Scope and Limitations of Absolute Configuration Determination of Allenic Natural Products Using C=C=C Stretching VCD Signal

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Supporting Information

Supporting Figures and Table

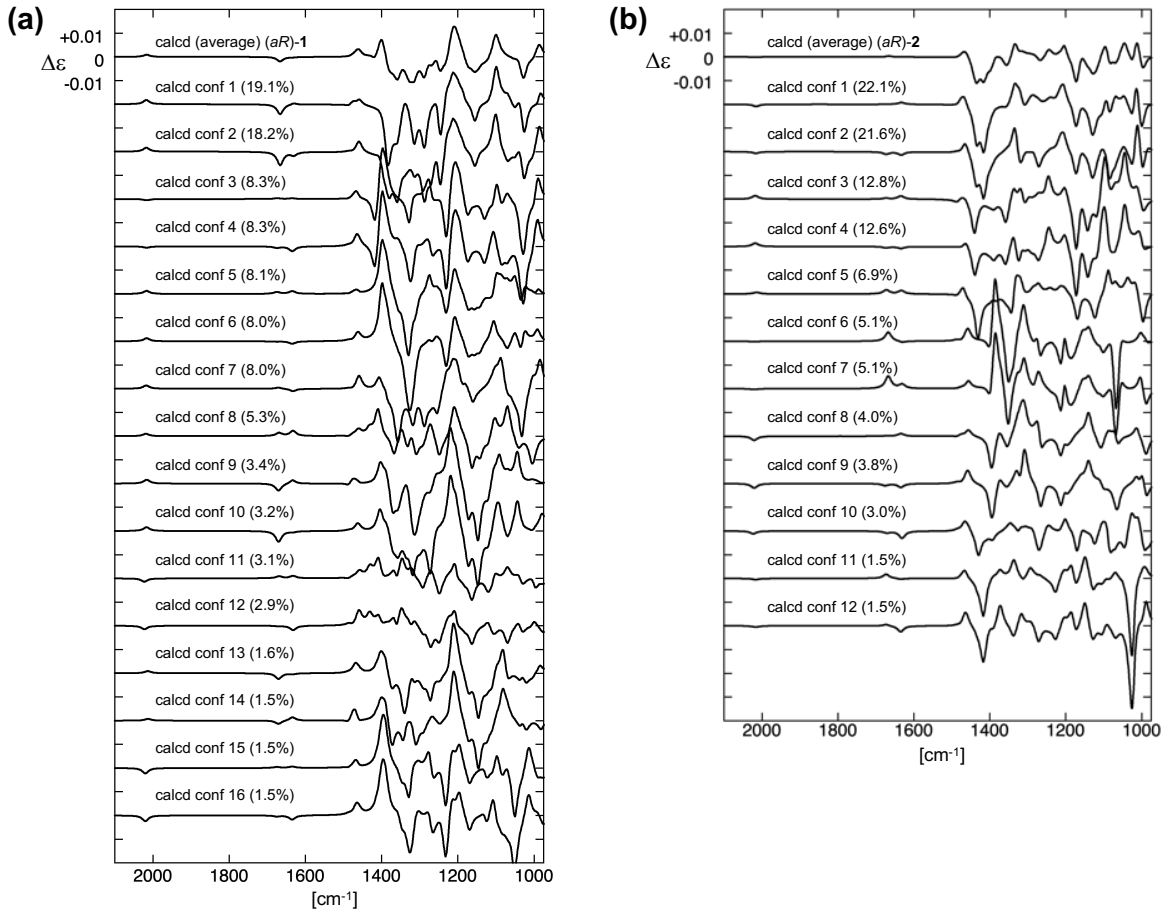


Fig. S1 Comparison of the intensity of ν_{as} C=C=C VCD signals of each predicted conformer of (a) (*aR*)-**1** and (b) (*aR*)-**2**. Calculation conditions: DFT/B3LYP/6-311+G(d,p). Scaling factor: 0.985.

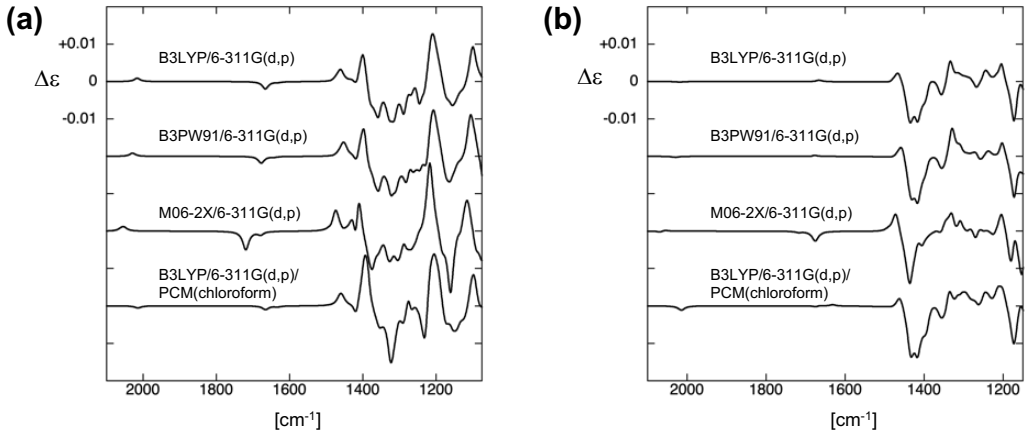


Fig. S2 Theoretical VCD spectra of (a) (*aR*)-**1** and (b) (*aR*)-**2** using different conditions. Scaling factor: 0.985.

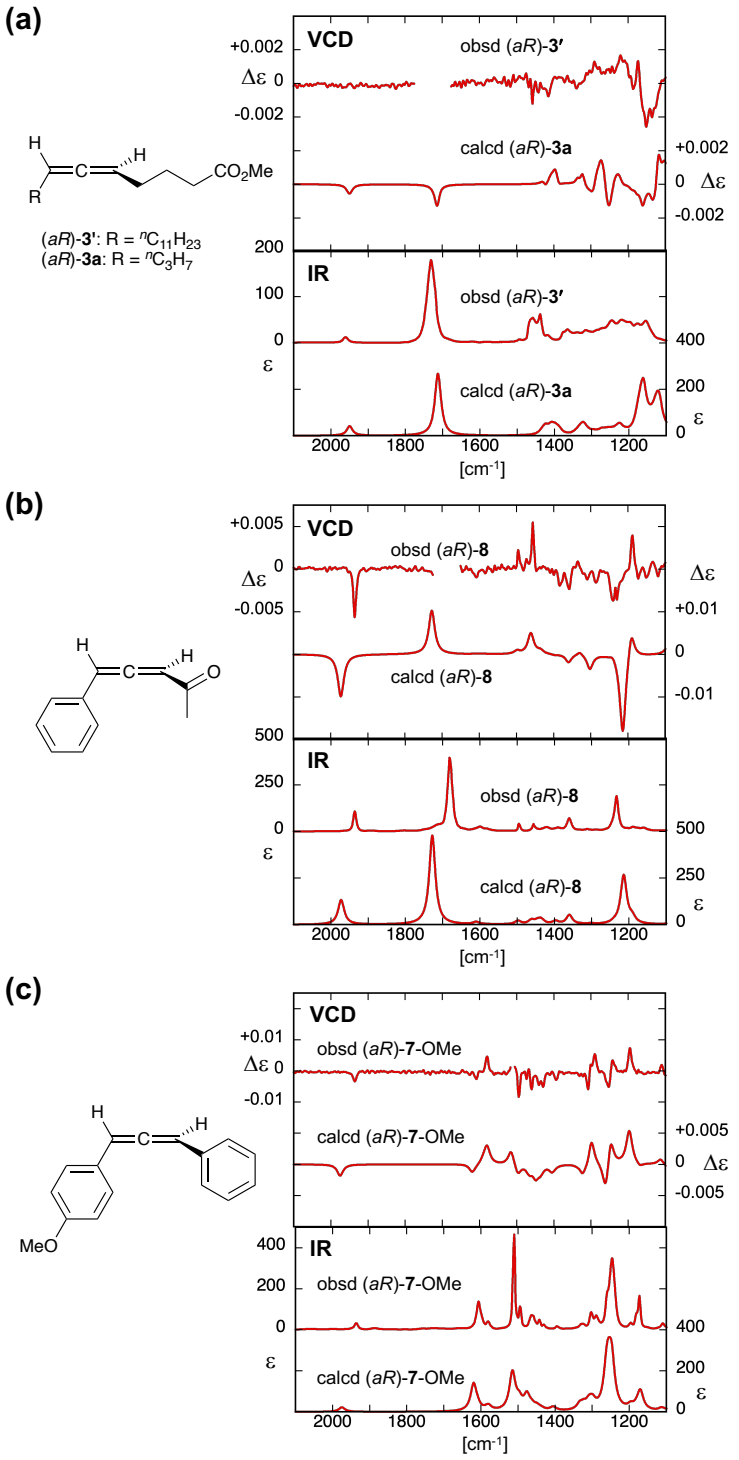


Fig. S3 Observed and calculated VCD/IR spectra of (a) **3′** and **3a**, (b) **8**, and (c) **7**-OMe. Measurement conditions: 1.5 M (for (*aR*)-**3′**), 0.8 M (for (*aR*)-**8**), or 0.3 M (for (*aR*)-**7**-OMe) in $CDCl_3$; *l* 85 μm (for (*aR*)-**3′** and (*aR*)-**7**-OMe) or 50 μm (for (*aR*)-**8**). Calculation conditions: DFT/B3LYP/6-311G(d,p). Scaling factors: 0.95 (for **3a**) or 0.98 (for **8** and **7**-OMe). Part of the observed spectra are omitted due to strong IR absorptions.

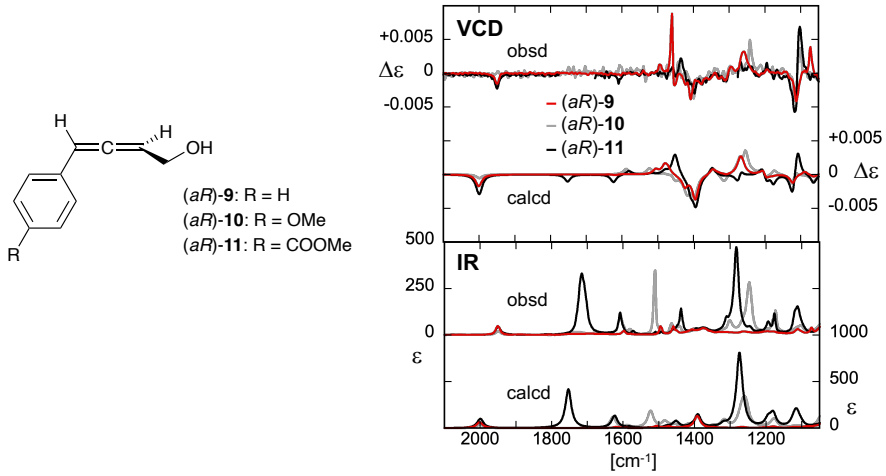


Fig. S4 Observed and calculated VCD/IR spectra of (*aR*)-**9** (red), (*aR*)-**10** (gray), and (*aR*)-**11** (black). Measurement conditions: 0.54-2.0 M in $CDCl_3$; *l* 50 μm. Calculation conditions: DFT/B3LYP/6-311G(d,p). Scaling factors: 0.985. The following regions of the observed VCD spectra are omitted due to strong IR absorption: 1530-1500 cm^{-1} for (*aR*)-**10** and 1775-1675 and 1300-1275 cm^{-1} for (*aR*)-**11**.

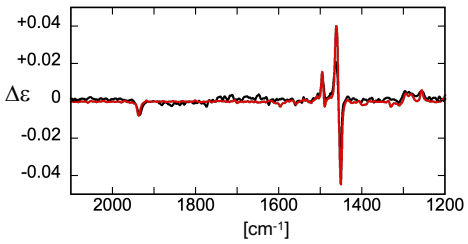


Fig. S5 Comparison of the observed VCD spectra of (*aR*)-**7** measured in $CDCl_3$ (red) and DMSO-d_6 (black) at 0.4 M.

Table S1 IR spectral similarity (S_{IR}) and VCD spectral similarity (S_{VCD}) obtained for the IR and VCD spectra of **1** and **2** using a numerical algorithm implemented in CompareVOA software.

Experimental spectra	Theoretical spectra	S_{IR}	S_{VCD}
(*aR*)-**1**	(*aR*)-**1**	95.0	79.0
(*aR*)-**1**	(*aS*)-**1**	95.5	56.5
(*aR*)-**2**	(*aR*)-**2**	96.1	62.3
(*aR*)-**2**	(*aS*)-**2**	93.8	32.1

Table S2 Electric dipole transition moments (μ), magnetic dipole transition moments (m), and the angles made by these two moments (ξ) calculated for the most stable conformers listed in Table 1.

	μ [10^{-20} esu cm]	m [10^{-24} esu cm]	ξ [deg]
(*aR*)-**1**	3.9	8.3	84.6
(*aR*)-**2**	3.7	12.0	94.2
(*aR*)-**3a**	7.6	5.5	97.3
(*aS*)-**4**	5.5	11.6	86.0
(*aR*)-**5**	5.9	11.8	83.1
(*aR*)-**6**	10.6	15.2	102.5
(*aR*)-**7**	7.6	13.9	98.4
(*aR*)-**8**	13.8	19.0	97.8
(*aR*)-**9**	10.1	10.6	100.6
(*aR*)-**10**	8.0	10.6	99.4
(*aR*)-**11**	12.9	19.4	96.6
(*aR*)-**7**-OMe	5.6	12.2	94.9

General Experimental and Computational Procedures

General Procedures

^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Varian Inova instrument at 25 °C. Chemical shift values (δ) are reported in ppm relative to tetramethylsilane or $CDCl_3$ (^{1}H δ 7.26 and ^{13}C δ 77.16). The following abbreviations were used for signal multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet. Electrospray ionization mass spectrometry and electron ionization mass spectrometry were measured on a Thermo Scientific Exactive and JEOL JMS-T100GCv, respectively. Optical rotations were measured on a JASCO P-1020 polarimeter at the sodium D-line under ambient temperature, and reported as $[\alpha]_D$ (concentration in grams/100 mL solvent). Enantioseparation of **5**, **6**, and **7** was performed on two JASCO PU-2086 intelligent pumps equipped with a JASCO MX-2080-31 solvent mixing module on a PU-2075 intelligent UV/Vis detector. Purchased chemicals were used without further purification.

VCD and IR spectra were measured on a BioTools Chiral*IR*-2X or JASCO FVS-6000 spectrometer with 4 cm^{-1} resolution for 3000 and 16 scans, respectively. All spectra were recorded using a BaF_2 cell at ambient temperature. When both enantiomers were available, VCD spectra were corrected by those of the corresponding enantiomers. The other spectra were corrected by solvent spectra obtained under the identical measurement conditions.

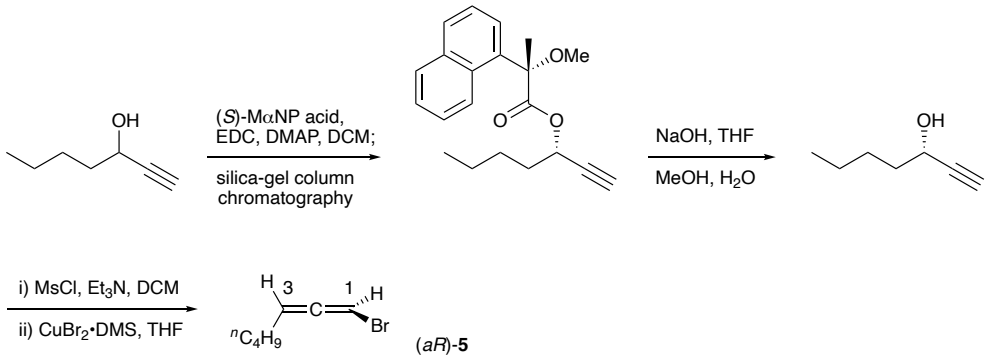
General Computational Details

Preliminary MMFF conformational search using a MonteCarlo algorithm of each molecule was performed on Spartan'20 software package.[1] When more than one stable geometry was predicted within 2-3 kcal/mol from the most stable, each conformer was optimized at DFT/B3LYP/6-31G(d) on Spartan'20. The optimized conformers within 1-2 kcal/mol energy window were further optimized at DFT/B3LYP/6-311G(d,p) on Gaussian 16 program.[2] The resultant conformers whose Boltzmann population is more than 1% were used for the following VCD/IR calculations. VCD/IR spectra of each conformer were calculated at DFT/B3LYP/6-311G(d,p). The calculated frequencies, dipole strengths, and rotational strengths were converted to VCD spectra on GaussView6 software using a peak half-width a half height of 10 cm^{-1}. The final spectra were obtained upon weighted average of the spectra of each conformer based on its Boltzmann population at 298 K.

Synthetic Procedures

Synthesis of (*aR*)-**1**, (*aR*)-**2**, and (*aS*)-**4** were reported previously,[3,4] while (*aR*)-**3′** was prepared using a reported procedure.[5]

Synthesis of (*aR*)-**5** ((*aR*)-1-bromohepta-1,2-diene)



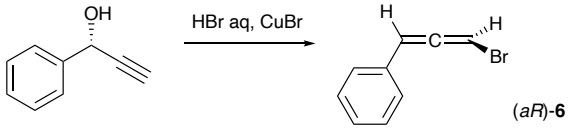
Esterification of hept-1-yn-3-ol with (*S*)-MαNP acid was performed using a similar procedure to that reported.[6] To hept-1-yn-3-ol (213 μL, 1.65 mmol) and (*S*)-MαNP acid (344 mg, 1.50 mmol) in DCM (5 mL) were added DMAP (367 mg) and EDC•HCl (316 mg) and the mixture was stirred at rt overnight. The mixture was then diluted with EtOAc, washed sequentially with 2 M NaOH aq and brine, and dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 8:1 to 1:1), which afforded (*S*)-hept-1-yn-3-ol (*S*)-MαNP ester (174 mg, 36%) along with (*R*)-hept-1-yn-3-ol (*S*)-MαNP ester (150 mg, 31%). The ^{1}H NMR spectra of both compounds were virtually identical with those reported.[7]

To (*S*)-hept-1-yn-3-ol (*S*)-MαNP ester (174 mg, 536 μmol) in THF (1 mL) and MeOH (2 mL) was added 2 M NaOH aq (2 mL) and the solution was stirred with refluxing at 70 °C overnight. The volume of organic solvent was then reduced using an evaporator, and then the mixture was diluted with Et_2O, washed with brine, and dried over $MgSO_4$. Removal of the solvent afforded (*S*)-hept-1-yn-3-ol[7] (60 mg, q.y.).

To (*S*)-hept-1-yn-3-ol (43 mg, 0.38 mmol) in DCM (1 mL) was added Et_3N (95 μL) and MsCl (44 μL) and the mixture was stirred at 0 °C for 1 h. The mixture was diluted with Et_2O, washed sequentially with 2 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the residue was dissolved in THF (2 mL) and added to a mixture of CuBr-dimethylsulfide (156 mg), LiBr (66 mg) and THF (0.5 mL) with stirring. The mixture was stirred at rt for overnight. The mixture was diluted with Et_2O, washed sequentially with 2 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane 100%), which afforded (*aR*)-**5** (23 mg, 34%) with >90%ee (checked by analytical Chiralpak IB). (*aR*)-**5**: ^{1}H NMR δ 5.93 (dt, H-1, *J* = 5.7, 2.3 Hz, 1H), 5.40 (td, H-3, *J* = 6.7, 5.6 Hz, 1H), 2.16 (m, H-4, 2H), 1.44 (m, H-5, 2H), 1.37 (m, H-6, 2H), 0.92 (t, H-7, *J* = 7.2 Hz, 3H); ^{13}C NMR δ 202.2 (C-2), 101.2 (C-3), 72.3 (C-1), 30.6 (C-

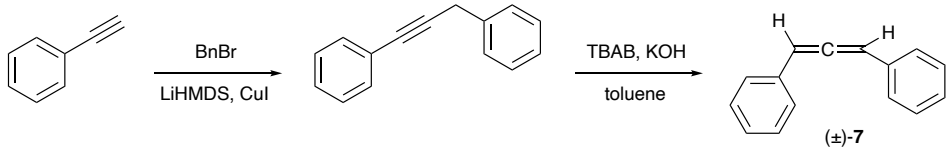
5), 28.2 (C-4), 22.2 (C-6), 14.0 (C-7); HRMS (EI) m/z calcd for $C_7H_{11}Br$ (M^+) 174.0044, found 174.0043; $[\alpha]_D$ -260 (*c* 1.0, $CHCl_3$).

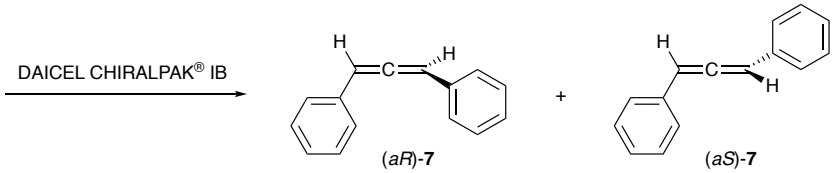
Synthesis of (*aR*)-**6** ((*aR*)-1-bromo-3-phenylpropa-1,2-diene)



Conversion from (*R*)-1-phenylprop-2-yl-1-ol to (*aR*)-**6** was carried out in a similar manner to a reported procedure.[8] To a mixture of conc HBr aq (226 μL) and CuBr (287 mg) was added (*R*)-1-phenylprop-2-yl-1-ol (124 μL, 1.00 mmol) and the mixture was stirred at rt for 15 mins. The mixture was diluted with hexane, washed sequentially with conc HBr aq, sat K_2CO_3 aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane 100%), which afforded (*aR*)-**6** (50 mg, 26%) with 29%ee. Its enantiomeric excess was enriched by semi-preparative chiral HPLC using a Daicel CHIRALPAK® IB column (1.0 cm $\phi \times$ 25 cm) using hexane only, which afforded (*aR*)-**5** with 91%ee. Its ^{1}H NMR spectra were virtually identical to those reported.[9] (*aR*)-**5**: $[\alpha]_D$ -764 (*c* 1.0, $CHCl_3$).

Synthesis of (*aR*)-**7** ((*aR*)-1,3-diphenylpropa-1,2-diene)



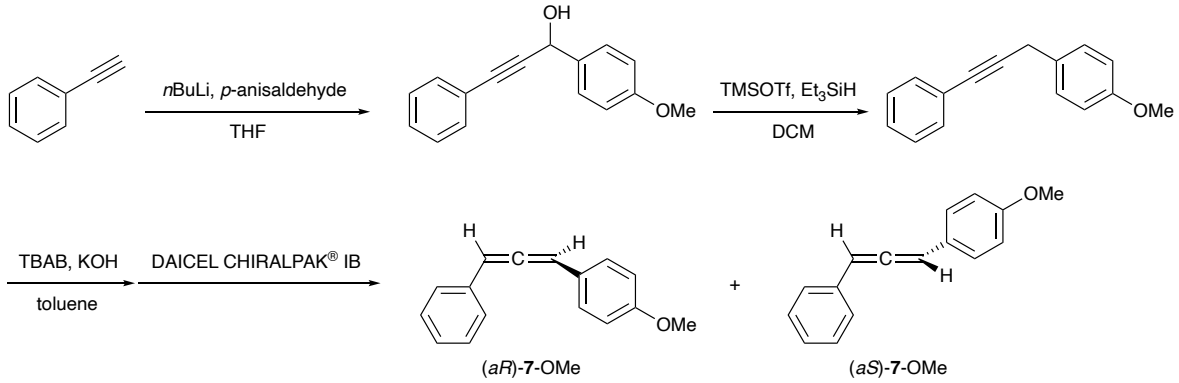


Synthesis of (±)-**7** was carried out in a similar manner to a reported procedure.[10] To a stirred solution of CuI (20 mg) and LiHMDS (2.4 mL, 1 M in THF) in dry toluene (8 mL) were added ethynylbenzene (330 µL, 3.00 mmol) and BnBr (238 μL, 2.00 mmol) dropwise under N_2 at rt. The mixture was refluxed at 90 °C for 1 h. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 25:1 to 10:1), which afforded 1,3-diphenylpropyne (83 mg, 22%).[10]

To 1,3-diphenylpropyne (83 mg, 0.43 mmol) in toluene (4 mL) were added TBAB (14 mg) and KOH (24 mg) and the mixture was stirred at rt for 1 h. The mixture was then concentrated *in vacuo* and the mixture purified by silica-gel column chromatography (hexane-EtOAc = 45:1 to 10:1) which afforded (±)-**7**[10] (35 mg, 42%).

Enantioseparation of (±)-**7** was carried out on a Daicel CHIRALPAK® IB column (1.0 cm $\phi \times$ 25 cm) using 100% hexane, which led to the first-eluted (*aR*)-**7** (98%ee) and the second-eluted (*aS*)-**7**. (*aR*)-**7**: $[\alpha]_D$ -766 (*c* 1.0, $CHCl_3$); lit[11] $[\alpha]_D$ -864 (*c* 0.59, $CHCl_3$). (*aS*)-**7**: $[\alpha]_D$ +735 (*c* 1.0, $CHCl_3$).

Synthesis of (*aR*)-**7**-OMe ((*aR*)-1-Methoxy-4-(3′-phenylpropa-1′,2′-dien-1′-yl)benzene)

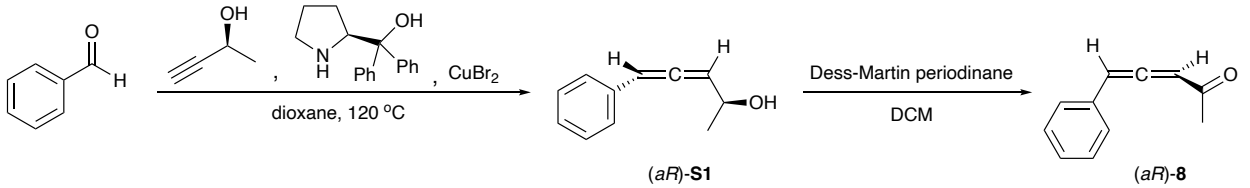


Conversion from ethynylbenzene to (±)-1-(4′-methoxyphenyl)-3-phenylprop-2-yn-1-ol was carried out in a similar manner to a reported procedure.[12] To a solution of ethynylbenzene (430 μL, 3.92 mmol) in THF (10 mL) was added *n*BuLi (2.6 M hexane solution, 1.5 mL) at -78 °C and stirred 20 min. To this solution *p*-anisaldehyde (476 μL) was added at -78 °C and stirred 40 min at rt. The mixture was added 2 M HCl aq and extracted with EtOAc. The organic layer was washed sequentially with sat $NaHCO_3$ aq and brine and dried over $MgSO_4$. Removal of the solvent afforded (±)-1-(4′-methoxyphenyl)-3-phenylprop-2-yn-1-ol[12] (886 mg, 90%).

To the obtained alcohol (200 mg, 839 μmol) in DCM (6 mL) was added TMSOTf (228 μL) and Et_3SiH (161 μL) at -78 °C and stirred 1 h. The mixture was added sat $NaHCO_3$ aq and extracted with $CHCl_3$. The organic layer was washed with brine and dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 100:0 to 83:17), which afforded 1-methoxy-4-(3′-phenylprop-2′-ynyl)benzene[13] (119 mg, 64%).

Conversion from 1-methoxy-4-(3′-phenylprop-2′-ynyl)benzene to (±)-**7**-OMe was carried out in a similar manner to a reported procedure.[14] To a solution of 1-methoxy-4-(3′-phenylprop-2′-ynyl)benzene (78 mg, 0.35 mmol) in toluene (3 mL) was added TBAB (12 mg) and KOH (20 mg) and the mixture was stirred at rt for 2 h. The mixture was then diluted with Et_2O, washed sequentially with sat $NaHCO_3$ aq and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was directed submitted to enantioseparation on a Daicel CHIRALPAK® IB column (1.0 cm $\phi \times$ 25 cm) using 100% hexane, which led to the first-eluted (*aR*)-**7**-OMe (8.0 mg, 98%ee) and the second-eluted (*aS*)-**7**-OMe (11.7 mg) (25% yield in total). Their ^{1}H NMR spectrum was virtually identical with that reported for (±)-**7**-OMe.[14] (*aR*)-**7**-OMe: $[\alpha]_D$ -563 (*c* 1.0, $CHCl_3$); lit[15] $[\alpha]_D$ -494 (*c* 1.2, $CHCl_3$, 90%ee). (*aS*)-**7**-OMe: $[\alpha]_D$ +534 (*c* 1.0, $CHCl_3$).

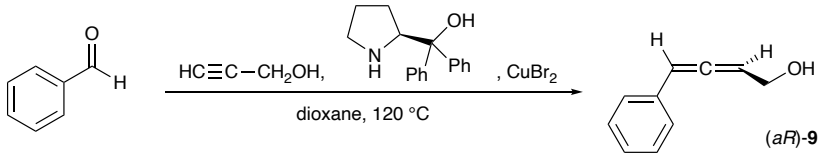
Synthesis of (*aR*)-**8** ((*aR*)-5-phenylpenta-3,4-dien-2-one)



To a solution of benzaldehyde (144 μL, 1.41 mmol), $CuBr_2$ (42 mg), and (*S*)-α,α-diphenyl-2-pyrrolidinemethanol (238 mg) in dioxane (20 mL) was added (*S*)-3-butyn-2-ol (111.2 μL) at rt and the mixture was refluxed at 120 °C overnight. The mixture was then diluted with EtOAc, washed sequentially with 2 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 4:1), which afforded (*aR*)-**S1**, (2*S*,4*aR*)-5-phenylpenta-3,4-dien-2-ol (80 mg, 35%). Its spectroscopic data were virtually identical to those reported for (±)-**S1**.[16] No ^1H NMR signal was detected for its allenic diastereomer, (2*S*,4*aS*)-5-phenylpenta-3,4-dien-2-ol. (*aR*)-**S1**: $[\alpha]_D$ -154 (*c* 1.0, $CHCl_3$).

To (*aR*)-**S1** (80 mg, 0.50 mmol) in DCM (10 mL) was added Dess-Martin periodinane (254 mg) and the mixture was stirred at rt for 3 h. The mixture was then diluted with Et_2O, washed with brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-Et_2O = 10:1), which afforded (*aR*)-**8** (22 mg, 28%). Its spectroscopic data were virtually identical to those reported for (±)-**8**.[17] (*aR*)-**8**: $[\alpha]_D$ -318 (*c* 1.0, $CHCl_3$).

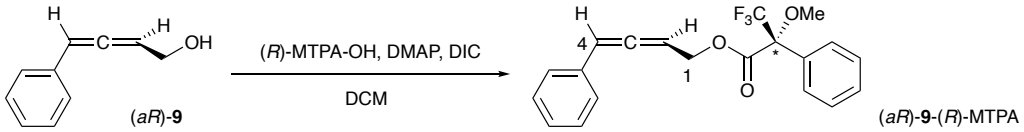
Synthesis of (*aR*)-**9** and (*aS*)-**9** ((*aR*)- and (*aS*)-4-phenylbuta-2,3-dien-1-ol)



To a solution of benzaldehyde (144 μL, 1.41 mmol), $CuBr_2$ (42 mg), and (*S*)-α,α-diphenyl-2-pyrrolidinemethanol (238 mg) in dioxane (20 mL) was added propargyl alcohol (83 μL) and the mixture was refluxed at 120 °C overnight. The mixture was then diluted with EtOAc, washed sequentially with sat NH_4Cl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 4:1 to 1:1), which afforded (*aR*)-**9** (75 mg, 36%). Its spectroscopic data spectra were virtually identical to those reported for (±)-**9**.[12] (*aR*)-**9**: $[\alpha]_D$ -208 (*c* 1.0, $CHCl_3$).

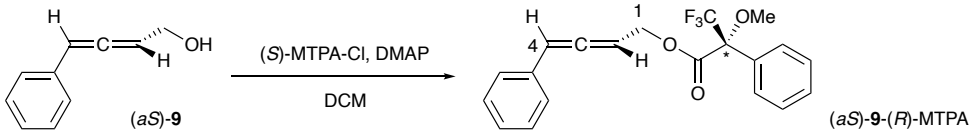
In a similar manner to the synthesis of (*aR*)-**9**, its enantiomer ((*aS*)-**9**) was synthesized by using (*R*)-α,α-diphenyl-2-pyrrolidinemethanol. (*aS*)-**9**: $[\alpha]_D$ +235 (*c* 1, $CHCl_3$); lit[18] for 86%ee (*aS*)-**9**: $[\alpha]_D$ +103.0 (*c* 0.49, $CHCl_3$).

Synthesis of (*aR*)-**9**-(*R*)-MTPA



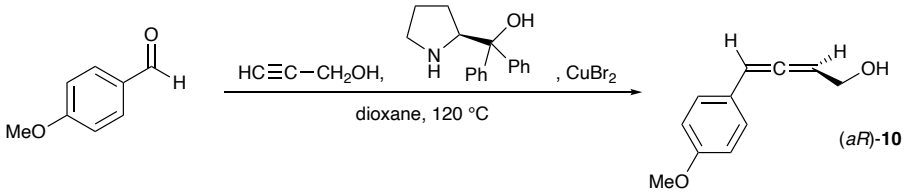
To a solution of (*R*)-MTPA-OH (35 mg), DMAP (20 mg), and DIC (24 μL, 0.15 mmol) in dry DCM (2 mL) was added a solution of (*aR*)-**9** (20 mg, 0.14 mmol) in DCM (1 mL) dropwise at 0 °C and the mixture was stirred at rt for 6 h. The mixture was then diluted with EtOAc, washed sequentially with 0.5 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, its ^{1}H NMR spectrum was measured, which confirmed the enantiomeric excess of (*aR*)-**9** to be >90%ee. The mixture was purified by silica-gel column chromatography (hexane-EtOAc = 10:1 to 3:1), which afforded (*aR*)-**9**-(*R*)-MTPA (10 mg, 20%). (*aR*)-**9**-(*R*)-MTPA: ^{1}H NMR ($CDCl_3$) δ 7.54 (d, *J* = 7.6 Hz, ArH, 2H), 7.44–7.35 (m, ArH, 3H), 7.33–7.20 (m, ArH, 5H), 6.31 (m, H-4, 1H), 5.76 (ddd, H-2, *J* = 6.6, 6.6, 6.6 Hz, 1H), 4.91 (m, C<u>H</u>$_2$O, 2H), 3.56 (s, OMe, 3H)., ^{13}C NMR ($CDCl_3$) δ 207.2 (C-3), 166.3 (CH_2-O-<u>C</u>=O), 132.9 (Ar), 132.1 (Ar), 129.6 (Ar), 128.7 (Ar), 128.4 (Ar), 127.5 (Ar), 127.3 (Ar), 127.0 (Ar), 97.0 (C-4), 90.0 (C-2), 84.6 (C*), 63.8 (C-1), 55.5 (OMe) (^{13}C NMR signal for CF_3 could not be detected); HRMS (ESI) m/z calcd for $C_{20}H_{17}F_3O_3Na$ $[M+Na]^+$ 385.1022, found 385.1023; $[\alpha]_D$ +15.7 (*c* 1.0, $CHCl_3$).

Synthesis of (*aS*)-**9**-(*R*)-MTPA



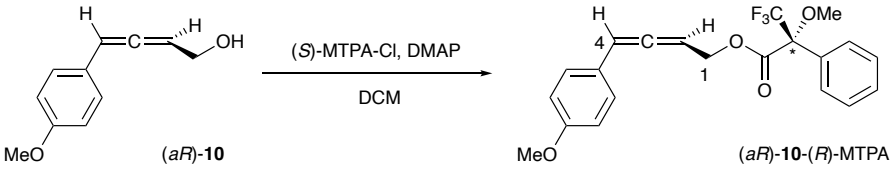
To a solution of (*aS*)-**9** (15 mg, 0.10 mmol) and DMAP (25 mg, 0.20 mmol) in dry DCM (2 mL) was added (*S*)-MTPA-Cl (28 μL, 0.15 mmol) and the mixture was stirred at rt for 30 mins. The mixture was then diluted with Et_2O, washed sequentially with 1 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 10:1 to 3:1) which afforded (*aS*)-**9**-(*R*)-MTPA (7 mg, 19%). (*aS*)-**9**-(*R*)-MTPA: ^{1}H NMR ($CDCl_3$) δ 7.55 (d, ArH, *J* = 7.2 Hz, 2H), 7.43–7.35 (m, ArH, 3H), 7.31–7.20 (m, ArH, 5H), 6.32 (m, H-4, 1H), 5.78 (ddd, H-2, *J* = 6.6, 6.6, 6.6 Hz, 1H), 4.91 (m, H-1, 2H), 3.56 (s, OMe, 3H)., ^{13}C NMR ($CDCl_3$) δ 207.4 (C-3), 166.3 (CH_2-O-<u>C</u>=O), 132.8 (Ar), 132.3 (Ar), 129.6 (Ar), 128.7 (Ar), 128.4 (Ar), 127.5 (Ar), 127.3 (Ar), 127.0 (Ar), 97.0 (C-4), 90.0 (C-2), 84.6 (C*), 63.9 (C-1), 55.5(OMe) (^{13}C NMR signal for CF_3 could not be detected); HRMS (ESI) m/z calcd for $C_{20}H_{17}F_3O_3Na$ $[M+Na]^+$ 385.1022, found 385.1026; $[\alpha]_D$ +64.1 (*c* 1.0, $CHCl_3$).

Synthesis of (*aR*)-**10** ((*aR*)-4-(4′-methoxyphenyl)buta-2,3-dien-1-ol)



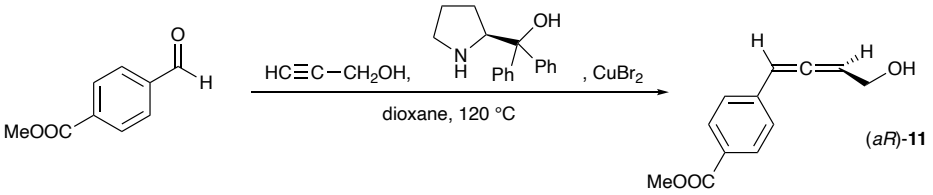
To a solution of *p*-anisaldehyde (134 μL, 1.10 mmol), $CuBr_2$ (32 mg), and (*S*)-α,α-diphenyl-2-pyrrolidinemethanol (185 mg) in dioxane (20 mL) was added propargyl alcohol (65 μL) and the mixture was refluxed at 120 °C overnight. The mixture was then diluted with EtOAc, washed sequentially with 2 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 4:1 to 1:1) which afforded (*aR*)-**10** (50 mg, 26%). Its spectroscopic data spectra were virtually identical to those reported for (±)-**10**.[19] (*aR*)-**10**: $[\alpha]_D$ -146 (*c* 1.0, $CHCl_3$).

Synthesis of (*aR*)-**10**-(*R*)-MTPA



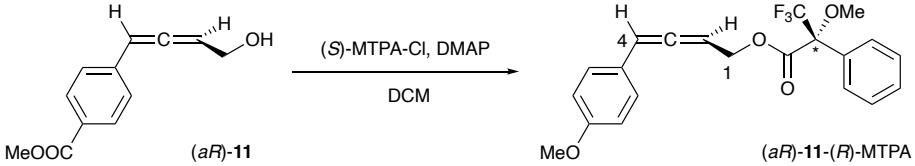
To a solution of (*aR*)-**10** (16 mg, 0.10 mmol) and DMAP (30 mg) in dry DCM (2 mL) was added (*S*)-MTPA-Cl (37 μL) and the mixture was stirred at rt for 30 mins. The mixture was then diluted with Et_2O, washed with 1 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, its ^1H NMR spectrum was measured, which confirmed the enantiomeric excess of (*aR*)-**10** to be >90%ee. The mixture was purified by silica-gel column chromatography (hexane-EtOAc = 10:1 to 4:1), which afforded (*aR*)-**10**-(*R*)-MTPA (15 mg, 38%). (*aR*)-**10**-(*R*)-MTPA: ^1H NMR δ 7.54 (d, ArH, *J* = 7.3 Hz, 2H), 7.43–7.34 (m, ArH, 3H), 7.17 (dd, ArH, *J* = 9.3, 9.3 Hz, 2H), 6.88–6.80 (m, ArH, 2H), 6.27 (dt, H-4, *J* = 6.5, 2.4 Hz, 1H), 5.74 (ddd, H-2, *J* = 6.8, 6.6, 6.6 Hz, 1H), 4.89 (m, H-1, 2H), 3.80 (s, ArO<u>Me</u>, 3H), 3.56 (s, C*OMe, 3H); ^{13}C NMR δ 206.8 (C-3), 166.3 (C=O), 159.2 (Ar), 132.2 (Ar), 129.6 (Ar), 128.6 (Ar), 128.4 (Ar), 127.3 (Ar), 125.1 (Ar), 114.2 (Ar), 96.4 (C-4), 89.9 (C-2), 84.6 (C*), 64.0 (C-1), 55.7 (OMe), 55.3 (OMe) (^{13}C NMR signal for CF_3 could not be detected); HRMS (ESI) m/z calcd for $C_{21}H_{19}F_3O_4Na$ $[M+Na]^+$ 415.1128, found 415.1130; $[\alpha]_D$ +12.6 (*c* 1.0, $CHCl_3$).

Synthesis of (*aR*)-**11** ((*aR*)-methyl 4-(4′-hydroxybuta-1′,2′-dien-1′-yl)-benzoate)



To a solution of methyl-4-formylbenzoate (163 mg, 1.00 mmol), $CuBr_2$ (30 mg, 0.13 mmol), and (*S*)-α,α-diphenyl-2-pyrrolidinemethanol (170 mg, 0.67 mmol) in dioxane (20 mL) was added propargyl alcohol (59 μL) and the mixture was refluxed at 120 °C overnight. The mixture was then diluted with EtOAc, washed sequentially with 2 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, the mixture was purified by silica-gel column chromatography (hexane-EtOAc = 4:1 to 1:1), which afforded (*aR*)-**11** (83 mg, 41%). (*aR*)-**11**: ^{1}H NMR δ 7.97 (d, ArH, *J* = 8.4 Hz, 2H), 7.35 (d, ArH, *J* = 8.4 Hz, 2H), 6.35 (dt, H-4, *J* = 6.1, 2.9 Hz, 1H), 5.85 (ddd, H-2, *J* = 6.1, 6.1, 6.1 Hz, 1H), 4.30 (m, H-1, 2H), 3.91 (s, COOMe, 3H); ^{13}C NMR ($CDCl_3$) δ 205.4 (C-3), 166.9 (C=O), 138.9 (Ar), 130.0 (Ar), 128.7 (Ar), 126.7 (Ar), 96.6 (C-4), 96.2 (C-2), 60.2 (C-1), 52.1 (OMe); HRMS (ESI) *m/z* calcd for $C_{12}H_{10}O_3$ $[M-H]^-$ 203.0714, found 203.0706; $[\alpha]_D$ -149 (*c* 1.0, $CHCl_3$).

Synthesis of (*aR*)-**11**-(*R*)-MTPA



To a solution of (*aR*)-**11** (4 mg, 0.02 mmol) and DMAP (15 mg, 0.12 mmol) in dry DCM (0.5 mL) at room temperature was added (*S*)-MTPA-Cl (13 μL, 0.07 mmol) and the mixture was stirred at room temperature for 20 mins. The mixture was then diluted with Et_2O, washed with 1 M HCl aq, sat $NaHCO_3$ aq, and brine, and then dried over $MgSO_4$. After removal of the solvent, its ^{1}H NMR spectrum was measured, which confirmed the enantiomeric excess of (*aR*)-**11** to be >90%ee. The mixture was purified by silica-gel column chromatography (hexane-EtOAc = 10:1 to 4:1) which afforded (*aR*)-**11**-(*R*)-MTPA (2 mg, 24%). (*aR*)-**11**-(*R*)-MTPA: 1H NMR ($CDCl_3$) δ 7.96 (d, ArH, *J* = 8.2 Hz, 2H), 7.53 (d, ArH, *J* = 6.8 Hz, 2H), 7.43–7.36 (m, ArH, 3H), 7.30 (d, ArH, *J* = 8.3 Hz, 2H), 6.33 (dt, H-4, *J* = 6.4, 2.4 Hz, 1H), 5.81 (ddd, H-2, *J* = 6.6, 6.6, 6.6 Hz, 1H), 4.92 (m, H-1, 2H), 3.91 (s, COOMe, 3H), 3.55 (s, OMe, 3H), ^{13}C NMR ($CDCl_3$) δ 208.0 (C-3), 166.8 (PhC=O), 166.3 (CH_2-O-C=O) 130.0 (Ar), 129.7 (Ar), 129.1 (Ar), 128.8 (Ar), 128.4 (Ar), 128.4 (Ar), 127.3 (Ar), 126.9 (Ar), 96.8 (C-4), 90.6 (C-2), 84.6 (C*), 63.4 (C-1), 55.7 (OMe), 52.3 (OMe) (^{13}C NMR signal for CF_3 could not be detected); HRMS (ESI) m/z calcd for $C_{22}H_{19}F_3O_5Na$ $[M+Na]^+$ 443.1077, found 443.1081; $[\alpha]_D$ -84.9 (*c* 1.0, $CHCl_3$).

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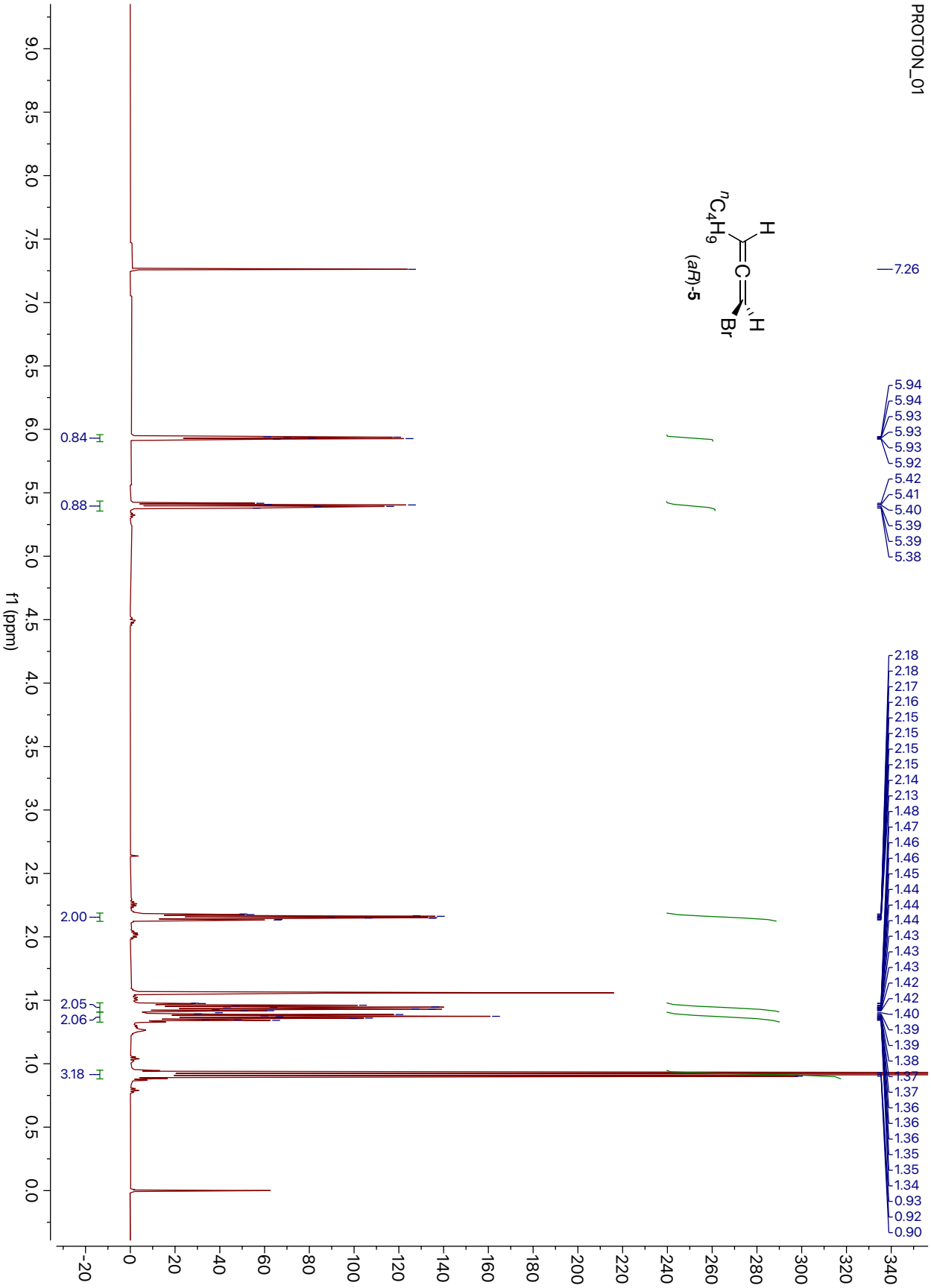
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5.38
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2.18
2.17
2.16
2.15
2.15
2.15
2.15
2.14
2.13
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1.45
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1.36
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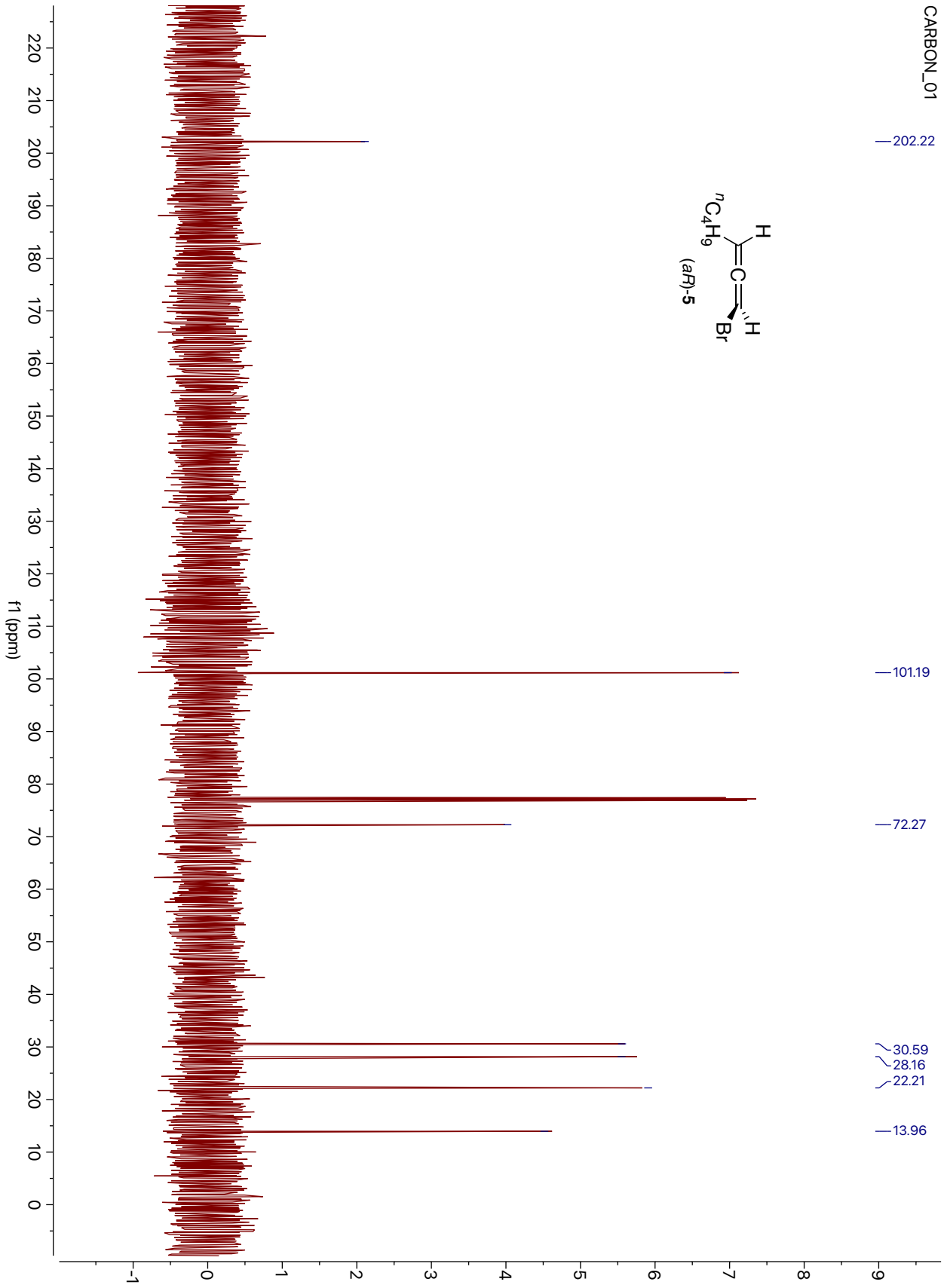
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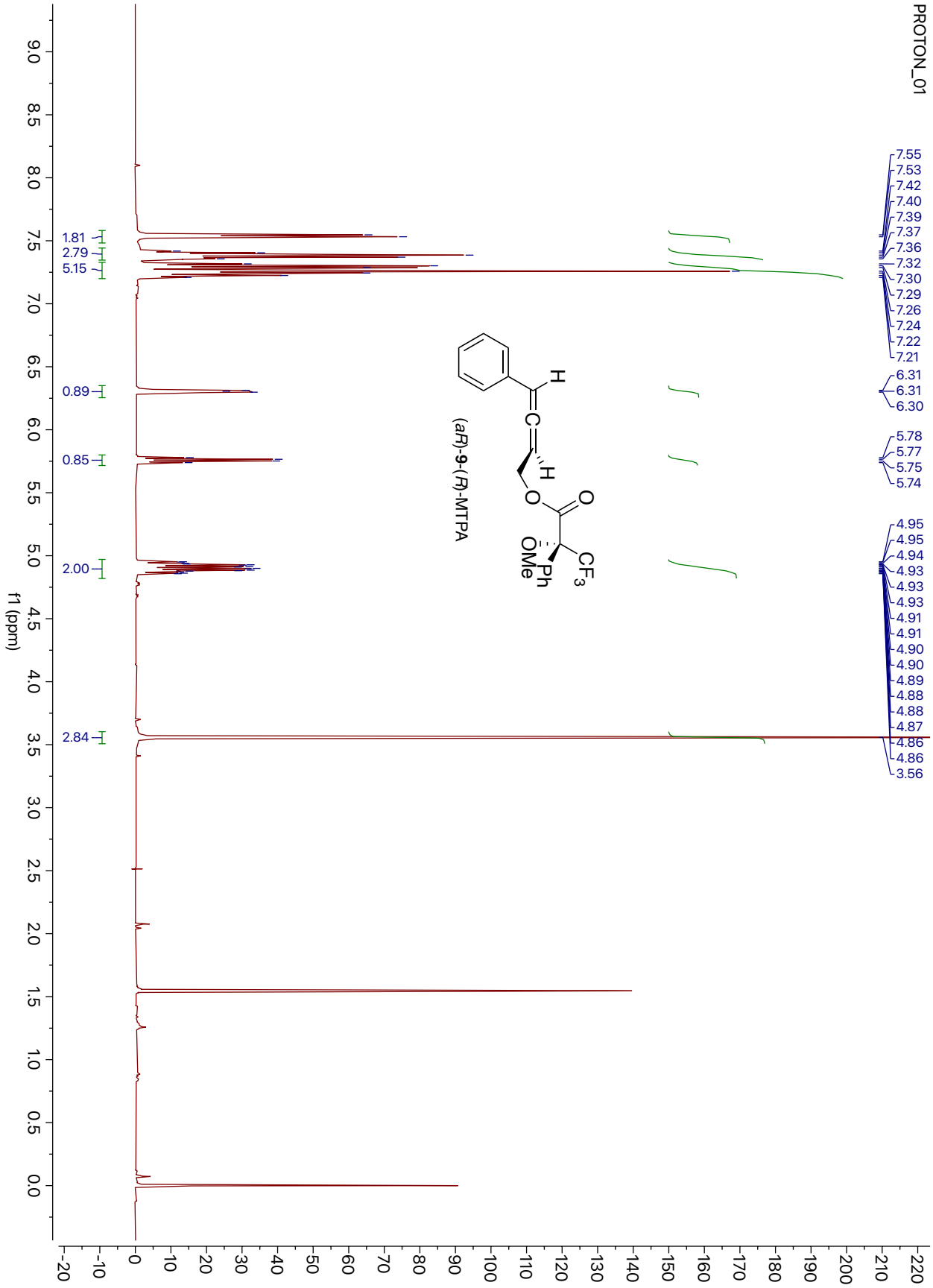
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7.36
7.32
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7.29
7.26
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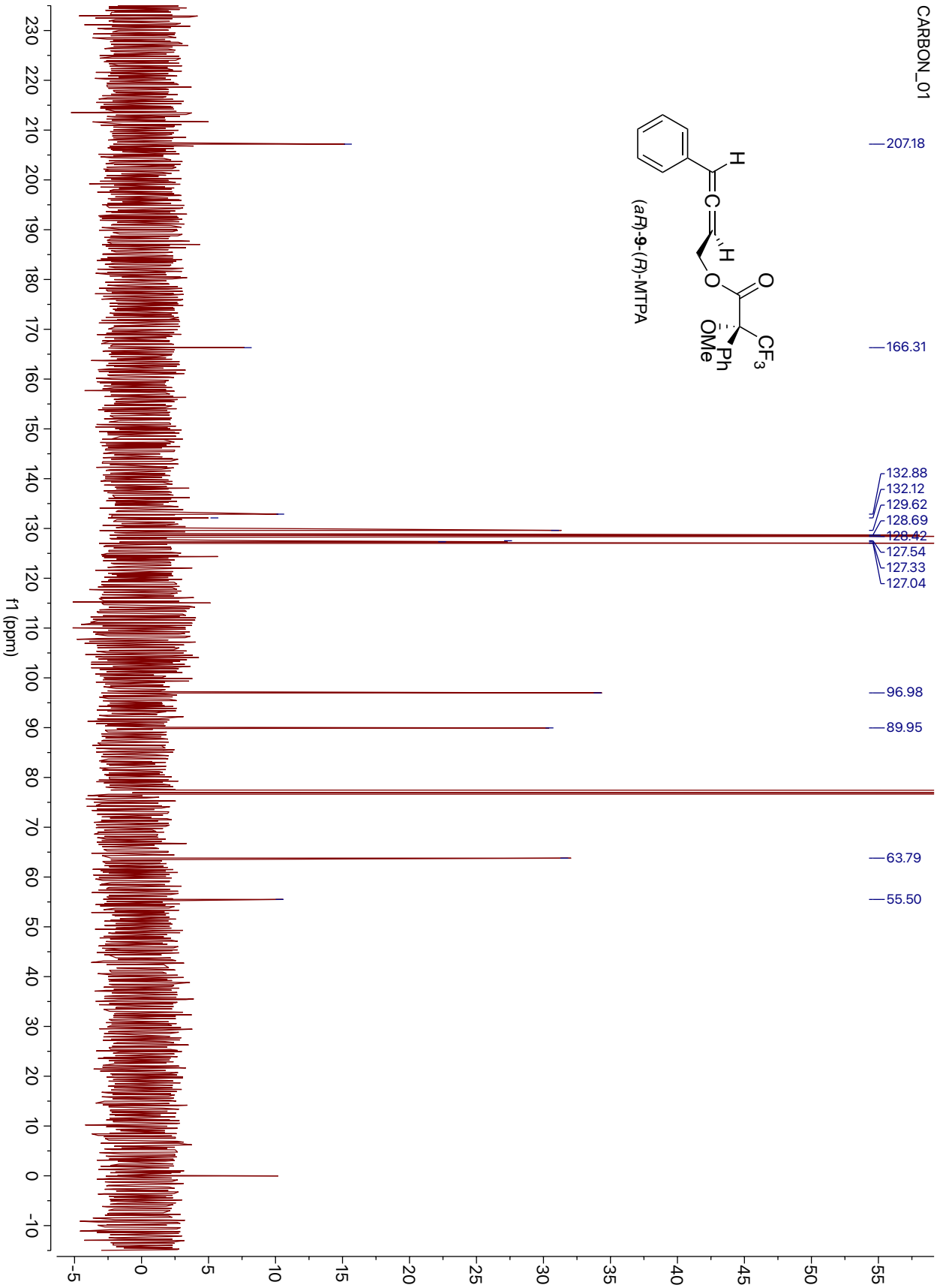
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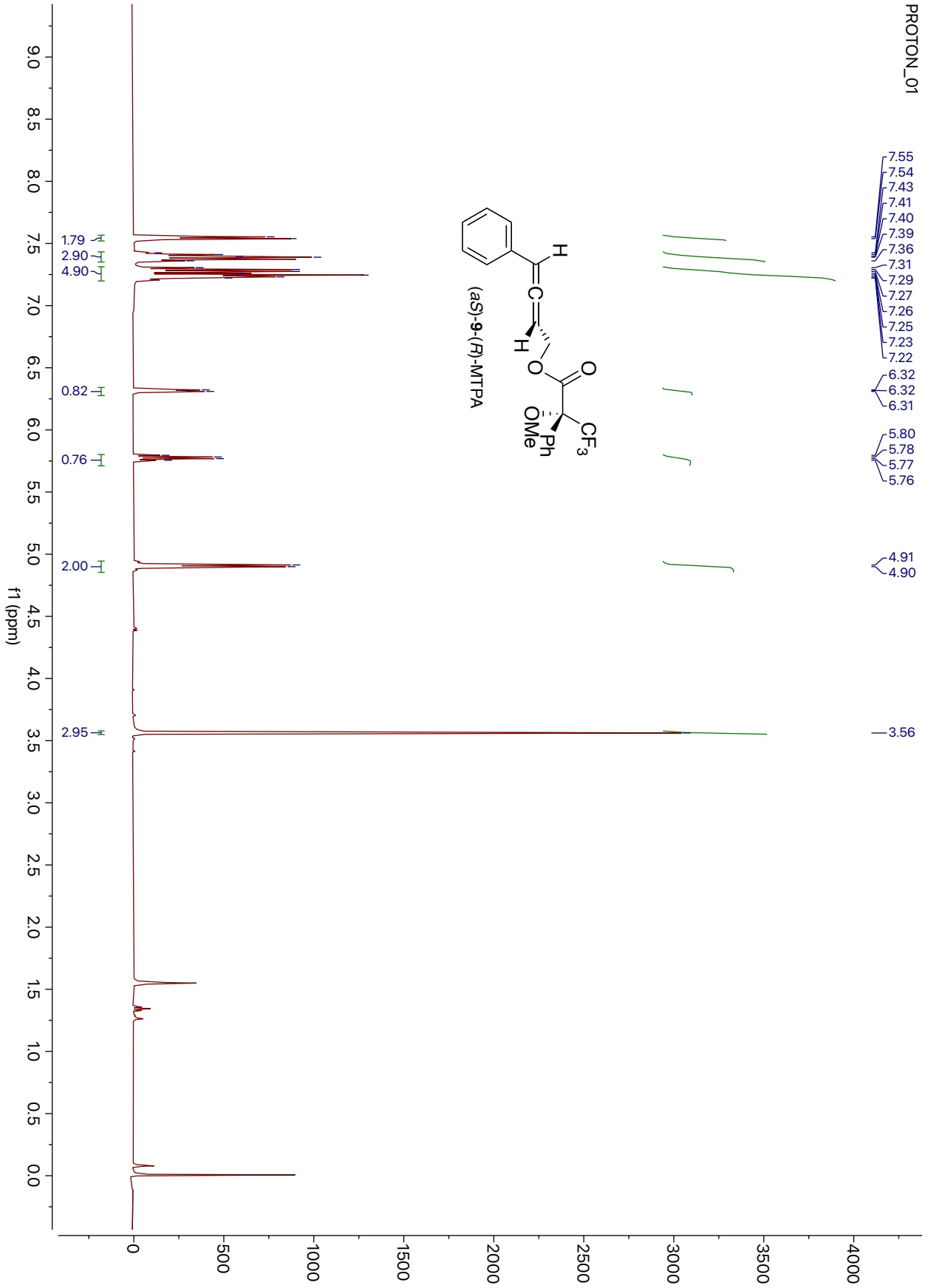
f1 (ppm)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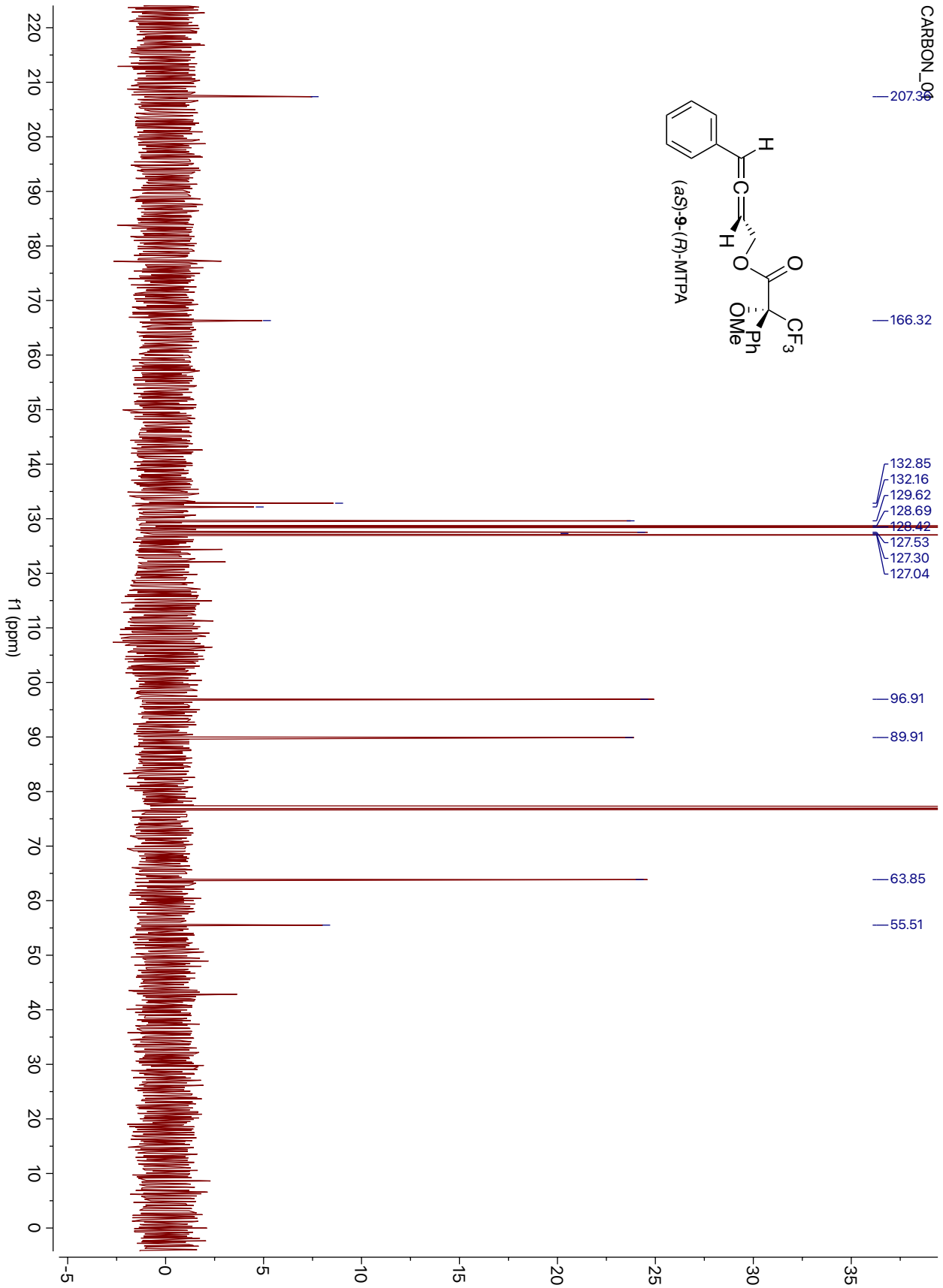
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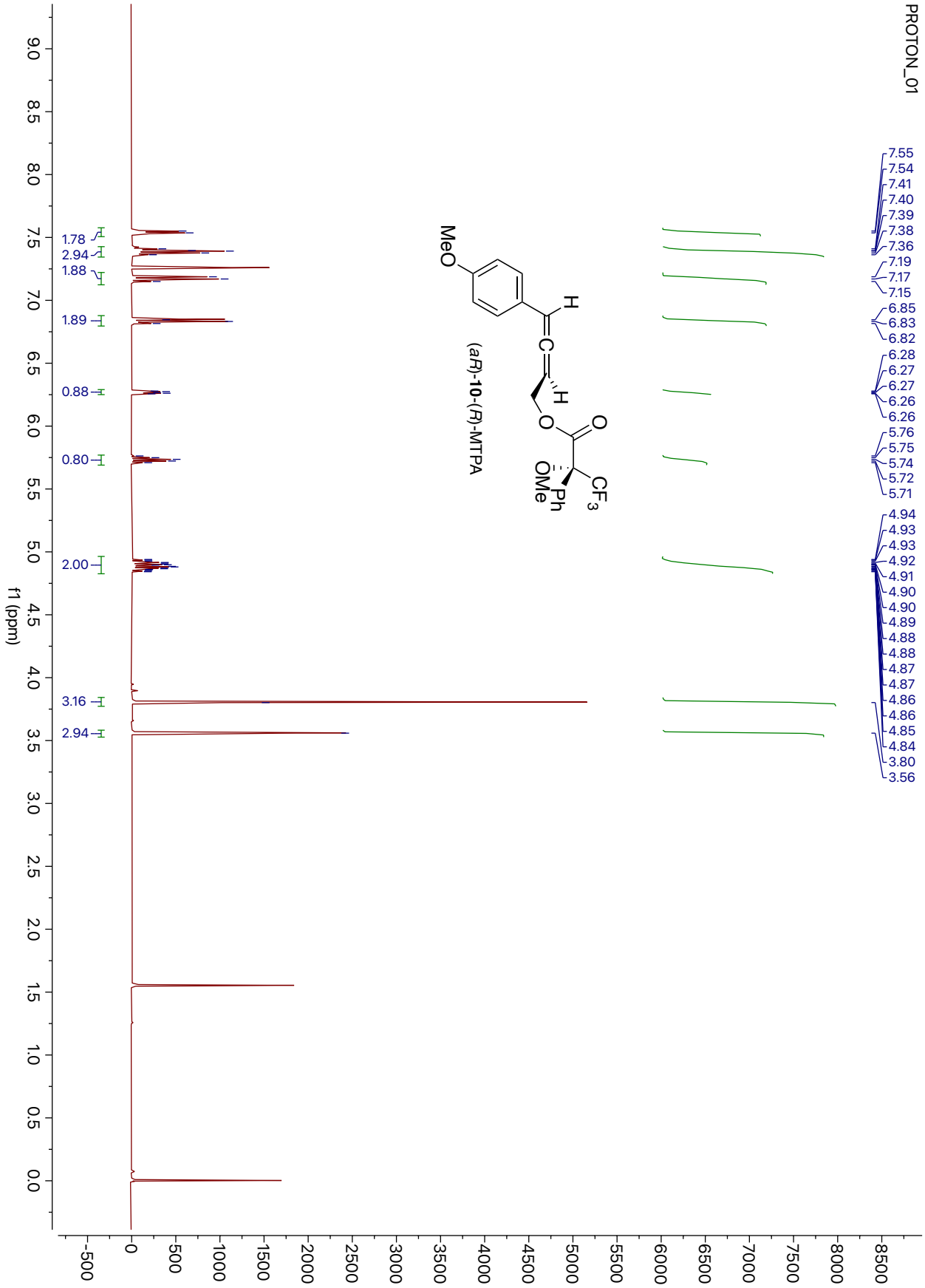
f1 (ppm)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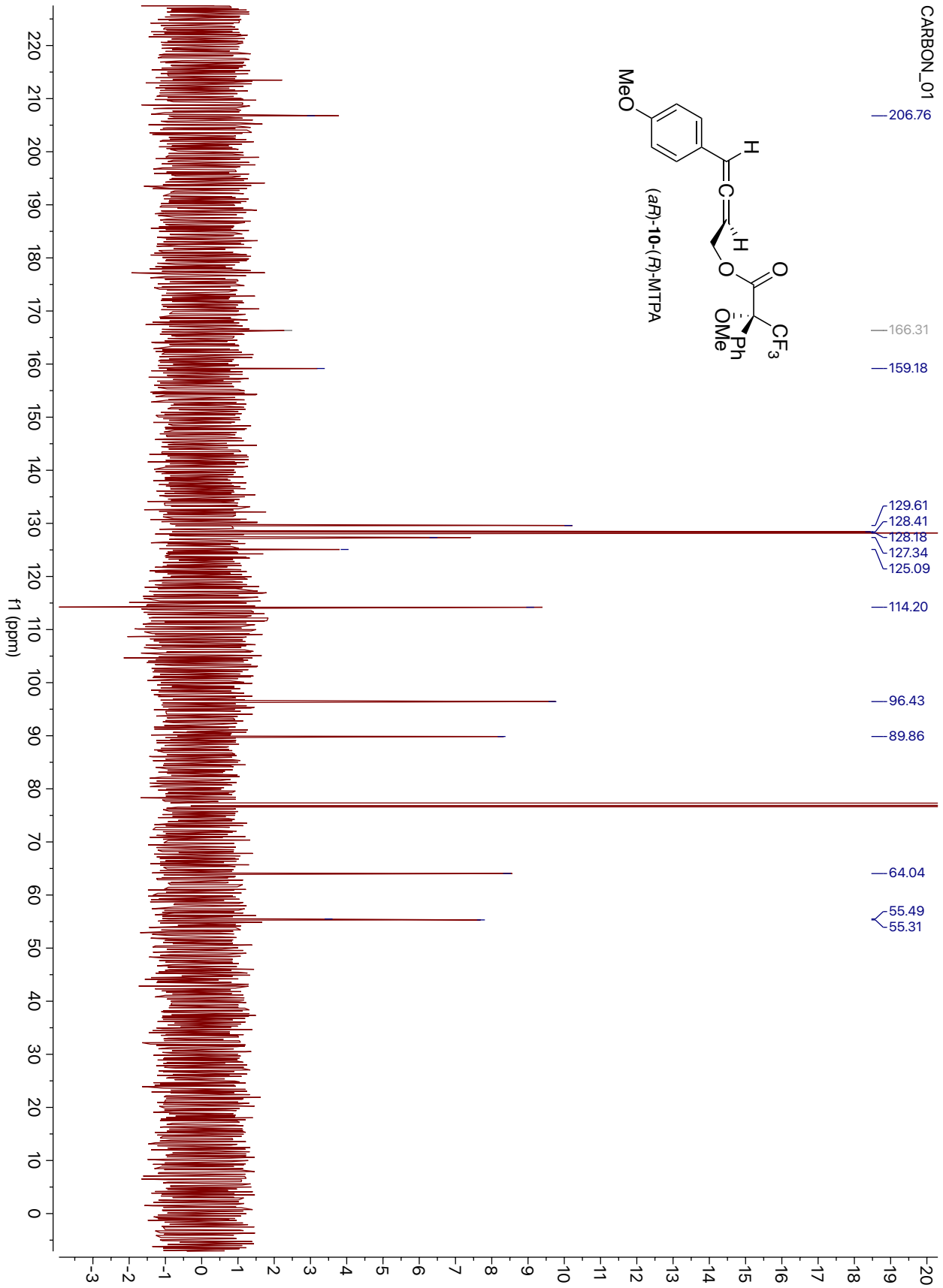
f1 (ppm)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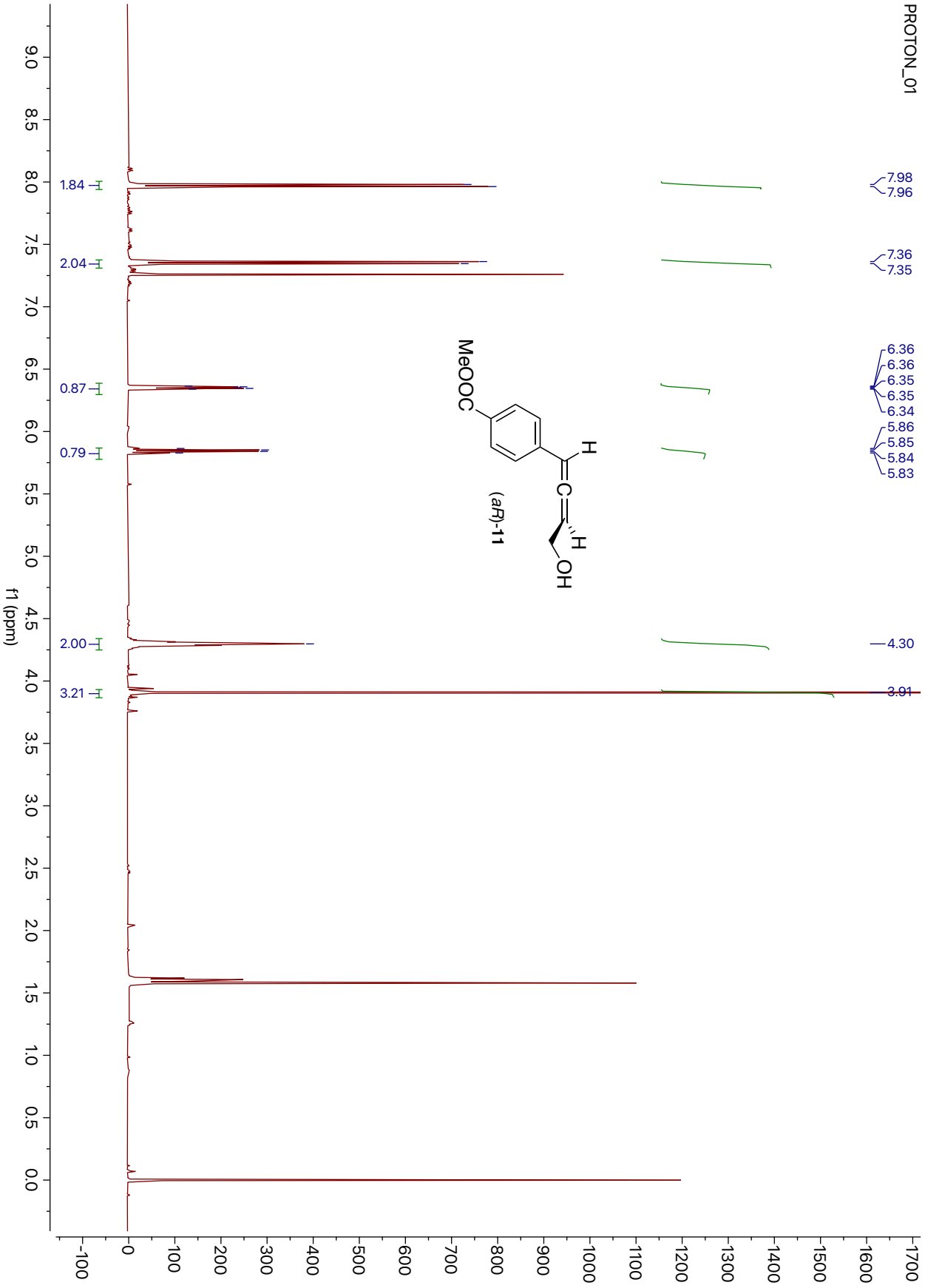
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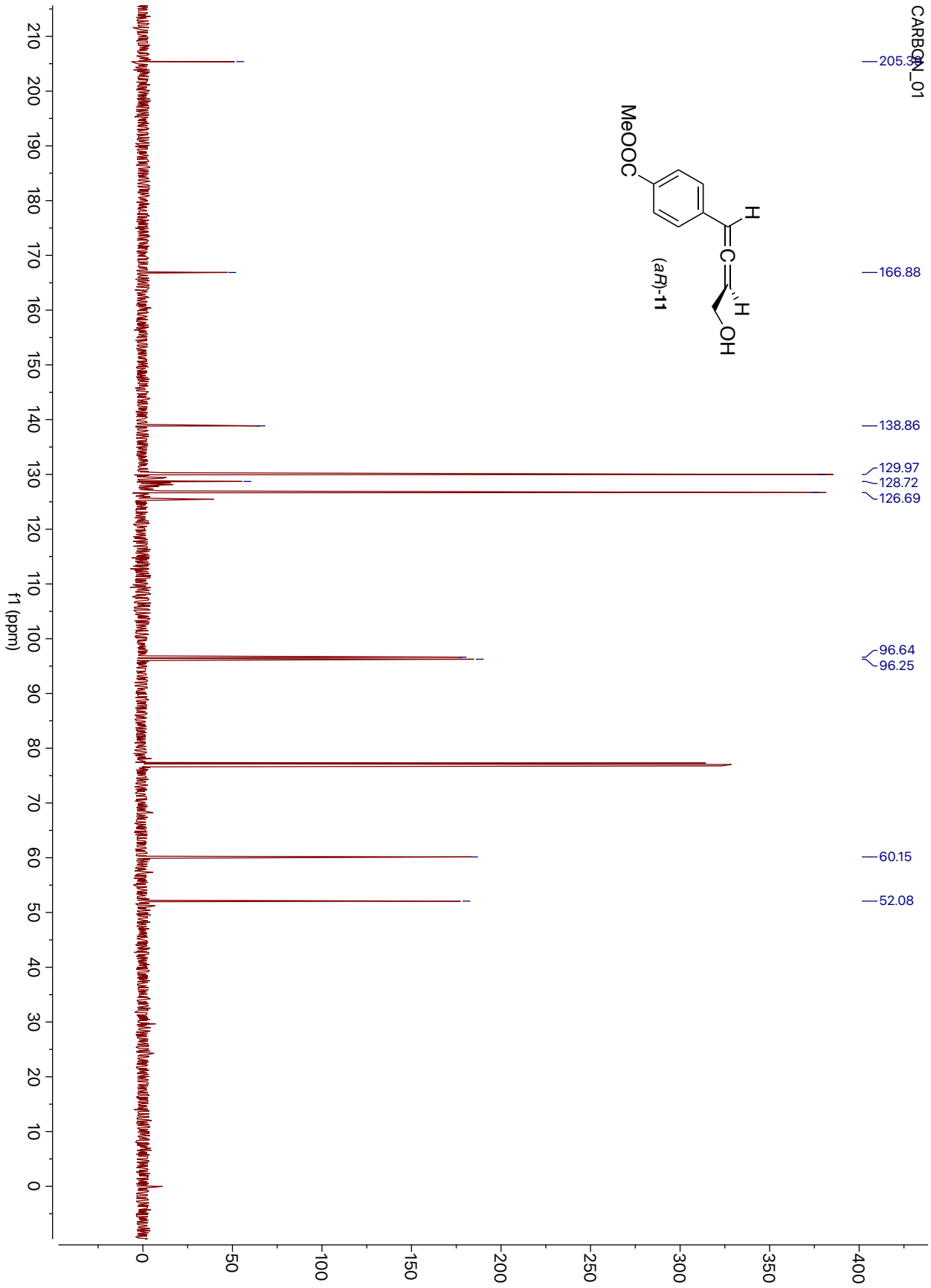
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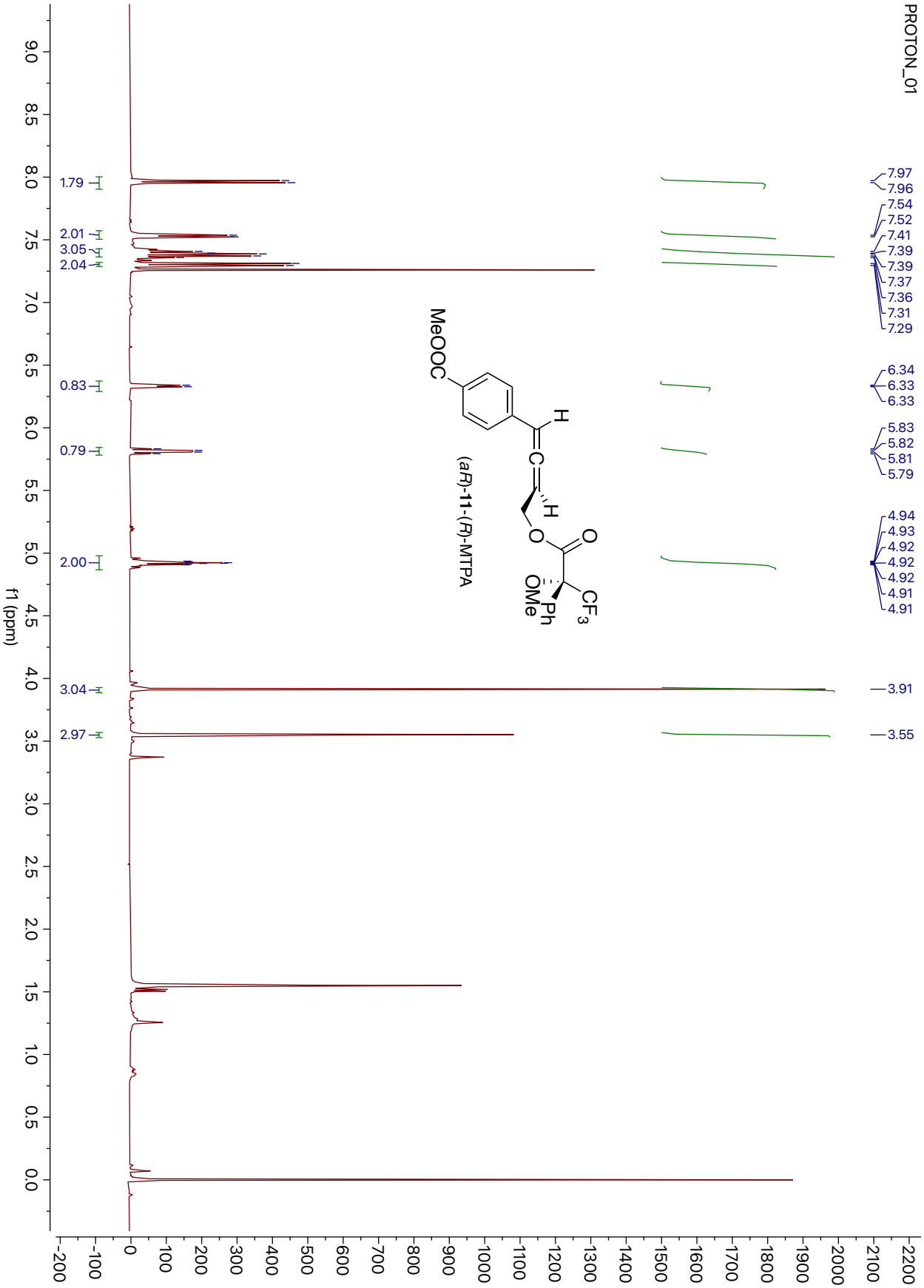
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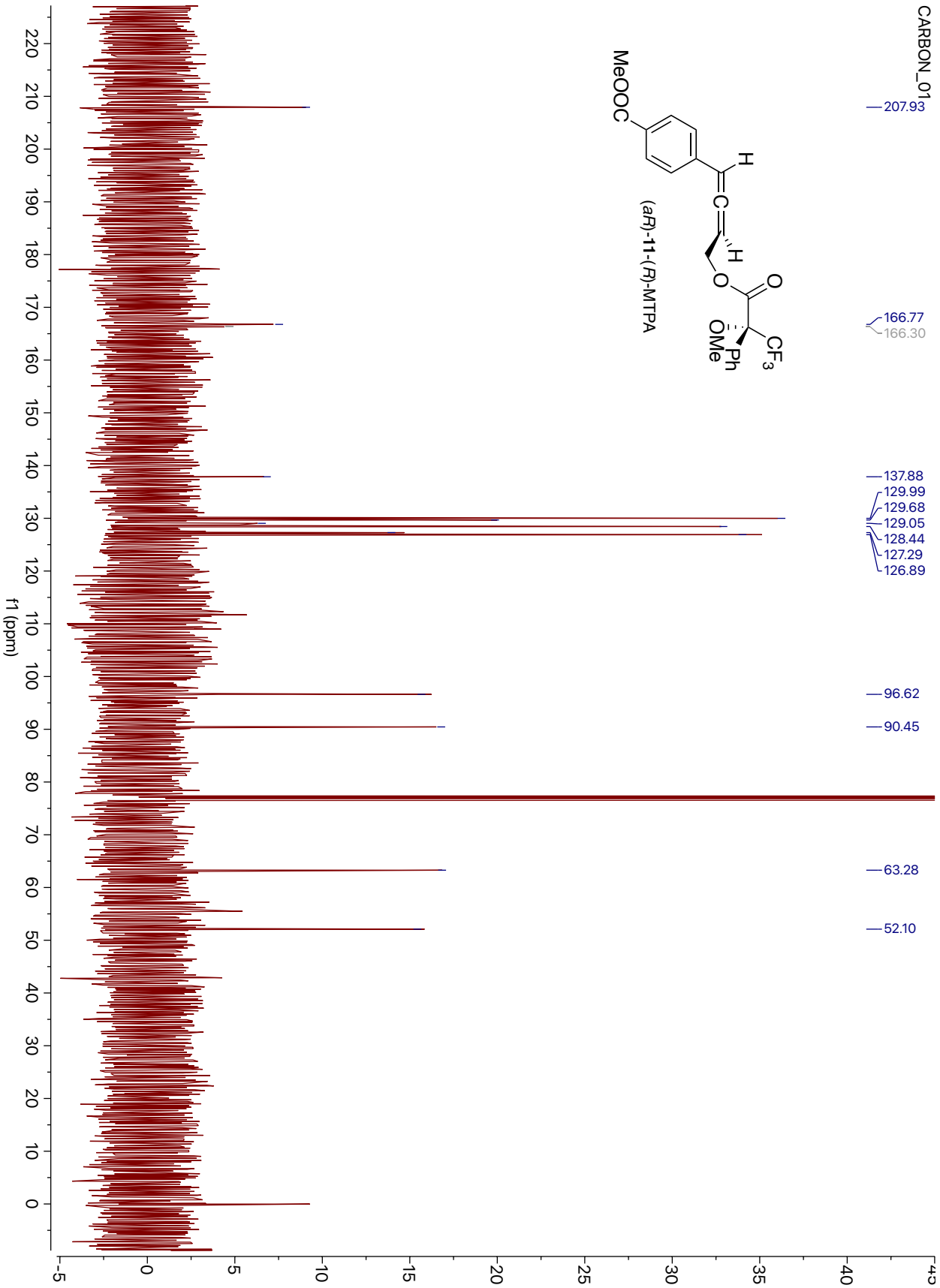
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MeOOC
(aR)-11-(R)-MTPA
f1 (ppm)

Cartesian Coordinates of Selected Conformers

The most stable conformer of (*aR*)-**1** optimized at B3LYP/6-311G(d,p)

C	2,880026	0,862279	1,064263
C	3,252978	1,107258	-0,396996
C	2,278792	2,209872	-0,803583
C	1,000167	1,797579	-0,032917
O	1,451261	1,073283	1,129453
H	3,363602	1,609936	1,706072
H	3,074256	0,205180	-0,987448
H	4,286770	1,423277	-0,532702
H	2,095408	2,228325	-1,881058
H	0,399086	1,122938	-0,652717
C	3,168209	-0,508774	1,624793
H	2,678201	-0,737028	2,569432
C	3,957612	-1,393603	1,080701
C	4,751014	-2,267750	0,546481
H	5,812547	-2,343894	0,734196
Br	4,131343	-3,606055	-0,697954
O	2,821680	3,448168	-0,360375
H	2,282112	4,156541	-0,731049
C	0,130476	2,945886	0,467553
H	0,725900	3,642385	1,053009
Br	0,459988	4,040670	-1,108495
C	1,058916	2,491692	1,314738
H	0,601539	1,876300	2,101302
O	1,625838	3,674397	1,879712
H	2,398684	3,409492	2,388694
C	2,094480	1,676700	0,595046
H	2,678051	2,205244	-0,154140
C	2,331628	0,381288	0,855189
H	1,722462	-0,115031	1,605514
C	3,350750	-0,398344	0,172958
H	3,938231	0,131945	-0,569233
C	3,610350	-1,697048	0,386768
Br	5,017247	-2,510308	-0,664217
C	2,939874	-2,644000	1,338906

H	2,353432	-2,059817	2,053077
H	3,709973	-3,162026	1,919018
C	2,030680	-3,678328	0,653688
H	1,226739	-3,186327	0,101420
H	2,595547	-4,296871	-0,046169
H	1,579387	-4,336327	1,400245

The most stable conformer of (*aR*)-**2** optimized at B3LYP/6-311G(d,p)

C	2,201675	1,233304	0,139936
C	2,378984	2,257985	-1,006777
C	1,276207	3,294600	-0,744732
C	0,157270	2,387017	-0,209626
O	0,872022	1,483400	0,670257
H	2,907530	1,412190	0,953581
H	2,222792	1,779258	-1,977264
H	3,368732	2,713698	-1,007218
H	0,979083	3,831708	-1,643822
H	-0,285597	1,815494	-1,033927
C	2,311754	-0,203162	-0,303730
H	1,576005	-0,539076	-1,033154
C	3,223138	-1,032933	0,127109
C	4,135221	-1,844294	0,561467
H	4,029570	-2,492535	1,419841
Br	5,853687	-2,023419	-0,290305
O	1,668700	4,288204	0,190724
H	1,906741	3,853379	1,017484
C	-0,951388	3,055106	0,597257
C	-1,861929	2,082219	1,388762
C	-2,451915	0,982635	0,539797
H	-2,968630	1,303957	-0,360986
C	-2,400226	-0,317608	0,857532
H	-1,898432	-0,597054	1,777212
C	-2,991388	-1,361495	0,036476
H	-3,484592	-1,034288	-0,873181
C	-2,971428	-2,673393	0,314154
Br	-3,816025	-3,870281	-0,954680
C	-2,364851	-3,371852	1,495978

H	-2,144802	-2,623253	2,261504
H	-3,111352	-4,046416	1,926952
C	-1,087874	-4,163617	1,168235
H	-0,309727	-3,503449	0,777260
H	-1,283555	-4,936667	0,422697
H	-0,703784	-4,650169	2,068371
H	-0,534743	3,782354	1,289076
Br	-2,038521	4,152197	-0,662503
H	-2,681687	2,683996	1,795496
O	-1,147318	1,606248	2,517589
H	-0,320221	1,229556	2,182577

The most stable conformer of (*aS*)-**1** optimized at B3LYP/6-311G(d,p)

C	-2,985227	2,242185	0,116847
C	-3,451708	1,915412	-1,310659
C	-3,619971	0,399992	-1,242243
C	-2,427073	-0,004432	-0,338258
O	-2,137964	1,148015	0,481186
H	-3,858572	2,261339	0,783384
H	-2,670513	2,181910	-2,027062
H	-4,383327	2,408130	-1,588794
H	-3,543587	-0,075202	-2,223879
H	-1,548579	-0,214089	-0,957822
C	-2,258420	3,551386	0,251511
H	-2,858227	4,439602	0,055793
C	-1,004920	3,696318	0,584308
C	0,228523	3,877302	0,931919
O	-4,886082	0,141679	-0,648645
H	-5,047294	-0,808348	-0,698315
C	-2,677815	-1,173025	0,609296
H	-3,553543	-0,978981	1,224036
Br	-3,209839	-2,783060	-0,468431
C	-1,495310	-1,478200	1,530204
H	-1,260942	-0,508124	1,989142
O	-1,983331	-2,387728	2,518051
H	-1,242046	-2,622765	3,085321
C	-0,266458	-2,015051	0,855064

H	-0,351865	-3,020821	0,452253
C	0,892460	-1,343482	0,764454
H	0,945803	-0,339682	1,176485
C	2,082897	-1,894232	0,138094
H	1,991743	-2,903173	-0,250390
C	3,259741	-1,262971	0,011786
Br	4,701813	-2,231770	-0,843263
C	3,636629	0,119417	0,456555
H	4,116400	0,637876	-0,379058
H	2,722716	0,676990	0,675698
C	4,567982	0,148967	1,680095
H	4,802179	1,181926	1,948547
H	5,506487	-0,369455	1,474691
H	4,096902	-0,330884	2,541537
H	0,581155	4,006067	1,945098
Br	1,671630	3,942956	-0,353028

The most stable conformer of (*aS*)-**2** optimized at B3LYP/6-311G(d,p)

C	2,398115	0,618550	0,793354
C	2,879964	1,238077	-0,518466
C	2,014104	2,499353	-0,613244
C	0,661717	1,976496	-0,107872
O	0,994048	0,970337	0,881656
H	2,908132	1,092662	1,640403
H	2,673236	0,567086	-1,357172
H	3,947261	1,463771	-0,511435
H	1,929605	2,887403	-1,631674
H	0,132460	1,483482	-0,929683
C	2,523830	-0,878259	0,933235
H	2,000088	-1,314686	1,781640
C	3,221269	-1,650656	0,146145
C	3,917686	-2,417770	-0,632370
O	2,469788	3,506989	0,286140
H	3,219982	3,955989	-0,113567
C	-0,254738	3,009720	0,545273
C	-1,483795	2,417560	1,279372
C	-2,306631	1,483296	0,425614

H	-2,638641	1,882734	-0,529427
C	-2,660966	0,245864	0,795519
H	-2,329794	-0,109018	1,765019
C	-3,471270	-0,630251	-0,034646
H	-3,786656	-0,226691	-0,991444
C	-3,848278	-1,876283	0,286691
Br	-4,916362	-2,850877	-1,005077
C	-3,544169	-2,655179	1,532858
H	-3,170317	-1,959776	2,288867
H	-4,477429	-3,069970	1,926602
C	-2,525490	-3,788953	1,328062
H	-2,348776	-4,313665	2,270419
H	-1,571083	-3,394405	0,970752
H	-2,886428	-4,515983	0,597995
H	0,307934	3,628851	1,237355
Br	-0,850958	4,279977	-0,876343
H	-2,114067	3,266354	1,566243
O	-1,049770	1,836582	2,498285
H	-0,309061	1,253424	2,274075
H	3,538433	-2,919783	-1,511113
Br	5,782591	-2,792484	-0,319428

The most stable conformer of (*aR*)-**3a** optimized at B3LYP/6-311G(d,p)

C	2,027086	-1,168328	-0,256696
C	0,785491	-1,244700	-0,654074
H	0,531793	-1,961465	-1,435481
C	3,271837	-1,084011	0,129328
H	3,604916	-1,717409	0,952261
C	4,309210	-0,160485	-0,468739
H	5,138306	-0,764398	-0,861452
H	3,875477	0,370961	-1,320906
C	4,870877	0,849920	0,545845
H	5,274408	0,307400	1,409082
H	4,047737	1,463402	0,927841
C	5,957780	1,749019	-0,049366
H	6,806074	1,159151	-0,410554
H	6,337502	2,457776	0,691475

H	5,573362	2,327059	-0,895426
C	-0,358521	-0,423267	-0,104109
H	-0,824841	0,129539	-0,926732
H	0,030309	0,311568	0,607504
C	-1,429722	-1,293432	0,576326
H	-0,969679	-1,843764	1,402705
H	-1,799876	-2,035977	-0,136553
C	-2,614525	-0,489529	1,116794
H	-2,285967	0,340716	1,749824
H	-3,245235	-1,116965	1,756904
C	-3,517270	0,067463	0,034274
O	-3,485114	-0,227263	-1,134952
O	-4,405135	0,943127	0,553501
C	-5,342384	1,510302	-0,379829
H	-4,817935	2,060367	-1,162680
H	-5,967405	2,180413	0,206176
H	-5,946098	0,726995	-0,840899

The most stable conformer of (*aS*)-**4** optimized at B3LYP/6-311G(d,p)

H	0,326061	3,236301	1,750188
C	-0,090530	2,657691	0,921161
C	1,211449	0,903279	-0,558345
C	-1,046846	0,384745	0,419925
C	0,231461	-0,203219	-0,160785
C	-0,806480	1,419499	1,496435
C	1,042626	2,269724	-0,026534
H	0,713478	-0,813777	0,610873
H	-0,172935	0,980648	2,278894
H	1,913482	2,922277	-0,017104
H	-1,742541	1,737282	1,956371
C	2,572353	0,432404	-1,051376
H	3,072929	1,298414	-1,496810
H	2,408244	-0,287480	-1,854160
C	3,432356	-0,142879	0,044455
H	3,830650	0,589122	0,745647
C	3,762681	-1,426164	0,237898
C	4,674865	-1,824697	1,371876

H	5,564043	-2,341537	0,991965
H	4,174510	-2,525283	2,050511
H	5,005880	-0,961732	1,952877
C	3,295767	-2,570311	-0,627675
H	2,931188	-3,391922	-0,001393
H	4,129745	-2,974386	-1,214127
H	2,491962	-2,296029	-1,309310
O	0,601475	1,940680	-1,360271
O	0,010945	-1,085336	-1,248966
H	-0,529945	-0,613320	-1,894168
O	-0,987977	3,533929	0,257592
H	-1,155841	3,141382	-0,609061
C	-2,228222	0,052552	-0,023898
C	-3,415292	-0,290809	-0,469248
H	-3,856301	0,293648	-1,275793
C	-4,219352	-1,417389	0,030697
C	-5,433071	-1,651949	-0,486220
H	-6,045669	-2,477282	-0,142750
H	-5,847068	-1,024077	-1,267740
C	-3,622260	-2,278948	1,112160
H	-2,673702	-2,711244	0,779128
H	-4,298242	-3,089097	1,389071
H	-3,404499	-1,687252	2,006905

The most stable conformer of (*aR*)-**5** optimized at B3LYP/6-311G(d,p)

C	1,795502	1,113589	0,317806
C	2,706869	0,054570	-0,326899
H	2,363587	2,044610	0,442930
H	2,141592	-0,876308	-0,448605
H	2,984140	0,380507	-1,337271
C	0,571122	1,406718	-0,514837
C	-0,663430	1,225300	-0,129351
C	-1,886353	1,050161	0,259781
H	-2,500533	1,788278	0,755192
Br	-2,832005	-0,617771	-0,000397
H	1,490372	0,789131	1,316121
H	0,744574	1,787838	-1,521628

C	3,977494	-0,216452	0,486605
H	4,535407	0,719955	0,607956
H	3,696818	-0,537104	1,496872
C	4,883978	-1,273028	-0,150927
H	5,209693	-0,965051	-1,149306
H	5,779568	-1,444758	0,452021
H	4,363862	-2,230259	-0,253461

The most stable conformer of (*aR*)-**6** optimized at B3LYP/6-311G(d,p)

C	-0,668382	0,867934	0,571080
C	0,504955	1,311672	0,182593
H	0,578417	2,364427	-0,087614
C	-1,828965	0,442690	0,948719
H	-2,201613	0,437460	1,963461
C	1,746065	0,530981	0,076948
C	4,151881	-0,894951	-0,152067
C	1,792808	-0,842388	0,364891
C	2,924528	1,173588	-0,327735
C	4,117924	0,466665	-0,441095
C	2,983973	-1,545761	0,250916
H	0,887656	-1,351642	0,675813
H	2,901277	2,234416	-0,554483
H	5,019970	0,979267	-0,755424
H	3,005020	-2,606293	0,475138
H	5,080049	-1,447902	-0,240224
Br	-3,131986	-0,276352	-0,294919

The most stable conformer of (*aR*)-**7** optimized at B3LYP/6-311G(d,p)

C	0,000020	1,299699	0,000406
C	1,176121	1,307555	-0,576591
H	1,327934	1,993918	-1,409940
C	-1,176022	1,307101	0,577528
H	-1,327372	1,991939	1,412215
C	-2,339666	0,476128	0,213603
C	-4,595751	-1,072525	-0,424134
C	-2,296489	-0,453828	-0,836747
C	-3,532696	0,613407	0,935654

C	-4,651133	-0,153512	0,620036
C	-3,412346	-1,218394	-1,150517
H	-1,379607	-0,571386	-1,403574
H	-3,581474	1,328581	1,750434
H	-5,565263	-0,032169	1,190487
H	-3,361795	-1,932697	-1,964891
H	-5,464981	-1,671061	-0,671883
C	2,339696	0,476218	-0,213272
C	4,595662	-1,073069	0,423349
C	2,296178	-0,455117	0,835841
C	3,533011	0,614560	-0,934649
C	4,651387	-0,152679	-0,619590
C	3,411975	-1,219997	1,149057
H	1,379074	-0,573504	1,402136
H	3,582058	1,330812	-1,748465
H	5,565739	-0,030504	-1,189508
H	3,361155	-1,935375	1,962471
H	5,464845	-1,671852	0,670665

The most stable conformer of (*aR*)-**8** optimized at B3LYP/6-311G(d,p)

C	-1,145701	-0,742013	-0,648419
C	0,025650	-1,244632	-0,349936
H	0,084649	-2,324274	-0,218152
C	-2,320926	-0,243067	-0,937005
H	-2,640968	-0,126359	-1,970178
C	1,283935	-0,498626	-0,169882
C	3,716806	0,854660	0,194527
C	2,445651	-1,195934	0,187813
C	1,361922	0,891812	-0,344582
C	2,566062	1,559226	-0,163415
C	3,651853	-0,525058	0,368780
H	2,400502	-2,271369	0,324532
H	0,473010	1,444787	-0,627161
H	2,610179	2,633529	-0,303043
H	4,540351	-1,081310	0,645432
H	4,655110	1,378931	0,334491
C	-3,327820	0,212377	0,073629

O	-4,383135	0,676427	-0,303210
C	-2,985387	0,071349	1,543030
H	-2,833308	-0,981042	1,798784
H	-3,801561	0,479085	2,137152
H	-2,055158	0,596044	1,776578

The most stable conformer of (*aR*)-**9** optimized at B3LYP/6-311G(d,p)

C	1,399117	-0,488387	0,439551
C	0,256771	-1,096610	0,226822
H	0,270578	-2,182546	0,144128
C	2,536530	0,118342	0,638184
H	2,889911	0,291577	1,654218
C	-1,065455	-0,458660	0,092569
C	-3,618348	0,686545	-0,173466
C	-2,191316	-1,258845	-0,144413
C	-1,242526	0,929944	0,194979
C	-2,504424	1,494214	0,063315
C	-3,456253	-0,692167	-0,276510
H	-2,071497	-2,334394	-0,225234
H	-0,381559	1,562544	0,380083
H	-2,623129	2,568985	0,145700
H	-4,314578	-1,328943	-0,459687
H	-4,602046	1,130396	-0,275806
C	3,459278	0,589470	-0,464927
H	3,603520	1,670538	-0,390639
H	3,012439	0,373642	-1,442799
O	4,763324	0,029166	-0,340315
H	4,669530	-0,928203	-0,384068

The most stable conformer of (*aR*)-**10** optimized at B3LYP/6-311G(d,p)

C	2,397820	0,501371	-0,419760
C	1,289179	1,173474	-0,219230
H	1,371556	2,252869	-0,096697
C	3,501156	-0,169561	-0,607716
H	3,875870	-0,329927	-1,618498
C	-0,074319	0,623577	-0,146879
C	-2,712524	-0,361834	0,001619

C	-0,345942	-0,748260	-0,302074
C	-1,155474	1,477906	0,082203
C	-2,464872	1,002616	0,157933
C	-1,637253	-1,233587	-0,229830
H	0,473634	-1,434764	-0,482641
H	-0,976598	2,541217	0,204950
H	-3,271483	1,700695	0,336963
H	-1,849546	-2,289226	-0,349377
C	4,358323	-0,736217	0,502829
H	4,442164	-1,820574	0,391551
H	3,893551	-0,530186	1,474523
O	5,697233	-0,250458	0,440515
H	5,655986	0,709243	0,507792
O	-3,943801	-0,942584	0,054989
C	-5,073622	-0,113353	0,286277
H	-5,007023	0,395644	1,254406
H	-5,935417	-0,778727	0,289210
H	-5,194970	0,631282	-0,508438

The most stable conformer of (*aR*)-**11** optimized at B3LYP/6-311G(d,p)

C	-3,149203	0,431676	0,421272
C	-2,151568	1,260424	0,220954
H	-2,385199	2,317318	0,102574
C	-4,141823	-0,392535	0,606741
H	-4,484777	-0,608809	1,618056
C	-0,725518	0,903171	0,143746
C	2,016056	0,296061	-0,015515
C	0,222134	1,911333	-0,088980
C	-0,272726	-0,417507	0,296394
C	1,077472	-0,718330	0,218282
C	1,574925	1,613176	-0,168029
H	-0,110221	2,937073	-0,208264
H	-0,991981	-1,207715	0,478758
H	1,417199	-1,738552	0,337651
H	2,308550	2,389173	-0,347716
C	-4,909376	-1,074892	-0,505568
H	-4,821751	-2,159487	-0,402108

H	-4,489257	-0,791823	-1,477988
O	-6,304820	-0,803018	-0,427887
H	-6,418569	0,149389	-0,512482
C	3,477315	0,032040	-0,109299
O	4,317071	0,878911	-0,309436
O	3,775664	-1,276300	0,055242
C	5,172023	-1,607947	-0,022310
H	5,224643	-2,683657	0,130645
H	5,733960	-1,081554	0,750794
H	5,575819	-1,338113	-0,999396

The most stable conformer of (*aR*)-**7**-OMe optimized at B3LYP/6-311G(d,p)

H	-0.583076	-0.446433	-1.299357
C	-1.466779	-0.156808	-0.74176
C	-3.746419	0.575452	0.685383
C	-1.383004	0.903476	0.179384
C	-2.653851	-0.83326	-0.945601
C	-3.8082	-0.473661	-0.233041
C	-2.540462	1.248968	0.880638
H	-2.721829	-1.650418	-1.653644
H	-2.50506	2.063164	1.597305
H	-4.618388	0.876935	1.249906
C	-0.133035	1.644956	0.420004
C	1.025188	1.441367	-0.158114
H	-0.194953	2.445337	1.158047
C	2.185185	1.253195	-0.737982
H	2.39257	1.804487	-1.65566
C	3.264889	0.360179	-0.274361
C	5.362843	-1.318853	0.549515
C	3.146696	-0.416563	0.888672
C	4.452518	0.27804	-1.013624
C	5.492428	-0.553364	-0.606043
C	4.184147	-1.245681	1.294311
H	2.232935	-0.363602	1.470097
H	4.559039	0.872781	-1.915161
H	6.403527	-0.602303	-1.192042
H	4.075646	-1.839441	2.195314

O	-4.925073	-1.203871	-0.508735
C	-6.126651	-0.889073	0.18011
H	-6.015711	-1.020455	1.262355
H	-6.874351	-1.58769	-0.191684
H	-6.453479	0.135629	-0.029606
H	6.170752	-1.967241	0.869057