Supporting Information

for

Diastereoselective access to *C*,*C*-glycosyl amino acids via iron-catalyzed, auxiliary-enabled MHAT coupling

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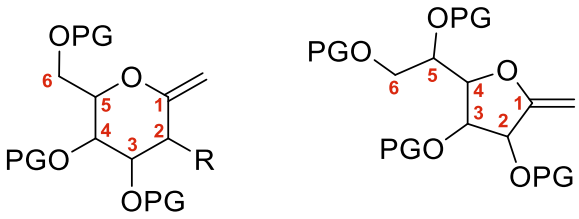
Contents

1. General information

Commercially available starting materials were purchased from commercial suppliers (Merck/Sigma-Aldrich, Alfa Aesar, Acros Organics, Fluorochem, Carbosynth) and were used without further purification. Tetrahydrofuran (THF) was distilled over Na/benzophenone ketyl under argon. Anhydrous reagent grade dichloromethane (stabilizer-free) and toluene were dried and stored over 4Å molecular sieves. Anhydrous reagent grade dimethylformamide (DMF) was purchased and used as received. Triethylamine (Et_3N), di*iso*propylamine (DIPA) and pyridine were distilled over KOH and stored over KOH under argon.

Reactions were performed using standard glassware or vials capped with Teflon septa under argon unless otherwise specified. Thin Layer Chromatographies (TLC) were performed on aluminium sheets coated with silica gel $60F_{254}$ purchased from E. Merck. Eluted TLC plates were revealed under UV light (254 nm) and with phosphomolybdic acid or potassium permanganate upon heating. Flash chromatographies were performed on silica gel 60 (230-400 mesh, 40-63 µm) purchased from E. Merck or using an automatic flash chromatography device.

Proton (^1H) and carbon (^{13}C) Nuclear Magnetic Resonance (NMR) spectra were recorded on a 400 MHz BRUKER Avance III spectrometer and/or a 500 MHz BRUKER Avance III spectrometer equipped with a direct X-^1H CPPBBO “Prodigy” 5 mm cryoprobe. Spectra were treated using Mestrenova© (Mestrelab) software. ^1H and ^{13}C chemical shifts (δ) are reported in parts per million (ppm) relative to the solvent signals: $CDCl_3$ (residual $CHCl_3$), δ_H = 7.26 ppm, δ_C = 77.16 ppm. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, b = broad), coupling constants (*J* expressed in Hz) and integration. Carbon multiplicities were assigned by Distortionless Enhancement by Polarisation Transfer (DEPT) experiments. ^1H and ^{13}C signals were assigned by 2D experiments (COSY, HSQC, HMBC and NOESY or ROESY) when required. Hydrogen and carbon numbering for furanosides and pyranosides compounds is defined as follows:



Infrared (IR) spectra were recorded on a PerkinElmer Spectrum One spectrophotometer and wavelengths are quoted in wave numbers (cm^{-1}). High Resolution Mass Spectra (HRMS) data were recorded on a BRUKER microTOF(I) spectrometer equipped with orthogonal electrospray interface (ESI). Atmospheric Pressure Mass Ionization (APCI) spectra were recorded on a THERMO TSQ Quantum spectrometer. Optical rotations were measured at 589 nm (sodium lamp) at 20 °C on an Anton Paar MCP200 polarimeter (path length = 1 dm); *C* is indicated in g/dL.

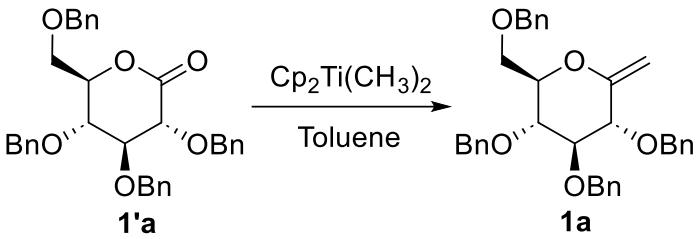
Known characterized compounds used for substrate syntheses were analyzed by ^1H NMR and references are given for further detail; full characterizations are reported if previously unavailable. New, purified intermediates were all fully characterized to the exception of few compounds whose unstability required immediate use.

2. Preparation and characterization of exo-glycals 1

General Procedure A for the lactone olefination with Petasis reagent (**GPA**)

To a solution of lactone (1 equiv) in dry toluene (0.05 M) under Ar was added a 0.76 M solution of dimethyltitanocene in toluene[1] (2.5 to 4 equiv depending on lactone). The reaction mixture was then heated to 90 °C for 16 h, protected from light with Al foil. The reaction mixture was then cooled to room temperature and Celite® (5.0 g/mmol of product) was added to the mixture before removing toluene by rotary evaporation. This adsorbed reaction mixture was then directly loaded onto a column using the appropriate eluent for purification.

2,3,4,6-Tetra-*O*-benzyl-*exo*-D-glucal (1a)[2]

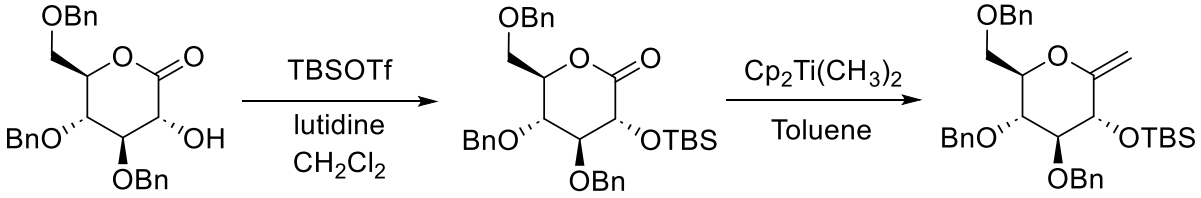


1'a **1a**

Following the **GPA** starting from 2,3,4,6-tetra-*O*-benzyl-D-gluconolactone (1'a)[3] (3.56 g, 6.60 mmol, 1 equiv) with dimethyltitanocene (0.76 M in toluene, 2.5 equiv), **1a** was yielded (2.45 g, 4.57 mmol, 69%) as a white solid after purification by column chromatography (SiO_2, Cyclohexane/EtOAc: 95/5 to 90/10).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.23 (m, 18 H, H_{Ar}), 7.17 – 7.12 (m, 2 H, H_{Ar}), 4.86 (d, *J* = 11.4 Hz, 1 H, OC$\underline{H_2}$Ph), 4.77 (d, *J* = 11.7 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.76 (d, *J* = 1.2 Hz, 1 H, overlapped C-1=C$\underline{H_2}$), 4.72 (d, *J* = 11.2 Hz, 1 H, OC$\underline{H_2}$Ph), 4.65 (d, *J* = 11.6 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.64 (d, *J* = 12.4 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.62 (d, *J* = 1.1 Hz, 1 H, overlapped C-1=C$\underline{H_2}$), 3.96 (dt, *J* = 7.3, 1.3 Hz, 1 H, H-2), 3.81-3.73 (m, 4 H, overlapped H-4, H-5, H-6 and H-6'), 3.70 (t, *J* = 7.3 Hz, 1 H, H-3), in accordance with literature data[2].

3,4,6-Tri-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl-*exo*-D-glucal (1b)



1'b **1b**

Step 1: Synthesis of 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl-D-gluconolactone (**1'b**)

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[1] T. R. Verhoeven *et al.*, *Org. Synth.,* 2002, **79**, 19.
[2] D. Tardieu *et al.*, *Org. Lett.,* 2019, **21**, 7262.
[3] J. Li *et al.*, *J. Carbohydr. Chem.,* 2016, **35**, 445.

To a solution of 3,4,6-tri-*O*-benzyl-D-gluconolactone[4] (313 mg, 0.70 mmol, 1.0 equiv) in dry CH_2Cl_2 (7.0 mL) under Ar at -78 °C was added 2,6-lutidine (0.20 mL, 1.74 mmol, 2.5 equiv). After 10 min, TBSOTf (0.24 mL, 1.05 mmol, 1.5 equiv) was added and the mixture was warmed to 0 °C and stirred for 1 h. The reaction mixture was then diluted with CH_2Cl_2 (30 mL) and washed with a 1 M aqueous solution of HCl (3 x 10 mL) and water (10 mL). The organic layer was then dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by column chromatography (SiO_2, Cyclohexane/EtOAc: 98/2 to 95/5), yielding **1'b** (270 mg, 0.48 mmol, 69%) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.29 (m, 13 H, H_{Ar}), 7.20-7.17 (m, 2 H, H_{Ar}), 4.80 (d, *J* = 11.5 Hz, 1 H, OC$\underline{H_2}$Ph), 4.69 (d, *J* = 12.4 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.67 (d, *J* = 11.0 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.59 (d, *J* = 12.0 Hz, 1 H, OC$\underline{H_2}$Ph), 4.52 (d, *J* = 11.0 Hz, 1 H , overlapped OC$\underline{H_2}$Ph), 4.50 (ddd, *J* = 8.5, 3.2, 2.3 Hz, 1 H, overlapped H-5), 4.48 (d, *J* = 12.0 Hz, 1 H , overlapped OC$\underline{H_2}$Ph), 4.31 (d, *J* = 6.7 Hz, 1 H, H-2), 3.97 (dd, *J* = 8.4, 6.1 Hz, 1 H, H-4), 3.81 (t, *J* = 6.5 Hz, 1 H, H-3), 3.74 (dd, *J* = 11.1, 2.4 Hz, 1 H , H-6), 3.66 (dd, *J* = 11.1, 2.4 Hz, 1 H, H-6'), 0.92 (s, 9H, Si$(CH_3)_2$C$(C\underline{H_3})_3$), 0.16 (s, 3H, Si$(C\underline{H_3})_2$C$(CH_3)_3$), 0.11 (s, 3H, Si$(C\underline{H_3})_2$C$(CH_3)_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.16 (C-1), 137.77 (Cq_{Ar}), 137.75 (Cq_{Ar}), 137.71 (Cq_{Ar}), 128.58 (2 x CH_{Ar}), 128.56 (2 x CH_{Ar}), 128.55 (2 x CH_{Ar}), 128.07 (2 x CH_{Ar}), 128.00 (2 x CH_{Ar}), 127.97 (2 x CH_{Ar}), 127.95 (2 x CH_{Ar}), 127.94 (2 x CH_{Ar}), 81.92 (C-3), 78.30 (C-5), 76.57 (C-4), 73.84 (O$\underline{C}H_2$Ph), 73.78 (O$\underline{C}H_2$Ph), 73.69 (O$\underline{C}H_2$Ph), 72.06 (C-2), 68.67 (C-6), 25.81 (3 x Si$(CH_3)_2$C$(\underline{C}H_3)_3$), 18.36 (Si$(CH_3)_2\underline{C}(CH_3)_3$), 5.12 (Si$(\underline{C}H_3)_2C(CH_3)_3$), 4.69 (Si$(\underline{C}H_3)_2C(CH_3)_3$).

Opt. rot. $[\alpha]_D^{20}$: +43.6 (*c* 1.07, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{33}H_{42}O_6SiK$ $[M+K]^+$: 601.2382, found: 601.2392.

IR (film) v : 2928, 2857, 1760, 1454, 1361, 1251, 1073, 837, 781, 734, 696 cm^{-1}.

Step 2 : Synthesis of 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl-*exo*-D-glucal (**1b**)

Following the **GPA** starting from **1'b** (100 mg, 0.18 mmol, 1 equiv) with dimethyltitanocene (0.76 M in toluene, 4 equiv), **1b** was yielded (98 mg, 0.17 mmol, 98%) as a pale-yellow oil after purification by column chromatography (SiO_2, Cyclohexane/EtOAc: 99/1 to 98/2).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41-7.22 (m, 13H, H_{Ar}), 7.10-7.05 (m, 2H, H_{Ar}), 4.92 (d, *J* = 11.5 Hz, 1 H, OC$\underline{H_2}$Ph), 4.82 (d, *J* = 11.5 Hz, 1 H, OC$\underline{H_2}$Ph), 4.77 (d, *J* = 10.8 Hz, 1 H, OC$\underline{H_2}$Ph), 4.75 (d, *J* = 1.6 Hz, 1 H, C-1=C$\underline{H_2}$), 4.71 (d, *J* = 1.7 Hz, 1 H , C-1=C$\underline{H_2}$), 4.66 (d, *J* = 12.1 Hz, 1 H, OC$\underline{H_2}$Ph), 4.54 (d, *J* = 12.1 Hz, 1 H , OC$\underline{H_2}$Ph), 4.50 (d, *J* = 10.8 Hz, 1 H, OC$\underline{H_2}$Ph), 4.09 (dt, *J* = 8.5, 1.7 Hz, 1 H, H-2), 3.80 (dd, *J* = 10.1, 8.6 Hz, 1 H, overlapped H-4), 3.77 (dd, *J* = 10.9, 2.3 Hz, 1 H , overlapped H-6), 3.75 (dd, *J* = 10.8, 3.5 Hz, 1 H, overlapped H-6'), 3.60 (ddd, *J* = 10.0, 3.4, 2.3 Hz, 1 H, H-5), 3.52 (t, *J* = 8.5 Hz, 1 H, H-3), 0.96 (s, 9H, Si$(CH_3)_2$C$(C\underline{H_3})_3$), 0.10 (s, 3H, Si$(C\underline{H_3})_2$C$(CH_3)_3$), 0.09 (s, 3H, Si$(C\underline{H_3})_2$C$(CH_3)_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.94 (C-1), 138.70 (Cq_{Ar}), 138.14 (Cq_{Ar}), 138.00 (Cq_{Ar}), 128.44 (2 x CH_{Ar}), 128.36 (2 x CH_{Ar}), 128.32 (2 x CH_{Ar}), 128.62 (2 x CH_{Ar}), 127.90 (2 x CH_{Ar}), 127.76 (CH_{Ar}), 127.71 (CH_{Ar}), 127.42 (CH_{Ar}), 127.40 (2 x CH_{Ar}),

[4] B. Vauzeilles *et al.*, *Tetrahedron Lett.*, 2001, **42**, 7269.

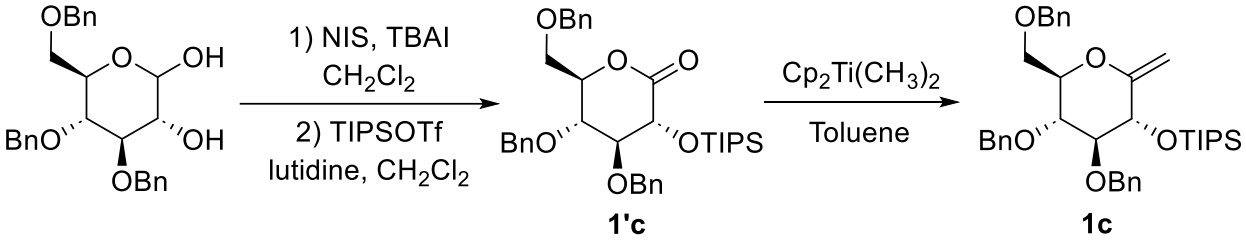
95.05 (C-1=$\underline{C}H_2$), 86.29 (C-3), 79.71 (C-5), 77.70 (C-4), 75.15 (O$\underline{C}H_2$Ph), 74.82 (O$\underline{C}H_2$Ph), 73.65 (O$\underline{C}H_2$Ph), 72.49 (C-2), 68.73 (C-6), 25.91 (Si(CH_3)$_2$C($\underline{C}H_3$)$_3$), 18.11 (Si(CH_3)$_2\underline{C}$(CH_3)$_3$), 4.62 (Si($\underline{C}H_3$)$_2$C(CH_3)$_3$), 4.84 (Si($\underline{C}H_3$)$_2$C(CH_3)$_3$).

Opt. rot. $[\alpha]_D^{20}$: +32.8 (*c* 1.09, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{34}H_{44}O_5SiNa$ $[M+Na]^+$: 583.2850, found: 583.2845.

IR (film): v 2928, 2857, 1661, 1454, 1360, 1252, 1085, 865, 837, 733, 697 cm^{-1}.

3,4,6-Tri-*O*-benzyl-2-*O*-triisopropylsilyl-*exo*-D-glucal (1c)



Step 1 : Synthesis of 3,4,6-tri-*O*-benzyl-2-*O*-triisopropylsilyl-D-gluconolactone (**1'c**)

To a solution of 3,4,6-tri-*O*-benzyl-D-glucopyranose[5] (mix of both anomers α/β : 1.0/0.3, 2.74 g, 6.08 mmol, 1 equiv) in anhydrous CH_2Cl_2 (12.5 mL), *n*-iodosuccinimide (3.01 g, 13.4 mmol, 2.2 equiv) and *n*-tetrabutylammonium iodide (670 mg, 1.82 mmol, 0.3 equiv) were added portionwise at 0 °C under Ar. The reaction was stirred for 40 h at room temperature, protected from light with Al foil. The mixture was then diluted with EtOAc (150 mL) and a saturated aqueous solution of $Na_2S_2O_3$ (150 mL) was added. Layers were separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were then washed with water (2 x 50 mL) and brine (3 x 50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. After complete removal of EtOAc the resulting hydroxylactone intermediate was then dissolved in anhydrous CH_2Cl_2 (60 mL) under Ar and the reaction mixture was cooled to -78 °C. To the mixture were then added freshly distilled 2,6-lutidine (2.13 mL, 18.3 mmol, 3 equiv) followed by TIPSOTf (2.45 mL, 9.12 mmol, 1.5 equiv). The reaction was then stirred for 10 min at -78 °C, then at 0 °C using an ice bath and left stirring until completion (typically 3-4 h). The reaction mixture was then diluted with CH_2Cl_2 (100 mL) and the organic layer was washed with a 1.0 M aqueous solution of HCl (3 x 50 mL) and with water (50 mL). The organic layer was then dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography (SiO_2, Cyclohexane/EtOAc: 99/1 to 95/5), yielding **1'c** (2.33 g, 3.84 mmol, 63% over two steps) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.26 (m, 13H, H_{Ar}), 7.19-7.10 (m, 2H, H_{Ar}), 4.84 (ddd, *J* = 9.2, 4.0, 2.2 Hz, 1H, H-5), 4.64 (d, *J* = 11.7 Hz, 1H, OC$\underline{H_2}$Ph), 4.60 (d, *J* = 12.1 Hz, 1H, OC$\underline{H_2}$Ph), 4.55 (d, *J* = 12.1 Hz, 1H, overlapped OC$\underline{H_2}$Ph), 4.54 (d, *J* = 11.4 Hz, 1H, overlapped OC$\underline{H_2}$Ph), 4.52 (d, *J* = 12.1 Hz, 1H, overlapped OC$\underline{H_2}$Ph), 4.45 (d, *J* = 4.1, 0.9 Hz, 1H, overlapped H-2), 4.44 (d, *J* = 11.4 Hz, 1H, overlapped OC$\underline{H_2}$Ph), 3.90 (ddd, *J* = 9.2, 3.2, 0.8 Hz, 1H, H-4), 3.84 (dd, *J* = 4.0, 3.2 Hz, 1H, H-

[5] M. Carpintero *et al.*, *J. Org. Chem.*, 2001, **66**, 1768.

3), 3.75 (dd, *J* = 11.3, 2.3 Hz, 1H, H-6), 3.68 (dd, *J* = 11.3, 4.0 Hz, 1H, H-6'), 1.16-1.02 (m, 21H, Si-CH and SiCH(CH$_3$)$_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.39 (C-1), 138.05 (Cq_{Ar}), 137.73 (Cq_{Ar}), 137.46 (Cq_{Ar}), 128.59 (2 x CH_{Ar}), 128.48 (2 x CH_{Ar}), 128.47 (2 x CH_{Ar}), 128.14 (CH_{Ar}), 128.01 (2 x CH_{Ar}), 127.99 (2 x CH_{Ar}), 127.97 (CH_{Ar}), 127.91 (2 x CH_{Ar}), 127.78 (CH_{Ar}), 81.05 (C-3), 77.72 (C-5), 76.92 (C-4), 73.63 (OCH$_2$Ph), 72.80 (OCH$_2$Ph), 72.40 (OCH$_2$Ph), 71.61 (C-2), 68.72 (C-6), 18.03 (3 SiCH(CH$_3$)$_2$), 17.94 (3 SiCH(CH$_3$)$_2$), 12.25 (3 SiCH(CH$_3$)$_2$).

Opt. rot. $[\alpha]_D^{20}$: +52.0 (*c* 1.03, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{36}H_{48}O_6SiNa$ $[M+Na]^+$: 627.3112, found: 627.3111.

IR (film): v 2943, 2866, 1761, 1454, 1091, 1070, 735, 695 cm^{-1}.

Step 2 : Synthesis of 3,4,6-tri-*O*-benzyl-2-*O*-triisopropylsilyl-*exo*-D-glucal (**1c**)

Following the **GPA** starting from 3,4,6-tri-*O*-benzyl-2-*O*-tri*iso*propylsilyl-D-gluconolactone (1.15 g, 1.90 mmol, 1 equiv) with dimethyltitanocene (0.76 M in toluene, 4 equiv), **1c** was yielded (790 mg, 1.31 mmol, 69%) as a pale-yellow oil after purification by column chromatography (SiO_2, Cyclohexane/EtOAc: 99/1 to 98/2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.22 (m, 13 H, H_{Ar}), 7.10-7.08 (m, 2 H, H_{Ar}), 4.78 (d, *J* = 11.8 Hz, 1 H, OCH$_2$Ph), 4.73 (d, *J* = 11.9 Hz, 1 H, OCH$_2$Ph), 4.66 (d, *J* = 9.3 Hz, 1 H, overlapped OCH$_2$Ph), 4.65 (d, *J* = 10.8 Hz, overlapped OCH$_2$Ph) 4.64 (t, *J* = 0.9 Hz, 1 H, overlapped C-1=CH$_2$), 4.55 (d, *J* = 12.2 Hz, 1 H, OCH$_2$Ph), 4.50 (t, *J* = 0.9 Hz, 1 H, C-1=CH$_2$), 4.46 (d, *J* = 11.1 Hz, 1 H, OCH$_2$Ph), 4.31 (d, *J* = 5.8 Hz, 1 H, H-2), 4.01 (ddd, *J* = 10.0, 4.0, 2.1 Hz, 1 H, H-5), 3.76 (overlapped dd, *J* = 11.2, 2.1 Hz, 1 H, H-6), 3.74 (dd, *J* = 10.0, 6.2 Hz, 1 H, overlapped H-4), 3.71 (dd, *J* = 11.2, 4.2 Hz, 1 H, overlapped H-6'), 3.62 (t, *J* = 6.0 Hz, 1 H, H-3), 1.15-1.02 (m, 21 H, Si-CH and SiCH(CH$_3$)$_2$).

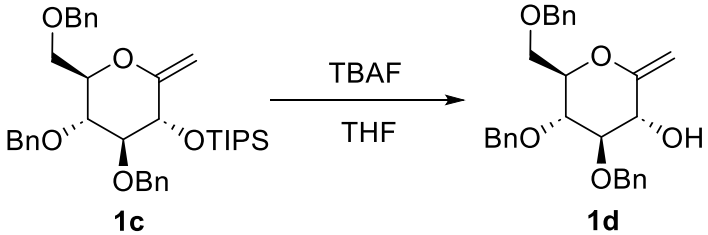
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.84 (C-1), 138.59 (CqAr), 138.33 (CqAr), 138.25 (CqAr), 128.48 (2 x CH_{Ar}), 128.41 (2 x CH_{Ar}), 128.40 (2 x CH_{Ar}), 128.05 (2 x CH_{Ar}), 127.94 (2 x CH_{Ar}), 127.74 (2 x CH_{Ar}), 127.60 (CH_{Ar}), 127.50 (2 x CH_{Ar}), 93.56 (C-1=CH$_2$), 85.06 (C-3), 78.43 (C-4), 77.36 (C-5), 73.75 (OCH$_2$Ph), 73.64 (OCH$_2$Ph), 73.54 (OCH2-Ph), 72.40 (C-2), 69.24 (C-6), 18.28 (SiCH(CH$_3$)$_2$), 12.80 (SiCH(CH$_3$)$_2$).

Opt. rot. $[\alpha]_D^{20}$: +31.0 (*c* 1.05, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{37}H_{50}O_5SiK$ $[M+K]^+$: 641.3059, found: 641.3057.

IR (film): v 2943, 2865, 1662, 1454, 1086, 733, 699 cm^{-1}.

3,4,6-Tri-*O*-benzyl-*exo*-D-glucal (1d)



1c **1d**

To a solution of 3,4,6-tri-*O*-benzyl-2-*O*-tri*iso*propylsilyl-*exo*-D-glucal (**1c**) (100 mg, 0.17 mmol, 1 equiv) in dry THF (0.7 mL) at 0 °C under Ar, was added a 1.0 M solution of TBAF in THF (0.25 mL, 0.25 mmol, 1.5 equiv). The reaction mixture was then stirred at room temperature for 1 h. The mixture was diluted with EtOAc (10 mL) and washed with a saturated aqueous solution of NH_4Cl (20 mL) and brine (20 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude product was purified by column chromatography (SiO_2, Pentane/Et_2O: 80/20), yielding **1d** (74.0 mg, 0.170 mmol, quant.) as a white solid.

^{1}H NMR (500 MHz, acetone d6) δ 7.60-7.15 (m, 15 H, H_{Ar}), 4.99 (d, *J* = 11.4 Hz, 1 H, OCH_2Ph), 4.84 (d, *J* = 11.0 Hz, 1 H, OCH_2Ph), 4.83 (d, *J* = 11.4 Hz, 1 H, OCH_2Ph), 4.79 (d, *J* = 5.5 Hz, 1 H, OH), 4.69 (d, *J* = 1.8 Hz, 1 H, C-1=CH_2), 4.63 (d, *J* = 10.9 Hz, 1 H, OCH_2Ph), 4.58 (d, *J* = 12.6 Hz, 1 H, OCH_2Ph), 4.57 (d, *J* = 1.6 Hz, 1 H, C-1=CH_2), 4.56 (d, *J* = 11.2 Hz, 1 H, OCH_2Ph), 4.11 (ddt, *J* = 8.5, 5.4, 1.8 Hz, 1 H, H-2), 3.80 (dd, *J* = 11.3, 2.6 Hz, 1 H, H-6), 3.77 (dd, *J* = 11.2, 3.5 Hz, 1 H, H-6'), 3.73 (dd, *J* = 9.8, 8.3 Hz, 1 H, H-4), 3.61 (ddd, *J* = 9.8, 3.6, 2.5 Hz, 1 H, H-5), 3.52 (t, *J* = 8.4 Hz, 1 H, H-3).

^{13}C NMR (125 MHz, acetone d6) δ 160.69 (C-1), 140.32 (Cq_{Ar}), 139.78 (Cq_{Ar}), 139.74 (Cq_{Ar}), 129.26 (2 x CH_{Ar}), 129.18 (2 x CH_{Ar}), 129.13 (2 x CH_{Ar}), 128.83 (2 x CH_{Ar}), 128.70 (4 x CH_{Ar}), 128.44 (CH_{Ar}), 128.42 (CH_{Ar}), 128.28 (CH_{Ar}), 93.27 (C-1=CH_2), 86.92 (C-3), 80.46 (C-5), 78.50 (C-4), 75.34 (OCH_2Ph), 75.26 (OCH_2Ph), 74.00 (OCH_2Ph), 72.55 (C-2), 70.21 (C-6).

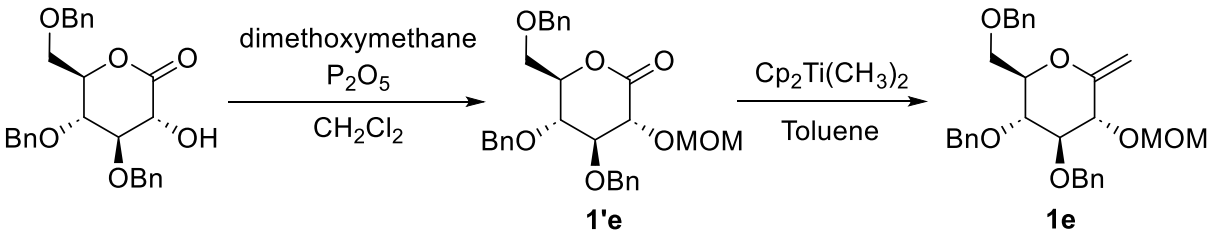
Opt. rot. $[\alpha]_D^{20}$: +66.2 (*c* 1.06, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{28}H_{30}O_5Na$ $[M+Na]^+$: 469.1985, found: 469.1960.

IR (film): v 3292, 3032, 2919, 1720, 1661, 1453, 1362, 1083, 875, 695 cm^{-1}.

Melting point: 112–113 °C (CH_2Cl_2/hexanes).

3,4,6-Tri-*O*-benzyl-2-*O*-methoxymethoxy-*exo*-D-glucal (1e)



Step 1 : Synthesis of 3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy-D-gluconolactone (**1'e**)

To a solution of 3,4,6-tri-*O*-benzyl-D-gluconolactone (**1d**) (200 mg, 0.45 mmol, 1.0 equiv) in dry CH_2Cl_2 (15 mL) under Ar was added dimethoxymethane (0.49 mL, 5.57 mmol, 12.5 equiv) and P_2O_5 (158 mg, 1.11 mmol, 2.5 equiv). The mixture was then stirred for 16 h at room temperature. The reaction mixture was then diluted with CH_2Cl_2 (10 mL) and a saturated aqueous solution of $NaHCO_3$ (10 mL) was added to quench the reaction. The organic layer was washed with water (15 mL) and brine (15 mL) then dried over Na_2SO_4, filtered and concentrated. The crude product was clean enough to avoid any further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 13 H, H_{Ar}), 7.20-7.17 (m, 2 H, H_{Ar}), 4.96 (d, *J* = 6.7 Hz, 1 H, $OC\underline{H_2}OCH_3$), 4.83 (d, *J* = 11.4 Hz, 1 H, $OC\underline{H_2}Ph$), 4.78 (d, *J* = 6.6 Hz, 1 H, $OC\underline{H_2}OCH_3$), 4.72 (d, *J* = 11.4 Hz, 1 H, $OC\underline{H_2}Ph$), 4.72 (d, *J* = 11.1 Hz, 1 H, $OC\underline{H_2}Ph$), 4.57 (d, *J* = 12.0 Hz, 1 H, $OC\underline{H_2}Ph$), 4.53 (d, *J* = 11.2 Hz, 1 H, $OC\underline{H_2}Ph$), 4.48 (d, *J* = 12.0 Hz, 1 H, $OC\underline{H_2}Ph$), 4.42 (ddd, *J* = 8.2, 3.3, 2.6 Hz, 1 H, overlapped H-5), 4.35 (d, *J* = 7.6 Hz, 1 H, H-2), 4.00 (dd, *J* = 8.2, 6.9 Hz, 1 H, H-4), 3.91 (dd, *J* = 7.7, 6.9 Hz, 1 H, H-3), 3.72 (dd, *J* = 11.0, 2.6 Hz, 1 H, H-6), 3.65 (dd, *J* = 11.0, 3.3 Hz, 1 H, H-6'), 3.42 (s, 3 H, $OCH_2OC\underline{H_3}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.41 (C-1), 137.69 (Cq_{Ar}), 137.67 (Cq_{Ar}), 137.56 (Cq_{Ar}), 128.62 (3 x CH_{Ar}), 128.60 (2 x CH_{Ar}), 128.17 (4 x CH_{Ar}), 128.60 (2 x CH_{Ar}), 128.17 (4 x CH_{Ar}), 128.10 (CH_{Ar}), 128.05 (2 x CH_{Ar}), 127.99 (CH_{Ar}), 127.93 (2 x CH_{Ar}), 96.89 ($O\underline{C}H_2OCH_3$), 80.79 (C-3), 78.63 (C-5), 76.33 (C-4), 74.14 ($O\underline{C}H_2Ph$), 74.13 ($O\underline{C}H_2Ph$), 73.95 (C-2), 73.71 ($O\underline{C}H_2Ph$), 68.45 (C-6), 56.47 ($OCH_2O\underline{C}H_3$).

Opt. rot. $[\alpha]_D^{20}$: +61.3 (*c* 0.91, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{29}H_{32}O_7Na$ $[M+Na]^+$: 515.2040, found: 515.2039.

IR (film): v 2900, 1759, 1497, 1457, 1362, 1212, 1152, 1097, 1073, 1039, 920, 739, 698 cm^{-1}.

Step 2 : Synthesis of 3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy-*exo*-D-glucal (**1e**)

Following the **GPA** starting from 3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy-D-gluconolactone (150 mg, 0.305 mmol, 1 equiv) with dimethyltitanocene (0.76 M in toluene, 2.5 equiv), **1e** was obtained (111 mg, 0.23 mmol, 74%) as a yellowish oil after purification by column chromatography (SiO_2, Cyclohexane/EtOAc: 95/5).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.26 (m, 5 H, H_{Ar}), 7.21-7.18 (m, 2 H, H_{Ar}), 7.15-7.06 (m, 8 H, H_{Ar}), 4.87 (t, *J* = 0.8 Hz, 1 H, C-1=$C\underline{H_2}$), 4.78 (d, *J* = 11.4 Hz, 1 H, $OC\underline{H_2}Ph$), 4.77 (d, *J* = 11.6 Hz, 1 H, $OC\underline{H_2}Ph$), 4.70 (d, *J* = 6.5 Hz, 1 H, $OC\underline{H_2}OCH_3$), 4.67 (t, *J* = 0.9 Hz, 1 H, C-1=$C\underline{H_2}$), 4.65 (d, *J* = 11.1 Hz, 1 H , $OC\underline{H_2}Ph$), 4.61 (d, *J* = 6.5 Hz, 1 H , $OC\underline{H_2}OCH_3$), 4.57 (d, *J* = 11.4 Hz, 1 H, $OC\underline{H_2}Ph$), 4.45 (d, *J* = 12.2 Hz, 1 H, $OC\underline{H_2}Ph$), 4.35 (d, *J* = 12.2 Hz, 1 H, $OC\underline{H_2}Ph$), 4.30 (dt, *J* = 7.0, 1.2 Hz, 1 H, H-2), 3.95 (dd, *J* = 10.0, 7.2 Hz, 1 H , H-4), 3.90 (dt, *J* = 10.0, 2.7 Hz, 1 H, H-5), 3.79 (t, *J* = 7.0 Hz, 1 H, H-3), 3.70 (d, *J* = 2.6 Hz, 2 H, H-6 + H-6'), 3.17 (s, 3 H, $OCH_2OC\underline{H_3}$).

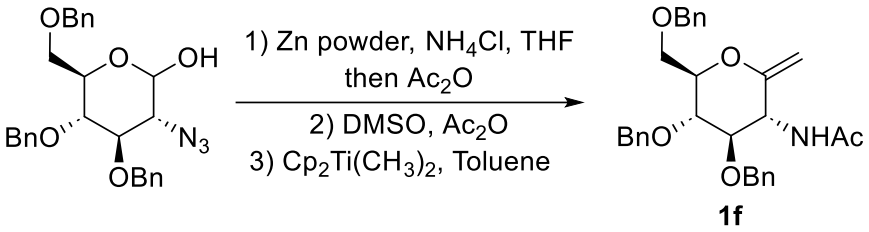
^{13}C NMR (125 MHz, $CDCl_3$) δ 157.21 (C-1), 139.12 (Cq_{Ar}), 139.05 (Cq_{Ar}), 138.97 (Cq_{Ar}), 128.59 (CH_{Ar}), 128.57 (CH_{Ar}), 128.50 (CH_{Ar}), 128.35 (3 x CH_{Ar}), 128.15 (2 x CH_{Ar}), 127.97 (2 x CH_{Ar}), 127.95 (3 x CH_{Ar}), 127.74 (CH_{Ar}), 127.71 (CH_{Ar}), 95.80 ($O\underline{C}H_2OCH_3$), 94.30 (C-1=$\underline{C}H_2$), 85.06 (C-3), 78.99 (C-5), 78.36 (C-4), 75.68 (C-2), 74.43 ($O\underline{C}H_2Ph$), 74.04 ($O\underline{C}H_2Ph$), 73.65 ($O\underline{C}H_2Ph$), 69.36 (C-6), 55.80 ($OCH_2O\underline{C}H_3$).

Opt. rot. $[\alpha]_D^{20}$: +33.3 (*c* 0.38, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{30}H_{34}O_6Na$ $[M+Na]^+$: 513.2248, found: 513.2245.

IR (film): v 2894, 1661, 1497, 1454, 1362, 1210, 1150, 1087, 1028 cm^{-1}.

2-Acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-*exo*-D-glucal (1f)[6]



1f

To a solution of 2-azido-3,4,5-tri-*O*-benzyl-2-deoxy-D-glucopyranose[7] (151 mg, 0.32 mmol, 1 equiv) in distilled THF (12.5 mL) under Ar, activated zinc powder (207 mg, 3.18 mmol, 10 equiv) and NH_4Cl (170 mg, 3.18 mmol, 10 equiv) were added. The reaction mixture was then refluxed for 5 min then cooled to room temperature, after what Ac_2O (0.75 mL, 7.94 mmol, 25 equiv) was added. The mixture was then stirred at room temperature during 1 h. A saturated aqueous solution of $NaHCO_3$ (50 mL) was then added and the mixture was stirred for 15 min. The reaction mixture was then filtered through a Celite® pad rinsed with EtOAc (150 mL). Layers were separated, and the aqueous layer was further extracted with EtOAc (30 mL). Organic layers were combined and washed with water (30 mL), brine (30 mL), were dried over Na_2SO_4, filtered and concentrated yielding the crude 2-acetamido-3,4,5-tri-*O*-benzyl-2-deoxy-D-glucopyranose intermediate (148 mg, 0.300 mmol, 94%) as a yellow amorphous solid, pure enough (according to ^1H NMR analysis) to be engaged in the next step without further purification.

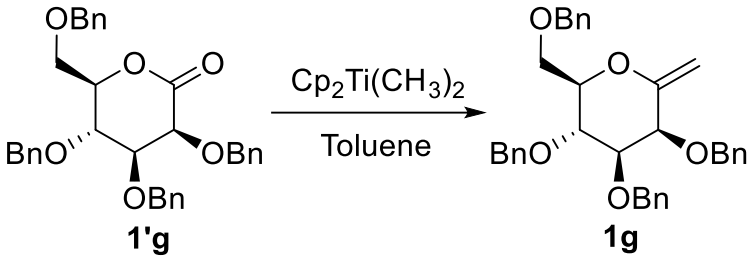
To a solution of 2-acetamido-3,4,5-tri-*O*-benzyl-2-deoxy-D-glucopyranose (139 mg, 0.28 mmol, 1 equiv) in dry DMSO (3.00 mL, 42.4 mmol, 150 equiv) under Ar, was added Ac_2O (0.90 mL, 9.90 mmol, 35 equiv) dropwise, and the mixture was stirred overnight at room temperature. The reaction mixture was dissolved in Et_2O (50 mL) and the mixture was washed with water (3 x 100 mL) and brine (2 x 100 mL). The organic layer was then dried over Na_2SO_4, filtered and concentrated yielding the crude 2-acetamido-3,4,5-tri-*O*-benzyl-2-deoxy-D-gluconolactone intermediate (**1'f**) (118 mg, 0.240 mmol, 85%) as a yellow amorphous solid. This lactone was found to be unstable on silica gel and was thus directly olefinated without purification.

Following the **GPA** starting from 2-acetamido-3,4,5-tri-*O*-benzyl-2-deoxy-D-gluconolactone **1'f** (110 mg, 0.22 mmol, 1 equiv) with dimethyltitanocene (0.76 M in toluene, 3 equiv), **1f** was yielded (36.0 mg, 0.0700 mmol, 33% over two steps) as a white amorphous solid after purification by column chromatography (SiO_2, Cyclohexane/EtOAc: 60/40 + 0.5% Et_3N).

^{1}H NMR (400 MHz, dimethyl sulfoxide-d6) δ 8.31 (d, *J* = 9.0 Hz, 1 H, N<u>H</u>(CO)CH_3), 7.31-7.23 (m, 13 H, HAr), 7.21-7.15 (m, 2 H, HAr), 4.76-4.65 (m, 3 H, OC<u>H_2</u>Ph), 4.59-4.47 (m, 4 H, OC<u>H_2</u>Ph and C1=C<u>H_2</u>), 4.42-4.35 (m, 2 H, C1=C<u>H_2</u> and H-2), 3.71-3.62 (m, 3 H, H-4, H-6 and H-6'), 3.57-3.48 (m, 2 H, H-3 and H5), 1.89 (s, 3 H, NH(CO)C<u>H_3</u>) ; in accordance with literature data.[6]

[6] Y. Leshch *et al.*, *Org. Lett.*, 2013, **15**, 4948.
[7] T. Yamanoi *et al.*, *Heterocycles*, 2012, **84**, 1335.

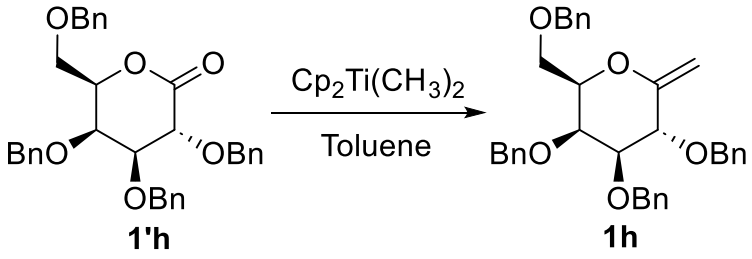
1-Methylidene-2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (1g)[8]



Following the **GPA** starting from 2,3,4,6-tetra-*O*-benzyl-D-mannolactone (**1'g**)[9] (500 mg, 0.93 mmol, 1 equiv) with dimethyltitanocene (0.76 M in toluene, 2.5 equiv), **1g** was yielded (364 mg, 0.68 mmol, 73%) as a yellow oil after purification by column chromatography (SiO_2, Cyclohexane/EtOAc: 95/5 to 90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.25 (m, 18 H, H_{Ar}), 7.19-7.17 (m, 2 H, H_{Ar}), 4.92 (d, *J* = 10.8 Hz, 1 H, OCH_2Ph), 4.83 (pseudo s, 1 H, C-1=CH_2), 4.76 (d, *J* = 12.6 Hz, 1 H, OCH_2Ph), 4.67 (d, *J* = 12.1 Hz, 1 H, OCH_2Ph), 4.62 (d, *J* =11.9 Hz, 1 H, OCH_2Ph), 4.59-4.51 (m, 3 H, OCH_2Ph), 4.43 (d, *J* = 12.6 Hz, 1 H, OCH_2Ph), 4.38 (d, *J* = 0.7 Hz, 1 H, C-1=CH_2), 4.17 (t, *J* = 9.2 Hz, 1 H, H-4), 4.07 (d, *J* = 3.3 Hz, 1 H, H-2), 3.81 (dd, *J* = 10.5, 4.0 Hz, 1 H, H-6), 3.78 (overlapped dd, *J* = 10.5, 2.4 Hz, 1 H, H-6'), 3.66 (dd, *J* = 9.1, 3.2 Hz, 1 H, H-3), 3.62 (m, 1 H, H-5) ; in accordance with literature data.[8]

2,3,4,6-Tetra-*O*-benzyl-*exo*-D-galactal (1h)[10]



Following the **GPA** starting from 2,3,4,6-tetra-*O*-benzyl-D-galactonolactone (**1'h**)[10] (350 mg, 0.65 mmol, 1 equiv) with dimethyltitanocene (0.76 M in toluene, 2.5 equiv), **1h** was yielded (318 mg, 0.559 mmol, 91%) as a yellow oil after purification by column chromatography (SiO_2, Cyclohexane/EtOAc: 95/5 to 90/10).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.27 (m, 20 H, H_{Ar}), 4.93 (d, *J* = 11.5 Hz, 1 H, OCH_2Ph), 4.78 (d, *J* = 11.9 Hz, 1 H, OCH_2Ph), 4.75 (d, *J* = 1.4 Hz, 1 H, overlapped C-1=CH_2), 4.75-4.70 (m, 3 H, overlapped OCH_2Ph), 4.71 (d, *J* = 1.3 Hz, 1 H, overlapped C-1=CH_2), 4.60 (d, *J* = 11.5 Hz, 1 H, OCH_2Ph), 4.52 (d, *J* = 11.8 Hz, 1 H, OCH_2Ph), 4.45 (d, *J* = 11.8 Hz, 1 H, OCH_2Ph), 4.37 (dt, *J* = 9.0, 1.5 Hz, 1 H, H-2), 4.06 (t, *J* = 2.4 Hz, 1 H, H-4), 3.82 (td, *J* = 6.3, 1.9 Hz, 1 H, H-5), 3.70 (dd, *J* = 9.7, 6.1 Hz, 1 H, H-6), 3.67 (dd, *J* = 9.0, 2.9 Hz, 1H, H-3), 3.63 (dd, *J* = 9.7, 6.6 Hz, 1H, H-6') ; in accordance with literature data.[10]

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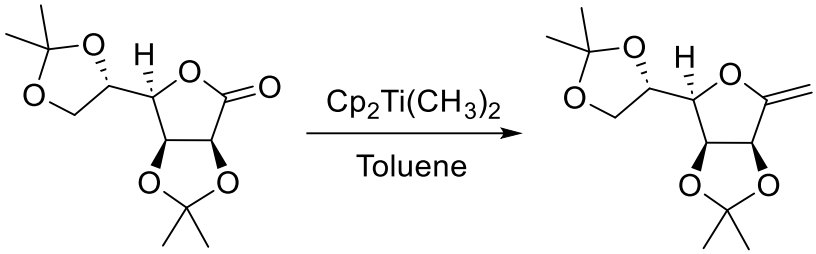
[8] J. Regier *et al.*, *J. Org. Chem.*, 2022, **87**, 524.
[9] J. Brunckova *et al.*, *Tetrahedron,* 1995, **51**, 11945.
[10] C. J.-M. Frédéric *et al.*, *Org. Lett.*, 2018, **20**, 6769.

1-Methylidene-2,3:5,6-di-*O*-*iso*propylidene-α-D-mannofuranoside (1i)[11]

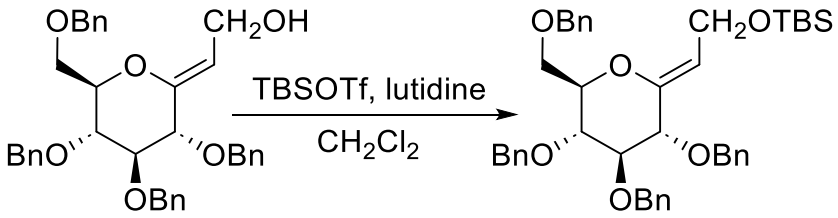


1'i **1i**

2,3,5,6-Di-*O*-*iso*propylidene-D-mannono-1,4-lactone (**1'i**)[2] (400 mg, 1.55 mmol, 1 equiv) and 2-(methylsulfonyl)benzo[d]thiazole (396 mg, 1.86 mmol, 1.2 equiv) were dissolved in dry THF (6 mL) under Ar and cooled to -78 °C. LiHMDS (1.0 M in THF, 3.72 mL, 3.72 mmol, 2.4 equiv) was then added dropwise over 5 min and the mixture was stirred at -78 °C for 2 h. The reaction was quenched by addition of AcOH (0.27 mL, 4.65 mmol, 3 equiv). The mixture was warmed up to room temperature then water (40 mL) was added and the aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The dark brown oil obtained was then dissolved in dry THF (15 mL) under Ar and DBU (0.46 mL, 3.01 mmol, 2 equiv) was added slowly at room temperature. The mixture turned immediately to an orange solution and was stirred at room temperature overnight. The reaction mixture was concentrated under reduced pressure and the obtained crude was purified by column chromatography (SiO_2, Cyclohexane/EtOAc: 90/10 to 80/20) yielding **1i** (228 mg, 0.89 mmol, 57%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (dt, *J* = 6.1, 1.2 Hz, 1 H, H-2), 4.65 (dd, *J* = 6.1, 4,3 Hz, 1 H, H- 3), 4.61 (t, *J* = 1.7 Hz, 1 H, C-1=C$\underline{H}_2$), 4.42 (dt, *J* = 8.4, 6.8 Hz, 1 H, H-5), 4.28 (dd, *J* = 2.0, 1.0 Hz, 1 H, C-1=C$\underline{H}_2$), 4.22 (dd, *J* = 8.6, 6.7 Hz, 1 H, H-6), 4.07 (dd, *J* = 8.4, 4.4 Hz, 1 H, H-4), 3.73 (dd, *J* = 8.6, 7.0 Hz, 1 H, H-6'), 1.47 (s, 3 H, C(C$\underline{H}_3$)$_2$), 1,46 (s, 3 H, C(C$\underline{H}_3$)$_2$), 1.40 (s, 3 H, C(C$\underline{H}_3$)$_2$), 1.34 (s, 3 H, C(C$\underline{H}_3$)$_2$) ; in accordance with literature data.[11]

Tert-butyldimethyl((*Z*)-2-(3,4,6-tri-*O*-benzyl-2-*O*-triisopropylsilyl)tetrahydro-2*H*-pyran-2-ylidene)ethoxy)silane (1j)[2]



1j

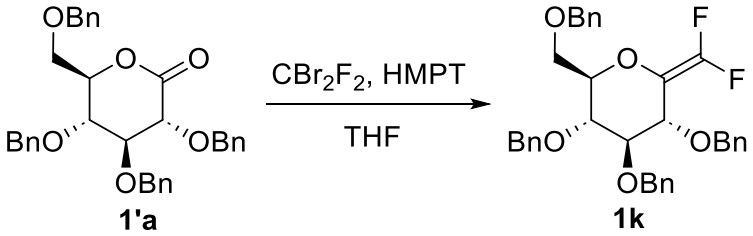
To a solution of *(Z)*-2-((3*R*,4*S*,5*R*,6*R*)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2*H*-pyran-2-ylidene)ethan-1-ol[2] (350 mg, 0.62 mmol, 1 equiv) in dry CH_2Cl_2 (15 mL) under Ar at 0 °C was added lutidine (0.11 mL, 0.93 mmol, 1.5 equiv) and TBSOTf (0.21 mL, 0.93 mmol, 1.5 equiv). The reaction mixture

[11] R. Csuk *et al.*, *Tetrahedron*, 1991, **47**, 1655.

was then stirred at room temperature for 2 h, then quenched by addition of a saturated aqueous solution of $NaHCO_3$ (10 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by column chromatography (SiO_2, Cyclohexane/EtOAc: 95/5) yielding **1j** (362 mg, 0.53 mmol, 86%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.06 (m, 20 H, H_{Ar}), 5.09 (td, *J* = 6.5, 1.2 Hz, 1 H, C<u>H</u>-C<u>H</u>$_2$-OH), 4.76 (d, *J* = 11.3 Hz, 1 H, OC<u>H</u>$_2$Ph), 4.70 (d, *J* = 10.7 Hz, 1 H, OC<u>H</u>$_2$Ph), 4.68 (d, *J* = 11.3 Hz, 1 H, OC<u>H</u>$_2$Ph), 4.62 (d, *J* = 11.2 Hz, 1 H, OC<u>H</u>$_2$Ph), 4.57 (d, *J* = 11.6 Hz, 1 H, OC<u>H</u>$_2$Ph), 4.54 (d, *J* = 10.4 Hz, 1 H, OC<u>H</u>$_2$Ph), 4.46 (d, *J* = 12.2 Hz, 1 H, OC<u>H</u>$_2$Ph), 4.45 (d, *J* = 11.1 Hz, 1 H, OC<u>H</u>$_2$Ph), 4.34 (ddd, *J* = 12.6, 6.7, 0.8 Hz, 1 H, CH-C<u>H</u>$_2$-OTBS), 4.26 (ddd, *J* = 12.8, 6.1, 1.2 Hz, 1 H, CH-C<u>H</u>$_2$-OTBS), 3.85 (dd, *J* = 6.5, 1.2 Hz, 1 H, H-2), 3.73-3.60 (m, 5 H, H-3, H-4, H-5, H-6 and H-6'), 0.83 (s, 9 H, OSi(CH$_3$)$_2$C(C<u>H</u>$_3$)$_3$), 0.00-0.01 (m, 6 H, OSi(C<u>H</u>$_3$)$_2$C(CH$_3$)$_3$) ; in accordance with literature data.[2]

2,6-Anhydro-1-deoxy-1,1-difluoro-3,4,5,7-tetrakis-*O*-benzyl-D-gluco-hept-1-enitol (1k)[12]



To a solution of 2,3,4,6-tetra-*O*-benzyl-D-gluconolactone[3] (200 mg, 0.37 mmol, 1 equiv) in distilled THF (20 mL) under Ar at -15 °C was added CBr_2F_2 (0.17 mL, 1.86 mmol, 5 equiv) followed by tris(dimethylamino)phosphine (340 µL, 1.86 mmol, 5 equiv). The reaction mixture was stirred at -15 °C for 1 h, then tris(dimethylamino)phosphine (0.68 mL, 3.71 mmol, 10 equiv) was added again and the reaction mixture was heated to 45 °C for 2 h. The mixture was then cooled to room temperature and was concentrated under vacuum. The obtained residue was dissolved in Et_2O (30 mL) and the solution was washed with water (2 x 15 mL), with a saturated aqueous solution of $CuSO_4$ (3 x 15 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude was purified by column chromatography (SiO_2, Cyclohexane/EtOAc: 98/2) yielding **1k** (101 mg, 0.180 mmol, 48%) as a colorless oil.

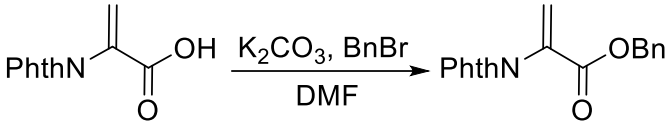
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.16 (m, 20 H, H_{Ar}), 4.73-4.38 (m, 8 H, OC<u>H</u>$_2$Ph), 4.25 (t, *J* = 3.8 Hz, 1 H), 4.07 (ddd, *J* = 9.8, 4.0, 2.6 Hz, 1 H, H-5), 3.87 (ddd, *J* = 5.7, 4.2, 1.5 Hz, 1 H, H-3), 3.78-3.72 (m, 3 H, H-4, H-6, H-6') ; in accordance with literature data.[12]

[12] J. Sarah Houlton *et al.*, *Tetrahedron*, 1993, **49**, 8087.

3. Preparation and characterization of radical acceptors 2

Achiral radical acceptors

Benzyl 2-(phthalimidoyl)acrylate (2a)



2' **2a**

To a solution of 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (1.00 g, 4.60 mmol, 1 equiv) in dry DMF (15.0 mL) under Ar were added K_2CO_3 (1.27 g, 9.21 mmol, 1.5 equiv) and BnBr (0.830 mL, 6.91 mmol, 1.5 equiv). The mixture was then stirred during 48 h at room temperature. The reaction mixture was then diluted with Et_2O (75 mL) and the organic layer was washed with water (2 x 50 mL) and brine (50 mL). The combined aqueous layers were extracted with Et_2O (3 x 30 mL). The combined organic layers were then washed with brine (2 x 50 mL), dried over Na_2SO_4, filtered and concentrated under vacuum.The crude ester was then purified by recrystallisation (EtOAc/*n*-hexane) yielding **2a** (985 mg, 3.21 mmol, 70%) as a yellowish amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (dd, J = 5.5, 3.1 Hz, 2 H, Ch from NPhth), 7.77 (dd, J = 5.5, 3.1 Hz, 2 H, CH from NPhth), 7.39-7.28 (m, 5 H, H_{Ar}), 6.71 (d, J = 0.7 Hz, 1 H, CH_2=Cq), 6.02 (d, J =0.7 Hz, 1 H, CH_2=Cq), 5.26 (s, 2 H, CH_2Ph).

^{13}C NMR (125 MHz, $CDCl_3$) δ 165.54 (CO from NPhth), 162.26 (COOBn), 135.27 (CqAr), 134.63 (CH from NPhth), 131.93 (Cq=CH_2), 129.28 (Cq from NPhth), 128.70 (2 x CH_{Ar}), 128.52 (CH_{Ar}), 128.41 (Cq=CH_2), 128.31 (2 x CH_{Ar}), 124.05 (CH from NPhth), 67.81 (CH_2Ph).

HRMS (*m/z*): calcd for $C_{18}H_{13}NO_4Na$ $[M+Na]^+$: 330.0737, found: 330.0745.

IR (film) ν: 1786, 1715, 1638, 1398, 1368, 1290, 1204, 1136, 1113, 886, 736, 714, 528 cm^{-1}.

p-Methoxybenzyl 2-(phthalimidoyl)acrylate (2b)

2' **2b**

To a solution of 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (397 mg, 2.53 mmol, 1 equiv) in dry DMF (7.50 mL) under Ar were added K_2CO_3 (636 mg, 2.30 mmol, 2 equiv) and 4-methoxybenzylchloride (0.340 mL, 2.53 mmol, 1.1 equiv). The mixture was then stirred during 16 h at room temperature. Then 0.3 equiv of 4-methoxybenzylchloride were added again. The reaction mixture was then stirred for

[13] Z. Wang *et al.*, *Angew. Chem., Int. Ed.*, 2023, **62**, e202305987.

72 additional hours. The reaction mixture was then diluted with Et_2O (35 mL) and the organic layer was washed with water (2 x 30 mL) and brine (2 x 30 mL). The combined aqueous layers were extracted with Et_2O (3 x 30 mL). The combined organic layers were then washed with brine (2 x 30 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The crude was recrystallized by dissolution in a minimum of CH_2Cl_2 on which a layer of hexane was added without perturbating the CH_2Cl_2-layer, yielding **2b** (535 mg, 1.59 mmol, 69%) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 5.5, 3.1 Hz, 2H, C<u>H</u> from NPhth), 7.77 (dd, J = 5.5, 3.1 Hz, 2H, C<u>H</u> from NPhth), 7.33-7.25 (m, 2H, H_{Ar}), 6.91-6.83 (m, 2H, H_{Ar}), 6.68 (d, J = 0.7 Hz, 1H, C<u>H_2</u>=Cq), 5.99 (d, J =0.7 Hz, 1H, C<u>H_2</u>=Cq), 5.19 (s, 2H, C<u>H_2</u>-Ar), 3.80 (s, 3H, Ar-OC<u>H_3</u>).

^{13}C NMR (100 MHz, $CDCl_3$) δ 166.53 (<u>C</u>O from NPhth), 162.23 (<u>C</u>OOPMB), 159.87 (CqAr), 134.60 (<u>C</u>H from NPhth), 131.94 (<u>Cq</u>=CH_2), 130.25 (CH_{Ar}), 129.38 (Cq from NPhth), 128.22 (<u>C</u>H_2=Cq), 127.38 (Cq_{Ar}), 124.03 (<u>C</u>H from NPhth), 114.07 (CH_{Ar}), 67.71 (<u>C</u>H_2-Ar), 55.39 (Ar-O<u>C</u>H_3).

HRMS (*m/z*): calcd for $C_{19}H_{15}NO_5Na$ $[M+Na]^+$: 360.0842, found: 360.0860.

IR (film): v 3022, 1720, 1515, 1392, 1287, 1248, 1140, 886, 748, 667 cm^{-1}.

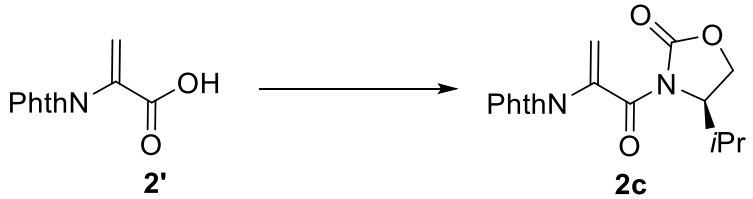
Enantiopure radical acceptors

General Procedure B for the synthesis of enantiopure radical acceptors (**GPB**)

To a solution of 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (1.3 equiv) in distilled THF (0.2 M) under Ar at -78 °C was added distilled Et_3N (1.9 equiv) and PivCl (1.4 equiv). The reaction mixture was stirred during 15 min at -78 °C then warmed to room temperature and stirred for 2 h. The reaction mixture was then cooled again to -78 °C and the corresponding oxazolidinone (1 equiv) and anhydrous LiCl (1.3 equiv) were added. The reaction mixture was then stirred for 16 h at room temperature. Celite® (5.0 g/mmol of product) was added to the mixture before removing the solvent by rotary evaporation. This adsorbed reaction mixture was then directly loaded onto a column of silica gel and eluted (Cyclohexane/EtOAc: 80/20) to afford the pure product.

Note : oxazolidinone-bearing DHA derivatives tend to decompose over time in wet $CDCl_3$, thus delayed 500 MHz ^{1}H and 125 MHz ^{13}C acquisitions may lead to impurities on NMR spectra initially showing pure product. Recrystallization of these compounds from hot solvents typically result in loss of material.

(R)-2-(3-(4-Isopropyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2c)



Following the **GPB** starting from 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (200 mg, 0.92 mmol) and commercially available *(R)*-4-isopropyloxazolidin-2-one (91 mg, 0.71 mmol), **2c** was obtained (90 mg, 0.28 mmol, 39%) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 5.5, 3.1 Hz, 2 H, C<u>H</u> from NPhth), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2 H, C<u>H</u> from NPhth), 6.12 (d, *J* = 1.5 Hz, 1H, Cq=C<u>H_2</u>), 5.82 (d, *J* = 1.4 Hz, 1 H, Cq=C<u>H_2</u>), 4.55 (dt, *J* = 8.4, 3.7 Hz, 1 H, <u>C</u>H-CH2-O), 4.32 (t, *J* = 8.8 Hz, 1 H, CH-C<u>H_2</u>-O), 4.22 (dd, *J* = 9.1, 3.7 Hz, 1 H, CH-C<u>H_2</u>-O), 2.51 (heptd, *J* = 7.0, 3.7 Hz, 1 H, C<u>H</u>-$(CH_3)_2$), 0.96 (d, *J* = 7.1 Hz, 3 H, CH-(C<u>H_3</u>)$_2$), 0.93 (d, *J* = 6.8 Hz, 3 H, CH-(C<u>H_3</u>)$_2$).

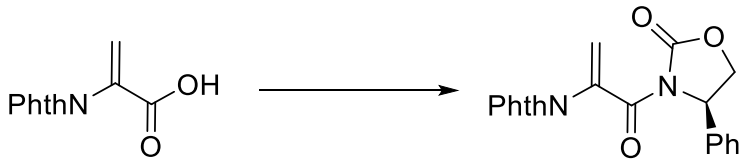
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.94 (2 x <u>C</u>O from NPhth), 164.33 (CH_2=Cq-(<u>C</u>O)), 153.31 (N-(<u>C</u>O)-O), 134.80 (2 x CH from NPhth), 131.59 (<u>C</u>q=CH_2), 131.54 (2 x Cq from NPhth), 124.15 (2x CH from NPhth), 117.56 (Cq=<u>C</u>H_2), 64.03 (O-<u>C</u>H_2-CH), 59.08 (O-CH_2-<u>C</u>H), 28.54 (<u>C</u>H$(CH_3)_2$), 18.20 (CH(<u>C</u>$H_3)_2$), 14.94 (<u>C</u>H$(CH_3)_2$).

Opt. rot. $[\alpha]_D^{20}$: -22.1 (*c* 1.10, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{17}H_{16}N_2O_5Na$ $[M+Na]^+$: 351.0951, found: 351.0967.

IR (film): v 2965, 1784, 1723, 1693, 1383, 1304, 1205, 886, 714 cm^{-1}.

(R)-2-(3-Oxo-3-(2-oxo-4-phenyloxazolidin-3-yl)prop-1-en-2-yl)phthalimide (2d)



2' **2d**

Following the **GPB** starting from 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (900 mg, 4.14 mmol) and commercially available *(R)*-4-phenyloxazolidin-2-one (520 mg, 3.18 mmol, 1 equiv), **2d** was obtained (180 mg, 0.5 mmol, 16%) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.1 Hz, 2 H, C<u>H</u> from NPhth), 7.75 (dd, *J* = 5.5, 3.1 Hz, 2 H, C<u>H</u> from NPhth), 7.48-7.31 (m, 5 H, H_{Ar}), 6.12 (d, *J* = 1.5 Hz, 1 H, Cq=CH_2), 5.86 (d, *J* = 1.5 Hz, 1 H, Cq=CH_2), 5.51 (dd, *J* = 8.7, 5.4 Hz, 1 H, C<u>H</u>-CH_2-O), 4.71 (t, *J* = 8.8 Hz, 1 H, CH-C<u>H_2</u>-O), 4.25 (dd, *J* = 8.9, 5.4 Hz, 1 H, CH-C<u>H_2</u>-O).

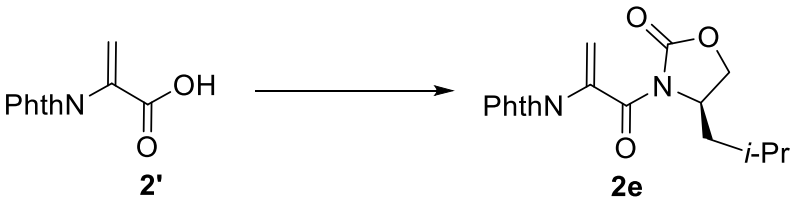
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.84 (2 x CO from NPhth), 163.78 (CH_2=Cq-(<u>C</u>O)), 152.96 (N-(<u>C</u>O)-O), 137.82 (Cq_{Ar}), 134.76 (2 x <u>C</u>H from NPhth), 131.47 (<u>C</u>q=CH_2), 131.00 (2 x Cq from NPhth), 129.22 (2 x CH_{Ar}), 128.95 (CH_{Ar}), 126.38 (2 x CH_{Ar}), 124.08 (2 x <u>C</u>H from NPhth), 118.82 (Cq=<u>C</u>H_2), 70.59 (CH-<u>C</u>H_2-O), 58.63 (<u>C</u>H-CH_2-O).

Opt. rot. $[\alpha]_D^{20}$: -71.8 (*c* 1.00, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{20}H_{14}N_2O_5Na$ $[M+Na]^+$: 385.0795, found: 385.0796.

IR (film): v 2923, 1784, 1721, 1381, 1321, 1208, 1082, 886, 754 cm^{-1}.

(R)-2-(3-(4-Isobutyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2e)



Following the **GPB** starting from 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (200 mg, 0.92 mmol) and commercially available *(R)*-4-isobutyloxazolidin-2-one (101 mg, 0.71 mmol, 1 equiv), **2e** was obtained (45 mg, 0.13 mmol, 18%) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, *J* =5.5, 3.1 Hz, 2 H, C<u>H</u> from NPhth), 7.76 (dd, *J* = 5.5, 3.1 Hz, 2 H, C<u>H</u> from NPhth), 6.10 (d, *J* = 1.3 Hz, 1 H, Cq=C<u>H$_2$</u>), 5.89 (d, *J* = 1.3H, 1 H, Cq=C<u>H$_2$</u>), 4.58 (dddd, *J* = 10.1, 7.9, 4.5, 3.5 Hz, 1 H, N-C<u>H</u>-CH$_2$), 4.45 (ddd, *J* = 8.7, 8.1, 0.8 Hz, 1 H, CH-C<u>H$_2$</u>-O), 4.09 (dd, *J* = 8.7, 4.6 Hz, 1 H, CH-C<u>H$_2$</u>-O), 2.06 (dddd, *J* = 13.5, 9.8, 3.2, 0.8 Hz, 1 H, C<u>H$_2$</u>-CH-(CH$_3$)$_2$), 1.70-1.58 (m, 1 H, C<u>H</u>-(CH$_3$)$_2$), 1.51 (ddd, *J* = 10.2, 1.4, 4.9 Hz, 1 H, C<u>H$_2$</u>-CH-(CH$_3$)$_2$), 1.00 (d, *J* = 6.6 Hz, 6 H, CH-(C<u>H$_3$</u>)$_2$).

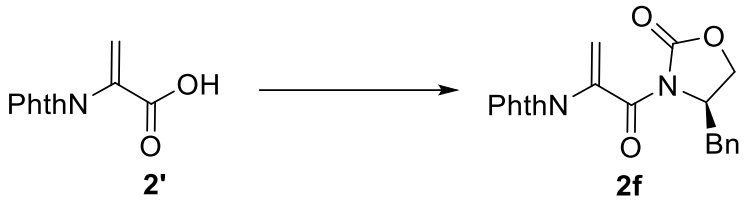
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.89 (2 x CO from NPhth), 164.21 (CH$_2$=Cq-(<u>C</u>O)), 152.91 (N-(<u>C</u>O)-O), 134.76 (CH from NPhth), 134.43 (CH from NPhth), 131.70 (<u>C</u>q=CH$_2$), 131.57 (2 x Cq from NPhth), 124.14 (CH from NPhth), 123.71 (CH from NPhth), 118.56 (Cq=<u>C</u>H$_2$), 68.59 (O-<u>C</u>H$_2$-CH), 53.79 (O-CH$_2$-<u>C</u>H), 40.99 (<u>C</u>H$_2$-CH-(CH$_3$)$_2$), 25.07 (<u>C</u>H(CH$_3$)$_2$), 23.60 (CH(<u>C</u>H$_3$)$_2$), 21.69 (<u>C</u>H(CH$_3$)$_2$).

Opt. rot. $[\alpha]_D^{20}$: -4.0 (*c* 1.25, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{18}H_{18}N_2O_5Na$ $[M+Na]^+$: 365.1108, found: 365.1110.

IR (film): v 2959, 1785, 1729, 1695, 1383, 1302, 1083, 886, 714 cm^{-1}.

(R)-2-(3-(4-Benzyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2f)



Following the **GPB** starting from 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (900 mg, 4.14 mmol) and commercially available *(R)*-4-benzyloxazolidin-2-one (564 mg, 3.18 mmol, 1 equiv), **2f** was yielded (780 mg, 2.07 mmol, 65%) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.5, 3.1 Hz, 2 H, C<u>H</u> from NPhth), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2 H, C<u>H</u> from NPhth), 7.37-7.24 (m, 5 H, H$_{Ar}$), 6.15 (d, *J* = 1.4 Hz, 1 H, Cq=C<u>H$_2$</u>), 5.91 (d, *J* = 1.4 Hz, 1 H, Cq=C<u>H$_2$</u>), 4.77 (dddd, *J* = 10.3, 7.8, 4.2, 3.4 Hz, 1 H, N-C<u>H</u>-CH$_2$Ph), 4.22 (dd, *J* = 9.3, 7.9 Hz, 1 H, O-C<u>H$_2$</u>-CH), 4.15 (dd, *J* = 9.1, 4.2 Hz, 1 H, O-C<u>H$_2$</u>-CH), 3.61 (dd, *J* = 13.5, 3.5 Hz, 1 H, C<u>H$_2$</u>Ph), 2.78 (dd, *J* = 13.5, 10.2 Hz, 1 H, C<u>H$_2$</u>Ph).

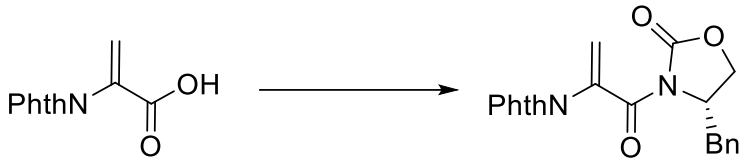
^{13}C NMR (100 MHz, $CDCl_3$) δ 165.94 (2 x CO from NPhth), 164.28 (CH_2=Cq-(<u>C</u>O)), 152.69 (N-(<u>C</u>O)-O-CH_2), 135.49 (Cq$_{Ar}$), 134.83 (2 x <u>C</u>H from NPhth), 131.61 (<u>C</u>q=CH_2), 131.57 (2 x Cq from NPhth), 129.52 (2 x <u>C</u>H$_{Ar}$), 129.14 (2 x <u>C</u>H$_{Ar}$), 127.47 (<u>C</u>H$_{Ar}$), 124.19 (2 x <u>C</u>H from NPhth), 118.37 (Cq=<u>C</u>H_2), 67.15 (O-<u>C</u>H_2-CH), 55.93 (O-CH_2-<u>C</u>H), 37.64 (<u>C</u>H_2Ph).

Opt. rot. $[\alpha]_D^{20}$: -19.5 (*c* 1.01, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{21}H_{16}N_2O_5Na$ $[M+Na]^+$: 399.0951, found: 399.0934.

IR (film): v 3029, 1788, 1723, 1694, 1384, 1354, 1306, 1233, 1082, 886, 713 cm^{-1}.

(S)-2-(3-(4-Benzyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2g)



2' **2g**

Following the **GPB** starting from 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (400 mg, 1.84 mmol) and commercially available *(S)*-4-benzyloxazolidin-2-one (251 mg, 1.41 mmol, 1 equiv), **2g** was obtained (330 mg, 0.85 mmol, 60%) as a white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.5, 3.0 Hz, 2 H, C<u>H</u> from NPhth), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2 H, C<u>H</u> from NPhth), 7.44-7.22 (m, 5 H, H$_{Ar}$), 6.15 (d, *J* = 1.4 Hz, 1 H, Cq=C<u>H</u>$_2$), 5.91 (d, *J* = 1.4 Hz, 1 H, Cq=C<u>H</u>$_2$), 4.77 (dddd, *J* = 10.2, 7.8, 4.2, 3.5 Hz, 1 H, N-C<u>H</u>-CH_2Ph), 4.22 (dd, *J* = 8.8, 8.0 Hz, 1 H, O-C<u>H</u>$_2$-CH), 4.15 (dd, *J* = 9.1, 4.1 Hz, 1 H, O-C<u>H</u>$_2$-CH), 3.61 (dd, *J* = 13.5, 3.4 Hz, 1 H, C<u>H</u>$_2$Ph), 2.78 (dd, *J* = 13.5, 10.2 Hz, 1 H, C<u>H</u>$_2$Ph).

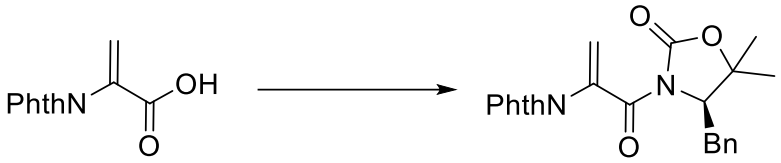
^{13}C NMR (125 MHz, $CDCl_3$) δ 165.94 (2 x CO from NPhth), 164.28 (CH_2=Cq-(<u>C</u>O)), 152.68 (N-(<u>C</u>O)-O-CH_2), 135.50 (Cq$_{Ar}$), 134.83 (2 x <u>C</u>H from NPhth), 131.61 (<u>C</u>q=CH_2), 131.58 (2 x Cq from NPhth), 129.52 (2 x <u>C</u>H$_{Ar}$), 129.14 (2 x <u>C</u>H$_{Ar}$), 127.47 (<u>C</u>H$_{Ar}$), 124.19 (2 x <u>C</u>H from NPhth), 118.35 (Cq=<u>C</u>H_2), 67.15 (O-<u>C</u>H_2-CH), 55.94 (O-CH_2-<u>C</u>H), 37.65 (<u>C</u>H_2Ph).

Opt. rot. $[\alpha]_D^{20}$: +13.3 (*c* 0.88, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{21}H_{16}N_2O_5Na$ $[M+Na]^+$: 399.0951, found: 399.0946.

IR (film): v 2925, 1788, 1724, 1694, 1384, 1306, 1234, 1082, 886, 713 cm^{-1}.

(R)-2-(3-(4-Benzyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2h)



2' **2h**

Following the **GPB** starting from 2-(1,3-dioxoisoindolin-2-yl)acrylic acid[13] (**2'**) (195 mg, 0.900 mmol) and *(R)*-4-benzyl-5,5-dimethyloxazolidin-2-one[14] (142 mg, 0.69 mmol, 1 equiv), **2h** was obtained (55 mg, 0.140 mmol, 20%) as a white amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.5, 3.1 Hz, 2 H, C<u>H</u> from NPhth), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2 H, C<u>H</u> from NPhth), 7.38-7.20 (m, 5 H, H_{Ar}), 6.12 (d, *J* = 1.3 Hz, 1 H, Cq=C<u>H_2</u>), 5.92 (d, *J* = 1.3 Hz, 1 H, Cq=C<u>H_2</u>), 4.58 (dd, *J* = 10.2, 3.7 Hz, 1 H, N-C<u>H</u>-CH_2Ph), 3.53 (dd, *J* = 14.4, 3.7 Hz, 1 H, C<u>H_2</u>-Ph), 2.87 (dd, *J* = 14.4, 10.2 Hz, 1 H, C<u>H_2</u>-Ph), 1.34 (s, 3 H, C(C<u>H_3</u>)$_2$), 1.29 (s, 3 H, C(C<u>H_3</u>)$_2$).

^{13}C NMR (100 MHz, $CDCl_3$) δ 165.98 (2 x CO from NPhth), 164.71 (CH_2=Cq-(<u>C</u>O)), 151.90 (N-(<u>C</u>O)-O-CH_2), 137.00 (Cq_{Ar}), 134.81 (2 x <u>C</u>H from NPhth), 131.78 (<u>C</u>q=CH_2), 131.62 (2 x Cq from NPhth), 129.25 (2 x <u>C</u>H_{Ar}), 128.86 (2 x <u>C</u>H_{Ar}), 127.04 (<u>C</u>H_{Ar}), 124.13 (2 x <u>C</u>H from NPhth), 118.77 (Cq=<u>C</u>H_2), 83.27 (CH-<u>C</u>(CH_3)$_2$), 64.51 (<u>C</u>H-C(CH_3)$_2$), 34.15 (<u>C</u>H_2-Ph), 28.21 (CH-C(<u>C</u>H_3)$_2$), 22.56 (CH-C(<u>C</u>H_3)$_2$).

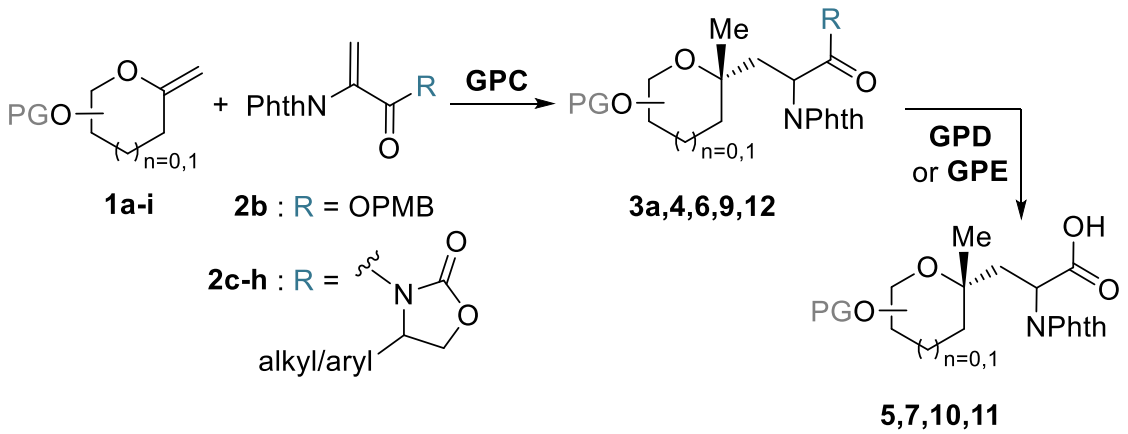
Opt. rot. $[\alpha]_D^{20}$: +31.1 (*c* 1.11, $CHCl_3$).

HRMS (*m/z*): calcd for $C_{23}H_{20}N_2O_5Na$ $[M+Na]^+$: 427.1264, found: 427.1258.

IR (film): v 1776, 1721, 1694, 1381, 1337, 1301, 1234, 1082, 886, 730, 713, 639 cm^{-1}.

[14] A. T. Herrmann *et al.*, *J. Am. Chem. Soc.*, 2012, **134**, 6976.

4. Synthesis and characterization of C,C-glycosyl aminoacid derivatives



General procedure C for the Fe-HAT coupling reaction (GPC)

*Example of protocol for 0.1 mmol of exo-glycal **1** (typically 30-35 mg):*

To a solution of *exo*-glycal (1 equiv) in previously degassed EtOH (0.03 M) under Ar at room temperature were added $Fe(acac)_3$ (10 mol%), Na_2HPO_4 (1.1 equiv) and the appropriate radical acceptor. The reaction mixture was then heated to 60 °C and phenylsilane (4 equiv) was added. The reaction mixture was then stirred under Ar at 60 °C for 4 h before being quenched by addition of brine (15 mL). The aqueous layer was then extracted with EtOAc (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum. The resulting crude coupling adduct was then hydrolyzed (see the general procedures D or E) or purified by chromatography (SiO_2, Cyclohexane/EtOAc).

General procedure D for the removal of oxazolidinone auxiliaries (GPD)

*(Following **GPC** the crude mixture is assumed to contain the Fe-HAT coupling adduct (1 equiv max) and the reduced acceptor (ca. 1 equiv))*

The crude was dissolved in H_2O/THF (1:2 v/v) (0.08 M) and the mixture was cooled to 0 °C and stirred. A solution of 30% aqueous H_2O_2 (10 equiv) and LiOH (4 equiv) in water (48 equiv) was added dropwise. The reaction mixture was then stirred for 15 min at 0 °C and 1.75 h at room temperature, after which a 2.0 M aqueous solution of sodium sulfite (9 equiv) was added at 0 °C and the reaction mixture was stirred for 10 additional min.

To the reaction mixture was then added a half saturated aqueous solution of $NaHCO_3$ (10 mL, pH ≃ 9-10). The mixture was then extracted with Et_2O (5 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum *(the reduced and hydrolyzed radical acceptor impurity (as carboxylate) remains in the basified water layer when extraction is performed with Et_2O)*. The crude mixture was purified by column chromatography (SiO_2, Cyclohexane/EtOAc: 80/20 + 1% AcOH) to obtain the desired deprotected carboxylic acid.

Chiral auxiliaries can be recovered by acidification of the aqueous layer (extracted previously with Et_2O) to pH = 2 then extraction with DCM. After drying over $MgSO_4$, filtration and concentration, the residue contains cleaved oxazolidinone and traces of (N-phtalimidoyl)alanine which can be removed by basic washes.

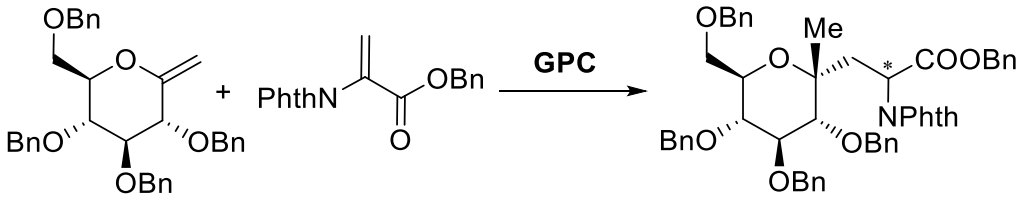
General procedure E for the deprotection of *p*-methoxybenzyl esters (GPE)

*(Following **GPC** the crude mixture is assumed to contain the Fe-HAT coupling adduct (1 equiv max) and the reduced acceptor (ca. 1 equiv))*

The crude was dissolved in dry CH_2Cl_2 (0.1 M). To this mixture under Ar was added 1.3-dimethoxybenzene (3 equiv) and TFA (14 equiv). The reaction mixture was stirred for 2 h at room temperature, then quenched by the addition of solid $NaHCO_3$ (≃ 50 mg) followed by a saturated aqueous solution of $NaHCO_3$ (10 mL). Most CH_2Cl_2 was then removed by rotary evaporation and the obtained mixture (pH ≃ 9) was extracted with Et_2O (5 x 10 mL). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under vacuum.

The residue was purified by column chromatography (SiO_2, Cyclohexane/EtOAc: 80/20 + 1% AcOH) to obtain the desired deprotected carboxylic acid.

Benzyl-2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoate (3a)



Following the **GPC** starting from **1a** (100 mg, 0.190 mmol, 1 equiv) and **2a** (115 mg, 0.370 mmol, 2 equiv), **3a** was yielded as a mixture of 2 diastereoisomers (d.r : 73:27, 122 mg, 0.140 mmol, 77%) as a colorless amorphous solid after purification of the crude by column chromatography (SiO_2, Cyclohexane/EtOAc: 95/5 to 85/15).

NMR attribution for the major diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.80 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.43-7.13 (m, 25 H, H_{Ar}), 5.27 (dd, *J* = 8.8, 2.0 Hz, 1 H, overlapped C-1-CH_2-C<u>H</u>), 5.23 (d, *J* = 12.4 Hz, 1 H, overlapped COOC<u>H_2</u>Ph), 5.12 (d, *J* = 12.4 Hz, 1 H, COOC<u>H_2</u>Ph),4.93 (d, *J* = 10.9 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.92 (d, *J* = 11.5 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.90 (d, *J* = 10.6 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.87 (d, *J* = 10.9 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.72 (d, *J* = 12.3 Hz, 1 H, OC<u>H_2</u>Ph), 4.69 (d, *J* = 11.7 Hz, 1 H, OC<u>H_2</u>Ph), 4.65 (d, *J* = 10.9 Hz, 1 H, OC<u>H_2</u>Ph), 4.60 (d, *J* = 12.2 Hz, 1 H, OC<u>H_2</u>Ph), 3.95 (t, *J* = 9.4 Hz, 1 H, H-3), 3.91 (dt, *J* = 10.2, 3.0 Hz, 1 H, H-5), 3.73 (d, *J* = 3.0 Hz, 2 H, H-6 and H-6'), 3.71 (t, *J* = 9.9 Hz, 1 H, H-4), 3.40 (d, *J* = 9.7 Hz, 1 H, overlapped H-2), 3.06 (dd, *J* = 16.5, 1.9 Hz, 1 H, C-1-C<u>H_2</u>-CH), 2.82 (dd, *J* = 16.3, 8.8 Hz, 1 H, C-1-C<u>H_2</u>-CH), 1.22 (s, 3 H, C1-C<u>H_3</u>).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.97 (<u>C</u>OOCH_2Ph), 167.70 (2 x CO from NPhth), 138.72 (Cq_{Ar}), 138.63 (Cq_{Ar}), 138.57 (Cq_{Ar}), 138.55 (Cq_{Ar}), 135.20 (Cq from COOCH_2<u>Ph</u>), 134.28 (2 x CH from NPhth), 132.05 (2 x Cq from NPhth), 128.61 (3 x CH_{Ar}), 128.50 (3 x CH_{Ar}), 128.44 (3 x CH_{Ar}), 128.41 (2 x CH_{Ar}), 128.38 (2 x CH_{Ar}), 128.01 (2 x CH_{Ar}), 127.96 (2 x CH_{Ar}), 127.91 (3 x CH_{Ar}), 127.86 (3 x CH_{Ar}), 127.54 (CH_{Ar}), 127.52 (CH_{Ar}),123.68 (2 x CH from NPhth), 86.77 (C-2), 83.94 (C-3), 79.02

(C-4), 76.65 (C-1), 75.70 (CH$_2$Ph), 75.61 (CH$_2$Ph), 74.94 (CH$_2$Ph), 73.53 (CH$_2$Ph), 72.68 (overlapped C-5), 69.17 (C-6), 67.88 (COOCH$_2$Ph), 47.52 (C-1-CH$_2$-CH), 29.32 (C-1-CH$_2$-CH), 25.33 (C-1-CH$_3$).

NMR attribution for the minor diastereoisomer:

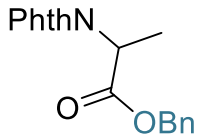
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.4, 3.0 Hz, 2 H, CH from NPhth), 7.71 (dd, J = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.43-7.13 (m, 25 H, H$_{Ar}$), 5.29-5.20 (m, 3 H, overlapped COOCH$_2$Ph and C-1-CH$_2$-CH), 4.99 (d, J = 11.3 Hz, 1 H, OCH$_2$Ph), 4.90 (d, J = 10.6 Hz, 2 H, 2 x overlapped OCH$_2$Ph), 4.82 (d, J = 10.8 Hz, 1 H, OCH$_2$Ph), 4.77 (d, J = 11.3 Hz, 1 H, OCH$_2$Ph), 4.53 (d, J = 10.7 Hz, 1 H, OCH$_2$Ph), 4.32 (d, J = 12.7 Hz, 1 H, OCH$_2$Ph), 4.18 (d, J = 12.7 Hz, 1 H, OCH$_2$Ph), 3.87 (t, J = 9.4 Hz, 1 H, H-3), 3.59 (t, J = 9.3 Hz, 1 H, H-4), 3.48 (ddd, J = 10.1, 3.8, 1.7 Hz, 1 H, overlapped H-5), 3.44 (dd, J = 9.3, 3.7 Hz, 1 H, overlapped H-6), 3.39 (d, J = 9.9 Hz, 1 H, overlapped H-2), 3.13 (dd, J = 9.3, 1.8 Hz, 1 H, H-6'), 2.91 (dd, J = 15.9, 3.8 Hz, 1 H, C-1-CH$_2$-CH), 2.88-2.79 (m, 1 H, overlapped C-1-CH$_2$-CH), 1.49 (s, 3 H, C1-CH$_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 169.59 (COOCH$_2$Ph), 167.81 (2 x CO from NPhth), 138.59 (Cq$_{Ar}$), 138.57 (Cq$_{Ar}$), 138.41 (Cq$_{Ar}$), 138.29 (Cq$_{Ar}$), 135.38 (Cq from COOCH$_2$Ph), 134.07 (2 x CH from NPhth), 132.15 (2 x Cq from NPhth), 128.66 (CH$_{Ar}$), 128.55 (CH$_{Ar}$), 128.46 (3 x CH$_{Ar}$), 128.36 (2 x CH$_{Ar}$), 128.34 (2 x CH$_{Ar}$), 128.32 (2 x CH$_{Ar}$), 128.30 (CH$_{Ar}$), 127.87 (2 x CH$_{Ar}$), 127.71 (3 x CH$_{Ar}$), 127.68 (3 x CH$_{Ar}$), 127.65 (2 x CH$_{Ar}$), 127.61 (2 x CH$_{Ar}$), 127.46 (CH$_{Ar}$), 123.53 (2 x CH from NPhth), 86.69 (C-2), 83.46 (C-3), 78.95 (C-4), 77.62 (C-1), 75.95 (CH$_2$Ph), 75.69 (CH$_2$Ph), 73.05 (CH$_2$Ph), 73.00 (CH$_2$Ph), 72.68 (overlapped C-5), 68.77 (C-6), 67.73 (COOCH$_2$Ph), 48.27 (C-1-CH$_2$-CH), 27.93 (C-1-CH$_2$-CH), 25.24 (C-1-CH$_3$).

HRMS (*m/z*): calcd for $C_{53}H_{51}NO_9Na$ $[M+Na]^+$: 868.3456, found: 868.3451.

IR (film): v 2923, 2854, 1744, 1714, 1454, 1386, 1259, 1087, 1067, 721, 696 cm^{-1}.

Benzyl 2-(phthalimidoyl)propanoate (4)



4

During column chromatography compound **4** was also isolated (63 mg, 0.200 mmol, 55% of the initial radical acceptor) as a white amorphous solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97-7.83 (m, 2 H, , CH from NPhth), 7.75-7.67 (m, 2 H, CH from NPhth), 7.37-7.22 (m, 5 H, HAr), 5.21 (d, J = 12.4 Hz, 1 H, (CO)CH$_2$Ph), 5.17 (d, J = 12.5 Hz, 1 H, (CO)CH$_2$Ph), 5.03 (q, J = 7.4 Hz, 1H, CH-CH$_3$), 1.73 (d, J = 7.4 Hz, 3 H, CH-CH$_3$)

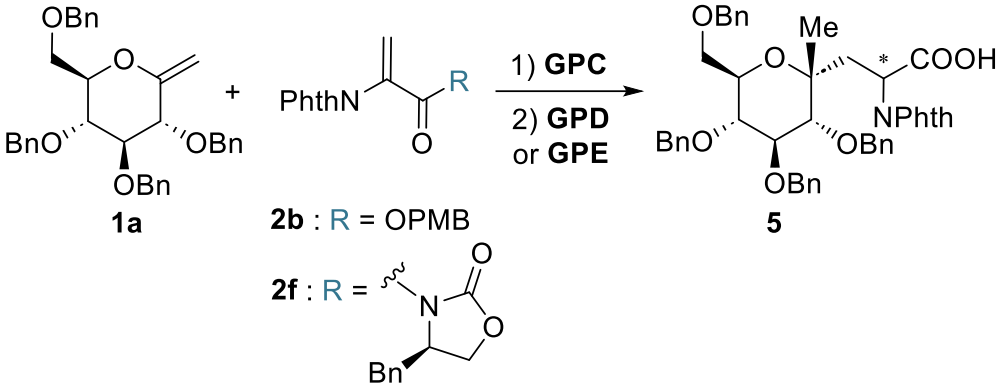
^{13}C NMR (125 MHz, $CDCl_3$) δ 169.71 ((CO)CH$_2$Ph), 167.52 (2 x CO from NPhth), 135.42 (CqAr), 134.26 (2 x CH from NPhth), 132.03 (2 x Cq from Nphth), 128.63 (2 x

CHAr), 128.40 (CHAr), 128.16 (2 x CHAr), 123.59 (2 x CH from NPhth), 67.58 ((CO)$\underline{C}H_2Ph$), 47.77 ($\underline{C}H$-CH_3), 47.77 (CH-$\underline{C}H_3$)

HRMS (*m/z*): calcd for $C_{18}H_{15}NO_4Na$ $[M+Na]^+$: 332.0893, found: 332.0895

IR (film): v 2923, 1780, 1713, 1388, 1223, 1146, 1078, 719 cm^{-1}

2-Phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoïc acid (5)



Using achiral acceptor 2b : Following the **GPC** and **GPE** (without intermediate purification) starting from **1a** (30.0 mg, 0.056 mmol, 1 equiv) and **2b** (37.7 mg, 0.110 mmol, 2 equiv), **5** was yielded as a mixture of 2 diastereoisomers (d.r : 73:27, 32.0 mg, 0.042 mmol, 76%) as a colorless amorphous solid.

With enantiopure acceptor 2f : Following the **GPC** and **GPD** (without intermediate purification) starting from **1a** (30.0 mg, 0.056 mmol, 1 equiv) and **2f** (42.1 mg, 0.110 mmol, 2 equiv), **5** was yielded as a mixture of 2 diastereoisomers (d.r : 88:12, 31.8 mg, 0.042 mmol, 75%) as a colorless amorphous solid.

NMR attribution for the major diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (dd, J = 5.4, 3.0 Hz, 2 H, CH from NPhth), 7.72 (dd, J = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.37-7.14 (m, 20 H, H_{Ar}), 5.14 (dd, J = 9.0, 2.0 Hz, 1 H, overlapped C-1-CH_2-$\underline{C}H$), 4.83 (d, J = 11.3 Hz, 2 H, overlapped O$\underline{C}H_2$Ph), 4.80 (d, J = 10.9 Hz, 2 H, overlapped O$\underline{C}H_2$Ph), 4.67 (d, J = 12.3 Hz, 1 H, O$\underline{C}H_2$Ph), 4.62 (d, J = 11.6 Hz, 1 H, O$\underline{C}H_2$Ph), 4.59 (d, J = 11.4 Hz, 1 H, overlapped O$\underline{C}H_2$Ph), 4.56 (d, J = 12.9 Hz, 1 H, overlapped O$\underline{C}H_2$Ph), 3.91 (t, J = 9.4 Hz, 1 H, H-3), 3.82 (dt, J = 10.2, 3.2 Hz, 1 H, overlapped H-5), 3.74 (d, J = 2.9 Hz, 2 H, H-6 and H-6'), 3.65 (t, J = 9.6 Hz, 1 H, H-4), 3.32 (d, J = 9.7 Hz, 1 H, overlapped H-2), 2.94 (dd, J = 16.1, 2.1 Hz, 1 H, C-1-C$\underline{H}_2$-CH), 2.76 (dd, J = 16.2, 9.2 Hz, 1 H, C-1-C$\underline{H}_2$-CH), 1.12 (s, 3 H, C1-C$\underline{H}_3$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.16 ($\underline{C}OOH$), 167.63 (2 x CO from NPhth), 138.77 (Cq_{Ar}), 138.55 (2 x Cq_{Ar}), 138.14 (overlapped Cq_{Ar}), 134.27 (2 x CH from NPhth), 132.07 (2 x Cq from NPhth), 128.55 (3 x CH_{Ar}), 128.46 (2 x CH_{Ar}), 128.44 (2 x CH_{Ar}), 128.40 (3 x CH_{Ar}), 128.21 (2 x CH_{Ar}), 127.92 (2 x CH_{Ar}), 127.90 (3 x CH_{Ar}), 127.56 (3 x CH_{Ar}), 123.73 (2 x CH from NPhth), 86.89 (C-2), 83.81 (C-3), 79.06 (C-4), 76.64 (C-1), 75.72 ($\underline{C}H_2$Ph), 75.65 ($\underline{C}H_2$Ph), 75.21 ($\underline{C}H_2$Ph), 73.59 ($\underline{C}H_2$Ph), 72.62 (C-5), 69.20 (C-6), 47.15 (overlapped C-1-CH_2-$\underline{C}H$), 28.98 (C-1-$\underline{C}H_2$-CH), 25.38 (C-1-$\underline{C}H_3$).

NMR attribution for the minor diastereoisomer:

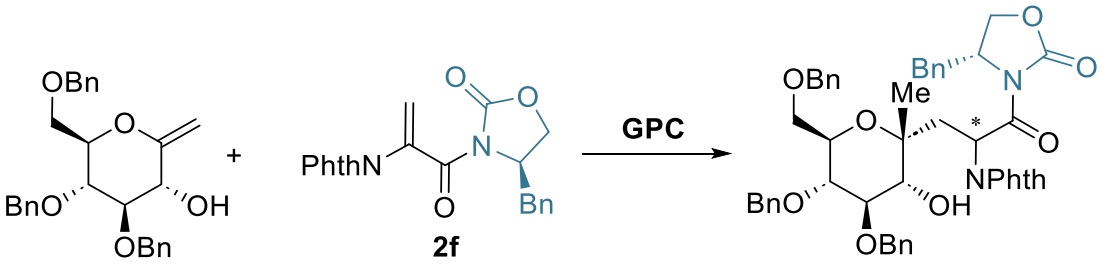
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.62 (dd, *J* = 5.4, 3.0 Hz, 2 H, CH from NPhth), 7.38-7.03 (m, 20 H, H_{Ar}), 5.14 (dd, *J* = 8.7, 4.1 Hz, 1 H, overlapped C-1-CH_2-CH), 4.91 (d, *J* = 11.3 Hz, 1 H, OCH_2Ph), 4.86 (d, *J* = 10.9 Hz, 2 H, 2 x overlapped OCH_2Ph), 4.74 (d, *J* = 10.7 Hz, 1 H, OCH_2Ph), 4.70 (d, *J* = 11.3 Hz, 1 H, OCH_2Ph), 4.45 (d, *J* = 10.8 Hz, 1 H, OCH_2Ph), 4.23 (d, *J* = 12.7 Hz, 1 H, OCH_2Ph), 4.08 (d, *J* = 12.7 Hz, 1 H, OCH_2Ph), 3.83 (t, *J* = 9.8 Hz, 1 H, overlapped H-3), 3.51 (t, *J* = 9.6 Hz, 1 H, H-4), 3.38 (ddd, *J* = 9.9, 4.0, 1.7 Hz, 1 H, H-5), 3.33 (dd, *J* = 10.1, 3.9 Hz, 1 H, overlapped H-6), 3.30 (d, *J* = 10.1 Hz, 1 H, overlapped H-2), 3.02 (dd, *J* = 10.7, 1.7 Hz, 1 H, H-6'), 2.73 (dd, *J* = 15.6, 4.1 Hz, 1 H, C-1-CH_2-CH), 2.74 (dd, *J* = 15.8, 9.3 Hz, 2 H, C-1-CH_2-CH), 1.39 (s, 3 H, C1-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.16 (COOH), 167.76 (2 x CO from NPhth), 138.50 (Cq_{Ar}), 138.38 (2 x Cq_{Ar}), 138.14 (overlapped Cq_{Ar}), 134.08 (2 x CH from NPhth), 132.14 (2 x Cq from NPhth), 128.55 (CH_{Ar}), 128.42 (2 x CH_{Ar}), 128.37 (2 x CH_{Ar}), 128.10 (2 x CH_{Ar}), 127.88 (CH_{Ar}), 127.81 (3 x CH_{Ar}), 127.75 (CH_{Ar}), 127.72 (CH_{Ar}), 127.66 (2 x CH_{Ar}), 127.64 (CH_{Ar}), 127.58 (CH_{Ar}), 127.48 (2 x CH_{Ar}), 127.43 (CH_{Ar}), 123.58 (2 x CH from NPhth), 86.64 (C-2), 83.40 (C-3), 79.01 (C-4), 77.60 (C-1), 76.02 (CH_2Ph), 75.15 (CH_2Ph), 73.03 (CH_2Ph), 72.92 (overlapped CH_2Ph), 72.92 (overlapped C-5), 68.73 (C-6), 47.15 (overlapped C-1-CH_2-CH), 27.70 (C-1-CH_2-CH), 25.11 (C-1-CH_3)

HRMS (*m/z*): calcd for $C_{46}H_{45}NO_9Na$ $[M+Na]^+$: 778.2987, found: 778.3020.

IR (film): v 3031, 2920, 1716, 1454, 1388, 1134, 1688, 737, 698 cm^{-1}.

2-(1-((*R*)-4-Benzyl-2-oxooxazolidin-3-yl)-3-(3,4,6-tri-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)-1-oxopropan-2-yl)phthalimide (6)



Following the **GPC** starting from **1d** (30.0 mg, 0.0670 mmol, 1 equiv) and **2f** (50.6 mg, 0.130 mmol, 2 equiv), **6** was yielded as a mixture of 2 diastereoisomers (d.r : 62:38, 13.0 mg, 0.016 mmol, 23%) as a white amorphous solid after purification of the crude by column chromatography (SiO_2, Cyclohexane/EtOAc: 85/15).

NMR attribution for the major diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.66 (dd, *J* = 5.4, 3.0 Hz, 2 H, CH from NPhth), 7.38-7.18 (m, 16 H, H_{Ar}), 7.22-7.12 (m, 4 H, H_{Ar}), 6.06 (dd, *J* = 9.9, 3.9 Hz, 1 H, C-1-CH_2-CH), 4.96 (d, *J* = 11.3 Hz, 1 H, OCH_2Ph), 4.75 (d, *J* = 11.2 Hz, 2 H, 2 x overlapped OCH_2Ph), 4.69 (dddd, *J* = 9.5, 7.8, 4.5, 3.3 Hz, 1 H, N-CH-CH_2Ph), 4.54 (d, *J* = 10.7 Hz, 1 H, OCH_2Ph), 4.32 (d, *J* =

12.7 Hz, 1 H, OCH_2Ph), 4.23 (dd, *J* = 9.1, 7.9 Hz, 1 H, (CO)-O-CH_2), 4.19 (dd, J = 9.1, 4.4 Hz, 1 H, (CO)-O-CH_2), 4.15 (d, *J* = 12.6 Hz, 1 H, OCH_2Ph), 3.71 (ddd, *J* = 9.2, 3.7, 1.9 Hz, 1 H, H-5), 3.62 (t, *J* = 9.5 Hz, 1 H, H-3), 3.59 (t, *J* = 9.4 Hz, 1 H, H-4), 3.53 (dd, *J* = 11.0, 3.4 Hz, 1 H, H-6), 3.38 (d, *J* = 9.9 Hz, 1 H, H-2), 3.34 (dd, *J* = 13.6, 3.1 Hz, 1 H, N-CH-CH_2Ph), 3.10 (dd, *J* = 11.0, 1.8 Hz, 1 H, H-6'), 2.84 (dd, J = 13.6, 9.3 Hz, 1 H, N-CH-CH_2Ph), 2.84 (dd, *J* = 15.3, 2.8 Hz, 1 H, C-1-CH_2-CH), 2.67 (dd, *J* = 15.2, 3.9 Hz, 1 H, C-1-CH_2-CH), 2.39 (s, 1 H, C-2-OH) 1.50 (s, 3 H, C1-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) *δ* 169.58 (CH-(CO)-N), 168.03 (2 x CO from NPhth), 152.87 (N-(CO)-O) 138.45 (3 x CqAr), 135.00 (CqAr) 134.12 (2 x CH from NPhth), 132.07 (2 x Cq from NPhth), 129.68 (2 x CHAr), 129.16 (2 x CHAr), 128.72 (2 x CHAr), 128.47 (2 x CHAr), 128.35 (2 x CHAr), 127.96 (CHAr), 127.91 (CHAr), 127.81 (3 x CHAr), 127.59 (2 x CHAr), 127.53 (2 x CHAr), 127.45 (CHAr), 123.54 (2 x CH from NPhth), 82.85 (C-3), 78.97 (C-4), 78.44 (C-2), 77.57 (C-1), 75.43 (CH_2Ph), 74.67 (CH_2Ph), 73.15 (CH_2Ph), 73.07 (C-5), 68.81 (C-6), 66.84 ((CO)-O-CH_2), 55.72 (N-CH-CH_2-Ph), 50.78 (C-1-CH_2-CH), 37.75 (N-CH-CH_2Ph), 26.07 (C-1-CH_2-CH), 24.98 (C-1-CH_3).

NMR attribution for the minor diastereoisomer:

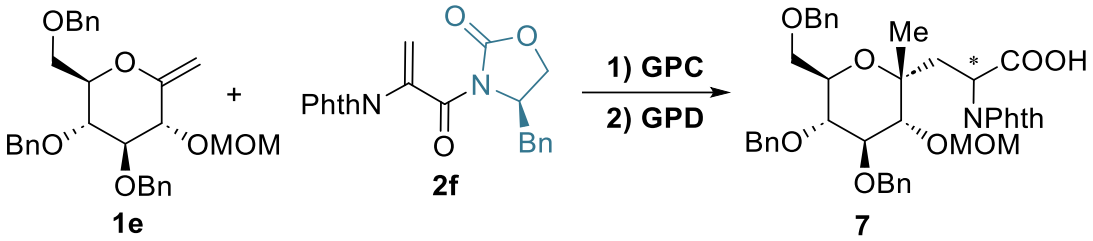
^{1}H NMR (500 MHz, $CDCl_3$) *δ* 7.85 (dd, *J* = 5.5, 3.0 Hz, 2H, CH from NPhth), 7.72 (dd, *J* = 5.5, 3.0 Hz, 2H, CH from NPhth), 7.38-7.18 (m, 16H, H_{Ar}), 7.22-7.12 (m, 4H, H_{Ar}), 6.02 (t, *J* = 6.0 Hz, 1H, C-1-CH_2-CH), 4.99 (d, *J* = 11.4 Hz, 1H, OCH_2Ph), 4.80 (d, *J* = 11.0 Hz, 1H, OCH_2Ph), 4.69 (d, *J* = 11.5 Hz, 1H, OCH_2Ph), 4.64-4.55 (m, 1H, N-CH-CH_2Ph), 4.62 (d, *J* = 11.8 Hz, 1H, OCH_2Ph), 4.60 (d, *J* = 10.5 Hz, 1H, OCH_2Ph), 4.52 (d, *J* = 11.8 Hz, 1H, OCH_2Ph), 4.05 (dd, *J* = 9.1, 3.3 Hz, 1H, (CO)-O-CH_2), 3.99 (ddd, *J* = 9.7, 3.8, 1.9 Hz, 1H, H-5), 3.99 (t, *J* = 9.0 Hz, 1H, (CO)-O-CH_2), 3.76 (t, *J* = 9.4 Hz, 1H, H-3), 3.72 (dd, *J* = 10.6, 3.8 Hz, 1H, H-6), 3.67 (dd, *J* = 11.0, 1.9 Hz, 1H, H-6'), 3.59 (t, *J* = 9.5 Hz, 1H, H-4), 3.45 (dd, *J* = 13.4, 3.3 Hz, 1H, N-CH-CH_2Ph), 3.38 (d, *J* = 9.3 Hz, 1H, H-2), 2.94 (dd, *J* = 15.3, 6.1 Hz, 1H, C-1-CH_2-CH), 2.56 (dd, *J* = 13.4, 10.3 Hz, 1H, N-CH-CH_2Ph), 2.45 (dd, *J* = 15.4, 5.8 Hz, 1H, C-1-CH_2-CH), 2.28 (s, 1H, C-2-OH) 1.48 (s, 3H, C1-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) *δ* 168.65 (CH-(CO)-N), 167.62 (2 x CO from NPhth), 152.65 (N-(CO)-O) 138.71 (3 x CqAr), 135.55 (CqAr) 134.22 (2 x CH from NPhth), 132.29 (2 x Cq from NPhth), 129.52 (2 x CHAr), 129.06 (2 x CHAr), 128.75 (2 x CHAr), 128.53 (2 x CHAr), 128.45 (2 x CHAr), 128.00 (CHAr), 127.94 (CHAr), 127.86 (3 x CHAr), 127.73 (2 x CHAr), 127.59 (2 x CHAr), 127.37 (CHAr), 123.63 (2 x CH from NPhth), 83.05 (C-3), 79.23 (C-4), 78.62 (C-2), 76.71 (C-1), 75.52 (CH_2Ph), 74.67 (CH_2Ph), 73.57 (CH_2Ph), 73.07 (C-5), 69.61 (C-6), 66.74 ((CO)-O-CH_2), 56.17 (N-CH-CH_2-O), 49.73 (C-1-CH_2-CH), 37.65 (N-CH-CH_2Ph), 30.16 (C-1-CH_2-CH), 26.02 (C-1-CH_3).

HRMS (*m/z*): calcd for $C_{49}H_{48}N_2O_{10}K$ $[M+K]^+$: 863.2941, found: 863.2934.

IR (film): v 3479, 2924, 1781, 1716, 1454, 1384, 1212, 1086, 910, 720, 699 cm^{-1}.

2-Phthalimidoyl-3-(3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy -1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (7)



Following the **GPC** and **GPD** (without intermediate purification) starting from **1e** (100 mg, 0.204 mmol, 1 equiv) and **2f** (153 mg, 0.408 mmol, 2 equiv), **7** was yielded as a mixture of 2 diastereoisomers (d.r : 94:6, 129 mg, 0.180 mmol, 89%) as a colorless amorphous solid.

NMR attribution for the major diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.40-7.11 (m, 15 H, H_{Ar}), 5.18 (dd, *J* = 9.3, 2.1 Hz, 1 H, C-1-CH_2-C<u>H</u>), 4.86 (d, *J* = 11.3 Hz, 1 H, OC<u>H_2</u>OCH_3), 4.86 (d, *J* = 11.3 Hz, 1 H, OC<u>H_2</u>Ph), 4.76 (d, *J* = 10.8 Hz, 1 H, OC<u>H_2</u>Ph), 4.75 (d, *J* = 11.1 Hz, 1 H, OC<u>H_2</u>Ph), 4.67 (d, *J* = 12.3 Hz, 1 H, OC<u>H_2</u>Ph), 4.56 (d, *J* = 12.3 Hz, 1 H, OC<u>H_2</u>Ph), 4.56 (d, *J* = 10.7 Hz, 1 H, OC<u>H_2</u>Ph), 4.55 (d, *J* = 6.4 Hz, 1 H, OC<u>H_2</u>OCH_3), 3.84 (t, *J* = 9.4 Hz, 1 H, H-3), 3.80 (ddd, *J* = 10.0, 4.0, 2.2 Hz, 1 H, H-5), 3.75-3.73 (m, 2 H, H-6 + H-6'), 3.61 (t, *J* = 9.6 Hz, 1 H, H-4), 3.37 (d, *J* = 9.4 Hz, 1 H, H-2), 3.26 (s, 3 H, OCH_2OC<u>H_3</u>), 2.89 (dd, *J* = 16.4, 2.0 Hz, 1 H, C-1-C<u>H_2</u>-CH), 2.75 (dd, *J* = 16.2, 9.2 Hz, 1 H, C-1-C<u>H_2</u>-CH), 1.21 (s, 3 H, OC<u>H_3</u>).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.05 (CH-(<u>C</u>O)-OH), 167.67 (2 x CO from NPhth), 138.68 (Cq_{Ar}), 138.53 (Cq_{Ar}), 137.99 (Cq_{Ar}), 134.32 (2 x CH from NPhth), 132.07 (2 x Cq from NPhth), 128.53 (2 x CHAr), 128.44 (3 x CH_{Ar}), 128.24 (2 x CH_{Ar}), 127.89 (2 x CH_{Ar}), 127.83 (CH_{Ar}), 127.78 (CH_{Ar}), 127.73 (2 x CH_{Ar}), 127.69 (CH_{Ar}), 127.57 (CH_{Ar}), 123.74 (2 x CH from NPhth) 98.85 (O<u>C</u>H_2OCH_3), 85.25 (C-2), 83.59 (C-3), 79.07 (C-4), 76.23 (C-1), 75.64 (O<u>C</u>H_2Ph), 75.18 (O<u>C</u>H_2Ph), 73.59 (O<u>C</u>H_2Ph), 72.64 (C-5), 69.17 (C-6), 56.36 (OCH_2O<u>C</u>H_3), 47.09 (C-1-CH_2-<u>C</u>H), 29.11 (C-1-<u>C</u>H_2-CH), 25.30 (C-1-<u>C</u>H_3).

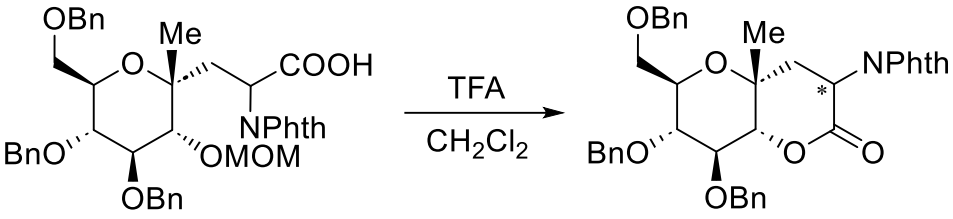
Tractable characteristic ^{1}H NMR signals for the minor diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.78 (m, 2 H, CH from NPhth), δ 7.68-7.65 (m, 2 H, CH from NPhth), 5.12 (dd, *J* = 9.2, 2.0 Hz, 1 H, C-1-CH_2-C<u>H</u>), 3.29 (s, 3H, OCH_2OC<u>H_3</u>), 2.47(dd, *J* = 12.2, 9.2 Hz, 1 H, C-1-C<u>H_2</u>-CH), 2.47(dd, *J* = 12.2, 1.9 Hz, 1 H, C-1-C<u>H_2</u>-CH), 1.16 (s, 3H, C-1-C<u>H_3</u>).

HRMS (*m/z*): calcd for $C_{41}H_{43}O_{10}NNa$ $[M+Na]^+$: 732.2779, found: 732.2796.

IR (film): v 2903, 1715, 1387, 1088, 1035, 737, 722, 699 cm^{-1}.

2-Phthalimidoyl-3-(3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy -1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid - lactonisation product (8)



7 **8**

To a solution of **7** (16 mg, 0.023 mmol, 1 equiv, d.r. 94:6) in CH_2Cl_2 (1 mL) was added TFA (0.17 mL, 2.29 mmol, 100 equiv). The reaction mixture was stirred for 16 h then diluted with EtOAc (5 mL) and concentrated under vacuum. The crude was then purified by column chromatography (SiO_2, Cyclohexane/EtOAc: 90:10) yielding **8** as a mixture of 2 diastereoisomers (11 mg, 0.017 mmol, 74%, d.r : 94:6) as an amorphous white solid.

NMR attribution for the major diastereoisomer:

^{1}H NMR (500 MHz, benzene-d6) δ 7.42 (dd, *J* = 5.4, 3.0 Hz, 2 H, CH from NPhth), 4.35-7.07 (m, 15 H, H_{Ar}), 6.83 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 5.49 (dd, *J* = 11.3, 8.4 Hz, 1 H, C-1-CH_2-C<u>H</u>), 4.75 (d, *J* = 11.5 Hz, 1 H, OC<u>H_2</u>Ph), 4.57 (d, *J* = 11.5 Hz, 1 H, OC<u>H_2</u>Ph), 4.44 (d, *J* = 12.1 Hz, 1 H, OC<u>H_2</u>Ph), 4.43 (d, *J* = 11.7 Hz, 1 H, OC<u>H_2</u>Ph), 4.35 (d, *J* = 4.0 Hz, 1 H, H-2), 4.30 (d, *J* = 12.2 Hz, 1 H, OC<u>H_2</u>Ph), 4.27 (d, *J* = 11.7 Hz, 1 H, OC<u>H_2</u>Ph), 4.04 (dd, *J* = 10.3, 6.9 Hz, 1 H, H-4), 3.90 (dd, *J* = 6.9, 4.0 Hz, 1 H, H-3), 3.64 (ddd, *J* = 10.2, 3.2, 1.9 Hz, 1 H, H-5), 3.60 (dd, *J* = 10.6, 3.1 Hz, 1 H, H-6), 3.45 (dd, *J* = 10.7, 2.0 Hz, 1 H, H-6'), 2.39 (dd, *J* = 13.6, 11.7 Hz, 1 H, C-1-C<u>H_2</u>-CH), 2.04 (dd, *J* = 13.7, 8.5 Hz, 1 H, C-1-C<u>H_2</u>-CH), 1.38 (s, 3 H, C-1-C<u>H_3</u>).

^{13}C NMR (125 MHz, benzene-d6) δ 167.38 (2 x CO from NPhth), 166.31 ((<u>C</u>O)O-C-2), 139.12 (Cq_{Ar}), 139.04 (Cq_{Ar}), 138.05 (Cq_{Ar}), 133.92 (2 x CH from NPhth), 132.28 (2 x Cq from NPhth), 128.72 (2 x CHAr), 128.59 (2 x CH_{Ar}), 128.52 (2 x CH_{Ar}), 128.38 (2 x CH_{Ar}), 128.35 (2 x CH_{Ar}), 128.16 (CH_{Ar}), 127.97 (CH_{Ar}), 127.87 (CH_{Ar}), 127.75 (CH_{Ar}), 127.71 (CH_{Ar}), 123.51 (2 x CH from NPhth) 83.98 (C-2), 82.33 (C-3), 76.80 (C-4), 73.98 (O<u>C</u>H_2Ph), 73.85 (C-5), 73.60 (O<u>C</u>H_2Ph), 72.54 (O<u>C</u>H_2Ph), 71.23 (C-1), 69.46 (C-6), 45.49 (C-1-CH_2-<u>C</u>H), 36.22 (C-1-<u>C</u>H_2-CH), 27.13 (C-1-<u>C</u>H_3).

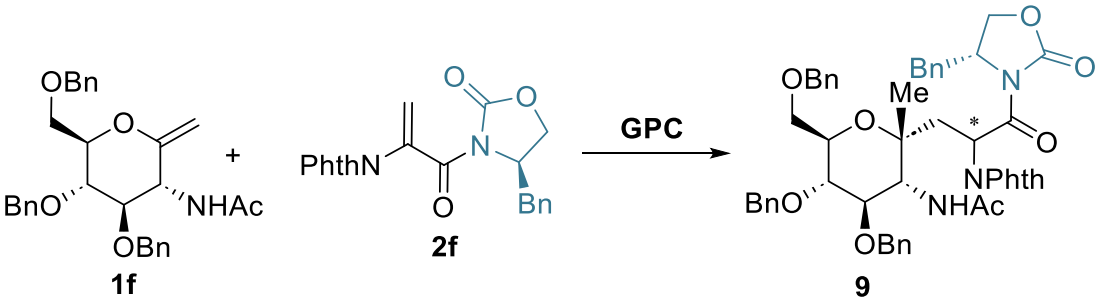
Tractable characteristic ^{1}H NMR signals for the minor diastereoisomer:

^{1}H NMR (500 MHz, benzene-d6) δ 5.15 (d, *J* = 10.9 Hz, 1 H, C<u>H_2</u>OPh), 5.06 (dd, *J* = 12.4, 7.9 Hz, 1 H, C-1-CH_2-C<u>H</u>), 4.97 (d, *J* = 10.8 Hz, 1 H, C<u>H_2</u>OPh), 2.97 (t, *J* = 12.4 Hz, 1 H, C-1-C<u>H_2</u>-CH), 1.40 (s, 3 H, C-1-C<u>H_3</u>), 1.35-1.30 (m, 1 H, C-1-C<u>H_2</u>-CH).

HRMS (*m/z*): calcd for $C_{39}H_{37}O_8NNa$ $[M+Na]^+$: 670.2411, found: 670.2397.

IR (film): v 2924, 1752, 1716, 1389, 1208, 1091, 720, 698 cm^{-1}.

2-(1-((*R*)-4-Benzyl-2-oxooxazolidin-3-yl)-3-(2-acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)-1-oxopropan-2-yl)phthalimide (9)



Following the **GPC** starting from **1f** (28.0 mg, 0.057 mmol, 1 equiv) and **2f** (43.2 mg, 0.110 mmol, 2 equiv), **9** was yielded as a mixture of 2 diastereoisomers (d.r : 77:23, 23.5 mg, 0.027 mmol, 47%) as a white amorphous solid after purification of the crude by column chromatography (SiO_2, Cyclohexane/EtOAc: 70/30).

NMR attribution for the major diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2 H, CH from NPhth), 7.77 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.39-7.13 (m, 20 H, H_{Ar}), 6.67 (d, *J* = 10.1 Hz, 1 H, NHAc), 5.88 (dd, *J* = 8.4, 3.1 Hz, 1 H, C-1-CH_2-CH), 4.87 (d, *J* = 11.6 Hz, 1 H, overlapped OCH_2Ph), 4.76 (d, *J* = 10.5 Hz, 1 H, overlapped OCH_2Ph), 4.75 (d, *J* = 11.4 Hz, 1 H, overlapped OCH_2Ph), 4.75-4.66 (m, 1 H, overlapped N-CH-CH_2Ph), 4.65 (d, *J* = 12.2 Hz, 1 H, overlapped OCH_2Ph), 4.55 (d, *J* = 11.6 Hz, 2 H, 2 x overlapped OCH_2Ph), 4.19 (t, *J* = 10.2 Hz, 1 H, H-2), 4.10 (dd, *J* = 8.9, 1.0 Hz, 1 H, overlapped (CO)-O-CH_2), 4.09 (dd, *J* = 9.1, 4.6 Hz, 1 H, overlapped (CO)-O-CH_2), 3.74-3.62 (m, 5H, H-3, H-4, H-5, H-6, H-6'), 3.60 (dd, *J* = 13.2, 3.1 Hz, 1 H, N-CH-CH_2Ph), 3.07 (dd, *J* = 14.6, 8.4 Hz, 1 H, C-1-CH_2-CH), 2.51 (dd, *J* = 13.5, 10.6 Hz, 1 H, N-CH-CH_2Ph), 2.12 (dd, *J* = 14.6, 3.3 Hz, 1 H, C-1-CH_2-CH), 1.95 (s, 3 H, NH(CO)CH_3), 1.29 (s, 3 H, C1-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.75 (CO from NHAc), 167.77 (2 x CO from NPhth), 167.57 (CH-(CO)-N), 152.81 (N-(CO)-O), 134.65 (Cq_{Ar}), 138.57 (Cq_{Ar}), 138.21 (Cq_{Ar}), 135.53 (Cq_{Ar}), 134.70 (overlapped 2 x CH from NPhth), 131.63 (2 x Cq from NPhth), 129.45 (2 x CH_{Ar}), 129.11 (2 x CH_{Ar}), 128.64 (2 x CH_{Ar}), 128.53 (2 x CH_{Ar}), 128.46 (2 x CH_{Ar}), 128.18 (2 x CH_{Ar}), 127.95 (2 x CH_{Ar}), 127.85 (2 x CH_{Ar}), 127.73 (2 x CH_{Ar}), 127.60 (1 x CH_{Ar}), 127.42 (1 x CH_{Ar}), 123.93 (2 x CH from NPhth), 81.10 (C-3), 79.38 (overlapped C-4), 76.06 (C-1), 75.00 (overlapped CH_2Ph), 74.87 (CH_2Ph), 73.61 (CH_2Ph), 73.03 (C-5), 69.52 (C-6), 66.99 (N-CH-CH_2-O), 58.36 (C-2), 56.09 (N-CH-CH_2-O), 49.88 (C-1-CH_2-CH), 37.68 (N-CH-CH_2Ph), 33.08 (C-1-CH_2-CH), 25.23 (C-1-CH_3), 23.56 (NH(CO)CH_3).

NMR attribution for the minor diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.70 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.39-7.13 (m, 20 H, H_{Ar}), 5.96 (dd, *J* = 10.2, 3.5 Hz, 1 H, C-1-CH_2-CH), 5.74 (d, *J* = 9.9 Hz, 1 H, NHAc), 4.87 (d, *J* = 11.6 Hz, 1 H, overlapped OCH_2Ph), 4.75 (d, *J* = 10.6 Hz, 1 H, overlapped OCH_2Ph), 4.69 (d, *J* = 11.7 Hz, 1 H, overlapped OCH_2Ph), 4.75-4.66 (m, 1 H, N-CH-CH_2Ph), 4.54 (d, *J* = 10.7 Hz, 1 H, overlapped OCH_2Ph), 4.51 (d, *J* = 12.4 Hz, 1 H, overlapped OCH_2Ph), 4.34 (d, *J* = 12.4 Hz, 1 H, overlapped OCH_2Ph), 4.27 (dd, *J* = 9.0, 1.5 Hz, 1 H, overlapped (CO)-O-CH_2), 4.27 (dd, *J* = 9.2, 4.5 Hz, 1 H, overlapped (CO)-O-

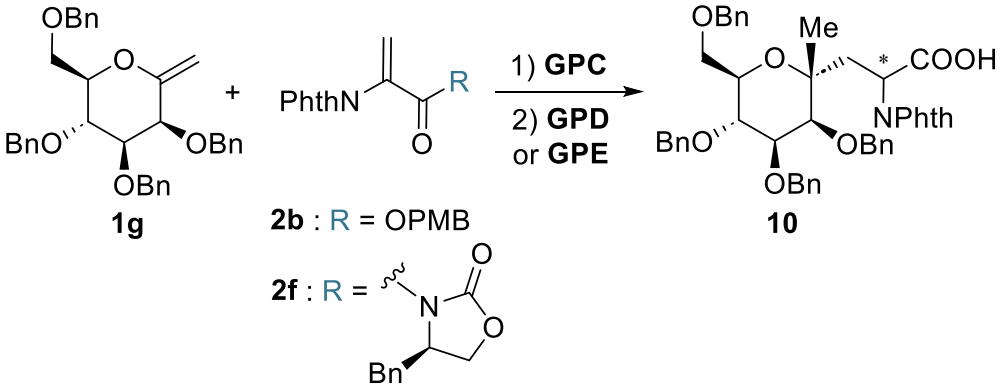
CH_2), 4.13 (t, *J* = 10.0 Hz, 1 H, overlapped H-2), 3.74-3.62 (m, 4 H, H-3, H-4, H-5 and H-6), 3.45 (dd, *J* = 11.8, 3.0 Hz, 1 H, H-6'), 3.30 (dd, *J* = 13.5, 3.1 Hz, 1 H, N-CH-CH_2Ph), 2.91 (dd, *J* = 13.5, 9.0 Hz, 1 H, N-CH-CH_2Ph), 2.90 (dd, *J* = 14.5, 10.3 Hz, 1 H, C-1-CH_2-CH), 2.33 (dd, *J* = 14.9, 3.6 Hz, 1 H, C-1-CH_2-CH), 1.92 (s, 3 H, NH(CO)CH_3), 1.26 (s, 3 H, C1-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 170.59 (CO from NHAc), 168.95 (CH-(CO)-N), 167.98 (2 x CO from NPhth), 153.20 (N-(CO)-O), 138.82 (Cq_{Ar}), 138.50 (Cq_{Ar}), 138.29 (Cq_{Ar}), 134.74 (overlapped Cq_{Ar}), 134.38 (2 x CH from NPhth), 131.83 (2 x Cq from NPhth), 129.70 (2 x CH_{Ar}), 129.21 (2 x CH_{Ar}), 128.59 (2 x CH_{Ar}), 128.53 (2 x CH_{Ar}), 128.41 (2 x CH_{Ar}), 128.22 (2 x CH_{Ar}), 127.89 (2 x CH_{Ar}), 127.80 (2 x CH_{Ar}), 127.76 (2 x CH_{Ar}), 127.52 (1 x CH_{Ar}), 127.42 (1 x CH_{Ar}), 123.72 (2 x CH from NPhth), 80.50 (C-3), 79.38 (overlapped C-4), 77.36 (C-1), 75.00 (overlapped CH_2Ph), 74.59 (CH_2Ph), 73.40 (CH_2Ph), 72.97 (C-5), 69.08 (C-6), 67.27 (N-CH-CH_2-O), 58.54 (C-2), 55.69 (N-CH-CH_2-O), 51.05 (C-1-CH_2-CH), 37.73 (N-CH-CH_2Ph), 28.62 (C-1-CH_2-CH), 25.01 (C-1-CH_3), 23.66 (NH(CO)CH_3).

HRMS (*m/z*): calcd for $C_{51}H_{51}N_3O_{10}Na$ $[M+Na]^+$: 888.3467, found: 888.3455.

IR (film): v 3301, 2925, 1783, 1720, 1659, 1548, 1454, 1385, 1280, 1214, 1093, 752, 720, 699 cm^{-1}.

2-Phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-mannopyranosyl)propanoïc acid (10)



With achiral acceptor 2b : Following the **GPC** and **GPE** (without intermediate purification) starting from **1g** (30.0 mg, 0.0560 mmol, 1 equiv) and **2b** (37.3 mg, 0.110 mmol, 2 equiv), **10** was yielded as a mixture of 2 diastereoisomers (d.r : 73:27, 38.7 mg, 0.051 mmol, 91%) as a colorless amorphous solid.

With enantiopure acceptor 2f : Following the **GPC** and **GPD** (without intermediate purification) starting from **1g** (30.0 mg, 0.056 mmol, 1 equiv) and **2f** (42.1 mg, 0.110 mmol, 2 equiv), **10** was yielded as a mixture of 2 diastereoisomers (d.r : 92:8, 28.9 mg, 0.038 mmol, 68%) as a colorless amorphous solid.

NMR attribution for the major diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.74 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.39-7.03 (m, 20 H, H_{Ar}), 5.17 (dd, *J* = 9.2, 2.2 Hz, 1 H, C-1-CH_2-CH), 4.83 (d, *J* = 11.4 Hz, 1 H, OCH_2Ph), 4.76 (d, *J* = 10.8 Hz, 1 H, OCH_2Ph), 4.74 (d, *J* = 11.2 Hz, 1 H, OCH_2Ph), 4.69 (d, *J* = 12.2 Hz, 1 H,

OC$\underline{H_2}$Ph), 4.66 (d, *J* = 11.6 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.60 (d, *J* = 11.5 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.52 (d, *J* = 10.7 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.50 (d, *J* = 11.4 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.05 (dd, *J* = 8.7, 2.8 Hz, 1 H, H-3), 3.97 (t, *J* = 9.3 Hz, 1 H, H-4), 3.82 (ddd, *J* = 9.6, 4.9, 2.2 Hz, 1 H, H-5), 3.74 (dd, *J* = 11.2, 2.1 Hz, 1 H, H-6), 3.70 (dd, *J* = 11.2, 4.9 Hz, 1 H, H-6'), 3.47 (d, *J* = 2.7 Hz, 1 H, H-2), 2.91 (dd, *J* = 15.6, 2.3 Hz, 1 H, C-1-C$\underline{H_2}$-CH), 2.50 (dd, *J* = 15.6, 9.1 Hz, 1 H, overlapped C-1-C$\underline{H_2}$-CH), 1.19 (s, 3H, C1-C$\underline{H_3}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.50 (overlapped $\underline{C}$OOH), 167.71 (overlapped 2 x CO from NPhth), 138.67 (overlapped Cq_{Ar}), 138.63 (overlapped Cq_{Ar}), 138.61 (overlapped Cq_{Ar}), 138.05 (overlapped Cq_{Ar}), 134.44 (2 x CH from NPhth), 131.96 (2 x Cq from NPhth), 128.51 (3 x CH_{Ar}), 128.44 (2 x CH_{Ar}), 128.39 (3 x CH_{Ar}), 128.29 (3 x CH_{Ar}), 128.05 (3 x CH_{Ar}), 128.01 (3 x CH_{Ar}), 127.57 (3 x CH_{Ar}), 123.80 (2 x CH from NPhth), 81.48 (C-3), 79.68 (C-2), 77.25 (C-1), 75.64 (C-4), 75.21 ($\underline{C}H_2$Ph), 75.12 ($\underline{C}H_2$Ph), 73.55 (C-5), 72.85 (2 x overlapped $\underline{C}H_2$Ph), 69.82 (C-6), 47.81 (overlapped C-1-CH_2-$\underline{C}$H), 32.89 (C-1-$\underline{C}H_2$-CH), 22.30 (C-1-$\underline{C}H_3$).

NMR attribution for the minor diastereoisomer:

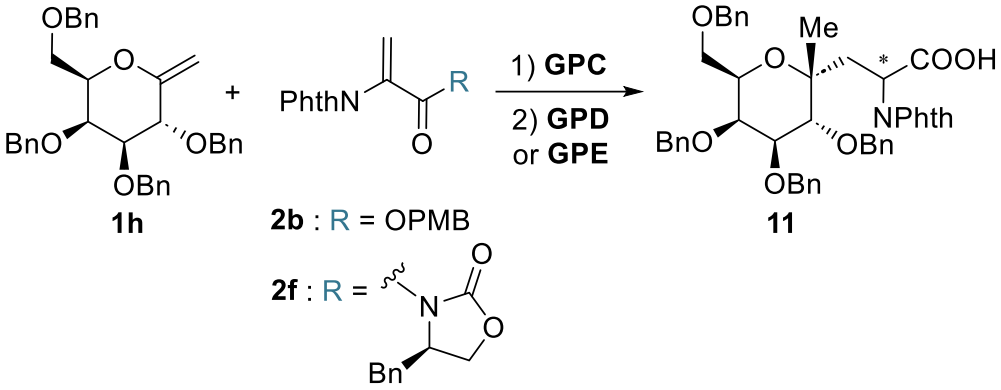
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 5.4, 3.0 Hz, 2 H, CH from NPhth), 7.64 (dd, *J* = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.39-7.03 (m, 20 H, H_{Ar}), 5.11 (dd, *J* = 9.4, 3.4 Hz, 1 H, C-1-CH_2-C$\underline{H}$), 4.91 (d, *J* = 11.4 Hz, 1 H, OC$\underline{H_2}$Ph), 4.72 (d, *J* = 10.7 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.69 (d, *J* = 12.2 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.58 (d, *J* = 11.6 Hz, 2 H, 2 x OC$\underline{H_2}$Ph), 4.42 (d, *J* = 10.7 Hz, 1 H, OC$\underline{H_2}$Ph), 4.29 (d, *J* = 12.5 Hz, 1 H, OC$\underline{H_2}$Ph), 4.07 (d, *J* = 9.1 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.01 (dd, *J* = 9.0, 2.6 Hz, 1 H, H-3), 3.90 (t, *J* = 9.2 Hz, 1 H, H-4), 3.53 (d, J = 2.6 Hz, 1 H, H-2), 3.41 (ddd, *J* = 9.4, 4.8, 1.9 Hz, 1 H, H-5), 3.37 (dd, *J* = 10.8, 4.7 Hz, 1 H, H-6), 3.15 (dd, *J* = 10.8, 1.9 Hz, 1 H, H-6'), 2.86 (dd, *J* = 16.2, 9.3 Hz, 1 H, C-1-C$\underline{H_2}$-CH), 2.24 (dd, *J* = 15.5, 3.4 Hz, 1 H, overlapped C-1-C$\underline{H_2}$-CH), 1.37 (s, 3 H, C1-C$\underline{H_3}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 172.50 (overlapped $\underline{C}$OOH), 167.71 (overlapped 2 x CO from NPhth), 138.67 (overlapped Cq_{Ar}), 138.63 (overlapped Cq_{Ar}), 138.61 (overlapped Cq_{Ar}), 138.05 (overlapped Cq_{Ar}), 134.16 (2 x CH from NPhth), 132.13 (2 x Cq from NPhth), 128.57 (2 x CH_{Ar}), 128.36 (2 x CH_{Ar}), 128.32 (2 x CH_{Ar}), 127.88 (2 x CH_{Ar}), 127.80 (2 x CH_{Ar}), 127.77 (3 x CH_{Ar}), 127.68 (2 x CH_{Ar}), 127.56 (2 x CH_{Ar}), 128.48 (2 x CH_{Ar}), 127.30 (CH_{Ar}), 123.66 (2 x CH from NPhth), 80.83 (C-3), 80.36 (C-2), 77.79 (C-1), 75.52 (C-4), 75.15 ($\underline{C}H_2$Ph), 75.04 ($\underline{C}H_2$Ph), 73.75 (C-5), 73.00 ($\underline{C}H_2$Ph), 72.82 (overlapped $\underline{C}H_2$Ph), 69.34 (C-6), 47.81 (overlapped C-1-CH_2-$\underline{C}$H), 32.00 (C-1-$\underline{C}H_2$-CH), 22.11 (C-1-$\underline{C}H_3$).

HRMS (*m/z*): calcd for $C_{46}H_{45}NO_9Na$ $[M+Na]^+$: 778.2987, found: 778.2982.

IR (film): v 3031, 2924, 1714, 1386, 1087, 724, 697 cm^{-1}.

2-Phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (11)



With enantiopure acceptor 2f : Following the **GPC** and **GPD** (without intermediate purification) starting from **1h** (25.8 mg, 0.048 mmol, 1 equiv) and **2f** (36.2 mg, 0.0960 mmol, 2 equiv), **11** was yielded as a mixture of 2 diastereoisomers (d.r : 96:4, 22.5 mg, 0.030 mmol, 62%) as a colorless amorphous solid.

With achiral acceptor 2b : Following the **GPC** and **GPE** (without intermediate purification) starting from **1h** (30.0 mg, 0.0560 mmol, 1 equiv) and **2b** (37.7 mg, 0.110 mmol, 2 equiv), **11** was yielded as a mixture of 2 diastereoisomere (d.r : 73:27, 39.4mg, 0.052 mmol, 93%) as a colorless amorphous solid.

NMR attribution for the major diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (dd, J = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.70 (dd, J = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.38-7.18 (m, 20 H, H_{Ar}), 5.15 (dd, J = 8.7, 2.2 Hz, 1 H, C-1-CH_2-C<u>H</u>), 4.91 (d, J = 11.8 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.89 (d, J = 12.1 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.68 (d, J = 12.2 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.64 (d, J = 11.8 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.61 (d, J = 11.7 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.57 (d, J = 11.7 Hz, 2 H, overlapped OC<u>H_2</u>Ph), 4.44 (d, J = 11.7 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.02 (s, 1 H, H-4), 3.94 (t, J = 6.5 Hz, 1 H, H-5), 3.82-3.79 (m, 2 H, overlapped H-2 and H-3), 3.63 (d, J = 6.4 Hz, 2 H, H-6 and H-6'), 2.90 (dd, J = 16.3, 2.4 Hz, 1 H, C-1-C<u>H_2</u>-CH), 2.67 (dd, J = 16.3, 8.8 Hz, 1 H, overlapped C-1-C<u>H_2</u>-CH), 1.13 (s, 3 H, C1-C<u>H_3</u>).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.68 (<u>C</u>OOH), 167.59 (2 x CO from NPhth), 139.07 (Cq_{Ar}), 138.83 (Cq_{Ar}), 138.63 (overlapped Cq_{Ar}), 138.05 (Cq_{Ar}), 134.26 (2 x CH from NPhth), 132.02 (2 x Cq from NPhth), 128.49 (4 x CH_{Ar}), 128.30 (2 x CH_{Ar}), 128.27 (2 x CH_{Ar}), 128.09 (2 x CH_{Ar}), 128.02 (3 x CH_{Ar}), 127.74 (2 x CH_{Ar}), 127.57 (3 x CH_{Ar}), 127.52 (2 x CH_{Ar}), 123.77 (2 x CH from NPhth), 82.87 (C-2), 81.30 (C-3), 76.95 (C-1), 75.77 (<u>C</u>H_2Ph), 74.61 (overlapped <u>C</u>H_2Ph), 74.51 (C-4), 73.65 (<u>C</u>H_2Ph), 72.61 (<u>C</u>H_2Ph), 71.02 (overlapped C-5), 69.22 (C-6), 47.33 (C-1-CH_2-<u>C</u>H), 29.12 (C-1-<u>C</u>H_2-CH), 25.36 (C-1-<u>C</u>H_3).

NMR attribution for the minor diastereoisomer:

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (dd, J = 5.3, 3.0 Hz, 2 H, CH from NPhth), 7.62 (dd, J = 5.5, 3.0 Hz, 2 H, CH from NPhth), 7.38-7.18 (m, 20 H, H_{Ar}), 5.18-5.11 (m, 1 H, overlapped C-1-CH_2-C<u>H</u>), 4.95 (d, J = 11.3 Hz, 1 H, OC<u>H_2</u>Ph), 4.84 (d, J = 11.6 Hz, 1 H, OC<u>H_2</u>Ph), 4.71 (d, J = 10.0 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.68 (d, J = 12.2 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.64 (d, J = 11.8 Hz, 1 H, overlapped OC<u>H_2</u>Ph), 4.61

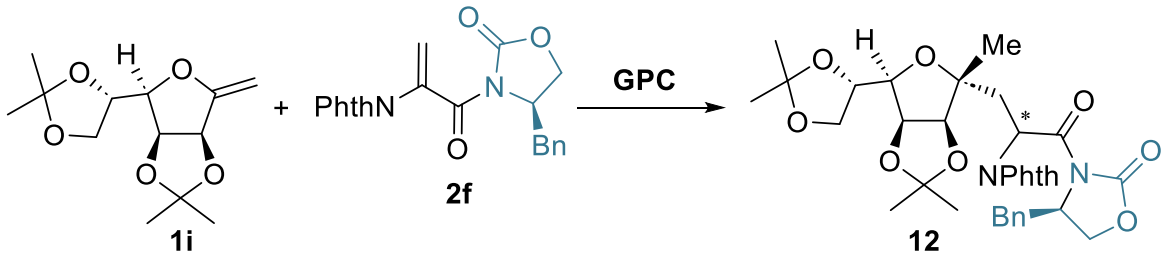
(d, *J* = 11.7 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 4.46 (d, *J* = 11.0 Hz, 1 H, overlapped OC$\underline{H_2}$Ph), 3.89-3.84 (m, 1 H, H-4), 3.80 (d, *J* = 10.5 Hz, 1 H, overlapped H-2), 3.71 (dd, *J* = 10.3, 2.8 Hz, 1 H, H-3), 3.51 (dd, *J* = 8.1, 5.2 Hz, 1 H, H-5), 3.28 (t, *J* = 8.4 Hz, 1 H, H-6), 2.85 (dd, *J* = 16.1, 10.7 Hz, 1 H, C-1-C$\underline{H_2}$-CH), 2.69 (dd, *J* = 8.6, 5.2 Hz, 1 H, overlapped H-6'), 2.66 (dd, *J* = 16.0, 3.5 Hz, 1 H, overlapped C-1-C$\underline{H_2}$-CH), 1.38 (s, 3 H, C1-C$\underline{H_3}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 174.32 (C$\underline{O}$OH), 167.79 (2 x CO from NPhth), 139.02 (Cq_{Ar}), 138.73 (Cq_{Ar}), 138.63 (overlapped Cq_{Ar}), 138.08 (Cq_{Ar}), 134.08 (2 x CH from NPhth), 132.17 (2 x Cq from NPhth), 128.40 (3 x CH_{Ar}), 128.27 (CH_{Ar}), 128.18 (2 x CH_{Ar}), 127.93 (3 x CH_{Ar}), 127.80 (3 x CH_{Ar}), 127.66 (2 x CH_{Ar}), 127.61 (3 x CH_{Ar}), 127.42 (3 x CH_{Ar}), 123.55 (2 x CH from NPhth), 82.50 (C-2), 80.87 (C-3), 78.11 (C-1), 76.09 (C$\underline{H_2}$Ph), 74.61 (overlapped C$\underline{H_2}$Ph), 74.41 (C-4), 72.98 (C$\underline{H_2}$Ph), 72.56 (C$\underline{H_2}$Ph), 71.02 (overlapped C-5), 68.69 (C-6), 48.35 (C-1-CH_2-C$\underline{H}$), 26.78 (C-1-C$\underline{H_2}$-CH), 24.89 (C-1-C$\underline{H_3}$).

HRMS (*m/z*): calcd for $C_{46}H_{45}NO_9Na$ $[M+Na]^+$: 778.2987, found: 778.2998.

IR (film): v 3030, 2917, 1716, 1388, 1088, 697 cm^{-1}.

2-(1-((*R*)-4-Benzyl-2-oxooxazolidin-3-yl)-3-((*3aS,4R,6aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2,4-trimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1-oxopropan-2-yl)phthalimide (12)



Following the **GPC** starting from **1i** (30 mg, 0.120 mmol, 1 equiv) and **2f** (88.1 mg, 0.230 mmol, 2 equiv), **12** was yielded as a mixture of 2 diastereoisomers (d.r : 84:16, 58.4 mg, 0.092 mmol, 79%) as a white amorphous solid after purification of the crude by column chromatography (SiO_2, Cyclohexane/EtOAc: 72:28).

NMR attribution for the major diastereoisomer :

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (ddd, *J* = 5.2, 3.1, Hz, 2 H, overlapped CH from NPhth), 7.73 (dd, *J* = 5.5, 3.1 Hz, 2 H, CH from NPhth), 7.36-7.15 (m, 5 H, H_{Ar}), 6.15 (dd, *J* = 9.2, 3.5 Hz, 1 H, C-1-CH_2-C$\underline{H}$), 4.79 (dddd, *J* = 10.3, 7.8, 3.3, 2.6 Hz, 1 H, N-C$\underline{H}$-CH_2-O), 4.75(dd, *J* = 6.2, 4.6 Hz, 1 H, H-3), 4.36 (d, *J* = 6.1 Hz, 1 H, H-2), 4.29 (q, *J* = 8.0 Hz, 1 H, overlapped H-5), 4.26-4.21 (m, 1 H, overlapped N-CH-C$\underline{H_2}$-O), 4.19 (dd, *J* = 8.1, 6.6 Hz, 1 H, H-6), 4.13 (dd, *J* = 8.9, 2.5 Hz, 1 H, N-CH-C$\underline{H_2}$-O), 4.02 (dd, *J* = 7.9, 4.6 Hz, 1 H, H-4), 3.68 (t, *J* = 7.6 Hz, 1 H, H-6'), 3.41 (dd, *J* = 13.4, 3.4 Hz, 1 H, N-CH-C$\underline{H_2}$Ph), 3.03 (dd, *J* = 14.3, 9.3 Hz, 1 H, C-1-C$\underline{H_2}$-CH), 2.62 (dd, *J* = 13.4, 10.4 Hz, 1 H, C$\underline{H_2}$Ph), 1.88 (dd, *J* = 14.3, 3.5 Hz, 1 H, C-1-C$\underline{H_2}$-CH), 1.54 (s, 3H, C1-C$\underline{H_3}$), 1.45 (s, 3 H, C$\underline{H_3}$-Cq-CH_3), 1.34 (s, 3 H, C$\underline{H_3}$-Cq-CH_3), 1.29 (s, 3 H, CH_3-Cq-C$\underline{H_3}$), 1.26 (s, 3 H, CH_3-Cq-C$\underline{H_3}$).

^{13}C NMR (125 MHz, $CDCl_3$) δ 167.68 (CH-(CO)-N), 152.83 (N-(CO)-O) 135.75 (Cq_{Ar}), 134.36 (2 x CH from NPhth), 131.90 (2 x Cq from NPhth), 129.54 (2 x CH_{Ar}), 128.99 (2 x CH_{Ar}), 127.32 (CH_{Ar}), 123.67 (2 x CH from NPhth), 112.81 (CH_3-Cq-CH_3), 109.46 (CH_3-Cq-CH_3), 86.32 (C-2), 84.34 (C-1), 81.95 (C-3), 81.18 (C-4), 76.91 (C-5), 66.70 (N-CH-CH_2-O), 66.38 (C-6), 56.12 (N-CH-CH_2-O), 49.19 (C-1-CH_2-CH), 37.72 (N-CH-CH_2Ph), 36.34 (C-1-CH_2-CH), 26.86 (CH_3-Cq-CH_3), 26.06 (CH_3-Cq-CH_3), 25.56 (CH_3-Cq-CH_3), 24.82 (CH_3-Cq-CH_3), 19.79 (C-1-CH_3).

NMR attribution for the minor diastereoisomer :

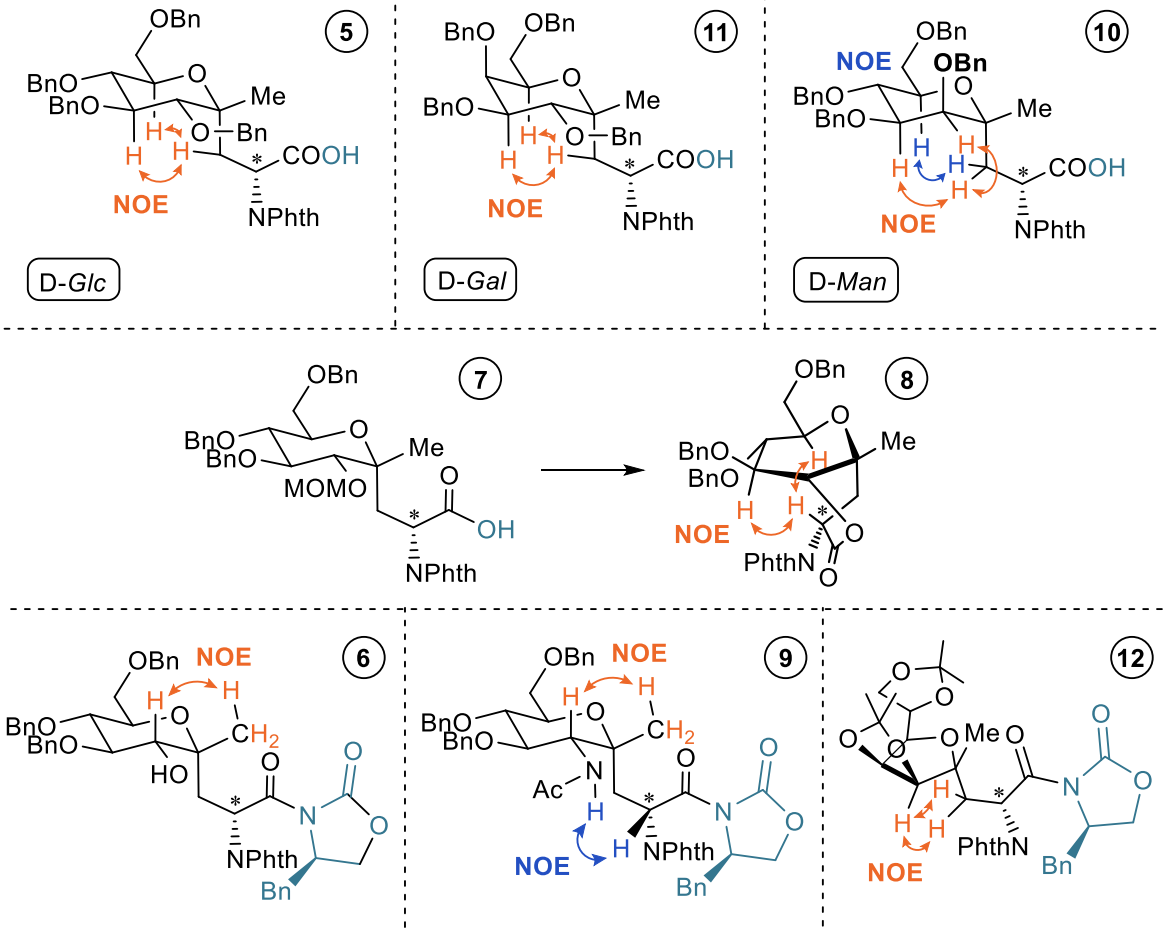
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 5.2, 3.1, Hz, 2 H, overlapped CH from NPhth), 7.70 (dd, *J* = 5.5, 3.1 Hz, 2 H, CH from NPhth), 7.36-7.15 (m, 5 H, 5 x H_{Ar}), 6.11 (dd, *J* = 11.6, 2.9 Hz, 1 H, C-1-CH_2-CH), 4.73-4.69 (m, 1 H, N-CH-CH_2-O), 4.38 (dd, *J* = 6.1, 4.5 Hz, 1 H, H-3), 4.44 (d, *J* = 6.1 Hz, 1 H, H-2), 4.29 (dd, *J* = 9.2, 8.2 Hz, 1 H, N-CH-CH_2-O), 4.26-4.21 (m, 1 H, overlapped N-CH-CH_2-O), 4.15-4.10 (m, 1 H, H-5), 4.11-4.09 (m, 1 H, H-6), 3.83 (dd, *J* = 7.7, 4.5 Hz, 1 H, H-4), 3.57 (t, *J* = 7.3 Hz, 1 H, H-6'), 3.29 (dd, *J* = 13.5, 3.2 Hz, 1 H, N-CH-CH_2Ph), 2.97 (dd, *J* = 14.4, 11.6 Hz, 1 H, C-1-CH_2-CH), 2.86 (dd, *J* = 13.5, 9.4 Hz, 1 H, N-CH-CH_2Ph), 1.97 (dd, *J* = 14.4, 2.9 Hz, 1 H, C-1-CH_2-CH), 1.45 (s, 3 H, C-1-CH_3), 1.41 (s, 3 H, CH_3-Cq-CH_3), 1.34 (s, 3 H, CH_3-Cq-CH_3), 1.26 (s, 3 H, CH_3-Cq-CH_3), 1.18 (s, 3 H, CH_3-Cq-CH_3).

^{13}C NMR (125 MHz, $CDCl_3$) δ 168.04 (CH-(CO)-N), 152.95 (N-(CO)-O) 134.79 (Cq_{Ar}), 133.95 (2 x CH from NPhth), 132.23 (2 x Cq from NPhth), 129.68 (CH_{Ar}), 129.16 (CH_{Ar}), 127.68 (CH_{Ar}), 123.85 (2 x CH from NPhth), 112.75 (CH_3-Cq-CH_3), 109.35 (CH_3-Cq-CH_3), 86.52 (C-2), 84.88 (C-1), 81.62 (C-3), 81.47 (C-4), 76.45 (C-5), 67.06 (N-CH-CH_2-O), 66.22 (C-6), 55.43 (N-CH-CH_2-O), 50.94 (C-1-CH_2-CH), 37.81 (N-CH-CH_2Ph), 32.21 (C-1-CH_2-CH), 26.79 (CH_3-Cq-CH_3), 25.97 (CH_3-Cq-CH_3), 25.29 (CH_3-Cq-CH_3), 24.80 (CH_3-Cq-CH_3), 18.64 (C-1-CH_3).

HRMS (*m/z*): calcd for $C_{34}H_{38}N_2O_{10}Na$ $[M+Na]^+$: 657.2419, found: 657.2413.

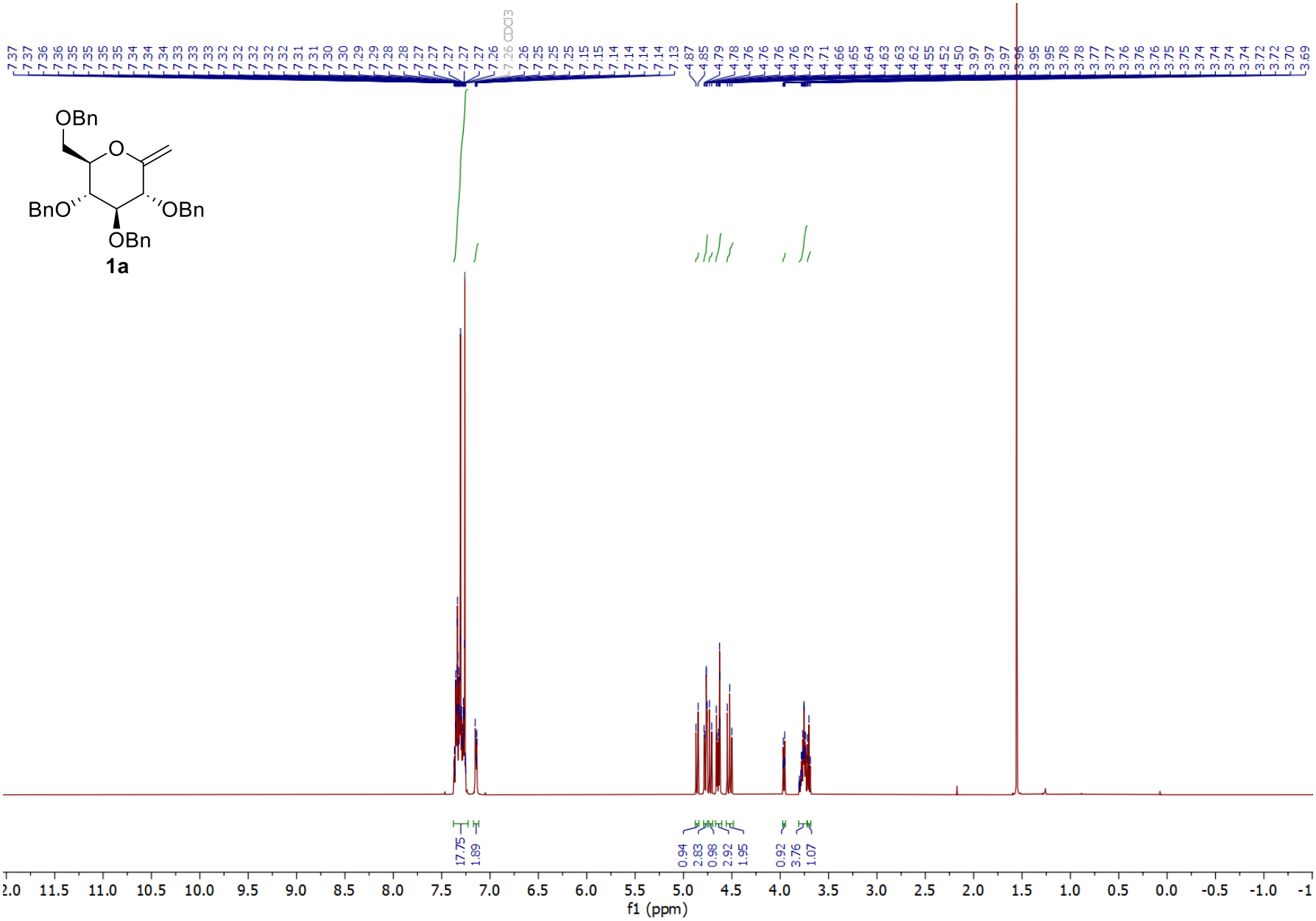
IR (film): v 2987, 2936, 1780, 1718, 1381, 1269, 1069, 909, 719, 648, 530 cm^{-1}.

5. Summary of NOESY interactions (for major diastereoisomers)

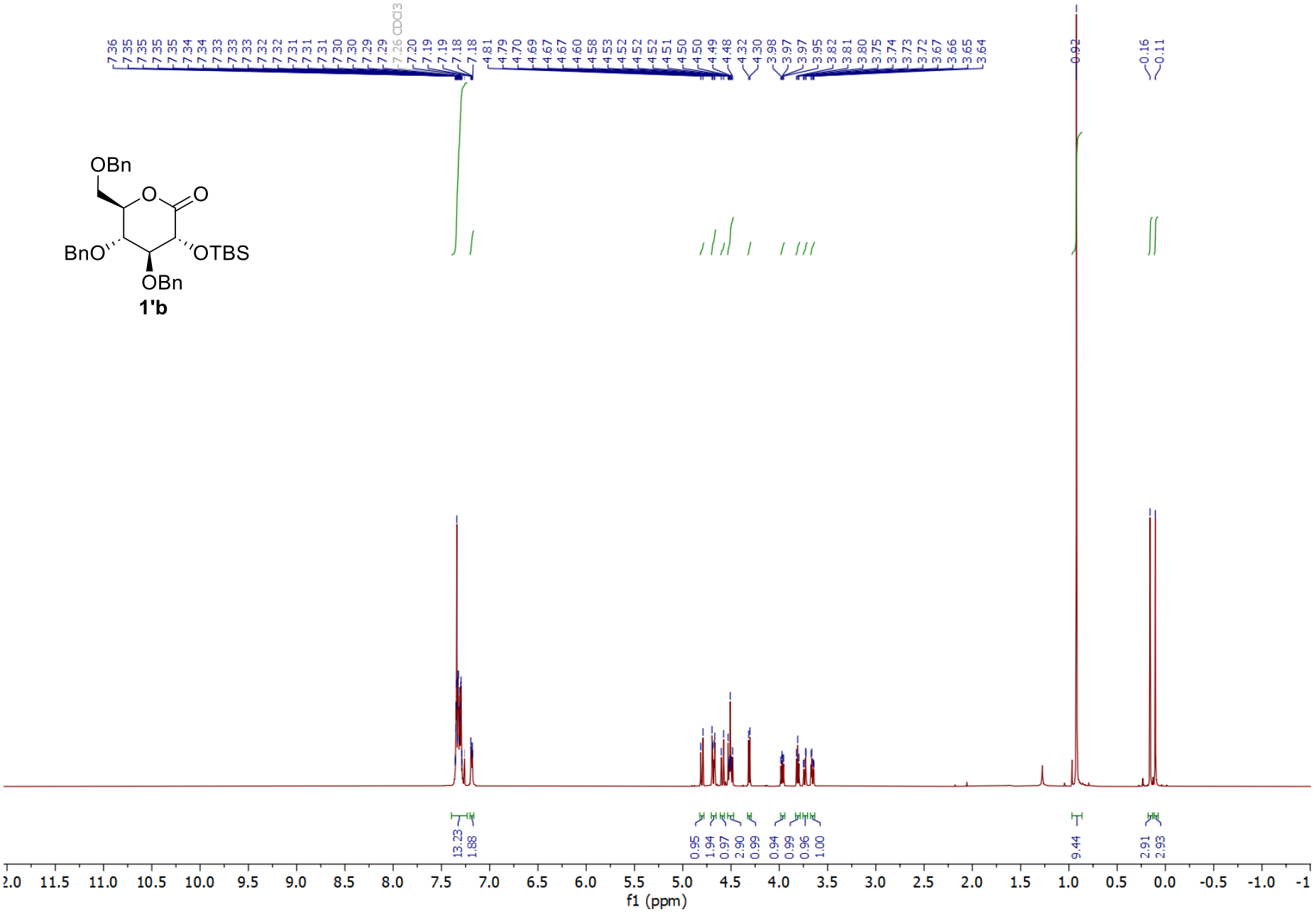


6. NMR Spectra

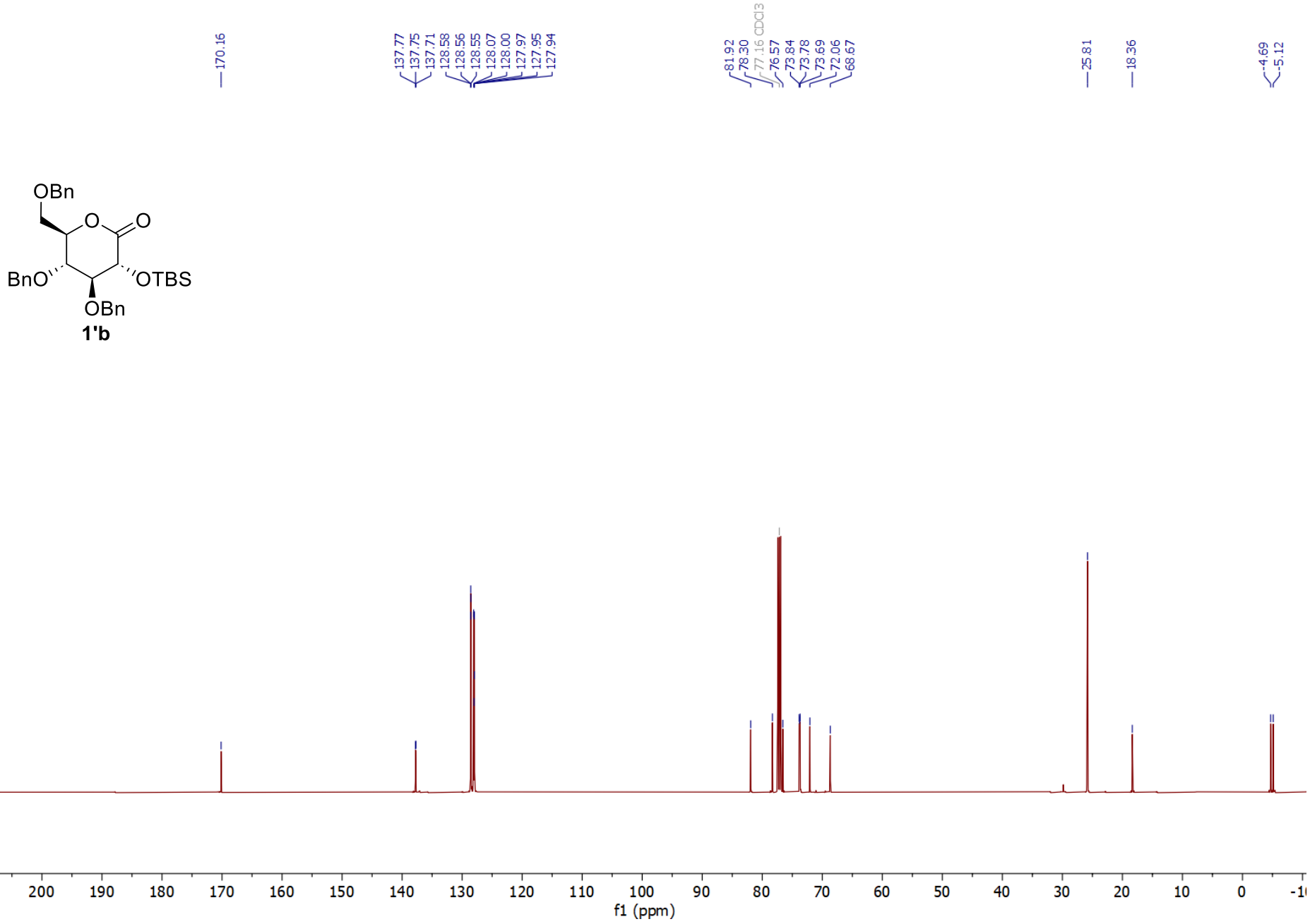
^{1}H NMR (500 MHz, $CDCl_3$) of 2,3,4,6-tetra-*O*-benzyl-*exo*-D-glucal (1a)



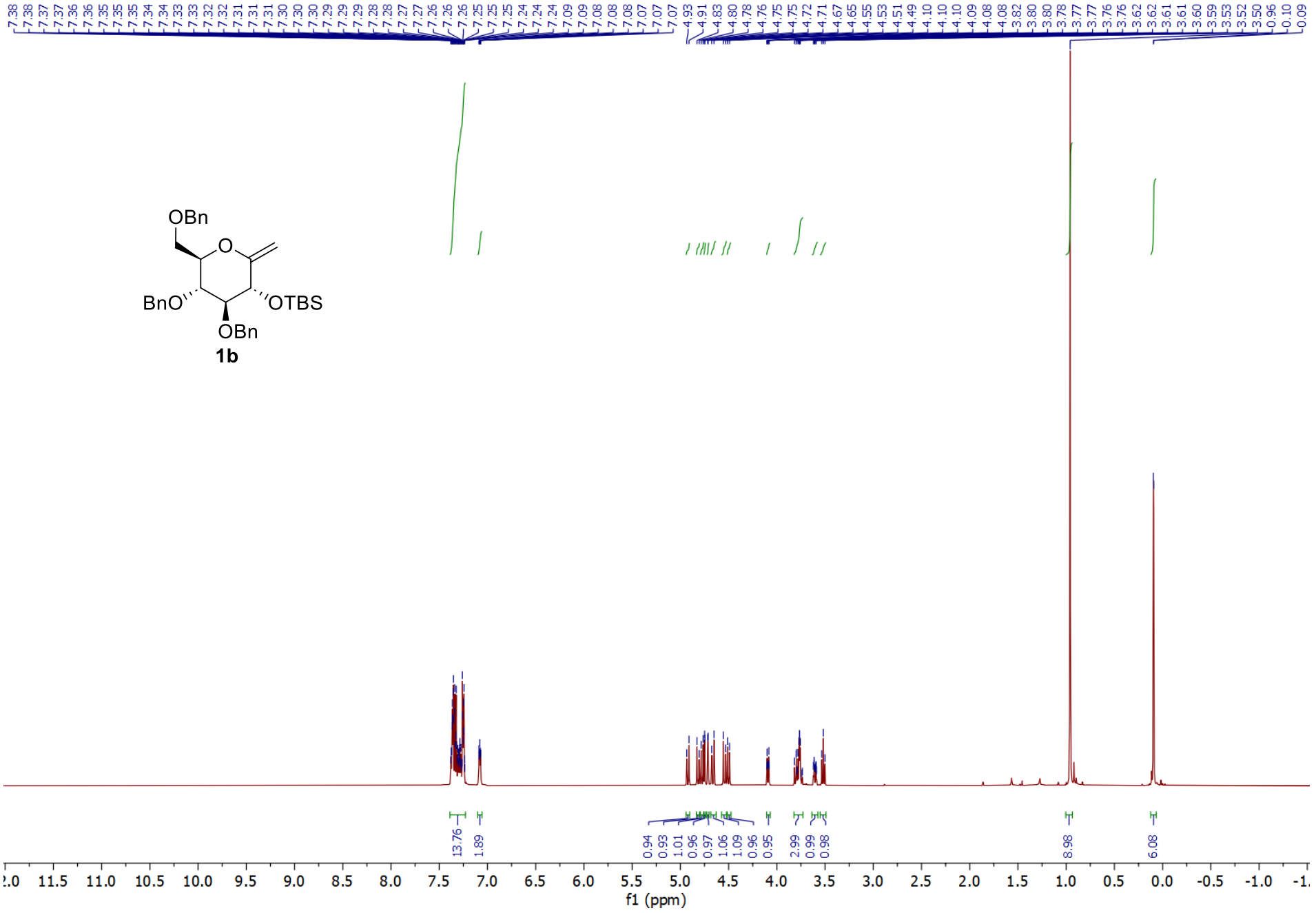
^{1}H NMR (500 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl-D-gluconolactone (1'b)



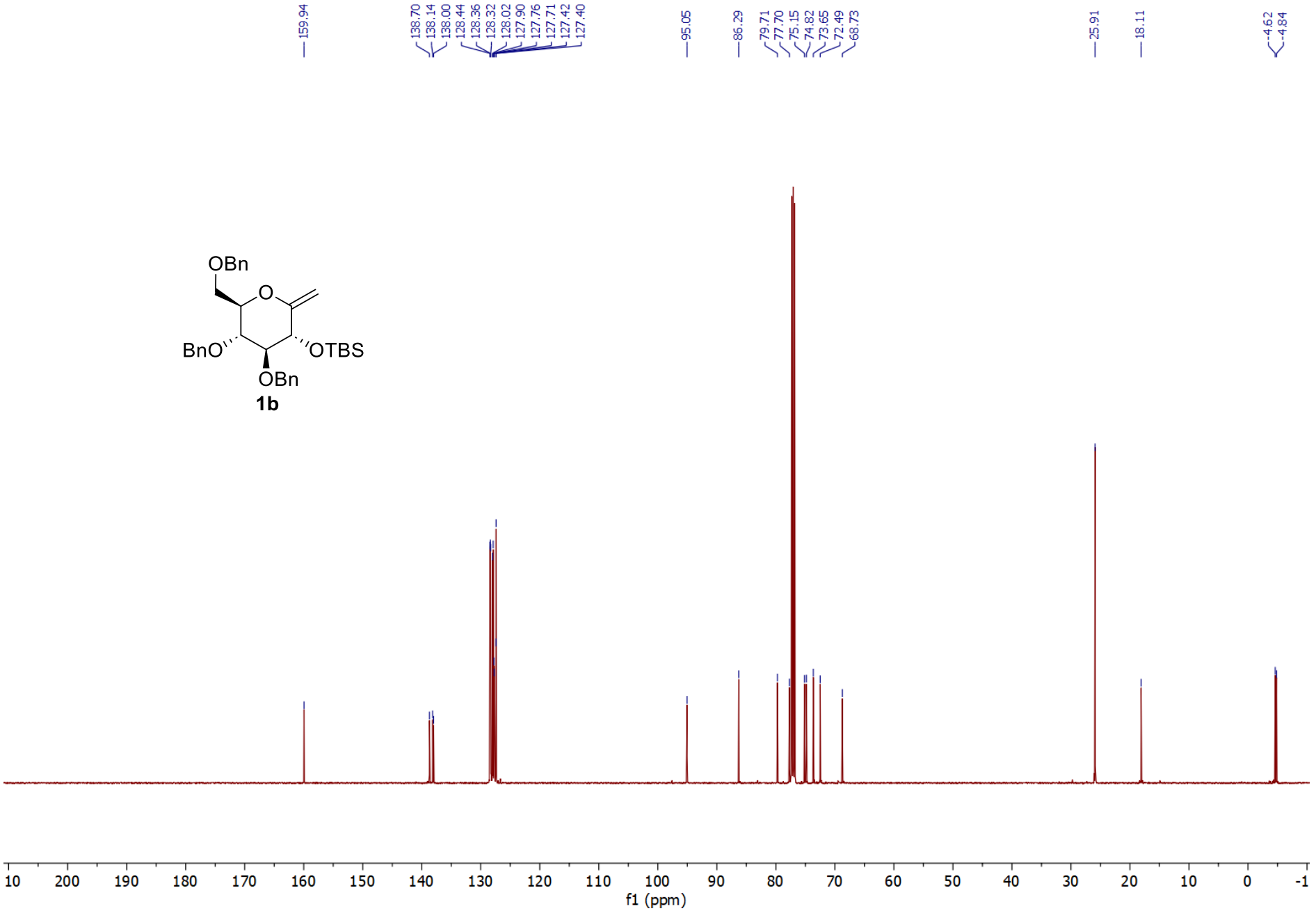
^{13}C NMR (125 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl-D-gluconolactone (1'b)



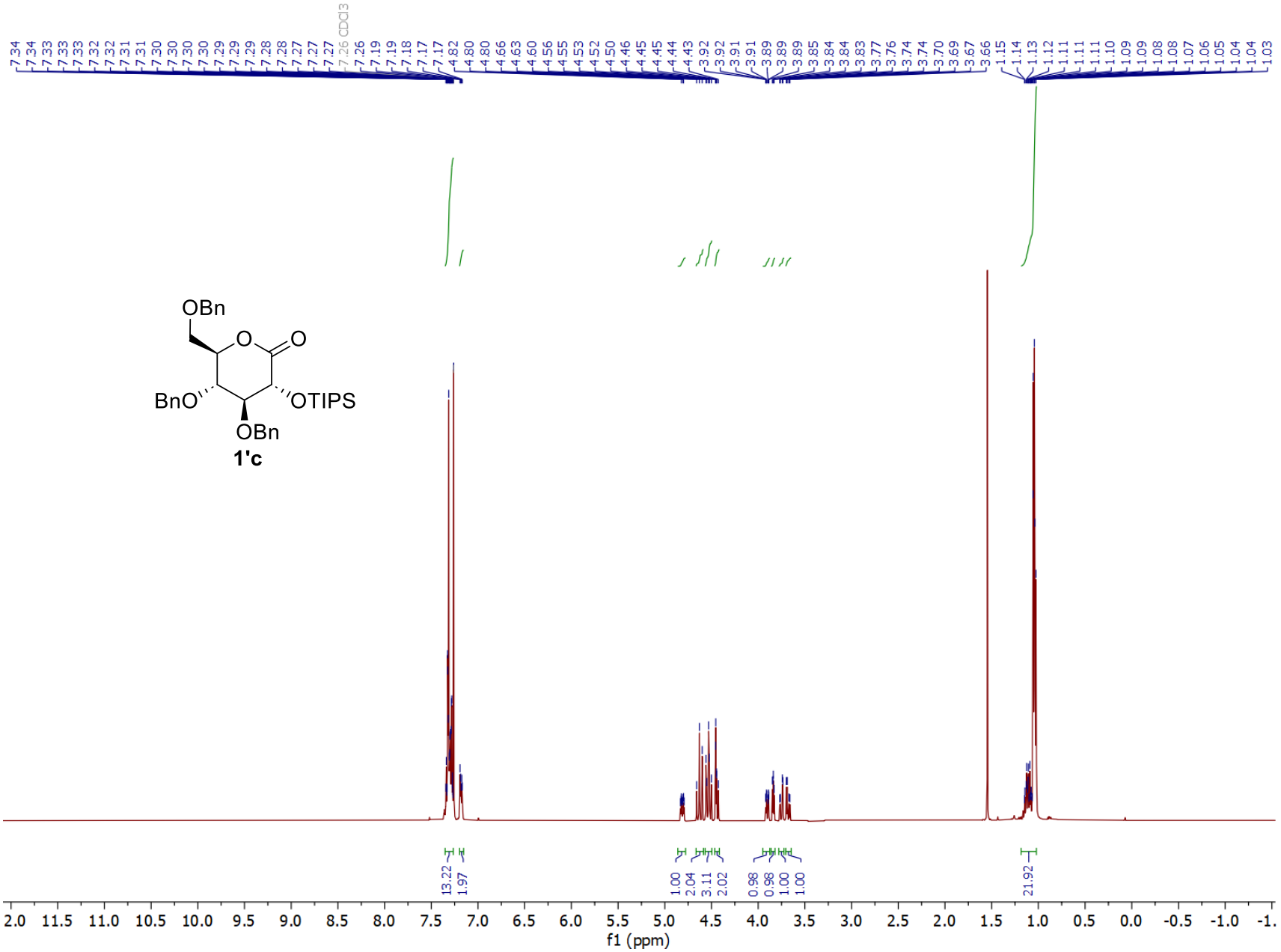
^{1}H NMR (500 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl-D-gluconolactone (1b)



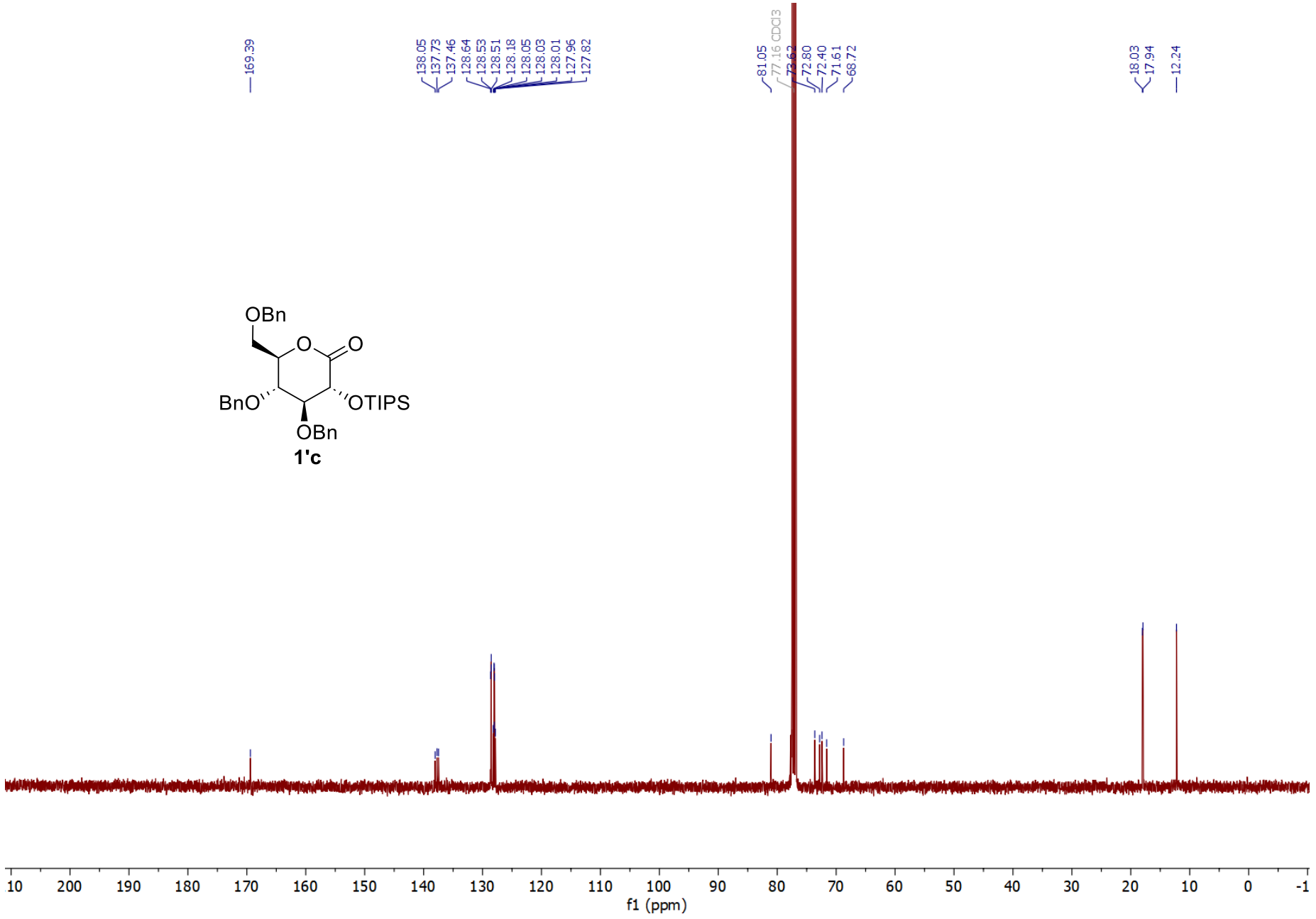
^{13}C NMR (125 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-*tert*-butyldimethylsilyl-D-gluconolactone (1b)



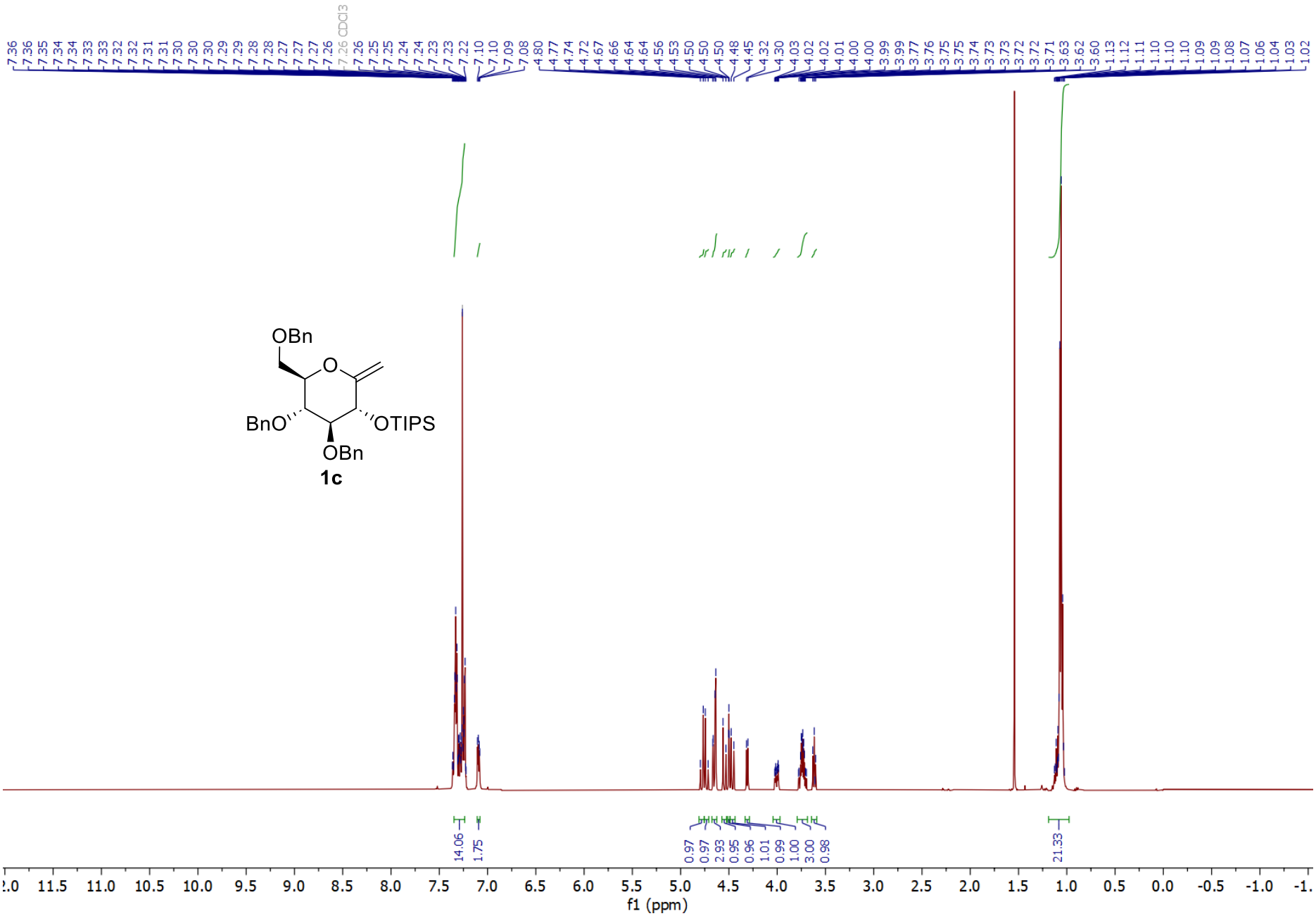
^{1}H NMR (400 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-triisopropylsilyl-D-gluconolactone (1'c)



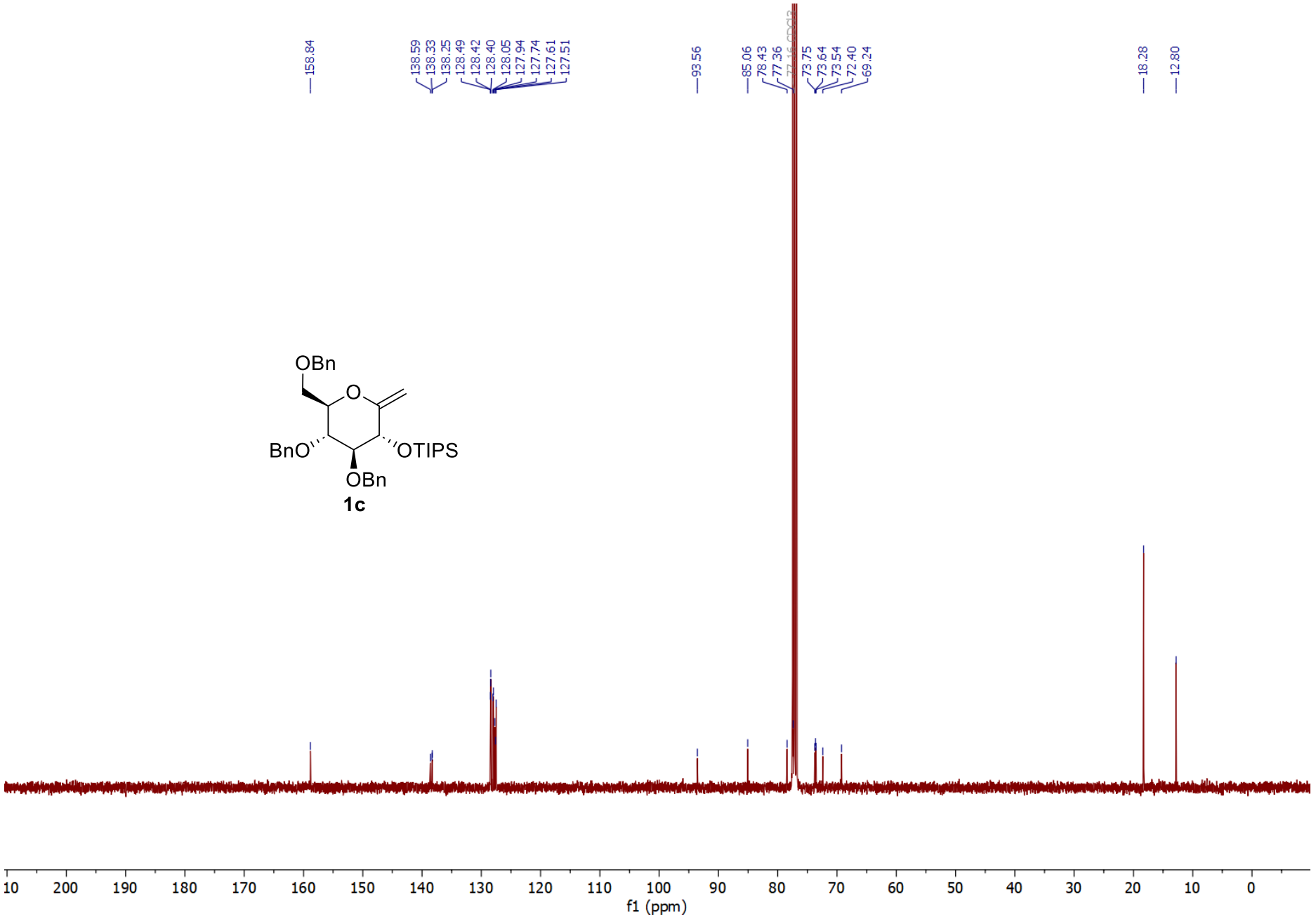
^{13}C NMR (100 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-triisopropylsilyl-D-gluconolactone (1'c)



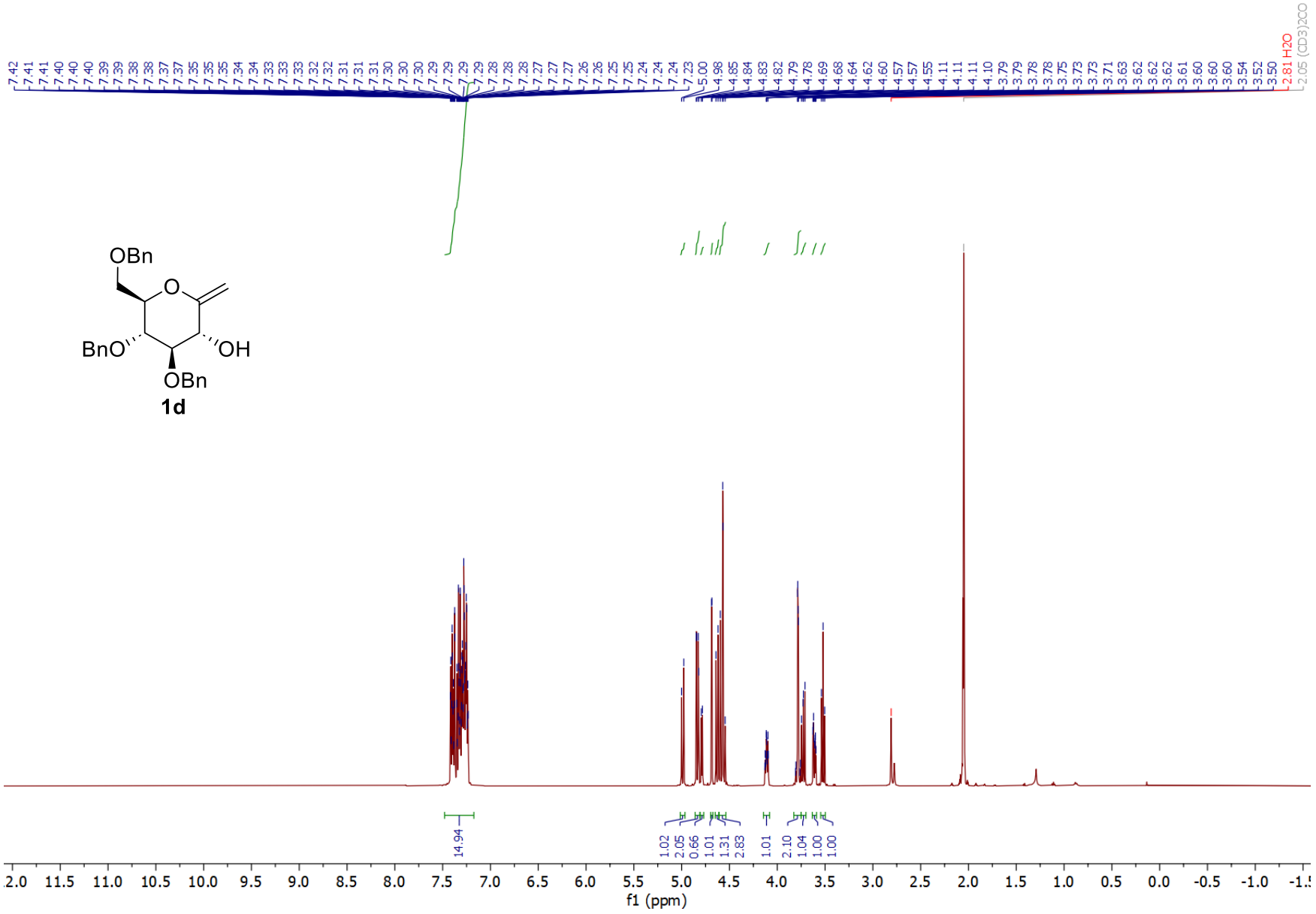
^{1}H NMR (400 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-triisopropylsilyl-*exo*-D-glucal (1c)



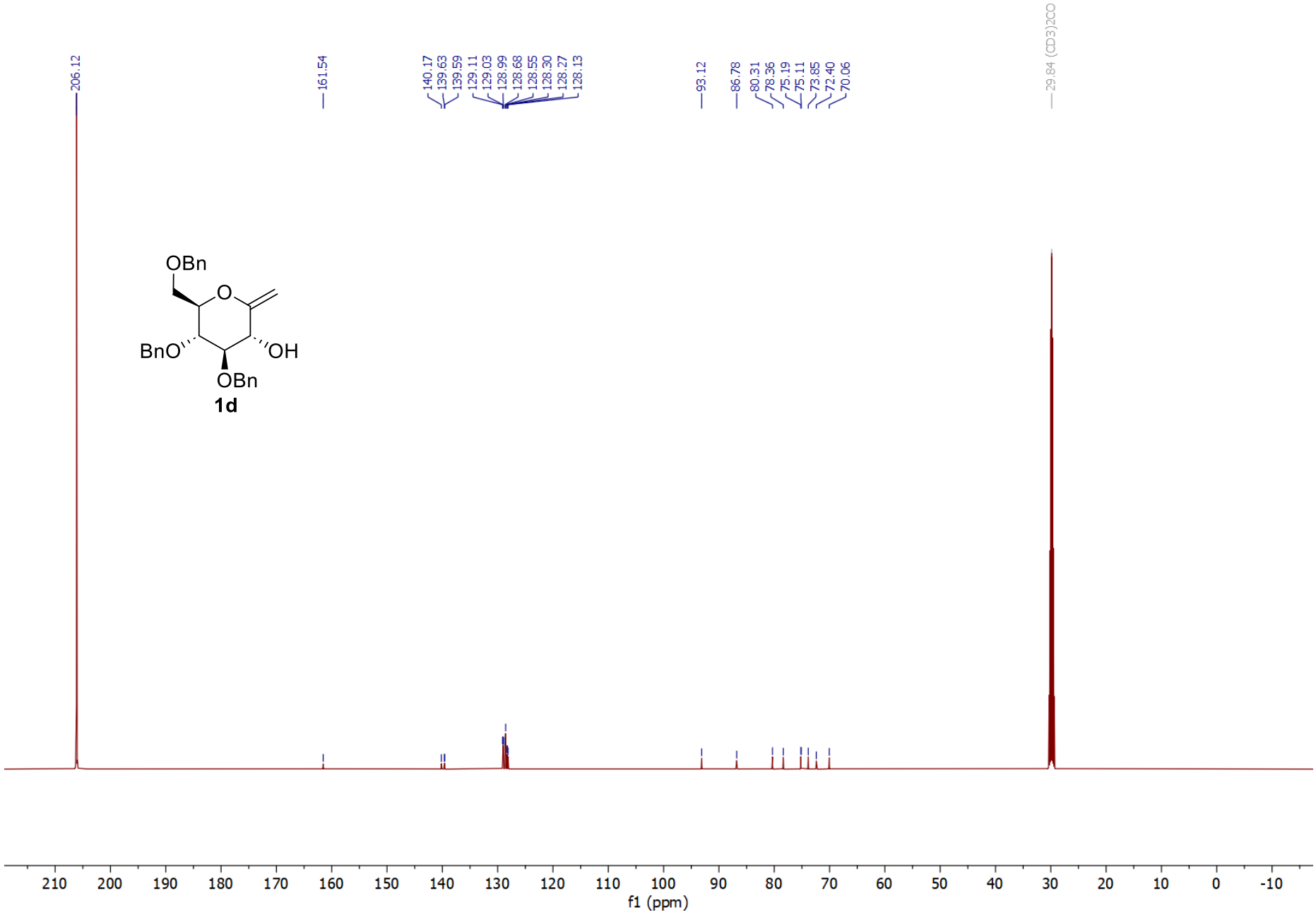
^{13}C NMR (100 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-triisopropylsilyl-*exo*-D-glucal (1c)



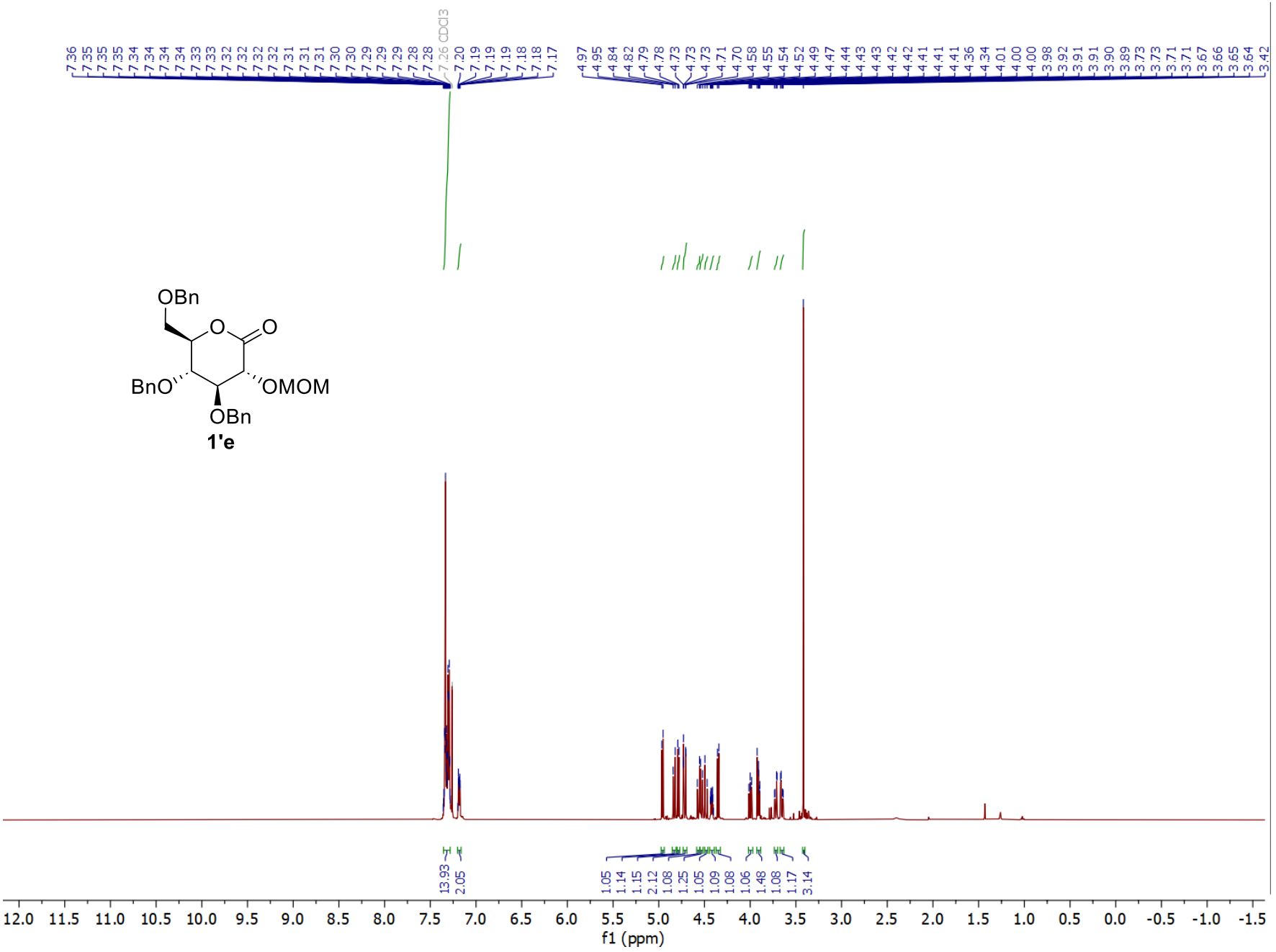
^{1}H NMR (400 MHz, acetone-d6) of 3,4,6-tri-*O*-benzyl-*exo*-D-glucal (1d)



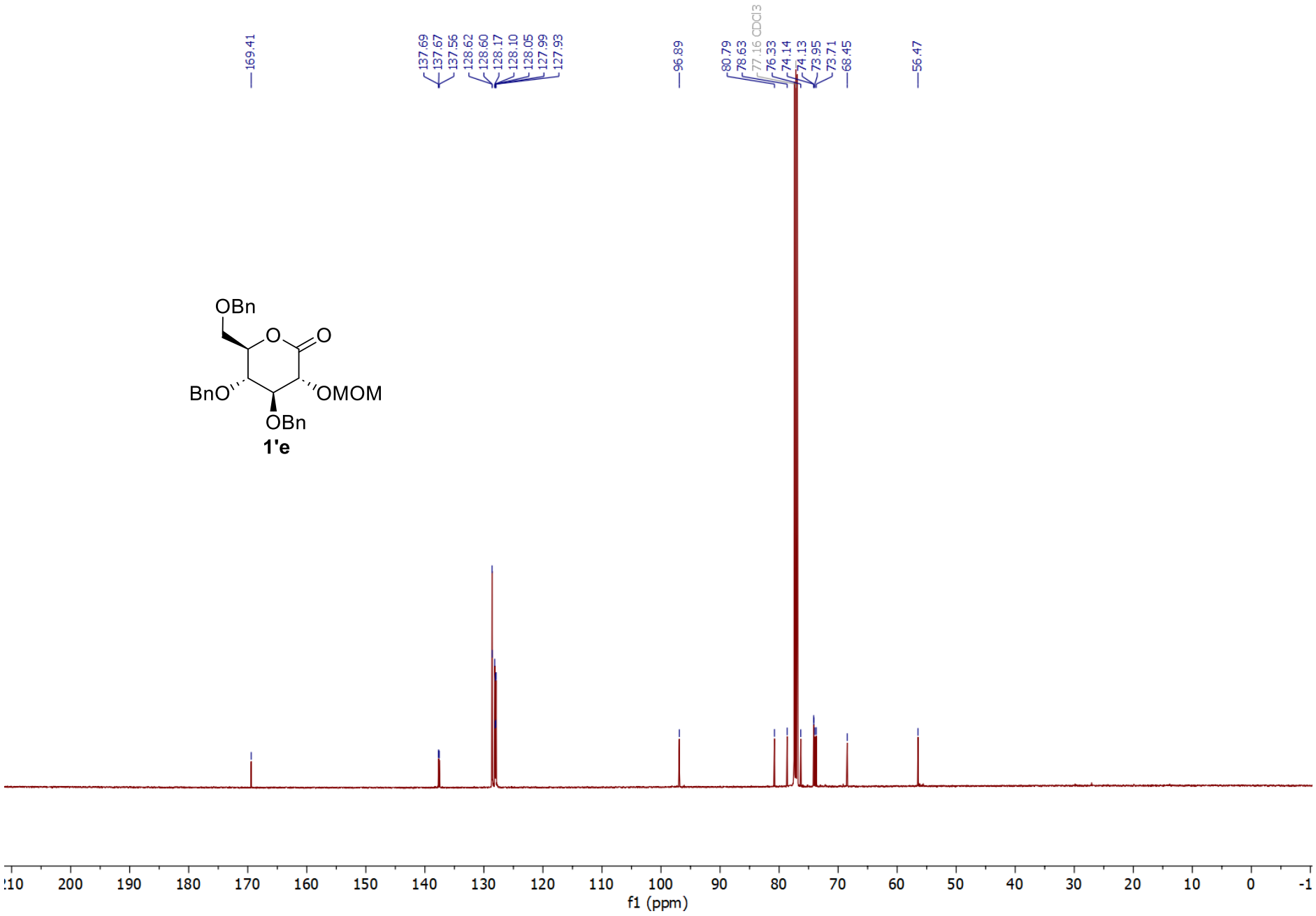
^{13}C NMR (100 MHz, acetone-d6) of 3,4,6-tri-*O*-benzyl-*exo*-D-glucal (1d)



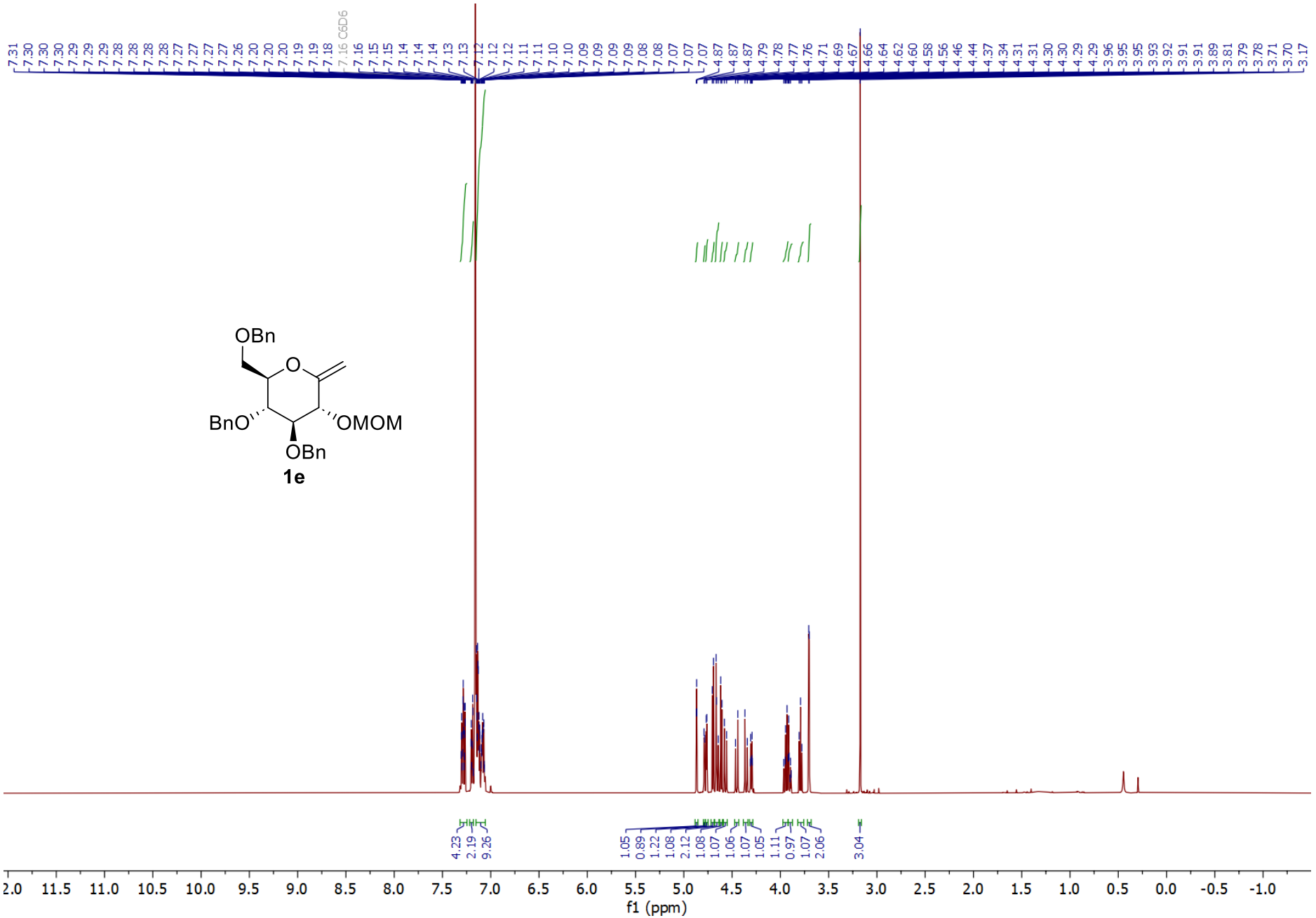
^{1}H NMR (500 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy-D-gluconolactone (1'e)



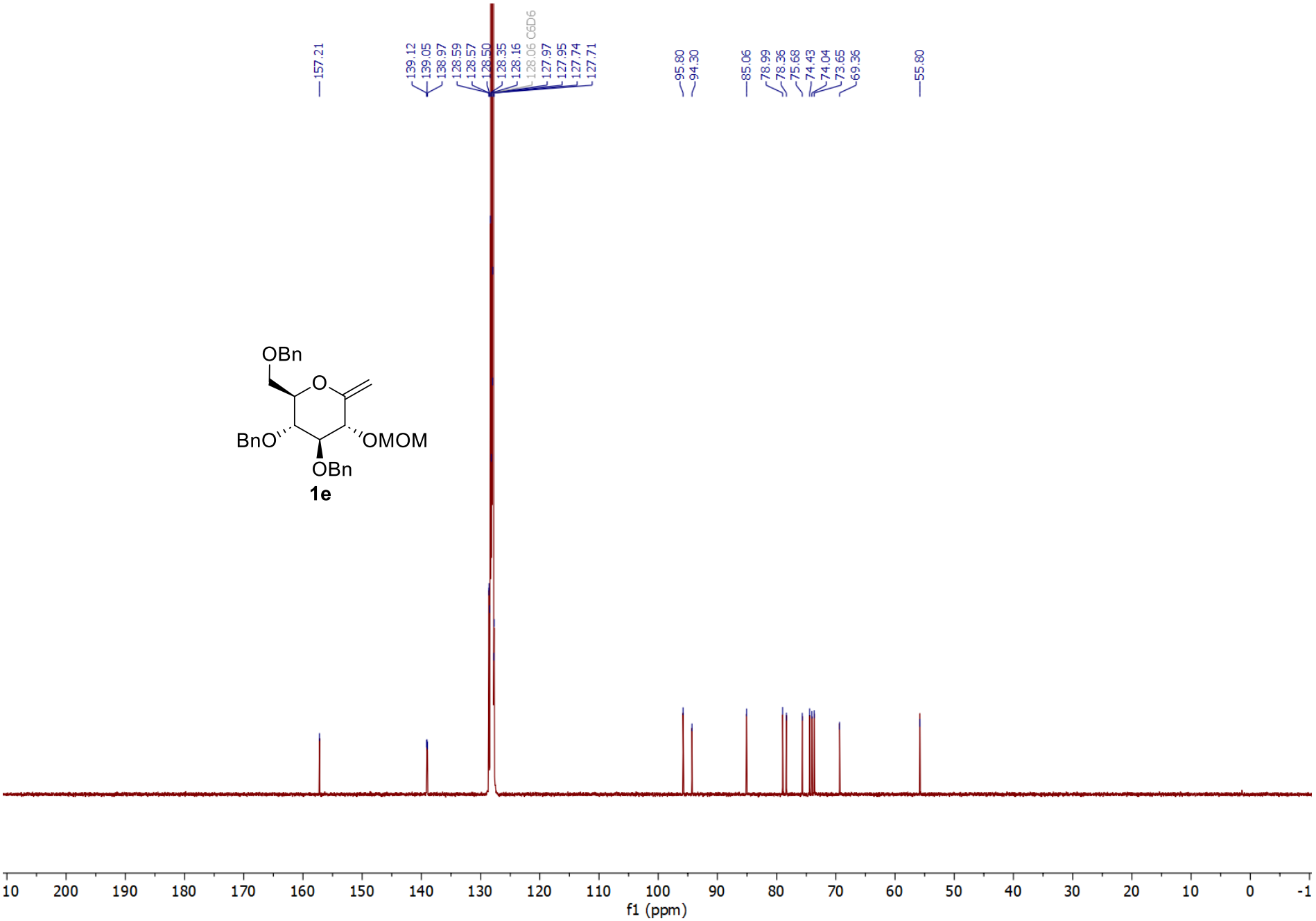
^{13}C NMR (125 MHz, $CDCl_3$) of 3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy-D-gluconolactone (1'e)



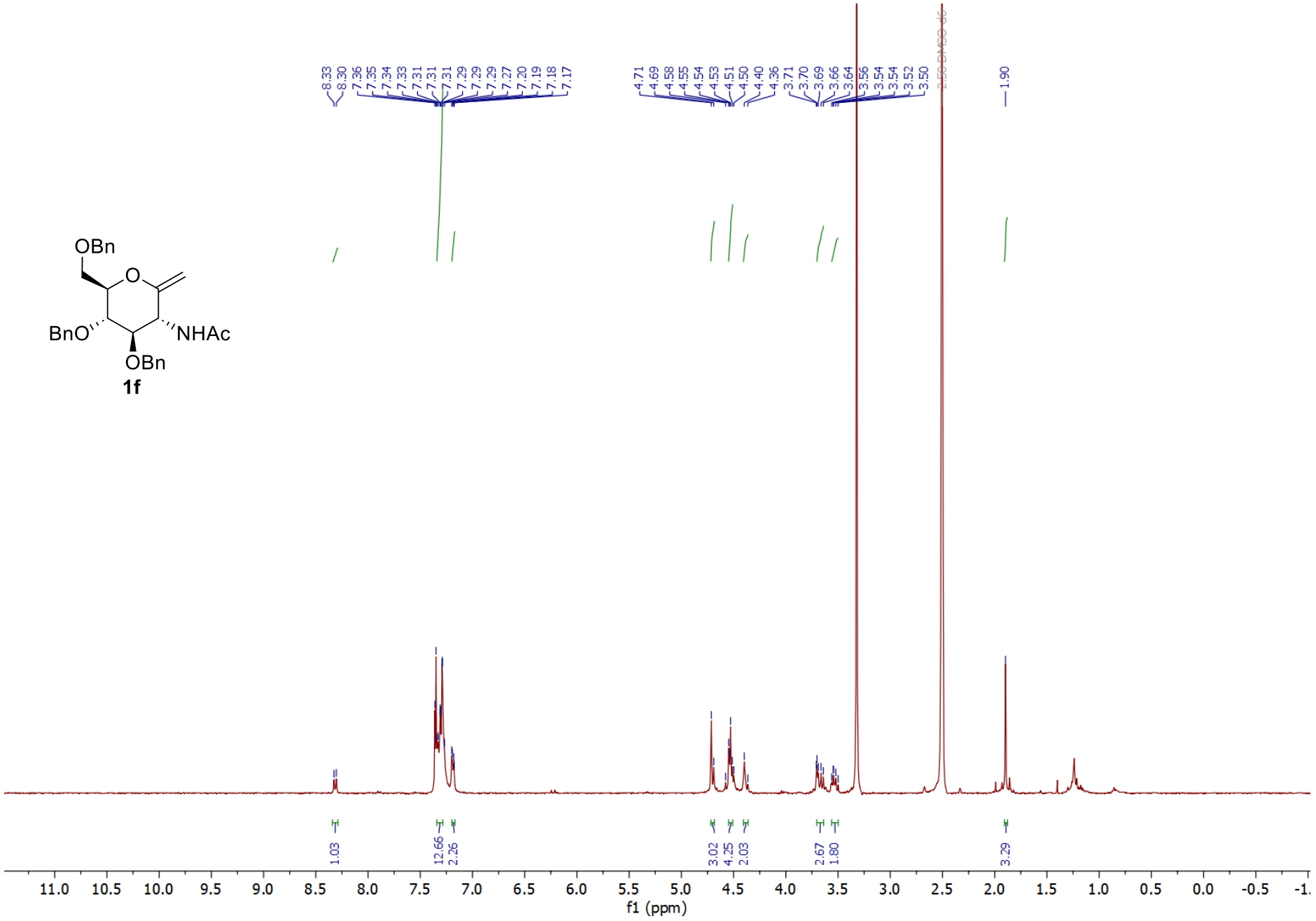
^{1}H NMR (500 MHz, benzene-d6) of 3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy-*exo*-D-glucal (1e)



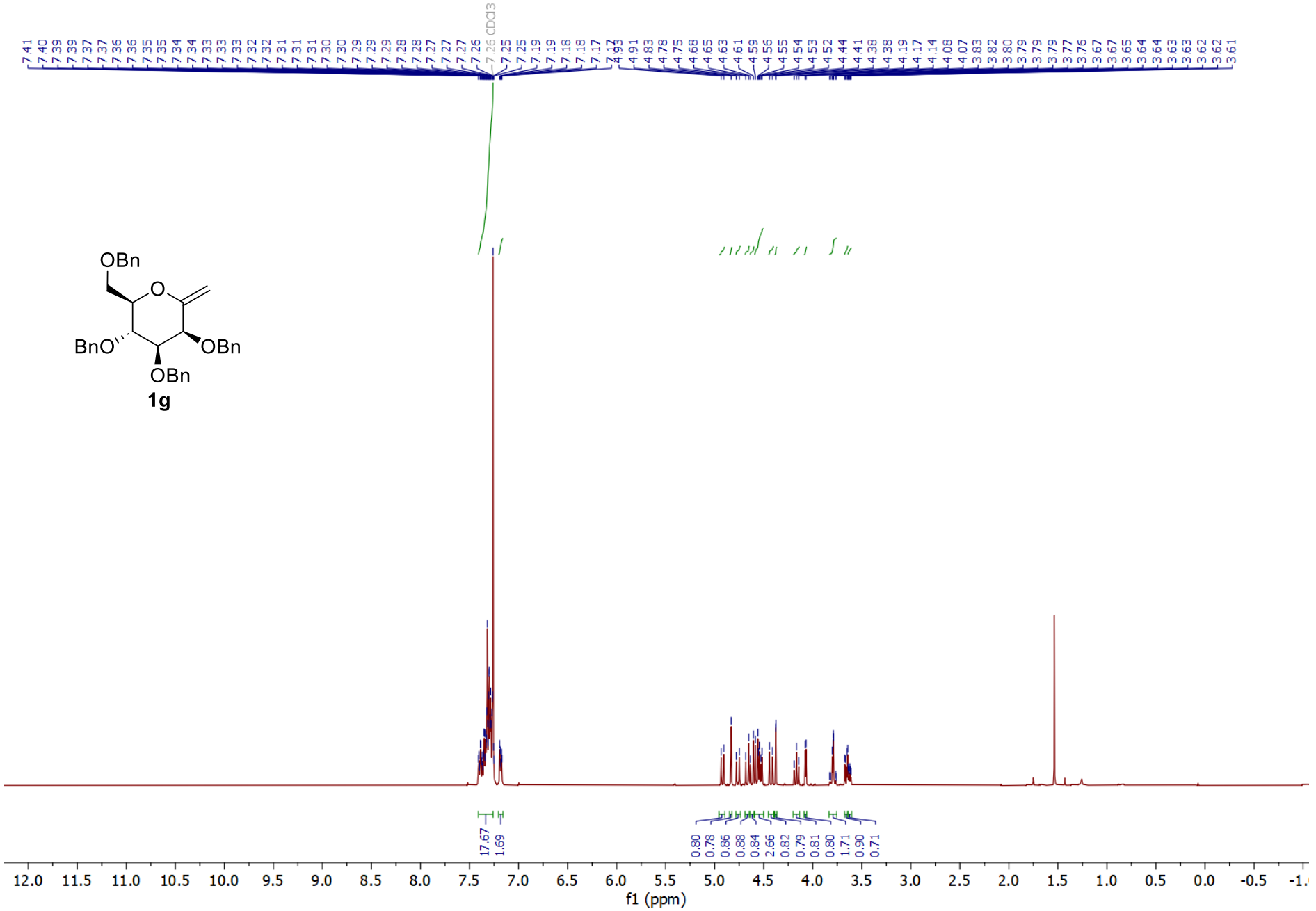
^{13}C NMR (125 MHz, benzene-d6) of 3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy-*exo*-D-glucal (1e)



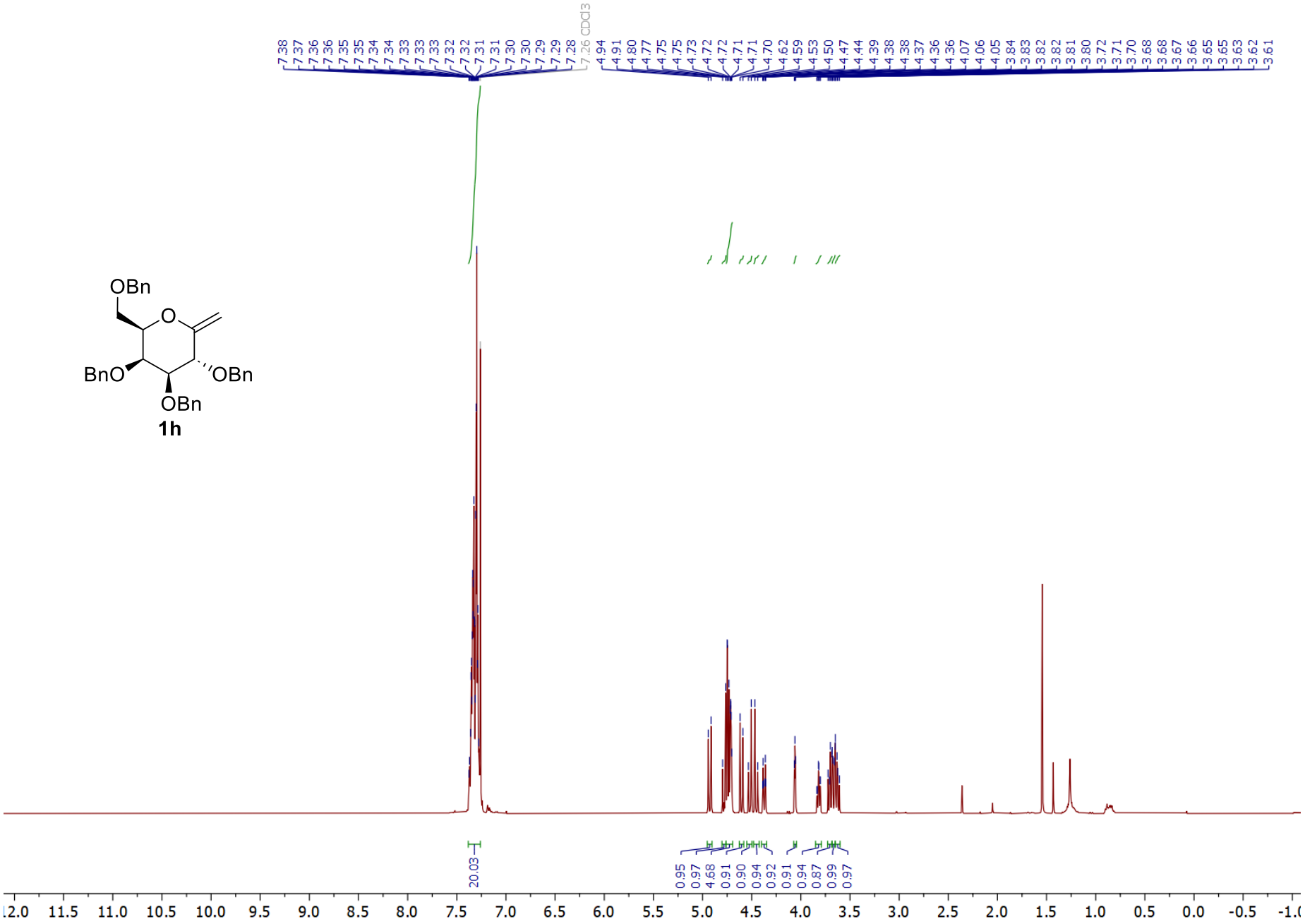
^{1}H NMR (400 MHz, DMSO-d6) of 2-acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-*exo*-D-glucal (1f)



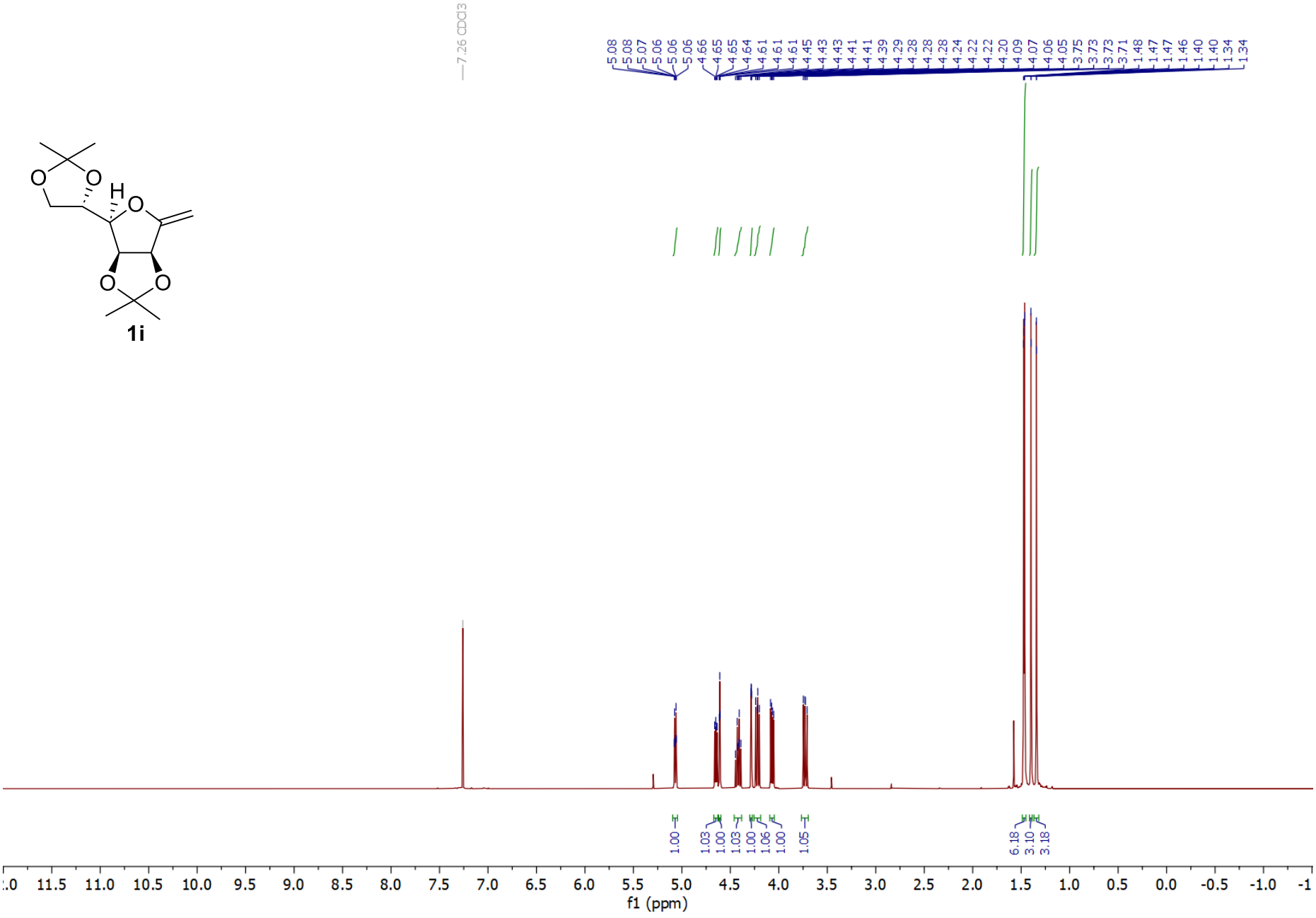
^{1}H NMR (400 MHz, $CDCl_3$) of 1-methylidene-2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (1g)



^{1}H NMR (400 MHz, $CDCl_3$) of 2,3,4,6-tetra-*O*-benzyl-*exo*-D-galactal (1h)

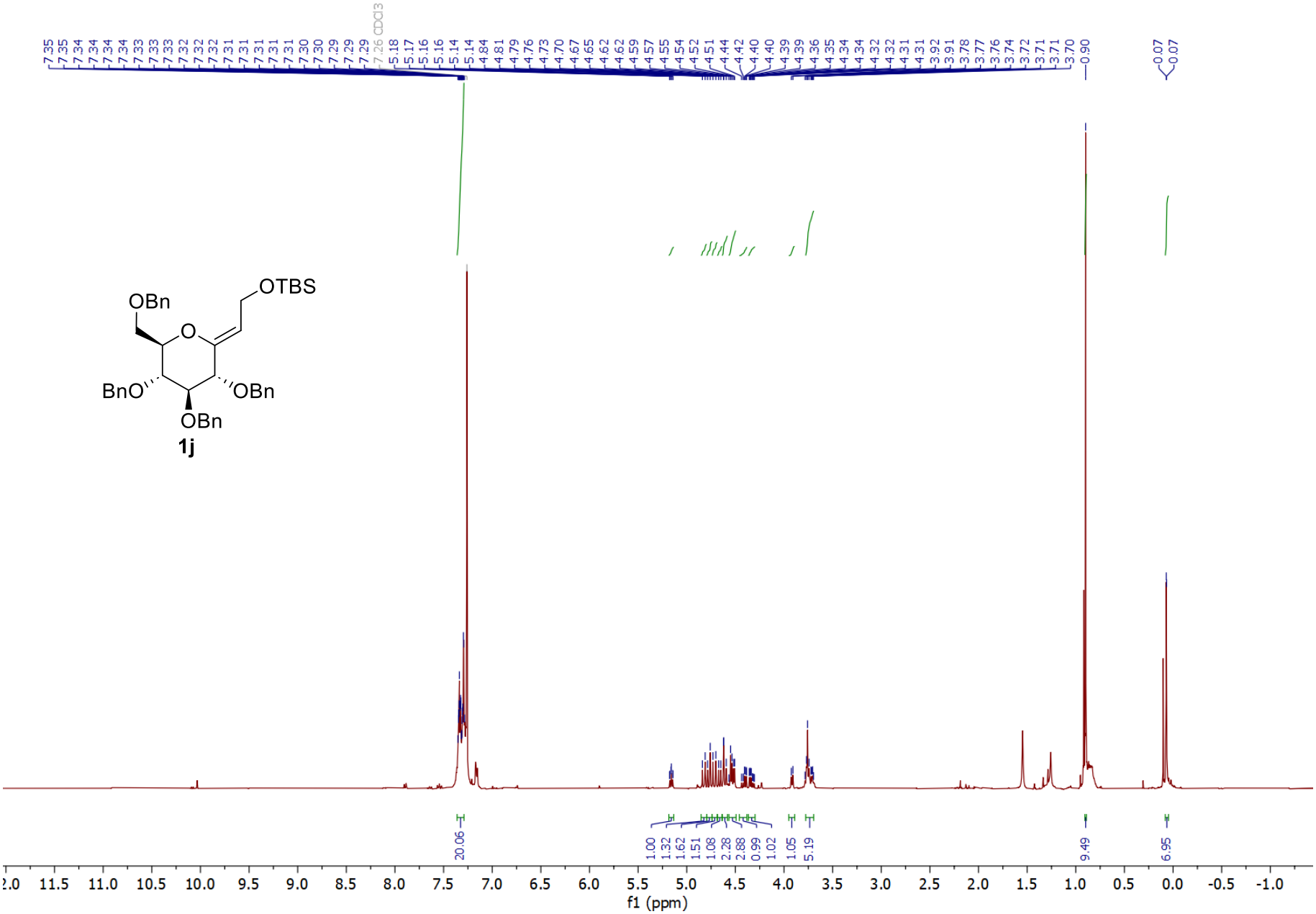


^{1}H NMR (400 MHz, $CDCl_3$) 1-methylidene-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranoside (1i)

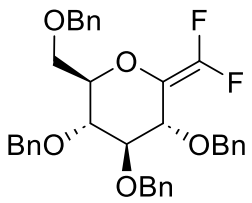


1i

^{1}H NMR (400 MHz, $CDCl_3$) *tert*-butyldimethyl((*Z*)-2-(3,4,6-tri-*O*-benzyl-2-*O*-triisopropylsilyl)tetrahydro-2H-pyran-2-ylidene)ethoxy)silane (1j)

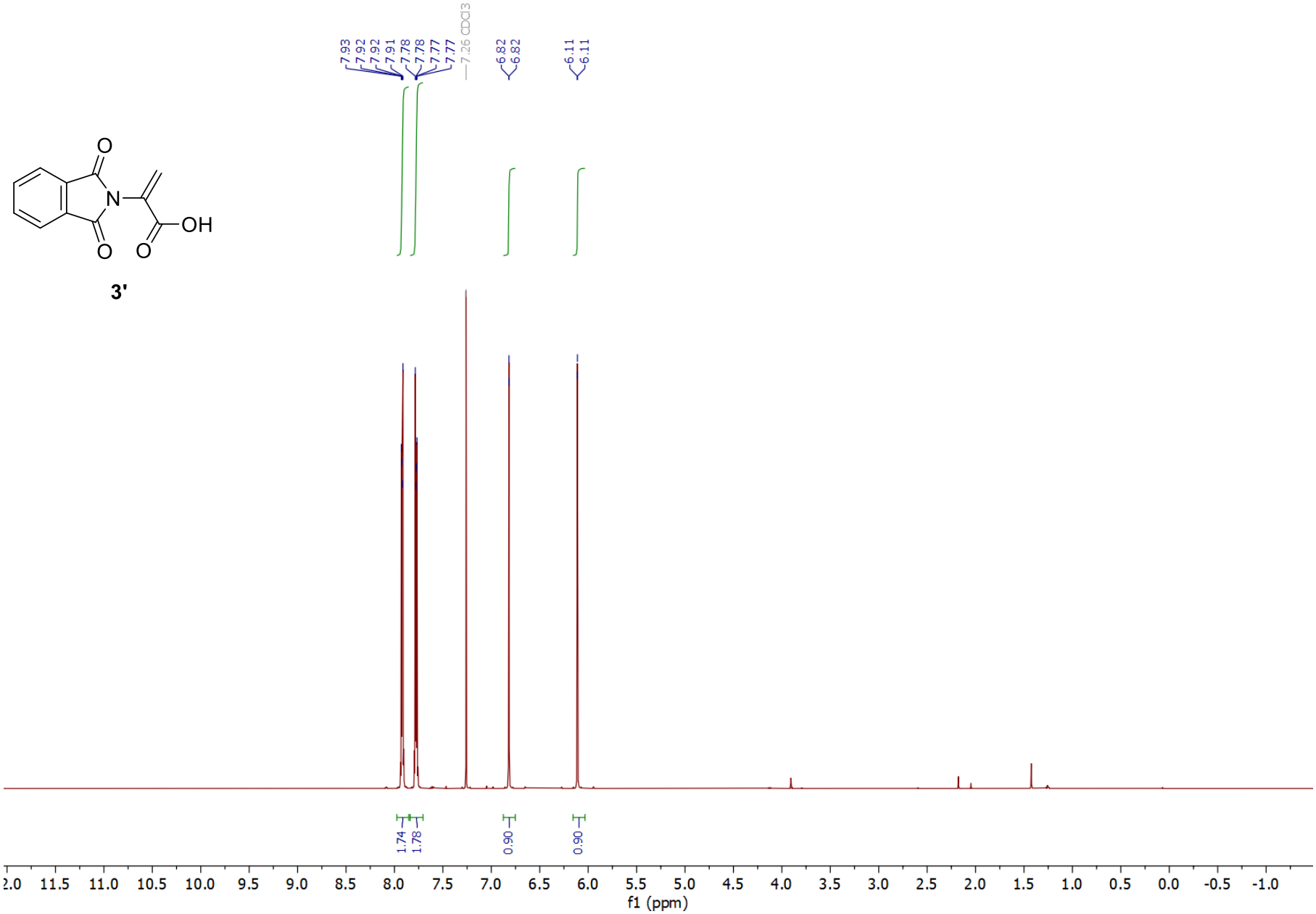


^{1}H NMR (400 MHz, $CDCl_3$) 2,6-anhydro-1-deoxy-1,1-difluoro-3,4,5,7-tetrakis-*O*-benzyl-D-gluco-heptI-enitol (1k)

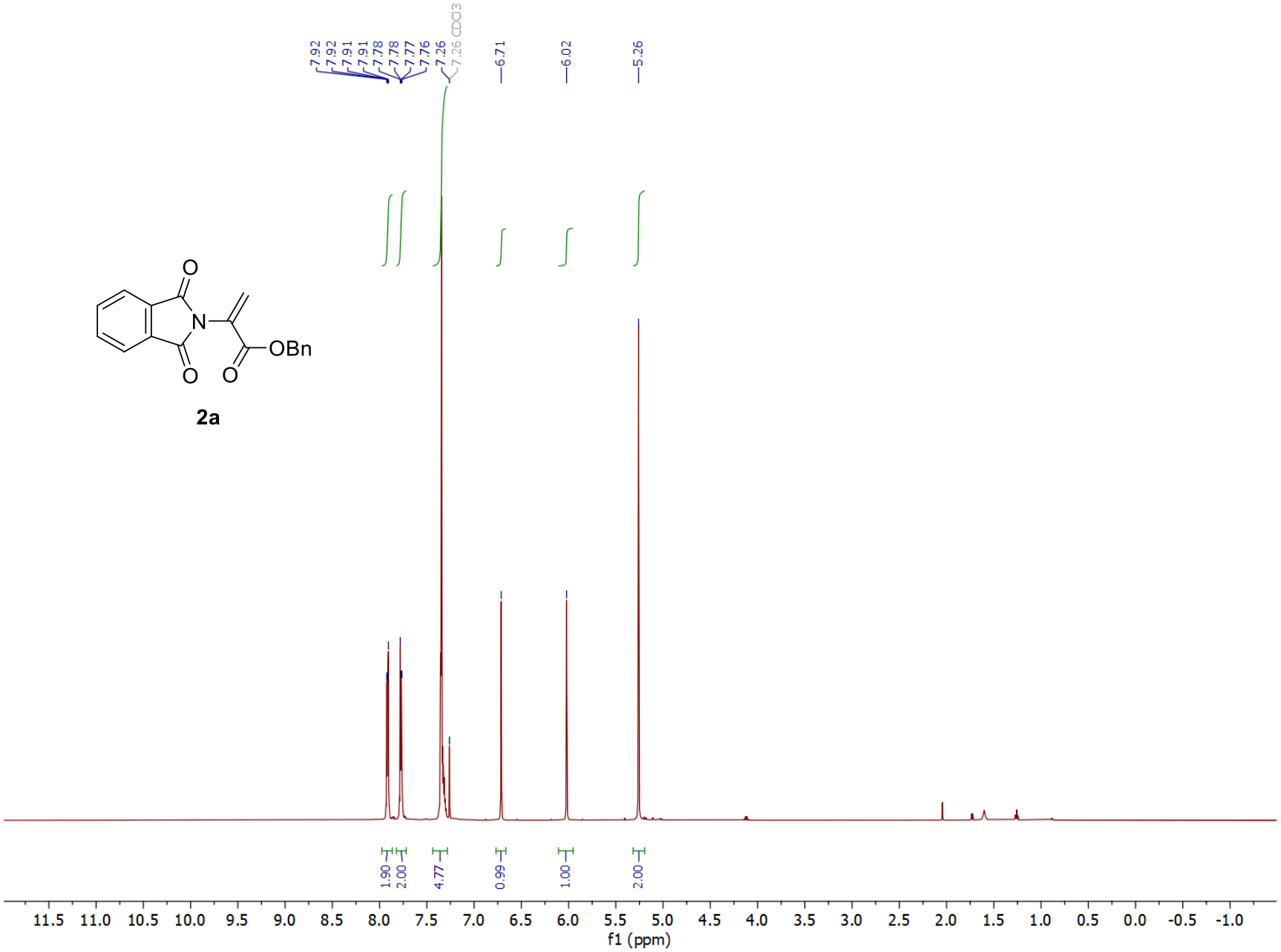


1k

^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1,3-dioxoisoindolin-2-yl)acrylic acid (2')

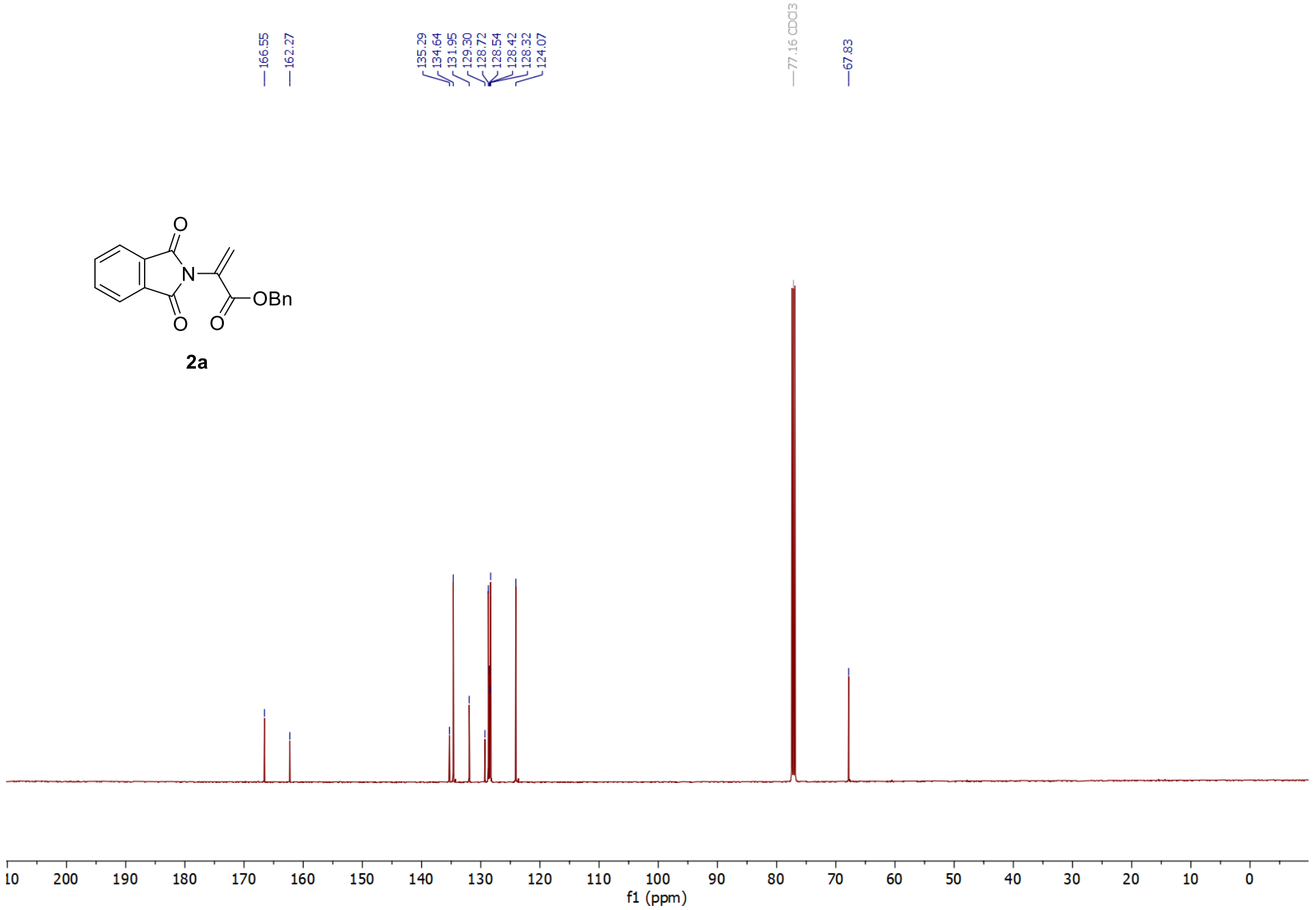


^{1}H NMR (500 MHz, $CDCl_3$) of benzyl 2-(phthalimidoyl)acrylate (2a)



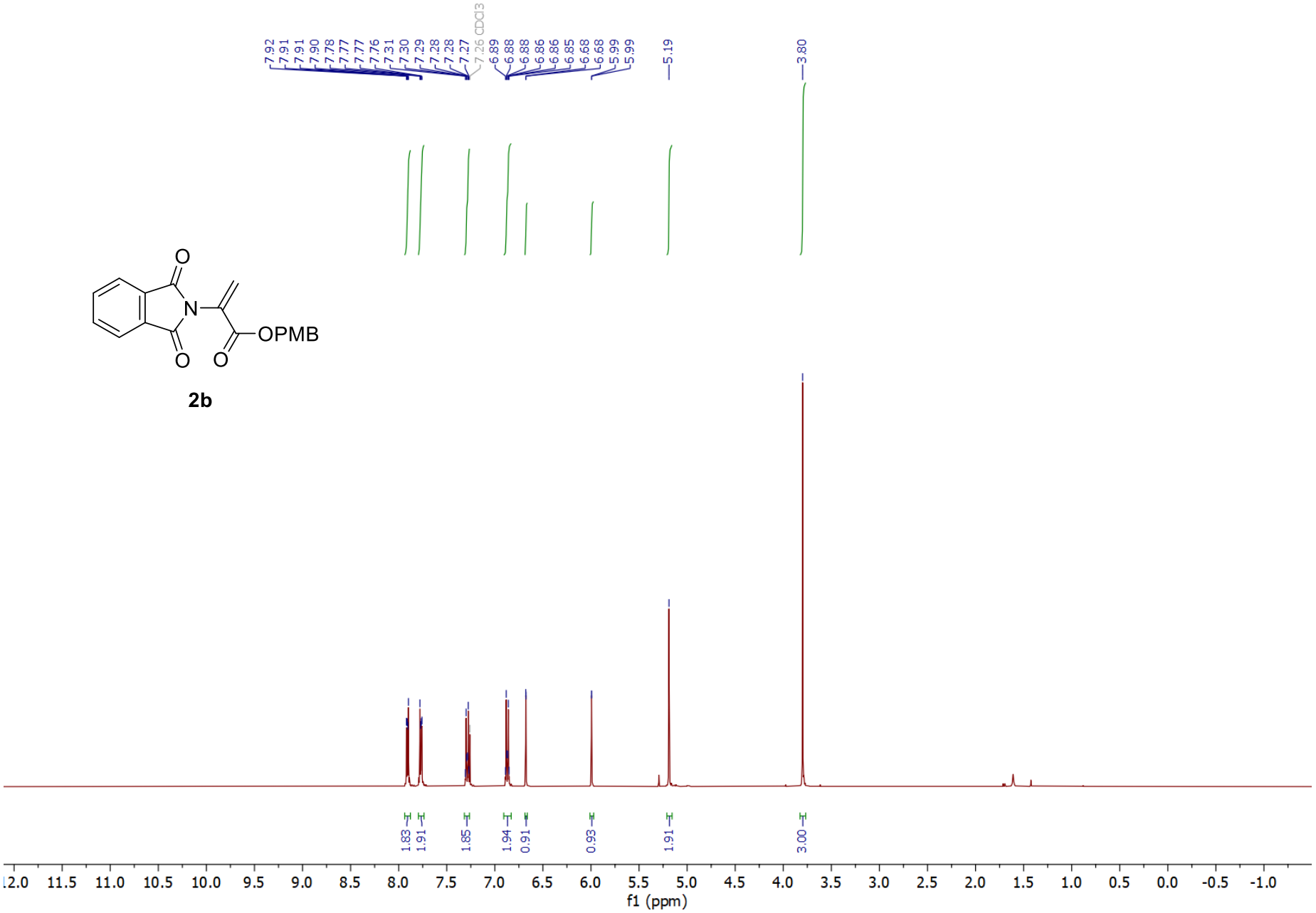
2a

^{13}C NMR (125 MHz, $CDCl_3$) of benzyl 2-(phthalimidoyl)acrylate (2a)



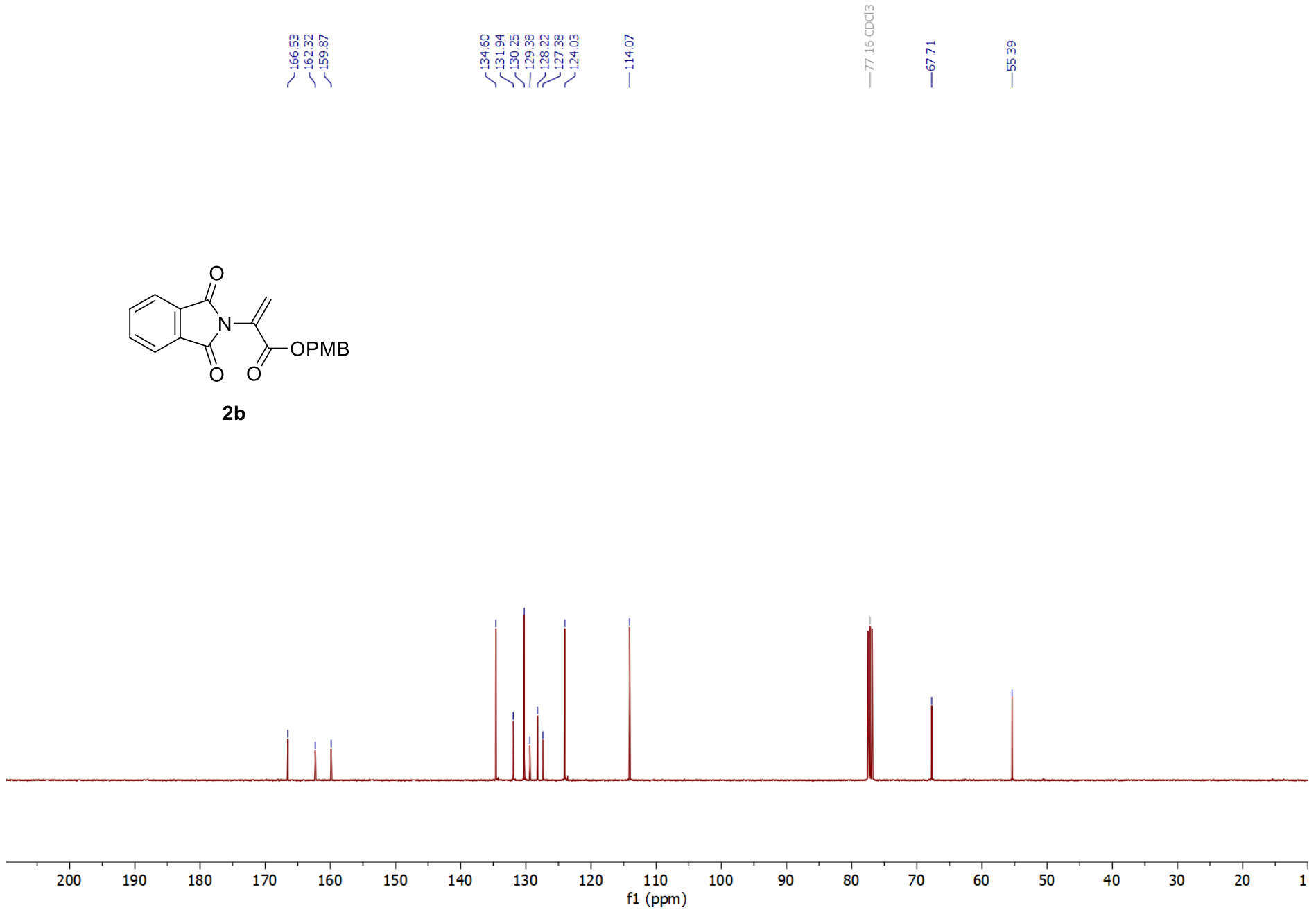
2a

^{1}H NMR (400 MHz, $CDCl_3$) of *p*-methoxybenzyl 2-(phthalimidoyl)acrylate (2b)



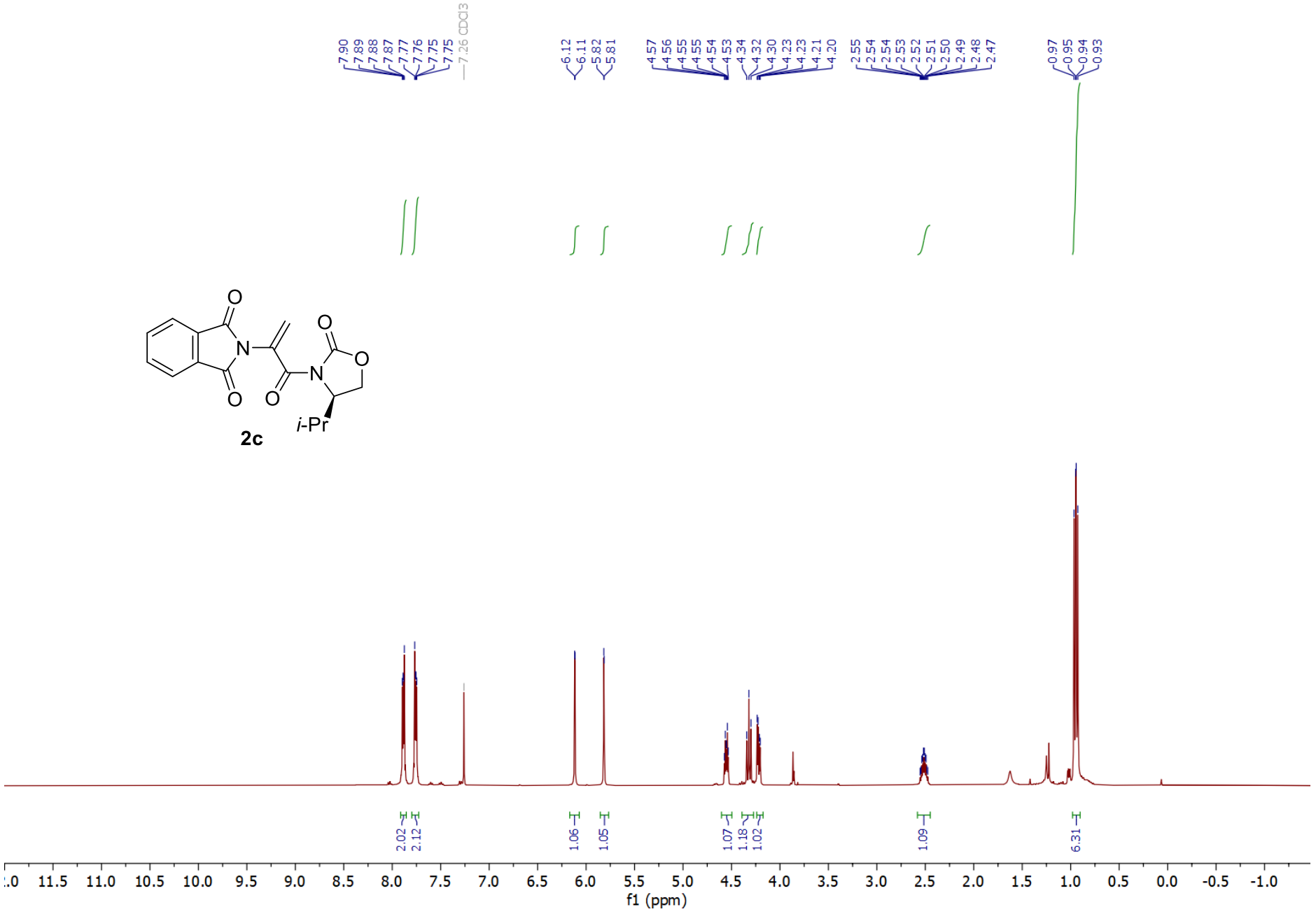
2b

^{13}C NMR (100 MHz, $CDCl_3$) of *p*-methoxybenzyl 2-(phthalimidoyl)acrylate (2b)

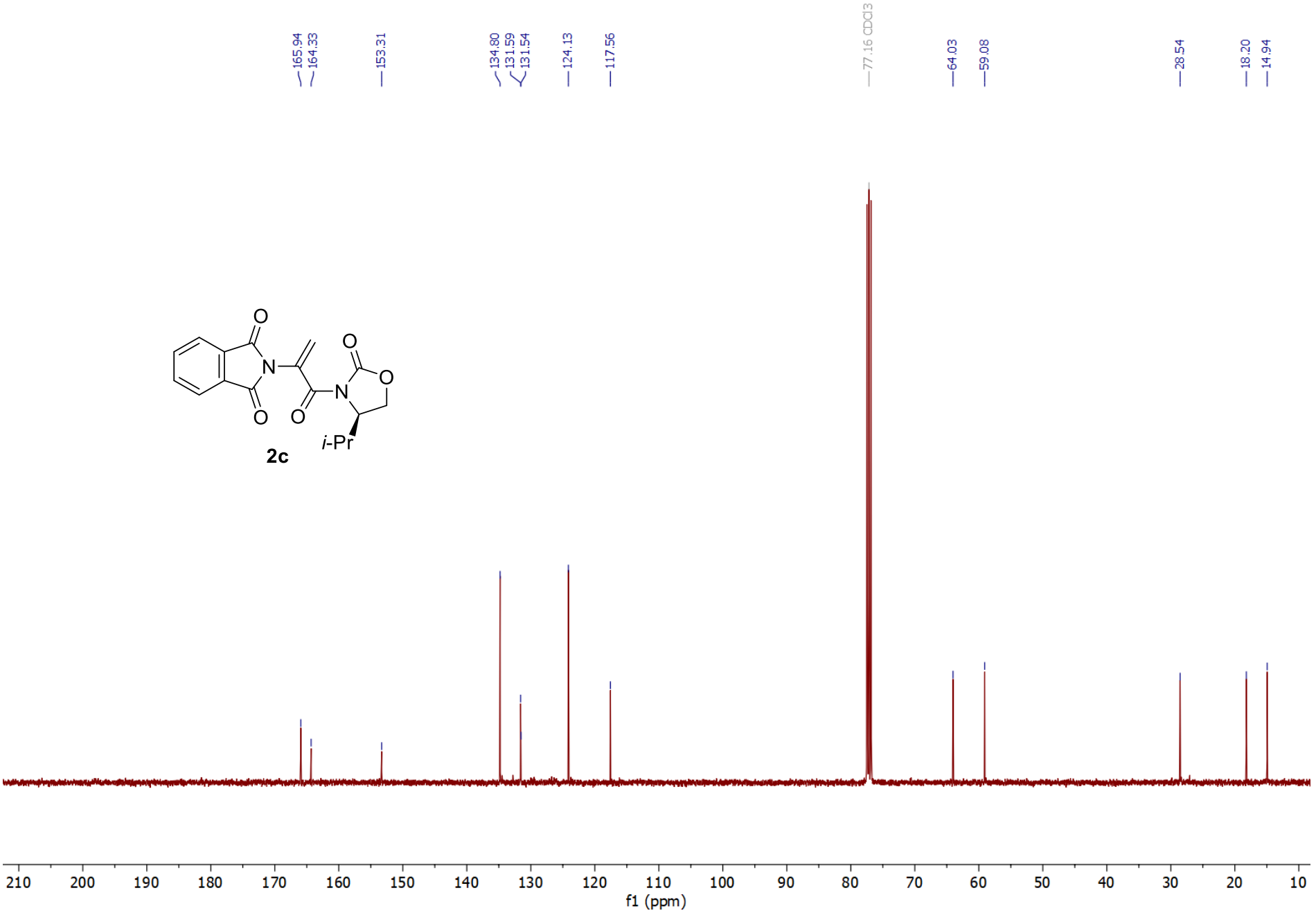


2b

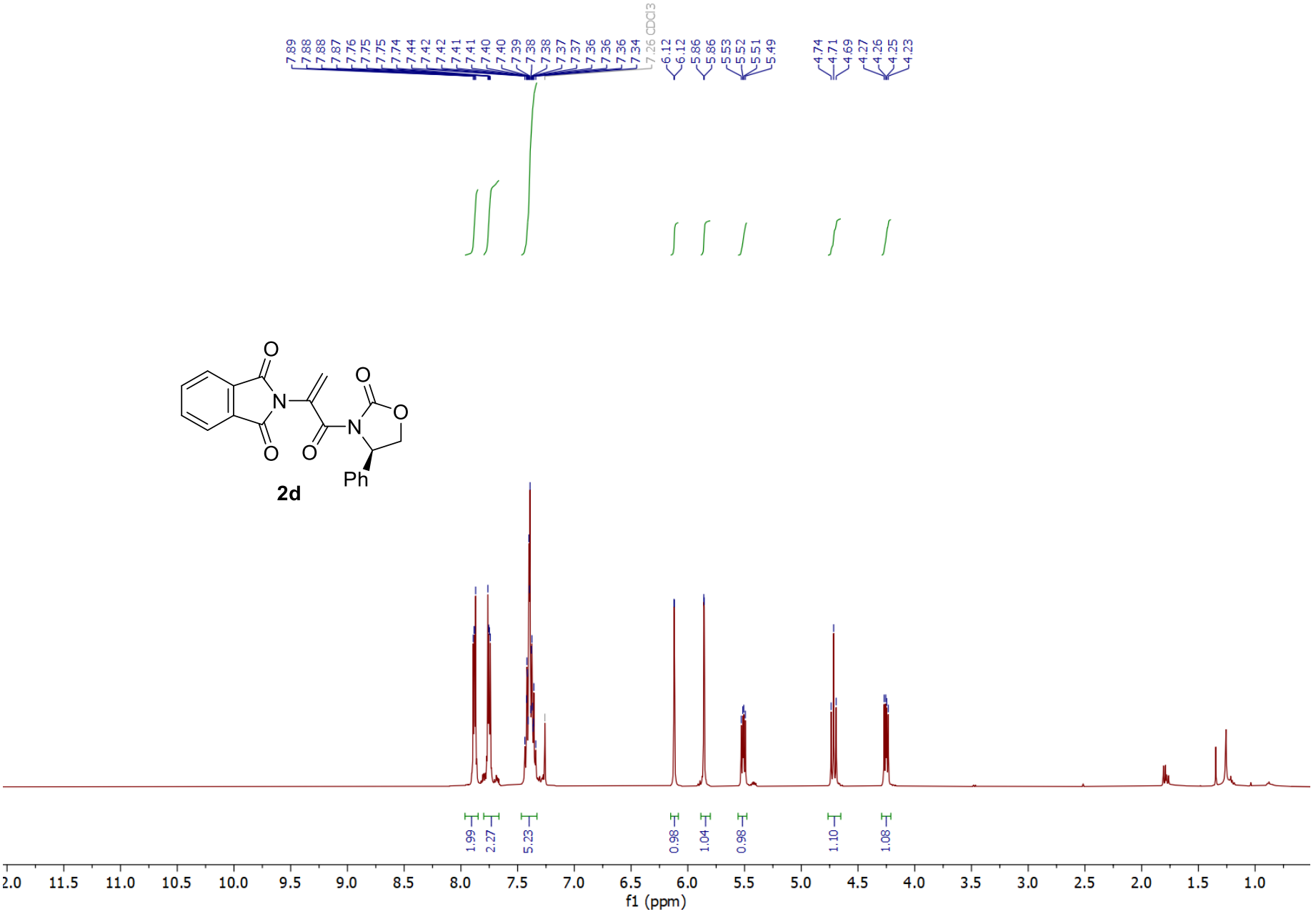
^{1}H NMR (400 MHz, $CDCl_3$) of *(R)*-2-(3-(4-Isopropyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2c)



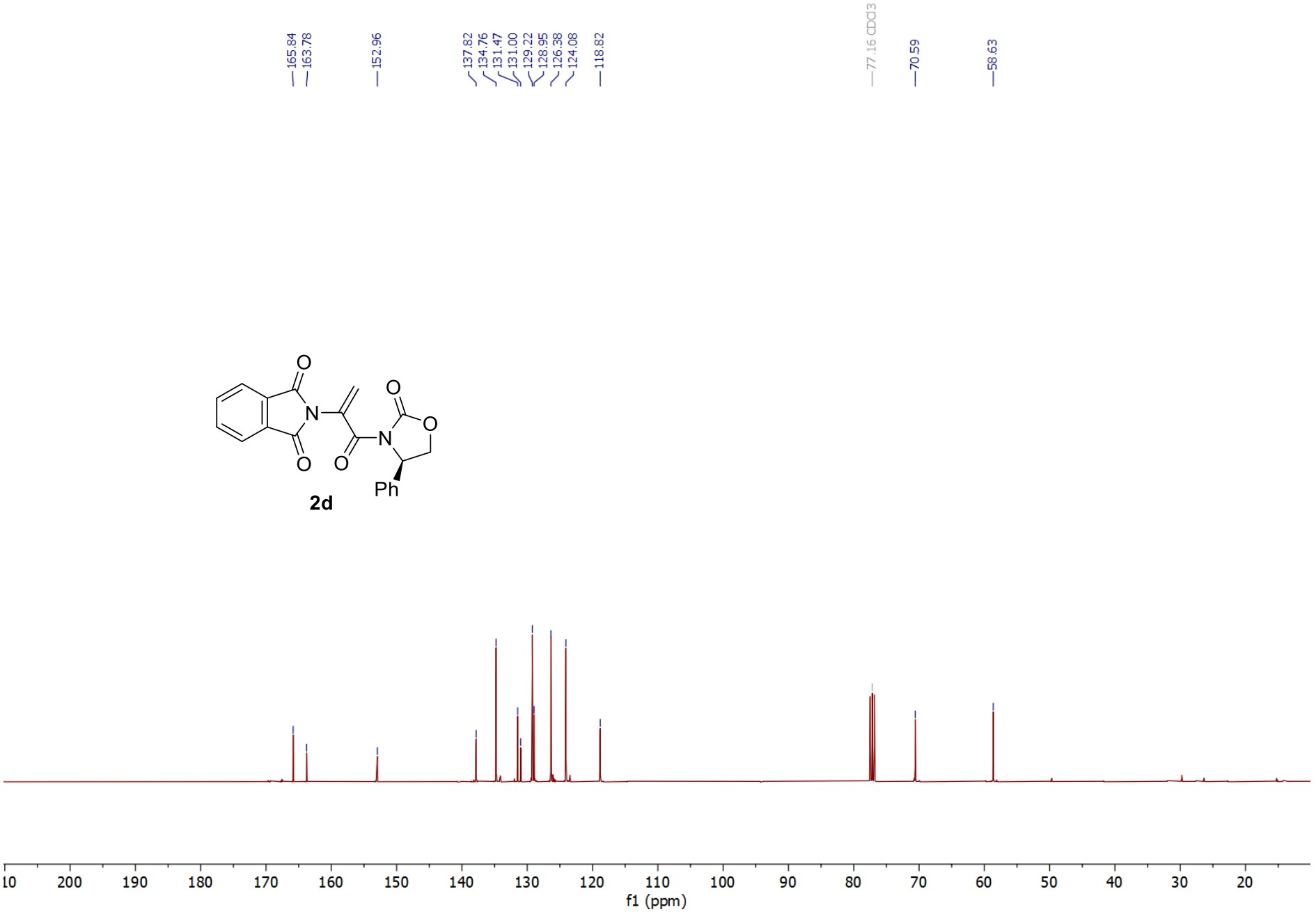
^{13}C NMR (100 MHz, $CDCl_3$) of *(R)*-2-(3-(4-Isopropyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2c)



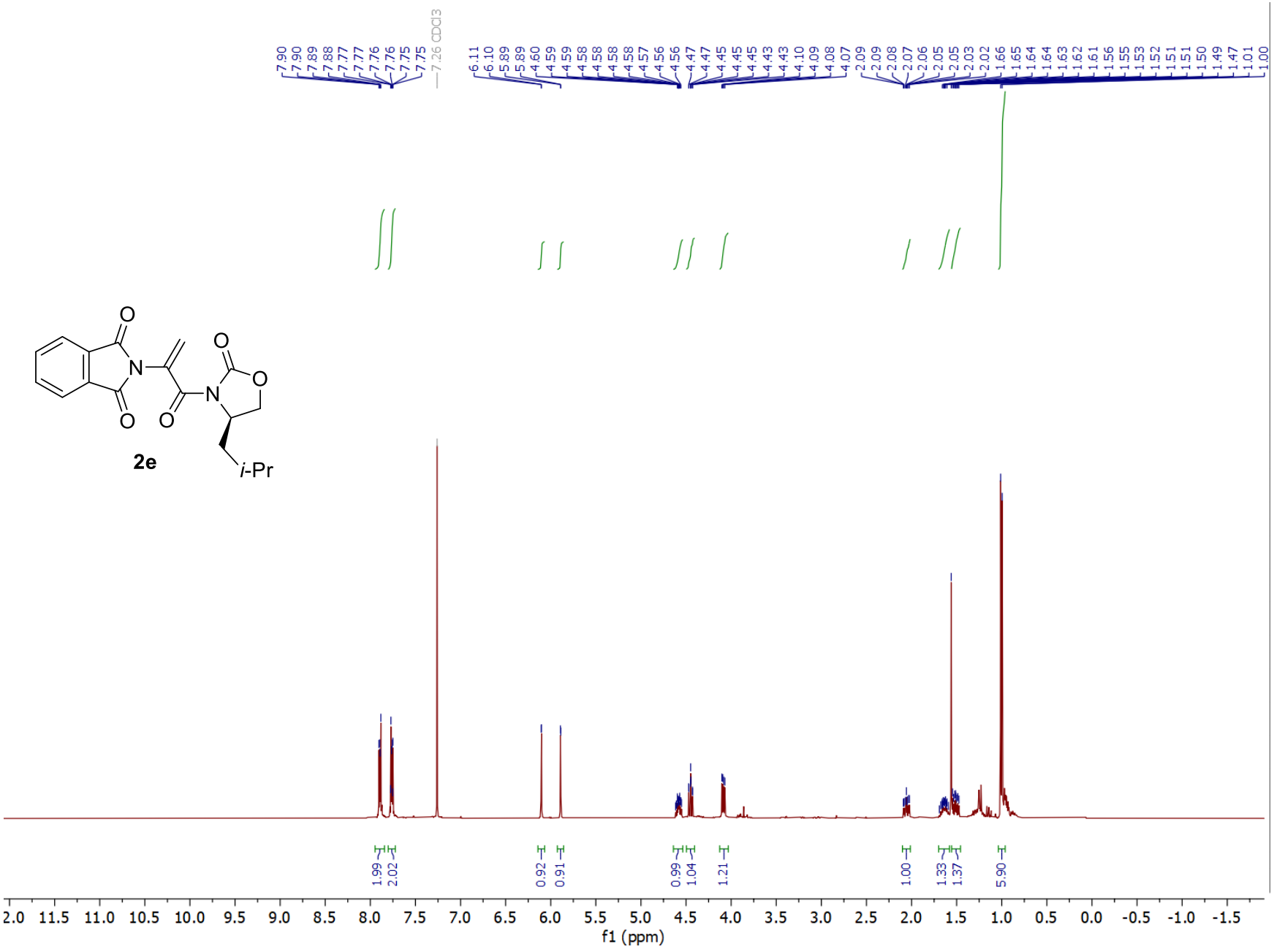
^{1}H NMR (400 MHz, $CDCl_3$) of *(R)*-2-(3-Oxo-3-(2-oxo-4-phenyloxazolidin-3-yl)prop-1-en-2-yl)phthalimide (2d)



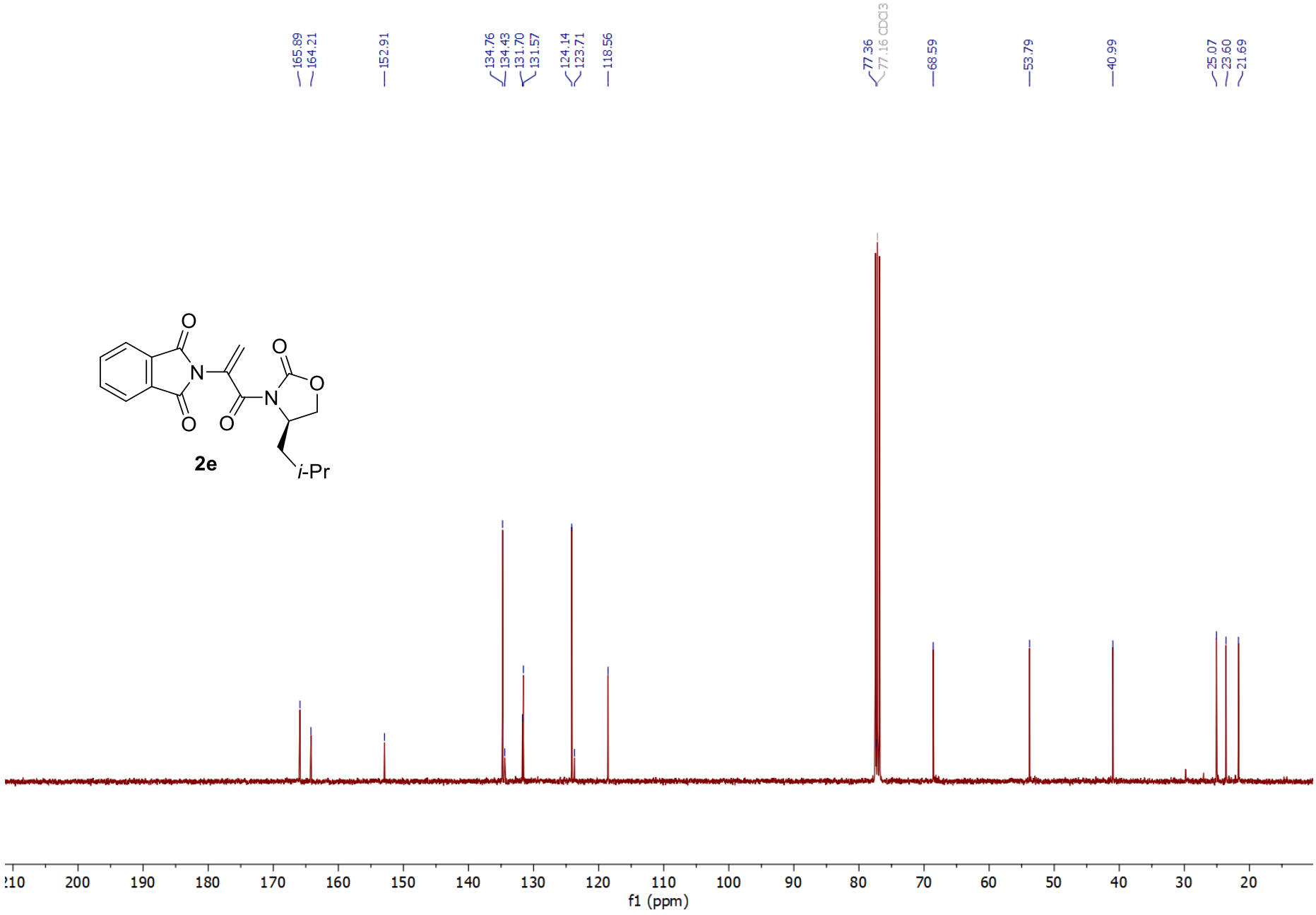
^{13}C NMR (100 MHz, $CDCl_3$) of *(R)*-2-(3-Oxo-3-(2-oxo-4-phenyloxazolidin-3-yl)prop-1-en-2-yl)phthalimide (2d)



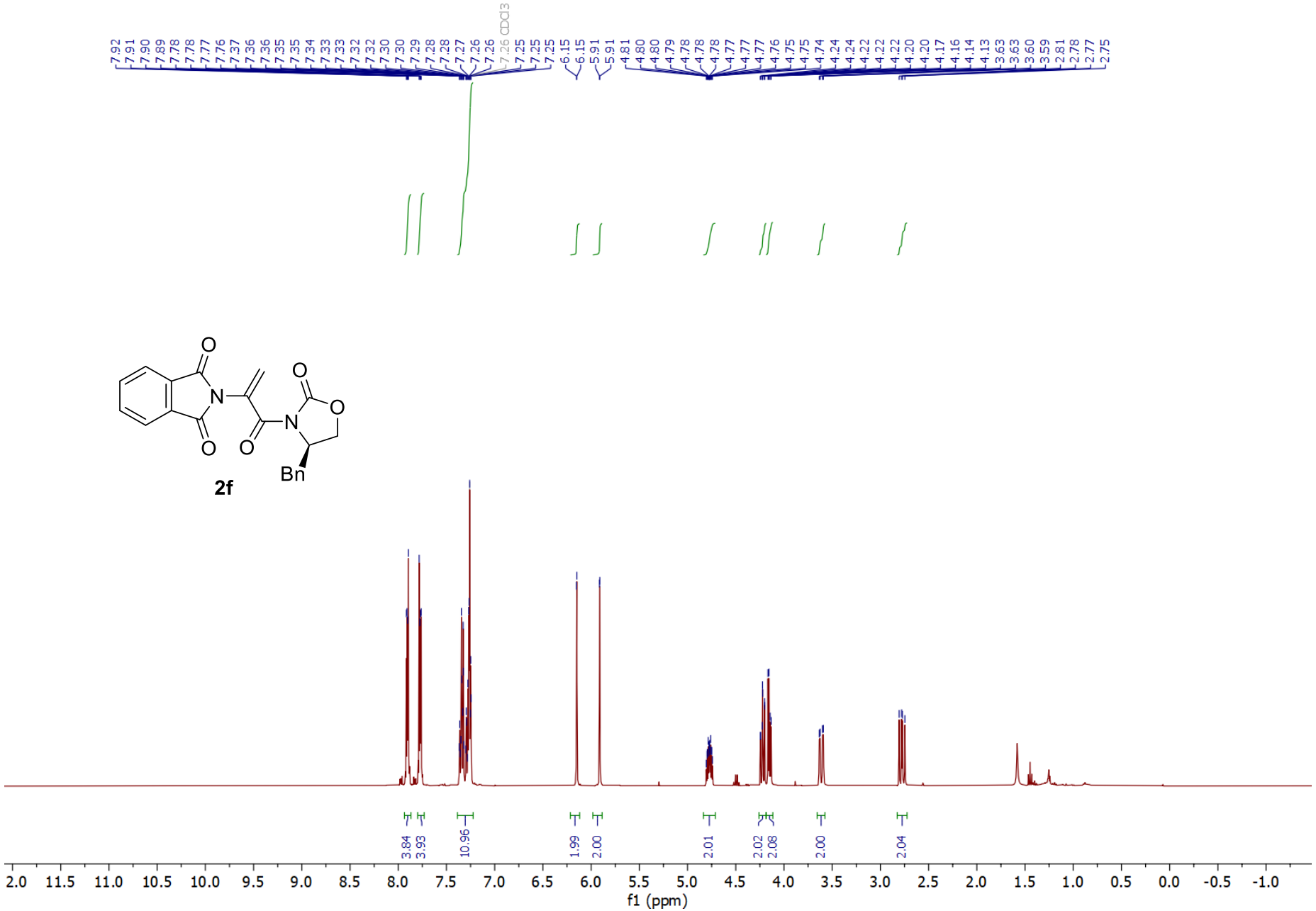
^{1}H NMR (400 MHz, $CDCl_3$) of *(R)*-2-(3-(4-Isobutyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2e)



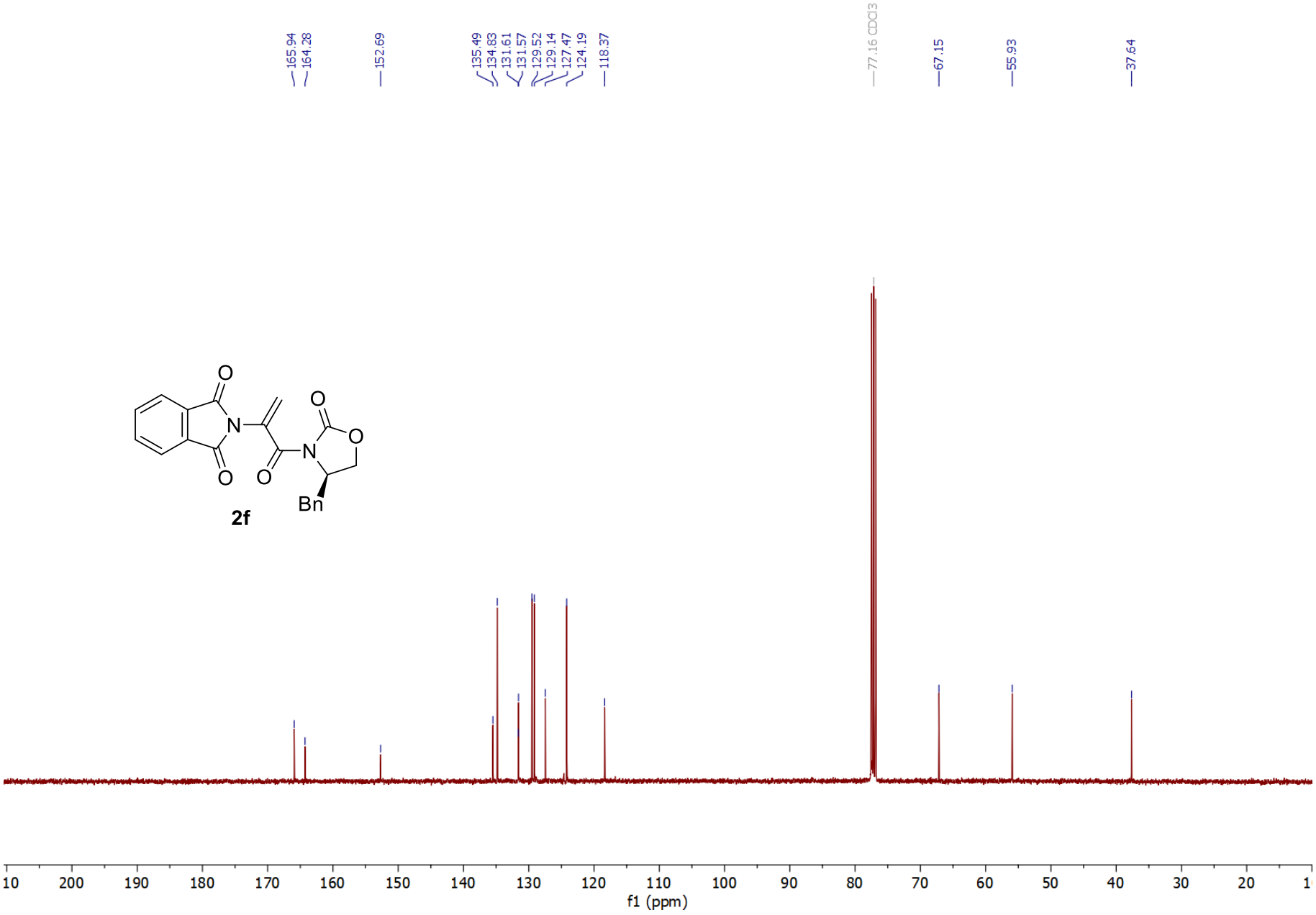
^{13}C NMR (100 MHz, $CDCl_3$) of *(R)*-2-(3-(4-Isobutyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2e)



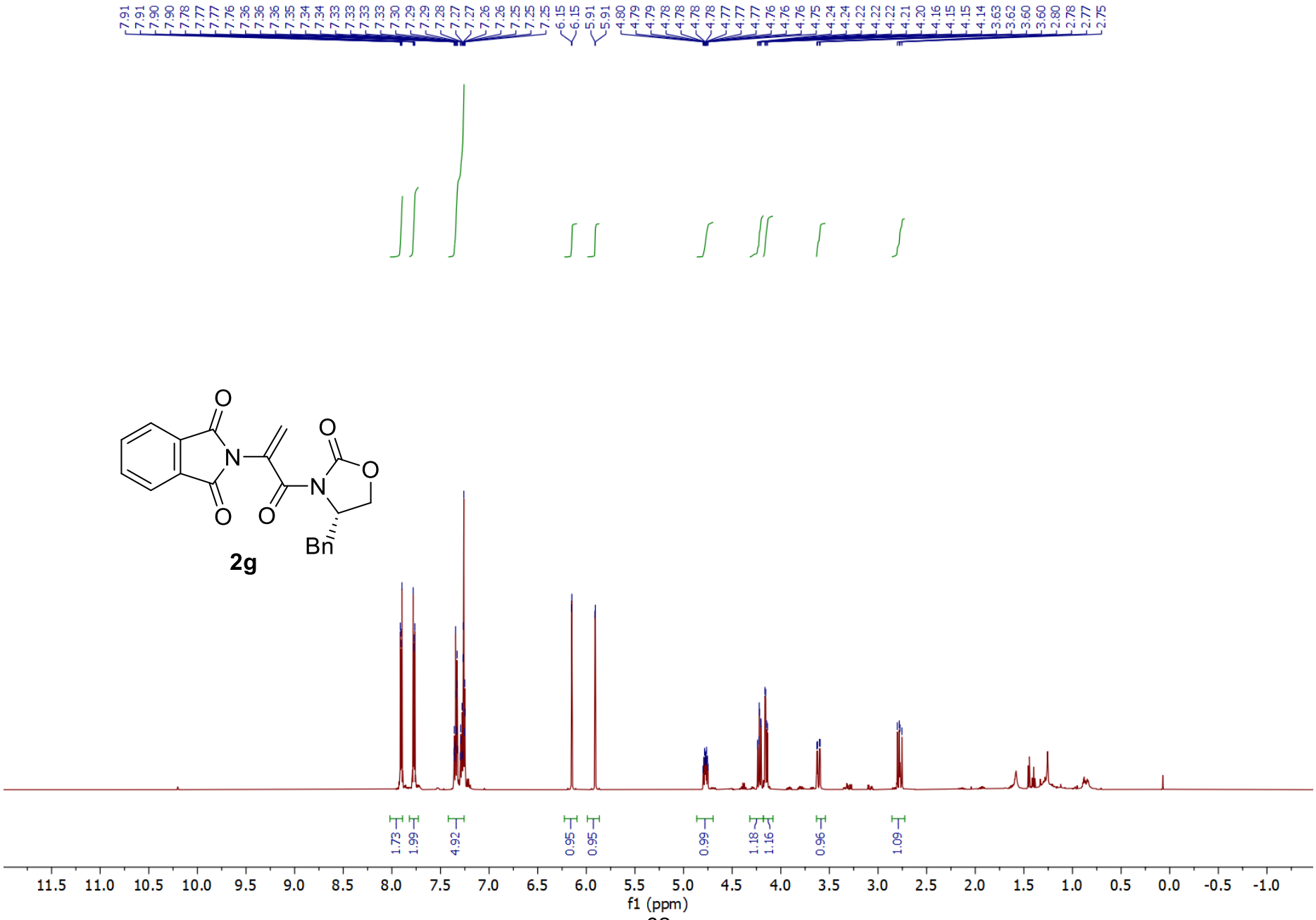
^{1}H NMR (400 MHz, $CDCl_3$) of *(R)*-2-(3-(4-Benzyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2f)



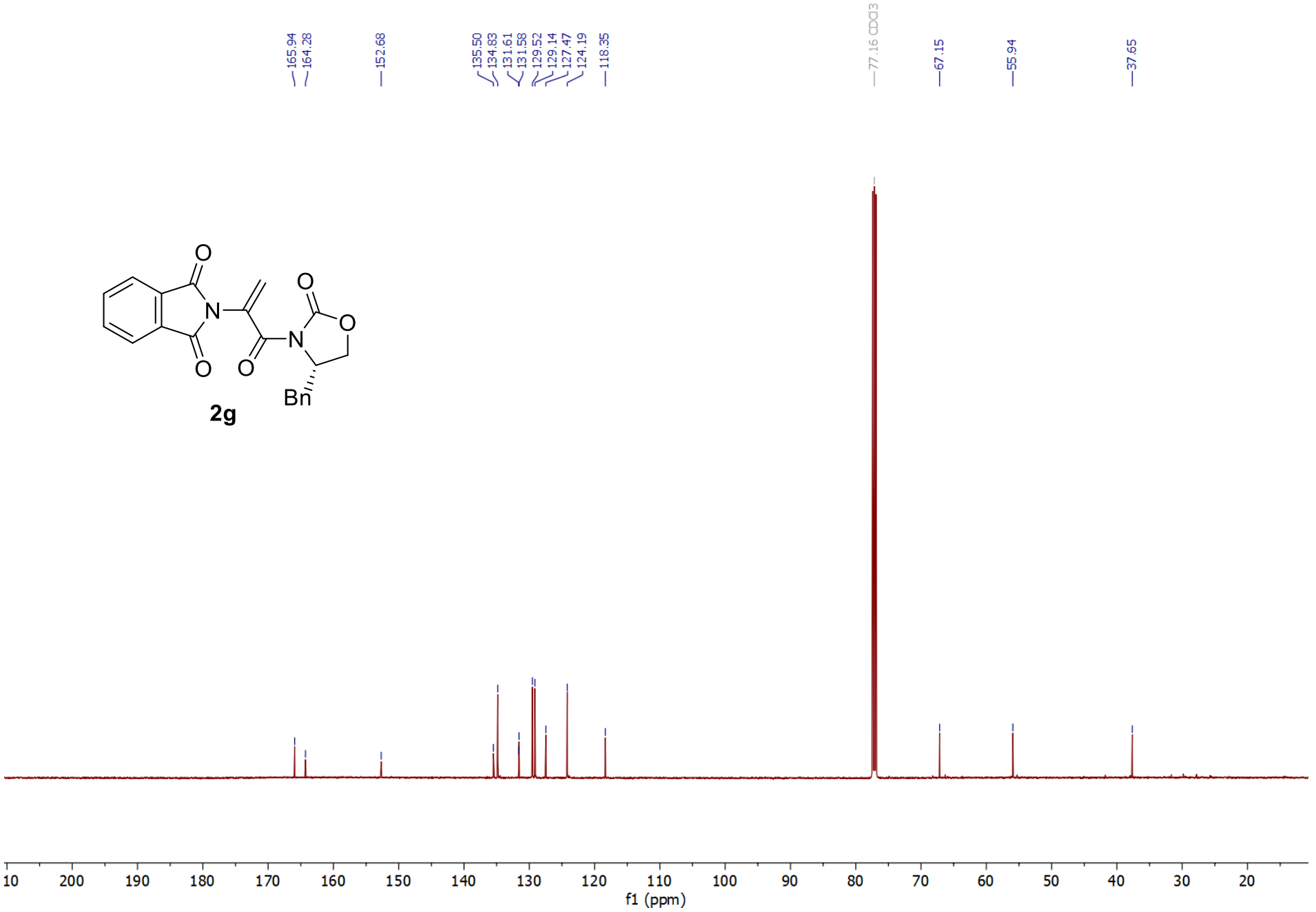
^{13}C NMR (100 MHz, $CDCl_3$) of *(R)*-2-(3-(4-Benzyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2f)



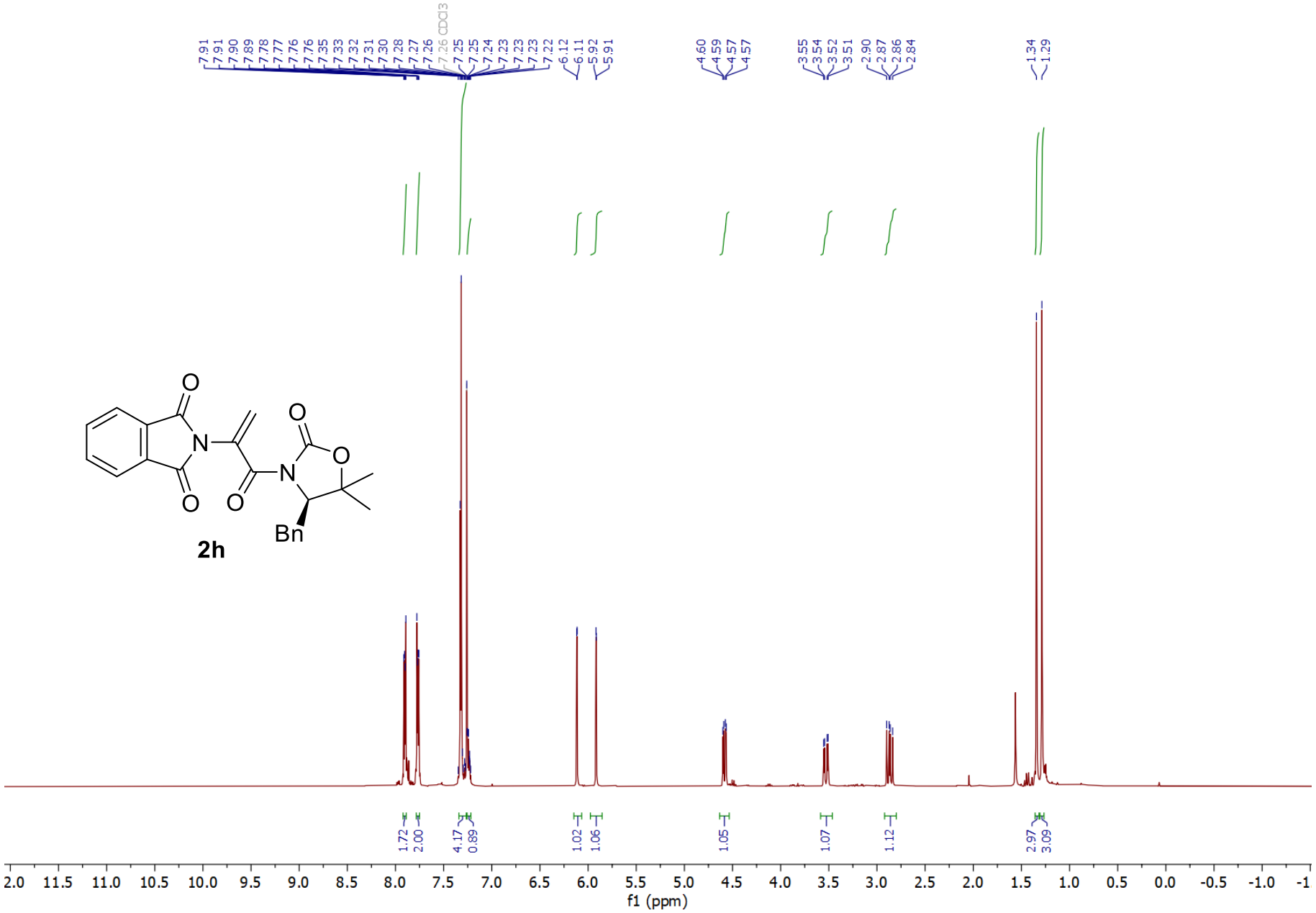
^{1}H NMR (500 MHz, $CDCl_3$) of *(S)*-2-(3-(4-Benzyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2g) *(impurities formed upon standing)*



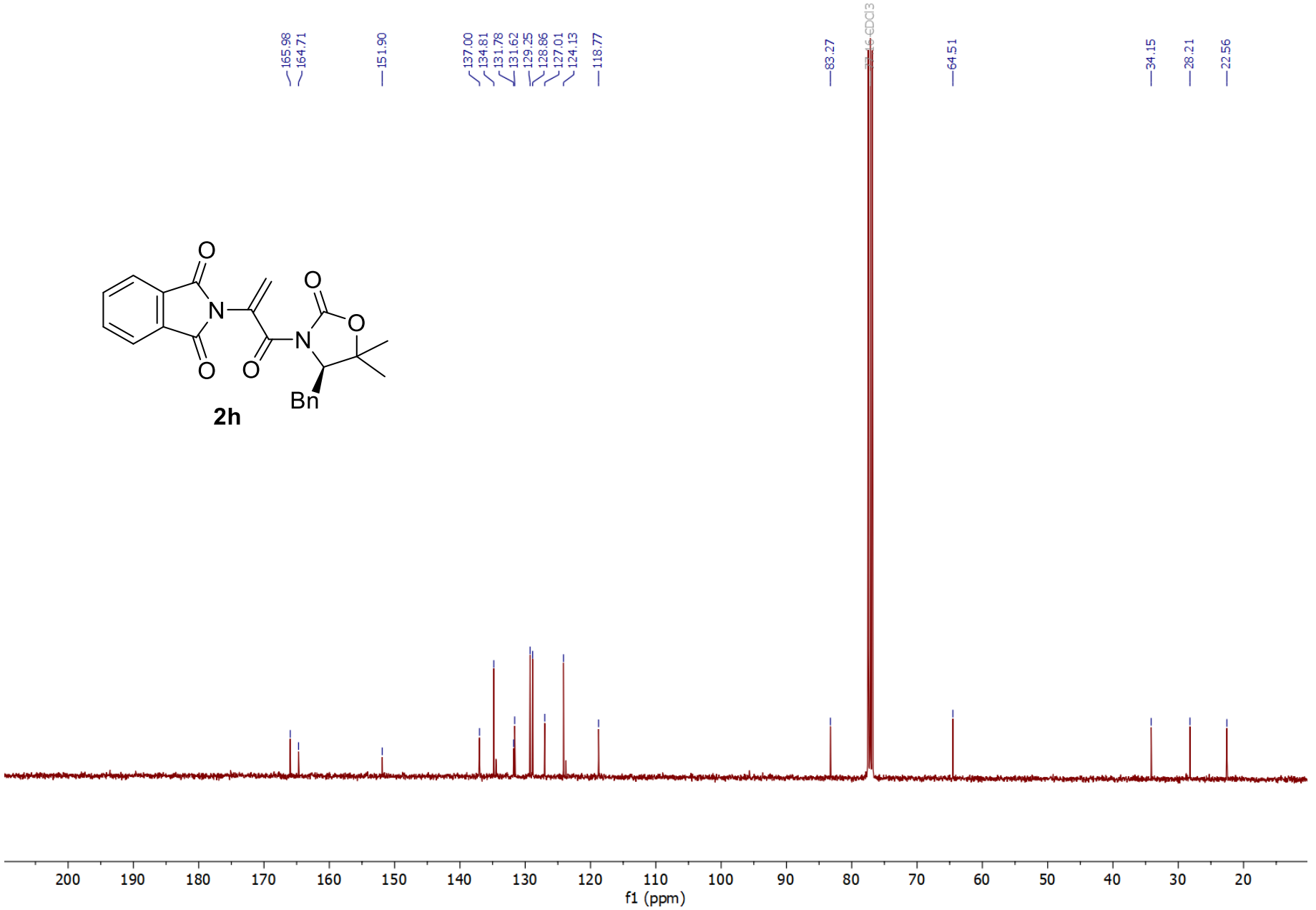
^{13}C NMR (125 MHz, $CDCl_3$) of *(S)*-2-(3-(4-Benzyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2g)



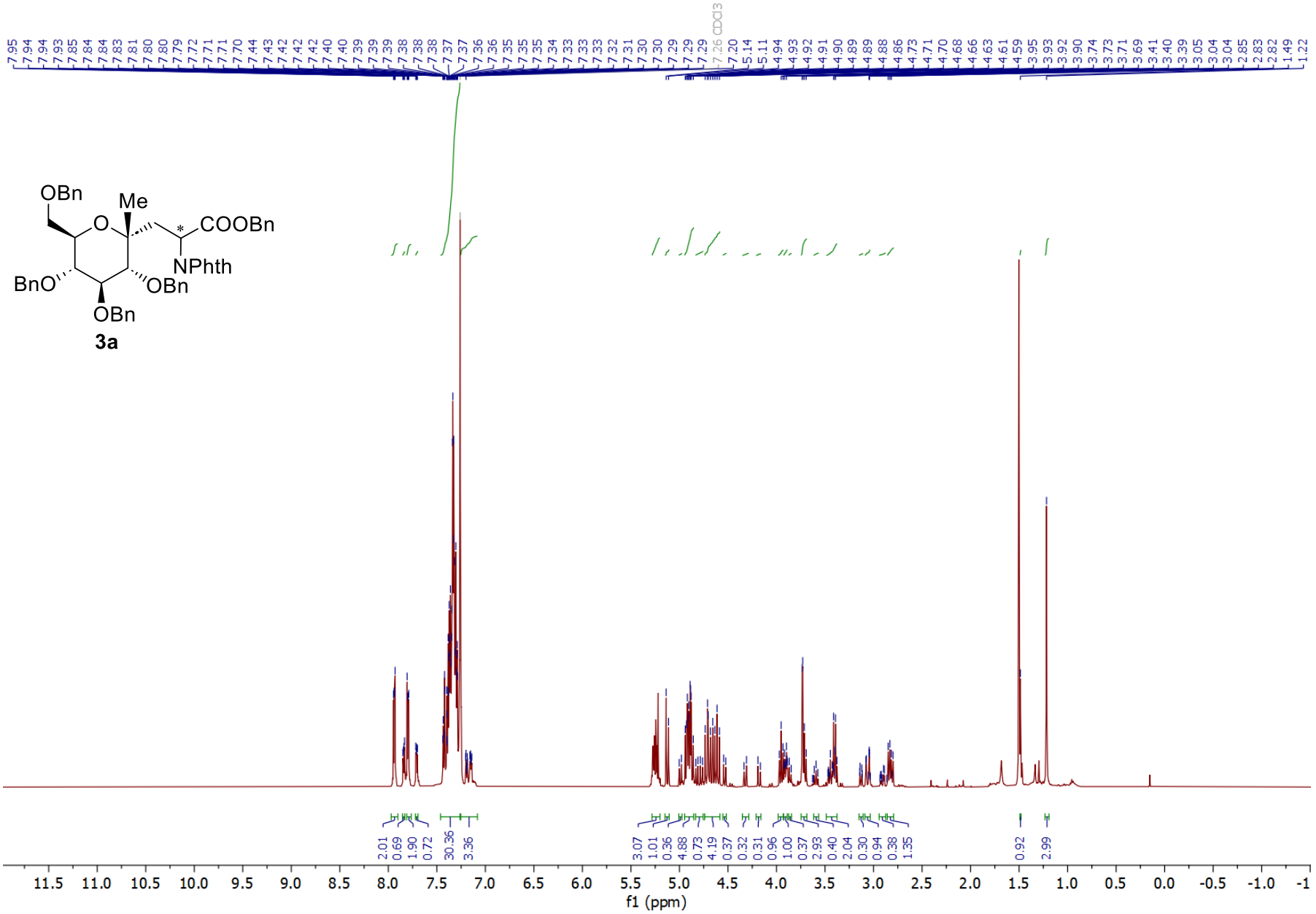
^{1}H NMR (400 MHz, $CDCl_3$) of *(R)*-2-(3-(4-Benzyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2h)



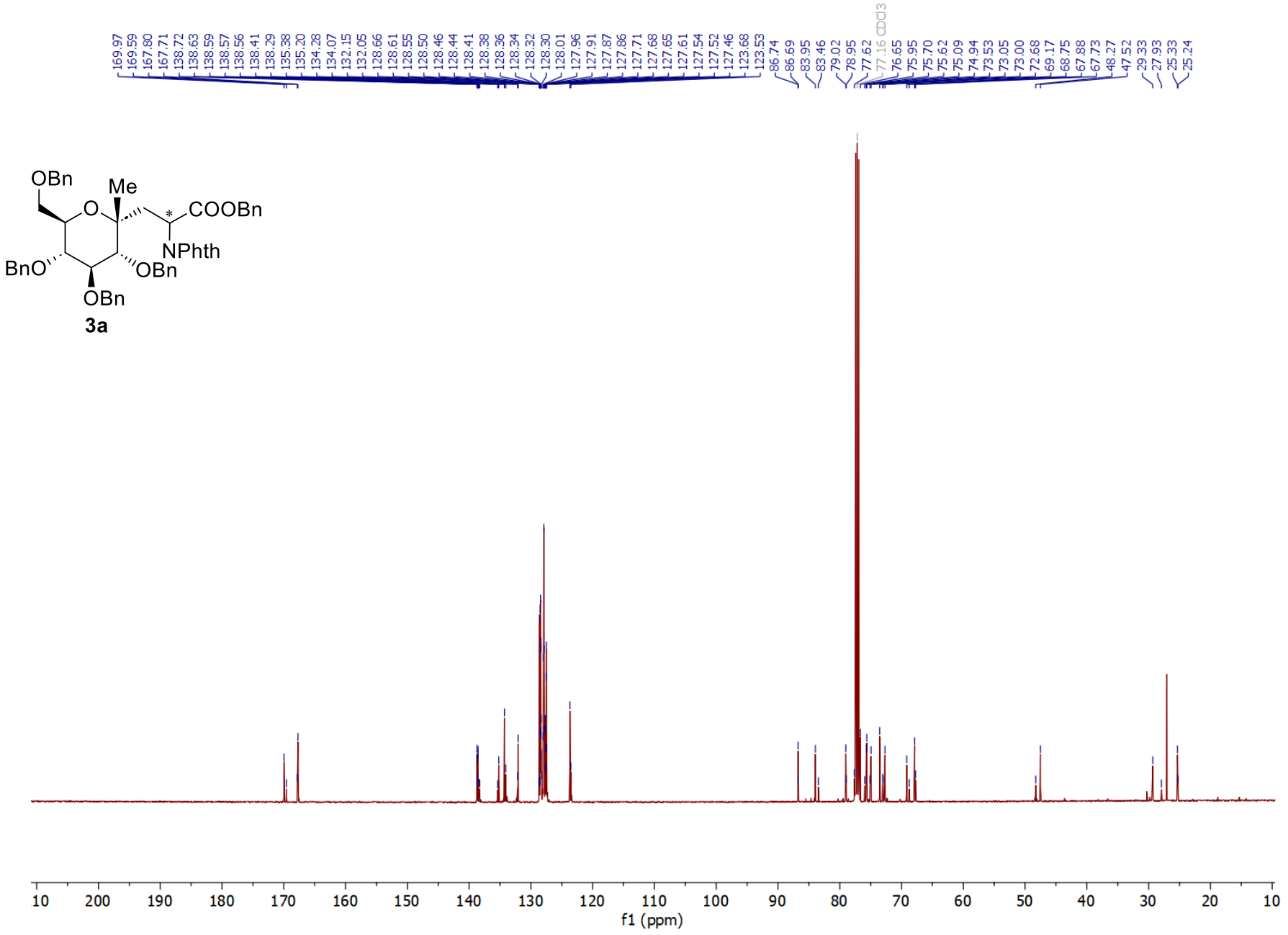
^{13}C NMR (100 MHz, $CDCl_3$) of *(R)*-2-(3-(4-Benzyl-5,5-dimethyl-2-oxooxazolidin-3-yl)-3-oxoprop-1-en-2-yl)phthalimide (2h)



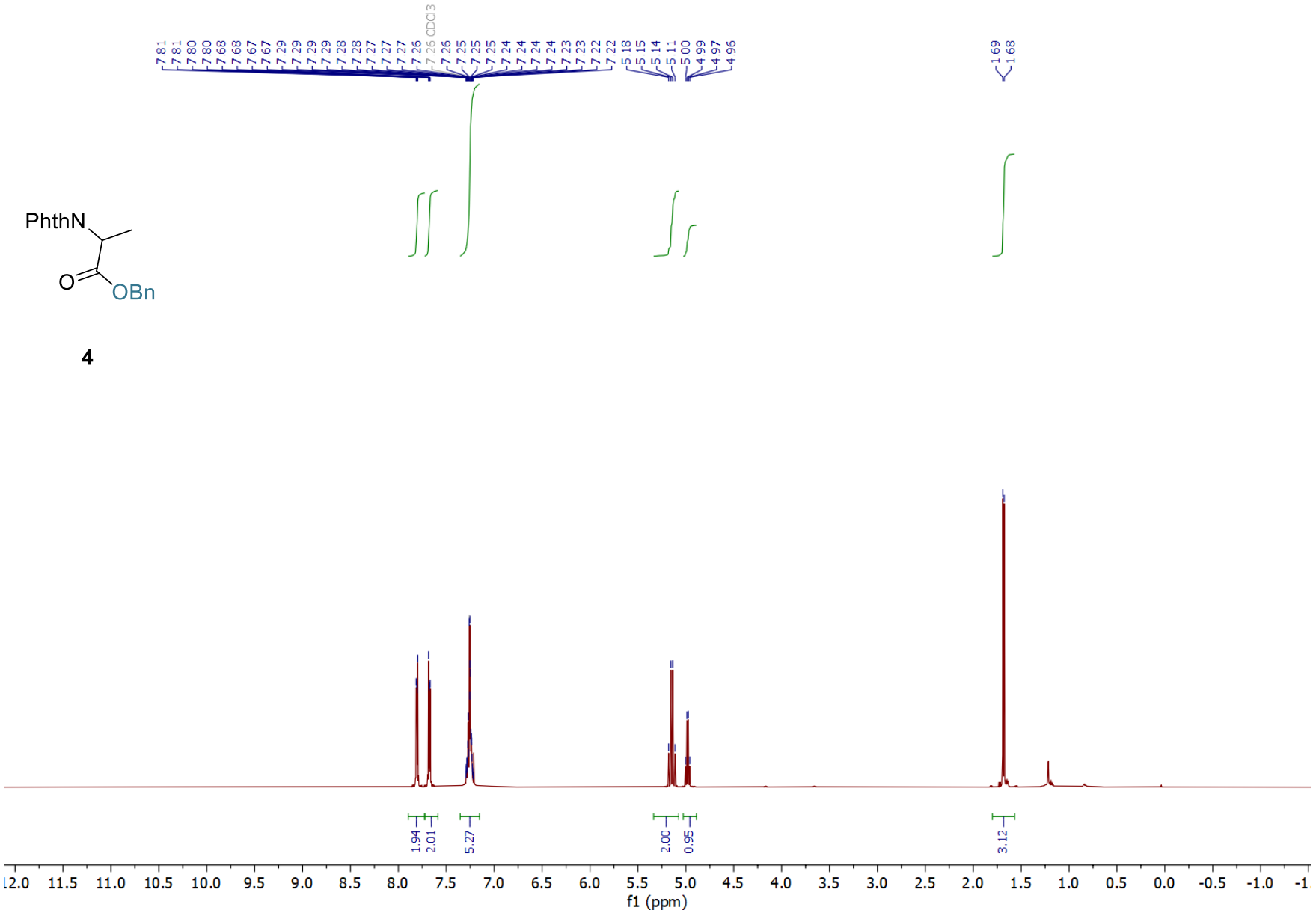
^{1}H NMR (500 MHz, $CDCl_3$) of benzyl-2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoate (3a)



^{13}C NMR (125 MHz, $CDCl_3$) of benzyl-2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoate (3a)

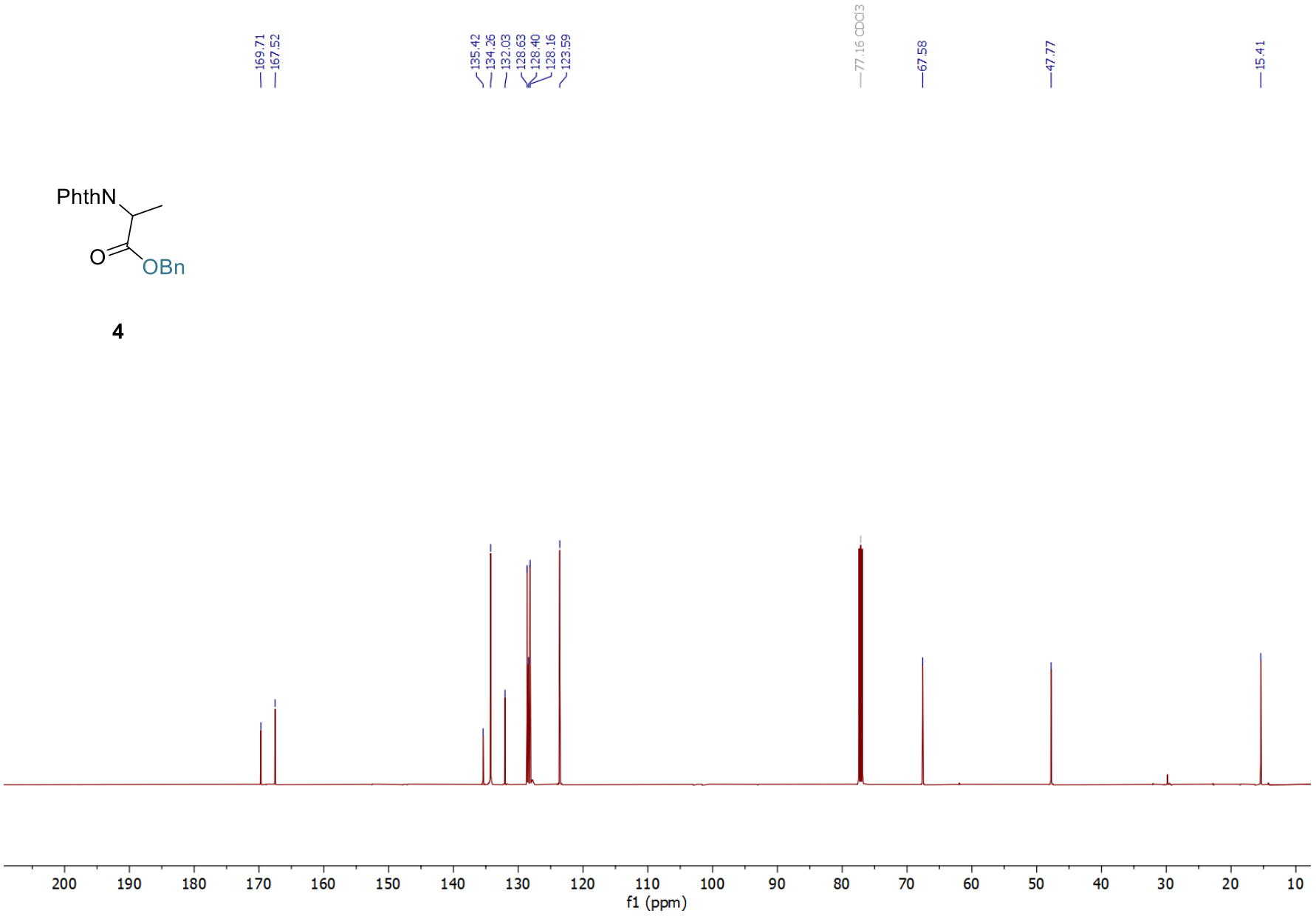


^{1}H NMR (500 MHz, $CDCl_3$) of benzyl 2-(phthalimidoyl)propanoate (4)



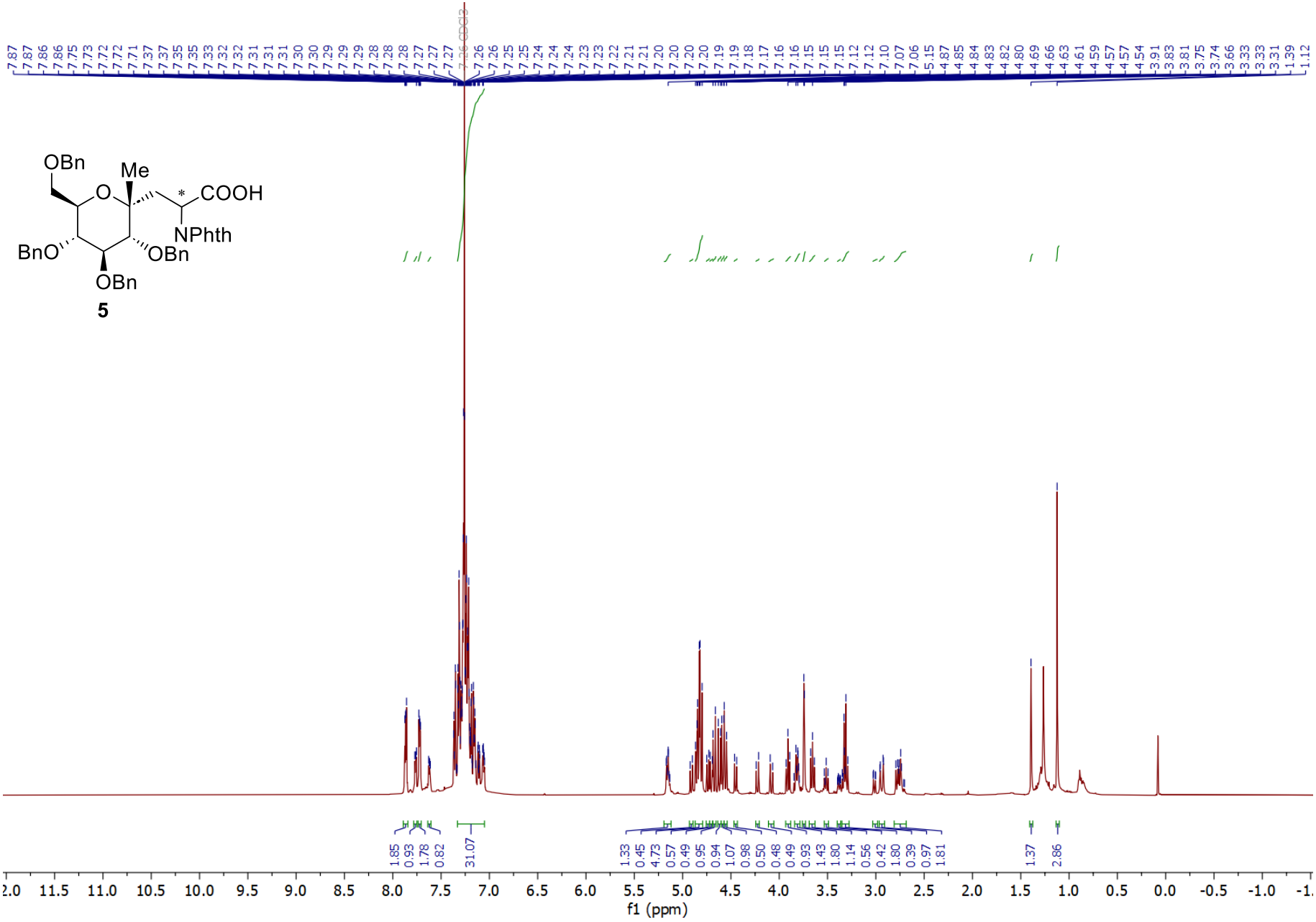
4

^{13}C NMR (125 MHz, $CDCl_3$) of benzyl 2-(phthalimidoyl)propanoate (4)

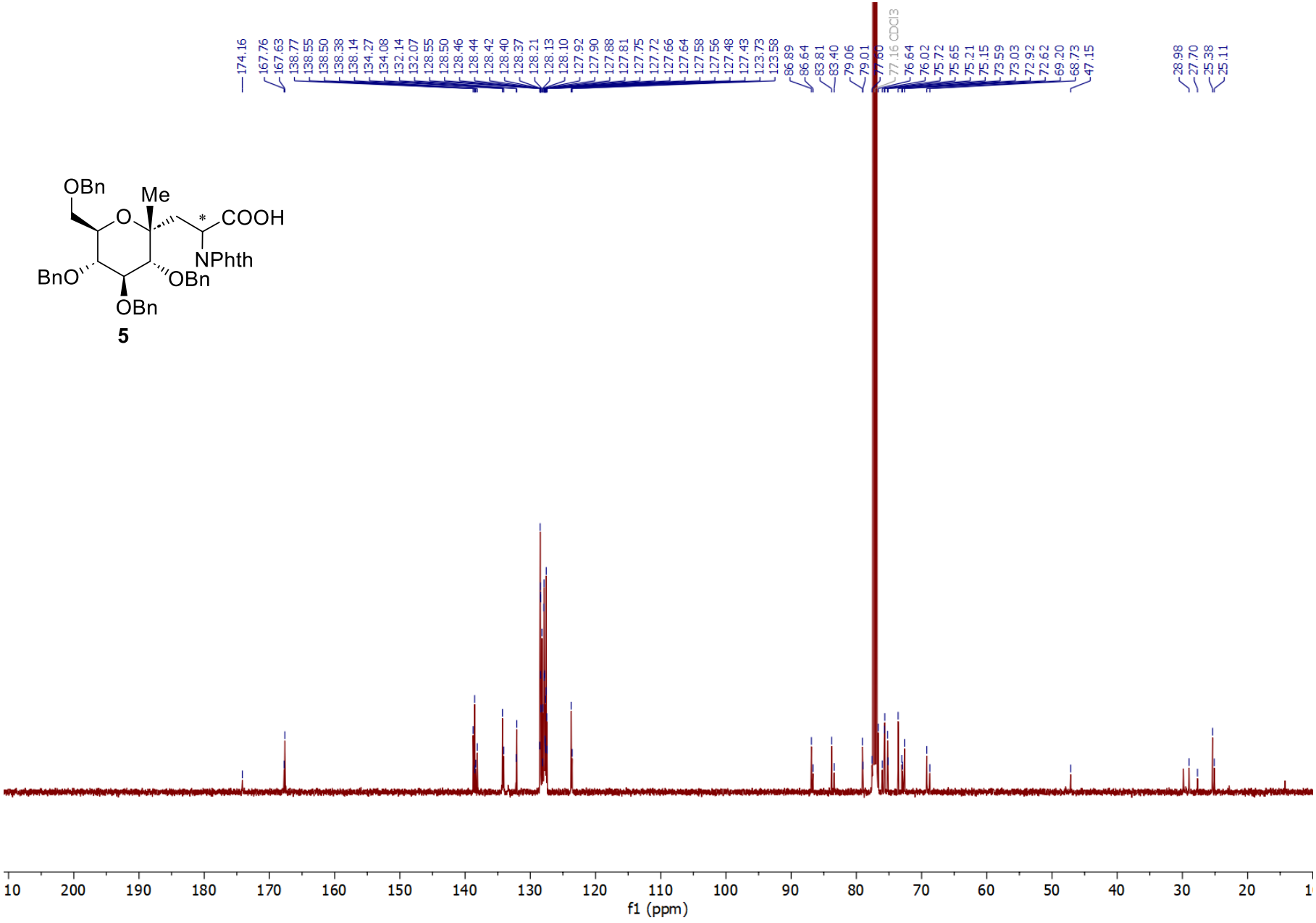


4

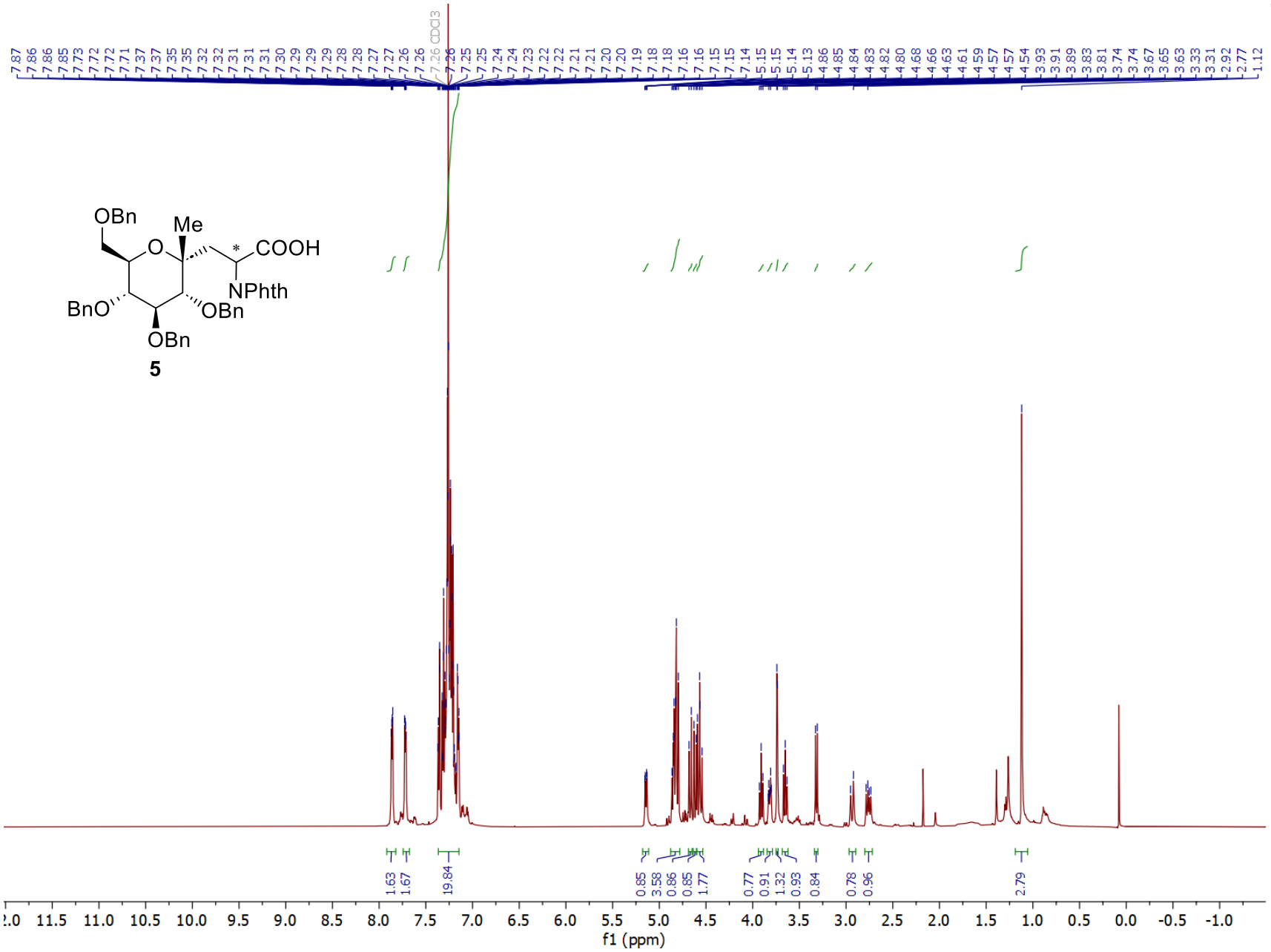
^{1}H NMR (500 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoïc acid (5) starting from an achiral acceptor (2b)



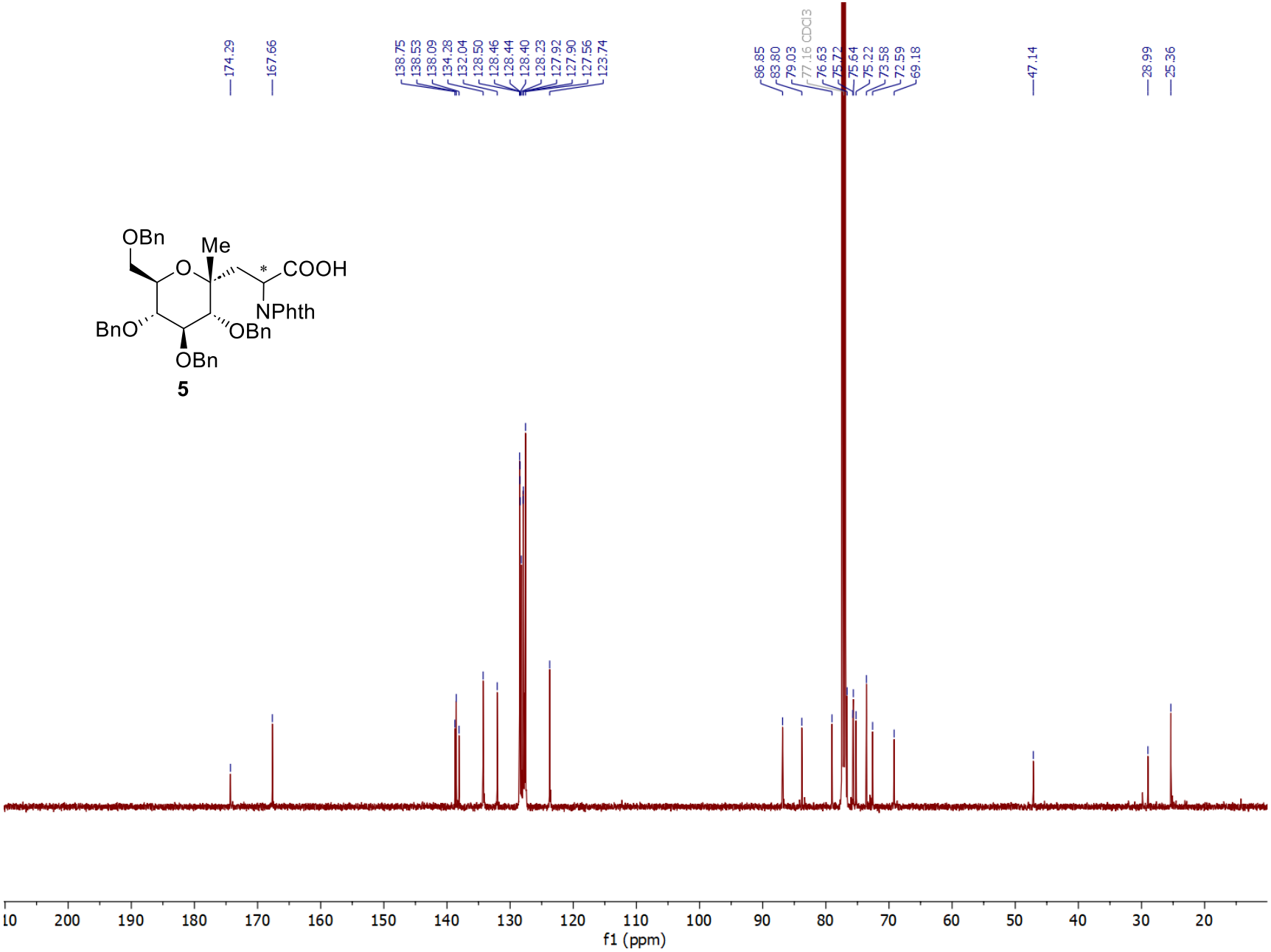
^{13}C NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoïc acid (5) starting from an achiral acceptor (2b)



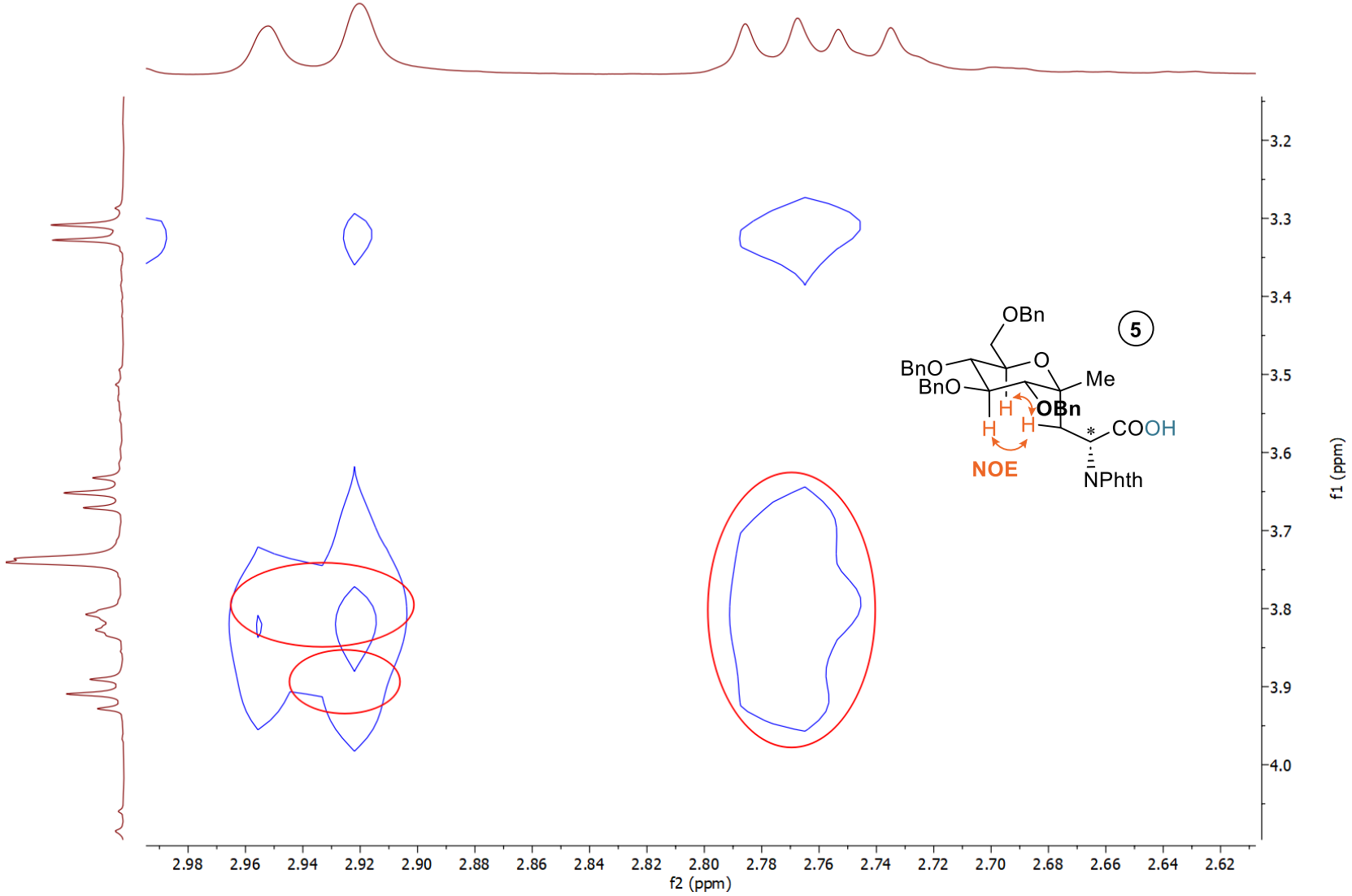
^{1}H NMR (500 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoïc acid (5) starting from an enantipure acceptor (2f)



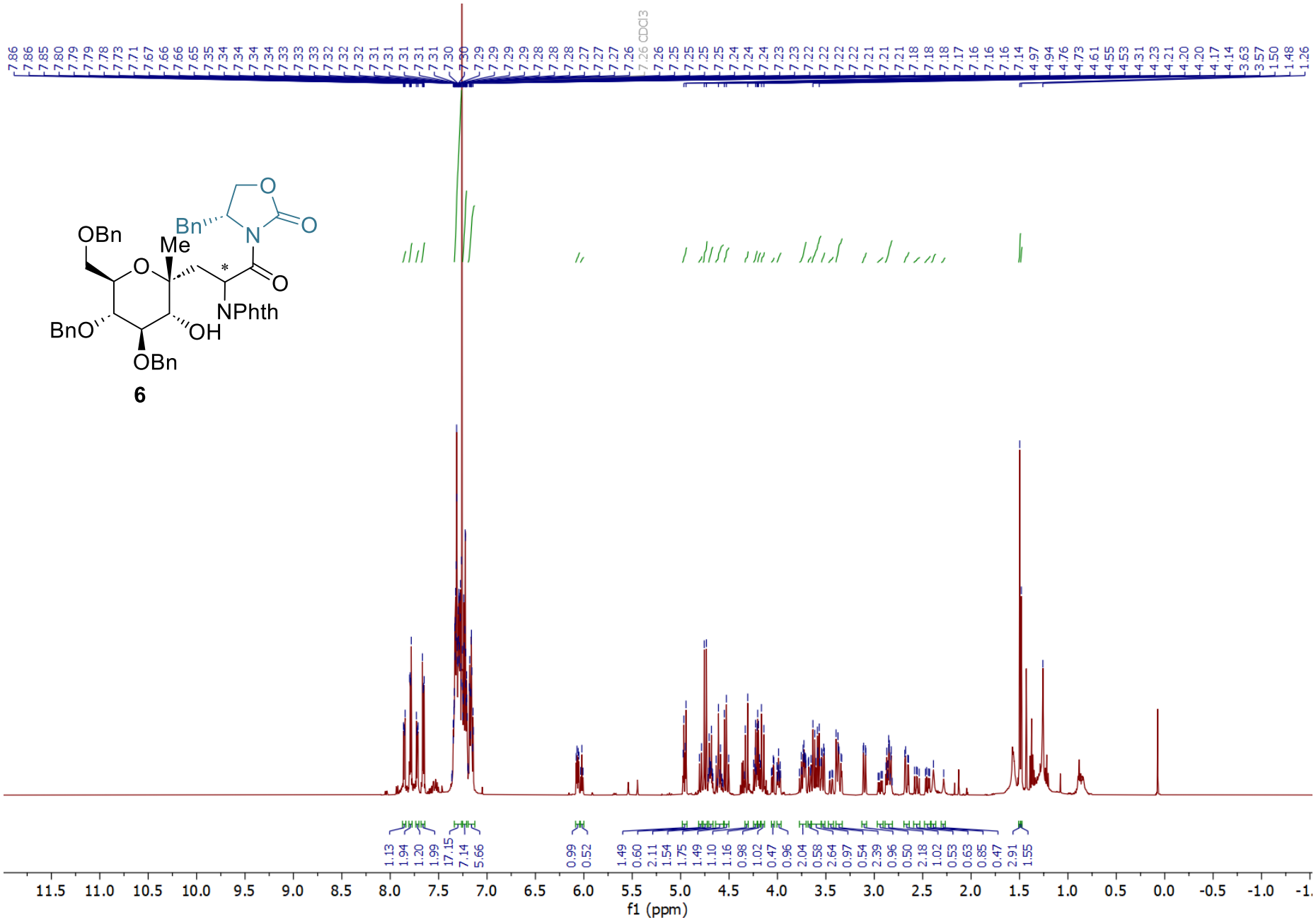
^{13}C NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoïc acid (5) starting from an enantipure acceptor (2f)



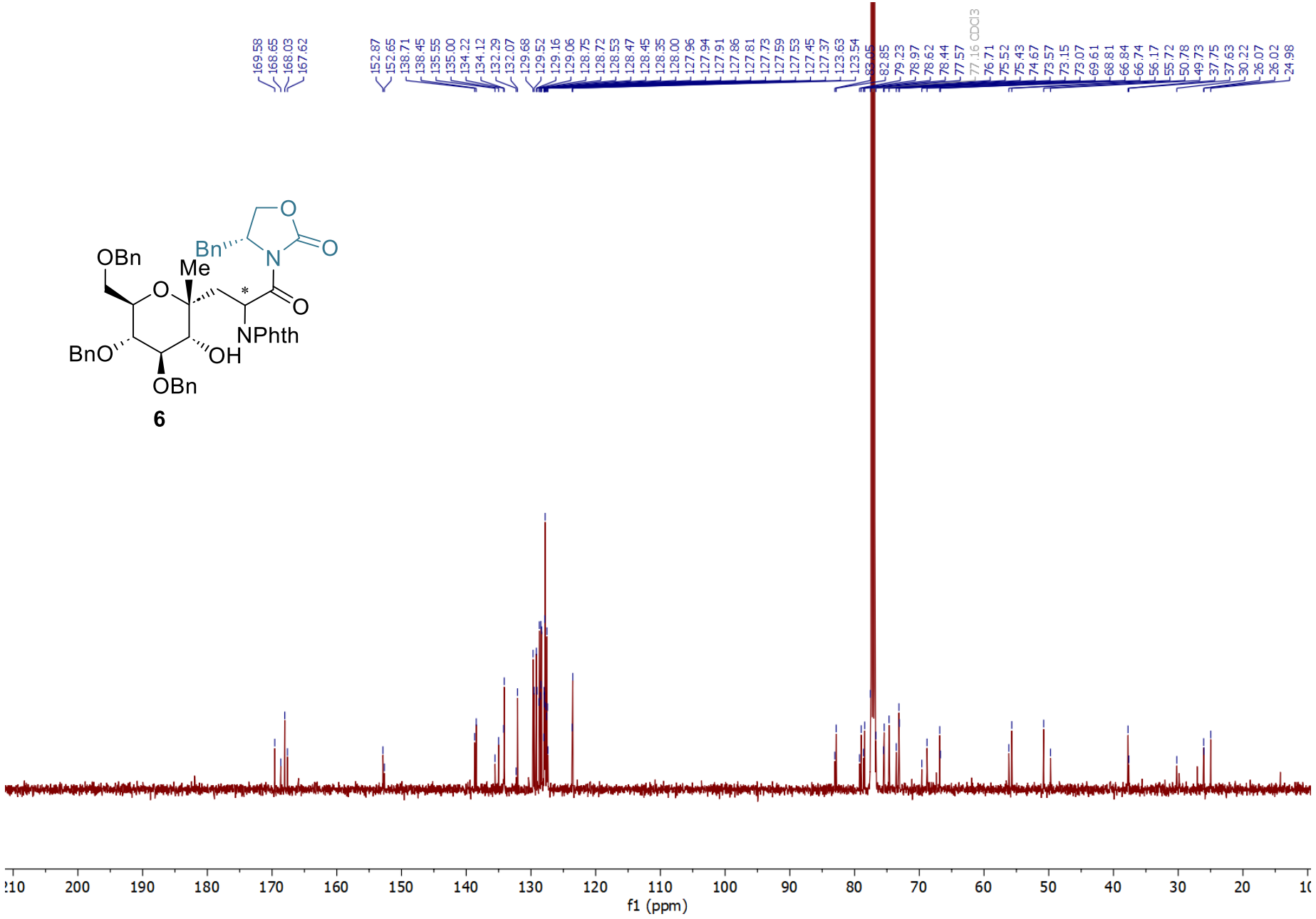
NOESY NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)propanoïc acid (5) starting from an enantipure acceptor (2f)



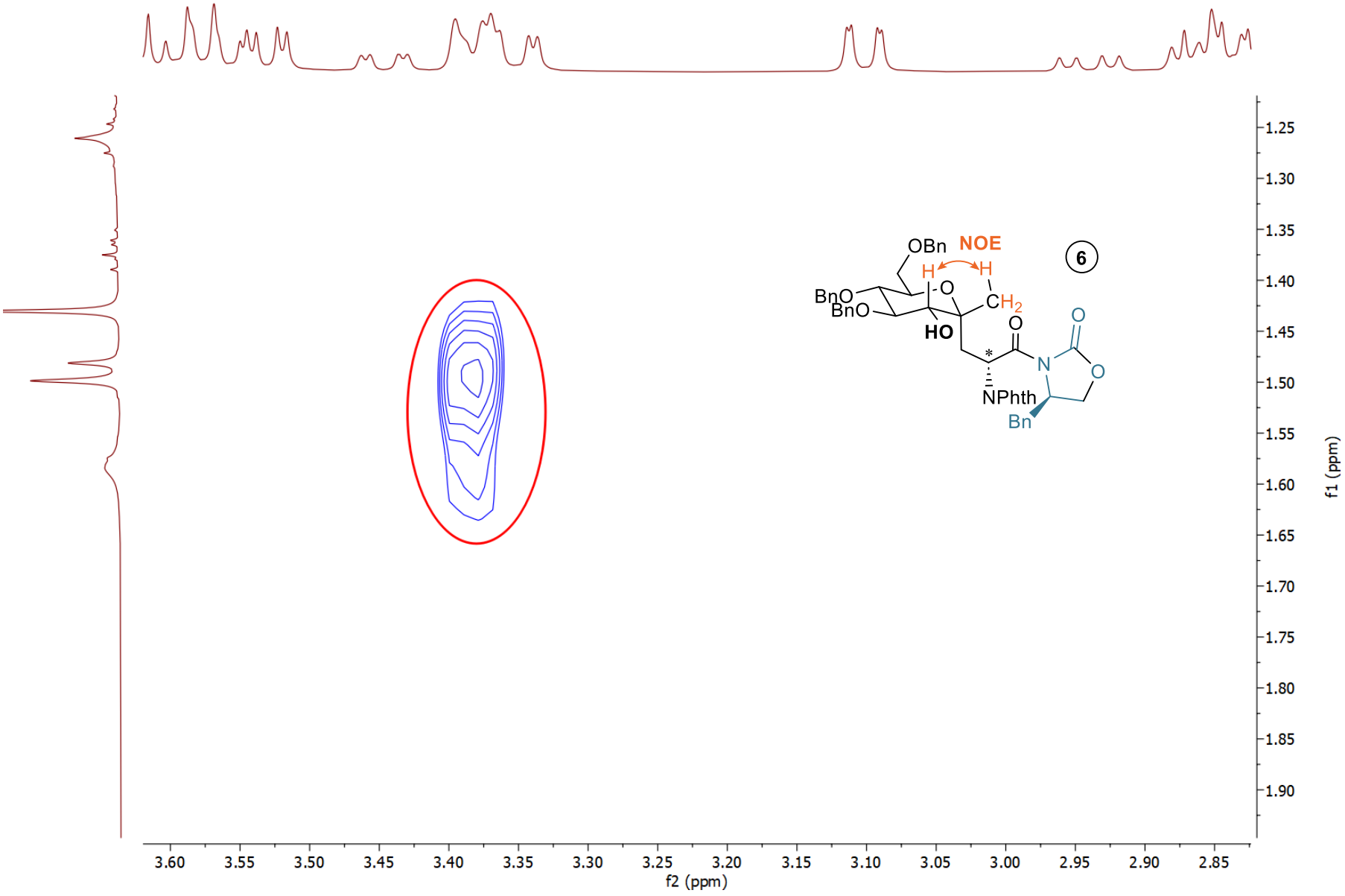
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-(3,4,6-tri-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)-1-oxopropan-2-yl)phthalimide (6)



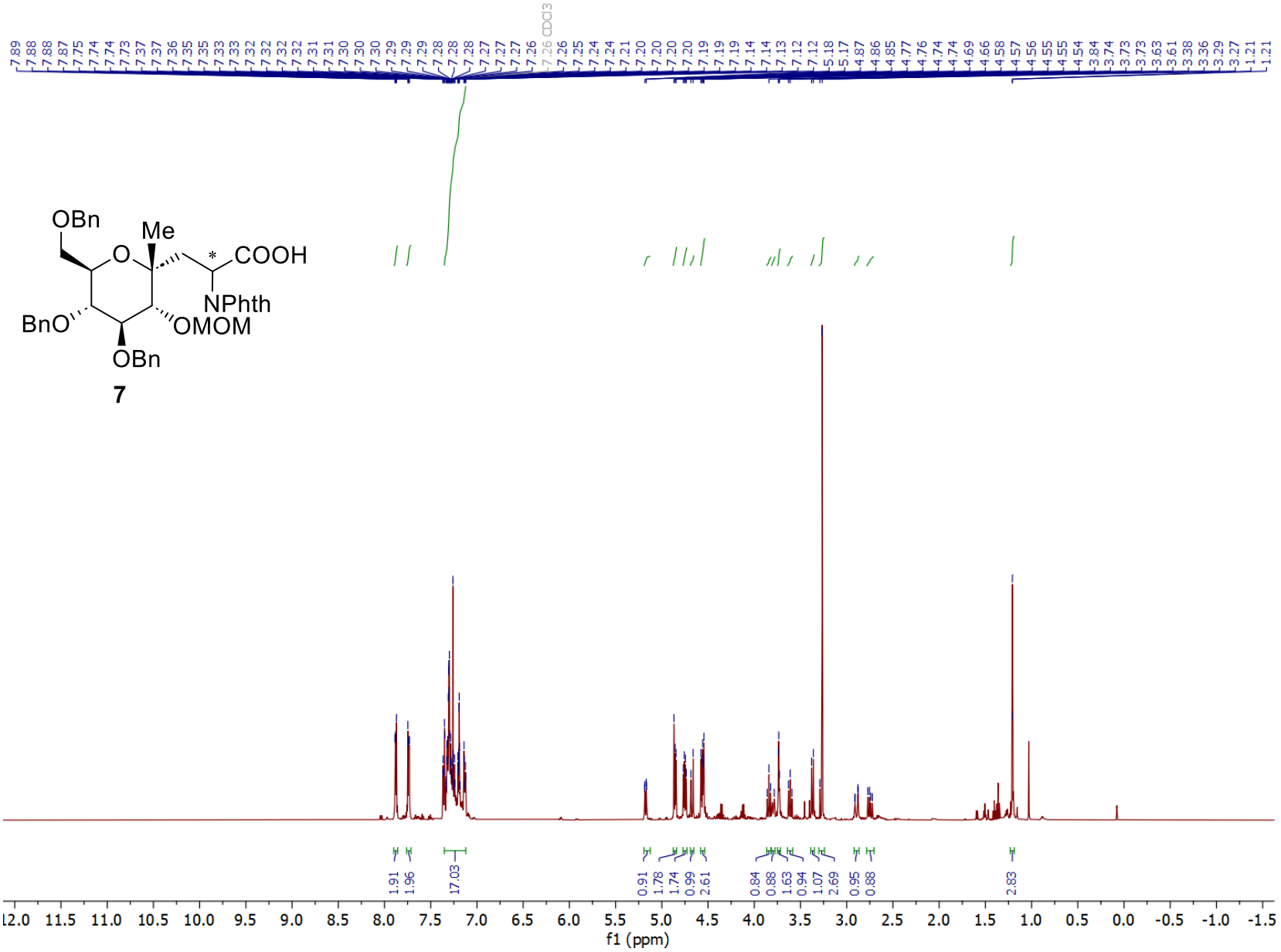
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-(3,4,6-tri-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)-1-oxopropan-2-yl)phthalimide (6)



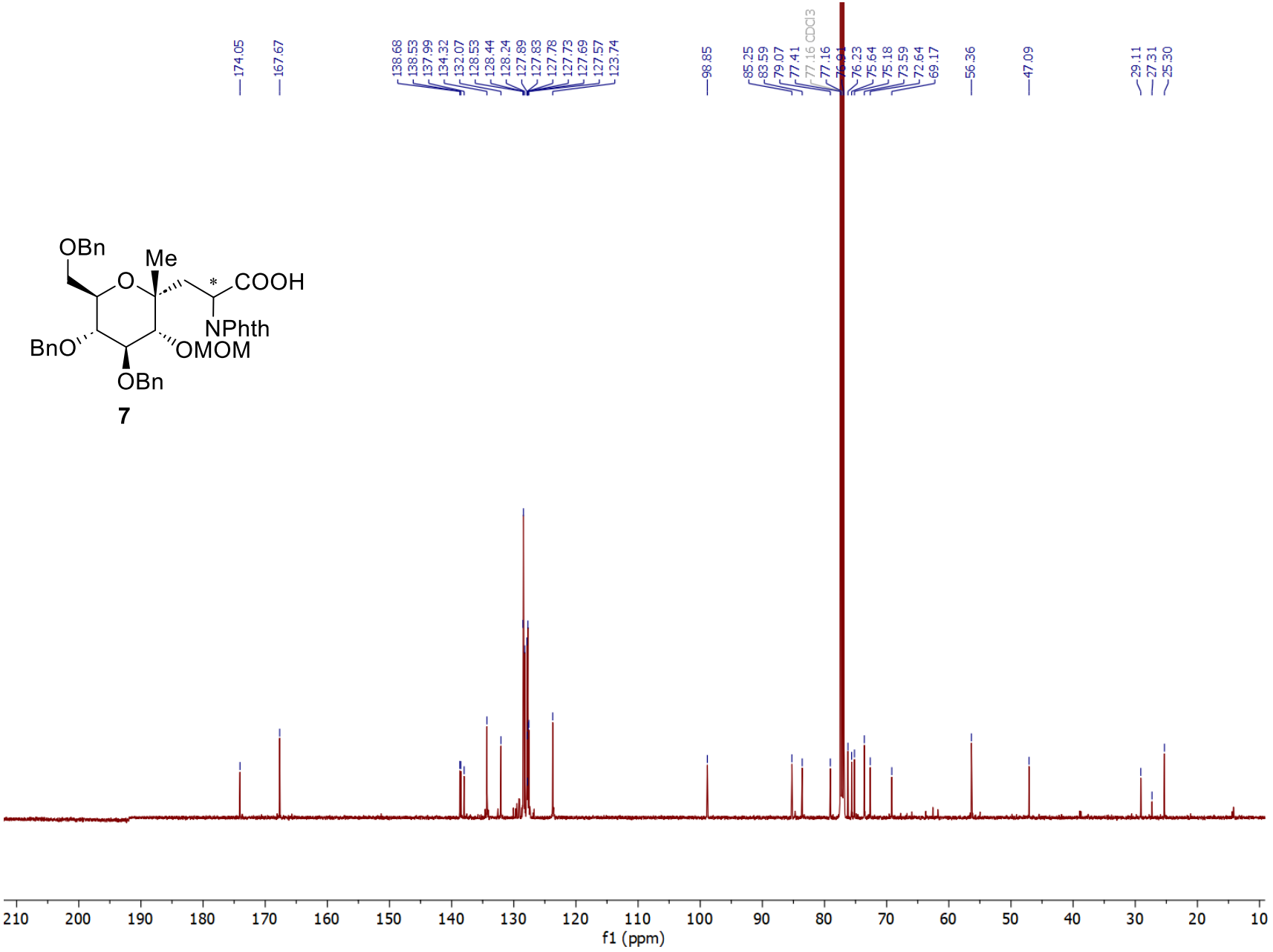
NOESY NMR (125 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-(3,4,6-tri-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)-1-oxopropan-2-yl)phthalimide (6)



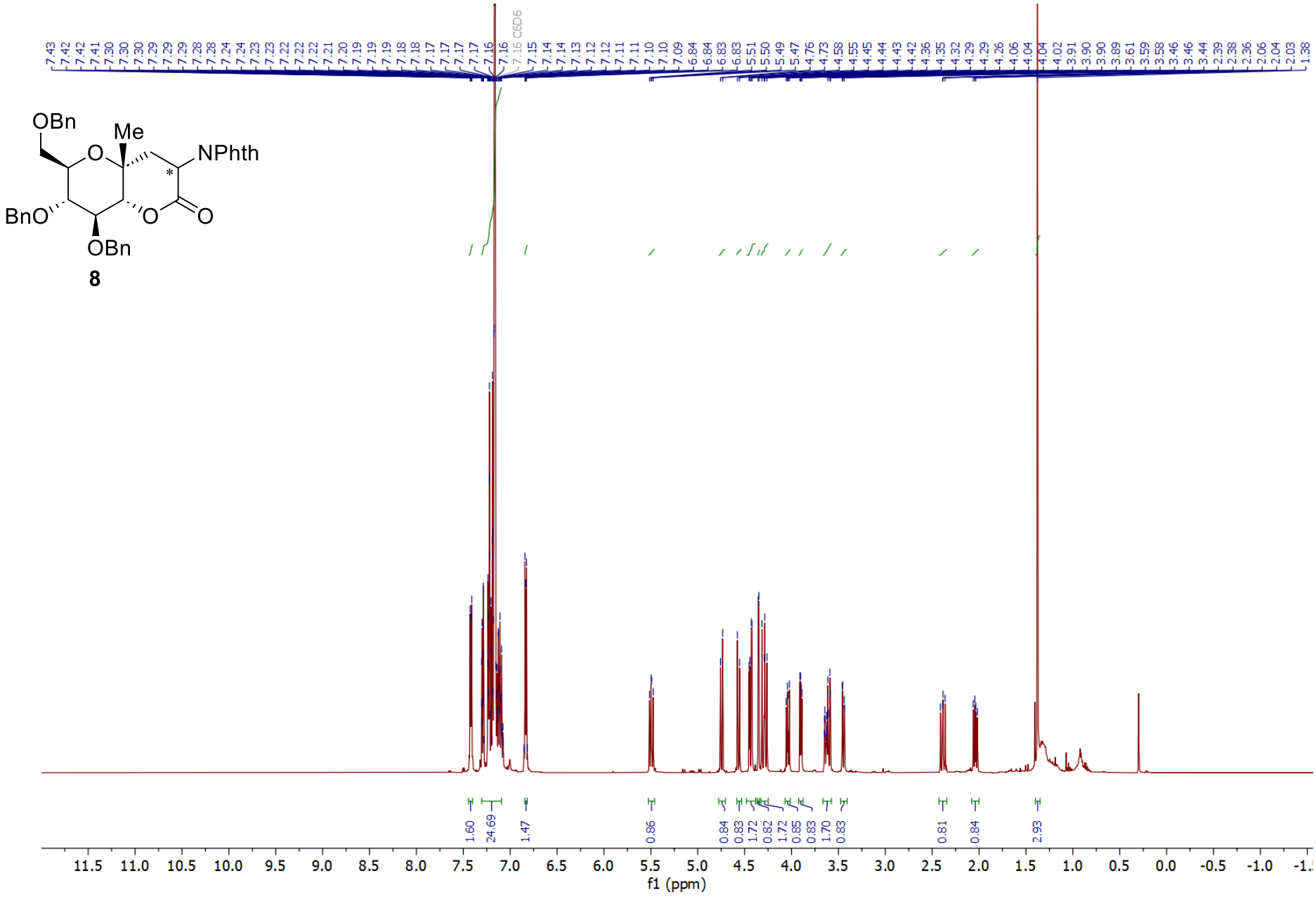
^{1}H NMR (500 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy -1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (7) starting from an enantipure acceptor (2f)



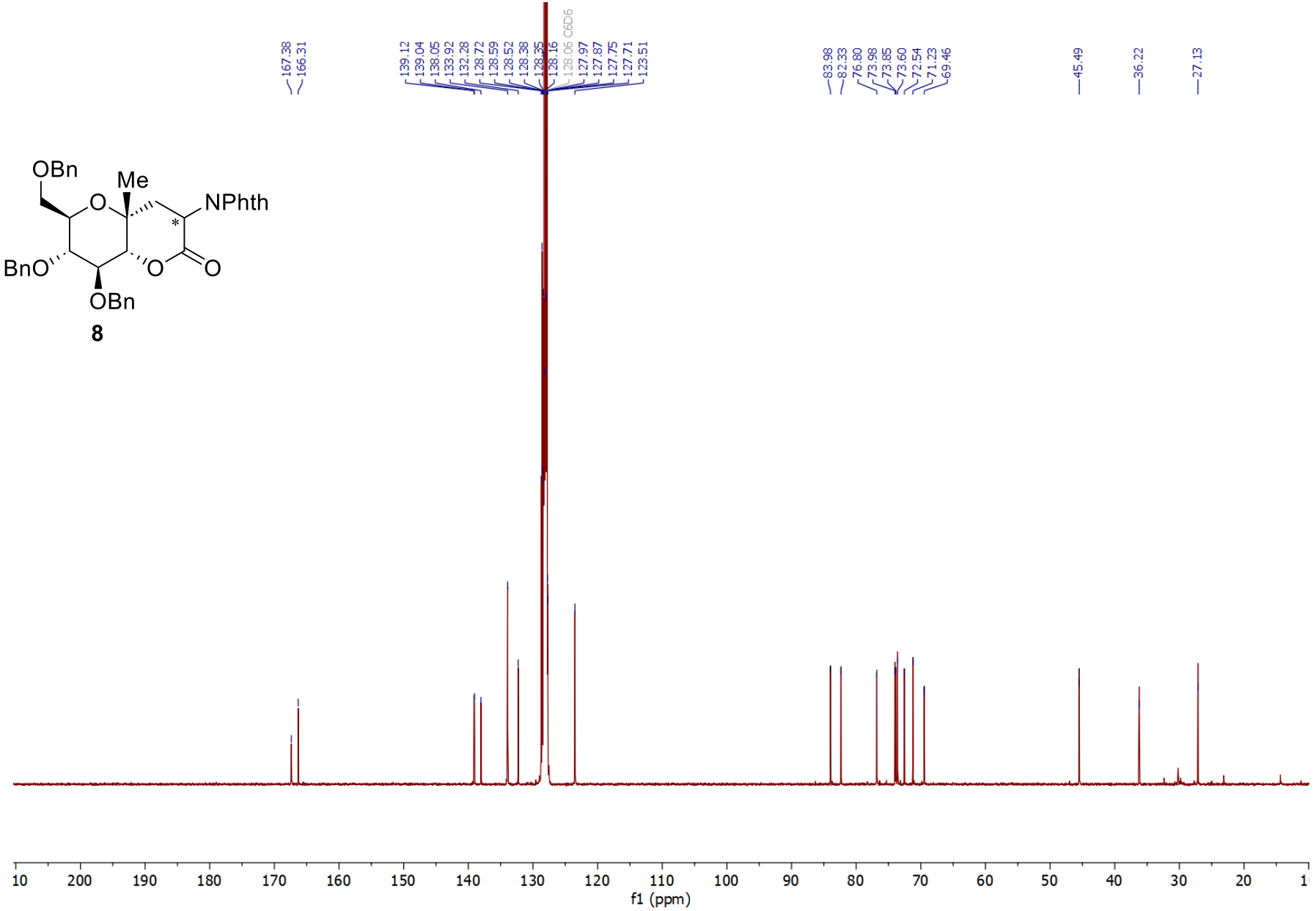
^{13}C NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy -1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (7) starting from an enantipure acceptor (2f)



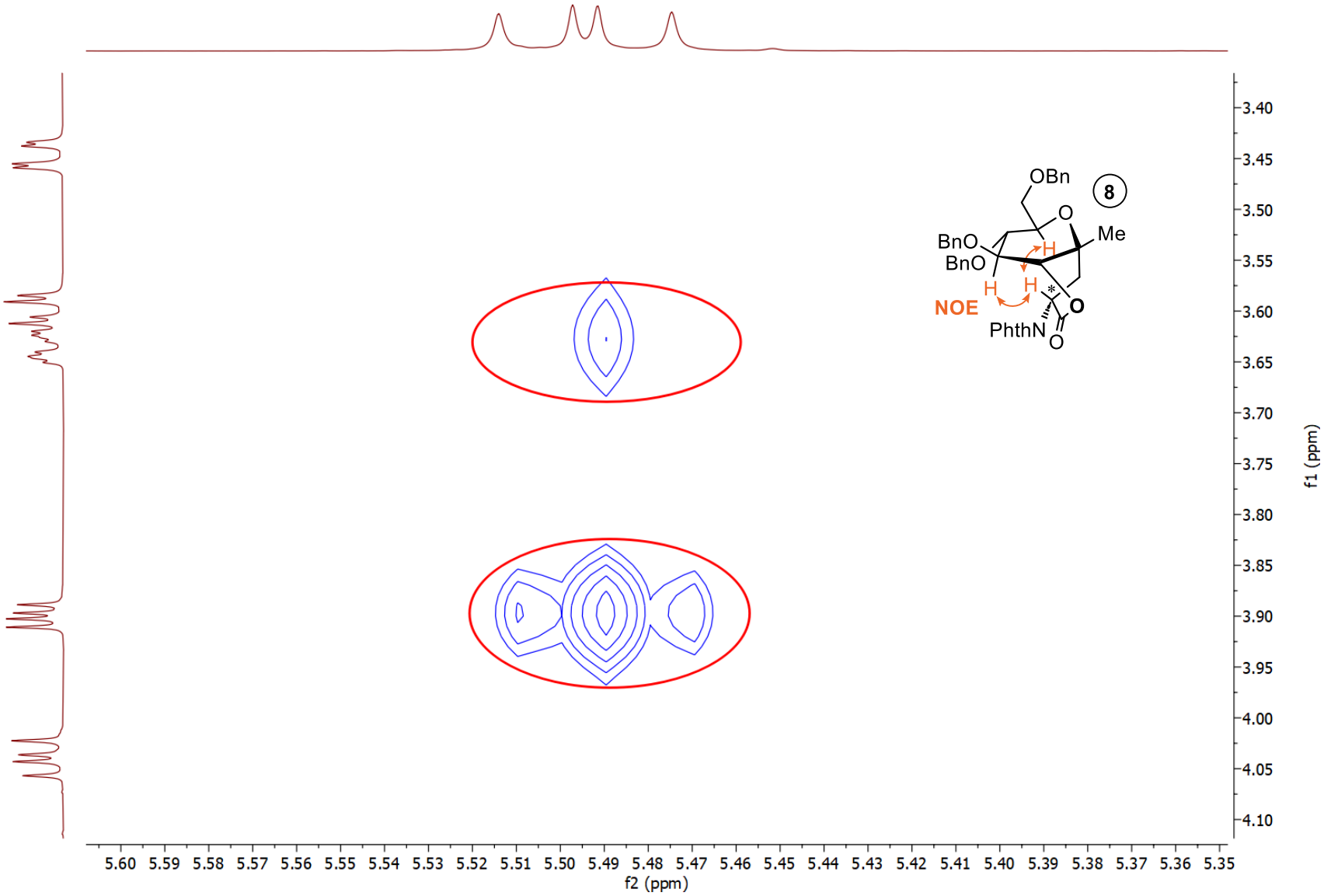
^{1}H NMR (500 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy -1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid - lactonisation product (8)



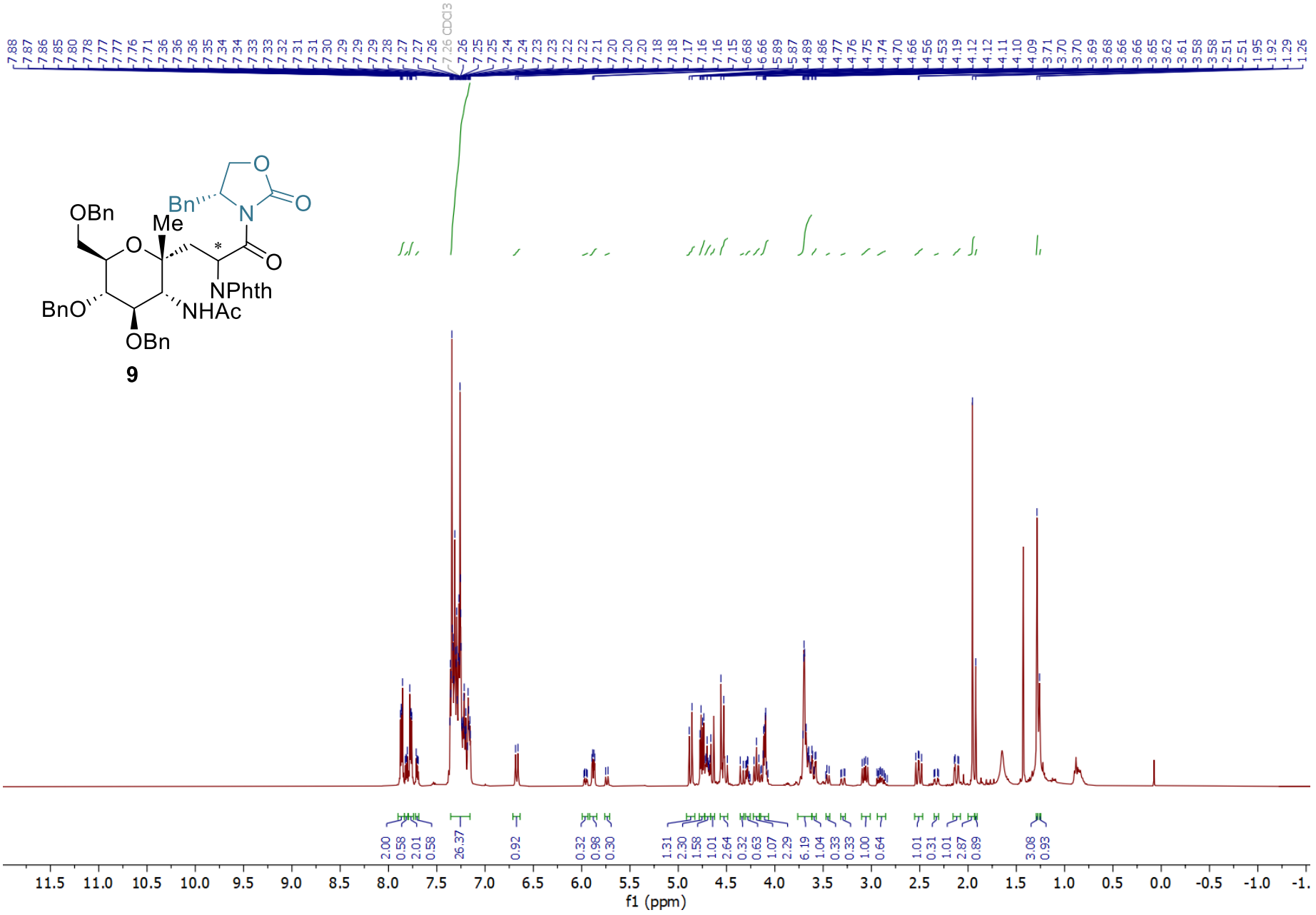
^{13}C NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy -1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid - lactonisation product (8)



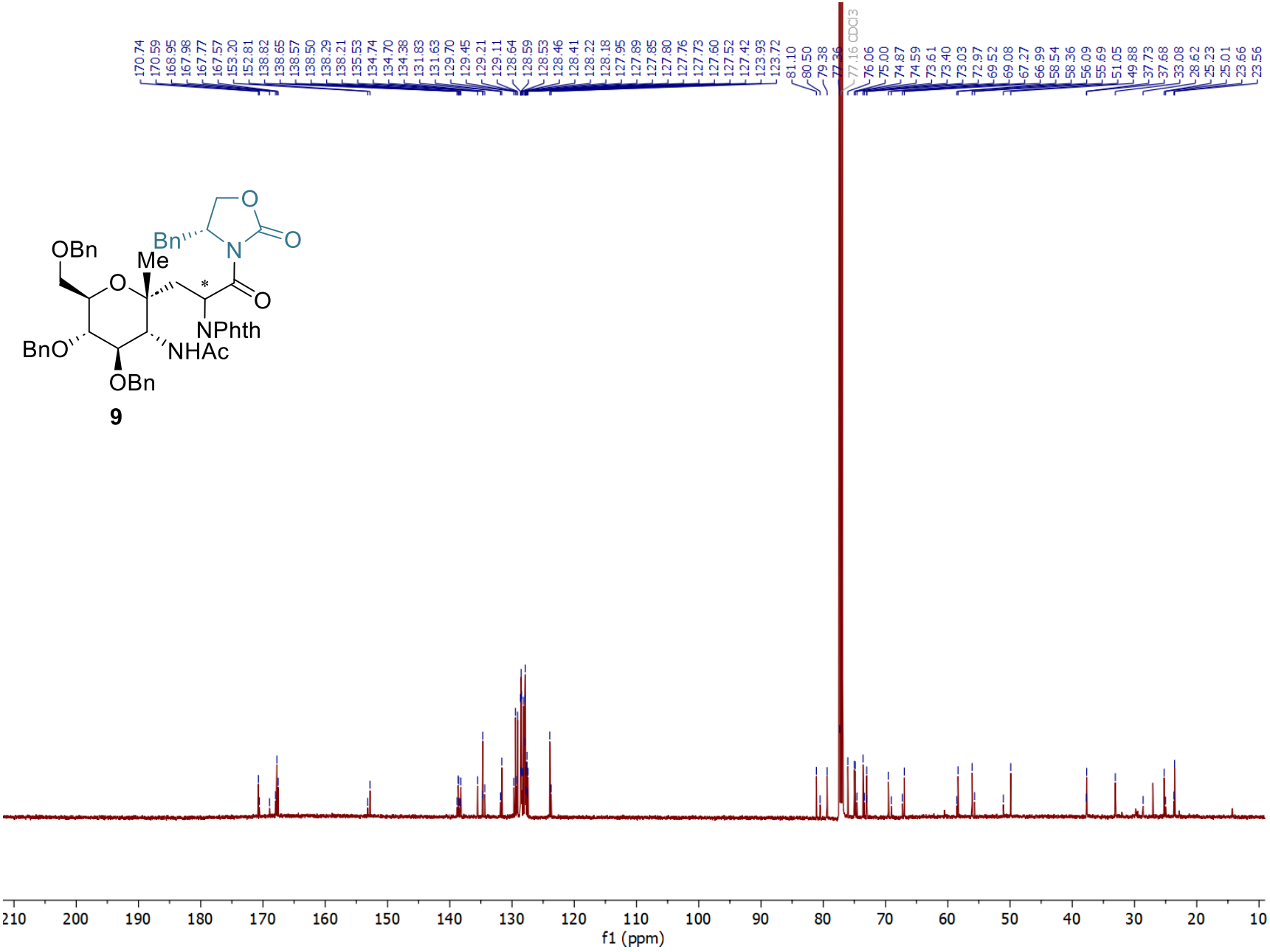
NOESY NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(3,4,6-tri-*O*-benzyl-2-*O*-methoxymethoxy -1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid - lactonisation product (8)



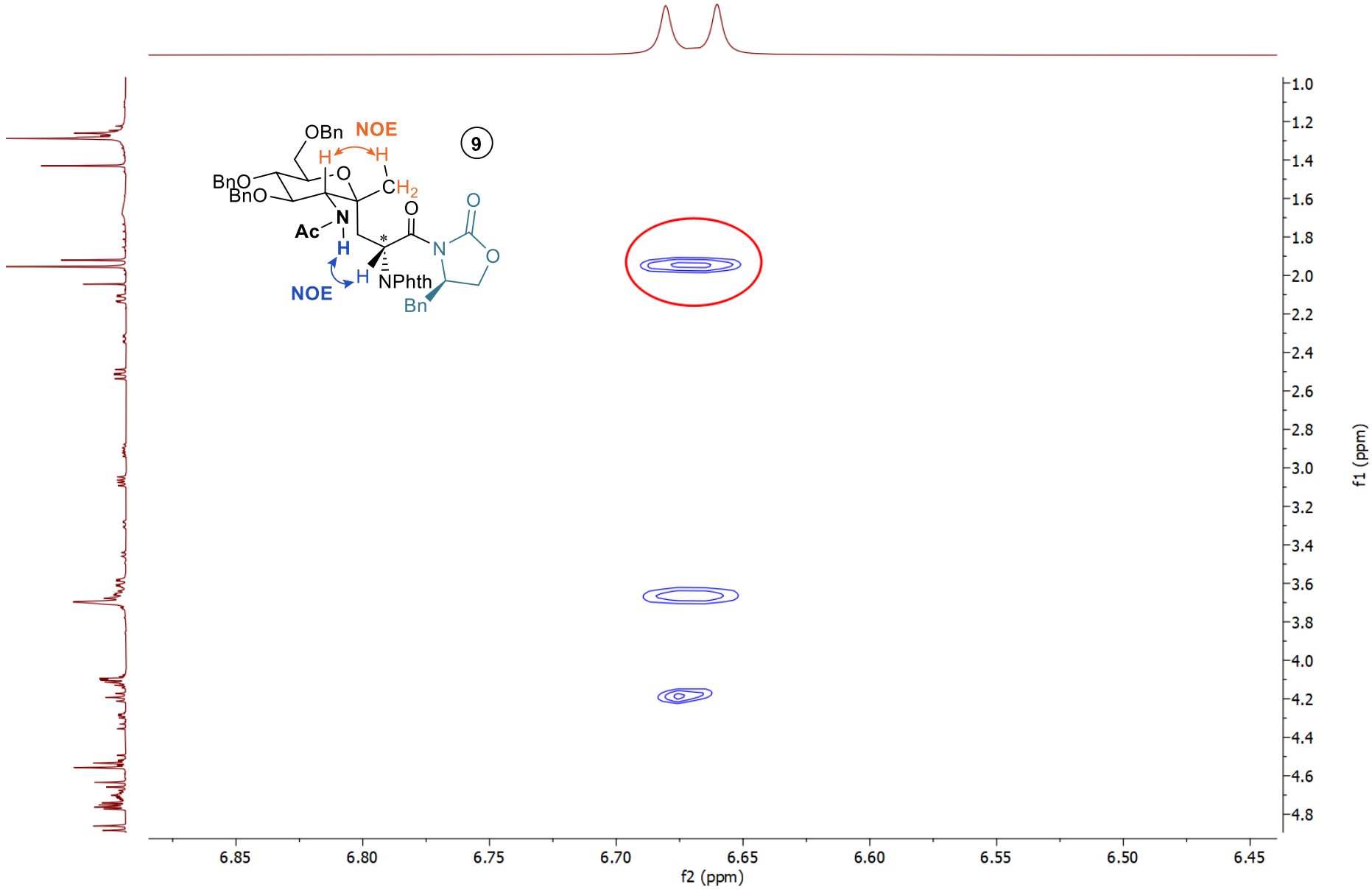
^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-(2-acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)-1-oxopropan-2-yl)phthalimide (9)



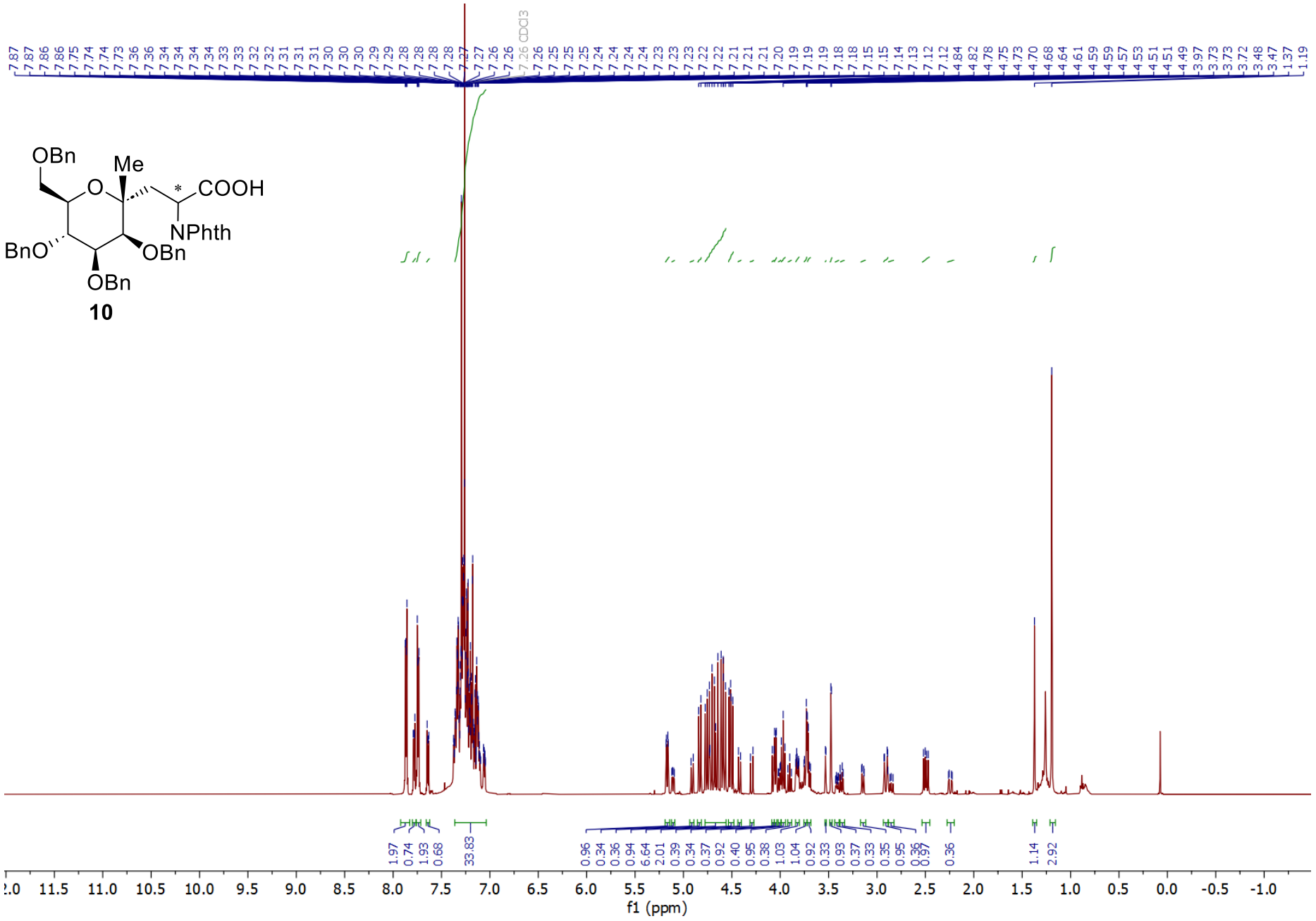
^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-(2-acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)-1-oxopropan-2-yl)phthalimide (9)



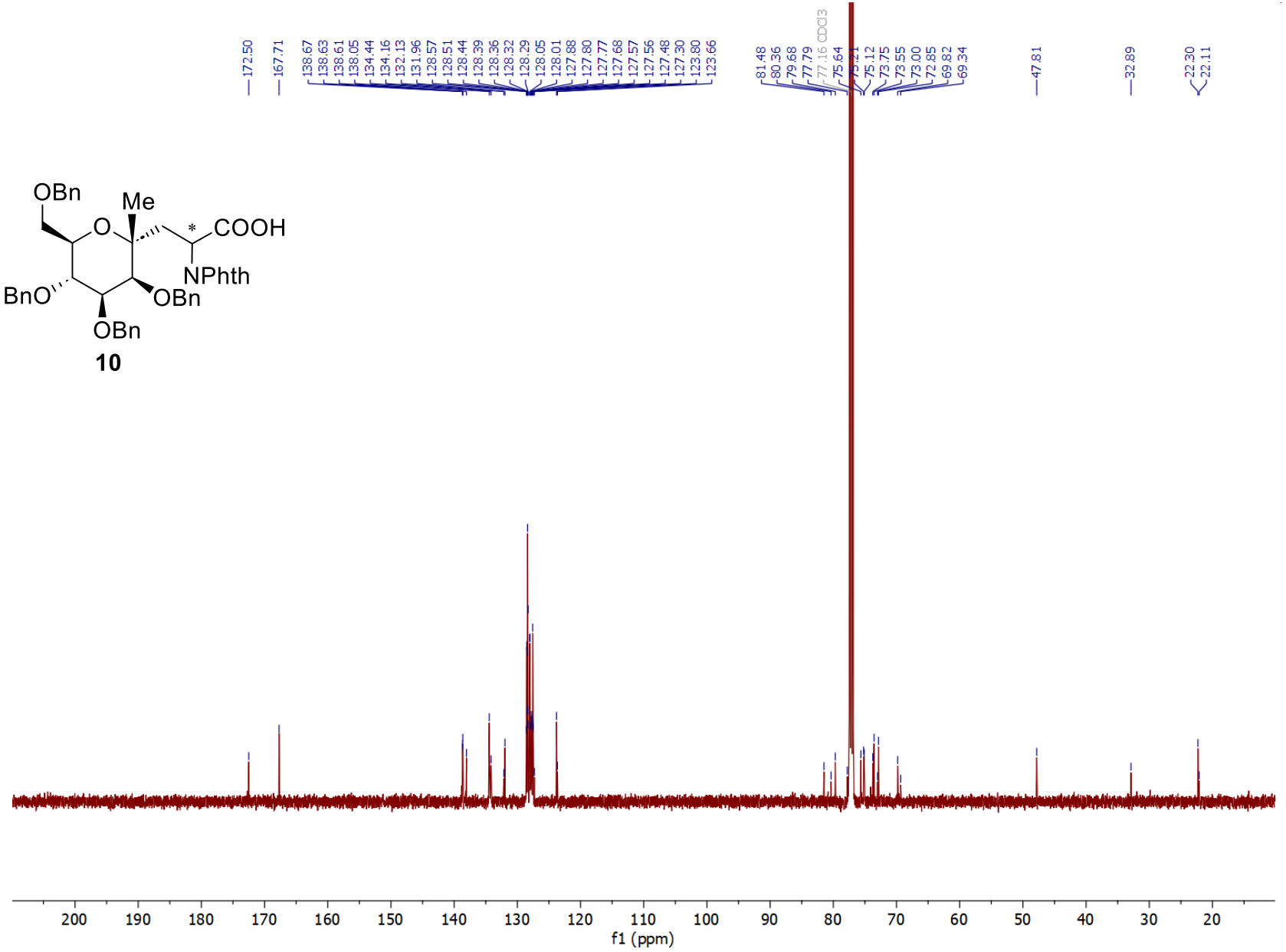
NOESY NMR (125 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-(2-acetamido-2-deoxy-3,4,6-tri-*O*-benzyl-1-methyl-1-deoxy-α-D-glucopyranosyl)-1-oxopropan-2-yl)phthalimide (9)



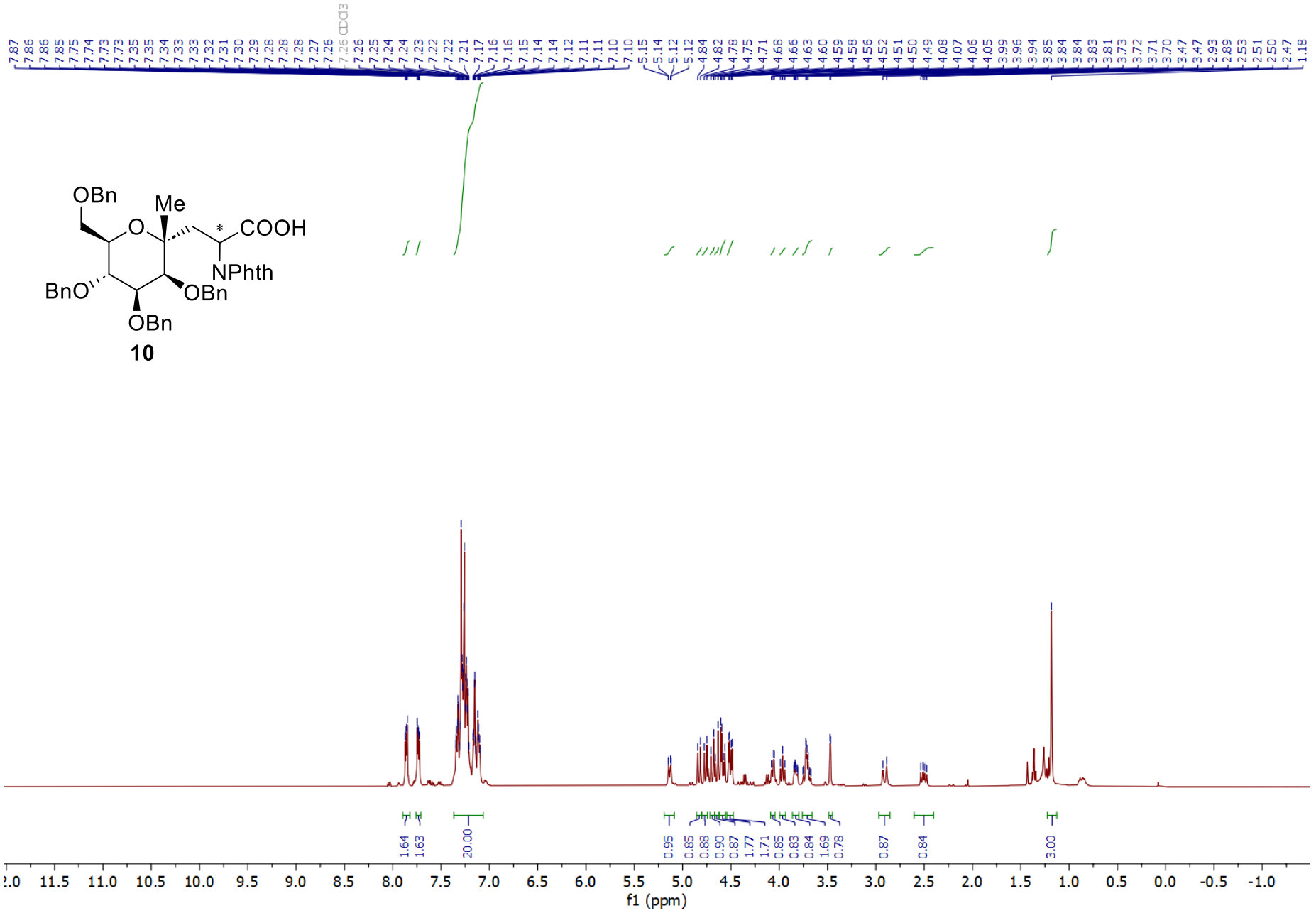
^{1}H NMR (500 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-mannopyranosyl)propanoïc acid (10) starting from an achiral acceptor (2b)



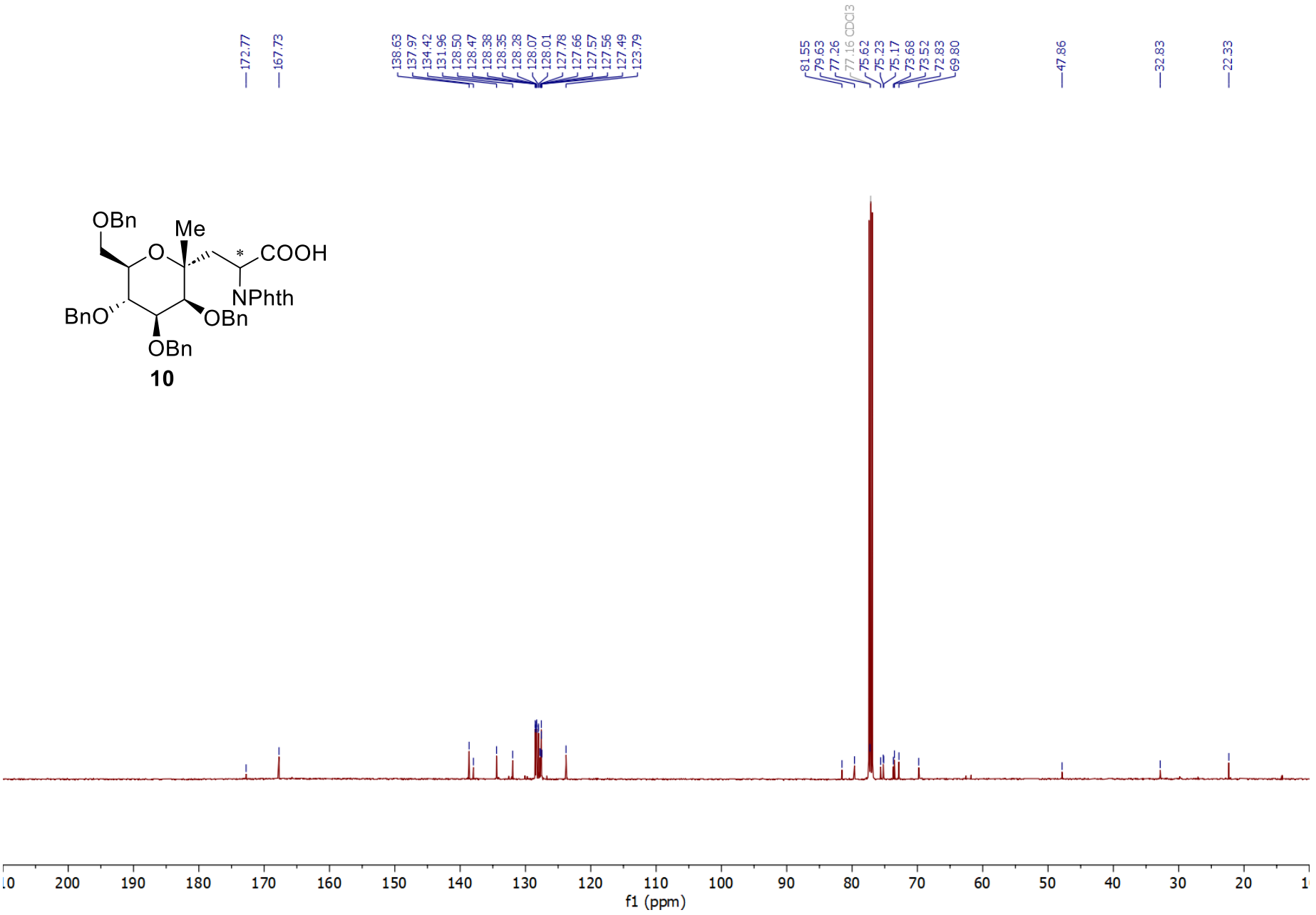
^{13}C NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-mannopyranosyl)propanoïc acid (10) starting from an achiral acceptor (2b)



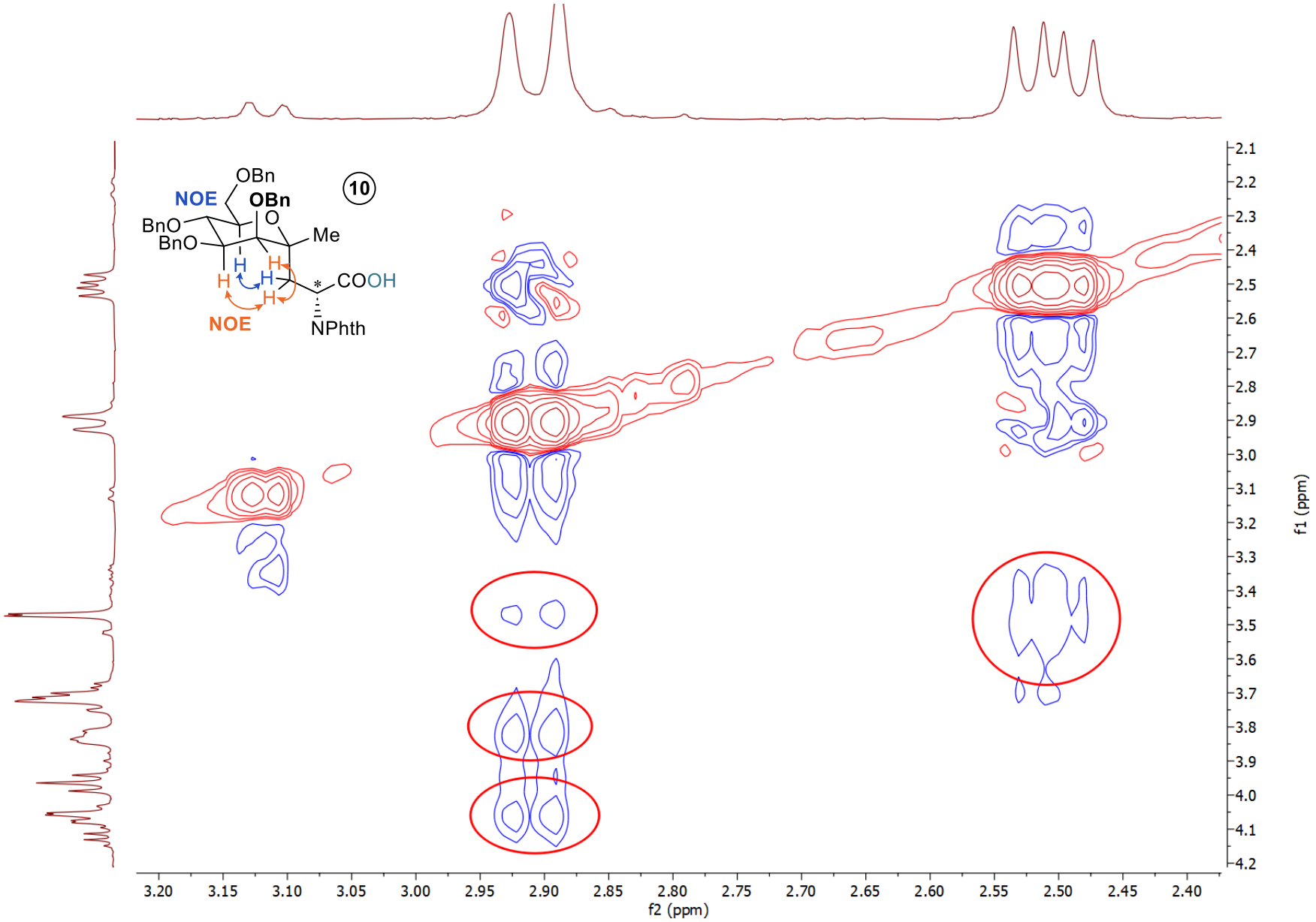
^{1}H NMR (500 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-mannopyranosyl)propanoïc acid (10) starting from an enantipure acceptor (2f)



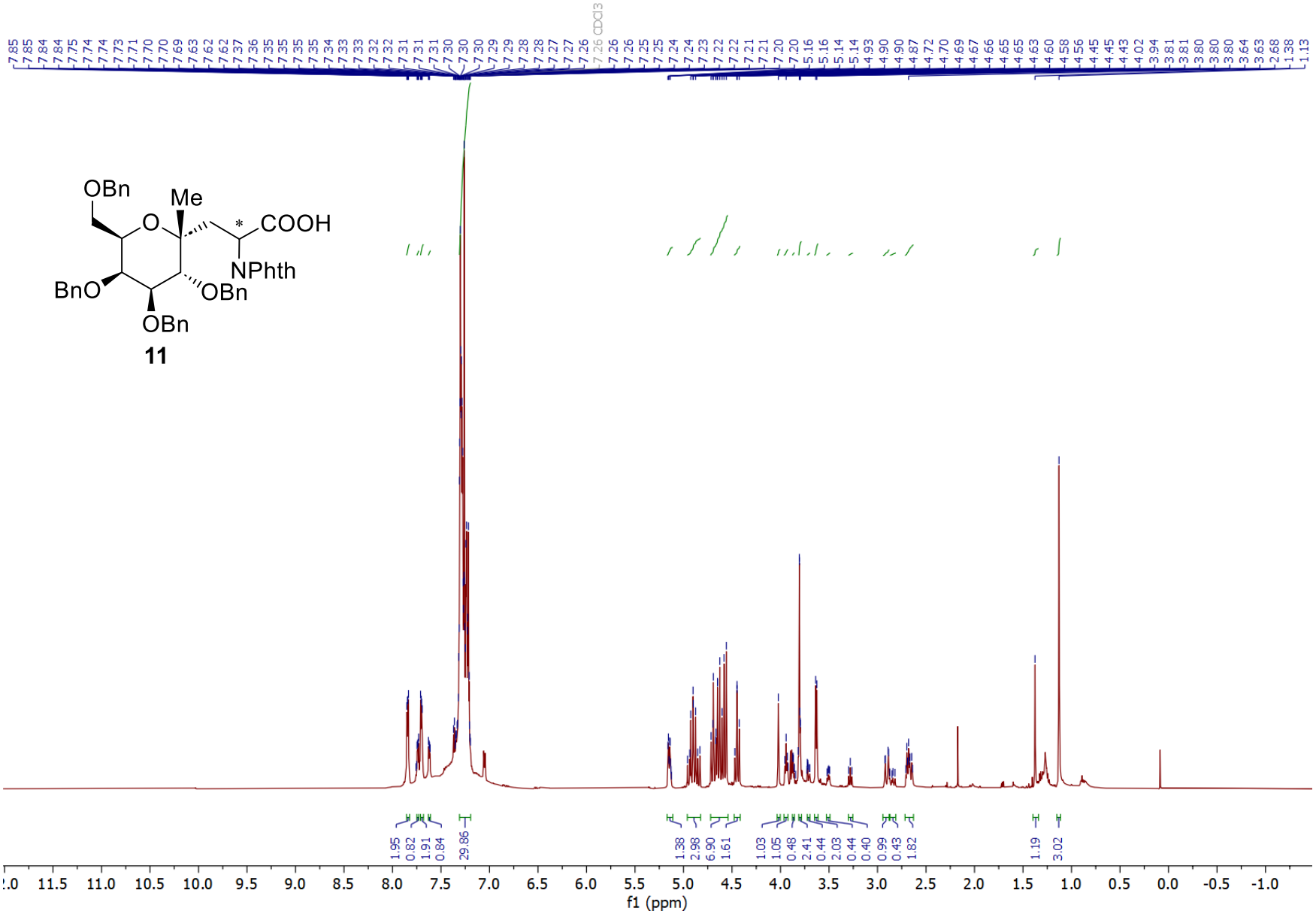
^{13}C NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-mannopyranosyl)propanoïc acid (10) starting from an enantipure acceptor (2f)



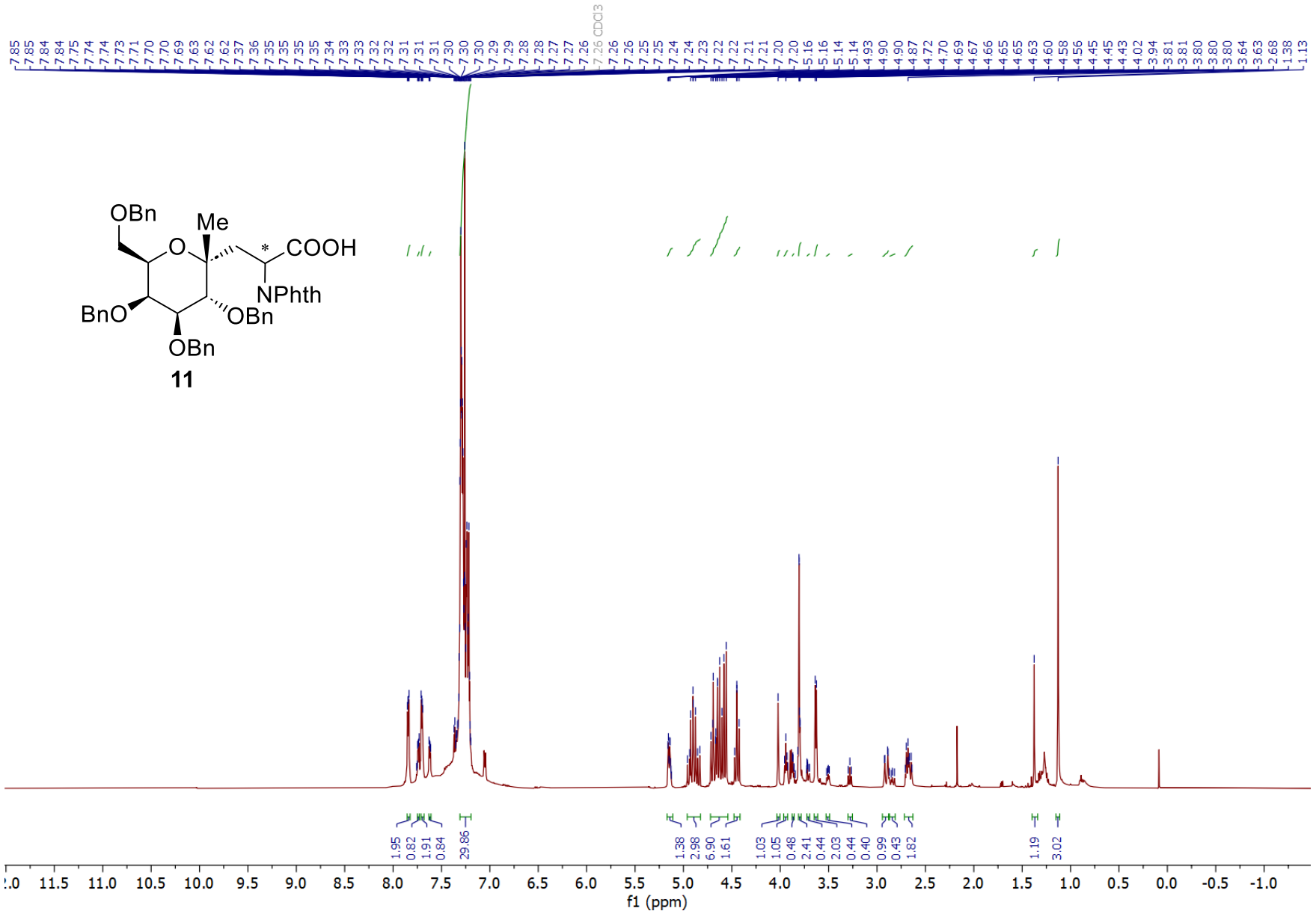
NOESY NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-mannopyranosyl)propanoïc acid (10) starting from an enantipure acceptor (2f)



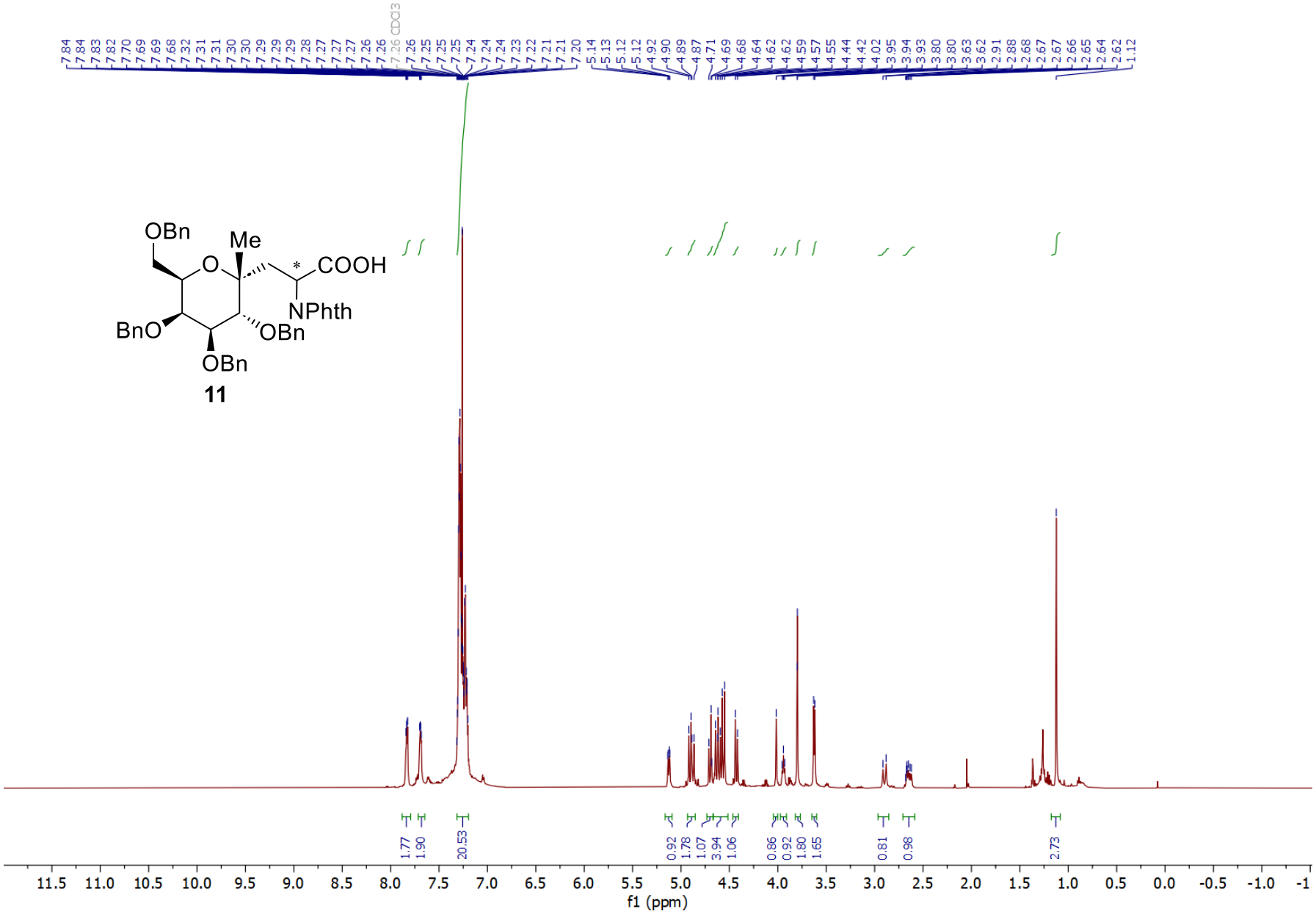
^{1}H NMR (500 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (11) starting from an achiral acceptor (2b)



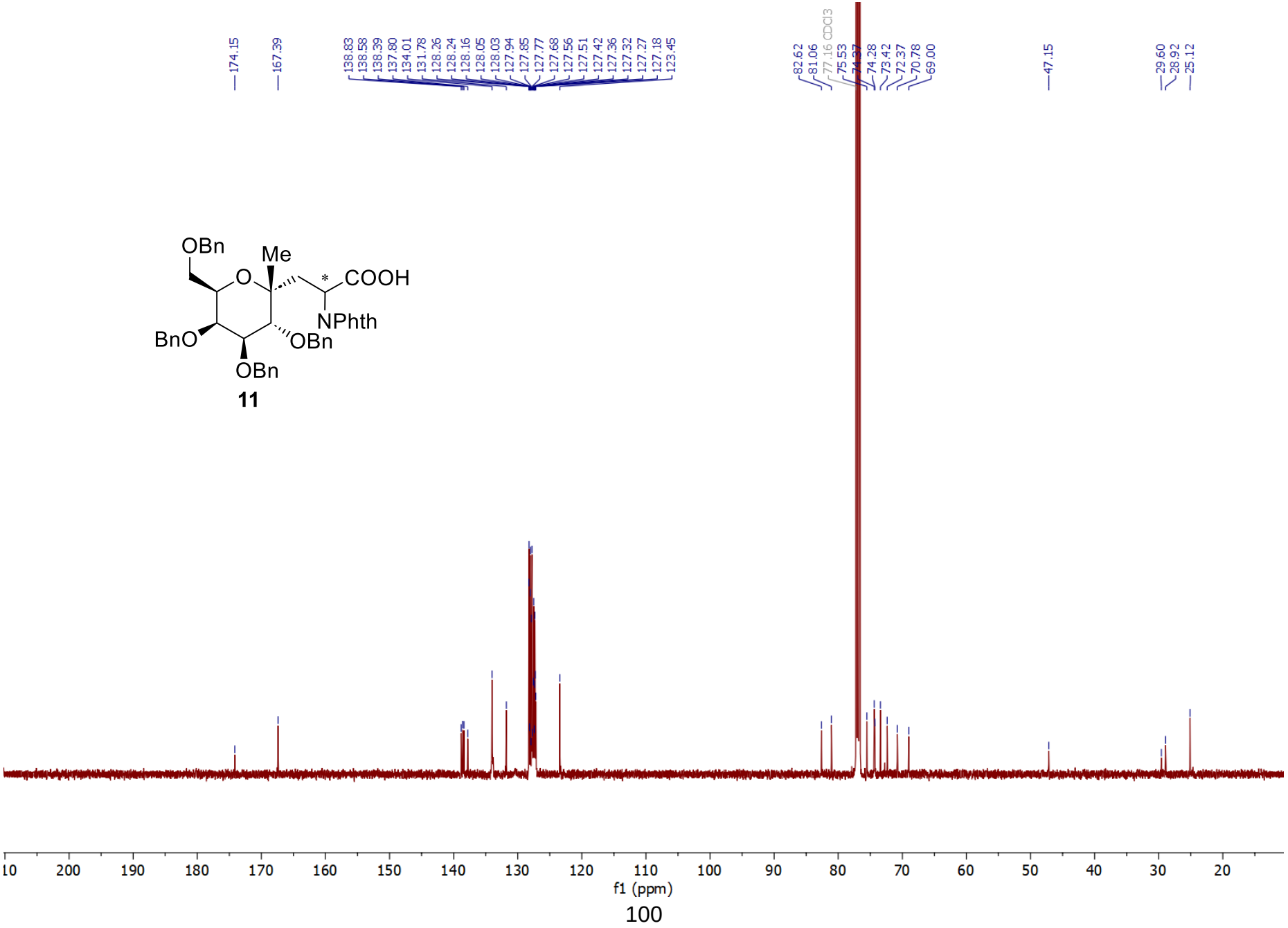
^{13}C NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (11) starting from an achiral acceptor (2b)



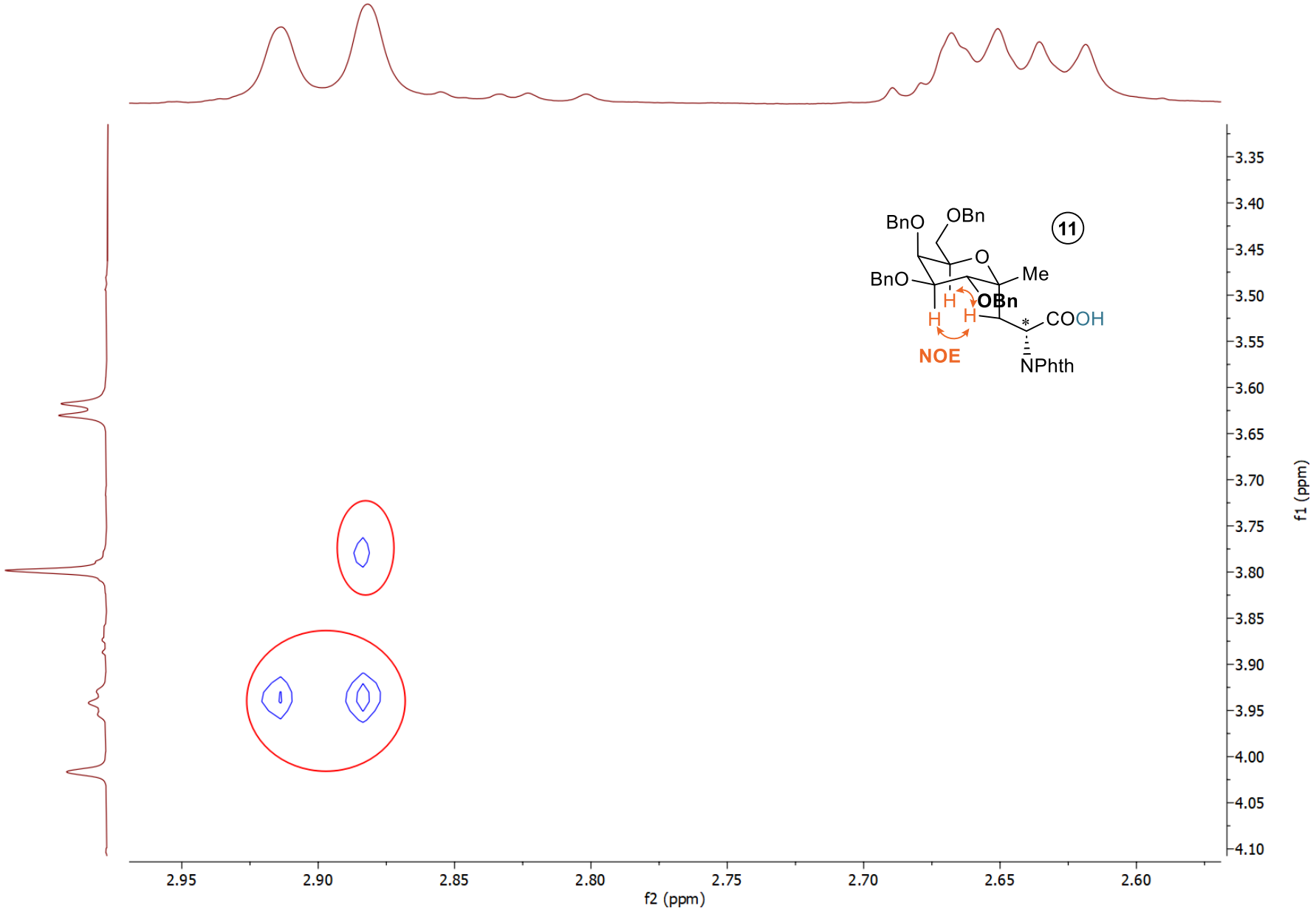
^{1}H NMR (500 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (11) starting from an enantipure acceptor (2f)



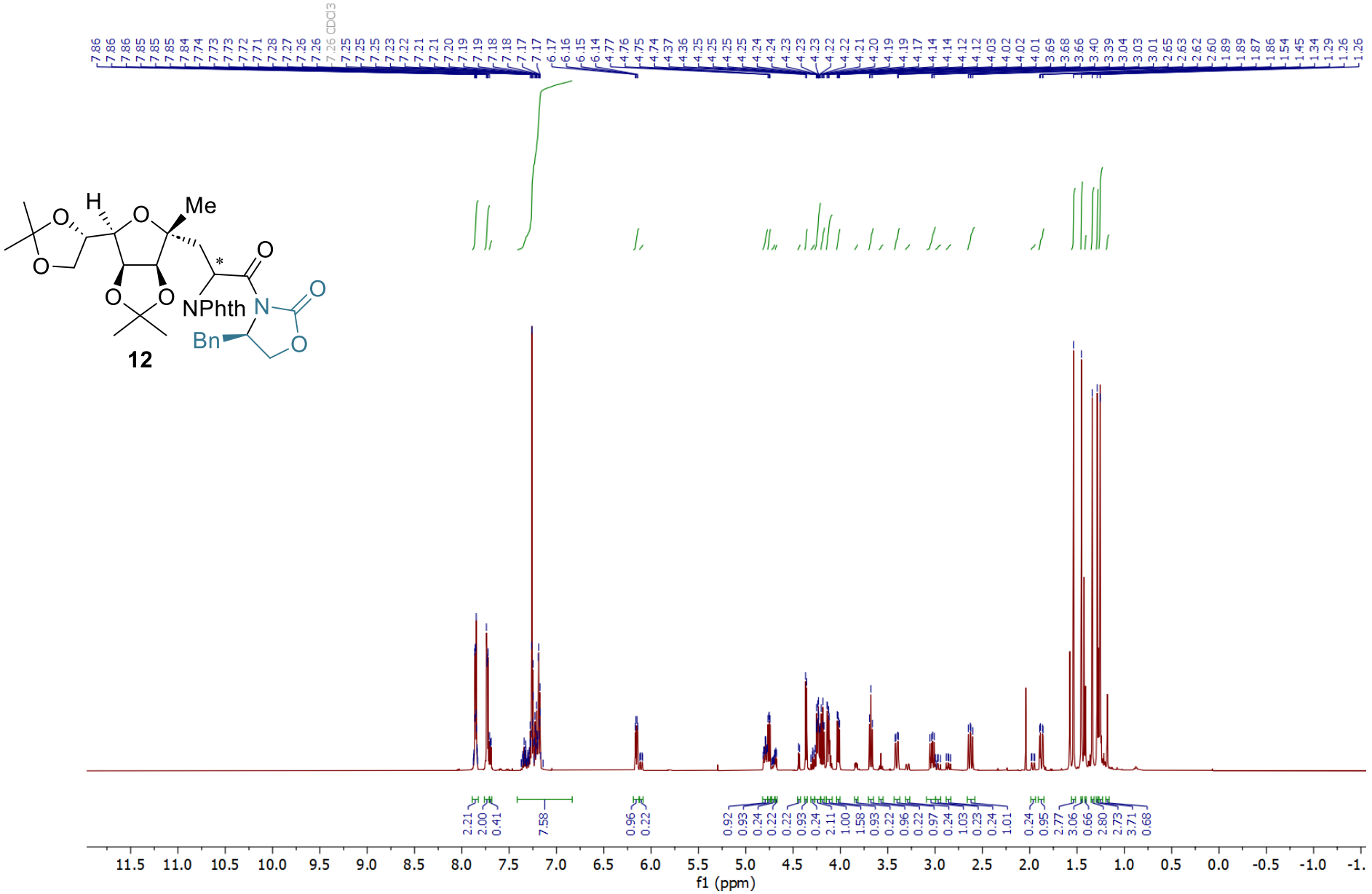
^{13}C NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (11) starting from an enantipure acceptor (2f)



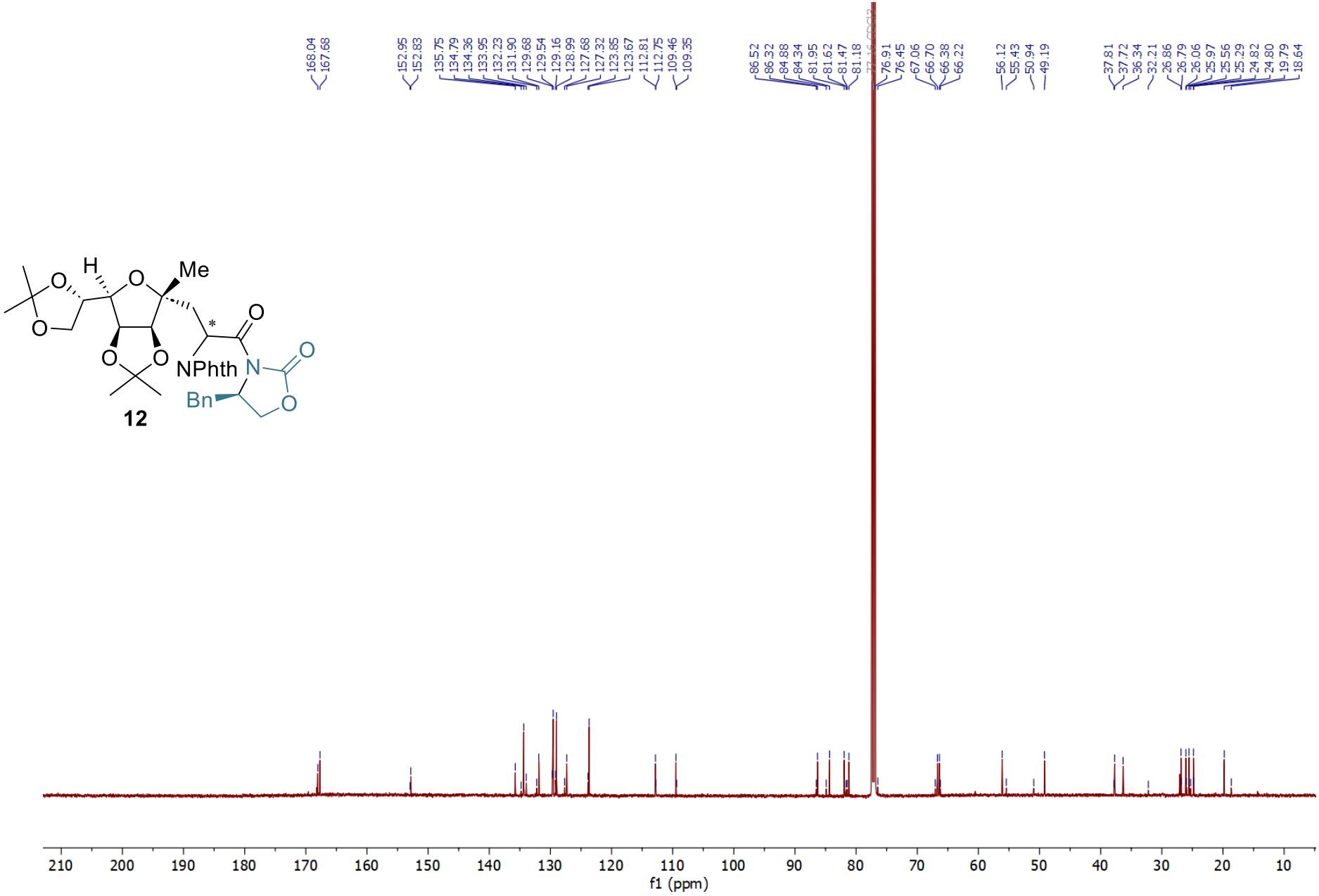
NOESY NMR (125 MHz, $CDCl_3$) of 2-phthalimidoyl-3-(2,3,4,6-tetra-*O*-benzyl-1-methyl-1-deoxy-α-D-galactopyranosyl)propanoïc acid (11) starting from an enantipure acceptor (2f)



^{1}H NMR (500 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-((*3aS,4R,6aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2,4-trimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1-oxopropan-2-yl)phthalimide (12)



^{13}C NMR (125 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-((*3aS,4R,6aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2,4-trimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1-oxopropan-2-yl)phthalimide (12)



NOESY NMR (125 MHz, $CDCl_3$) of 2-(1-((*R*)-4-benzyl-2-oxooxazolidin-3-yl)-3-((*3aS,4R,6aS*)-6-((*S*)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2,4-trimethyltetrahydrofuro[3,4-d][1,3]dioxol-4-yl)-1-oxopropan-2-yl)phthalimide (12)