

**Bismuth triflate-catalyzed Wagner-Meerwein rearrangements in terpenes. Application to the synthesis of the 18 $\alpha$ -oleanane core and A-*neo*-18 $\alpha$ -oleanene compounds from lupanes .**

**Jorge A. R. Salvador,<sup>\*a,b</sup> Rui M. A. Pinto,<sup>a</sup> Rita C. Santos,<sup>a</sup> Christophe Le Roux,<sup>c</sup>  
Ana Matos Beja<sup>d</sup> and José A. Paixão<sup>d</sup>**

<sup>a</sup>Laboratório de Química Farmacêutica, Faculdade de Farmácia, Universidade de Coimbra, 3000-295 Coimbra, Portugal. Fax: +351 239 827126; Tel: +351 239 859950

<sup>b</sup>Instituto Pedro Nunes-Labpharm, Rua Pedro Nunes, 3030-199 Coimbra, Portugal

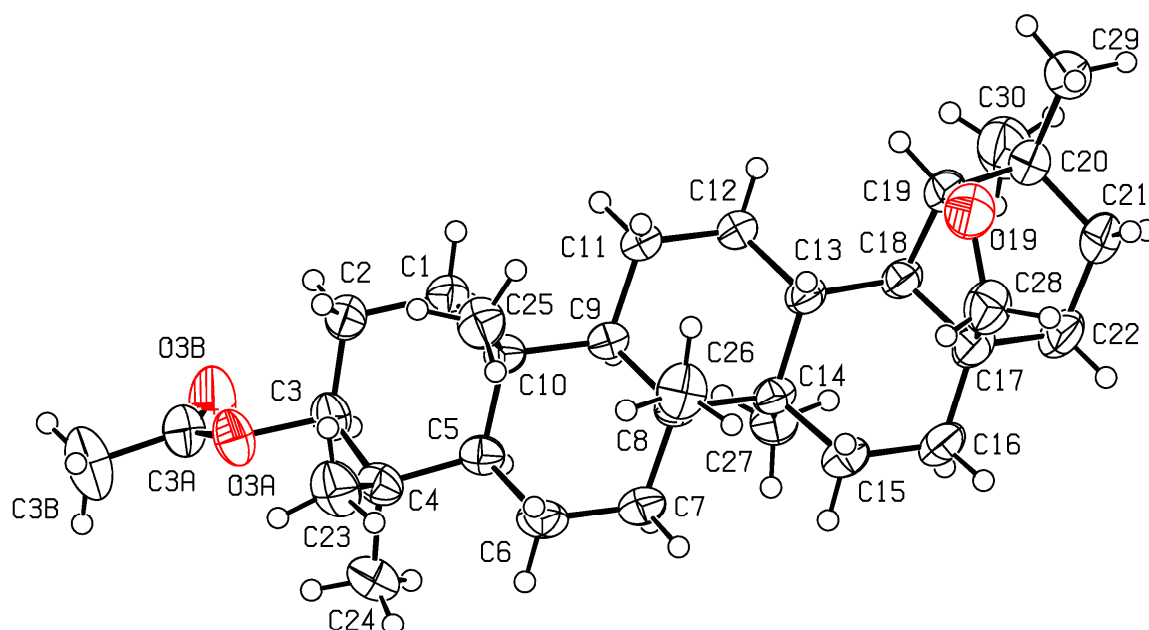
<sup>c</sup>Laboratoire Hétérochimie Fondamentale et Appliquée, Université Paul Sabatier, 118, route de Narbonne, 31062 Toulouse Cedex 9, France

<sup>d</sup>CEMDRX, Departamento de Física, Faculdade de Ciências e Tecnologia, Universidade de Coimbra, 3004-516 Coimbra, Portugal

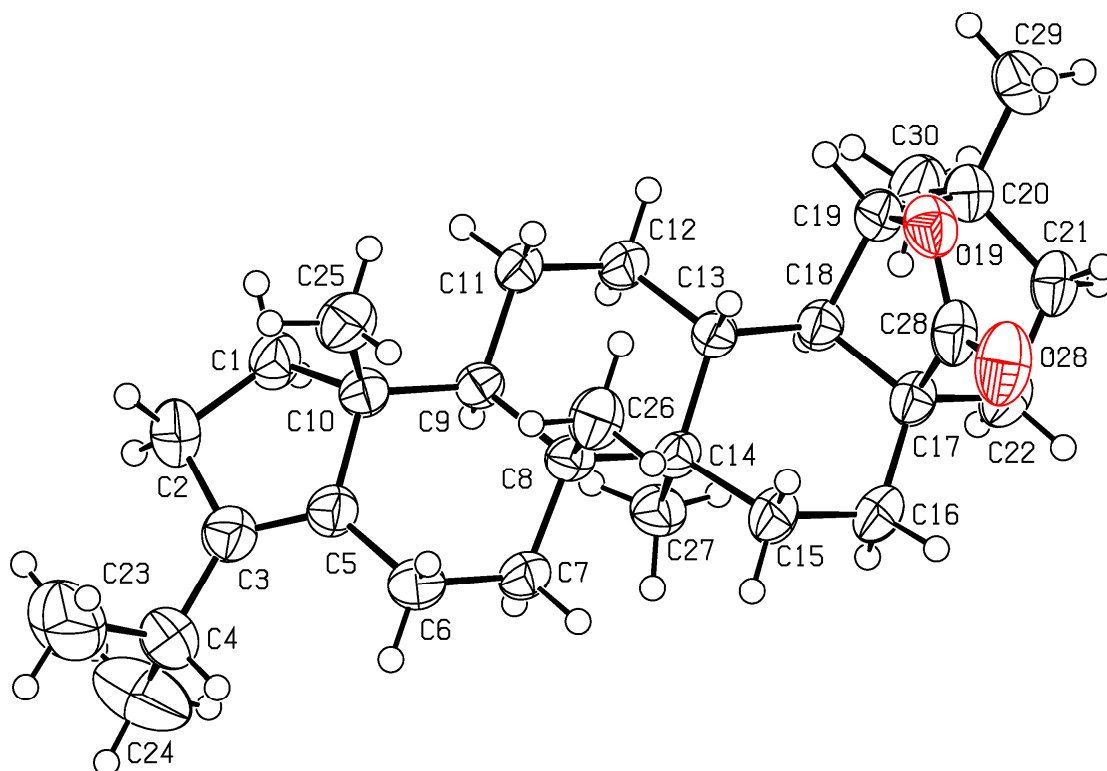
;E-mail: [salvador@ci.uc.pt](mailto:salvador@ci.uc.pt)

**Supplementary Data**

Single crystal X-ray diffraction data for compound <b>5</b> .....	2
Single crystal X-ray diffraction data for compound <b>17</b> .....	3
NMR data for compound <b>7</b> .....	4
NMR data for compound <b>11</b> .....	11
NMR data for compound <b>14</b> .....	17
NMR data for compound <b>16</b> .....	24

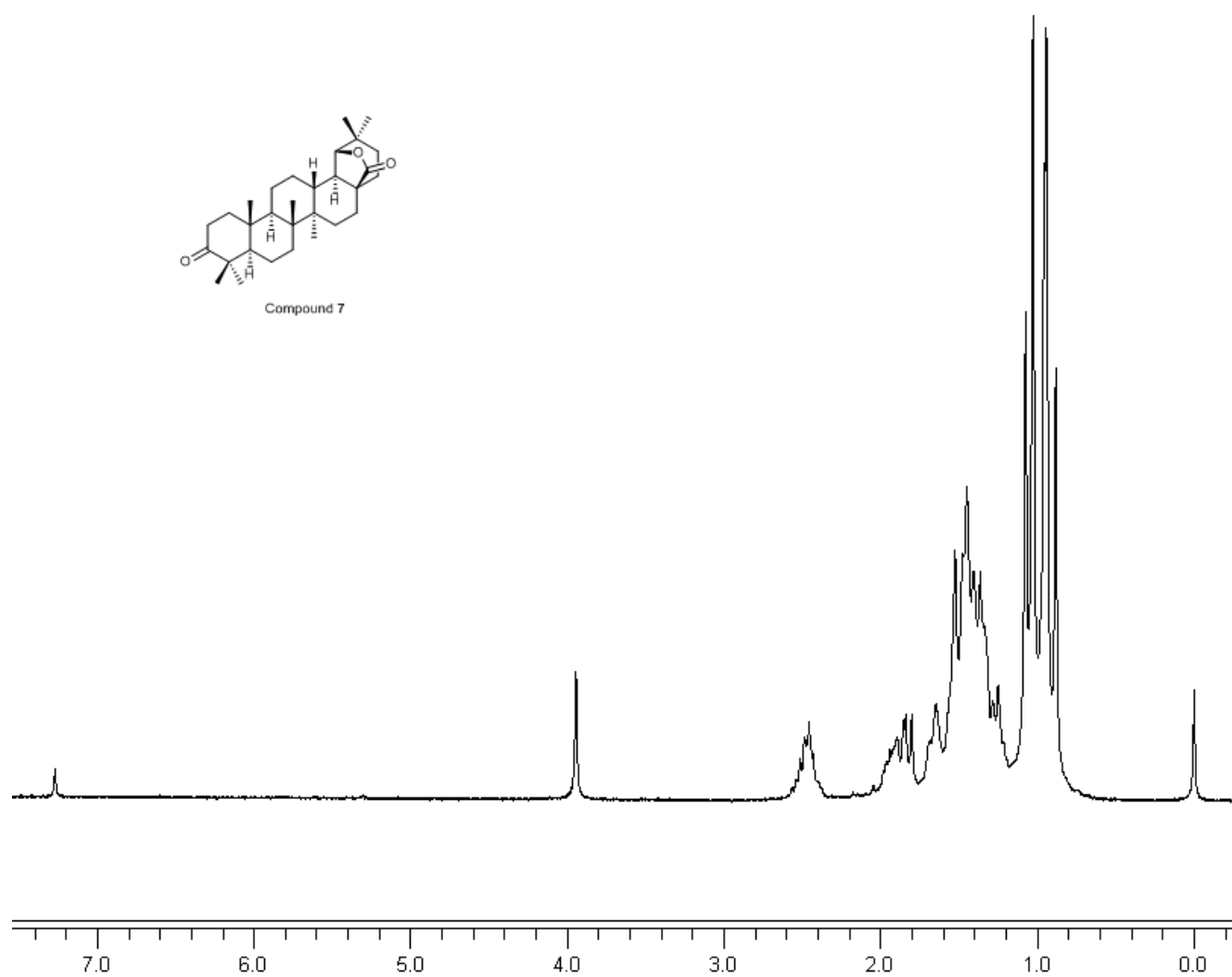
Single crystal X-ray diffraction data for compound **5**ORTEP diagram of compound **5** (50% probability level, H atoms of arbitrary sizes)

**Crystal data for compound 5.**  $C_{32}H_{52}O_3$ ,  $M = 484.76$ , monoclinic,  $a = 13.3520(2)$ ,  $b = 6.54000(10)$ ,  $c = 32.4439(5)$  Å,  $V = 2798.13(7)$  Å<sup>3</sup>,  $T = 293(2)$  K, space group  $C2$ ,  $Z = 4$ , 26879 reflections measured, 3074 unique ( $R_{int} = 0.027$ ) which were used in all calculations. Final  $R$  indices:  $R1 = 0.036$  for 2759 reflections with  $I > 2\sigma(I)$ ,  $wR(F^2)$  was 0.099 (all data).

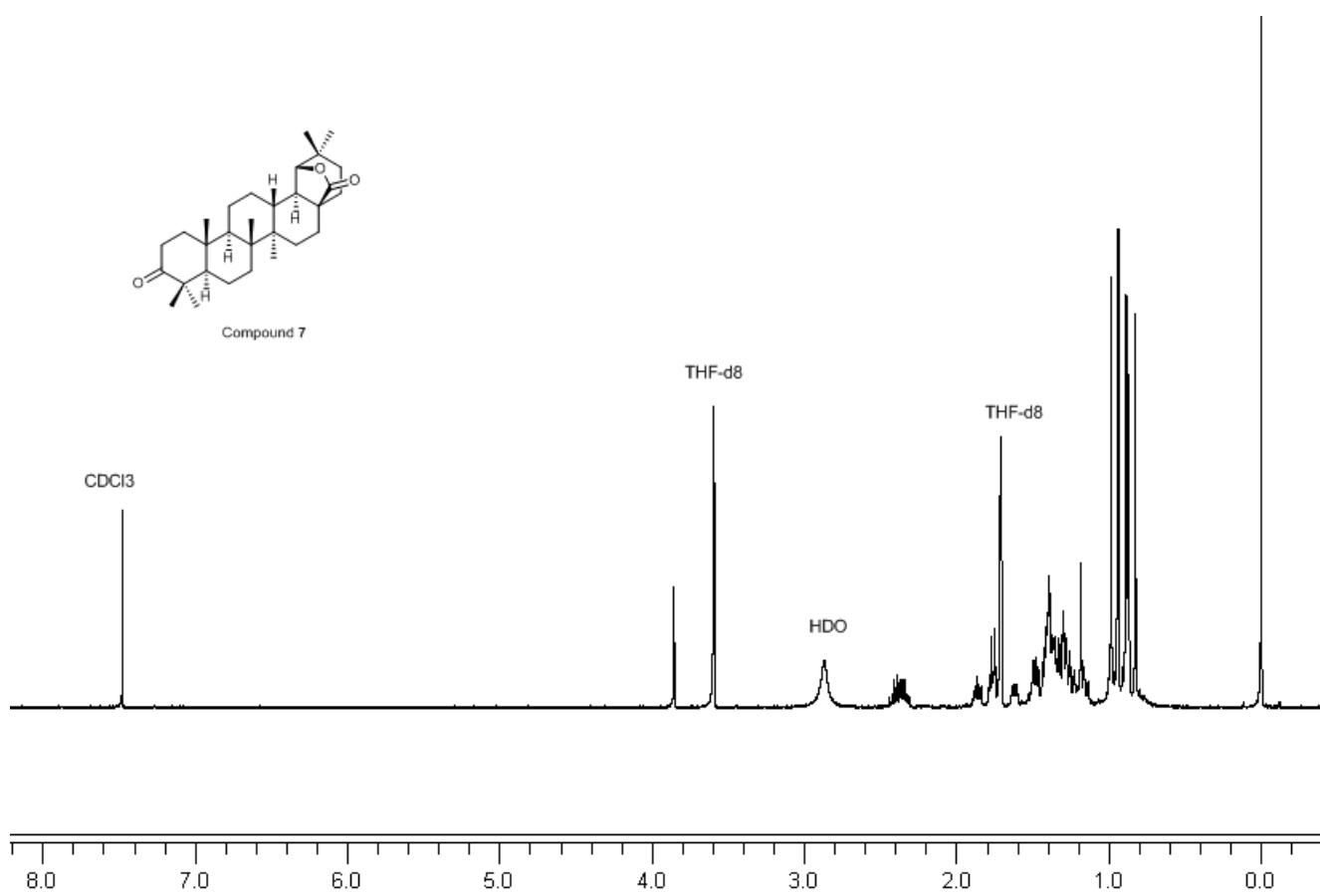
Single crystal X-ray diffraction data for compound **17**ORTEP diagram of compound **17** (50% probability level, H atoms of arbitrary sizes)

**Crystal data for compound 17.**  $C_{30}H_{46}O_2$ ,  $M = 438.67$ , monoclinic,  $a = 13.2214(4)$ ,  $b = 6.4962(2)$ ,  $c = 29.8420(9)$  Å,  $V = 2558.00(13)$  Å<sup>3</sup>,  $T = 293(2)$  K, space group  $C2$ ,  $Z = 4$ , 22819 reflections measured, 2655 unique ( $R_{int} = 0.061$ ) which were used in all calculations. Final  $R$  indices:  $R1 = 0.046$  for 1677 reflections with  $I > 2\sigma(I)$ ,  $wR(F^2)$  was 0.116 (all data).

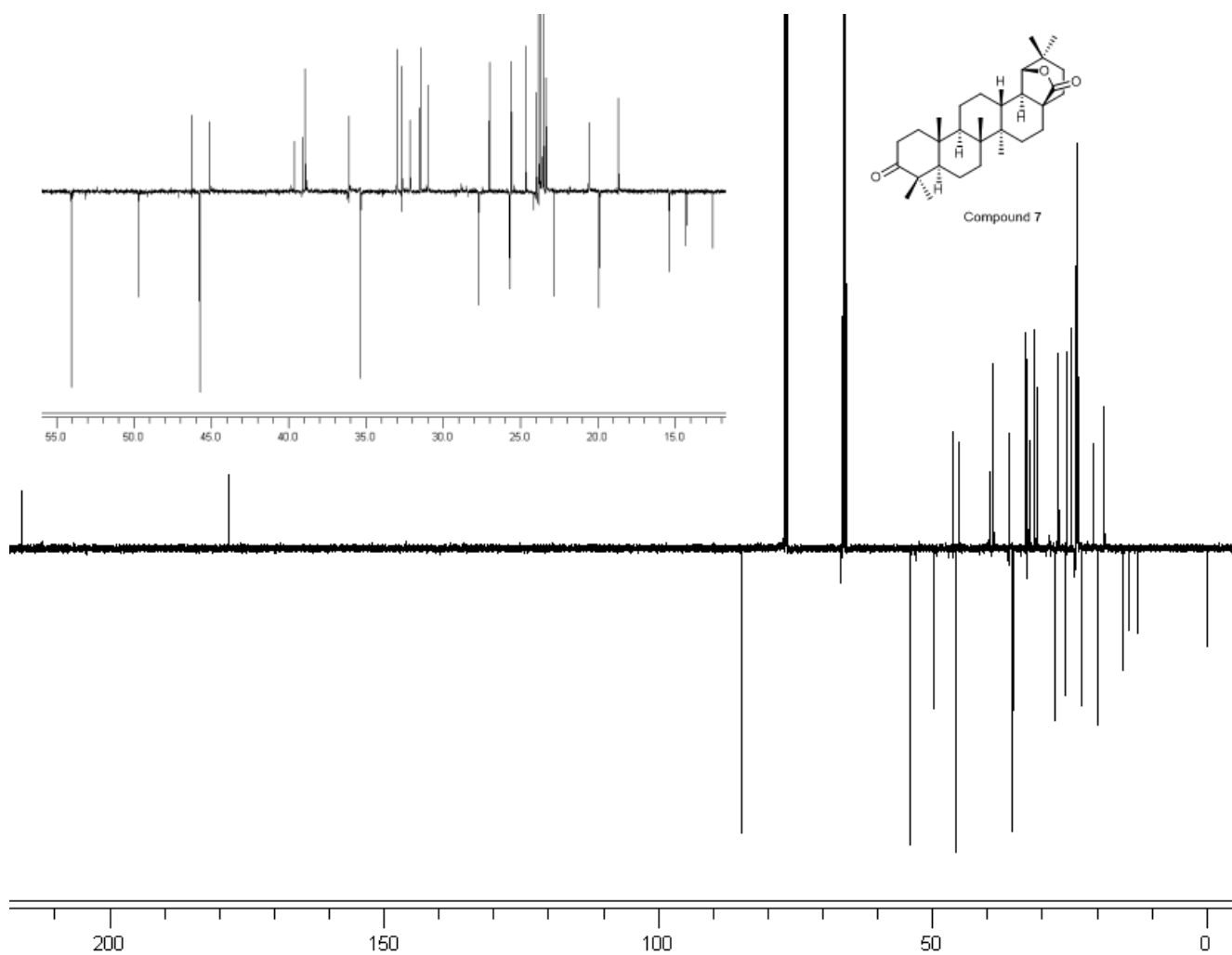
NMR data for compound **7**



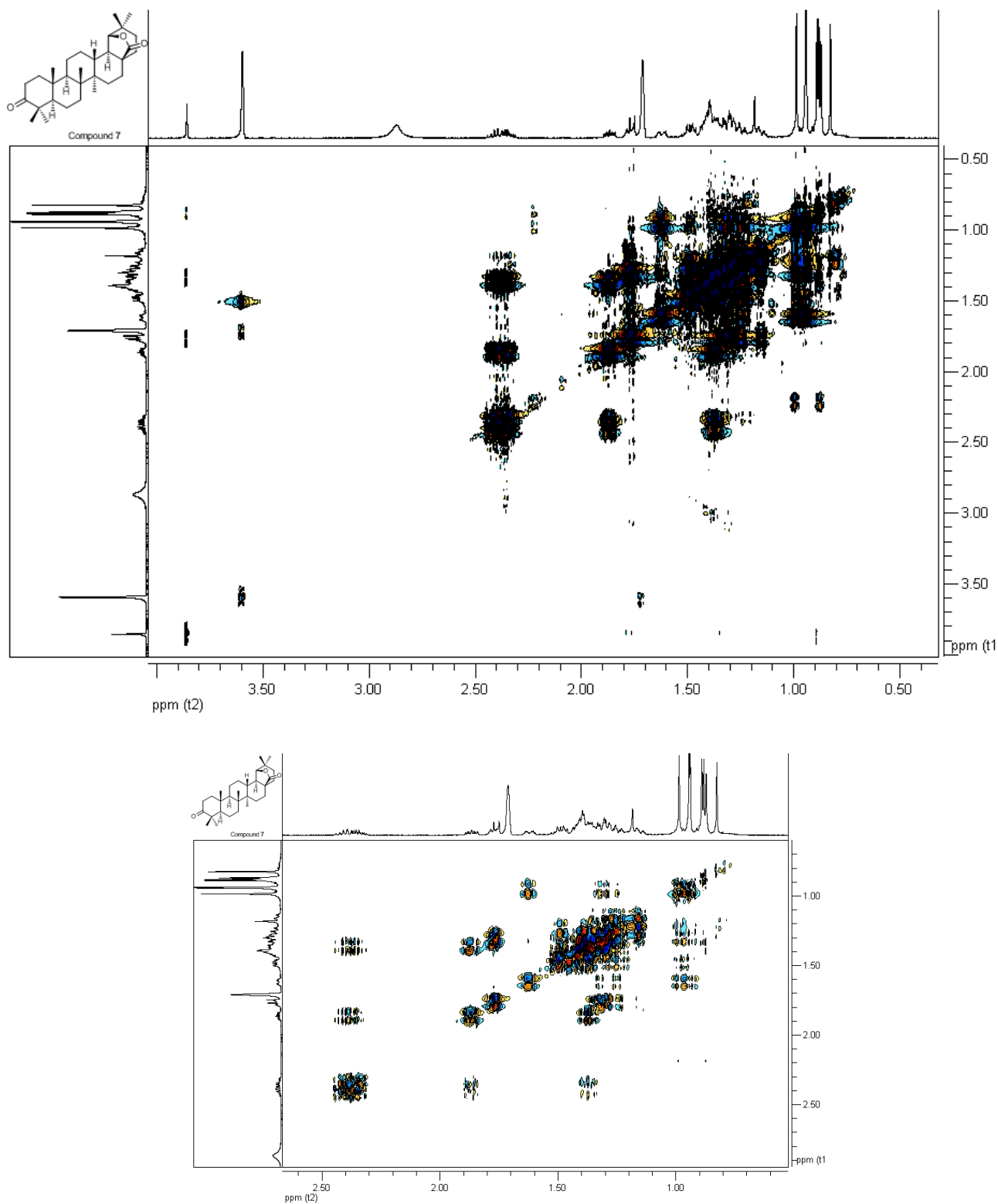
**Fig. S1.** <sup>1</sup>H NMR of compound **7** in CDCl<sub>3</sub>.

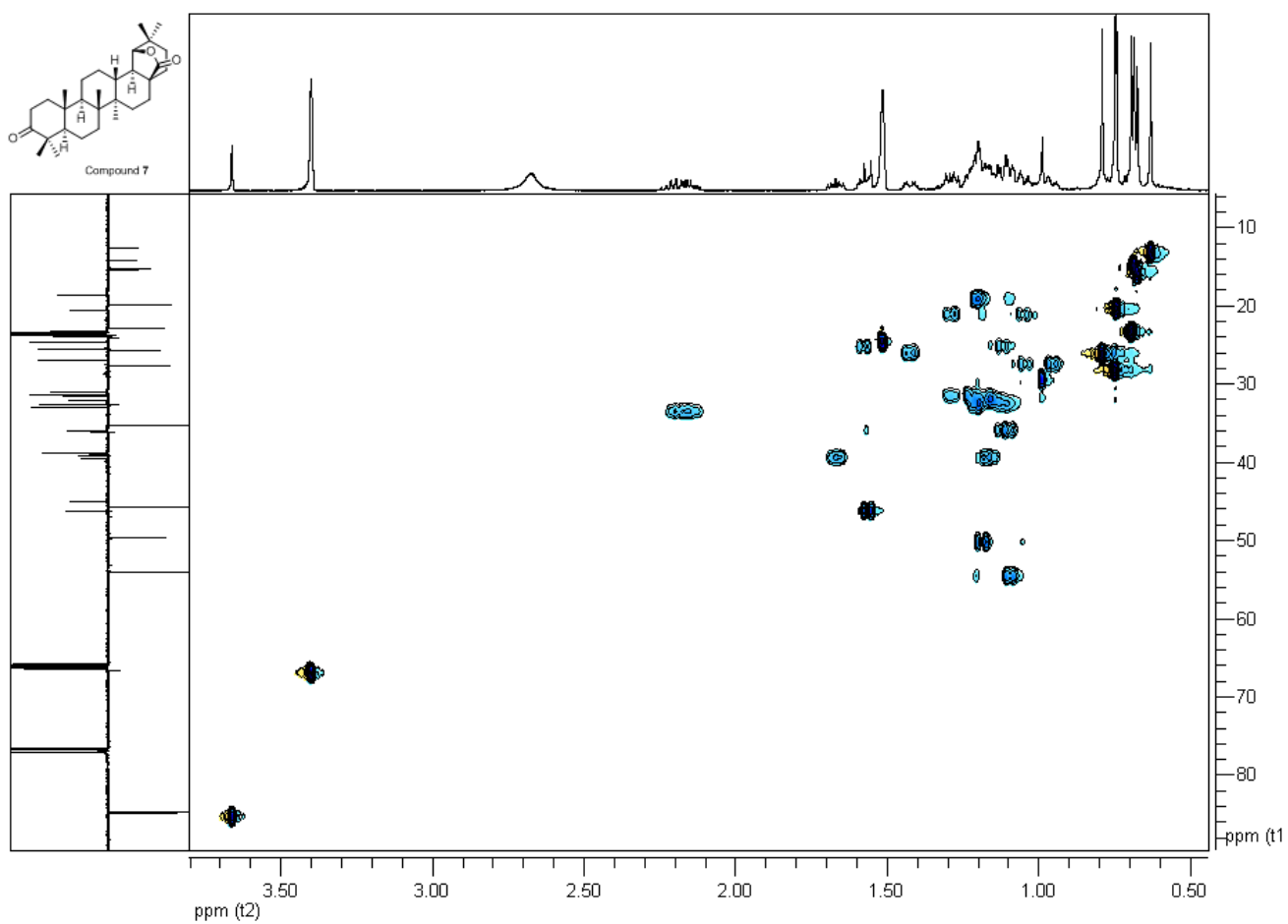


**Fig. S2.**  $^1\text{H}$  NMR of compound 7 in  $\text{CDCl}_3/\text{THF-}d_8$ .



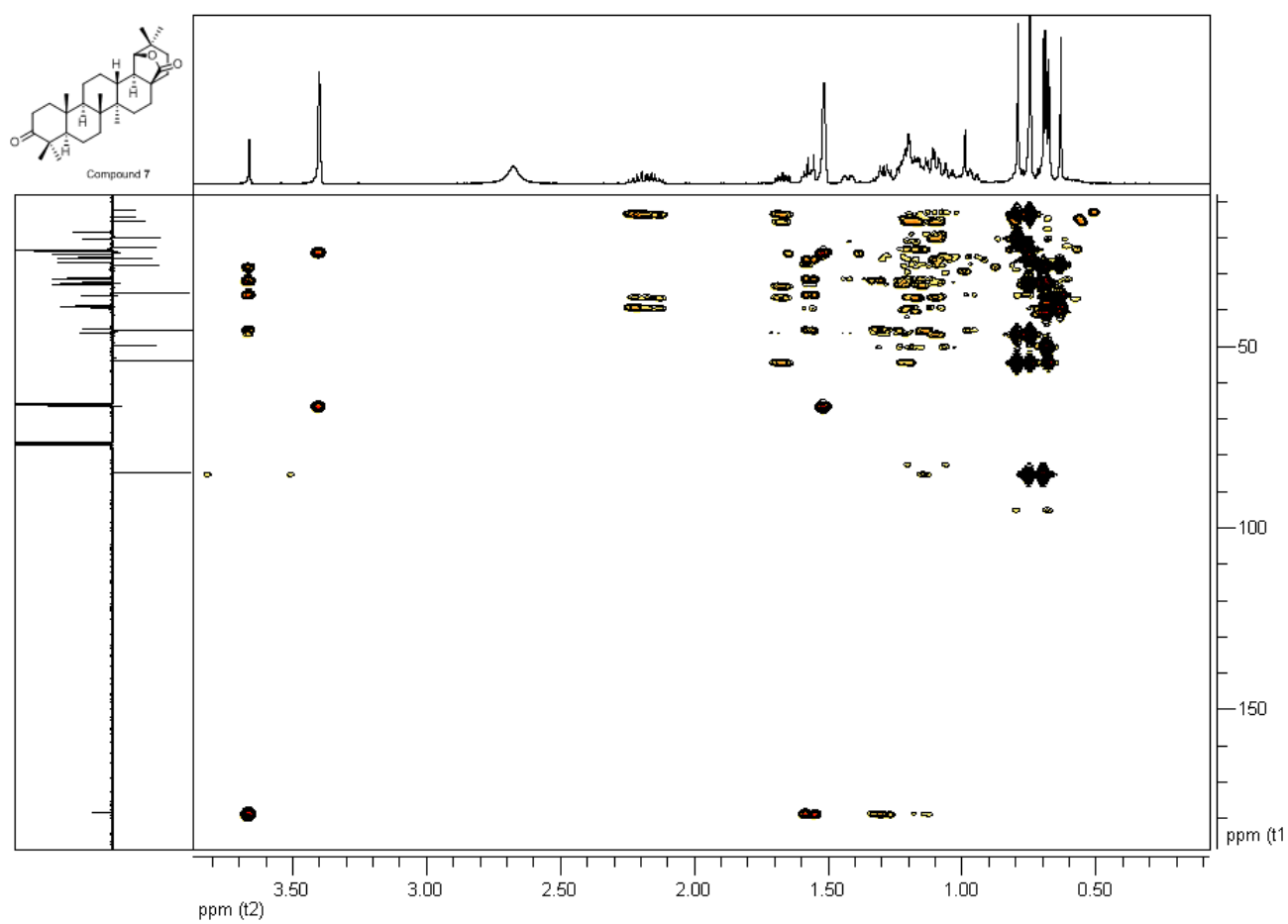
**Fig. S3.**  $^{13}\text{C}$  NMR/J-MOD of compound 7 in  $\text{CDCl}_3/\text{THF}-d_8$ .

**Fig. S4.**  $^1\text{H}$ - $^1\text{H}$  COSY of compound 7 in  $\text{CDCl}_3/\text{THF-}d_8$ .

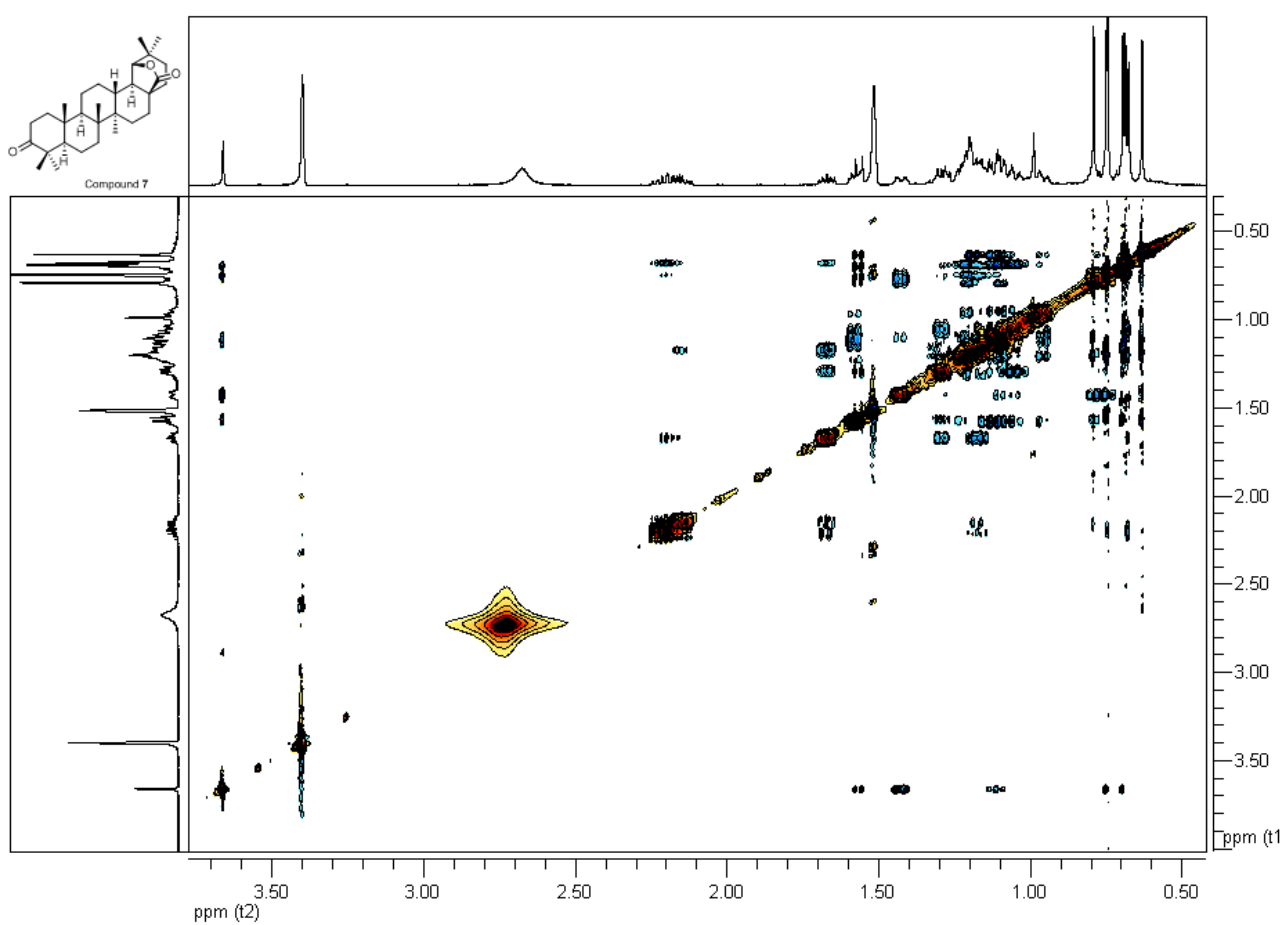


**Fig. S5.** HSQC of compound **7** in CDCl<sub>3</sub>/THF-*d*<sub>8</sub>.



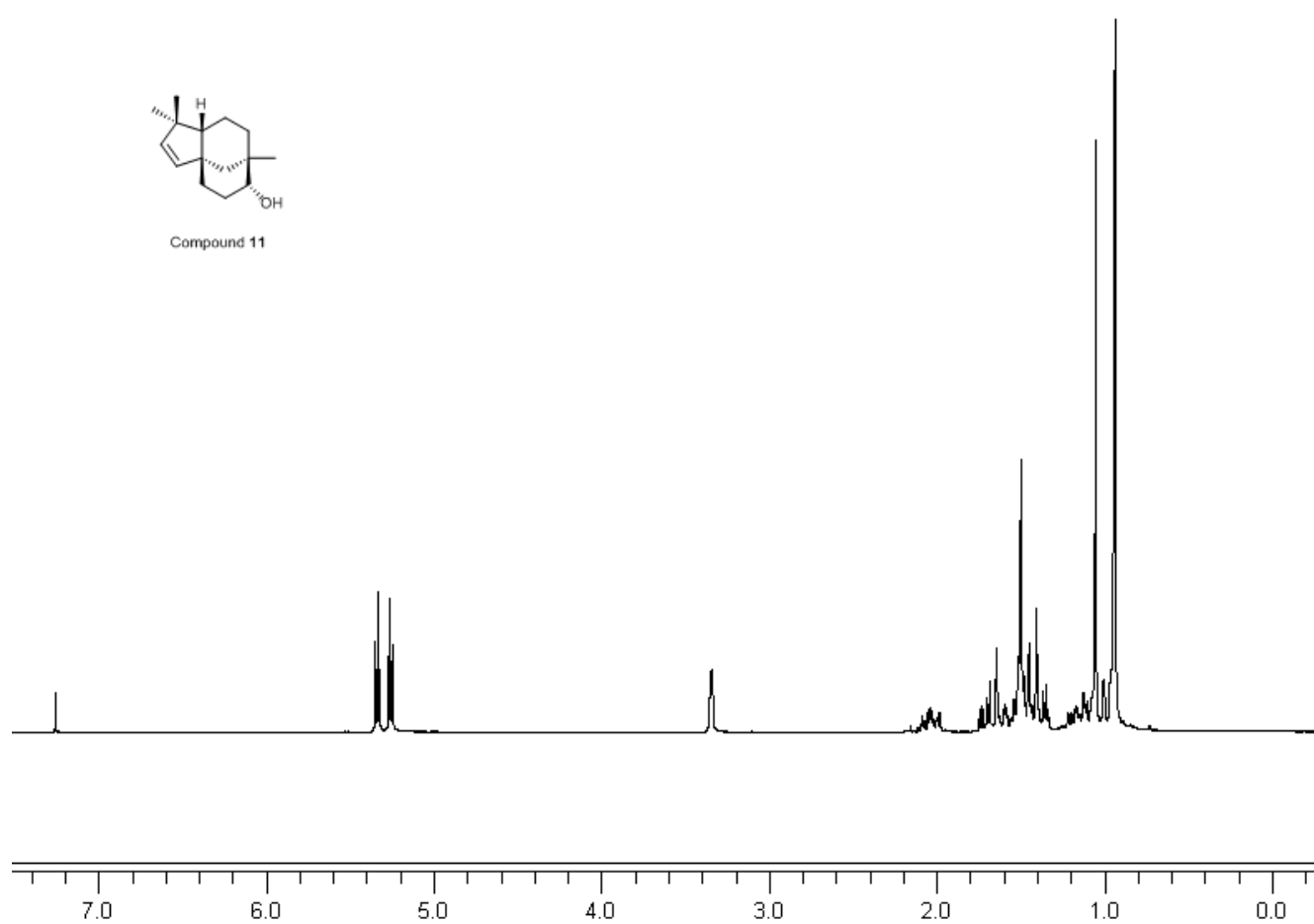


**Fig. S6.** HMBC of compound 7 in CDCl<sub>3</sub>/THF-*d*<sub>8</sub>.

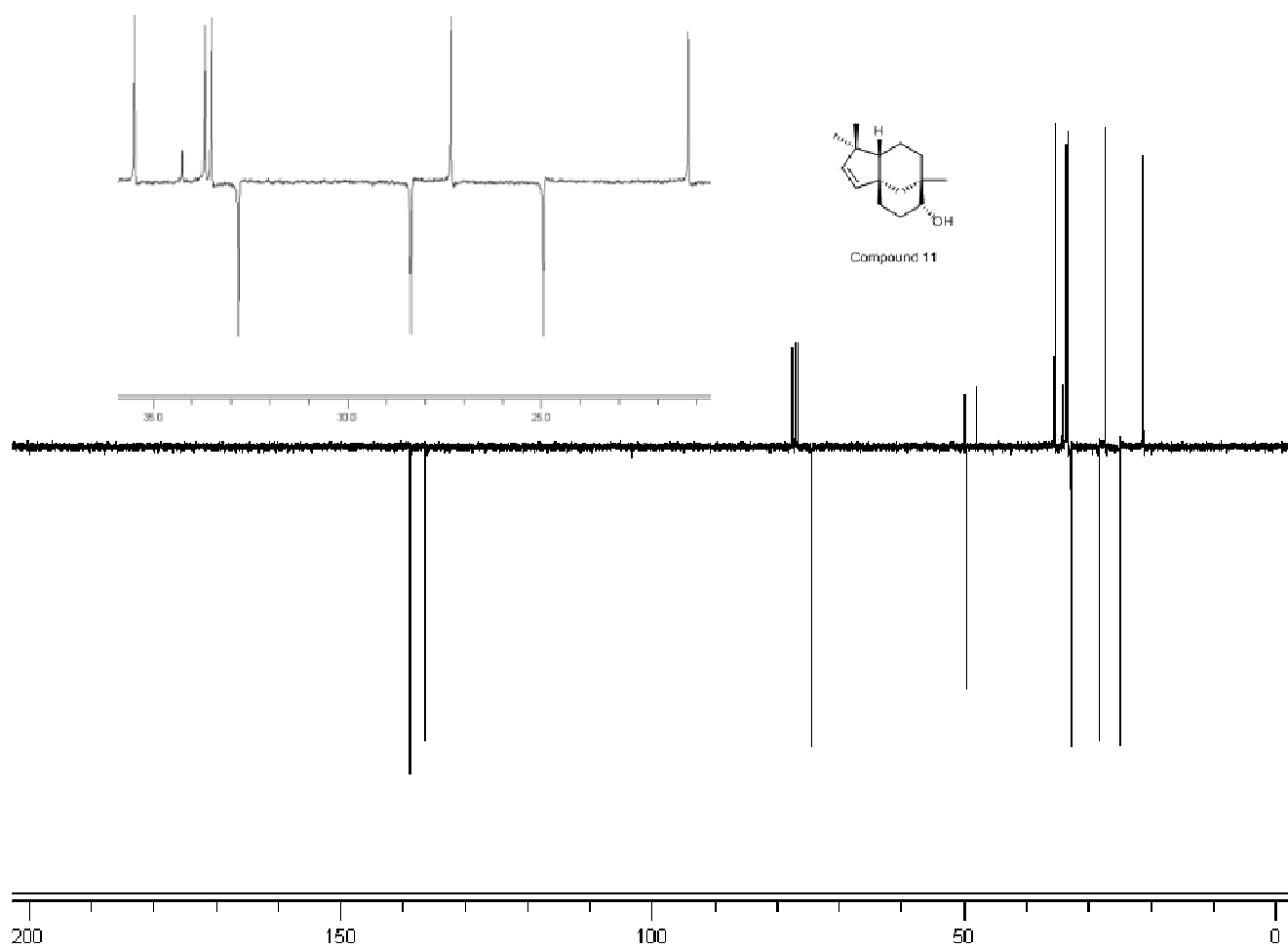


**Fig. S7.** NOESY of compound **7** in  $\text{CDCl}_3/\text{THF-}d_8$ .

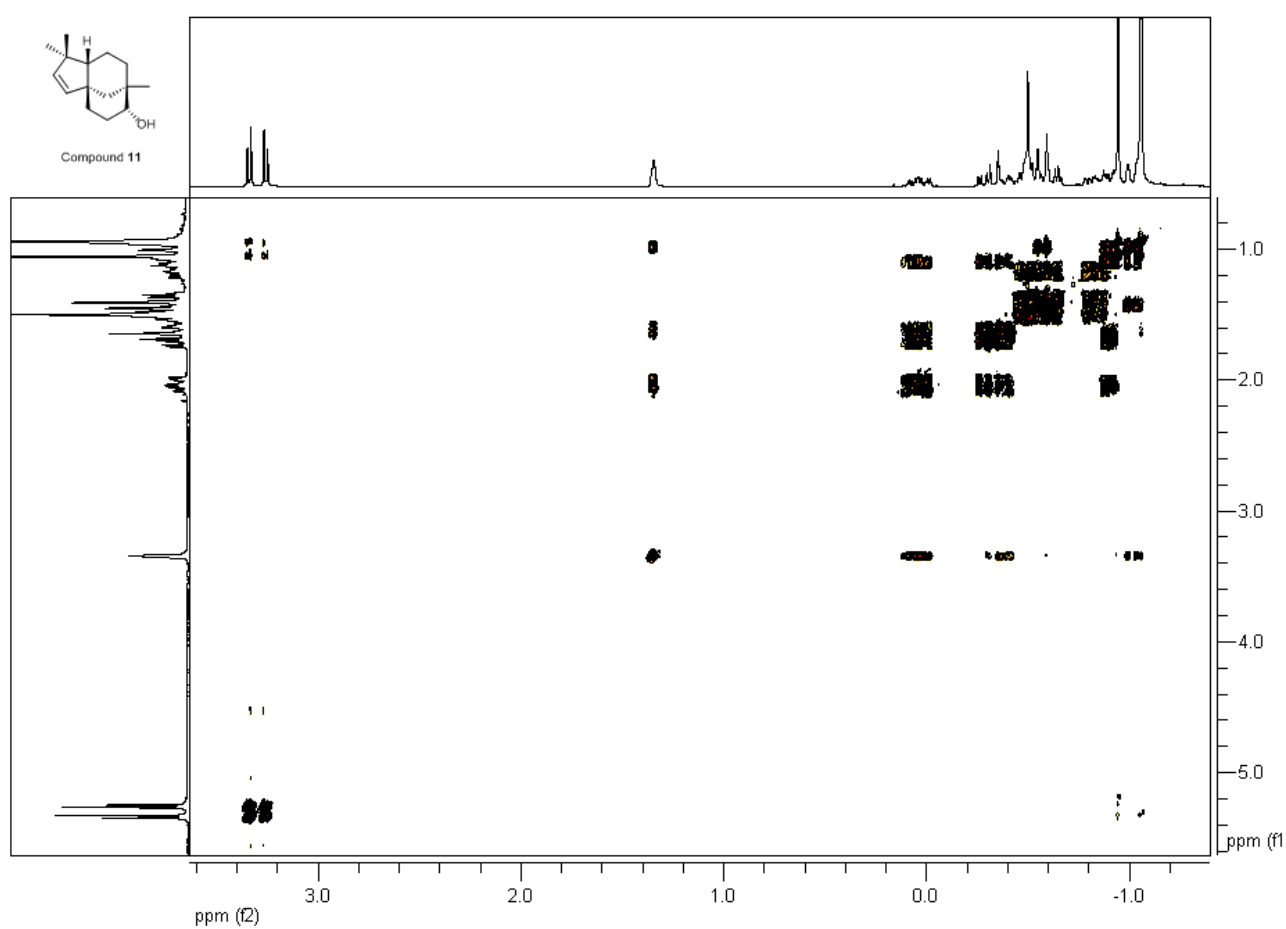
NMR data for compound **11**



**Fig. S8.**  $^1\text{H}$  NMR of compound **11** in  $\text{CDCl}_3$ .



**Fig. S9.**  $^{13}\text{C}$  NMR/J-MOD of compound 11 in  $\text{CDCl}_3$ .

**Fig. S10.**  $^1\text{H}$ - $^1\text{H}$  COSY of compound 11 in  $\text{CDCl}_3$ .

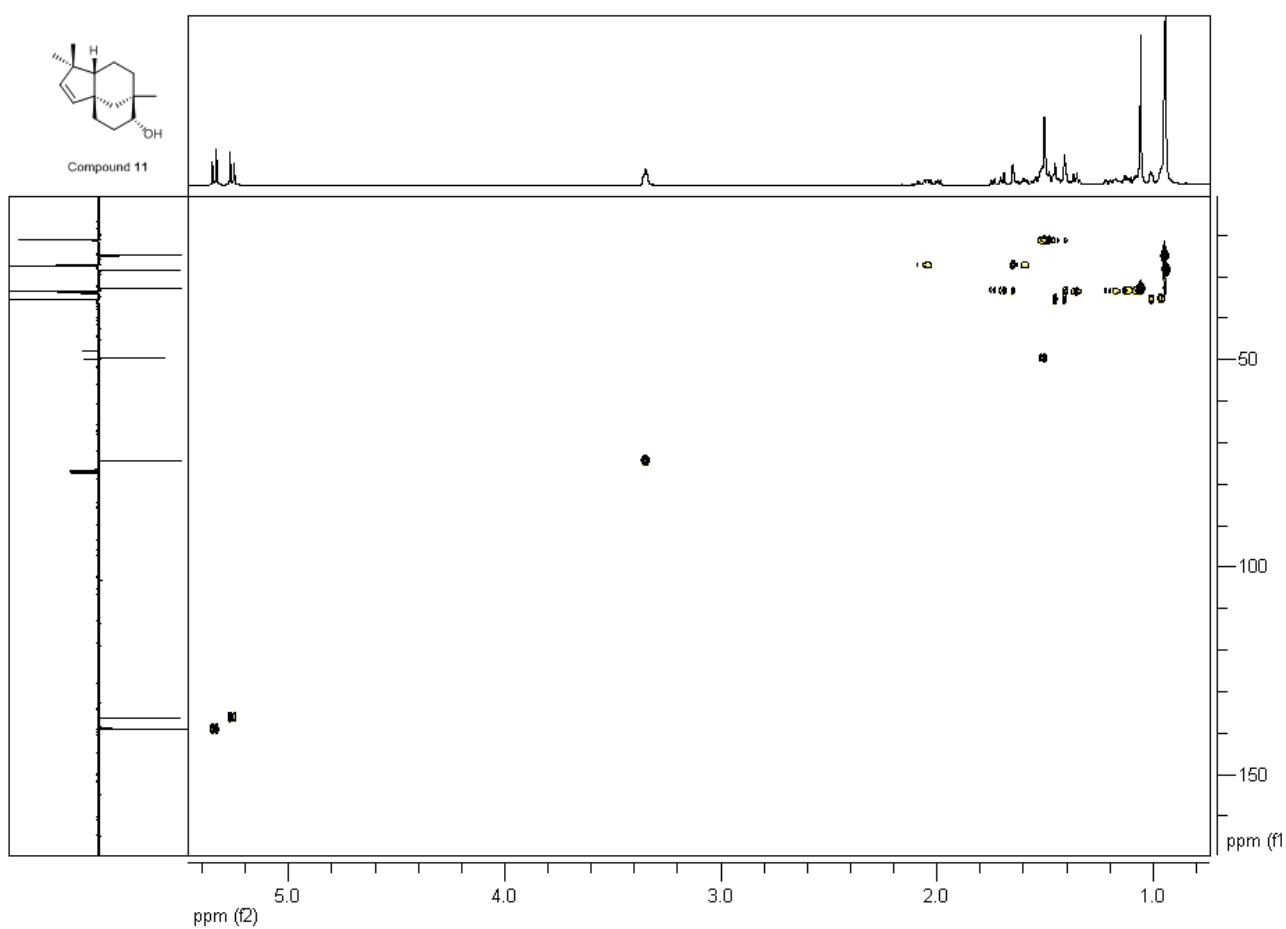
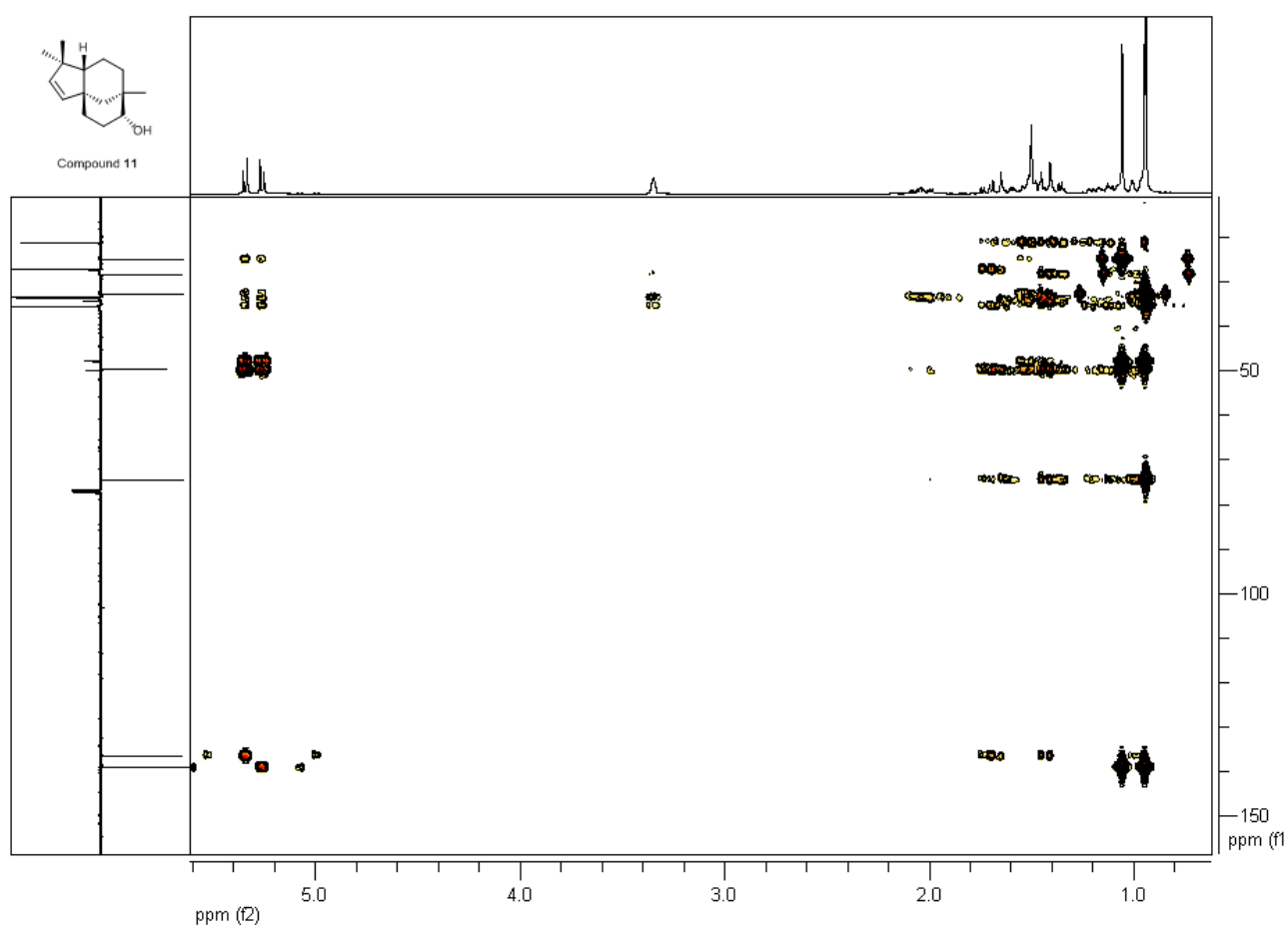
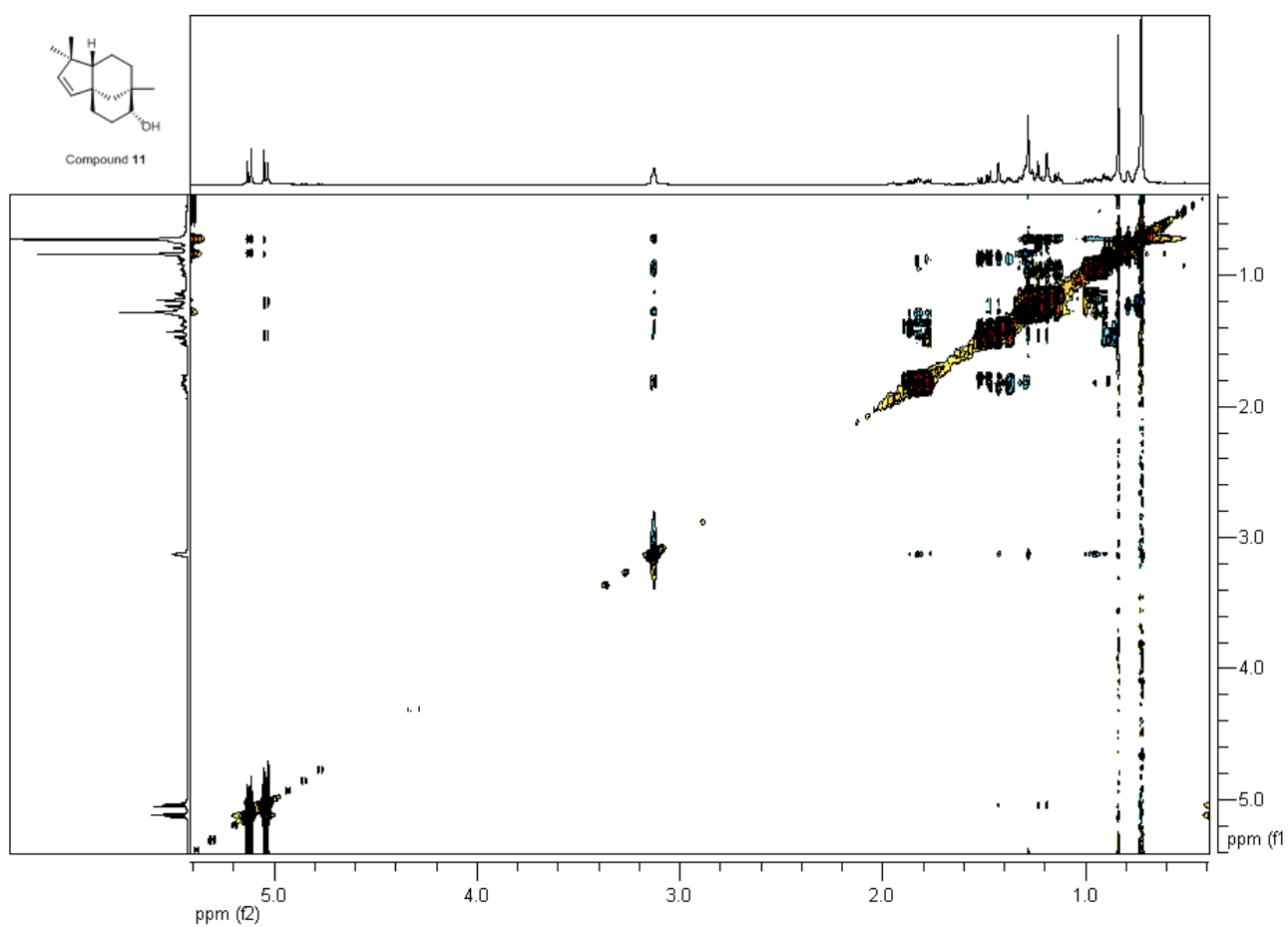


Fig. S11. HSQC of compound 11 in CDCl<sub>3</sub>.

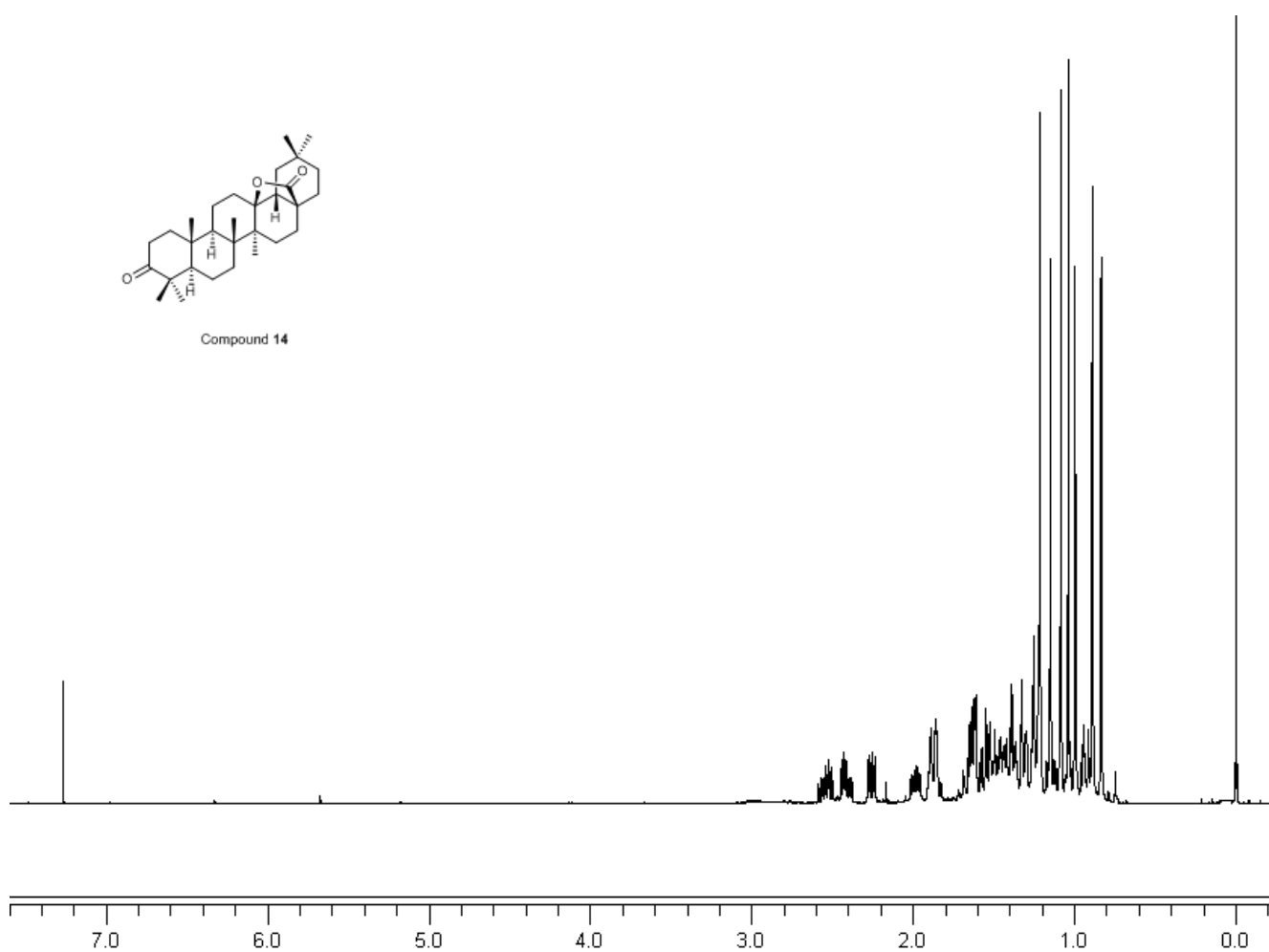
**Fig. S12.** HMBC of compound **11** in CDCl<sub>3</sub>.



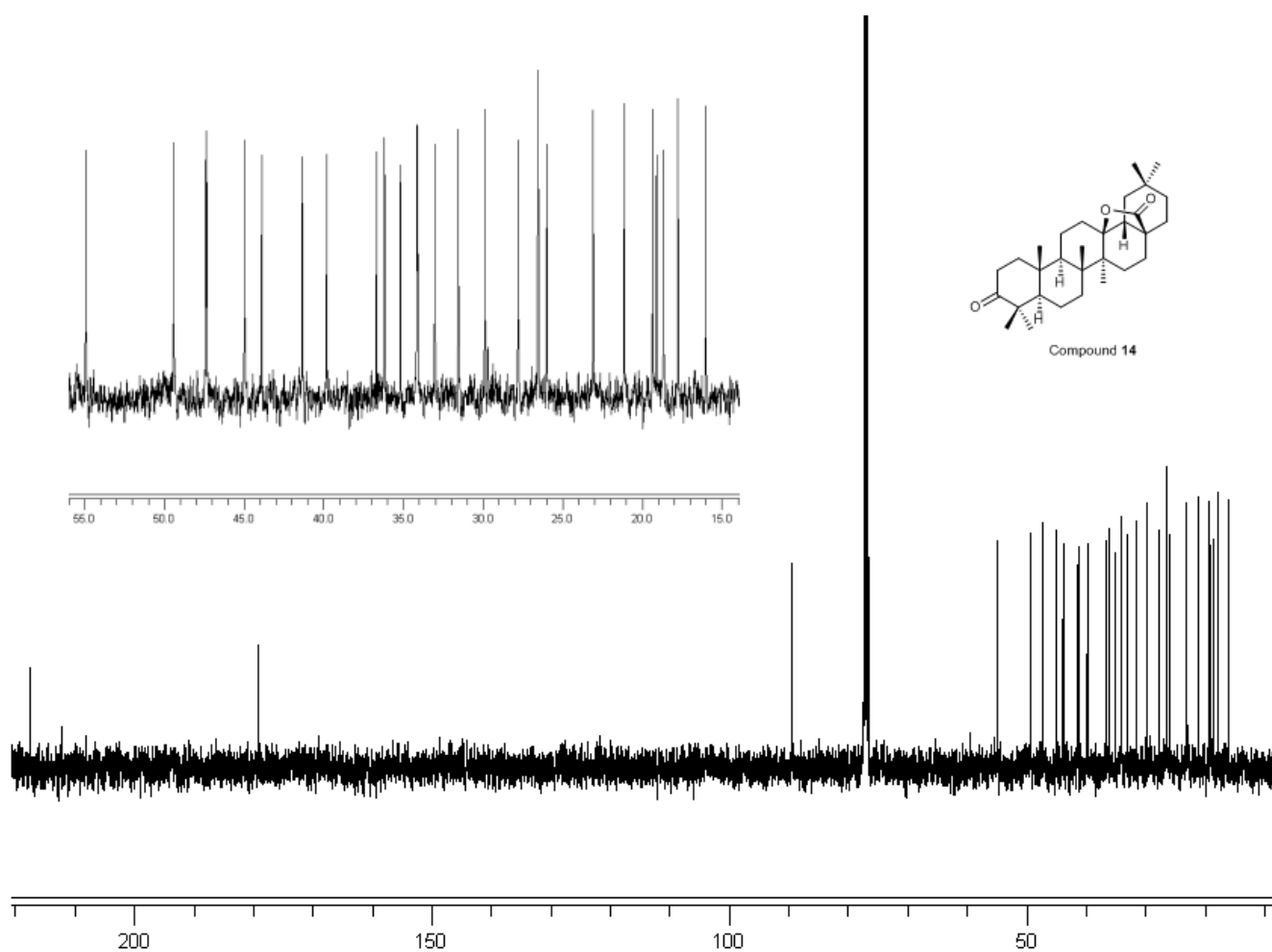
**Fig. S13.** NOESY of compound 7 in  $\text{CDCl}_3$ .



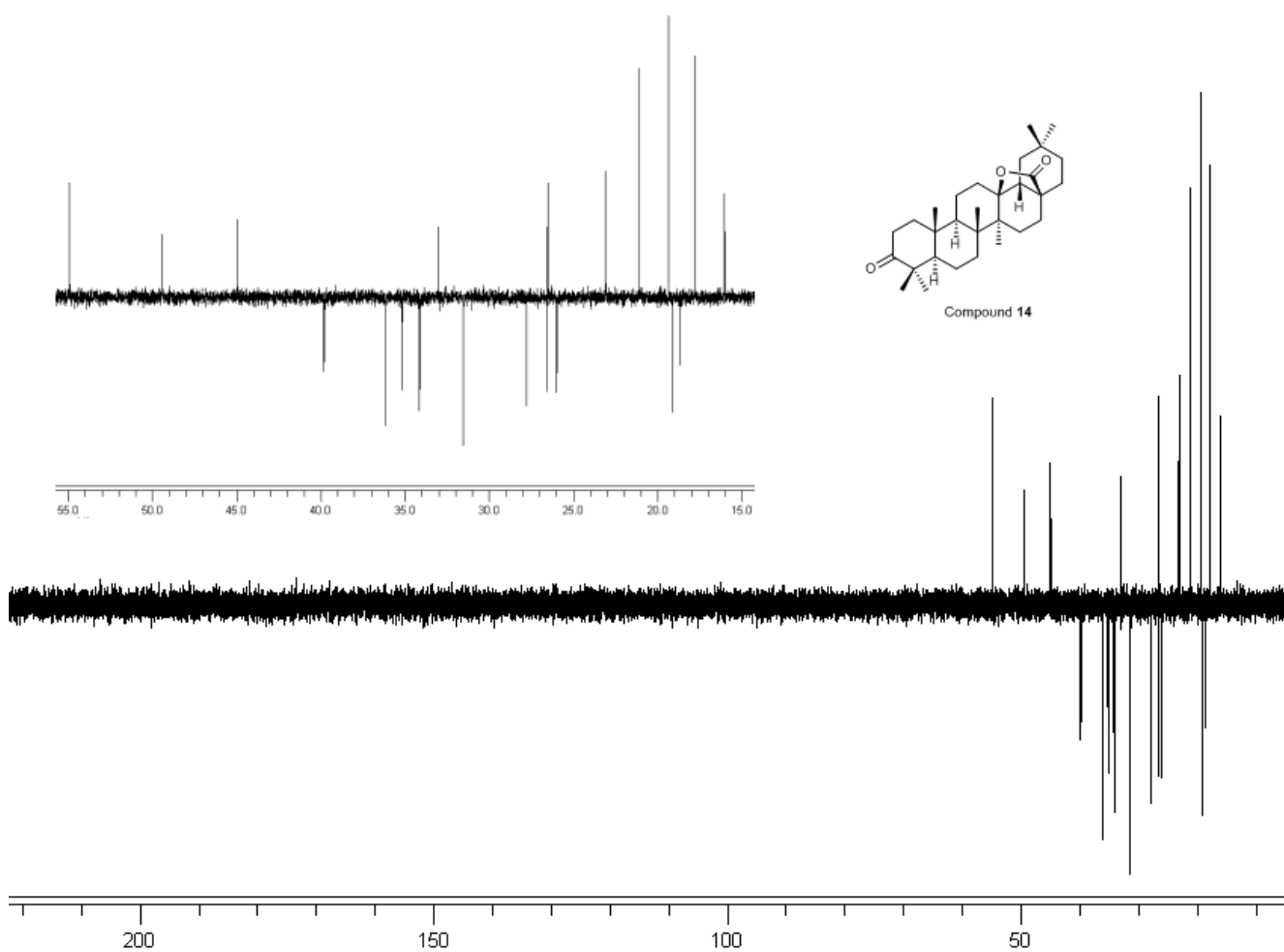
NMR data for compound **14**



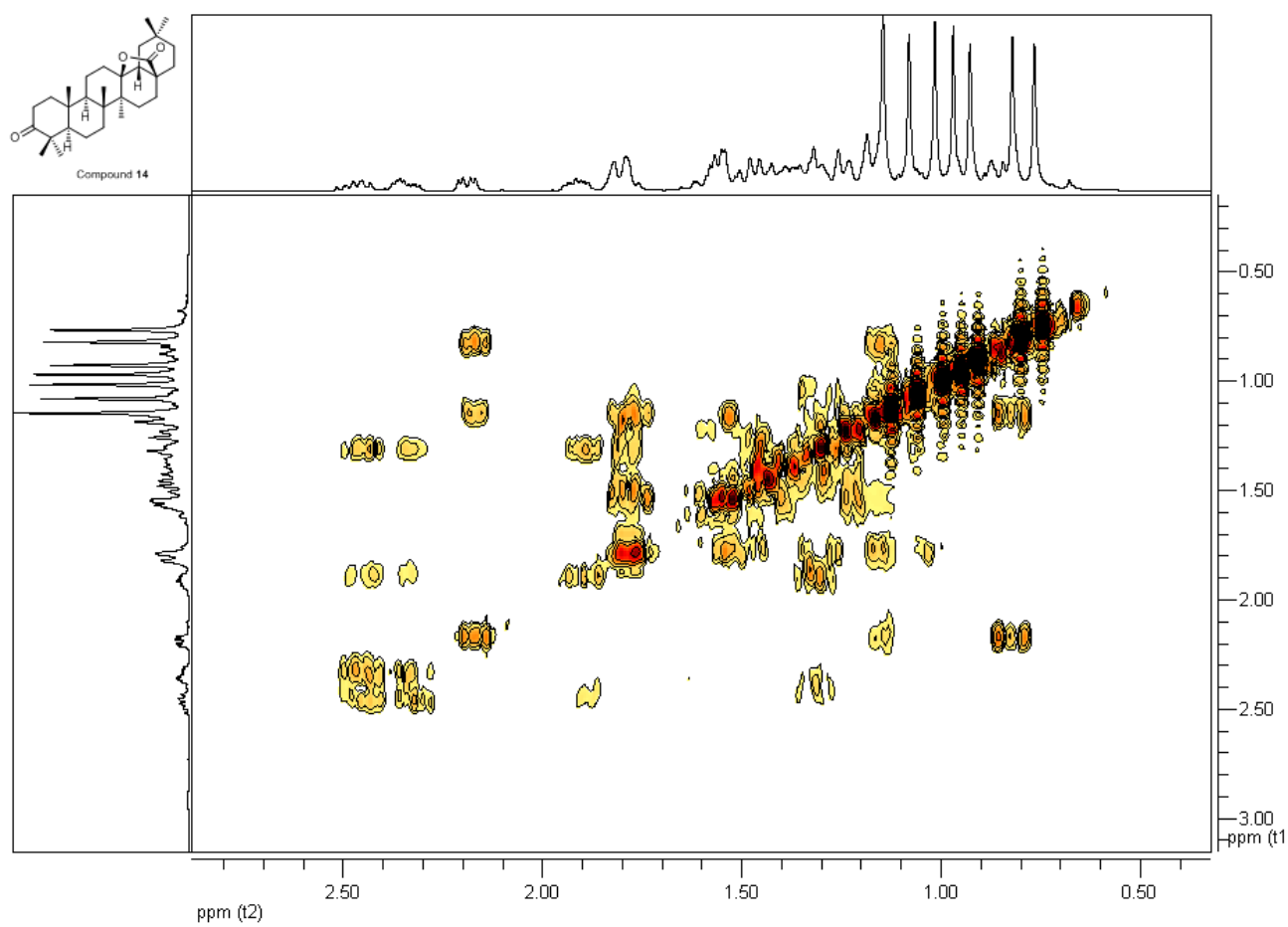
**Fig. S14.** <sup>1</sup>H NMR of compound **14** in CDCl<sub>3</sub>.



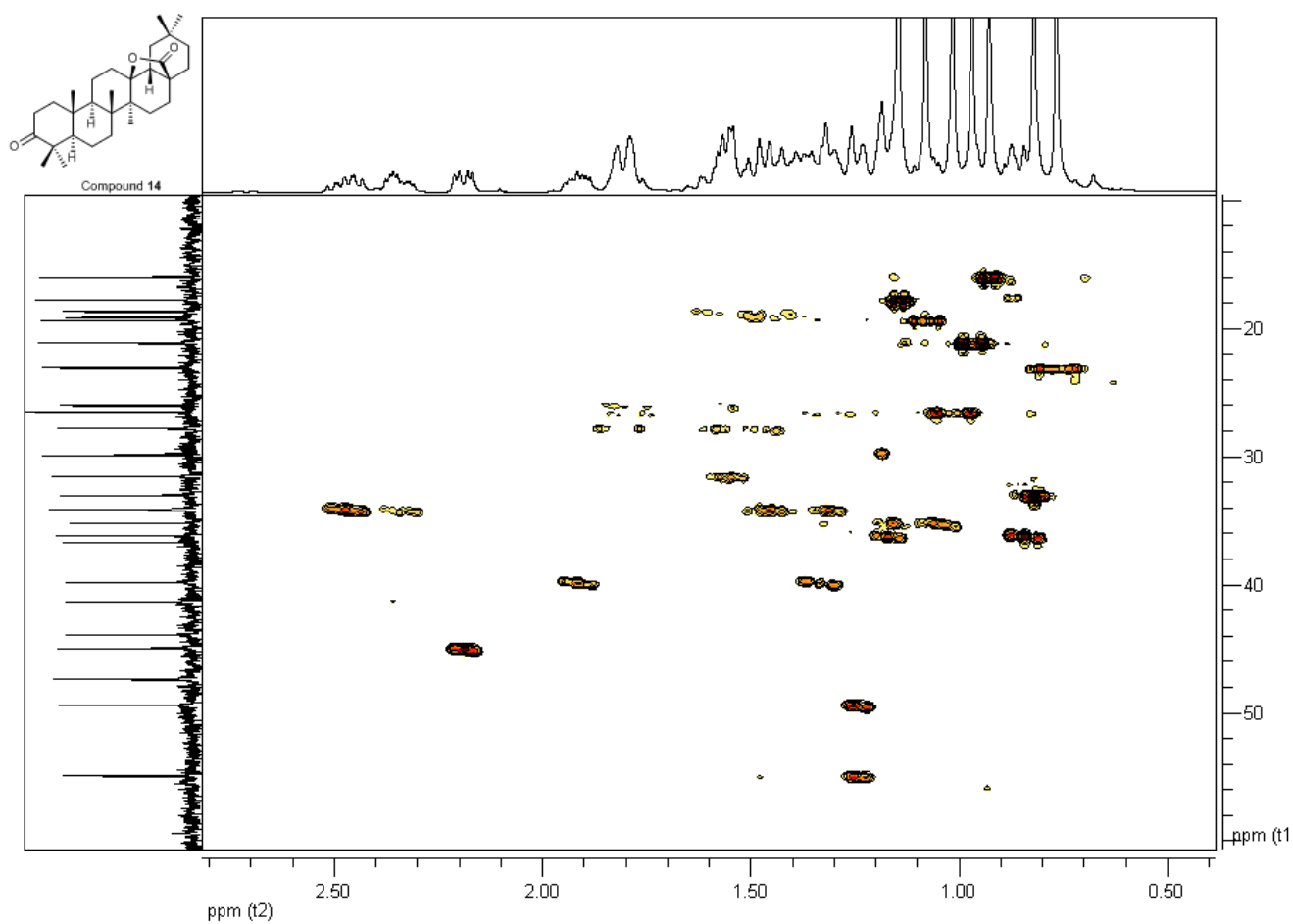
**Fig. S15.**  $^{13}\text{C}$  NMR of compound 14 in  $\text{CDCl}_3$ .



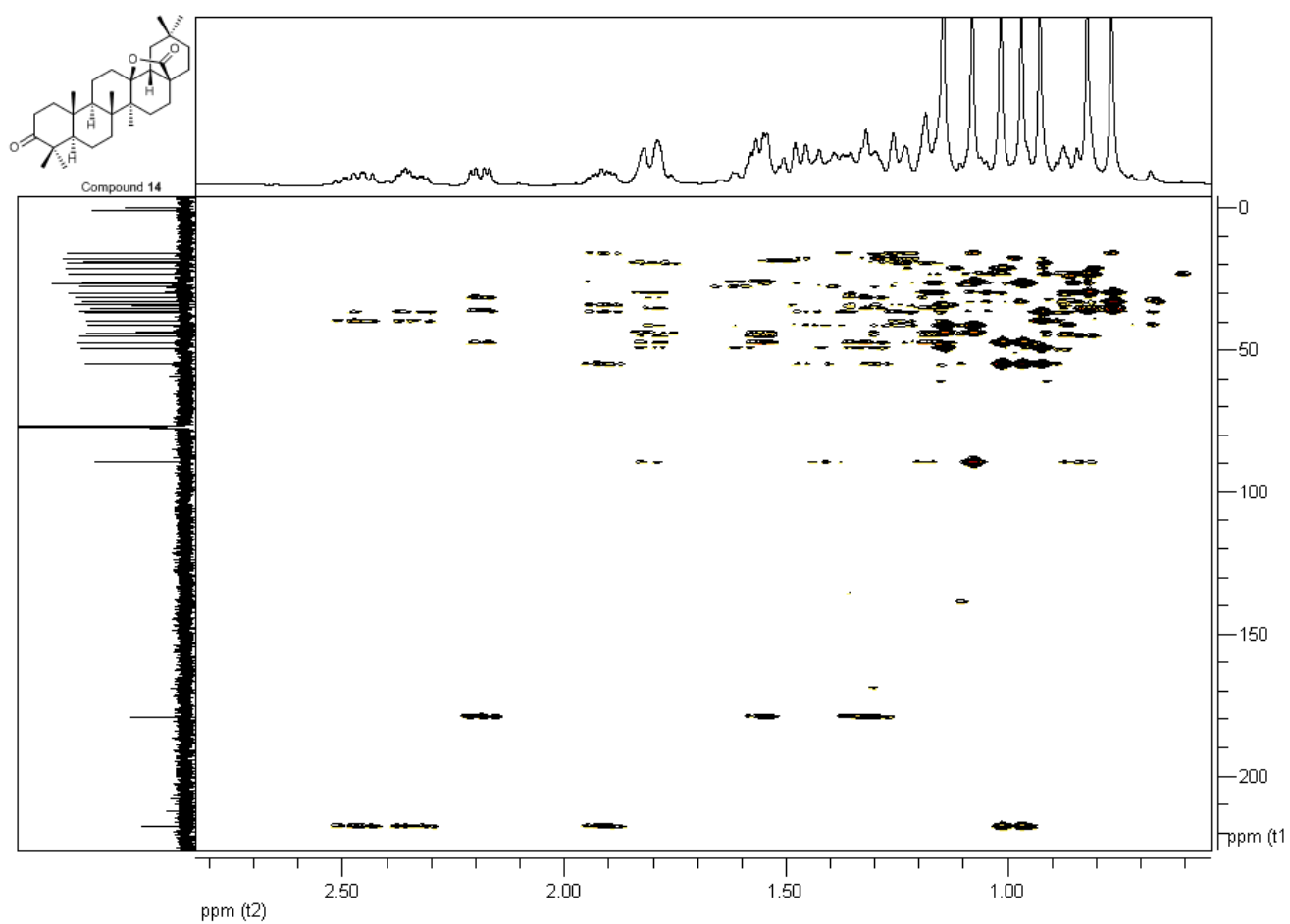
**Fig. S16.** DEPT 135 of compound **14** in CDCl<sub>3</sub>.



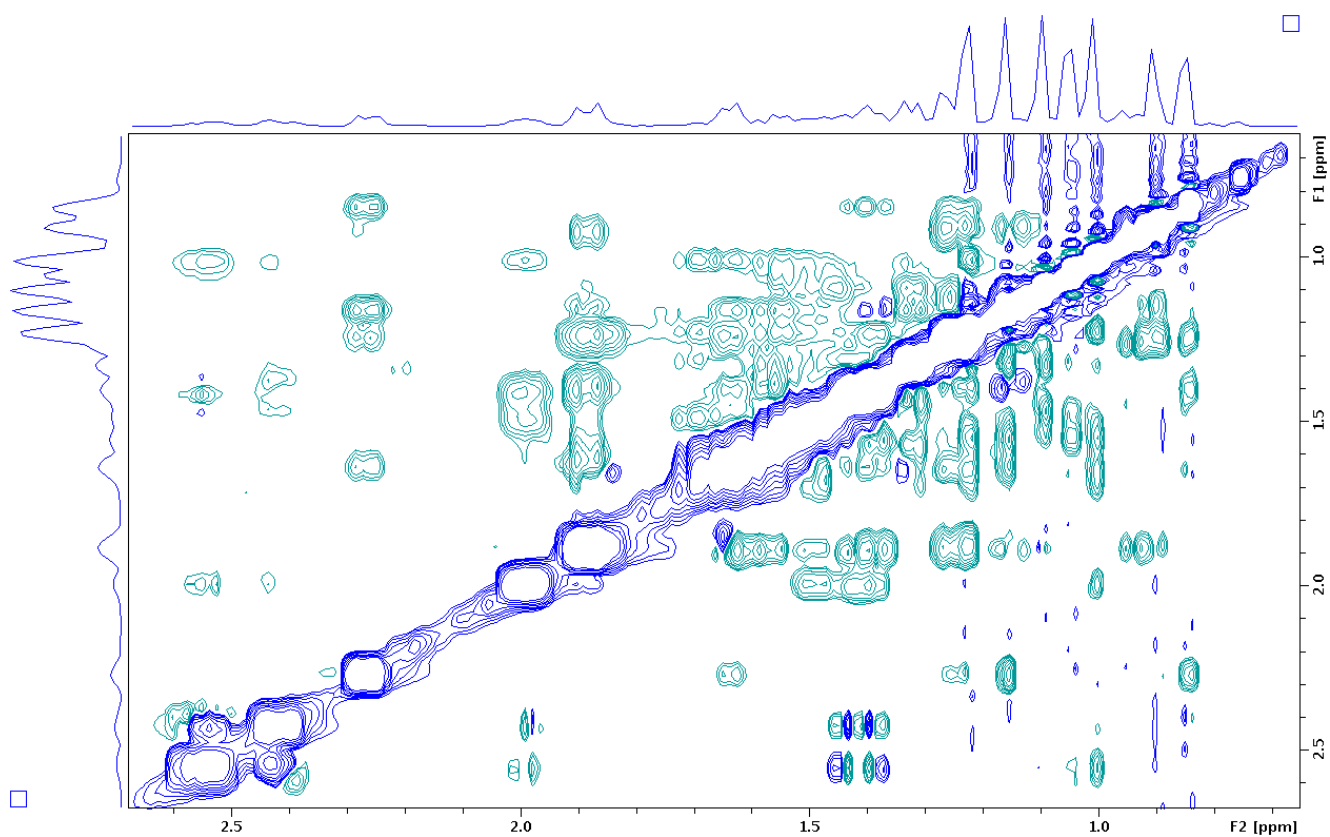
**Fig. S17.**  $^1\text{H}$ - $^1\text{H}$  COSY of compound **14** in  $\text{CDCl}_3$ .



**Fig. S18.** HMQC of compound **14** in  $\text{CDCl}_3$ .

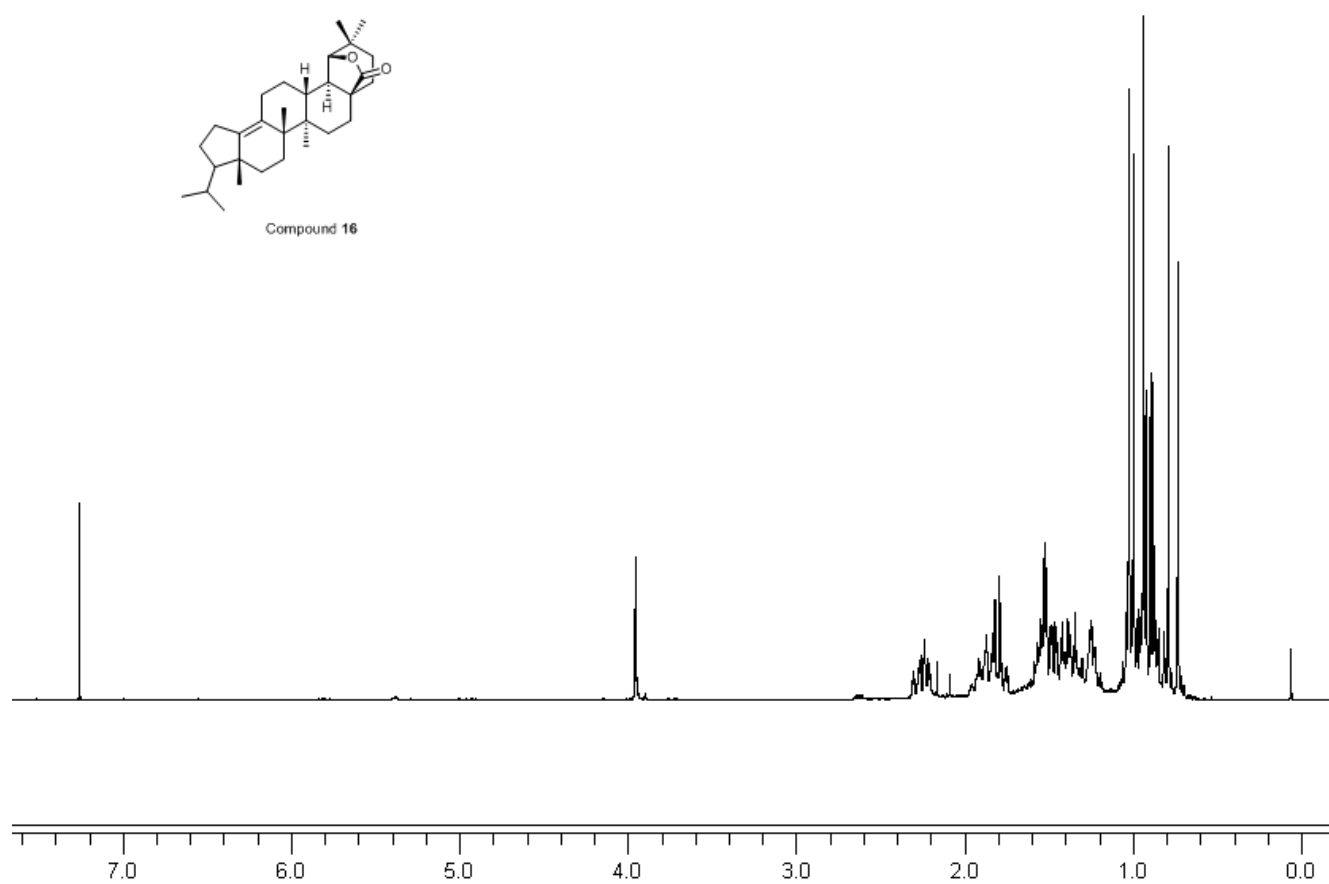


**Fig. S19.** HMBC of compound **14** in  $\text{CDCl}_3$ .



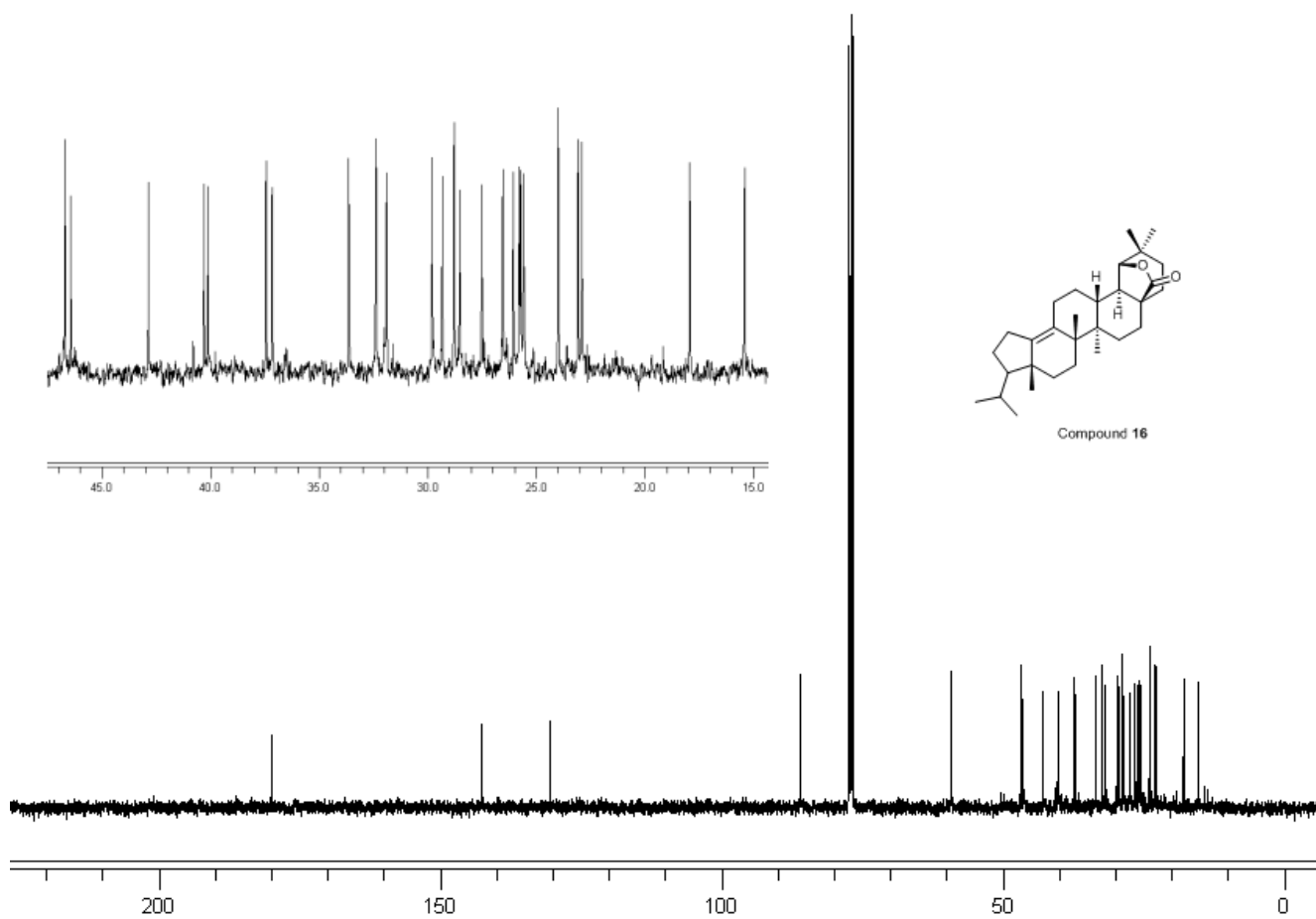
**Fig. S20.** NOESY of compound **14** in CDCl<sub>3</sub>.

NMR data for compound **16**

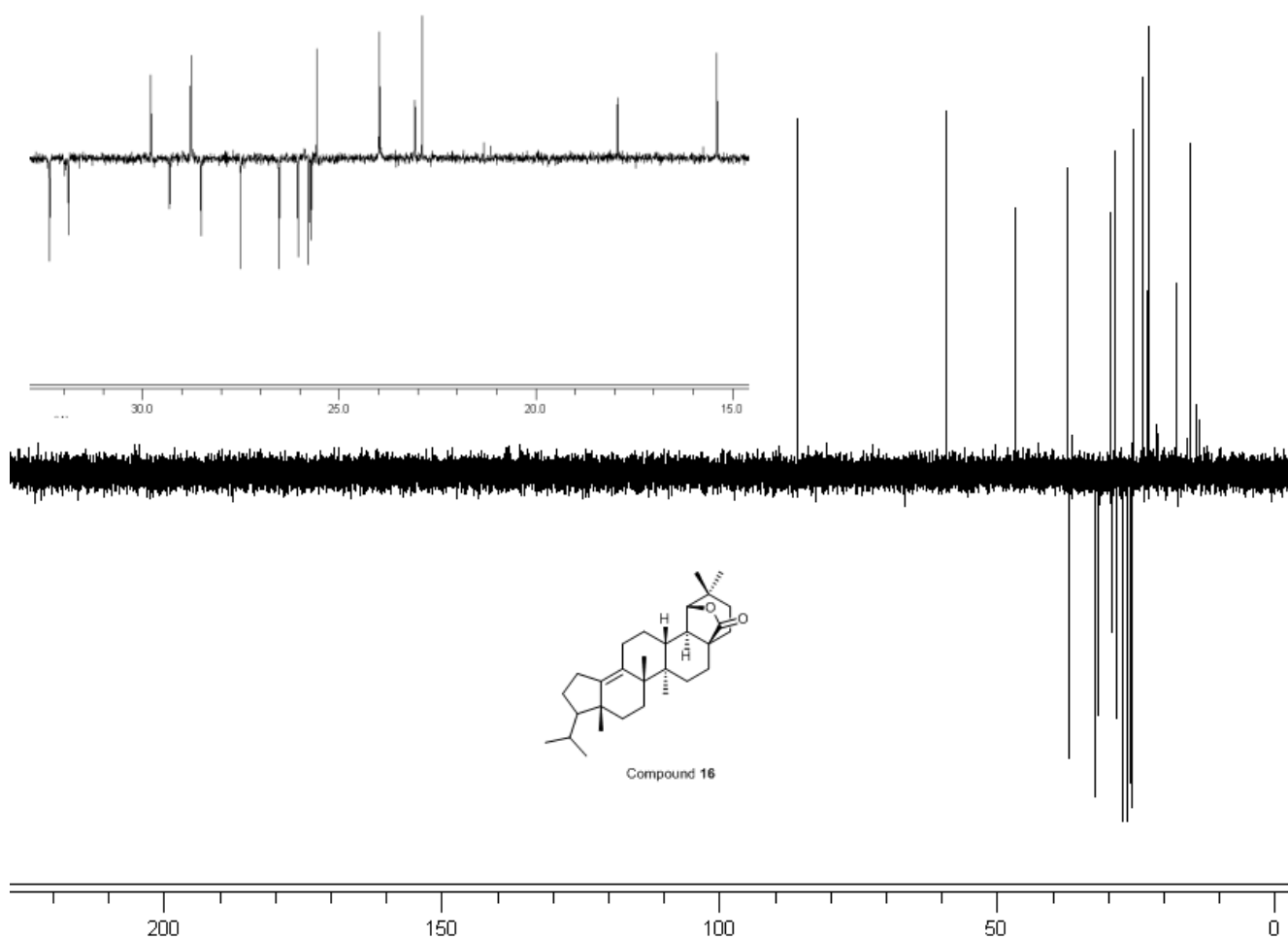


**Fig. S21.** <sup>1</sup>H NMR of compound **16** in CDCl<sub>3</sub>.

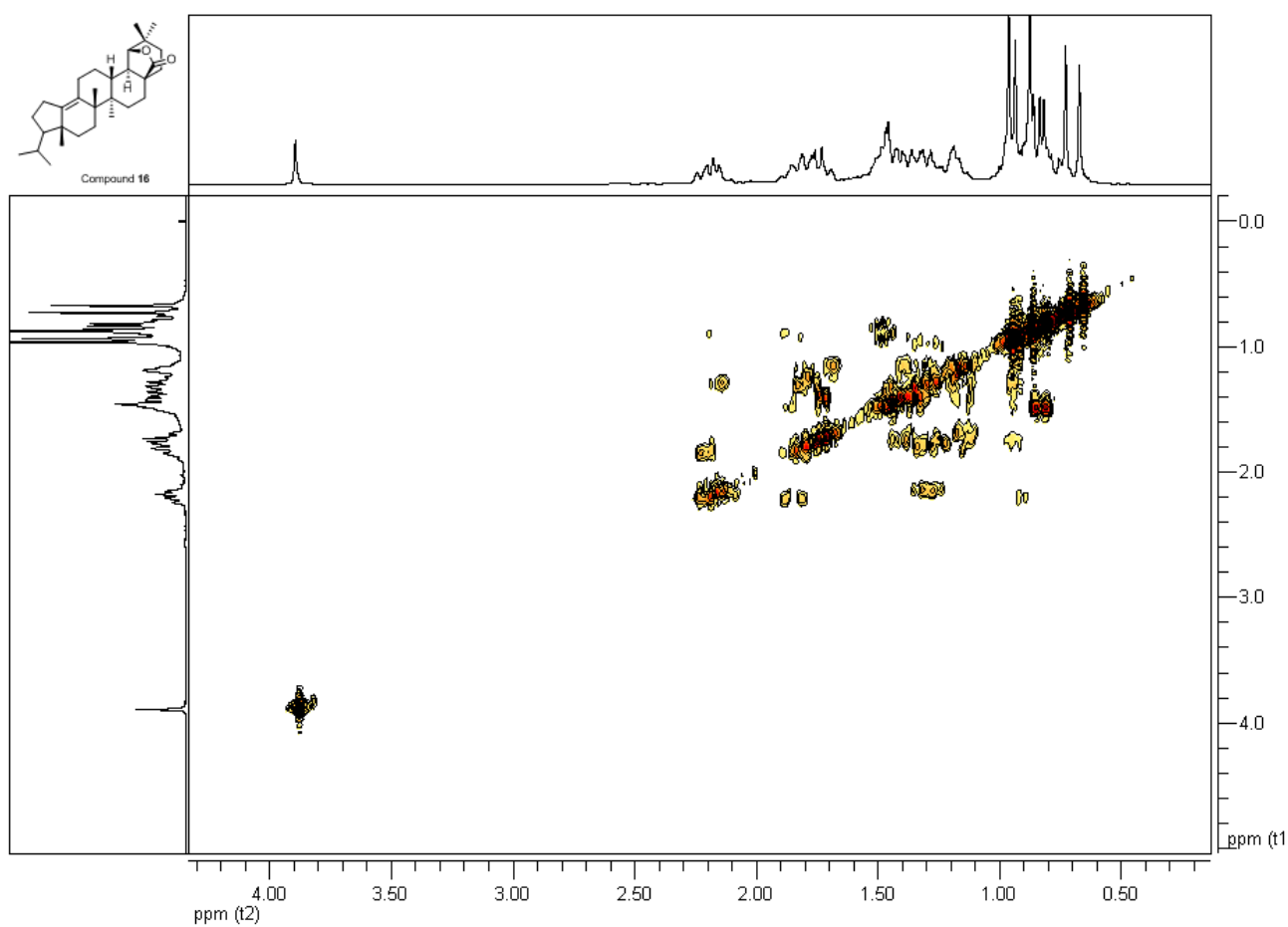




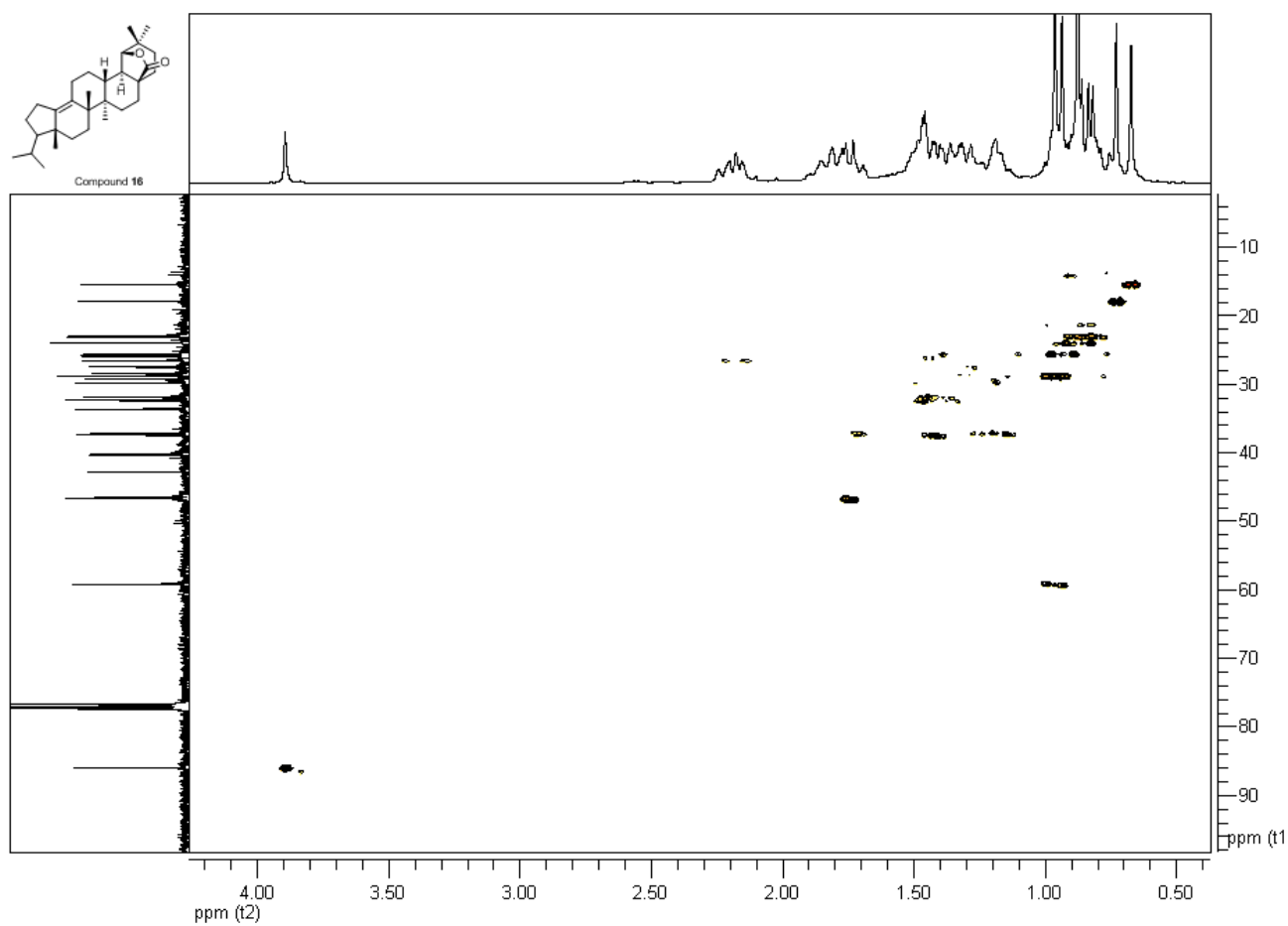
**Fig. S22.**  $^{13}\text{C}$  NMR of compound 16 in  $\text{CDCl}_3$ .



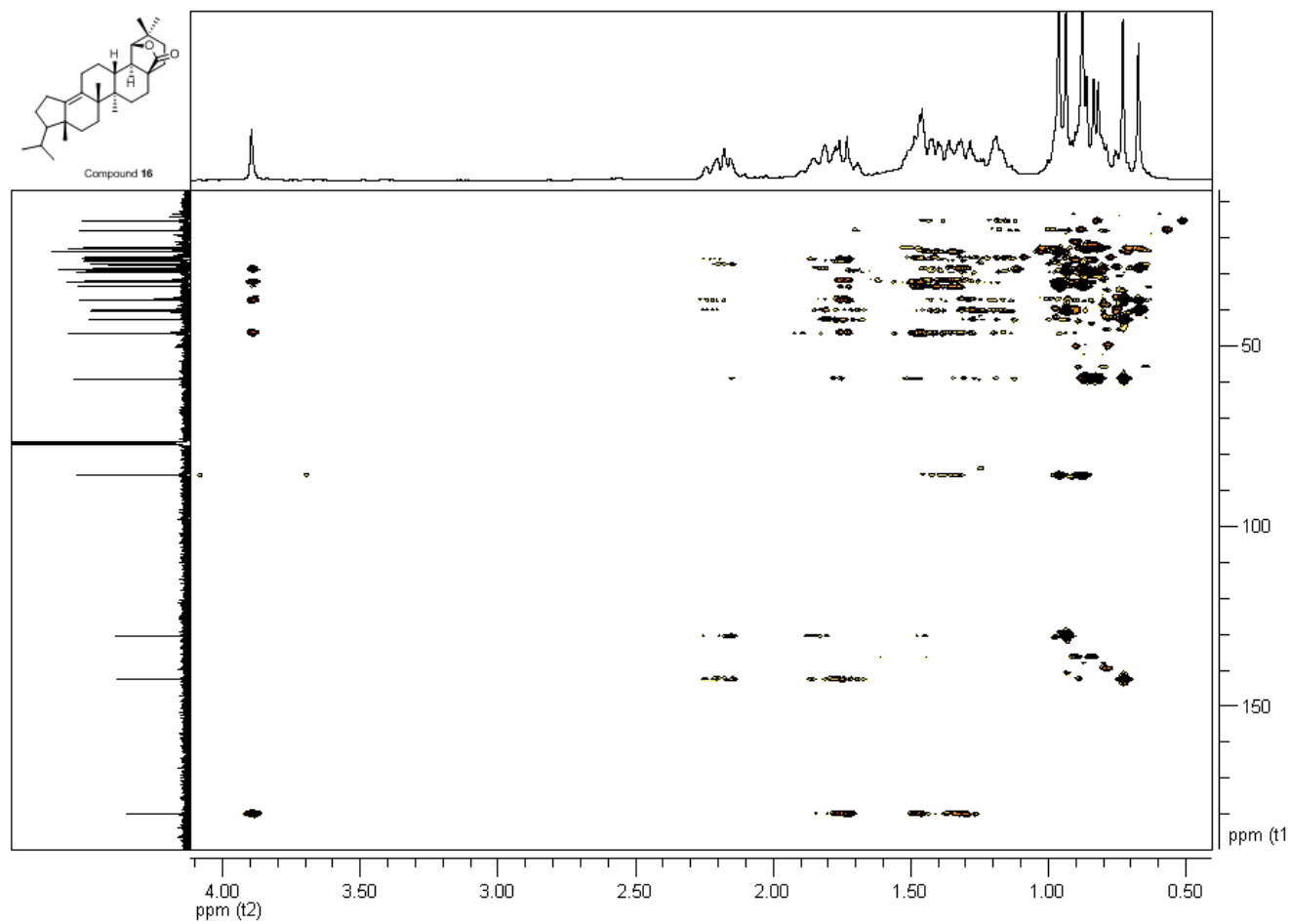
**Fig. S23.** DEPT 135 of compound **16** in CDCl<sub>3</sub>.

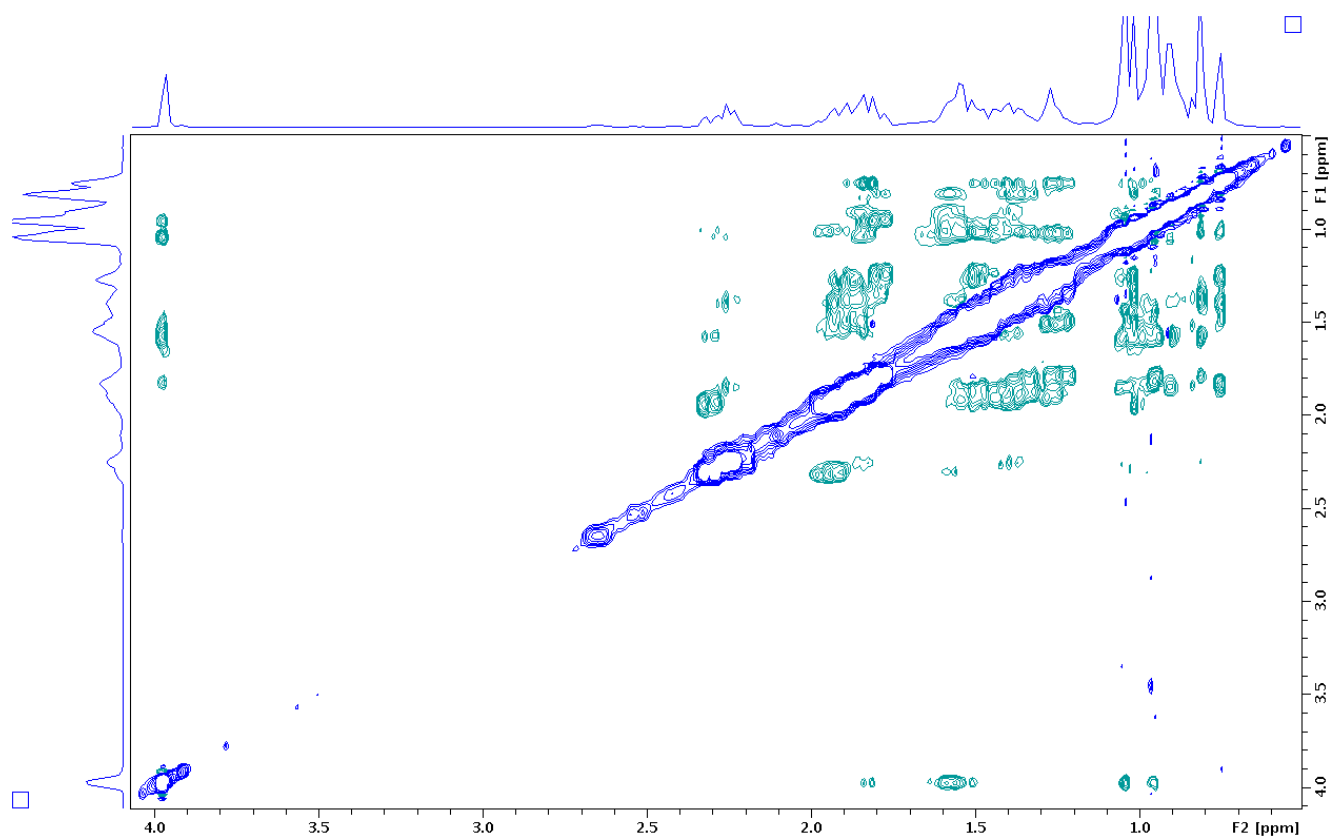


**Fig. S24.**  $^1\text{H}$ - $^1\text{H}$  COSY of compound **16** in  $\text{CDCl}_3$ .



**Fig. S25.** HMQC of compound 16 in CDCl<sub>3</sub>.

**Fig. S26.** HMBC of compound **16** in  $\text{CDCl}_3$ .



**Fig. S27.** NOESY of compound **16** in  $\text{CDCl}_3$ .