Supplementary Material (ESI) for Chemical Communications

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Challenging the absence of observable hydrogens in the assignment of absolute configurations by NMR: application to primary alcohols

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Table 1S. $\Delta\delta^{RS}$ values for Pg, L and Cβ–H substituents at 298 y 213K of 9-AMA esters of alcohols **1**, **7-8**, **10-14**, **16**, **18**, **20**, **21**, **23**. (Solvent for the ^{1}H-NMR spectra: CD_2Cl_2:CS_2 1:4).

^{1}H NMR and ^{13}C NMR spectra of selected compounds

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Conformational Studies

Figure 11S. (a) Main conformers for (*R*)-9-AMA esters of Type A primary alcohols. (b) *Idem.* for (*S*)-9-AMA esters.

Figure 12S (a) Main conformers of (*R*)-9-AMA esters of Type A primary alcohols (stick models). (b) *Idem.* for (*S*)-9-AMA esters (stick models).

Experimental Section

General Esterification Procedure.

Esters **2-3, 9-10, 13** were prepared by treatment of the alcohol (1 equivalent) with the corresponding (*R*) and (*S*)-MPA (1.1 equivalents) in the presence of EDC[1] (1.1 equivalents) and DMAP (catalytic) in dry CH_2Cl_2, under a nitrogen atmosphere. The reaction was stirred at room temperature for 3-8 hours. The organic layer was sequentially washed with water, HCl (1M), water, $NaHCO_3$(sat) and water, then dried (Na_2SO_4) and concentrated under reduced pressure to obtain the corresponding ester. Final purification was achieved by flash column chromatography on silica gel 230-400 mesh (elution with 8:2 to 7:3 hexane/ethyl acetate mixtures, 90-95% yields after purification). All compounds were characterized by optical rotation, NMR (1D,2D) and MS(EI).

NMR spectroscopy.

^1H and ^{13}C NMR spectra were recorded at 250.13 MHz and 62.83 MHz respectively. ^1H chemical shifts are internally referenced to the TMS signal (0.00 ppm) for spectra recorded in $CDCl_3$. ^{13}C chemical shifts are internally referenced to $CDCl_3$ (77.0 ppm). *J* values are recorded in Hz.

Low temperature ^1H spectra were recorded at 500.13 MHz.The solvent used was a mixture of CD_2Cl_2/CS_2 in a 1:4 ratio.

References:

[1]M. K. Dharon, K. O.Richard, K. Ramasamy, *J. Org. Chem.* **1982**, 47(10), 1962-1965.

Spectroscopic data

(*R*)-9-AMA ester of (*R*)-glycidol [(*R*)-2]

$[\alpha]_D$= +3.7 (c= 0.38, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.33 (dd, J = 2.6 Hz, 5.2 Hz, 1H), 2.58 (dd, J = 4.1Hz, 4.6 Hz, 1H), 2.83-2.89 (m, 1H), 3.43 (s, 3H), 3.99 (dd, J = 6.2 Hz, 11.9 Hz, 1H), 4.28 (dd, 3.6 Hz, 12.4 Hz, 1H), 6.33 (s, 1H), 7.46-7.59 (m, 4H), 8.01-8.03 (m, 2H), 8.51-8.57 (m, 3H); ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 44.4, 48.8, 57.5, 65.6, 124.3, 125.0, 126.6, 127.2, 129.2, 129.4, 130.6, 131.4, 134.1, 171.1; MS (EI) m/z % 338 (M^+).

(*S*)-9-AMA ester of (*R*)-glycidol [(*S*)-2]

$[\alpha]_D$= +14.6 (c= 0.40, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.25 (dd, J = 2.6 Hz, 5.2 Hz, 1H), 2.54 (dd, J = 4.1Hz, 5.2 Hz, 1H), 3.01-3.07 (m, 1H), 3.41 (s, 3H), 3.87 (dd, J = 5.2 Hz, 12.4 Hz, 1H), 4.42 (dd, 3.1 Hz, 12.4 Hz, 1H), 6.32 (s, 1H), 7.45-7.59 (m, 4H), 8.01-8.03 (m, 2H), 8.49-8.56 (m, 3H); ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 44.2, 48.9, 57.4, 64.6, 124.2, 125.0, 126.6, 126,7, 127.1, 129.1, 129.4, 130.5, 131.4, 133.4, 134.0, 171.1; MS (EI) m/z % 338 (M^+).

(*R*)-9-AMA ester of (*S*)-2-chloro-1-propanol [(*R*)-3]

$[\alpha]_D$= -122.5 (c= 1.1, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 1.11 (d, J = 6.2 Hz, 3H), 3.44 (s, 3H), 3.72-3.92 (m, 1H), 4.03 (dd, J = 6.3 Hz, 11.4 Hz, 1H), 4.23 (dd, J = 7.3 Hz, 11.4 Hz, 1H), 6.33 (s, 1H), 7.45-7.58 (m, 4H), 8.01-8.05 (m, 2H), 8.49-8.57 (m, 3H) ; ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 57.8, 63.4, 80.6, 123.4, 124.5, 125.5, 127.2, 129.6, 130.0, 130.8, 131.4, 152.2, 171.2; MS (EI) m/z % 358 (M^+).

(*S*)-9-AMA ester of (*S*)-2-chloro-1-propanol [(*S*)-3]

$[\alpha]_D$= -38.4 (c= 0.26, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 0.99 (d, J = 6.7 Hz, 3H), 3.44 (s, 3H), 3.84-3.95 (m, 1H), 4.08 (dd, J = 6.2 Hz, 11.4 Hz, 1H), 4.17 (dd, J = 6.2 Hz, 11.4 Hz, 1H), 6.3 (s, 1H), 7.45-7.59 (m, 4H), 8.01-8.05 (m, 2H), 8.50-8.57 (m, 3H) ; ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 57.8, 62.4, 80.3, 122.9, 124.6, 125.5, 126.8, 127.2, 129.6, 129.9, 130.8, 131.8, 151.2, 171.1; MS (EI) m/z % 358 (M^+).

(*R*)-9-AMA ester of (*R*)-2-hydroxy-2-phenylpropanol [(*R*)-9]

$[\alpha]_D$= -11.5 (c= 3.67, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 3.40 (s, 3H), 4.18 (dd, J = 6.8 Hz, 11.2 Hz, 1H), 4.22 (dd, J = 4.4 Hz, 11.2 Hz, 1H), 4.60-4.66 (m, 1H), 6.29 (s, 1H), 6.96-7.00 (m, 2H), 7.06-7.17 (m, 3H), 7.45-7.59 (m, 4H), 8.02-8.06 (m, 2H), 8.50-8.57 (m, 3H); ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 57.5, 69.6, 71.8, 77.1,

124.1, 125.1, 125.8, 126.7, 127.9, 128.2, 129.2, 129.4, 130.5, 131.4, 139.1, 171.2; MS (EI) m/z % 386 (M^+).

(*S*)-9-AMA ester of (*R*)-2-hydroxy-2-phenylpropanol [(S)-9]

$[\alpha]_D$= +8.3 (c= 2.6, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 3.44 (s, 3H), 4.04 (dd, J = 7.9 Hz, 11.2 Hz, 1H), 4.31 (dd, J = 3.6 Hz, 11.5 Hz, 1H), 4.59 (dd, J = 3.6 Hz, 7.9 Hz, 1H), 6.30 (s, 1H), 7.00-7.05 (m, 2H), 7.13-7.18 (m, 3H), 7.50-7.60 (m, 4H), 8.03-8.07 (m, 2H), 8.52-8.55 (m, 3H); ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 57.5, 69.6, 71.8, 77.1, 124.1, 125.1, 125.8, 126.7, 127.9, 128.2, 129.2, 129.4, 130.5, 131.4, 139.1, 171.2; MS (EI) m/z % 386 (M^+).

(*R*)-9-AMA ester of (*R*)-2-methoxy-2-phenylethanol [(*R*)-10]

$[\alpha]_D$= +8.5 (c= 0.28, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.86 (s, 3H), 3.40 (s, 3H), 4.01 (dd, J = 4.6 Hz, 6.7 Hz, 1H), 4.09 (dd, J = 4.6 Hz, 10.9 Hz, 1H), 4.29 (dd, J = 6.7 Hz, 10.9 Hz, 1H), 6.29 (s, 1H), 6.91-6.94 (m, 2H), 7.05-7.15 (m, 3H), 7.25-8.56 (m, 9H); ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 56.4, 57.5, 68.0, 80.9, 124.3, 124.8, 126.4, 126.8, 126.9, 127.1, 127.9, 128.1, 128.4, 128.5, 129.0, 129.2, 130.6, 131.4, 133.4, 134.0, 137.4, 171.1; MS (EI) m/z % 416 (M^+).

(*S*)-9-AMA ester of (*R*)-2-methoxy-2-phenylethanol [(*S*)-10]

$[\alpha]_D$= +24.9 (c= 1.30, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 2.78 (s, 3H), 3.43 (s, 3H), 3.99 (dd, J = 3.6 Hz, 7.2 Hz, 1H), 4.11 (dd, J = 7.2 Hz, 10.8 Hz, 1H), 4.20 (dd, J = 3.6 Hz, 10.8 Hz, 1H), 6.28 (s, 1H), 6.94-6.99 (m, 2H), 7.08-7.18 (m, 3H), 7.25-8.56 (m, 9H); ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 56.5, 57.5, 68.0, 80.9, 124.5, 124.9, 126.5, 126.8, 126.9, 127.1, 127.9, 128.1, 128.4, 128.5, 129.1, 130.5, 131.4, 133.4, 134.0, 137.4, 171.1; MS (EI) m/z % 416 (M^+).

(*R*)-9-AMA ester of (*R*)-2-acetoxy-2-phenylpropanol [(*R*)-13]

$[\alpha]_D$= -131.3 (c= 3.20, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 1.56 (s, 3H), 3.42 (s, 3H), 4.09 (dd, J = 8.5 Hz,11.5 Hz, 1H), 4.36 (dd, J = 3.8 Hz, 11.8 Hz, 1H), 5.82 (dd, J = 3.8 Hz, 8.7 Hz ,1H), 6.20 (s, 1H), 7.04-7.08 (m, 2H), 7.12-7.20 (m, 3H), 7.45-7.58 (m, 4H), 8.00-8.04 (m, 2H), 8.28-8.63 (m, 3H); ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 20.4, 57.5, 66.5, 72.4, 124.1, 125.0, 126.4, 126.5, 126.8, 128.4, 128.5, 129.1, 129.2, 130.4, 131.4, 135.8, 169.6, 171.2; MS (EI) m/z % 428 (M^+).

(*S*)-9-AMA ester of (*R*)-2-acetoxy-2-phenylpropanol [(S)-13]

$[\alpha]_D$= +119.2 (c= 0.76, $CHCl_3$); ^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 1.57 (s, 3H), 3.41 (s, 3H), 4.14 (dd, J = 6.6 Hz,11.5 Hz, 1H), 4.50 (dd, J = 3.6 Hz, 11.5 Hz, 1H), 5.62

(dd, J = 3.6 Hz, 6.3 Hz ,1H), 6.26 (s, 1H), 6.75-6.78 (m, 2H), 6.96-7.14 (m, 3H), 7.45-7.47 (m, 4H), 8.03-8.07 (m, 2H), 8.50-8.52 (m, 3H); ^{13}C NMR (62.83 MHz, $CDCl_3$) δ 20.3, 57.5, 66.0, 72.6, 124.3, 125.0, 126.3, 126.6, 126.9, 128.1, 129.1, 129.3, 130.5, 131.4, 136.0, 169.4, 170.9; MS (EI) m/z % 428 (M^+).

^{1}H-NMR data of 9-AMA esters of β–chiral primary alcohols at 213 K.

[213K] (*R*)-9-AMA ester of (*R)*-glycidol [(*R*)-2]

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 2.21 (dd, J = 2.0 Hz, 4.7 Hz, 1H), 2.46 (dd, J = 4.0Hz, 4.7 Hz, 1H), 2.68-2.72 (m, 1H), 3.37 (s, 3H), 3.81 (dd, J = 6.7 Hz, 12.2 Hz, 1H), 4.15 (dd, 3.3 Hz, 12.2 Hz, 1H), 6.15 (s, 1H), 7.23-8.44 (m, 9H).

[213K] (*R*)-9-AMA ester of (*R)*-glycidol [(*R*)-2]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.29-2.30 (m, 1H), 2.56-2.58 (m, 1H), 2.73-2.78 (m, 1H), 3.20 (s, 3H), 3.67 (dd, J = 8.1 Hz, 12.2 Hz, 1H), 4.24 (d, 12.8 Hz, 1H), 6.21 (s, 1H), 7.31-8.46 (m, 9H).

[213K] (*S*)-9-AMA ester of (*R)*-glycidol [(*S*)-2]

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 2.13 (dd, J = 2.7 Hz, 5.4 Hz, 1H), 2.42 (dd, J = 4.0Hz, 4.7 Hz, 1H), 2.86-2.89 (m, 1H), 3.35 (s, 3H), 3.63 (dd, J = 5.4 Hz, 12.2 Hz, 1H), 4.32 (dd, 2.7 Hz, 12.2 Hz, 1H), 6.10 (s, 1H), 7.38-8.43 (m, 9H).

[213K] (*S*)-9-AMA ester of (*R)*-glycidol [(*S*)-2]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.17-2.20 (m, 1H), 2.46-2.52 (m, 1H), 2.95-2.99 (m, 1H), 3.20 (s, 3H), 3.26 (dd, J = 6.1 Hz, 12.2 Hz, 1H), 4.54 (d, 12.2 Hz, 1H), 6.18 (s, 1H), 7.40-8.46 (m, 9H).

[298K] (*R*)-9-AMA ester of (*S*)-2-chloro-1-propanol [(*R*)-3]

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 1.09 (d, J = 6.8 Hz, 3H), 3.37 (s, 3H), 3.70-3.76 (m, 1H), 3.87 (dd, J = 6.0 Hz, 11.2 Hz, 1H), 4.12 (dd, J = 7.2 Hz, 11.6 Hz, 1H), 6.14 (s, 1H), 7.39-8.4 (m, 9H).

[213K] (*R*)-9-AMA ester of (*S*)-2-chloro-1-propanol [(*R*)-3]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 1.12 (d, J = 6.4 Hz, 3H), 3.22 (s, 3H), 3.63-3.70 (m, 1H), 3.73 (dd, J = 4.4 Hz, 12.2 Hz, 1H), 4.12 (dd, J = 8.4 Hz, 12.2 Hz, 1H), 6.12 (s, 1H), 7.39-8.46 (m, 9H).

[298K] (*S*)-9-AMA ester of (*S*)-2-chloro-1-propanol [(*S*)-3]

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 1.01 (d, J = 6.4 Hz, 3H), 3.44 (s, 3H), 3.80-3.87 (m, 1H), 4.02 (dd, J = 6.4 Hz, 11.2 Hz, 1H), 4.08 (dd, J = 6.0 Hz, 11.2 Hz, 1H), 6.20 (s, 1H), 7.45-8.49 (m, 9H).

[213K] (*S*)-9-AMA ester of (*S*)-2-chloro-1-propanol [(*S*)-3]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 0.98 (d, J = 6.0 Hz, 3H), 3.27 (s, 3H), 3.82-3.89 (m, 1H), 3.91 (dd, J = 6.4 Hz, 11.2 Hz, 1H), 4.06 (dd, J = 5.2 Hz, 10.8 Hz, 1H), 6.20 (s, 1H), 7.40-8.44 (m, 9H)

[298K] (*R*)-9-AMA ester of (*R*)-3-bromine-2-methyl-1-propanol [(*R*)-8]^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 0.54 (d, J = 6.5 Hz, 3H), 1.77-1.83 (m, 1H), 2.76 (dd, J = 5.5 Hz, 9.9 Hz, 1H), 2.84 (dd, J = 5.5 Hz, 9.9 Hz, 1H), 3.38 (s, 3H), 3.87 (dd, J = 6.5 Hz, 10.9 Hz, 1H), 3.90 (dd, J = 5.1 Hz, 10.9 Hz, 1H), 6.11 (s, 1H), 7.39-8.44 (m, 9H)..

[213K] (*R*)-9-AMA ester of (*R*)-3-bromine-2-methyl-1-propanol [(*R*)-8]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 0.54 (d, J = 6.5 Hz, 3H), 1.77-1.85 (m, 1H), 2.72 (dd, J = 4.8 Hz, 9.9 Hz, 1H), 2.86 (dd, J = 5.1 Hz, 9.6 Hz, 1H), 3.26 (s, 3H), 3.78 (dd, J = 7.2 Hz, 10.9 Hz, 1H), 3.90 (dd, J = 5.1 Hz, 10.9 Hz, 1H), 6.16 (s, 1H), 7.40-8.46 (m, 9H).

[298K] (*S*)-9-AMA ester of (*R*)-3-bromine-2-methyl-1-propanol [(*S*)-8]

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 0.69 (d, J = 6.9 Hz, 3H), 1.66-1.73 (m, 1H), 2.67 (dd, J = 5.1 Hz, 9.9 Hz, 1H), 2.71 (dd, J = 5.1 Hz, 9.9 Hz, 1H), 3.38 (s, 3H), 3.76 (dd, J = 7.5 Hz, 10.9 Hz, 1H), 3.96 (dd, J = 5.1 Hz, 10.9 Hz, 1H), 6.11 (s, 1H) 7.39-8.44 (m, 9H).

[213K] (*S*)-9-AMA ester of (*R*)-3-bromine-2-methyl-1-propanol [(*S*)-8]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 0.72 (d, J = 6.6 Hz, 3H), 1.63-1.70 (m, 1H), 2.72-2.81 (m, 2H), 3.25 (s, 3H), 3.73 (dd, J = 9.7 Hz, 10.4 Hz, 1H), 3.88 (dd, J = 4.5 Hz, 11.1 Hz, 1H), 6.16 (s, 1H) 7.44-8.43 (m, 9H).

[213K] (*R*)-9-AMA ester of (*R*)-2-hydroxy-2-phenylpropanol [(*R*)-9]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.86 (s, 3H), 3.85 (dd, J = 7.7 Hz, 11.2 Hz, 1H), 4.28 (dd, J = 3.4 Hz, 11.2 Hz, 1H), 4.88-4.89 (m, 1H), 4.99 (br s, 1H), 6.18 (s, 1H), 7.05-7.08 (m, 2H), 7.12-7.15 (m, 3H), 7.42-7.52 (m, 4H), 7.95-7.99 (m, 2H), 8.29-8.46 (m, 3H).

[213K] (*S*)-9-AMA ester of (*R*)-2-hydroxy-2-phenylpropanol [(S)-9]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.98 (s, 3H), 3.88-3.91 (m, 1H), 4.16-4.21 (m, 1H), 4.69-4.71 (m, 1H), 6.26 (s, 1H), 7.18-7.22 (m, 5H), 7.42-7.44 (m, 4H), 7.96-7.99 (m, 2H), 8.25-8.45(m, 3H).

[298K] (*R*)-9-AMA éster de (*R*)-2-metoxi-2-feniletanol [(*R*)-10]

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 2.75 (s, 3H), 3.33 (s, 3H), 3.87 (dd, J = 4.7 Hz, 13.5 Hz, 1H), 3.89 (dd, J = 4.7 Hz, 13.5 Hz, 1H), 4.07-4.11 (m, 1H), 6.06 (s, 1H), 6.84-6.85 (m, 2H), 7.02-7.08 (m, 3H), 7.40-8.43 (m, 9H).

[213K] (*R*)-9-AMA ester of (*R*)-2-methoxy-2-phenylethanol [(*R*)-10]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.50 (s, 3H), 3.24 (s, 3H), 3.71-3.77 (m, 2H), 4.10-4.16 (m, 1H), 6.19 (s, 1H), 6.86-6.88 (m, 2H), 7.08-7.12 (m, 3H), 7.40-8.52 (m, 9H).

[298K] (*S*)-9-AMA ester of (*R*)-2-methoxy-2-phenylethanol [(*S*)-10]

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 2.69 (s, 3H), 3.35 (s, 3H), 3.89-3.96 (m, 3H), 6.08 (s, 1H), 6.88-6.90 (m, 2H), 7.06-7.10 (m, 3H), 7.38-8.43 (m, 9H).

[213K] (*S*)-9-AMA ester of (*R*)-2-methoxy-2-phenylethanol [(*S*)-10]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.42 (s, 3H), 3.27 (s, 3H), 3.80-3.84 (m, 1H), 3.91-3.98 (m, 2H), 6.19 (s, 1H), 6.90-6.92 (m, 2H), 7.12-7.15 (m, 3H), 7.43-8.52 (m, 9H).

[298K] (*R*)-9-AMA ester of (2*R*, 3*R*)-*trans*-phenyl-glycidol [(*R*)-11]: ^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.68-2.70 (m, 1H), 3.24 (s, 1H), 3.38 (s, 3H), 3.99 (dd, J = 5.4 Hz, 12.2 Hz, 1H), 4.21 (dd, J = 4.0 Hz, 12.2 Hz, 1H), 6.15 (s, 1H), 6.48-6.87 (m, 2H), 7.13-7.39 (m, 3H), 7.30-7.56 (m, 4H), 7.90-7.92 (m, 2H), 8.35-8.44 (m, 3H).

[213K] (*R*)-9-AMA ester of (2*R*, 3*R*)-*trans*-phenyl-glycidol [(*R*)-11]: ^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.69-2.71 (m, 1H), 3.21 (s, 1H), 3.29 (s, 3H), 3.88 (dd, J = 6.7 Hz, 12.2 Hz, 1H), 4.26 (dd, J = 2.7 Hz, 12.2 Hz, 1H), 6.19 (s, 1H), 6.85-6.86 (m, 2H), 7.15-7.16 (m, 3H), 7.30-7.56 (m, 4H), 7.92-8.00 (m, 2H), 8.33-8.49 (m, 3H).

[298K] (*S*)-9-AMA ester of (2*R*, 3*R*)-*trans*-phenyl-glycidol [(*S*)-11]: ^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.95-2.97 (m, 1H), 3.25 (s, 1H), 3.48 (s, 3H), 4.02 (dd, J = 4.7 Hz, 12.2 Hz, 1H), 4.40 (dd, J = 1.3 Hz, 12.2 Hz, 1H), 6.25 (s, 1H), 6.89-6.90 (m, 2H), 7.21-7.24 (m, 3H), 7.39-7.55 (m, 4H), 7.46-7.54 (m, 2H), 8.01-8.03 (m, 2H), 8.47-8.57 (m, 3H).

[213K] (*S*)-9-AMA ester of (2*R*, 3*R*)-*trans*-phenyl-glycidol [(*S*)-11]: ^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 2.93-2.94 (m, 1H), 3.12 (s, 1H), 3.28 (s, 3H), 3.67 (dd, J = 4.7 Hz, 12.2 Hz, 1H), 4.46 (dd, J = 1.3 Hz, 12.2 Hz, 1H), 6.20 (s, 1H), 6.76-6.78 (m, 2H), 7.15-7.18 (m, 3H), 7.39-7.55 (m, 4H), 7.94-8.01 (m, 2H), 8.31-8.56 (m, 3H).

[298K] (*R*)-9-AMA ester of (*S*)-2-acetoxypropanol [(*R*)-12]:

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 0.77 (d, J= 6.7 Hz, 3H), 1.54 (s, 3H), 3.37 (s, 3H), 3.87 (dd, J= 5.3 Hz, 10.7 Hz, 1H), 4.03 (dd, J= 2.7 Hz, 10.8 Hz, 1H), 4.61-4.57 (m, 1H), 6.09 (s, 1H), 7.37-8.44 (m, 9H).

[213K] (*R*)-9-AMA ester of (*S*)-2-acetoxypropanol [(*R*)-12]:

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 0.73 (d, J= 5.4 Hz, 3H), 1.44 (s, 3H), 3.25 (s, 3H), 3.74 (dd, J= 6.7 Hz, 12.0 Hz, 1H), 4.18 (dd, J= 2.7 Hz, 12.0 Hz, 1H), 4.53-4.58 (m, 1H), 6.16 (s, 1H), 7.37-8.43 (m, 9H).

[298K] (*S*)-9-AMA ester of (*S*)-2-acetoxypropanol [(*S*)-12]:

^{1}H-RMN (500.13 MHz, $CDCl_3$) δ (ppm): 0.90 (d, J= 7.3 Hz, 3H), 1.58 (s, 3H), 3.39 (s, 3H), 3.61 (dd, J= 7.3 Hz, 11.7 Hz, 1H), 4.15 (dd, J= 2.9 Hz, 11.7 Hz, 1H), 4.85-4.90 (m, 1H), 6.06 (s, 1H), 7.37-8.42 (m, 9H).

[213K] (*S*)-9-AMA ester of (*S*)-2-acetoxypropanol [(*S*)-12]:

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 1.05 (d, J= 5.8 Hz, 3H), 1.73 (s, 3H), 3.23 (s, 3H), 3.26 (dd, J= 8.8 Hz, 11.7 Hz, 1H), 4.36 (dd, J= 2.9 Hz, 11.7 Hz, 1H), 5.04-5.10 (m, 1H), 6.06 (s, 1H), 7.38-8.40 (m, 9H).

[298K] (*R*)-9-AMA ester of (*R*)-2-acetoxy-2-phenylpropanol [(*R*)-13]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 1.57 (s, 3H), 3.38 (s, 3H), 3.88 (dd, J = 10.3 Hz,12.0 Hz, 1H), 4.25 (dd, J = 3.4 Hz, 12.0 Hz, 1H), 5.73 (dd, J = 3.4 Hz, 10.3 Hz ,1H), 6.08 (s, 1H), 6.99-8.42 (m, 13H).

[213K] (*R*)-9-AMA ester of (*R*)-2-acetoxy-2-phenylpropanol [(*R*)-13]

^{1}H-NMR (500.13 MHz, $CDCl_3$) δ (ppm): 1.55 (s, 3H), 3.28 (s, 3H), 3.66 (dd, J = 10.3 Hz,12.0 Hz, 1H), 4.23 (dd, J = 3.4 Hz, 12.0 Hz, 1H), 5.76 (dd, J = 3.4 Hz, 10.3 Hz ,1H), 6.13 (s, 1H), 7.04-7.06 (m, 2H), 7.12-7.18 (m, 3H), 7.37-7.54 (m, 4H), 7.92-7.98 (m, 2H), 8.27-8.51 (m, 3H).

[298K] (*S*)-9-AMA ester of (*R*)-2-acetoxy-2-phenylpropanol [(S)-13]

^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 1.51 (s, 3H), 3.36 (s, 3H), 4.03 (dd, J = 6.9 Hz,12.0 Hz, 1H), 4.29 (dd, J = 3.4 Hz, 12.0 Hz, 1H), 5.50 (dd, J = 2.6 Hz, 6.9 Hz ,1H), 6.07 (s, 1H), 6.73-8.41 (m, 3H).

[213K] (*S*)-9-AMA ester of (*R*)-2-acetoxy-2-phenylpropanol [(S)-13]

^{1}H-NMR (250.13 MHz, $CDCl_3$) δ (ppm): 1.34 (s, 3H), 3.29 (s, 3H), 3.81 (dd, J = 6.9 Hz,12.0 Hz, 1H), 4.45 (dd, J = 3.4 Hz, 12.0 Hz, 1H), 5.38 (dd, J = 2.6 Hz, 6.9 Hz ,1H), 6.14 (s, 1H), 6.55 (d, J = 6.8 Hz, 2H), 6.90 (t, J = 7.7 Hz, 2H), 7.04 (t, J = 6.8 Hz, 1H), 7.41-7.55 (m, 4H), 7.97-8.06 (m, 2H), 8.24-8.53 (m, 3H).

Table 1. $\Delta\delta^{RS}$ values for Pg, L and Cβ–H substituents at 298 and 213K of 9-AMA esters of alcohols **1**, **7-8**, **10-14**, **16**, **18**, **20**, **21**, **23** (CD_2Cl_2:CS_2 1:4).

		$\Delta\delta^{RS}$ values (ppm)		
Alcohol	T (K)	Cβ-H	Pg	L
2	298	-0.18		+0.04, +0.08
2	213	-0.22	-	+0.08, +0,11
3	298	-0.01	-	+0.12
3	213	-0.21	-	+0.14
8	298	+0.09	+0.00, +0.09	-0.17
8	213	+0.14	+0.03, +0.12	-0.18
9	298	+0.04		-0.04, -0.06
9	213	+0.18		-0.06, -0.10
10	298	+0.02	+0.08	-0.04, -0.02
10	213	+0.21	+0.08	-0.05, -0.02
11	298	-0.19	+0.13,+0.02,+0.10	-
11	213	-0.26	+0.06,-0.04,+0.05	-
12	298	-0.23	-0.02	-0.13
12	213	-0.43	-0.17	-0.27
13	298	+0.21	+0.01	+0.31
13	298	+0.47	+0.21	+0.49

^{1}H NMR and ^{13}C NMR spectra of selected compounds

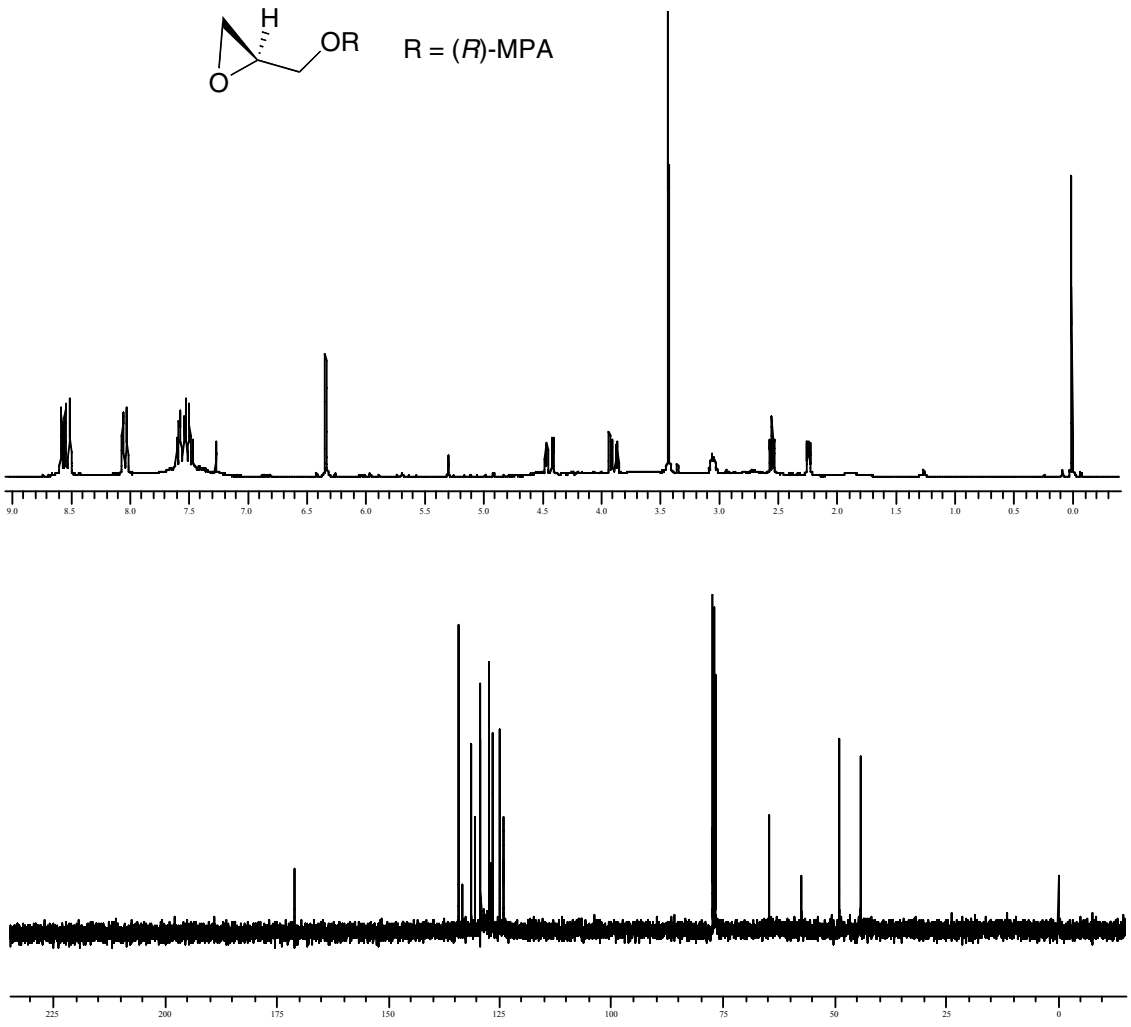

Figure 1S. (*R*)-9-AMA ester of (*R)*-glycidol [(*R*)-2]

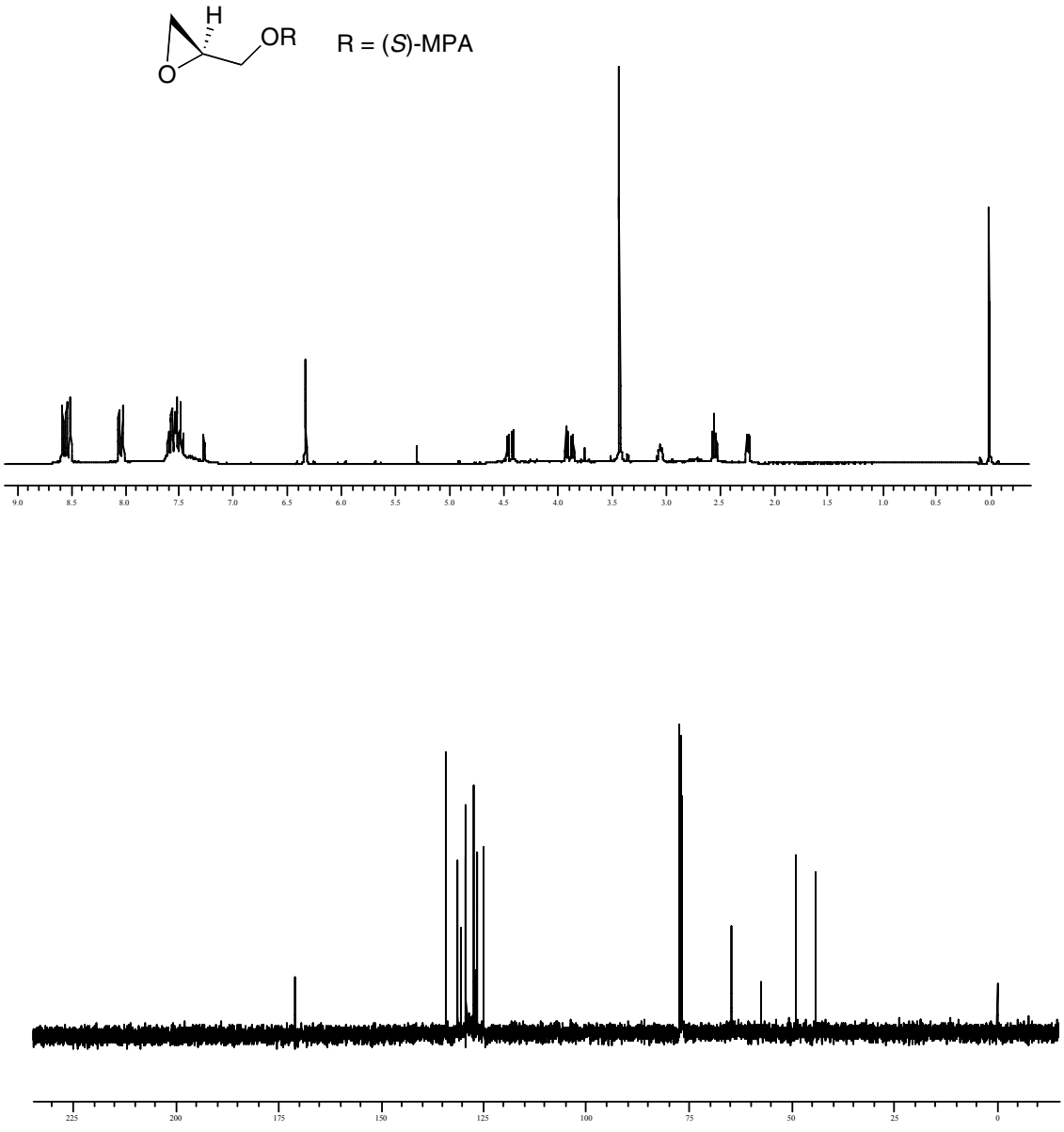

Figure 2S. (*S*)-9-AMA ester of (*R)*-glycidol [(*S*)-2]

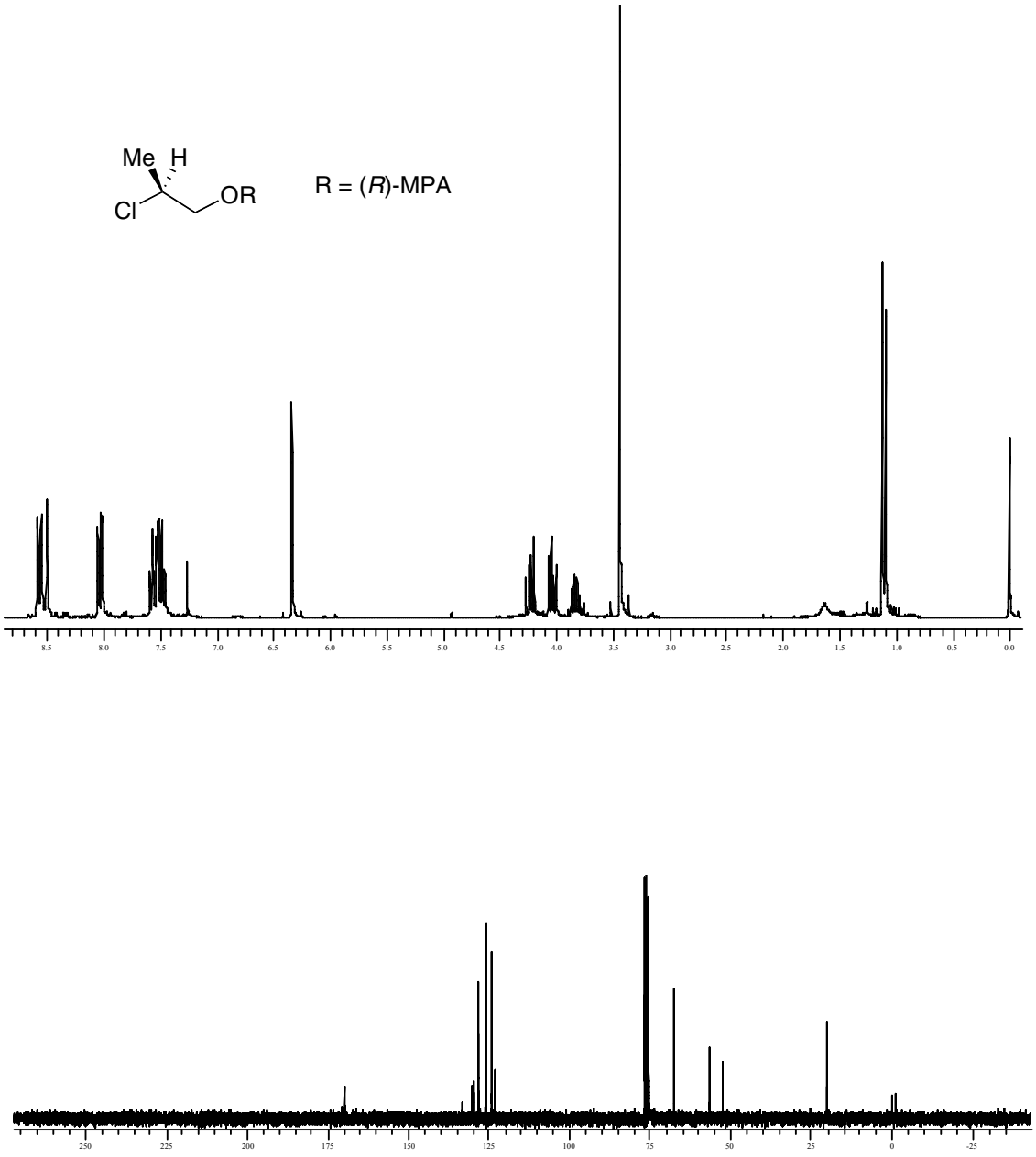

Figure 3S. (*R*)-9-AMA ester of (*S*)-2-chloro-1-propanol [(*R*)-3]

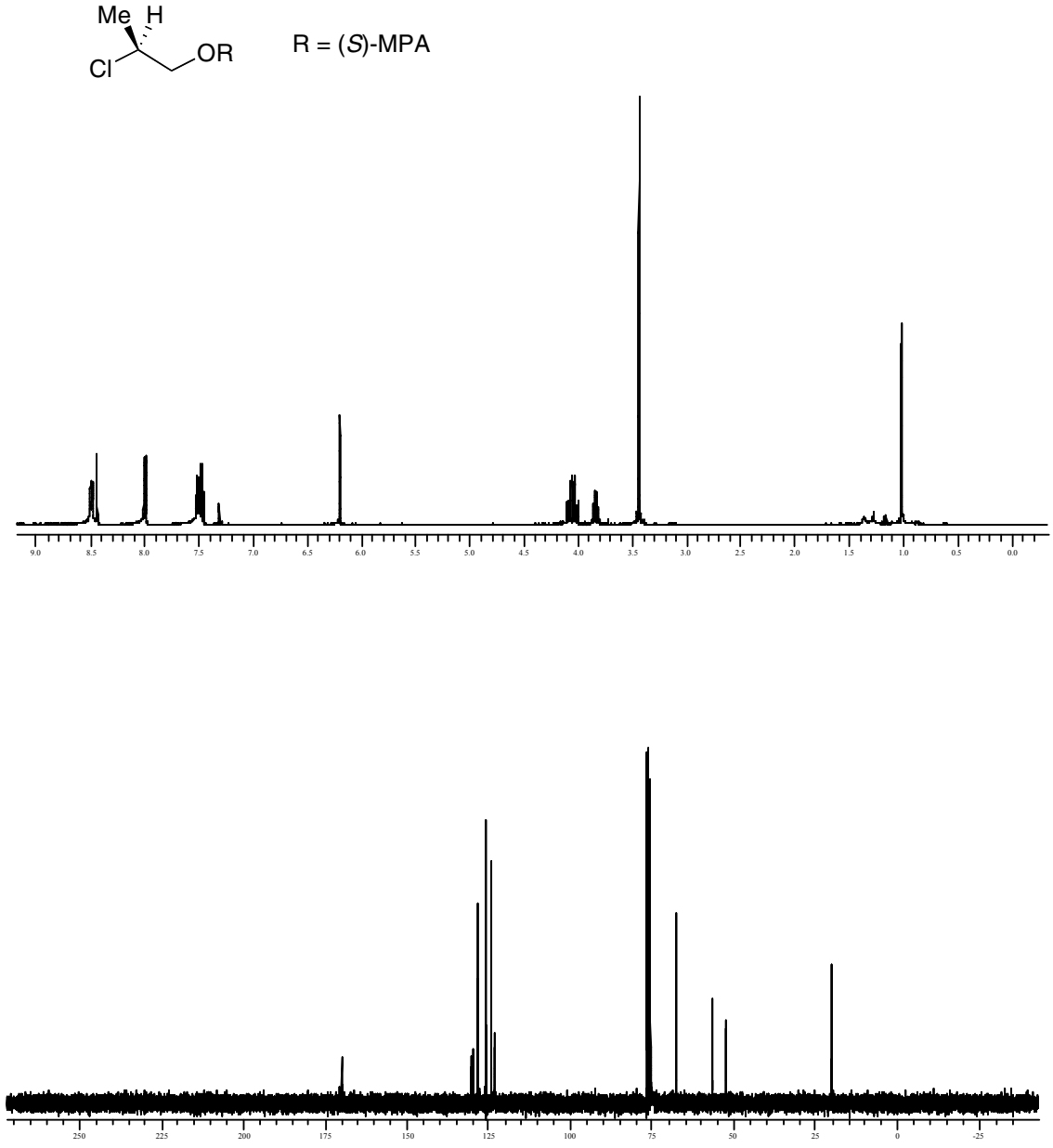

Figure 4S. (*S*)-9-AMA ester of (*S*)-2-chloro-1-propanol [(*S*)-3]

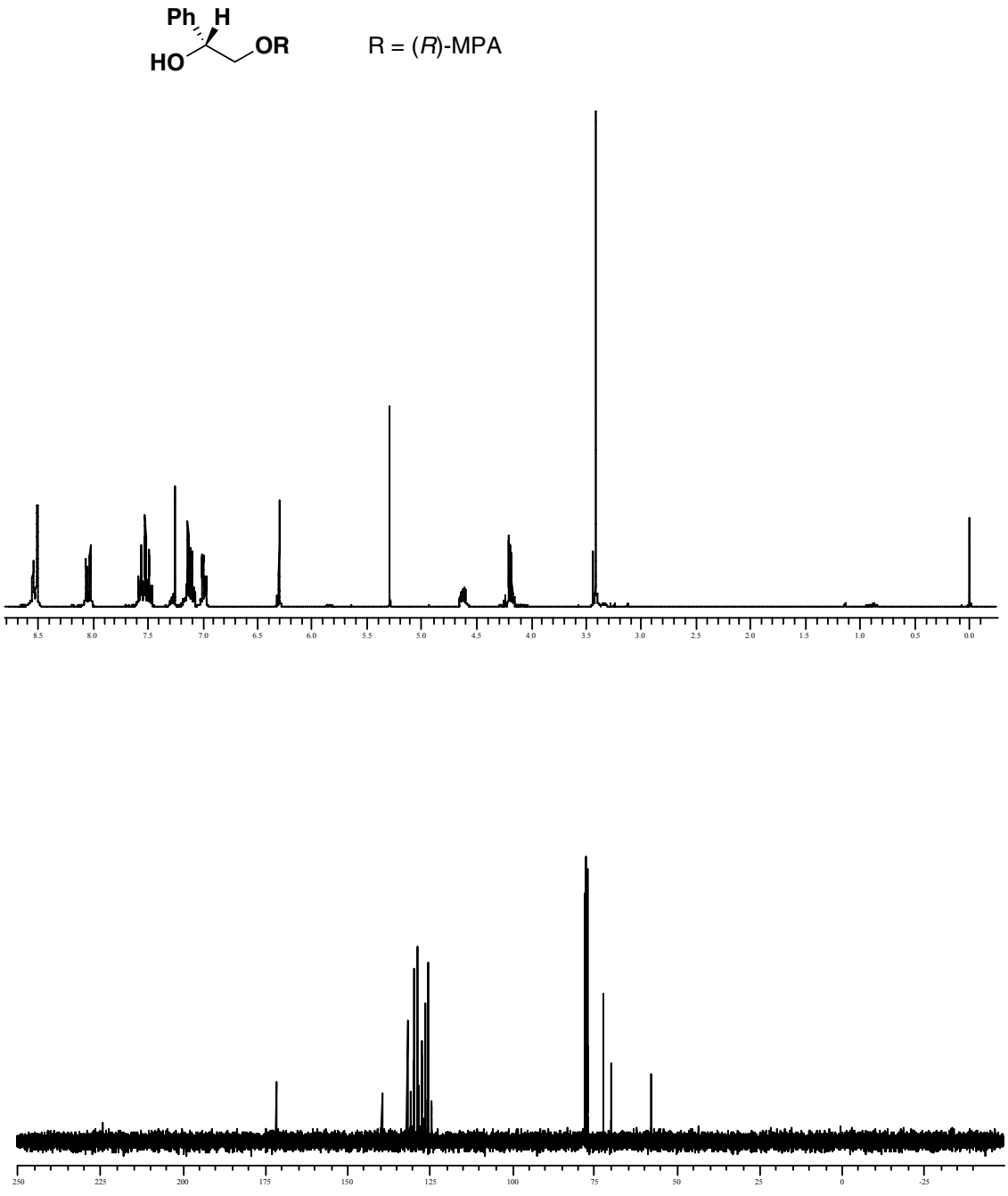

Figure 5S. (*R*)-9-AMA ester of (*R*)-2-hydroxy-2-phenylpropanol [(*R*)-9]

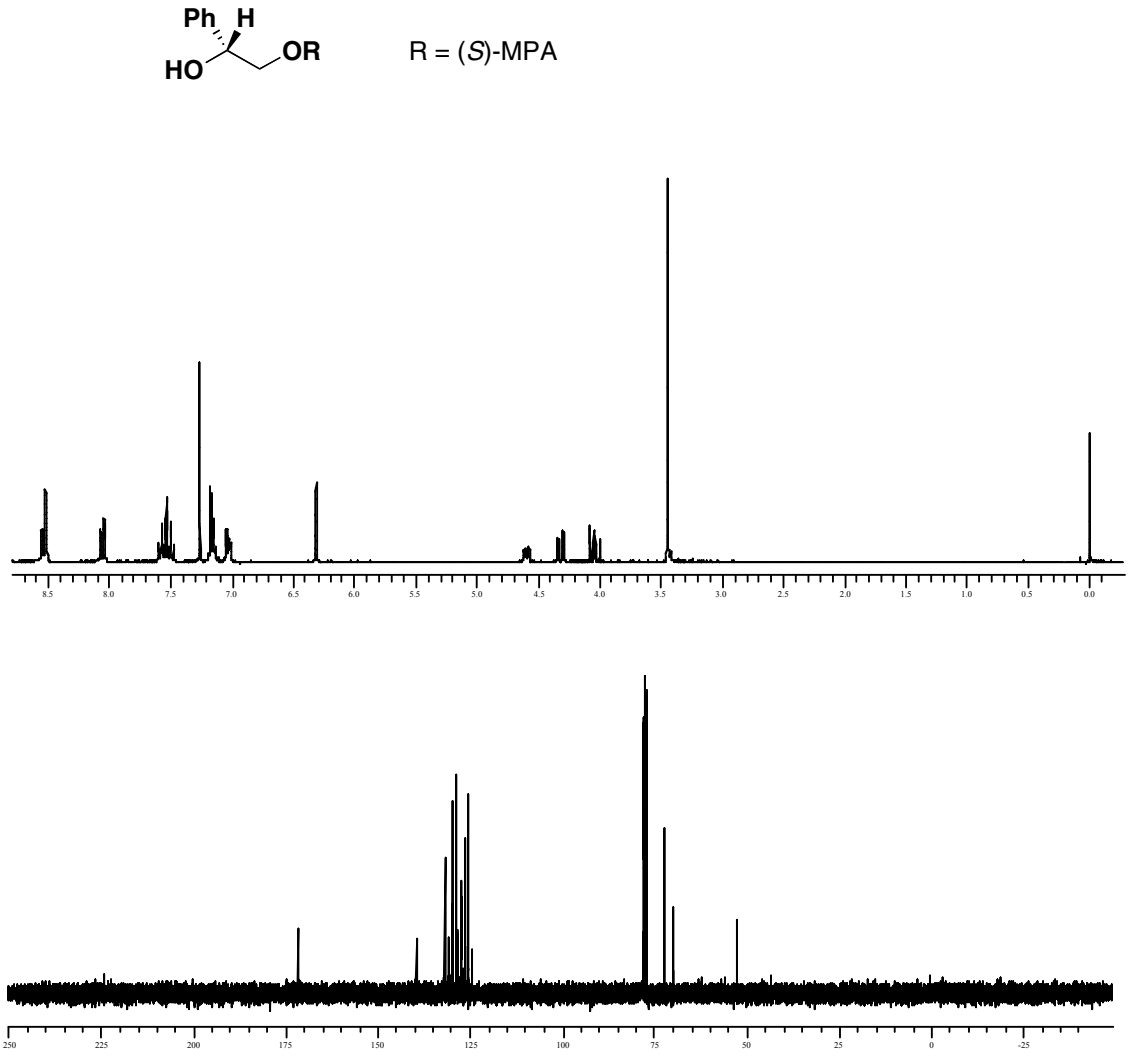

Figure 6S. (*S*)-9-AMA ester of (*R*)-2-hydroxy-2-phenylpropanol [(S)-9]

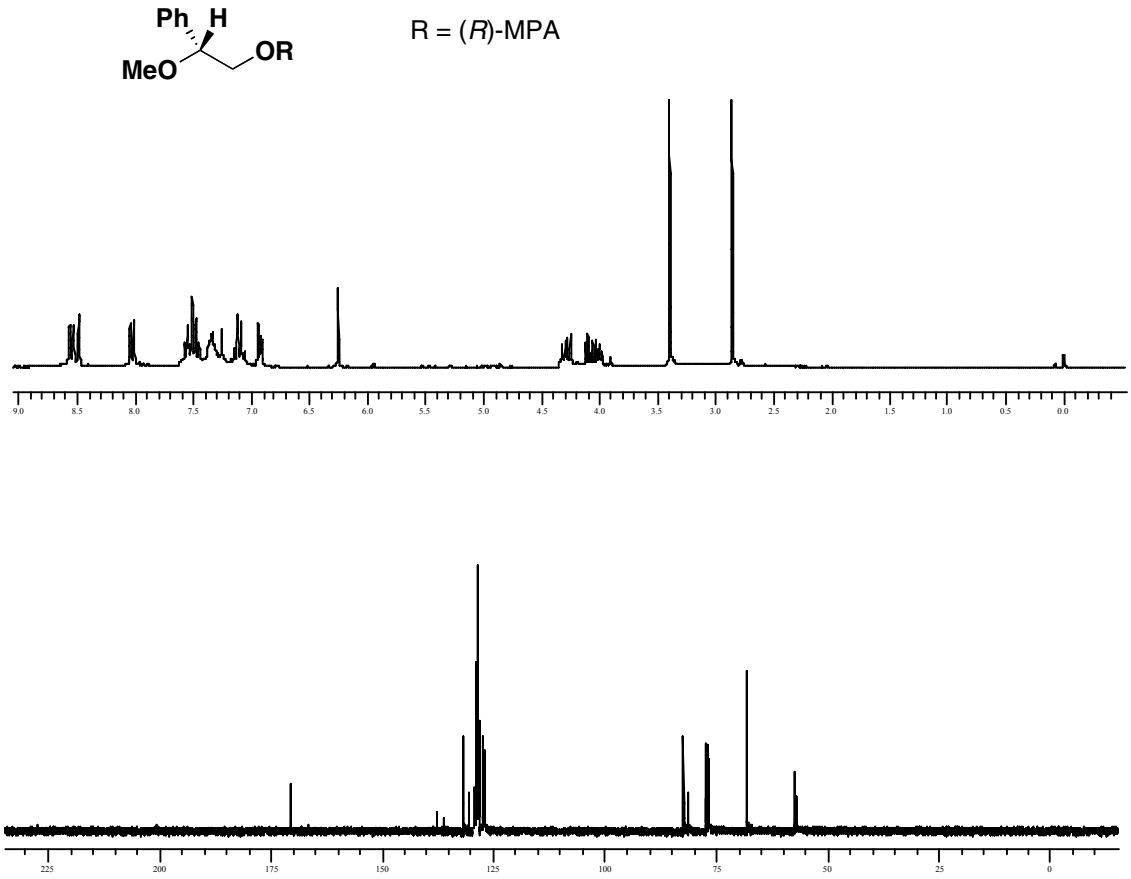

Figure 7S. (*R*)-9-AMA ester of (*R*)-2-methoxy-2-phenylethanol [(*R*)-10]

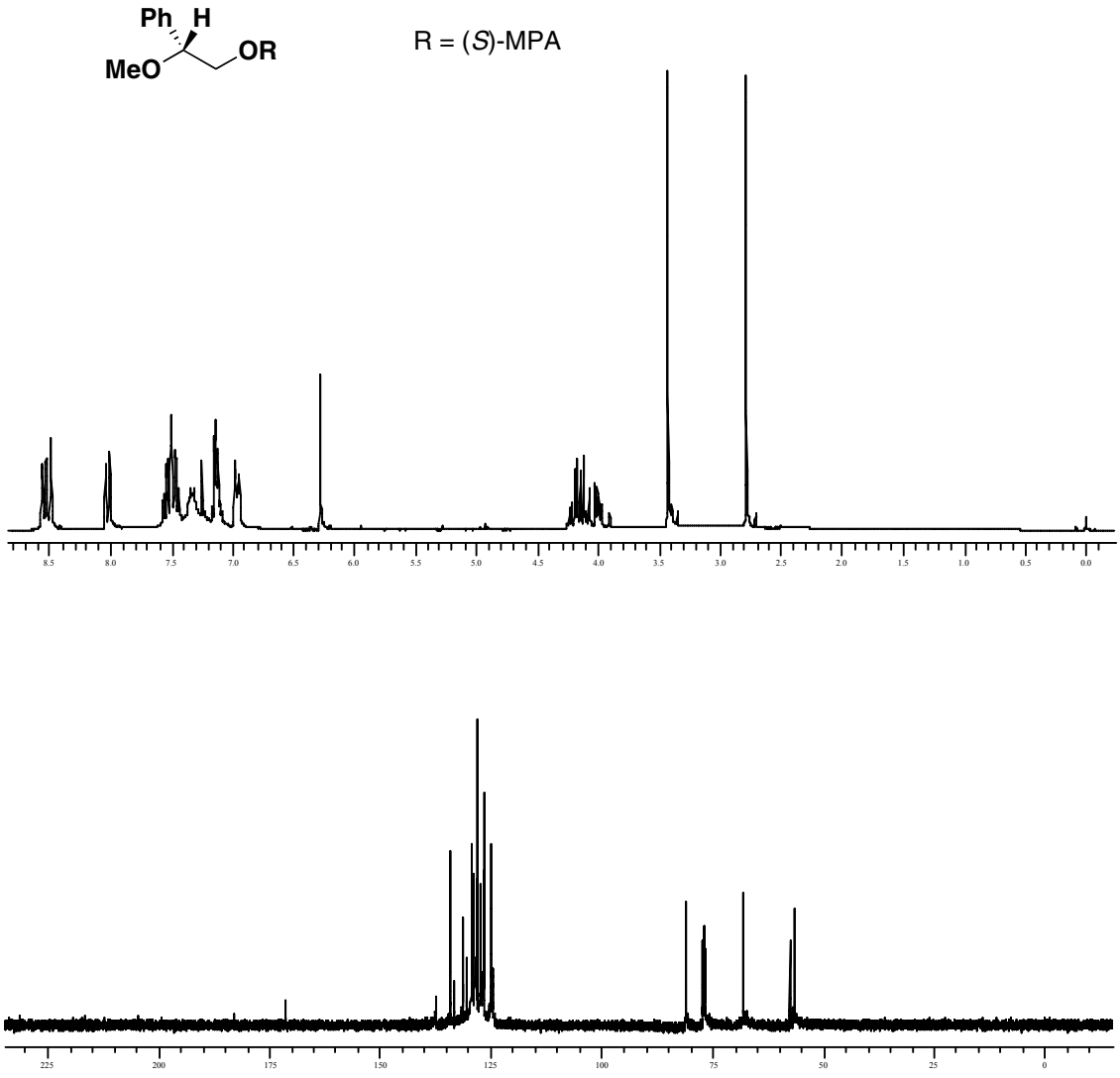

Figure 8S. (*S*)-9-AMA ester of (*R*)-2-methoxy-2-phenylethanol [(*S*)-10]

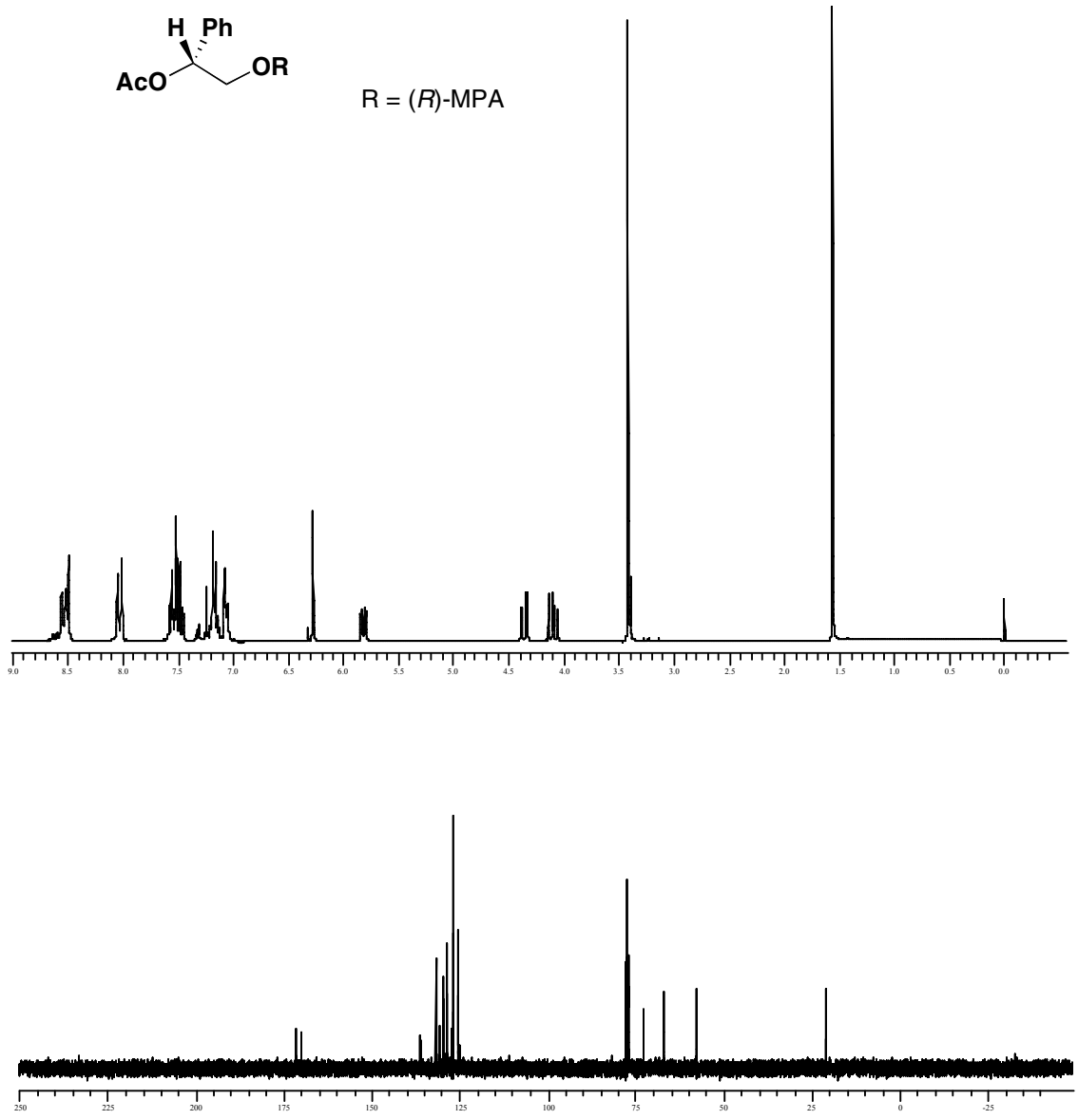

Figure 9S. (*R*)-9-AMA ester of (*R*)-2-acetoxy-2-phenylpropanol [(*R*)-13]

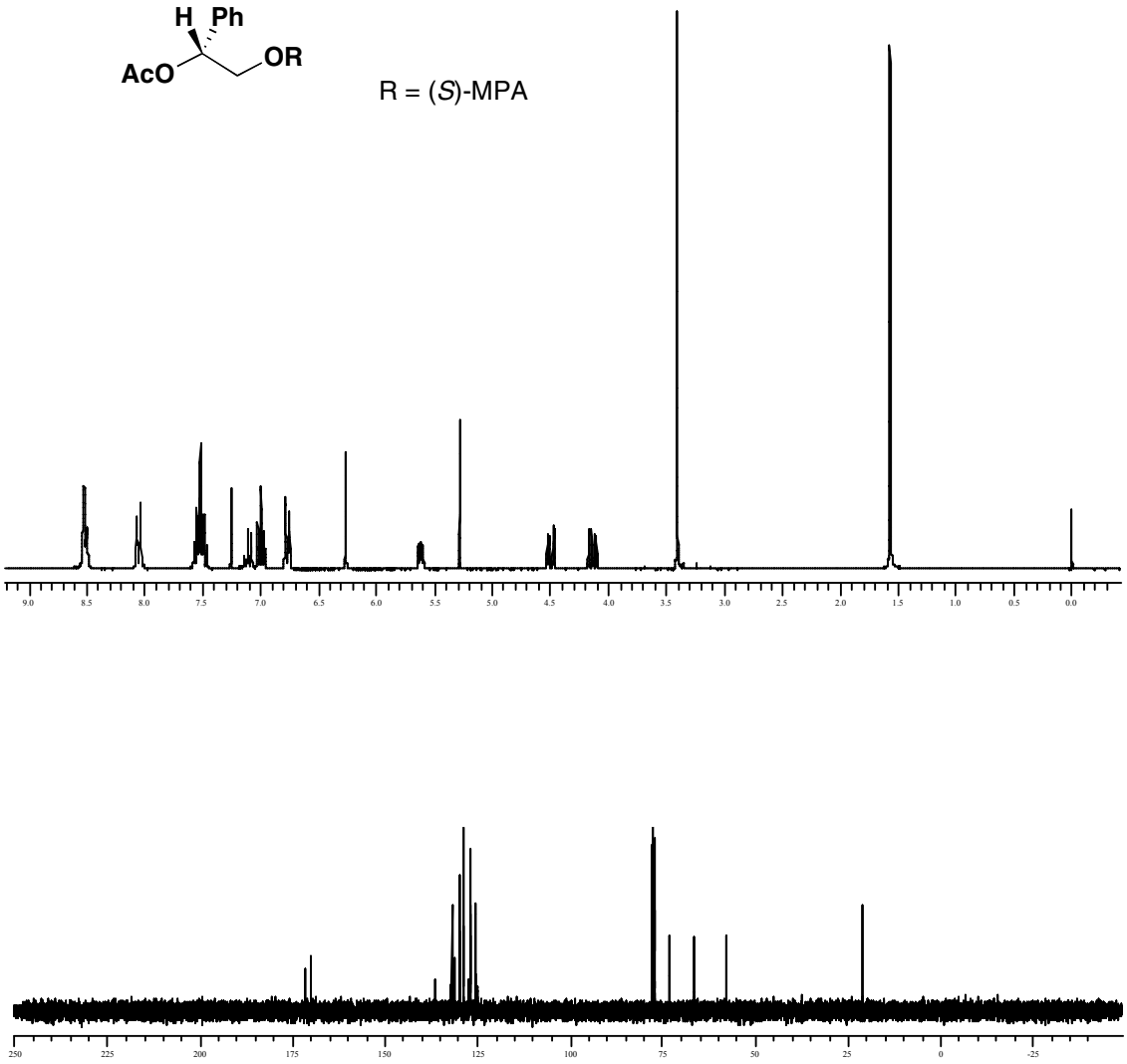

Figure 10S. (*S*)-9-AMA ester of (*R*)-2-acetoxy-2-phenylpropanol [(S)-13]

Conformational studies

The conformational studies [energy minimization by semiempirical (AM1), and DFT (B3LYP)] were performed using Gaussian 98. They conclude that (*R*)-9-AMA esters of Type A primary alcohols present two major conformers: [(G-), A, SP] and [(G-), +AC, SP], as shown in Fig. 11Sa and Fig. 12Sa. For its part, (*S*)-9-AMA esters of Type A primary alcohols present two major conformers: [(A), A, SP] and [(A), -AC, SP], as shown in Fig. 11Sb and Fig. 12b.

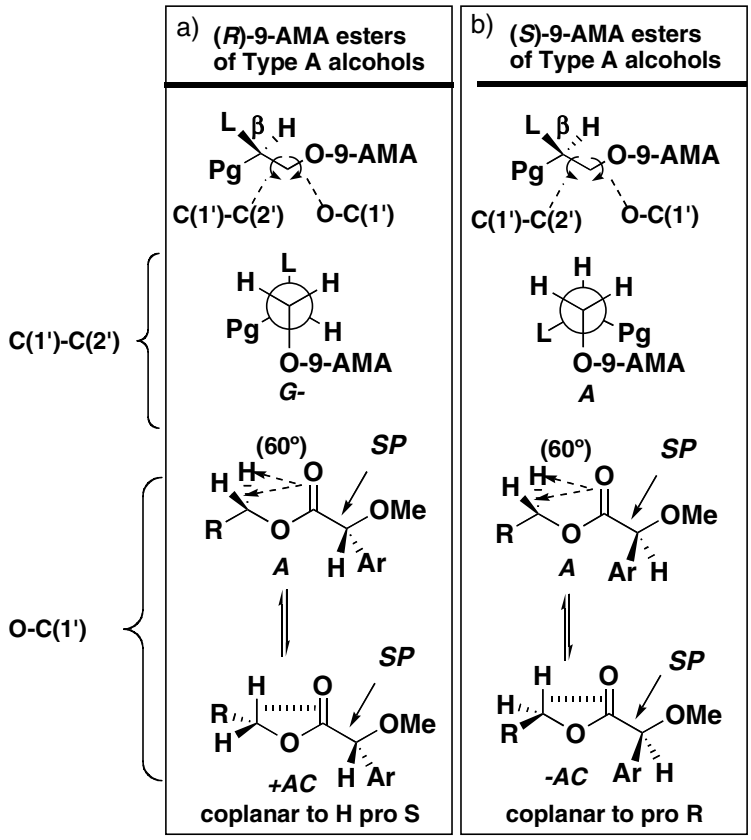

Fig. 11S (a) Main conformers for (*R*)-9-AMA esters of Type A primary alcohols. (b) *Idem* for (*S*)-9-AMA esters. In both cases, the C(1')-C(2') conformations are described in relation to the position of Cβ-H to O-9-AMA and the O-C(1') conformations are described in relation to the carbonyl group of the auxiliary to O-9-AMA. The SP conformation correspond to the 9-AMA moiety (OMe synperiplanar to the carbonyl group). Labels are taken as suggested in: J. Michl and R. West, *Acc. Chem. Res.* 2000, **33**, 821.

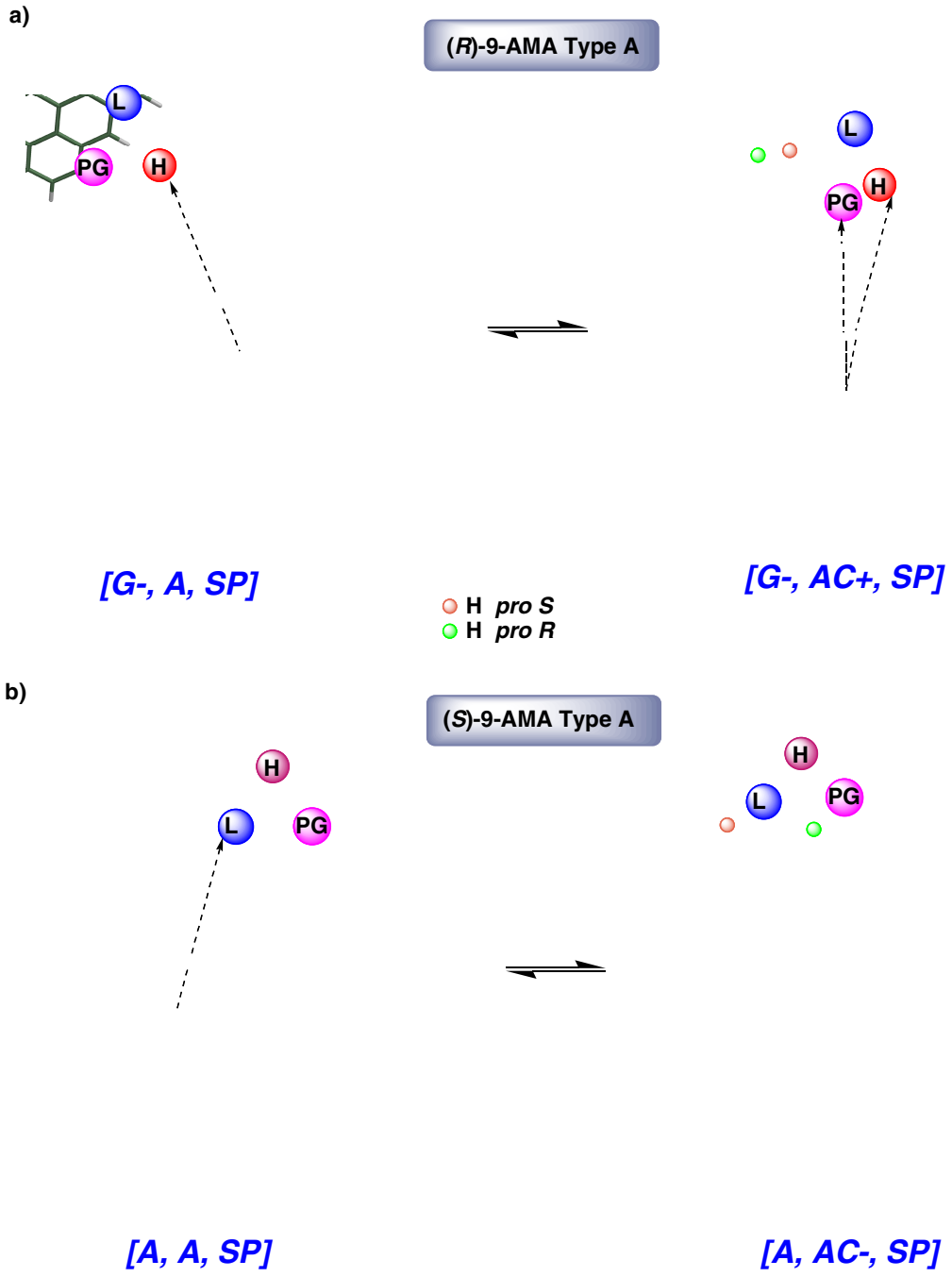

Fig. 12S (a) Main conformers of (*R*)-9-AMA esters of Type A primary alcohols (stick models). (b) *Idem* for (*S*)-9-AMA esters (stick models).