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Supporting Information

for the article

NMR Analysis of Chiral Alcohols and Amines: Development of Environmentally Benign "In Tube" Procedure with High Efficiency and Improved Detection Limit

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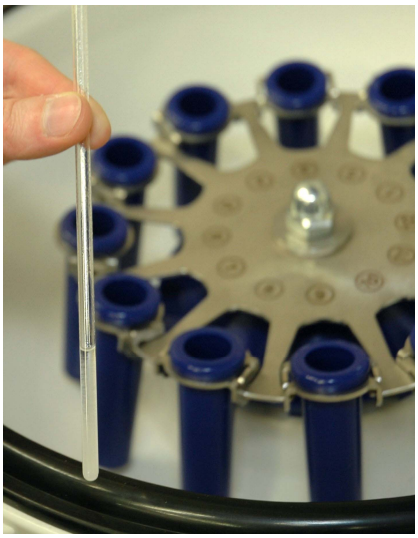
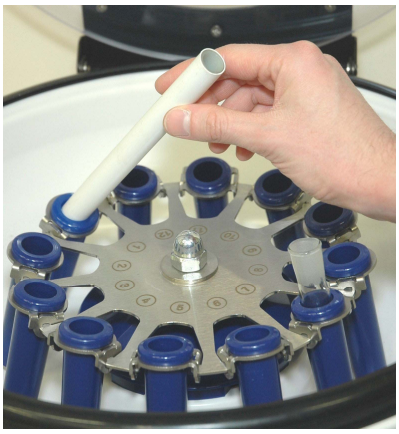
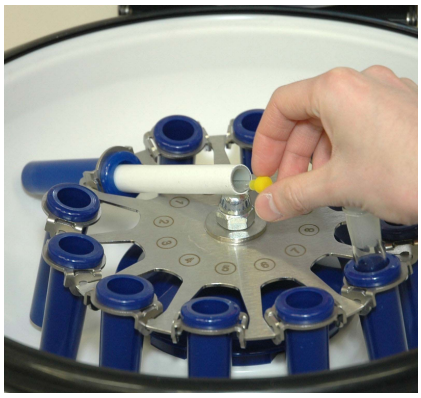
1) Description of centrifugation of NMR tubes.

NMR tube should be put inside a suitable metal or metal-plastic tube of appropriate length (Figure S1). Such cover prevents NMR tube from possible breakage during centrifugation. The sample in centrifuge was balanced in a regular way by test-tube with water placed on the opposite side. According to our experience centrifugation at 500 - 1000 rpm for 5 min was enough for the studied samples. Depending on the type of centrifuge device another type of cover may be necessary.

It should be pointed out that centrifugation was helpful for both types of samples – with solid particles precipitated to the bottom and with solid particles floated to the top of the solution (i.e. more heavy component - particles or liquid - was faster moving to the bottom of the sample tube).

		
a	**b**	**c**

d	**e**

Figure S1. NMR tube centrifugation. a) NMR tube to be centrifuged; b) insertion of metal-plastic tube into centrifuge; c) insertion of NMR tube into centrifuge; d) centrifugation in progress; e) NMR tube ready for spectral analysis.

2) Derivatization of a mixture of *R*- and *S*-methylmandelates with MPA and MTPA in various deuterated solvents in NMR tube.

Figure S2 shows representative fragments of the ^{1}H NMR spectra of diastereomers after derivatization in different deuterated solvents. Signals assigned to the diastereomers of *R*- and *S*-methylmandelate are marked in red and blue respectively, signals of unreacted alcohol are marked in green. Left column corresponds to MPA esters and right column corresponds to MTPA ones. See Table 1 in the article for the yields and ratios of diastereomers.

3) Influence of water impurities on DCC-promoted derivatization of mixture of *R*- and *S*-methylmandelates with MPA and MTPA in NMR tube in $CDCl_3$.

Figure S3 shows representative fragments of the ^{1}H NMR spectra of diastereomers after derivatization in the presence of various amounts of added water. Signals assigned to the diastereomers of *R*- and *S*-methylmandelate are marked in red and blue respectively, signals of unreacted alcohol are marked in green. Left column corresponds to MPA esters and right column corresponds to MTPA ones. See Table 2 in the article for the yields and ratios of diastereomers.

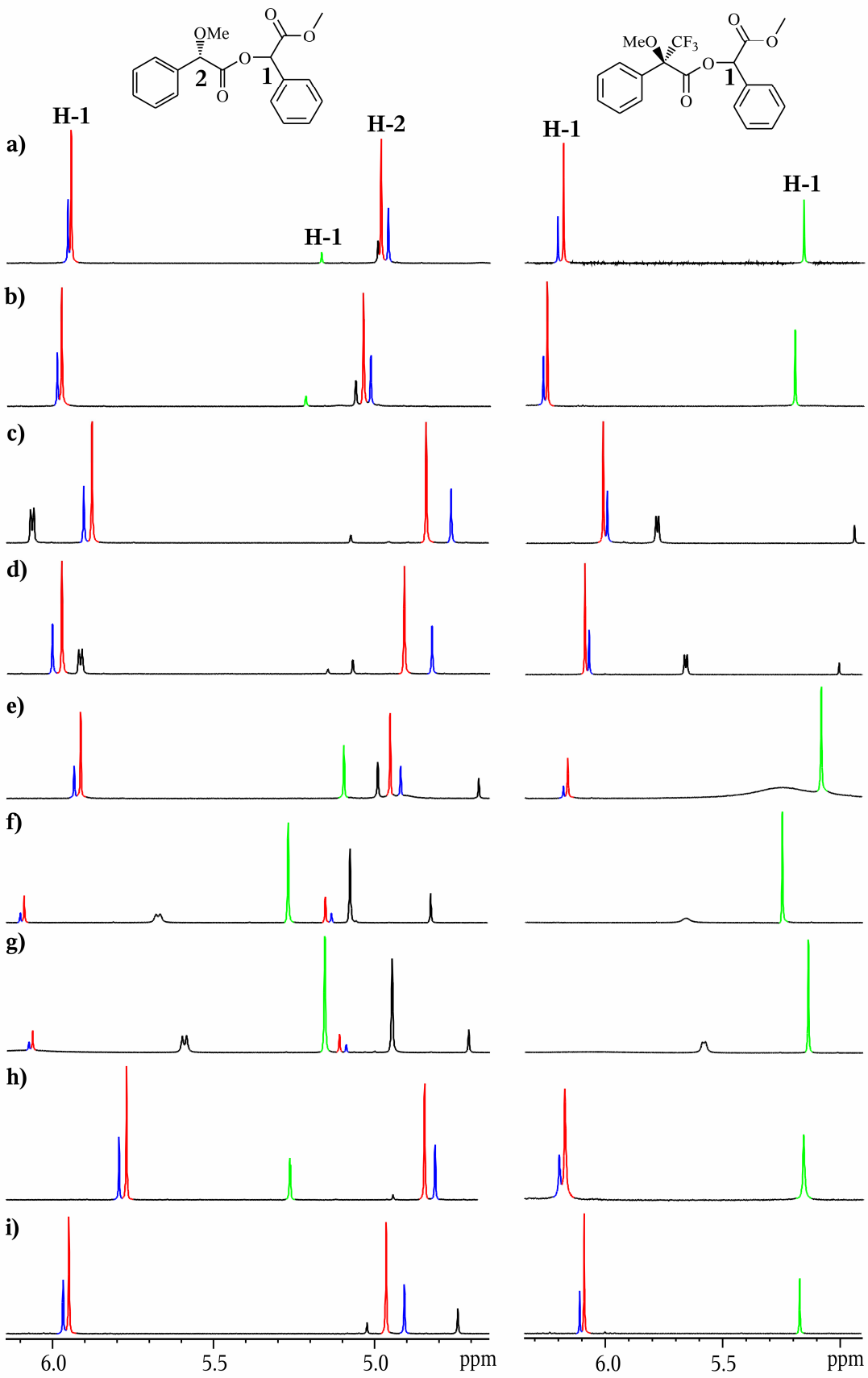


Figure S2. Representative fragments of ^{1}H NMR spectra of diastereomers of *R*- and *S*-methylmandelate formed in NMR tube in different solvents a) CD_3CN; b) acetone-d_6; c) toluene-d_8; d) benzene-d_6; e) THF-d_8; f) DMF-d_7; g) DMSO-d_6; h) CS_2/CD_2Cl_2 (4/1); i) $CDCl_3$.

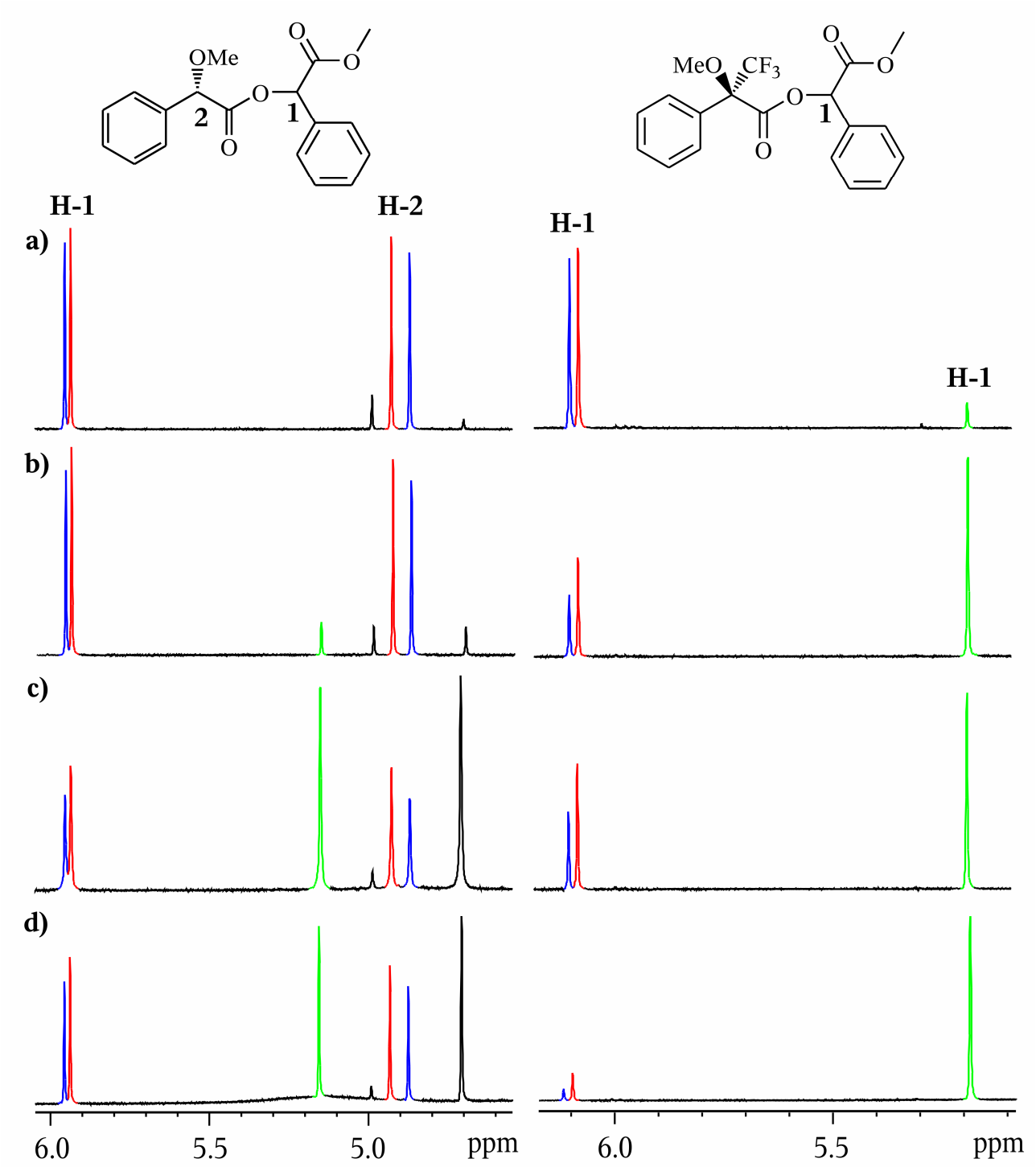
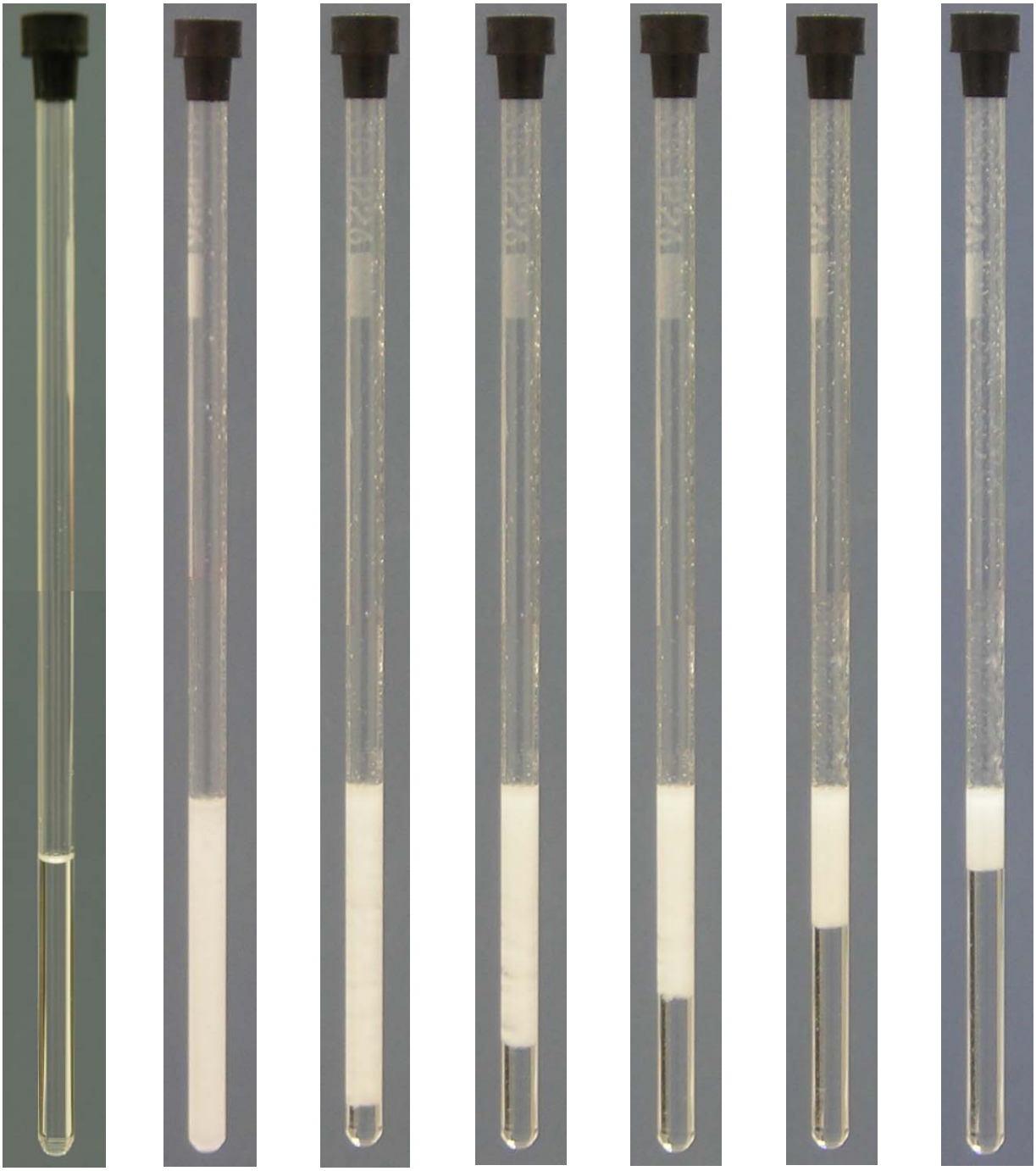


Figure S3. Representative fragments of ^{1}H NMR spectra showing influence of water on diastereomers yield and ratio. Quantities of added water: a) 0 equiv; b) 0.1 equiv; c) 0.5 equiv; d) 1 equiv.

4) Typical derivatization procedure of chiral alcohols and amines using *R*-MTPA or *S*-MPA in $CDCl_3$.

Figure S4 shows the pictures of the NMR tube at various time intervals during derivatization process without centrifugation.



a **b** **c** **d** **e** **f** **g**

Figure S4. "In tube" derivatization of chiral alcohols and amines with *R*-MTPA or *S*-MPA directly in NMR tube. **a** – solution of MTPA or MPA and analyzed sample in $CDCl_3$; **b** – after addition of DCC/DMAP and shaking for 1 min; **c** – after standing for 10 min; **d** – after standing for 20 min; **e** – after standing for 30 min; **f** – after standing for 45 min; **g** – after standing for 60 min.

Figure S5 shows NMR spectra with various amounts of diastereomers – MPA esters of *R*- and *S*-methylmandelate (corresponding signals marked in red and blue, respectively; signals of unreacted alcohol are marked in green) in $CDCl_3$ and C_6D_6. See Table 3 in the article for details.

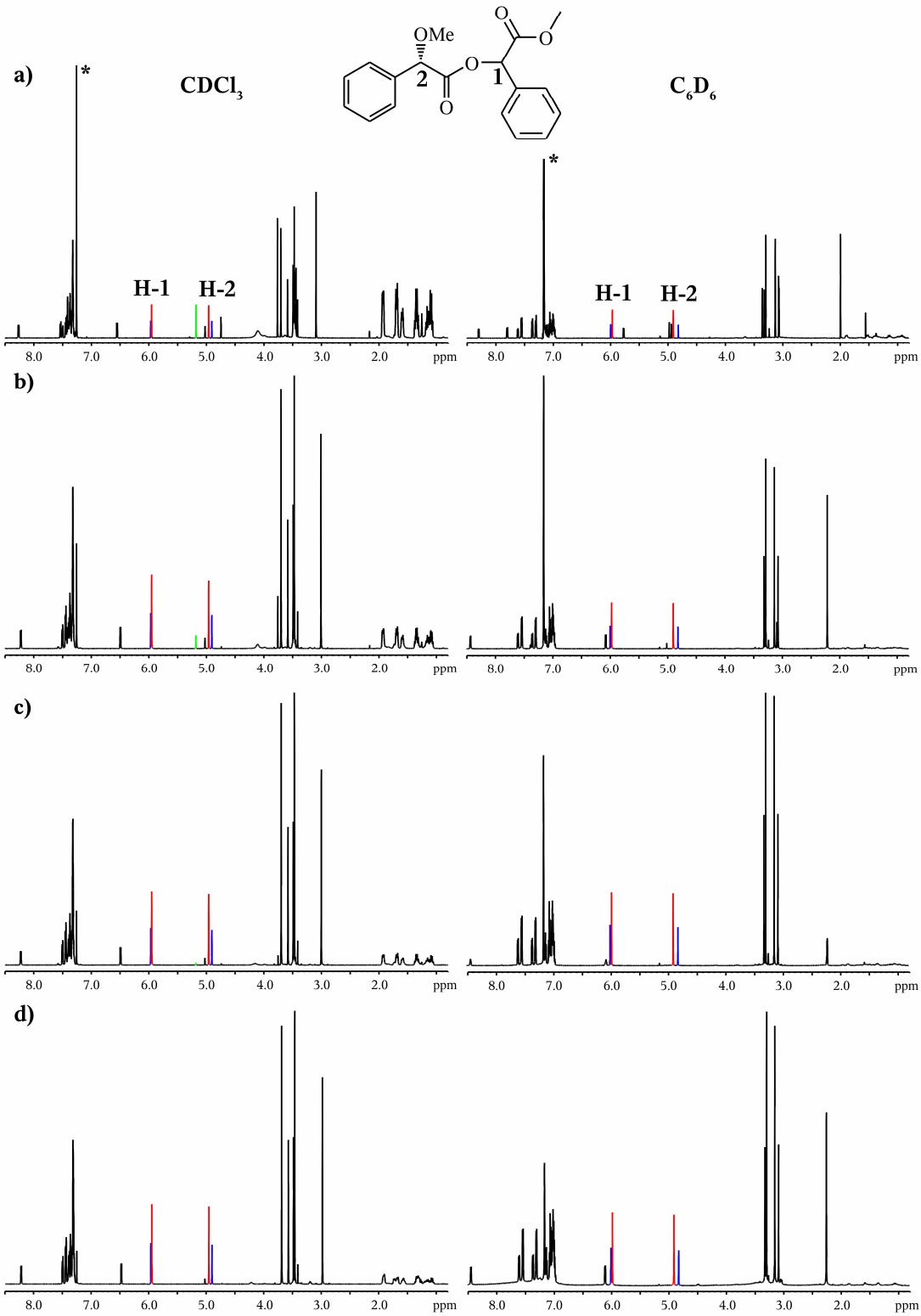


Figure S5. NMR spectra with various amounts of diastereomers – MPA esters of *R*- and *S*-methylmandelate in $CDCl_3$ (left column) and C_6D_6 (right column). The amount of the analyzed

sample: a) 0.9 mg, b) 4.5 mg, c) 9.0 mg, d) 18.0 mg. Signals of deuterated solvents are marked with an asterisk.

5) Increasing water tolerance by using an excess of DCC.

Commercially available NMR solvent was utilized without preliminary drying by molecular sieves.

Table S1. Influence of amount of DCC on the yield and R/S ratio of derivatization of mixture of *R*- and *S*-methylmandelates (70:30 molar ratio) with *S*-MPA (in $CDCl_3$).

Entry	Amount of added DCC, equiv [a]	Method of derivatization [b]	Conversion, % (R/S ratio)
1	1.1	C	84 (71.4:28.6)
2	1.5	C	95 (67.4:32.6)
3	2.0	C	100 (69.3:30.7)

[a] Based on the initial amount of *S*-MPA. [b] See Experimental part in the article for description of Method C.

6) The measured Δδ values in ^{1}H, ^{13}C and ^{19}F NMR spectra of diastereomers 1 – 18.

The summary of measured Δδ values is presented in Table S2. Completely resolved signals which can be used for measurement of diastereomers' ratio are given (See Scheme 3 in the article for structural summary). Signals of the diastereomers which are incompletely resolved or overlapped with other components of the mixture but still can be used for determination of absolute configuration are shown in *italic*.

Table S2. Differences in the ^{1}H, ^{13}C and ^{19}F NMR chemical shifts for diastereomers **1-18**.

Diastereomer	Δδ ^{1}H, ppm	Δδ ^{13}C, ppm	Δδ ^{19}F, ppm
1	0.141 (MeO in MTPA) 0.030 (MeO in alcohol) 0.019 (CHO)	0.153 (MeO in MTPA) 0.054 (MeO in alcohol)	0.289
2	0.024 (CHO) 0.022 (MeO in MTPA) *0.024 (Me)*	0.180 (MeO) *0.056 (CH_2O)* *0.026 (Me)*	0.275
3	0.074 (CHO)	0.303 (MeO)	0.222 (CF_3 in alcohol) 0.046 (CF_3 MTPA)
4	0.106 (<u>Me</u>CH_2) 0.011 (MeO) *0.077 (Me)*	0.350 (Me) 0.269 (<u>Me</u>CH_2) 0.125 (CHO)	0.025
5	0.045 (CH) 0.031 (MeO) *0.069 (Me)*	0.390 (MeO) 0.224 (CHO) 0.131 (Me) 0.107 (CH) *0.193 (<u>C</u>CH)*	0.260

6	0.056 (NH) *0.045 (MeCH)* *0.030 ($MeCH_2$)*	0.165 ($MeCH_2$) 0.126 (CHN) 0.069 (CH_2CH) 0.054 (CH_2CH_2CH)	0.089
7	0.039 (MeO) *0.040 (MeCH)*	0.223 (MeCH) 0.097 (CHN)	0.182
8	*0.016 (Me)*	0.238 (CHO) 0.016 (Me) *0.055 (CH_2N)*	0.040
9	0.207 ($MeCH_2$) *0.129 (Me)*	0.400 (Me) 0.310 ($MeCH_2$) 0.253 (MeO) *0.068 (CH_2)*	
10	0.038 ($MeCH_2$) 0.016 (MeO)	0.443 (MeCH) 0.157 ($CH_2CH_2CH_2Me$) 0.128 (CHO MPA) 0.110 (CHO in alcohol) 0.104 (CH_2CH_2CH) *0.376 (CH_2CH_2Me)* *0.096 ($MeCH_2$)* *0.023 (CH_2CHO)*	
11	0.086 (CH) *0.136 (Me)*	0.208 (Me) 0.162 (CHO MPA) 0.100 (CH) 0.069 (CHO in alcohol) *0.292 (CCH)*	
12	0.126 (MeO in alcohol) 0.075 (Me) 0.060 (CHO in alcohol) 0.026 (CHO MPA) 0.024 (MeO MPA)	0.209 (CHO MPA) 0.171 (MeO in alcohol) 0.091 (Me)	
13	0.118 (MeO in alcohol) 0.055 (CHO MPA) 0.016 (CHO in alcohol)	0.167 (MeO in alcohol) 0.109 (CHO MPA) 0.087 (CHO in alcohol)	
14	0.052 (CHO MPA) 0.019 (CHO in alcohol)	0.118 (Me) 0.097 (CHO MPA) 0.054 (CHO in alcohol) *0.156 (CH_2)*	
15	0.027 (CHO MPA)	0.394 (COO)	0.018
16		0.093 (CHO MPA) 0.088 (CH_2Br) 0.059 *(CH_2O)*	
17	0.040 (CHO) 0.036 (MeO) *0.066 (Me)*	0.226 (CHN) 0.112 (MeCHN) 0.073 (MeO)	0.217
18	0.063 ($MeCH_2$) 0.011 (MeO) *0.077 (Me)*	0.211 (MeCHN) 0.176 (CHN) 0.124 (MeO) 0.100 (CH_2CH_2CH) 0.096 (CHO) 0.084 ($MeCH_2$) 0.082 (CH_2CH) *0.035 (CH_2Me)*	

7) Spectral data for the studied compounds.

***(R)*-MTPA ester of *(R)*-methylmandelate (1-RR)**: ^{1}H NMR 3.688 (s, OMe MTPA, 3 H); 3.765 (s, OMe alcohol, 3 H); 6.100 (s, CHO, 1H); 7.268-7.461 (m, meta-, para-H Ph MTPA, Ph, 8H); 7.614-7.648 (m, ortho-H Ph MTPA, 2H). ^{13}C NMR 52.975 (OMe alcohol); 55.803 (OMe MTPA); 76.034 (CHO); 84.744 (COMe MTPA); 127.662 (Ph); 127.996 (Ph); 128.522 (Ph); 128.971 (Ph); 129.591 (Ph); 129.817 (Ph); 132.052 (Ph); 132.743 (Ph); 166.319 (COO MTPA); 168.559 (COO). ^{19}F NMR -72.274.

***(R)*-MTPA ester of *(S)*-methylmandelate (1-RS)**: ^{1}H NMR 3.547 (s, OMe MTPA, 3 H); 3.735 (s, OMe alcohol, 3 H); 6.116 (s, CHO, 1H); 7.268-7.461 (m, meta-, para-H Ph MTPA, Ph, 8H); 7.569-7.600 (m, ortho-H Ph MTPA, 2H). ^{13}C NMR 52.921 (OMe alcohol); 55.650 (OMe MTPA); 76.034 (CHO); 84.869 (COMe MTPA); 127.662 (Ph); 127.878 (Ph); 128.481 (Ph); 129.043 (Ph); 129.682 (Ph); 129.862 (Ph); 131.802 (Ph); 132.854 (Ph); 166.235 (COO MTPA); 168.307 (COO). ^{19}F NMR -72.563.

***(R)*-MTPA ester of *(R)*-ethylmandelate (2-RR)**: ^{1}H NMR 1.238 (t, Me, 3H, J= 7.12 Hz); 3.692 (s, OMe, 3 H); 4.135-4.295 (m, CH_2O, 2H); 6.067 (s, CHO, 1H); 7.268-7.472 (m, meta-, para-H Ph MTPA, Ph, 8H); 7.615-7.662 (m, ortho-H Ph MTPA, 2H). ^{13}C NMR 14.080 (Me); 55.797 (OMe); 62.234 (CH_2O); 76.253 (CHO); 85.193 (COMe); 127.473 (Ph); 127.677 (Ph); 127.973 (Ph); 128.507 (Ph); 129.495 (Ph); 129.813 (Ph); 132.083 (Ph); 132.882 (Ph); 166.318 (COO MTPA); 168.067 (COO). ^{19}F NMR -72.260.

***(R)*-MTPA ester of *(S)*-ethylmandelate (2-RS)**: ^{1}H NMR 1.214 (t, Me, 3H, J= 7.12 Hz); 3.670 (s, OMe, 3 H); 4.135-4.295 (m, CH_2O, 2H); 6.091 (s, CHO, 1H); 7.268-7.472 (m, meta-, para-H Ph MTPA, Ph, 8H); 7.568-7.609 (m, ortho-H Ph MTPA, 2H). ^{13}C NMR 14.054 (Me); 55.617 (OMe); 62.178 (CH_2O); 76.201 (CHO); 85.402 (COMe); 127.473 (Ph); 127.607 (Ph); 127.897 (Ph); 128.507 (Ph); 129.591 (Ph); 129.854 (Ph); 131.826 (Ph); 132.995 (Ph); 166.239 (COO MTPA); 167.841 (COO). ^{19}F NMR -72.535.

***(R)*-MTPA ester of *(R)*-α-(trifluoromethyl)benzyl alcohol (3-RR)**: ^{1}H NMR 3.603 (s, OMe, 3H); 6.257 (q, CHO, 1H, J= 6.63 Hz); 7.264-7.484 (m, Ph, 10H). ^{13}C NMR 55.896 (OMe); 73.664 (q, CHO, J= 33.71 Hz); 127.289 (Ph); 128.206 (Ph); 128.576 (Ph); 128.824 (Ph); 129.951 (Ph); 130.401 (Ph); 131.628 (Ph); 164.850 (COO). ^{19}F NMR -72.332 (CF_3 MTPA); -76.175 (d, CF_3 alcohol, J= 6.89 Hz).

***(R)*-MTPA ester of *(S)*-α-(trifluoromethyl)benzyl alcohol (3-RS)**: ^{1}H NMR 3.480 (s, OMe, 3H); 6.331 (q, CHO, 1H, J= 6.63 Hz); 7.264-7.484 (m, Ph, 10H). ^{13}C NMR 55.593 (OMe); 73.446 (q, CHO, J= 33.71 Hz); 127.587 (Ph); 127.912 (Ph); 128.652 (Ph); 129.055 (Ph); 130.034 (Ph); 130.545 (Ph); 131.454 (Ph); 165.077 (COO). ^{19}F NMR -72.286 (CF_3 MTPA); -76.397 (d, CF_3 alcohol, J= 6.89 Hz).

***(R)*-MTPA ester of *(R)*-butan-2-ol (4-RR)**: ^{1}H NMR 0.938 (t, Me, 3H, J= 7.27 Hz); 1.254 (d, Me, 3H, J= 6.26 Hz); 1.552-1.716 (m, CH_2, 2H); 3.565 (s, OMe, 3H); 5.052-5.127 (m, CHO, 1H); 7.374-7.409 (m, meta-, para-H Ph, 3H); 7.514-7.556 (m, ortho-H Ph, 2H). ^{13}C NMR 9.804 (CH_2Me); 19.132 (Me); 55.485 (OMe); 75.557 (CHO); 84.686 (COMe); 127.557 (Ph); 128.476 (Ph); 129.633 (Ph); 166.334 (COO). ^{19}F NMR -72.023.

***(R)*-MTPA ester of *(S)*-butan-2-ol (4 RS)**: ^{1}H NMR 0.832 (t, Me, 3H, J= 7.27 Hz); 1.331 (d, Me, 3H, J= 6.26 Hz); 1.552-1.716 (m, CH_2, 2H); 3.554 (s, OMe, 3H); 5.052-5.127 (m, CHO, 1H); 7.374-7.409 (m, meta-, para-H Ph, 3H); 7.514-7.556 (m, ortho-H Ph, 2H). ^{13}C NMR 9.535 (CH_2Me); 19.482 (Me); 55.485 (OMe); 75.432 (CHO); 84.728 (COMe); 127.464 (Ph); 128.476 (Ph); 129.633 (Ph); 166.280 (COO). ^{19}F NMR -71.998.

***(R)*-MTPA ester of *(R)*-3-butyn-2-ol (5-RR)**: ^{1}H NMR 1.532 (d, Me, 3H, J= 6.68 Hz); 2.535 (d, CH, 1H, J= 1.95 Hz); 3.588 (s, OMe, 3H); 5.602-5.669 (m, CHO, 1H); 7.380-7.442 (m, meta-, para-H Ph, 3H); 7.511-7.557 (m, ortho-H Ph, 2H). ^{13}C NMR 20.956 (Me); 55.187 (OMe); 62.445 (CHO); 74.354 (CH); 80.841 (CCH); 85.005 (COMe); 127.580 (Ph); 127.984 (Ph); 129.794 (Ph); 132.333 (Ph); 165.717 (COO). ^{19}F NMR -72.242.

***(R)*-MTPA ester of *(S)*-3-butyn-2-ol (5-RS)**: ^{1}H NMR 1.601 (d, Me, 3H, J= 6.68 Hz); 2.490 (d, CH, 1H, J= 1.95 Hz); 3.557 (s, OMe, 3H); 5.602-5.669 (m, CHO, 1H); 7.380-7.442 (m, meta-, para-H Ph, 3H); 7.511-7.557 (m, ortho-H Ph, 2H). ^{13}C NMR 21.087 (Me); 55.577 (OMe); 62.221 (CHO); 74.247 (CH); 80.648 (CCH); 84.823 (COMe); 127.450 (Ph); 127.984 (Ph); 129.794 (Ph); 132.063 (Ph); 165.611 (COO). ^{19}F NMR -72.502.

***(R)*-MTPA ester of *(R)*-2-heptylamine (6-RR)**: ^{1}H NMR 0.884 (t, Me, 3H, J= 6.95 Hz); 1.135 (d, Me, 3H, J= 6.58 Hz); 1.203-1.395 (m, CH_2, 6H); 1.448-1.501 (m, CH_2, 2H); 3.412 (s, Me, 3H); 3.988-4.067 (m, CHN, 1H); 6.516 (br. d, NH, 1H, J= 7.28 Hz); 7.376-7.408 (m, meta-, para-H Ph, 3H); 7.503-7.551 (m, ortho-H Ph, 2H). ^{13}C NMR 14.069 (Me); 20.841 (Me); 22.663 (CH_2); 25.754 (CH_2); 31.692 (CH_2); 36.813 (CH_2); 45.675 (CHN); 55.034 (OMe); 84.028 (COMe); 127.834 (Ph); 128.635 (Ph); 129.521 (Ph); 132.974 (Ph); 165.520 (CON). ^{19}F NMR -69.336.

***(R)*-MTPA ester of *(S)*-2-heptylamine (6-RS)**: ^{1}H NMR 0.854 (t, Me, 3H, J= 6.95 Hz); 1.180 (d, Me, 3H, J= 6.58 Hz); 1.203-1.395 (m, CH_2, 6H); 1.448-1.501 (m, CH_2, 2H); 3.422 (s, Me, 3H); 3.988-4.067 (m, CHN, 1H); 6.460 (br. d, NH, 1H, J= 7.28 Hz); 7.376-7.408 (m, meta-, para-H Ph, 3H); 7.503-7.551 (m, ortho-H Ph, 2H). ^{13}C NMR 14.069 (Me); 21.006 (Me); 22.663 (CH_2); 25.754 (CH_2); 31.638 (CH_2); 36.744 (CH_2); 45.549 (CHN); 55.034 (OMe); 84.219 (COMe); 127.834 (Ph); 128.593 (Ph); 129.521 (Ph); 133.038 (Ph); 165.520 (CON). ^{19}F NMR -69.425.

***(R)*-MTPA ester of *(R)*-α-methylbenzylamine (7-RR)**: ^{1}H NMR 1.507 (d, Me, 3H, J= 6.88 Hz); 3.369 (s, Me, 3H); 5.147-5.222 (m, CHN, 1H); 6.972 (br. t, NH, 1H); 7.228-7.309 (m, Ph, 5H); 7.387-7.446 (m, meta-, para-H Ph MTPA, 3H); 7.524-7.564 (m, ortho-H Ph MTPA, 2H). ^{13}C NMR 21.371 (Me); 48.928 (CHN); 55.060 (OMe); 84.047 (COMe); 126.310 (Ph); 127.721 (Ph); 127.799

(Ph); 128.708 (Ph); 128.900 (Ph); 129.564 (Ph); 132.853 (Ph); 142.478 (Ph); 165.536 (CON). ^{19}F NMR -69.236.

***(R)*-MTPA ester of *(S)*-α-methylbenzylamine (7-RS)**: ^{1}H NMR 1.547 (d, Me, 3H, J= 6.88 Hz); 3.409 (s, Me, 3H); 5.147-5.222 (m, CHN, 1H); 6.972 (br. t, NH, 1H); 7.228-7.309 (m, Ph, 5H); 7.387-7.446 (m, meta-, para-H Ph MTPA, 3H); 7.524-7.564 (m, ortho-H Ph MTPA, 2H). ^{13}C NMR 21.594 (Me); 49.025 (CHN); 55.060 (OMe); 84.281 (COMe); 126.310 (Ph); 127.679 (Ph); 127.863 (Ph); 128.608 (Ph); 128.880 (Ph); 129.616 (Ph); 132.631 (Ph); 142.604 (Ph); 165.464 (CON). ^{19}F NMR -69.419.

***(R)*-MTPA ester of *(R)*-1-amino-2-propanol (8-RR)**: ^{1}H NMR 1.183 (d, Me, 3H, J= 6.30 Hz); 3.136-3.264 (m, CH_2N, 2H); 3.417 (s, OMe, 3H); 3.908-3.994 (m, CHO, 1H); 4.071-4.224 (br. s, OH, 1H); 7.183-7.259 (br. s, NH, 1H); 7.336-7.435 (m, meta-, para-H Ph, 3H); 7.511-7.558 (m, ortho-H Ph, 2H). ^{13}C NMR 21.055 (Me); 46.801 (CH_2N); 55.092 (OMe); 67.339 (CHO); 84.175 (COMe); 127.842 (Ph); 132.630 (Ph); 128.711 (Ph); 129.635 (Ph); 167.285 (CON). ^{19}F NMR -69.422.

***(R)*-MTPA ester of *(S)*-1-amino-2-propanol (8-RS)**: ^{1}H NMR 1.199 (d, Me, 3H, J= 6.30 Hz); 3.136-3.264 (m, CH_2N, 2H); 3.417 (s, OMe, 3H); 3.908-3.994 (m, CHO, 1H); 4.071-4.224 (br. s, OH, 1H); 7.183-7.259 (br. s, NH, 1H); 7.336-7.435 (m, meta-, para-H Ph, 3H); 7.511-7.558 (m, ortho-H Ph, 2H). ^{13}C NMR 21.142 (Me); 26.746 (CH_2N); 55.092 (OMe); 67.131 (CHO); 84.374 (COMe); 132.674 (Ph); 127.842 (Ph); 132.630 (Ph); 128.711 (Ph); 129.635 (Ph); 167.285 (CON). ^{19}F NMR -69.462.

***(S)*-MPA ester of *(R)*-butan-2-ol (9-SR)**: ^{1}H NMR 0.858 (t, Me, 3H, J= 7.37 Hz); 1.086 (d, Me, 3H, J= 6.29 Hz); 3.419 (s, OMe, 3H); 4.738 (s, CHO MPA, 1H); 4.841-4.932 (m, CHO alcohol, 1H); 7.291-7.393 (m, meta-, para-H Ph, 3H); 7.424-7.460 (m, ortho-H Ph, 2H). ^{13}C NMR 9.719 (Me); 19.240 (Me); 28.820 (CH_2); 57.407 (OMe); 73.433 (CHO alcohol); 82.980 (CHO MPA); 127.214 (Ph); 128.635 (Ph); 128.718 (Ph); 136.583 (Ph); 170.576 (COO).

***(S)*-MPA ester of *(S)*-butan-2-ol (9-SS)**: ^{1}H NMR 0.651 (t, Me, 3H, J= 7.37 Hz); 1.215 (d, Me, 3H, J= 6.29 Hz); 3.416 (s, OMe, 3H); 4.726 (s, CHO MPA, 1H); 4.841-4.932 (m, CHO alcohol, 1H); 7.291-7.393 (m, meta-, para-H Ph, 3H); 7.424-7.460 (m, ortho-H Ph, 2H). ^{13}C NMR 9.409 (Me); 19.640 (Me); 28.752 (CH_2); 57.154 (OMe); 73.433 (CHO alcohol); 82.940 (CHO MPA); 127.325 (Ph); 128.635 (Ph); 128.806 (Ph); 136.710 (Ph); 170.576 (COO).

***(S)*-MPA ester of *(R)*-octan-2-ol (10-SR)**: ^{1}H NMR 0.870 (t, Me, 3H, J= 7.14 Hz); 1.041-1.303 (m, CH_2, 8H); 1.087 (d, Me, 3H, J= 6.02 Hz); 1.415-1.503 (m, CH_2, 2H); 3.417 (s, OMe, 3H); 4.732 (s, CHO MPA, 1H); 4.897-4.997 (m, CHO alcohol, 1H); 7.289-7.378 (m, meta-, para-H Ph, 3H); 7.405-7.461 (m, ortho-H Ph, 2H). ^{13}C NMR 14.175 (Me); 19.765 (Me); 22.660 (CH_2); 25.376 (CH_2); 29.125 (CH_2); 31.819 (CH_2); 35.897 (CH_2); 57.423 (OMe); 72.265 (CHO alcohol); 82.978 (CHO MPA); 127.199 (Ph); 128.645 (Ph); 128.689 (Ph); 136.554 (Ph); 170.557 (COO).

***(S)*-MPA ester of *(S)*-octan-2-ol (10-SS)**: ^{1}H NMR 0.832 (t, Me, 3H, J= 7.14 Hz); 0.942-1.024 (m, CH_2, 2H); 1.041-1.303 (m, CH_2, 8H); 1.215 (d, Me, 3H, J= 6.02 Hz); 3.412 (s, OMe, 3H); 4.716 (s, CHO MPA, 1H); 4.897-4.997 (m, CHO alcohol, 1H); 7.289-7.378 (m, meta-, para-H Ph, 3H); 7.405-7.461 (m, ortho-H Ph, 2H). ^{13}C NMR 14.155 (Me); 20.208 (Me); 22.564 (CH_2); 24.997 (CH_2); 28.968 (CH_2); 31.715 (CH_2); 35.874 (CH_2); 57.381 (OMe); 72.155 (CHO alcohol); 82.850 (CHO MPA); 127.344 (Ph); 128.645 (Ph); 128.733 (Ph); 136.683 (Ph); 170.557 (COO).

***(S)*-MPA ester of *(R)*-3-butyn-2-ol (11-SR)**: ^{1}H NMR 1.375 (d, Me, 3H, J= 6.37 Hz); 2.452 (d, CH, 1H, J= 2.20 Hz); 3.427 (s, OMe, 3H); 4.784 (s, CHO MPA, 1H); 5.449-5.510 (m, CHO alcohol, 1H); 7.311-7.388 (m, meta-, para-H Ph, 3H); 7.422-7.468 (m, ortho-H Ph, 2H). ^{13}C NMR 21.057 (Me); 57.548 (OMe); 61.068 (CH); 73.515 (CHO alcohol); 81.728 (CCH); 82.716 (CHO MPA); 127.366 (Ph); 128.720 (Ph); 128.905 (Ph); 135.921 (Ph); 169.785 (COO).

***(S)*-MPA ester of *(S)*-3-butyn-2-ol (11-SS)**: ^{1}H NMR 1.511 (d, Me, 3H, J= 6.37 Hz); 2.366 (d, CH, 1H, J= 2.20 Hz); 3.425 (s, OMe, 3H); 4.781 (s, CHO MPA, 1H); 5.449-5.510 (m, CHO alcohol, 1H); 7.311-7.388 (m, meta-, para-H Ph, 3H); 7.422-7.468 (m, ortho-H Ph, 2H). ^{13}C NMR 21.265 (Me); 57.522 (OMe); 60.968 (CH); 73.446 (CHO alcohol); 81.436 (CCH); 82.554 (CHO MPA); 127.366 (Ph); 128.757 (Ph); 128.905 (Ph); 136.069 (Ph); 169.669 (COO).

***(S)*-MPA ester of *(R)*-methyllactate (12-SR)**: ^{1}H NMR 1.419 (d, Me, 3H, J= 6.91 Hz); 3.450 (s, OMe MPA, 3H); 3.721 (s, OMe alcohol, 3H); 3.868 (s, CHO MPA, 1H); 5.121 (q, CHO alcohol, 1H, J= 6.91 Hz); 7.311-7.397 (m, meta-, para-H Ph, 3H); 7.444-7.491 (m, ortho-H Ph, 2H). 13C NMR 16.970 (Me); 52.474 (OMe alcohol); 57.646 (OMe MPA); 69.213 (CHO alcohol); 82.630 (CHO MPA); 127.449 (Ph); 128.733 (Ph); 128.940 (Ph); 136.073 (Ph); 170.276 (COOMe); 170.895 (COO).

***(S)*-MPA ester of *(S)*-methyllactate (12-SS)**: ^{1}H NMR 1.494 (d, Me, 3H, J= 6.91 Hz); 3.474 (s, OMe MPA, 3H); 3.595 (s, OMe alcohol, 3H); 4.842 (s, CHO MPA, 1H); 5.179 (q, CHO alcohol, 1H, J= 6.91 Hz); 7.311-7.397 (m, meta-, para-H Ph, 3H); 7.444-7.491 (m, ortho-H Ph, 2H). ^{13}C NMR 16.879 (Me); 52.303 (OMe alcohol); 57.621 (OMe MPA); 69.244 (CHO alcohol); 82.421 (CHO MPA); 127.480 (Ph); 128.733 (Ph); 128.888 (Ph); 135.936 (Ph); 170.276 (COOMe); 170.629 (COO).

***(S)*-MPA ester of *(R)*-methylmandelate (13-SR)**: ^{1}H NMR 3.471 (s, OMe MPA, 3H); 3.702 (s, OMe alcohol, 3H); 4.961 (s, CHO MPA, 1H); 5.953 (s, CHO alcohol, 1H); 7.302-7.461 (m, Ph, 8H); 7.491-7.515 (m, ortho-H Ph MPA, 2H). ^{13}C NMR 52.806 (OMe alcohol); 57.717 (OMe MPA); 74.955 (CHO alcohol); 82.545 (CHO MPA); 127.354 (Ph); 127.523 (Ph); 128.747 (Ph); 128.817 (Ph); 128.966 (Ph); 129.293 (Ph); 133.433 (Ph); 168.998 (COOMe); 170.245 (COO MPA).

***(S)*-MPA ester of *(S)*-methylmandelate (13-SS)**: ^{1}H NMR 3.491 (s, OMe MPA, 3H); 3.584 (s, OMe alcohol, 3H); 4.906 (s, CHO MPA, 1H); 5.969 (s, CHO alcohol, 1H); 7.302-7.461 (m, Ph, 10H). ^{13}C NMR 52.639 (OMe alcohol); 57.717 (OMe MPA); 74.868 (CHO alcohol); 82.436 (CHO

MPA); 127.440 (Ph); 127.664 (Ph); 128.747 (Ph); 128.817 (Ph); 128.920 (Ph); 129.447 (Ph); 133.559 (Ph); 168.701 (COOMe); 170.274 (COO MPA).

***(S)*-MPA ester of *(R)*-ethylmandelate (14-SR)**: ^{1}H NMR 1.181 (t, Me, 3H, J= 7.17 Hz); 3.471 (s, OMe, 3H); 4.110-4.235 (m, CH_2O, 2H); 4.958 (s, CHO MPA, 1H); 5.921 (s, CHO alcohol, 1H); 7.285-7.470 (m, Ph, 8H); 7.494-7.523 (m, ortho-H Ph MPA, 2H). ^{13}C NMR 14.056 (Me); 57.716 (OMe MPA); 61.939 (CH_2O); 75.035 (CHO alcohol); 82.451 (CHO MPA); 127.395 (Ph); 127.480 (Ph); 128.733 (Ph); 128.760 (Ph); 128.944 (Ph); 129.197 (Ph); 133.544 (Ph); 168.503 (COOEt); 170.262 (COO MPA).

***(S)*-MPA ester of *(S)*-ethylmandelate (14-SS)**: ^{1}H NMR 1.074 (t, Me, 3H, J= 7.17 Hz); 3.493 (s, OMe, 3H); 3.994-4.110 (m, CH_2O, 2H); 4.906 (s, CHO MPA, 1H); 5.940 (s, CHO alcohol, 1H); 7.285-7.470 (m, Ph, 10H). ^{13}C NMR 13.938 (Me); 57.745 (OMe MPA); 61.783 (CH_2O); 75.132 (CHO alcohol); 82.505 (CHO MPA); 127.395 (Ph); 127.480 (Ph); 128.733 (Ph); 128.760 (Ph); 128.917 (Ph); 129.352 (Ph); 133.698 (Ph); 168.209 (COOEt); 170.262 (COO MPA).

***(S)*-MPA ester of *(R)*-α-(trifluoromethyl)benzyl alcohol (15-SR)**: ^{1}H NMR 3.432 (s, OMe, 3H); 4.930 (s, CHO MPA, 1H); 6.084-6.161 (m, CHO alcohol, 1H); 7.189-7.239 (m, Ph, 2H), 7.283-7.327 (m, Ph, 1H); 7.327-7.437 (m, Ph, 7H). ^{13}C NMR 57.578 (OMe); 72.497 (q, CHO alcohol, J= 33.55); 82.352 (CHO MPA); 127.607 (Ph); 127.663 (Ph); 128.579 (Ph); 128.820 (Ph); 128.884 (Ph); 129.209 (Ph); 129.856 (Ph); 168.560 (COO). ^{19}F NMR -76.599.

***(S)*-MPA ester of *(S)*-α-(trifluoromethyl)benzyl alcohol (15-SS)**: ^{1}H NMR 3.425 (s, OMe, 3H); 4.903 (s, CHO MPA, 1H); 6.084-6.161 (m, CHO alcohol, 1H); 7.327-7.437 (m, Ph, 8H); 7.442-7.475 (m, ortho-H Ph MPA, 2H). ^{13}C NMR 57.578 (OMe); 72.449 (q, CHO alcohol, J= 33.55); 82.570 (CHO MPA); 127.607 (Ph); 127.663 (Ph); 128.579 (Ph); 128.820 (Ph); 129.142 (Ph); 130.112 (Ph); 168.954 (COO). ^{19}F NMR -76.581.

***(S)*-MPA ester of *(R)*-2,3-dibromo-1-propanol (16-SR)**: ^{1}H NMR 3.446 (s, OMe, 3H); 3.451 (dd, CH_2Br, 1H, J_1= 10.67 Hz, J_2= 9.33 Hz); 3.555-3.601 (m, CH_2Br, 1H); 4.213-4.272 (m, CHBr, 1H); 4.501 (dd, CH_2O, 1H, J_1= 5.13 Hz, J_2= 4.02 Hz); 4.553 (dd, CH_2O, 1H, J_1= 5.38 Hz, J_2= 5.09 Hz); 4.835 (s, CHO MPA, 1H); 7.326-7.402 (m, meta-, para-H Ph, 3H); 7.442-7.481 (m, ortho-H Ph MPA, 2H). ^{13}C NMR 31.927 (CH_2Br); 46.444 (CHBr); 57.642 (OMe); 65.562 (CH_2O); 82.580 (CHO MPA); 127.393 (Ph); 128.878 (Ph); 129.117 (Ph); 136.037 (Ph); 170.092 (COO).

***(S)*-MPA ester of *(S)*-2,3-dibromo-1-propanol (16-SS)**: ^{1}H NMR 3.444 (s, OMe, 3H); 3.555-3.601 (m, CH_2Br, 1H); 3.659 (dd, CH_2Br, 1H, J_1= 5.13 Hz, J_2= 2.31 Hz); 4.213-4.272 (m, CHBr, 1H); 4.481 (dd, CH_2O, 1H, J_1= 5.13 Hz, J_2= 4.02 Hz); 4.573 (dd, CH_2O, 1H, J_1= 5.38 Hz, J_2= 5.09 Hz); 4.831 (s, CHO MPA, 1H); 7.326-7.402 (m, meta-, para-H Ph, 3H); 7.442-7.481 (m, ortho-H Ph MPA, 2H). ^{13}C NMR 32.015 (CH_2Br); 46.433 (CHBr); 57.642 (OMe); 65.621 (CH_2O); 82.487 (CHO MPA); 127.376 (Ph); 128.838 (Ph); 129.081 (Ph); 135.960 (Ph); 170.092 (COO).

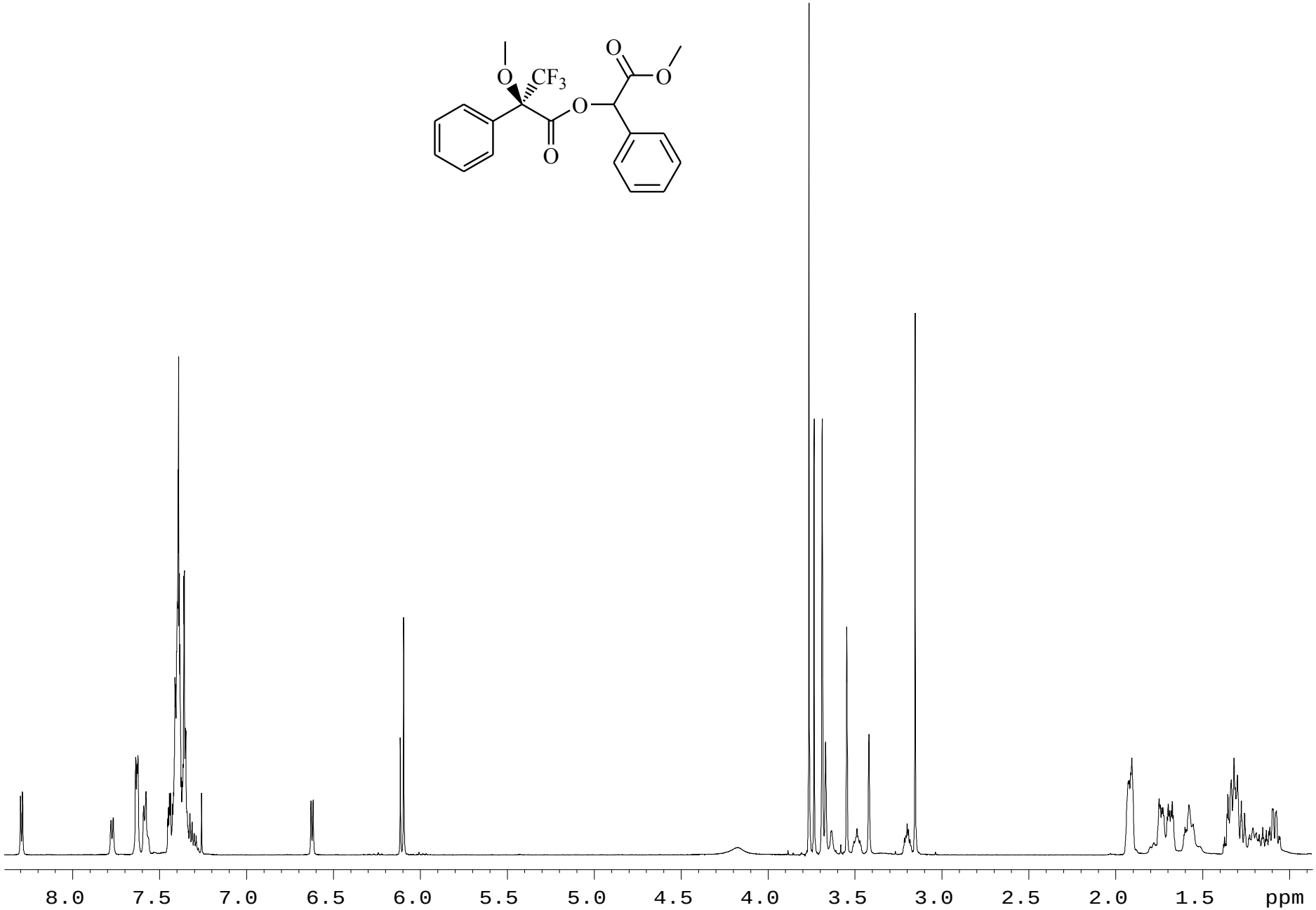
***(S)*-MPA ester of *(R)*-4-fluoro-α-methylbenzylamine (17-SR)**: ^{1}H NMR 1.464 (d, Me, 3H, J= 6.92 Hz); 3.326 (s, OMe, 3H); 4.587 (s, CHO MPA, 1H); 5.045-5.136 (m, CHN, 1H); 6.904-6.983 (m, NH, 1H); 7.006-7.056 (m, ArF, 2H); 7.277-7.436 (m, Ph, 7H). ^{13}C NMR 21.845 (Me); 47.800 (CHN); 57.307 (OMe); 83.868 (CHO); 115.590 (d, ArF, J_{C-F}= 21.39 Hz); 127.128 (Ph); 128.030 (d, ArF, J_{C-F}= 7.22 Hz); 128.592 (Ph); 128.815 (Ph); 137.132 (Ph); 139.113 (d, ArF, J_{C-F}= 3.63 Hz); 161.202 (ArF); 169.769 (CON). ^{19}F NMR -115.905.

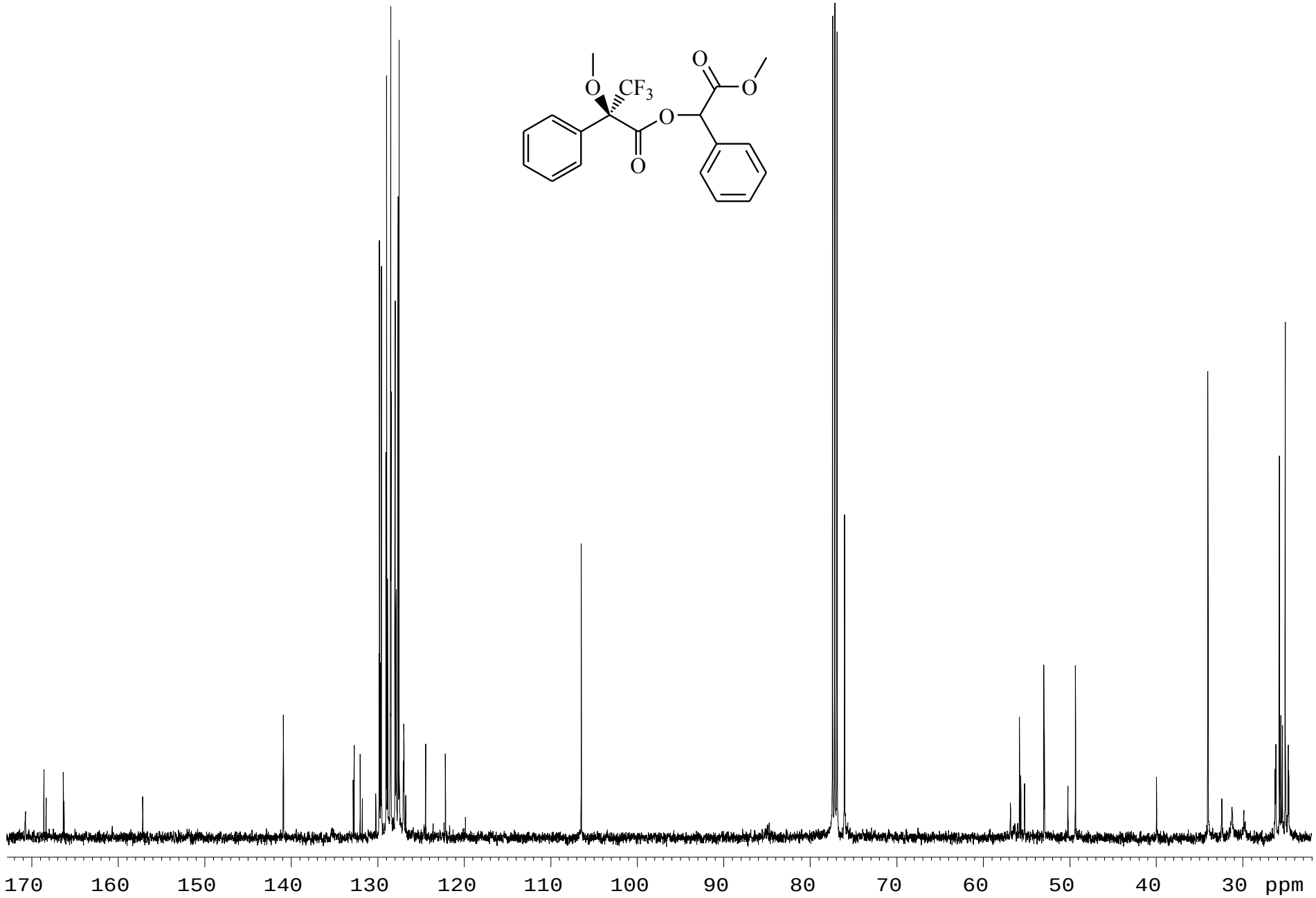
***(S)*-MPA ester of *(S)*-4-fluoro-α-methylbenzylamine (17-SS)**: ^{1}H NMR 1.530 (d, Me, 3H, J= 6.92 Hz); 3.362 (s, OMe, 3H); 4.627 (s, CHO MPA, 1H); 5.045-5.136 (m, CHN, 1H); 6.904-6.983 (m, ArF, NH, 3H); 7.166-7.213 (m, ArF, 2H); 7.277-7.436 (m, Ph, 5H). ^{13}C NMR 21.957 (Me); 47.574 (CHN); 57. 234 (OMe); 83.957 (CHO); 115.495 (d, ArF, J_{C-F}= 21.39 Hz); 127.128 (Ph); 127.775 (d, ArF, J_{C-F}= 7.22 Hz); 128.592 (Ph); 128.815 (Ph); 137.061 (Ph); 138.988 (d, ArF, J_{C-F}= 3.63 Hz); 161.117 (ArF); 169.727 (CON). ^{19}F NMR -116.122.

***(S)*-MPA ester of *(R)*-2-heptylamine (18-SR)**: ^{1}H NMR 0.827 (t, Me, 3H, J= 6.95 Hz); 1.099 (d, Me, 3H, J= 6.53 Hz); 1.124-1.264 (m, CH_2, 6H); 1.387-1.441 (m, CH_2, 2H); 3.356 (s, OMe, 3H); 3.916-4.008 (m, CHN, 1H); 4.576 (s, CHO MPA, 1H); 6.438-6.543 (br. m, NH, 1H); 7.282-7.399 (m, Ph, 5H). ^{13}C NMR 14.038 (Me); 21.212 (Me); 22.642 (CH_2); 25.095 (CH_2); 31.692 (CH_2); 37.077 (CH_2); 44.792 (CHN); 57.240 (OMe); 84.137 (CHO); 127.101 (Ph); 128.621 (Ph); 128.806 (Ph); 137.497 (Ph); 169.783 (CON).

***(S)*-MPA ester of *(S)*-2-heptylamine (18-SS)**: ^{1}H NMR 0.890 (t, Me, 3H, J= 6.95 Hz); 1.124-1.264 (m, CH_2, 6H); 1.176 (d, Me, 3H, J= 6.53 Hz); 1.449-1.517 (m, CH_2, 2H); 3.367 (s, OMe, 3H); 3.916-4.008 (m, CHN, 1H); 4.582 (s, CHO MPA, 1H); 6.438-6.543 (br. m, NH, 1H); 7.282-7.399 (m, meta-, para-H Ph, 3H); 7.406-7.438 (m, ortho-H Ph, 2H). ^{13}C NMR 14.122 (Me); 21.001 (Me); 22.677 (CH_2); 25.095 (CH_2); 31.792 (CH_2); 36.995 (CH_2); 44.968 (CHN); 57.364 (OMe); 84.041 (CHO); 127.101 (Ph); 128.621 (Ph); 128.806 (Ph); 137.470 (Ph); 169.811 (CON).

^{1}H, ^{13}C and ^{19}F NMR spectra of *(R)*-MTPA ester of *(R)*-methyl mandelate **(1-RR)** and *(S)*-methyl mandelate **(1-RS)** (ratio 70:30).

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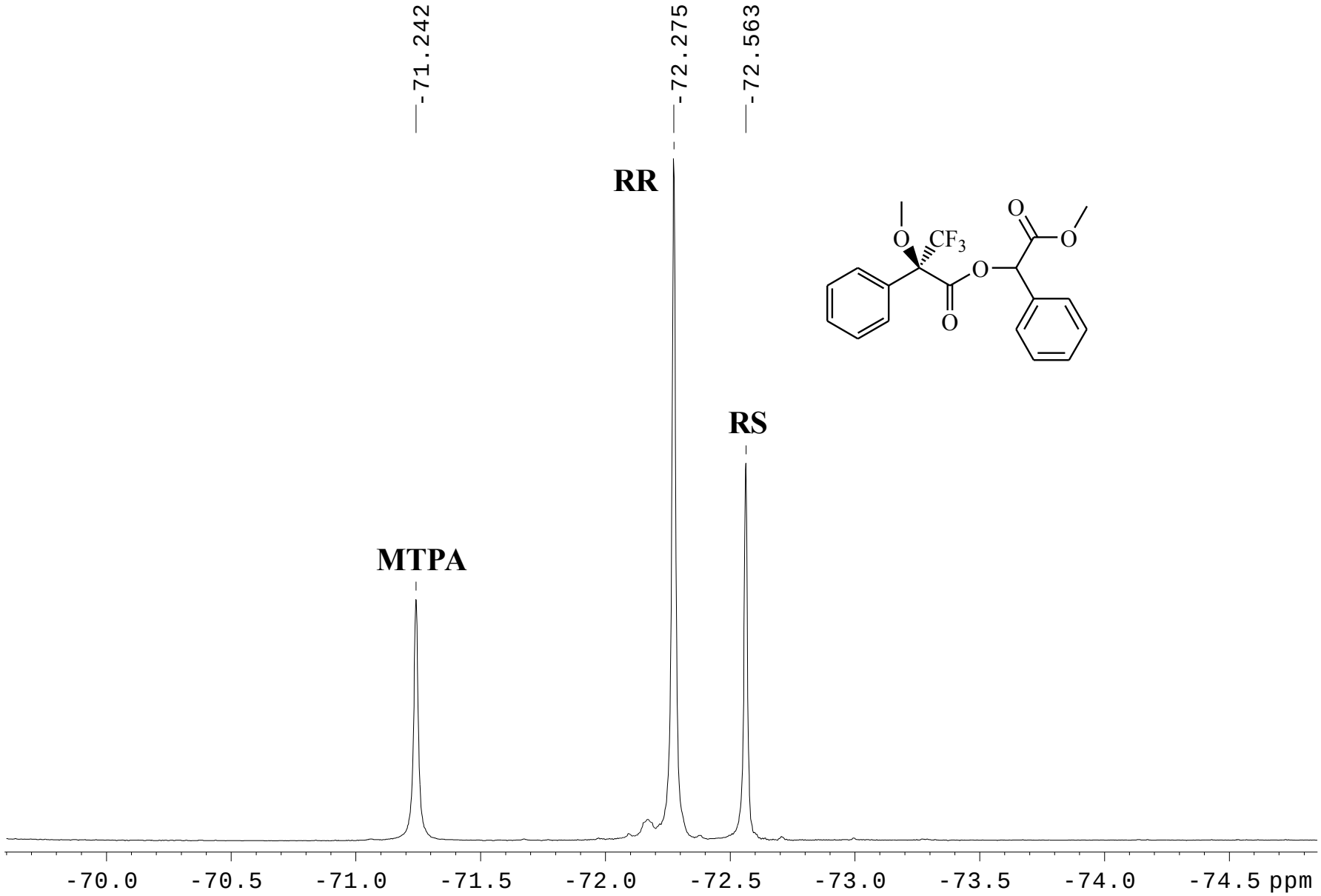
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RR
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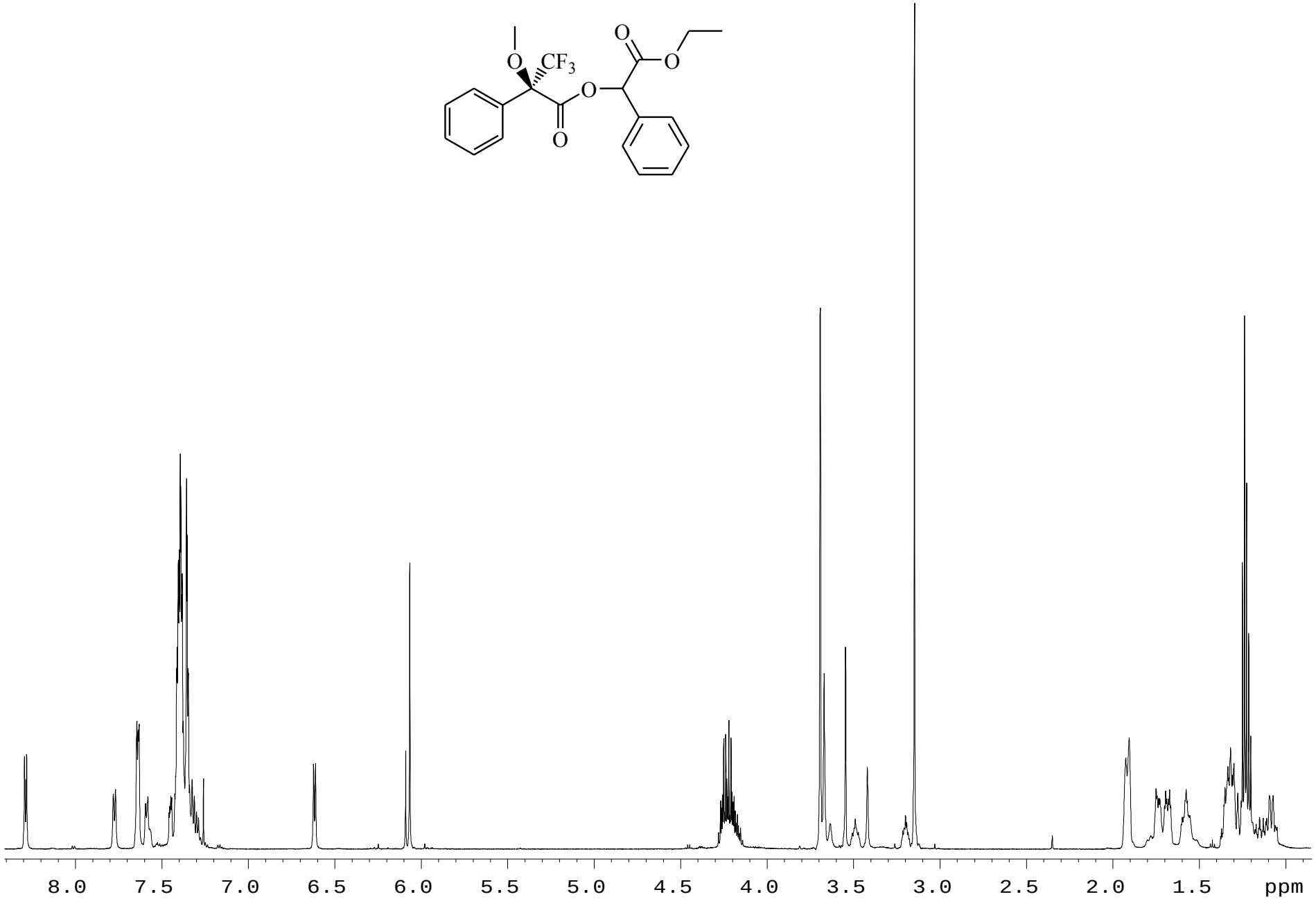
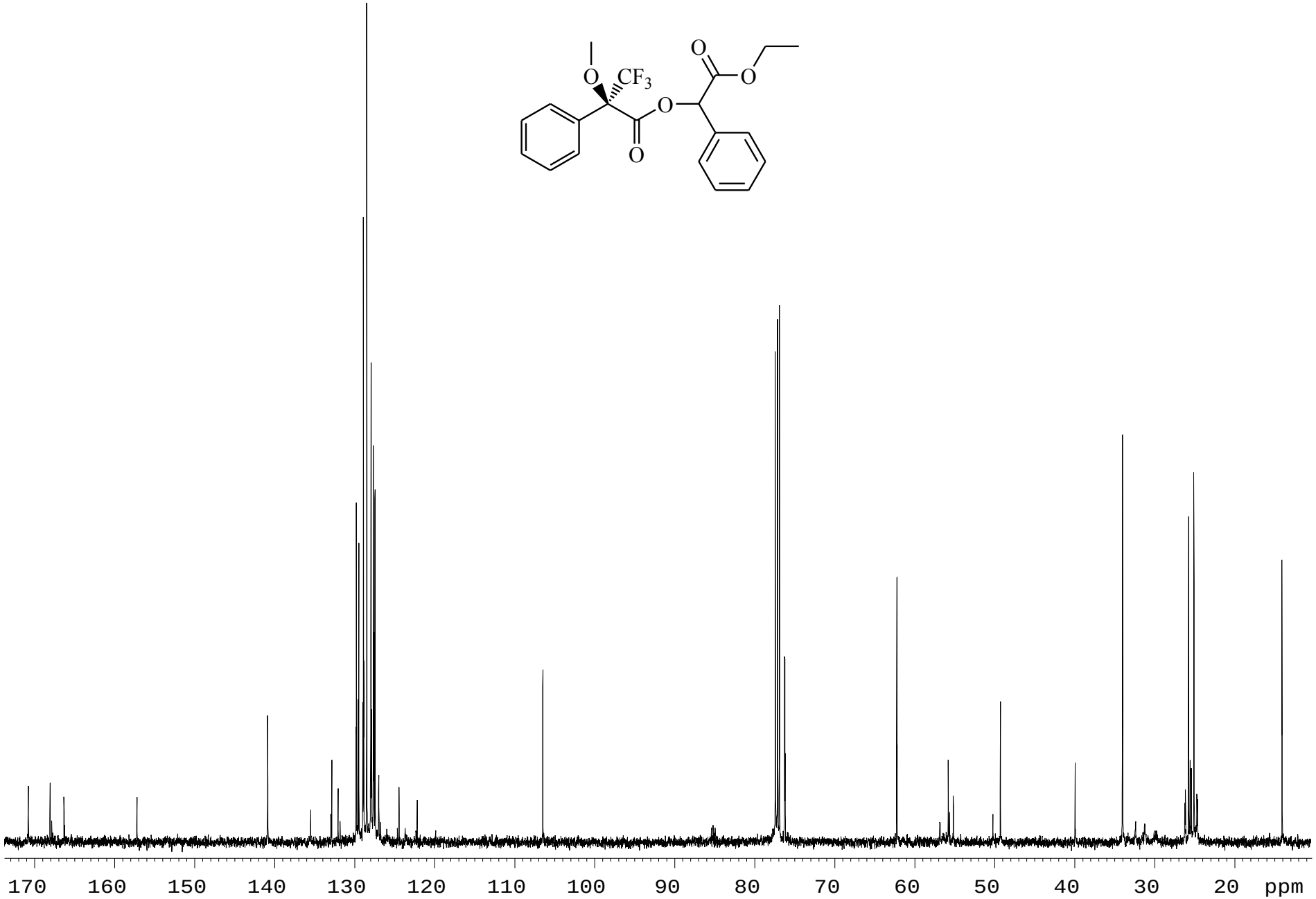
-71.5
-72.0
-72.5
-73.0
-73.5
-74.0
-74.5 ppm

^{1}H, ^{13}C and ^{19}F NMR spectra of *(R)*-MTPA ester of *(R)*-ethyl mandelate **(2-RR)** and *(S)*-ethyl mandelate **(2-RS)** (ratio 75:25).

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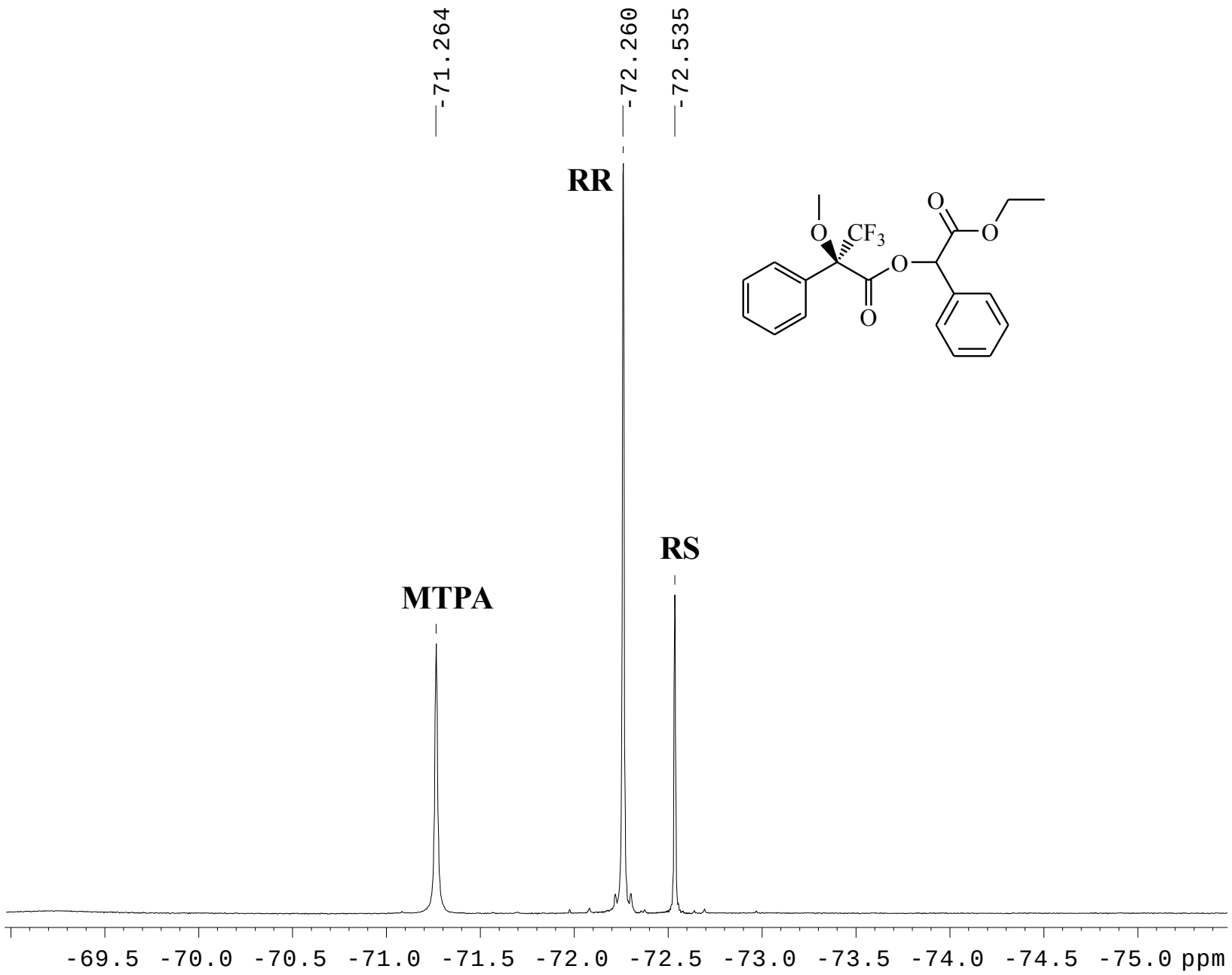
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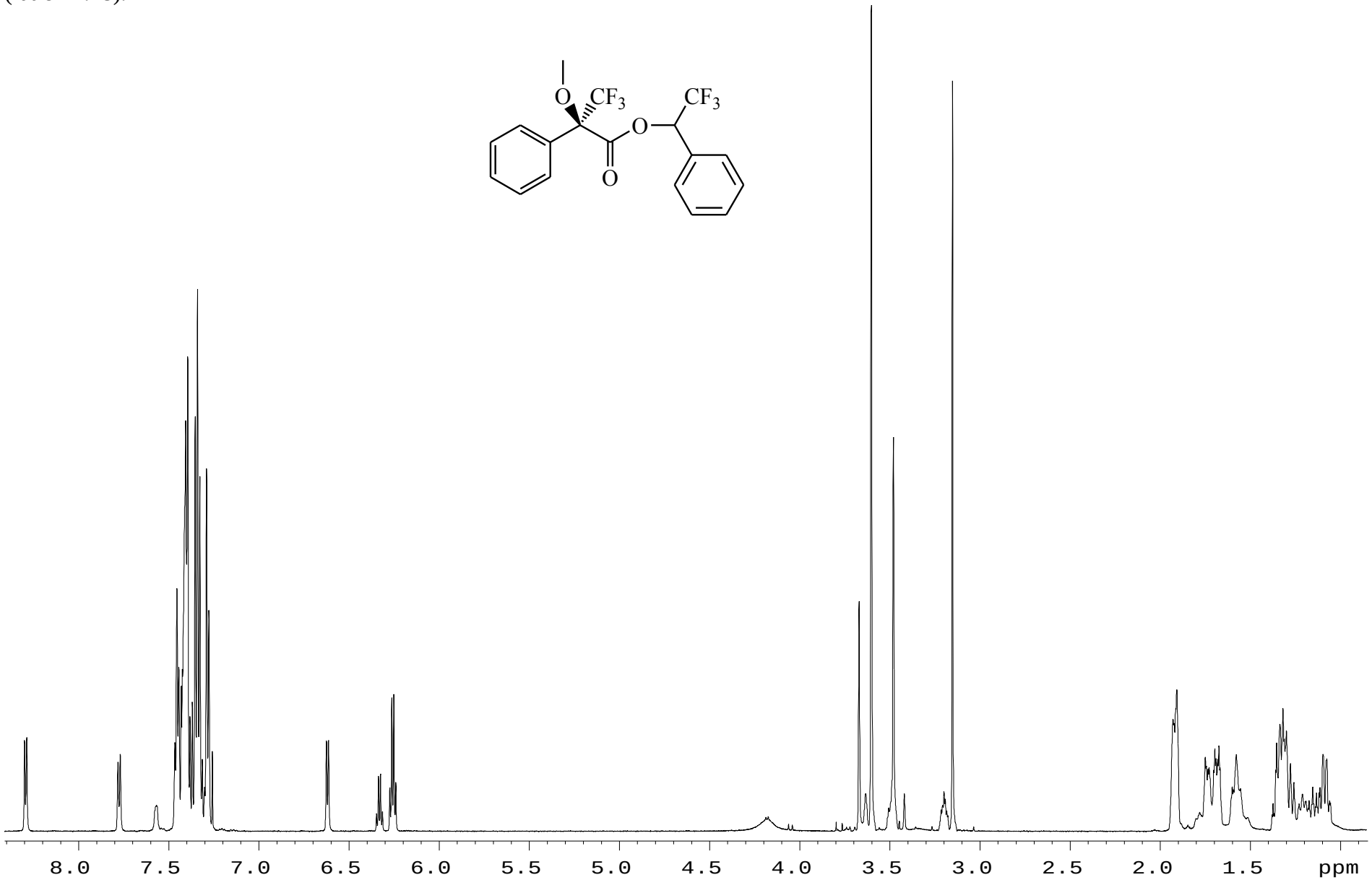
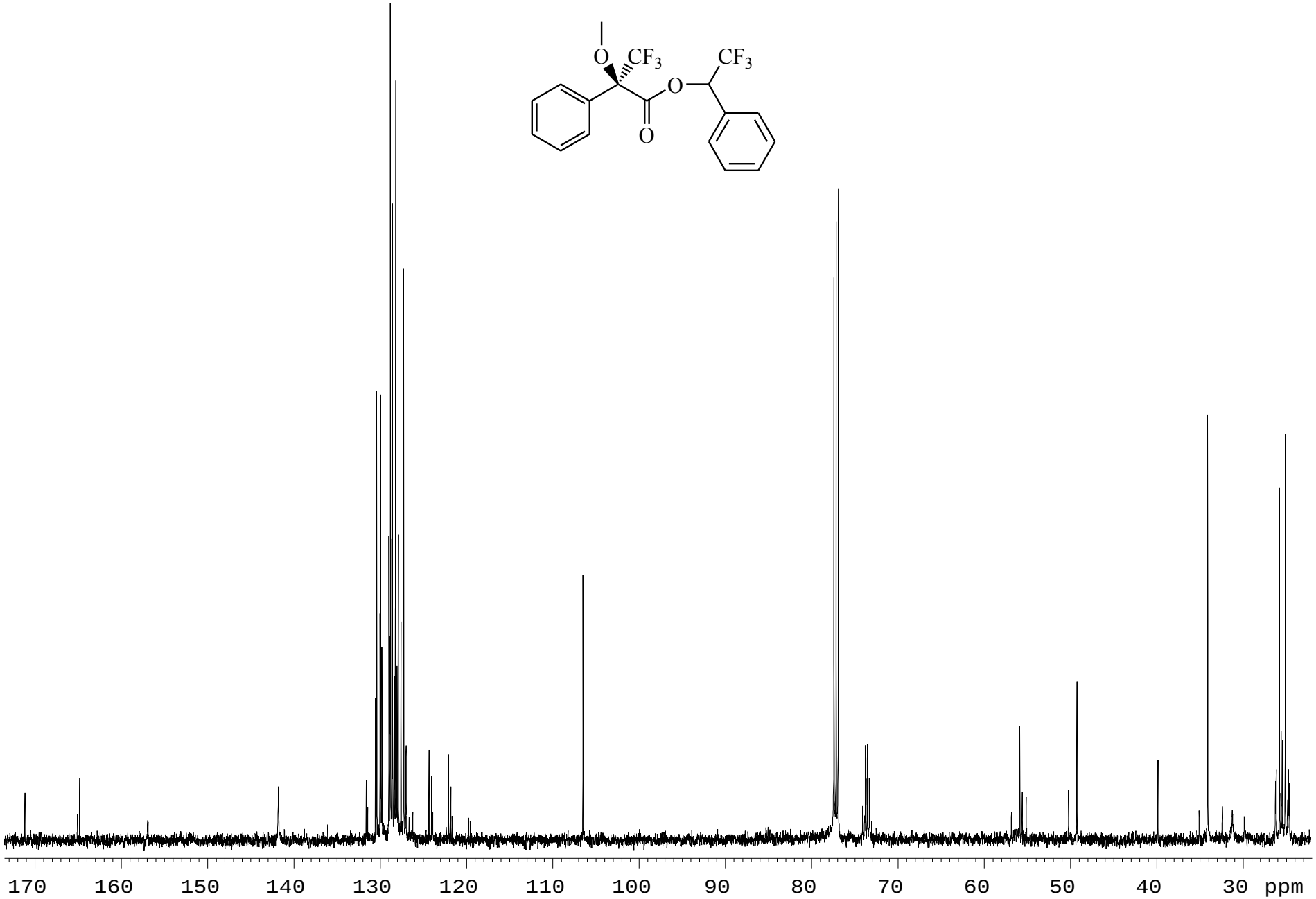
^{1}H, ^{13}C and ^{19}F NMR spectra of *(R)*-MTPA ester of *(R)*-α-(trifluoromethyl)benzyl alcohol **(3-RR)** and *(S)*-α-(trifluoromethyl)benzyl alcohol **(3-RS)** (ratio 72:28).

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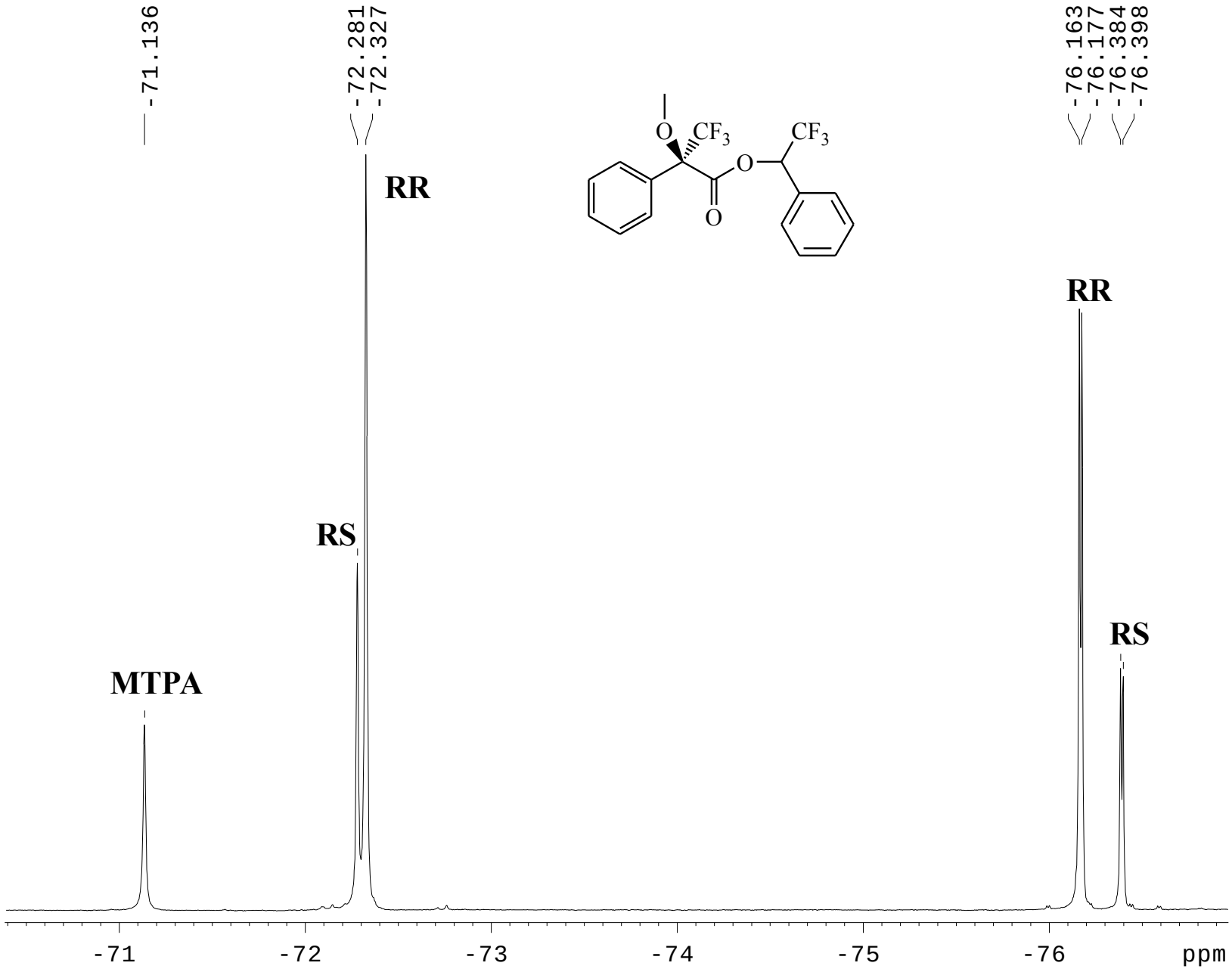
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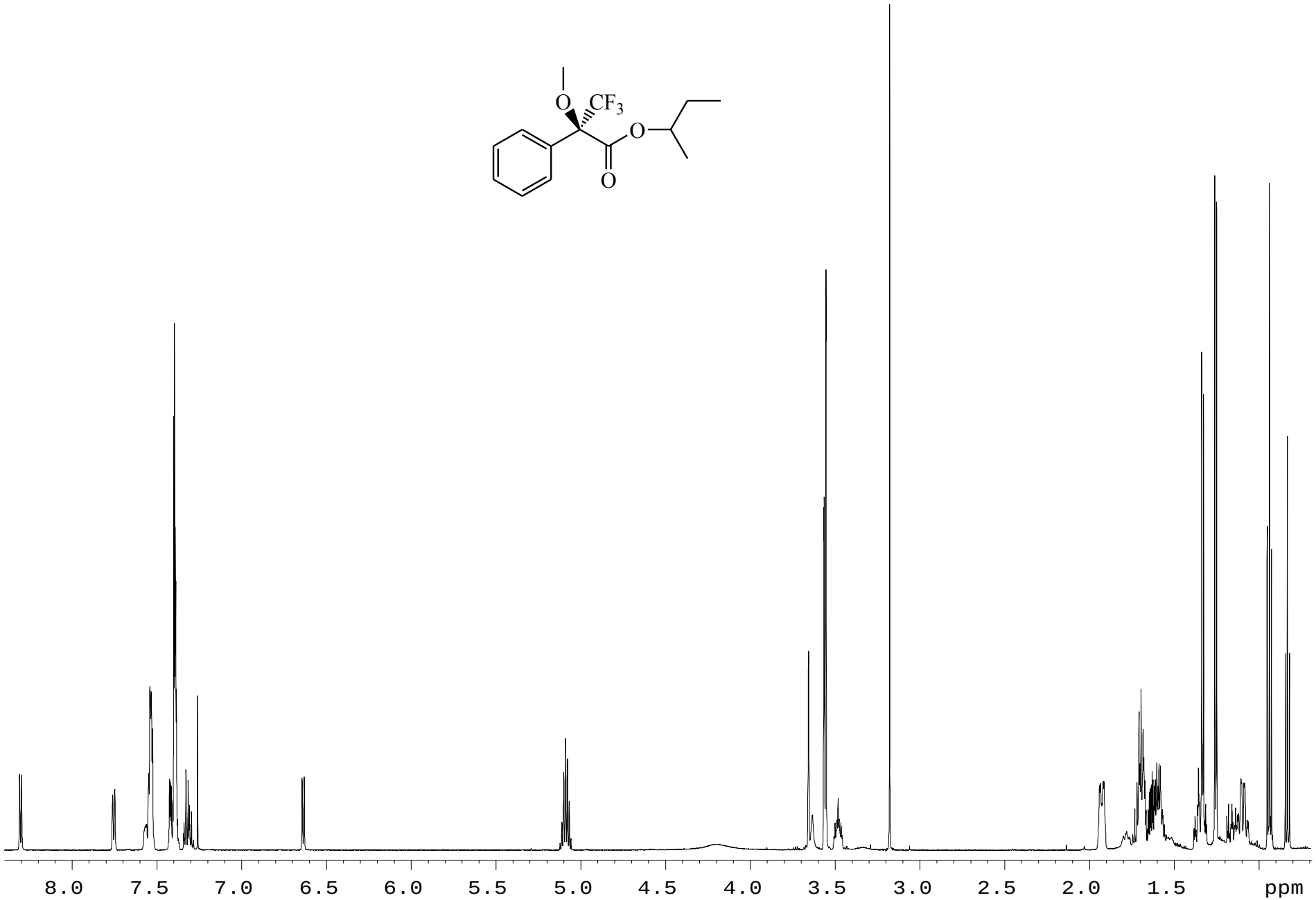
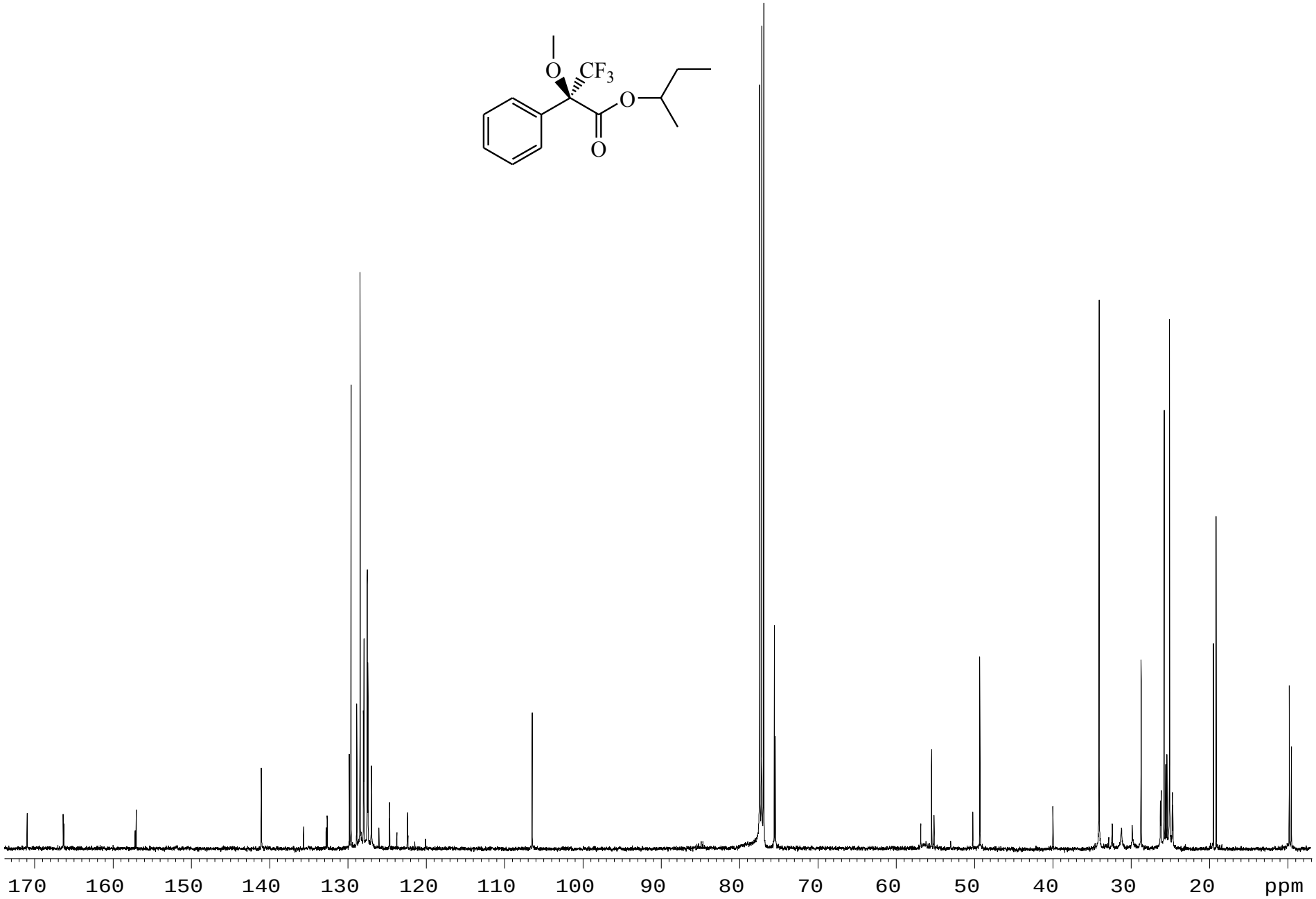
^{1}H, ^{13}C and ^{19}F NMR spectra of *(R)*-MTPA ester of *(R)*-butan-2-ol **(4-RR)** and *(S)*-butan-2-ol **(4-RS)** (ratio 61:39).

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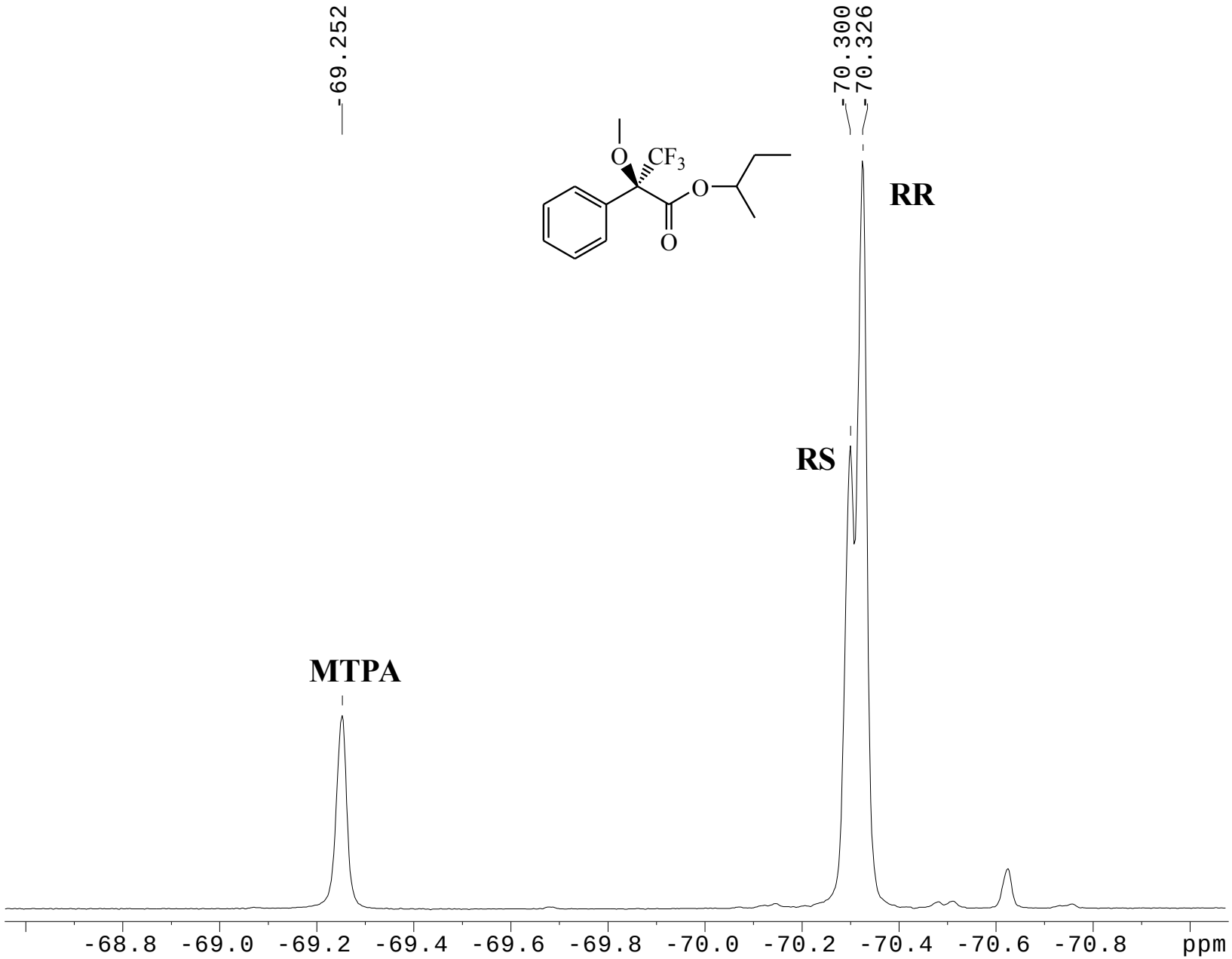
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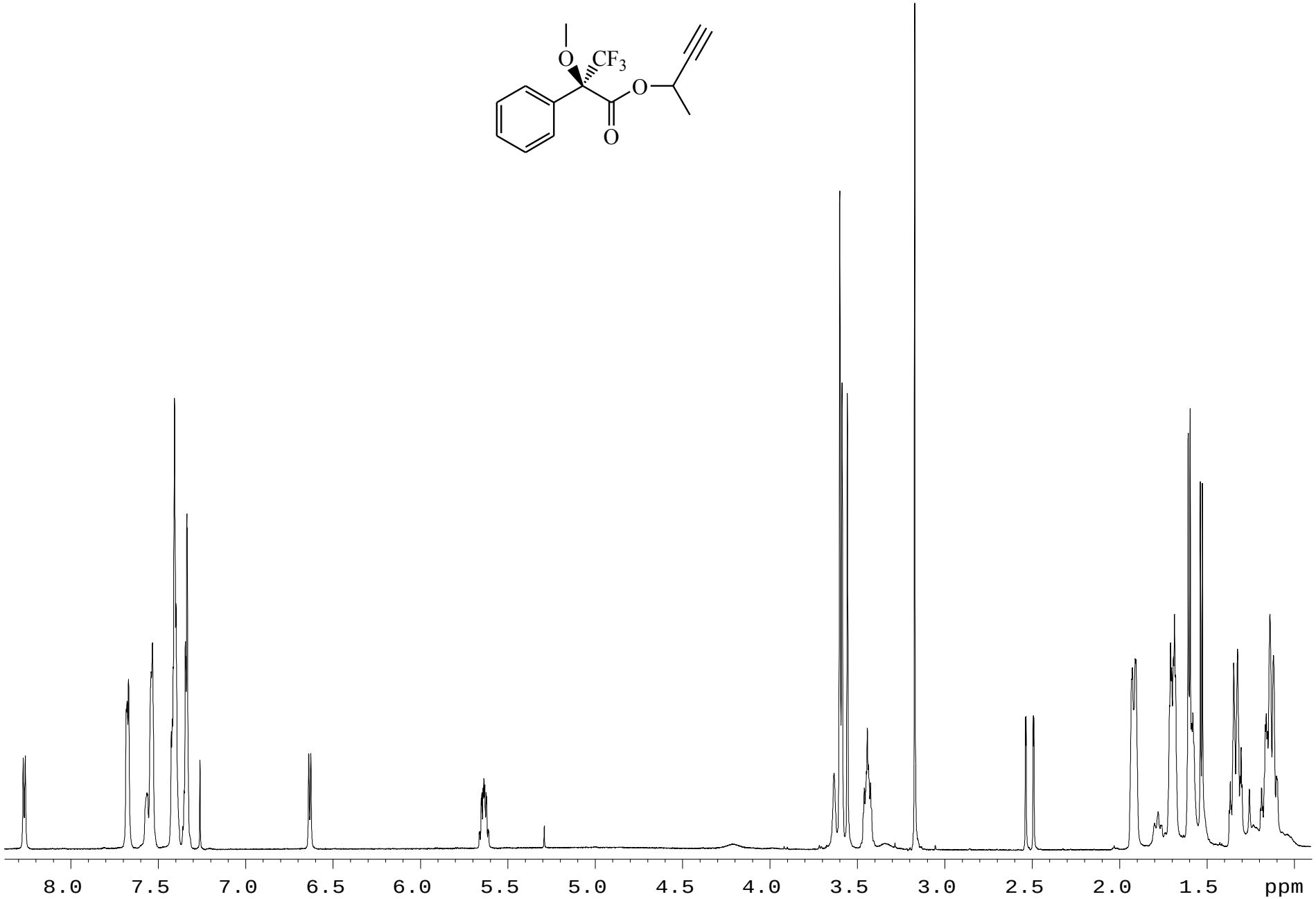
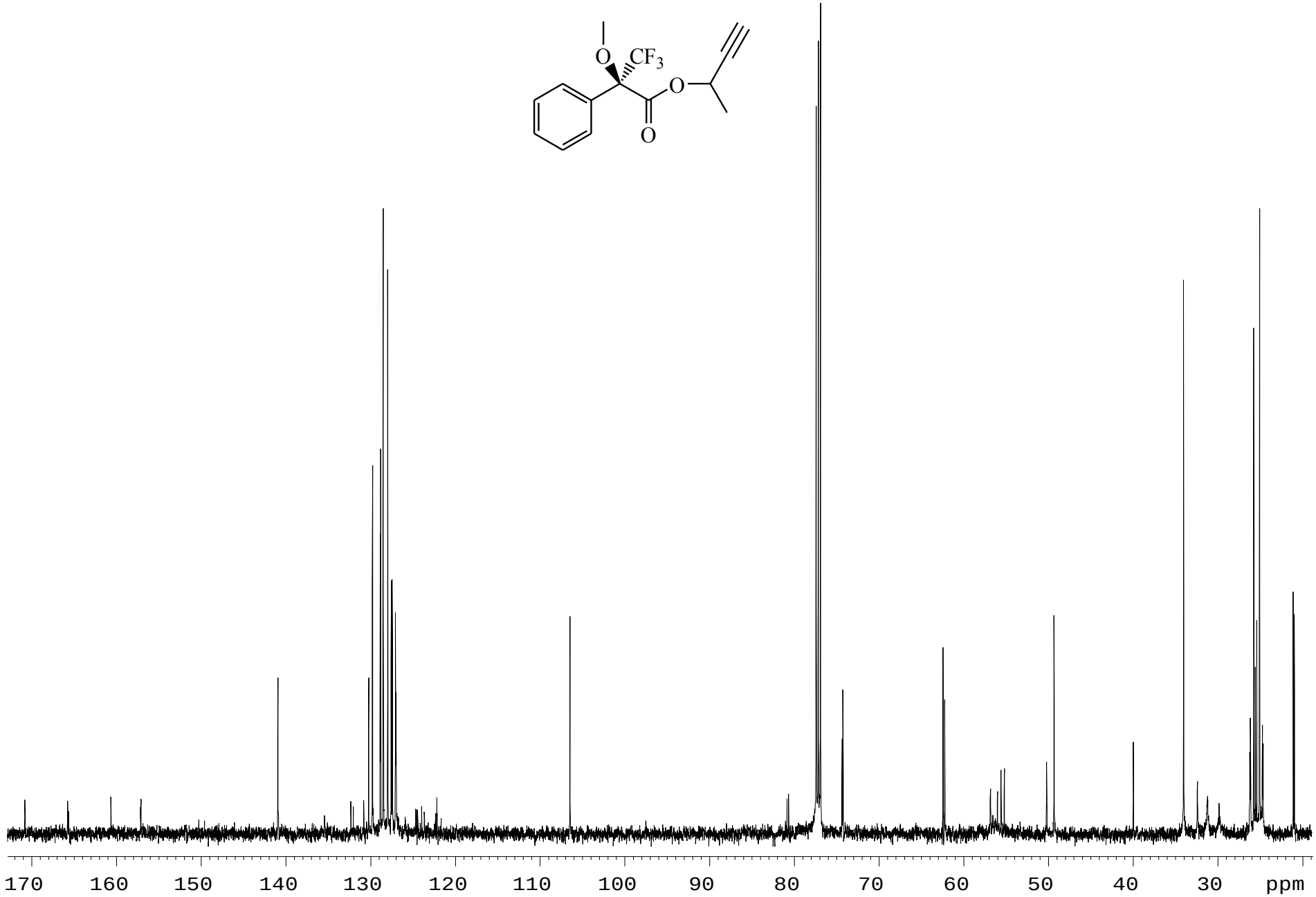
ppm

^{1}H, ^{13}C and ^{19}F NMR spectra of *(R)*-MTPA ester of *(R)*-butyn-2-ol **(5-RR)** and *(S)*-butyn-2-ol **(5-RS)** (ratio 50:50).

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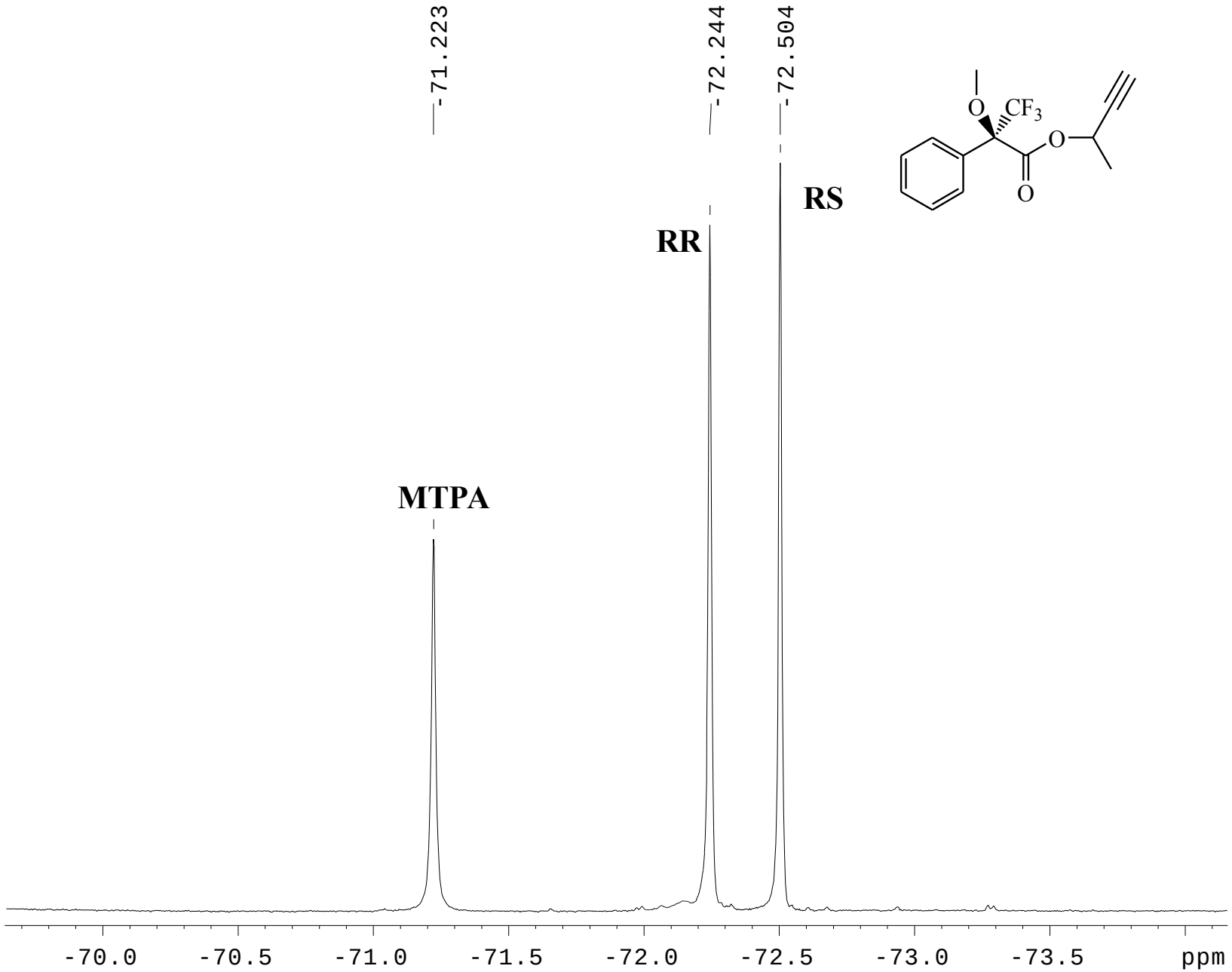
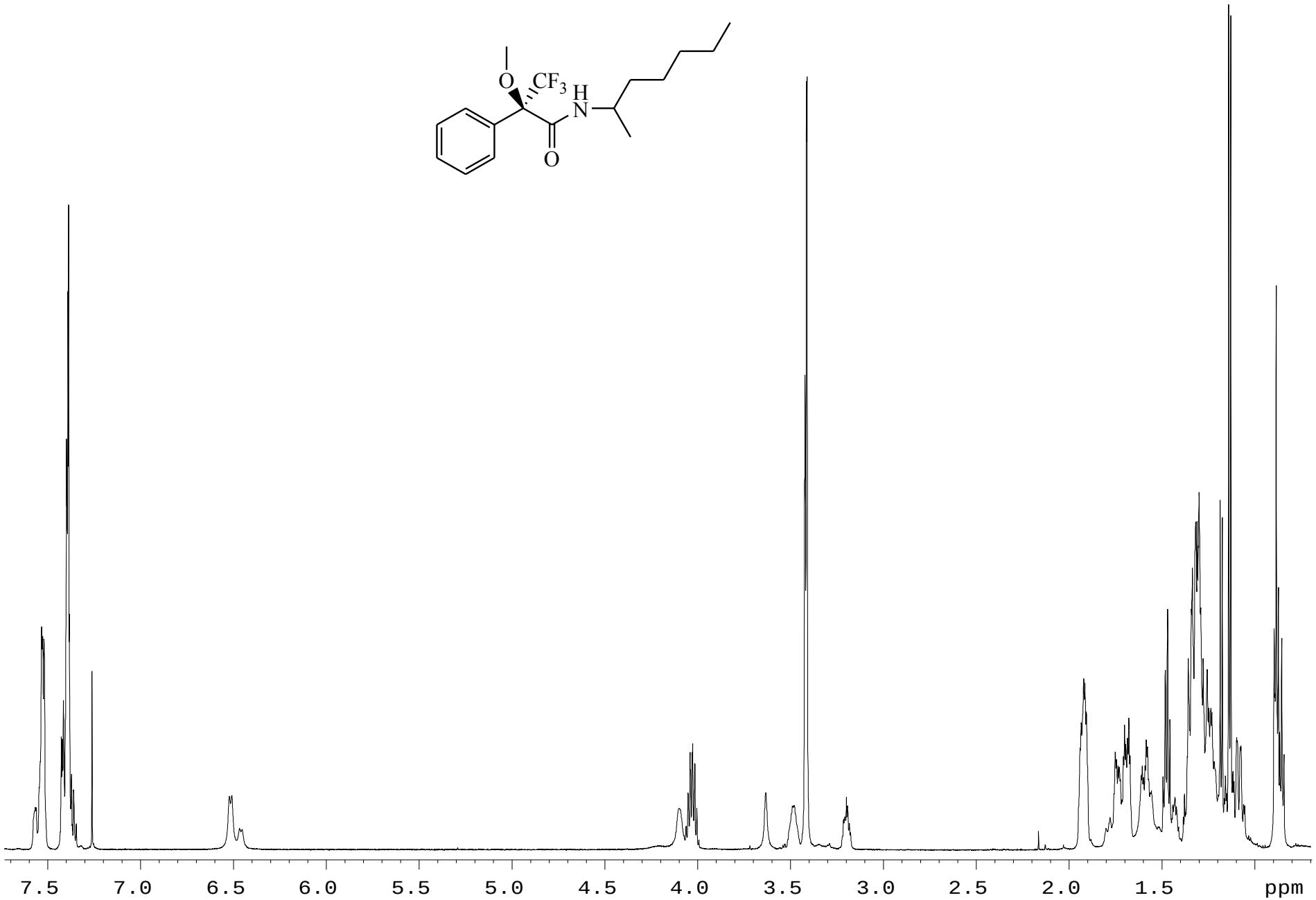
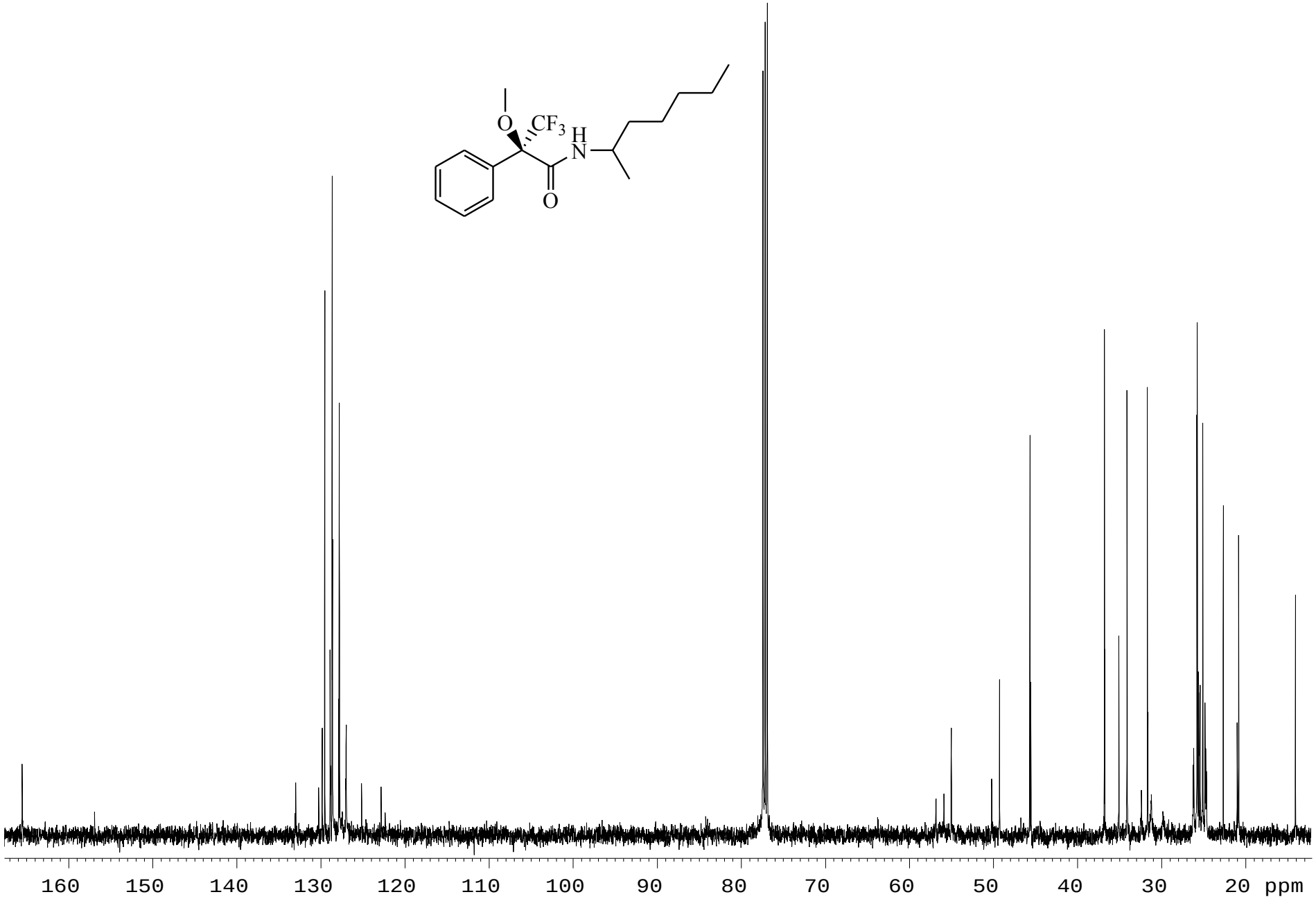
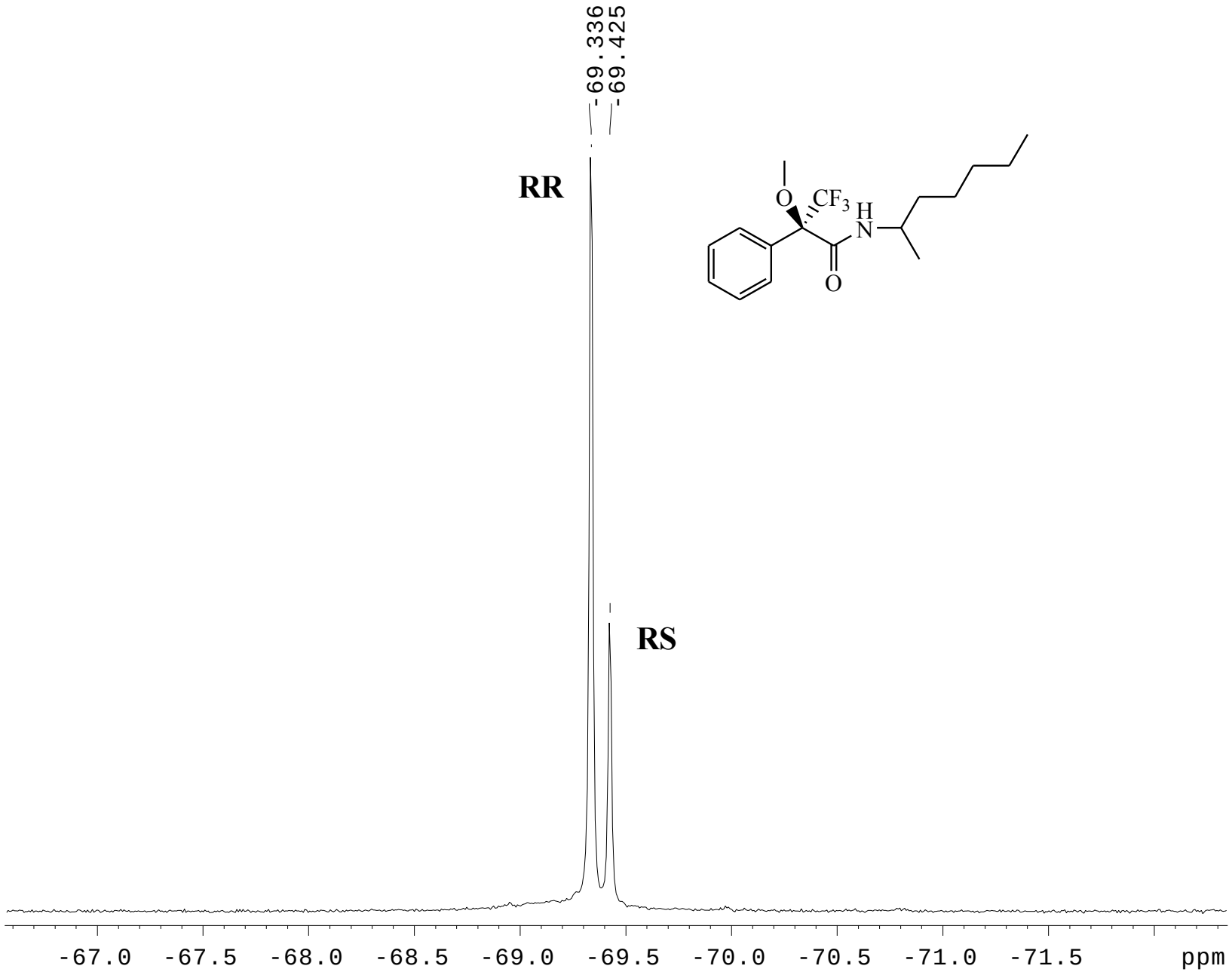
30
ppm


-71.223
-72.244
-72.504
MTPA
RR
RS
O
CF3
O
O
-70.0
-70.5
-71.0
-71.5
-72.0
-72.5
-73.0
-73.5
ppm

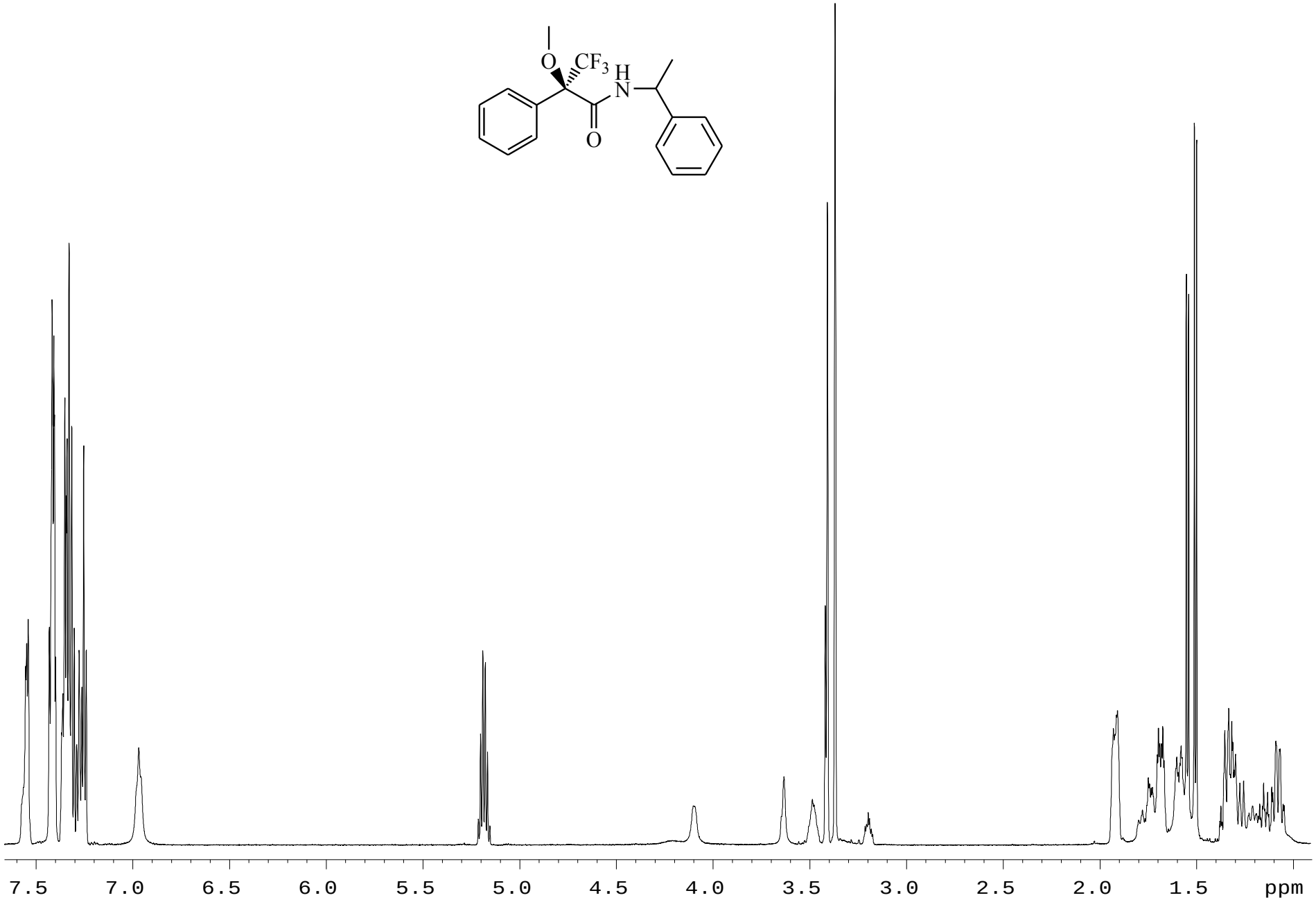
^{1}H, ^{13}C and ^{19}F NMR spectra of *(R)*-MTPA ester of *(R)*-2-heptylamine **(6-RR)** and *(S)*-2-heptylamine **(6-RS)** (ratio 73:27).

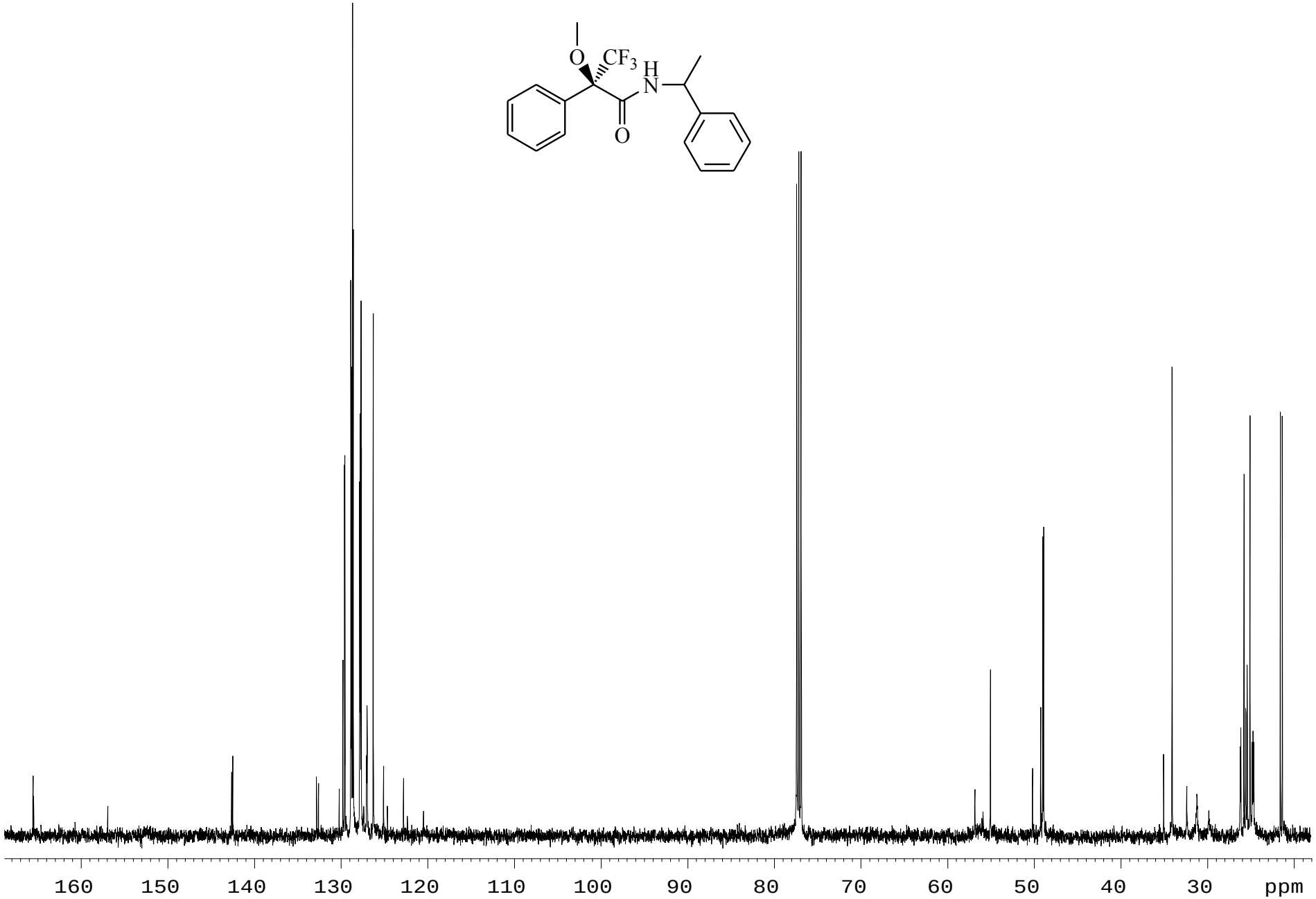


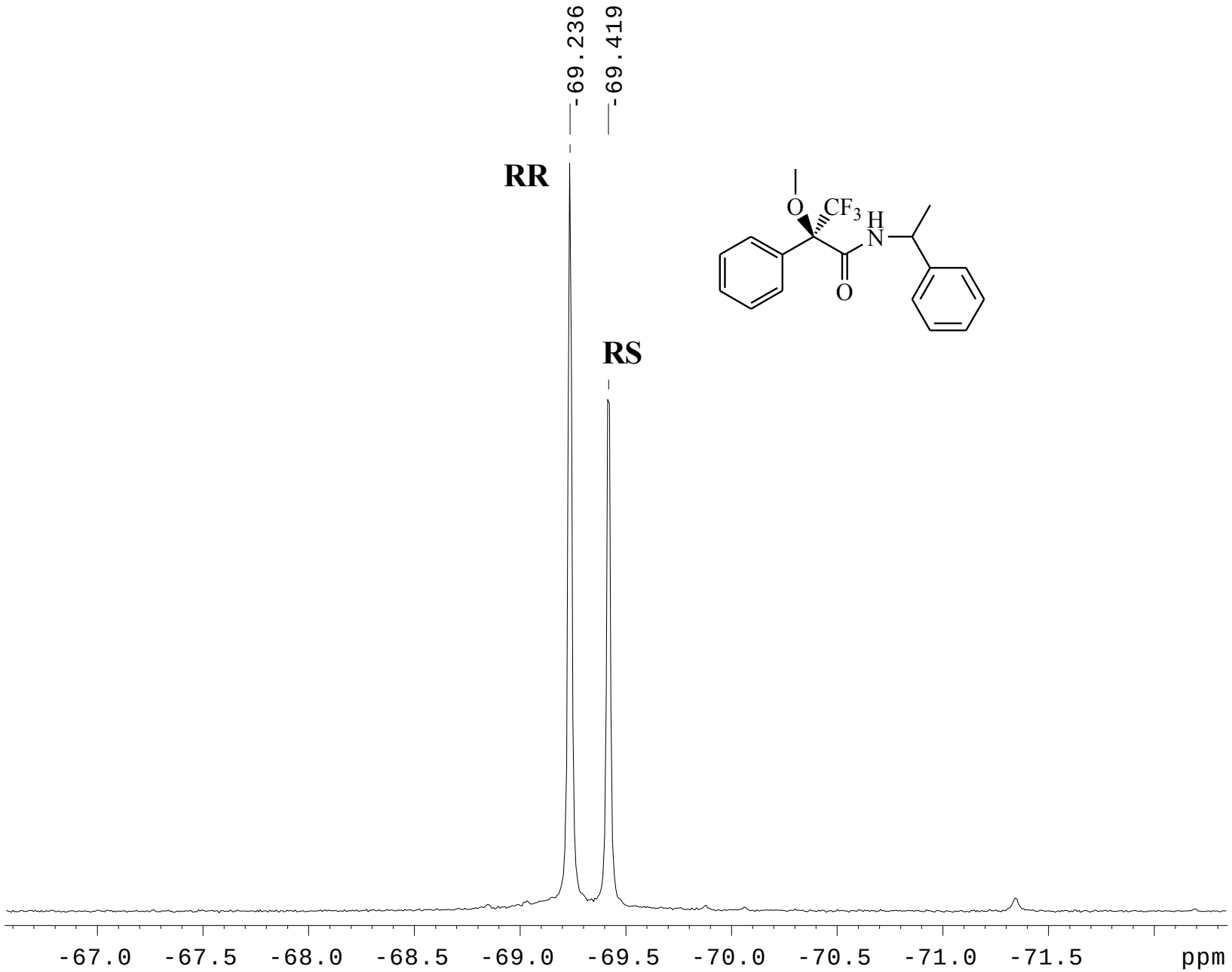

O
CF3
H
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


-69.336
-69.425
RR
RS
O
CF3
H
N
O
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
-70.5
-71.0
-71.5
ppm

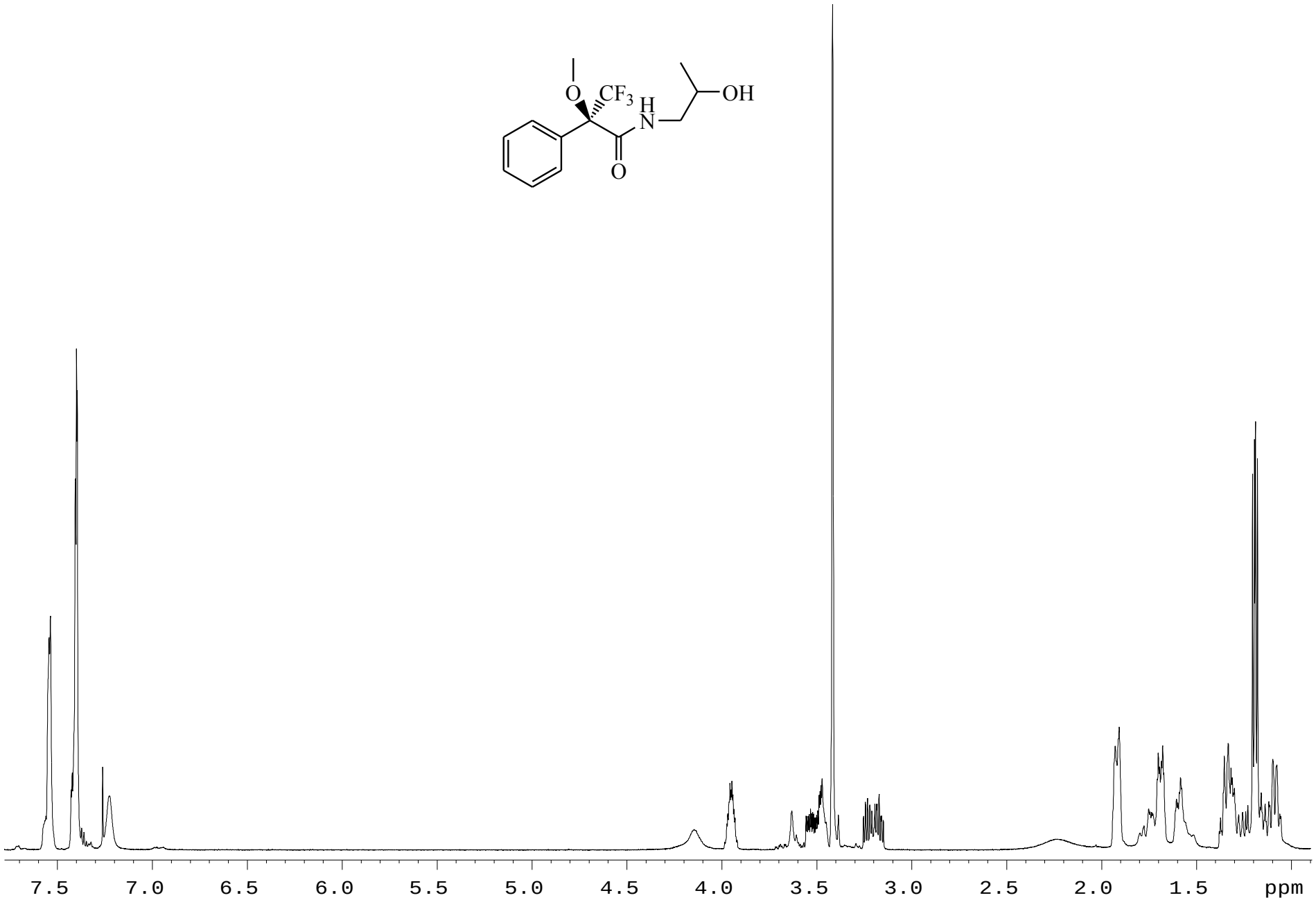
^{1}H, ^{13}C and ^{19}F NMR spectra of *(R)*-MTPA ester of *(R)*-α-methylbenzylamine **(7-RR)** and *(S)*-α-methylbenzylamine **(7-RS)** (ratio 57:43).

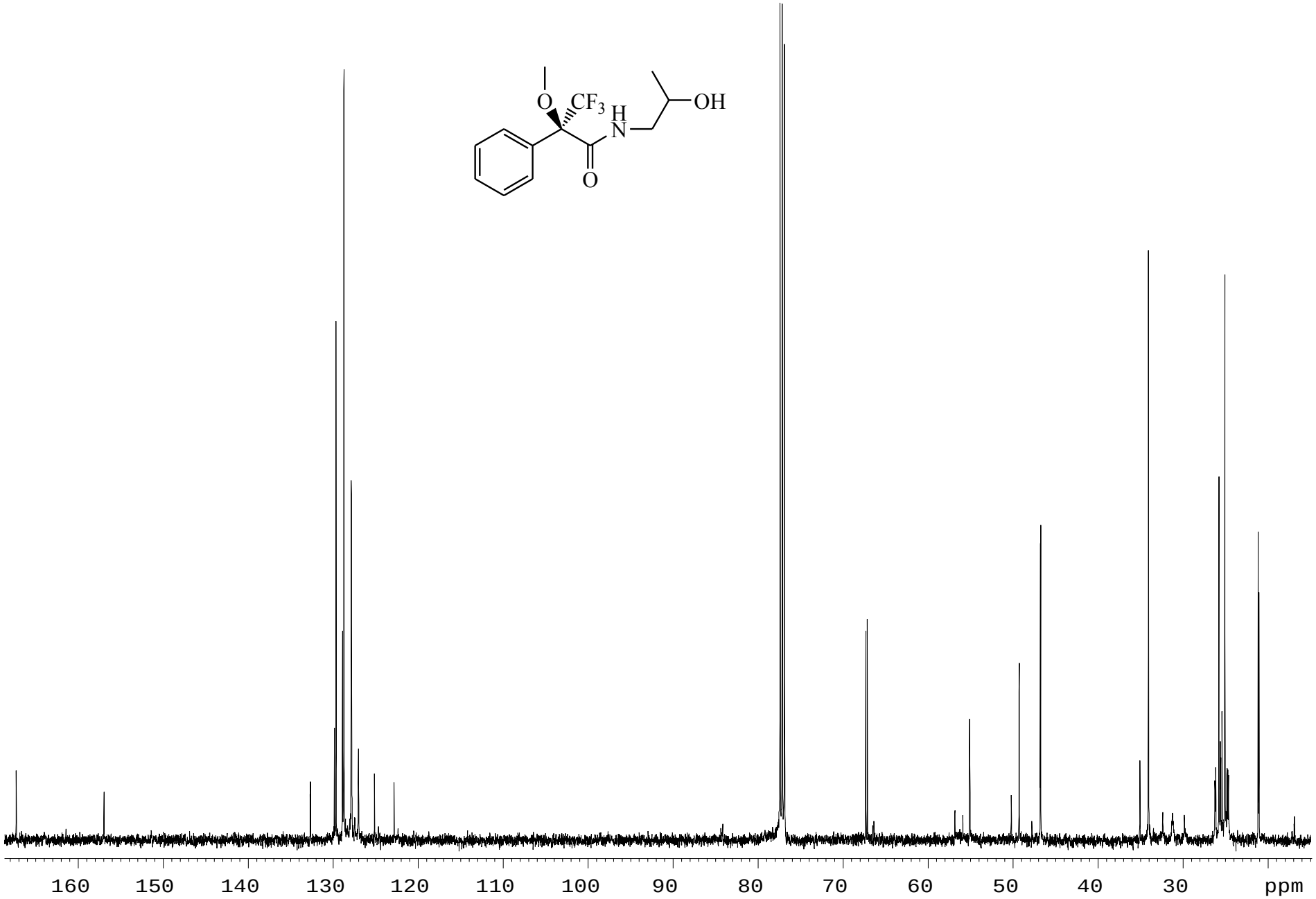


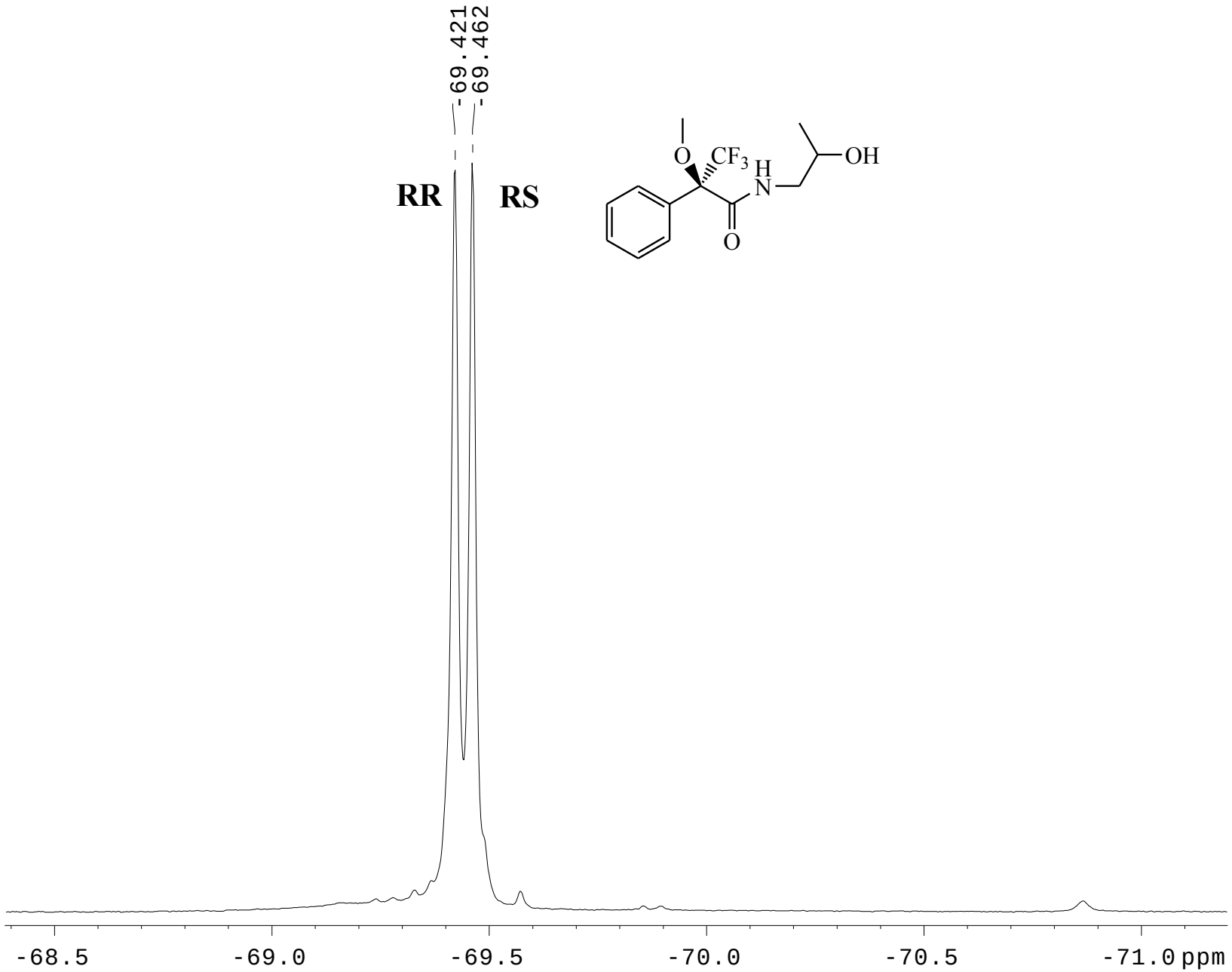

O
CF3
H
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


-69.236
-69.419
RR
RS
O
CF3
H
N
O
-67.0
-67.5
-68.0
-68.5
-69.0
-69.5
-70.0
-70.5
-71.0
-71.5
ppm

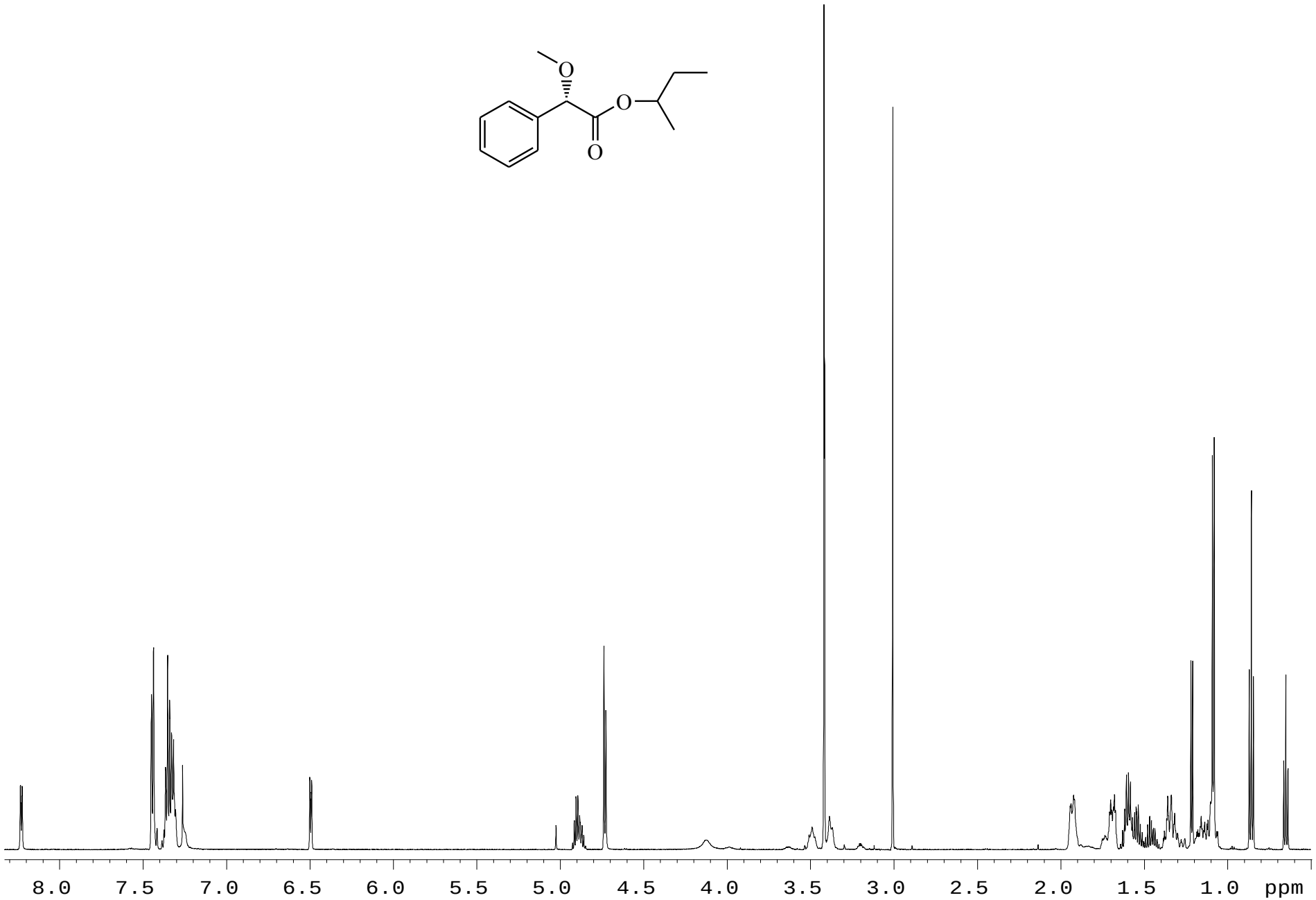
^{1}H, ^{13}C and ^{19}F NMR spectra of *(R)*-MTPA ester of *(R)*-1-amino-2-propanol **(8-RR)** and *(S)*-1-amino-2-propanol **(8-RS)** (ratio 50:50).

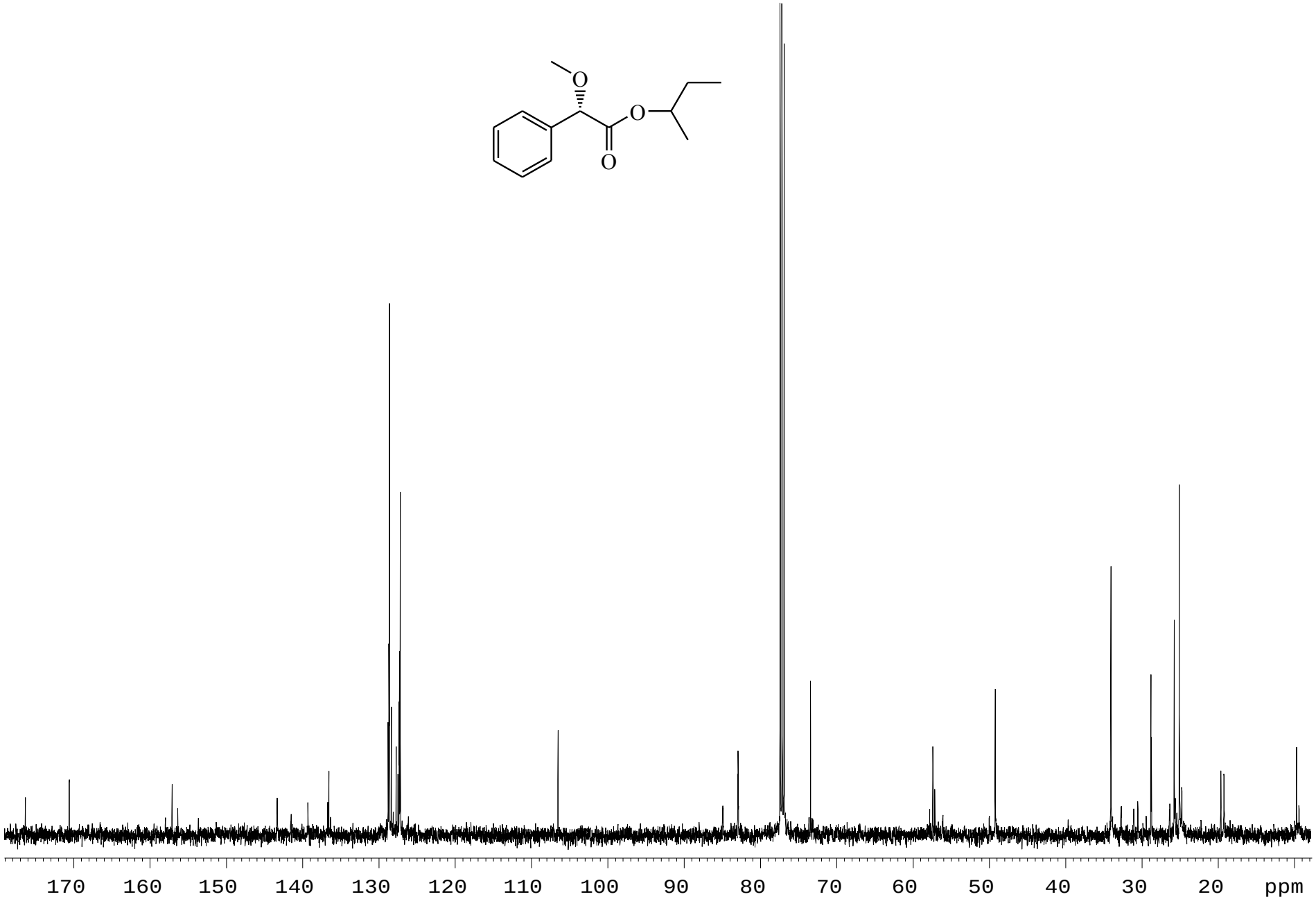



O
CF3
H
N
OH
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

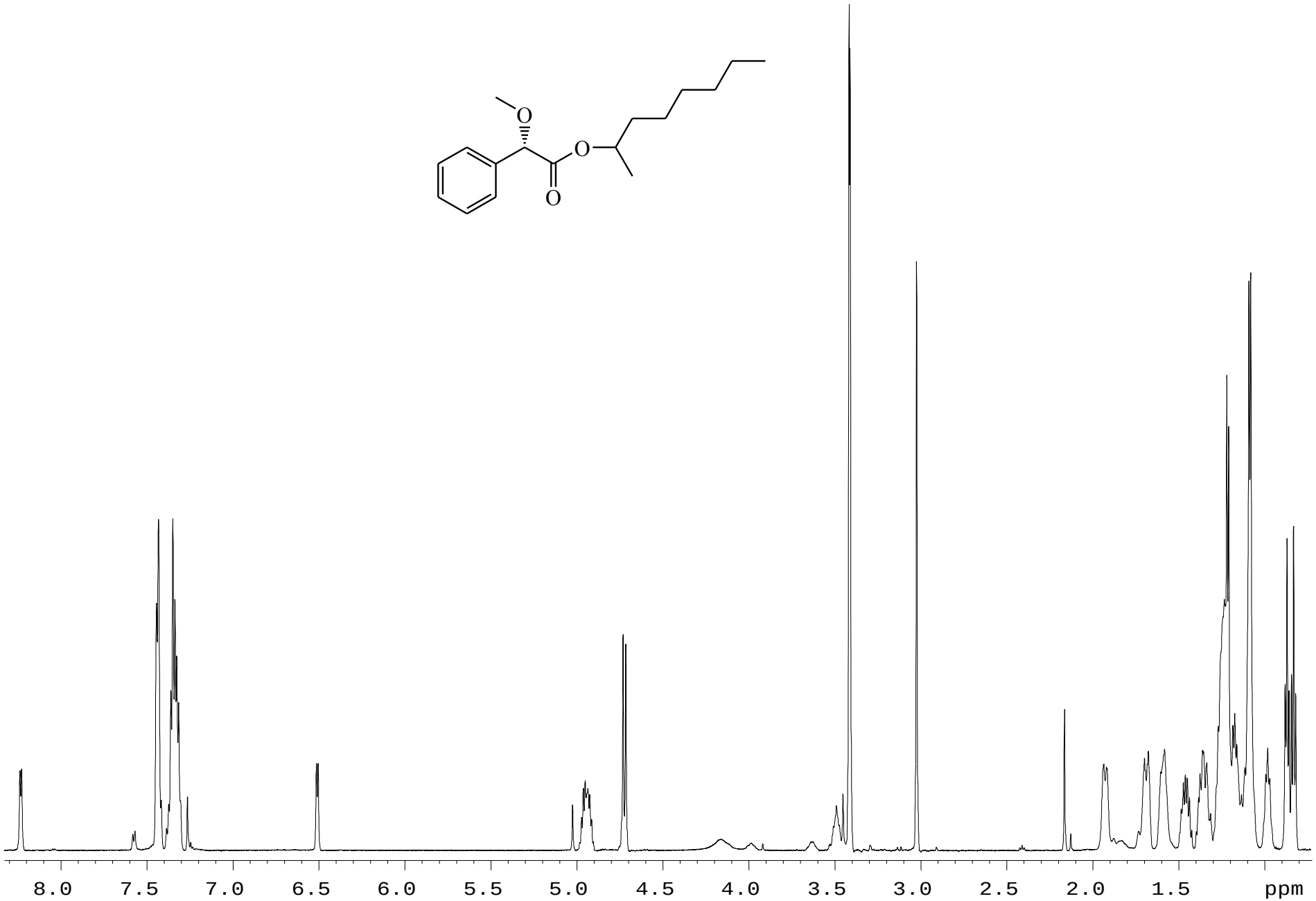

-69.421
-69.462
RR
RS
O
CF3
H
N
OH
O
-68.5
-69.0
-69.5
-70.0
-70.5
-71.0 ppm

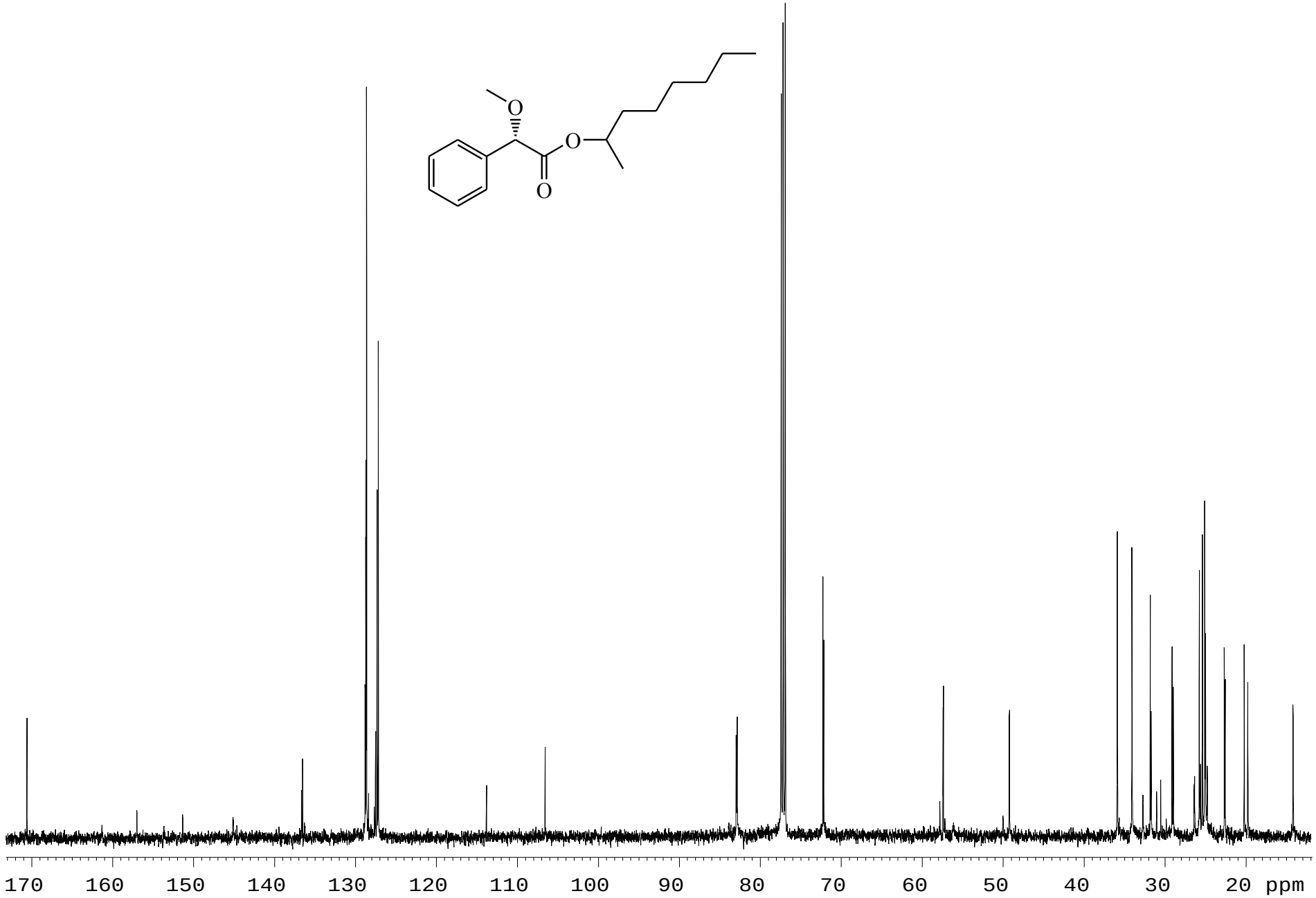
^{1}H and ^{13}C NMR spectra of *(S)*-MPA ester of *(R)*-butan-2-ol **(9-SR)** and *(S)*-butan-2-ol **(9-SS)** (ratio 70:30).



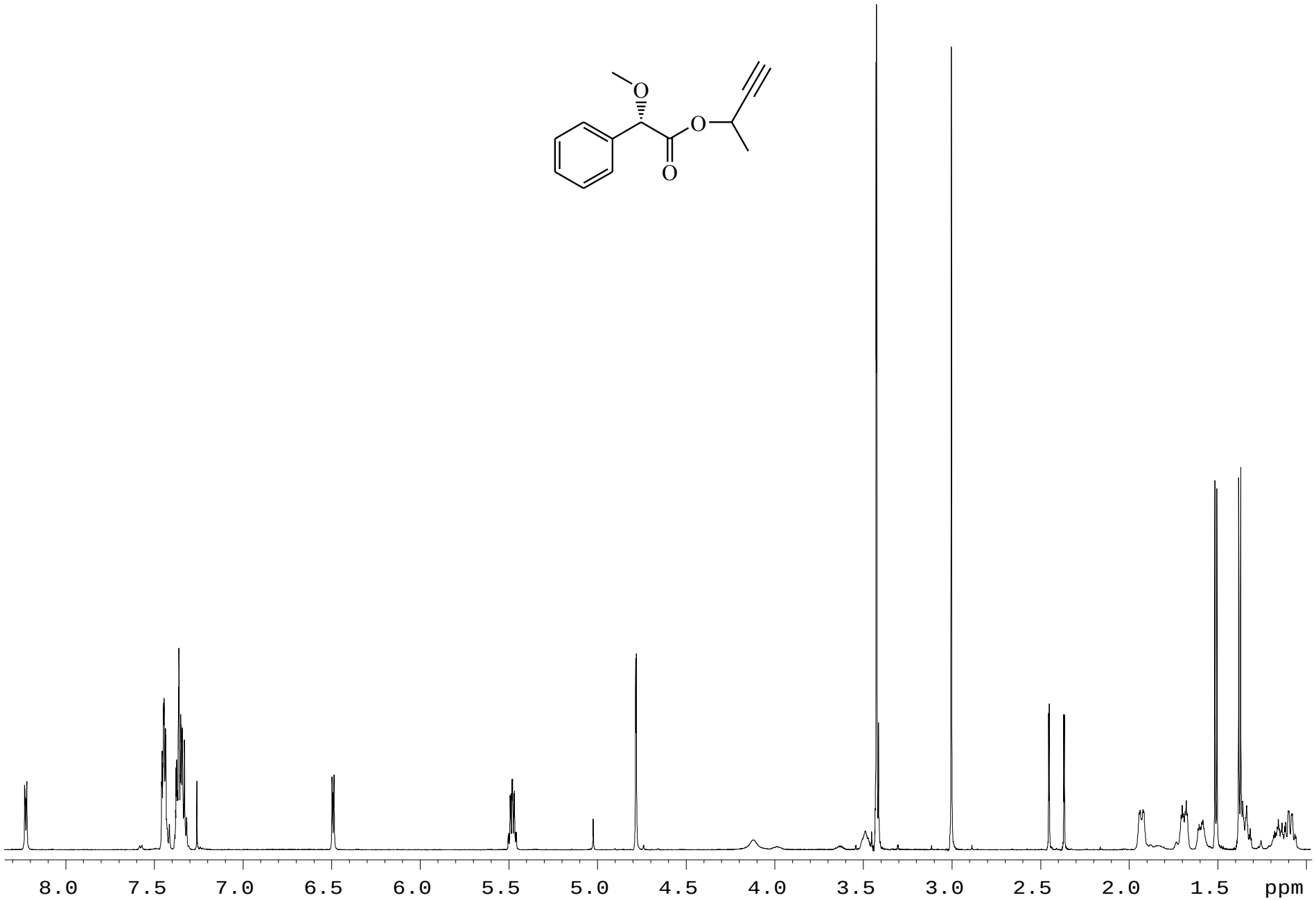

O
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

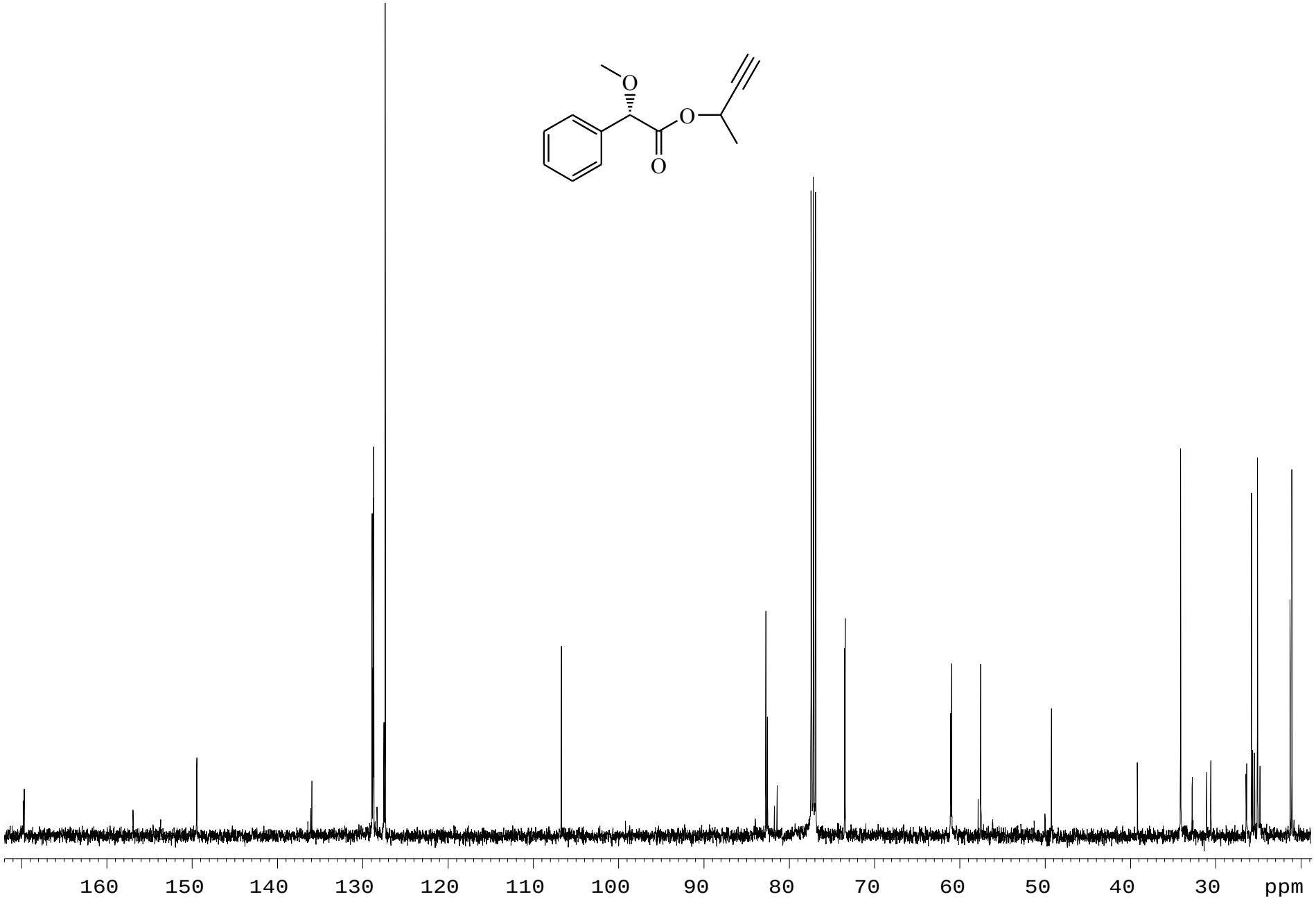
^{1}H and ^{13}C NMR spectra of *(S)*-MPA ester of *(R)*-octan-2-ol **(10-SR)** and *(S)*-octan-2-ol **(10-SS)** (ratio 50:50).



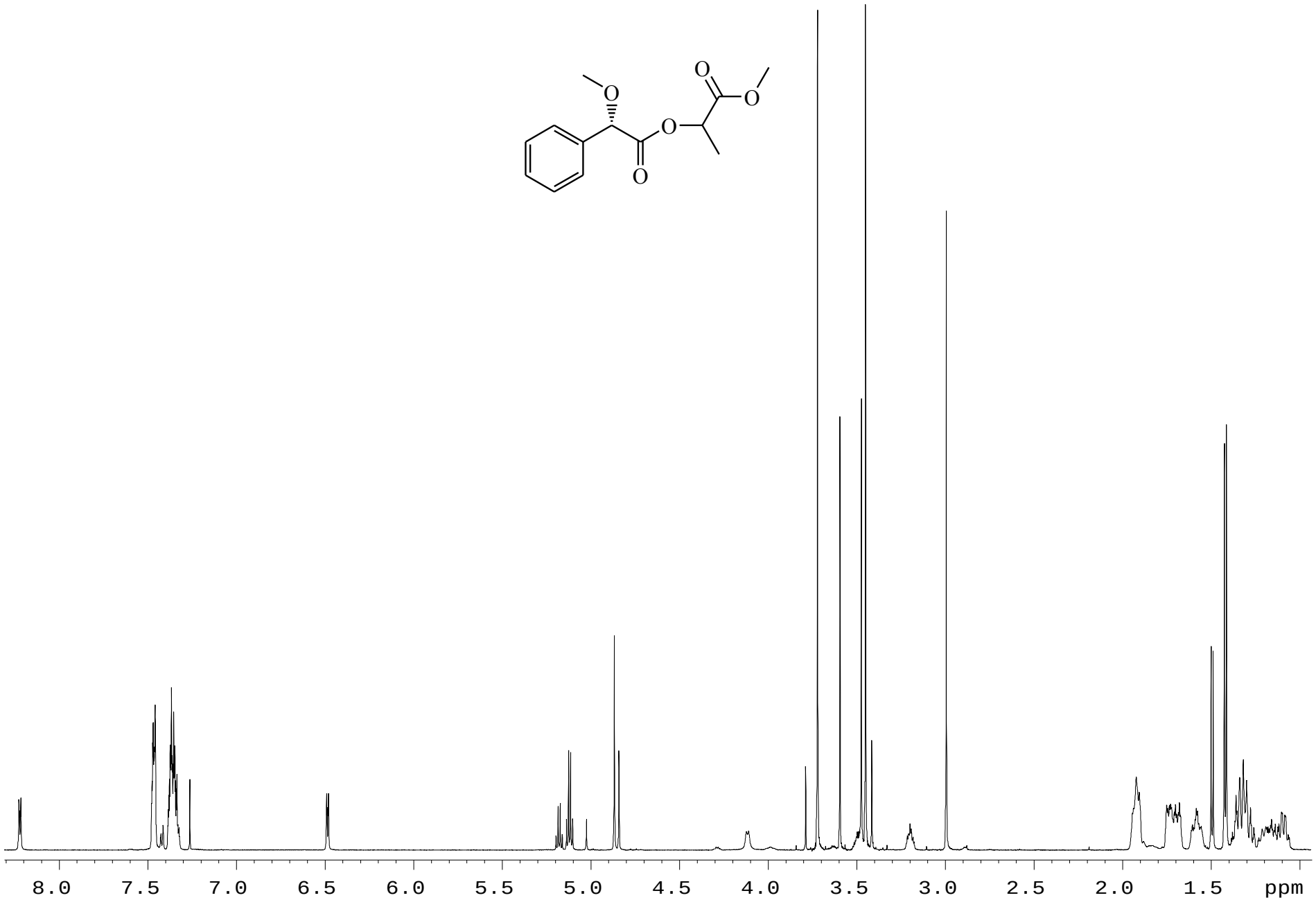

O
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20 ppm

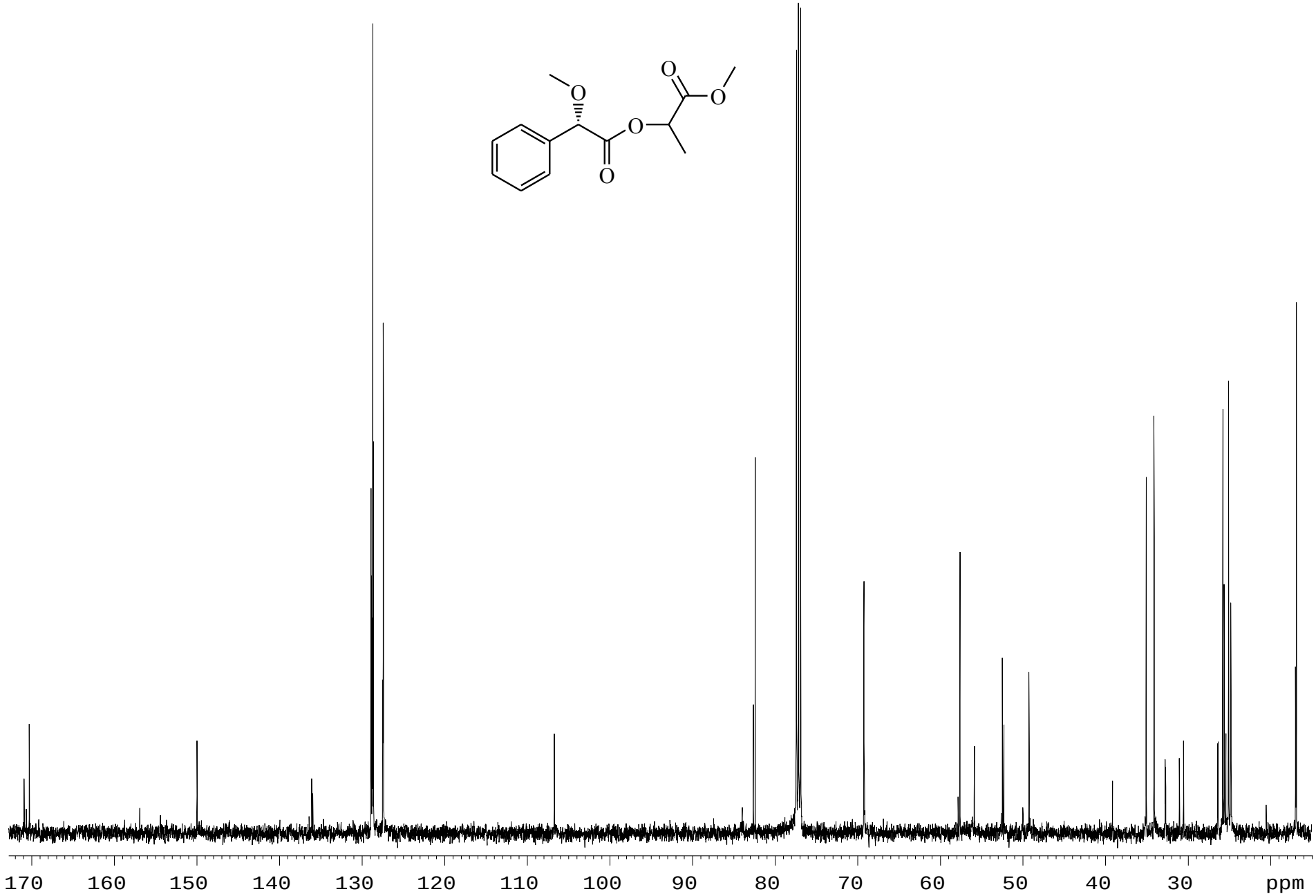
^{1}H and ^{13}C NMR spectra of *(S)*-MPA ester of *(R)*-3-butyn-2-ol **(11-SR)** and *(S)*-3-butyn-2-ol **(11-SS)** (ratio 50:50).



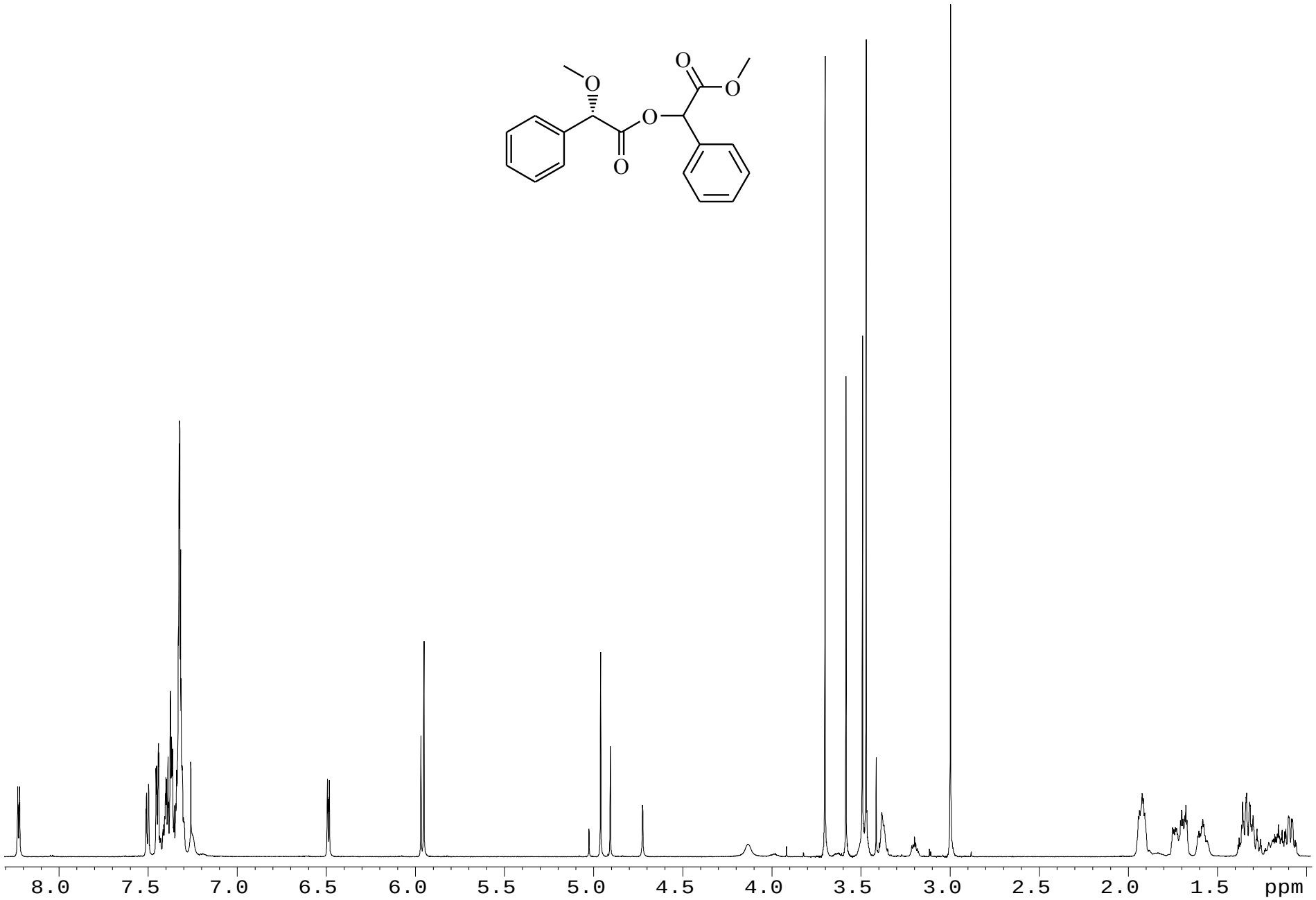

O
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

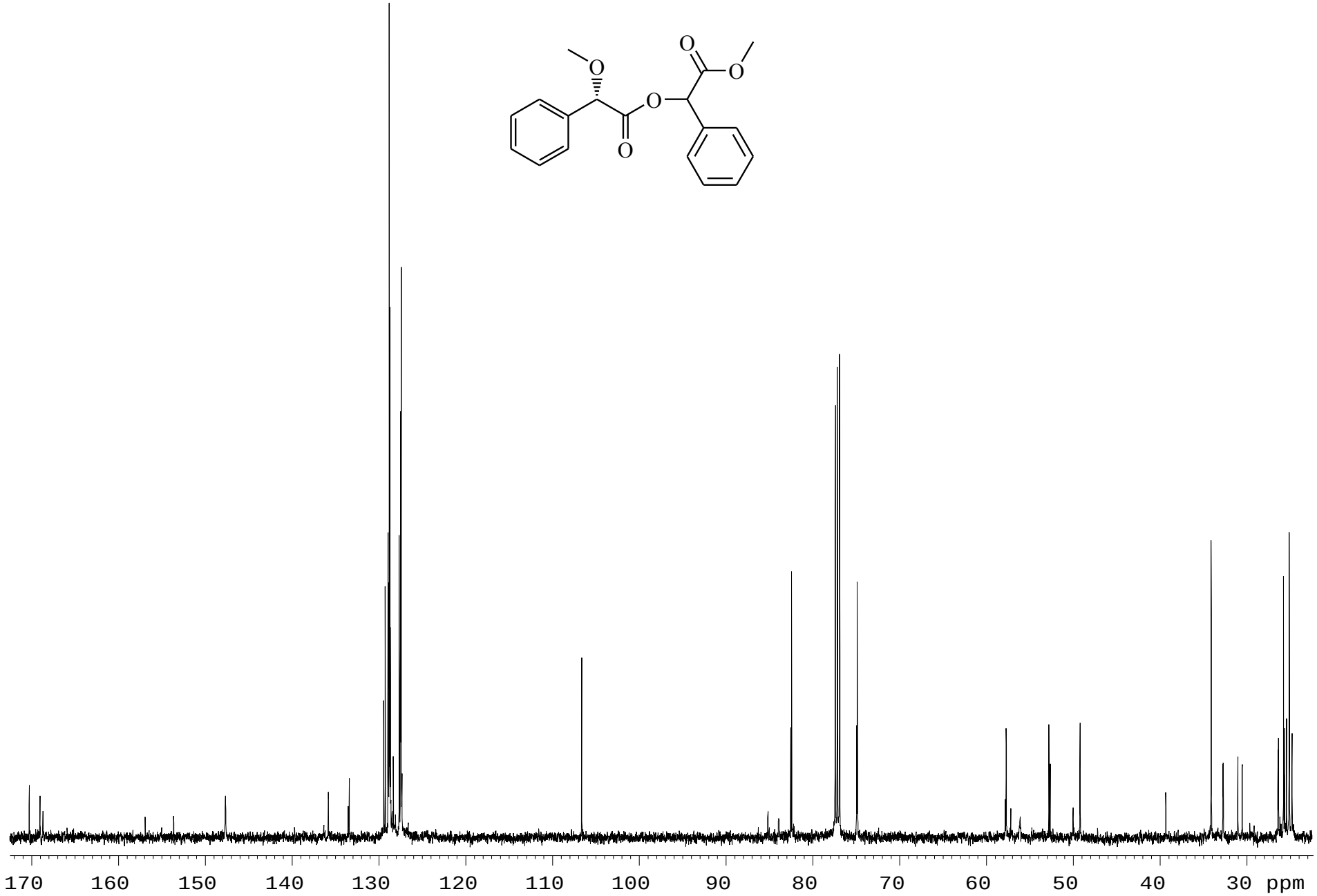
^{1}H and ^{13}C NMR spectra of *(S)*-MPA ester of *(R)*-methyl lactate **(12-SR)** and *(S)*-methyl lactate **(12-SS)** (ratio 67:33).



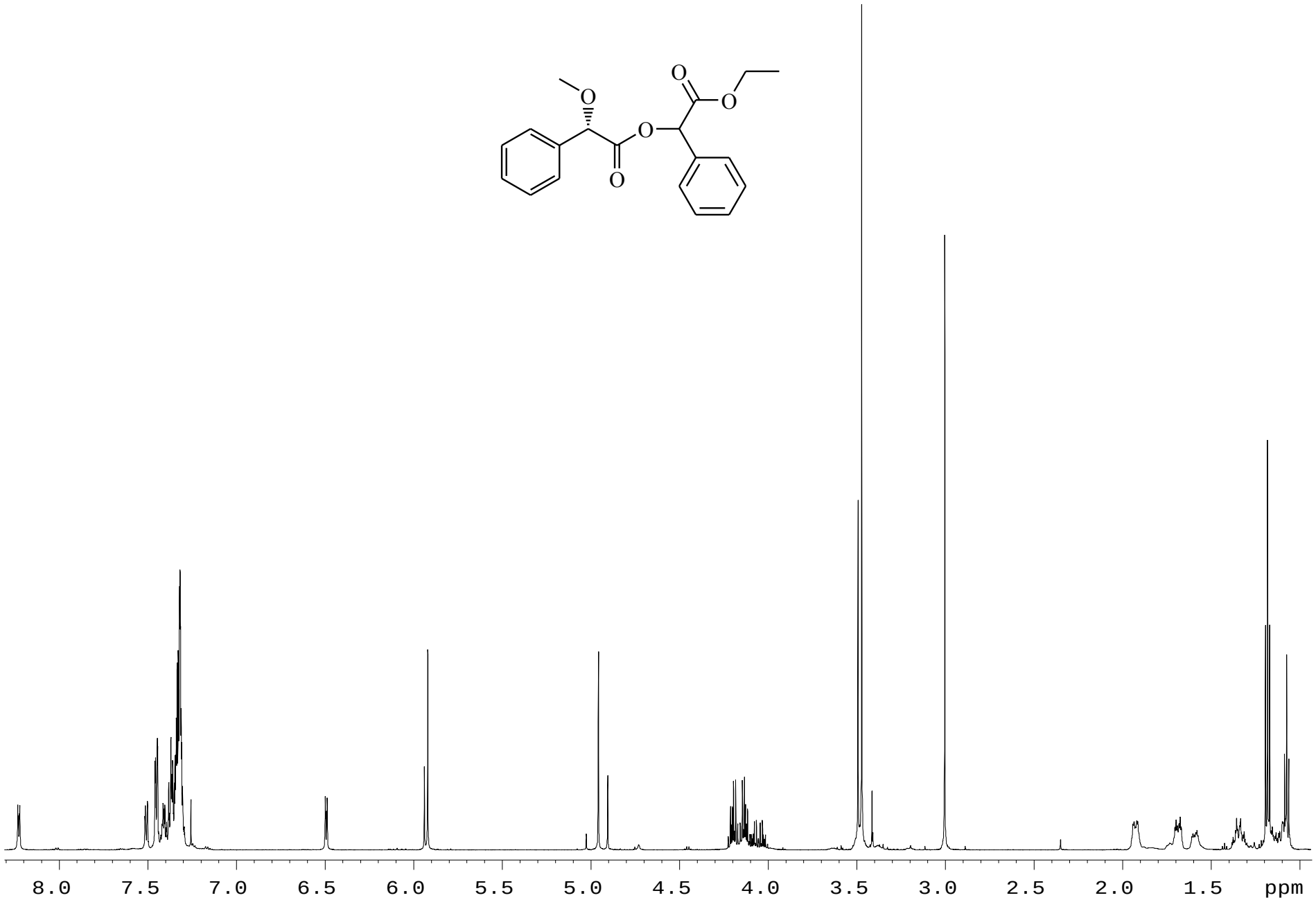

O
O
O
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

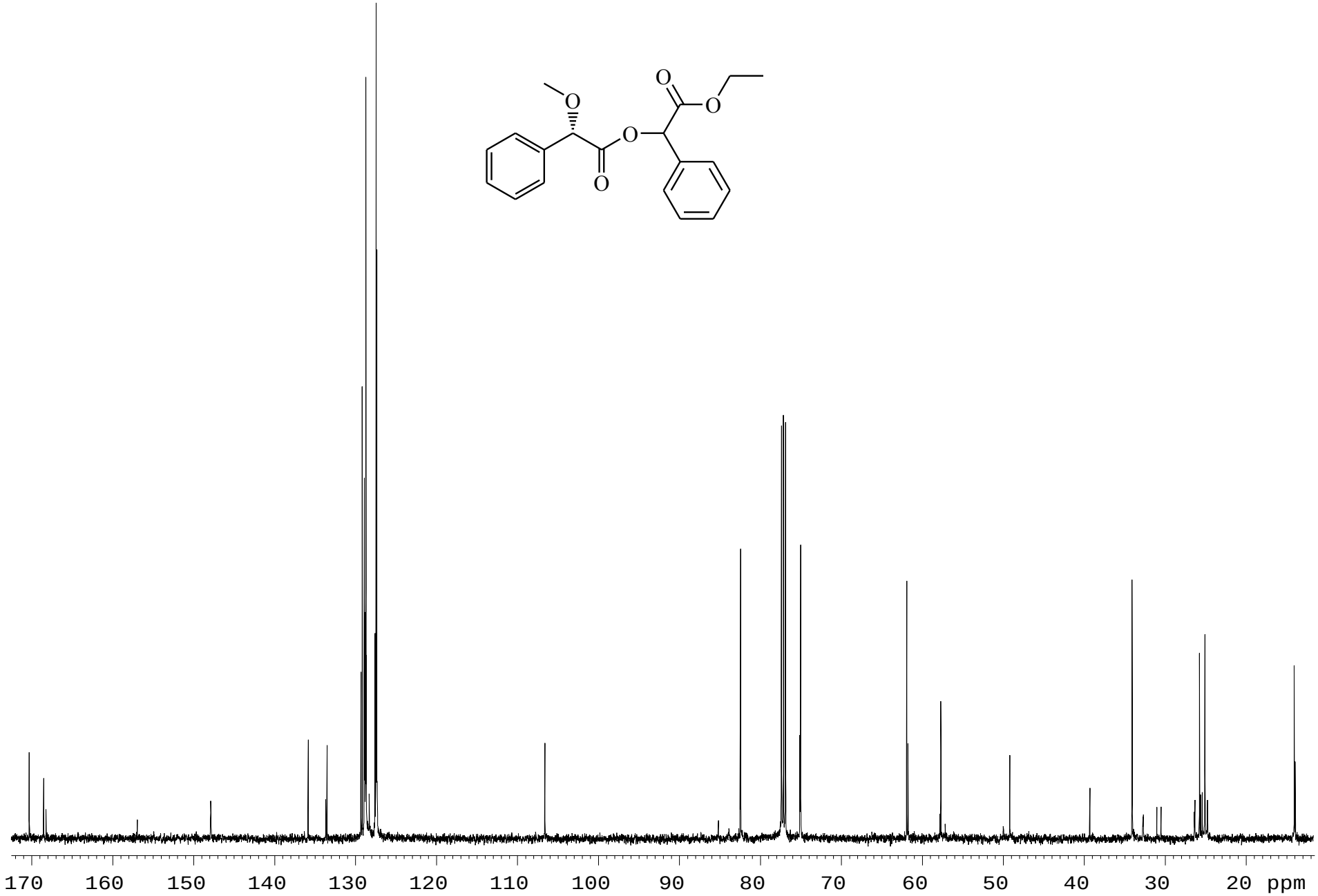
^{1}H and ^{13}C NMR spectra of *(S)*-MPA ester of *(R)*-methyl mandelate **(13-SR)** and *(S)*-methyl mandelate **(13-SS)** (ratio 66:34).



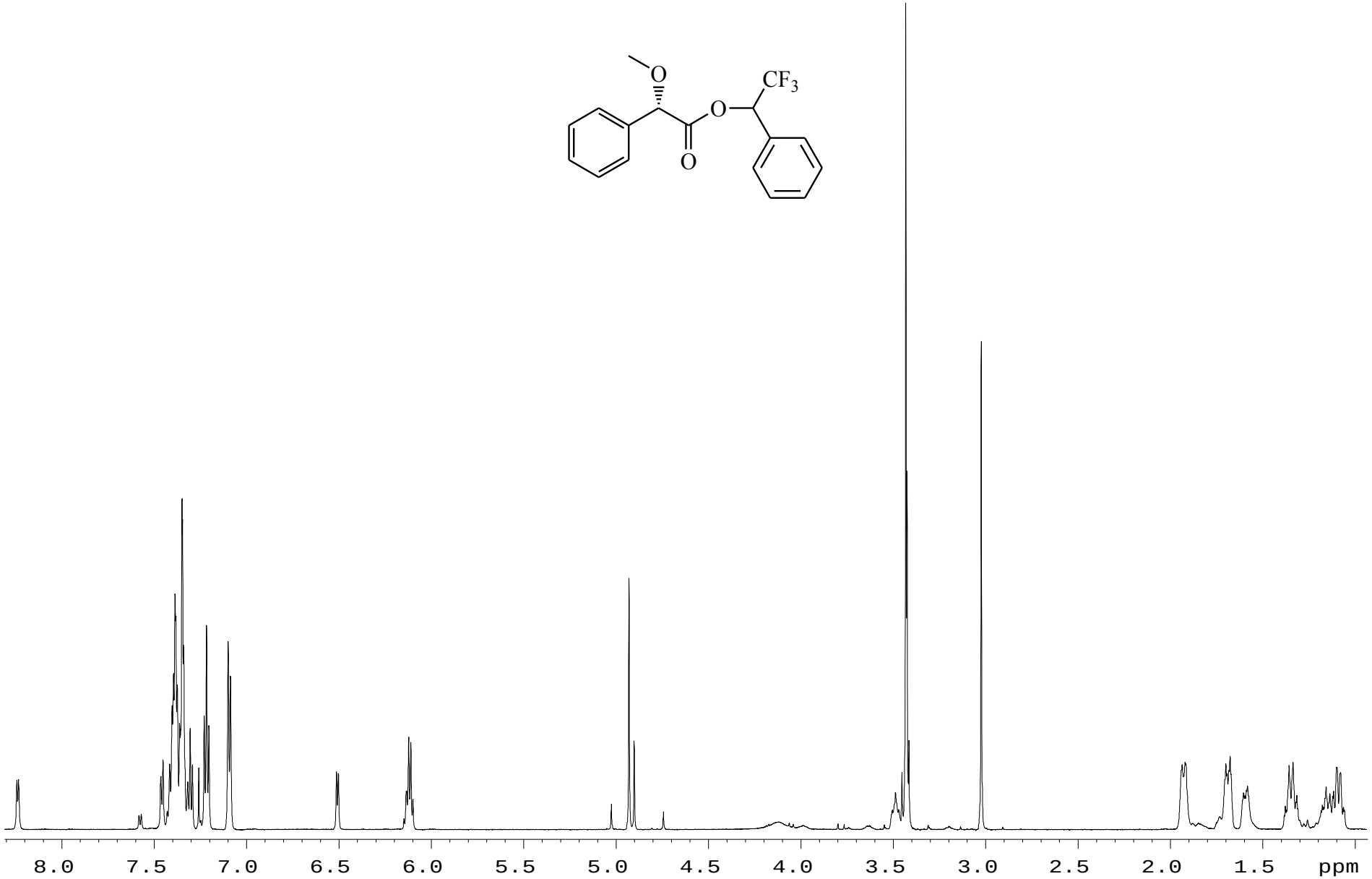

O
O
O
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

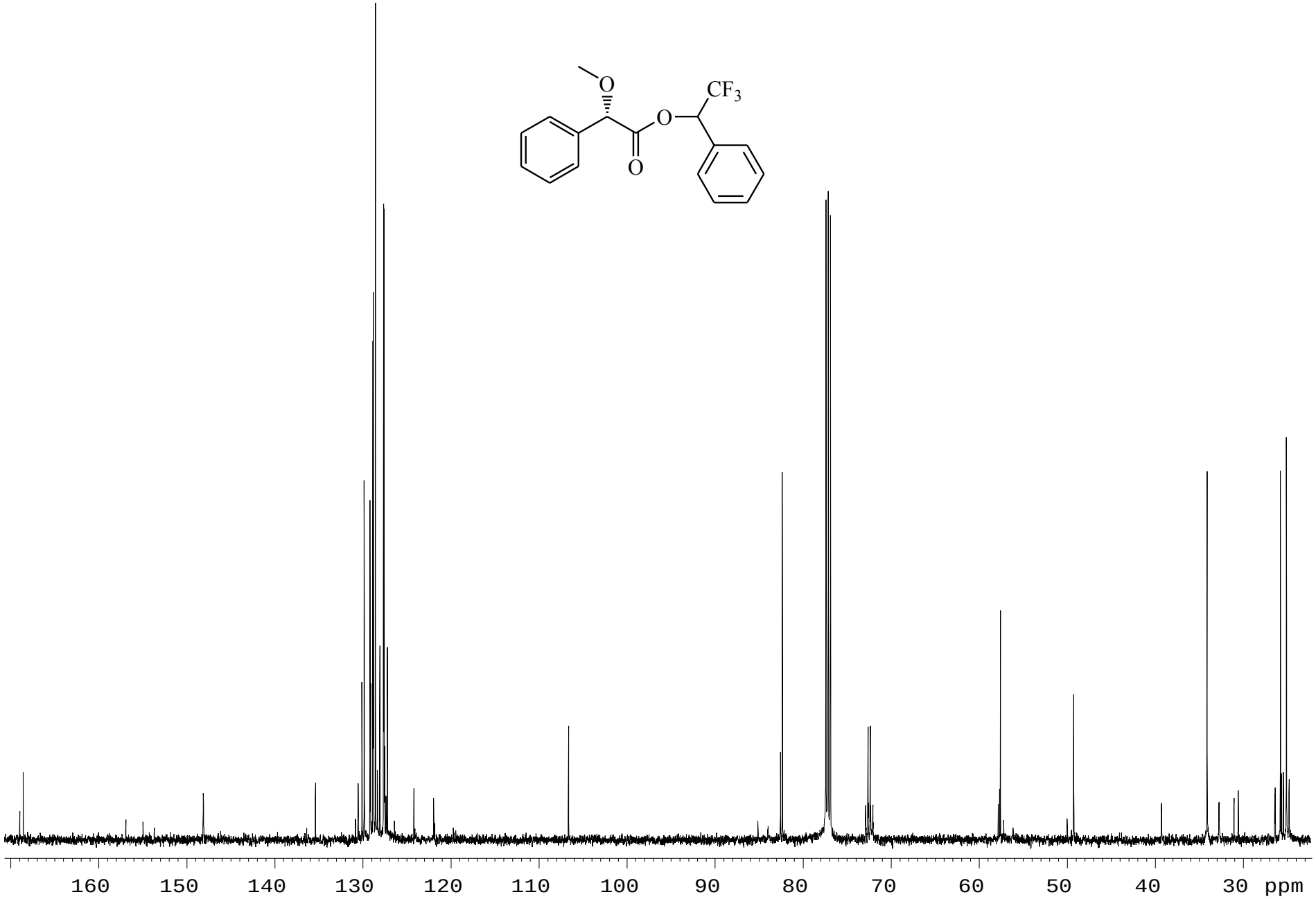
^{1}H and ^{13}C NMR spectra of *(S)*-MPA ester of *(R)*-ethyl mandelate **(14-SR)** and *(S)*-ethyl mandelate **(14-SS)** (ratio 73:27).

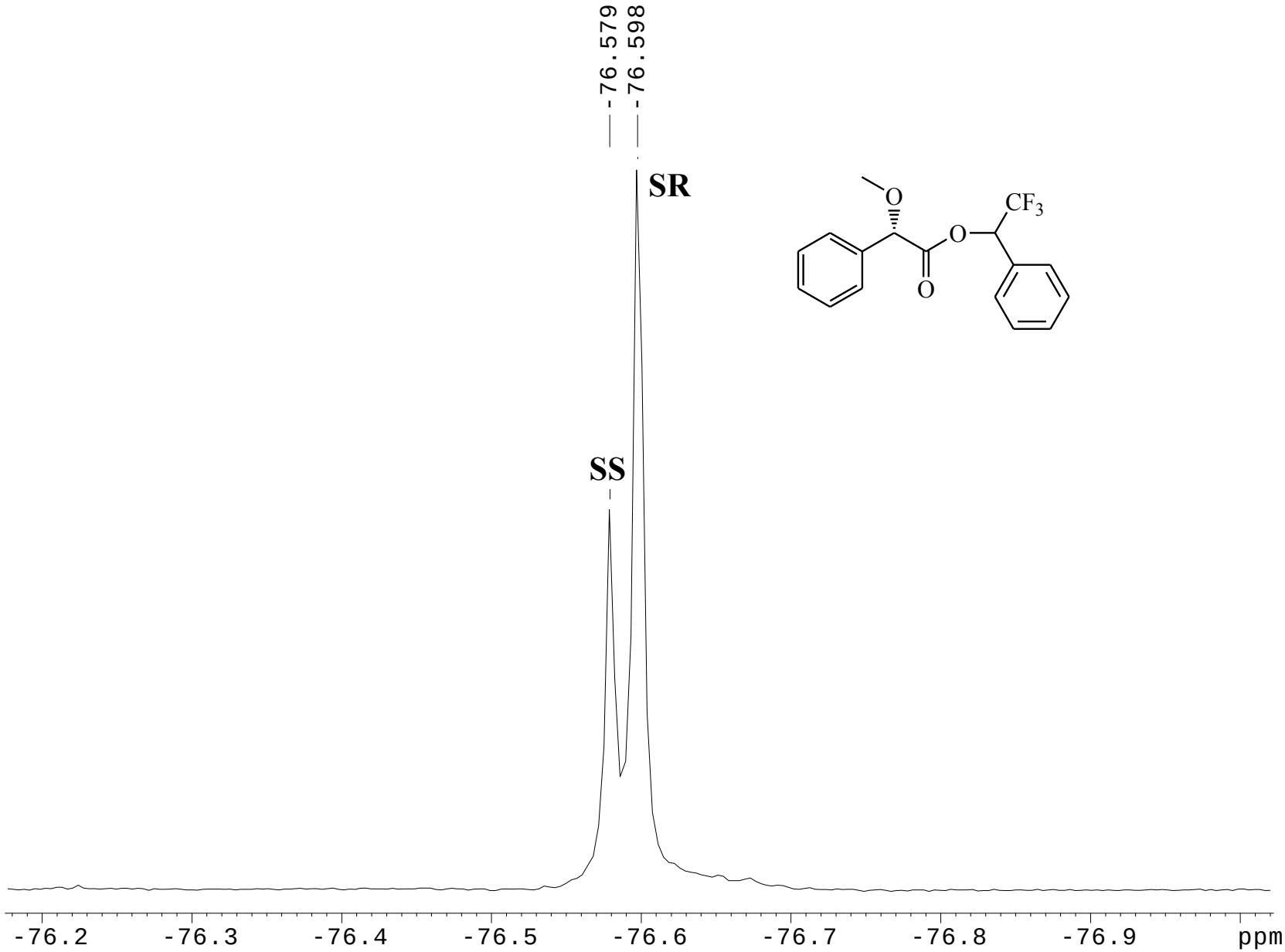



O
O
O
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

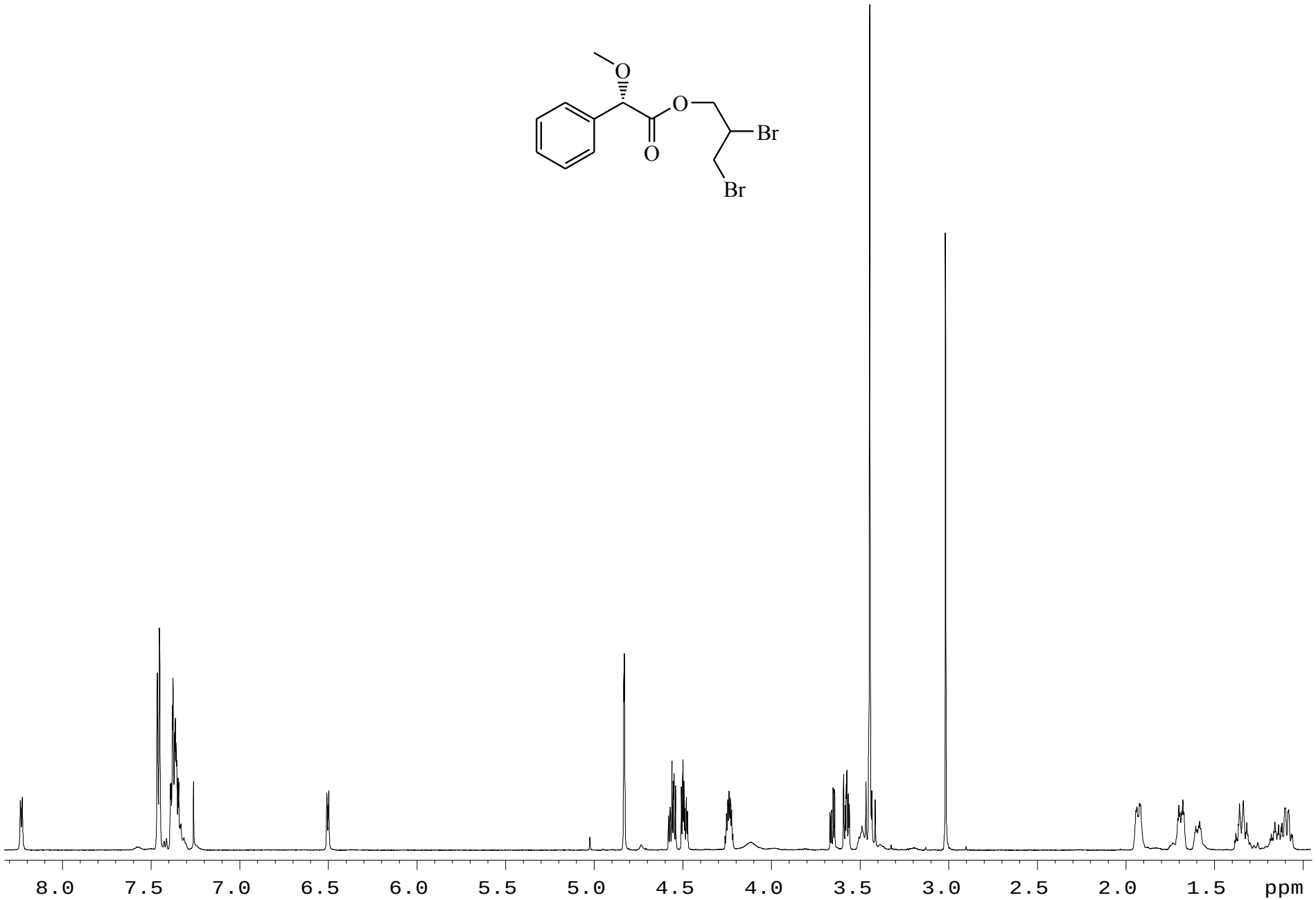
^{1}H, ^{13}C and ^{19}F NMR spectra of *(S)*-MPA ester of *(R)*-α-(trifluoromethyl)benzyl alcohol **(15-SR)** and *(S)*-α-(trifluoromethyl)benzyl alcohol **(15-SS)** (ratio 75:25).

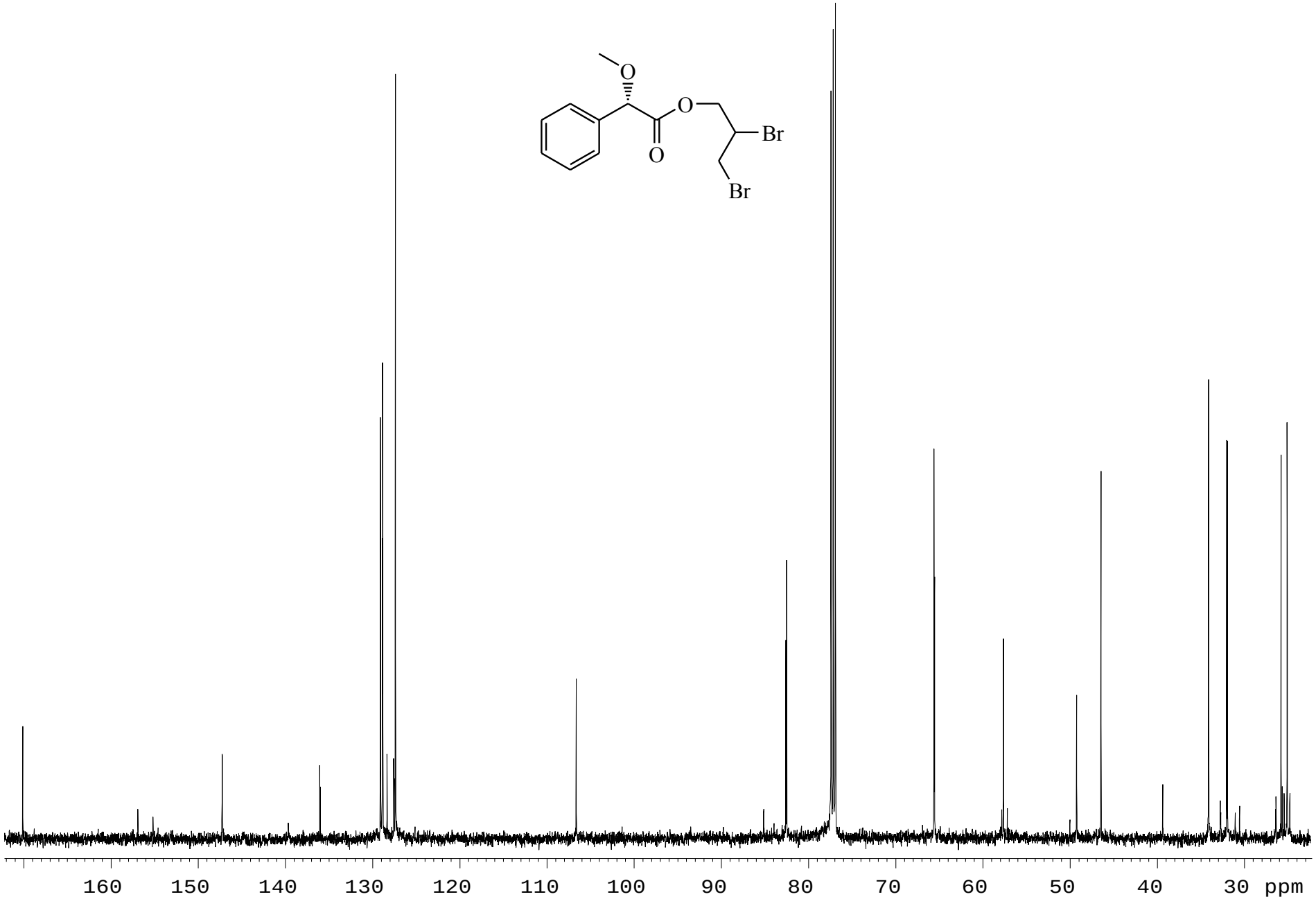



O
CF3
O
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

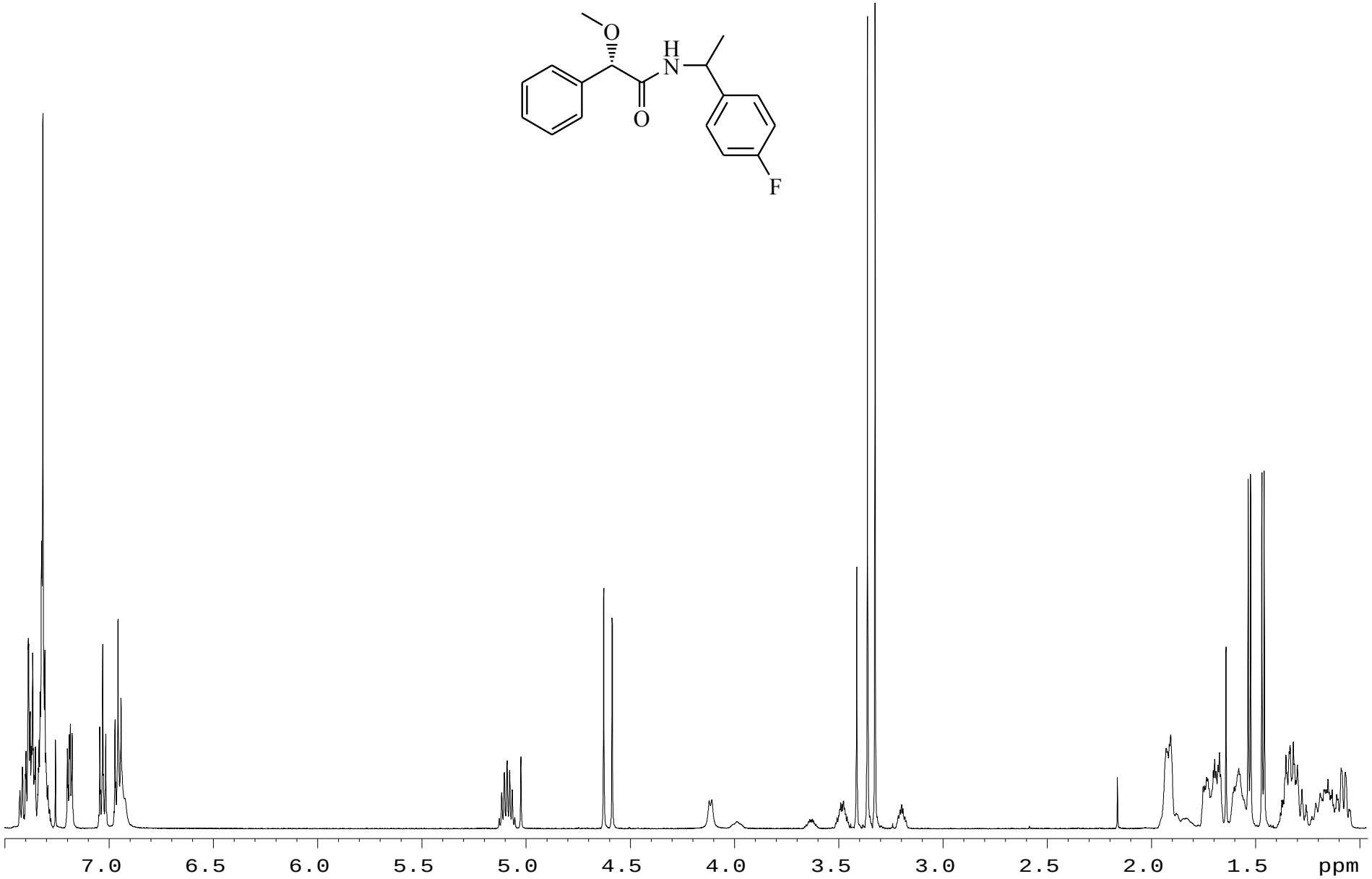

-76.579
-76.598
SR
SS
O
CF3
O
O
-76.2
-76.3
-76.4
-76.5
-76.6
-76.7
-76.8
-76.9
ppm

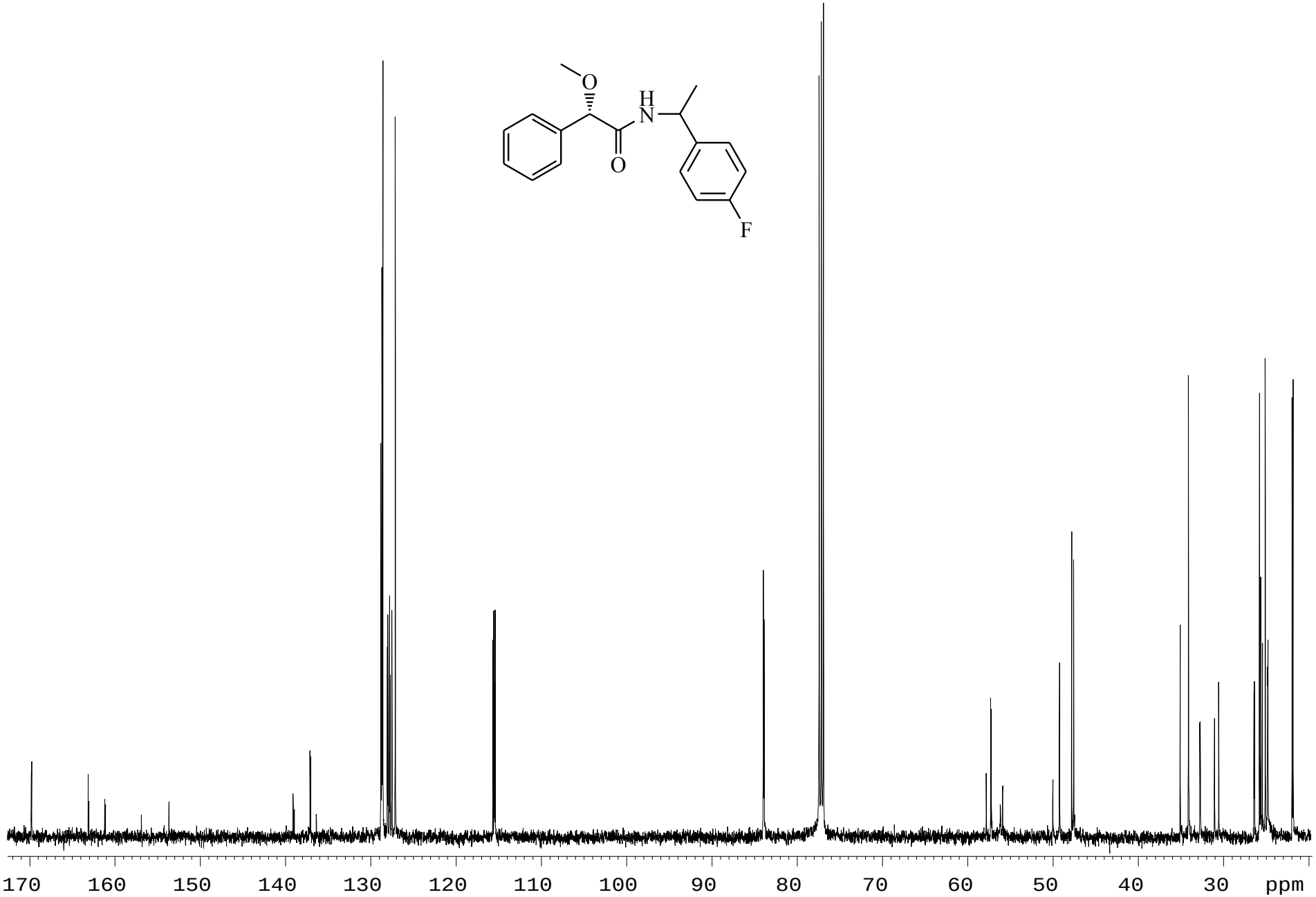
^{1}H and ^{13}C NMR spectra of *(S)*-MPA ester of *(R)*-2,3-dibromo-1-propanol **(16-SR)** and *(S)*-2,3-dibromo-1-propanol **(16-SS)** (ratio 50:50).

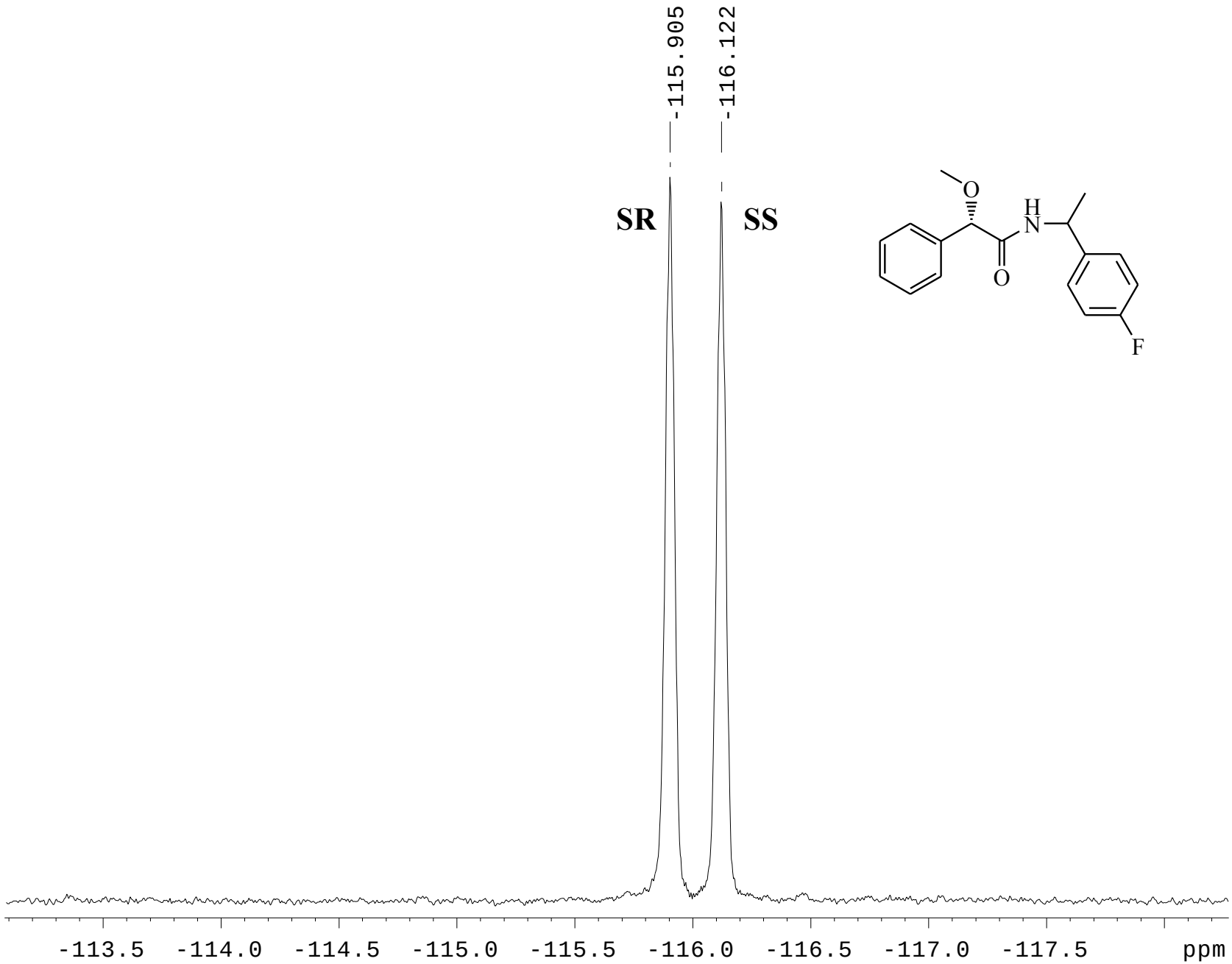



O
O
O
Br
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm

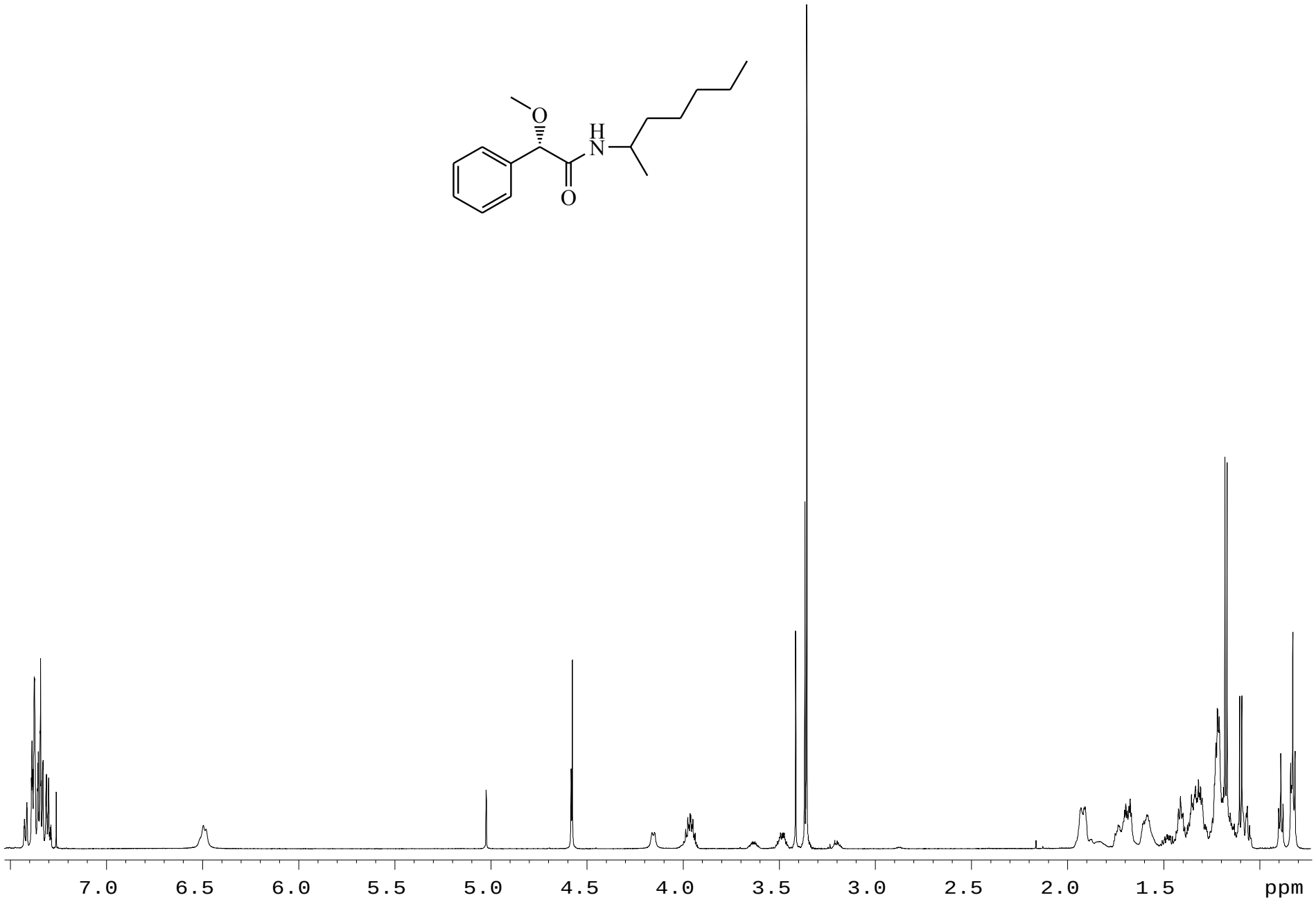
^{1}H, ^{13}C and ^{19}F NMR spectra of *(S)*-MPA ester of *(R)*-4-fluoro-α-methylbenzylamine **(17-SR)** and *(S)*-4-fluoro-α-methylbenzylamine **(17-SS)** (ratio 50:50).

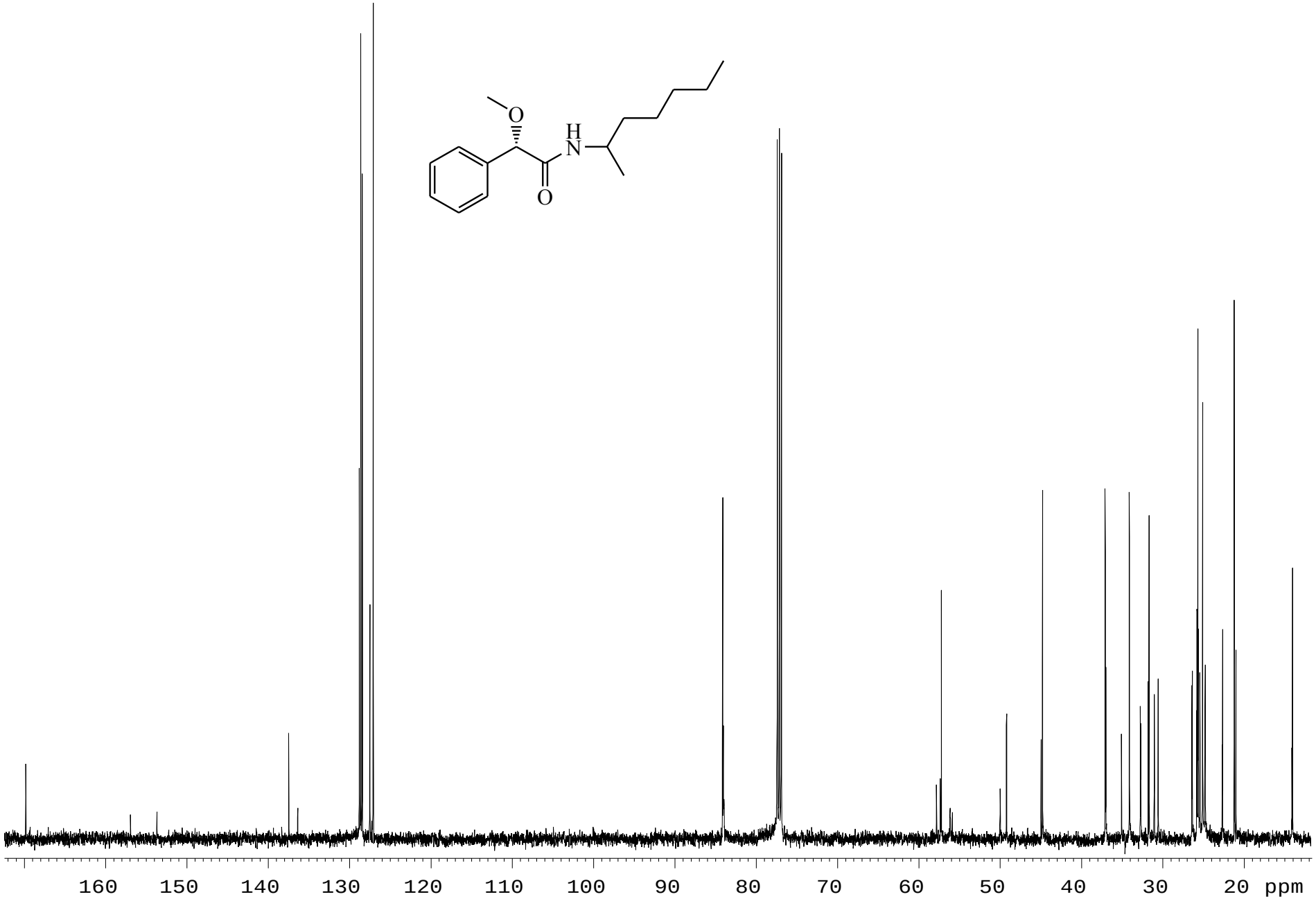



O
H
N
O
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm


-115.905
-116.122
SR
SS
O
H
N
O
F
-113.5
-114.0
-114.5
-115.0
-115.5
-116.0
-116.5
-117.0
-117.5
ppm

^{1}H and ^{13}C NMR spectra of *(S)*-MPA ester of *(R)*-2-heptylamine **(18-SR)** and *(S)*-2-heptylamine **(18-SS)** (ratio 74:26).




O
H
N
O
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm