

## Electronic Supporting Information

# **Sterically controlled diastereoselectivity in thio-Staudinger cycloadditions of alkyl/alkenyl/aryl-substituted thioketenes**

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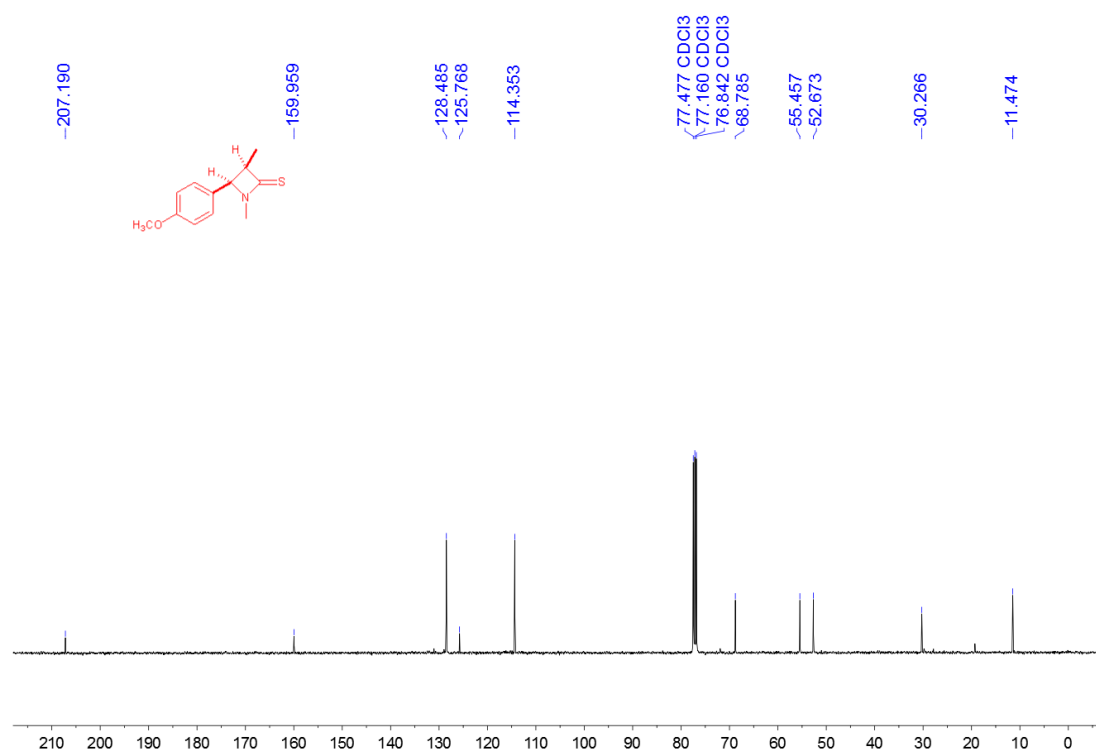
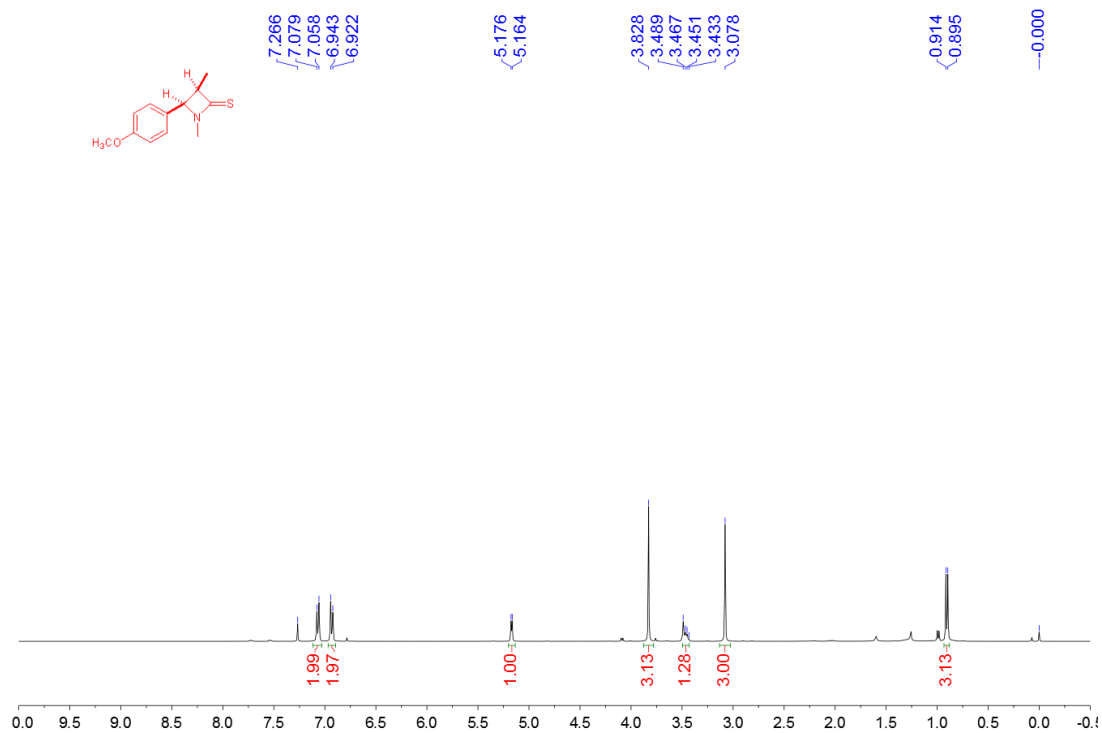
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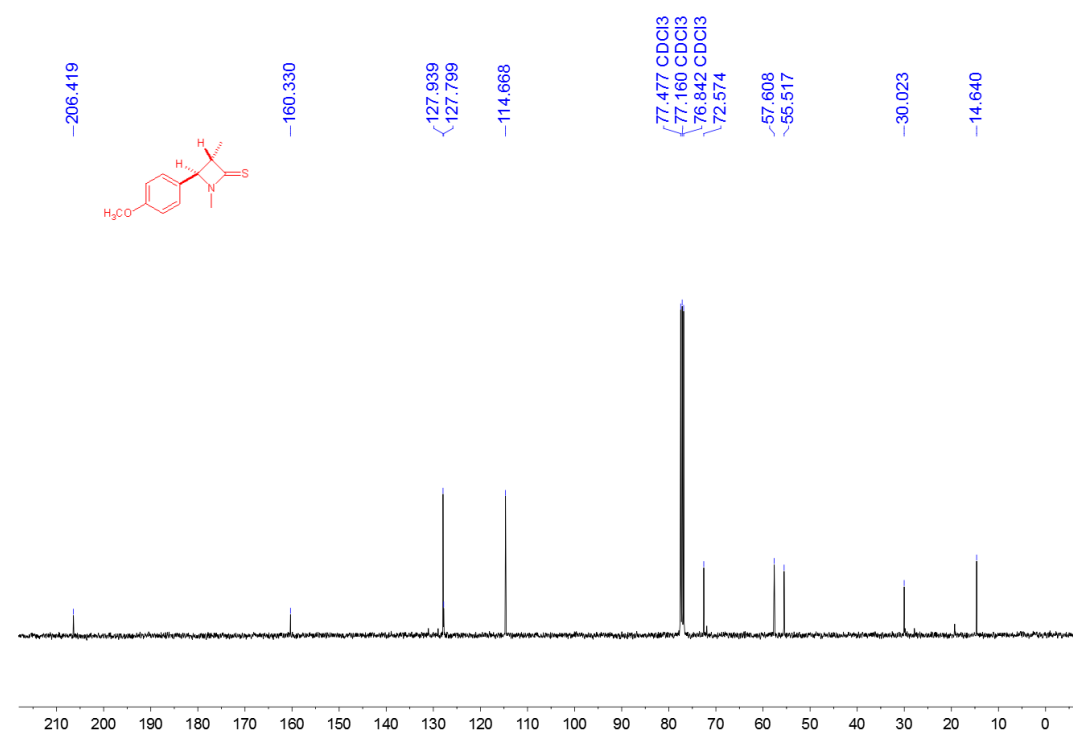
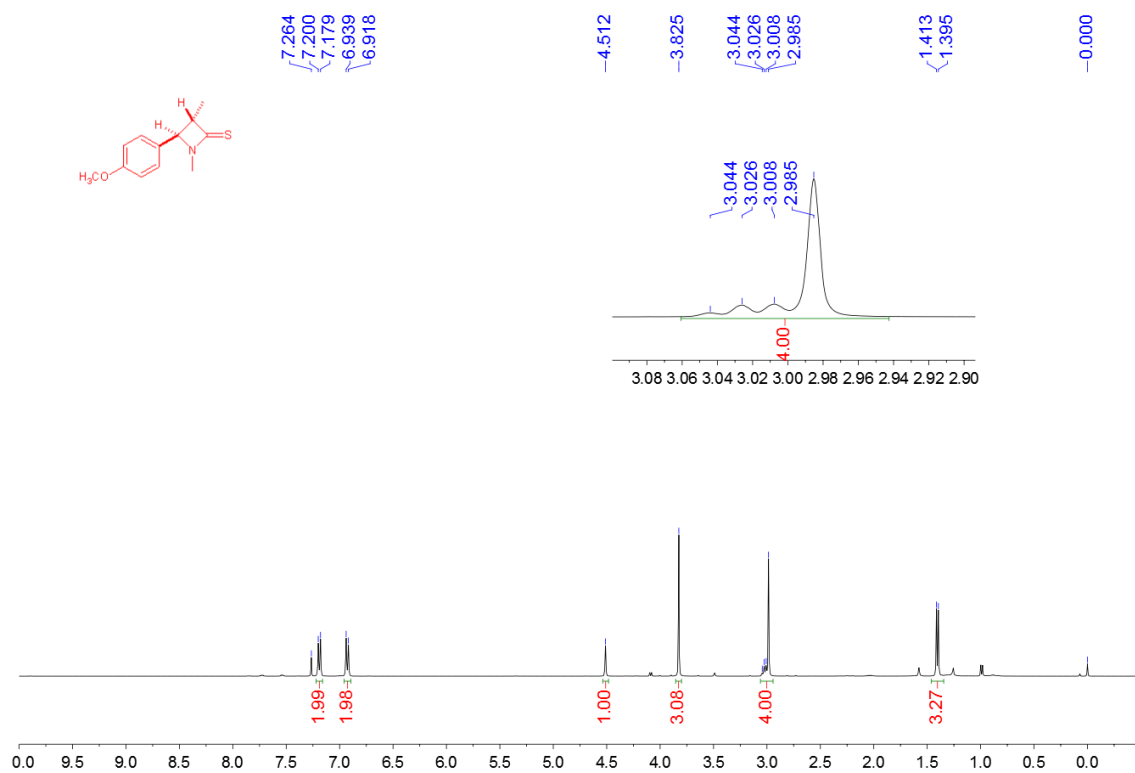
1. Copies of <sup>1</sup> H and <sup>13</sup> C NMR Spectra of β-thiolactams.....	S2
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# 1. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of $\beta$ -thiolactams.

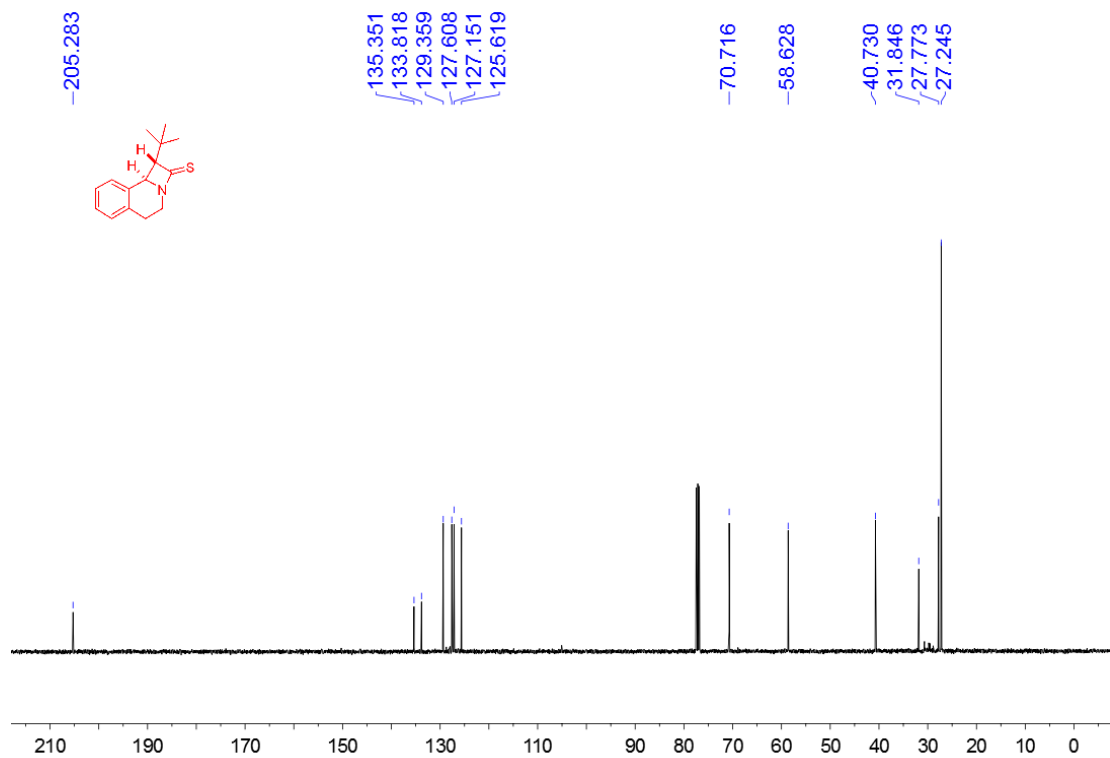
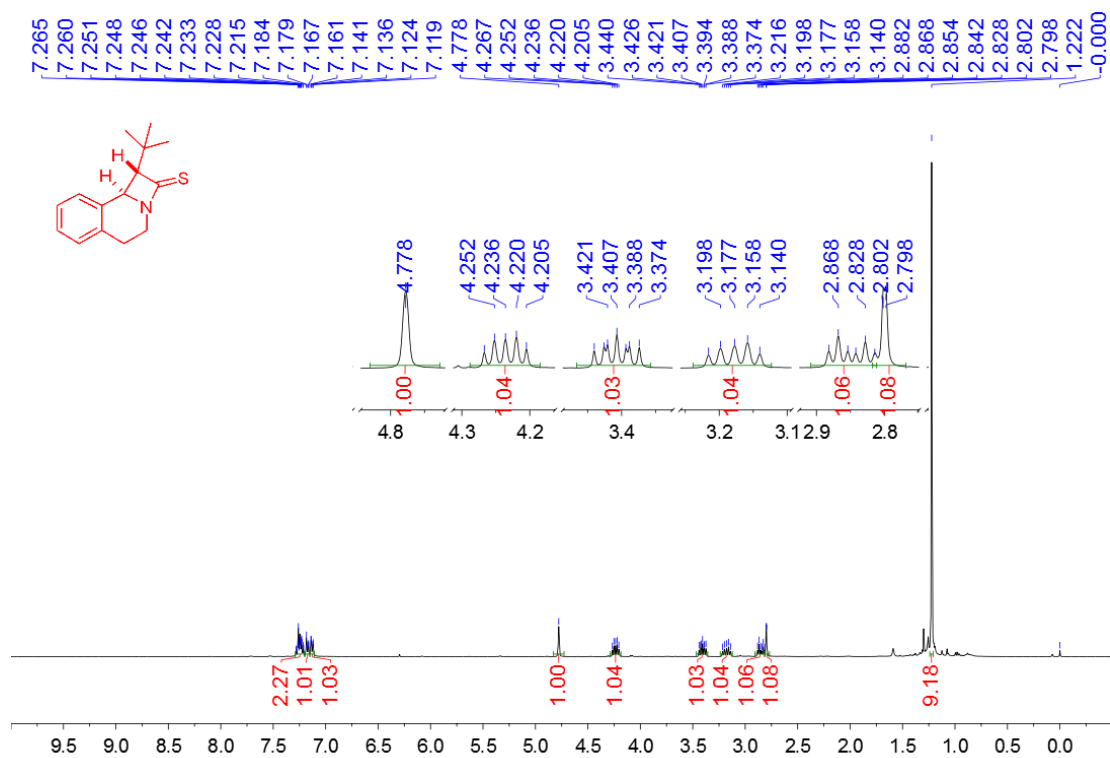
## *cis*-4-(4-Methoxyphenyl)-1,3-dimethylazetidine-2-thione (3I)

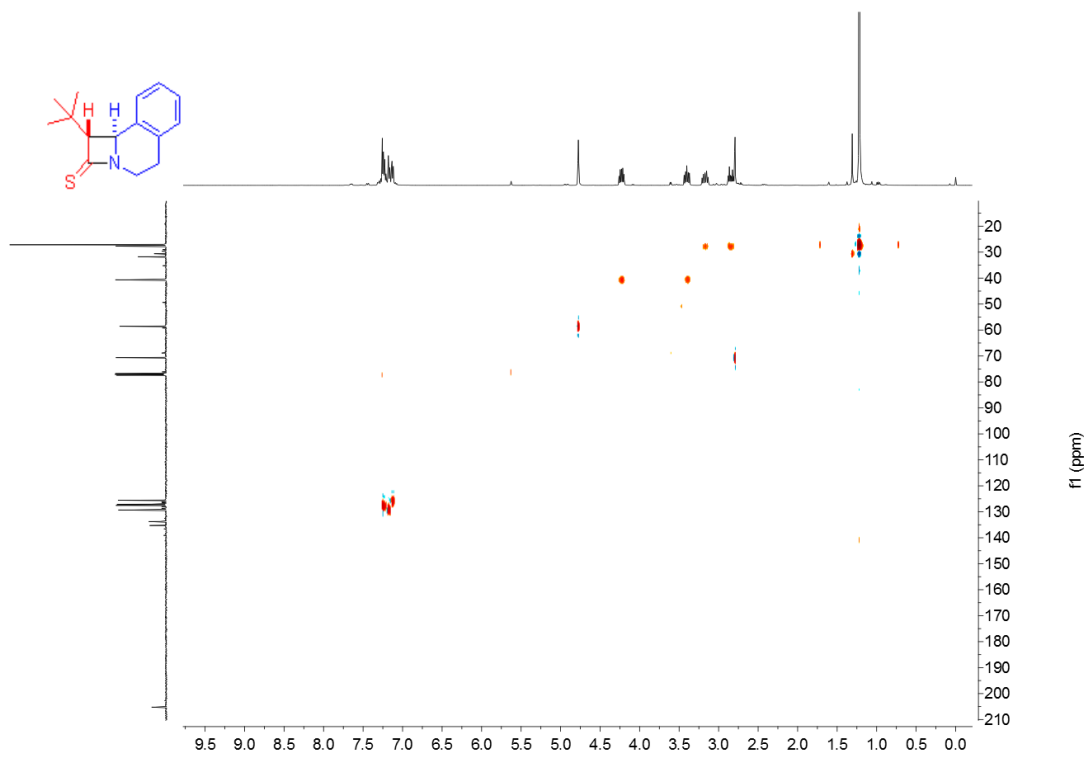


***trans*-4-(4-Methoxyphenyl)-1,3-dimethylazetidine-2-thione (4I)**

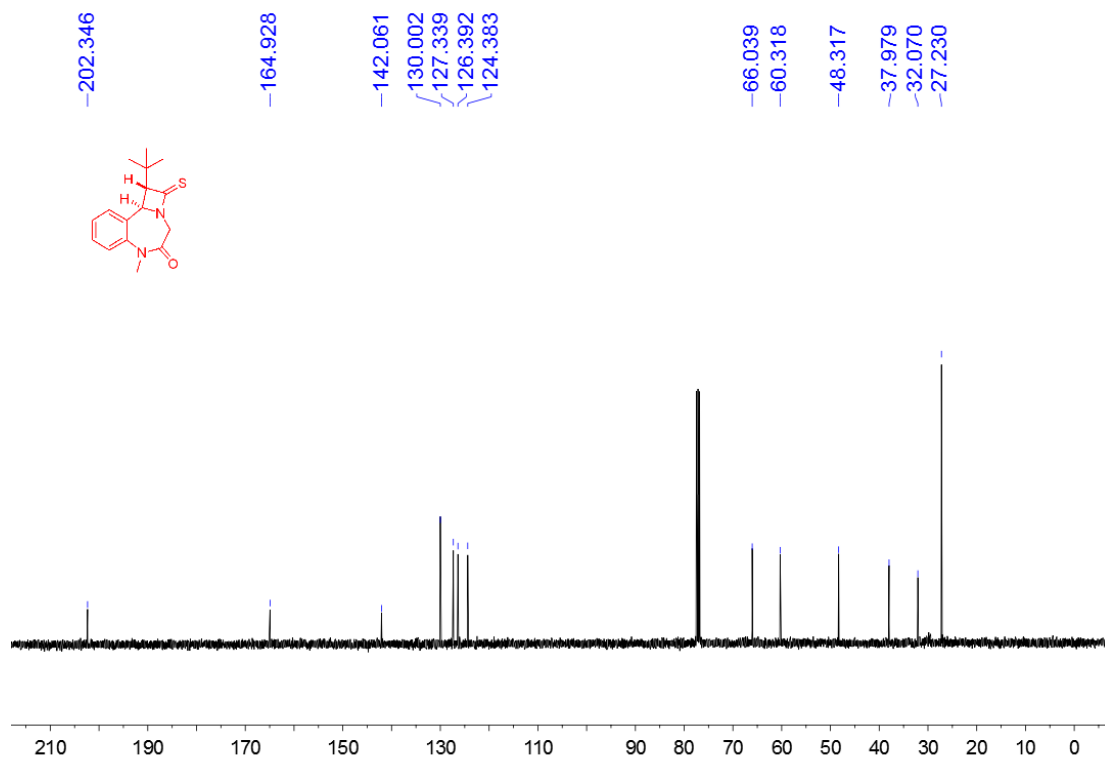
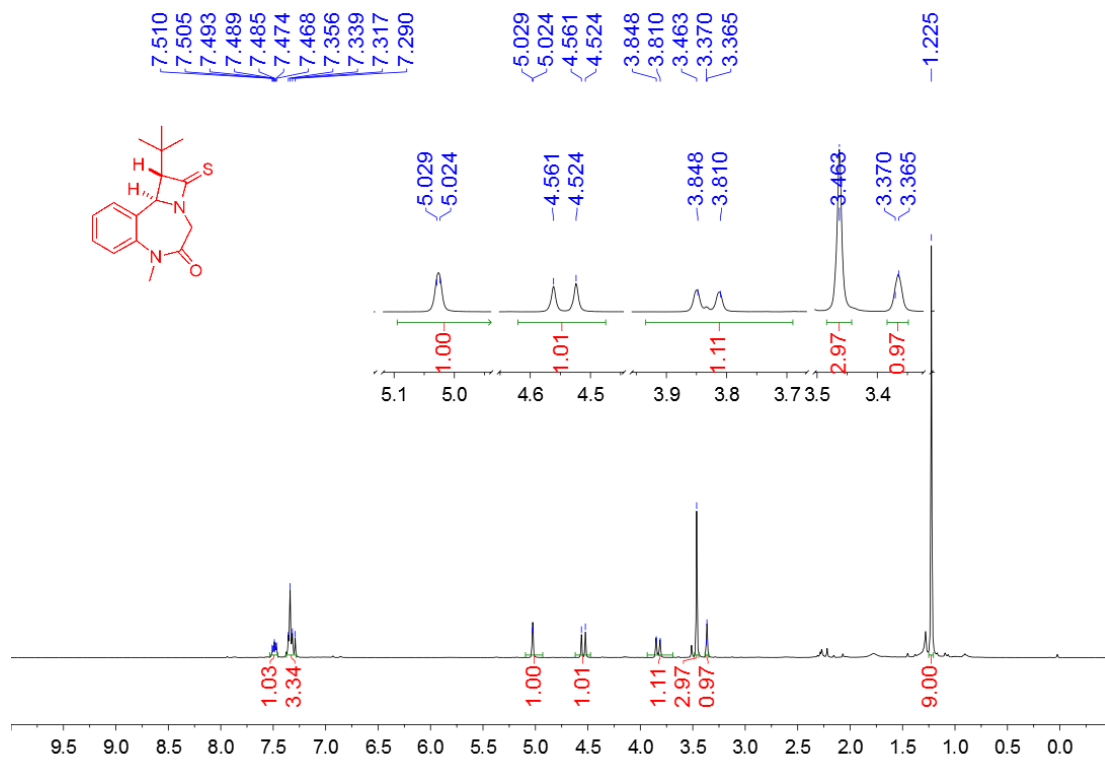


*rel*(1*S*,9*bR*)-1-(*tert*-Butyl)-1,4,5,9*b*-tetrahydro-2*H*-azeto[2,1-*a*]isoquinoline-2-thione (7k)



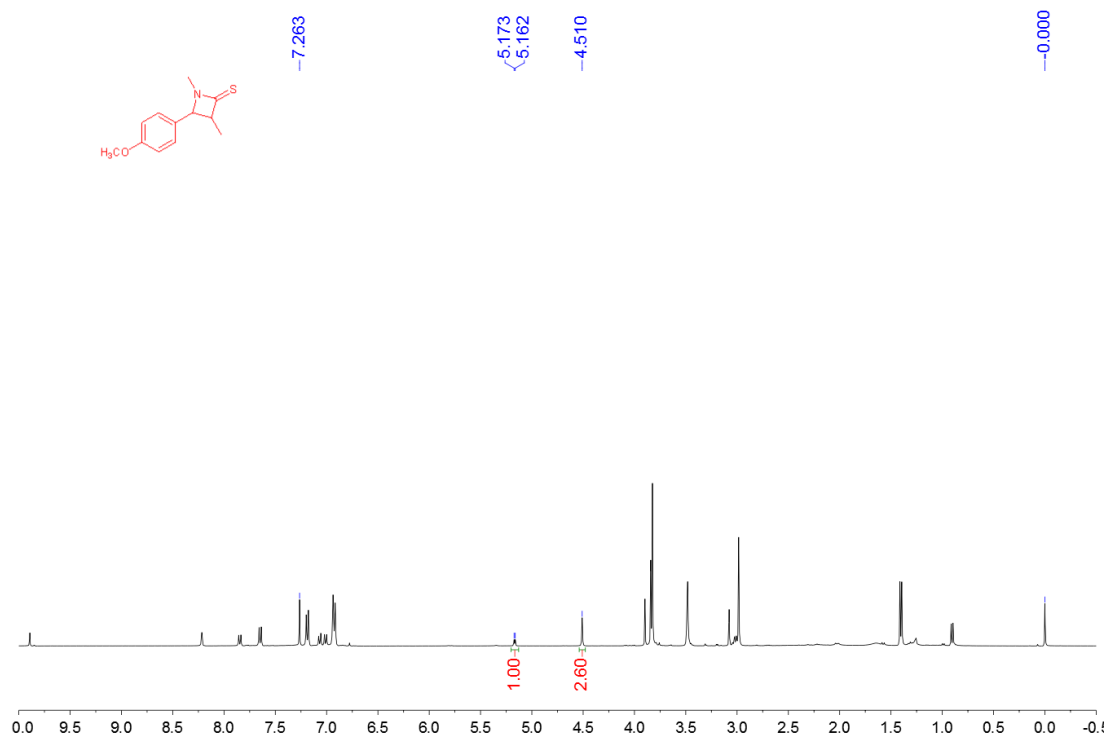


***rel*(1*S*,10*bR*)-1-(*tert*-Butyl)-6-methyl-2-thioxo-1,2,6,10*b*-tetrahydroazeto[1,2-*d*]benzo[*f*][1,4]diazepin-5(4*H*)-one (10)**



## 2. Copies of $^1\text{H}$ NMR of reaction mixtures.

$^1\text{H}$  NMR of crude reaction mixture for the reaction of **2a** and **9b**. [*trans/cis* = 76:24]



$^1\text{H}$  NMR of crude epimerization mixture for **3l**. [*trans/cis* = 52:48]

