## **SUPPORTING INFORMATION**

## One-Pot Reductive Coupling of *N*-Acylcarbamates with Activated Alkenes: Application to the Asymmetric Synthesis of Pyrrolo[1,2-*a*]azepin-5-one Ring System and (–)-Xenovenine

Xue-Kui Liu, <sup>a</sup> Xiao Zheng, <sup>a</sup> Yuan-Ping Ruan, <sup>a</sup> Jie Ma, <sup>a</sup> and Pei-Qiang Huang\* <sup>a, b</sup>

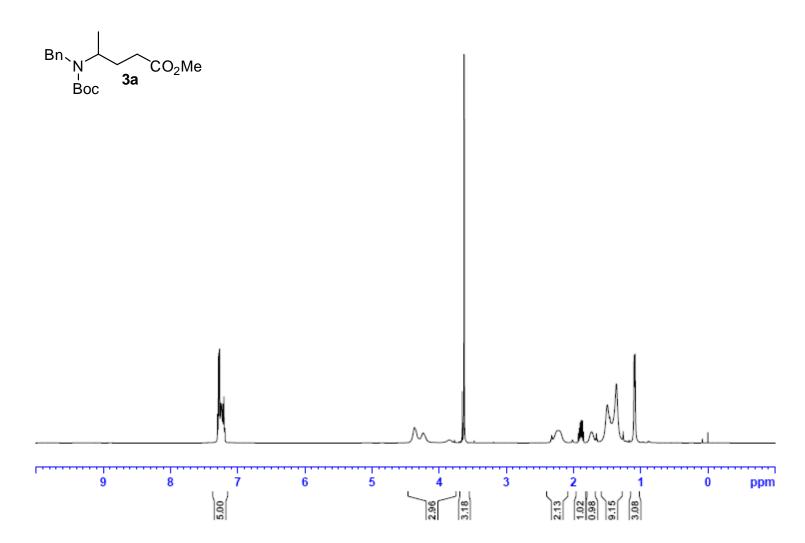
E-mail: pqhuang@xmu.edu.cn

## **Contents**

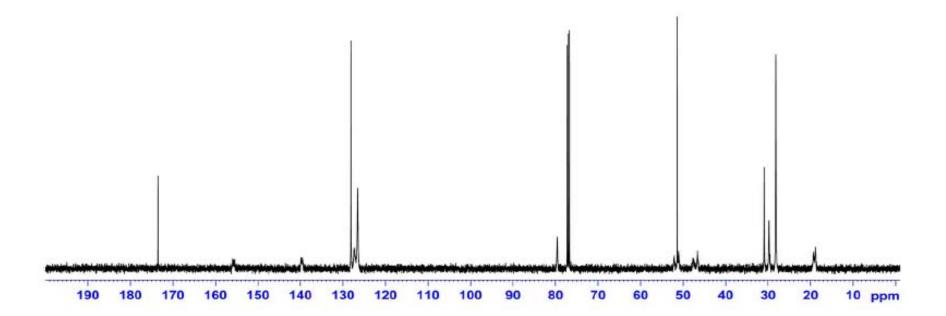
<sup>1</sup> H and <sup>13</sup> C NMR Spectra of all New Compounds and	S-2
(-)-Xenovenine	
Variable Temperature <sup>1</sup> H NMR of Compound 3e	S-11
2D-COSY Spectrum of Compound 16	S-59
2D-NOESY Spectrum of Compound 16	S-60
1D-GOESY Spectrum of Compound 16	S-61

<sup>&</sup>lt;sup>a</sup> Department of Chemistry and The Key Laboratory for Chemical Biology of Fujian Province, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, P. R. China; <sup>b</sup> The State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, P. R. China

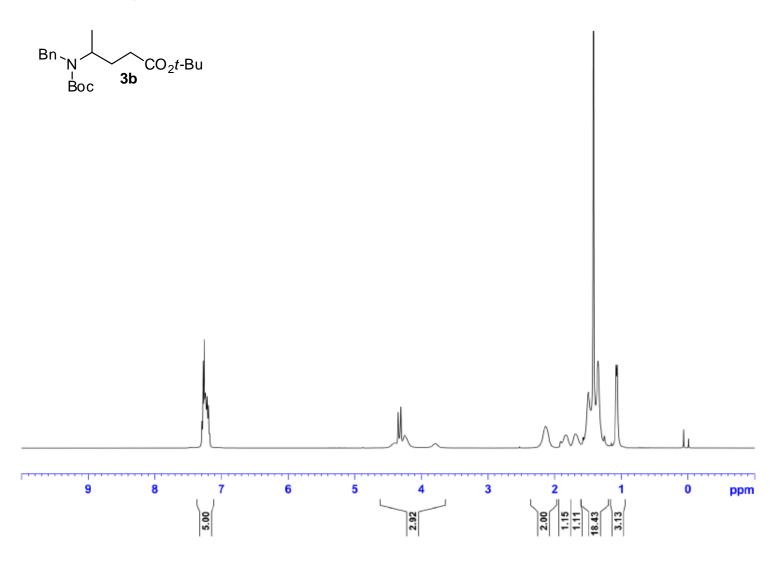
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **3a**:

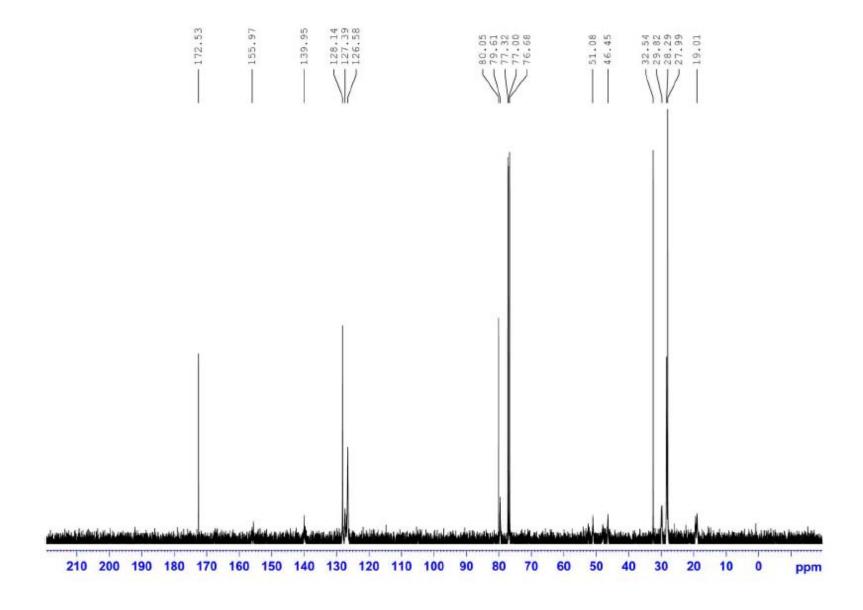




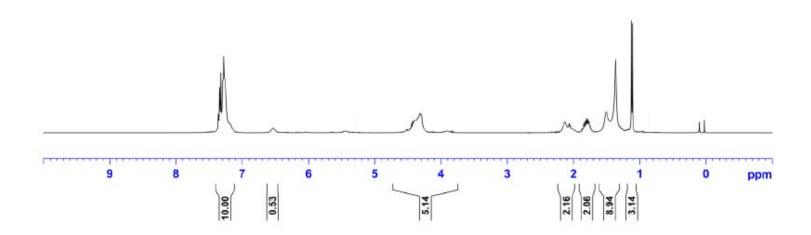


<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **3b**:

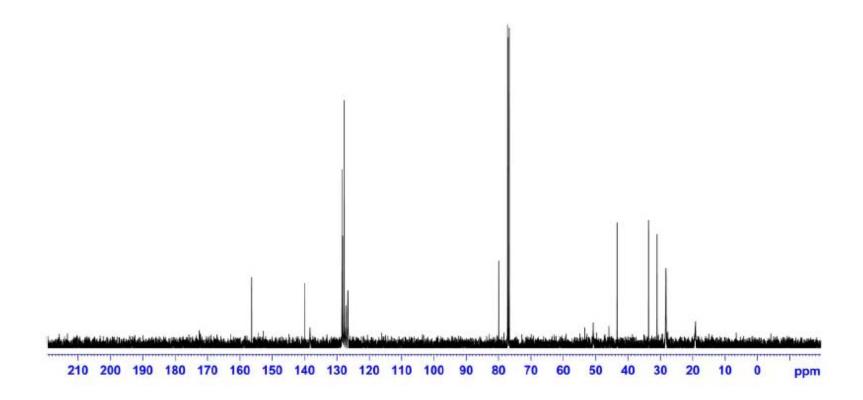




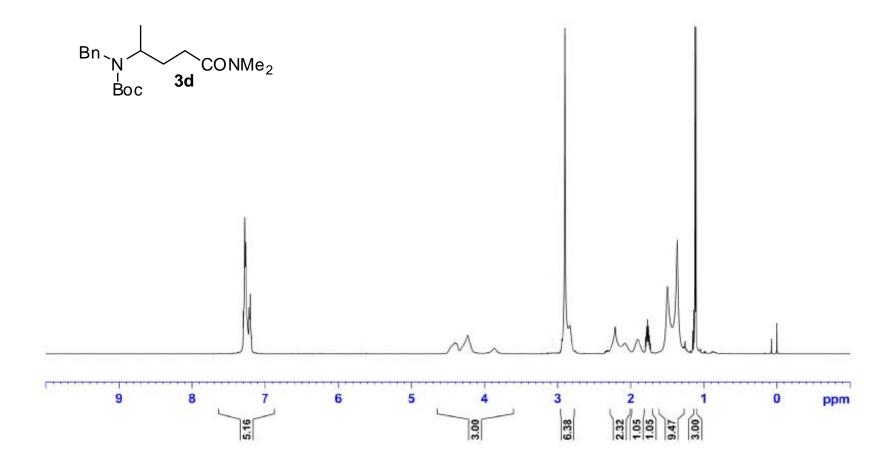
 $^{1}\text{H}$  NMR and  $^{13}\text{C}$  NMR data of compound 3c:

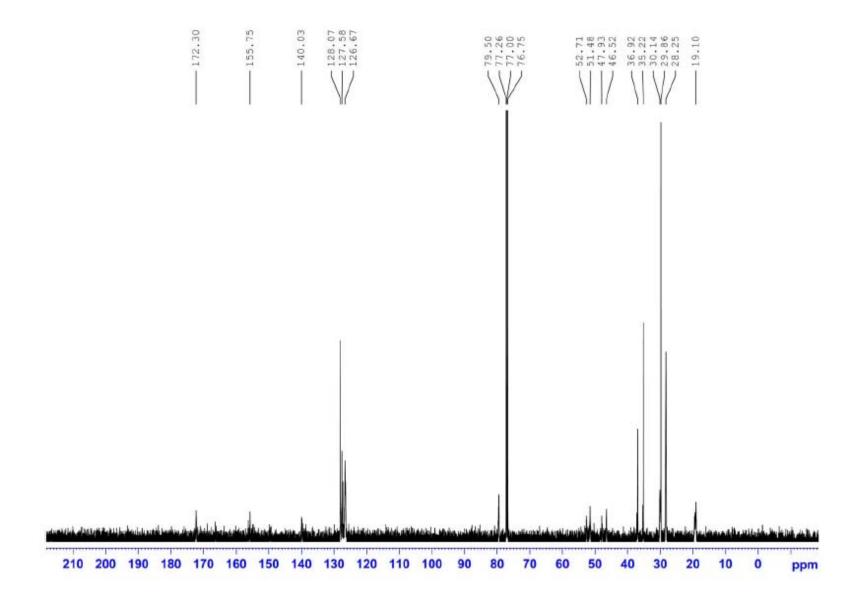




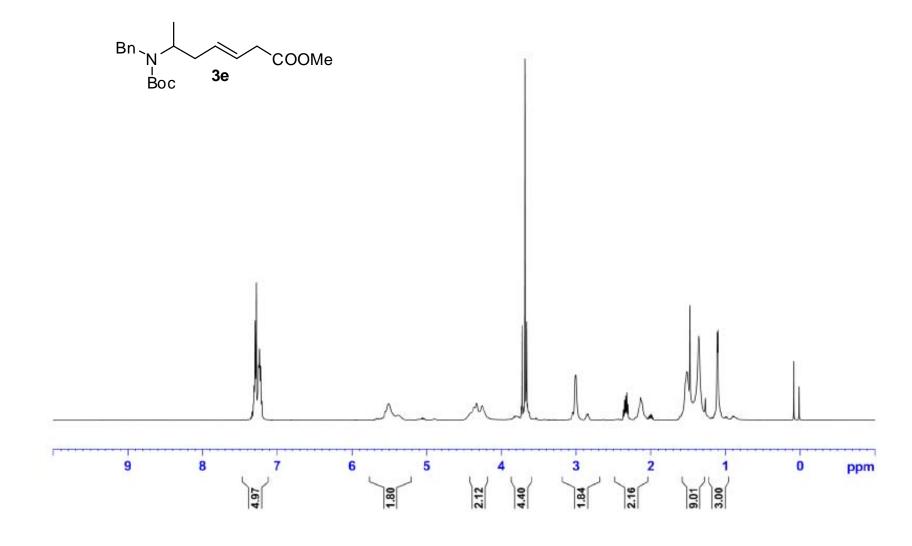


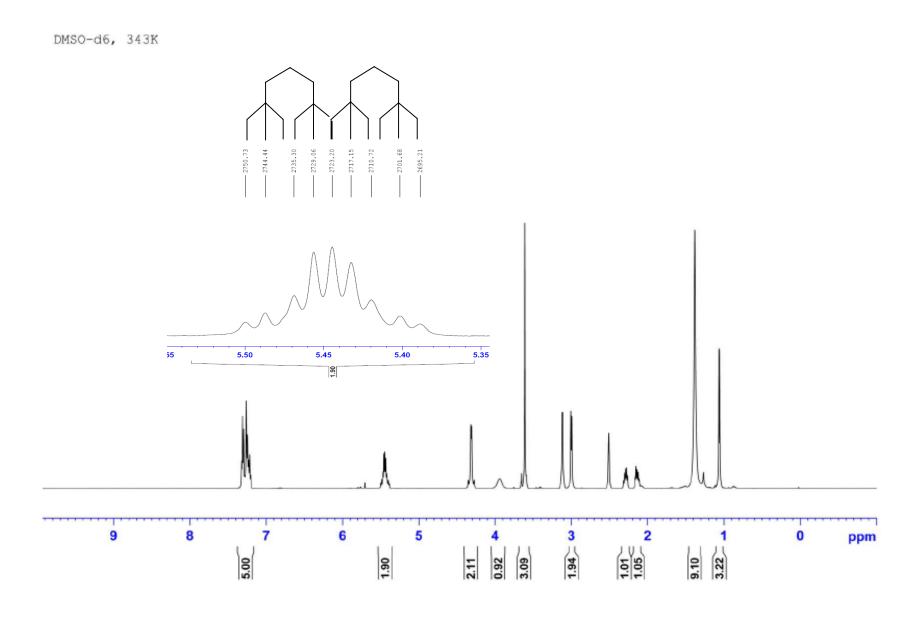
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **3d**:

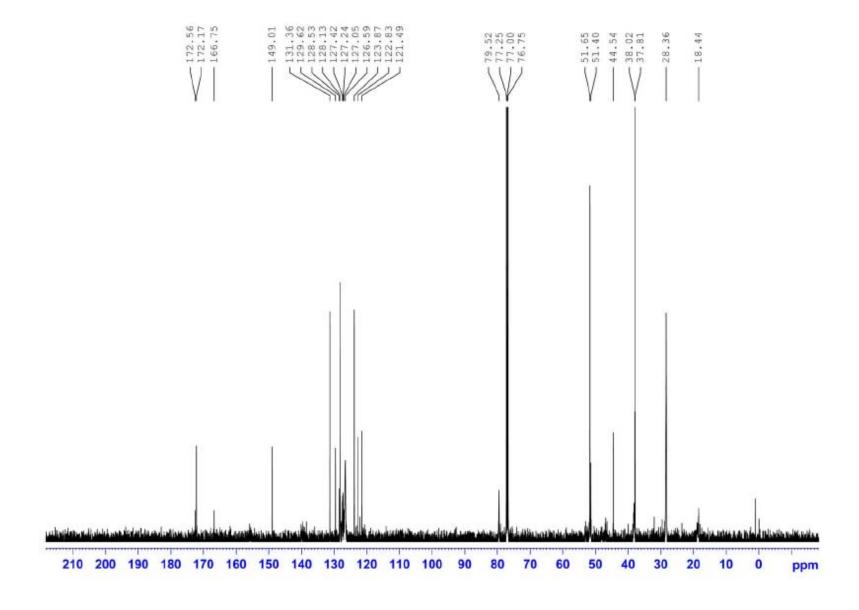




<sup>1</sup>H NMR, VT <sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **3e**:

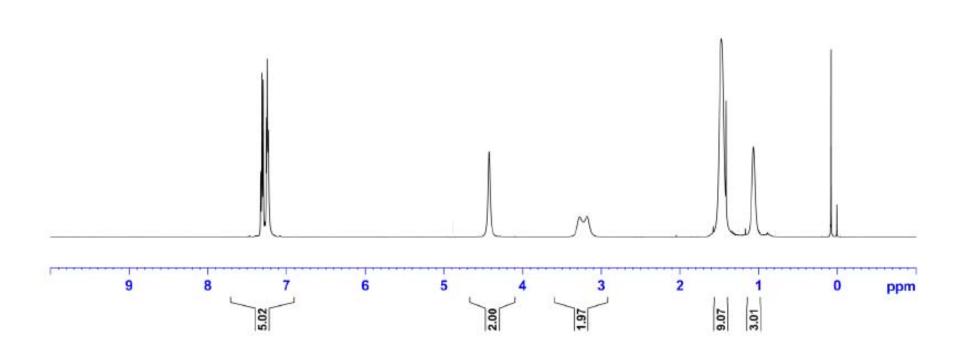


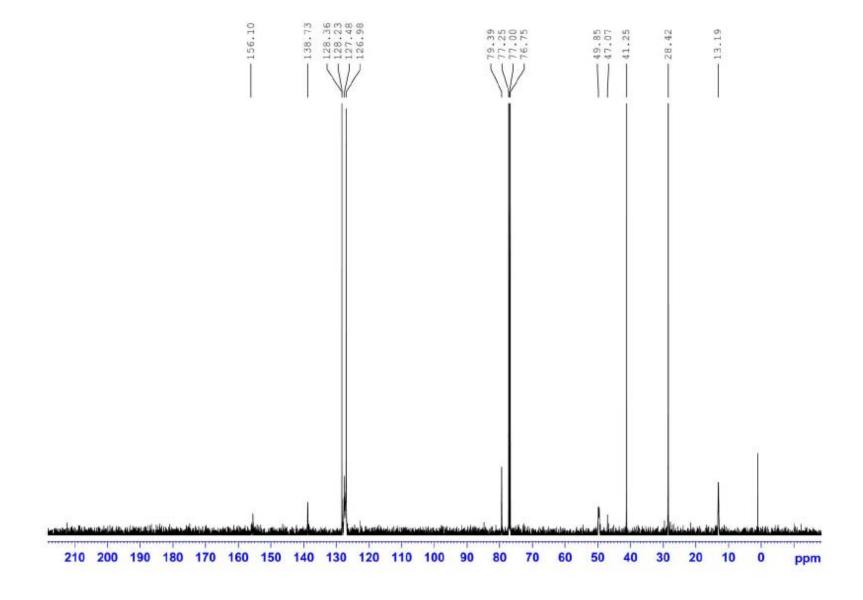




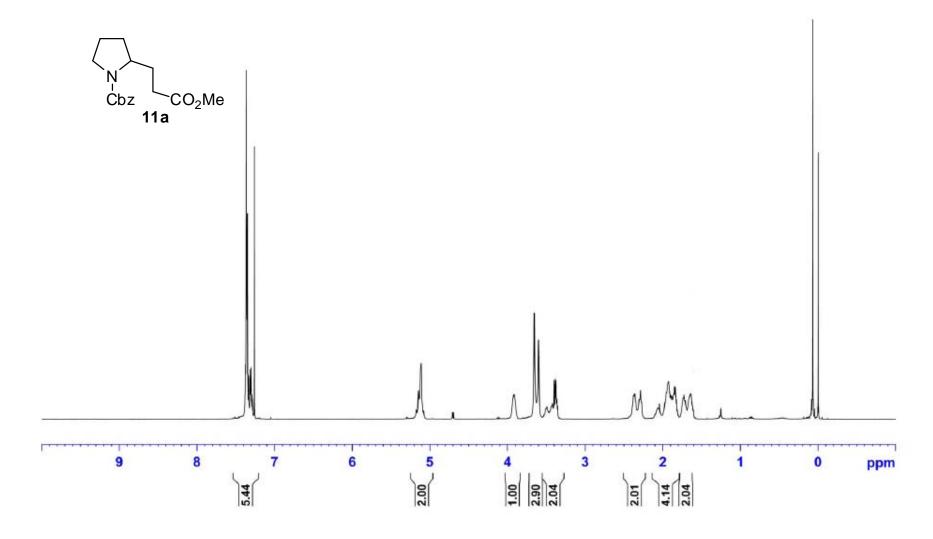
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **9**:

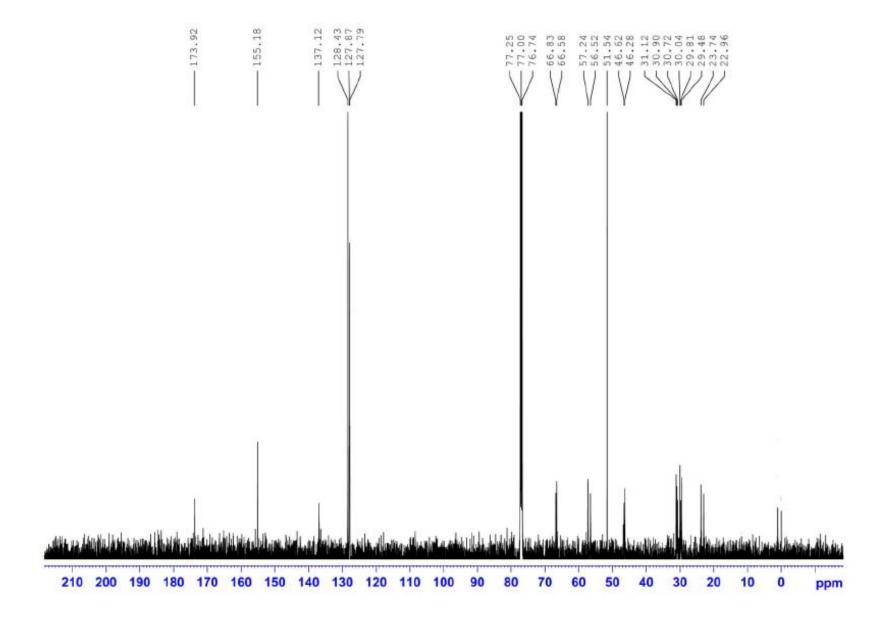




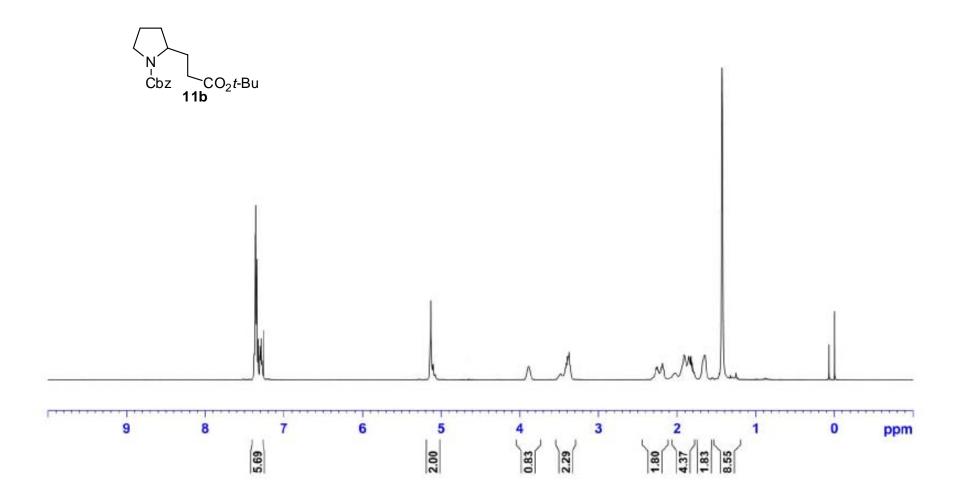


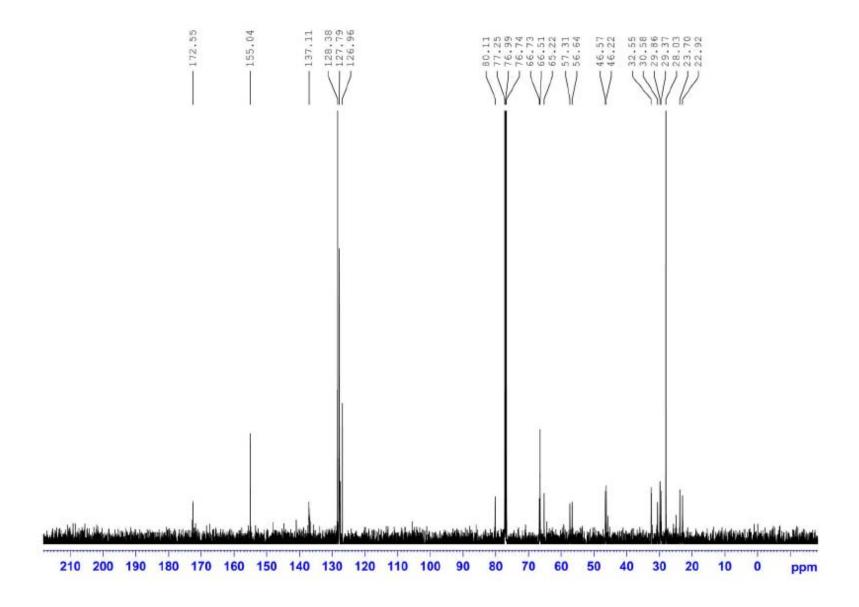
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **11a**:



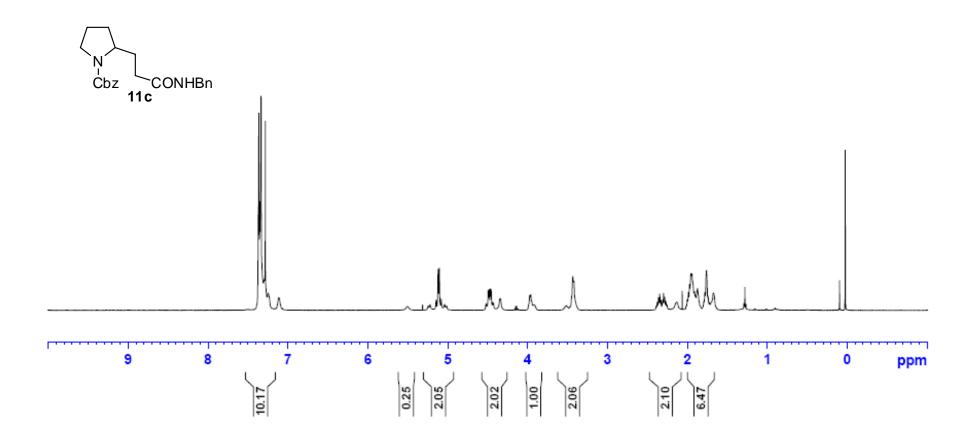


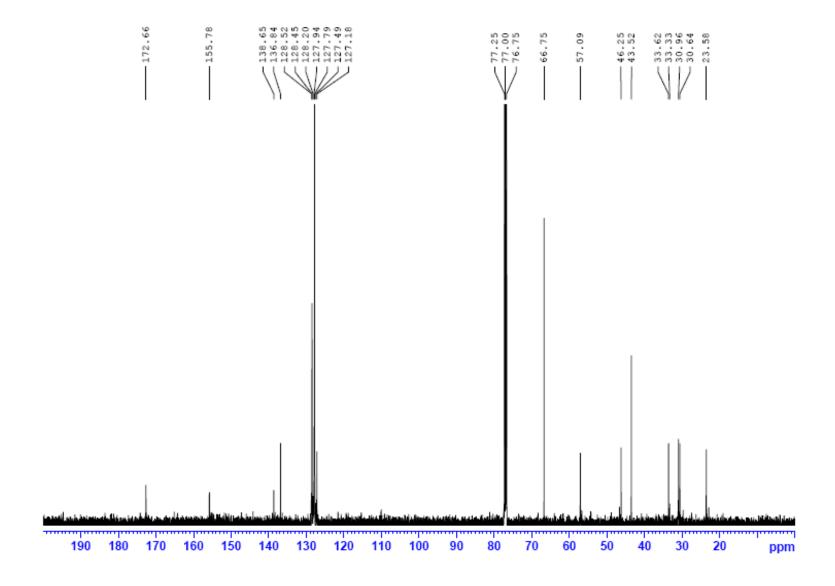
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **11b**:



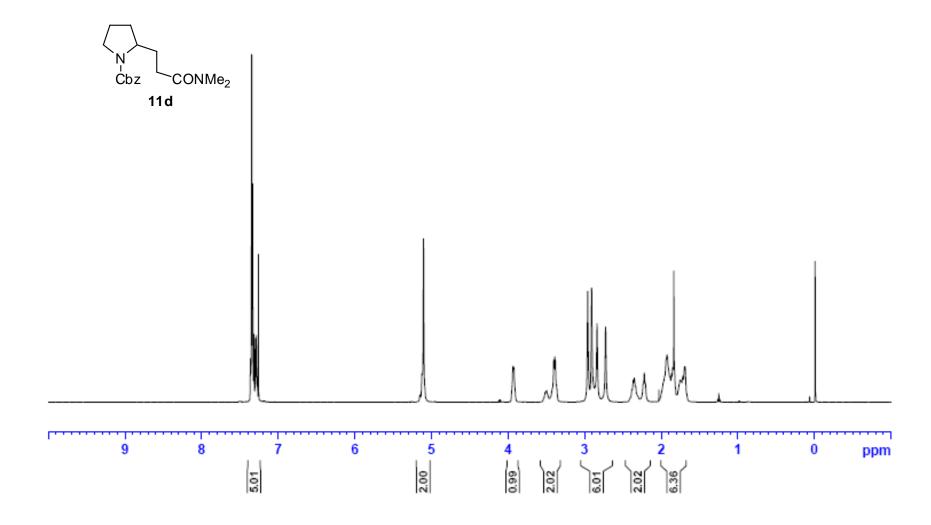


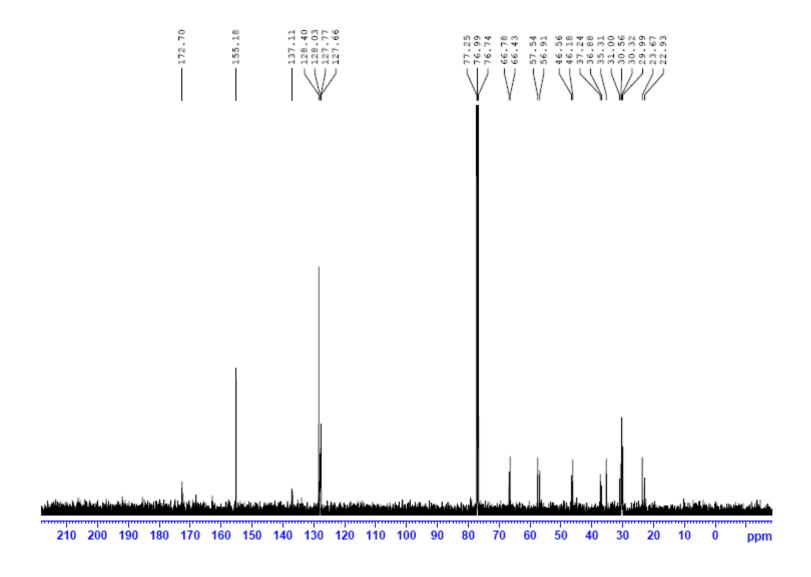
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **11c**:



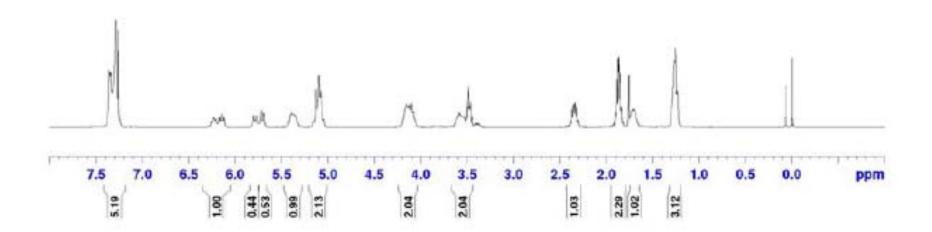


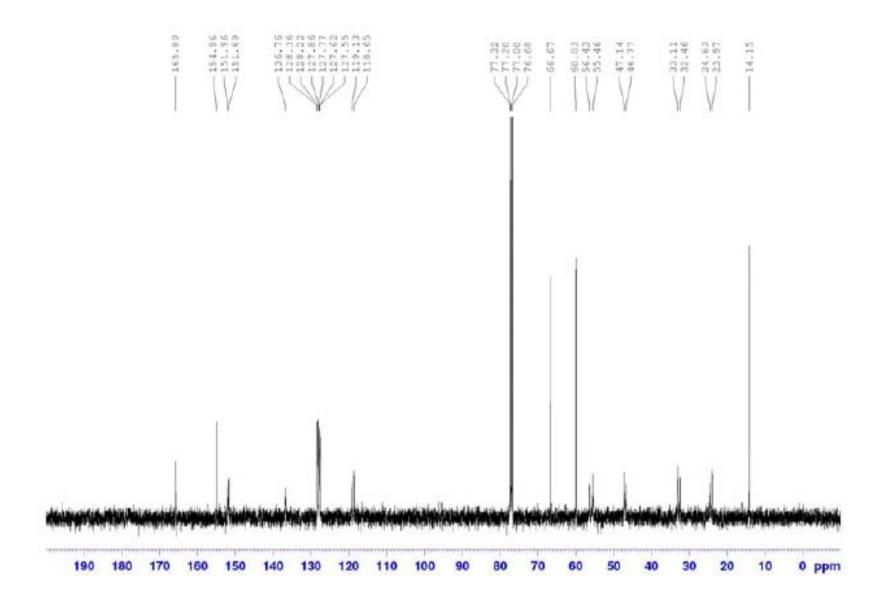
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **11d**:



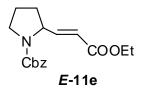


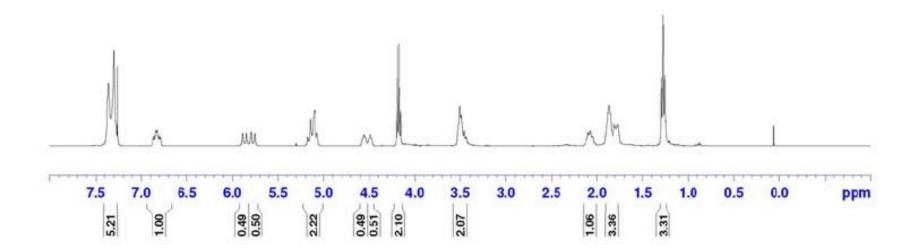
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **Z-11e**:

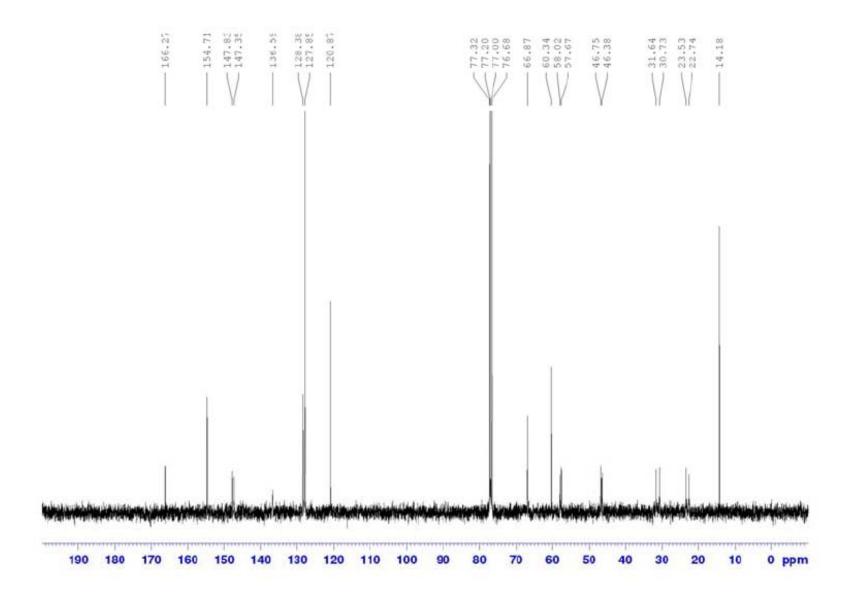




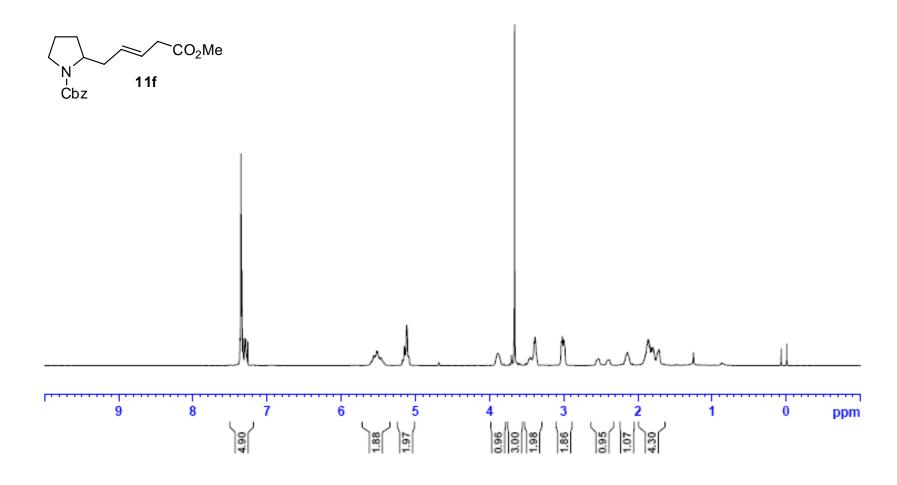
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound *E***-11e**:

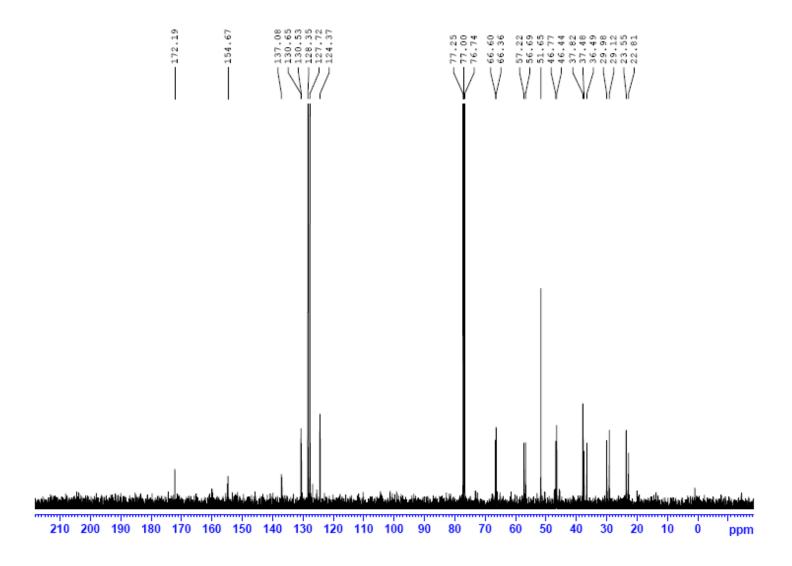




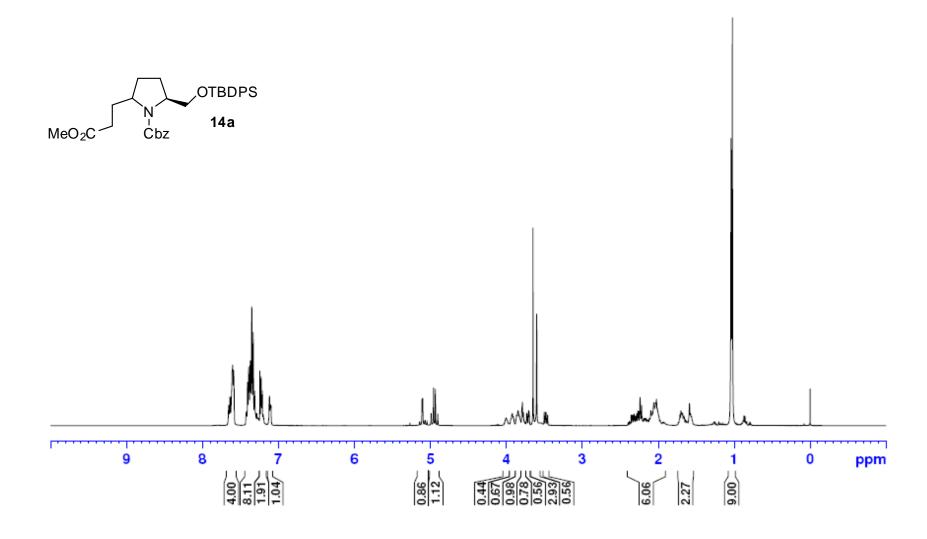


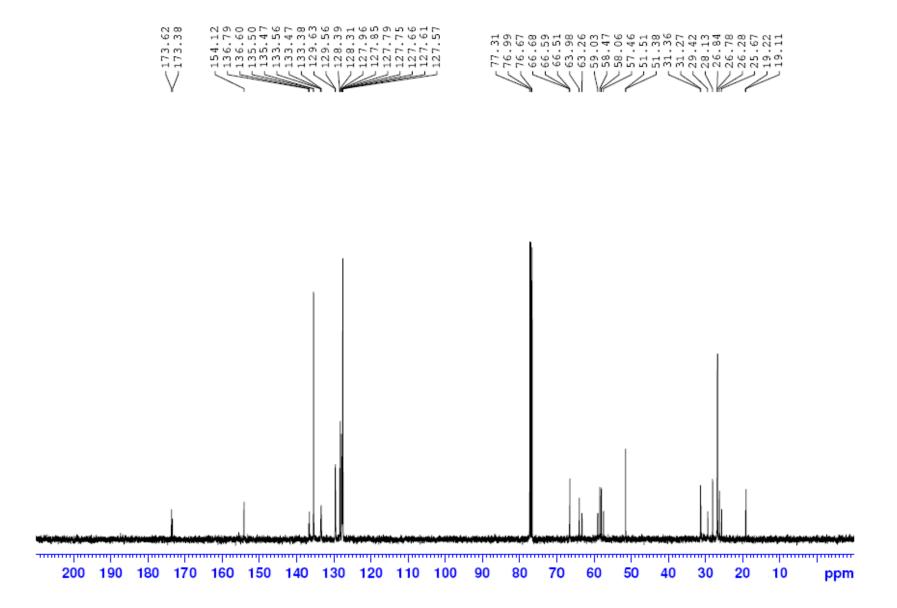
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **11f**:



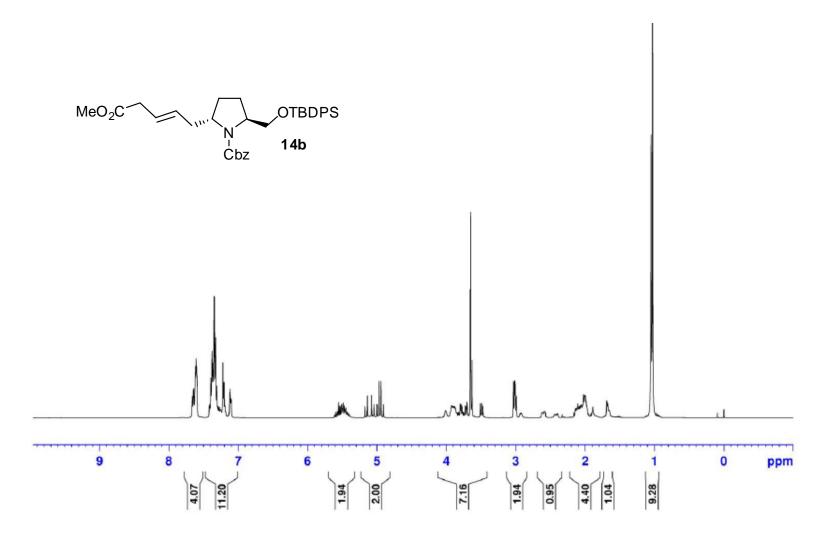


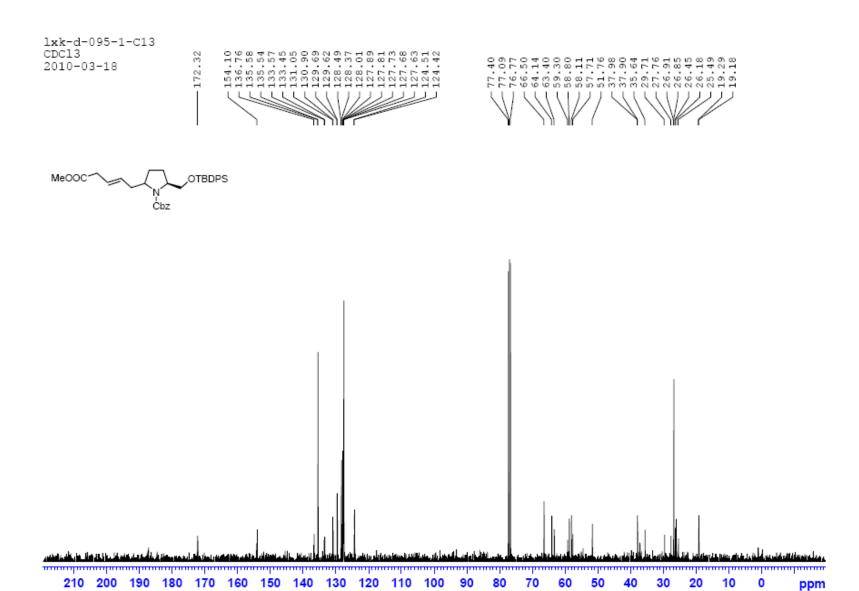
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **14a**:



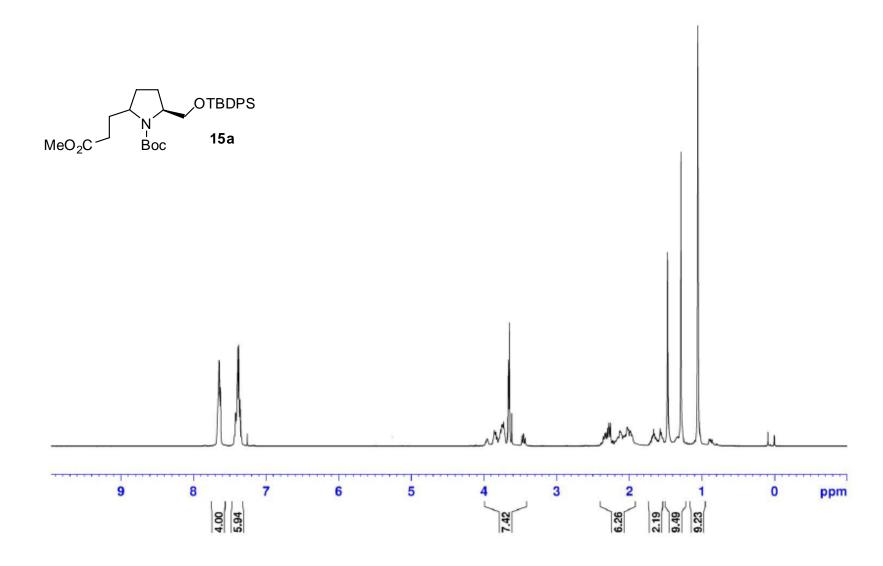


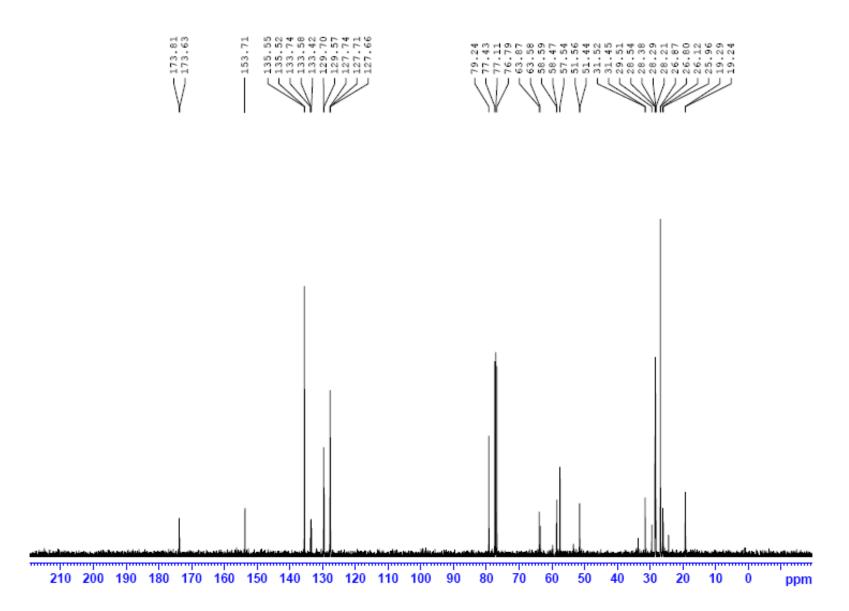
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **14b**:



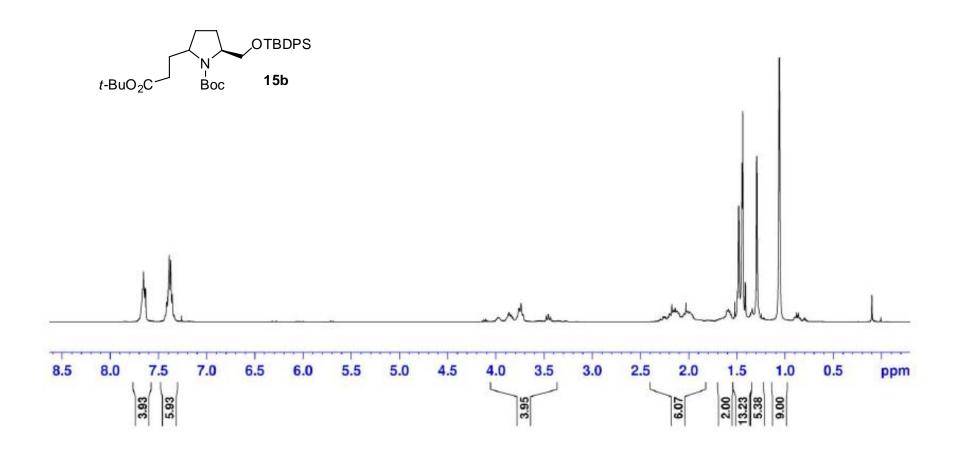


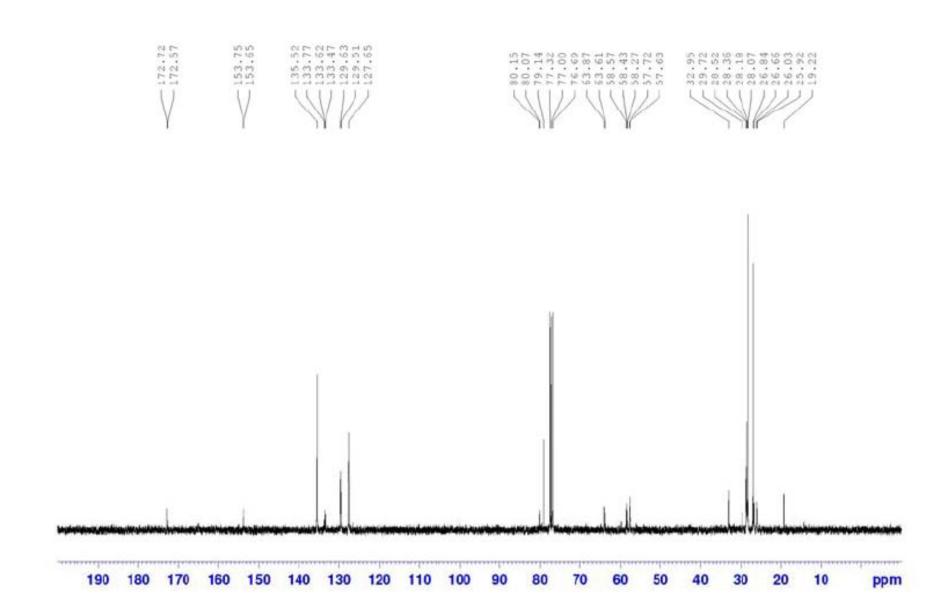
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **15a**:



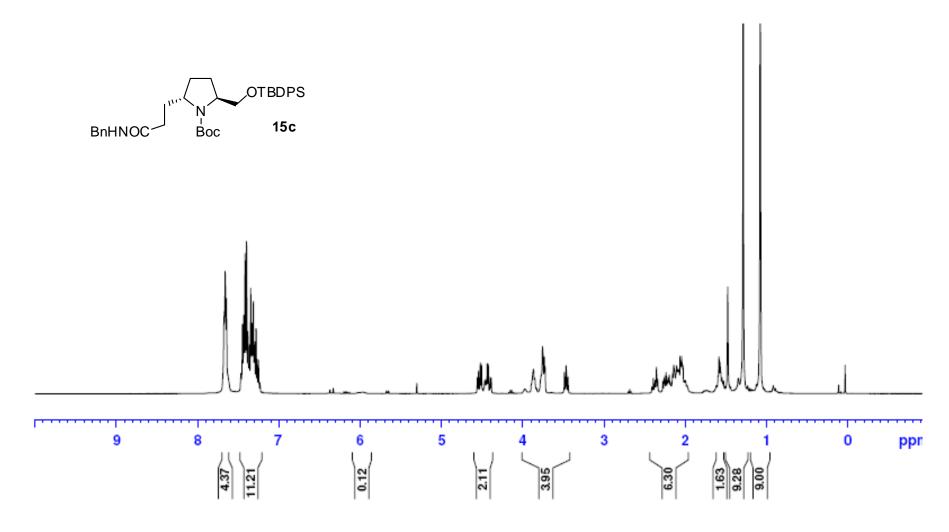


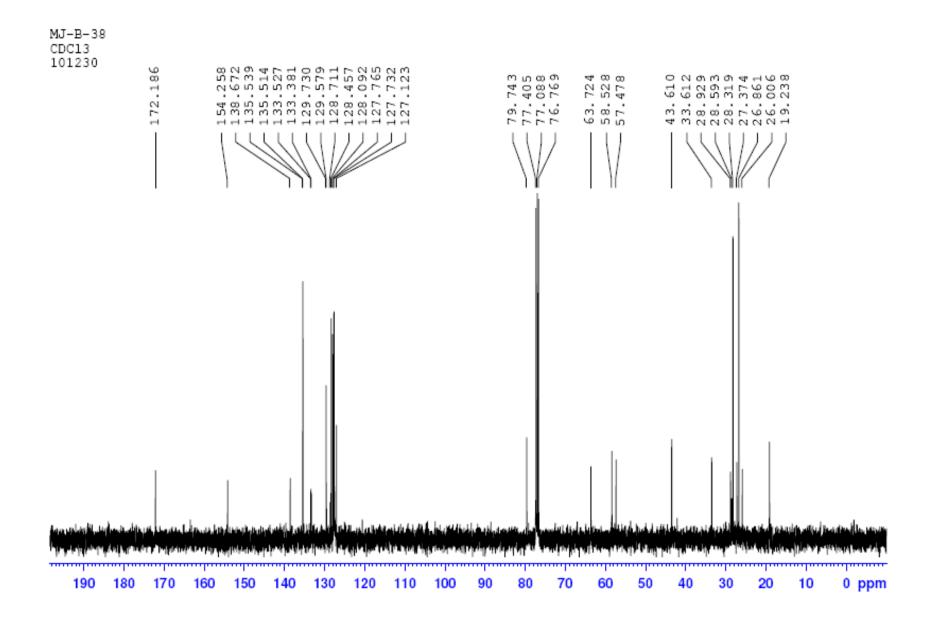
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **15b**:



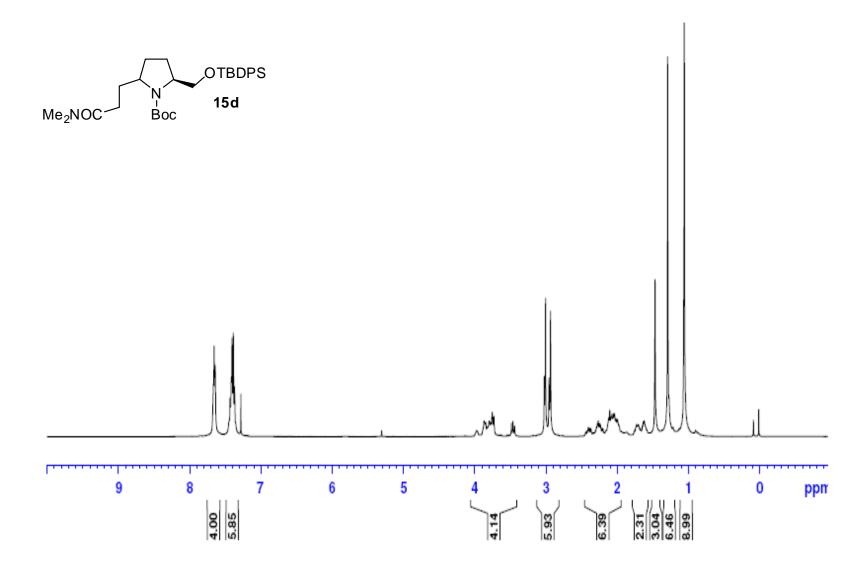


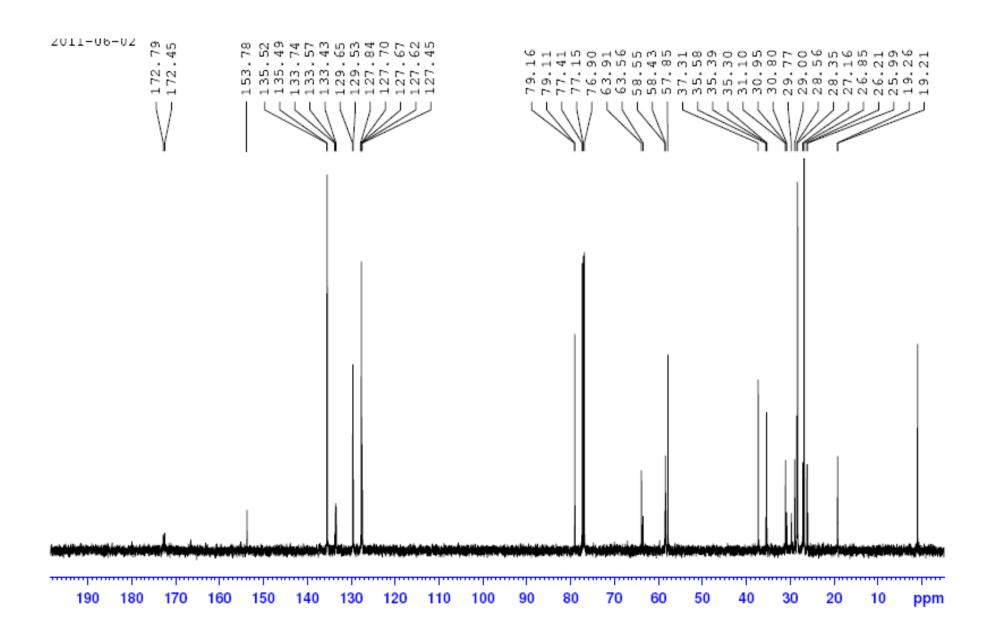
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **15c**:

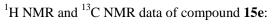


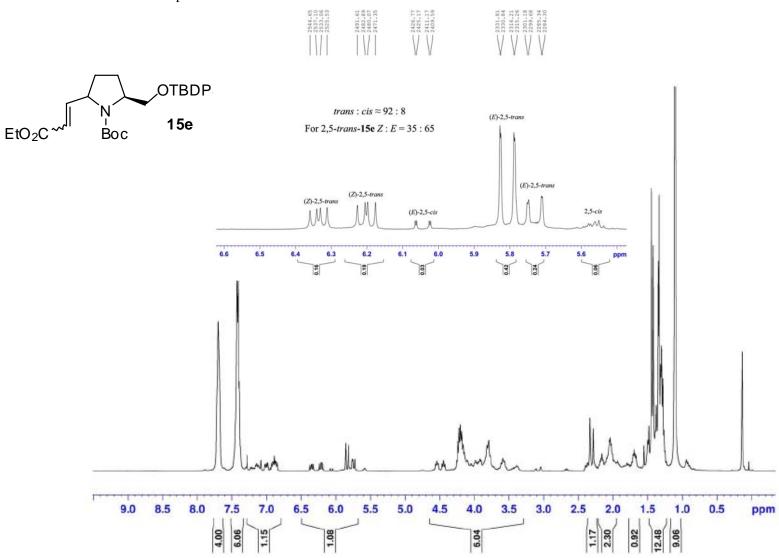


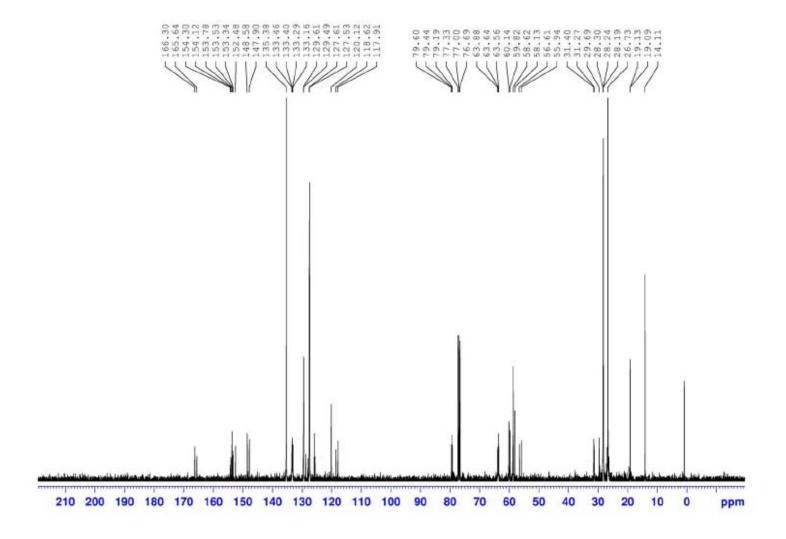
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **15d**:



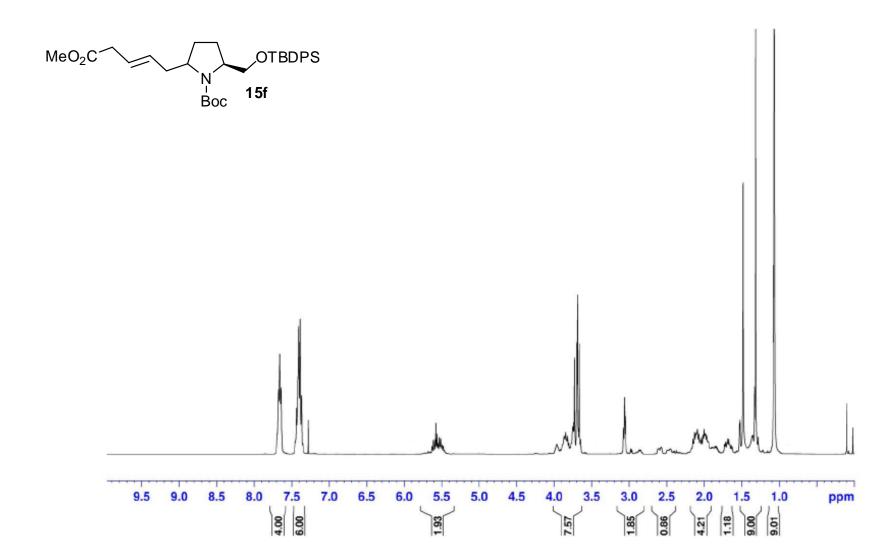


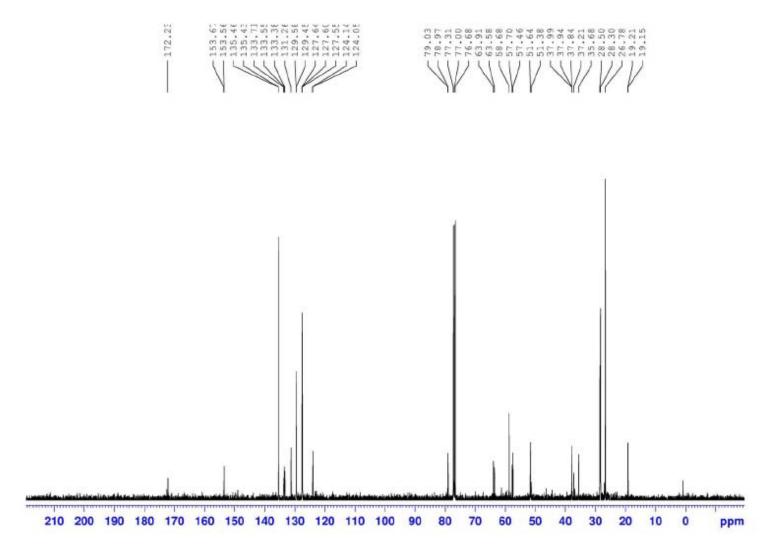




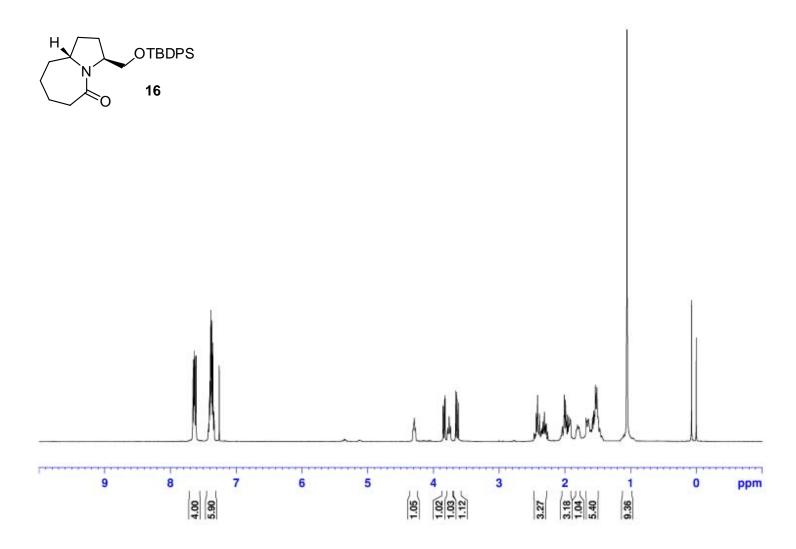


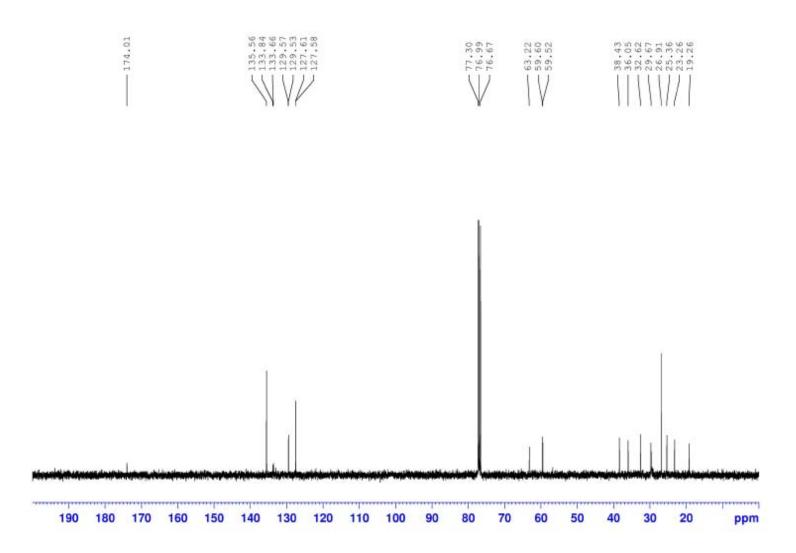
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **15f**:



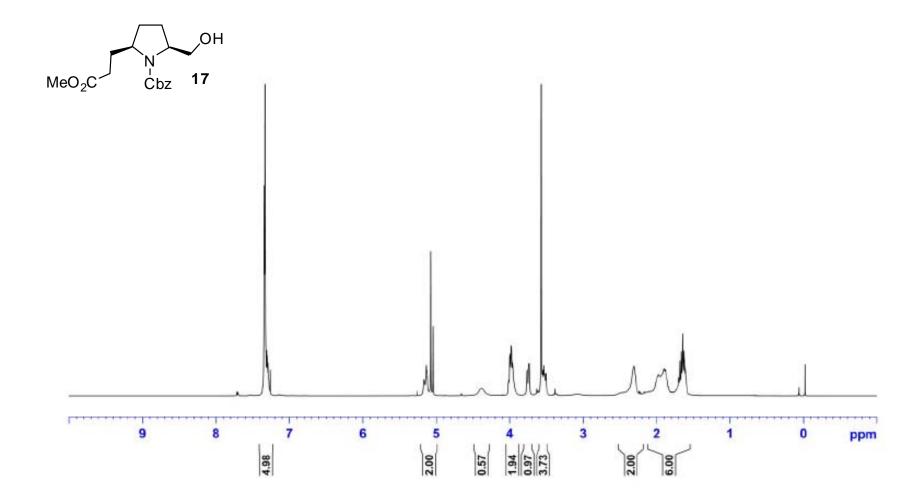


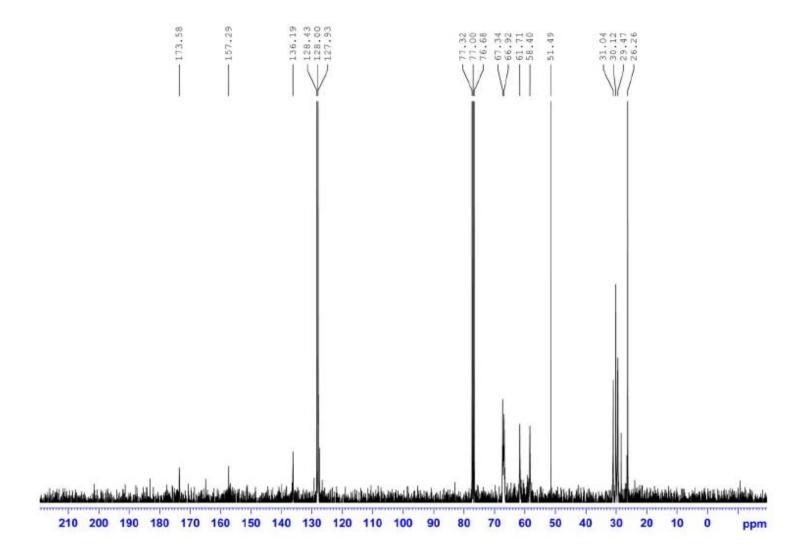
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **16**:



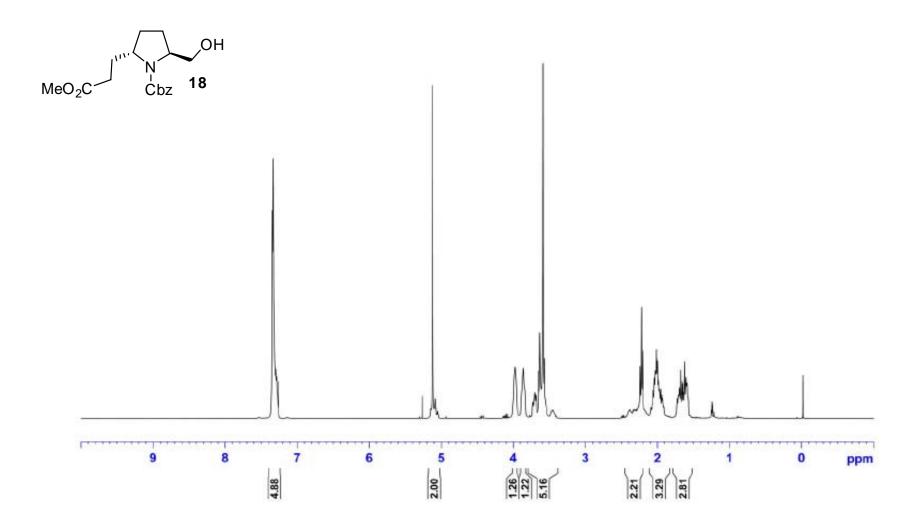


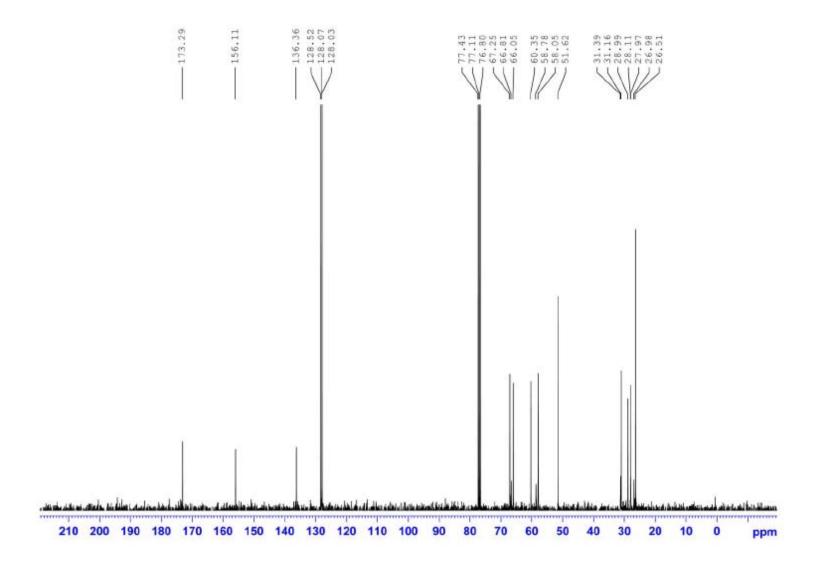
 $^{1}\text{H NMR}$  and  $^{13}\text{C NMR}$  data of compound 17:



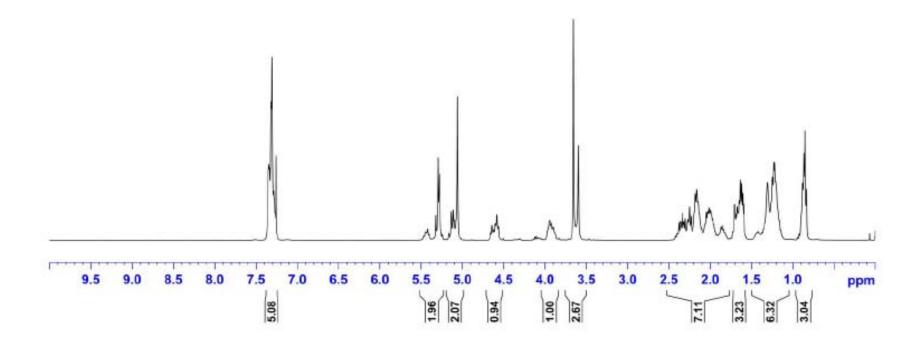


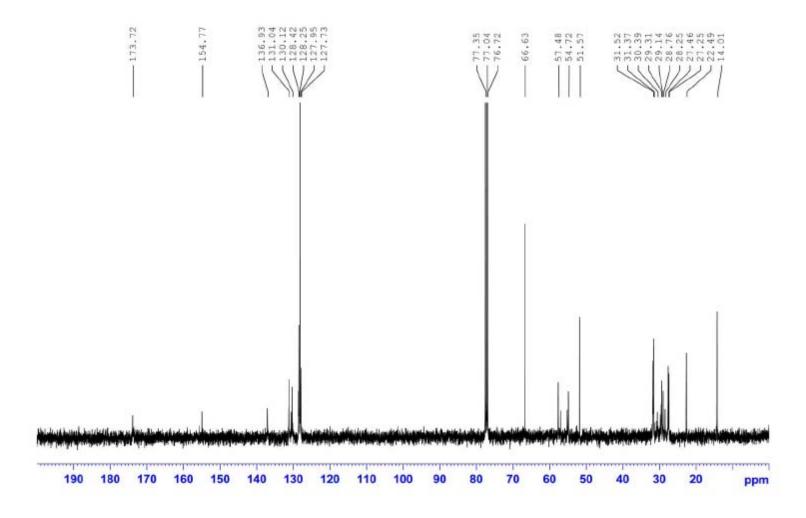
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **18**:



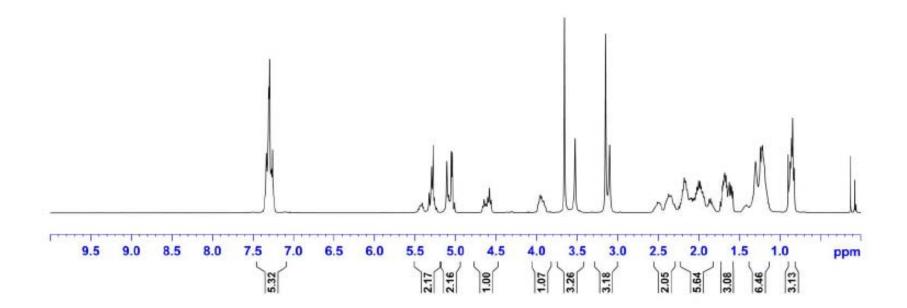


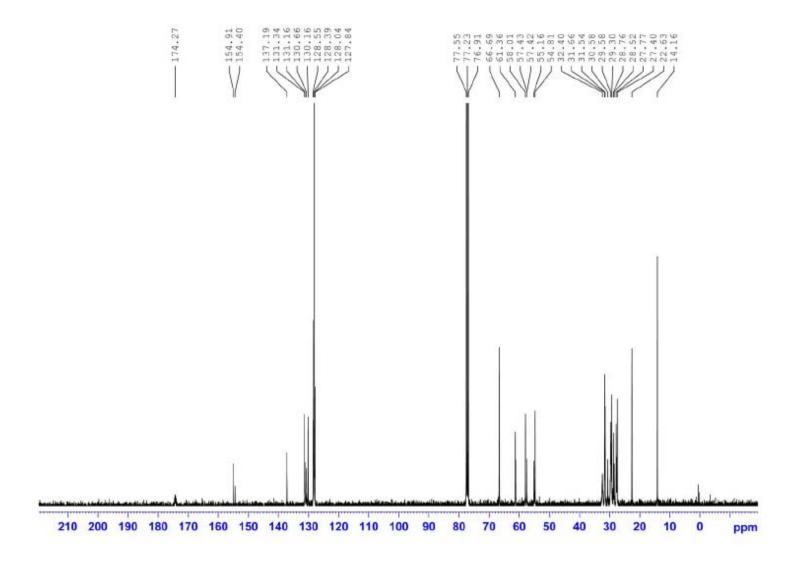
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **19**:



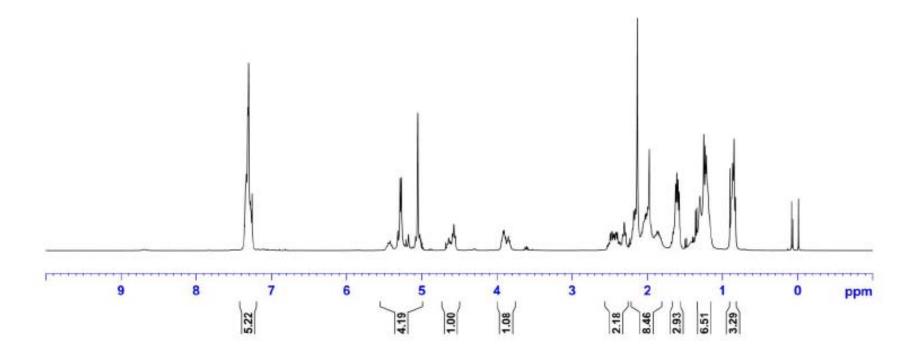


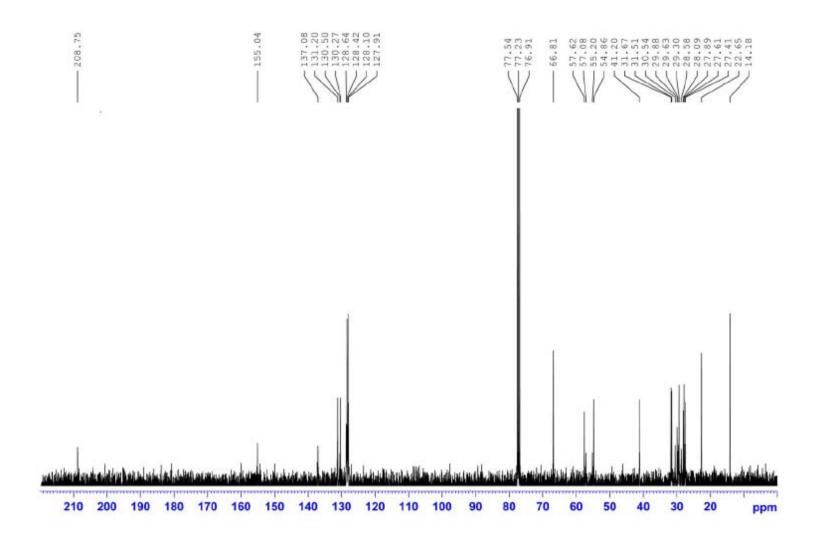
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **20**:



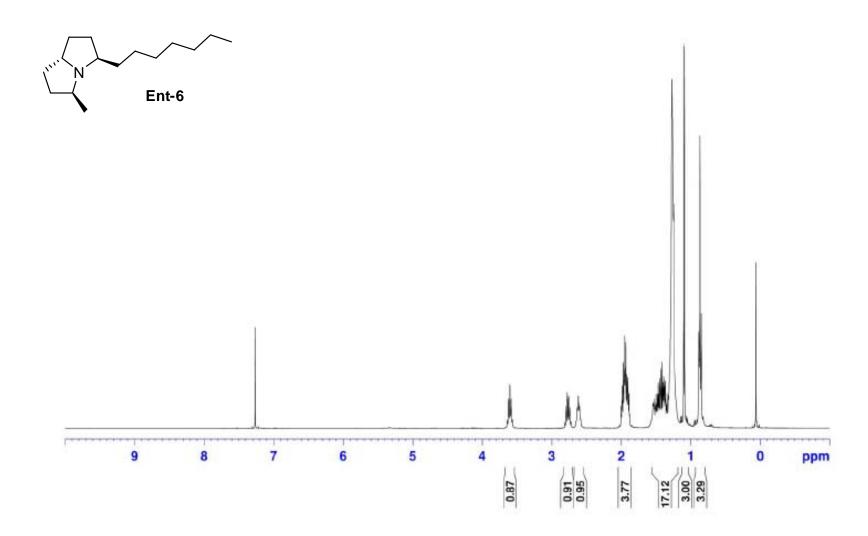


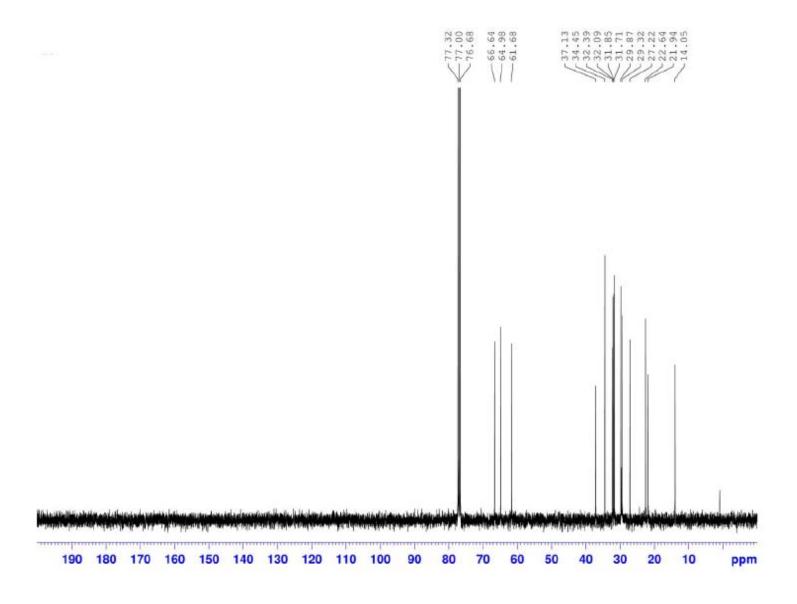
<sup>1</sup>H NMR and <sup>13</sup>C NMR data of compound **21**:



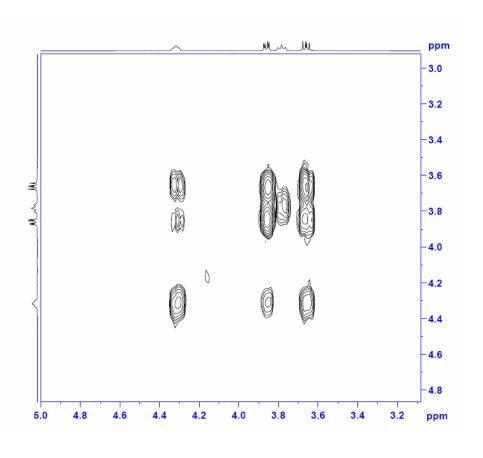


<sup>1</sup>H NMR and <sup>13</sup>C NMR data of (–)-xenovenine (ent-6) :



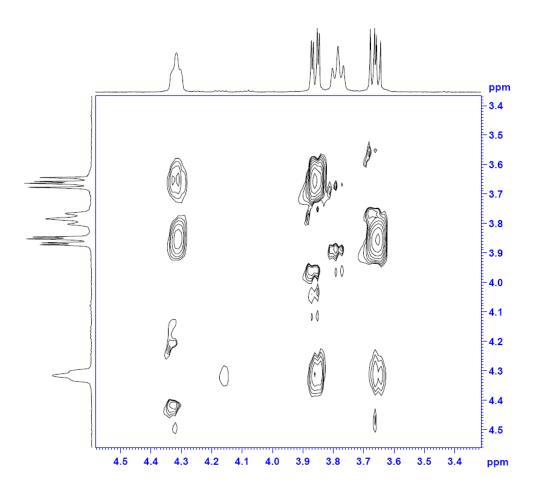


2D-COSY of compound **16**:



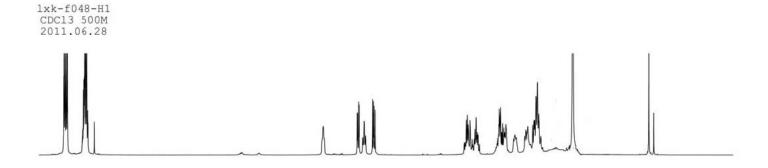
<sup>1</sup>H-<sup>1</sup>H COSY

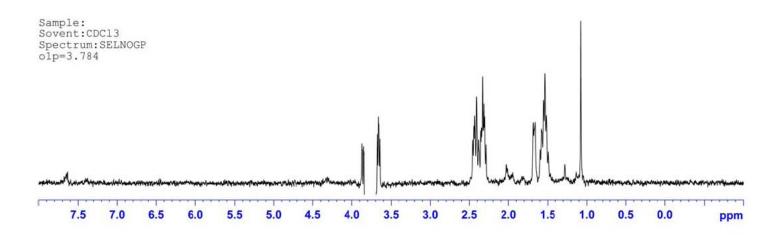
## 2D-NOESY of compound **16**:



2D NOESY

## 1D-GOESY of compound **16**:





1D GOESY