# Enantioselective synthesis of all diastereomers of heptadeca-1-ene-4,6-diyne-3,8,9,10-tetrol; Putative structure of a conjugated diyne natural product isolated from *Hydrocotyle leucocephala*

*Kavirayani R. Prasad* and Bandita Swain*

Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India

## Supplementary information

S4-S7 : General procedures and NMR spectral data

S 8: $^{1}H$ and $^{13}C$ spectrum of Compound **7**

S 9: $^{1}H$ and $^{13}C$ spectrum of Compound **5**

S 10: $^{1}H$ and $^{13}C$ spectrum of Compound **8**

S 11: H and $^{13}C$ spectrum of Compound **9**

S 12: $^{1}H$ and $^{13}C$ spectrum of silyloxy ether of **9**

S 13: $^{1}H$ and $^{13}C$ spectrum of Compound **4**

S 14: $^{1}H$ and $^{13}C$ spectrum of Compound **10**

S 15: $^{1}H$ and $^{13}C$ spectrum of Compound **11**

S 16: $^{1}H$ and $^{13}C$ spectrum of Compound **3**

S 17: $^{1}H$ and $^{13}C$ spectrum of *p*-nitrobenzoate of **18**

S 18: $^{1}H$ and $^{13}C$ spectrum of Compound **18**

S 19: $^{1}H$ and $^{13}C$ spectrum of Compound **19**

S 20: $^{1}H$ and $^{13}C$ spectrum of 2-*epi*-**4**

S 21: $^{1}H$ and $^{13}C$ spectrum of 3-*epi*-**10**

S 22: $^{1}H$ and $^{13}C$ spectrum of intermediate Compound for synthesis of **17**

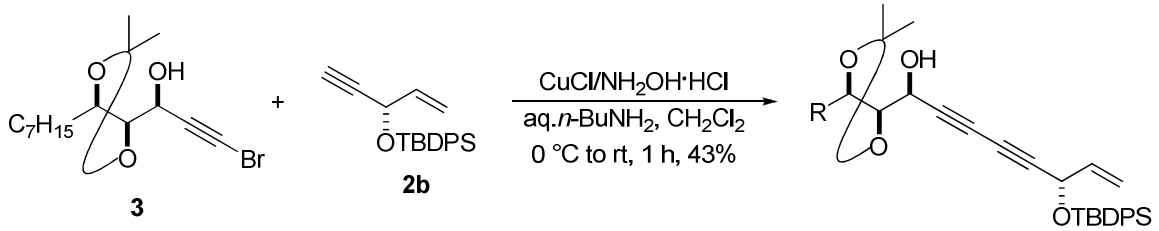
S 23: $^{1}H$ and $^{13}C$ spectrum of 3-*epi*-**11**

S 24: $^{1}H$ and $^{13}C$ spectrum of Compound **17**

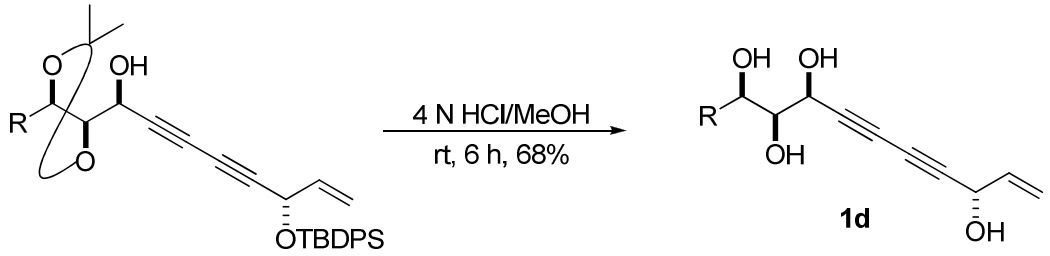
S 25: $^{1}H$ and $^{13}C$ spectrum of Compound **24**

S 26: $^{1}H$ and $^{13}C$ spectrum of Compound **22**
S 27: $^{1}H$ and $^{13}C$ spectrum of 1-benzyloxy **22**
S 28: $^{1}H$ and $^{13}C$ spectrum of Compound **25**
S 29: $^{1}H$ and $^{13}C$ spectrum of Compound **26**
S 30: $^{1}H$ and $^{13}C$ spectrum of Compound **27**
S 31: $^{1}H$ and $^{13}C$ spectrum of Compound **28**
S 32: $^{1}H$ and $^{13}C$ spectrum of Compound **29**
S 33: $^{1}H$ and $^{13}C$ spectrum of Compound **21**
S 34: $^{1}H$ and $^{13}C$ spectrum of Compound **12**
S 35: $^{1}H$ and $^{13}C$ spectrum of Compound **13**
S 36: $^{1}H$ and $^{13}C$ spectrum of Compound **14**
S 37: $^{1}H$ and $^{13}C$ spectrum of Compound **15**
S 38: $^{1}H$ and $^{13}C$ spectrum of Compound **2a**
S 39: $^{1}H$ and $^{13}C$ spectrum of Compound **16**
S 40: $^{1}H$ spectrum of Compound **1c**
S 41: $^{13}C$ spectrum of Compound **1c**
S 42: $^{1}H$ and $^{13}C$ spectrum of 3-*epi*-16
S 43: $^{1}H$ and $^{13}C$ spectrum of Compound **1d**
S 44: $^{1}H$ and $^{13}C$ spectrum of Compound **20**
S 45: $^{1}H$ and $^{13}C$ spectrum of Compound **1e**
S 46: $^{1}H$ and $^{13}C$ spectrum of intermediate Compound for synthesis of **1f**
S 47: $^{1}H$ and $^{13}C$ spectrum of Compound **1f**
S 48: $^{1}H$ and $^{13}C$ spectrum of 3,8-bis-*epi*-**16**
S 49: $^{1}H$ and $^{13}C$ spectrum of Compound **1g**
S 50: $^{1}H$ and $^{13}C$ spectrum of intermediate Compound for synthesis of **1h**
S 51: $^{1}H$ and $^{13}C$ spectrum of Compound **1h**

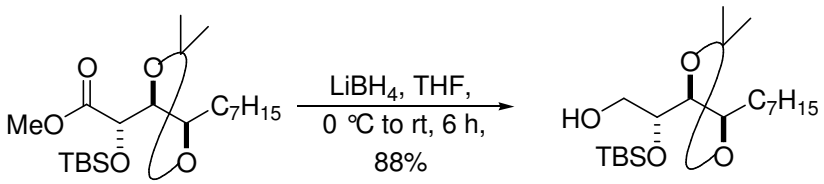
**General Procedures:** Column chromatography was performed on silica gel, Acme grade 100-200 mesh. TLC plates were visualized either with UV, in an iodine chamber, or with phosphomolybdic acid spray, unless noted otherwise. Unless stated otherwise, all reagents were purchased from commercial sources and used without additional purification. THF was freshly distilled over Na-benzophenone ketyl. Melting points were uncorrected. Unless stated otherwise, $^{1}H$ NMR and $^{13}C$ NMR spectra were recorded either on a 400 or on a 300 MHz machine in $CDCl_3$ as solvent with TMS as reference unless otherwise indicated. Unless stated otherwise, all the reactions were performed under inert atmosphere.



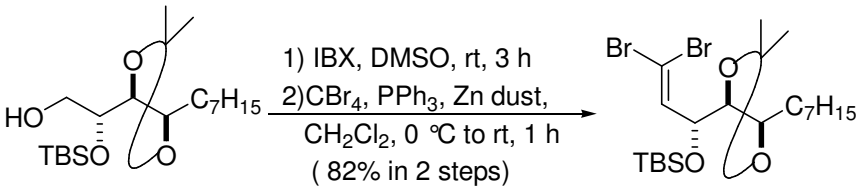

Compound was synthesized following the same procedure described for the synthesis of **16** in 43% yield. $R_f$ 0.4 (1:9 EtOAc/petroleum ether); $[\alpha]_D^{26}$ + 132.3 (*c* 1.30, $CHCl_3$); IR (neat) 3421, 2954, 2931, 2858, 1250, 1214, 1111, 1059 $cm^{-1}$; $^{1}H$ NMR (300 MHz, $CDCl_3$) δ 7.74–7.64 (m, 4H), 7.44–7.37 (m, 6H), 5.84 (ddd, 1H, *J* = 16.8, 10.1, 5.4 Hz), 5.27 (d, 1H, *J* = 16.9 Hz), 5.13 (d, 1H, *J* = 10.1 Hz), 4.84 (d, 1H, *J* = 5.3 Hz), 4.39 (t, 1H, *J* = 4.9 Hz), 3.95 (dt, 1H, *J* = 7.7, 4.1 Hz), 3.74 (dd, 1H, *J* = 7.6, 4.8 Hz), 2.48 (brd, 1H, *J* = 5.6 Hz), 1.65–1.23 (m, 18 H), 1.09 (s, 9H), 0.87 (t, 3H, *J* = 7 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 135.8, 135.5, 135.3, 132.6, 132.4, 129.5, 127.22, 127.20, 115.7, 109.1, 82.6, 78.7, 77.2, 70.0, 69.0, 64.5, 62.8, 32.1, 31.3, 29.1, 28.7, 27.1, 26.6, 26.4, 25.5, 22.2, 18.9, 13.7; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{36}H_{48}O_4Si$, 595.3220; found, 595.3221.



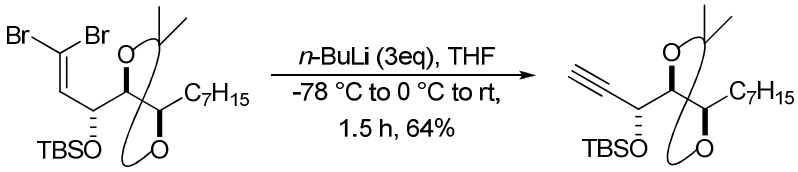

Compound **1d** was synthesized following same procedure described for the synthesis of **1c** as a white solid in 68% yield. $R_f$ 0.5 (3:2 EtOAc/petroleum ether); mp 111–112 °C; $[\alpha]_D^{26}$ + 34.4 (*c* 1.40, MeOH); IR (KBr) 3271, 2918, 2851, 1431, 1079, 1015 $cm^{-1}$; $^{1}H$ NMR (400 MHz, $CD_3OD$) δ 5.91 (ddd, 1H, *J* = 16.7, 10.1, 5.4 Hz), 5.40 (dd, 1H, *J* = 17.0, 1.1 Hz), 5.19 (dd, 1H, *J* = 10.1, 1.1 Hz), 4.44 (d, 1H, *J* = 7.5 Hz), 3.76 (t, 1H, *J* = 5.8 Hz), 3.38 (d, 1H, *J* = 7.5 Hz), 3.30 (s, 1H), 1.57–1.33 (m, 12H), 0.90 (t, 3H, *J* = 6.5 Hz); $^{13}C$ NMR (100 MHz, $CD_3OD$) δ 138.0, 116.6, 79.9, 79.6, 77.6, 72.0, 70.4, 70.0, 65.4, 63.8, 34.9, 33.0, 30.7, 30.4, 26.9, 23.7, 14.4; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{17}H_{26}O_4$, 317.1729; found, 317.1714.



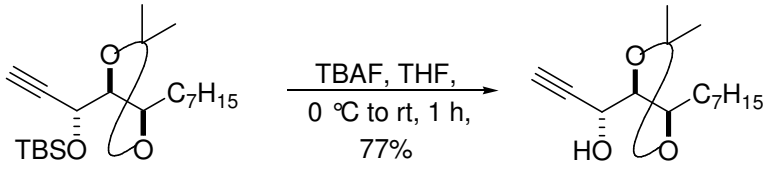

Reaction is performed similar to that described for the synthesis of **4** in 88% yield as colorless oil. $R_f$ 0.5 (3:7 EtOAc/petroleum ether); $[\alpha]_D^{26}$ + 12.1 (*c* 3.50, $CHCl_3$); IR (neat) 3490, 2955, 2930, 1464, 1255 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.92–3.87 (m, 1H), 3.73–3.66 (m, 4H), 2.25–2.22 (m, 1H), 1.71–1.20 (m, 18H), 0.96–0.84 (m, 12H), 0.12 (s, 3H), 0.10 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 108.6, 81.2, 80.4, 73.9, 65.0, 34.6, 31.6, 29.6, 29.1, 27.3, 27.0, 26.2, 25.6, 22.5, 17.8, 14.0, –4.4, –4.6; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{20}H_{42}O_4Si$, 397.2750; found, 397.2754.



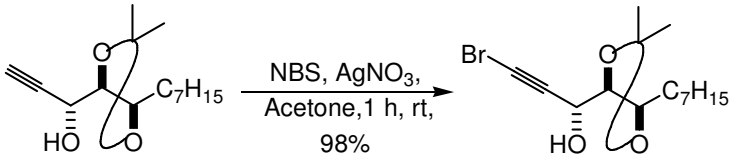

Dibromoolefin is synthesized following the same procedure described for compound **10** in 82% yield. $R_f$ 0.6 (5:95 EtOAc/petroleum ether); $[\alpha]_D^{26}$ + 8.5 (*c* 3.30, $CHCl_3$); IR (neat) 2954, 2930, 2858, 1253, 1076 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 6.40 (d, 1H, *J* = 8.4 Hz), 4.34–4.33 (brm, 1H), 3.94–3.90 (brm, 1H), 3.61 (t, 1H, *J* = 6.3 Hz), 1.60–1.28 (m, 18H), 0.88 (s, 12H), 0.11 (s, 3H), 0.09 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 138.7, 109.0, 90.9, 82.8, 78.5, 74.5, 34.3, 31.7, 29.6, 29.1, 27.5, 26.8, 26.1, 25.7, 22.6, 14.0, –4.4, –4.8; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{21}H_{40}Br_2O_3Si$, 551.1098; found, 551.1053.




alkyne is synthesized following the same procedure that is described for the synthesis of **11** in 64% yield as colorless oil. $R_f$ 0.5 (5:95 EtOAc/petroleum ether); $[\alpha]_D^{26}$ – 10.3 (*c* 2.20, $CHCl_3$); IR (neat) 3312,2955, 2930, 2858, 1464, 1253, 1087 $cm^{-1}$. $^1H$ NMR (400 MHz, $CDCl_3$) δ 4.39 (dd, 1H, *J* = 5.7, 2.1 Hz), 4.01 (dt, 1H, *J* = 8.4, 3.1 Hz), 3.71 (dd, 1H, *J* = 7.1, 5.8 Hz), 2.46 (d, 1H, *J* = 2.1 Hz), 1.75–1.26 (m, 18H), 0.91–0.85 (m, 12H), 0.16 (s, 3H), 0.12 (s, 3H); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 108.9, 83.0, 78.5, 73.9, 63.9, 34.5, 31.7, 29.6, 29.1, 27.5, 27.0, 26.1, 25.7, 22.6, 18.1, 14.0, –4.7, –5.0; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{21}H_{40}O_3Si$, 391.2644; found, 391.2636.

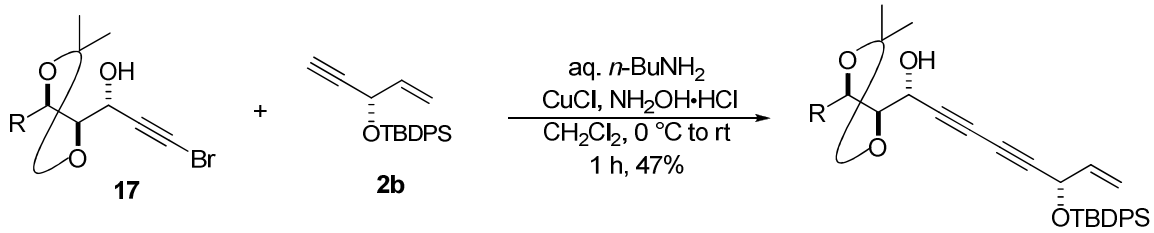



Silyl deprotection is performed following the same procedure that is described for the synthesis of **11** in 77% yield as colorless oil. $R_f$ 0.6 (1:4 EtOAc/petroleum ether); $[\alpha]_D^{26}$ + 22.7 (*c* 2.30, $CHCl_3$); IR (neat) 3437, 3311, 2928, 2858, 1372 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 4.55–4.47 (m, 1H), 4.07 (dt, 1H, *J* = 8.1, 3.6 Hz), 3.79 (dd, 1H, *J* = 7.8, 3.8 Hz), 2.61 (d, 1H, *J* = 5.4 Hz), 2.54 (d, 1H, *J* = 2.2 Hz), 1.80–1.49 (m, 3H), 1.43 (s, 6H), 1.38–1.25 (m, 9H), 0.88 (t, 3H, *J* = 6.7 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 109.0, 82.3, 80.8, 77.3, 75.0, 62.2, 33.9, 31.7, 29.5, 29.0, 27.4, 26.8, 25.9, 22.5, 14.0; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{15}H_{26}O_3$, 277.1780; found, 277.1779.



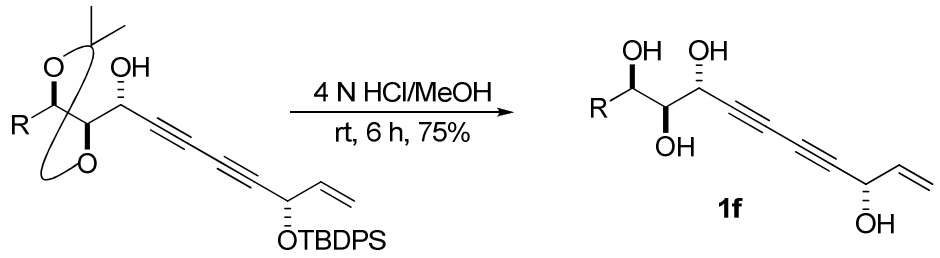

**17**

Bromo alkyne is prepared following the same procedure that is described for the synthesis of **3** 98% yield. $R_f$ 0.6 (1:4 EtOAc/petroleum ether); $[\alpha]_D^{26}$ + 13.8 (*c* 3.0, $CHCl_3$); IR (neat) 3444, 2927, 2858, 1493 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 4.51 (t, 1H, *J* = 4.5 Hz), 4.05 (dt, 1H, *J* = 7.9, 3.9 Hz), 3.78 (dd, 1H, *J* = 7.8, 3.4 Hz), 2.74–2.69 (m, 1H), 1.77–1.28 (m, 18 H), 0.88 (t, 3H, *J* = 6.8 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 109.3, 82.5, 77.3, 77.2, 63.2, 47.4, 33.8, 31.7, 29.5, 29.1, 27.5, 26.8, 25.9, 22.6, 14.0; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{15}H_{25}BrO_3$, 355.0885; found, 355.0891.

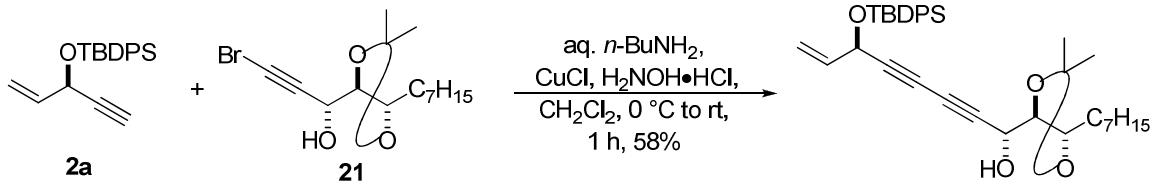



**17** **2b**

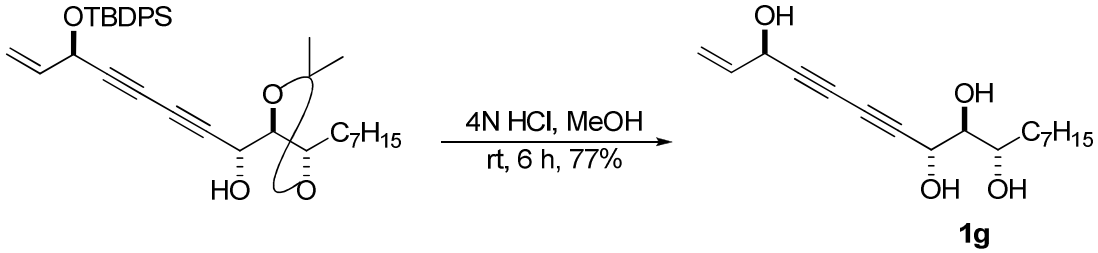
The diyne was synthesized following the same procedure described for the synthesis of **16**. Yield 47% (colorless oil). $R_f$ 0.4 (1:9 EtOAc/petroleum ether); $[\alpha]_D^{26}$ – 85.8 (*c* 3.20, $CHCl_3$); IR (neat) 3421, 2955, 2931, 2858, 1111, 1060 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.73–7.64 (m, 4H), 7.44–7.35 (m, 6H), 5.84 (ddd, 1H, *J* = 16.6, 10.1, 5.4 Hz), 5.28 (d, 1H, *J* = 16.9 Hz), 5.13 (d, 1H, *J* = 10.1 Hz), 4.84 (d, 1H, *J* = 5.3 Hz), 4.53 (s, 1H), 4.03 (dt, 1H, *J* = 7.9, 4.0 Hz), 3.78 (dd, 1H, *J* = 7.8, 3.5 Hz), 2.47 (brs, 1H), 1.66–1.27 (m, 18H), 1.08–1.07 (m, 9H), 0.87 (t, 3H, *J* = 6.8 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 136.2, 135.9, 135.7, 134.7, 133.0, 132.7, 129.9, 129.6, 127.7, 127.61, 127.60, 116.1, 109.3, 82.5, 78.9, 77.3, 76.4, 71.1, 69.3, 64.8, 63.1, 33.7, 31.7, 29.5, 29.1, 27.5, 26.8, 26.7, 26.5, 25.9, 22.6, 19.3, 14.1; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{36}H_{48}O_4Si$, 595.3220; found, 595.3224.




Compound **1f** was synthesized following a similar procedure that is described for the synthesis of **1c**. Yield 75% (Gummy mass). $R_f$ 0.5 (3:2 EtOAc/petroleum ether); $[\alpha]_D^{26}$ + 28.2 (*c* 1.10, MeOH); IR (KBr) 3365, 2926, 2856, 2429, 1022 $cm^{-1}$; $^1H$ NMR (400 MHz, $CD_3OD$) δ 5.90 (ddd, 1H, *J* = 16.9, 10.1, 5.5 Hz), 5.39 (d, 1H, *J* = 17.0 Hz), 5.18 (d, 1H, *J* = 10.1 Hz), 4.42 (d, 1H, *J* = 7.3 Hz), 3.84–3.75 (m, 1H), 3.37 (dd, 1H, *J* = 2.4, 7.3 Hz), 3.30 (s, 1H), 1.57–1.30 (m, 12H), 0.90 (t, 3H, *J* = 6.9 Hz); $^{13}C$ NMR (100 MHz, $CD_3OD$) δ 136.6, 115.1, 80.0, 77.5, 75.2, 69.6, 68.9, 68.1, 63.2, 62.4, 33.1, 31.6, 29.3, 29.0, 25.5, 22.3, 13.0; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{17}H_{26}O_4$, 317.1729; found, 317.1713.

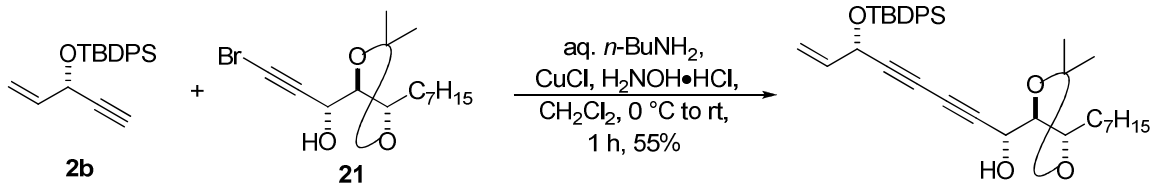



Compound diyne was synthesized following the same procedure as for **16.** Yield 58%. $R_f$ 0.4 (1:9 EtOAc/petroleum ether); $[\alpha]_D^{26}$ + 155.3 (*c* 2.90, $CHCl_3$); IR (neat) 3414, 2953, 2930, 2858, 1112, 1059 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.74–7.65 (m, 4H), 7.43–7.37 (m, 6H), 5.85 (ddd, 1H, *J* = 16.7, 10.1, 5.4 Hz), 5.29 (d, 1H, *J* = 16.9 Hz), 5.12 (d, 1H, *J* = 10.1 Hz), 4.84 (d, 1H, *J* = 5.3 Hz), 4.40 (m, 1H), 4.20 (dt, 1H, *J* = 10.1, 5.8 Hz), 4.13–4.09 (m, 1H), 2.46 (brs, 1H), 1.75–1.24 (m, 18H), 1.09 (s, 9H), 0.88 (t, 3H, *J* = 6.9 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 136.3, 135.9, 135.7, 134.8, 133.0, 132.8, 129.8, 127.61, 127.60, 116.1, 108.6, 79.7, 78.7, 78.0, 77.2, 70.9, 69.7, 64.9, 63.0, 31.7, 29.5, 29.2, 28.8, 27.3, 27.0, 26.8, 26.5, 25.3, 22.6, 19.3, 14.1; HRMS (*m/z*): $[M + Na]^+$ calcd for $C_{36}H_{48}O_4Si$, 595.3220; found, 595.3205.



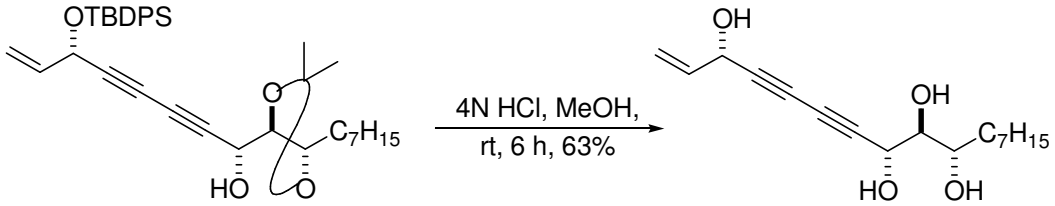

**Preparation of 1g:** Compound **1g** was synthesized following the same procedure as for **1c.** Yield 77% (Yellow oil). $R_f$ 0.5 (3:2 EtOAc/petroleum ether); $[\alpha]_D^{26}$ – 41.7 (*c* 2.3, MeOH); IR (neat) 3352, 2954, 2925, 2855, 1406, 1021 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.91 (ddd, 1H, *J* = 16.6, 10.1, 5.3 Hz), 5.46 (d, 1H, *J* = 16.9 Hz), 5.24 (d, 1H, *J* = 10.1 Hz), 4.93 (d, 1H, *J* = 4.4 Hz), 4.75 (brs, 2H), 4.52 (brs, 1H), 3.98 (brs, 1H), 3.68–3.65 (brm, 2H), 3.42 (brs, 1H), 1.76–1.27 (m, 12H), 0.88 (t, 3H, *J* = 6.9 Hz); $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 135.6, 117.4, 78.4, 78.1, 76.4, 72.9, 70.5, 70.2, 64.7, 63.1, 33.3, 31.9,

29.7, 29.4, 25.6, 22.6, 14.1; HRMS (*m/z*): [M + Na]$^+$ calcd for $C_{17}H_{26}O_4$, 317.1729; found, 317.1713.



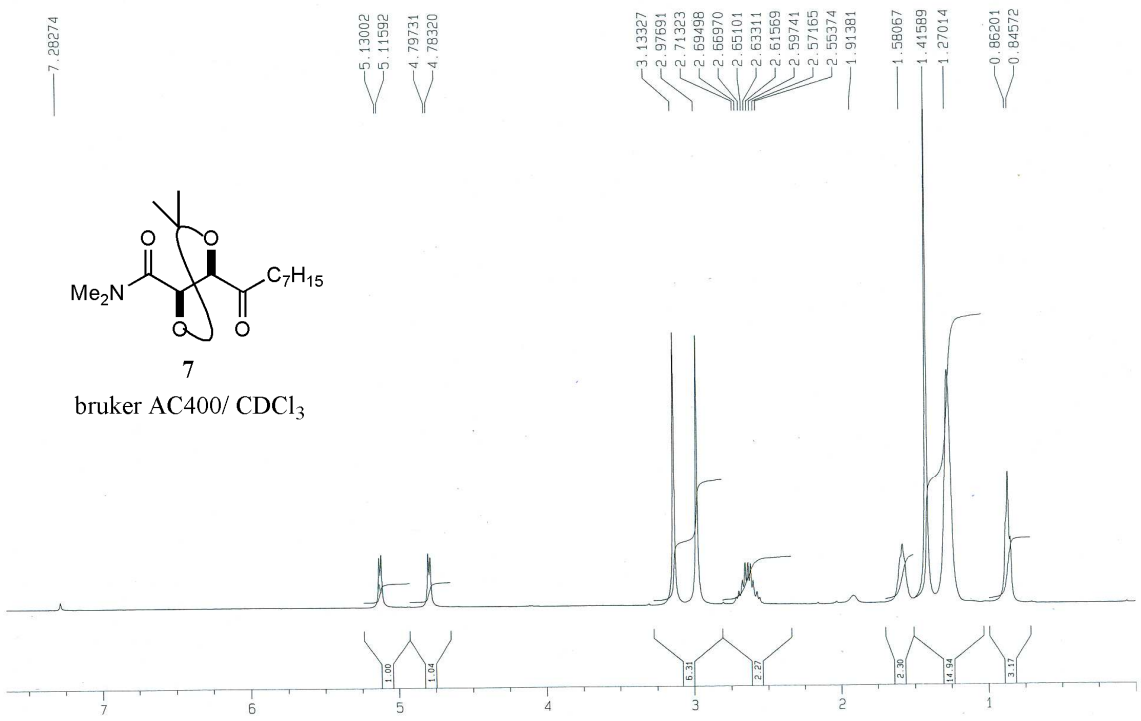

**2b** **21**

Conjugated diyne was synthesized following the same procedure as for **16**. Yield 55% (colorless oil). $R_f$ 0.4 (1:9 EtOAc/petroleum ether); $[\alpha]_D^{26}$ – 72.6 (*c* 2.5, $CHCl_3$); IR(neat) 3414, 2954, 2930, 2858, 1111, 1058, 702 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) δ 7.74–7.64 (m, 4H), 7.43–7.36 (m, 6H), 5.84 (ddd, 1H, *J* = 16.9, 10.1, 5.4 Hz), 5.27 (dd, 1H, *J* = 17.0, 1.2 Hz), 5.12 (d, 1H, *J* = 10.1 Hz), 4.83 (d, 1H, *J* = 5.3 Hz), 4.40 (dd, 1H, *J* = 7.1, 5.0 Hz), 4.20 (ddd, 1H, *J* = 13.5, 6.1, 4.4 Hz), 4.09 (m, 1H), 2.23 (brd, 1H, *J* = 7.3 Hz), 1.76–1.21 (m, 18H), 1.08–1.04 (m, 9H), 0.87 (t, 3H, *J* = 7 Hz); $^{13}$C NMR (100 MHz, $CDCl_3$) δ 136.3, 135.9, 135.8, 134.8, 133.0, 132.8, 129.8, 129.6, 127.7, 127.61, 127.60, 116.1, 108.6, 79.7, 78.7, 78.0, 77.2, 70.9, 69.7, 64.9, 63.0, 31.7, 29.5, 29.2, 28.8, 27.3, 27.0, 26.8, 26.5, 25.3, 22.6, 19.3, 14.0; HRMS (*m/z*): [M + Na]$^+$ calcd for $C_{36}H_{48}O_4Si$, 595.3220; found, 595.3213.




**1h**

Compound **1h** was synthesized following the same procedure as for **1c.** Yield 63% (Gummy mass). $R_f$ 0.5 (3:2 EtOAc/petroleum ether); $[\alpha]_D^{26}$ + 11.9 (*c* 1.4, MeOH); IR (neat) 3305, 2918, 1453, 1290, 1071, 1013 cm$^{-1}$; $^1$H NMR (400 MHz, $CD_3OD$) δ 5.91 (ddd, 1H, *J* = 16.9, 10.1, 5.5 Hz), 5.40 (d, 1H, *J* = 17 Hz), 5.19 (d, 1H, *J* = 10.1 Hz), 4.64 (d, 1H, *J* = 3.9 Hz), 3,56–3.52 (m, 1H), 3.44 (dd, 1H, *J* = 8.1, 4.0 Hz), 3.31 (brs, 1H), 1.78–1.32 (m, 12H), 0.91 (t, 3H, *J* = 6.9 Hz); $^{13}$C NMR (100 MHz, $CD_3OD$) δ 138.1, 116.6, 79.9, 78.8, 78.4, 73.1, 70.5, 70.2, 65.6, 63.8, 34.2, 33.0, 30.8, 30.5, 26.4, 23.7, 14.4; HRMS (*m/z*): [M + Na]$^+$ calcd for $C_{17}H_{26}O_4$, 317.1729; found, 317.1724.

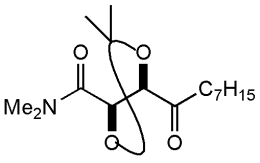






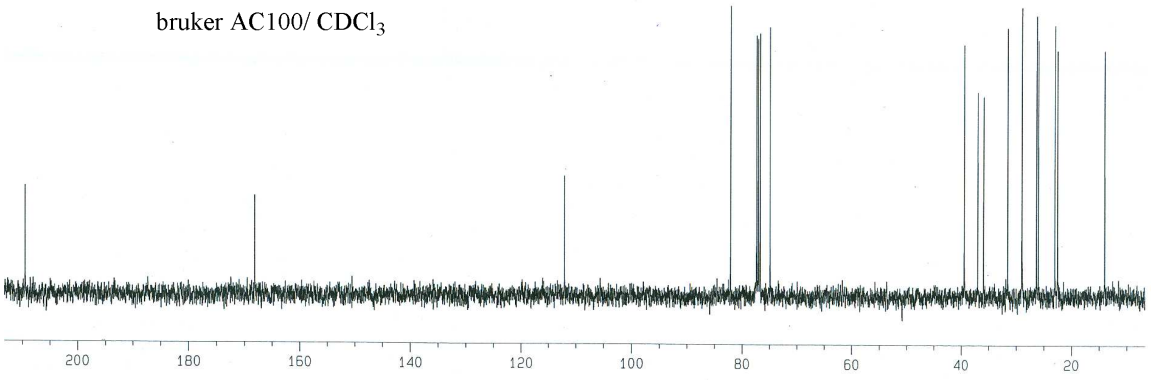
7

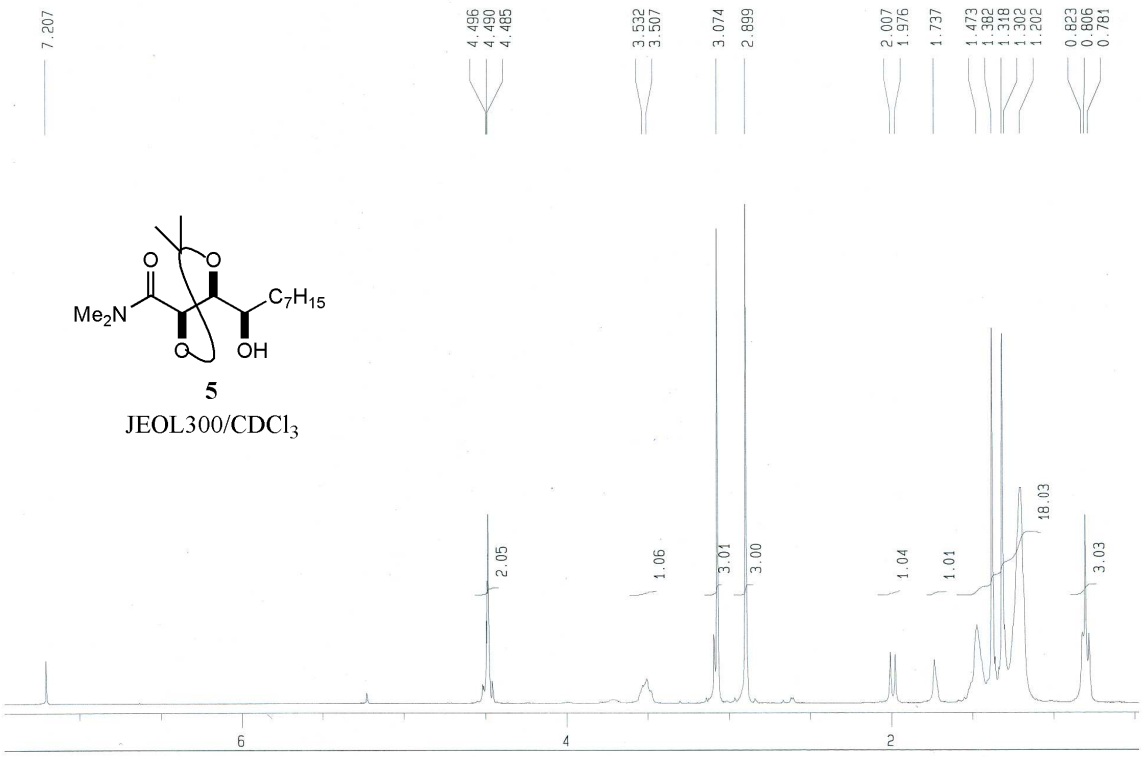
bruker AC400/ $CDCl_3$


7

bruker AC100/ $CDCl_3$



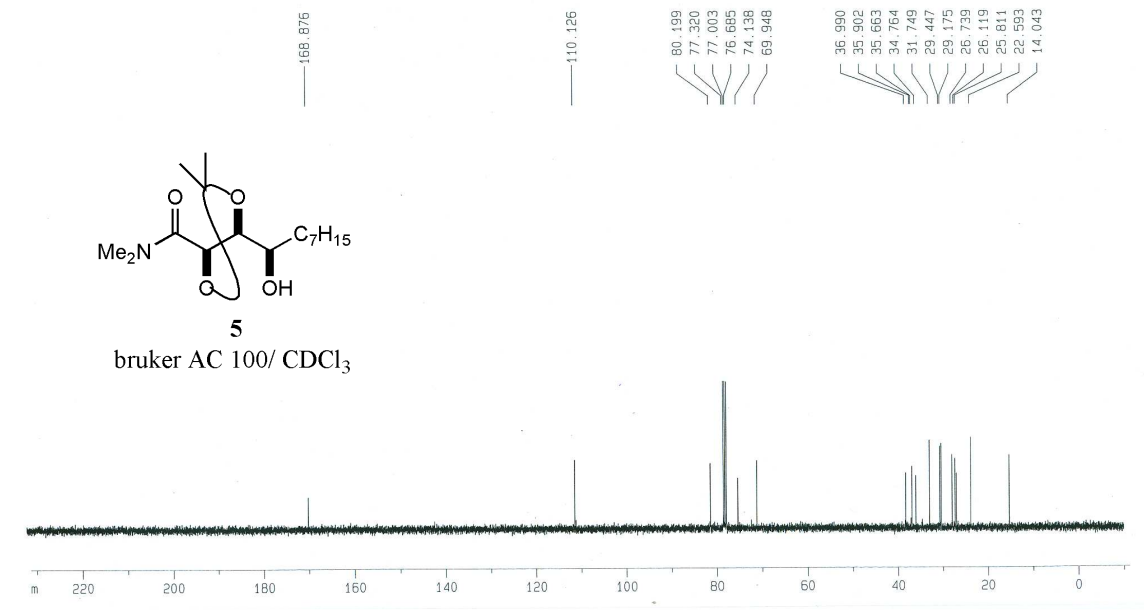






**5**

JEOL300/$CDCl_3$

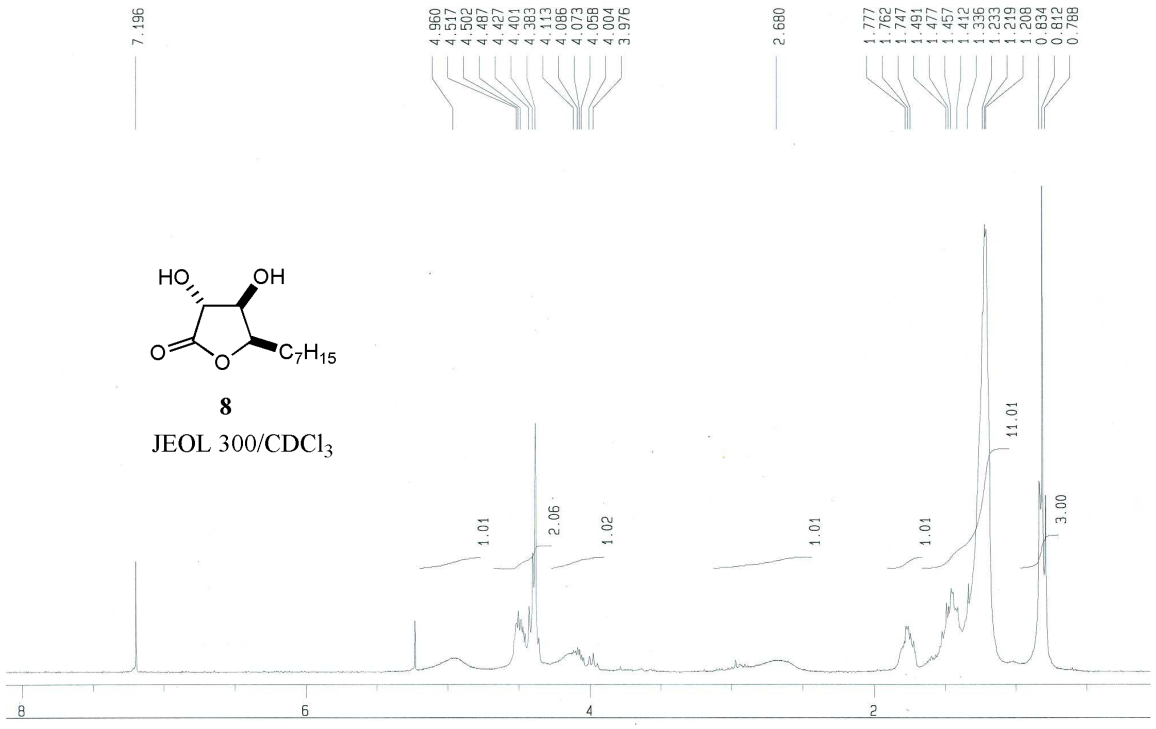






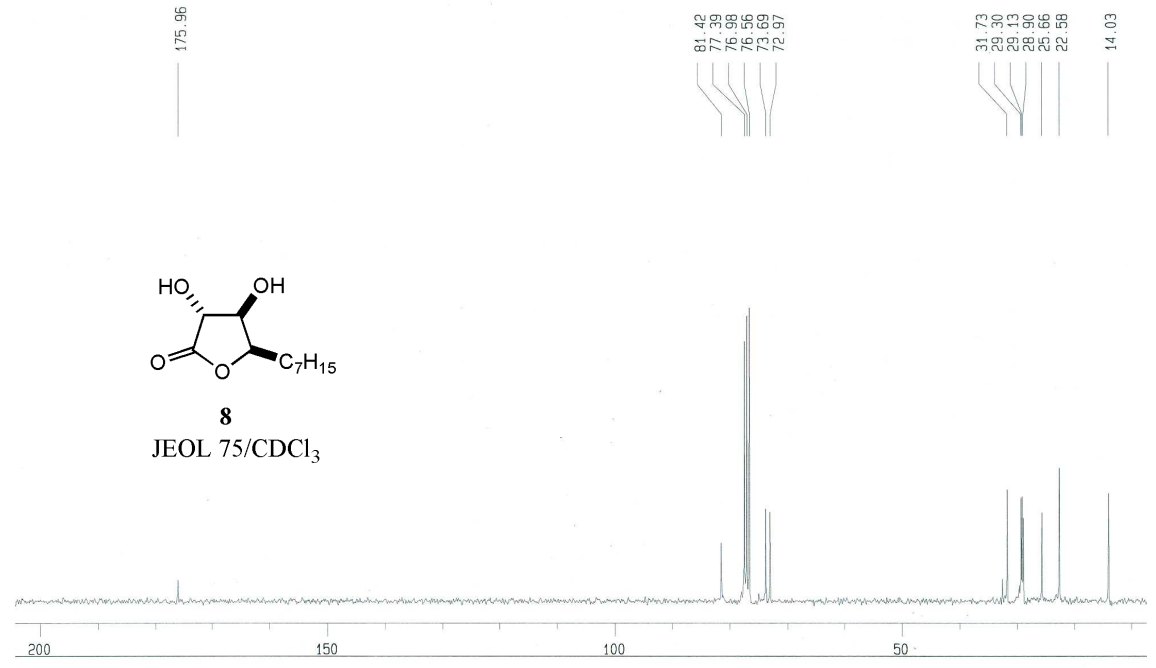
**5**

bruker AC 100/ $CDCl_3$



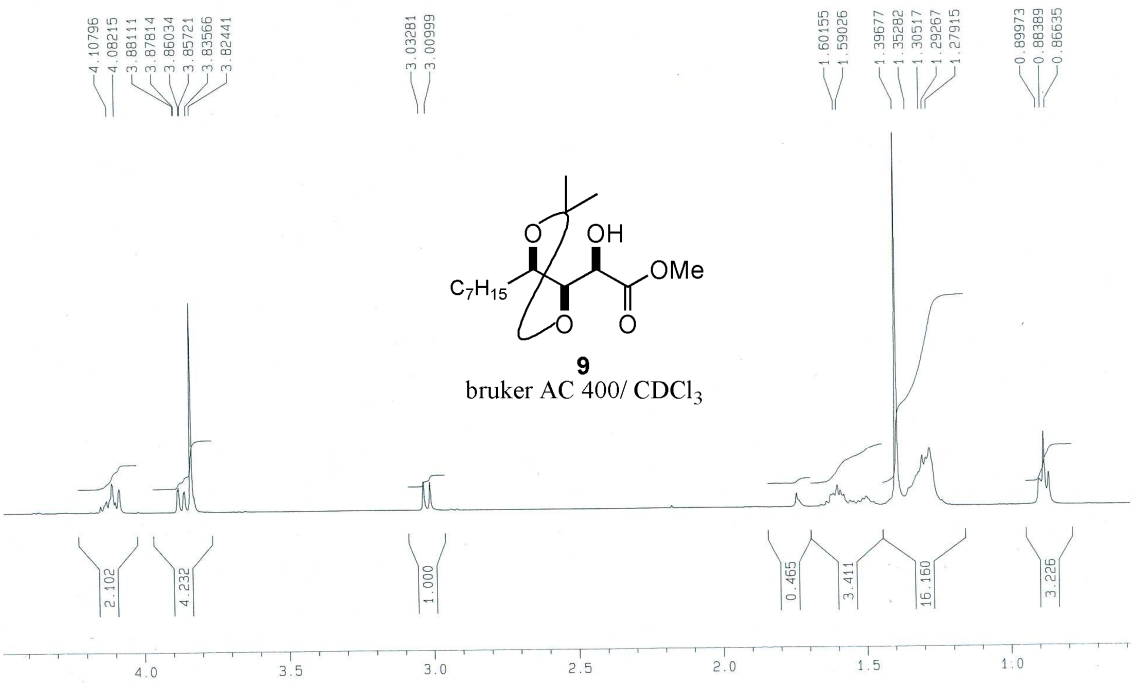

**8**

JEOL 300/$CDCl_3$



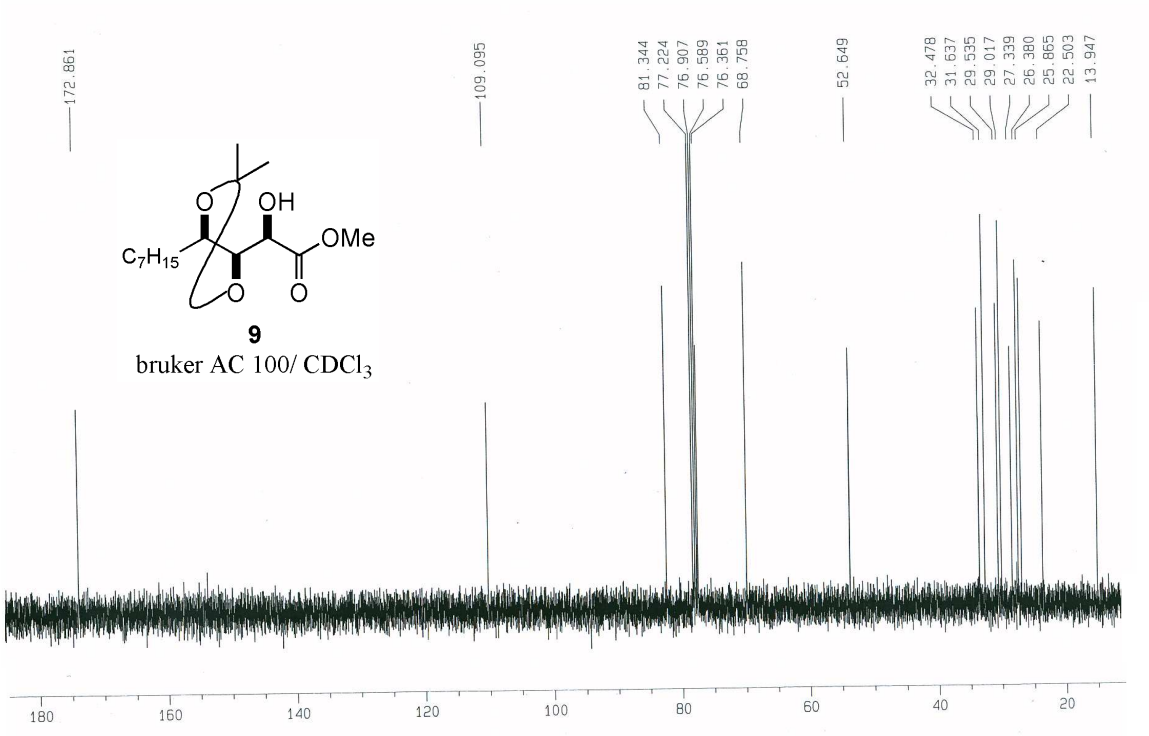

**8**

JEOL 75/$CDCl_3$



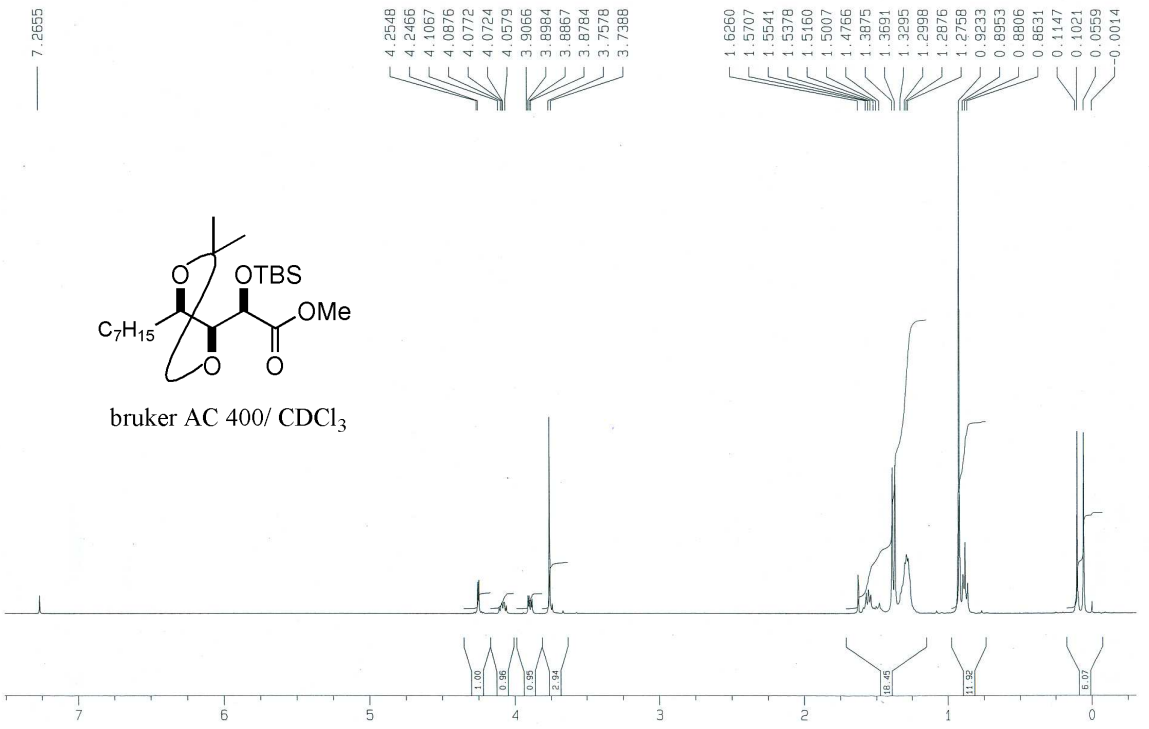

**9**

bruker AC 400/ $CDCl_3$

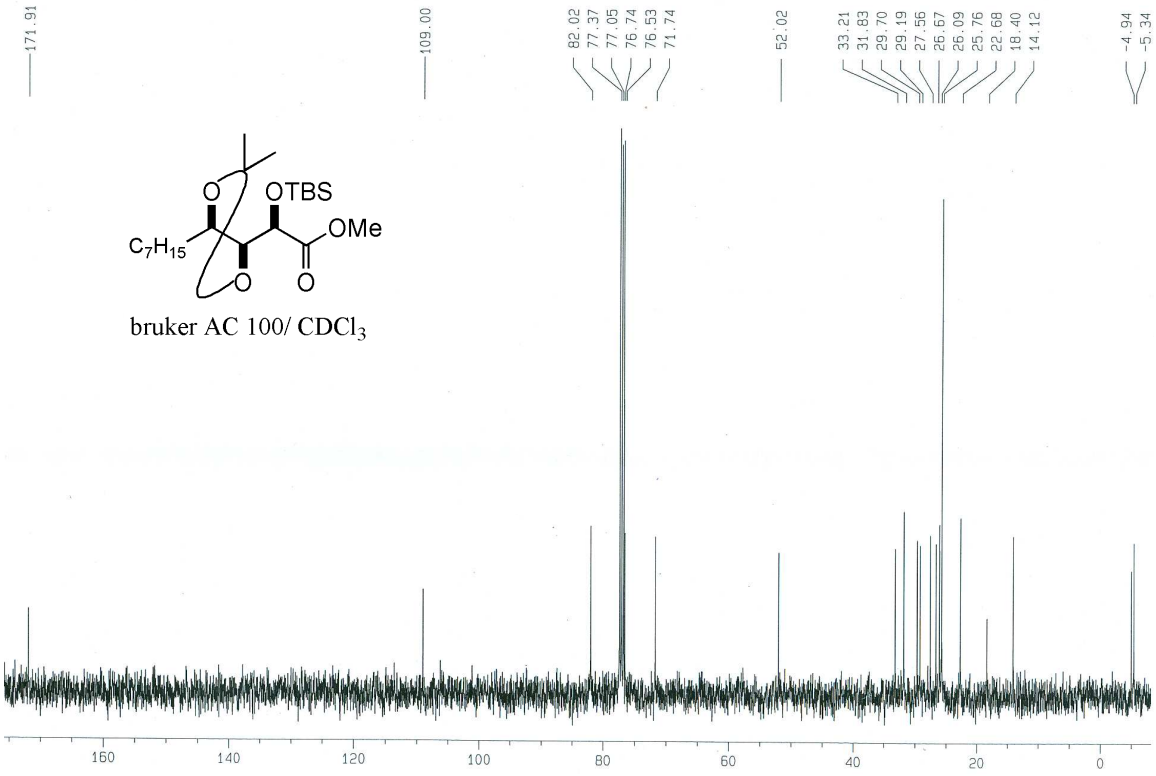



**9**

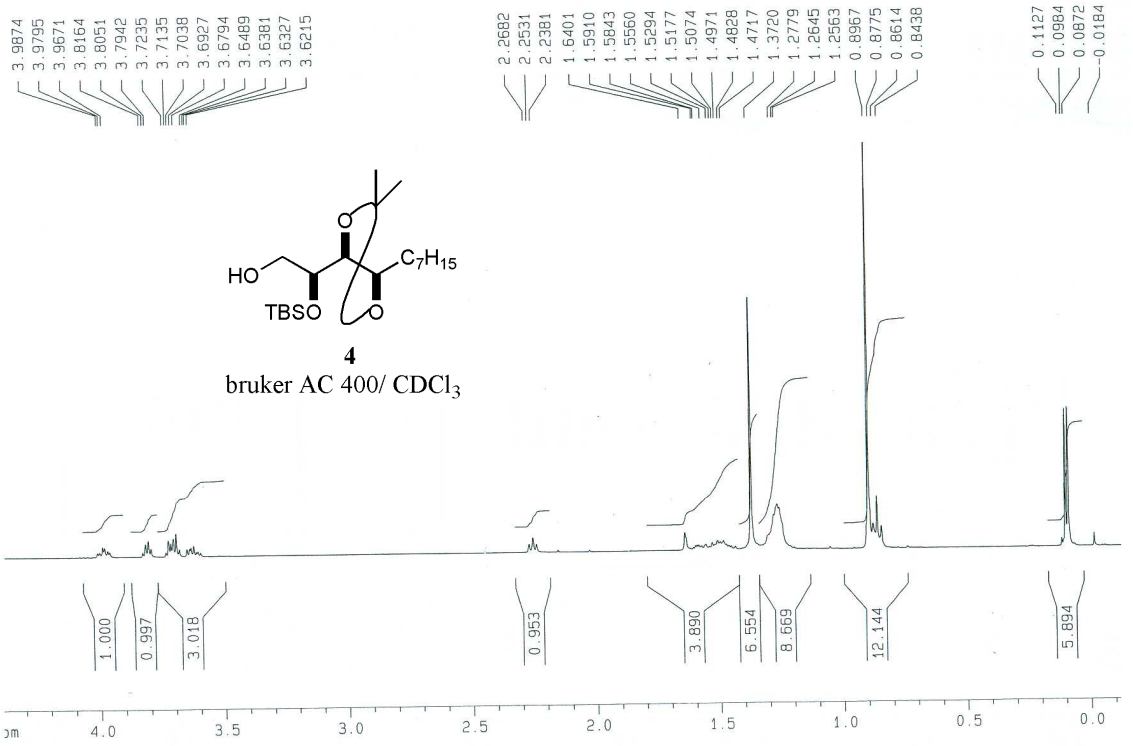
bruker AC 100/ $CDCl_3$




bruker AC 400/ $CDCl_3$

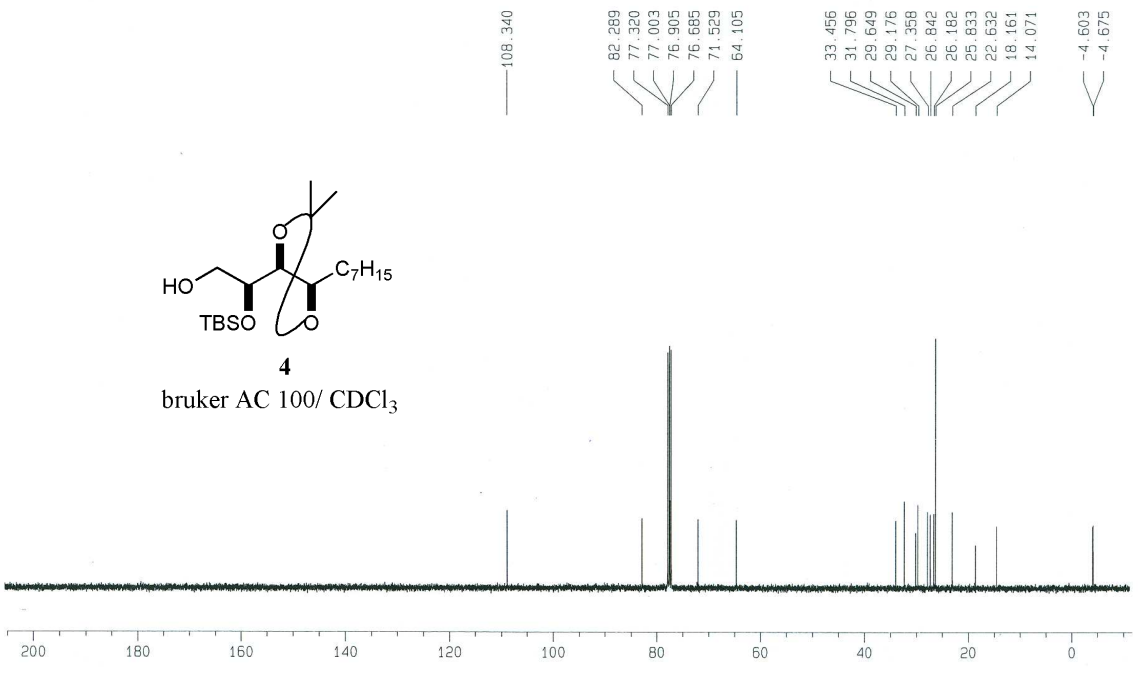



bruker AC 100/ $CDCl_3$



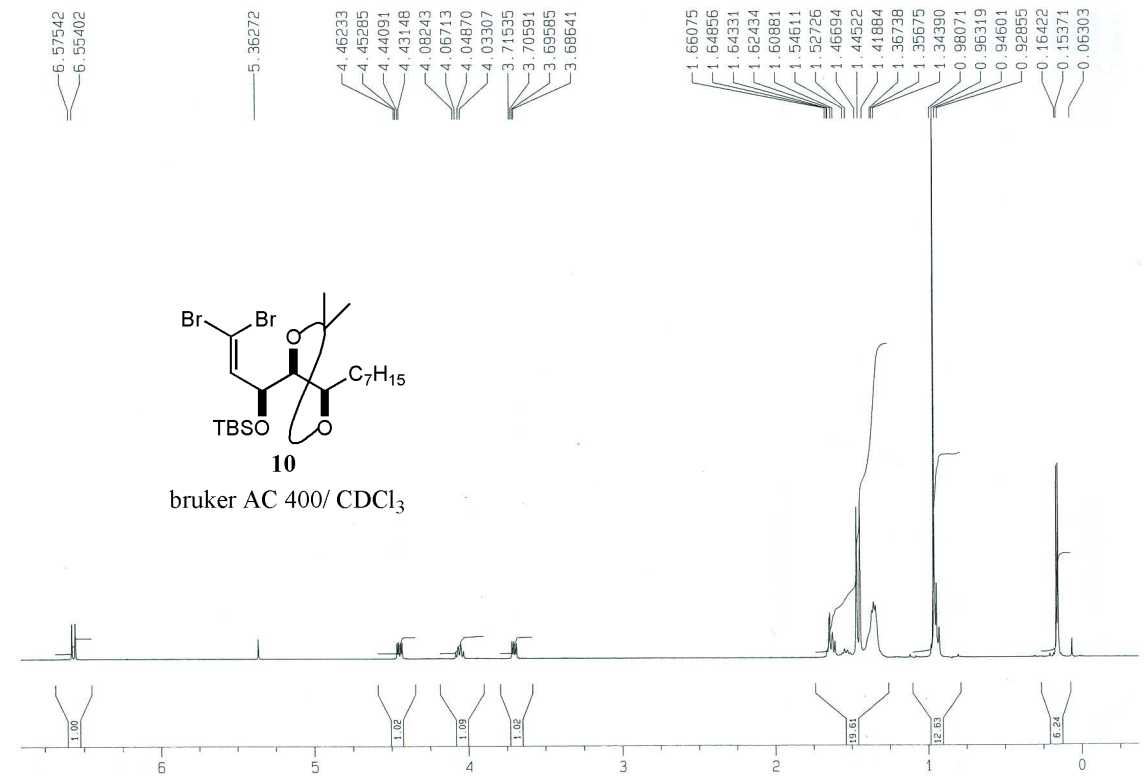

**4**

bruker AC 400/ $CDCl_3$



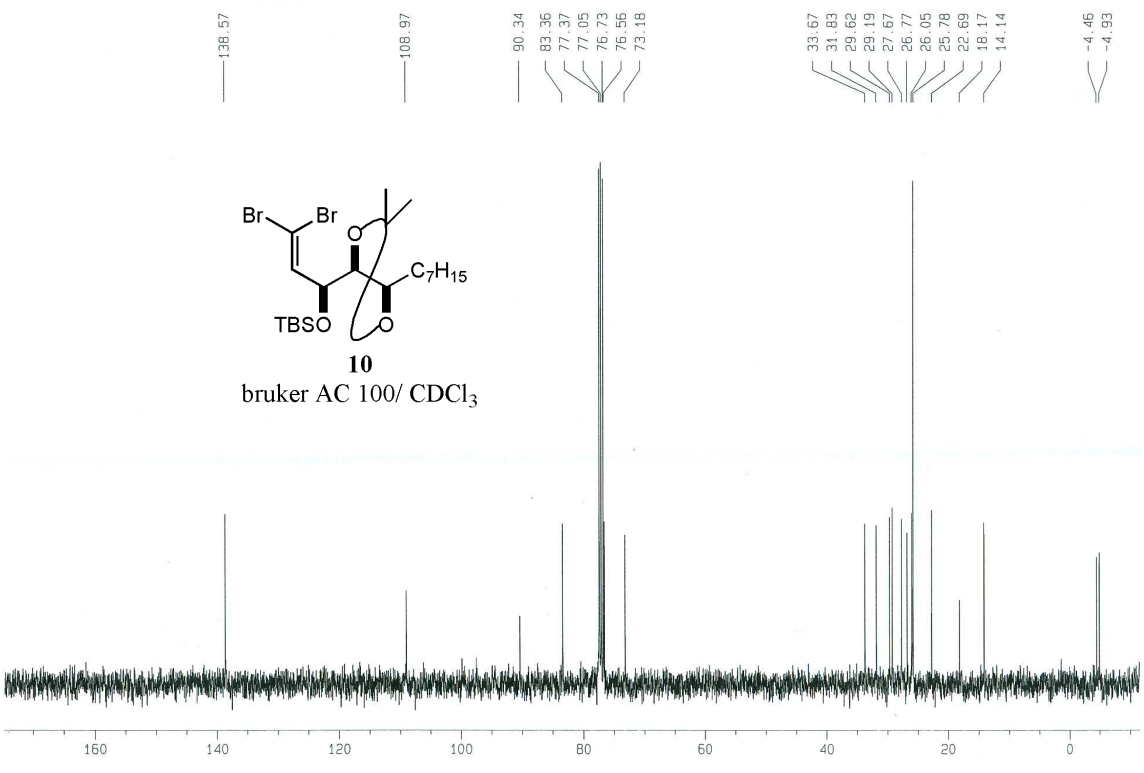

**4**

bruker AC 100/ $CDCl_3$



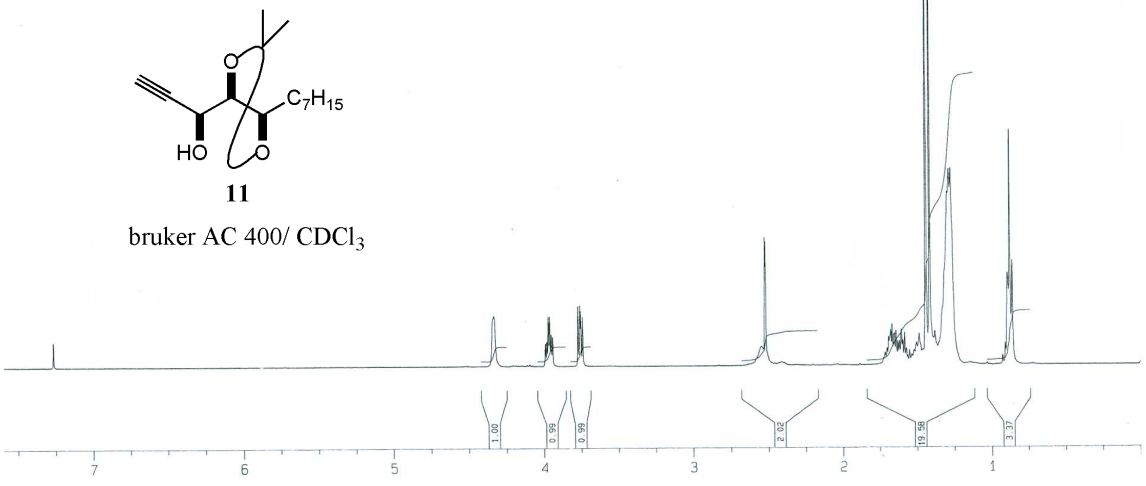

**10**

bruker AC 400/ $CDCl_3$




**10**

bruker AC 100/ $CDCl_3$

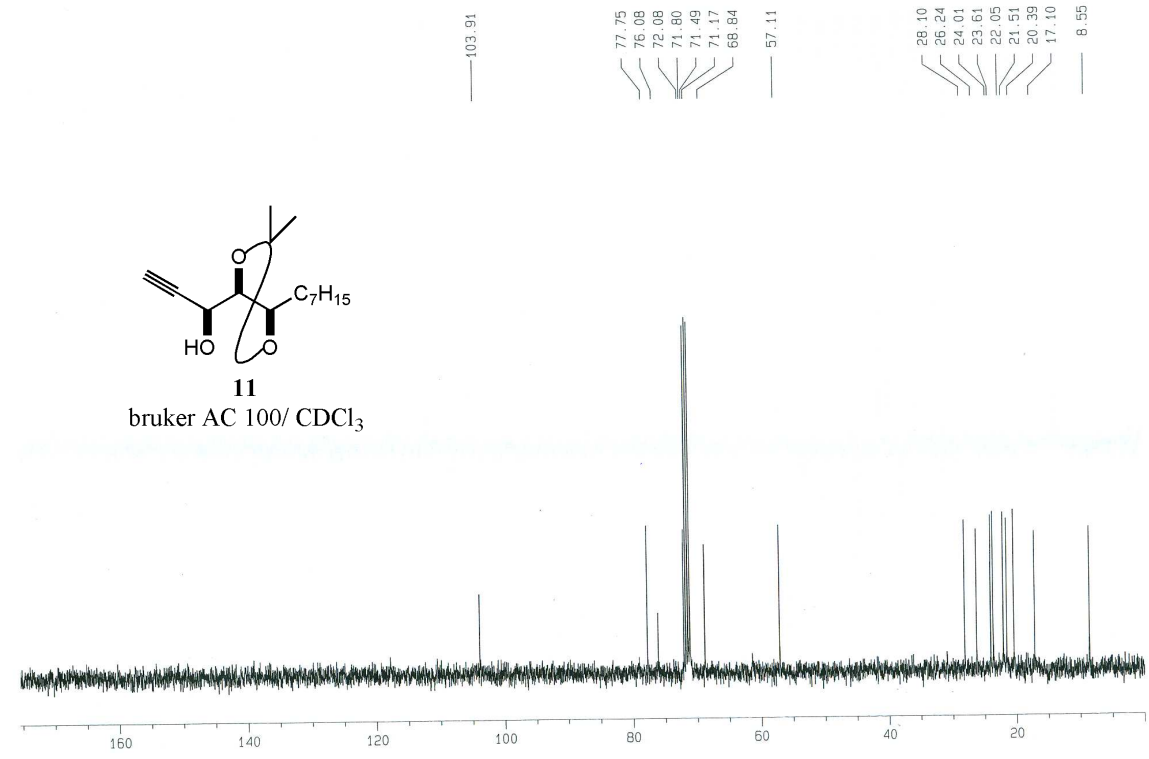






**11**

bruker AC 400/ $CDCl_3$

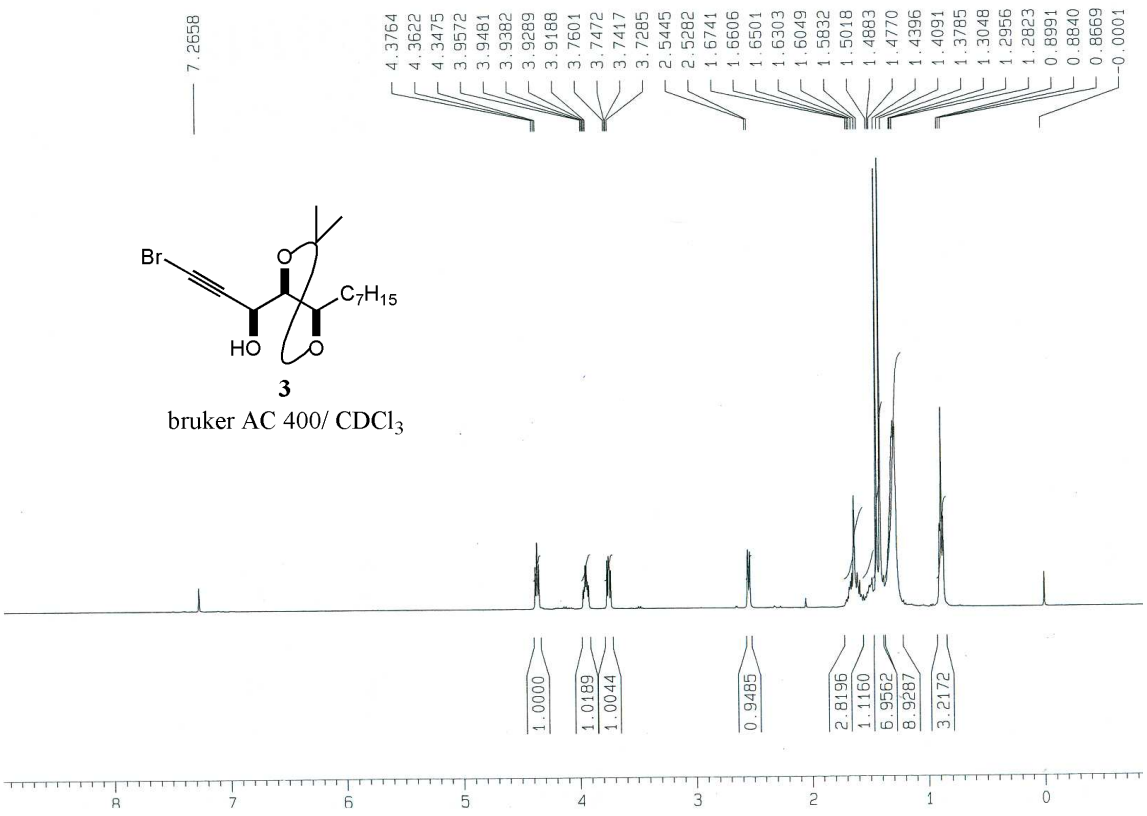






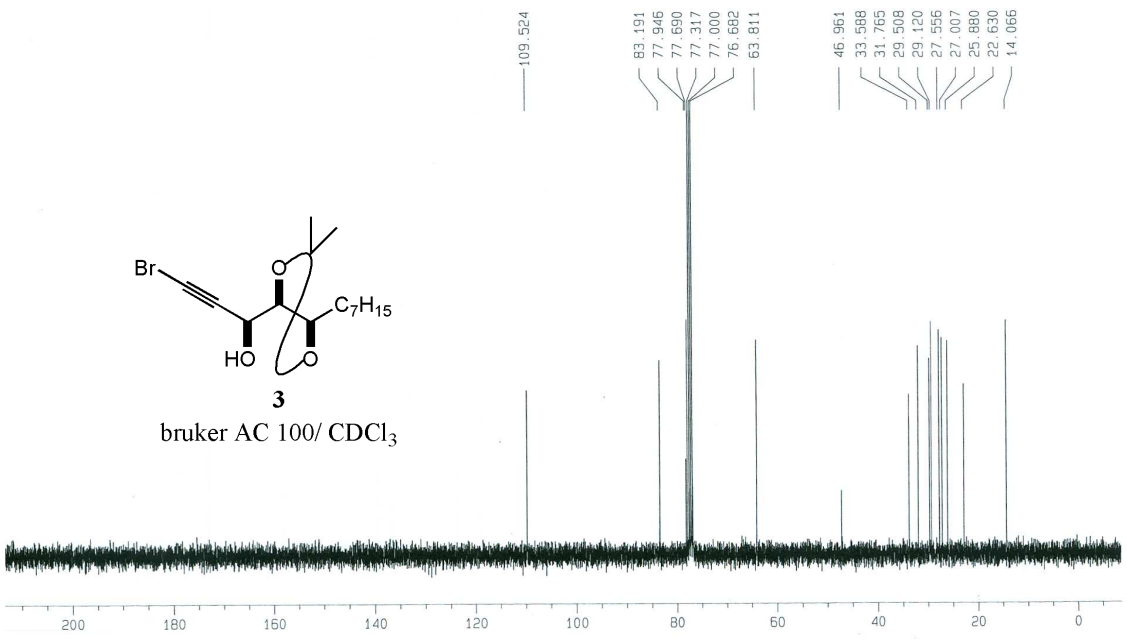
**11**

bruker AC 100/ $CDCl_3$



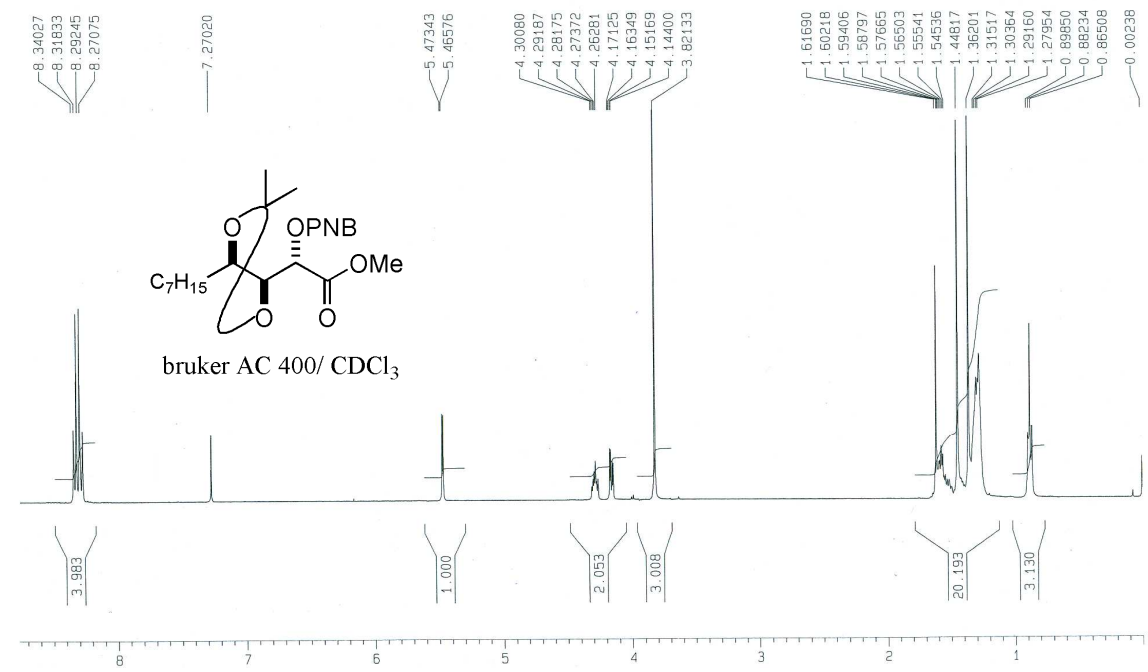

**3**

bruker AC 400/ $CDCl_3$

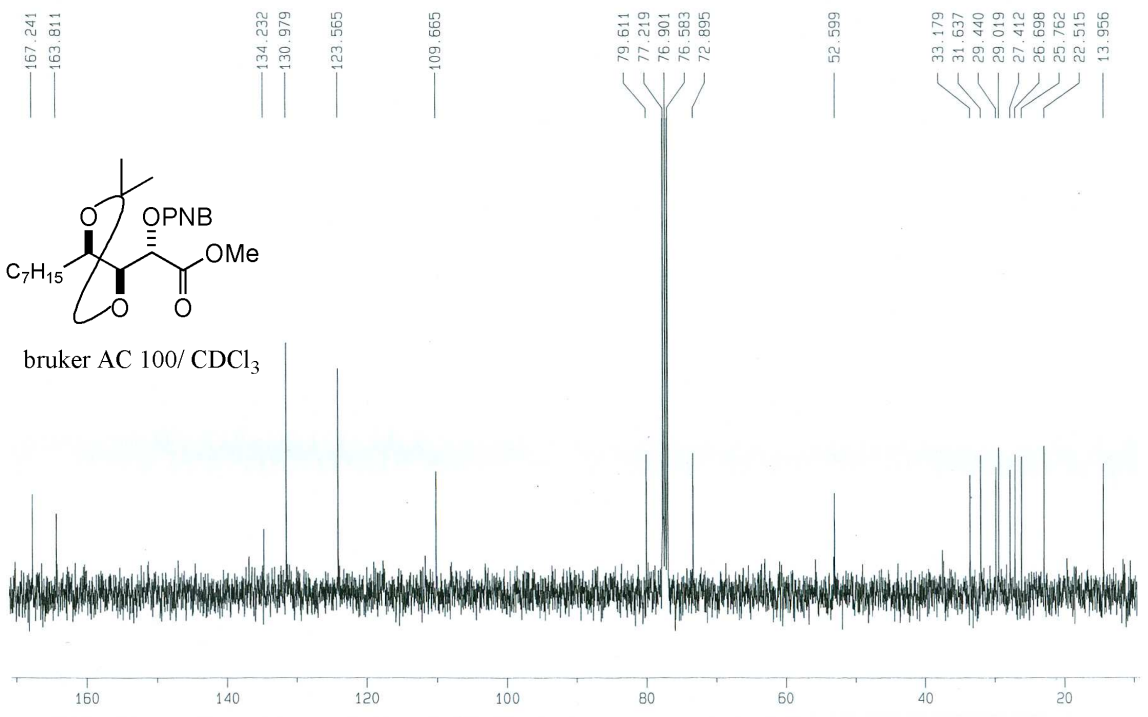



**3**

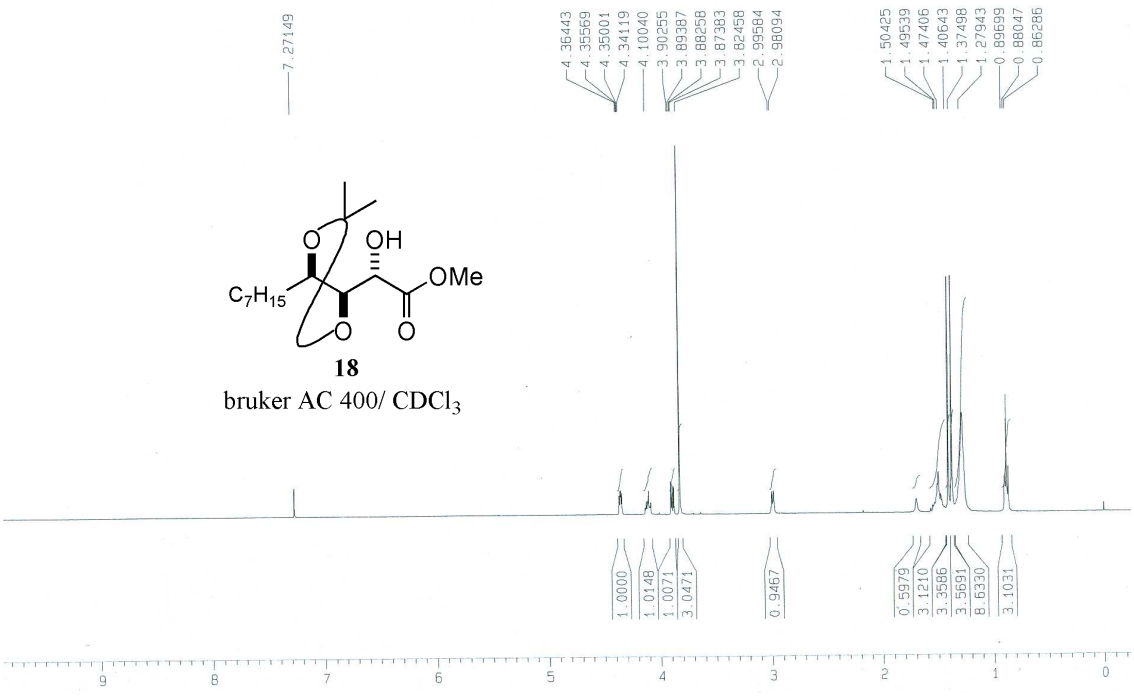
bruker AC 100/ $CDCl_3$




bruker AC 400/ $CDCl_3$

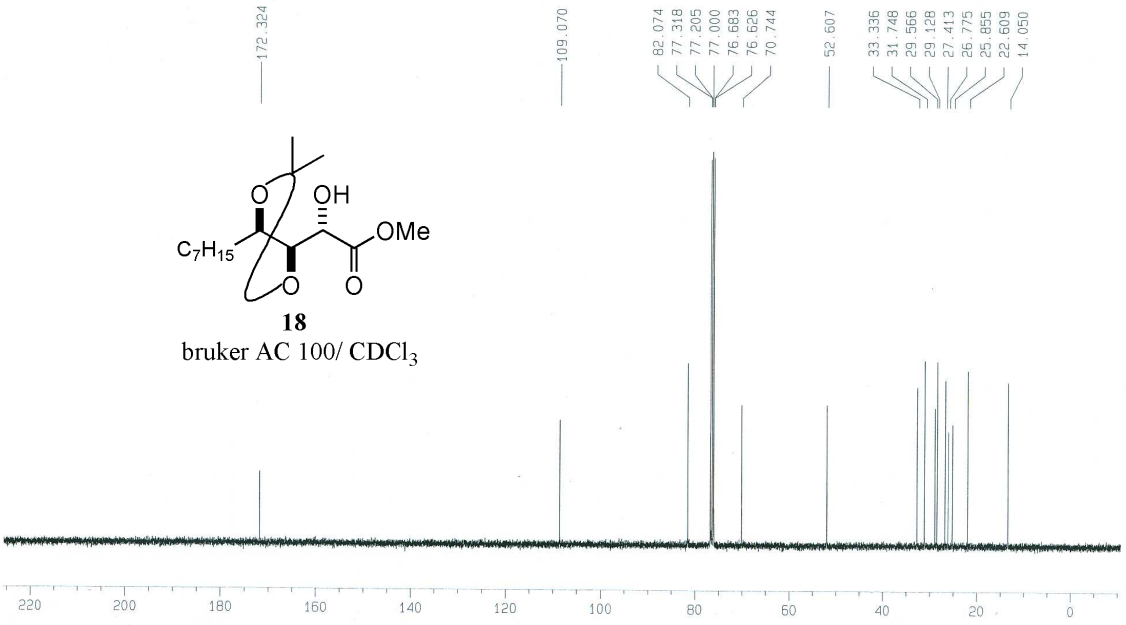



bruker AC 100/ $CDCl_3$



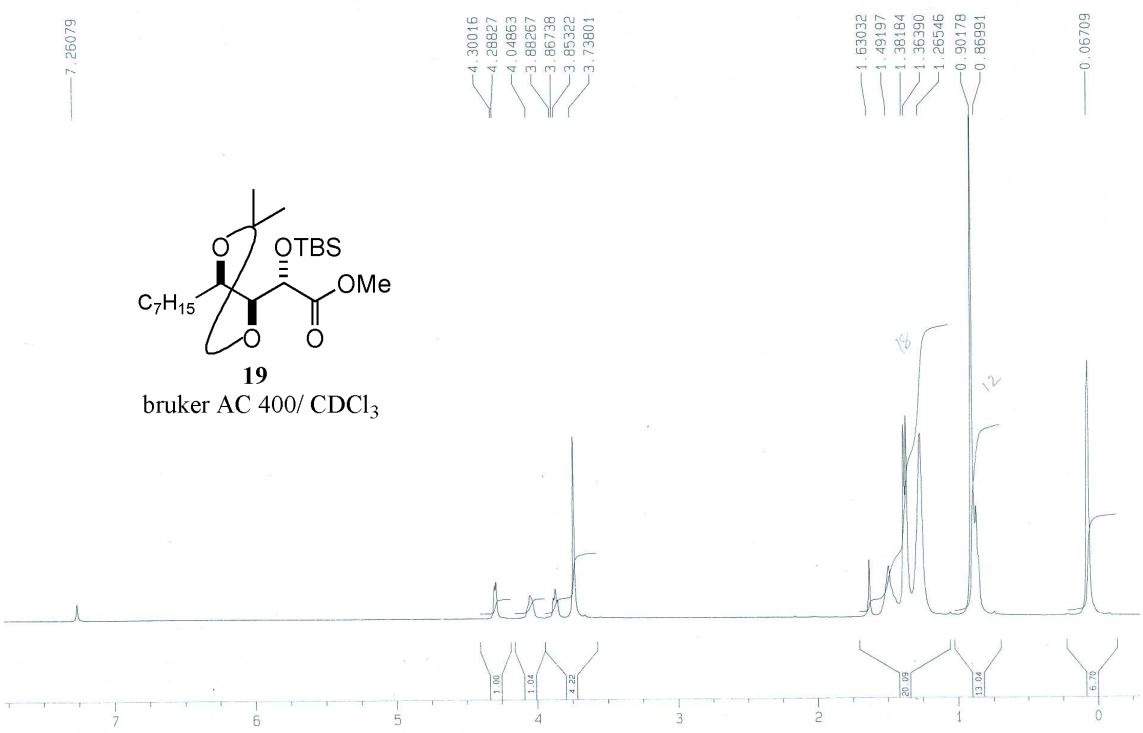

**18**

bruker AC 400/ $CDCl_3$



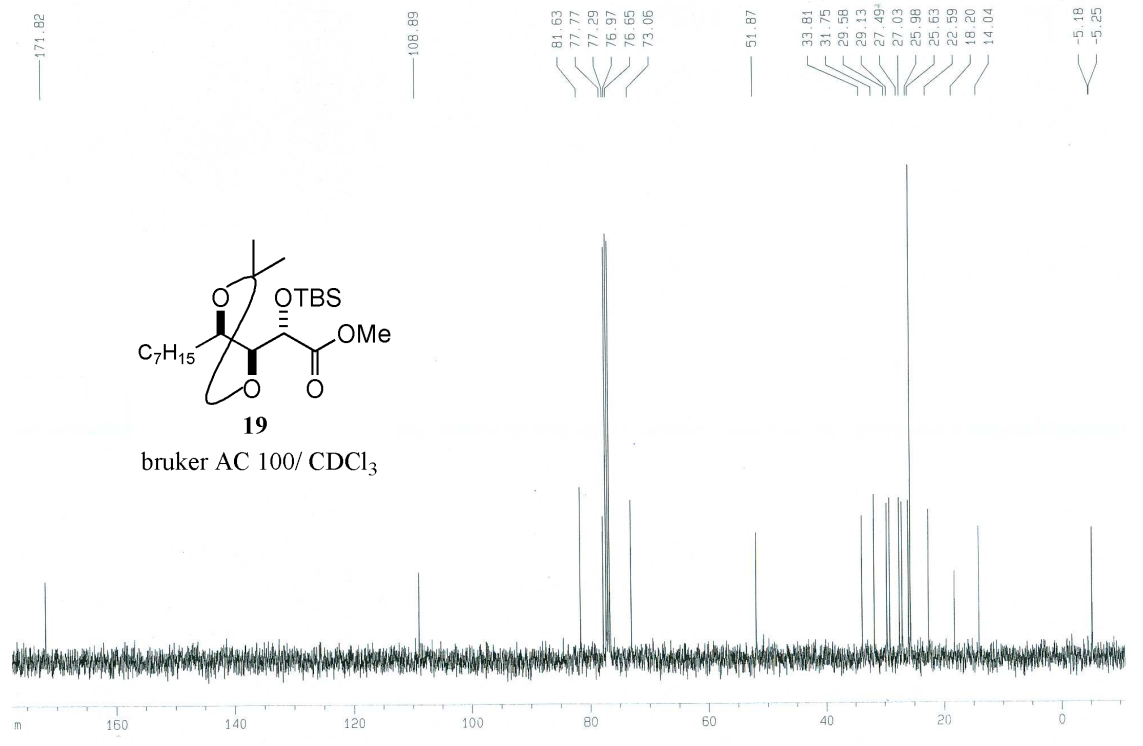

**18**

bruker AC 100/ $CDCl_3$



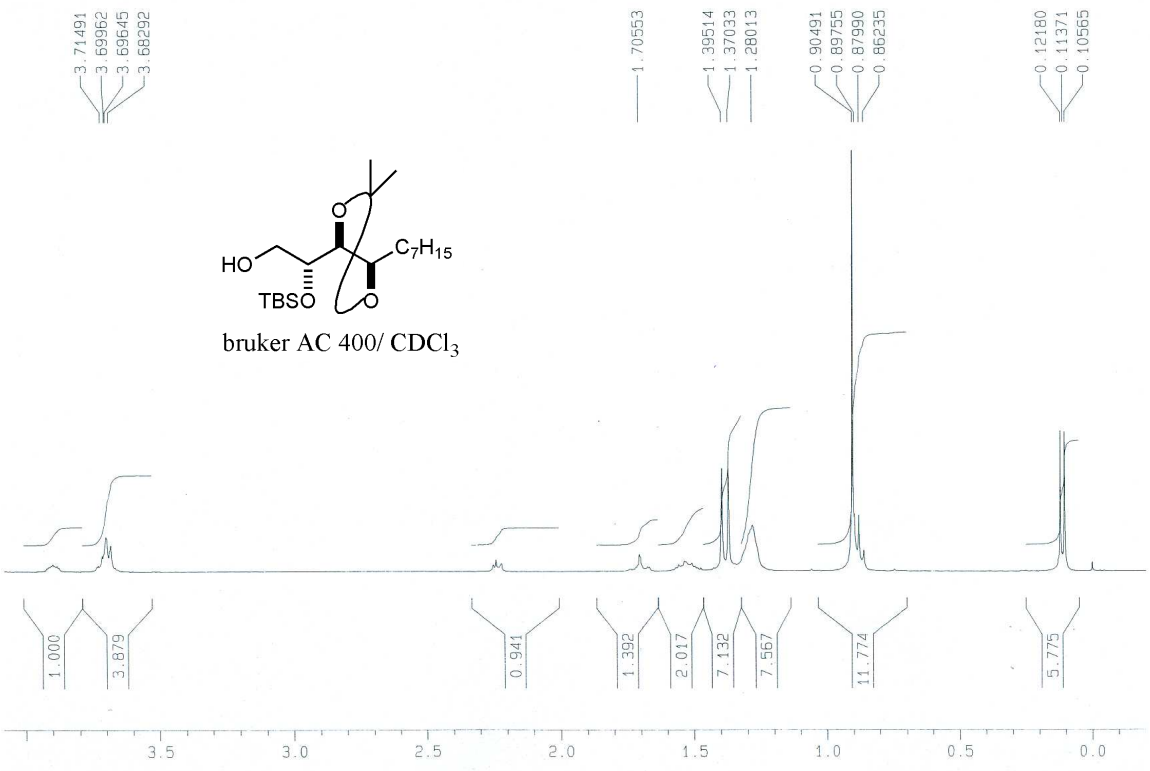

**19**

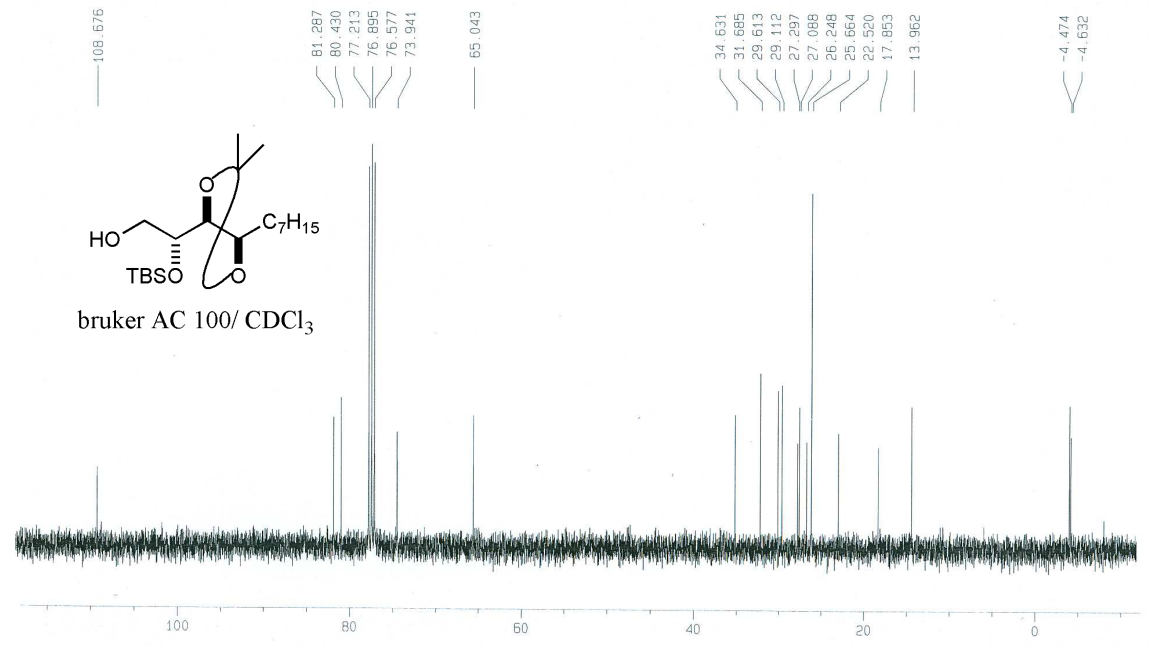
bruker AC 400/ $CDCl_3$

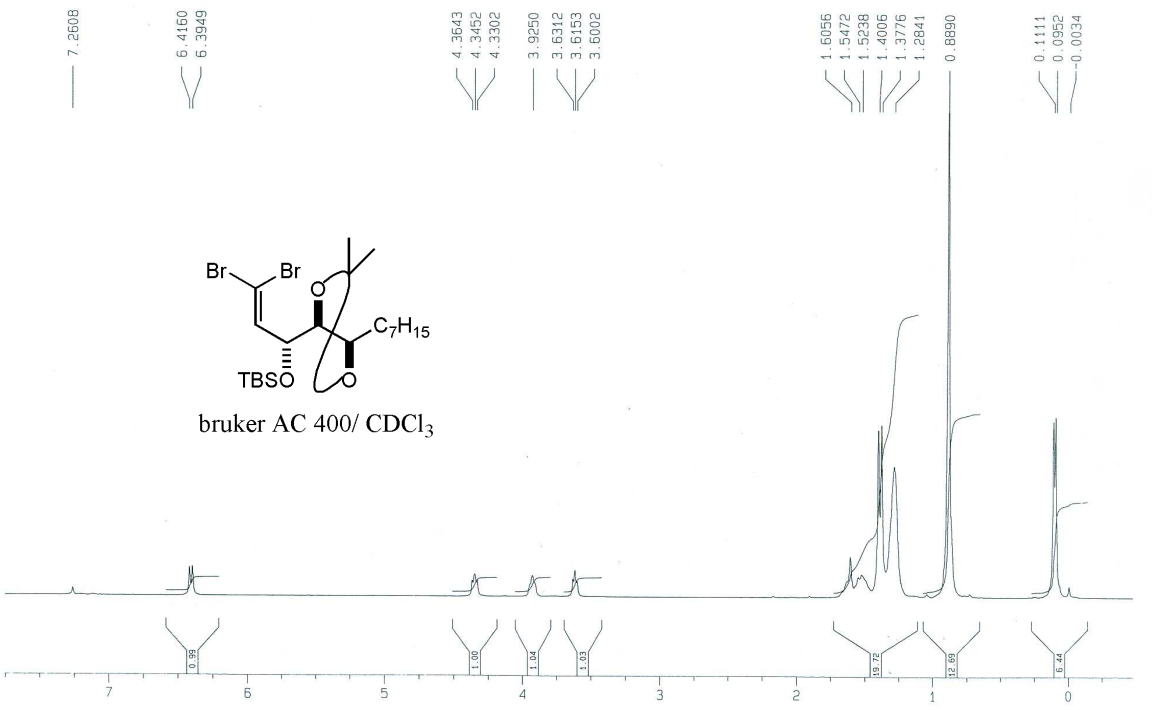



**19**

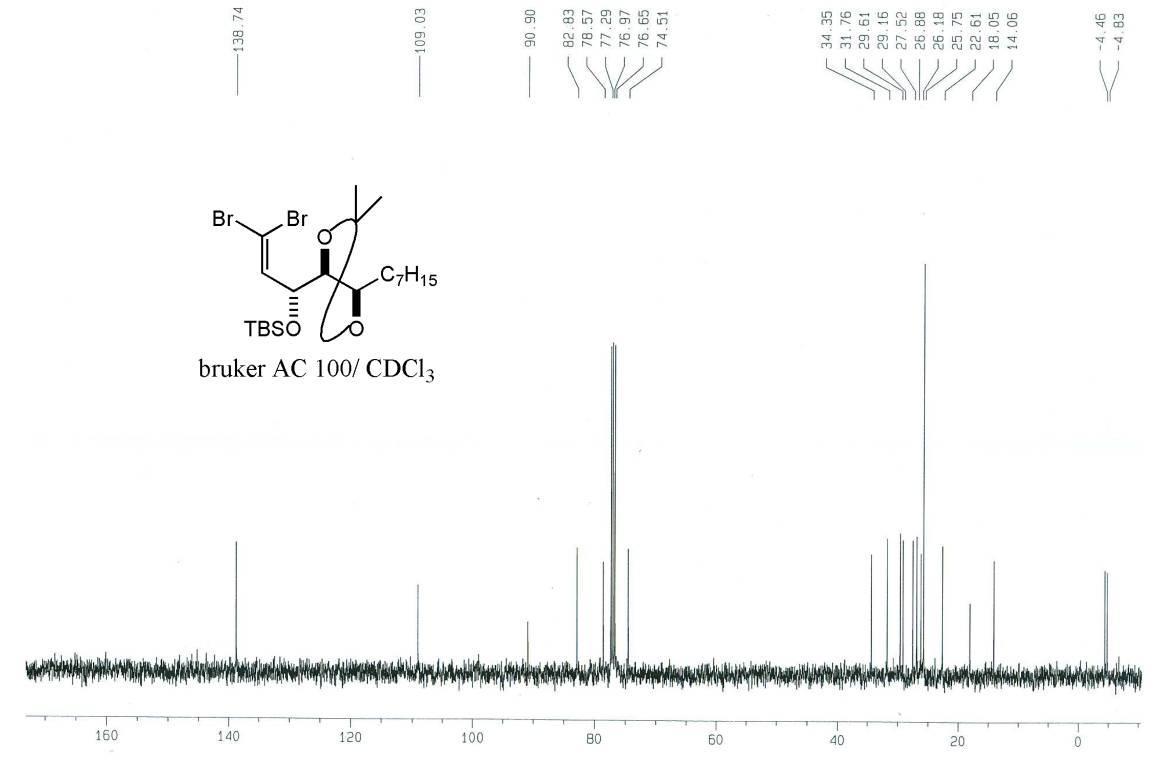
bruker AC 100/ $CDCl_3$


3.71491
3.69962
3.69645
3.68292
1.70553
1.39514
1.37033
1.28013
0.90491
0.89755
0.87990
0.86235
0.12180
0.11371
0.10565
HO
TBSO
C7H15
O
O
bruker AC 400/ CDCl3
1.000
3.879
0.941
1.392
2.017
7.132
7.567
11.774
5.775
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

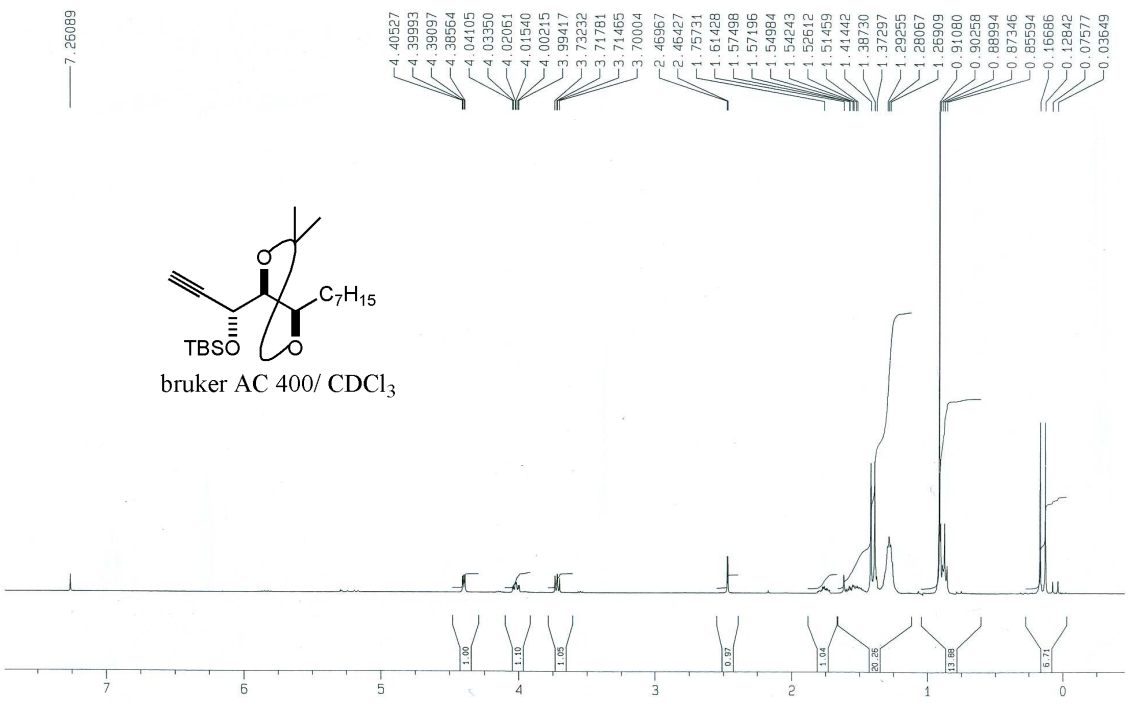

108.676
81.287
80.430
77.213
76.895
76.577
73.941
65.043
34.631
31.685
29.613
29.112
27.297
27.088
26.248
25.664
22.520
17.853
13.962
-4.474
-4.632
HO
TBSO
C7H15
O
O
bruker AC 100/ CDCl3
100
80
60
40
20
0




bruker AC 400/ $CDCl_3$



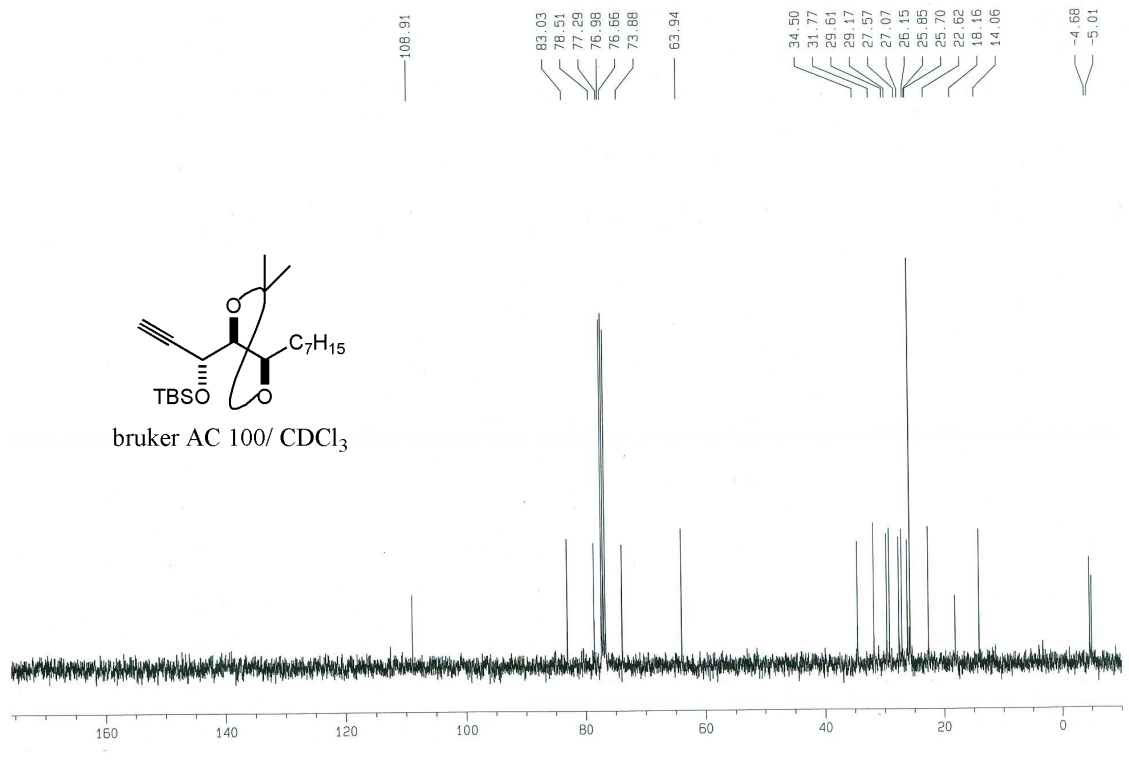

bruker AC 100/ $CDCl_3$







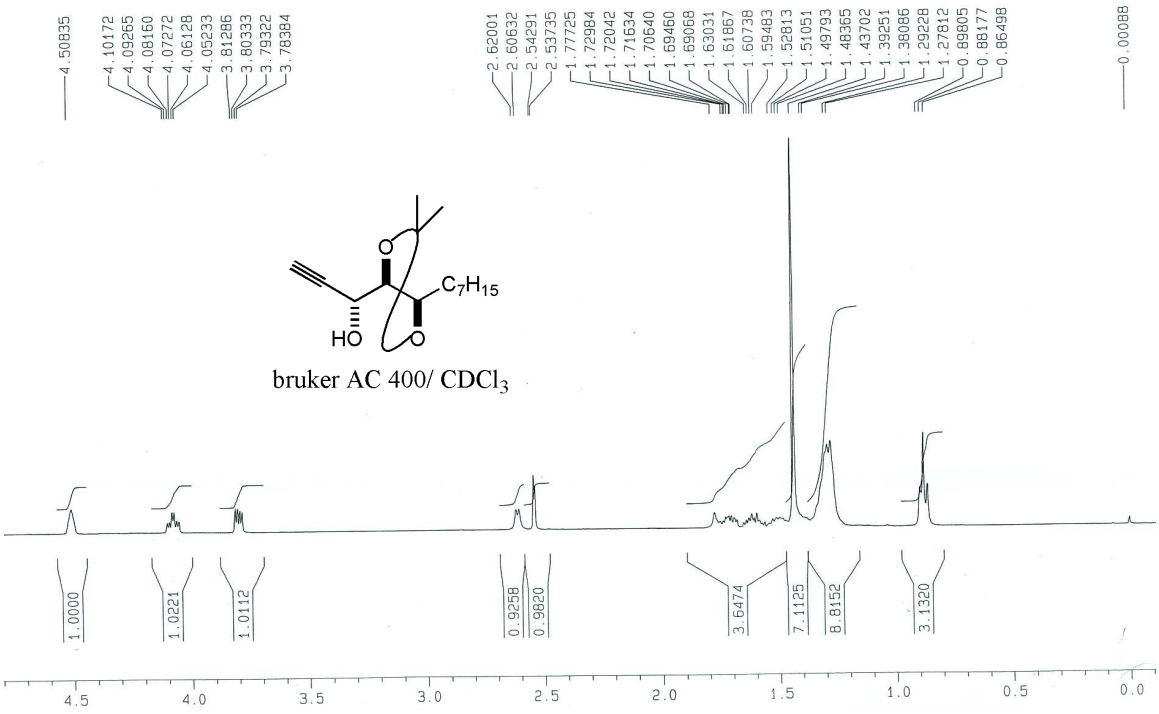
bruker AC 400/ $CDCl_3$







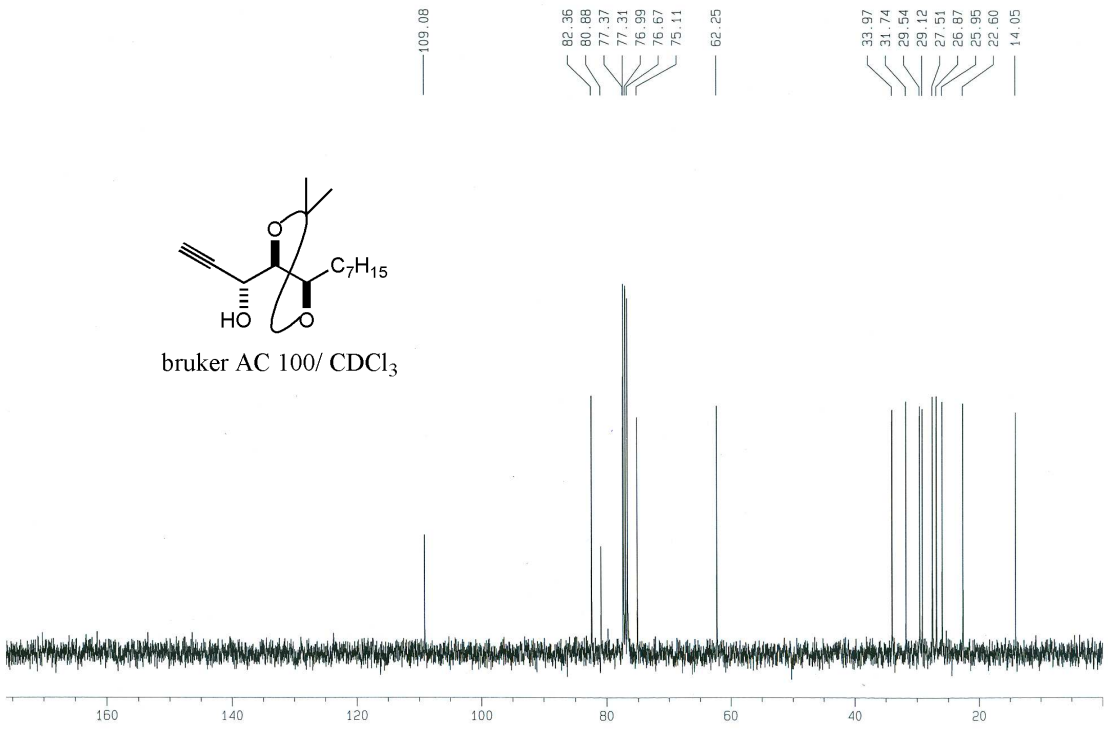
bruker AC 100/ $CDCl_3$







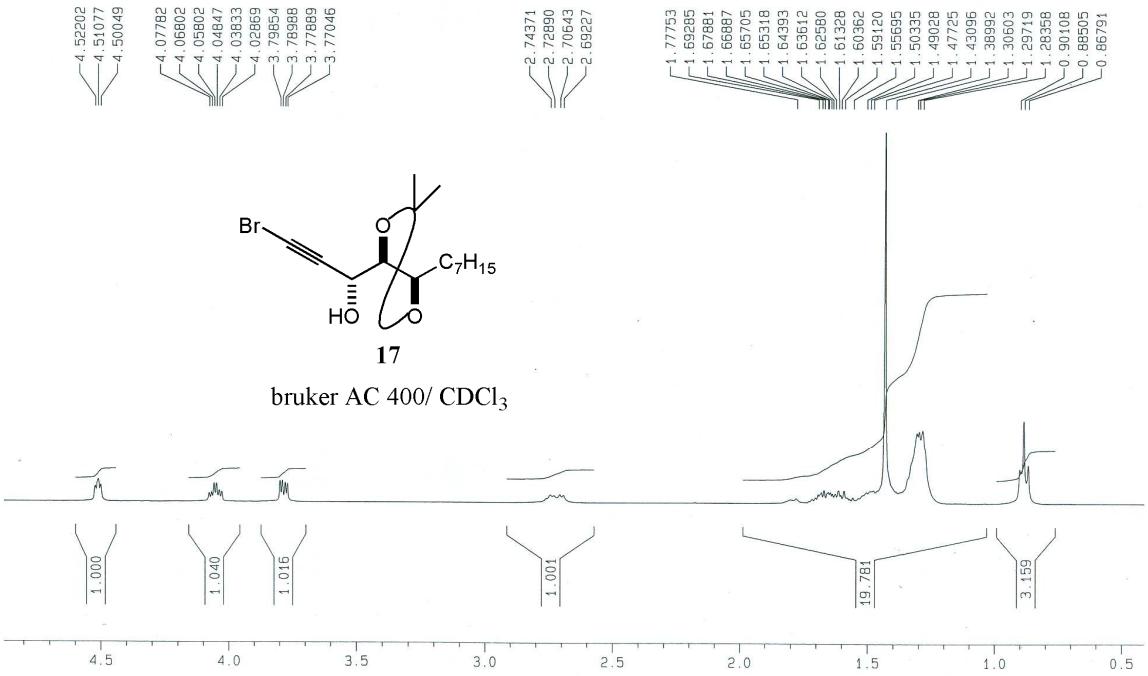
bruker AC 400/ $CDCl_3$





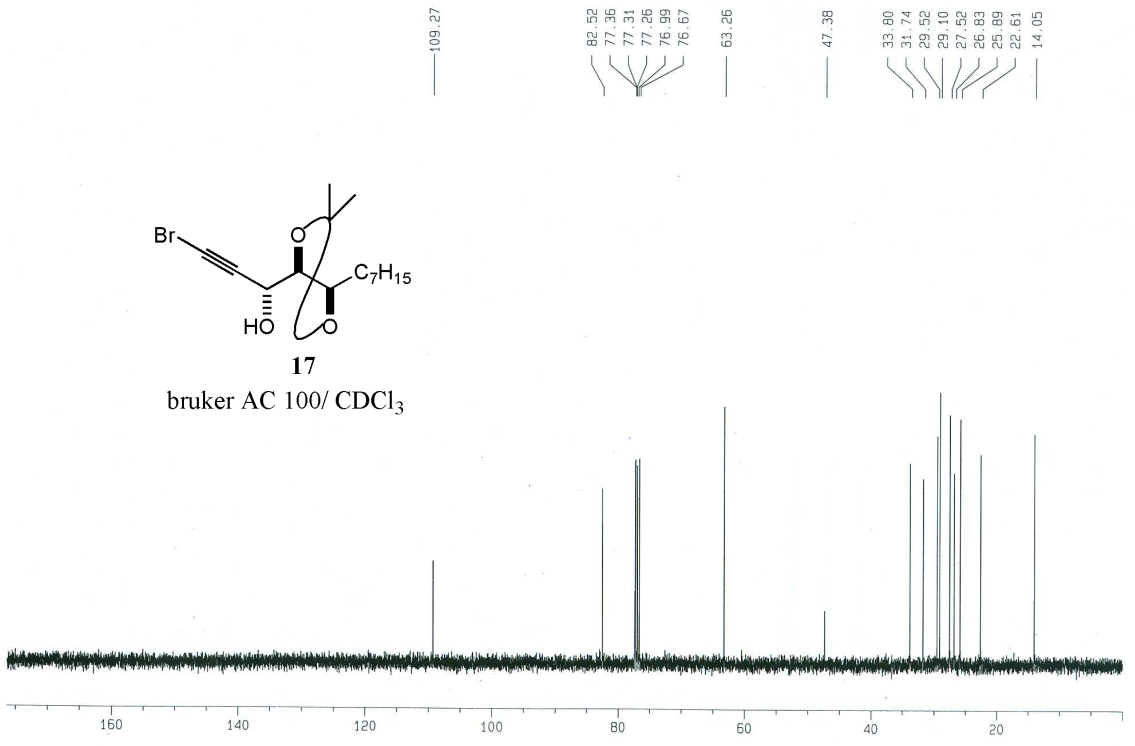


bruker AC 100/ $CDCl_3$



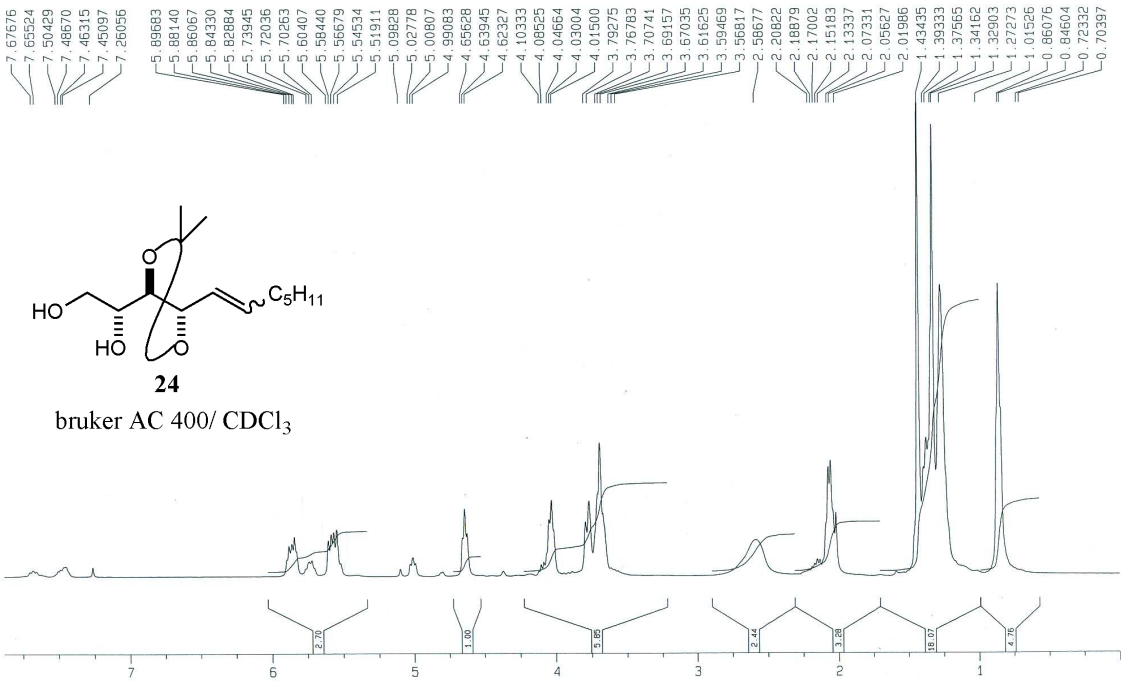

**17**

bruker AC 400/ $CDCl_3$



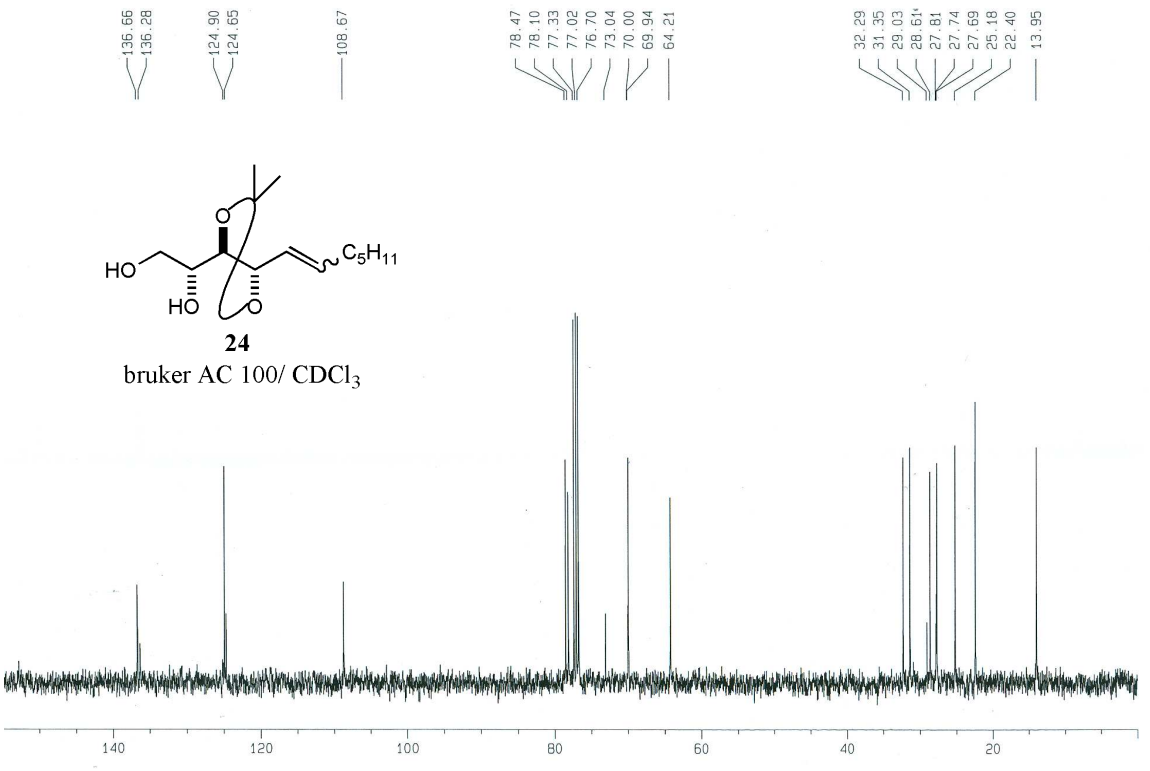

**17**

bruker AC 100/ $CDCl_3$



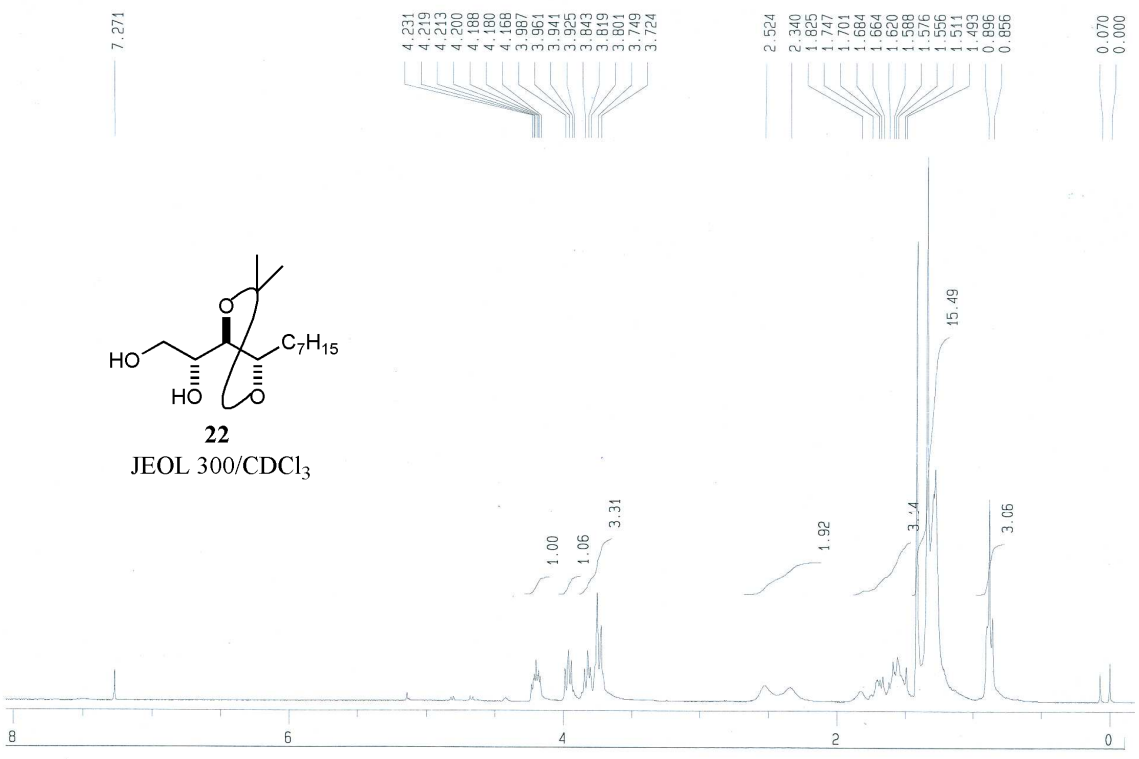

**24**

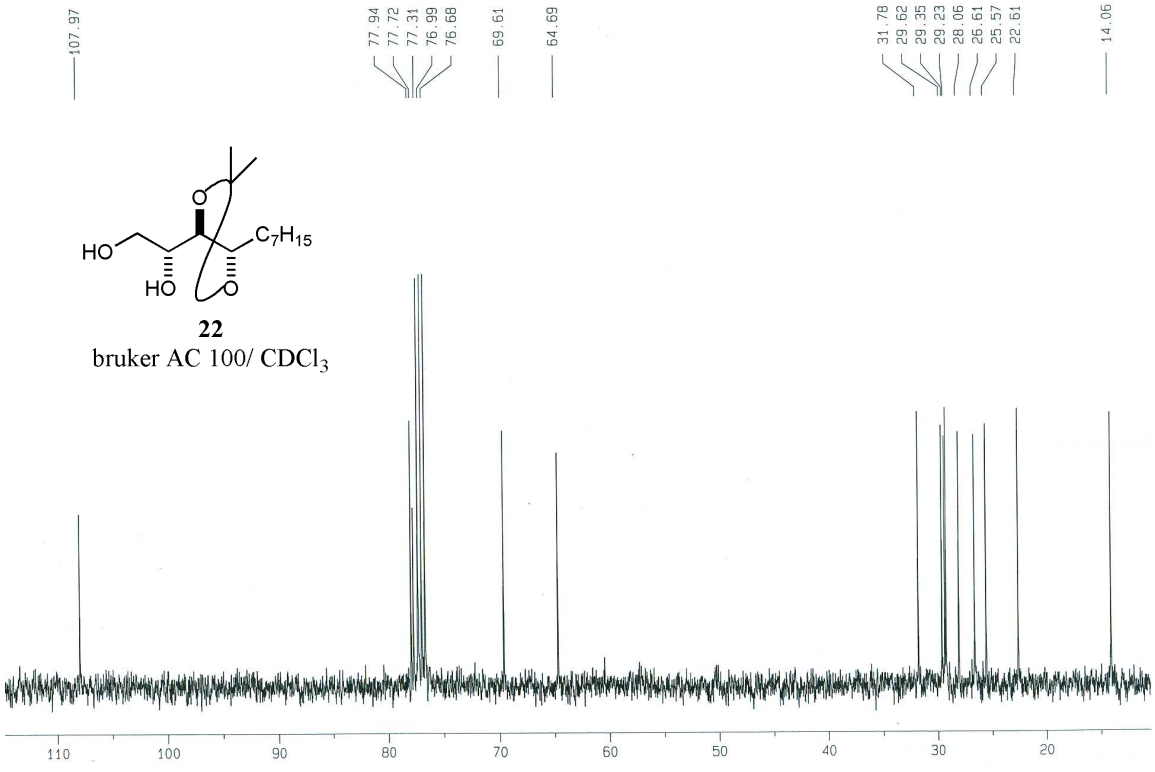
bruker AC 400/ $CDCl_3$

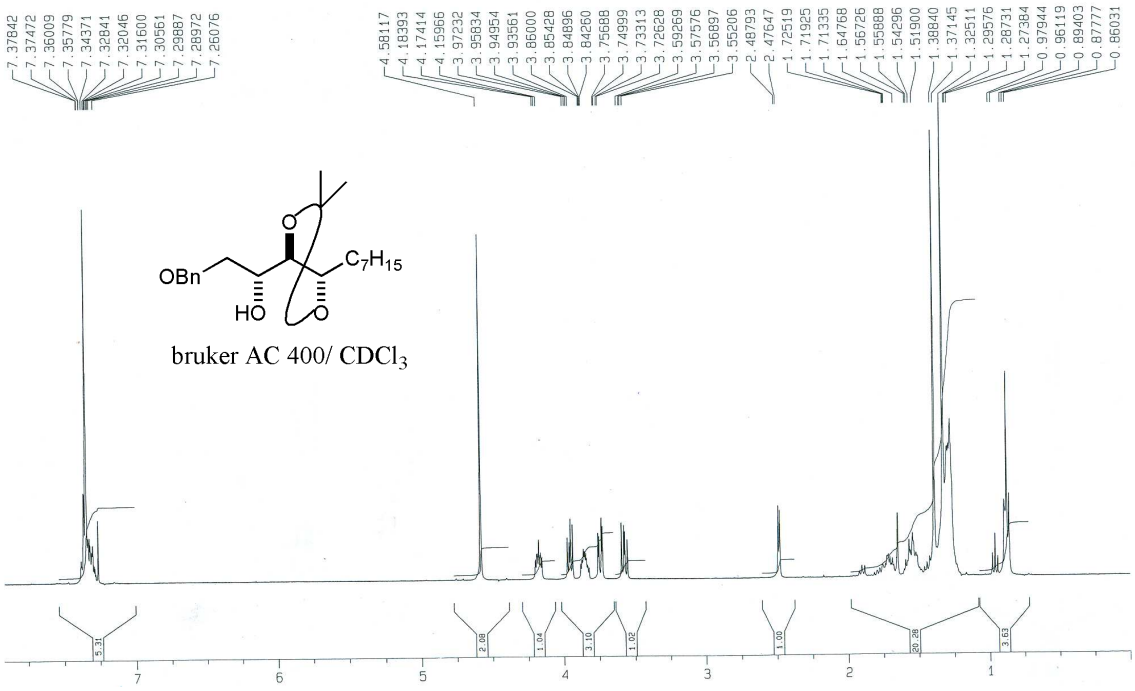


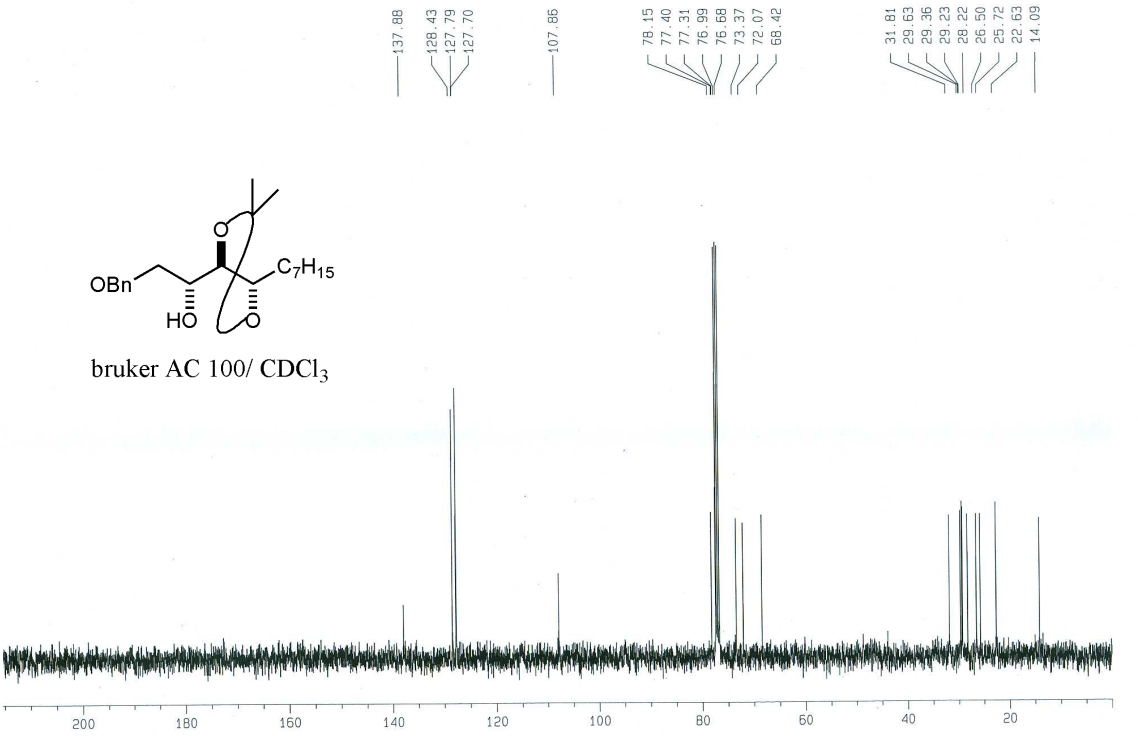

**24**

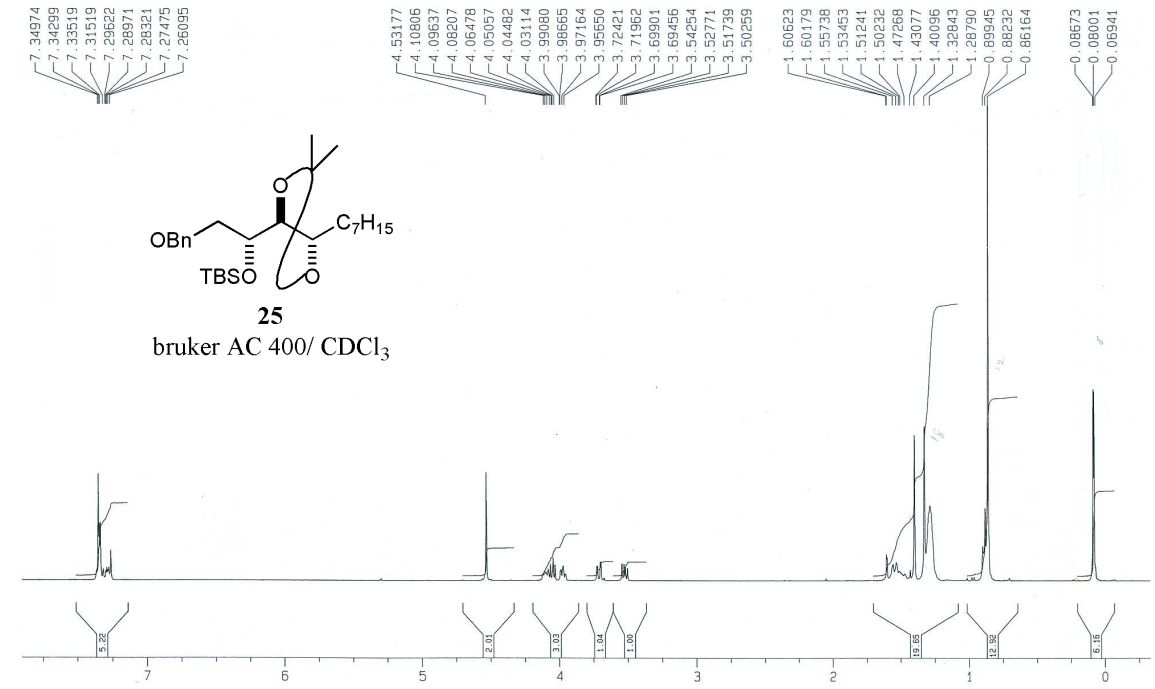
bruker AC 100/ $CDCl_3$


7.271
4.231
4.219
4.213
4.200
4.188
4.180
4.168
3.987
3.961
3.941
3.925
3.843
3.819
3.801
3.749
3.724
2.524
2.340
1.825
1.747
1.701
1.684
1.664
1.620
1.588
1.576
1.556
1.511
1.493
0.896
0.856
0.070
0.000
HO
HO
C7H15
22
JEOL 300/CDCl3
1.00
1.06
3.31
1.92
3.44
15.49
3.06
8
6
4
2
0


107.97
77.94
77.72
77.31
76.99
76.68
69.61
64.69
31.78
29.62
29.35
29.23
28.06
26.61
25.57
22.61
14.06
HO
HO
C7H15
22
bruker AC 100/ CDCl3
110
100
90
80
70
60
50
40
30
20

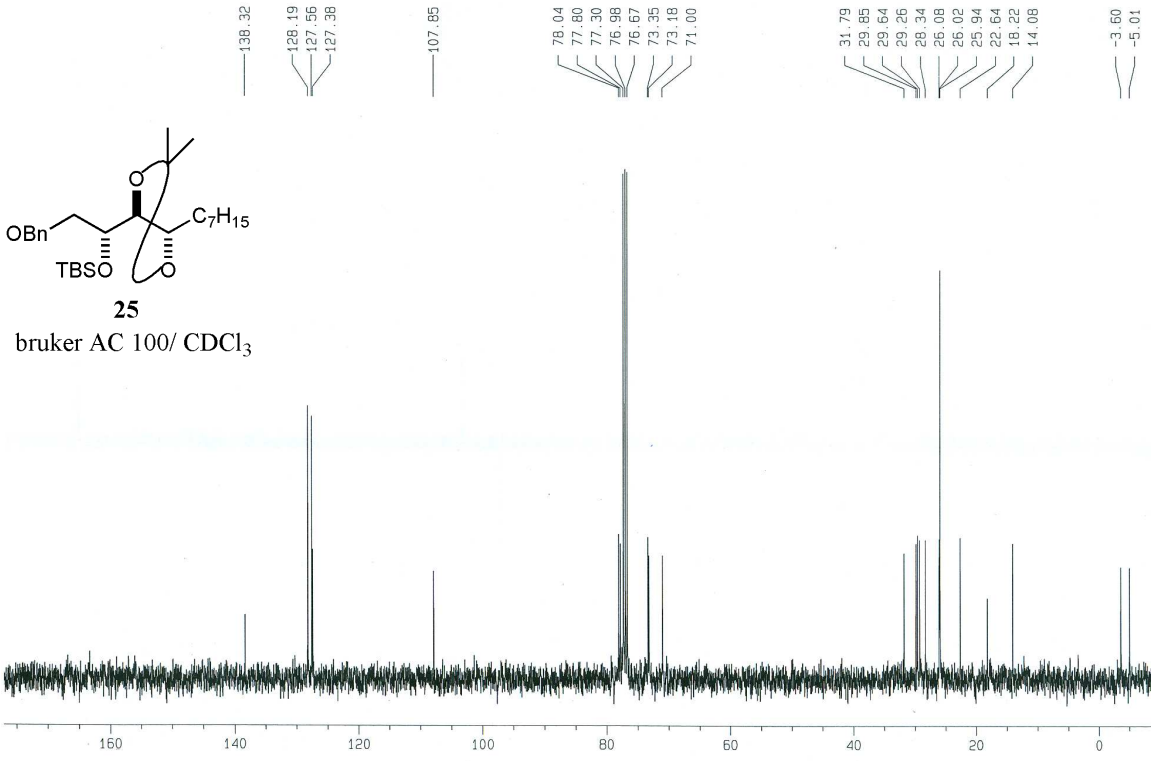

7.37842
7.37472
7.36009
7.35779
7.34371
7.32841
7.32046
7.31600
7.30561
7.29887
7.28972
7.26076
4.58117
4.18393
4.17414
4.15966
3.97232
3.95834
3.94954
3.93561
3.86000
3.85428
3.84896
3.84260
3.75688
3.74999
3.73313
3.72628
3.59269
3.57576
3.56897
3.55206
2.48793
2.47647
1.72519
1.71925
1.71335
1.64768
1.56726
1.55888
1.54296
1.51900
1.38840
1.37145
1.32511
1.29576
1.28731
1.27384
0.97944
0.96119
0.89403
0.87777
0.86031
OBn
C7H15
HO
O
O
bruker AC 400/ CDCl3
5.31
2.08
1.04
3.10
1.02
1.00
20.28
3.63
7
6
5
4
3
2
1


137.88
128.43
127.79
127.70
107.86
78.15
77.40
77.31
76.99
76.68
73.37
72.07
68.42
31.81
29.63
29.36
29.23
28.22
26.50
25.72
22.63
14.09
OBn
C7H15
HO
O
O
bruker AC 100/ CDCl3
200
180
160
140
120
100
80
60
40
20



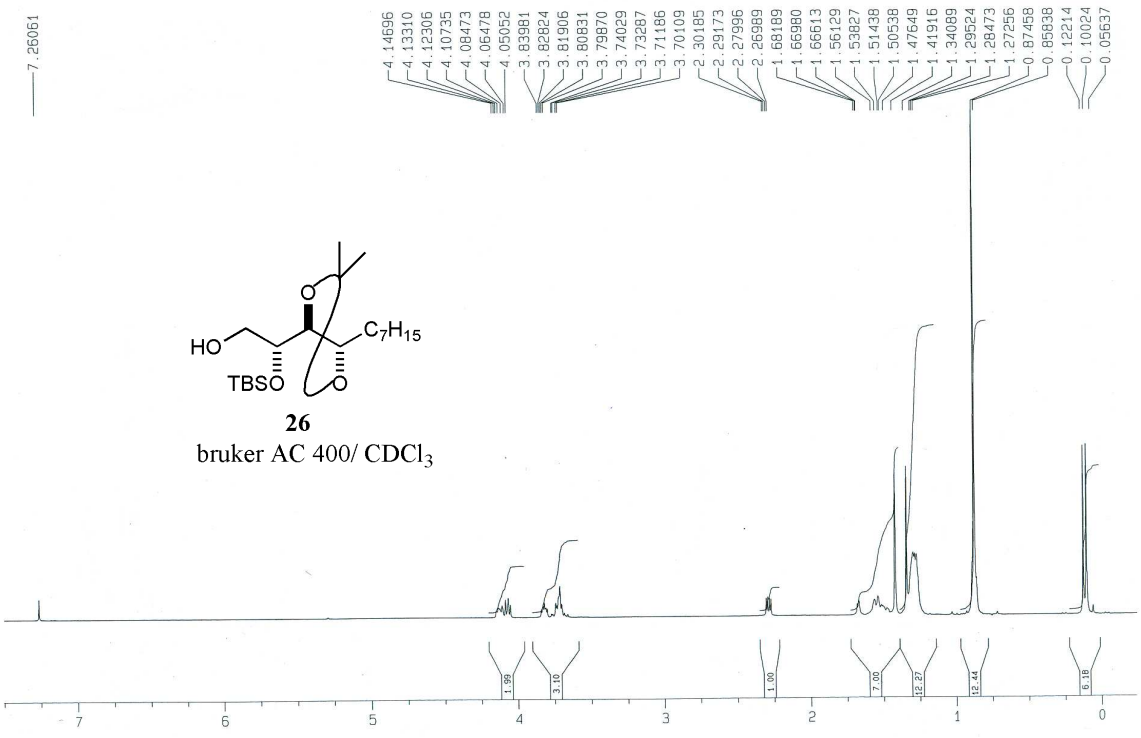

**25**

bruker AC 400/ $CDCl_3$



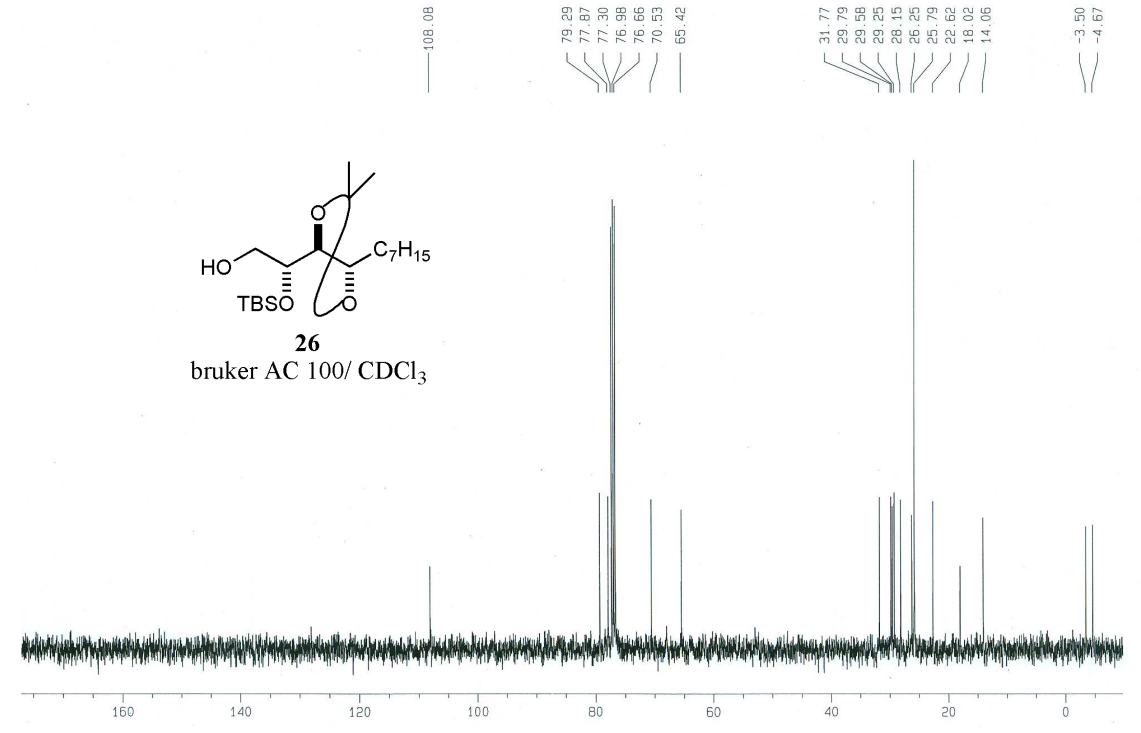

**25**

bruker AC 100/ $CDCl_3$



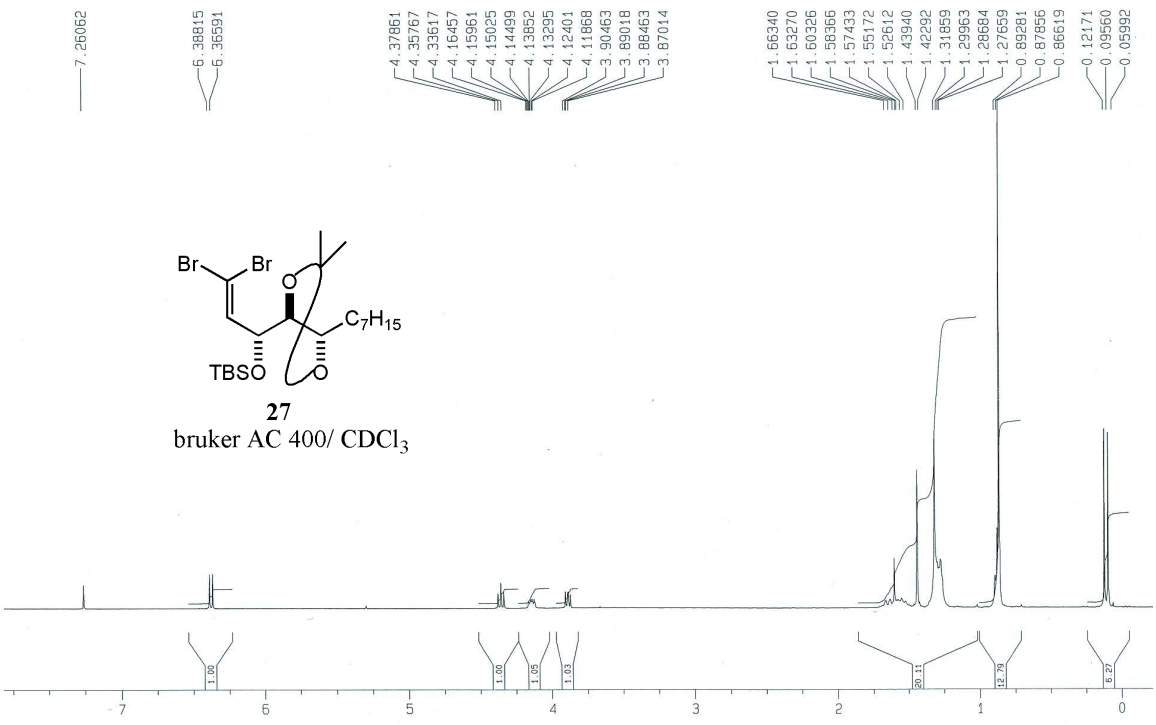

**26**

bruker AC 400/ $CDCl_3$

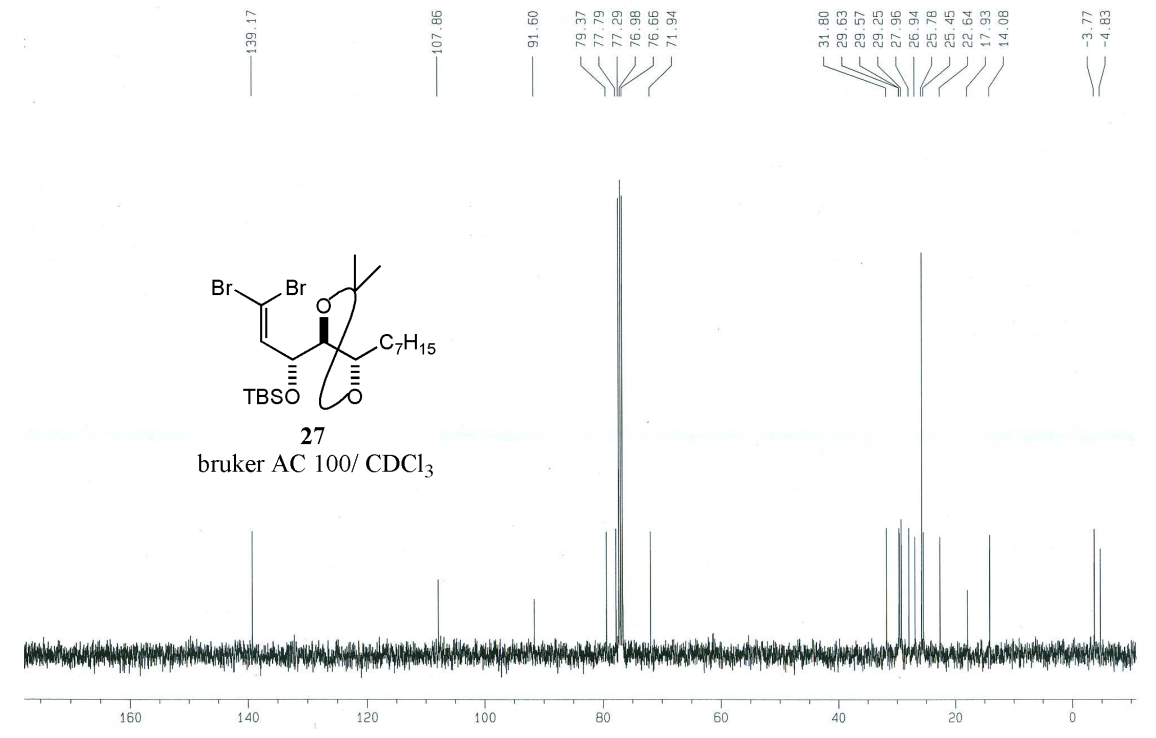



**26**

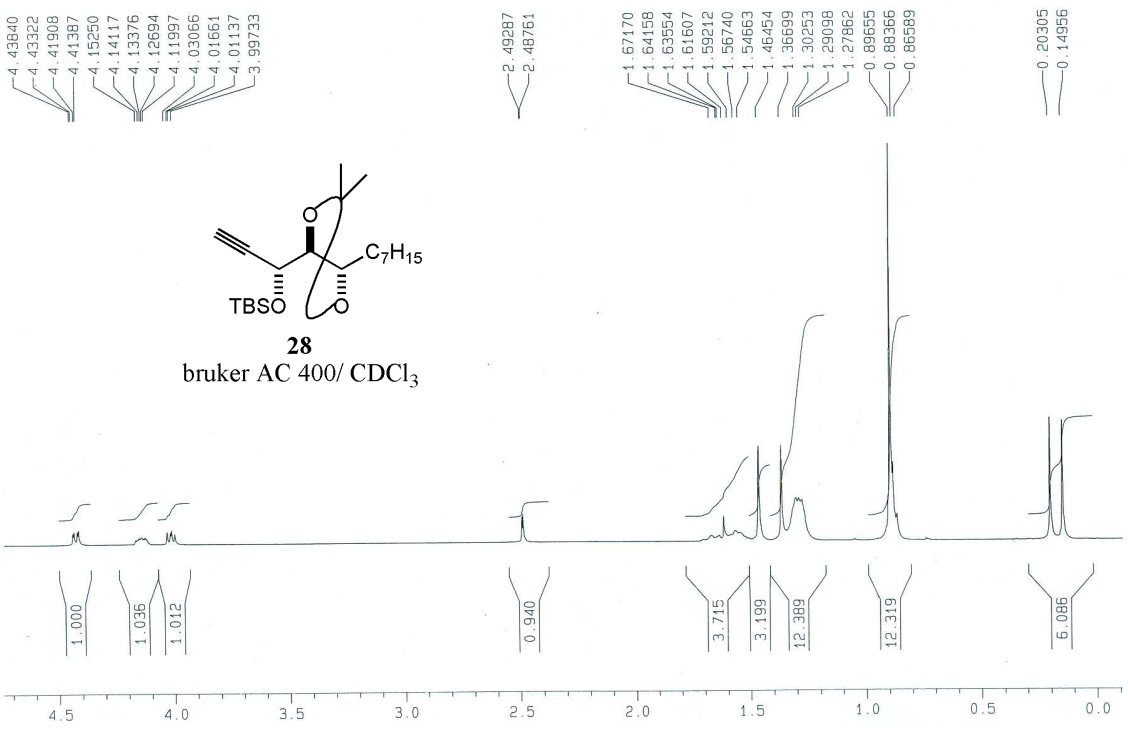
bruker AC 100/ $CDCl_3$




**27**
bruker AC 400/ $CDCl_3$

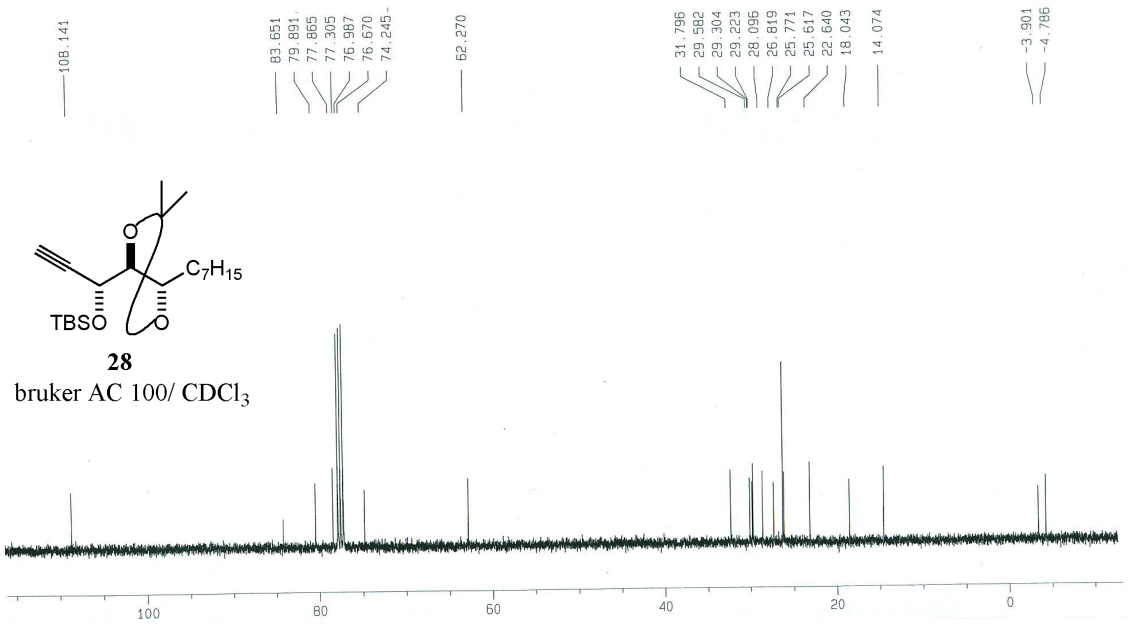



**27**
bruker AC 100/ $CDCl_3$



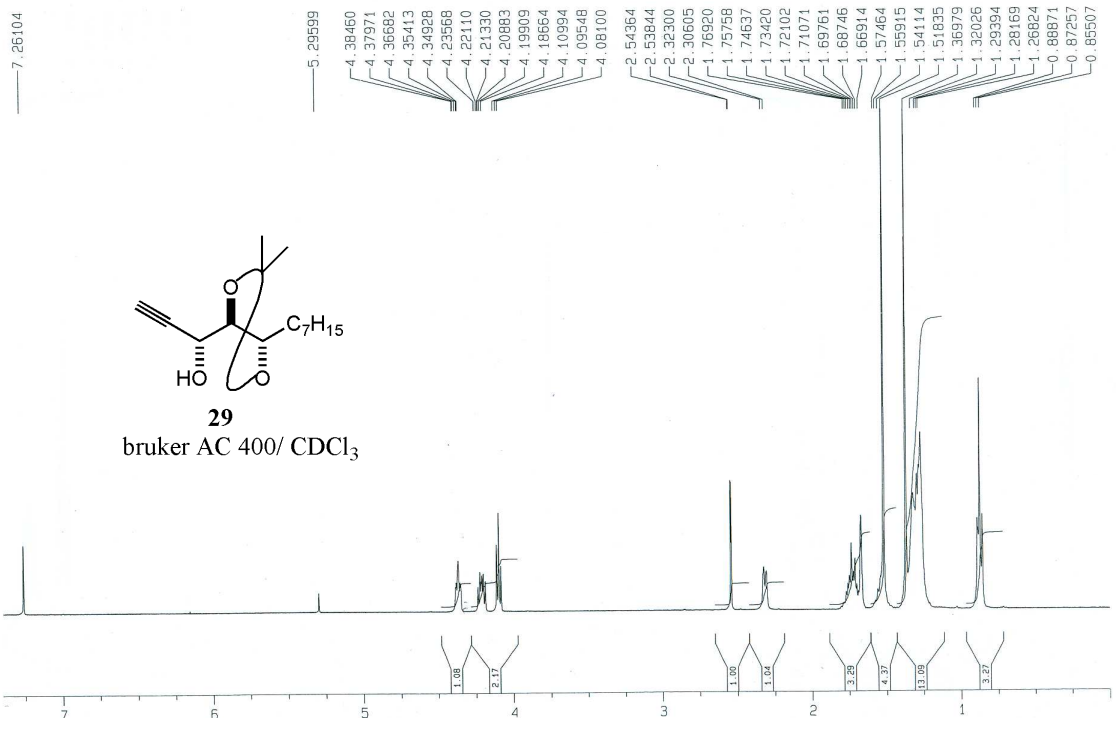

**28**

bruker AC 400/ $CDCl_3$




**28**

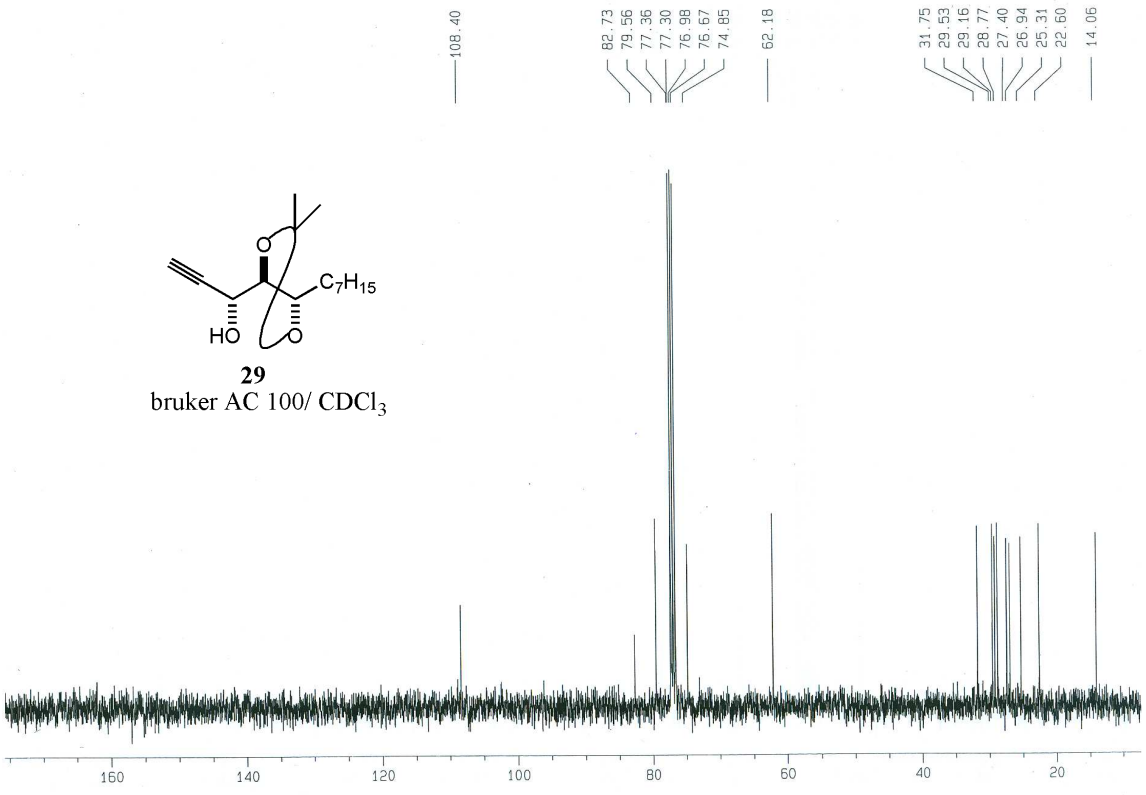
bruker AC 100/ $CDCl_3$







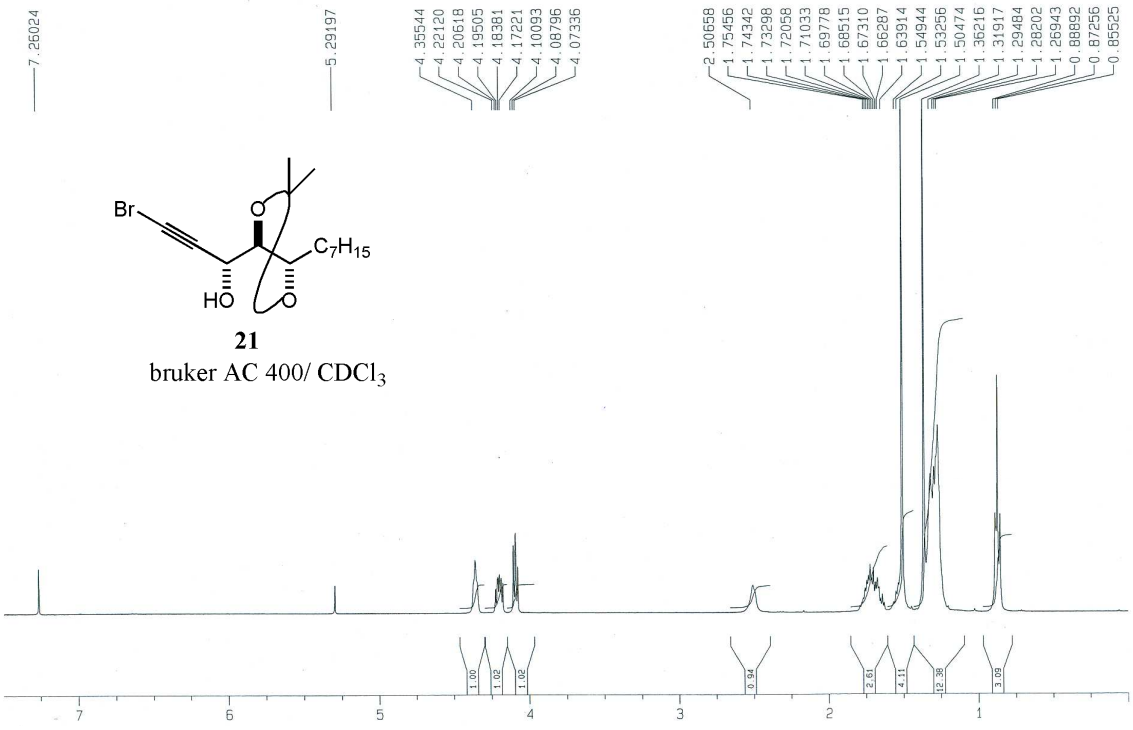
**29**
bruker AC 400/ $CDCl_3$





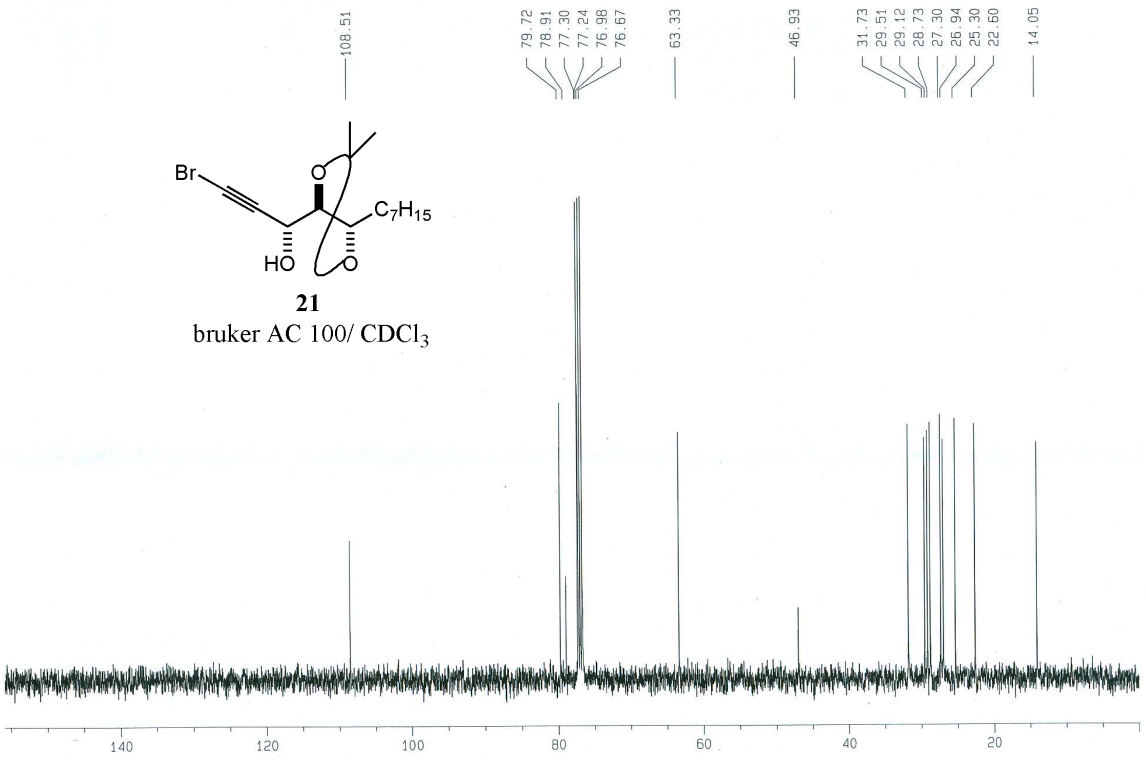


**29**
bruker AC 100/ $CDCl_3$



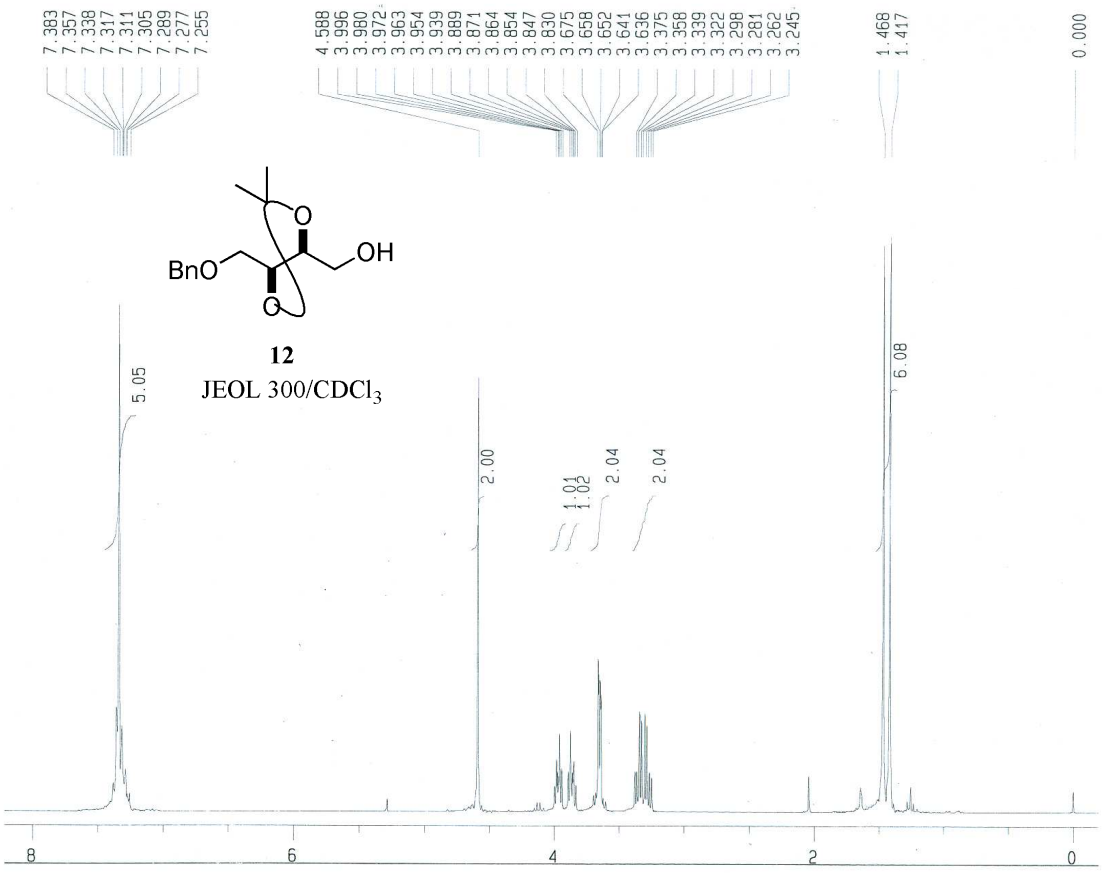

**21**

bruker AC 400/ $CDCl_3$



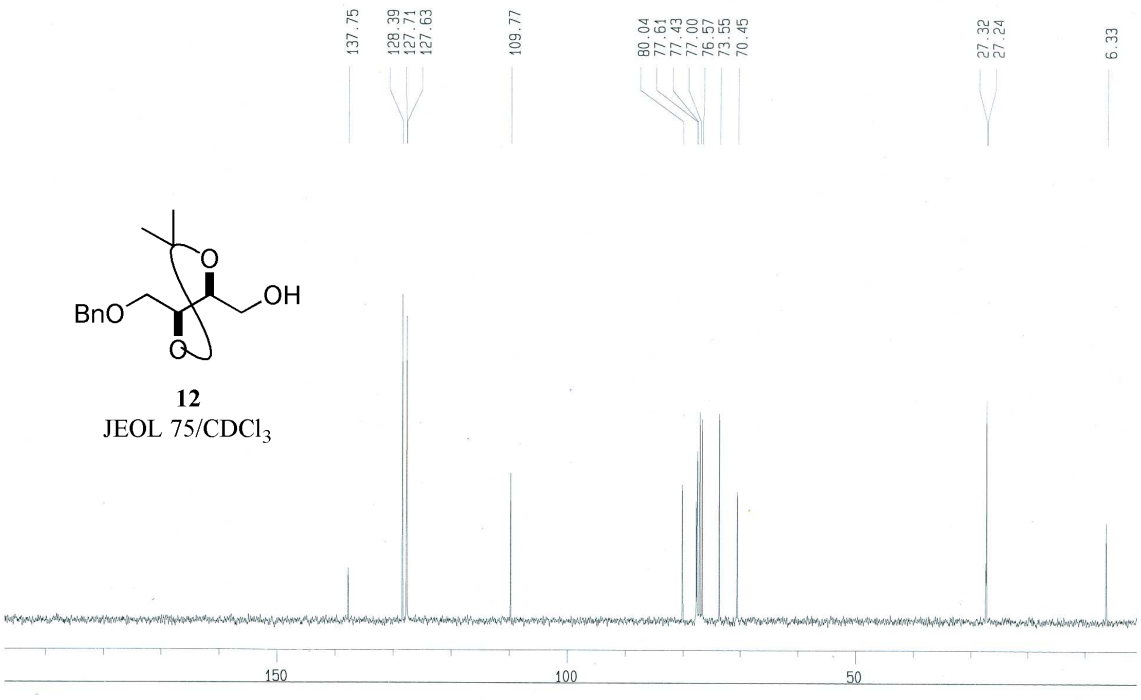

**21**

bruker AC 100/ $CDCl_3$



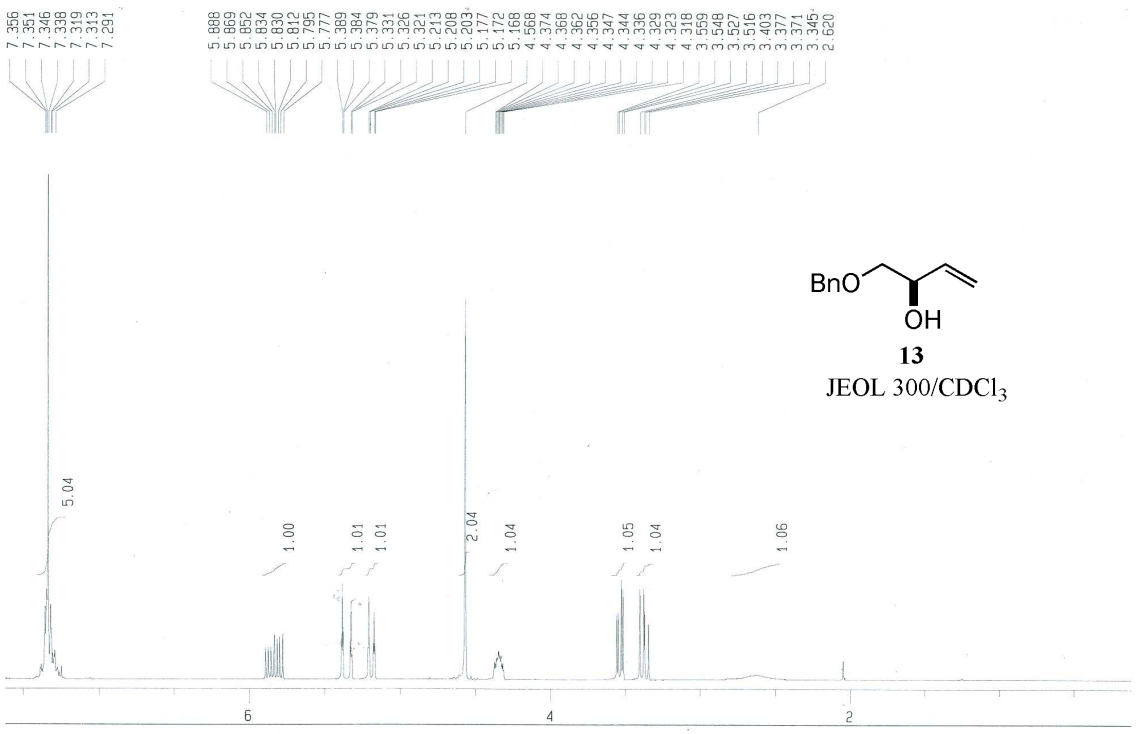

**12**

JEOL 300/$CDCl_3$




**12**

JEOL 75/$CDCl_3$

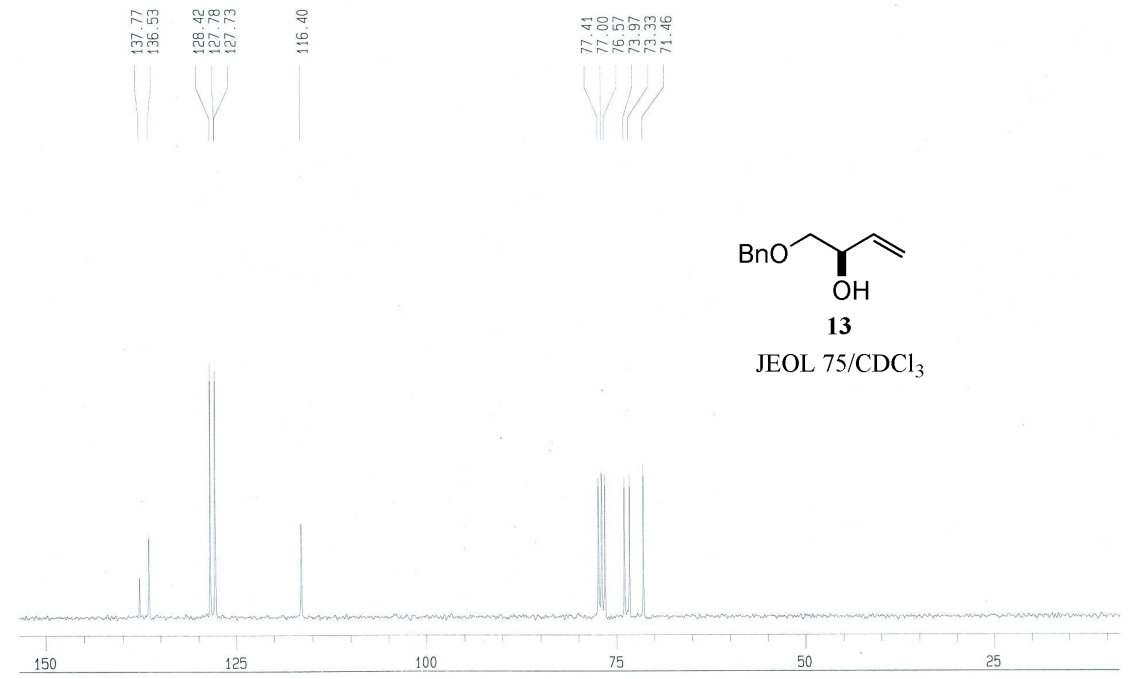






**13**

JEOL 300/$CDCl_3$

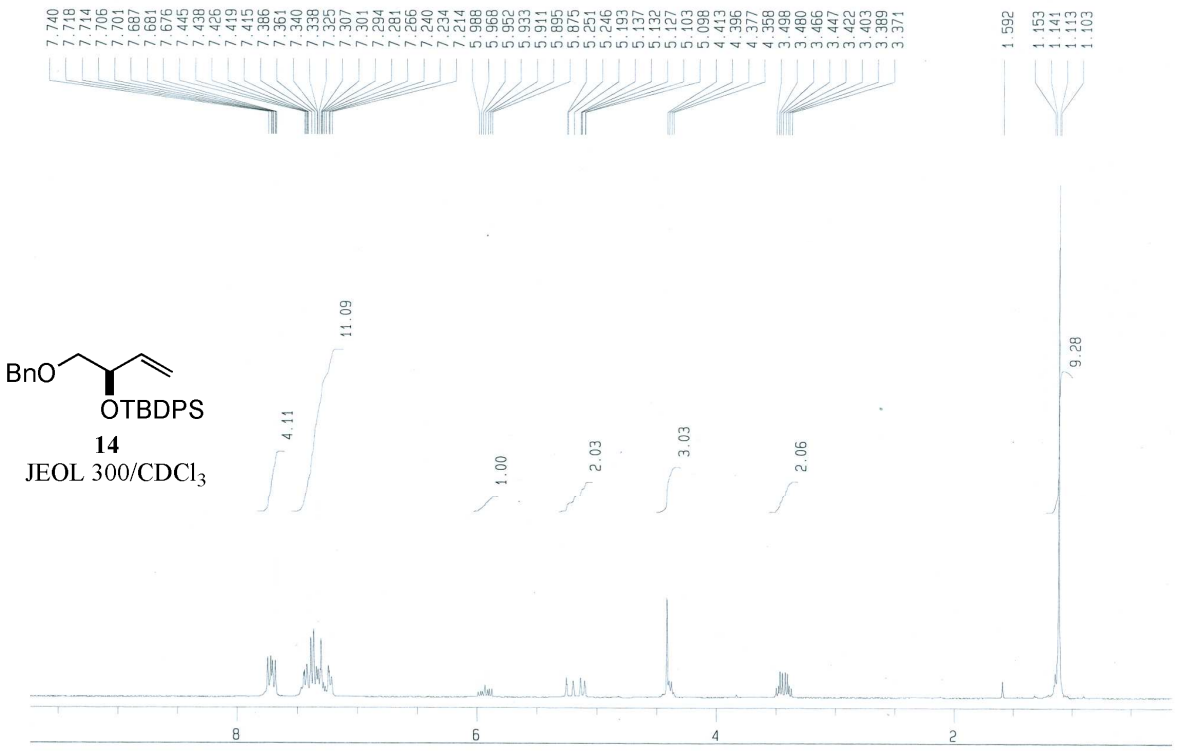


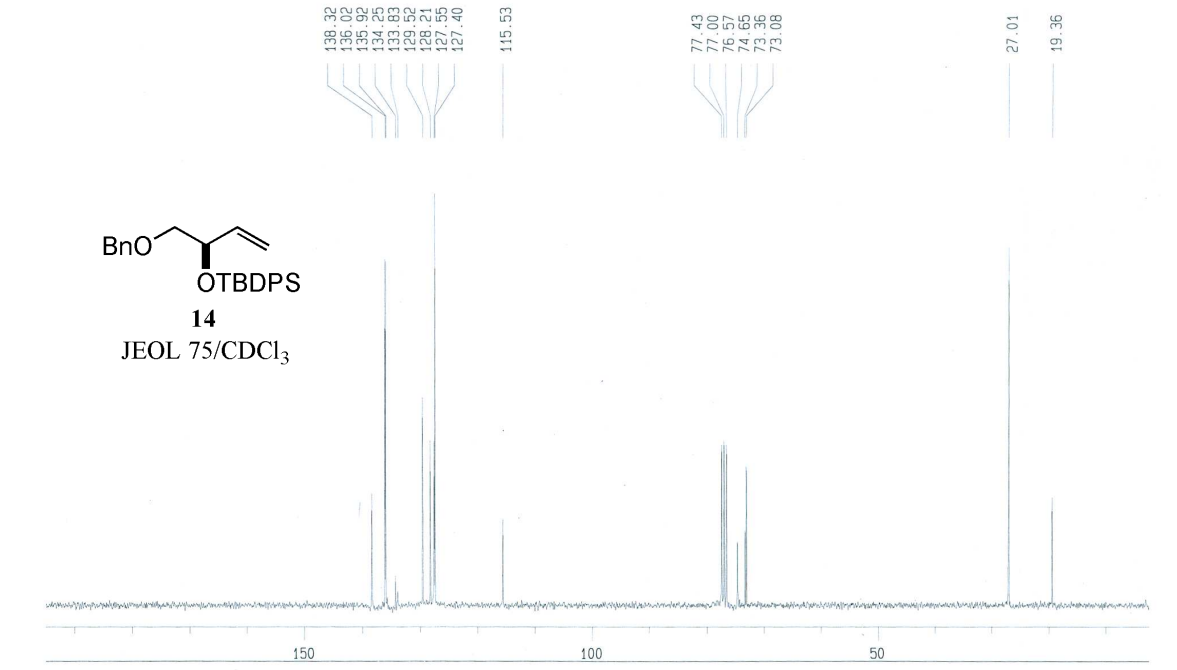


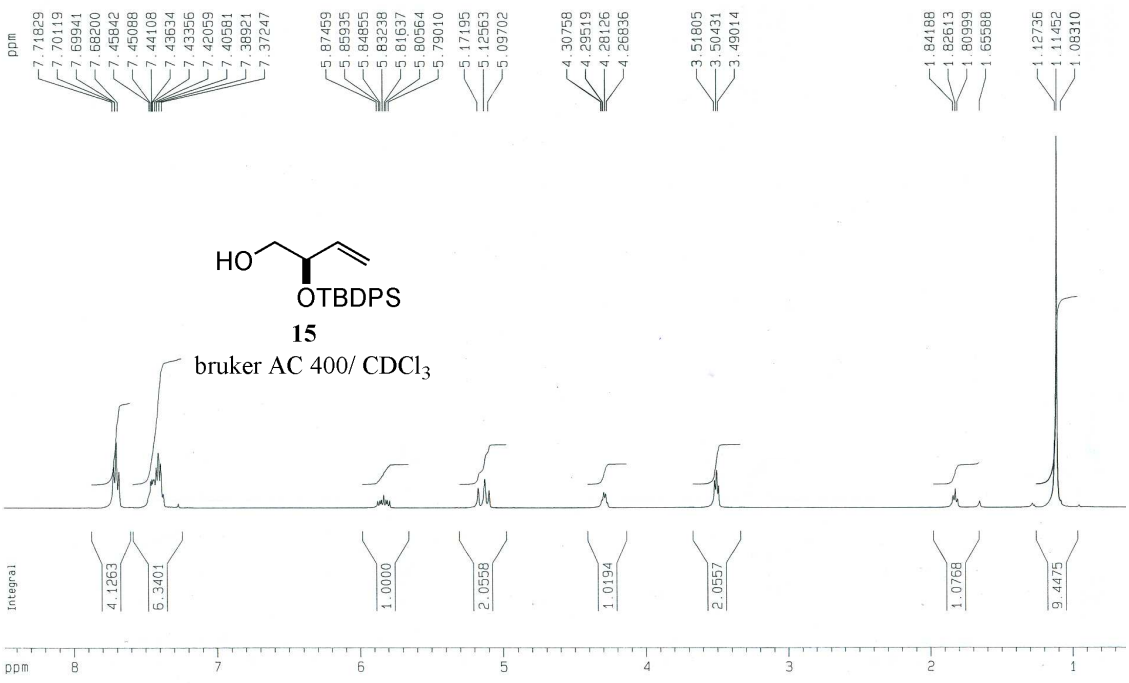


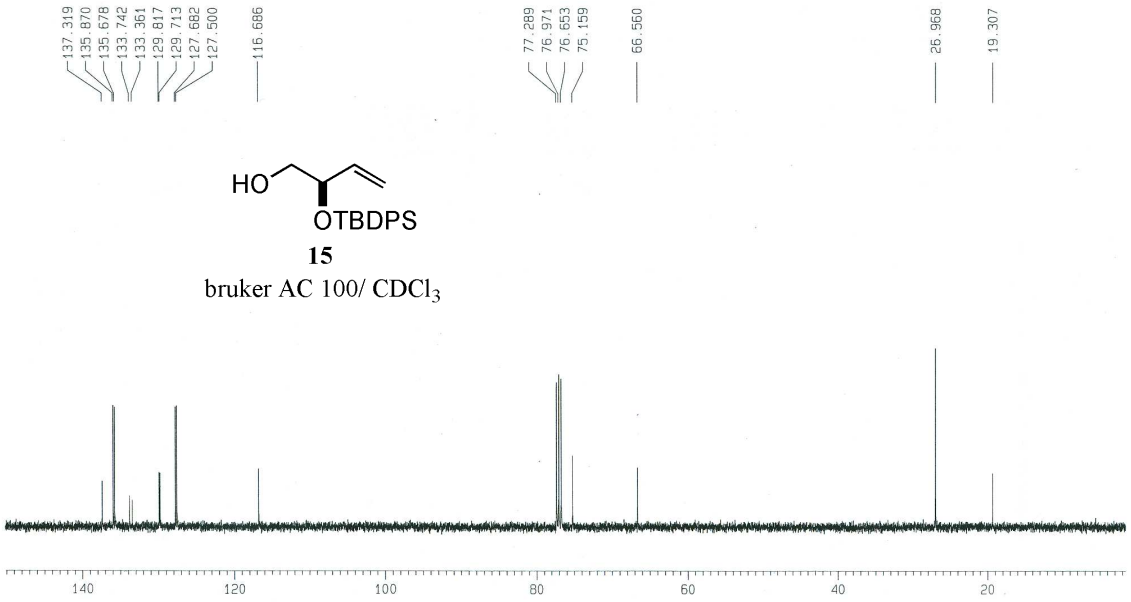
**13**

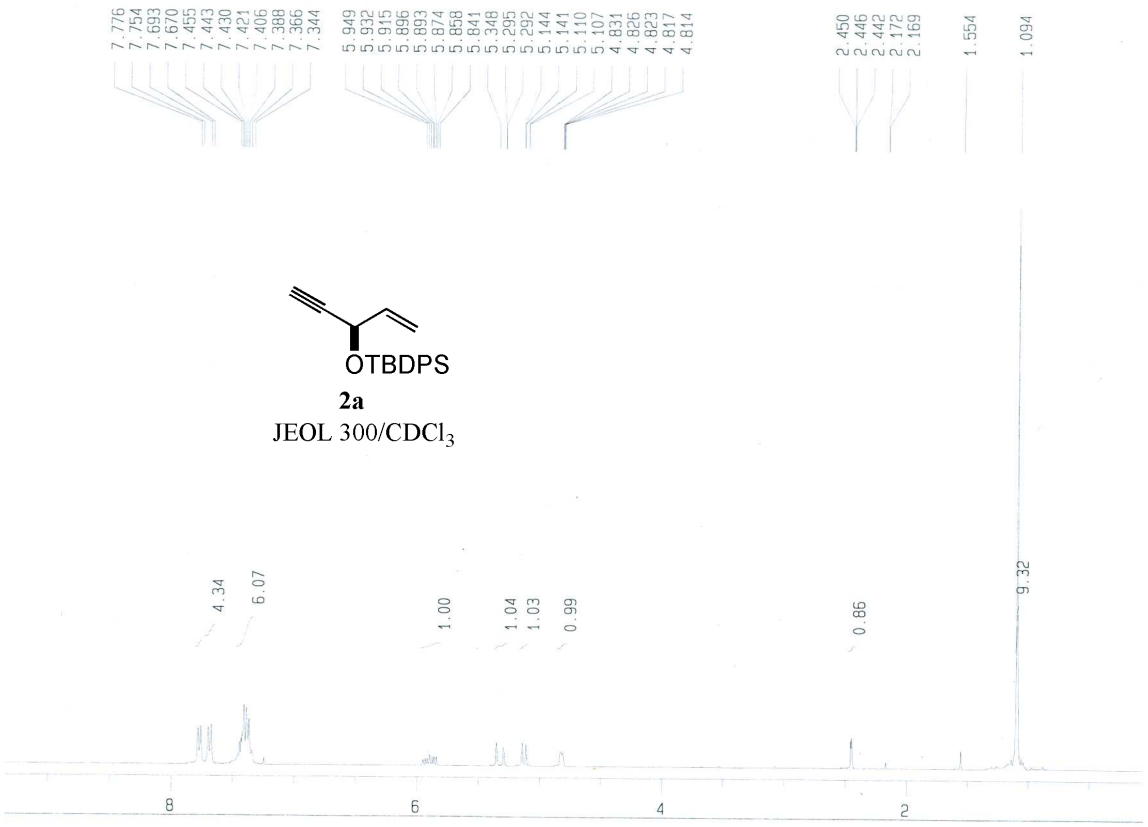
JEOL 75/$CDCl_3$


BnO
OTBDPS
14
JEOL 300/CDCl3
7.740
7.718
7.714
7.706
7.701
7.687
7.681
7.676
7.445
7.438
7.426
7.419
7.415
7.386
7.361
7.340
7.338
7.325
7.307
7.301
7.294
7.281
7.266
7.240
7.234
7.214
5.988
5.968
5.952
5.933
5.911
5.895
5.875
5.251
5.246
5.193
5.137
5.132
5.127
5.103
5.098
4.413
4.396
4.377
4.358
3.498
3.480
3.466
3.447
3.422
3.403
3.389
3.371
1.592
1.153
1.141
1.113
1.103
4.11
11.09
1.00
2.03
3.03
2.06
9.28
8
6
4
2


BnO
OTBDPS
14
JEOL 75/CDCl3
138.32
136.02
135.92
134.25
133.83
129.52
128.21
127.55
127.40
115.53
77.43
77.00
76.57
74.65
73.36
73.08
27.01
19.36
150
100
50


ppm
7.71829
7.70119
7.69941
7.68200
7.45842
7.45088
7.44108
7.43634
7.43356
7.42059
7.40581
7.38921
7.37247
5.87459
5.85935
5.84855
5.83238
5.81637
5.80564
5.79010
5.17195
5.12563
5.09702
4.30758
4.29519
4.28126
4.26836
3.51805
3.50431
3.49014
1.84188
1.82613
1.80999
1.65588
1.12736
1.11452
1.08310
HO
OTBDPS
15
bruker AC 400/ CDCl3
Integral
4.1263
6.3401
1.0000
2.0558
1.0194
2.0557
1.0768
9.4475
ppm
8
7
6
5
4
3
2
1


137.319
135.870
135.678
133.742
133.361
129.817
129.713
127.682
127.500
116.686
77.289
76.971
76.653
75.159
66.560
26.968
19.307
HO
OTBDPS
15
bruker AC 100/ CDCl3
140
120
100
80
60
40
20

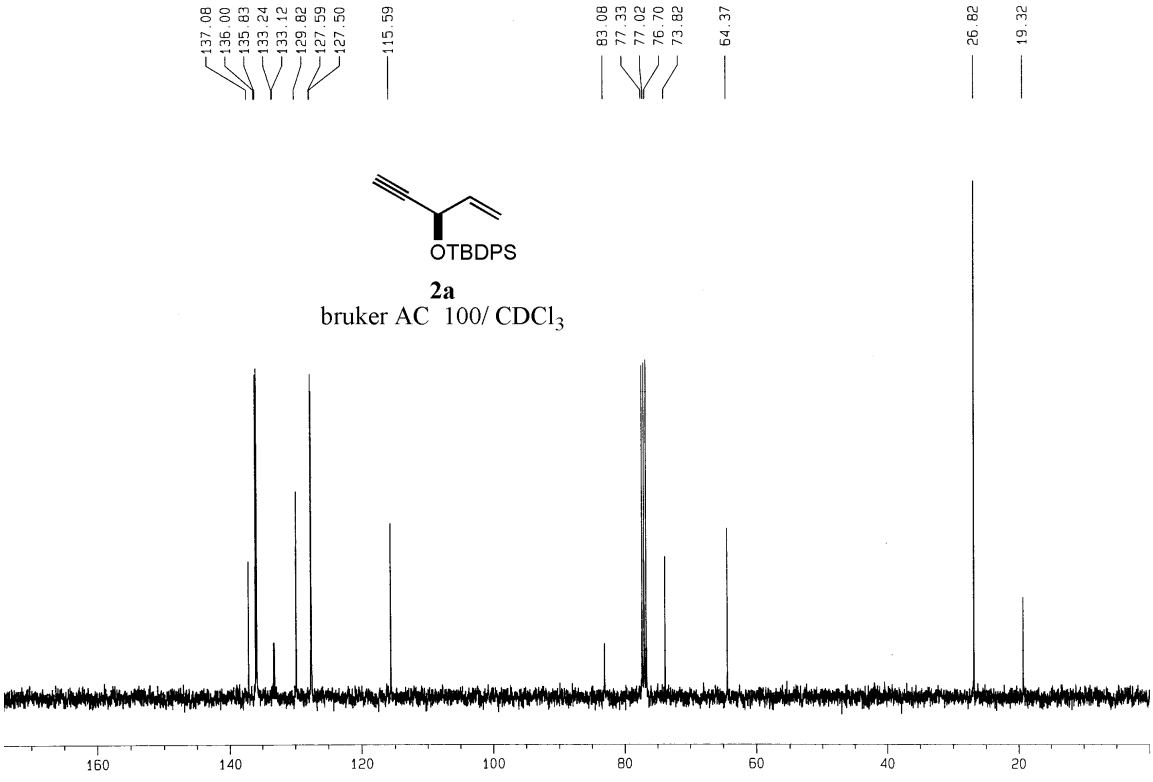






**2a**

JEOL 300/$CDCl_3$

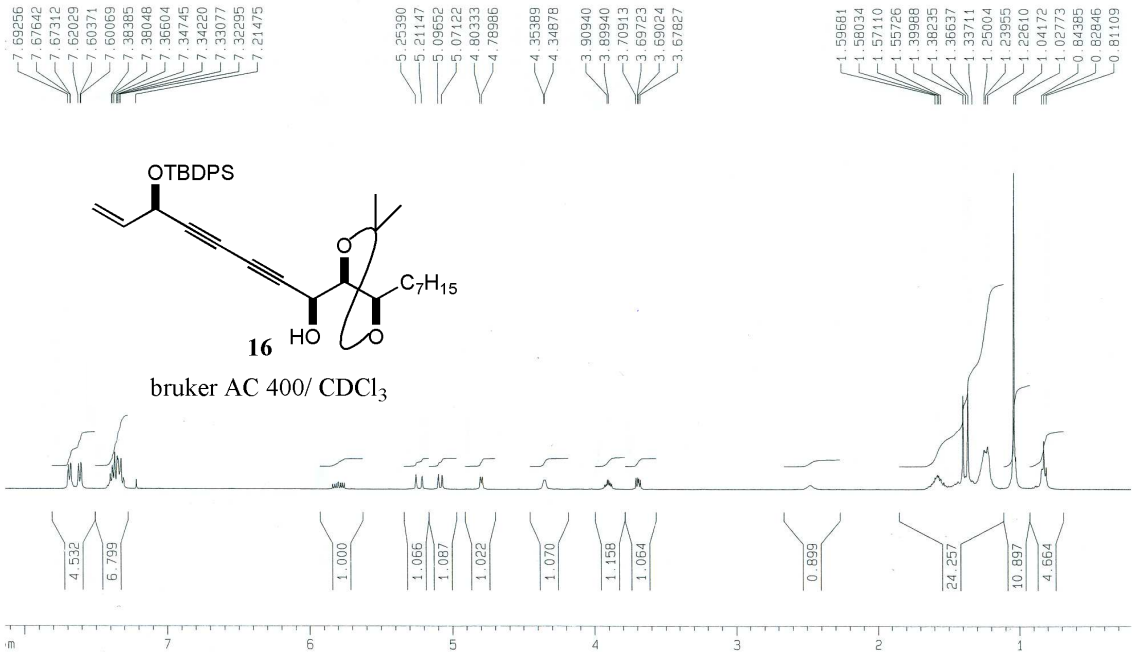


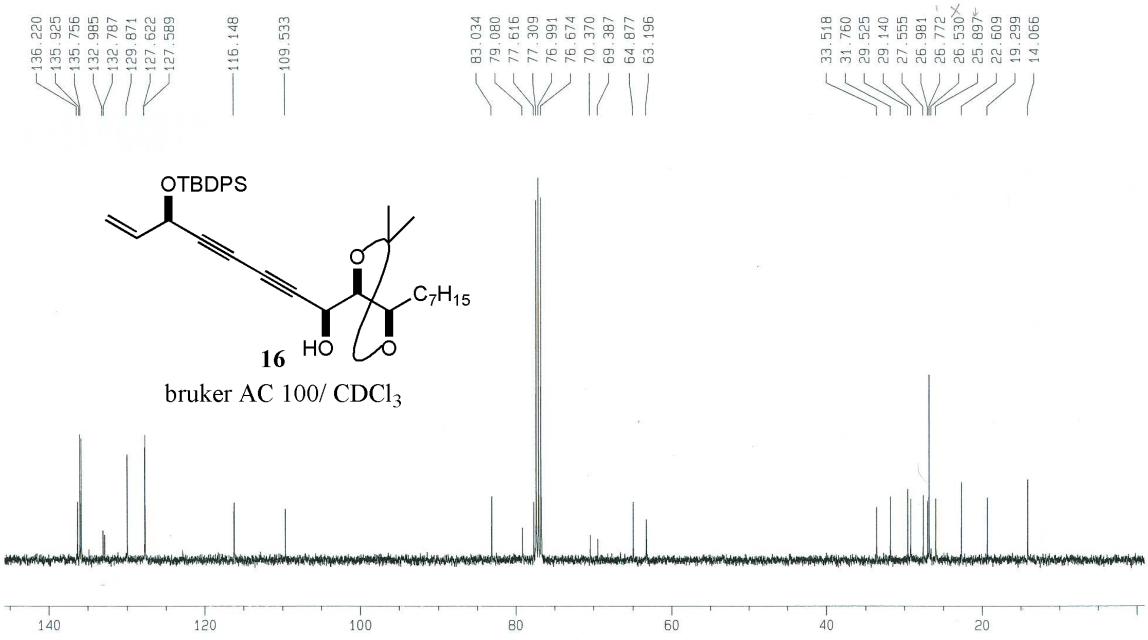


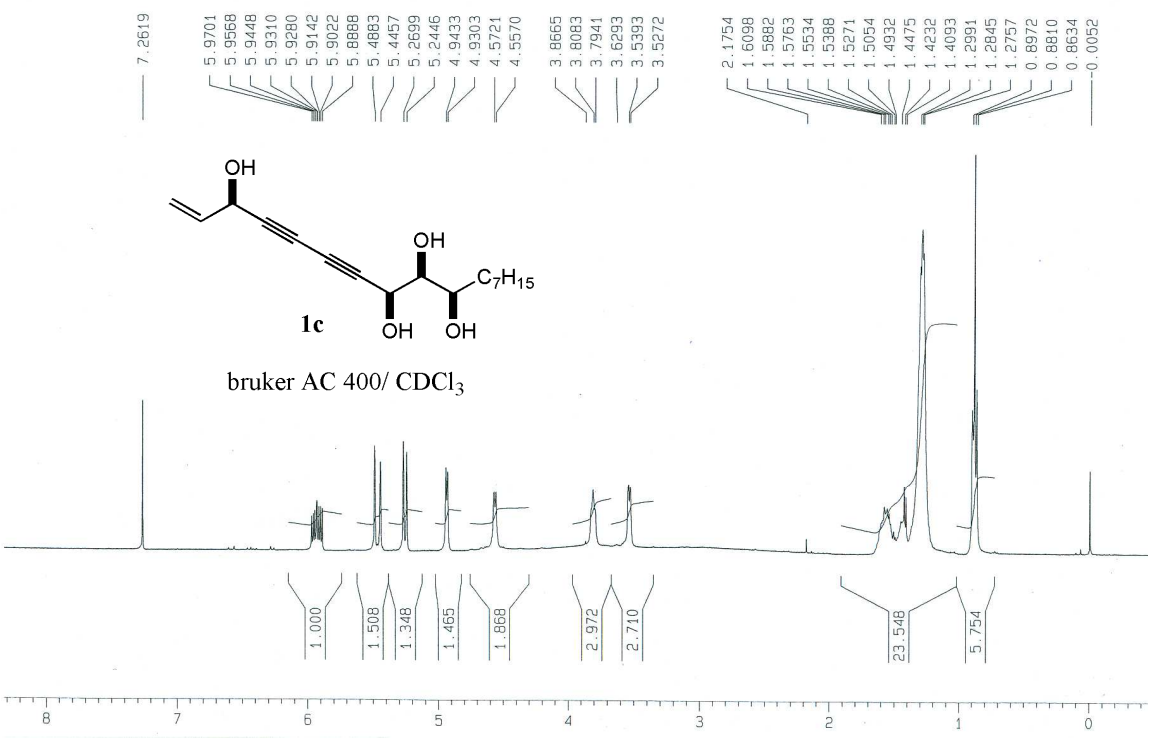


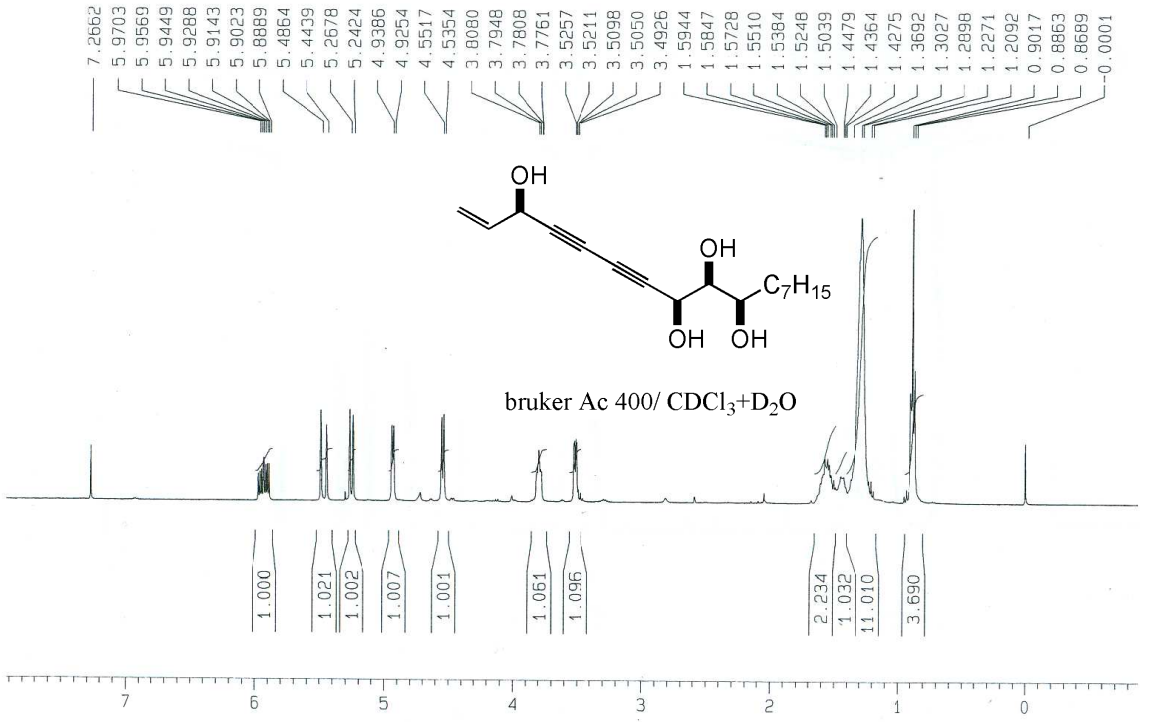
**2a**

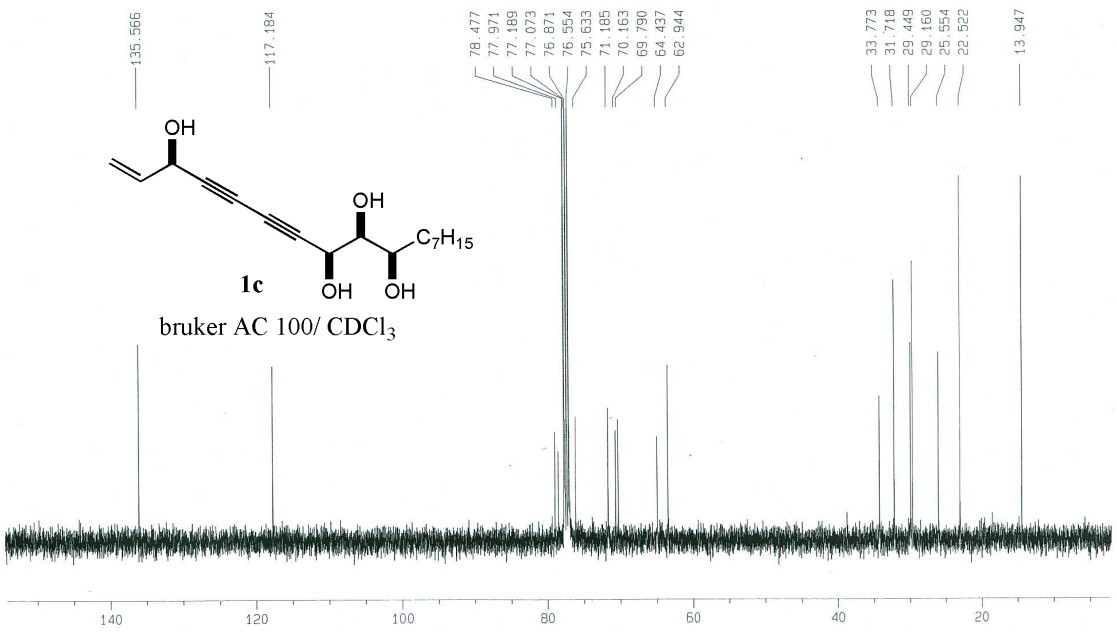
bruker AC 100/ $CDCl_3$

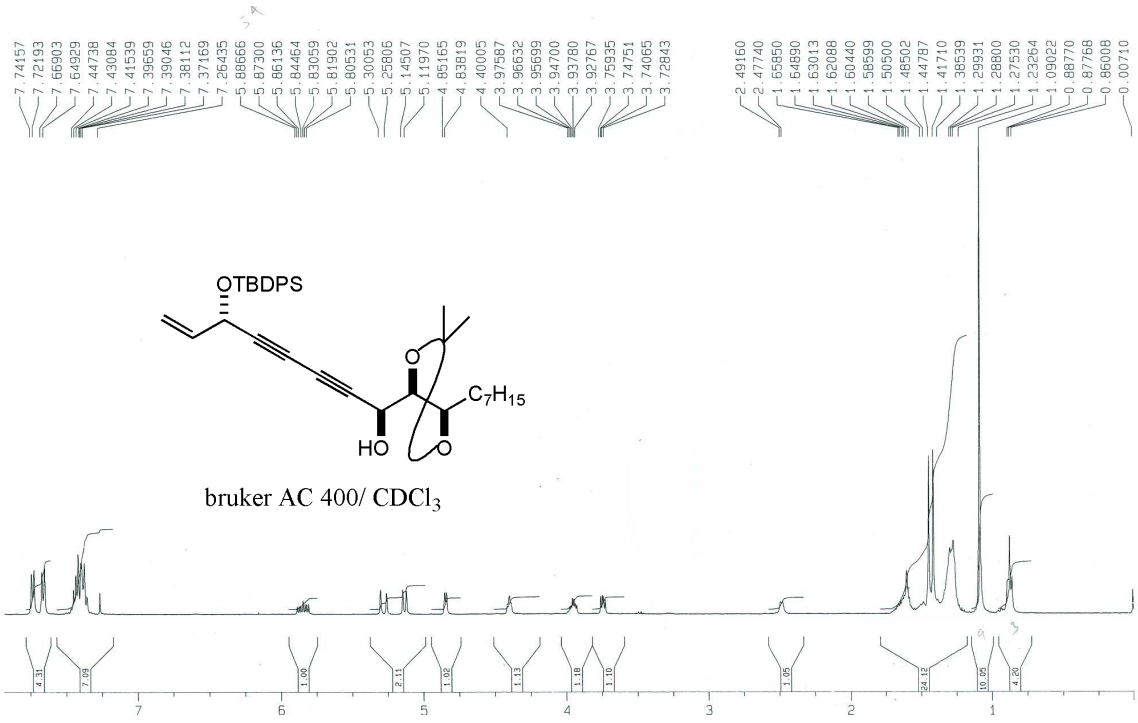

OTBDPS
C7H15
HO
16
bruker AC 400/ CDCl3


OTBDPS
C7H15
HO
16
bruker AC 100/ CDCl3

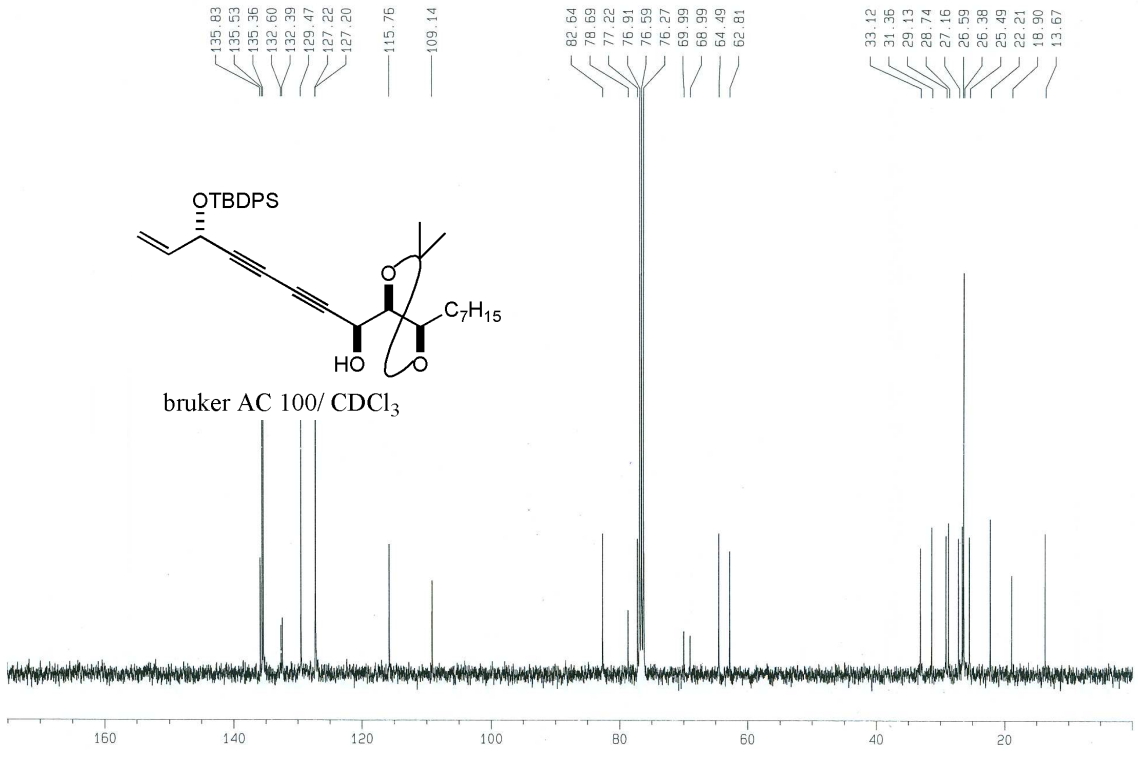

7.2619
5.9701
5.9568
5.9448
5.9310
5.9280
5.9142
5.9022
5.8888
5.4883
5.4457
5.2699
5.2446
4.9433
4.9303
4.5721
4.5570
3.8665
3.8083
3.7941
3.6293
3.5393
3.5272
2.1754
1.6098
1.5882
1.5763
1.5534
1.5388
1.5271
1.5054
1.4932
1.4475
1.4232
1.4093
1.2991
1.2845
1.2757
0.8972
0.8810
0.8634
-0.0052
OH
OH
$C_7H_{15}$
OH
OH
1c
bruker AC 400/ $CDCl_3$
1.000
1.508
1.348
1.465
1.868
2.972
2.710
23.548
5.754
8
7
6
5
4
3
2
1
0


7.2662
5.9703
5.9569
5.9449
5.9288
5.9143
5.9023
5.8889
5.4864
5.4439
5.2678
5.2424
4.9386
4.9254
4.5517
4.5354
3.8080
3.7948
3.7808
3.7761
3.5257
3.5211
3.5098
3.5050
3.4926
1.5944
1.5847
1.5728
1.5510
1.5384
1.5248
1.5039
1.4479
1.4364
1.4275
1.3692
1.3027
1.2898
1.2271
1.2092
0.9017
0.8863
0.8689
-0.0001
OH
OH
$C_7H_{15}$
OH
OH
bruker Ac 400/ $CDCl_3$+$D_2O$
1.000
1.021
1.002
1.007
1.001
1.061
1.096
2.234
1.032
11.010
3.690
7
6
5
4
3
2
1
0

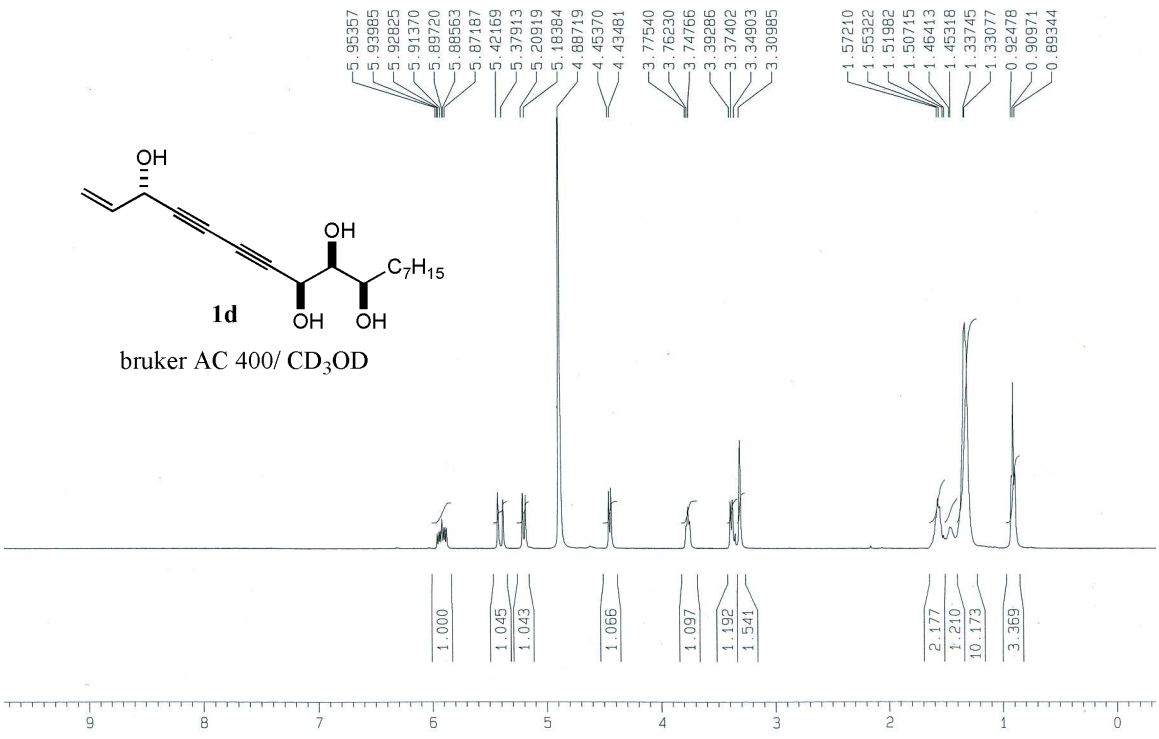

135.566
117.184
78.477
77.971
77.189
77.073
76.871
76.554
75.633
71.185
70.163
69.790
64.437
62.944
33.773
31.718
29.449
29.160
25.554
22.522
13.947
OH
OH
$C_7H_{15}$
OH
OH
1c
bruker AC 100/ $CDCl_3$
140
120
100
80
60
40
20



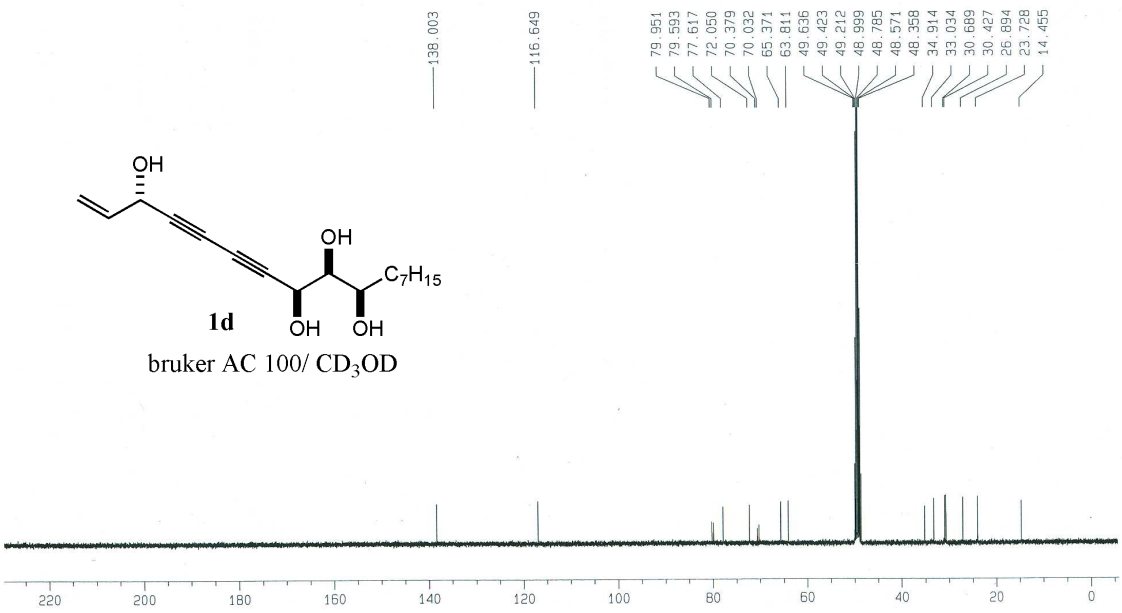

bruker AC 400/ $CDCl_3$



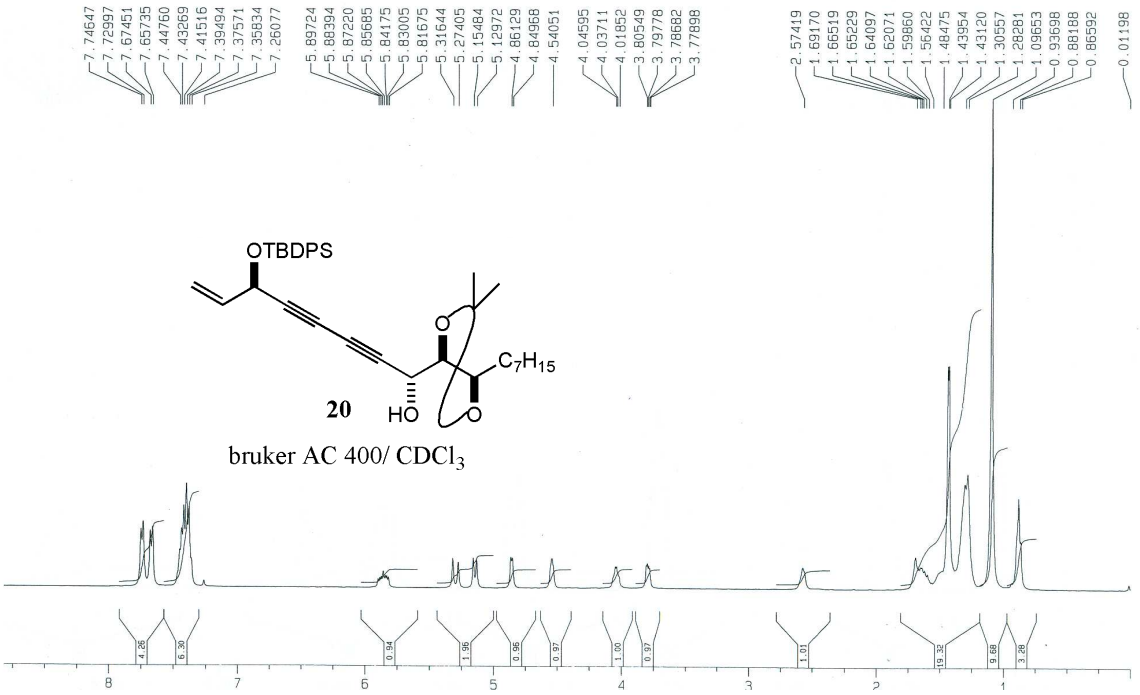

bruker AC 100/ $CDCl_3$



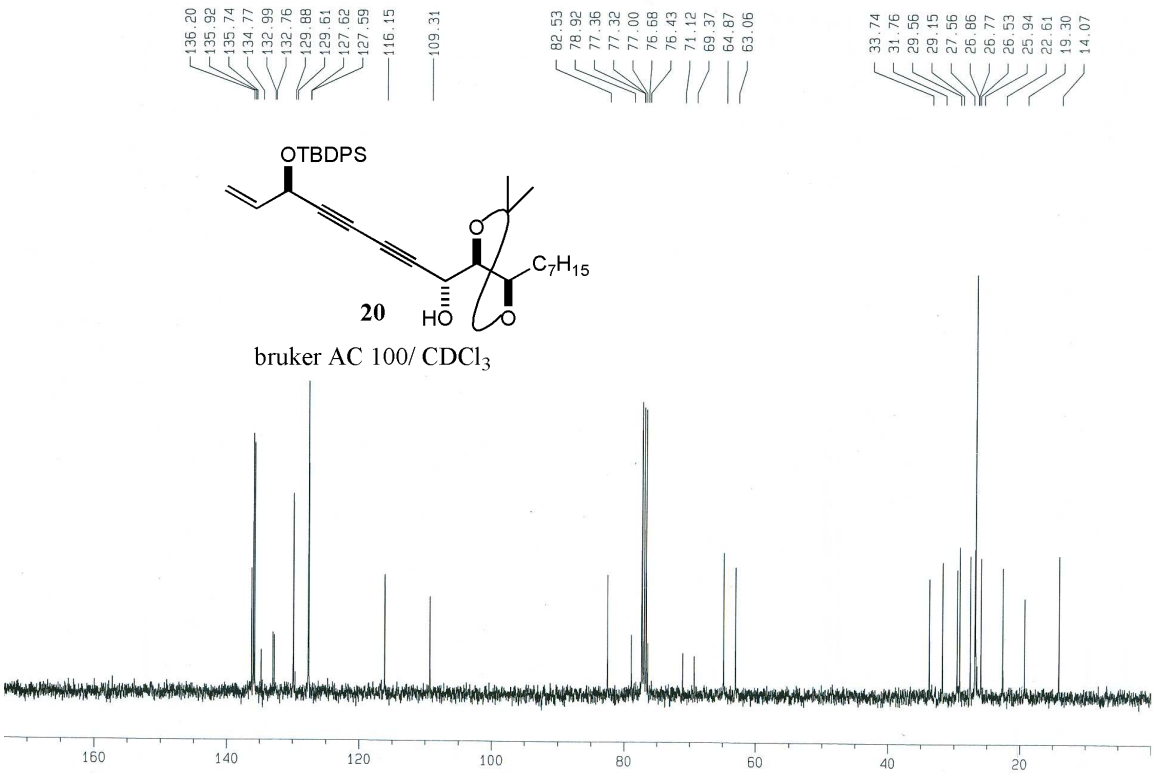

bruker AC 400/ $CD_3OD$



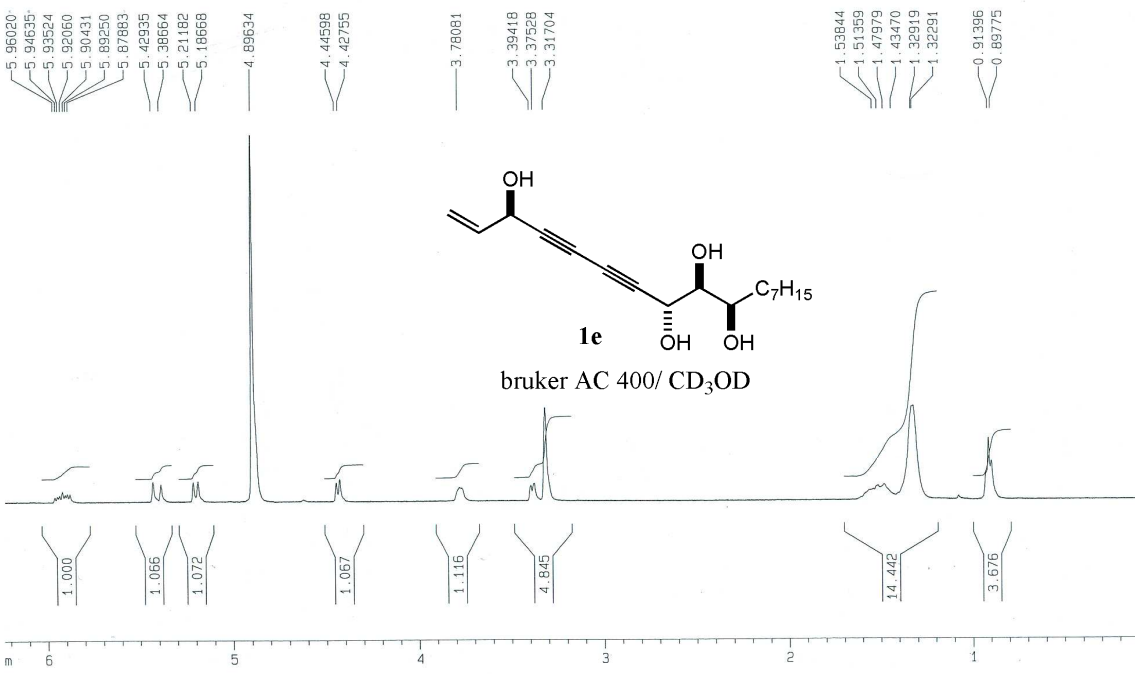

bruker AC 100/ $CD_3OD$



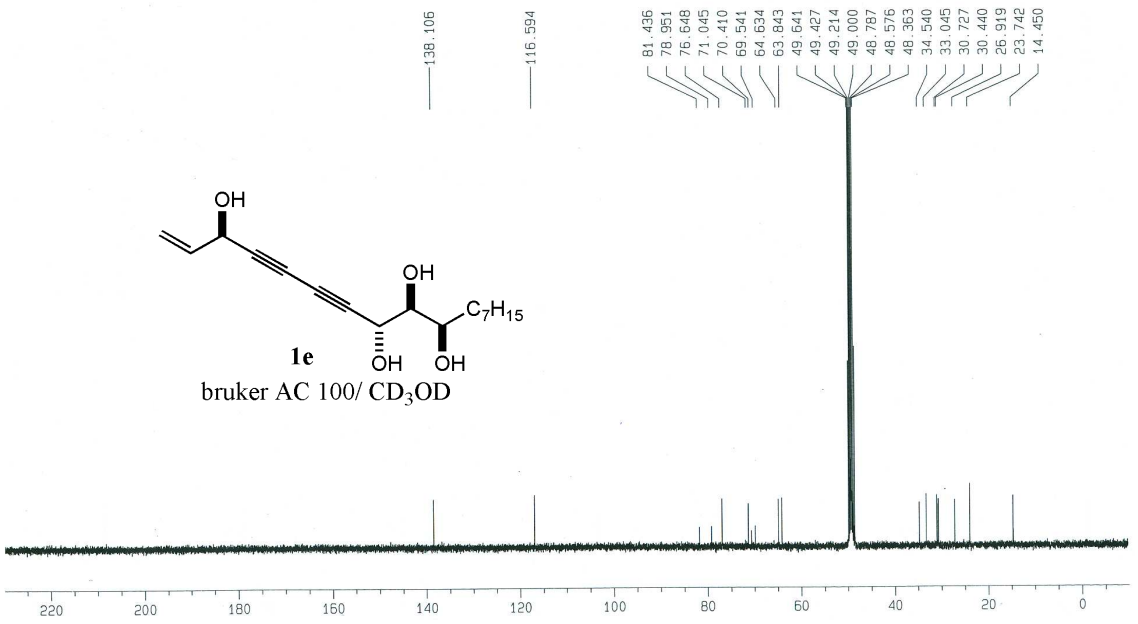

bruker AC 400/ $CDCl_3$



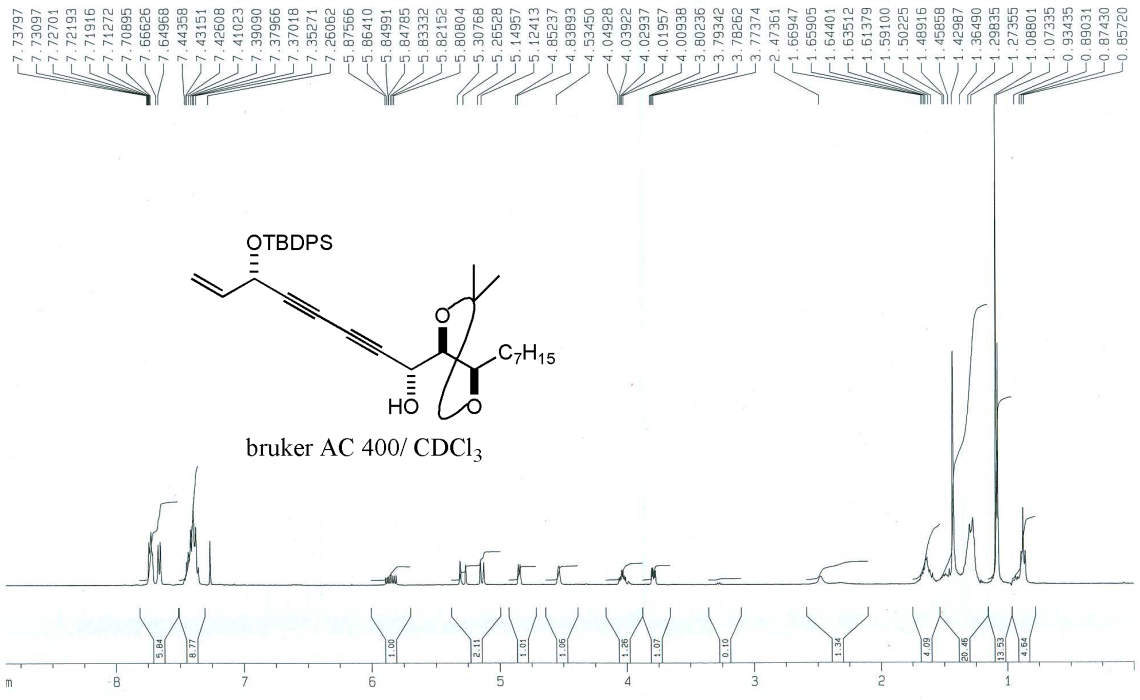

bruker AC 100/ $CDCl_3$

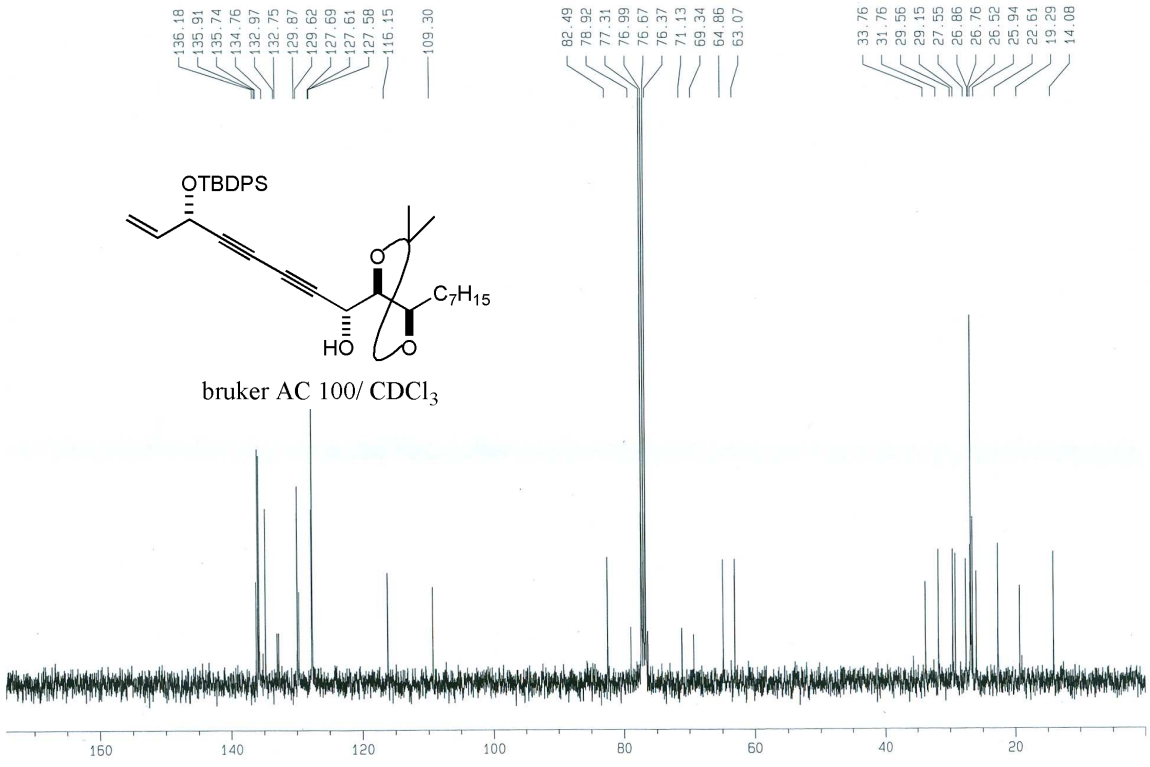


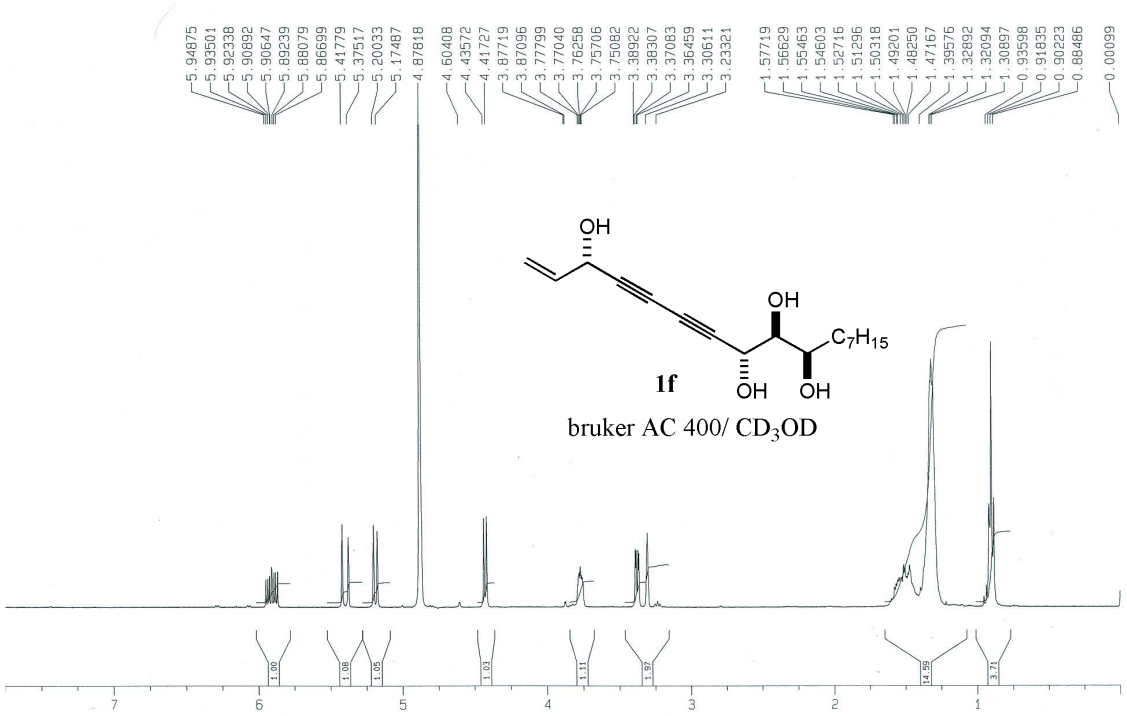

bruker AC 400/ $CD_3OD$

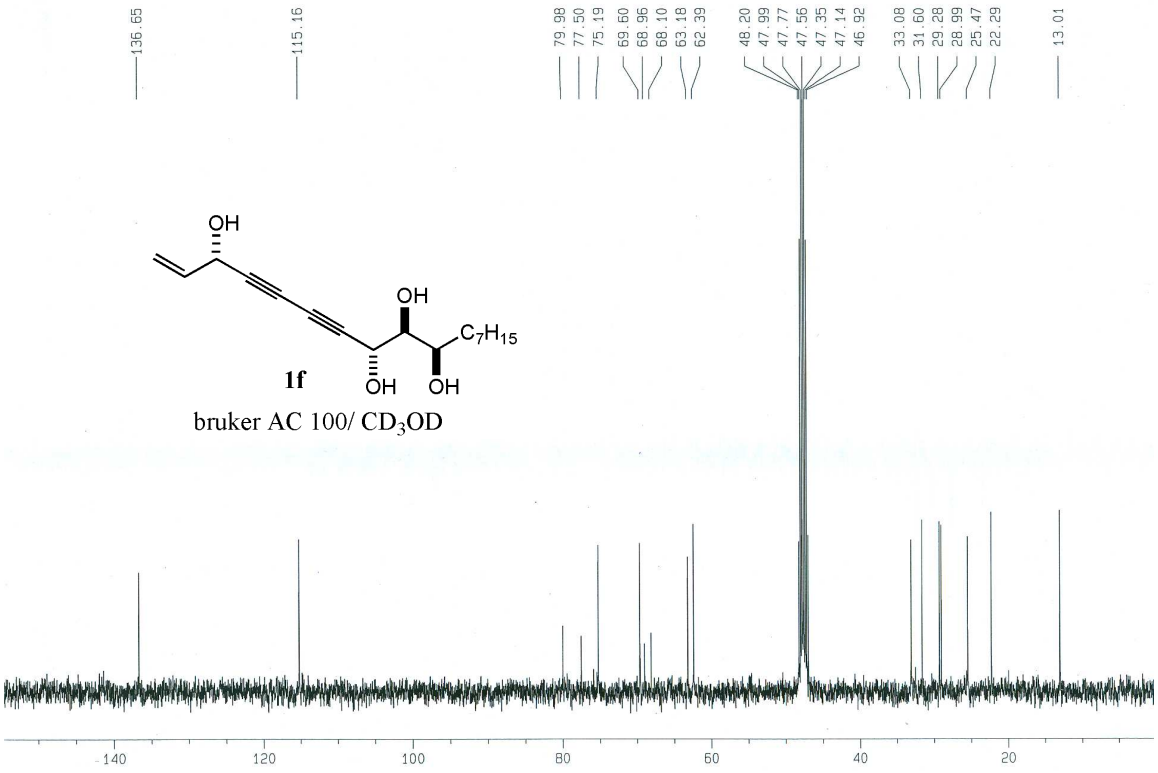


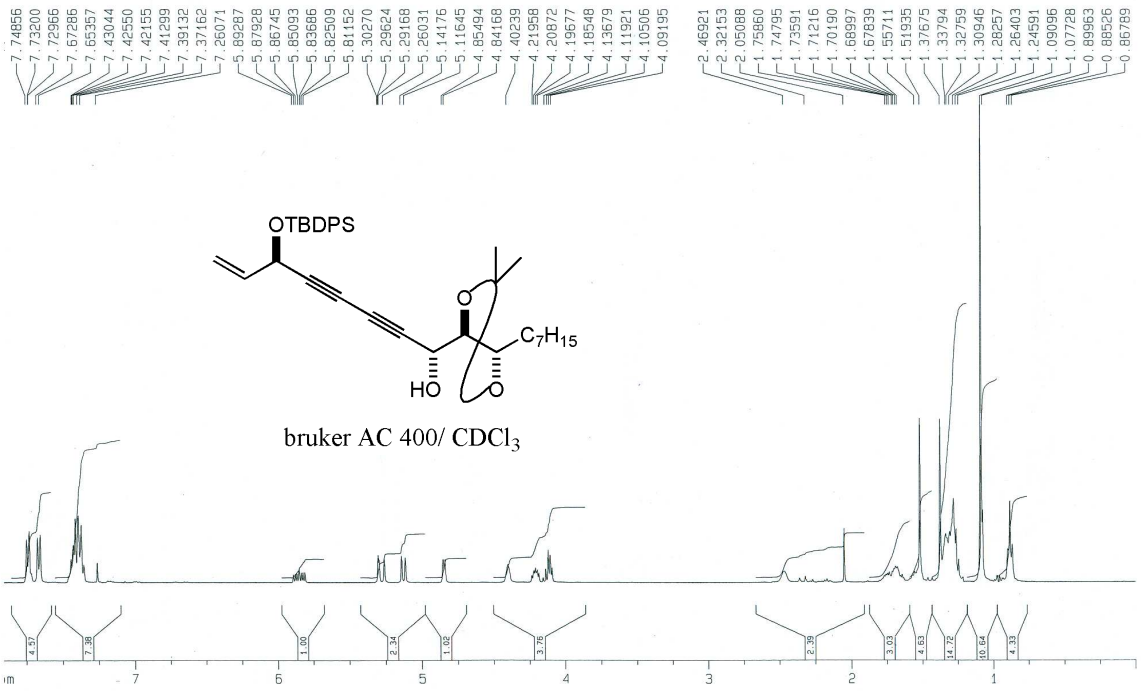

bruker AC 100/ $CD_3OD$

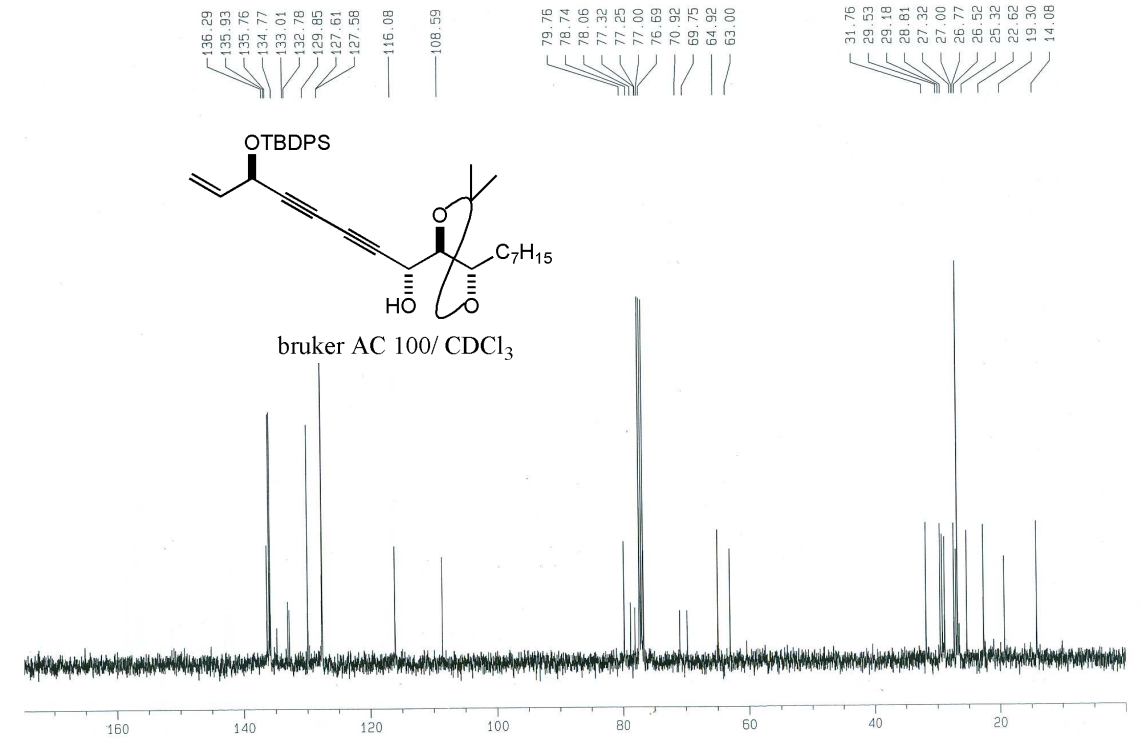

OTBDPS
C7H15
HO
O
O
bruker AC 400/ CDCl3

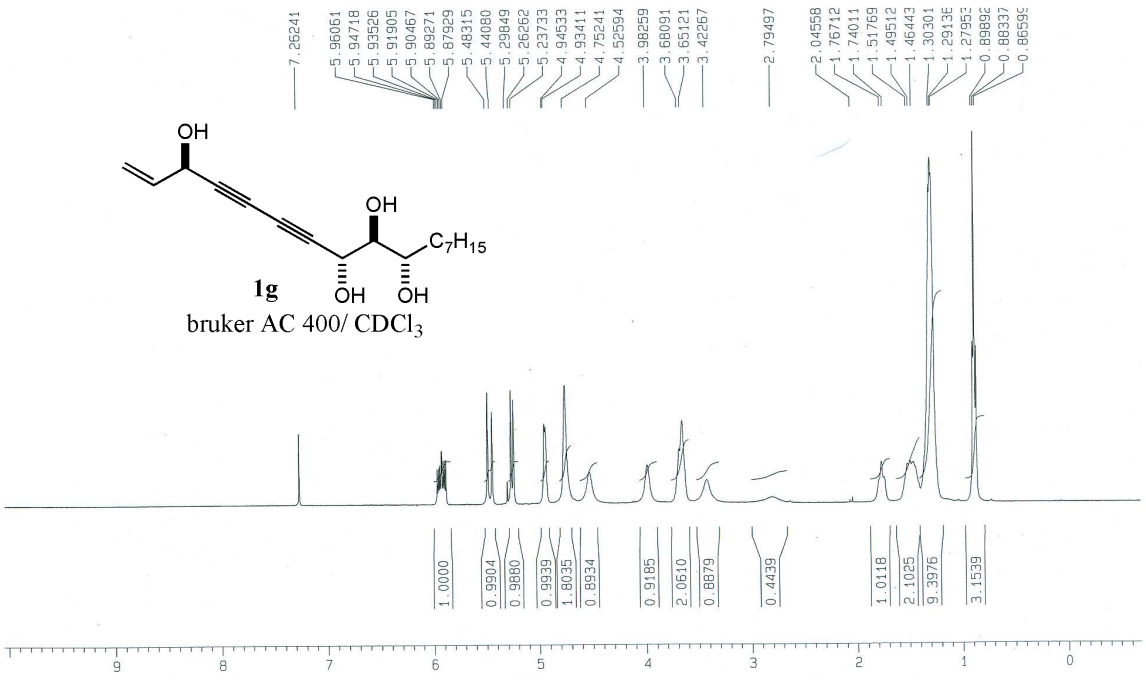

OTBDPS
C7H15
HO
O
O
bruker AC 100/ CDCl3


5.94875
5.93501
5.92338
5.90892
5.90647
5.89239
5.88079
5.86699
5.41779
5.37517
5.20033
5.17487
4.87818
4.60408
4.43572
4.41727
3.87719
3.87096
3.77799
3.77040
3.76258
3.75706
3.75082
3.38922
3.38307
3.37083
3.36459
3.30611
3.23321
1.57719
1.56629
1.55463
1.54603
1.52716
1.51296
1.50318
1.49201
1.48250
1.47167
1.39576
1.32892
1.32094
1.30897
0.93598
0.91835
0.90223
0.88486
0.00099
OH
OH
C7H15
OH
OH
1f
bruker AC 400/ CD3OD
1.00
1.08
1.05
1.03
1.11
1.97
14.99
3.71
7
6
5
4
3
2
1

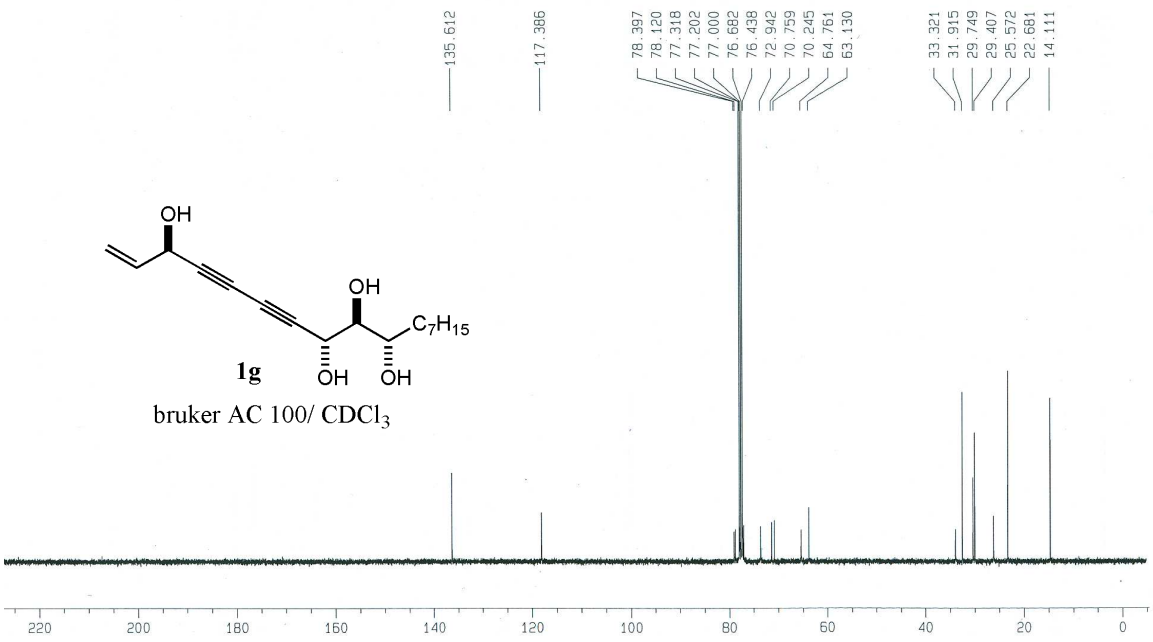

136.65
115.16
79.98
77.50
75.19
69.60
68.96
68.10
63.18
62.39
48.20
47.99
47.77
47.56
47.35
47.14
46.92
33.08
31.60
29.28
28.99
25.47
22.29
13.01
OH
OH
C7H15
OH
OH
1f
bruker AC 100/ CD3OD
140
120
100
80
60
40
20


OTBDPS
O
C7H15
HO
O
bruker AC 400/ CDCl3

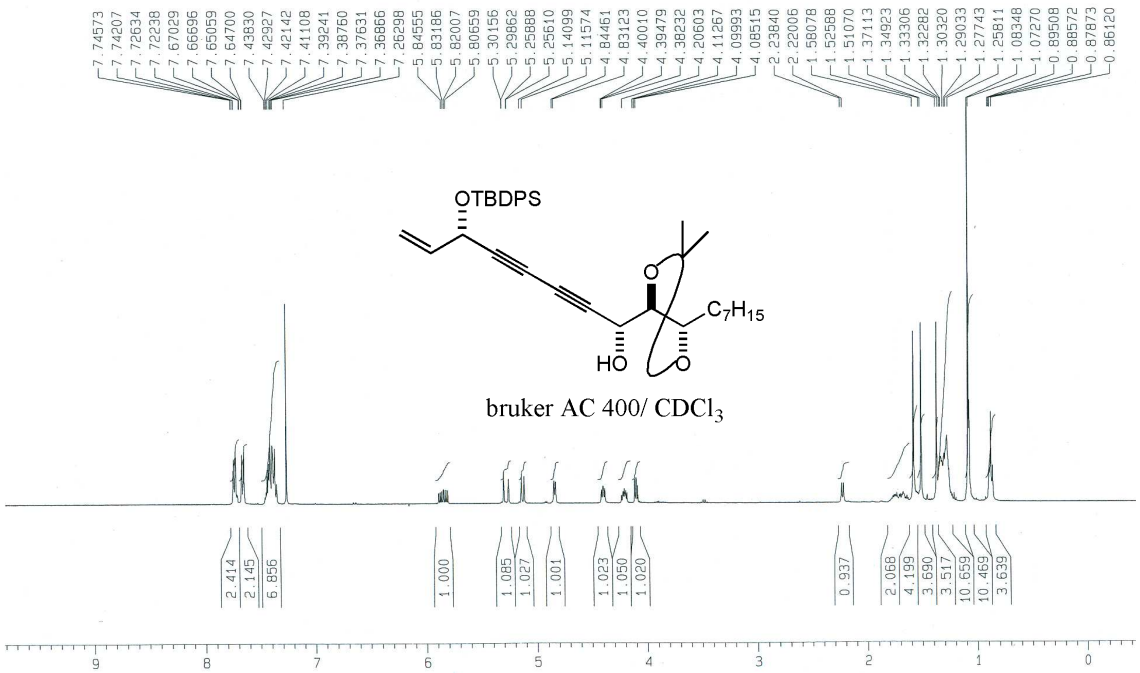

OTBDPS
O
C7H15
HO
O
bruker AC 100/ CDCl3



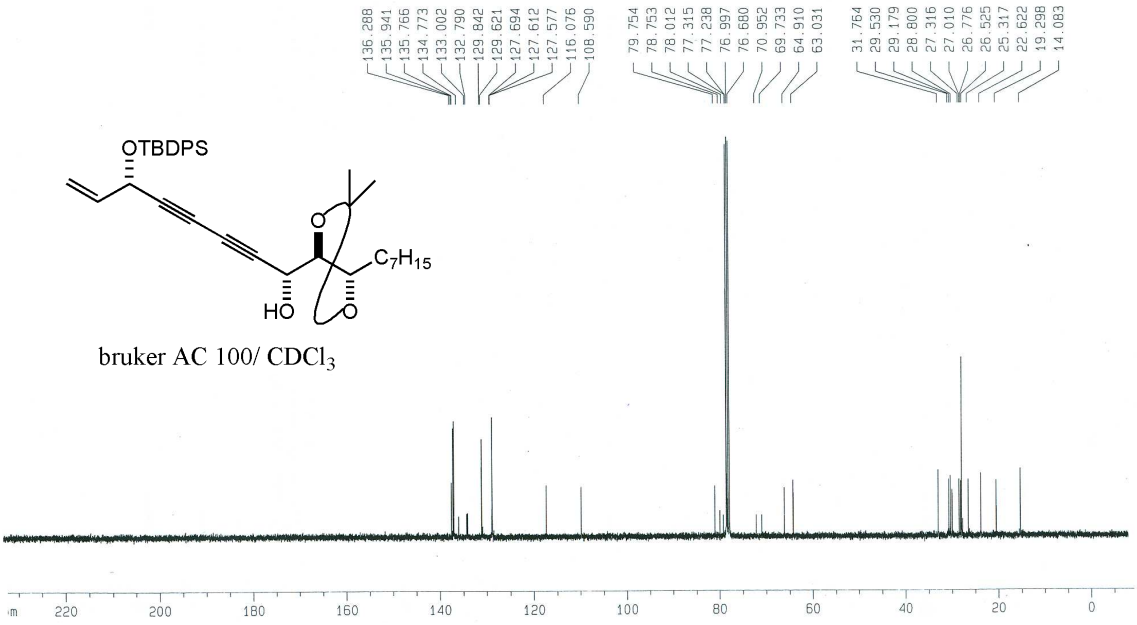

bruker AC 400/ $CDCl_3$



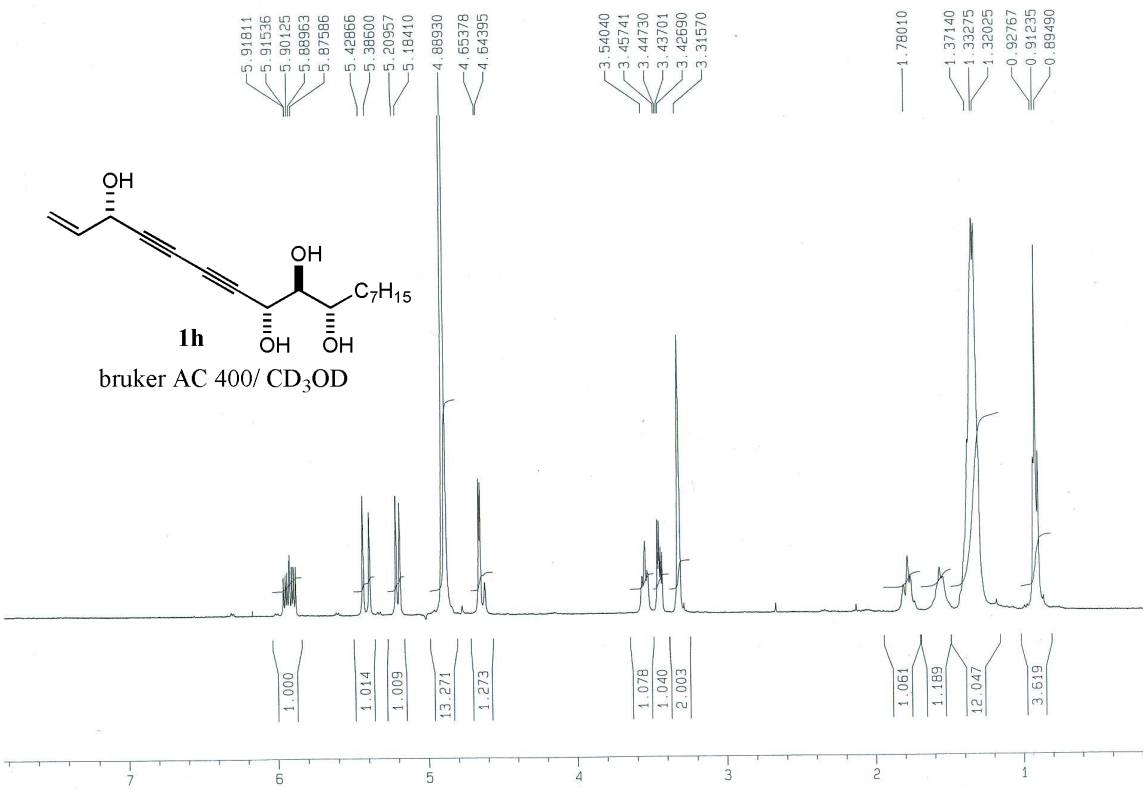

bruker AC 100/ $CDCl_3$



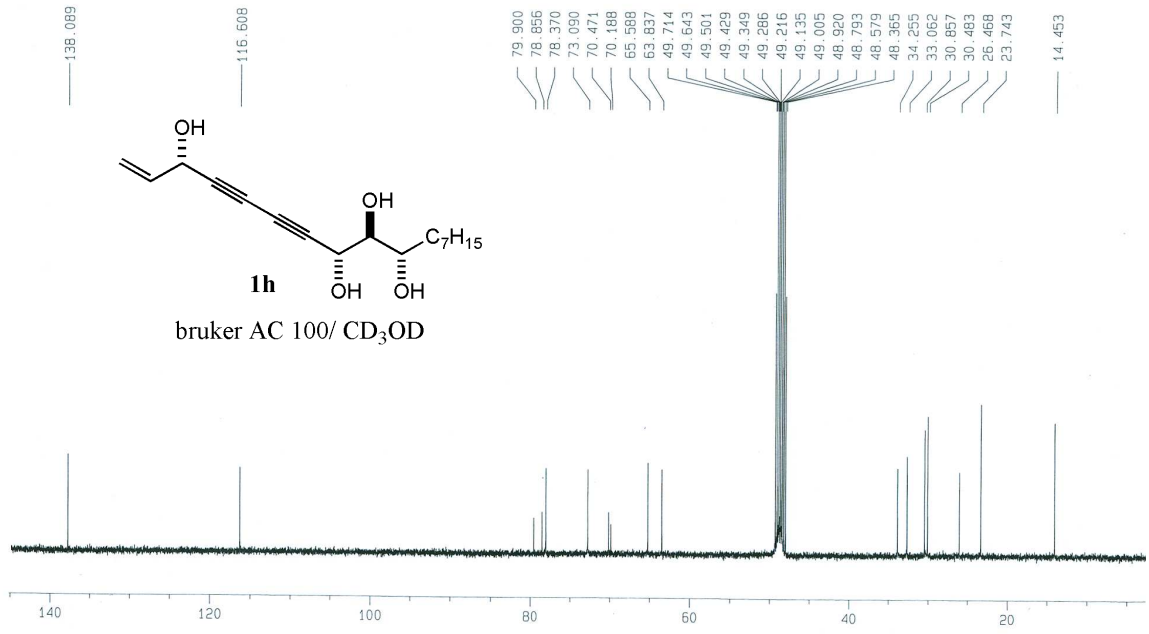

bruker AC 400/ $CDCl_3$




bruker AC 100/ $CDCl_3$




bruker AC 400/ $CD_3OD$




bruker AC 100/ $CD_3OD$