Stereoselective synthesis of 3-oxo-2-*C*-branched glycosides from 2,3-unsaturated sugars *via* [3,3] sigmatropic rearrangement

Intzar Ali, Sravani Gundumalla and Ramu Sridhar Perali*

e-mail: p_ramu_sridhar@uohyd.ac.in

Table of Contents

General Information:

All the reactions were carried out under nitrogen or argon atmosphere and monitored by thin layer chromatography (TLC) using silica gel GF_{254} plates with detection by charring with 5% (v/v) H_2SO_4 in methanol or by phosphomolybdic acid (PMA) stain or by ultraviolet (UV) detection. All the chemicals were purchased from Sigma-Aldrich or TCI Chemical Company. Solvents used in the reactions were distilled over dehydrated agents. Silica-gel (100-200 mesh) was used for column chromatography. ^{1}H, ^{13}C, DEPT, COSY, and NOESY spectra were recorded on Bruker 400 MHz or 500 MHz spectrometer. ^{1}H NMR chemical shifts were reported in ppm (δ) with TMS as internal standard (δ 0.00) and ^{13}C NMR were reported in chemical shifts with solvent reference ($CDCl_3$, δ 77.00). High resolution mass spectra (HRMS) were recorded on Bruker maXis ESI-QTOF spectrometer.

General Procedures:

2.1 Iodo-acetalyzation of glycals (General Procedure A):

To a stirred solution of protected glycal in acetonitrile (10 mL/mmol) under inert atmosphere was added benzyl alcohol (5 eq) followed by *N*-iodosuccinimide (1.5 eq) at 0 ˚C. The reaction was allowed to room temperature and stirred until starting material is disappeared. The reaction was quenched with saturated solution of sodium thiosulphate and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography using hexanes and ethyl acetate to give pure 2-deoxy 2-iodo glycoside.

2.2 Dehydrohalogenation-synthesis of vinyl ether (General procedure B):

To a stirred solution of 2-deoxy 2-iodo glycoside in toluene (10 mL/mmol) under inert atmosphere was added DBU (1.1 eq) at room temperature. The reaction mass was heated at 80 ˚C for 24 h. After complete conversion of starting material (monitored by TLC), solvent was removed under reduced pressure to obtain crude product which was purified over basic alumina using hexanes and ethyl acetate to obtain vinyl ether.

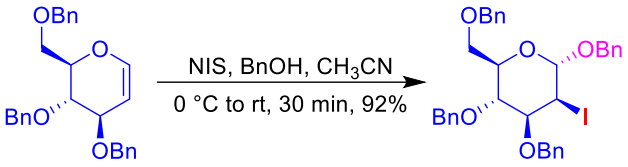
2.3 [3,3] sigmatropic rearrangement (Claisen rearrangement) (General procedure C):

Vinyl glycoside (2.4 mmol, 1 equiv.) was mixed with *N,N-dimethylaniline* (0.2 mL) in nitrobenzene (10 mL), and the mixture was heated at 150–170 ˚C until the starting material was completely consumed (5–6 h). The resulting mixture was instantly loaded onto a silica gel

column, and the product was purified by eluting with hexanes and ethyl acetate to obtain the 3-oxo-2-*C*-branched glycoside derivative.

2.4 General procedure for 3-*O*-alkylation of glycal derivative (General Procedure D): The 3-hydroxy glycal was dissolved in anhydrous THF (3 mL/mmol) under an inert atmosphere and the mixture was cooled to 0 °C. NaH (1.5 eq, 60%) was added portion-wise with stirring over a period of 20 minutes. After continued stirring for a further 1 hour at 0 °C, alkyl halide (1.25 eq) and TBAI (0.1 eq) were added at 0 °C and the mixture was stirred overnight at 25 °C. After completion of the reaction (monitored by TLC) cold water was added dropwise and the obtained solution was extracted with ethyl acetate. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to obtain the crude alkyl protected glycal derivative that was purified by silica gel column chromatography using hexanes and ethyl acetate to give pure 3-*O*-alkylated glycal derivative.

Experimental procedures and spectral data:



4 **5**

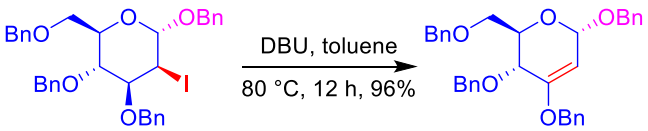
(2*S*,3*S*,4*S*,5*R*,6*R*)-2,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)-3-iodotetrahydro-2*H*-pyran (5): Compound **5** was synthesized from tribenzyl D-glucal **4**[1] (1 g, 2.40 mmol) by following general **procedure A.**

Yield: 1.43 g, 92 % colourless gel. R_f = 0.5 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.44 (m, 20H), 5.46 (s, 1H), 4.88-4.92 (m, 1H), 4.78 (d, 1H, *J* = 15.0 Hz), 4.75 (s, 1H), 4.72 (s, 1H), 4.58-4.61 (m, 2H), 4.53-4.56 (d, 2H), 4.51 (d, 1H, *J* = 15.0 HZ), 3.97-3.99 (m, 2H), 3.83-3.86 (m, 1H), 3.75 (8, 1H, *J*= 13.5 Hz), 3.40-3.43 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 138.1, 137.6, 136.8, 128.4, 128.3, 128.3, 128.2, 128.0, 128.0, 127.9, 127.9, 127.7, 127.6, 127.6, 127.4, 100.6, 76.7, 75.8, 75.2, 73.3, 72.3, 70.9, 69.4, 68.7, 33.4.

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{34}H_{35}IO_5NH_4$ 668.1873, found 668.1871



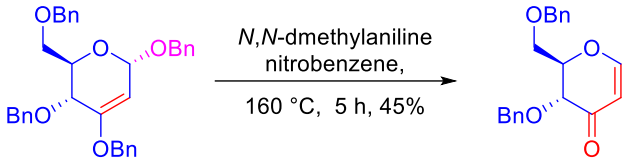
5 6

(2*R*,3*R*,6*S*)-3,4,6-tris(benzyloxy)-2-((benzyloxy)methyl)-3,6-dihydro-2*H*-pyran (6): Compound **6** was synthesized from **5** (1 g, 1.53 mmol) by following **general procedure B.** Yield: 771.1 mg, 96%, colorless gel. R_f = 0.4 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 126.1 (*c* 0.98, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.41 (m, 20H), 5.36 (d, 1H, *J* = 4.5 Hz), 4.88-4.96 (m, 3H), 4.81 (t, 2H, *J* = 16.0 Hz), 4.67 (d, 1H, *J* = 15.5 Hz), 4.63 (d, 1H, *J* = 14.5 Hz), 4.52 (d, 1H, *J* = 15.0 Hz), 4.47 (d, 1H, *J* = 14.0 Hz), 4.34 (d, 1H, *J* = 12.0 Hz), 4.21- 4.25 (m, 1H), 3.72-3.76 (m, 1H), 3.64 (dd , 1H, J_1 = 2.5, J_2 = 27 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 138.2, 138.2, 138.1, 136.4 , 128.4 , 128.3(2), 128.2, 128.1, 128.0, 127.9, 127.9, 127.6, 127.6, 127.6, 127.5, 95.8, 95.4, 74.1, 73.3, 71.1, 69.8, 69.7, 69.4, 68.6

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{34}H_{34}O_5NH_4$ 540.2750, found 540.2755



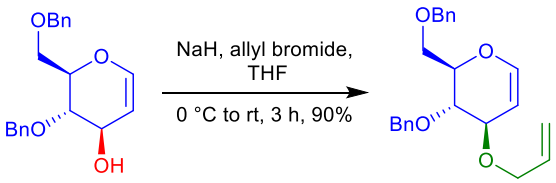
6 3

(2*R*,3*R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-2,3-dihydro-4*H*-pyran-4-one (3): Compound **3** was synthesized from **6** (500 mg, 0.95 mmol) by following general **procedure C.** Yield: 139.6 mg, 45%, colorless gel. R_f = 0.6 (15% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.35 (m, 11H), 5.38 (d, 1H, *J* = 6.0 Hz), 5.07 (d, 1H, *J* = 11.0 Hz), 4.57-4.61 (m, 2H), 4.52 (d, 1H, *J* = 12.0 Hz), 4.43 (dt, 1H, *J* =3.0 Hz, 11.5 Hz), 4.24 (d, 1H, *J* = 12.0 Hz), 3.80 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 193.5, 162.2, 137.5, 137.4, 128.5, 128.4, 128.3, 128.0, 127.9, 127.8, 105.2, 81.0, , 74.6, 74.1, 73.6, 67.9.

HRMS (ESI-TOF) *m/z*: [M+H]$^+$ calcd for $C_{20}H_{20}O_4H$ 325.1431, found 325.1431.



9 10

(2*R*,3*S*,4*R*)-4-(allyloxy)-3-(benzyloxy)-2-((benzyloxy)methyl)-3,4-dihydro-2H-pyran (10):

Compound **10** was synthesized from **9**[2] (500 mg, 1.53 mmol) by following general **procedure D.** Yield: 505.2 mg, 90%, colorless gel. R_f = 0.8 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 56.8 (*c* 0.25, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.36 (m, 10H), 6.43 (dd, 1H, *J* = 0.5 Hz, *J* = 6.0 Hz), 5.90-5.98 (m, 1H), 5.31 (dd, 1H, *J* = 1.5 Hz, *J* = 17.0 Hz), 5.20 (dd, 1H, *J* = 1.5 Hz, *J* = 10.5 Hz), 4.85-4.87 (m, 2H), 4.67 (d, 1H, *J* = 11.5 Hz), 4.62 (d, 1H, *J* = 12.0 Hz), 4.58 (d, 1H, *J* = 12.0 Hz), 4.12-4.16 (m, 2H), 4.03-4.09 (m, 2H), 3.83- 3.84 (m 1H), 3.79-3.81 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.6, 138.2, 138.0, 134.8, 128.4, 128.3, 127.9, 127.8, 127.7, 127.6, 116.8, 100.1, 76.7, 75.7, 74.3, 73.7, 73.5, 69.4, 68.5.

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{23}H_{26}O_4Na$ 389.1729, found 389.1724

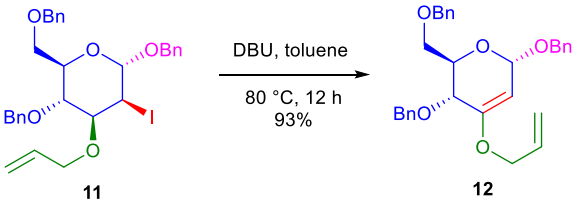
10 **11**

(2*S*,3*S*,4*S*,5*R*,6*R*)-4-(allyloxy)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3-iodotetrahydro-2*H*-pyran (11): Compound **11** was synthesized from **10** (300 mg, 0.81 mmol) by following general **procedure A.** Yield: 442.5 mg, 90%, colorless gel. R_f = 0.8 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 37.3 (*c* 0.55, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24-7.7.40 (m, 15H), 5.94-6.00 (m, 1H), 5.37 (d, 1H, *J* = 17.5 Hz), 5.33 (s, 1H), 5.22 (d, 1H, *J* = 10.0 Hz), 4.89 (d, 1H, *J* = 11.0 Hz), 4.74 (d, 1H, *J* = 12.0 Hz), 4.70 (d, 1H, *J* = 11.5), 4.49-4.58 (m, 4H), 4.18 (dd, 1H, *J* = 5.5 Hz, *J* = 12.5 Hz), 4.04 (dd, 1H, *J* = 5.5 Hz, *J* = 13.0 Hz), 3.89-3.95 (m, 2H), 3.80 (dd, 1H, *J* = 3.5 Hz, *J* = 10.5 Hz), 3.71 (d, 1H, *J* = 10.5 Hz), 3.26-3.29 (m, 1H).

^{13}C NMR (125 MHz, $CDCl_3$): δ, 138.4, 138.2, 136.9, 134.3, 128.4, 128.3, 128.3, 128.1, 128.0, 128.0, 127.7, 127.6, 127.4, 117.3, 100.7, 76.7, 76.0, 75.2, 73.4, 72.4, 70.0, 69.5, 68.9, 33.7.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{30}H_{33}IO_5Na$ 623.1265, found 623.1266



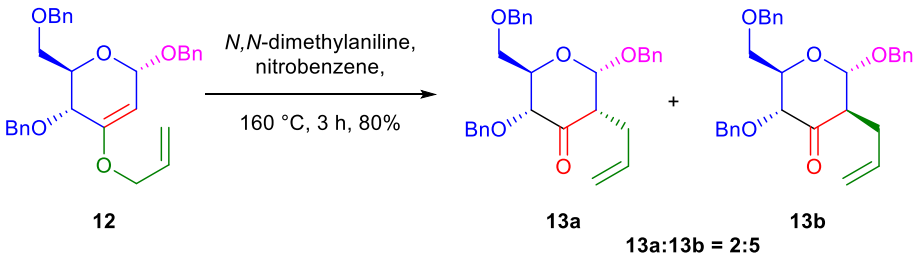
11 **12**

(2*R*,3*R*,6*S*)-4-(allyloxy)-3,6-bis(benzyloxy)-2-((benzyloxy)methyl)-3,6-dihydro-2*H*-pyran (12): Compound **12** was synthesized from **11** (300 mg, 0.49 mmol) by following general **procedure B.** Yield: 219.5 mg, 93%, colorless gel. R_f = 0.7 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.7.38 (m, 15H), 5.98-6.0 (m, 1H), 5.37-5.41 (m, 1H), 5.32 (d, 1H, *J* = 3.5 Hz), 5.26-5.29 (m, 1H), 4.92 (d, 1H, *J* = 11.0 Hz), 4.82 (d, 1H, *J* = 3.5 Hz), 4.80 (d, 1H, *J* = 12.0 Hz), 4.65 (d, 1H, *J* = 12.5), 4.60 (d, 1H, *J* = 12.0 Hz), 4.50 (d, 1H, J = 12.5 Hz), 4.47 (d, 1H, *J* = 11.5 Hz), 4.35-4.38 (m, 1H), 4.29-4.30 (m, 1H), 4.27 (s, 1H), 4.17-4.20 (m, 1H). 3.71 (dd, 1H, *J* = 4.0 Hz, *J* = 10.5 Hz), 3.61 (dd, 1H, *J* = 2.5 Hz, *J* = 11.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 138.4, 138.2, 138.1, 132.7, 128.3(3), 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 117.5, 95.7, 95.3, 74.0, 73.3, 71.1, 69.7, 69.7, 68.7, 68.1.

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ calcd for $C_{30}H_{32}O_5NH_4$ 490.2588, found 495.2589



(2*S*,3*S*,5*R*,6*R*)-3-allyl-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-4*H*-pyran-4-one (13a Minor) and (2*S*,3*R*,5*R*,6*R*)-3-allyl-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-4*H*-pyran-4-one (13b Major): Compounds **13a** and **13b** were obtained as a mixture from **12** (200 mg, 0.42 mmol) by following general **procedure C**. Combined yield: 159.9 mg, 80%, (13a:13b in 2:5 ratio), colourless gel. R_f = 0.7. (10% EtOAc/hexane). Both the diastereomers were separated by flash column chromatography.

Compound 13a: 46 mg, 23%. $[\alpha]_D^{25}$ = 122.0 (*c* 0.50, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.7.36 (m, 15H), 5.68-5.75 (m, 1H, H-8), 5.20 (d, 1H, *J* = 3.5 Hz, H-1), 4.99-5.04 (m, 2H, H-9), 4.91(d, 1H, *J* = 11.0 Hz,), 4.68 (d, 1H, *J* = 12.0 Hz), 4.65 (d, 1H, *J* = 12.5 Hz), 4,53-4.55 (m, 1H), 4.47 (d, 1H, *J* = 12.0 Hz), 4.41 (d, 1H, *J* = 11.0 Hz), 4.25 (d, 1H, *J* = 10.0 Hz, H-4), 4.07 (d, 1H, *J* = 9.5 Hz, H-5), 3.79-3.82 (m, 1H, H-6a), 3.71-3.73 (m, 1H, H-6b), 2.80-2.84 (m, 1H, H-2), 2.57-2.62 (m, 1H, H-7a), 2.18-2,24 (m, 1H, H-7b).

^{13}C NMR (125 MHz, $CDCl_3$): δ 204.5, 137.9, 137.5, 136.8, 135.0, 128.4, 128.3(2), 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 116.9, 100.0, 79.0, 73.6, 73.3, 73.3, 69.3, 68.5, 53.3, 28.1.

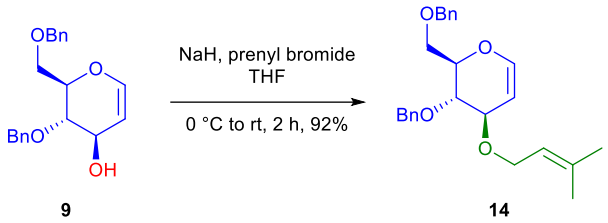
HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{30}H_{32}O_5Na$ 495.2147, found 495.2145.

Compound 13b: 114 mg, 57%. $[\alpha]_D^{25}$ = 87.7 (*c* 0.30, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.34 (m, 15H), 5.68-5.73 (m, 1H, H-8), 5.09-5.19 (m, 1H, H-9), 5.06 (d, 1H, *J* = 18 Hz, H-1), 4.99 (d, 1H, *J* =11.5), 4.85-4.91 (m,1H), 4.66-4.72 (m, 2H), 4.49-4.57 (m, 2H), 4.41 (d, 1H, *J* = 9 Hz), 4,27 (dd, 1H, *J* = 2 Hz, *J* = 10 Hz, H-4), 4.06-4.12 (m, 1H, H-5), 3.75 (dd, 2H, *J* = 10.5 Hz, *J* = 30 Hz, H-6), 2.78-2.88 (m, 1H, H-2), 2.27-2.61 (m, 2H, H-7).

^{13}C NMR (125 MHz, $CDCl_3$): δ 206.6, 138.1, 137.3, 136.9, 133.8, 128.5, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.6, 117.7, 100.7, 73.6, 73.5, 73.3, 72.9, 69.1, 68.7, 56.0, 34.1.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{30}H_{32}O_5Na$ 495.2147, found 495.2145.



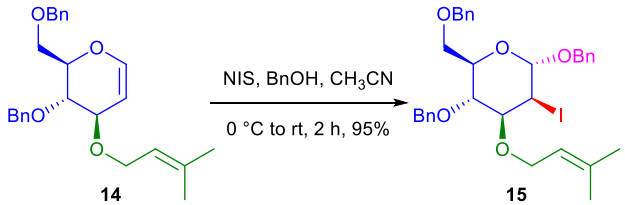
9 **14**

(2*R*,3*S*,4*R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-((3-methylbut-2-en-1-yl)oxy)-3,4-dihydro-2*H*-pyran (14): Compound **14** was synthesized from **9**[2] (400 mg, 1.22 mmol) by following general **procedure D.** Yield: 444.7 mg, 92%, colorless gel. R_f = 0.5 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 18.5 (*c* 0.20, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.37 (m, 10H), 6.44 (d, 1H, *J* = 6.0 Hz), 5.38 (t, 1H, *J* = 5.5 Hz), 4.88-4.90 (m, 2H), 4.58-4.69 (m, 3H), 4.11-4.15 (m, 2H), 4.02-4.10 (m, 2H), 3.78-3.84 (m, 3H), 1.77 (s, 3H), 1.69 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.4, 138.3, 138.0, 136.8, 128.3, 128.3, 127.8, 127.7, 127.6, 127.6, 121.1, 100.3, 76.7, 75.4, 74.3, 73.6, 73.4, 68.6, 64.9, 25.7, 18.0.

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{25}H_{30}O_4H$ 395.2222, found 395.2217



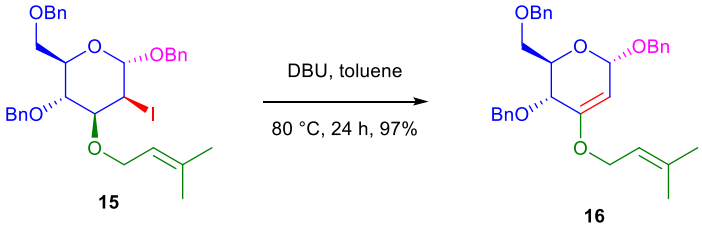
14 **15**

(2*S*,3*S*,4*S*,5*R*,6*R*)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3-iodo-4-((3-methylbut-2-en-1-yl) oxy) tetrahydro-2*H*-pyran (15): Compound **15** was synthesized from **14** (300 mg, 0.76 mmol) by following general **procedure A.** Yield: 454.1 mg, 95%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 38.8 (*c* 0.25, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.25-7.41 (m, 15H), 5.43-5.47 (m, 1H), 5.35 (s, 1H), 4.93 (d, 1H, *J* = 10.5 Hz), 4.75 (d, 1H, *J* = 12.0 Hz), 4.73 (d, 1H, *J* = 12.0 Hz), 4.59 (d, 1H, *J* = 1.5 Hz), 4.57 (d, 1H, *J* = 12.0 Hz), 4.51-4.53 (m, 2H), 4.19 (dd, 1H, J = 7.0 Hz), 3.93-4.00 (m, 2H), 3.89 (t, 1H, *J* = 8.5 Hz), 3.82 (dd, 1H, *J* = 4.5 Hz, *J* = 11.0 Hz), 3.74 (dd, 1H, *J* = 2.0 Hz, *J* = 11.0 Hz), 3.26 (dd, 1H, *J* = 4.5 Hz, *J* = 8.5 Hz), 1.78 (s, 3H), 1.71 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4(2), 137.5, 136.9, 128.4, 128.3, 128.3(2) , 128.0, 128.0, 127.9, 127.6, 127.4, 120.6, 100.7, 76.5, 75.8, 75.2, 73.3, 72.4, 69.4, 68.9, 65.3, 34.0, 25.8, 18.1.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{32}H_{37}IO_5Na$ 651.1583, found 651.1578

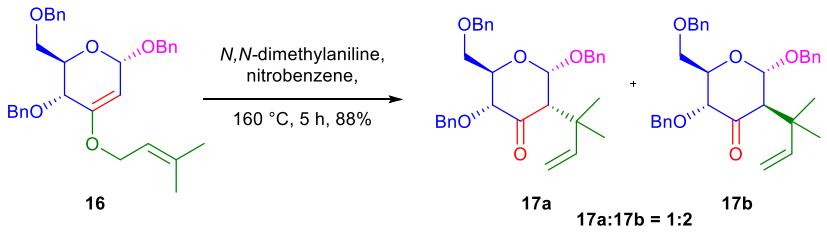


(2*R*,3*R*,6*S*)-3,6-bis(benzyloxy)-2-((benzyloxy)methyl)-4-((3-methylbut-2-en-1-yl)oxy)-3,6-dihydro-2*H*-pyran (16): Compound **16** was synthesized from **15** (350 mg, 0.55 mmol) by following general **procedure B.** Yield: 270.3 mg, 97%, colorless gel. R_f = 0.5 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23-7.34 (m, 15H), 5.39-5.42 (m, 1H), 5.29 (d, 1H, *J* = 3.5 Hz), 4.85 (d, 1H, *J* = 11.0), 4.78 (d, 1H, *J* = 3.5 Hz), 4.76 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 12.0 Hz), 4.57 (d, 1H, *J* = 11.5 Hz), 4.46 (d, 1H, *J* = 12.0 Hz), 4.42 (d, 1H, *J* = 11.0 Hz), 4.29 (dd, 1H, *J* = 6.5 Hz, *J* = 11.5 Hz), 4.21-4.24 (m, 2H), 4.14-4.17 (m, 1H), 3.67 (dd, 1H, *J* = 4.0 Hz, *J* = 10.5 Hz), 3.58 (dd, 1H, *J* = 2 Hz, *J* = 10.5 Hz), 1.76 (s, 3H), 1.67 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 138.5, 138.3, 138.2, 137.7, 128.3 (2), 128.2, 128.1, 128.1, 127.9, 127.6, 127.5, 127.5, 119.3, 95.5, 95.2, 73.7, 73.3, 71.1, 69.7, 69.6, 68.7, 64.3, 25.7, 18.2

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ calcd for $C_{32}H_{36}O_5NH_4$ 518.2906, found 518.2901



(2*S*,3*S*,5*R*,6*R*)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3-(2-methylbut-3-en-2-yl)tetrahydro-4*H*-pyran-4-one(17a) and **(2*S*,3*R*,5*R*,6*R*)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3-(2-methylbut-3-en-2-yl)tetrahydro-4*H*-pyran-4-one (17b):**

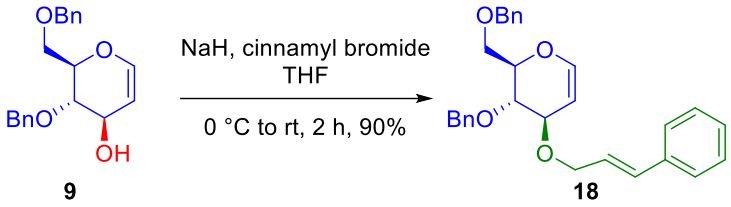
Compounds **17a** and **17b** were obtained as inseparable mixture from **16** (200 mg, 0.399 mmol) by following general **procedure C**. Combined yield: 176 mg, 88%, **17a**:**17b** in 1:2 ratio), colorless gel. R_f = 0.5. (10% EtOAc/hexane).

Selected data for Major Product 17b:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.35 (m, 15H), 5.93 (dd, 1H, *J* = 11 Hz, *J* = 17.5 Hz) 5.21 (s, 1H), 4.95-4.98 (m, 1H), 4.91 (d, 1H, *J* = 11.0 Hz), 4.86 (d, 1H, *J* = 11.0 Hz), 4.64-4.69 (m, 2H), 4.49-4.53 (m, 3H), 4.23 (d, 1H, *J* = 10.0 Hz), 4.12-4.14 (m, 1H), 4.75-4.78 (m, 1H), 3.72 (dd, 1H, *J* = 2.0 Hz, *J* = 11.0 Hz), 2.63 (s, 1H), 1.10 (s, 3H), 1.09 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 206.3, 145.3, 138.2, 137.3, 137.1, 128.5, 128.4, 128.3 (3), 127.7 (2), 127.6, 127.4, 112.5, 99.0, 78.5, 73.4, 73.2, 72.2, 69.0, 68.8, 65.9, 37.8, 27.7, 24.6.

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ calcd for $C_{32}H_{36}O_5NH_4$ 518.2906, found 518.2907.



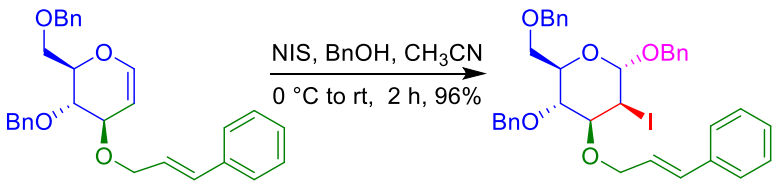
9 **18**

(2*R*,3*S*,4*R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-(cinnamyloxy)-3,4-dihydro-2*H*-pyran (18): Compound **18** was synthesized from **9**[2] (400 mg, 1.22 mmol) by following general **procedure D.** Yield: 488.1 mg, 90%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 0.8 (*c* 0.25, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.39 (m, 15H), 6.63 (d, 1H, *J* = 15.5 Hz), 6.46 (d, 1H, *J* = 6.0 Hz), 6.30 (dt, 1H, J = 6.0 Hz, *J* = 10.0 Hz), 4.88-4.91 (m, 2H), 4.71 (d, 1H, *J* = 11.5 Hz), 4.64 (d, 1H, *J* = 12.0 Hz), 4.60 (d, 1H, *J* = 12.0 Hz), 4.28-4.32 (m, 1H), 4.20-4.24 (m, 2H), 4.08-4.12 (m, 1H), 3.88 (dd, 1H, *J* = 6.5 Hz, *J* = 8.5 Hz), 3.80-3.85 (m, 2H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.7, 138.2, 137.9, 136.6, 132.2, 128.5, 128.4, 128.3, 127.9, 127.7, 127.7, 127.6, 127.6, 126.4, 126.1, 100.1, 76.7, 75.7, 74.4, 73.8, 73.5, 69.1, 68.5

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{29}H_{30}O_4Na$ 465.2036, found 465.2035



18 **19**

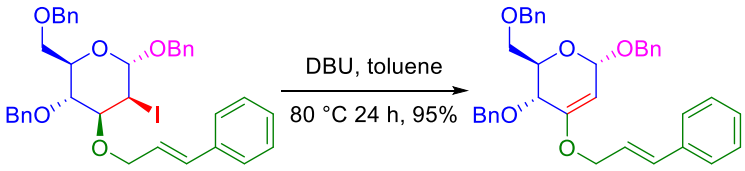
(2S,3S,4S,5R,6R)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-4-(cinnamyloxy)-3-iodotetrahydro-2H-pyran (19): Compound **19** was synthesized from **18** (400 mg, 0.90 mmol)

by following general **procedure A.** Yield: 587.1 mg, 96%, colorless gel. R_f = 0.7 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 16.1 (*c* 0.75, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.44 (m, 20H), 6.69 (d, 1H, *J* = 16.0 Hz), 6.35 (dt, 1H, *J* = 6.0 Hz, *J* = 15.5 Hz), 5.36 (s, 1H), 4.95 (d, 1H, *J* = 11.0 Hz), 4.78(d, 1H, *J* = 12.5 Hz), 4.73 (d, 1H, *J* = 11.5 Hz), 4.56-4.61 (m, 3H), 4.52 (d, 1H, *J* = 12.0 Hz), 4.36 (dd, 1H, *J* = 6.0 Hz, *J* = 12.5 Hz), 4.23 (dd, 1H, *J* = 6.0 Hz, *J* = 12.5 Hz), 3.96 (m, 2H), 3.83-3.86 (m, 1H), 3.75 (d, 1H, *J* = 10.5 Hz), 3.38 (t, 1H, *J* = 4.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 138.2, 136.8, 136.5, 132.8, 128.5, 128.4(2), 128.3, 128.3, 128.0, 128.0, 127.9, 127.7, 127.6, 127.5, 126.5, 125.5, 100.7, 76.7, 76.1, 75.2, 73.4, 72.4, 69.8, 69.4, 68.8, 33.9

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{36}H_{37}IO_5Na$ 699.1578, found 699.1578



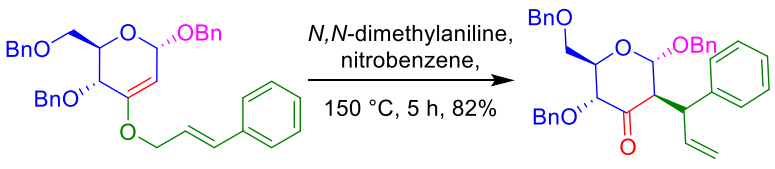
19 **20**

(2*R*,3*R*,6*S*)-3,6-bis(benzyloxy)-2-((benzyloxy)methyl)-4-(cinnamyloxy)-3,6-dihydro-2*H*-pyran (20): Compound **20** was synthesized from **19** (400 mg, 0.59 mmol) by following general procedure B. Yield: 308.1 mg, 95%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 55.1 (*c* 0.22, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.38 (m, 20H), 6.69 (d, 1H, *J* = 16.0 Hz), 6.35 (dt, 1H, *J* = 6.0 Hz, *J* = 16 Hz), 5.33 (d, 1H, *J* = 3.5 Hz), 4.92 (d, 1H, *J* = 11.5 Hz), 4.88 (d, 1H, *J* = 3.5 Hz), 4.80 (d, 1H, *J* = 11.5 Hz), 4.65 (d, 1H, *J* = 12.5 Hz), 4.61 (d, 1H, *J* = 11.5 Hz), 4.49-4.54 (m, 3H), 4.20-4.45 (m, 1H), 4.30 (d, 1H, *J* = 9.5 Hz), 4.19-4.22 (m, 1H), 3.72 (dd, 1H, *J* = 4.0 Hz, *J* = 10.5 Hz), 3.62 (dd, 1H, *J* = 2.0 Hz, *J* = 10.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.8, 138.4, 138.3, 138.2, 136.4, 133.0, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.9, 127.6, 127.6, 127.5, 126.5, 123.9, 95.9, 95.4, 74.0, 73.4, 71.3, 69.8, 68.8, 68.0

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{36}H_{36}O_5Na$ 571.2455, found 571.2454



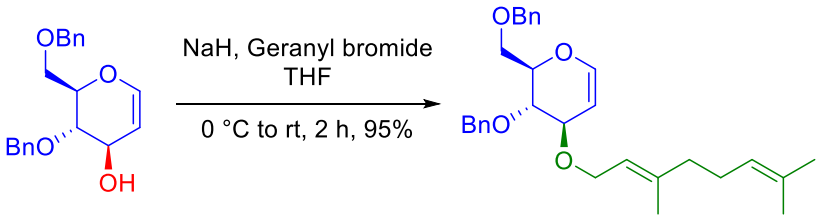
20 **21**

(2*S*,3*R*,5*R*,6*R*)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3-((*R*)-1-phenylallyl)tetrahydro-4*H*-pyran-4-one (21) : Compound **21** was synthesized from **20** (245.9 mg, 0.54 mmol) by following general **procedure C.** Yield: 245.9 mg, 82%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 70.8 (*c* 0.25, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.37 (m, 20H), 5.88-5.97 (m, 1H), 5.06 (d, 1H, *J* = 7.6 Hz), 5.03 (s, 1H), 4.88 (d, 1H, *J* = 11.2 Hz), 4.76 (s, 1H), 4.70 (d, 1H, *J* = 12.0 Hz), 4.60 (d, 1H, *J* = 12.0 Hz), 4.55 (d, 1H, *J* = 12.0 Hz), 4.43 (d, 1H, *J* = 11.2 Hz), 4.33-4.38 (m, 2H), 4.08-4.11 (m, 1H), 3.83 (dd, 1H, *J* = 3.6 Hz, *J* = 10.8 Hz), 3.72-3.77 (m, 2H), 3.11 (d, 1H, *J* = 11.6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 205.6, 140.6, 138.3, 138.1, 137.4, 136.9, 129.0, 128.4, 128.4, 128.4, 128.3, 128.0, 127.6(2), 127.5(3), 127.2, 116.2, 99.9, 77.4, 73.6, 73.4, 73.1, 69.3, 68.8, 61.9, 50.6

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{36}H_{36}O_5Na$ 571.2455, found 571.2454



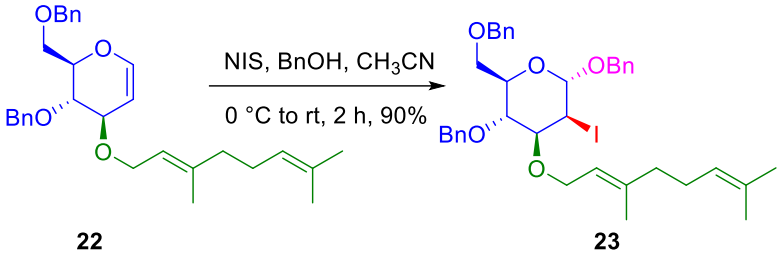
9 **22**

(2*R*,3*S*,4*R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-(((E)-3,7-dimethylocta-2,6-dien-1-yl)oxy)-3,4-dihydro-2*H*-pyran (22): Compound **22** was synthesized from **9**[2] (500 mg, 1.53 mmol) by following general **procedure D.** Yield: 673.24 mg, 95%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 6.6 (*c* 0.30, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.39 (m, 10H), 6.46 (dd, 1H, *J* = 1.0 Hz, *J* = 6.0 Hz), 5.39-5.42 (m, 1H), 5.13-5.16 (m, 1H), 4.89-4.92 (m, 2H), 4.70 (d, 1H, *J* = 11.5 Hz), 4.65 (d, 1H, *J* = 12.5 Hz), 4.60 (d, 1H, *J* = 12.0 Hz), 4.16-4.20 (m, 2H), 4.07-4.12 (m, 2H), 3.82-3.87 (m, 3H), 2.12-2.18 (m, 2H), 2.07-2.10 (m, 2H), 1.73 (d, 3H, *J* = 1.0 Hz), 1.70 (s, 3H), 1.65 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 140.1, 138.4, 138.1, 131.7, 128.4, 128.4, 127.9, 127.8, 127.7, 127.7, 124.0, 121.0, 100.5, 76.8, 75.6 , 74.4, 73.7, 73.5, 68.7, 65.1, 39.6, 26.4, 25.8, 17.8, 16.6

HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{30}H_{38}O_5H$ 463.2843, found 463.2844.



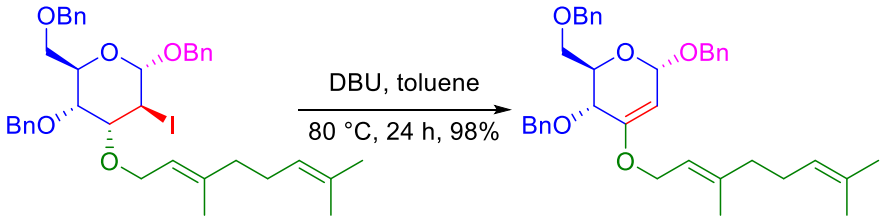
22 **23**

(2*S*,3*S*,4*S*,5*R*,6*R*)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-4-(((E)-3,7-dimethylocta-2,6-dien-1-yl) oxy)-3-iodotetrahydro-2*H*-pyran (23): Compound **23** was synthesized from **22** (500 mg, 1.08 mmol) by following general **procedure A.** Yield: 677.7 mg, 90%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 73.2 (*c* 0.25, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21-7.41 (m, 15H), 5.44 (t, 1H, *J* = 6.5 Hz), 5.34 (s, 1H), 5.11 (t, 1H, *J* = 6.5 Hz), 4.92 (d, 1H, *J* = 10.5 Hz), 4.74 (d, 1H, *J* = 12.5 Hz), 4.71 (d, 1H, *J* = 12.5 Hz), 4.56-4.58 (m, 2H), 4.49-4.52 (m, 2H), 4.20 (dd, 1H, *J* = 7.0 Hz), 4.00 (dd, 1H, *J* = 6.5 Hz, *J* = 11.0 Hz), 3.92-3.95 (m, 1H), 3.86-3.91 (m, 1H), 3.81 (dd, 1H, *J* = 4.5 Hz, *J* = 10.5 Hz), 3.71-3.73 (m, 1H), 3.25 (dd, 1H, *J* = 4.0 Hz, *J* = 8.5 Hz), 2.09-2.12 (m, 2H), 2.04-2.07 (m, 2H), 1.69 (s, 6H), 1.61 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.8, 138.5, 137.0, 131.7, 128.5, 128.3, 128.3(2), 128.1, 128.0 (2), 127.6(2), 127.5, 123.9, 120.4, 100.8, 76.6, 75.9, 75.2, 73.4, 72.5, 69.5, 69.0, 65.5, 39.6, 34.2, 26.4, 25.7, 17.7, 16.6

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ calcd for $C_{37}H_{45}IO_5H$ 714.2655, found 714.2650.



23 **24**

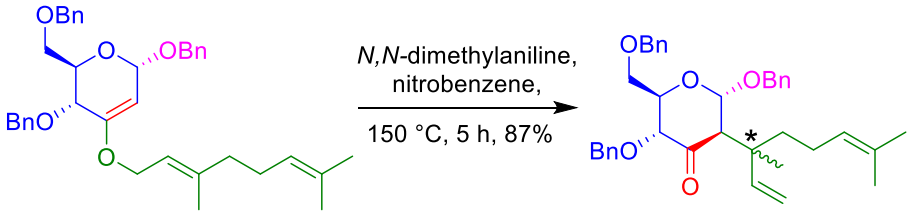
(2*R*,3*R*,6*S*)-3,6-bis(benzyloxy)-2-((benzyloxy)methyl)-4-(((E)-3,7-dimethylocta-2,6-dien-1-yl)oxy)-3,6-dihydro-2*H*-pyran (24): Compound **24** was synthesized from **23** (500 mg, 0.71 mmol) by following general procedure B. Yield: 399.9 mg, 98%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 84.0 (*c* 0.17, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23-7.35 (m, 15H), 5.41 (t, 1H, *J* = 6.5 Hz), 5.29 (d, 1H, *J* = 4.0 Hz), 5.07-5.10 (m, 1H), 4.85 (d, 1H, *J* = 10.5 Hz), 4.78 (d, 1H, *J* = 3.5 Hz), 4.76 (d, 1H, *J* = 11.5 Hz), 4.61 (d, 1H, *J* = 12.5 Hz), 4.57 (d, 1H, *J* = 12.0 Hz), 4.46 (d, 1H, *J* = 12.5 Hz),

4.43 (d, 1H, *J* = 11.0 Hz), 4.31 (dd, 1H, *J* = 6.5 Hz, *J* = 11.5 Hz), 4.24-4.26 (m, 1H), 4.22 (d, 1H, *J* = 9.5 Hz), 4.14-4.17 (m, 1H), 3.67 (dd, 1H, *J* = 4.0 Hz, *J* = 10.5 Hz), 3.58 (dd, 1H, J = 2.0 Hz, J = 10.5 Hz), 2.08-2.11 (m, 2H), 2.03-2.06 (m, 2H), 1.66 (s, 6H), 1.59 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 141.0, 138.5, 138.3, 138.2, 131.8, 128.4, 128.2 (2), 128.1, 127.9, 127.6 (3), 123.8, 119.1, 95.5, 95.3, 73.8, 73.4, 71.1, 69.8, 69.7, 68.8, 64.3, 39.5, 26.4, 25.7, 17.7, 16.6

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{37}H_{44}O_5Na$ 591.3086, found 591.3084.



24 **25** (* 5:1 mixture)

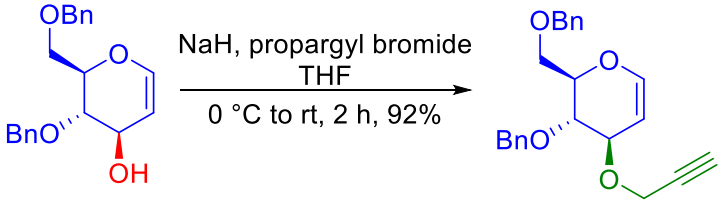
(2*S*,3*R*,5*R*,6*R*)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3-(3,7-dimethylocta-1,6-dien-3-yl)tetrahydro-4*H*-pyran-4-one (25): Compound **25** was synthesized as an inseparable diastereomeric mixture from **24** (250 mg, 0.43 mmol) by following general **procedure C.** Yield: 217.4 mg, 87%, colorless gel. R_f = 0.5. (10% EtOAc/hexane).

Selected data for major diastereomer of 25:

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.36 (m, 15H), 5.88 (dd, 1H, *J* = 10.8 Hz, *J* = 17.6 Hz), 5.21 (s, 1H), 5.04-5.07 (m, 2H), 4.89 (d, 1H, *J* = 17.2 Hz), 4.88-4.93 (m, 2H), 4.84 (d, 1H, *J* = 11.2 Hz), 4.69 (d, 1H, *J* = 12.0 Hz), 4.65 (d, 1H, *J* = 12.0 Hz), 4.52 (d, 1H, *J* = 2.8 Hz), 4.50 (d, 1H, *J* = 3.2 Hz), 4.44 (d, 1H, *J* = 11.2 Hz), 4.18 (d, 1H, *J* = 10.0 Hz), 4.07-4.12 (m, 1H), 3.77 (dd, 1H, *J* = 4.0 Hz, *J* = 10.4 Hz), 3.72 (dd, 1H, *J* = 2.0 Hz, *J* = 10.8 Hz), 2.75 (s, 1H), 1.93-2.03 (m, 1H), 1.82-1.90 (m, 1H), 1.70 (s, 3H), 1.60 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 206.1, 143.6, 138.2, 137.3, 137.1, 131.8, 128.5, 128.4, 128.3, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 124.0, 113.4, 98.2, 78.7, 73.3, 73.2, 72.3, 69.0, 68.9, 65.2, 40.7, 39.6, 25.7, 22.5, 21.6, 17.7.

HRMS (ESI-TOF) *m/z*: [M+H] calcd for $C_{37}H_{44}O_5H$ 569.3262, found 569.3267.



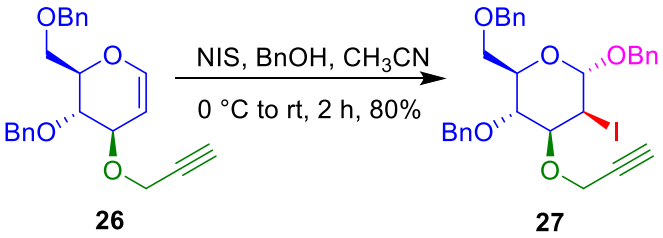
9 **26**

(2*R*,3*S*,4*R*)-3-(benzyloxy)-2-((benzyloxy)methyl)-4-(prop-2-yn-1-yloxy)-3,4-dihydro-2*H*-pyran (26): Compound **26** was synthesized from **9**[2] (400 mg, 1.22 mmol) by following general **procedure D.** Yield: 410.8 mg, 92%, colourless gel. R_f = 0.5 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 55.8 (*c* 0.50, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.38 (m, 10H), 6.46 (dd, 1H, *J* = 1.5 Hz, *J* = 7.5 Hz), 4.90 (dd, 1H, *J* = 3.5 Hz, *J* = 8.0 Hz), 4.89 (d, 1H, *J* = 13.0 Hz), 4.68 (d, 1H, *J* = 14.0 Hz), 4.62 (s, 1H), 4.61 (s, 1H), 4.33-4.36 (m, 1H), 4.25-4.26 (m, 2H), 4.08-4.13 (m, 1H), 3.80-3.87 (m, 3H), 2.46 (t, 1H, *J* = 5.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 145.1, 138.2, 138.0, 128.4(2), 128.0, 127.8 (2), 127.7, 99.4, 80.0, 76.8, 75.4, 74.5, 74.2, 73.7, 73.5, 68.5, 55.9

HRMS (ESI-TOF) *m/z*: $[M+NH_4]^+$ calcd for $C_{23}H_{24}O_4NH_4$ 382.2013, found 382.2013



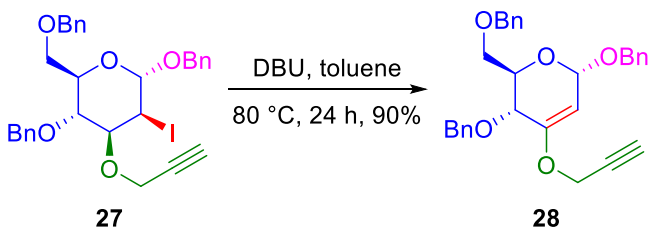
26 **27**

(2*S*,3*S*,4*S*,5*R*,6*R*)-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)-3-iodo-4-(prop-2-yn-1-yloxy)tetrahydro-2*H*-pyran (27): Compound **27** was synthesized from **26** (300 mg, 0.82 mmol) by following general **procedure A.** Yield: 394.19 mg, 80%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 30.5 (*c* 0.35, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.44 (m, 15H), 5.34 (s, 1H), 4.90 (d, 1H, *J* = 10.5 Hz), 4.78 (d, 1H, *J* = 12.0 Hz), 4.73 (d, 1H, *J* = 12.0 Hz), 4.60 (dd, 1H, *J* = 1. Hz, *J* = 4.5 Hz), 4.58 (d, 1H, *J* = 12.0 Hz), 4.53 (t, 2H, *J* = 10.0 Hz), 4.38 (dd, 1H, *J* = 2.0 Hz, *J* = 15.0 Hz), 4.28 (dd, 1H, *J* = 2.5, *J* = 16.0 Hz), 3.95 (d, 2H, *J* = 5.5 Hz), 3.81-3.84 (m, 1H), 3.73 (d, 1H, *J* = 10.5 Hz), 3.50-3.52 (m, 1H), 2.49 (t, 1H, *J* = 2.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4, 138.2, 136.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.8, 127.7, 127.5, 100.7, 79.3, 76.7, 76.0, 75.3, 75.1, 73.4, 72.4, 69.5, 68.8, 56.8, 33.1.

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{30}H_{31}IO_5Na$ 621.1108, found 621.1107



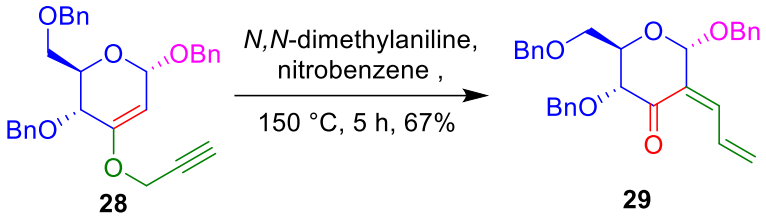
27 **28**

(2*R*,3*R*,6*S*)-3,6-bis(benzyloxy)-2-((benzyloxy)methyl)-4-(prop-2-yn-1-yloxy)-3,6-dihydro-2H-pyran (28): Compound **28** was synthesized from **27** (300 mg, 0.50 mmol) by following general procedure **B**. Yield: 212.2 mg, 90%, colorless gel. R_f = 0.5 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 24.2 (*c* 0.70, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.37 (m, 15H), 5.33 (d, 1H, *J* = 3.5 Hz), 4.88-4.93 (m, 2H), 4.79 (d, 1H, *J* = 12.0 Hz), 4.64 (d, 1H, *J* = 12.0 Hz), 4.60 (d, 1H, J = 12.0 Hz), 4.54 (dd, 1H, *J* = 2.5 Hz, *J* = 10.5), 4.45-4.51 (m, 3H), 4.28 (d, 1H, *J* = 9.0 Hz), 4.16-4.21 (m, 1H), 3.70 (dd, 1H, *J* = 4.0 Hz, *J* = 10.5 Hz), 3.61 (dd, 1H, *J* = 2.0 Hz, *J* = 10.5 Hz), 2.54 (t, 1H, *J* = 2.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9, 138.3, 138.1(2), 128.4(3), 128.3, 128.2, 128.1, 127.9, 127.7, 127.6, 96.7, 95.1, 77.9, 75.7, 74.1, 73.4, 71.0, 69.9, 69.7, 68.6, 55.2

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{30}H_{30}O_5Na$ 493.1985, found 493.1986.



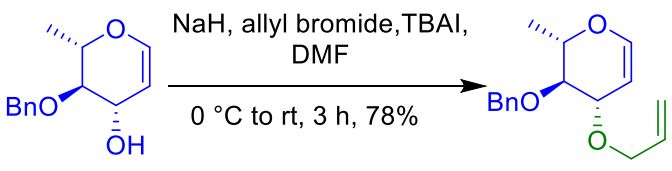
28 **29**

(2*S*,5*R*,6*R*,*Z*)-3-allylidene-2,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-4*H*-pyran-4-one (29): Compound **29** was synthesized from **28** (200 mg, 0.42 mmol) by following general **procedure C.** Yield: 133.9 mg, 67%, colorless gel. R_f = 0.5. (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 32.0 (*c* 0.05, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.36 (m, 15H), 7.17 (d, 1H, *J* = 15.0 Hz), 6.30-6.39 (m, 1H), 5.77 (m, 2H), 5.65 (d, 1H, *J* = 12.5 Hz), 5.10 (d, 1H, *J* = 13.5 Hz), 4.81 (d, 1H, *J* = 15.0 Hz), 4.67 (d, 1H, *J* = 15.0 Hz), 4.53-4.63 (m, 3H), 4.35-4.39 (m, 1H), 4.12 (d, 1H, *J* = 13.0 Hz), 3.76 (dd, 1H, *J* = 5.0 Hz, *J* = 13.0 Hz), 3.68 (dd, 1H, *J* = 2.5 Hz, *J* = 13.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 197.1, 139.4(2), 137.9, 137.7, 137.0, 132.1, 130.6, 129.7, 128.4, 128.4, 128.4, 128.3, 128.3, 128.0, 127.8, 127.7, 95.2, 77.2, 74.7, 73.5, 69.3, 69.1, 68.7

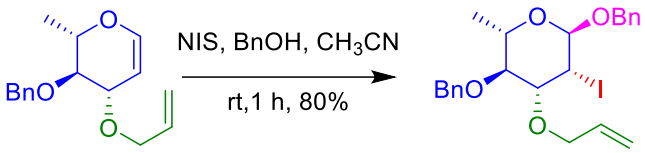
HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{30}H_{30}O_5Na$ 493.1985, found 493.1985



S1 **30**

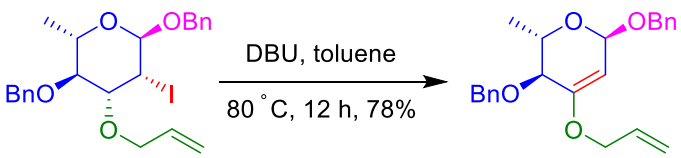
(2*S*,3*S*,4*S*)-4-(allyloxy)-3-(benzyloxy)-2-methyl-3,4-dihydro-2*H*-pyran (30): Compound **30** was synthesized from **S1** (500 mg, 2.27 mmol) by following general **procedure D.** Yield: 460.9 mg, 78%, colorless gel. R_f = 0.7 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = 6.1 (*c* 0.75, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.37 (m, 5H), 6.34 (dd, 1H, *J* = 1.0 Hz, *J* = 6.0 Hz), 5.90-5.98 (m, 1H), 5.28-5.33 (m, 1H), 5.17-5.19 (m, 1H), 4.88 (d, 1H, *J* = 11.5 Hz), 4.82 (dd, 1H, *J* = 2.5 Hz, *J* = 6.0 Hz), 4.70 (d, 1H, *J* = 11.5 Hz), 4.12-4.15 (m, 2H), 4.02-4.06 (m, 1H), 3.91-3.96 (m, 1H), 3.42 (dd, 1H, *J* = 6.5 Hz), 1.37 (d, 3H, *J* = 6.0 Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 144.7, 138.3 , 135.0, 128.4, 128.0, 127.8, 116.8, 100.3, 79.5, 76.5, 74.1, 74.0, 69.5, 17.5
HRMS (ESI-TOF) *m/z*: [M+H] calc for $C_{16}H_{20}O_3H$ 261.1491, found 261.1493.



30 **31**

(2*R*,3*R*,4*R*,5*S*,6*S*)-4-(allyloxy)-2,5-bis(benzyloxy)-3-iodo-6-methyltetrahydro-2*H*-pyran (31): Compound **31** was synthesized from **30** (400 mg, 1.15 mmol) by following general **procedure A.** Yield: 607.7 mg, 80%, colorless gel. R_f = 0.5 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = -28.8 (*c* 2.00, $CHCl_3$).
^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.39 (m, 10H), 5.97-6.04 (m, 1H), 5.39 (dd, 1H, *J* = 1.5 Hz, *J* = 17.5 Hz), 5.24 (d, 2H, *J* = 10 Hz), 4.98 (d, 1H, *J* = 10.5 Hz), 4.69 (d, 1H, *J* = 12.0 Hz), 4.67 (d, 1H, *J* = 11 Hz), 4.56 (d, 1H, *J* = 4.0 Hz), 4.50 (d, 1H, *J* = 12 Hz), 4.19 (dd, 1H, *J* = 5.5 Hz, *J* = 12.5 Hz), 4.05 (dd, 1H, *J* =5.5 Hz, *J* = 12.5 Hz), 3.87-3.93 (m, 1H), 3.51 (t, 1H, *J* = 9.0 Hz), 3.23 (dd, 1H, *J* = 4 Hz, *J* = 8.5 Hz), 1.36 (d, 3H, *J* = 6.0 Hz).
^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 136.9, 134.3, 128.4, 128.3, 128.1, 127.9, 127.9, 127.7, 117.2, 100.7, 81.6, 76.6, 75.4, 69.9, 69.4, 68.4, 34.4, 17.9.
HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{23}H_{27}IO_4Na$ 517.0852, found 517.0856.



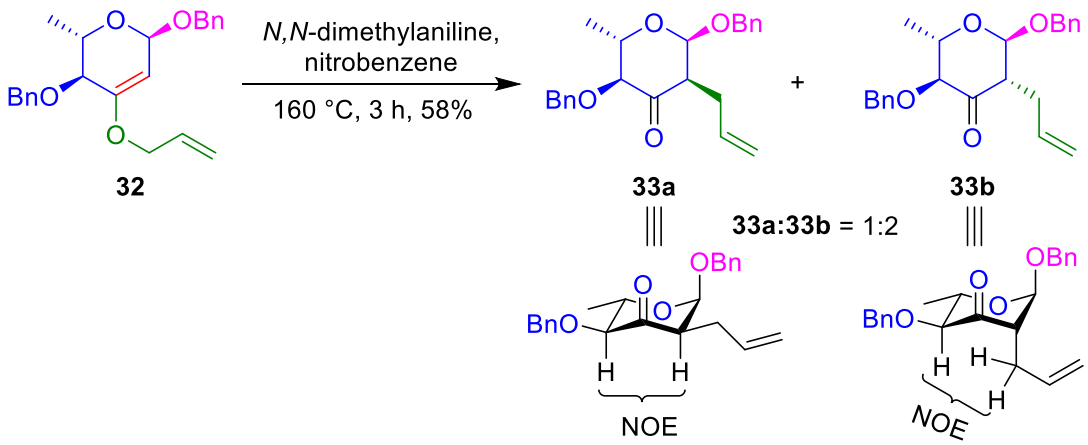
31 **32**

(2*S*,3*S*,6*R*)-4-(allyloxy)-3,6-bis(benzyloxy)-2-methyl-3,6-dihydro-2*H*-pyran (32): Compound **32** was synthesized from **31** (300 mg, 0.60 mmol) by following general **procedure B.** Yield: 173.4 mg, 78%, colorless gel. R_f = 0.4 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = -100.6 (*c* 0.50, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.36 (m, 10H), 5.96-6.03 (m, 1H), 5.36 (dd, 1H, *J* = 1.5 Hz, *J* = 17.5), 5.25 (dd, 1H, *J* = 1.0 Hz, *J* = 10.5 Hz), 5.20 (d, 1H, *J* = 3.5 Hz), 4.93 (d, 1H, *J* = 11.0 Hz), 4.78 (d, 1H, *J* = 3.0 Hz), 4.74 (d, 1H, *J* = 12.0 Hz), 4.59 (d, 1H, *J* = 11.0 Hz), 4.57 (d, 1H, *J* = 12.0 Hz), 4.32-4.35 (m, 1H), 4.24-4.28 (m, 1H), 4.12-4.16 (m, 1H), 3.77 (d, 1H, *J* = 9.0 Hz), 1.24 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 138.4, 138.3, 132.7, 128.5, 128.3, 128.2, 128.1, 127.9, 127.6, 127.5, 117.5, 95.8, 95.2, 73.8, 69.6, 68.1, 66.1, 18.2

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{23}H_{26}O_4NH_4$ 384.2174, found 384.2175.



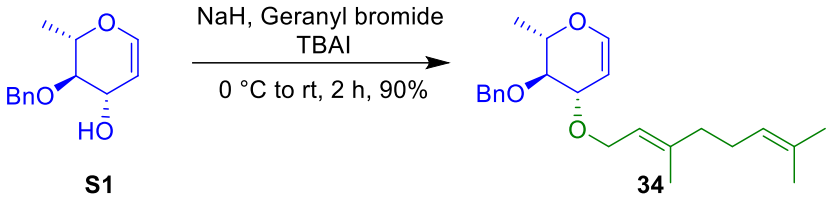
(2*R*,3*R*,5*S*,6*S*)-3-allyl-2,5-bis(benzyloxy)-6-methyltetrahydro-4H-pyran-4-one (33a) and (2*R*,3*S*,5*S*,6*S*)-3-allyl-2,5-bis(benzyloxy)-6-methyltetrahydro-4H-pyran-4-one (33b): Compounds **33a** and **33b** were was synthesized from **32** (200 mg, 0.42 mmol) by following general **procedure C.** Yield: 159.9 mg, 58%, **33a**:**33b** (1:2). colorless gel. R_f = 0.7. (10% EtOAc/hexane). $[\alpha]_D^{25}$ = -37.0 (*c* 0.10, $CHCl_3$).

Selected data for the mixture 33a and 33b:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.39 (m, 15H), 5.67-5.76 (m, 1.5H), 5.05-5.11 (m, 3H), 4.96-5.01 (m, 1.5H), 4.91-4.94 (m, 2H), 4.69 (dd, 1.5H, *J* = 3.5, 12 Hz), 4.45-4.52 (m, 3H), 4.07-4.14 (m, 1.5H), 3.74 (d, 1H, *J* = 10 Hz), 3.69 (d, 0.5H, *J* = 10 Hz), 2.75-2.81 (m, 1.5H), 2.57-2.62 (m, 0.5H), 2.37-2.49 (m, 2H), 2.19-2.25 (m, 0.5H), 1.40 (d, 1.5H, *J* = 6 Hz), 1.38 (d, 3H, *J* = 6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 206.2, 204.0, 137.3, 136.9, 136.8, 135.1, 133.8, 128.3, 128.3,128.2, 127.9, 127.8, 127.7, 117.7, 116.9, 100.5, 99.6, 84.5, 82.0, 73.1, 73.0, 70.1, 69.4, 69.1, 69.0, 56.0, 53.5, 34.3, 28.1, 18.9, 18.8.

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{23}H_{26}O_4NH_4$ 384.2174, found 384.2172.

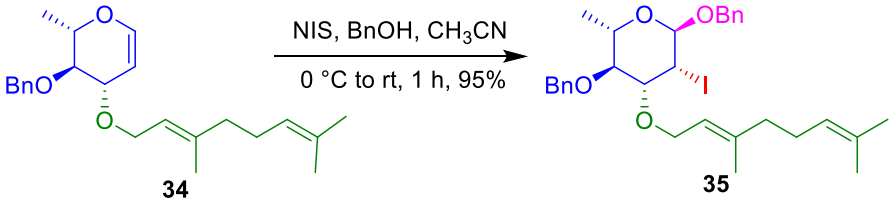


(2*S*,3*S*,4*S*)-3-(benzyloxy)-4-(((E)-3,7-dimethylocta-2,6-dien-1-yl)oxy)-2-methyl-3,4-dihydro-2*H*-pyran (34): Compound **34** was synthesised from **S1** 500 mg, 2.27 mmol) by following general **procedure D.** Yield: 728.32 mg, 90%, colorless gel. R_f = 0.6 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.40 (m, 5H), 6.36-6.37 (m, 1H), 5.38-5.41 (m, 1H), 5.10-5.13 (m, 1H), 4.93 (d, 1H, *J* = 11.35 Hz), 4.85-4.87 (m, 1H), 4.73 (d, 1H, *J* = 11.35 Hz), 4.12-4.19 (m, 2H), 4.06-4.09 (m, 1H), 3.92-3.98 (m, 1H), 3.42-3.45 (m, 1H), 2.11-2.14 (m, 2H), 2.04-2.08 (m, 2H), 1.70 (s, 6H), 1.62 (s, 3H), 1.39 (d, 3H, J = 6.4 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.5, 140.0, 138.4, 131.6, 128.3, 127.9, 127.6, 123.9, 121.0, 100.6, 79.5, 76.2, 73.9(2), 65.0, 39.6, 26.3, 25.6, 17.7, 17.5, 16.5

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{23}H_{32}O_3Na$ 379.2249, found 379.2252



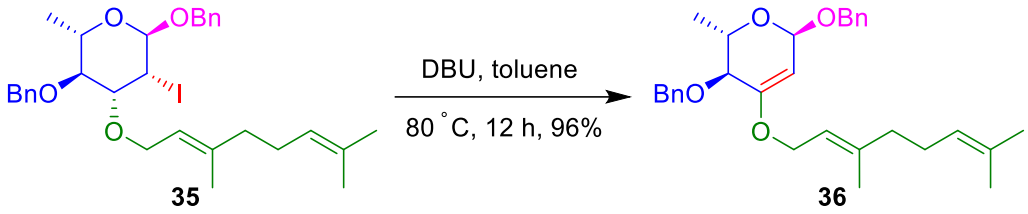
(2*R*,3*R*,4*R*,5*S*,6*S*)-2,5-bis(benzyloxy)-4-(((E)-3,7-dimethylocta-2,6-dien-1-yl)oxy)-3-iodo-6-methyltetrahydro-2*H*-pyran (35): Compound **35** was synthesized from **34** (400 mg, 1.12 mmol) by following general **procedure A.** Yield: 627.7 mg, 95%, colorless gel. R_f = 0.7 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.36 (m, 10H), 5.42-5.45 (m, 1H), 5.22 (s, 1H), 5.09-5.11 (m, 1H), 4.97 (d, 1H, *J* = 11.0 Hz), 4.66-4.69 (m, 1H), 4.63 (d, 1H, *J* = 11.0 Hz), 4.56 (dd, 1H, *J* = 1.5 Hz, *J* = 4.0 Hz), 4.47 (d, 1H, *J* = 12.0 Hz), 4.19 (dd, 1H, *J* = 7.0 Hz, *J* = 11.5 Hz), 3.99 (dd, 1H, *J* = 6.5 Hz, *J* = 11.0 Hz), 3.84-3.88 (m, 1H), 3.45 (t, 1H, *J* = 9.0 Hz), 3.18

(dd, 1H, *J* = 4.0 Hz, *J* = 8.5 Hz), 2.08-2.13 (m, 2H), 2.03-2.06 (m, 2H), 1.68 (s, 6H), 1.60 (s, 3H), 1.33 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 138.5, 137.0, 131.6, 128.4, 128.3, 128.0, 127.9, 127.9, 127.6, 123.9, 120.4, 100.7, 81.6, 76.4, 75.4, 69.4, 68.5, 65.4, 39.6, 35.0, 26.3, 25.6, 18.0, 17.7, 16.6

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{30}H_{39}IO_4Na$ 613.1791, found 613.1790.

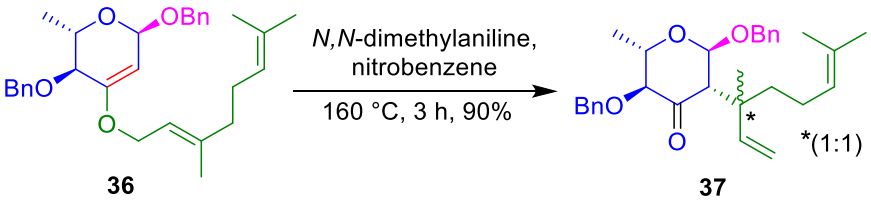


(2*S*,3*S*,6*R*)-3,6-bis(benzyloxy)-4-(((E)-3,7-dimethylocta-2,6-dien-1-yl)oxy)-2-methyl-3,6-dihydro-2*H*-pyran(36): Compound **36** was synthesized from **35** 450 mg, 0.76 mmol) by following general procedure B. Yield: 328.1 mg, 96%, colorless gel. R_f = 0.6 (10%EtOAc/hexane). $[\alpha]_D^{25}$ = -10.0 (*c* 0.05, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.36 (m, 10H), 5.41-5.44 (m, 1H), 5.20 (d, 1H, *J* = 3.5 Hz), 5.08-5.11 (m, 1H), 4.88 (d, 1H, *J* = 11.0 Hz), 4.78 (d, 1H, *J* = 3.0 Hz), 4.74 (d, 1H, *J* = 12.0 Hz), 4.58 (d, 1H, *J* = 11.0 Hz), 4.57 (d, 1H, *J* = 11.5 Hz), 4.32 (dd, 1H, *J* = 6.5 Hz, *J* = 11.5 Hz), 4.25 (dd, 1H, *J* = 6.5, *J* = 11.5 Hz), 4.10-4.16 (m, 1H), 3.75 (d, 1H, *J* = 9.0 Hz), 2.09-2.12 (m, 2H), 2.04-2.07 (m, 2H), 1.67 (s, 6H), 1.60 (s, 3H), 1.24 (d, 3H, *J* = 6.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 140.9, 138.5, 138.4, 131.8, 128.3(2), 128.2(2), 128.0, 127.6, 127.5, 123.8, 119.1, 95.3(2), 73.5, 69.6, 66.1, 64.3, 39.5, 26.3, 25.7, 18.2, 17.7, 16.6

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{30}H_{38}O_4Na$ 485.2668, found 485.2666.

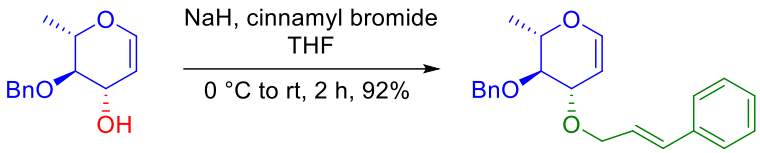


(2*R*,3*S*,5*S*,6*S*)-2,5-bis(benzyloxy)-3-(3,7-dimethylocta-1,6-dien-3-yl)-6-methyltetrahydro-4H-pyran-4-one (37): Compound **37** was synthesized from **36** (300 mg, 0.64 mmol) by following general **procedure C.** Obtained as an inseparable mixture in 1:1 ratio at the newly

generated quaternary stereo-centre. Yield: 269.9 mg, 90%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = -112.0 (*c* 0.05, $CHCl_3$).

^{13}C NMR (125 MHz, $CDCl_3$) (Inseparable mixture): δ 205.7 (2), 143.7(2), 137.8, 137.4, 137.2, 136.7, 128.5, 128.4, 128.3, 128.2, 128.1, 127.9 (2), 127.8 (2), 127.6 (2), 124.0 (2), 120.4, 113 (2), 101.6, 98.5, 85.3, 84.9, 83.9, 75.2, 72.9, 71.4, 71.2, 70.1, 68.8, 68.7, 65.1, 40.5, 39.6, 39.4, 33.3, 26.3, 25.6 (2), 22.4, 21.8, 18.8, 17.7, 17.6, 16.7.

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{30}H_{38}O_4NH_4$ 480.3114, found 480.3120.



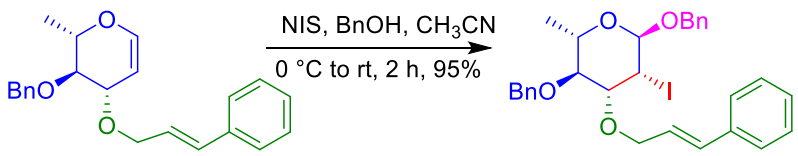
S1 **38**

(2*S*,3*S*,4*S*)-3-(benzyloxy)-4-(cinnamyloxy)-2-methyl-3,4-dihydro-2*H*-pyran(38): Compound **38** was synthesized from **S1** (500 mg, 2.27 mmol) by following general **procedure D.** Yield: 702.5 mg, 92%, colorless gel. R_f = 0.7 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.39 (m, 10H), 6.62 (d, 1H, *J* = 16.0 Hz), 6.37 (dd, 1H, *J* = 1.0 Hz, *J* = 6.0 Hz), 6.30 (dt, 1H, J = 6.0 Hz, J = 16.0 Hz), 4.92 (d, 1H, *J* = 11.0 Hz), 4.87 (dd, 1H, *J* = 2.5 Hz, *J* = 6.0 Hz), 4.75 (d, 1H, *J* = 11.0 Hz), 4.29-4.33 (m, 1H), 4.19-4.29 (m, 2H), 3.93-3.99 (m, 1H), 3.47 (dd, 1H, *J* = 6.5 Hz, *J* = 9.0 Hz), 1.40 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8, 138.3, 136.7, 132.2, 128.5, 128.4, 127.9, 127.7, 127.6, 126.4, 126.2, 100.3, 79.6, 76.4, 74.1, 74.0, 69.2, 17.5

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{22}H_{24}O_3Na$ 359.1623, found 359.1622



38 **39**

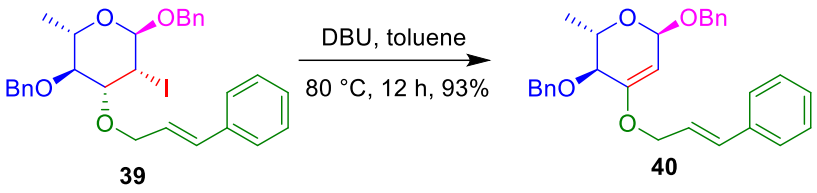
(2*R*,3*R*,4*R*,5*S*,6*S*)-2,5-bis(benzyloxy)-4-(cinnamyloxy)-3-iodo-6-methyltetrahydro-2*H*-pyran (39): Compound **39** was synthesized from **38** (400 mg, 1.18 mmol) by following general **procedure A.** Yield: 644.4 mg, 95%, colorless gel. R_f = 0.7 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.27-7.38 (m, 15H), 6.67 (d, 1H, *J* = 16.0 Hz), 6.32 (dt, 1H, J = 6.0 Hz, J = 15.5 Hz), 5.23 (s, 1H), 4.99 (d, 1H, *J* = 11.0 Hz), 4.68 (bs, 1H), 4.66 (d, 1H, *J* = 2.5 Hz), 4.57 (dd, 1H, *J* = 1.5 Hz, *J* = 4.0 Hz), 4,47 (d, 1H, *J* = 11.5 Hz), 4.31-4.35 (m, 1H),

4.18-4.22 (m, 1H), 3.86-3.92 (m, 1H), 3.51 (t, 1H, *J* = 9.0 Hz), 3.27 (dd, 1H, *J* = 4.0 Hz, *J* = 8.5 Hz), 1.35 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4, 137.0, 136.6, 132.7, 128.5, 128.4, 128.4, 128.0, 127.9, 127.9, 127.7, 127.7, 126.5, 125.6, 100.7, 81.7, 76.6, 75.5, 69.7, 69.4, 68.6, 34.7, 18.0

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{29}H_{31}IO_4Na$ 593.1165, found 593.1161.



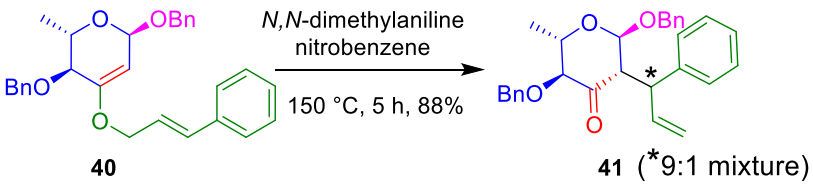
39 **40**

(2*S*,3*S*,6*R*)-3,6-bis(benzyloxy)-4-(cinnamyloxy)-2-methyl-3,6-dihydro-2*H*-pyran (40): Compound **40** was synthesized from **39** (400 mg, 0.70 mmol) by following general procedure **B**. Yield: 288.5 mg, 93%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = -32.0 (*c* 0.05, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.38 (m, 15H), 6.68 (d, 1H, *J* = 16.0 Hz), 6.34 (dt, 1H, J = 5.5 Hz, J = 16.0 Hz), 5.22 (d, 1H, *J* = 3.5 Hz), 4.94 (d, 1H, *J* = 11.5 Hz), 4.85 (d, 1H, *J* = 3.5 Hz), 4.76 (d, 1H, *J* = 12.0 Hz), 4.63 (d, 1H, *J* = 11.0 Hz), 4.58 (d, 1H, *J* = 12.0 Hz), 4.48-4.52 (m, 1H), 4.39-4.43 (m, 1H), 4.14-4.19 (m, 1H), 3.80 (d, 1H, *J* = 9.0 Hz), 1.26 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.7, 138.4, 138.3, 136.4, 133.0, 128.6, 128.3, 128.3, 128.1, 127.9 (2), 127.6, 127.5, 126.5, 123.9, 95.9, 95.2, 77.1, 73.7, 69.6, 67.9, 66.1, 18.2

HRMS (ESI-TOF) *m/z*: $[M+Na]^+$ calcd for $C_{29}H_{30}O_5Na$ 469.1997, found 469.1985.



40 **41** (*9:1 mixture)

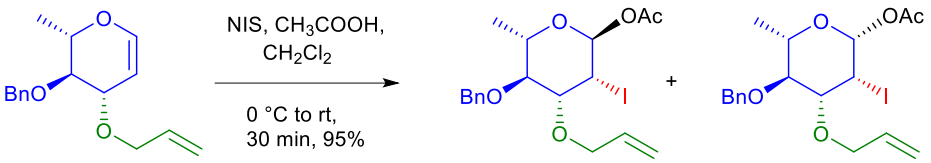
(2*R*,3S,5*S*,6*S*)-2,5-bis(benzyloxy)-6-methyl-3-(1-phenylallyl)tetrahydro-4*H*-pyran-4-one (41): Compound **41** was synthesized (an inseparable mixture of diastereomers at the allylic position) from **40** (200 mg, 0.45 mmol) by following general **procedure C.** Combined yield: 175.9 mg, 88%, colorless gel. R_f = 0.6 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = -96.6 (*c* 0.55, $CHCl_3$).

Data for the major diastereomer of 41:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.13-7.36 (m, 15H), 5.86-5.94 (m, 1H), 5.04 (s, 1H), 5.01 (d, 1H, *J* = 5.0 Hz), 4.90 (d, 1H, *J* = 11.5 Hz), 4.63 (s, 1H), 4.53 (d, 1H, *J* = 12.0 Hz), 4.43 (d, 1H, *J* = 12.0 Hz), 4.28 (d, 1H, *J* = 12.0 Hz), 4.03-4.09 (m, 1H), 3.77 (d, 1H, *J* = 9.5 Hz), 3.61 (dd, 1H, *J* = 10.0 Hz, *J* = 12.0 Hz), 3.06 (d, 1H, *J* = 12.0 Hz), 1.37 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 205.2, 140.6, 138.1, 137.4, 136.9, 129.0, 128.4, 128.3, 128.2, 128.0, 127.6, 127.5, 127.3, 127.2, 116.1, 99.6, 83.0, 72.8, 69.8, 69.2, 62.0, 50.9, 18.9

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{29}H_{30}O_4Na$ 465.2042, found 465.2045



30 **42α** **42β**

(2*S*,3*R*,4*R*,5*S*,6*S*)-4-(allyloxy)-5-(benzyloxy)-3-iodo-6-methyltetrahydro-2*H*-pyran-2-yl acetate (42*α*) and (2R,3R,4R,5S,6S)-4-(allyloxy)-5-(benzyloxy)-3-iodo-6-methyltetrahydro-2H-pyran-2-yl acetate (42β):): Compounds **42*α*** and **42β** were synthesized from **30** (700 mg, 2.63 mmol) by following general **procedure A. 42*α*** yield: 580 mg, 50%, colorless gel. R_f = 0.4 (10% EtOAc/hexane). **42β** yield: 500 mg, 45%, colorless gel. R_f = 0.35 (10% EtOAc/hexane).

Compound 42*α*:

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31-7.43 (m, 5H), 6.35 (d, 1H, *J* = 1.5 Hz), 5.97-6.04 (m, 1H), 5.39 (dq, 1H, J = 1.5 Hz, *J* = 17.5 Hz), 5.25 (dq, 1H, *J* = 1.5 Hz, *J* = 10.5), 4.97 (d, 1H, *J* = 10.5 Hz), 4.50 (dd, 1H, *J* = 1.5 Hz, *J* = 4 Hz), 4.20 (ddt, 1H, *J* = 1.5 Hz, *J* = 5.5 Hz, *J* = 12.5 Hz), 4.06 (ddt, 1H, *J* = 1 Hz, *J* = 5.5 Hz, *J* = 12.5 Hz), 3.89-3.95 (m, 1H), 3.53 (t, 1H, *J* = 9 Hz), 3.12 (q, 1H, *J* = 4.5 Hz), 2.09 (s, 3H), 1.35 (d, 3H, *J* = 6.5).

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.7, 138.1, 134.2, 128.5, 128.2, 127.9, 117.7, 95.3, 81.1, 76.1, 75.6, 70.8, 70.1, 31.9, 20.9, 18.1.

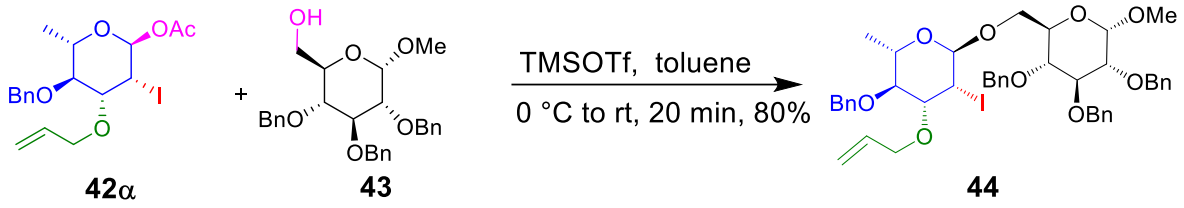
HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{18}H_{23}IO_5Na$ 469.0488, found 469.0486.

Compound 42β: $[\alpha]_D^{25}$ = -51.9 (*c* 2.13, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.37 (m, 5H), 5.98-6.06 (m, 1H), 5.78 (d, 1H, *J* = 9.5), 5.31 (d, 1H, *J* = 17.5 Hz), 5.20 (d, 1H, *J* = 10 Hz), 4.84 (d, 1H, *J* = 11 Hz), 4.63 (d, 1H, *J* = 10.5), 4.36-4.43 (m, 2H), 3.89 (t, 1H, *J* = 10 Hz), 3.53-3.60 (m, 2H), 3.16 (t, 1H, *J* = 9 Hz), 2.13 (s, 3H), 1.29 (d, 3H, *J* = 6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 168.9, 137.6, 134.3, 128.5, 128.0, 117.5, 94.0, 85.1, 84.5, 75.4, 74.6, 72.5, 30.7, 20.8, 17.6.

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{18}H_{23}IO_5Na$ 469.0488, found 469.0486.



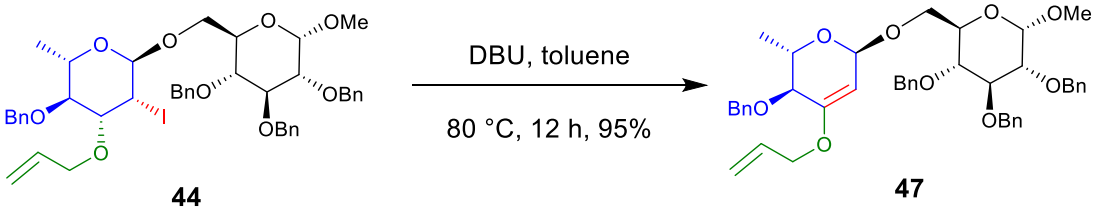
42α **43** **44**

(2*S*,3*S*,4*R*,5*R*,6*R*)-4-(allyloxy)-3-(benzyloxy)-5-iodo-2-methyl-6-(((3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methoxy)tetrahydro-2*H*-pyran (44): To a stirred solution of donor sugar **42*α*** (330 mg, 1.0 eq) and acceptor sugar **43** (376 mg, 1.1 eq) in anhydrous toluene (10 mL/mmol) under an inert atmosphere was added 4 Å molecular sieves and the solution was stirred for 20 min at room temperature. The reaction mixture was further cooled to 0 ˚C. TMSOTf (0.4 eq) was added dropwise to the above reaction mixture, and stirring was continued at 0 °C. After completion of the reaction (~20 min, monitored by TLC) triethylamine (0.6 mmol) at the same temperature to quench the reaction. The solvent was removed under reduced pressure to obtain the crude product, which was purified by column chromatography using hexane and ethyl acetate to obtain the glycosylated product **44** as a single diastereomer (α only) in 80% (502.0 mg). $[\alpha]_D^{25}$ = 40.8 (*c* 1.13, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.32-7.36 (m, 20H), 5.92-6.00 (m, 1H), 5.34 (dd, 1H, *J* = 1.5 Hz, *J* = 17.5 Hz), 5.19 (dd, 1H, *J* = 1.0 Hz, *J* = 10.0 Hz), 5.00 (d, 1H, *J* = 11.5 Hz), 4.99 (bs, 1H), 4.93 (d, 1H, *J* = 11.0 Hz), 4.89 (d, 1H, *J* = 11.0 Hz), 4.82 (d, 1H, *J* = 10.5 Hz), 4.79 (d, 1H, *J* = 12.5 Hz), 4.67 (d, 1H, *J* = 12.0 Hz), 4.61 (d, 1H, *J* = 11.0 Hz), 4.54-4.57 (m, 2H), 4.34-4.35 (m, 1H), 4.11-4.15 (m, 1H), 3.97-4.01 (m, 2H), 3.77-3.80 (m, 2H), 3.69-3.72 (m, 1H), 3.50 (dd, 1H, *J* = 3.5 Hz, *J* = 13.5 Hz), 3.38-3.46 (m, 3H), 3.35 (s, 3H), 3.09 (dd, 1H, *J* = 4.0 Hz, *J* = 8.5 Hz), 1.27 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.6, 138.3, 138.0, 134.4, 128.4(3), 128.3 (2), 128.2(2), 128.0(2), 127.9, 127.8, 127.7, 127.6, 117.3, 101.3, 97.8, 82.1, 81.6, 80.0, 77.4, 76.3, 75.8, 75.4, 74.8, 73.3, 69.9, 69.8, 68.2, 66.4, 55.0, 34.3, 17.9

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{44}H_{51}IO_9NH_4$ 868.2932, found 868.2932.



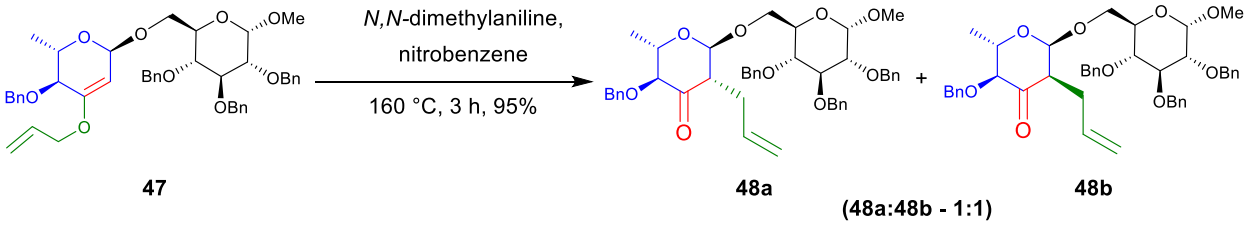
44 **47**

(2*S*,3*S*,6*R*)-4-(allyloxy)-3-(benzyloxy)-2-methyl-6-(((3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methoxy)-3,6-dihydro-2*H*-pyran (47): Compound **47** was synthesized from **44** (100 mg, 0.11 mmol) by following general procedure B. Yield: 80.7 mg, 97%, colorless gel. R_f = 0.5 (20% EtOAc/hexane). $[\alpha]_D^{25}$ = -23.2 (*c* 0.52, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.30-7.38 (m, 20H), 5.98-6.05 (m, 1H), 5.40 (dd, 1H, *J* = 1.5 Hz, *J* = 17.5 Hz), 5.27 (dd, 1H, *J* = 1.5 Hz, *J* = 12.0 Hz), 5.03 (d, 1H, *J* = 4.0 Hz), 5.02 (d, 1H, 11.5 Hz), 4.94 (d, 1H, *J* = 11.0 Hz), 4.91 (d, 1H, *J* = 11.0 Hz), 4.84 (d, 1H, *J* = 11.0 Hz), 4.81 (d, 1H, *J* = 12.5 Hz), 4.69 (d, 1H, *J* = 4.0 Hz), 4.68 (d, 1H, *J* = 12.5 Hz), 4.59-4.61 (m, 3H), 4.30-4.34 (m, 1H), 4.23-4.27 (m, 1H), 4.08-4.13 (m, 1H), 4.03 (t, 1H, *J* = 9.0 Hz), 3.93 (dd, 1H, *J* = 2.0 Hz, *J* = 11.0 Hz), 3.76-3.79 (m, 1H), 3.74 (d, 1H, *J* = 9.0 Hz), 3.62 (dd, 1H, *J* = 5.0 Hz, *J* = 11.0 Hz), 3.51-3.57 (m, 2H), 3.39 (s, 3H), 1.26 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 138.8, 138.5, 138.3, 138.2, 132.8, 128.4(3), 128.2, 128.1(2), 128.1, 127.9 (2), 127.8, 127.7, 127.6, 127.5, 117.5, 98.0, 96.2, 95.6, 82.1, 80.0, 77.9, 77.0, 75.7, 74.9, 74.0, 73.3, 70.1, 68.0, 66.5, 66.1, 55.1, 18.2

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{44}H_{50}O_9NH_4$ 740.3799, found 740.3799.



47 48a (48a:48b - 1:1) 48b

(2*R*,3*S*,5*S*,6*S*)-3-allyl-5-(benzyloxy)-6-methyl-2-(((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methoxy)tetrahydro-4*H*-pyran-4-one (48a) and **(2*R*,3*R*,5*S*,6*S*)-3-allyl-5-(benzyloxy)-6-methyl-2-(((2*R*,3*R*,4*S*,5*R*,6S)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2*H*-pyran-2-yl)methoxy)tetrahydro-4*H*-pyran-4-one** (**48b**) :

Compounds **48a** and **48b** were synthesized from **47** (70 mg, 0.09 mmol) by following general **procedure C.** Combine yield: 60.8 mg, 95%, colourless gel. R_f = 0.5 (20% EtOAc/hexane).

Compound **48a**: $[\alpha]_D^{25}$ = -20.3 (*c* 0.30, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.30-7.35 (m, 20H), 5.61-5.69 (m, 1H), 5.04-5.08 (m, 1H), 5.04 (s, 1H), 4.98 (d, 1H, *J* = 11.0 Hz), 4.88 (dd, 2H, *J*= 3.0 Hz, *J* = 11.5 Hz), 4.78 (dd, 2H, *J* = 8.0 Hz, *J* = 10.5 Hz), 4.73 (s, 1H), 4.64 (d, 1H,

J = 12.0 Hz), 4.52 (d, 1H, *J* = 2.0 Hz), 4.51 (d, 1H, *J* = 5.5 Hz), 4.45 (d, 1H, *J* = 11.5 Hz), 4.02-4.06 (m, 1H), 3.96 (t, 1H, *J* = 7.5 Hz), 3.78 (dd, 1H, *J* = 2.0 Hz, *J* = 11.0 Hz), 3.69-3.728 (m, 1H), 3.69 (d, 1H, *J* = 10.0 Hz), 3.48-3.50 (m, 2H), 3.43 (dd, 1H, *J* = 9.0 Hz, *J* = 10.0 Hz), 3.37 (s, 1H), 3.33 (s, 3H), 2.63 (t, 1H, *J* = 8.0 Hz), 2.31-2.39 (m, 2H), 1.30 (d, 3H, *J* = 6.5 Hz).

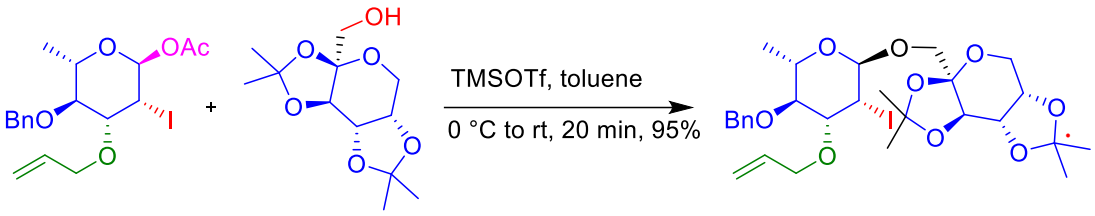
^{13}C NMR (125 MHz, $CDCl_3$): δ 206.1, 138.8, 138.3, 138.1, 137.4, 133.9, 128.5(2), 128.4(3), 128.2, 128.0, 128.0, 127.9, 127.8, 127.7, 127.6, 117.9, 101.4, 97.9, 82.1 (2), 80.1, 77.3, 75.7, 74.9, 73.5, 73.2, 69.7, 69.0, 66.2, 56.1, 55.1, 34.5, 18.8

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{44}H_{50}O_9NH_4$ 740.3799, found 740.3797.

Compound **48b**: $[\alpha]_D^{25}$ = -2.0 (*c* 0.10, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.25-7.37 (m, 20H), 5.64-5.72 (m, 1H), 4.98-5.0 (m, 2H), 4.97 (d, 1H, *J* = 10.7 Hz), 4.83- 4.86 (m, 2H), 4.81-4.82 (m, 1H), 4.77-4.79 (m, 2H), 4.68 (t, 2H, *J* = 10.6 Hz), 4.59 (d, 1H, *J*= 3.5 Hz), 4.40 (d, 1H, *J*= 11.5 Hz), 4.21 (dd, 1H, *J* = 3.5 Hz, *J* =11.5 Hz), 3.97 (t, 1H, *J* = 9.0 Hz), 3.7 (dd, 1H, *J* = 2.9, *J* = 9.9 Hz), 3.68 (d, 1H, *J* = 9.1 Hz), 3.60- 3.66 (m, 2H), 3.57 (t, 1H, *J* = 9.2 Hz), 3.50 (dd, 1H, *J* = 3.5, *J* = 9.5 Hz), 3.34 (s, 3H), 2.92-2.96 (m, 1H), 2.59-2.65 (m, 1H), 2.36-2.43 (m, 1H), 1.33 (d, 3H, *J* = 6.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): 206.8, 138.7, 138.3, 138.1, 137.2, 134.6, 128.5, 128.5, 128.4, 128.4(2), 128.1(4), 127.9, 127.8, 127.7, 117.2, 101.1, 98.2, 82.5, 82.0, 80.0, 77.6, 75.9, 75.2, 73.5, 73.2, 71.9, 69.9, 67.1, 56.1, 55.2, 29.6, 19.0.

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{44}H_{50}O_9NH_4$ 740.3799, found 740.3794.



42α **45** **46**

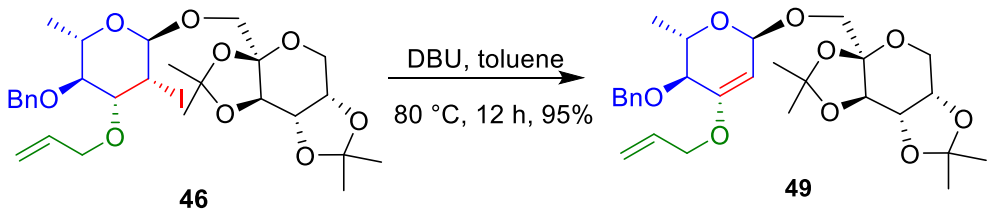
(3a*R*,5a*S*,8a*S*,8b*R*)-3a-((((2*S*,3*R*,4*R*,5*S*,6*S*)-4-(allyloxy)-5-(benzyloxy)-3-iodo-6-methyltetrahydro-2*H*-pyran-2-yl)oxy)methyl)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (46): To a stirred solution of donor sugar **42α** (100 mg, 1.0 eq) and acceptor sugar **45** (64 mg, 1.1 eq) in anhydrous toluene (10 mL/mmol) under an inert atmosphere was added 4 Å molecular sieves and the solution was stirred for 20 min at rt. The reaction mixture was further cooled to 0 ˚C. TMSOTf (0.4 eq) was added dropwise to the above reaction mixture, and stirring was continued at 0 °C. After completion of the reaction

(monitored by TLC) it was quenched by triethylamine (0.6 mmol) at the same temperature. The solvent was removed under reduced pressure to obtain the crude product, which was purified by column chromatography using hexane and ethyl acetate to obtain the glycosylated product **46** as a single diastereomer (α only) in 95% (137.5 mg) yield. $[\alpha]_D^{25}$ = -18.4 (*c* 0.68, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.36 (m, 5H), 5.91-5.99 (m, 1H), 5.32 (dd, 1H, *J* = 1.5 Hz, *J* = 17.0 Hz), 5.22 (s, 1H), 5.18 (dd, 1H, *J* = 1.5 Hz, *J* = 10.5 Hz), 4.93 (d, 1H, *J* = 11.0 Hz), 4.63 (d, 1H, *J* = 10.5 Hz), 4.57 (dd, 1H, *J* = 2.5 Hz, *J* = 7.5 Hz), 4.52 (d, 1H, *J* = 4.0 Hz), 4.31 (d, 1H, *J* = 2.5 Hz), 4.21 (d, 1H, *J* = 8.0 Hz), 4.13-4.17 (m, 1H), 4.00-4.03 (m, 1H), 3.88 (dd, 1H, *J* = 1.5 Hz, *J* = 12.5 Hz), 3.76-3.79 (m, 1H), 3.72 (d, 1H, *J* = 13.0 Hz), 3.69 (d, 1H, *J* = 10.5 Hz), 3.56 (d, 1H, *J* = 11.0 Hz), 3.46 (t, 1H, *J* = 9.0 Hz), 3.08 (dd, 1H, *J* = 4.0 Hz, *J* = 8.5 Hz), 1.53 (s, 3H), 1.43 (s, 3H), 1.37 (s, 3H), 1.31 (s, 3H), 1.29 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.3, 134.4, 128.5, 128.3, 127.9, 117.6, 108.9, 108.5, 102.1, 101.6, 81.5, 76.5, 75.7, 70.9, 70.1, 69.9, 69.8, 68.7, 67.7, 61.1, 33.7, 26.6, 25.8, 25.4, 23.9, 17.8

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{28}H_{39}IO_9Na$ 669.1536, found 669.1537.



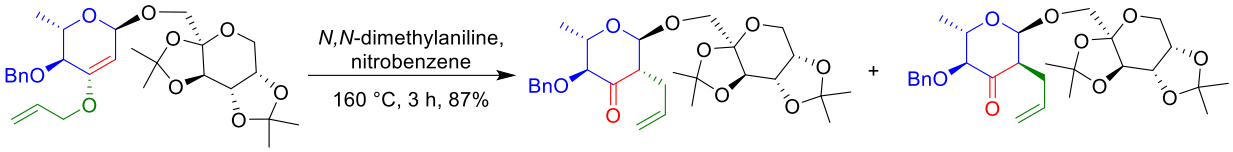
46 **49**

(3a*R*,5a*S*,8a*S*,8b*R*)-3a-((((2*R*,5*S*,6*S*)-4-(allyloxy)-5-(benzyloxy)-6-methyl-5,6-dihydro-2*H*-pyran-2-yl)oxy)methyl)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran (49): Compound **49** was synthesized from **46** (150 mg, 0.232 mmol) by following general procedure **B**. Yield: 116.6 mg, 95%, colureless gel. R_f = 0.5 (20% EtOAc/hexane). $[\alpha]_D^{25}$ = -50.0 (*c* 0.05, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28-7.38 (m, 5H), 5.95-6.02 (m, 1H), 5.36 (dd, 1H, *J* = 1.5Hz, *J* = 17.5 Hz), 5.24 (dd, 1H, *J* = 1.5 Hz, *J* = 10.5 Hz), 5.14 (d, 1H, *J* = 3.5 Hz), 4.94 (d, 1H, *J* = 11.0 Hz), 4.76 (d, 1H, *J* = 3.0 Hz), 4.59 (d, 1H, *J* = 11.0 Hz), 4.56 (dd, 1H, *J* = 2.5 Hz, *J* = 8.0 Hz), 4.38 (d, 1H, *J* = 2.5 Hz), 4.20-4.32 (m, 3H), 4.00-4.06 (m, 1H), 3.90 (dd, 1H, *J* = 2.0 Hz, *J* = 13.0 Hz), 3.78 (d, 1H, *J* = 10.5 Hz), 3.75 (d, 1H, *J* = 9.0 Hz), 3.72 (d, 1H, *J* = 13.0 Hz), 3.62 (d, 1H, *J* = 10.5 Hz), 1.53 (s, 3H), 1.46 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H), 1,26 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 138.3, 132.7, 128.3(3), 127.7, 117.5, 108.8, 108.4, 102.6, 95.7, 95.6, 76.7, 74.4, 71.0, 70.1, 70.0, 68.1, 66.2, 61.0, 26.6, 25.9, 25.5, 24.0, 18.0

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{28}H_{38}O_9Na$ 541.2414, found 541.2419.



49 **50a** **(50a:50b** = 1:1) **50b**

(2*R*,3*S*,5*S*,6*S*)-3-allyl-5-(benzyloxy)-6-methyl-2-(((3a*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methoxy)tetrahydro-4*H*-pyran-4-one (50a) and **(2*R*,3*R*,5*S*,6*S*)-3-allyl-5-(benzyloxy)-6-methyl-2-(((3a*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-tetramethyltetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-3a-yl)methoxy)tetrahydro-4*H*-pyran-4-one (50b):** Compounds **50a:50b** were synthesized from **49** (100 mg, 0.19 mmol) by following **general procedure C.** Combined yield: 86.91 mg, 87%, colorless gel. R_f = 0.5. (20% EtOAc/hexane).

Compound **50a**: **^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.32-7.39 (m, 5H), 5.65-5.73 (m, 1H), 5.11 (s, 1H), 5.07-5.09(m, 1H), 4.94 (s, 1H), 4.91 (d, 1H, *J* = 12.0 Hz), 4.57(dd, 1H, *J* = 2.5 Hz, *J* = 8.0 Hz), 4.48 (d, 1H, *J* = 11.5 Hz), 4.34 (d, 1H, *J* = 3.0 Hz), 4.22 (d, 1H, *J* = 8.0 Hz), 3.98-4.03 (m, 1H), 3.92 (dd, 1H, *J* = 2.0 Hz, *J*= 12.9 Hz), 3.69-3.75 (m, 3H), 3.56 (d, 1H, *J* = 10.5 Hz), 2.75 (t, 1H, *J* = 6.5 Hz), 2.35-2.49 (m, 2H), 1.54 (s, 3H), 1.45 (s, 3H), 1.36-1.38(m, 6H), 1.33 (s, 3H).

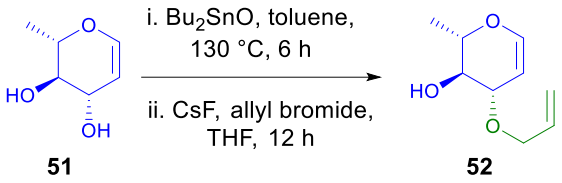
^{13}C NMR (125 MHz, $CDCl_3$): δ 206.2, 137.2, 133.6, 128.5, 128.4, 128.1, 118.0, 108.8, 108.7, 102.0, 101.5, 82.0, 73.2, 70.9, 69.8, 69.7, 69.6, 67.2, 61.0, 56.2, 34.4, 26.6, 25.8, 25.3, 23.9, 18.7.

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{28}H_{38}O_9Na$ 541.2414, found 541.2419.

Compound **50b: ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.32-7.41 (m, 5H), 5.73-5.81 (m, 1H), 5.11-5.17 (m, 1H), 5.07 (d, 1H, *J* = 10.1 Hz), 5.03 (d, 1H, *J* = 4.0 Hz), 4.95 (d, 1H, *J* = 11.5 Hz), 4.56 (dd, 1H, *J* = 2.5 Hz, *J* = 8.0 Hz), 4.50 (d, 1H, *J* = 11.5 Hz), 4.30 (d, 1H, *J* = 2.5 Hz), 4.22 (dd, 1H, *J* = 1.0 Hz, *J*= 8.0 Hz), 3.98-4.02 (m, 1H), 3.94 (dd, 1H, *J* = 1.5 Hz, *J* = 13.0 Hz), 3.77 (d, 1H, *J* = 10.0 Hz), 3.96-3.374 (m, 2H), 3.43 (d, 1H, *J* = 10.0 Hz), 2.75-2.79 (m, 1H), 2.49-2.55 (m, 1H), 2.25-2.32 (m, 1H), 1.54 (s, 3H), 1.45 (s, 3H), 1.40 (s, 3H), 1.36 (d, 3H, *J* = 6.5 Hz), 1.32 (s, 3H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 204.0, 137.4, 134.9, 128.5, 128.4, 128.1, 117.4, 108.8, 108.8, 101.7, 100.7, 84.6, 73.1, 71.0, 70.4, 69.8, 69.5, 67.9, 61.0, 53.5, 27.9, 26.6, 25.9, 25.7, 23.8, 18.8.

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{28}H_{38}O_9NH_4$ 536.2860, found 536.2863.



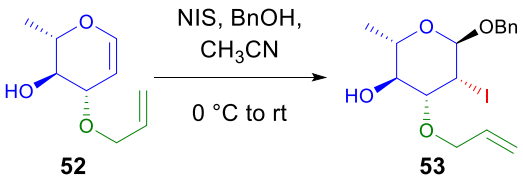
51 **52**

(2*S*,3*S*,4*S*)-4-(allyloxy)-2-methyl-3,4-dihydro-2H-pyran-3-ol (52): Compound **51** (3 g, 1eq) and Bu_2SnO (6.3 g, 1.1 eq) were suspended in toluene at room temperature. The reaction mixture was stirred at reflux at 130 °C under Dean-Stark conditions for 6 h, then cooled to room temperature. The solvent was removed in vacuo. The resulting resulting solid CsF (7 g, 2 eq) was added and the mixture was suspended in THF, then allyl bromide (2.2 mL, 1.1 eq) was added at room temperature. The reaction mixture was stirred for 12 h, then imidazole (2.8 g, 1.8 eq) was added and allowed to stir for 1 h. The crude residue was filtered through a celite pad and washed with ethyl acetate and concentrated in vacuo. The crude residue was purified by flash column chromatography on silica gel. Yield: 2.3 g, 60%, R_f = 0.5 (20% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 6.27 (dd, 1H, *J* = 1 Hz, *J* = 6 Hz), 5.85-5.92 (m, 1H), 5.25 (dq, 1H, *J* = 1.5 Hz, *J* = 17.5 Hz), 5.12-5.15 (m, 1H), 4.74 (dd, 1H, *J* = 2.5 Hz, *J* = 6.5 Hz), 4.09 (ddt, 1H, *J* = 1.5 Hz, *J* = 5.5 Hz, *J* = 13 Hz), 4.00 (ddt, 1H, *J* = 1.5 Hz, *J* = 5.5 Hz, *J* = 13 Hz), 3.93 (dt, 1H, *J* = 2 Hz, *J* = 7 Hz), 3.79-3.85 (m, 1H), 3.47-3.51 (m, 1H), 3.43 (bs, 1H), 1.32 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 144.8, 134.8, 117.1, 99.8, 76.7, 74.5, 72. 4, 69.3, 17.1.

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_9H_{14}O_3Na$ 193.0841, found 193.0839.



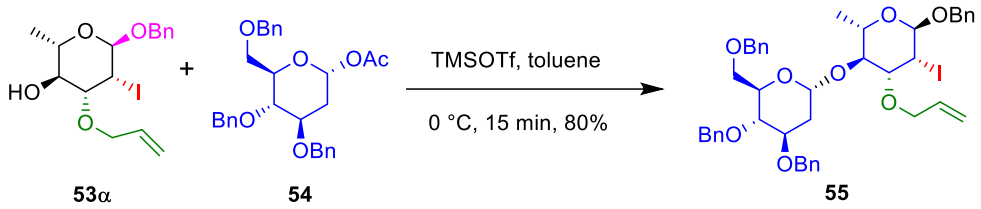
52 **53**

(2*S*,3*S*,4*R*,5*R*,6*R*)-4-(allyloxy)-6-(benzyloxy)-5-iodo-2-methyltetrahydro-2*H*-pyran-3-ol (53): Compound **53** was synthesized from **52** (1g, 1eq) by following general **procedure A.** Yield: 1.8 g, 80%, colorless gel. R_f = 0.5 (20% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33-7.41 (m, 5H), 5.95-6.03 (m, 1H), 5.37 (dd, 1H, *J* = 1.5 Hz, *J* = 17.5 Hz), 5.25-5.27 (m, 2H), 4.72 (d, 1H, *J* = 6 Hz), 4.50-4.53 (m, 2H), 4.15 (ddt, 1H, *J* = 1.5 Hz, *J* = 6 Hz, *J* = 12.5 Hz), 3.86-3.90 (m, 1H), 3.91-3.96 (m, 1H), 3.65 (t, 1H, *J* = 9.5), 3.03 (dd, 1H, *J* = 4 Hz, *J* = 9 Hz), 2.73 (bs, 1H), 1.38 (d, 3H, *J* = 6 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.0, 133.9, 128.5, 128.4, 127.8, 118.1, 101.0, 76.1, 73.5, 69.5 (2), 68.9, 32.6, 17.8.

HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{16}H_{21}IO_4Na$ 427.0382, found 427.0380.



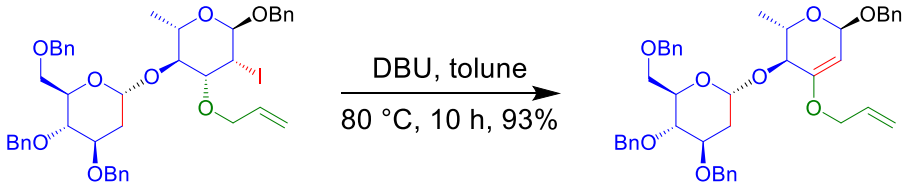
53α **54** **55**

(2*R*,3*R*,4*R*,6*S*)-4-(allyloxy)-2-(benzyloxy)-5-(((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)-3-iodo-6-methyltetrahydro-2*H*-pyran (55): To a stirred solution of donor sugar **54** (200 mg, 1.0 eq) and acceptor sugar **53*α*** (186.63 mg, 1.1 eq) in anhydrous toluene (10 mL/mmol) under an inert atmosphere was added 4 Å molecular sieves and the solution was stirred for 20 min at rt. The reaction mixture was further cooled to 0 ˚C. TMSOTf (0.4 eq) was added dropwise to the above reaction mixture, and stirring was continued at 0 °C. The reaction was monitored by TLC and quenched by triethylamine (0.6 mmol) at the same temperature and allowed to room temperature. The solvent was removed under reduced pressure to obtain the crude product, which was purified by column chromatography using hexane and ethyl acetate to obtain the glycosylated product **55** of as a single diastereomer (α only) in 80% (274.9 mg) yield.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23-7.38 (m, 20H), 5.90-5.98 (m, 1H), 5.28-5.32 (m, 1H), 5.23 (d, 1H, *J* = 1.5 Hz), 5.18 (d, 1H, *J* = 3.0 Hz), 5.15 (dd, 1H, *J* = 1.5 Hz, *J* = 10.0 Hz), 4.91 (d, 1H, *J* = 11.0 Hz), 4.68-4.72 (m, 4H), 4.58 (d, 1H, *J* = 11.0 Hz), 4.53 (dd, 1H, *J* = 1.5 Hz, *J* = 4.0 Hz), 4.51 (d, 1H, *J* = 6.0 Hz), 4.49 (d, 1H, *J* = 6.0 Hz), 4.14-4.17 (m, 1H), 4.01-4.06 (m, 1H), 3.91-3.98 (m, 2H), 3.85 (dd, 1H, *J* = 6.5 Hz, *J* = 9.0 Hz), 3.81 (dd, 1H, *J* = 3.0 Hz, *J* = 10.5 Hz), 3.67-3.74 (m, 3H), 3.08 (dd, 1H, *J* = 4.0 Hz, *J* = 8.5 Hz), 2.27-2.31(m, 1H), 1.73-1.79 (m, 1H), 1.31 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.9, 138.7, 138.3, 137.0, 134.2, 128.5, 128.3, 128.2, 128.2(2), 127.9 (2), 127.6 (2), 127.5 (2), 127.3, 117.8, 100.5, 97.9, 78.4, 78.2, 77.3, 75.2, 74.7, 73.4, 71.8, 71.0, 69.9, 69.5, 68.9, 68.9, 35.5, 33.9, 18.3

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{43}H_{49}IO_8NH_4$ 838.2816, found 838.2816.



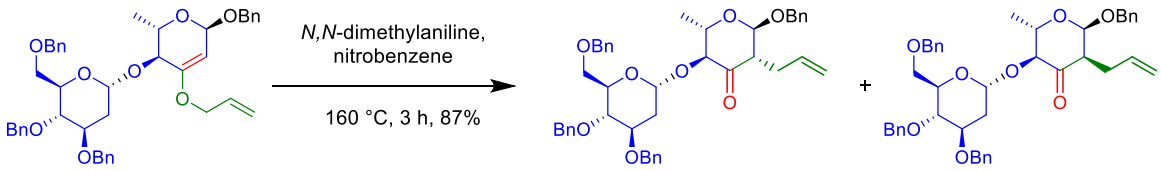
55 **58**

(2*S*,3*S*,6*R*)-4-(allyloxy)-6-(benzyloxy)-3-(((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)-2-methyl-3,6-dihydro-2*H*-pyran(58): Compound **58** was synthesized from **55** (170 mg, 0.20 mmol) by following **general procedure B**. Yield: 133.4 mg, 93%, colorless gel. R_f = 0.5 (20% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20-7.37 (m, 20H), 5.89-5.94 (m, 1H), 5.30 (dd, 1H, *J* = 1.0 Hz, *J* = 17.0 Hz), 5.17-5.20 (m, 2H), 5.09 (d, 1H, *J* = 3.0 Hz), 4.90 (d, 1H, *J* = 11.0 Hz), 4.78 (d, 1H, *J* = 2.5 Hz), 4.75 (d, 1H, *J* = 12.0 Hz), 4.65-4.67 (m, 3H), 4.58 (d, 1H, *J* = 12.5 Hz), 4.56 (d, 1H, *J* = 12.5 Hz), 4.48 (d, 1H, *J* = 12.5 Hz), 4.19-4.26 (m, 4H), 3.96-4.00 (m, 2H), 3.79 (dd, 1H, *J* = 3.0 Hz, *J* = 10.5 Hz), 3.69 (t, 1H, *J* = 9.5 Hz), 3.61 (dd, 1H, *J* = 1.5 Hz, *J* = 10.5 Hz), 2.30 (dd, 1H, *J* = 5.0 Hz, *J* = 12.0 Hz), 1.74 (td, 1H, *J* = 3.5 Hz, *J* = 12.5 Hz), 1.25 (d, 3H, *J* = 6.5 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 139.0, 138.8, 138.4, 138.3, 132.6, 128.4 (2), 128.3, 128.2, 128.0, 127.9, 127.6, 127.6(2), 127.5 (2), 127.4, 118.5, 97.9, 96.9, 95.1, 78.3, 77.5, 75.9, 74.6, 73.5, 72.0, 71.3, 69.6, 69.0, 68.5, 67.0, 35.9, 18.4

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{43}H_{48}O_8NH_4$ 710.3693, found 710.3693.



58 **59a** **(59a: 59b= 10:1)** **59b**

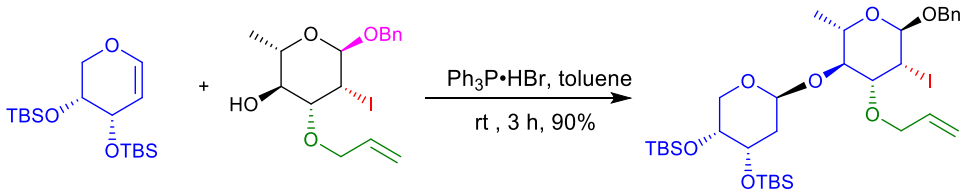
(2*R*,3*S*,5*S*,6*S*)-3-allyl-2-(benzyloxy)-5-(((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)-6-methyltetrahydro-4*H*-pyran-4-one (59a) and **(2*R*,3*R*,5*S*,6*S*)-3-allyl-2-(benzyloxy)-5-(((2*R*,4*R*,5*S*,6*R*)-4,5-bis(benzyloxy)-**

6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-yl)oxy)-6-methyltetrahydro-4*H*-pyran-4-one (59b): Compounds **59a:59b** were synthesized from **58** (100 mg, 0.14 mmol) by following general **procedure C.** Obtained as an inseparable mixture. Combined yield: 86.65 mg, 87%, colorless gel. R_f = 0.5 (20% EtOAc/hexane).

Compound 59a (selected data for the major product**): ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.25-7.36 (m, 20H), 5.59-5.67 (m, 1H), 5.06 (dd, 1H, *J* = 1.0 Hz, *J* = 17.0 Hz), 4.96-4.99 (m, 2H), 4.89 (d, 2H, *J* = 11.0 Hz), 4.65-4.67 (m, 3H), 4.59 (d, 1H, *J* = 12.0 Hz), 4.54 (d, 1H, *J* = 11.0 Hz), 4.48 (d, 1H, *J* = 12.5 Hz), 4.44 (d, 1H, *J* = 12.0 Hz), 4.33-4.36 (m, 1H), 4.03-4.10 (m, 2H), 3.96 (d, 1H, *J* = 9.5 Hz), 3.78 (dd, 1H, *J* = 3.0 Hz, *J* = 13.5 Hz), 3.66 (t, 1H, *J* = 9.5 Hz), 3.49 (dd, 1H, *J* = 2.0 Hz, *J* = 10.5 Hz), 2.71 (t, 1H, *J* = 8.0 Hz), 2.33-2.43 (m, 3H), 1.74-1.80 (m, 1H), 1.33 (d, 3H, *J* = 6.0 Hz).

^{13}C NMR (125 MHz, $CDCl_3$): δ 204.2, 138.9, 138.8, 138.2, 137.0, 133.8, 128.4, 128.4, 128.3, 128.2, 127.9, 127.8, 127.8, 127.7, 127.6, 127.6, 127.5, 127.4, 117.8, 100.6, 99.5, 82.0, 78.2, 77.5, 74.6, 73.4, 72.2, 71.4, 69.8, 69.1, 68.6, 56.4, 35.6, 34.4, 18.6

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{43}H_{48}O_8NH_4$ 710.3693, found 710.3695.



56 53a 57

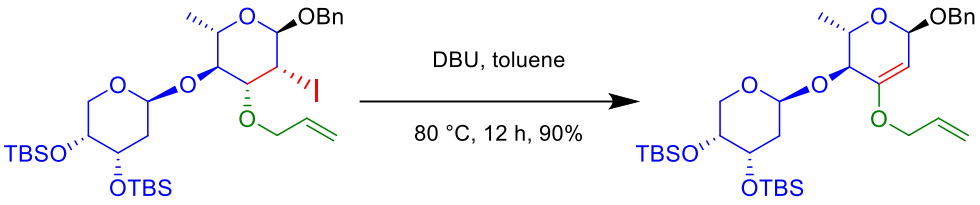
(((3*R*,4*S*,6*S*)-6-(((2*S*,4*R*,5*R*,6*R*)-4-(allyloxy)-6-(benzyloxy)-5-iodo-2-methyltetrahydro-2*H*-pyran-3-yl) oxy)tetrahydro-2*H*-pyran-3,4-diyl)bis(oxy))bis(tert-butyldimethylsilane) (57): To a stirred solution of donor sugar **56** (100 mg, 1.0 eq) and the acceptor sugar **53α** (135.9 mg, 1.2 eq) in anhydrous toluene (10 mL/mmol) under an inert atmosphere was added 4 Å molecular sieves and the solution was stirred for 1 h. $Ph_3P{\cdot}HBr$ (0.8 eq) was added to the above-stirred solution, and stirring was continued for 3 h. After the complete consumption of the starting material, the solvent was concentrated under reduced pressure to obtain the crude product, which was purified by column chromatography using hexane and ethyl acetate to obtain the glycosylated product **57** as a single diastereomer (β only) in 90% (201.0 mg) yield. $[\alpha]_D^{25}$ = -50.6 (*c* 0.73, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-7.37 (m, 5H), 5.89-5.93 (m, 1H), 5.28-5.31 (m, 1H), 5.16-5.19 (m, 3H), 4.67 (d, 1H, *J* = 11.5 Hz), 4.45-4.48 (m, 2H), 4.05-4.09 (m, 1H), 3.97-4.00 (m, 1H), 3.89-3.93 (m, 1H), 3.76-3.81 (m, 1H), 3.69-3.71 (m, 1H), 3.60-3.66 (m, 4H),

3.08 (dd, 1H, *J* = 4.0 Hz, *J* = 8.5 Hz), 2.01-2.06 (m, 1H), 1.34 (d, 3H, *J* = 6.5 Hz), 0.90 (s, 9H), 0.89 (s, 9H), 0.06-0.07 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 137.1, 134.4, 128.5, 128.0(2), 117.4, 100.7, 99.6, 79.3, 76.3, 70.0, 69.6, 69.4, 68.3, 68.1, 68.0, 64.8, 33.8, 26.0 (2), 18.3 (2), 18.2, -4.4 (2), -4.7, -4.8

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{33}H_{57}IO_7Si_2NH_4$ 766.3031, found 766.3029



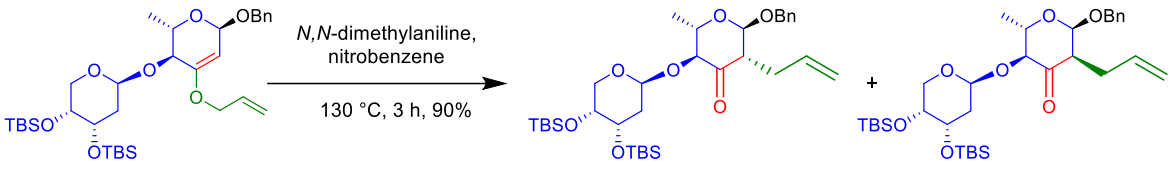
57 **60**

(((3*R*,4*S*,6*S*)-6-(((2*S*,6*R*)-4-(allyloxy)-6-(benzyloxy)-2-methyl-3,6-dihydro-2*H*-pyran-3-yl)oxy)tetrahydro-2*H*-pyran-3,4-diyl)bis(oxy))bis(tert-butyldimethylsilane) (60): Compound **60** was synthesized from **57** (200 mg, 0.285 mmol) by following general procedure B. Yield: 147.1 mg, 90%, colorless gel. R_f = 0.6 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.29-739 (m, 5H), 5.90-5.98 (m, 1H), 5.30 (dd, 1H, *J* = 1.5 Hz, *J* = 17.5 Hz), 5.20-5.24 (m, 3H), 4.76 (d, 1H, *J* = 11.5 Hz), 4.72 (d, 1H, *J* = 3.5 Hz), 4.58 (d, 1H, *J* = 12.0 Hz), 4.21-4.30 (m, 2H), 4.03-4.07 (m, 1H), 3.99-4.02 (m, 1H), 3.93 (d, 1H, *J* = 9.0 Hz), 3.69-3.74 (m, 2H), 3.65 (dd, 1H, *J* = 6.0 Hz, *J* = 11.0 Hz), 2.04-2.09 (m, 1H), 1.64-1.69 (m, 1H), 1.32 (d, 3H, *J* = 6.5 Hz), 0.92 (s, 9H), 0.91 (s, 9H), 0.07-0.09 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ157.6, 138.4, 132.8, 128.4(2), 128.0(2), 127.5, 117.6, 99.9, 95.2, 95.2, 75.2, 70.1, 69.6, 68.1, 68.0, 66.5, 64.8, 26.0, 26.0, 18.4, 18.3, 18.2, -4.4 (2), -4.7, -4.8

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{33}H_{56}O_7Si_2NH_4$ 638.3908, found 638.3908.



60 **61a** **61b**

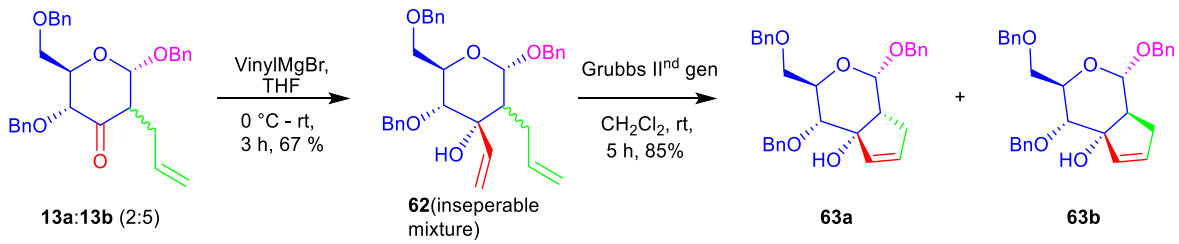
(61a: 61b = 10:1)

(2*R*,3*S*,5*S*,6*S*)-3-allyl-2-(benzyloxy)-5-(((2*S*,4*S*,5*R*)-4,5-bis((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-6-methyltetrahydro-4*H*-pyran-4-one (61a) and **(2*R*,3*R*,5*S*,6*S*)-3-allyl-2-(benzyloxy)-5-(((2*S*,4*S*,5*R*)-4,5-bis((*tert*-butyldimethylsilyl)oxy)tetrahydro-2*H*-pyran-2-yl)oxy)-6-methyltetrahydro-4*H*-pyran-4-one (61b):** Compounds **61a** and **61b** were synthesized from **60** (100 mg, 0.61 mmol) by following **general procedure C**. Obtained as an inseparable mixture. Combined yield: 89.9 mg, 90%, colorless gel. R_f = 0.5 (10% EtOAc/hexane). $[\alpha]_D^{25}$ = -80.0 (*c* 0.13, $CHCl_3$).

Compound 61a (selected data for the major compound)**: ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.27-7.34 (m, 5H), 5.60-5.68 (m, 1H), 5.08 (dd, 1H, *J* = 1.5 Hz, *J* = 17.0 Hz), 5.03-5.05 (m, 1H), 4.95-4.98 (m, 1H), 4.90 (s, 1H), 4.66 (d, 1H, *J* = 12.0 Hz), 4.48 (d, 1H, *J* = 12.0 Hz), 3.99-4.08 (m, 3H), 3.71-3.75 (m, 1H), 3.64 (dd, 1H, *J* = 2.5 Hz, *J* = 11.5 Hz), 3.58 (dd, 1H, *J* = 6.0 Hz, *J* = 11.5 Hz), 2.92-2.95 (m, 1H), 2.71 (t, 1H, *J* = 8.0 Hz), 2.37-2.45 (m, 1H), 2.12-2.17 (m, 1H), 1.71-1.77(m, 1H), 1.39 (d, 3H, *J* = 6.0 Hz), 0.89 (s, 9H), 0.89 (s, 9H), 0.06-0.08 (m, 12H).

^{13}C NMR (125 MHz, $CDCl_3$): δ 205.8, 137.1, 133.7, 128.4, 127.8, 127.7, 117.8, 100.6, 97.9, 79.2, 69.9, 69.2, 69.0, 67.6, 65.2, 56.1, 34.3, 25.9, 19.0, 18.2, 18.2, -4.4, -4.5, -4.7, -4.8.

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{33}H_{56}O_7Si_2NH_4$ 638.3908, found 638.3906.



13a:**13b** (2:5) **62**(inseperable mixture) **63a** **63b**

(1*S*,3*R*,4*R*,4a*S*,7a*R*)-1,4-bis(benzyloxy)-3-((benzyloxy)methyl)-3,4,7,7a-tetrahydrocyclopenta[c]pyran-4a(1*H*)-ol (63a) and **(1*S*,3*R*,4*R*,4*aR*,7*aR*)-1,4-bis(benzyloxy)-3-((benzyloxy)methyl)-3,4,7,7a-tetrahydrocyclopenta[c]pyran-4a(1*H*)-ol (63b):** To a stirred solution containing diastereomeric mixture of **13a: 13b** (100 mg, 0.21 mmol) in dry THF (5 mL) at 0 ˚C was added vinyl magnesium bromide (0.5 mL, 0.42 mmol).

The reaction mixture was allowed to come to room temperature and stirred for 3 h. After completion of the reaction, it was quenched by addition of saturated NH_4Cl solution**.** The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and filtered to obtain the crude mixture which was subjected to flash column chromatography to obtain an inseparable mixture of diastereomers **62 (**70 mg, 67%) as a colorless gel. R_f = 0.6 (20% EtOAc/hexane).

The diastereomeric mixture **62** (60 mg, 0.11 mmol) was dissolved in dichloromethane (2 mL) and to this Grubbs IInd generation catalyst (18.6 mg, 0.023 mmol) was added. The mixture was stirred at room temperature. After 5 h the solution was made into a slurry and column chromatography over silica gel provided compounds **63a** (17 mg, Yield:30%) as a colourless gel. R_f = 0.4 (20% EtOAc/hexane) $[\alpha]_D^{25}$ = 67.2 (*c* 0.13, $CHCl_3$).

and **63b** (31.1 mg, Yield: 55%), as a colourless gel. R_f = 0.45 (20% EtOAc/hexane). $[\alpha]_D^{25}$ = 94.6 (*c* 0. 07, $CHCl_3$).

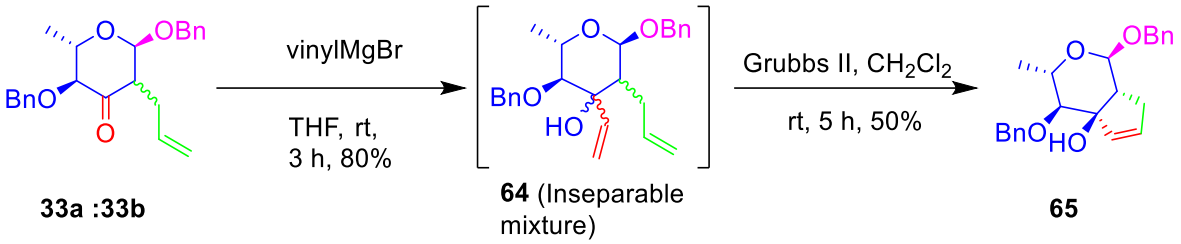
Compound **63a : ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.27-7.37 (m, 15H), 6.00-6.07 (m, 2H, H-8 & H-9), 5.19 (d, 1H, *J* = 3.0 Hz, H-1), 4.81 (d, 1H, *J* = 12.0 Hz), 4.65 (d, 2H, *J* = 12.0 Hz), 4.58 (d, 1H, *J* = 11.5 Hz), 4.56 (d, 1H, *J* = 12.0 Hz), 4.55 (d, 1H, J = 12.0 Hz) 4.53 (bs, 1H), 4.11 (m, 1H), 3.84 (dd, 1H, *J* = 3.5 Hz, *J* = 10.5 Hz, H-5), 3.75 (dd, 1H, *J* = 2.0 Hz, *J* = 10.5 Hz, H-6), 3.71 (d, 1H, J = 10.0 Hz, H-4), 2.57-2.63 (m, 1H, H-7a), 2.22-2.27 (m, 1H, H-7b), 2.08-2.12 (m, 1H, H-2).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.1, 136.9, 135.7, 134.7, 128.4 (2), 128.3, 128.2, 127.9(2), 127.8(2), 127.7, 127.6, 98.5, 81.2, 78.4, 73.7, 73.4, 70.0, 69.9, 68.9, 49.2, 30.1.

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{30}H_{32}O_5NH_4$ 490.2593, found 490.2594.
Compound **63b : ^{1}H NMR (500 MHz, $CDCl_3$):** δ 7.21-7.36 (m, 15H), 5.77-5.82 (m, 2H, H-8 & H-9), 4.92 (s, 1H, H-1), 4.74 (d, 1H, *J* = 12.0 Hz), 4.66 (d, 1H, *J* = 12.5 Hz), 4.51-4.59 (m, 4H), 4.04-4.06 (m, 1H), 3.74 (dd, 1H, *J* = 4.0, 11.0 Hz, H-5), 3.64 (dd, 1H, *J* = 2.0 Hz, *J* = 11.0 Hz, H-6), 3,59 (d, 1H, *J* = 10.0 Hz, H-4), 3.07 (bs, 1H), 2.43-2.54 (m, 2H, H-2 & H-7a), 2.23-2.29 (m, 1H, H-7b).

^{13}C NMR (125 MHz, $CDCl_3$): δ 138.4, 138.1, 137.9, 137.7, 130.3, 128.5, 128.4, 128.3, 128.3, 128.0, 128.0, 127.9, 127.6, 127.5, 97.6, 82.2, 78.6, 74.8, 73.6, 69.1, 68.8, 65.1, 50.6, 33.9.

HRMS (ESI-TOF) *m/z*: [M+NH_4] calcd for $C_{30}H_{32}O_5NH_4$ 490.2593, found 490.2594.



33a :33b **64** (Inseparable mixture) **65**

(1*R*,3*S*,4*S*,4*aR*,7*aR*)-1,4-bis(benzyloxy)-3-methyl-3,4,7,7a tetrahydrocyclopenta[c]pyran-4a(1*H*)-ol (65): To a stirred solution containing diastereomeric mixture of **33a: 33b** (100 mg, 0.27 mmol) in dry THF (5 mL) at 0 ˚C was added vinyl magnesium bromide (0.7 mL, 0.54 mmol). The reaction mixture was allowed to come to room temperature and stirred for 3 h. After completion of the reaction, it was quenched by addition of saturated NH_4Cl solution**.** The layers were separated and the aqueous layer was extracted with ethyl acetate. The combined organic layer was dried over Na_2SO_4 and filtered to obtain the crude mixture which was subjected to flash column chromatography to obtain an inseparable mixture of diastereomers **64 (**86 mg, 80%) as a colorless gel. R_f = 0.6 (5% EtOAc/hexane).

The diastereomeric mixture **64** (70 mg, 0.17 mmol) was dissolved in dichloromethane (3 mL) and to this Grubbs IInd generation catalyst (29.7 mg, 0.035 mmol) was added. The mixture was stirred at room temperature. After 5 h the solution was made into a slurry and column chromatography over silica gel provided compound **65** (32.5 mg, 50%), as a colourless gel.

R_f = 0.5 (10% EtOAc/hexane).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26-7.37 (m, 10H), 5.86-5.87 (m, 1H, H-9), 5.79-5.87 (m, 1H, H-8), 4.81 (s, 1H, H-1), 4.72 (d, 1H, *J* = 12.5 Hz), 4.66 (d, 1H, *J* = 11.5 Hz), 4.63 (d, 1H, *J* = 11.0 Hz), 4.55 (d, 1H, *J* = 12.5 Hz), 4.00-4.05 (m, 1H, H-5), 3.13 (d, 1H, *J* = 10.0 Hz, H-4), 3.08 (bs, 1H), 2.50-2.54 (m, 1H, H-2), 2.44-2.49 (m, 1H, H-7a), 2.18-2.24 (m, 1H, H-7b), 1.24 (d, 3H, *J* = 6.5 Hz, H-6).

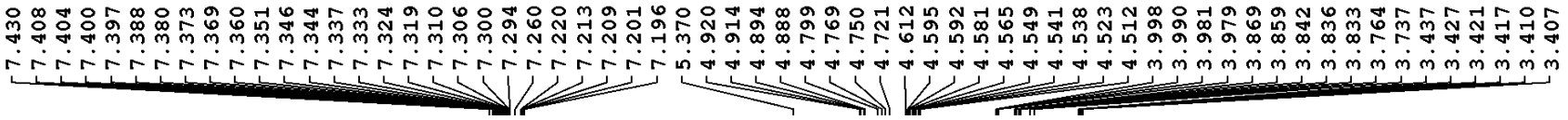
^{13}C NMR (125 MHz, $CDCl_3$): δ 138.7, 137.9, 137.6, 130.2, 128.5, 28.4, 128.1, 128.0, 128.0, 127.6, 97.2, 84.8, 82.1, 75.3, 68.8, 61.4, 50.8, 34.0, 17.7.

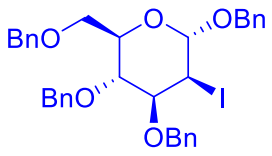
HRMS (ESI-TOF) *m/z*: [M+Na] calcd for $C_{23}H_{26}O_4Na$ 389.1729, found 389.1728.

References:

1. Colgan, A. C., Muller-Bunz, H. and McGarrigle, E. M., Benzylation Reactions in DMF Lead to an Impurity Which Acts as an Organocatalyst Poison in Thiourea-Catalyzed Glycosylations, *J. Org. Chem.,* 2016, **81**, 11394-11396.

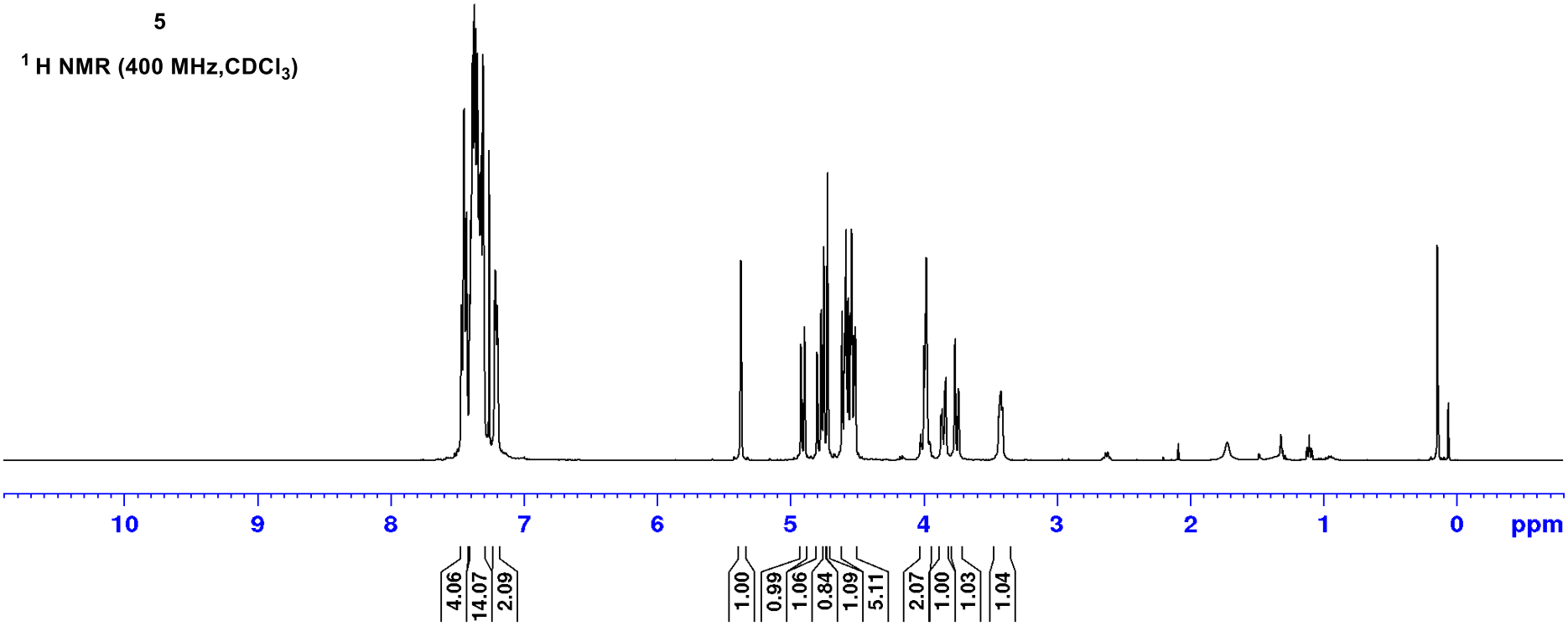
2. Kalikanda, J. and Li, Z., Study of the stereoselectivity of 2-azido-2-deoxygalactosyl donors: remote protecting group effects and temperature dependency, *J.Org. Chem.,* 2011, **76**, 5207-5218.

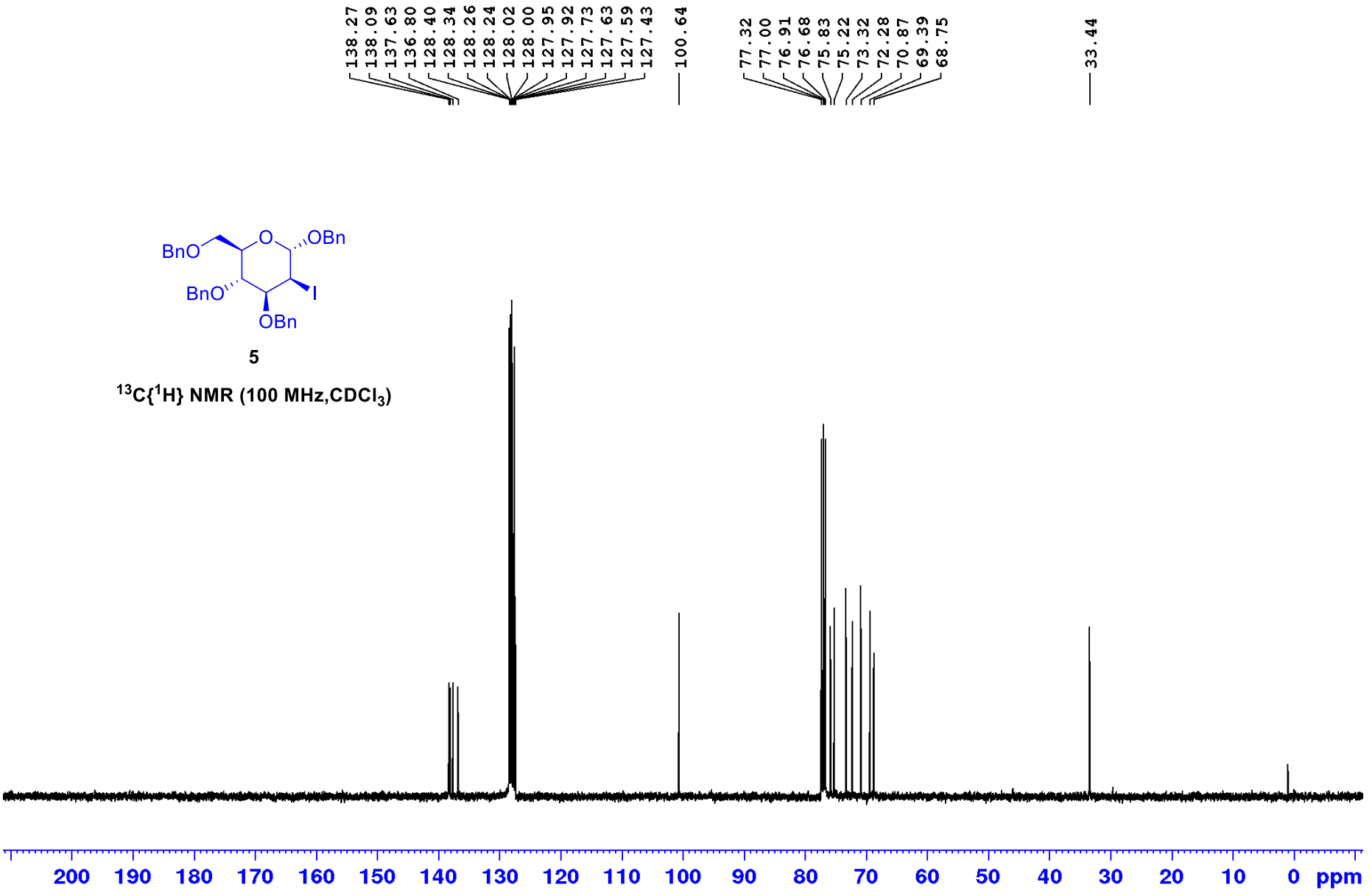




5

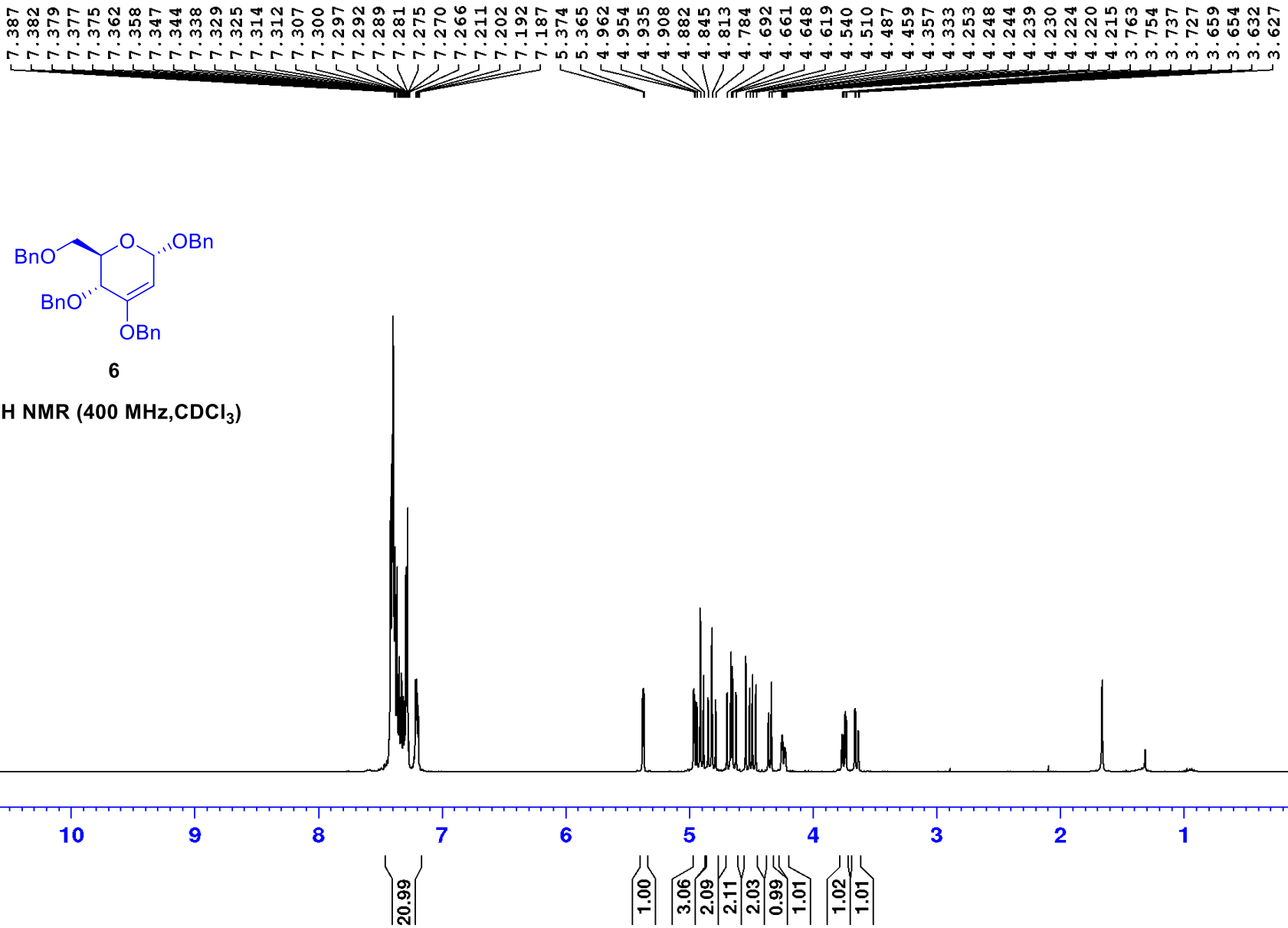
^{1}H NMR (400 MHz,$CDCl_3$)





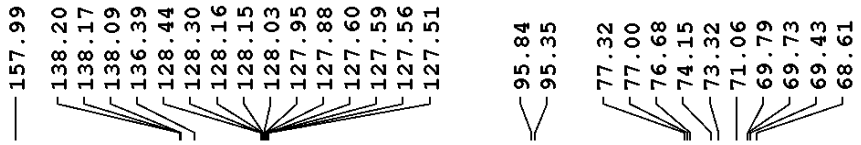
5

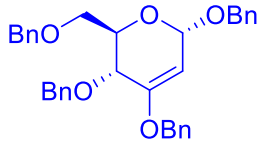
$^{13}C\{^{1}H\}$ NMR (100 MHz,$CDCl_3$)



6

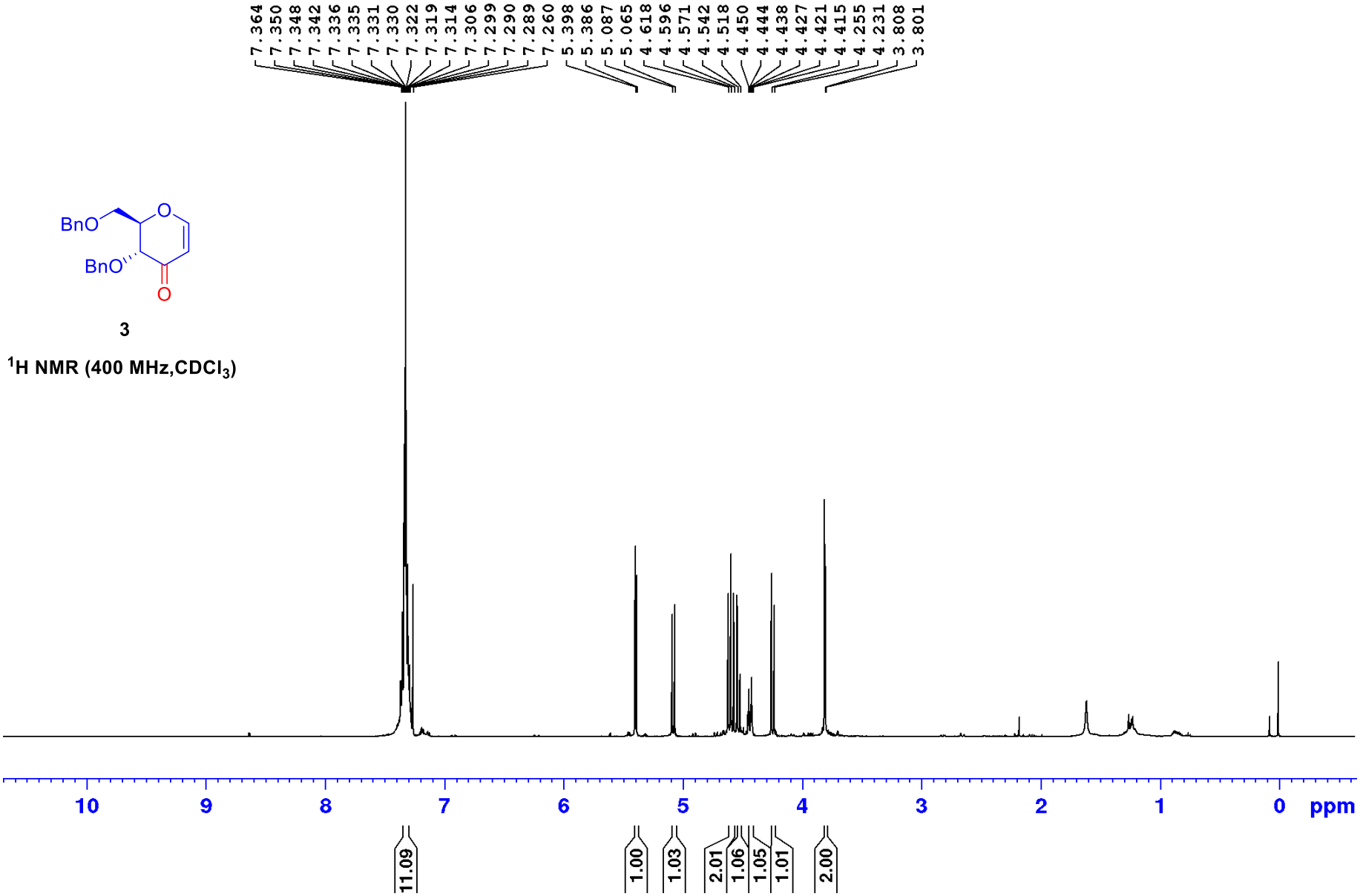
^{1}H NMR (400 MHz,$CDCl_3$)





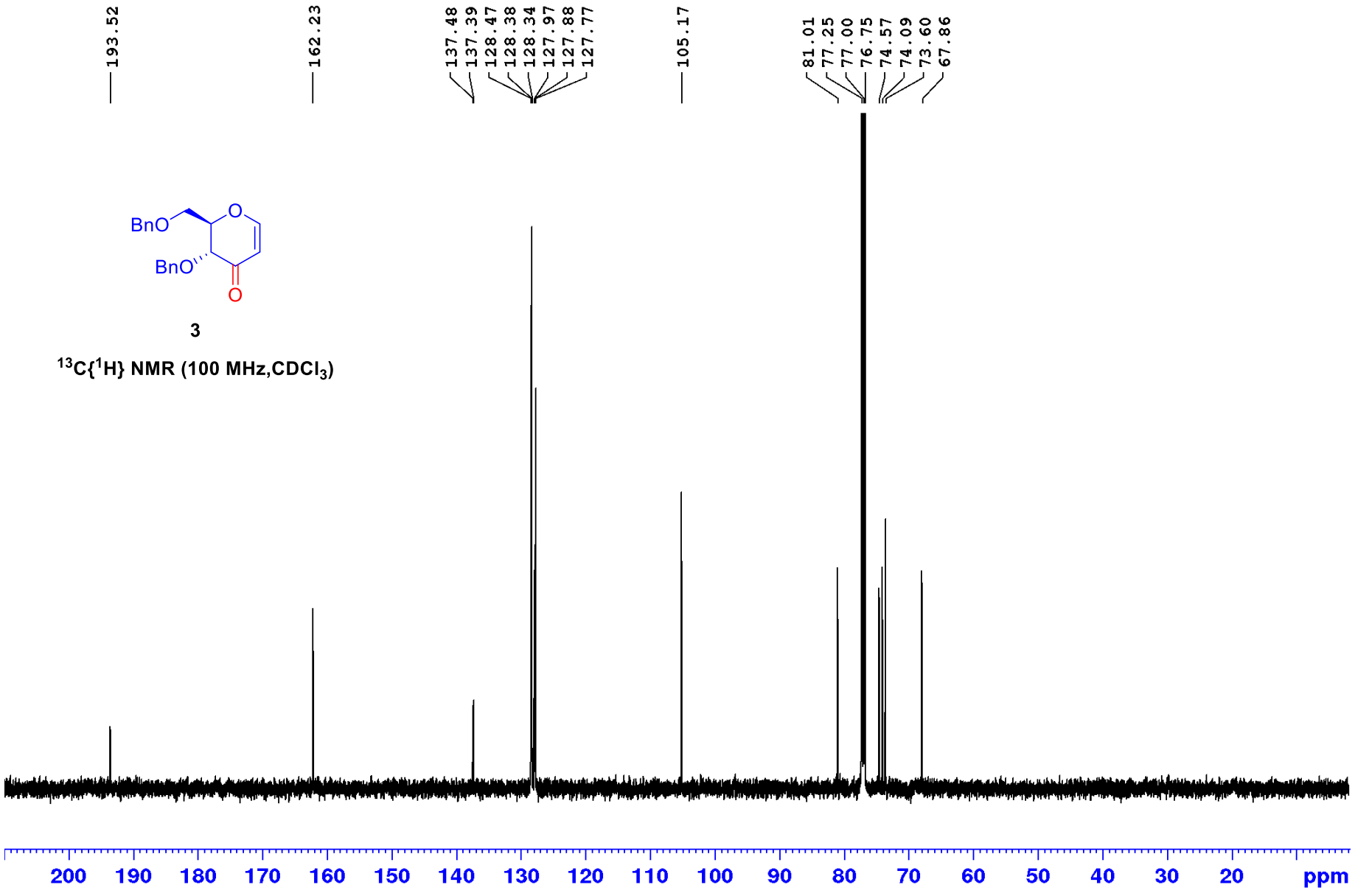
6

$^{13}C\{^{1}H\}$ NMR (100 MHz,$CDCl_3$)



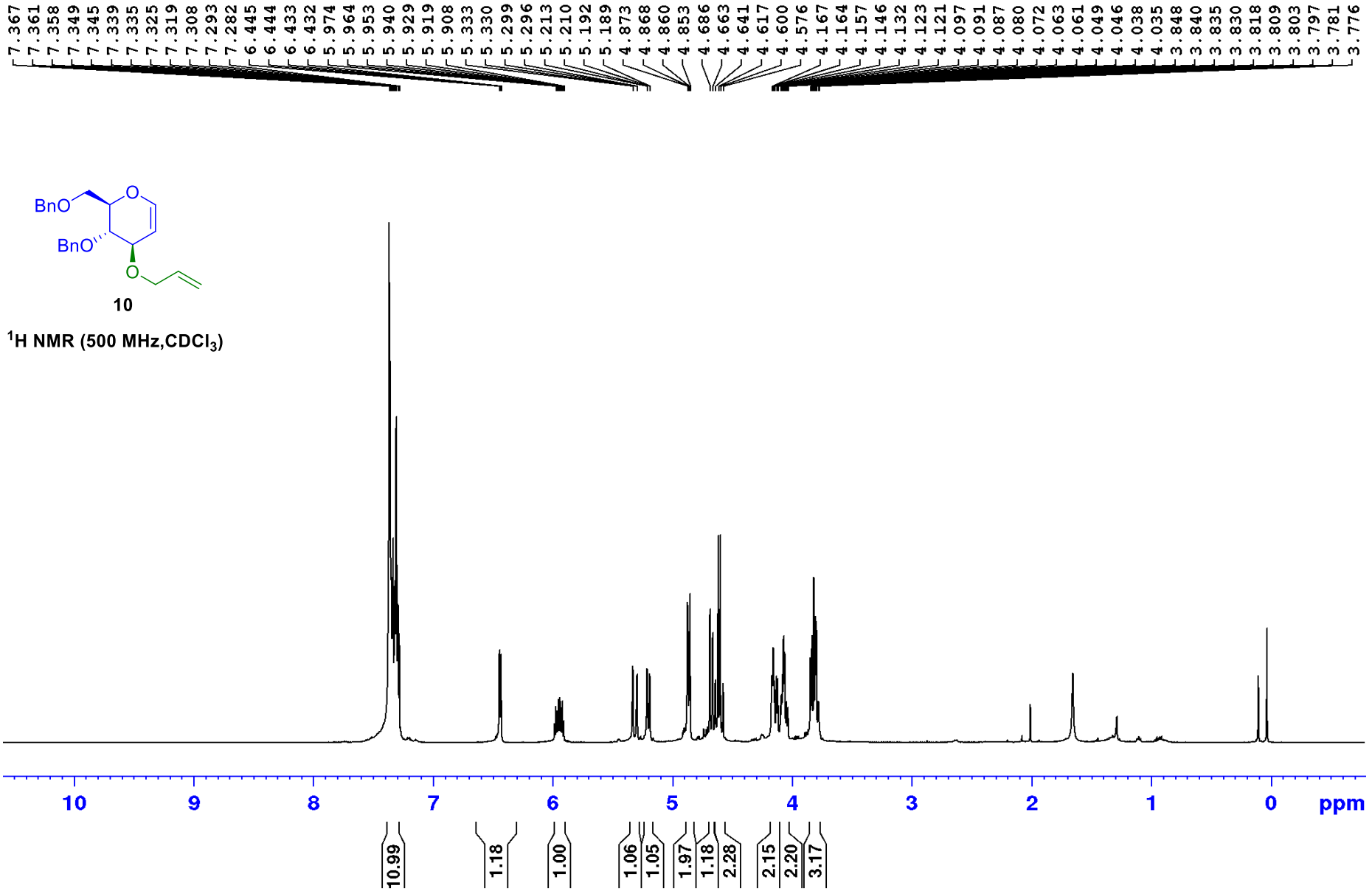
3

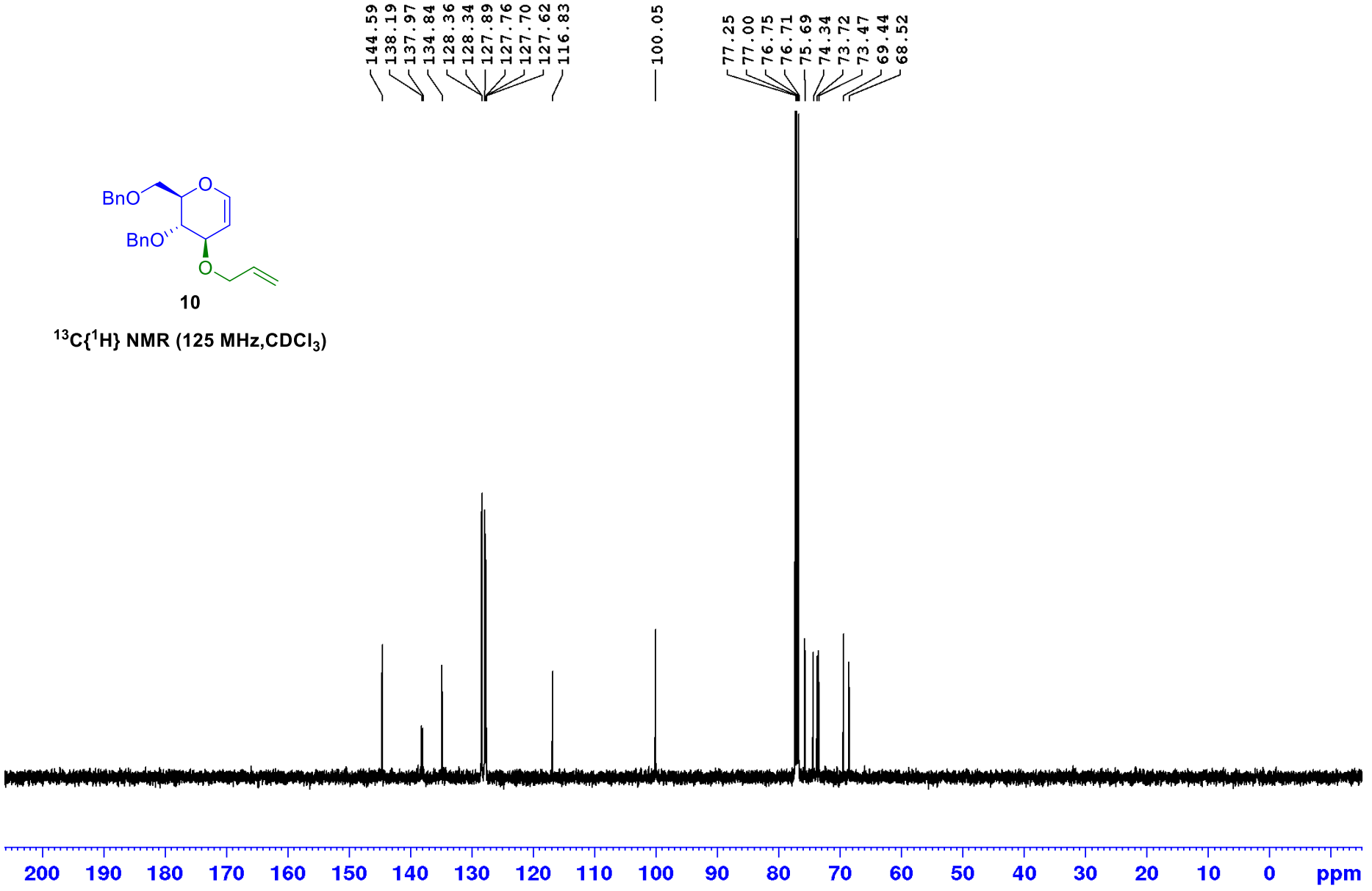
^{1}H NMR (400 MHz,$CDCl_3$)



3

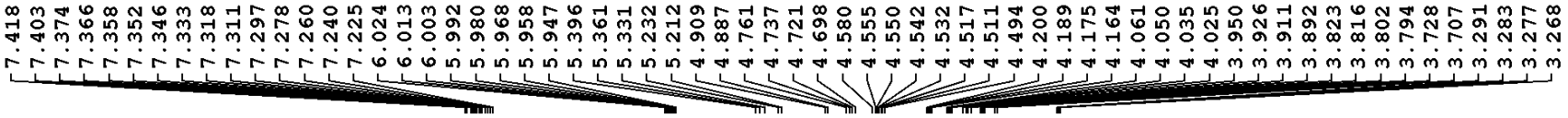
$^{13}C\{^{1}H\}$ NMR (100 MHz,$CDCl_3$)

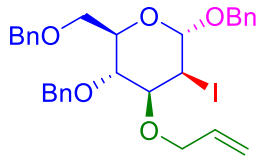

7.367
7.361
7.358
7.349
7.345
7.339
7.335
7.325
7.319
7.308
7.293
7.282
6.445
6.444
6.433
6.432
5.974
5.964
5.953
5.940
5.929
5.919
5.908
5.333
5.330
5.299
5.296
5.213
5.210
5.192
5.189
4.873
4.868
4.860
4.853
4.686
4.663
4.641
4.617
4.600
4.576
4.167
4.164
4.157
4.146
4.132
4.123
4.121
4.097
4.091
4.087
4.080
4.072
4.063
4.061
4.049
4.046
4.038
4.035
3.848
3.840
3.835
3.830
3.818
3.809
3.803
3.797
3.781
3.776
BnO
BnO
O
O
10
1H NMR (500 MHz,CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
10.99
1.18
1.00
1.06
1.05
1.97
1.18
2.28
2.15
2.20
3.17



10

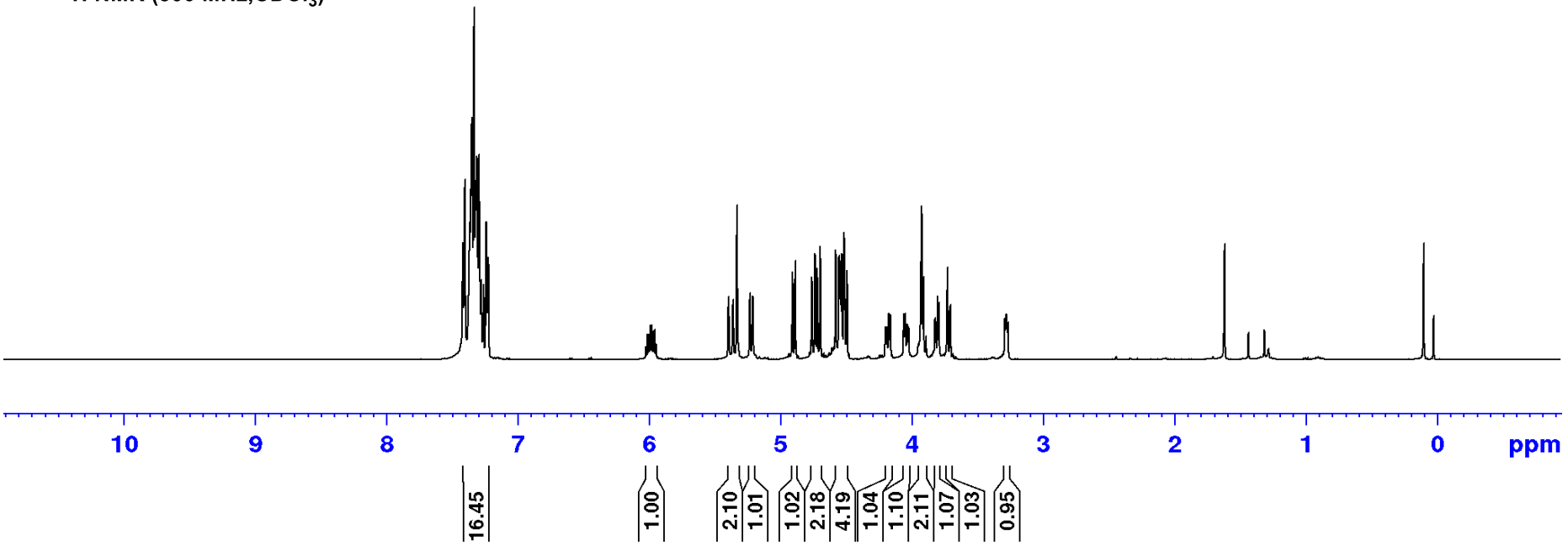
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)

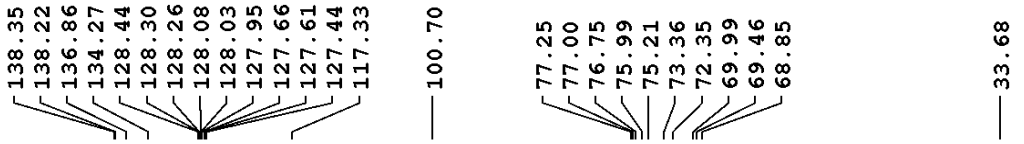


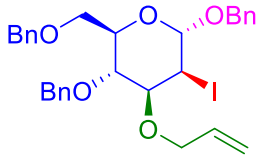


11

^{1} H NMR (500 MHz,$CDCl_3$)

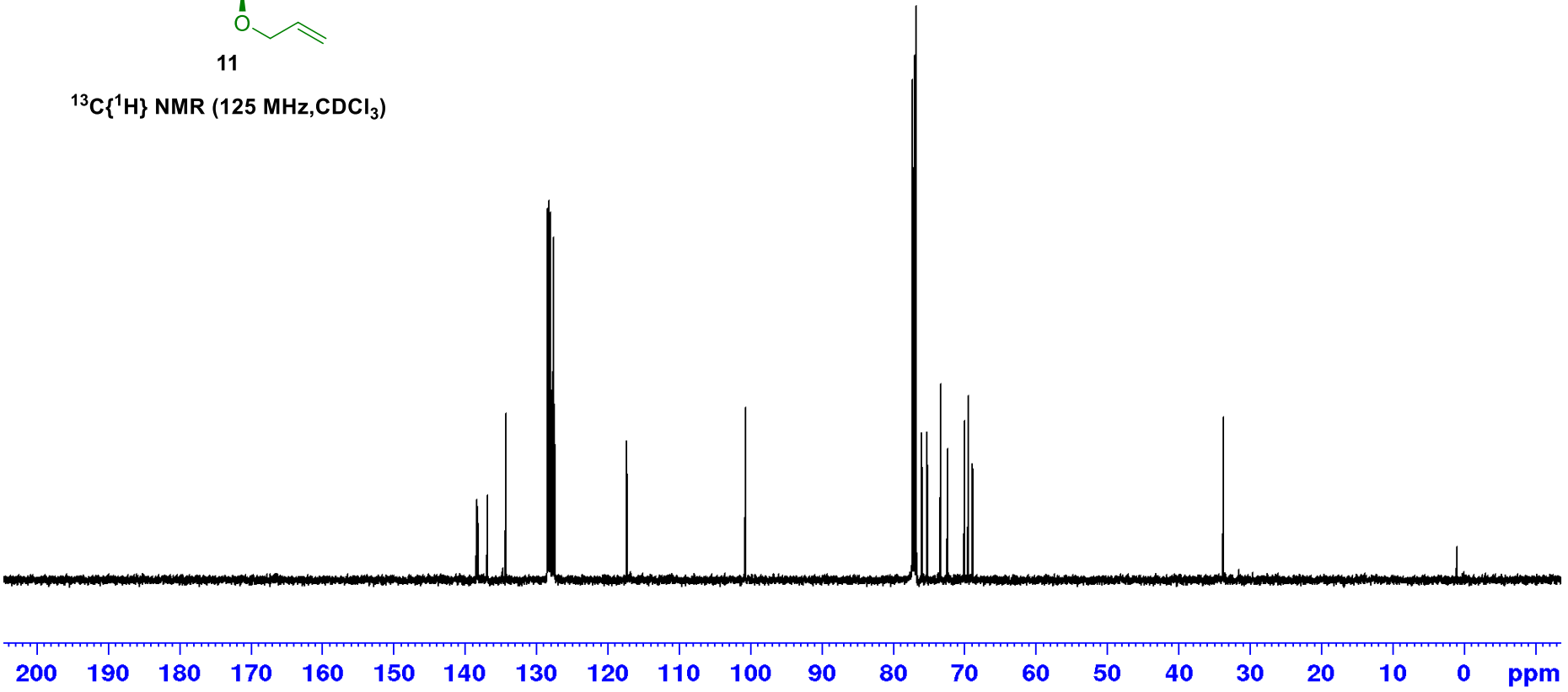


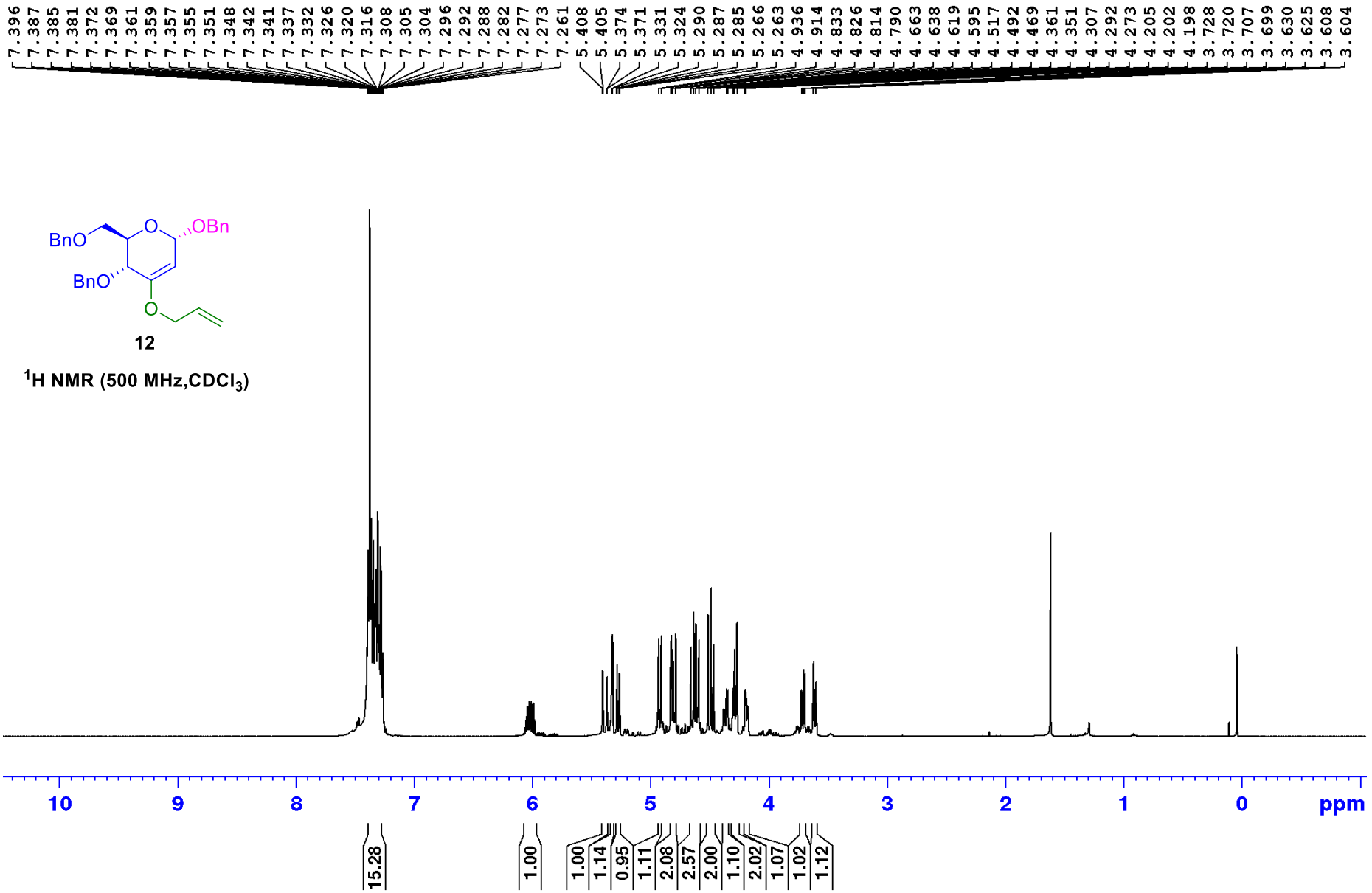


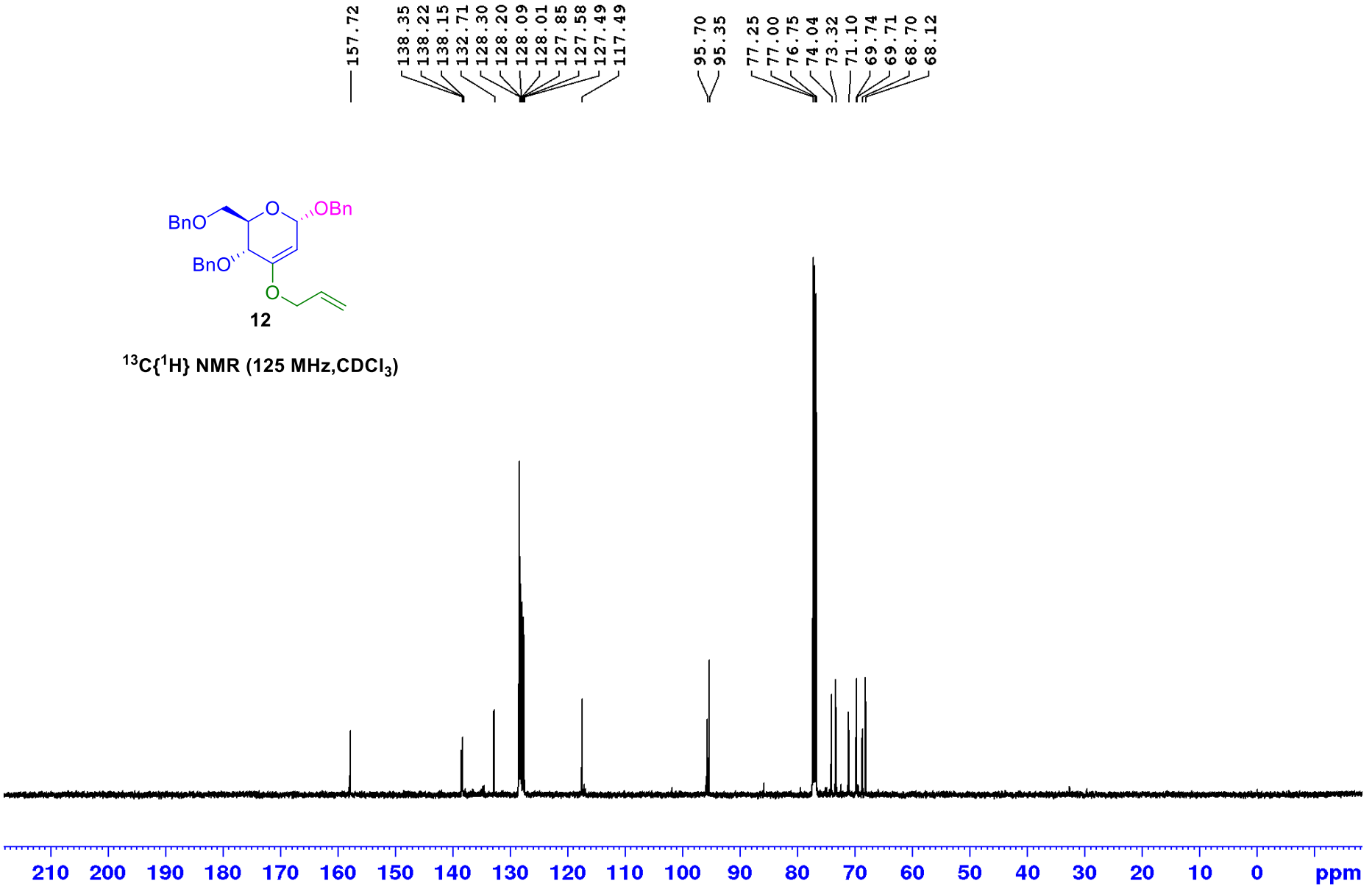


11

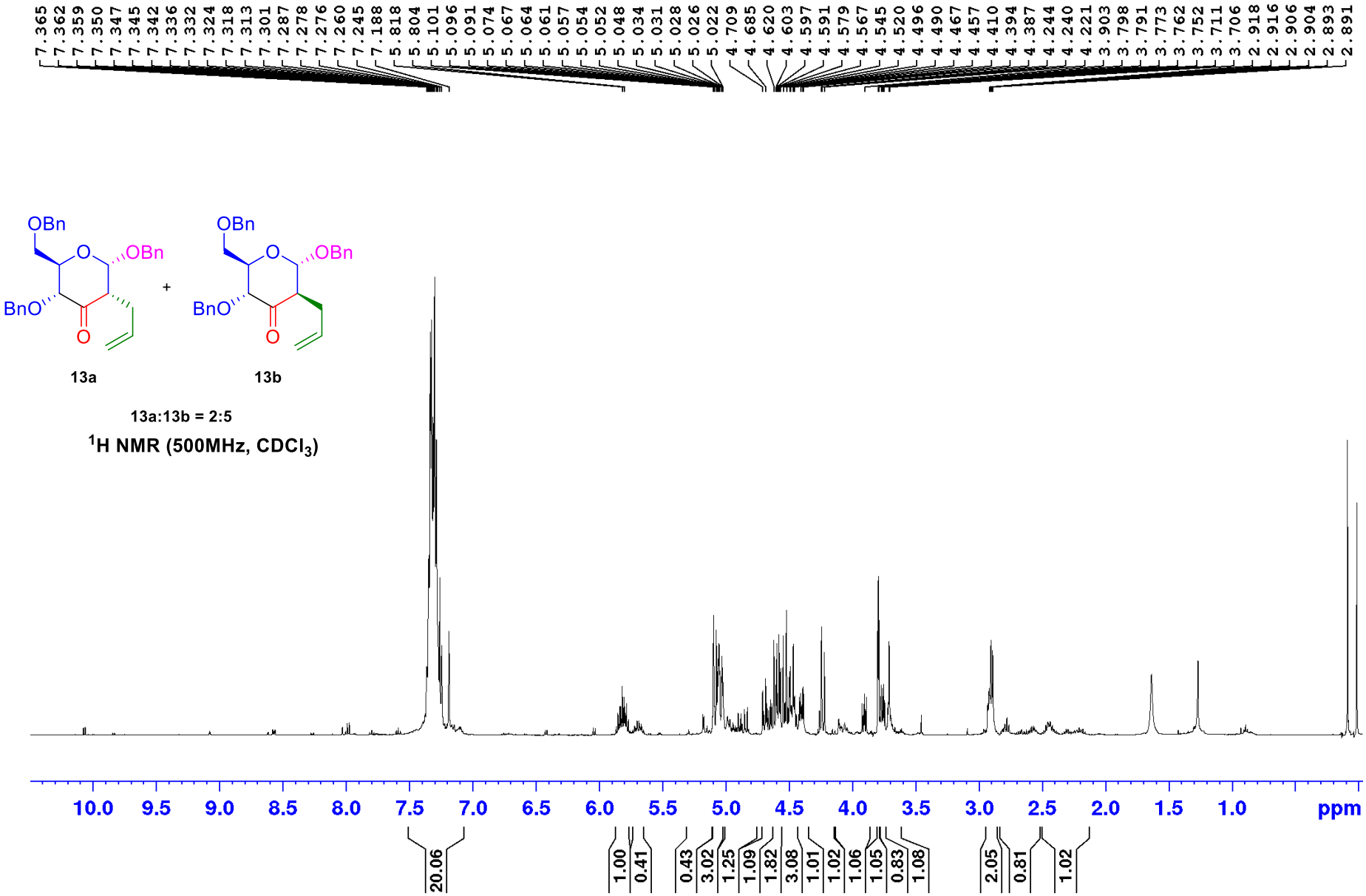
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)

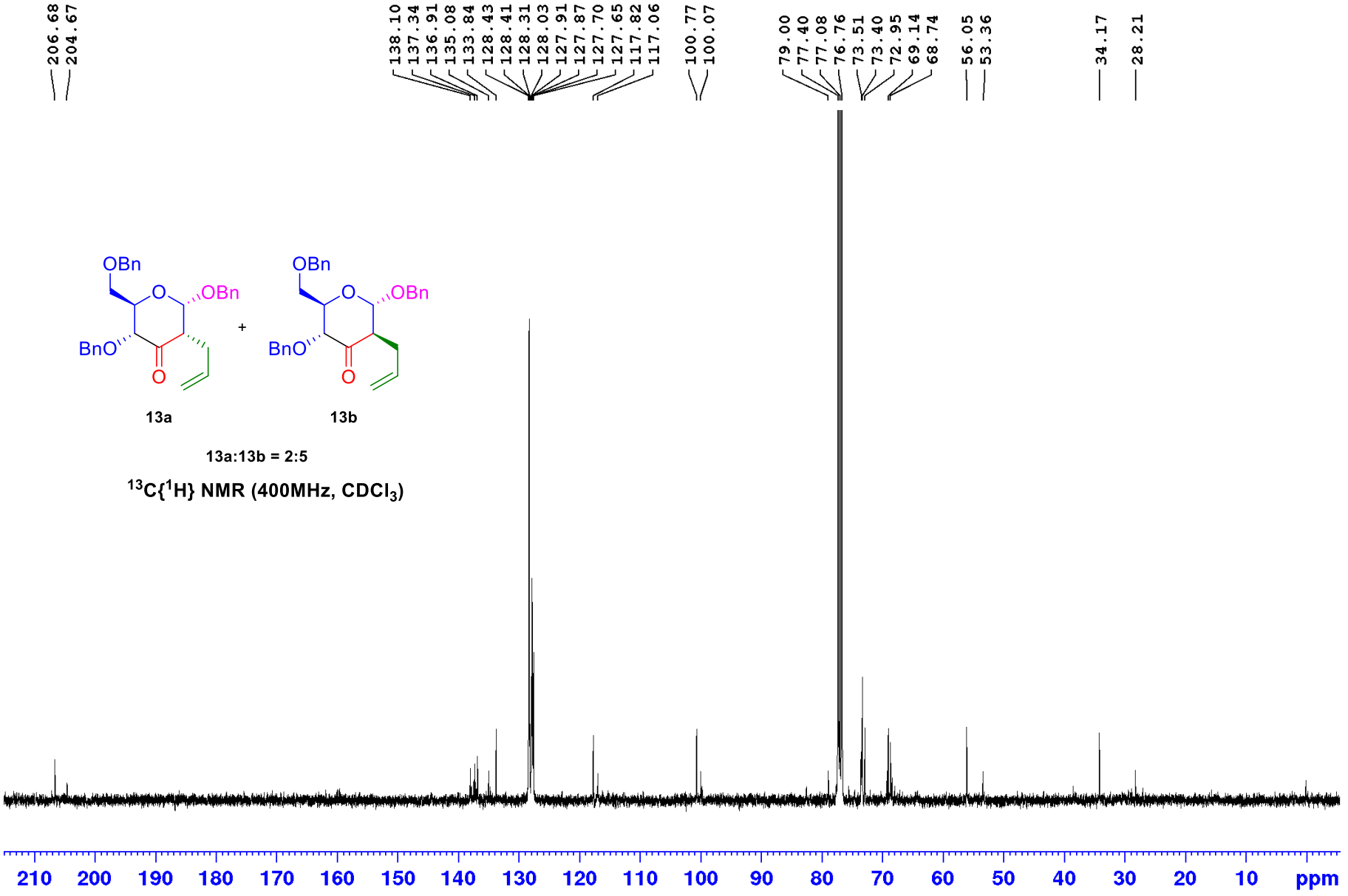


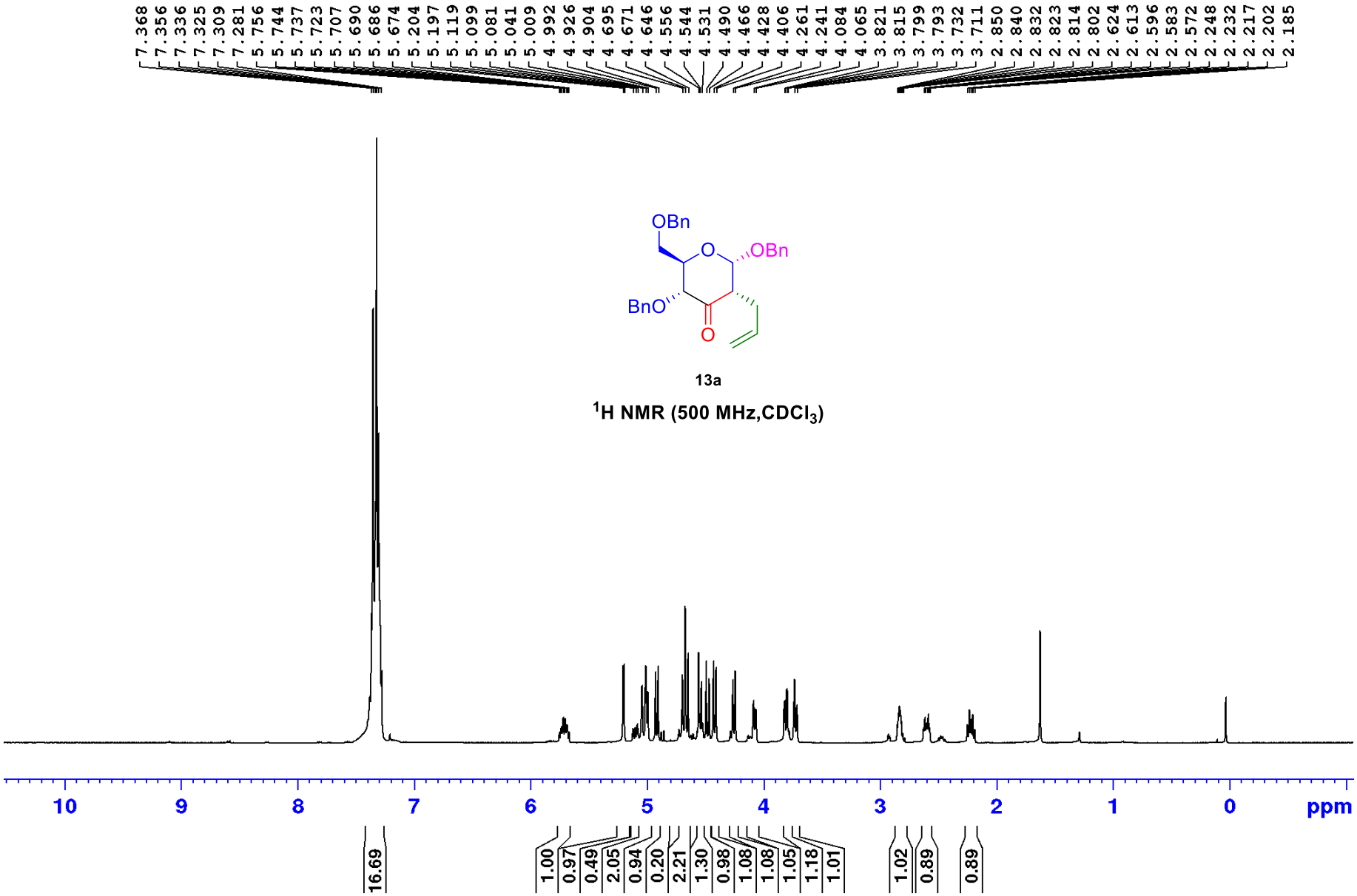

7.396
7.387
7.385
7.381
7.372
7.369
7.361
7.359
7.357
7.355
7.351
7.348
7.342
7.341
7.337
7.332
7.326
7.320
7.316
7.308
7.305
7.304
7.296
7.292
7.288
7.282
7.277
7.273
7.261
5.408
5.405
5.374
5.371
5.331
5.324
5.290
5.287
5.285
5.266
5.263
4.936
4.914
4.833
4.826
4.814
4.790
4.663
4.638
4.619
4.595
4.517
4.492
4.469
4.361
4.351
4.307
4.292
4.273
4.205
4.202
4.198
3.728
3.720
3.707
3.699
3.630
3.625
3.608
3.604
BnO
OBn
BnO
O
O
12
1H NMR (500 MHz,CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
15.28
1.00
1.00
1.14
0.95
1.11
2.08
2.57
2.00
1.10
2.02
1.07
1.02
1.12

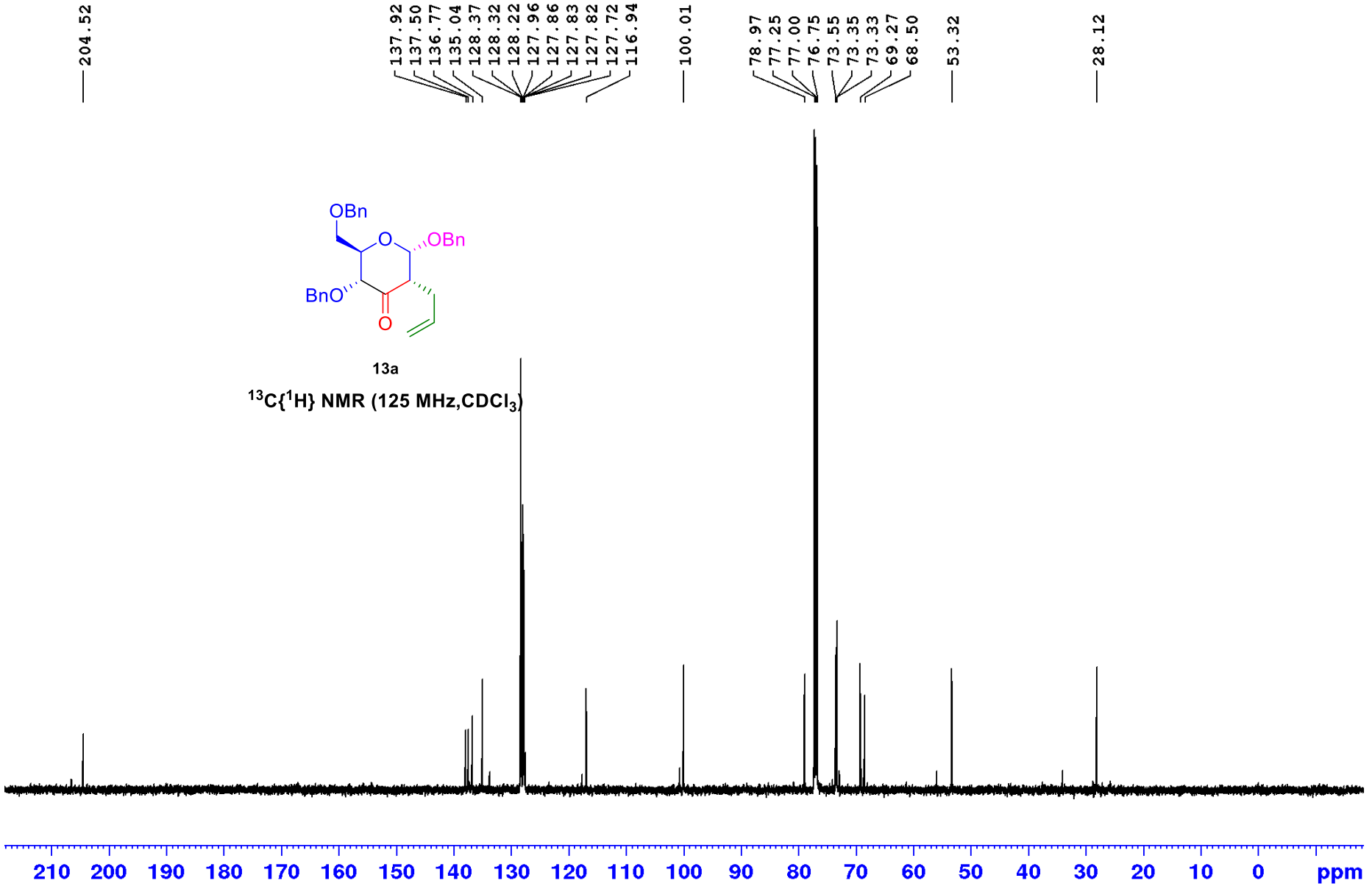


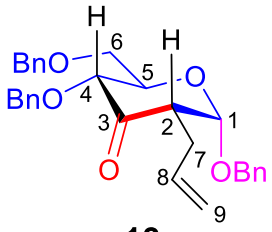
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)


7.365
7.362
7.359
7.350
7.347
7.345
7.342
7.336
7.332
7.324
7.318
7.313
7.301
7.287
7.278
7.276
7.260
7.245
7.188
5.818
5.804
5.101
5.096
5.091
5.074
5.067
5.064
5.061
5.057
5.054
5.052
5.048
5.034
5.031
5.028
5.026
5.022
4.709
4.685
4.620
4.603
4.597
4.591
4.579
4.567
4.545
4.520
4.496
4.490
4.467
4.457
4.410
4.394
4.387
4.244
4.240
4.221
3.903
3.798
3.791
3.773
3.762
3.752
3.711
3.706
2.918
2.916
2.906
2.904
2.893
2.891
OBn
OBn
BnO
O
O
13a
+
OBn
OBn
BnO
O
O
13b
13a:13b = 2:5
1H NMR (500MHz, CDCl3)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
20.06
1.00
0.41
0.43
3.02
1.25
1.09
1.82
3.08
1.01
1.02
1.06
1.05
0.83
1.08
2.05
0.81
1.02


206.68
204.67
138.10
137.34
136.91
135.08
133.84
128.43
128.41
128.31
128.03
127.91
127.87
127.70
127.65
117.82
117.06
100.77
100.07
79.00
77.40
77.08
76.76
73.51
73.40
72.95
69.14
68.74
56.05
53.36
34.17
28.21
OBn
OBn
BnO
O
O
+
OBn
OBn
BnO
O
O
13a
13b
13a:13b = 2:5
$^{13}C\{^{1}H\}$ NMR (400MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

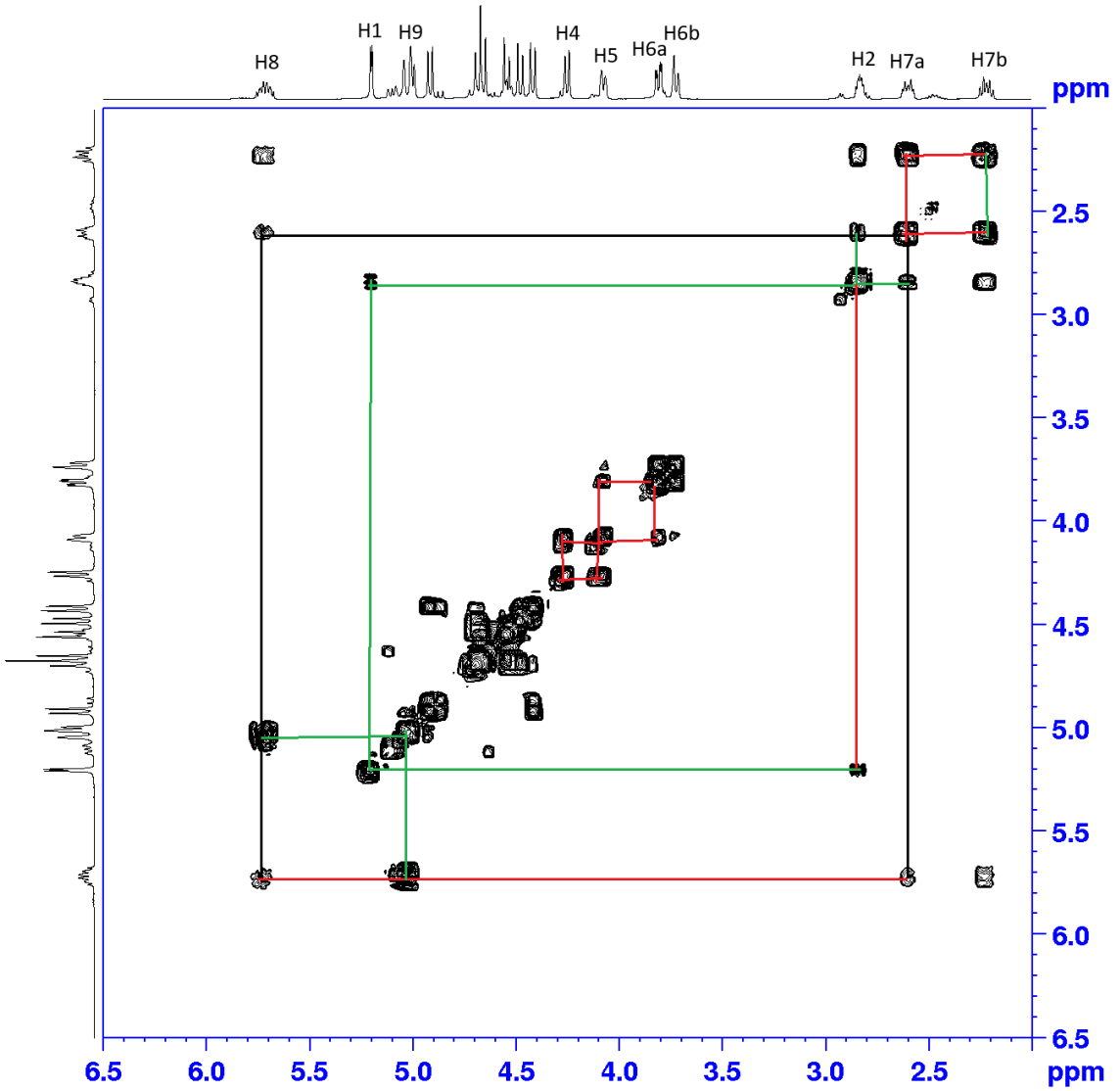

7.368
7.356
7.336
7.325
7.309
7.281
5.756
5.744
5.737
5.723
5.707
5.690
5.686
5.674
5.204
5.197
5.119
5.099
5.081
5.041
5.009
4.992
4.926
4.904
4.695
4.671
4.646
4.556
4.544
4.531
4.490
4.466
4.428
4.406
4.261
4.241
4.084
4.065
3.821
3.815
3.799
3.793
3.732
3.711
2.850
2.840
2.832
2.823
2.814
2.802
2.624
2.613
2.596
2.583
2.572
2.248
2.232
2.217
2.202
2.185
OBn
O
OBn
BnO
O
13a
1H NMR (500 MHz,CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
16.69
1.00
0.97
0.49
2.05
0.94
0.20
2.21
1.30
0.98
1.08
1.08
1.05
1.18
1.01
1.02
0.89
0.89

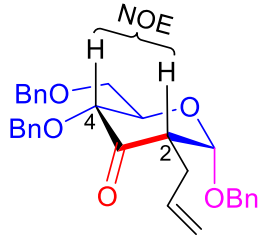

204.52
137.92
137.50
136.77
135.04
128.37
128.32
128.22
127.96
127.86
127.83
127.82
127.72
116.94
100.01
78.97
77.25
77.00
76.75
73.55
73.35
73.33
69.27
68.50
53.32
28.12
OBn
O
OBn
BnO
O
13a
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



13a

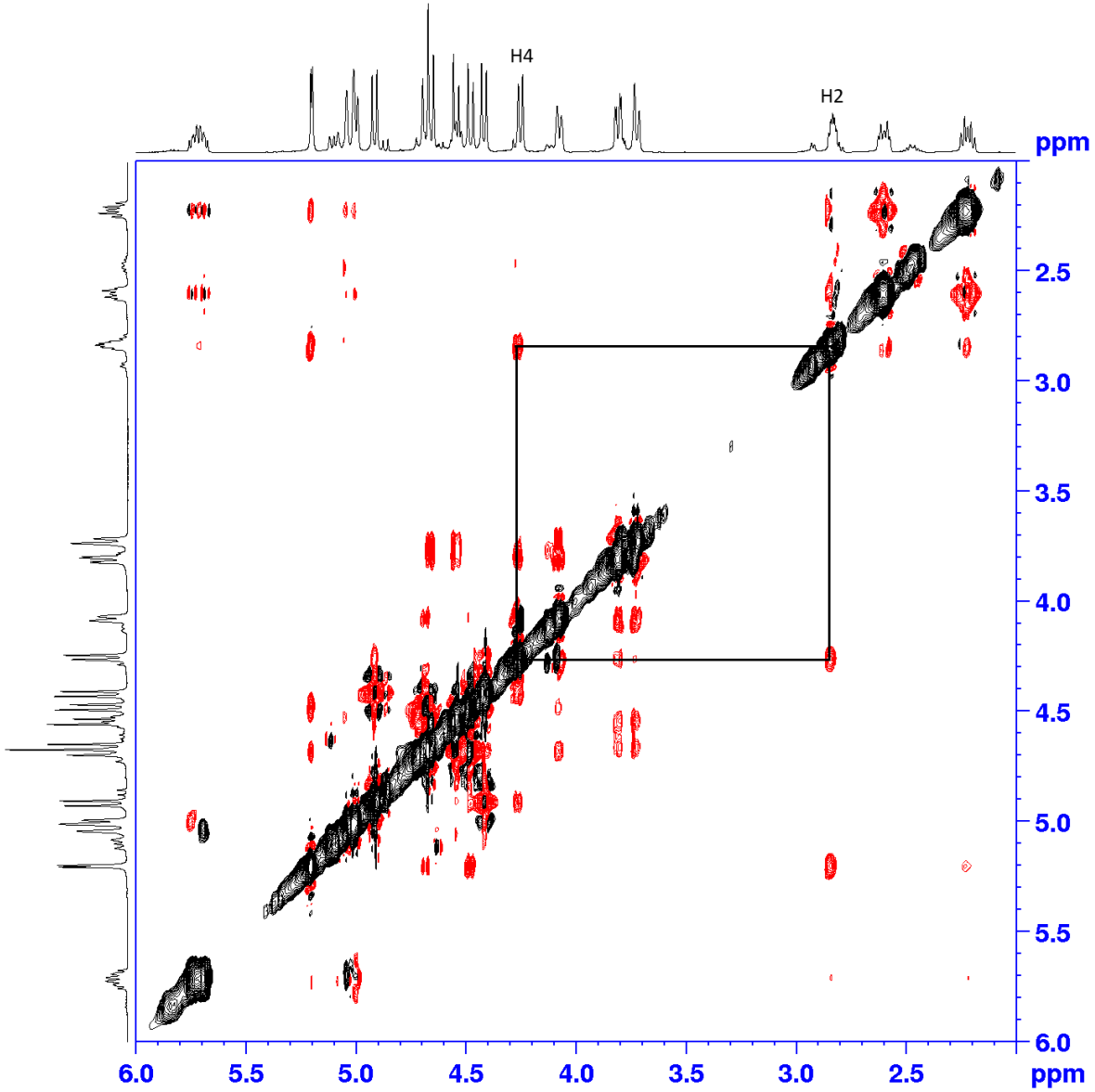
^{1}H-^{1}H COSY (500 MHz, $CDCl_3$)

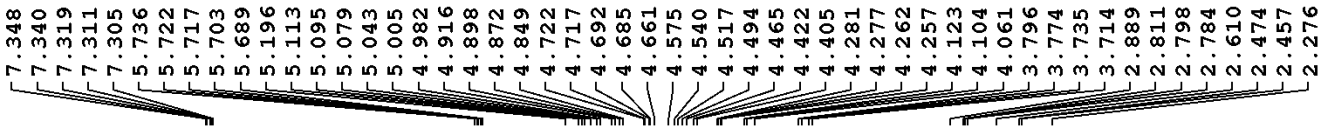


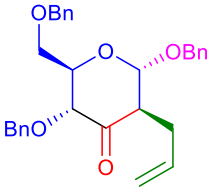


13a

^{1}H-^{1}H NOESY (500 MHz, $CDCl_3$)

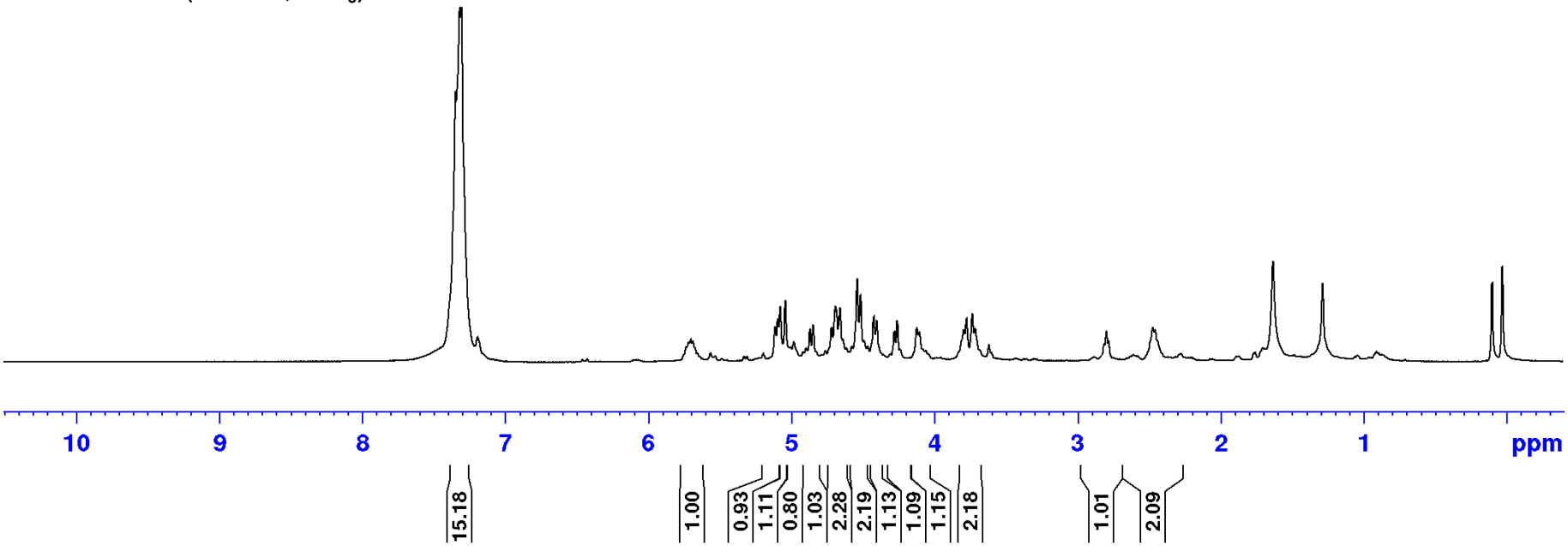


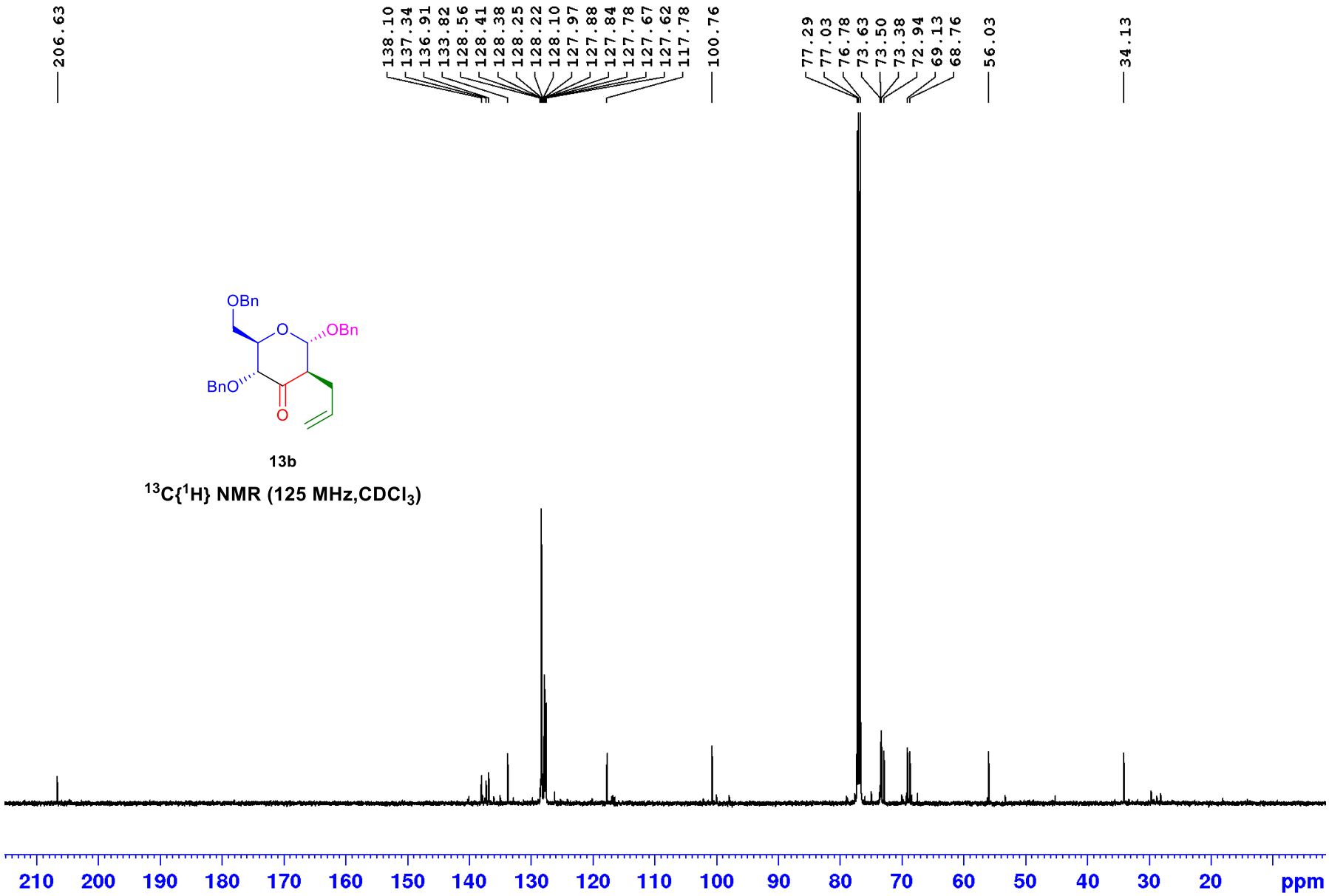




13b

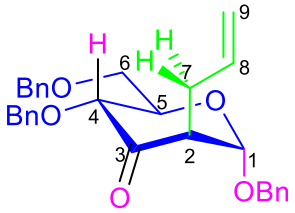
^{1}H NMR (500 MHz,$CDCl_3$)





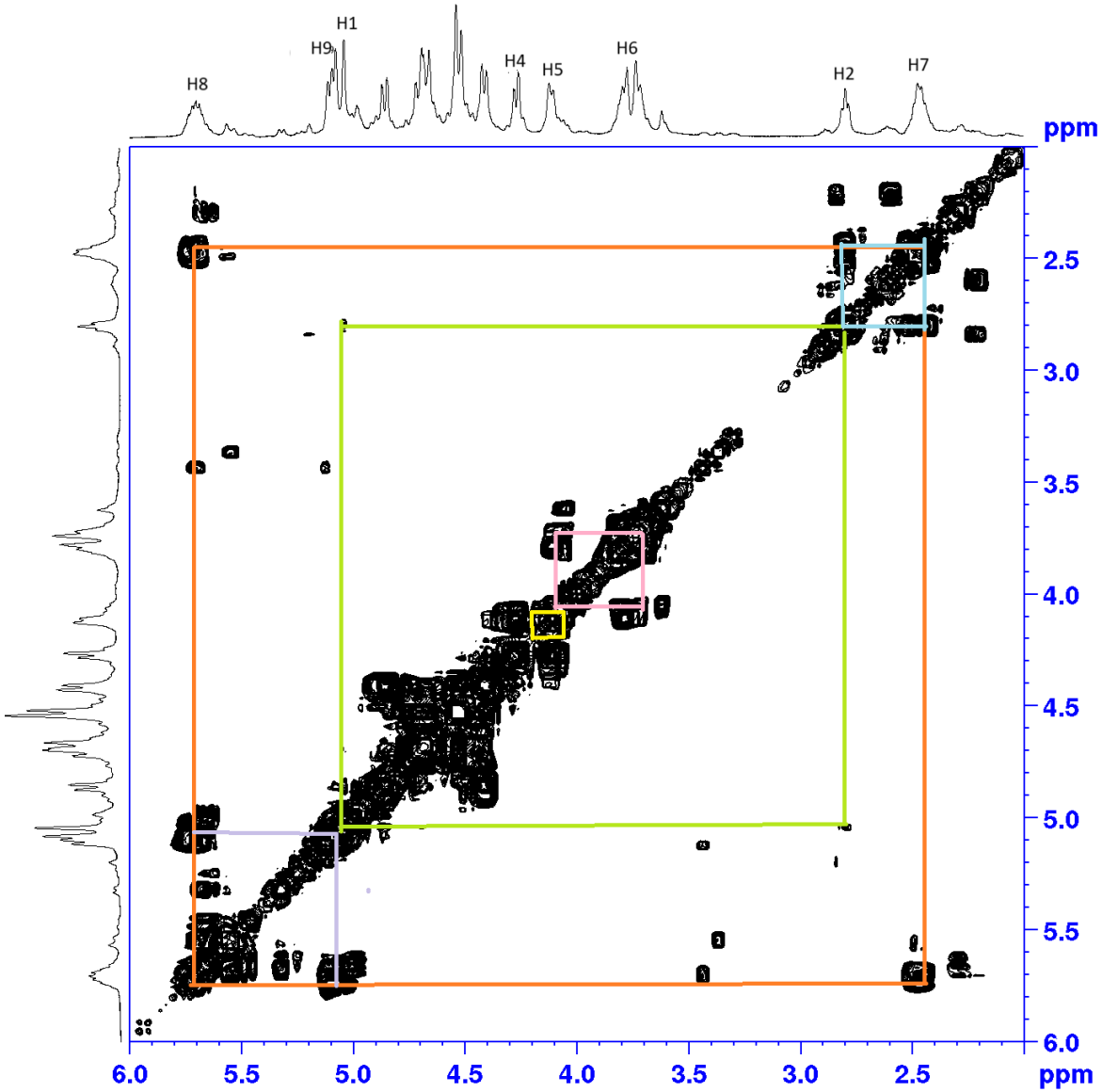
13b

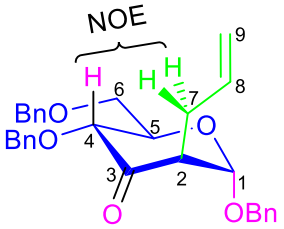
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)



13b

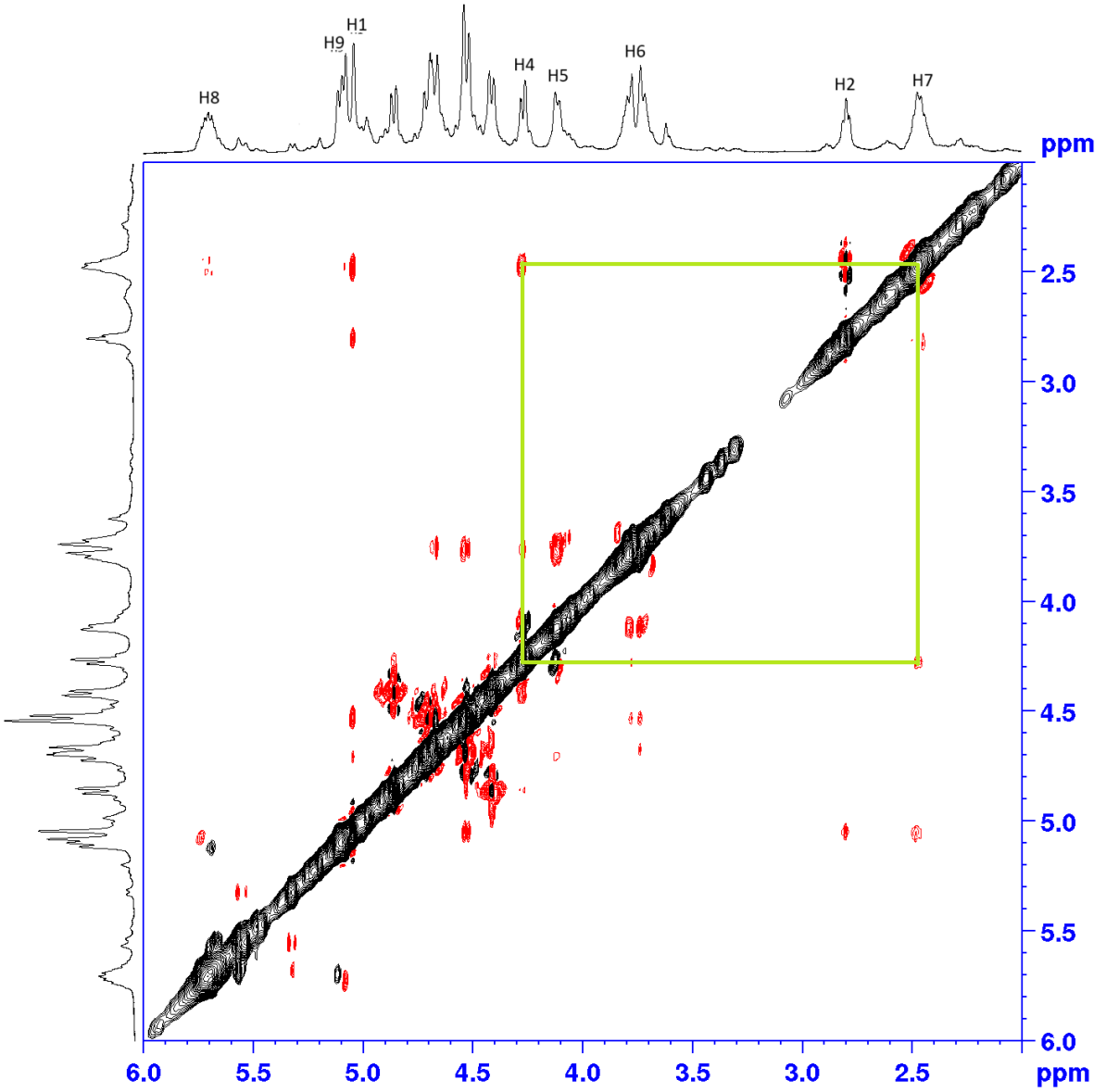
^{1}H-^{1}H COSY (500 MHz, $CDCl_3$)

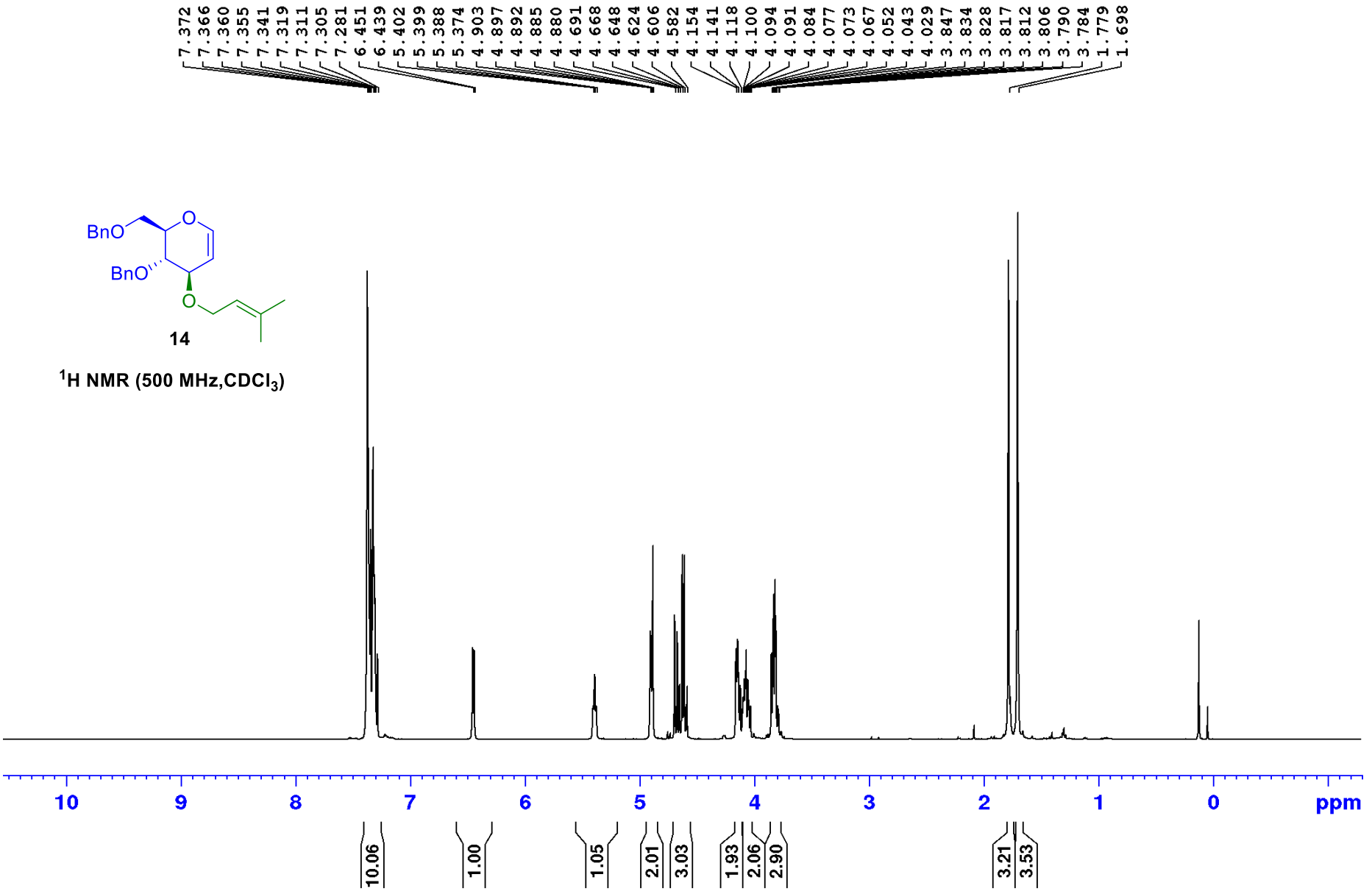


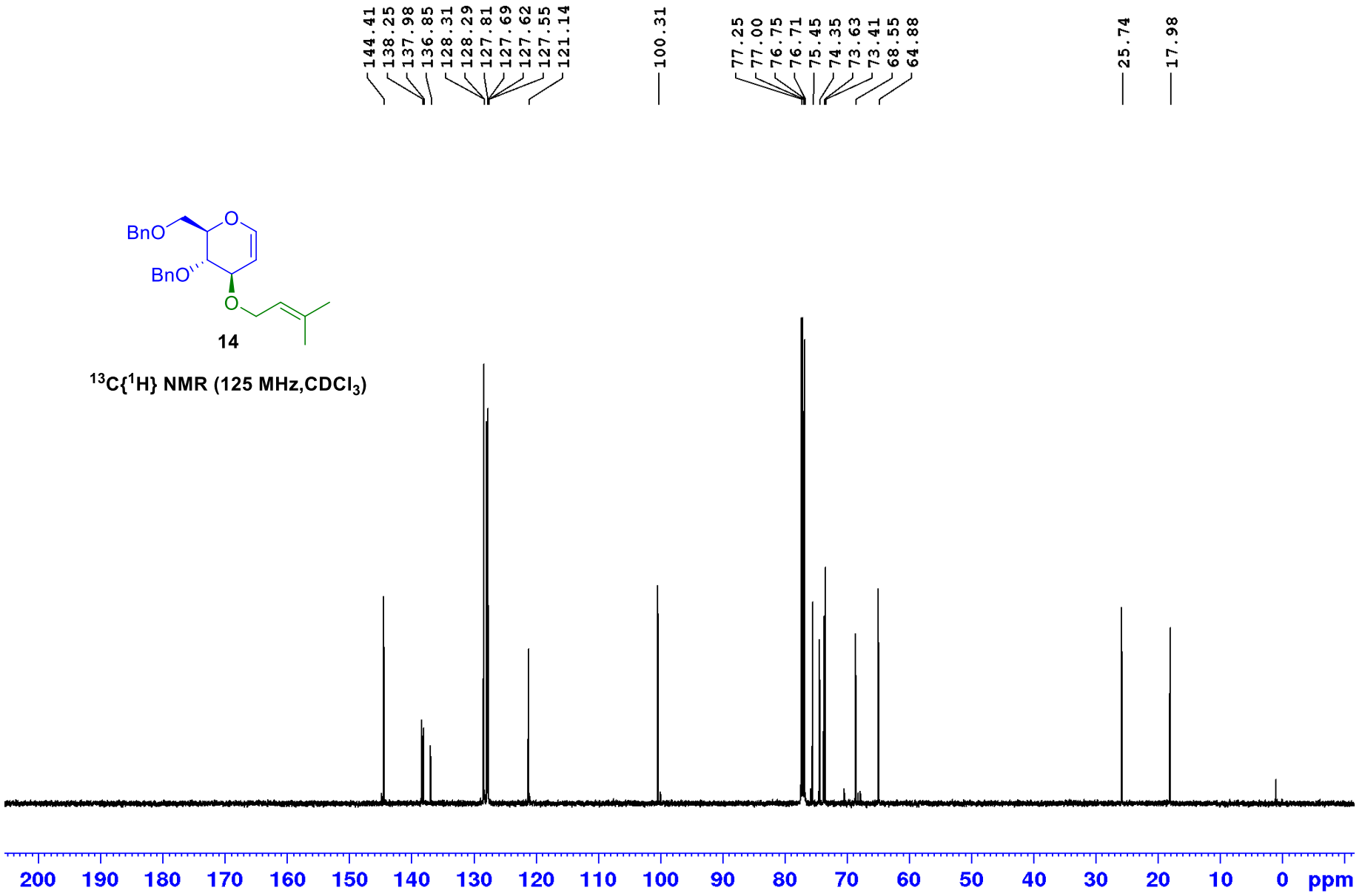


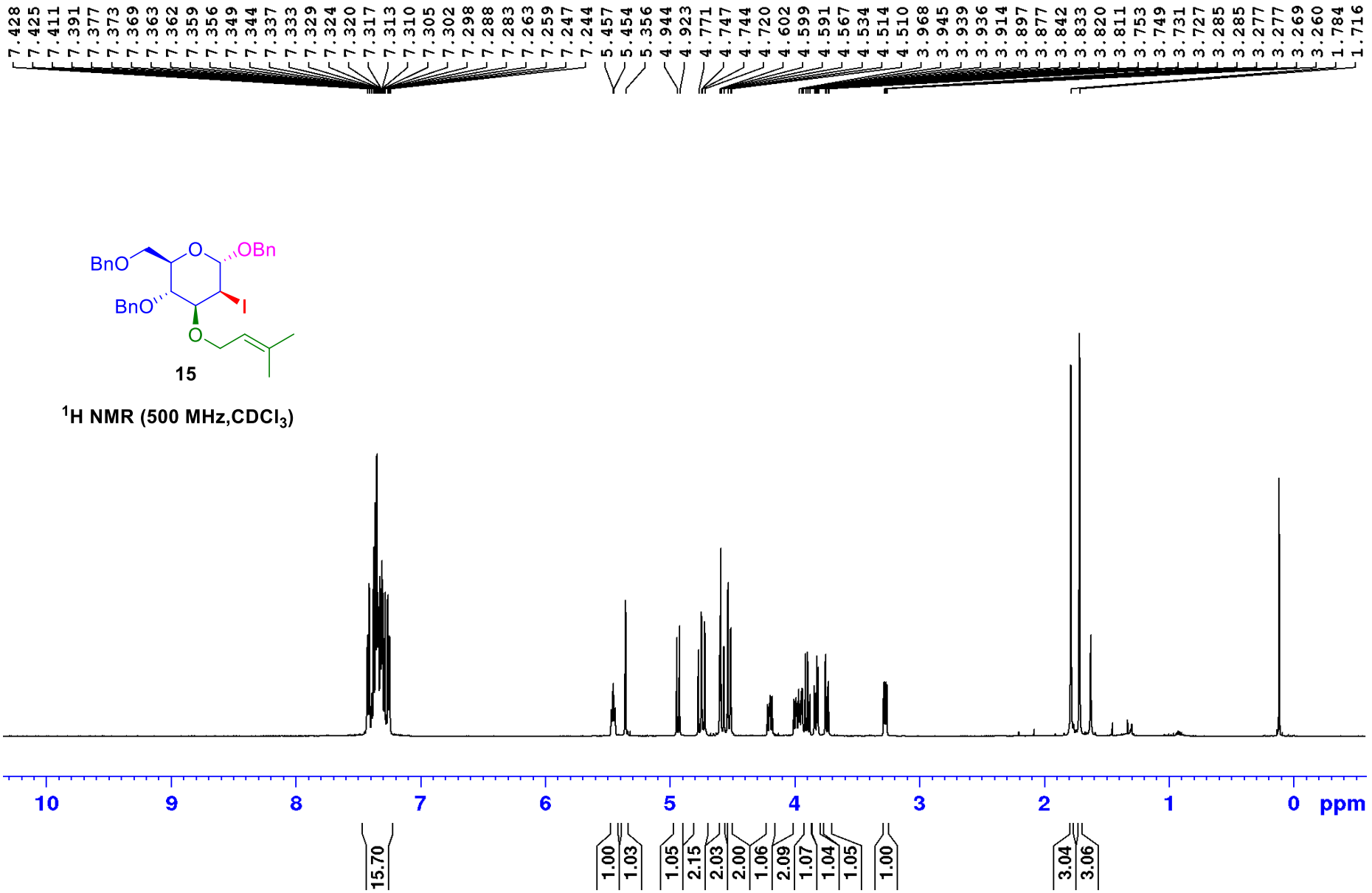
13b

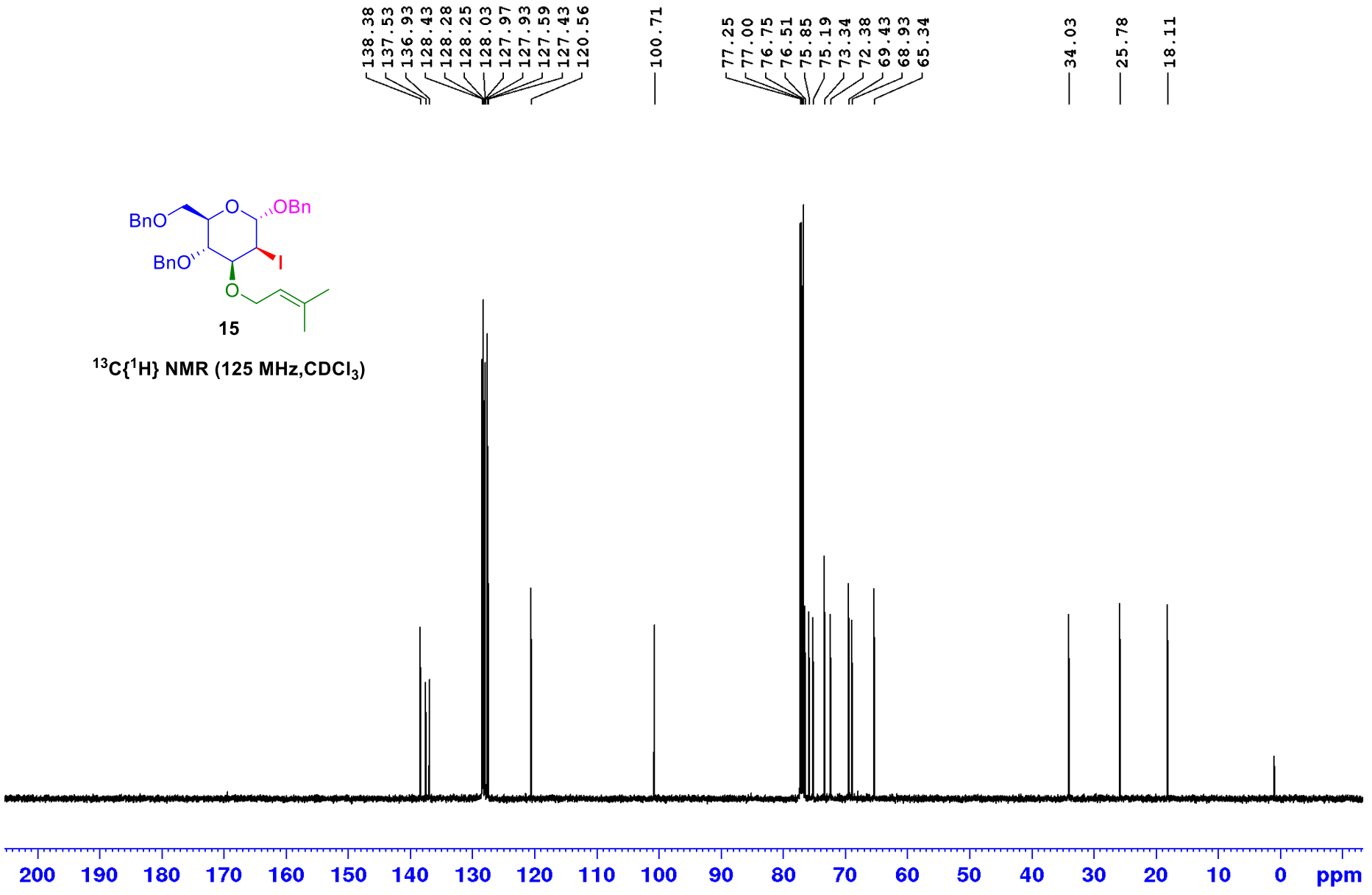
^{1}H-^{1}H NOESY (500 MHz, $CDCl_3$)

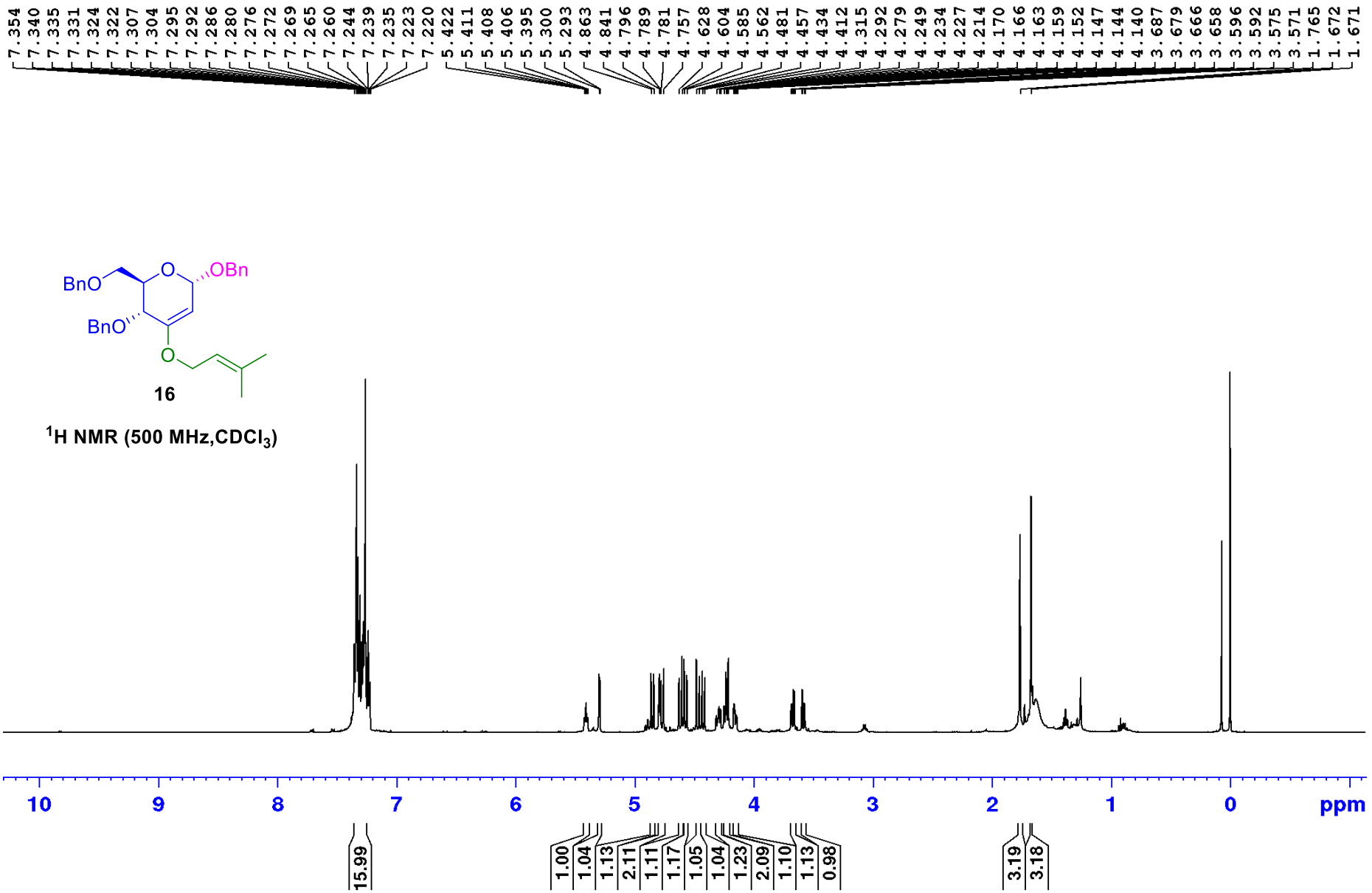


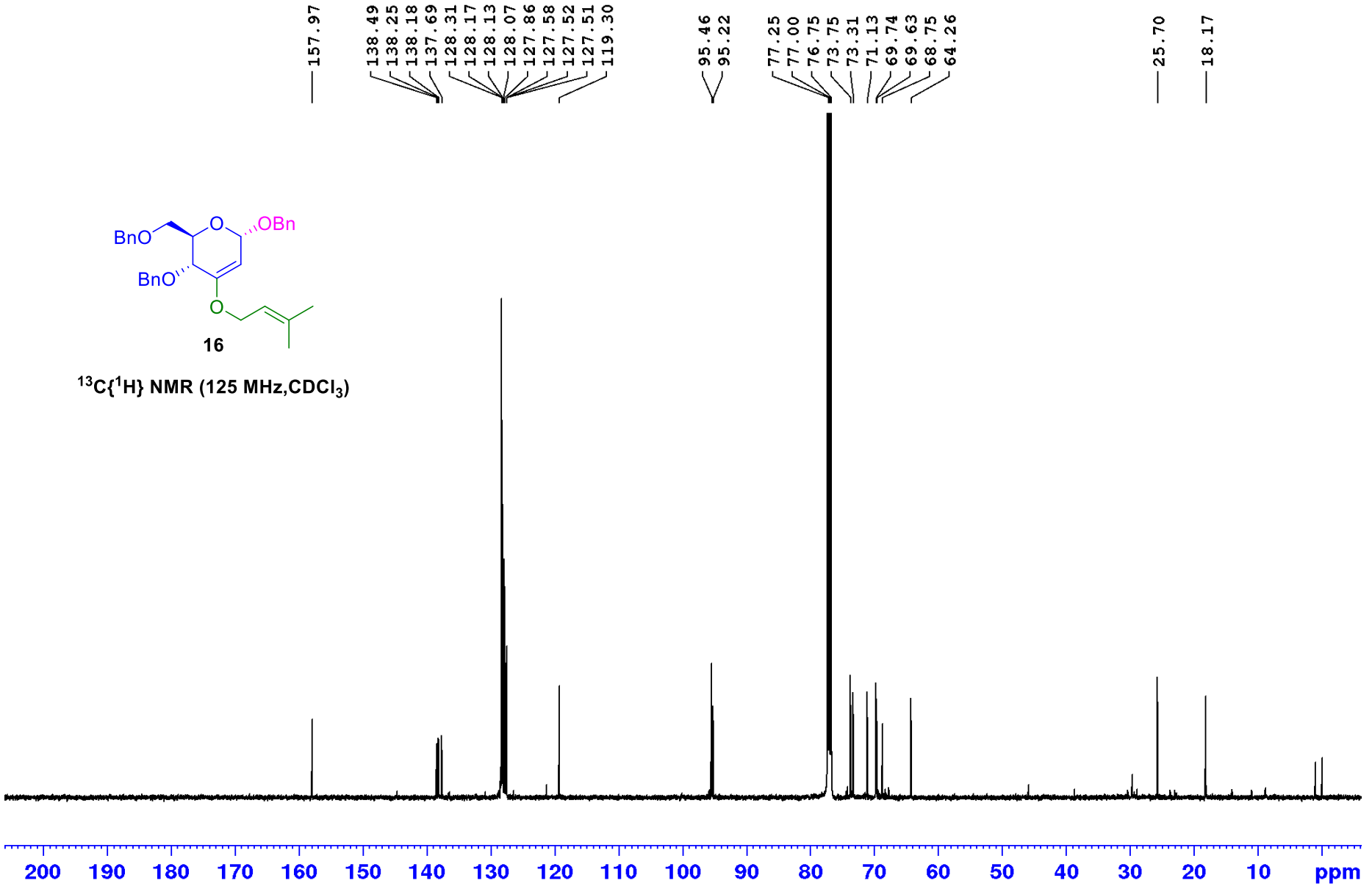

7.372
7.366
7.360
7.355
7.341
7.319
7.311
7.305
7.281
6.451
6.439
6.402
5.399
5.388
5.374
4.903
4.897
4.892
4.885
4.880
4.691
4.668
4.648
4.624
4.606
4.582
4.154
4.141
4.118
4.100
4.094
4.091
4.084
4.077
4.073
4.067
4.052
4.043
4.029
3.847
3.834
3.828
3.817
3.812
3.806
3.790
3.784
1.779
1.698
BnO
BnO
O
O
14
^{1}H NMR (500 MHz,CDCl$_3$)
10
9
8
7
6
5
4
3
2
1
0
ppm
10.06
1.00
1.05
2.01
3.03
1.93
2.06
2.90
3.21
3.53


144.41
138.25
137.98
136.85
128.31
128.29
127.81
127.69
127.62
127.55
121.14
100.31
77.25
77.00
76.75
76.71
75.45
74.35
73.63
73.41
68.55
64.88
25.74
17.98
BnO
BnO
O
O
14
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


7.428
7.425
7.411
7.391
7.377
7.373
7.369
7.363
7.362
7.359
7.356
7.349
7.344
7.337
7.333
7.329
7.324
7.320
7.317
7.313
7.310
7.305
7.302
7.298
7.288
7.283
7.263
7.259
7.247
7.244
5.457
5.454
5.356
4.944
4.923
4.771
4.747
4.744
4.720
4.602
4.599
4.591
4.567
4.534
4.514
4.510
3.968
3.945
3.939
3.936
3.914
3.897
3.877
3.842
3.833
3.820
3.811
3.753
3.749
3.731
3.727
3.285
3.285
3.277
3.277
3.269
3.260
1.784
1.716
BnO
O
OBn
BnO
I
O
15
^{1}H NMR (500 MHz,CDCl$_3$)
10
9
8
7
6
5
4
3
2
1
0
ppm
15.70
1.00
1.03
1.05
2.15
2.03
2.00
1.06
2.09
1.07
1.04
1.05
1.00
3.04
3.06

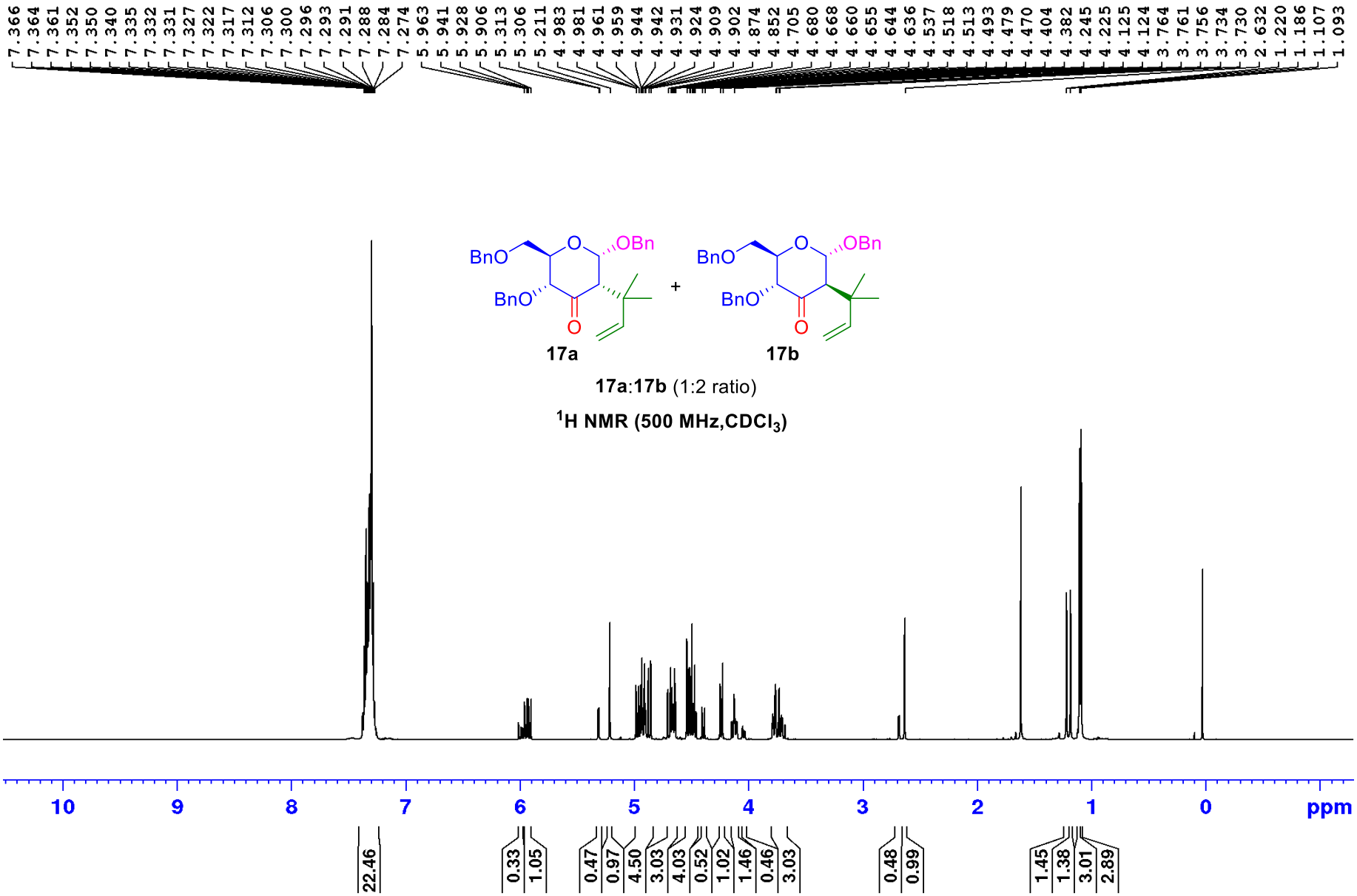

138.38
137.53
136.93
128.43
128.28
128.25
128.03
127.97
127.93
127.59
127.43
120.56
100.71
77.25
77.00
76.75
76.51
75.85
75.19
73.34
72.38
69.43
68.93
65.34
34.03
25.78
18.11
BnO
OBn
BnO
I
O
O
15
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

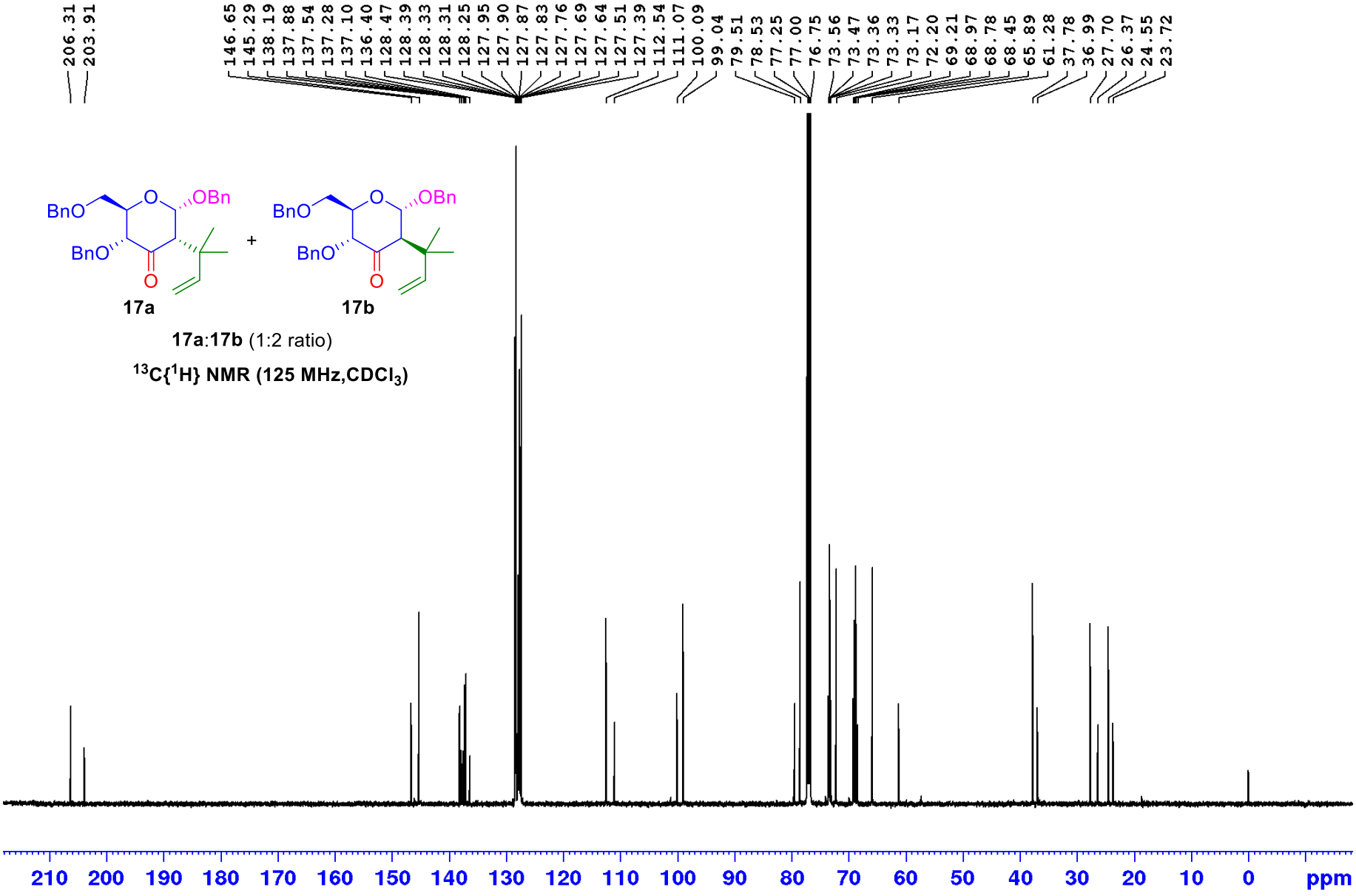

7.354
7.340
7.335
7.331
7.324
7.322
7.307
7.304
7.295
7.292
7.286
7.280
7.276
7.272
7.269
7.265
7.260
7.244
7.239
7.235
7.223
7.220
5.422
5.411
5.408
5.406
5.395
5.300
5.293
4.863
4.841
4.796
4.789
4.781
4.757
4.628
4.604
4.585
4.562
4.481
4.457
4.434
4.412
4.315
4.292
4.279
4.249
4.234
4.227
4.214
4.170
4.166
4.163
4.159
4.152
4.147
4.144
4.140
3.687
3.679
3.666
3.658
3.596
3.592
3.575
3.571
1.765
1.672
1.671
BnO
O
OBn
BnO
O
16
1H NMR (500 MHz,CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
15.99
1.00
1.04
1.13
2.11
1.11
1.17
1.05
1.04
1.23
2.09
1.10
1.13
0.98
3.19
3.18

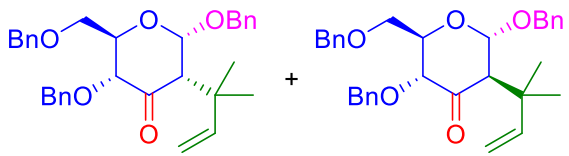


16

$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)


7.366 7.364 7.361 7.352 7.350 7.340 7.335 7.332 7.331 7.327 7.322 7.317 7.312 7.306 7.300 7.296 7.293 7.291 7.288 7.284 7.274
5.963 5.941 5.928 5.906 5.313 5.306 5.211 4.983 4.981 4.961 4.959 4.944 4.942 4.931 4.924 4.909 4.902 4.874 4.852 4.705 4.680 4.668 4.660 4.655 4.644 4.636 4.537 4.518 4.513 4.493 4.479 4.470 4.404 4.382 4.245 4.225 4.125 4.124 3.764 3.761 3.756 3.734 3.730 2.632 1.220 1.186 1.107 1.093
BnO
OBn
BnO
O
O
17a
+
BnO
OBn
BnO
O
O
17b
17a:17b (1:2 ratio)
1H NMR (500 MHz,CDCl3)
10 9 8 7 6 5 4 3 2 1 0 ppm
22.46
0.33 1.05
0.47 0.97 4.50 3.03 4.03 0.52 1.02 1.46 0.46 3.03
0.48 0.99
1.45 1.38 3.01 2.89

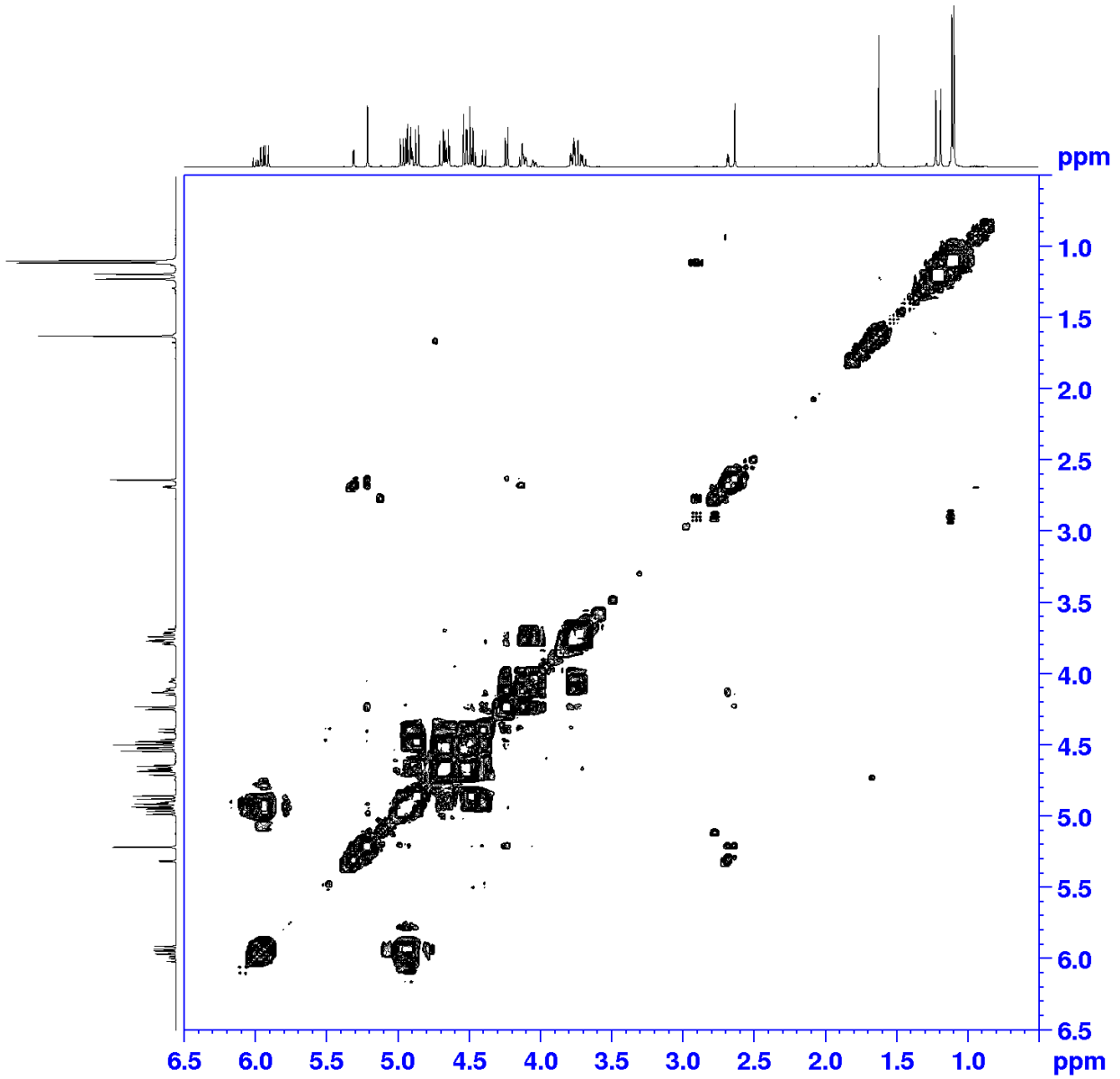

206.31
203.91
146.65
145.29
138.19
137.88
137.54
137.28
137.10
136.40
128.47
128.39
128.33
128.31
128.25
127.95
127.90
127.87
127.83
127.76
127.69
127.64
127.51
127.39
112.54
111.07
100.09
99.04
79.51
78.53
77.25
77.00
76.75
73.56
73.47
73.36
73.33
73.17
72.20
69.21
68.97
68.78
68.45
65.89
61.28
37.78
36.99
27.70
26.37
24.55
23.72
BnO
OBn
BnO
O
O
+
BnO
OBn
BnO
O
O
17a
17b
17a:17b (1:2 ratio)
13C{1H} NMR (125 MHz,CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

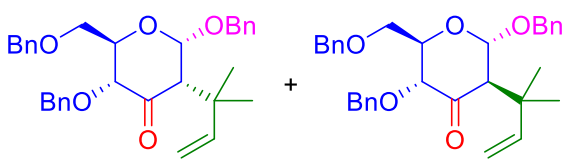


17a **17b**

17a:**17b** (1:2 ratio)

^{1}H-^{1}H COSY, (500 MHz,$CDCl_3$)

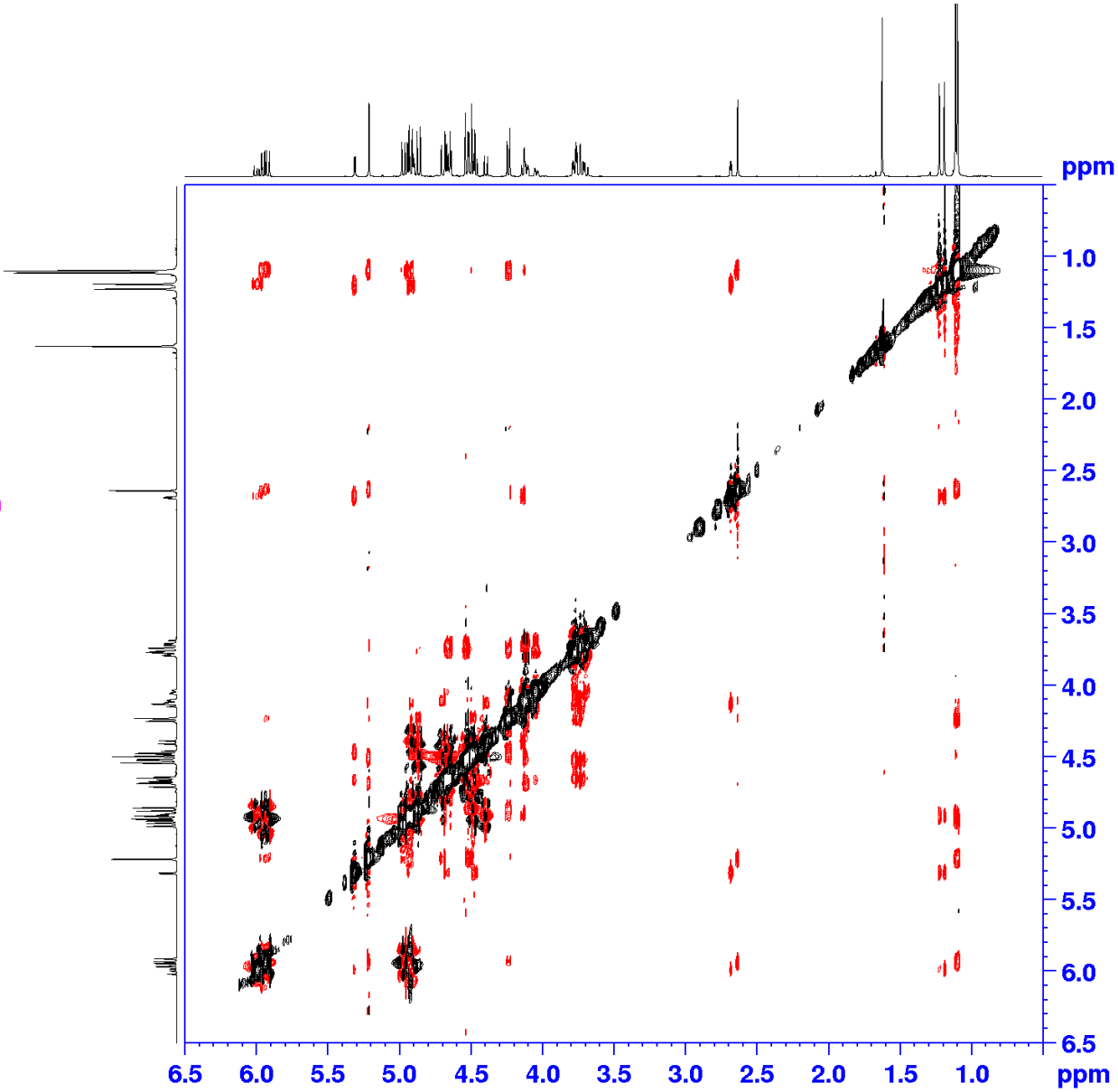


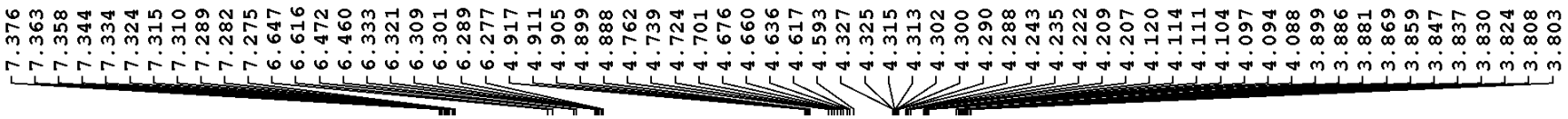


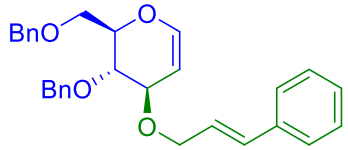
17a **17b**

17a:**17b** (1:2 ratio)

^{1}H-^{1}H NOESY, (500 MHz,CDCl$_3$)

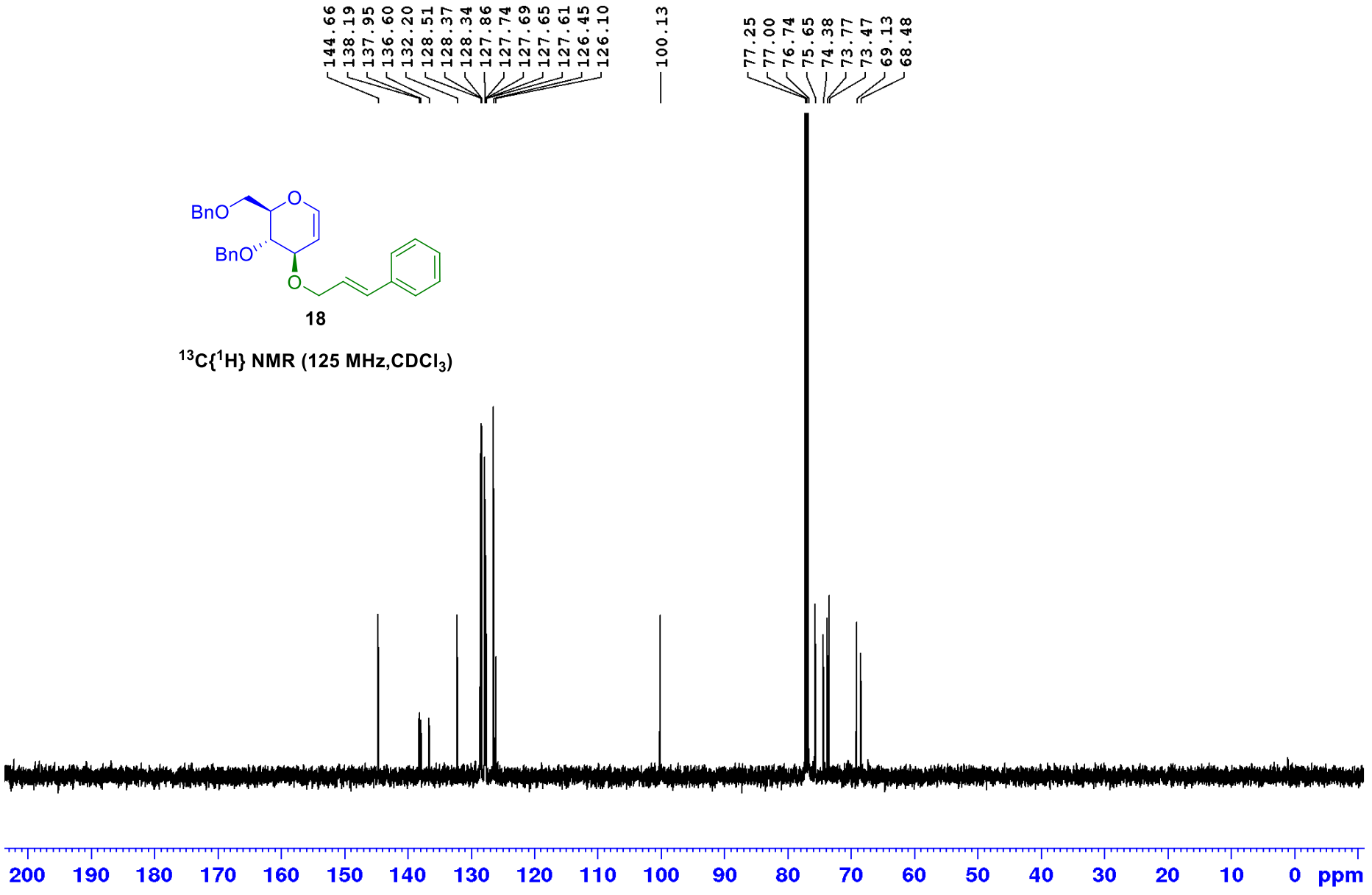




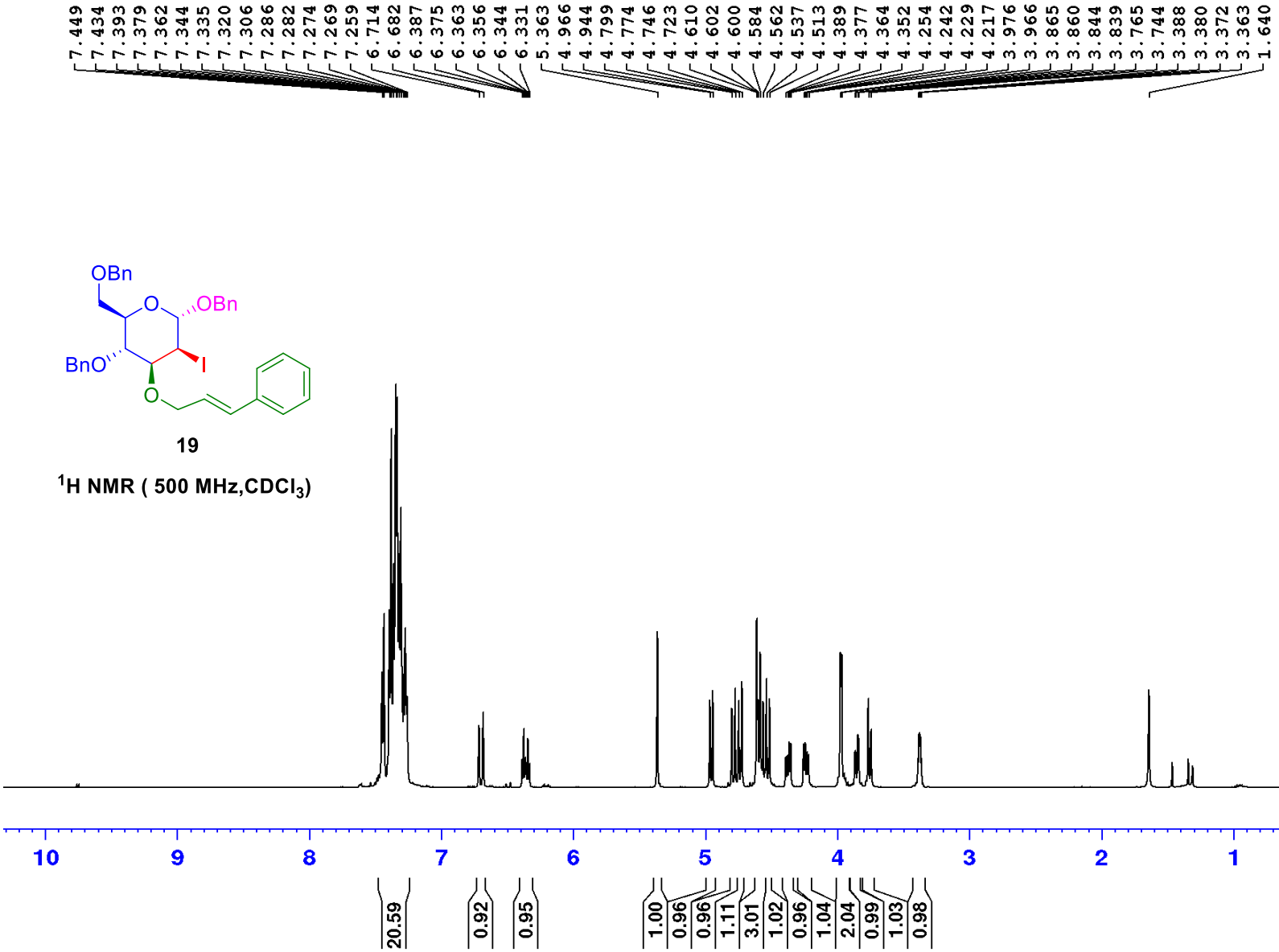


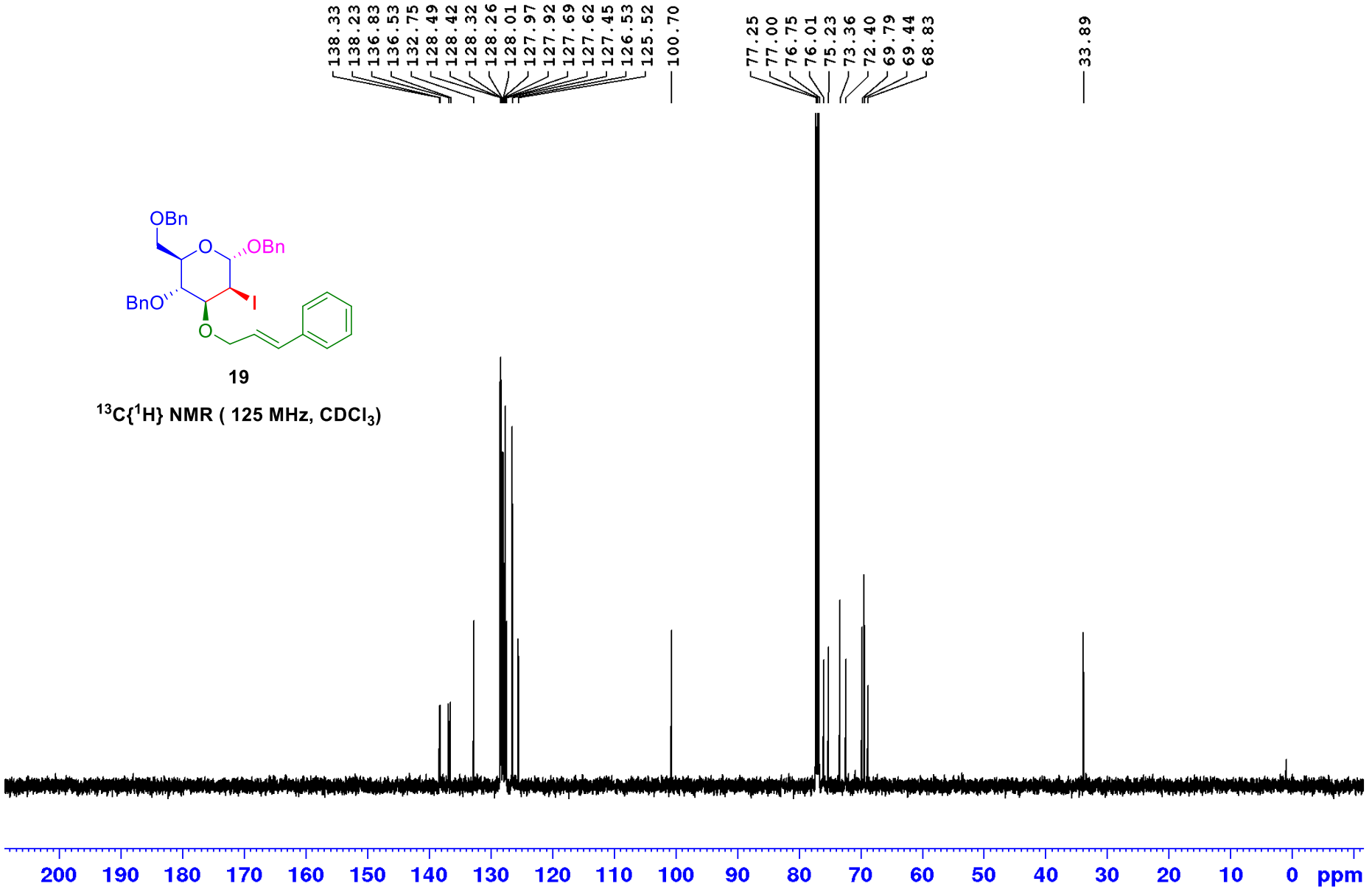
18

^{1}H NMR (500 MHz,$CDCl_3$)



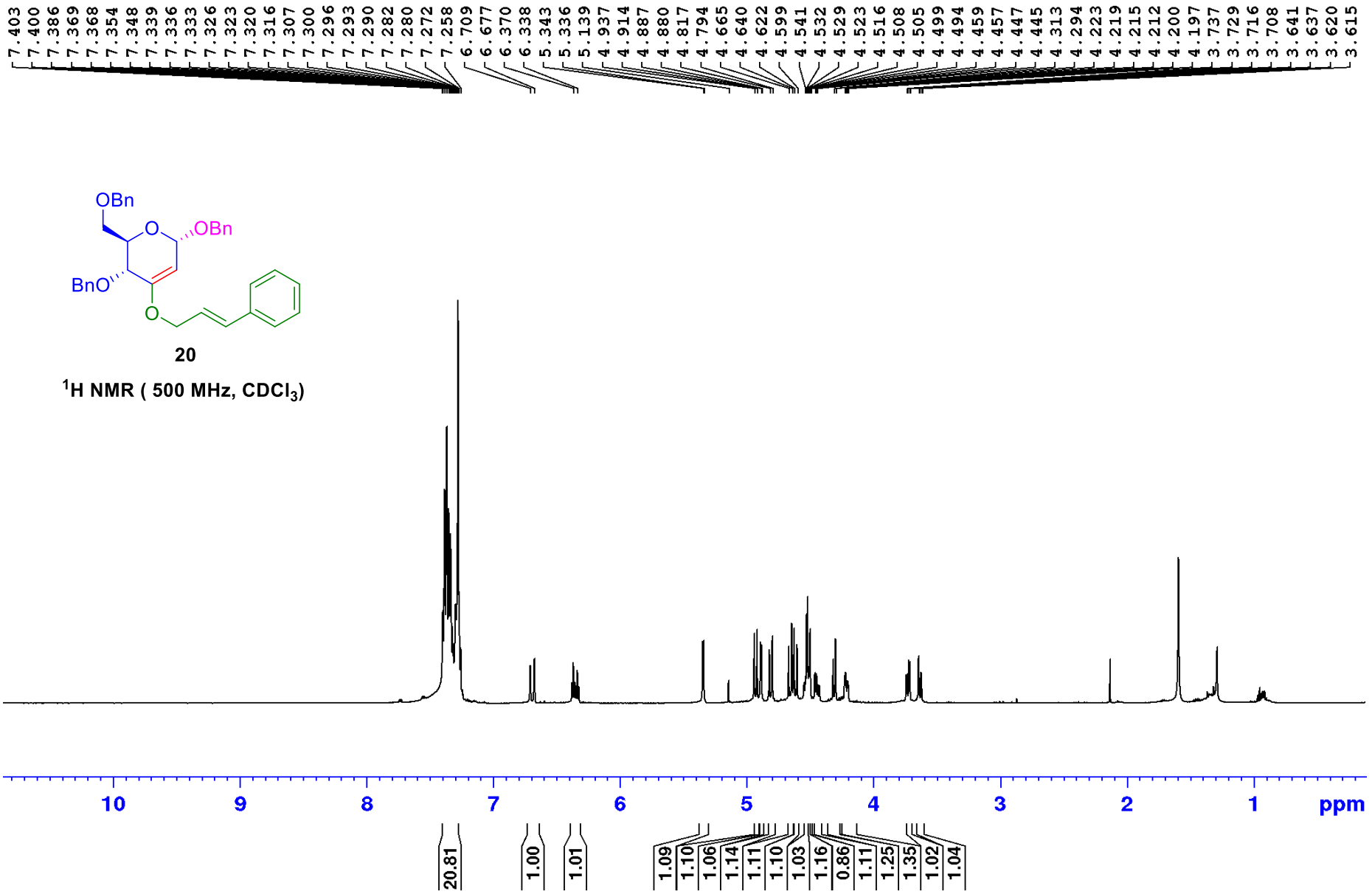
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)


7.449
7.434
7.393
7.379
7.362
7.344
7.335
7.320
7.306
7.286
7.282
7.274
7.269
7.259
6.714
6.682
6.387
6.375
6.363
6.356
6.344
6.331
5.363
4.966
4.944
4.799
4.774
4.746
4.723
4.610
4.602
4.600
4.584
4.562
4.537
4.513
4.389
4.377
4.364
4.352
4.254
4.242
4.229
4.217
3.976
3.966
3.865
3.860
3.844
3.839
3.765
3.744
3.388
3.380
3.372
3.363
1.640
OBn
OBn
BnO
I
O
O
19
1H NMR (500 MHz,CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
20.59
0.92
0.95
1.00
0.96
0.96
1.11
3.01
1.02
0.96
1.04
2.04
0.99
1.03
0.98



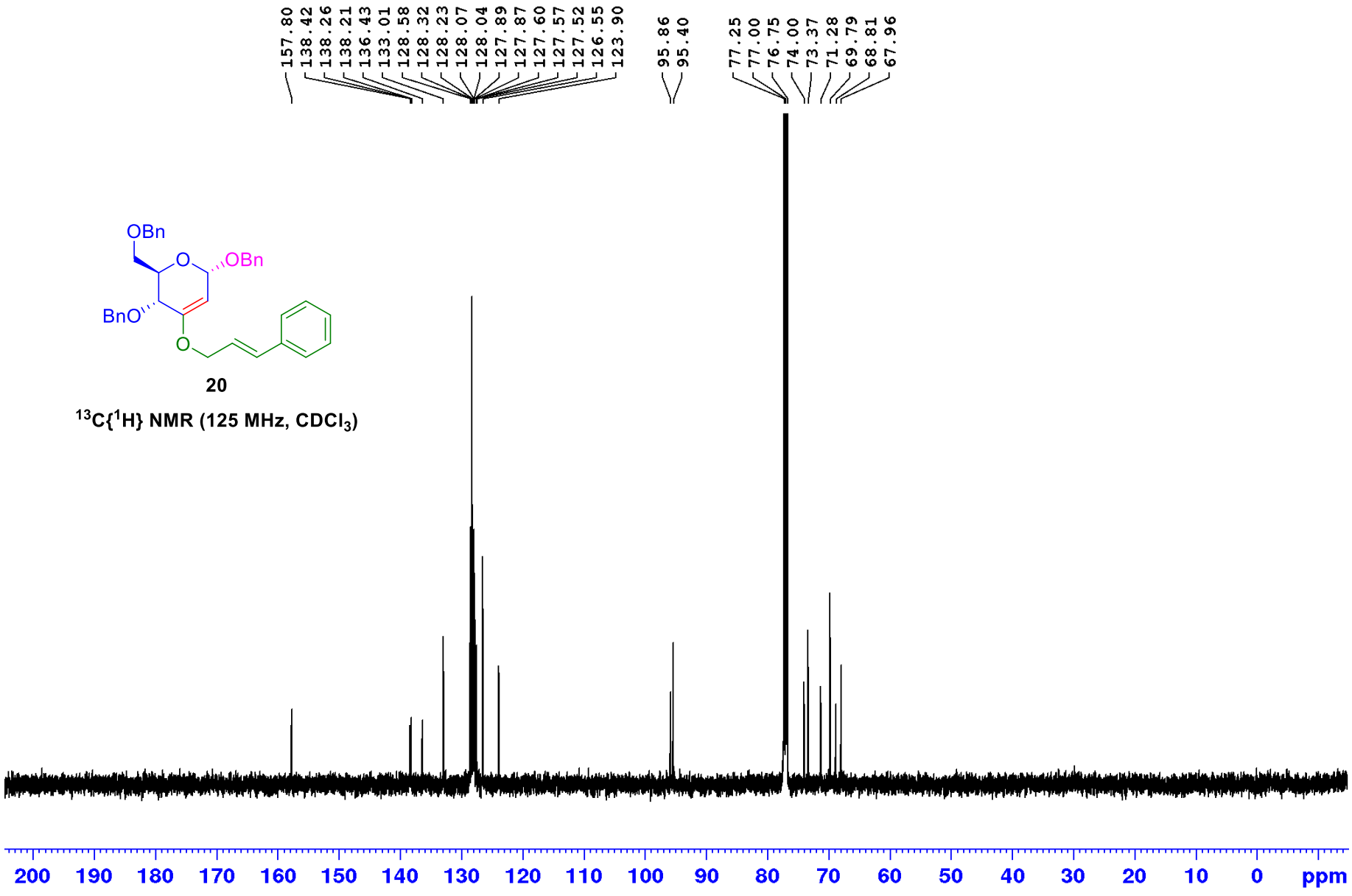
19

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



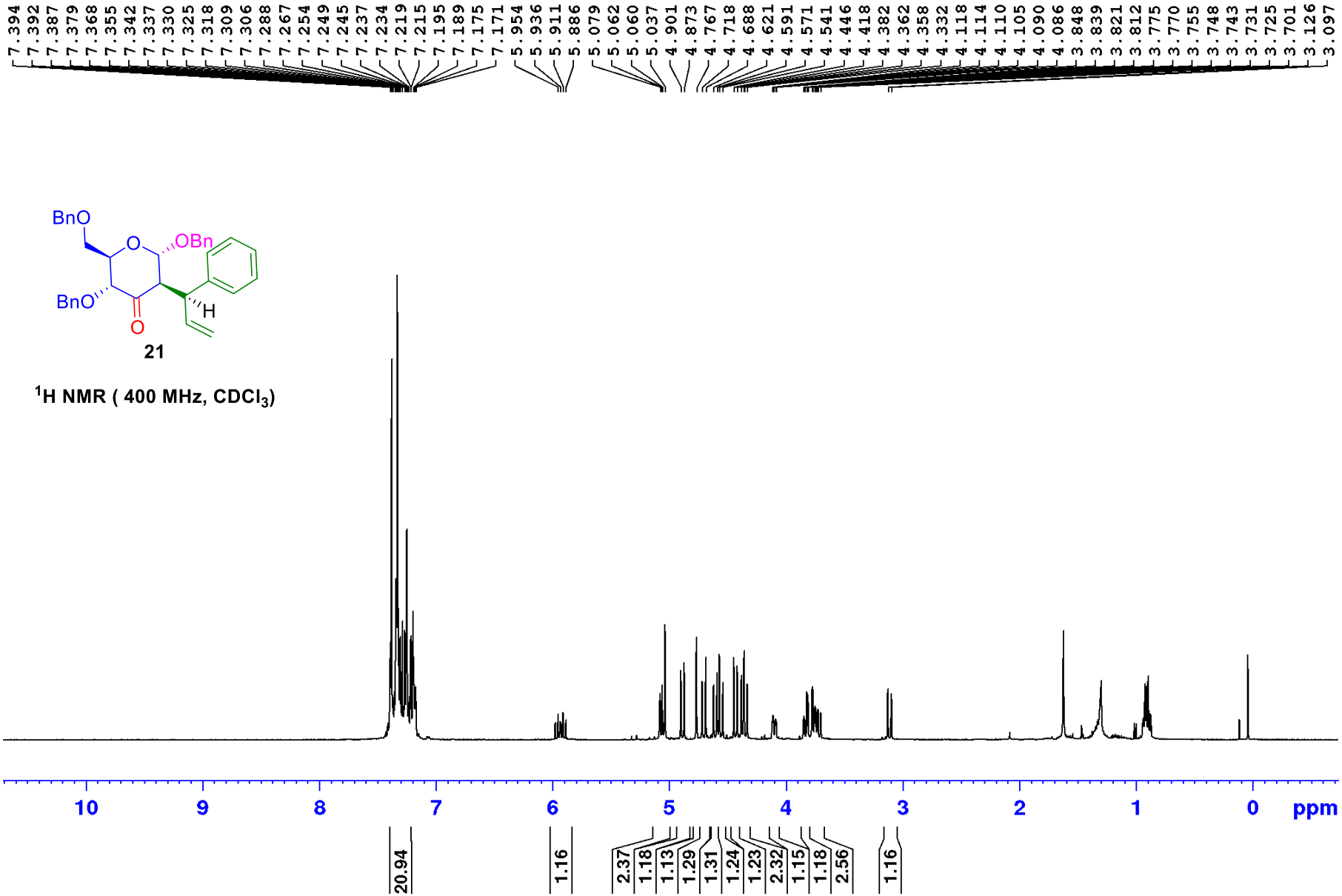
20

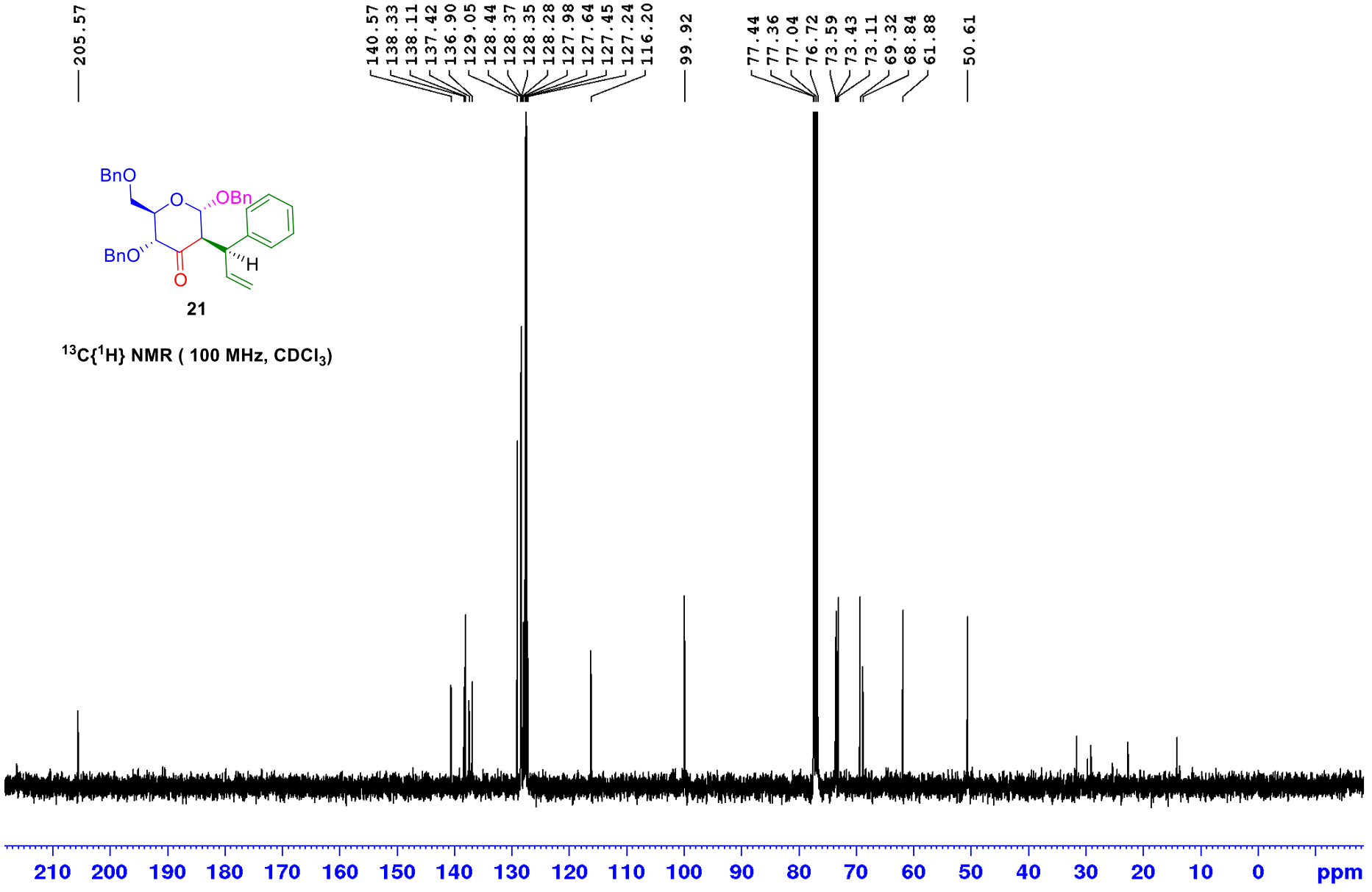
^{1}H NMR (500 MHz, $CDCl_3$)



20

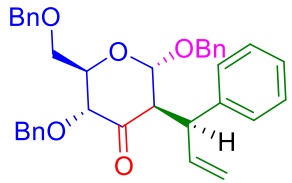
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)


7.394
7.392
7.387
7.379
7.368
7.355
7.342
7.337
7.330
7.325
7.318
7.309
7.306
7.288
7.267
7.254
7.249
7.245
7.237
7.234
7.219
7.215
7.195
7.189
7.175
7.171
5.954
5.936
5.911
5.886
5.079
5.062
5.060
5.037
4.901
4.873
4.767
4.718
4.688
4.621
4.591
4.571
4.541
4.446
4.418
4.382
4.362
4.358
4.332
4.118
4.114
4.110
4.105
4.090
4.086
3.848
3.839
3.821
3.812
3.775
3.770
3.755
3.748
3.743
3.731
3.725
3.701
3.126
3.097
BnO
O
OBn
BnO
H
O
21
1H NMR (400 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
20.94
1.16
2.37
1.18
1.13
1.29
1.31
1.24
1.23
2.32
1.15
1.18
2.56
1.16



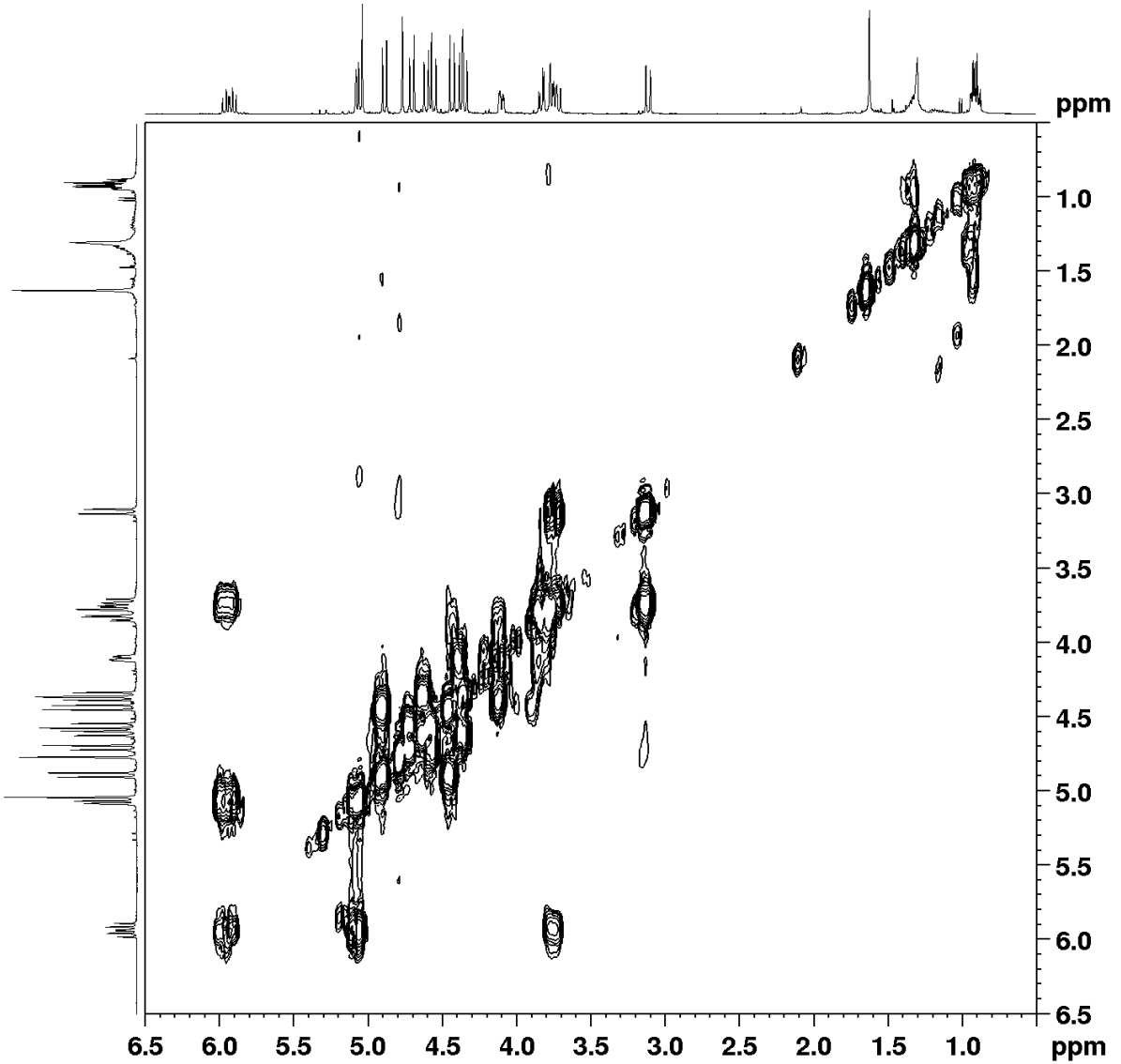
21

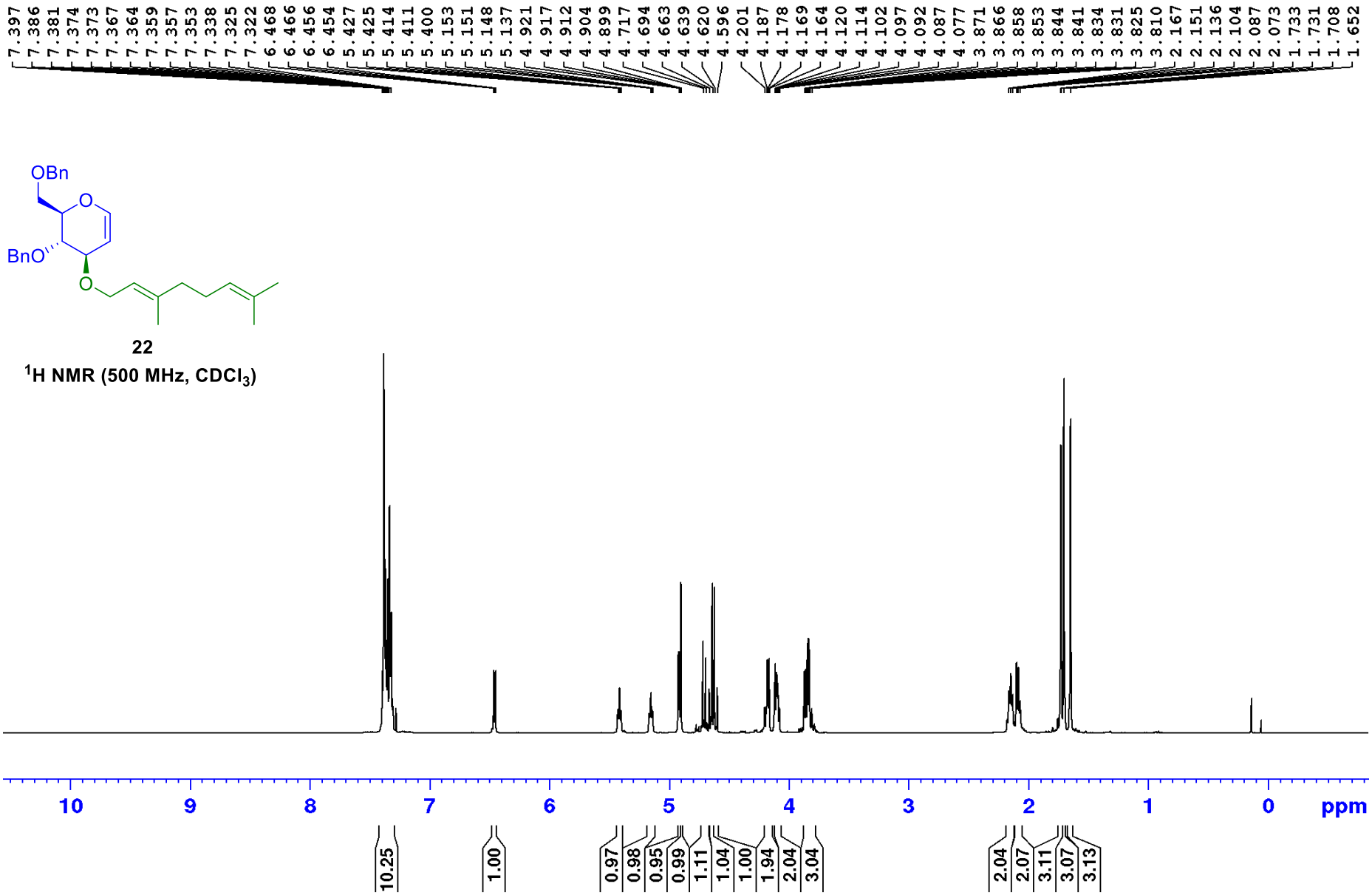
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

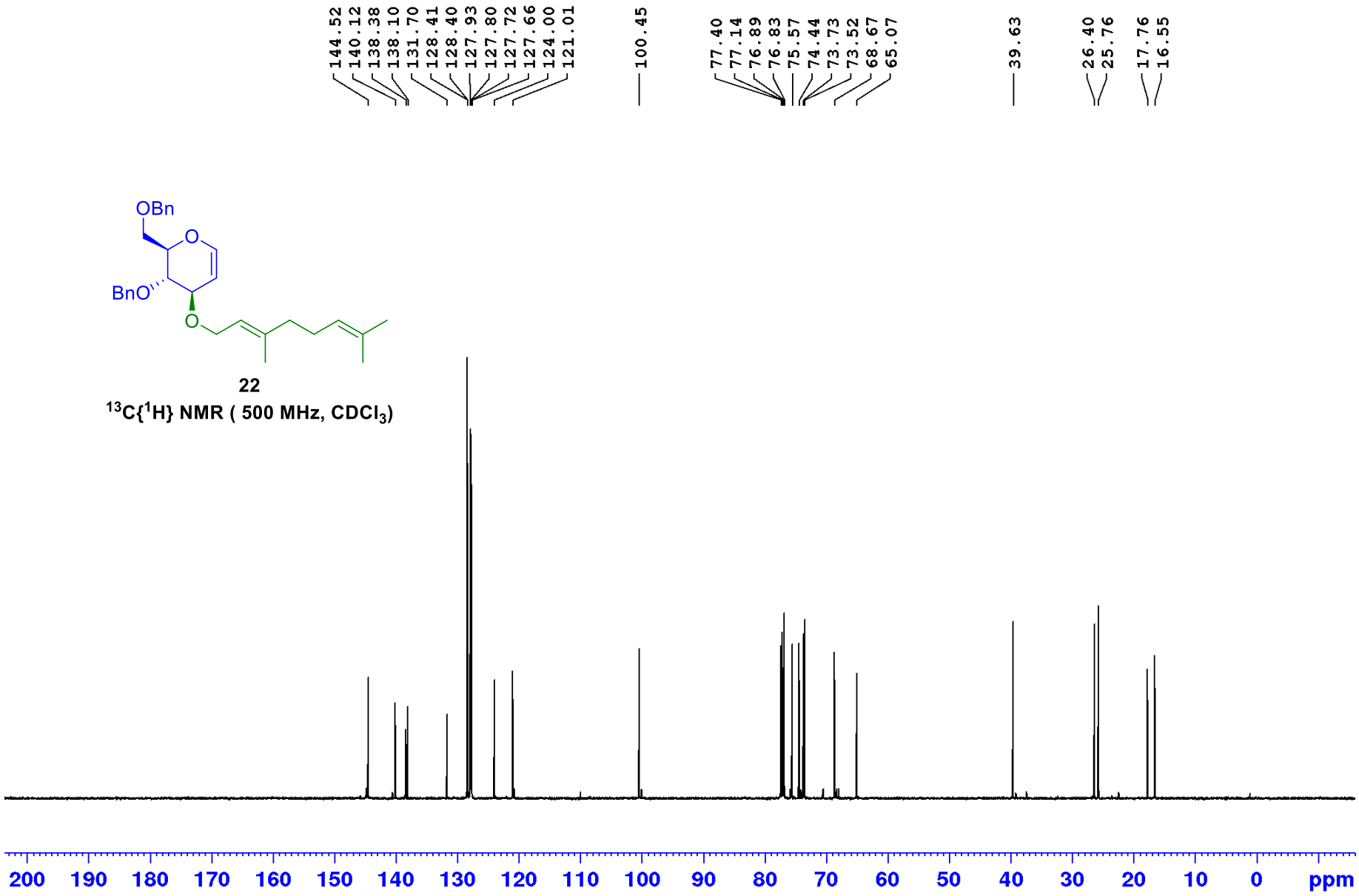


21

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

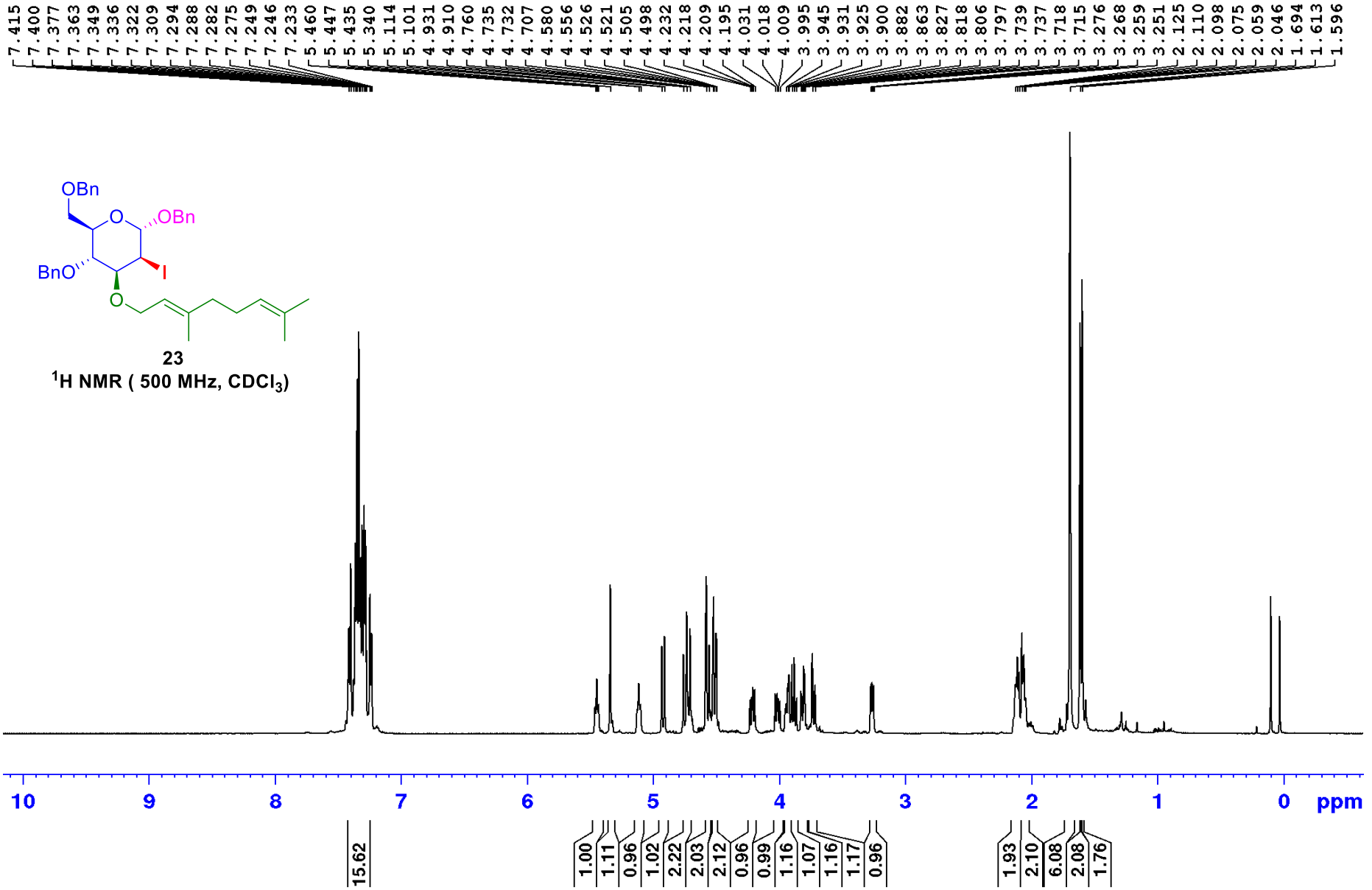


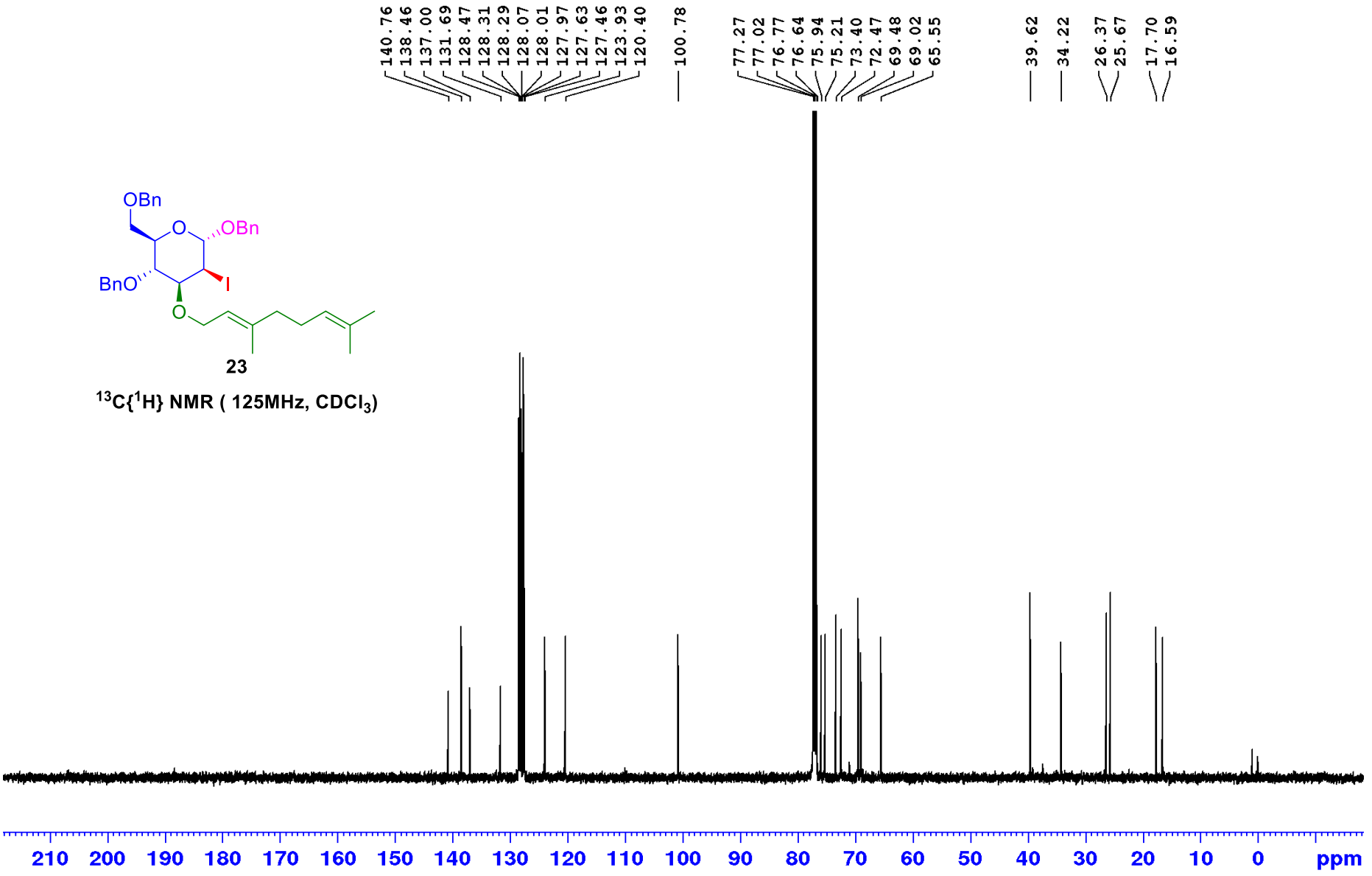

7.397
7.386
7.381
7.374
7.373
7.367
7.364
7.359
7.357
7.353
7.338
7.325
7.322
6.468
6.466
6.456
6.454
5.427
5.425
5.414
5.411
5.400
5.153
5.151
5.148
5.137
4.921
4.917
4.912
4.904
4.899
4.717
4.694
4.663
4.639
4.620
4.596
4.201
4.187
4.178
4.169
4.164
4.120
4.114
4.102
4.097
4.092
4.087
4.077
3.871
3.866
3.858
3.853
3.844
3.841
3.834
3.831
3.825
3.810
2.167
2.151
2.136
2.104
2.087
2.073
1.733
1.731
1.708
1.652
OBn
O
BnO
O
22
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
10.25
1.00
0.97
0.98
0.95
0.99
1.11
1.04
1.00
1.94
2.04
3.04
2.04
2.07
3.11
3.07
3.13



22

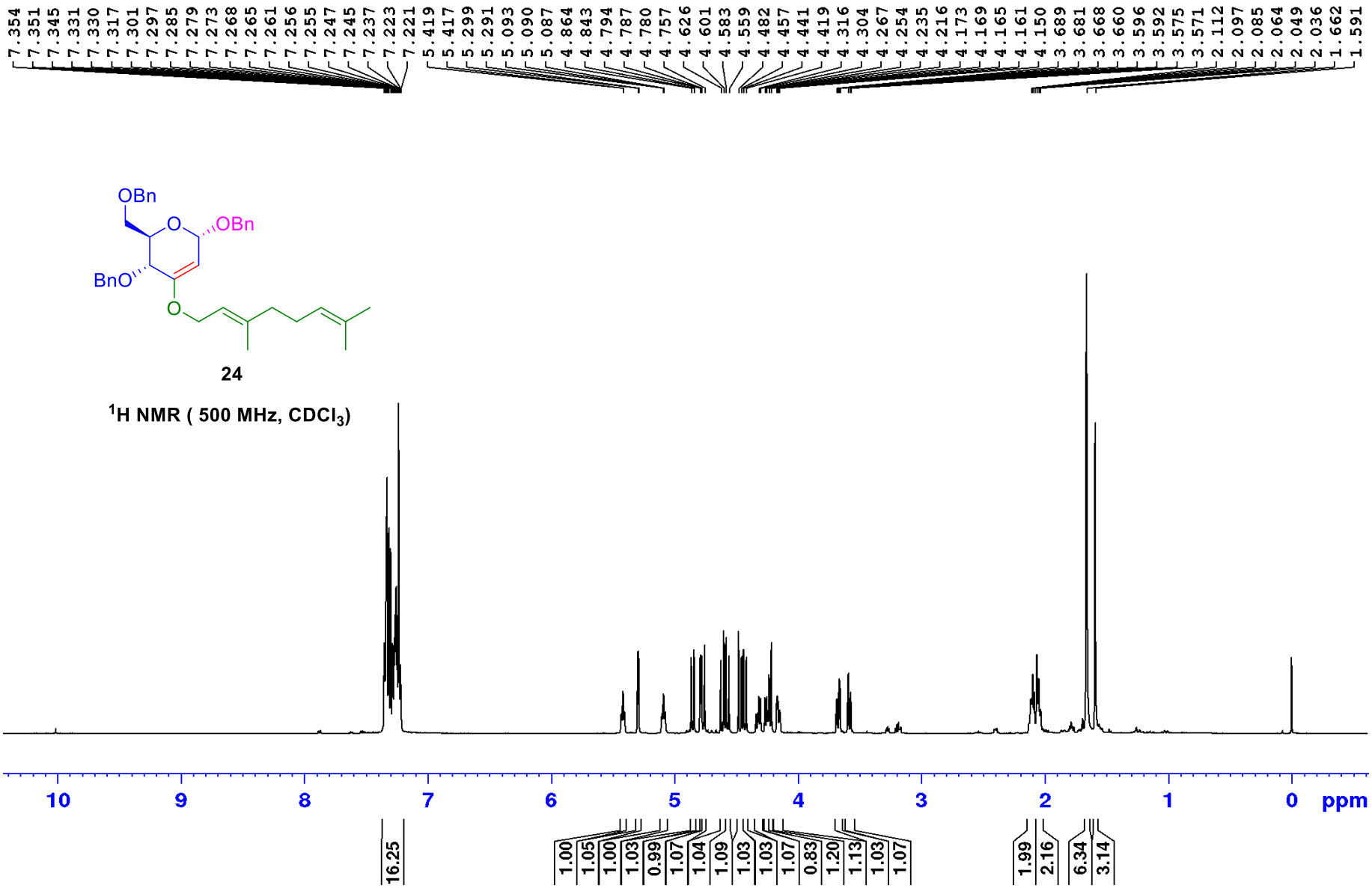
$^{13}C\{^{1}H\}$ NMR (500 MHz, $CDCl_3$)

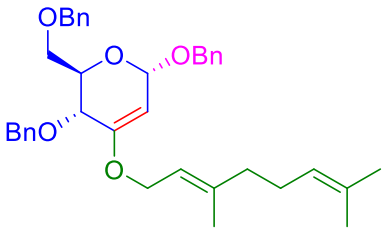

7.415
7.400
7.377
7.363
7.349
7.336
7.322
7.309
7.294
7.288
7.282
7.275
7.249
7.246
7.233
5.460
5.447
5.435
5.340
5.114
5.101
4.931
4.910
4.760
4.735
4.732
4.707
4.580
4.556
4.526
4.521
4.505
4.498
4.232
4.218
4.209
4.195
4.031
4.018
4.009
3.995
3.945
3.931
3.925
3.900
3.882
3.863
3.827
3.818
3.806
3.797
3.739
3.737
3.718
3.715
3.276
3.268
3.259
3.251
2.125
2.110
2.098
2.075
2.059
2.046
1.694
1.613
1.596
OBn
O
OBn
BnO
I
O
23
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
15.62
1.00
1.11
0.96
1.02
2.22
2.03
2.12
0.96
0.99
1.16
1.07
1.16
1.17
0.96
1.93
2.10
6.08
2.08
1.76



23

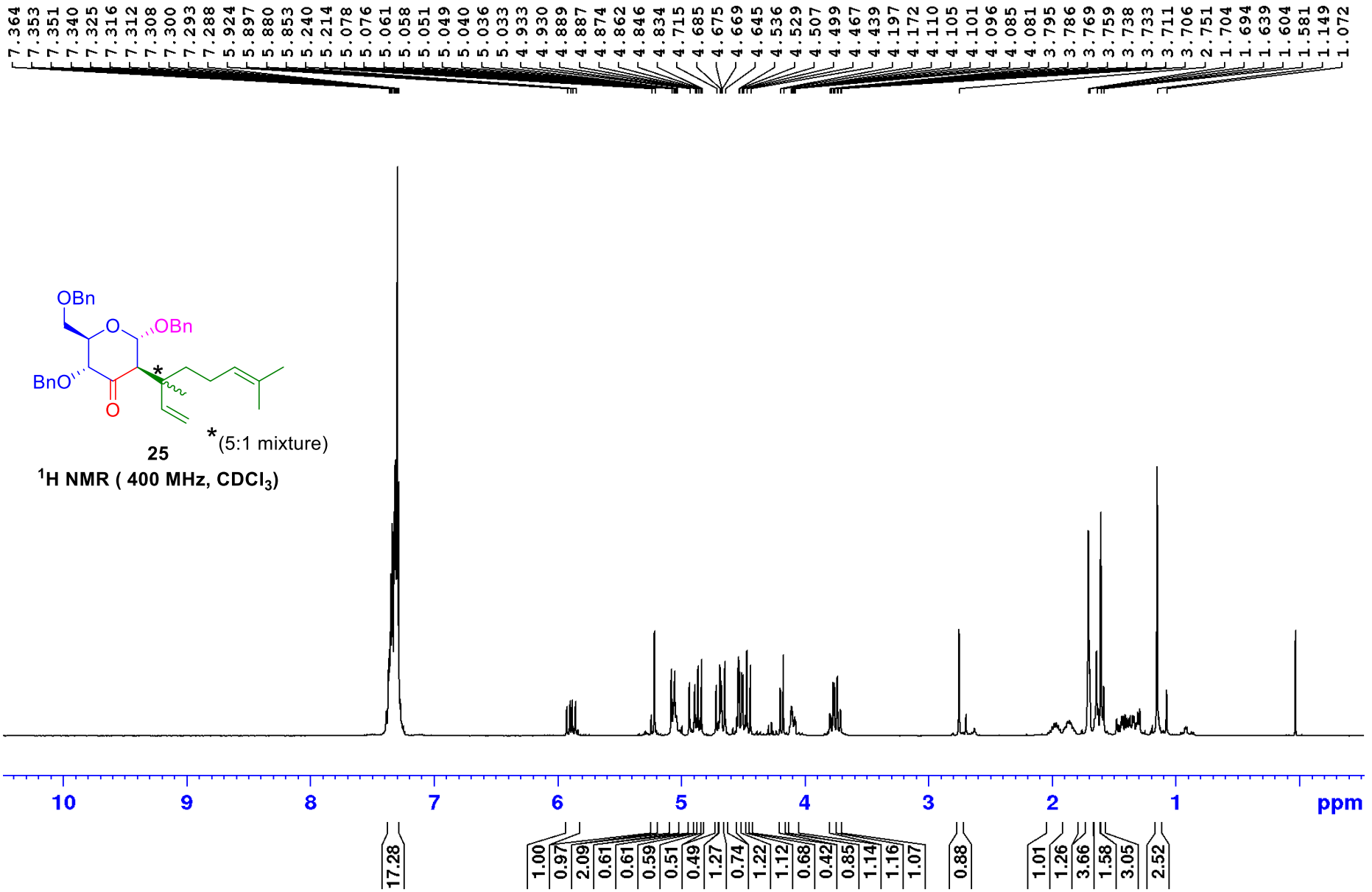
$^{13}C\{^{1}H\}$ NMR (125MHz, $CDCl_3$)

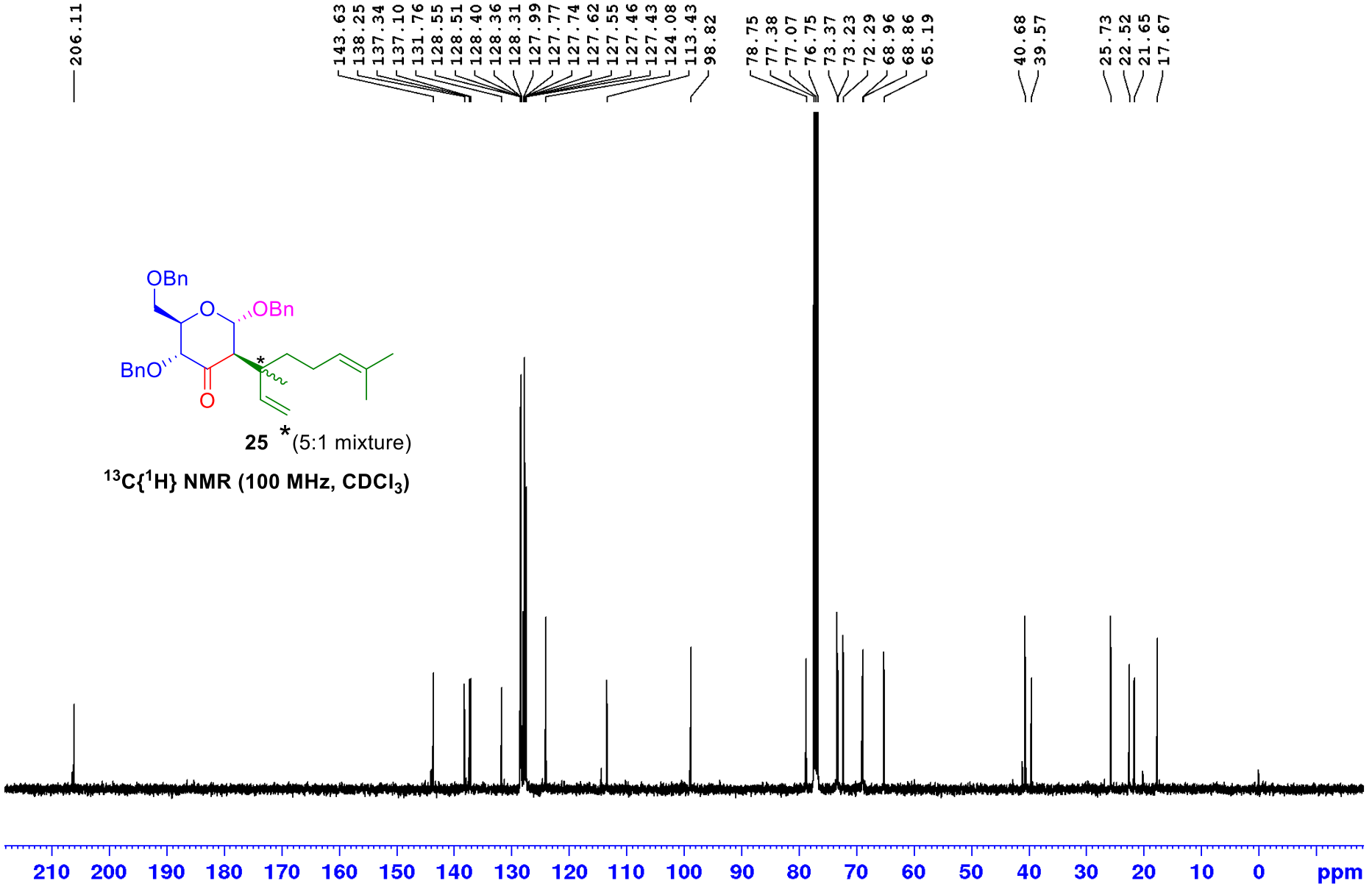

7.354
7.351
7.345
7.331
7.330
7.317
7.301
7.297
7.285
7.279
7.273
7.268
7.265
7.261
7.256
7.255
7.247
7.245
7.237
7.223
7.221
5.419
5.417
5.299
5.291
5.093
5.090
5.087
4.864
4.843
4.794
4.787
4.780
4.757
4.626
4.601
4.583
4.559
4.482
4.457
4.441
4.419
4.316
4.304
4.267
4.254
4.235
4.216
4.173
4.169
4.165
4.161
4.150
3.689
3.681
3.668
3.660
3.596
3.592
3.575
3.571
2.112
2.097
2.085
2.064
2.049
2.036
1.662
1.591
OBn
O
OBn
BnO
O
24
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
16.25
1.00
1.05
1.00
1.03
0.99
1.07
1.04
1.09
1.03
1.03
1.07
0.83
1.20
1.13
1.03
1.07
1.99
2.16
6.34
3.14



24

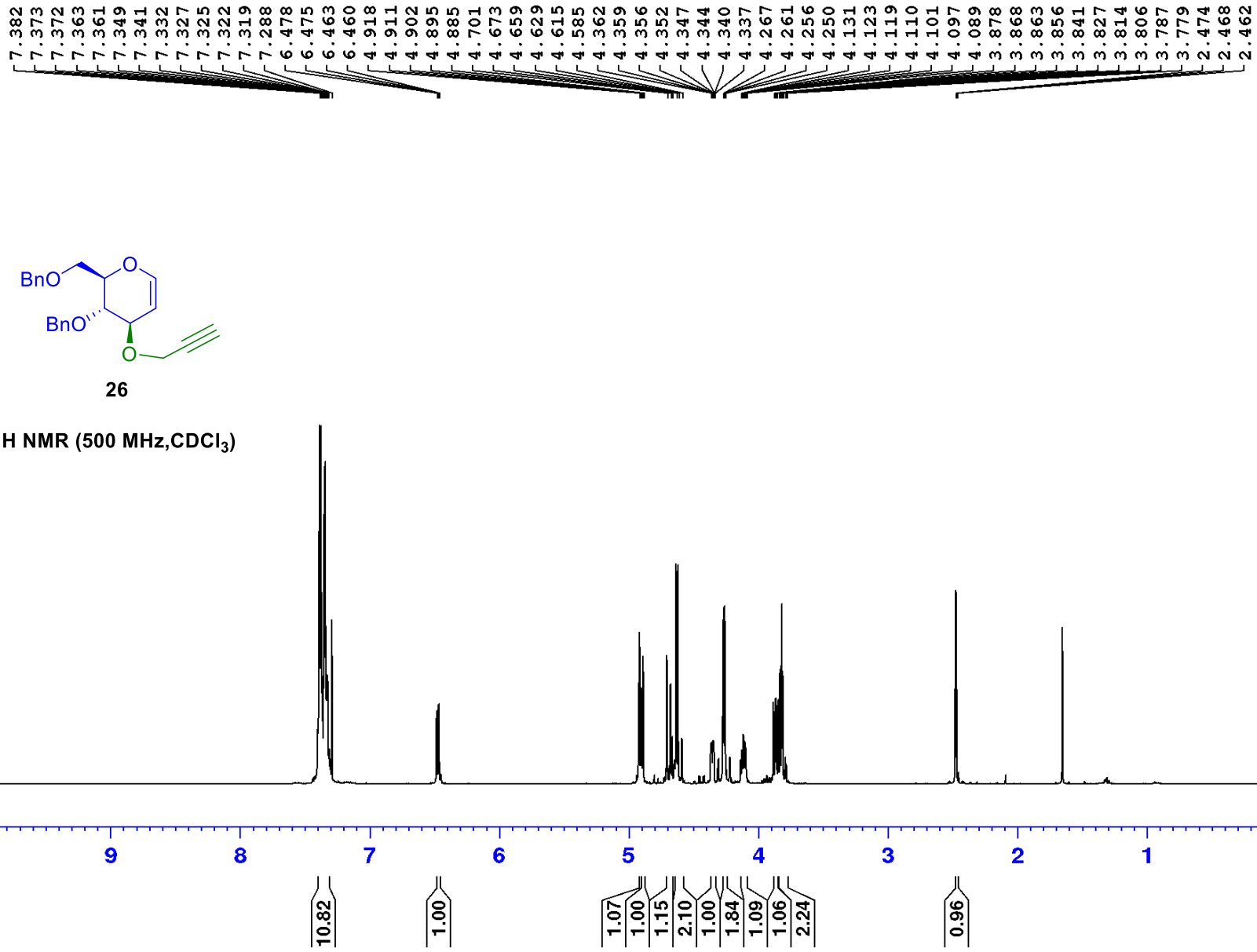
$^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl)

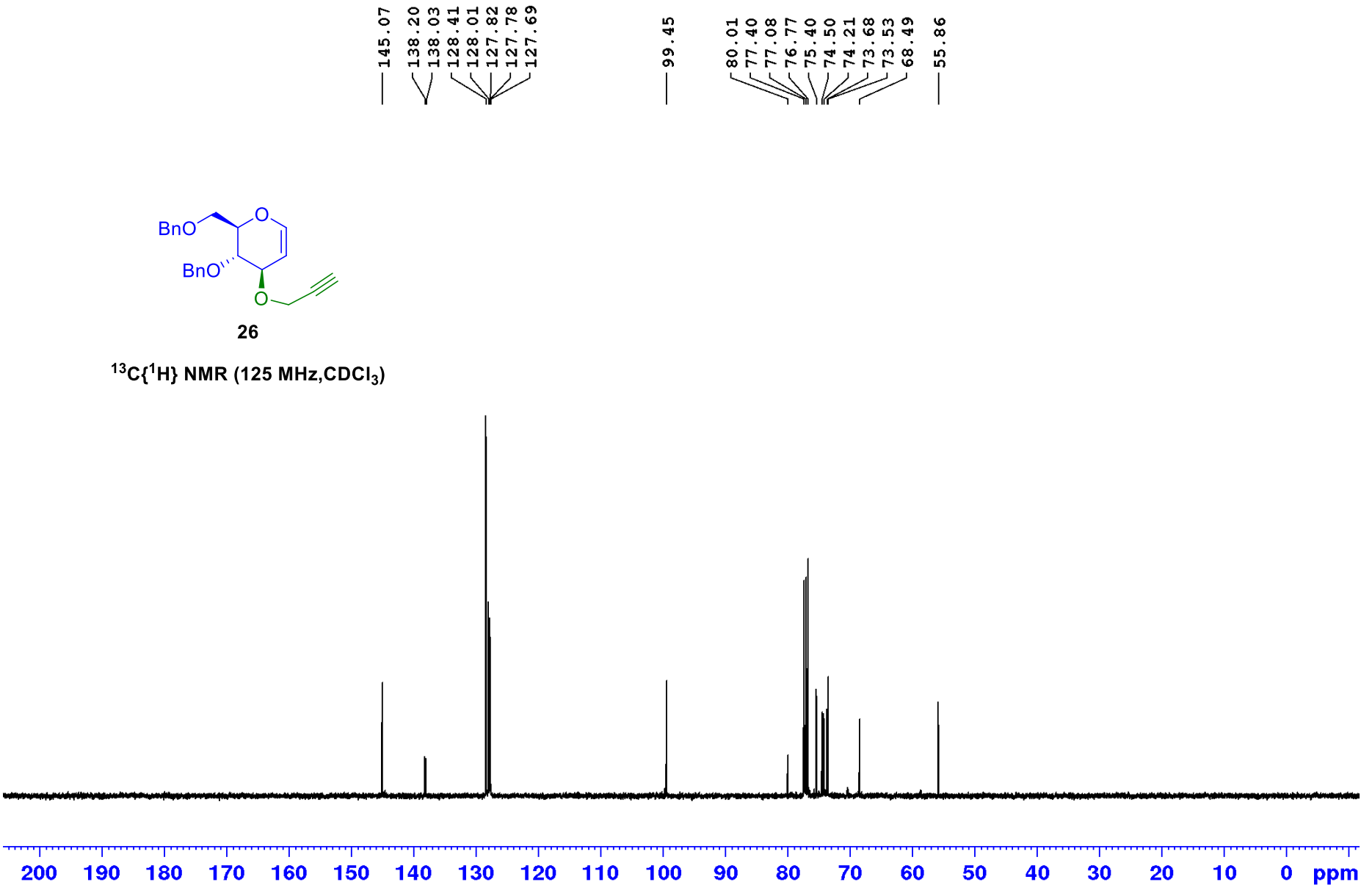

7.364
7.353
7.351
7.340
7.325
7.316
7.312
7.308
7.300
7.293
7.288
5.924
5.897
5.880
5.853
5.240
5.214
5.078
5.076
5.061
5.058
5.051
5.049
5.040
5.036
5.033
4.933
4.930
4.889
4.887
4.874
4.862
4.846
4.834
4.715
4.685
4.675
4.669
4.645
4.536
4.529
4.507
4.499
4.467
4.439
4.197
4.172
4.110
4.105
4.101
4.096
4.085
4.081
3.795
3.786
3.769
3.759
3.738
3.733
3.711
3.706
2.751
1.704
1.694
1.639
1.604
1.581
1.149
1.072
OBn
O
OBn
BnO
O
*
*(5:1 mixture)
25
1H NMR (400 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
ppm
17.28
1.00
0.97
2.09
0.61
0.61
0.59
0.51
0.49
1.27
0.74
1.22
1.12
0.68
0.42
0.85
1.14
1.16
1.07
0.88
1.01
1.26
3.66
1.58
3.05
2.52



25 * (5:1 mixture)

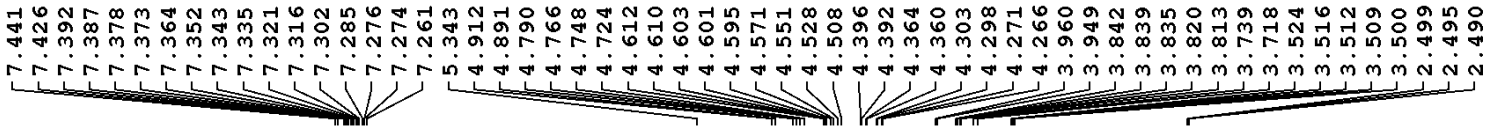
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)

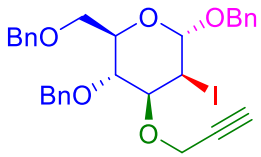

7.382
7.373
7.372
7.363
7.361
7.349
7.341
7.332
7.327
7.325
7.322
7.319
7.288
6.478
6.475
6.463
6.460
4.918
4.911
4.902
4.895
4.885
4.701
4.673
4.659
4.629
4.615
4.585
4.362
4.359
4.356
4.352
4.347
4.344
4.340
4.337
4.267
4.261
4.256
4.250
4.131
4.123
4.119
4.110
4.101
4.097
4.089
3.878
3.868
3.863
3.856
3.841
3.827
3.814
3.806
3.787
3.779
2.474
2.468
2.462
BnO
BnO
O
O
26
1H NMR (500 MHz,CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
10.82
1.00
1.07
1.00
1.15
2.10
1.00
1.84
1.09
1.06
2.24
0.96



26

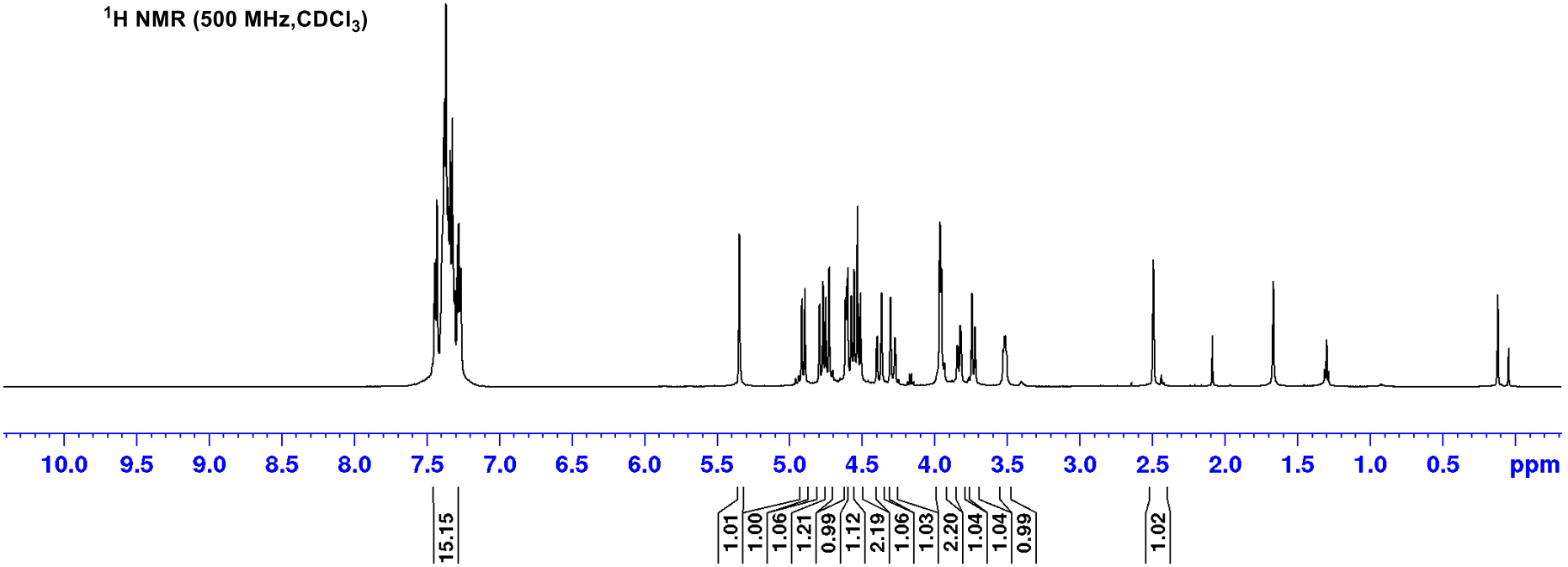
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)

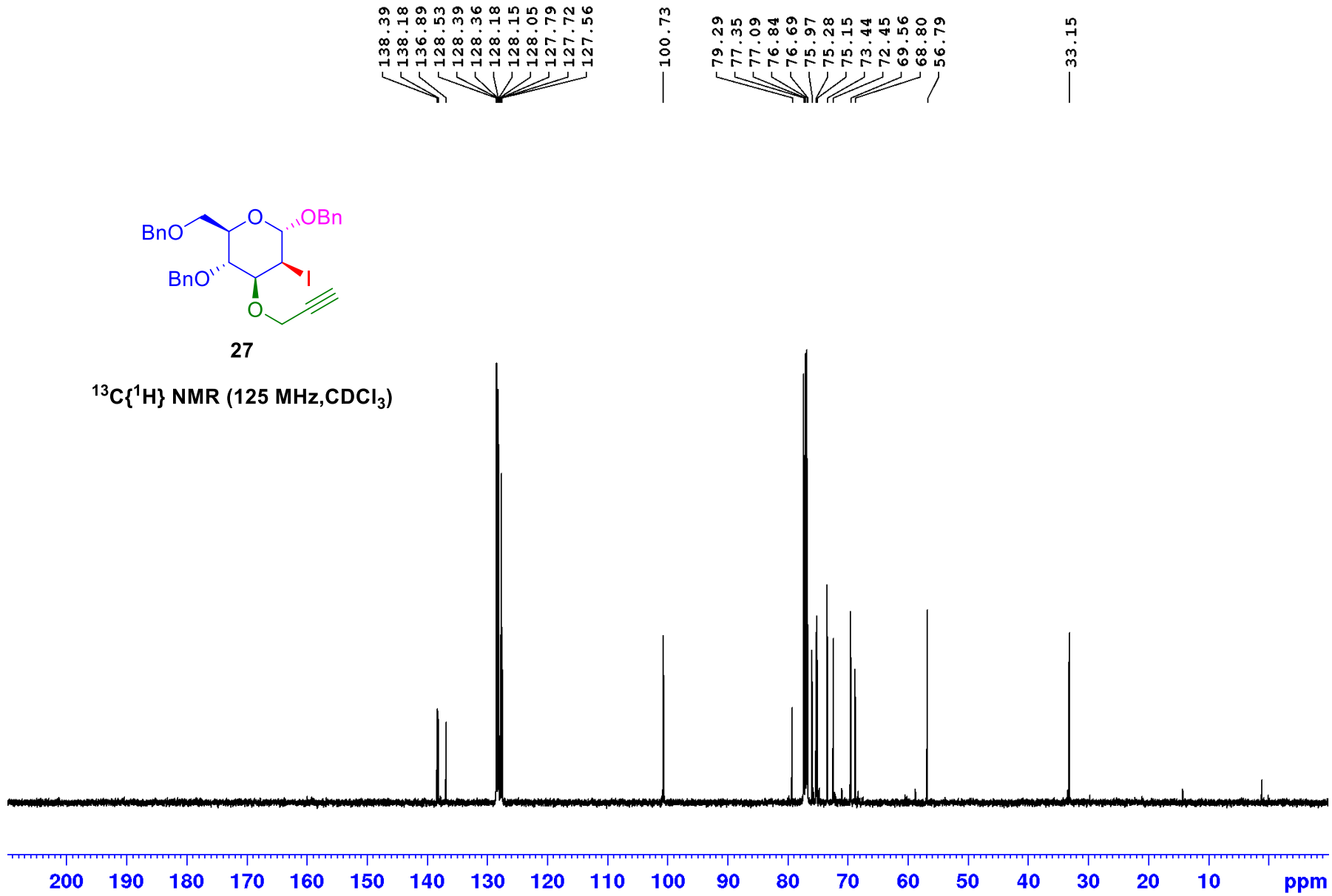


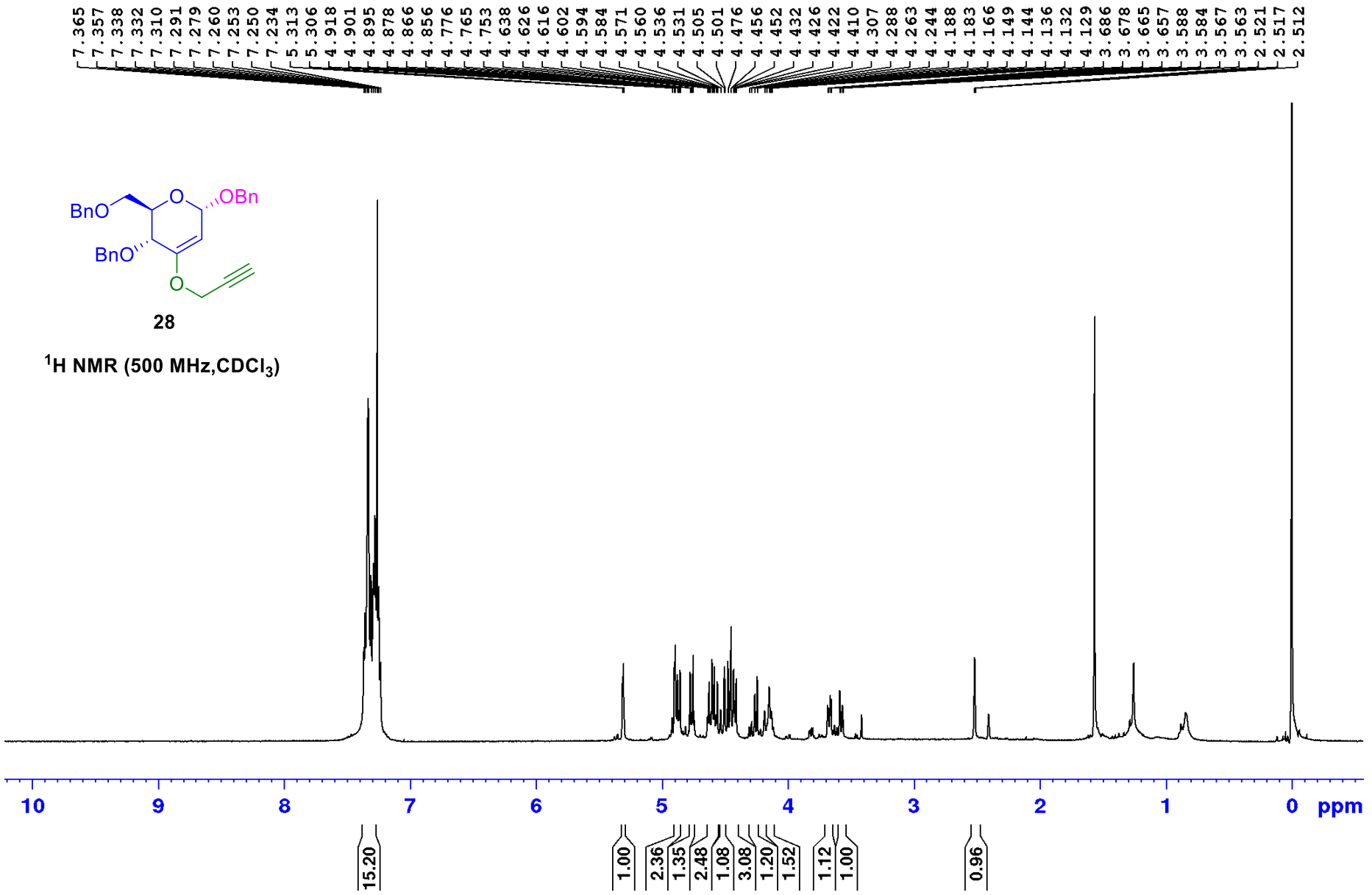


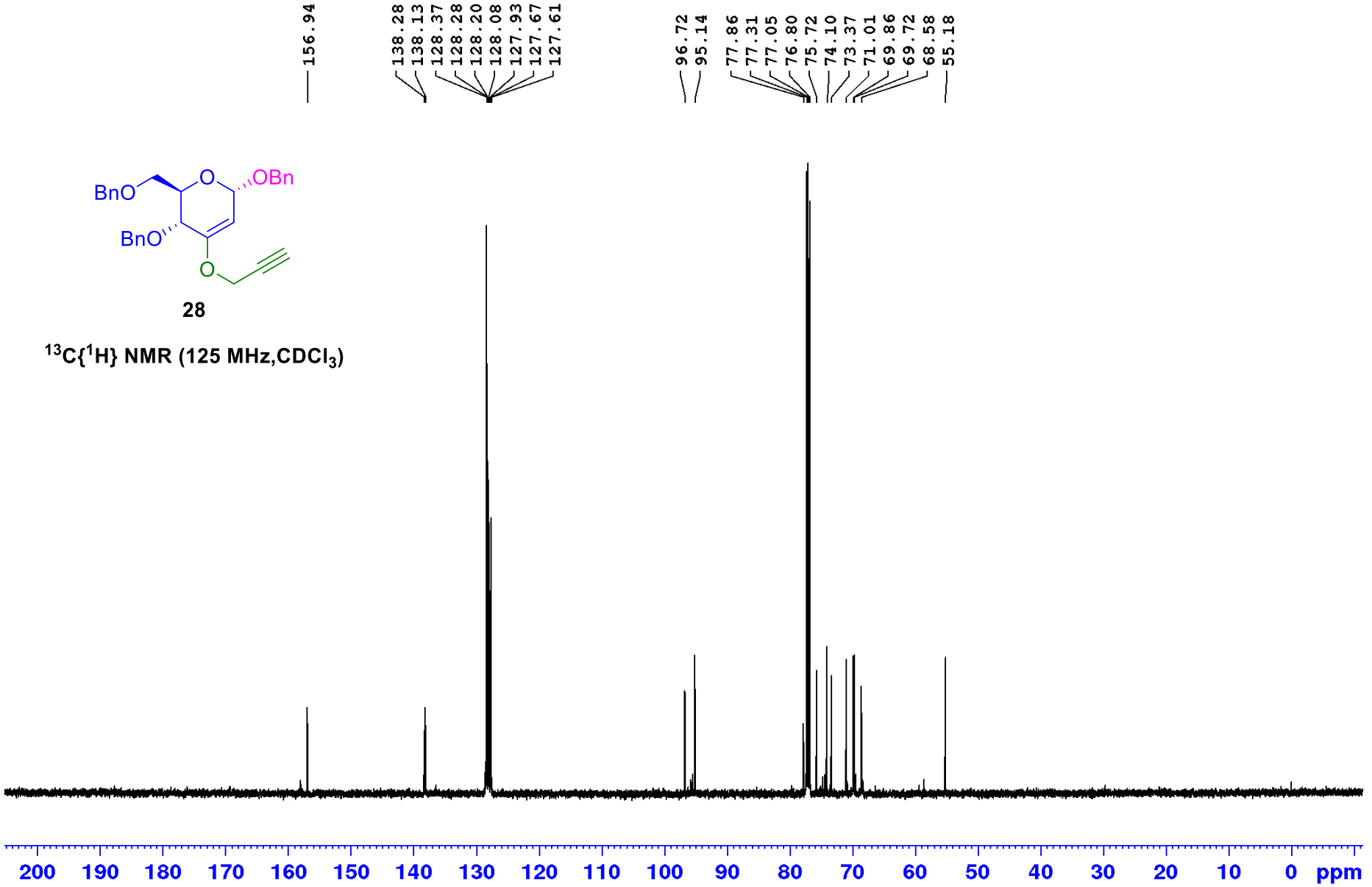
27

^{1}H NMR (500 MHz,$CDCl_3$)



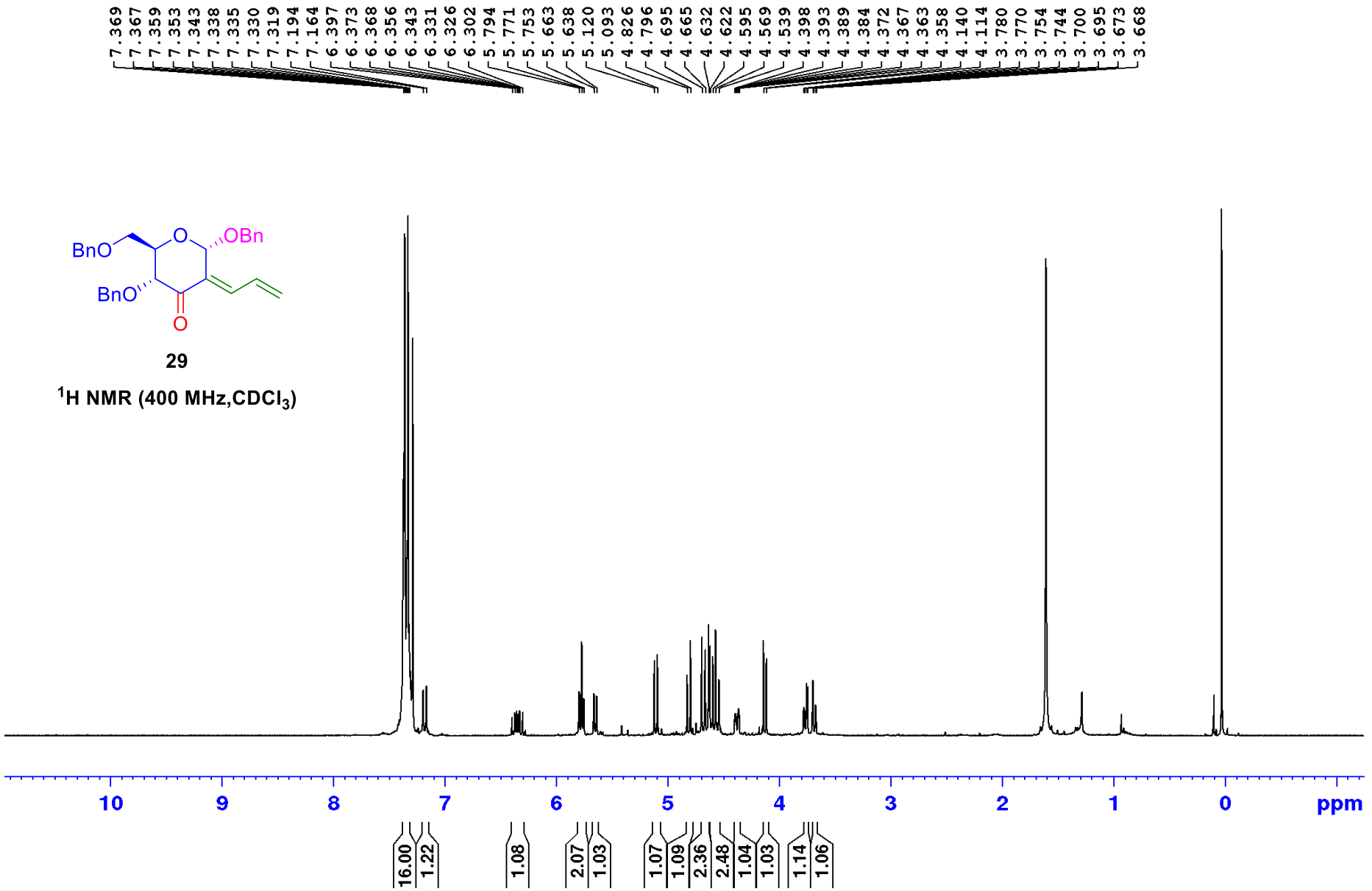

138.39
138.18
136.89
128.53
128.39
128.36
128.18
128.15
128.05
127.79
127.72
127.56
100.73
79.29
77.35
77.09
76.84
76.69
75.97
75.28
75.15
73.44
72.45
69.56
68.80
56.79
33.15
BnO
O
OBn
BnO
I
O
27
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

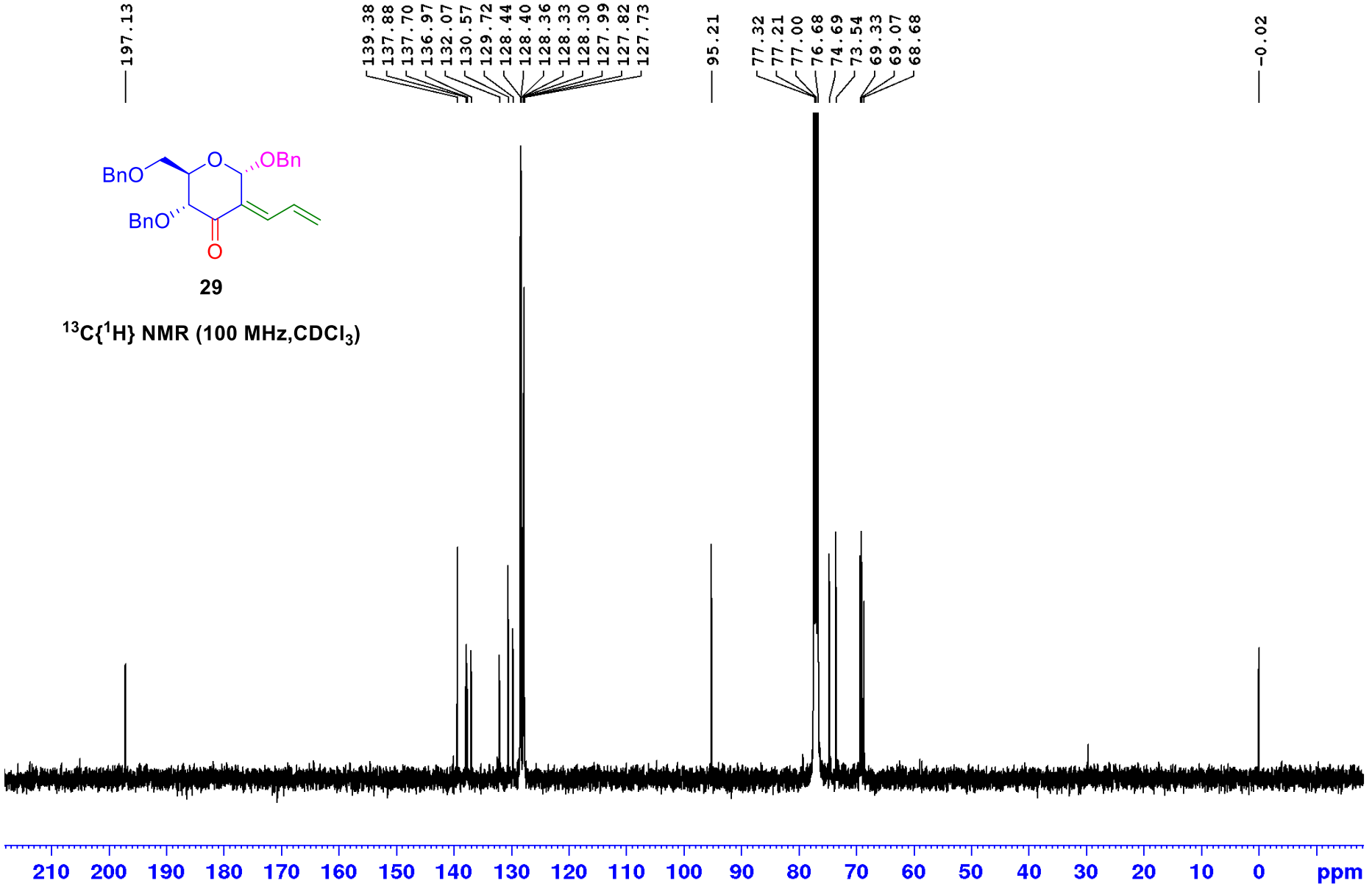

7.365
7.357
7.338
7.332
7.310
7.291
7.279
7.260
7.253
7.250
7.234
5.313
5.306
4.918
4.901
4.895
4.878
4.866
4.856
4.776
4.765
4.753
4.638
4.626
4.616
4.602
4.594
4.584
4.571
4.560
4.536
4.531
4.505
4.501
4.476
4.456
4.452
4.432
4.426
4.422
4.410
4.307
4.288
4.263
4.244
4.188
4.183
4.166
4.149
4.144
4.136
4.132
4.129
3.686
3.678
3.665
3.657
3.588
3.584
3.567
3.563
2.521
2.517
2.512
BnO
OBn
BnO
O
O
28
1H NMR (500 MHz,CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
15.20
1.00
2.36
1.35
2.48
1.08
3.08
1.20
1.52
1.12
1.00
0.96



28

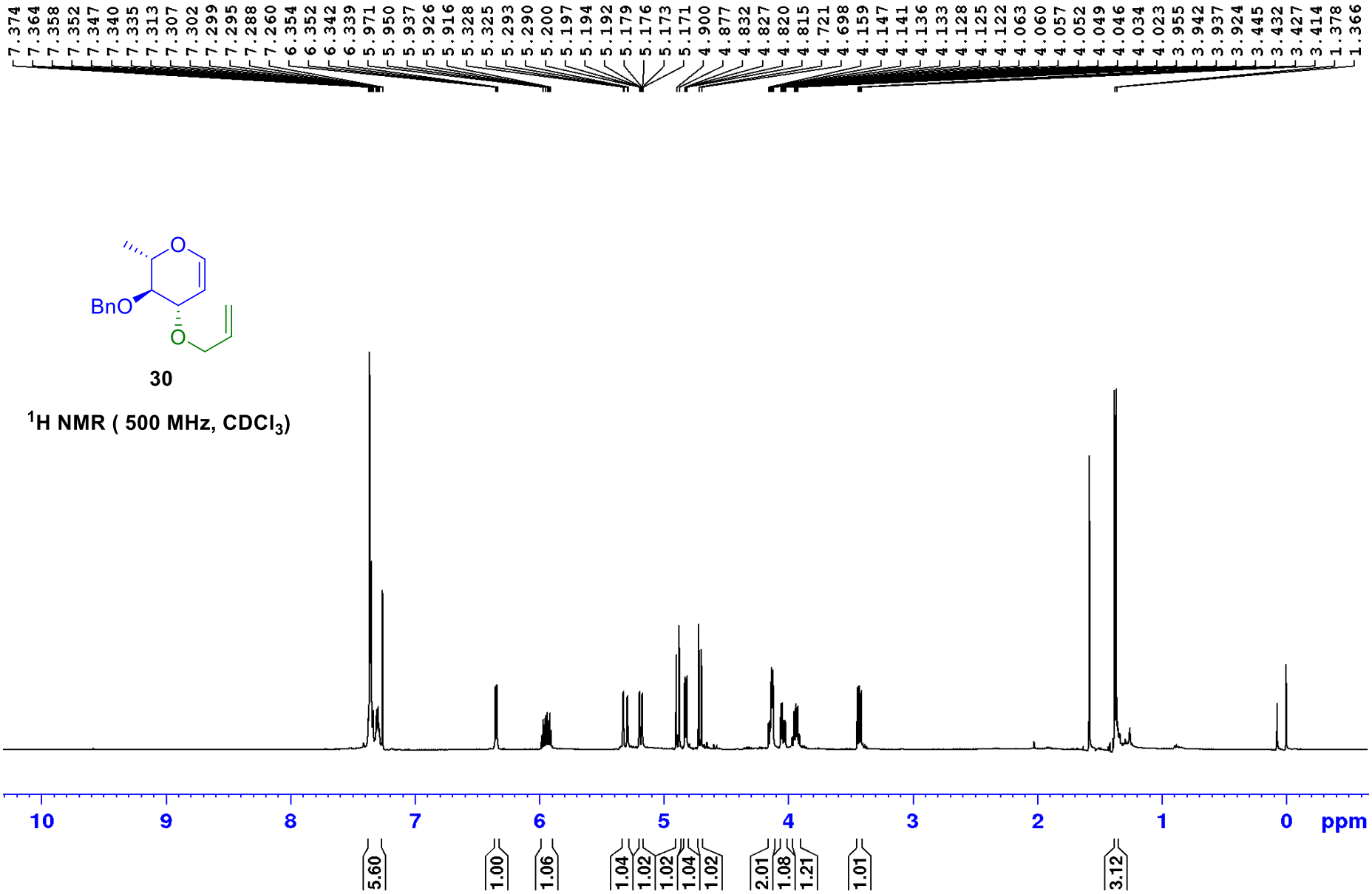
$^{13}C\{^{1}H\}$ NMR (125 MHz,$CDCl_3$)

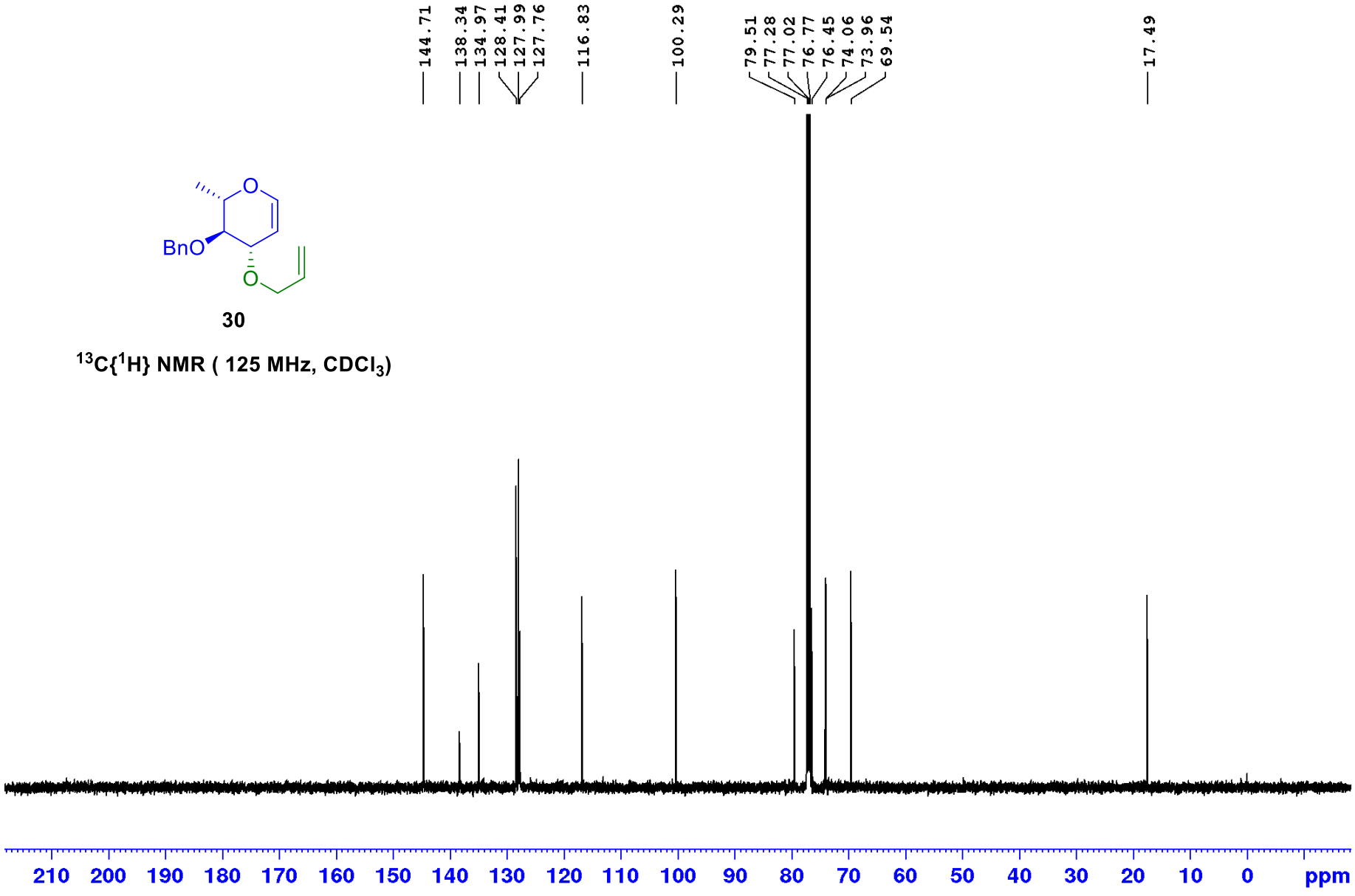

7.369
7.367
7.359
7.353
7.343
7.338
7.335
7.330
7.319
7.194
7.164
6.397
6.373
6.368
6.356
6.343
6.331
6.326
6.302
5.794
5.771
5.753
5.663
5.638
5.120
5.093
4.826
4.796
4.695
4.665
4.632
4.622
4.595
4.569
4.539
4.398
4.393
4.389
4.384
4.372
4.367
4.363
4.358
4.140
4.114
3.780
3.770
3.754
3.744
3.700
3.695
3.673
3.668
BnO
OBn
BnO
O
O
29
1H NMR (400 MHz,CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
16.00
1.22
1.08
2.07
1.03
1.07
1.09
2.36
2.48
1.04
1.03
1.14
1.06



29

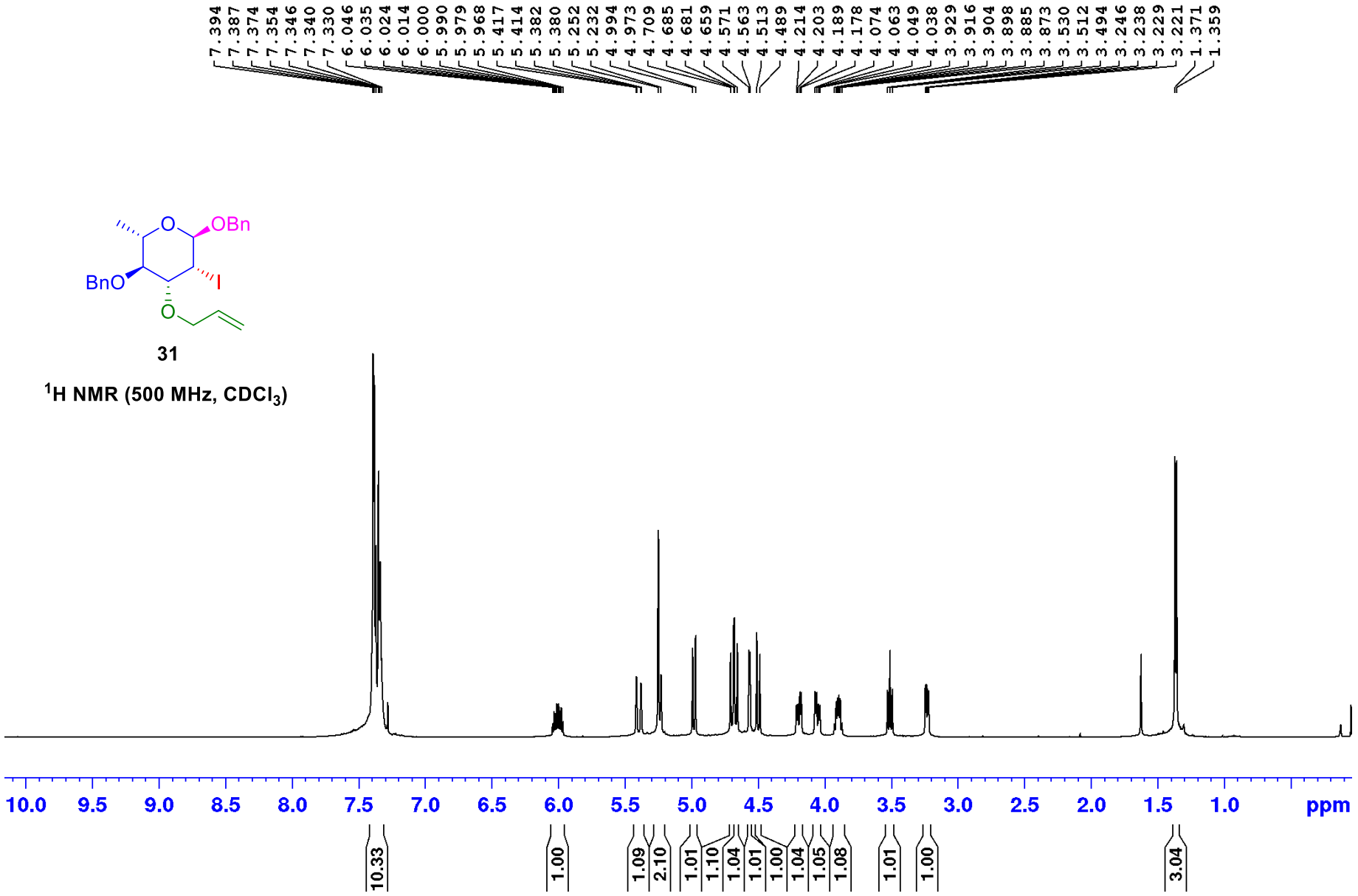
$^{13}C\{^{1}H\}$ NMR (100 MHz,$CDCl_3$)

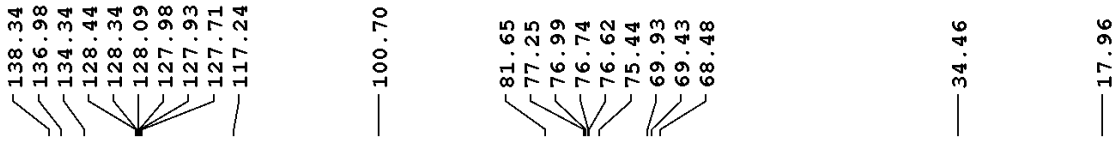

7.374
7.364
7.358
7.352
7.347
7.340
7.335
7.313
7.307
7.302
7.299
7.295
7.288
7.260
6.354
6.352
6.342
6.339
5.971
5.950
5.937
5.926
5.916
5.328
5.325
5.293
5.290
5.200
5.197
5.194
5.192
5.179
5.176
5.173
5.171
4.900
4.877
4.832
4.827
4.820
4.815
4.721
4.698
4.159
4.147
4.141
4.136
4.133
4.128
4.125
4.122
4.063
4.060
4.057
4.052
4.049
4.046
4.034
4.023
3.955
3.942
3.937
3.924
3.445
3.432
3.427
3.414
1.378
1.366
BnO
O
O
30
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
5.60
1.00
1.06
1.04
1.02
1.02
1.04
1.02
2.01
1.08
1.21
1.01
3.12

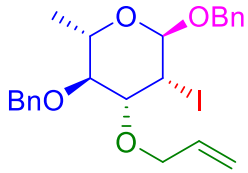


30

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

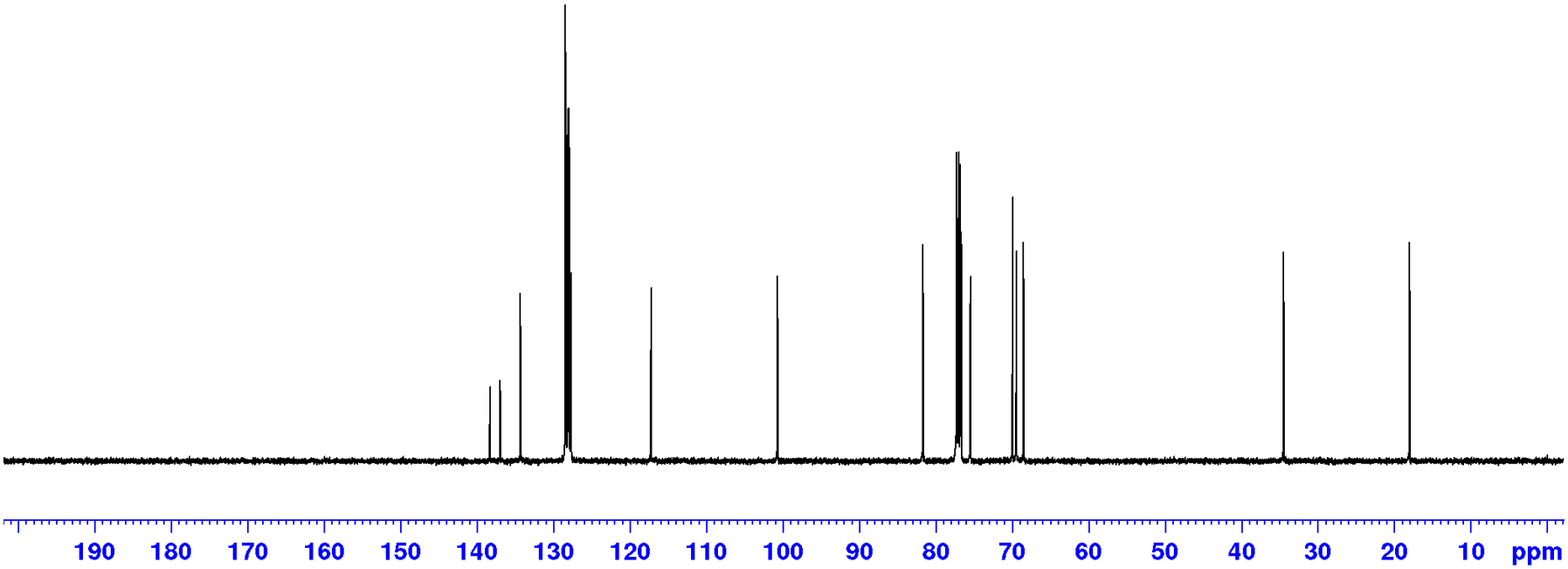

7.394
7.387
7.374
7.354
7.346
7.340
7.330
6.046
6.035
6.024
6.014
6.000
5.990
5.979
5.968
5.417
5.414
5.382
5.380
5.252
5.232
4.994
4.973
4.709
4.685
4.681
4.659
4.571
4.563
4.513
4.489
4.214
4.203
4.189
4.178
4.074
4.063
4.049
4.038
3.929
3.916
3.904
3.898
3.885
3.873
3.530
3.512
3.494
3.246
3.238
3.229
3.221
1.371
1.359
O
OBn
BnO
I
O
31
1H NMR (500 MHz, CDCl3)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
10.33
1.00
1.09
2.10
1.01
1.10
1.04
1.01
1.00
1.04
1.05
1.08
1.01
1.00
3.04

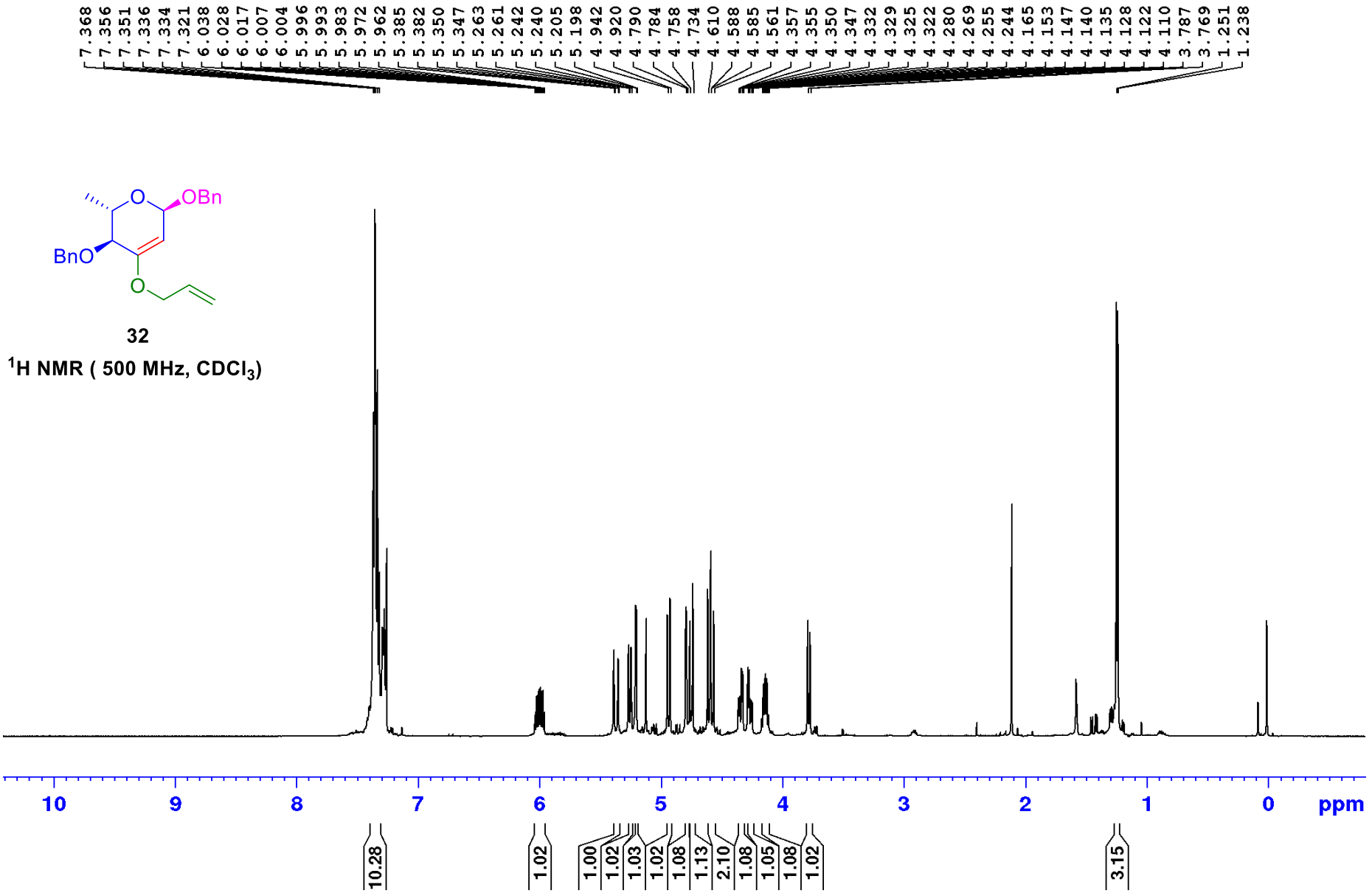


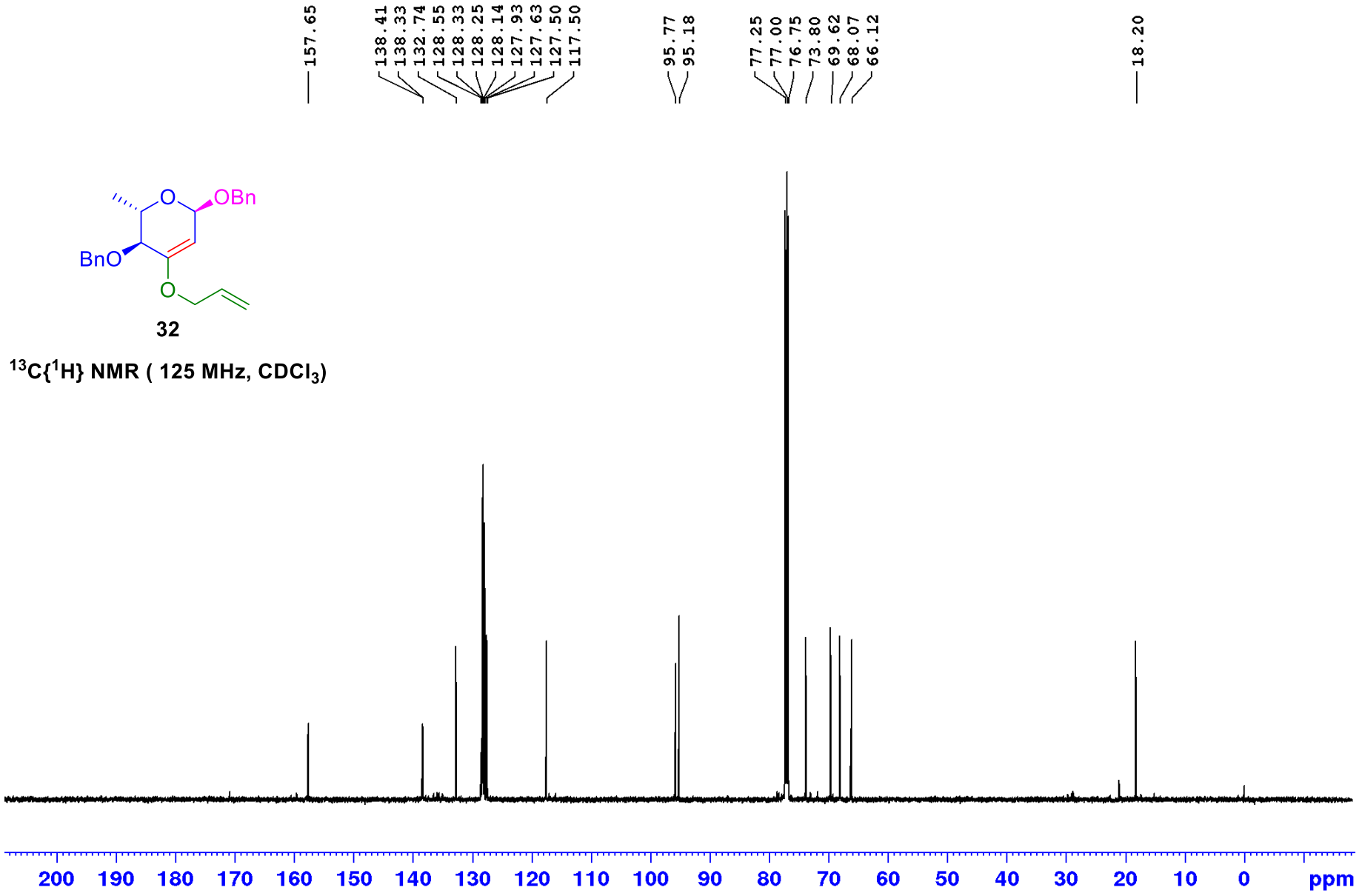


31

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

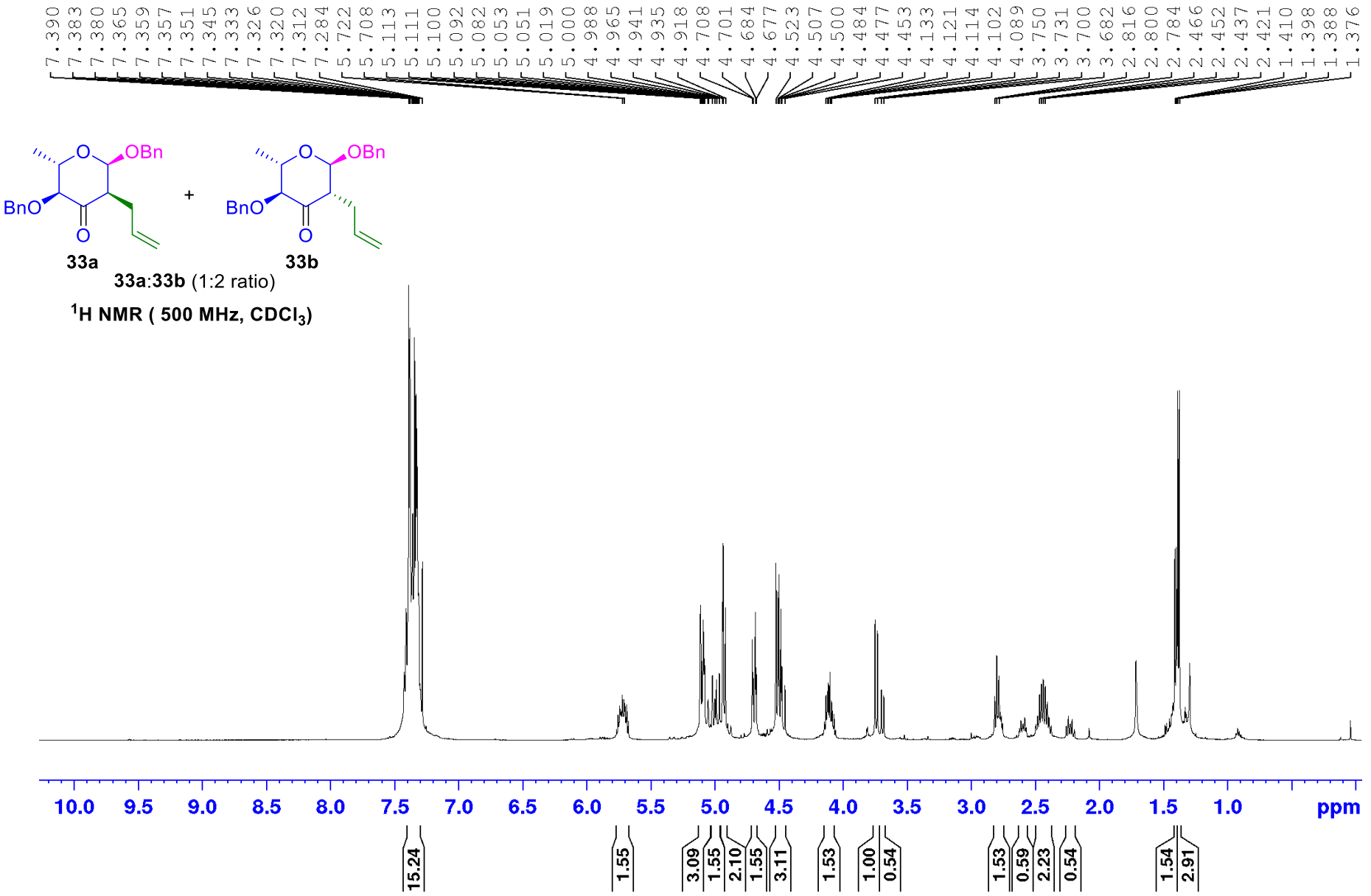


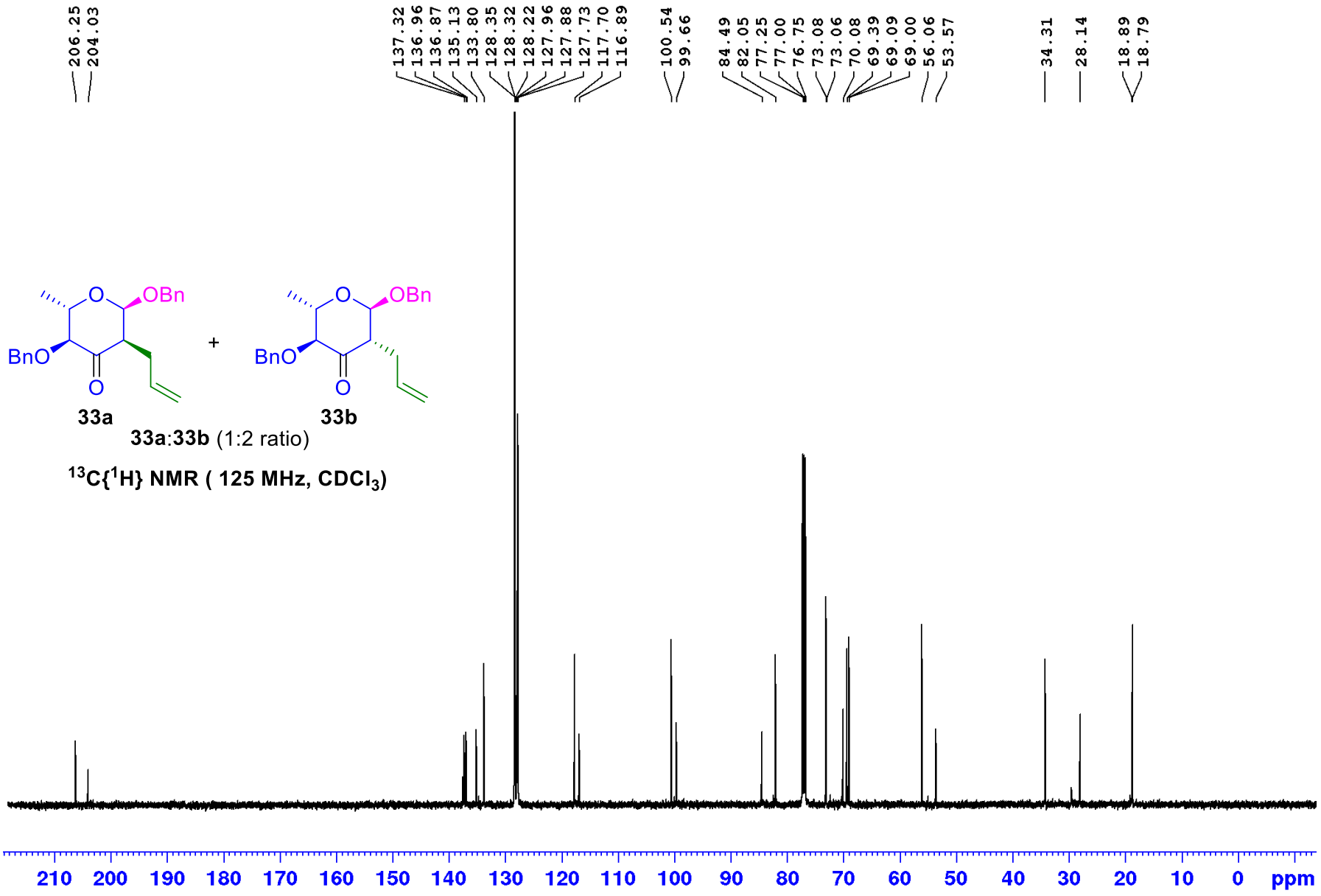

7.368
7.356
7.351
7.336
7.334
7.321
6.038
6.028
6.017
6.007
6.004
5.996
5.993
5.983
5.972
5.962
5.385
5.382
5.350
5.347
5.263
5.261
5.242
5.240
5.205
5.198
4.942
4.920
4.790
4.784
4.758
4.734
4.610
4.588
4.585
4.561
4.357
4.355
4.350
4.347
4.332
4.329
4.325
4.322
4.280
4.269
4.255
4.244
4.165
4.153
4.147
4.140
4.135
4.128
4.122
4.110
3.787
3.769
1.251
1.238
O
OBn
BnO
O
32
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
10.28
1.02
1.00
1.02
1.03
1.02
1.08
1.13
2.10
1.08
1.05
1.08
1.02
3.15

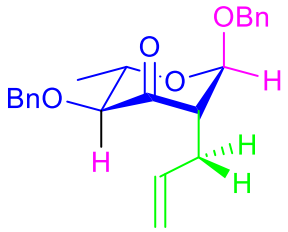


32

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

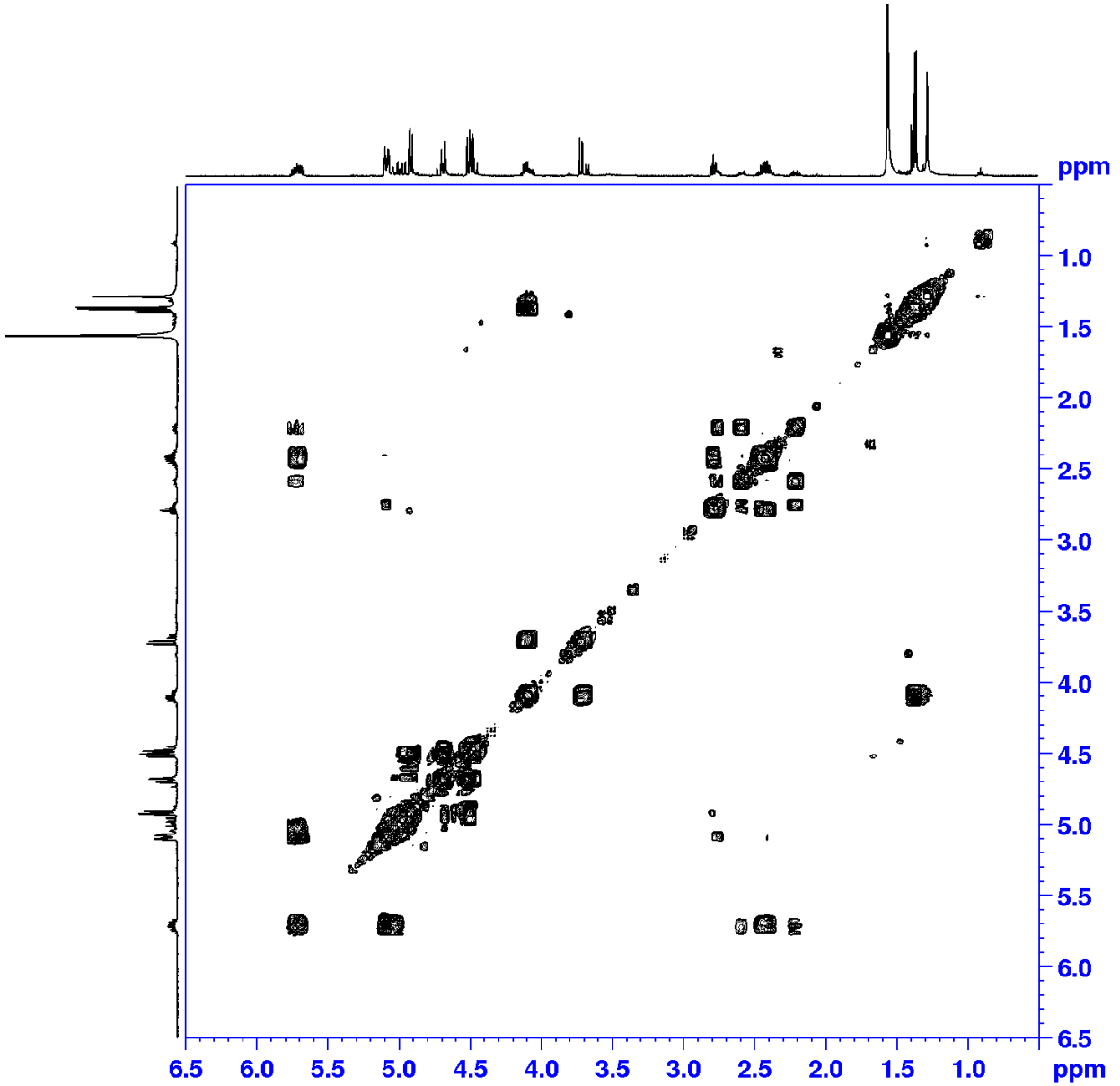

7.390
7.383
7.380
7.365
7.359
7.357
7.351
7.345
7.333
7.326
7.320
7.312
7.284
5.722
5.708
5.113
5.111
5.100
5.092
5.082
5.053
5.051
5.019
5.000
4.988
4.965
4.941
4.935
4.918
4.708
4.701
4.684
4.677
4.523
4.507
4.500
4.484
4.477
4.453
4.133
4.121
4.114
4.102
4.089
3.750
3.731
3.700
3.682
2.816
2.800
2.784
2.466
2.452
2.437
2.421
1.410
1.398
1.388
1.376
BnO
OBn
O
33a
33b
33a:33b (1:2 ratio)
1H NMR (500 MHz, CDCl3)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
15.24
1.55
3.09
1.55
2.10
1.55
3.11
1.53
1.00
0.54
1.53
0.59
2.23
0.54
1.54
2.91

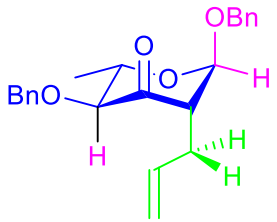

206.25
204.03
137.32
136.96
136.87
135.13
133.80
128.35
128.32
128.22
127.96
127.88
127.73
117.70
116.89
100.54
99.66
84.49
82.05
77.25
77.00
76.75
73.08
73.06
70.08
69.39
69.09
69.00
56.06
53.57
34.31
28.14
18.89
18.79
OBn
BnO
O
+
OBn
BnO
O
33a
33b
33a:33b (1:2 ratio)
13C{1H} NMR (125 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm



33a

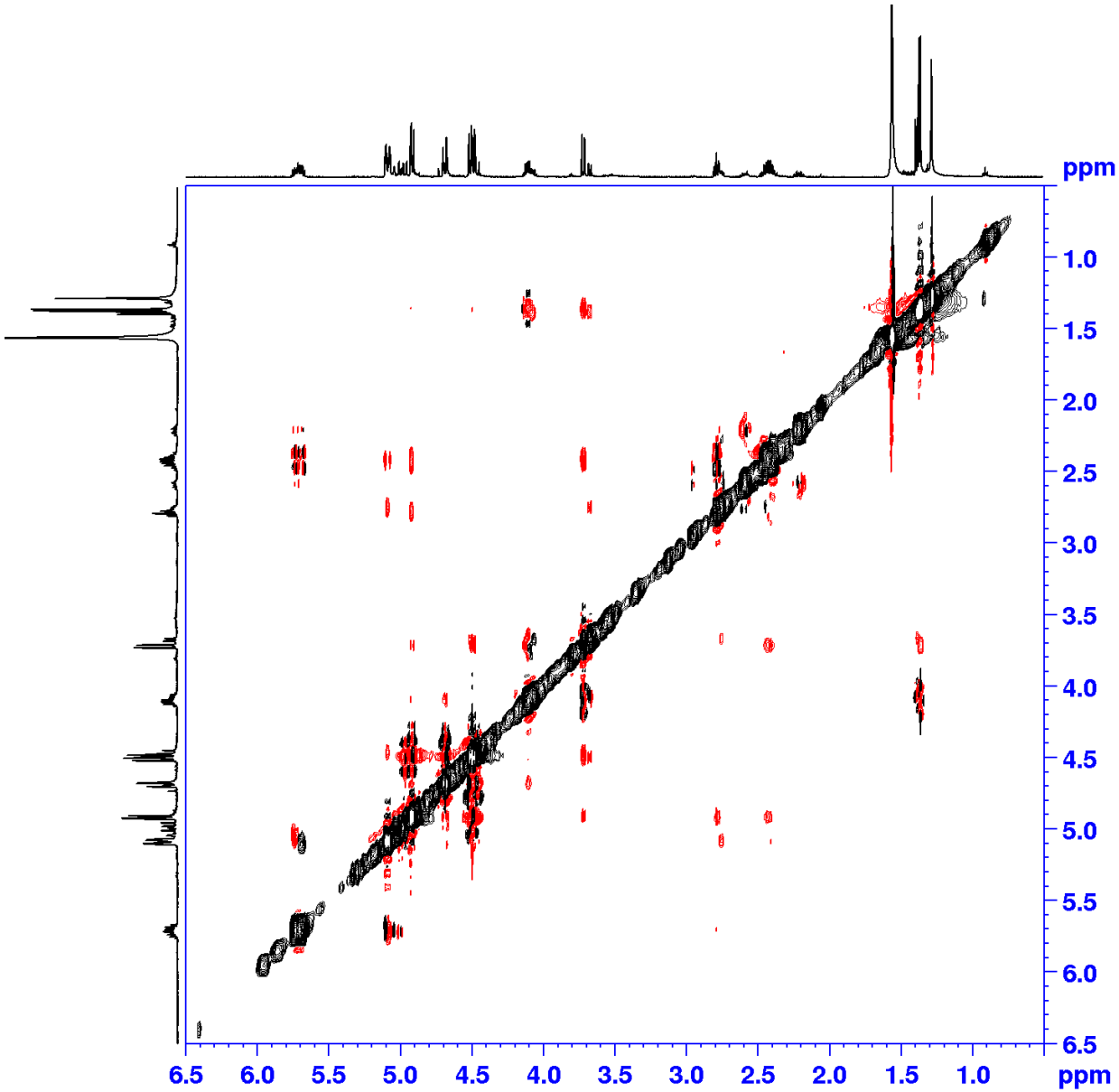
^{1}H-^{1}H COSY (500 MHz, $CDCl_3$)

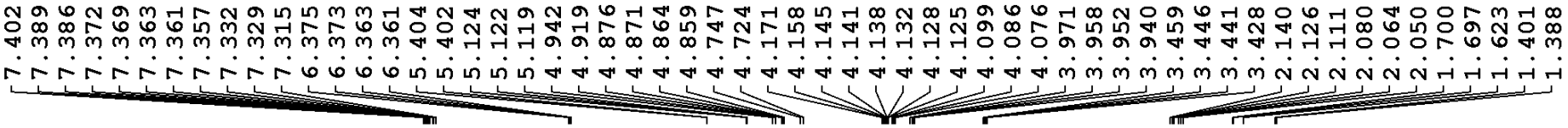


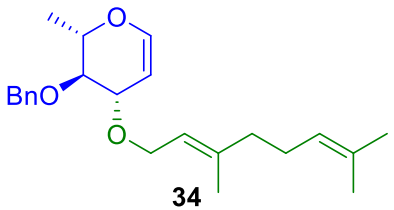


33a

^{1}H-^{1}H NOESY (500 MHz, $CDCl_3$)

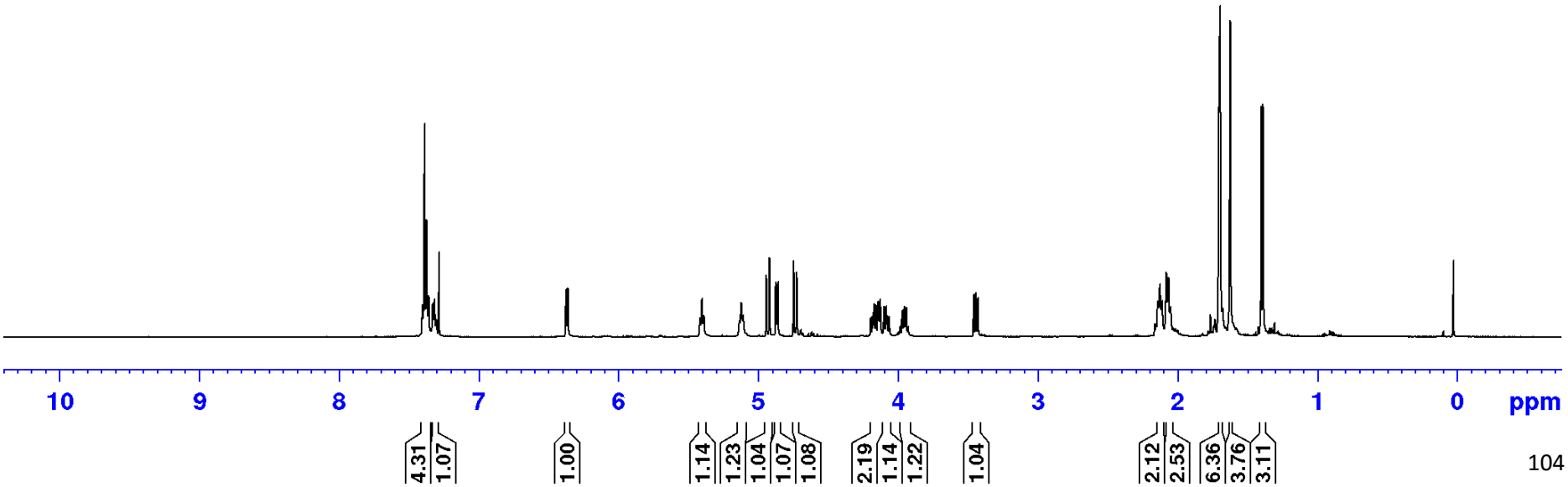


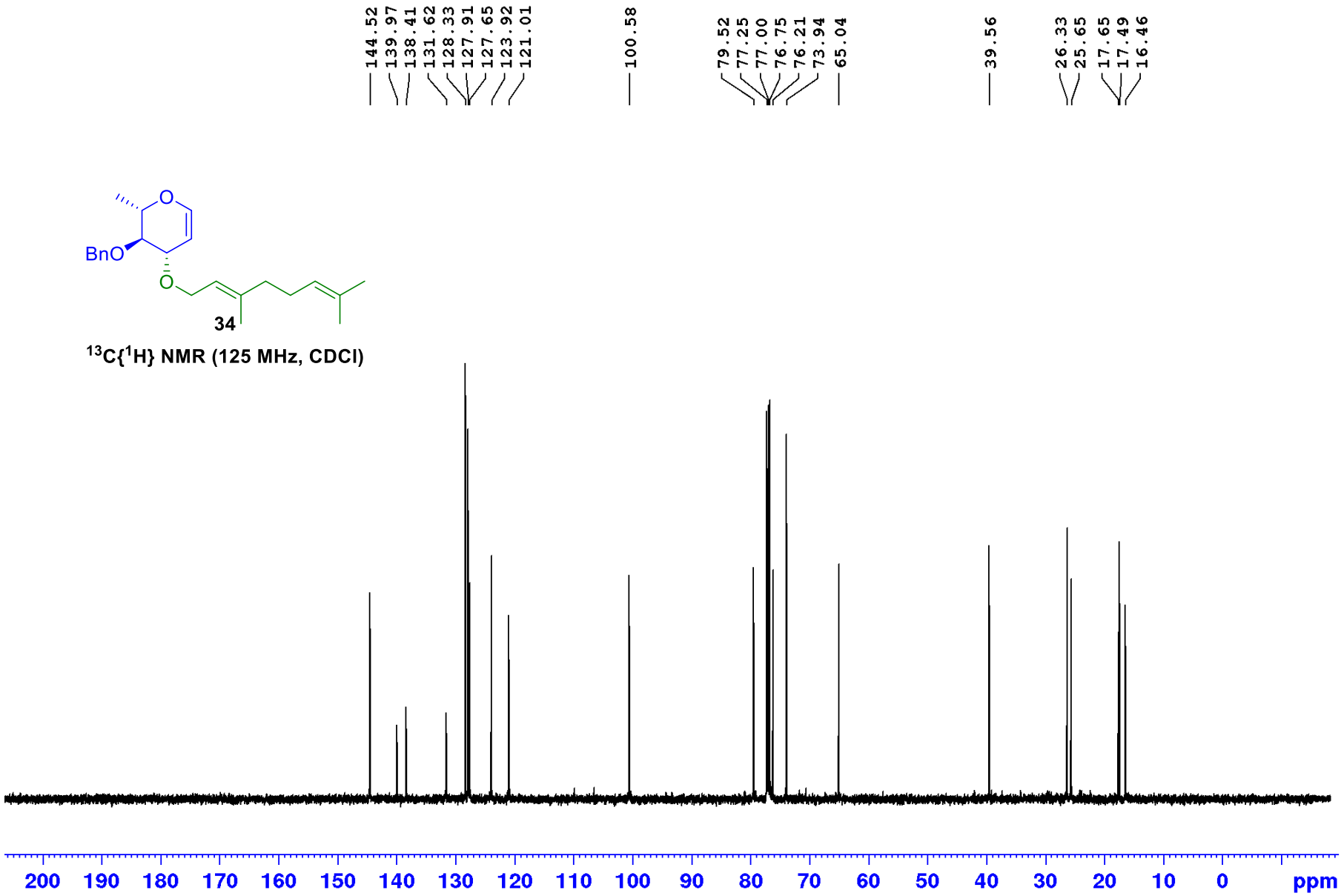


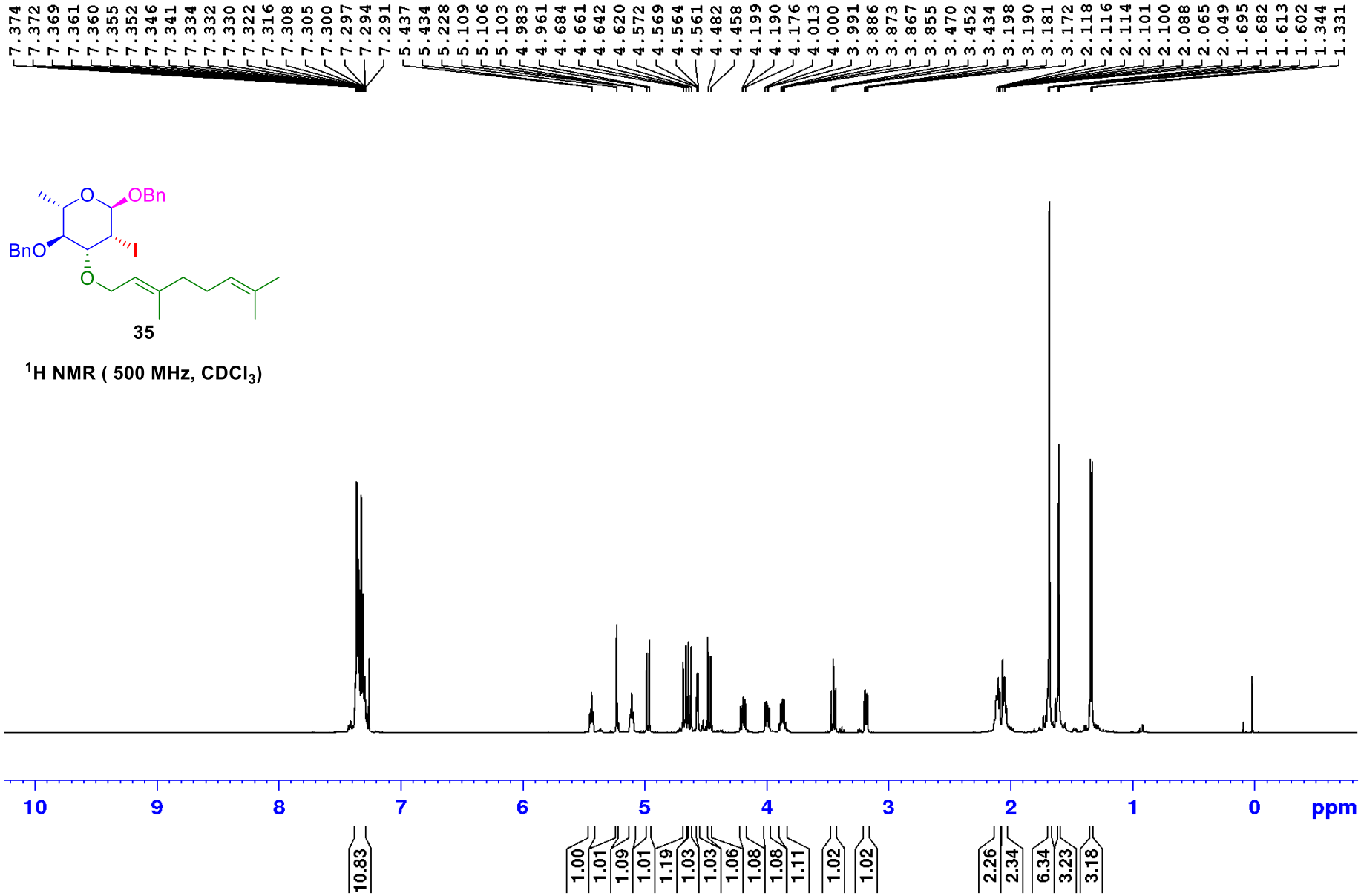


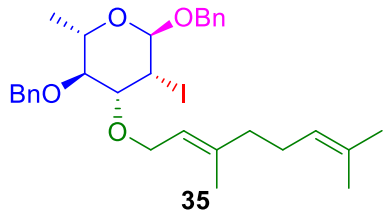
34

^{1}H NMR (500 MHz, $CDCl_3$)



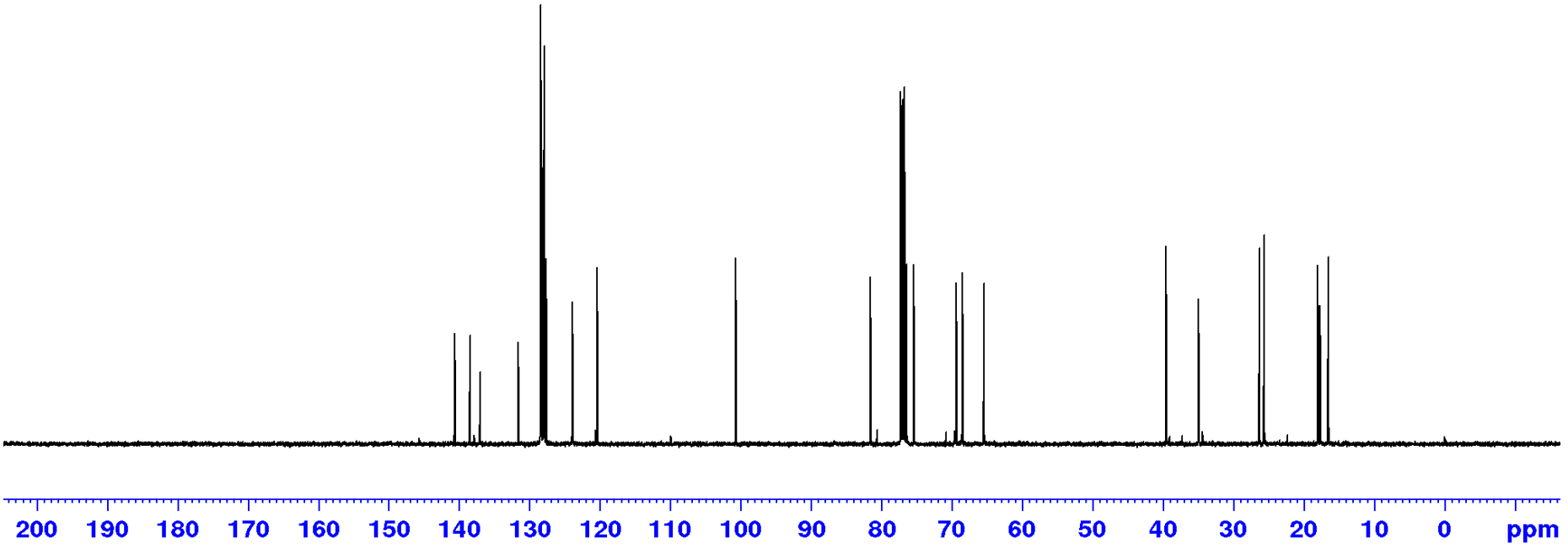

144.52
139.97
138.41
131.62
128.33
127.91
127.65
123.92
121.01
100.58
79.52
77.25
77.00
76.75
76.21
73.94
65.04
39.56
26.33
25.65
17.65
17.49
16.46
BnO
O
O
34
$^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

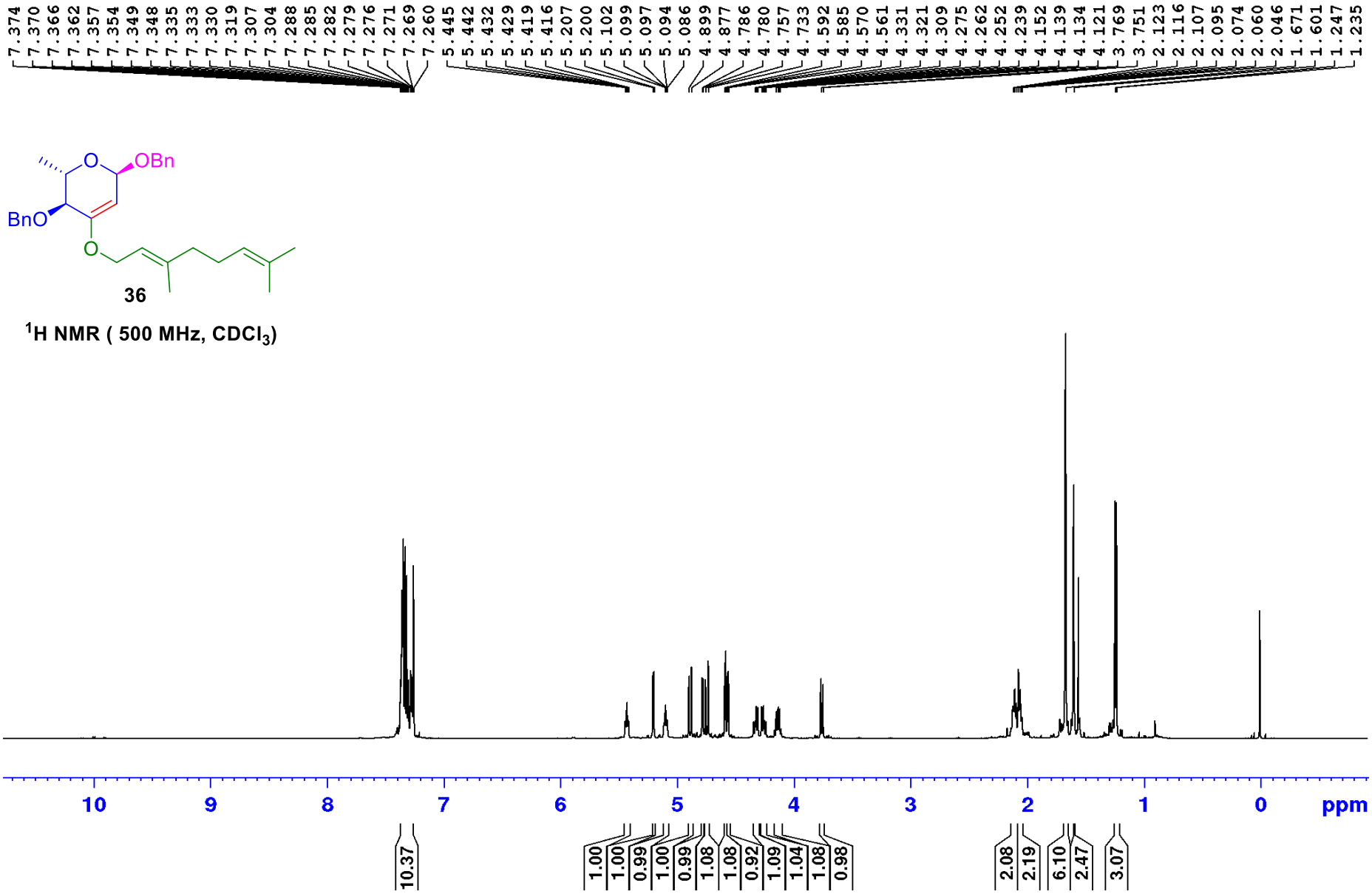

7.374
7.372
7.369
7.361
7.360
7.355
7.352
7.346
7.341
7.334
7.332
7.330
7.322
7.316
7.308
7.305
7.300
7.297
7.294
7.291
5.437
5.434
5.228
5.109
5.106
5.103
4.983
4.961
4.684
4.661
4.642
4.620
4.572
4.569
4.564
4.561
4.482
4.458
4.199
4.190
4.176
4.013
4.000
3.991
3.886
3.873
3.867
3.855
3.470
3.452
3.434
3.198
3.190
3.181
3.172
2.118
2.116
2.114
2.101
2.100
2.088
2.065
2.049
1.695
1.682
1.613
1.602
1.344
1.331
OBn
BnO
I
O
O
35
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
10.83
1.00
1.01
1.09
1.01
1.19
1.03
1.03
1.06
1.08
1.08
1.11
1.02
1.02
2.26
2.34
6.34
3.23
3.18



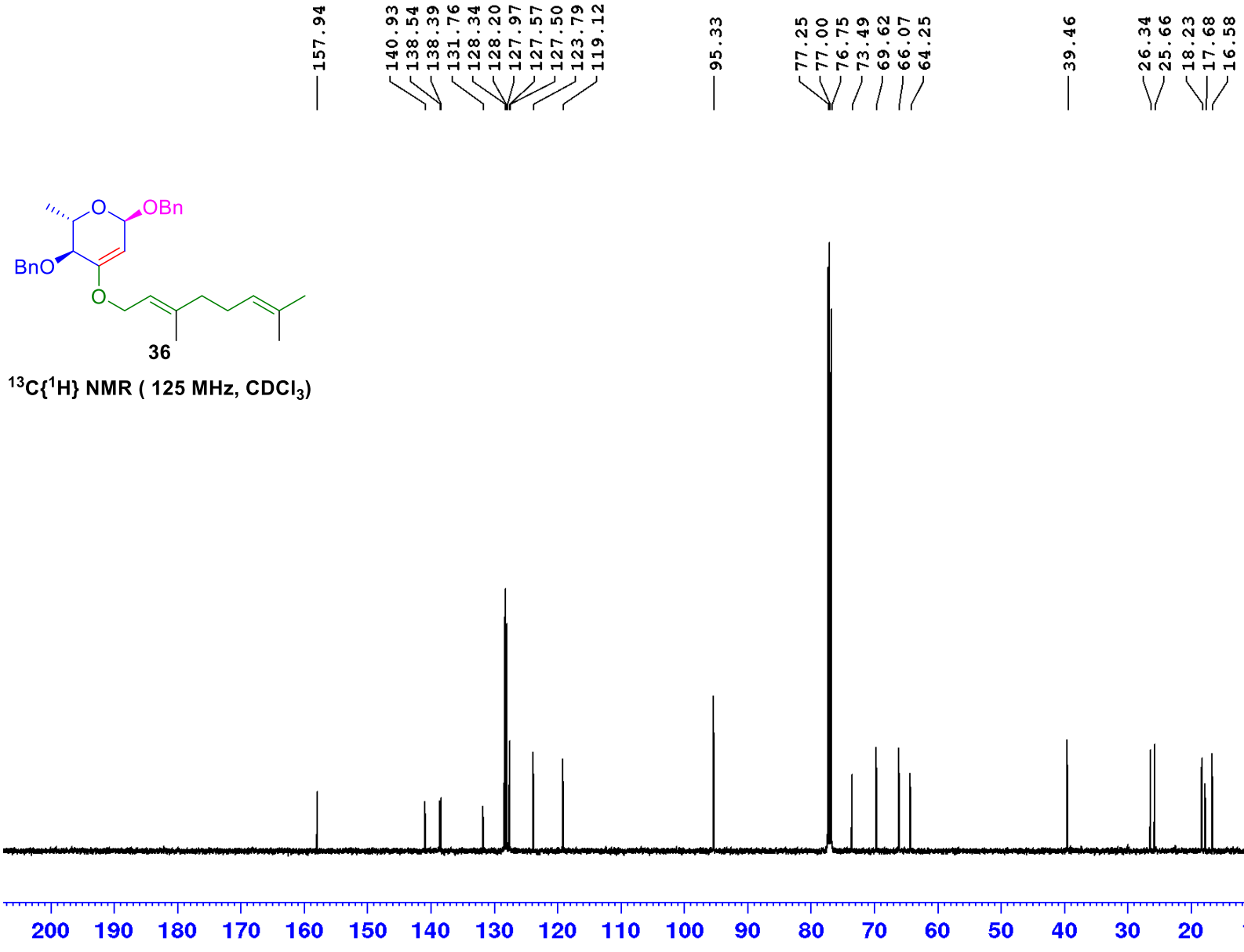
35

$^{13}C\{^{1}H\}$ NMR (125 MHz, CDCl)

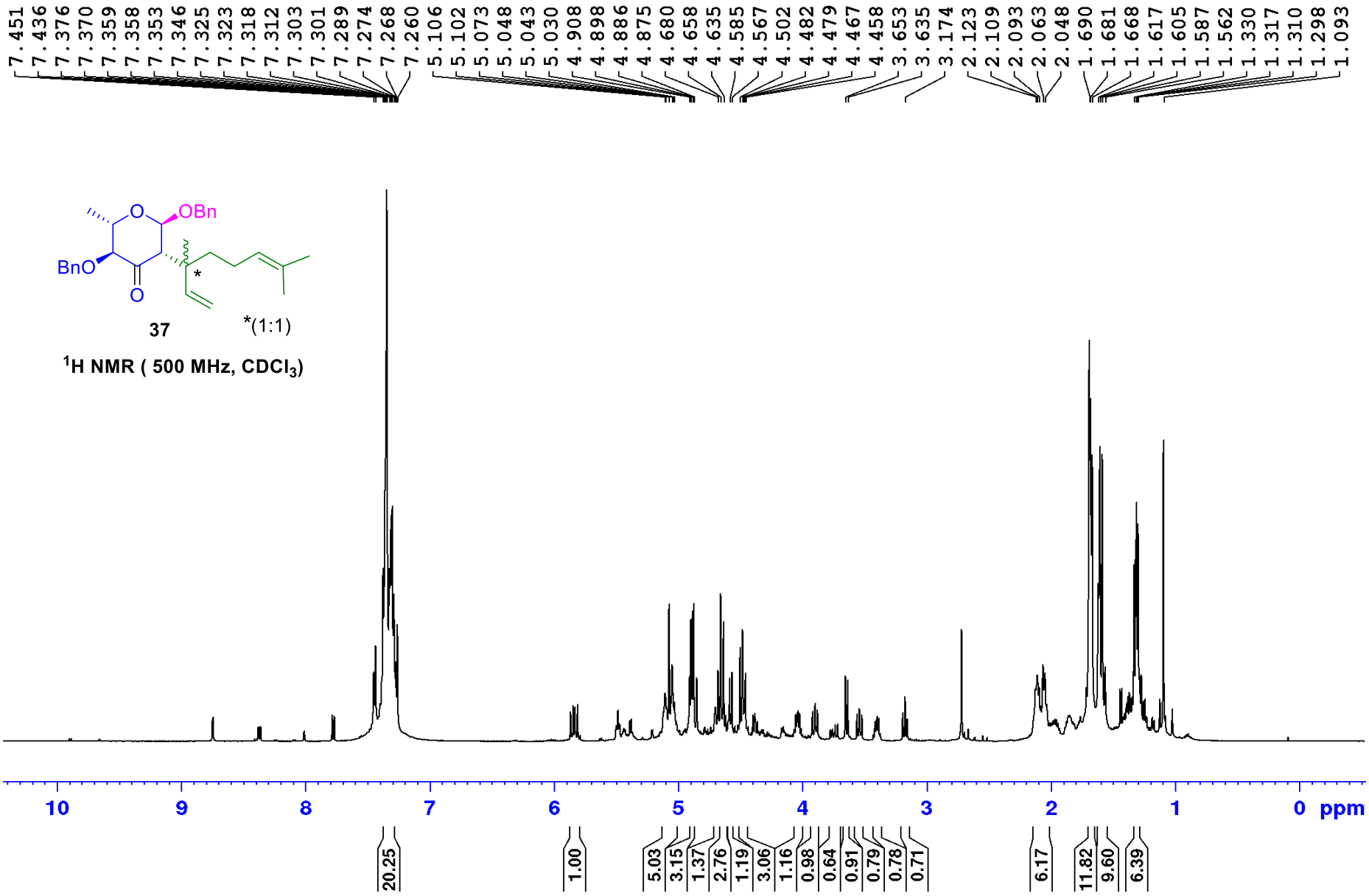


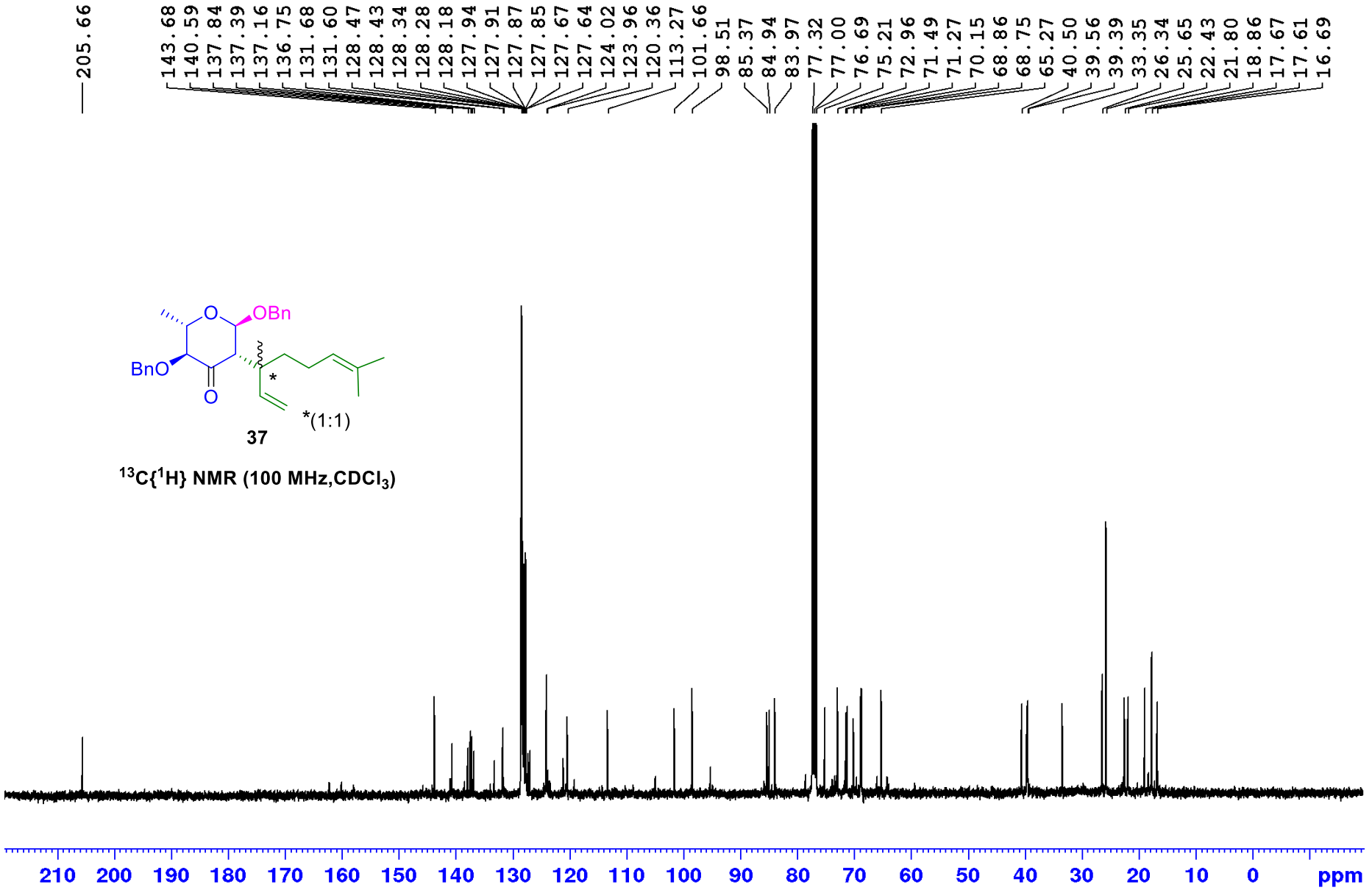


^{1}H NMR (500 MHz, $CDCl_3$)



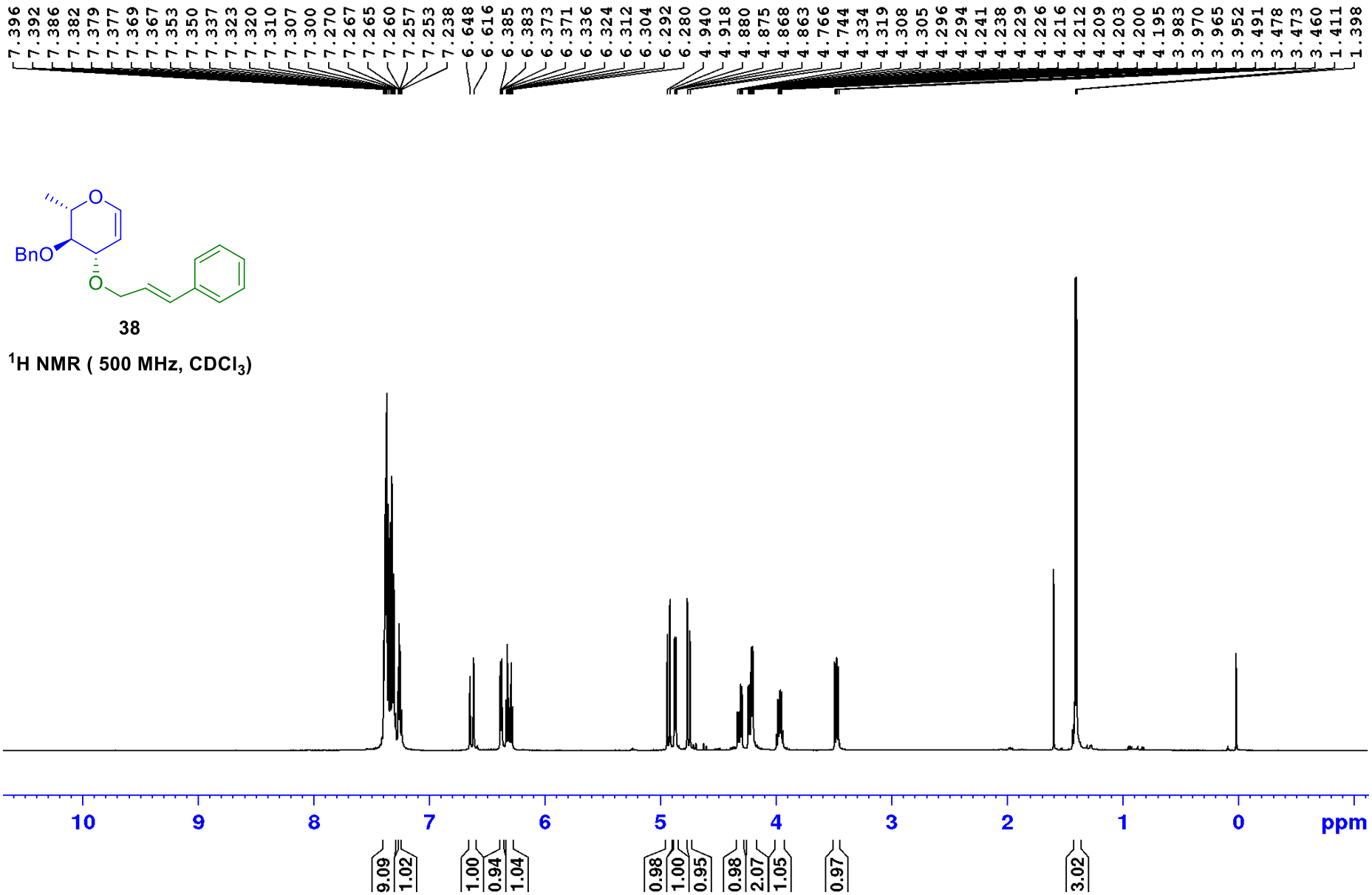
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

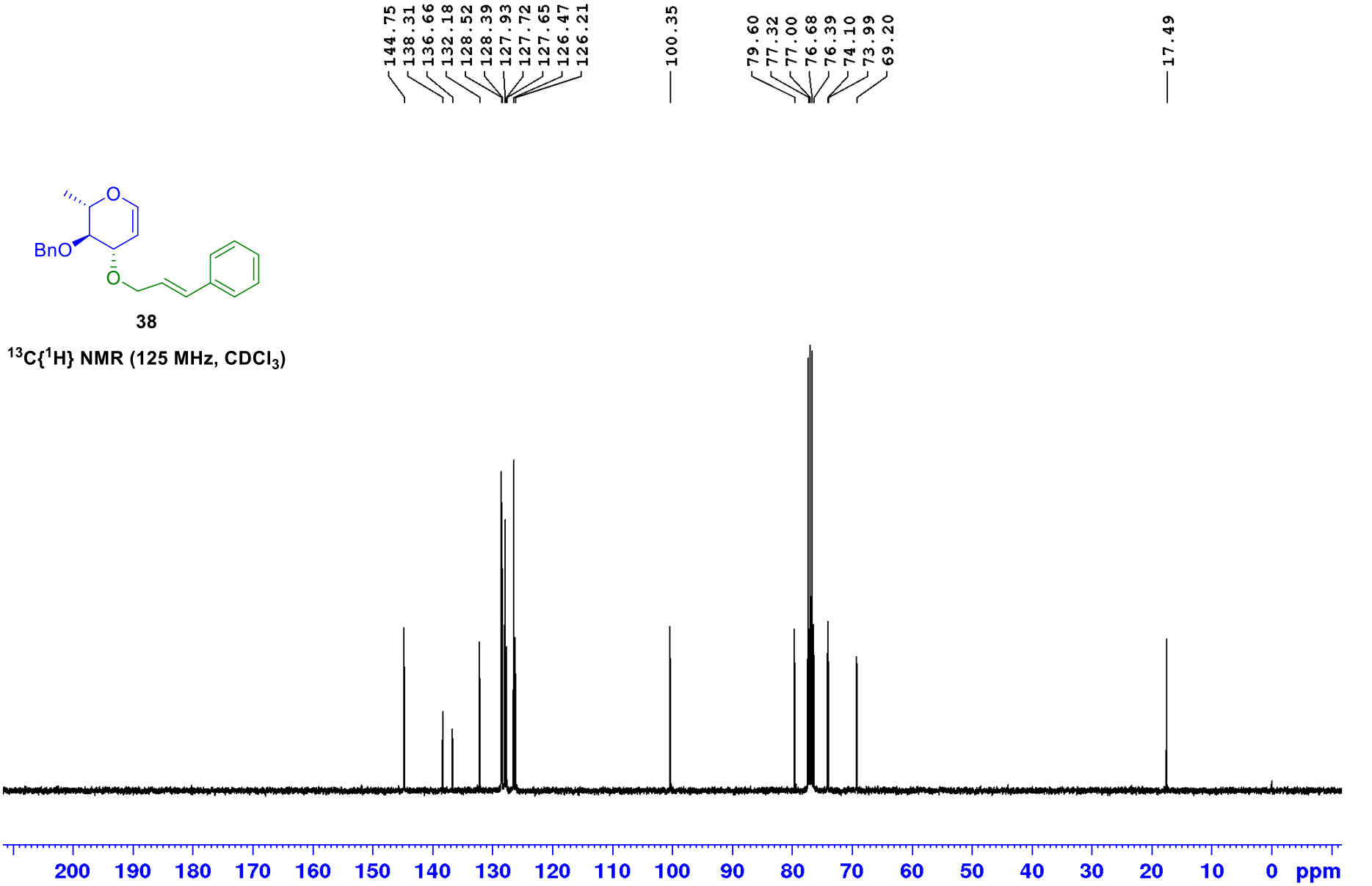

7.451
7.436
7.376
7.370
7.359
7.358
7.353
7.346
7.325
7.323
7.318
7.312
7.303
7.301
7.289
7.274
7.268
7.260
5.106
5.102
5.073
5.048
5.043
5.030
4.908
4.898
4.886
4.875
4.680
4.658
4.635
4.585
4.567
4.502
4.482
4.479
4.467
4.458
3.653
3.635
3.174
2.123
2.109
2.093
2.063
2.048
1.690
1.681
1.668
1.617
1.605
1.587
1.562
1.330
1.317
1.310
1.298
1.093
OBn
BnO
O
O
*
37
*(1:1)
^{1}H NMR (500 MHz, CDCl$_3$)
10
9
8
7
6
5
4
3
2
1
0
ppm
20.25
1.00
5.03
3.15
1.37
2.76
1.19
3.06
1.16
0.98
0.64
0.91
0.79
0.78
0.71
6.17
11.82
9.60
6.39

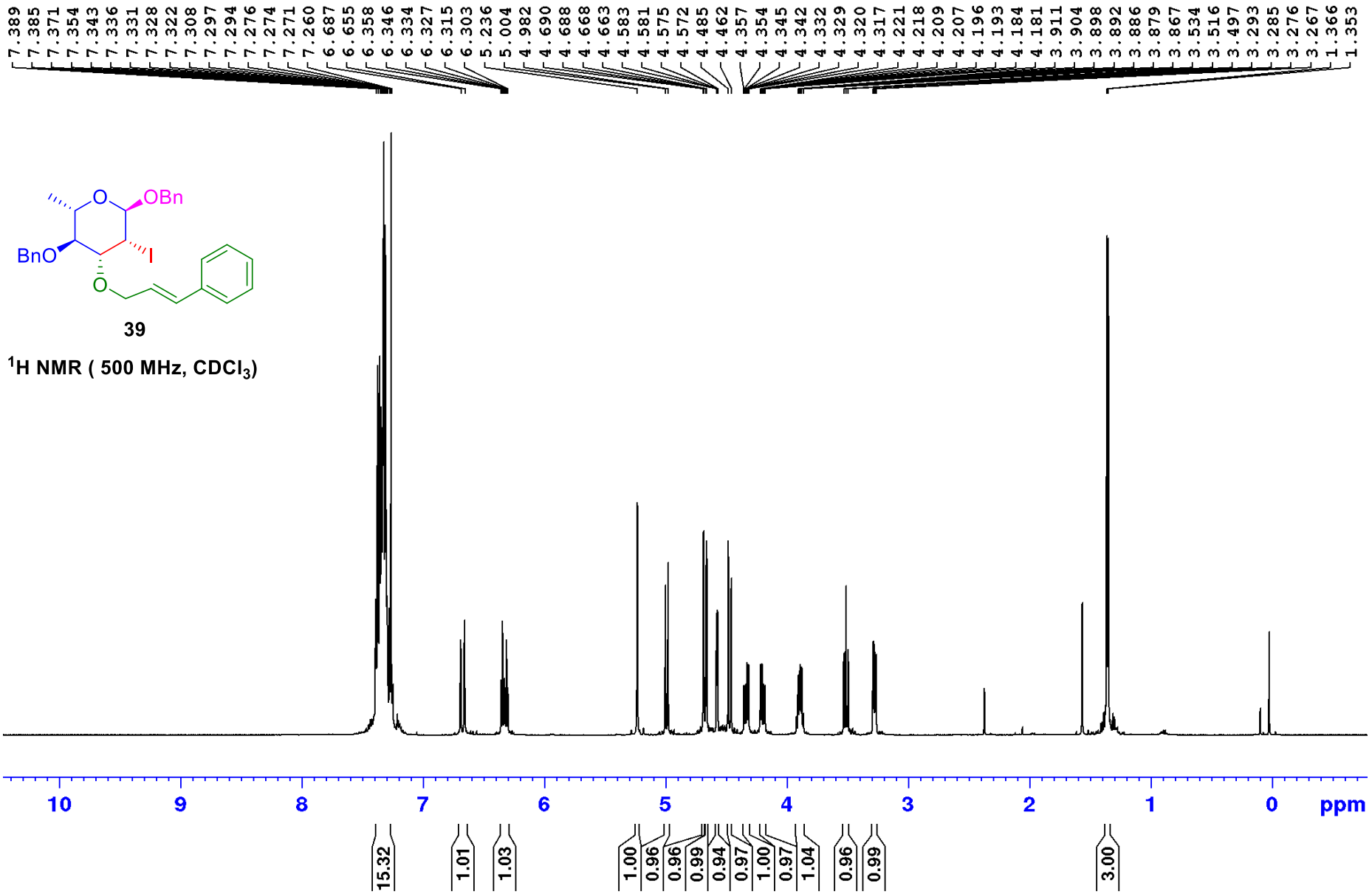


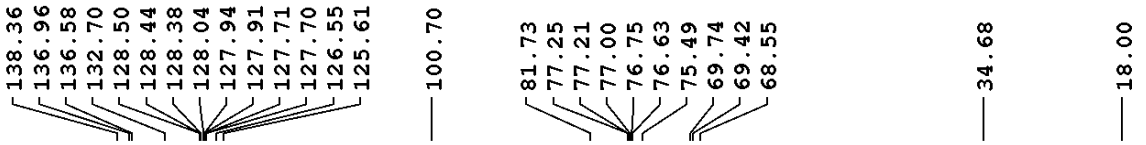
37

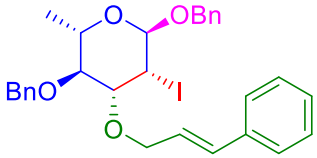
$^{13}C\{^{1}H\}$ NMR (100 MHz,$CDCl_3$)


7.396
7.392
7.386
7.382
7.379
7.377
7.369
7.367
7.353
7.350
7.337
7.323
7.320
7.310
7.307
7.300
7.270
7.267
7.265
7.260
7.257
7.253
7.238
6.648
6.616
6.385
6.383
6.373
6.371
6.336
6.324
6.312
6.304
6.292
6.280
4.940
4.918
4.880
4.875
4.868
4.863
4.766
4.744
4.334
4.319
4.308
4.305
4.296
4.294
4.241
4.238
4.229
4.226
4.216
4.212
4.209
4.203
4.200
4.195
3.983
3.970
3.965
3.952
3.491
3.478
3.473
3.460
1.411
1.398
BnO
O
O
38
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
9.09
1.02
1.00
0.94
1.04
0.98
1.00
0.95
0.98
2.07
1.05
0.97
3.02


144.75
138.31
136.66
132.18
128.52
128.39
127.93
127.72
127.65
126.47
126.21
100.35
79.60
77.32
77.00
76.68
76.39
74.10
73.99
69.20
17.49
BnO
O
O
38
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

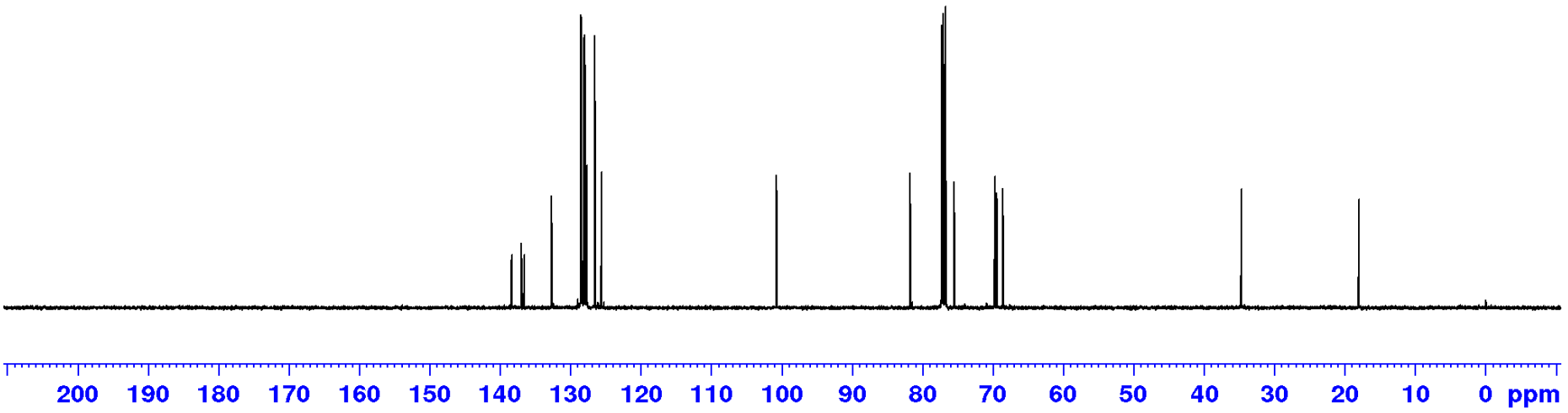

7.389
7.385
7.371
7.354
7.343
7.336
7.331
7.328
7.322
7.308
7.297
7.294
7.276
7.274
7.271
7.260
6.687
6.655
6.358
6.346
6.334
6.327
6.315
6.303
5.236
5.004
4.982
4.690
4.688
4.668
4.663
4.583
4.581
4.575
4.572
4.485
4.462
4.357
4.354
4.345
4.342
4.332
4.329
4.320
4.317
4.221
4.218
4.209
4.207
4.196
4.193
4.184
4.181
3.911
3.904
3.898
3.892
3.886
3.879
3.867
3.534
3.516
3.497
3.293
3.285
3.276
3.267
1.366
1.353
O
OBn
BnO
I
O
39
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
15.32
1.01
1.03
1.00
0.96
0.96
0.99
0.94
0.97
1.00
0.97
1.04
0.96
0.99
3.00

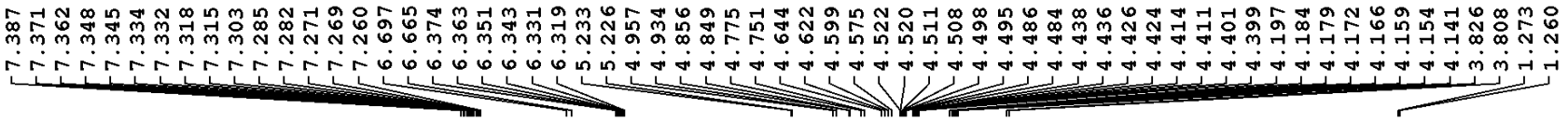


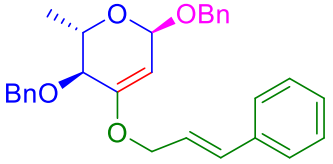


39

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

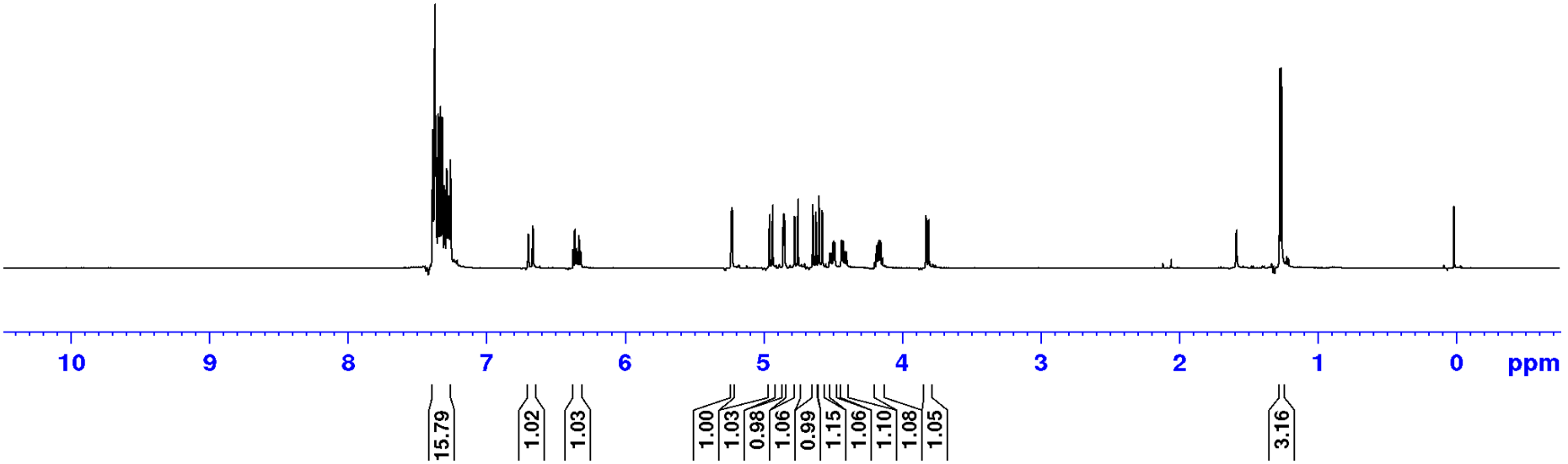


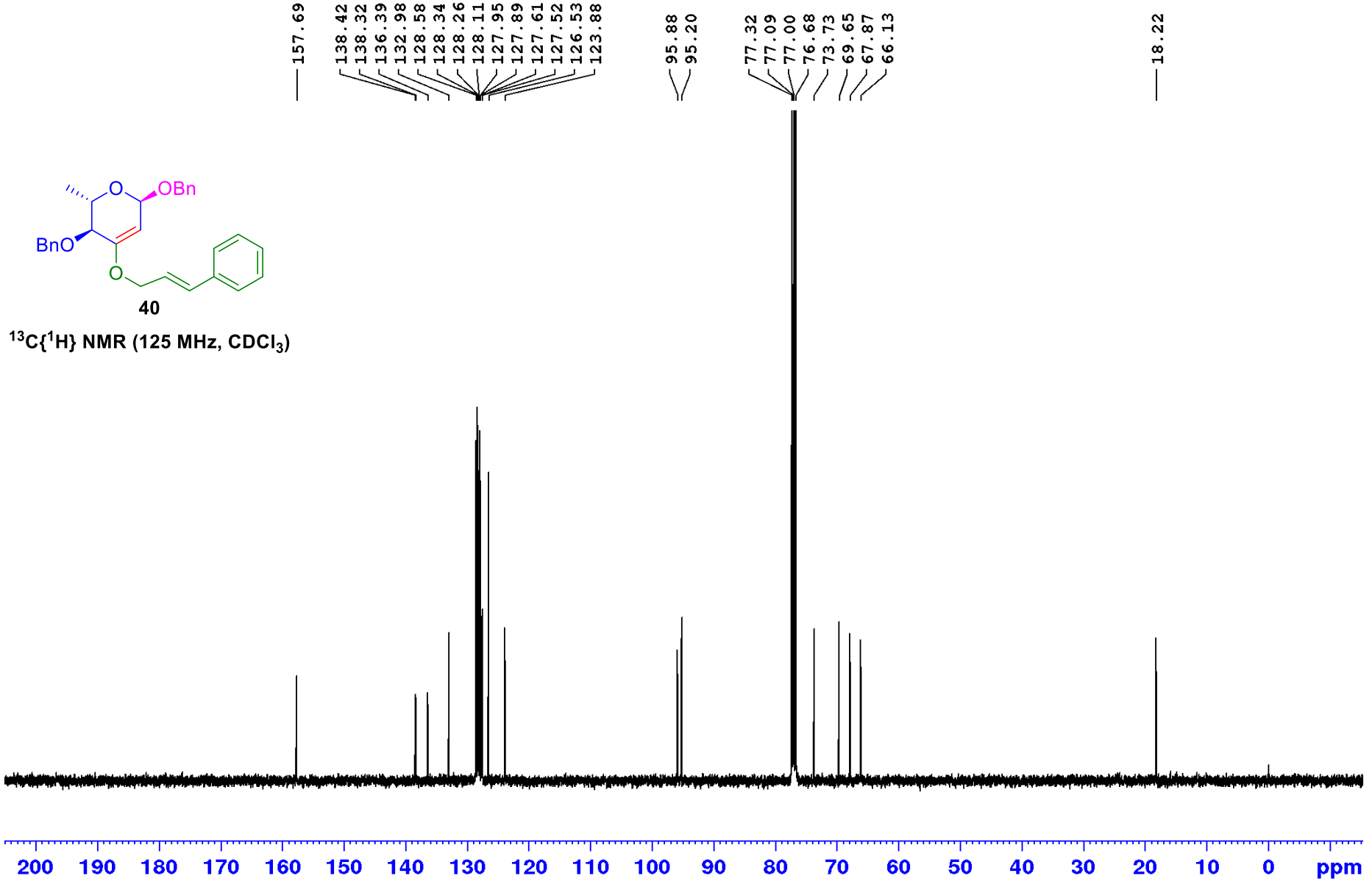




40

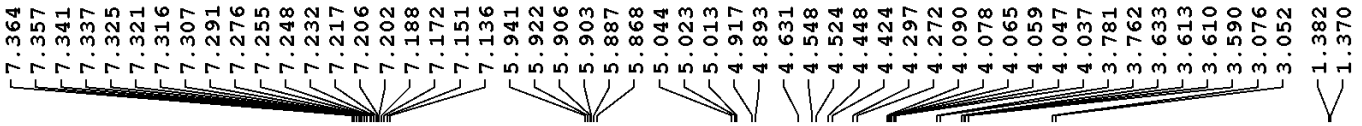
^{1}H NMR (500 MHz, $CDCl_3$)

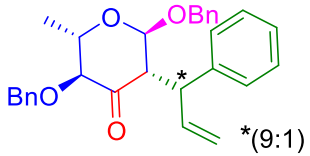




40

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

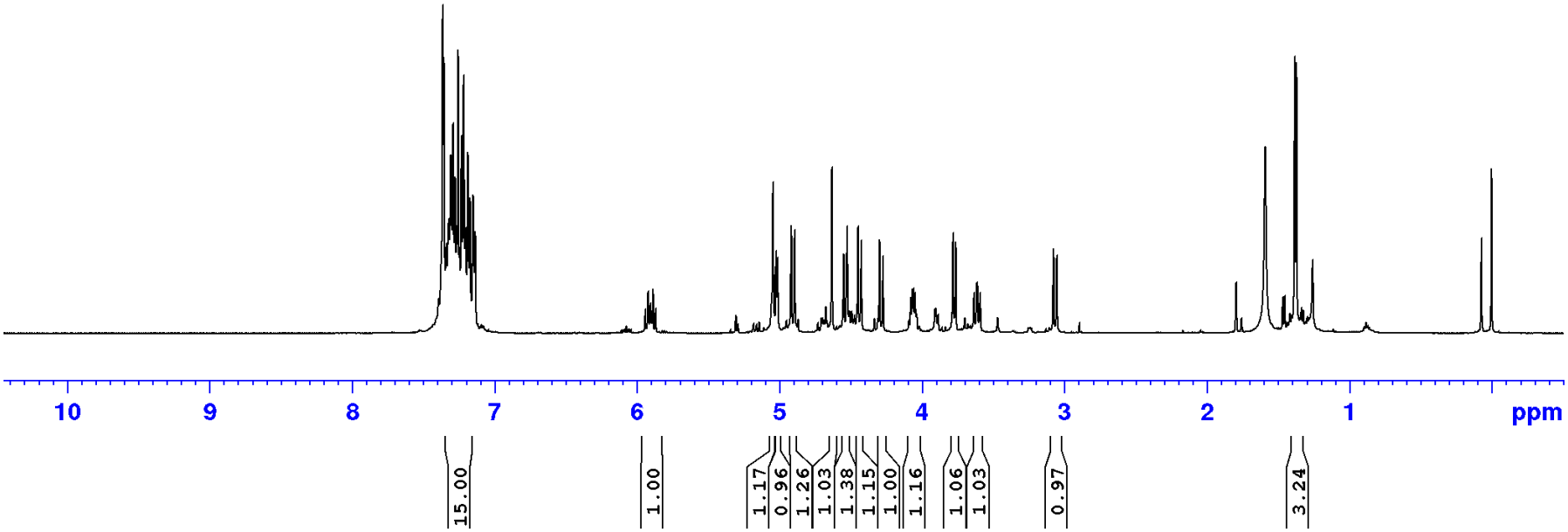


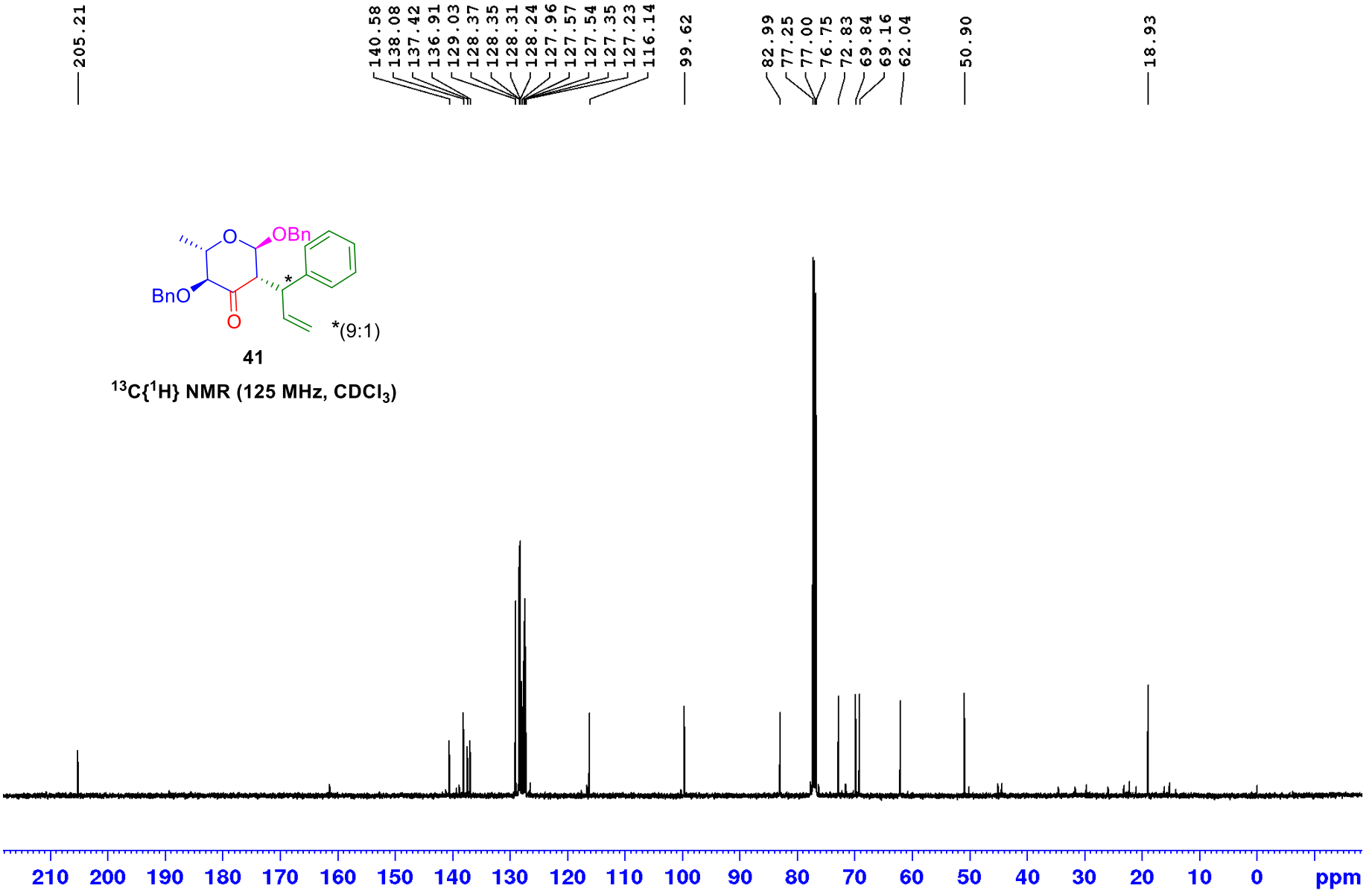


*(9:1)

41

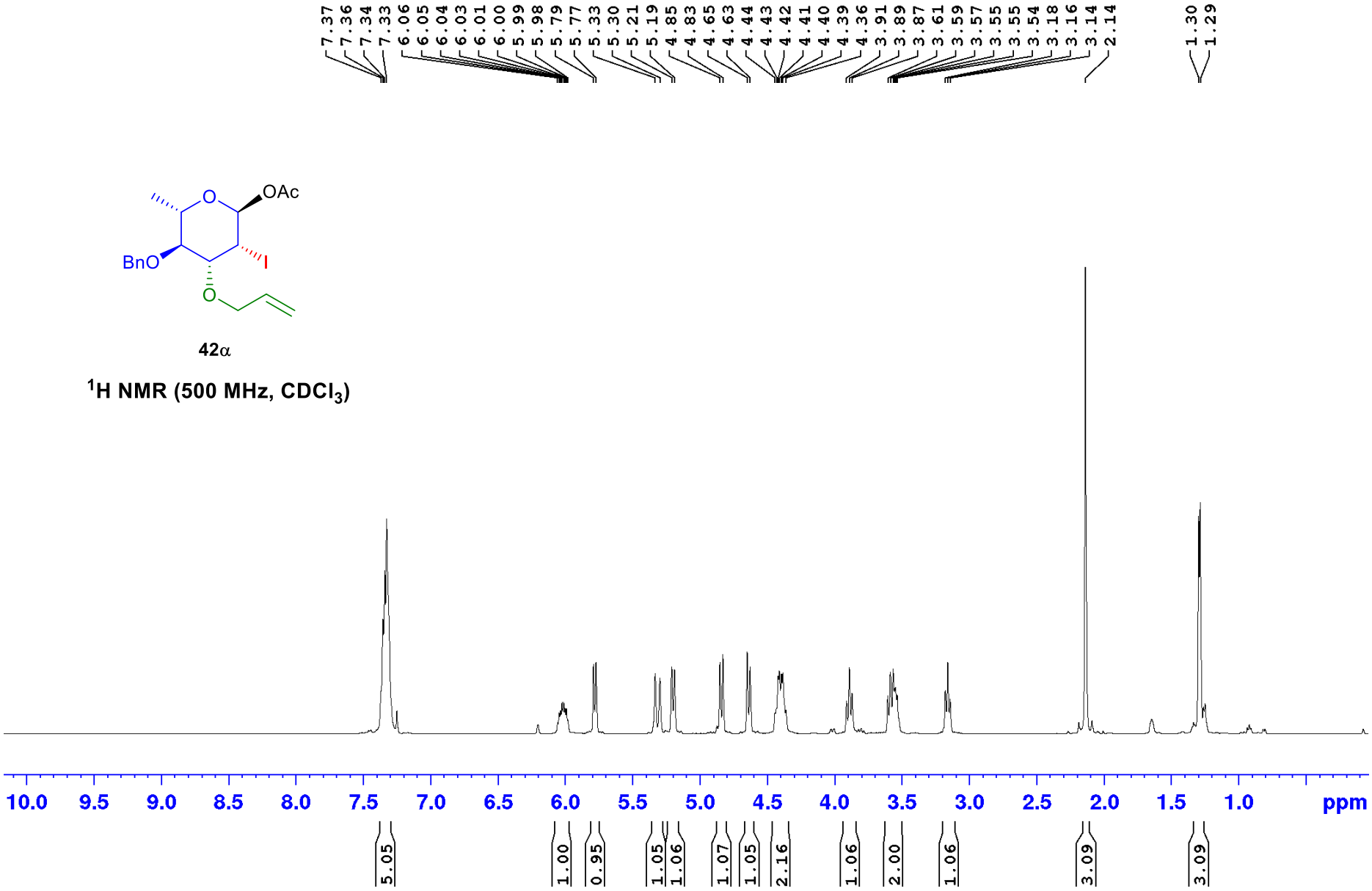
^{1}H NMR (500 MHz, $CDCl_3$)





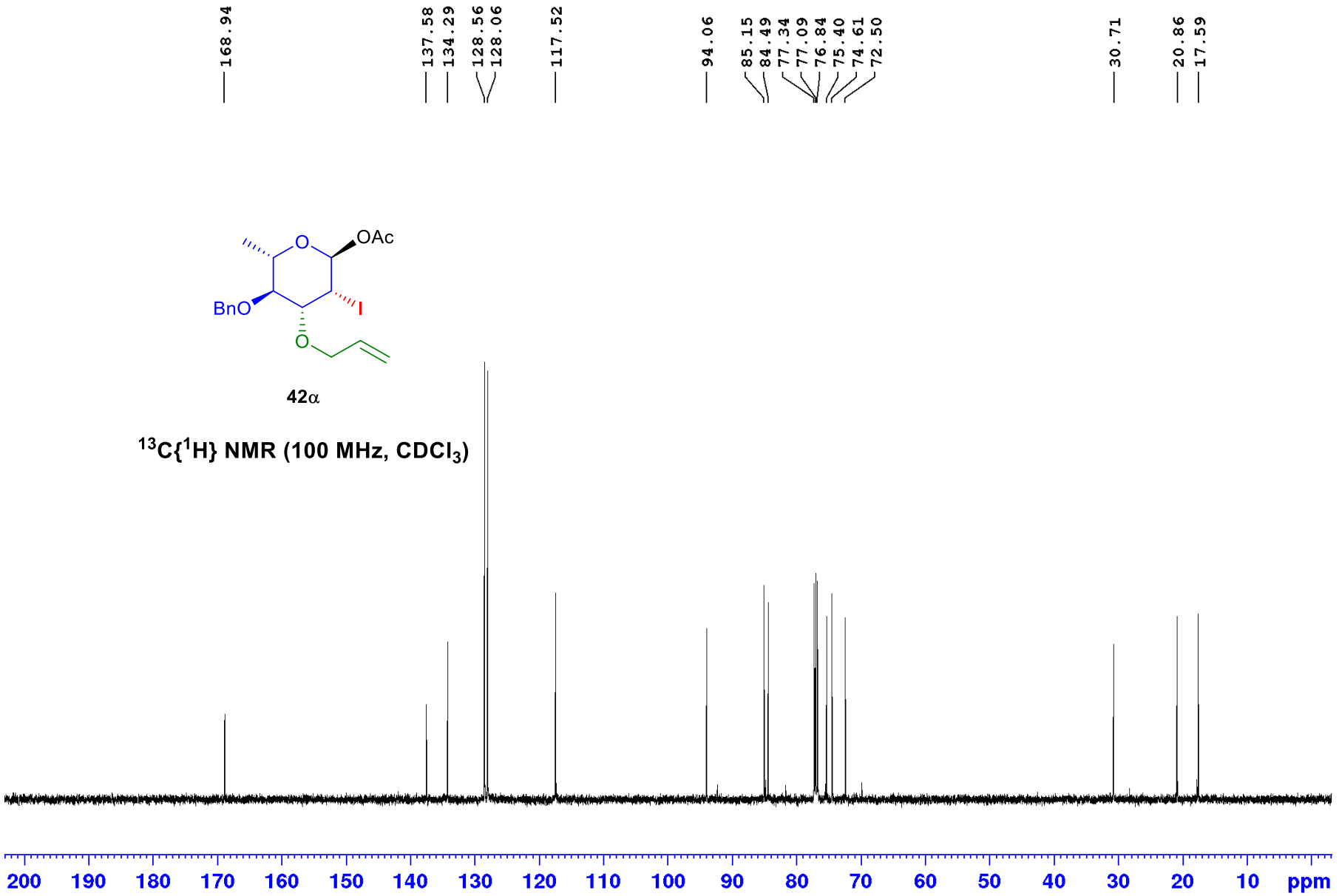
41

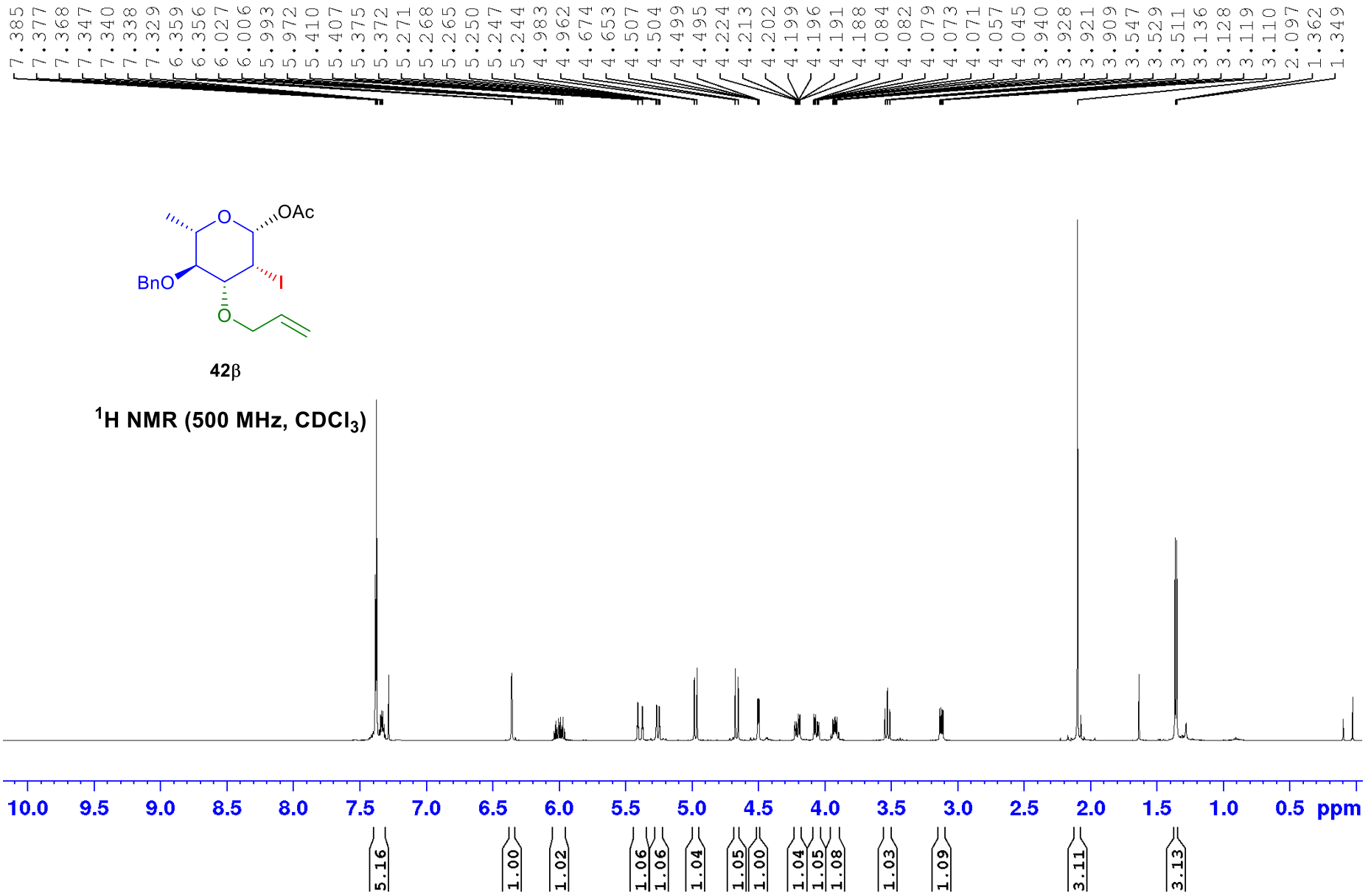
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

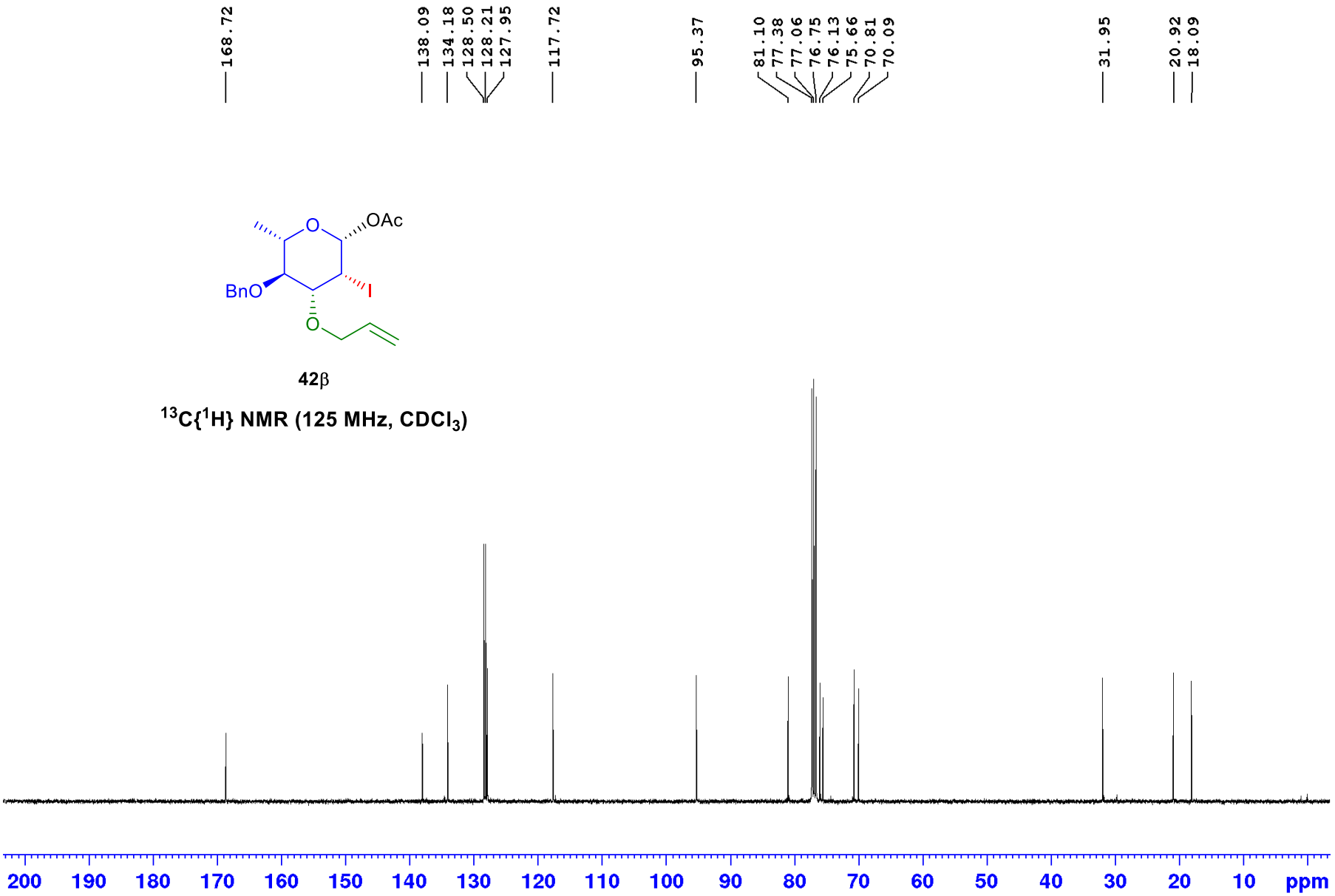


42α

^{1}H NMR (500 MHz, $CDCl_3$)

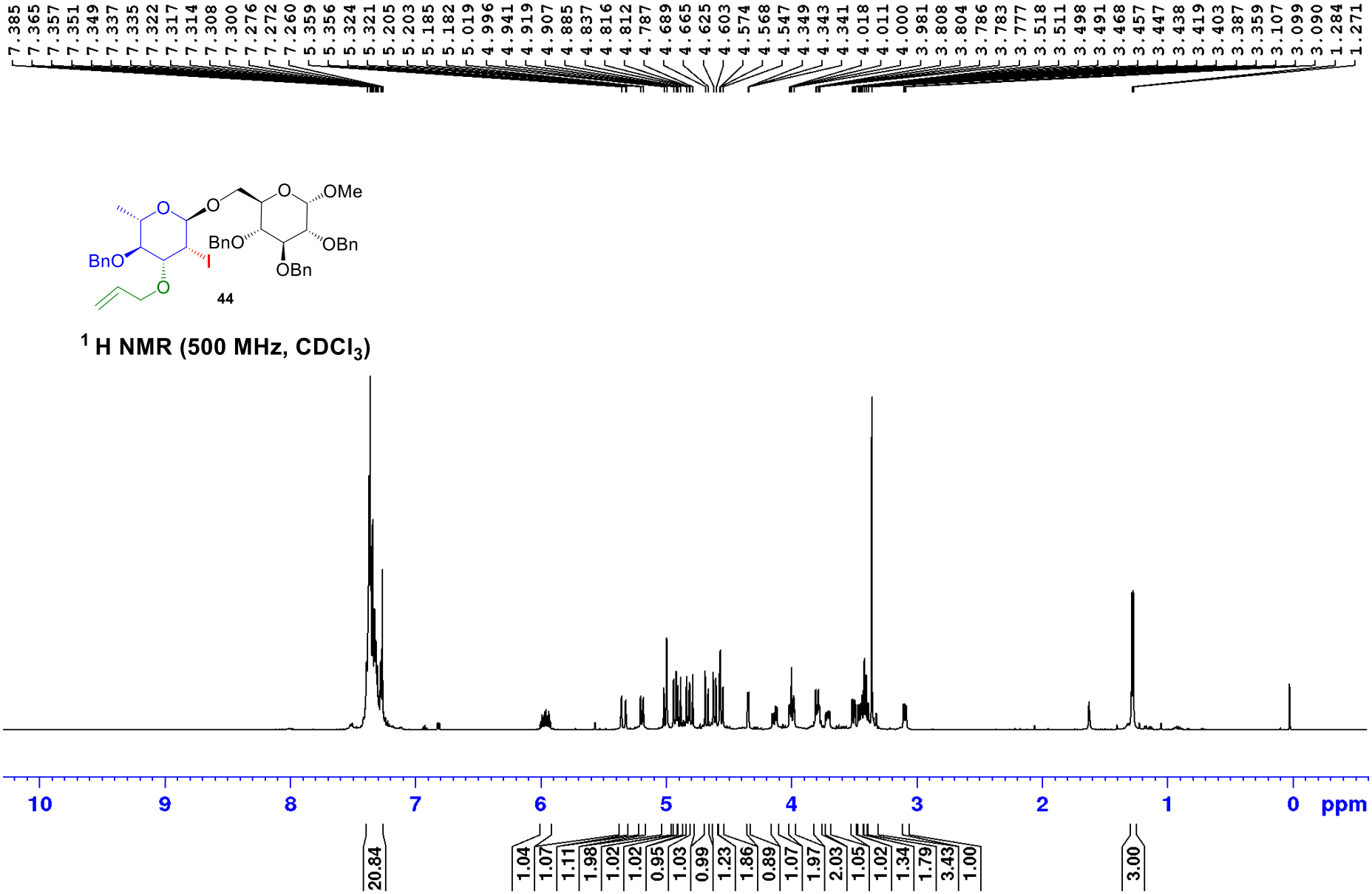

168.94
137.58
134.29
128.56
128.06
117.52
94.06
85.15
84.49
77.34
77.09
76.84
75.40
74.61
72.50
30.71
20.86
17.59
OAc
O
BnO
I
O
42α
$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

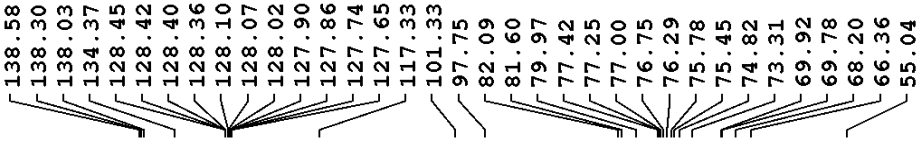

7.385
7.377
7.368
7.347
7.340
7.338
7.329
6.359
6.356
6.027
6.006
5.993
5.972
5.410
5.407
5.375
5.372
5.271
5.268
5.265
5.250
5.247
5.244
4.983
4.962
4.674
4.653
4.507
4.504
4.499
4.495
4.224
4.213
4.202
4.199
4.196
4.191
4.188
4.084
4.082
4.079
4.073
4.071
4.057
4.045
3.940
3.928
3.921
3.909
3.547
3.529
3.511
3.136
3.128
3.119
3.110
2.097
1.362
1.349
OAc
BnO
O
I
42β
1H NMR (500 MHz, CDCl3)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
5.16
1.00
1.02
1.06
1.06
1.04
1.05
1.00
1.04
1.05
1.08
1.03
1.09
3.11
3.13

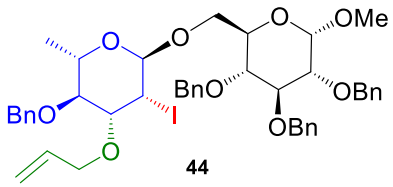


42β

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

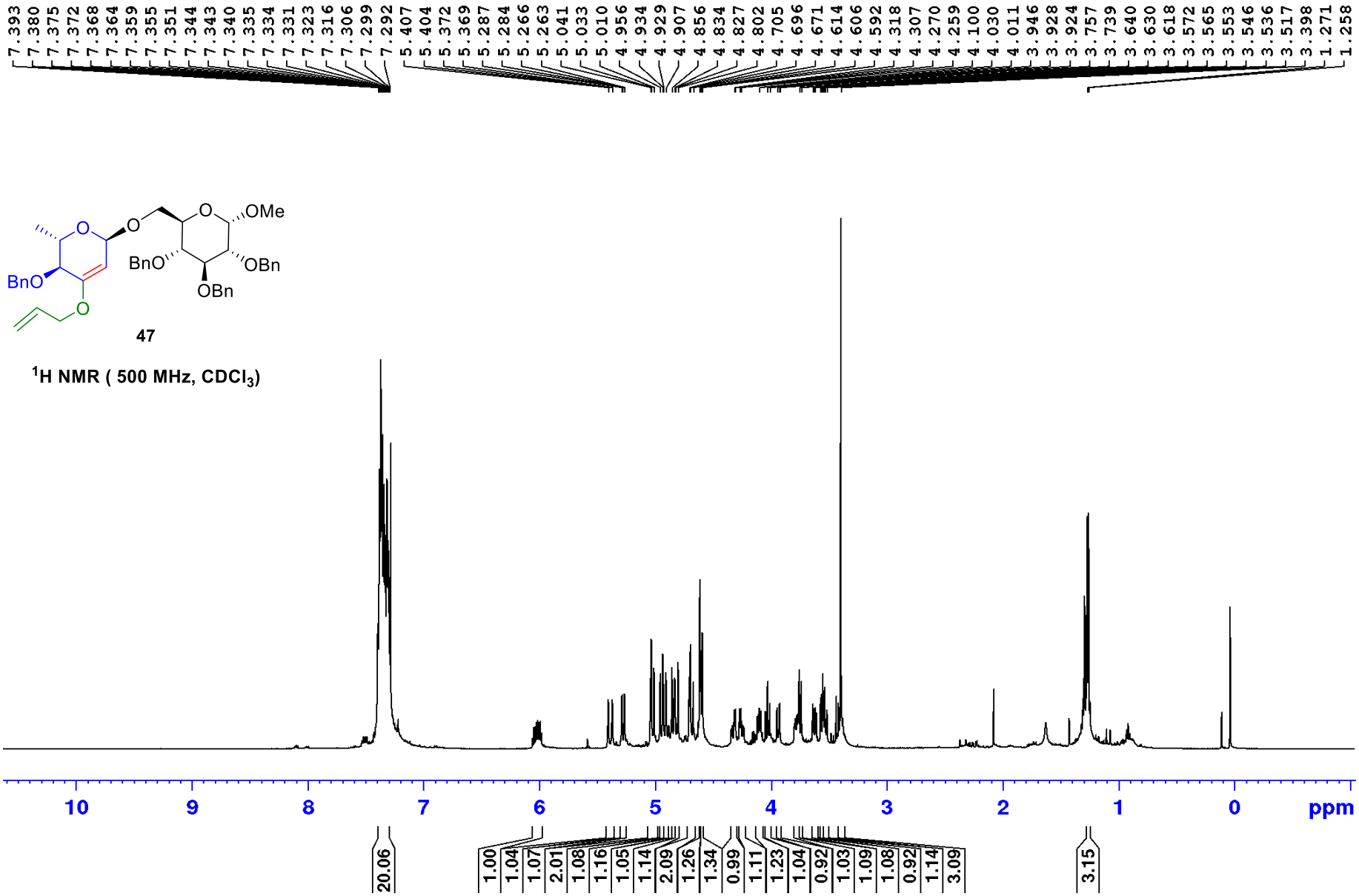

7.385
7.365
7.357
7.351
7.349
7.337
7.335
7.322
7.317
7.314
7.308
7.300
7.276
7.272
7.260
5.359
5.356
5.324
5.321
5.205
5.203
5.185
5.182
5.019
4.996
4.941
4.919
4.907
4.885
4.837
4.816
4.812
4.787
4.689
4.665
4.625
4.603
4.574
4.568
4.547
4.349
4.343
4.341
4.018
4.011
4.000
3.981
3.808
3.804
3.786
3.783
3.777
3.518
3.511
3.498
3.491
3.468
3.457
3.447
3.438
3.419
3.403
3.387
3.359
3.107
3.099
3.090
1.284
1.271
OMe
OBn
OBn
BnO
BnO
O
O
O
O
O
I
44
1 H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
20.84
1.04
1.07
1.11
1.98
1.02
1.02
0.95
1.03
0.99
1.23
1.86
0.89
1.07
1.97
2.03
1.05
1.02
1.34
1.79
3.43
1.00
3.00

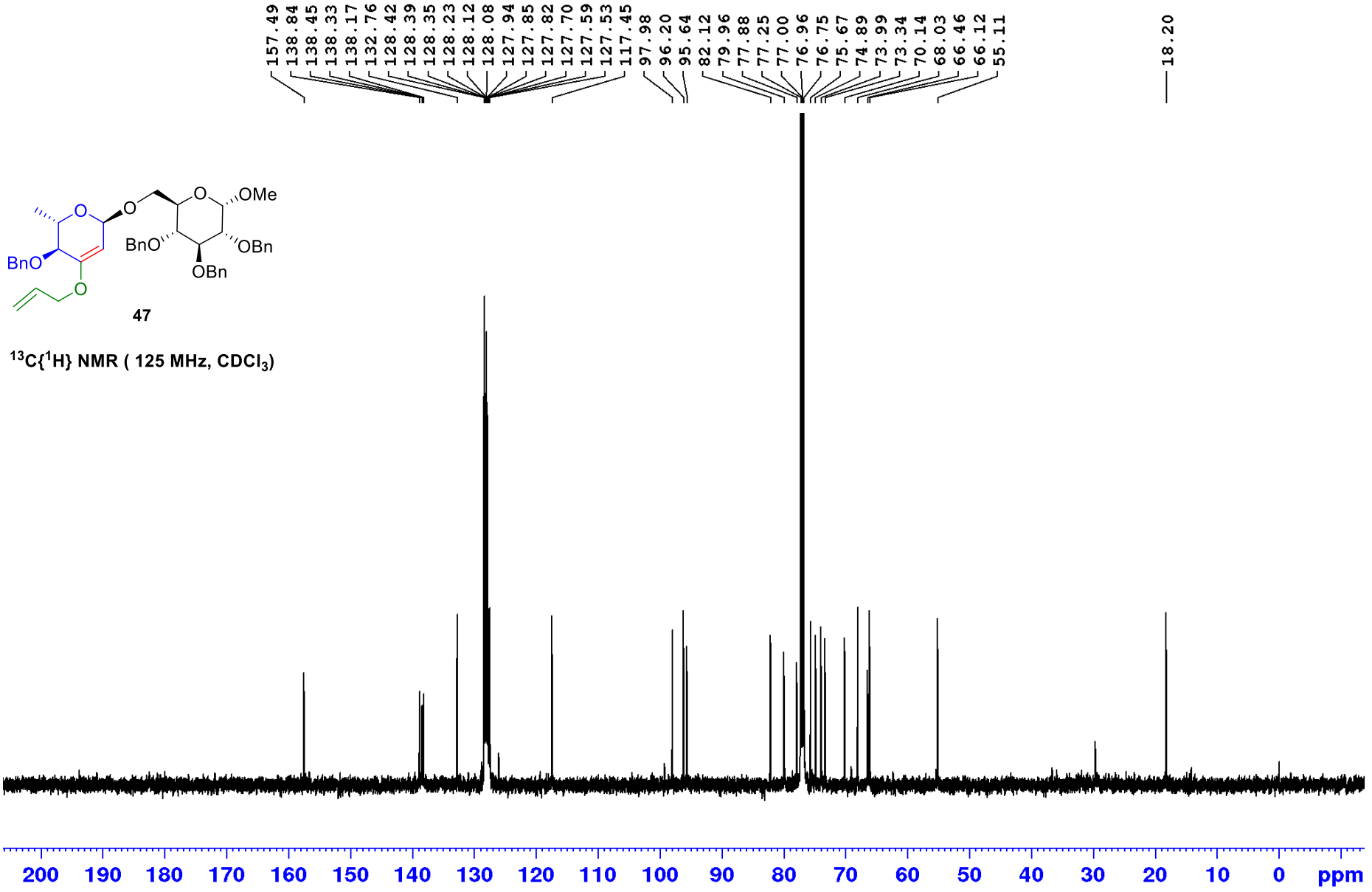




44

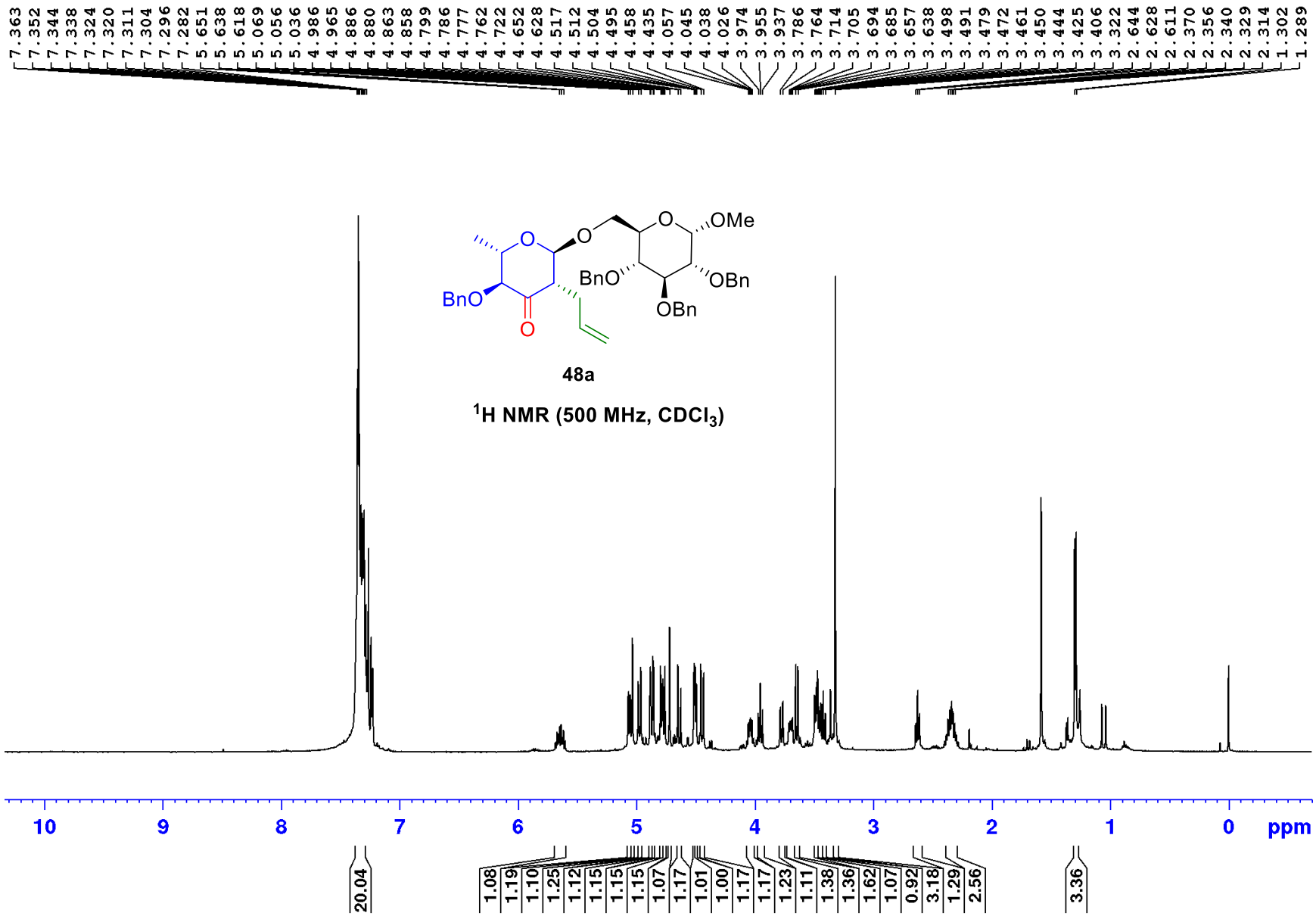
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

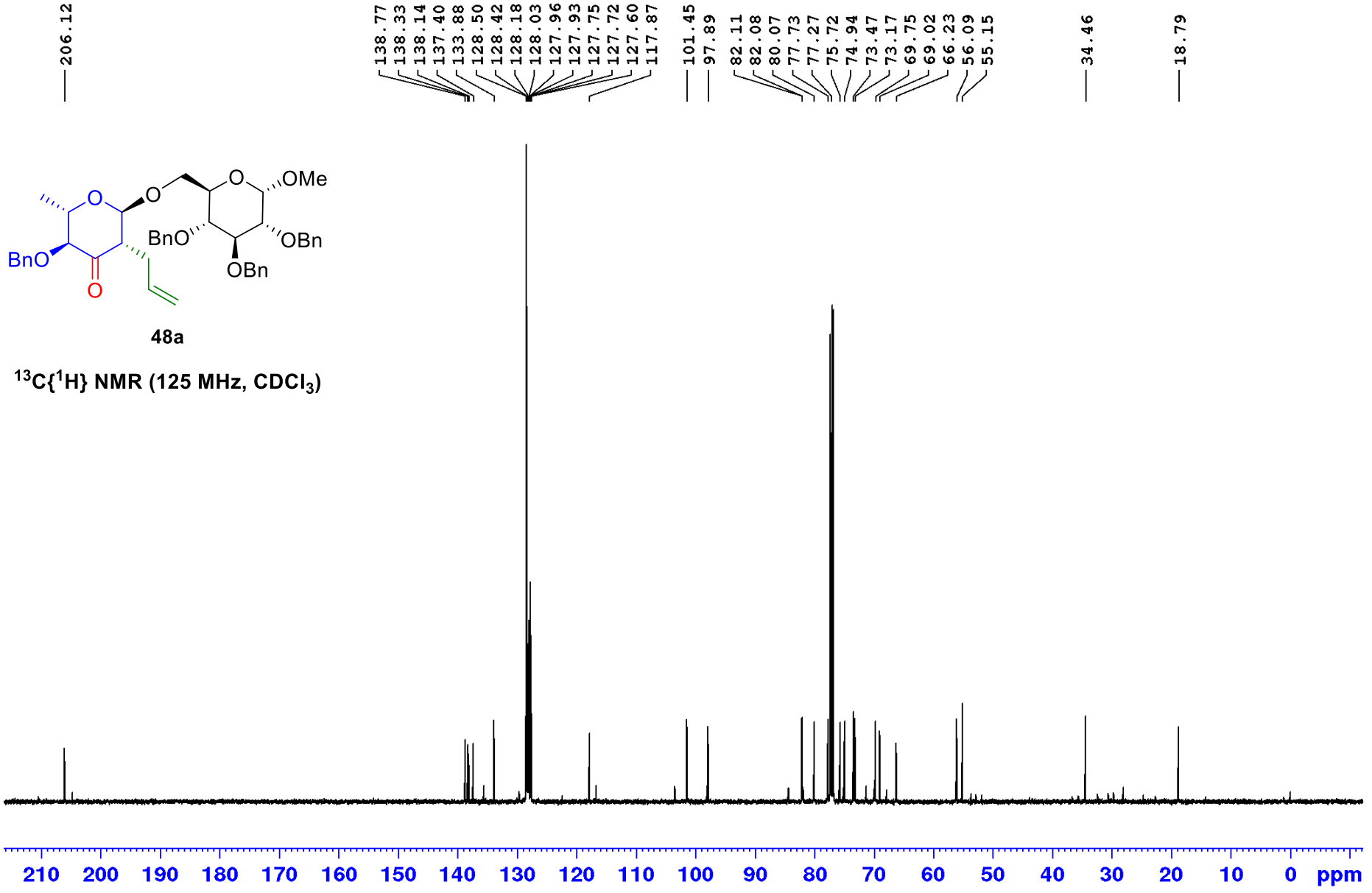

7.393 7.380 7.375 7.372 7.368 7.364 7.359 7.355 7.351 7.344 7.343 7.340 7.335 7.334 7.331 7.323 7.316 7.306 7.299 7.292
5.407 5.404 5.372 5.369 5.287 5.284 5.266 5.263 5.041 5.033 5.010 4.956 4.934 4.929 4.907 4.856 4.834 4.827 4.802 4.705 4.696 4.671 4.614 4.606 4.592 4.318 4.307 4.270 4.259 4.100 4.030 4.011 3.946 3.928 3.924 3.757 3.739 3.640 3.630 3.618 3.572 3.565 3.553 3.546 3.536 3.517 3.398 1.271 1.258
O
O
O
OMe
BnO
OBn
BnO
OBn
O
47
1H NMR (500 MHz, CDCl3)
10 9 8 7 6 5 4 3 2 1 0 ppm
20.06
1.00 1.04 1.07 2.01 1.08 1.16 1.05 1.14 2.09 1.26 1.34 0.99 1.11 1.23 1.04 0.92 1.03 1.09 1.08 0.92 1.14 3.09
3.15



47

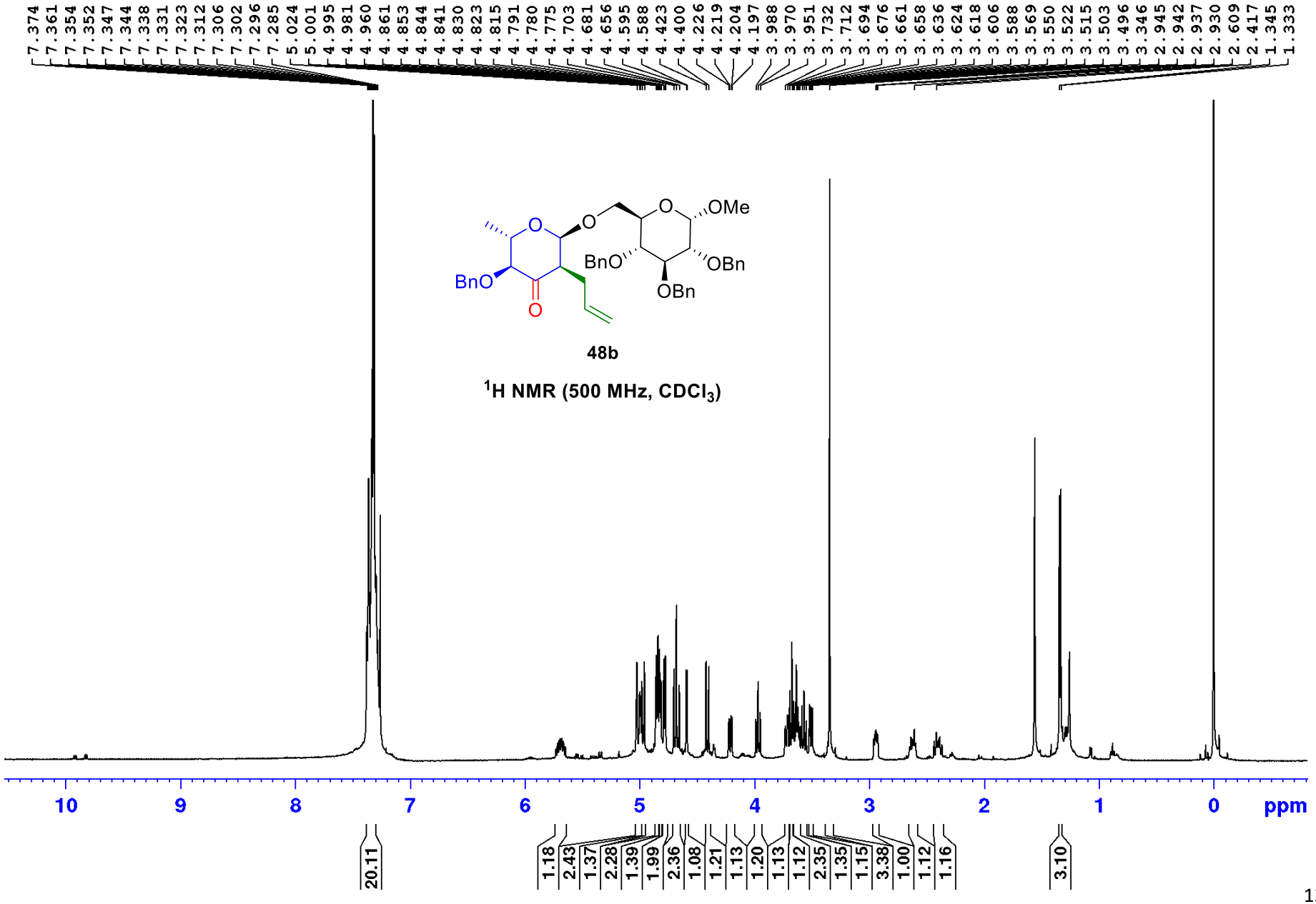
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

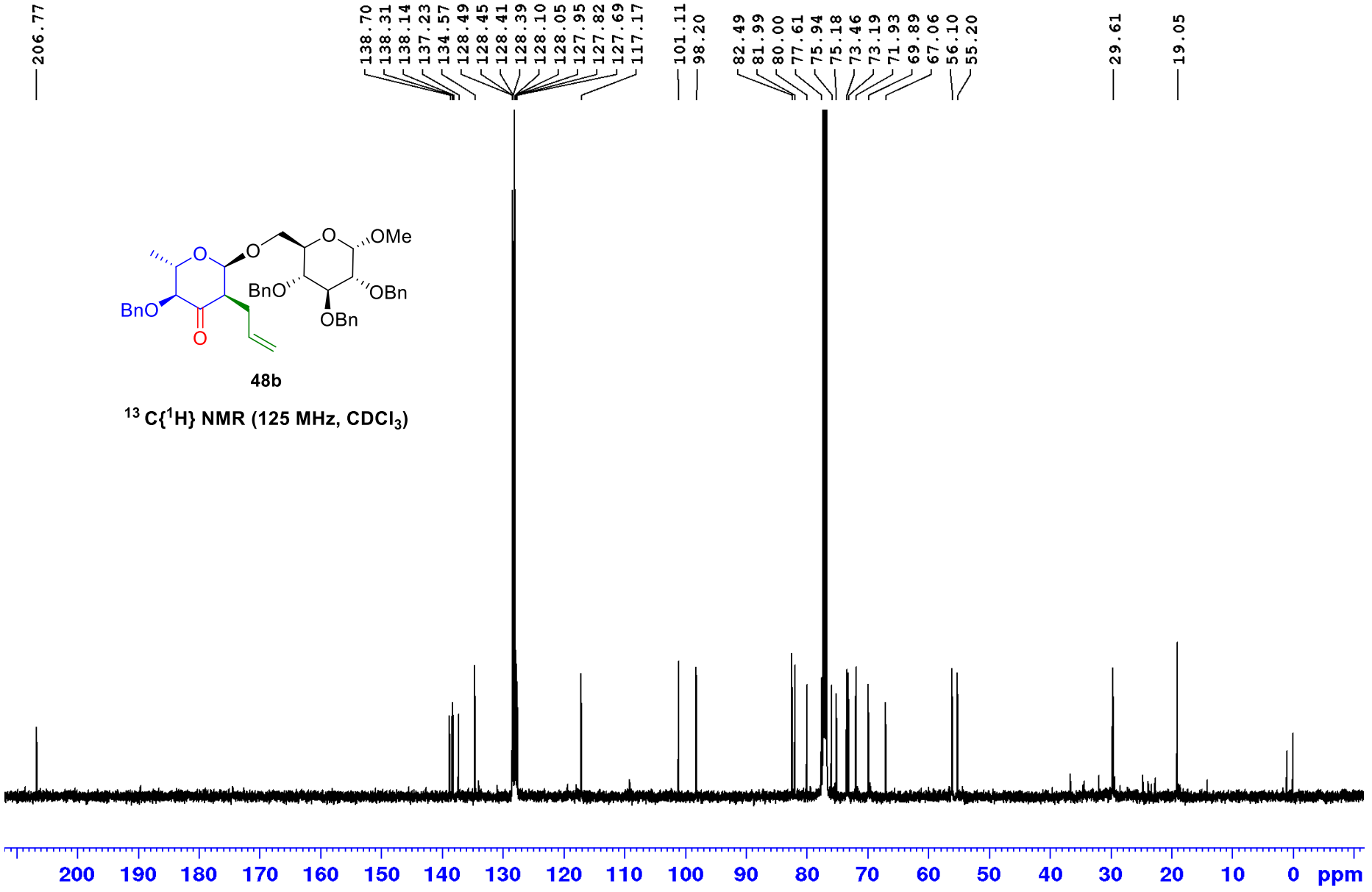

7.363
7.352
7.344
7.338
7.324
7.320
7.311
7.304
7.296
7.282
5.651
5.638
5.618
5.069
5.056
5.036
4.986
4.965
4.886
4.880
4.863
4.858
4.799
4.786
4.777
4.762
4.722
4.652
4.628
4.517
4.512
4.504
4.495
4.458
4.435
4.057
4.045
4.038
4.026
3.974
3.955
3.937
3.786
3.764
3.714
3.705
3.694
3.685
3.657
3.638
3.498
3.491
3.479
3.472
3.461
3.450
3.444
3.425
3.406
3.322
2.644
2.628
2.611
2.370
2.356
2.340
2.329
2.314
1.302
1.289
OMe
OBn
OBn
BnO
BnO
O
O
O
O
48a
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
20.04
1.08
1.19
1.10
1.25
1.12
1.15
1.15
1.15
1.07
1.17
1.01
1.00
1.17
1.17
1.23
1.11
1.38
1.36
1.62
1.07
0.92
3.18
1.29
2.56
3.36



48a

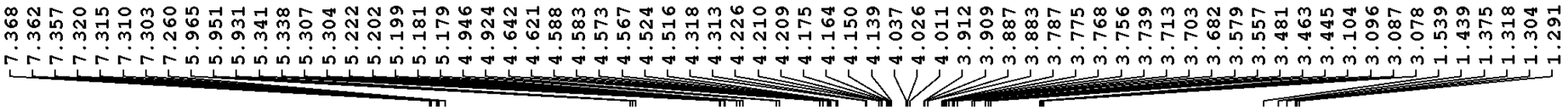
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

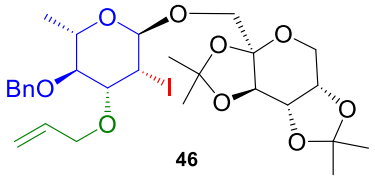

7.374
7.361
7.354
7.352
7.347
7.344
7.338
7.331
7.323
7.312
7.306
7.302
7.296
7.285
5.024
5.001
4.995
4.981
4.960
4.861
4.853
4.844
4.841
4.830
4.823
4.815
4.791
4.780
4.775
4.703
4.681
4.656
4.595
4.588
4.423
4.400
4.226
4.219
4.204
4.197
3.988
3.970
3.951
3.732
3.712
3.694
3.676
3.661
3.658
3.636
3.624
3.618
3.606
3.588
3.569
3.550
3.522
3.515
3.503
3.496
3.346
2.945
2.942
2.937
2.930
2.609
2.417
1.345
1.333
OMe
OBn
OBn
BnO
BnO
O
O
O
O
48b
1H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
20.11
1.18
2.43
1.37
2.28
1.39
1.99
2.36
1.08
1.21
1.13
1.20
1.13
1.12
2.35
1.35
1.15
3.38
1.00
1.12
1.16
3.10



48b

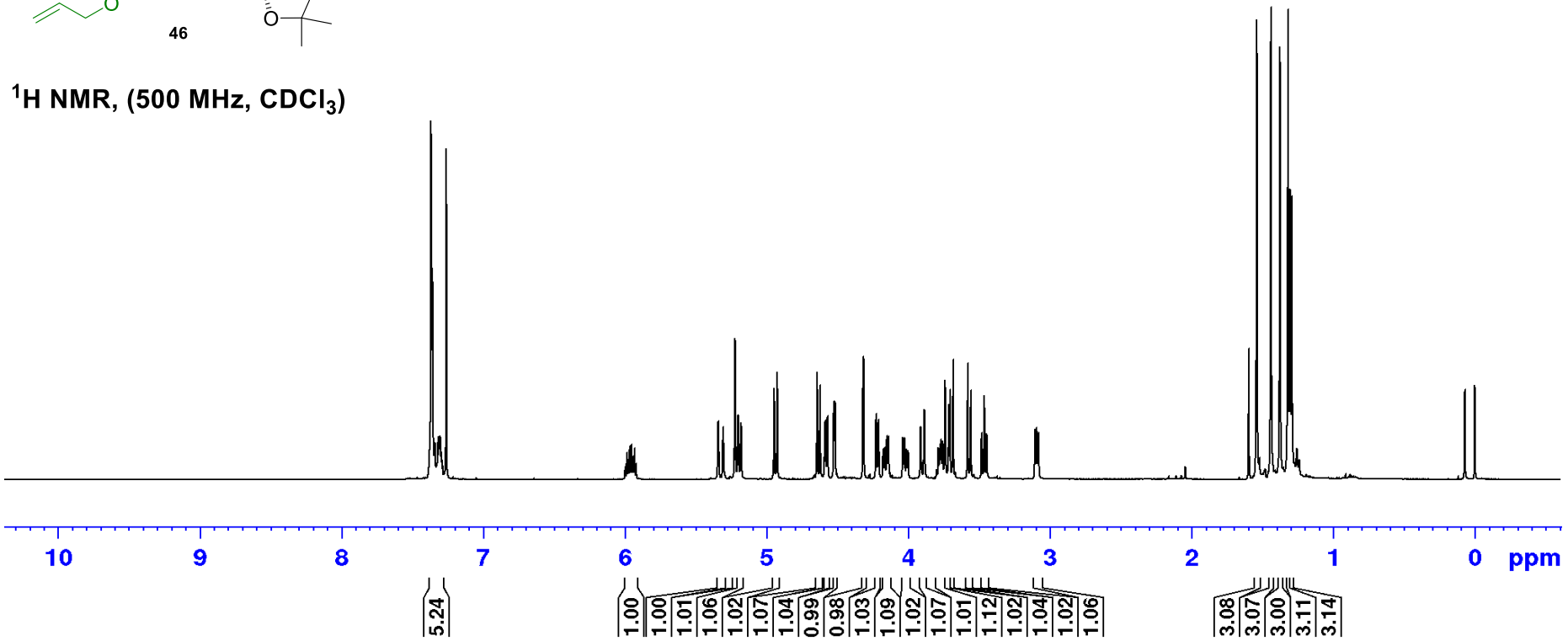
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

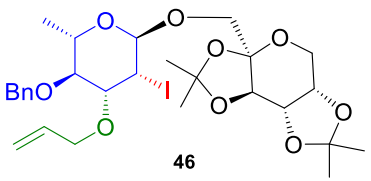




46

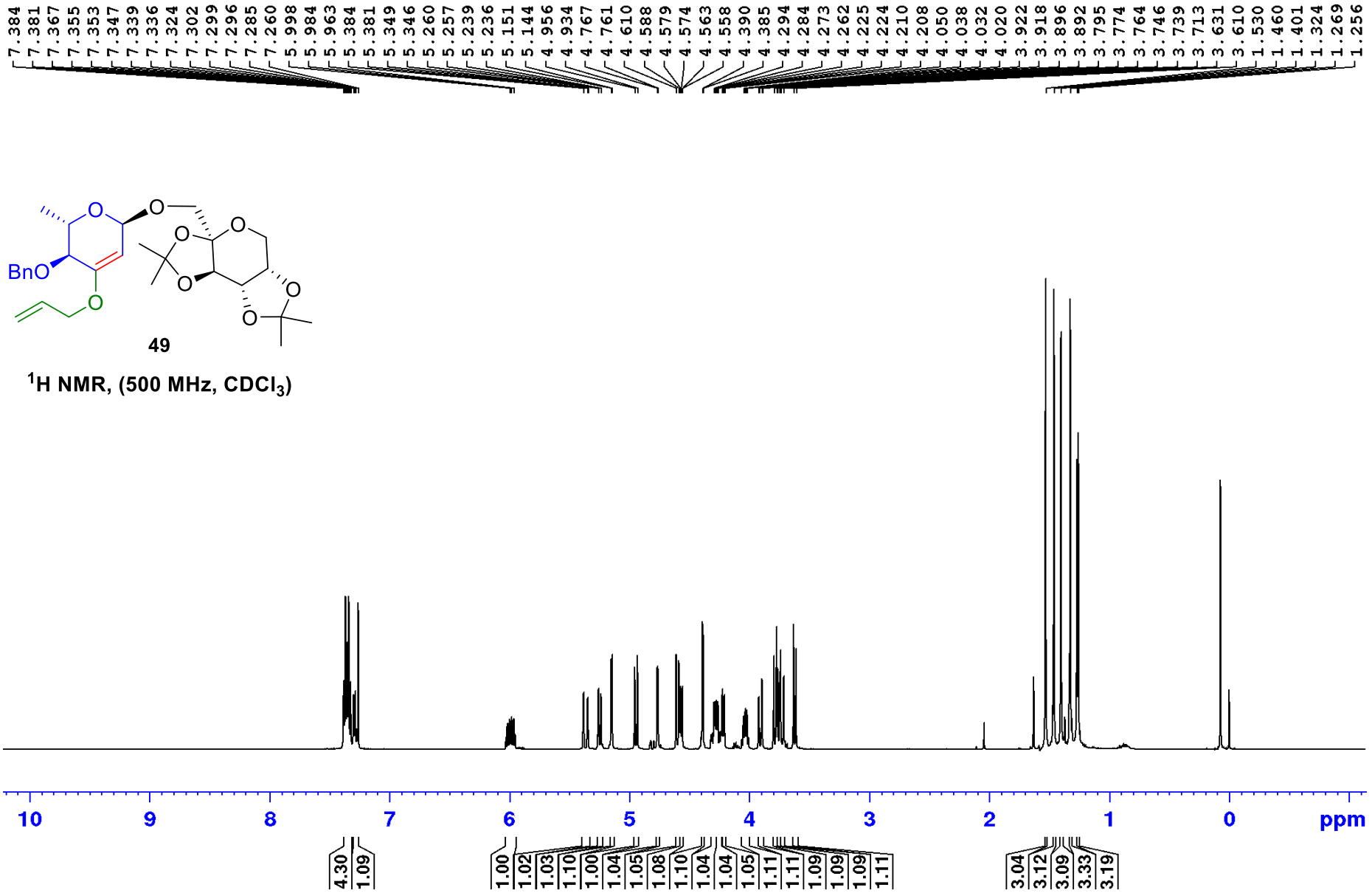
^{1}H NMR, (500 MHz, $CDCl_3$)

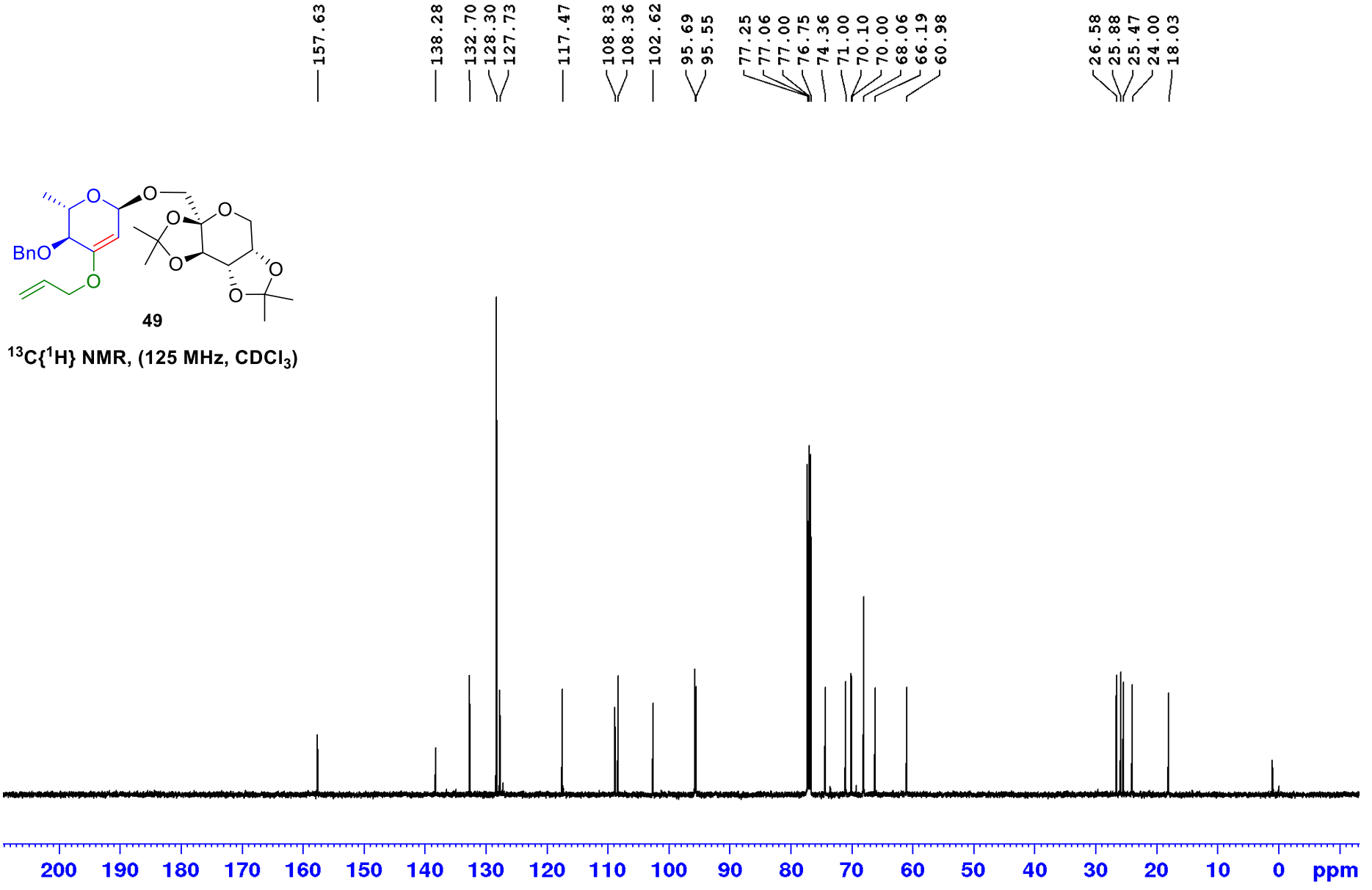




46

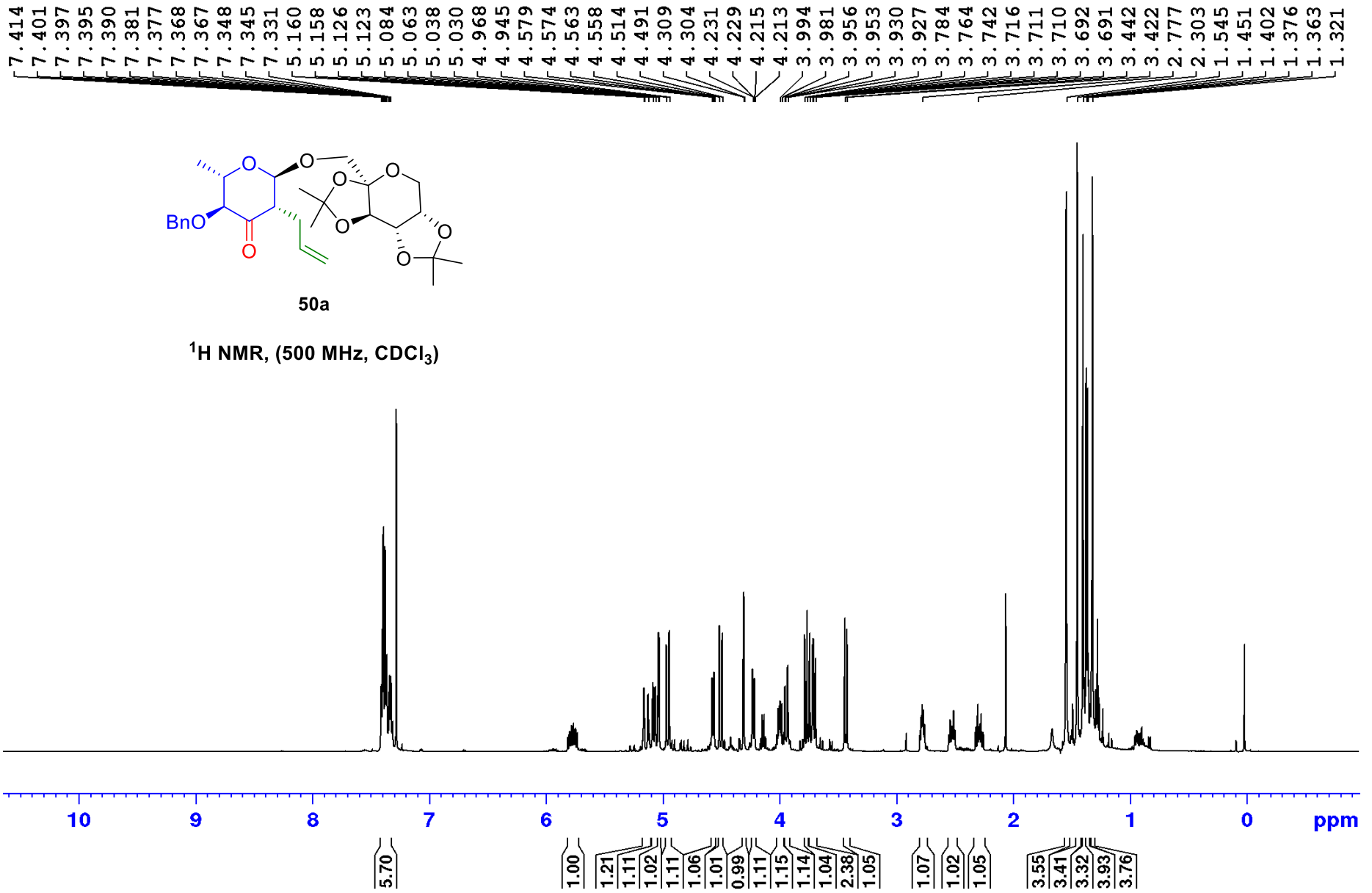
$^{13}C\{^{1}H\}$ NMR, (125 MHz, $CDCl_3$)


7.384
7.381
7.367
7.355
7.353
7.347
7.339
7.336
7.324
7.302
7.299
7.296
7.285
7.260
5.998
5.984
5.963
5.384
5.381
5.349
5.346
5.260
5.257
5.239
5.236
5.151
5.144
4.956
4.934
4.767
4.761
4.610
4.588
4.579
4.574
4.563
4.558
4.390
4.385
4.294
4.284
4.273
4.262
4.225
4.224
4.210
4.208
4.050
4.038
4.032
4.020
3.922
3.918
3.896
3.892
3.795
3.774
3.764
3.746
3.739
3.713
3.631
3.610
1.530
1.460
1.401
1.324
1.269
1.256
BnO
O
O
O
O
O
O
O
O
49
1H NMR, (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
4.30
1.09
1.00
1.02
1.03
1.10
1.00
1.04
1.05
1.08
1.10
1.04
1.04
1.05
1.11
1.11
1.09
1.09
1.09
1.11
3.04
3.12
3.09
3.33
3.19



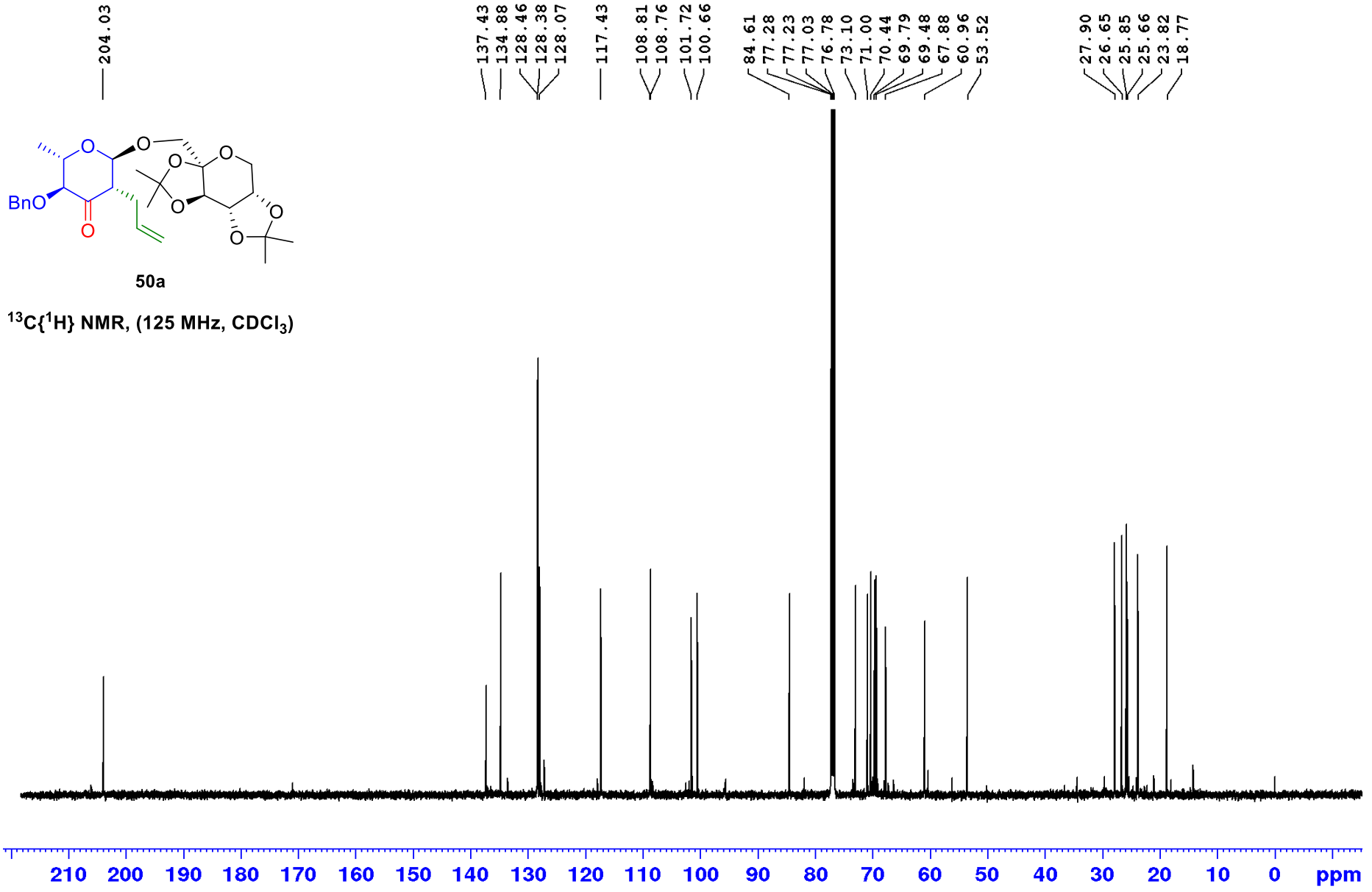
49

$^{13}C\{^{1}H\}$ NMR, (125 MHz, $CDCl_3$)



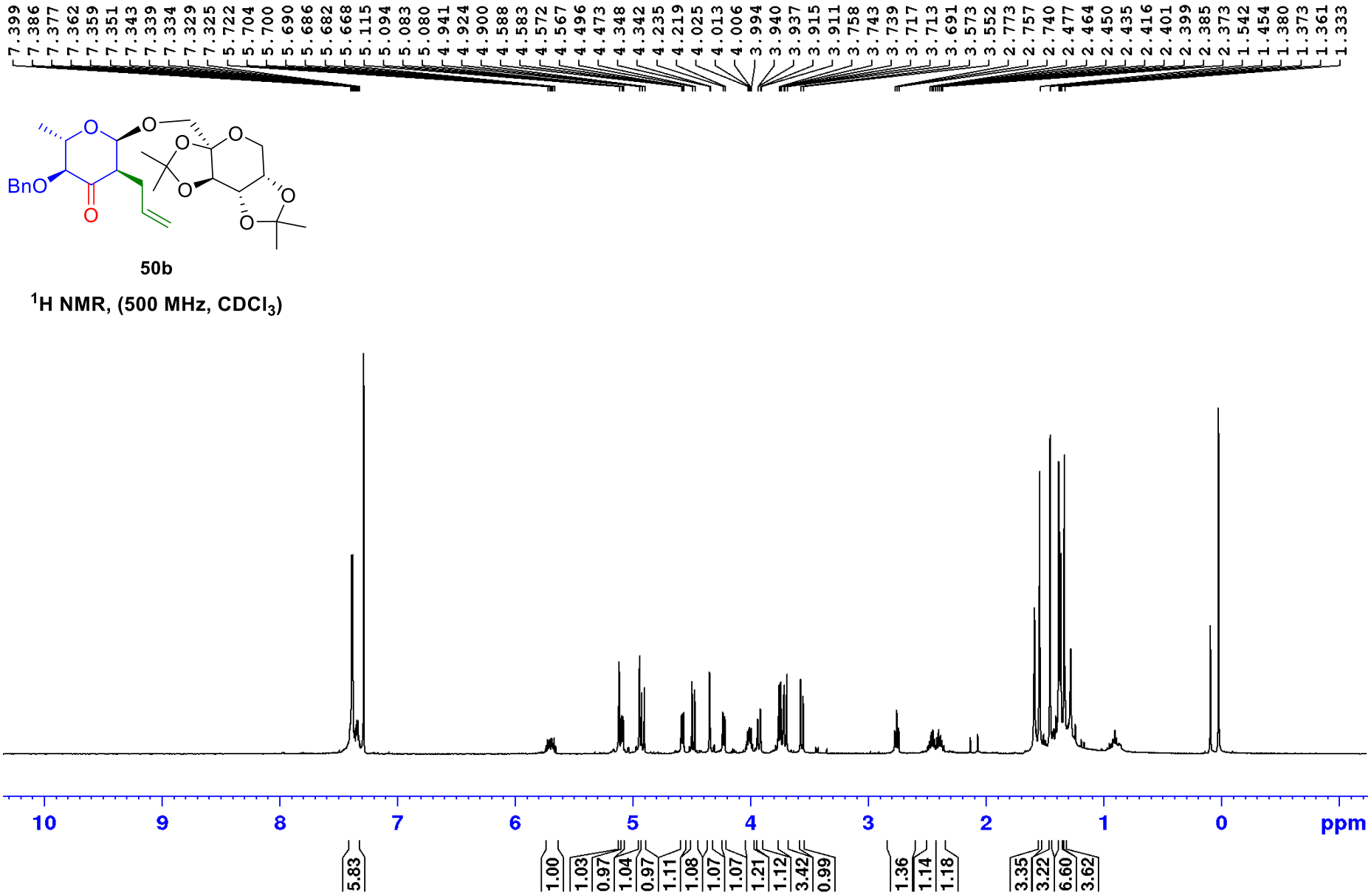
50a

^{1}H NMR, (500 MHz, $CDCl_3$)



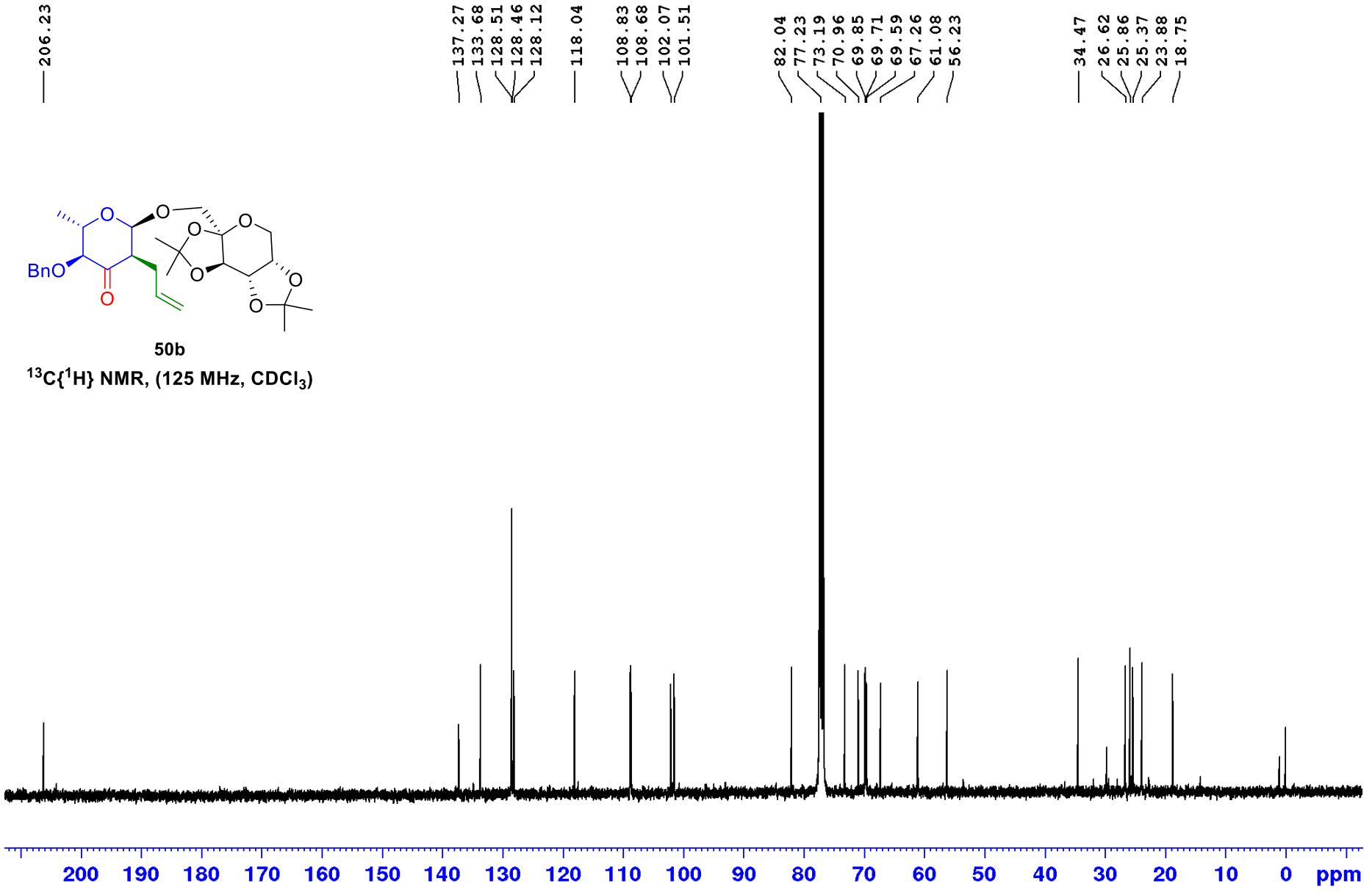
50a

$^{13}C\{^{1}H\}$ NMR, (125 MHz, $CDCl_3$)



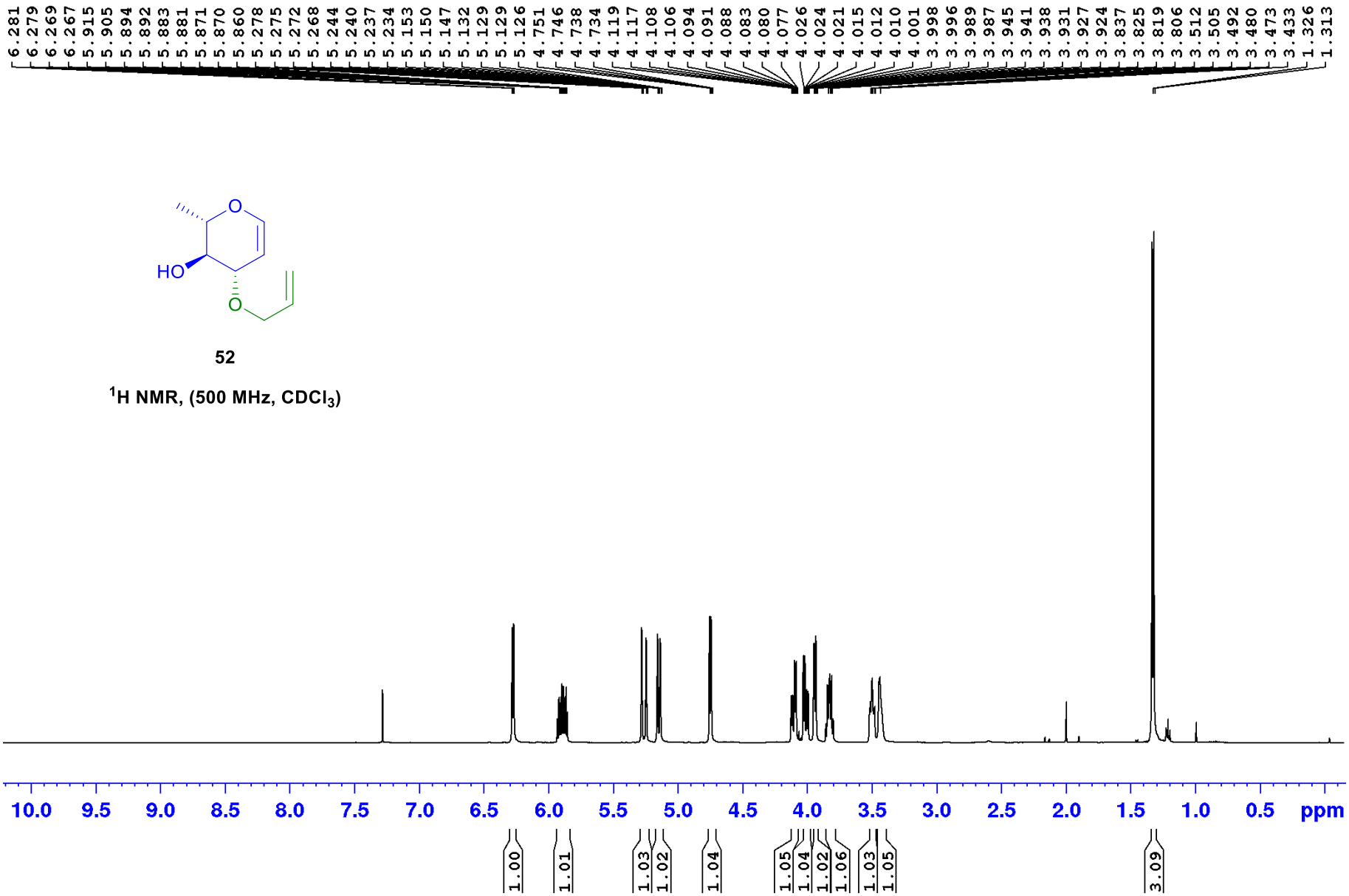
50b

^{1}H NMR, (500 MHz, $CDCl_3$)



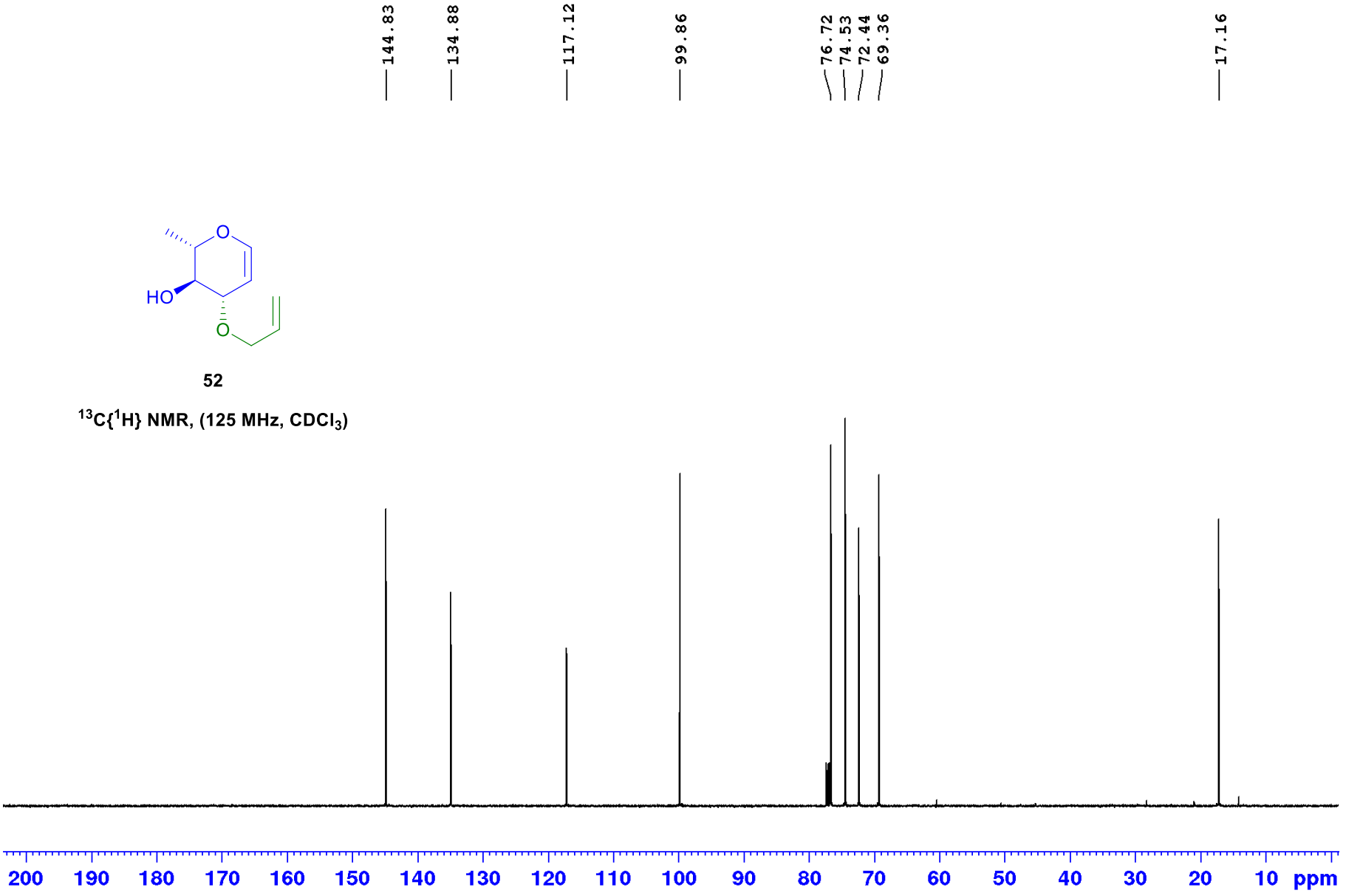
50b

$^{13}C\{^{1}H\}$ NMR, (125 MHz, $CDCl_3$)



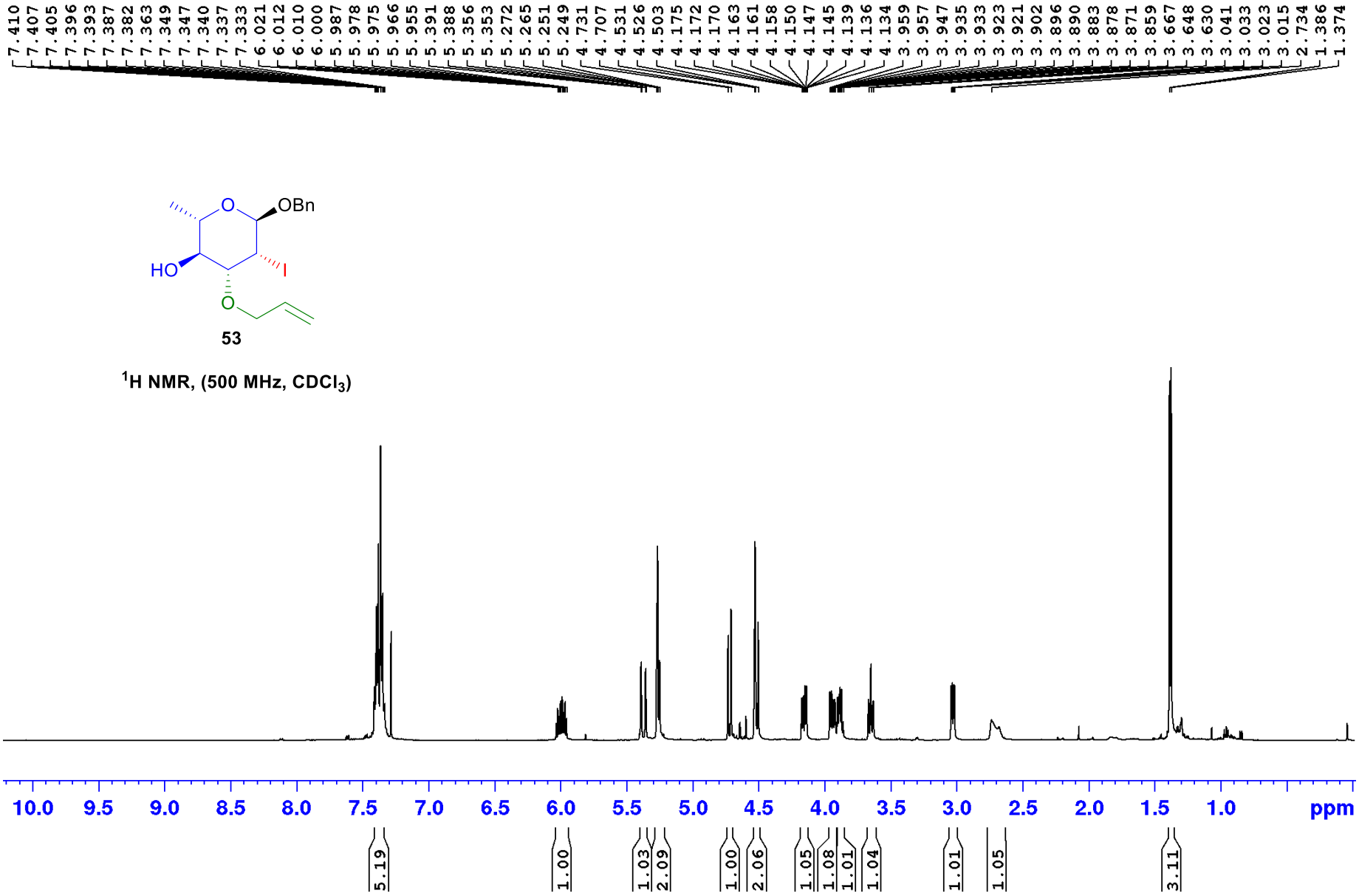
52

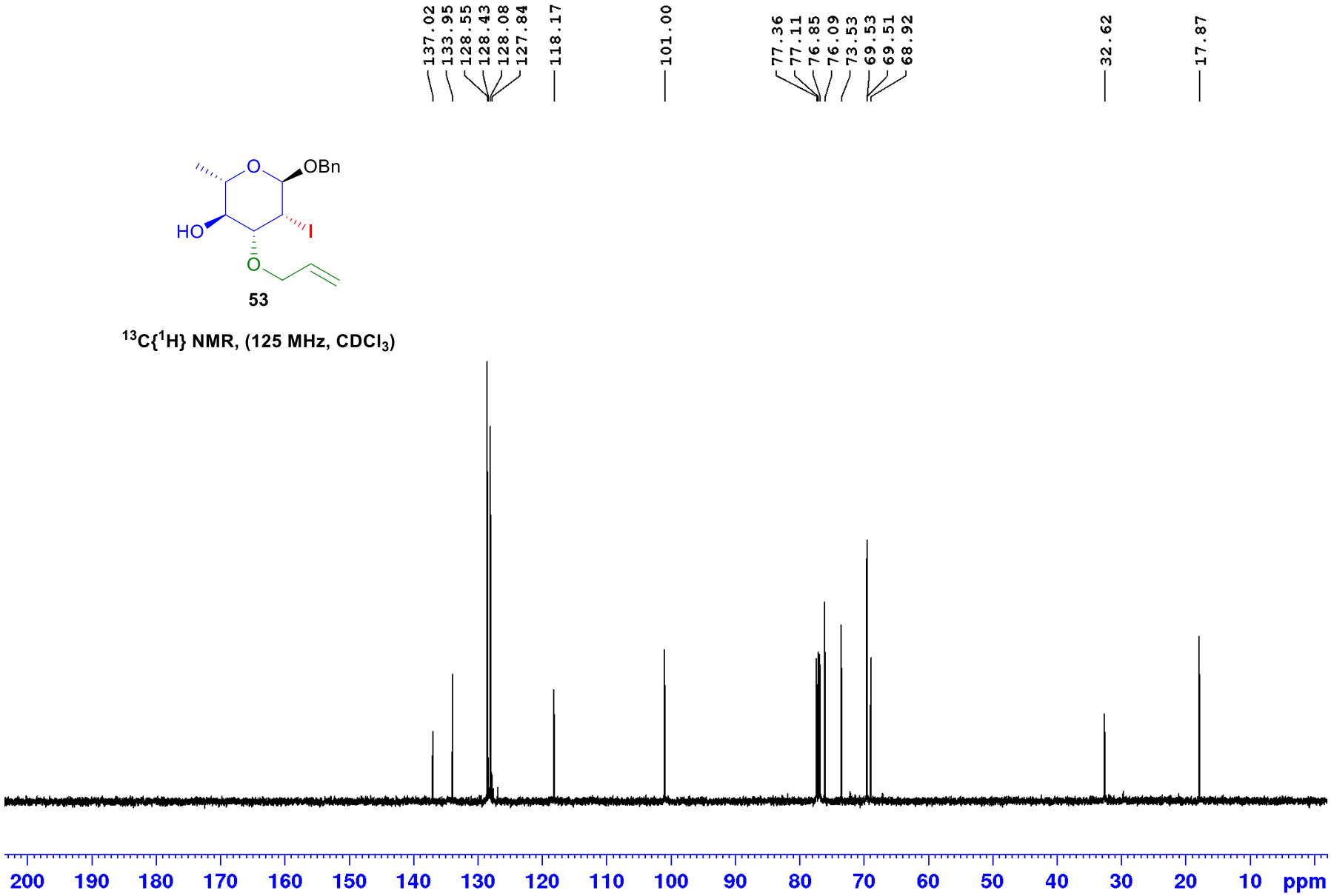
^{1}H NMR, (500 MHz, $CDCl_3$)



52

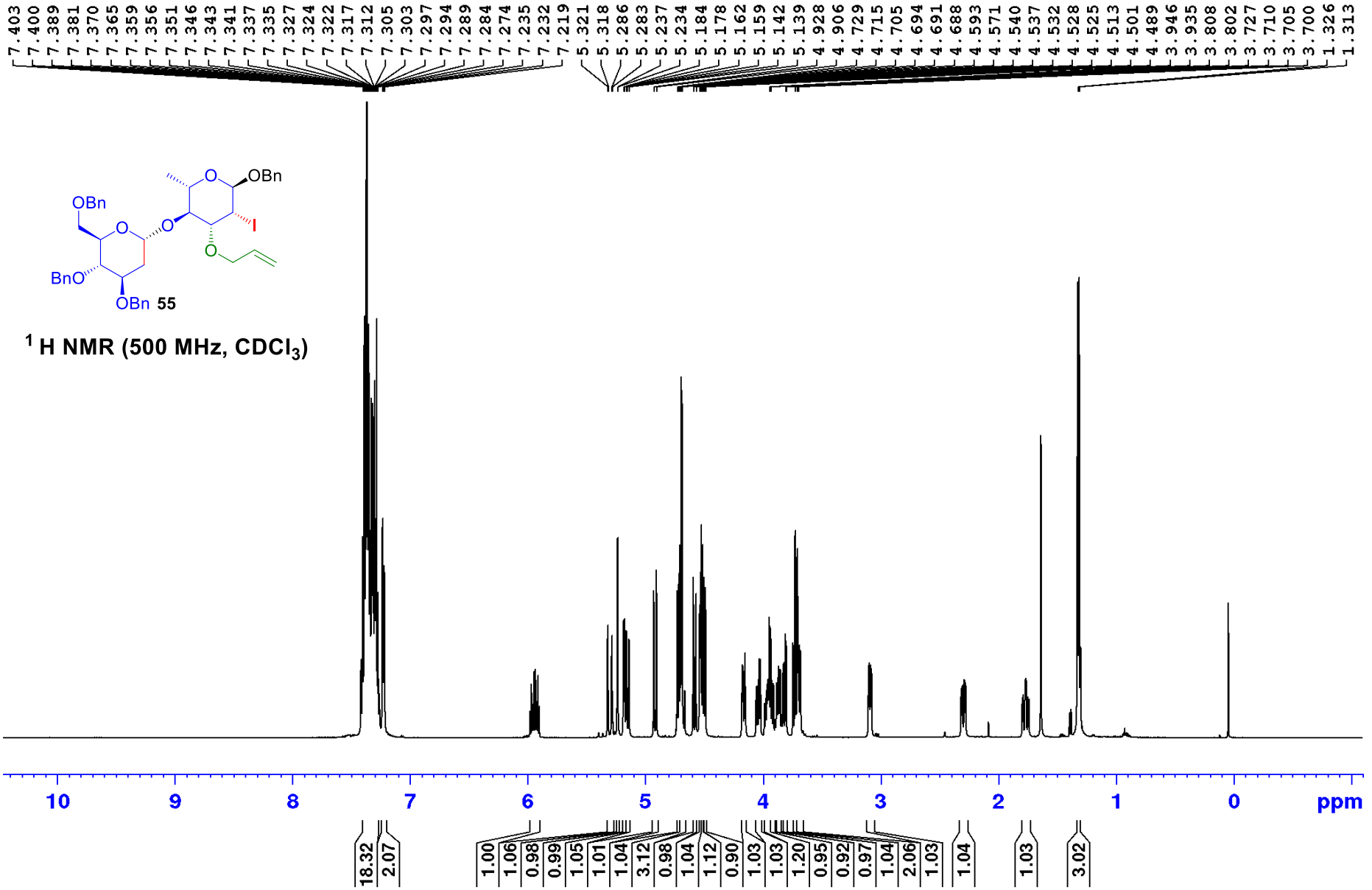
$^{13}C\{^{1}H\}$ NMR, (125 MHz, $CDCl_3$)

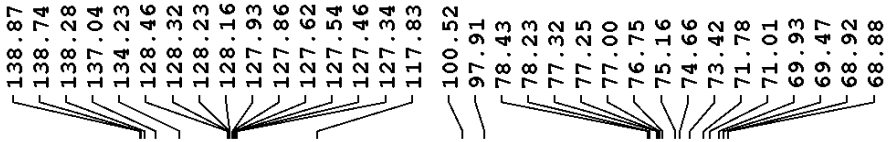

7.410
7.407
7.405
7.396
7.393
7.387
7.382
7.363
7.349
7.347
7.340
7.337
7.333
6.021
6.012
6.010
6.000
5.987
5.978
5.975
5.966
5.955
5.391
5.388
5.356
5.353
5.272
5.265
5.251
5.249
4.731
4.707
4.531
4.526
4.503
4.175
4.172
4.170
4.163
4.161
4.158
4.150
4.147
4.145
4.139
4.136
4.134
3.959
3.957
3.947
3.935
3.933
3.923
3.921
3.902
3.896
3.890
3.883
3.878
3.871
3.859
3.667
3.648
3.630
3.041
3.033
3.023
3.015
2.734
1.386
1.374
OBn
HO
I
O
O
53
^{1}H NMR, (500 MHz, CDCl$_3$)
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5.19
1.00
1.03
2.09
1.00
2.06
1.05
1.08
1.01
1.04
1.01
1.05
3.11

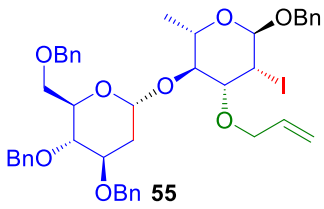


53

$^{13}C\{^{1}H\}$ NMR, (125 MHz, $CDCl_3$)

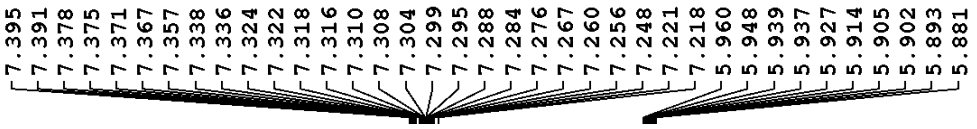

7.403
7.400
7.389
7.381
7.370
7.365
7.359
7.356
7.351
7.346
7.343
7.341
7.337
7.335
7.327
7.324
7.322
7.317
7.312
7.305
7.303
7.297
7.294
7.289
7.284
7.274
7.235
7.232
7.219
5.321
5.318
5.286
5.283
5.237
5.234
5.184
5.178
5.162
5.159
5.142
5.139
4.928
4.906
4.729
4.715
4.705
4.694
4.691
4.688
4.593
4.571
4.540
4.537
4.532
4.528
4.525
4.513
4.501
4.489
3.946
3.935
3.808
3.802
3.727
3.710
3.705
3.700
1.326
1.313
OBn
OBn
O
O
O
I
O
BnO
OBn
55
1 H NMR (500 MHz, CDCl3)
10
9
8
7
6
5
4
3
2
1
0
ppm
18.32
2.07
1.00
1.06
0.98
0.99
1.05
1.01
1.04
3.12
0.98
1.04
1.12
0.90
1.03
1.03
1.20
0.95
0.92
0.97
1.04
2.06
1.03
1.04
1.03
3.02

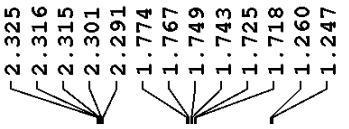


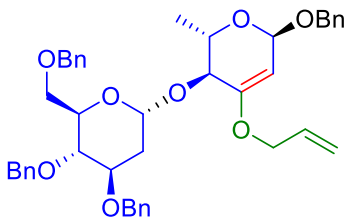


55

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

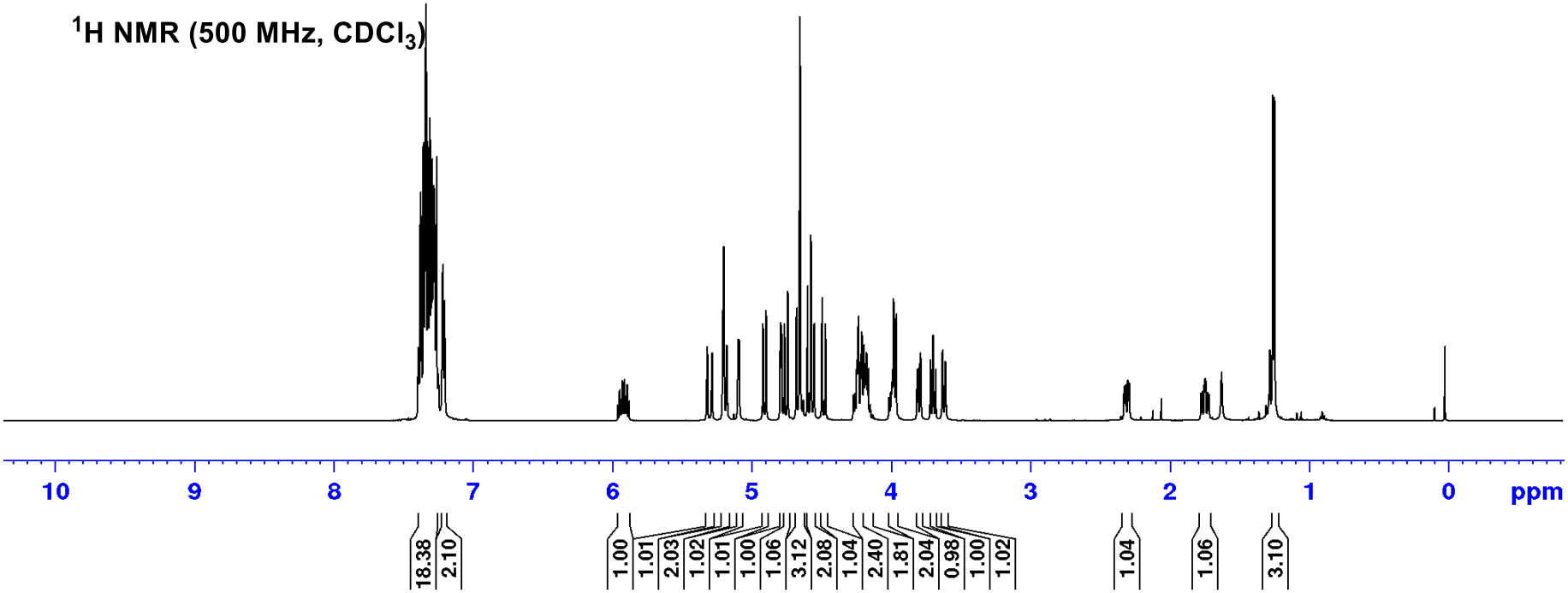


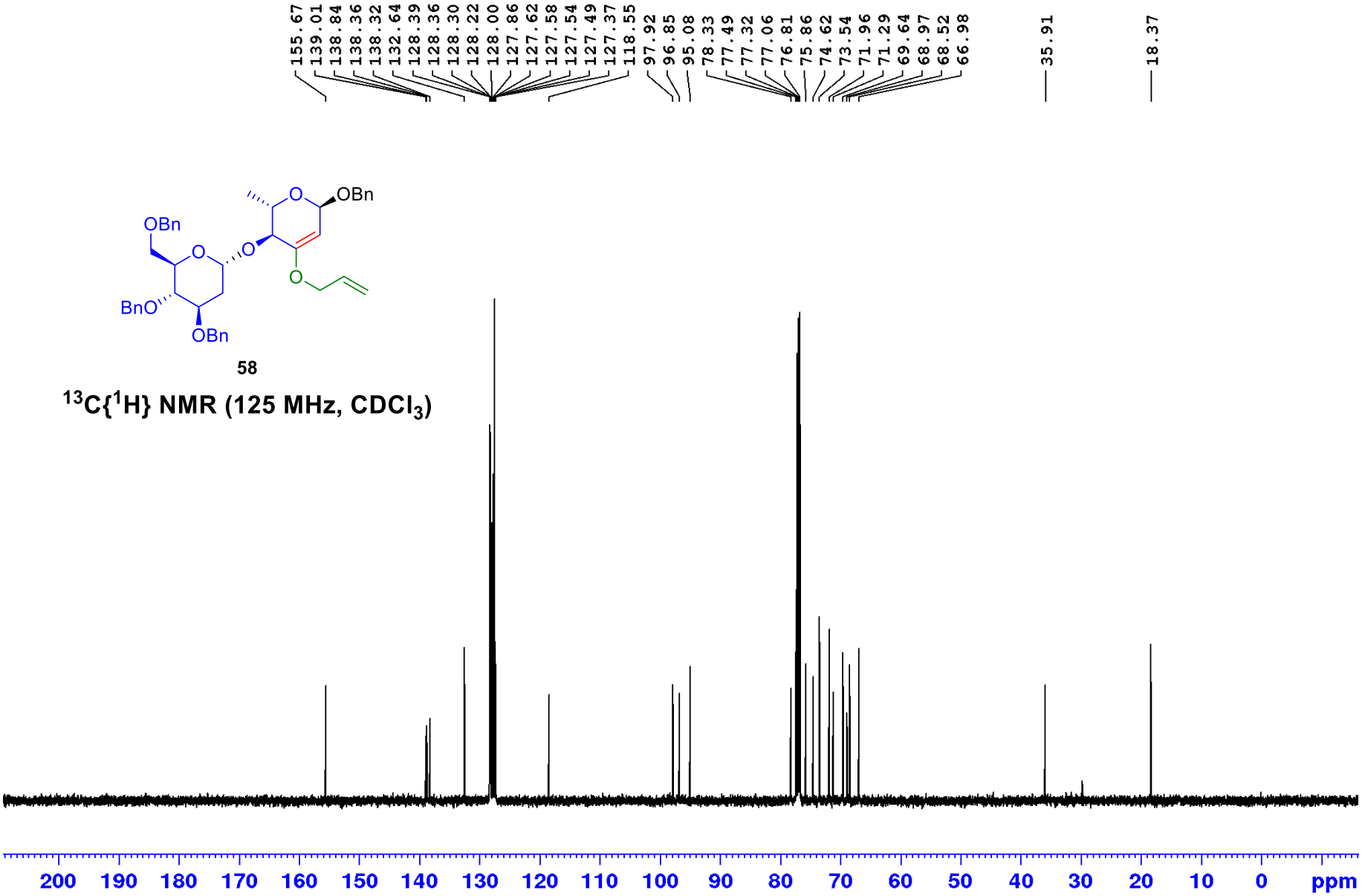


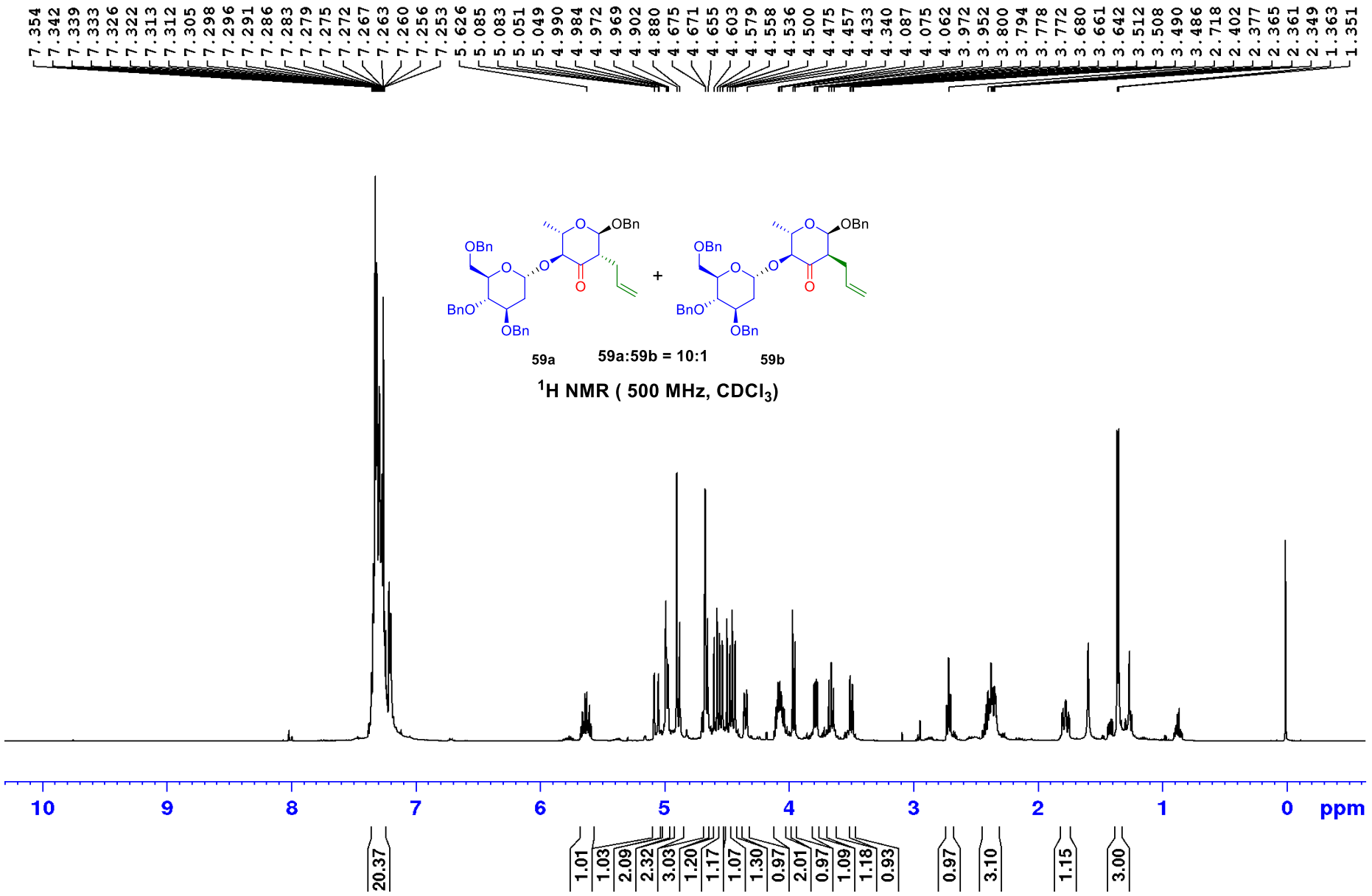


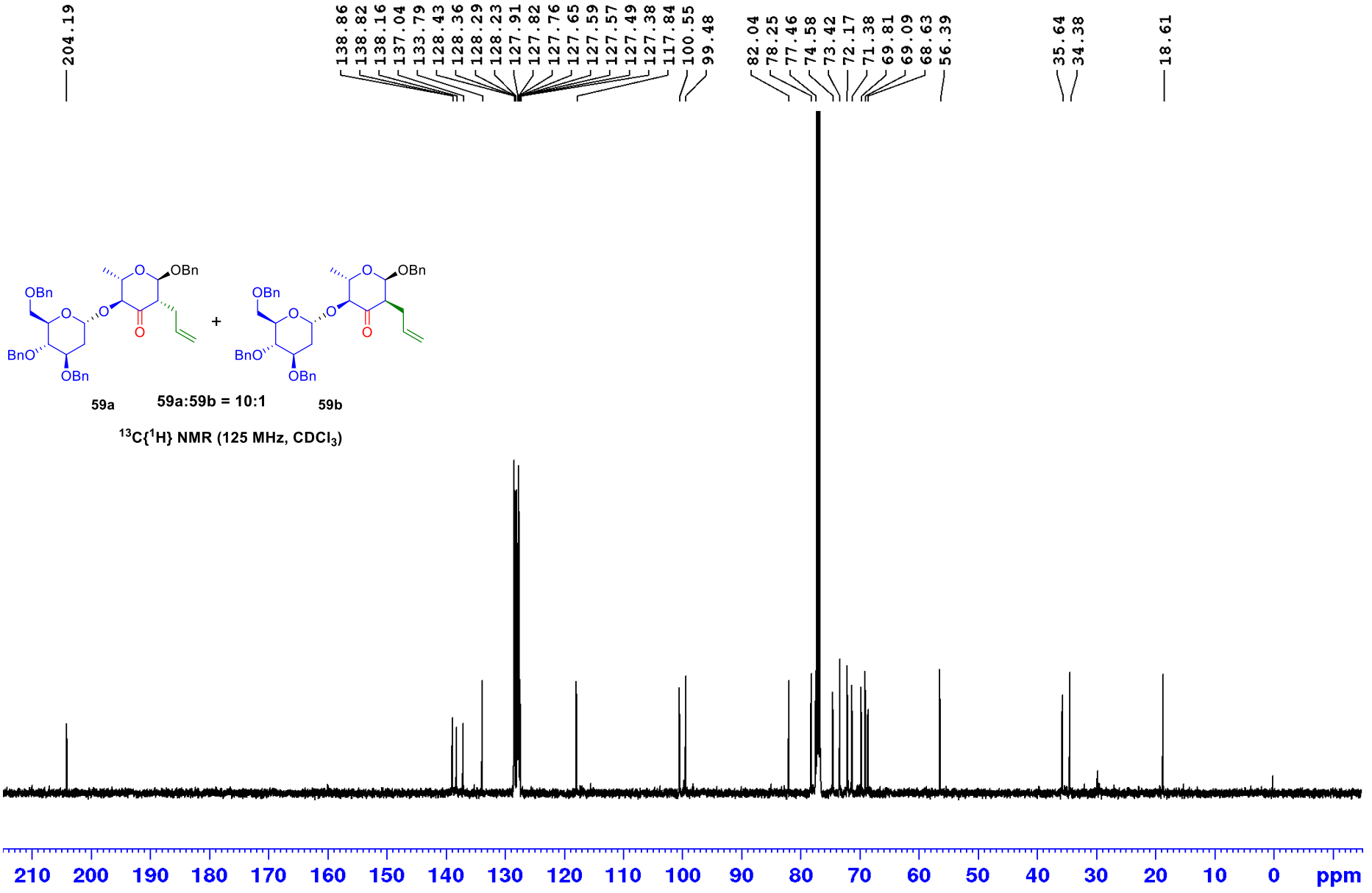
58

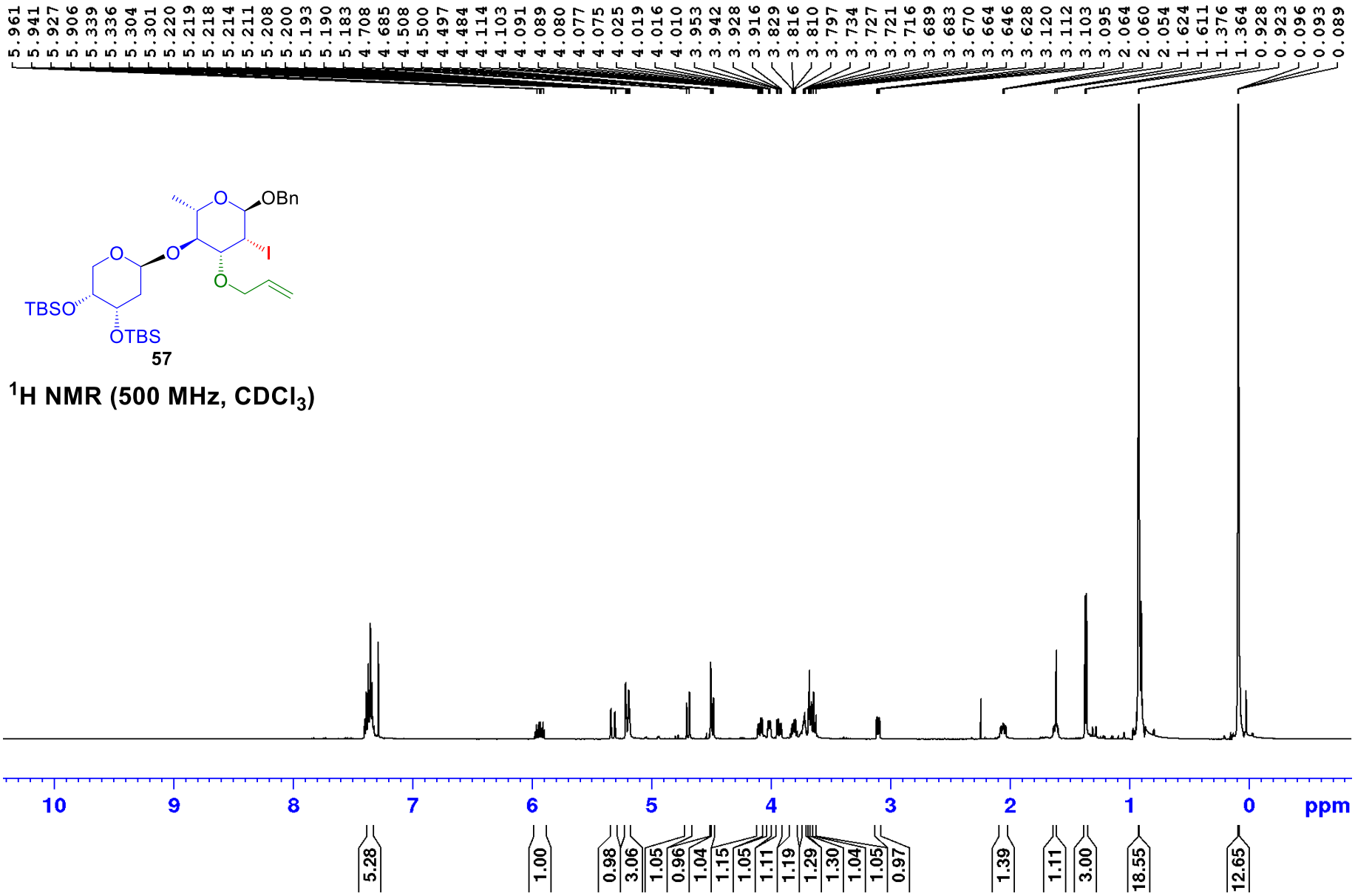
^{1}H NMR (500 MHz, $CDCl_3$)




155.67
139.01
138.84
138.36
138.32
132.64
128.39
128.36
128.30
128.22
128.00
127.86
127.62
127.58
127.54
127.49
127.37
118.55
97.92
96.85
95.08
78.33
77.49
77.32
77.06
76.81
75.86
74.62
73.54
71.96
71.29
69.64
68.97
68.52
66.98
35.91
18.37
OBn
OBn
BnO
OBn
O
O
O
O
58
13C{1H} NMR (125 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

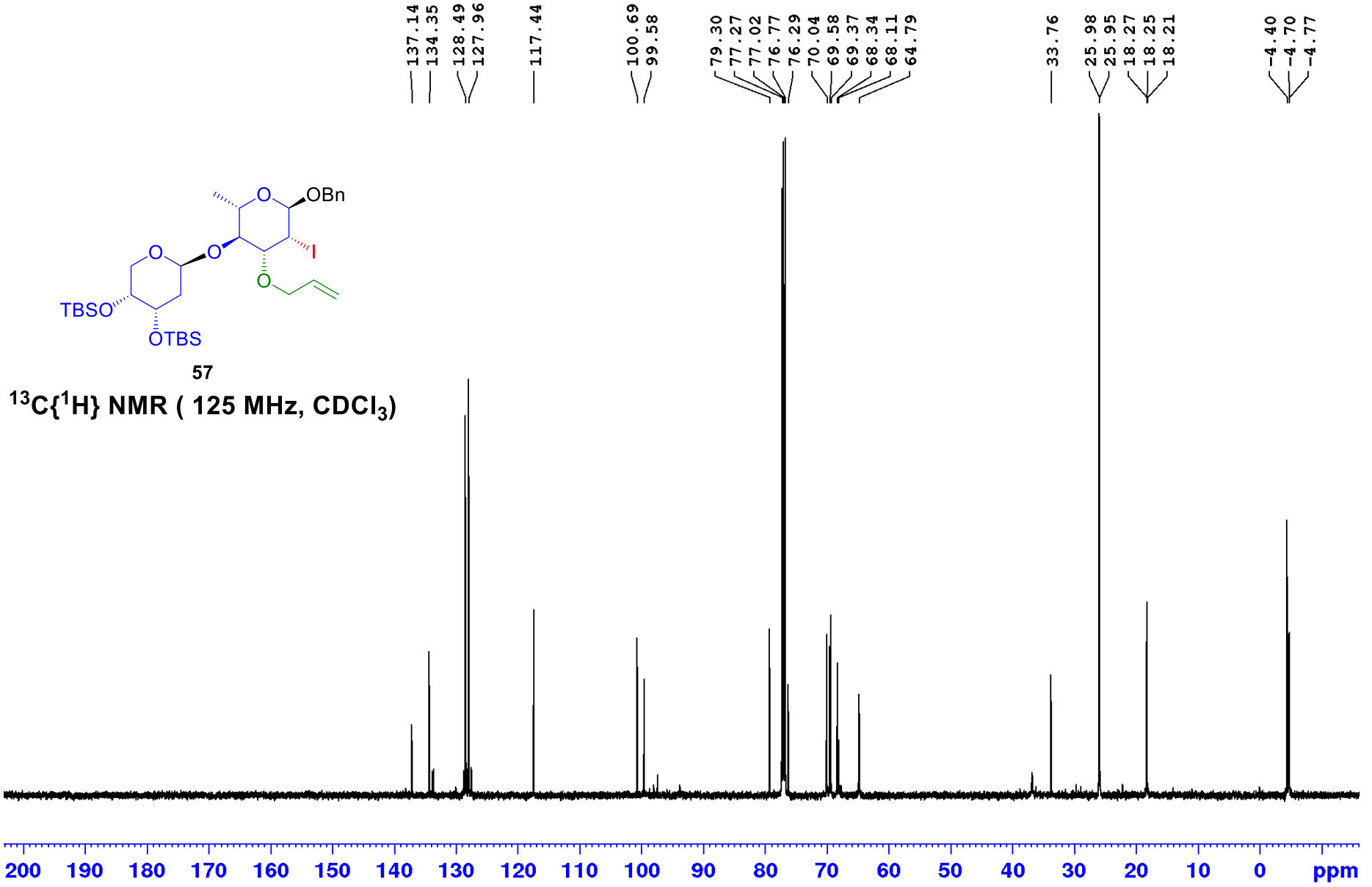

7.354 7.342 7.339 7.333 7.326 7.322 7.313 7.312 7.305 7.298 7.296 7.291 7.286 7.283 7.279 7.275 7.272 7.267 7.263 7.260 7.256 7.253
5.626 5.085 5.083 5.051 5.049 4.990 4.984 4.972 4.969 4.902 4.880 4.675 4.671 4.655 4.603 4.579 4.558 4.536 4.500 4.475 4.457 4.433 4.340 4.087 4.075 4.062 3.972 3.952 3.800 3.794 3.778 3.772 3.680 3.661 3.642 3.512 3.508 3.490 3.486 2.718 2.402 2.377 2.365 2.361 2.349 1.363 1.351
OBn
BnO
OBn
O
+
59a
59a:59b = 10:1
59b
^{1}H NMR (500 MHz, CDCl$_3$)
10 9 8 7 6 5 4 3 2 1 0 ppm
20.37
1.01 1.03 2.09 2.32 3.03 1.20 1.17 1.07 1.30 0.97 2.01 0.97 1.09 1.18 0.93
0.97
3.10
1.15
3.00


204.19
138.86
138.82
138.16
137.04
133.79
128.43
128.36
128.29
128.23
127.91
127.82
127.76
127.65
127.59
127.57
127.49
127.38
117.84
100.55
99.48
82.04
78.25
77.46
74.58
73.42
72.17
71.38
69.81
69.09
68.63
56.39
35.64
34.38
18.61
OBn
BnO
59a
59a:59b = 10:1
59b
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



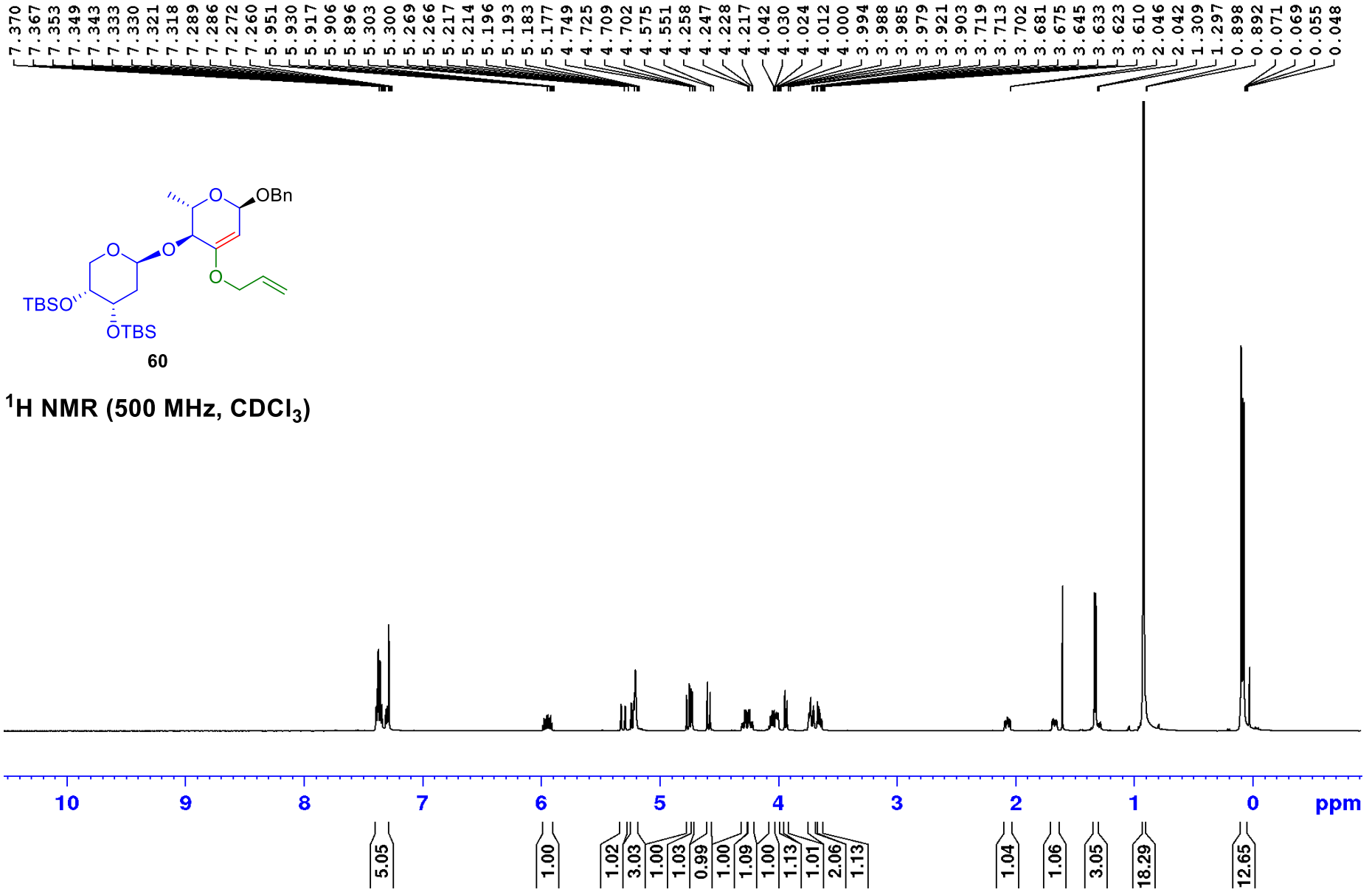
57

^{1}H NMR (500 MHz, $CDCl_3$)



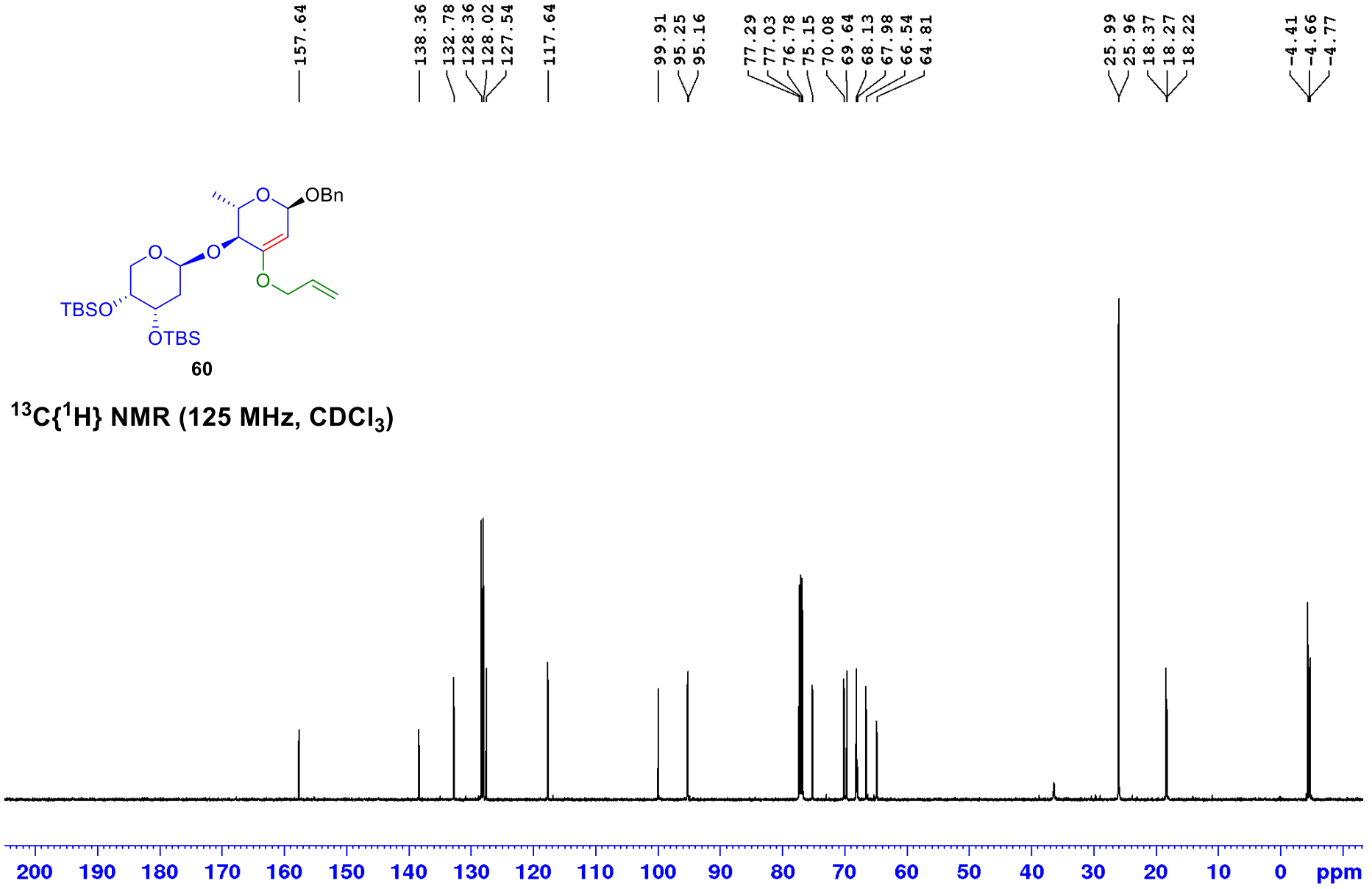
57

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)



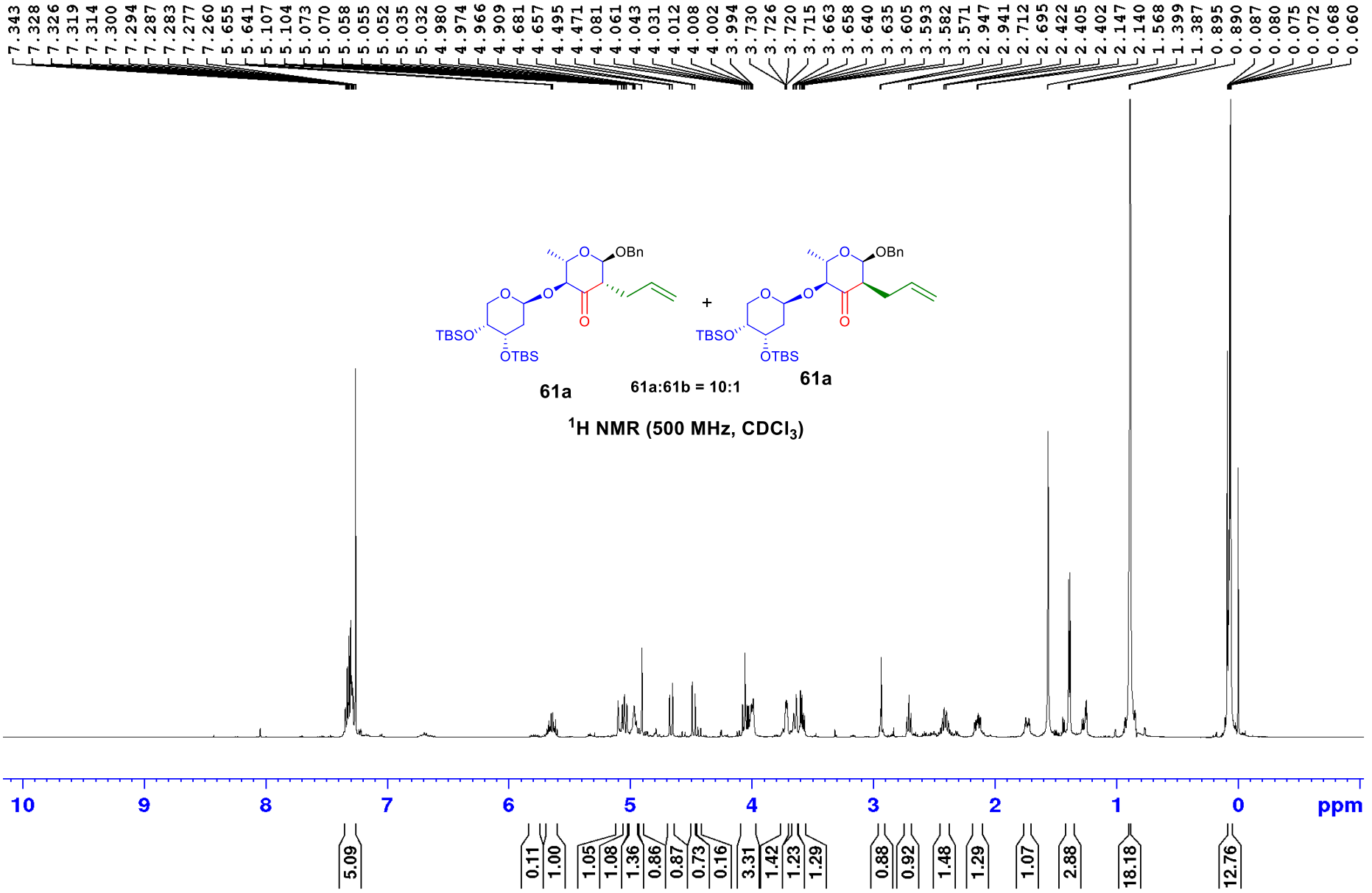
60

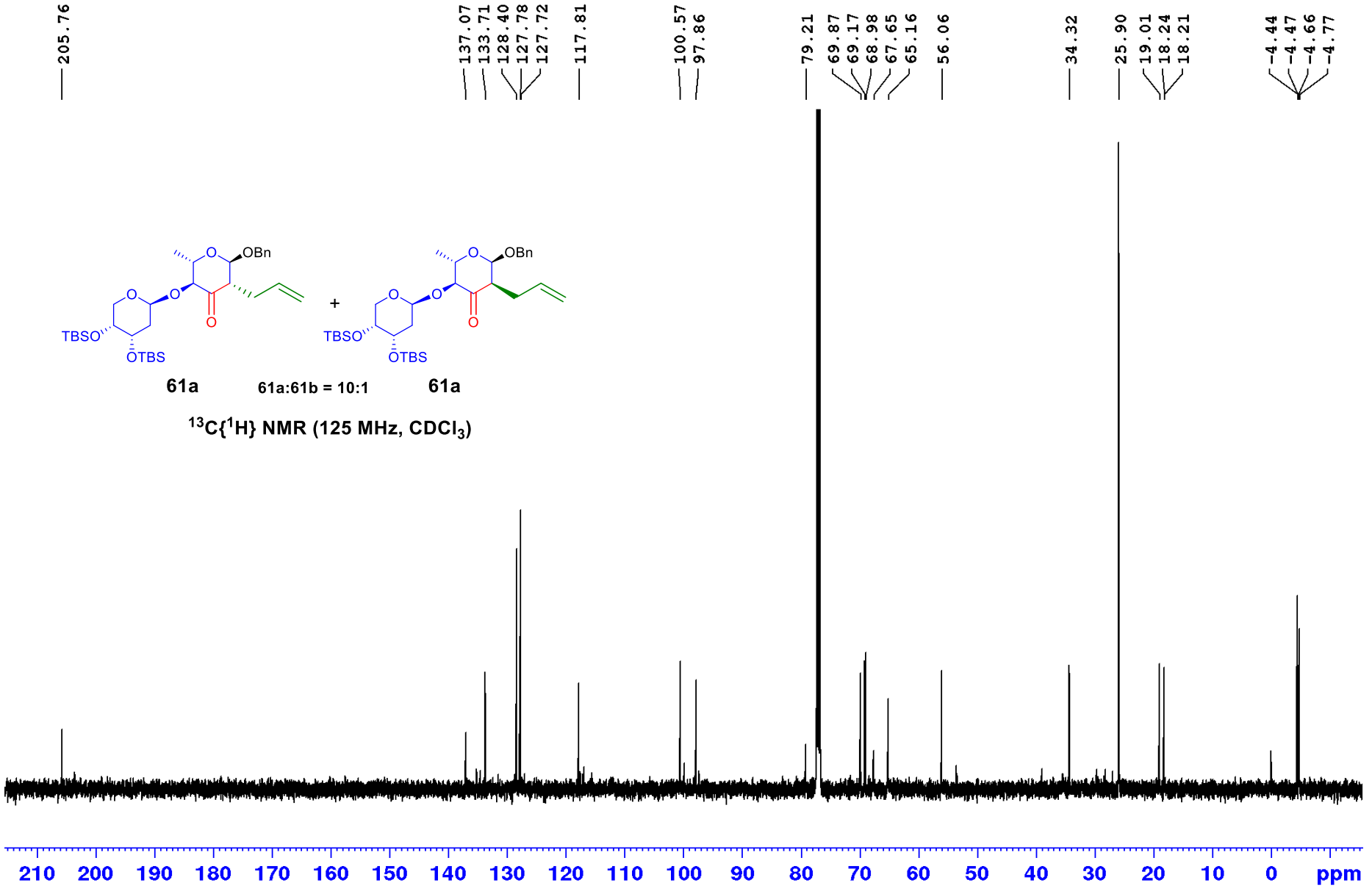
^{1}H NMR (500 MHz, $CDCl_3$)

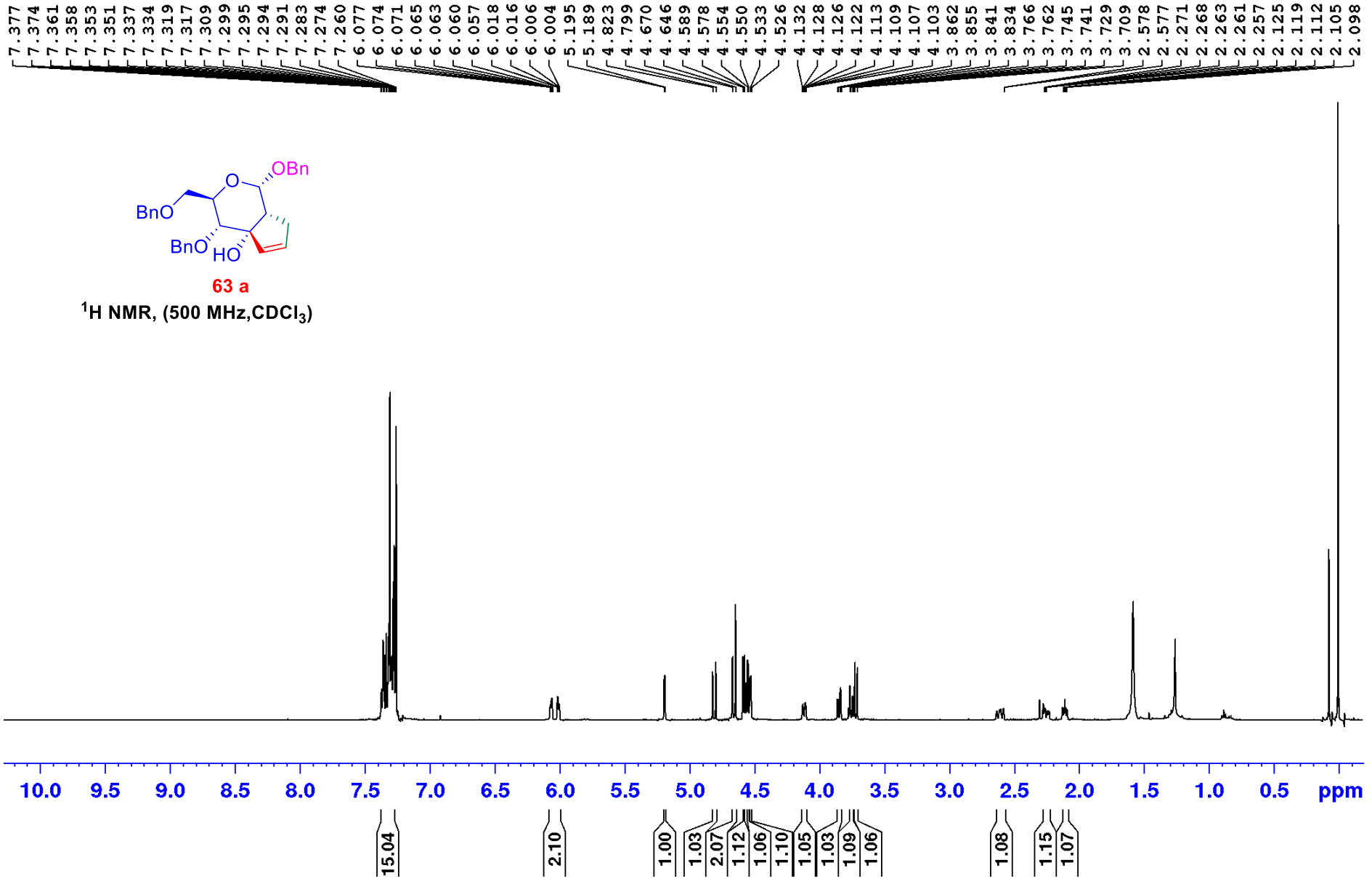


60

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

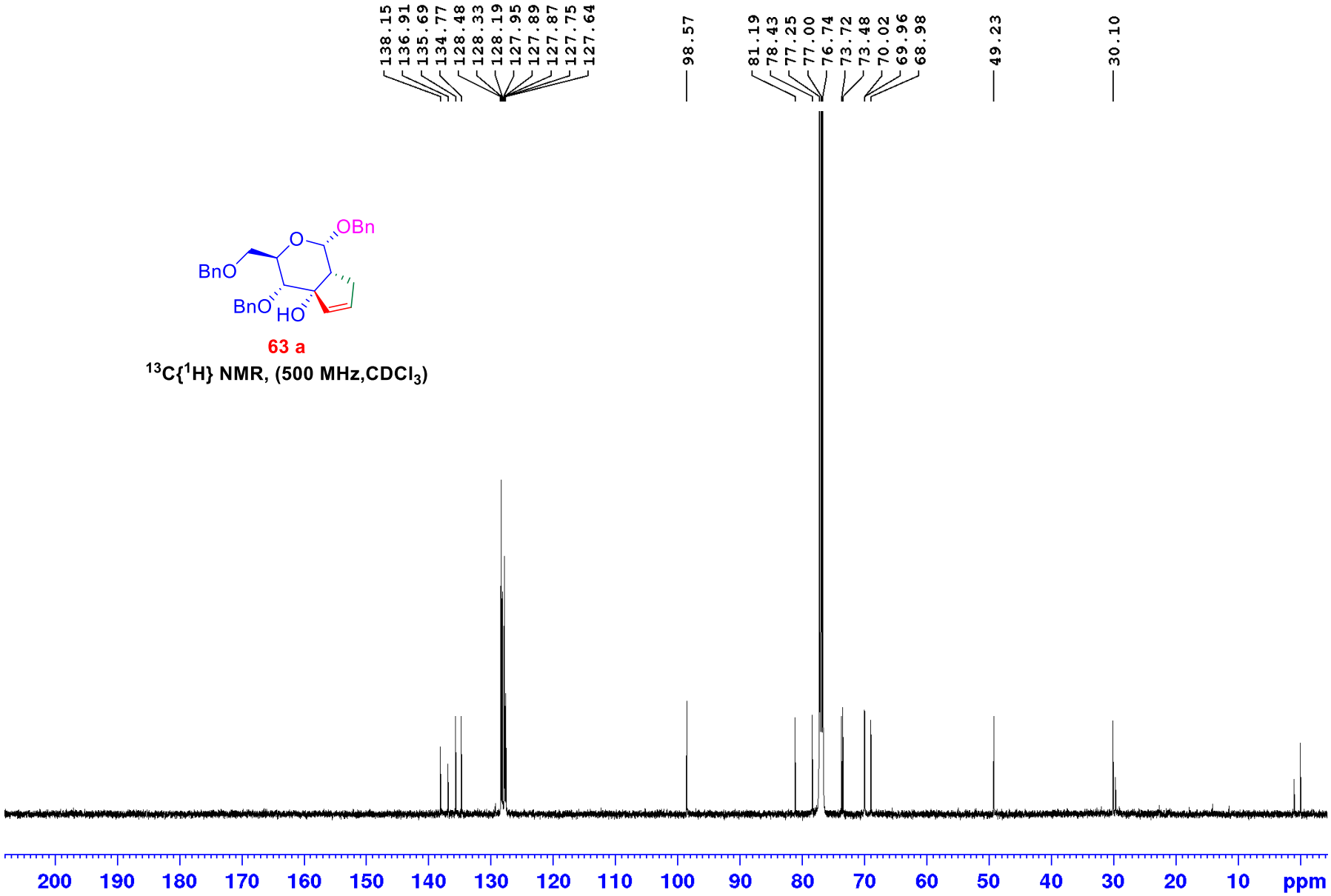

7.343
7.328
7.326
7.319
7.314
7.300
7.294
7.287
7.283
7.277
7.260
5.655
5.641
5.107
5.104
5.073
5.070
5.058
5.055
5.052
5.035
5.032
4.980
4.974
4.966
4.909
4.681
4.657
4.495
4.471
4.081
4.061
4.043
4.031
4.012
4.008
4.002
3.994
3.730
3.726
3.720
3.715
3.663
3.658
3.640
3.635
3.605
3.593
3.582
3.571
2.947
2.941
2.712
2.695
2.422
2.405
2.402
2.147
2.140
1.568
1.399
1.387
0.895
0.890
0.087
0.080
0.075
0.072
0.068
0.060
OBn
TBSO
OTBS
61a
61a:61b = 10:1
61a
^{1}H NMR (500 MHz, CDCl$_3$)
10
9
8
7
6
5
4
3
2
1
0
ppm
5.09
0.11
1.00
1.05
1.08
1.36
0.86
0.87
0.73
0.16
3.31
1.42
1.23
1.29
0.88
0.92
1.48
1.29
1.07
2.88
18.18
12.76


205.76
137.07
133.71
128.40
127.78
127.72
117.81
100.57
97.86
79.21
69.87
69.17
68.98
67.65
65.16
56.06
34.32
25.90
19.01
18.24
18.21
-4.44
-4.47
-4.66
-4.77
OBn
TBSO
OTBS
+
OBn
TBSO
OTBS
61a
61a:61b = 10:1
61a
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm



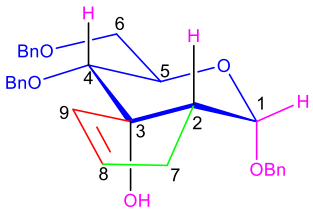
63 a

^{1}H NMR, (500 MHz,$CDCl_3$)



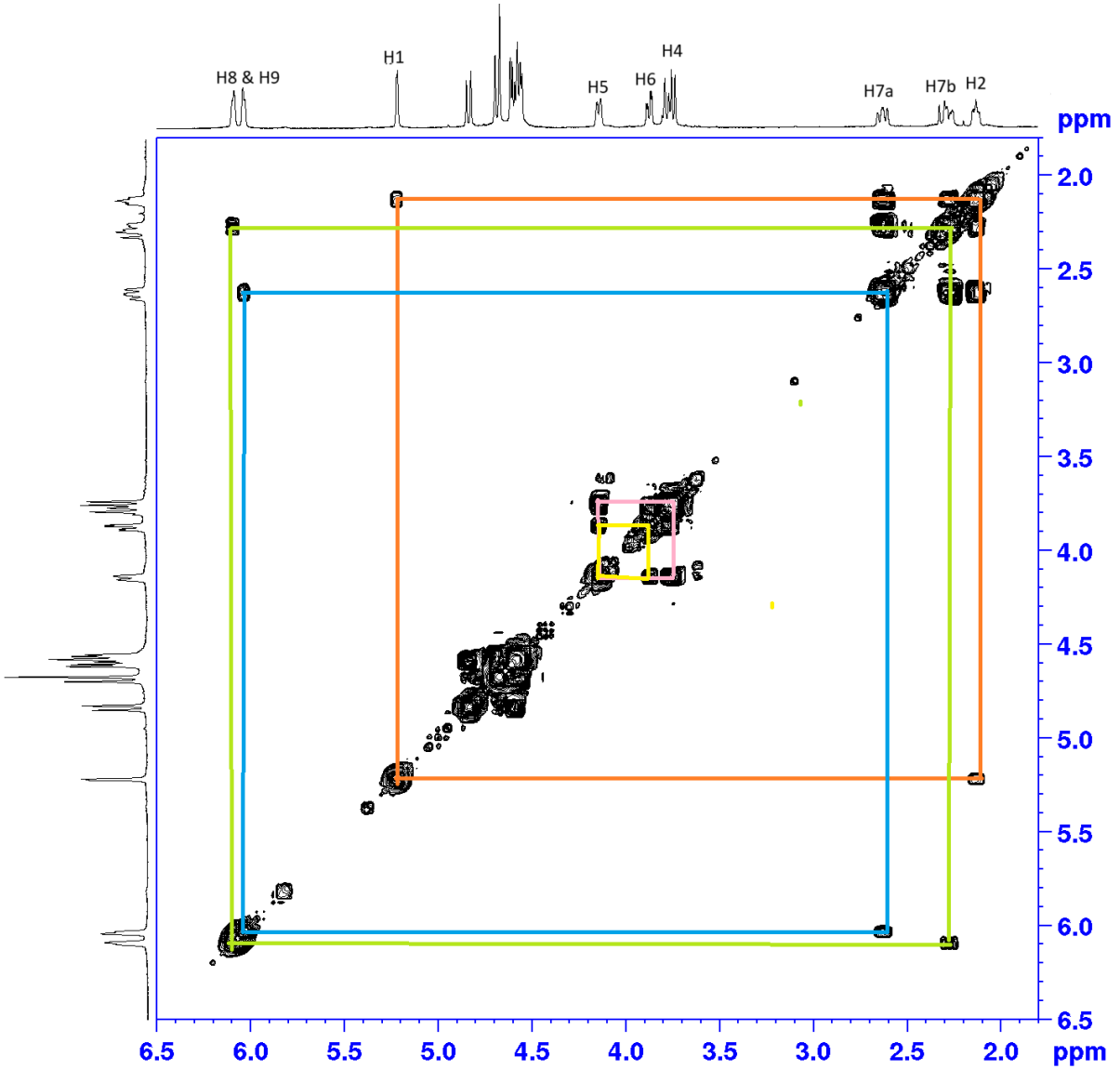
63 a

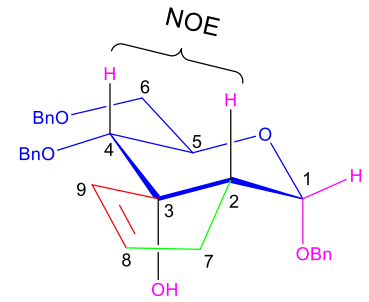
$^{13}C\{^{1}H\}$ NMR, (500 MHz,$CDCl_3$)



63 a

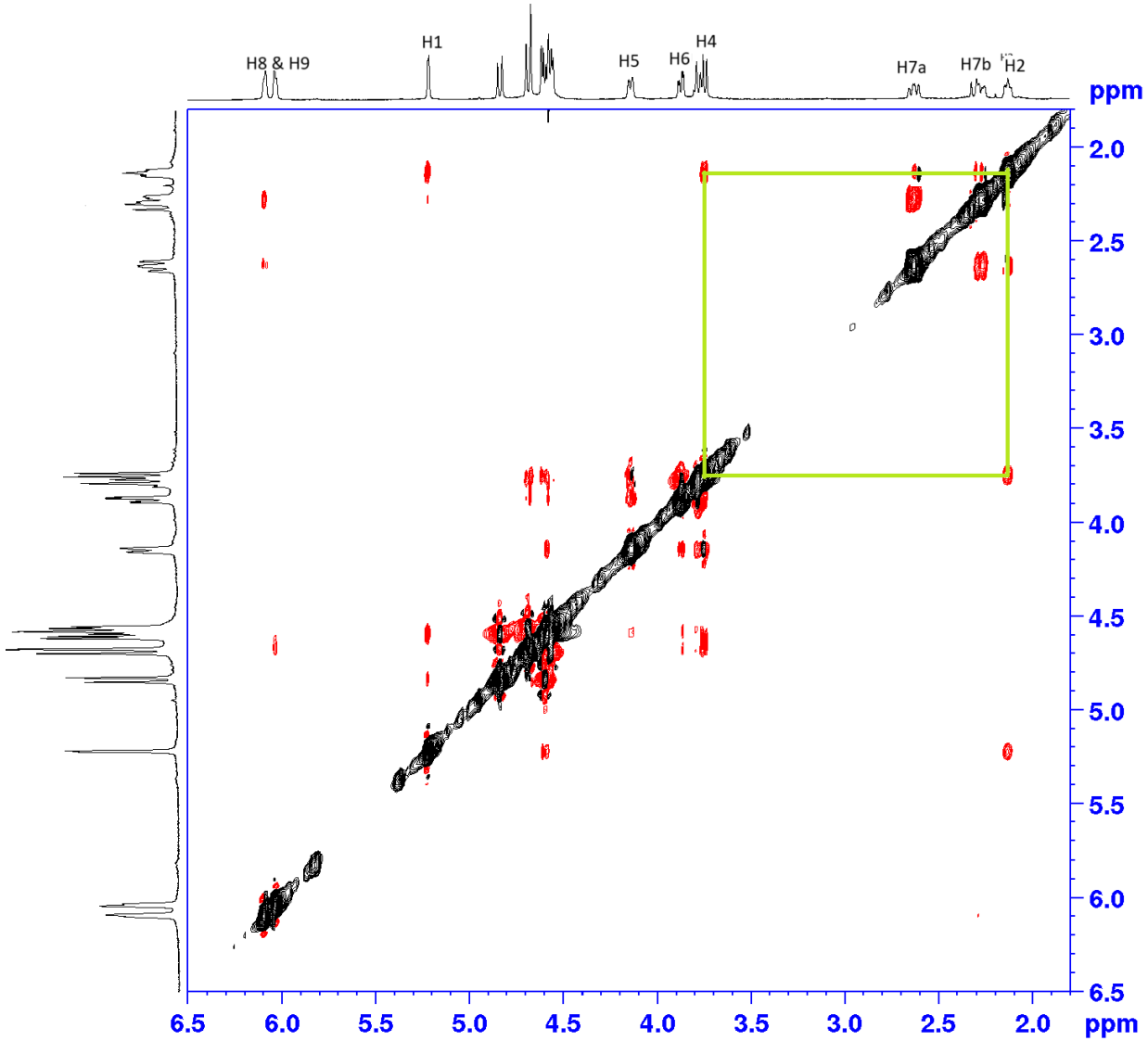
^{1}H-^{1}H COSY, (500 MHz,$CDCl_3$)

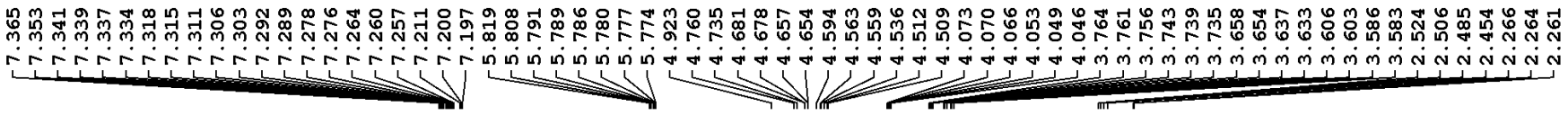


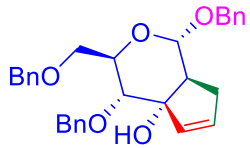


63 a

^{1}H-^{1}H NOESY, (500 MHz,$CDCl_3$)

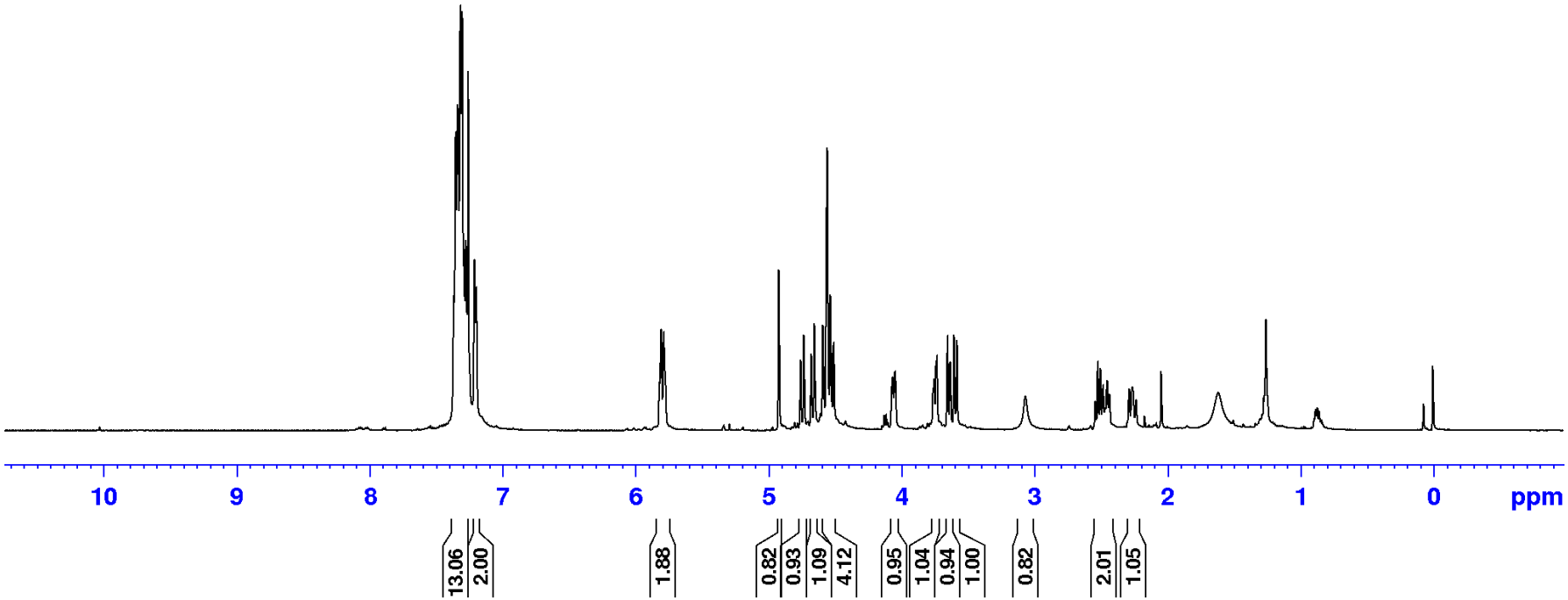


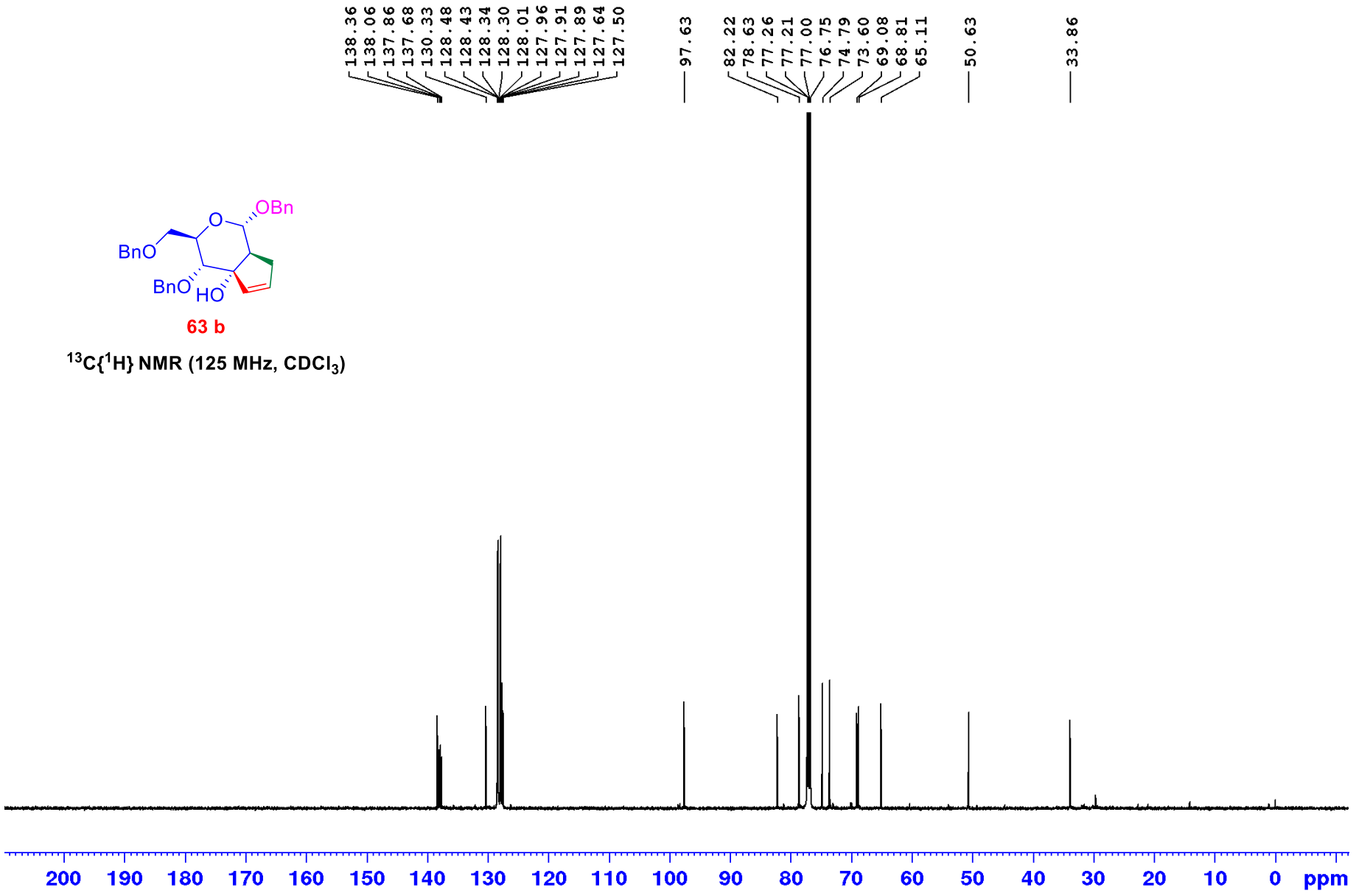


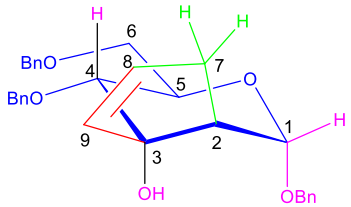


63 b

^{1}H NMR (500 MHz, $CDCl_3$)

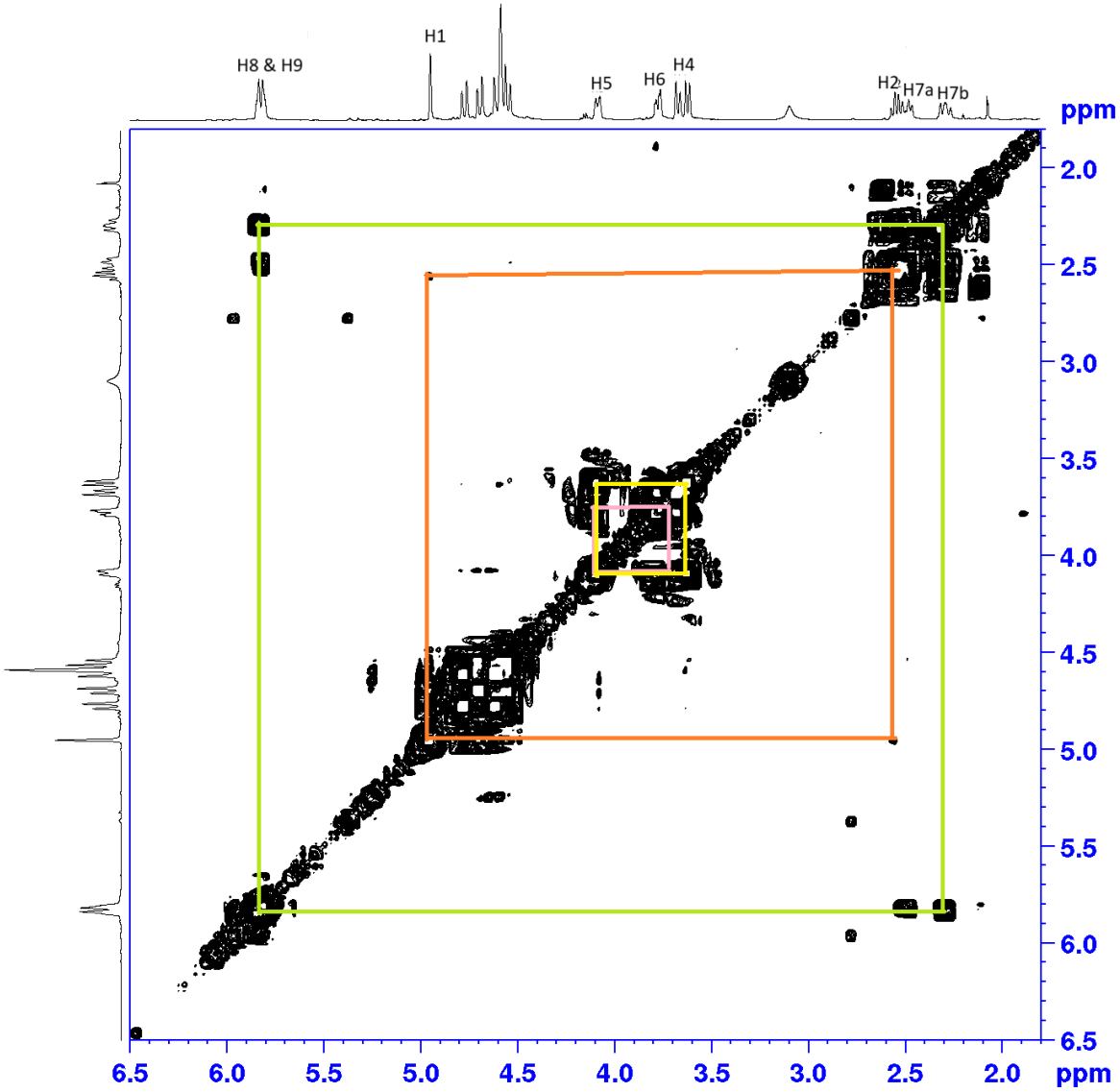



138.36
138.06
137.86
137.68
130.33
128.48
128.43
128.34
128.30
128.01
127.96
127.91
127.89
127.64
127.50
97.63
82.22
78.63
77.26
77.21
77.00
76.75
74.79
73.60
69.08
68.81
65.11
50.63
33.86
OBn
O
BnO
BnO
HO
63 b
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

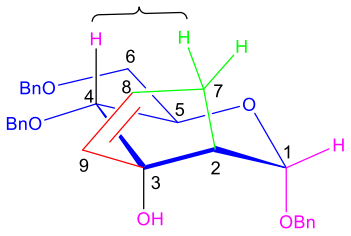


63 b

^{1}H-^{1}H COSY, (500 MHz,$CDCl_3$)

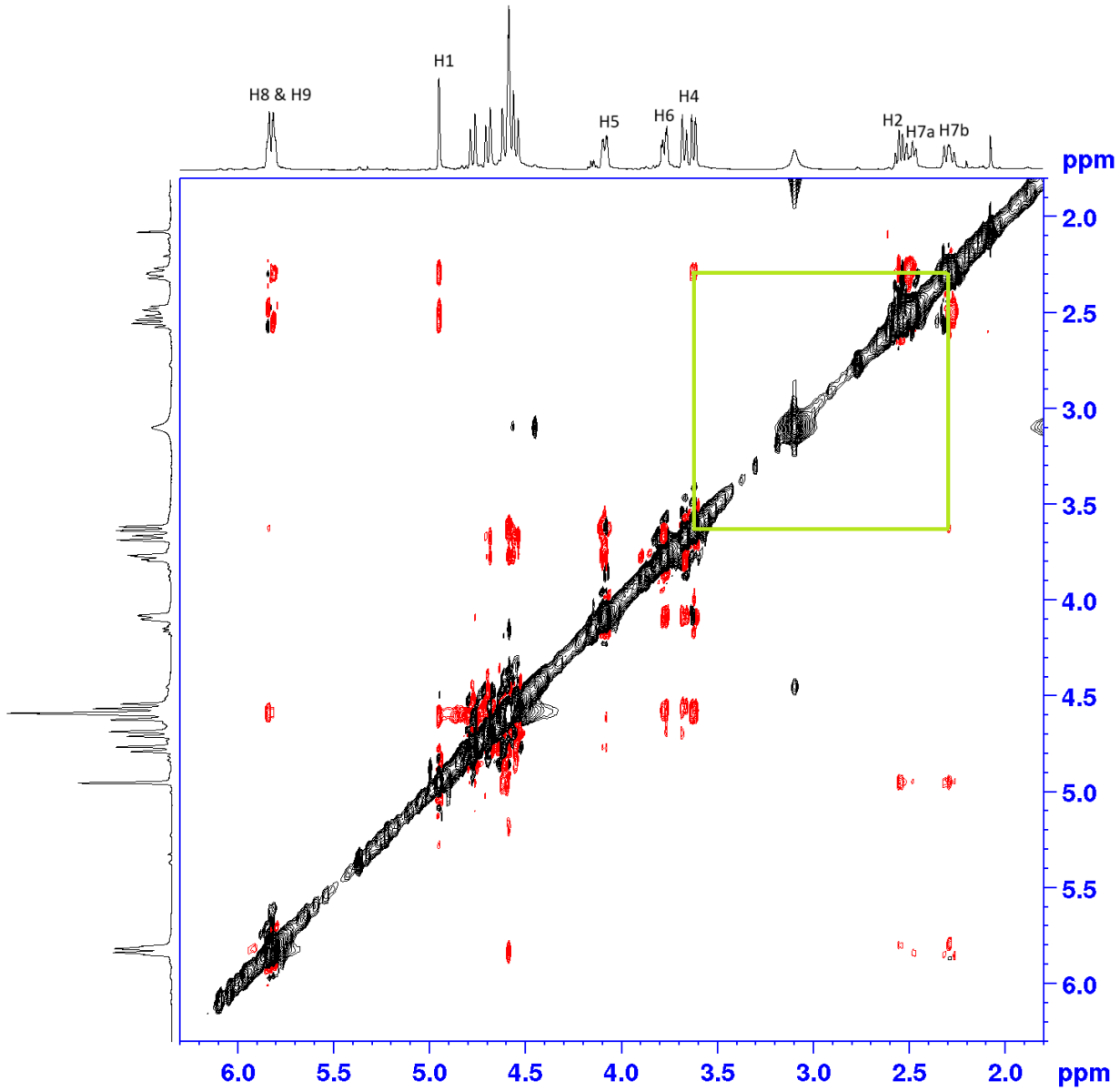


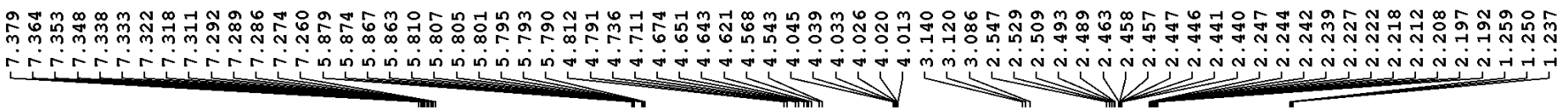
NOE

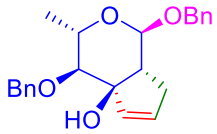


63 b

^{1}H-^{1}H NOESY, (500 MHz,$CDCl_3$)

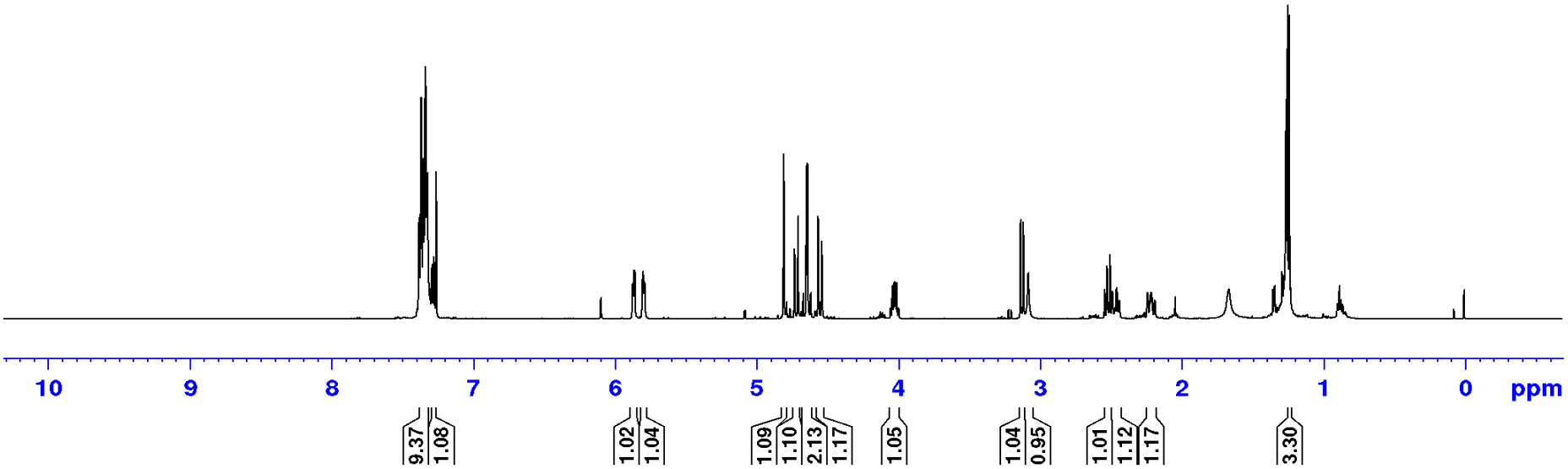


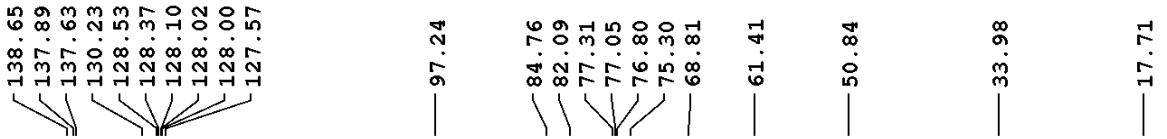


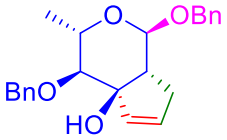


65

^{1}H NMR (500 MHz, $CDCl_3$)

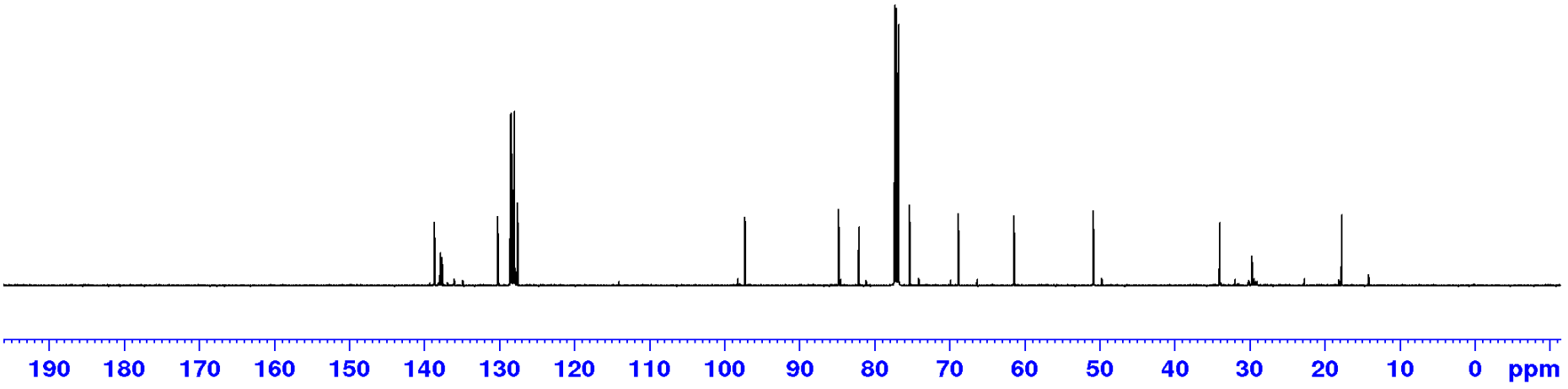


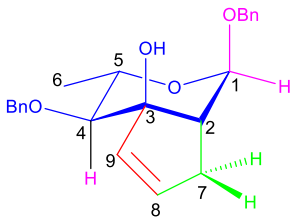




65

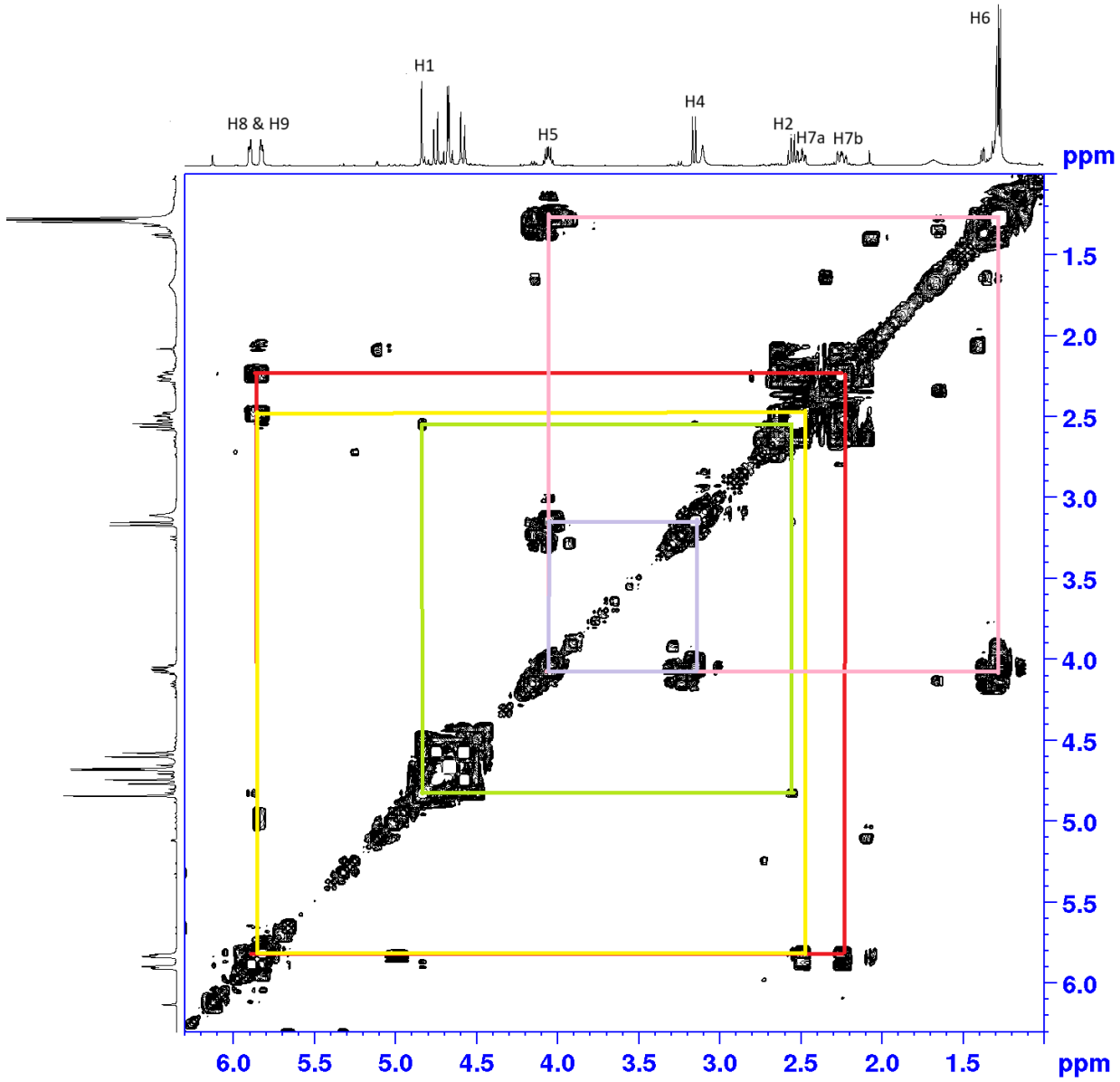
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$)

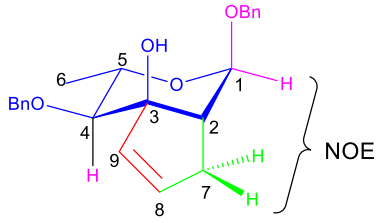




65

^{1}H-^{1}H COSY, (500 MHz,$CDCl_3$)





65

^{1}H-^{1}H NOESY, (500 MHz,$CDCl_3$)