

## Electronic Supplementary Information

### **Annuloselectivity and stereochemistry in the sulfa-Staudinger cycloadditions of cyclic imines**

**Zhanhui Yang, and Jiayi Xu\***

State Key Laboratory of Chemical Resource Engineering,  
Department of Organic Chemistry, Faculty of Science,  
Beijing University of Chemical Technology,  
Beijing 100029, People's Republic of China.

Fax: +0-8610-6443-5565.

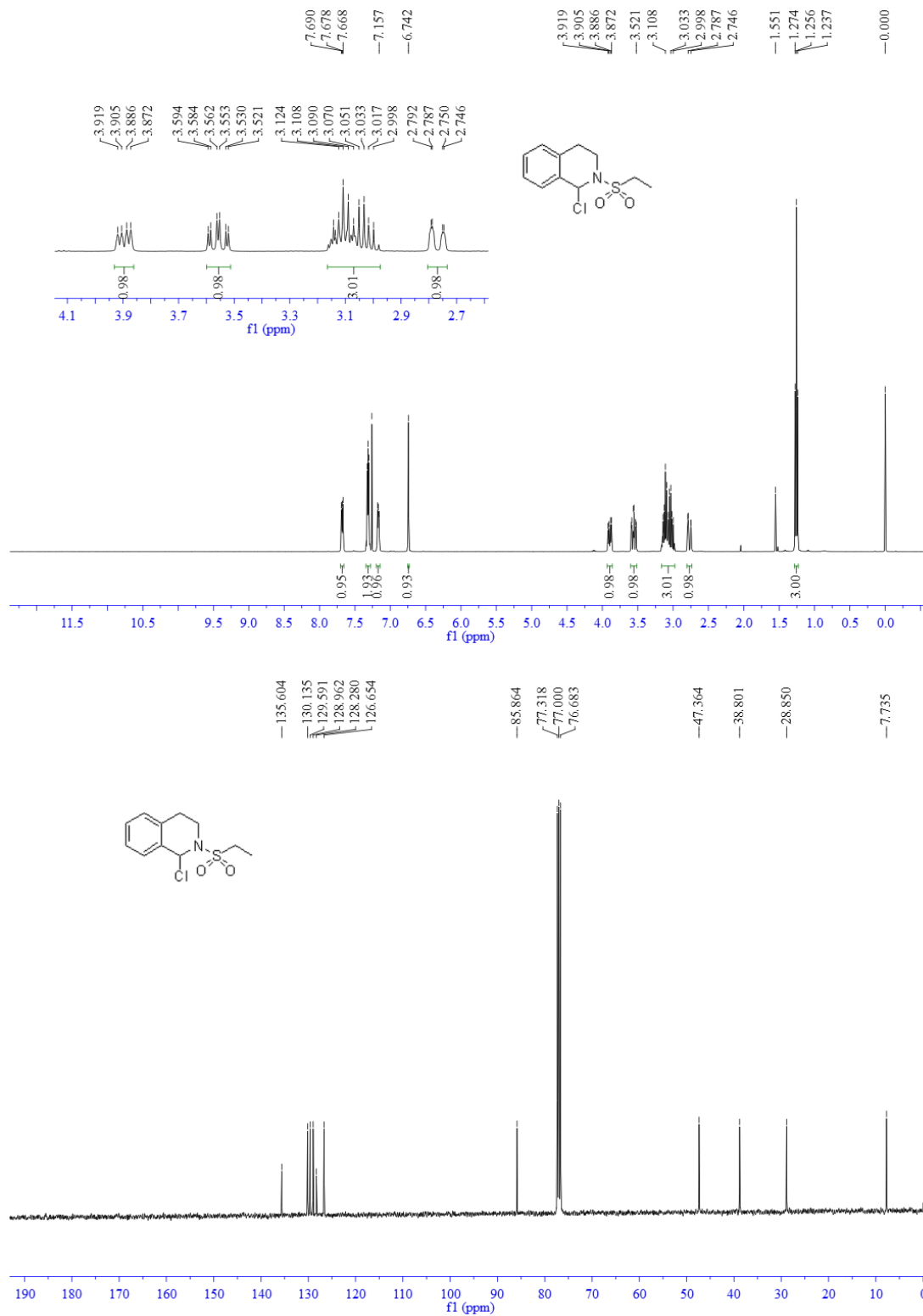
E-mail: [jxxu@mail.buct.edu.cn](mailto:jxxu@mail.buct.edu.cn).

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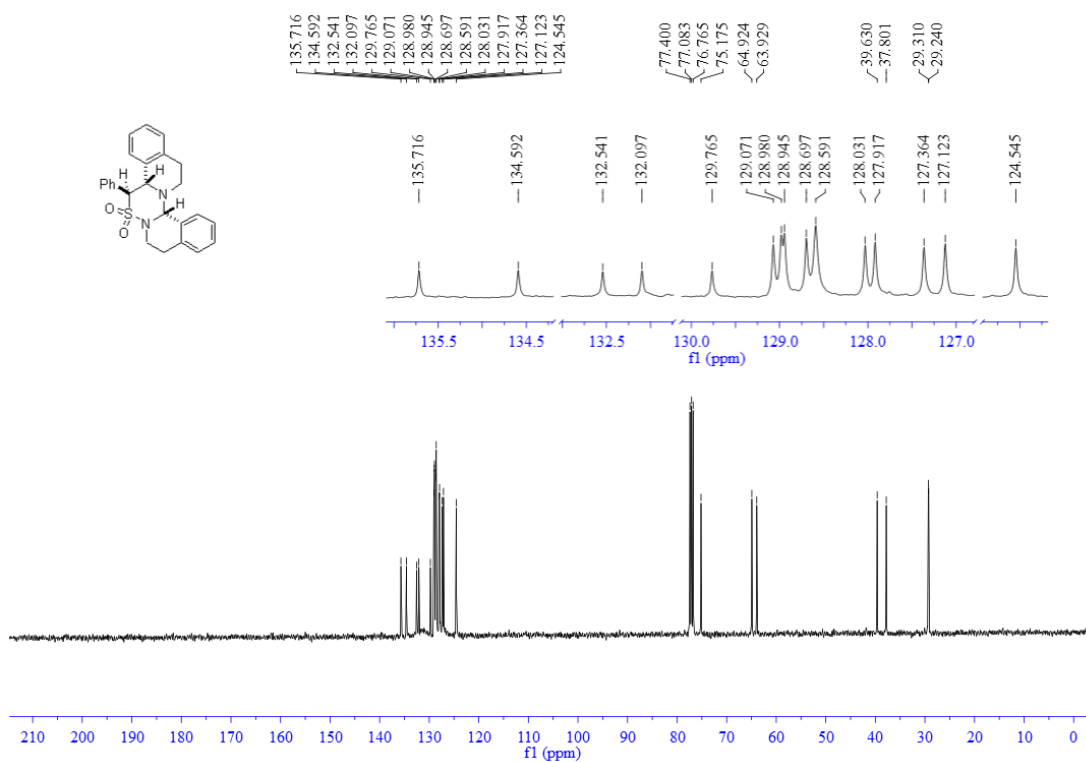
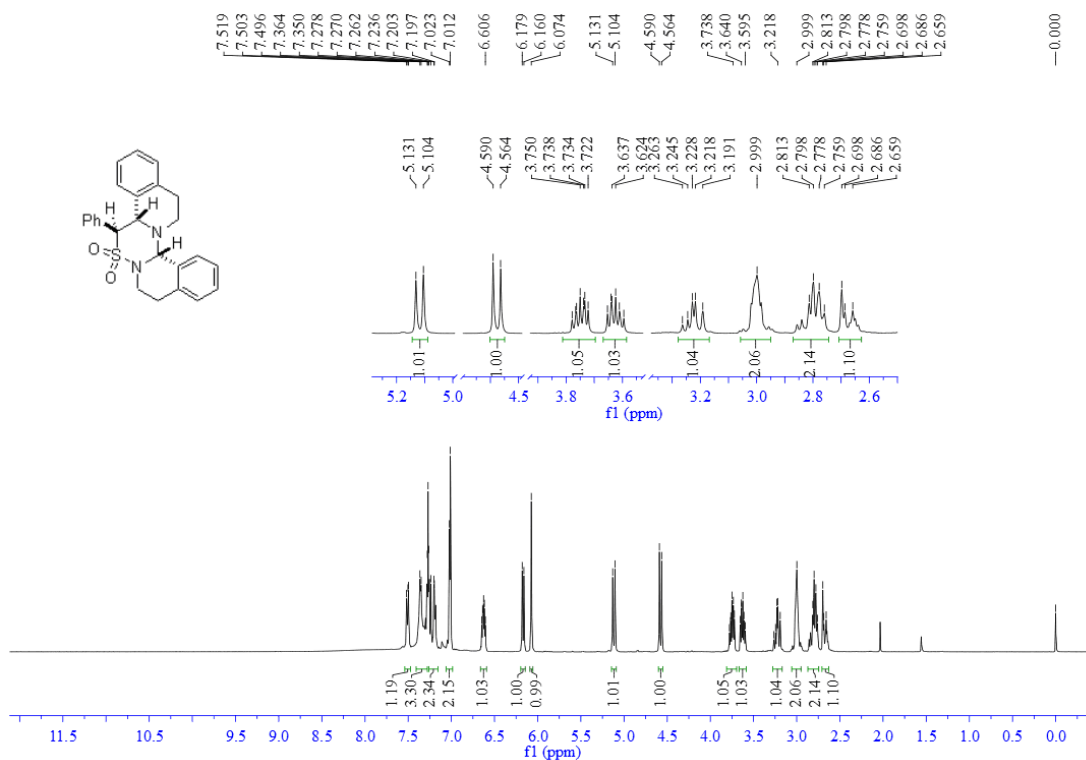
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# 1. Copies of $^1\text{H}$ and $^{13}\text{C}$ spectra of products

## 1-Chloro-2-(ethylsulfonyl)-1,2,3,4-tetrahydroisoquinoline (7)



***rel*(4*R*,5*R*,13*bR*)-5-Phenyl-4*b*,5,9,13*b*,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*]dii  
soquinoline 6,6-dioxide (8)**

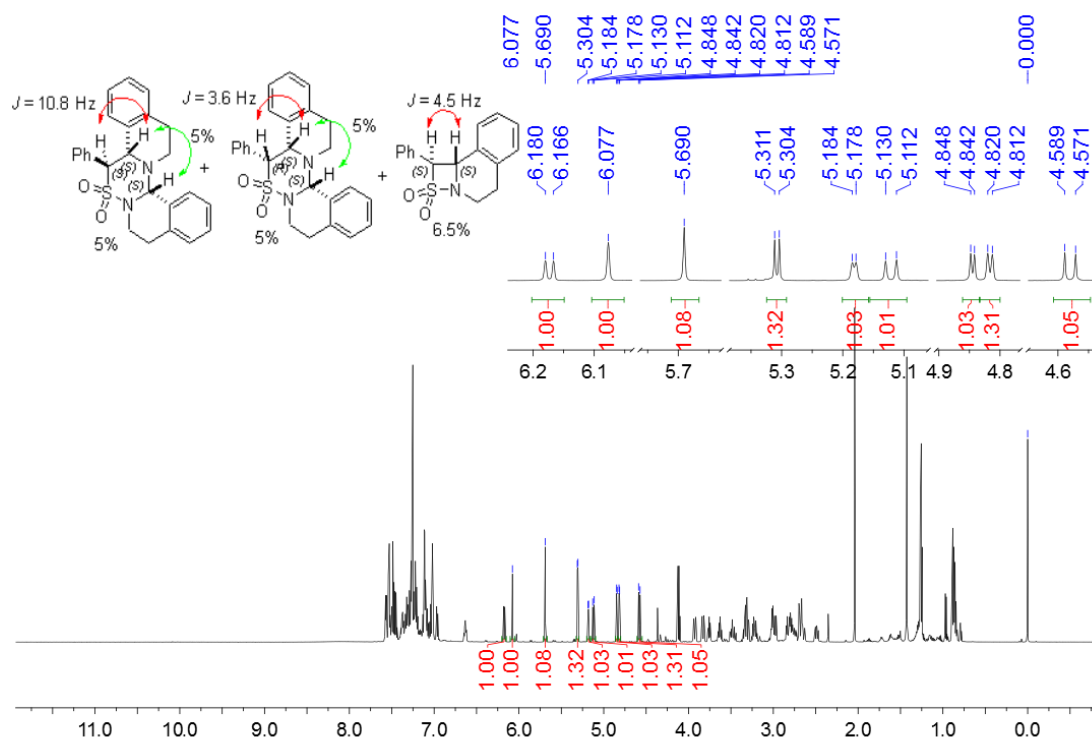


***rel(4bR,5S,13bR)*-5-Phenyl-4b,5,9,13b,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*]diiisoquinoline 6,6-dioxide (9)**

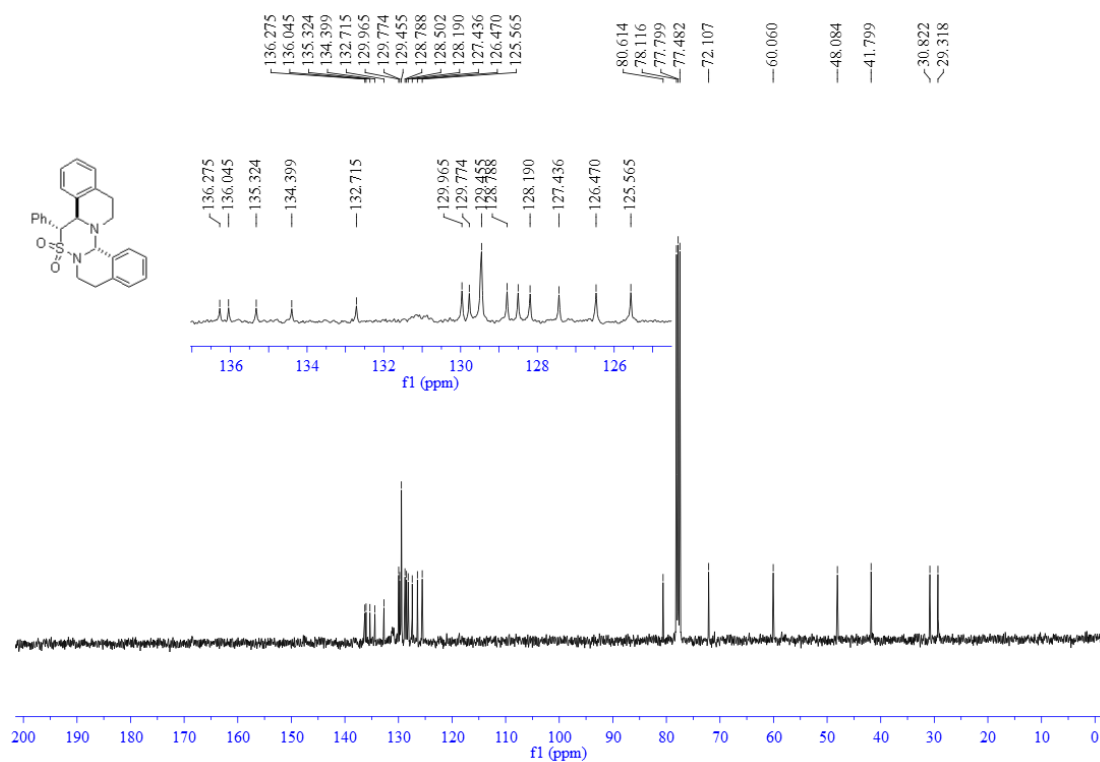
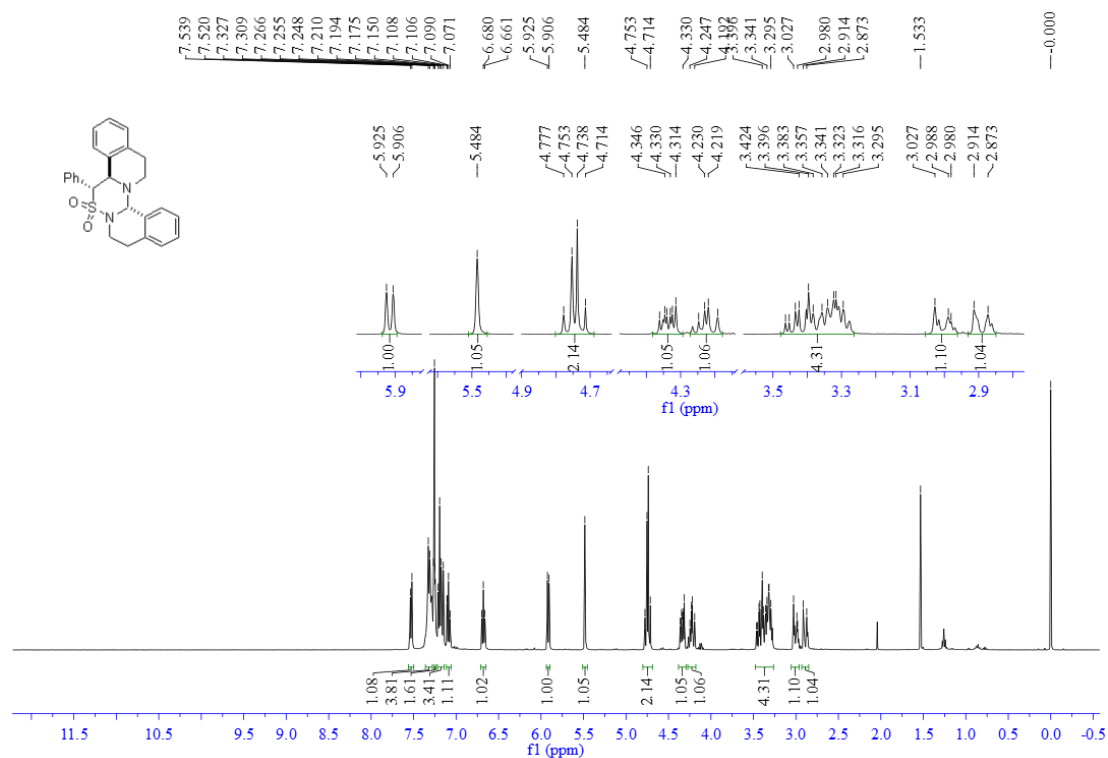
White solid (5% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.69 (s, 1H in NCHN), 5.18 (d, *J* = 3.6 Hz, 1H in CHN), 4.84 (d, *J* = 3.6 Hz, 1H in CHS).

***rel(1S,9bS)*-1-Phenyl-1,4,5,9b-tetrahydro[1,2]thiazeto[3,2-*a*]isoquinoline 2,2-dioxide (11)**

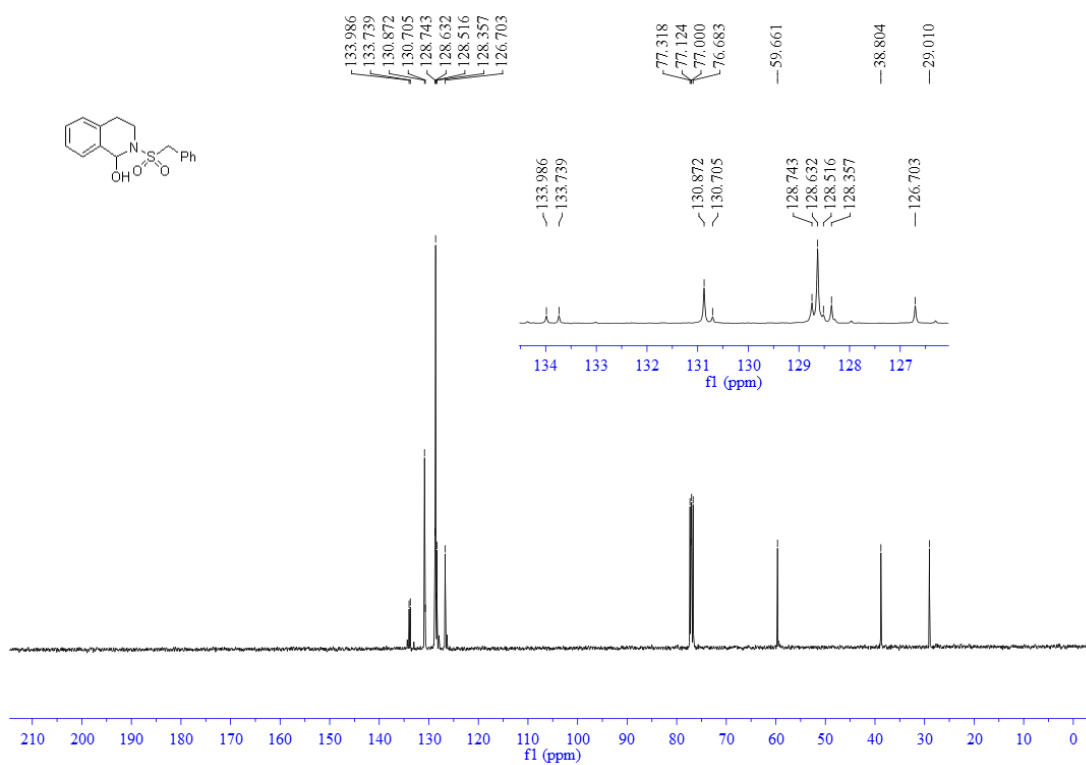
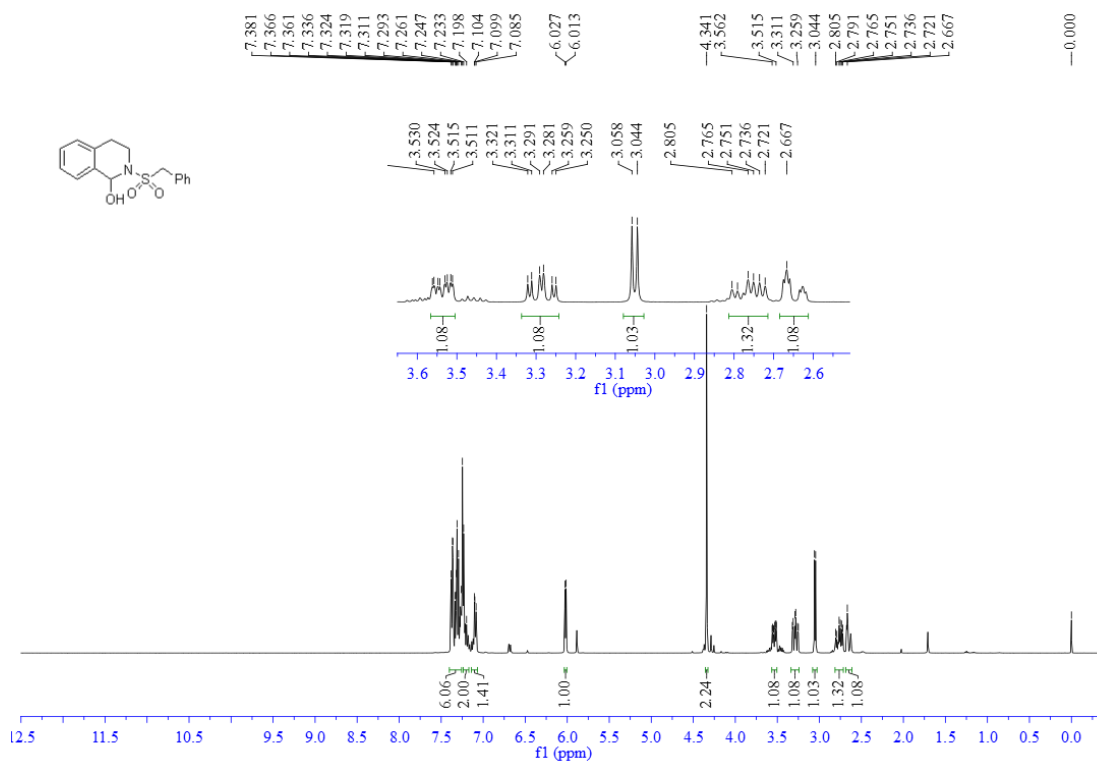
White solid (6.5% yield). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 5.31 (d, *J* = 4.5 Hz, 1H in CHN), 4.82 (d, *J* = 4.5 Hz, 1H in CHS). HRMS (ESI) calcd for C<sub>16</sub>H<sub>16</sub>NO<sub>2</sub>S (M + H<sup>+</sup>) *m/z* 286.0896, found 286.0893.



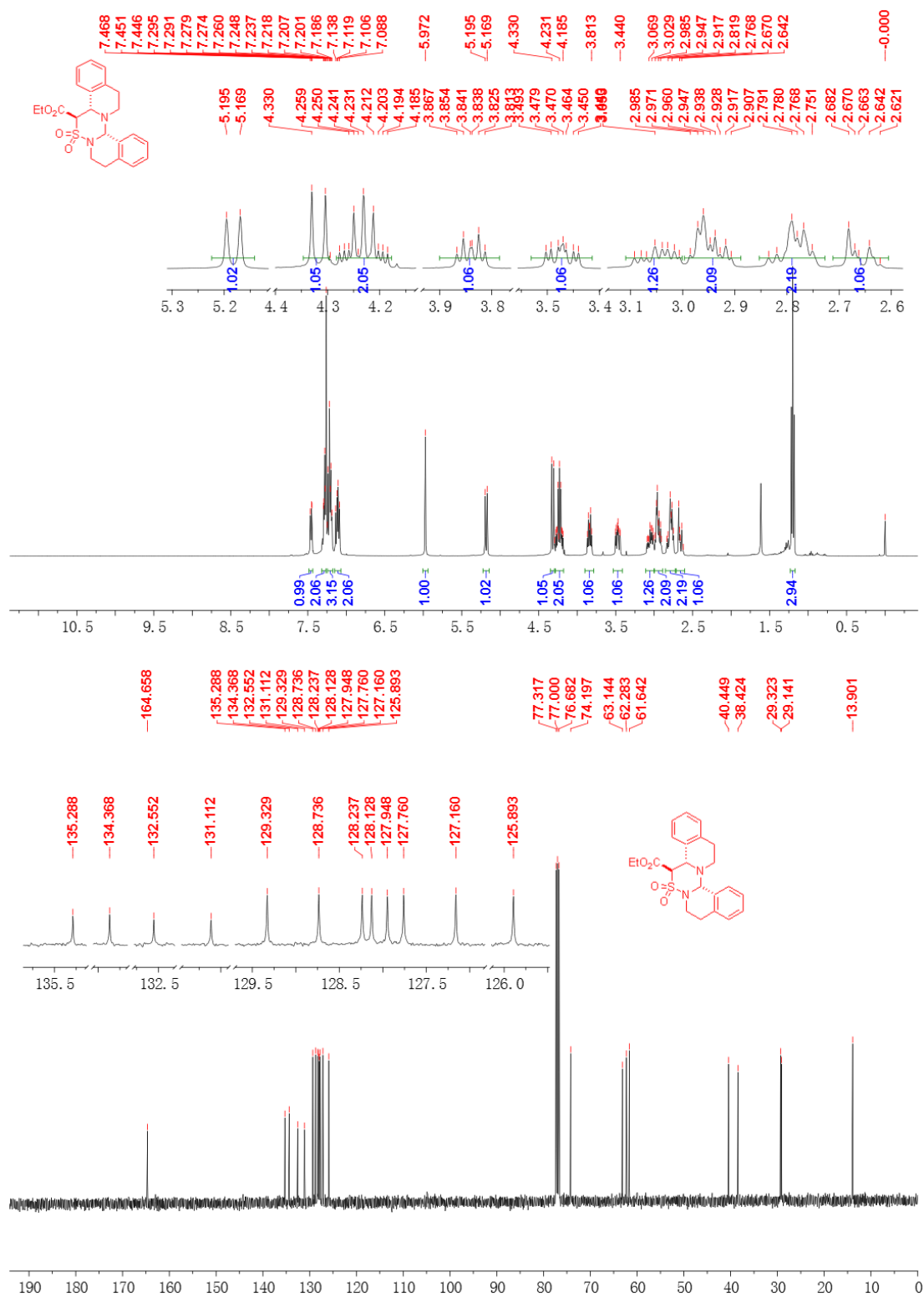
*rel*(4*bR*,5*R*,13*bS*)-5-Phenyl-4*b*,5,9,13*b*,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*]  
 diisoquinoline 6,6-dioxide (10)



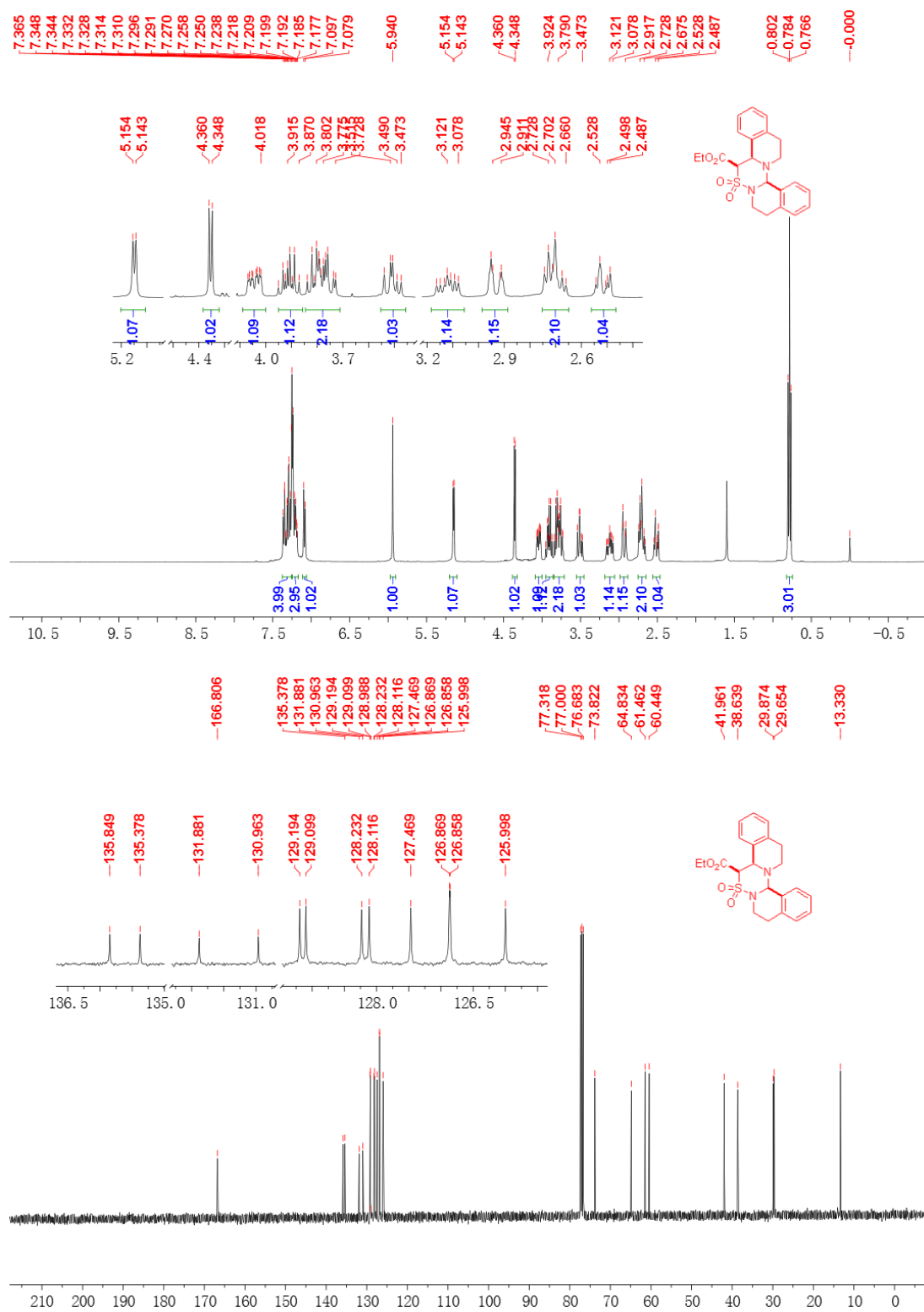
**2-(Benzyloxy)isoquinolin-1-ol (12)**



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

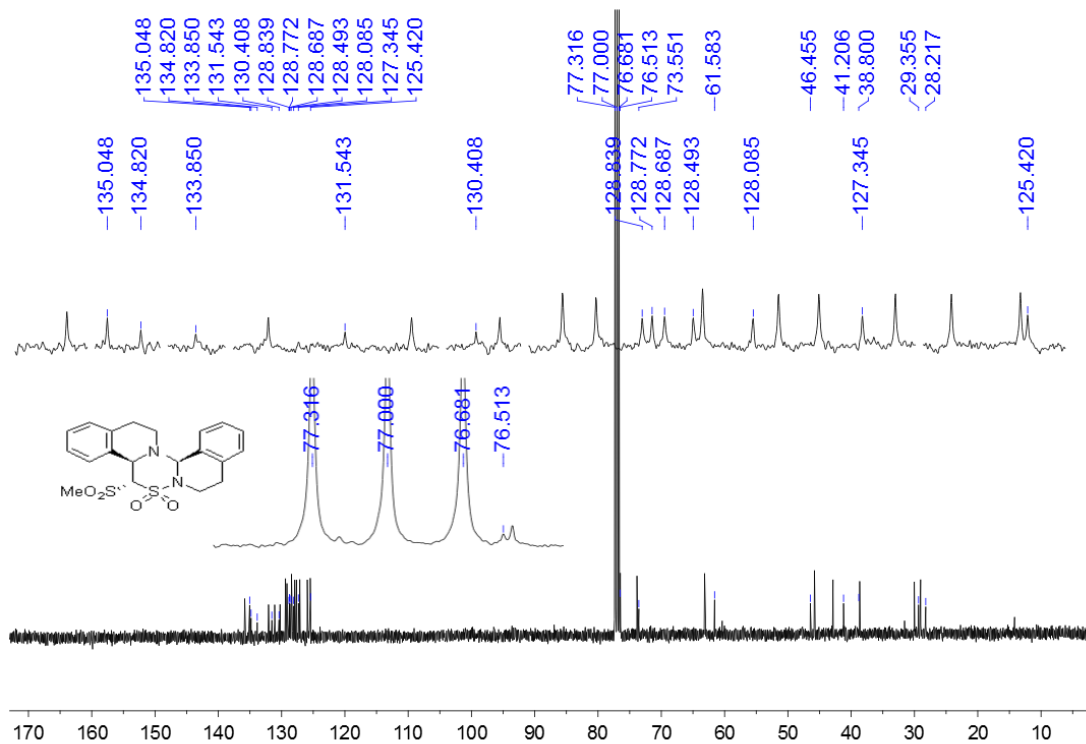
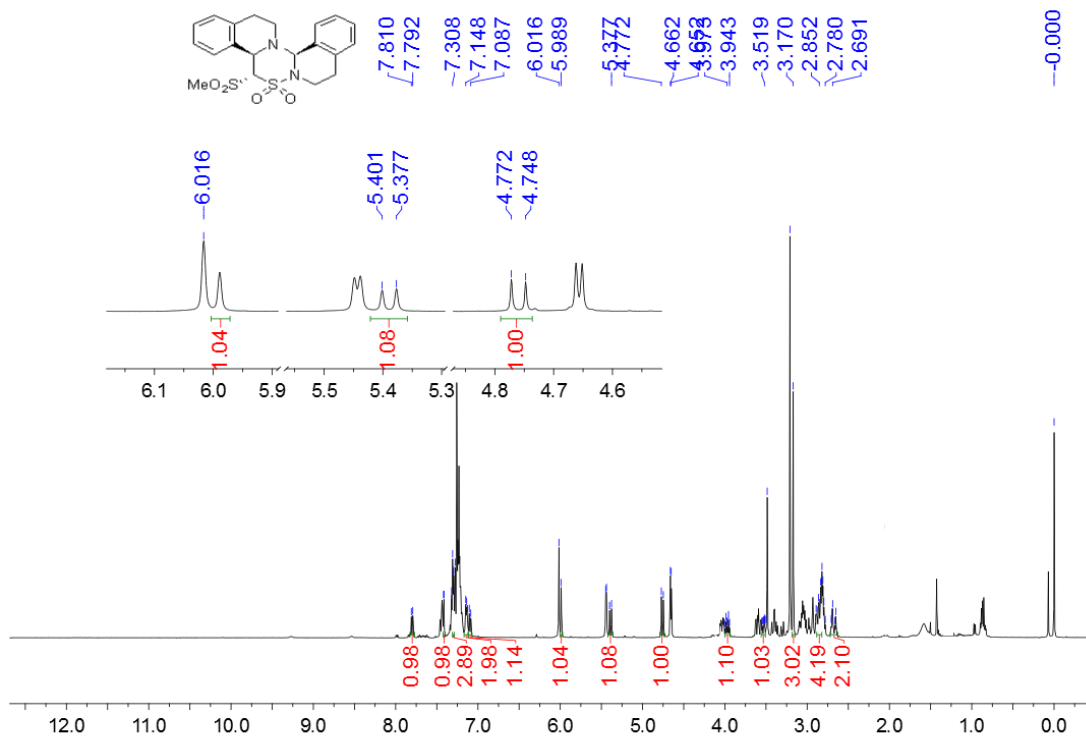


Ethyl *rel*(4*bR*,5*R*,13*bR*)-4*b*,5,9,13*b*,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*] diisoquinoline-5-carboxylate 6,6-dioxide (14)

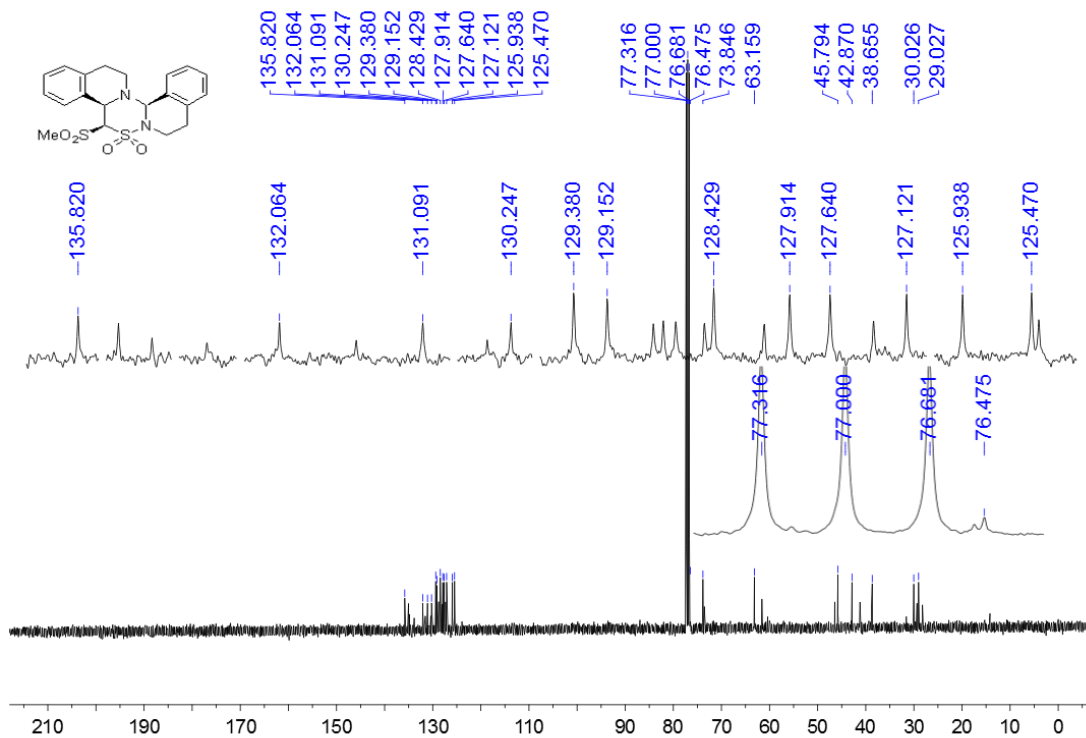
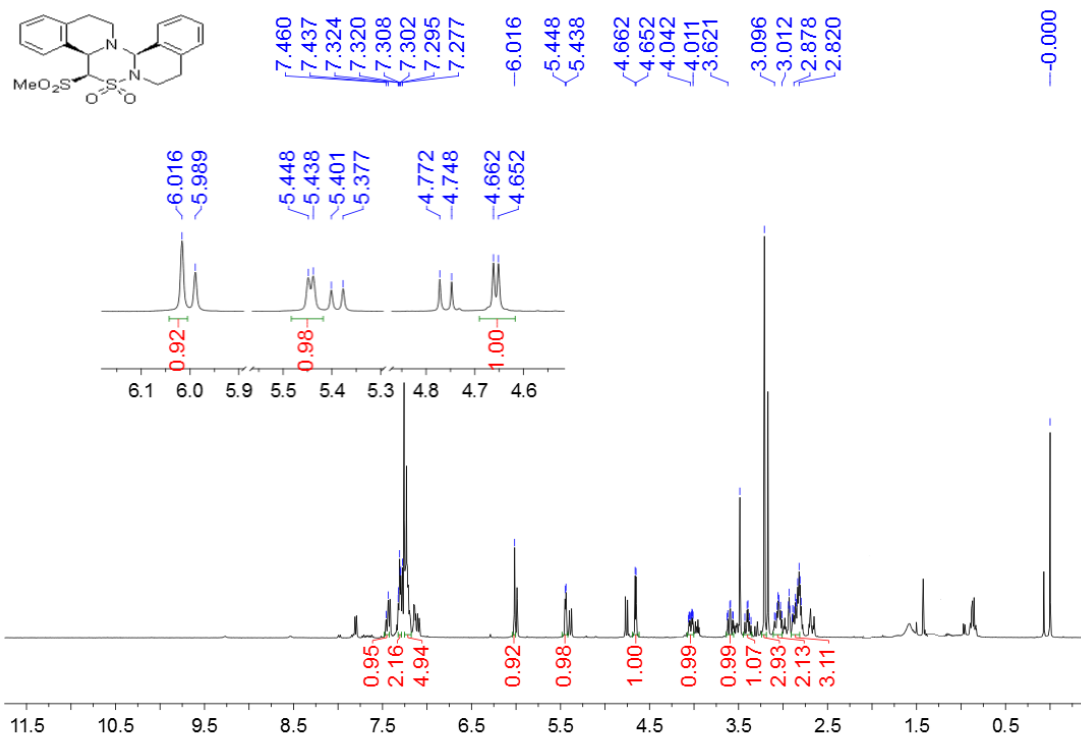




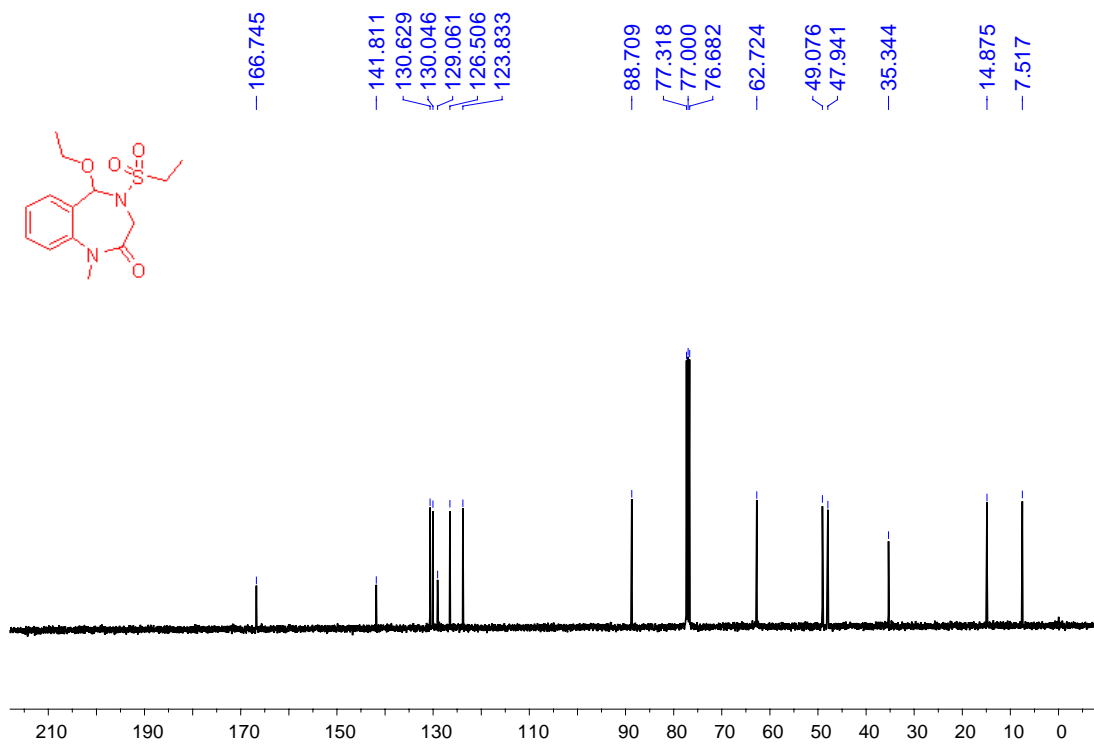
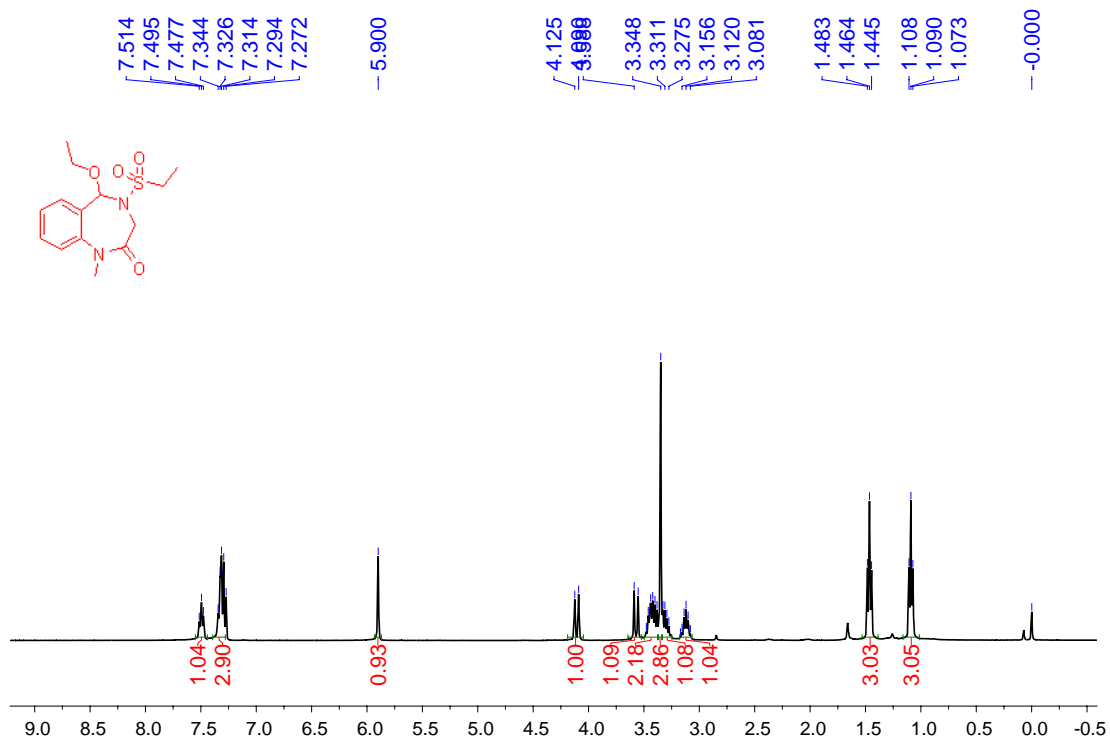
***rel*(4*bR*,5*S*,13*bR*)-5-(methylsulfonyl)-4*b*,5,9,13*b*,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*]diisoquinoline 6,6-dioxide (15)**



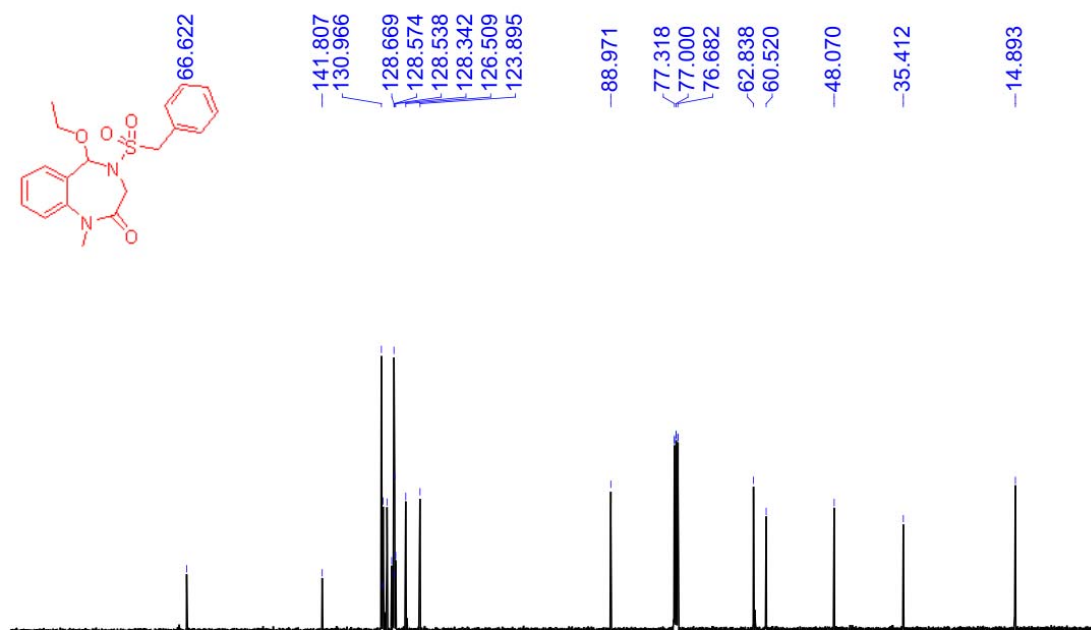
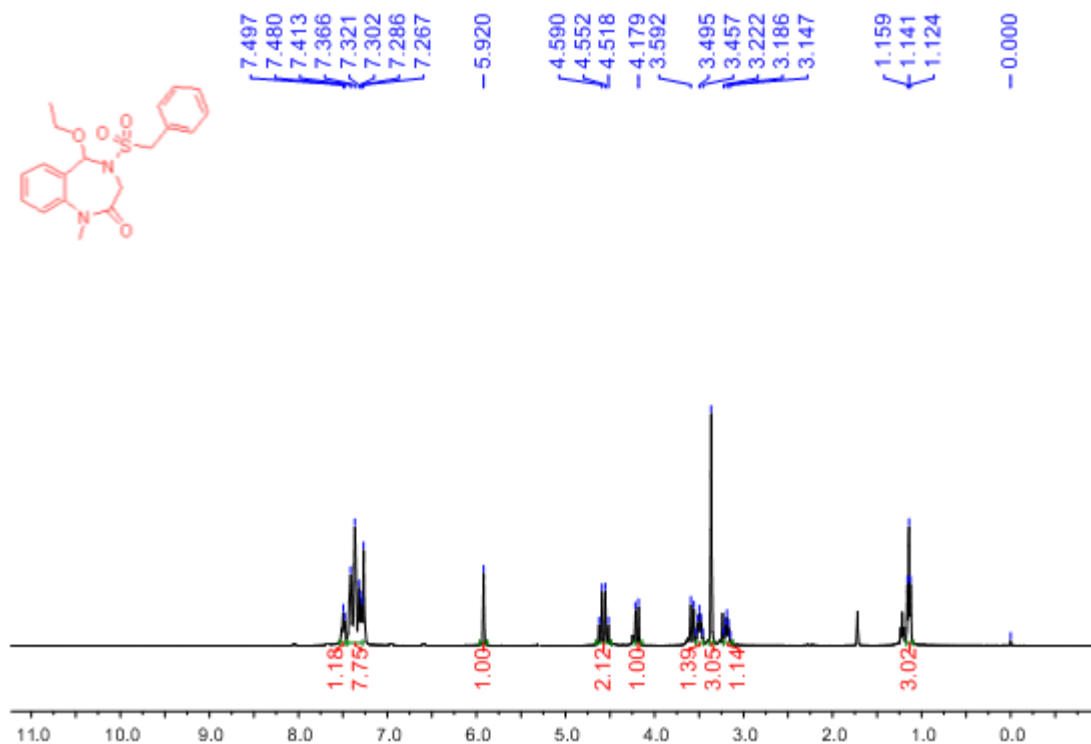
***rel(4bR,5R,13bR)*-5-(methylsulfonyl)-4b,5,9,13b,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*]diisoquinoline 6,6-dioxide (16)**



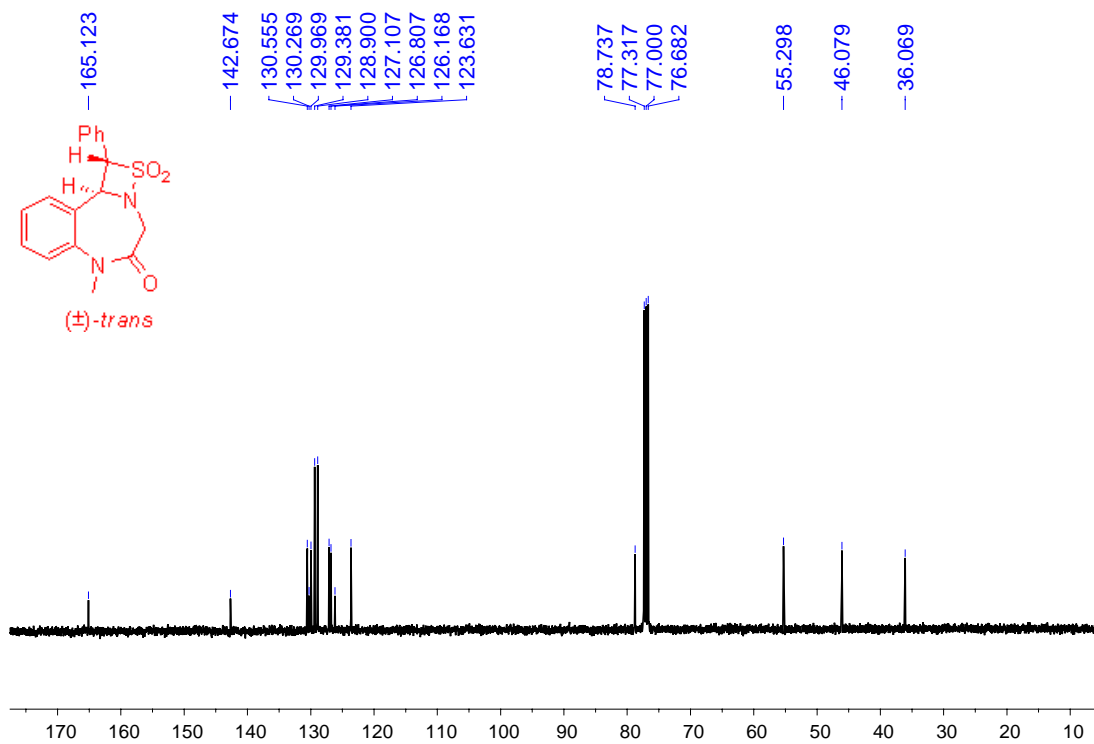
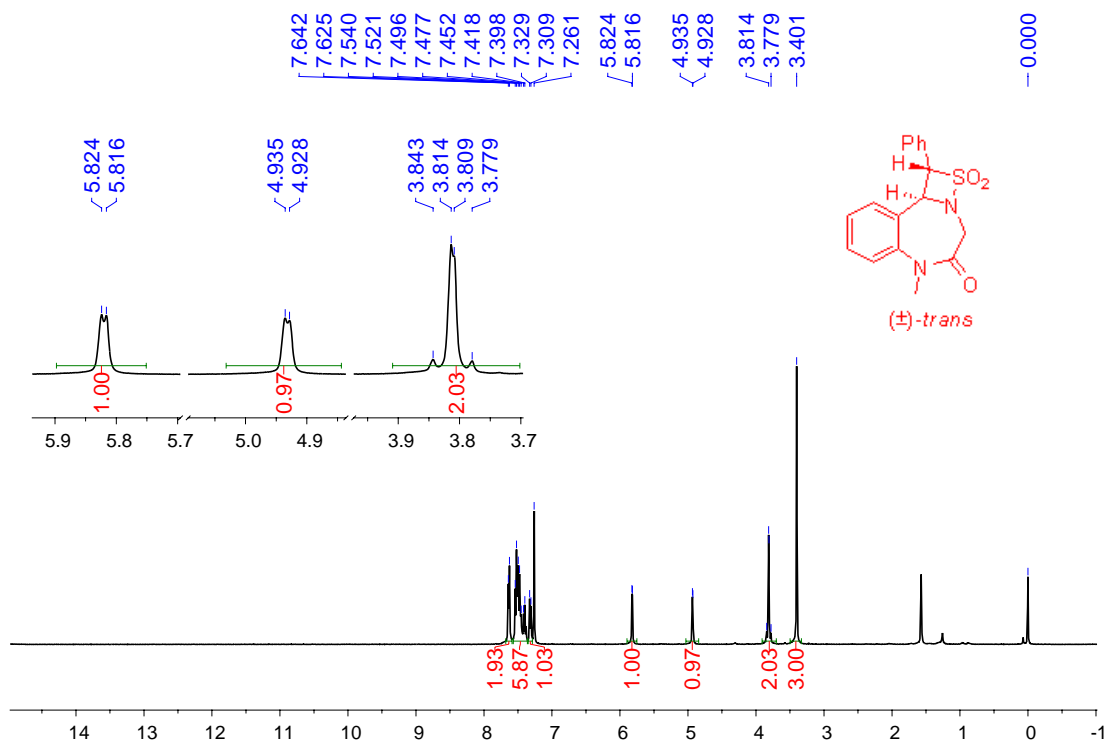
**5-Ethoxy-4-(ethylsulfonyl)-1-methyl-4,5-dihydro-1H-benzo[f][1,4]diazepin-2(3H)-one (18a)**



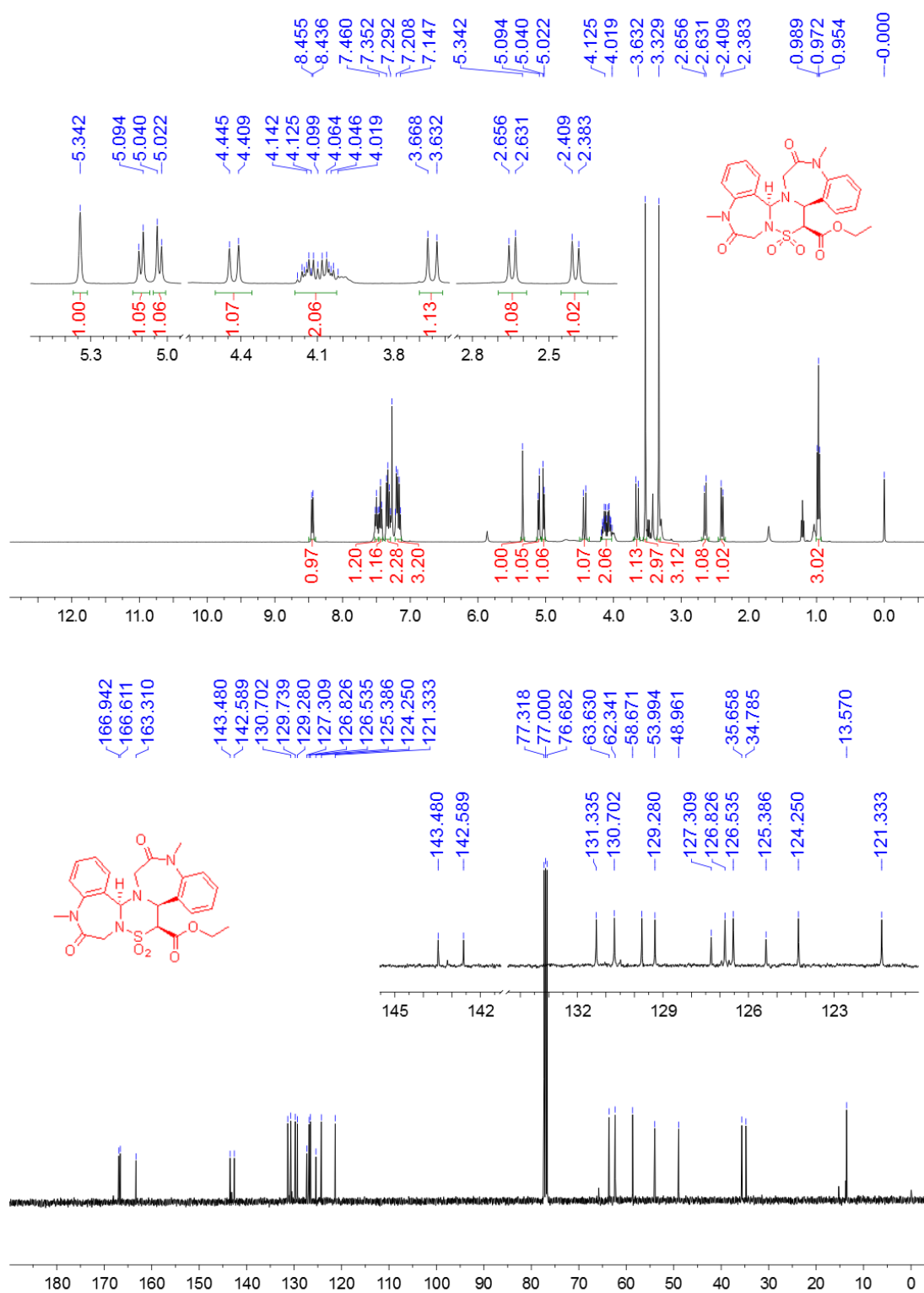
**4-(Benzylsulfonyl)-5-ethoxy-1-methyl-4,5-dihydro-1*H*-benzo[*f*][1,4]diazepin-2(3*H*)-one (18b)**



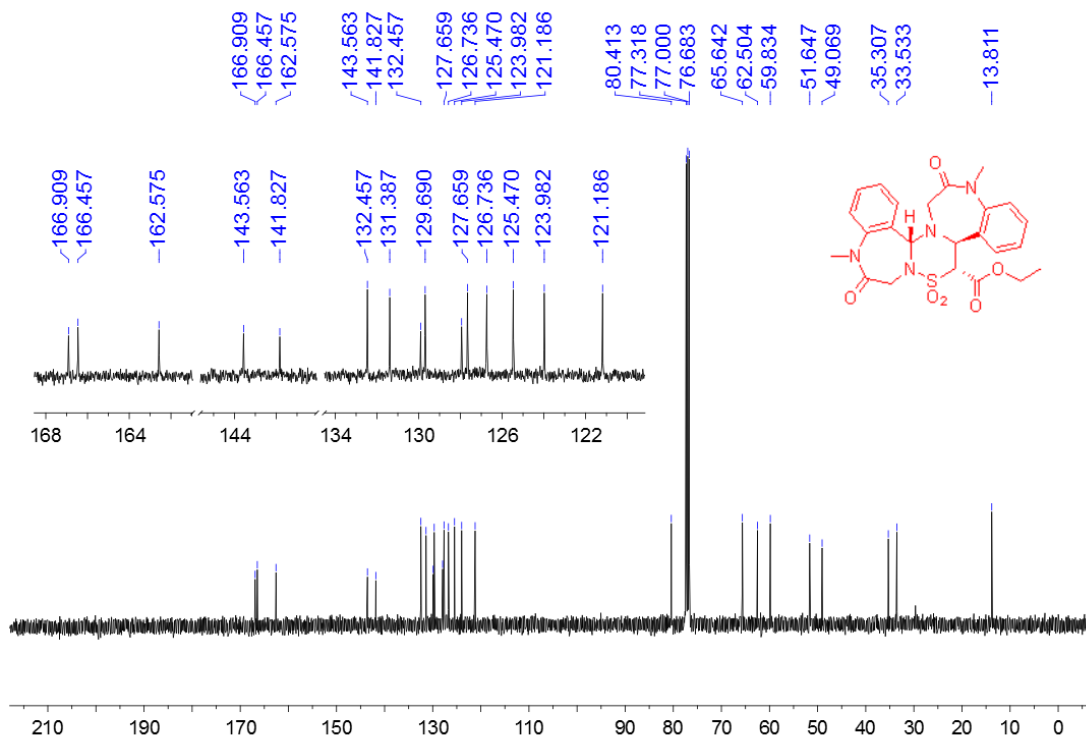
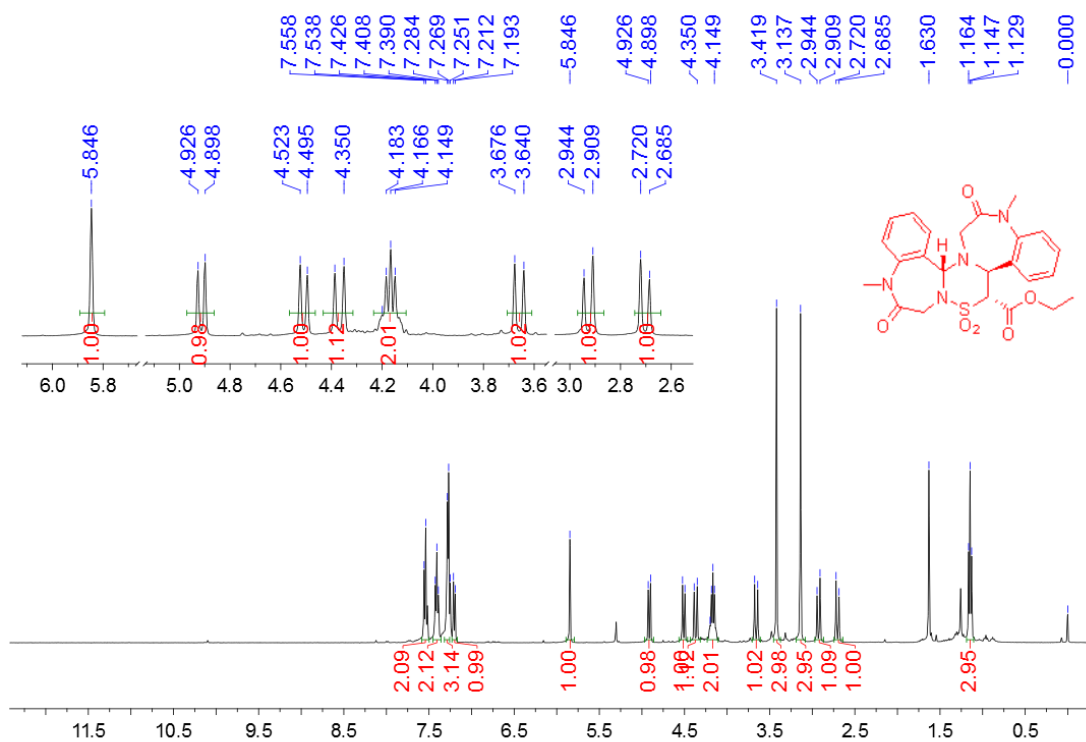
***trans*-6-Methyl-1-phenyl-1,10b-dihydro-6*H*-benzo[*f*][1,2]thiazeto[2,3-*d*][1,4]diazepin-5(4*H*)-one 2,2-dioxide (19)**



**Ethyl *rel*(2*S*,10*R*,11*S*)-1,5,8,14-tetraza-9-thiadibenzo[*c*,*l*]tricyclo[9.5.0.0<sup>2,8</sup>]hexadecane-6,15-dione-10-carboxylate 9,9-dioxide (20)**

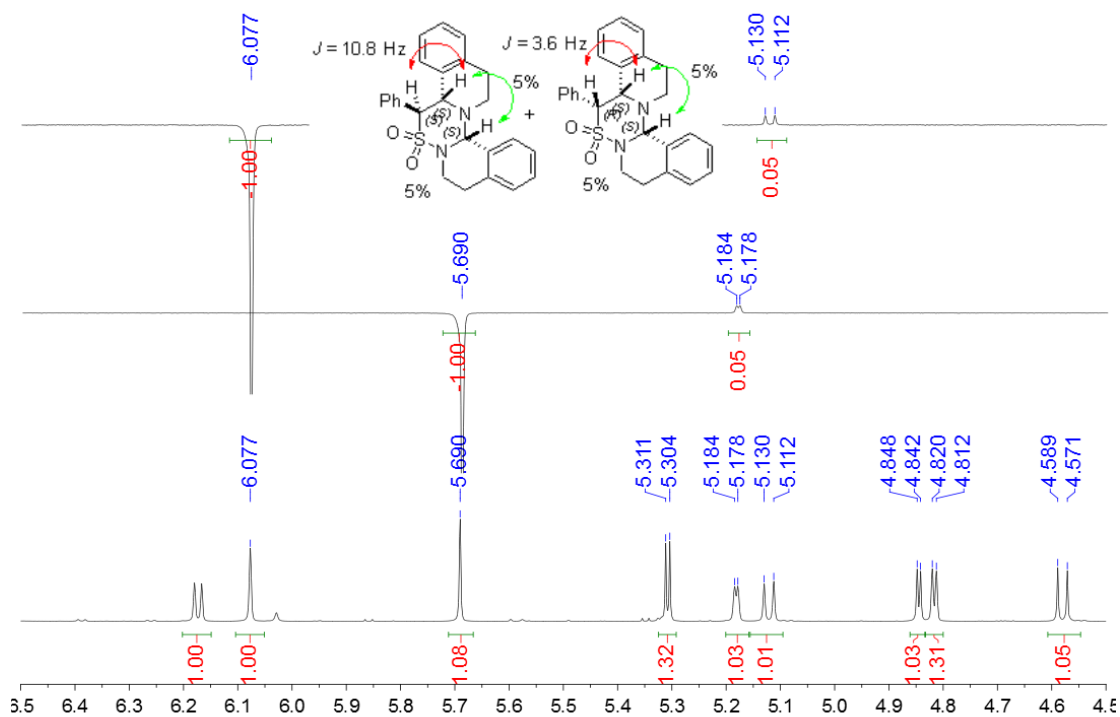
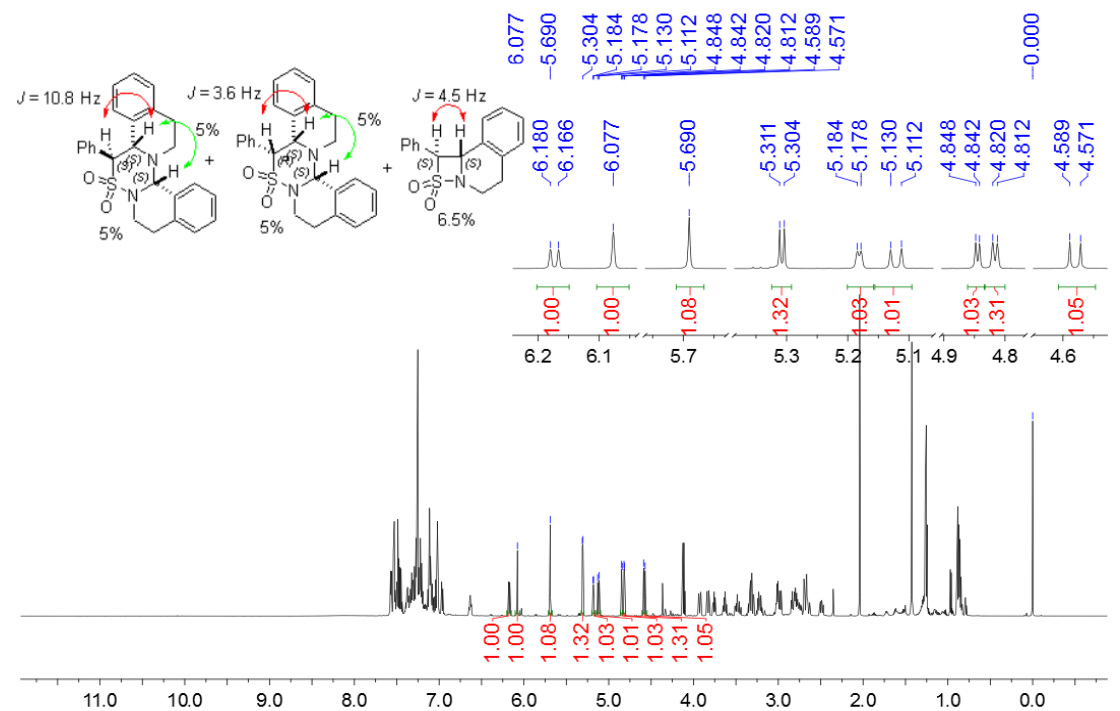


Ethyl *rel*(2*R*,10*S*,11*S*)-1,5,8,14-tetraza-9-thiadibenzo[*c,l*]tricyclo[9.5.0.0<sup>2,8</sup>]hexadecane-6,15-dione-10-carboxylate 9,9-dioxide (21)



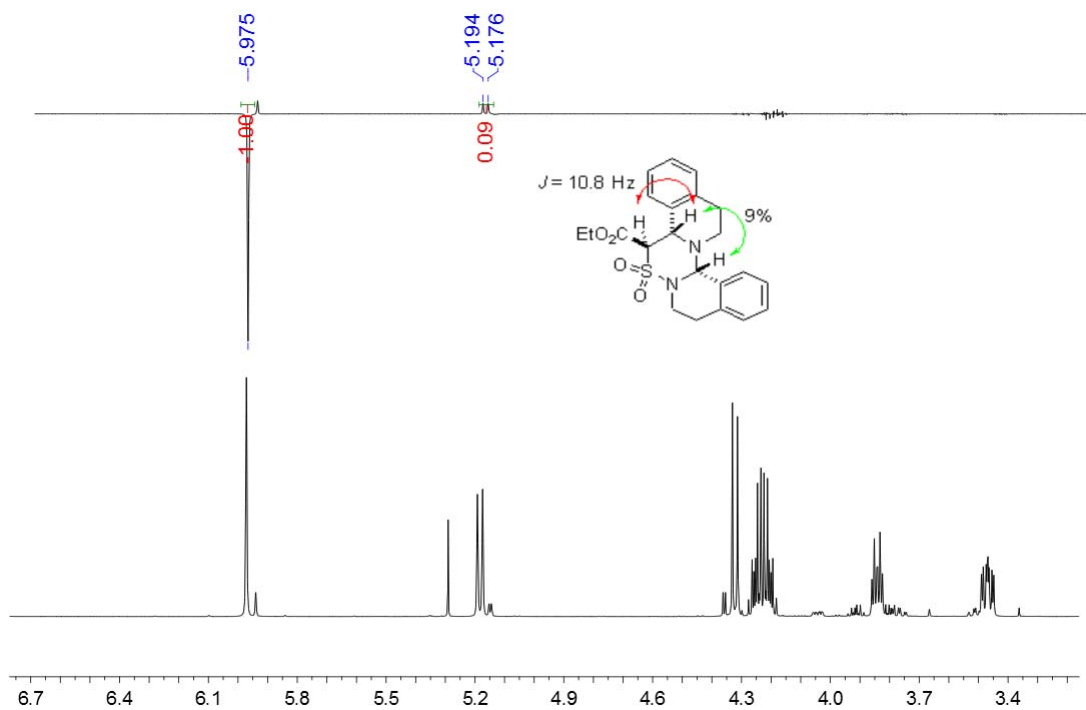
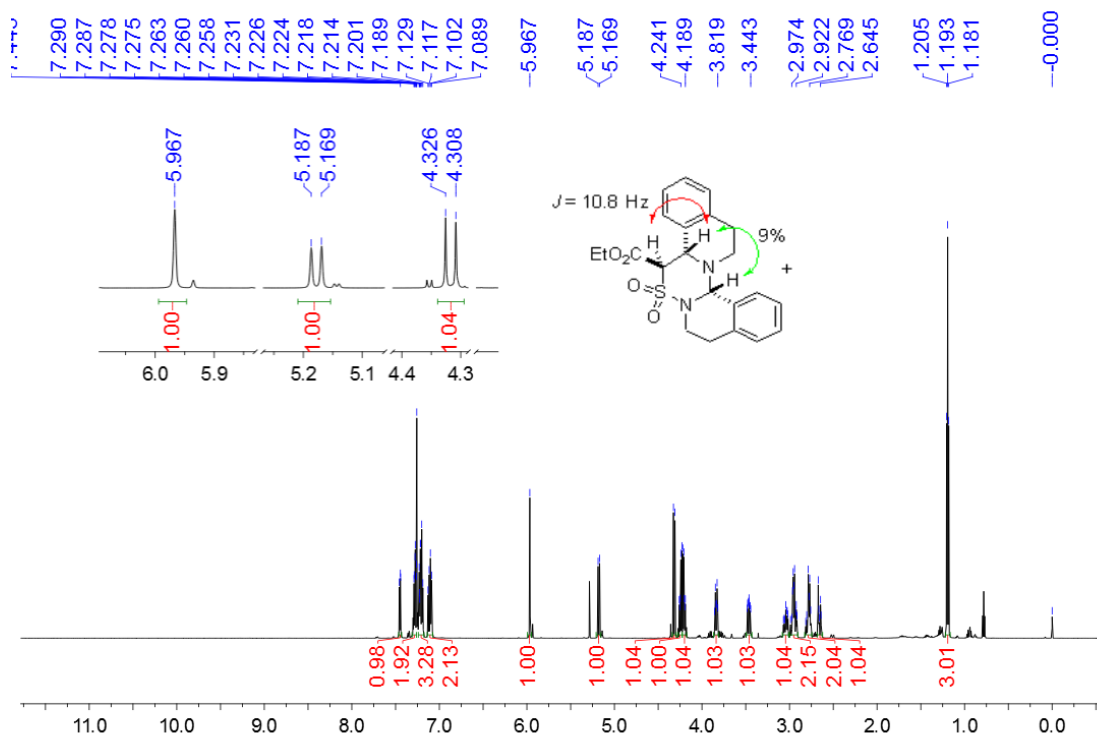
## 2. NOE spectra of [2<sup>s</sup> + 2<sup>i</sup> + 2<sup>i</sup>] annuladducts

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

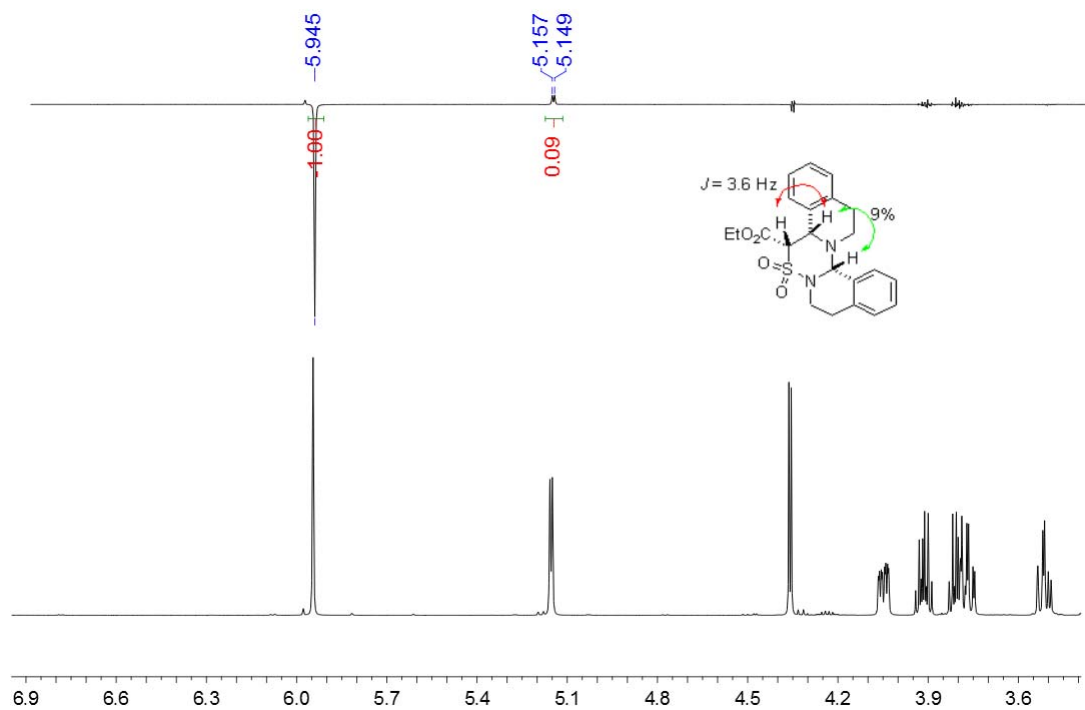
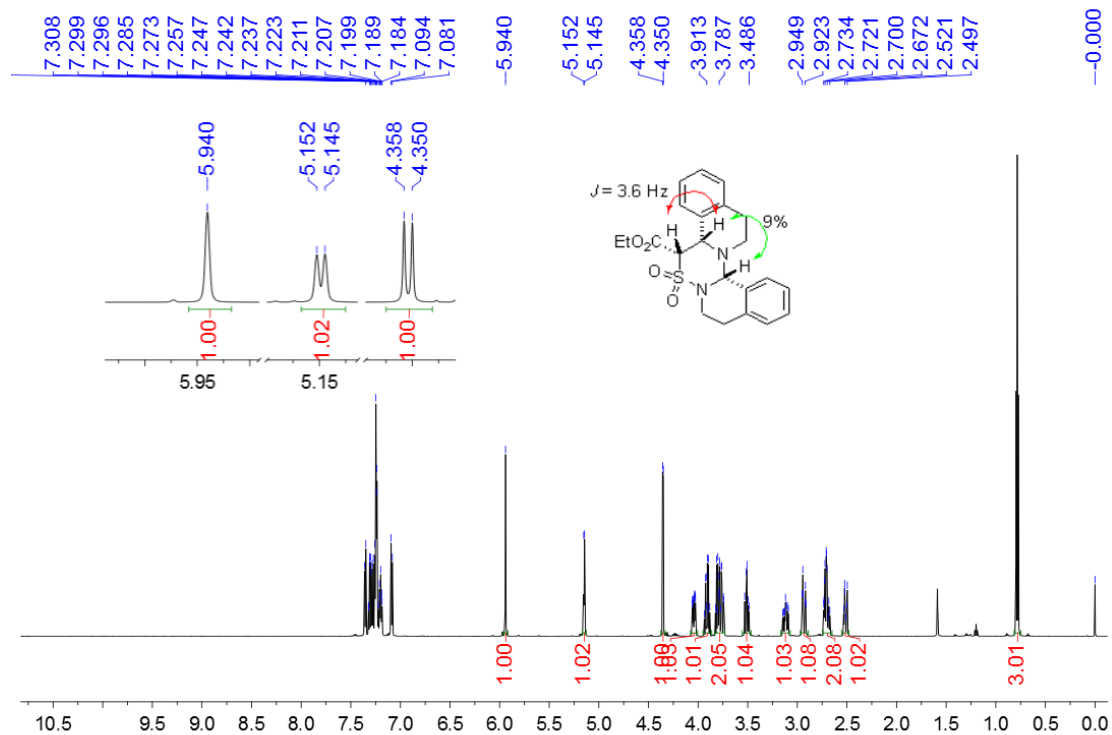




Ethyl *rel*(4*R*,5*R*,13*bS*)-4*b*,5,9,13*b*,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*] diisoquinoline-5-carboxylate 6,6-dioxide (13)

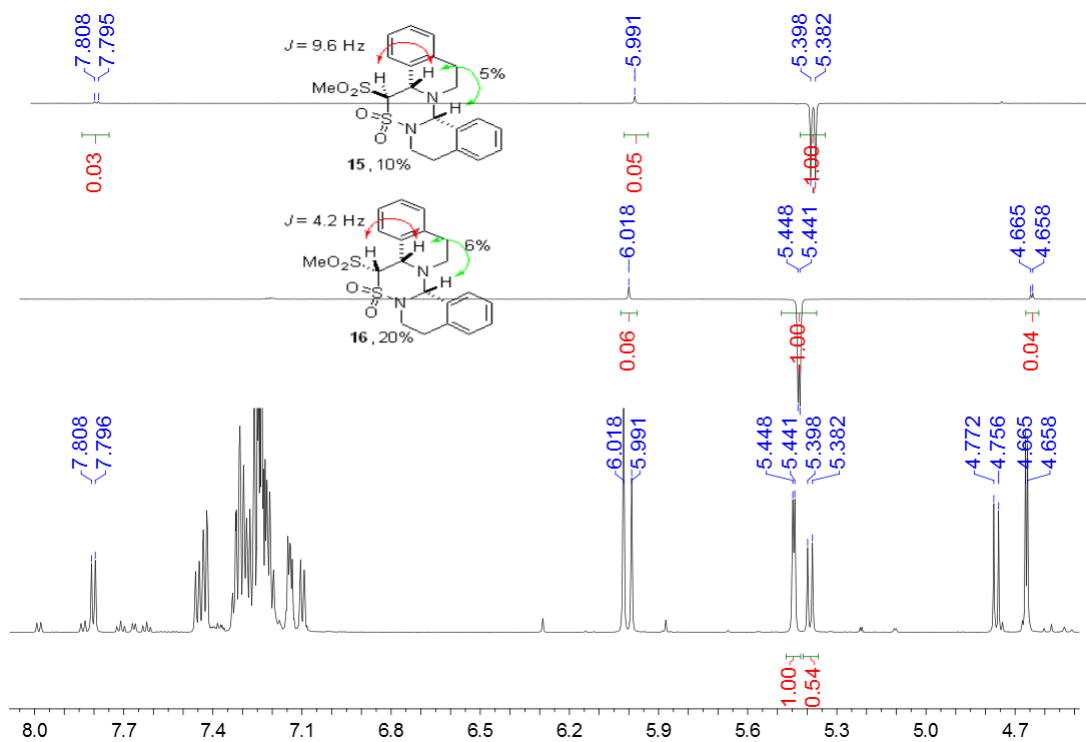
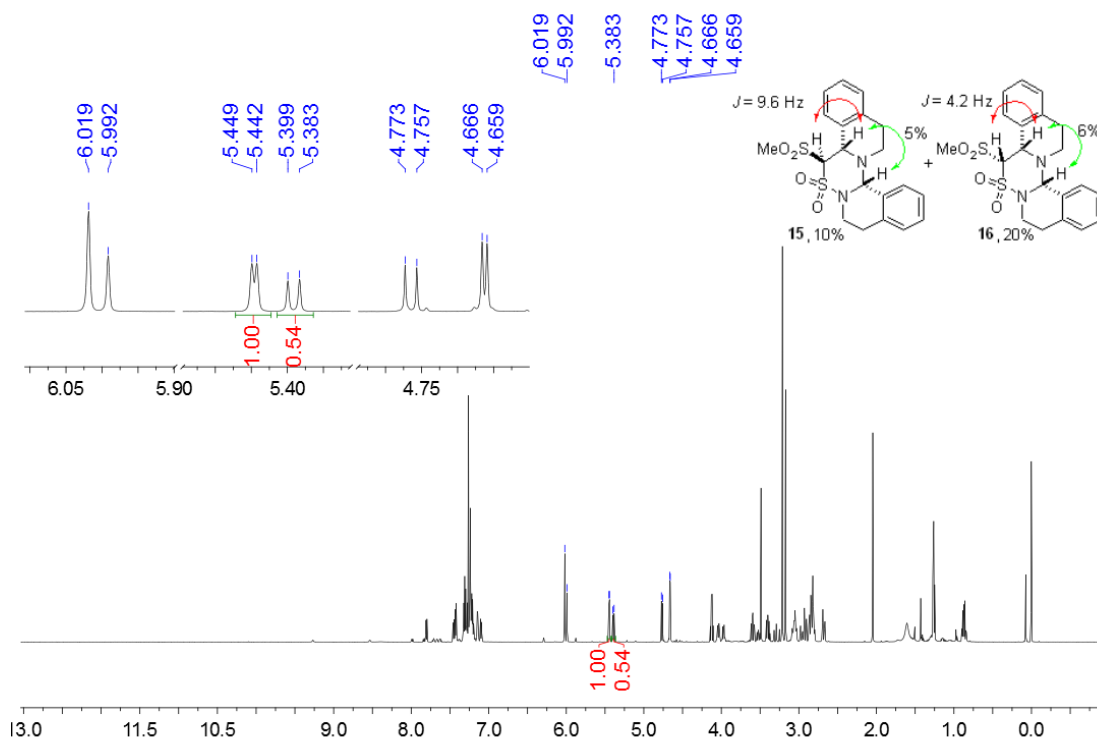


Ethyl *rel*(4*bR*,5*R*,13*bR*)-4*b*,5,9,13*b*,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*] diisoquinoline-5-carboxylate 6,6-dioxide (14)

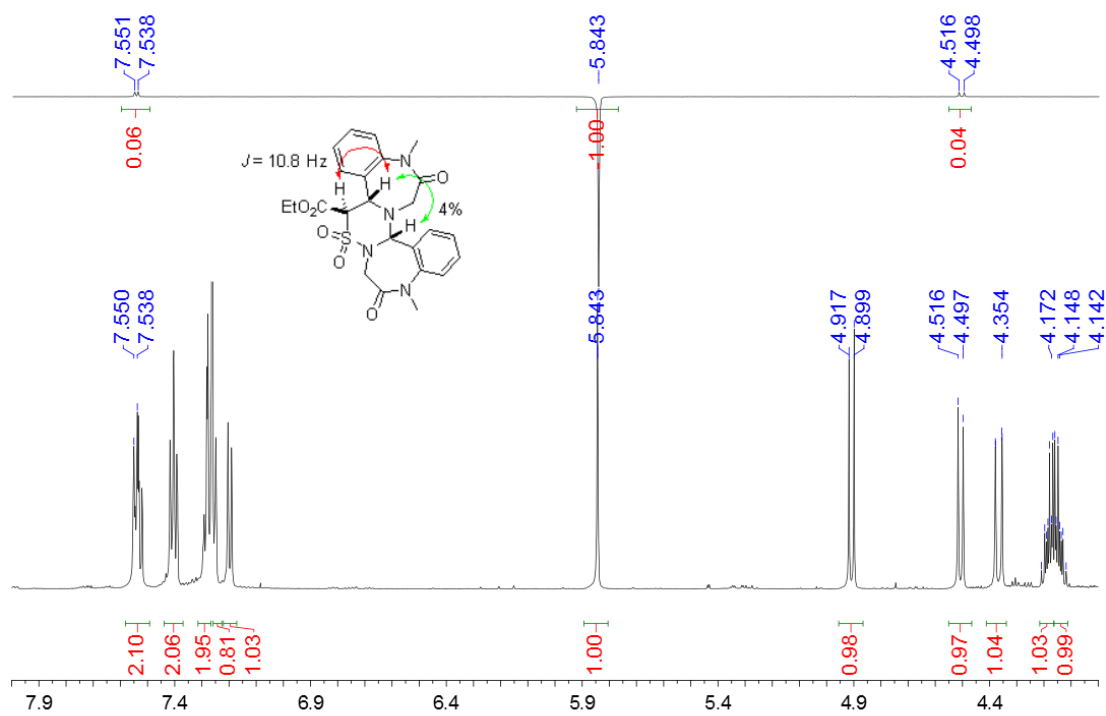
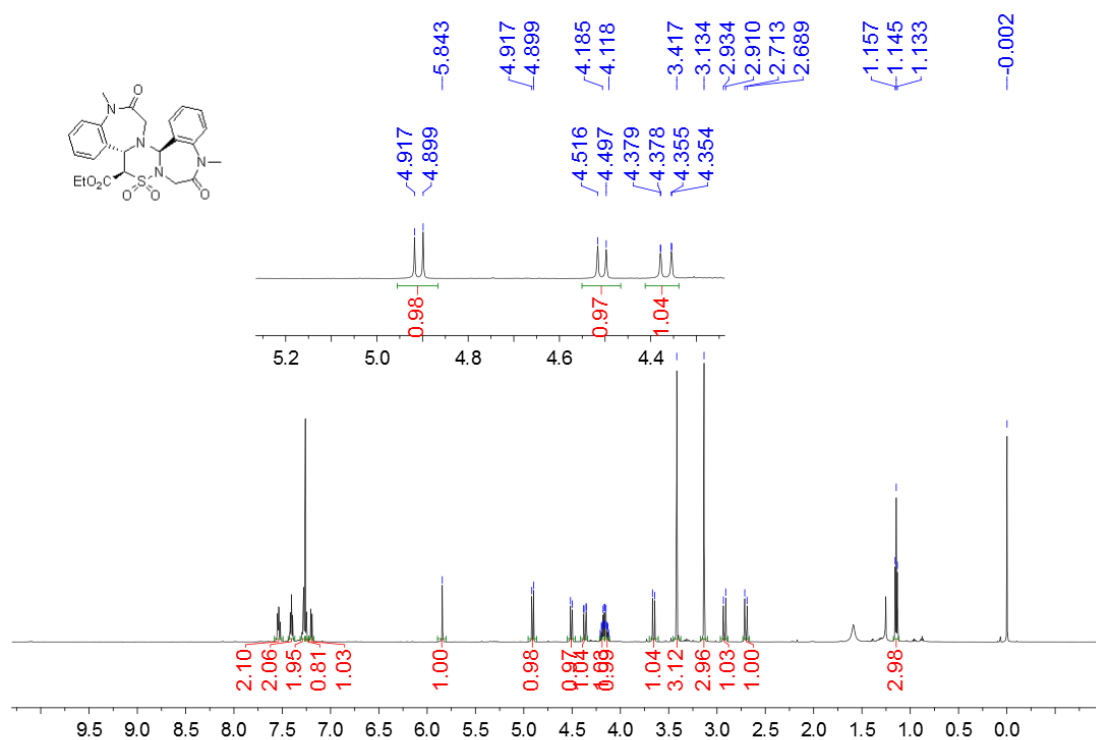


*rel*(4*bR*,5*S*,13*bR*)-5-(Methylsulfonyl)-4*b*,5,9,13*b*,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*]diisoquinoline 6,6-dioxide (15)

*rel*(4*bR*,5*R*,13*bR*)-5-(Methylsulfonyl)-4*b*,5,9,13*b*,15,16-hexahydro-8*H*-[1,2,4]thiadiazino[3,2-*a*:5,4-*a'*]diisoquinoline 6,6-dioxide (16)



Ethyl *rel*(2*S*,10*R*,11*S*)-1,5,8,14-tetraza-9-thiadibenzo[*c,l*]tricyclo[9.5.0.0<sup>2,8</sup>]hexadecane-6,15-dione-10-carboxylate 9,9-dioxide (20)



Ethyl *rel*(2*R*,10*S*,11*S*)-1,5,8,14-tetraza-9-thiadibenzo[*c*,*l*]tricyclo[9.5.0.0<sup>2,8</sup>]hexadecane-6,15-dione-10-carboxylate 9,9-dioxide (21)

