Combined coinage metal catalysis in natural product synthesis: total synthesis of (+)-varitriol and seven analogs†

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Supporting Information

General information

All reactions were performed in heat gun-dried glassware under an argon atmosphere and all solvents were dried if not noted otherwise. Solvents came from the solvent purification system MB-SPS 800 of MBRAUN GmbH. Column chromatography was carried out with ACROS silica gel (0.035-0.070 mm). ^{1}H, ^{13}C, COSY and NOESY spectra were recorded with Bruker DRX 400 and DRX 500 spectrometers at room temperature in $CDCl_3$ or $(CD_3)_2CO$. The signals of the undeuterated solvent were used as the standard ($CDCl_3$: ^{1}H NMR: δ = 7.26; ^{13}C NMR: δ = 77.0; acetone-d_6: ^{1}H NMR: δ = 2.05; ^{13}C: δ = 30.8). *J* values were given in Hz. Carbon atoms were assigned with APT experiments. IR spectra were measured with a Nicolet Avatar 320 FT-IR as a liquid film between NaCl plates. FAB mass spectra was measured with a Jeol SX102A spectrometer, ESI spectra with a LTQ ORBITRAP equipped with a Hypersil gold column (diameter 50 x 1 mm, particle size 1.9 µm). Optical rotations were determined with a Perkin-Elmer 341 polarimeter. Enantiomer excess (*ee*) was determined with a KNAUER chiral HPLC (250 x 4.6 mm Eurocel 01, 5 µm). Melting point were measured with a Reichert thermovar melting point apparatus and are uncorrected.

Synthetic procedures

(2-(Chloromethyl)-6-methoxyphenyl)methanol (8). To a solution of ethyl 6-chloromethyl-2-methoxybenzoate **7** (2.70 g, 11.8 mmol) in THF (30 mL) was added DIBAL-H (1 M in hexane; 29.2 mL, 29.2 mmol) at 0°C. After being stirred at 0°C for 1 h, the reaction mixture was quenched with H_2O (10 mL). The emulsion was added to a solution of patassium-sodium-tartrate (23.4 g, 82.9 mmol) in H_2O (66 mL). After stirring at room temperature for 3 h and extraction with CH_2Cl_2 (4 × 40 mL), the organic layer was dried with $MgSO_4$, and concentrated under vacuum. The residue was purified by column chromatography using cyclohexane/AcOEt (2:1) to give **8** (2.12 g, 11.4 mmol, 97%) as a colorless solid, mp 51-52°C. IR (ν cm^{-1}): 3376 (OH), 2937, 2838, 1589, 1471, 1269, 1005, 748. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (1H, dd, *J* 8.3, 7.6), 6.98 (1H, d, *J* 7.6), 6.91 (1H, d, *J* 8.3), 4.84 (2H, d, *J* 4.5), 4.69 (2H, s), 3.87 (3H, s), 2.44 (OH, brs). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 137.0 (2 C), 129.2 (CH), 127.7 (C), 122.5, 111.3 (2 CH), 56.6 (CH_2), 55.7 (CH_3), 43.9 (CH_2). EI-HRMS *m*/*z*: found 186.0433, calcd for $C_9H_{11}O_2Cl$ (M^+): 186.0442.

***tert*-Butyl(2-(chloromethyl)-6-methoxybenzyloxy)dimethylsilane (9).**[1] To a solution of **8** (2.12 g, 11.4 mmol) in DMF (50 mL) were added TBSCl (2.58 g, 17.1 mmol) and imidazole (2.33 g, 34.2 mmol) at 0°C. After being stirred at 0°C for 4 h, the reaction mixture was quenched with aq. satd. NH_4Cl soln. (50 mL). Then H_2O (200 mL) was added. After extraction with a 1:1-mixture of isohexane and Et_2O (4 × 100 mL), the organic layer was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using cyclohexane/AcOEt (50:1) to give **9** (3.32 g, 11.0 mmol, 96%) as a

[1] *(a)* R. T. Clemens and M. P. Jennings, *Chem. Commun.*, 2006, 2720; *(b)* K. C. Nicolaou, T. Ladduwahetty and E. M. Elisseou, *J. Chem. Soc., Chem. Commun.*, 1985, 1580; *(b)* K. C. Nicolaou, C. V. C. Prasad, P. K. Somers and C. K. Hwang, *J. Am. Chem. Soc.*, 1989, **111**, 5335.

colorless oil. IR (ν cm^{-1}): 2955, 2929, 2856, 1621, 1384, 1122, 837. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26 (1H, dd, *J* 8.3, 7.6), 7.03 (1H, d, *J* 7.6), 6.86 (1H, d, *J* 8.3), 4.91 (2H, s), 4.81 (2H, s), 3.83 (3H, s), 0.90 (9H, s), 0.07 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.2, 138.6 (2 C), 129.0 (CH), 127.7 (C), 122.5, 111.1 (2 CH), 55.6 (CH_3), 55.5, 43.7 (2 CH_2). CI-HRMS *m*/*z*: found 265.1611, calcd for $C_{15}H_{25}O_2Si$ $(M\text{-}Cl)^+$: 265.1618.

Diethyl 2-((*tert*-butyldimethylsilyloxy)methyl)-3-methoxybenzylphosphonate (2). A mixture of **9** (809 mg, 2.69 mmol) and triethylphosphite (1.10 g, 6.62 mmol) was stirred under reflux (ca 170°C) for 3 h. After cooling to ambient temperature, the residue was purified by column chromatography using cyclohexane/AcOEt (1:1) to give **2** (1.04 g, 2.58 mmol, 96%) as a colorless oil. IR (ν cm^{-1}): 2955, 2929, 2856, 1588, 1471, 1251, 1052, 1028, 838. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18 (1H, dd, *J* 8.2, 7.6), 6.95 (1H, dd, *J* 7.6, J_{HP} 2.1), 6.76 (1H, d, *J* 8.2), 4.89 (2H, s), 3.95-4.05 (4H, m), 3.80 (3H, s), 3.43 (2H, d, J_{HP} 21.8), 1.24 (6H, t, *J* 7.1), 0.88 (9H, s), 0.04 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4 (C, d, J_{CP} 3.1), 133.2 (C, d, J_{CP} 8.8), 128.4 (CH, d, J_{CP} 3.4), 128.1 (C, d, J_{CP} 7.5), 123.4 (CH, d, J_{CP} 5.0), 109.4 (CH, d, J_{CP} 3.7), 61.9 (2CH_2, d, J_{CP} 6.7), 55.9 (CH_2), 55.4 (CH_3), 30.0 (CH_2, d, J_{CP} 120.5), 25.9 (3CH_3), 18.3 (C), 16.3 (2CH_3, d, J_{CP} 6.0), -5.4 (2CH_3). ESI-HRMS *m*/*z*: found 425.1882, calcd for $C_{19}H_{35}O_5NaPSi$ $(M+Na)^+$: 425.1884.

***tert*-Butyl(2-(chloromethyl)benzyloxy)dimethylsilane (11).** To a solution of **10**[2] (870 mg, 5.56 mmol) in DMF (28 mL) were added TBSCl (1.26 g, 8.34 mmol) and imidazole (1.14 g, 16.7 mmol) at 0°C. After being stirred at 0°C for 2 h, the reaction mixture was quenched with aq. satd. NH_4Cl soln. (30 mL). Then H_2O (140 mL) was added. After extraction with a 1:1-mixture of isohexane and Et_2O (3 × 90 mL), the organic layer was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using cyclohexane/AcOEt (50:1) to give **11** (1.50 g, 5.54 mmol, quant.) as a light yellow oil. The NMR data are in accordance with those reported in the literature.[3]

Diethyl 2-((*tert*-butyldimethylsilyloxy)methyl)benzylphosphonate (12). A mixture of **11** (1.50 g, 5.54 mmol) and triethylphosphite (1.84 g, 11.1 mmol) was stirred under reflux (ca 155°C) for 5 h. After cooling to ambient temperature, the residue was purified by column chromatography using cyclohexane/AcOEt (2:1) to give **12** (1.87 g, 2.58 mmol, 91%) as a light yellow oil. IR (ν cm^{-1}): 2956, 2930, 2857, 1472, 1252, 1055, 1028, 964, 838. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40 (1H, d, *J* 6.5), 7.16-7.29 (3H, m), 4.82 (2H, s), 3.91-4.02 (4H, m), 3.23 (2H, d, J_{HP} 21.8), 1.21 (6H, t, *J* 7.1), 0.92 (9H, s), 0.08 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 139.6 (C, d, J_{CP} 6.6), 130.7 (CH, d, J_{CP} 5.5), 129.0 (C, d, J_{CP} 9.6), 127.4 (CH, d, J_{CP} 3.0), 127.0 (CH, d, J_{CP} 3.2), 126.9 (CH, d, J_{CP} 3.7), 63.3 (CH_2), 62.0 (2CH_2, d, J_{CP} 6.8), 30.0 (CH_2, d, J_{CP} 138.3), 25.9 (3CH_3), 18.3 (C), 16.3 (2CH_3, d, J_{CP} 6.0), -5.3 (2CH_3). EI-HRMS *m*/*z*: found 372.1870, calcd for $C_{18}H_{33}O_4PSi$ (M^+): 372.1880.

((2*R*,3*R*)-3-(Prop-1-ynyl)oxiran-2-yl)methanol (14).[4] To a suspension of powdered, activated molecular sieves (4 Å, 6 g) in CH_2Cl_2 (100 mL) were added D-(−)-DET (1.48 g, 7.2 mmol) and Ti(O*i*-Pr)$_4$ (1.71 g, 6.0 mmol) at −30°C. After stirring at −30°C for 20 min, **13** (2.88 g, 30.0 mmol) was added dropweise over 10 min. The mixture was stirred for additional 40 min at −30°C then cooled to −50°C. *tert*-Butylhydroperoxide (TBHP, 3.76 M solution in toluene,

[2] W. E. Lindsell, D. D. Palmer, P. N. Preston and G. M. Rosair, *Organometallics*, 2005, **24**, 1119.
[3] B. Bradshaw, P. Evans, E. J. Thomas, R. H. Davies and K. J. Broadley, *Org. Biomol. Chem.*, 2008, **6**, 2138.
[4] *(a)* J. G. Hill, K. B. Sharpless, C. M. Exon and R. Regenye, *Org. Synth.*, 1985, **63**, 66; *(b)* Y. Gao, R. M. Hanson, J. M. Klunder, S. K. Ko, H. Masamune and K. B. Sharpless, *J. Am. Chem. Soc.*, 1987, **109**, 5765;

47.9 mL, 180 mmol, predried with 4.8 g powdered, activated molecular sieves (4Å))[5] was slowly added over a period of 10 min. The reaction mixture was further stirred at –30°C for 1 h before it was put in a fridge with an inner temperature of –23°C. After 4 days the reaction mixture t was ransferred into a bigger flask at 0°C, leaving the molecular behind. To this mixture was added a precooled (icebath) solution of $FeSO_4 \bullet 7\ H_2O$ (180 g, 648 mmol) and tartaric acid (3.6 g, 24 mmol) in H_2O (720 mL). The mixture was stirred at 0°C for 1 h and then allowed to warm up to room temperature. After extraction with Et_2O (6 × 300 mL), the organic layer was dried with $MgSO_4$ and concentrated under vacuum (up to 300 mbar). The crude product, which was a mixture of **14** and D-(–)-DET in toluene, was direct applied in the next step.
An analytically pure sample was obtained according to the original literature procedure[4] and purification of the crude product by column chromatography using cyclohexane/AcOEt (2:1). Data for **14**: Light yellow oil; 91% *ee*. $[\alpha]_D^{20} = -3.1$ (*c* 1, $CHCl_3$). IR (ν cm^{-1}): 3405 (OH), 2921, 2243 (C≡C), 1438, 1066, 1024, 858. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.90 (1H, d, *J* 12.9), 3.66 (1H, d, *J* 12.9), 3.38 (1H, s), 3.24 (1H, s), 2.14 (OH, brs), 1.83 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 81.0, 75.0 (2 C), 60.3 (CH_2), 59.9, 43.0 (2 CH), 3.5 (CH_3). EI-HRMS *m*/*z*: found 112.0518, calcd for $C_6H_8O_2$ (M^+): 112.0519.

(2*R*,3*R*)-2-(Benzyloxymethyl)-3-(prop-1-ynyl)oxirane (6). To a suspension of NaH (60% disp. in oil, 1.8 g, 45 mmol) in THF (300 mL) was added crude **14** at 0°C. After being stirred at room temperature for 15 min, BnBr (7.68g, 45 mmol) and TBAI (0.554 g, 1.5 mmol) were added. The reaction mixture was stirred at room temperature for 22 h and then was quenched with aq. satd. NH_4Cl soln. (65 mL). After extraction with Et_2O (3 × 130 mL), the organic layer was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using cyclohexane/AcOEt (20:1) to give **6** (2.88 g, 14.2 mmol, 47% for two steps) as a yellow oil. $[\alpha]_D^{20} = +9.1$ (*c* 1.2, $CHCl_3$). IR (ν cm^{-1}): 3400 (OH), 3030, 2919, 2858, 2242 (alkyne), 1454, 1096, 739. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-7.38 (5H, m), 4.56 (2H, s), 3.71 (1H, dd, *J* 11.7, 2.2), 3.52 (1H, dd, *J* 11.7, 4.5), 3.29 (2H, m), 1.84 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.6 (C), 128.3, 127.7, 127.7 (5 CH), 80.7, 75.2 (2 C), 73.3, 68.9 (2 CH_2), 58.6, 43.2 (2 CH), 3.6 (CH_3). EI-HRMS *m*/*z*: found 202.0985, calcd for $C_{13}H_{14}O_2$ (M^+): 202.0988.

(2*R*,3*S*,4*R*,5*S*)- and (2*R*,3*R*,4*S*,5*S*)-2-(Benzyloxymethyl)-5-methyltetrahydrofuran-3,4-diol (15/16).[6] To a 1:1-mixture of *t*-butanol and H_2O (88 mL) were added at room temperature under air $K_3Fe(CN)_6$ (8.69 g, 26.4 mmol), $NaHCO_3$ (2.22 g, 26.4 mmol), Na_2CO_3 (2.80 g, 26.4 mmol), $K_2OsO_2(OH)_4$ (32.5 mg, 0.0881 mmol) and $(DHQD)_2PYR$ (389 mg, 0.441 mmol). After stirring for 10 min, $MeSO_2NH_2$ (1.67 g, 17.6 mmol) was added and the mixture was stirred until both phases were clear (ca. 15 min). Then the reaction mixture was cooled to 2°C and **4** (1.80 g, 8.81 mmol) was added. After being strongly stirred at 2°C for 64 h, the reaction was quenched with aq. satd. $Na_2S_2O_3$ soln. (70 mL) at 2°C and further stirred for 1 h at room temperature. After extraction with ethyl acetate (5 × 75 mL), the organic layer was washed with aq. KOH (2 M, 2 × 75 mL), dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using cyclohexane/AcOEt (1:2) to give a mixture of **15** and **16** (2.06 g, 8.64 mmol, 98%, *dr* = 78:22) as a yellow oil. Data for the mixture of **15** and **16**: IR (ν cm^{-1}): 3390 (OH), 2928, 1454, 1384, 1096, 740. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27-7.39 (5H+1.5H m), 4.52-4.60 (2H+0.6H, m), 4.07-4.12 (0.3H, m), 3.94-3.99 (1H, m), 3.89-3.93 (1H, m), 3.86-3.89 (0.3H, m), 3.77-3.85 (1.3H, m), 3.63-3.68

[5] J. G. Hill, B. E. Rossiter and K. B. Sharpless, *J. Org. Chem.*, 1983, **48**, 3707
[6] *(a)* H. C. Kolb, M. S. VanNieuwenhze and K. B. Sharpless, *Chem. Rev.*, 1994, **94**, 2483; *(b)* A. B. Zaitsev and H. Adolfsson, *Synthesis*, 2006, 1725.

(1.3H, m), 3.54-3.68 (2.6H, m), 2.85-3.10 (2.6H, m), 1.28 (3H, d, *J* 6.3), 1.28 (0.9H, d, *J* 6.3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.8, 136.6 (2 C), 128.7, 128.4, 128.2, 127.9, 127.7 (10 CH), 82.6, 79.3, 77.7, 76.2, 75.7 (5 CH), 74.0 (CH_2), 74.0 (CH), 73.6 (CH_2), 72.7, 72.5 (2 CH), 70.7, 68.6 (2 CH_2), 18.7, 14.3 (2 CH_3). ESI-HRMS *m*/*z*: found 239.1280, calcd for $C_{13}H_{19}O_4$ $(M+H)^+$: 239.1278.

(3a*R*,4*R*,6*S*,6a*S*)- and (3a*S*,4*R*,6*S*,6a*R*)-4-(Benzyloxymethyl)-2,2,6-trimethyltetrahydro-furo-[3,4-*d*][1,3]dioxole (17/18). To a solution of the mixture of **15** and **16** (1.22 g, 5.12 mmol) in DMF (20 mL) were added PPTS (129 mg, 0.512 mmol) and 2,2-dimethoxypropane (1.60 g, 15.4 mmol) at room temperature. After being stirred at this temperature for 23 h, the reaction mixture was diluted with H_2O (150 mL). After extraction with Et_2O/isohexane (2:1, 3 × 100 mL), the organic layer was dried with $MgSO_4$ and concentrated under vacuum. The residue was purified by column chromatography using cyclohexane/AcOEt (7:1) to give **17** (1.01 g, 3.63 mmol, 71%) as a colorless oil and **18** (0.287 g, 1.03 mmol, 20%) as a colorless solid. Data for **17**: $[\alpha]_D^{20}$ = +10.4 (*c* 1.2, $CHCl_3$). IR (ν cm^{-1}): 3030, 2933, 1454, 1382, 1212, 1076, 867. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.26-7.37 (5H, m), 4.59 (2H, s), 4.56 (1H, dd, *J* 6.9, 4.5), 4.25 (1H, dd, *J* 6.7, 5.1), 4.04-4.09 (1H, m), 3.94-4.02 (1H, m), 3.53-3.63 (2H, m), 1.53 (3H, s), 1.33 (3H, s), 1.32 (3H, d, *J* 6.4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.9, (C), 128.3, 127.7, 127.6 (5 CH), 114.5 (C), 85.9, 83.0, 82.3, 80.6 (4 CH), 73.5, 70.4 (2 CH_2), 27.3, 25.4, 18.9 (3 CH_3). NOSY (500 MHz, $CDCl_3$) showed it was the *cis*-*trans*-*cis*-product. ESI-HRMS *m*/*z*: found 279.1594, calcd for $C_{16}H_{23}O_4$ $(M+H)^+$: 279.1591. Data for **18**: mp 33-35°C. $[\alpha]_D^{20}$ = –22.0 (*c* 1.2, $CHCl_3$). IR (ν cm^{-1}): 3030, 2935, 1454, 1381, 1209, 1100, 1010, 899. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24-7.38 (5H, m), 4.64-69 (2H, m), 4.49-4.56 (2H, m), 3.75-3.82 (1H, m), 3.67-3.74 (2H, m), 3.60-3.67 (1H, m), 1.46 (3H, s), 1.34 (3H, d, *J* 6.4), 1.31 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.0 (C), 128.2, 127.8, 127.5 (5 CH), 112.1 (C), 82.0, 81.4, 80.3, 77.6 (4 CH), 73.4, 68.1 (2 CH_2), 25.8, 24.9, 13.3 (3 CH_3). ESI-HRMS *m*/*z*: found 279.1592, calcd for $C_{16}H_{23}O_4$ $(M+H)^+$: 279.1591.

((3a*R*,4*R*,6*S*,6a*S*)-2,2,6-Trimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methanol (19). To a solution of **17** (1.08 g, 3.88 mmol) in THF (27 mL) was added Pd (10 wt% on activated carbon, 206 mg, 0.194 mmol) at room temperature. Then a balloon with H_2 was attached. After being strongly stirred at room temperature for 3 h, the reaction mixture was filtered through celite and the residue was washed with ethyl acetate (500 mL). The solvent was removed under vacuum to afford crude **19** (740 mg) as a light yellow oil.
An analytically pure sample was obtained by column chromatography using cyclohexane/AcOEt (2:1). $[\alpha]_D^{20}$ = +9.8 (*c* 1.25, $CHCl_3$). IR (ν cm^{-1}): 3434 (OH), 2935, 1455, 1383, 1213, 1078, 865. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.63 (1H, dd, *J* 7.0, 4.5), 4.23 (1H, dd, *J* 6.8, 5.4), 3.95-4.03 (2H, m), 3.79-3.86 (1H, m), 3.64-3.72 (1H, m), 1.90 (OH, brs), 1.53 (3H, s), 1.34 (3H, s), 1.32 (3H, d, *J* 6.4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 114.8 (C), 86.1, 84.1, 81.6, 80.5 (4 CH), 62.8 (CH_2), 27.4, 25.4, 18.8 (3 CH_3). ESI-HRMS *m*/*z*: found 189.1121, calcd for $C_9H_{17}O_4$ $(M+H)^+$: 189.1121.

((3a*S*,4*R*,6*S*,6a*R*)-2,2,6-Trimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methanol (20). Debenzylation of **18** (602 mg, 2.16 mmol) according to the procedure used for **19** gave crude **20** (425 mg) as a colorless oil. An analytically pure sample was obtained by column chromatography using cyclohexane/ AcOEt (2:1). $[\alpha]_D^{20}$ = –8.7 (*c* 1.1, $CHCl_3$). IR (ν cm^{-1}): 3433 (OH), 2937, 1456, 1381, 1210, 1125, 1074, 1009, 900, 870. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.70 (1H, dd, *J* 6.1, 3.9), 4.54 (1H, dd, *J* 6.1, 3.7), 3.81-3.92 (2H, m), 3.61-3.67 (1H, m), 3.56-3.61 (1H, m), 2.64 (OH, brs), 1.44 (3H, s), 1.30 (3H, s), 1.28 (3H, d, *J* 6.4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 112.2 (C), 82.1, 81.5, 81.1, 77.5 (4 CH), 60.8 (CH_2), 25.7, 24.7, 13.2 (3 CH_3). ESI-HRMS *m*/*z*: found 189.1120, calcd for $C_9H_{17}O_4$ $(M+H)^+$: 189.1121.

(3a*S*,4*S*,6*S*,6a*S*)-2,2,6-Trimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carbaldehyde (3). To a solution of DMP (0.992 g, 2.34 mmol) in CH_2Cl_2 (30 mL) was added a solution of **19** (400 mg, crude product) in CH_2Cl_2 (10 mL) at room temperature. After being stirred at room temperature for 22 h, the reaction was quenched with aq. satd. Na_2CO_3 soln. (30 mL). After addition of aq. satd. $Na_2S_2O_3$ soln. (40 mL), the mixture was stirred until both phases were clear (ca. 30 min). After extraction with CH_2Cl_2 (5 × 70 mL), the organic layer was concentrated under vacuum giving the crude aldehyde **3** (380 mg) as a light yellow oil. Analytical data of the crude product: IR (ν cm^{-1}): 2982, 2935, 1732 (C=O), 1382, 1212, 1078, 866. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.72 (1H, s, CHO), 4.92 (1H, dd, *J* 6.3, 2.7), 4.33-4.38 (2H, m), 4.26-3.33 (1H, dq, *J* 6.7, 2.4), 1.52 (3H, s), 1.33 (3H, s), 1.19 (3H, d, *J* 6.7). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.1 (CHO), 113.9 (C), 88.8, 85.5, 81.6, 81.5 (4 CH), 26.8, 25.2, 18.8 (3 CH_3). EI-HRMS *m*/*z*: found 171.0652, calcd for $C_8H_{11}O_4$ $(M\text{-}CH_3)^+$: 171.0652.

(3a*R*,4*S*,6*S*,6a*R*)-2,2,6-Trimethyltetrahydrofuro[3,4-*d*][1,3]dioxole-4-carbaldehyde (21). Oxidation of **20** (338 mg, 1.80 mmol) according to the procedure used for **3** gave crude **21** (310 mg) as a colorless oil. Analytical data of the crude product: IR (ν cm^{-1}): 2986, 2936, 1737 (C=O), 1384, 1211, 1107, 1073, 1009, 874. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.63 (1H, s, CHO), 5.02 (1H, dd, *J* 5.9, 4.4), 4.61 (1H, dd, *J* 5.9, 3.6), 3.96 (1H, d, *J* 4.3), 3.75 (1H, dq, *J* 6.3, 3.6), 1.44 (3H, s), 1.40 (3H, d, *J* 6.3), 1.29 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 198.7 (CHO), 113.1 (C), 85.2, 82.6, 81.8, 78.3 (4 CH), 25.7, 24.7, 13.3 (3 CH_3). EI-HRMS *m*/*z*: found 171.0655, calcd for $C_8H_{11}O_4$ $(M\text{-}CH_3)^+$: 171.0652.

Diethyl 3-methoxybenzylphosphonate (23). A mixture of 3-methoxybenzyl chloride (1.00 g, 6.39 mmol) and triethylphosphite (0.956 g, 5.75 mmol) was stirred under reflux (ca 170°C) for 3 h. After cooling to ambient temperature, the residue was purified by column chromatography using cyclohexane/AcOEt (1:2) to give **23** (0.965 g, 3.74 mmol, 65%) as a colorless oil. IR (ν cm^{-1}): 2983, 1602, 1384, 1252, 1027, 964. The NMR data are in accordance with those reported in the literature.[7] EI-HRMS *m*/*z*: found 258.1006, calcd for $C_{12}H_{19}O_4P$ (M^+): 258.1015.

***tert*-Butyldimethyl(2-((*E*)-2-((3a*R*,4*R*,6*S*,6a*S*)-2,2,6-trimethyltetrahydrofuro[3,4-*d*][1,3]-dioxol-4-yl)vinyl)benzyloxy)silane (25).** HWE-reaction according to the general procedure (reaction time: 15 h) of **12** (488 mg, 1.31 mmol) and **3** (crude product, 114 mg) gave **25** (125 mg, 0.309 mmol, 49% for 3 steps) as a yellow oil. $[\alpha]_D^{20}$ = +30.9 (*c* 1.3, $CHCl_3$). IR (ν cm^{-1}): 2930, 2858, 1384, 1258, 1079, 837. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (1H, dd, *J* 7.0, 1.6), 7.41 (1H, dd, *J* 7.0, 1.1), 7.19-7.29 (2H, m), 6.93 (1H, d, *J* 15.7, HC=C), 6.14 (1H, dd, *J* 15.7, 6.9, HC=C), 4.77 (2H, s), 4.55 (1H, dd, *J* 6.9, 4.9), 4.43-4.49 (1H, m), 4.35 (1H, dd, *J* 6.9, 4.7), 4.01-4.09 (1H, m), 1.58 (3H, s), 1.37 (3H, d, *J* 7.1), 1.36 (3H, s), 0.93 (9H, s), 0.09 (6H, s). ^{13}C NMR (100 MHz, acetone-d6) δ: 140.0, 136.9 (2 C), 131.8, 130.2, 129.4, 129.3, 129.2, 127.5 (4 CH + 2 H<u>C</u>=C), 116.1 (C), 88.0, 87.4, 86.8, 81.9 (4 CH), 65.0 (CH_2), 28.7 (CH_3), 27.3 (C(<u>C</u>H_3)$_3$), 26.7, 20.6 (2 CH_3), 19.8 (<u>C</u>$(CH_3)_3$), -4.1 (2CH_3). EI-HRMS *m*/*z*: found 404.2373, calcd for $C_{23}H_{36}O_4Si$ (M^+): 404.2377.

(3a*R*,4*R*,6*S*,6a*S*)-4-(3-Methoxystyryl)-2,2,6-trimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (26). HWE-reaction according to the general procedure (at 40°C for 22 h) of **23** (58 mg, 0.226 mmol) and **3** (crude product, 21 mg) gave **26** (16 mg, 0.0551 mmol, 47% for 3 steps) as a yellow oil. $[\alpha]_D^{20}$ = +36.7 (*c* 1.65, $CHCl_3$). IR (ν cm^{-1}): 2978, 2933, 1599, 1383, 1157, 1078, 865. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17-7.23 (1H, m), 6.98 (1H, d, *J* 7.6), 6.92 (1H, s), 6.80

[7] M. J. Mphahlele, A. Pienaar and T. A. Modro, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1455.

(1H, dd, *J* 8.1, 2.2), 6.68 (1H, d, *J* 15.9, HC=C), 6.24 (1H, dd, *J* 15.9, 6.7, HC=C), 4.55 (1H, dd, *J* 6.9, 5.2), 4.40-4.46 (1H, m), 4.35 (1H, dd, *J* 6.9, 4.8), 4.00-4.08 (1H, m), 3.81 (3H, s, OCH_3), 1.58 (3H, s), 1.37 (3H, d, *J* 6.4), 1.36 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 137.8 (2 C), 132.3, 129.5, 127.3, 119.3 (4 CH), 115.1 (C), 113.6, 111.7 (2 CH), 86.2, 85.6, 84.7, 80.2 (4 CH), 55.2 (OCH_3), 27.4, 25.5, 19.0 (3 CH_3). ESI-HRMS *m*/*z*: found 291.1592, calcd for $C_{17}H_{23}O_4$ (M^+): 291.1591.

3a*S*,4*S*,6*R*,6a*R*)-2,2,4-Trimethyl-6-styryltetrahydrofuro-[3,4-*d*][1,3]dioxole (27). HWE-reaction according to the general procedure (at 40°C for 24 h) of **24** (120 mg, 0.524 mmol) and **3** (crude product, 65 mg) gave **27** (42 mg, 0.161 mmol, 45% for 3 steps) as a yellow oil. $[\alpha]_D^{20}$ = +41.1 (*c* 1.5, $CHCl_3$). IR (ν cm^{-1}): 2979, 2934, 1382, 1212, 1078, 864. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.20-7.41 (5H, m), 6.71 (1H, t, *J* 15.9), 6.25 (1H, dd, *J* 15.9, 6.7), 4.55 (1H, dd, *J* 7.0, 5.1), 4.44 (1H, m), 4.35 (1H, dd, 7.0, 4.8), 4.00-4.08 (1H, m), 1.58 (3H, s), 1.38 (3H, d, *J* 6.5), 1.36 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.4 (C), 132.5, 128.5, 127.8, 127.0, 126.6 (5 CH + 2 HC=C), 115.1 (C), 86.2, 85.6, 84.8, 80.2 (4 CH), 27.4, 25.5, 19.0 (3 CH_3). ESI-HRMS *m*/*z*: found 261.1486, calcd for $C_{16}H_{21}O_3$ (M^+): 261.1485.

***tert*-Butyl(2-methoxy-6-((*E*)-2-((3a*S*,4*R*,6*S*,6a*R*)-2,2,6-trimethyltetrahydrofuro[3,4-*d*]-[1,3]dioxol-4-yl)vinyl)benzyloxy)dimethylsilane (28).** HWE-reaction according to the general procedure (at 65°C for 21 h) of **2** (285 mg, 0.708 mmol) and **21** (crude product, 60 mg) gave **25** (52 mg, 0.120 mmol, 36% for 3 steps) as a light yellow oil. $[\alpha]_D^{20}$ = –61.5 (*c* 1.5, $CHCl_3$). IR (ν cm^{-1}): 2933, 2855, 1579, 1472, 1380, 1253, 1066, 837. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.17-7.24 (3H, m), 6.74-6.80 (1H, m), 6.30 (1H, dd, *J* 16.0, 7.8, HC=C), 4.84 (1H, d, *J* 11.2), 4.79 (1H, d, *J* 11.2, AB-system), 4.68-4.72 (1H, m), 4.59-4.64 (1H, m), 4.11 (1H, dd, *J* 7.6, 3.6), 3.80 (3H, s), 3.67-3.75 (1H, m), 1.52 (3H, s), 1.38 (3H, d, *J* 6.3), 1.34 (3H, s), 0.88 (9H, s), 0.05 (3H, s), 0.03 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.2, 138.6 (2 C), 132.2, 128.4 (2 CH), 126.4 (C), 125.7, 119.0 (2 CH), 112.1 (C), 109.9 (CH), 83.4, 82.9, 82.5, 77.4 (4 CH), 55.9 (CH_2), 55.6 (OCH_3), 26.0 ($C(\underline{C}H_3)_3$), 25.1, 23.8 (2 CH_3), 18.4 ($\underline{C}(CH_3)_3$), 13.5 (CH_3), -5.2 ($2CH_3$). ESI-HRMS *m*/*z*: found 452.2825, calcd for $C_{24}H_{42}O_5NSi$ $(M+NH_4)^+$: 452.2827.

***tert*-Butyldimethyl(2-((*E*)-2-((3a*S*,4*R*,6*S*,6a*R*)-2,2,6-trimethyltetrahydrofuro[3,4-*d*][1,3]-dioxol-4-yl)vinyl)benzyl-oxy)silane (29).** HWE-reaction according to the general procedure (reaction time: 8 h) of **12** (352 mg, 0.946 mmol) and **21** (crude product, 80 mg) gave **29** (56 mg, 0.138 mmol, 31% for 3 steps) as a light yellow oil. $[\alpha]_D^{20}$ = –41.5 (*c* 2.45, $CHCl_3$). IR (ν cm^{-1}): 2931, 2856, 1383, 1256, 1098, 1073, 837. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.51 (1H, dd, *J* 6.8, 1.8), 7.39 (1H, dd, *J* 6.6, 1.5), 7.22 (2H, m), 6.92 (1H, d, *J* 15.9, HC=C), 6.25 (1H, d, *J* 15.9, 7.8, HC=C), 4.79 (1H, d, *J* 13.2), 4.74 (1H, d, *J* 13.1, AB-system with last signal), 4.69 (1H, dd, *J* 6.0, 3.8), 4.60 (1H, dd, *J* 5.9, 3.7), 4.09 (1H, dd, *J* 7.6, 3.5), 3.70 (1H, dq, *J* 6.3, 3.7), 1.51 (3H, s), 1.36 (3H, d, *J* 6.3), 1.32 (3H, s), 091 (9H, s), 0.07 (3H, s), 0.06 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 138.2, 134.6 (2 C), 131.1, 127.7, 127.1, 126.7, 126.2, 125.6 (4 CH + 2 HC=C), 112.2 (C), 83.3, 82.8, 82.5, 77.5 (4 CH), 63.1 (CH_2), 26.0 (CH_3), 25.9 ($C(\underline{C}H_3)_3$), 25.1, (CH_3), 18.4 ($\underline{C}(CH_3)_3$), 13.5 (CH_3), -5.2 ($2CH_3$). EI-HRMS *m*/*z*: found 404.2368, calcd for $C_{23}H_{36}O_4Si$ (M^+): 404.2377.

(3a*S*,4*R*,6*S*,6a*R*)-4-(3-Methoxystyryl)-2,2,6-trimethyltetrahydrofuro[3,4-*d*][1,3]dioxole (30). HWE-reaction according to the general procedure (reaction time: 8 h) of **23** (305 mg, 1.18 mmol) and **21** (crude product, 90 mg) gave **30** (60 mg, 0.207 mmol, 42% for 3 steps) as a light yellow oil. $[\alpha]_D^{20}$ = –67.8 (*c* 0.93, $CHCl_3$). IR (ν cm^{-1}): 2935, 2837, 1599, 1383, 1265, 1163, 1097, 1036. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.18-7.25 (1H, m), 6.96 (1H, s), 6.80 (1H, dd, *J* 8.0, 2.1), 6.68 (1H, d, *J* 16.0, HC=C), 6.37 (1H, dd, *J* 16.0, 7.8, HC=C), 4.70 (1H, dd, *J*

6.0, 3.8), 4.63 (1H, dd, *J* 5.9, 3.7), 4.09 (1H, dd, *J* 7.7, 3.6), 3.80 (3H, s, OCH_3), 3.71 (1H, dq, *J* 6.3, 3.7), 1.53 (3H, s), 1.38 (3H, d, *J* 6.4), 1.34 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.6, 137.9 (2 C), 134.3, 129.3, 123.9, 119.5, 113.5 (5 CH), 112.2 (C), 111.9 (CH), 83.2, 82.5, 82.4, 77.4 (4 CH), 55.2 (OCH_3), 26.0, 25.0, 13.4 (3 CH_3). EI-HRMS *m*/*z*: found 290.1509, calcd for $C_{17}H_{22}O_4$ (M^+): 290.1513.

(3a*R*,4*S*,6*R*,6a*S*)-2,2,4-Trimethyl-6-styryltetrahydrofuro[3,4-*d*][1,3]dioxole (31). HWE-reaction according to the general procedure (reaction time: 14 h) of **24** (216 mg, 0.946 mmol) and **21** (crude product, 83 mg) gave **31** (58 mg, 0.207 mmol, 49% for 3 steps) as a colorless oil. $[\alpha]_D^{20}$ = –48.1 (*c* 1.65, $CHCl_3$). IR (ν cm^{-1}): 2979, 2935, 1368, 1209, 1096, 1032, 968. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.40-7.45 (2H, d, *J* 7.3), 7.27-7.33 (2H, m), 6.91 (1H, d, *J* 16.1, HC=C), 6.38 (1H, dd, *J* 16.1, 7.8, HC=C), 4.71 (1H, dd, *J* 6.0, 3.7), 4.62 (1H, dd, *J* 6.0, 3.7), 4.10 (1H, dd, *J* 7.6, 3.5), 3.71 (1H, dq, *J* 6.3, 3.6), 1.54 (3H, s), 1.38 (3H, d, *J* 6.3), 1.35 (3H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.5 (C), 134.5 (CH), 128.4 (2CH), 127.8 (CH), 126.8 (2CH), 123.5 (CH), 112.2 (C), 83.2, 82.6, 82.5, 77.4 (4 CH), 26.0, 25.0, 13.4 (3 CH_3). EI-HRMS *m*/*z*: found 260.1410, calcd for $C_{16}H_{20}O_3$ (M^+): 260.1407.

(2*R*,3*S*,4*R*,5*S*)-2-(2-(Hydroxymethyl)styryl)-5-methyltetrahydrofuran-3,4-diol (32). Deprotection of **25** (43 mg, 0.106 mmol) according to the general procedure (5.4 mL 1 M HCl, 18 eq, 18 h) and column chromatography using CH_2Cl_2/acetone (2:1) gave **32** (12 mg, 0.0479 mmol, 45%) as a colorless oil. $[\alpha]_D^{20}$ = +17.5 (*c* 0.55, $CHCl_3$). IR (ν cm^{-1}): 3379 (OH), 2928, 1454, 1384, 1221, 1092, 1010, 754. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50 (1H, d, *J* 7.5), 7.21-7.29 (3H, m), 6.98 (1H, d, *J* 15.7, HC=C), 6.08 (1H, dd, *J* 15.8, 7.2, HC=C), 4.73 (1H, d, *J* 12.3), 4.61 (1H, d, *J* 12.3), 4.27 (1H, t, *J* 6.4), 3.85-3.90 (1H, m), 3.78-3.85 (2H, m), 3.64 (1H, brs, OH), 3.22 (1H, brs, OH), 2.96 (1H, brs, OH), 1.29 (3H, d, *J* 6.4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 135.6 (2 C), 129.9, 129.6, 129.0, 128.4, 128.0, 1276.3 (4 CH + 2 HC=C), 84.0, 80.0, 76.1, 75.4 (4 CH), 63.3 (CH_2), 19.2 (CH_3). ESI-HRMS *m*/*z*: found 501.2478, calcd for $C_{28}H_{37}O_8$ $(2M+H)^+$: 501.2483.

(2*R*,3*S*,4*R*,5*S*)-2-(3-Methoxystyryl)-5-methyltetrahydrofuran-3,4-diol (33). Deprotection of **26** (33 mg, 0.114 mmol) according to the general procedure (2.1 mL 1 M HCl, 18 eq, 28 h) and column chromatography using cyclohexane/AcOEt (2:1) gave **33** (25 mg, 0.10 mmol, 88%) as a colorless oil. $[\alpha]_D^{20}$ = +22.0 (*c* 1.45, $CHCl_3$). IR (ν cm^{-1}): 3391 (OH), 2930, 1580, 1455, 1269, 1089, 1047, 778. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.19-7.25 (1H, m), 6.98 (1H, d, *J* 7.7), 6.93 (1H, s), 6.80 (1H, dd, *J* 8.1, 2.1), 6.87 (1H, d, *J* 15.8, HC=C), 6.20 (1H, dd, *J* 15.9, 7.0, HC=C), 4.30 (1H, t, *J* 6.3), 3.87-3.97 (2H, m), 3.80 (3H, OCH_3), 3.74-3.82 (1H, m), 2.75 (OH, brd, *J* 5.6), 2.69 (OH, bd, *J* 5.4), 1.36 (3H, d, *J* 6.4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 137.7 (2 C), 132.5, 129.5, 127.5, 119.3, 113.6, 111.7 (4 CH + 2 HC=C), 84.1, 79.7, 76.2, 75.5 (4 CH), 55.2 (OCH_3), 19.0 (3 CH_3). EI-HRMS *m*/*z*: found 250.1206, calcd for $C_{14}H_{18}O_4$ (M^+): 250.1200.

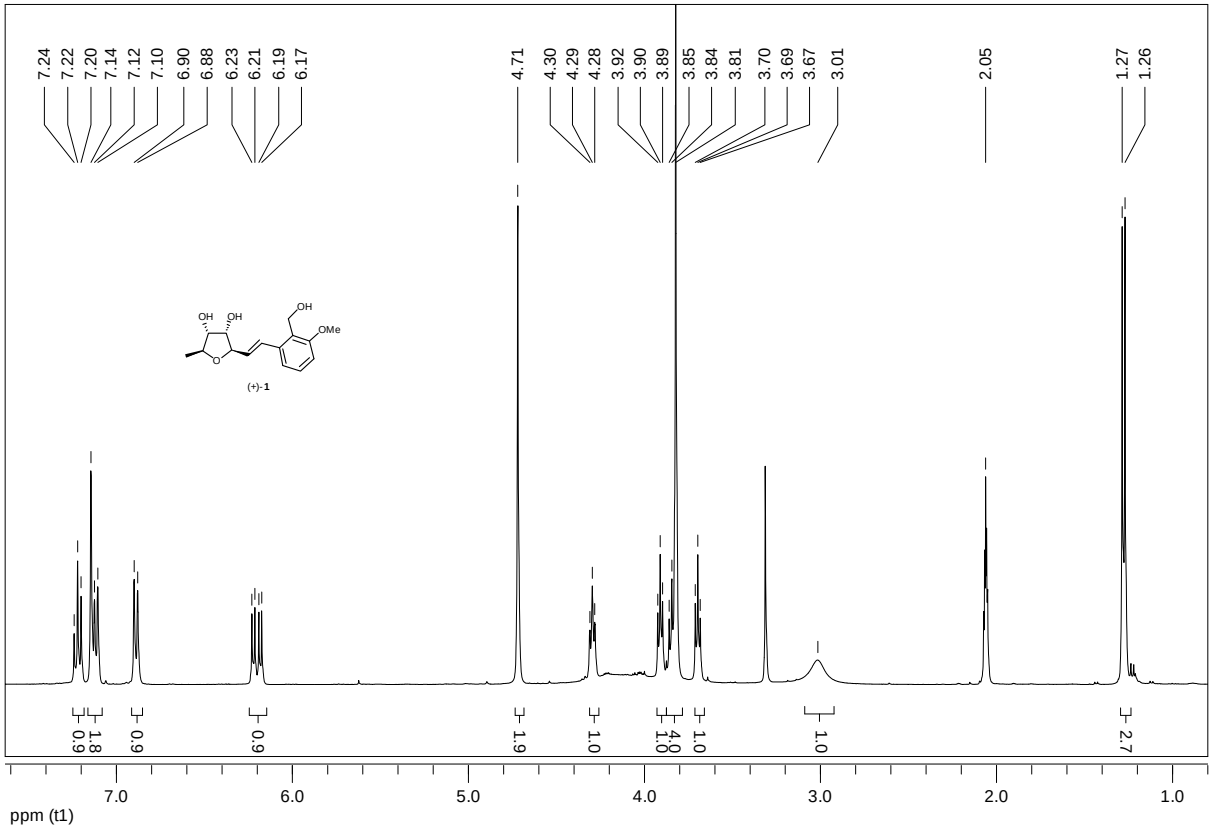
(2*S*,3*R*,4*S*,5*R*)-2-Methyl-5-styryltetrahydrofuran-3,4-diol (34). Deprotection of **27** (28 mg, 0.108 mmol) according to the general procedure (2.0 mL 1 M HCl, 18 eq, 27 h) and column chromatography using cyclohexane/AcOEt (2:1) gave **34** (19 mg, 0.0862 mmol, 80%) as a colorless solid, mp 76-78°C. $[\alpha]_D^{20}$ = +27.9 (*c* 0.95, $CHCl_3$). IR (ν cm^{-1}): 3431 (OH), 2928, 1384, 1221, 1092, 967, 747. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21-7.42 (5H, m), 6.70 (1H, d, *J* 15.9, HC=C), 6.21 (1H, dd, *J* 15.9, 7.0, HC=C), 4.31 (1H, d, *J* 6.4), 3.88-3.93 (2H, m), 3.74-3.81 (1H, m), 2.60-2.80 (2H, brs, OH), 1.36 (3H, d, *J* 6.3). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.3 (C), 137.2 (CH), 128.5 (2CH), 127.9 (CH), 127.2 (2CH), 126.6 (CH), 84.2, 79.7, 76.2, 75.5 (4 CH), 19.0 (3 CH_3). EI-HRMS *m*/*z*: found 220.1099, calcd for $C_{13}H_{16}O_3$ (M^+): 220.1094.

(2*R*,3*R*,4*S*,5*S*)-2-(2-(Hydroxymethyl)-3-methoxystyryl)-5-methyltetrahydrofuran-3,4-diol (35). Deprotection of **28** (49 mg, 0.113 mmol) according to the general procedure (8.1 mL 1 M HCl, 72 eq, 52 h) and column chromatography using CH_2Cl_2/acetone (2:1) gave **35** (29 mg, 0.103 mmol, 91%) as a colorless oil. $[\alpha]_D^{20}$ = +1.5 (*c* 1.4, CH_3OH). IR (ν cm^{-1}): 3391 (OH), 2934, 1578, 1471, 1384, 1264, 1074, 1000, 795. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (1H, t, *J* 8.0), 7.09 (1H, d, *J* 7.7), 7.03 (1H, d, *J* 15.9, HC=C), 6.82 (1H, d, *J* 8.2), 6.17 (1H, dd, *J* 15.9, 6.4, HC=C), 4.79 (2H, brs), 4.47 (1H, t, *J* 6.1), 4.28-4.35 (1H, m), 4.07-4.12 (1H, m), 3.95-4.04 (1H, m), 3.85 (3H, s, OCH_3), 2.96 (1H, brs, OH), 2.80 (1H, brs, OH), 2.51 (1H, brs, OH), 1.34 (3H, d, *J* 6.4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 137.9 (2 C), 130.2, 129.6, 128.9 (3 CH), 126.0 (C), 119.4, 109.7 (2 CH), 80.7, 74.1, 73.2 (4 CH), 56.4 (CH_2), 55.6 (OCH_3), 14.8 (CH_3). ESI-HRMS *m*/*z*: found 303.1204, calcd for $C_{15}H_{20}O_5Na$ $(M+Na)^+$: 303.1203.

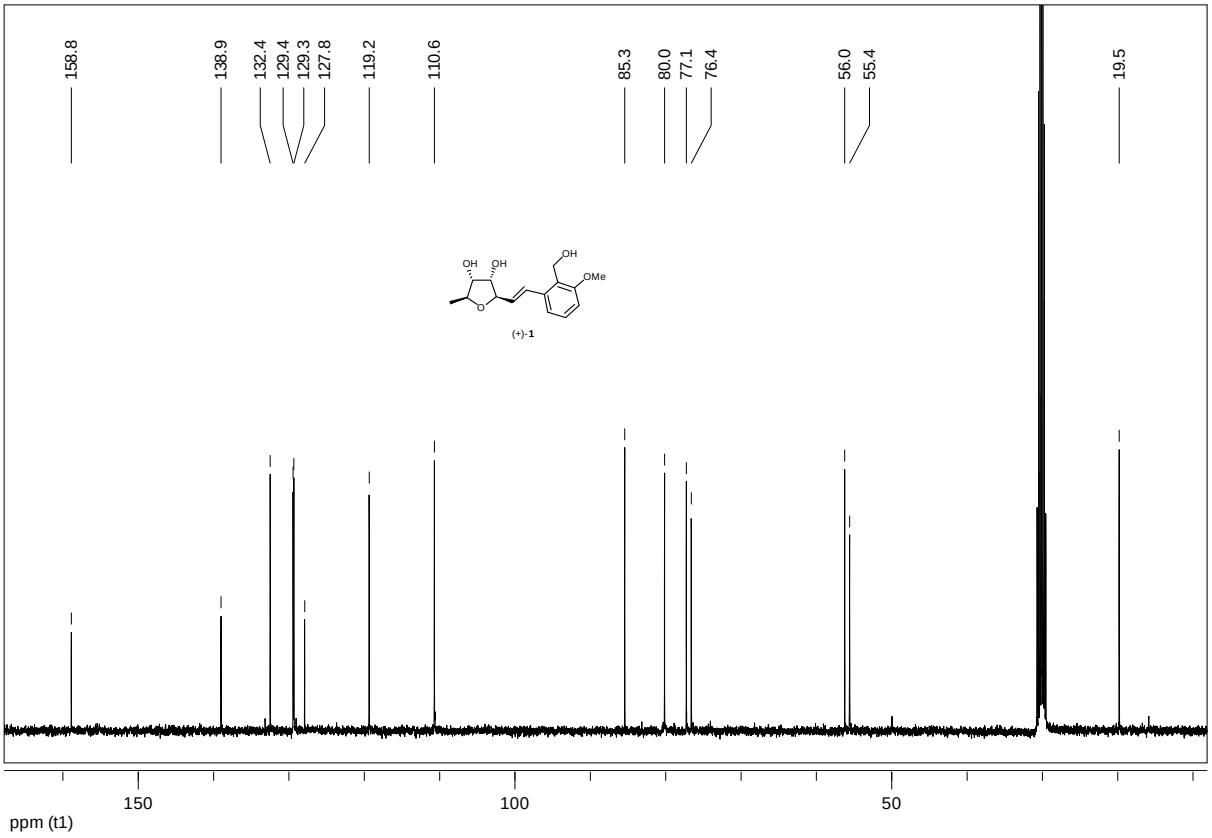
(2*R*,3*R*,4*S*,5*S*)-2-(2-(Hydroxymethyl)styryl)-5-methyltetrahydrofuran-3,4-diol (36). Deprotection of **29** (40 mg, 0.0989 mmol) according to the general procedure (4.5 mL 2 M HCl, 90 eq, 18 h) and column chromatography using CH_2Cl_2/acetone (5:1) gave **36** (17 mg, 0.0679 mmol, 69%) as a colorless oil. $[\alpha]_D^{20}$ = +6.7 (*c* 0.8, $CHCl_3$). IR (ν cm^{-1}): 3366 (OH), 2930, 1384, 1113, 1073, 995, 755. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (1H, d, *J* 7.3), 7.21-7.32 (3H, m), 6.09 (1H, d, *J* 15.9, HC=C), 6.16 (1H, dd, *J* 15.9, 6.2, HC=C), 4.74 (1H, d, *J* 12.3), 4.66 (1H, d, *J* 12.3, AB-system with last signal), 4.49 (1H, t, *J* 6.1), 4.28-4.34 (1H, m), 4.03-4.07 (1H, m), 3.95-4.03 (1H, m), 2.83 (3H, brs, OH), 1.34 (3H, d, *J* 6.4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 137.4, 136.2 (2 C), 130.0, 128.9, 128.8, 128.4, 127.8, 126.8 (4 CH + 2 HC=C), 80.4, 76.6, 74.2, 73.3 (4 CH), 63.7 (CH_2), 14.8 (CH_3). ESI-HRMS *m*/*z*: found 501.2478, calcd for $C_{28}H_{37}O_8$ $(2M+H)^+$: 501.2483.

(2*R*,3*R*,4*S*,5*S*)-2-(3-Methoxystyryl)-5-methyltetrahydrofuran-3,4-diol (37). Deprotection of **30** (19 mg, 0.0654 mmol) according to the general procedure (7.8 mL 1 M HCl, 120 eq, 48 h) and column chromatography using cyclohexane/AcOEt (2:1) gave **37** (11 mg, 0.0439 mmol, 67%) as a colorless oil. $[\alpha]_D^{20}$ = –17.5 (*c* 0.5, $CHCl_3$). IR (ν cm^{-1}): 3435 (OH), 2934, 1599, 1384, 1267, 1157, 1047, 780. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.23 (1H, t, *J* 7.9), 7.00 (1H, d, *J* 7.7), 6.95 (1H, s), 6.81 (1H, dd, *J* 8.2, 2.2), 6.68 (1H, d, *J* 16.0, HC=C), 6.30 (1H, dd, *J* 16.0, 6.7, HC=C), 4.46 (1H, dt, *J* 6.2, 0.8), 4.34 (1H, q, *J* 5.5), 4.19 (1H, q, *J* 5.1), 4.01 (1H, qd, *J* 6.4, 4.8), 3.81 (3H, s), 2.52 (1H, brd, *J* OH), 2.38 (1H, brd, *J* OH), 1.36 (3H, d, *J* 6.4). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.7, 137.7 (2 C), 133.6, 129.5, 125.3, 119.4, 113.8, 1117.7 (4 CH + 2 HC=C), 80.9, 73.9, 73.3 (4 CH), 55.2 (OCH_3), 14.8 (CH_3). EI-HRMS *m*/*z*: found 250.1196, calcd for $C_{14}H_{18}O_4$ (M^+): 250.1200.

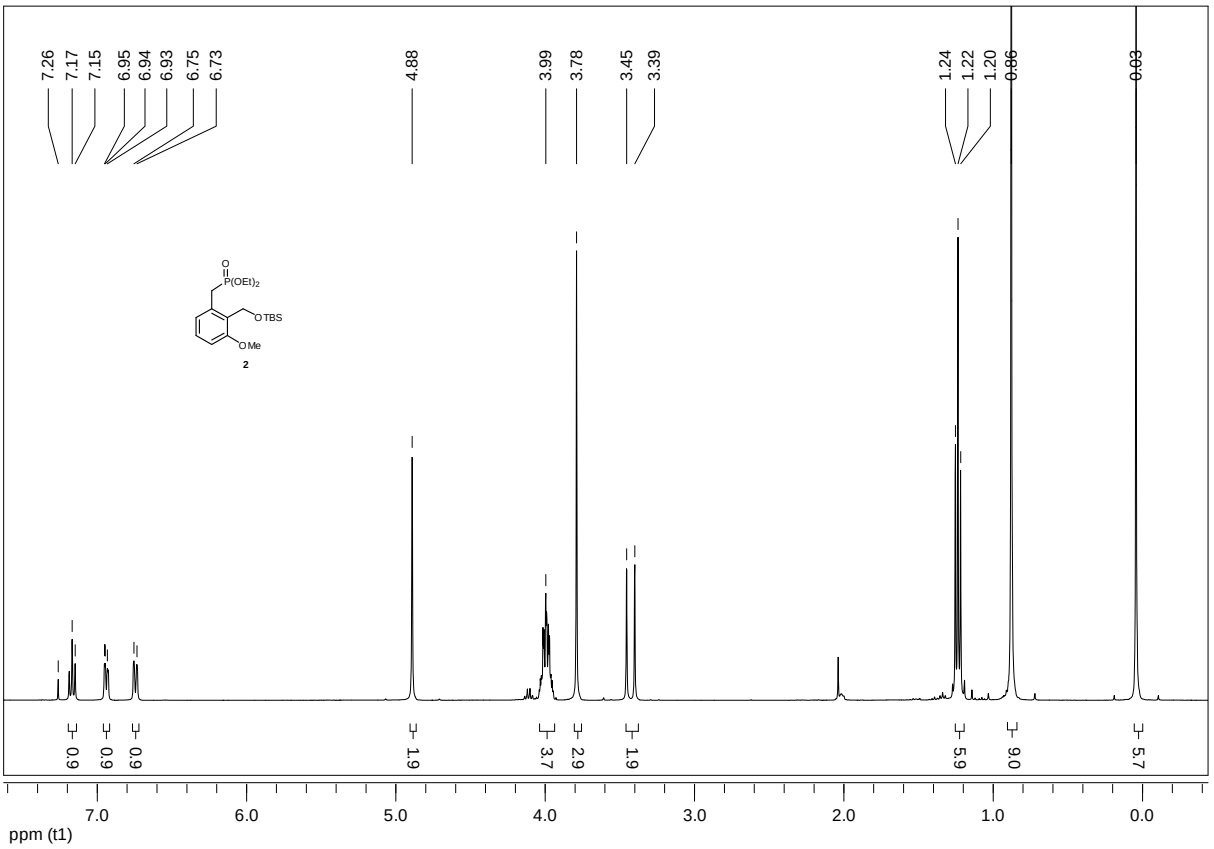
(2*S*,3*S*,4*R*,5*R*)-2-Methyl-5-styryltetrahydrofuran-3,4-diol (38). Deprotection of **31** (29 mg, 0.111 mmol) according to the general procedure (10 mL 1 M HCl, 90 eq, 27 h) and column chromatography using cyclohexane/AcOEt (2:1) gave **38** (18 mg, 0.0817 mmol, 74%) as a colorless solid, mp 87-89°C. $[\alpha]_D^{20}$ = –21.8 (*c* 0.9, $CHCl_3$). IR (ν cm^{-1}): 3398 (OH), 3026, 2933, 1384, 1114, 1073, 969, 750. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.22-7.45 (5H, m), 7.00 (1H, d, *J* 7.7), 6.95 (1H, s), 6.81 (1H, dd, *J* 8.2, 2.2), 6.72 (1H, d, *J* 16.0, HC=C), 6.31 (1H, dd, *J* 16.0, 6.6, HC=C), 4.32-4.39 (1H, m), 4.16-4.22 (1H, m), 4.02 (1H, qd, *J* 6.4, 4.9), 2.45 (1H, brs, OH), 2.29 (1H, brs, OH), 1.36 (3H, d, *J* 6.5). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 136.2 (C), 133.7 (CH), 128.5 (2CH), 128.0(CH), 126.7 (2CH), 124.9 (CH), 80.9, 73.9, 73.4 (4 CH), 14.8 (CH_3). EI-HRMS *m*/*z*: found 220.1083, calcd for $C_{13}H_{16}O_3$ (M^+): 220.1094.



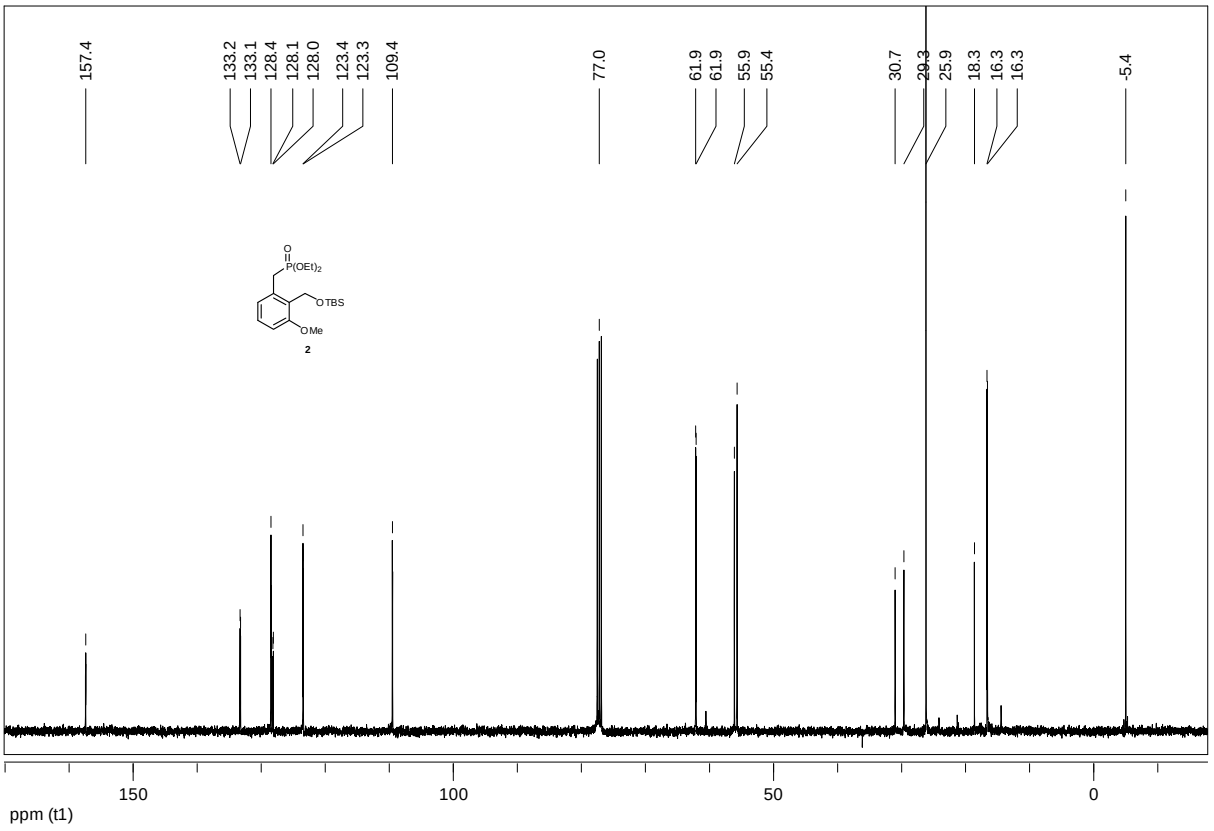
^{1}H NMR (400 MHz, acetone-d_6)



^{13}C NMR (100 MHz, acetone-d_6)



^{1}H-NMR (400 MHz, $CDCl_3$)



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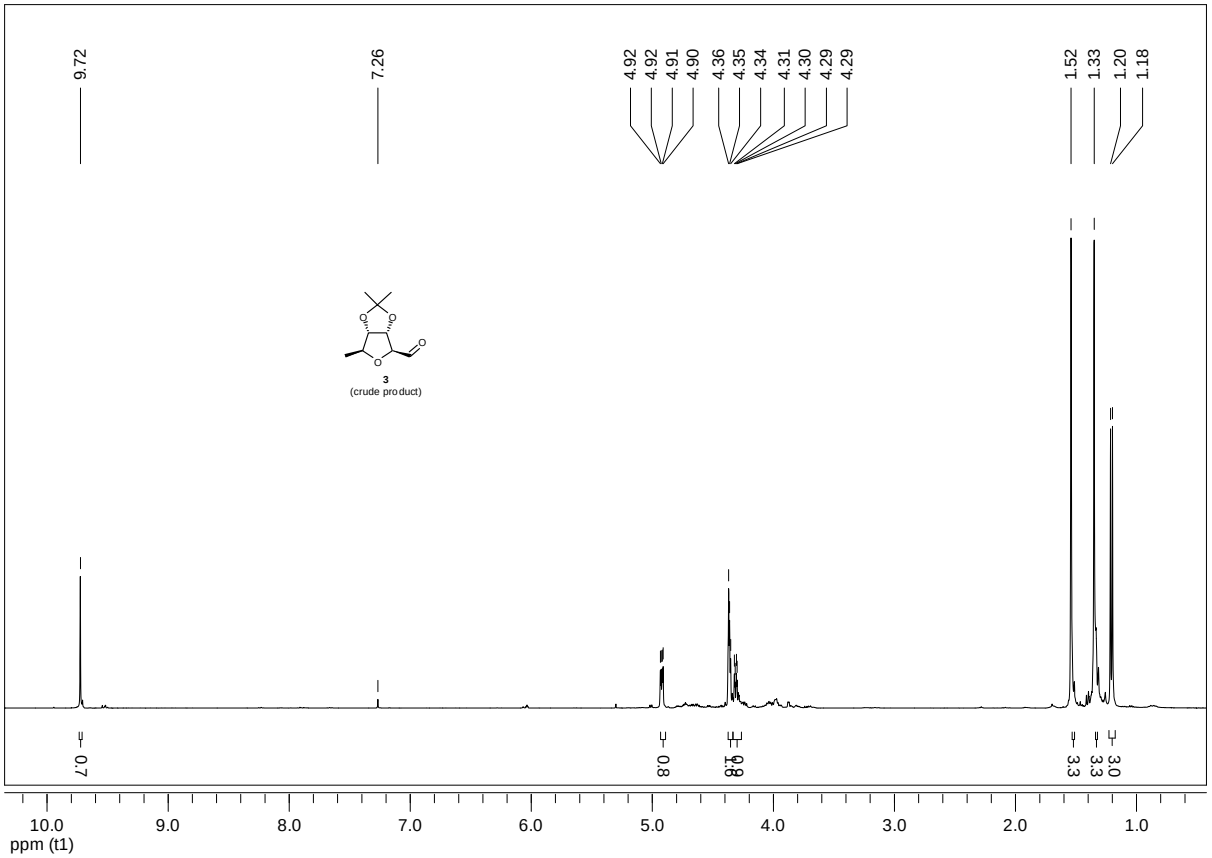

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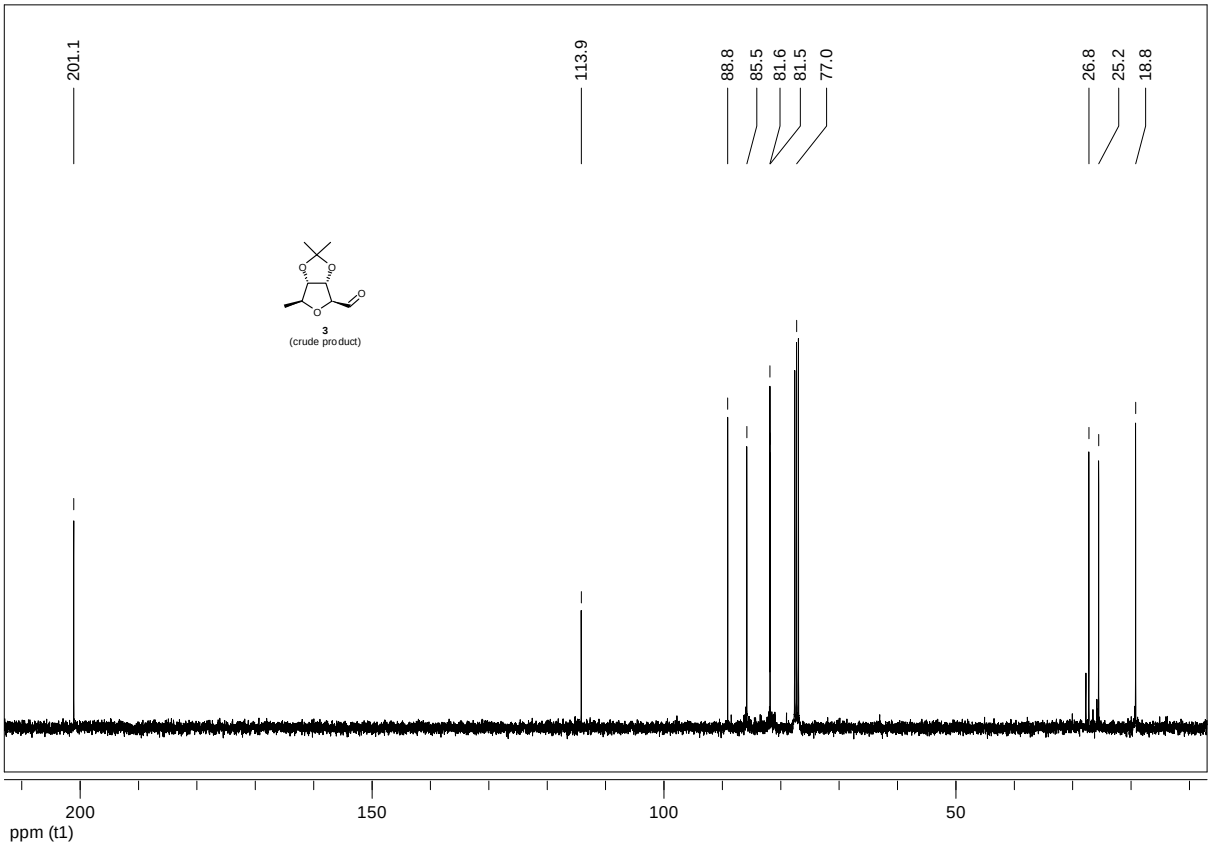

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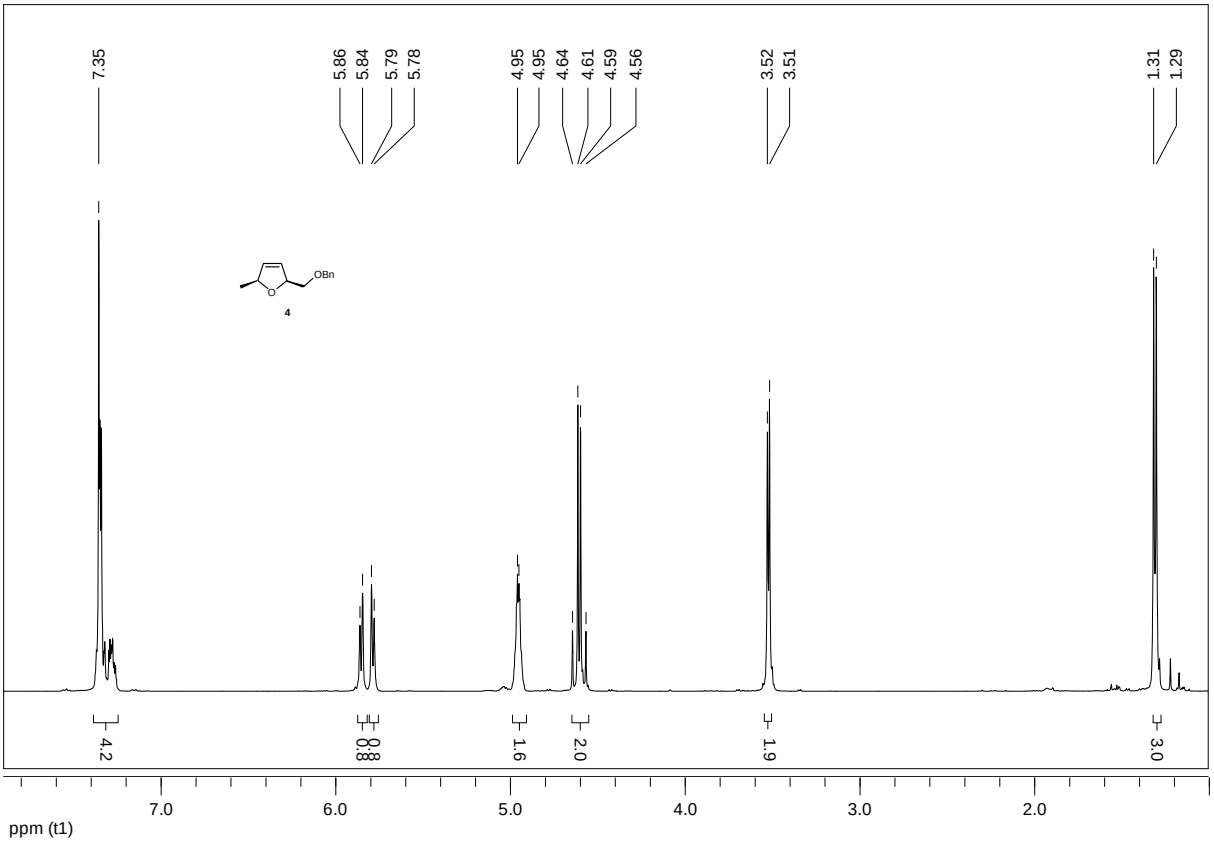

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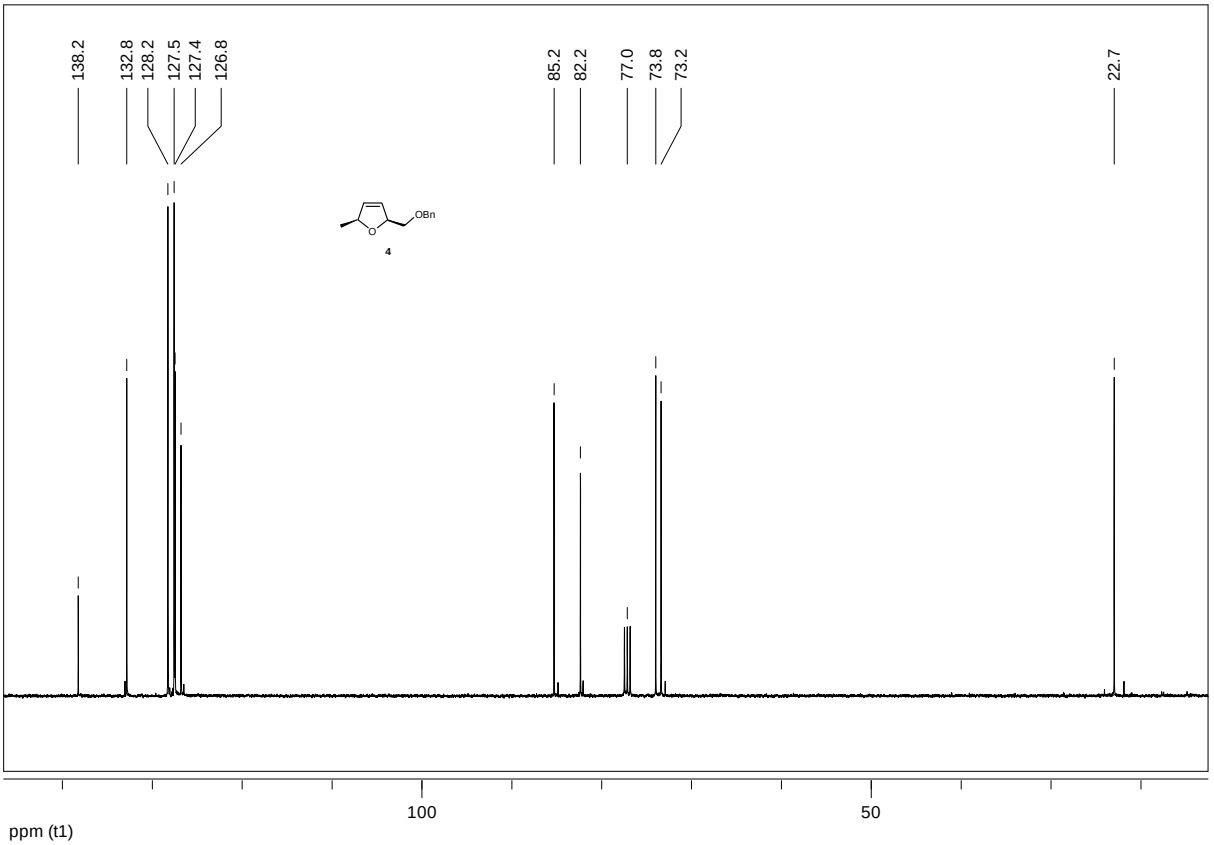

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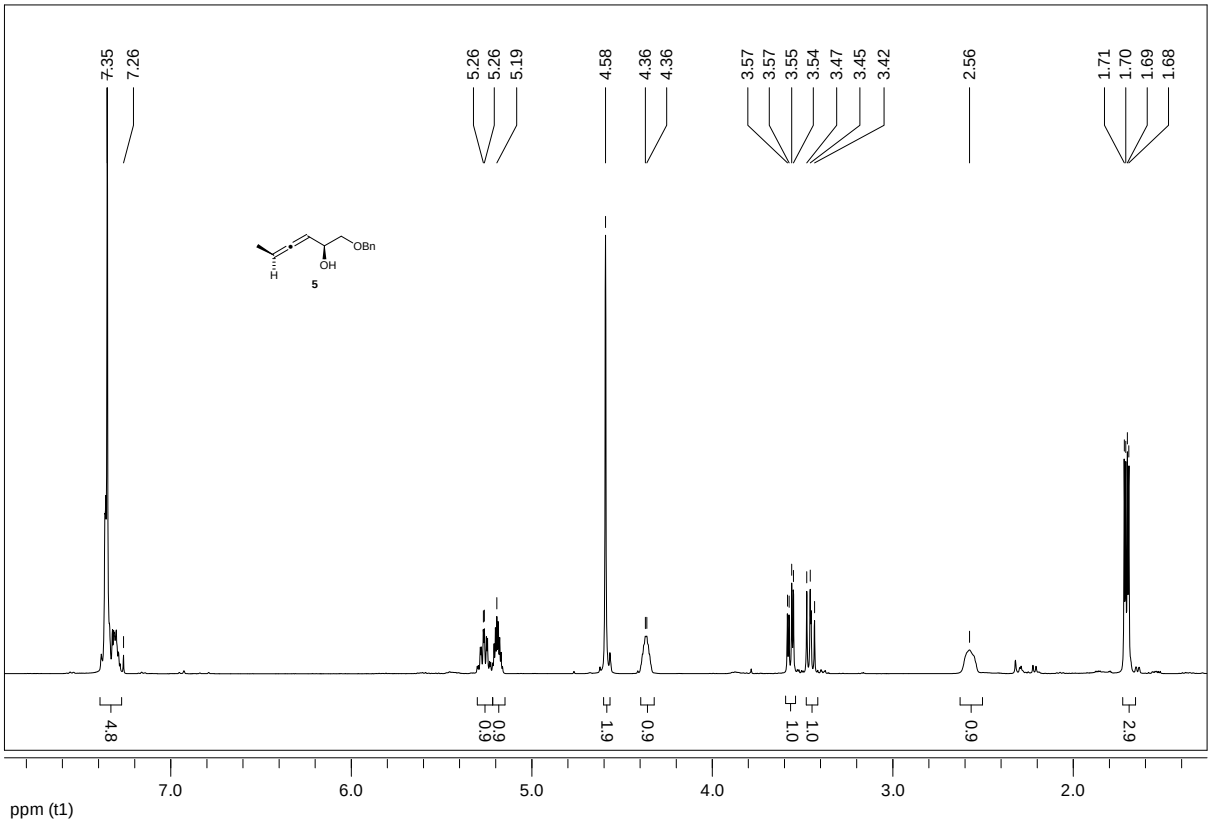

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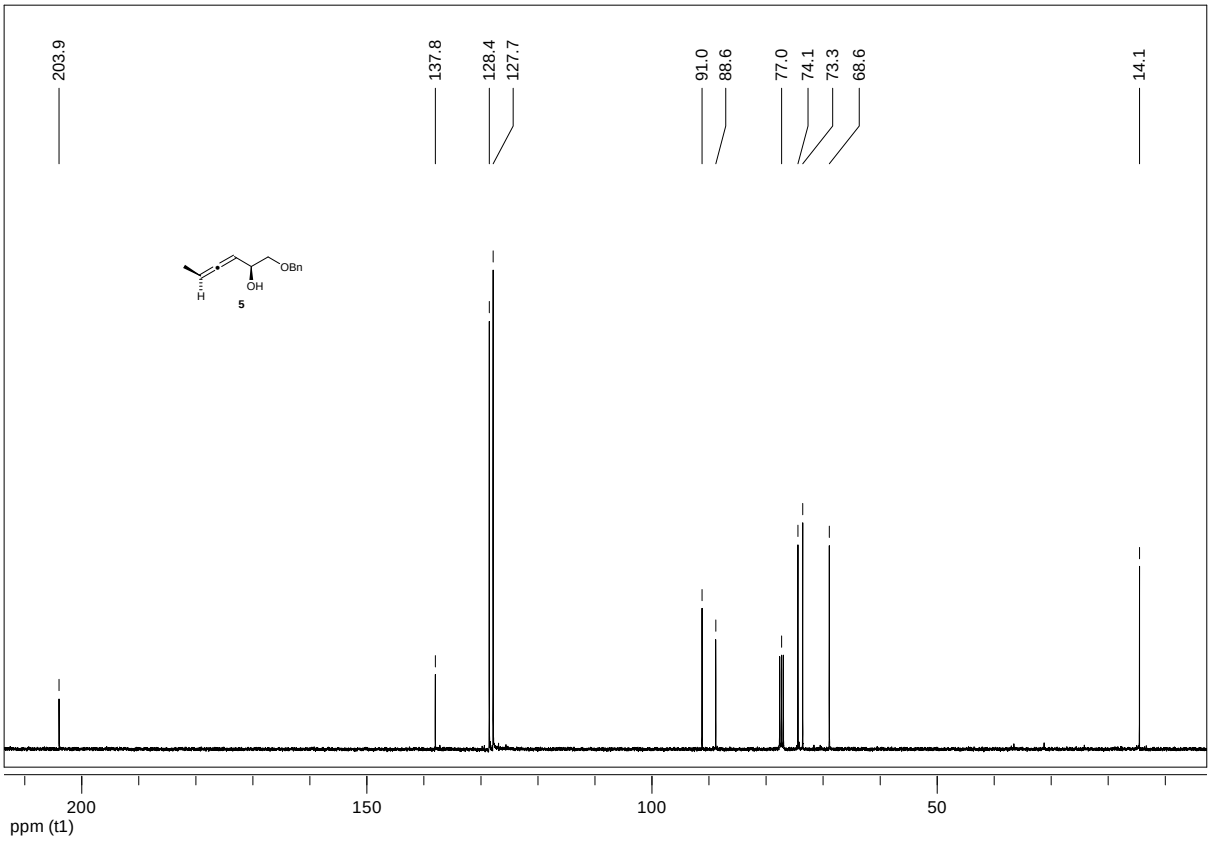

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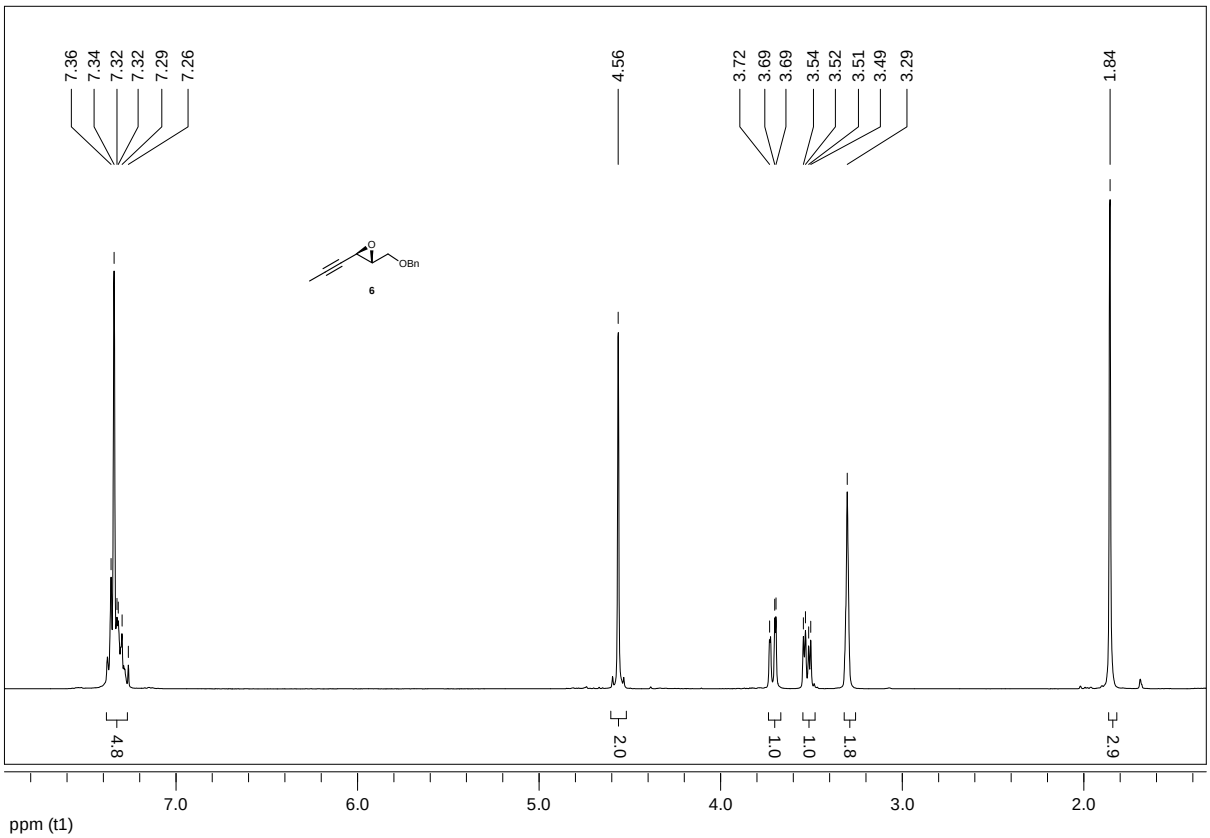

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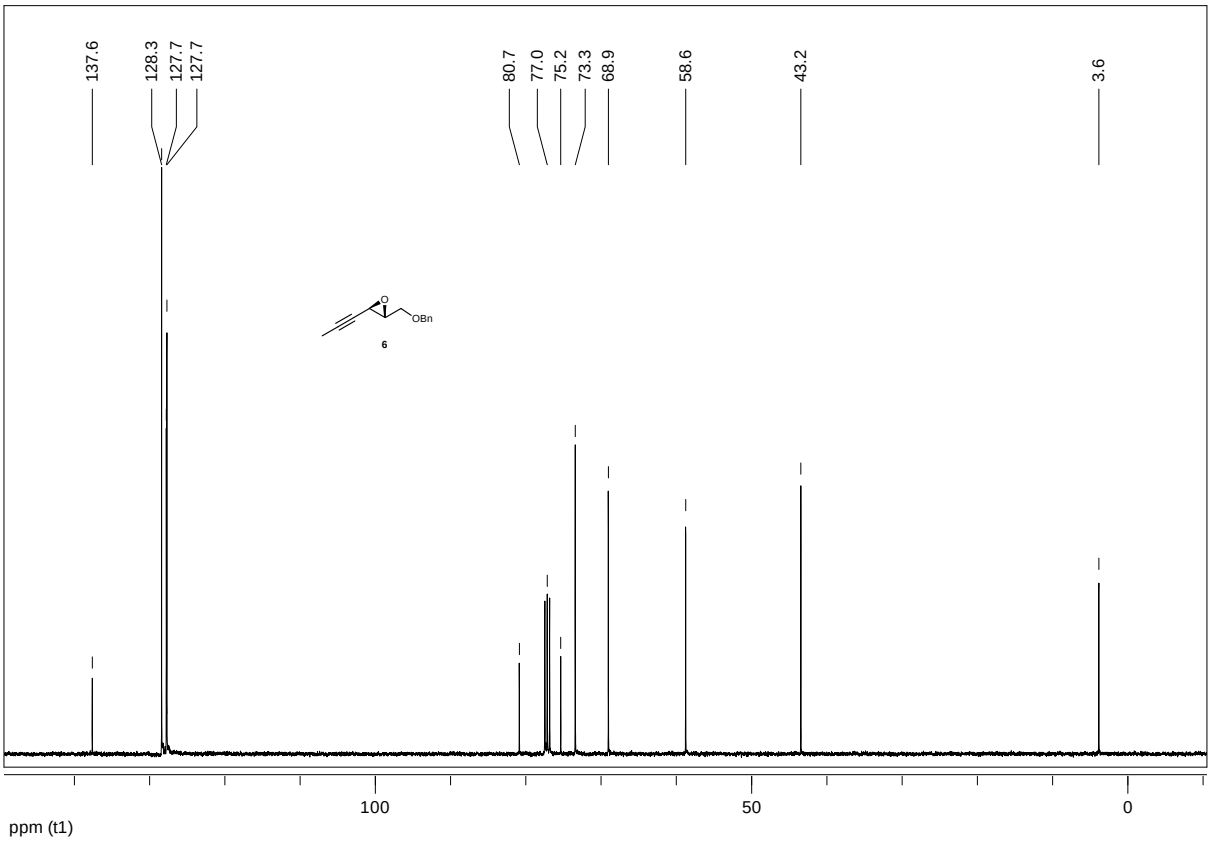

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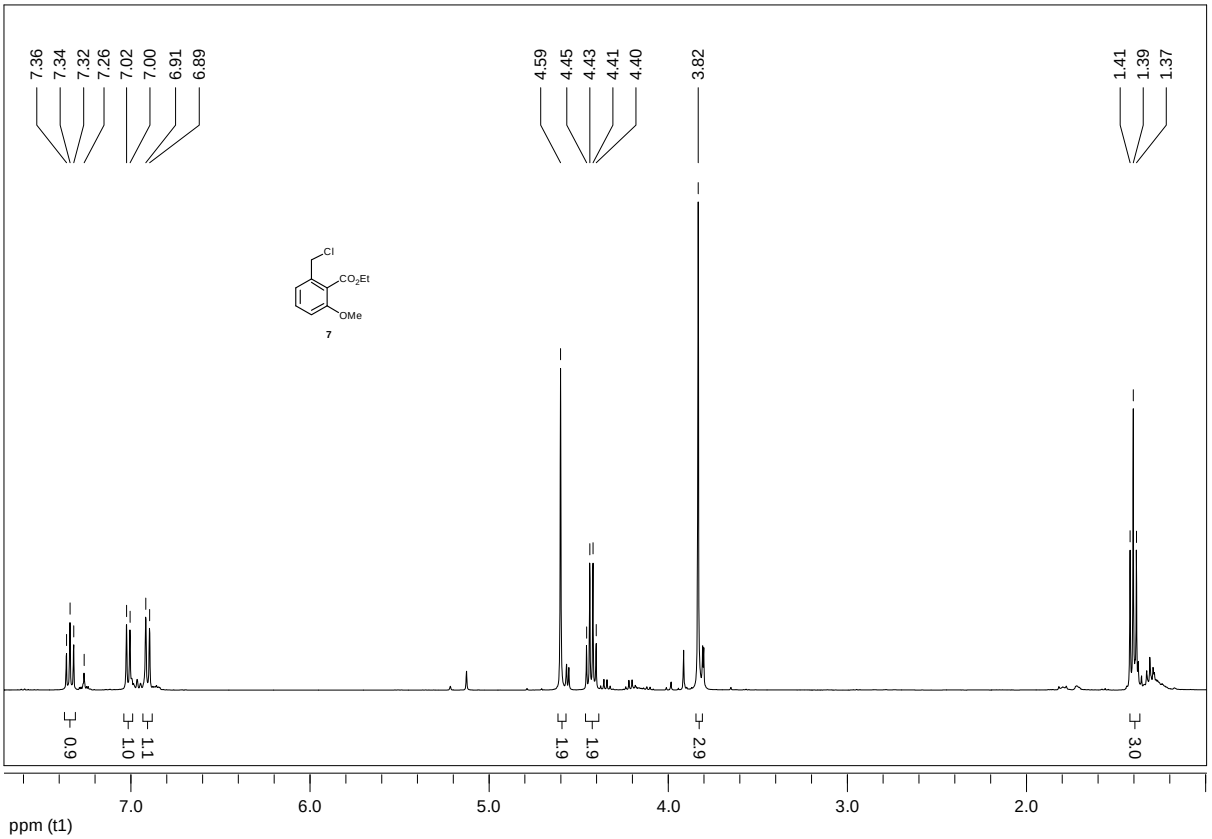

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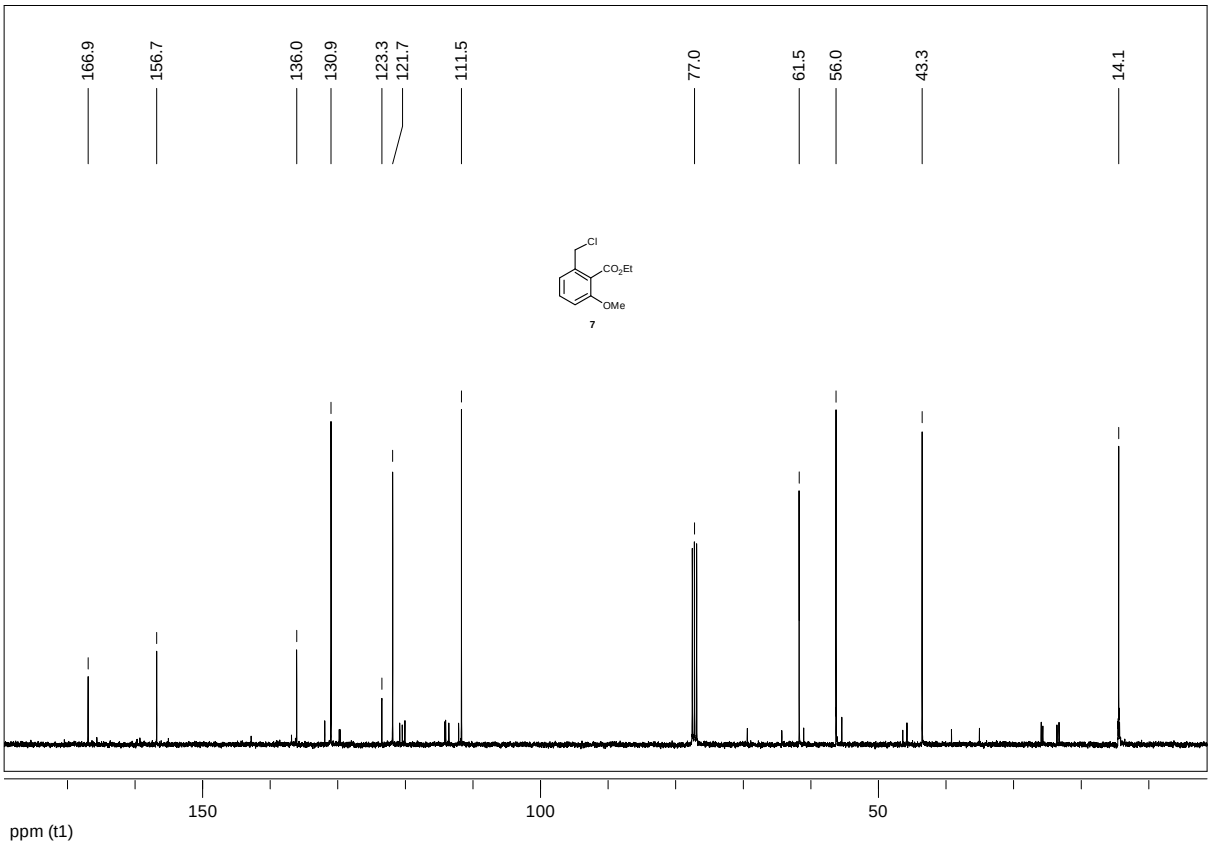

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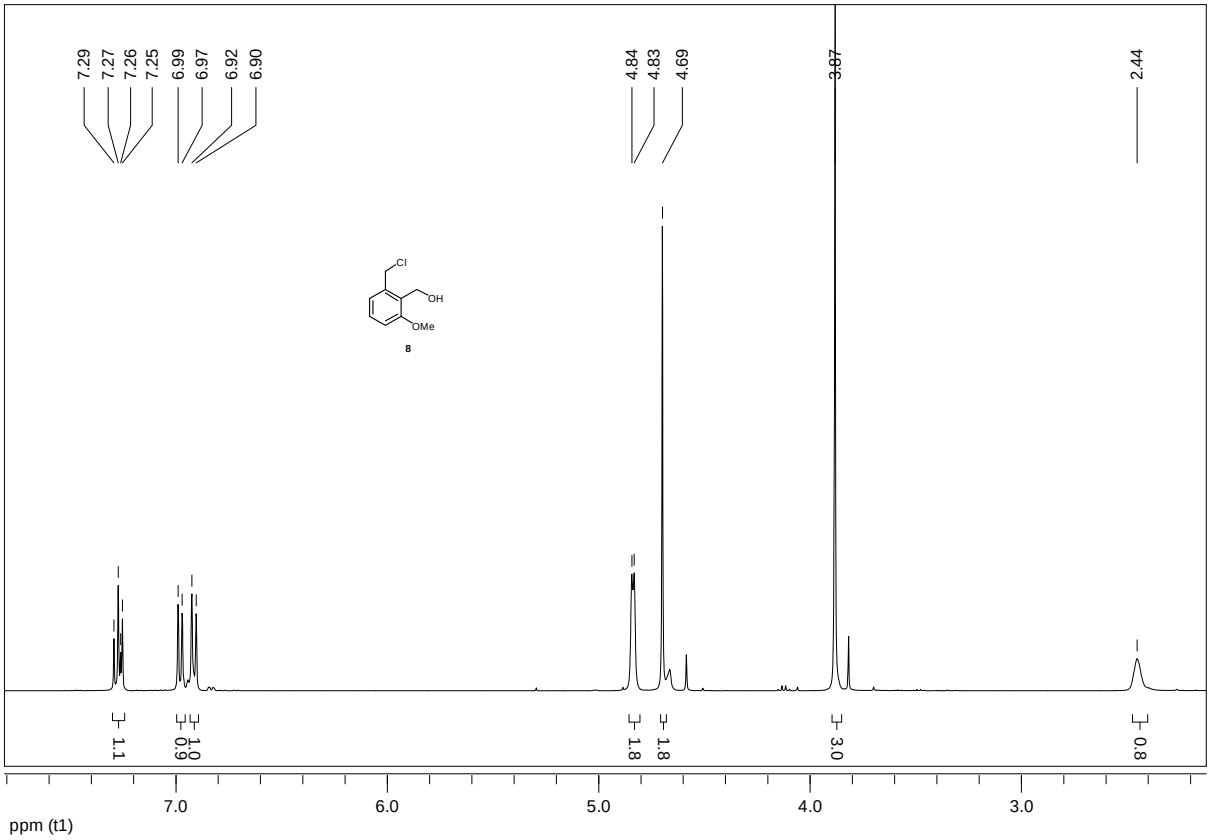

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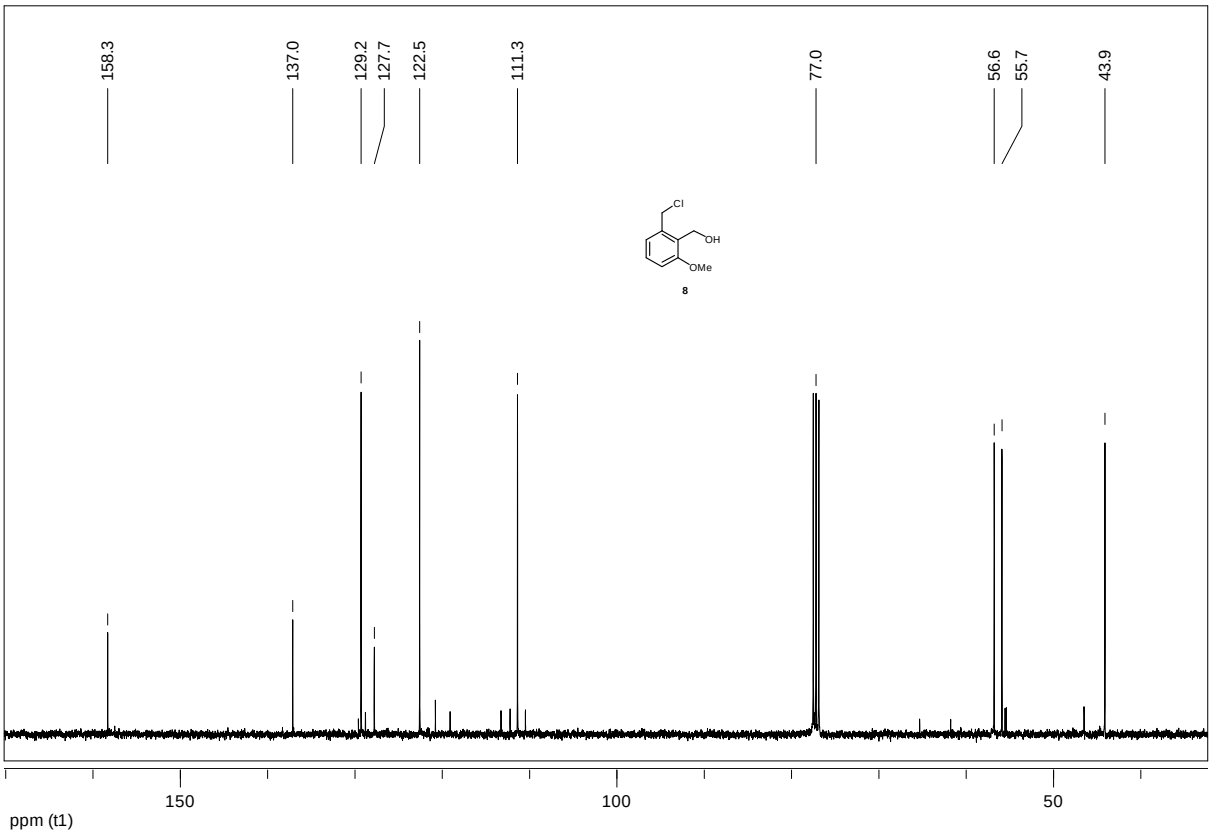

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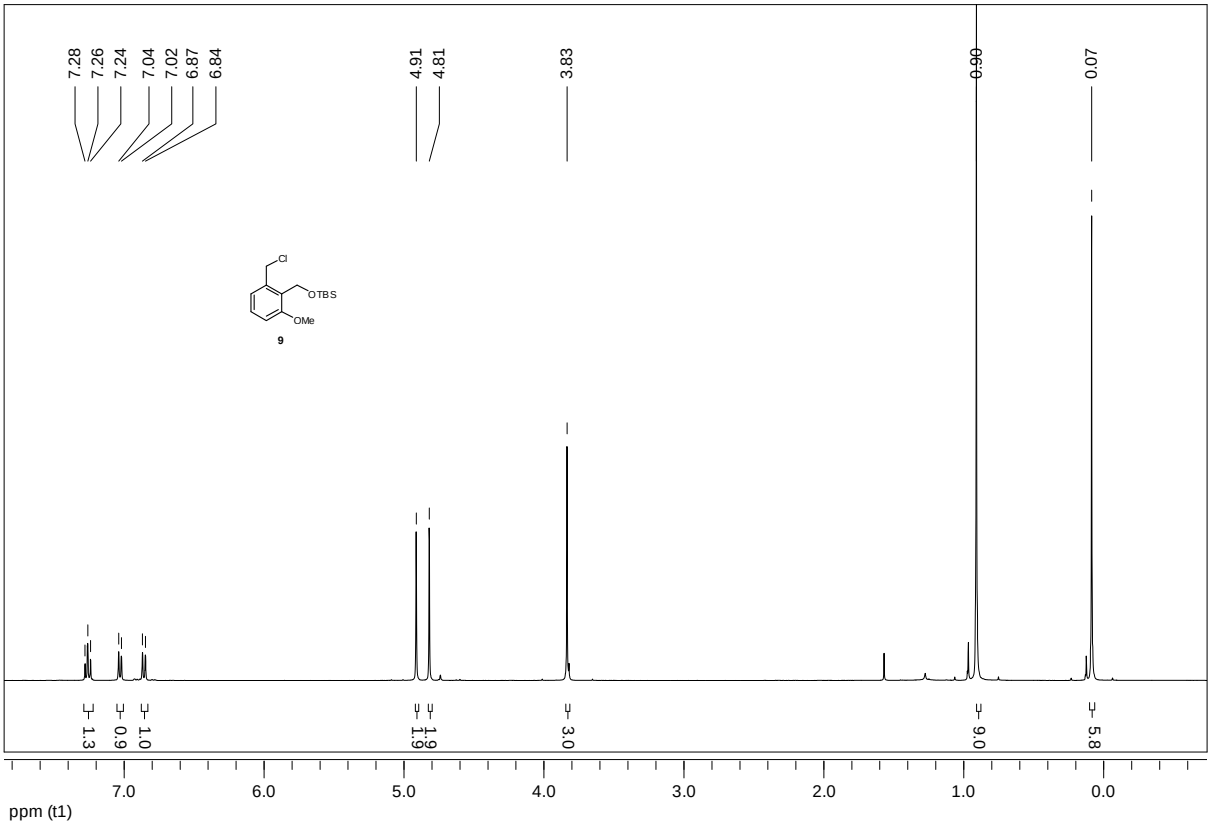

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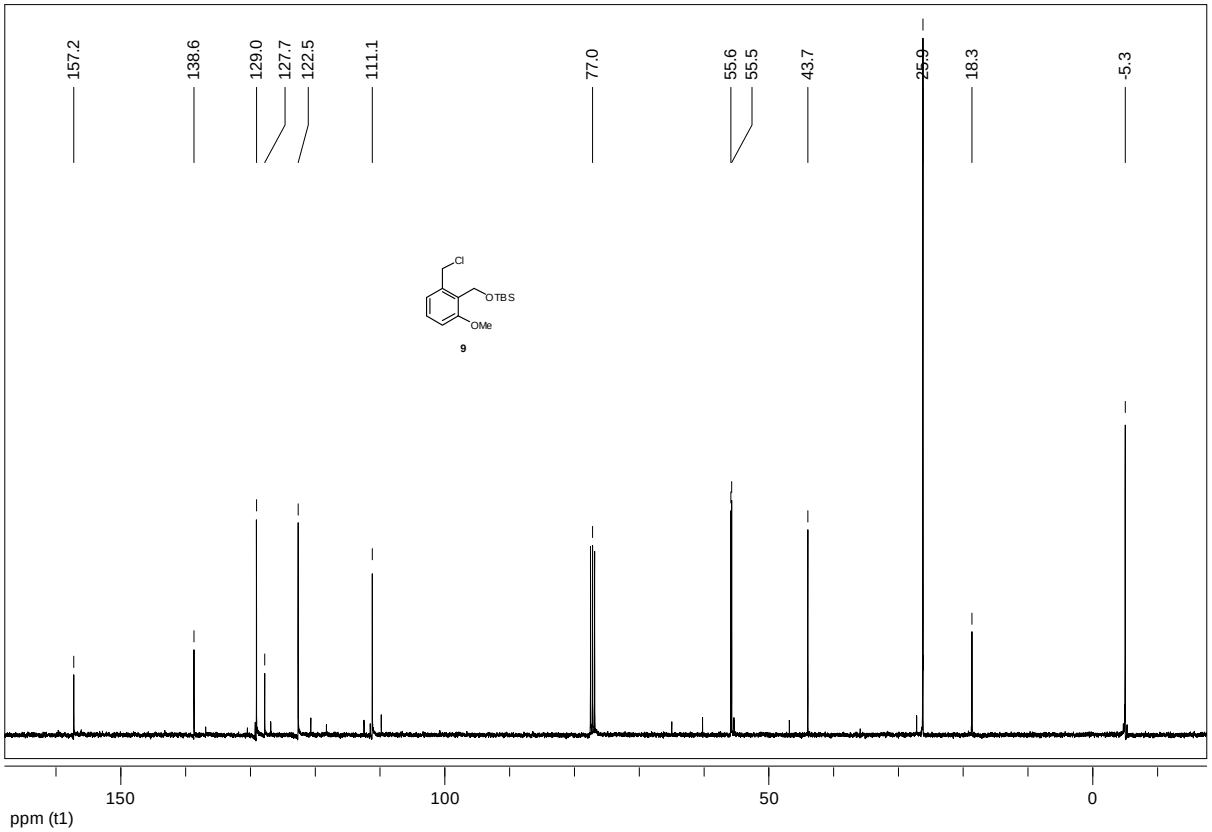

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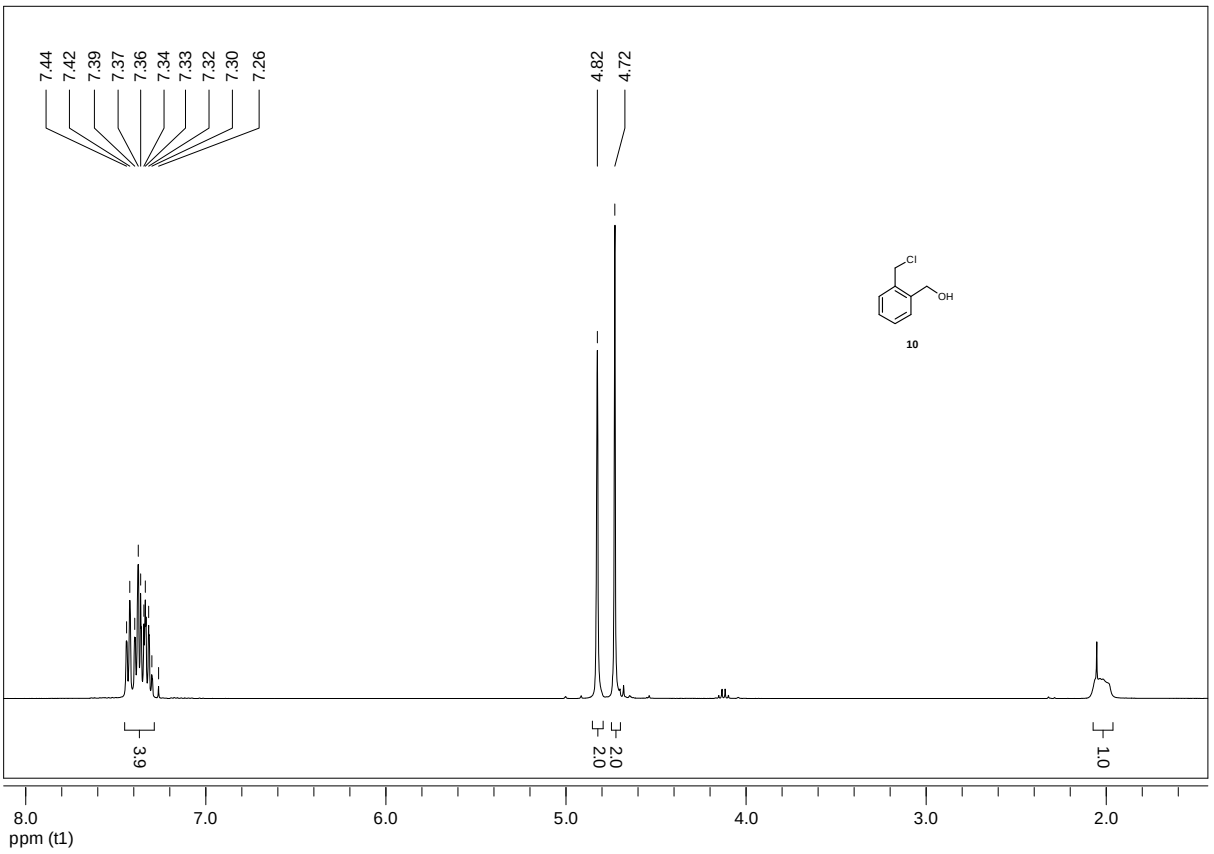

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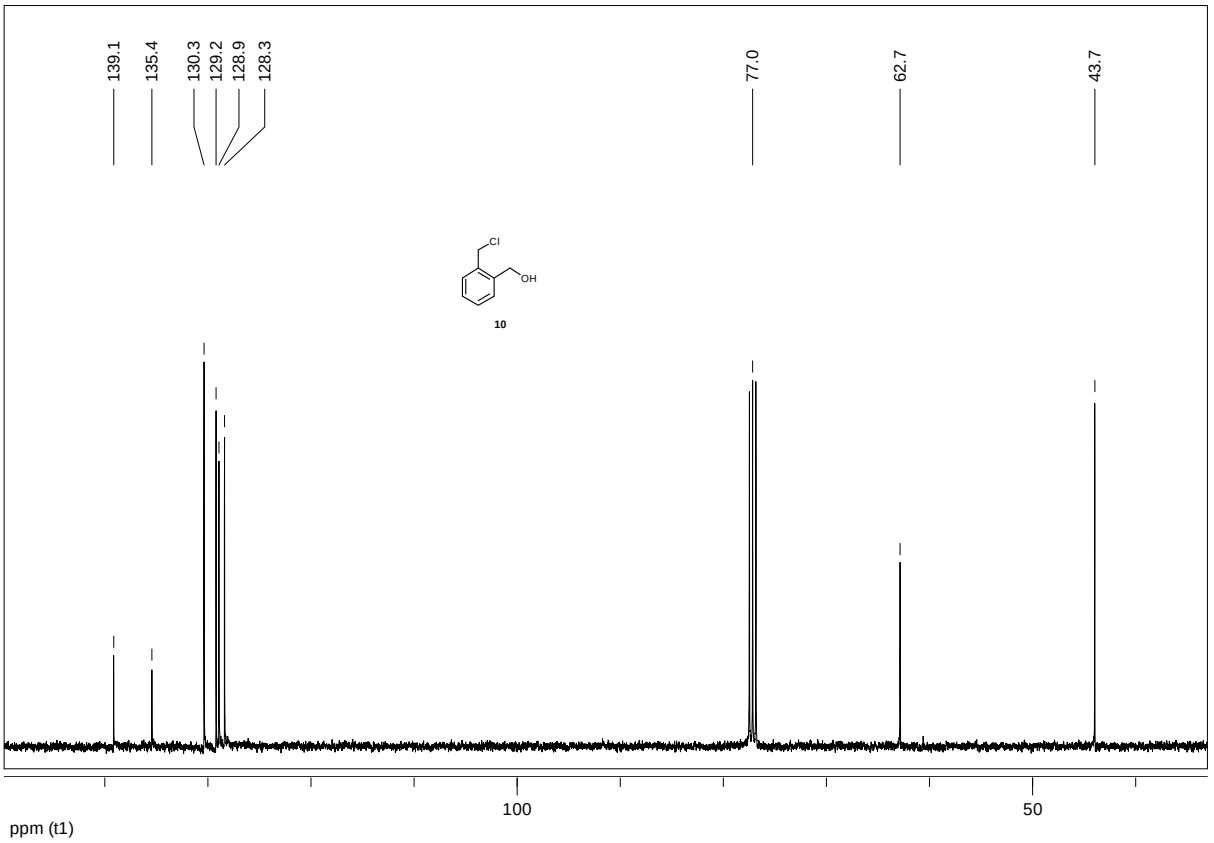

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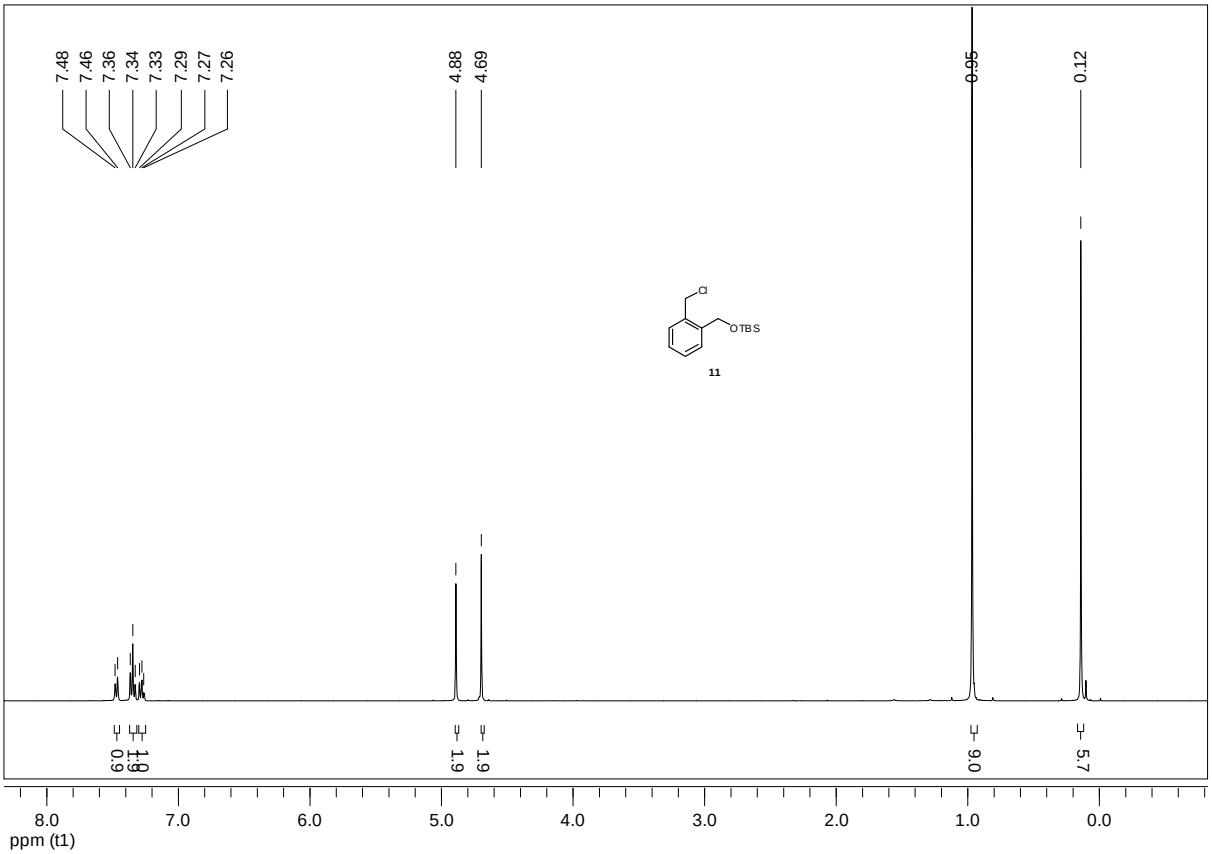

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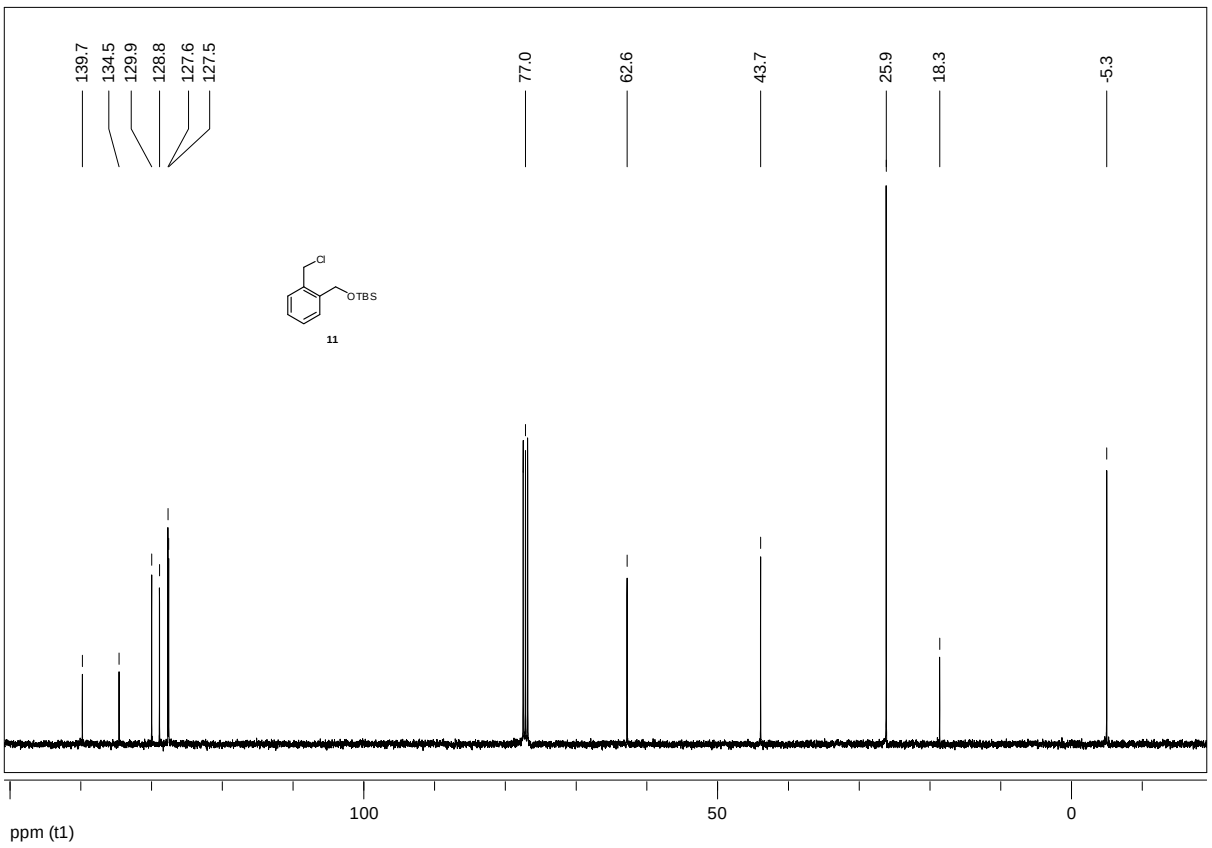

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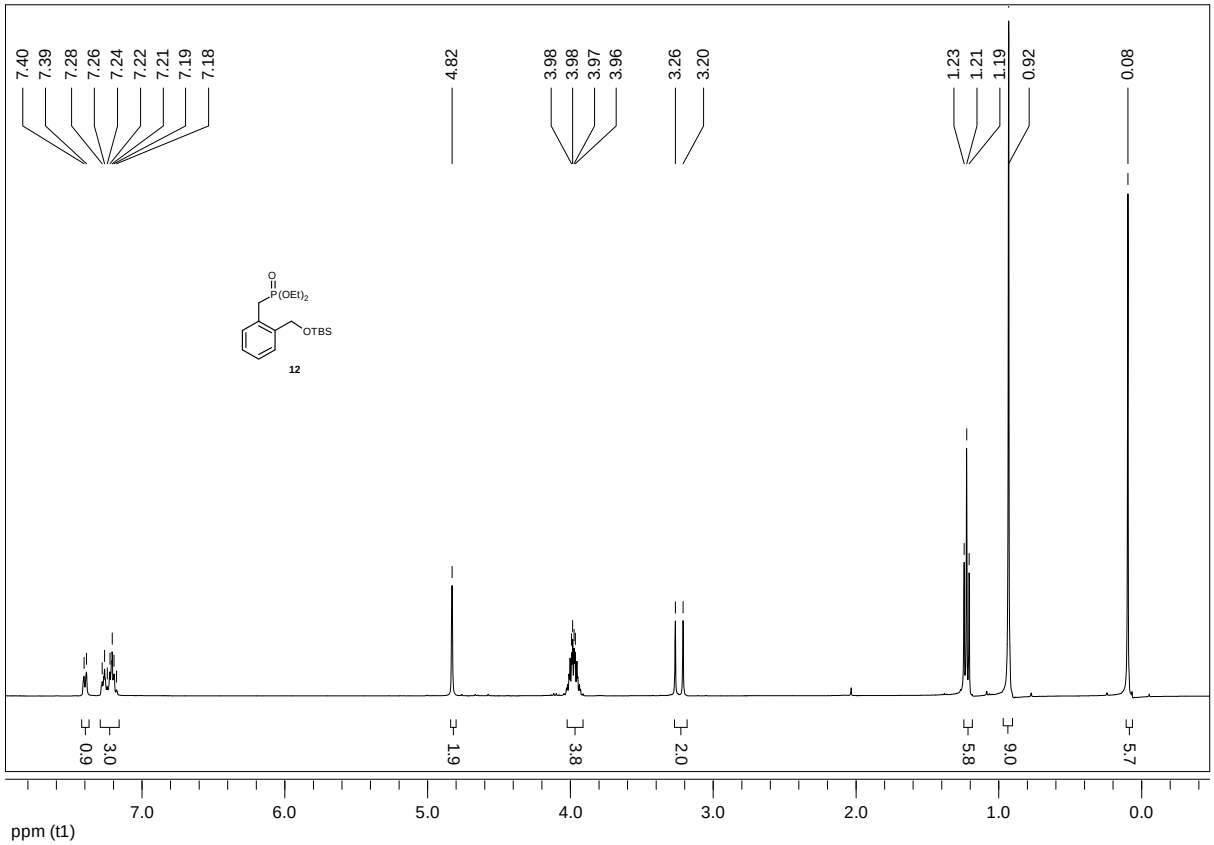

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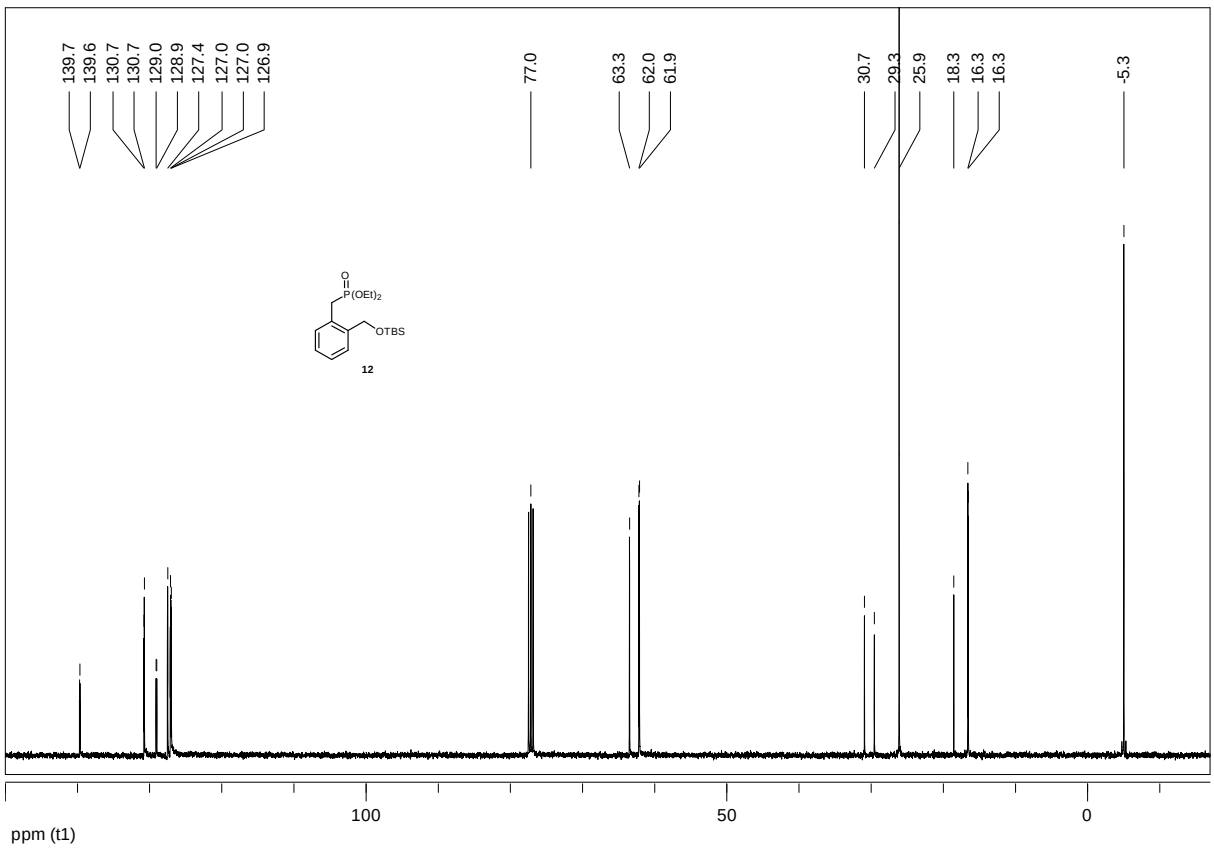

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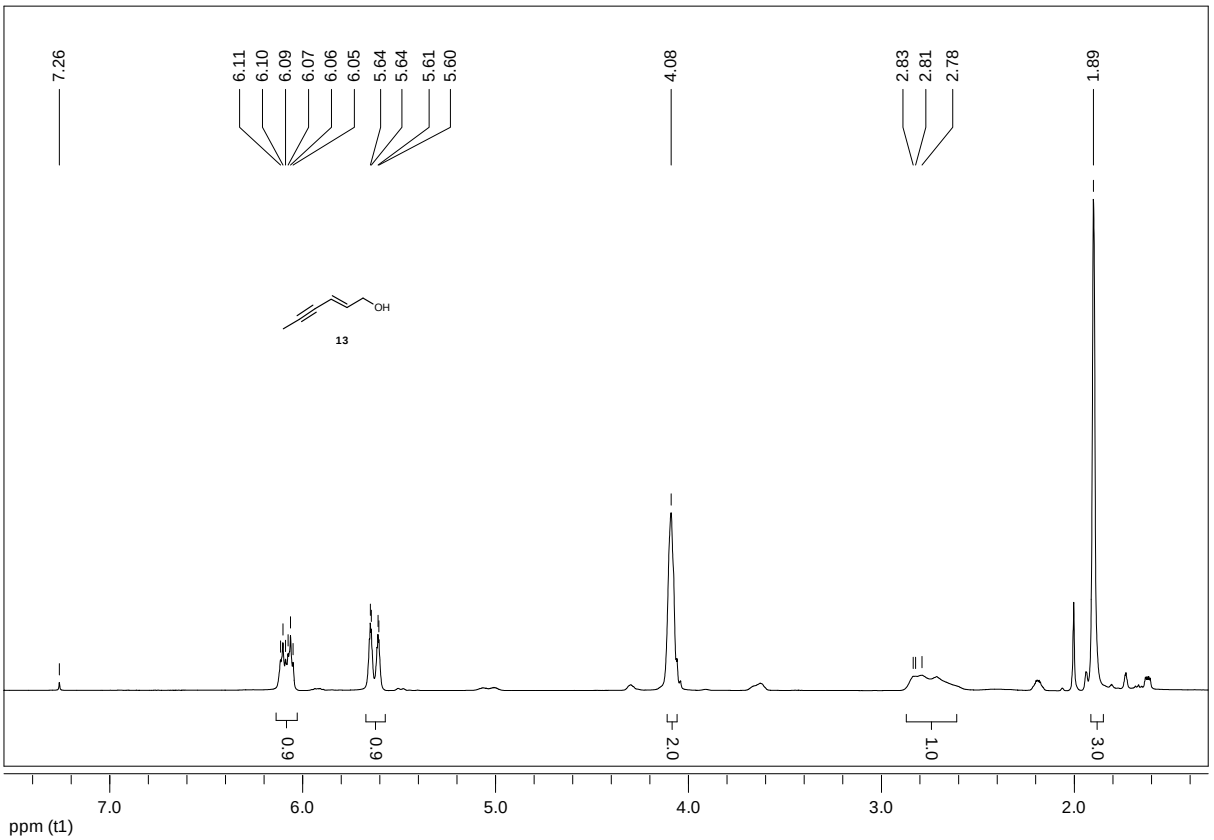

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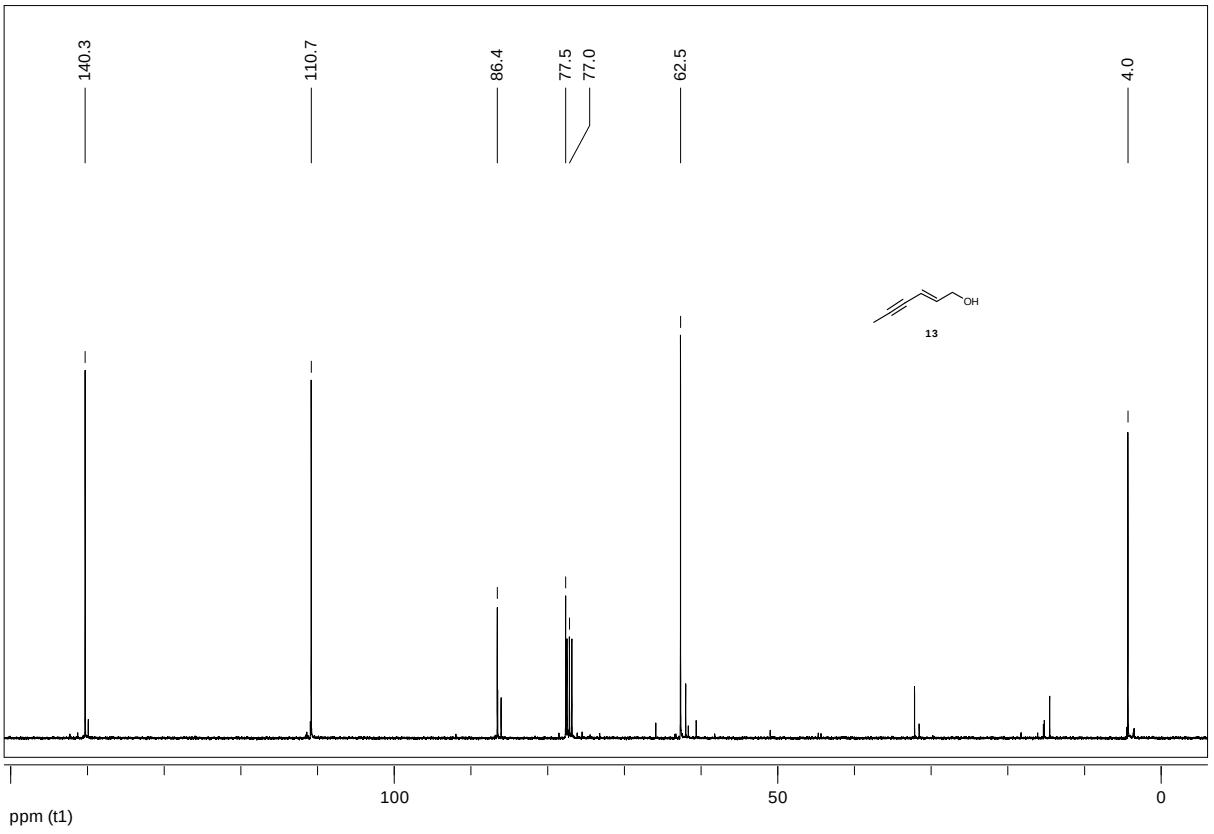

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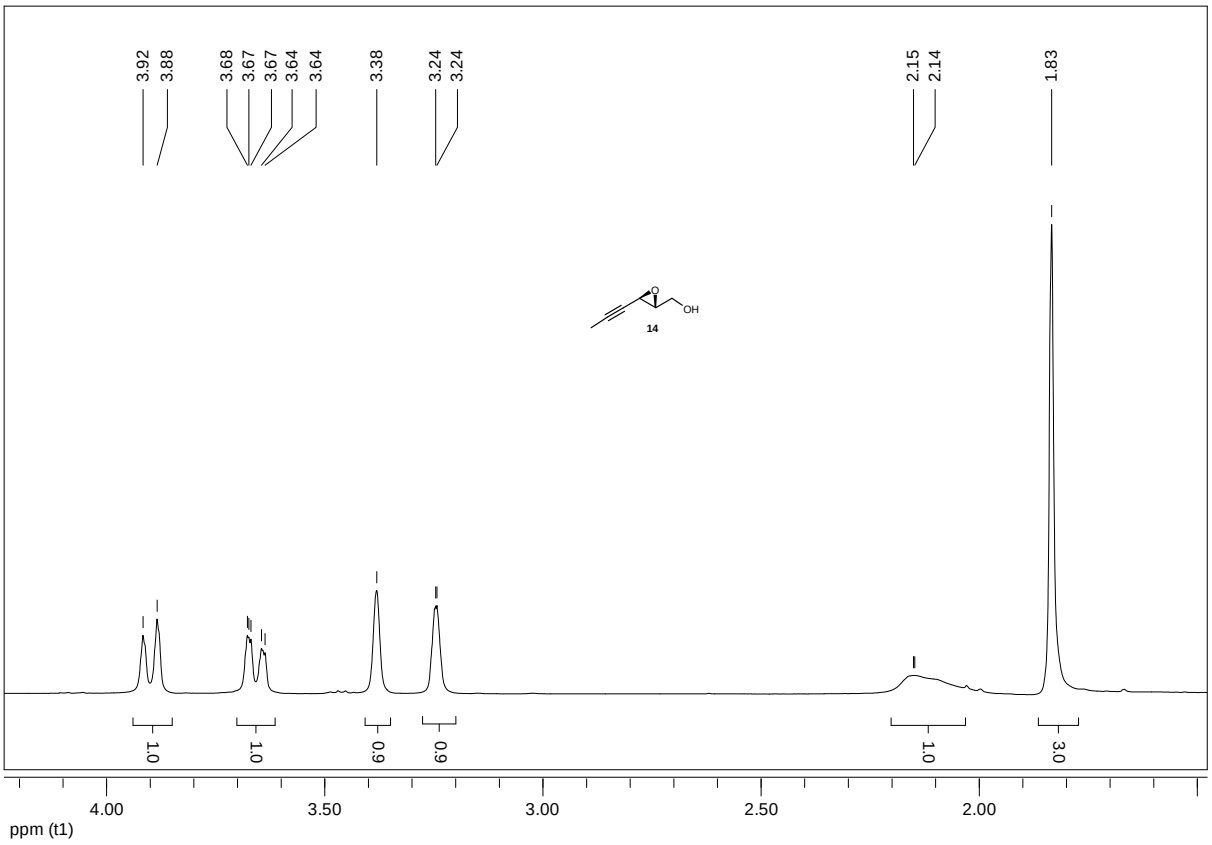

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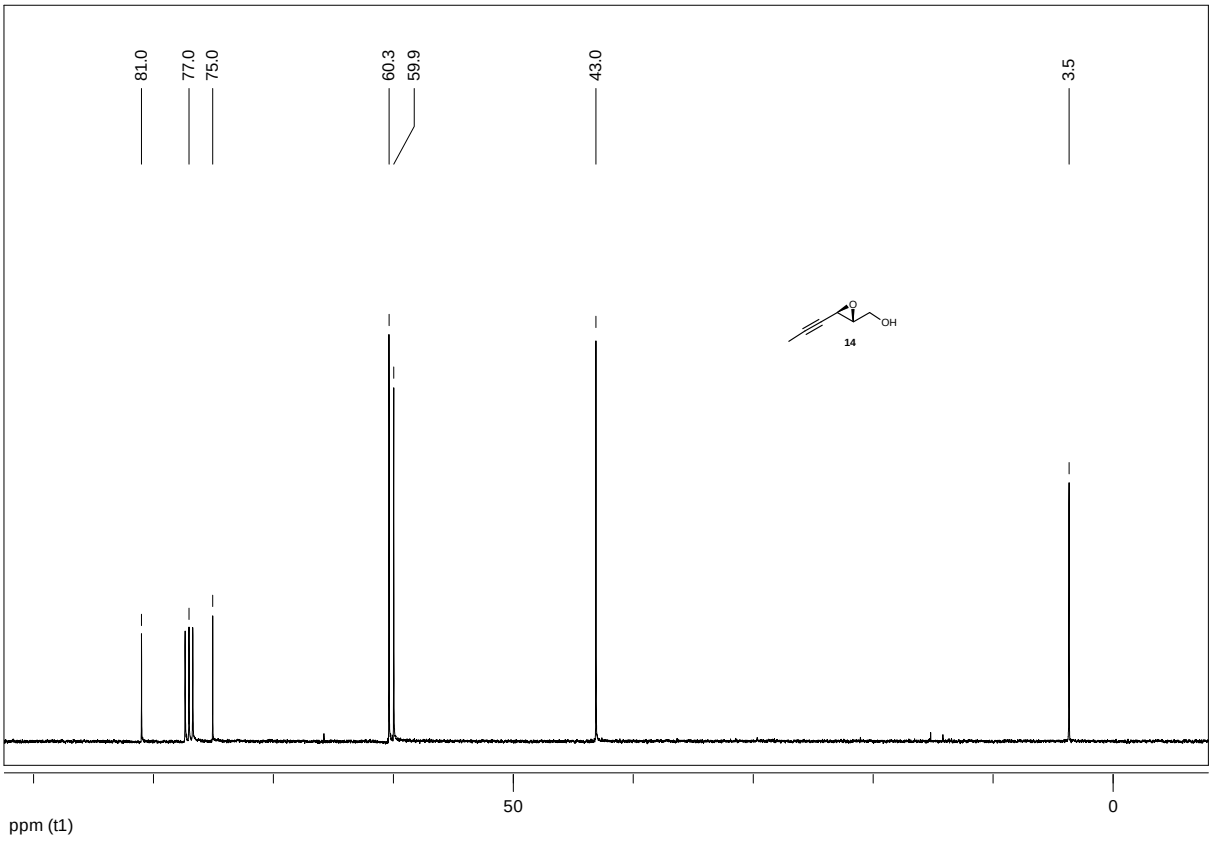

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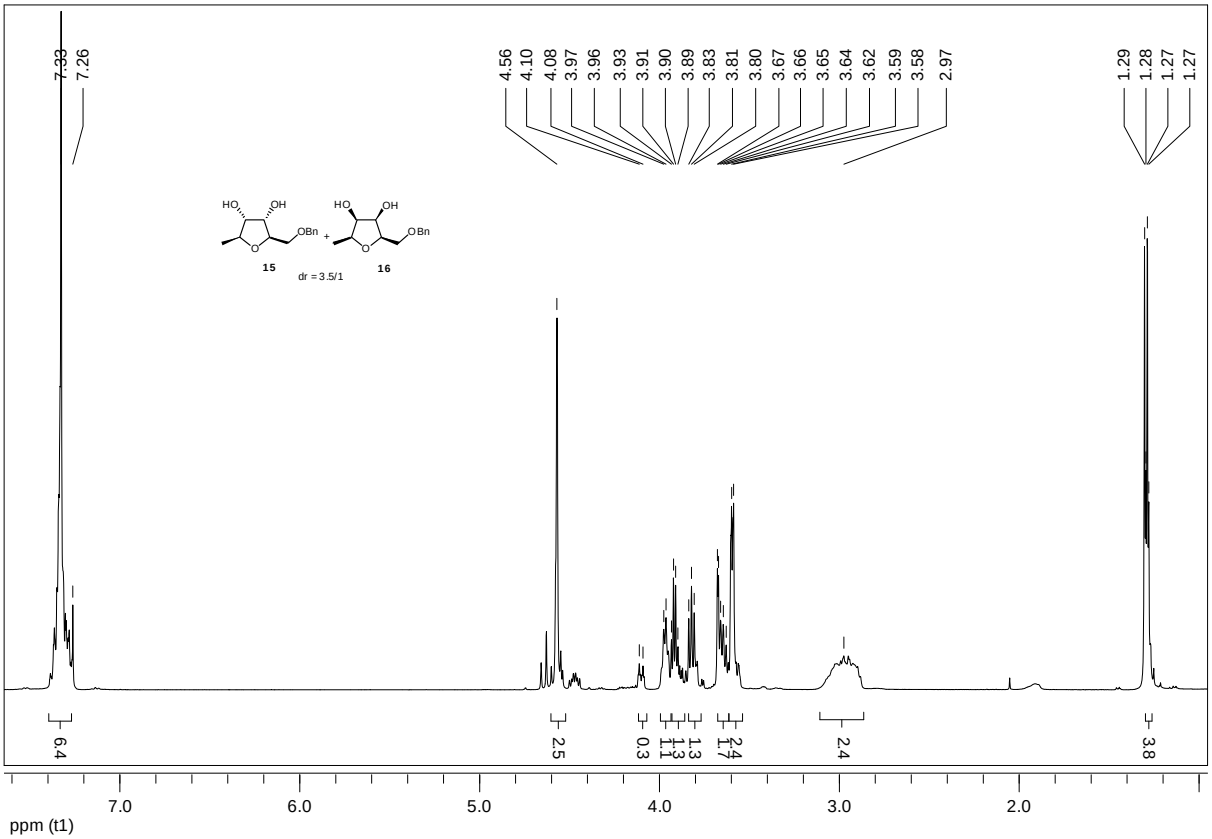

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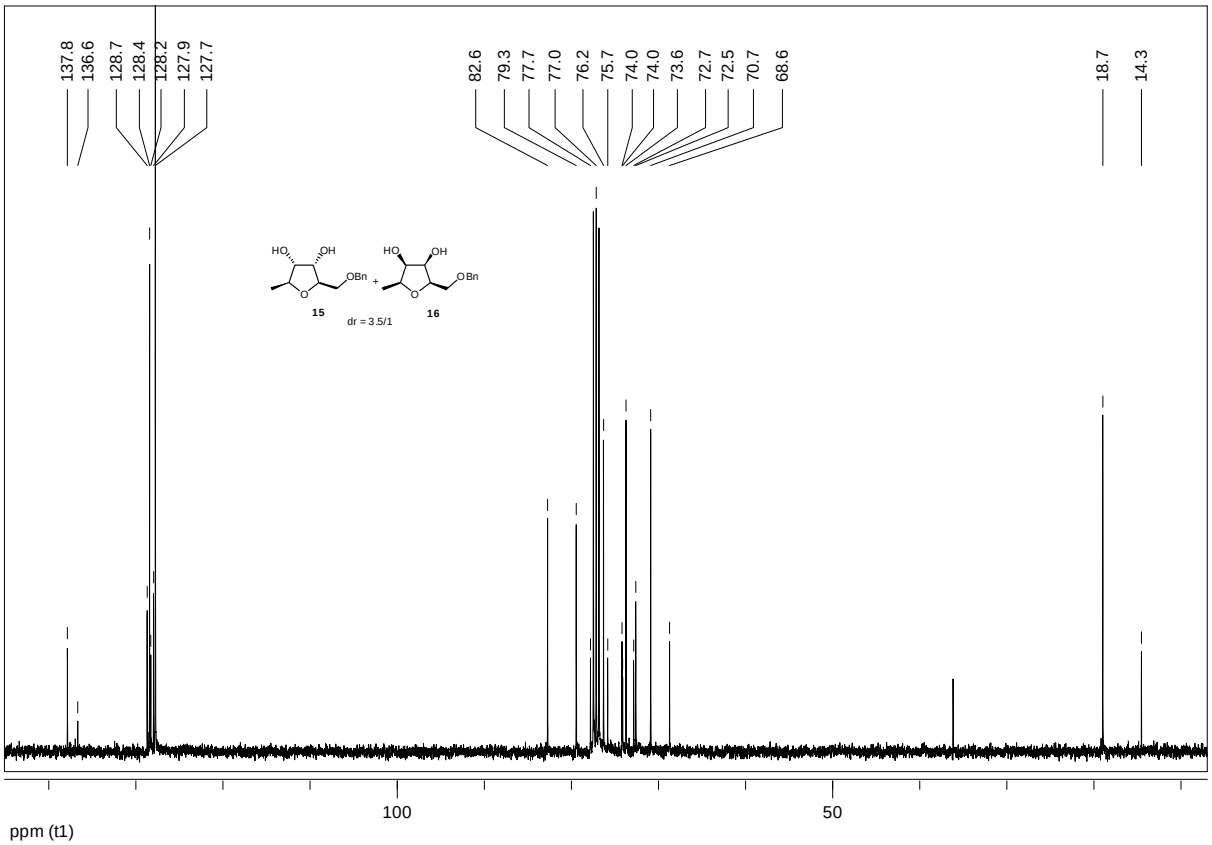

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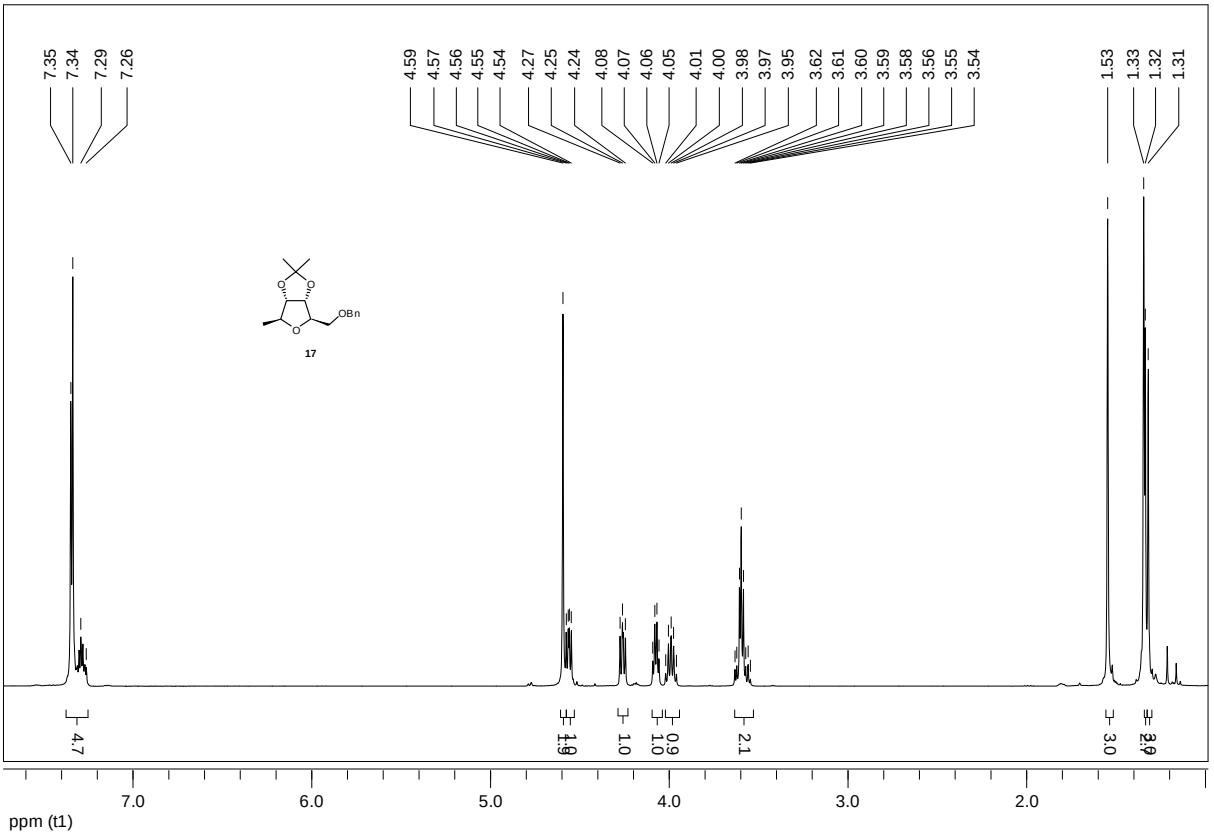

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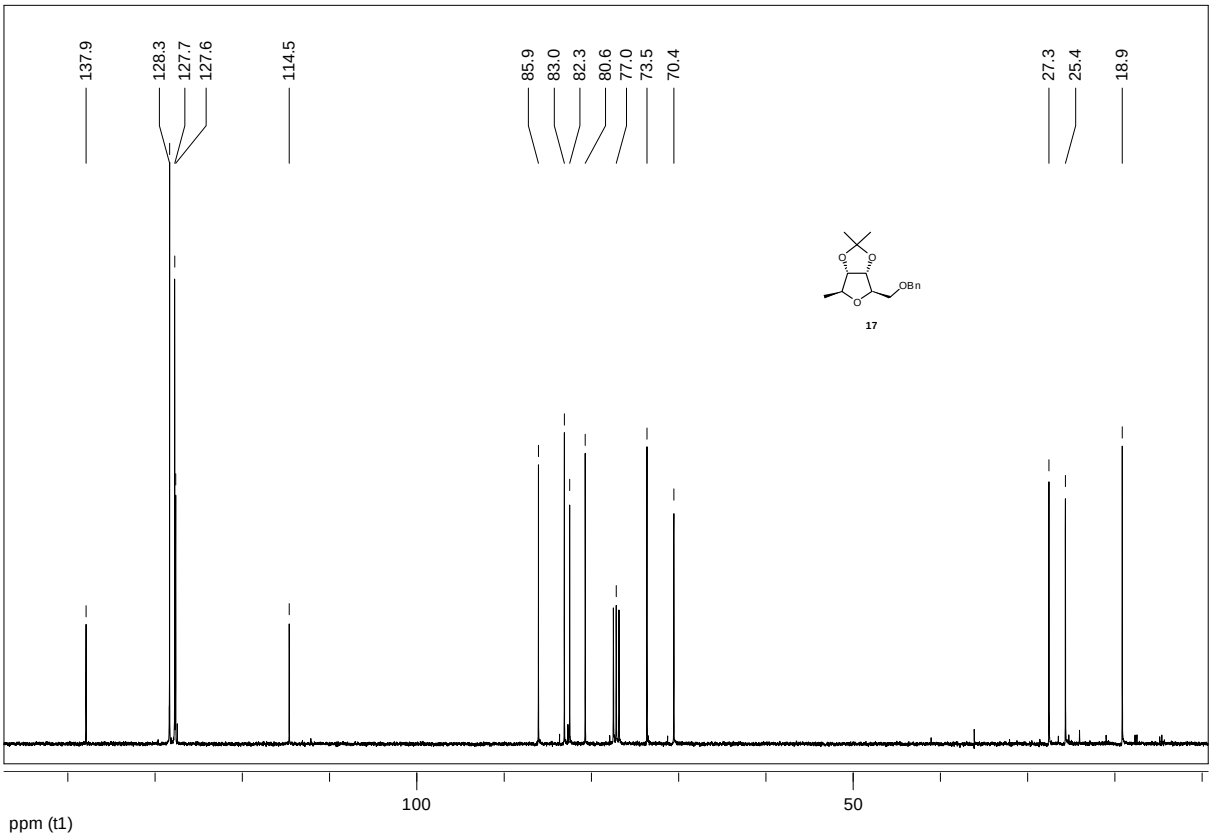
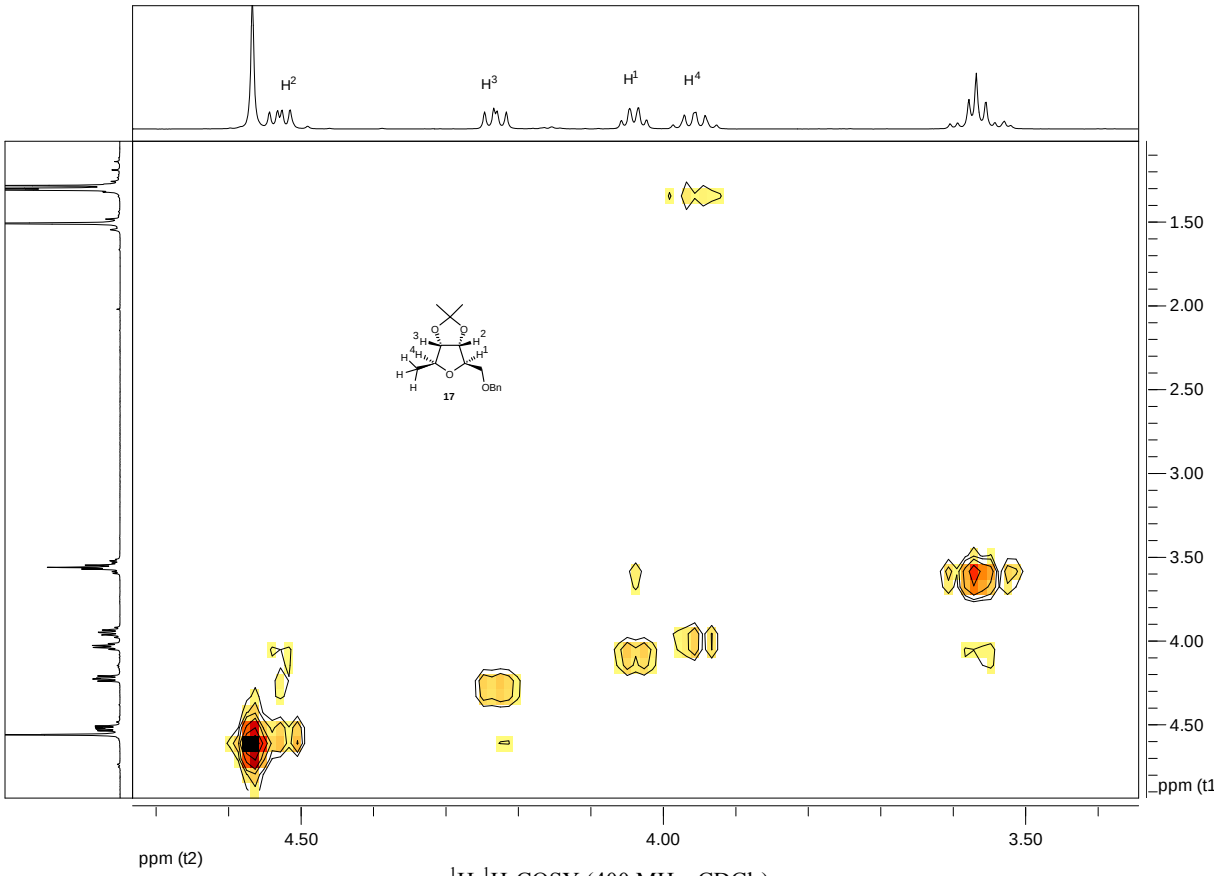
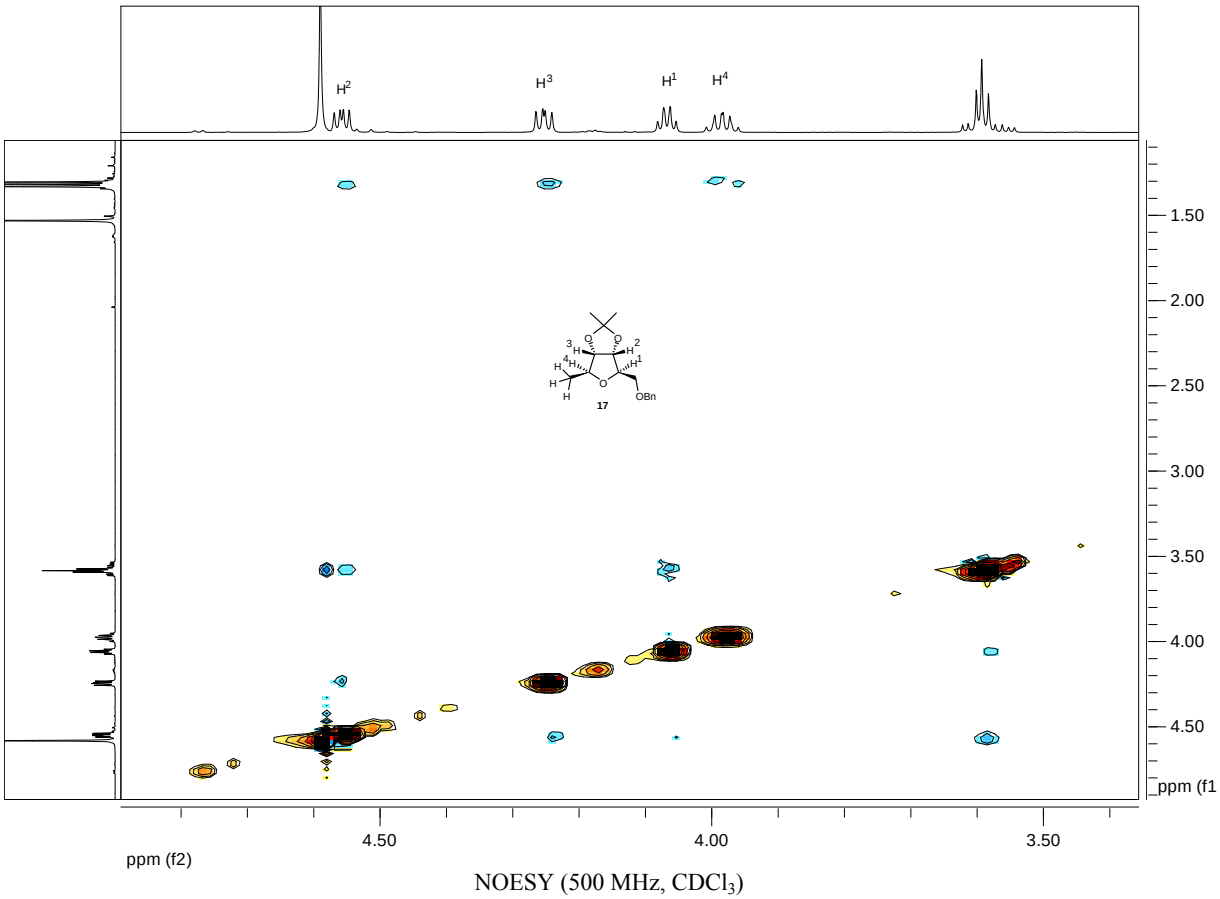


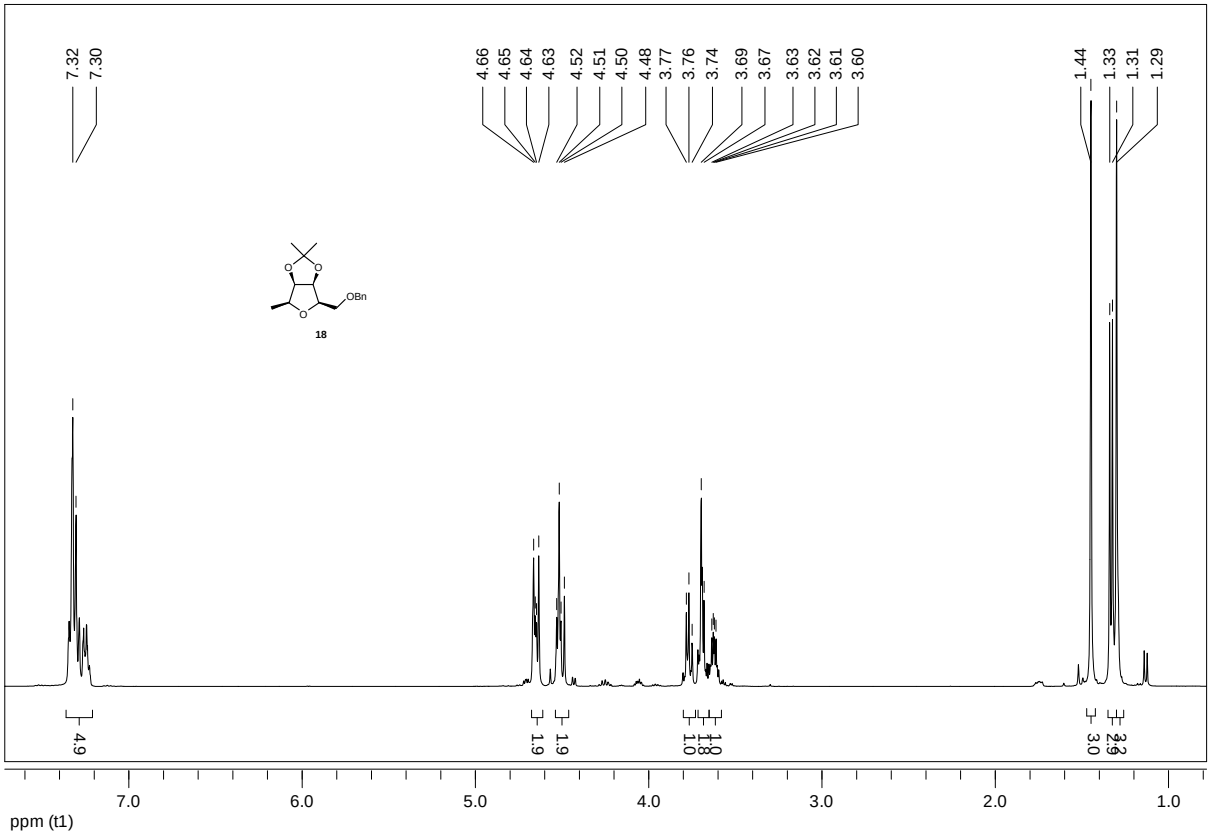
^{13}C-NMR (100 MHz, $CDCl_3$)



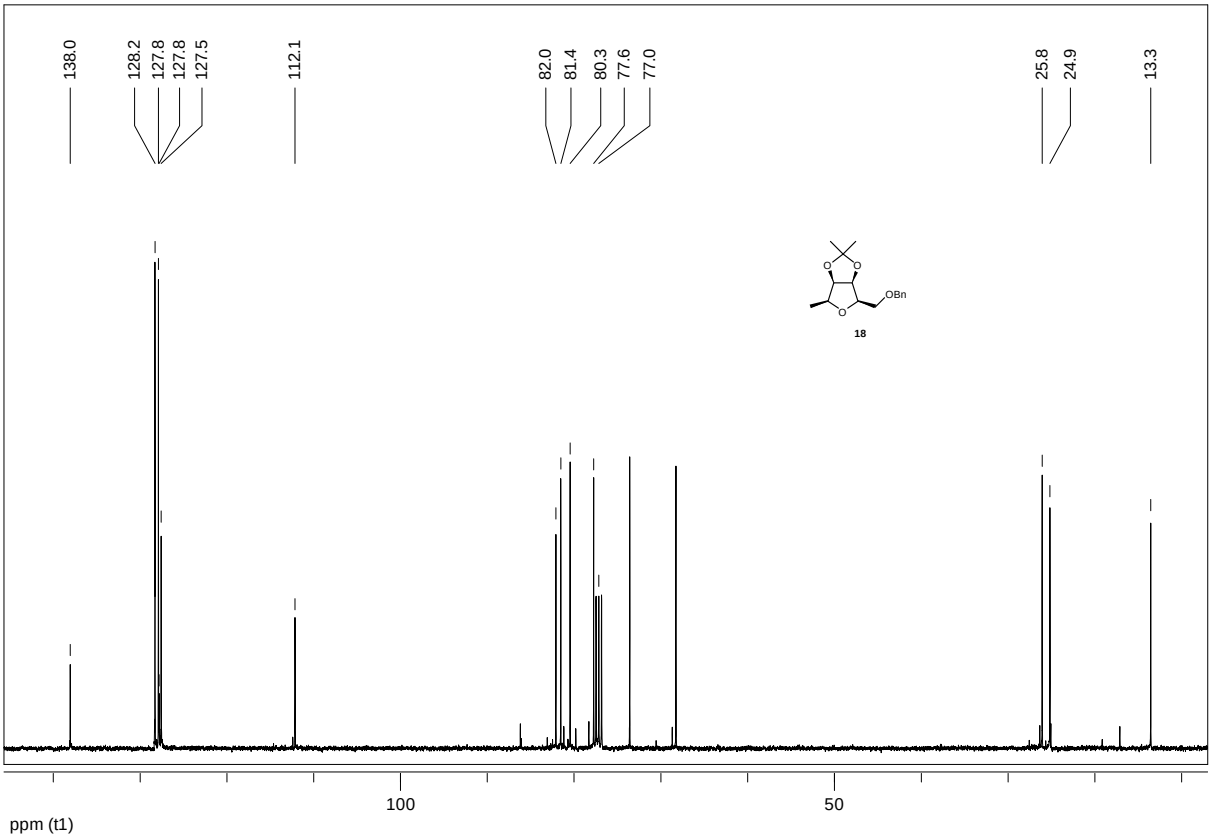
^{1}H-^{1}H-COSY (400 MHz, $CDCl_3$)



NOESY (500 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)



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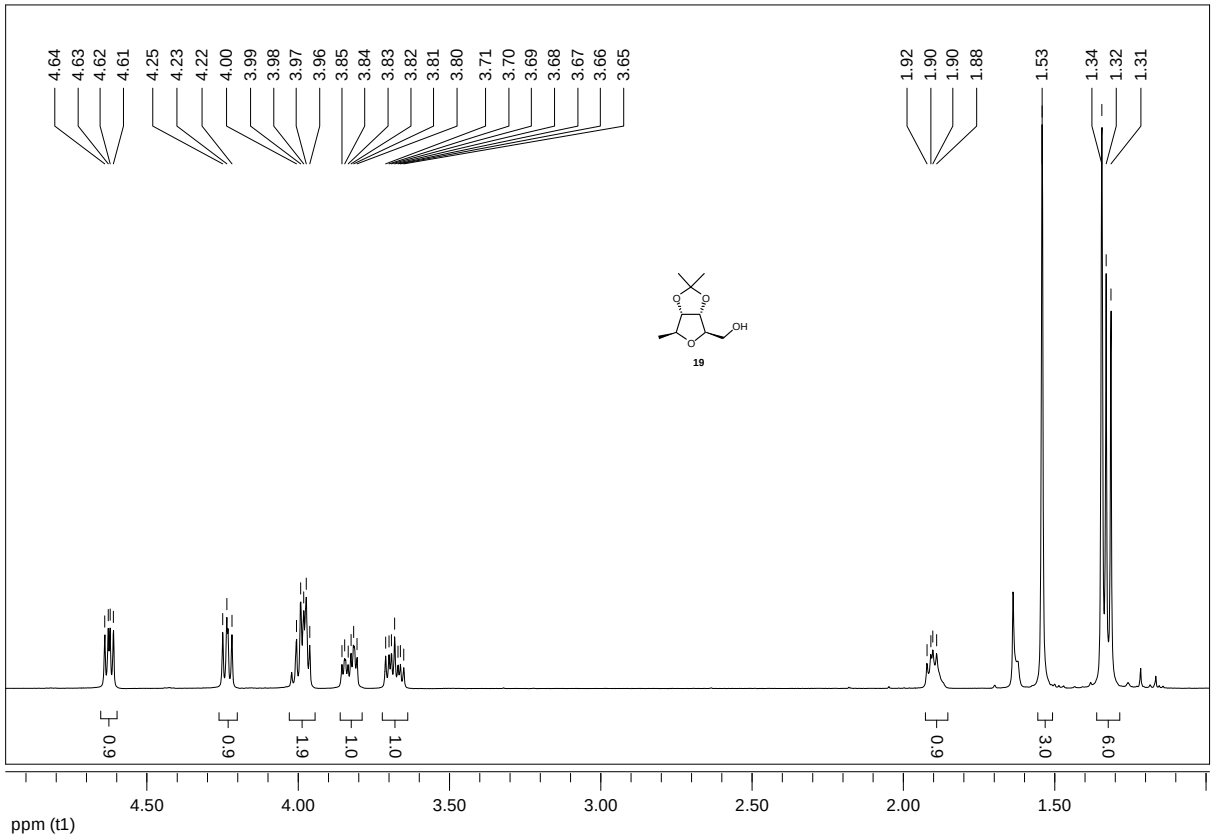

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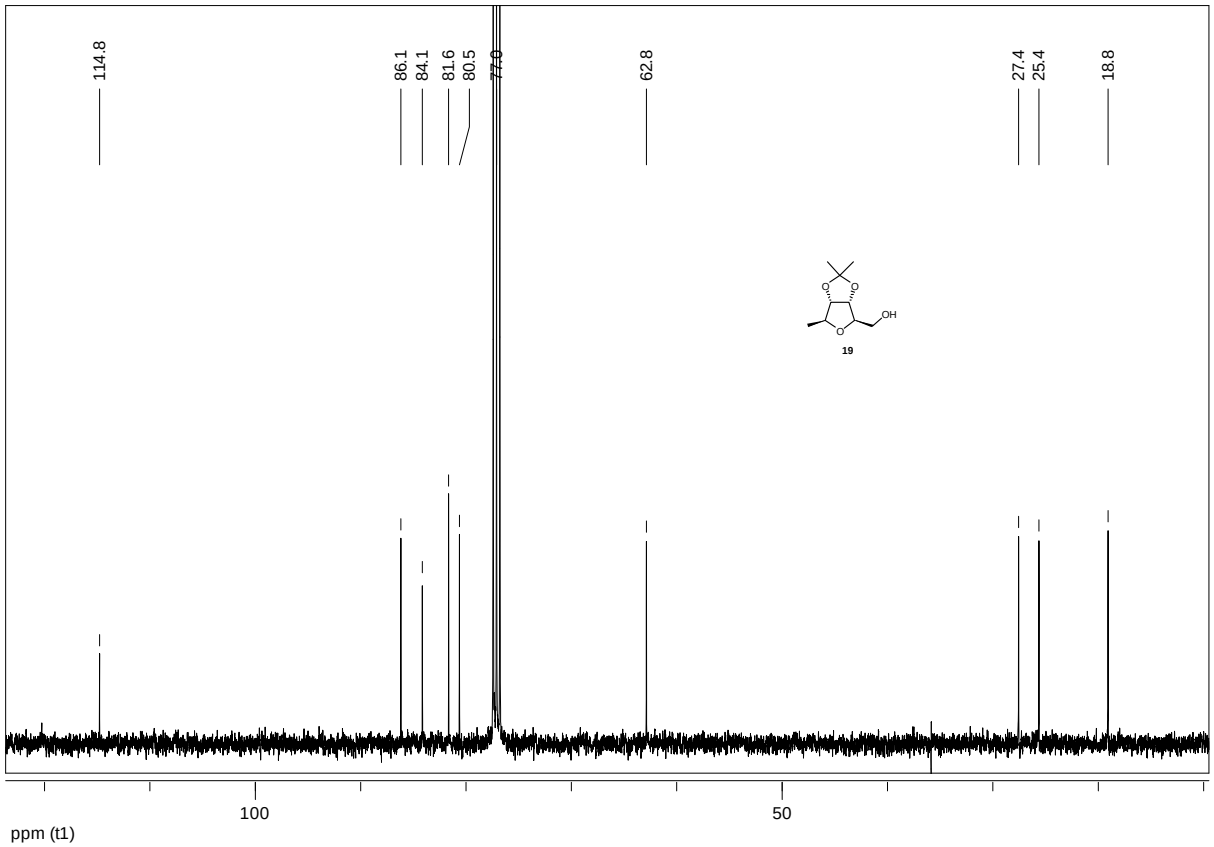

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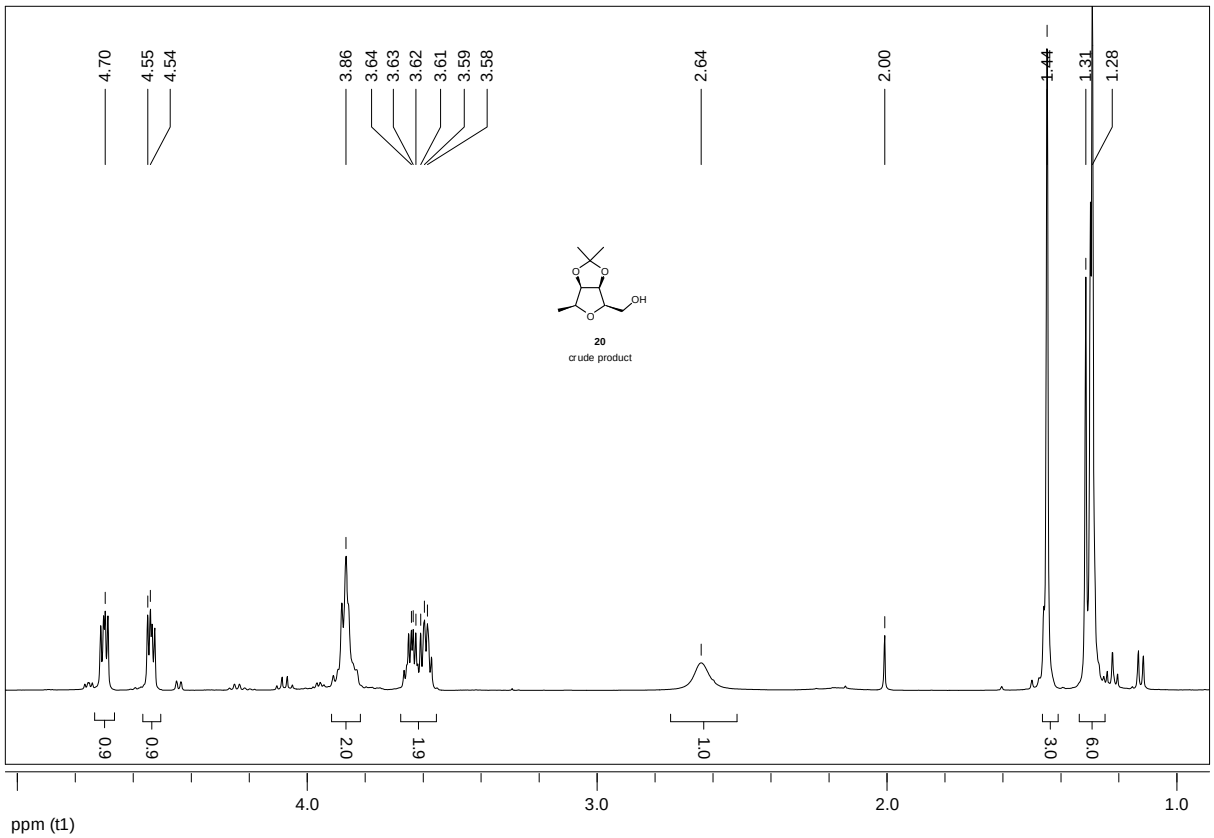

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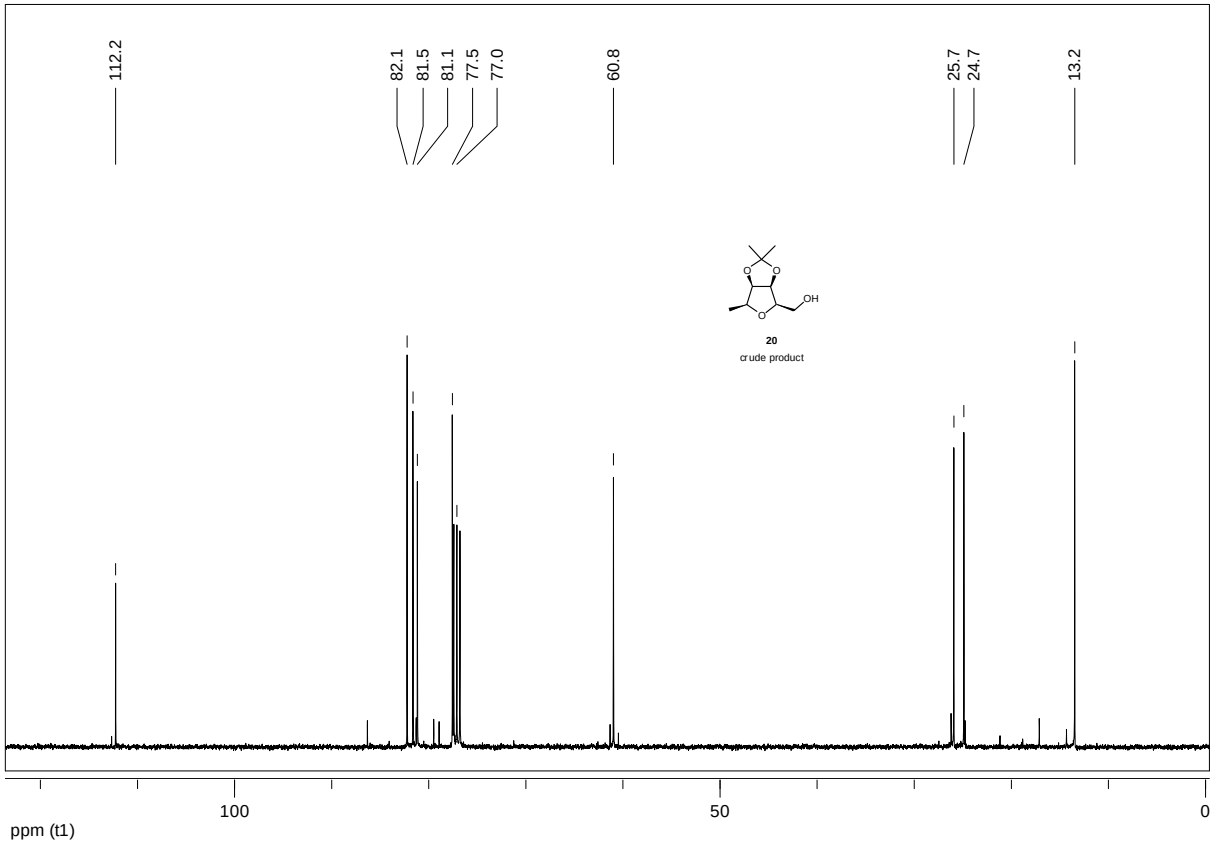
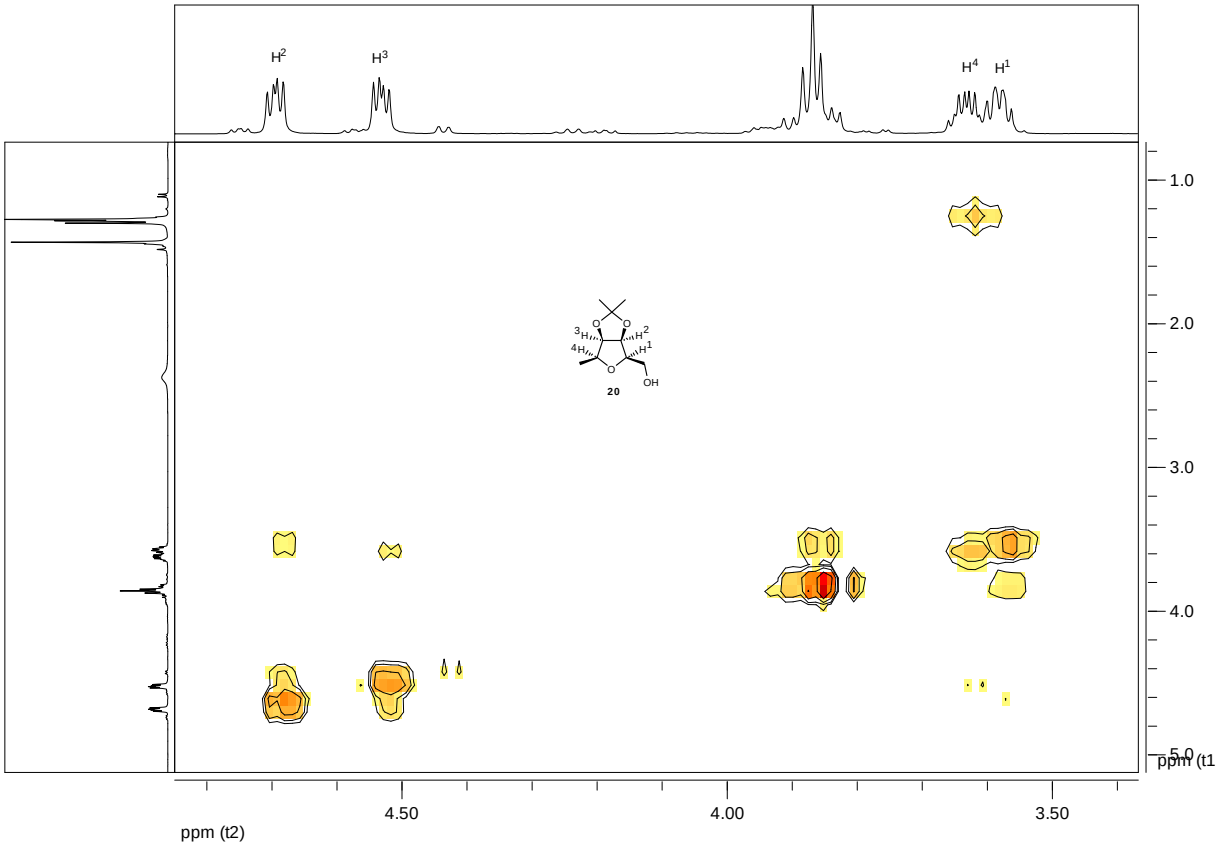
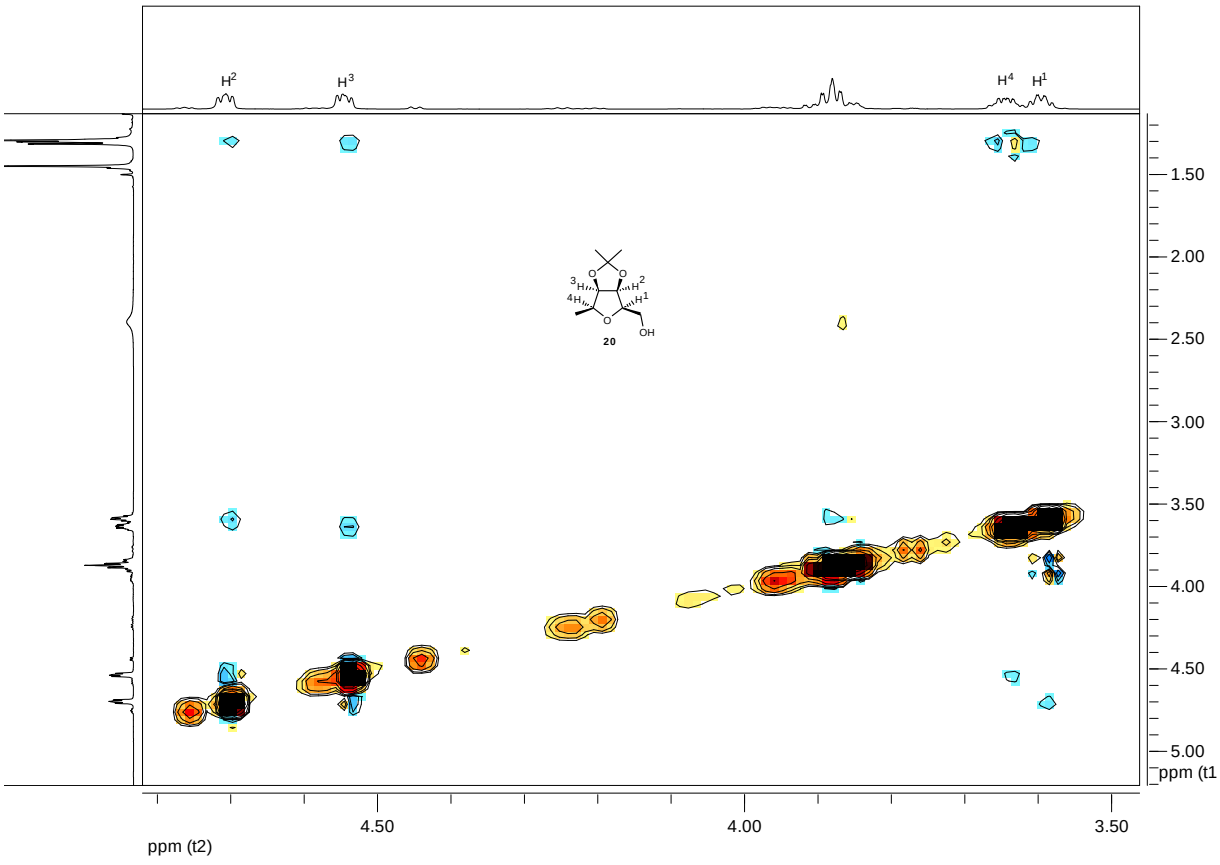


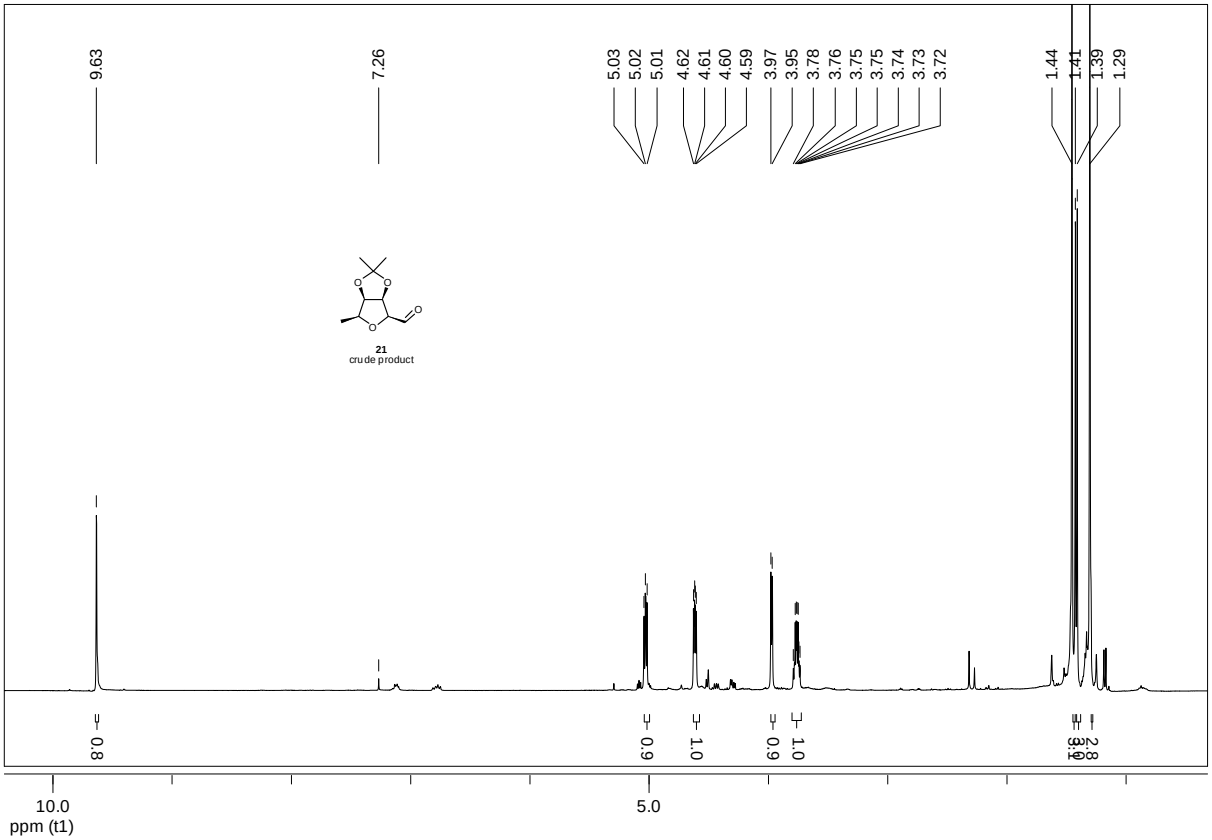
^{13}C-NMR (100 MHz, $CDCl_3$)



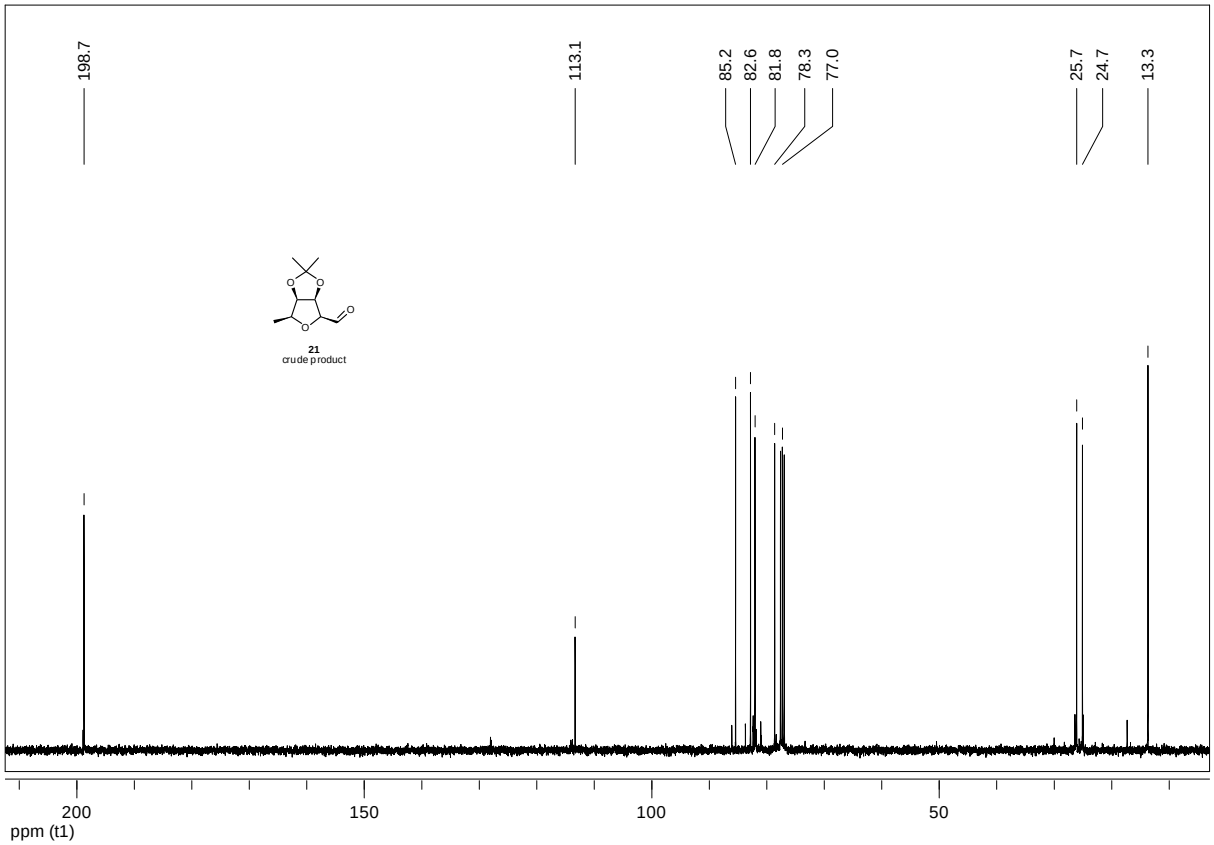
^{1}H-^{1}H-COSY (400 MHz, $CDCl_3$)



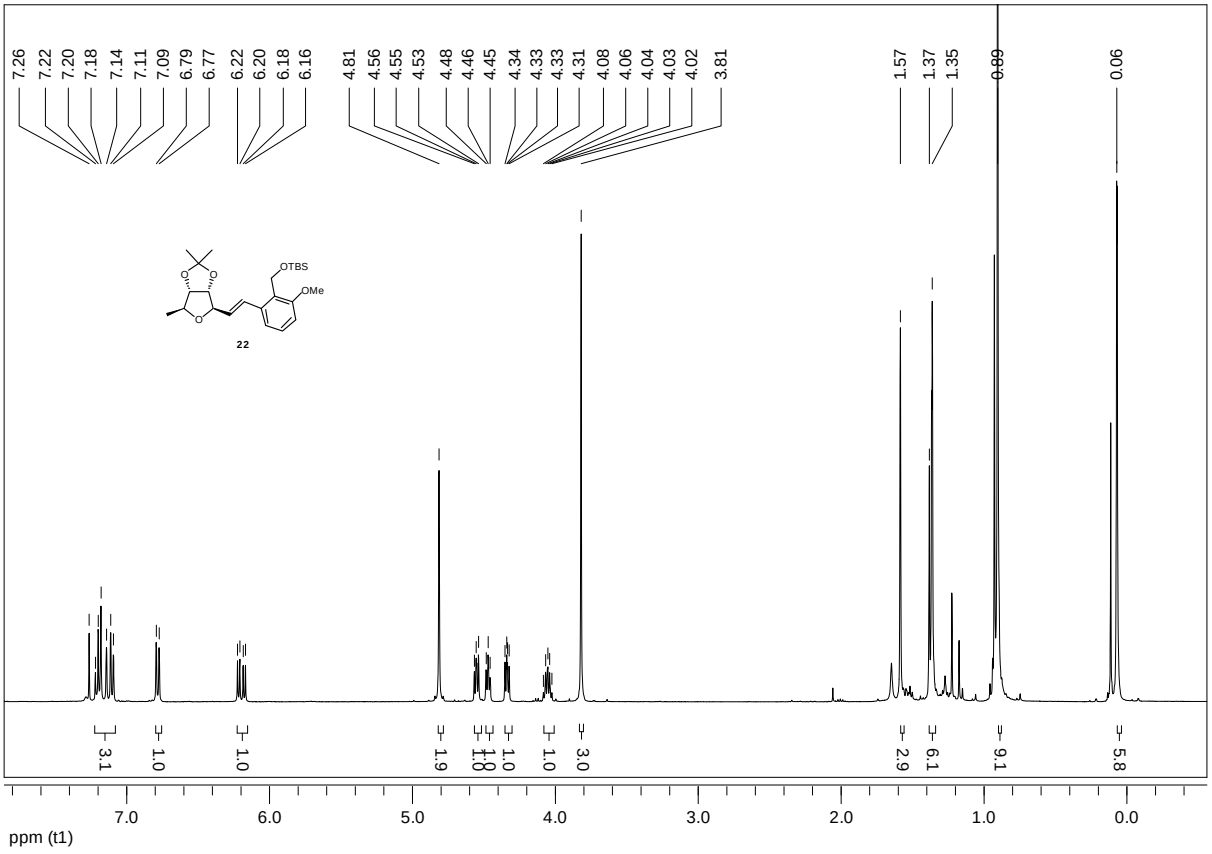
NOESY (500 MHz, $CDCl_3$)



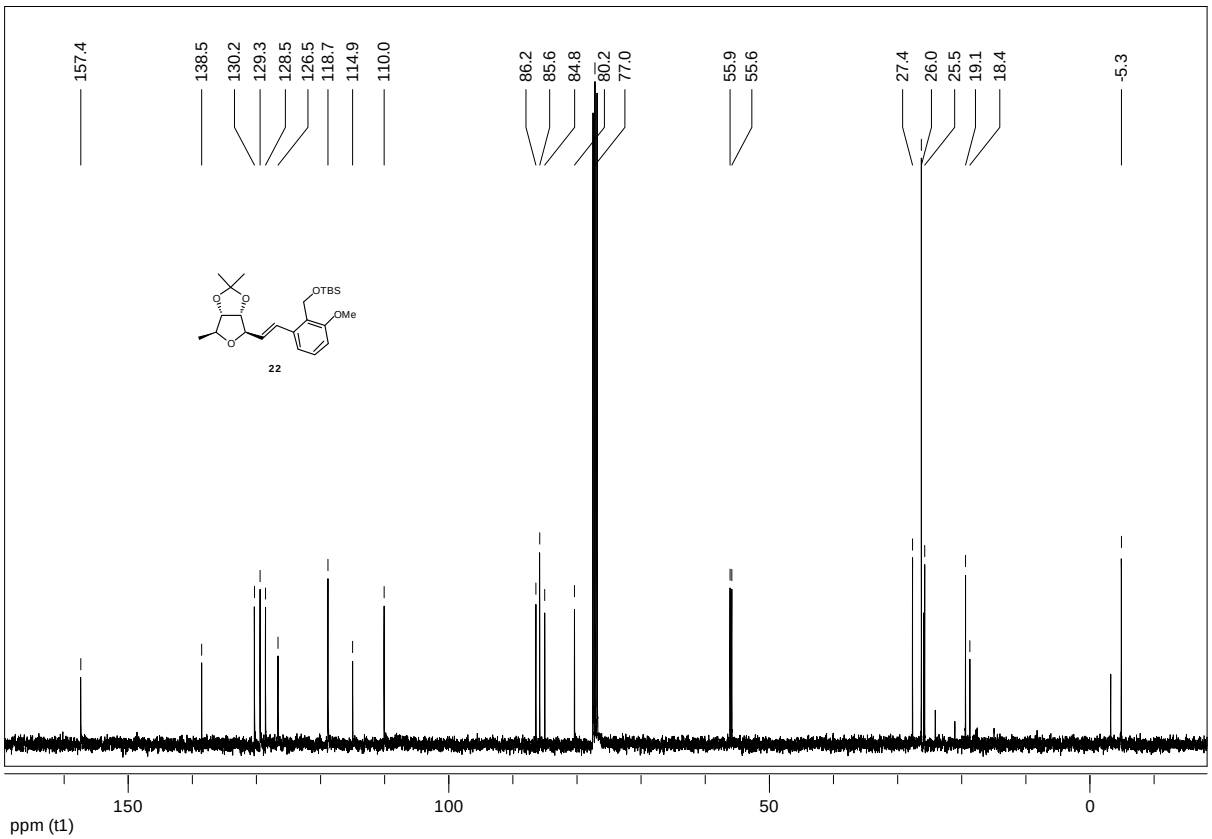
^{1}H-NMR (400 MHz, $CDCl_3$)



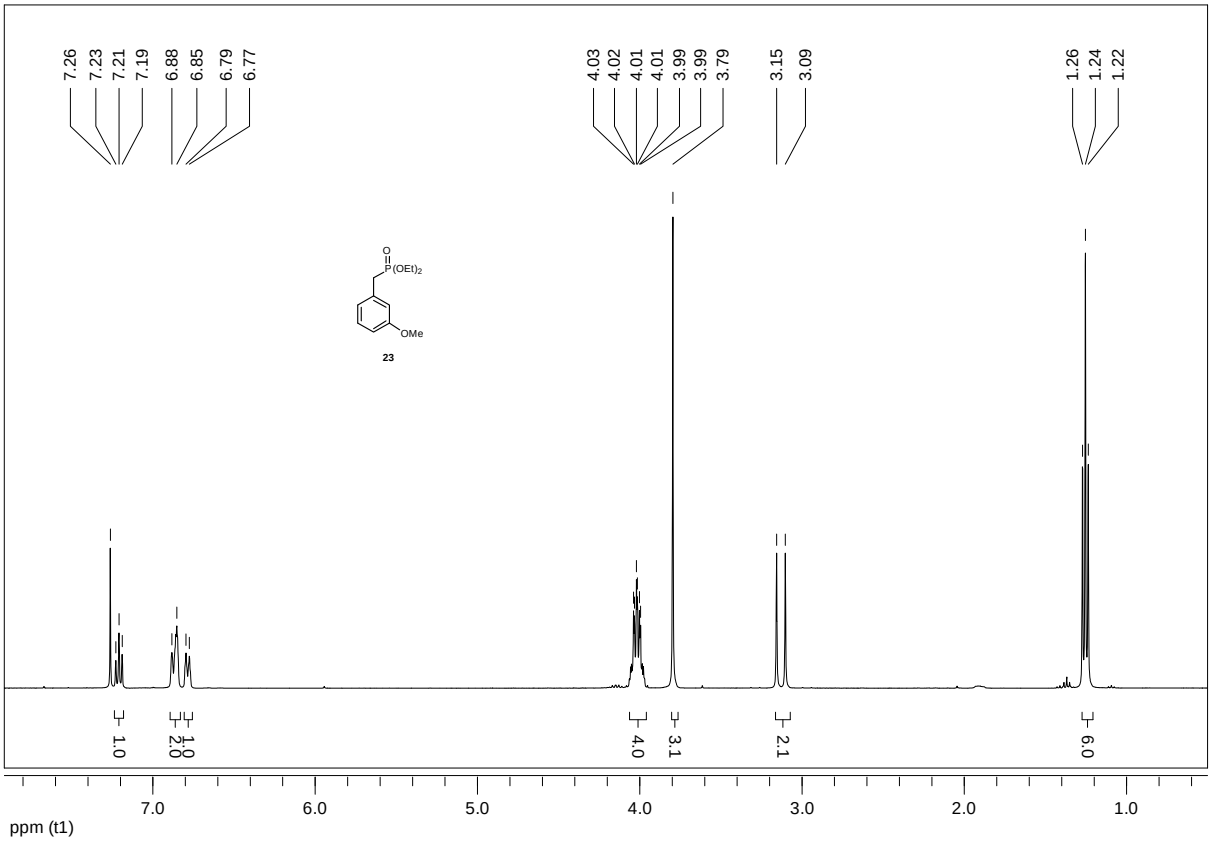
^{13}C-NMR (100 MHz, $CDCl_3$)



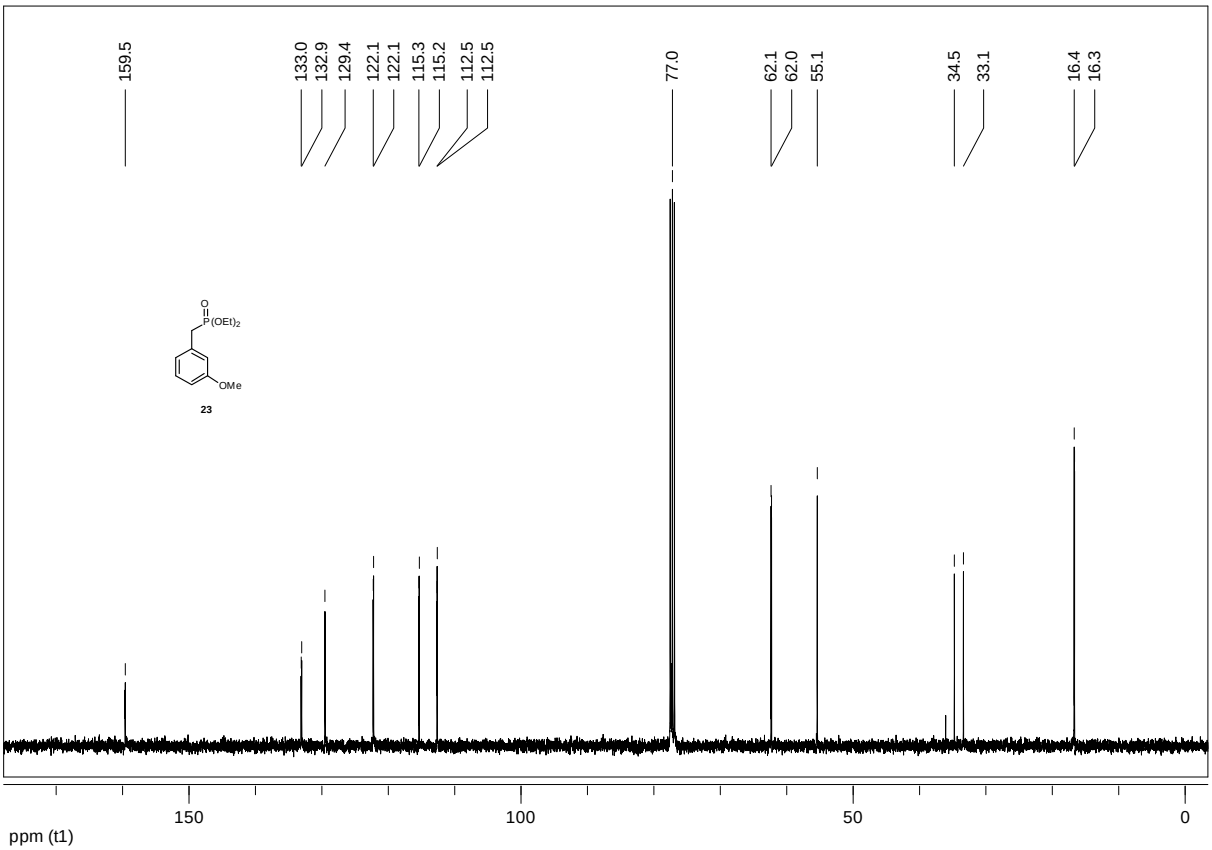
^{1}H-NMR (400 MHz, $CDCl_3$)



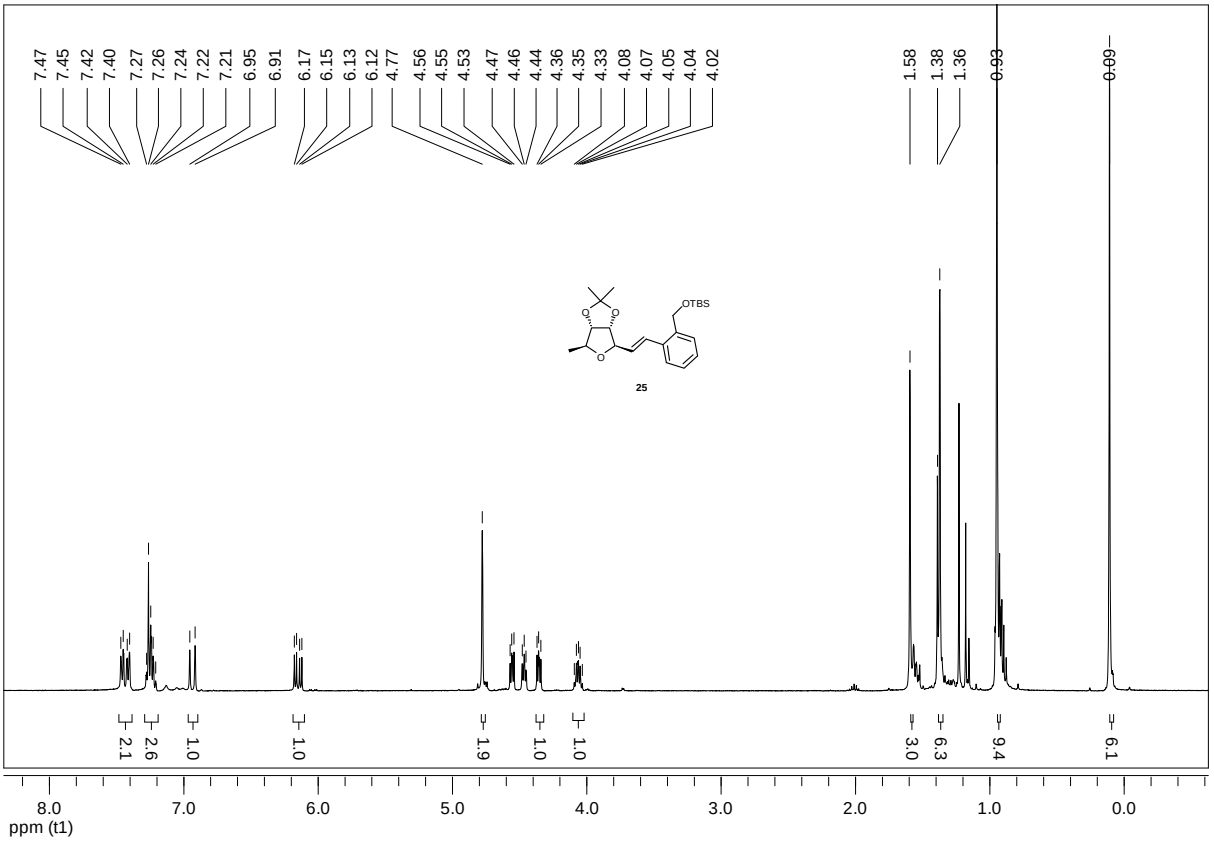
^{13}C-NMR (100 MHz, $CDCl_3$)



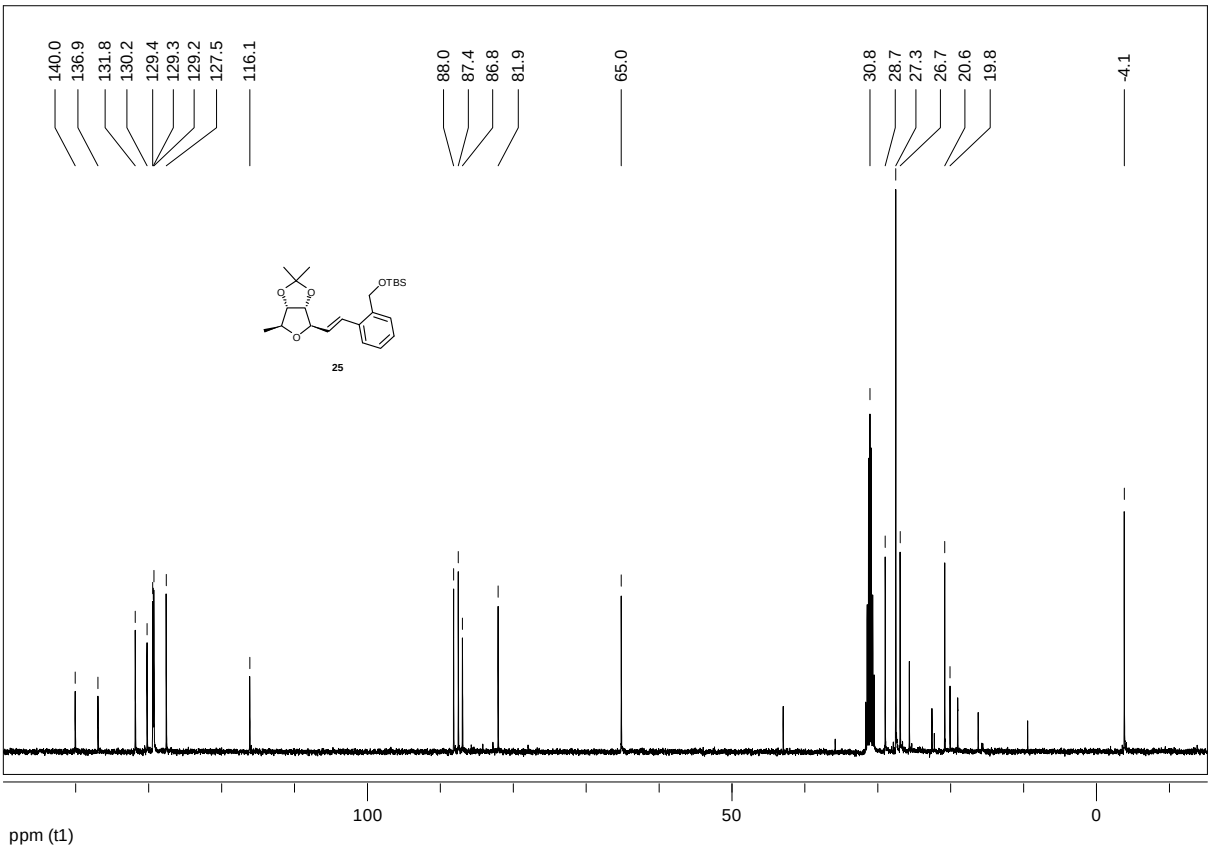
^{1}H-NMR (400 MHz, $CDCl_3$)



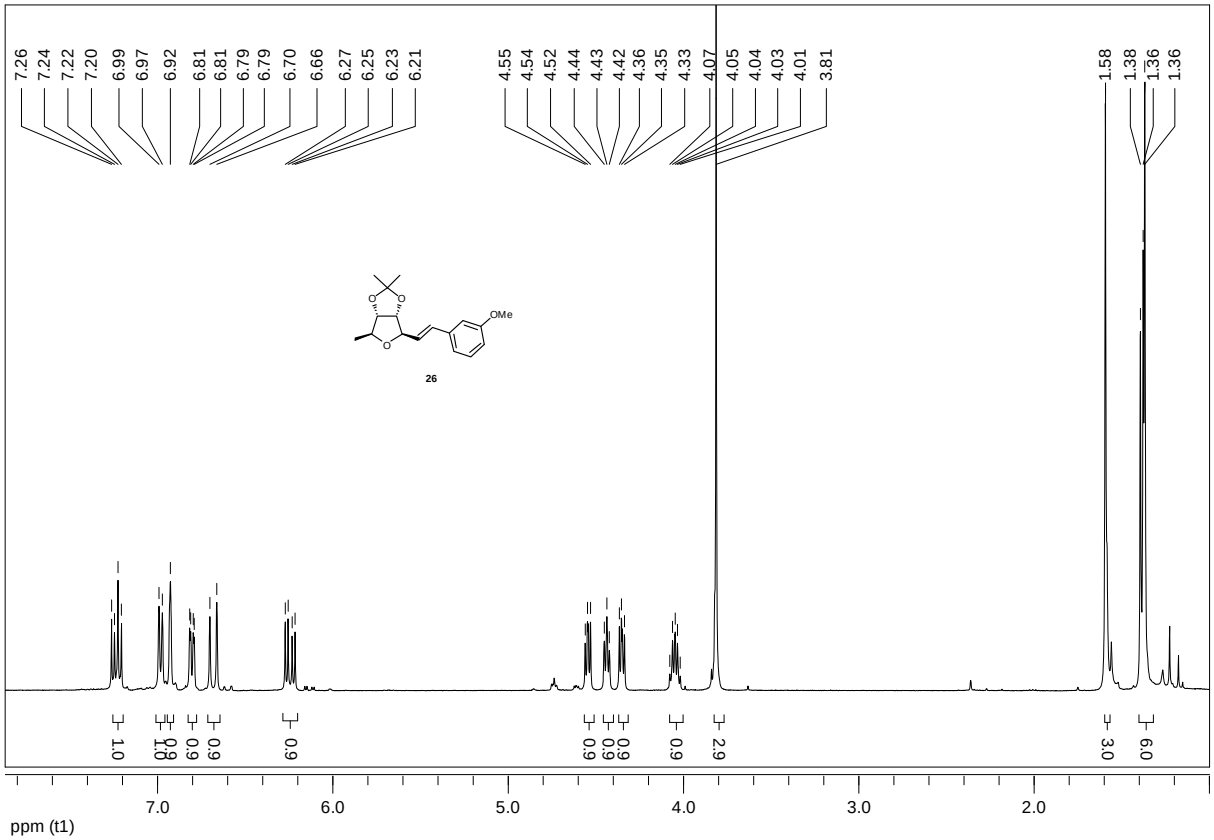
^{13}C-NMR (100 MHz, $CDCl_3$)



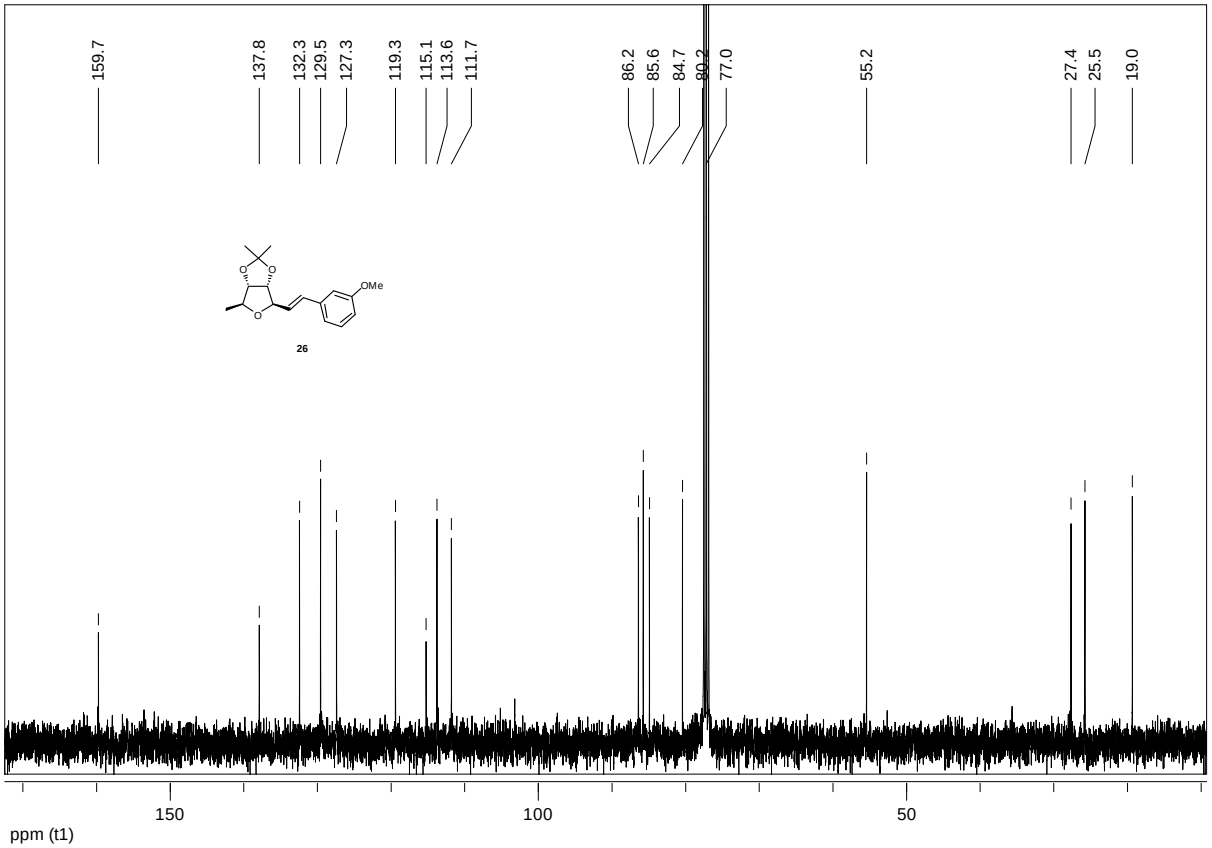
^{1}H-NMR (400 MHz, $CDCl_3$)



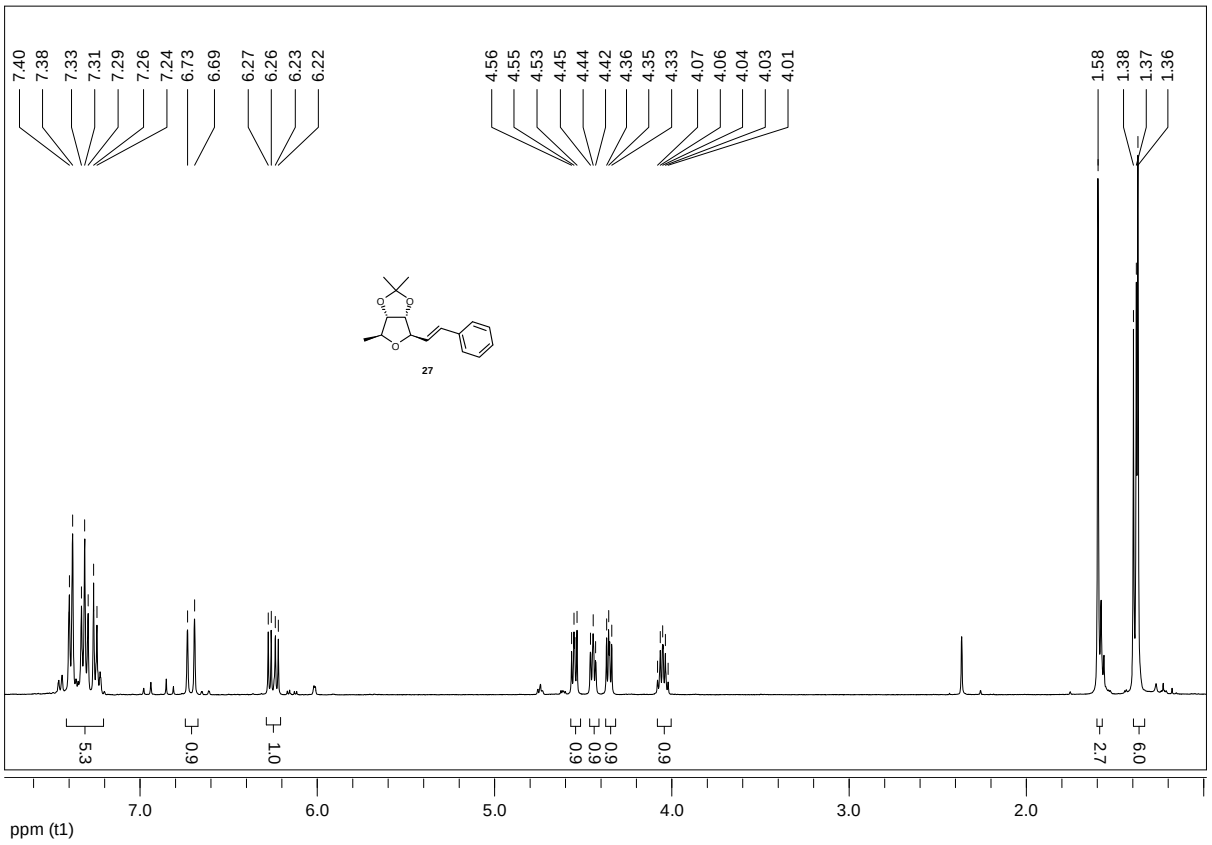
^{13}C-NMR (100 MHz, acetone-d_6)



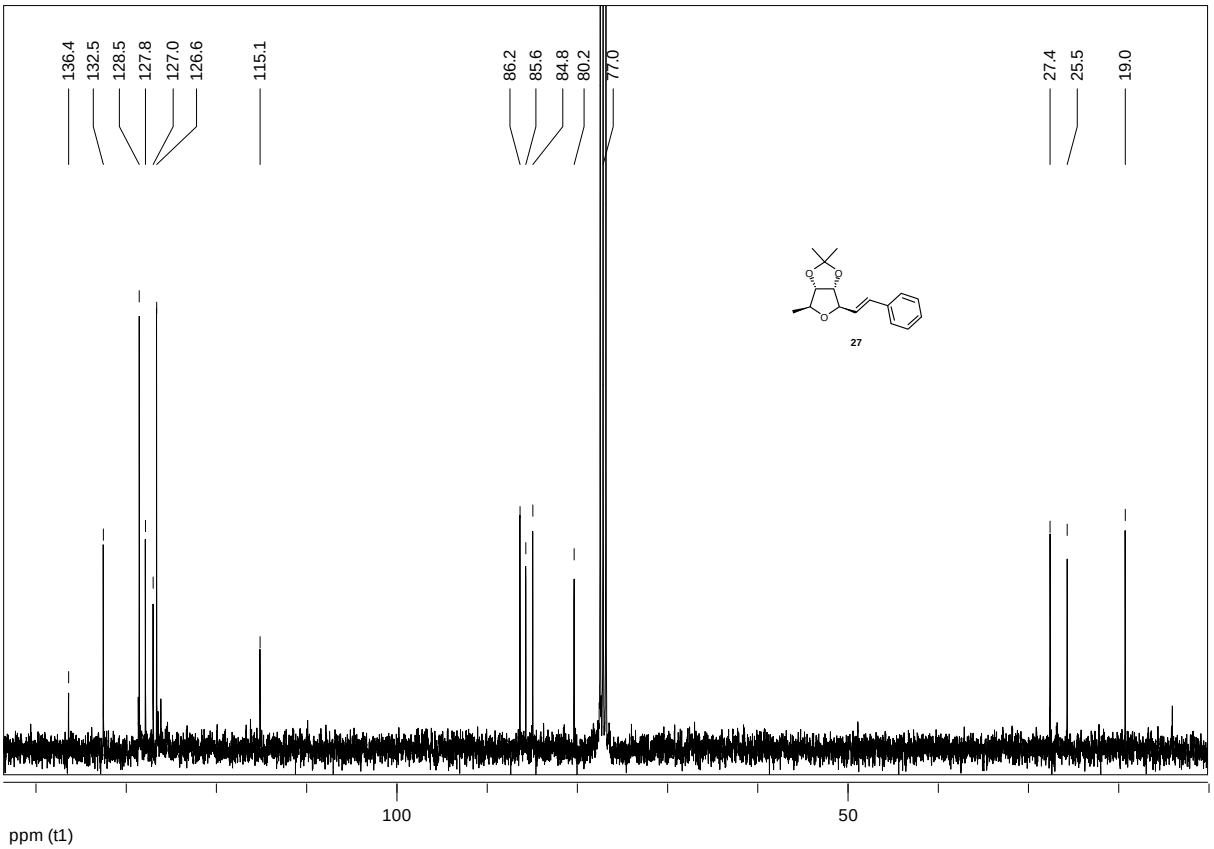
^{1}H-NMR (400 MHz, $CDCl_3$)



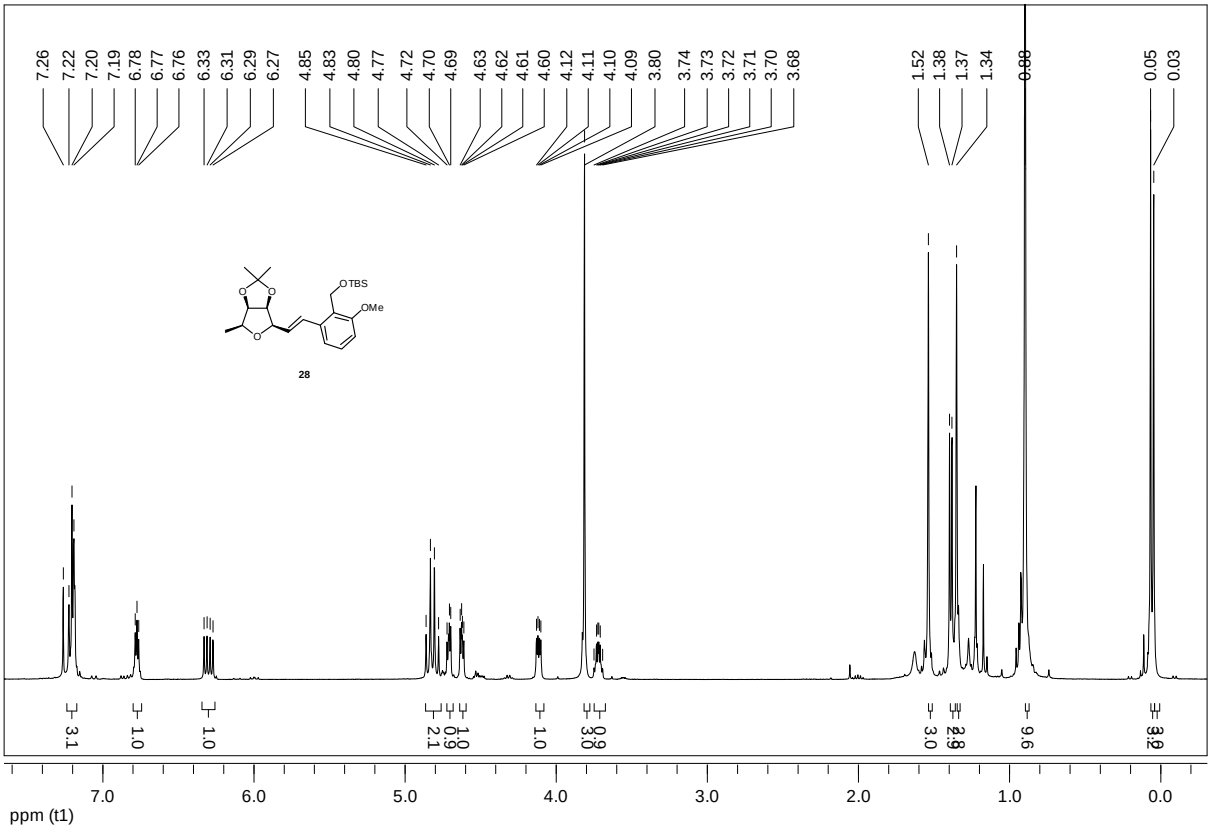
^{13}C-NMR (100 MHz, $CDCl_3$)



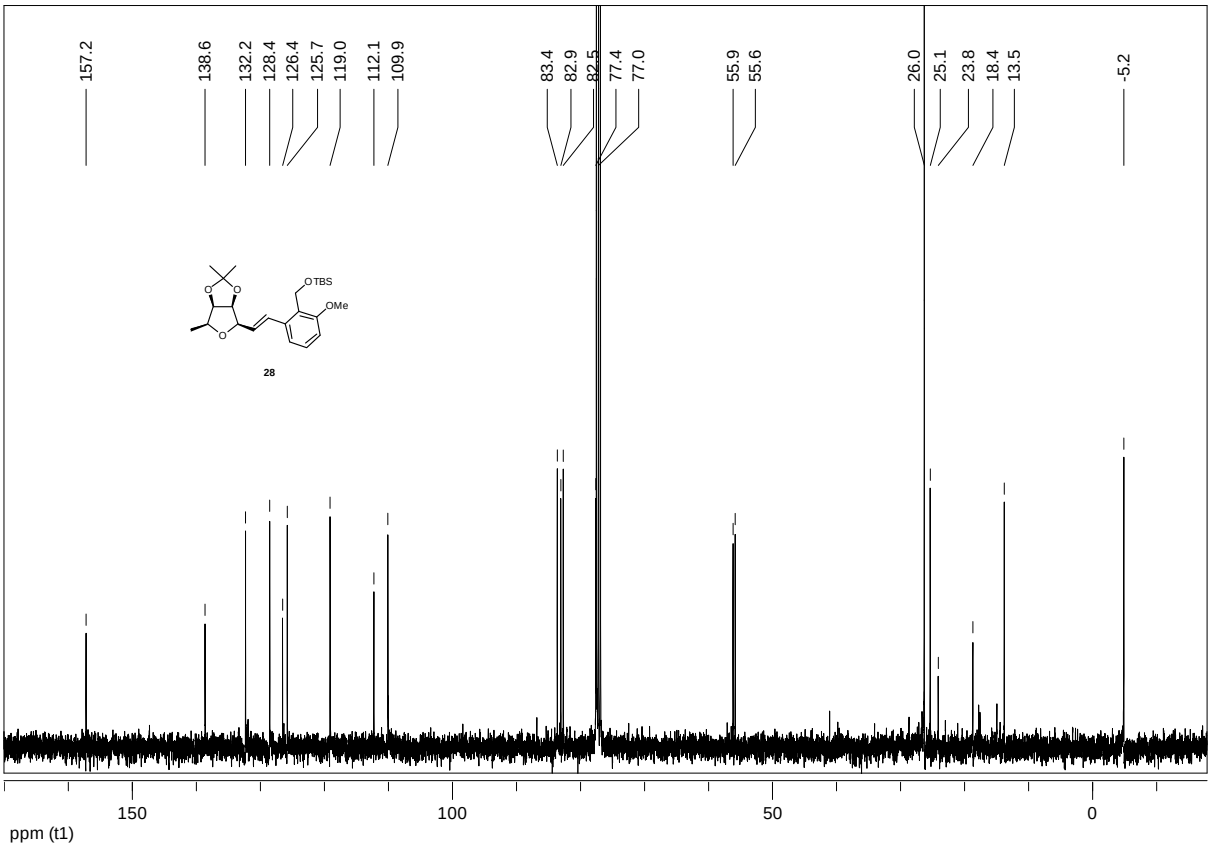
^{1}H-NMR (400 MHz, $CDCl_3$)



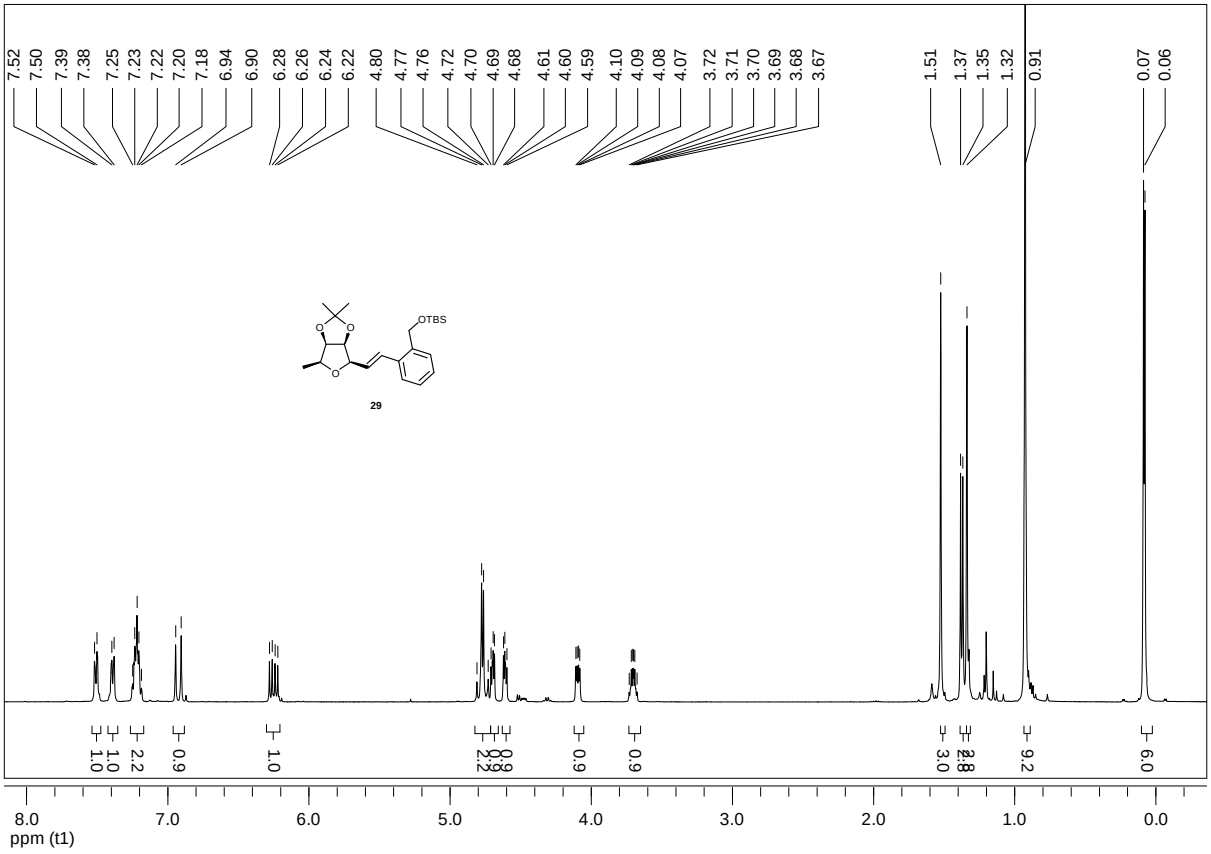
^{13}C-NMR (100 MHz, $CDCl_3$)



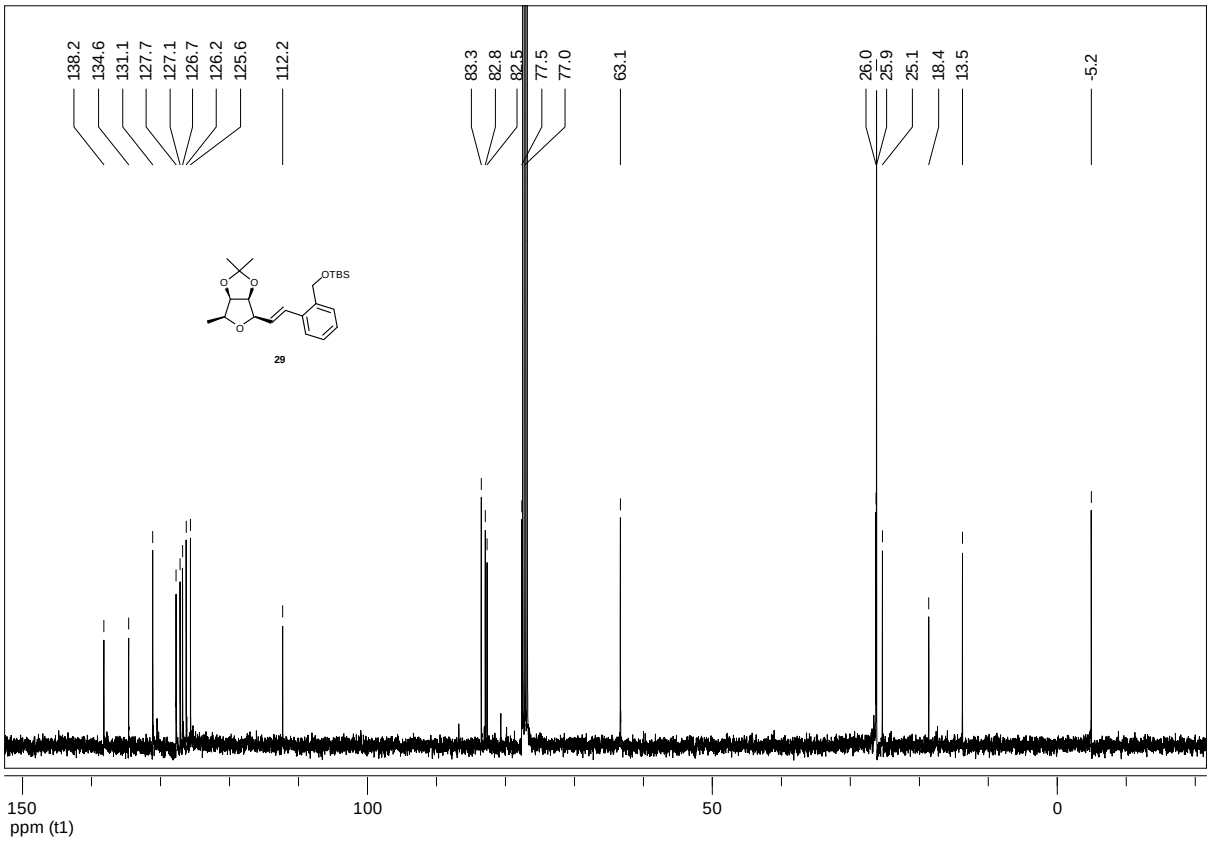
^{1}H-NMR (400 MHz, $CDCl_3$)



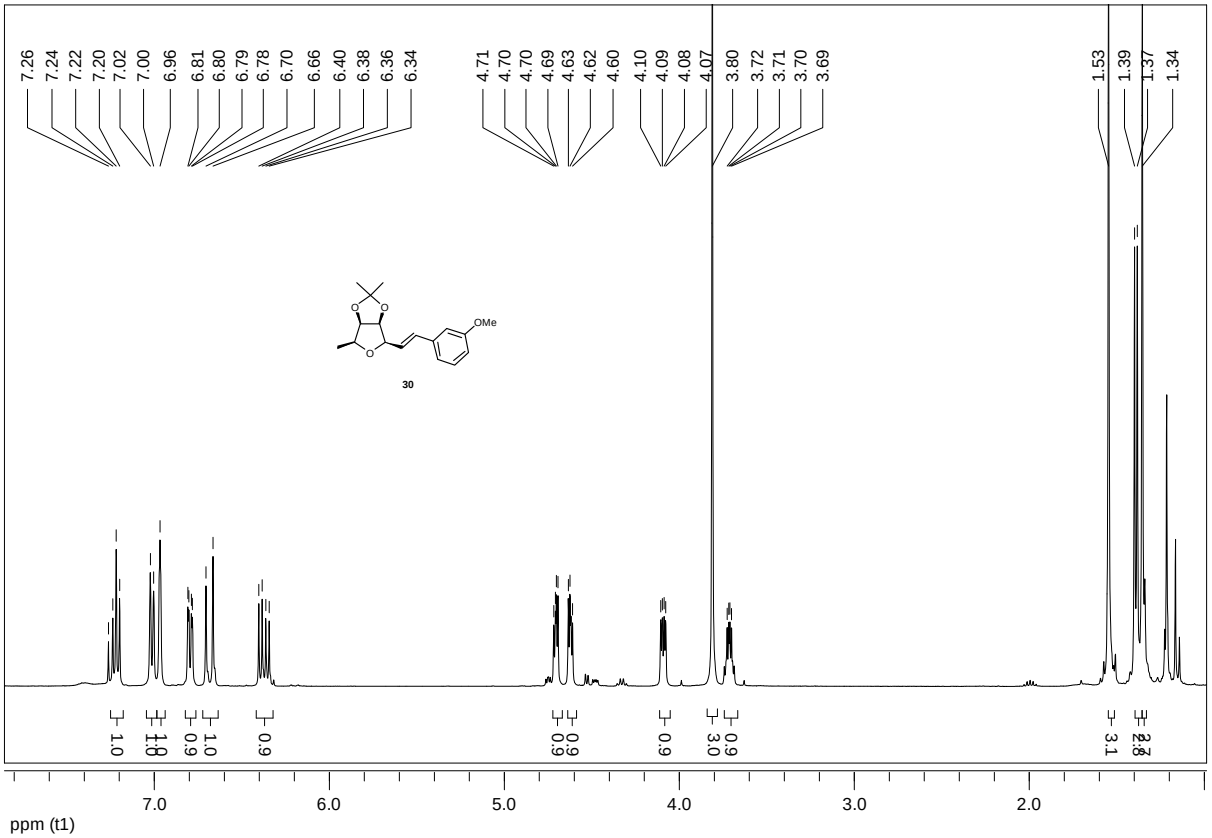
^{13}C-NMR (100 MHz, $CDCl_3$)



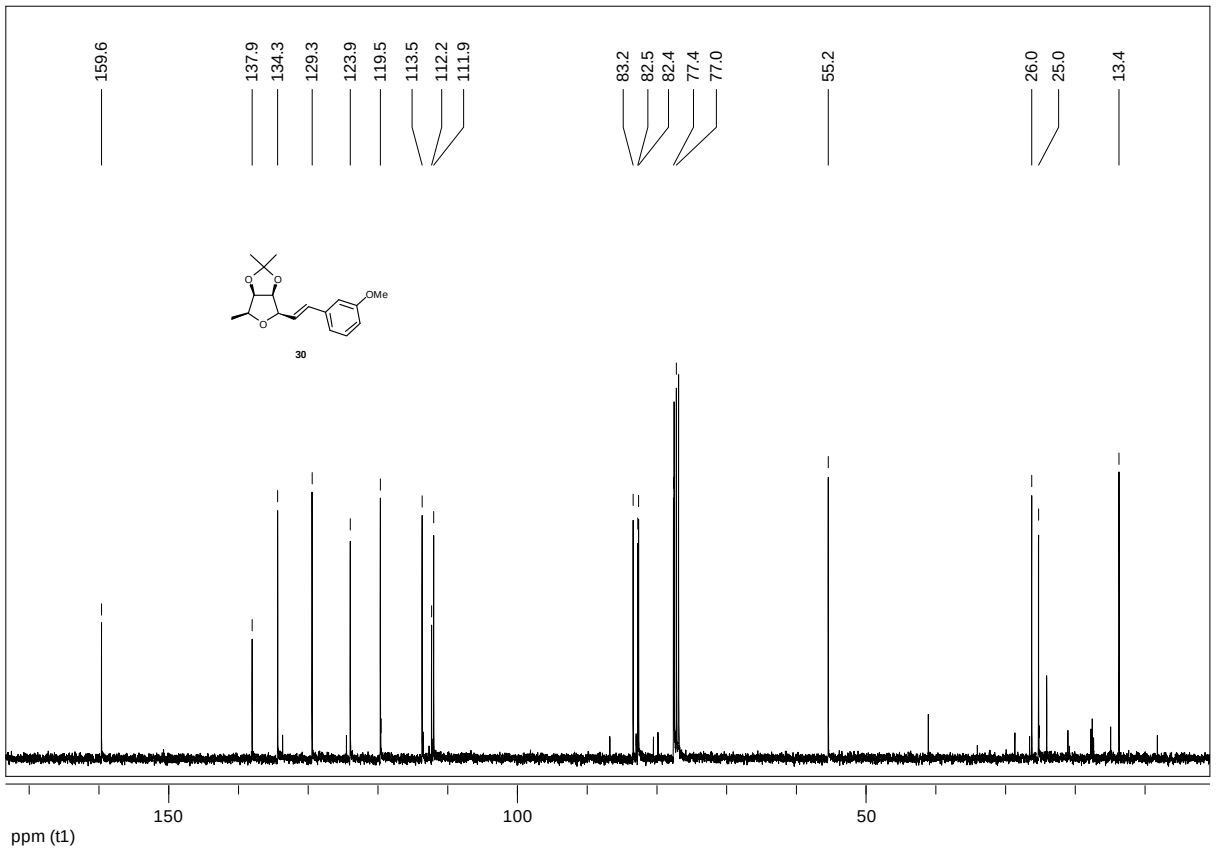
^{1}H-NMR (400 MHz, $CDCl_3$)



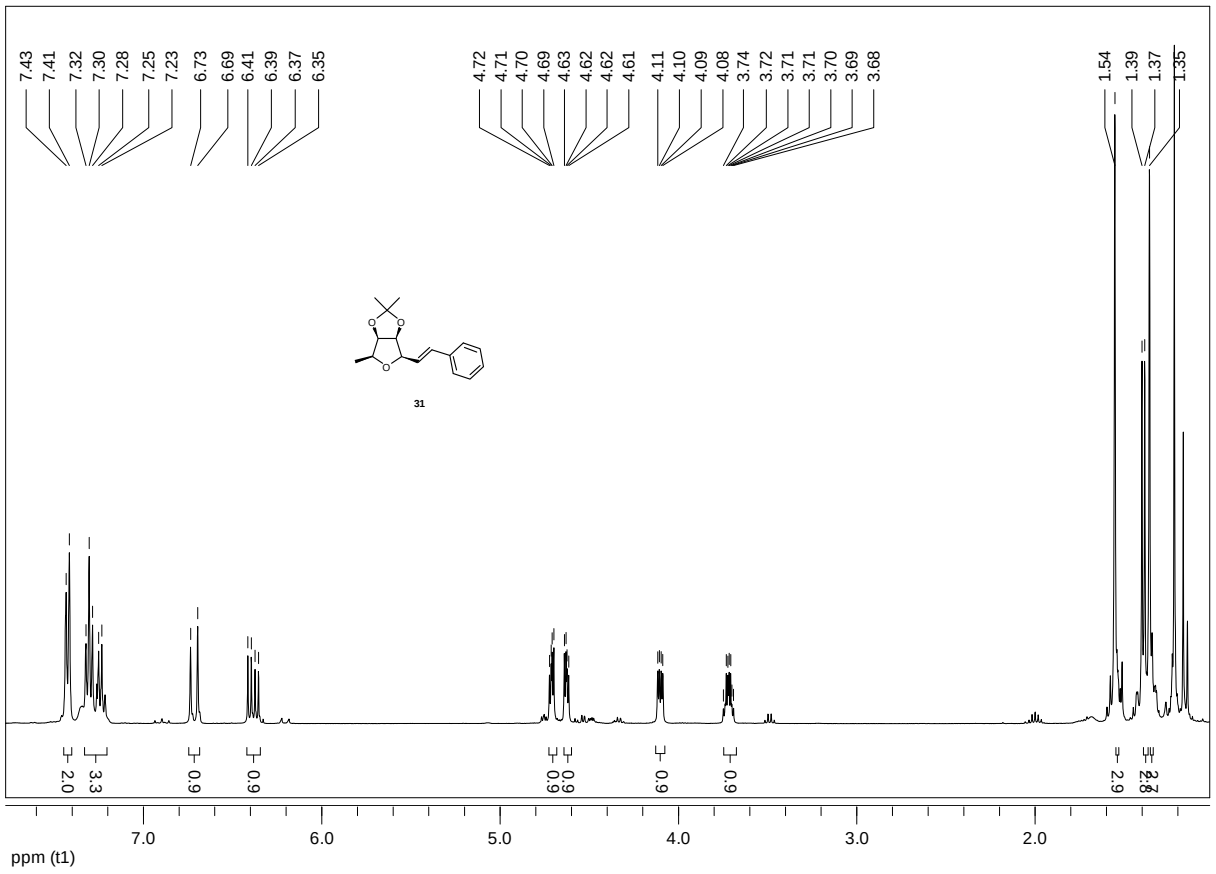
^{13}C-NMR (100 MHz, $CDCl_3$)



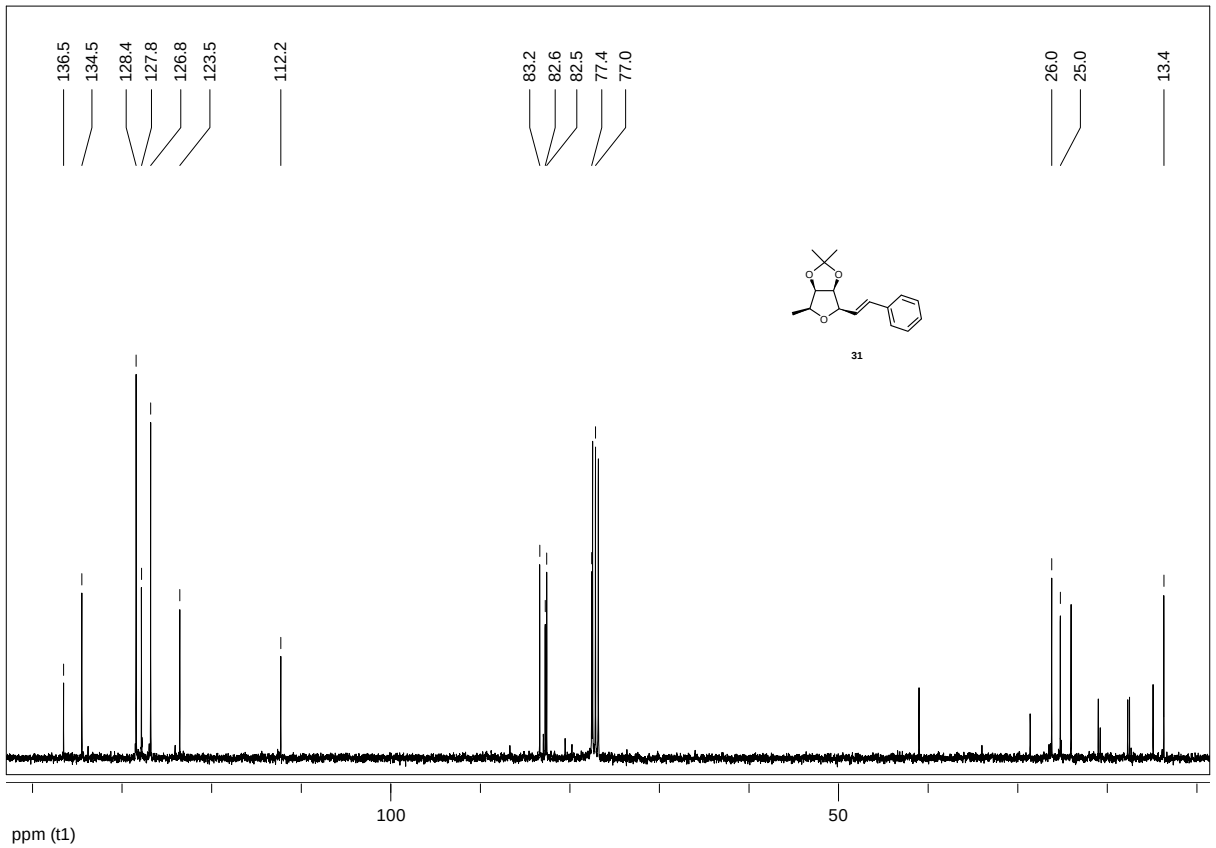
^{1}H-NMR (400 MHz, $CDCl_3$)



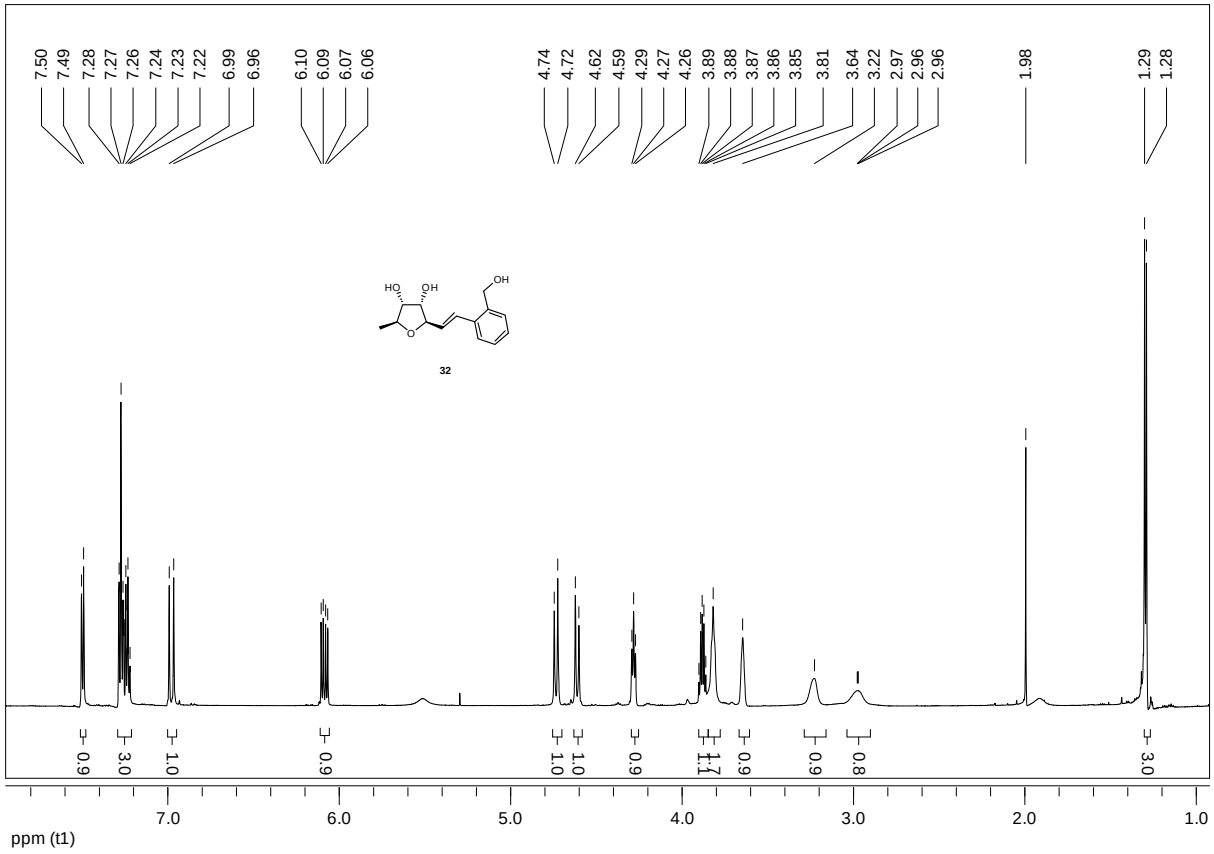
^{13}C-NMR (100 MHz, $CDCl_3$)



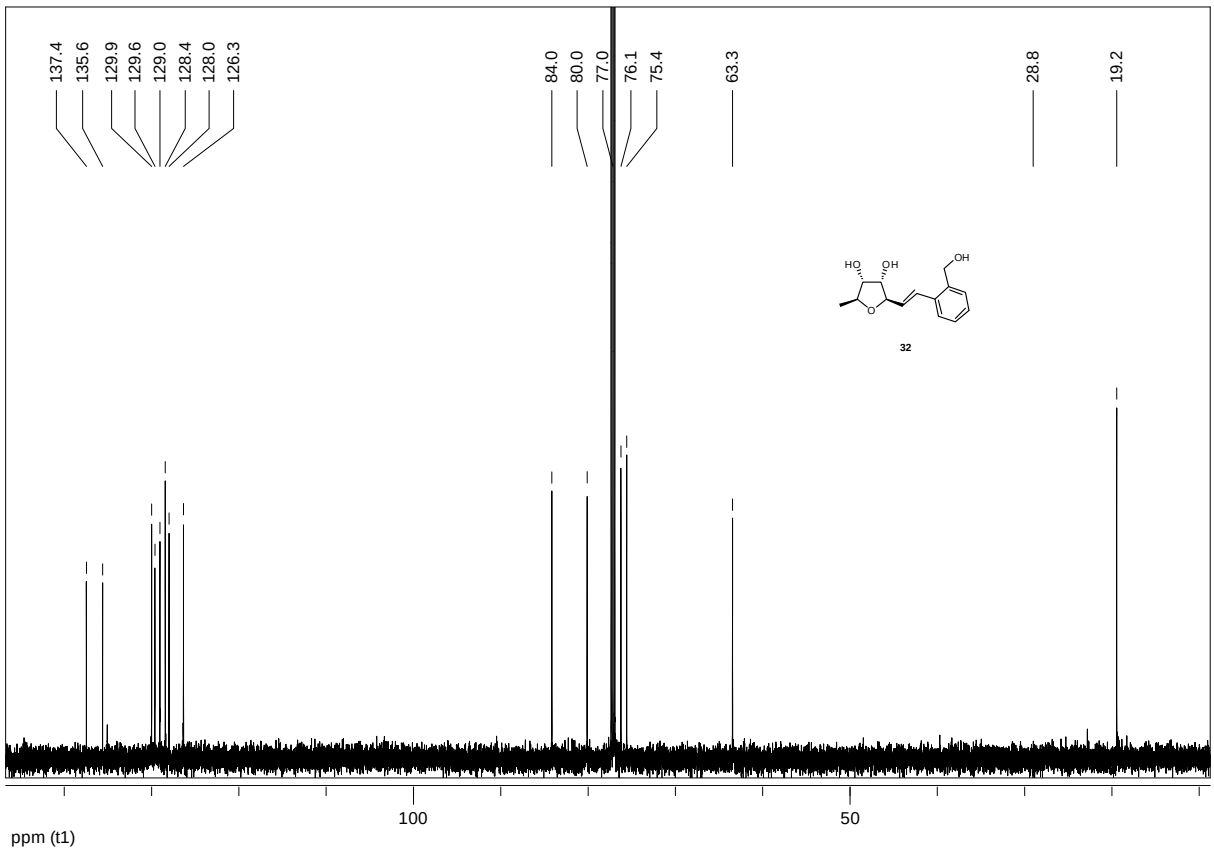
^{1}H-NMR (400 MHz, $CDCl_3$)



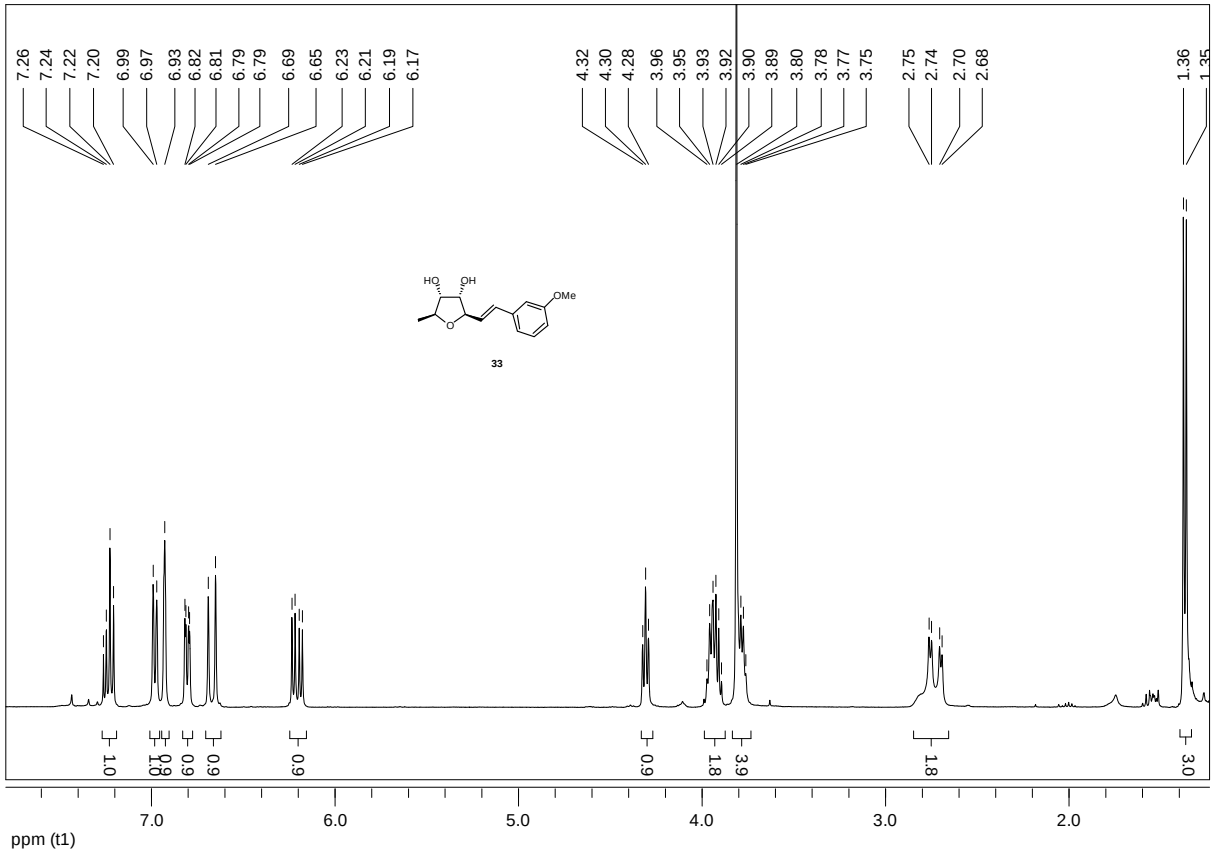
^{13}C-NMR (100 MHz, $CDCl_3$)



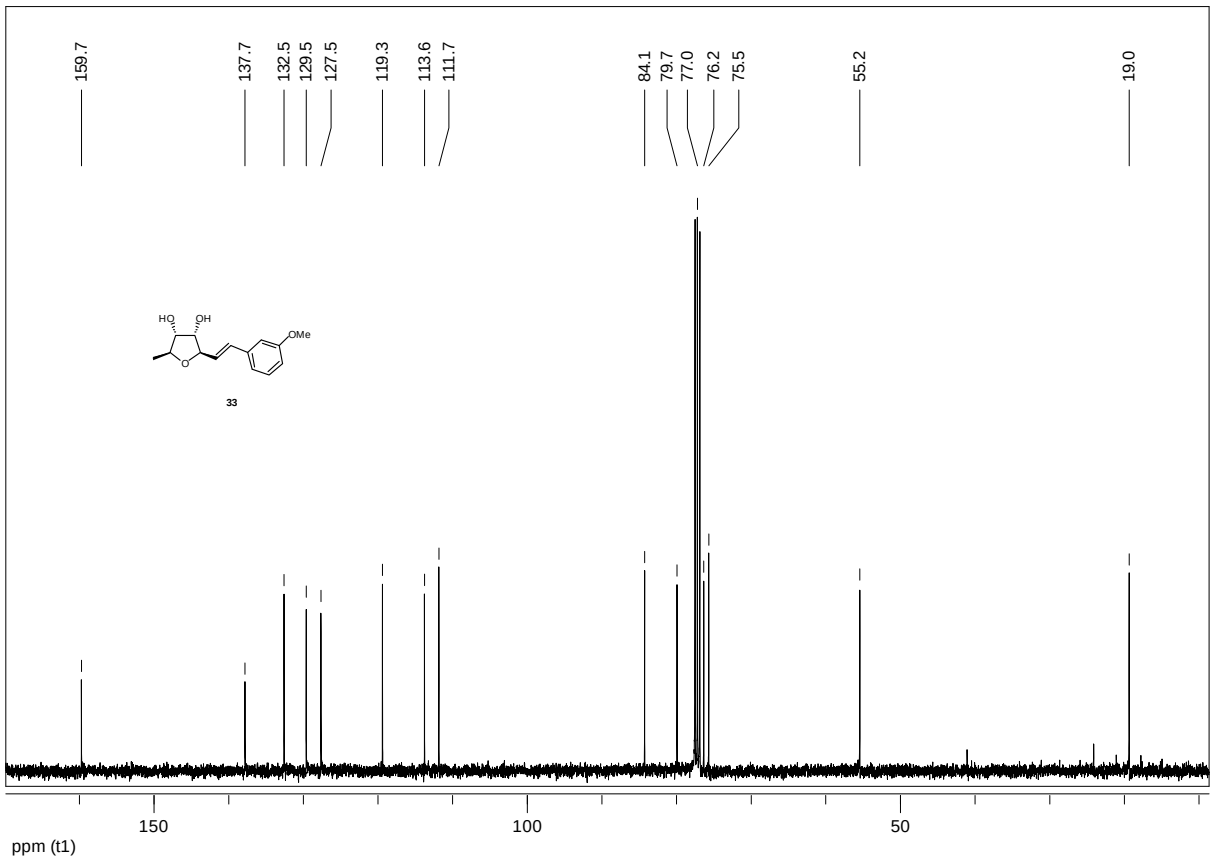
^{1}H-NMR (400 MHz, $CDCl_3$)



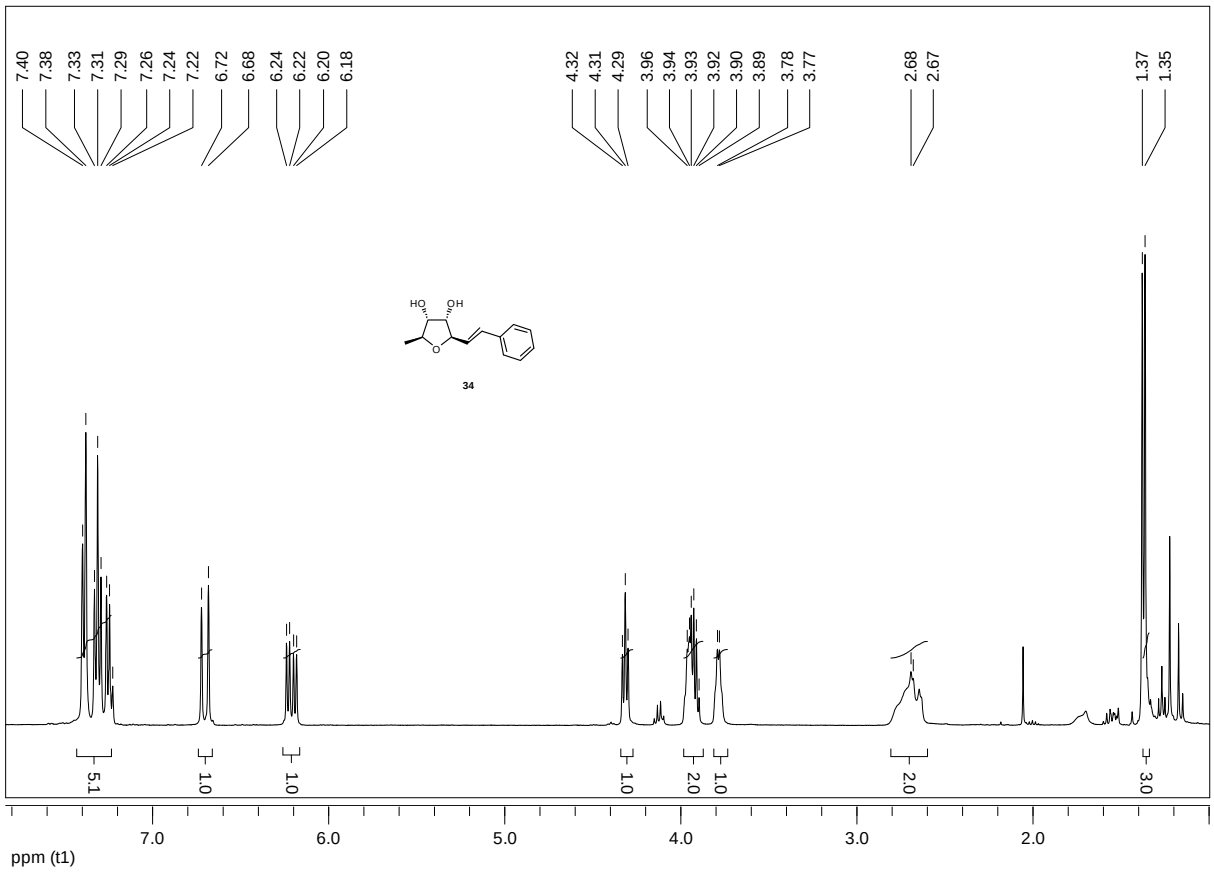
^{13}C-NMR (100 MHz, $CDCl_3$)



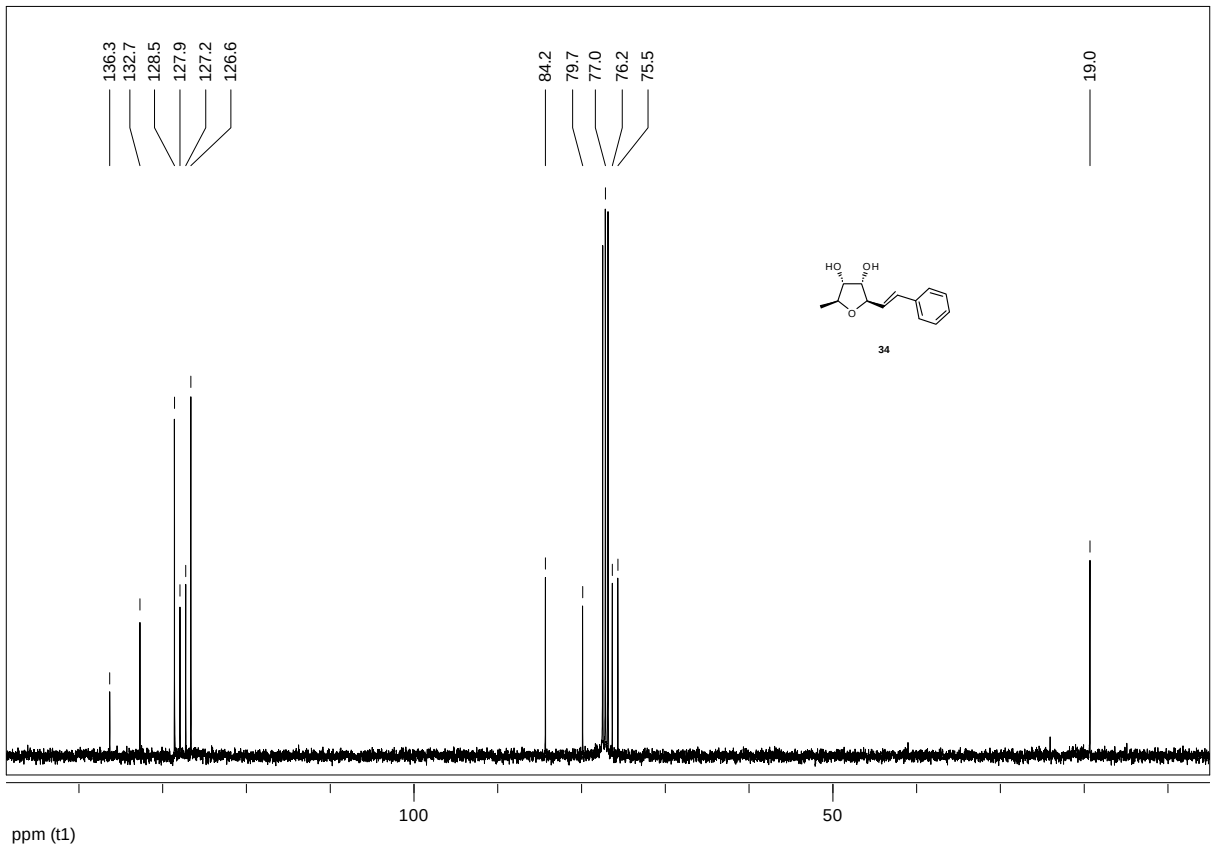
^{1}H-NMR (400 MHz, $CDCl_3$)



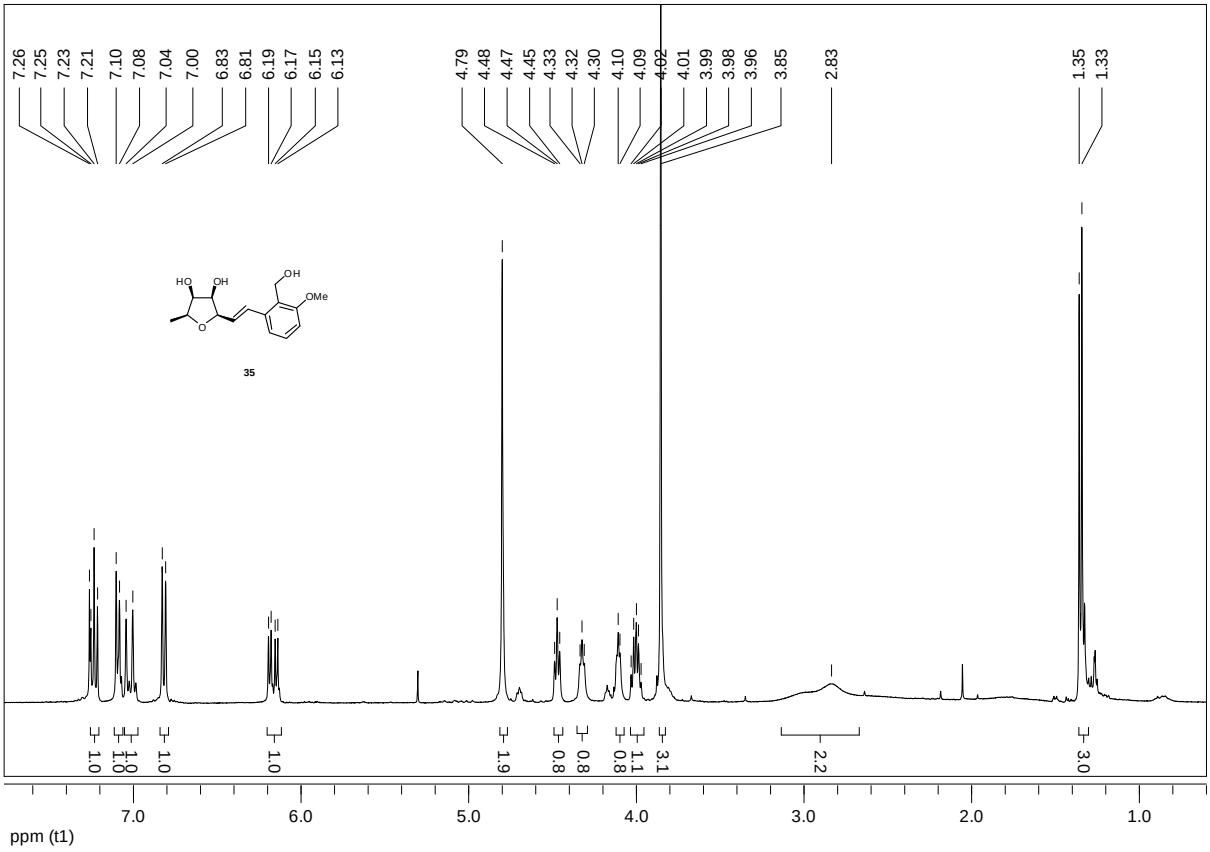
^{13}C-NMR (100 MHz, $CDCl_3$)



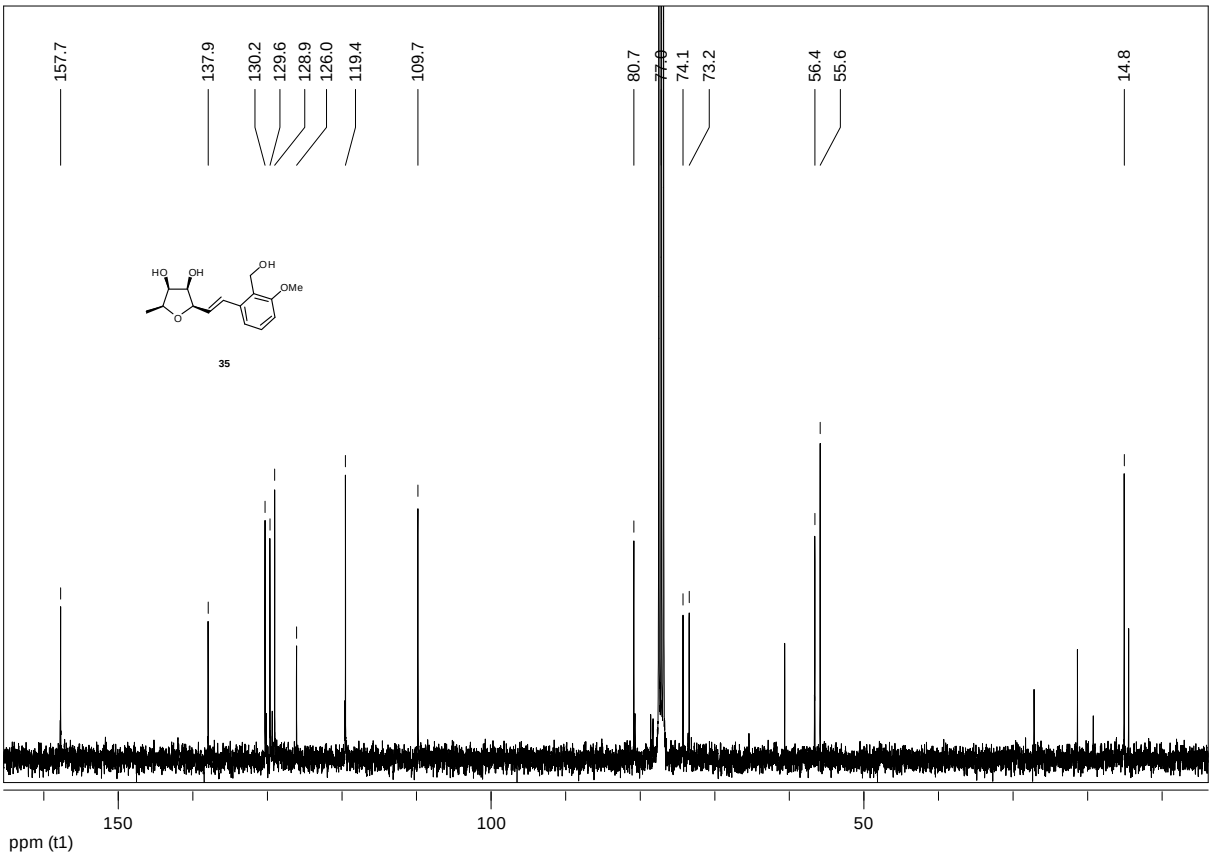
^{1}H-NMR (400 MHz, $CDCl_3$)



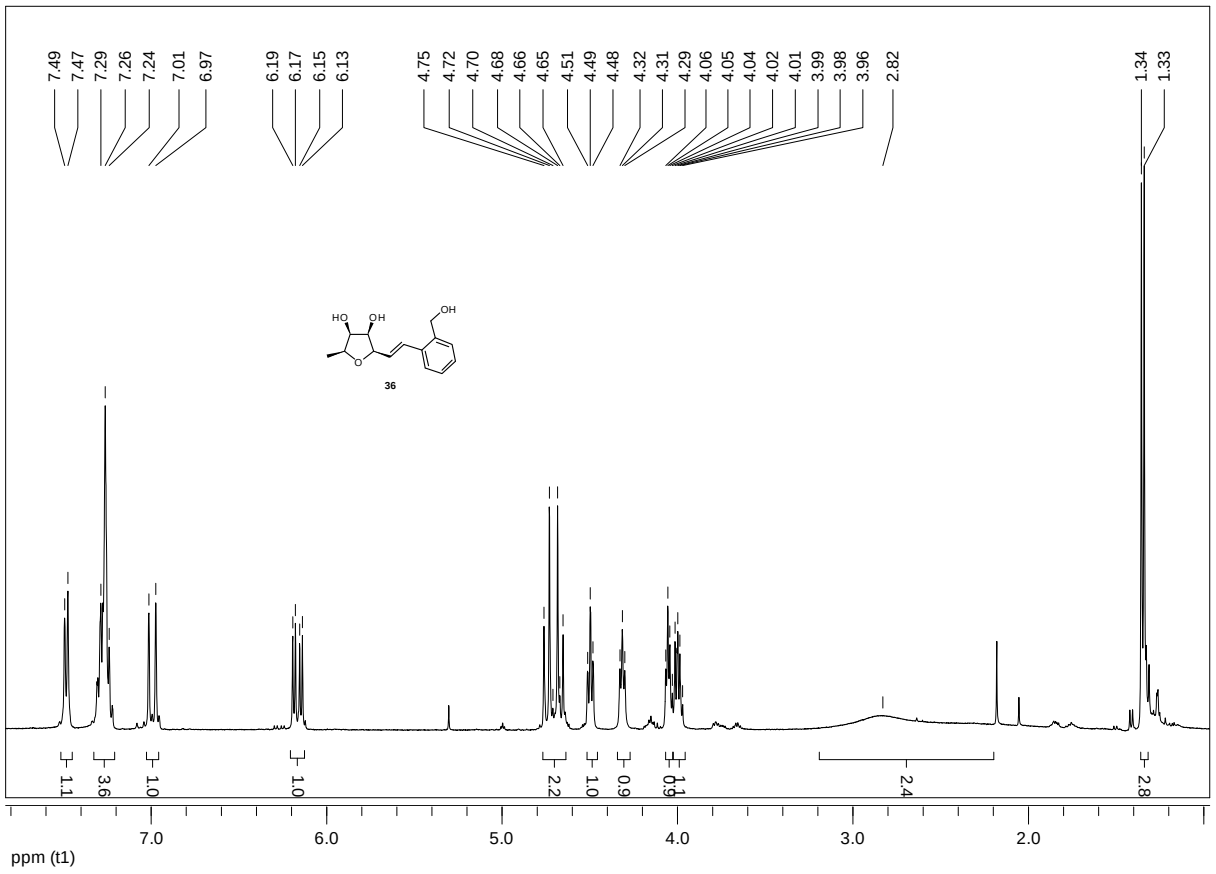
^{13}C-NMR (100 MHz, $CDCl_3$)



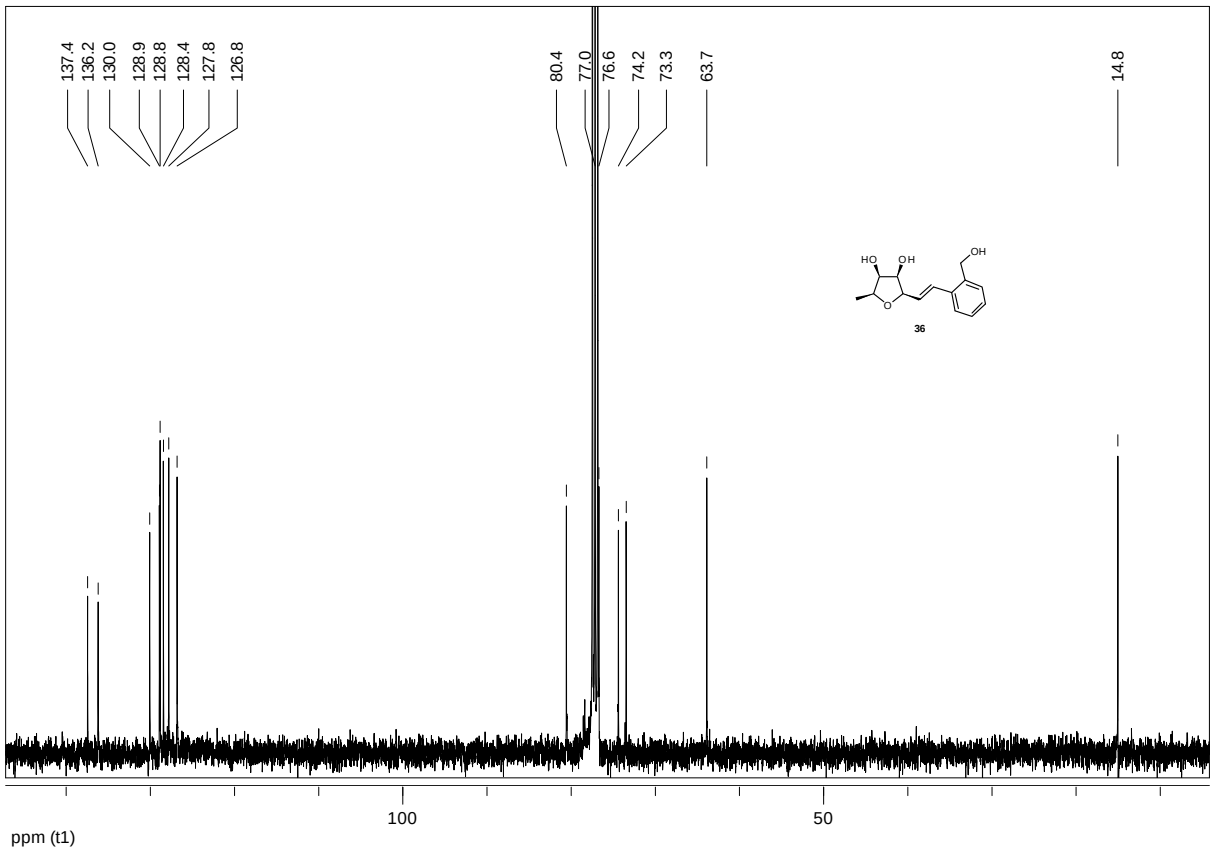
^{1}H-NMR (400 MHz, $CDCl_3$)



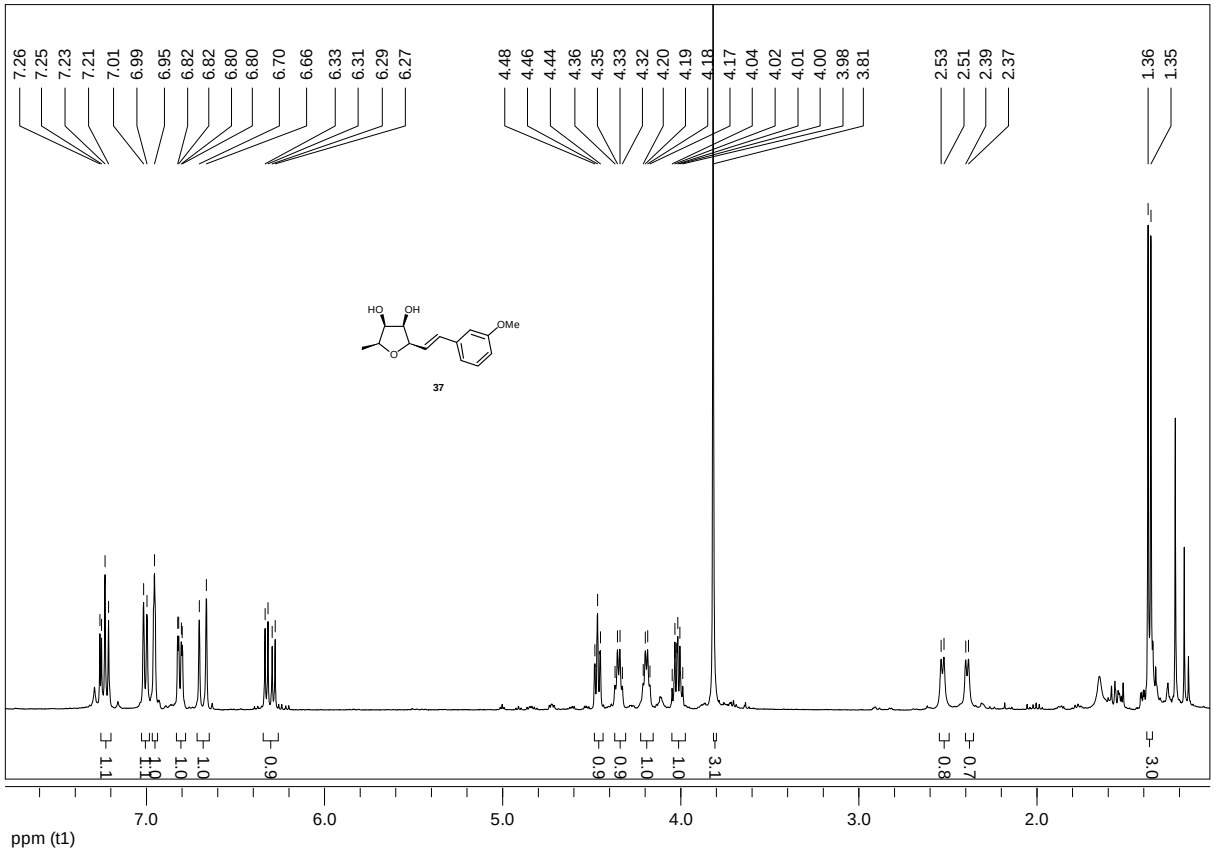
^{13}C-NMR (100 MHz, $CDCl_3$)



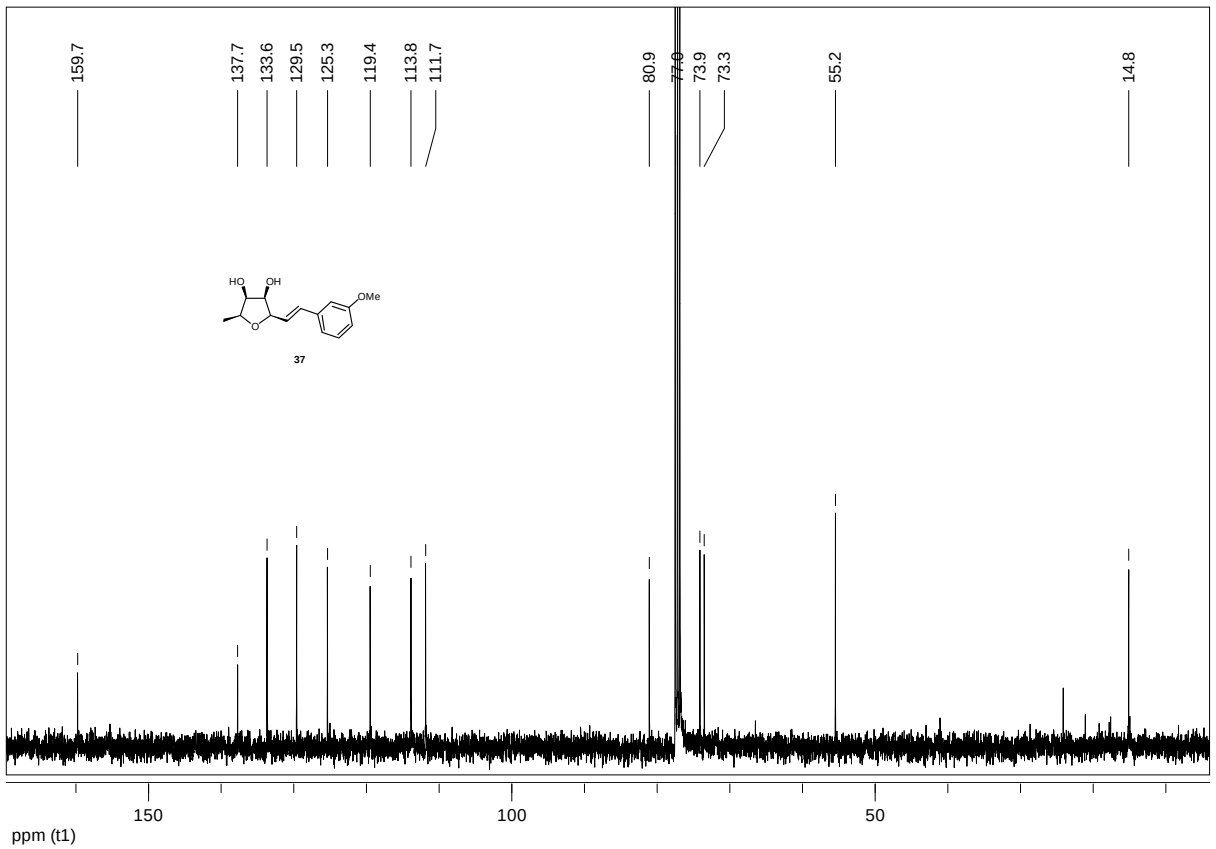
^{1}H-NMR (400 MHz, $CDCl_3$)



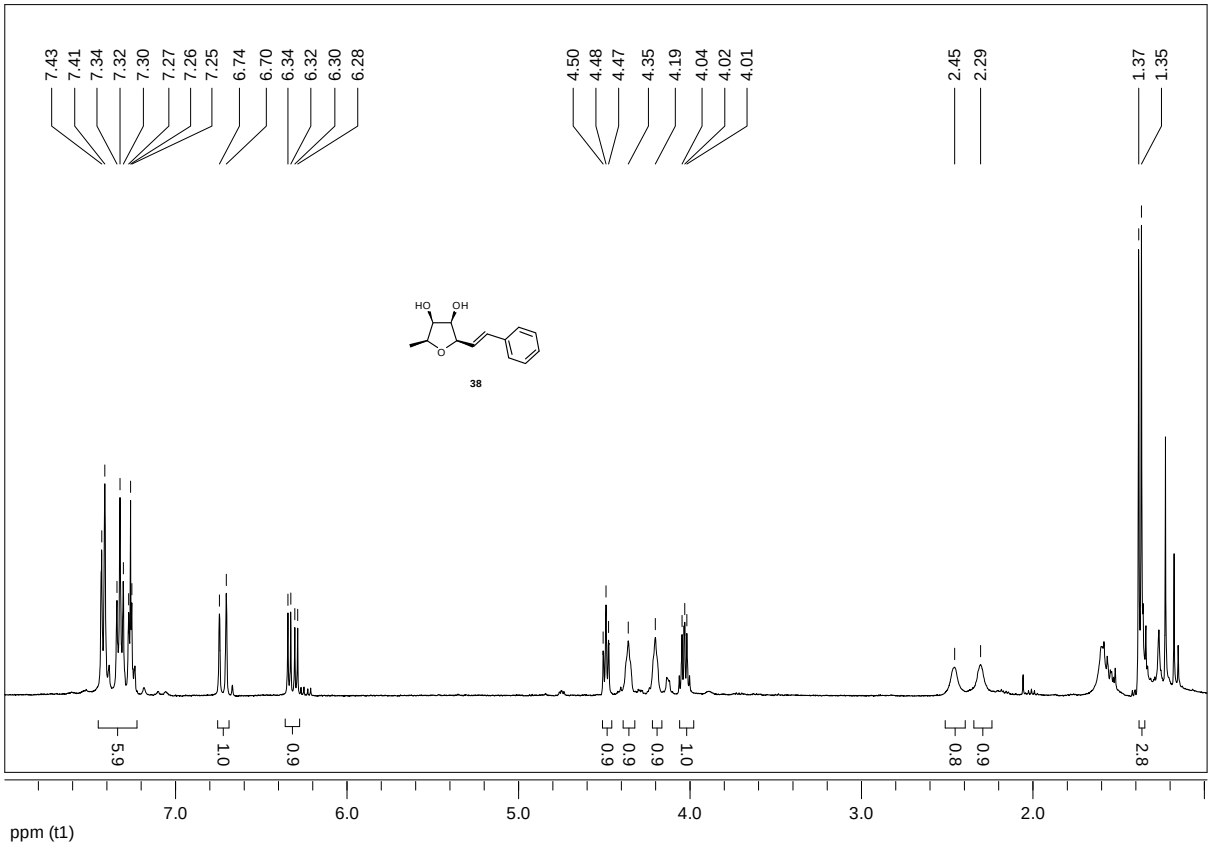
^{13}C-NMR (100 MHz, $CDCl_3$)



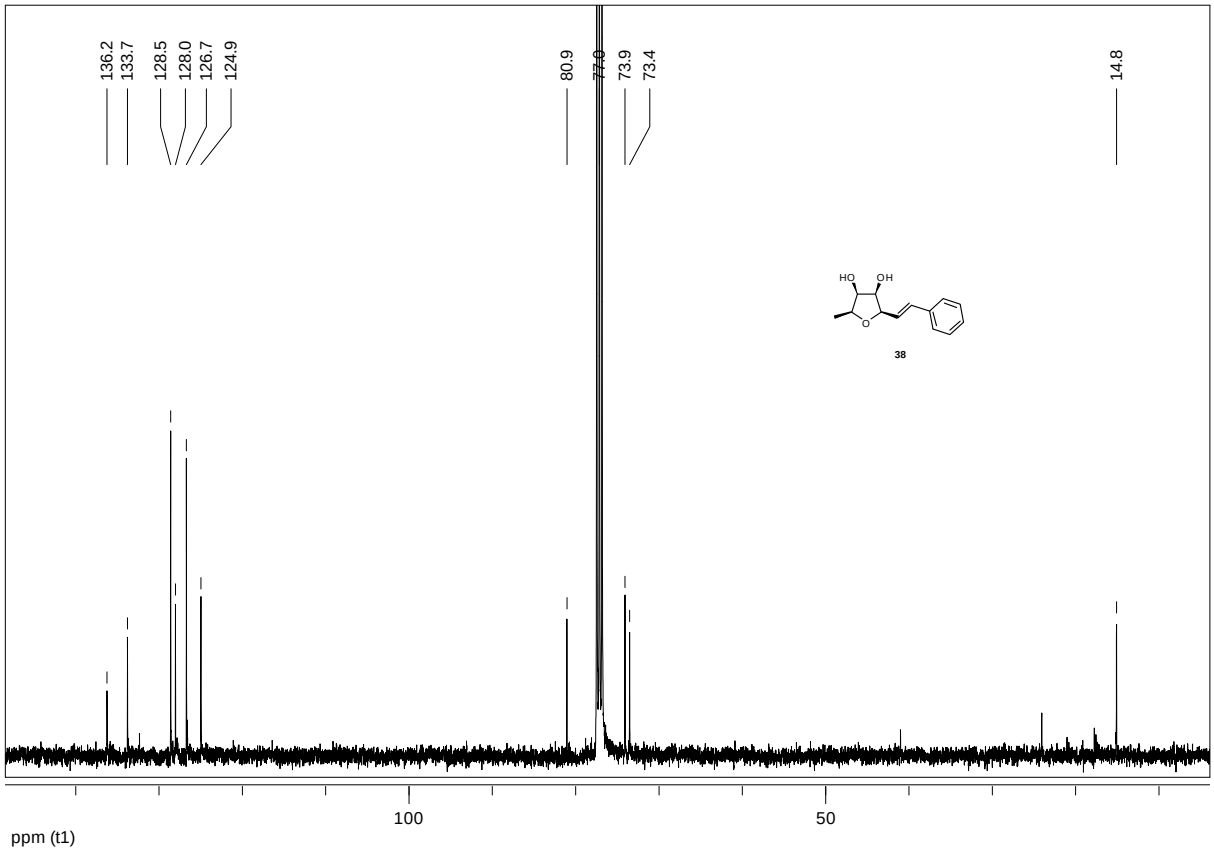
^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (400 MHz, $CDCl_3$)