Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Stereoselective ozonolysis of TMS-substituted allylic alcohol derivatives and synthesis of 14*R*,15*S*- and 14*S*,15*S*-diHETE

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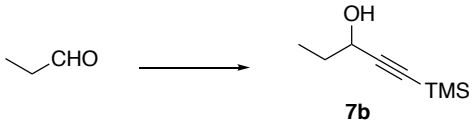
Experimental

General methods for ESI

The ^{1}H (300 and 400 MHz) and ^{13}C NMR (75 and 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 EI and FAB ionization modes. The solvents that were distilled prior to use were THF (from Na/benzophenone), Et_2O (from Na/benzophenone) and CH_2Cl_2 (from CaH_2). The reaction products were purified by chromatography on silica gel (Kanto, spherical silica gel 60N). Following reactions are described in the ESI: synthesis of **9b**, **9c**, **13b** and **13c**; ozonolysis and subsequent conversion to diols **11b**, **11c**, **15b** and **15c**; synthesis of **24** and **25**.

Preparation of 9b,c and 13b,c

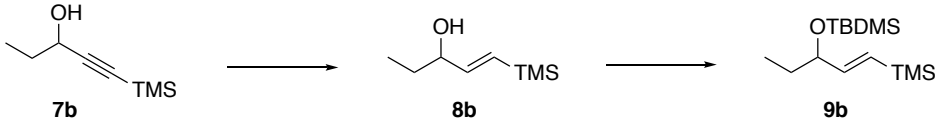
1-(Trimethylsilyl)pent-1-yn-3-ol (7b)



7b

According to the procedure for the synthesis of **7a**, a solution of propionaldehyde (467 mg, 8.04 mmol, 1.0 equiv) in THF (10 mL) was added to a solution of trimethylsilylacetylene (1.66 mL, 12.0 mmol, 1.5 equiv) and *n*-BuLi (6.0 mL, 1.6 M in hexane, 9.6 mmol, 1.2 equiv) in THF (16 mL) at –78 °C and the solution was warmed to rt over 3 h to afford alcohol **7b** (1.09 g, 87%): colorless liquid; R_f 0.38 (hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 1.00 (t, J = 7.5 Hz, 3 H), 1.64–1.77 (m, 2 H), 1.80 (d, J = 5.7 Hz, 1 H), 4.31 (dt, J = 5.7, 6.3 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.15, 9.4, 30.6, 63.8, 89.0, 106.9. The ^{1}H and ^{13}C NMR spectra were identical with those reported.[S1]

(*E*)-*tert*-Butyldimethyl[(1-(trimethylsilyl)pent-1-en-3-yl)oxy]silane (9b)

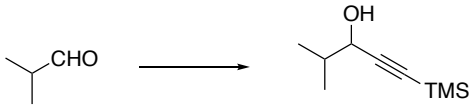


7b **8b** **9b**

According to the procedure for the synthesis of **9a** from **7a**, Red-Al (1.90 mL, 3.6 M in toluene, 6.84 mmol, 2.0 equiv) was added to an ice-cold solution of alcohol **7b** (527 mg, 3.37 mmol, 1.0 equiv) in Et_2O (7 mL), and the solution was stirred at rt for 3 h to afford allylic alcohol **8b** (465 mg, 87%). A solution of **8b** (197 mg, 1.24 mmol, 1.0 equiv), TBDMSCl (294 mg, 1.95 mmol, 1.6 equiv) and imidazole (175 mg, 2.57 mmol, 2.1 equiv) in DMF (2.5 mL) was stirred at rt for 3 h to afford silyl ether **9b** (309 mg, 91%): colorless

liquid; R_f 0.90 (hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.02 (s, 3 H), 0.04 (s, 3 H), 0.05 (s, 9 H), 0.86 (t, J = 6.9 Hz, 3 H), 0.89 (s, 9 H), 1.48 (quint., J = 6.9 Hz, 2 H), 3.98 (q, J = 5.7 Hz, 1 H), 5.74 (d, J = 18.9 Hz, 1 H), 5.95 (dd, J = 18.9, 5.7 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.7 (+), –4.2 (+), –1.2 (+), 9.9 (+), 18.5 (–), 26.1 (+), 30.8 (–), 77.2 (+), 128.6 (+), 149.3 (+); HRMS (EI$^+$) calcd for $C_{14}H_{32}OSi_2$ [M$^+$] 272.1992, found 272.1992.

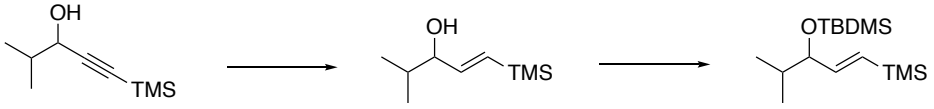
4-Methyl-1-(trimethylsilyl)pent-1-yn-3-ol (7c)



7c

According to the procedure for the synthesis of **7a**, a solution of isobutyraldehyde (580 mg, 8.06 mmol, 1.0 equiv) in THF (10 mL) was added to a solution of trimethylsilylacetylene (1.66 mL, 12.0 mmol, 1.5 equiv) and *n*-BuLi (6.0 mL, 1.6 M in hexane, 9.6 mmol, 1.2 equiv) in THF (16 mL) at –78 °C and the solution was warmed to rt over 3 h to afford alcohol **7c** (1.28 g, 93%): colorless liquid; R_f 0.45 (hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.17 (s, 9 H), 0.98 (d, J = 6.9 Hz, 3 H), 1.00 (d, J = 6.6 Hz, 3 H), 1.77 (d, J = 5.7 Hz, 1 H), 1.80–1.94 (m, 1 H), 4.15 (t, J = 5.7 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ –0.1, 17.4, 18.1, 34.3, 68.1, 89.9, 105.8. The ^{1}H NMR spectrum was revised. The ^{13}C NMR spectrum was identical with that reported.[S2]

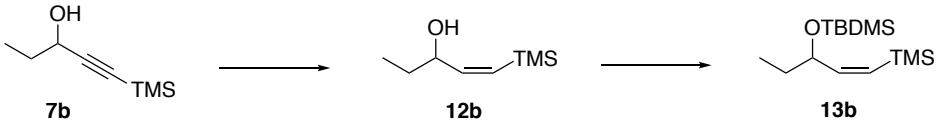
(*E*)-*tert*-Butyldimethyl[(4-methyl-1-(trimethylsilyl)pent-1-en-3-yl)oxy]silane (9c)



7c **8c** **9c**

According to the procedure for the synthesis of **9a** from **7a**, Red-Al (2.00 mL, 3.6 M in toluene, 7.20 mmol, 2.0 equiv) was added to an ice-cold solution of alcohol **7c** (605 mg, 3.55 mmol, 1.0 equiv) in Et_2O (7 mL), and the solution was stirred at rt for 3 h to produce allylic alcohol **8c** (491 mg, 80%). A solution of **8c** (172 mg, 0.995 mmol, 1.0 equiv), TBDMSCl (230 mg, 1.53 mmol, 1.5 equiv) and imidazole (141 mg, 2.07 mmol, 2.1 equiv) in DMF (2 mL) was stirred at rt for 3 h to afford silyl ether **9c** (237 mg, 83%): colorless liquid; R_f 0.88 (hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.02 (s, 3 H), 0.02 (s, 3 H), 0.06 (s, 9 H), 0.83 (d, J = 6.9 Hz, 3 H), 0.87 (d, J = 6.9 Hz, 3 H), 0.89 (s, 9 H), 1.64 (d of sept., J = 5.7, 6.9 Hz, 1 H), 3.76 (t, J = 5.7 Hz, 1 H), 5.73 (d, J = 18.9 Hz, 1 H), 5.94 (dd, J = 18.9, 6.0 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.8 (+), –4.0 (+), –1.2 (+), 18.0 (+), 18.4 (–), 18.7 (+), 26.0 (+), 34.4 (+), 81.1 (+), 129.9 (+), 148.2 (+); HRMS (EI$^+$) calcd for $C_{15}H_{34}OSi_2$ [M$^+$] 286.2148, found 286.2155.

(*Z*)-*tert*-Butyldimethyl[(1-(trimethylsilyl)pent-1-en-3-yl)oxy]silane (13b)

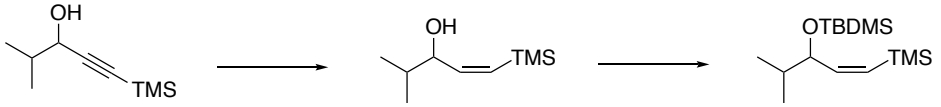


7b **12b** **13b**

According to the procedure for the synthesis of **13a** from **7a**, alcohol **7b** (536 mg, 3.43

mmol, 1.0 equiv) in MeOH (2 mL) was added to a mixture of $Ni(OAc)_2 \cdot 4H_2O$ (1.03 g, 4.14 mmol, 1.2 equiv), $NaBH_4$ (158 mg, 4.18 mmol, 1.2 equiv) and ethylenediamine (0.47 mL, 6.96 mmol, 2.0 equiv) in MeOH (5 mL), and the mixture was stirred at rt for 5 h under hydrogen to afford allylic alcohol **12b** (433 mg, 80%). A solution of **12b** (202 mg, 1.28 mmol, 1.0 equiv), TBDMSCl (291 mg, 1.93 mmol, 1.5 equiv) and imidazole (176 mg, 2.59 mmol, 2.0 equiv) in DMF (2.5 mL) was stirred at rt for 3 h to afford silyl ether **13b** (319 mg, 91%): colorless liquid; R_f 0.85 (hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.03 (s, 3 H), 0.05 (s, 3 H), 0.12 (s, 9 H), 0.88 (s, 9 H), 0.90 (t, J = 7.2 Hz, 3 H), 1.31–1.60 (m, 2 H), 4.15 (dt, J = 5.4, 8.4 Hz, 1 H), 5.44 (d, J = 14.7 Hz, 1 H), 6.21 (dd, J = 14.7, 8.4 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.4 (+), –3.9 (+), 0.5 (+), 10.1 (+), 18.3 (–), 26.0 (+), 31.9 (–), 74.6 (+), 127.4 (+), 152.4 (+); HRMS (EI$^+$) calcd for $C_{14}H_{32}OSi_2$ [M$^+$] 272.1992, found 272.1997.

(*Z*)-*tert*-Butyldimethyl[(4-methyl-1-(trimethylsilyl)pent-1-en-3-yl)oxy]silane (13c)

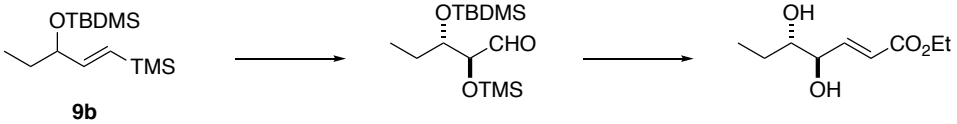


7c **12c** **13c**

According to the procedure for the synthesis of **13a** from **7a**, alcohol **7c** (498 mg, 2.92 mmol, 1.0 equiv) in MeOH (2 mL) was added to a mixture of $Ni(OAc)_2 \cdot 4H_2O$ (883 mg, 3.54 mmol, 1.2 equiv), $NaBH_4$ (134 mg, 3.54 mmol, 1.2 equiv) and ethylenediamine (0.40 mL, 5.92 mmol, 2.0 equiv) in MeOH (4 mL), and the mixture was stirred at rt for 8 h under hydrogen to afford allylic alcohol **12c** (384 mg, 76%). A solution of **12c** (340 mg, 1.97 mmol, 1.0 equiv), TBDMSCl (448 mg, 2.97 mmol, 1.5 equiv) and imidazole (271 mg, 3.98 mmol, 2.0 equiv) in DMF (4 mL) was stirred at rt for 3 h to afford silyl ether **13c** (521 mg, 92%): colorless liquid; R_f 0.85 (hexane/EtOAc 9:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.00 (s, 3 H), 0.04 (s, 3 H), 0.12 (s, 9 H), 0.879 (d, J = 6.3 Hz, 3 H), 0.88 (s, 9 H), 0.884 (d, J = 6.6 Hz, 3 H), 1.60 (d of sept., J = 4.8, 6.6 Hz, 1 H), 4.00 (dd, J = 9.0, 4.8 Hz, 1 H), 5.48 (d, J = 14.4 Hz, 1 H), 6.22 (dd, J = 14.4, 9.0 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –4.5 (+), –3.7 (+), 0.6 (+), 16.9 (+), 18.4 (–), 19.5 (+), 26.0 (+), 35.7 (+), 77.4 (+), 128.4 (+), 151.3 (+); HRMS (EI$^+$) calcd for $C_{15}H_{34}OSi_2$ [M$^+$] 286.2148, found 286.2147.

Ozonolysis and conversion to 11b,c and 15b,c

Ethyl (4*R,5*S**,*E*)-4,5-dihydroxyhept-2-enoate (11b)**

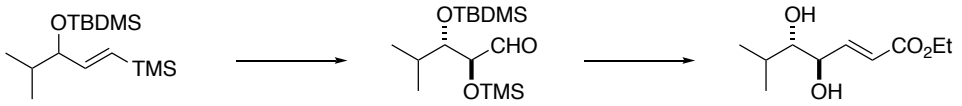


9b **10b** **11b**

According to the procedure for the synthesis of **11a** from **9a**, a solution of **9b** (*E*/*Z* 94:6 by ^{1}H NMR, 154 mg, 0.565 mmol, 1.0 equiv) in EtOAc (8 mL) at −78 °C was gently bubbled with O_3 in O_2 and then the product was treated with Ph_3P (713 mg, 2.72 mmol, 5 equiv) to afford aldehyde **10b**, which was dissolved in THF (1 mL) and added to a mixture of NaH (60 wt %, 30 mg, 0.75 mmol, 1.3 equiv) and $(EtO)_2P(O)CH_2CO_2Et$ (0.160 mL,

0.799 mmol, 1.4 equiv) in THF (2 mL). The mixture was stirred at rt for 1 h to afford the silyl ether of **11b**. A solution of the silyl ether of **11b** and TBAF (1.0 M in THF, 2.75 mL, 2.75 mmol, 5 equiv) in THF (6 mL) was stirred at rt for 1 h to afford a mixture of diol **11b** and the *syn* isomer **15b** (*anti*/*syn* 80:20 by ^{1}H NMR, 49 mg, 47% over three steps): colorless liquid; R_f 0.33 (hexane/EtOAc 1:1). The *anti* isomer **11b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (t, J = 7.2 Hz, 3 H), 1.28 (t, J = 7.2 Hz, 3 H), 1.46 (quint., J = 7.2 Hz, 2 H), 2.62 (br s, 1 H), 2.98 (br s, 1 H), 3.62–3.71 (m, 1 H), 4.19 (q, J = 7.2 Hz, 2 H), 4.27–4.34 (m, 1 H), 6.09 (d, J = 15.6 Hz, 1 H), 6.96 (dd, J = 15.6, 5.1 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 10.3 (+), 14.2 (+), 25.0 (–), 60.7 (–), 74.0 (+), 75.7 (+), 122.4 (+), 146.0 (+), 166.6 (–). The ^{1}H NMR spectrum was identical with that of the minor component in the diol derived from *Z*-olefin **13b**.

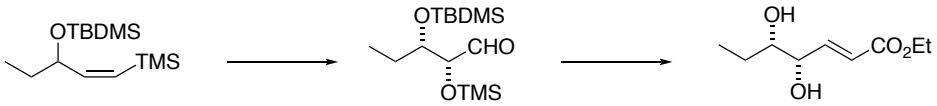
Ethyl (4*R,5*S**,*E*)-4,5-dihydroxy-6-methylhept-2-enoate (11c)**



9c **10c** **11c**

According to the procedure for the synthesis of **11a** from **9a**, a solution of silyl ether **9c** (*E*/*Z* 91:9 by ^{1}H NMR, 151 mg, 0.527 mmol, 1.0 equiv) in EtOAc (7 mL) at −78 °C was gently bubbled with O_3 in O_2 and then the product was treated with Ph_3P (674 mg, 2.57 mmol, 5 equiv) to afford aldehyde **10c**, which was dissolved in THF (1 mL) and added to a mixture of NaH (60 wt %, 29 mg, 0.725 mmol, 1.4 equiv) and $(EtO)_2P(O)CH_2CO_2Et$ (0.150 mL, 0.749 mmol, 1.4 equiv) in THF (2 mL). The mixture was stirred at rt for 2 h to afford the silyl ether of **11c**. A solution of the silyl ether of **11c** and TBAF (1.0 M in THF, 2.60 mL, 2.60 mmol, 5 equiv) in THF (5 mL) was stirred at rt for 1 h to afford a mixture of diol **11c** and the *syn* isomer **15c** (*anti*/*syn* 82:18 by ^{1}H NMR, 61 mg, 58% over three steps): colorless liquid; R_f 0.45 (hexane/EtOAc 1:1). The *anti* isomer **11c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (d, J = 6.9 Hz, 3 H), 0.97 (d, J = 6.9 Hz, 3 H), 1.26 (t, J = 7.2 Hz, 3 H), 1.66 (octet, J = 6.9 Hz, 1 H), 2.88 (br s, 1 H), 3.28–3.46 (m, 2 H), 4.16 (q, J = 7.2 Hz, 2 H), 4.30–4.39 (m, 1 H), 6.08 (d, J = 15.6 Hz, 1 H), 6.99 (dd, J = 15.6, 5.7 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 14.2 (+), 18.8 (+), 18.9 (+), 30.4 (+), 60.7 (–), 72.0 (+), 79.5 (+), 122.8 (+), 145.8 (+), 166.6 (–). The ^{1}H NMR spectrum was identical with that of the minor component in the diol derived from *Z*-olefin **13c**.

Ethyl (4*S,5*S**,*E*)-4,5-dihydroxyhept-2-enoate (15b)**

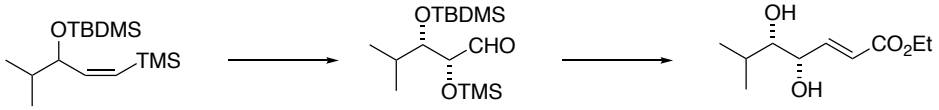


13b **14b** **15b**

According to the procedure for the synthesis of **11a** from **9a**, a solution of silyl ether **13b** (*Z*/*E* 96:4 by ^{1}H NMR, 153 mg, 0.561 mmol, 1.0 equiv) in EtOAc (8 mL) at −78 °C was gently bubbled with O_3 in O_2 and then the product was treated with Ph_3P (714 mg, 2.72 mmol, 5 equiv) to afford aldehyde **14b**, which was dissolved in THF (1 mL) and added to a mixture of NaH (60 wt %, 30 mg, 0.75 mmol, 1.3 equiv) and $(EtO)_2P(O)CH_2CO_2Et$ (0.160 mL, 0.799 mmol, 1.4 equiv) in THF (2 mL). The mixture was stirred at rt for 1 h to afford

the silyl ether of **15b**. A solution of the silyl ether of **15b** and TBAF (1.0 M in THF, 2.75 mL, 2.75 mmol, 5 equiv) in THF (6 mL) was stirred at rt for 1 h to afford a mixture of diol **15b** and the *anti* isomer **11b** (*syn*/*anti* 84:16 by ^{1}H NMR, 46 mg, 44% over three steps): colorless liquid; R_f 0.33 (hexane/EtOAc 1:1). The *syn* isomer **15b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.97 (t, J = 7.2 Hz, 3 H), 1.27 (t, J = 7.2 Hz, 3 H), 1.39–1.67 (m, 2 H), 3.03 (br s, 2 H), 3.45 (dt, J = 8.8, 4.4 Hz, 1 H), 4.11 (t, J = 5.1 Hz, 1 H), 4.17 (q, J = 7.2 Hz, 2 H), 6.10 (d, J = 15.6 Hz, 1 H), 6.91 (dd, J = 15.6, 5.1 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 10.0 (+), 14.2 (+), 26.0 (–), 60.7 (–), 73.8 (+), 75.4 (+), 122.2 (+), 147.3 (+), 166.7 (–). The reported ^{1}H NMR spectrum was updated from that reported. The ^{13}C NMR spectrum was identical with that reported.[S3]

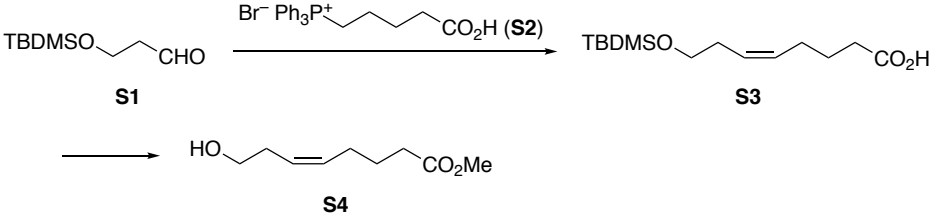
Ethyl (4*S,5*S**,*E*)-4,5-dihydroxy-6-methylhept-2-enoate (15c)**



According to the procedure for the synthesis of **11a** from **9a**, a solution of silyl ether **13c** (*Z*/*E* 94:6 by ^{1}H NMR, 152 mg, 0.530 mmol, 1.0 equiv) in EtOAc (7 mL) at −78 °C was gently bubbled with O_3 in O_2 and then the product was treated with Ph_3P (681 mg, 2.60 mmol, 5 equiv) to afford aldehyde **14c**, which was dissolved in THF (1 mL) and added to a mixture of NaH (60 wt %, 28 mg, 0.70 mmol, 1.3 equiv) and $(EtO)_2P(O)CH_2CO_2Et$ (0.150 mL, 0.749 mmol, 1.4 equiv) in THF (2 mL). The mixture was stirred at rt for 2 h to afford the silyl ether of **15c**. A solution of the silyl ether of **15c** and TBAF (1.0 M in THF, 2.60 mL, 2.60 mmol, 5 equiv) in THF (5 mL) was stirred at rt for 1 h to afford a mixture of diol **15c** and the *anti* isomer **11c** (*syn*/*anti* 90:10 by ^{1}H NMR, 39 mg, 37% over three steps): colorless liquid; R_f 0.45 (hexane/EtOAc 1:1). The *syn* isomer **15c**: ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.98 (d, J = 6.6 Hz, 3 H), 0.99 (d, J = 6.6 Hz, 3 H), 1.30 (t, J = 7.2 Hz, 3 H), 1.85 (octet, J = 6.6 Hz, 1 H), 2.75 (br s, 1 H), 3.13 (br s, 1 H), 3.29 (t, J = 5.1 Hz, 1 H), 4.20 (q, J = 7.2 Hz, 2 H), 4.27–4.35 (m, 1 H), 6.13 (d, J = 15.6 Hz, 1 H), 6.94 (dd, J = 15.6, 5.1 Hz, 1 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ 14.3 (+), 17.1 (+), 19.7 (+), 30.0 (+), 60.7 (–), 71.9 (+), 78.7 (+), 122.1 (+), 147.7 (+), 166.6 (–). The ^{1}H and ^{13}C NMR spectra were identical with those reported.[S4]

Preparation of phosphonium salt 24

Methyl (*Z*)-8-hydroxyoct-5-enoate (S4)

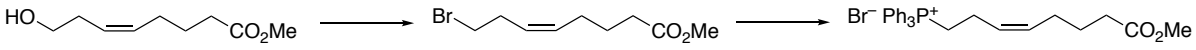


To an ice-cold suspension of phosphonium salt **S2** (4.20 g, 9.47 mmol, 1.5 equiv) in THF (50 mL) was added NaHMDS (1.0 M in THF, 9.50 mL, 9.50 mmol, 1.5 equiv). The resulting reddish-orange mixture was stirred at 0 °C for 1 h and cooled to −90 °C. A

solution of aldehyde **S1** (1.19 g, 6.32 mmol, 1.0 equiv) in THF (12 mL) was added to the mixture dropwise. After 2 h, the mixture was warmed to rt over 1 h before addition of saturated NH_4Cl solution (aq.). The resulting mixture was extracted with Et_2O three times. The combined extracts were dried over $MgSO_4$ and concentrated to afford a residue, which was purified by chromatography on silica gel (hexane/EtOAc 9:1 to 2:1) to give olefin **S3** (1.28 g, 74%): colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.05 (s, 6 H), 0.89 (s, 9 H), 1.70 (quint., J = 7.2 Hz, 2 H), 2.11 (q, J = 6.8 Hz, 2 H), 2.26 (q, J = 6.8 Hz, 2 H), 2.36 (t, J = 7.2 Hz, 2 H), 3.61 (t, J = 6.8 Hz, 2 H), 5.38–5.47 (m, 2 H); ^{13}C–APT NMR (75 MHz, $CDCl_3$) δ –5.2 (+), 18.5 (–), 24.6 (–), 26.0 (+), 26.7 (–), 31.1 (–), 33.5 (–), 63.0 (–), 127.1 (+), 130.2 (+), 180.1 (–).

A solution of silyl ether **S3** (1.42 g, 5.21 mmol, 1.0 equiv) and *p*-TsOH·H_2O (186 mg, 1.08 mmol, 0.2 equiv) in MeOH (7 mL) and THF (3.5 mL) was stirred at 40 °C for 1 h and diluted with saturated $NaHCO_3$ solution (aq.). The resulting mixture was extracted with Et_2O three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc 2:1) to afford hydroxy ester **S4** (755 mg, 84%): colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.69 (quint., J = 7.2 Hz, 2 H), 1.78 (br s, 1 H), 2.10 (q, J = 7.2 Hz, 2 H), 2.25–2.36 (m, 4 H), 3.62 (t, J = 6.4 Hz, 2 H), 3.65 (s, 3 H), 5.36–5.55 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.2, 26.0, 30.3, 32.8, 50.9, 61.4, 126.3, 130.2, 173.7. The ^{1}H and ^{13}C NMR spectra were identical with those reported.[S5]

(*Z*)-(8-methoxy-8-oxooct-3-en-1-yl)triphenylphosphonium bromide (24)



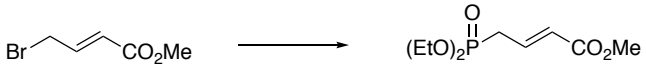
S4 **S5** **24**

To an ice-cold solution of hydroxy ester **S4** (299 mg, 1.74 mmol, 1.0 equiv) and PPh_3 (644 mg, 2.46 mmol, 1.4 equiv) in CH_2Cl_2 (4 mL) was added CBr_4 (799 mg, 2.41 mmol, 1.4 equiv). The solution was stirred at rt for 1 h and diluted with saturated $NaHCO_3$ solution (aq.). The resulting mixture was extracted with CH_2Cl_2 three times. The combined extracts were dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (hexane/EtOAc 9:1) to afford the corresponding bromide **S5** (397 mg, 97%): colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.71 (quint., J = 7.2 Hz, 2 H), 2.09 (q, J = 7.2 Hz, 2 H), 2.32 (t, J = 7.2 Hz, 2 H), 2.60 (q, J = 7.2 Hz, 2 H), 3.36 (t J = 7.2 Hz, 2 H), 3.67 (s, 3 H), 5.36–5.45 (m, 1 H), 5.46–5.55 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.6, 26.7, 30.7, 32.4, 33.3, 51.5, 127.0, 131.6, 173.9. The ^{1}H and ^{13}C NMR spectra were identical with those reported.[S5,S6]

A mixture of bromide **S5** (384 mg, 1.63 mmol, 1.0 equiv) and PPh_3 (867 mg, 3.31 mmol, 2.0 equiv) in MeCN (2 mL) was heated under reflux for 17 h, cooled to rt, and concentrated. The residue was purified by chromatography on silica gel (CH_2Cl_2 to CH_2Cl_2/MeOH 9:1) to afford phosphonium salt **24** (837 g, quant.): creamy gum; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.54 (quint., J = 7.2 Hz, 2 H), 1.83 (q, J = 7.2 Hz, 2 H), 2.17 (t, J = 7.2 Hz, 2 H), 2.34–2.46 (m, 2 H), 3.56 (s, 3 H), 3.74–3.84 (m, 2 H), 5.33 (dt, J = 10.8, 7.2 Hz, 1 H), 5.60 (dt, J = 10.8, 7.2 Hz, 1 H), 7.65–7.73 (m, 6 H), 7.74–7.86 (m, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 22.9 (d, J = 48 Hz), 24.4, 26.5, 33.2, 51.5, 118.1 (d, J = 86 Hz), 127.2 (d, J = 15 Hz), 130.5 (d, J = 12 Hz), 131.1, 133.7 (d, J = 10 Hz), 135.1, 173.9. The ^{1}H and ^{13}C NMR spectra were identical with those reported.[S6]

Preparation of phosphonate 25

Methyl (*E*)-4-(diethoxyphosphoryl)but-2-enoate (25)



S6 **25**

According to the literature procedure,[S7] a mixture of methyl 4-bromocrotonate (**S6**) (3.97 g, 22.2 mmol, 1.0 equiv) and $(EtO)_3P$ (4.64 mL, 26.8 mmol, 1.2 equiv) was stirred at 120 °C for 1 h, cooled to rt and purified by chromatography on silica gel (CH_2Cl_2/THF 19:1) to give phosphonate **25** (4.73 g, 90%): yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.0 Hz, 6 H), 2.73 (dd, J = 22.8, 8.0 Hz, 2 H), 3.73 (s, 3 H), 4.03–4.17 (m, 4 H), 5.96 (dd, J = 15.6, 5.2 Hz, 1 H), 6.88 (sextet, J = 8.0 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.3 (d, J = 6 Hz), 30.5 (d, J = 137 Hz), 51.4, 62.1, 125.2 (d, J = 14 Hz), 137.7 (d, J = 11 Hz), 165.9. The ^{1}H and ^{13}C NMR spectra were identical with those reported.[S7]

References

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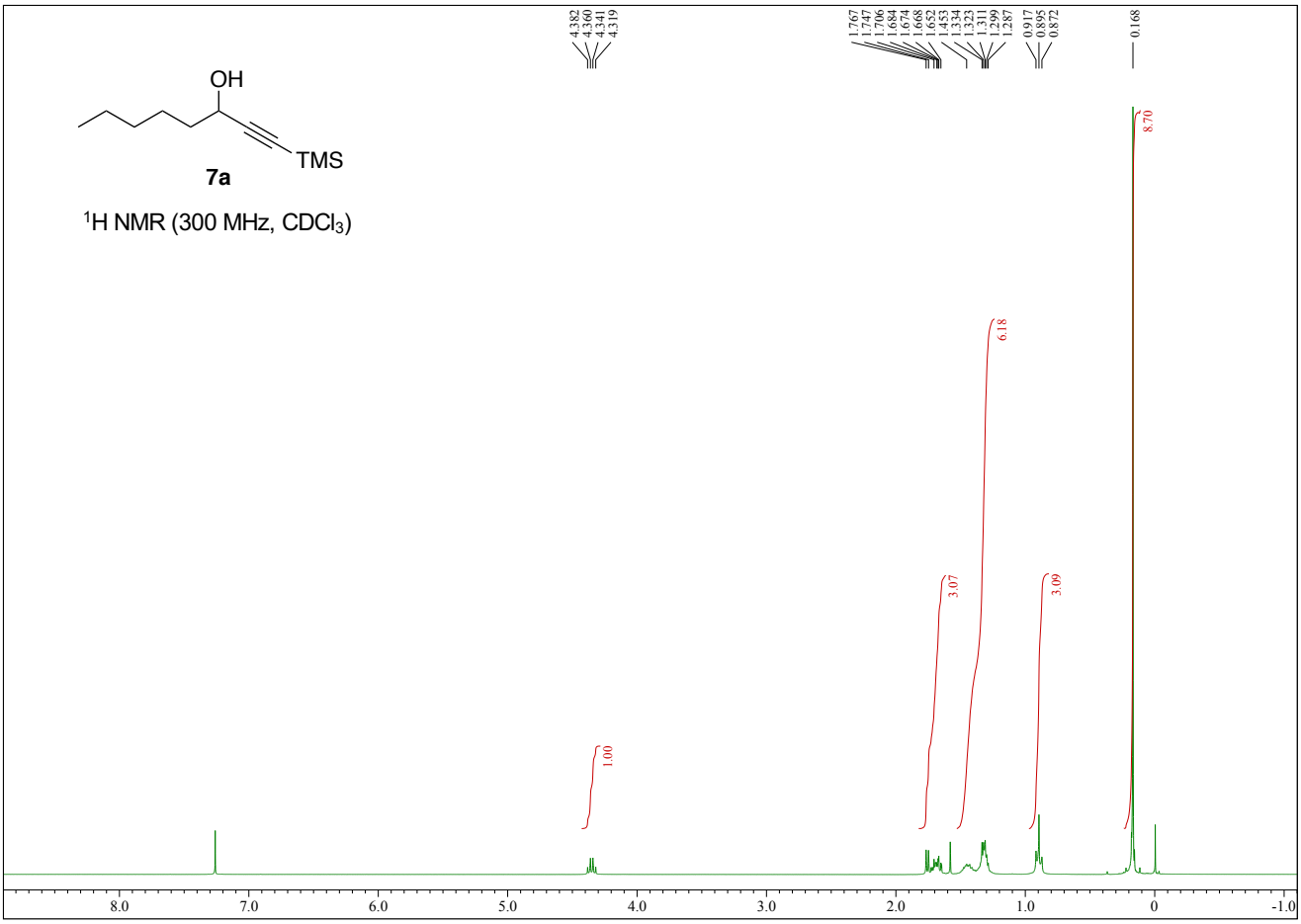
S5 X. Han, S. N. Crane and E. J. Corey, *Org. Lett.*, 2000, **2**, 3437.

S6 (*a*) S. P. Nikas, M. D'Souza and A. Makriyannis, *Tetrahedron*, 2012, **68**, 6329; (*b*) J. Sandri and J. Viala, *J. Org. Chem.*, 1995, **60**, 6627.

S7 R. D. C. Pullin, A. H. Rathi, E. Y. Melikhova, C. Winter, A. L. Thompson and T. J. Donohoe, *Org. Lett.*, 2013, **15**, 5492.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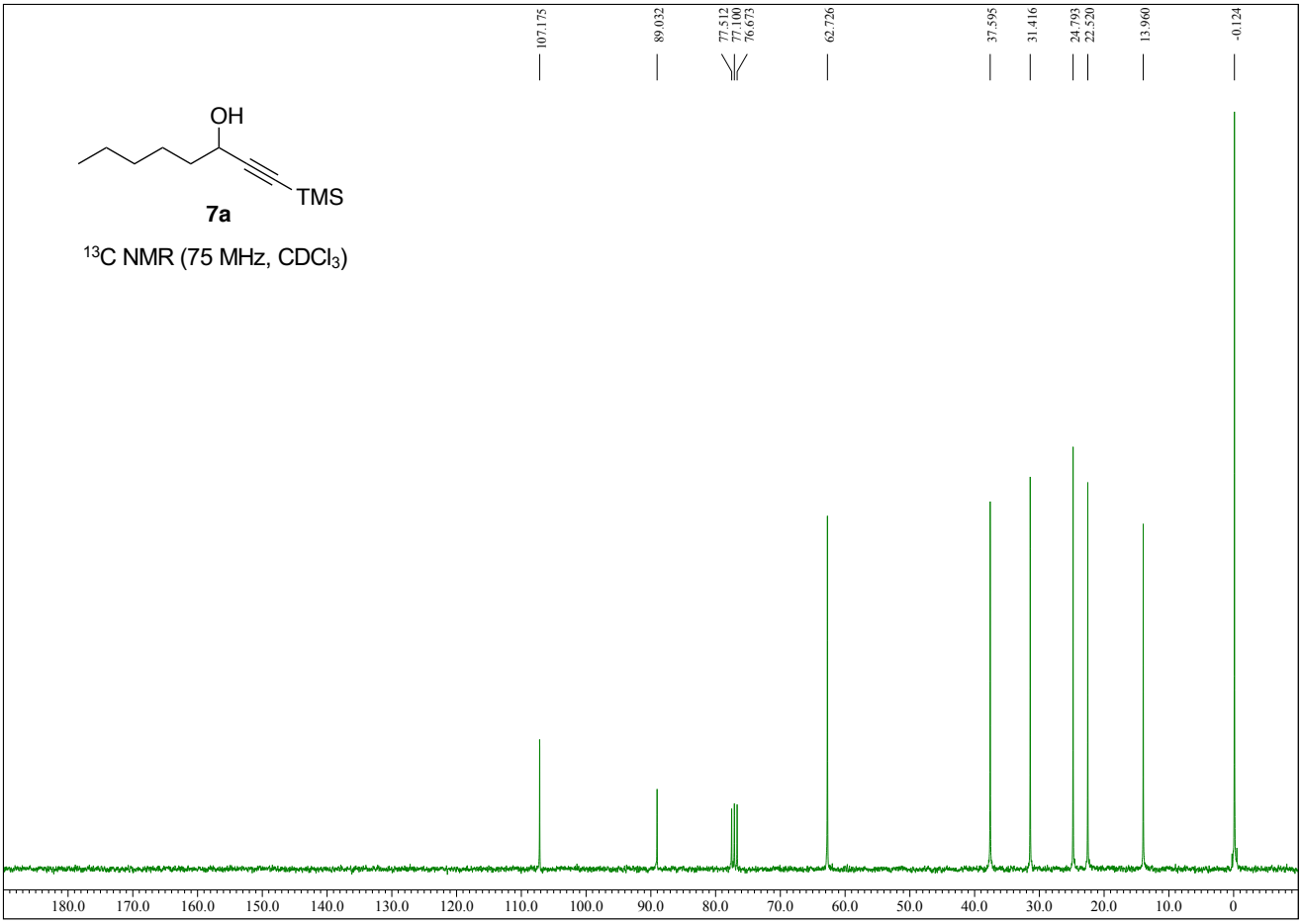
TMS
7a
^{1}H NMR (300 MHz, $CDCl_3$)
4.382
4.360
4.341
4.319
1.767
1.747
1.706
1.684
1.674
1.668
1.653
1.455
1.334
1.323
1.311
1.299
1.287
0.917
0.895
0.872
0.168
8.70
6.18
3.07
3.09
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0


OH
TMS
7a
^{13}C NMR (75 MHz, $CDCl_3$)
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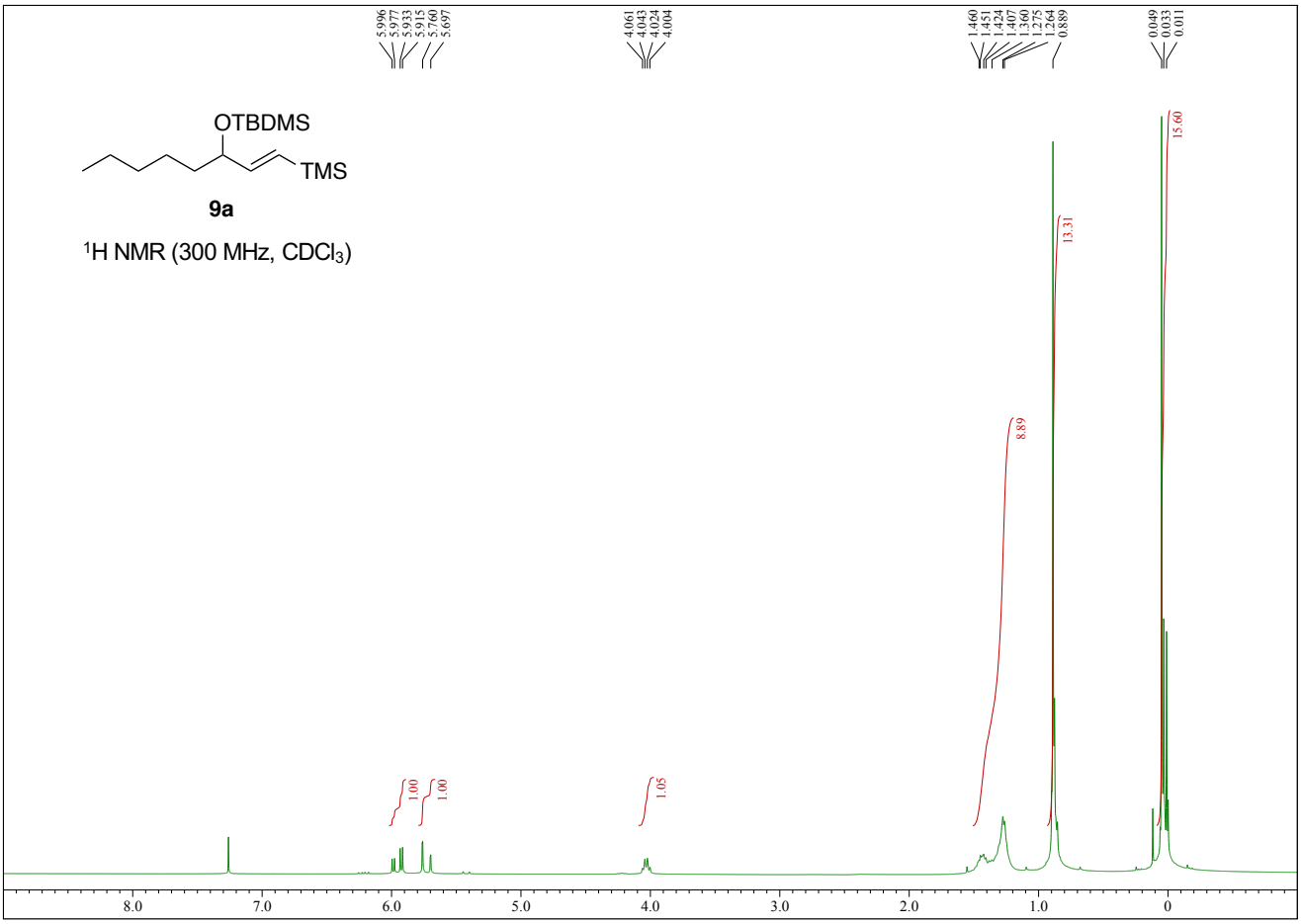
89.032
77.512
77.100
76.673
62.726
37.595
31.416
24.793
22.520
13.960
-0.124
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0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TMS
9a
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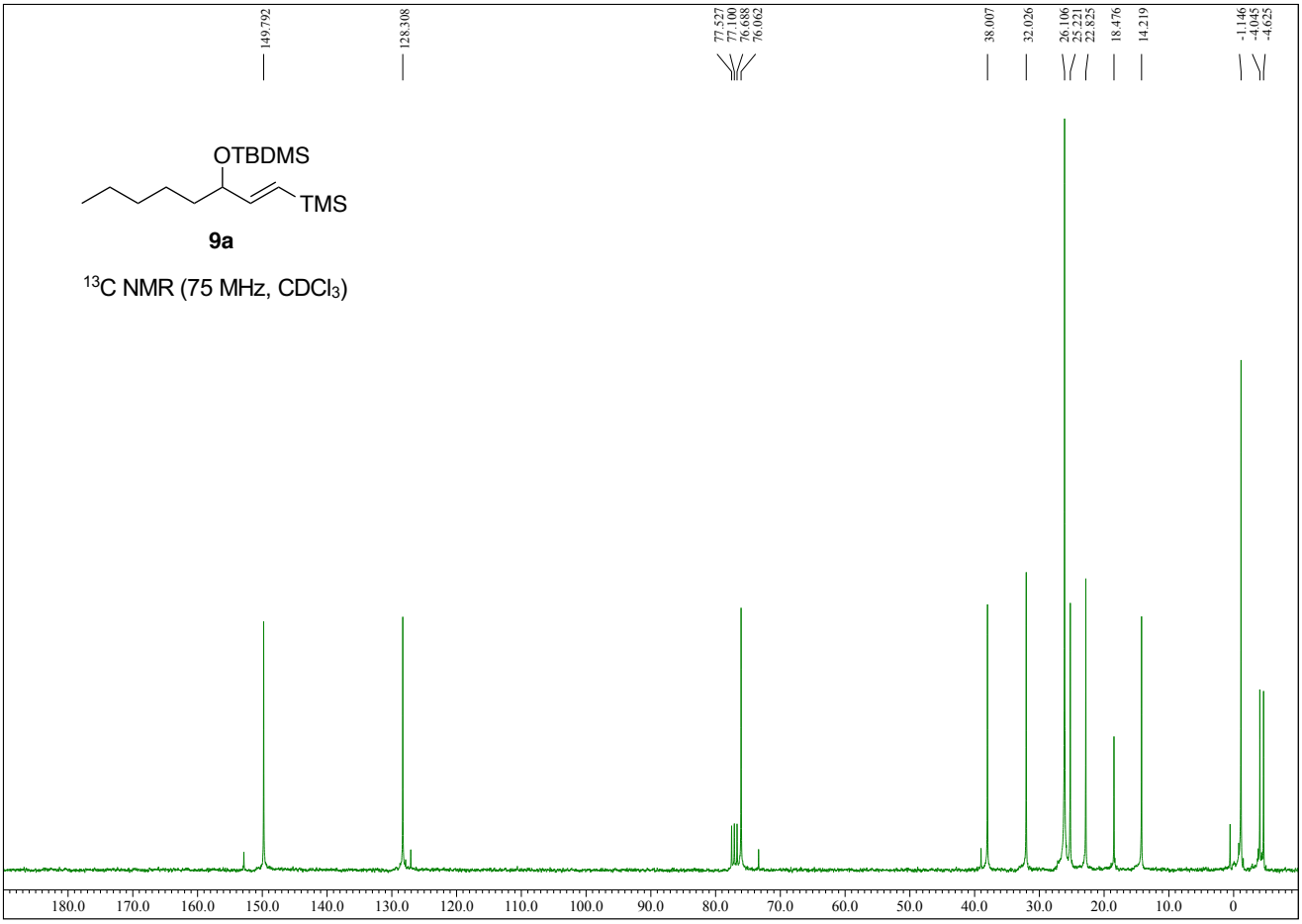
5.933
5.915
5.760
5.697
4.061
4.043
4.024
4.004
1.460
1.451
1.424
1.407
1.360
1.275
1.264
0.889
0.049
0.033
0.011
15.60
13.31
8.89
1.00
1.00
1.05
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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TMS
9a
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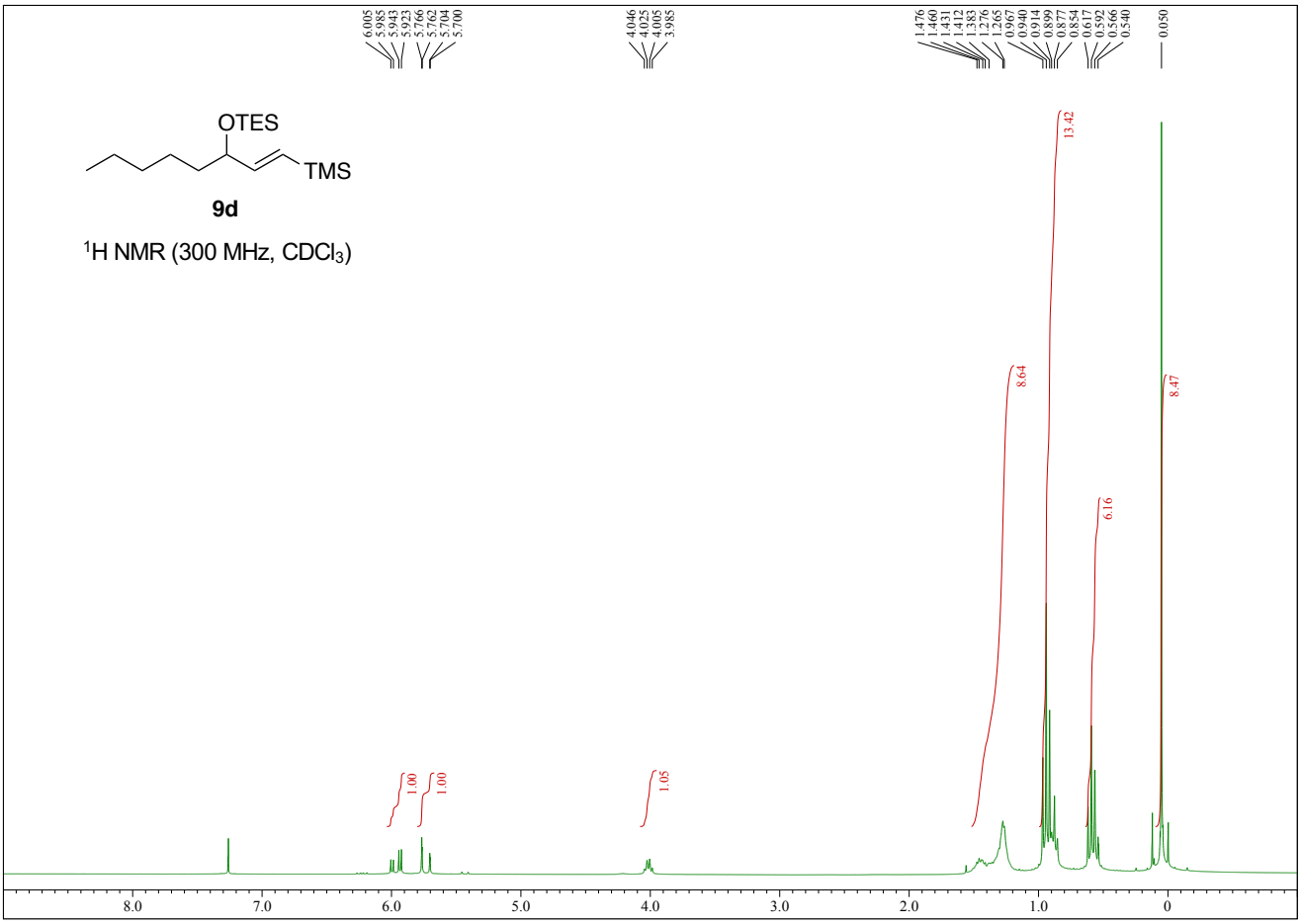
77.527
77.100
76.688
76.062
38.007
32.026
26.106
25.221
22.825
18.476
14.219
-1.146
-4.045
-4.625
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0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TMS
9d
1H NMR (300 MHz, CDCl3)
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5.985
5.943
5.923
5.766
5.762
5.704
5.700
4.046
4.025
4.005
3.985
1.476
1.460
1.431
1.412
1.383
1.276
1.265
0.967
0.940
0.914
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0.877
0.854
0.617
0.592
0.566
0.540
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13.42
8.64
8.47
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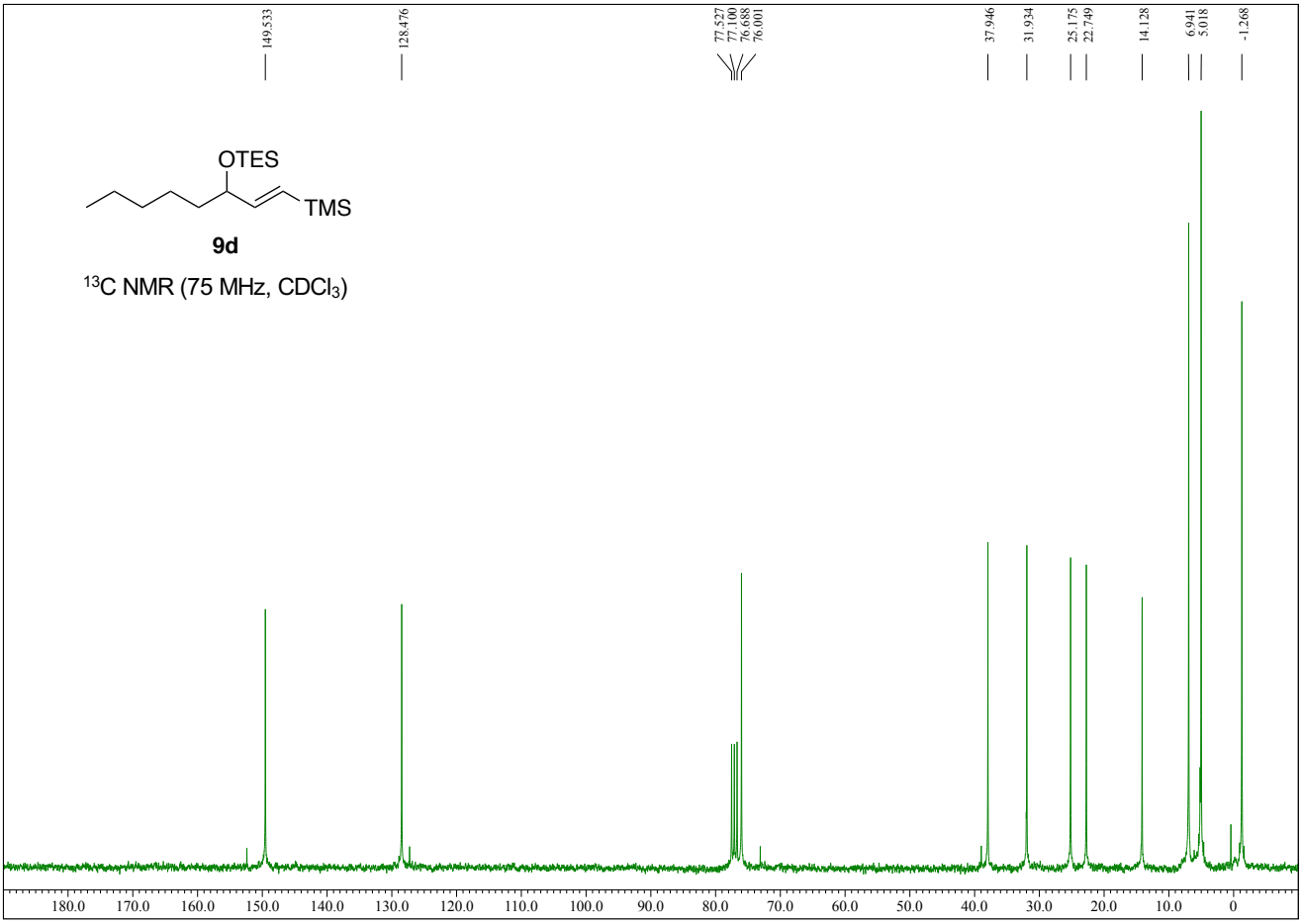
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9d
13C NMR (75 MHz, CDCl3)
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77.527
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76.688
76.001
37.946
31.934
25.175
22.749
14.128
6.941
5.018
-1.268
180.0
170.0
160.0
150.0
140.0
130.0
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90.0
80.0
70.0
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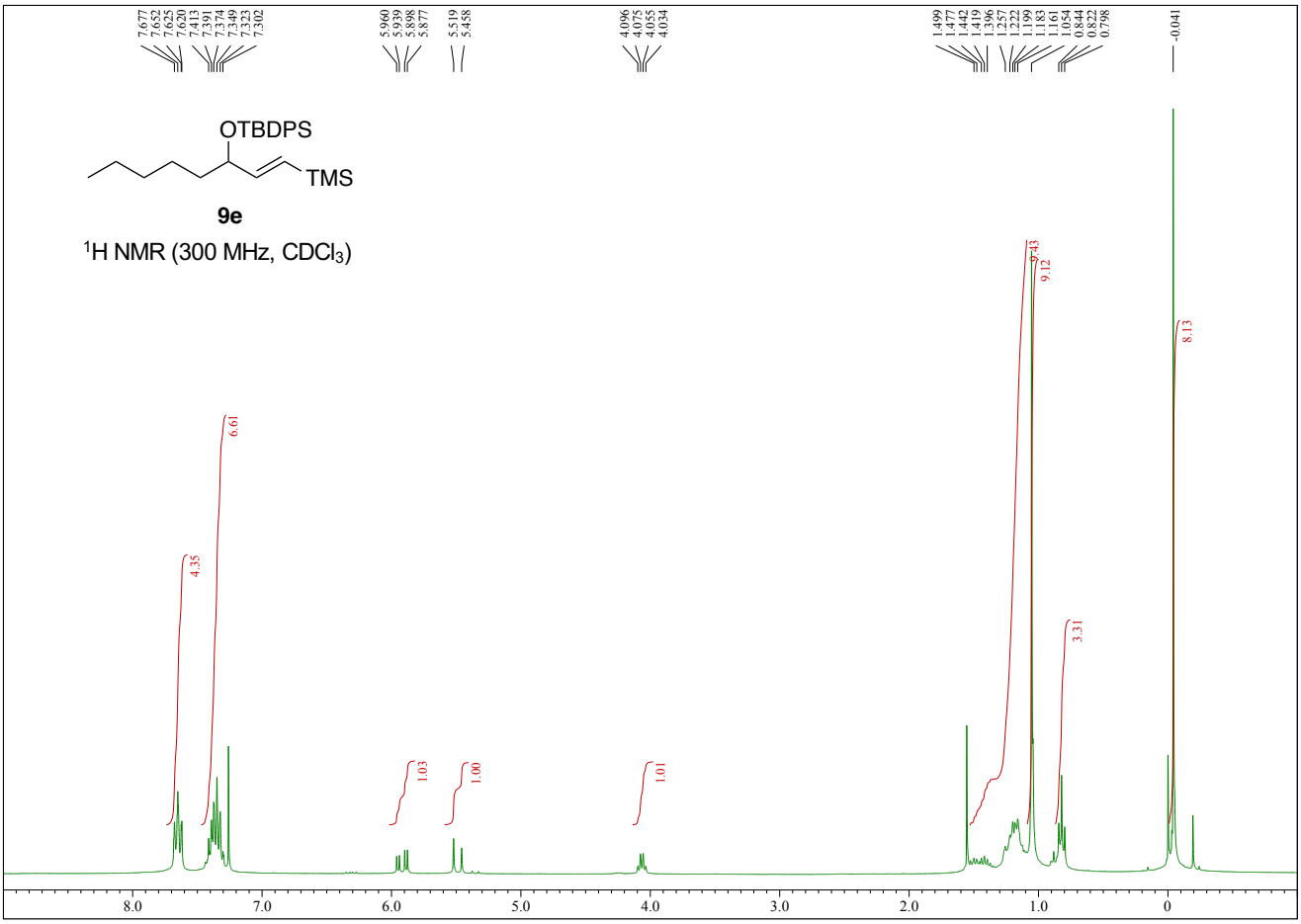
40.0
30.0
20.0
10.0
0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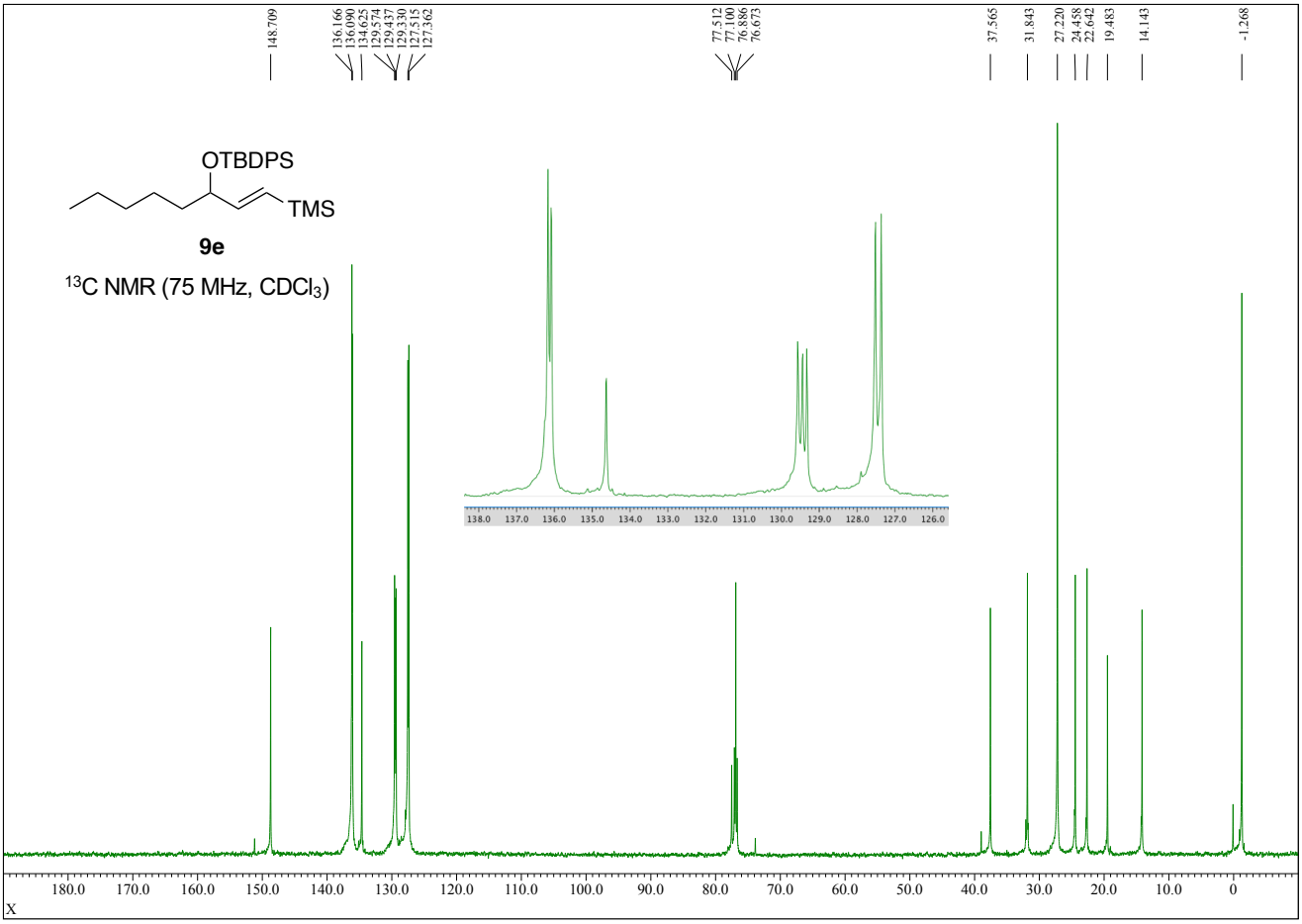
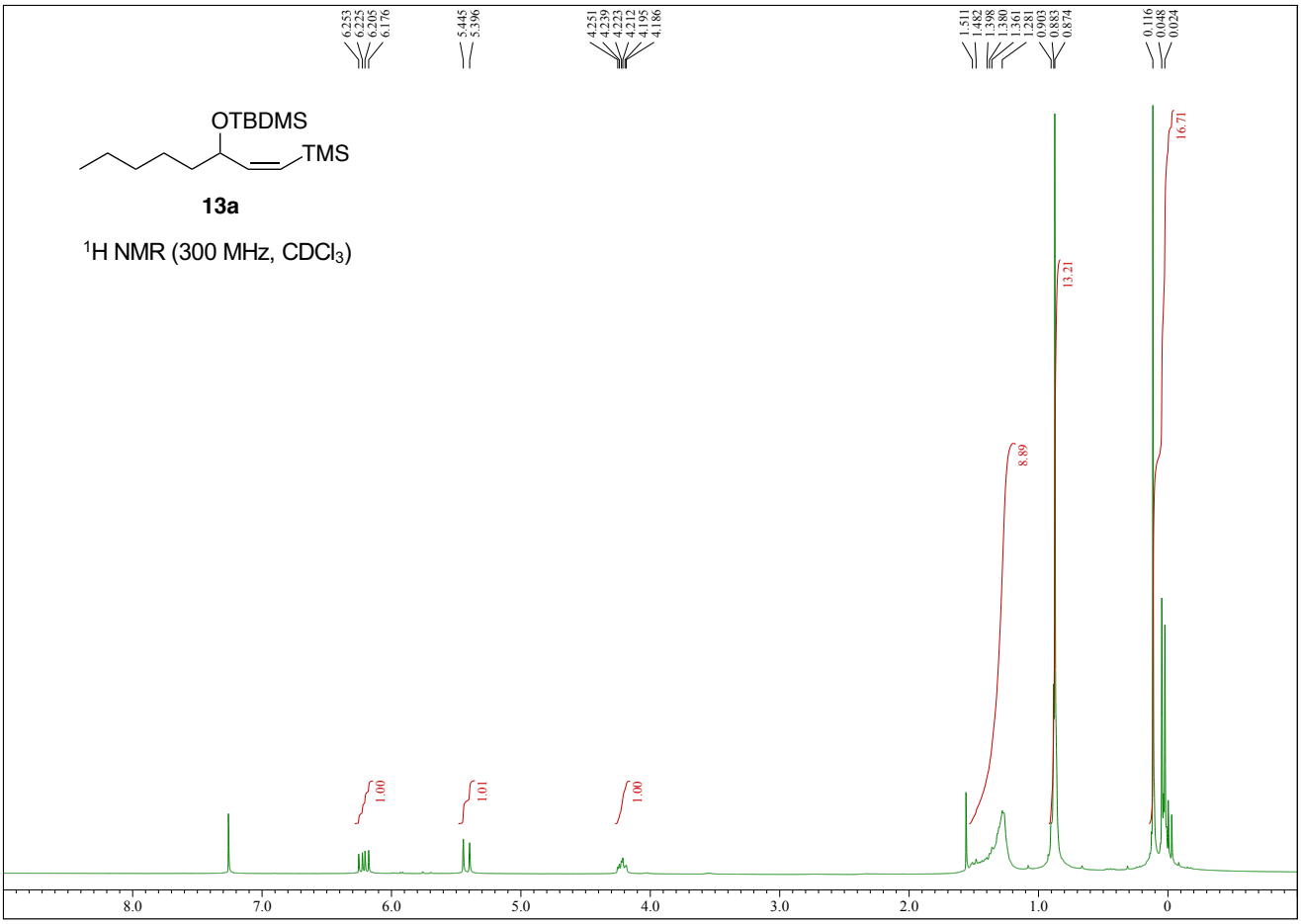
TMS
9e
1H NMR (300 MHz, CDCl3)


OTBDPS
TMS
9e
13C NMR (75 MHz, CDCl3)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6.205
6.176
5.445
5.396
4.251
4.239
4.223
4.212
4.195
4.186
1.511
1.482
1.398
1.380
1.361
1.281
0.903
0.883
0.874
0.116
0.048
0.024
16.71
13.21
8.89
1.00
1.01
1.00
OTBDMS
TMS
13a
^{1}H NMR (300 MHz, $CDCl_3$)
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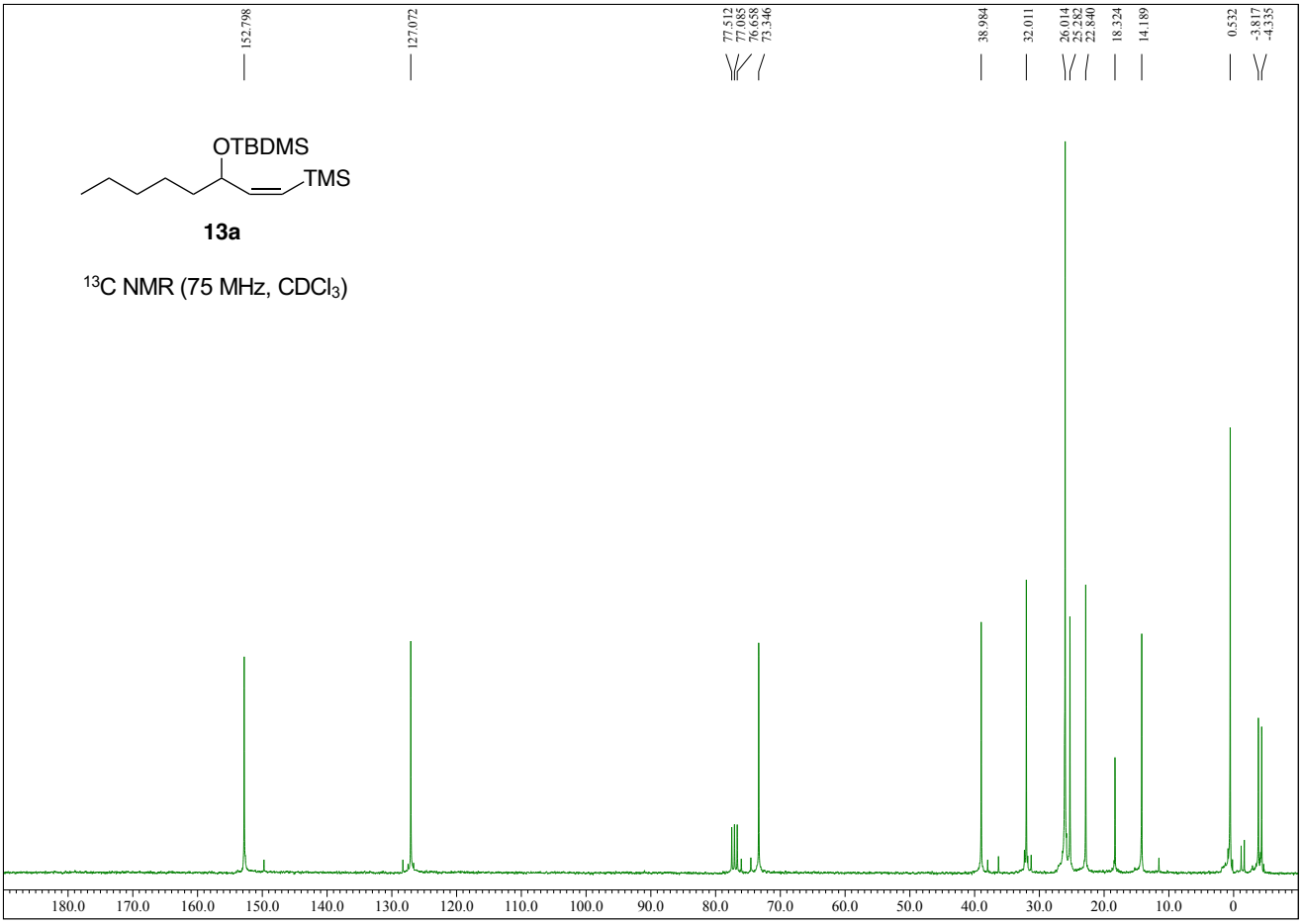
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0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76.658
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25.282
22.840
18.324
14.189
0.532
-3.817
-4.335
OTBDMS
TMS
13a
^{13}C NMR (75 MHz, $CDCl_3$)
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
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70.0
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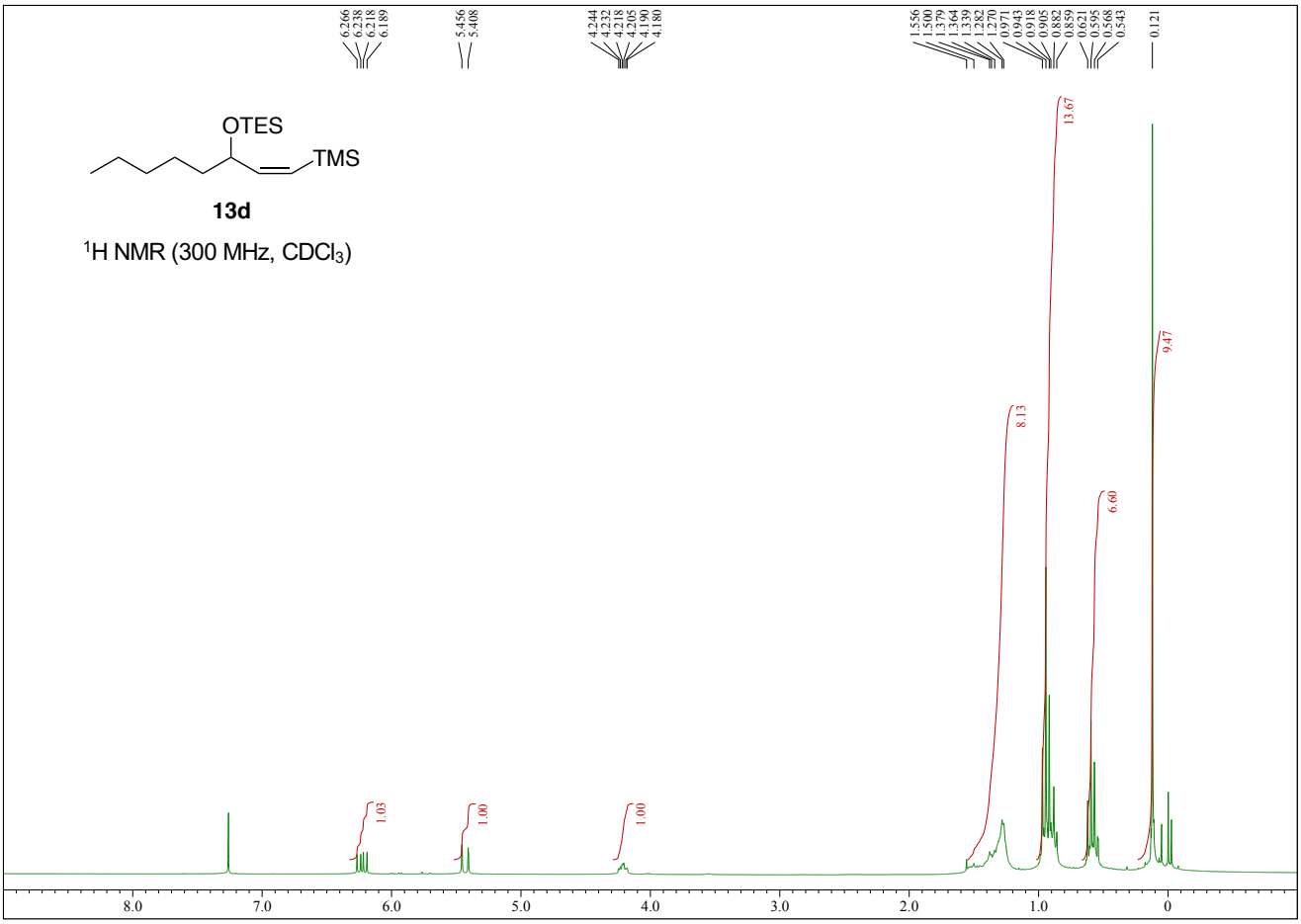
20.0
10.0
0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4.232
4.218
4.205
4.190
4.180
1.556
1.500
1.379
1.364
1.339
1.282
1.270
0.971
0.943
0.918
0.905
0.882
0.859
0.621
0.595
0.568
0.543
0.121
OTES
TMS
13d
1H NMR (300 MHz, CDCl3)
13.67
9.47
8.13
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1.00
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7.0
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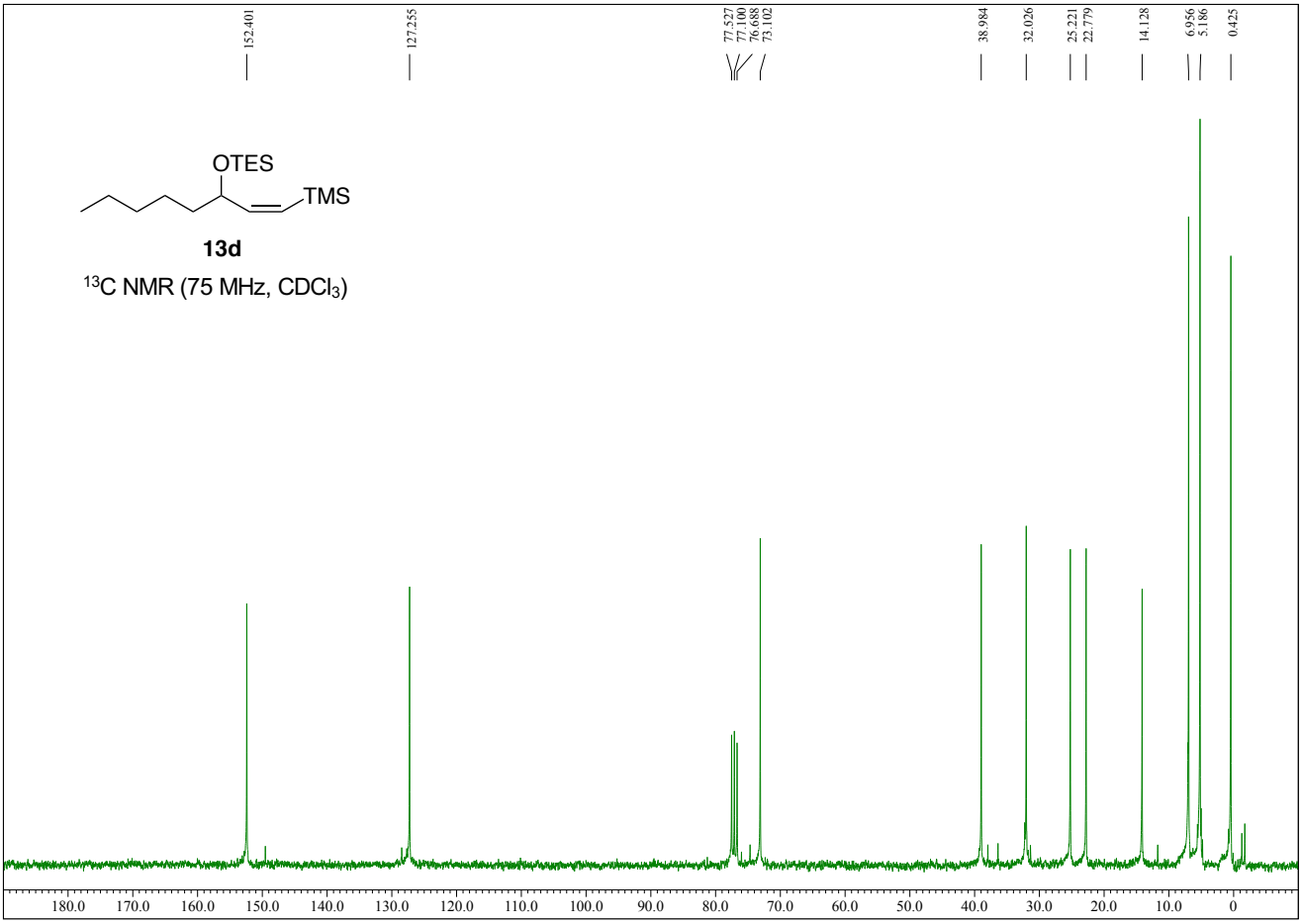
4.0
3.0
2.0
1.0
0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76.688
73.102
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22.779
14.128
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5.186
0.425
OTES
TMS
13d
13C NMR (75 MHz, CDCl3)
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150.0
140.0
130.0
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110.0
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90.0
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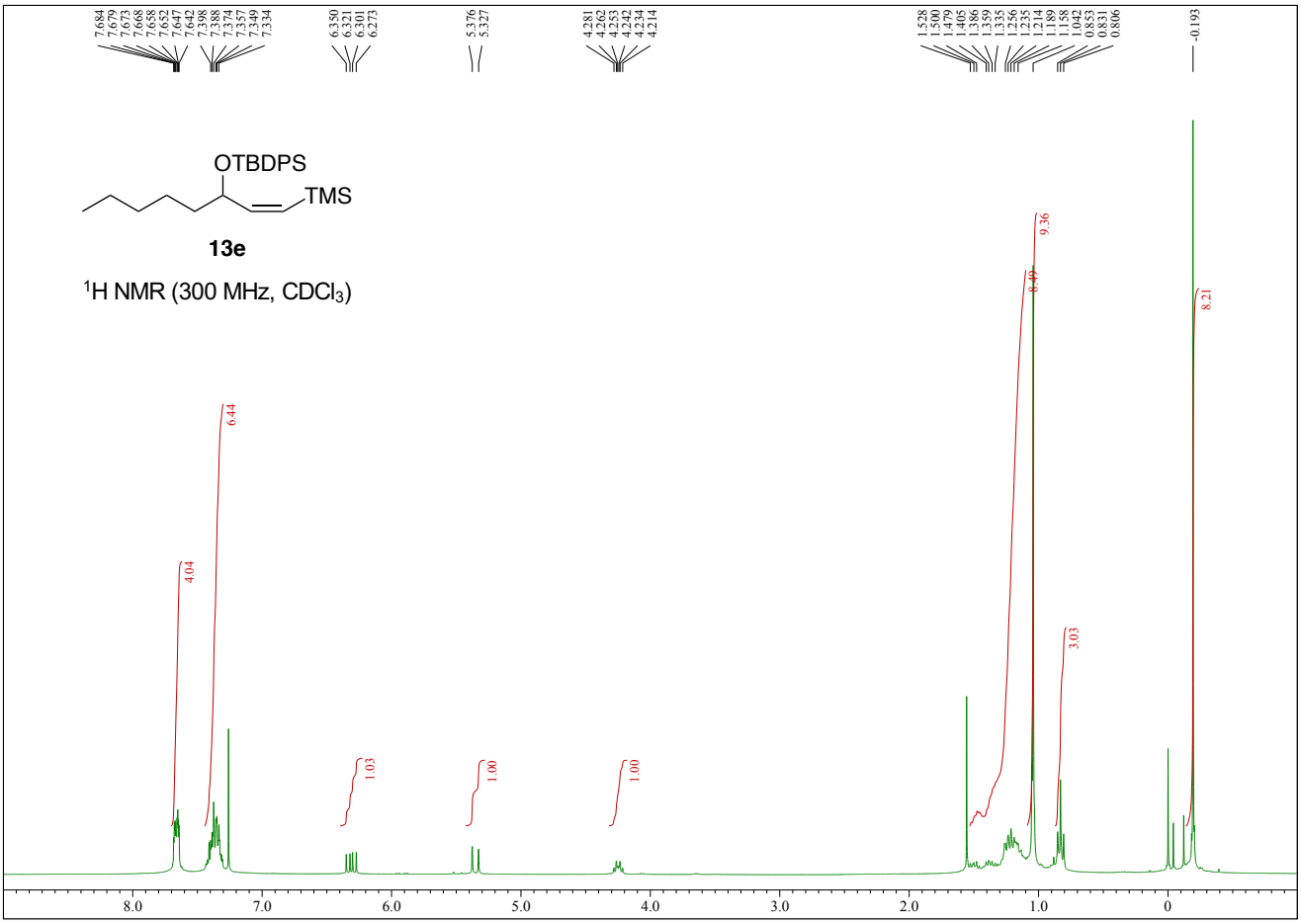
20.0
10.0
0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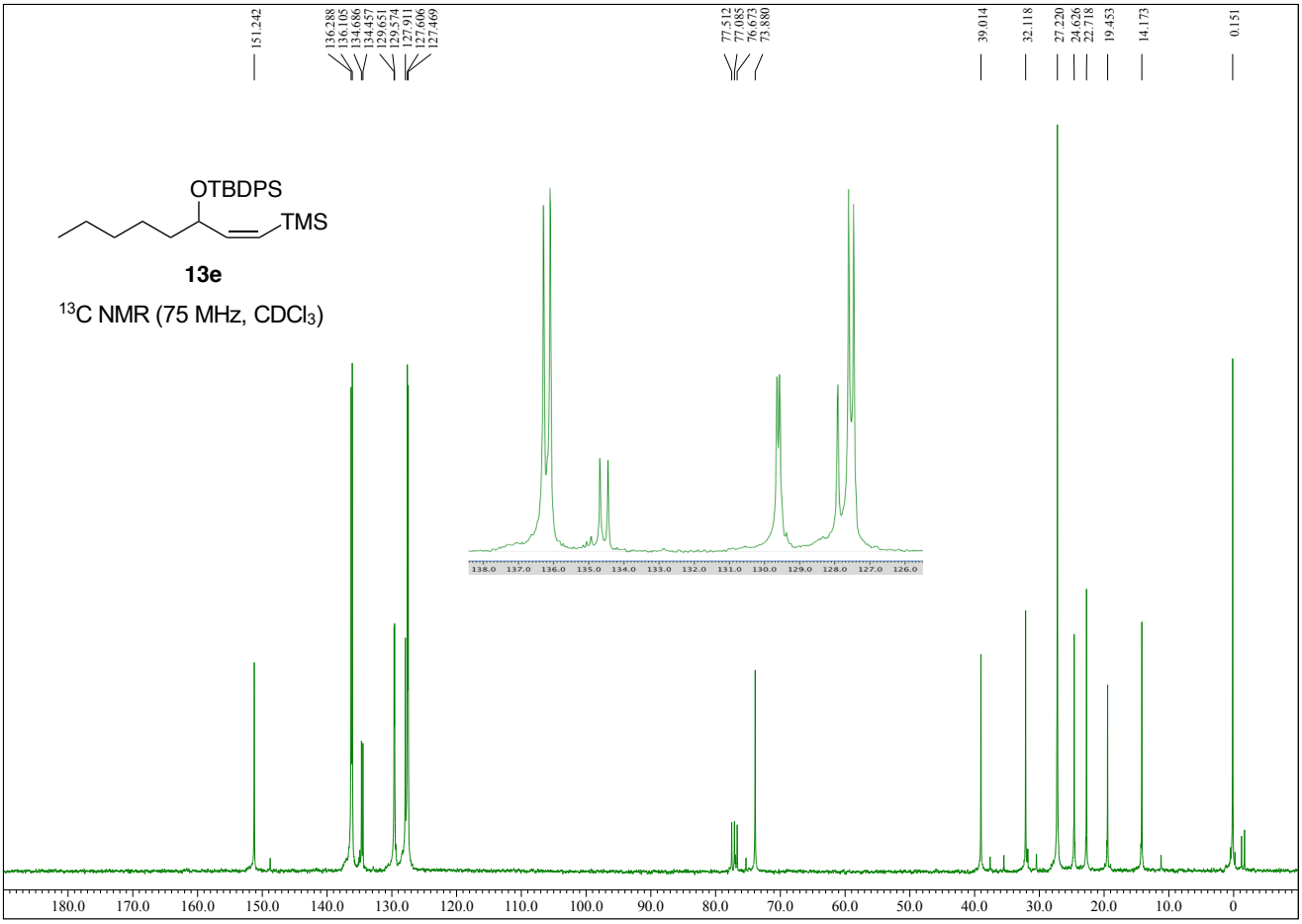
TMS
13e
1H NMR (300 MHz, CDCl3)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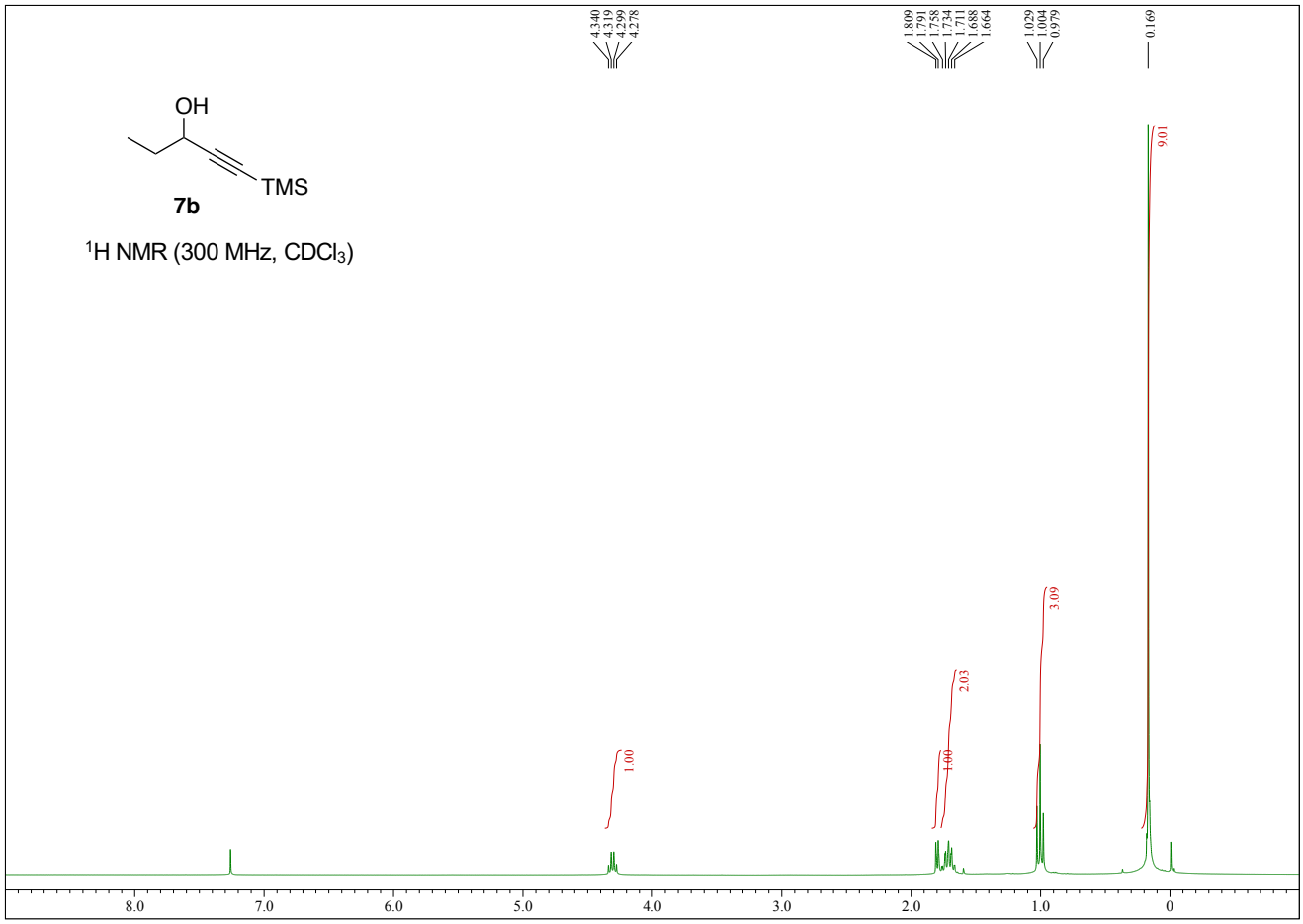
TMS
13e
13C NMR (75 MHz, CDCl3)



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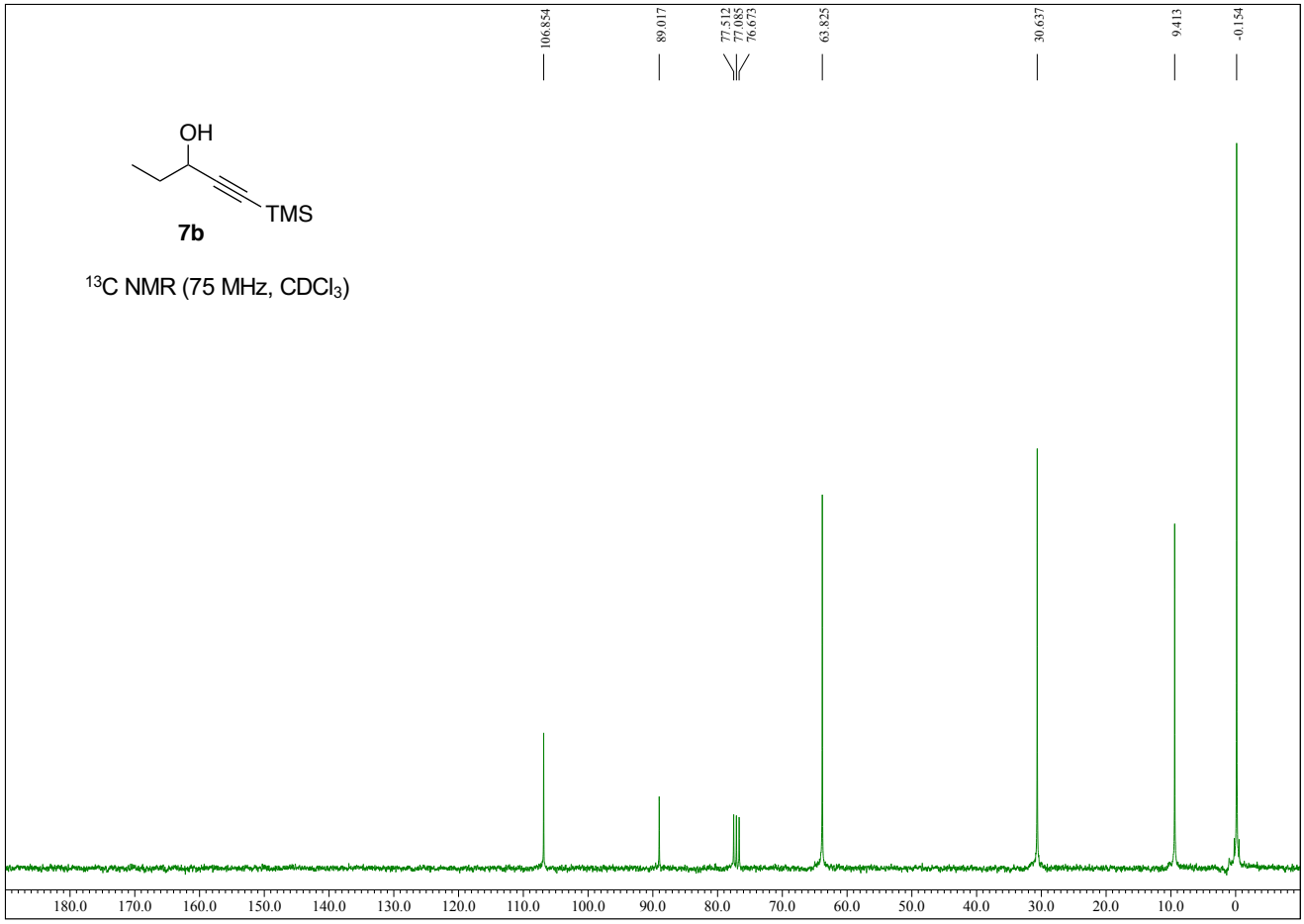
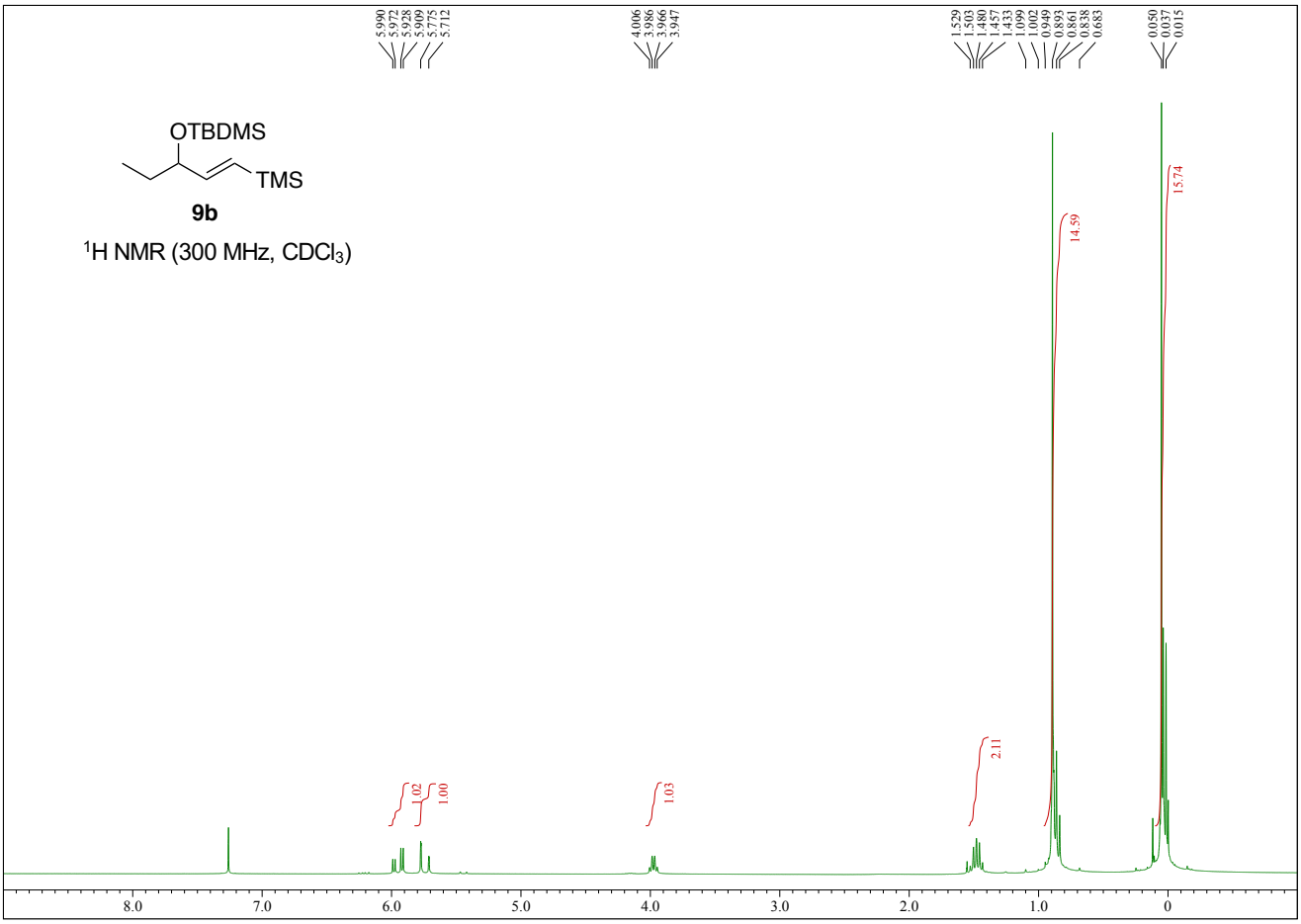


^{13}C NMR (75 MHz, $CDCl_3$)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TMS
9b
1H NMR (300 MHz, CDCl3)
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5.909
5.795
5.712
4.006
3.986
3.966
3.947
1.529
1.503
1.480
1.457
1.433
1.099
1.002
0.949
0.893
0.861
0.838
0.683
0.050
0.037
0.015
15.74
14.59
2.11
1.03
1.02
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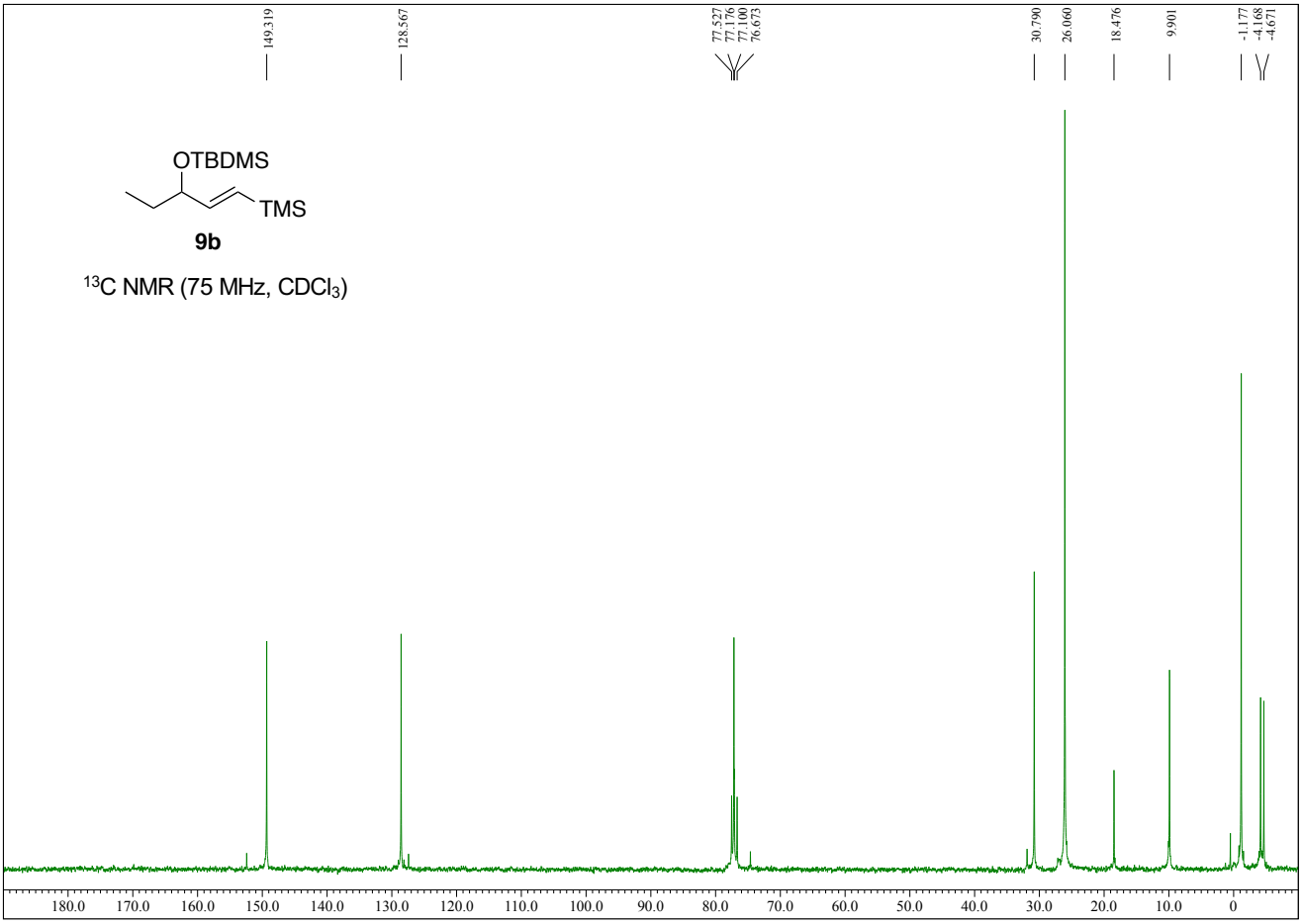
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TMS
9b
13C NMR (75 MHz, CDCl3)
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77.176
77.100
76.673
30.790
26.060
18.476
9.901
-1.177
-4.168
-4.671
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160.0
150.0
140.0
130.0
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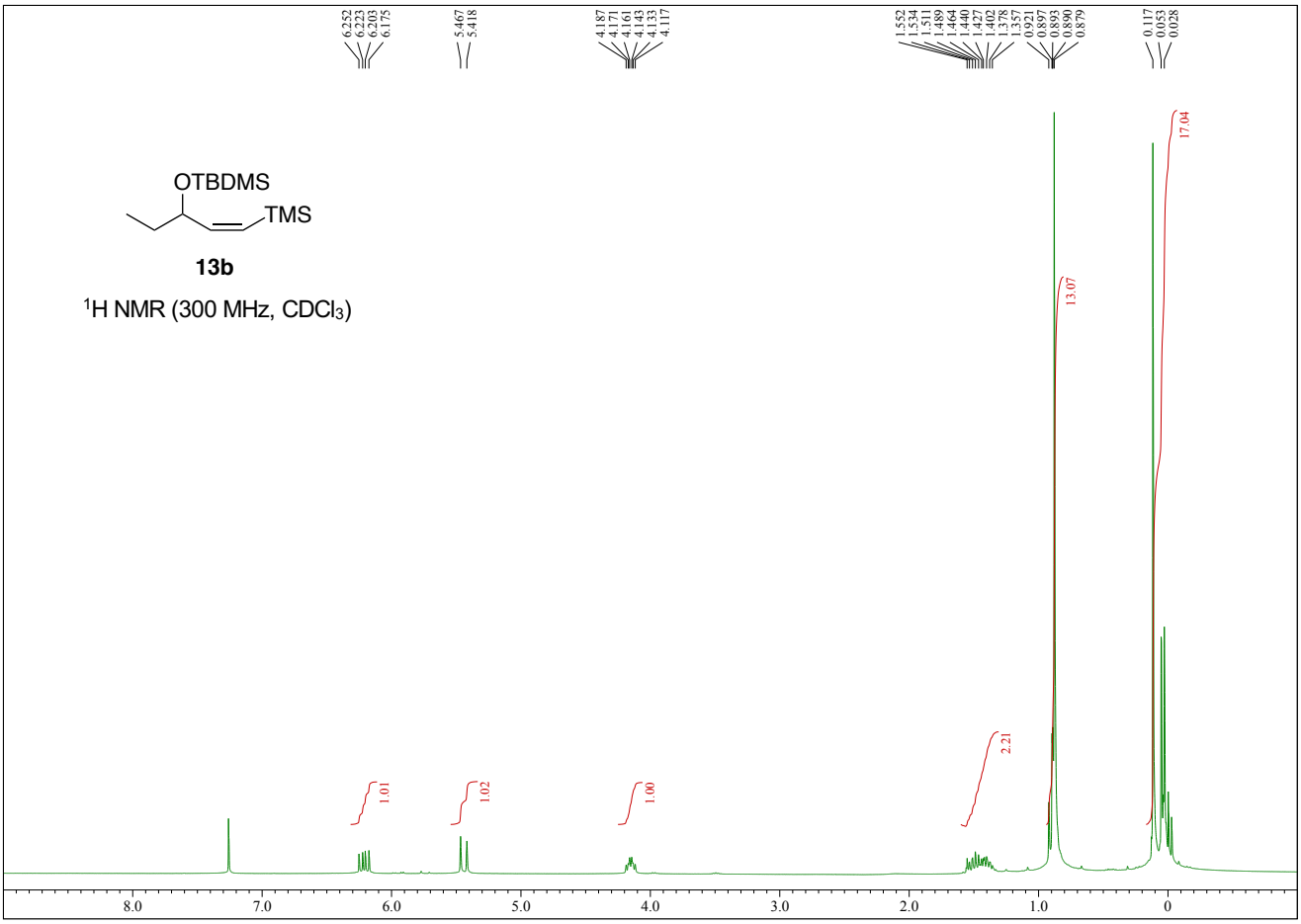
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TMS
13b
1H NMR (300 MHz, CDCl3)
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6.175
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5.418
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4.171
4.161
4.143
4.133
4.117
1.552
1.534
1.511
1.489
1.464
1.440
1.427
1.402
1.378
1.357
0.921
0.907
0.893
0.890
0.879
0.117
0.053
0.028
17.04
13.07
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1.02
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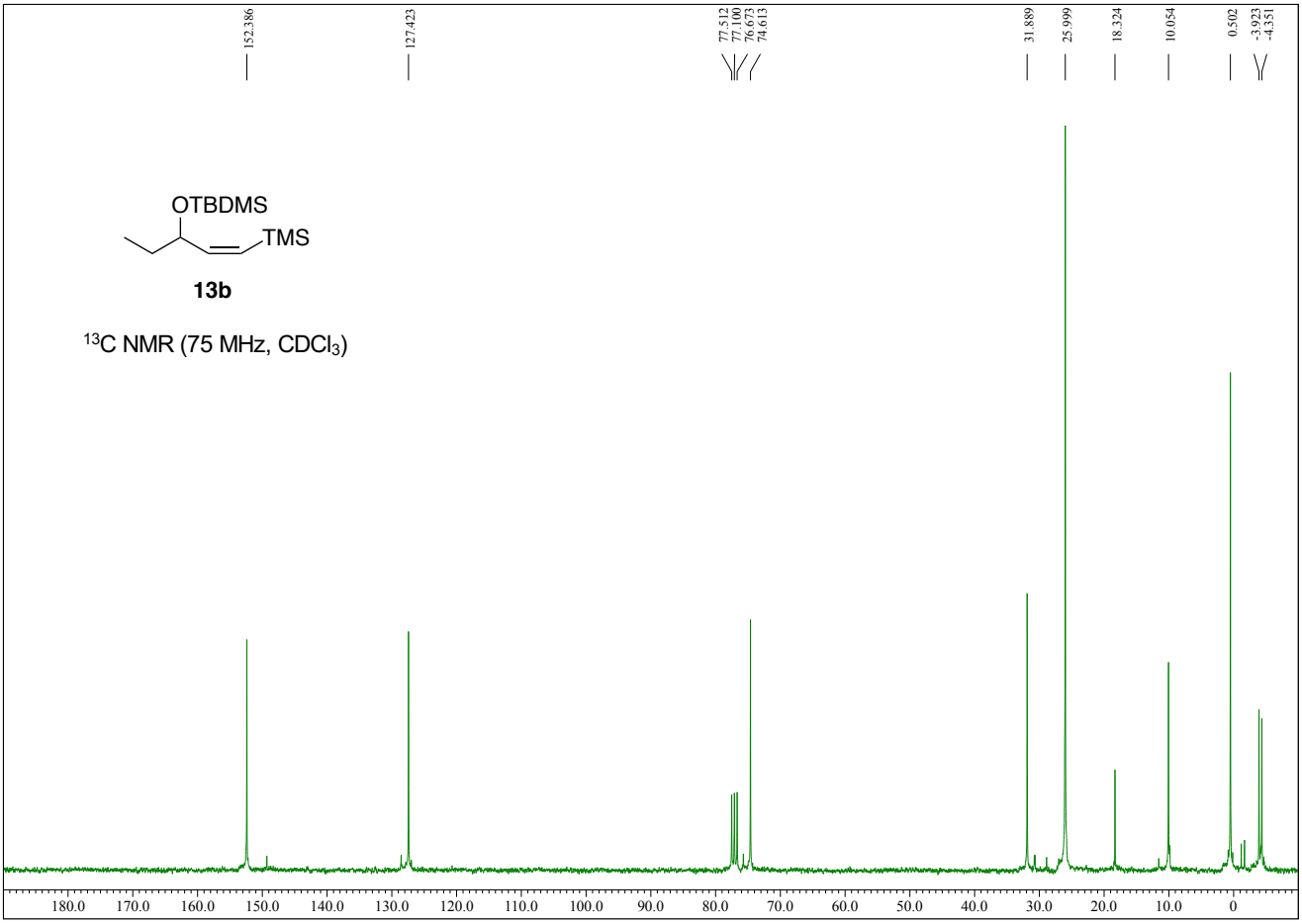
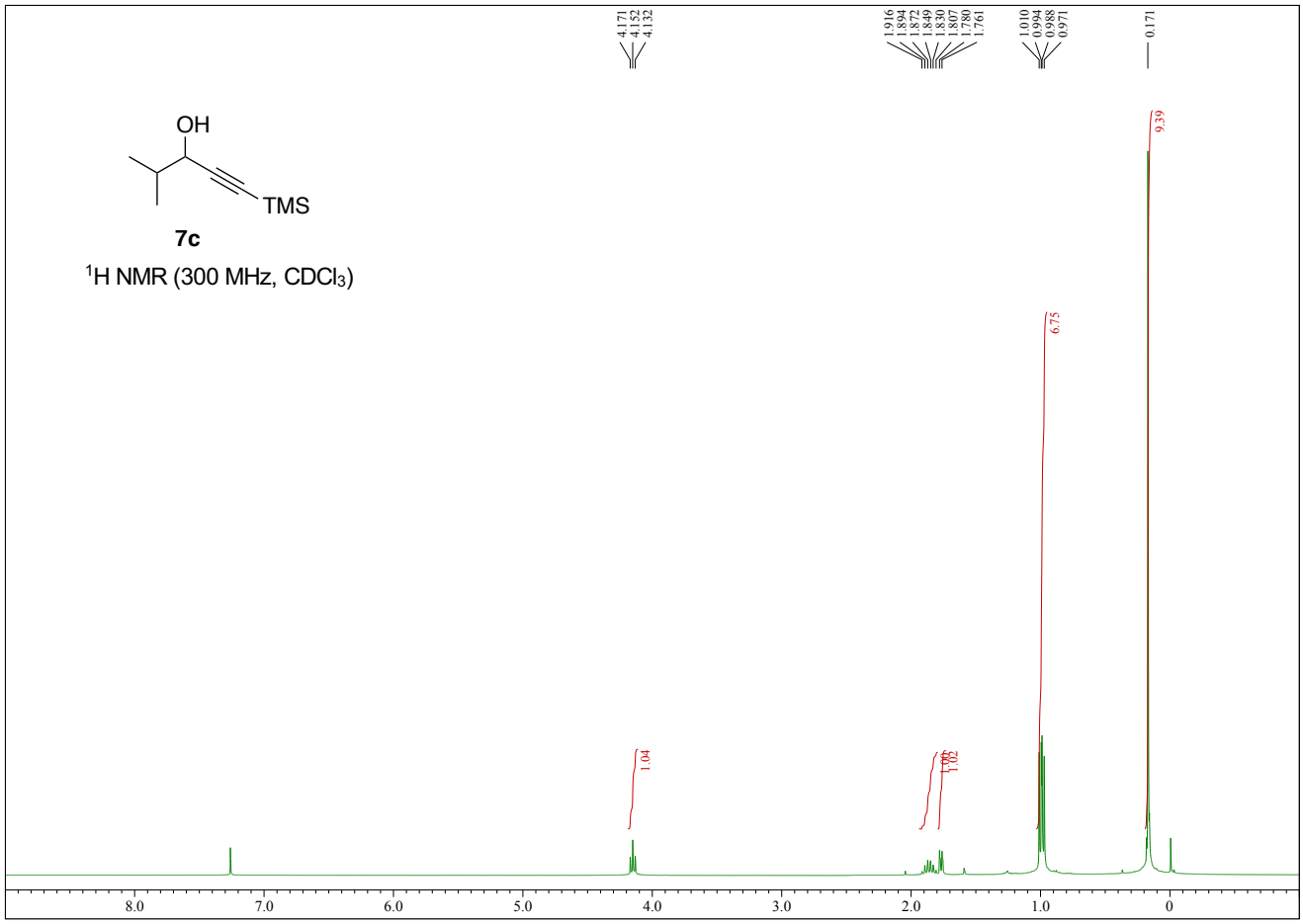
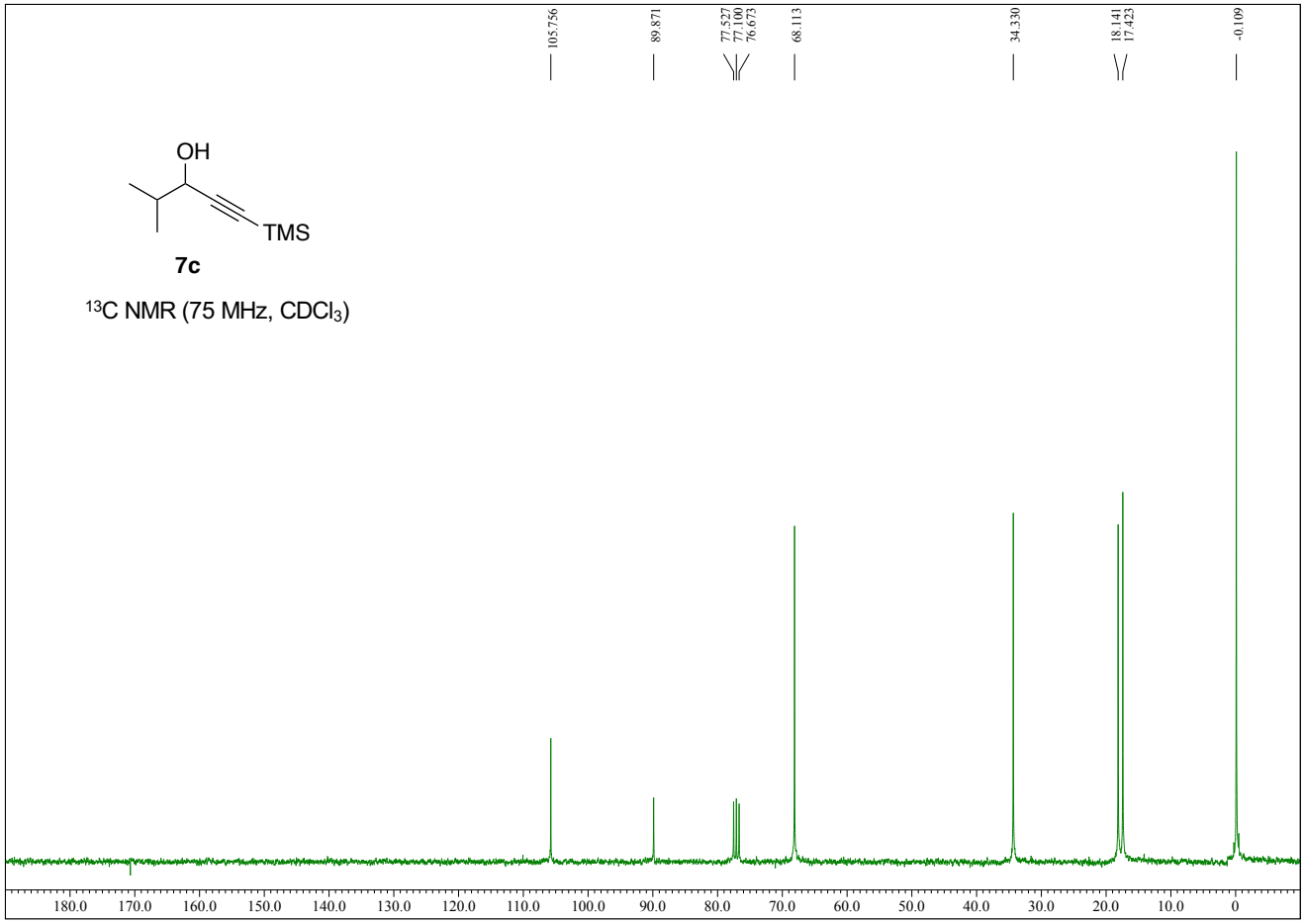

OTBDMS
TMS
13b
13C NMR (75 MHz, CDCl3)
152.386
127.423
77.512
77.100
76.673
74.613
31.889
25.999
18.324
10.054
0.502
-3.923
-4.351
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0



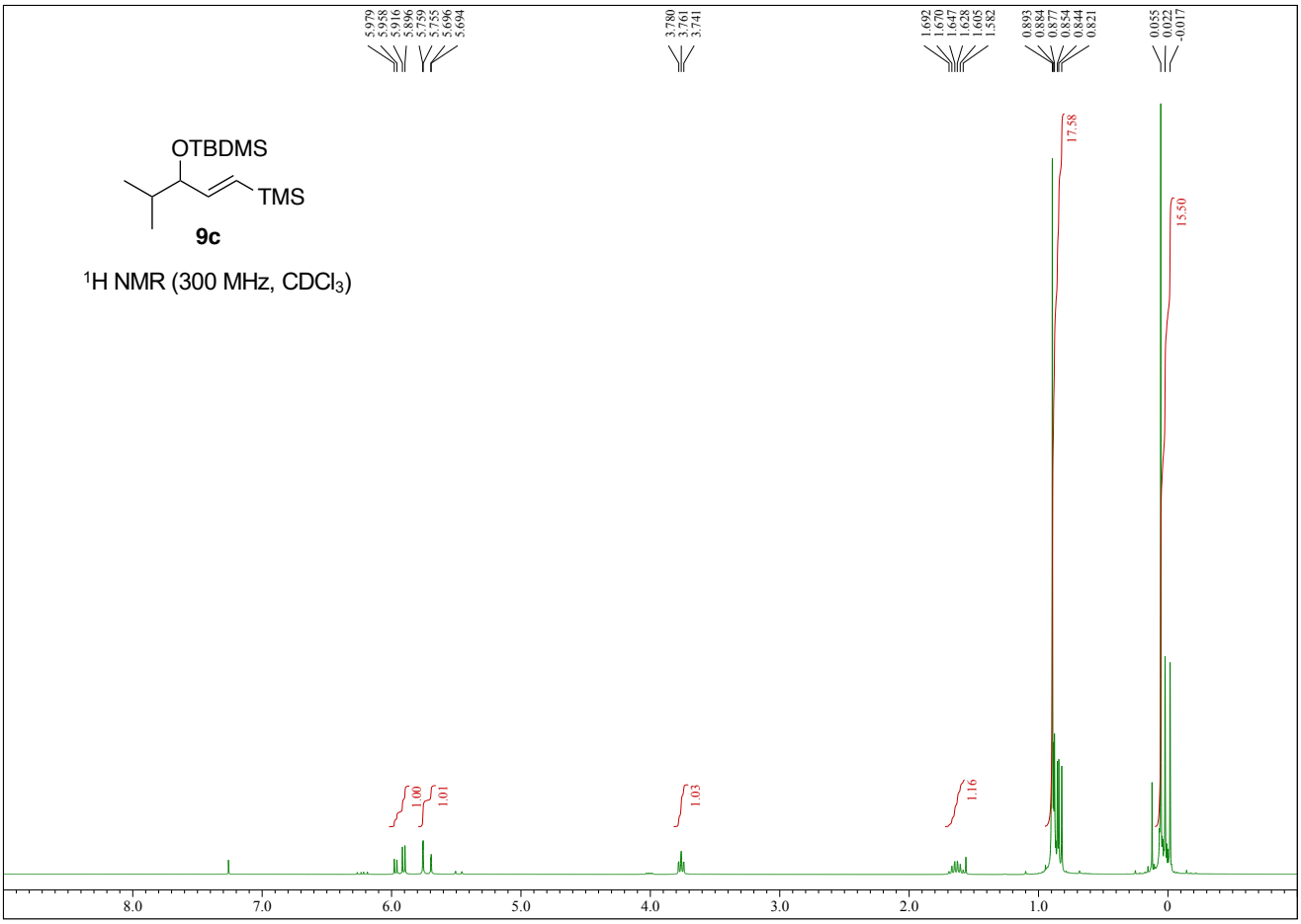
7c

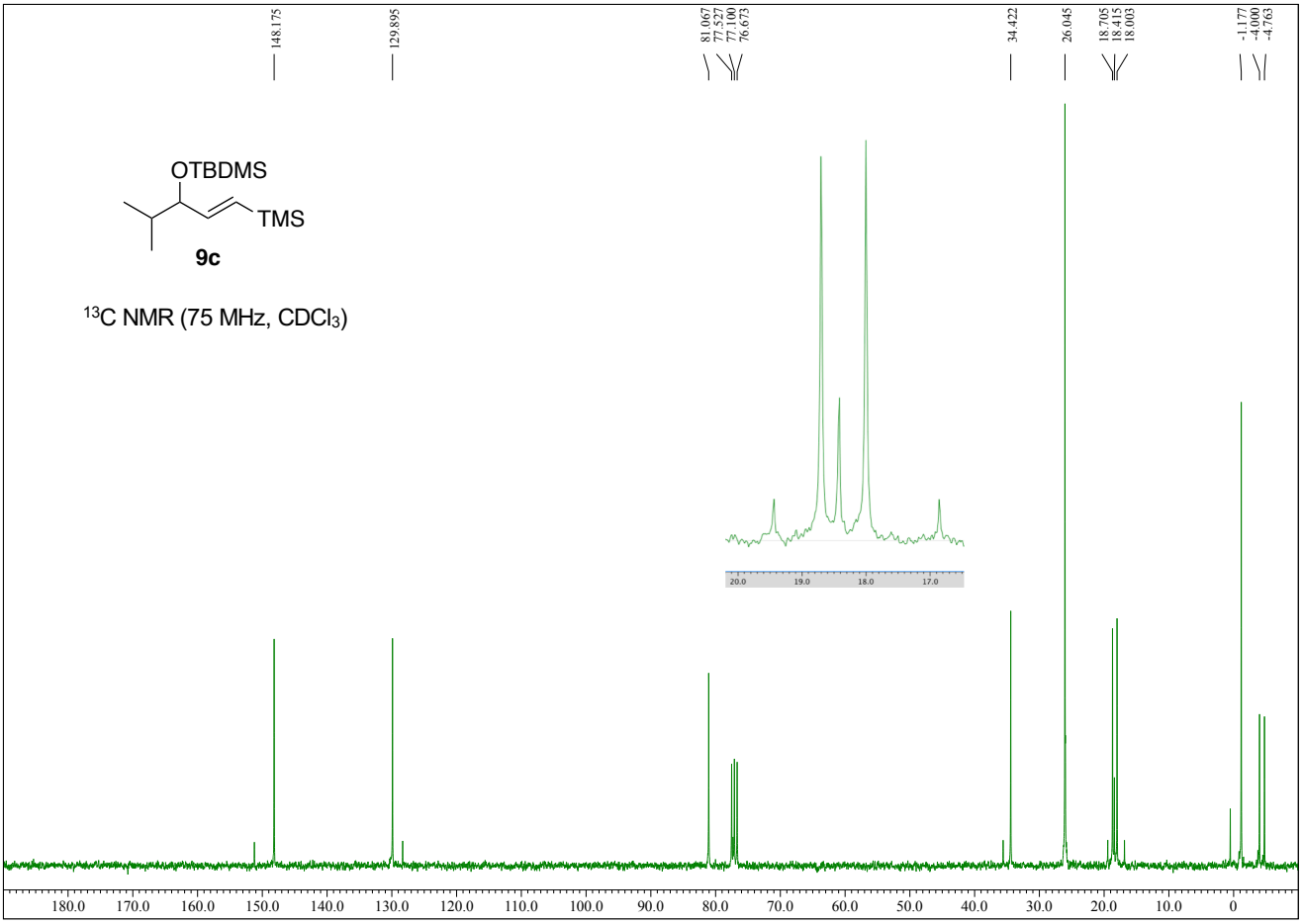
^{1}H NMR (300 MHz, $CDCl_3$)

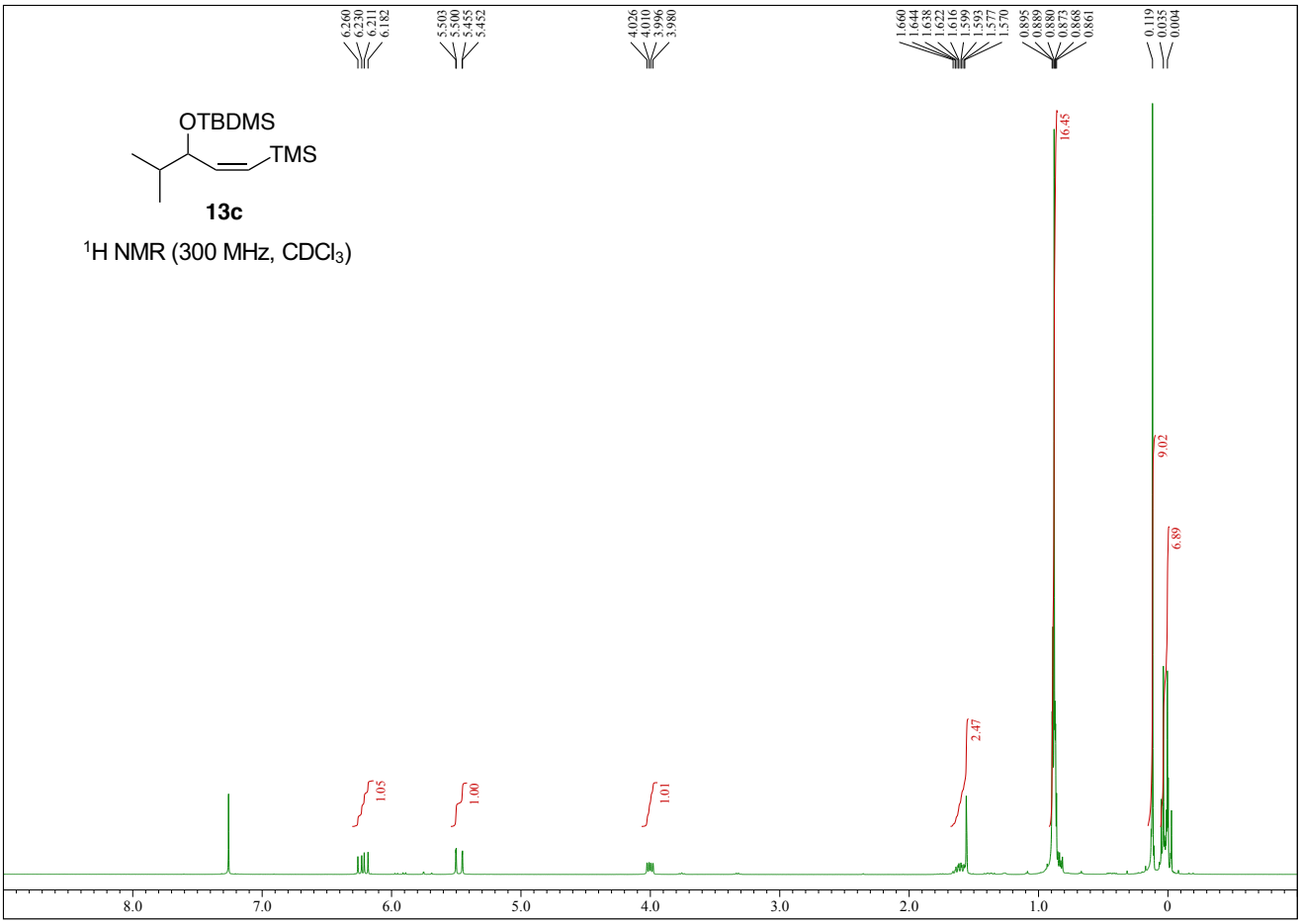


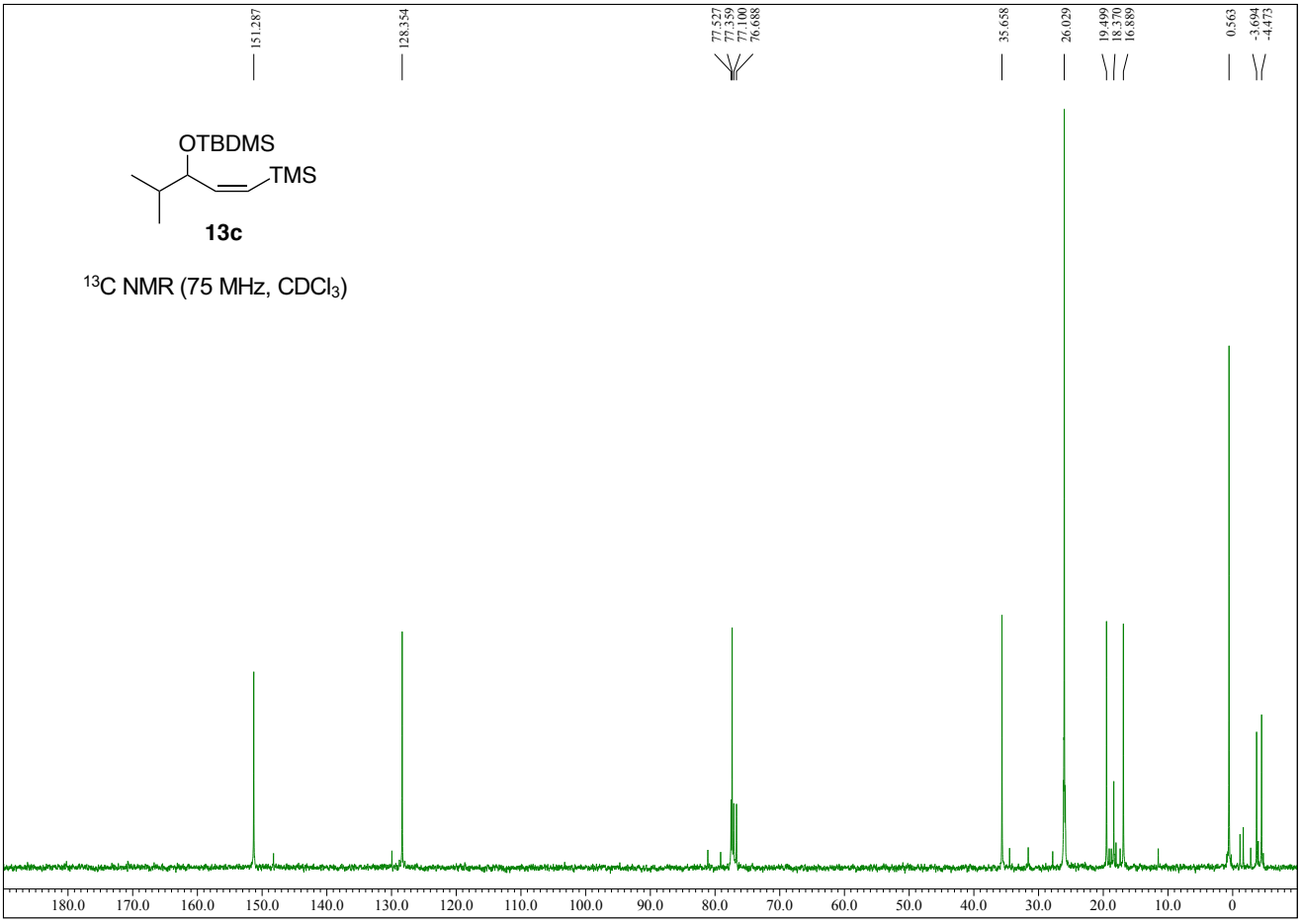
7c

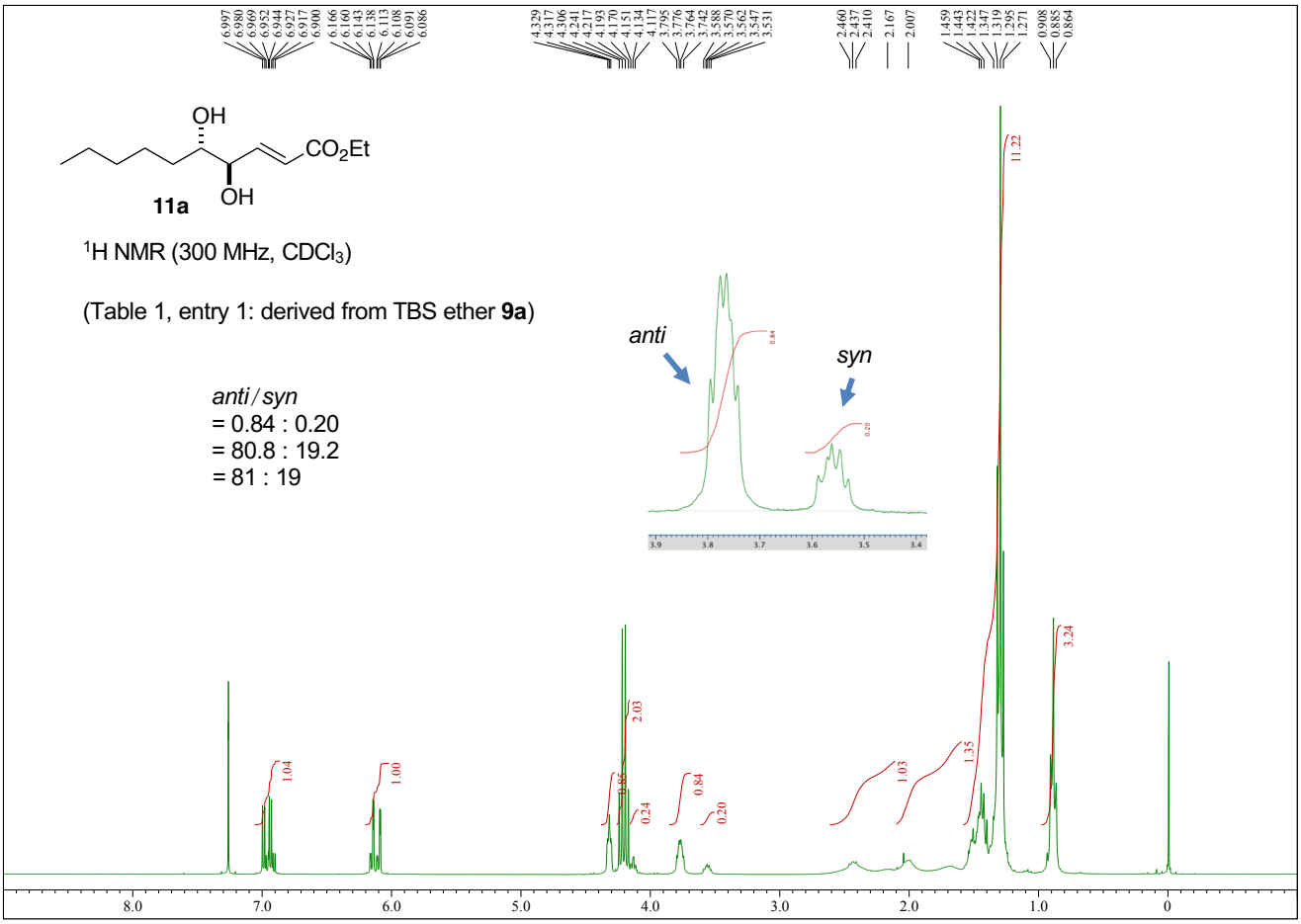
^{13}C NMR (75 MHz, $CDCl_3$)


OTBDMS
TMS
9c
1H NMR (300 MHz, CDCl3)


OTBDMS
TMS
9c
13C NMR (75 MHz, CDCl3)


OTBDMS
TMS
13c
1H NMR (300 MHz, CDCl3)
6.260
6.230
6.211
6.182
5.503
5.500
5.455
5.452
4.026
4.010
3.996
3.980
1.660
1.644
1.638
1.622
1.616
1.599
1.593
1.577
1.570
0.895
0.889
0.880
0.873
0.868
0.861
0.119
0.035
0.004
16.45
9.02
6.89
2.47
1.05
1.00
1.01
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

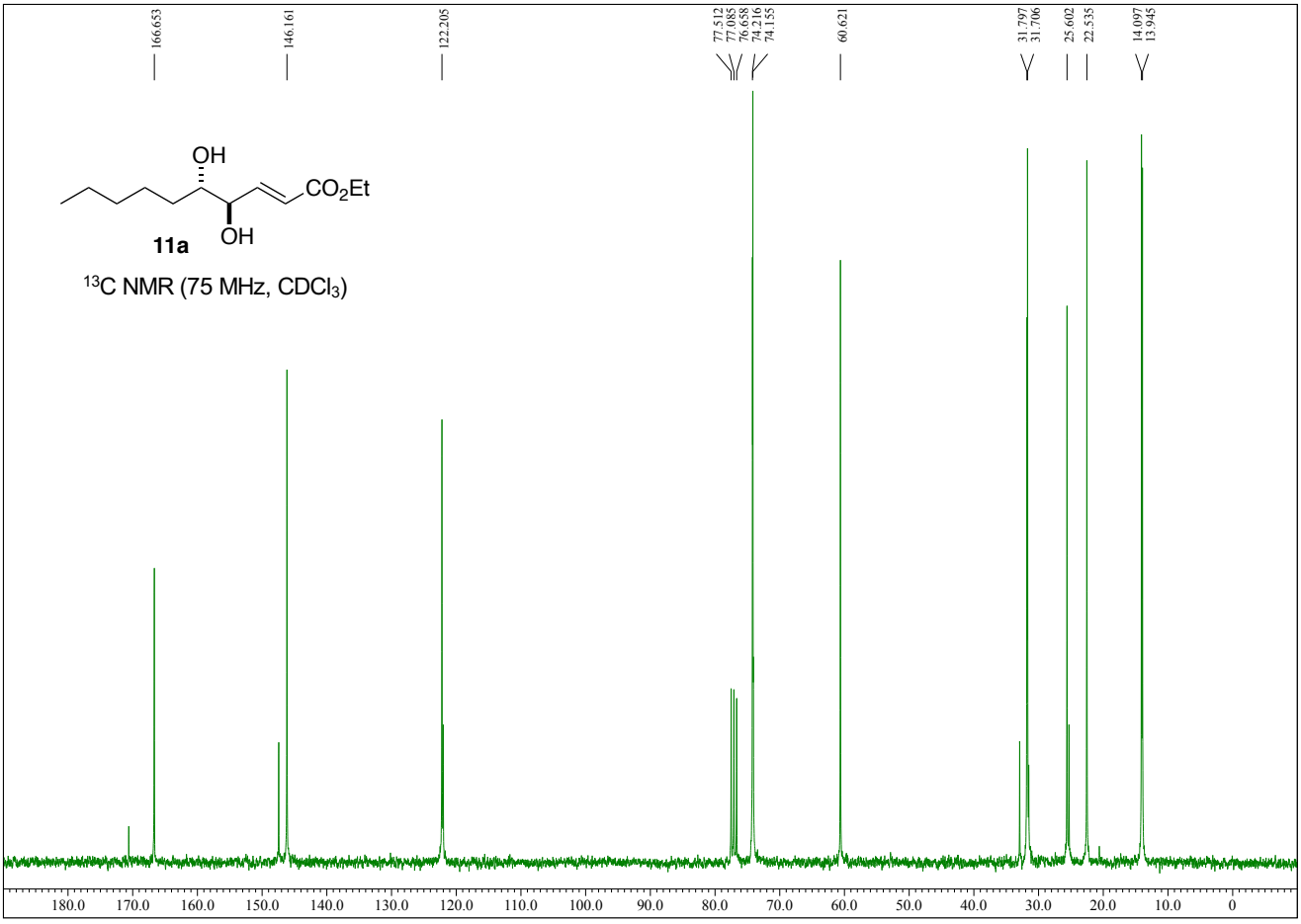

OTBDMS
TMS
13c
13C NMR (75 MHz, CDCl3)
151.287
128.354
77.527
77.359
77.100
76.688
35.658
26.029
19.499
18.370
16.889
0.563
-3.694
-4.473
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0



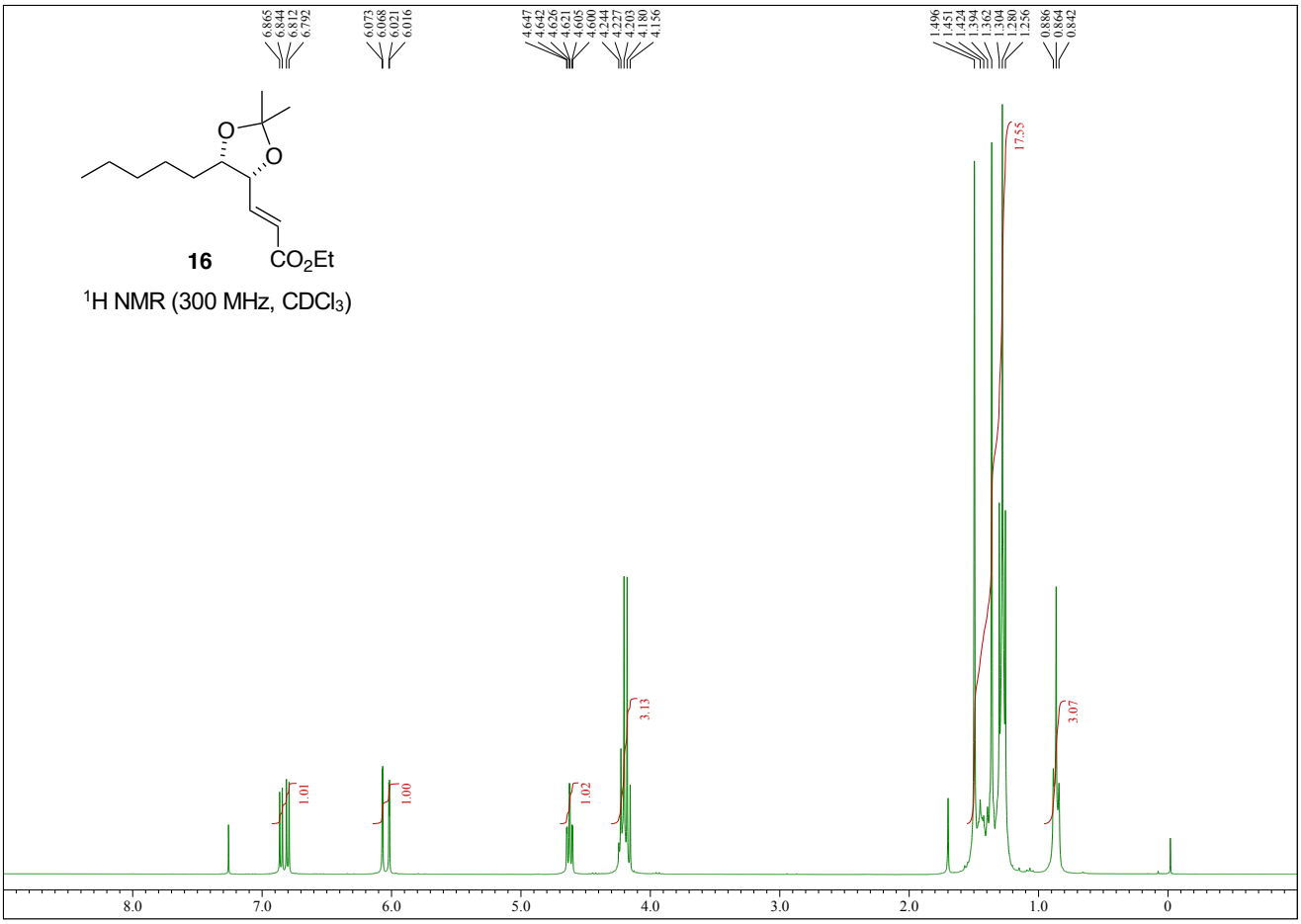
^{1}H NMR (300 MHz, $CDCl_3$)

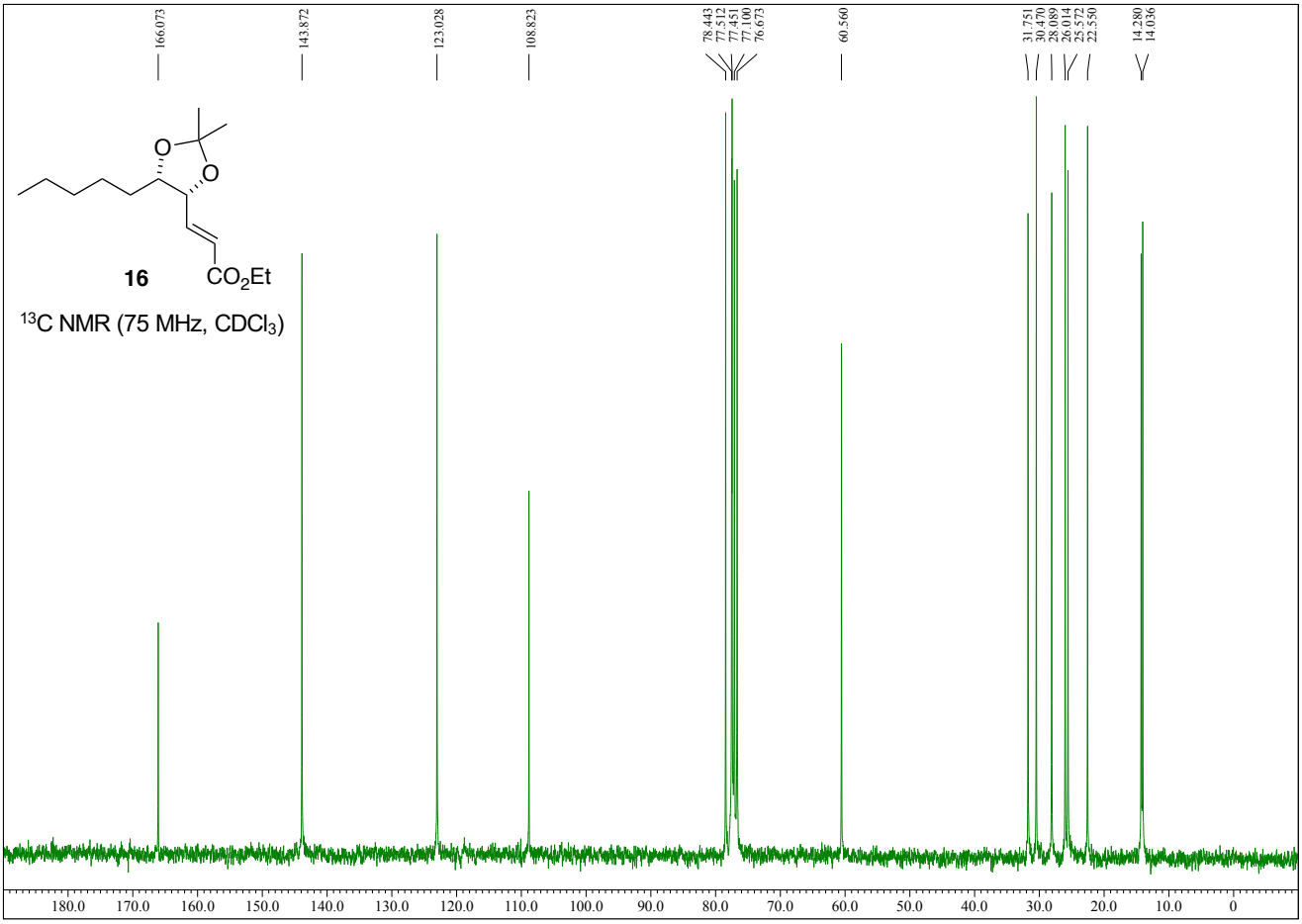
(Table 1, entry 1: derived from TBS ether **9a**)

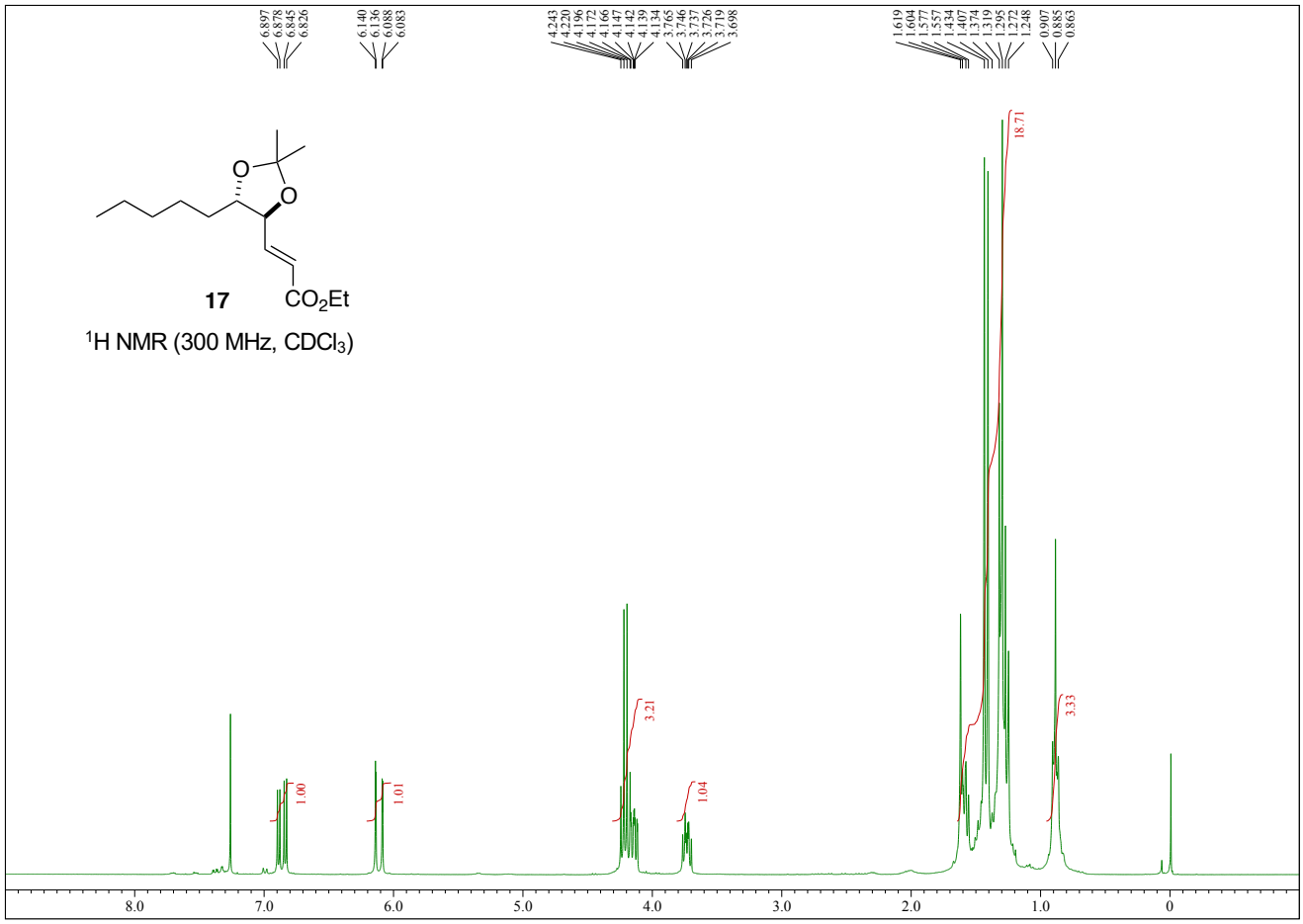
anti / *syn*
= 0.84 : 0.20
= 80.8 : 19.2
= 81 : 19



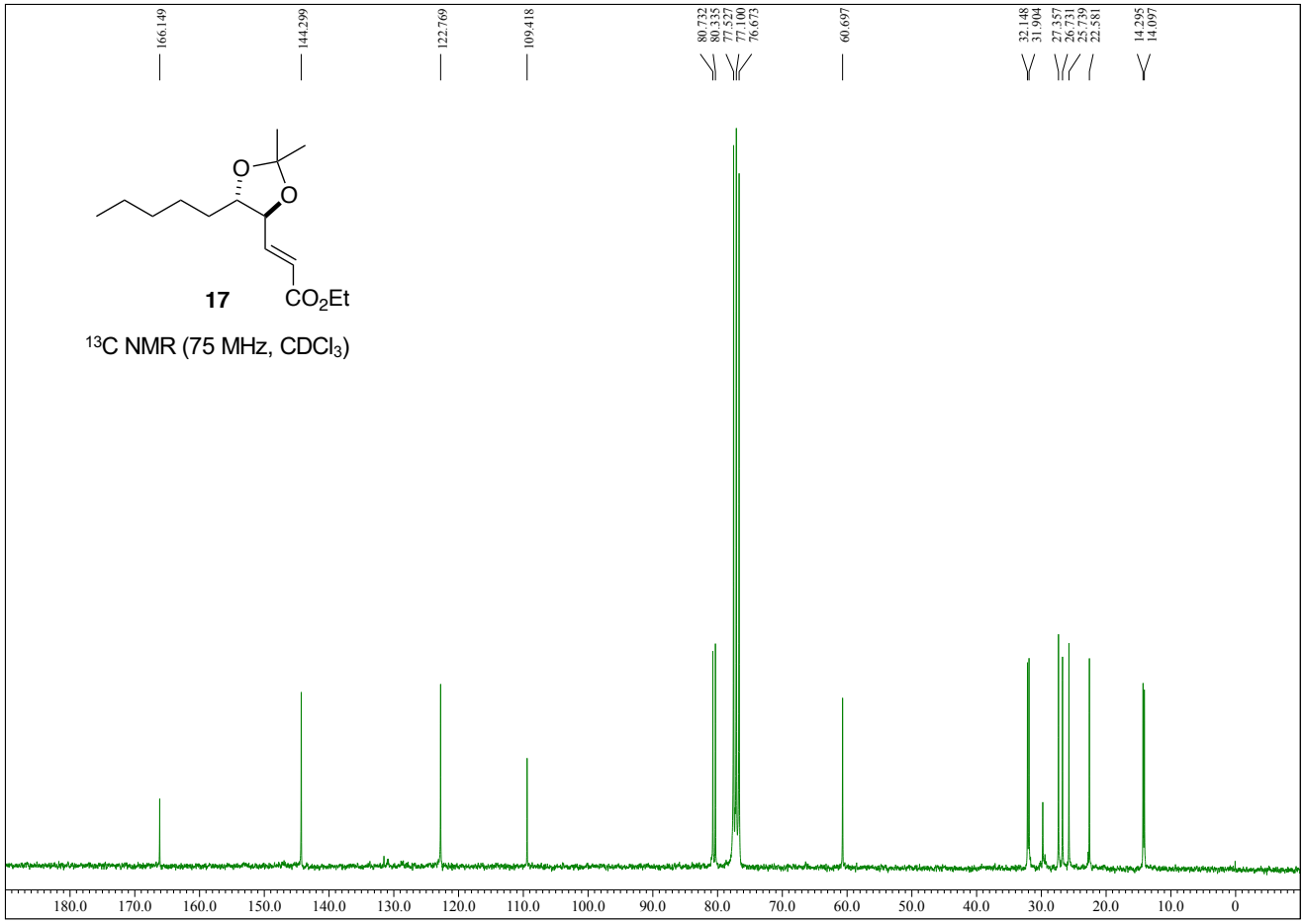
^{13}C NMR (75 MHz, $CDCl_3$)


6.865
6.844
6.812
6.792
6.073
6.068
6.021
6.016
4.647
4.642
4.626
4.621
4.605
4.600
4.244
4.227
4.203
4.180
4.156
1.496
1.451
1.424
1.394
1.342
1.304
1.280
1.256
0.886
0.864
0.842
17.55
3.13
3.07
1.01
1.00
1.02
O
O
16
CO2Et
1H NMR (300 MHz, CDCl3)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

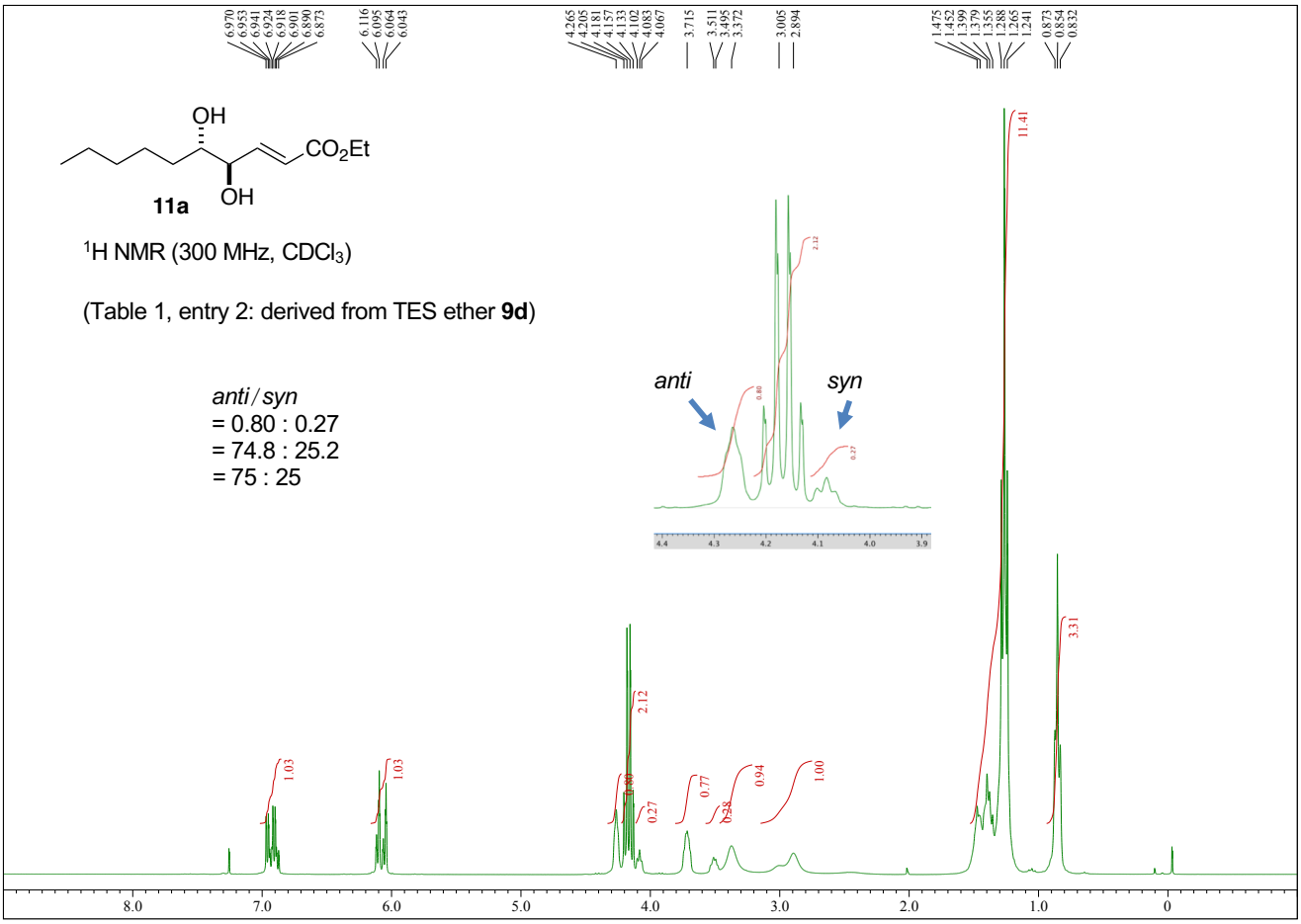

166.073
143.872
123.028
108.823
78.443
77.512
77.451
77.100
76.673
60.560
31.751
30.470
28.089
26.014
25.572
22.550
14.280
14.036
O
O
16
CO2Et
13C NMR (75 MHz, CDCl3)
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0



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



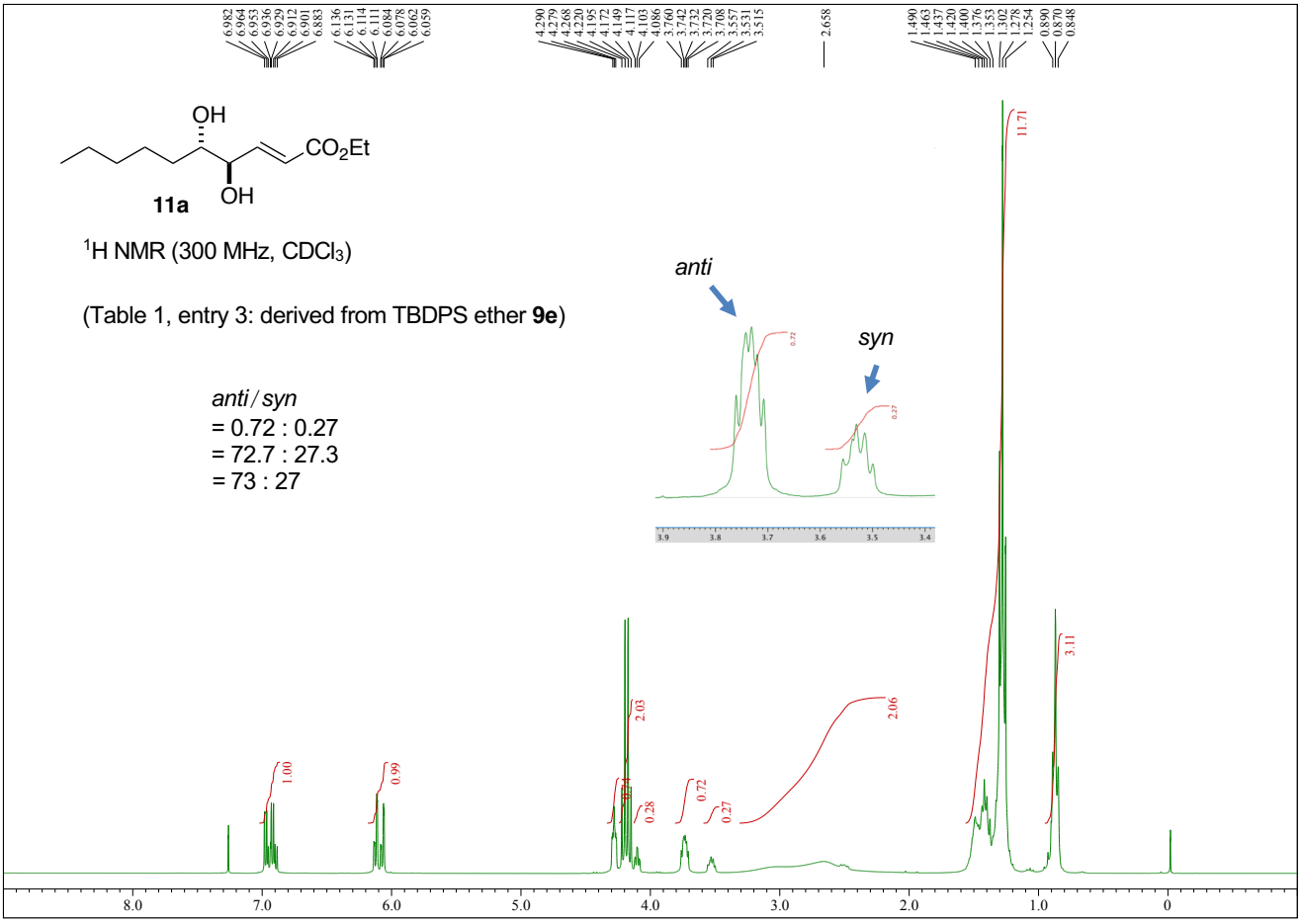
^{13}C NMR (75 MHz, $CDCl_3$)



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

(Table 1, entry 2: derived from TES ether **9d**)

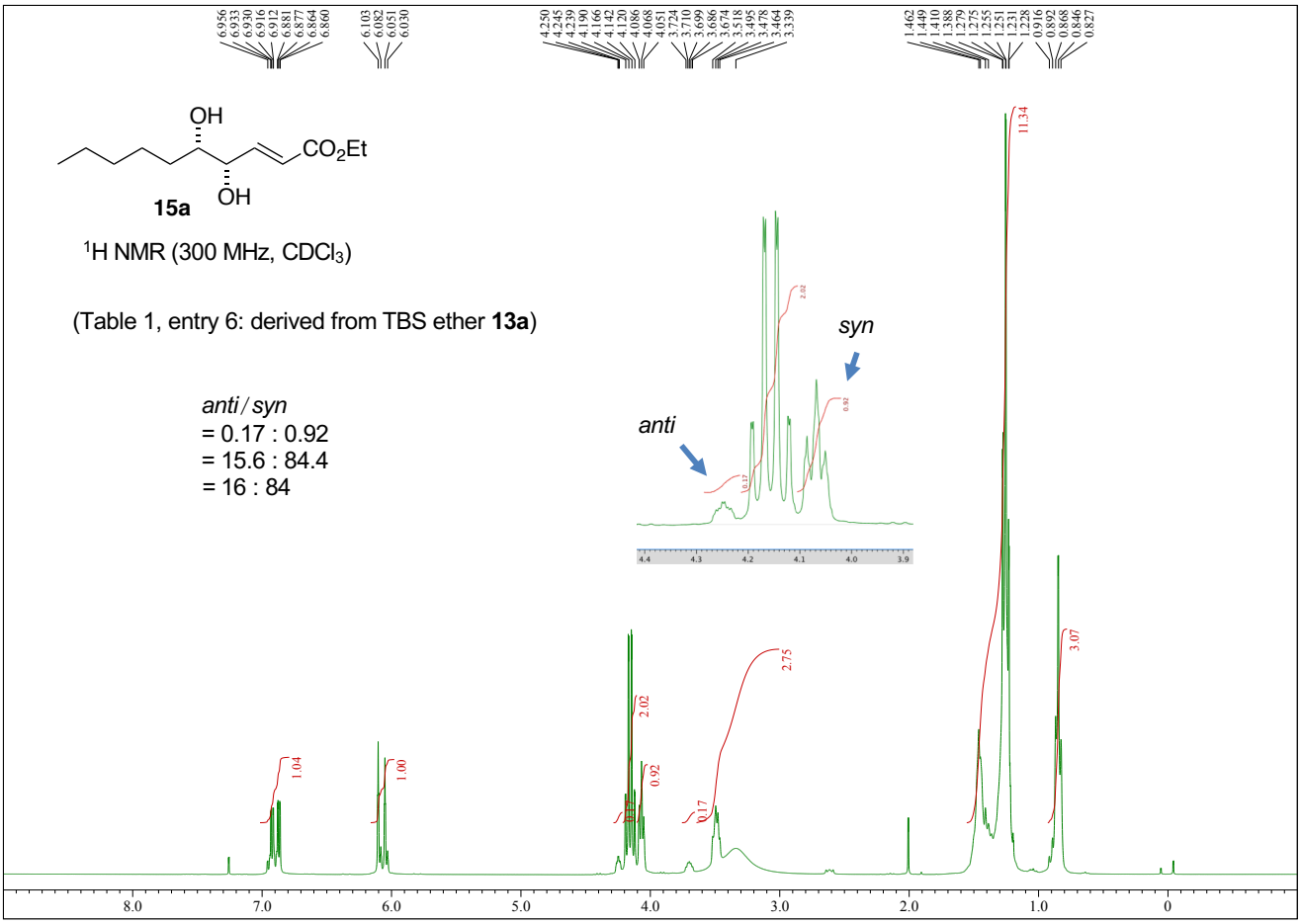
anti / *syn*
= 0.80 : 0.27
= 74.8 : 25.2
= 75 : 25

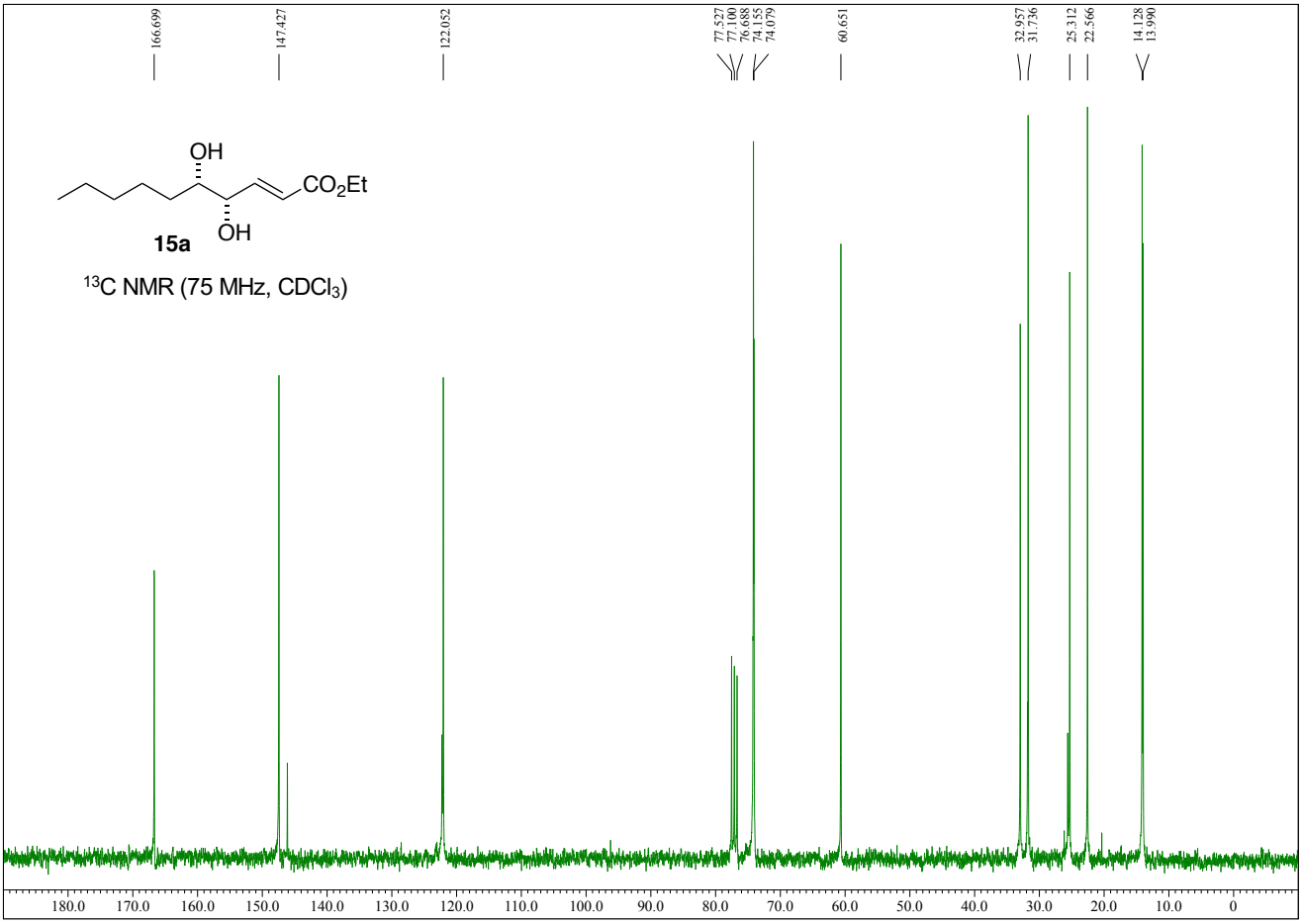


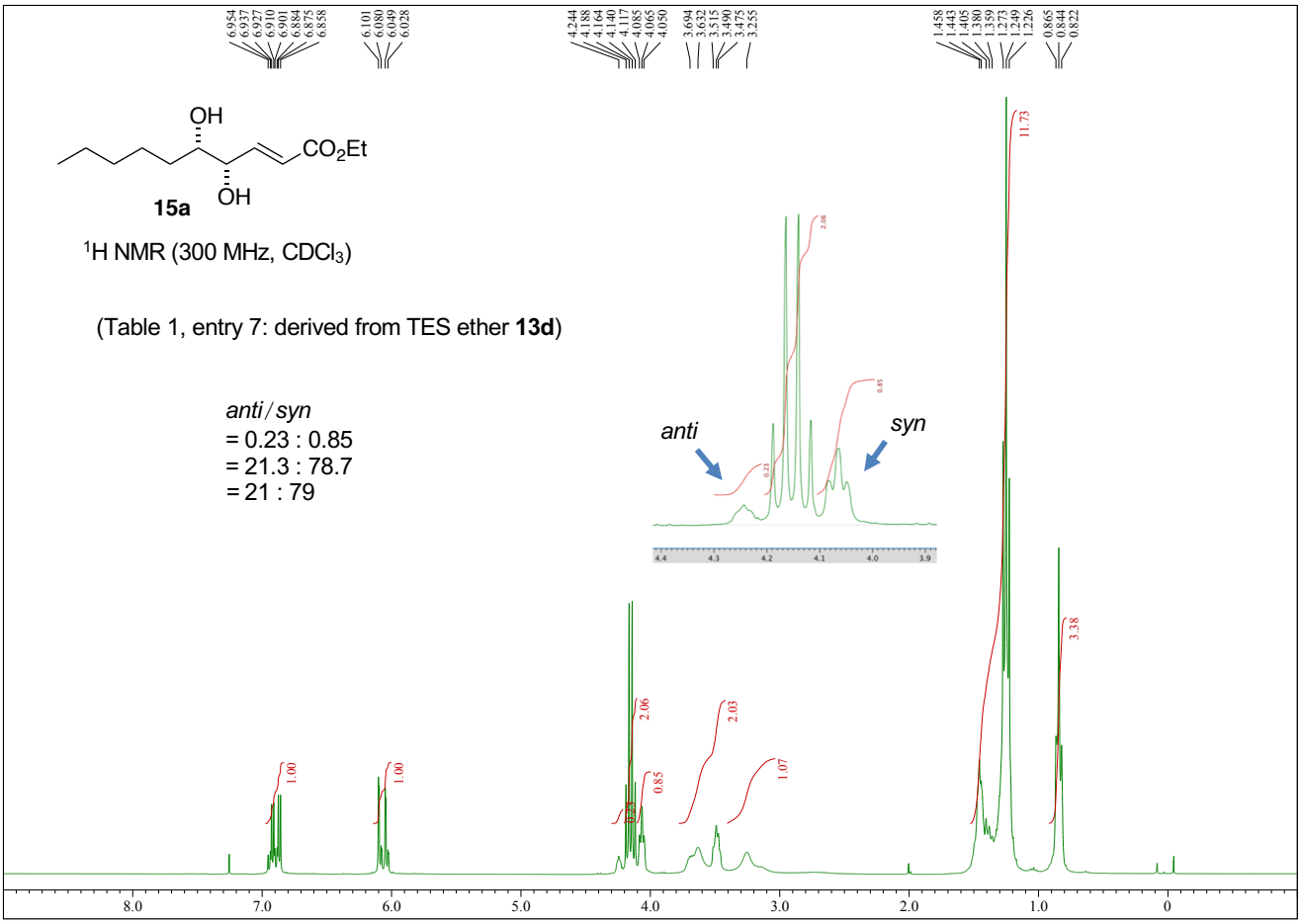
^{1}H NMR (300 MHz, $CDCl_3$)

(Table 1, entry 3: derived from TBDPS ether **9e**)

anti / *syn*
= 0.72 : 0.27
= 72.7 : 27.3
= 73 : 27


OH
CO2Et
OH
15a
1H NMR (300 MHz, CDCl3)
(Table 1, entry 6: derived from TBS ether 13a)
anti / syn
= 0.17 : 0.92
= 15.6 : 84.4
= 16 : 84
anti
syn

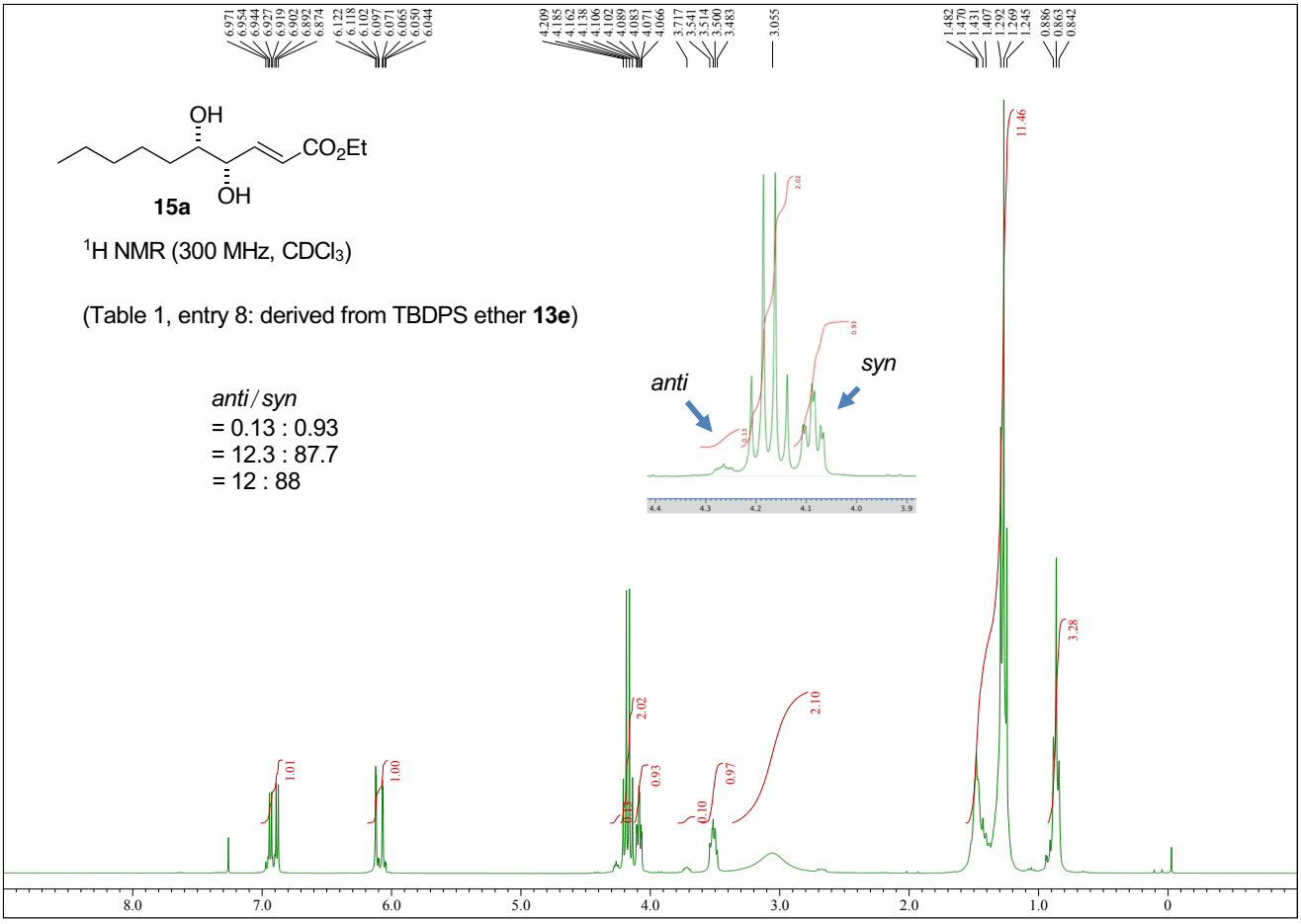

OH
CO2Et
OH
15a
13C NMR (75 MHz, CDCl3)



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

(Table 1, entry 7: derived from TES ether **13d**)

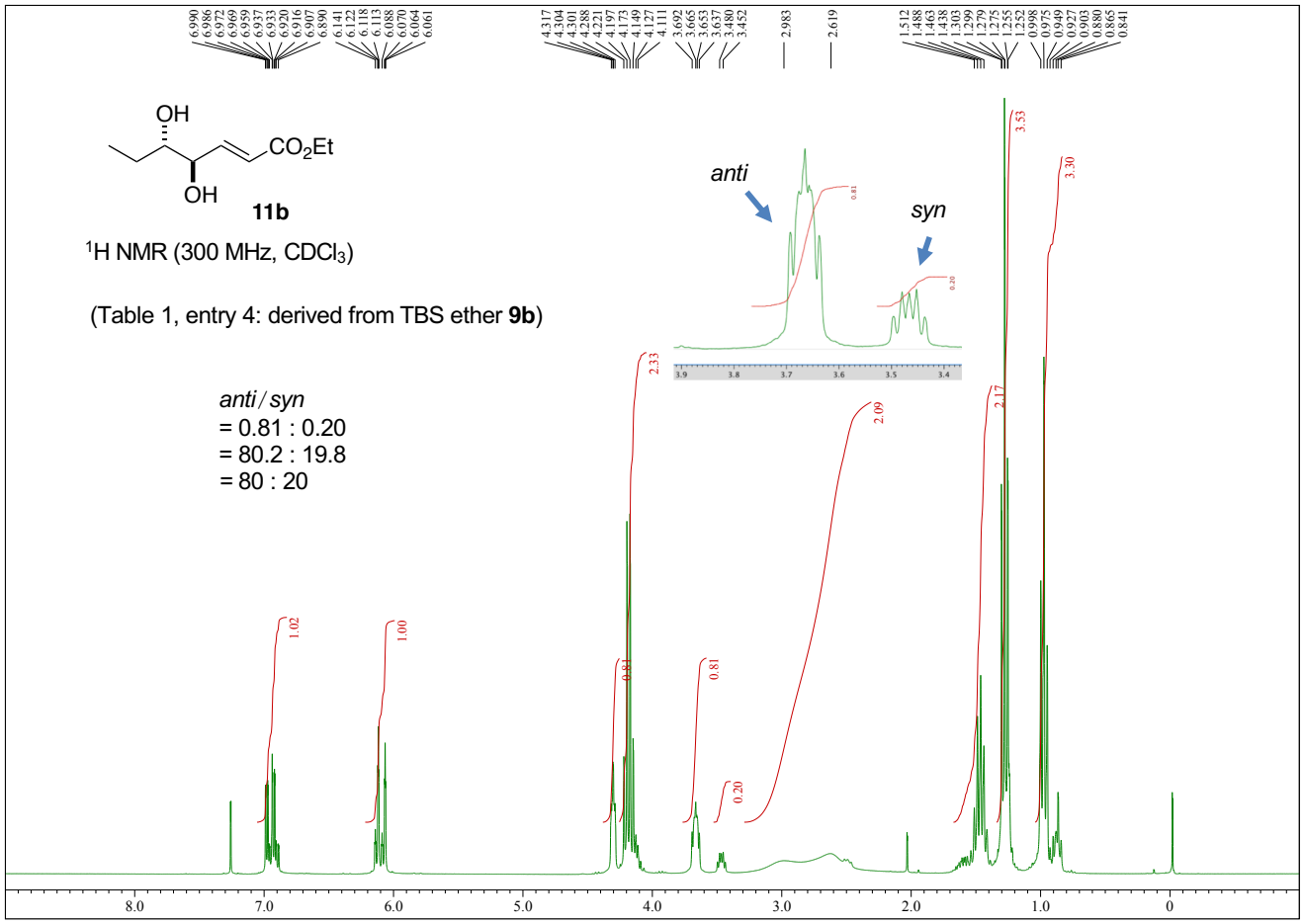
anti / *syn*
= 0.23 : 0.85
= 21.3 : 78.7
= 21 : 79

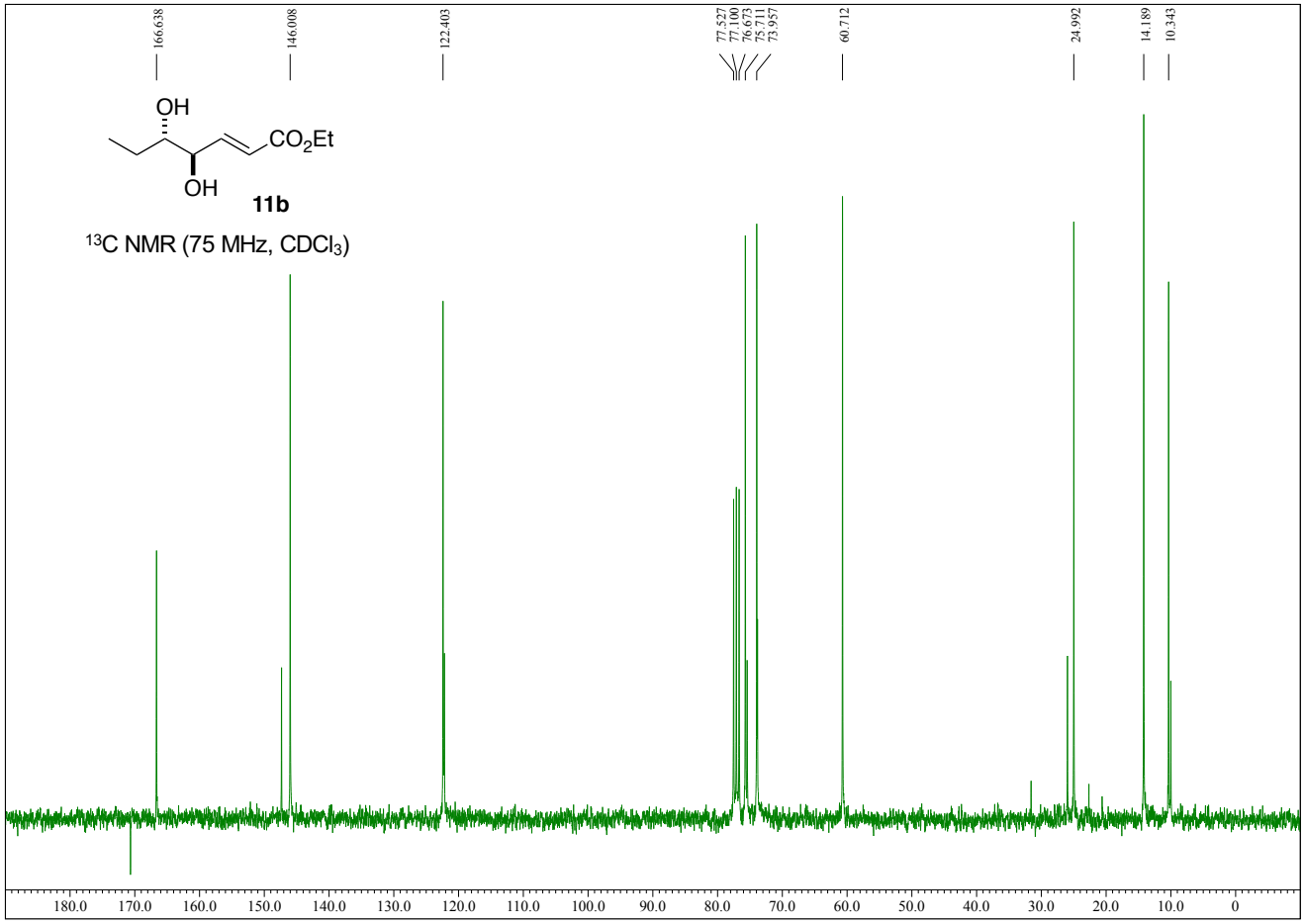


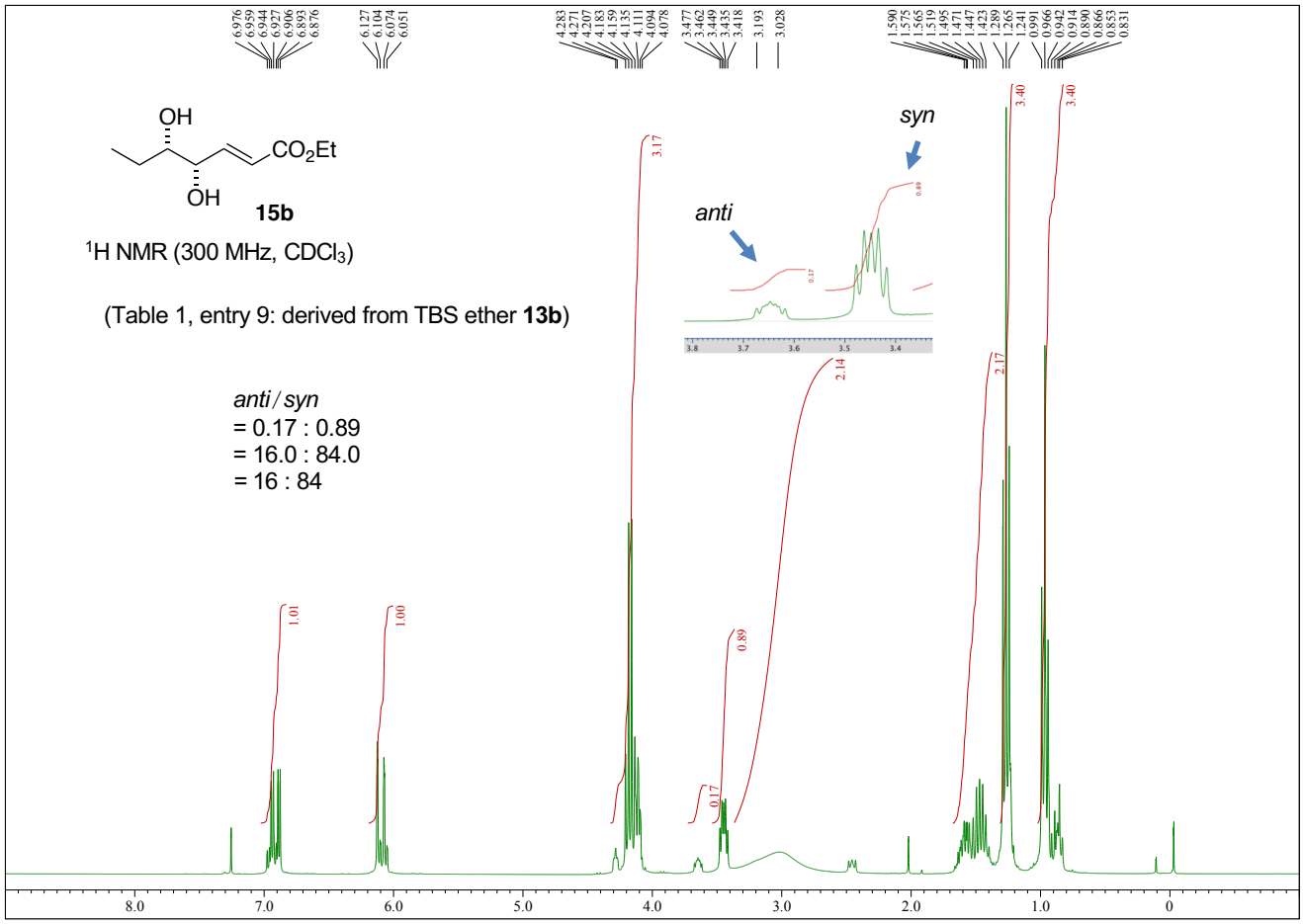
^{1}H NMR (300 MHz, $CDCl_3$)

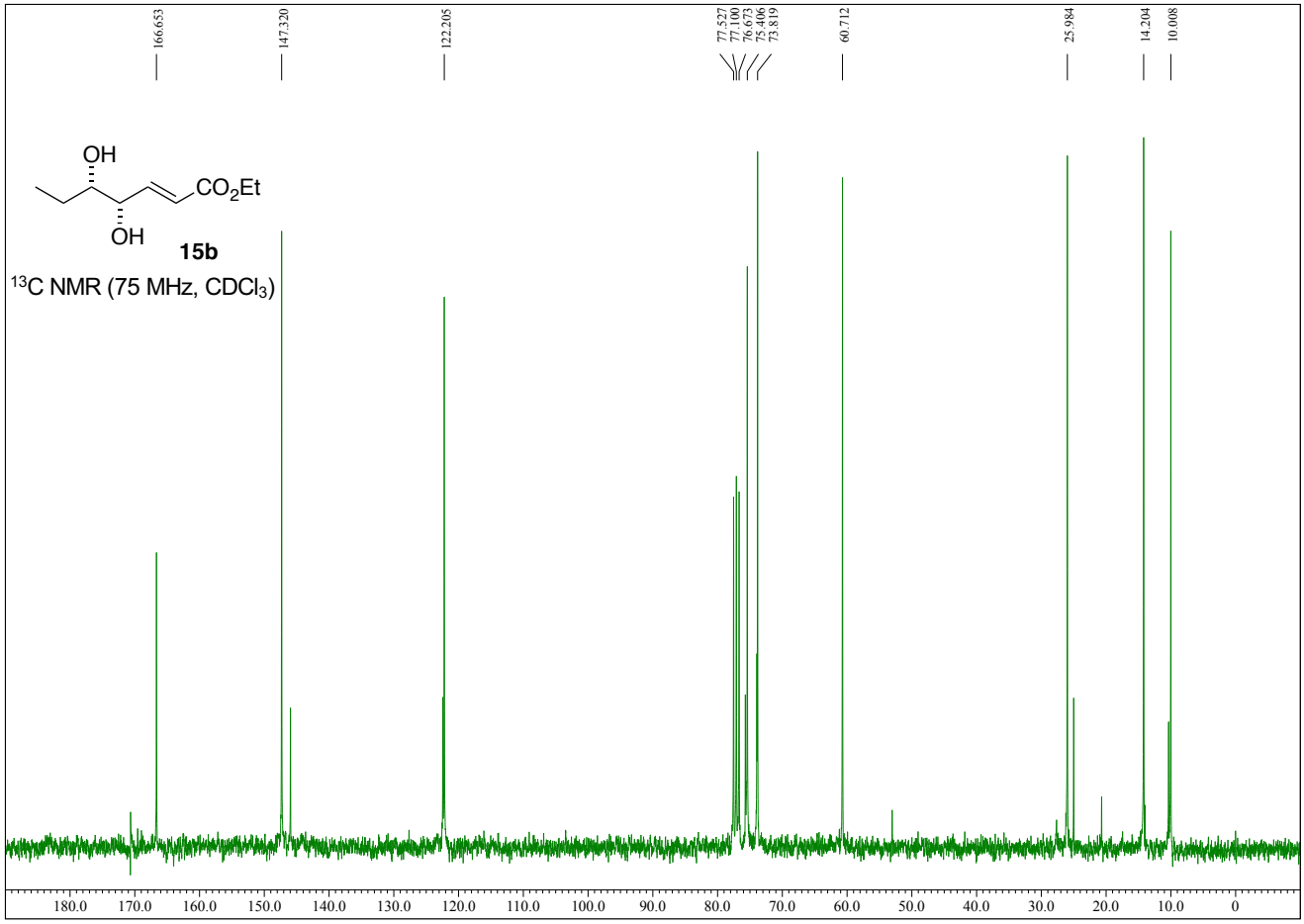
(Table 1, entry 8: derived from TBDPS ether **13e**)

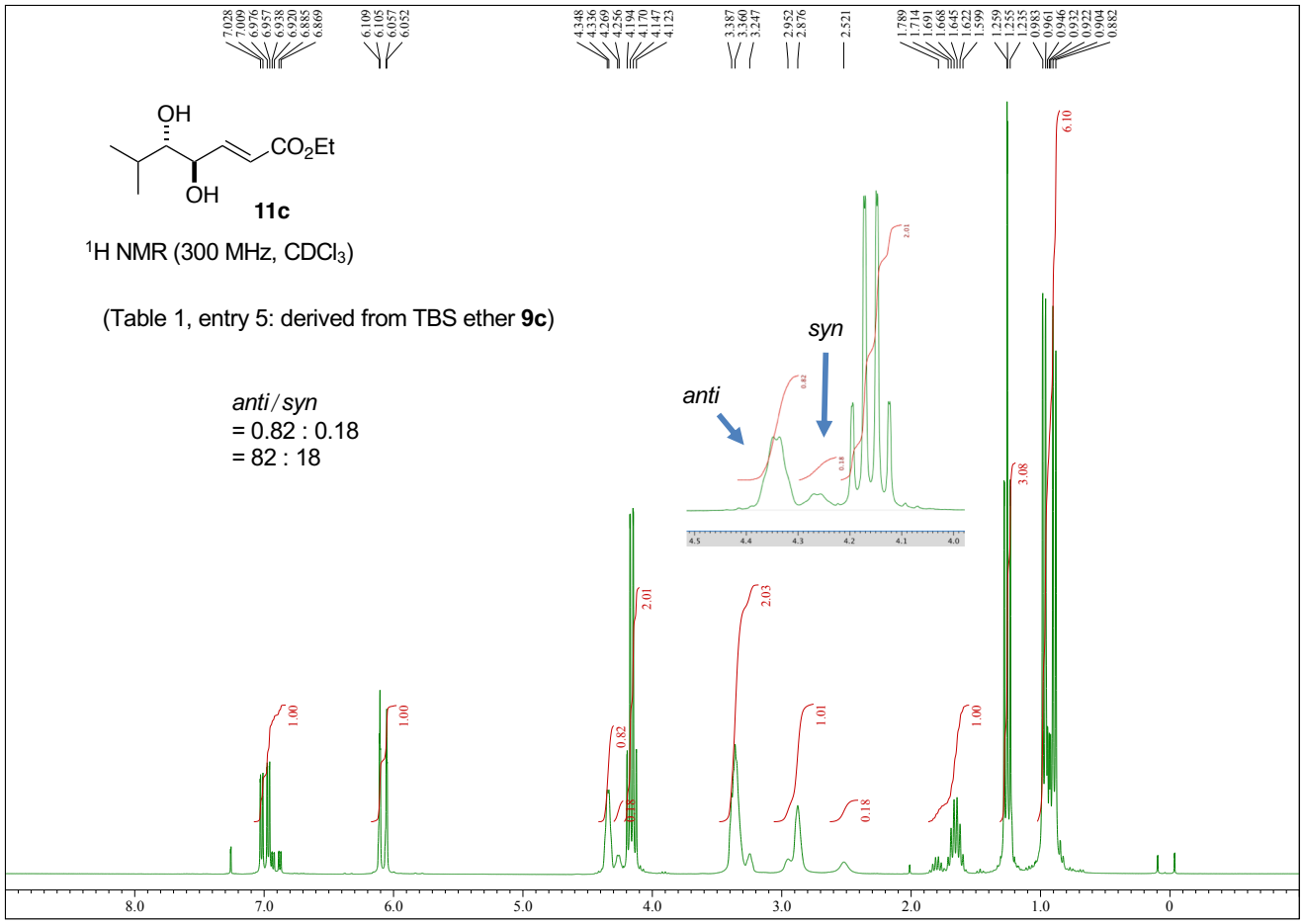
anti / *syn*
= 0.13 : 0.93
= 12.3 : 87.7
= 12 : 88

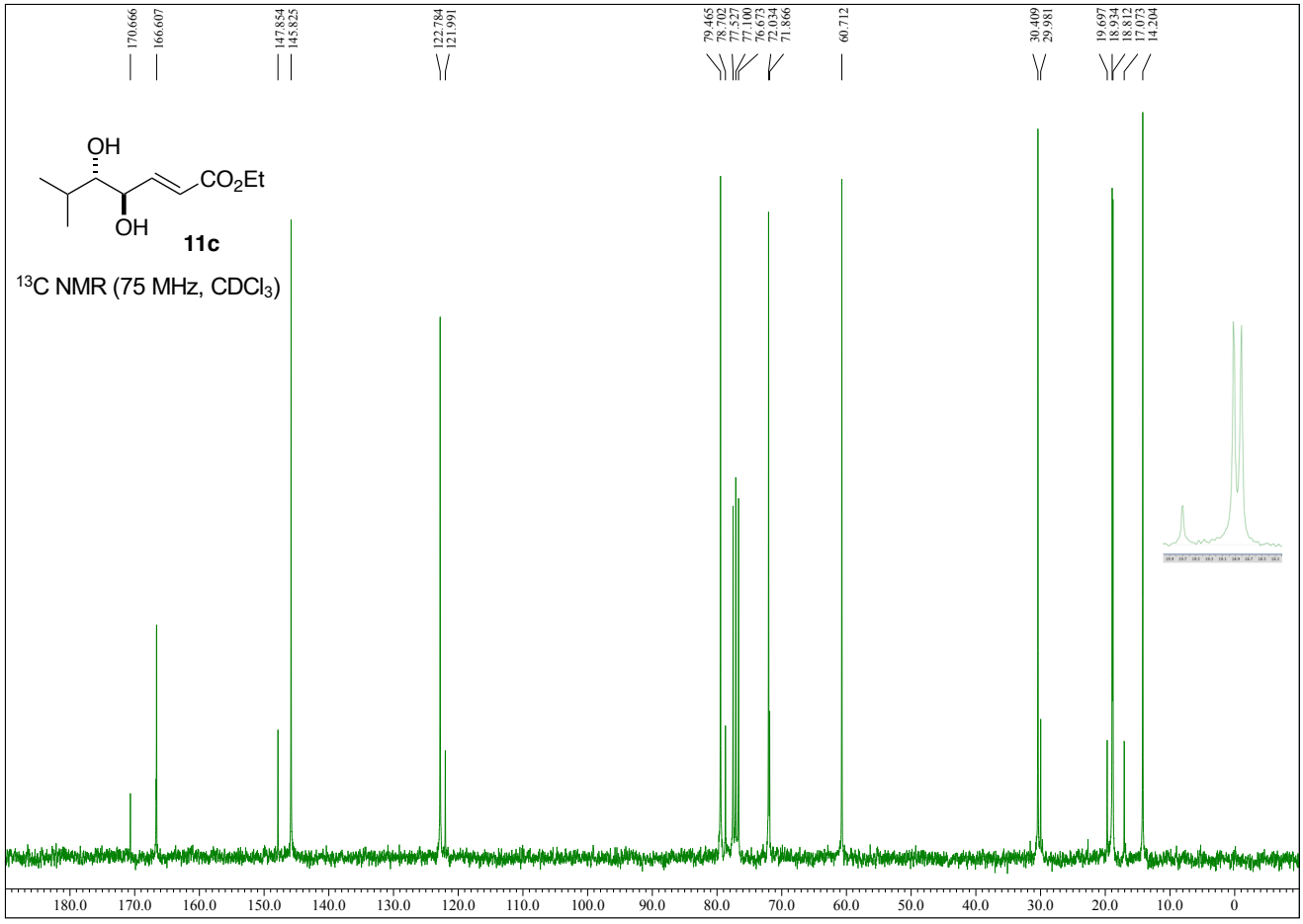

OH
CO2Et
OH
11b
1H NMR (300 MHz, CDCl3)
(Table 1, entry 4: derived from TBS ether 9b)
anti / syn
= 0.81 : 0.20
= 80.2 : 19.8
= 80 : 20
anti
syn

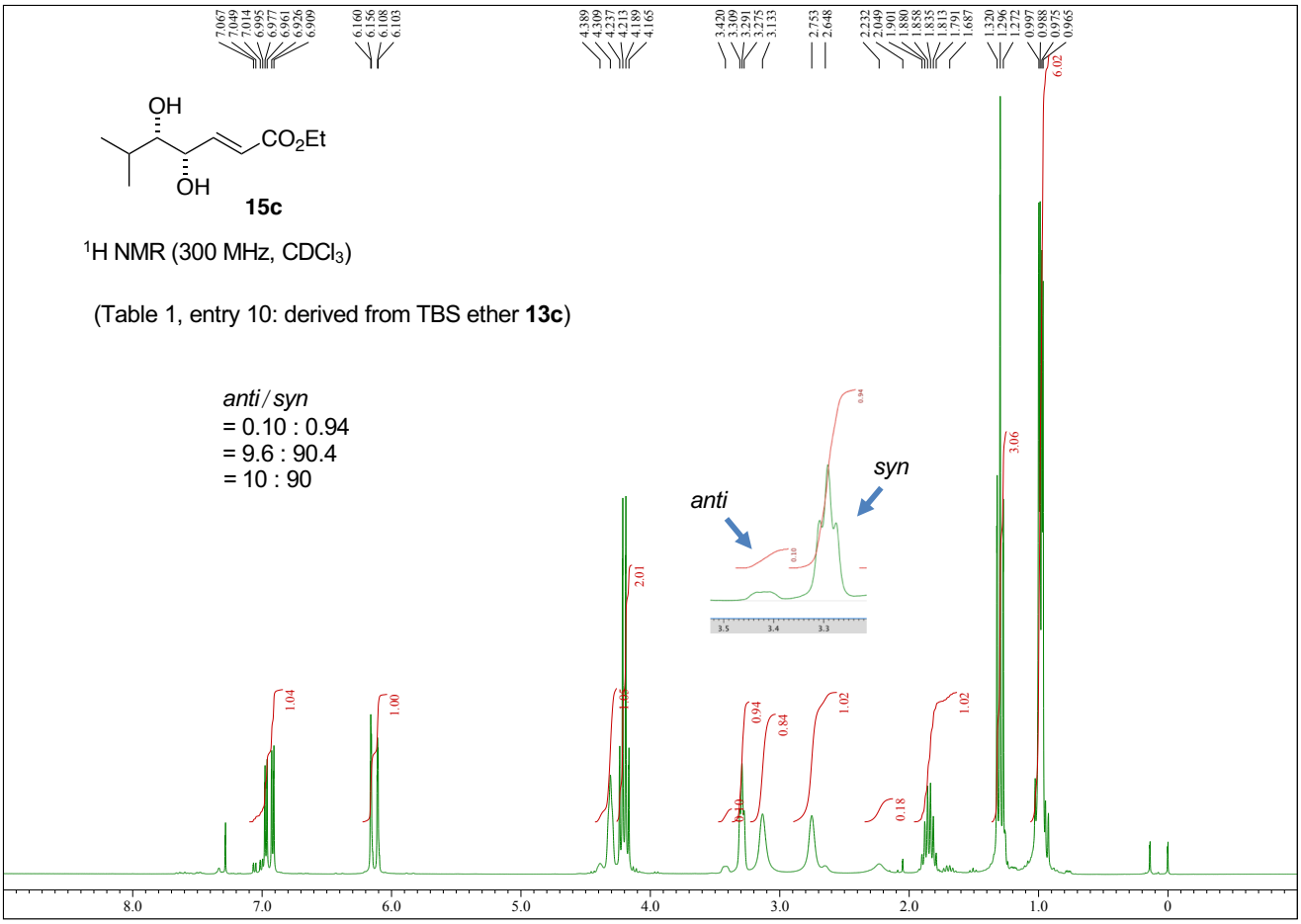

OH
CO2Et
OH
11b
13C NMR (75 MHz, CDCl3)


OH
CO2Et
OH
15b
1H NMR (300 MHz, CDCl3)
(Table 1, entry 9: derived from TBS ether 13b)
anti / syn
= 0.17 : 0.89
= 16.0 : 84.0
= 16 : 84
syn
anti


OH
CO2Et
OH
15b
13C NMR (75 MHz, CDCl3)


OH
CO2Et
OH
11c
1H NMR (300 MHz, CDCl3)
(Table 1, entry 5: derived from TBS ether 9c)
anti/syn
= 0.82 : 0.18
= 82 : 18
anti
syn

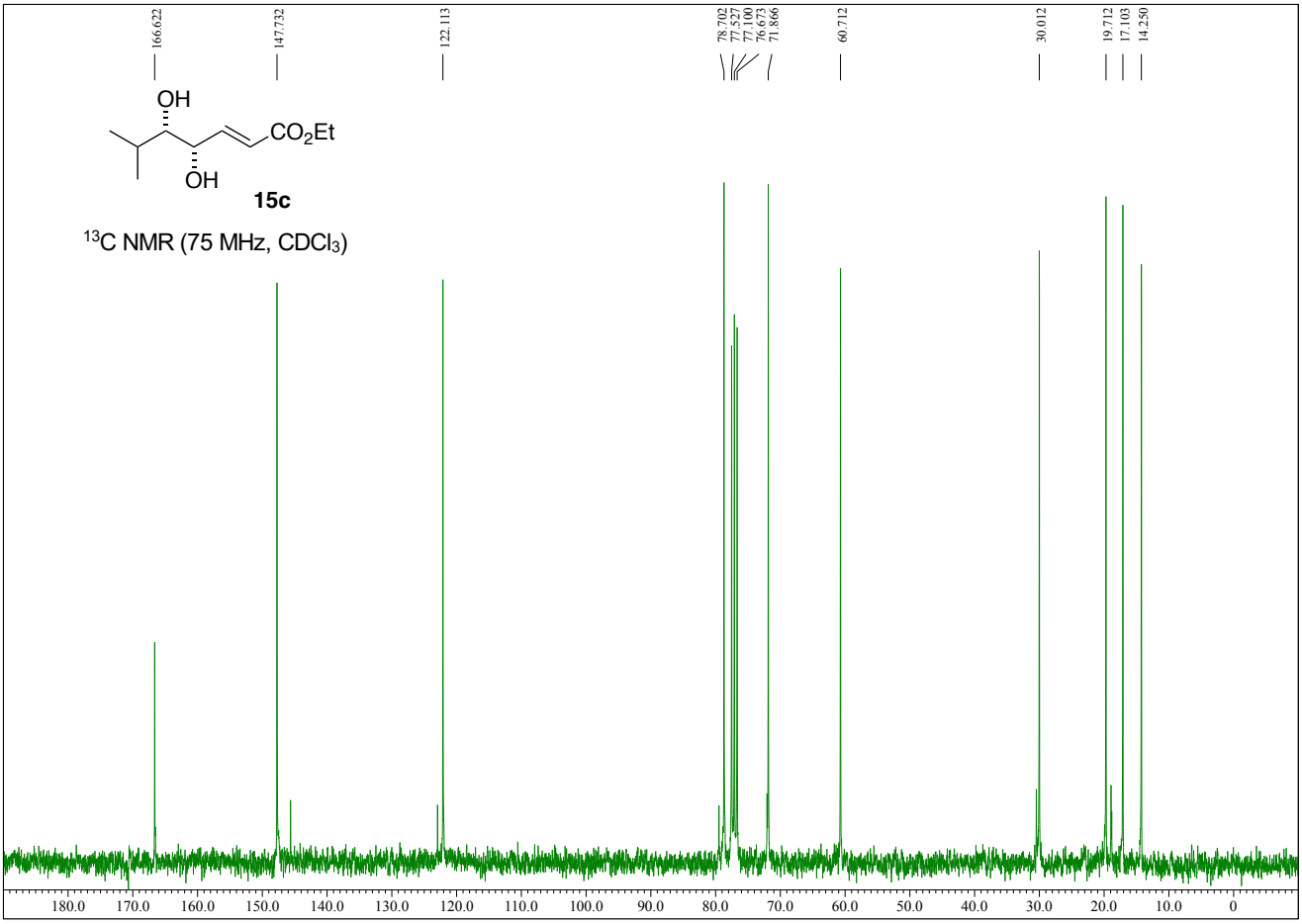

OH
CO2Et
OH
11c
13C NMR (75 MHz, CDCl3)



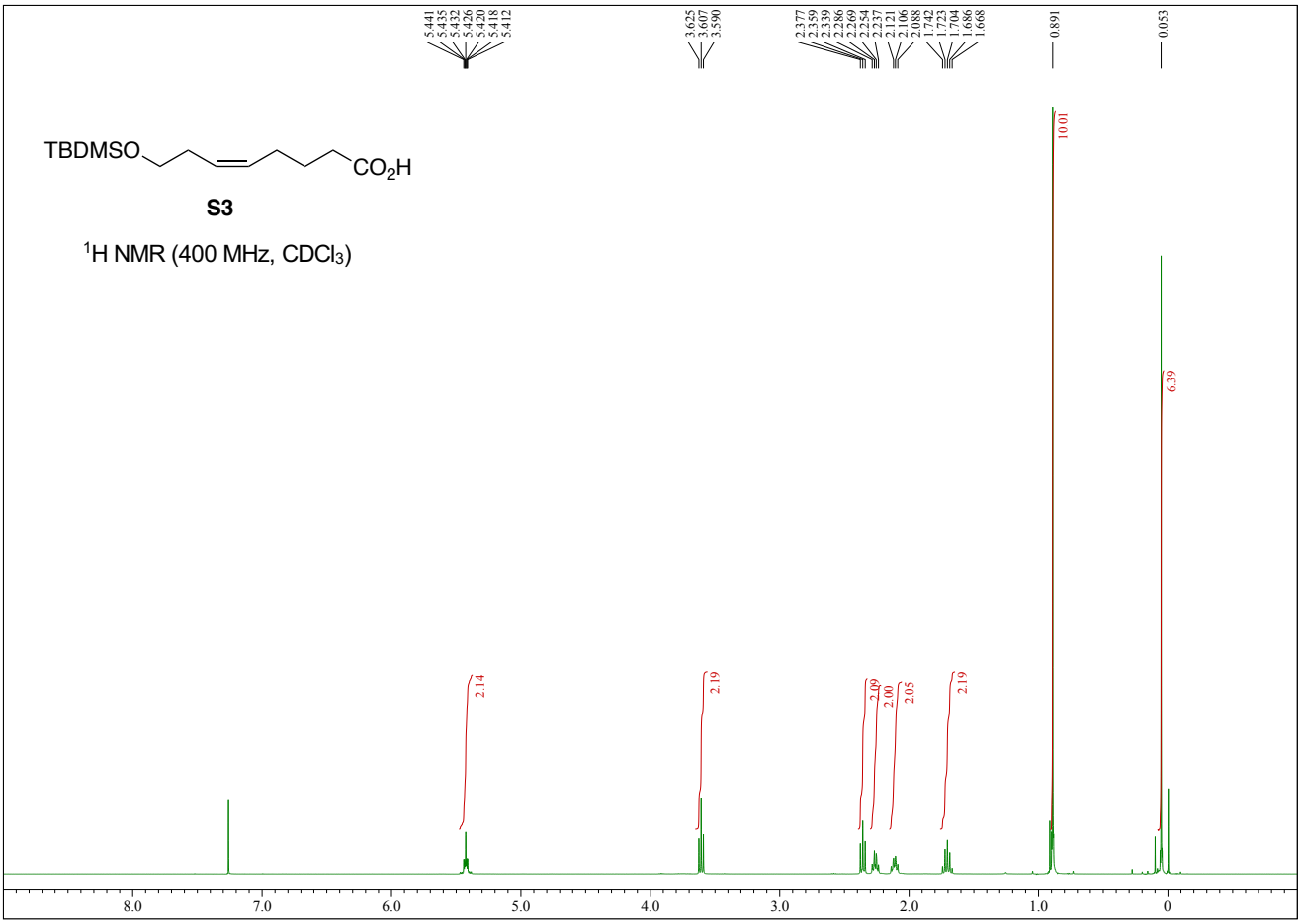
^{1}H NMR (300 MHz, $CDCl_3$)

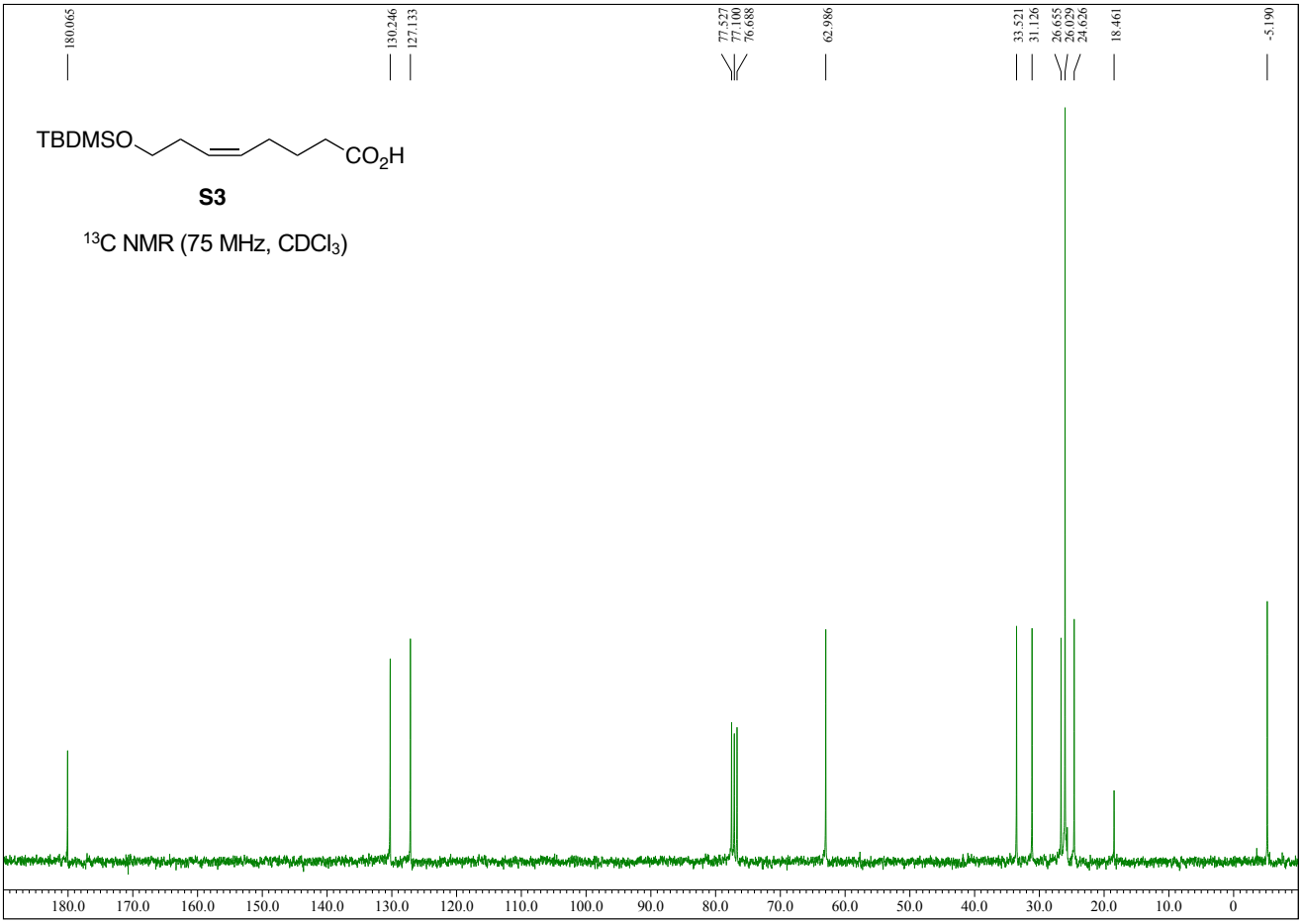
(Table 1, entry 10: derived from TBS ether **13c**)

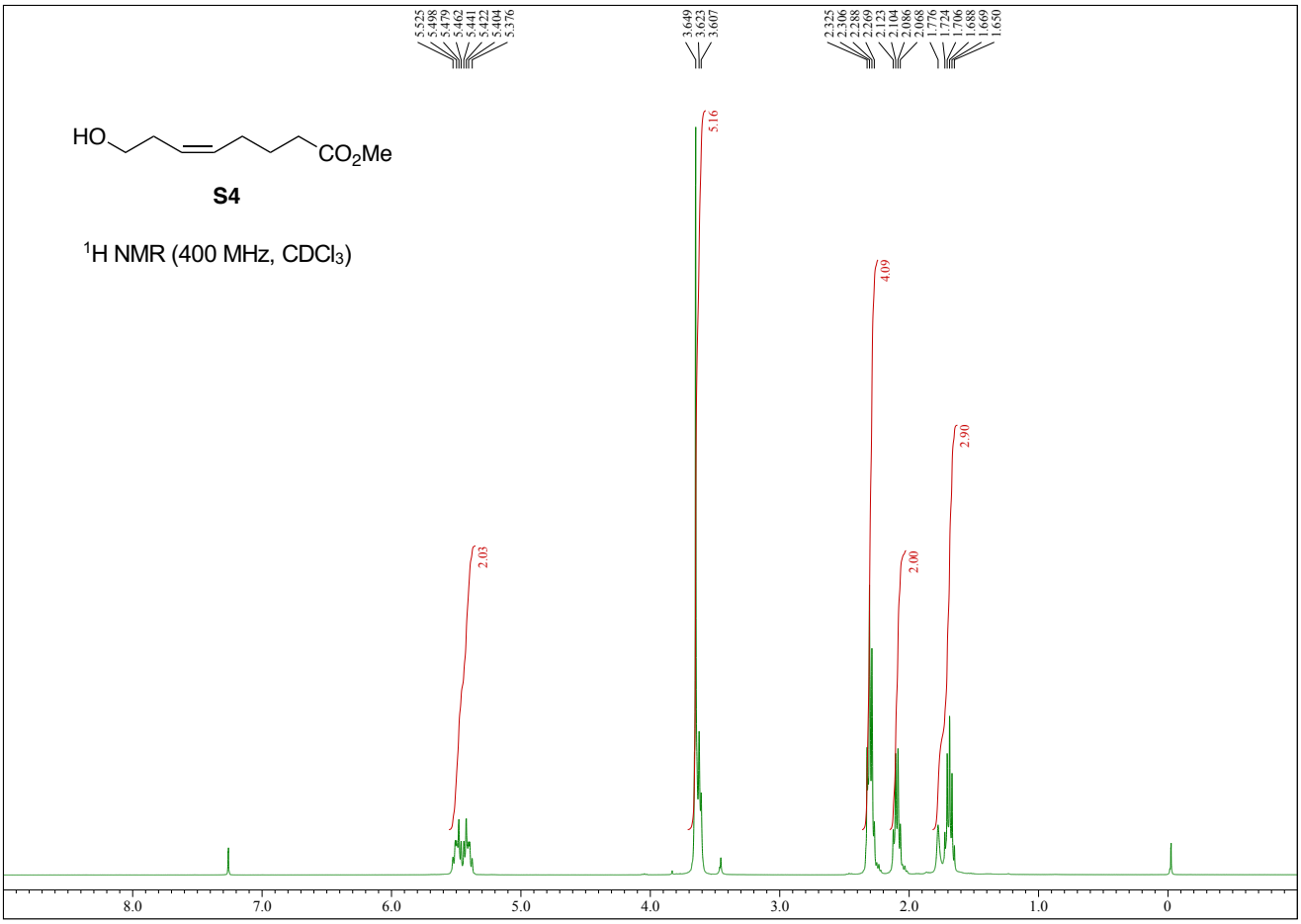
anti / *syn*
= 0.10 : 0.94
= 9.6 : 90.4
= 10 : 90

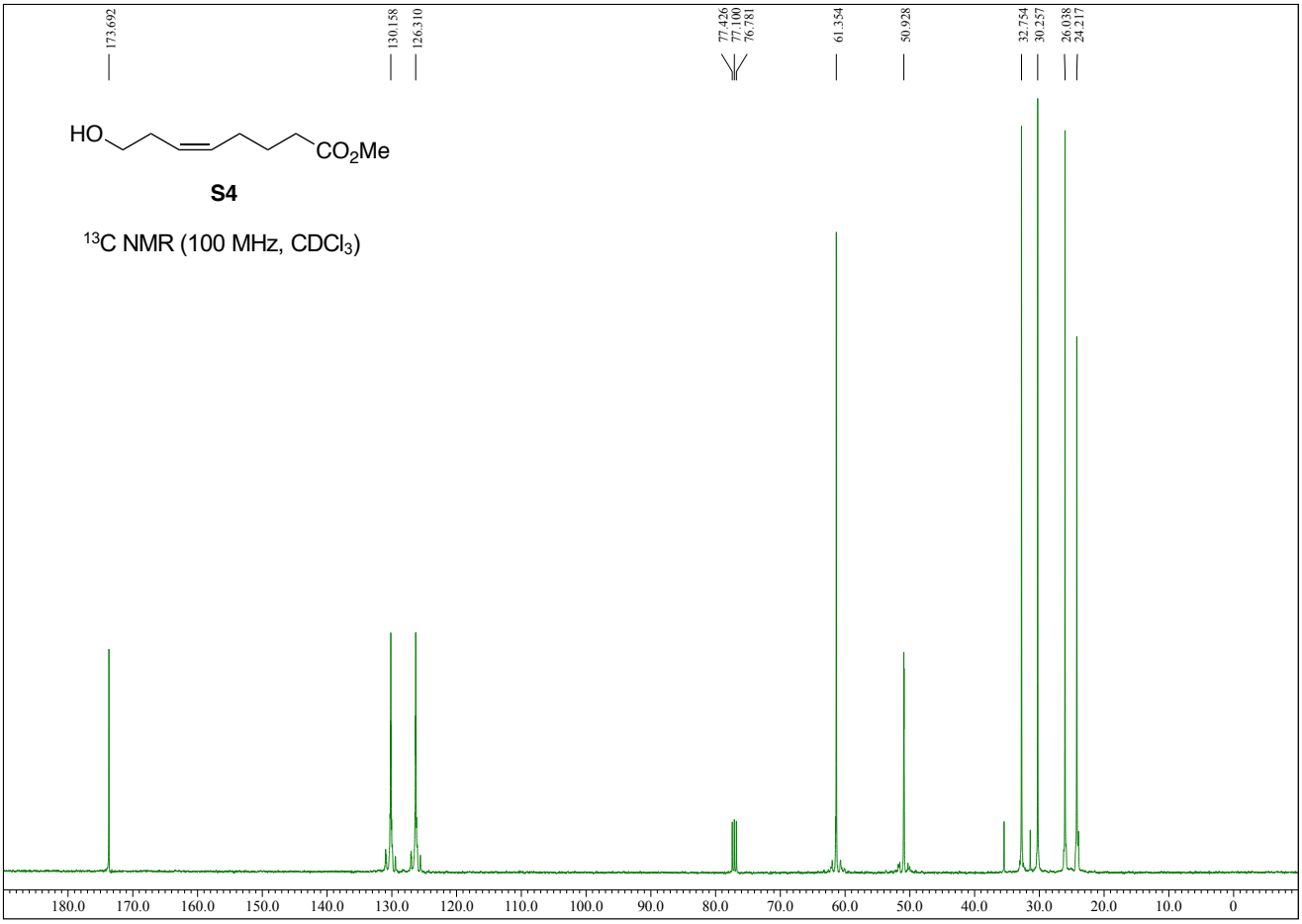


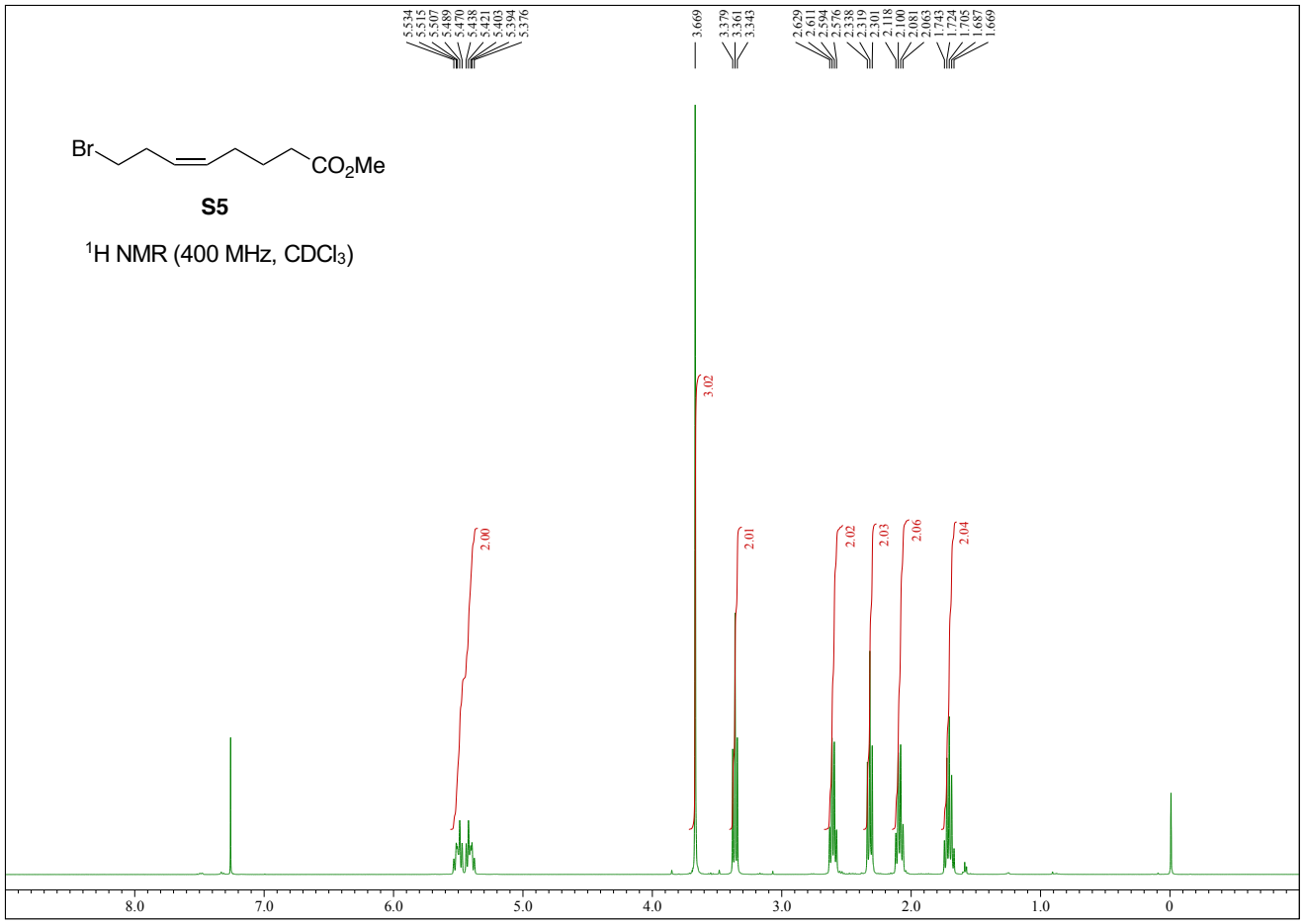
^{13}C NMR (75 MHz, $CDCl_3$)

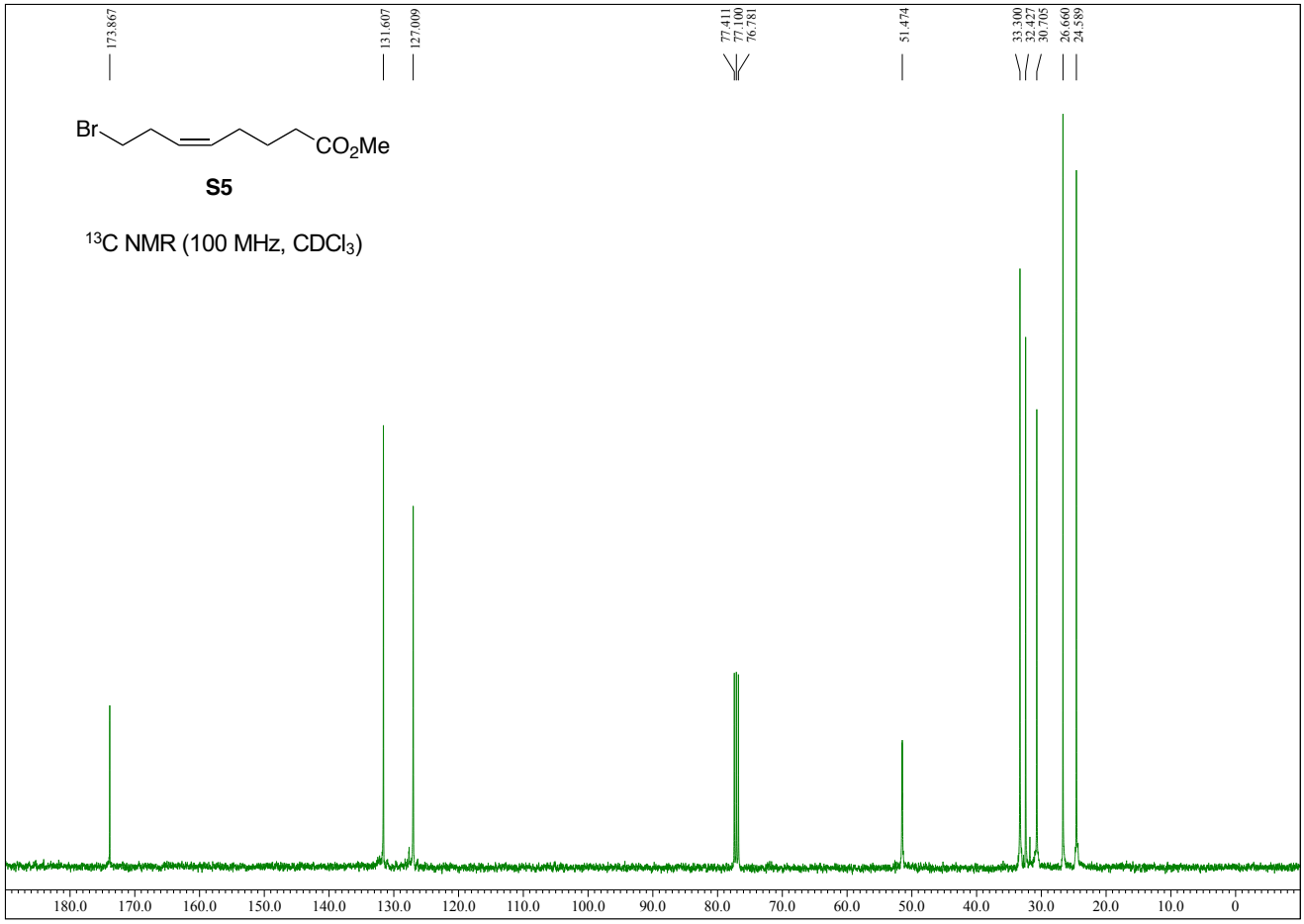

TBDMSO
CO2H
S3
1H NMR (400 MHz, CDCl3)

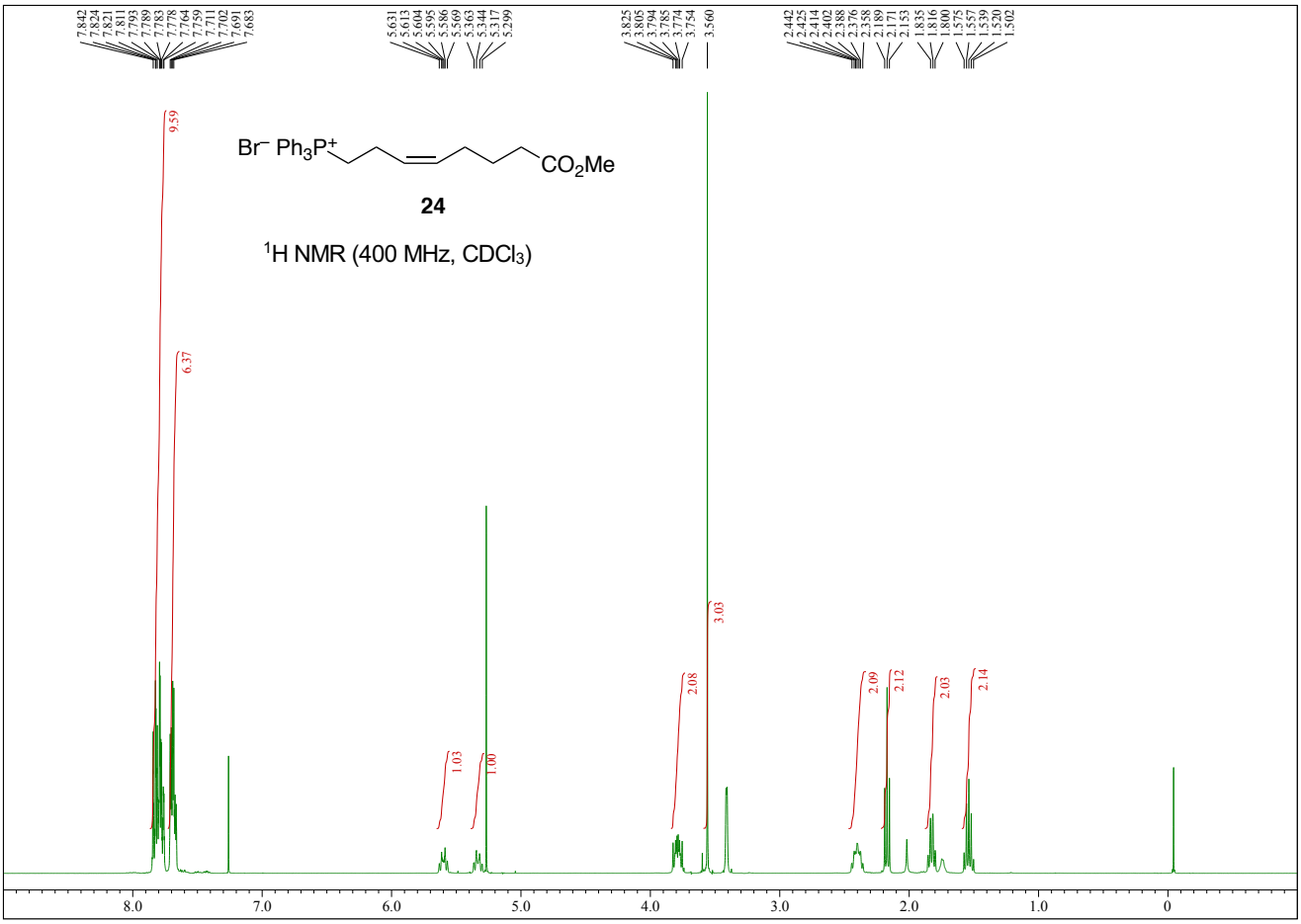

TBDMSO
CO2H
S3
13C NMR (75 MHz, CDCl3)

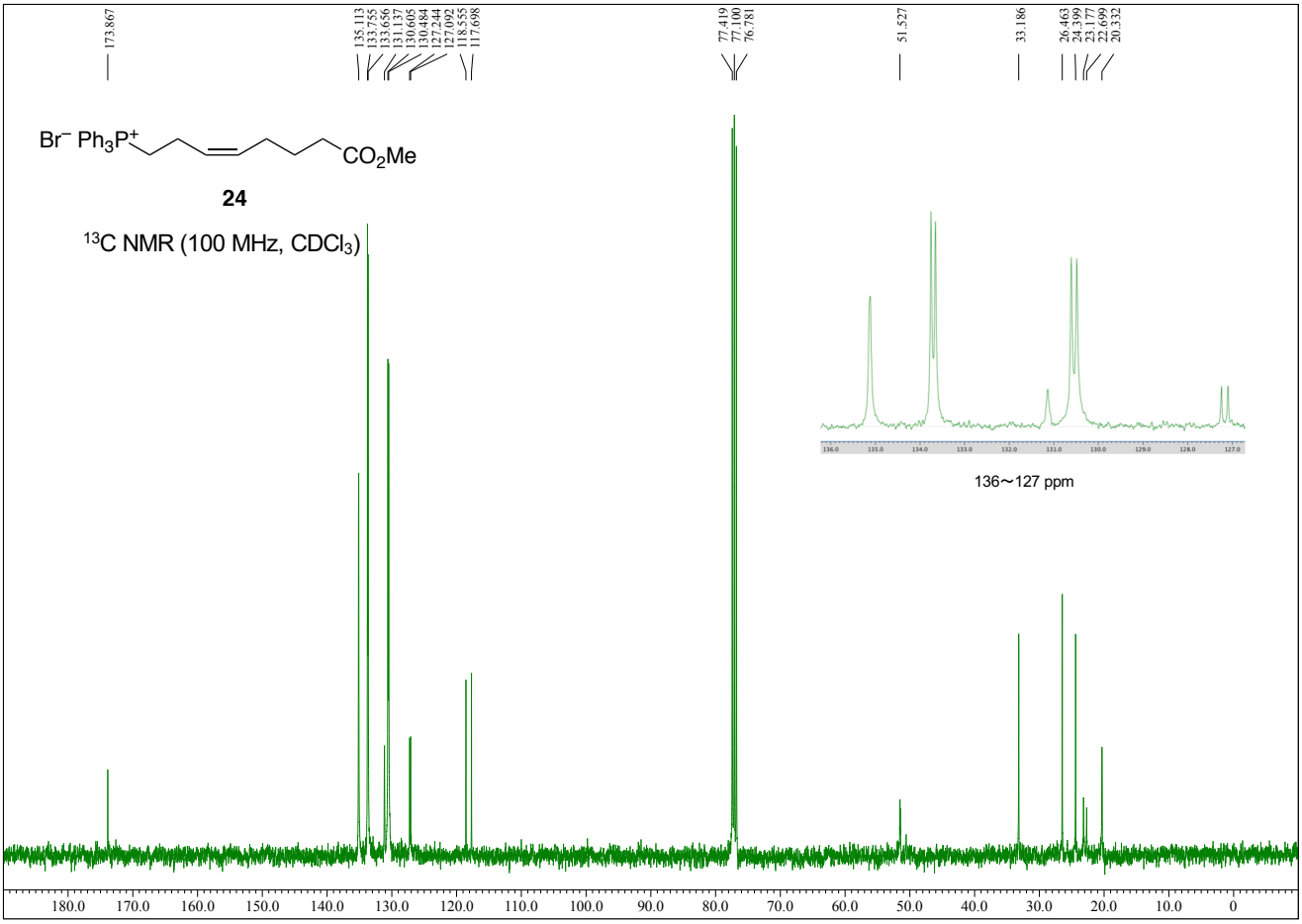

HO
CO2Me
S4
1H NMR (400 MHz, CDCl3)
5.525
5.498
5.479
5.462
5.441
5.422
5.404
5.376
3.649
3.623
3.607
2.325
2.306
2.288
2.269
2.123
2.104
2.086
2.068
1.776
1.724
1.706
1.688
1.669
1.650
5.16
4.09
2.90
2.03
2.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

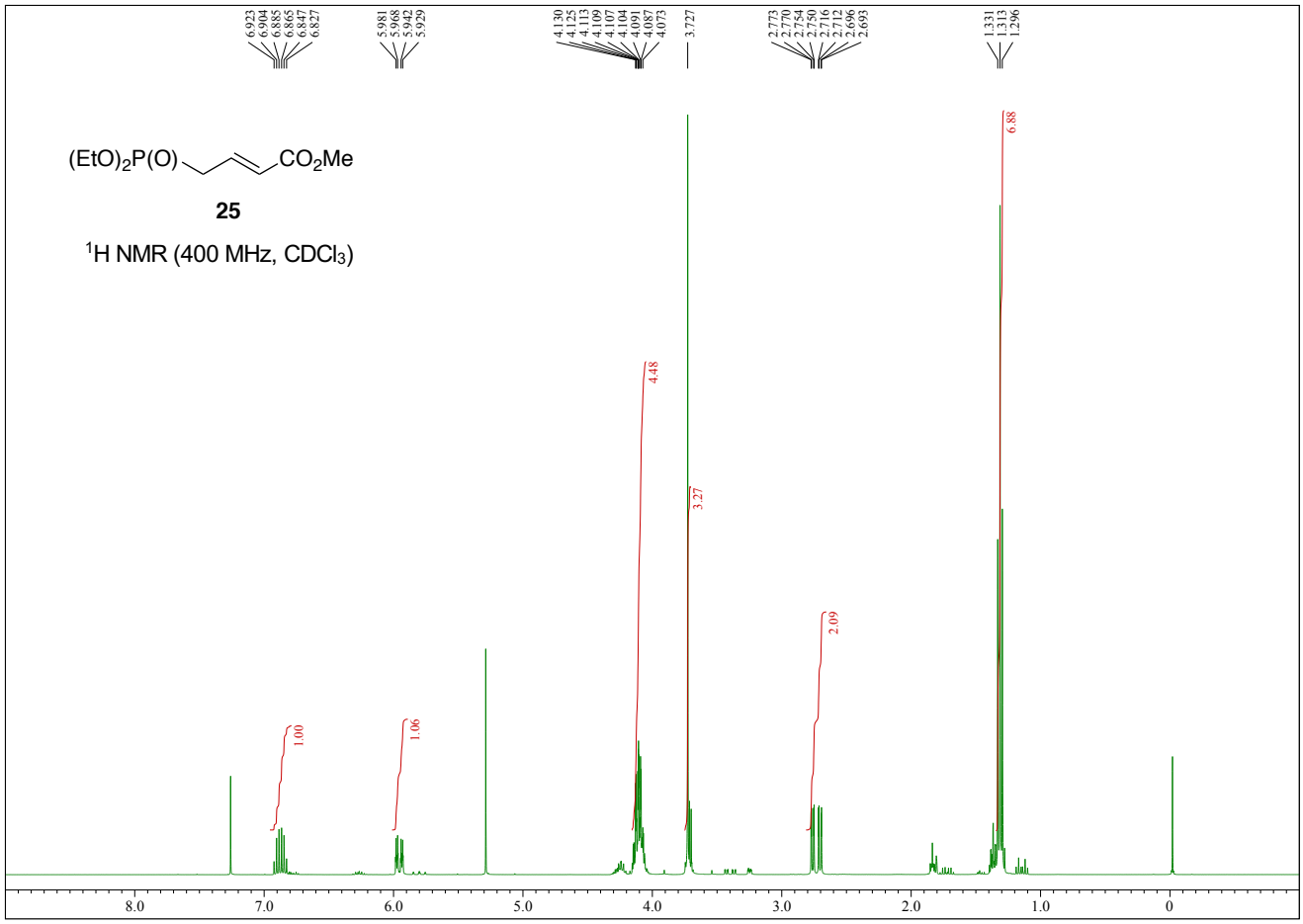

HO
CO2Me
S4
13C NMR (100 MHz, CDCl3)
173.692
130.158
126.310
77.426
77.100
76.781
61.354
50.928
32.754
30.257
26.038
24.217
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0


Br
CO2Me
S5
1H NMR (400 MHz, CDCl3)
5.534
5.515
5.507
5.489
5.470
5.438
5.421
5.403
5.394
5.376
3.669
3.379
3.361
3.343
2.629
2.611
2.594
2.576
2.338
2.319
2.301
2.118
2.100
2.081
2.063
1.743
1.724
1.705
1.687
1.669
3.02
2.00
2.01
2.02
2.03
2.06
2.04
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


Br
CO2Me
S5
13C NMR (100 MHz, CDCl3)
173.867
131.607
127.009
77.411
77.100
76.781
51.474
33.300
32.427
30.705
26.660
24.589
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


Br⁻ Ph3P+
CO2Me
24
1H NMR (400 MHz, CDCl3)

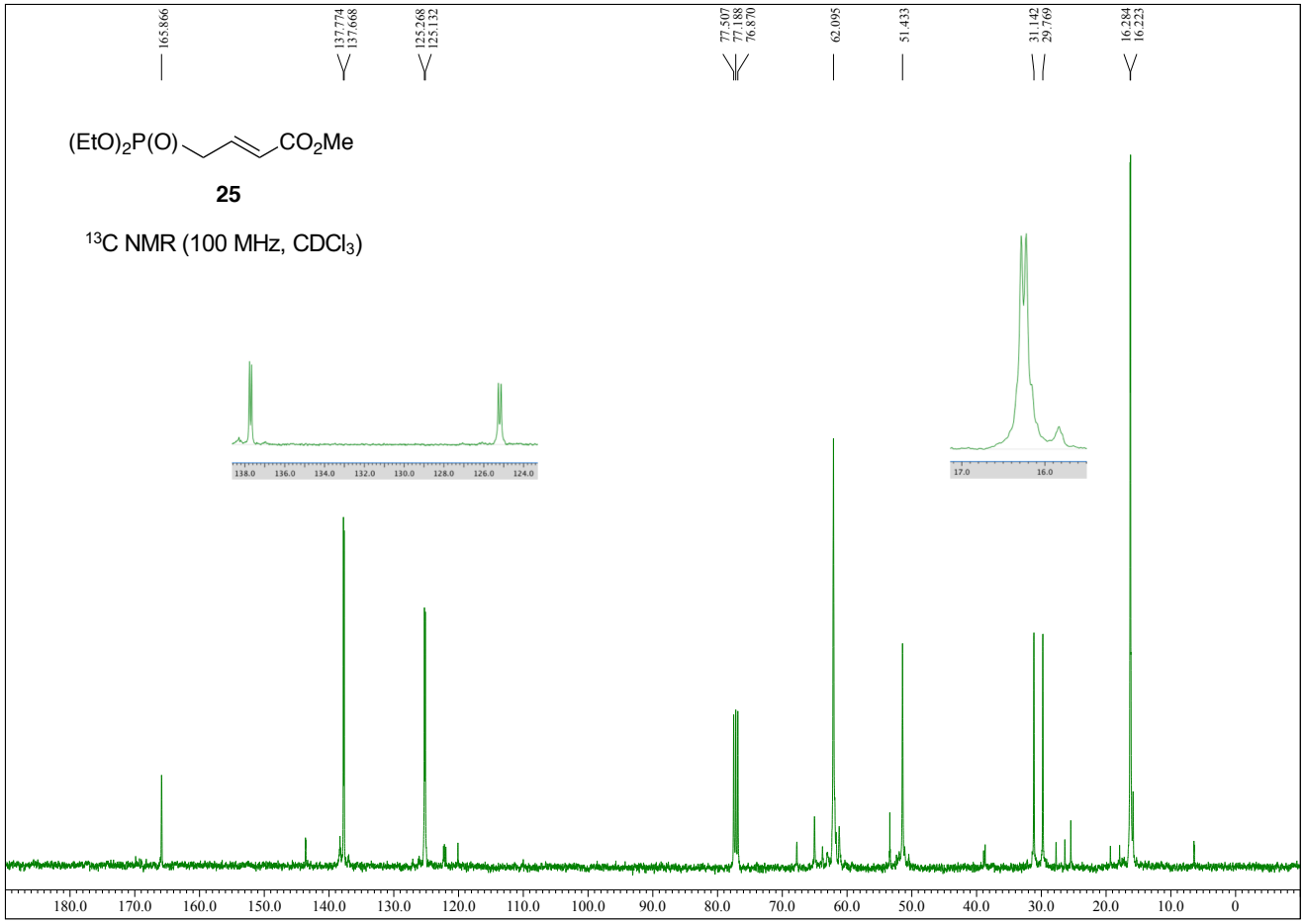

Br⁻ Ph3P+
CO2Me
24
13C NMR (100 MHz, CDCl3)
136~127 ppm



$(EtO)_2P(O)$ CO_2Me

25

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

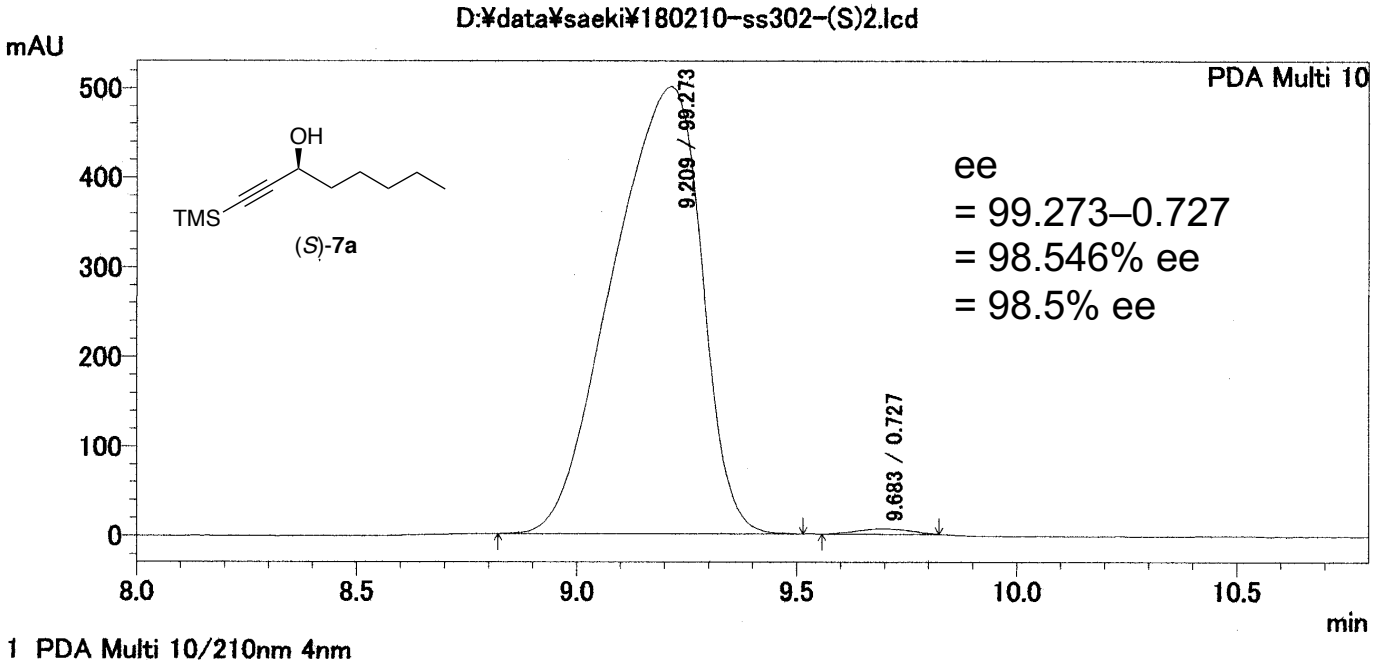


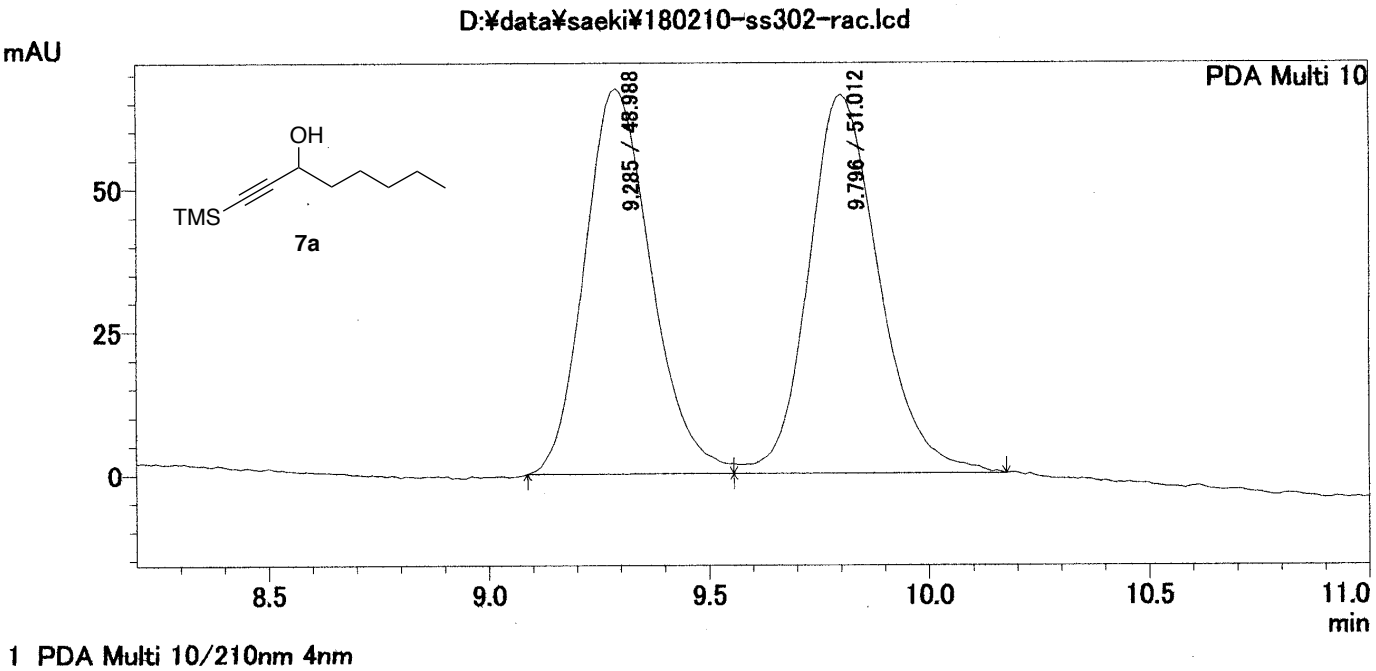
$(EtO)_2P(O)$ CO_2Me

25

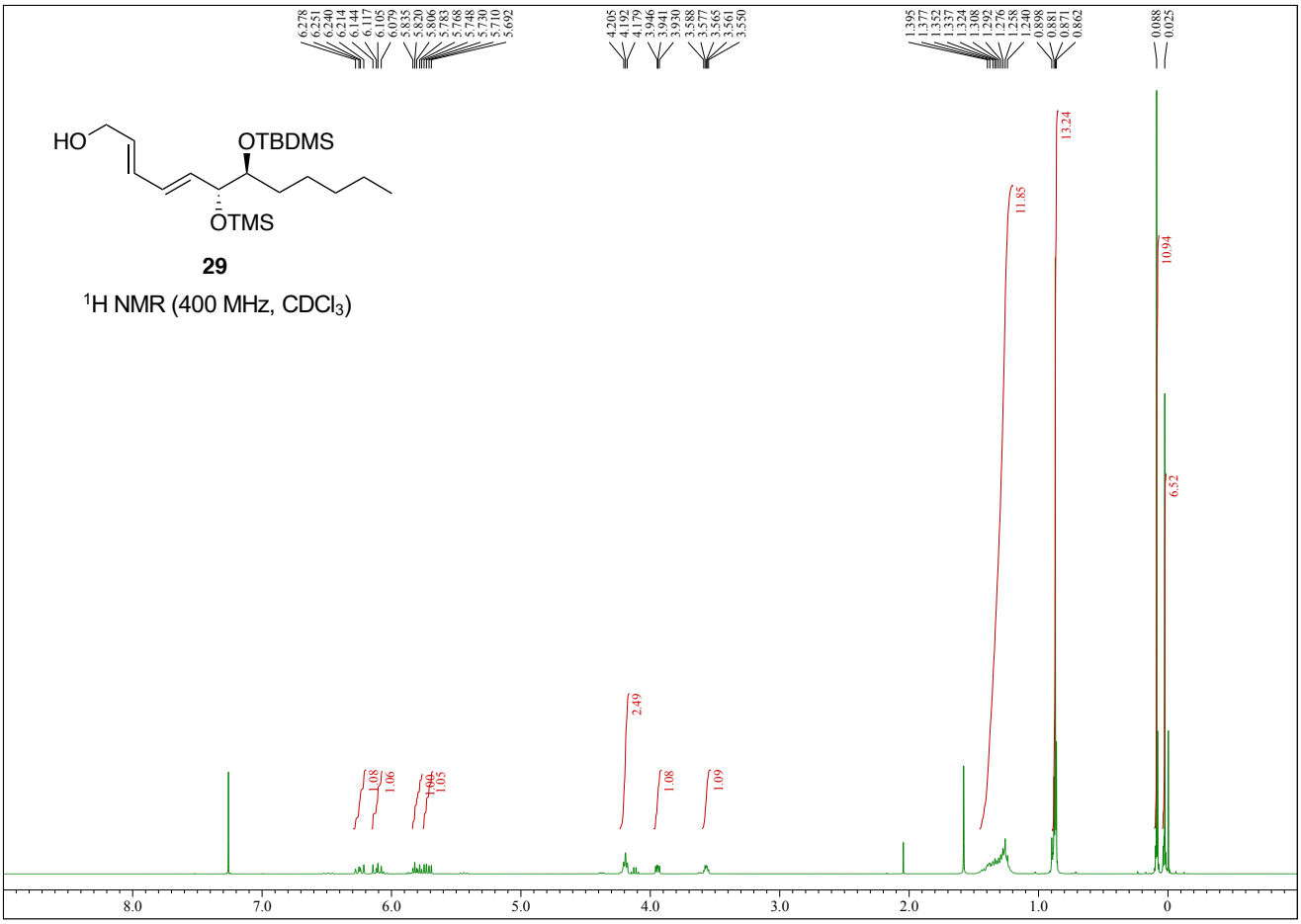
^{13}C NMR (100 MHz, $CDCl_3$)

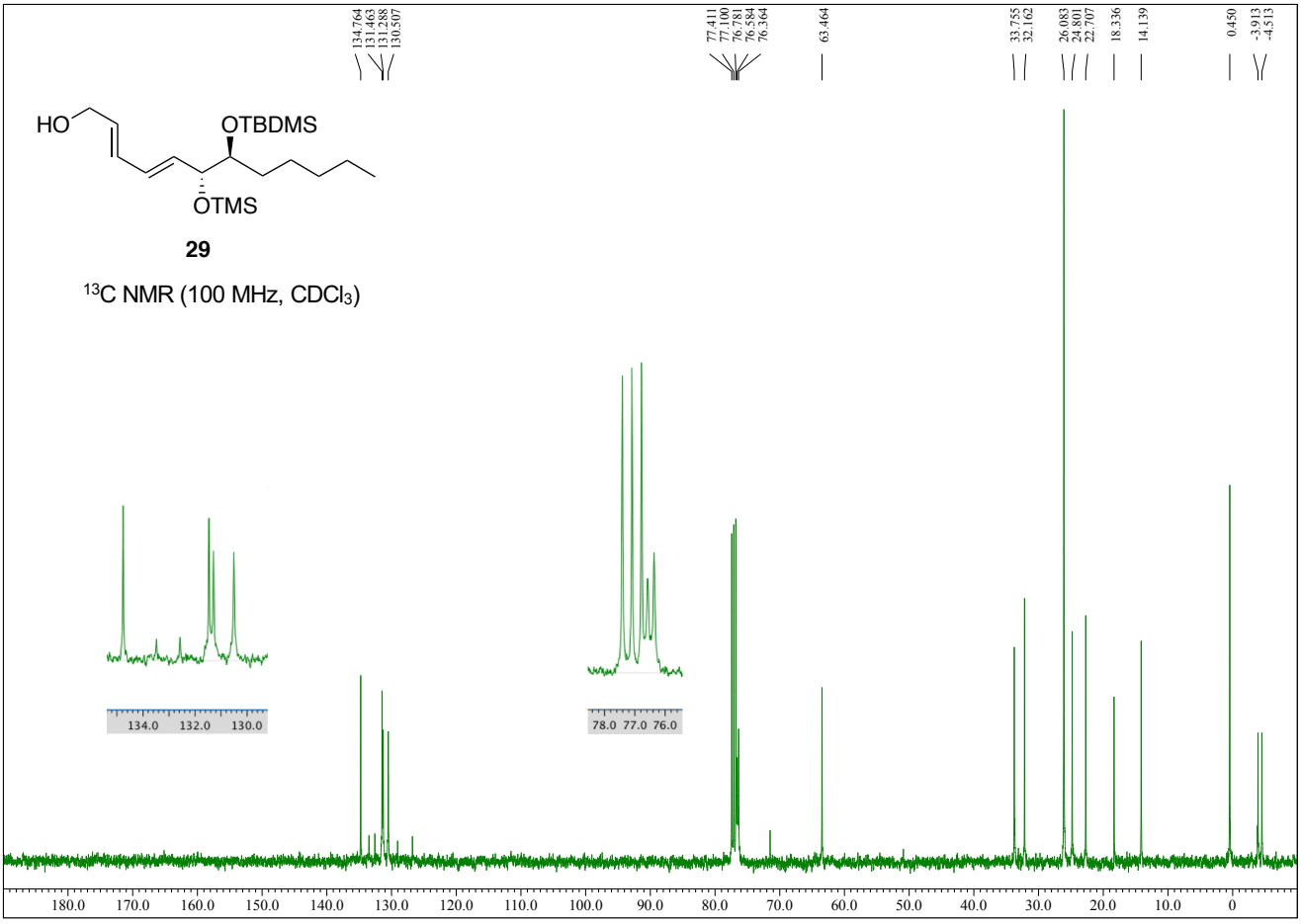
Determination of the enantiomeric purity of (*S*)-**7a** for the synthesis of 14*R*,15*S*-diHETE (**22**)

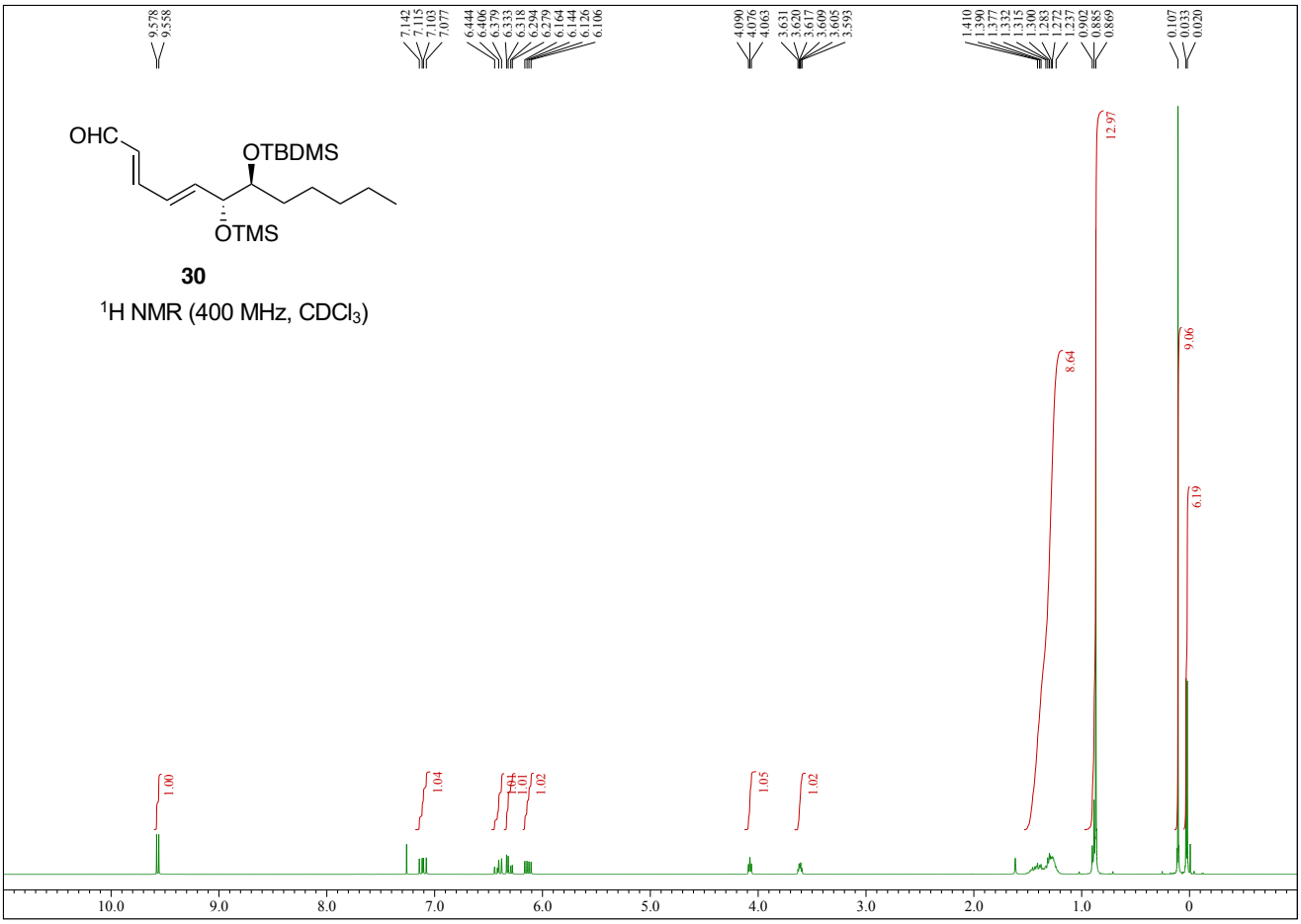


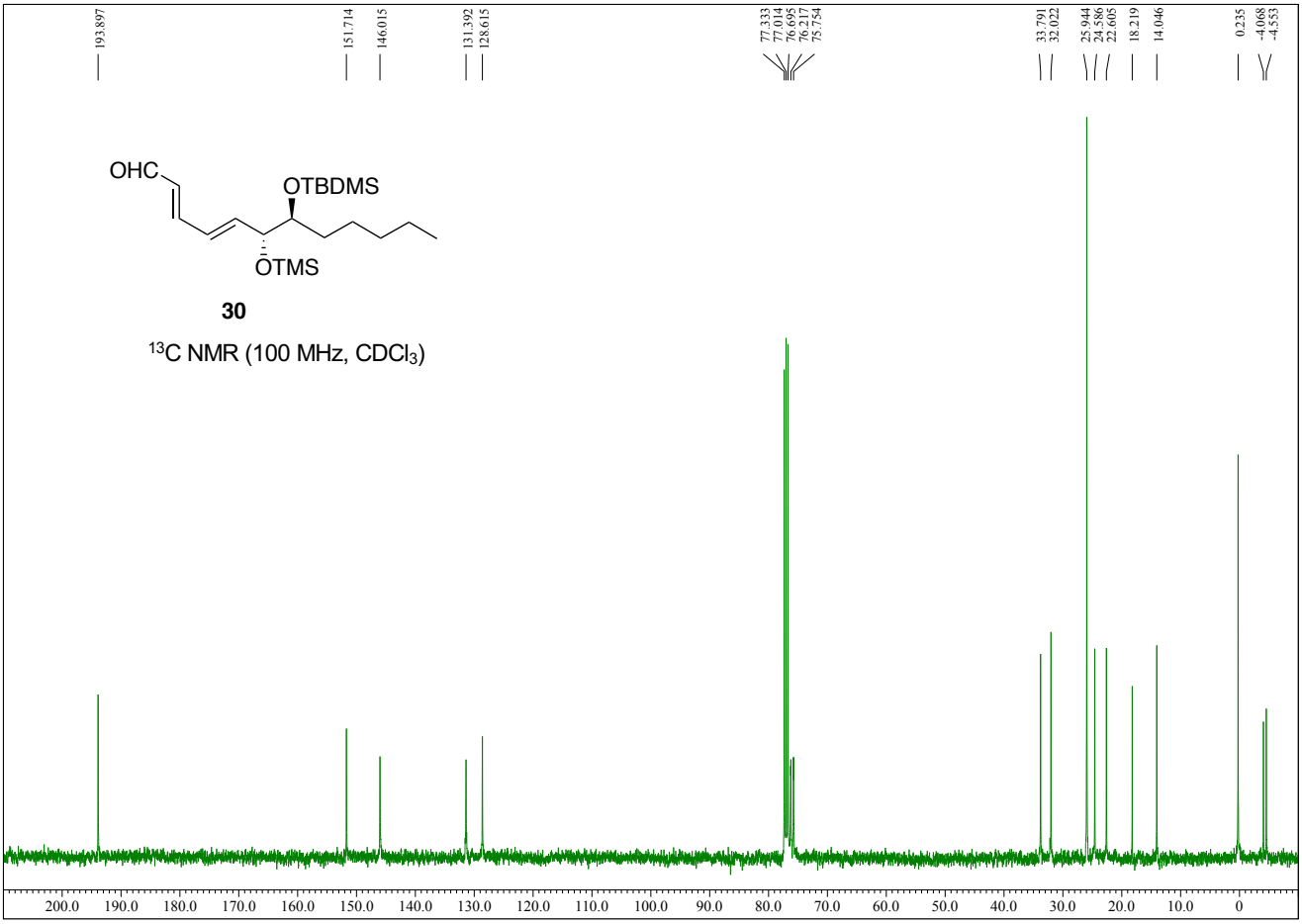


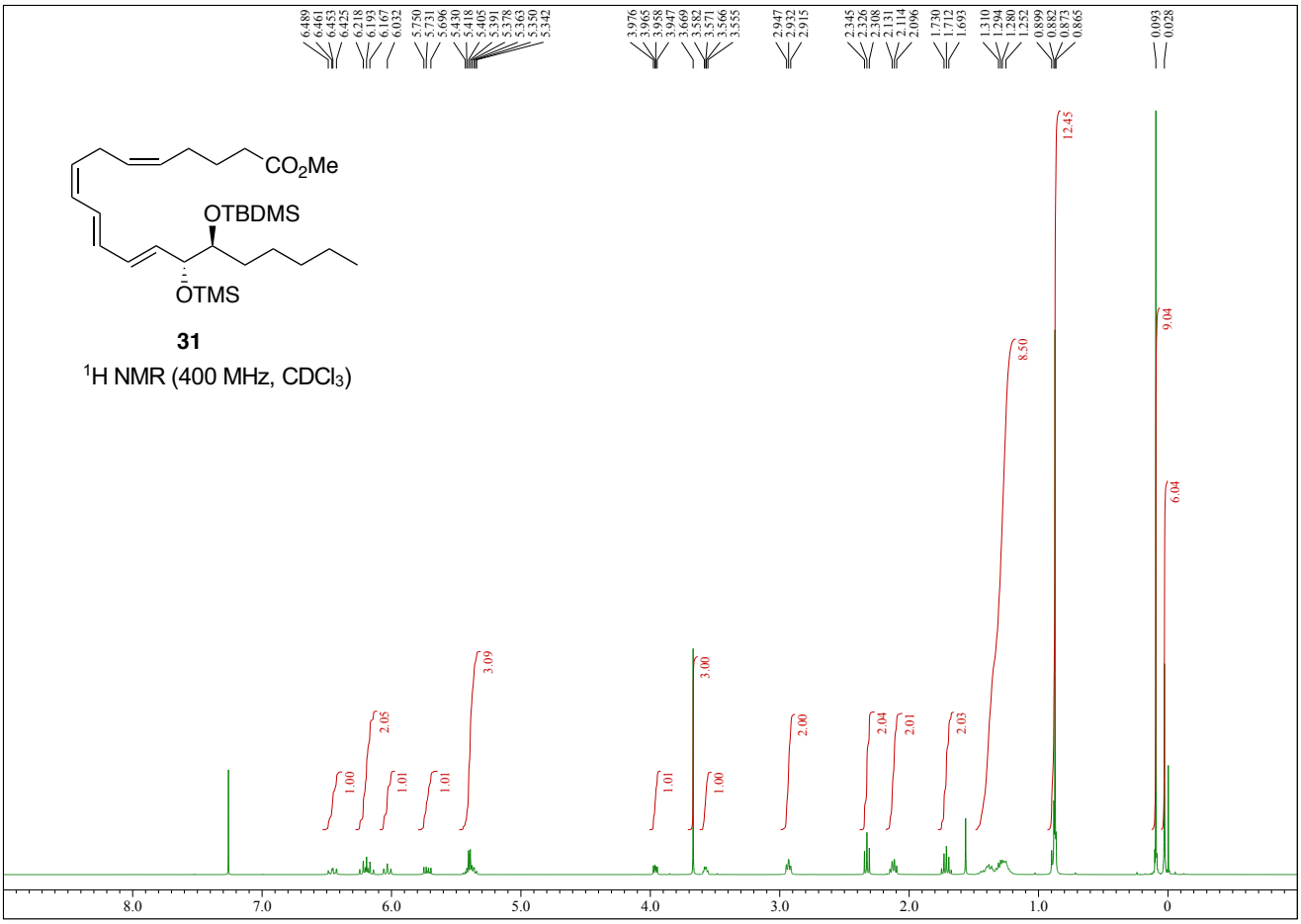
Conditions : Chirapak AD-H, hexane/*i*-PrOH = 99/1, 1.0 mL/min, 35 ºC


HO
OTBDMS
OTMS
29
1H NMR (400 MHz, CDCl3)


HO
OTBDMS
OTMS
29
13C NMR (100 MHz, CDCl3)

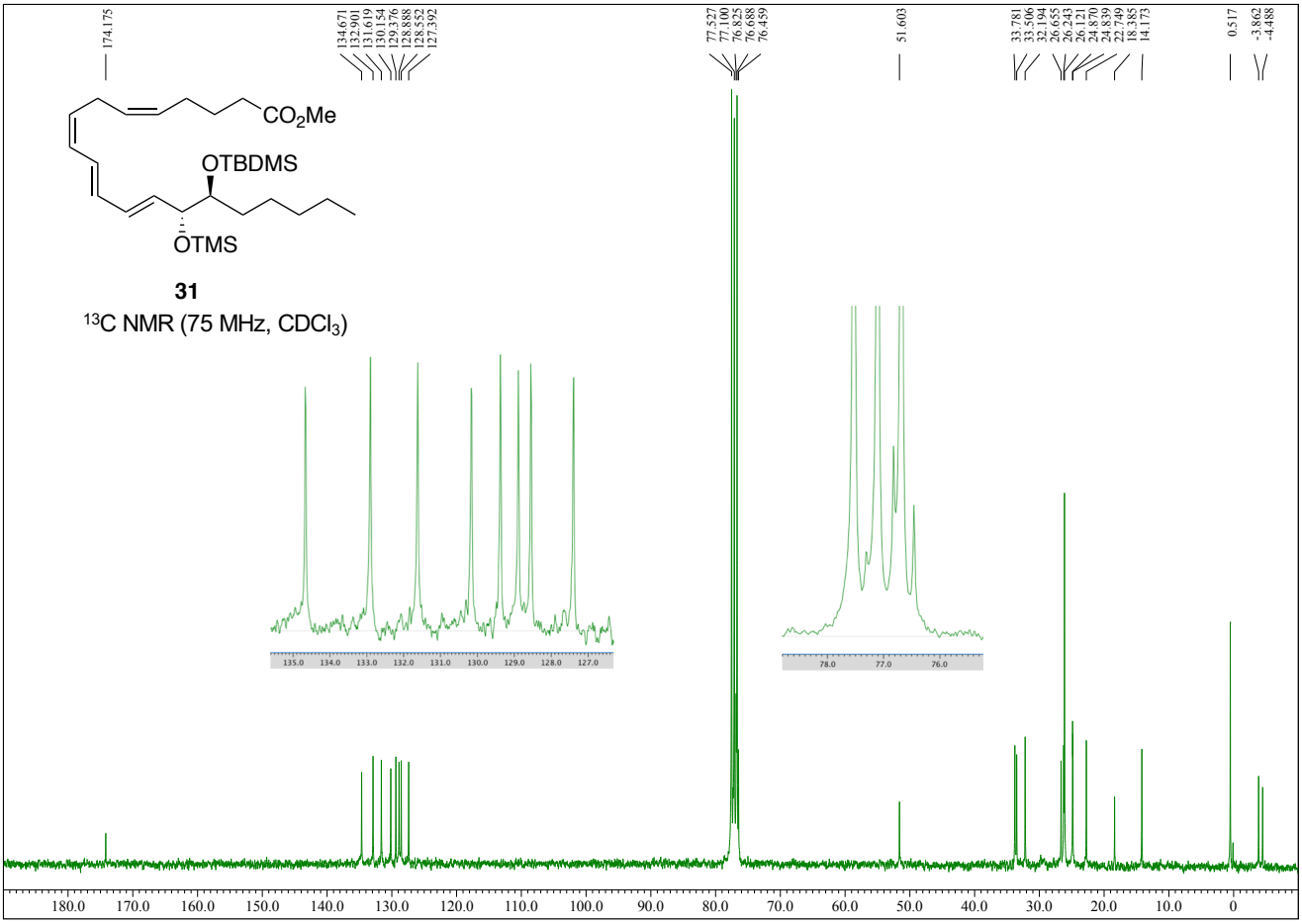

OHC
OTBDMS
OTMS
30
1H NMR (400 MHz, CDCl3)


OHC
OTBDMS
OTMS
30
13C NMR (100 MHz, CDCl3)



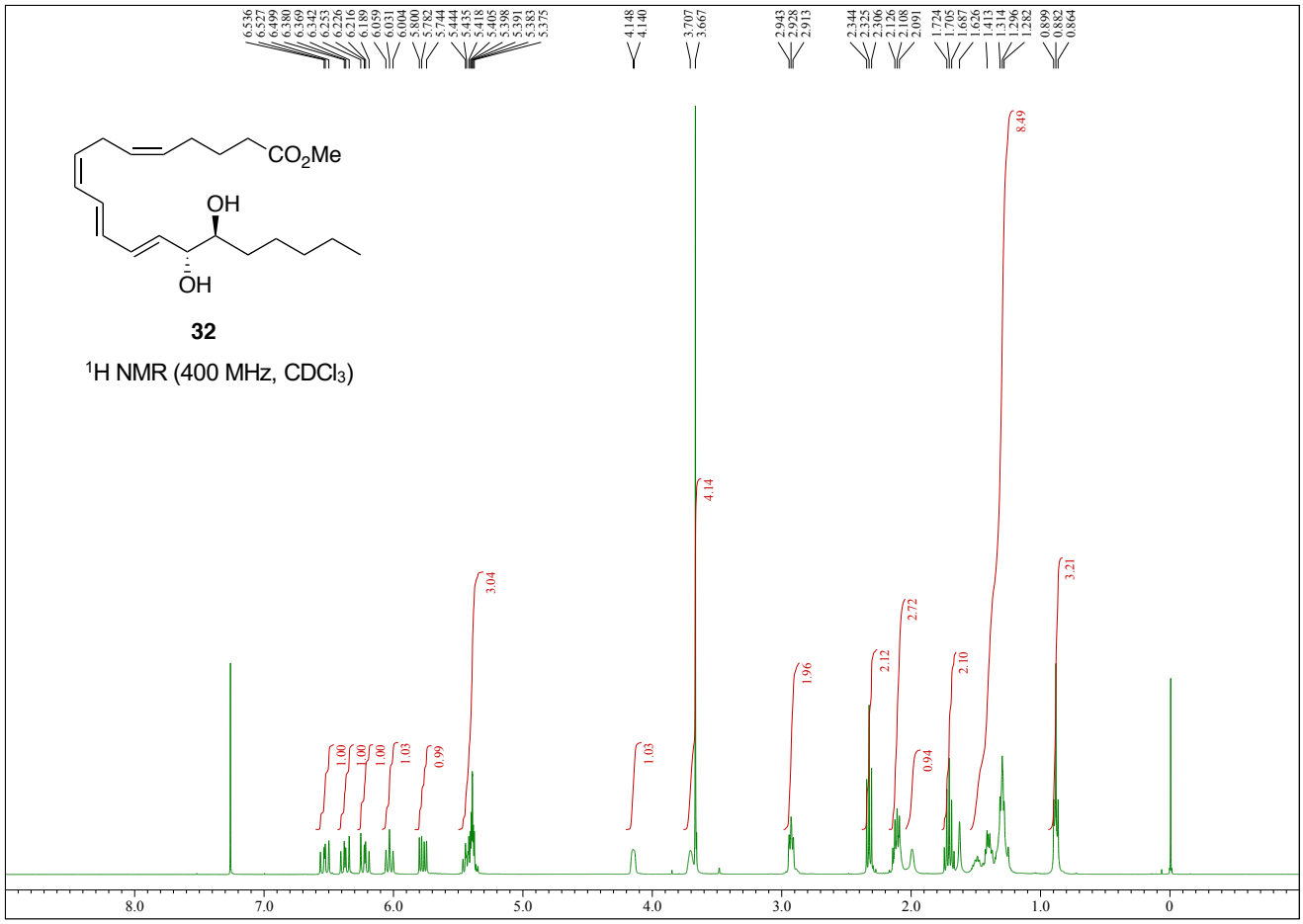
31

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



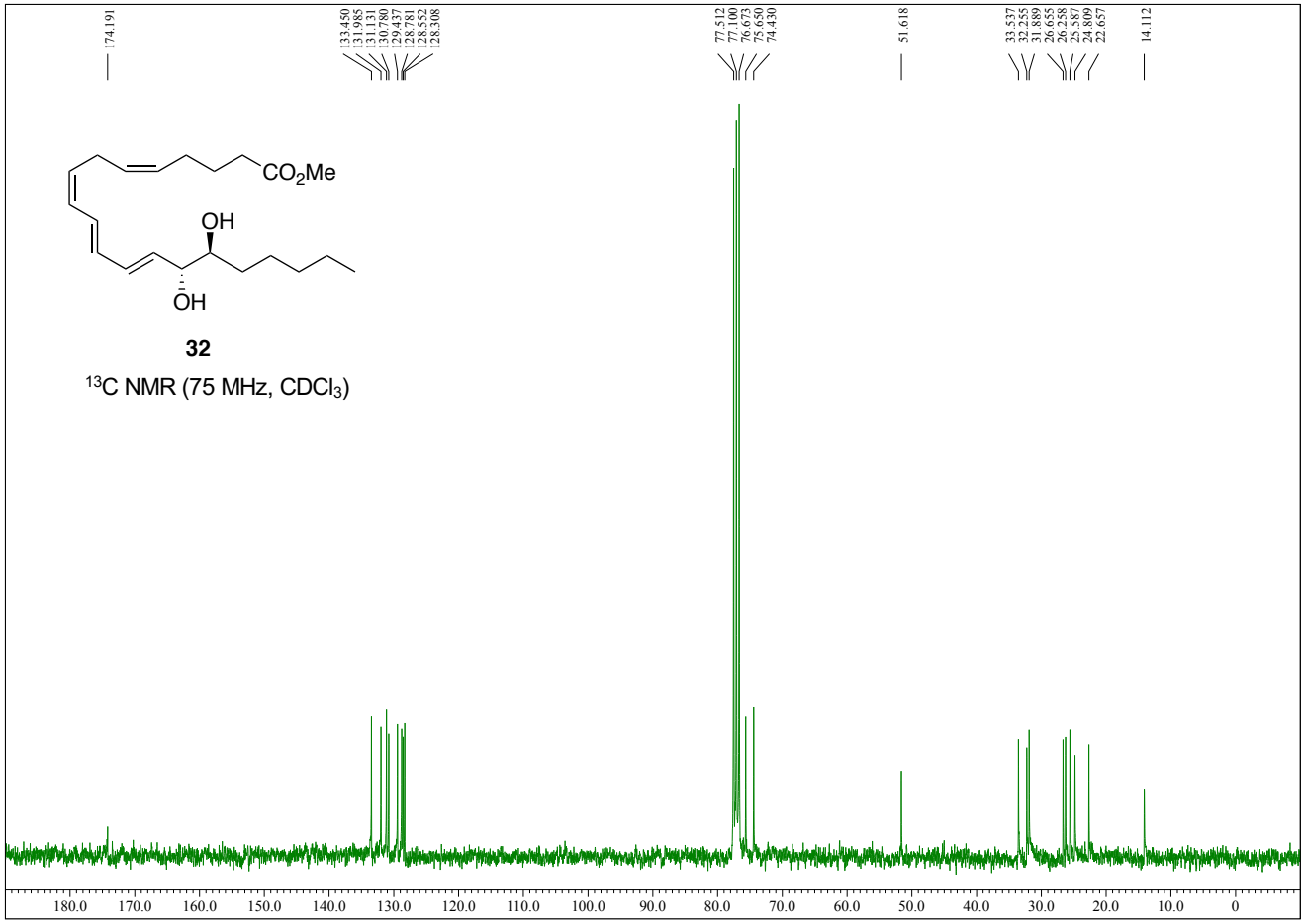
31

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



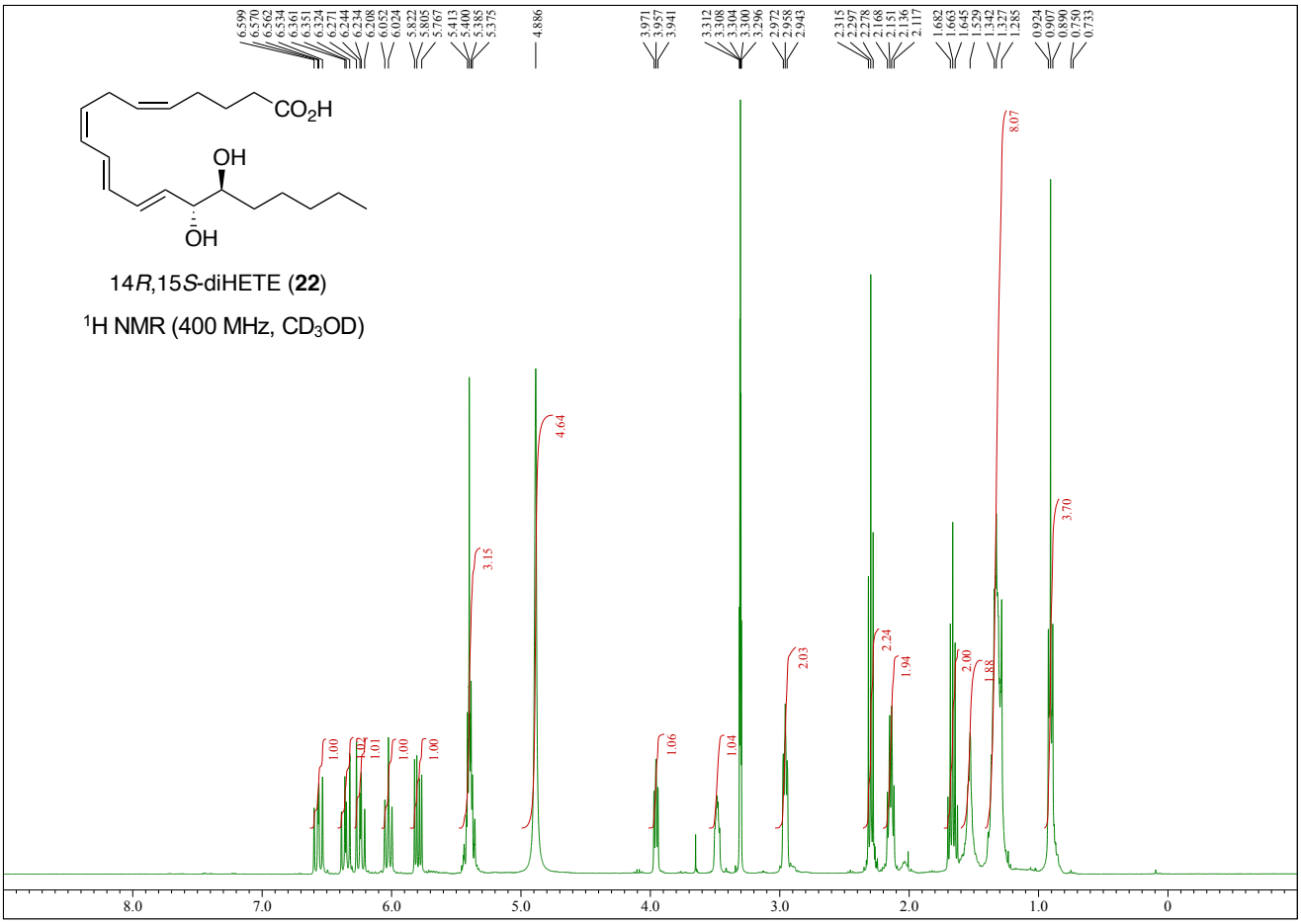
32

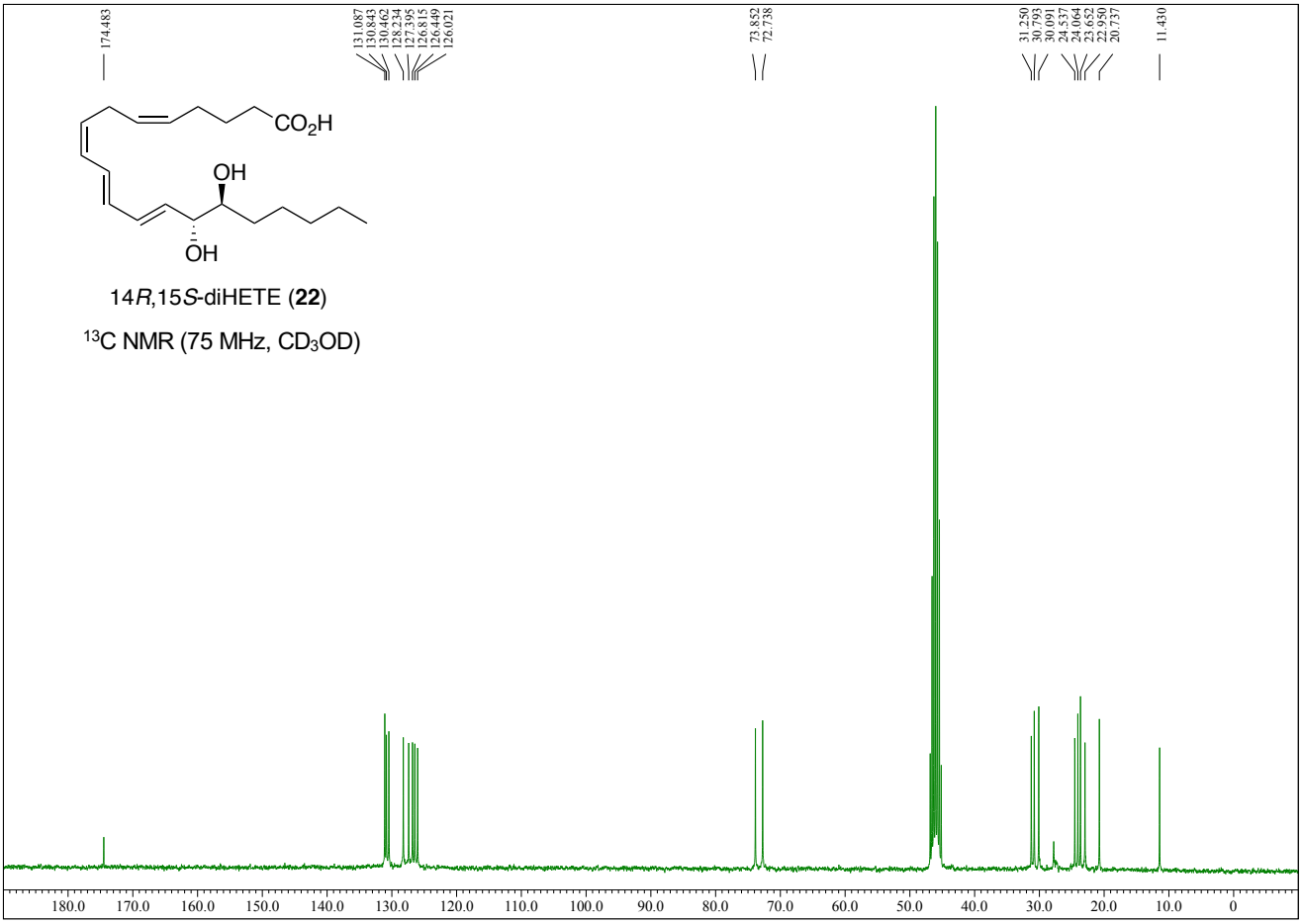
^{1}H NMR (400 MHz, $CDCl_3$)



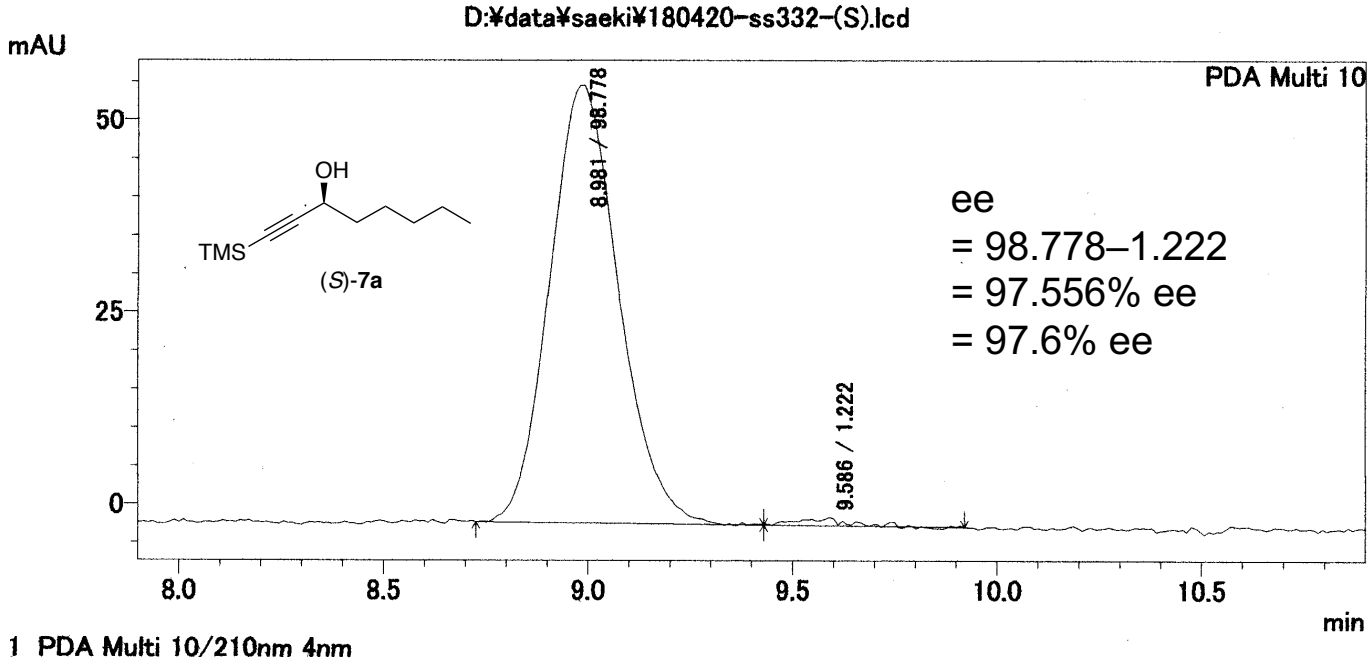
32

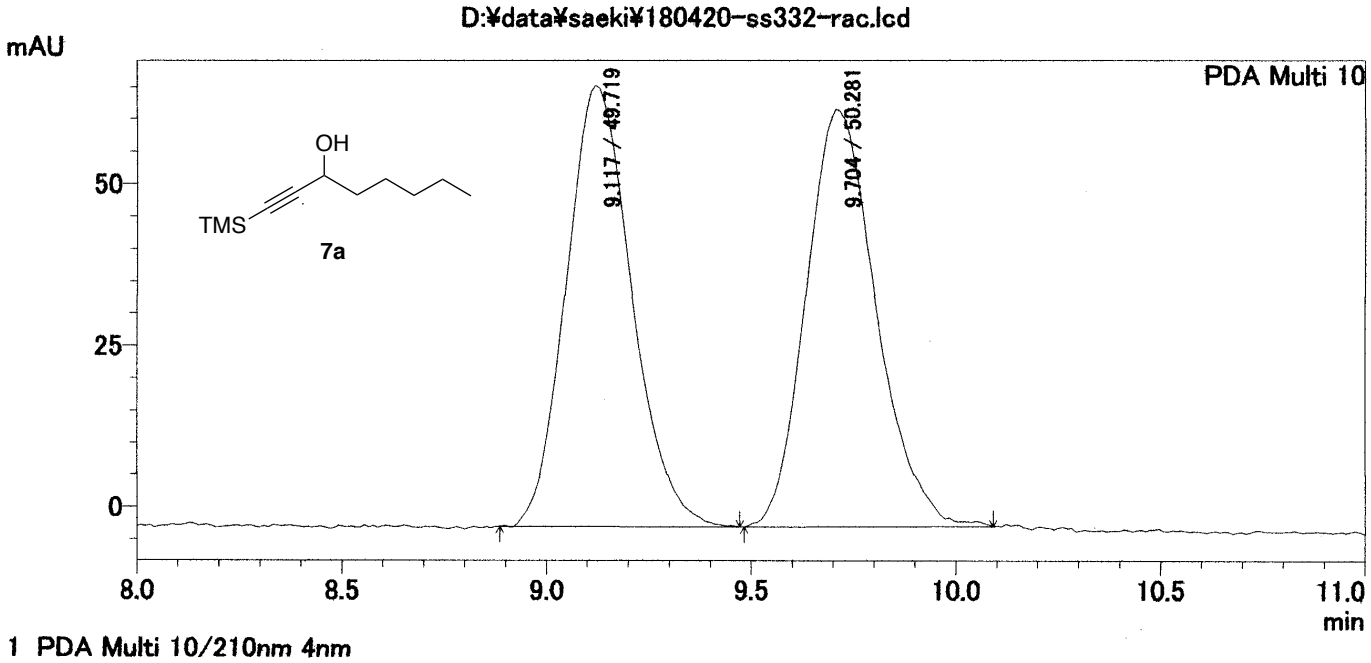
^{13}C NMR (75 MHz, $CDCl_3$)


CO2H
OH
OH
14R,15S-diHETE (22)
1H NMR (400 MHz, CD3OD)

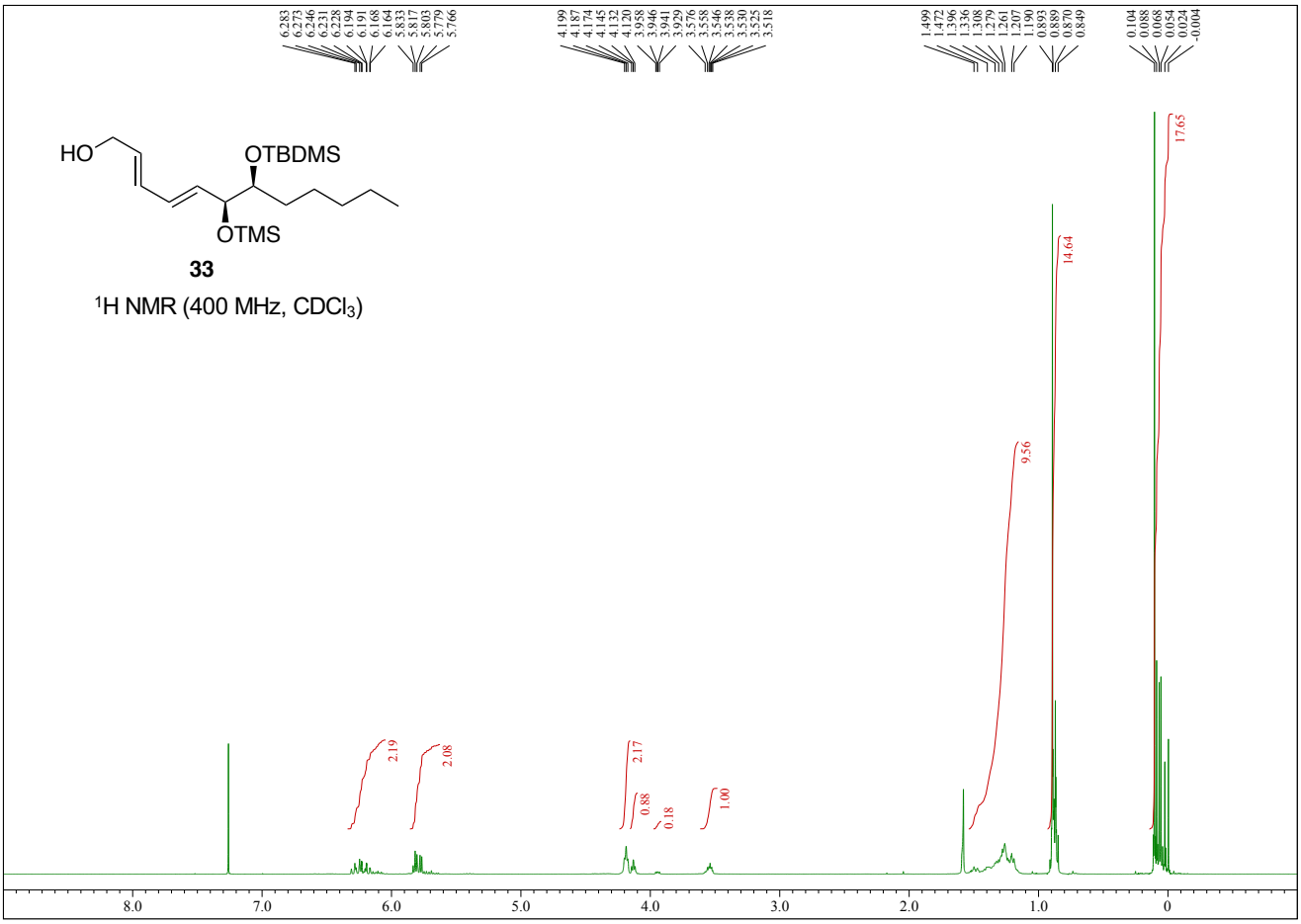

CO2H
OH
OH
14R,15S-diHETE (22)
13C NMR (75 MHz, CD3OD)

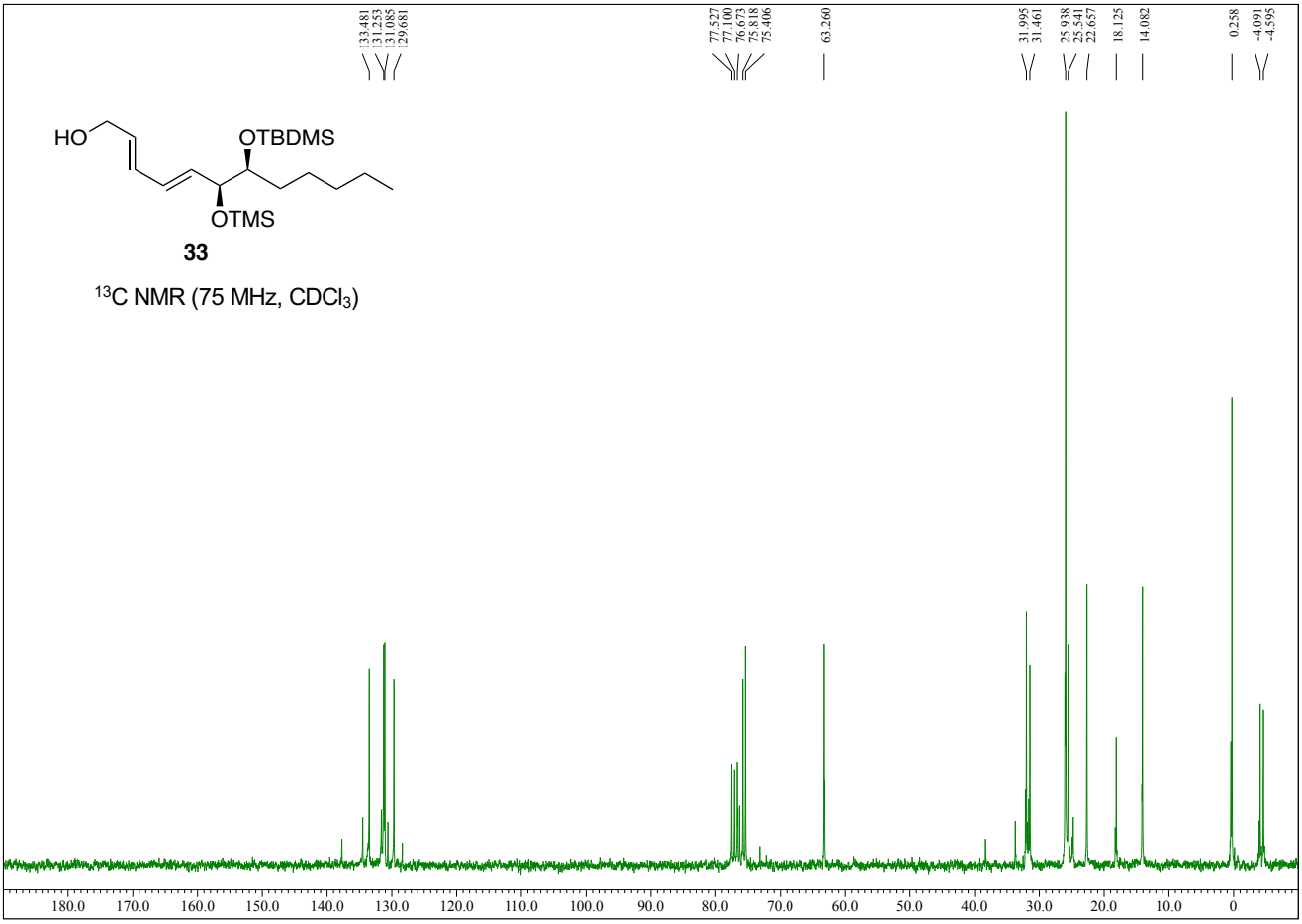
Determination of the enantiomeric purity of (*S*)-**7a** for the synthesis of 14*S*,15*S*-diHETE (**23**)

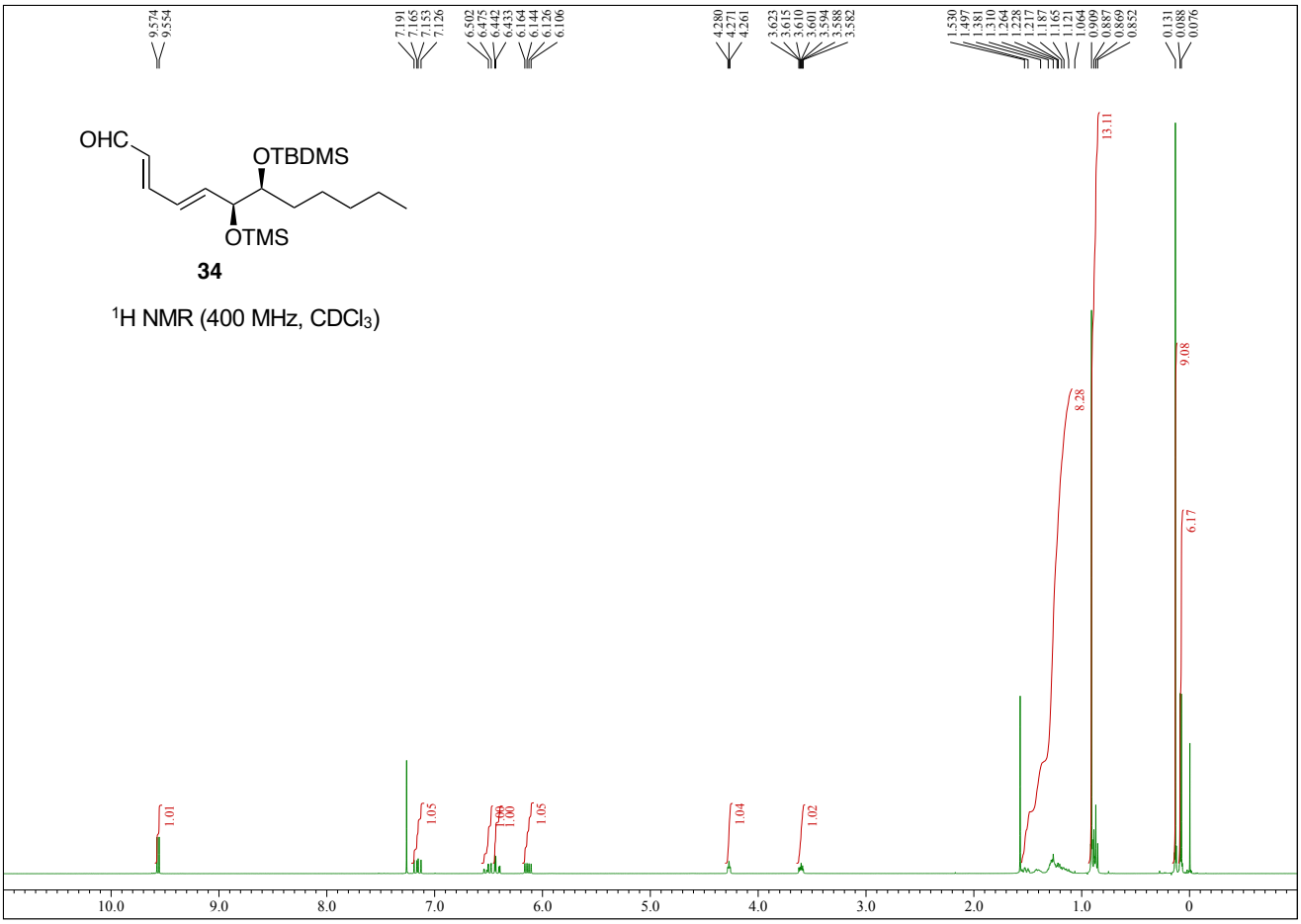


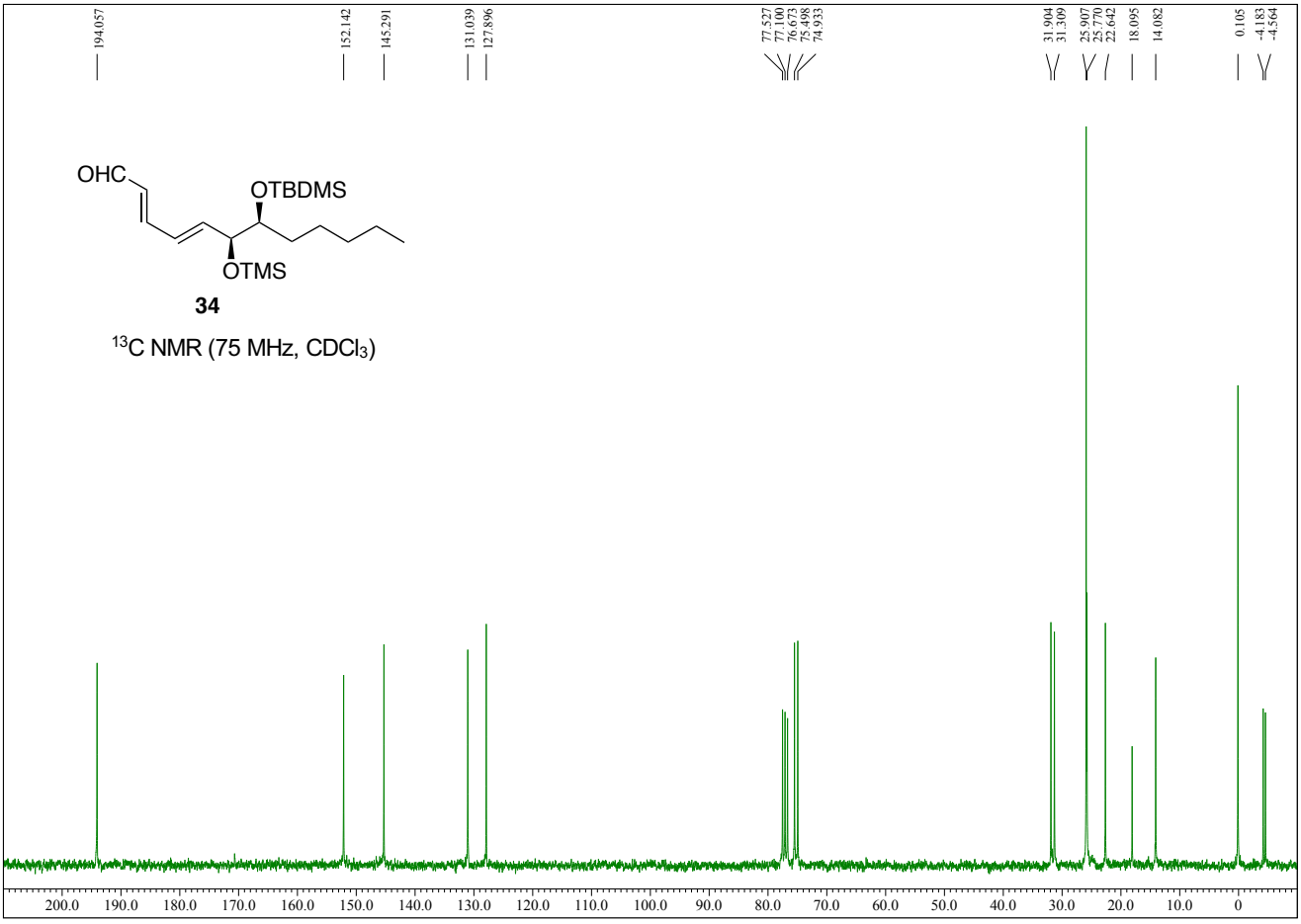


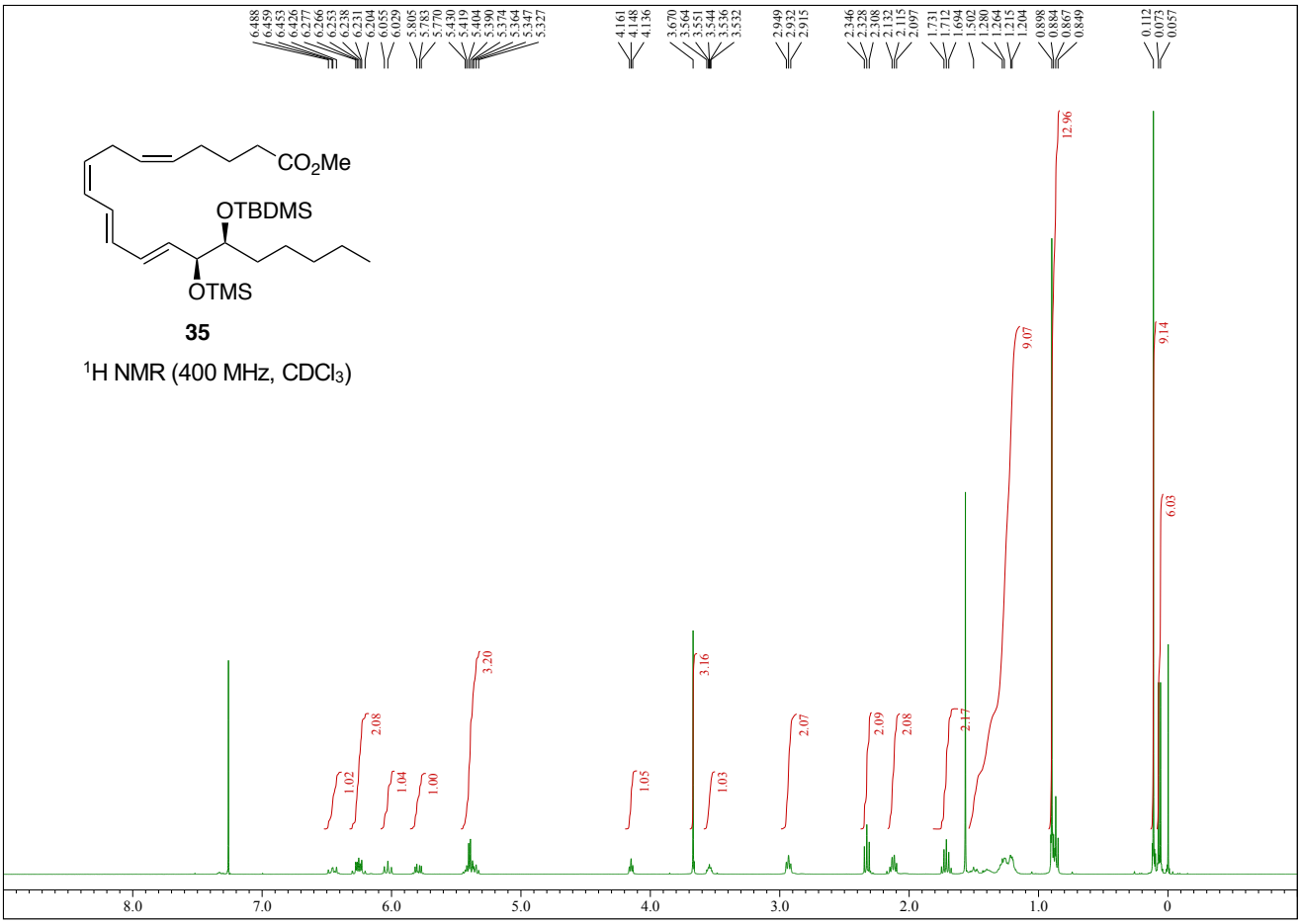
Conditions : Chiralpak AD-H, hexane/*i*-PrOH = 99/1, 1.0 mL/min, 35 ºC


HO
OTBDMS
OTMS
33
1H NMR (400 MHz, CDCl3)
6.283
6.273
6.246
6.231
6.208
6.194
6.191
6.168
6.164
5.833
5.817
5.803
5.779
5.766
4.199
4.187
4.174
4.145
4.132
4.120
3.958
3.946
3.941
3.929
3.576
3.558
3.546
3.538
3.530
3.525
3.518
1.499
1.472
1.396
1.336
1.308
1.279
1.261
1.207
1.190
0.893
0.889
0.870
0.849
0.104
0.088
0.068
0.054
0.024
-0.004
17.65
14.64
9.56
2.19
2.08
2.17
0.88
0.18
1.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


HO
OTBDMS
OTMS
33
13C NMR (75 MHz, CDCl3)
133.481
131.253
131.085
129.681
77.527
77.100
76.673
75.818
75.406
63.260
31.995
31.461
25.938
25.541
22.657
18.125
14.082
0.258
-4.091
-4.595
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

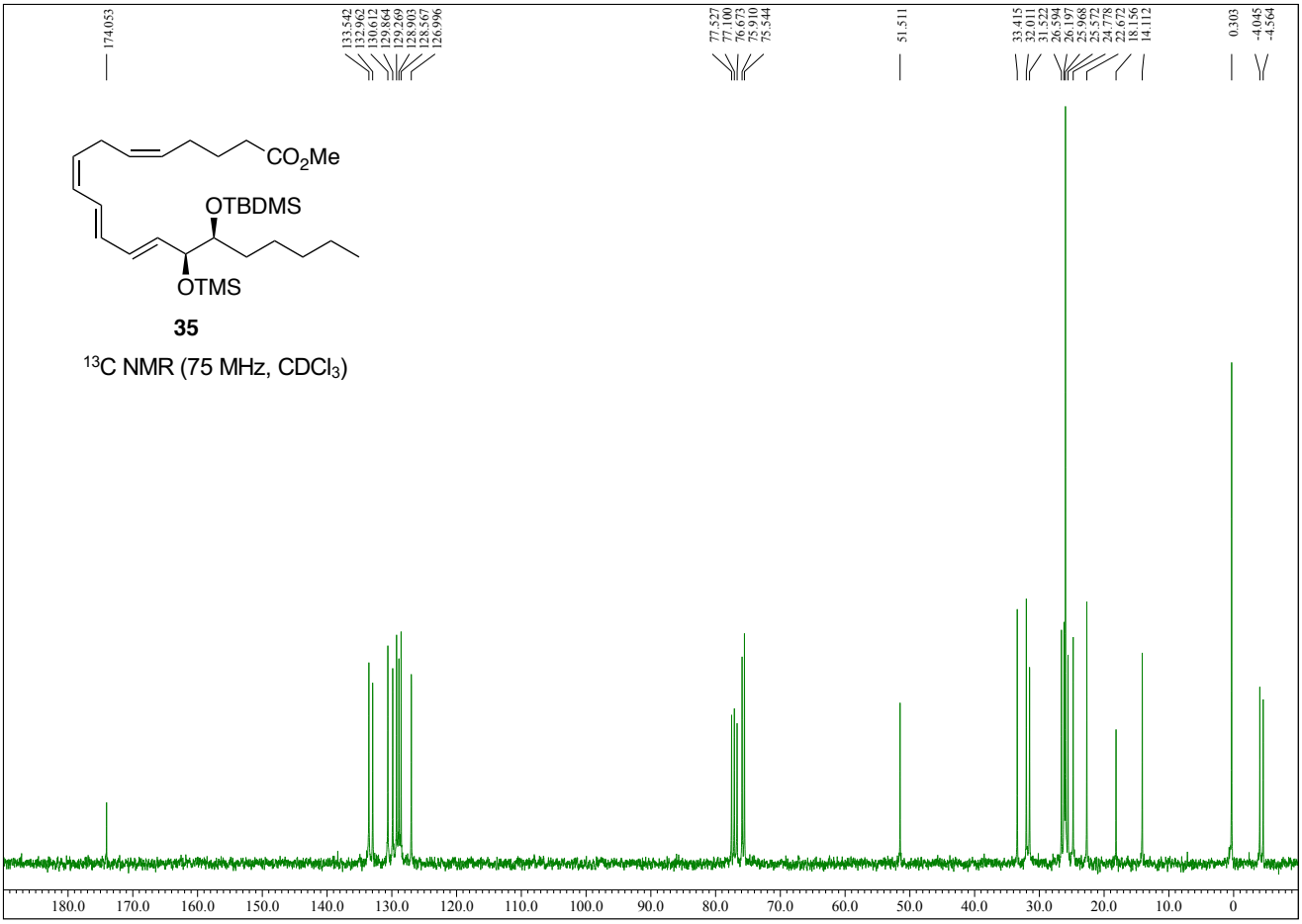

OHC
OTBDMS
OTMS
34
^{1}H NMR (400 MHz, CDCl$_3$)


OHC
OTBDMS
OTMS
34
^{13}C NMR (75 MHz, CDCl$_3$)



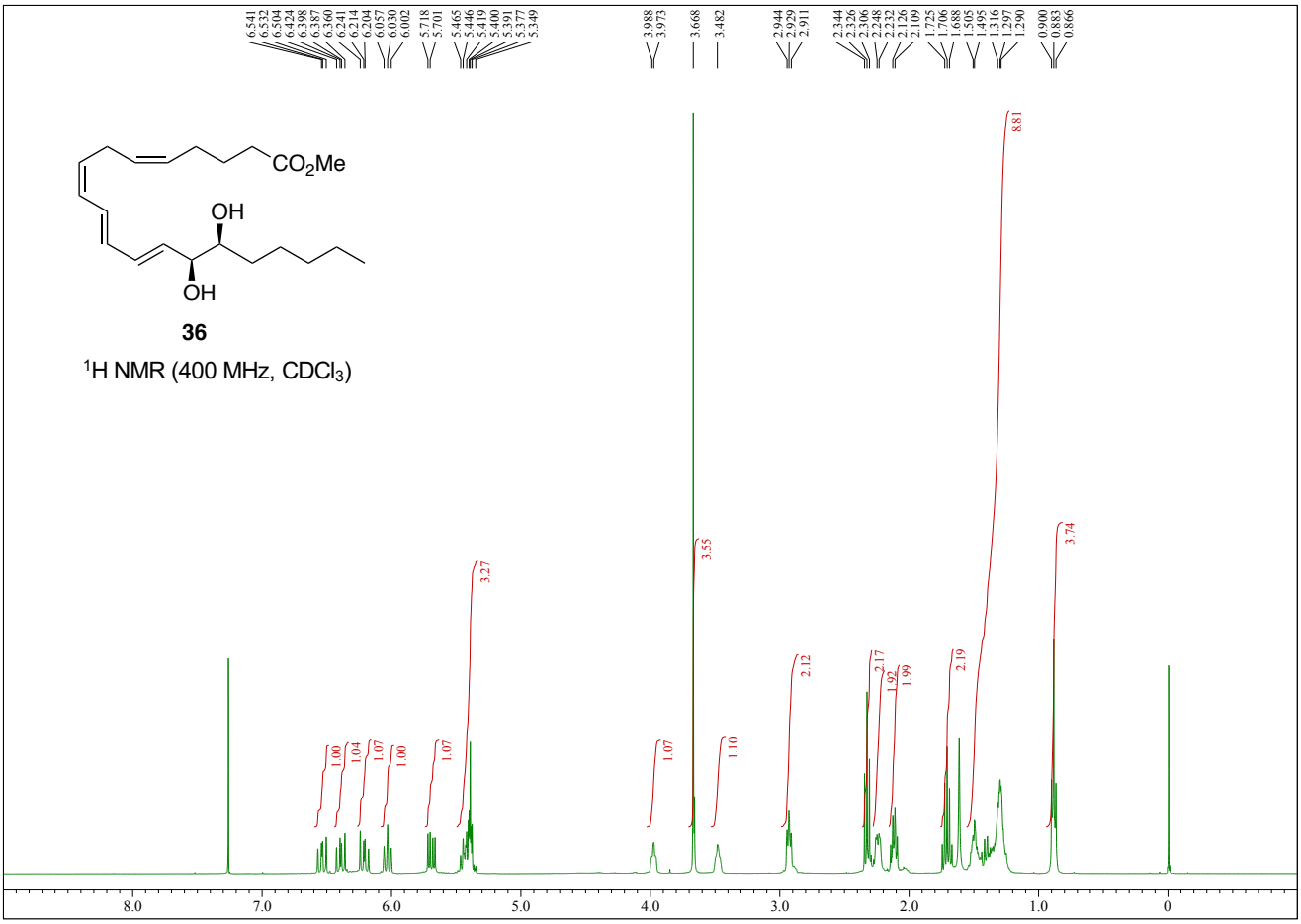
35

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



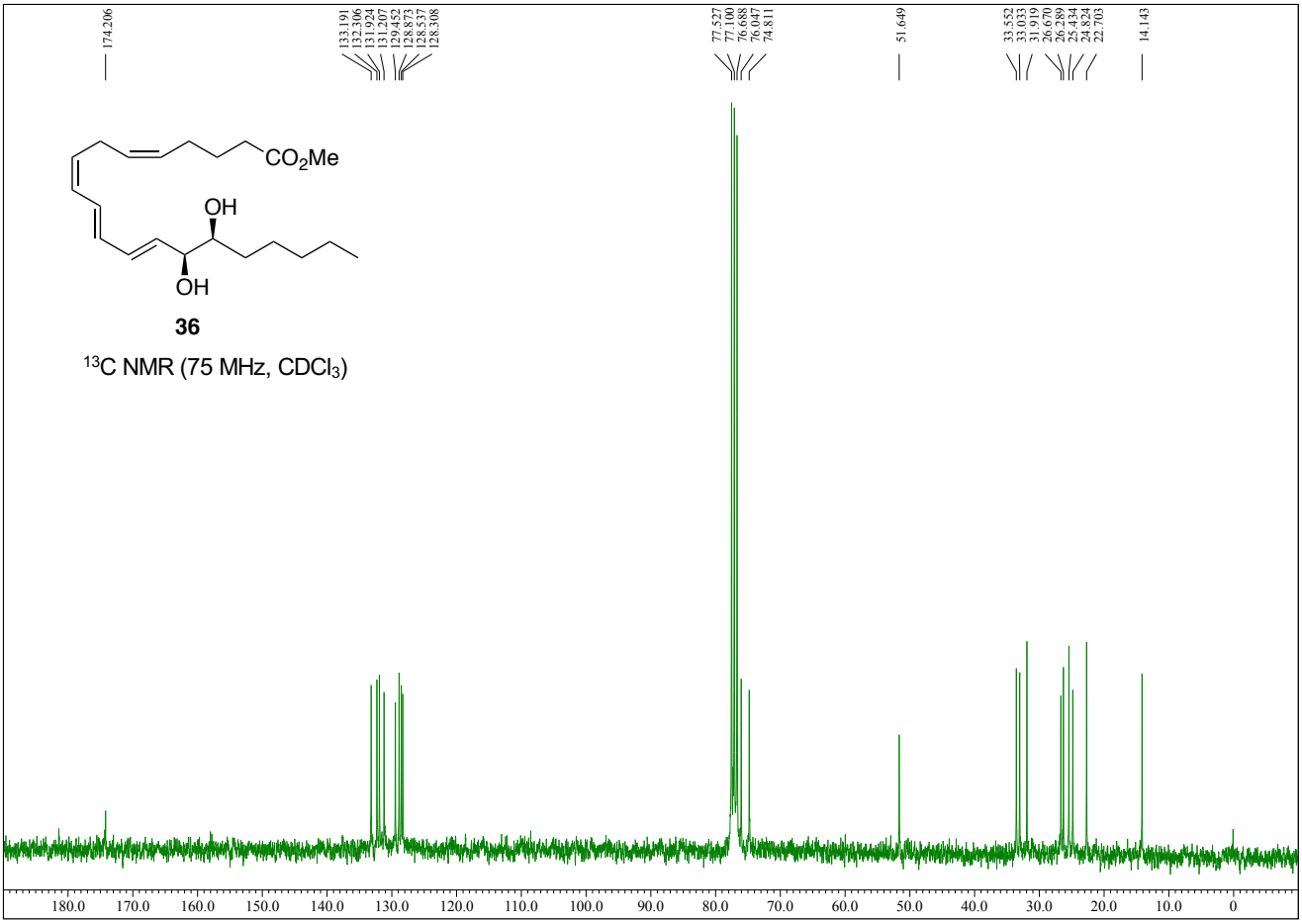
35

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



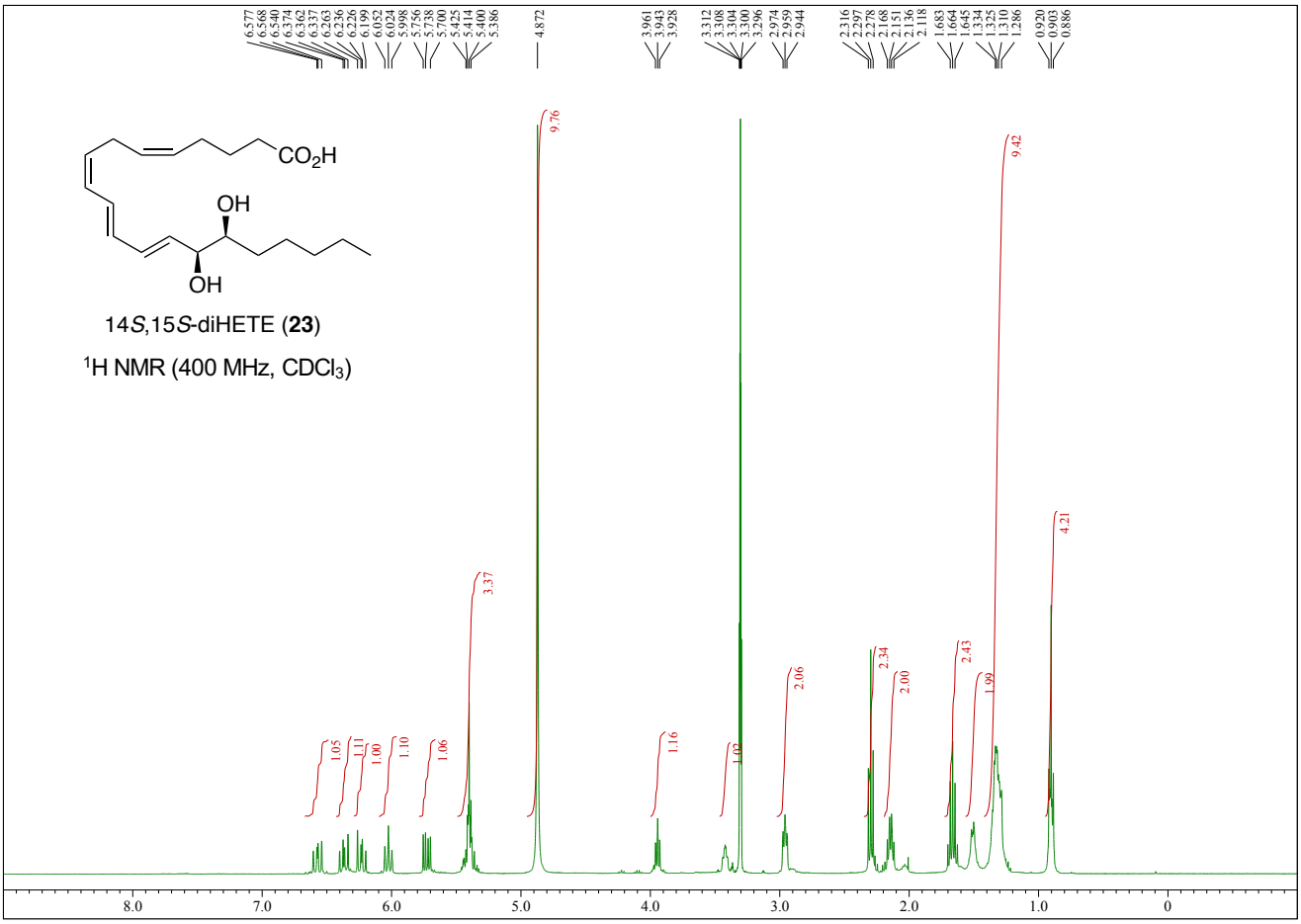
36

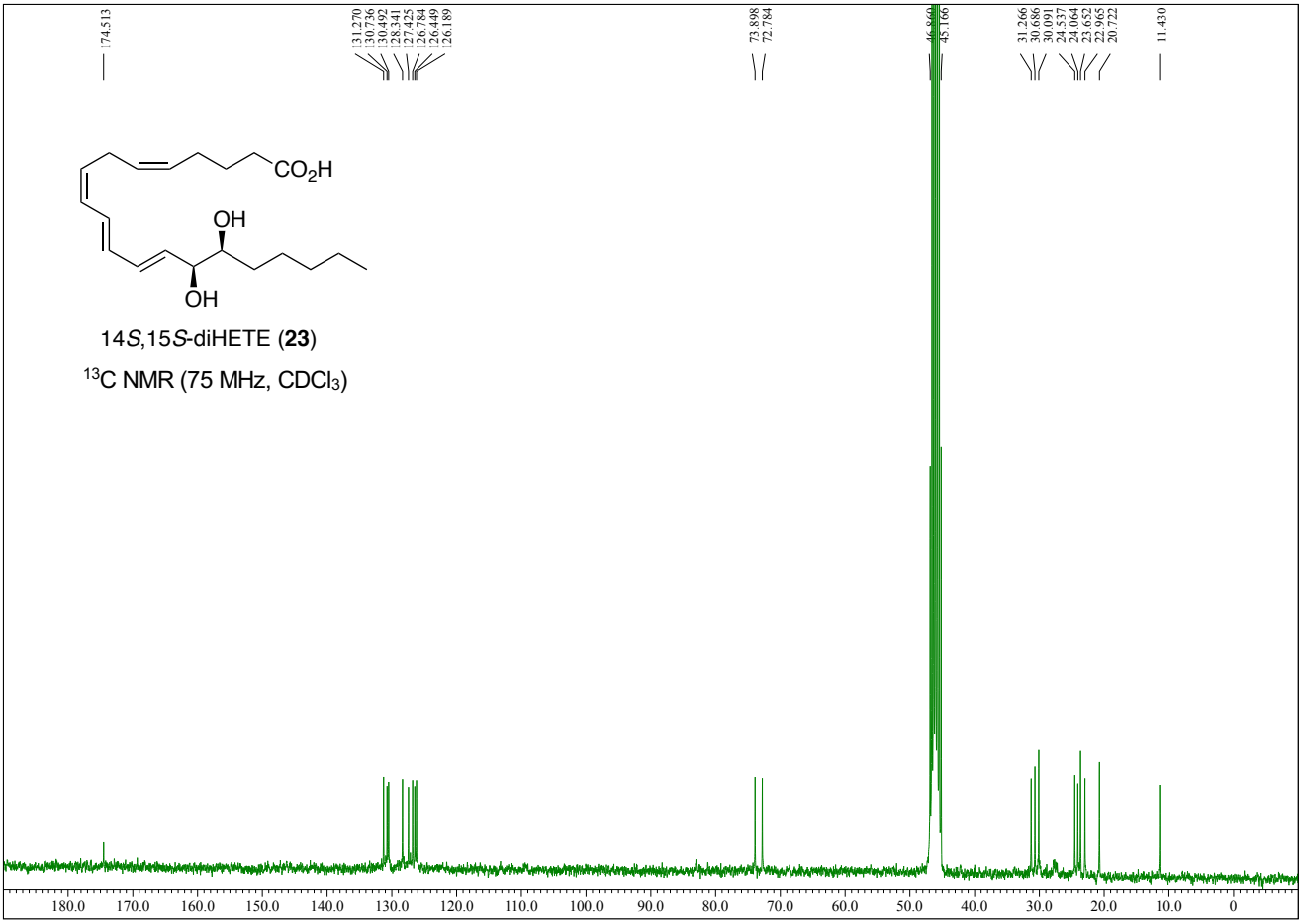
^{1}H NMR (400 MHz, $CDCl_3$)



36

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


CO2H
OH
OH
14S,15S-diHETE (23)
1H NMR (400 MHz, CDCl3)


CO2H
OH
OH
14S,15S-diHETE (23)
13C NMR (75 MHz, CDCl3)