Supporting Information

Stereoselective Synthesis of Protected 1,2-Diols and 1,2,3-Triols by a Tandem Hydroboration-Coupling Sequence

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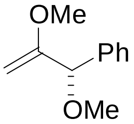
General. ^{1}H and ^{13}C NMR: Bruker Avance 400, spectra were recorded at 295 K in $CDCl_3$; chemical shifts are calibrated to the residual proton and carbon resonance of the solvent: $CDCl_3$ (δH 7.25, δC 77.0 ppm), C_6D_6 (δH, 7.16, δC 128.0 ppm). IR: Jasco FT/IR-430. Optical rotation: Jasco polarimeter P-1020, reported in degree $[\alpha]_D$ (c [g/100 mL], solvent). EI-MS: Finnigan Triple-Stage-Quadrupol (TSQ-70). HRMS (FT-ICR): Bruker Daltonic APEX 2 with electron spray ionization (ESI). Flash chromatography: Merck silica gel 43-60 µm; Machery Nagel aluminium oxide 90 active basic (Al_2O_3, 63-200 µm), Thin-layer chromatography Machery-Nagel Polygram Sil G/UV_{254}. All solvents used in the reactions were purified before use. Dry diethyl ether, tetrahydrofuran, and toluene were distilled from sodium and benzophenone, whereas dry dichloromethane, dimethylformamide, pyridine, and triethylamine were distilled from CaH_2. Petroleum ether with a boiling range of 40-60^{o}C was used. Reactions were generally run under nitrogen atmosphere. All commercially available compounds (Acros, Aldrich, Fluka, Merck) were used as received unless stated otherwise. Assignments of ^{1}H and ^{13}C resonances for complicated structures were confirmed by 2D experiments.

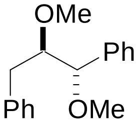
General Procedure 1 for Petasis Olefination: To a stirred solution of the substrate (1 equiv, 0.25 M) in dry THF was added the Petasis reagent (3 equiv, solution in toluene (10 % wt)). The resulting orange reaction mixture was warmed to 65 °C and stirred in the dark under an argon atmosphere till more than 90% of the starting material was consumed (as indicated by TLC). The solution was cooled to room temperature and the titanium compounds were precipitated by addition of a large excess of petroleum ether (ca. 50 mL/mmol of substrate). The resulting heterogeneous mixture was poured onto a basic alumina column and eluted quickly. In order to ensure that the entire product was out of the column, the alumina bed was flushed with a petroleum ether/ethyl acetate (4:1) mixture. The column fractions were pooled together and concentrated. In cases where the stability of the product was good, it was column chromatographed on alumina to obtain the pure compound.

General procedure 2 for the tandem hydroboration-Suzuki coupling reaction: A THF solution of the substrate (1 equiv, 0.33 M) in a Schlenk flask was thoroughly degassed by freeze-pump-thaw method. Then 9-BBN (1.2 equiv, 0.5 M solution in THF) was added at 0 °C under an argon atmosphere. The resulting reaction mixture was allowed to stir at room temperature for about 6 hours. Meanwhile, in a separate Schlenk flask, a solution of the halide (or triflate) (1.2 equiv), triphenyl arsine (0.05 equiv), cesium carbonate (2 equiv), water (30 equiv), in DMF (2 mL/ mmol of halide (or triflate)) was degassed by the same method. For the coupling of triflate **21**, KBr (1.2 equiv) was added at this point. This flask was purged with argon and under a continuous flow of argon, $PdCl_2$(dppf) (0.05 equiv) was added. To the resulting red suspension was added the above mixture from the hydroboration reaction. This was then stirred under argon at room temperature for a further 14-16 hours. The reaction was worked up by addition of saturated NH_4Cl solution (15 mL/mmol of substrate). The resulting mixture was poured into a separating funnel and the layers were separated. The aqueous layer was extracted twice with ethyl acetate and the combined organic extracts were washed successively with saturated $Na_2S_2O_3$, water and brine. The organic phase was dried over anhydrous $MgSO_4$, filtered, concentrated under reduced pressure, and flash column chromatographed on silica, eluting with a petroleum ether/ethyl acetate mixture to afford the pure product.



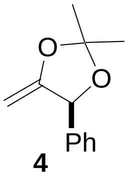
1

[(1*S*)-1,2-Dimethoxyprop-2-enyl]benzene (1): This enol ether was prepared according to general procedure 1. Yield = 67 mg (56%), colorless oil. This compound was utilized immediately after workup. R_f = 0.5 (petroleum ether/ethyl acetate, 9:1). ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.53 (d, *J* = 7.3 Hz, 2H, aromatic), 7.05-7.22 (m, 3H, aromatic), 4.55 (br s, 1H, PhCH), 4.50 (d, *J* = 1.8 Hz, 1H, C=C*H*$_2$), 3.97 (d, *J* = 2.0 Hz, 1H, C=C*H*$_2$), 3.18 (s, 3H, OMe), 3.07 (s, 3H, OMe). HRMS (ESI): calcd for $C_{11}H_{14}NaO_2$ $[M+Na]^+$ 201.08860, found 201.08867.



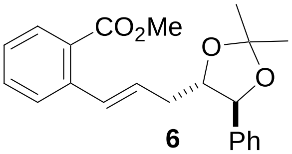
2

[(1*S*,2*R*)-1,2-Dimethoxy-3-phenylpropyl]benzene: The tandem hydroboration/cross coupling reaction to give compound **2** was performed according to general procedure 2. Yield = 7 mg (35%), colorless oil; R_f = 0.5 (petroleum ether/ethyl acetate, 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40-7.15 (m, 10H, aromatic), 4.08 (d, *J* = 5.8 Hz, 1H, PhC*H*(OMe)), 3.45 (ddd, *J* = 8.3, 5.8, 3.3 Hz, 1H, CH_2C*H*(OMe)), 3.25 (s, 3H, OMe), 2.99 (s, 3H, OMe), 2.94 (dd, *J* = 14.1, 3.3 Hz, 1H, CH_2), 2.77 (dd, *J* = 14.1, 8.3 Hz, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 139.3 (2 C, quaternary C, aromatic), 129.6, 128.1, 127.7, 125.9 (CH, aromatic), 86.2 (Ph*C*H(OMe)), 84.8 (CH_2*C*H(OMe)), 58.9 (OMe), 56.9 (OMe), 36.9 (CH_2). HRMS (ESI): calcd for $C_{17}H_{20}NaO_2$ (M+Na) 279.13555, found 279.13550.



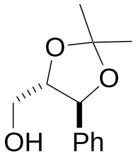
4

(5*S*)-2,2-Dimethyl-4-methylene-5-phenyl-1,3-dioxolane (4): This enol ether was prepared according to general procedure 1. Purification was done by chromatography on Al_2O_3 (petroleum ether/ethyl acetate, 18:1). Yield = 188 mg (92%), slightly yellow oil; R_f = 0.5 (petroleum ether/ethyl acetate, 18:1); ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.35 (dd, *J* = 8.3, 1.3 Hz, 2H, aromatic H), 7.06-7.15 (m, 3H, aromatic H), 5.42 (br s, 1H, PhCH), 4.49 (dd like t, *J* = 1.8, 2.3 Hz, 1H, C=CH_2), 3.66 (t, *J* = 1.8 Hz, 1 H, C=CH_2), 1.49 (s, 3H, CH_3), 1.32 (s, 3H, CH_3); ^{13}C NMR (C_6D_6, 100 MHz): δ = 160.8 (CH_2=*C*), 139.5 (C, aromatic), 128.64 128.57, 128.3 (CH, aromatic), 110.9 (C, acetonide), 80.5 (*C*H_2=C), 80.0 (*C*HPh), 26.7 (acetonide Me), 25.0 (acetonide Me).



6

Methyl 2-{(1*E*)-3-[(4*S*,5*S*)-2,2-dimethyl-5-phenyl-1,3-dioxolan-4-yl]prop-1-enyl}benzoate (6): This dioxolane derivative was prepared according to general procedure 2. Compound **6** was obtained as a 7:1 mixture of *E*/*Z* isomers. It is advisable to store it at -20 °C to prevent isomerization of the olefin. Yield = 22 mg (62%), colorless oil; $[\alpha]^{20}_D$ = -28.6 (*c* 0.8, CH_2Cl_2); R_f = 0.35 (petroleum ether/ethyl acetate, 9:1); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.84 (d, *J* = 8.6 Hz, 1H, aromatic H (H-6)), 7.43-7.18 (m, 9H, aromatic H, C*H*=CHCH_2), 6.09 (td, *J* = 14.2, 7.1 Hz, 1H, CH=C*H*CH_2), 4.68 (d, *J* = 8.3 Hz, 1H, CHPh), 3.98-3.90 (m, 1H, CH_2C*H*OR) 3.88 (s, 3H, OMe), 2.68-2.51 (m, 2H, CH_2), 1.58 (s, 3H, CH_3), 1.52(s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.9 (C=O), 139.1 (C, aromatic), 137.6 (C, aromatic), 132.0, 131.2, 130.3, 128.6 (CH, aromatic), 128.2 (CH=*C*HCH_2), 127.4, 127.0 (CH, aromatic), 126.8 (*C*H=CHCH_2), 108.8 (C, acetonide), 82.59 (Ph*C*HOR), 82.6 (CH_2*C*HOR), 52.0 (OMe), 34.7 (CH_2), 27.3 (CH_3), 27.1 (CH_3); HRMS (ESI): calcd for $C_{22}H_{24}NaO_4$ $[M+Na]^+$: 375.15668, found 375.15683.



7

[(4*S*,5*S*)-2,2-Dimethyl-5-phenyl-1,3-dioxolan-4-yl]methanol (7): To a stirred solution of enol ether **4** (188 mg, 0.99 mmol) in dry THF (3 mL) was added 9-BBN (2.37 mL, 1.18 mmol, 0.5 M in THF), at 0 °C. The cooling bath was removed and the mixture stirred for 6 h at room temperature. The mixture was then cooled again in an ice-bath and aqueous NaOH (1 mL, 5% soln) was added followed by H_2O_2 (1 mL, 30 % aqueous soln). The reaction mixture was brought up to room temperature and stirred for about 30 minutes before it was diluted with water (10 mL) and poured into a separating funnel. The mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to yield 171 mg (83%) of the two easily separable diastereomers (ratio = 7:1) as colorless oils. The spectral data were in excellent agreement with that reported in literature.[1] Data for the major isomer: R_f = 0.3 (petroleum ether/ethyl acetate, 3:1); ^{1}H NMR (C_6D_6, 400 MHz): δ = 7.36 (d, *J* = 7.1 Hz, 2H, CH, aromatic), 7.19-7.07 (m, 3H, aromatic), 4.96 (d, *J* = 8.6 Hz, 1H, CHPh), 3.76-3.70 (ddd, *J* = 8.6, 3.8, 2.8 Hz, 1H, C*H*CH_2), 3.70-3.63 (m, 1H, CH_2), 3.51-3.42 (m, 1H, CH_2), 2.73 (dd like t, *J* = 6.6, 5.6 Hz, 1H, OH), 1.49 (s, 3H,

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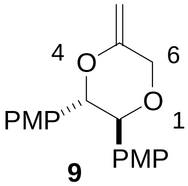
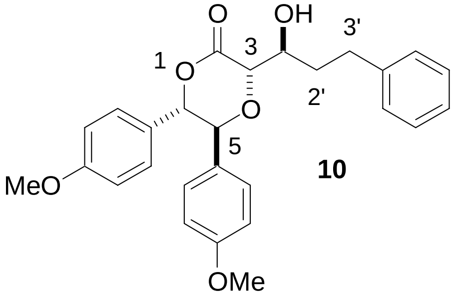
[1] Lombardo, M.; Licciulli, S.; Trombini, C. *Tetrahedron: Asymmetry* 2004, *15*, 289-292.

CH_3), 1.46 (s, 3H, CH_3); ^{13}C NMR (C_6D_6, 100 MHz): δ = 138.8 (C, aromatic), 128.7, 128.3, 126.8 (CH, aromatic), 109.1 (C, acetonide), 84.3 (CHPh), 79.0 (CH_2*C*H), 60.5 (CH_2), 27.2 (2 CH_3, acetonide); HRMS (ESI): calcd for $C_{12}H_{16}NaO_3$ $[M+Na]^+$: 231.09917, found 231.09915.



9

(2*R*,3*R*)-2,3-Bis(4-methoxyphenyl)-5-methylene-1,4-dioxane (9): This enol ether was prepared according to general procedure 1. Yield = 69 mg (68 %), slightly yellow oil; R_f = 0.3 (petroleum ether/ethyl acetate, 4:1). This compound was utilized immediately after workup. ^{1}H NMR (C_6D_6, 400 MHz): δ = 6.99 (d, *J* = 8.6 Hz, 2H, aromatic), 6.97 (d, *J* = 8.6 Hz, 2H, aromatic), 6.62 (d, *J* = 8.6 Hz, 2H, aromatic), 6.60 (d, *J* = 8.6 Hz, 2H, aromatic), 4.81 (d, *J* = 9.3 Hz, 1H, H-3), 4.69 (s, 1 H, C=CH_2), 4.48 (d, *J* = 9.3 Hz, 1H, H-2), 4.28 (d, *J* = 13.1 Hz, 1H, H-6), 4.24 (d, *J* = 13.1 Hz, 1H, H-6), 4.19 (s, 1H, C=CH_2), 3.18 (s, 3H, OMe), 3.17 (s, 3H, OMe).



10

(3*S*,5*S*,6*S*)-3-[(1*S*)-3-Phenyl-1-hydroxypropyl]-5,6-bis-(4-methoxyphenyl)-[1,4]-dioxan-2-one (10): To a cooled solution (-78 °C) of dioxanone[2] **8** (0.233 g, 0.740 mmol) in dry CH_2Cl_2 (20 mL) were added in a dropwise fashion Et_3N (0.26 mL, 1.86 mmol) followed by *c*Hex$_2$BOTf (1.85 mL, 1.0 M in abs. hexane) under a nitrogen atmosphere. The resulting solution was stirred at -78 °C for 3 h before freshly distilled 3-phenylpropanal (0.119 g, 0.888 mmol) was added in dry CH_2Cl_2 (1 mL) dropwise over 10 min at this temperature. The resulting solution was stirred at -78 °C for 12 h at which time it was quenched by the addition of pH 7 buffer (2.5 mL), MeOH (2 mL) and 30% aqueous H_2O_2 (0.5 mL). The solution was vigorously stirred for 1 h and then warmed to room temperature before it was diluted with Et_2O (50 mL). The aqueous layer was extracted with Et_2O (4 × 50 mL) and the combined organic layers were washed with dilute $NaHCO_3$ solution (30 mL). Drying of the combined organic layers with anhydrous $MgSO_4$ was followed by filtration, and concentration of the filtrate to afford 0.9 g of crude product as a yellow oil, which was used in the next step without further purification. During flash chromatography retro aldol reaction might take place. The selectivity was found to be 10:1 (*anti*/*anti*) via ^{1}H NMR and LC-MS of the crude reaction material. R_f = 0.27 (petroleum ether/EtOAc, 3:1); $[\alpha]^{20}_D$ = -119.5 (*c* 1.0, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 7.34-7.29 (m, 2H, CH, Ph), 7.26-7.19 (m, 3H, CH, Ph), 7.02-6.95 (m, 4H, CH, PMP), 6.82-6.77 (m, 4H, CH, PMP), 5.42 (d, *J* = 9.0 Hz, 1H, H-6), 4.85 (d, *J* = 9.0 Hz, 1H, H-5), 4.5 (d, *J* = 6.0 Hz, 1H, H-3), 4.21-4.15 (m, 1H, C*H*OH), 3.80 (s, 3H, *p*CH_3OPh), 3.79 (s, 3H, *p*CH_3OPh), 3.22 (br s, 1H, OH), 3.00-2.90 (m, 1H, CH_2), 2,84-2.74 (m, 1H, CH_2), 2.22-2.13 (m, 1H, CH_2), 2.06-1.96 (m, 1H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz) δ = 170.5 (C=O), 160.0, 159.7 (both *C*OMe of PMP), 141.6 (C, Ph), 128.7, 128.5, 128.4, 128.3, 127.7, 126.4, 125.9, 113.7 (CH, Ph and PMP), 84.8 (6-C), 78.1 (5-C), 75.7 (3-CH), 71.7 (*C*HOH), 55.2 (both *p*CH_3OPh), 34.7, 31.4 (CH_2); HRMS (ESI) $[M+Na]^+$ calcd for $C_{27}H_{28}NaO_6$: 503.20402, found 503.20393.

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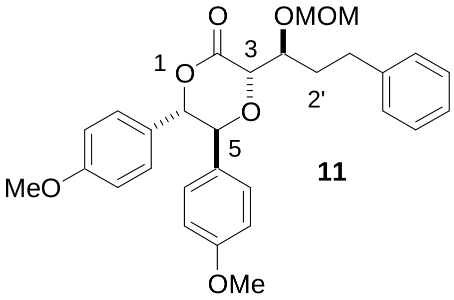
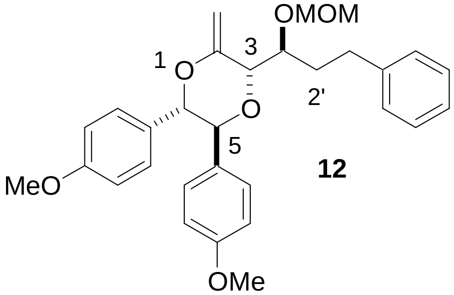
[2] Andrus, M. B.; Meredith, E. L.; Simmons, B. L.; Sekhar, B. B. V. S.; Hicken, E. J. *Org. Lett.* **2002**, *4*, 3549-3552.



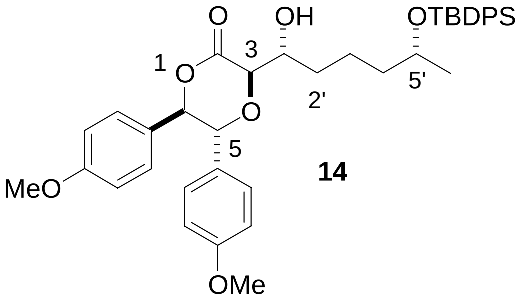
11

(3*S*,5*S*,6*S*)-3-[(1*S*)-3-Phenyl-1-(methoxymethoxy)propyl]-5,6-bis-(4-methoxyphenyl)-[1,4]-dioxan-2-one (11): To a stirred, cooled (0 °C) solution of crude aldol product (0.9 g) in CH_2Cl_2 (90 mL) were added *N*,*N*-diisopropylethylamine (15.4 mL, 11.6 g, 90.0 mmol), chloromethylmethyl ether (3.42 mL, 3.62 g, 45.0 mmol), and tetrabutylammonium iodide (665 mg, 1.80 mmol). The reaction mixture was protected from light and allowed to reach room temperature within 12 h. After stirring for 3 days, saturated aqueous $NaHCO_3$ solution (100 mL) was added followed by Et_2O (150 mL). The organic layer was washed with 1 N HCl (50 mL) and brine (30 ml), and the basic aqueous layer was extracted with Et_2O (2 × 50 ml). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Flash chromatography of the residue provided the MOM ether as slightly yellow oil, yield 0.18 g (50%). $R_f = 0.3$ (petroleum ether/EtOAc, 3:1); $[\alpha]^{20}_{D} = -68.9$ (*c* 0.45, CH_2Cl_2); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.30-7.25 (m, 2H, Ph)), 7.22-7.17 (m, 3H, Ph), 7.02-6.95 (m, 4H, PMP), 6.77-6.72 (m, 4H, PMP), 5.40 (d, *J* = 8.5 Hz, 1H, H-6), 4.95 (d, J = 8.5 Hz, 1H, H-5), 4.89 (d, *J* = 3.0 Hz, 1H, H-3), 4.79 (dd, *J* = 7.0, 17.0 Hz, 2H, CH_2OCH_3), 4.23-4.16 (m, 1H, H-1’), 3.75 (s, 3H, *p*CH_3OPh), 3.74 (s, 3H, *p*CH_3OPh), 3.43 (s, 3H, CH_2OCH_3), 2.87-2.78 (m, 1H, CH_2), 2.77-2.67 (m, 1H, CH_2), 2.21-2.05 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.9 (C=O), 159.8, 159.7 (both *C*OMe of PMP), 141.5 (C, Ph), 128.6, 128.5, 128.4, 128.3, 127.9, 127.0, 125.9, 113.7, 113.6 (CH, Ph and PMP), 97.0 (CH_2 of MOM), 84.6 (6-C), 80.55 (5-C), 78.1 (3-C), 74.7 (*C*HOMOM), 56.0 (CH_3 of MOM), 55.1 (both *p*CH_3OPh), 32.6, 32.1 (CH_2); HRMS (ESI) $[M+MeOH+Na]^+$ calcd for $C_{30}H_{36}NaO_8$: 547.23060, found 547.23024.



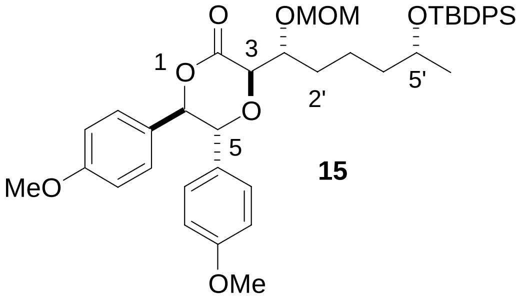
12

(3*S*,5*S*,6*S*)-2-Methylidene-3-[(1*S*)-3-phenyl-1-(methoxymethoxy)propyl]-5,6-bis[4-(methyloxy)phenyl]-3-propyl-1,4-dioxane (12): This enol ether was prepared according to general procedure 1. Purification was done by chromatography on Al_2O_3 (petroleum ether/ethyl acetate, 4:1). Yield = 25 mg (67%), colorless oil; $R_f = 0.45$ (petroleum ether/ethyl acetate, 4:1); $[\alpha]^{20}_{D} = -166.3$ (*c* 1.12, CH_2Cl_2); ^1H NMR (C_6D_6, 400 MHz): δ = 7.23 (d, *J* = 7.3 Hz, 2H, Ph), 7.16-7.12 (m, 2H, Ph), 7.07-7.02 (m, 1H, ph), 6.95 (d, *J* = 8.6 Hz, 2H, PMP), 6.92 (d, *J* = 8.6 Hz, 2H, PMP), 6.62 (d, *J* = 8.6 Hz, 2H, PMP), 6.60 (d, *J* = 8.6 Hz, 2H, PMP), 4.91 (d, *J* = 7.1 Hz, 1H, CH_2OCH_3), 4.88 (s, 1H, $C=CH_2$), 4.79 (d, *J* = 9.6 Hz, 1H, H-6), 4.64 (d, *J* = 7.1 Hz, 1 H, CH_2OCH_3), 4.62-4.55 (m, 1H, H-1’), 4.57 (s, 1H, $C=CH_2$), 4.54 (d, *J* = 9.4 Hz, 1H, H-3), 4.33 (d, *J* = 9.6 Hz, 1H, H-5), 3.33 (s, 3H, CH_2OCH_3), 3.18 (s, 6H, OMe), 2.99-2.85 (m, 2H, H-3’), 2.37-2.35 (m, 1H, H-2’), 2.11-2.00 (m, 1H, H-2’); ^{13}C NMR (C_6D_6, 100 MHz): δ = 159.9, 159.8 (*C*OMe of PMP), 156.7 ($C=CH_2$), 142.8 (C, Ph), 130.0, 129.9 (C, PMP), 129.2-126.0 (CH, aromatic), 113.6 (CH, aromatic), 97.6 (CH_2OCH_3), 96.3 ($C=CH_2$), 86.0 (3-C), 77.2 (1’-C), 75.5 (5-C), 74.6 (6-C), 55.6 (CH_2OCH_3), 54.6 (2 OMe), 33.8 (2’-C), 30.9 (3’-C); HRMS (ESI): calcd for $C_{30}H_{34}NaO_6$ $[M+Na]^+$: 513.22476, found 513.22506.



14

(3*R*,5*R*,6*R*)-3-[(1*R*,5R)-5-(*tert*-Butyldiphenylsilyloxy)-1-hydroxyhexyl]-5,6-bis-(4-methoxyphenyl)-[1,4]-dioxan-2-one (14): To a cooled (-78 °C) solution of dioxanone *ent*-**8** (0.233 g, 0.740 mmol) in dry CH_2Cl_2 (20 mL) was added in a dropwise fashion Et_3N (0.26 mL, 1.86 mmol) followed by *c*Hex_2BOTf (1.85 mL, 1.0 M in abs. hexane) under a nitrogen atmosphere. The resulting solution was stirred at -78 °C for 3 h at which time (5*R*)-5-(*tert*-butyldiphenylsilyloxy)hexanal[3] (**13**) (0.314 g, 0.888 mmol), dissolved in dry CH_2Cl_2 (1 mL) was added dropwise over 10 min. The resulting solution was stirred at -78 °C for 12 h before it was quenched at that same temperature by the addition of pH 7 buffer (2.5 mL), MeOH (2 mL) and 30% aqueous H_2O_2 (0.5 mL). The mixture was stirred vigorously for 1 h and then warmed to room temperature when it was diluted with Et_2O (50 mL). The aqueous layer was extracted with Et_2O (4 × 50 mL) and the combined organic layers were washed with dilute $NaHCO_3$ solution (30 mL). The combined organic layers were dried with anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford 1.0 g of crude product as a yellow oil, which was used for the next step without further purification (approximately half of the product decomposes during flash chromatography on silica gel (petroleum ether/EtOAc, 2:1)). The selectivity was found to be 9:1 (*anti*/*anti*) according to ^1H NMR and LC-MS of the crude reaction material. Data for the purified product: R_f = 0.48 (petroleum ether/EtOAc, 2:1); ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.68-7.63 (m, 4H, aromatic TBDPS), 7.41-7.30 (m, 6H, aromatic TBDPS), 6.98 (d, *J* = 8.5 Hz, 2H, CH, PMP), 6.94 (d, *J* = 8.5 Hz, 2H, CH, PMP), 6.76 (d, *J* = 8.5 Hz, 2H, CH, PMP), 6.74 (d, *J* = 8.5 Hz, 2H, CH, PMP), 5.37 (d, *J* = 9.0 Hz, 1H, H-6), 4.87 (d, *J* = 9.0 Hz, 1H, H-5), 4.43 (d, *J* = 5.5 Hz, 1H, H-3), 4.08-4.02 (m, 1H, C*H*OH), 3.83 (dd, *J* = 6.0, 11.5 Hz, 1H, H-5'), 3.76 (s, 3H, CH_3OPh), 3.75 (s, 3H, CH_3OPh), 2.86 (d, *J* = 5.0 Hz, 1H, OH), 1.92-1.35 (m, 6H, $(CH_2)_3$), 1.06-1.00 (m, 12H, 3 CH_3 *t*Bu, CH_3CHOTBDPS); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 170.2 (C=O), 160.0 (*C*OMe), 159.7 (*C*OMe), 135.9, 135.8 (aromatic TBDPS), 134.8, 134.6 (aromatic TBDPS), 129.5, 129.4 (aromatic TBDPS), 128.7, 128.5, 127.9 (aromatic PMP), 127.5, 127.4 (aromatic TBDPS), 126.6, 113.8 (aromatic PMP), 85.0 (6-C), 77.9 (5-C), 76.0 (3-C), 73.0 (CHOH), 69.4 (5-C), 55.2 (CH_3O), 39.1, 33.3 (2'-C, 4'-C), 27.0 (3 CH_3 *t*Bu), 23.1 (6'-C), 20.9 (3'-C), 19.3 (quat. C, *t*Bu); HRMS (ESI): $[M+Na]^+$ calcd for $C_{40}H_{48}NaO_7Si$: 723.33236, found 723.33153.



15

(3*R*,5*R*,6*R*)-3-[(1*R*,5*R*)-5-(*tert*-Butyldiphenylsilyloxy)-1-(methoxymethoxy)hexyl]-5,6-bis-(4-methoxyphenyl)-[1,4]-dioxan-2-one (15): To a stirred, cooled (0 °C) solution of crude aldol product **14** (1.0 g) in CH_2Cl_2 (30 mL) were added *N*,*N*-diisopropylethylamine (5.1 mL, 3.86 g, 30.0 mmol), chloromethylmethyl ether (1.14 mL, 1.20 g, 15.0 mmol), and tetrabutylammonium iodide (222 mg, 0.60 mmol). The reaction mixture was protected from light and allowed to reach room temperature within 12 h. After stirring for 3 days, saturated aqueous $NaHCO_3$ solution (40 mL) was added followed by Et_2O (50 mL). The organic layer was washed with 1 N HCl (150 mL) and brine (10 mL), and the basic aqueous layer was extracted with Et_2O (2 × 25 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo. Flash chromatography of the residue provided the MOM ether as a slightly yellow oil, yield 0.24 g (45% for two steps from aldehyde). R_f = 0.18 (petroleum ether/EtOAc, 5:1); ^1H NMR (400 MHz, $CDCl_3$): δ = 7.70-7.65 (m, 4H, aromatic TBDPS), 7.42-7.33 (m, 6H, aromatic TBDPS), 7.00 (d, *J*

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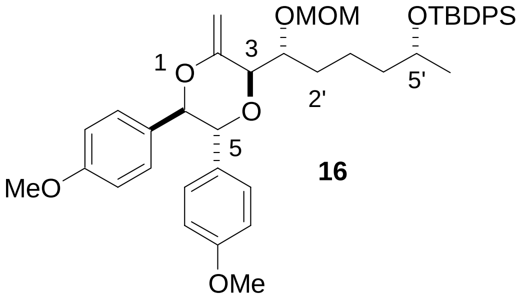
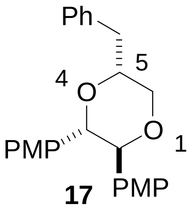
[3] Haynes, R. K.; Lam, W. W. L.; Yeung, L.-L.; Williams, I. D.; Ridley, A. C.; Starling, S. M.; Vonwiller, S. C.; Hambley, T. W.; Lelandais, P. *J. Org. Chem.* **1997**, *62*, 4552-4553.

= 3.0 Hz, 2H, CH, PMP), 6.97 (d, *J* = 3.0 Hz, 2H, CH, PMP), 6.77 (d, *J* = 2.0 Hz, 2H, CH, PMP), 6.74 (d, *J* = 2.0 Hz, 2H, CH, PMP), 5.39 (d, *J* = 8.5 Hz, 1H, H-6), 4.98 (d, *J* = 8.5 Hz, 1H, H-5), 4.77 (d, *J* = 2.5 Hz, 1H, H-3), 4.73 (dd, *J* = 7.0, 10.0 Hz, 2H, OC*H*$_2$OCH$_3$), 4.10-4.04 (m, 1H, 5'-H), 3.88-3.80 (m, 1H, H-5'), 3.76 (s, 3H, CH$_3$OPh), 3.75 (s, 3H, CH$_3$OPh), 3.37 (s, 3H, C*H*$_3$OCH$_2$O), 1.76-1.65 (m, 2H, H-2'), 1.55-1.42 (m, 3H, CH$_2$), 1.40-1.30 (m, 1H, CH$_2$), 1.06-1.01 (m, 12H, 3 CH$_3$ *t*Bu, H-6'); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 167.8 (C=O), 156.8, 159.7 (*C*OMe of PMP), 135.8, 134.8, 134.4 129.5, 129.4 (aromatic of TBDPS), 128.7, 128.6, 128.0 (aromatic of PMP), 127.5, 127.4 (aromatic of TBDPS), 127.1, 113.7, 113.6 (aromatic of PMP), 96.7 (*C*H$_2$OCH$_3$), 84.8 (6-C), 81.1 (5-C), 78.0 (3-C), 74.8 (*C*HOMOM), 69.4 (5'-C), 56.0 (CH$_2$O*C*H$_3$), 55.2 (*p*CH$_3$OPh), 39.3, 31.0 (2'-C, 4'-C), 27.0 (3 CH$_3$ of *t*Bu), 23.2 (6'-C), 21.7 (3'-C), 19.2 (C of *t*Bu); HRMS (ESI) [M+Na]$^+$ calcd for C$_{42}$H$_{52}$NaO$_8$Si: 735.33237, found 735.33270.



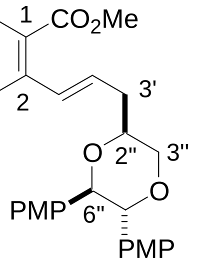
16

(3*R*,5*R*,6*R*)-3-[(1*R*,5*R*)-5-(*tert*-Butyldiphenylsilyloxy)-1-(methoxymethoxy)hexyl]-2-methylidene-5,6-bis-(4-methoxyphenyl)-[1,4]-dioxan-2-one (16): This enol ether was prepared according to general procedure 1. Purification was done by chromatography on Al$_2$O$_3$ (petroleum ether/ethyl acetate, 9:1). Yield = 149 mg (91%), slightly yellow oil; R$_f$ = 0.35 (petroleum ether/ethyl acetate, 9:1); $[\alpha]^{20}_D$ = +63.8 (*c* 0.8, CH$_2$Cl$_2$); ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 7.84-7.75 (m, 4H, aromatic), 7.24-7.17 (m, 6H, aromatic), 7.02 (d, *J* = 8.6 Hz, 2 H, PMP), 6.99 (d, *J* = 8.6 Hz, 2 H, PMP), 6.61 (d, *J* = 8.6 Hz, 4H, PMP), 4.91 (s, 1H, C=C*H*$_2$), 4.87 (d, *J* = 6.8 Hz, 1H, C*H*$_2$OCH$_3$), 4.84 (d, *J* = 9.6 Hz, 1H, H-6), 4.82 (d, *J* = 9.6 Hz, 1H, H-5), 4.68 (d, *J* = 6.8 Hz, 1H, C*H*$_2$OCH$_3$), 4.60 (s, 1H, C=CH$_2$), 4.59 (m, 1H, H-1'), 4.36 (d, *J* = 9.3 Hz, 1H, H-3), 3.92 (sextet, *J* = 6.1 Hz, 1H, H-5'), 3.32 (s, 3H, CH$_2$OC*H*$_3$), 3.19 (s, 3H, OMe), 3.18 (s, 3H, OMe), 1.93-1.84 (m, 1H, H-2'), 1.79-1.60 (m, 3H, CH$_2$), 1.60-1.43 (m, 2H, H-3', H-4'), 1.18 (s, 9H, *t*Bu), 1.06 (d, *J* = 6.1 Hz, 3H, H-6'); ^{13}C NMR (C$_6$D$_6$, 100 MHz): δ = 159.92, 159.90 (*C*OMe of PMP), 156.8 (C-2), 136.3 (aromatic), 135.2, 135.0 (aromatic of TBDPS), 130.1 (C, PMP), 130.0 (C, PMP), 129.8-127.8 (CH, aromatic), 113.7 (4 CH, PMP), 96.9 (*C*H$_2$OCH$_3$), 96.3 (C=*C*H$_2$), 86.0 (3-C), 77.7 (1'-C), 75.4 (5-C), 74.3 (6-C), 70.0 (5'C), 55.7 (CH$_2$O*C*H$_3$), 54.6 (2 OMe), 40.1 (4'-C), 31.9 (2'-C), 27.3 (3 CH$_3$, *t*Bu), 23.2 (6'-C), 20.3 (3'-C), 19.5 (C, *t*Bu); HRMS (ESI): calcd for C$_{43}$H$_{54}$NaO$_7$Si [M+Na]$^+$: 733.35310, found 733.35347.



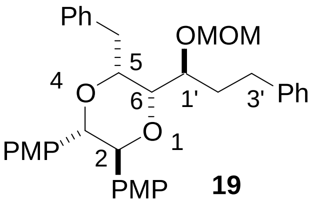
17

(2*S*,3*S*,5*R*)-5-Benzyl-2,3-bis(4-methoxyphenyl)-1,4-dioxane (17): This dioxane derivative was prepared according to general procedure 2. Yield = 46 mg (72%), colorless oil; $[\alpha]^{20}_D$ = -43.4 (*c* 1.0, CH$_2$Cl$_2$); R$_f$ = 0.4 (petroleum ether/ethyl acetate, 3:1); ^{1}H NMR (CDCl$_3$, 400 MHz): δ = 7.32-7.17 (m, 5H, aromatic), 6.94 (d, *J* = 8.6 Hz, 2H, PMP), 6.91 (d, *J* = 8.6 Hz, 2H, PMP), 6.70 (d, *J* = 8.6 Hz, 2H, PMP), 6.68 (d, *J* = 8.6 Hz, 2H, PMP), 4.41 (d, *J* = 8.8 Hz, 1H, H-2), 4.22 (d, *J* = 8.8 Hz, 1H, H-3), 4.10 (dddd, *J* = 10.6, 7.3, 5.6, 2.5 Hz, 1H, H-5), 3.93 (dd, *J* = 11.4, 2.5 Hz, 1H, H-6), 3.73 (s, 3H, OMe), 3.71 (s, 3H, OMe), 3.59 (dd like t, *J* = 11.4, 10.6 Hz, 1H, H-6), 3.0 (dd, *J* = 14.0, 5.6 Hz, 1H, C*H*$_2$Ph), 2.77 (dd, *J* = 14.0, 7.3 Hz, 1H, CH$_2$Ph); ^{13}C NMR (CDCl$_3$, 100 MHz): δ = 159.0 (*C*OMe of PMP), 137.4 (C, Ph), 130.4 (C, PMP), 130.1 (C, PMP), 129.3, 128.6, 128.4, 126.4 (CH, aromatic), 113.3 (2 CH, PMP-aromatic), 113.2 (2 CH, PMP-aromatic), 83.7 (5-C), 83.3 (2-C), 76.1 (3-C), 70.8 (6-C), 55.1 (2 OMe), 38.6 (*C*H$_2$Ph); HRMS (ESI) calcd for C$_{25}$H$_{26}$NaO$_4$ [M+Na]$^+$ 413.17233, found 413.17241.



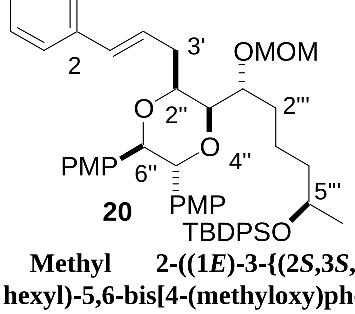
18

Methyl 2-{(1*E*)-3-[(2*S*,5*R*,6*R*)-5,6-bis(4-methoxyphenyl)-1,4-dioxan-2-yl]prop-1-enyl}benzoate (18): This dioxane derivative was prepared according to general procedure 2. Yield = 89 mg (87%), colorless foam. This compound was obtained as a 9:1 mixture of *E*/*Z* isomers. It is advisable to store this compound at -20 °C in order to avoid isomerization of the olefin. R_f = 0.4 (petroleum ether/ethyl acetate, 9:1); $[\alpha]^{20}_D$ = +55.7 (*c* 1.4, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78 (d, *J* = 7.8 Hz, 1H, H-6), 7.45 (d, *J* = 7.8 Hz, 1H, H-3), 7.35 (t, *J* = 7.8 Hz, 1H, H-5), 7.19 (t, *J* = 7.8 Hz, 1H, H-4), 7.17 (d, *J* = 14.2 Hz, 1H, H-1’), 6.89 (d, *J* = 8.6 Hz, 2H, PMP), 6.87 (d, *J* = 8.6 Hz, 2H, PMP), 6.63 (d, *J* = 8.6 Hz, 2H, PMP), 6.62 (d, *J* = 8.6 Hz, 2H, PMP), 6.11 (ddd, *J* = 14.2 Hz, 7.3, 7.0 Hz, 1H, H-2’), 4.36 (d, *J* = 9.0 Hz, 1H, H-5’’), 4.19 (d, *J* = 9.0 Hz, 1H, H-6’’), 4.0 (dd, *J* = 11.3, 2.3 Hz, H-3’’), 3.98-3.90 (m, 1H, H-2’’), 3.79 (3H, CO_2Me), 3.64 (s, 6H, 2 OMe), 3.59 (dd like t, *J* = 11.3, 10.6 Hz, 1H, H-3’’), 2.56-2.46 (m, 1H, H-3’), 2.46-2.36 (m, 1H, H-3’); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.8 (C, C=O), 159.0 (2 C, *C*OMe of PMP), 139.1 (2-C), 132.0 (4-C), 131.2 (6-C), 130.4, 130.3, 130.1, 128.7, 128.1, 128.6, 127.3 (CH, aromatic), 128.0 (2’C), 126.8 (1’-C), 113.23 (CH, PMP), 113.20 (CH, aromatic), 83.6 (6’’-C), 83.3 (5’’-C), 75.1 (2’’-C), 71.0 (3’’-C), 55.0 (2 OMe), 52.0 (CO_2Me), 35.7 (3’-C); HRMS (ESI): calcd for $C_{29}H_{30}NaO_6$ $[M+Na]^+$: 497.19346, found 497.19317.



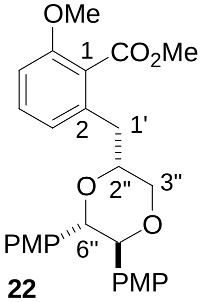
19

(2S,3*S*,5*R*,6*S*)-2,3-Bis[4-(methyloxy)phenyl]-6-[(1*S*)-3-phenyl-1-(methoxymethoxy)propyl]-5-(phenylmethyl)-1,4-dioxane (19): This dioxane derivative was prepared according to general procedure 2. Yield = 18 mg (76%), colorless oil; R_f = 0.35 (petroleum ether/ethyl acetate, 3:1); $[\alpha]^{20}_D$ = +4.1 (*c* 0.81, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.30-7.13 (m, 10H, aromatic), 6.90 (d, *J* = 8.8 Hz, 2H, PMP), 6.86 (d, *J* = 8.8 Hz, 2H, PMP), 6.71 (d, *J* = 8.8 Hz, 2H, PMP), 6.70 (d, *J* = 8.8 Hz, 2H, PMP), 4.89 (d, *J* = 6.8 Hz, 1H, CH_2OCH_3), 4.86 (d, *J* = 6.8 Hz, 1H, CH_2OCH_3), 4.61 (ddd, *J* = 8.6, 4.6, 2.8 Hz, 1H, H-5), 4.40 (d, *J* = 9.6 Hz, 1H, H-3), 4.39-4.33 (m, 1H, H-1’), 4.29 (d, *J* = 9.6 Hz, 1H, H-2), 3.89 (dd, *J* = 9.1, 2.8 Hz, 1H, H-6), 3.75 (s, 6H, 2 OMe), 3.53 (s, 3H, CH_2OCH_3), 3.03 (dd, *J* = 14.2, 4.6 Hz, 1H, CH_2Ph), 2.87 (dd, *J* = 14.2, 8.6 Hz, 1H, CH_2Ph), 2.84 (dd like t, *J* = 8.3, 7.8 Hz, 2H, H-3’), 2.33-2.21 (m, 1H, H-2’), 2.09-1.97 (m, 1H, H-2’); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.1, 159.0 (*C*OMe of PMP), 142.71 (C, Ph), 139.6 (C, Ph), 130.4 (C, PMP), 130.2 (C, PMP), 129.2, 128.8, 128.6, 128.3, 128.2 (CH, aromatic), 126.1 (CH, aromatic), 125.7 (CH, aromatic), 113.3 (CH, PMP), 113.2 (CH, PMP), 97.1 (CH_2OCH_3), 84.5 (6-C), 80.6 (1’-C), 77.8 (5-C), 74.7 (3-C), 73.7 (2-C), 56.4 (CH_2OCH_3), 55.1 (2 OMe), 38.0 (CH_2Ph), 33.1 (2’-C), 29.7 (3’-C); HRMS (ESI): calcd for $C_{36}H_{40}NaO_6$ $[M+Na]^+$: 591.27171, found 591.27203.



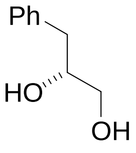
20

Methyl 2-((1*E*)-3-{(2*S*,3*S*,5*R*,6*R*)-3-((1*R*,5*R*)-5-{(*tert*-Butyldiphenylsilyloxy)}-1-{[(methyloxy)methyl]oxy}-hexyl)-5,6-bis[4-(methyloxy)phenyl]-1,4-dioxan-2-yl}-1-propenyl)benzoate (20): This dioxane derivative was prepared according to general procedure 2. This compound was obtained as a 10:1 mixture of *E*/*Z* isomers. It is advisable to store this compound at -20 °C in order to avoid isomerization of the olefin. Yield = 180 mg (74%), slightly yellow oil; R_f = 0.4 (petroleum ether/ethyl acetate, 4:1); $[\alpha]^{20}_{D}$ = +8.9 (*c* 0.9, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (dd, *J* = 7.8, 1.0 Hz, 1H, H-6), 7.66-7.57 (m, 4H, aromatic), 7.52 (d, *J* = 7.8 Hz, 1H, H-3), 7.44-7.19 (m, 9H, aromatic, H-1’), 6.94 (d, *J* = 8.6 Hz, 2H, PMP), 6.88 (d, *J* = 8.6 Hz, 2H, PMP), 6.72 (d, *J* = 8.6 Hz, 2H, PMP), 6.68 (d, *J* = 8.6 Hz, 2H, PMP), 6.26 (ddd, *J* = 14.4, 8.1, 7.1 Hz, 1H, H-2’), 4.77 (d, *J* = 6.8 Hz, 1H, CH_2OCH_3), 4.74 (d, *J* = 6.8 Hz, 1H, CH_2OCH_3), 4.51-4.43 (m, 1H, H-2’’), 4.43 (d, *J* = 9.4 Hz, 1H, H-6’’), 4.31 (d, *J* = 9.4 Hz, 1H, H-5’’), 4.25-4.18 (m, 1H, H-5’’’), 3.86 (s, 3H, CO_2Me), 3.78 (dd, *J* = 8.9, 2.5 Hz, 1H, H-3’’), 3.76 (m, 1H, H-1’’’), 3.74 (s, 3H, OMe), 3.73 (s, 3H, OMe), 3.40 (s, 3H, CH_2OCH_3), 2.69-2.48 (m, 2H, H-3’), 1.84-1.30 (m, 6H, CH_2), 1.0 (s, 9H, *t*Bu), 0.96 (d, *J* = 6.1 Hz, 3H, H-6’’’); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.0 (C=O), 159.1 (2 *C*OMe of PMP), 139.3 (2-C), 135.84, 135.80 (CH, aromatic), 134.9 (C, SiPh), 134.6 (C, SiPh), 131.9 (CH, aromatic), 130.5 (2’-H), 130.3, 130.2, 129.35, 129.31, 128.74, 128.68 (CH, aromatic), 128.2 (1-C), 127.4, 127.3 (CH, aromatic), 126.7 (CH, C9), 113.3 (PMP), 113.2 (PMP), 96.8 (CH_2OCH_3), 84.6 (2-C’’), 79.6 (3’’-C), 77.9 (1’’’-C), 74.7 (6’’-C), 73.4 (5’’-C), 69.6 (5’’’-C), 56.3 (CH_2OCH_3), 55.2 (OMe), 55.1 (OMe), 52.0 (CO_2Me), 39.8 (4’’’-C), 35.8 (2’’’-C), 30.7 (3’-C), 27.0 (3 CH_3, *t*Bu), 22.8 (6’’’-C), 19.1 (3’’’-C), 18.9 (*t*Bu); HRMS (ESI): calcd for $C_{53}H_{68}NO_9Si$ $[M+NH_4]^+$: 890.46579, found 890.46626.



22

Methyl 2-{[(2*R*,5*S*,6*S*)-5,6-bis(4-methoxyphenyl)-1,4-dioxan-2-yl]methyl}-6-methoxybenzoate (22): This dioxane derivative was prepared according to general procedure 2 with added KBr (1.2 equiv). Yield = 108 mg (53%), colorless foam; R_f = 0.2 (petroleum ether/ethyl acetate, 2:1); $[\alpha]^{20}_{D}$ = -25.1 (*c* 1.1, CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (t, *J* = 8.3 Hz, 1H, H-4), 6.93 (d, *J* = 8.6 Hz, 2H, PMP), 6.92 (d, *J* = 8.3 Hz, 1H, H-3), 6.90 (d, *J* = 8.6 Hz, 2H, PMP), 6.80 (d, *J* = 8.3 Hz, 1H, H-5), 6.70 (d, *J* = 8.6 Hz, 2H, PMP), 6.68 (d, *J* = 8.6 Hz, 2H, PMP), 4.39 (d, *J* = 8.9 Hz, 1H, H-5’’), 4.22 (d, *J* = 8.9 Hz, 1H, H-6’’), 4.11 (dddd, *J* = 10.9, 7.0, 6.1, 2.5 Hz, 1H, H-2’’), 3.91 (dd, *J* = 11.1, 2.5 Hz, 1H, H-3’’), 3.90 (s, 3H, OMe), 3.82 (s, 3H, CO_2Me), 3.74 (s, 3H, OMe), 3.72 (s, 3H, OMe), 3.57 (dd like t, *J* = 11.1, 10.9 Hz, 1H, H-3’’), 2.94 (dd, *J* = 14.0, 6.1 Hz, 1H, H-1’), 2.72 (dd, *J* = 14.0, 7.0 Hz, H-1’); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 168.6 (C=O), 159.1, 159.0 (*C*OMe of PMP), 156.4 (6-C), 135.9 (2-C), 130.4 (C, PMP), 130.3 (4-C), 130.1 (C, PMP), 128.7 (CH, PMP), 128.6 (CH, PMP), 124.0 (1-C), 122.6 (3-C), 113.3 (2 CH, PMP), 113.18 (2 CH, PMP), 109.2 (5-C), 83.7 (2’’-C), 83.3 (5’’-C), 75.8 (6’’-C), 70.8 (3’’-C), 55.9 (OMe), 55.1 (2 OMe), 52.3 (CO_2Me), 35.7 (1’-C); HRMS (ESI): calcd for $C_{28}H_{30}NaO_7$ $[M+Na]^+$: 501.18837, found 501.18819.



23

(2*R*)-3-Phenylpropane-1,2-diol (23): To a stirred solution of the dioxane **17** (38 mg, 97 μmols) in CH_3CN/H_2O mixture (9:1) (2 mL), was added CAN (117 mg, 0.21 mmol). The resulting yellow solution was stirred at room temperature for 2 h, during which the starting material was completely consumed. The mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure, the crude product loaded onto a silica column and chromatographed using petroleum ether/ethyl acetate (1:1) as eluent to afford pure diol **23** as a colorless oil, 12.7 mg (86%). R_f = 0.3 (petroleum ether/ethyl acetate, 1:1); $[\alpha]^{20}_{D}$ = +20.4 (*c* 1.0, $CHCl_3$); ref.[4] $[\alpha]^{20}_{D}$ = +15.0 (*c* 1.0,

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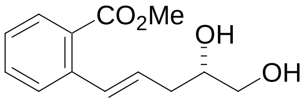
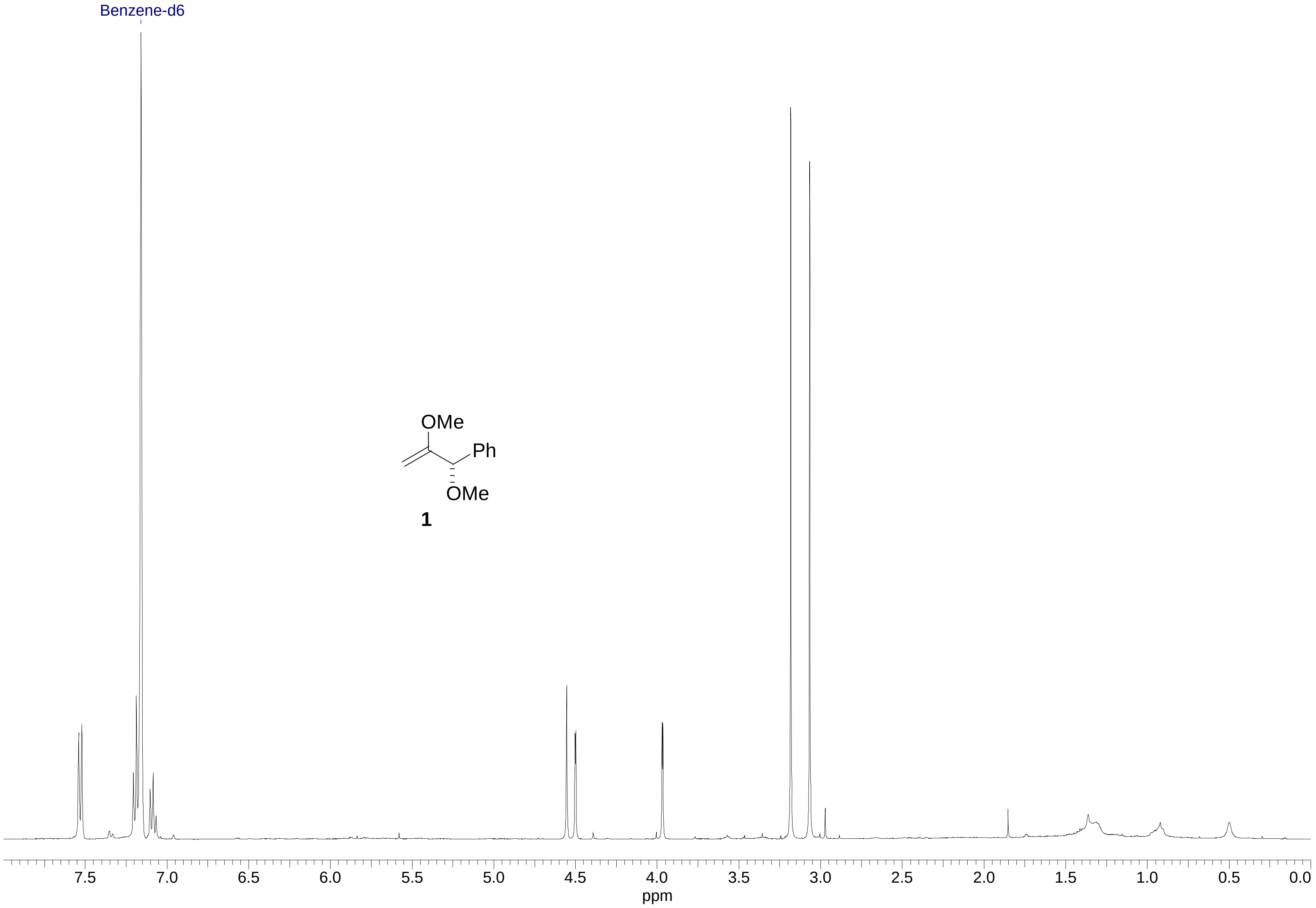
[4] Ramachary, D. B.; Barbas, C. F., III *Org. Lett.* **2005**, *7*, 1577-1580.

$CHCl_3$); ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35-7.17 (m, 5H, aromatic), 3.99-3.87 (m, 1H, H-2), 3.68 (dd, *J* = 11.1, 2.8 Hz, 1H, H-1), 3.50 (dd, *J* = 11.1, 7.1 Hz, 1H, H-1), 2.84-2.69 (m, 2H, H-3), 2.13 (br s, 2H, OH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 137.7 (C, Ph), 129.3 (2 CH, Ph), 128.6 (2 CH, Ph), 73.0 (CH, 2-C), 66.0 (1-C), 39.8 (3-C); HRMS (ESI): calcd for $C_9H_{12}NaO_2$ $[M+Na]^+$: 175.07295, found 175.07445.



24

(*S*,*E*)-Methyl 2-(4,5-dihydroxypent-1-enyl)benzoate (24): To a stirred solution of the dioxane **18** (40 mg, 84.3 μmol) in CH_3CN/H_2O (9:1) (2 mL), was added CAN (102 mg, 0.186 mmol). The resulting solution was stirred at room temperature for 3 h, during which the starting material was almost completely consumed. The mixture was diluted with water (10 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated under reduced pressure and the crude residue was purified by flash chromatography (petroleum ether/ethyl acetate, 2:8) to afford the pure diol **24** as a colorless gel, 16.2 mg (81%). NMR analysis indicated a ratio of 8:1 (*E:Z*). R_f = 0.25 (petroleum ether/ethyl acetate, 2:8); $[\alpha]^{20}_D$ = + 7.9 (*c* 1.1, CH_2Cl_2). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82 (d, *J* = 7.8 Hz, 1H, H-3), 7.43-7.38 (m, 2H, aromatic), 7.28-7.20 (m, 1H, aromatic), 7.09 (d, *J* = 15.9 Hz, 1H, H-1’), 5.96 (ddd, *J* = 15.9, 7.9, 7.3 Hz, 1H, H-2’), 3.82 (s, 3H, CO_2Me), 3.81-3.75 (m, 1H, H-4´), 3.70-3.62 (m, 1H, H-5’), 3.56-3.46 (m, 1H, H-5’), 2.81 (br s, 1H, OH), 2.41-2.32 (m, 2H, H-3’, OH), 2.31-2.25 (m, 1H, H-3’). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 167.8 (C, C=O), 139.7 (C, 1-C), 132.9, 132.3, 130.3, 127.0 (CH, aromatic), 128.3 (CH, 2’-C), 127.3 (C, 2-C), 127.7 (CH, 1’-C), 71.3 (CH, 4’-C), 66.3 (CH_2, 5’-C), 52.2 (CH_3, CO_2Me), 37.0 (CH_2, 3’-C). HRMS: calcd for $C_{13}H_{16}NaO_4$ $[M+Na]^+$: 259.09408, found 259.09413.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Ph
OMe
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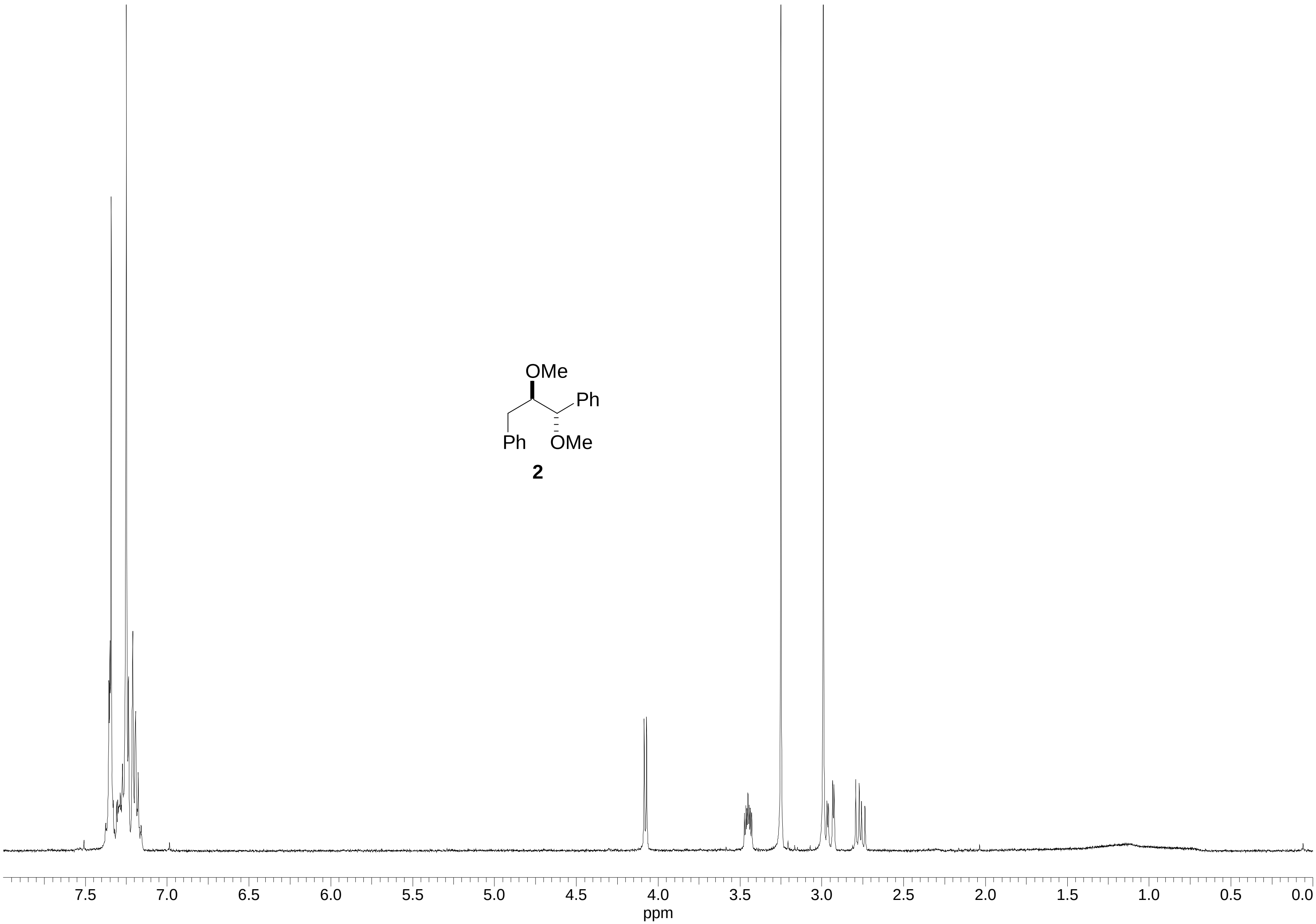
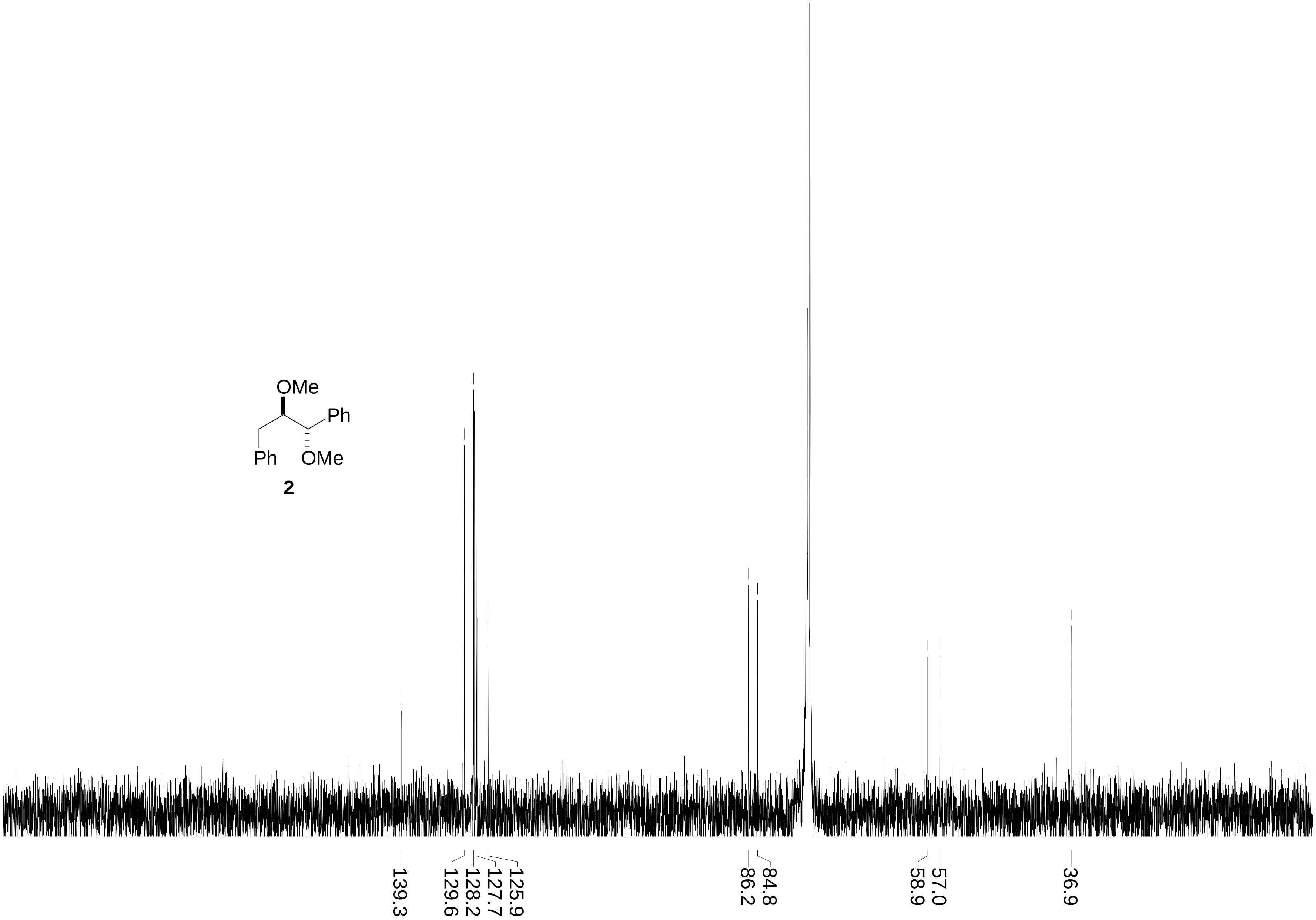
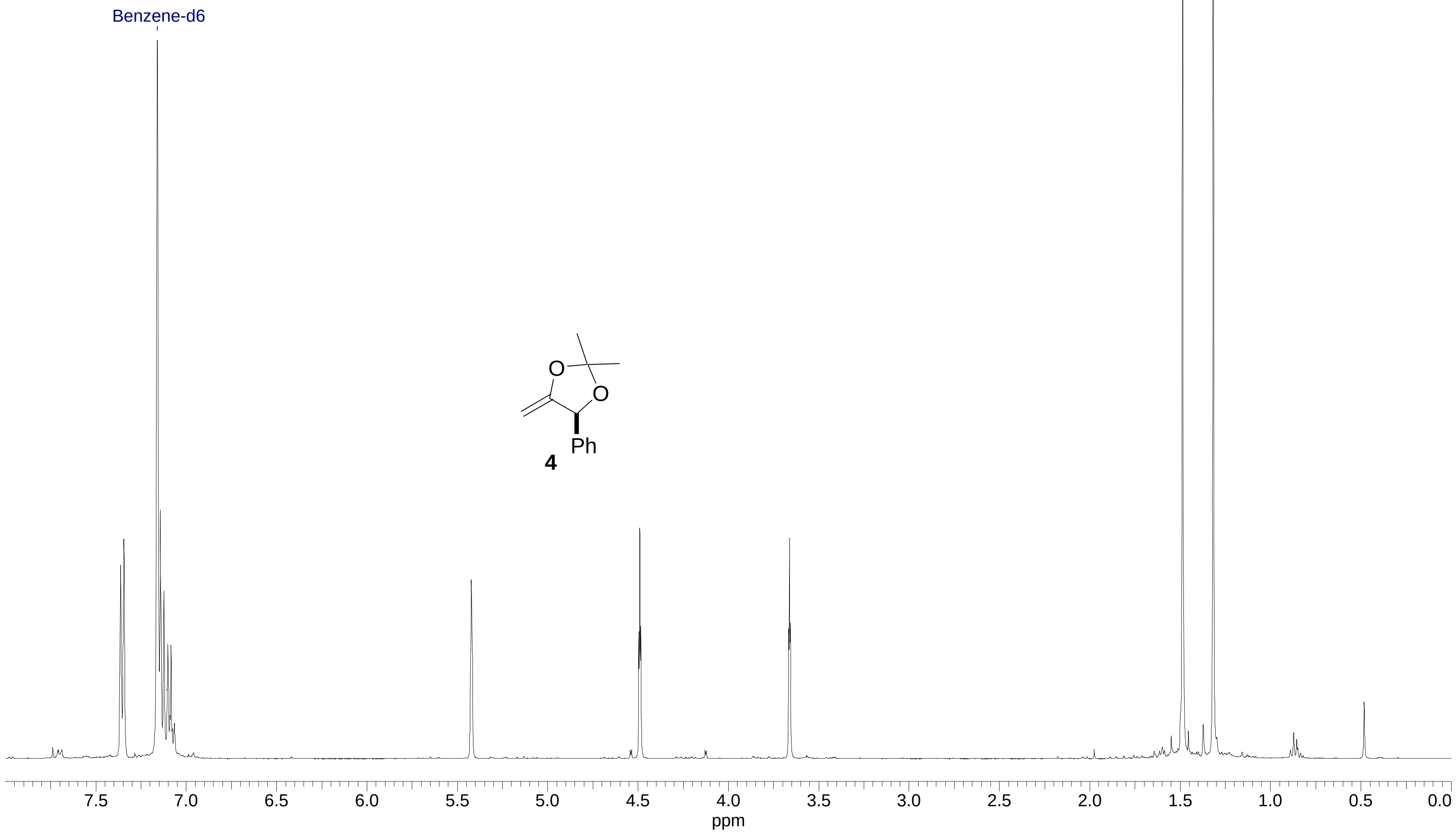
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



2



2


Benzene-d6
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O
Ph
4
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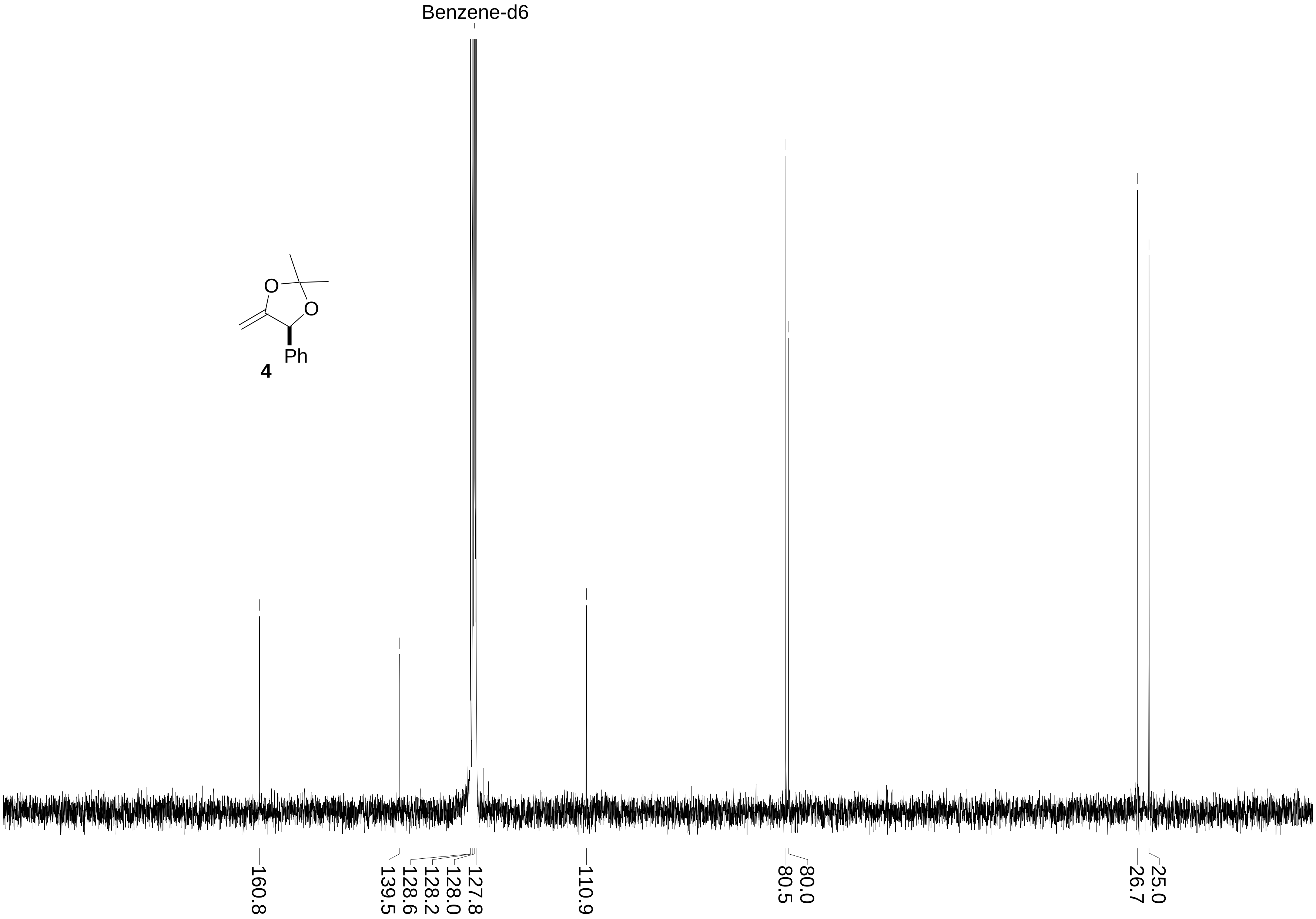
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Benzene-d6
O
O
Ph
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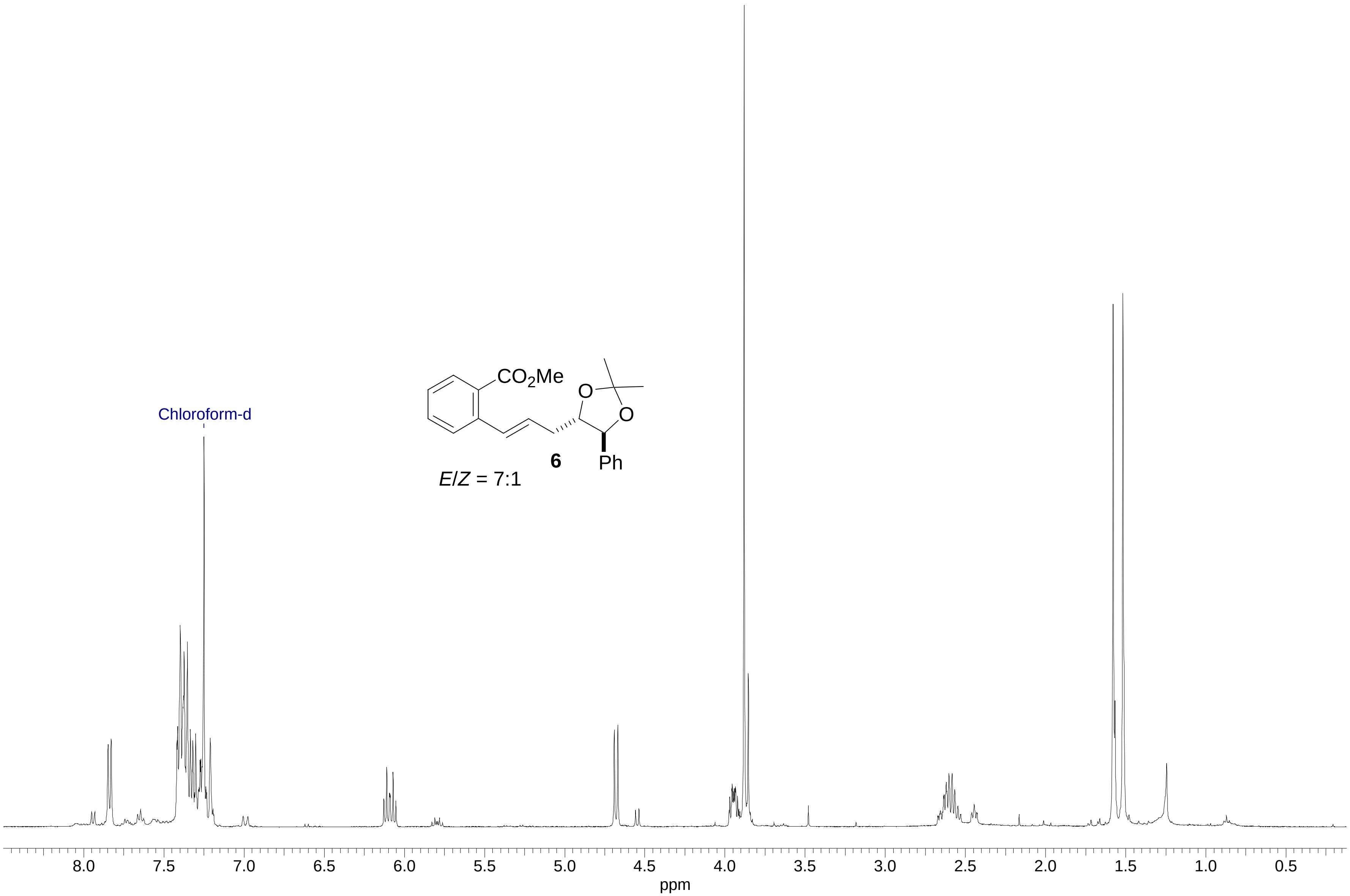
128.2
128.0
127.8
110.9
80.5
80.0
26.7
25.0

4


CO2Me
O
O
Ph
6
E/Z = 7:1
Chloroform-d
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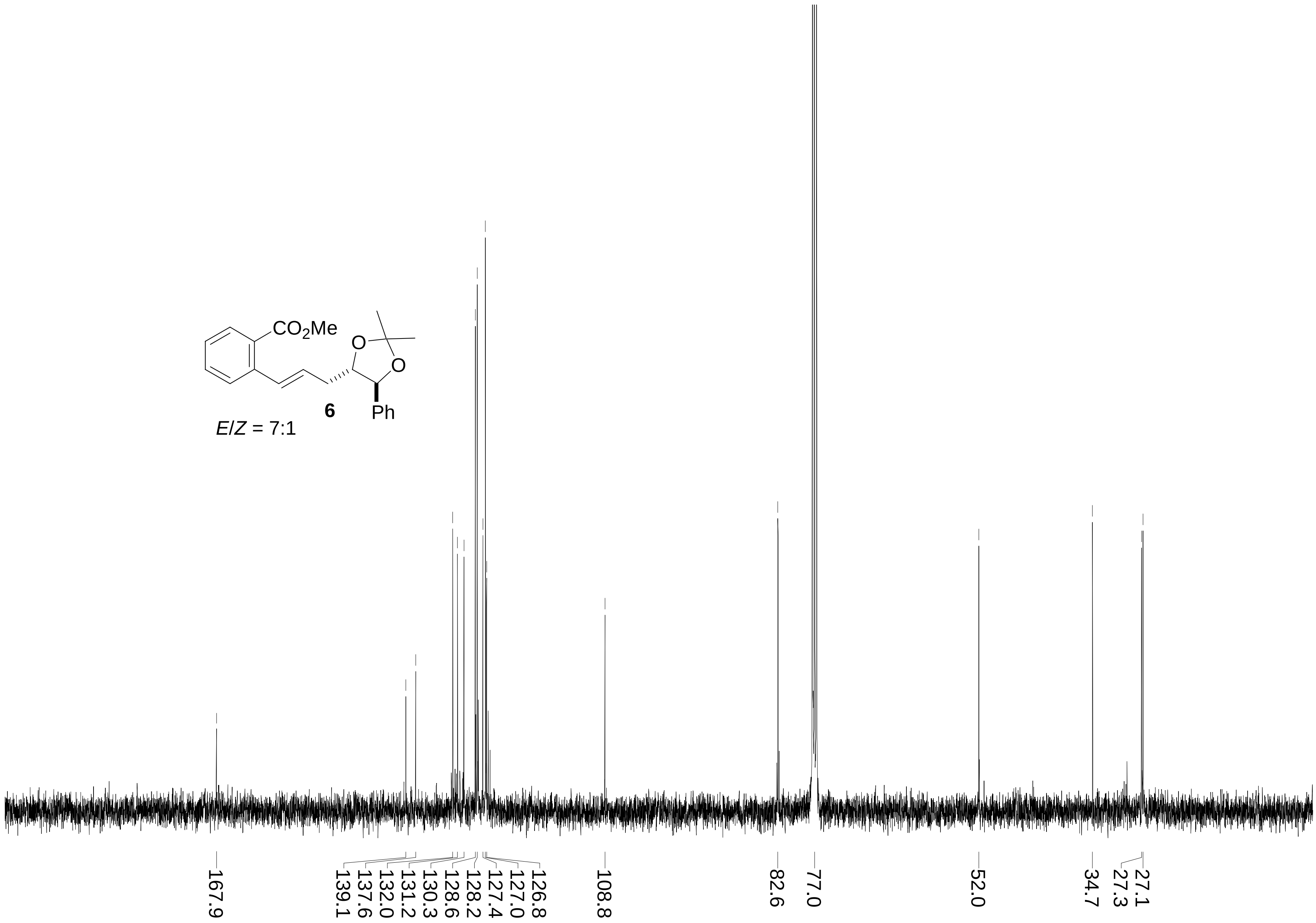
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm


CO2Me
O
O
Ph
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137.6
132.0
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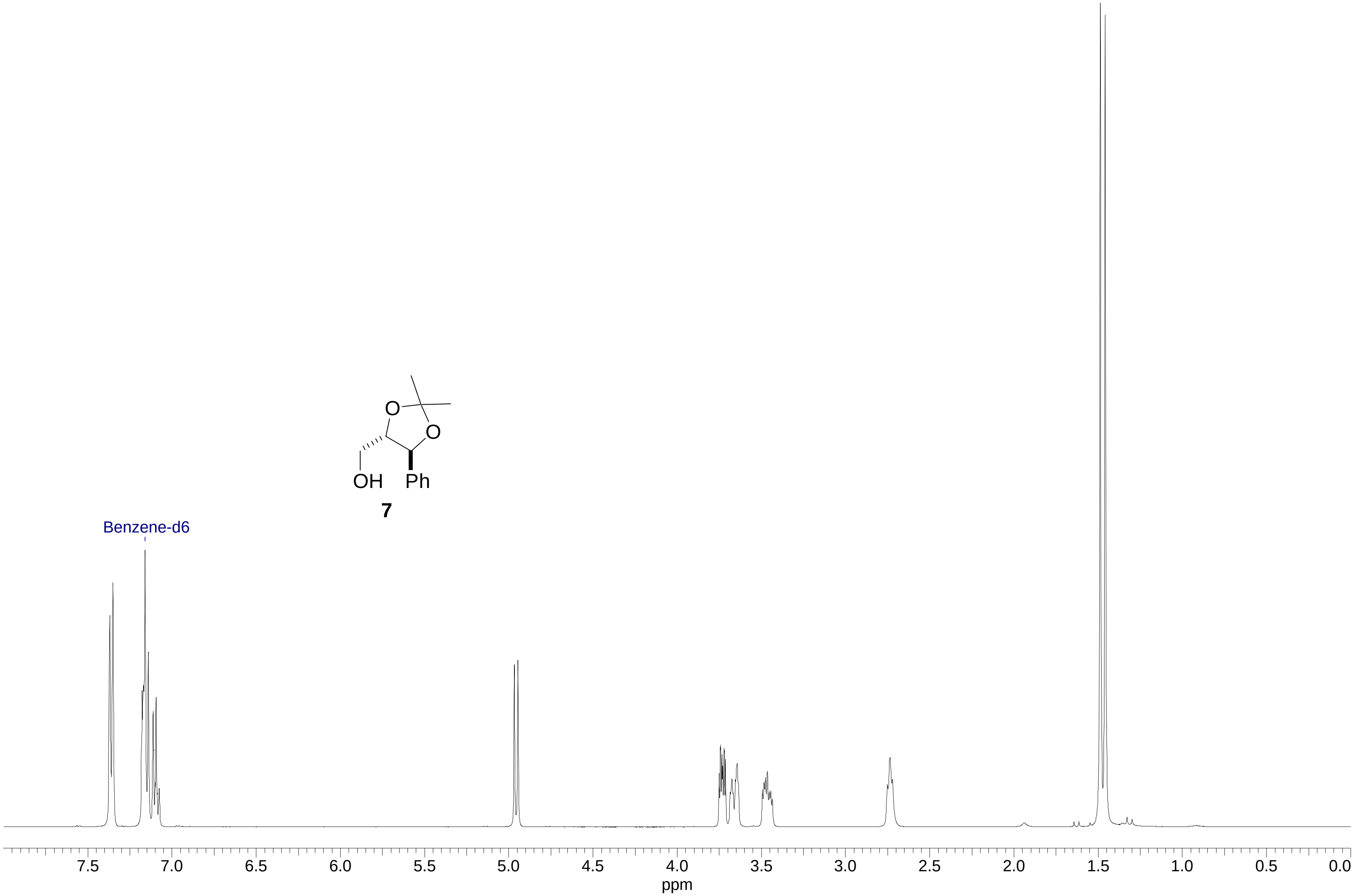
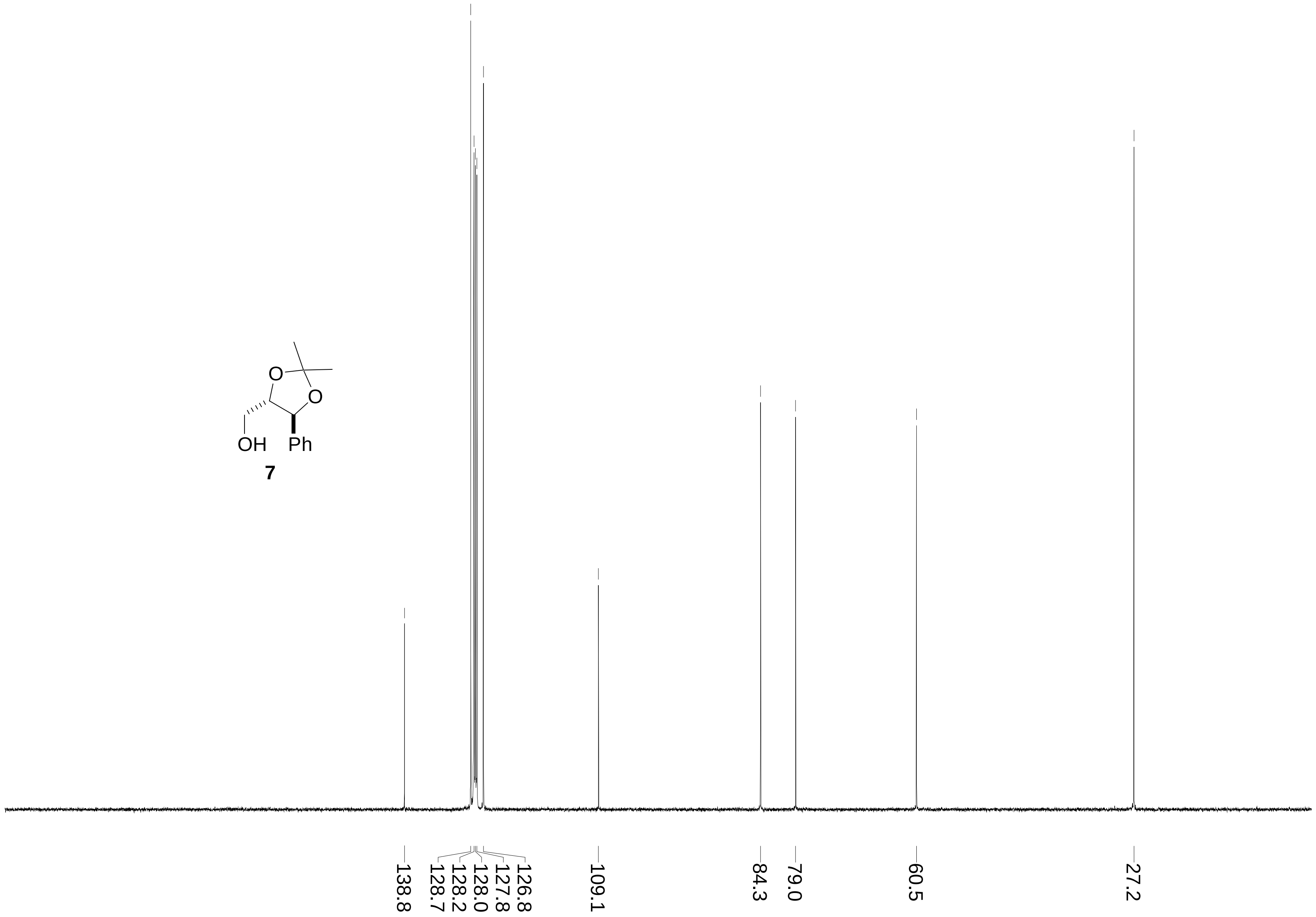
130.3
128.6
128.2
127.4
127.0
126.8
108.8
82.6
77.0
52.0
34.7
27.3
27.1

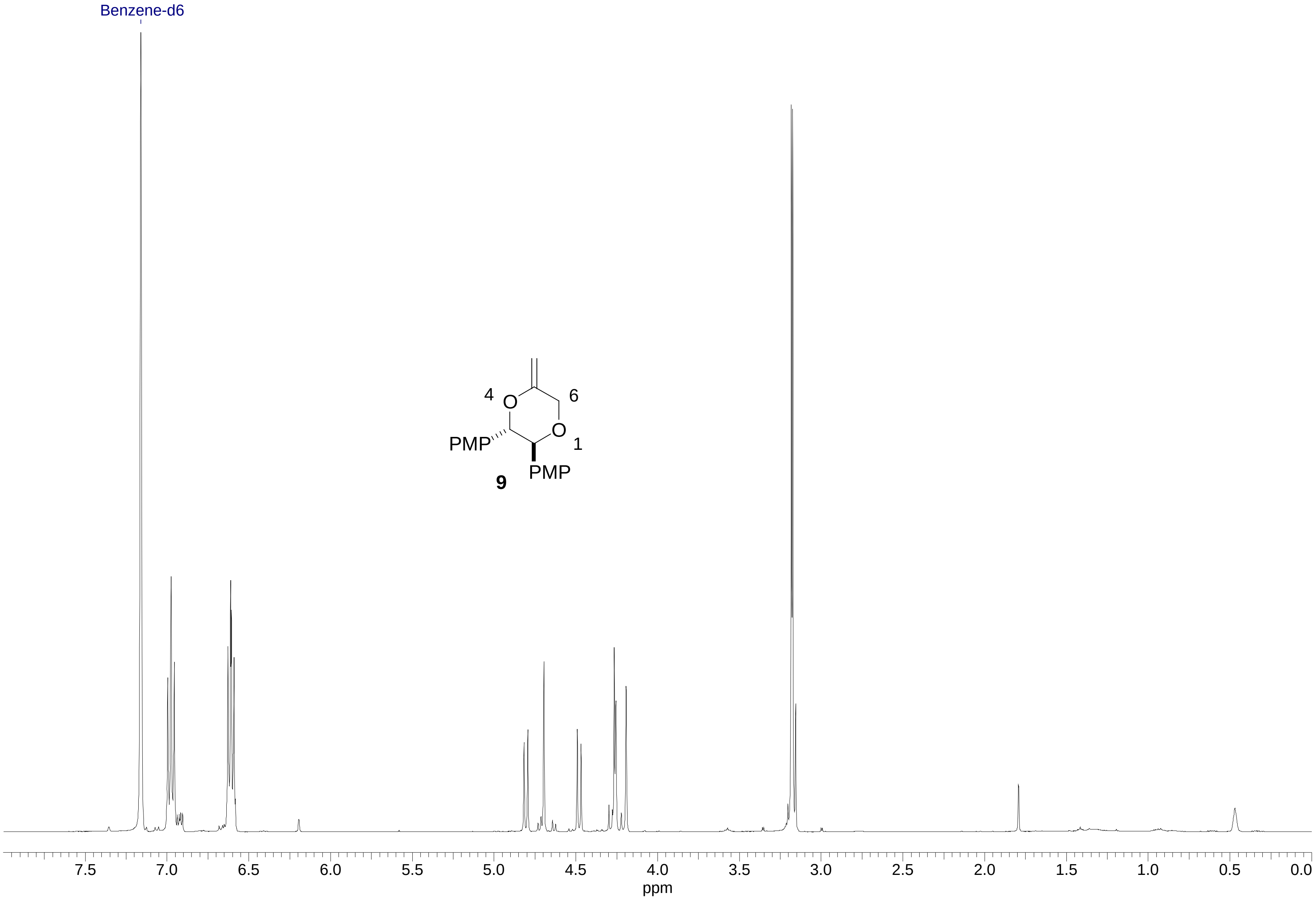
6

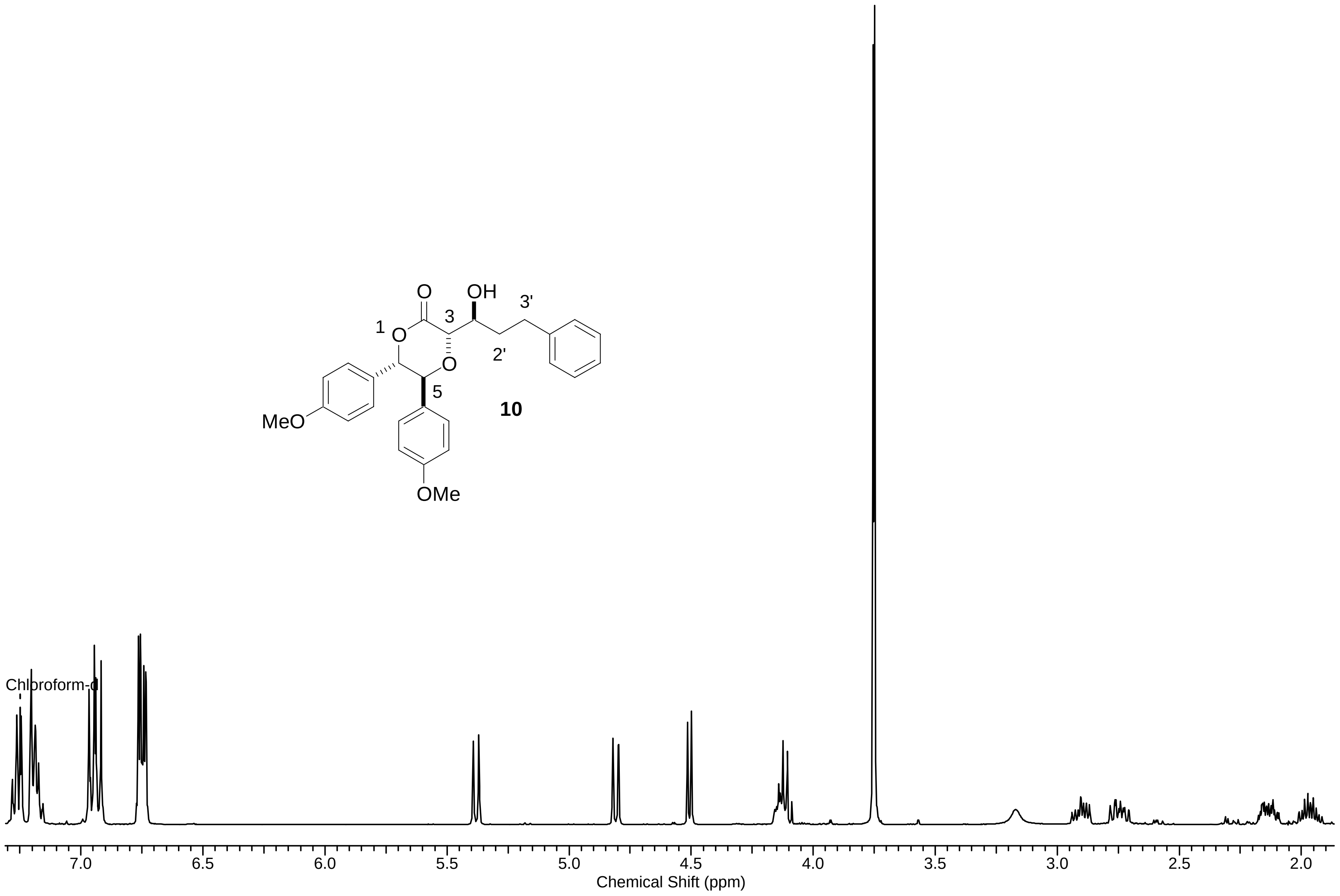
E/*Z* = 7:1


O
O
OH
Ph
Benzene-d6
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

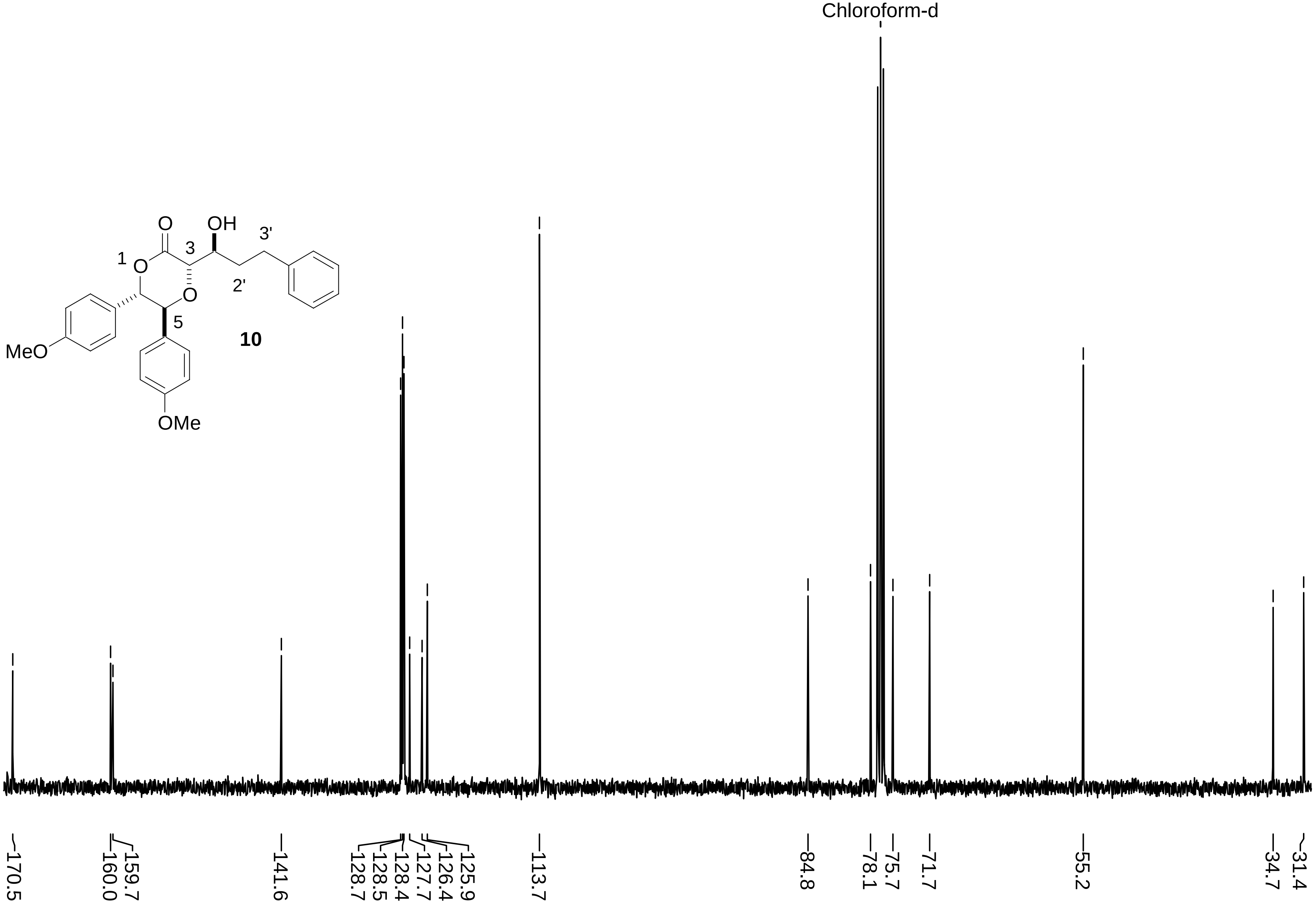
7


O
O
OH
Ph
7
138.8
128.7
128.2
128.0
127.8
126.8
109.1
84.3
79.0
60.5
27.2

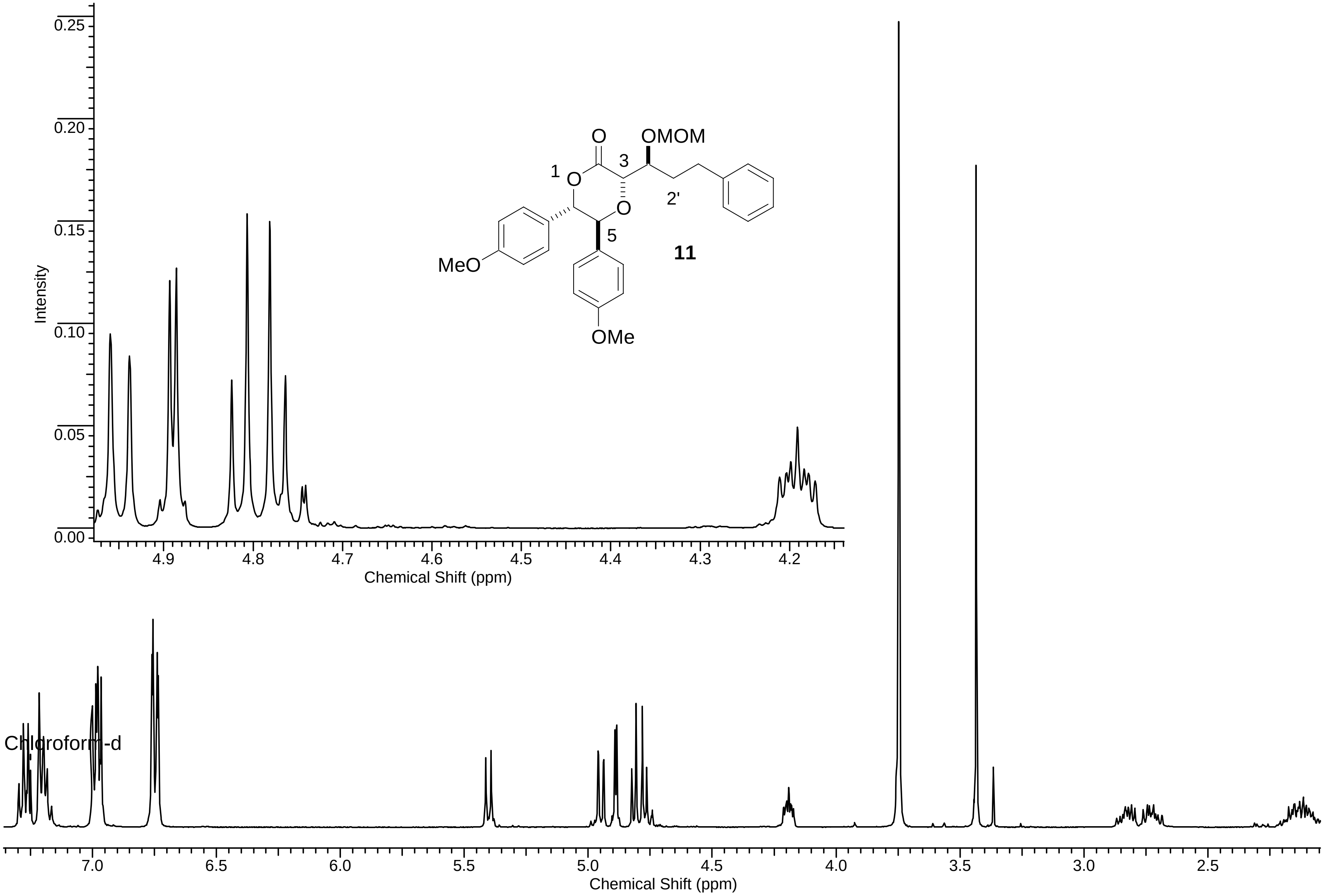

Benzene-d6
4
6
O
O
1
PMP
PMP
9
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


O
OH
3'
1
O
3
2'
O
5
MeO
OMe
Chloroform-d
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)

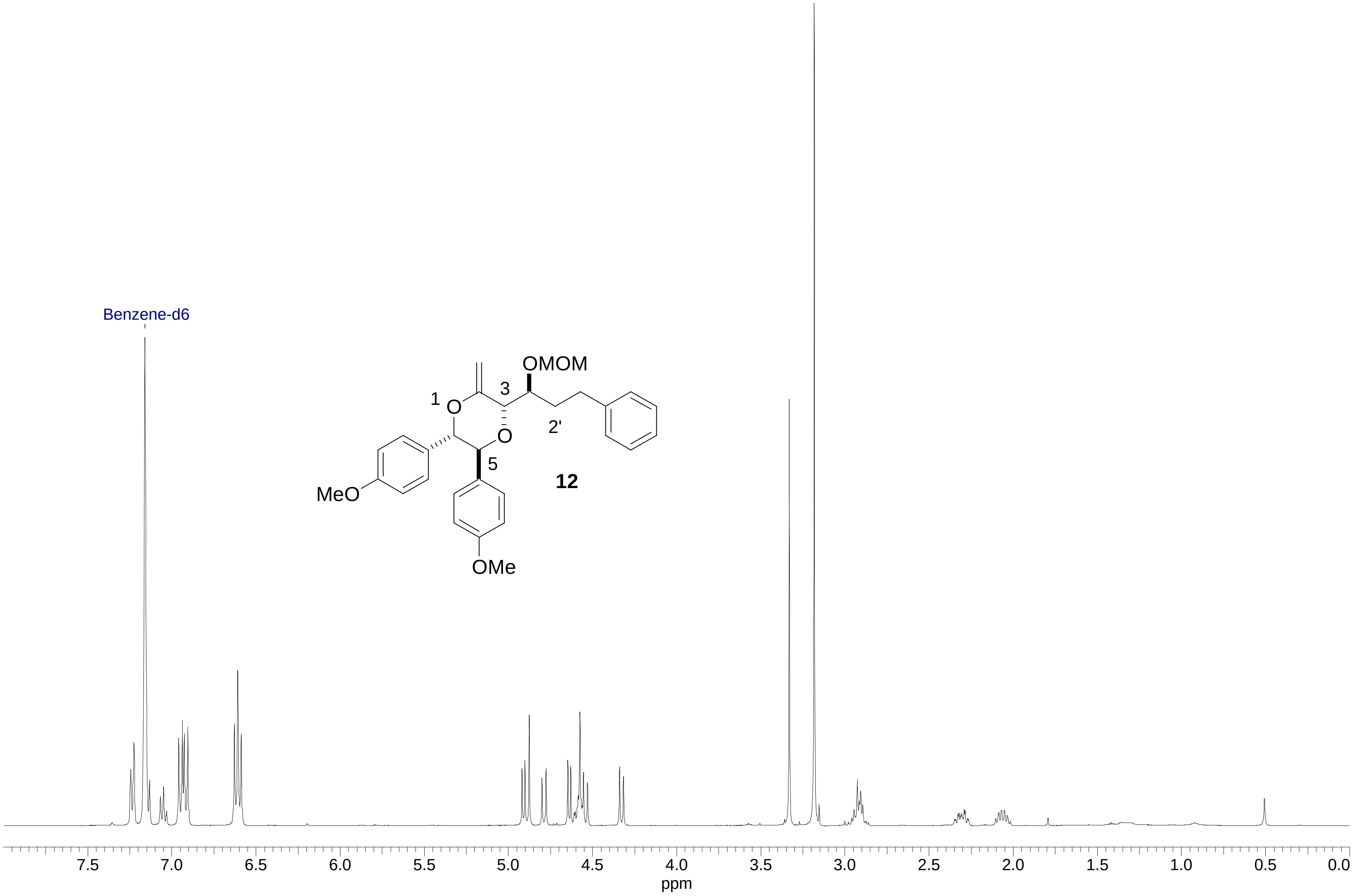
10


10

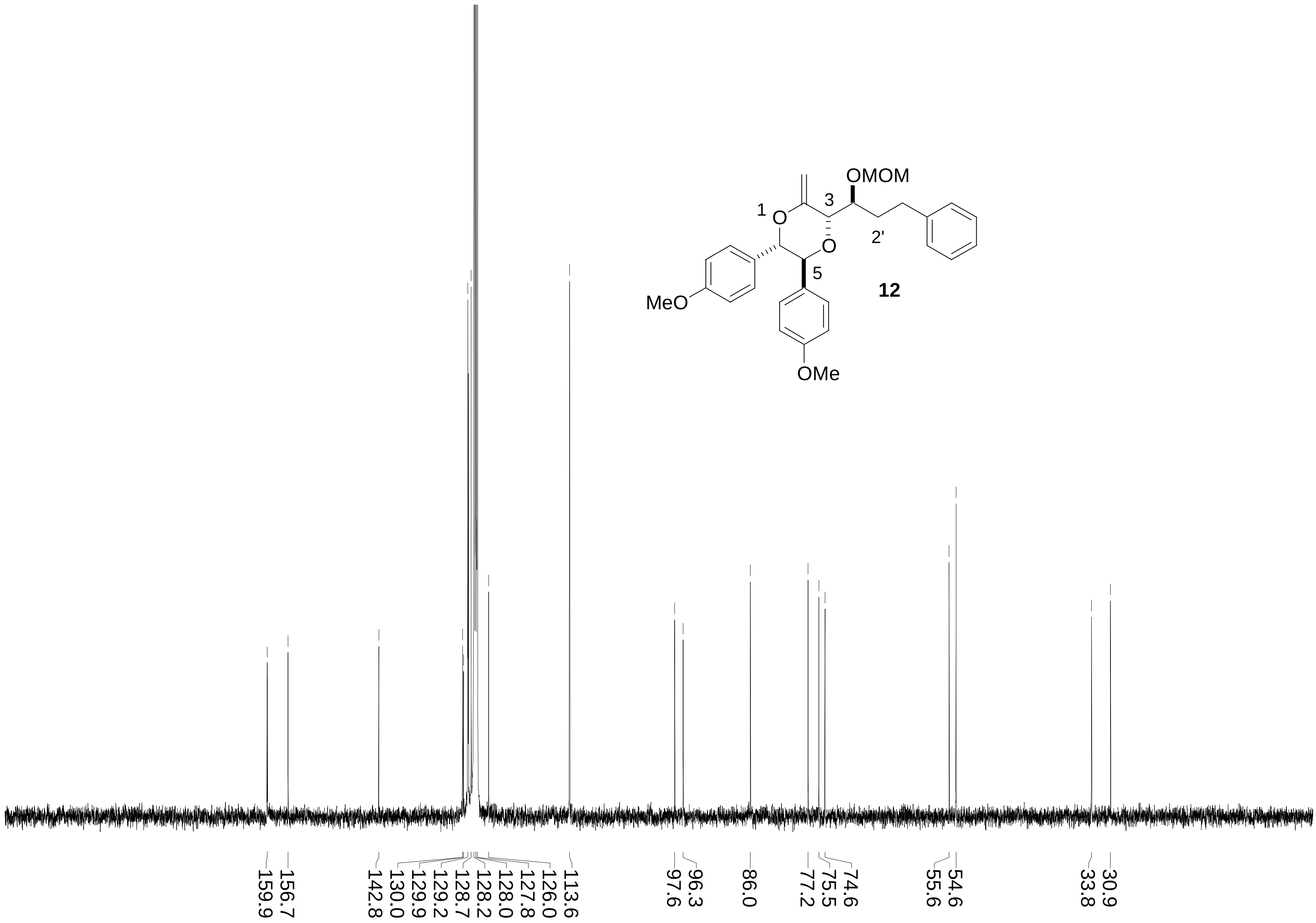
Chloroform-d
O
OH
3'
1
O
3
2'
O
5
MeO
OMe
170.5
160.0
159.7
141.6
128.7
128.5
128.4
127.7
126.4
125.9
113.7
84.8
78.1
75.7
71.7
55.2
34.7
31.4



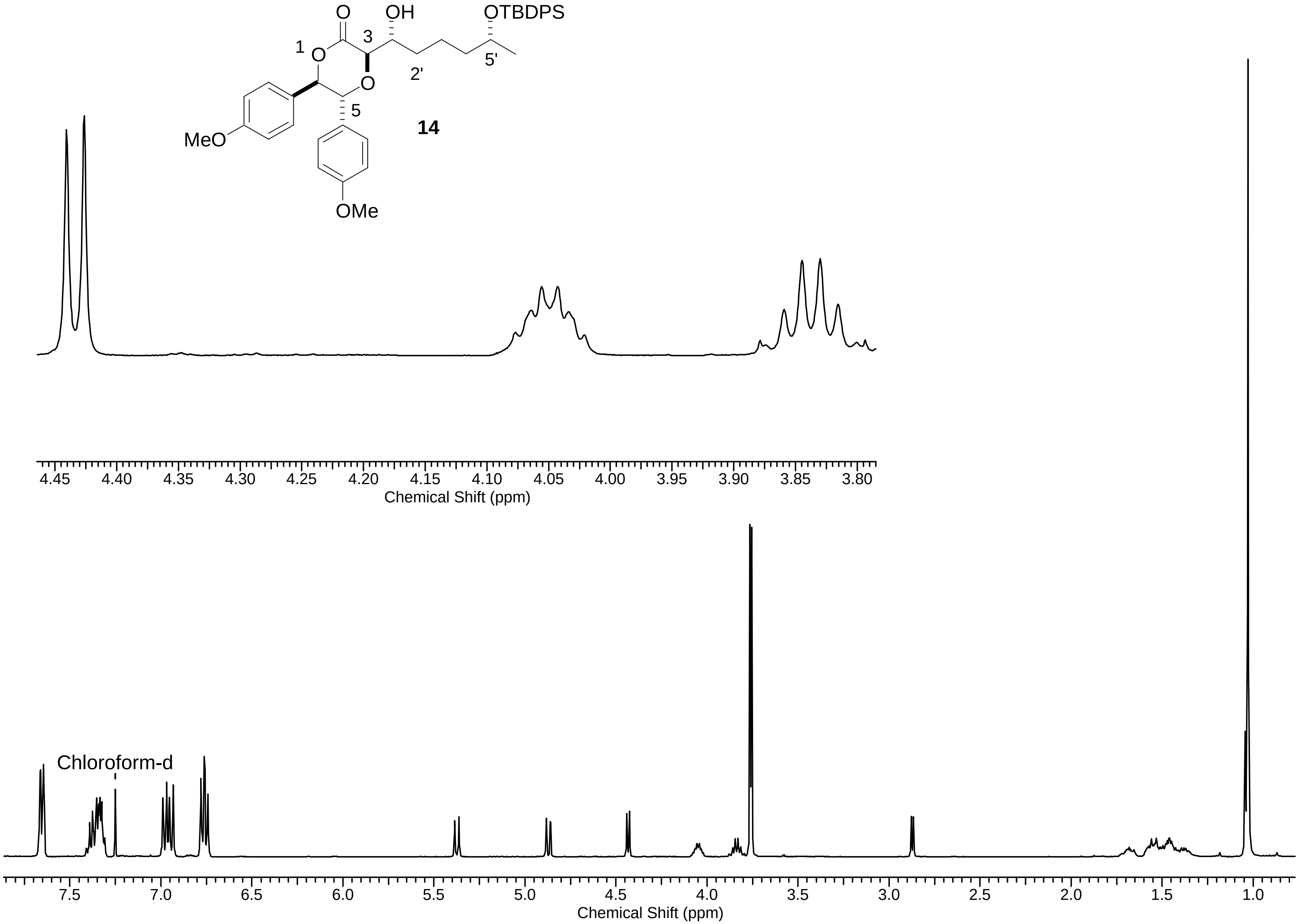
0.25
0.20
0.15
0.10
0.05
0.00
Intensity
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
Chemical Shift (ppm)
O
OMOM
1
3
O
O
2'
5
MeO
OMe
11
Chloroform-d
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
Chemical Shift (ppm)

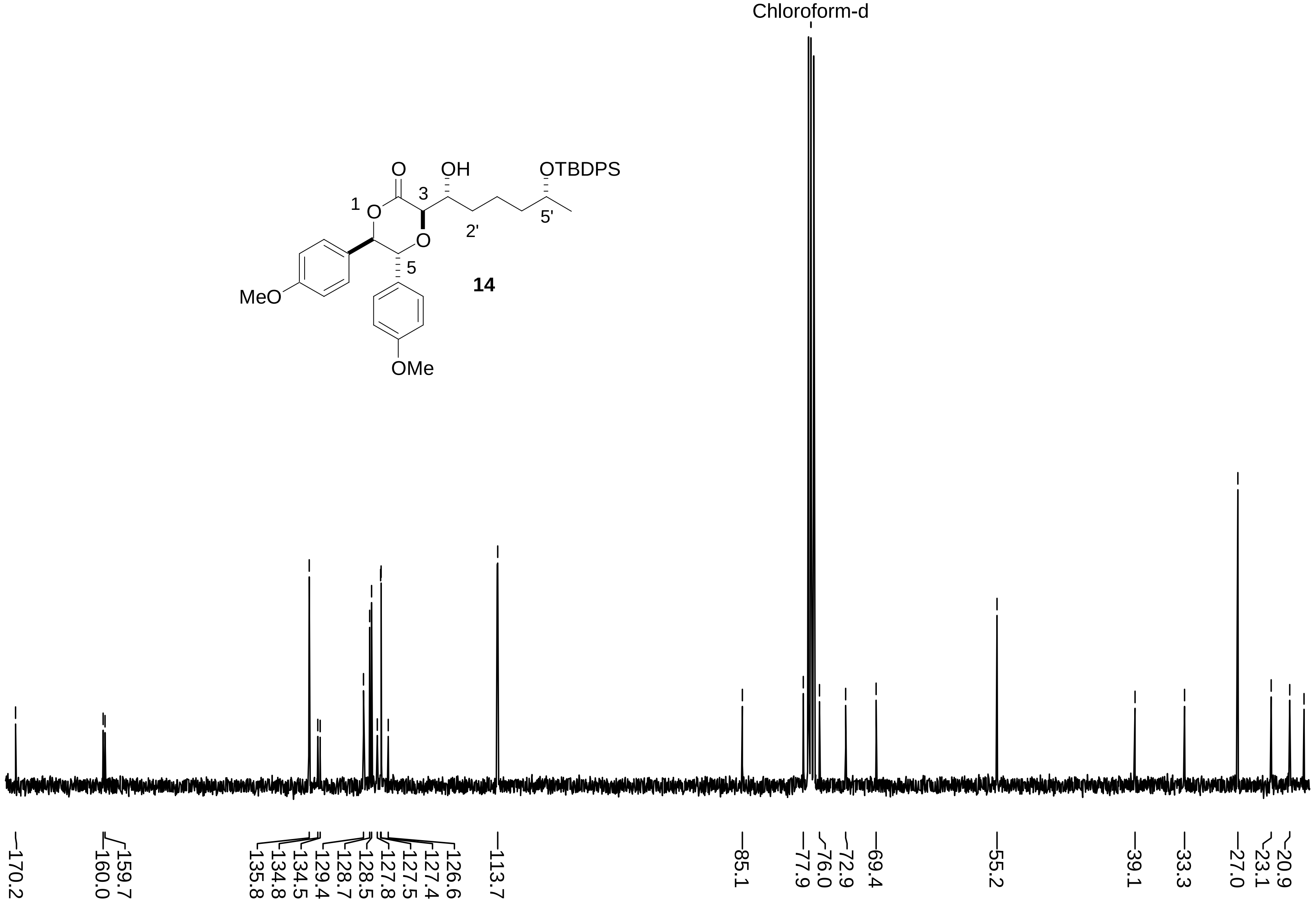

Benzene-d6
OMOM
1
O
3
O
2'
5
MeO
OMe
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

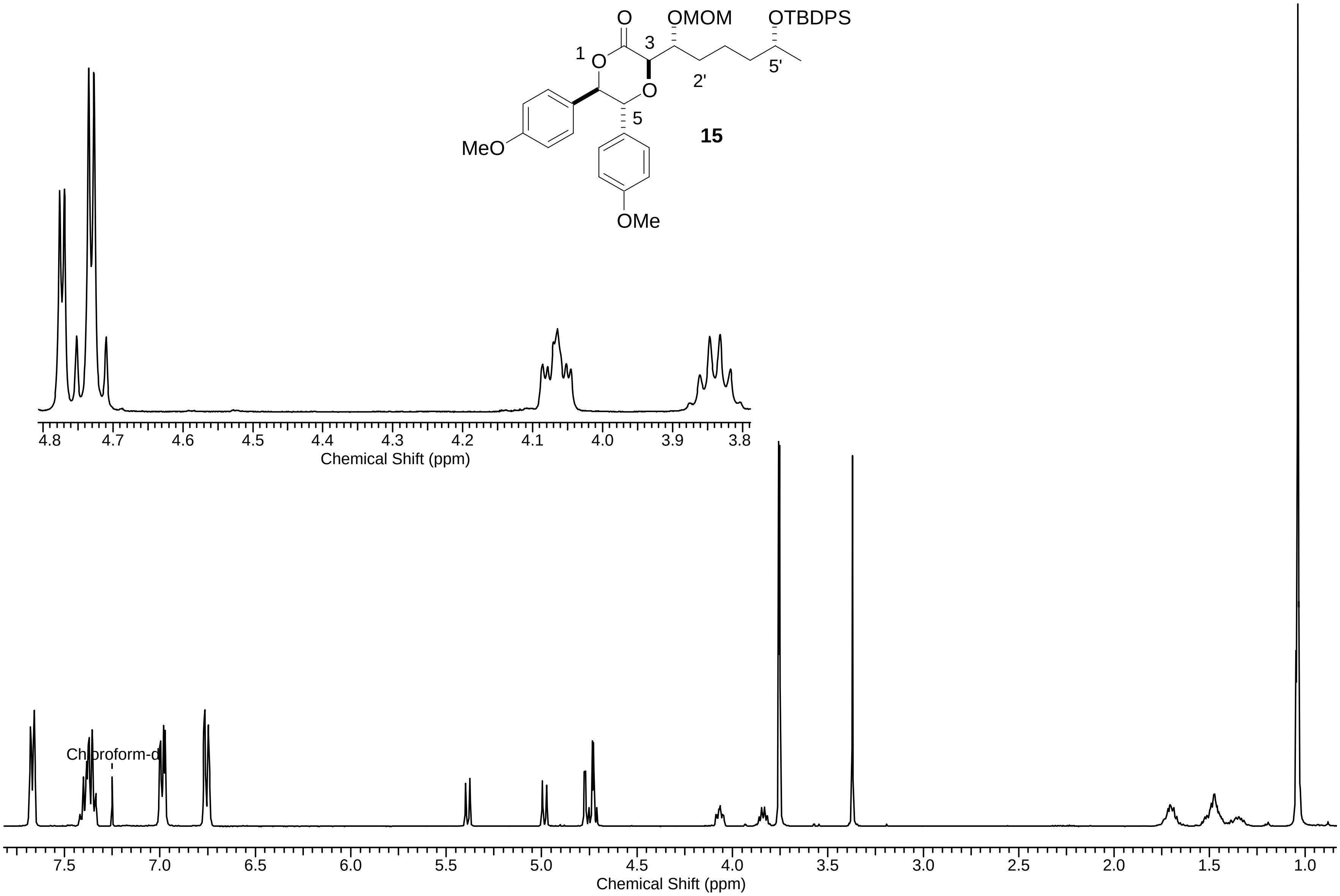
12


OMOM
1
O
3
O
2'
5
MeO
OMe
159.9
156.7
142.8
130.0
129.9
129.2
128.7
128.2
128.0
127.8
126.0
113.6
97.6
96.3
86.0
77.2
75.5
74.6
55.6
54.6
33.8
30.9

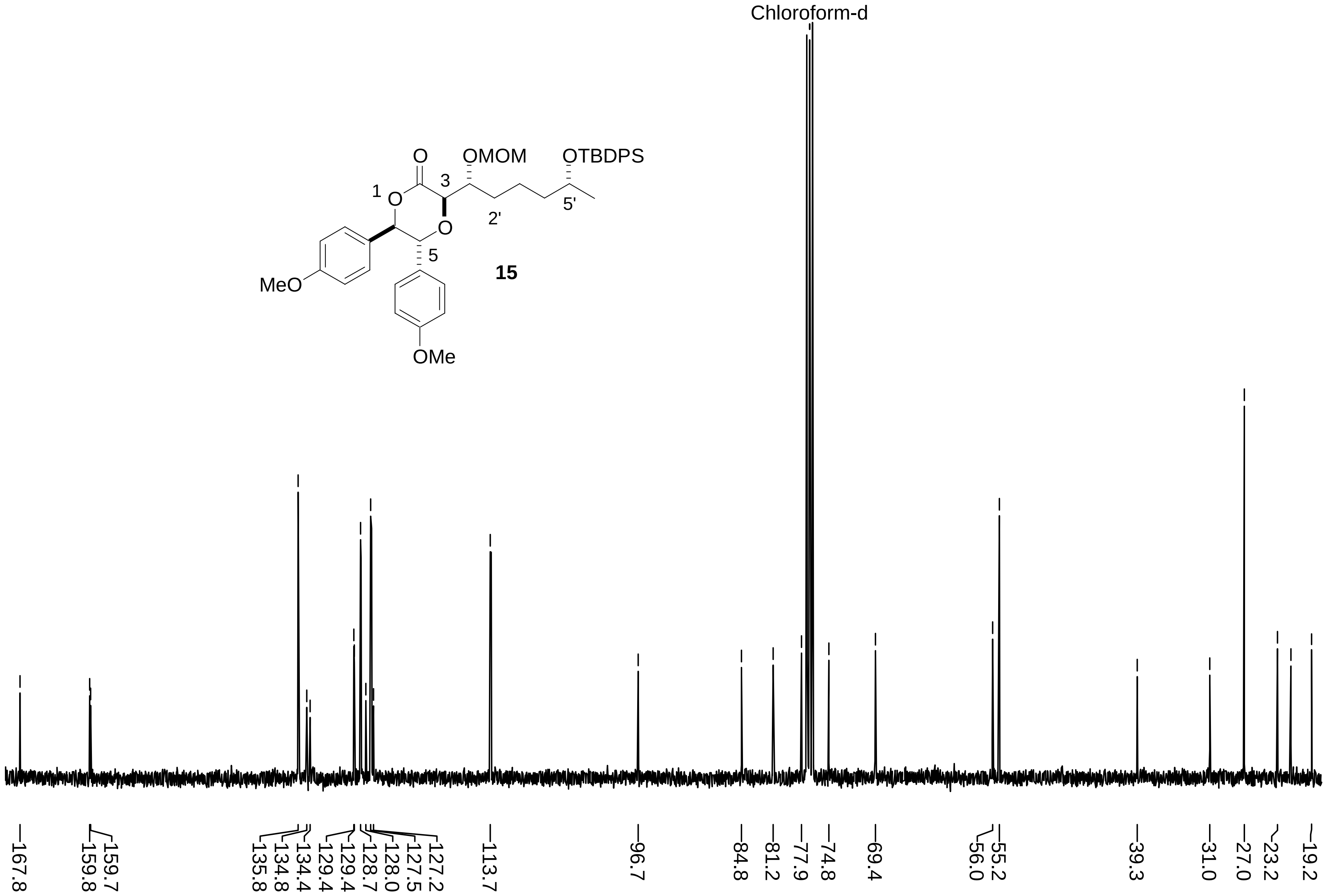
12

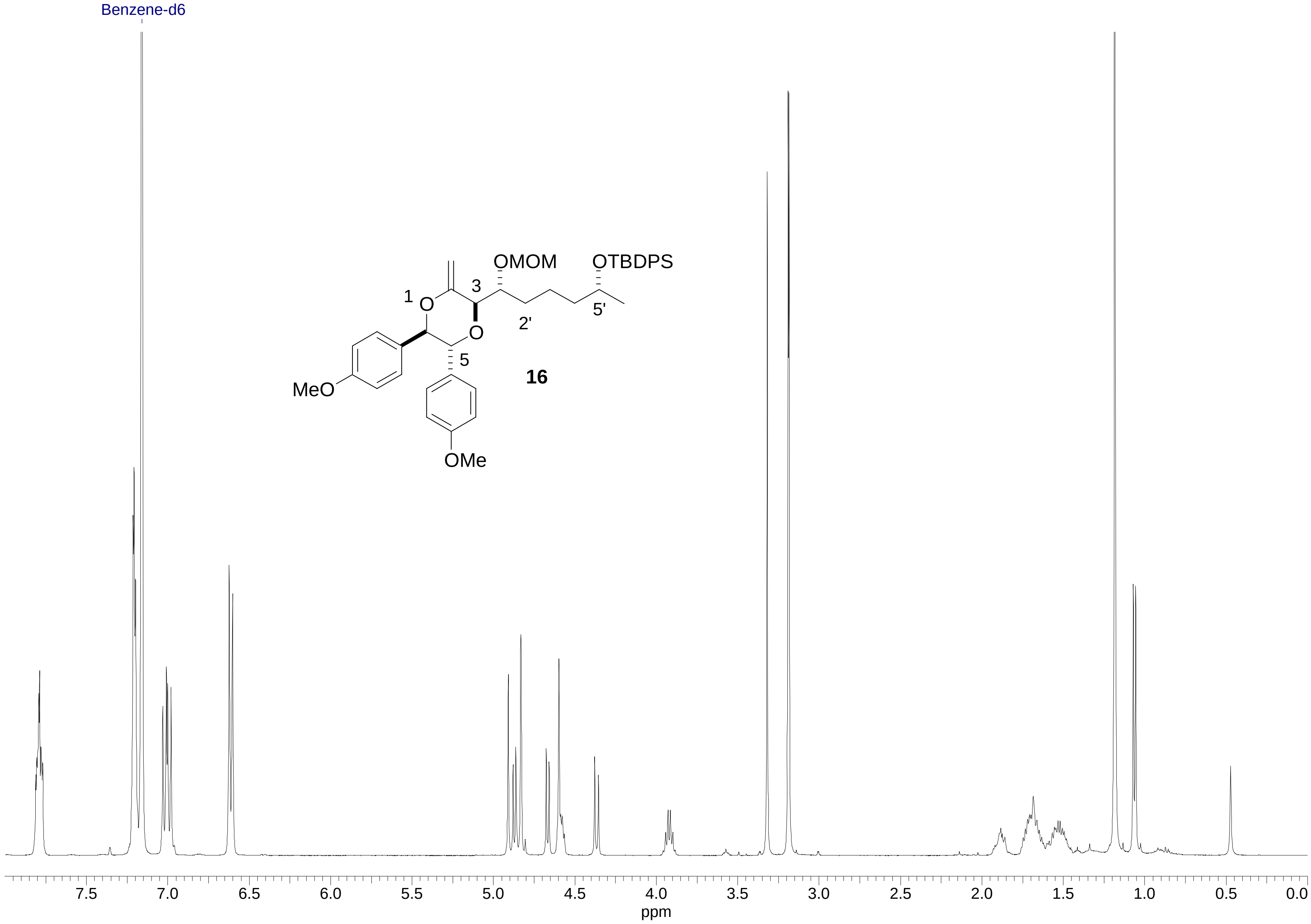

O
OH
OTBDPS
1
3
2'
5'
O
O
5
MeO
OMe
14
4.45
4.40
4.35
4.30
4.25
4.20
4.15
4.10
4.05
4.00
3.95
3.90
3.85
3.80
Chemical Shift (ppm)
Chloroform-d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)


Chloroform-d
O
OH
OTBDPS
1
O
3
O
2'
5'
5
MeO
OMe
14
170.2
160.0
159.7
135.8
134.8
134.5
129.4
128.7
128.5
127.8
127.5
127.4
126.6
113.7
85.1
77.9
76.0
72.9
69.4
55.2
39.1
33.3
27.0
23.1
20.9


O
OMOM
OTBDPS
1
O
3
2'
5'
O
5
MeO
OMe
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
3.8
Chemical Shift (ppm)
Chloroform-d
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
Chemical Shift (ppm)

15


Chloroform-d
O
OMOM
OTBDPS
1
3
O
O
2'
5'
5
MeO
OMe
15
167.8
159.8
159.7
135.8
134.8
134.4
129.4
129.4
128.7
128.0
127.5
127.2
113.7
96.7
84.8
81.2
77.9
74.8
69.4
56.0
55.2
39.3
31.0
27.0
23.2
19.2


Benzene-d6
OMOM
OTBDPS
1
O
3
O
2'
5'
5
MeO
OMe
16
7.5
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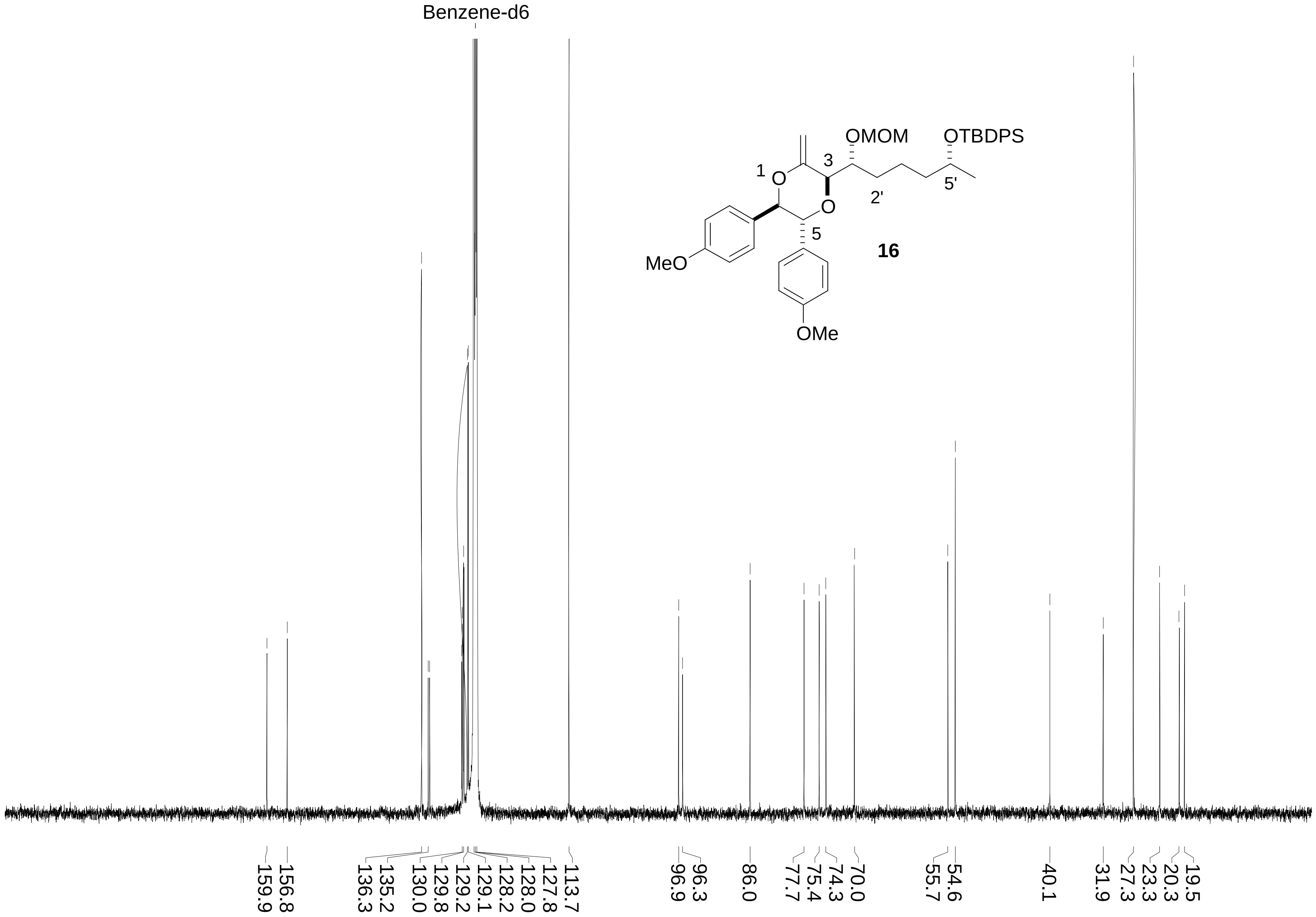
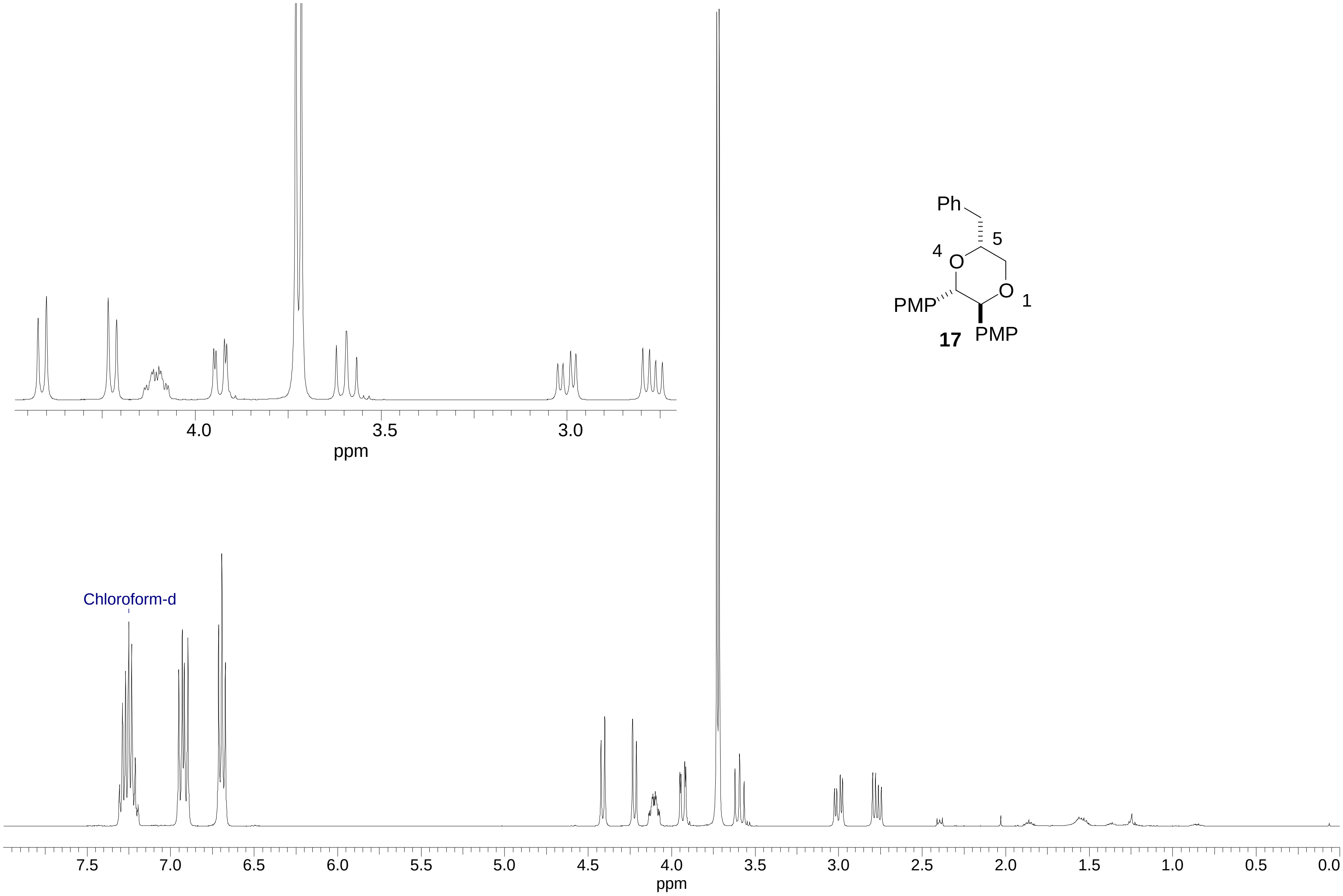
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


Benzene-d6
OMOM
OTBDPS
1
3
O
O
2'
5'
5
MeO
OMe
16
159.9
156.8
136.3
135.2
130.0
129.8
129.2
129.1
128.2
128.0
127.8
113.7
96.9
96.3
86.0
77.7
75.4
74.3
70.0
55.7
54.6
40.1
31.9
27.3
23.3
20.3
19.5



Chloroform-d
4.0
3.5
3.0
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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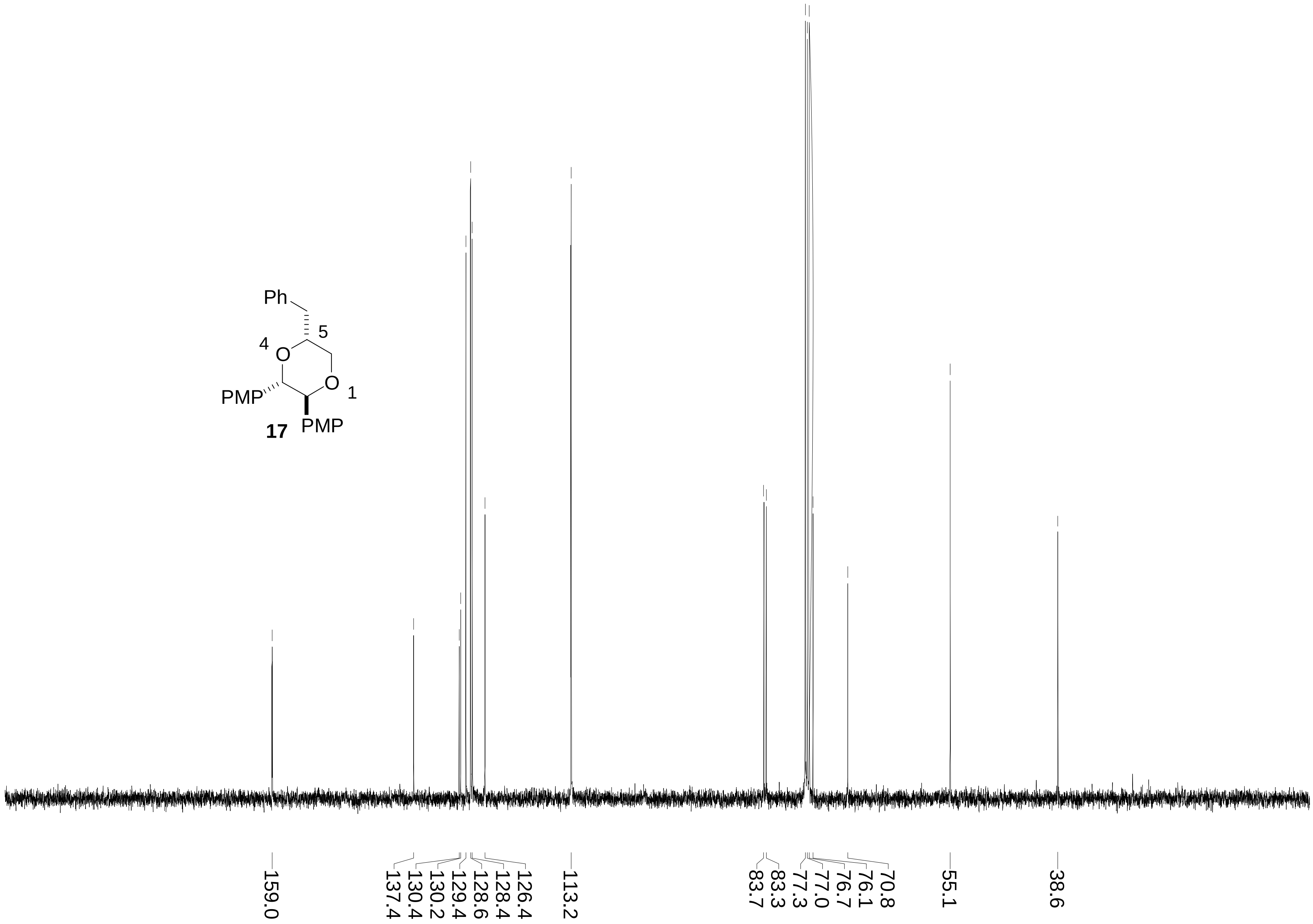
1.0
0.5
0.0
ppm

Ph
5
4
O
O
1
PMP
PMP

17


Ph
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4
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PMP
PMP
17
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130.4
130.2
129.4
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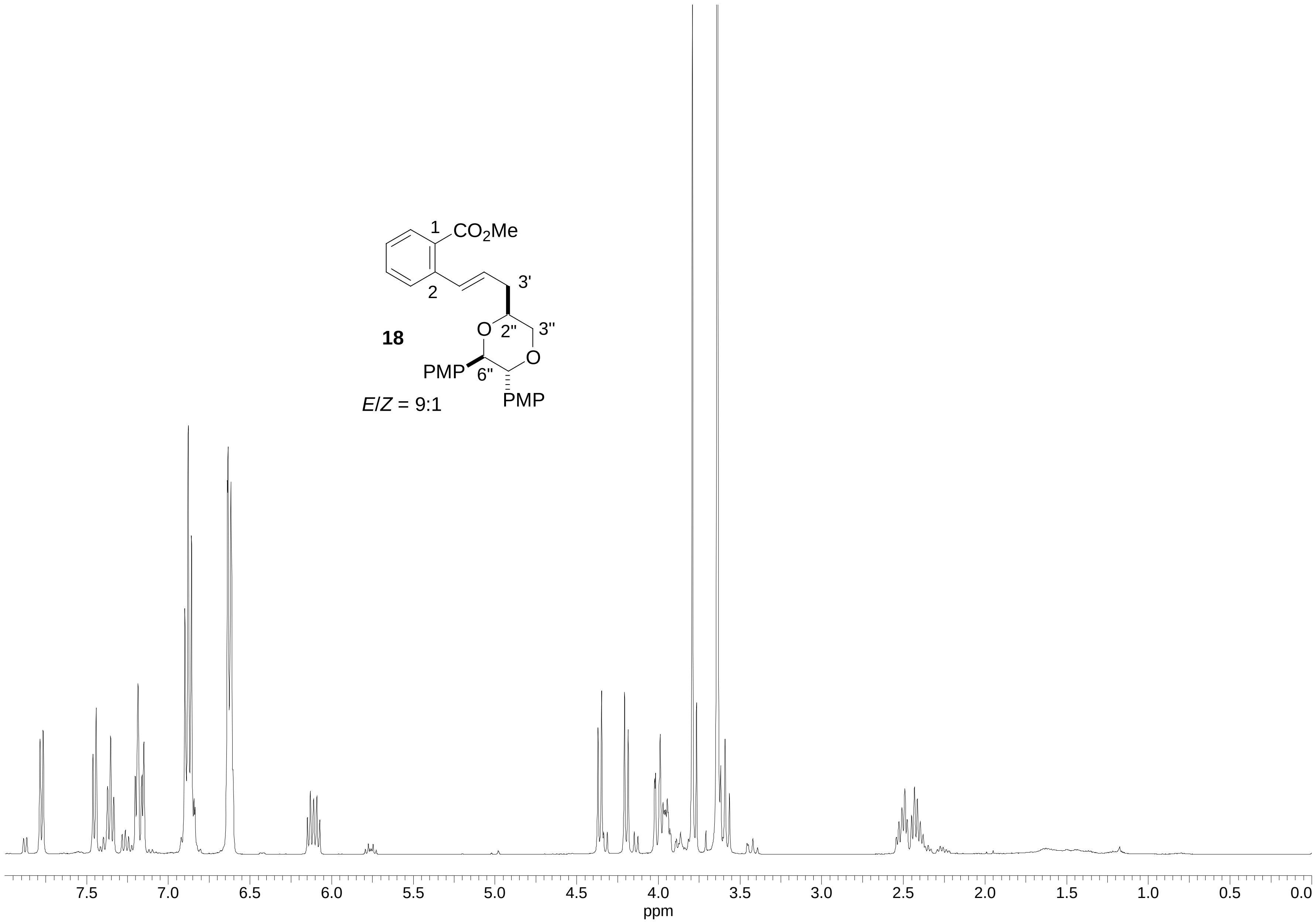
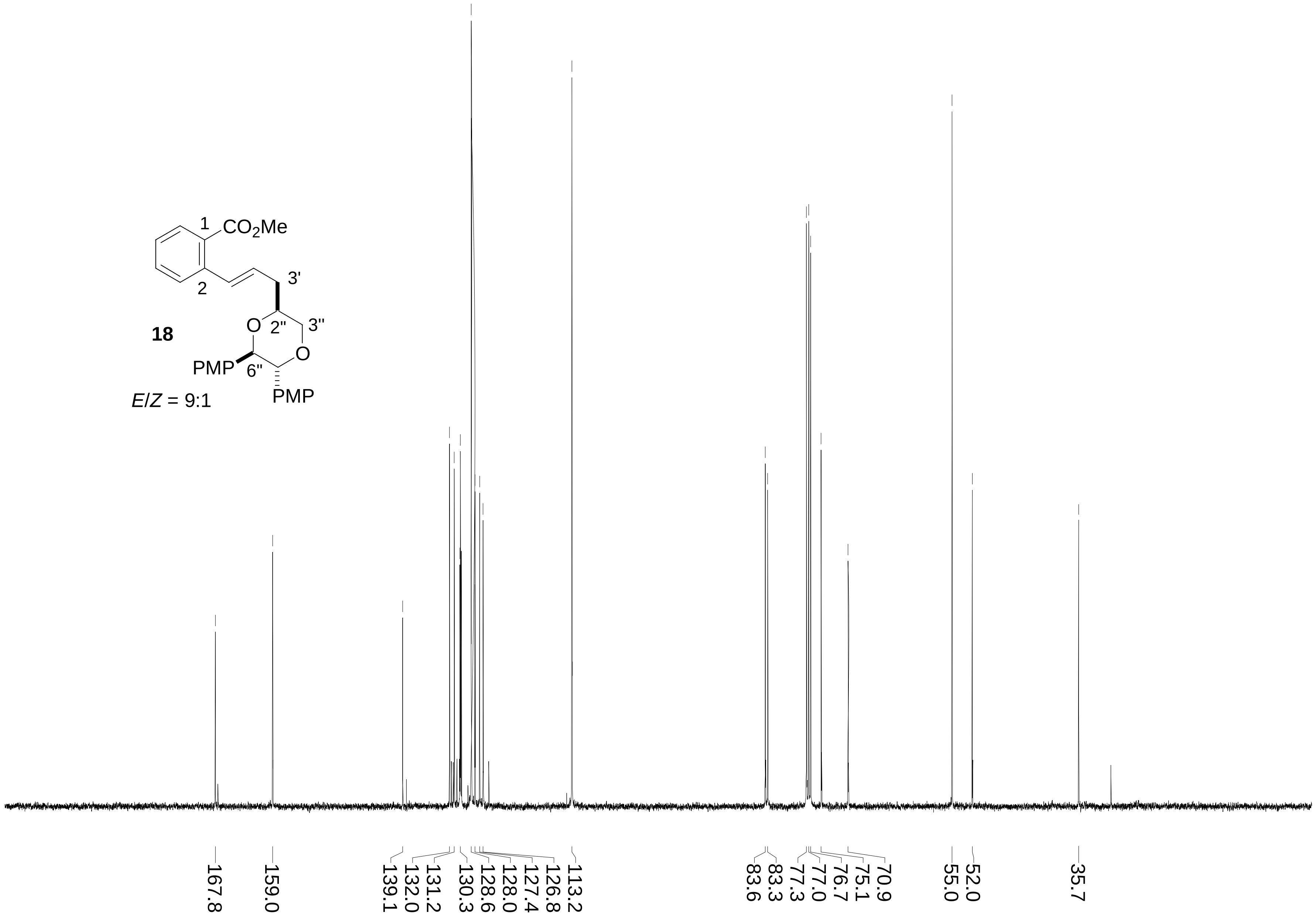
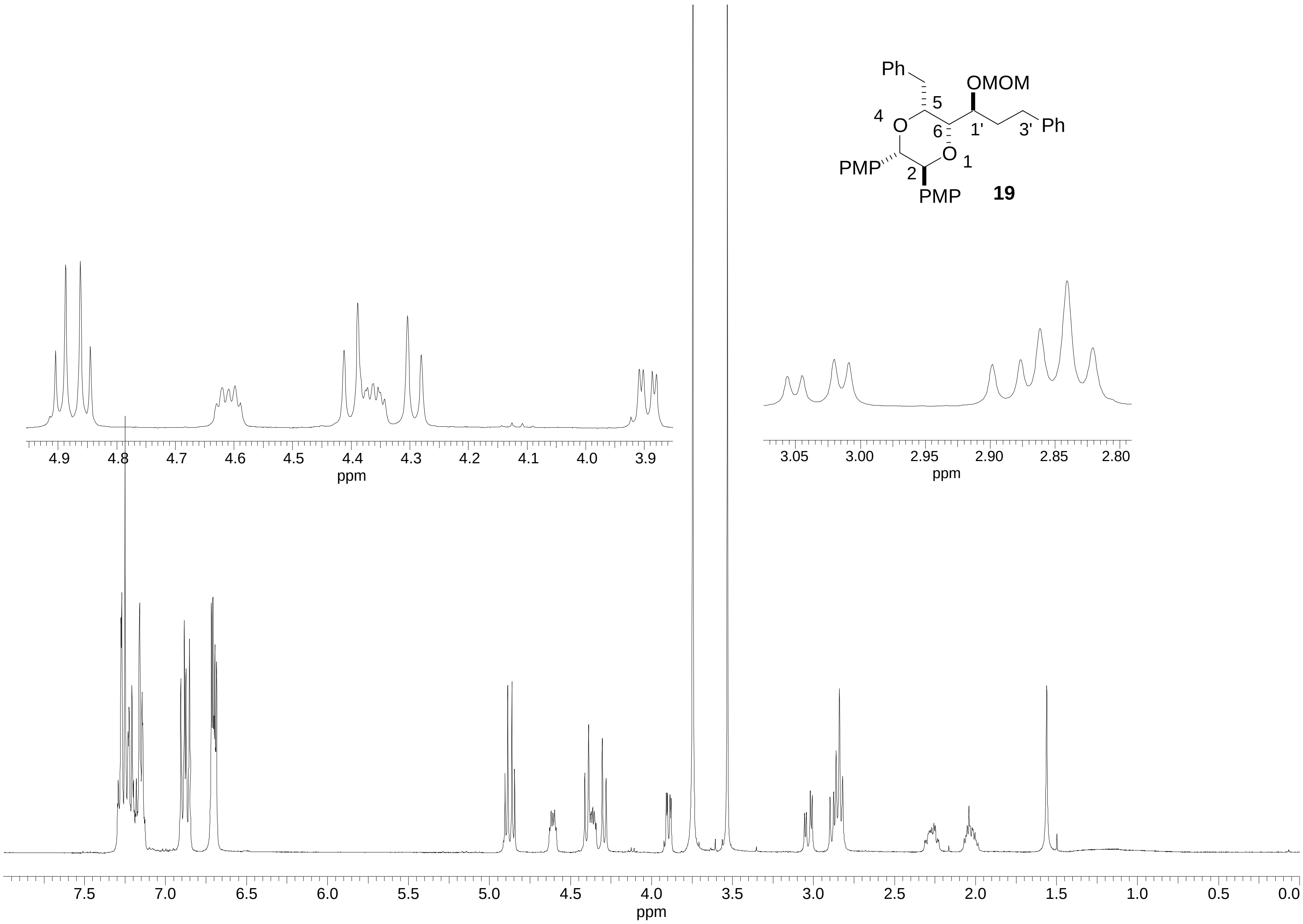
128.4
126.4
113.2
83.7
83.3
77.3
77.0
76.7
76.1
70.8
55.1
38.6


1
CO2Me
2
3'
O
2"
3"
O
PMP
6"
PMP
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

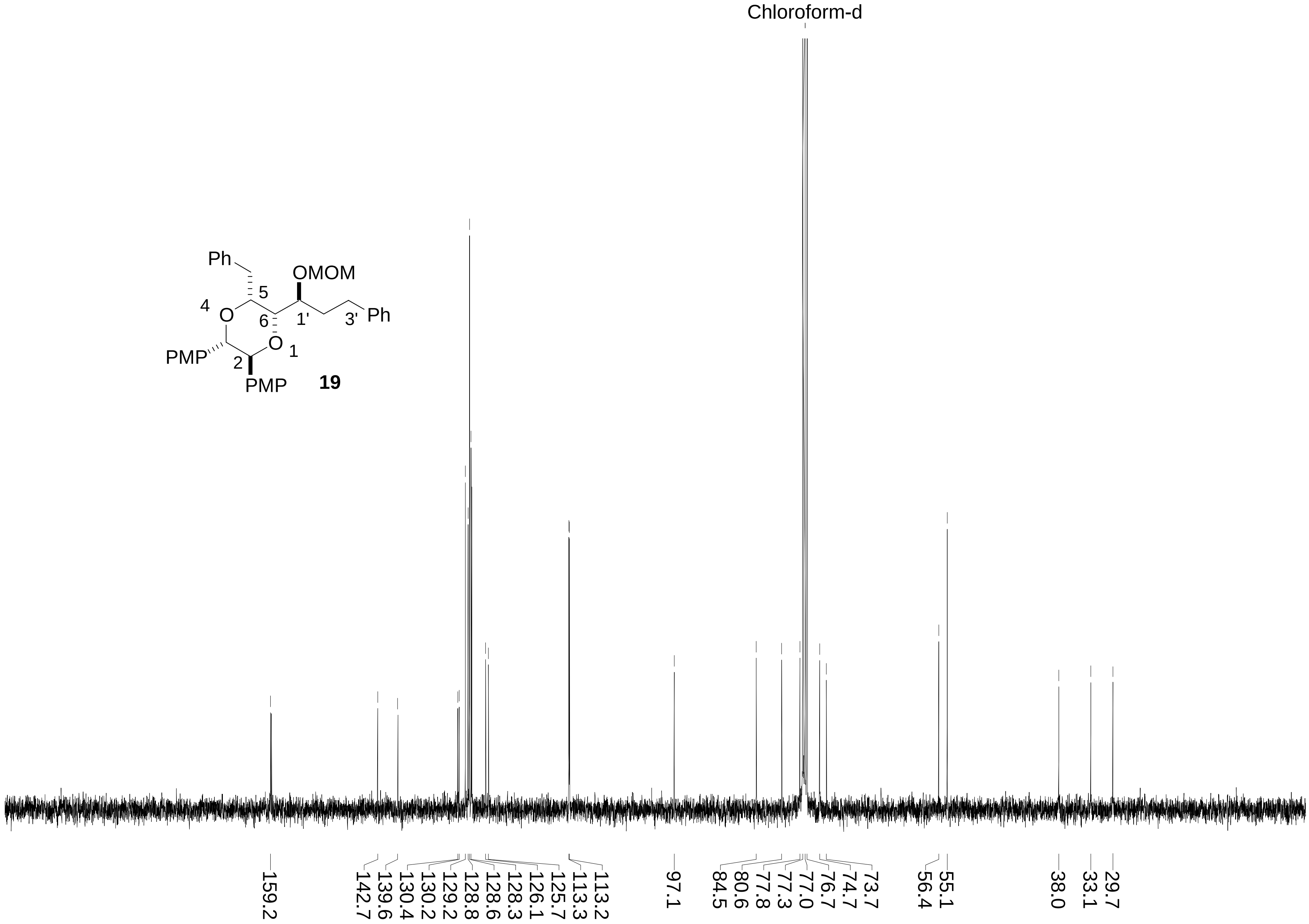
18

E/*Z* = 9:1

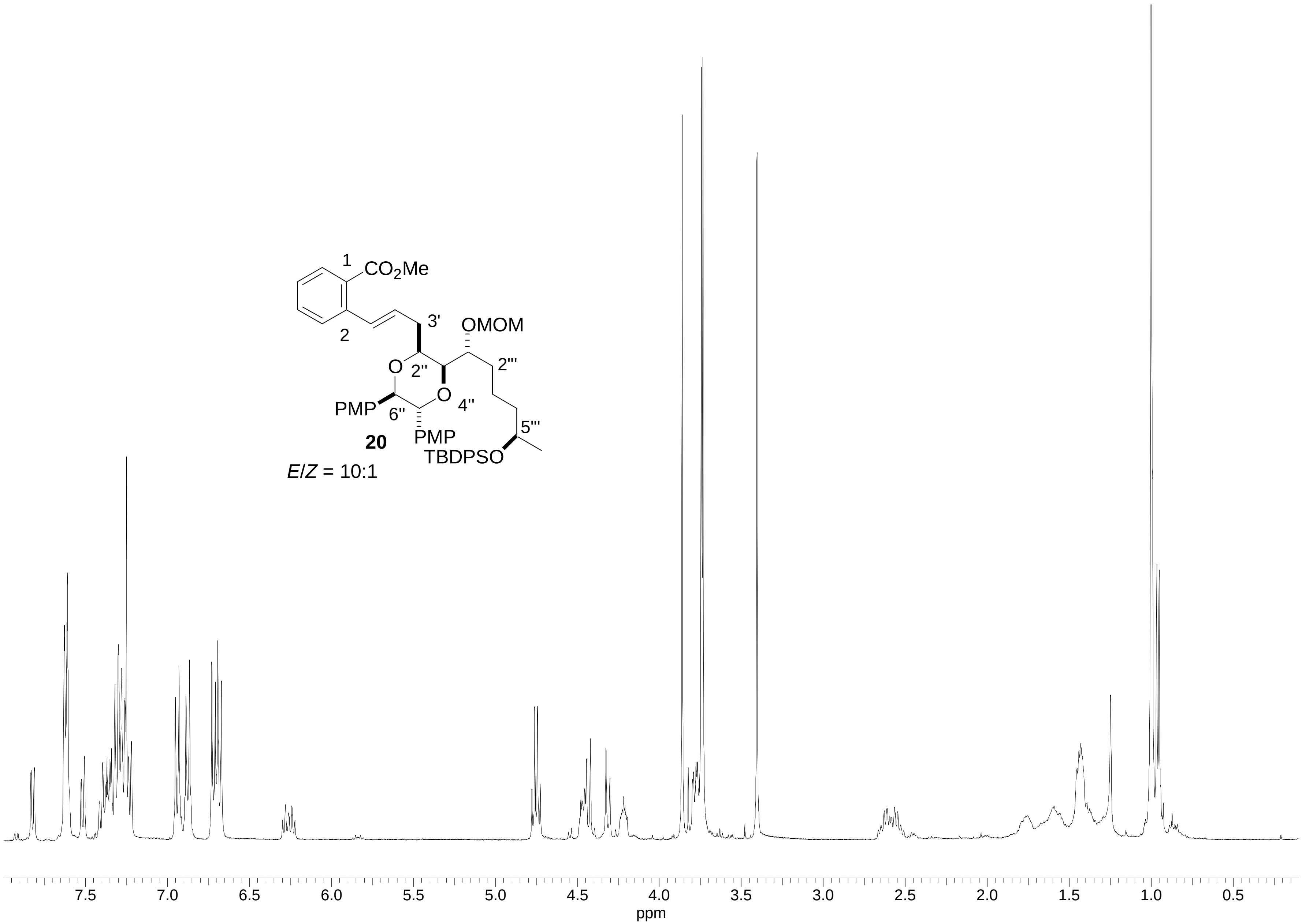

1
CO2Me
2
3'
2"
3"
O
O
PMP
6"
PMP
18
E/Z = 9:1
167.8
159.0
139.1
132.0
131.2
130.3
128.6
128.0
127.4
126.8
113.2
83.6
83.3
77.3
77.0
76.7
75.1
70.9
55.0
52.0
35.7


Ph
OMOM
5
4
O
6
1'
3'
Ph
O
1
PMP
2
PMP
4.9
4.8
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
3.9
ppm
3.05
3.00
2.95
2.90
2.85
2.80
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

19

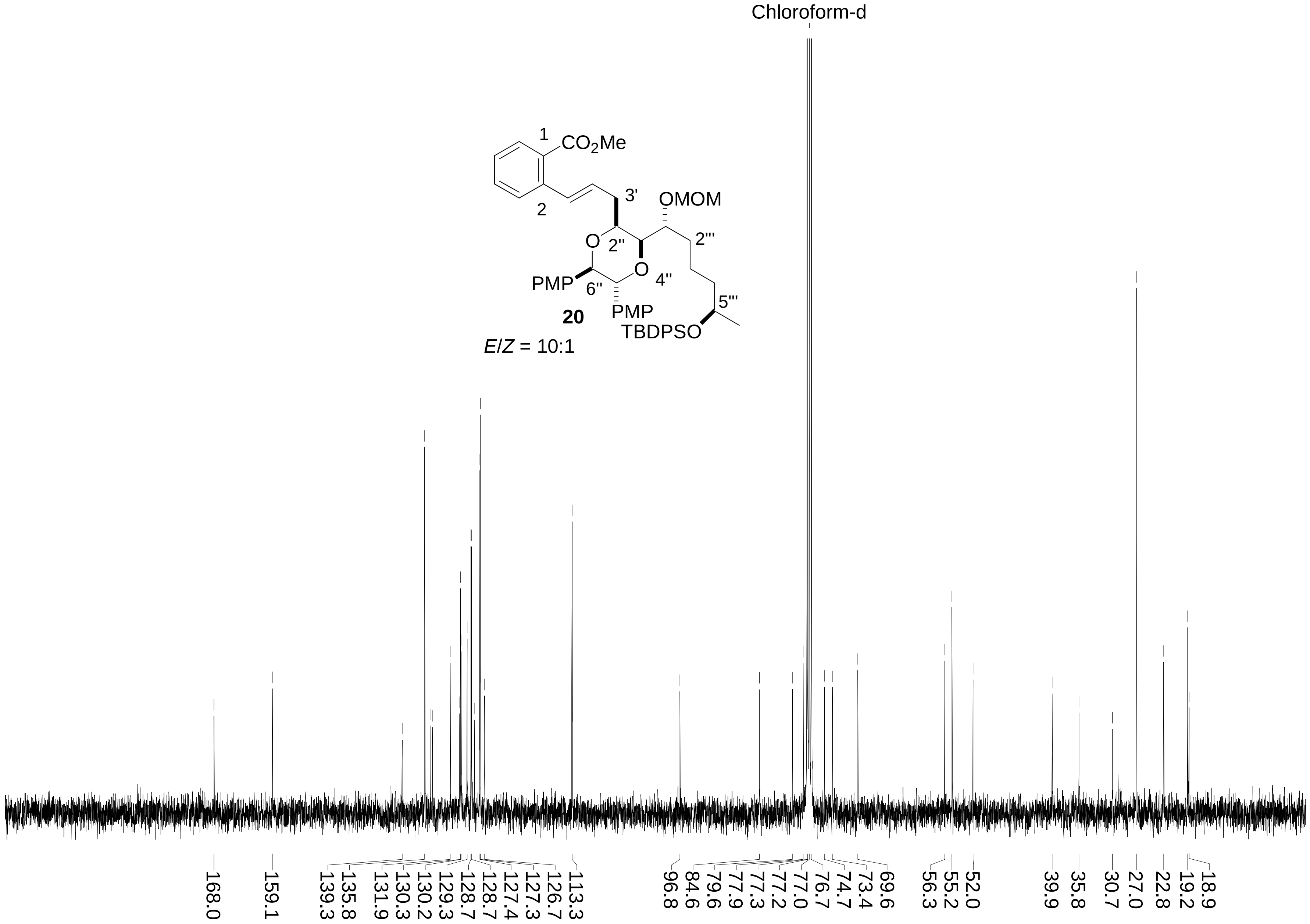

Ph
OMOM
5
4
O
6
1'
3'
Ph
PMP
2
O
1
PMP
Chloroform-d
159.2
142.7
139.6
130.4
130.2
129.2
128.8
128.6
128.3
126.1
125.7
113.3
113.2
97.1
84.5
80.6
77.8
77.3
77.0
76.7
74.7
73.7
56.4
55.1
38.0
33.1
29.7

19


1
CO2Me
2
3'
OMOM
O
2''
2'''
O
PMP
6''
4''
PMP
5'''
TBDPSO
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

20

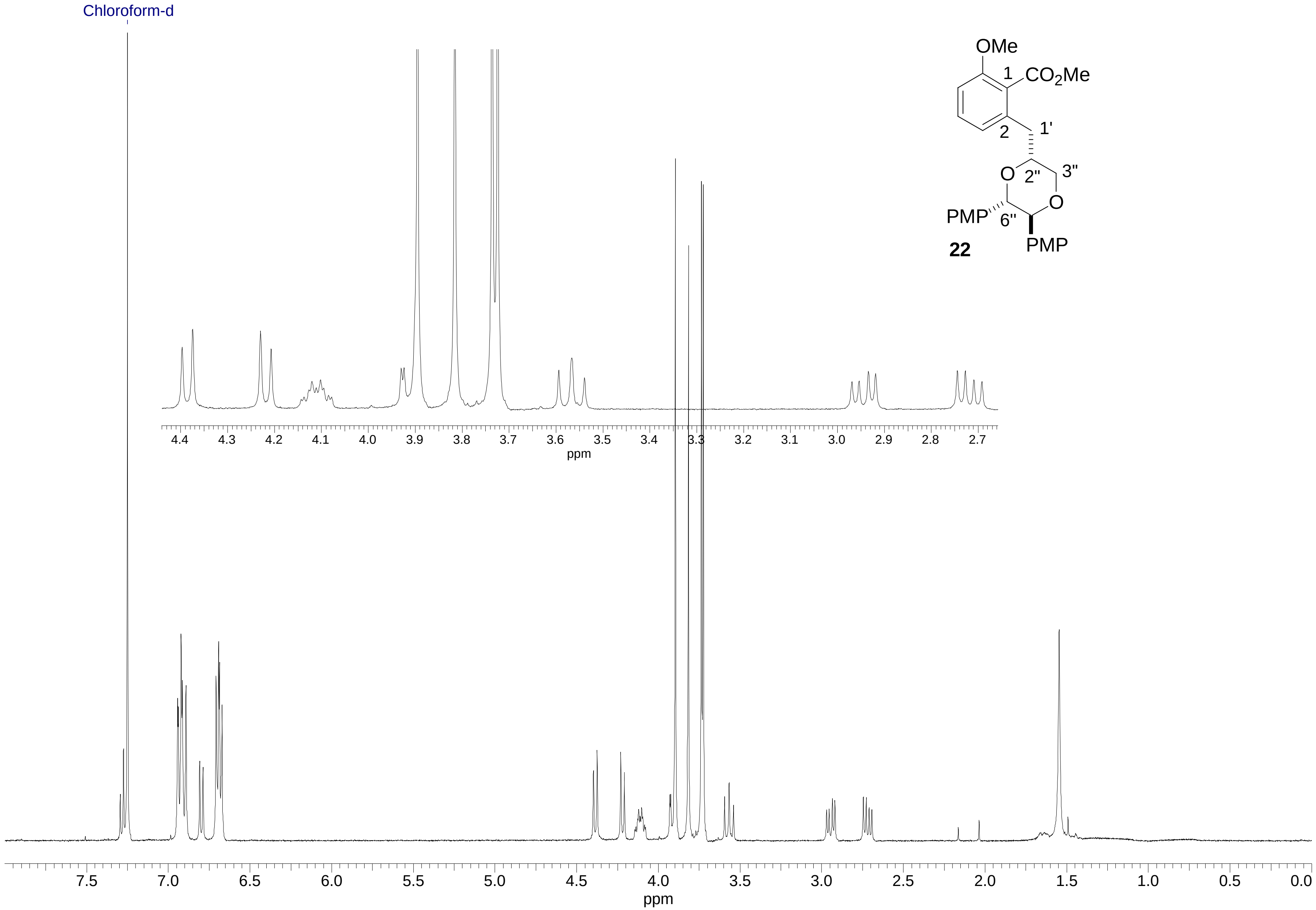
E/*Z* = 10:1



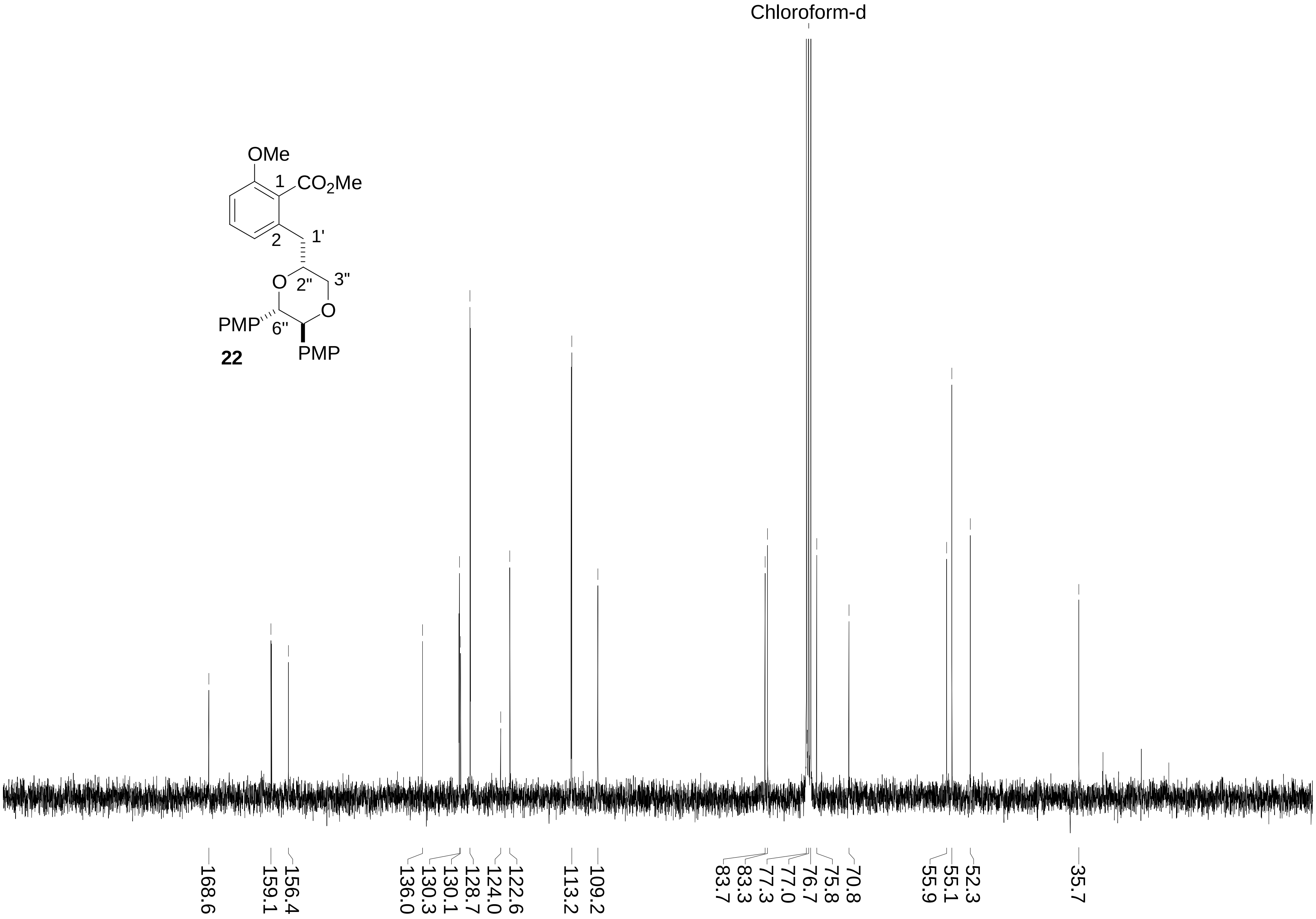
Chloroform-d
1
CO_2Me
2
3'
OMOM
2'''
O
2''
O
4''
PMP
6''
PMP
5'''
TBDPSO
168.0
159.1
139.3
135.8
131.9
130.3
130.2
129.3
128.7
128.7
127.4
127.3
126.7
113.3
96.8
84.6
79.6
77.9
77.3
77.2
77.0
76.7
74.7
73.4
69.6
56.3
55.2
52.0
39.9
35.8
30.7
27.0
22.8
19.2
18.9

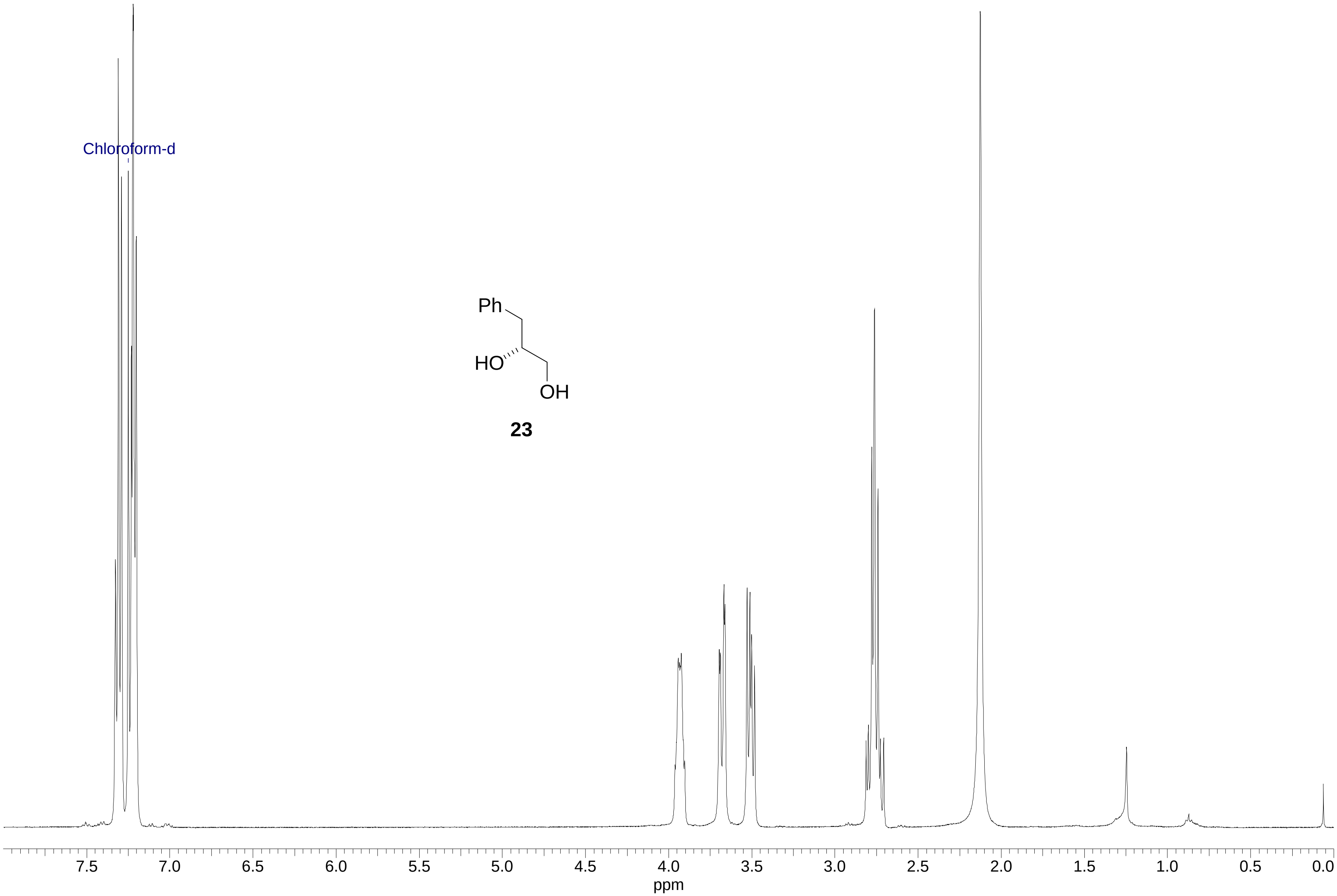
20

E/*Z* = 10:1

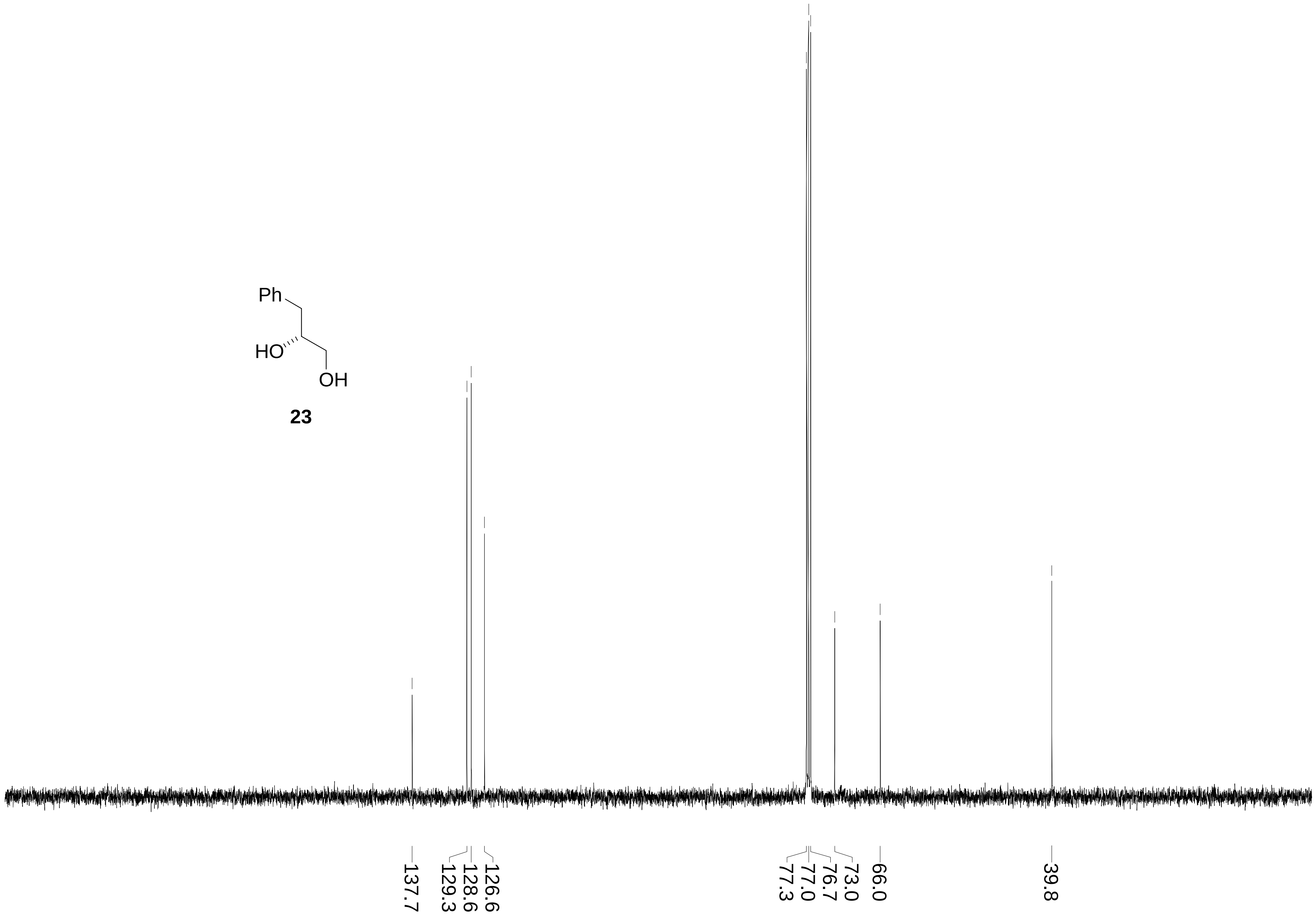

Chloroform-d
OMe
1
CO2Me
2
1'
O
2"
3"
O
PMP
6"
PMP
4.4
4.3
4.2
4.1
4.0
3.9
3.8
3.7
3.6
3.5
3.4
3.3
3.2
3.1
3.0
2.9
2.8
2.7
ppm
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

22

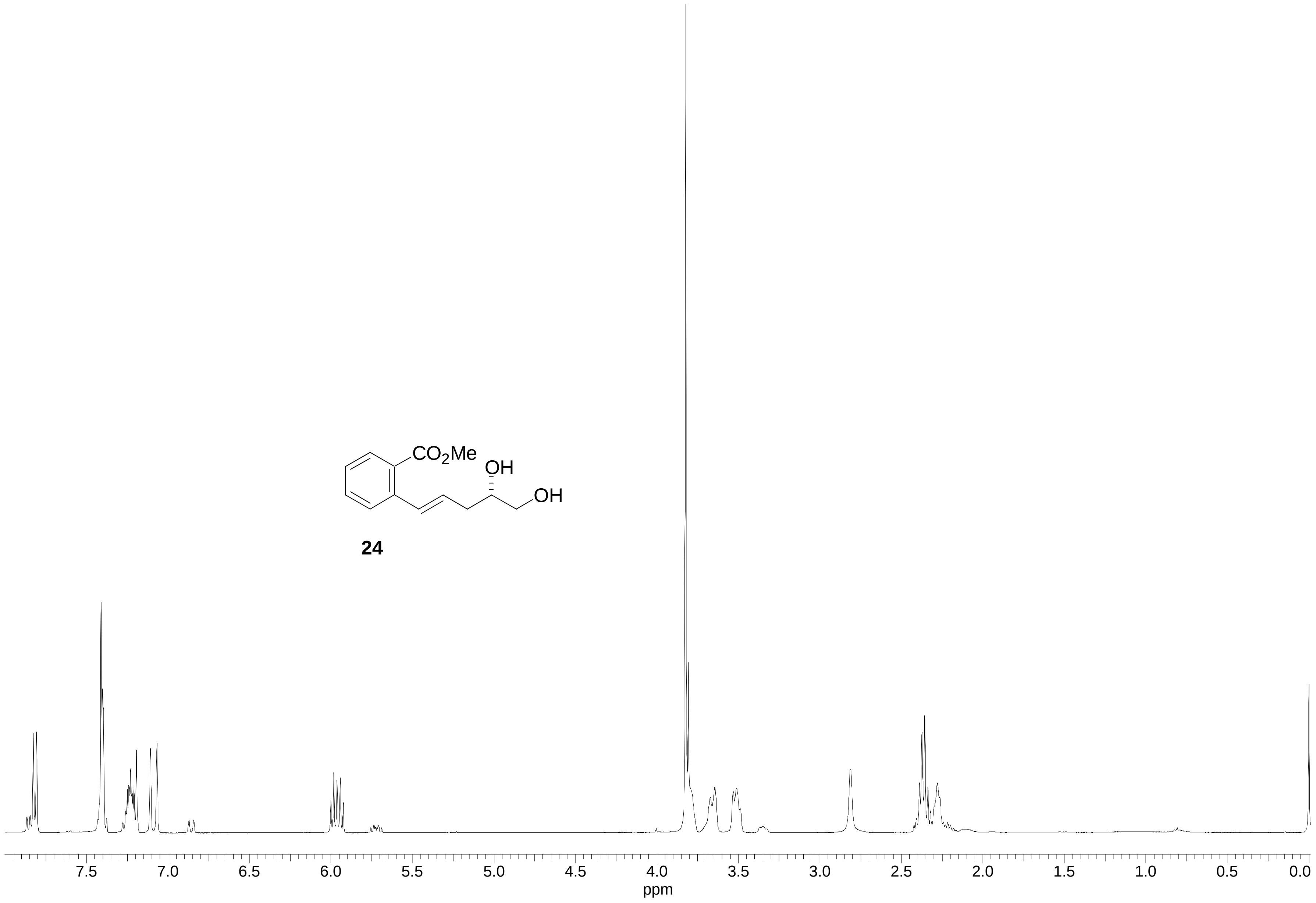

Chloroform-d
OMe
1
CO2Me
2
1'
O
2"
3"
O
PMP
6"
PMP
22
168.6
159.1
156.4
136.0
130.3
130.1
128.7
124.0
122.6
113.2
109.2
83.7
83.3
77.3
77.0
76.7
75.8
70.8
55.9
55.1
52.3
35.7


Chloroform-d
Ph
HO
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

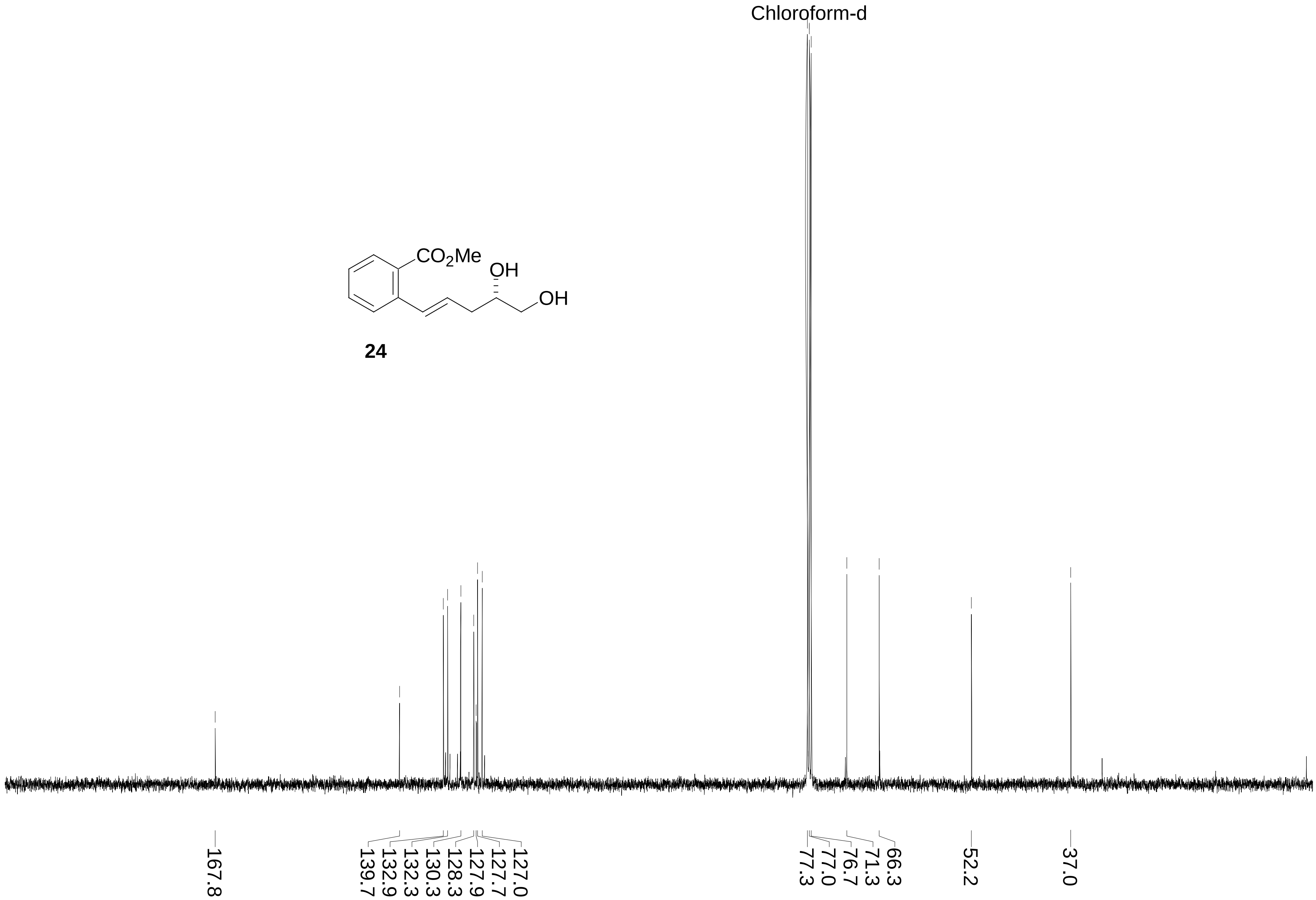
23



23



24


Chloroform-d
CO2Me
OH
OH
24
167.8
139.7
132.9
132.3
130.3
128.3
127.9
127.7
127.0
77.3
77.0
76.7
71.3
66.3
52.2
37.0