

Electronic Supplementary Information (ESI)

The assignment of absolute configuration of cyanohydrins by NMR

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MPA esters of cyanohydrins: general experimental procedure. The MPA esters were prepared by treatment of the cyanohydrin (1.0 equivalent) with the corresponding (*R*) and (*S*)-MPA (1.25 equivalents) in the presence of 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 1.25 equivalents) and catalytic DMAP (20 mol%) in dry CH₂Cl₂ and under a nitrogen atmosphere. The reaction mixtures were stirred at r.t. for 2 h. Next, the organic layers were sequentially washed with water, HCl (1N), water, NaHCO₃ (sat) and water. Then, the layers were dried (anh. NaSO₄) and concentrated under reduced pressure to provide the corresponding esters. If needed, further purification was achieved by means of flash column chromatography (silica gel 230-400; elution with 9:1 to 4:1 hexanes/ethyl acetate mixtures; 63-95% yields after purification).

NMR Spectroscopy. 1D ¹H and ¹³C and 2D COSY, TOCSY, HSQC and HMBC spectra of samples in CDCl₃ were recorded in 250, 300, 400 and 500 MHz. Chemical shifts (ppm) are internally referenced to the TMS signal (0 ppm) in ¹H-NMR spectra. ¹³C-NMR spectra are referenced to the CDCl₃ signal. ¹H and ¹³C-NMR spectra of MPA derivatives of compounds **1-13** and 9-AMA derivatives of compound **2** are shown in next pages.

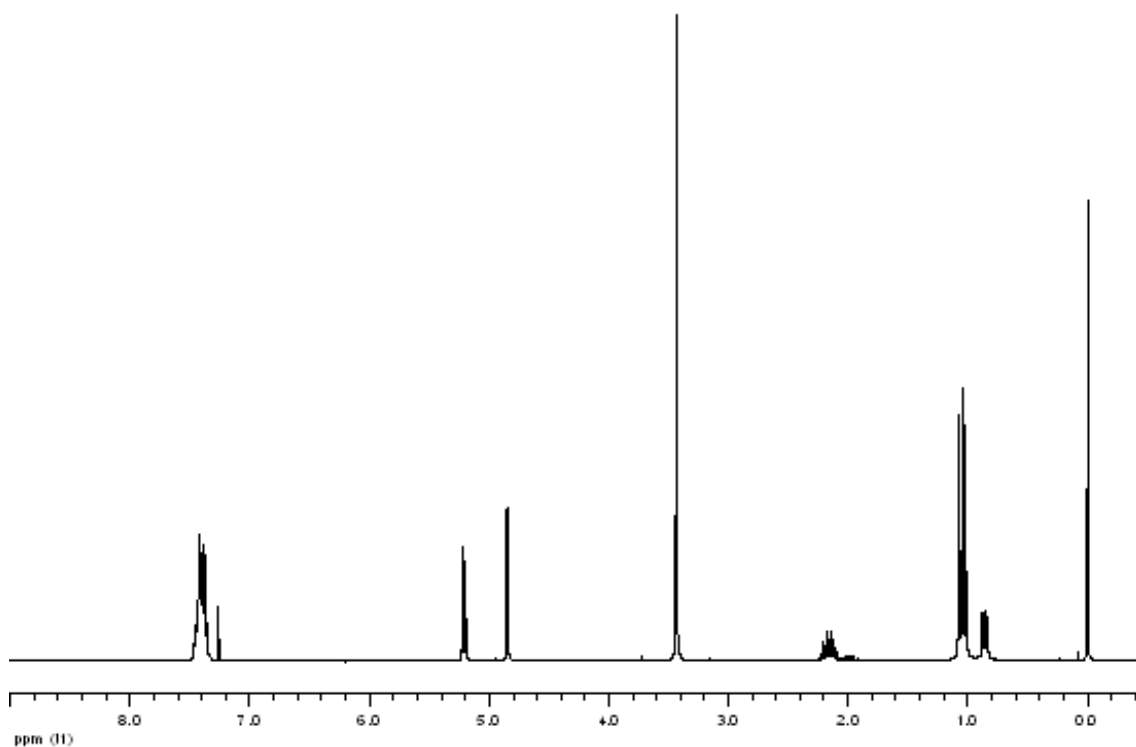


Figure 1S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **1** (250.13 MHz, CDCl_3 , dr 85/15).

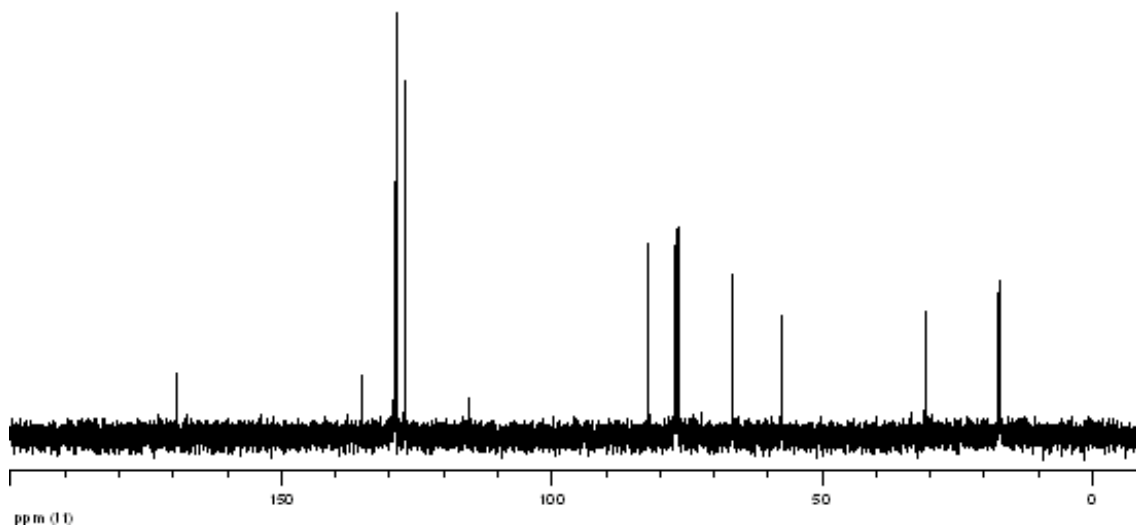


Figure 2S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **1** (75.46 MHz, CDCl_3 , dr 85/15).

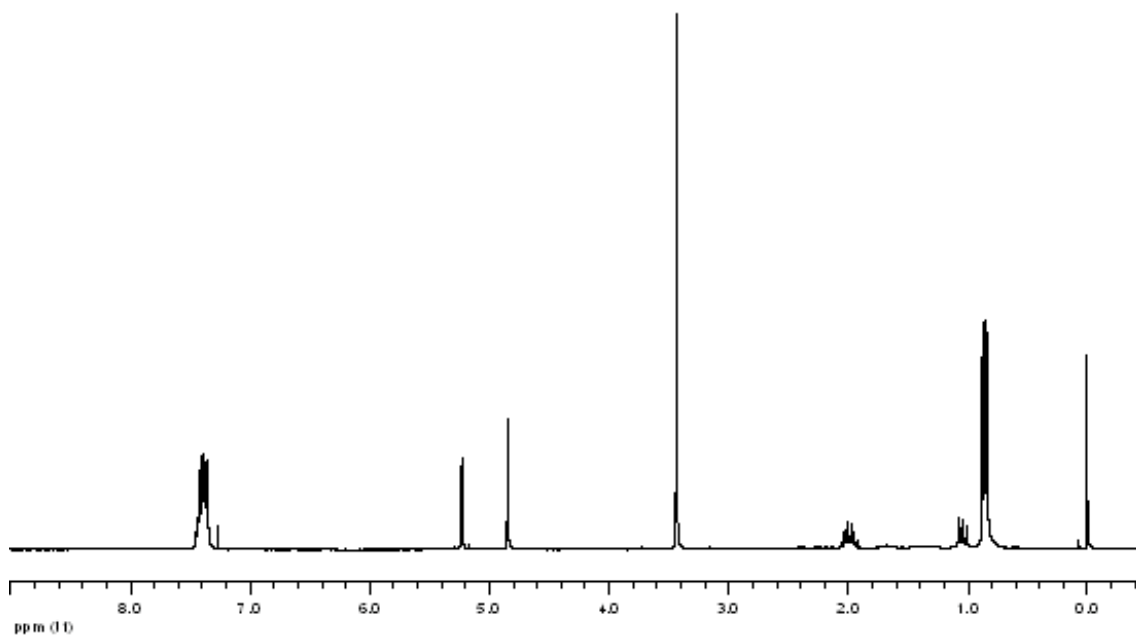


Figure 3S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **1** (250.13 MHz, CDCl_3 , dr 88/12).

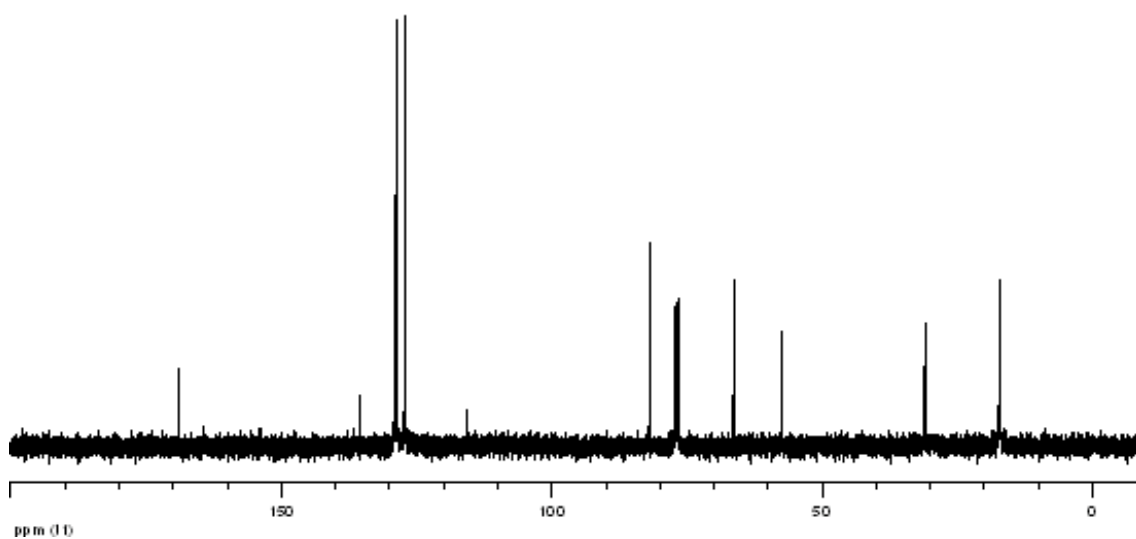


Figure 4S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **1** (75.46 MHz, CDCl_3 , dr 88/12).

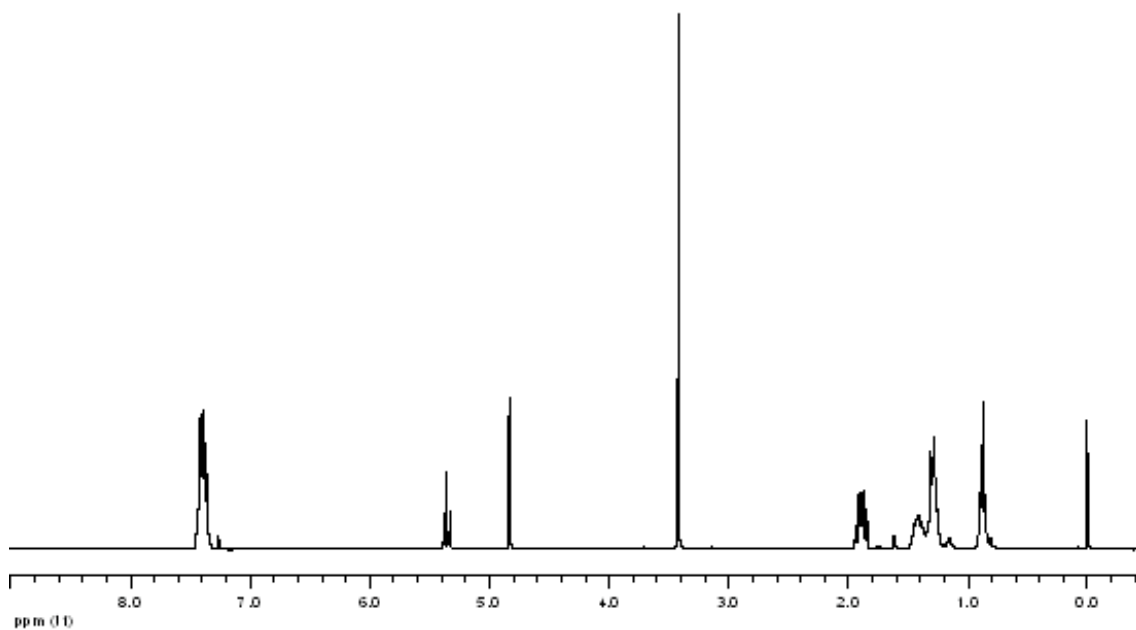


Figure 5S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **2** (250.13 MHz, CDCl_3).

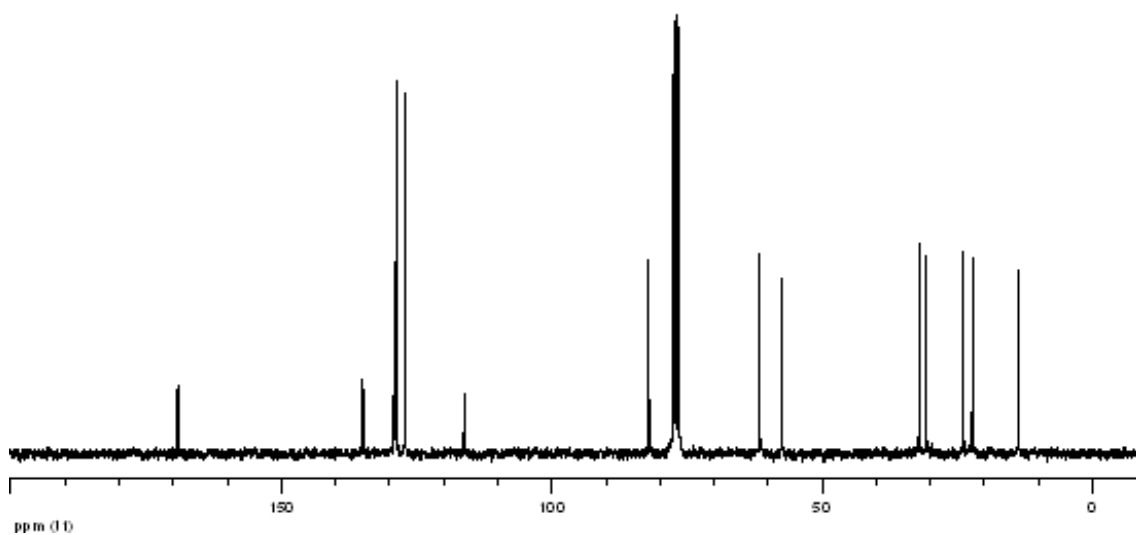


Figure 6S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **2** (62.90 MHz, CDCl_3).

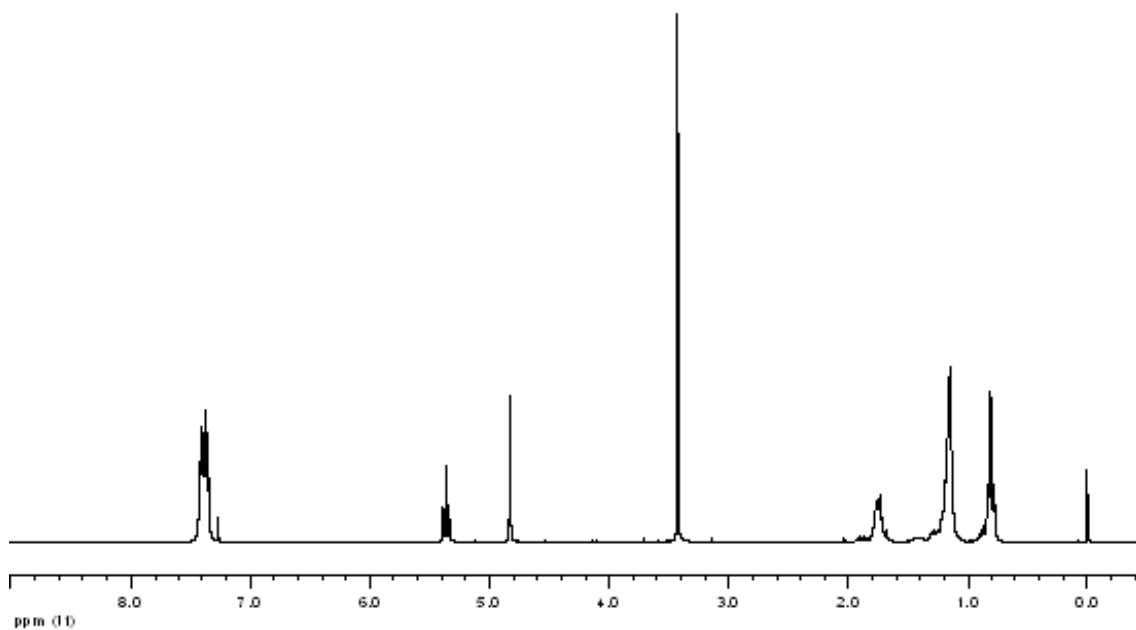


Figure 7S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **2** (250.13 MHz, CDCl_3).

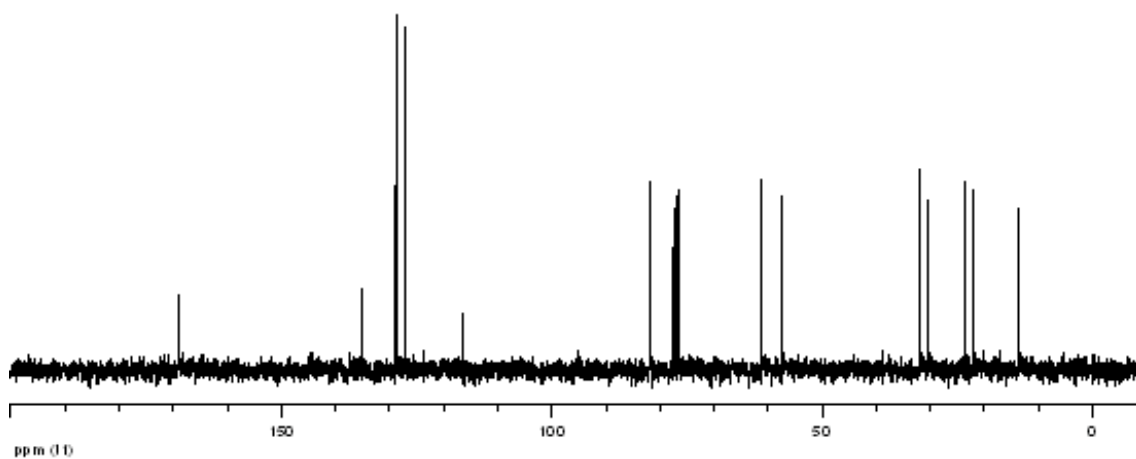


Figure 8S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **2** (62.90 MHz, CDCl_3).

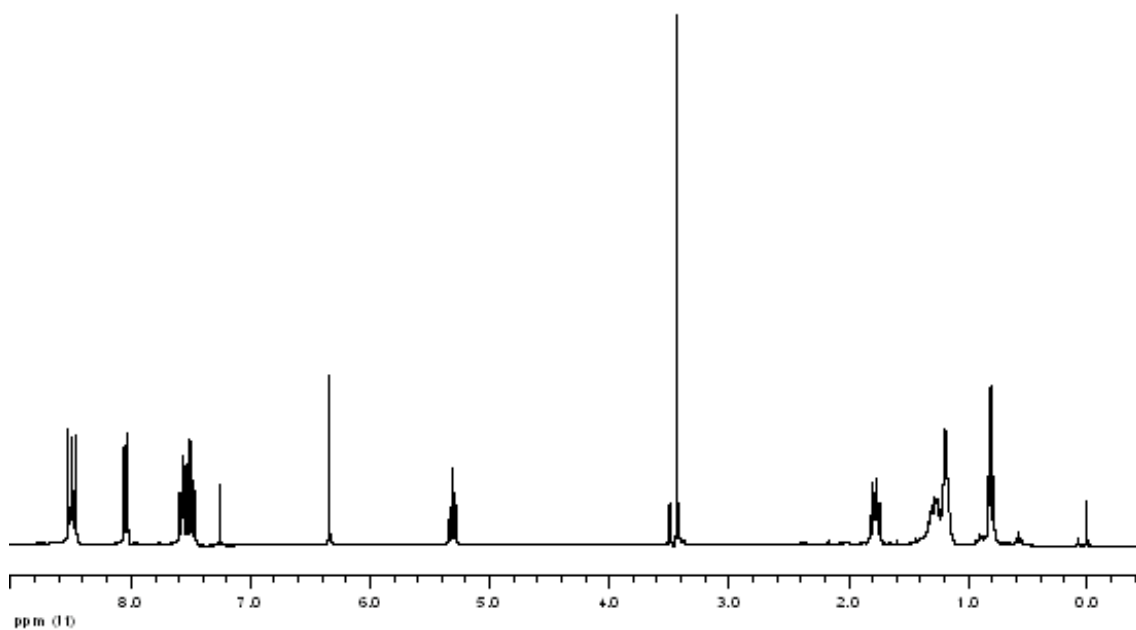


Figure 9S. ^1H -NMR spectrum of (*R*)-9-AMA ester of compound **2** (300.07 MHz, CDCl_3).

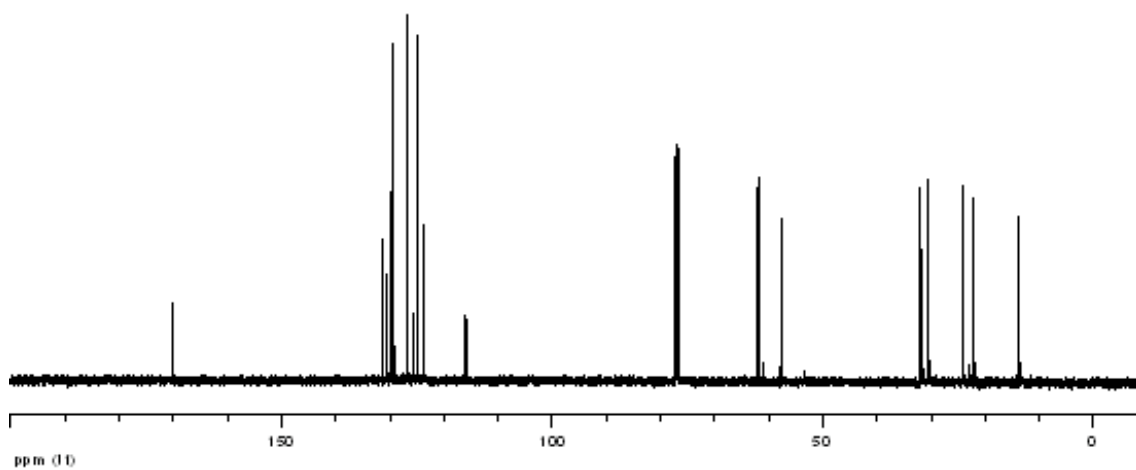


Figure 10S. ^{13}C -NMR spectrum of (*R*)-9-AMA ester of compound **2** (100.58 MHz, CDCl_3).

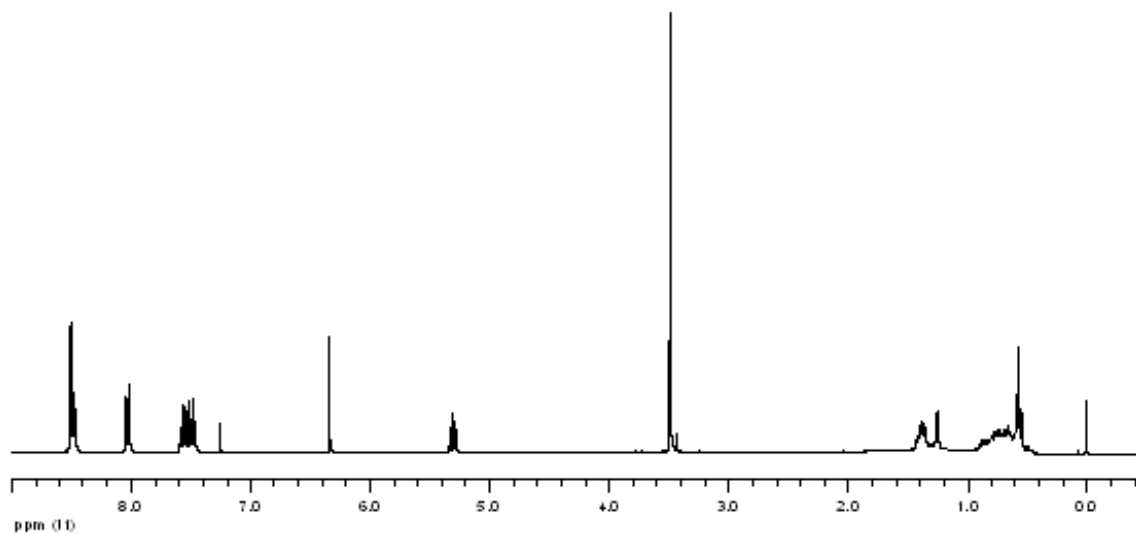


Figure 11S. ^1H -NMR spectrum of (*S*)-9-AMA ester of compound **2** (300.07 MHz, CDCl_3).

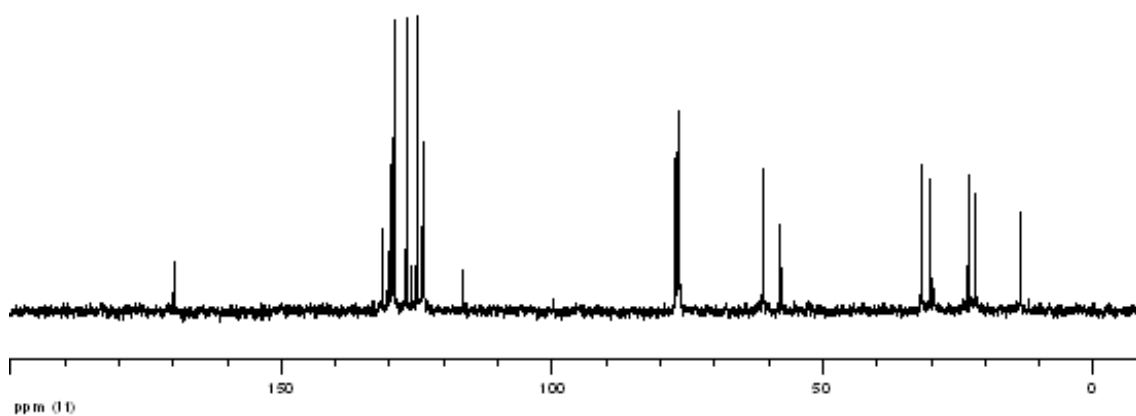


Figure 12S. ^{13}C -NMR spectrum of (*S*)-9-AMA ester of compound **2** (75.46 MHz, CDCl_3).

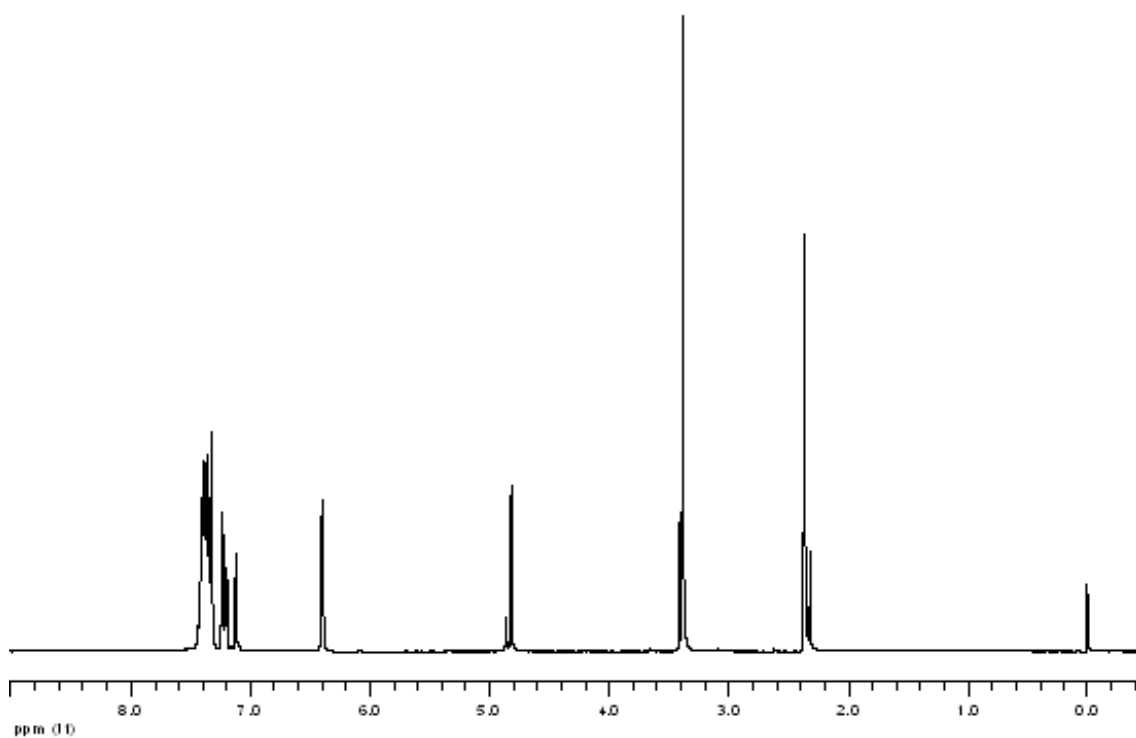


Figure 13S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **3** (250.13 MHz, CDCl_3 , dr 84/16).

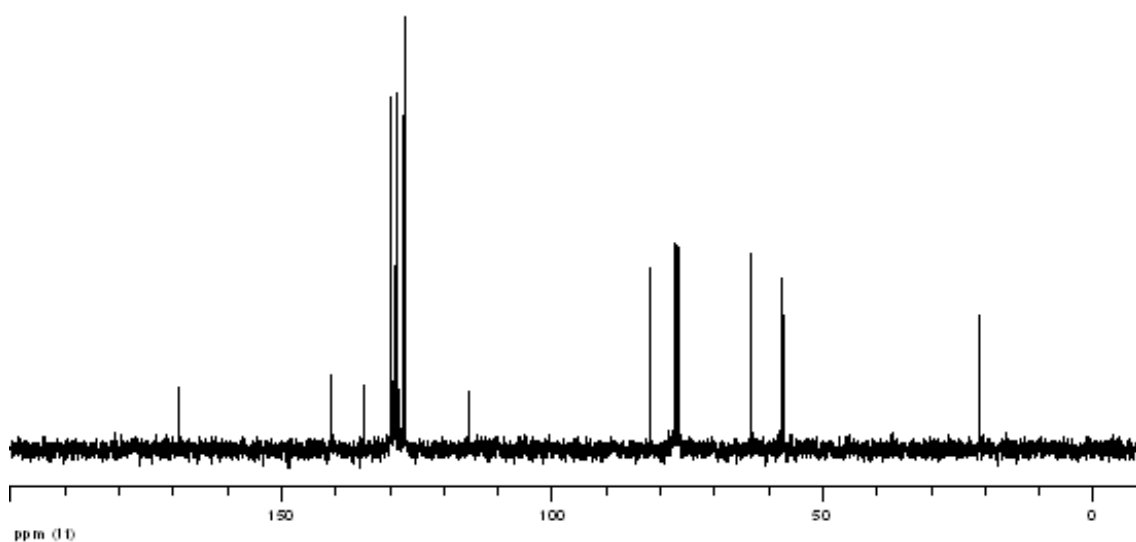


Figure 14S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **3** (62.90 MHz, CDCl_3 , dr 84/16).

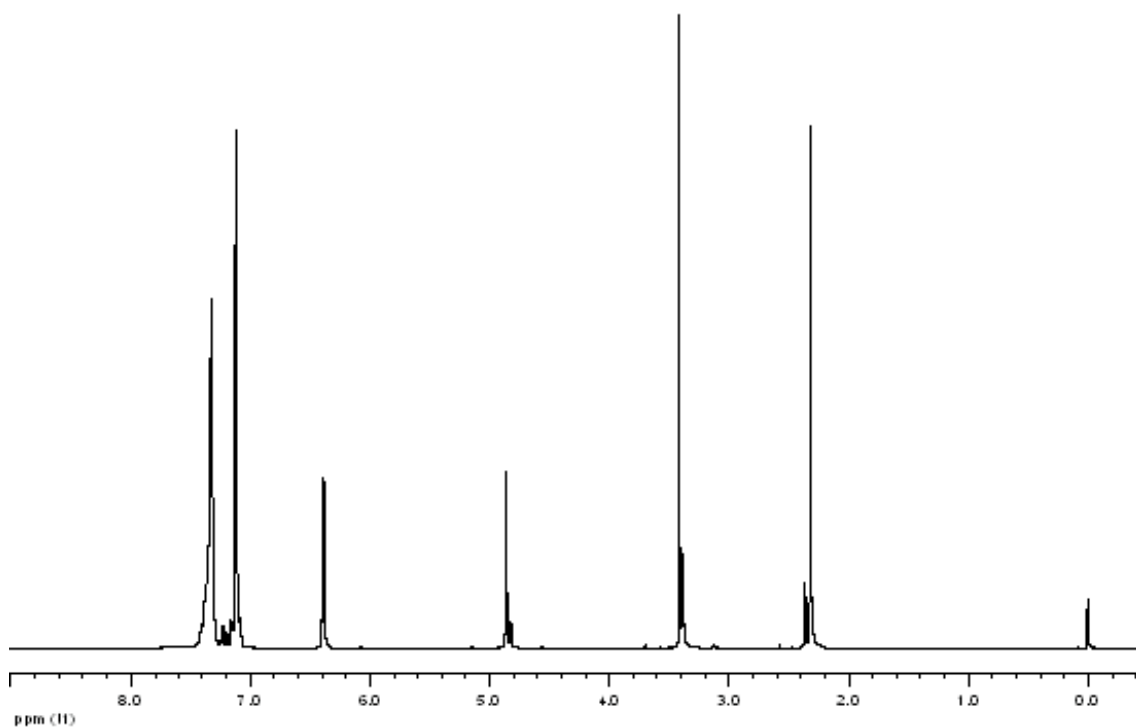


Figure 15S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **3** (250.13 MHz, CDCl_3 , dr 89/11).

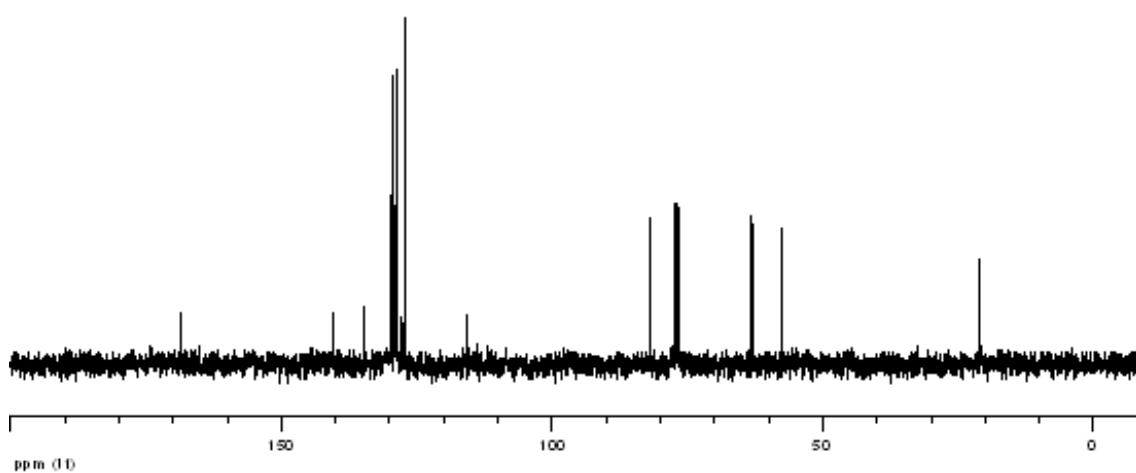


Figure 16S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **3** (62.90 MHz, CDCl_3 , dr 89/11).

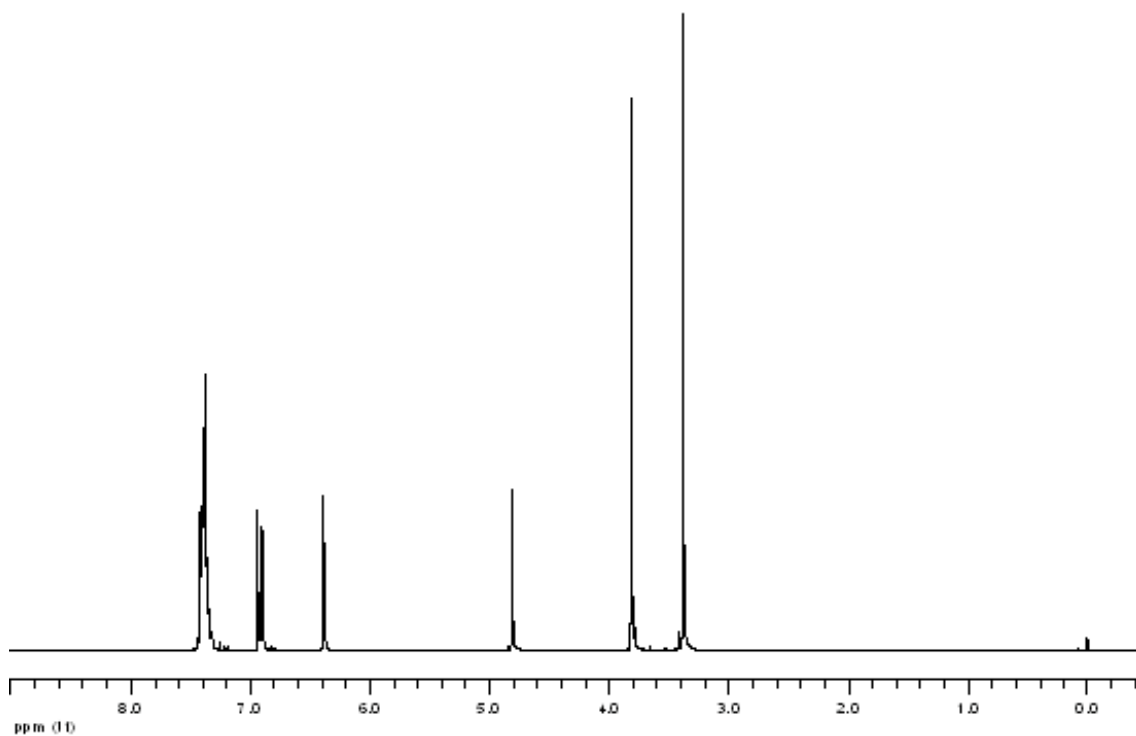


Figure 17S. ¹H-NMR spectrum of (*R*)-MPA ester of compound **4** (250.13 MHz, CDCl₃).

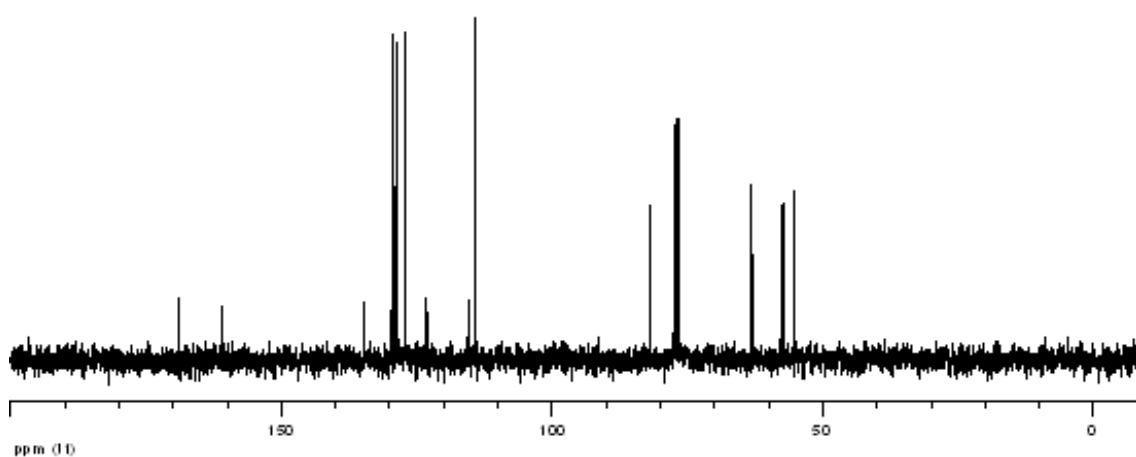


Figure 18S. ¹³C-NMR spectrum of (*R*)-MPA ester of compound **4** (62.90 MHz, CDCl₃).

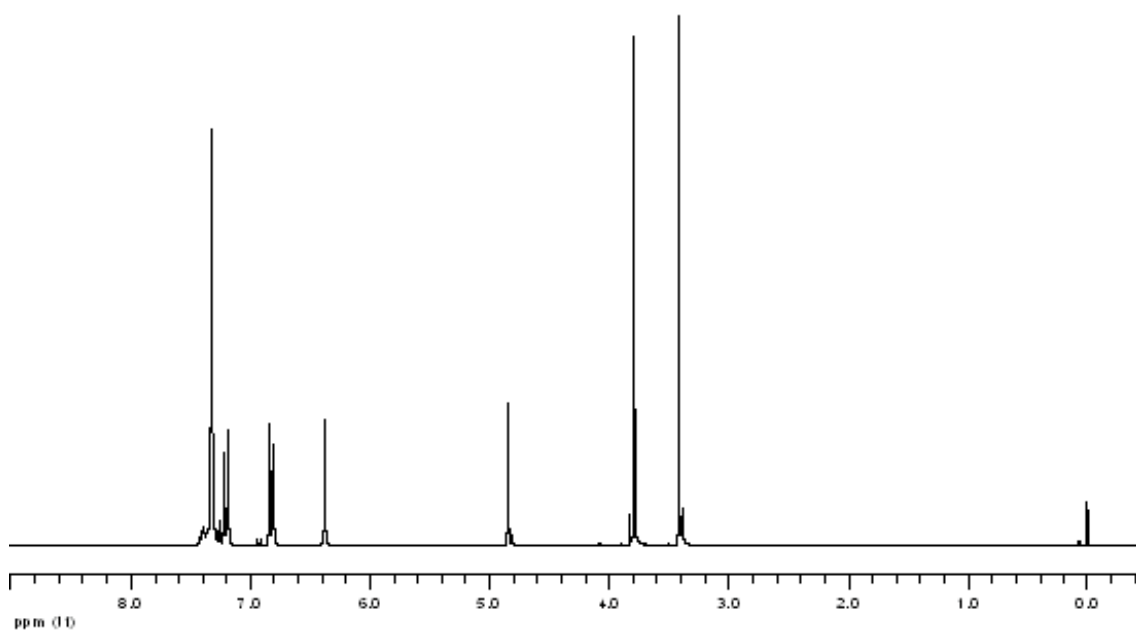


Figure 19S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **4** (250.13 MHz, CDCl_3).

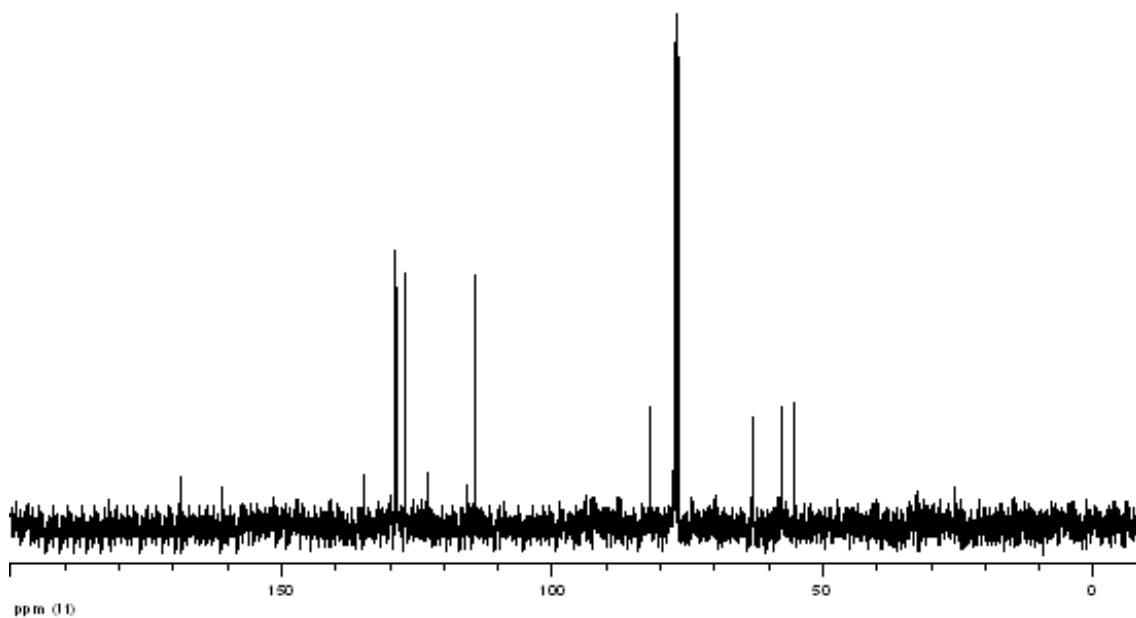


Figure 20S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **4** (62.90 MHz, CDCl_3).

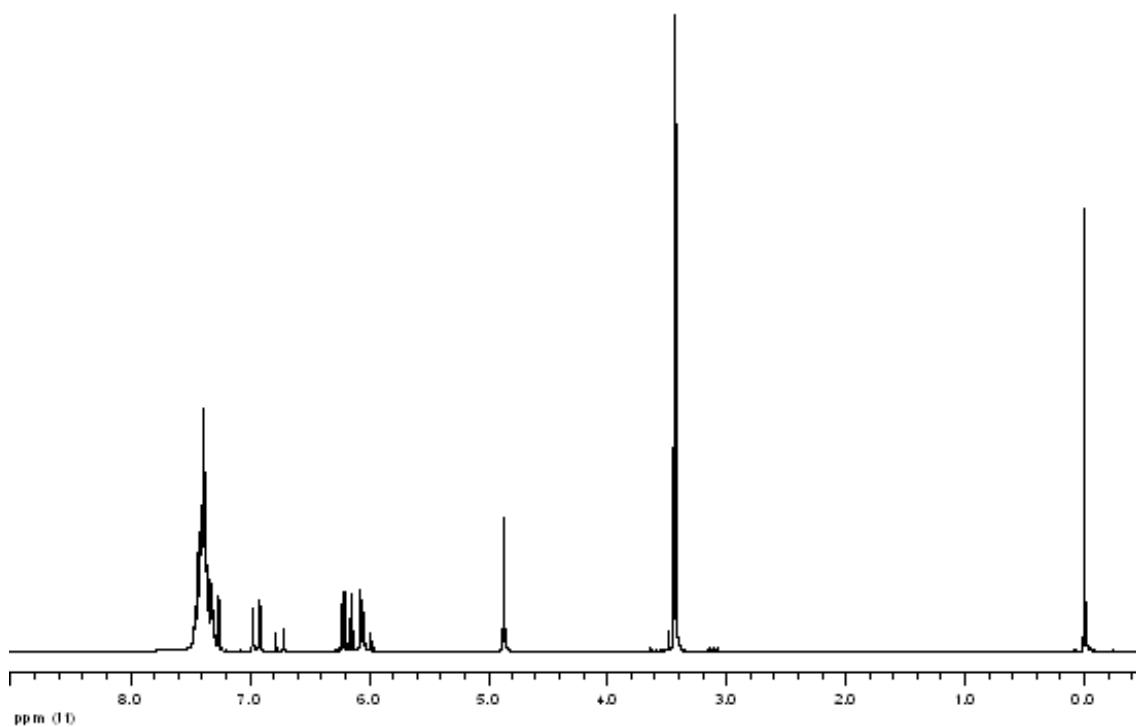


Figure 21S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **5** (250.13 MHz, CDCl_3 , dr 81/19).

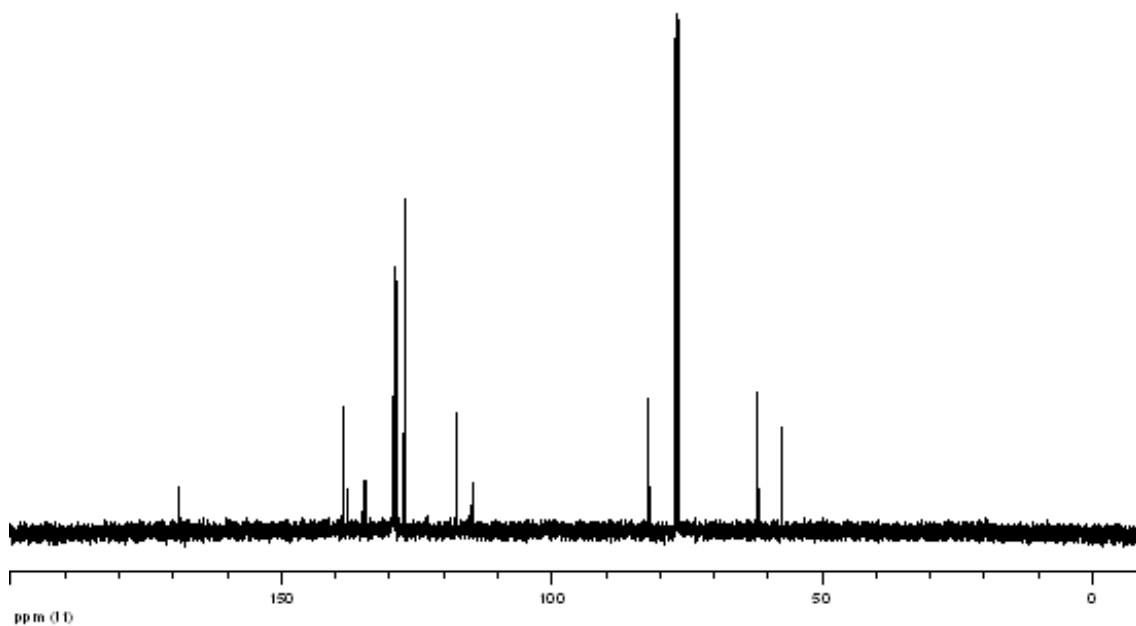


Figure 22S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **5** (100.58 MHz, CDCl_3 , dr 81/19).

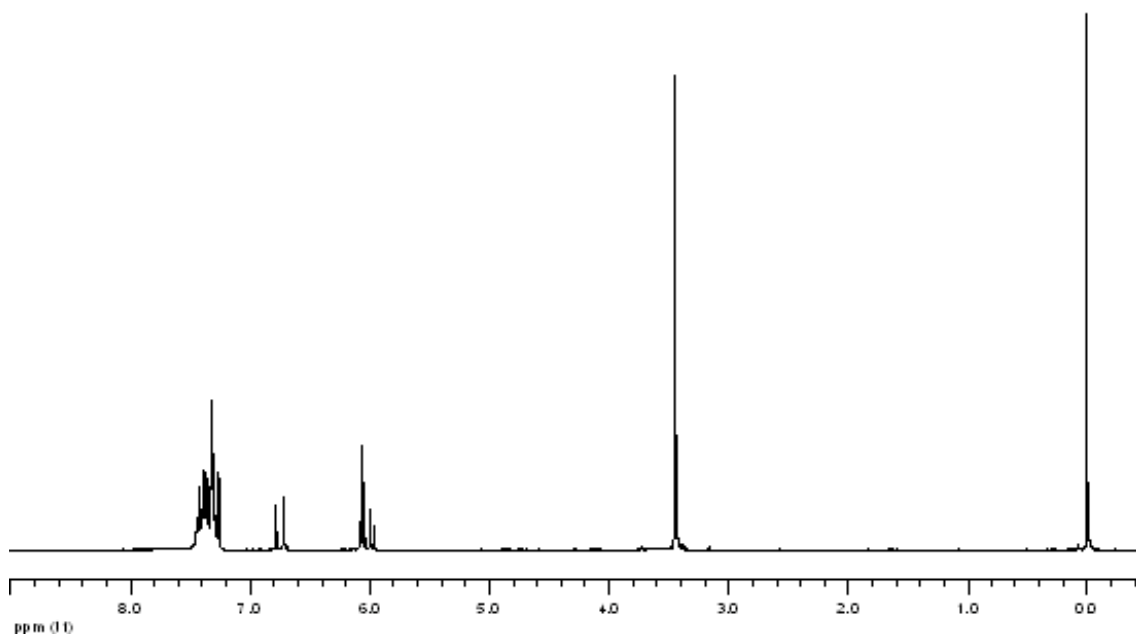


Figure 23S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **5** (250.13 MHz, CDCl_3).

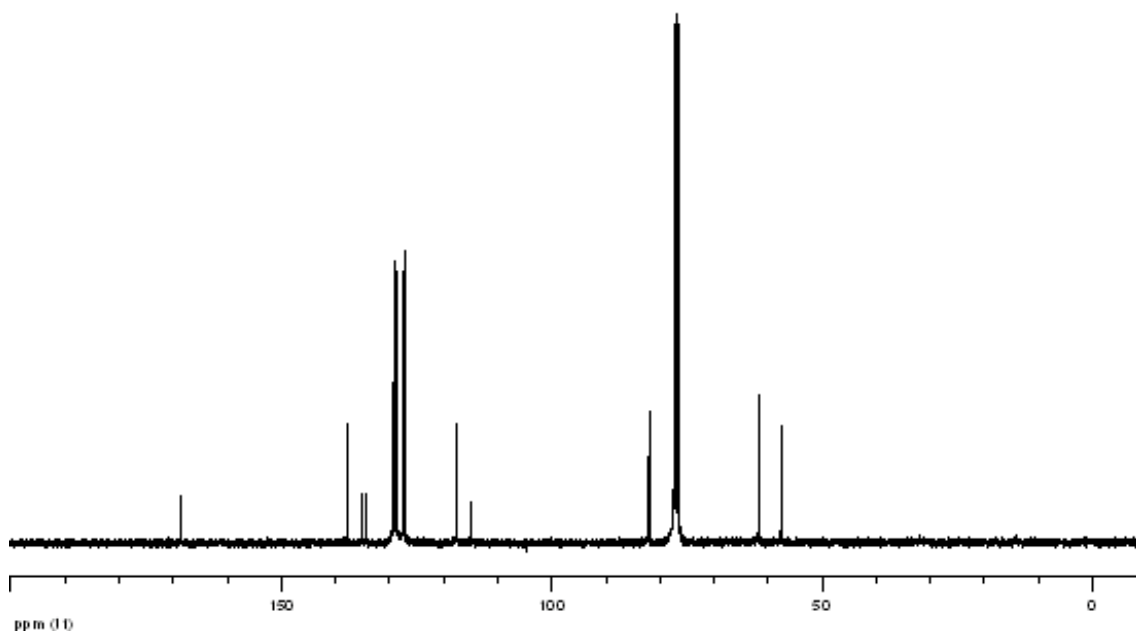


Figure 24S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **5** (75.46 MHz, CDCl_3).

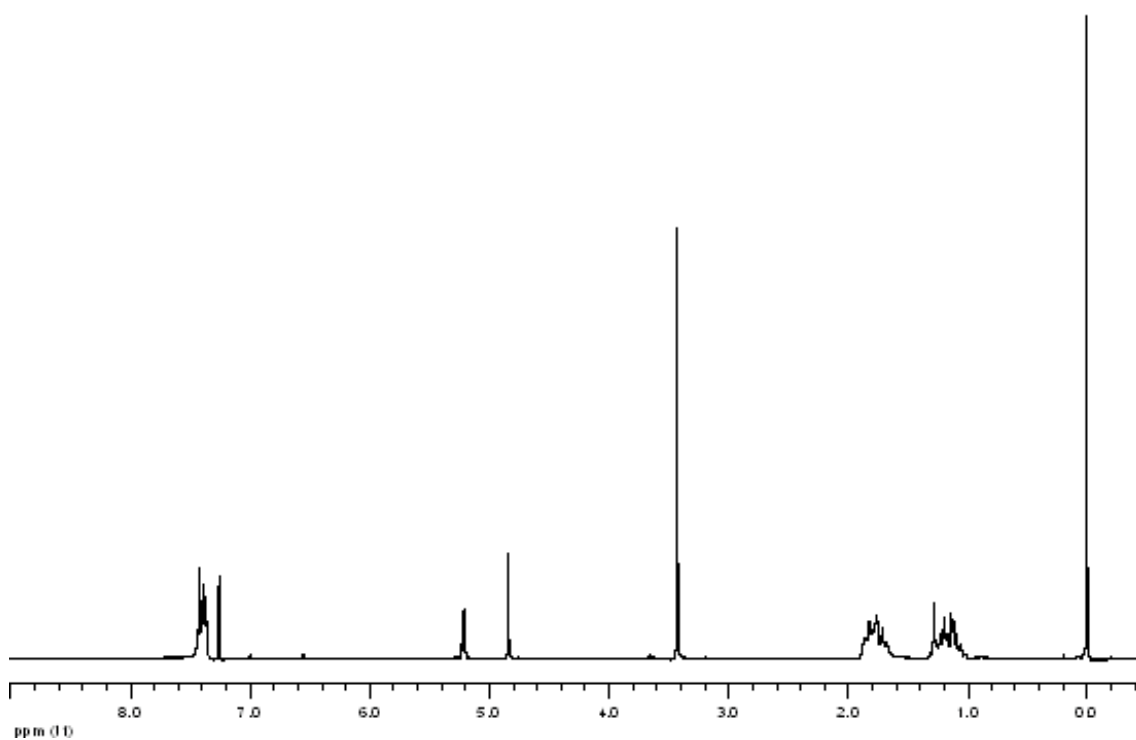


Figure 25S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **6** (300.07 MHz, CDCl_3).

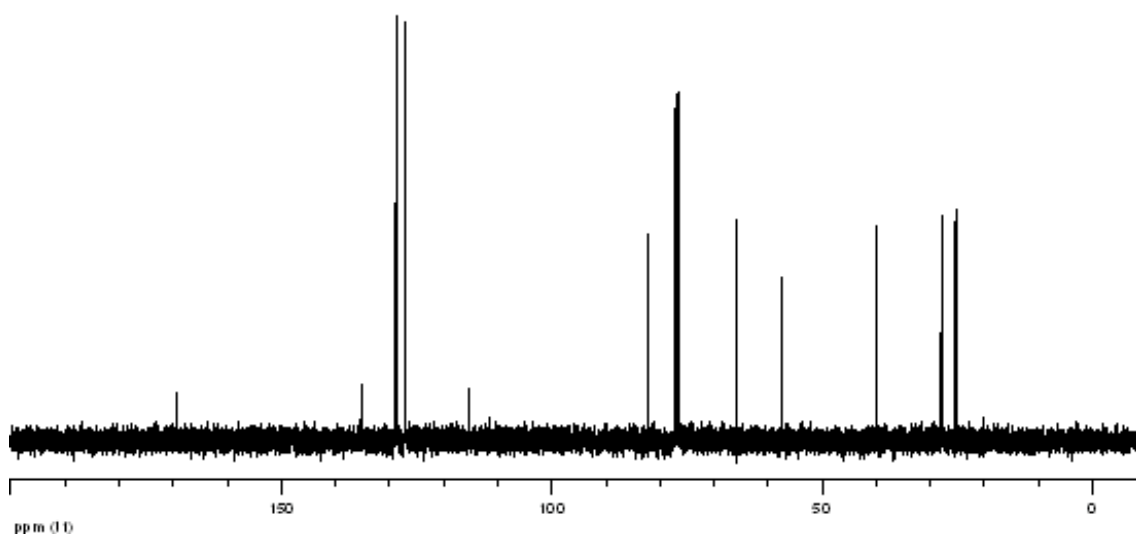


Figure 26S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **6** (75.46 MHz, CDCl_3).

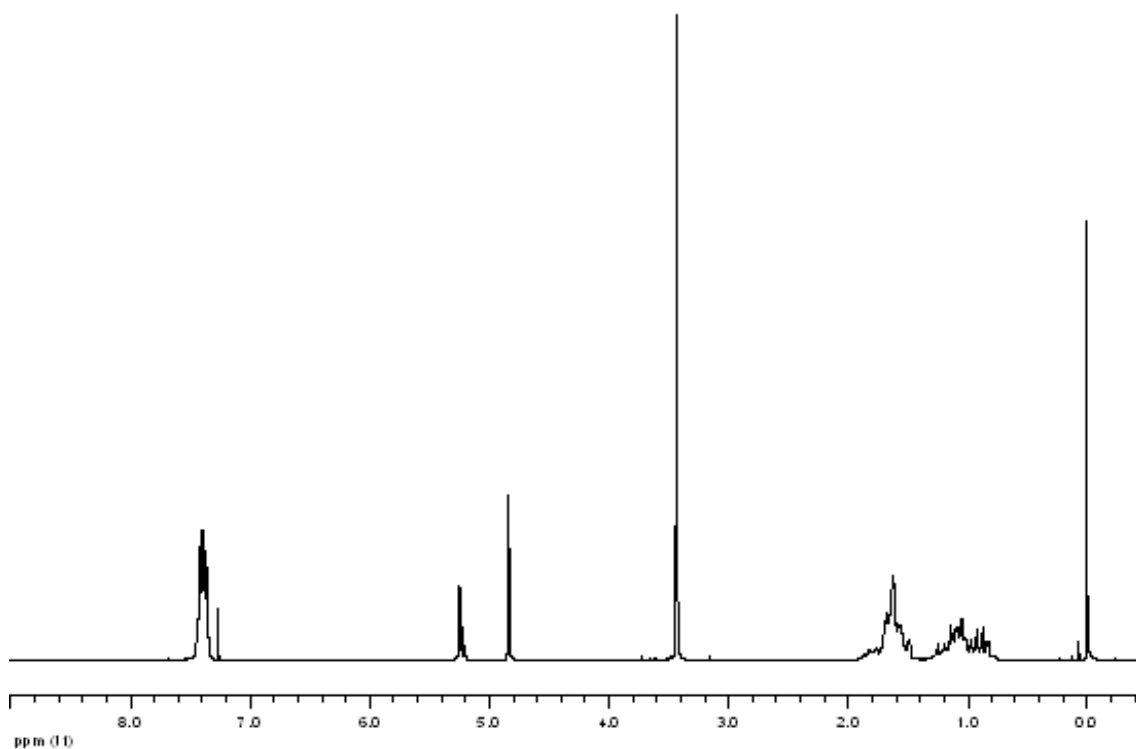


Figure 27S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **6** (250.13 MHz, CDCl_3 , dr 85/15).

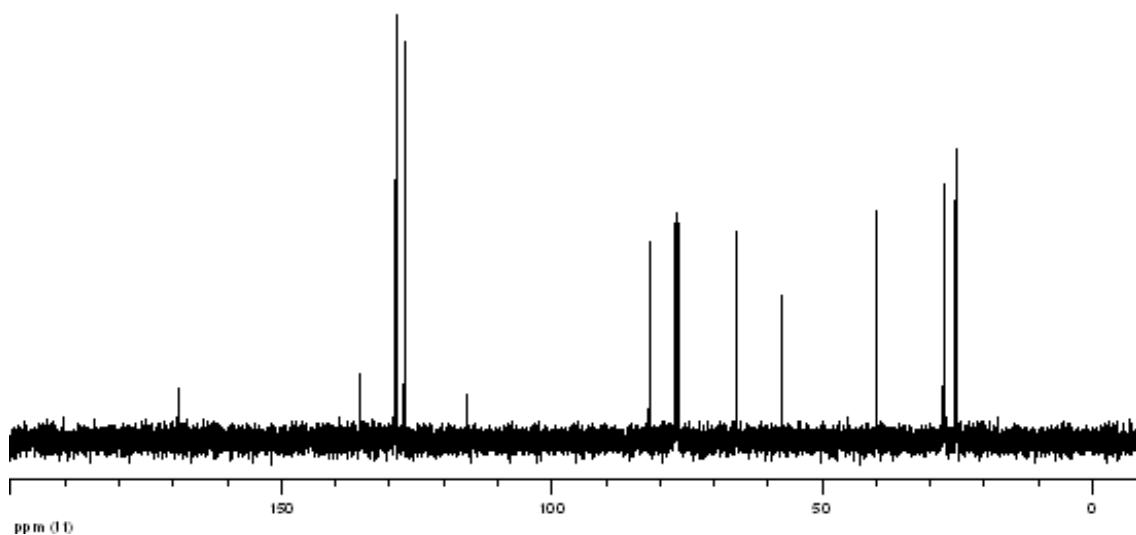


Figure 28S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **6** (75.46 MHz, CDCl_3 , dr 85/15).

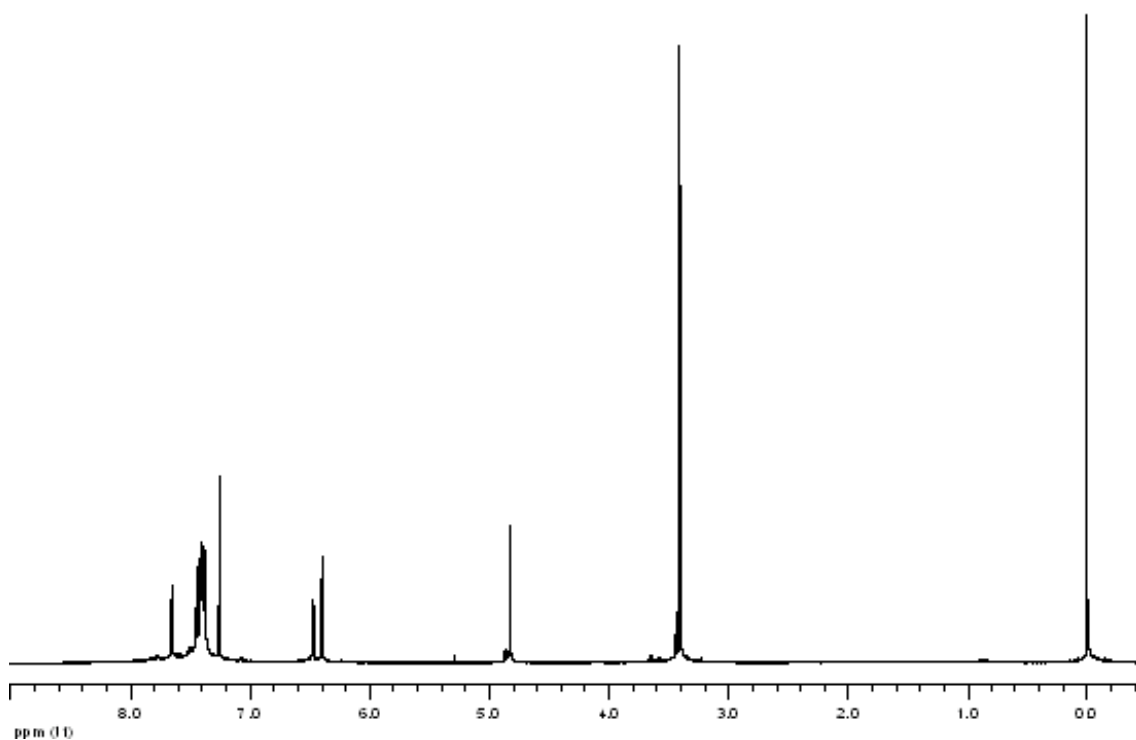


Figure 29S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **7** (399.97 MHz, CDCl_3).

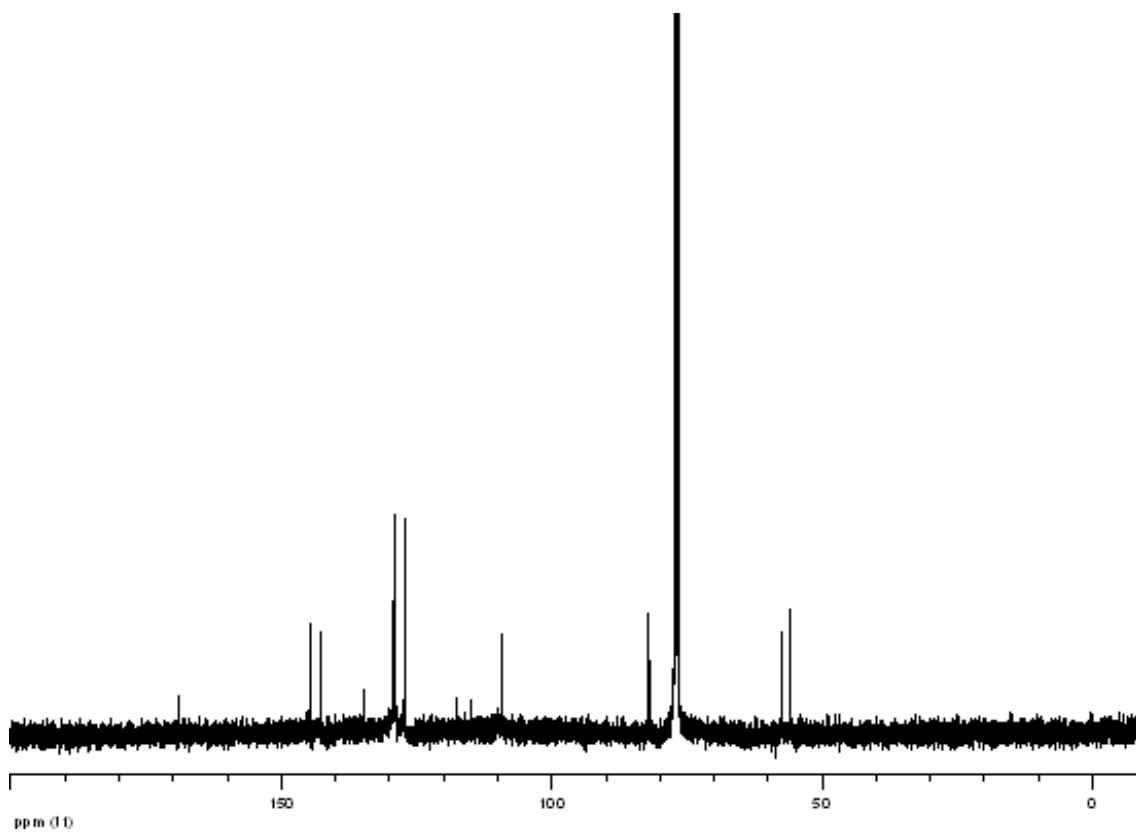


Figure 30S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **7** (100.58 MHz, CDCl_3).

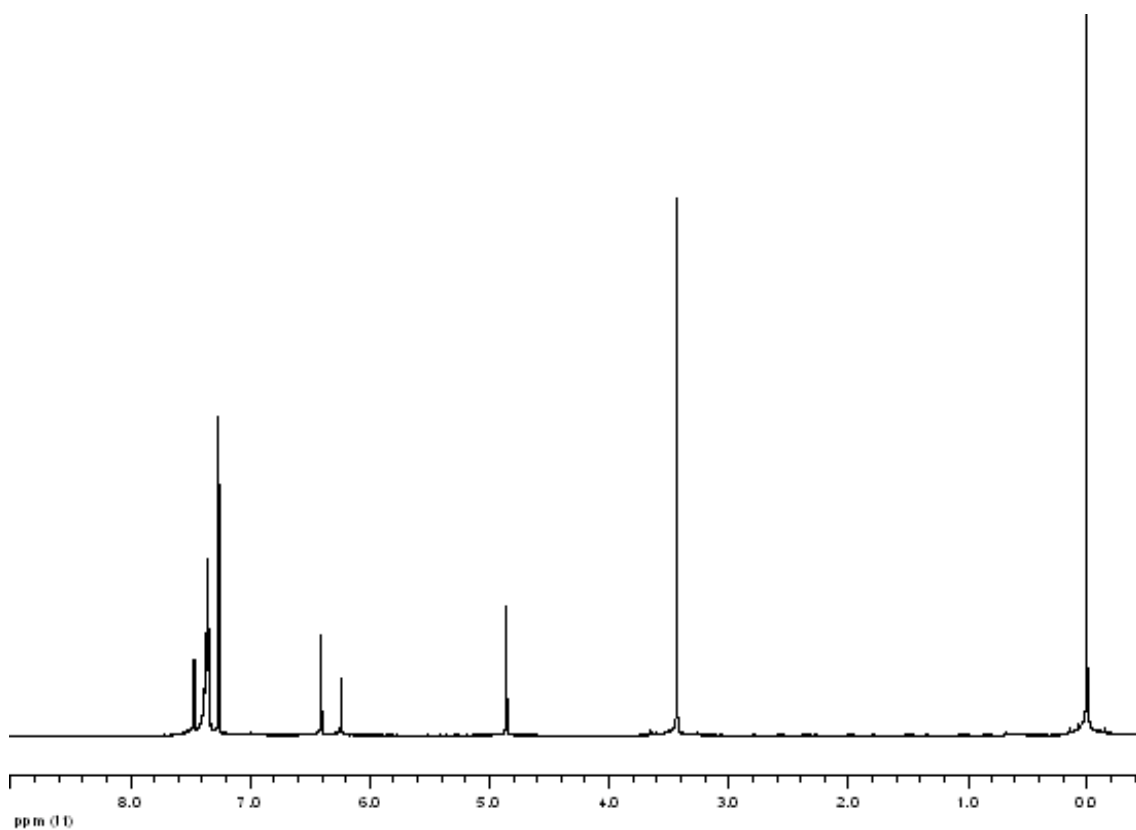


Figure 31S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **7** (399.97 MHz, CDCl_3).

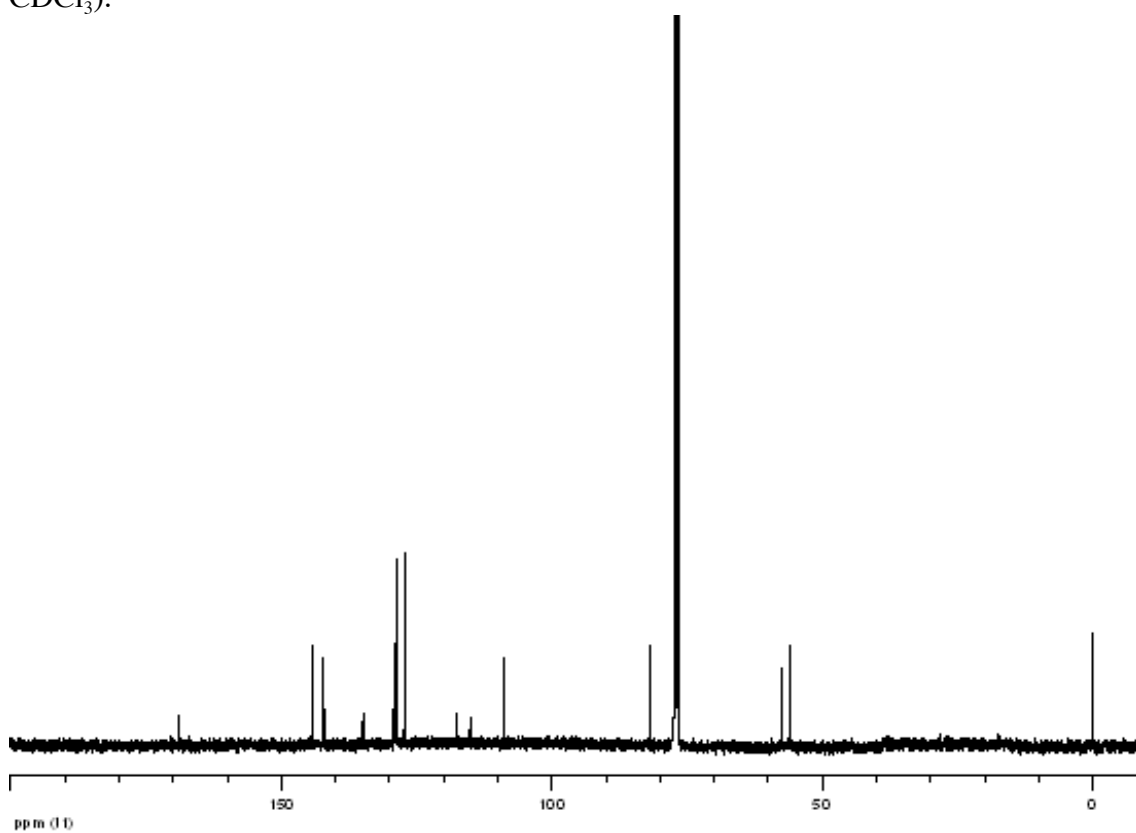


Figure 32S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **7** (100.58 MHz, CDCl_3).

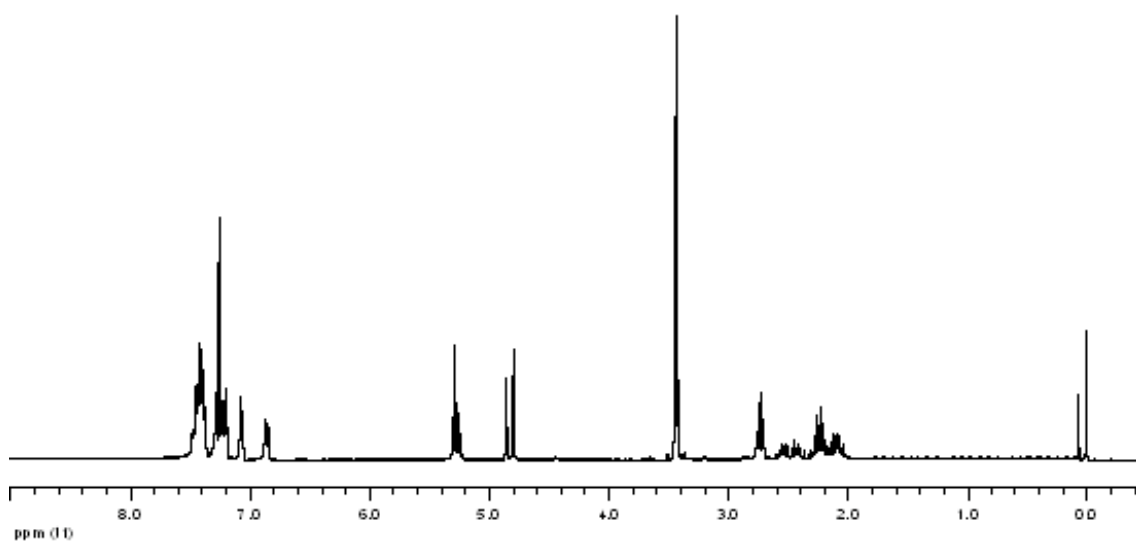


Figure 33S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **8** (250.13 MHz, CDCl_3 , dr 57/43).

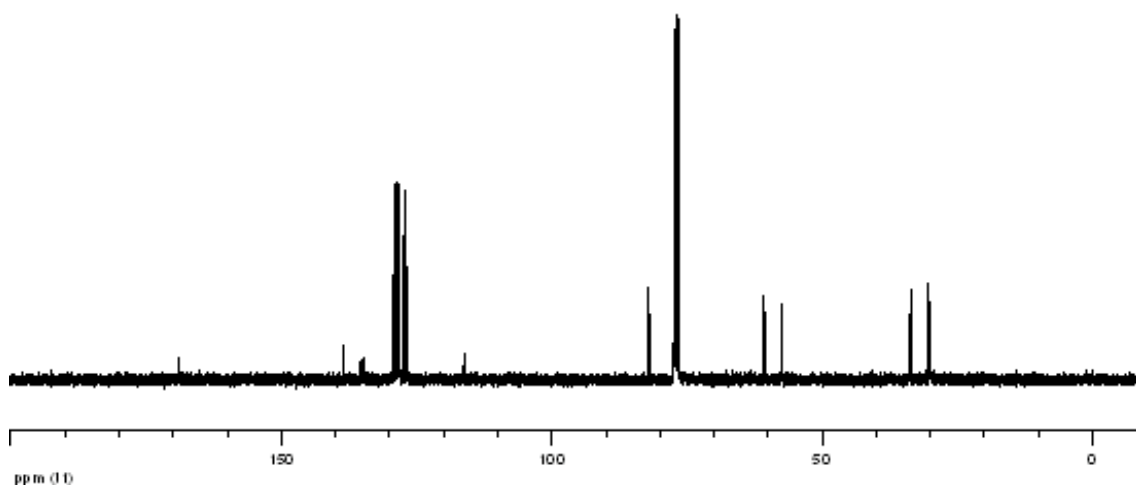


Figure 34S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **8** (75.46 MHz, CDCl_3 , dr 57/43).

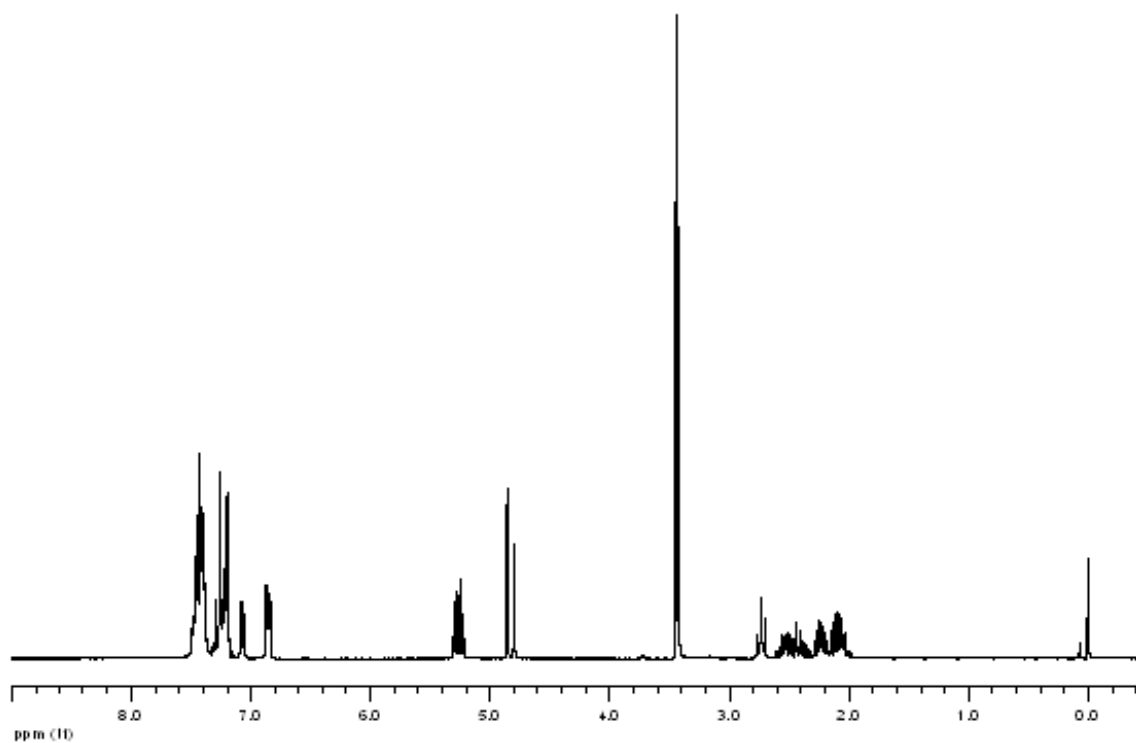


Figure 35S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **8** (250.13 MHz, CDCl_3 , dr 61/39).

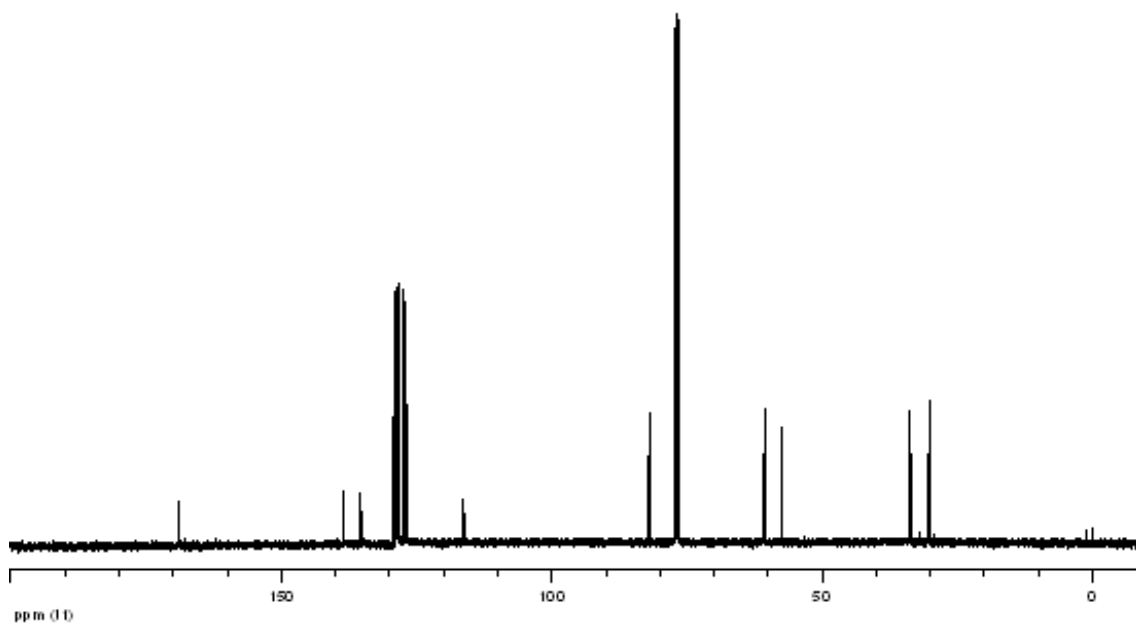


Figure 36S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **8** (100.58 MHz, CDCl_3 , dr 61/39).

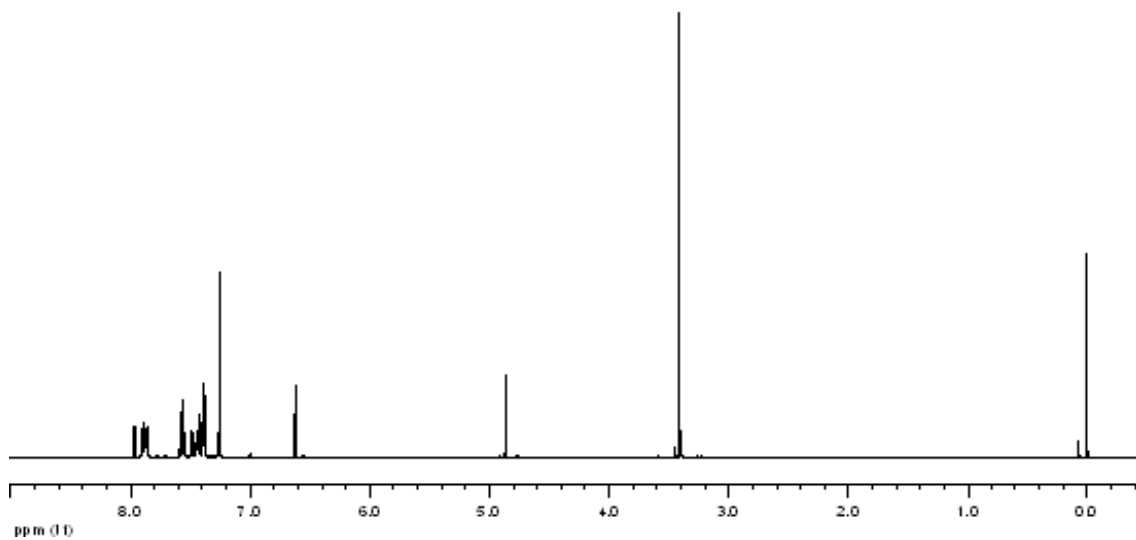


Figure 37S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **9** (399.97 MHz, CDCl_3).

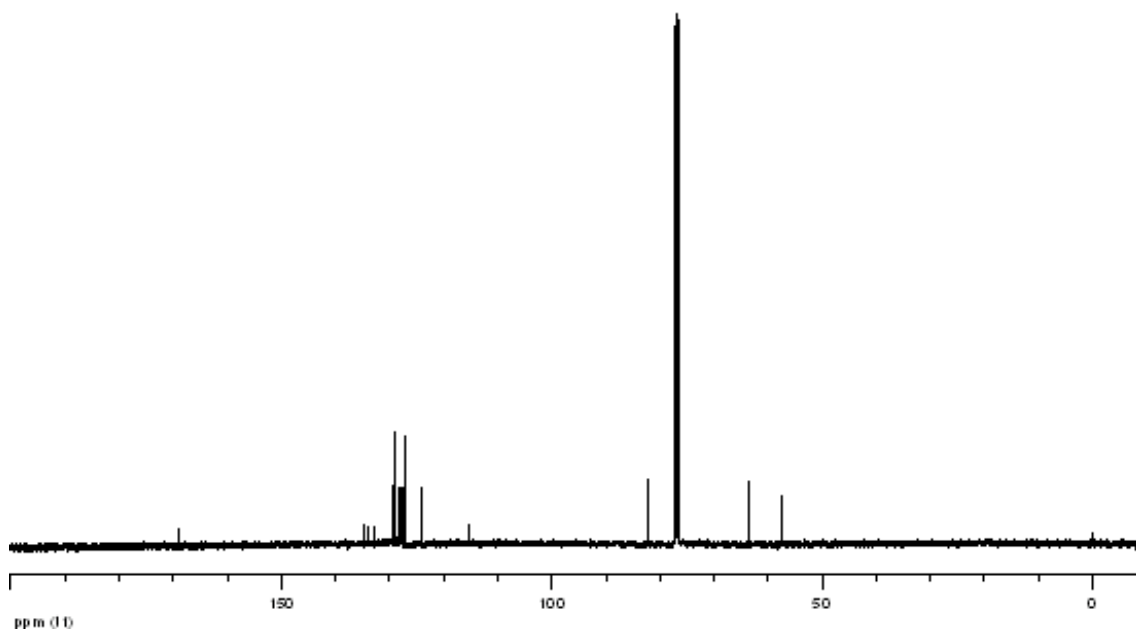


Figure 38S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **9** (100.58 MHz, CDCl_3).

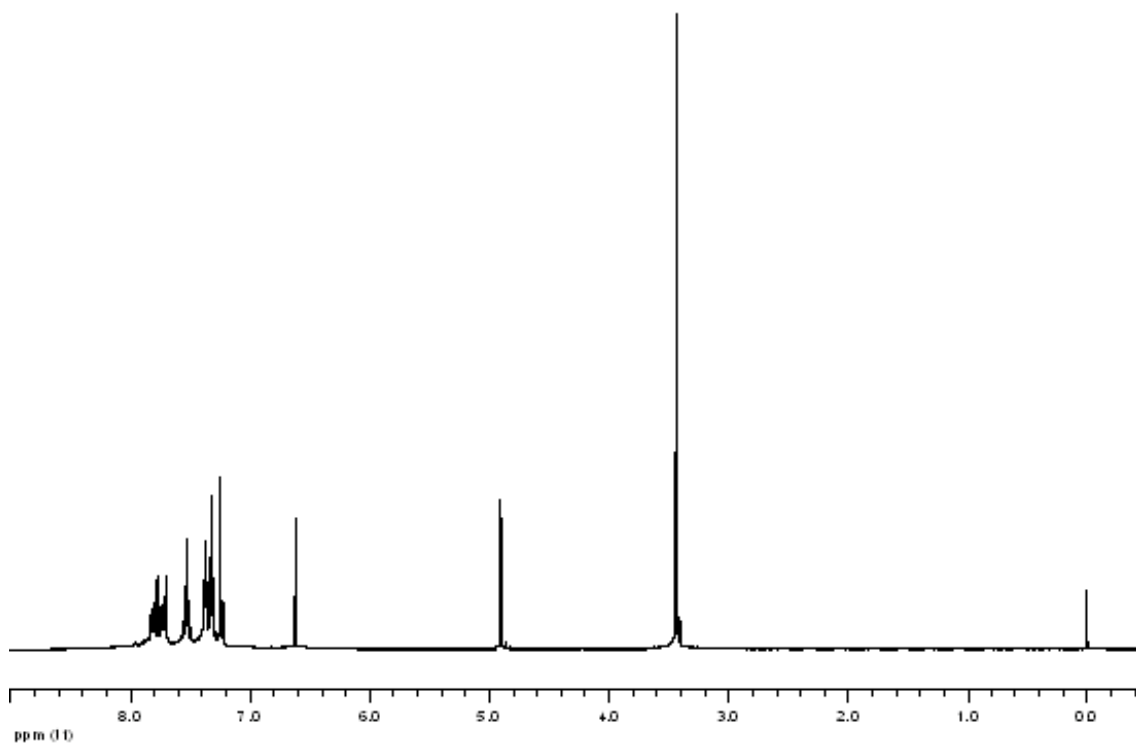


Figure 39S. ¹H-NMR spectrum of (*S*)-MPA ester of compound **9** (399.97 MHz, CDCl₃).

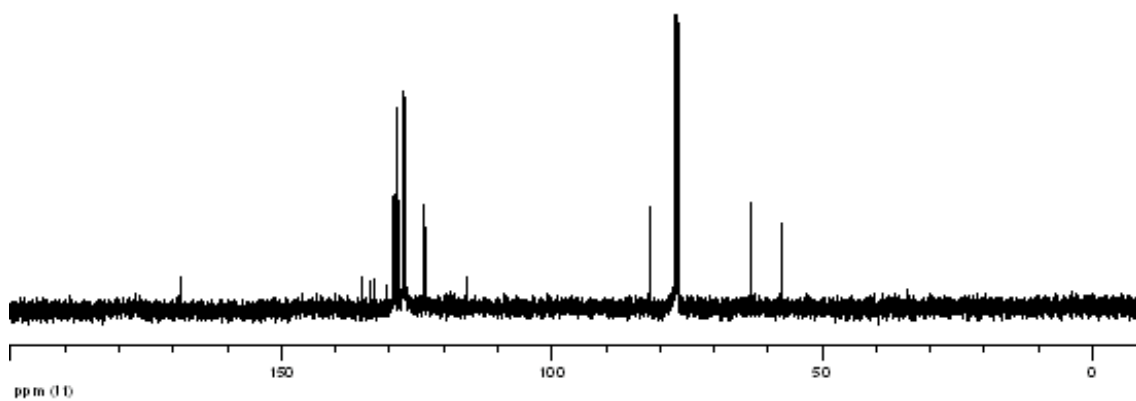


Figure 40S. ¹³C-NMR spectrum of (*S*)-MPA ester of compound **9** (100.58 MHz, CDCl₃).

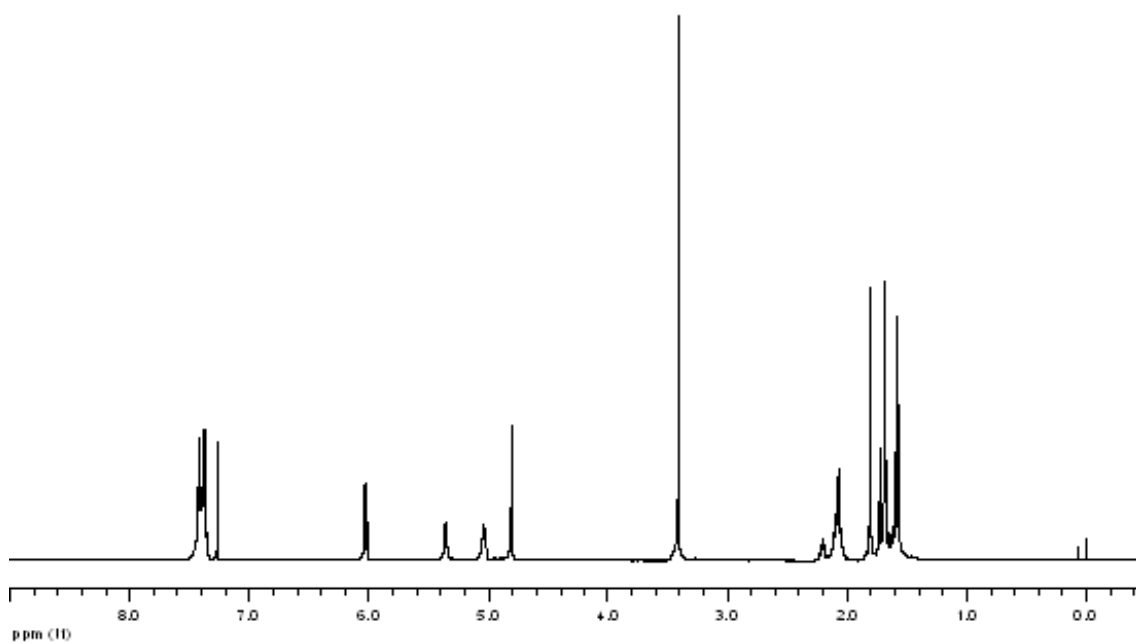


Figure 41S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **10** (500.13 MHz, CDCl_3 , dr 74/26).

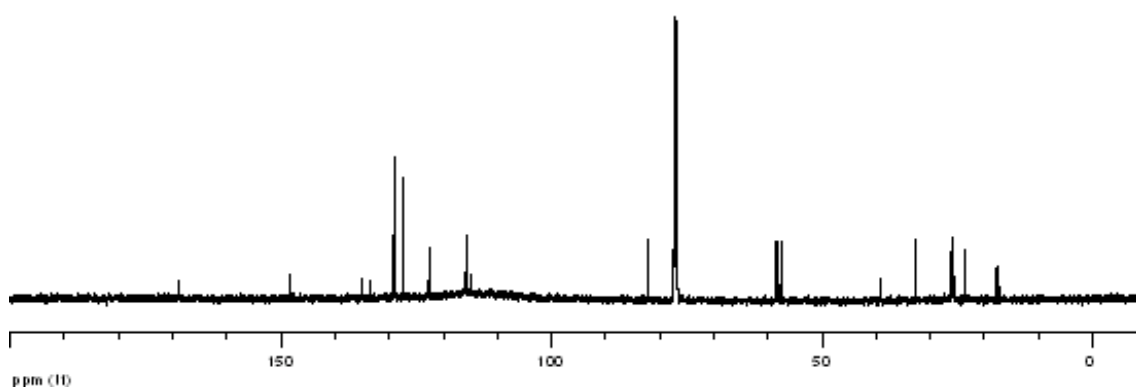


Figure 42S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **10** (125.77 MHz, CDCl_3 , dr 74/26).

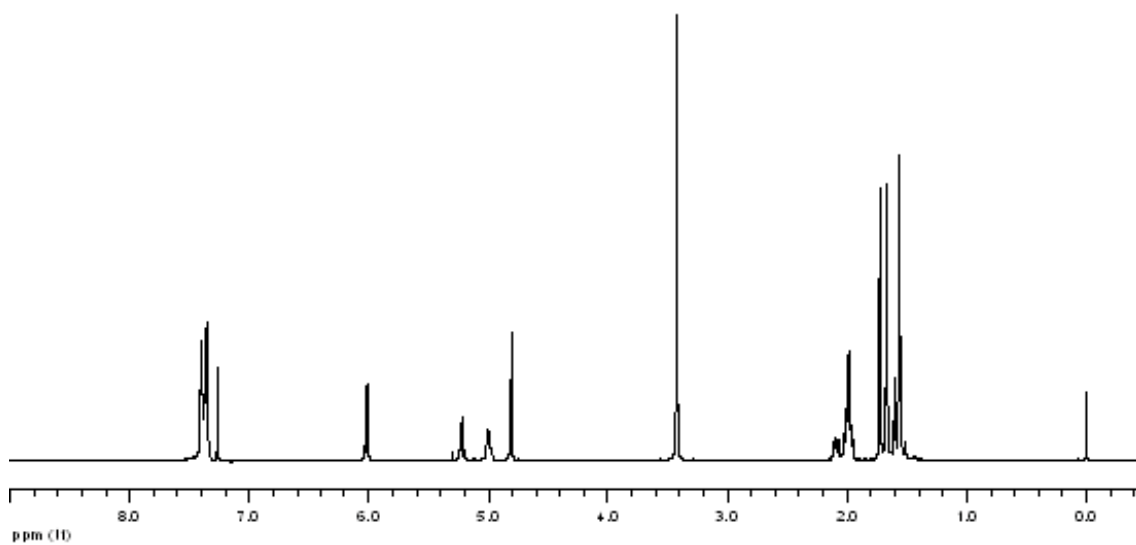


Figure 43S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **10** (500.13 MHz, CDCl_3).

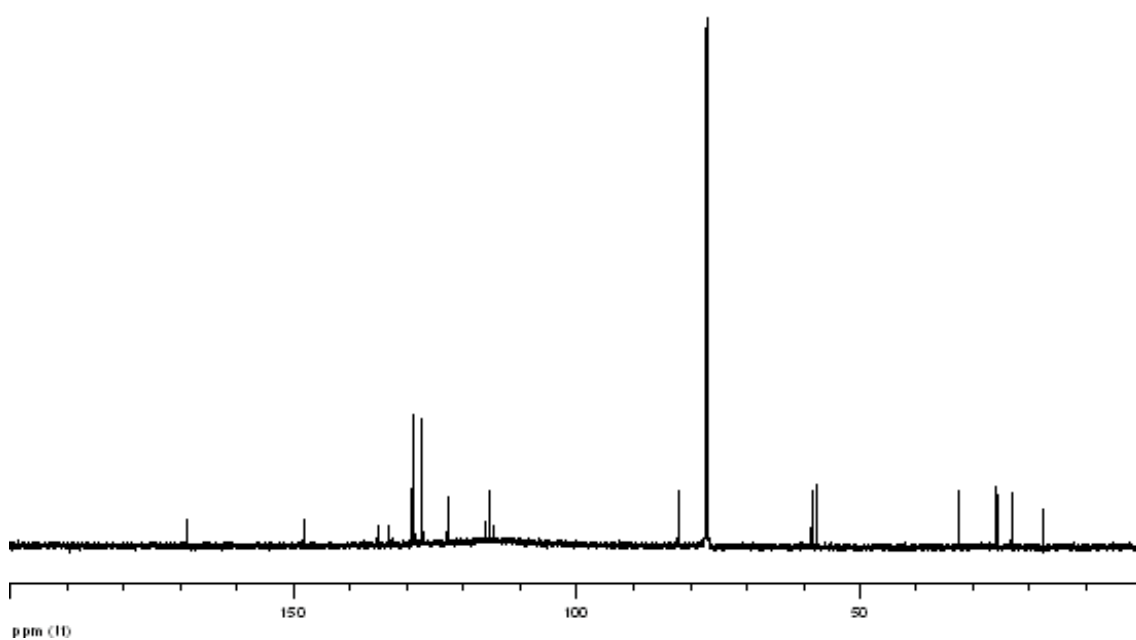


Figure 44S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **10** (125.77 MHz, CDCl_3).

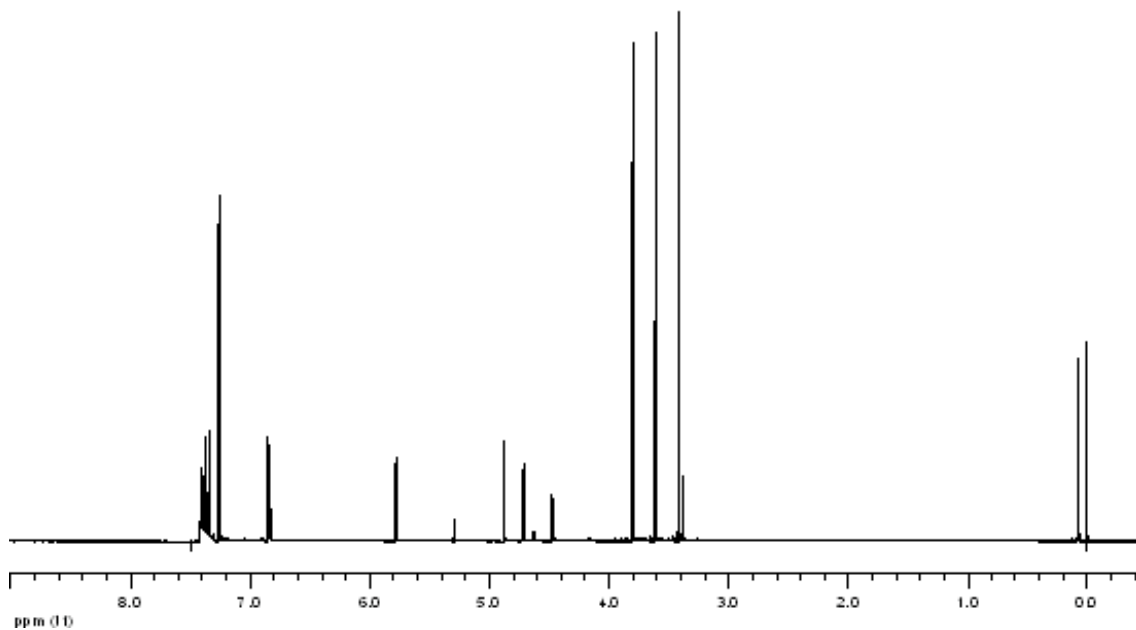


Figure 45S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **11** (500.13 MHz, CDCl_3).

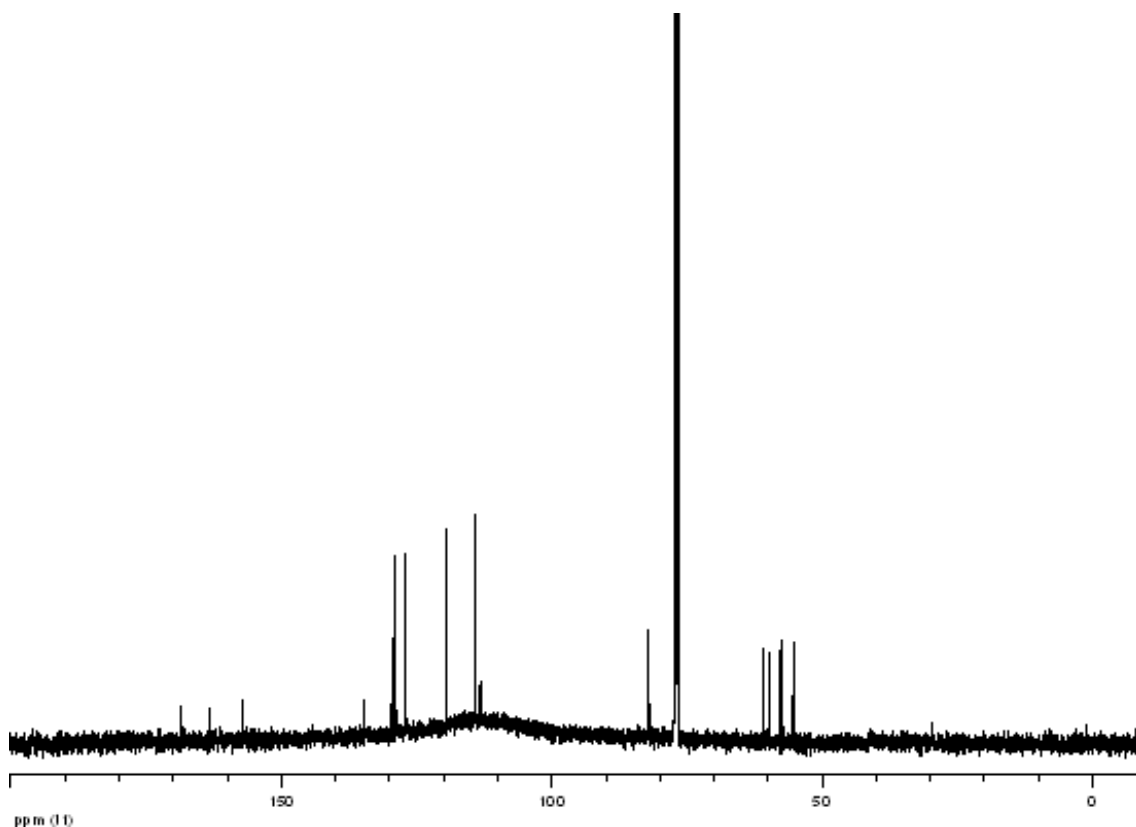


Figure 46S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **11** (125.77 MHz, CDCl_3).

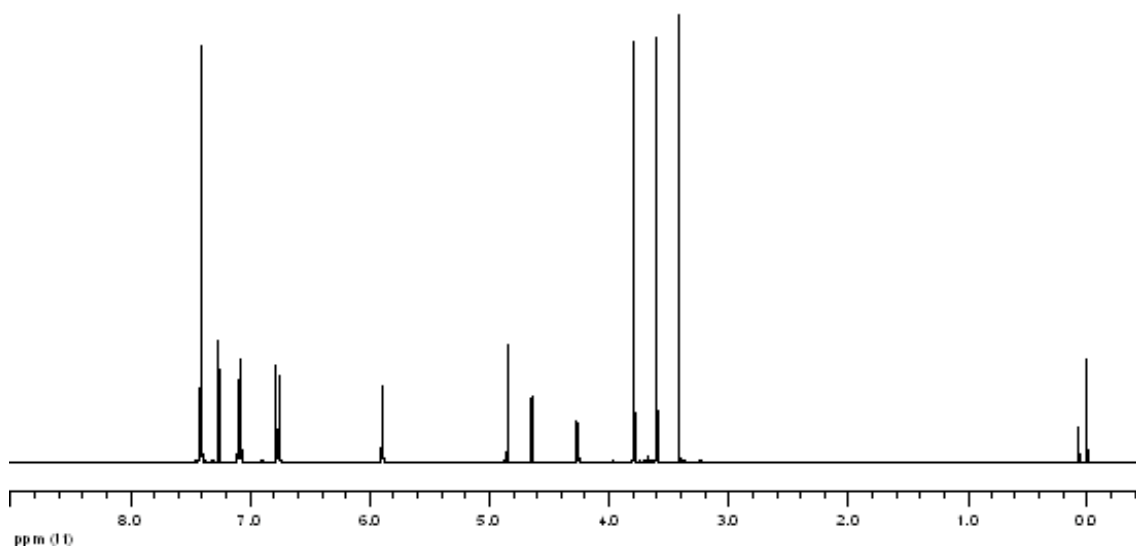


Figure 47S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **11** (399.97 MHz, CDCl_3).

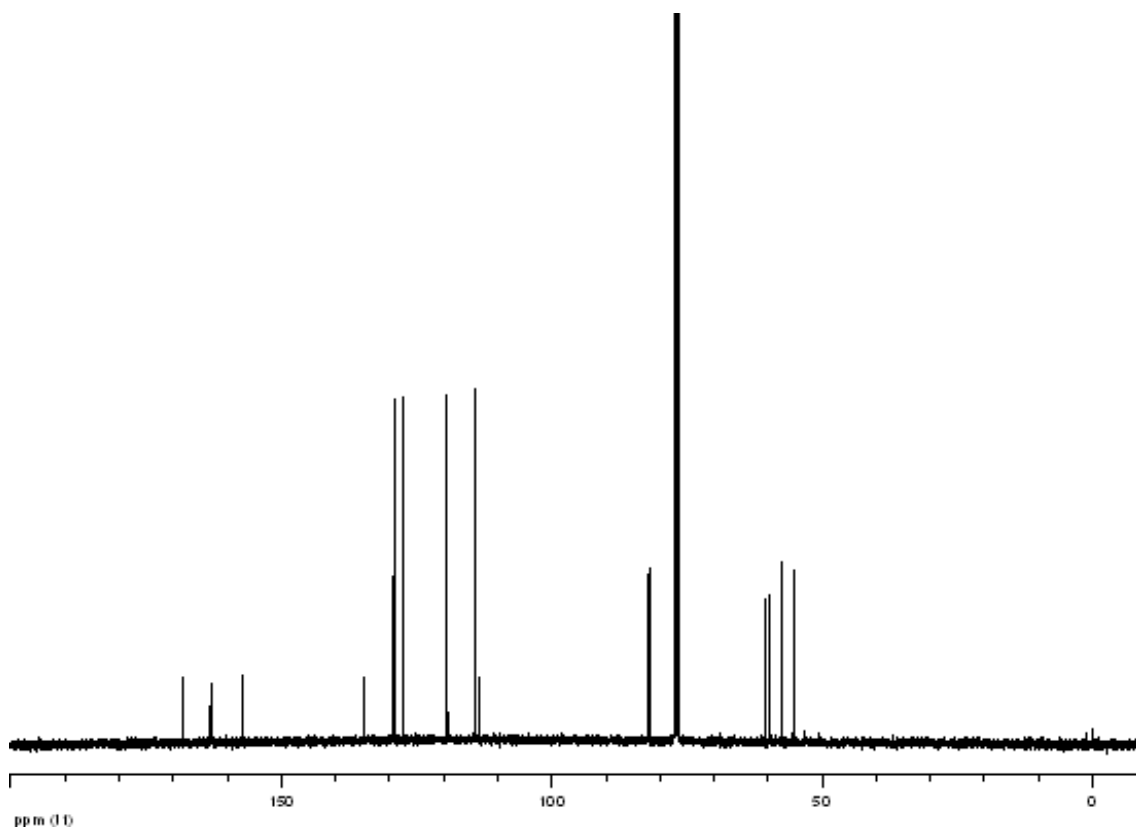


Figure 48S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **11** (100.58 MHz, CDCl_3).

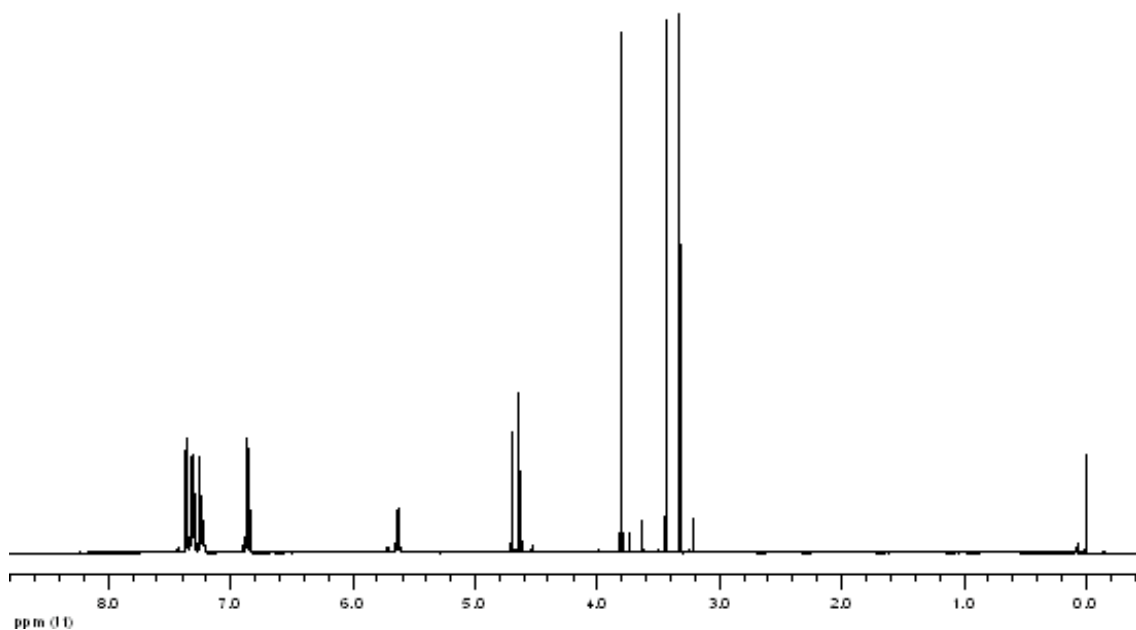


Figure 49S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **12** (399.97 MHz, CDCl_3 , dr 95/5).

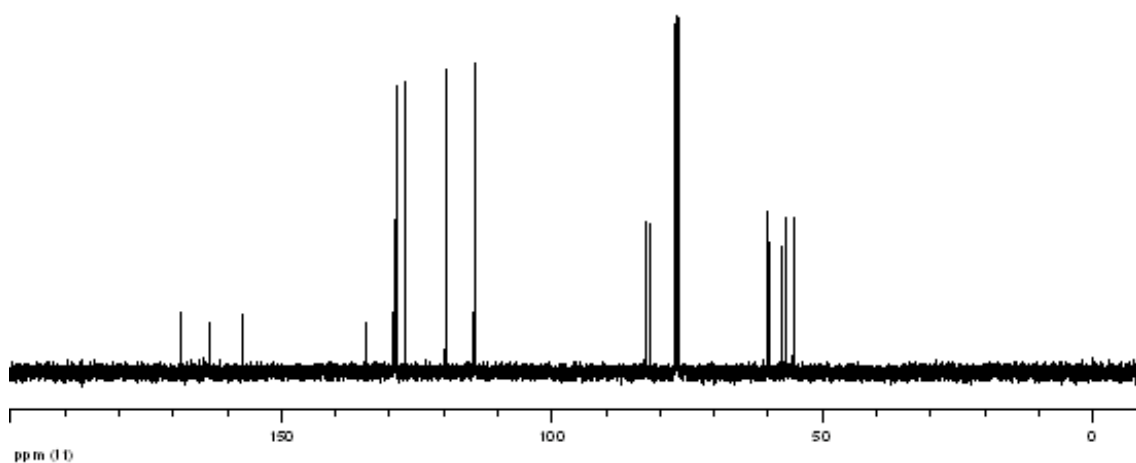


Figure 50S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **12** (100.58 MHz, CDCl_3 , dr 95/5).

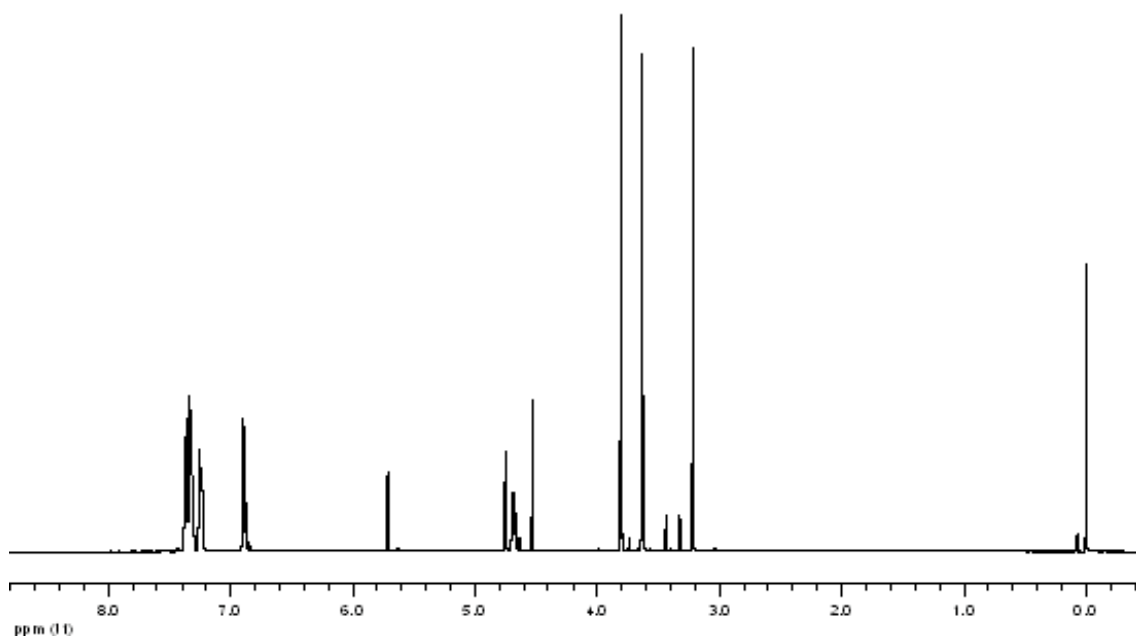


Figure 51S. ^1H -NMR spectrum of (*S*)-MPA ester of compound **12** (399.97 MHz, CDCl_3 , dr 94/6).

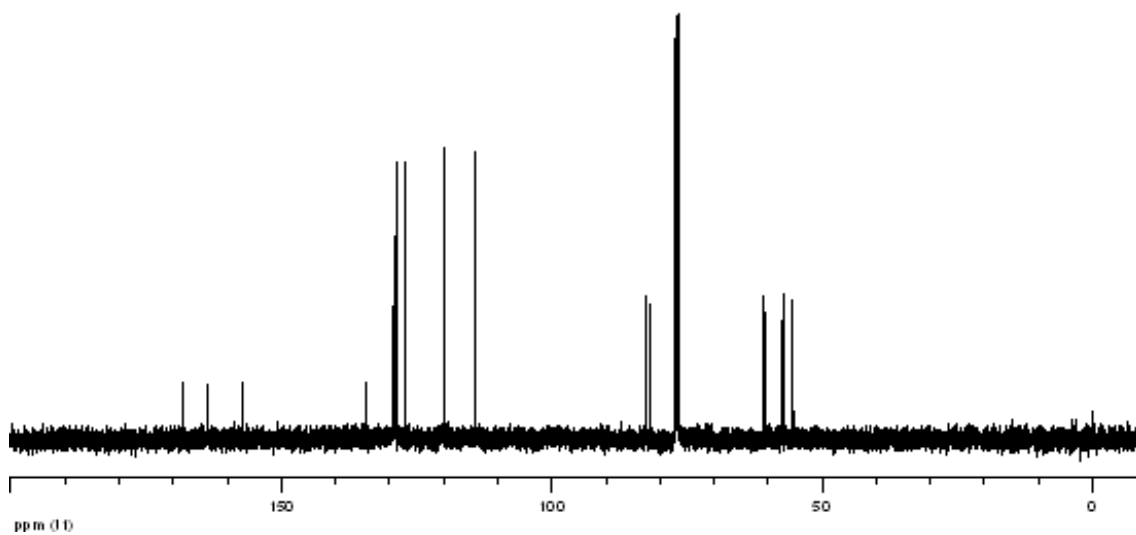


Figure 52S. ^{13}C -NMR spectrum of (*S*)-MPA ester of compound **12** (100.58 MHz, CDCl_3 , dr 94/6).

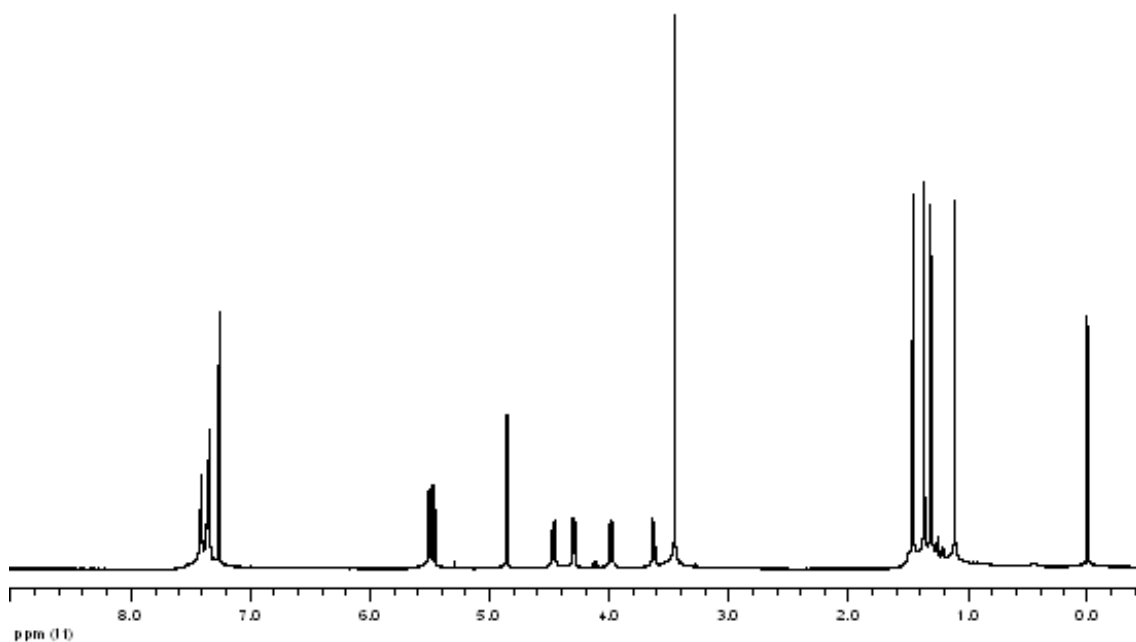


Figure 53S. ^1H -NMR spectrum of (*R*)-MPA ester of compound **13** (399.97 MHz, CDCl_3).

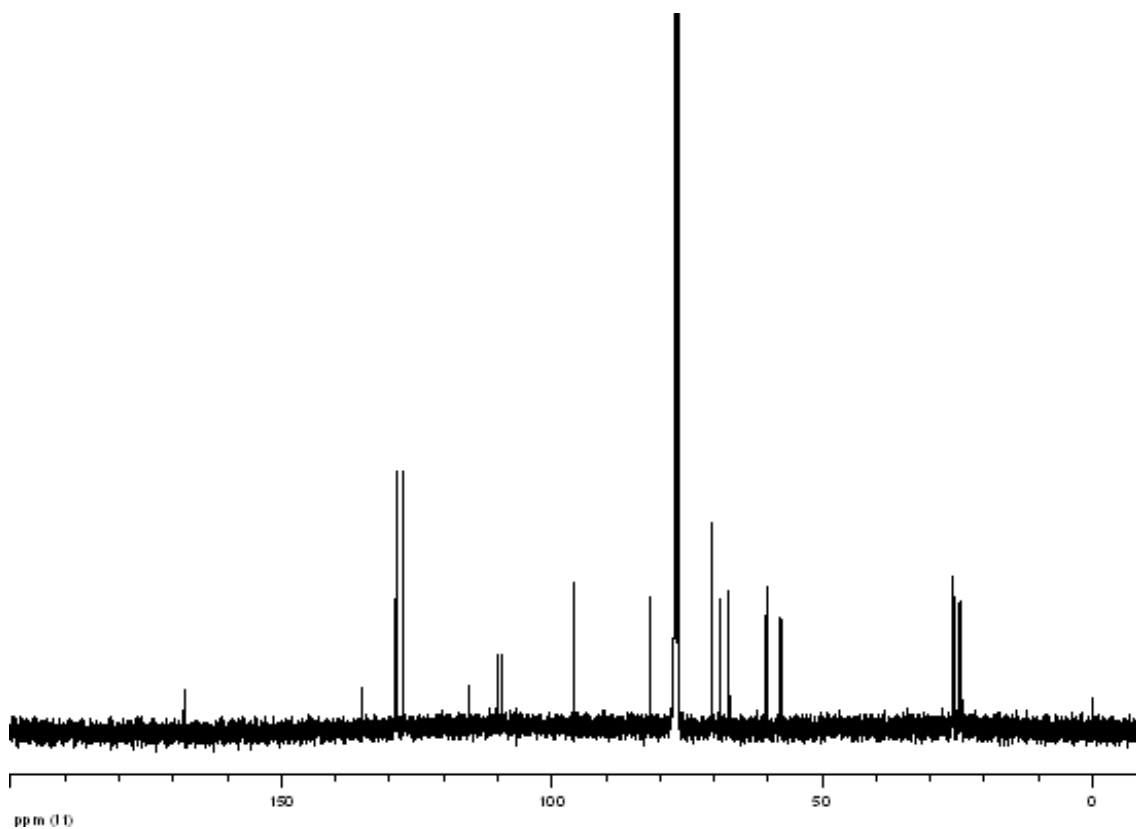


Figure 54S. ^{13}C -NMR spectrum of (*R*)-MPA ester of compound **13** (100.58 MHz, CDCl_3).

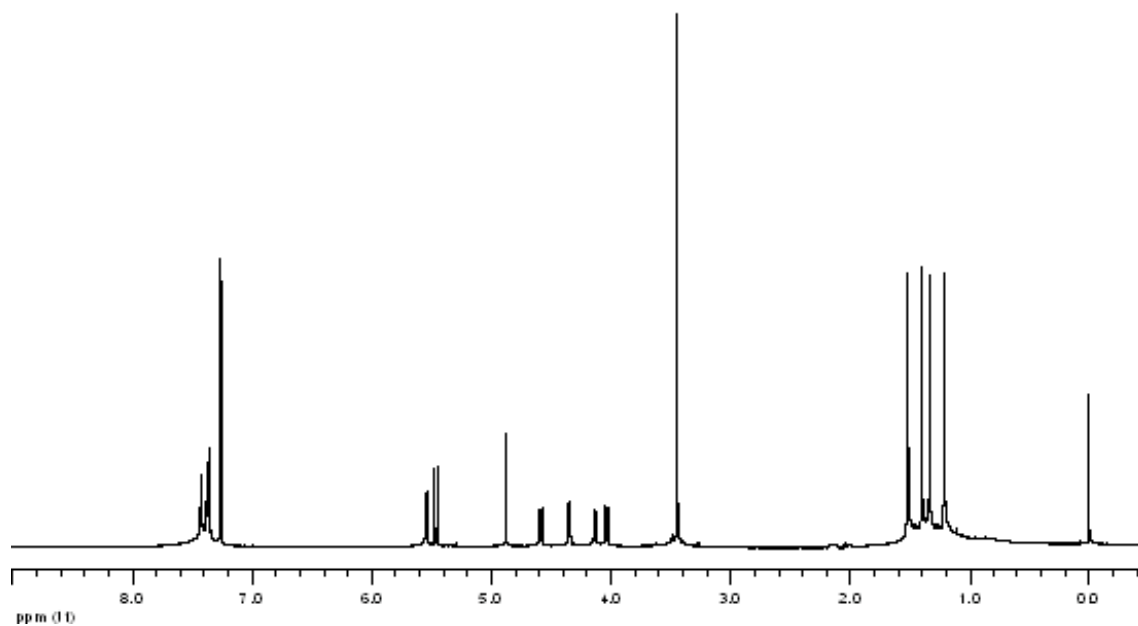


Figure 55S. ¹H-NMR spectrum of (*S*)-MPA ester of compound **13** (399.97 MHz, CDCl₃).

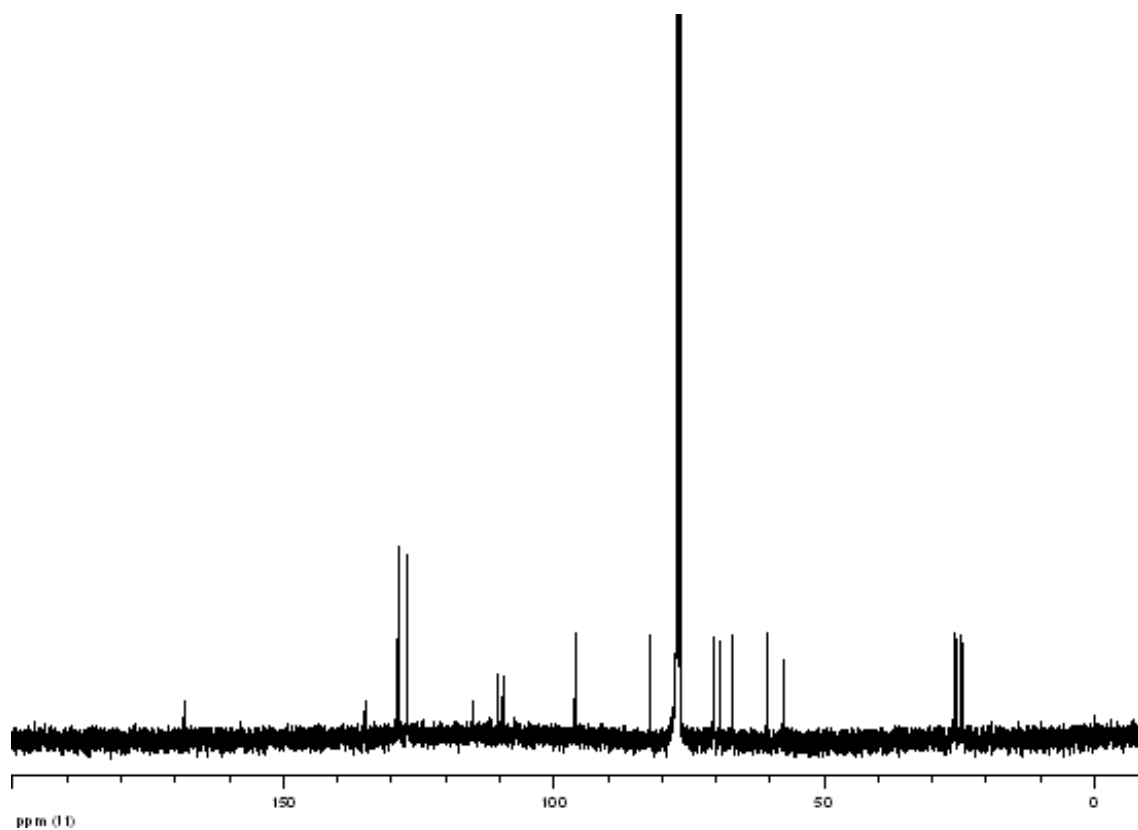


Figure 56S. ¹³C-NMR spectrum of (*S*)-MPA ester of compound **13** (100.58 MHz, CDCl₃).