

**Mechanistic and chiroptical studies on the desulfurization of  
epidithiodioxopiperazines reveal universal retention of configuration at the  
bridgehead carbon atoms**

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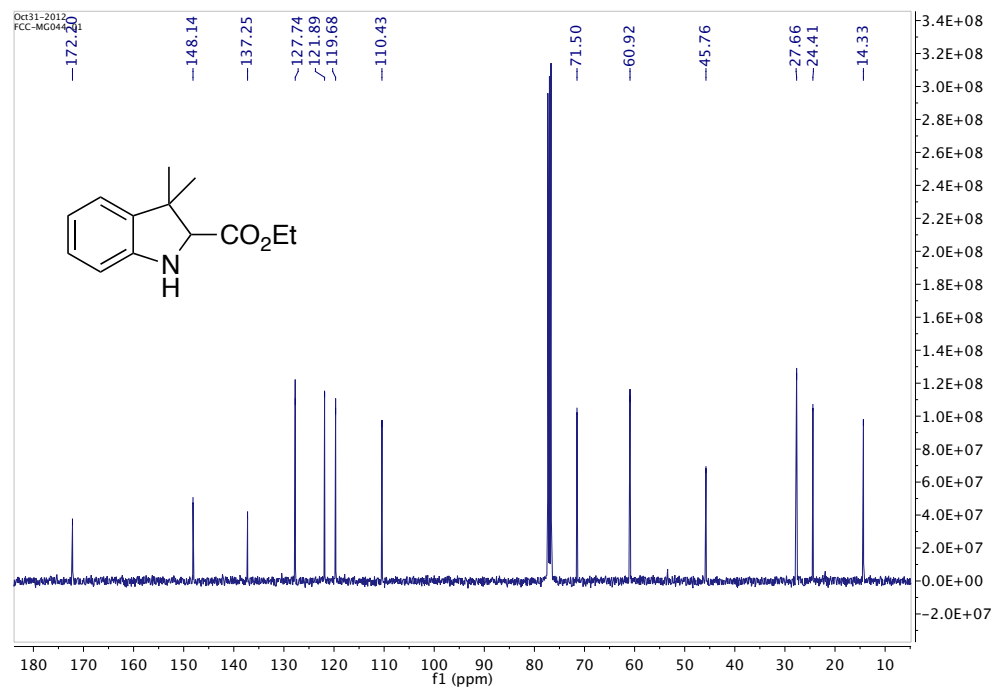
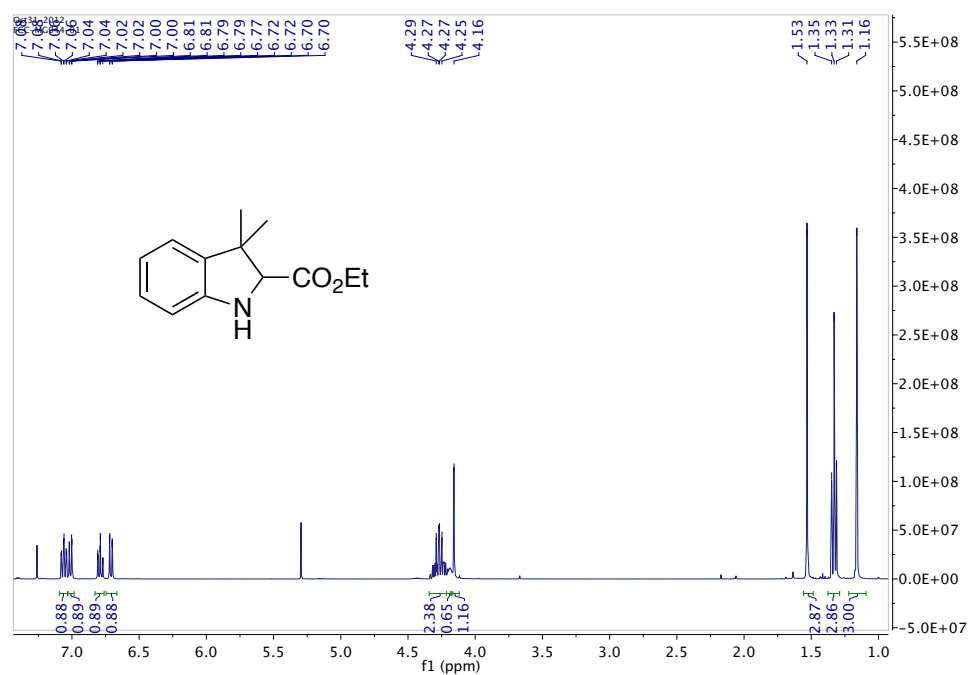
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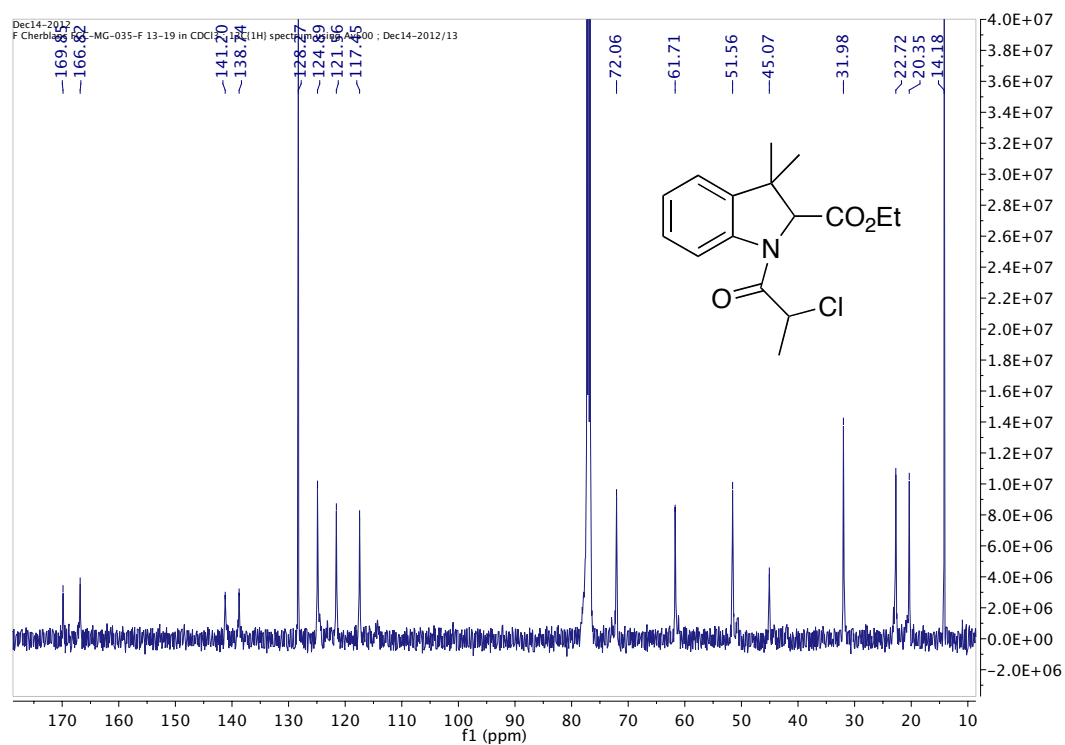
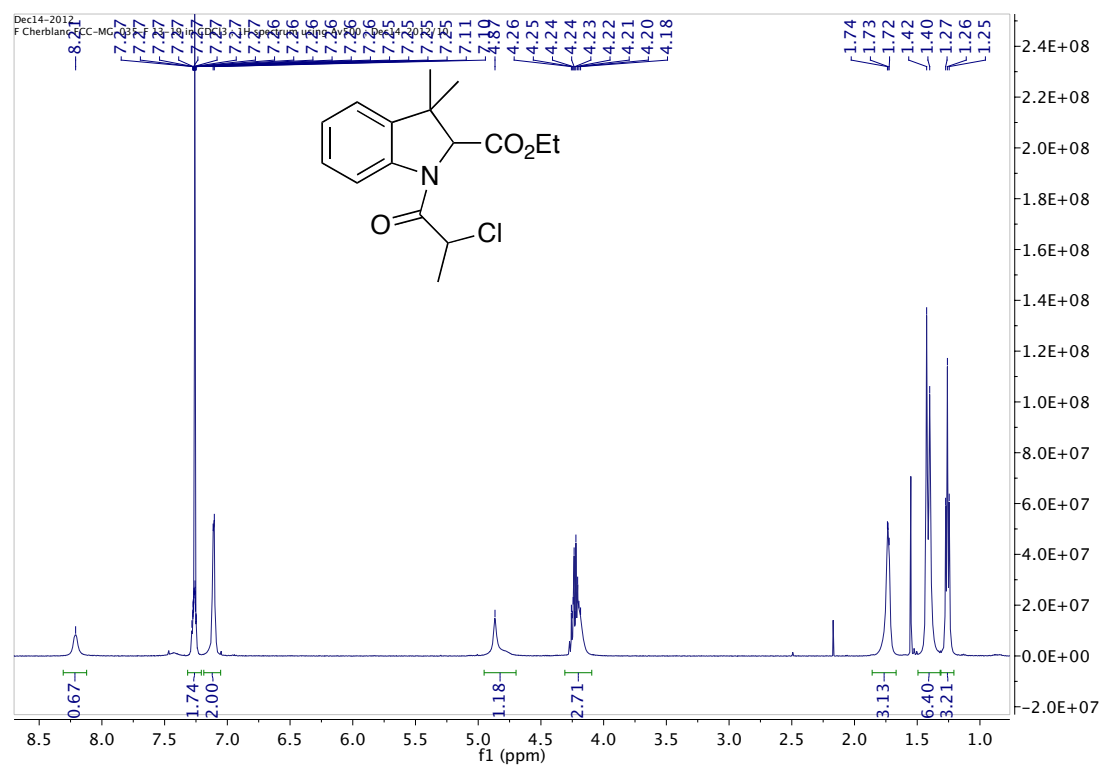
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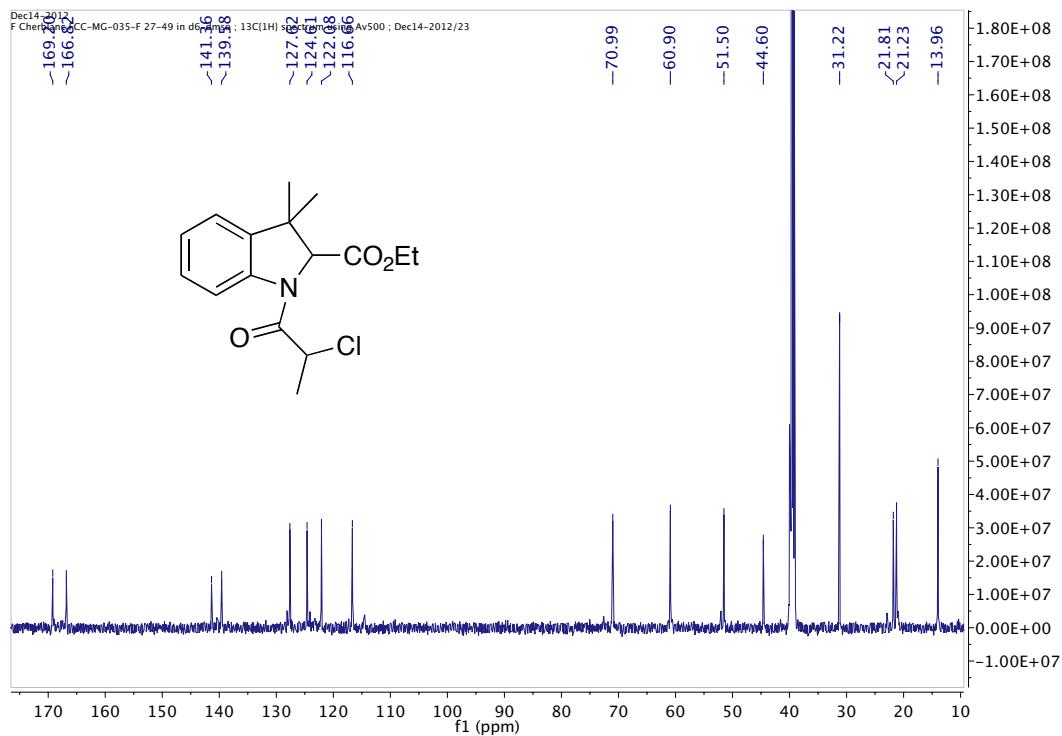
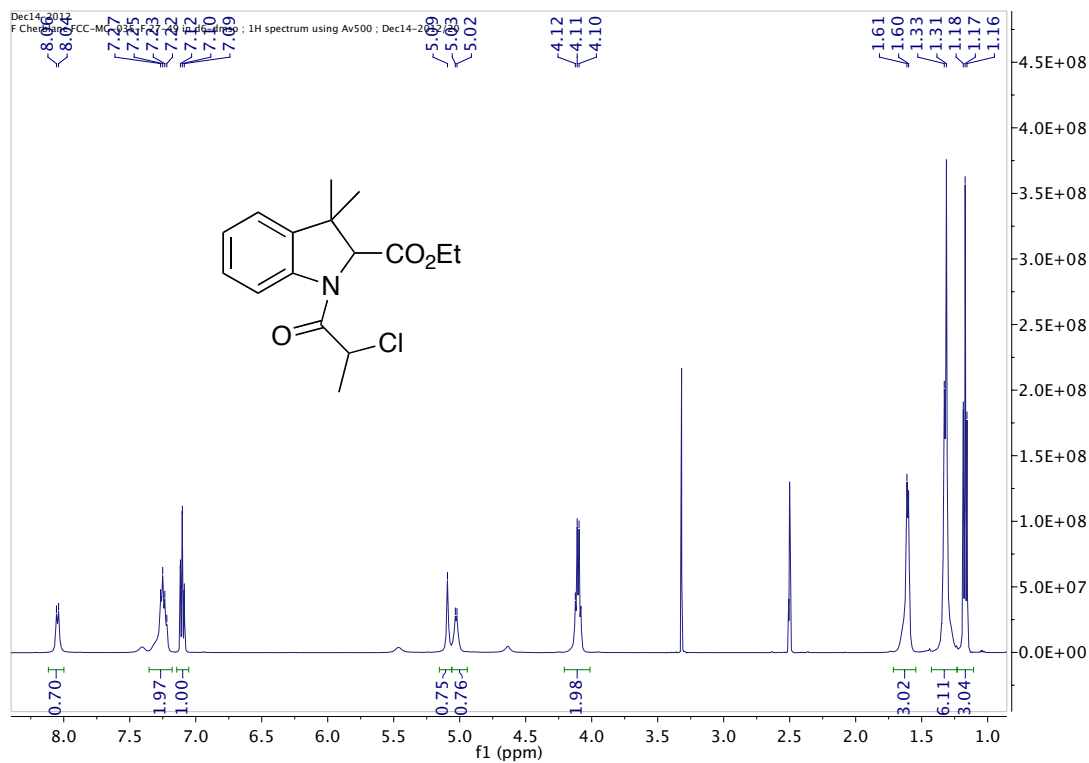
1. <sup>1</sup> H/ <sup>13</sup> C NMR spectra compound <b>10 – 13, 1, 8</b>	S2
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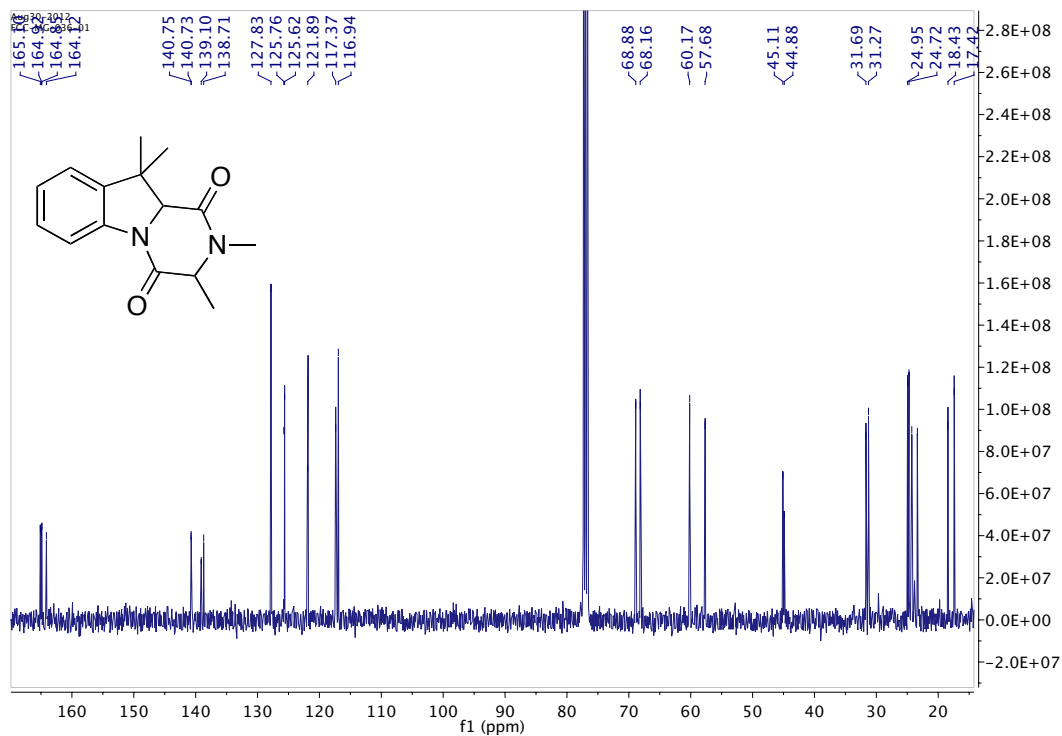
## 1. NMR spectra compound 7 – 13

### Ethyl 3,3-dimethylindoline-2-carboxylate (10)<sup>1</sup>

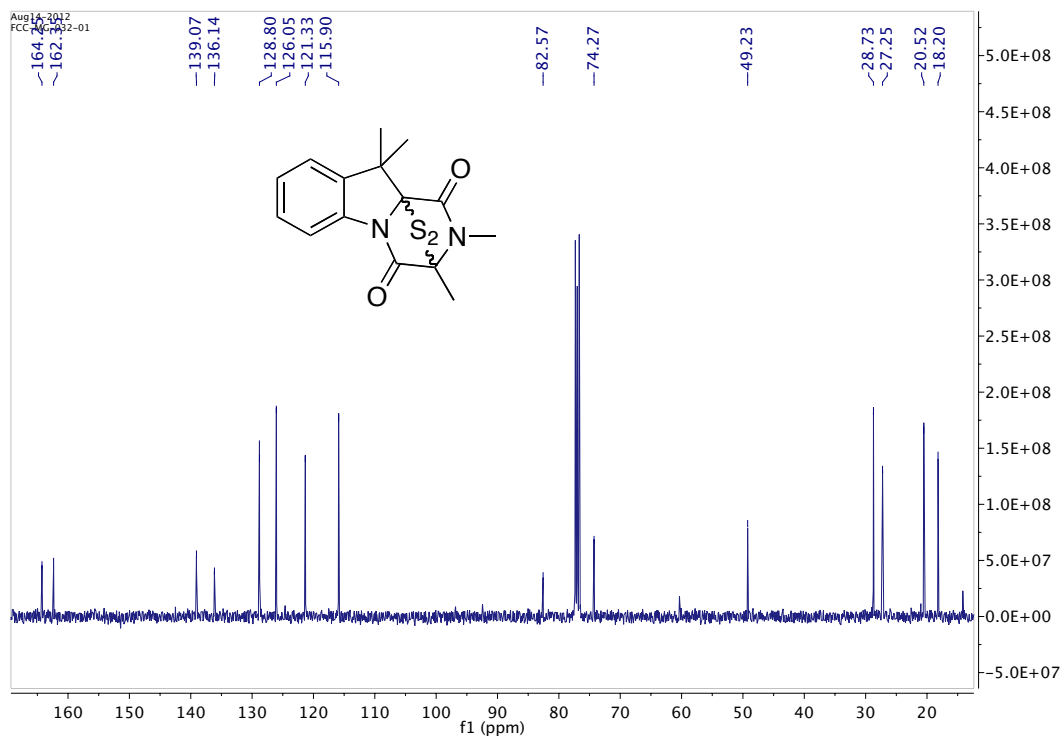
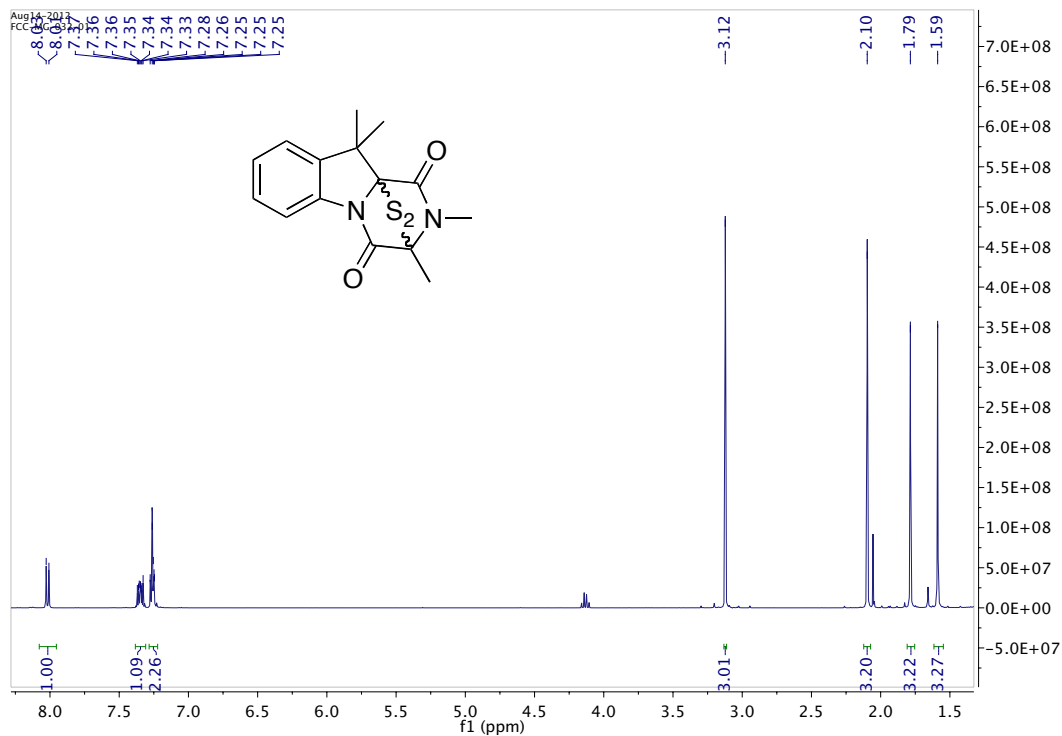


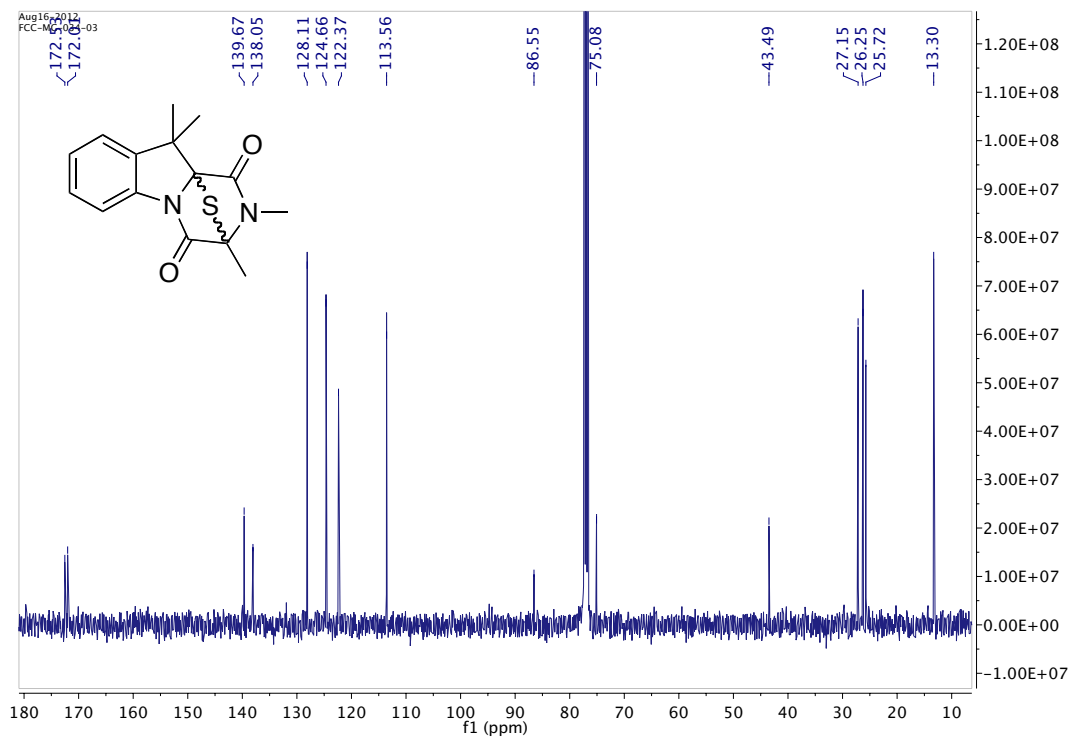
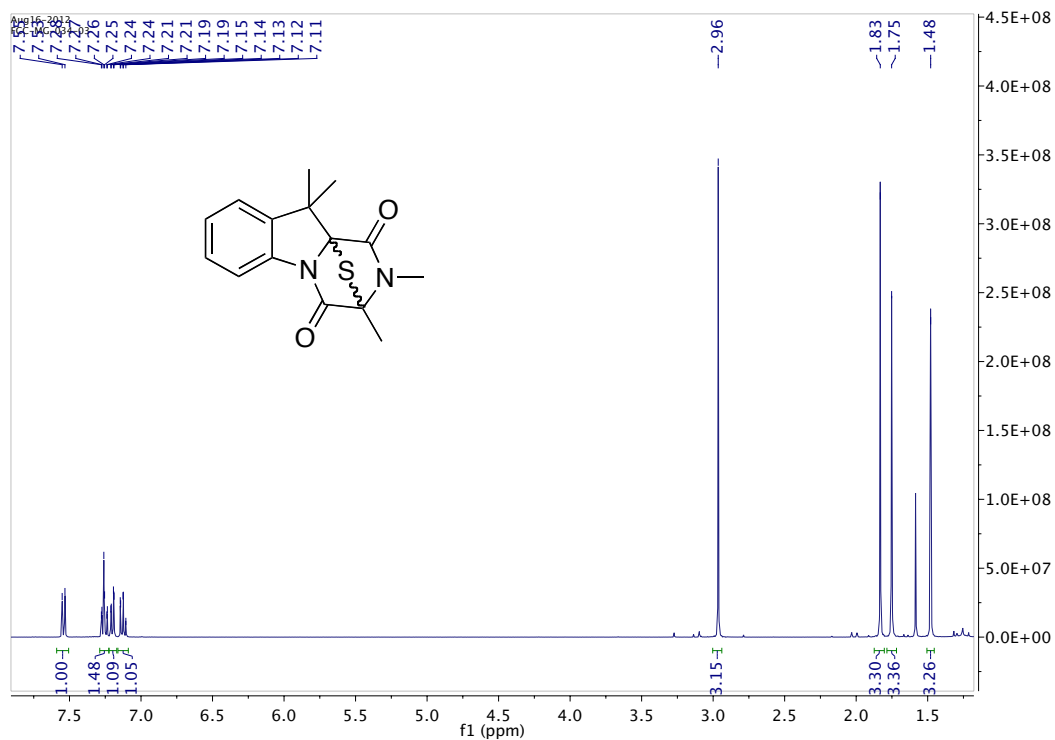
**Ethyl 1-(2-chloropropanoyl)-3,3-dimethylindoline-2-carboxylate (11)****diastereoisomer 1**

**Ethyl 1-(2-chloropropanoyl)-3,3-dimethylindoline-2-carboxylate (11)****diastereoisomer 2 (in  $d_6$ -DMSO)**

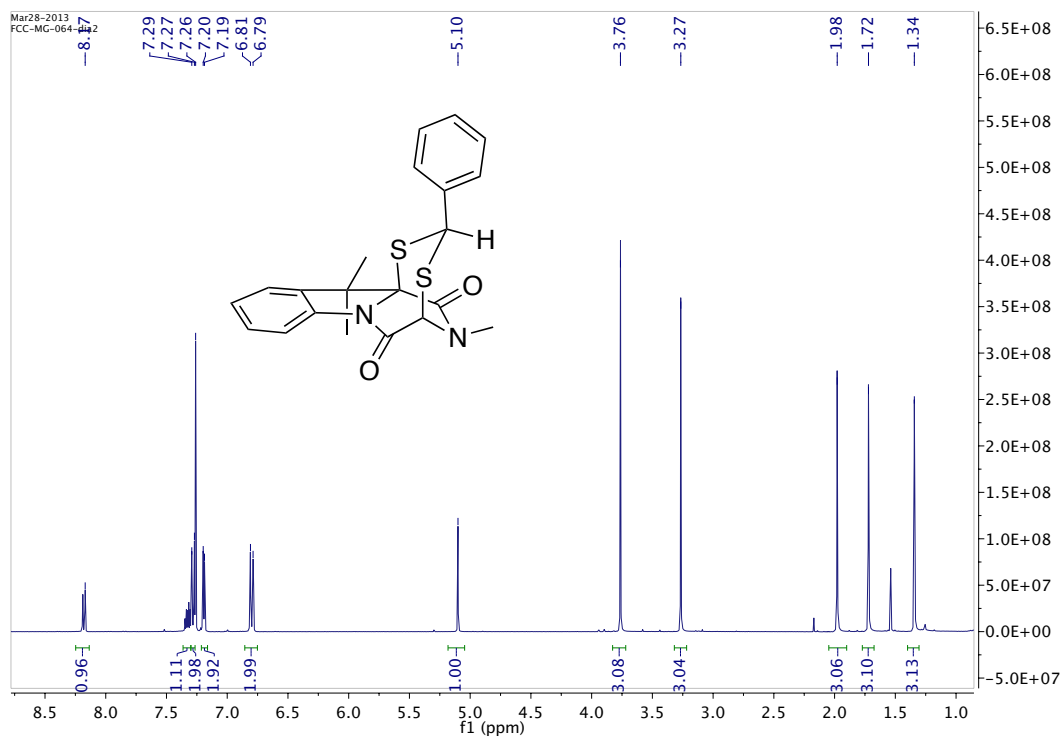


**2,3,10,10-Tetramethyl-2,3-dihydro-1*H*-3,10a-epithiopyrazino[1,2-*a*]indole-1,4(10*H*)-dione 11-sulfide (7)<sup>2</sup>**



**2,3,10,10-Tetramethyl-2,3-dihydro-1*H*-3,10a-epithiopyrazino[1,2-*a*]indole-1,4(10*H*)-dione (8)<sup>2</sup>**

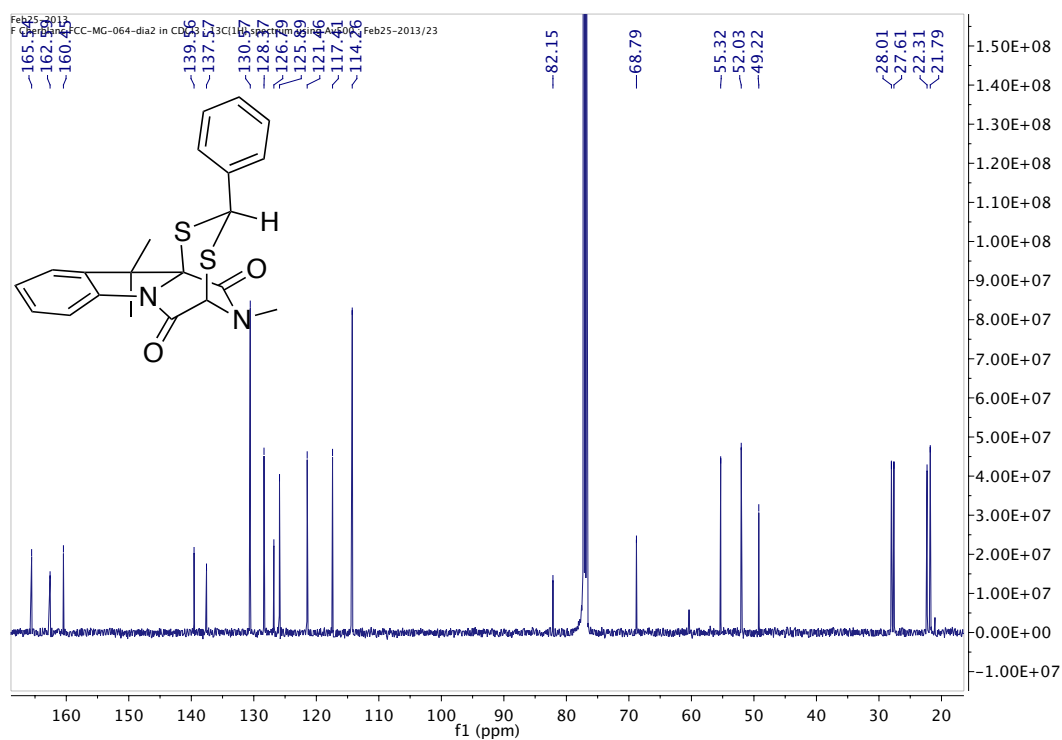
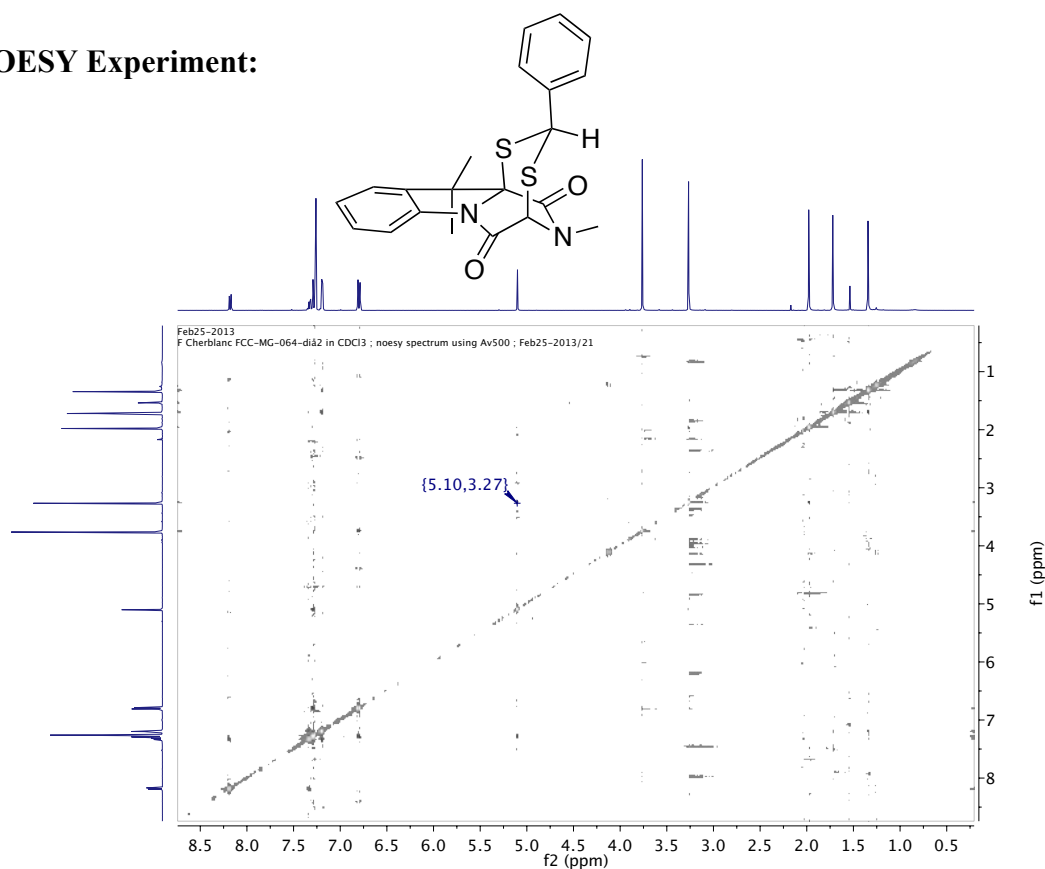
**2-(4-Methoxyphenyl)-4,11,11,13-tetramethyl-4*H*-4,11a-(epiminomethano)[1,3,5]dithiazepino[5,4-*a*]indole-5,12(11*H*)-dione (13, *syn* diastereoisomer)**





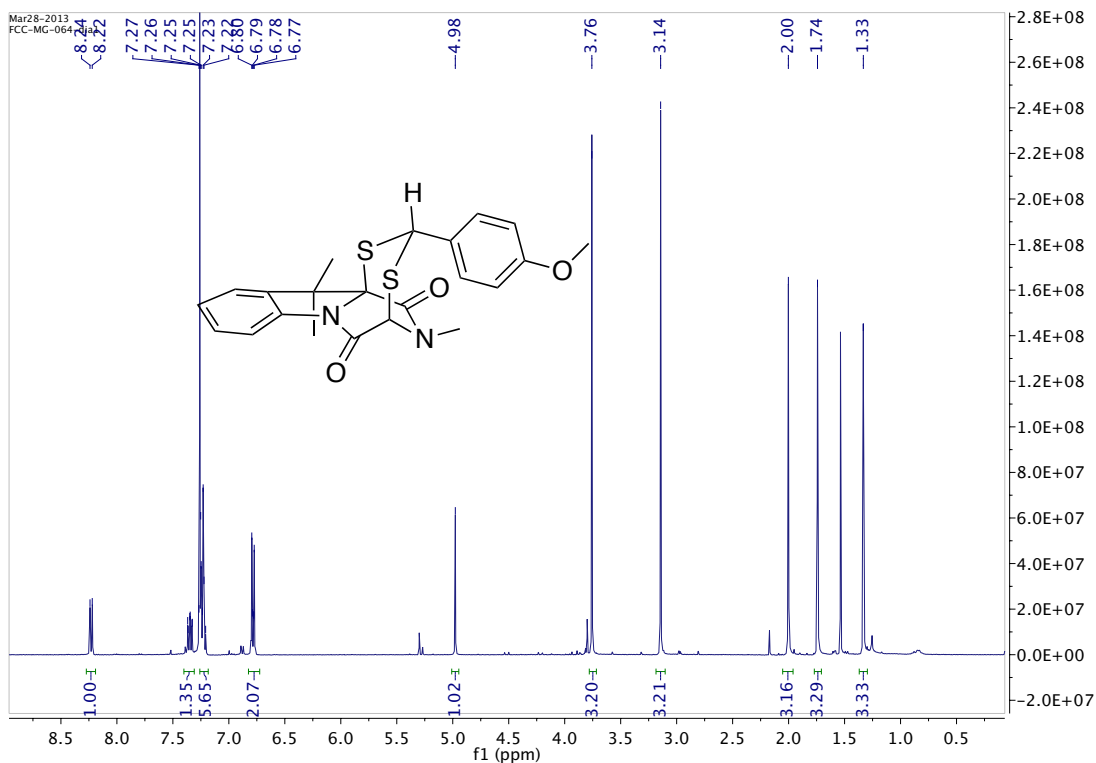
# Supporting Information

## NOESY Experiment:

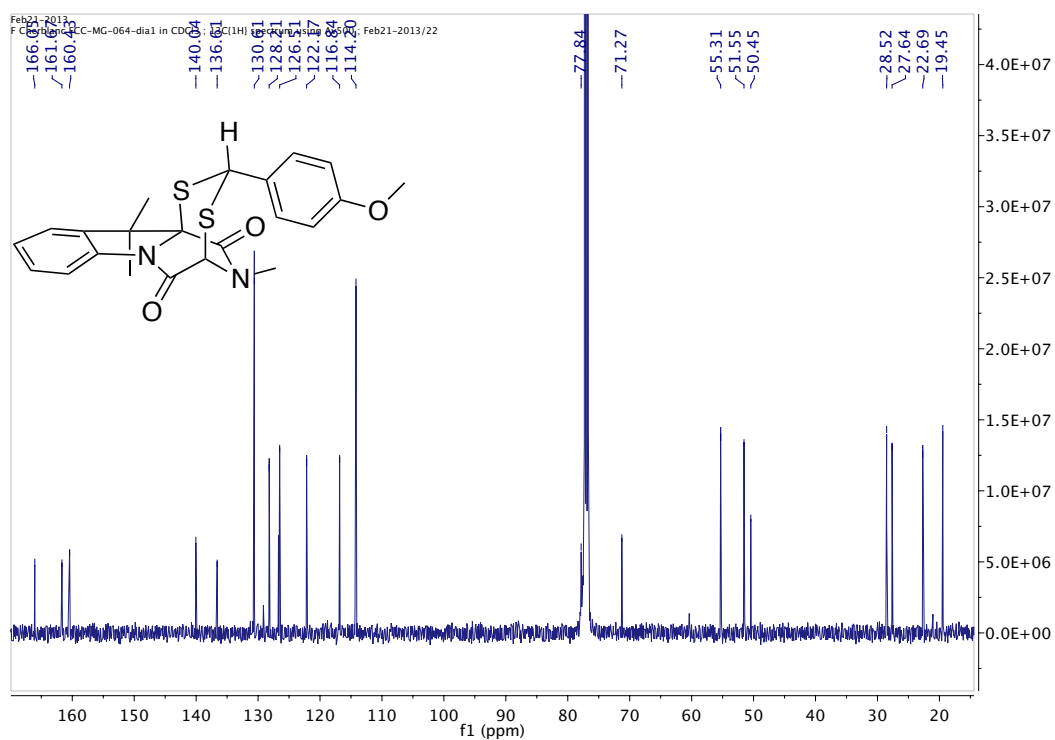
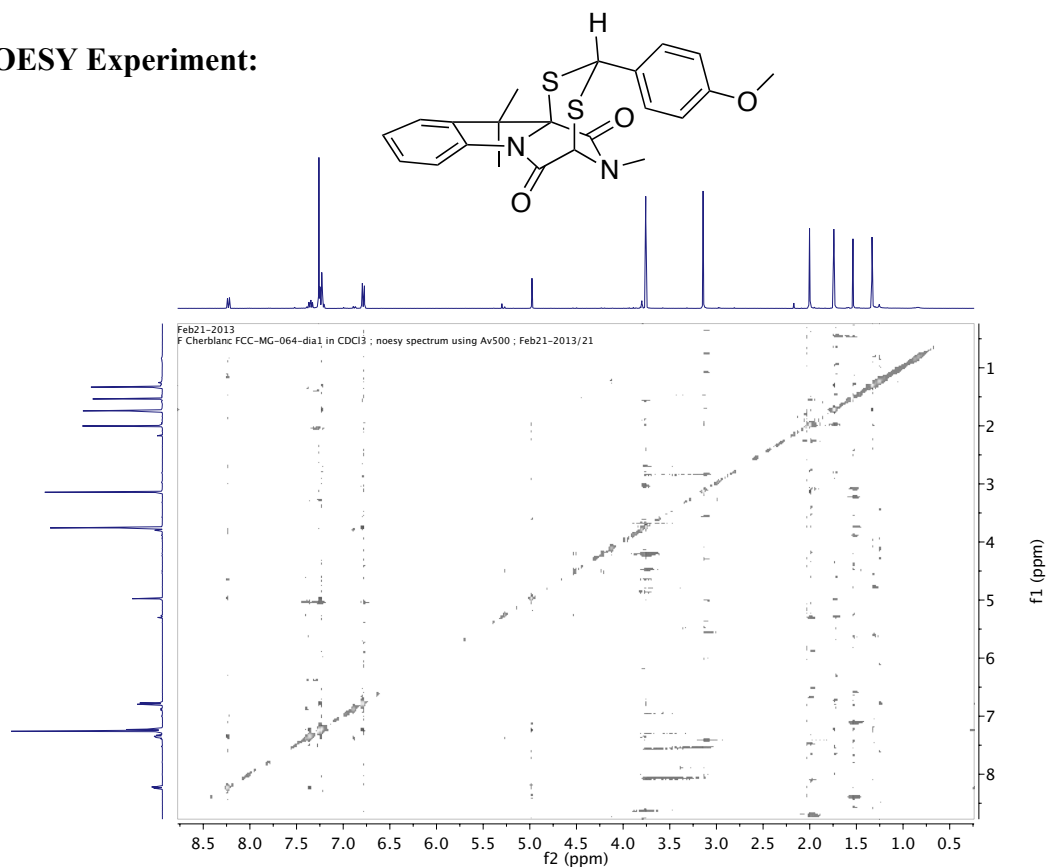


**2-(4-Methoxyphenyl)-4,11,11,13-tetramethyl-4*H*-4,11a-**

**(epiminomethano)[1,3,5]dithiazepino[5,4-*a*]indole-5,12(11*H*)-dione – (13, *anti* diastereoisomer)**



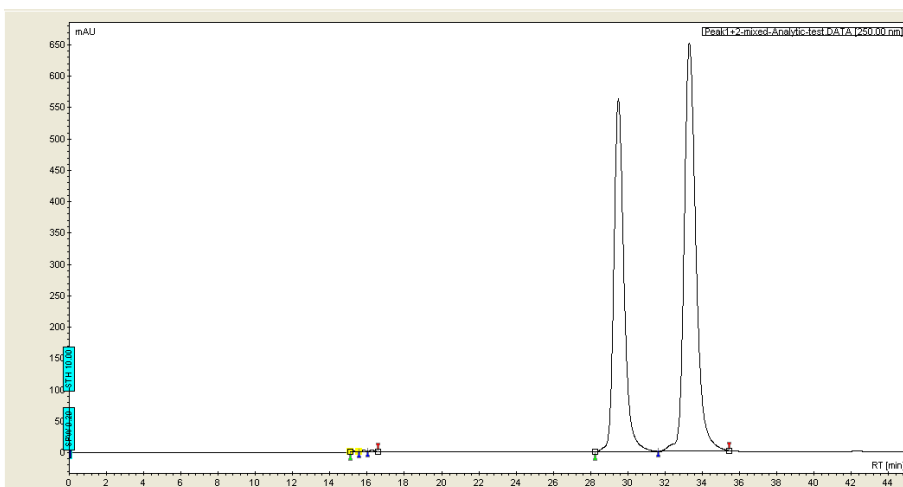
**NOESY Experiment:**



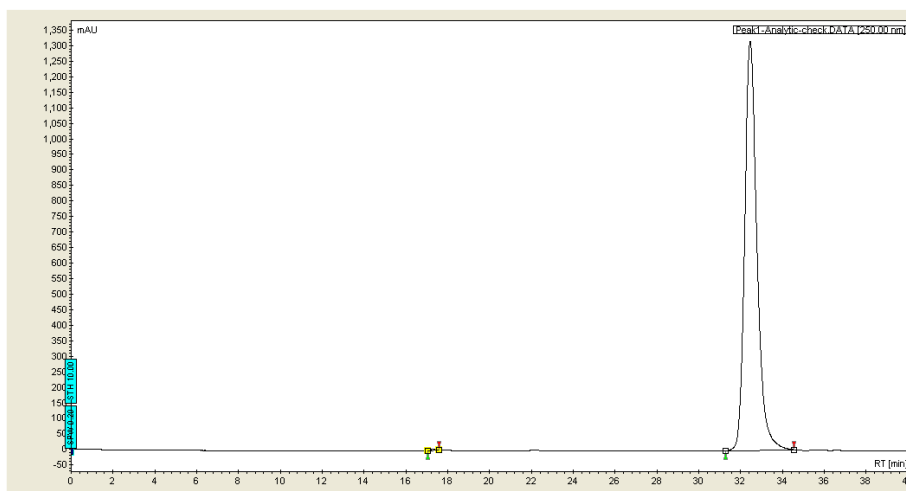
## 2. HPLC Traces compounds 7, 8 and 13

*Traces obtained on ODH column (analytical or semi-preparative).*

(±)-7 (Hexane – Isopropanol, 50:50)

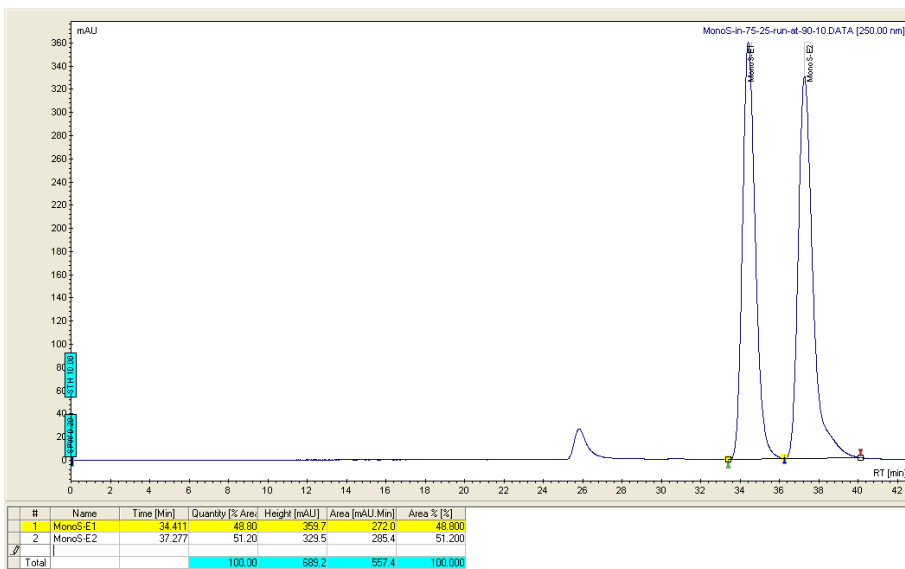


7 (First enantiomer separated, Hexane – Isopropanol, 50:50)



## Supporting Information

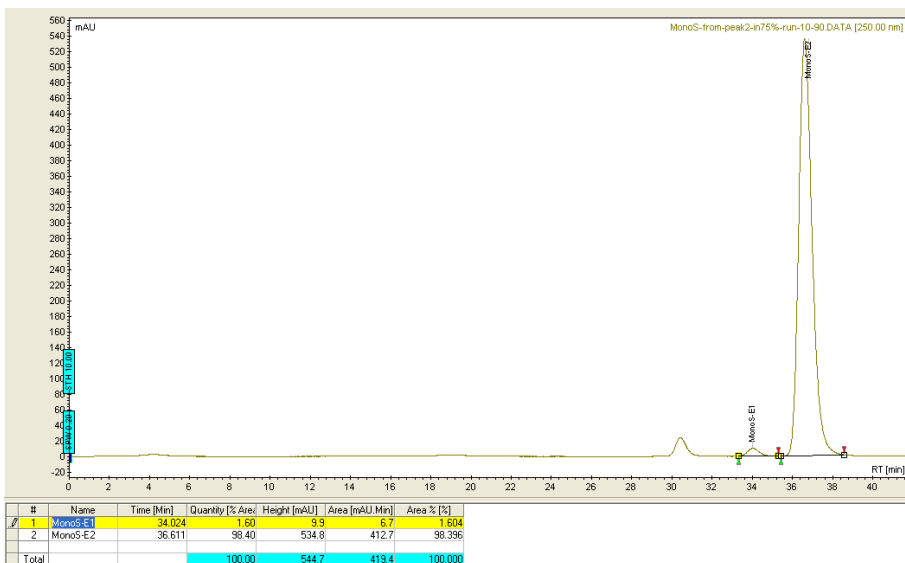
(±)-**8** obtained by reaction of (±)-**7** (Hexane – Isopropanol, 90:10)



**8** obtained by reaction of the first enantiomer of **7** (Hexane – Isopropanol, 90:10)

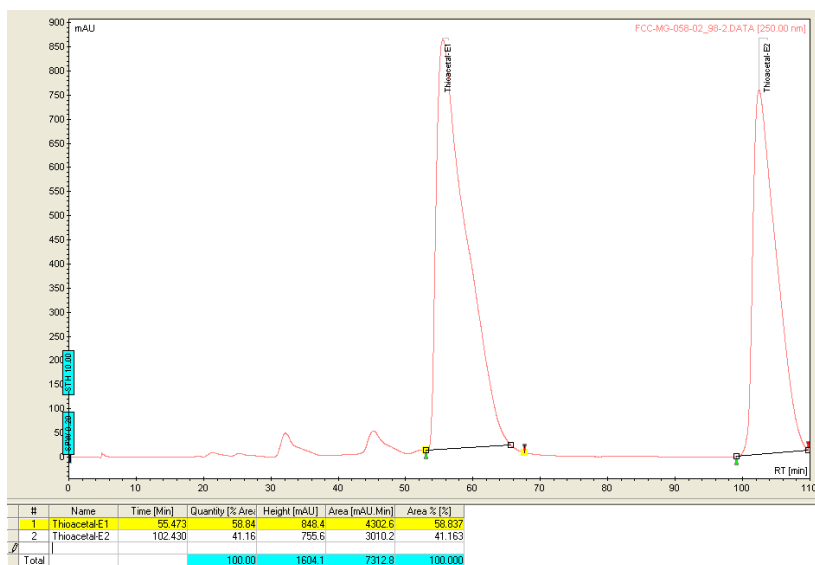


**8** obtained by reaction of second enantiomer of **7** (Hexane – Isopropanol, 90:10)

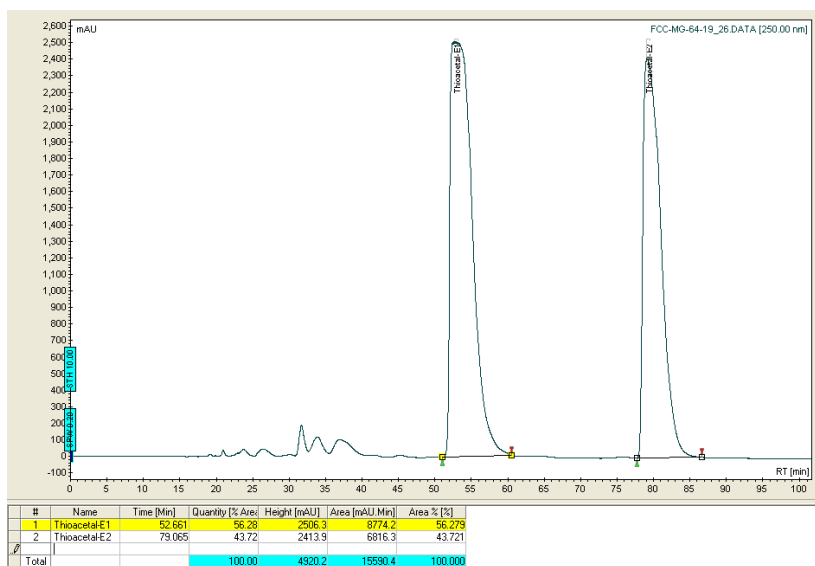


## Supporting Information

**13** obtained by reaction of ( $\pm$ )-**7** (Hexane – Isopropanol, 98:2)

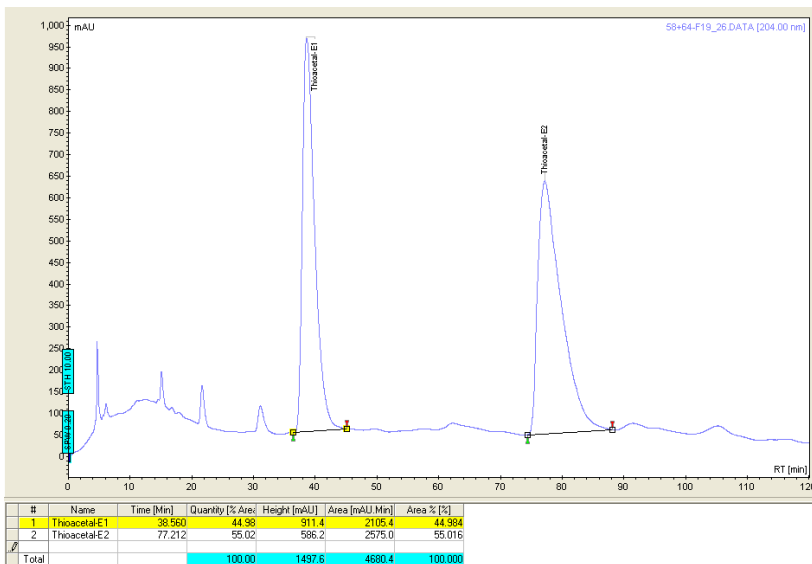


**13** obtained by reaction of ( $\pm$ )-**8**, diastereoisomer 2 (Hexane – Isopropanol, 98:2)

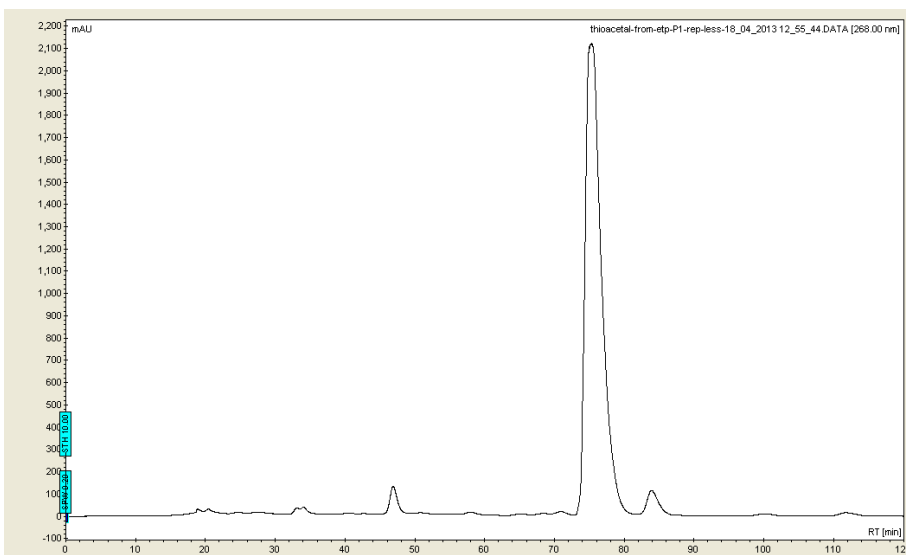


## Supporting Information

Mix **13** obtained by reaction of (±)-**7** and **13** obtained by reaction of (±)-**8**,  
diastereoisomer 2 (Hexane – Isopropanol, 98:2)



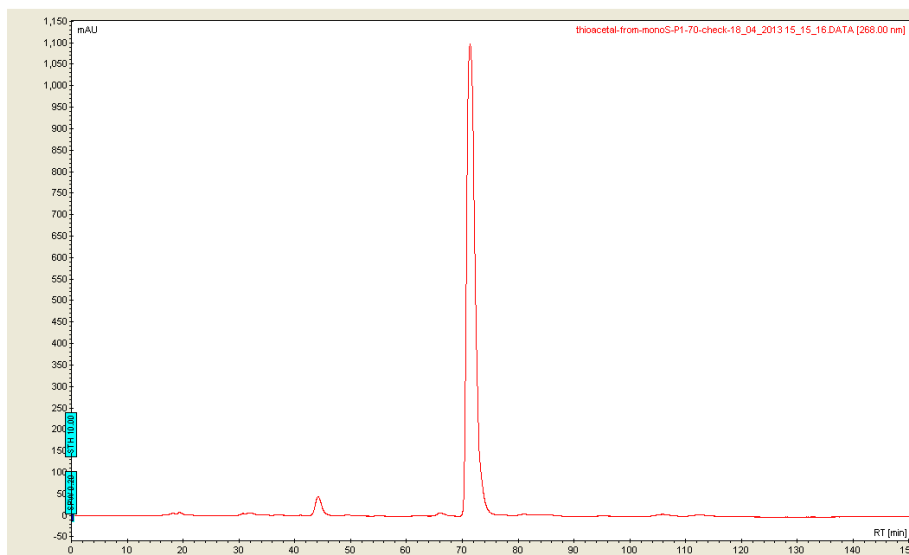
**13** obtained by reaction of **7**, first enantiomer (Hexane – Isopropanol, 98:2)



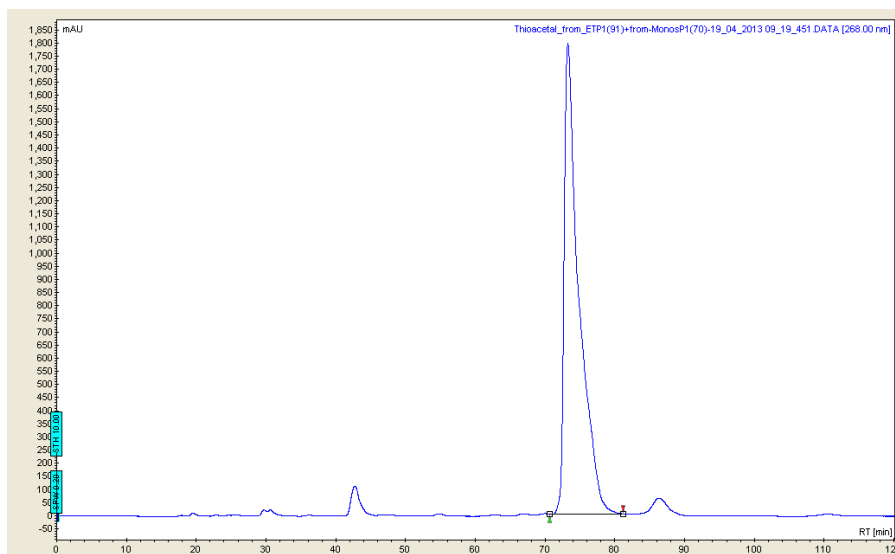


## Supporting Information

**13** obtained by reaction of **8**, first enantiomer (Hexane – Isopropanol, 98:2)



Mix **13** obtained by reaction of **7** first enantiomer and **13** obtained by reaction of **8**, first enantiomer (dia2) (Hexane – Isopropanol, 98:2)



### 3. References

- (1) Rueping, M.; Brinkmann, C.; Antonchick, A. P.; Atodiresei, I. *Org. Lett.* **2010**, *12*, 4604.
- (2) Ottenheijm, H. C. J.; Herscheid, J. D. M.; Kerkhoff, G. P. C.; Spande, T. *F. J. Org. Chem.* **1976**, *41*, 3433.