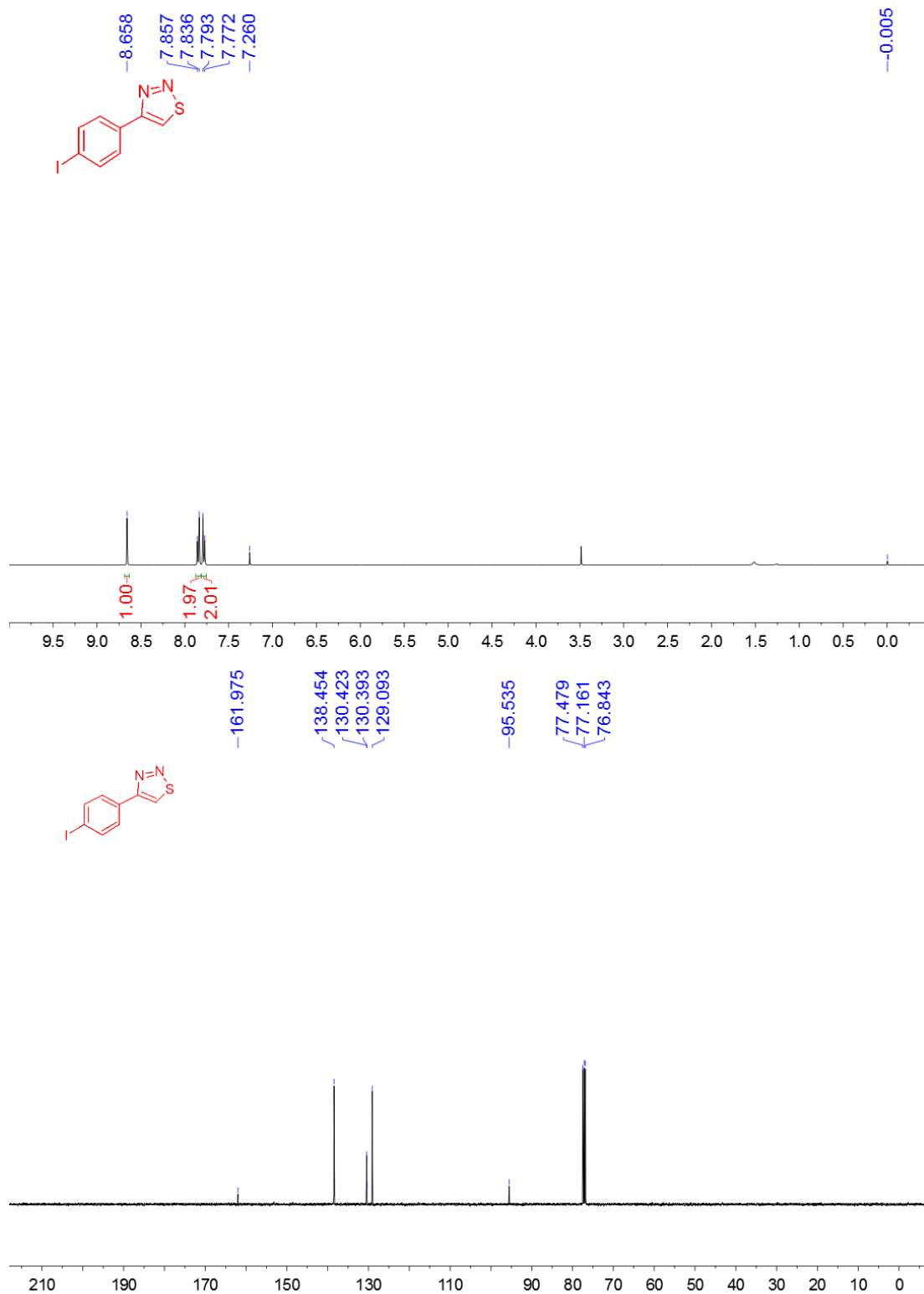
[†] These two authors contributed equally.

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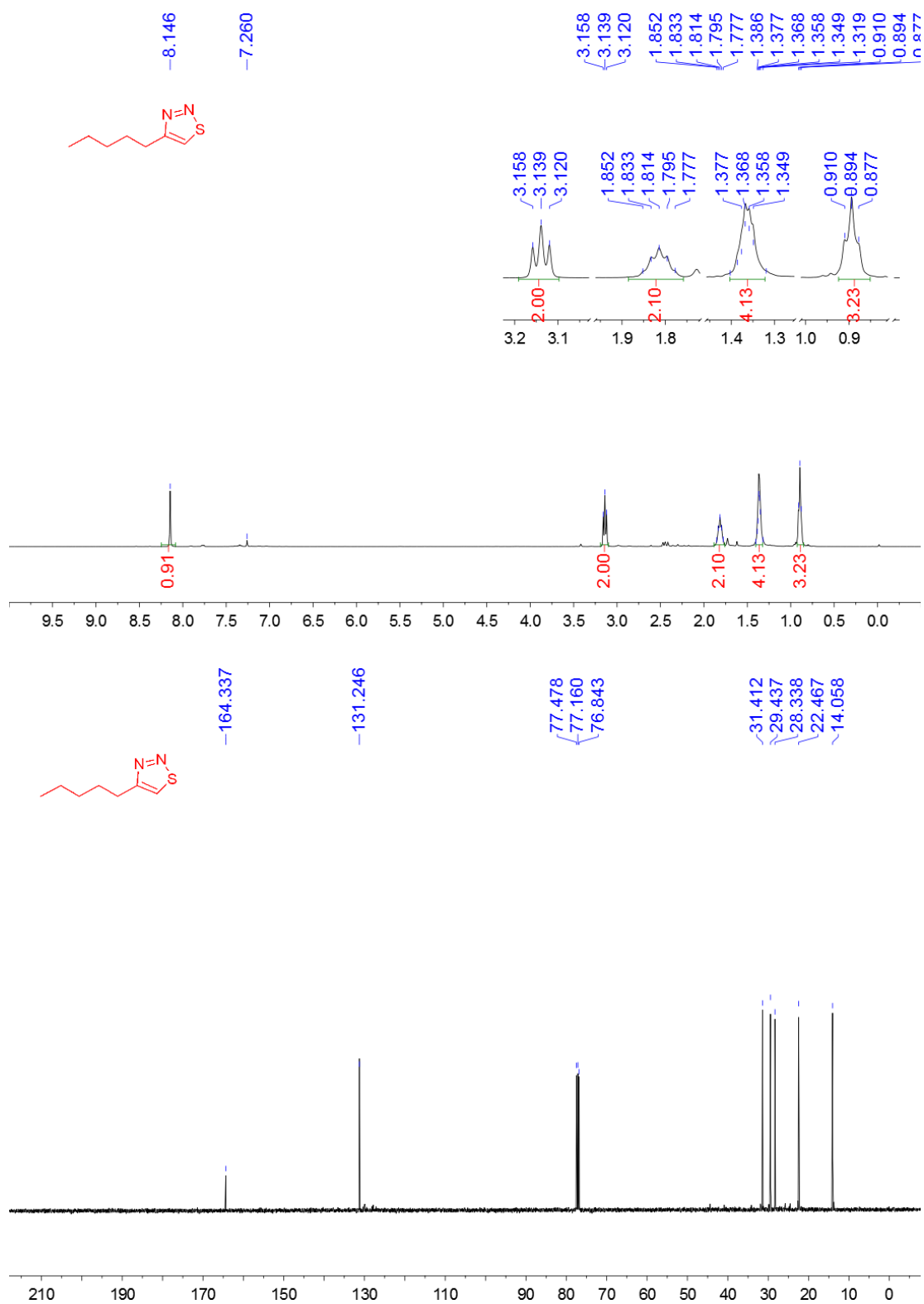
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1. ^1H and ^{13}C NMR Spectra of Unknown Compounds

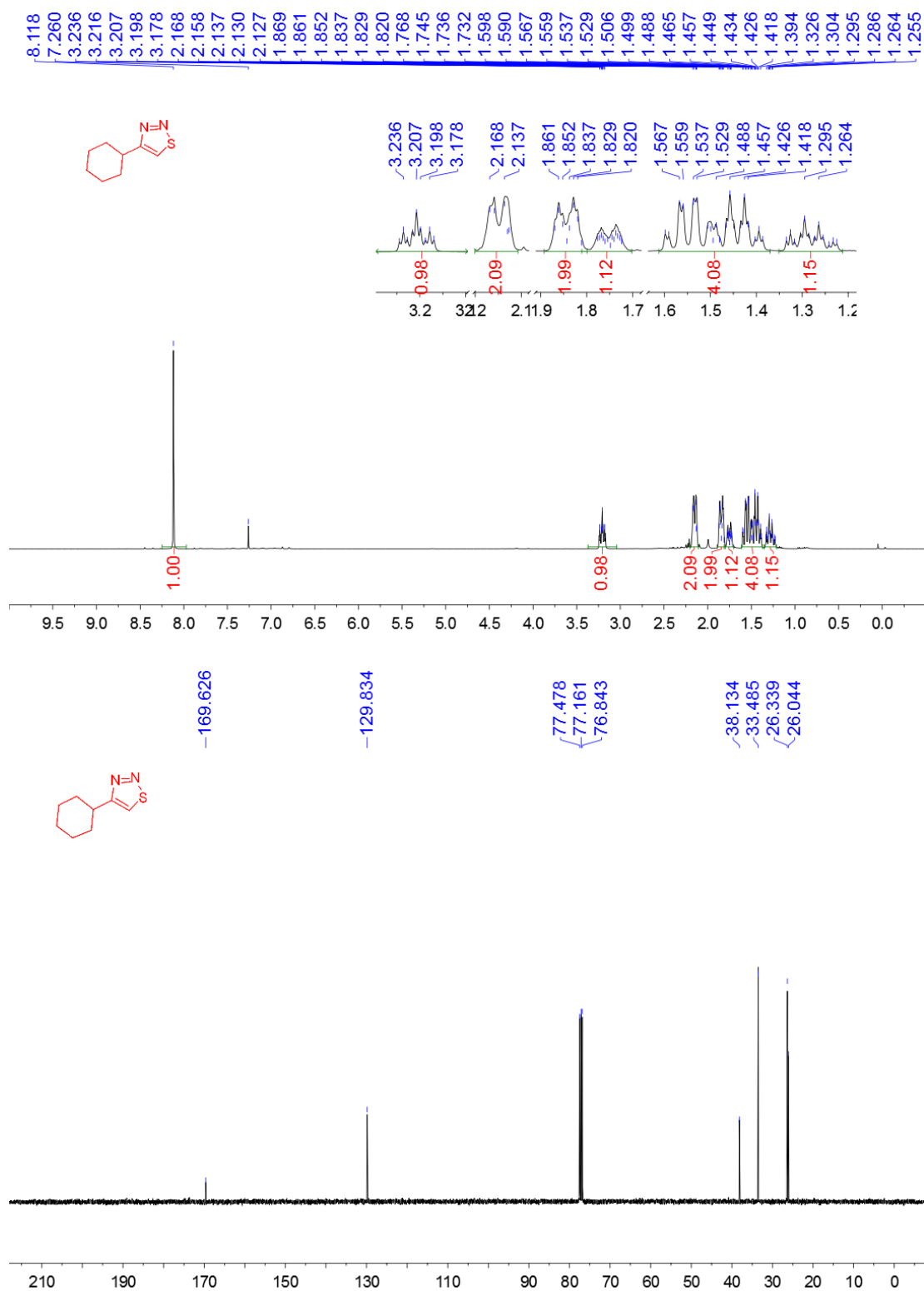
4-(4-Iodophenyl)-1,2,3-thiadiazole (6d)



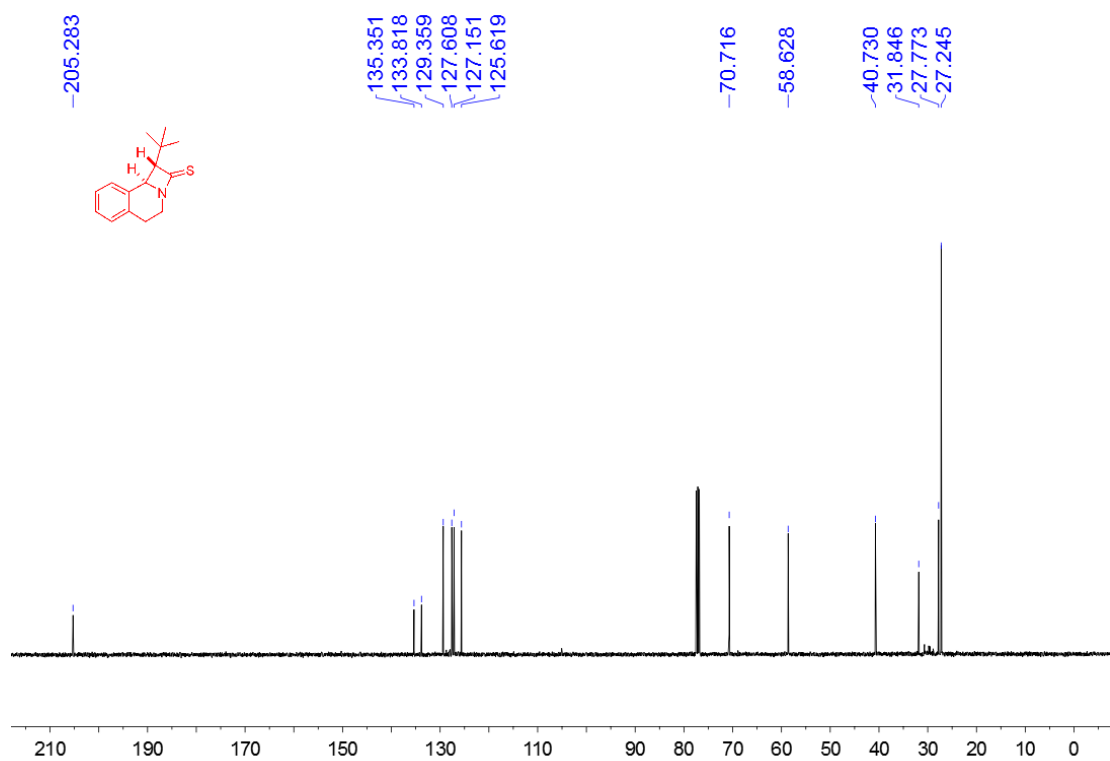
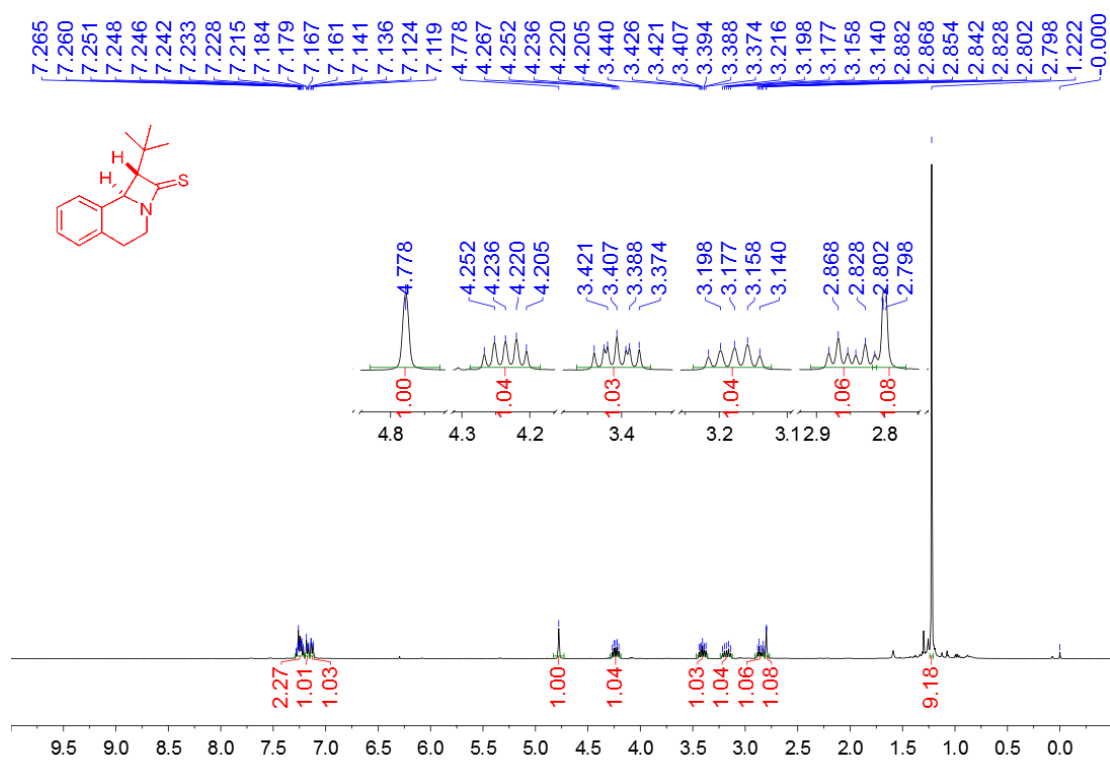
4-Pentyl-1,2,3-thiadiazole (6j)



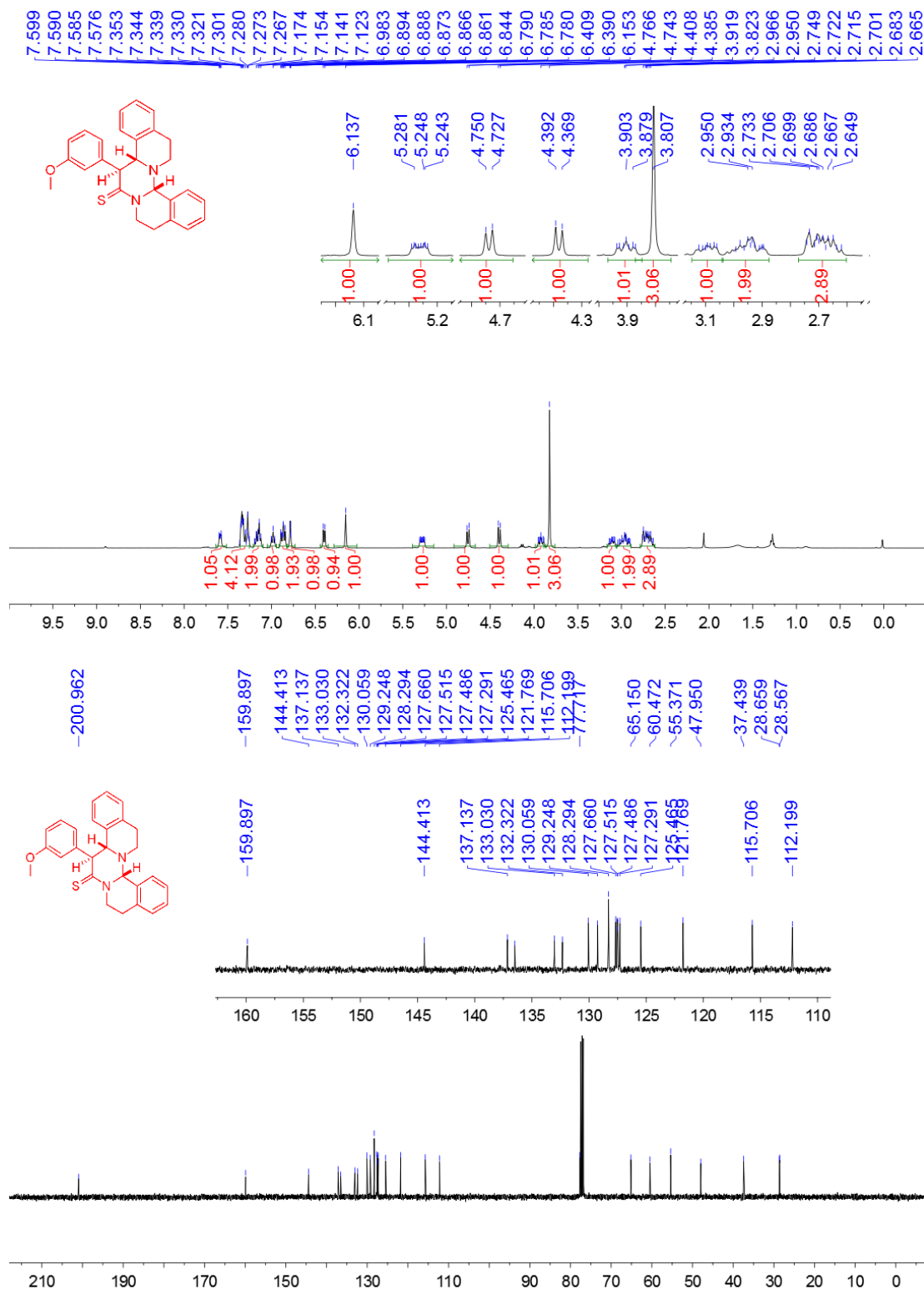
4-Cyclohexyl-1,2,3-thiadiazole (6l)



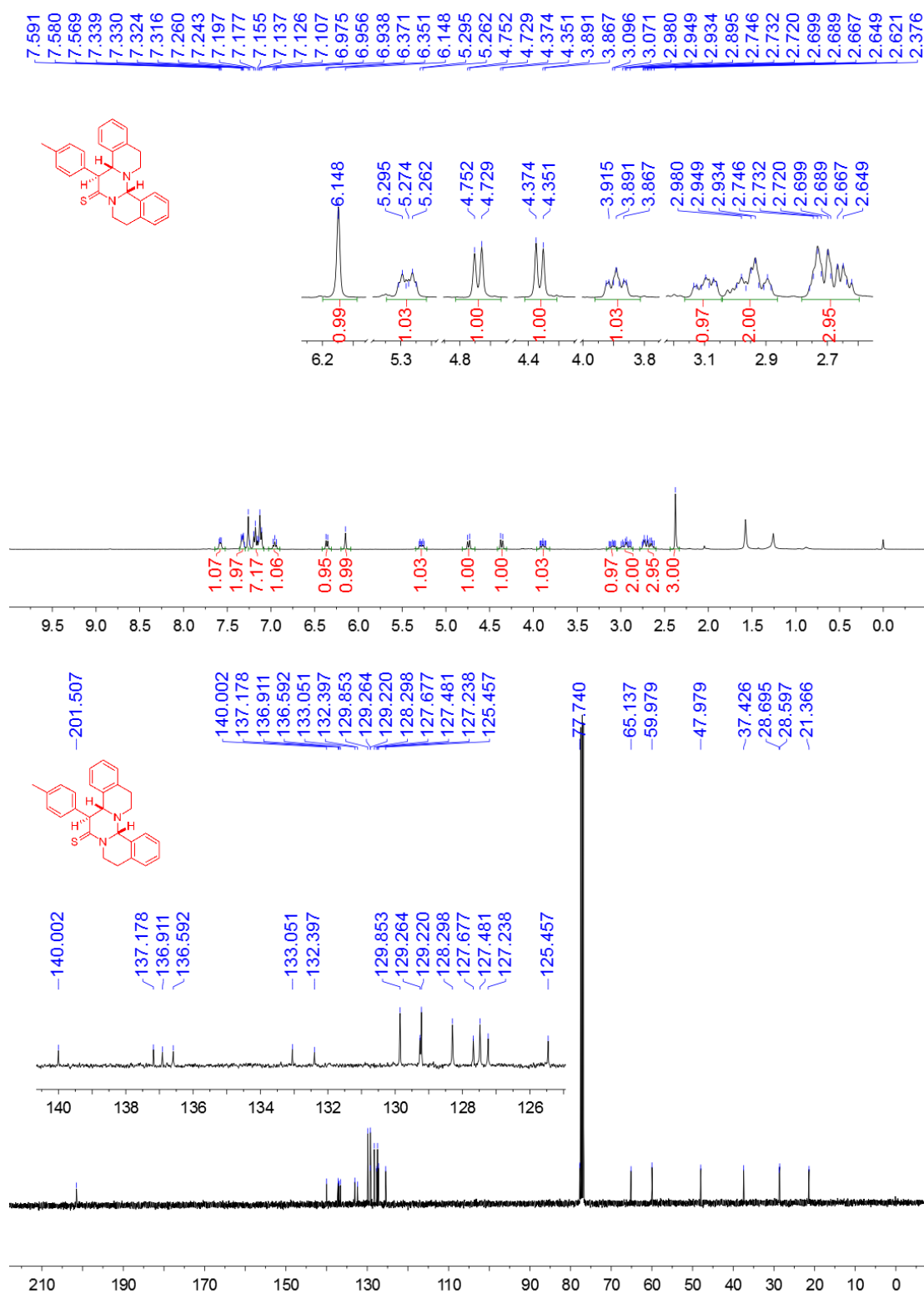
rel(1S,9bR)-1-(tert-Butyl)-1,4,5,9b-tetrahydro-2H-azeto[2,1-a]isoquinoline-2-thione (3n)



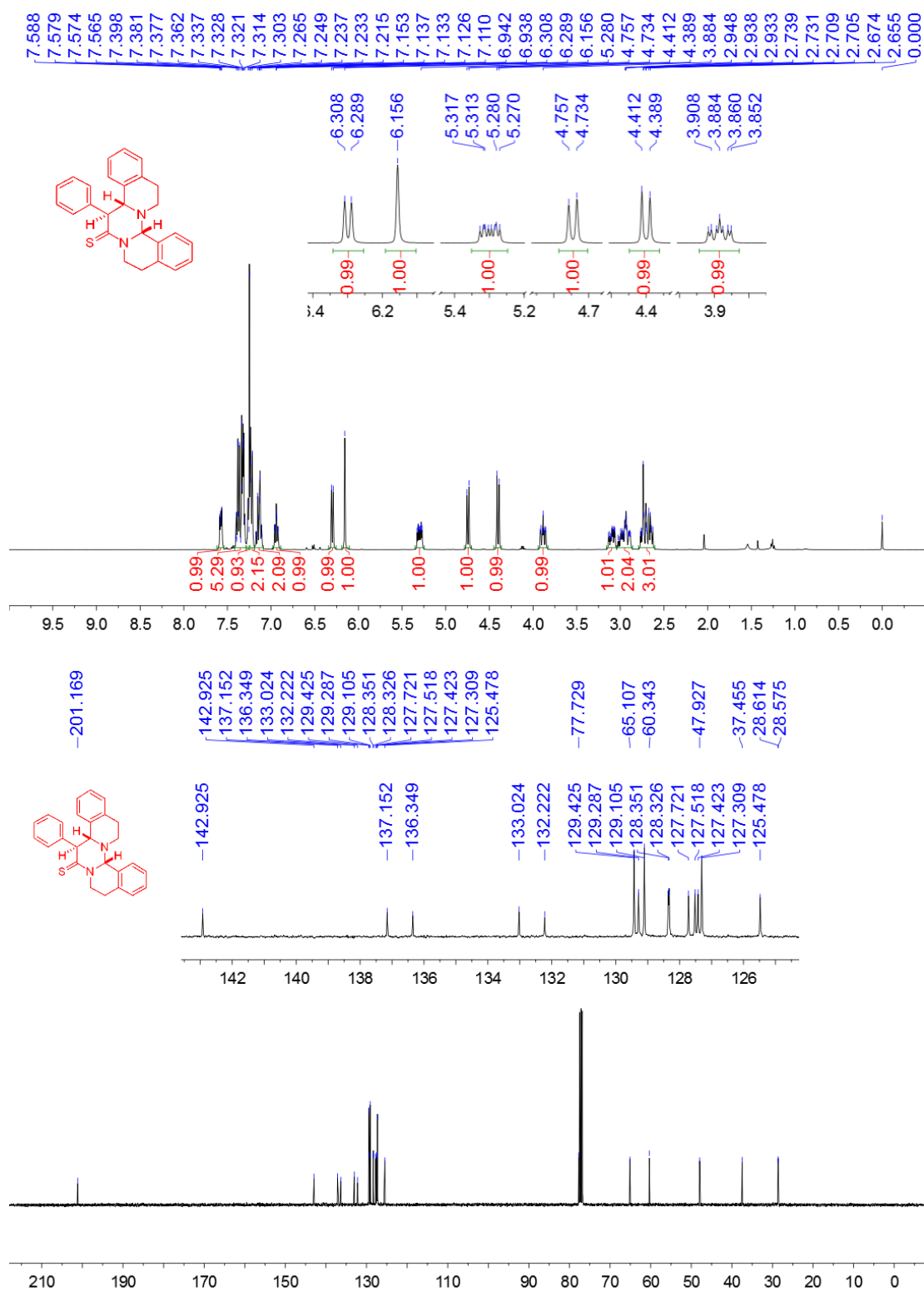
***rel*(4b*R*,5*S*,13b*S*)-5-(3-Methoxyphenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4a)**



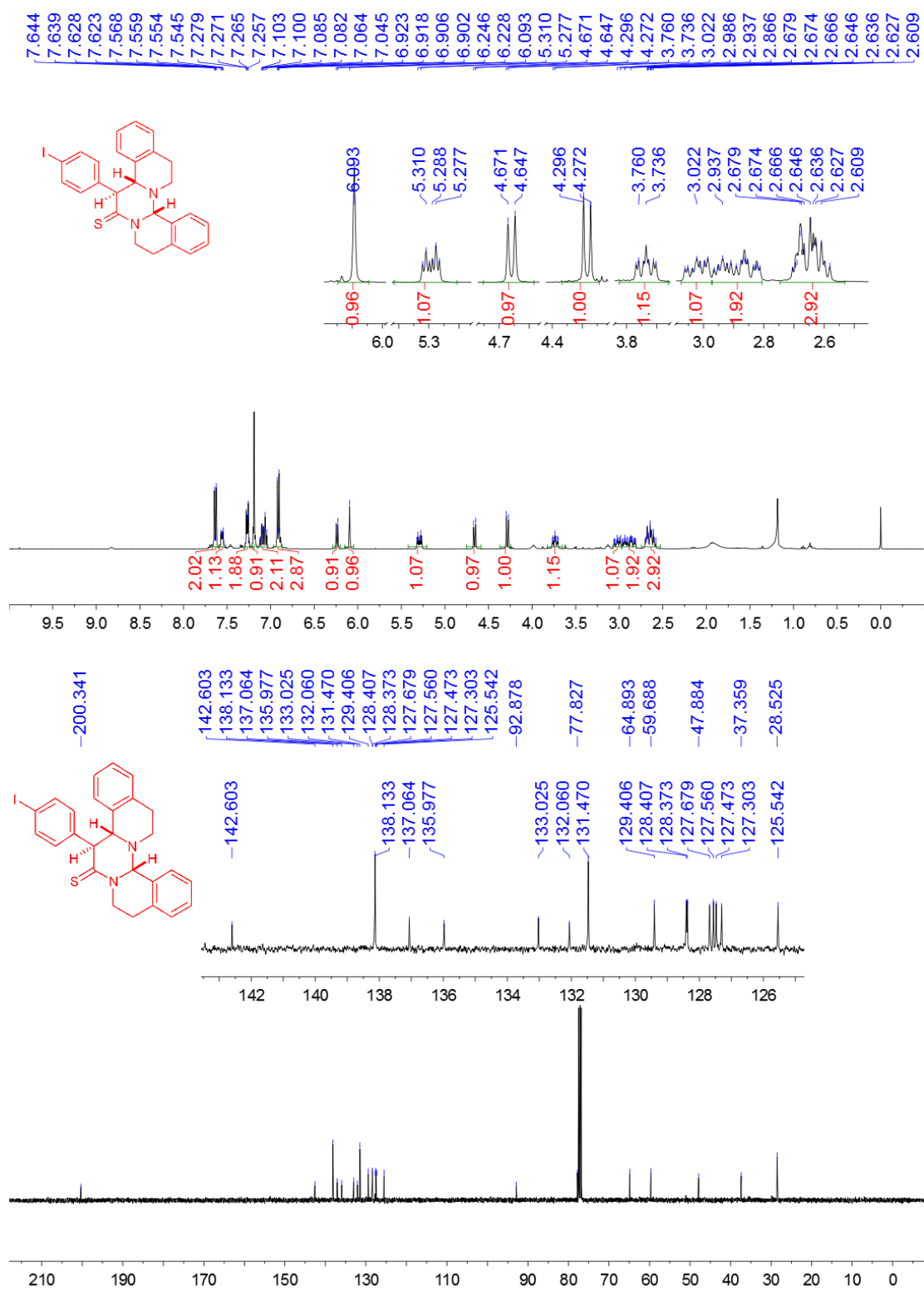
***rel*(4*bR*,5*S*,13*bS*)-5-(4-Methylphenyl)-4*b*,5,9,13*b*,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4*b*)**



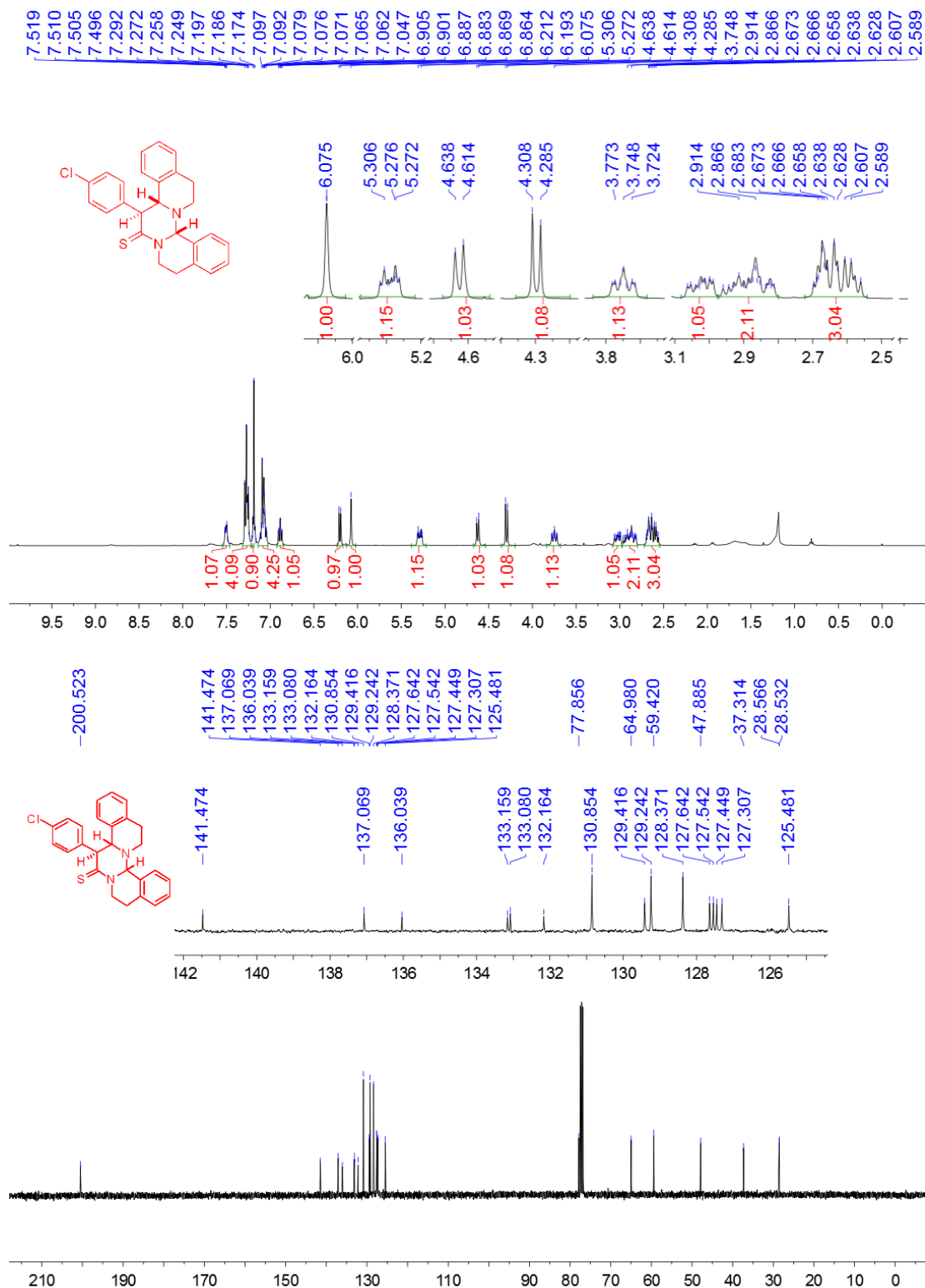
***rel*(4*bR*,5*S*,13*bS*)-5-Phenyl-4*b*,5,9,13*b*,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4c)**



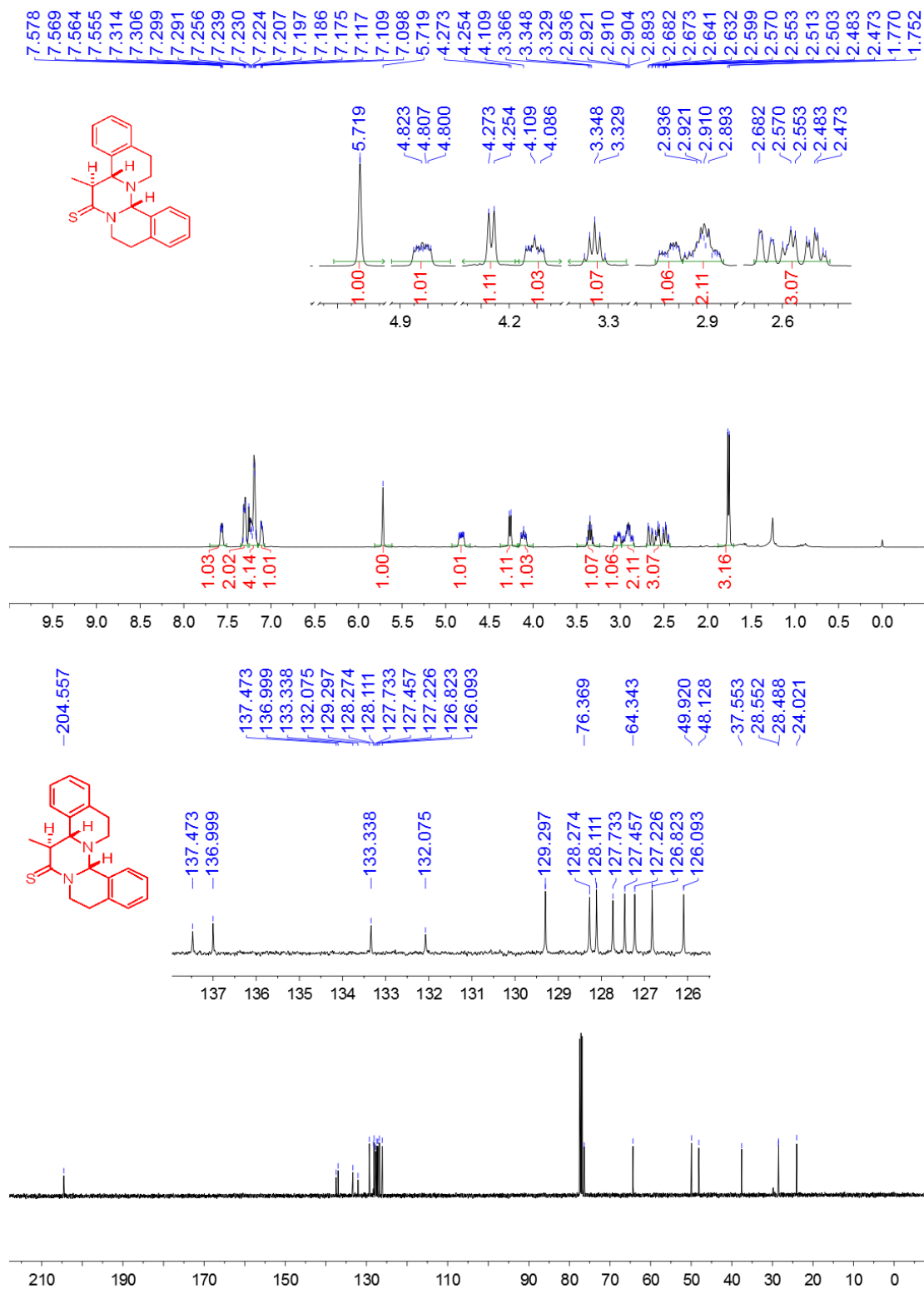
***rel*(4*bR*,5*S*,13*bS*)-5-(4-Iodophenyl)-4*b*,5,9,13*b*,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]*di*isoquinoline-6-thione (4*d*)**



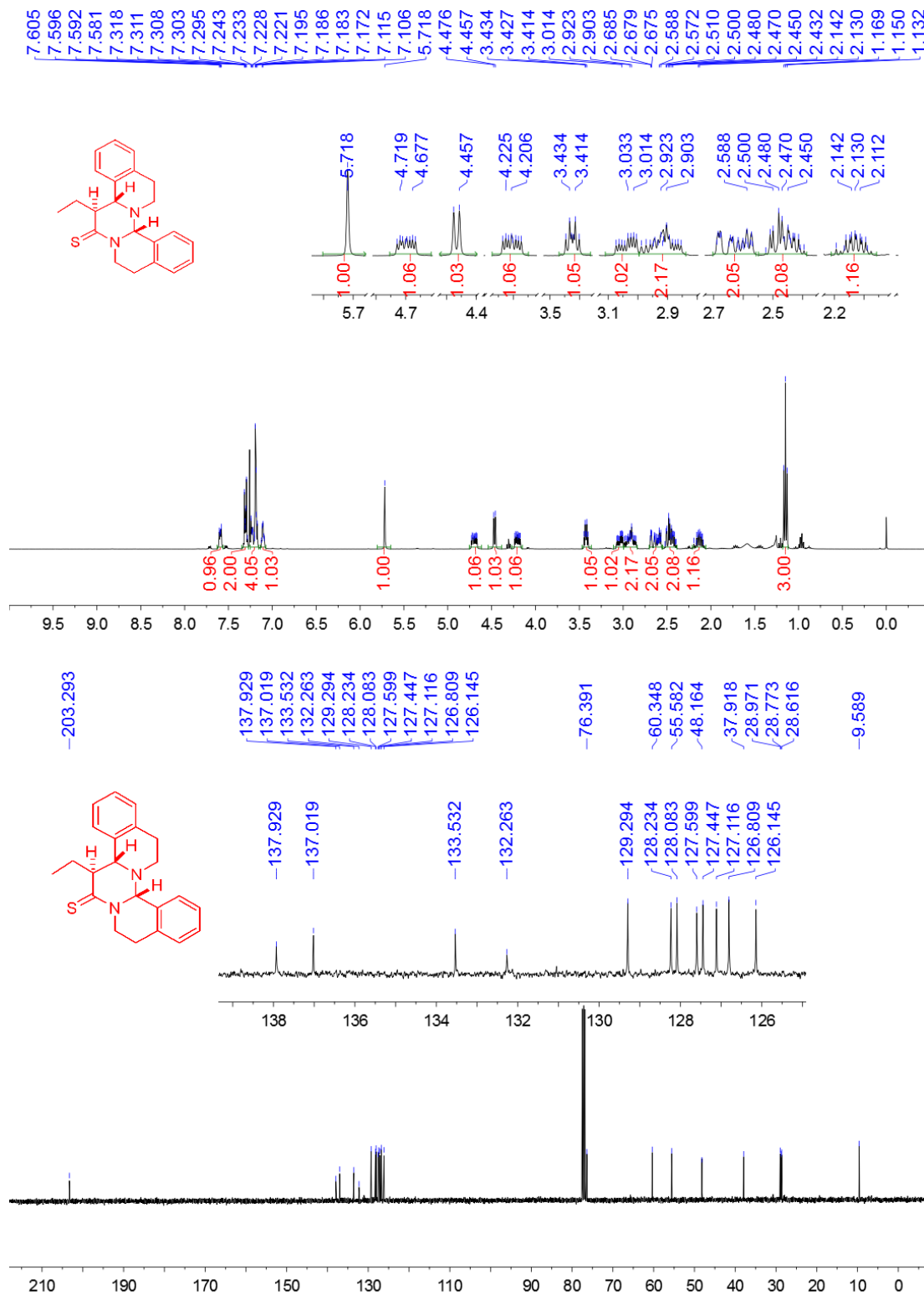
***rel*(4b*R*,5*S*,13b*S*)-5-(4-Chlorophenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4e)**



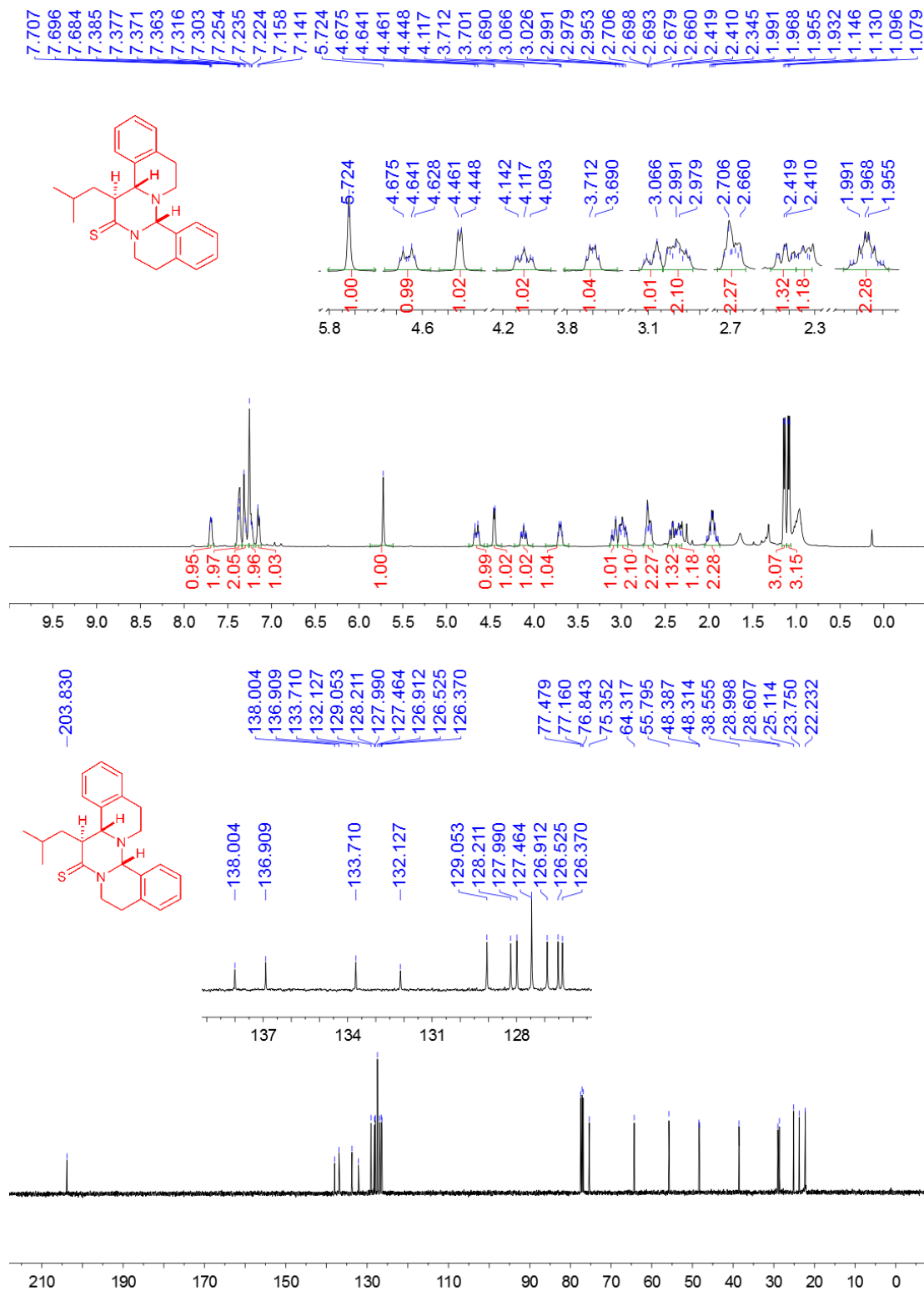
***rel*(4b*R*,5*S*,13b*S*)-5-Methyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4g)**



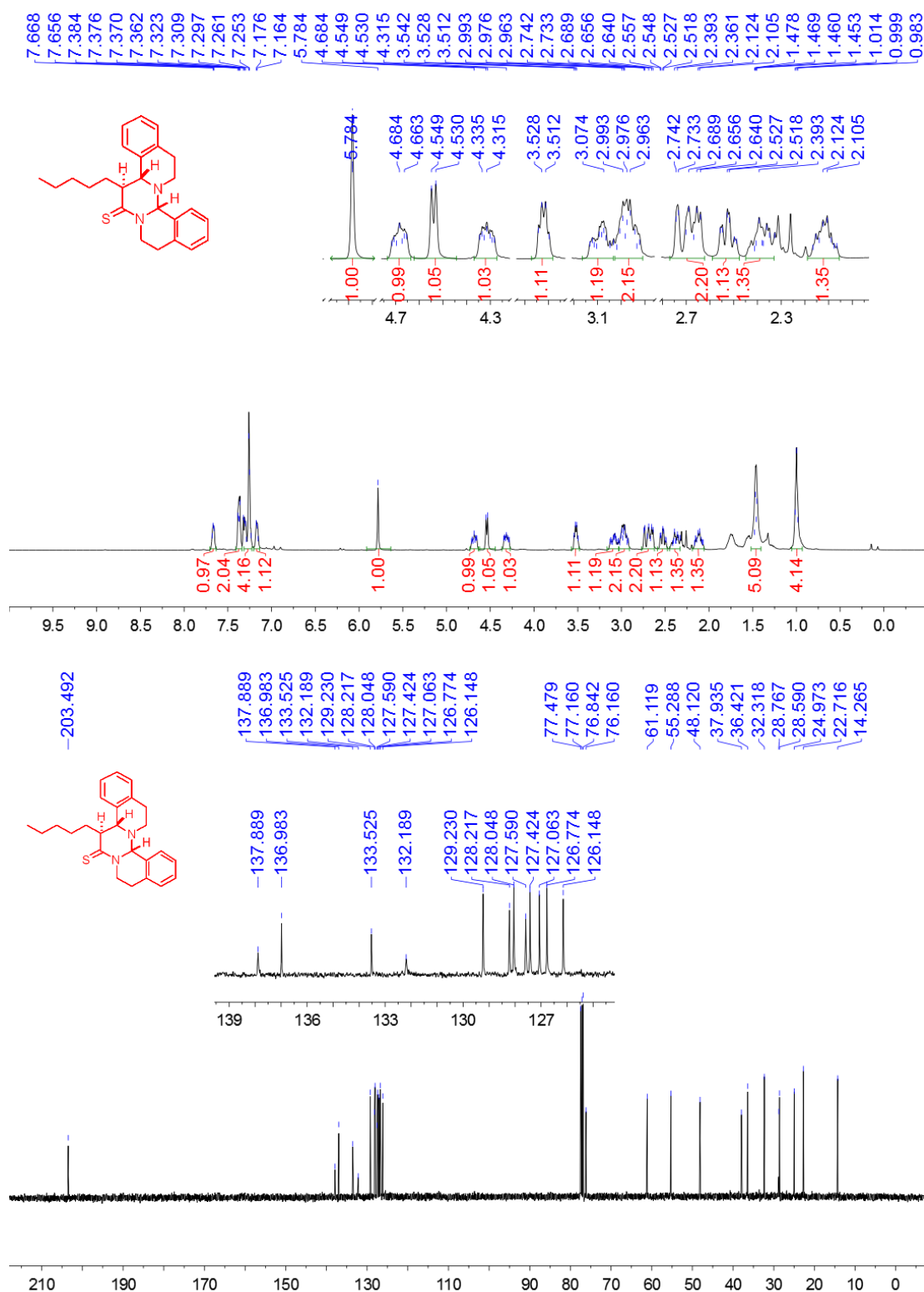
***rel*(4*bR*,5*S*,13*bS*)-5-Ethyl-4*b*,5,9,13*b*,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4*h*)**



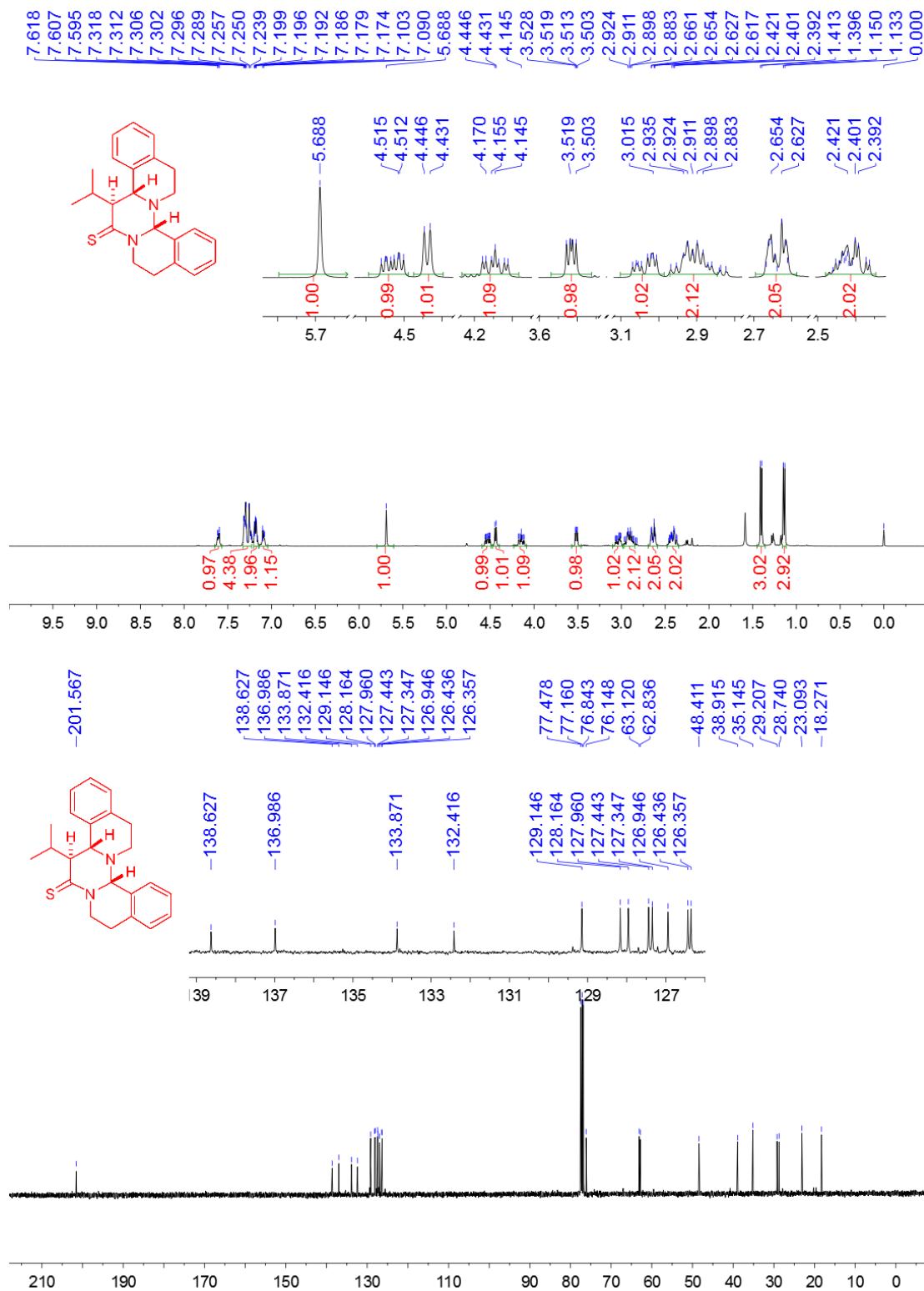
rel(4bR,5S13bS)-5-Isobutyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4i)



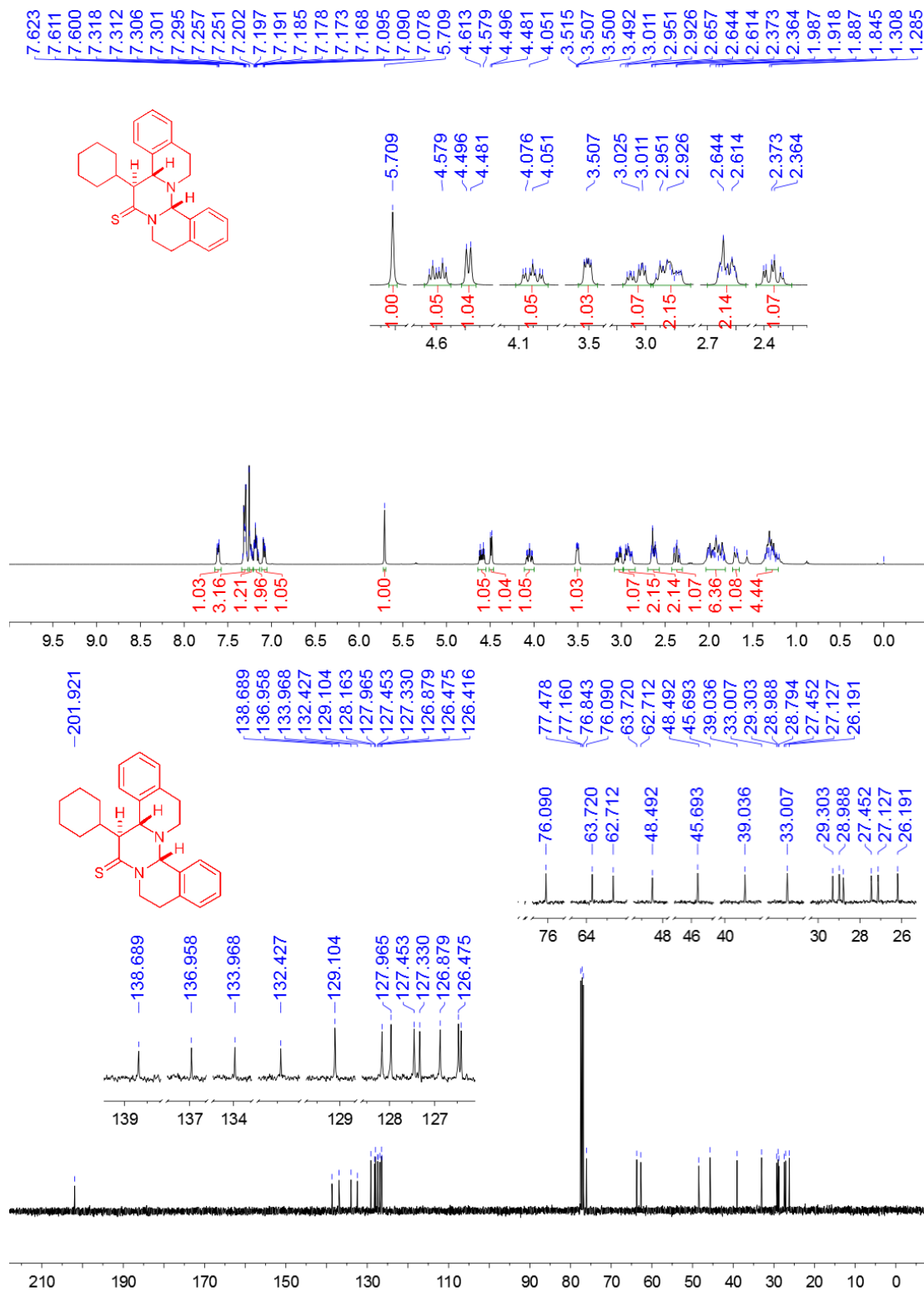
***rel*(4b*R*,5*S*,13b*S*)-5-Pentyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4j)**



***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)**

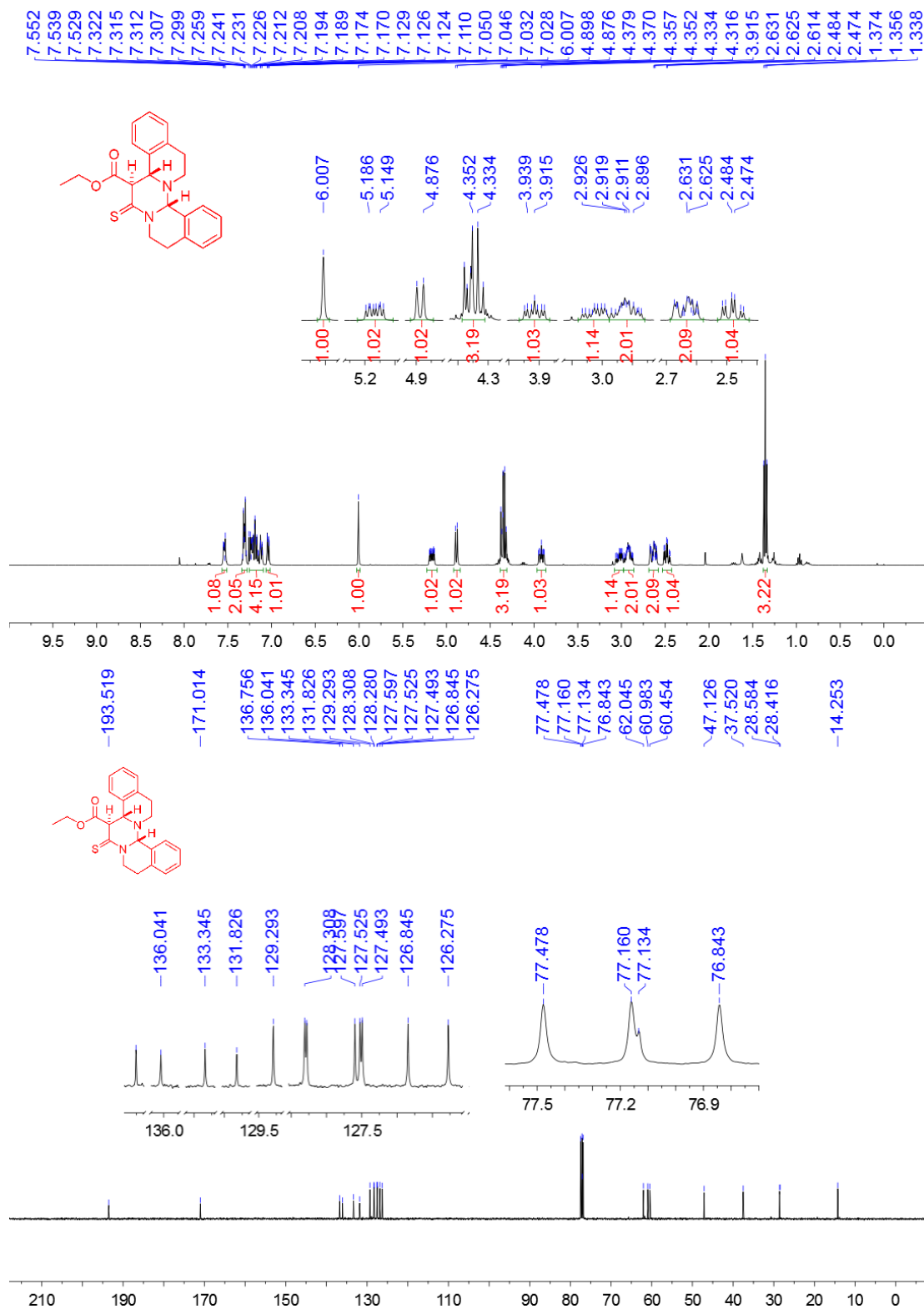


***rel*(4b*R*,5*S*,13b*S*)-5-Cyclohexyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4l)**



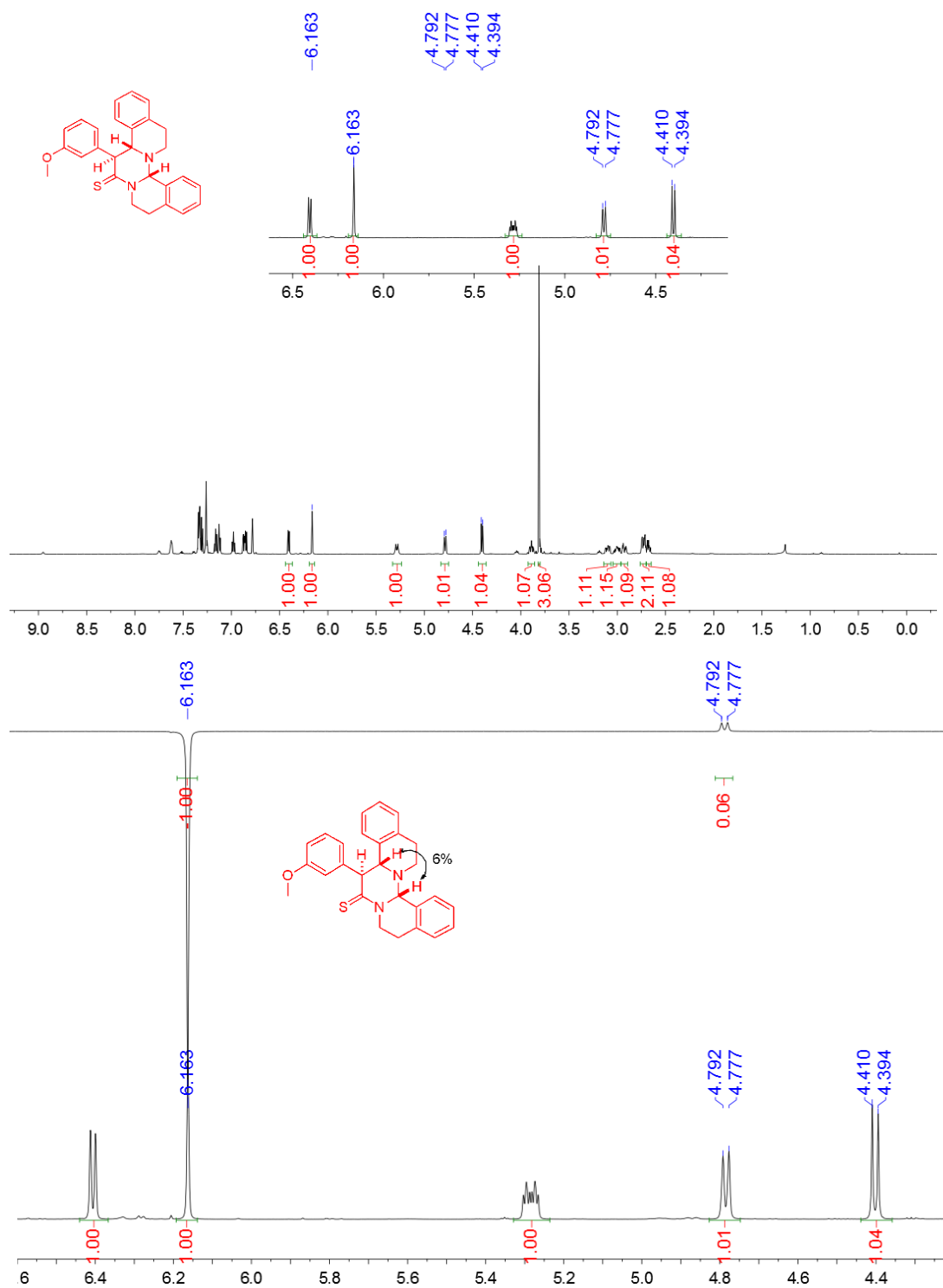
Ethyl

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

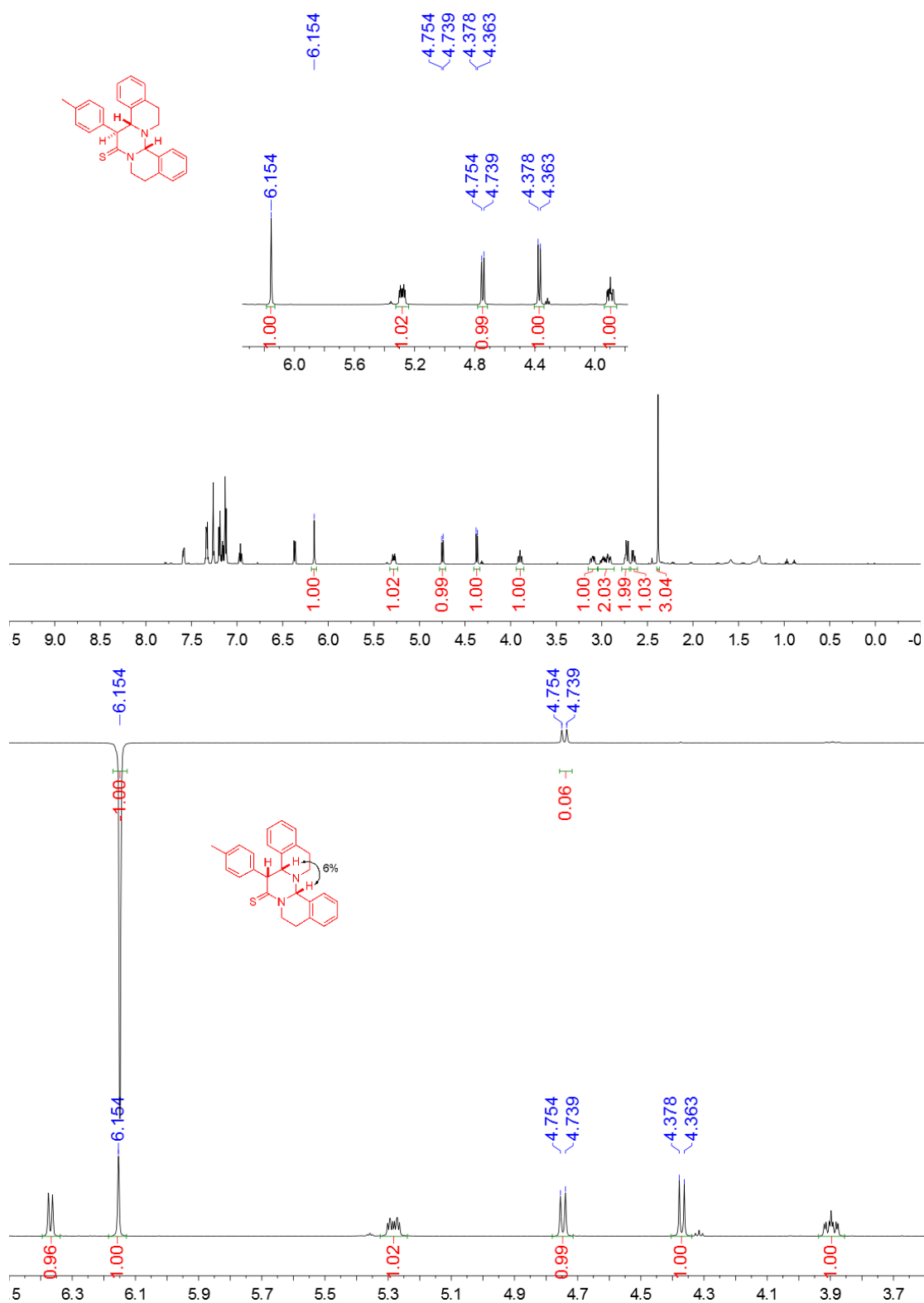


2. One-dimension NOE Spectra of [2^t + 2ⁱ + 2ⁱ] Annuladducts (600 MHz)

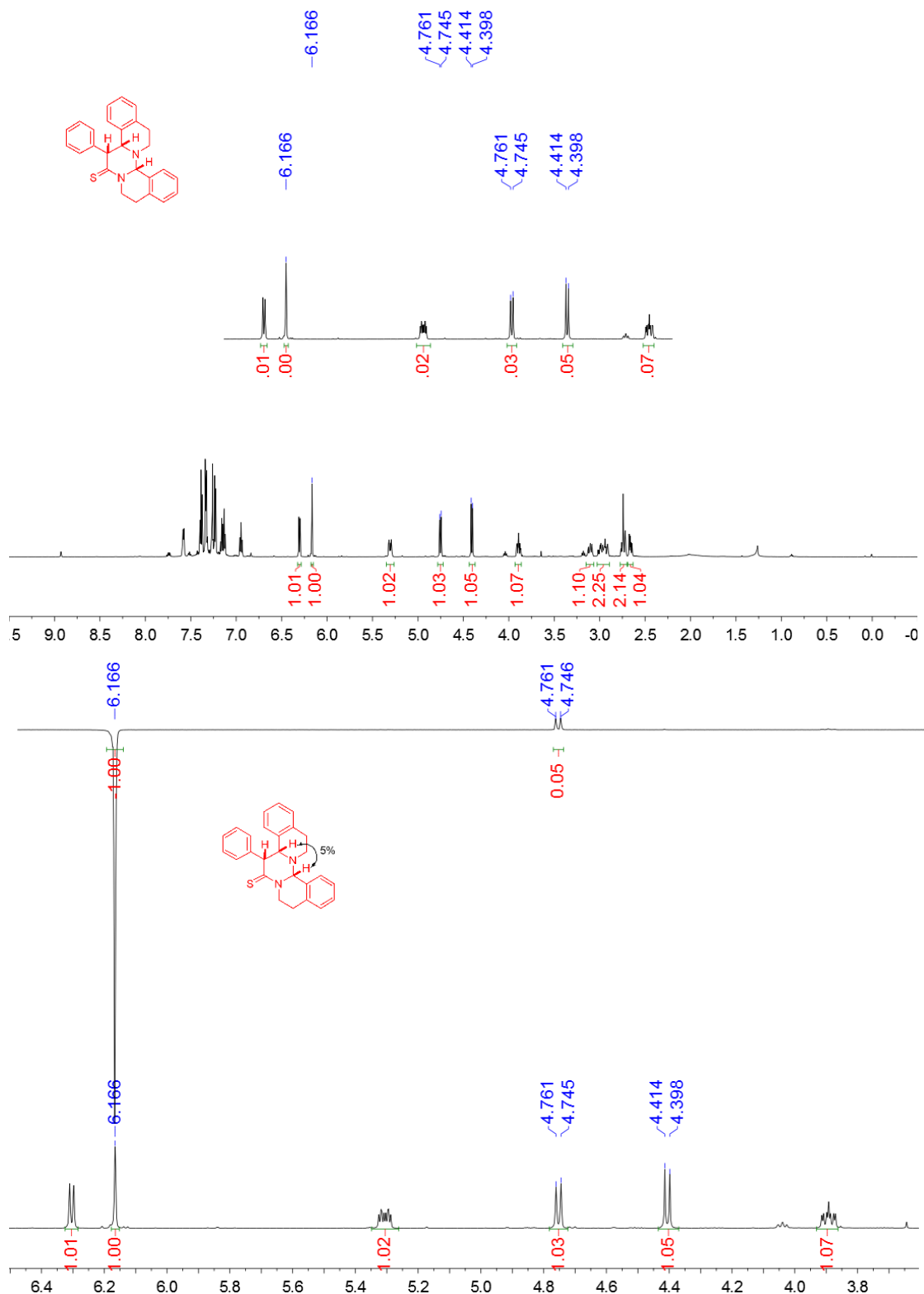
rel(4*bR*,5*S*,13*bS*)-5-(3-Methoxyphenyl)-4*b*,5,9,13*b*,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4*a*):



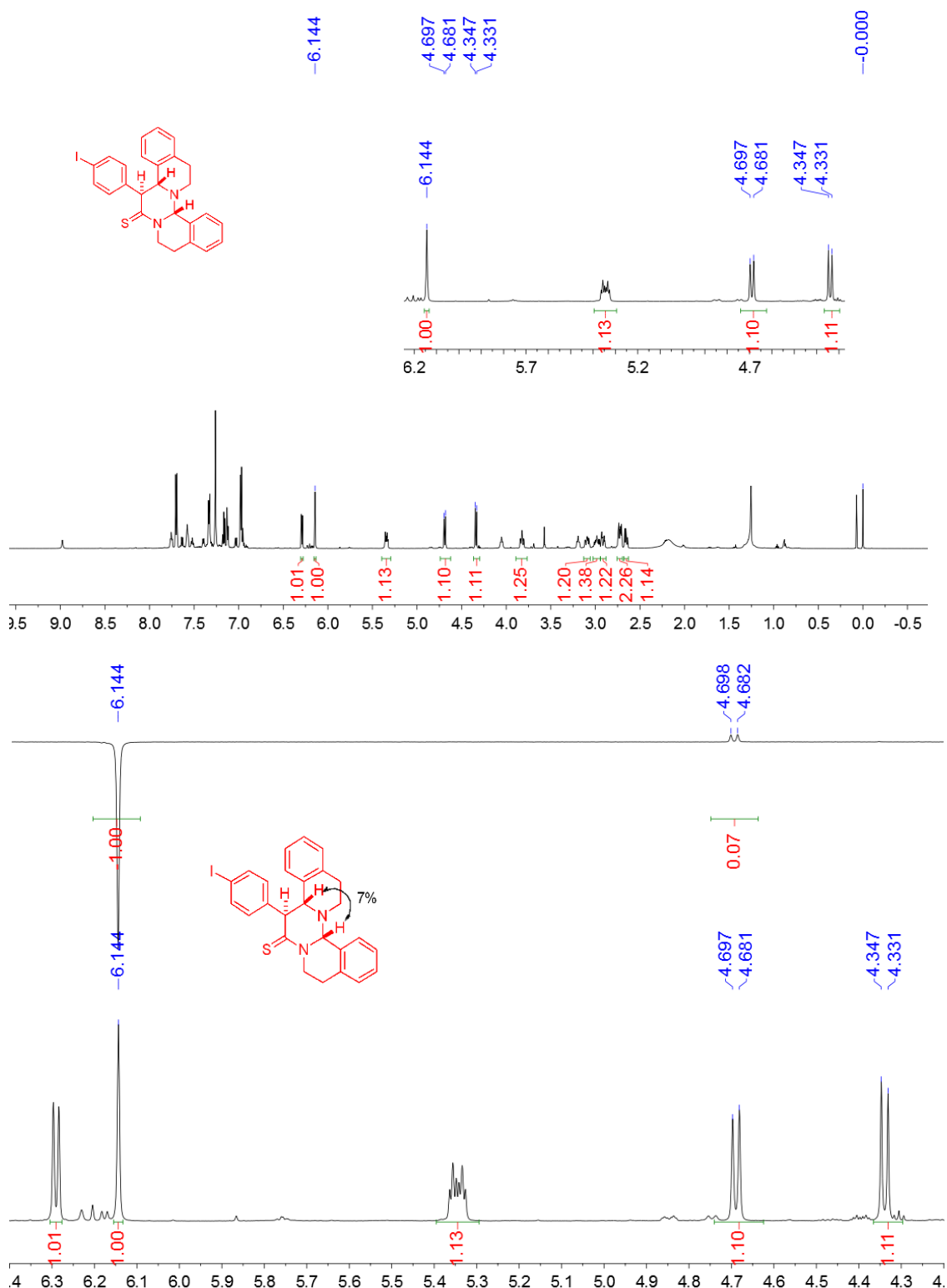
***rel*(4b*R*,5*S*,13b*S*)-5-(4-Methylphenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4b):**



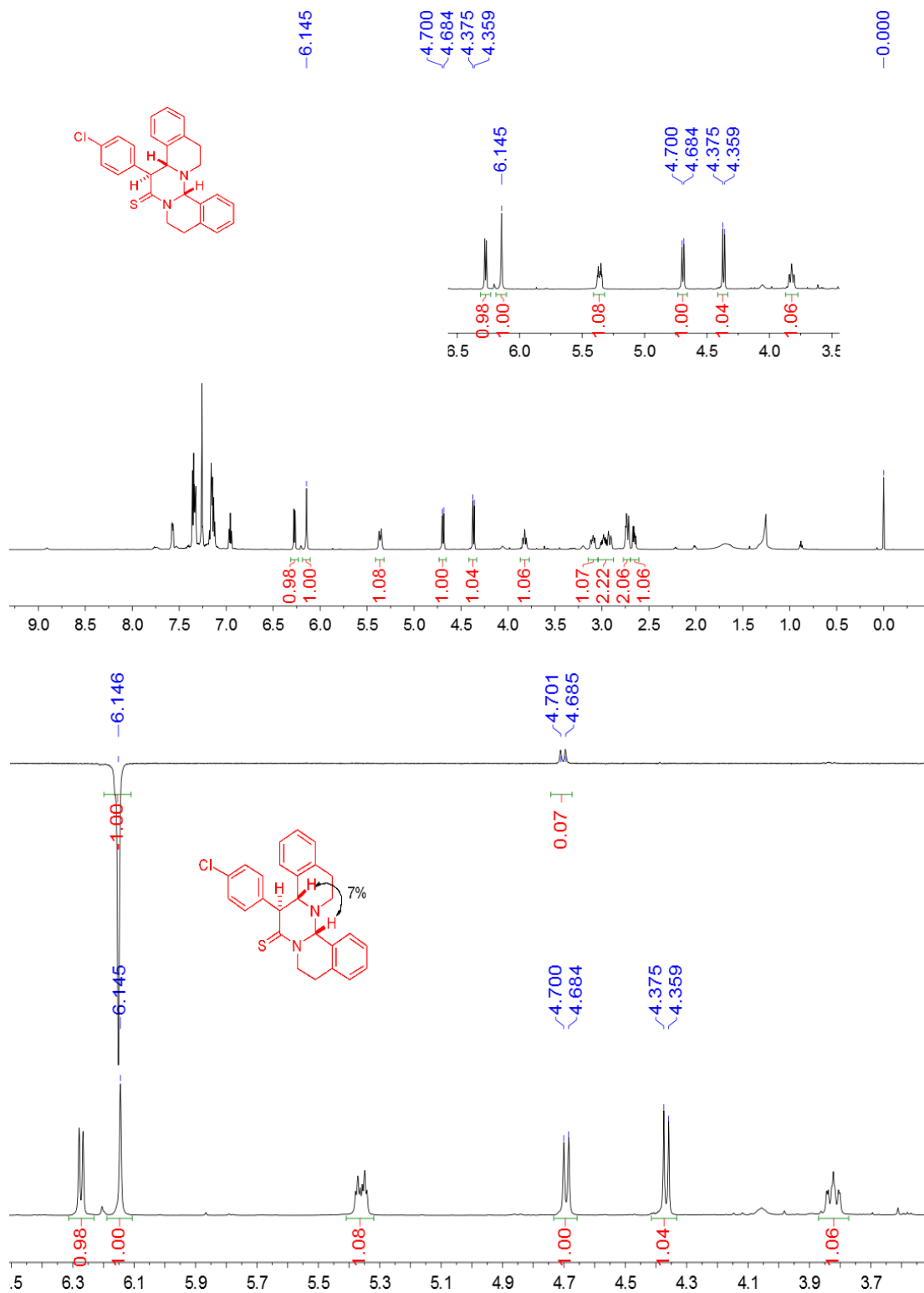
***rel*(4b*R*,5*S*,13b*S*)-5-Phenyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4c):**



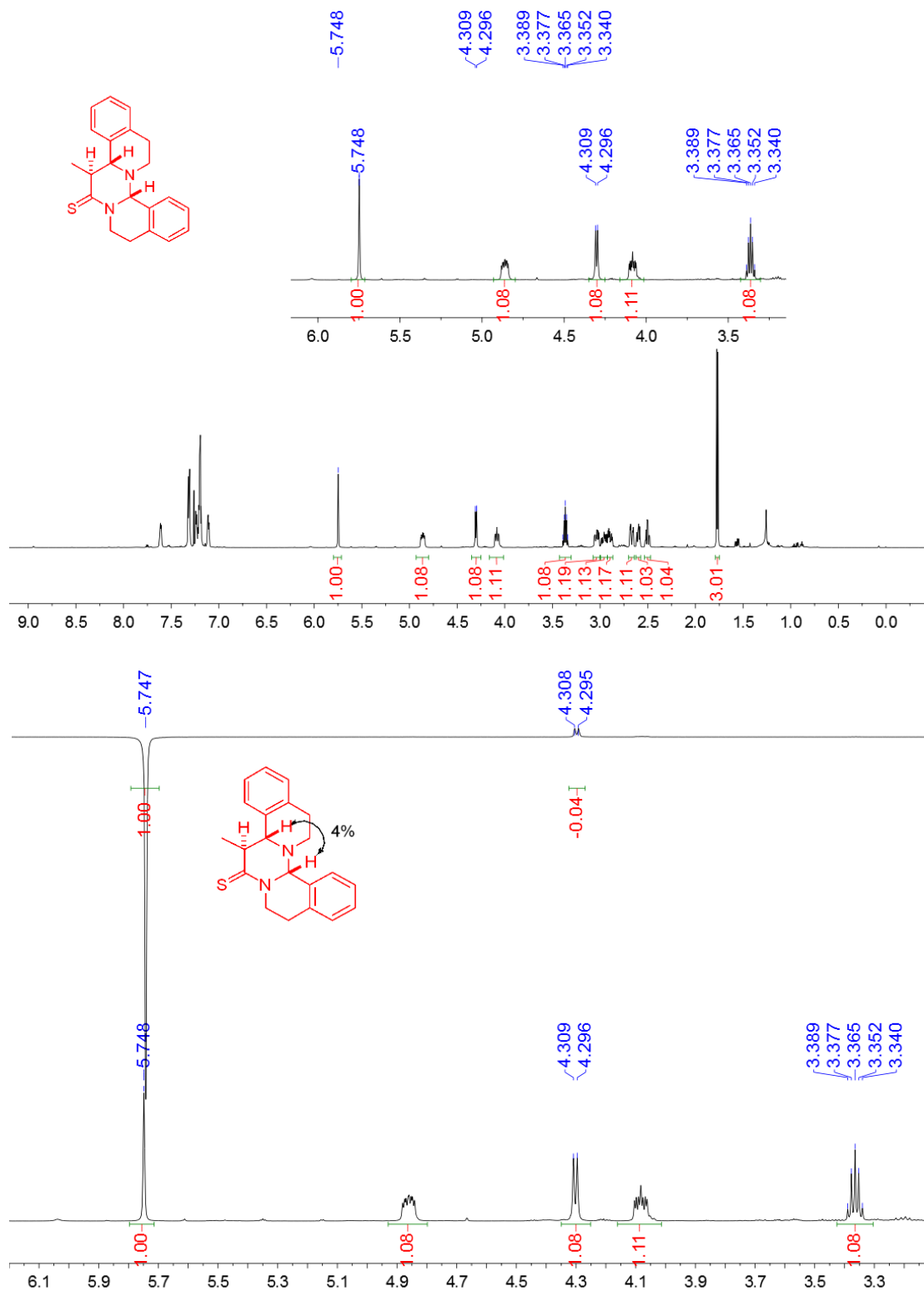
***rel*(4*bR*,5*S*,13*bS*)-5-(4-Iodophenyl)-4*b*,5,9,13*b*,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]
[diisoquinoline-6-thione (4*d*):**



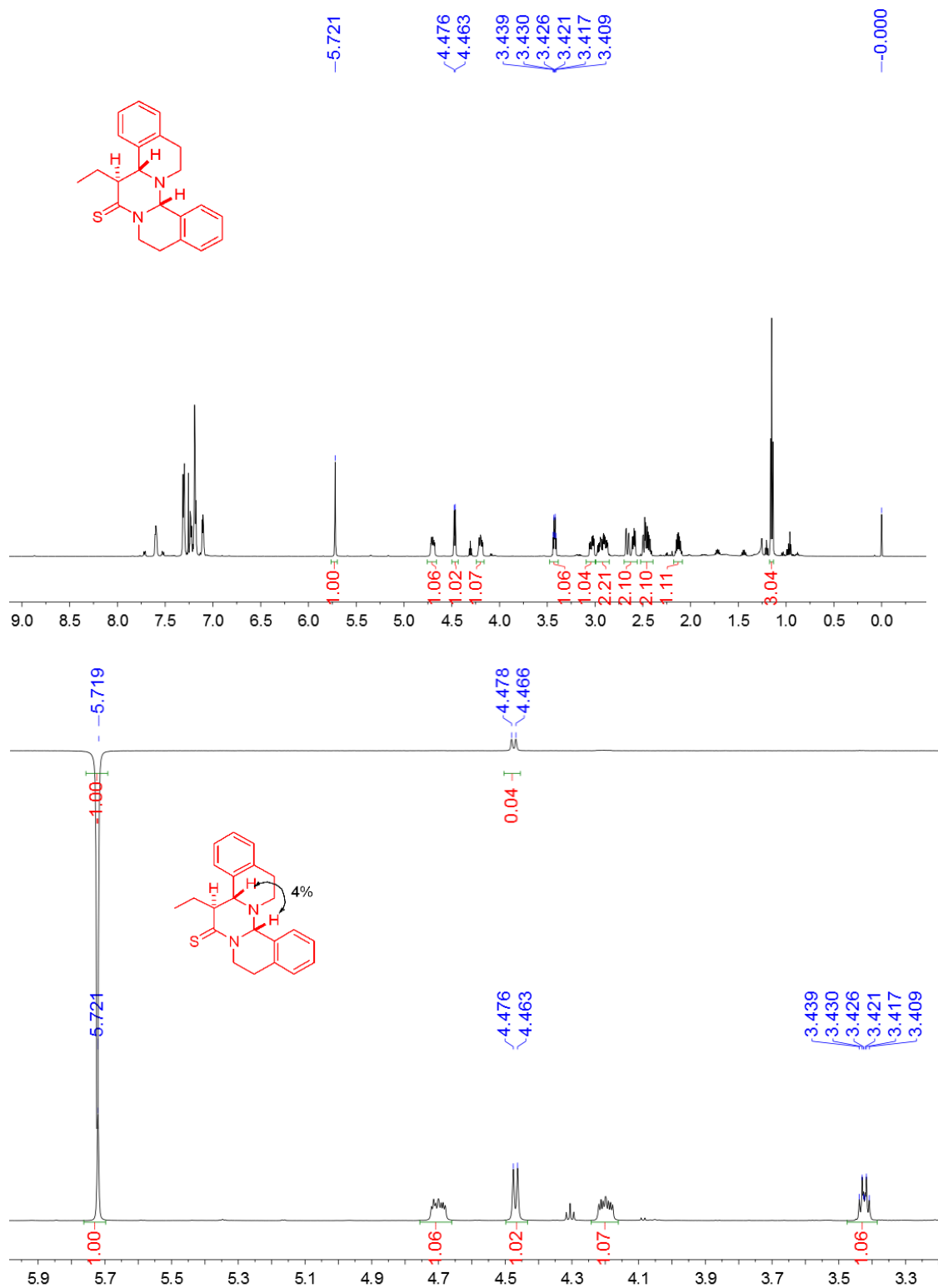
***rel*(4b*R*,5*S*,13b*S*)-5-(4-Chlorophenyl)-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4e):**



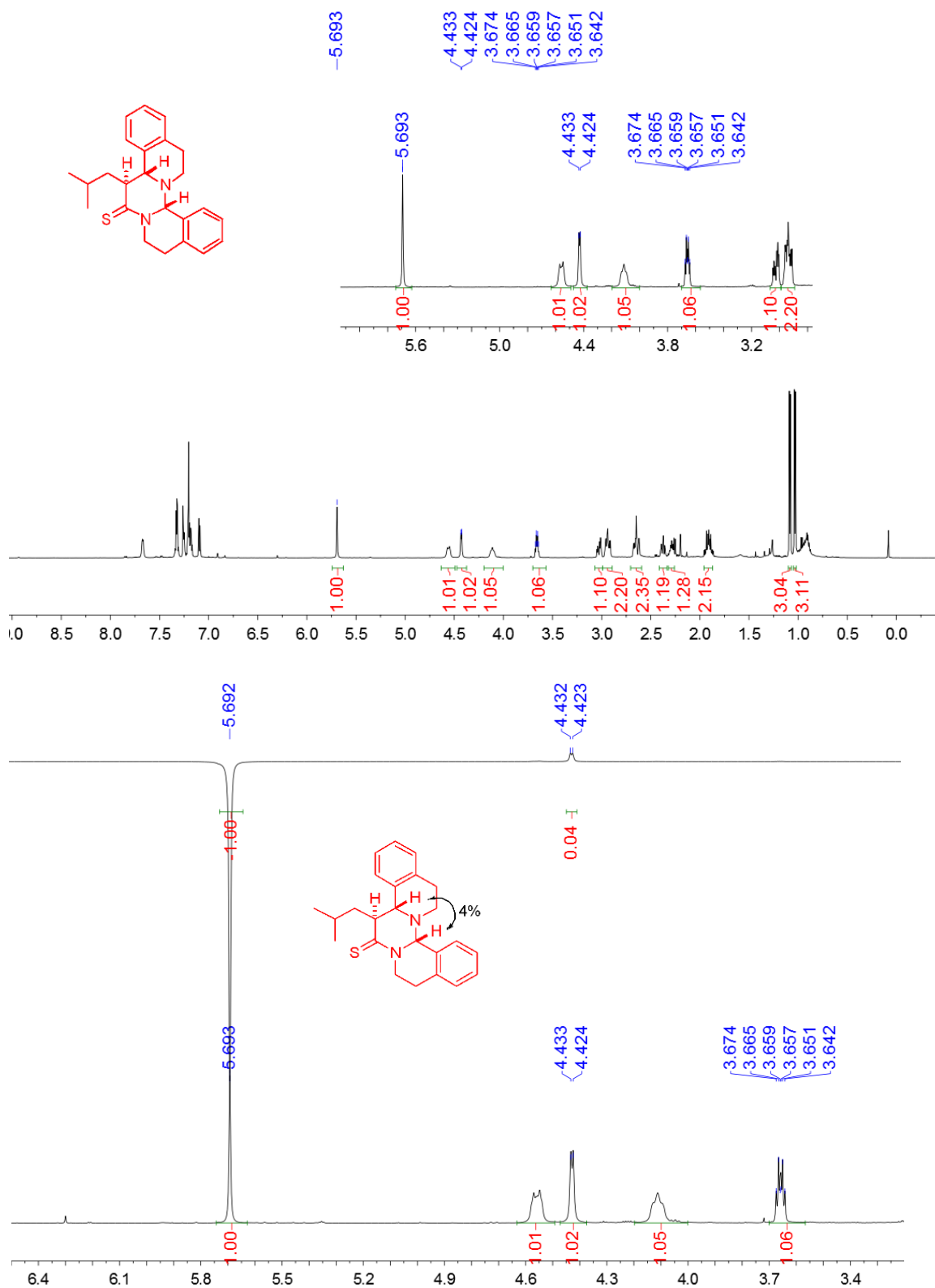
***rel*(4b*R*,5*S*,13b*S*)-5-Methyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4g):**



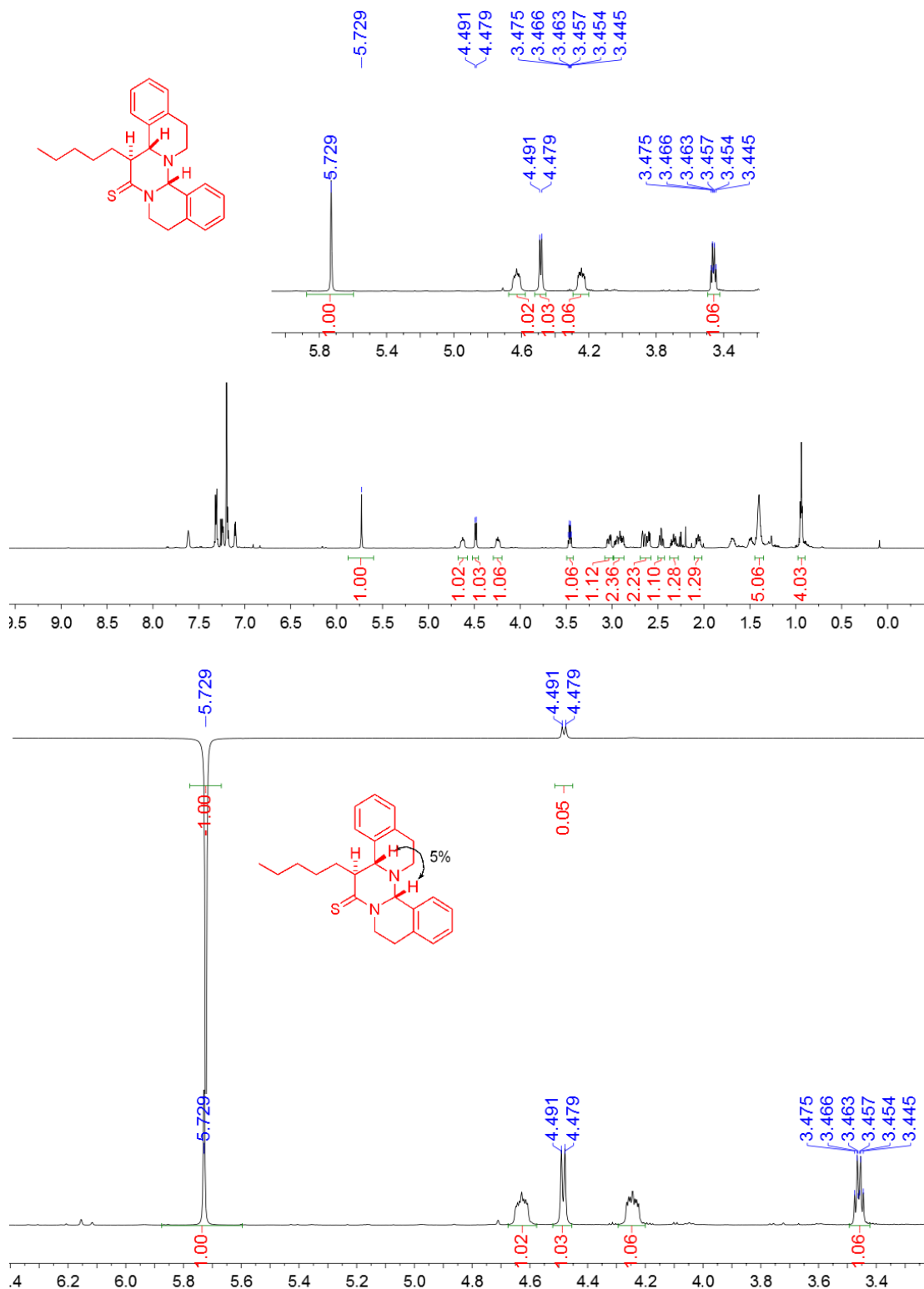
***rel*(4b*R*,5*S*,13b*S*)-5-Ethyl-4b,5,9,13b,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4h):**



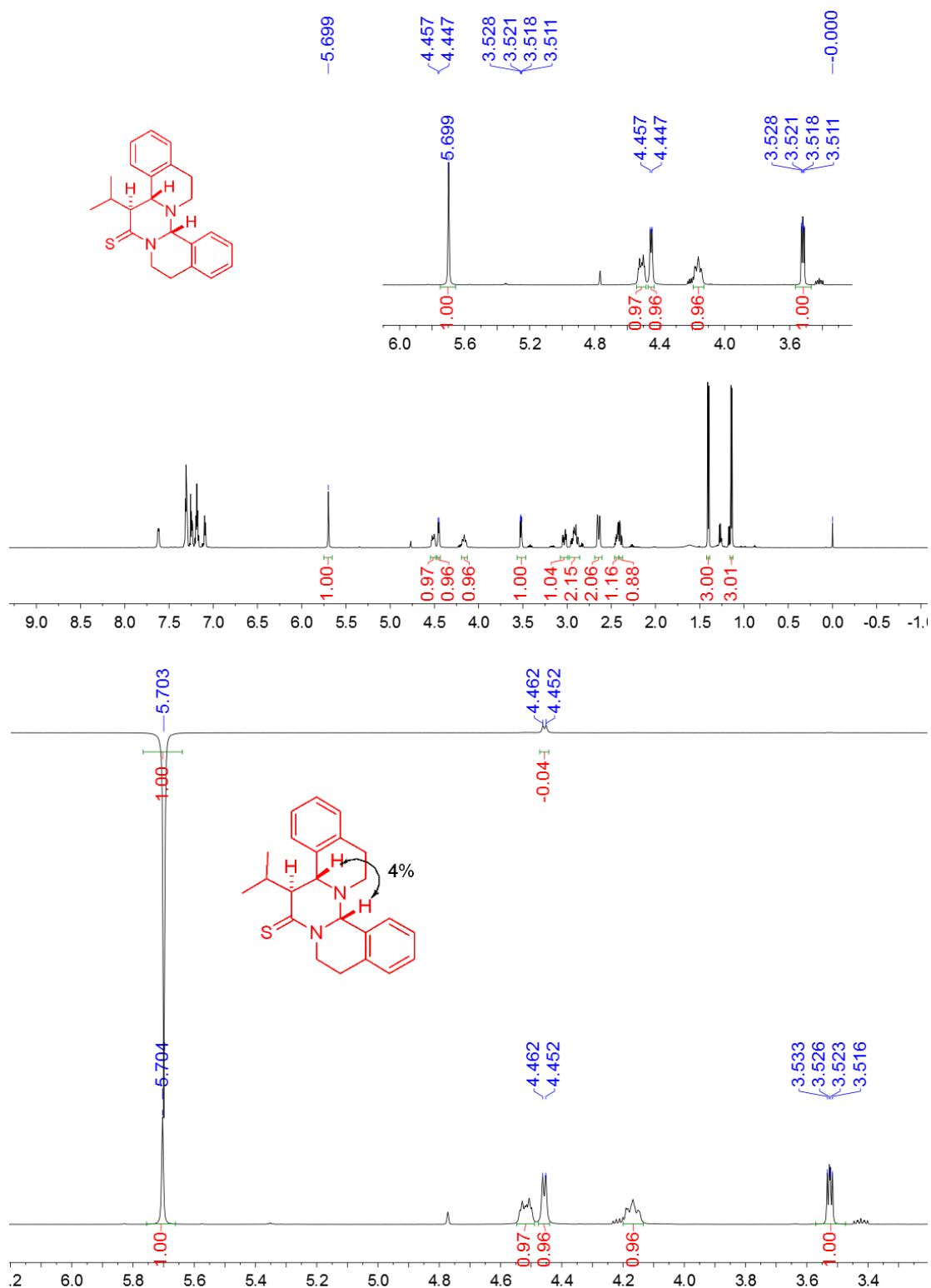
***rel*(4*bR*,5*S*13*bS*)-5-Isobutyl-4*b*,5,9,13*b*,15,16-hexahydro-6*H*,8*H*-pyrimido[2,1-*a*:4,3-*a'*]diisoquinoline-6-thione (4*i*):**



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



The figure displays two ^1H NMR spectra of compound **10**. The top spectrum is the full ^1H NMR (400 MHz, CDCl_3) showing peaks from 0 to 10 ppm. The bottom spectrum is an expanded view of the 3.4–5.8 ppm region. Both spectra include chemical shift labels, integration values, and the chemical structure of compound **10**.

Chemical structure of compound 10: O=C1N2C(=O)N(C1)Cc3ccccc3[C@H]2Cc4ccccc4

Top Spectrum (Full ^1H NMR):

- Chemical shift range: 0.0 to 10.0 ppm.
- Integration values (red): 0.98, 3.01, 1.03, 2.03, 0.98, 1.00, 1.01, 1.01, 1.00, 0.99, 1.02, 2.03, 2.03, 1.00, 6.29, 1.02, 4.37.
- Chemical shift labels (blue): 5.709, 4.493, 4.483, 3.511, 3.505, 3.501, 3.495.

Bottom Spectrum (Expanded View):

- Chemical shift range: 3.3 to 6.1 ppm.
- Integration values (red): 1.00, 1.01, 1.01, 1.00, 0.99.
- Chemical shift labels (blue): 5.709, 4.493, 4.483, 3.511, 3.505, 3.501, 3.495.

Ethyl

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

