A New Method of Deuterium Incorporation to TMS-Epoxyalcohol using Sodium Methylsulfinylmethylide-d_6 (NaDMSO-d_6)

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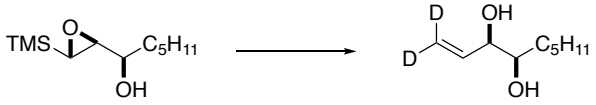
General.

The ^{1}H (300 or 400 MHz) and ^{13}C NMR (75 or 100 MHz) spectroscopic data were recorded in $CDCl_3$ using Me_4Si (δ = 0 ppm) and the centerline of the triplet (δ = 77.1 ppm), respectively, as internal standards. Signal patterns are indicated as br s (broad singlet), s (singlet), d (doublet), t (triplet), q (quartet), and m (multiplet). Coupling constants (*J*) are given in Hertz (Hz). Chemical shifts of carbons are accompanied by minus (for C and CH_2) and plus (for CH and CH_3) signs of the attached proton test (APT) experiments. High-resolution mass spectroscopy (HRMS) was performed with a double-focusing mass spectrometer with an ionization mode of positive FAB or EI as indicated for each compound. The solvents that were distilled prior to use are THF (from Na/benzophenone) and CH_2Cl_2 (from CaH_2). After the reactions were completed, the organic extracts were concentrated by using an evaporator, and then the residues were purified by chromatography on silica gel (Kanto, spherical silica gel 60N). DMSO-d_6 (deuteration degree minimum 99.96%) in ampoules was purchased from Merck.

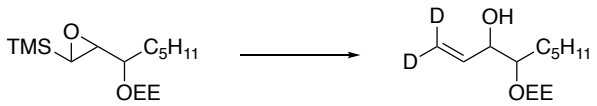
(3*R,4*R**)-Non-1-ene-1,1-d_2-3,4-diol (2s).**



1s **2s**

According to the conversion of **1a** to **2a** described in the text, syn epoxy alcohol **1s** (98 mg, 0.45 mmol) in THF (2 mL) was added to a mixture of oil-free NaH (prepared by washing NaH (60% wt% in mineral oil, 139 mg, 3.48 mmol) with hexane) and DMSO-d_6 (0.60 mL, 8.48 mmol). The mixture was stirred at rt for 3 h to afford diol **2s** (47 mg, 65%): liquid; R_f 0.37 (hexane/EtOAc 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 7.2 Hz, 3 H), 1.22–1.58 (m, 8 H), 2.20 (br s, 1 H), 2.24 (br s, 1 H), 3.44–3.52 (m, 1 H), 3.94 (t, *J* = 6.4 Hz, 1 H), 5.82–5.89 (m, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 14.1 (+), 22.6 (–), 25.3 (–), 31.9 (–), 32.8 (–), 74.5 (+), 76.3 (+), 116.8 (quint., *J* = 24 Hz) (–), 137.5 (+). The ^{13}C and ^{13}C–APT NMR spectra were identical with those reported for the non-deuterated anti diol except for the carbon bearing deuterium atoms.[S1]

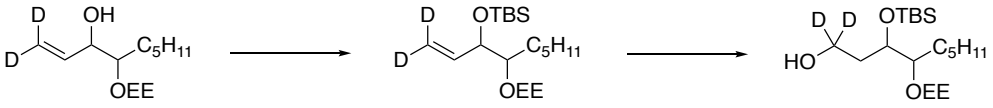
4-(1-Ethoxyethoxy)non-1-en-1,1-d_2-3-ol (6a/s).



5a/s **6a/s**

According to the conversion of **1a** to **2a** described in the text, the α-ethyoxyethyl ether **5a/s** (96 mg, 0.333 mmol) in THF (2 mL) was added to a mixture of oil-free NaH (prepared by washing NaH (60% wt% in mineral oil, 113 mg, 2.83 mmol) with hexane) and DMSO-d_6 (0.60 mL, 8.48 mmol). The mixture was stirred at rt for 2.5 h to afford alcohol **6a/s** (51 mg, 66%): liquid; R_f 0.42, 0.35 (hexane/EtOAc 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (t, J = 6.8 Hz, 3 H), 1.18–1.65 (m, 14 H), 2.70 (d, J = 5.2 Hz, 0.25 H), 2.74 (d, J = 4.2 Hz, 0.25 H), 3.33 (dt, J = 3.2, 8.0 Hz, 0.25 H), 3.46–3.76 (m, 2.75 H), 3.90–4.18 (m, 1.5 H), 4.56–4.64 (m, 0.5 H), 4.78 (q, J = 5.2 Hz, 0.25 H), 4.88 (q, J = 5.2 Hz, 0.25 H), 5.74–5.92 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.1, 15.17, 15.24, 20.1, 20.2, 20.4, 22.6, 25.0, 25.59, 25.63, 30.4, 31.5, 31.80, 31.87, 31.92, 32.04, 61.0, 61.1, 61.2, 61.7, 74.2, 74.3, 74.8, 75.4, 78.4, 79.6, 84.1, 84.3, 99.2, 100.2, 101.9, 102.0, 116.1 (m), 136.5, 136.6, 137.2, 137.7; HRMS (FAB$^+$) calcd for $C_{13}H_{24}D_2O_3Na$ [(M+Na)$^+$] 255.1905, found 255.1904.

3-[(*tert*-Butyldimethylsilyl)oxy]-4-(1-ethoxyethoxy)nonan-1,1-d_2-1-ol (10)



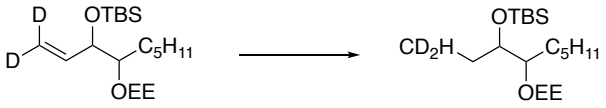
6a/s **9** **10**

A solution of alcohol **6a/s** (1.03 g, 4.43 mmol), imidazole (740 mg, 10.9 mmol), and TBSCl (840 mg, 5.57 mmol) in CH_2Cl_2 (10 mL) was stirred overnight at rt and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2 twice. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to afford **9** (1.27 g, 83%): liquid; R_f 0.71 (hexane/EtOAc 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02, 0.03, 0.04, 0.05, and 0.07 (5 s, total 6 H), 0.82–0.98 (m, 3 H) 0.89, 0.897, 0.899, and 0.904 (4 s, total 9 H), 1.10–1.64 (m, 14 H), 3.30–3.81 (m, 3 H), 4.04 (dd, J = 6.9 Hz, 3.3 Hz, 0.25 H), 4.14 (dd, J = 6.3 Hz, 3.6

Hz, 0.25 H), 4.20 (t, J = 5.4 Hz, 0.25 H), 4.38 (t, J = 4.5 Hz, 0.25 H), 4.71 (q, J = 5.4 Hz, 0.25 H), 4.78–4.89 (m, 0.5 H), 4.92 (q, J = 5.4 Hz, 0.25 H), 5.80–6.00 (m, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.92 (+), –4.82 (+), –4.78 (+), –4.5 (+), –4.32 (+), –4.27 (+), 14.1 (+), 15.36 (+), 15.43 (+), 18.2 (–), 18.3 (–), 20.3 (+), 20.5 (+), 20.6 (+), 22.6 (–), 22.7 (–), 25.3 (–), 25.57 (–), 25.60 (–), 25.7 (–), 25.86 (+), 25.94 (+), 29.0 (–), 29.8 (–), 30.6 (–), 31.7 (–), 32.0 (–), 32.1 (–), 32.2 (–), 59.8 (–), 60.0 (–), 60.2 (–), 61.2 (–), 73.8 (+), 74.2 (+), 76.9 (+), 77.0 (+), 78.7 (+), 79.4 (+), 80.7 (+), 81.1 (+), 99.3 (+), 100.0 (+), 100.6 (+), 100.9 (+), ca. 115 (m) (–), 137.0 (+), 137.2 (+), 137.8 (+), 138.5 (+).

To an ice-cold solution of olefin **9** (95 mg, 0.27 mmol) was added dropwise $(Sia)_2BH$ (0.50 M in THF, 3.0 mL, 1.50 mmol), freshly prepared by mixing BH_3·THF (1.0 M in THF, 3.0 mL, 3.0 mmol) and 2-methyl-2-butene (2.0 M in THF, 3.0 mL, 6.0 mmol) at 0 °C for 30 min. The solution was stirred at 0 °C for 1 h, and aqueous 2 N NaOH (2.8 mL, 5.6 mmol) and H_2O_2 (35 wt% in H_2O, 0.50 mL, 5.7 mmol) were added. The mixture was stirred between 0 °C and rt for 15 min and extracted with Et_2O twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford alcohol **10** (74 mg, 74%): liquid; R_f 0.48, 0.45 (hexane/EtOAc 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.09 (s, 6 H), 0.82–1.00 (m, 3 H), 0.883, 0.887, 0.897, and 0.903 (4 s, total 9 H), 1.13–1.94 (m, 16 H), 2.28, 2.52, and 2.91 (3 br s, total 1 H), 3.38–4.12 (m, 4 H), 4.67 (q, J = 5.4 Hz, 0.25 H), 4.74–4.84 (m, 0.5 H), 4.98 (q, J = 5.4 Hz, 0.25 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.9 (+), –4.8 (+), –4.7 (+), –4.40 (+), –4.35 (+), –4.27 (+), 14.1 (+), 15.3 (+), 15.4 (+), 17.9 (–), 18.0 (–), 18.1 (–), 20.3 (+), 20.6 (+), 20.7 (+), 22.6 (–), 25.5 (–), 25.8 (+), 25.9 (+), 26.0 (+), 26.17 (–), 26.21 (–), 28.4 (–), 28.6 (–), 31.0 (–), 31.95 (–), 32.00 (–), 32.1 (–), 32.3 (–), 33.7 (–), 34.1 (–), 34.3 (–), 35.1 (–), 59.7 (–), 60.4 (–), 60.7 (–), 61.4 (–), 71.1 (+), 71.8 (+), 73.0 (+), 73.1 (+), 78.1 (+), 79.1 (+), 81.5 (+), 81.6 (+), 99.0 (+), 99.9 (+), 101.1 (+), 101.7 (+); HRMS (FAB$^+$) calcd for $C_{19}H_{40}D_2O_4SiNa$ [$(M+Na)^+$] 387.2876, found 387.2883.

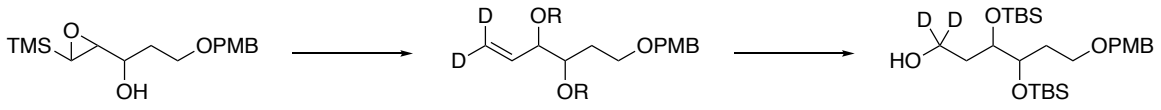
5-(Ethyl-2,2-*d*$_2$)-2,2,3,3,8-pentamethyl-6-pentyl-4,7,9-trioxa-3-silaundecane (11)



9 **11**

Olefin **9** (ca. 90 mg) was treated with charcoal (24 mg) in EtOAc (1 mL) at rt for 6 h to absorb impurities, filtered through a pad of Celite, and purified by chromatography on silica gel (hexane/EtOAc) before use. A mixture of **9** (43 mg, 0.12 mmol) and 10% Pd/C (17 mg, 0.16 mmol) in EtOAc (0.5 mL) under hydrogen was stirred at rt for 5 h. The resulting mixture was filtered through a pad of silica gel and concentrated to give **11** (40 mg, 92%): liquid; R_f 0.57 (hexane/EtOAc 20:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.06 (s, 6 H), 0.83–1.72 (m, 29 H), 3.29–3.90 (m, 4 H), 4.61–4.95 (m, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.5 (+), –4.2 (+), –4.1 (+), 14.1 (+), 15.4 (+), 15.5 (+), 18.1 (–), 20.4 (+), 20.6 (+), 20.7 (+), 21.0 (+), 22.70 (–), 22.73 (–), 25.6 (–), 25.9 (+), 26.0 (+), 26.1 (+), 26.26 (–), 26.30 (–), 28.5 (–), 28.8 (–), 30.4 (–), 31.7 (–), 31.9 (–), 32.0 (–), 32.1 (–), 32.2 (–), 32.3 (–), 59.8 (–), 59.9 (–), 60.7 (–), 60.9 (–), 74.5 (+), 75.2 (+), 76.4 (+), 76.6 (+), 78.6 (+), 78.8 (+), 80.8 (+), 81.2 (+), 99.1 (+), 99.9 (+), 100.1 (+), 101.0 (+); HRMS (FAB^+) calcd for $C_{19}H_{40}D_2O_3SiNa$ [$(M+Na)^+$] 371.2926, found 371.2923.

3,4-Bis[(*tert*-butyldimethylsilyl)oxy]-6-[(4-methoxybenzyl)oxy]hexan-1,1-d_2-1-ol (16)



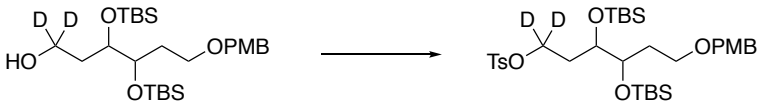
13 **14**, R = H; **15**, R = TBS **16**

According to the conversion of **1a** to **2a** described in the text, epoxy alcohol **13** (254 mg, 0.818 mmol) in THF (2 mL) was added to a mixture of oil-free NaH (prepared by washing NaH (60% wt% in mineral oil, 264 mg, 6.60 mmol) with hexane) and DMSO-d_6 (1.40 mL, 19.8 mmol). The mixture was stirred at rt for 2 h to afford diol **14** (144 mg, 69%): liquid; R_f 0.25 (hexane/EtOAc 2:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.64–1.96 (m, 2 H), 2.57 (d, J = 4.2 Hz, 0.5 H), 2.73 (d, J = 4.5 Hz, 0.5 H), 3.26 (d, J = 3.0 Hz, 0.5 H), 3.28 (d, J = 3.3 Hz, 0.5 H), 3.53–3.89 (m, 3 H), 3.81 (s, 3 H), 3.92–4.00 (m, 0.5 H), 4.09–4.17 (m, 0.5 H), 4.46 (s, 2 H), 5.76–5.96 (m, 1 H), 6.88 (d, J = 9.0 Hz, 2 H), 7.25 (d, J = 9.0 Hz, 2 H).

To an ice-cold solution of diol **14** (144 mg, 0.566 mmol) in CH_2Cl_2 (2 mL) were added 2,6-lutidine (0.80 mL, 6.91 mmol) and TBSOTf (0.70 mL, 3.05 mmol). The solution was stirred at rt for 3.5 h and diluted with saturated $NaHCO_3$. The resulting mixture was extracted with CH_2Cl_2 twice. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc) to afford **15** (239 mg, 87%): liquid; R_f 0.61, 0.56 (hexane/EtOAc 15:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.04~+0.16 (m, 12 H), 0.80–1.00 (m, 18 H), 1.24–2.02 (m, 2 H), 3.46–3.86 (m, 3 H), 3.80 (s, 3 H), 3.96–4.02 (m, 0.5 H), 4.13–4.18 (m, 0.5 H), 4.34–4.46 (m, 2 H), 5.74–5.84 (m, 0.5 H), 5.92–6.02 (m, 0.5 H), 6.86 (d, J = 8.7 Hz, 1 H), 6.87 (d, J = 8.7 Hz, 1 H), 7.22–7.29 (m, 2 H).

To an ice-cold solution of olefin **15** (56 mg, 0.12 mmol) was added dropwise $(Sia)_2BH$ (0.50 M in THF, 2.0 mL, 1.00 mmol), freshly prepared by mixing BH_3·THF (1.0 M in THF, 2.3 mL, 2.30 mmol) and 2-methyl-2-butene (2.0 M in THF, 2.3 mL, 4.60 mmol) at 0 °C for 30 min. The solution was stirred at rt for 1 h, and aqueous 2 N NaOH (2.0 mL, 4.00 mmol) and H_2O_2 (35 wt% in H_2O, 0.35 mL, 4.01 mmol) were added. The mixture was stirred at 0 °C to rt for 1 h and extracted with Et_2O twice. The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated to give a residue, which was purified by chromatography on silica gel (hexane/EtOAc) to afford alcohol **16** (37 mg, 64%): liquid; R_f 0.47, 0.40 (hexane/EtOAc 5:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.05, 0.07, 0.08, 0.10, and 0.12 (5 s, total 12 H), 0.87, 0.88, 0.89, and 0.90 (4 s, total 18 H), 1.52–2.17 (m, 4 H), 2.46 (br s, 0.3 H), 2.70 (br s, 0.7 H), 3.43–3.58 (m, 2 H), 3.72–3.92 (m, 2 H), 3.81 (s, 3 H), 4.36–4.47 (m, 2 H), 6.86 (d, J = 8.7 Hz, 0.6 H), 6.87 (d, J = 8.7 Hz, 1.4 H), 7.25 (d, J = 8.7 Hz, 2 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.9 (+), –4.84 (+), –4.76 (+), –4.2 (+), –4.1 (+), –4.0 (+), –3.9 (+), 18.3 (–), 25.9 (+), 26.08 (+), 26.14 (+), 30.5 (–), 33.9 (–), 34.1 (–), 34.7 (–), 55.4 (+), 66.8 (–), 67.0 (–), 71.8 (+), 72.3 (–), 72.7 (–), 73.8 (+), 74.1 (+), 113.7 (+), 113.8 (+), 129.1 (+), 129.3 (+), 130.6 (–), 159.2 (–); HRMS (FAB^+) calcd for $C_{26}H_{49}D_2O_5Si_2$ $[(M+H)^+]$ 501.3401, found 501.3407.

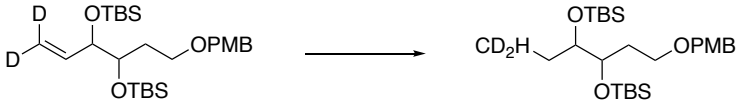
3,4-Bis[(*tert*-butyldimethylsilyl)oxy]-6-[(4-methoxybenzyl)oxy]hexyl-1,1-d_2-4-methylbenzenesulfonate (17)



16 **17**

To an ice-cold solution of alcohol **16** (668 mg, 1.33 mmol), Et_3N (0.40 mL, 2.87 mmol), and DMAP (17.0 mg, 0.139 mmol) in CH_2Cl_2 (4 mL) were added TsCl (398 mg, 2.09 mmol). The solution was stirred at rt for 1.5 h and diluted with saturated $NaHCO_3$ at 0 °C. The resulting mixture was extracted with CH_2Cl_2 twice. The combined extracts were dried over $MgSO_4$ and concentrated to afford a residual oil, which was purified by chromatography on silica gel (hexane/EtOAc) to give tosylate **17** (763 mg, 87%): liquid; R_f 0.34, 0.28 (hexane/EtOAc 10:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.05~+0.04 (m, 12 H), 0.77–0.92 (m, 18 H), 1.20–2.08 (m, 4 H), 2.44 (s, 3 H), 3.38–3.54 (m, 2 H), 3.64–3.86 (m, 2 H), 3.80 and 3.81 (2 s, total 3 H), 4.39 (s, 2 H), 6.82–6.90 (m, 2 H), 7.18–7.28 (m, 2 H), 7.32 (d, J = 8.1 Hz, 2 H), 7.77 (d, J = 8.1 Hz, 2 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –5.1 (+), –5.0 (+), –4.9 (+), –4.21 (+), –4.15 (+), –4.0 (+), –3.9 (+), 17.9 (–), 18.16 (–), 18.20 (–), 21.7 (+), 25.79 (+), 25.82 (+), 26.0 (+), 29.8 (–), 30.1 (–), 31.7 (–), 33.9 (–), 55.3 (+), 66.7 (–), 67.0 (–), 70.6 (+), 71.0 (+), 72.4 (–), 72.7 (–), 73.9 (+), 77.3 (+), 113.7 (+), 113.8 (+), 127.9 (+), 128.0 (+), 129.0 (+), 129.3 (+), 129.8 (+), 130.5 (–), 130.8 (–), 133.3 (–), 144.7 (–), 159.0 (–), 159.2 (–); HRMS (FAB$^+$) calcd for $C_{33}H_{55}D_2O_7SSi_2$ [(M+H)$^+$] 655.3489, found 655.3471.

5-(Ethyl-2,2-*d*$_2$)-6-{2-[(4-methoxybenzyl)oxy]ethyl}-2,2,3,3,8,8,9,9-octamethyl-4,7-dioxa-3,8-disiladecane (18)



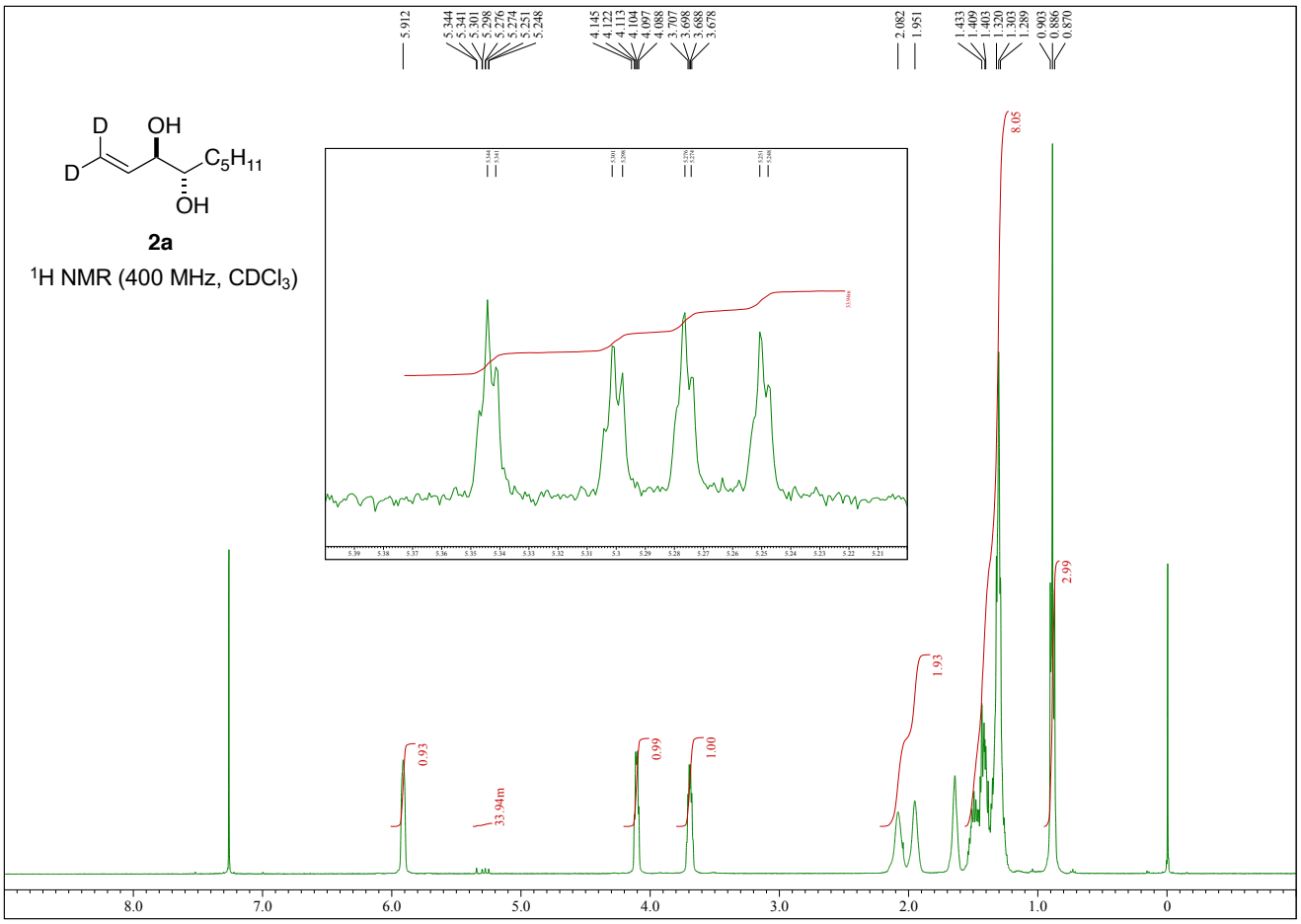
15 **18**

A mixture of olefin **15** (39 mg, 0.081 mmol) and 10% Pd/C (9 mg, 0.085 mmol) in EtOAc (0.5 mL) under hydrogen was stirred at rt for 2.5 h. The resulting mixture was filtered through a pad of silica gel and concentrated to give **18** (38 mg, 96%): liquid; R_f 0.56 (hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.01~+0.16 (m, 12 H), 0.86, 0.87, 0.88, 0.89 (4 s, total 18 H), 1.22–2.08 (m, 5 H), 3.40–3.58 (m, 3 H), 3.68–3.82 (m, 1 H),

3.80 (s, 3 H), 4.34–4.46 (m, 2 H), 6.86 (d, J = 8.7 Hz, 0.6 H), 6.87 (d, J = 8.7 Hz, 1.4 H), 7.25 (d, J = 8.7 Hz, 2 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.7 (+), –4.5 (+), –4.2 (+), –4.1 (+), –4.0 (+), –3.9 (+), 18.0 (–), 18.1 (–), 18.28 (–), 18.34 (–), 25.88 (+), 25.95 (+), 26.01 (+), 26.11 (+), 30.4 (–), 32.9 (–), 35.7 (–), 55.3 (+), 67.1 (–), 67.5 (–), 72.0 (+), 72.3 (–), 72.6 (–), 72.8 (+), 76.9 (+), 78.0 (+), 113.7 (+), 113.8 (+), 129.1 (+), 129.2 (+), 129.3 (+), 130.8 (–), 130.96 (–), 131.01 (–), 159.0 (–), 159.1 (–).

Reference

S1. Y. Nanba, R. Shinohara, M. Morita, and Y. Kobayashi, *Org. Biomol. Chem*., 2017, **15**, 8614.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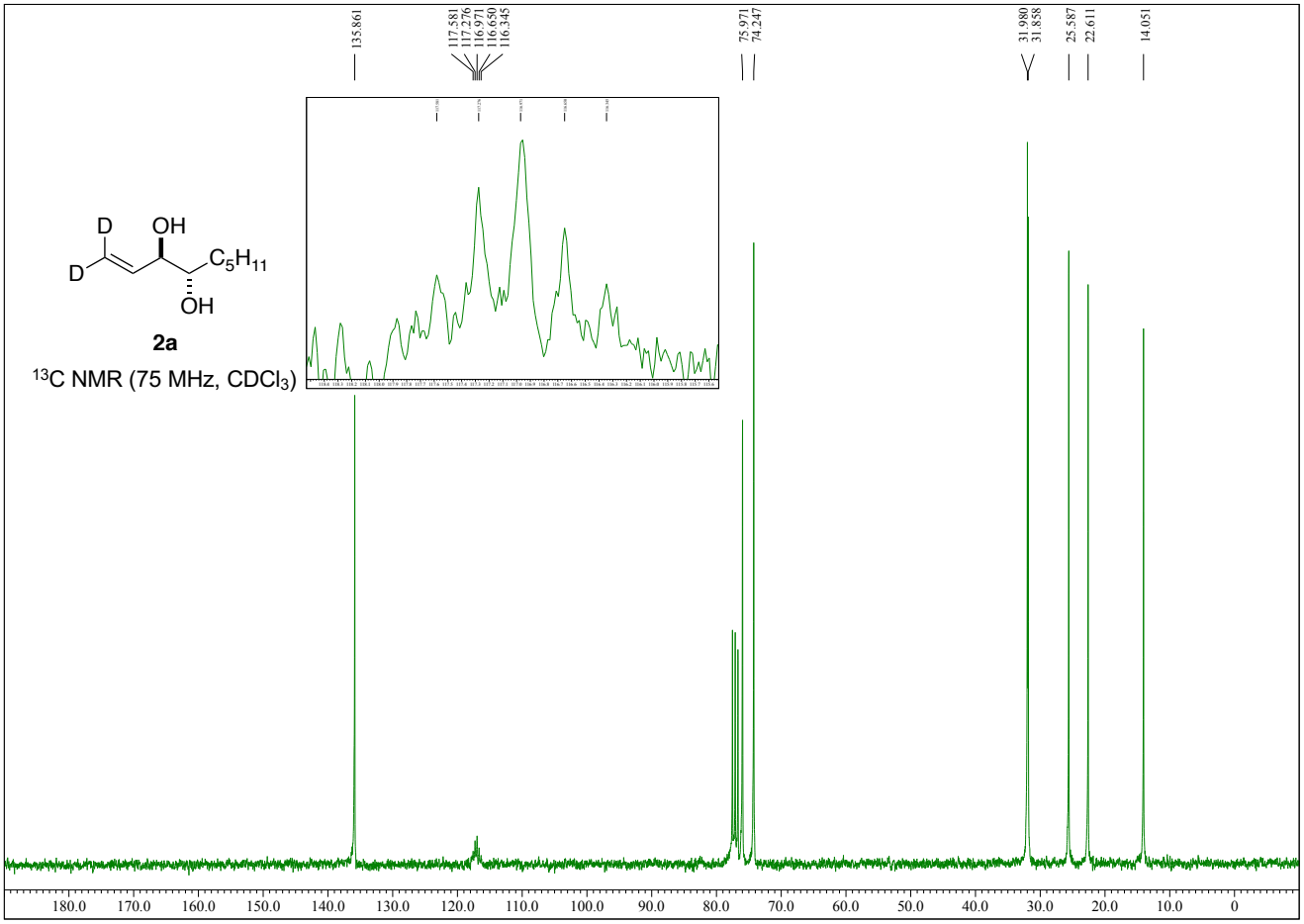
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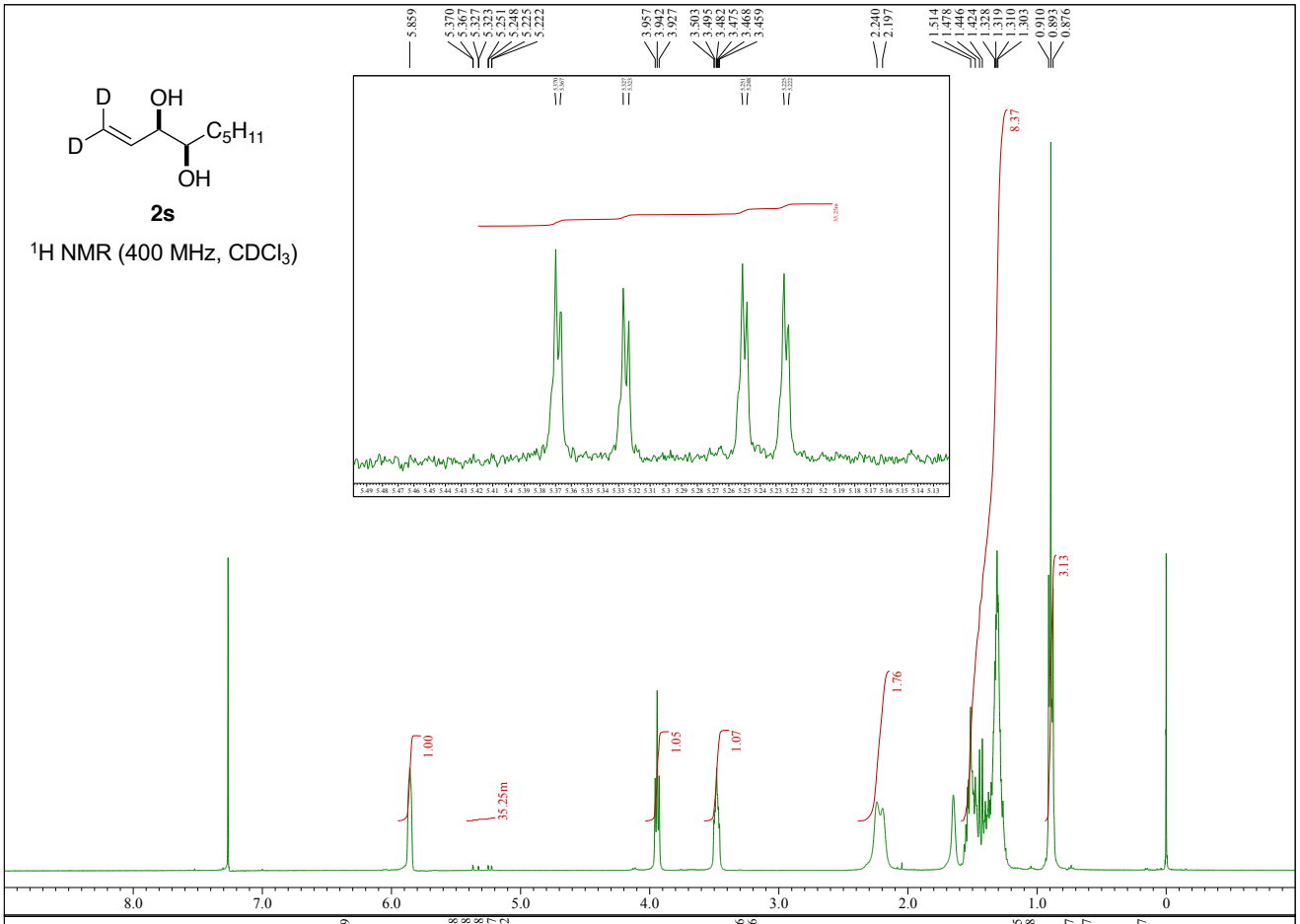
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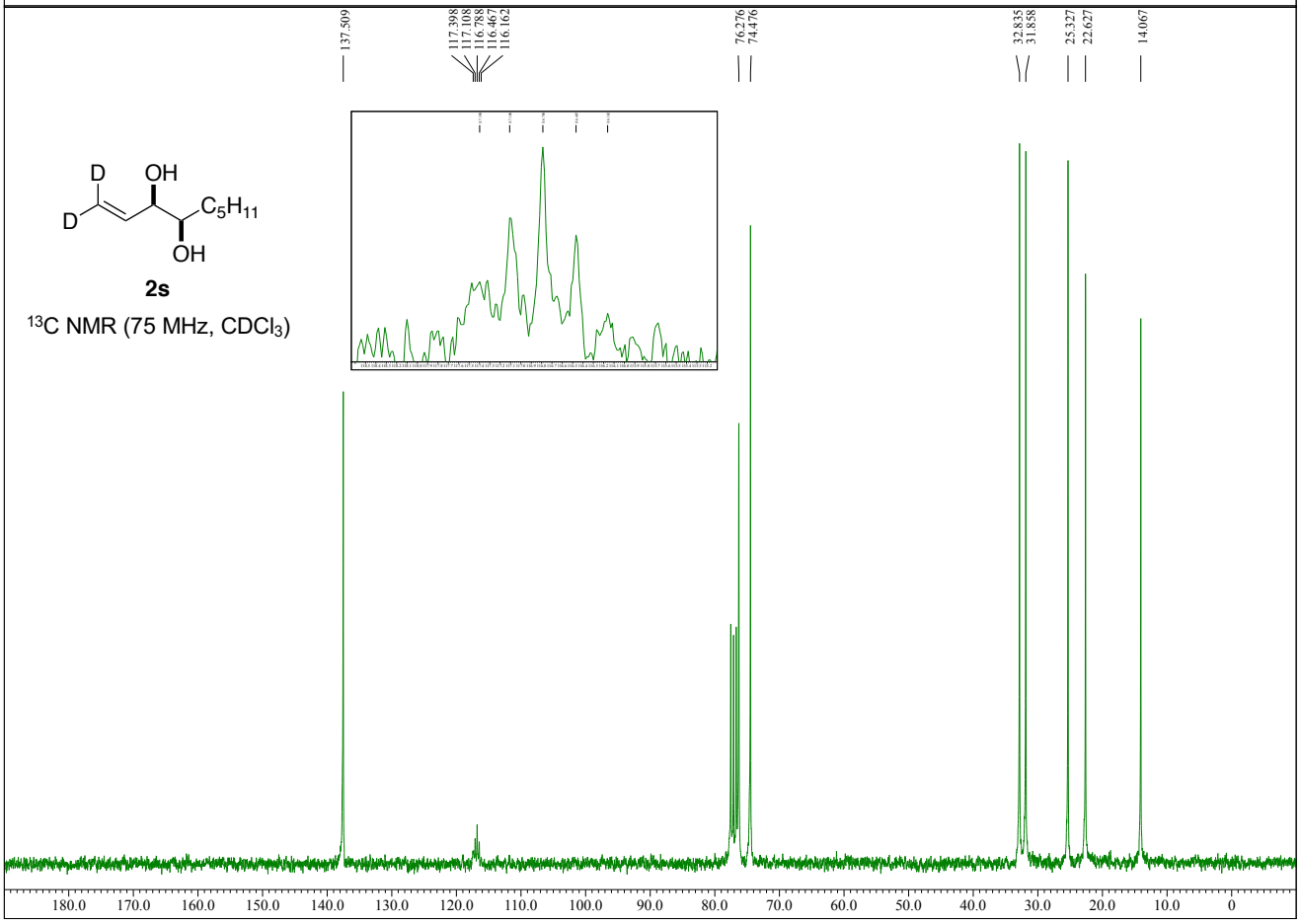
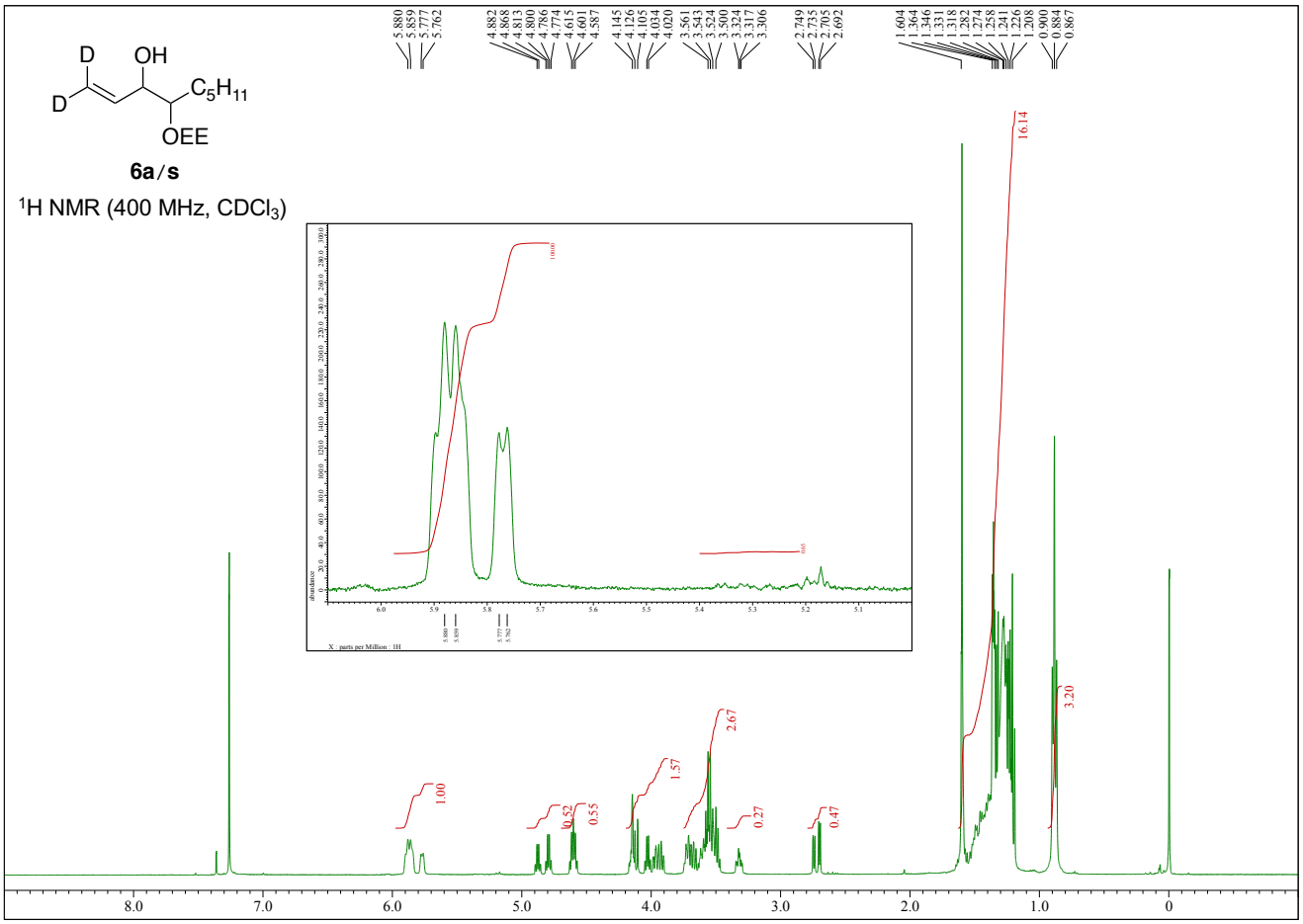
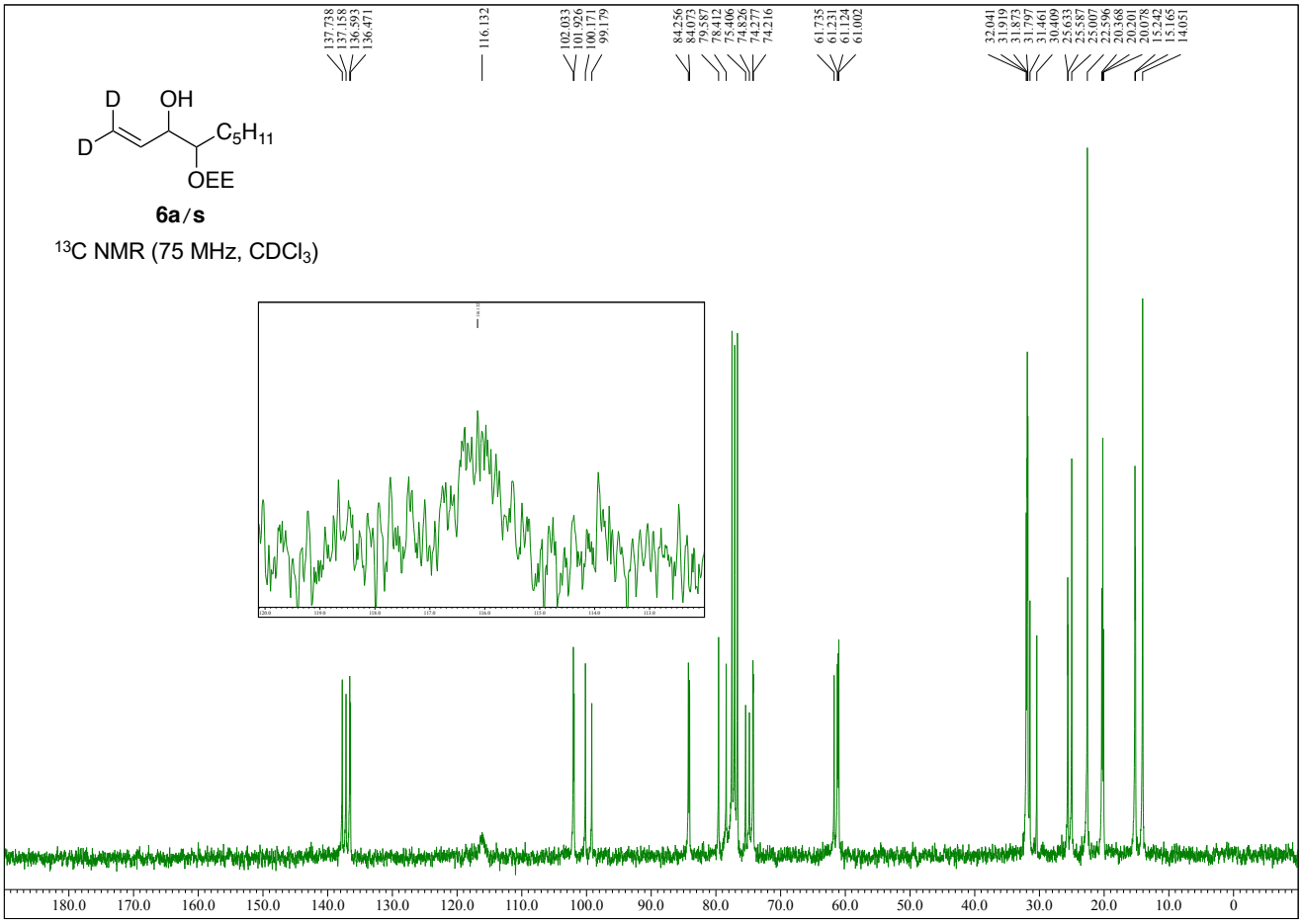
C_5H_{11}
OH
2s
^{1}H NMR (400 MHz, $CDCl_3$)
5.859
5.370
5.367
5.327
5.323
5.251
5.248
5.225
5.222
3.957
3.947
3.927
3.503
3.495
3.482
3.475
3.468
3.459
2.240
2.197
1.514
1.478
1.446
1.424
1.328
1.319
1.310
1.303
0.910
0.893
0.876
8.37
3.13
1.76
1.00
35.25m
1.05
1.07
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


D
OH
D
C_5H_{11}
OH
2s
^{13}C NMR (75 MHz, $CDCl_3$)
137.509
117.398
117.108
116.788
116.467
116.162
76.276
74.476
32.835
31.858
25.327
22.627
14.067
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0



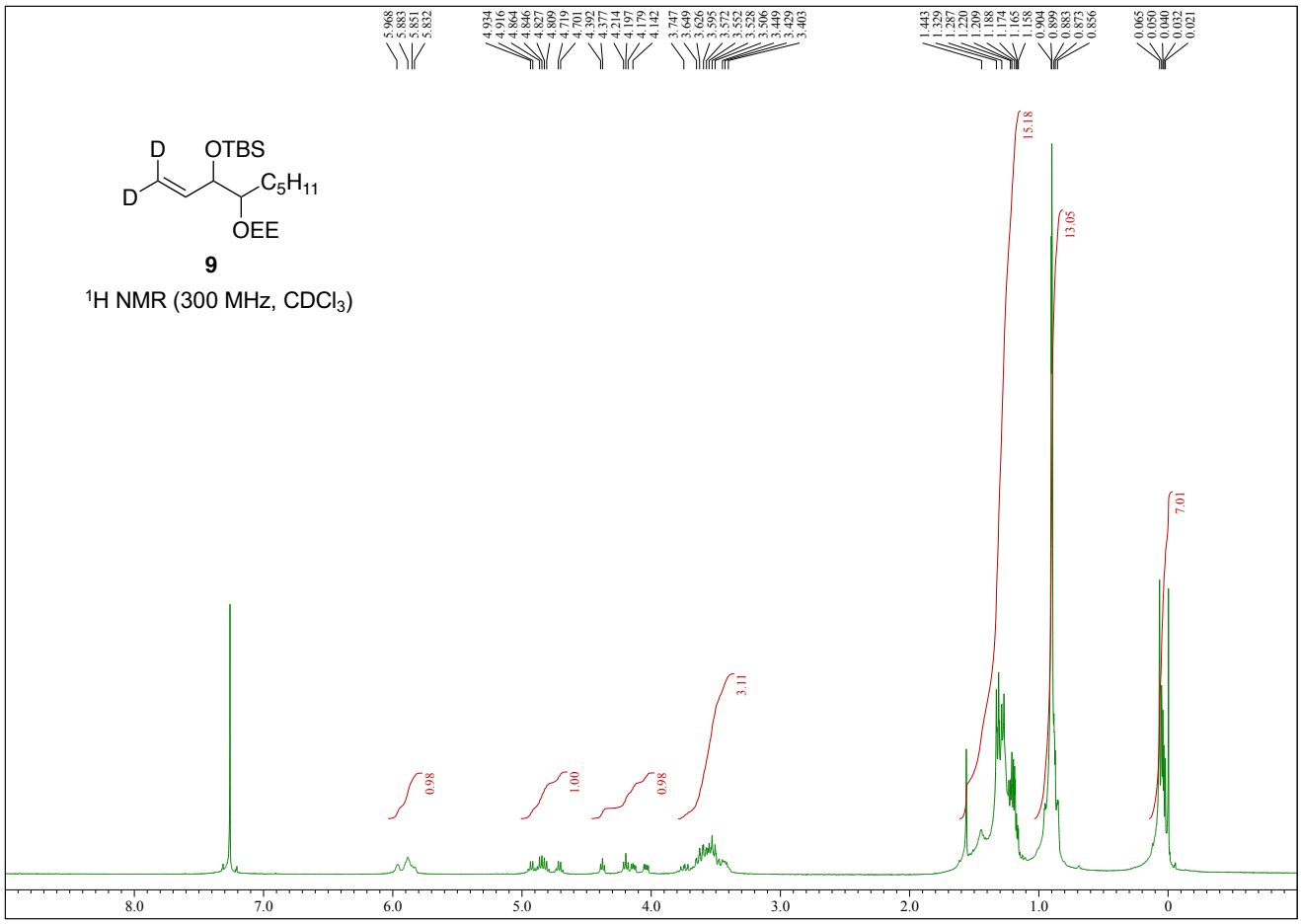
6a/s

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



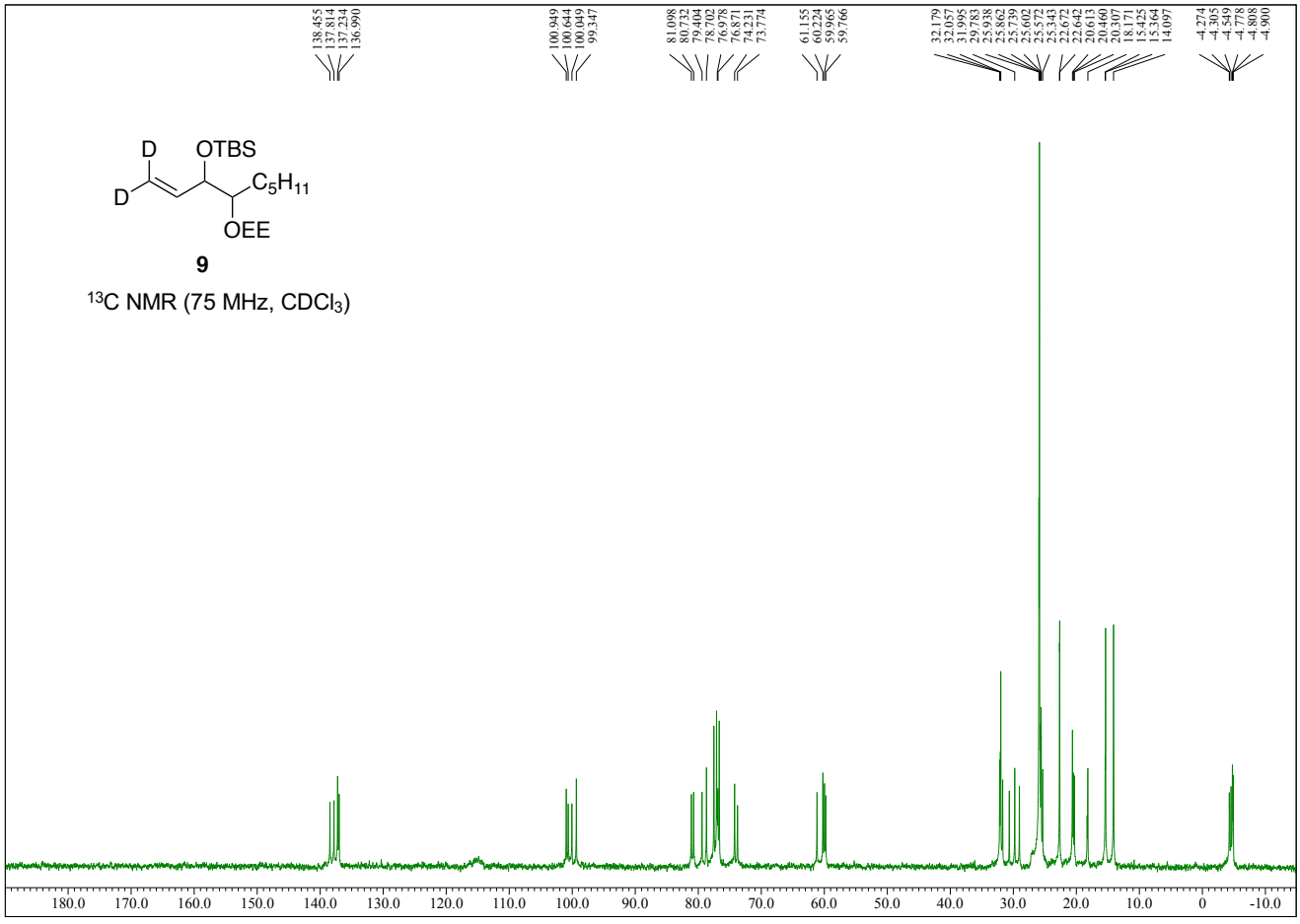
6a/s

^{13}C NMR (75 MHz, $CDCl_3$)



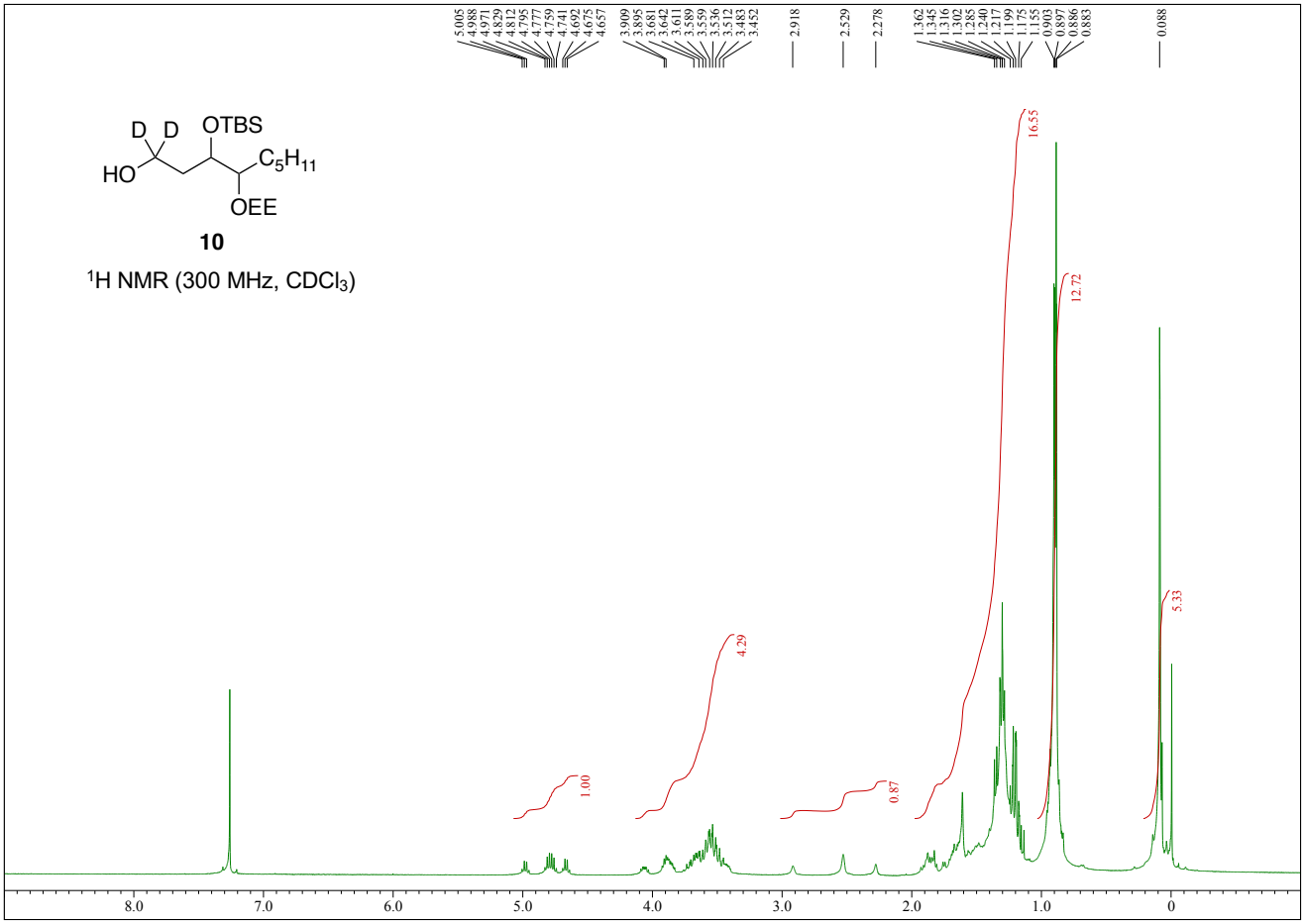
9

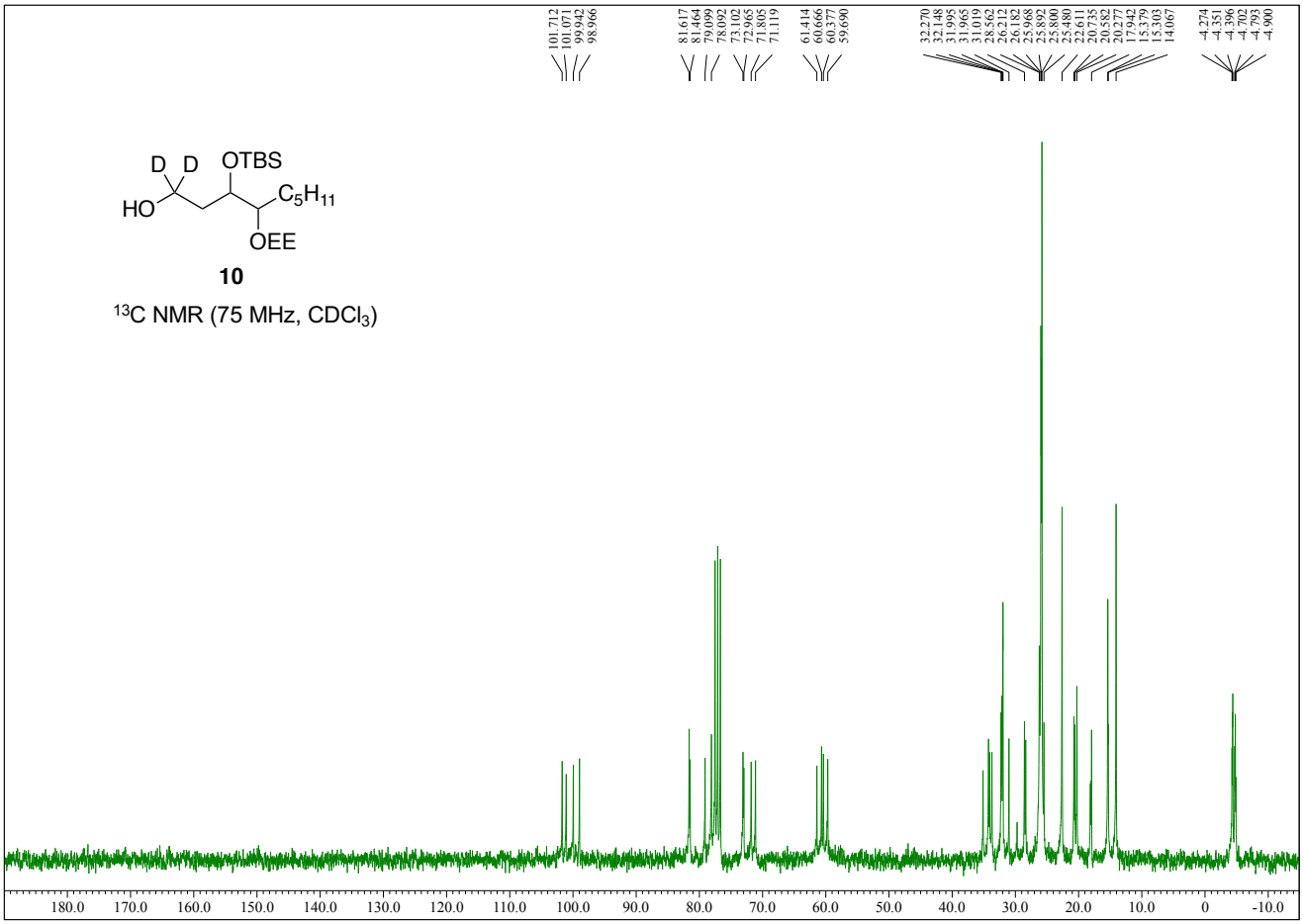
^{1}H NMR (300 MHz, $CDCl_3$)

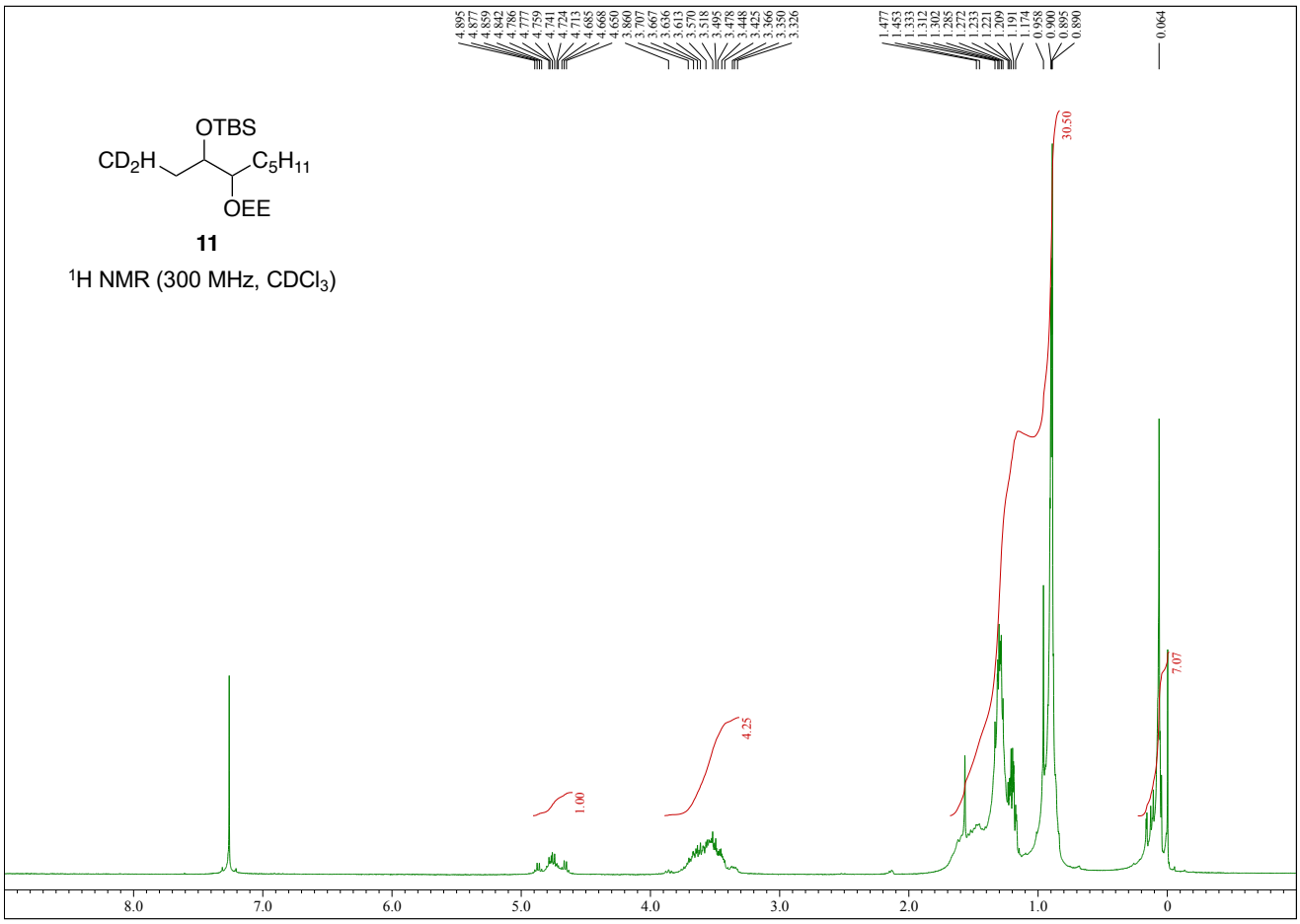


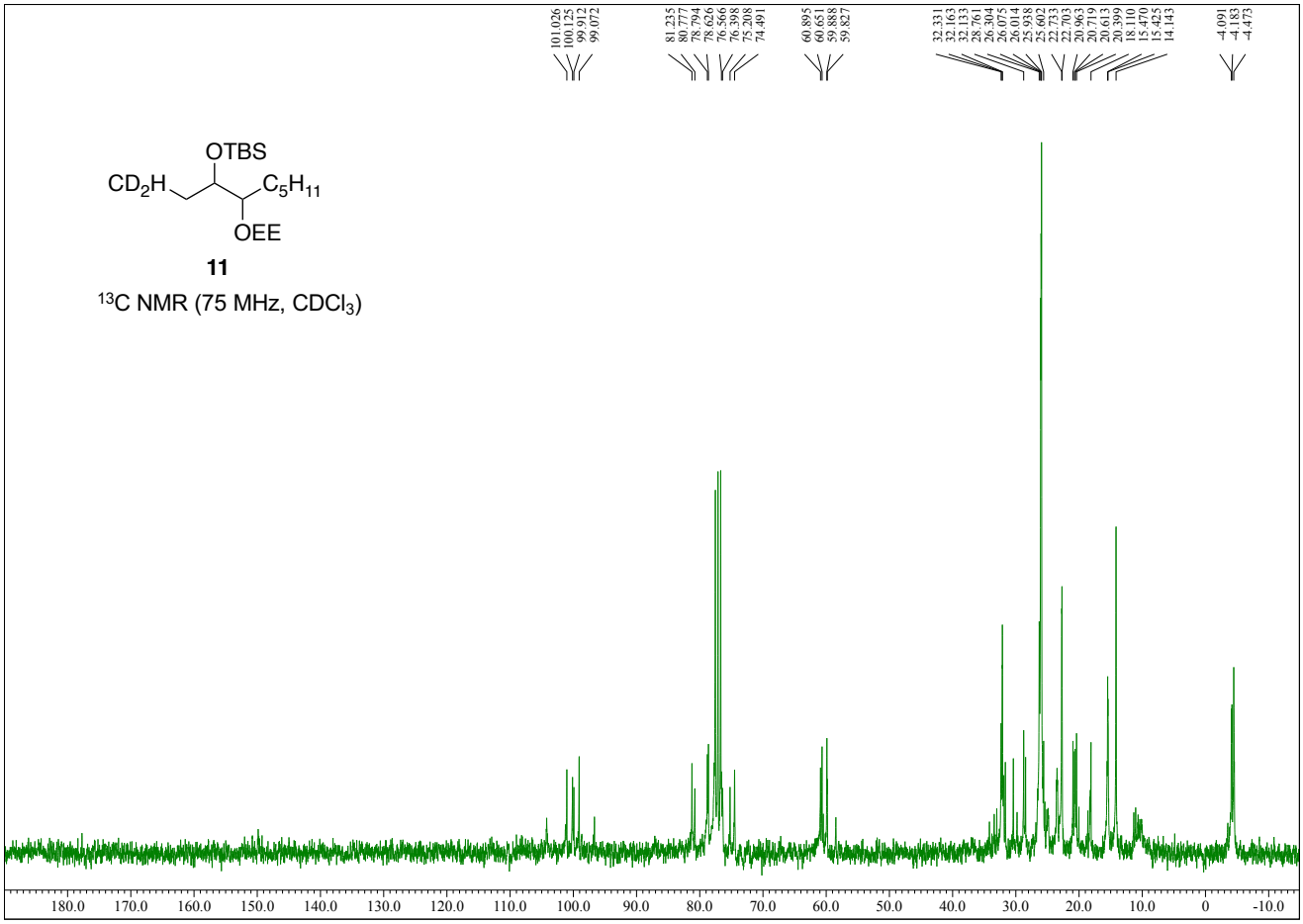
9

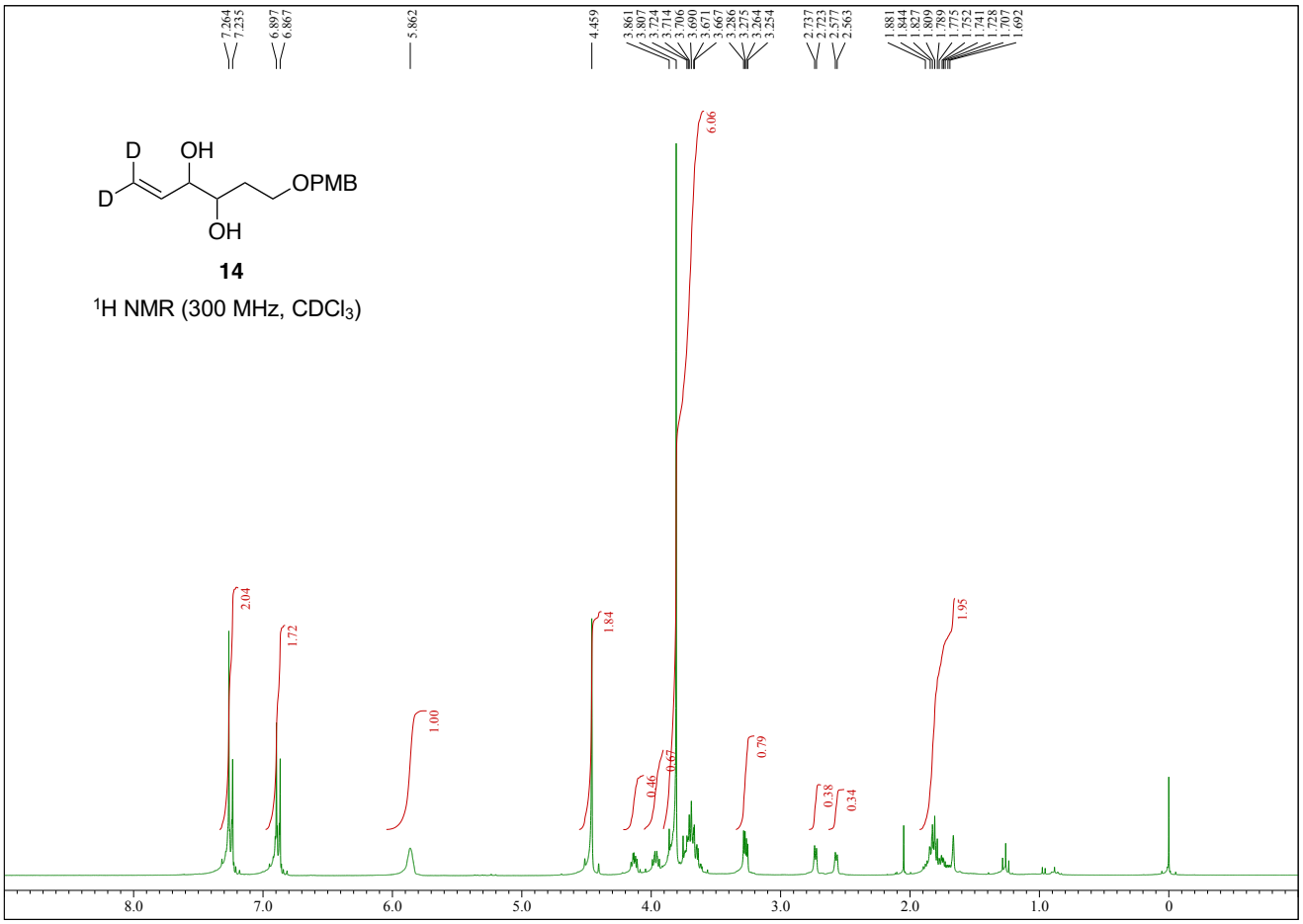
^{13}C NMR (75 MHz, $CDCl_3$)


D D OTBS
HO
C_5H_{11}
OEE
10
^{1}H NMR (300 MHz, $CDCl_3$)
16.55
12.72
5.33
4.29
1.00
0.87


D D OTBS
HO
C_5H_{11}
OEE
10
^{13}C NMR (75 MHz, $CDCl_3$)

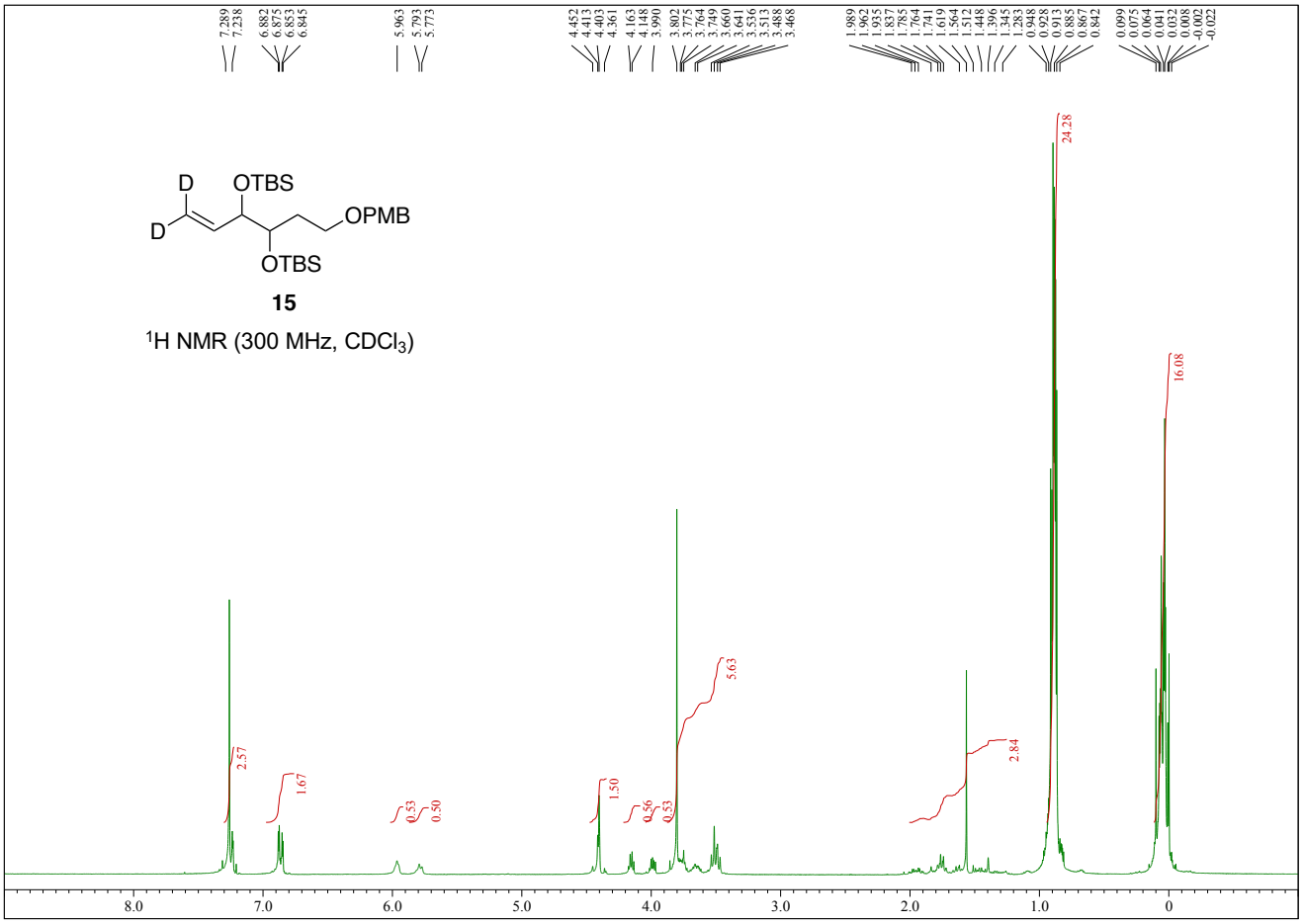

OTBS
CD2H
C5H11
OEE
11
1H NMR (300 MHz, CDCl3)
4.895
4.877
4.859
4.842
4.786
4.777
4.759
4.741
4.724
4.713
4.685
4.668
4.650
4.460
3.707
3.667
3.636
3.613
3.570
3.518
3.495
3.478
3.448
3.425
3.366
3.350
3.326
1.477
1.453
1.333
1.312
1.302
1.285
1.272
1.253
1.231
1.209
1.191
1.174
0.958
0.900
0.895
0.890
0.064
30.50
7.07
4.25
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


OTBS
CD2H
C5H11
OEE
11
13C NMR (75 MHz, CDCl3)
101.026
100.125
99.912
99.072
81.235
80.777
78.794
78.626
76.566
76.398
75.208
74.491
60.895
60.651
59.888
59.827
32.331
32.163
32.133
28.761
26.804
26.075
26.014
25.938
25.602
22.733
22.703
20.963
20.719
20.613
20.399
18.110
15.470
15.425
14.143
-4.091
-4.183
-4.473
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0



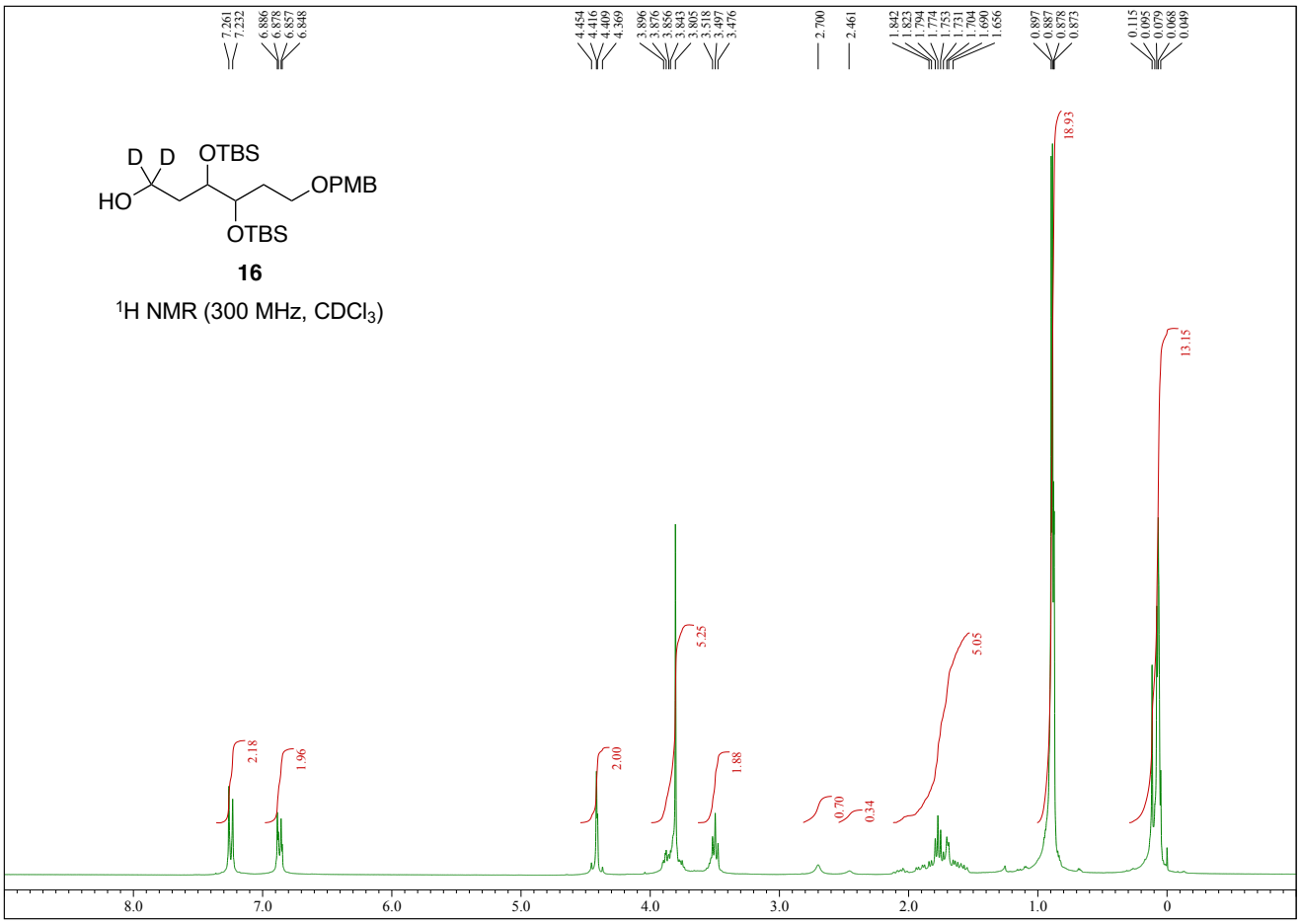
14

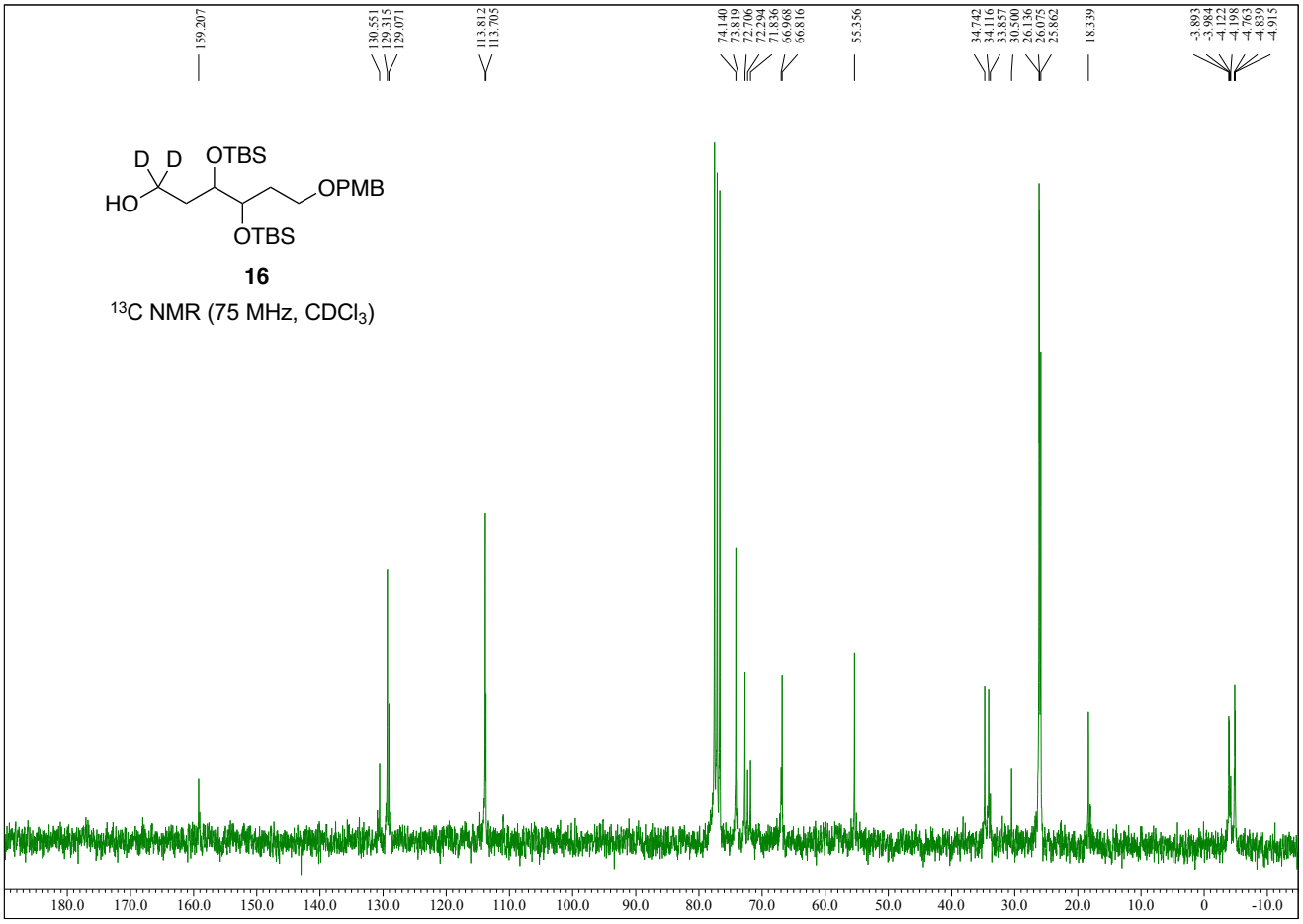
^{1}H NMR (300 MHz, $CDCl_3$)

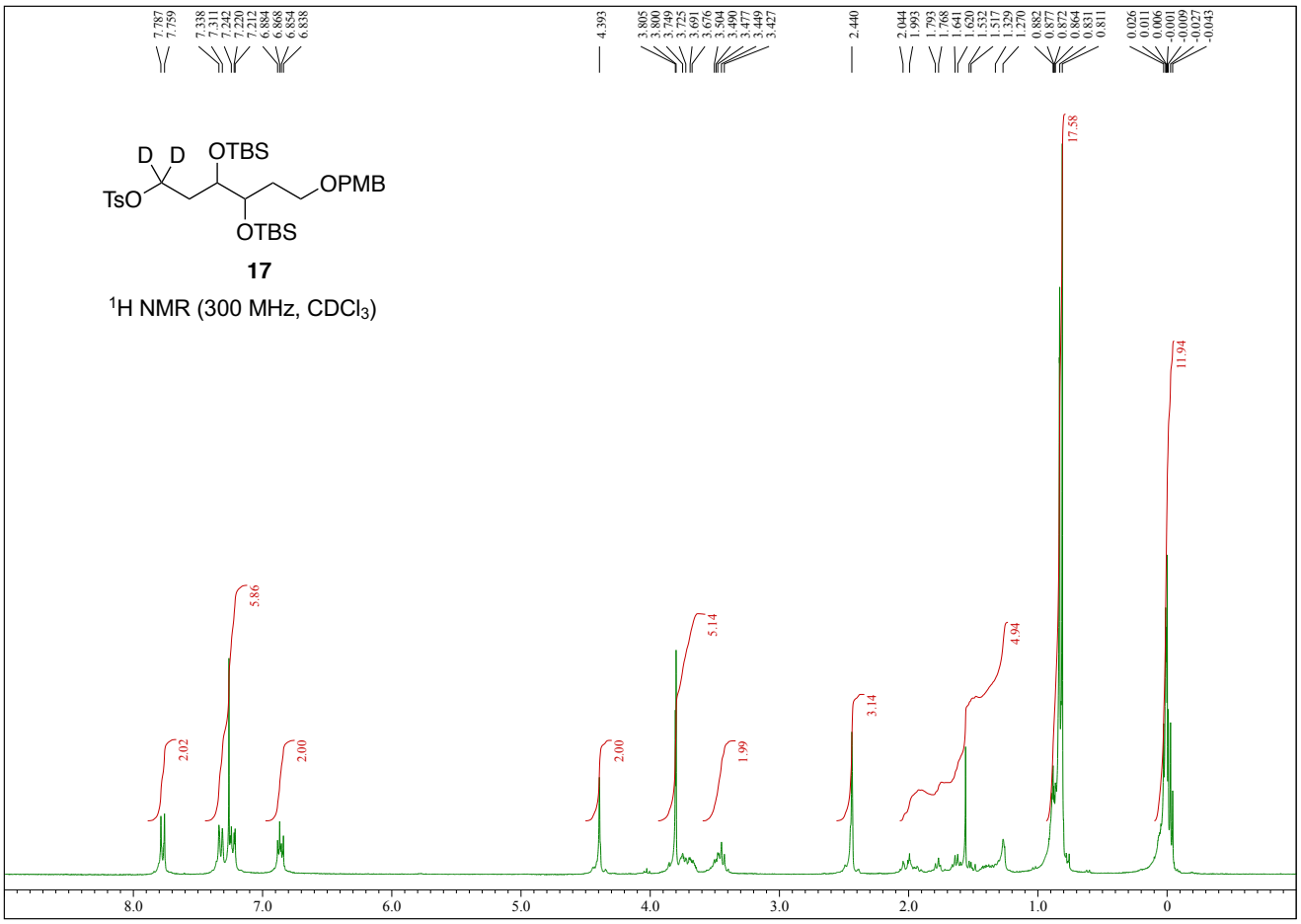


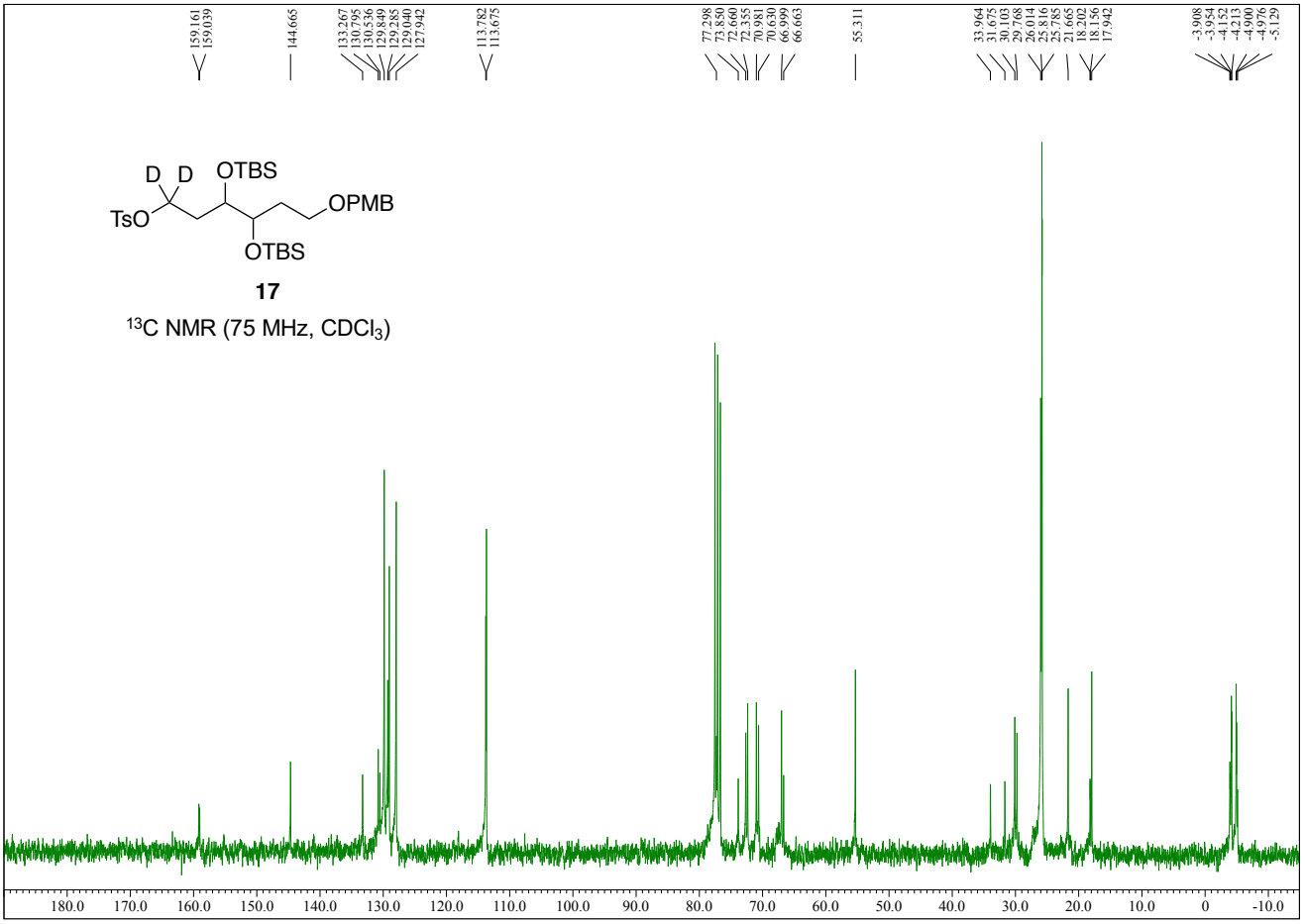
15

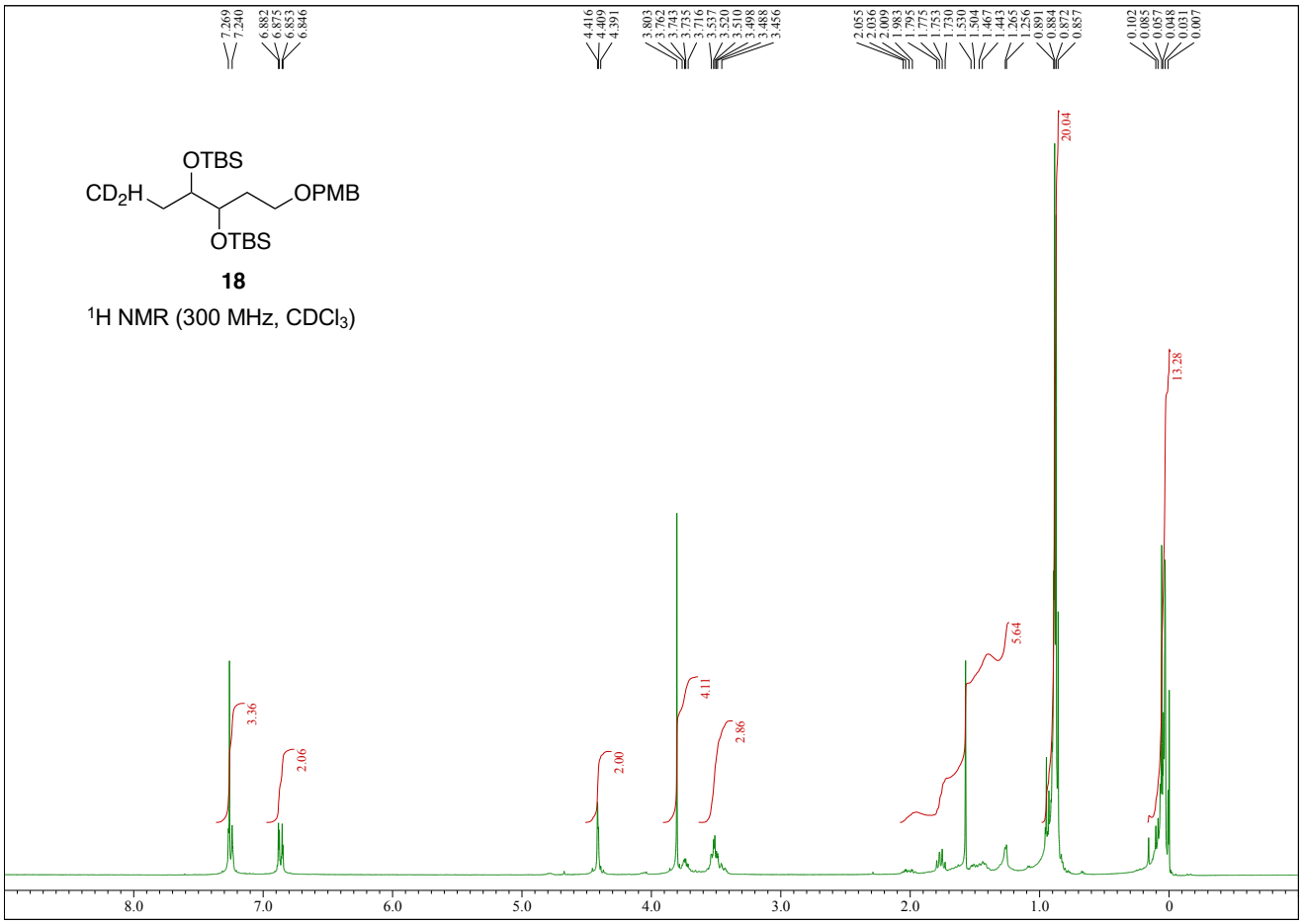
^{1}H NMR (300 MHz, $CDCl_3$)

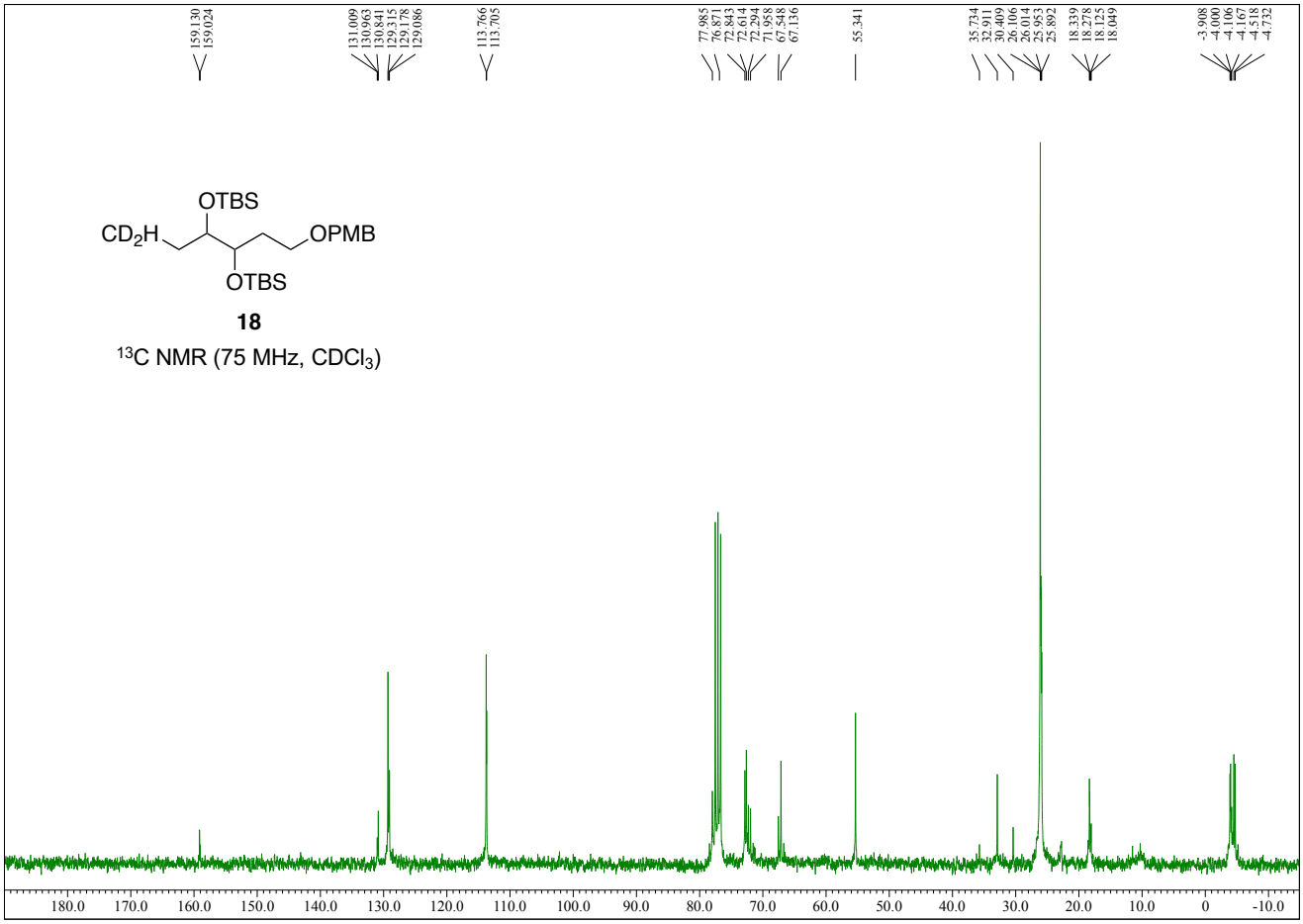

D D OTBS
HO OPMB
OTBS
16
1H NMR (300 MHz, CDCl3)


D D OTBS
HO OPMB
OTBS
16
13C NMR (75 MHz, CDCl3)


D D OTBS
TsO
OPMB
OTBS
17
1H NMR (300 MHz, CDCl3)


D D OTBS
TsO
OPMB
OTBS
17
13C NMR (75 MHz, CDCl3)


OTBS
CD2H
OPMB
OTBS
18
1H NMR (300 MHz, CDCl3)
7.269
7.240
6.882
6.875
6.853
6.846
4.416
4.409
4.391
3.803
3.762
3.743
3.735
3.716
3.577
3.520
3.510
3.498
3.488
3.456
2.055
2.036
2.009
1.983
1.795
1.775
1.753
1.730
1.530
1.504
1.467
1.443
1.265
1.256
0.891
0.884
0.872
0.857
0.102
0.085
0.057
0.048
0.031
0.007
20.04
13.28
5.64
4.11
3.36
2.86
2.06
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


OTBS
CD2H
OPMB
OTBS
18
13C NMR (75 MHz, CDCl3)
159.130
159.024
131.009
130.963
130.841
129.315
129.178
129.086
113.766
113.705
77.985
76.871
72.843
72.614
72.294
71.958
67.548
67.136
55.341
35.734
32.911
30.409
26.106
26.014
25.953
25.892
18.339
18.278
18.175
18.049
-3.908
-4.000
-4.106
-4.167
-4.518
-4.732
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0