Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Access to *C*-aryl/alkenylglycosides by directed Pd-catalyzed C-H functionalisation of the anomeric position in glycal-type substrates.

Morgane de Robichon, Andrea Bordessa, Maciej Malinowski, Jacques Uziel, Nadège Lubin-Germain and Angélique Ferry*.

LCB laboratory – University of Cergy-Pontoise, 5 mail Gay-Lussac, 95031 Cergy-Pontoise cedex.

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General experimental methods

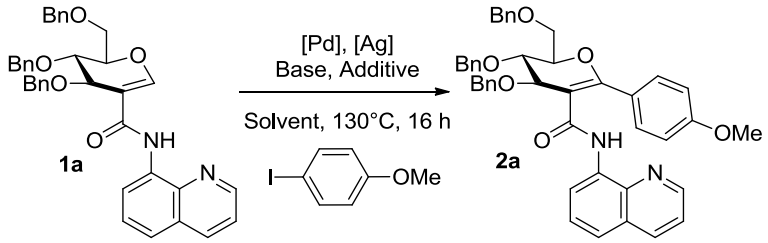
All chemical operations were carried out using standard Schlenk tubes. Acetonitrile and DMF were purified before use by distillation under an argon atmosphere. Other solvents were used without further purification. The "Cyclo" abbreviation will be used to name cyclohexane. Commercially available chemicals were used as received unless otherwise stated. Reactions were monitored by thin-layer chromatography on silica gel plates (60 F254 aluminum sheets) which were rendered visible by ultraviolet and/or spraying with vanillin (15%) + sulfuric acid (2,5%) in EtOH followed by heating. ^{1}H NMR (400 MHz), ^{13}C NMR (100.5 MHz), and ^{19}F NMR spectra (376.2 MHz) were recorded at 298 K unless otherwise stated. Chemical shifts are given in ppm (δ) and are referenced to the internal solvent signal or to TMS used as an internal standard. Multiplicities are declared as follows: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quadruplet), dd (doublet of doublet), ddd (doublet of doublet of doublet), dt (doublet of triplet), m (multiplet). Coupling constants *J* are given in Hz. Infrared spectra (IR) were recorded on a FT-IR system using diamond window Dura SamplIR II, and the data are reported in reciprocal centimeters (cm^{-1}) in the range 4000−600 cm^{-1}. Optical rotations were measured on a polarimeter at 589 nm. [α] is expressed in $deg \cdot cm^3 \cdot g^{-1} \cdot dm^{-1}$, and c is expressed in g/100 cm^3. HRMS were determined on a TOF mass analyzer coupled with electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI). Compounds 2-iodo-3,4,6-tri-*O*-benzyl-D-glucal, 2-iodo-3,4,6-tri-*O*-benzyl-D-galactal and 2-iodo-3,6-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-glucal were prepared according to the literature[1,2,3]: corresponding glycal was dissolved in dry acetonitrile (8 mL/mmol), and the resulting mixture was heated to 80 °C. At this temperature, *N*-iodosuccinimide (1.2 equiv) and silver nitrate (20 mol %) were added. The resulting mixture was stirred at 80 °C for 2−7 h. The mixture was filtrated on Celite and concentrated. The obtained crude was purified on silica gel and furnished the corresponding 2-iodoglycal.

[1] S. Dharuman and Y. D. Vankar *Org. Lett*. 2014, **16**, 1172.

[2] (a) M. K. Spassova, W. G. Bornmann, G. Ragupathi, G. Sukenick, P. O. Livingston and S. J. Danishefsky, *J. Org. Chem.* 2005, **70**, 3383. (b) D. Ruhela, P. Chatterjee and R. A. Vishwakarma *Org. Biomol. Chem*. 2005, **3**, 1043.

[3] M. de Robichon, A. Bordessa, N. Lubin-Germain and A. Ferry *J. Org. Chem*. 2019, **6**, 3328.

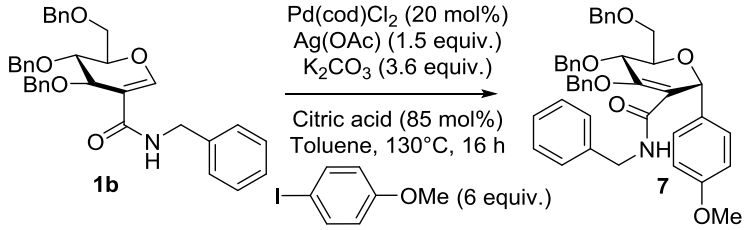
Optimization of the C-H functionalisation reaction



Entry	[Pd] (x mol%)	[Ag] (x equiv.)	Base (x equiv.)	Additive (x mol%)	Solvent	Yield[b] : **2a**/**1a**
1	$Pd(OAc)_2$ (20)	AgOAc (3.5)	-	-	Toluene (1 mL)	19%/42%
2	$Pd(OAc)_2$ (20)	AgOAc (3.5)	**K_2CO_3** (2.6)	-	Toluene (1 mL)	34%/0%
3	$Pd(OAc)_2$ (20)	**Ag_2CO_3** (3.5)	K_2CO_3 (2.6)	-	Toluene (1 mL)	26%/6%
4	$Pd(OAc)_2$ (20)	AgOAc (3.5)	K_2CO_3 (2.6)	-	**DMF** (1 mL)	3%/97%
5	$Pd(OAc)_2$ (20)	AgOAc (3.5)	K_2CO_3 (2.6)	-	**Dioxane** (1 mL)	14%/44%
6	$Pd(OAc)_2$ (20)	AgOAc (3.5)	K_2CO_3 (2.6)	-	**tBuOH** (1 mL)	0%/100%
7	$Pd(OAc)_2$ (20)	AgOAc (3.5)	K_2CO_3 (2.6)	**PPh_3** (40)	Toluene (1 mL)	13%/32%
8	$Pd(OAc)_2$ (20)	AgOAc (3.5)	K_2CO_3 (2.6)	**Citric acid** (85)	Toluene (1 mL)	36%/64%
9	**$Pd(cod)Cl_2$** (20)	AgOAc (3.5)	K_2CO_3 (2.6)	Citric acid (85)	Toluene (1 mL)	60%/40% *Isolated **2a** :* 46%
10	$Pd(cod)Cl_2$ **(10)**	AgOAc (3.5)	K_2CO_3 (2.6)	Citric acid (85)	Toluene (1 mL)	25%/35%
11	**$PdCl_2(MeCN)_2$** (20)	AgOAc (3.5)	K_2CO_3 (2.6)	Citric acid (85)	Toluene (1 mL)	19%/50%
12	$Pd(cod)Cl_2$ (20)	AgOAc **(1.5)**	K_2CO_3 (2.6)	Citric acid (85)	Toluene (1 mL)	46%/32%
13	$Pd(cod)Cl_2$ (20)	AgOAc (1.5)	K_2CO_3 **(3.6)**	Citric acid (85)	Toluene (1 mL)	52%/37%
14	$Pd(cod)Cl_2$ (20)	AgOAc (1.5)	K_2CO_3 (3.6)	Citric acid (85)	Toluene **(2 mL)**	61%/34%
15[c]	$Pd(cod)Cl_2$ (20)	AgOAc (1.5)	K_2CO_3 (3.6)	Citric acid (85)	Toluene (2 mL)	72%/26% *Isolated **2a** :* 58%
16[d]	$Pd(cod)Cl_2$ (20)	AgOAc (1.5)	K_2CO_3 (3.6)	Citric acid (85)	Toluene (2 mL)	0%
17[e]	$Pd(cod)Cl_2$ (20)	AgOAc (1.5)	K_2CO_3 (3.6)	Citric acid (85)	Toluene (2 mL)	traces

[a] Conditions: **1a** (0.085 mmol), [Pd] (x mol%), [Ag] (x equiv.), Base (x equiv.), Additive (x mol%), 4-iodoanisole (6 equiv.), Solvent at 130 °C for 16 h under air. [b] Yields were determined by ^{1}H-NMR using acetophenone as internal reference. [c] Catalytic system ([Pd], [Ag], Base and Additive) was added in two halves : one at t_0 and the other one at t_{+3h}. [d] 4-Bromoanisole (6 equiv.) was used instead of 4-iodoanisole. [e] Benzylamine was used as directing group instead of aminoquinoline. Structure of the undesired product[4] was determined by ^{1}H NMR and confirmed by mass (reaction presented in scheme 1).

[4] (a) T. Shengbiao, Z. Qiannan, X. De-Cai, J. Shende, L. Qin and Y. Xin-Shan *Org. Lett.* 2018, **20**, 3079. (b) M. Lei, L. Gao and J.-S. Yang *Tetrahedron Lett.* 2009, **50**, 5135.



Scheme 1: Undesired reactivity observed with **1b** as starting substrate in the optimized conditions.

^{1}H NMR of **7** (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m, 1H), 7.39 – 7.31 (m, 5H), 7.31 – 7.26 (m, 7H), 7.23 – 7.17 (m, 5H), 7.09 (d, *J* = 7.1 Hz, 2H), 7.01 (dd, *J* = 6.3, 2.7 Hz, 2H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.83 (s, 1H), 5.11 (d, *J* = 10.9 Hz, 1H), 4.81 (d, *J* = 11.0 Hz, 1H), 4.64 (d, *J* = 6.6 Hz, 1H), 4.59 (d, *J* = 11.1 Hz, 1H), 4.50 (d, *J* = 10.3 Hz, 2H), 4.43 (d, *J* = 12.0 Hz, 1H), 4.37 – 4.26 (m, 2H), 4.05 – 4.00 (m, 1H), 3.77 (s, *J* = 5.7 Hz, 3H), 3.64 (dd, *J* = 10.4, 4.2 Hz, 1H), 3.52 (dd, *J* = 10.5, 4.0 Hz, 1H); HRMS (TOF ES+) for (M+H)+ $C_{42}H_{42}NO_6^+$ (*m/z*): calc. 656.3007; found 656.3018.

[b] The NMR yield of **2a** was determined with acetophenone as internal reference: 10 µL of acetophenone (1 equiv. compared to compound **1a**) was added after filtration of the crude on celite, and then the crude was concentrated. The NMR yield of **2a** on the ^{1}H NMR spectra could be determined by analytical signals:

s at 2.6 ppm (CH_3 of acetophenone - calibrated for 3H) compared with the integrations of product signals:

- s at 9.76 ppm (NH of product **2a**)
- m at 8.79 – 8.77 ppm, dd at 8.31 ppm and dd at 8.04 ppm (aromatic H of aminoquinoline of **2a**)

The yield of reaction was determined with the mean value of these integrations.

Conversion of **1a** was determined in the same mixture by integration of:

- s at 10.55 ppm (amide proton of **1a**)
- dd at 8.83 ppm, at 8.37 ppm and at 8.12 ppm (aromatic H of aminoquinoline of **1a**)

The mean value of these integrations was calculated determining the conversion of reaction.

General procedures

General procedure for the aminocarbonylation reaction:

In a Schlenk tube were added $Pd(OAc)_2$ (0.1 equiv.), PPh_3 (0.2 equiv.), K_2CO_3 (2 equiv.), $Mo(CO)_6$ (4.2 equiv.), and the corresponding 2-iodoglycal (1 equiv.). Dioxane (1 mL) and the amine (2equiv.) were then added. The resulting mixture was stirred at 80 °C overnight. The mixture was concentrated under vacuum and the crude was finally purified on silica gel using the indicated solvent. The product was washed with HCl (1M) to remove excess of aminoquinoline.

General procedure for the C-H functionalisation reaction:

Catalytic system: $Pd(cod)Cl_2$ (0.2 equiv.), AgOAc (1.5 equiv.), K_2CO_3 (3.6 equiv.) and citric acid (0.85 equiv.). In a Schlenk tube were added the half of the catalytic system, the corresponding iodide (6 equiv.) (except for compound **2n**: 0.5 equiv.), compound **1a** (1 equiv.) and toluene (2 mL). The resulting mixture was stirred for 3 h at 130 °C. Then the other half of the catalytic system was added at room temperature in the Schlenk tube. The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. The crude was finally purified on silica gel using the indicated solvent.

Characterization data

*2-N-(quinolin-8-yl)carbamoyl-3,4,6-tri-O-benzyl-D-glucal (**1a**).* **1a** was obtained following the general procedure of aminocarbonylation: $Pd(OAc)_2$ (82.8 mg; 0.1 equiv.; 0.369 mmol), PPh_3 (193.4 mg; 0.2 equiv.; 0.738 mmol), K_2CO_3 (1.0 g; 2 equiv.; 7.374 mmol), $Mo(CO)_6$ (4.1 g; 4.2 equiv.; 15.486 mmol), 8-aminoquinoline (1.1 g; 2 equiv.; 7.374 mmol), 2-iodo-3,4,6-tri-*O*-benzyl-D-glucal (2.0 g; 1 equiv.; 3.687 mmol), dioxane (40 mL). The resulting mixture was stirred at 80 °C overnight. The mixture was concentrated under vacuum and **1a** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 80:20) as yellowish oil (1.86 g; 3.169 mmol; 85 %). The product was washed with HCl (1M) to remove excess of aminoquinoline. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.55 (s, 1H), 8.83 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.37 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.12 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.78 (s, 1H), 7.57 – 7.53 (m, 1H), 7.48 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.36 – 7.28 (m, 12H), 7.25 – 7.22 (m, 4H), 5.08 (d, *J* = 11.3 Hz, 1H), 4.70 – 4.63 (m, 4H), 4.55 – 4.54 (m, 1H), 4.47 (d, *J* = 11.9 Hz, 1H), 4.40 (d, *J* = 11.9 Hz, 1H), 4.06 (t, *J* = 2.7 Hz, 1H), 3.82 (dd, *J* = 10.4, 7.0 Hz,1H), 3.66 (dd, *J* = 10.5, 5.2 Hz,1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 153.4, 148.0, 138.7, 137.9, 137.7, 137.5, 136.3, 135.2, 128.7, 128.5, 128.4, 128.1, 128.0, 127.8, 127.7, 127.5, 121.5, 121.2, 116.8, 108.3, 76.3, 73.5, 71.8, 71.0, 70.6, 70.5, 67.6; IR (cm^{-1}): 3345, 3063, 3031, 2922, 2866, 1676, 1617, 1527, 1195; $[\alpha]^{20}_D$ = +20.3 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+Na)+ $C_{37}H_{34}N_2NaO_5^+$ (*m/z*): calc. 609.2365; found 609.2368.

*2-N-(quinolin-8-yl)carbamoyl-1-(4-methoxyphenyl)-3,4,6-tri-O-benzyl-D-glucal (**2a**).* **2a** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 4-iodoanisole (119.7 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3

(21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2a** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 90:10) as yellowish oil (34 mg; 0.049 mmol; 58 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.79 – 8.77 (m, 1H), 8.31 (dd, *J* = 4.2, 1.6 Hz,1H), 8.04 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.51 – 7.47 (m, 3H), 7.41 (dd, *J* = 8.2, 1.1 Hz, 2H), 7.36 – 7.27 (m, 12H), 7.25 (s, 1H), 7.22 – 7.20 (m, 2H), 6.70 (d, *J* = 8.8 Hz, 2H), 4.87 (dd, *J* = 2.5, 1.8 Hz, 1H), 4.78 (d, *J* = 11.4 Hz, 1H), 4.71 (d, *J* = 12.0 Hz, 2H), 4.65 (d, *J* = 11.4 Hz, 1H), 4.64 (d, *J* = 12.0 Hz, 1H), 4.59 (s, 2H), 4.06 – 4.01 (m, 2H), 3.80 (dd, *J* = 10.6, 4.6 Hz,1H), 3.60 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.3, 161.2, 157.4, 147.5, 138.6, 138.6, 138.2, 138.0, 135.9, 135.2, 130.8, 128.6, 128.3, 128.0, 127.9, 127.8, 127.6, 127.4, 126.9, 121.3, 121.0, 116.1, 113.6, 108.3, 76.9, 73.4, 72.8, 72.7, 72.5, 71.7, 68.0, 55.3; IR (cm^{-1}): 3333, 2927.8, 2858, 1654, 1606, 1577, 1522, 1497, 1484, 1454, 1425, 1385, 1327, 1253, 1175, 1100, 1070, 1028; $[\alpha]^{20}_{D}$ = +23.5 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{44}H_{41}N_2O_6^+$ (*m/z*): calc. 693.2959; found 693.2975.

2-N-(quinolin-8-yl)carbamoyl-1-phenyl-3,4,6-tri-O-benzyl-D-glucal ***(2b)****.* **2b** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then iodobenzene (57.3 µL, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2b** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 90:10) as yellowish oil (34 mg; 0.051 mmol; 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 8.79 – 8.77

(m, 1H), 8.30 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.03 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.58 – 7.56 (m, 2H), 7.52 – 7.48 (m, 2H), 7.41 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.37 – 7.27 (m, 13H), 7.22 – 7.19 (m, 4H), 4.88 (dd, *J* = 2.5, 1.8 Hz, 1H), 4.80 (d, *J* = 11.3 Hz, 1H), 4.73 (d, *J* = 12.1 Hz, 2H), 4.66 (d, *J* = 11.8 Hz, 2H), 4.60 (s, 2H), 4.08 – 4.04 (m, 2H), 3.83 (dd, *J* = 10.6, 4.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 157.3, 147.5, 138.5, 138.2, 137.9, 135.9, 135.0, 134.6, 129.9, 129.2, 128.6, 128.5, 128.3, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.4, 121.3, 121.0, 116.1, 109.2, 76.8, 73.4, 72.7 (2C), 72.5, 71.8, 67.9; IR (cm^{-1}): 3335, 3062, 3030, 2918, 2861, 1656, 1596, 1577, 1520, 1484, 1454, 1424, 1385, 1327, 1261, 1207, 1163, 1088, 1071, 1028, 1002; $[\alpha]^{20}_D$ = +17.9 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{43}H_{39}N_2O_5^+$ (*m/z*): calc. 663.2859; found 663.2848.

*2-N-(quinolin-8-yl)carbamoyl-1-(4-methylphenyl)-3,4,6-tri-O-benzyl-D-glucal (**2c**).* **2c** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 4-iodotoluene (111.5 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2c** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 85:15) as a white oil (38 mg; 0.056 mmol; 66 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.66 (s, 1H), 8.68 (d, J = 7.7 Hz, 1H), 8.19 (dd, J = 4.2, 1.5 Hz, 1H), 7.93 (dd, J = 8.3, 1.6 Hz, 1H), 7.41 – 7.37 (m, 2H), 7.36 – 7.28 (m, 5H), 7.28 – 7.24 (m, 2H), 7.23 – 7.14 (m, 8H), 7.12 – 7.09 (m, 3H), 6.90 (d, J = 7.9 Hz, 2H), 4.77 (dd, J = 2.5, 1.8 Hz, 1H), 4.69 (d, J = 11.4 Hz, 1H), 4.64 – 4.58 (m, 2H), 4.58 – 4.53 (m, 2H), 4.49 (s, 2H), 3.96 – 3.91 (m, 2H), 3.72 (dd, J = 10.6, 4.7 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 157.7, 147.4, 140.1, 138.5, 138.2, 137.9, 135.9, 135.2, 131.7, 129.1, 128.9,

128.6, 128.5, 128.3, 128.0, 127.9, 127.9, 127.8, 127.6, 127.4, 121.2, 121.0, 116.1, 108.6, 76.9, 73.4, 72.8, 72.5 (2C), 71.8, 68.0, 21.4; IR (cm^{-1}) : 3332, 3062, 3030, 2920, 2859, 1653, 1520, 1483, 1454, 1424, 1384, 1326, 1088, 1069; $[\alpha]^{20}_D$ = +24.6 (1.00, $CHCl_3$), HRMS (TOF ES+) for (M+H)+ $C_{44}H_{41}N_2O_5^+$ (*m/z*): calc. 677.3010; found 677.2983.

*2-N-(quinolin-8-yl)carbamoyl-1-(4-methylbenzoate)-3,4,6-tri-O-benzyl-D-glucal (**2d**).* **2d** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: Pd(cod)Cl_2 (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then methyl 4-iodobenzoate (134 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: Pd(cod)Cl_2 (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2d** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 90:10) as yellowish oil (28 mg; 0.039 mmol; 46 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.76 – 8.74 (m, 1H), 8.27 (dd, *J* = 4.1, 1.2 Hz, 1H), 8.04 – 8.02 (m, 1H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.48 (m, 1H), 7.44 – 7.42 (m, 1H), 7.39 – 7.25 (m, 14H), 7.22 – 7.20 (m, 2H), 4.84 – 4.84 (m, 1H), 4.81 (d, *J* = 11.3 Hz, 1H), 4.73 (d, *J* = 11.9 Hz, 2H), 4.66 (d, *J* = 12.3 Hz, 1H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.59 (s, 2H), 4.08 – 4.03 (m, 2H), 3.83 (s, 3H), 3.81 – 3.79 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 166.5, 156.0, 147.7, 139.2, 138.4, 138.3, 138.0, 137.8, 136.0, 134.8, 131.1, 129.4, 129.2, 128.6, 128.6, 128.4, 128.0, 127.9, 127.7, 127.4, 121.4, 116.3, 110.2, 77.0, 73.4, 72.7, 72.6, 72.3, 71.9, 67.7, 52.2; IR (cm^{-1}): 3336, 3063, 3031, 2950, 2921, 2861, 2245, 1948, 1721, 1658, 1608, 1577, 1520, 1497, 1484, 1454, 1435, 1425, 1407, 1385, 1326, 1277, 1207, 1178, 1163, 1138, 1102, 1070, 1028, 1020; $[\alpha]^{20}_D$ = +28.6 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{45}H_{41}N_2O_7^+$ (*m/z*): calc. 721.2908; found 721.2918.

*2-N-(quinolin-8-yl)carbamoyl-1-(4-cyanophenyl)-3,4,6-tri-O-benzyl-D-glucal (**2e**).* **2e** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 4-iodobenzonitrile (117 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2e** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 9:1) as yellowish oil (23 mg; 0.033 mmol; 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (s, 1H), 8.73 – 8.71 (m, 1H), 8.30 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.09 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.55 – 7.45 (m, 6H), 7.38 – 7.31 (m, 10H), 7.25 – 7.21 (m, 4H), 4.82 – 4.79 (m, 2H), 4.74 – 4.70 (m, 2H), 4.65 (d, *J* = 12.0 Hz, 1H), 4.64 (d, *J* = 11.4 Hz, 1H), 4.57 (d, *J* = 1.2 Hz, 2H), 4.06 – 4.01 (m, 2H), 3.76 (dd, *J* = 10.7, 4.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 155.0, 147.8, 139.3, 138.4, 138.1, 137.9, 137.6, 136.3, 134.6, 131.9, 129.8, 128.7, 128.6, 128.4, 128.2, 128.0, 128.0, 127.9, 127.8, 127.4, 121.6, 118.5, 116.5, 113.2, 110.7, 77.2, 73.4, 72.7, 72.5, 72.1, 72.0, 67.6; IR (cm^{-1}): 3340, 3064, 3032, 2958, 2928, 2859, 2228, 1725, 1660, 1628, 1605, 1577, 1522, 1485, 1454, 1425, 1385, 1327, 1261, 1164, 1071, 1028; $[\alpha]^{20}_D$ = +4.8 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{44}H_{38}N_3O_5^+$ (*m/z*): calc. 688.2806; found 688.2811.

*2-N-(quinolin-8-yl)carbamoyl-1-(4-nitrophenyl)-3,4,6-tri-O-benzyl-D-glucal (**2f**).* **2f** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 1-iodo-4-nitrobenzene (127.3 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv.,

0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2f** was obtained after purification on silica gel (eluent: Toluene/EtOAc 95:5) as yellowish oil (23 mg; 0.032 mmol; 38 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.60 (d, *J* = 7.3 Hz, 1H), 8.14 (dd, *J* = 4.2, 1.6 Hz, 1H), 7.98 – 7.90 (m, 3H), 7.58 (d, *J* = 8.6 Hz, 2H), 7.41 – 7.33 (m, 3H), 7.28 – 7.24 (m, 3H), 7.23 – 7.18 (m, 6H), 7.17 – 7.14 (m, 3H), 7.13 – 7.09 (m, 3H), 4.71 (d, *J* = 11.4 Hz, 1H), 4.69 – 4.66 (m, 1H), 4.65 – 4.61 (m, 1H), 4.59– 4.52 (m, 3H), 4.50 – 4.42 (m, 2H), 3.97 – 3.90 (m, 2H), 3.66 (dd, *J* = 10.7, 4.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 154.8, 148.4, 147.7, 141.2, 138.4, 138.0, 137.9, 137.6, 136.2, 134.6, 130.1, 128.7, 128.6, 128.4, 128.2, 128.0, 128.0, 127.9, 127.8, 127.8, 127.4, 123.3, 121.7, 121.6, 116.5, 110.9, 73.4, 72.7, 72.5, 72.0, 67.5; IR (cm^{-1}) : 3338, 3064, 3031, 2919, 2860, 1659, 1595, 1519, 1484, 1344, 1326, 1087, 1069; $[\alpha]^{19}_D$ = +42.5 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{43}H_{38}N_3O_7^+$ (*m/z*): calc. 708.2710; found 708.2715.

*2-N-(quinolin-8-yl)carbamoyl-1-(4-trifluoromethylphenyl)-3,4,6-tri-O-benzyl-D-glucal (**2g**).* **2g** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 4-iodotrifluoromethylbenzene (75 µL, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc

and then concentrated under vacuum. **2g** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 9:1) as yellowish oil (31 mg; 0.042 mmol; 50 %). ^{1}H NMR (400 MHz, $CDCl_3$) 9.59 (s, 1H), 8.64 (d, *J* = 7.5 Hz, 1H), 8.14 (d, *J* = 4.0 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.33 (d, *J* = 8.2 Hz, 4H), 7.29 – 7.25 (m, 4H), 7.23 – 7.13 (m, 7H), 7.13 – 7.09 (m, 3H), 4.75 – 4.68 (m, 2H), 4.67 – 4.58 (m, 2H), 4.55 (d, *J* = 11.6 Hz, 2H), 4.48 (s, 2H), 3.98 – 3.91 (m, 2H), 3.68 (dd, *J* = 10.7, 4.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.3, 155.6, 147.6, 138.3, 138.0, 137.8, 136.2, 134.7, 131.6 (q, $J_{C\text{-}F}$ = 32.5 Hz), 129.6, 128.6, 128.6, 128.4, 128.1, 128.0, 127.9, 127.9, 127.7, 127.4, 125.1, 125.1, 123.9 (q, $J_{C\text{-}F}$ = 272.2 Hz), 121.5, 121.4, 116.4, 110.3, 77.0, 73.4, 72.8, 72.5, 72.3, 71.9, 67.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.6; IR (cm^{-1}): 3339, 3031, 2926, 1659, 1522, 1485, 1324, 1166, 1126, 1109, 1067; $[\alpha]^{20}_{D}$ = +119.7 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{44}H_{38}F_3N_2O_5^+$ (*m/z*): calc. 731.2733; found 731.2735.

*2-N-(quinolin-8-yl)carbamoyl-1-(4-chlorophenyl)-3,4,6-tri-O-benzyl-D-glucal (**2h**).* **2h** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 1-chloro-4-iodobenzene (121.9 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2h** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 9:1) as yellowish oil (28 mg; 0.040 mmol; 46 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H), 8.77 – 8.75 (m, 1H), 8.34 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.07 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.50 – 7.48 (m, 2H), 7.44 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.37 – 7.27 (m, 3H), 7.23 – 7.21 (m, 3H), 7.18 (d, *J* = 8.5 Hz, 2H),

4.84 (dd, *J* = 2.6, 1.8 Hz, 1H), 4.80 (d, *J* = 11.3 Hz, 1H), 4.74 – 4.70 (m, 2H), 4.66 – 4.63 (m, 2H), 4.58 (s, 2H), 4.06 – 4.01 (m, 2H), 3.79 (dd, *J* = 10.6, 4.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 156.0, 147.7, 138.5, 138.4, 138.1, 137.8, 136.0, 134.9, 133.2, 130.6, 128.6, 128.5, 128.5, 128.4, 128.0, 127.9, 127.9, 127.7, 127.4, 121.5, 121.3, 116.3, 109.6, 77.0, 73.4, 72.7, 72.6, 72.5, 71.8, 67.8; IR (cm^{-1}): 3328, 3089, 3063, 3031, 2924, 2866, 1681, 1596, 1577, 1526, 1488, 1454, 1425, 1400, 1377, 1327, 1311, 1279, 1260, 1218, 1091, 1028, 1015; $[\alpha]^{20}_D$ = +12.3 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{43}H_{38}ClN_2O_5^+$ (*m/z*): calc. 697.2469; found 697.2460.

*2-N-(quinolin-8-yl)carbamoyl-1-(3-methoxyphenyl)-3,4,6-tri-O-benzyl-D-glucal (**2i**).* **2i** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (9.8 mg, 0.2 equiv., 0.034 mmol), AgOAc (42.7 mg, 1.5 equiv., 0.256 mmol), K_2CO_3 (84.8 mg, 3.6 equiv., 0.614 mmol) and citric acid (27.9 mg, 0.85 equiv., 0.145 mmol). Then 3-iodoanisole (244 µL mg, 6 equiv., 2.045 mmol), the compound **1a** (200 mg, 1 equiv., 0.341 mmol) and toluene (8 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (9.8 mg, 0.2 equiv., 0.034 mmol), AgOAc (42.7 mg, 1.5 equiv., 0.256 mmol), K_2CO_3 (84.8 mg, 3.6 equiv., 0.614 mmol) and citric acid (27.9 mg, 0.85 equiv., 0.145 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2i** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 9:1) as yellowish oil (184 mg; 0.266 mmol; 78 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 8.79 – 8.77 (m, 1H), 8.34 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.42 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.38 – 7.27 (m, 12H), 7.22 – 7.20 (m, 2H), 7.15 (d, *J* = 7.5 Hz, 1H), 7.10 – 7.06 (m, 2H), 6.72 (dd, *J* = 8.0, 2.0 Hz, 1H), 4.88 – 4.88 (m, 1H), 4.79 (d, *J* = 11.3 Hz, 1H), 4.74 – 4.71 (m, 2H), 4.67 – 4.64 (m, 2H), 4.60 (s, 2H), 4.08 – 4.03 (m, 2H), 3.82 (dd, *J* = 10.6, 4.7 Hz, 1H), 3.59 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 159.5, 156.9, 147.6, 138.5, 138.2, 137.9, 135.9, 135.8, 135.1, 129.3, 128.6, 128.3, 128.0, 128.0, 127.8, 127.6, 127.4, 121.7, 121.4, 121.1, 116.7, 116.0, 113.6, 109.3, 76.8, 73.4, 72.8, 72.6, 72.5, 71.8, 67.9, 55.3; IR (cm^{-1}): 3329,

3063, 3031, 2924, 2855, 2360, 1725, 1655, 1597, 1579, 1522, 1485, 1454, 1425, 1385, 1327, 1288, 1263, 1210, 1182, 1158, 1138, 1088, 1071, 1028; $[\alpha]^{20}_{D}$ = +5.5 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{44}H_{41}N_2O_6^+$ (*m/z*): calc. 693.2959; found 693.2990.

*2-N-(quinolin-8-yl)carbamoyl-1-(3,4,5-methoxyphenyl)-3,4,6-tri-O-benzyl-D-glucal (**2j**).* **2j** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 5-iodo-1,2,3-trimethoxybenzene (150.0 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2j** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 90:10) as yellowish oil (43 mg; 0.057 mmol; 67 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.65 (s, 1H), 8.81 – 8.79 (m, 1H), 8.40 (dd, *J* = 4.1, 1.6 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.52 – 7.48 (m, 2H), 7.42 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.37 – 7.23 (m, 14H), 6.79 (s, 2H), 4.89 – 4.88 (m, 1H), 4.81 – 4.78 (m, 2H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.66 (d, *J* = 11.3 Hz, 1H), 4.65 (d, *J* = 12.4 Hz, 1H), 4.63 (s, 1H), 4.13 (dd, *J* = 10.7, 7.6 Hz, 1H), 4.01 – 4.00 (m, 1H), 3.84 – 3.78 (m, 2H), 3.59 (s, 6H), 3.54 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.2, 156.4, 153.1, 147.7, 139.5, 138.4, 138.3, 138.2, 137.9, 136.0, 135.1, 129.8, 128.6, 128.5, 128.0, 127.8, 127.8, 127.7, 127.6, 127.3, 121.5, 121.2, 109.3, 106.4, 76.8, 73.3, 72.9, 72.5, 72.2, 71.7, 67.8, 60.7, 56.0 (2C); IR (cm^{-1}): 3334, 3030, 2937, 2248, 1652, 1582, 1520, 1504, 1484, 1454, 1424, 1414, 1385, 1340, 1326, 1237, 1209, 1174, 1125, 1086, 1070, 1027, 1002; $[\alpha]^{20}_{D}$ = +12.0 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{46}H_{45}N_2O_8^+$ (*m/z*): calc. 753.3170; found 753.3184.

*2-N-(quinolin-8-yl)carbamoyl-1-(5-Boc-indole)-3,4,6-tri-O-benzyl-D-glucal (**2k**).* **2k** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 1-Boc-5-iodoindole (175.4 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2k** was obtained after purification on silica gel (eluent: Toluene/EtOAc 98:2) as yellowish oil (27 mg; 0.034 mmol; 40 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.64 (s, 1H), 8.75 – 8.74 (m, 1H), 7.96 – 7.93 (m, 2H), 7.85 – 7.78 (m, 2H), 7.49 – 7.44 (m, 3H), 7.38 – 7.27 (m, 12H), 7.25 – 7.17 (m, 4H), 7.13 (dd, *J* = 8.2, 4.3 Hz, 1H), 6.45 (d, *J* = 3.6 Hz, 1H), 4.91 (dd, *J* = 2.4, 1.7 Hz, 1H), 4.81 (d, *J* = 11.4 Hz, 1H), 4.77 – 4.72 (m, 2H), 4.67 (d, *J* = 11.3 Hz, 1H), 4.66 (d, *J* = 12.1 Hz, 1H), 4.61 (s, 2H), 4.10 – 4.04 (m, 2H), 3.85 (dd, *J* = 10.7, 4.7 Hz, 1H), 1.6 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.4, 158.1, 149.6, 147.2, 141.0, 138.6, 138.5, 138.3, 138.0, 135.7, 135.2, 130.6, 129.2, 128.7, 128.6, 128.6, 128.4, 128.0, 127.9, 127.9, 127.8, 127.7, 127.6, 127.3, 127.1, 126.4, 125.6, 125.4, 122.3, 121.0, 120.9, 116.1, 116.1, 114.9, 108.9, 107.7, 83.9, 73.4, 72.7 (2C), 72.6, 71.7, 68.0, 65.5, 28.3 (3C); IR (cm^{-1}): 3034, 2924, 2856, 1734, 1684, 1528, 1487, 1455, 1425, 1370, 1334, 1232, 1159, 1134, 1083, 1026; $[\alpha]^{20}_D$ = +35.7 (0.66, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{50}H_{48}N_3O_7^+$ (*m/z*): calc. 802.3487; found 802.3506.

*2-N-(quinolin-8-yl)carbamoyl-1-(3-ethyl-cis-acrylate)-3,4,6-tri-O-benzyl-D-glucal (**2l**).* **2l** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036

mmol). Then ethyl cis-3-iodoacrylate (66 µL, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2l** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 9:1 then 85:15) as a mixture of two isomers as yellowish oil (31 mg; 0.045 mmol; 54 %, ratio E/Z: 75/25). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.92 – 8.87 (m, 1H), 8.22 – 8.17 (m, 1H), 7.94 – 7.92 (m, 0.25H), 7.87 – 7.85 (m, 0.75H) 7.71 – 7.68 (m, 1H), 7.65 – 7.60 (m, 1.50H), 7.45 – 7.39 (m, 2.50H), 7.38 – 7.36 (m, 1H), 7.35 – 7.27(m, 12.75H), 7.25 (s, 0.25H), 5.80 (d, *J* = 14.2, 0.75H), 5.13 (d, *J* = 11.0, 0.25H), 4.94 – 4.92 (m, 0.25H), 4.88 (d, *J* = 11.7, 0.75H), 4.84 – 4.82 (m, 0.25H), 4.79 (d, *J* = 11.8, 0.75H), 4.71 – 4.67 (m, 1H), 4.66 – 4.53 (m, 5H), 4.50 (dd, *J* = 3.5, 1.2, 0.75H), 4.47 (dd, *J* = 2.4, 1.5, 0.25H), 4.09 – 4.08 (m, 0.25H), 4.02 – 4.00 (m, 0.75H), 3.95 – 3.87 (m, 1.25H), 3.79 – 3.75 (m, 0.75 H), 3.42 – 3.31 (m, 1H), 3.29 – 3.20 (m, 1H), 1.18 (t, *J* = 6.5, 0.75H), 0.64 (t, *J* = 6.9, 2.25H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.4, 170.0, 164.1, 162.0, 150.6, 145.2, 140.8, 140.8, 138.3, 138.2, 137.9, 137.9, 137.5, 137.3, 136.2, 134.2, 134.2, 131.6, 129.7, 129.6, 129.0, 128.7, 128.7, 128.6, 128.5, 128.4, 128.3, 128.3, 128.2, 128.1, 128.1, 128.0, 127.9, 127.8, 127.8, 127.7, 127.7, 126.2, 121.5, 103.8, 103.1, 97.9, 97.7, 81.0, 80.9, 73.5 (2C), 73.4, 73.1, 72.5, 72.4, 72.1, 71.6, 68.2, 68.1, 67.6, 66.2, 60.2 (2C), 13.6 (2C); IR (cm^{-1}): 3063, 3031, 2956, 2927, 2870, 1728, 1714, 1669, 1640, 1596, 1522, 1498, 1475, 1454, 1427, 1407, 1369, 1326, 1301, 1243, 1179, 1152, 1089, 1070, 1028; $[\alpha]^{20}_D$ = +7.7 (1.00, $CHCl_3$); HRMS (TOF ES-) for (M-H)- $C_{42}H_{39}N_2O_7^-$ (*m/z*): calc. 683.2757; found 683.2761.

*2-N-(quinolin-8-yl)carbamoyl-1-(4,4-N-Boc-O-tBu-L-phenylalanine)-3,4,6-tri-O-benzyl-D-glucal (**2m**).* **2m** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7

mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then *N*-Boc-4-iodophenylalanine-*O*-tBu (228.7 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2m** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 9:1 then 85:15) as yellowish oil (47 mg; 0.052 mmol; 61 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.78 (s, 1H), 8.77 – 8.75 (m, 1H), 8.31 (dd, *J* = 4.1, 1.4 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.51 – 7.47 (m, 3H), 7.43 – 7.41 (m, 2H), 7.36 – 7.29 (m, 12H), 7.25 – 7.24 (m, 1H), 7.20 – 7.19 (m, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 4.84 – 4.74 (m, 3H), 4.71 – 4.63 (m, 3H), 4.59 (s, 2H), 4.36 – 4.31 (m, 1H), 4.08 – 4.01 (m, 2H), 3.81 (dd, *J* = 10.6, 4.6 Hz, 1H), 2.96 (dd, *J* = 13.7, 6.1 Hz, 1H), 2.85 (dd, *J* = 13.4, 5.3 Hz, 1H), 1.41 (s, 9H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 167.0, 156.9, 155.2, 147.7, 138.5, 138.5, 138.4, 138.3, 137.9, 136.0, 135.1, 129.4, 129.2, 128.6, 128.6, 128.3, 128.0, 127.9, 127.8, 127.6, 127.4, 121.4, 121.1, 116.2, 109.1, 82.3, 79.8, 73.4, 72.9, 72.6 (2C), 71.8, 67.9, 60.5, 54.6, 37.7, 28.5 (3C), 28.0 (3C); IR (cm^{-1}): 3431, 3336, 3064, 3033, 2977, 2929, 2867, 2361, 2340, 1714, 1657, 1609, 1577, 1522, 1497, 1485, 1455, 1425, 1386, 1367, 1327, 1250, 1153, 1091, 1069, 1028; $[\alpha]^{20}_D$ = +21.8 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{55}H_{60}N_3O_9^+$ (*m/z*): calc. 906.4330; found 906.4343.

*1,4-di(2-N-(quinolin-8-yl)carbamoyl-3,4,6-tri-O-benzyl-D-glucal)-phenyl (**2n**).* **2n** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 1,4-diiodobenzene (14 mg, 0.5 equiv., 0.43 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then

the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2n** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 9:1 then 8:2) as yellowish oil (40 mg; 0.032 mmol; 76 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 2H), 8.63 – 8.61 (m, 2H), 8.28 (dd, *J* = 4.2, 1.5 Hz, 2H), 7.77 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.44 – 7.40 (m, 5H), 7.35 – 7.27 (m, 25H), 7.24 – 7.22 (m, 4H), 7.19 – 7.17 (m, 4H), 7.06 (dd, *J* = 8.3, 4.2 Hz, 2H), 4.78 – 4.73 (m, 4H), 4.67 – 4.56 (m, 12H), 4.02 – 3.96 (m, 4H), 3.78 (dd, *J* = 10.6, 4.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.1, 155.8, 147.2, 138.5, 138.2, 138.0, 136.0, 129.0, 128.6, 128.3, 128.0, 128.0, 127.9, 127.6, 121.6, 121.3, 114.2, 109.6, 77.4, 73.6, 73.0, 72.8, 72.3, 71.8, 68.0; IR (cm^{-1}): 2925, 2855, 1734, 1684, 1527, 1488, 1455, 1370, 1328, 1084, 1027; $[\alpha]^{20}_D$ = -5.69 (0.28, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{80}H_{71}N_4O_{10}^+$ (*m/z*): calc. 1247.5170; found 1247.5183.

*2-N-(quinolin-8-yl)carbamoyl1-(4-chloro-3-(4-ethoxybenzyl)-benzene)-3,4,6-tri-O-benzyl-D-glucal (**2o**).* **2o** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 1-chloro-2-(4-ethoxybenzyl)-4-iodobenzene (190.5 mg, 6 equiv., 0.511 mmol), the compound **1a** (50 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **2o** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 90:10 then 80:20) as yellowish oil (60 mg; 0.036 mmol; 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.67 (s, 1H), 8.76 – 8.74 (m, 1H), 8.21 (dd, *J* = 4.1,

1.1 Hz, 1H), 8.05 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.45 – 7.43 (m, 1H), 7.39 – 7.18 (m, 19H), 6.73 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 8.5 Hz, 2H), 4.81 – 4.81 (m, 1H), 4.75 (d, *J* = 11.4 Hz, 1H), 4.71 – 4.66 (m, 2H), 4.62 (d, *J* = 12.1 Hz, 1H), 4.61 (d, *J* = 11.3 Hz, 1H), 4.55 (s, 2H), 4.02 – 3.97 (m, 2H), 3.85 (q, *J* = 7.0 Hz, 2H), 3.79 – 3.65 (m, 3H), 1.34 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5, 157.3, 156.0, 147.7, 139.0, 138.4, 138.1, 137.8, 136.1, 135.9, 134.9, 133.3, 131.8, 130.6, 129.7, 129.5, 128.6, 128.6, 128.5, 128.4, 128.0, 128.0, 127.9, 127.8, 127.7, 127.4, 121.4, 121.2, 116.3, 114.3, 109.5, 77.0, 73.4, 72.8, 72.6, 72.5, 71.8, 67.8, 63.3, 38.3, 15.0; IR (cm^{-1}): 3338, 3029, 2923, 2856, 1709, 1670, 1611, 1596, 1524, 1510, 1477, 1453, 1424, 1362, 1325, 1309, 1242, 1176, 1088, 1041, 1026; $[\alpha]^{20}_D$ = +20.3 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{52}H_{48}ClN_2O_6^+$ (*m/z*): calc. 831.3201; found 831.3210.

*2-N-(quinolin-8-yl)carbamoyl-1-(3,4,5-methoxyphenyl)-3,4,6-tri-O-benzyl-D-galactal (**3a**).* 2-*N*-(quinolin-8-yl)carbamoyl-3,4,6-tri-*O*-benzyl-D-galactal (**S1**) was obtained following the general procedure of aminocarbonylation: $Pd(OAc)_2$ (12.8 mg; 0.1 equiv.; 0.057 mmol), PPh_3 (29.9 mg; 0.2 equiv.; 0.114 mmol), K_2CO_3 (157.9 mg; 2 equiv.; 1.143 mmol), $Mo(CO)_6$ (633.8 mg; 4.2 equiv.; 2.4 mmol), 8-aminoquinoline (164.8 mg; 2 equiv.; 1.143 mmol), 2-iodo-3,4,6-tri-*O*-benzyl-D-galactal (310 mg; 1 equiv.; 0.572 mmol), dioxane (6.2 mL). The resulting mixture was stirred at 80 °C overnight. The mixture was concentrated under vacuum and **S1** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 85:15) as yellowish oil (280 mg; 0.477 mmol; 83 %). The product was washed with HCl (1M) to remove excess of aminoquinoline and was directly engaged in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.81 – 8.79 (m, 1H), 8.32 – 8.31 (m, 1H), 8.10 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.60 (s, 1H), 7.54 – 7.50 (m, 1H), 7.47 – 7.45 (m, 1H), 7.39 – 7.27 (m, 15H), 7.25 (s, 1H), 5.20 (d, *J* = 11.1 Hz, 1H), 5.12 (d, *J* = 11.2 Hz, 1H), 4.78 – 4.74 (m, 2H), 4.66 (d, *J* = 11.8 Hz, 1H), 4.59 – 4.56 (m, 2H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.09 (t, *J* = 3.8 Hz, 1H), 4.02 (dd, *J* = 11.1, 8.5 Hz, 1H), 3.87 (dd, *J* = 11.2, 2.9 Hz,1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 153.1, 148.0, 138.8, 138.6, 138.0, 137.7, 136.3, 135.2, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 121.6, 121.3, 116.9, 109.9, 76.6, 73.6, 73.6, 73.4, 72.8, 69.6, 67.8; IR

(cm^{-1}): 3368, 3277, 2926, 1670, 1607, 1527, 1488, 1454, 1425, 1386, 1325, 1208, 1103; $[\alpha]^{20}_D$ = -87.4 (0.61, $CHCl_3$). **3a** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: Pd(cod)Cl_2 (2.2 mg, 0.2 equiv., 0.008 mmol), AgOAc (9.6 mg, 1.5 equiv., 0.058 mmol), K_2CO_3 (19.0 mg, 3.6 equiv., 0.138 mmol) and citric acid (6.3 mg, 0.85 equiv., 0.033 mmol). Then 5-iodo-1,2,3-trimethoxybenzene (134.7 mg, 6 equiv., 0.458 mmol), the compound **S1** (44.8 mg, 1 equiv., 0.076 mmol) and toluene (1.8 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: Pd(cod)Cl_2 (2.2 mg, 0.2 equiv., 0.008 mmol), AgOAc (9.6 mg, 1.5 equiv., 0.058 mmol), K_2CO_3 (19.0 mg, 3.6 equiv., 0.138 mmol) and citric acid (6.3 mg, 0.85 equiv., 0.033 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **3a** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 70:30) as yellowish oil (41 mg; 0.055 mmol; 72 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.76 – 8.74 (m, 1H), 8.39 (dd, *J* = 4.0, 1.3 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.51 – 7.47 (m, 2H), 7.43 – 7.30 (m, 14H), 7.22 – 7.21 (m, 2H), 6.73 (s, 2H), 5.04 – 5.03 (m, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.84 – 4.82 (m, 2H), 4.73 (d, *J* = 12.1 Hz, 1H), 4.68 (s, 1H), 4.39 (dd, *J* = 11.5, 9.3 Hz, 1H), 4.15 – 4.12 (m, 1H), 4.03 (dd, *J* = 11.7, 2.0 Hz, 1H), 3.91 – 3.82 (m, 2H), 3.55 (s, 6H), 3.51 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 155.6, 153.1, 147.7, 139.5, 139.1, 138.5, 138.3, 137.9, 136.0, 135.0, 129.6, 128.7, 128.5, 128.2, 128.1, 127.8, 127.8, 127.7, 127.7, 127.3, 127.2, 121.5, 121.4, 115.8, 110.3, 106.2, 76.2, 74.8, 74.5, 73.3, 72.1, 70.2, 67.7, 60.7, 56.0 (2C); IR (cm^{-1}): 3332, 3088, 3064, 3030, 3003, 2934, 1732, 1653, 1583, 1521, 1503, 1484, 1454, 1424, 1414, 1385, 1361, 1327, 1279, 1238, 1209, 1176, 1126, 1103, 1073, 1028, 1005; $[\alpha]^{20}_D$ = -4.2 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{46}H_{45}N_2O_8^+$ (*m/z*): calc. 753.3170; found 753.3167.

*2-N-(quinolin-8-yl)carbamoyl-1-(4-methylbenzoate)-3,4,6-tri-O-benzyl-D-galactal (**3b**).* 2-*N*-(quinolin-8-yl)carbamoyl-3,4,6-tri-*O*-benzyl-D-galactal (**S1**) was obtained following the general procedure of aminocarbonylation: $Pd(OAc)_2$ (12.8 mg; 0.1 equiv.; 0.057 mmol), PPh_3 (29.9 mg; 0.2

equiv.; 0.114 mmol), K_2CO_3 (157.9 mg; 2 equiv.; 1.143 mmol), $Mo(CO)_6$ (633.8 mg; 4.2 equiv.; 2.4 mmol), 8-aminoquinoline (164.8 mg; 2 equiv.; 1.143 mmol), 2-iodo-3,4,6-tri-*O*-benzyl-D-galactal (310 mg; 1 equiv.; 0.572 mmol), dioxane (6.2 mL). The resulting mixture was stirred at 80 °C overnight. The mixture was concentrated under vacuum and **S1** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 85:15) as yellowish oil (280 mg; 0.477 mmol; 83 %). The product was washed with HCl (1M) to remove excess of aminoquinoline and was directly engaged in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.61 (s, 1H), 8.81 – 8.79 (m, 1H), 8.32 – 8.31 (m, 1H), 8.10 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.60 (s, 1H), 7.54 – 7.50 (m, 1H), 7.47 – 7.45 (m, 1H), 7.39 – 7.27 (m, 15H), 7.25 (s, 1H), 5.20 (d, *J* = 11.1 Hz, 1H), 5.12 (d, *J* = 11.2 Hz, 1H), 4.78 – 4.74 (m, 2H), 4.66 (d, *J* = 11.8 Hz, 1H), 4.59 – 4.56 (m, 2H), 4.45 (d, *J* = 11.9 Hz, 1H), 4.09 (t, *J* = 3.8 Hz, 1H), 4.02 (dd, *J* = 11.1, 8.5 Hz, 1H), 3.87 (dd, *J* = 11.2, 2.9 Hz,1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 153.1, 148.0, 138.8, 138.6, 138.0, 137.7, 136.3, 135.2, 128.7, 128.6, 128.3, 128.2, 128.1, 128.0, 127.9, 127.6, 127.5, 121.6, 121.3, 116.9, 109.9, 76.6, 73.6, 73.6, 73.4, 72.8, 69.6, 67.8; IR (cm^{-1}): 3368, 3277, 2926, 1670, 1607, 1527, 1488, 1454, 1425, 1386, 1325, 1208, 1103; $[\alpha]^{20}_D$ = -87.4 (0.61, $CHCl_3$). **3b** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (1.8 mg, 0.2 equiv., 0.007 mmol), AgOAc (7.9 mg, 1.5 equiv., 0.047 mmol), K_2CO_3 (15.6 mg, 3.6 equiv., 0.113 mmol) and citric acid (5.1 mg, 0.85 equiv., 0.027 mmol). Then methyl 4-iodobenzoate (98.6 mg, 6 equiv., 0.376 mmol), the compound **S1** (36.8 mg, 1 equiv., 0.063 mmol) and toluene (1.5 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (1.8 mg, 0.2 equiv., 0.007 mmol), AgOAc (7.9 mg, 1.5 equiv., 0.0.47 mmol), K_2CO_3 (15.6 mg, 3.6 equiv., 0.113 mmol) and citric acid (5.1 mg, 0.85 equiv., 0.027 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **3b** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 80:20) as a colorless oil (24 mg; 0.033 mmol; 53 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.60 (s, 1H), 8.70 (d, *J* = 7.3 Hz, 1H), 8.25 (dd, *J* = 4.1, 1.4 Hz,

1H), 8.02 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.51 – 7.22 (m, 15H), 7.21 – 7.14 (m, 3H), 4.98 (dd, *J* = 4.0, 1.1 Hz, 1H), 4.93 (d, *J* = 11.3 Hz, 1H), 4.82-4.77 (m, 2H), 4.74-4.70 (m, 2H), 4.67 – 4.59 (m, 2H), 4.28 (dd, *J* = 11.5, 8.8 Hz, 1H), 4.16 – 4.12 (m, 1H), 4.00 (dd, *J* = 11.6, 2.2 Hz, 1H), 3.81 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6, 166.3, 154.8, 147.7, 138.9, 138.9, 138.4, 138.3, 137.9, 136.0, 134.7, 131.1, 129.4, 129.0, 128.7, 128.6, 128.2, 128.1, 127.8, 127.6, 127.3, 121.5, 121.3, 116.3, 111.3, 76.4, 74.6, 74.1, 73.4, 72.3, 70.6, 67.6, 52.2; IR (cm^{-1}): 3338, 3063, 3030, 2867, 1721, 1655, 1520, 1483, 1326, 1277, 1102, 1057; $[\alpha]^{20}_D$ = +139.5 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{45}H_{41}N_2O_7^+$ (*m/z*): calc. 721.2914; found 721.2923.

*2-N-(quinolin-8-yl)carbamoyl-1-4-(3,4,5-methoxyphenyl)-3-O-benzyl-4,6-O-isopropylidene-D-glucal (**4a**).* 3-Hydroxy-4,6-*O*-isopropylidene-D-glucal and 3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal were prepared according to the literature.[1,5,6] 2-Iodo-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal was synthesized following the described procedure:[6] 3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal (546 mg, 1.98 mmol) was dissolved in dry acetonitrile (14 mL) under argon and the resulting mixture was heated to 80 °C. At this temperature, *N*-iodosuccinimide (533 mg, 2.37 mmol, 1.2 equiv.) and silver nitrate (67 mg, 0.40 mmol, 20 mol%) were added. The resulting mixture was stirred at 80 °C for 3.5 h. The mixture was filtrated on celite with EtOAc and concentrated. The obtained crude was purified on silica gel (eluent: Cyclo/EtOAc 95:5) and furnished the 2-iodo-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal as a colorless oil (300 mg, 0.75 mmol, 38 %) which was directly engaged in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 1H), 7.36 – 7.26 (m, 4H), 6.66 (d, *J* = 1.2 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.12 – 4.05 (m, 2H), 3.96 – 3.93 (m, 1H), 3.86 – 3.78 (m, 2H), 1.47 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 138.3, 128.4, 128.3, 127.8, 99.7, 77.2, 74.3, 73.4, 72.6, 70.3, 61.5, 29.1, 19.1; IR (cm^{-1}): 3411, 3065, 3031, 2993, 2879, 1727, 1665, 1618, 1530, 1497, 1454, 1374, 1268,

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1219, 1201, 1168, 1135, 1112, 1085, 1069, 1028, 1016; $[\alpha]^{20}_D$ = +5.7 (1.00, $CHCl_3$). 2-*N*-(quinolin-8-yl)carbamoyl-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal (**S2**) was obtained following the general procedure of aminocarbonylation: $Pd(OAc)_2$ (15.6 mg; 0.1 equiv.; 0.07 mmol), PPh_3 (36.5 mg; 0.2 equiv.; 0.139 mmol), K_2CO_3 (192.4 mg; 2 equiv.; 1.392 mmol), $Mo(CO)_6$ (771.9 mg; 4.2 equiv.; 2.924 mmol), 8-aminoquinoline (200.7 mg; 2 equiv.; 1.392 mmol), 2-iodo-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal (280 mg; 1 equiv.; 0.696 mmol), dioxane (8 mL). The resulting mixture was stirred at 80 °C overnight. The mixture was concentrated under vacuum and **S2** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 85:15) as yellowish oil (151 mg; 0.338 mmol; 49 %). The product was washed with HCl (1M) to remove excess of aminoquinoline and was directly engaged in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 8.84 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.42 (dd, *J* = 4.1, 1.5 Hz,1H), 8.11 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.72 (s, 1H), 7.56 – 7.47 (m, 3H), 7.44 – 7.42 (m, 2H), 7.34 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.24 – 7.22 (m, 2H), 5.31 (d, *J* = 11.9 Hz, 1H), 5.10 (d, *J* = 11.9 Hz, 1H), 4.79 – 4.77 (m, 1H), 4.26 – 4.22 (m, 1H), 4.04 (dd, *J* = 8.5, 3.4 Hz,1H), 3.90 – 3.87 (m, 2H), 1.45 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 155.6, 148.1, 139.0, 138.9, 136.2, 135.4, 128.3, 128.1, 127.6, 121.5, 117.4, 111.0, 99.9, 74.0, 72.9, 72.4, 70.6, 61.5, 29.1, 18.8; IR (cm^{-1}): 3277, 3063, 2993, 2879, 1668, 1602, 1595, 1528, 1488, 1463, 1455, 1425, 1384, 1324, 1272, 1222, 1187, 1166, 1139, 1121, 1103, 1082, 1056, 1040, 1026, 1018; $[\alpha]^{20}_D$ = +18.4 (0.63, $CHCl_3$). **4a** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (1.6 mg, 0.2 equiv., 0.006 mmol), AgOAc (7.0 mg, 1.5 equiv., 0.042 mmol), K_2CO_3 (14.0 mg, 3.6 equiv., 0.101 mmol) and citric acid (4.6 mg, 0.85 equiv., 0.024 mmol). Then 5-iodo-1,2,3-trimethoxybenzene (98.8 mg, 6 equiv., 0.336 mmol), the compound **S2** (25 mg, 1 equiv., 0.056 mmol) and toluene (1.3 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (1.6 mg, 0.2 equiv., 0.006 mmol), AgOAc (7.0 mg, 1.5 equiv., 0.042 mmol), K_2CO_3 (14.0 mg, 3.6 equiv., 0.101 mmol) and citric acid (4.6 mg, 0.85 equiv., 0.024 mmol). The resulting mixture was stirred at 130 °C overnight.

The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **4a** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 90:10 then 85:15) as yellowish oil (25 mg; 0.041 mmol; 73 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.77 – 8.75 (m, 1H), 8.42 – 8.41 (m, 1H), 8.09 – 8.07 (m, 1H), 7.51 – 7.45 (m, 2H), 7.36 – 7.32 (m, 3H), 7.19 – 7.18 (m, 3H), 6.76 (s, 2H), 4.99 – 4.93 (m, 2H), 4.78 (d, *J* = 7.0 Hz, 1H), 4.34 (dd, *J* = 9.6, 7.3 Hz, 1H), 4.12 – 3.97 (m, 3H), 3.66 (s, 9H), 1.54 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 157.3, 153.0, 148.0, 139.3, 138.7, 138.6, 136.1, 135.1, 129.4, 128.2, 128.0, 127.9, 127.5, 127.3, 121.6, 121.5, 116.6, 111.4, 105.6, 99.8, 76.2, 74.2, 73.5, 70.1, 61.8, 60.8, 56.1 (2C), 29.2, 19.2; IR (cm^{-1}): 3338, 2993, 2936, 1713, 1665, 1583, 1522, 1484, 1454, 1424, 1415, 1385, 1349, 1325, 1293, 1268, 1240, 1222, 1200, 1171, 1151, 1126, 1103, 1083, 1064, 1051, 1028, 1004; $[\alpha]^{20}_{D}$ = -5.9 (0.96, $CHCl_3$); HRMS (TOF ES+) for (M-H2+K)+ (partial deprotection of the isopropylidene group) $C_{35}H_{38}KN_2O_8^+$ (*m/z*): calc. 653.2265; found 653.2280.

*2-N-(quinolin-8-yl)carbamoyl-1-4-(4-trifluoromethylphenyl)-3-O-benzyl-4,6-O-isopropylidene-D-glucal (**4b**).* 3-Hydroxy-4,6-*O*-isopropylidene-D-glucal and 3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal were prepared according to the literature.[1,5,6] 2-Iodo-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal was synthesized following the described procedure:[6] 3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal (546 mg, 1.98 mmol) was dissolved in dry acetonitrile (14 mL) under argon and the resulting mixture was heated to 80 °C. At this temperature, *N*-iodosuccinimide (533 mg, 2.37 mmol, 1.2 equiv.) and silver nitrate (67 mg, 0.40 mmol, 20 mol%) were added. The resulting mixture was stirred at 80 °C for 3.5 h. The mixture was filtrated on celite with EtOAc and concentrated. The obtained crude was purified on silica gel (eluent: Cyclo/EtOAc 95:5) and furnished the 2-iodo-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal as a colorless oil (300 mg, 0.75 mmol, 38 %) which was directly engaged in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.1 Hz, 1H), 7.36 – 7.26 (m, 4H), 6.66 (d, *J* = 1.2 Hz, 1H), 4.79 (d, *J* = 11.4 Hz, 1H), 4.74 (d, *J* = 11.5 Hz, 1H), 4.12 – 4.05 (m, 2H), 3.96 – 3.93 (m, 1H), 3.86 – 3.78 (m, 2H), 1.47 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.9, 138.3, 128.4, 128.3, 127.8, 99.7, 77.2, 74.3, 73.4, 72.6, 70.3, 61.5, 29.1,

19.1; IR (cm^{-1}): 3411, 3065, 3031, 2993, 2879, 1727, 1665, 1618, 1530, 1497, 1454, 1374, 1268, 1219, 1201, 1168, 1135, 1112, 1085, 1069, 1028, 1016; $[\alpha]^{20}_D$ = +5.7 (1.00, $CHCl_3$). 2-*N*-(quinolin-8-yl)carbamoyl-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal (**S2**) was obtained following the general procedure of aminocarbonylation: $Pd(OAc)_2$ (15.6 mg; 0.1 equiv.; 0.07 mmol), PPh_3 (36.5 mg; 0.2 equiv.; 0.139 mmol), K_2CO_3 (192.4 mg; 2 equiv.; 1.392 mmol), $Mo(CO)_6$ (771.9 mg; 4.2 equiv.; 2.924 mmol), 8-aminoquinoline (200.7 mg; 2 equiv.; 1.392 mmol), 2-iodo-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal (280 mg; 1 equiv.; 0.696 mmol), dioxane (8 mL). The resulting mixture was stirred at 80 °C overnight. The mixture was concentrated under vacuum and **S2** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 85:15) as yellowish oil (151 mg; 0.338 mmol; 49 %). The product was washed with HCl (1M) to remove excess of aminoquinoline and was directly engaged in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 1H), 8.84 (dd, *J* = 7.5, 1.3 Hz, 1H), 8.42 (dd, *J* = 4.1, 1.5 Hz,1H), 8.11 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.72 (s, 1H), 7.56 – 7.47 (m, 3H), 7.44 – 7.42 (m, 2H), 7.34 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.24 – 7.22 (m, 2H), 5.31 (d, *J* = 11.9 Hz, 1H), 5.10 (d, *J* = 11.9 Hz, 1H), 4.79 – 4.77 (m, 1H), 4.26 – 4.22 (m, 1H), 4.04 (dd, *J* = 8.5, 3.4 Hz,1H), 3.90 – 3.87 (m, 2H), 1.45 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.7, 155.6, 148.1, 139.0, 138.9, 136.2, 135.4, 128.3, 128.1, 127.6, 121.5, 117.4, 111.0, 99.9, 74.0, 72.9, 72.4, 70.6, 61.5, 29.1, 18.8; IR (cm^{-1}): 3277, 3063, 2993, 2879, 1668, 1602, 1595, 1528, 1488, 1463, 1455, 1425, 1384, 1324, 1272, 1222, 1187, 1166, 1139, 1121, 1103, 1082, 1056, 1040, 1026, 1018; $[\alpha]^{20}_D$ = +18.4 (0.63, $CHCl_3$). **4b** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: $Pd(cod)Cl_2$ (1.6 mg, 0.2 equiv., 0.006 mmol), AgOAc (7.0 mg, 1.5 equiv., 0.042 mmol), K_2CO_3 (14.0 mg, 3.6 equiv., 0.101 mmol) and citric acid (4.6 mg, 0.85 equiv., 0.024 mmol). Then 4-iodotrifluoromethylbenzene (49 µL, 6 equiv., 0.336 mmol), the compound **S2** (25 mg, 1 equiv., 0.056 mmol) and toluene (1.3 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: $Pd(cod)Cl_2$ (1.6 mg, 0.2 equiv., 0.006 mmol), AgOAc (7.0 mg, 1.5 equiv., 0.042 mmol), K_2CO_3 (14.0 mg, 3.6 equiv., 0.101 mmol) and

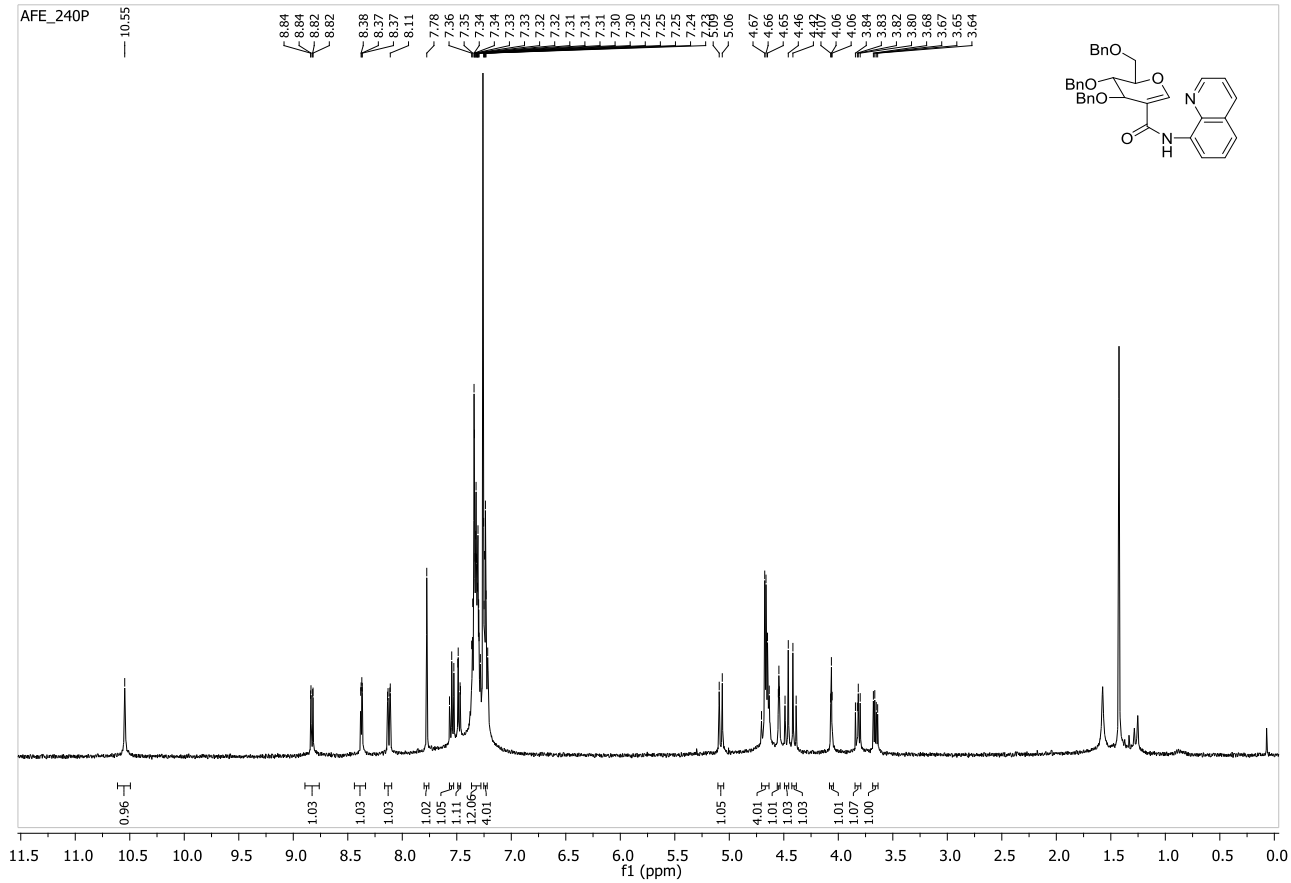
citric acid (4.6 mg, 0.85 equiv., 0.024 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **4b** was obtained after purification on silica gel (eluent: Toluene/EtOAc 98:2) as yellowish oil (20 mg; 0.034 mmol; 60 %). ^{1}H NMR (400 MHz, $CDCl_3$) 10.69 (s, 1H), 8.69 (dd, *J* = 5.7, 3.3 Hz, 1H), 8.34 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.10 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.51 – 7.48 (m, 3H), 7.40 – 7.31 (m, 5H), 7.21 – 7.19 (m, 2H), 5.05 – 4.97 (m, 2H), 4.78 (d, *J* = 7.0 Hz, 1H), 4.34 (dd, *J* = 9.9, 7.0 Hz, 1H), 4.12 – 3.95 (m, 3H), 1.52 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.5, 157.2, 147.5, 138.6, 138.6, 137.8, 134.6, 131.5 (q, $J_{C\text{-}F}$ = 34.3 Hz), 128.9, 128.1, 128.0, 127.8, 127.4, 127.3, 125.1, 123.8 (q, $J_{C\text{-}F}$ = 272.0 Hz), 121.8, 121.3, 112.1, 99.8, 76.0, 73.7, 73.2, 70.2, 61.6, 29.0, 19.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.7; IR (cm^{-1}): 3336, 2994, 2927, 1668, 1617, 1597, 1576, 1524, 1486, 1456, 1425, 1409, 1385, 1324, 1269, 1244, 1219, 1201, 1168, 1125, 1112, 1082, 1067, 1092; $[\alpha]^{20}_{D}$ = +20.2 (0.44, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{33}H_{30}F_3N_2O_5^+$ (*m/z*): calc. 591.2107; found 591.2108.

*2-N-(quinolin-8-yl)carbamoyl-1-(4,4-N-Boc-O-tBu-L-phenylalanine)-3,6-di-O-benzyl-4-O-(2,3,4,6-tetra-O-benzyl-β-D-galactopyranosyl)-D-glucal (**5**).* 2-*N*-(quinolin-8-yl)carbamoyl-3,6-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-*β*-D-galactopyranosyl)-D-glucal (**S3**) was obtained following the general procedure of aminocarbonylation: $Pd(OAc)_2$ (6.9 mg; 0.1 equiv.; 0.031 mmol), PPh_3 (16.4 mg; 0.2 equiv.; 0.062 mmol), K_2CO_3 (87.4 mg; 2 equiv.; 0.615 mmol), $Mo(CO)_6$ (341.2 mg; 4.2 equiv.; 1.292 mmol), 8-aminoquinoline (88.7 mg; 2 equiv.; 0.615 mmol), 2-iodo-3,6-di-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-β-D-galactopyranosyl)-D-glucal (300 mg; 1 equiv.; 0.308 mmol), dioxane (3.5 mL). The resulting mixture was stirred at 80 °C overnight. The mixture was concentrated under vacuum and **S3** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 80:20) as yellowish oil (198 mg; 0.194 mmol; 63 %). The product was washed with HCl (1M) to remove excess of aminoquinoline and was directly engaged in the next step. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s, 1H), 8.86 – 8.84 (m, 1H), 8.30 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.11 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.82 (s, 1H), 7.57 – 7.53 (m, 2H), 7.48 – 7.46 (m, 1H), 7.38 – 7.19 (m, 30H), 5.23 (d, *J* = 11.3 Hz,

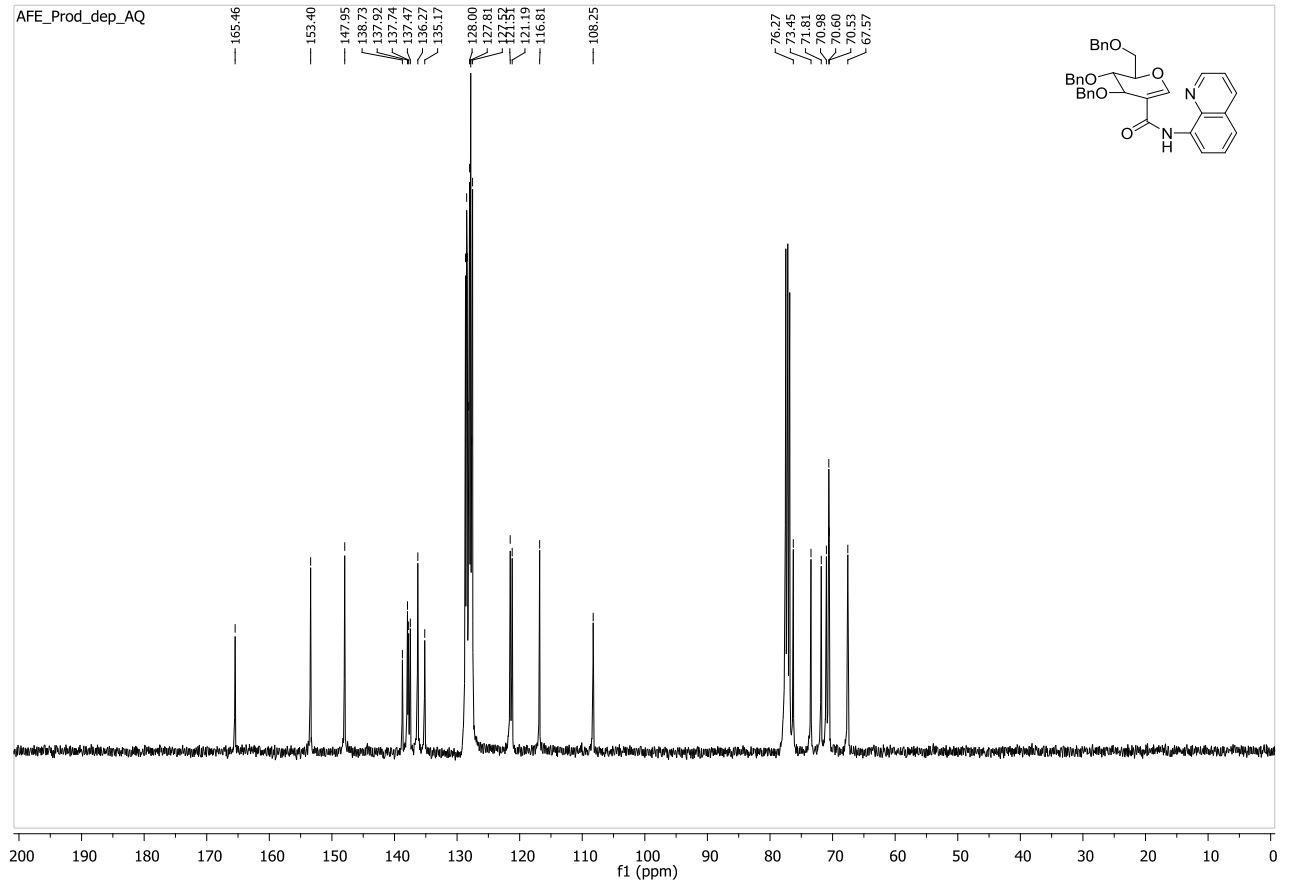
1H), 4.94 – 4.86 (m, 3H), 4.78 (d, *J* = 11.8 Hz, 1H), 4.72 – 4.67 (m, 4H), 4.61 (d, *J* = 11.8 Hz, 1H), 4.54 (d, *J* = 7.7 Hz, 1H), 4.44 – 4.32 (m, 5H), 3.85 – 3.79 (m, 3H), 3.62 (dd, *J* = 10.3, 5.6 Hz, 1H), 3.58 – 3.42 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 153.5, 147.9, 138.8, 138.5, 138.3, 138.0, 137.8, 136.3, 135.3, 129.1, 128.6, 128.5, 128.3, 128.0, 127.9, 127.8, 127.8, 127.7, 127.6, 125.4, 121.5, 121.1, 117.0, 108.0, 103.4, 82.1, 79.1, 76.2, 75.5, 74.6, 73.9, 73.6, 73.5, 73.4 (2C), 71.2, 71.0, 70.5, 69.2, 67.3; IR (cm^{-1}): 3340, 3088, 3063, 3030, 2914, 2866, 1725, 1676, 1617, 1596, 1528, 1496, 1487, 1454, 1425, 1385, 1365, 1325, 1287, 1264, 1194, 1176, 1157, 1095, 1072, 1028, 1002; $[\alpha]^{20}_D$ = +15.6 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+Na)+ $C_{64}H_{62}N_2NaO_{10}^+$ (*m/z*): calc. 1041.4302; found 1041.4308. **5** was obtained following the general procedure of C-H functionalisation: in a Schlenk tube was added the half of catalytic system: Pd(cod)Cl_2 (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). Then 3-iodoanisole (61 µL, 6 equiv., 0.511 mmol), the compound **S3** (87 mg, 1 equiv., 0.085 mmol) and toluene (2 mL) were added. The resulting mixture was stirred for 3 h at 130 °C. Then the other half of catalytic system was added at room temperature in the Schlenk tube: Pd(cod)Cl_2 (2.5 mg, 0.2 equiv., 0.009 mmol), AgOAc (10.7 mg, 1.5 equiv., 0.064 mmol), K_2CO_3 (21.2 mg, 3.6 equiv., 0.154 mmol) and citric acid (7.0 mg, 0.85 equiv., 0.036 mmol). The resulting mixture was stirred at 130 °C overnight. The mixture was filtrated on celite with EtOAc and then concentrated under vacuum. **5** was obtained after purification on silica gel (eluent: Cyclo/EtOAc 90:10) as yellowish oil (47 mg; 0.035 mmol; 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.90 (s, 1H), 8.76 – 8.74 (m, 1H), 8.23 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.04 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.49 – 7.45 (m, 4H), 7.42 – 7.40 (m, 2H), 7.34 – 7.16 (m, 30H), 6.98 (d, *J* = 7.9 Hz, 2H), 4.95 (d, *J* = 11.7 Hz, 1H), 4.89 – 4.66 (m, 10H), 4.62 – 4.53 (m, 4H), 4.44 – 4.43 (m, 1H), 4.41 – 4.33 (m, 2H), 4.09 – 4.01 (m, 1H), 3.89 (d, *J* = 2.8 Hz, 1H), 3.84 (dd, *J* = 9.7, 7.8 Hz, 1H), 3.79 (dd, *J* = 10.6, 4.9 Hz, 1H), 3.55 – 3.54 (m, 2H), 3.49 (dd, *J* = 9.7, 2.8 Hz, 1H), 2.97 – 2.85 (m, 2H), 1.40 (s, 9H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 166.8, 157.4, 155.2, 147.6, 138.8, 138.7, 138.6, 138.6, 138.5, 138.2, 137.9, 135.9, 135.2, 133.5, 129.4, 129.2,

128.5, 128.5, 128.4, 128.3, 128.3, 128.2, 128.0, 127.9, 127.8, 127.8, 127.7, 127.4, 127.3, 121.3, 121.0, 116.4, 116.3, 116.3, 108.7, 103.0, 82.2, 82.2, 79.8, 79.2, 77.2, 76.4, 75.3, 75.2, 74.7, 73.7 (2C), 73.3, 73.2, 72.3, 72.1, 68.9, 67.7, 54.6, 37.8, 28.4 (3C), 28.0 (3C); IR (cm^{-1}): 3339, 3064, 3031, 2975, 2927, 2867, 1714, 1659, 1522, 1497, 1485, 1454, 1425, 1367, 1327, 1257, 1209, 1154, 1095, 1074, 1028; $[\alpha]^{20}_{D}$ = +2.5 (1.00, $CHCl_3$); HRMS (TOF ES+) for (M+H)+ $C_{82}H_{88}N_3O_{14}^{+}$ (*m/z*): calc. 1338.6266; found 1338.6290.

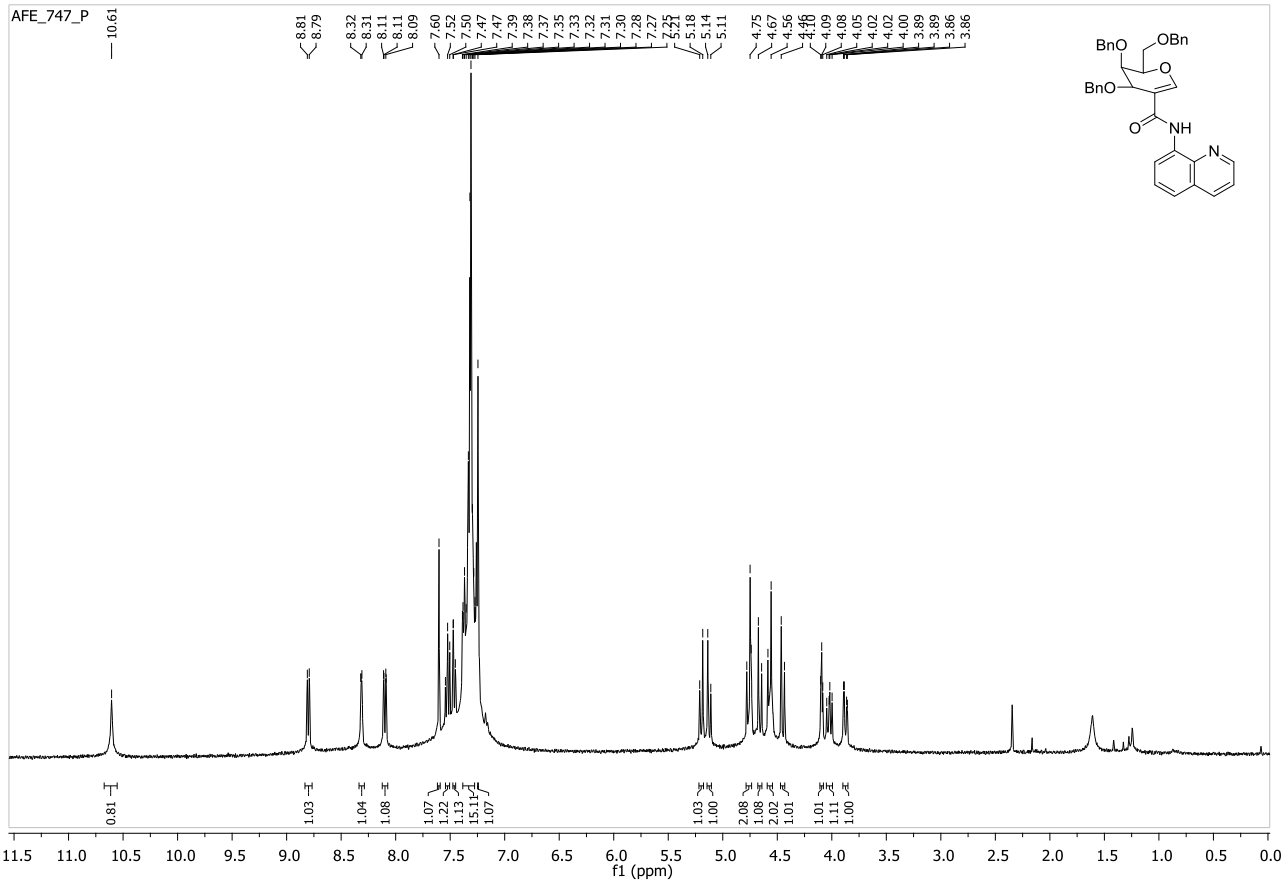
^{1}H-NMR spectrum of **1a**



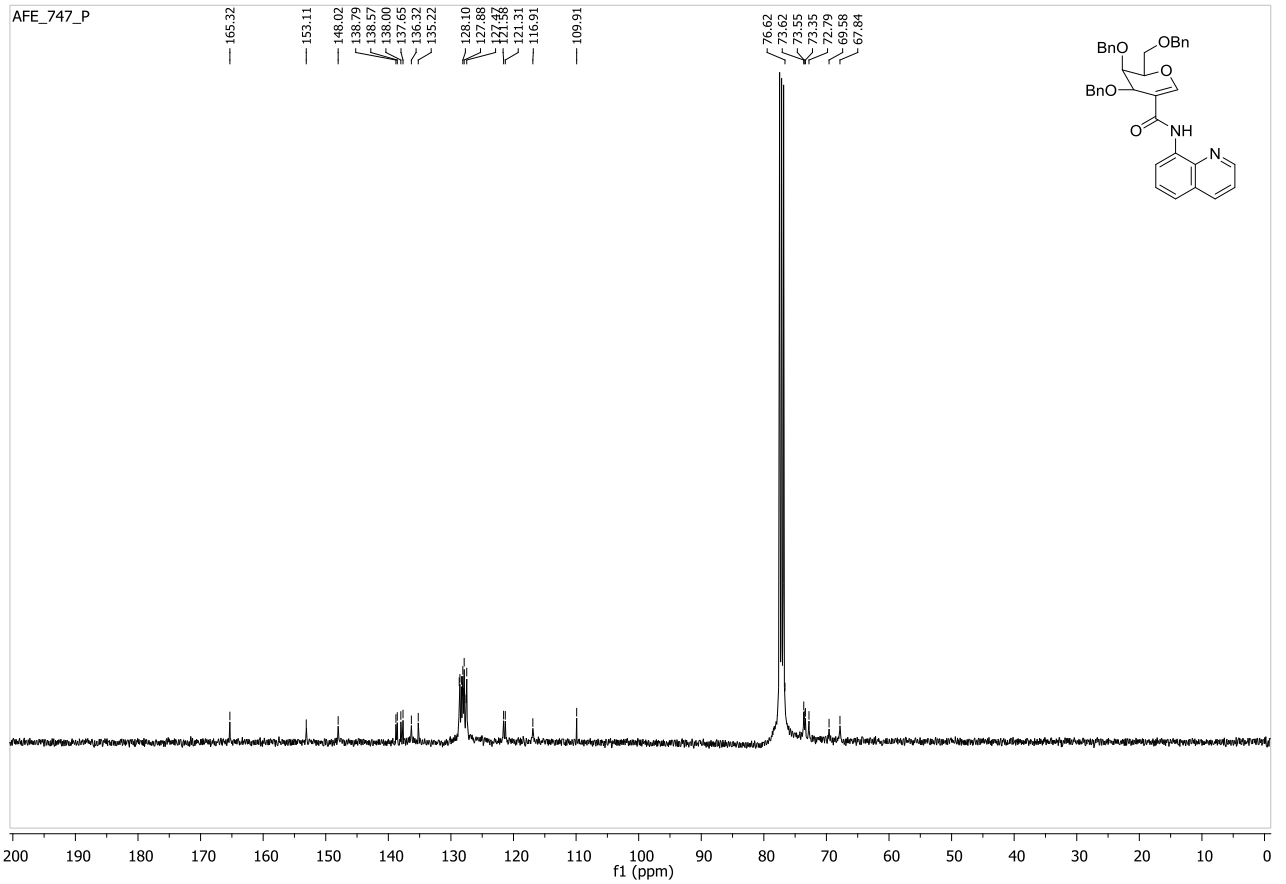
^{13}C-NMR spectrum of **1a**



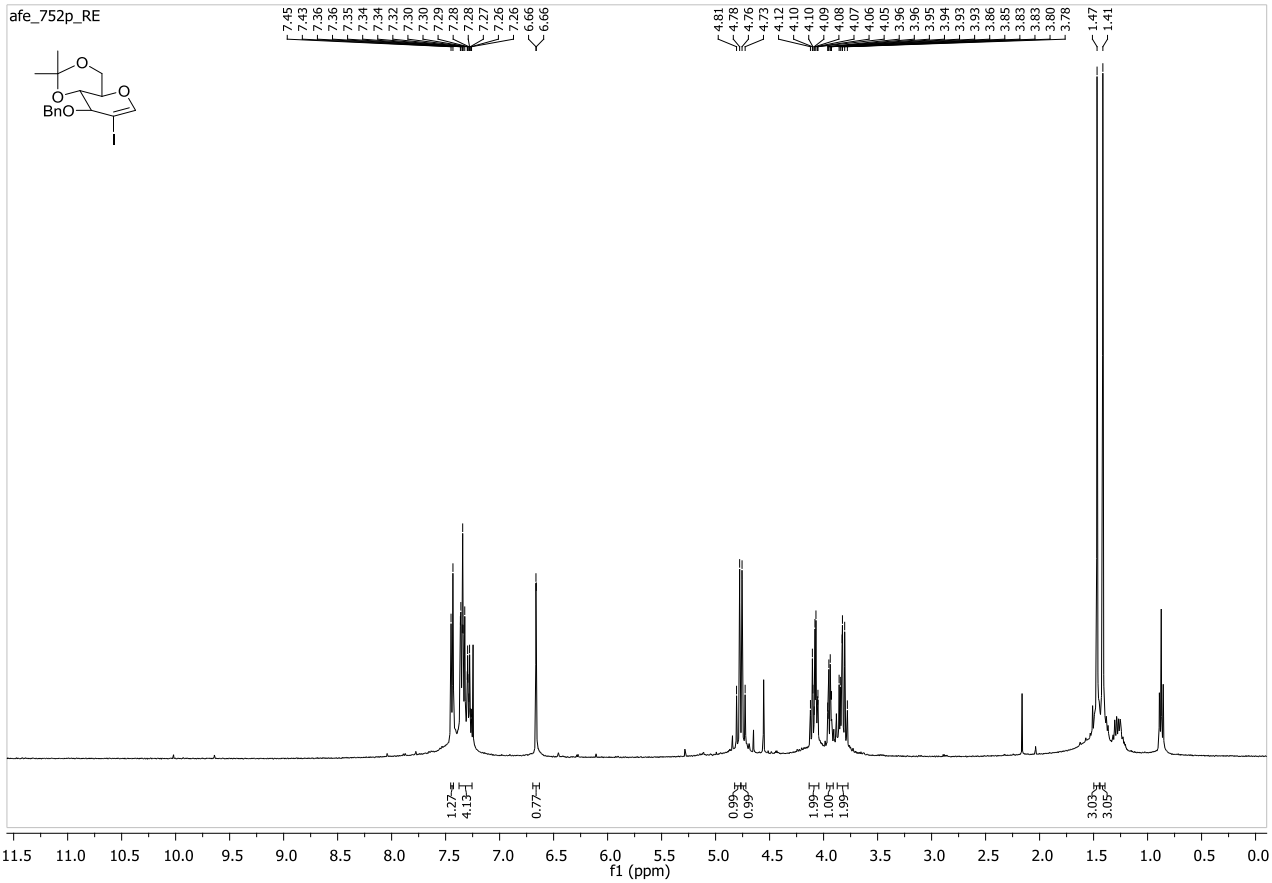
^{1}H-NMR spectrum of **S1**



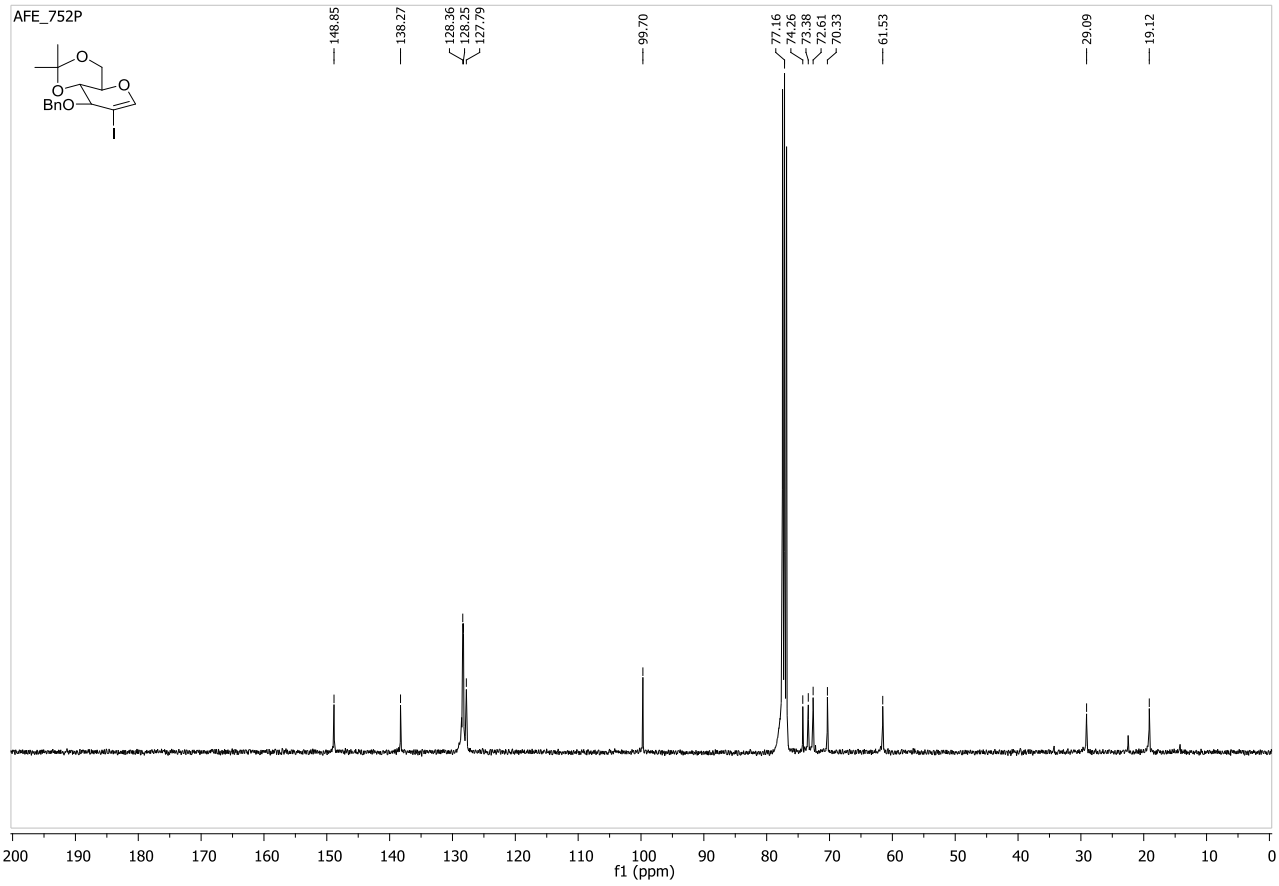
^{13}C-NMR spectrum of **S1**



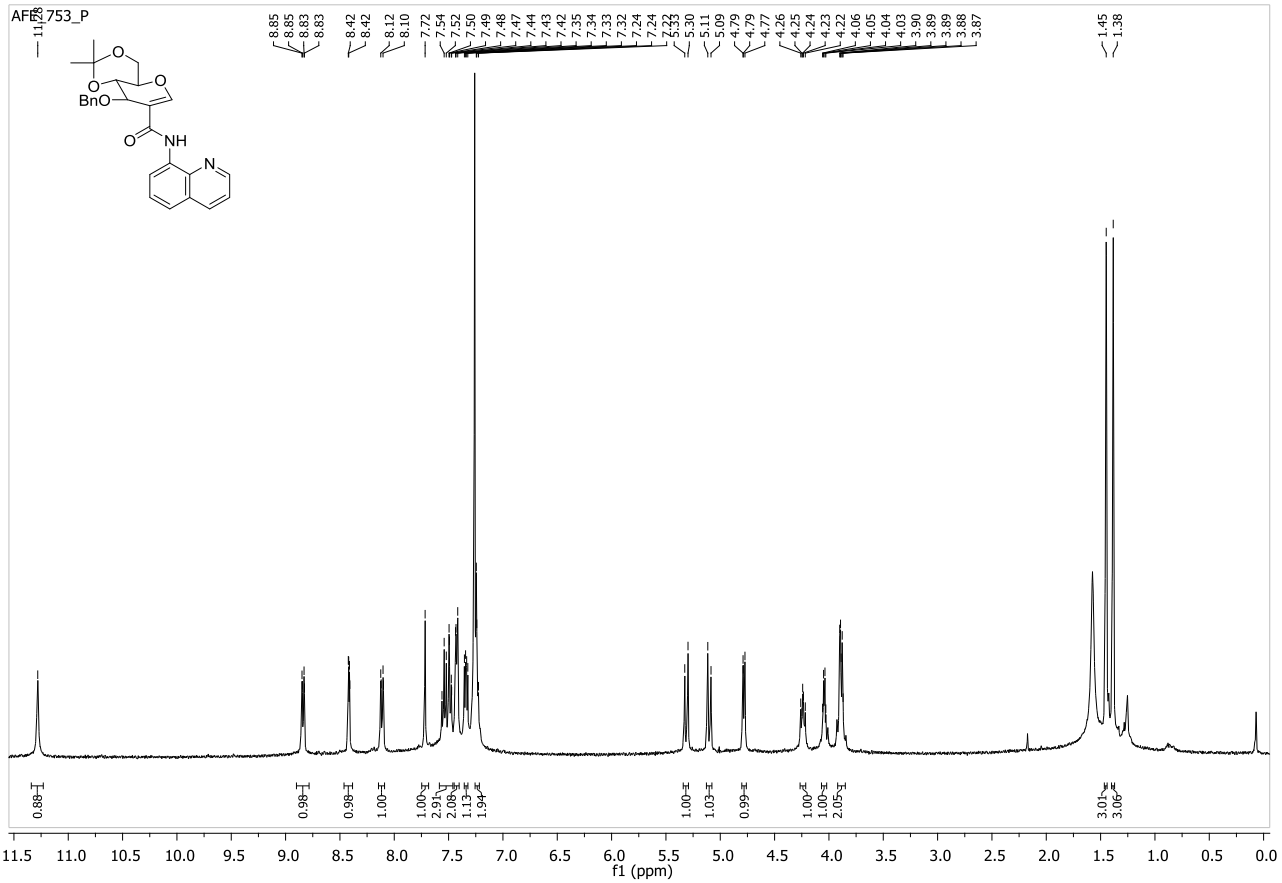
^{1}H-NMR spectrum of 2-iodo-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal



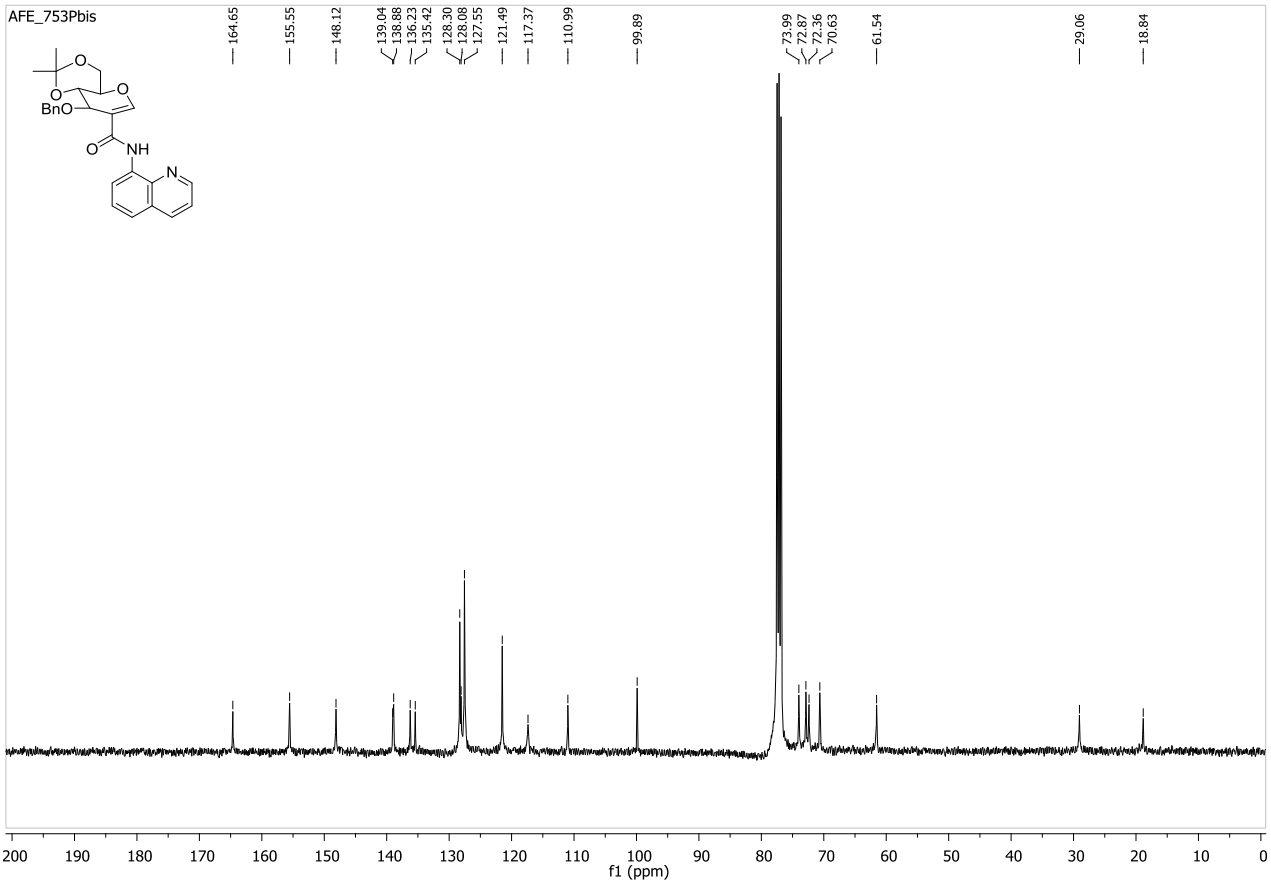
^{13}C-NMR spectrum of 2-iodo-3-*O*-benzyl-4,6-*O*-isopropylidene-D-glucal



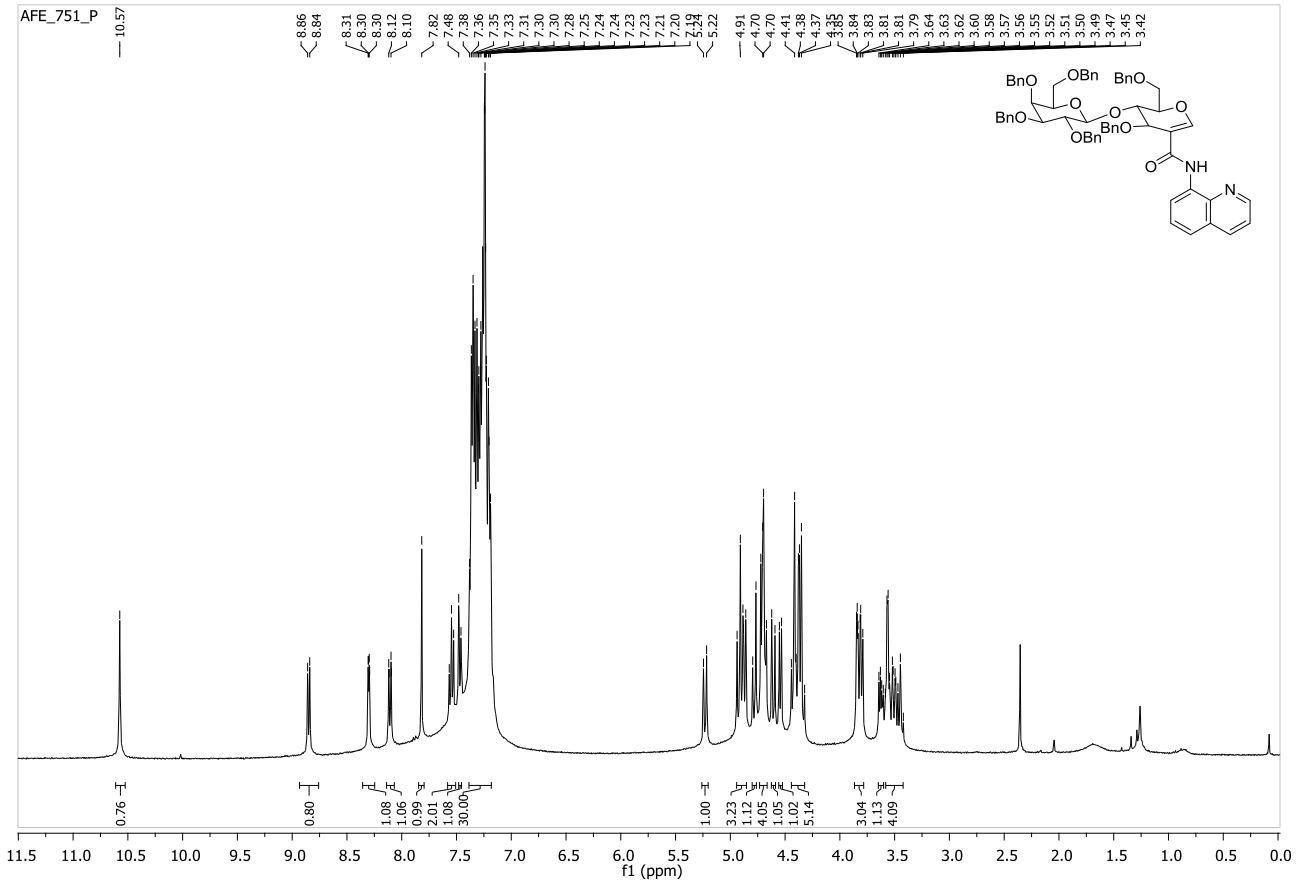
^{1}H-NMR spectrum of **S2**



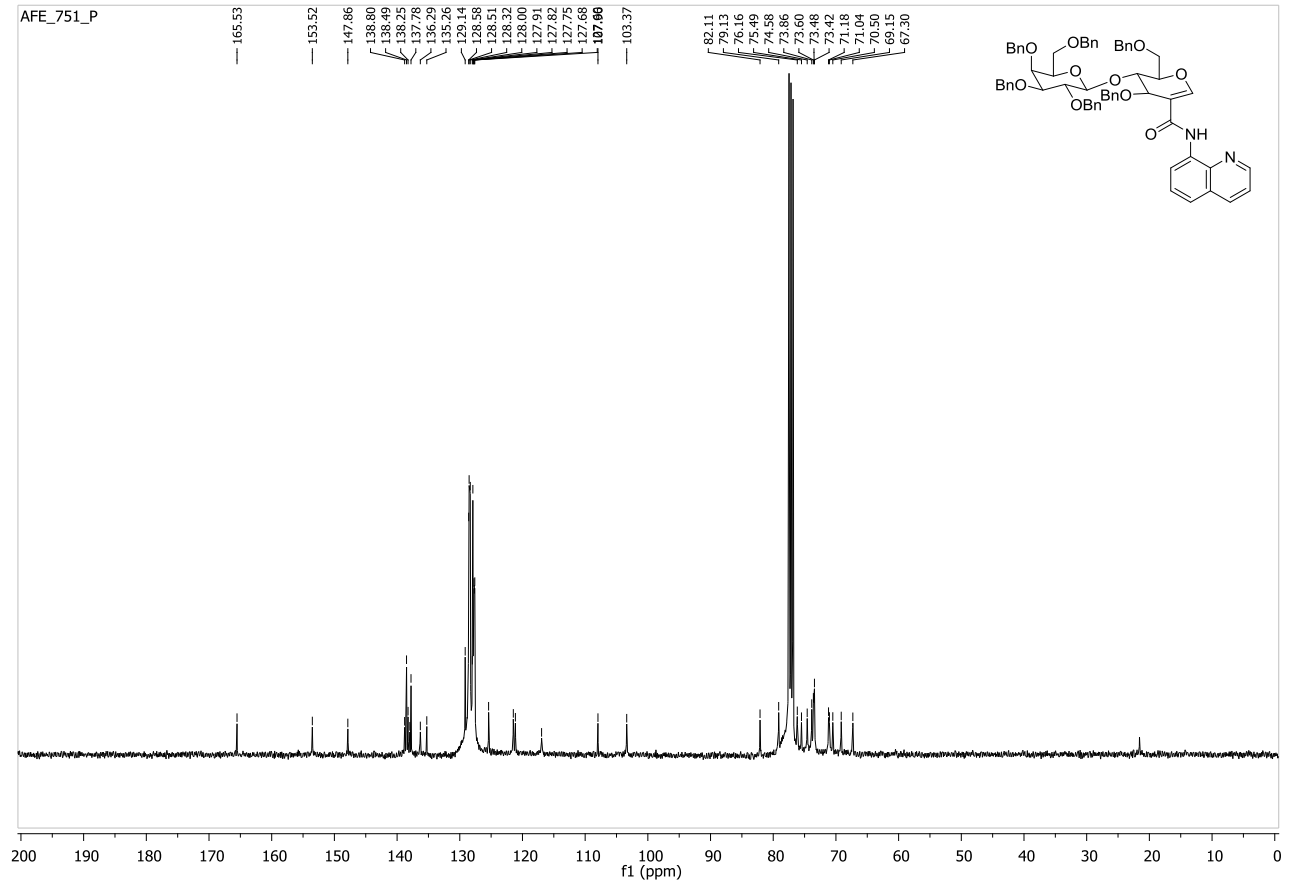
^{13}C-NMR spectrum of **S2**



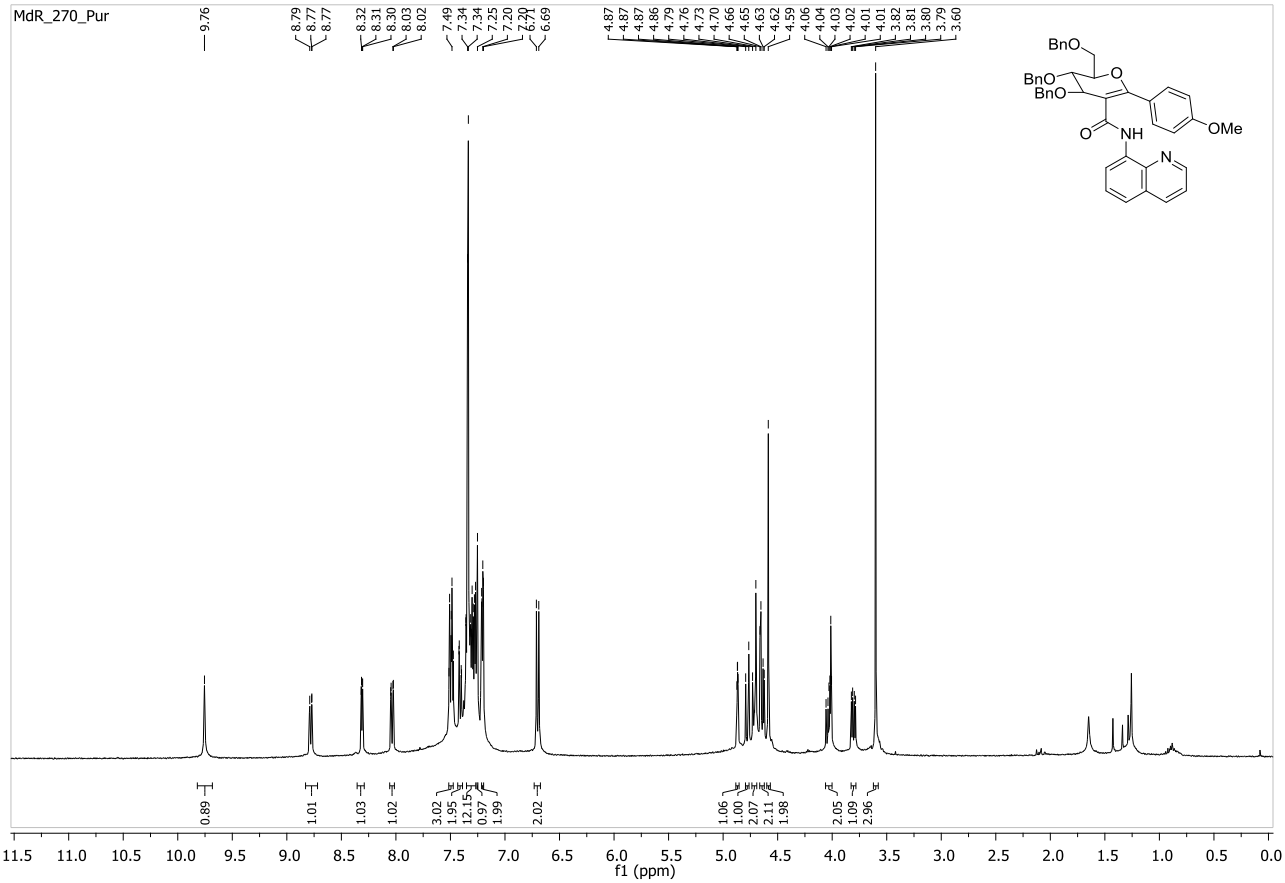
^{1}H-NMR spectrum of **S3**



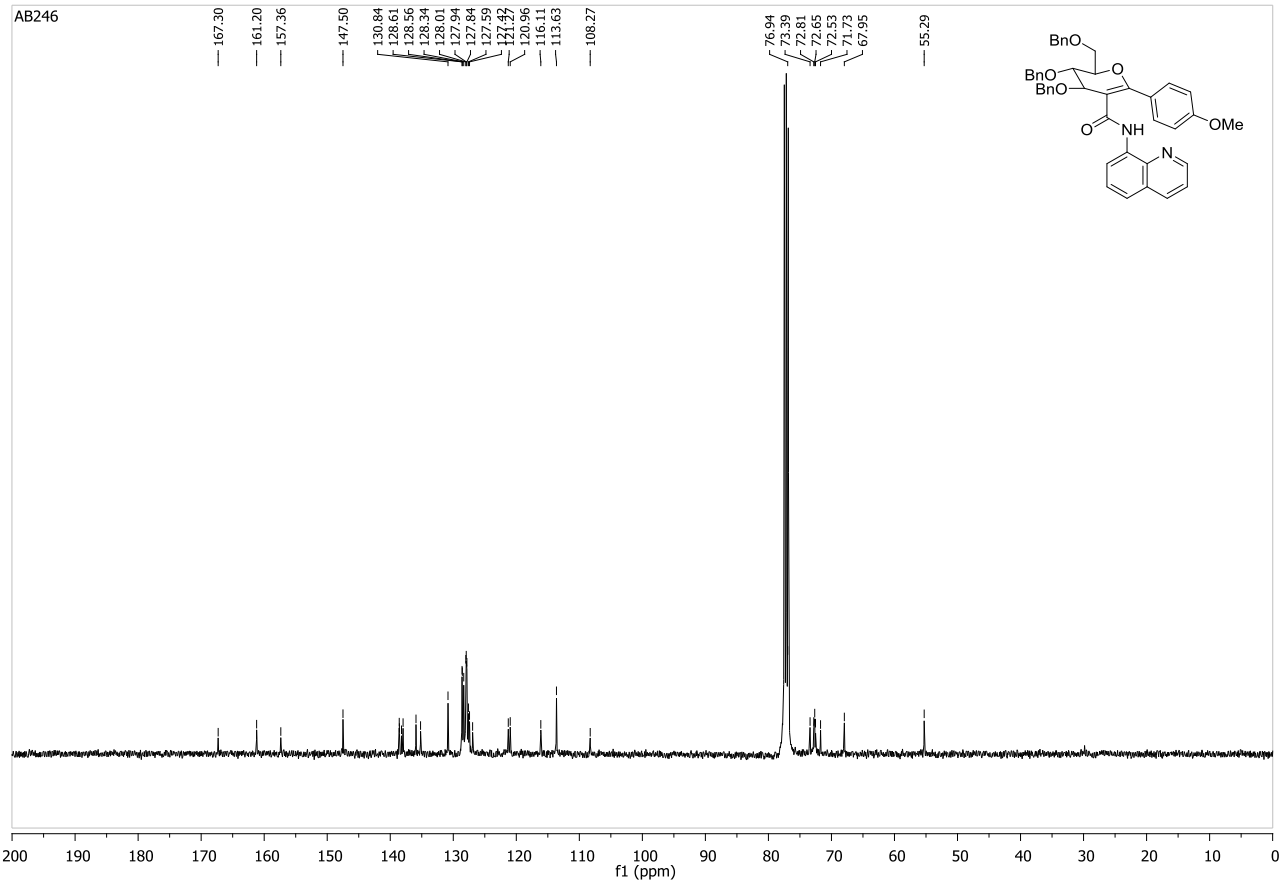
^{13}C-NMR spectrum of **S3**



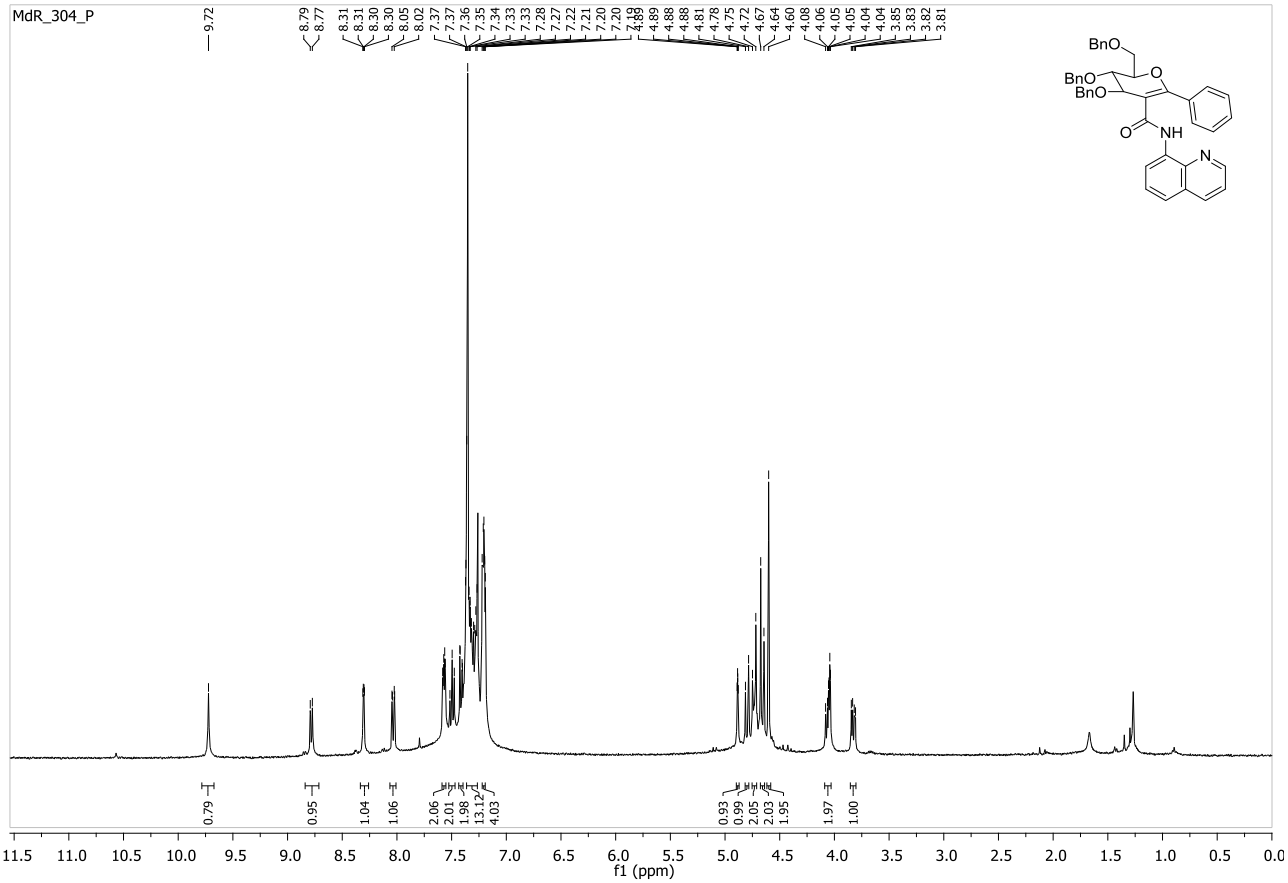
^{1}H-NMR spectrum of **2a**



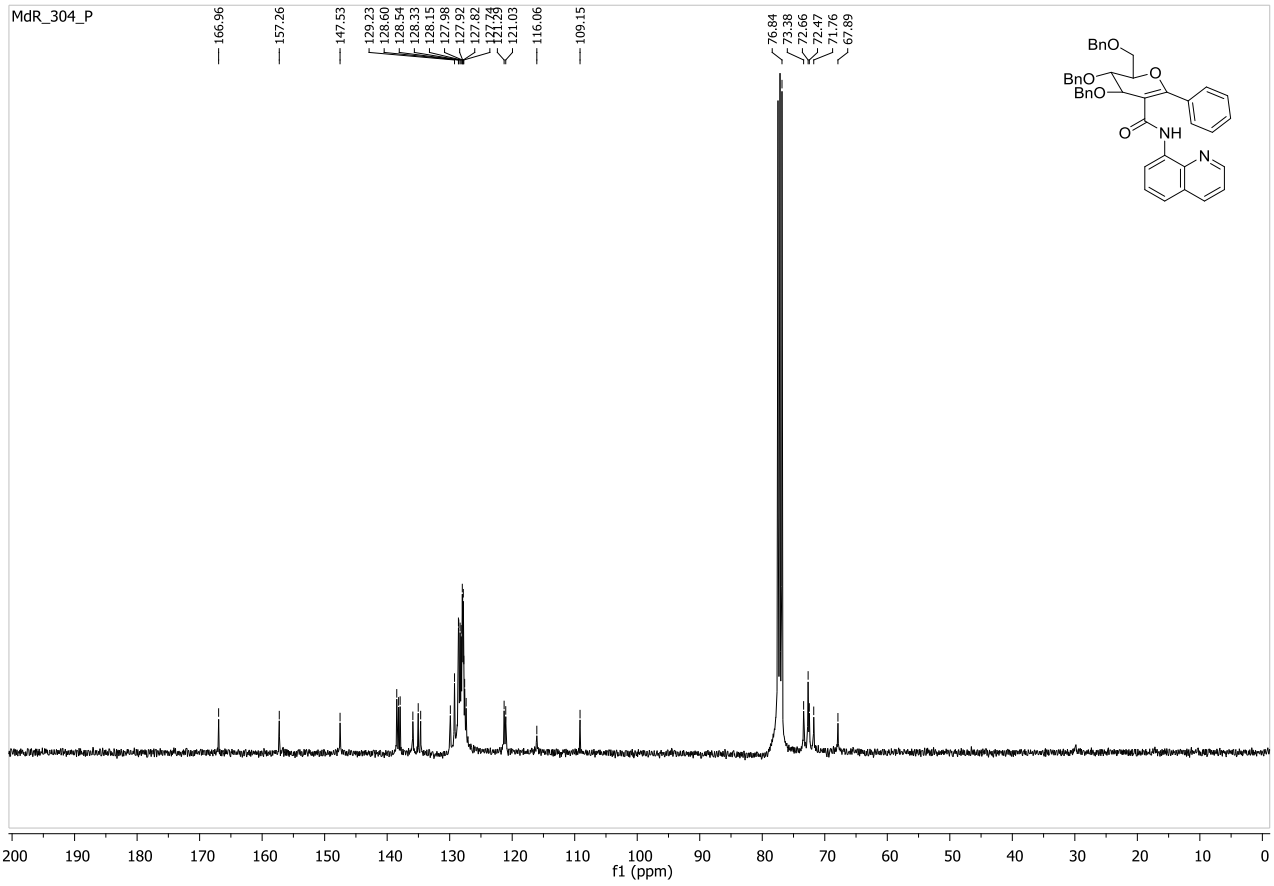
^{13}C-NMR spectrum of **2a**



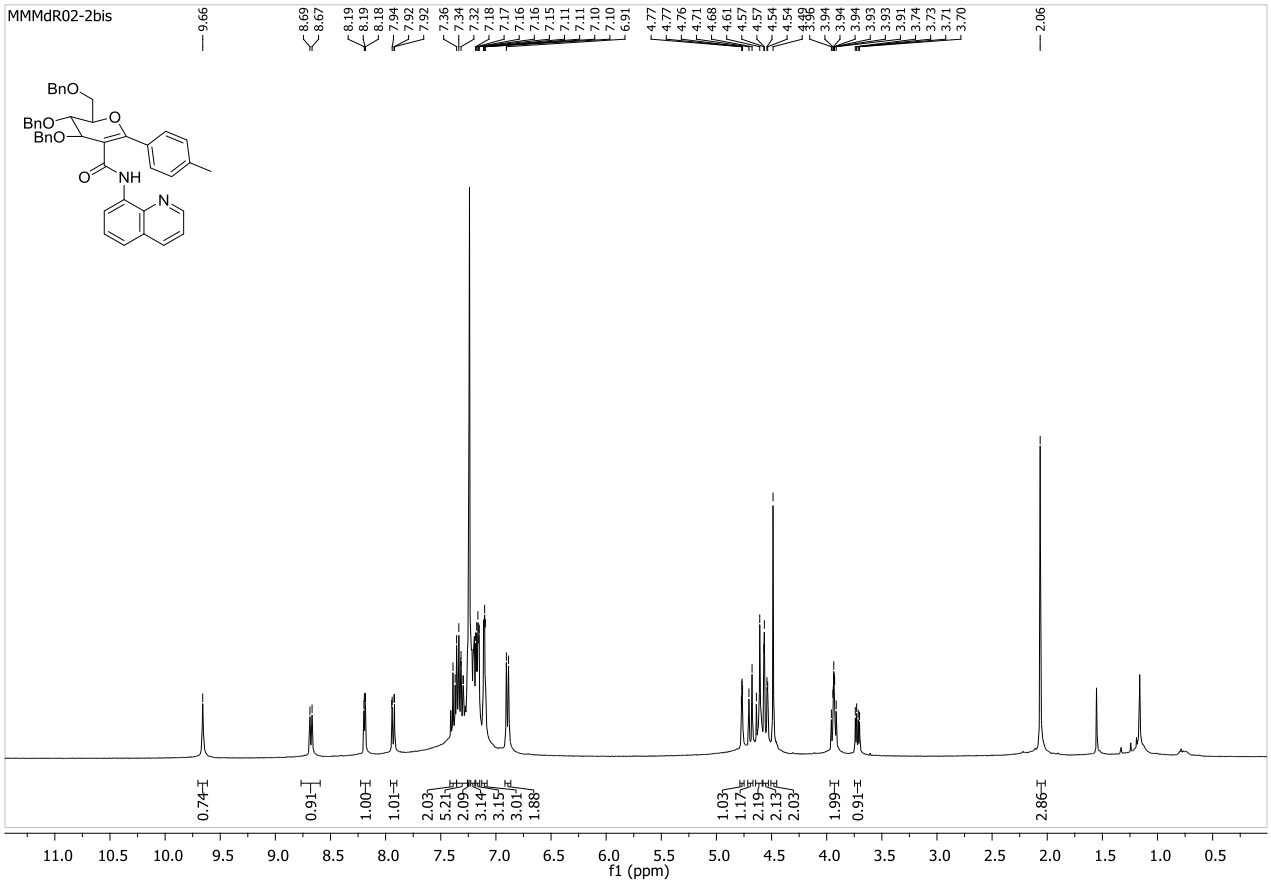
^{1}H-NMR spectrum of **2b**



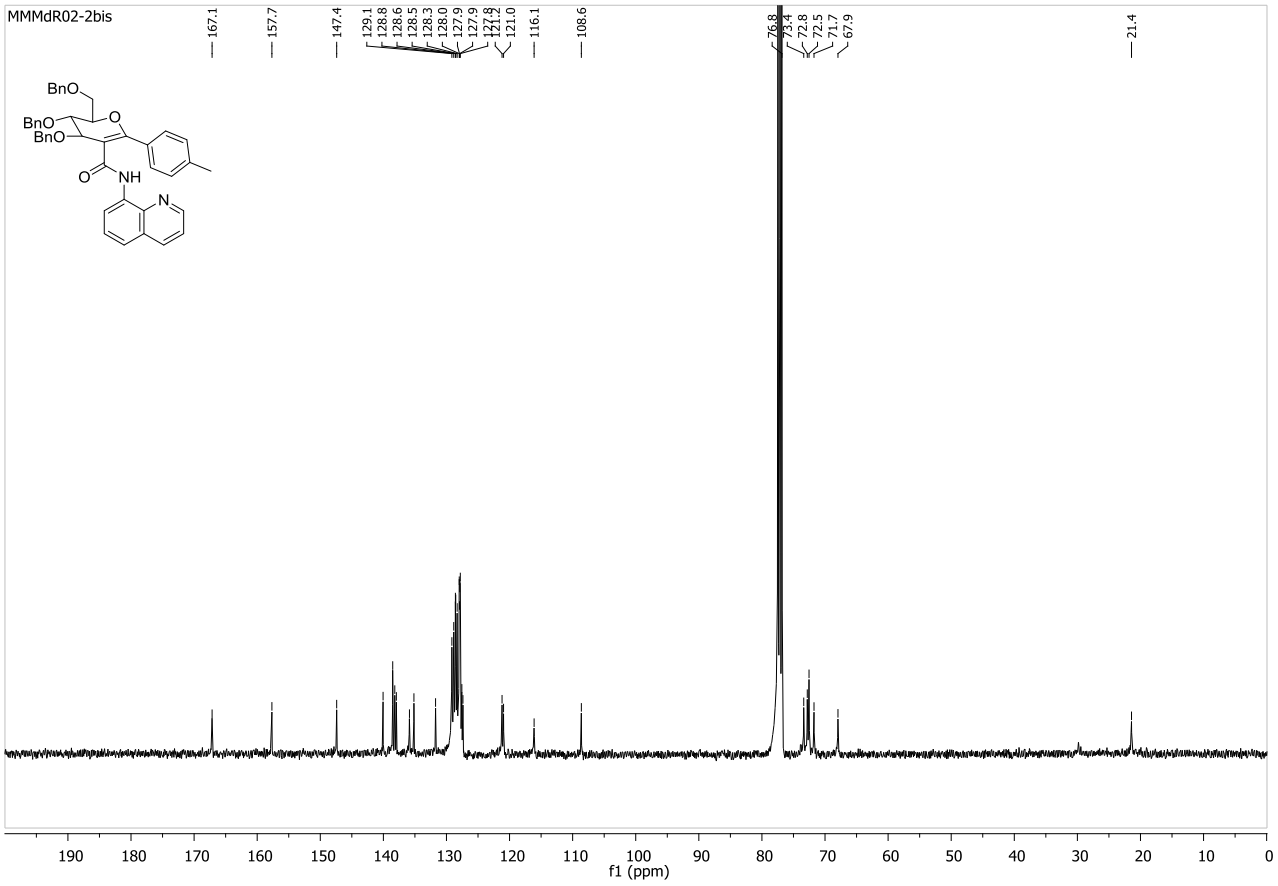
^{13}C-NMR spectrum of **2b**



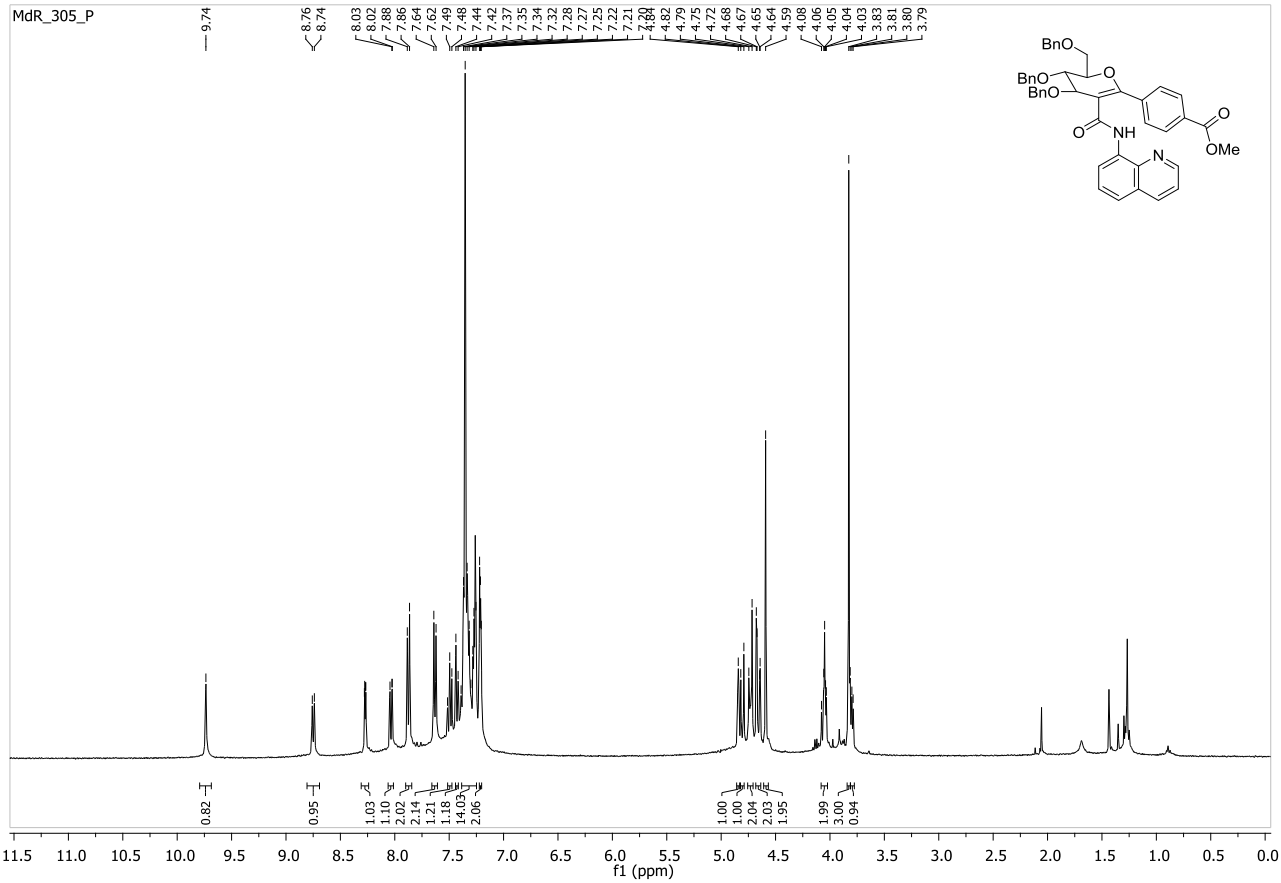
^{1}H-NMR spectrum of **2c**



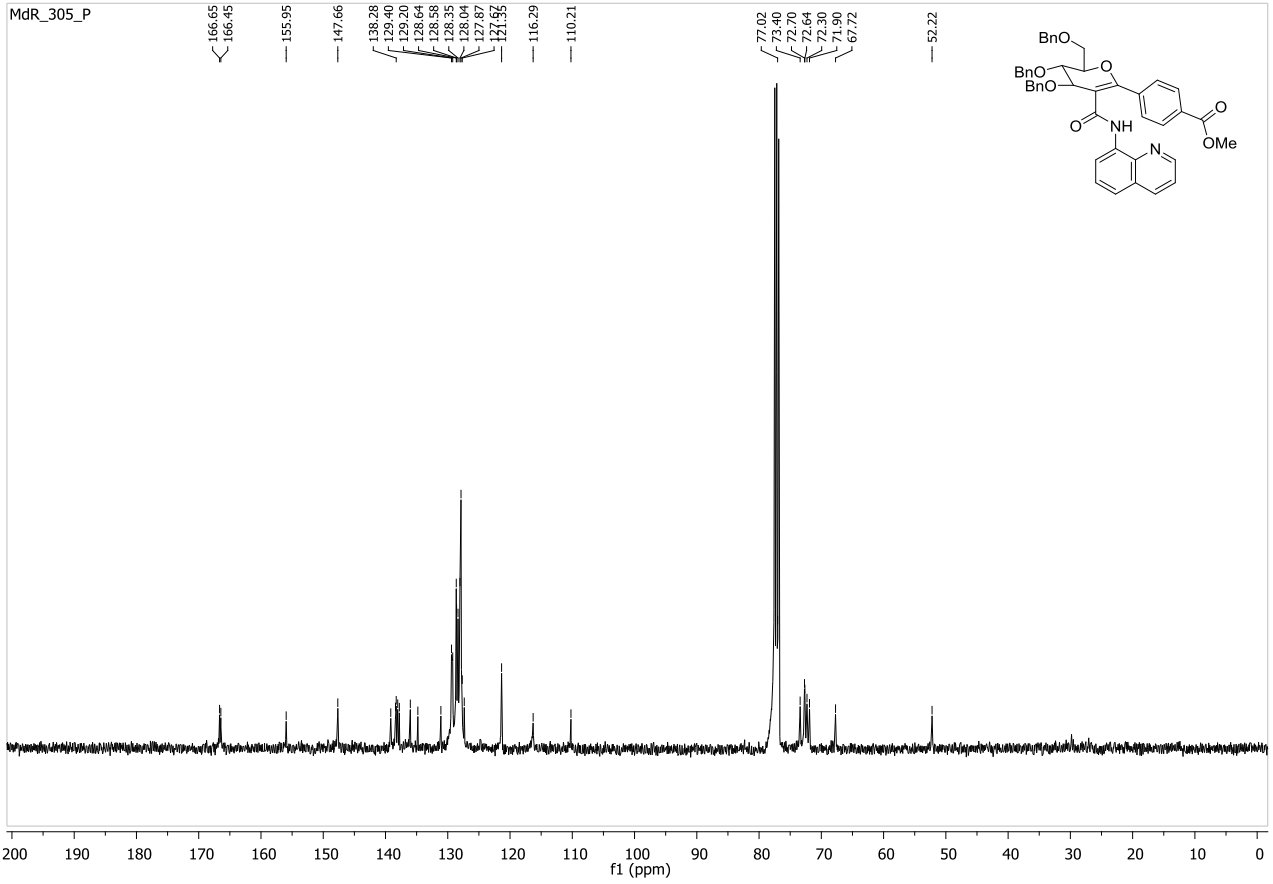
^{13}C-NMR spectrum of **2c**



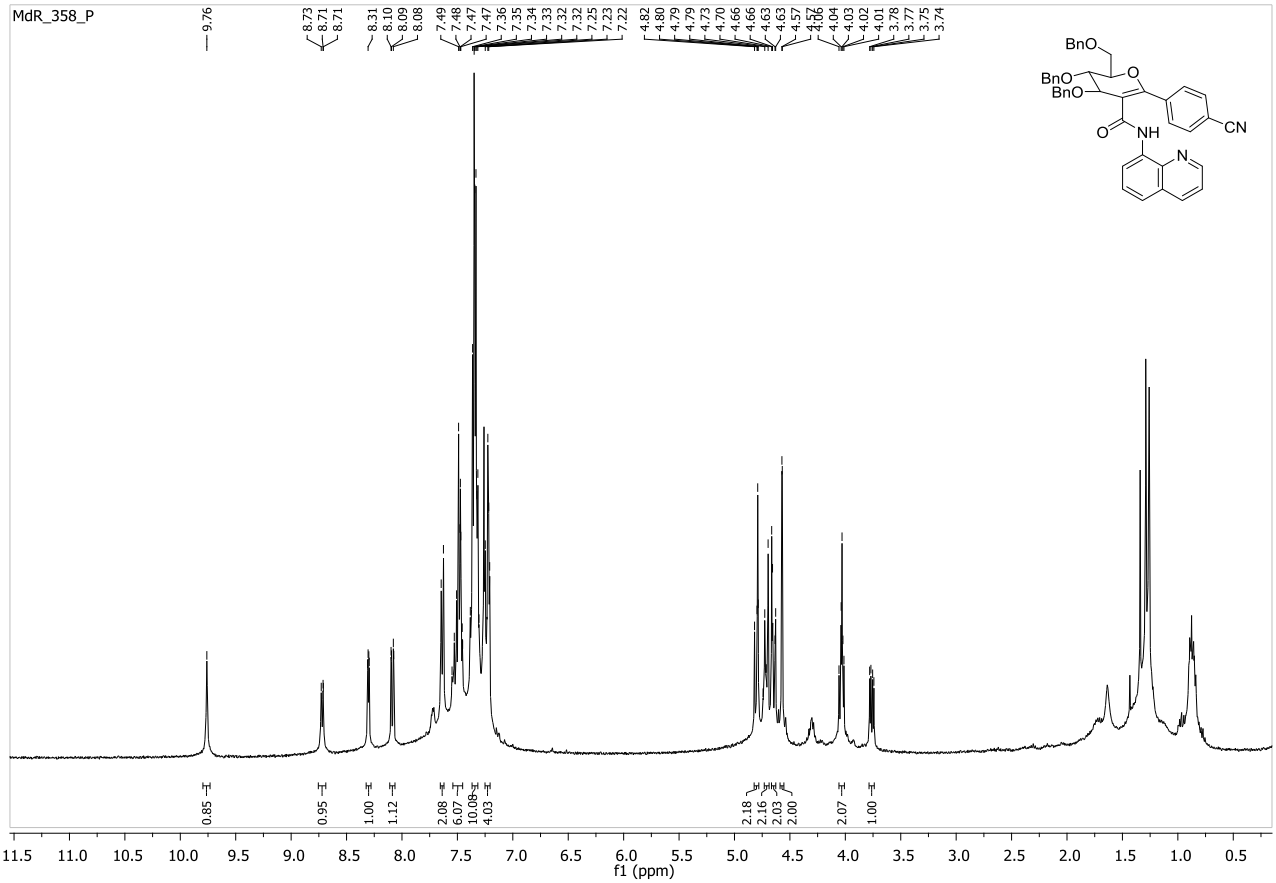
^{1}H-NMR spectrum of **2d**



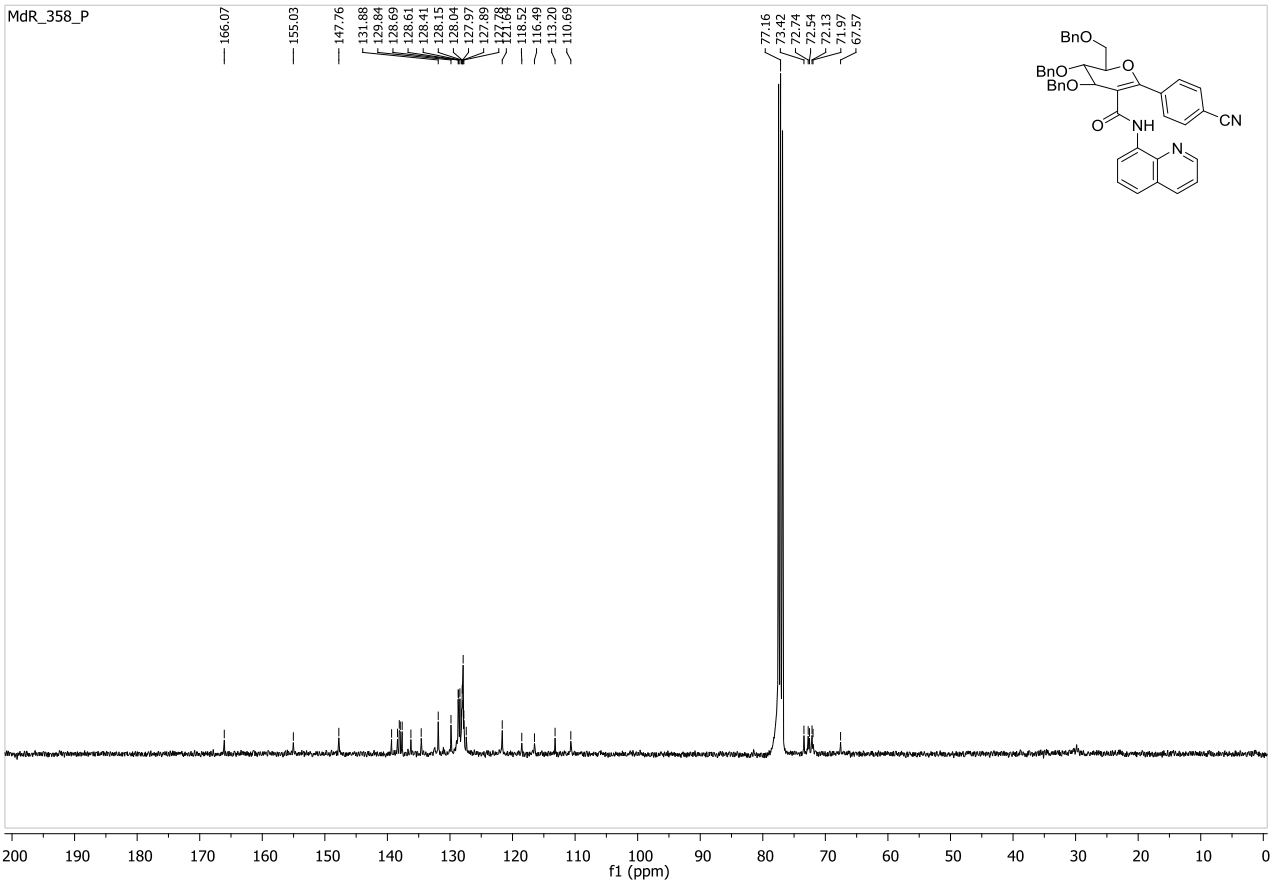
^{13}C-NMR spectrum of **2d**



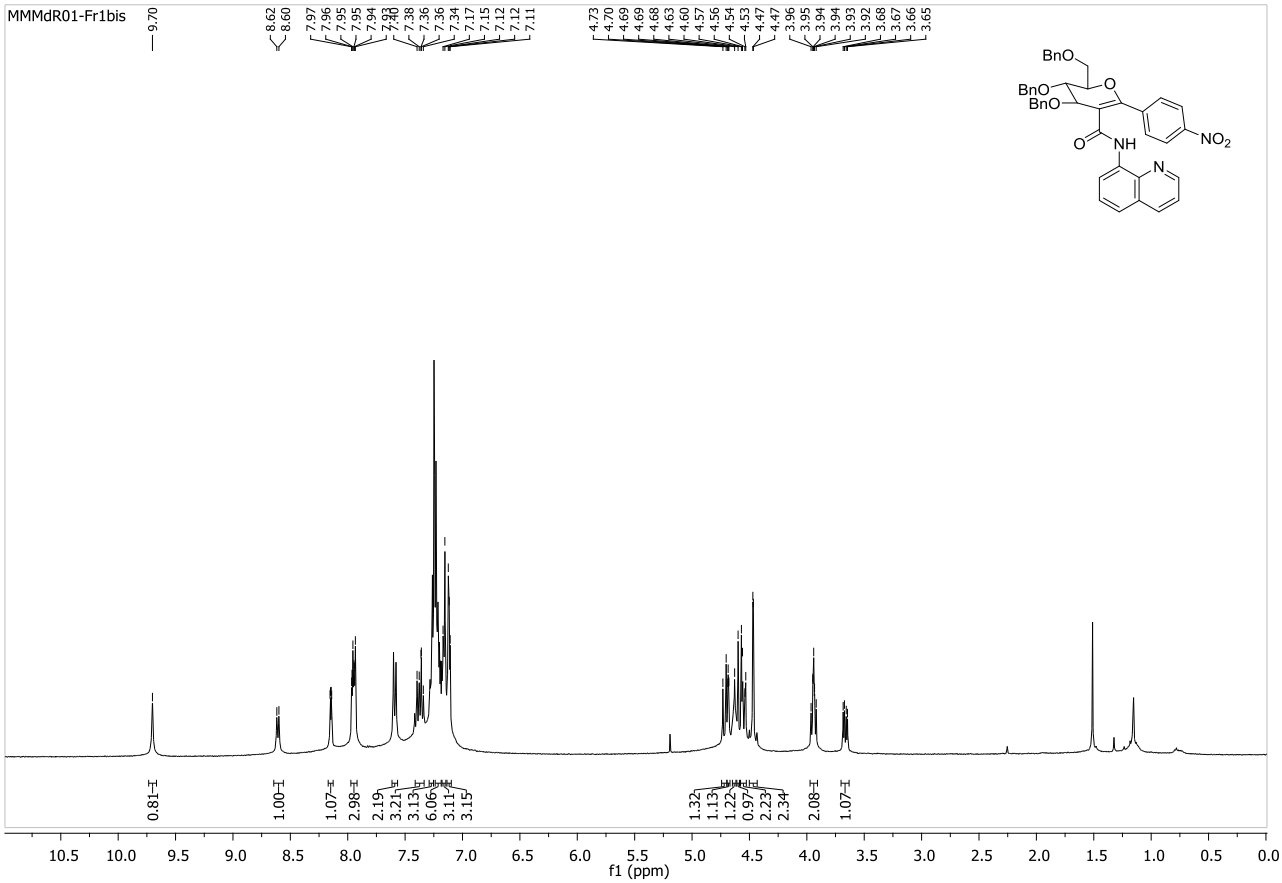
^{1}H-NMR spectrum of **2e**



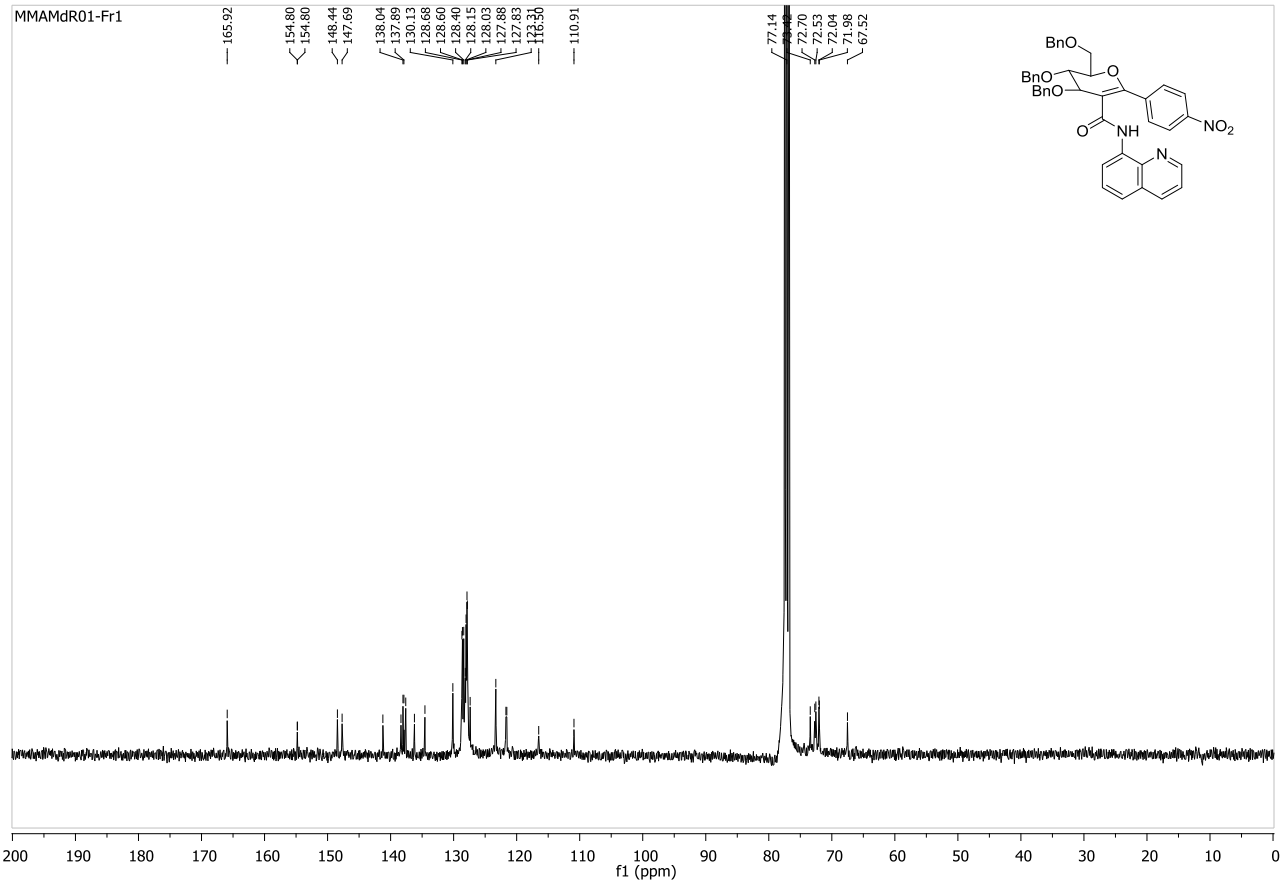
^{13}C-NMR spectrum of **2e**



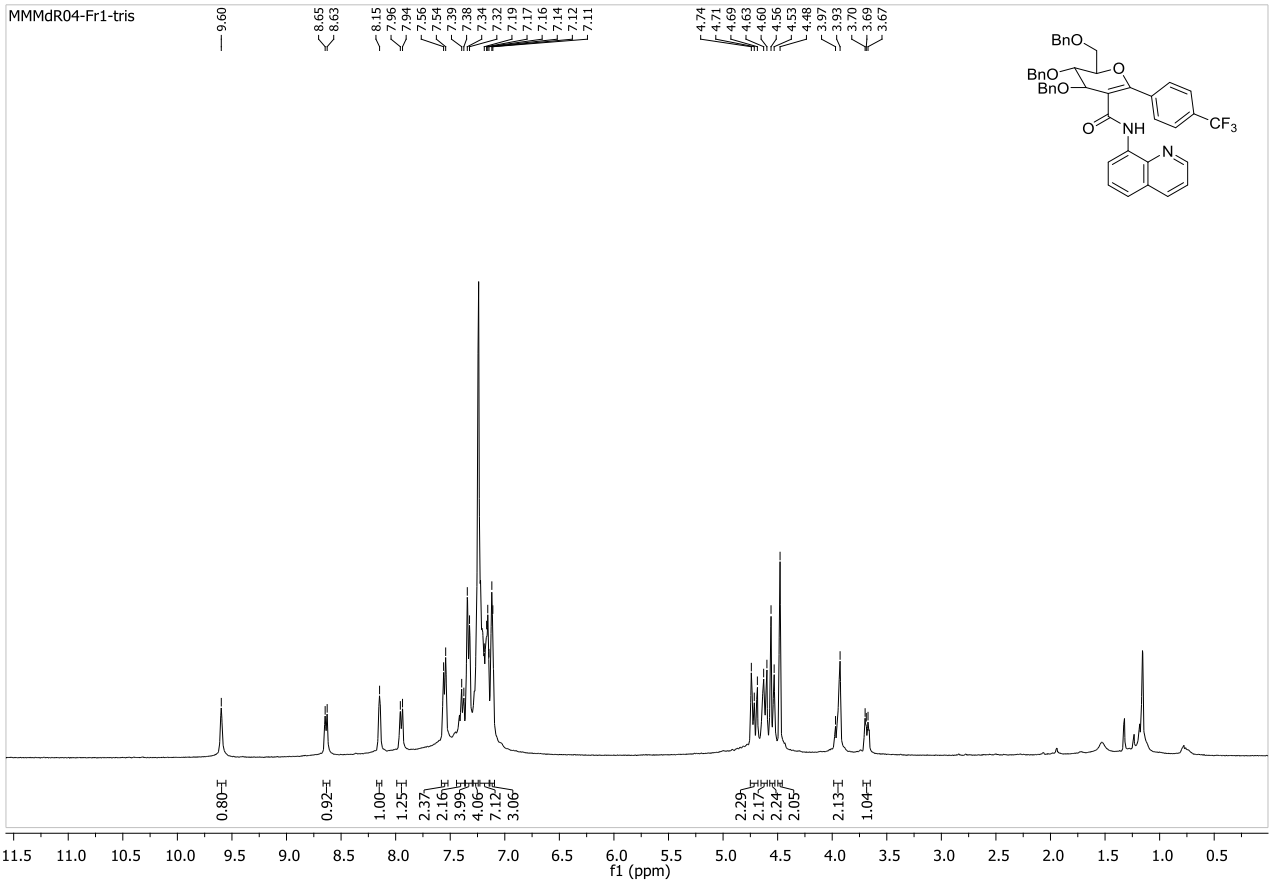
^{1}H-NMR spectrum of **2f**



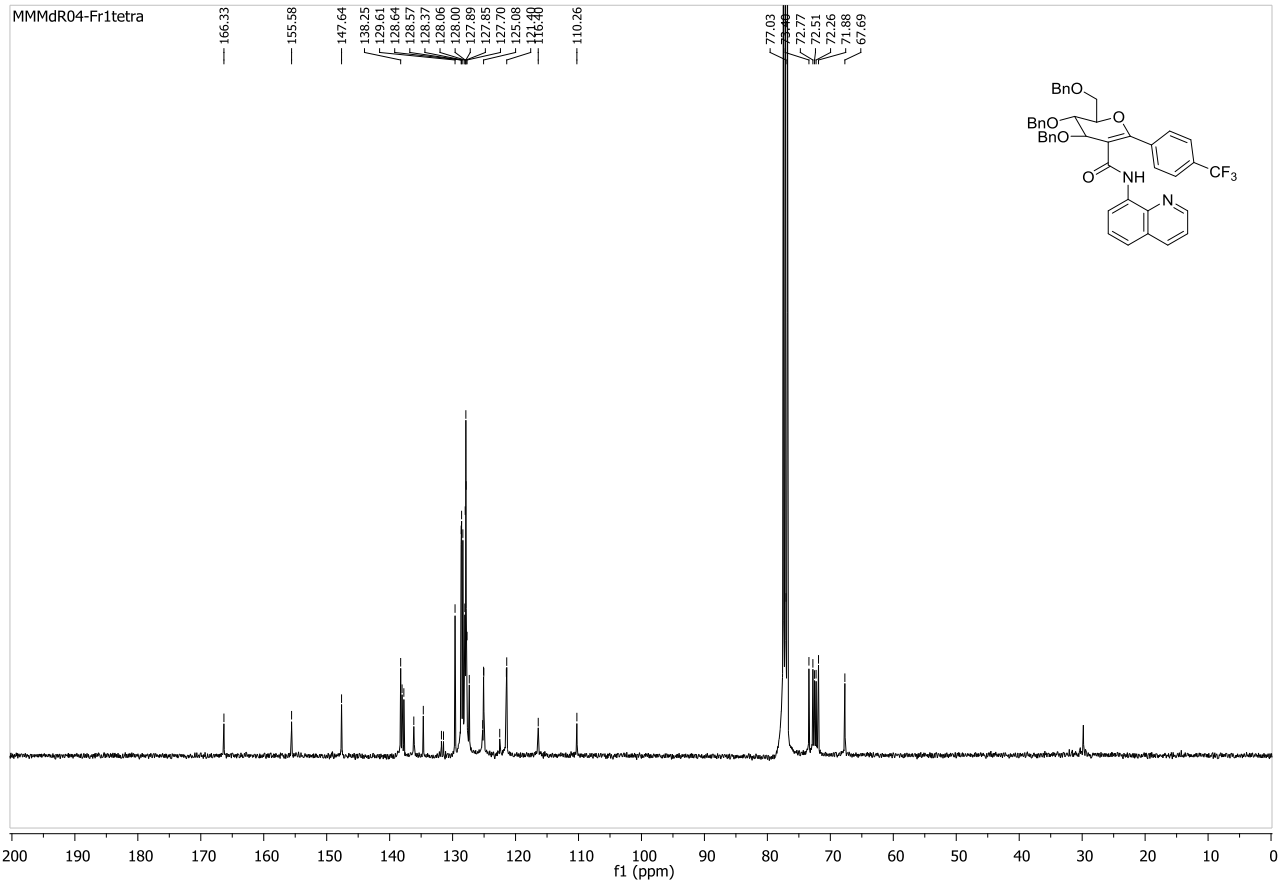
^{13}C-NMR spectrum of **2f**



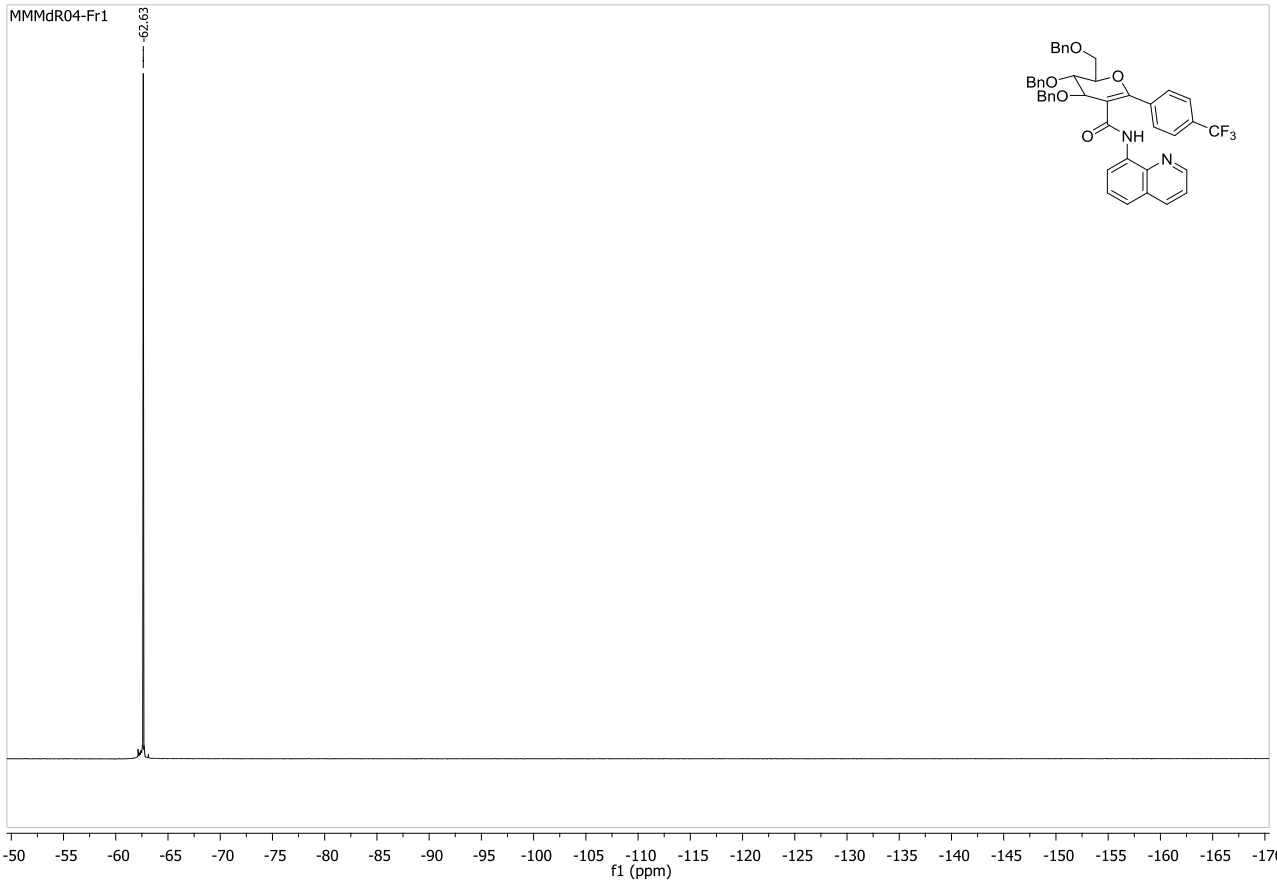
^{1}H-NMR spectrum of **2g**



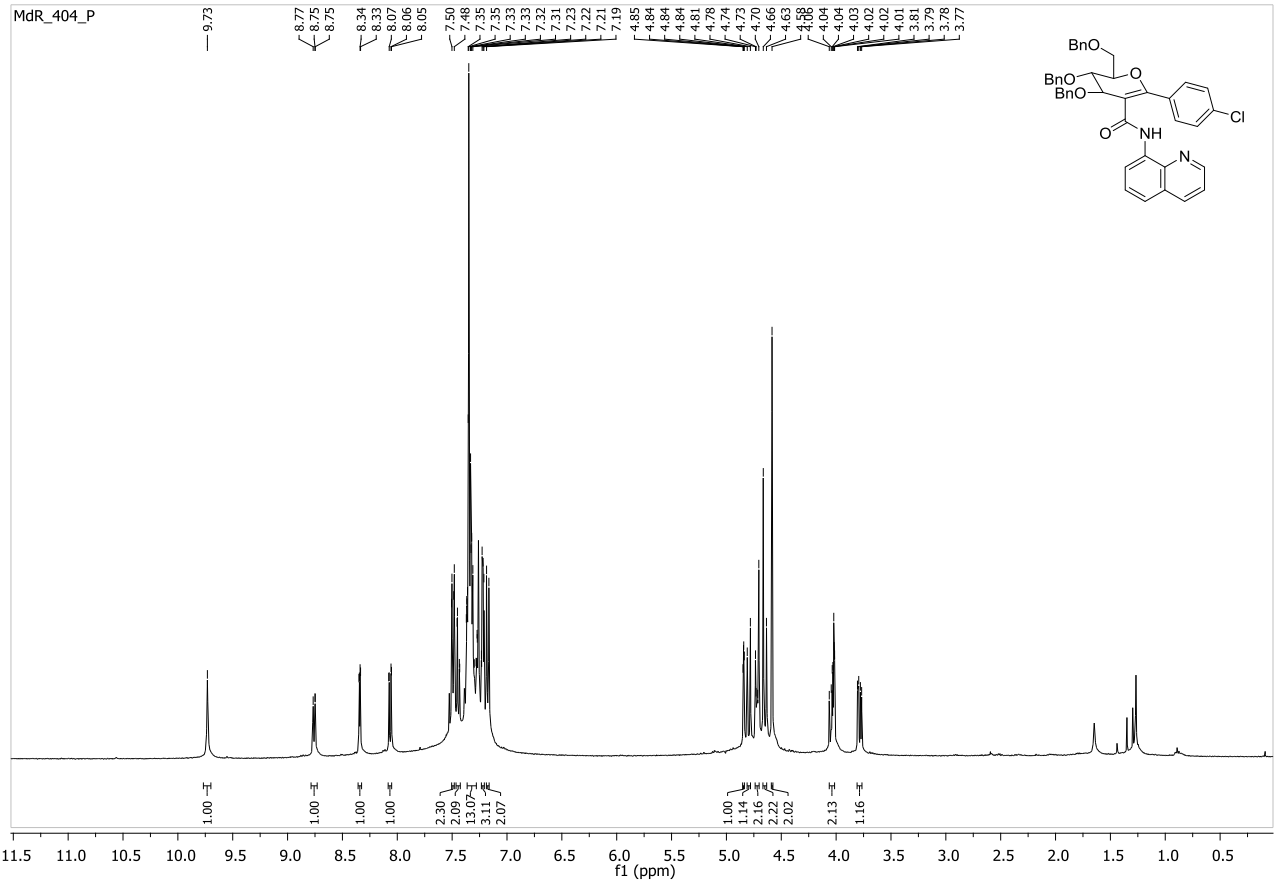
^{13}C-NMR spectrum of **2g**



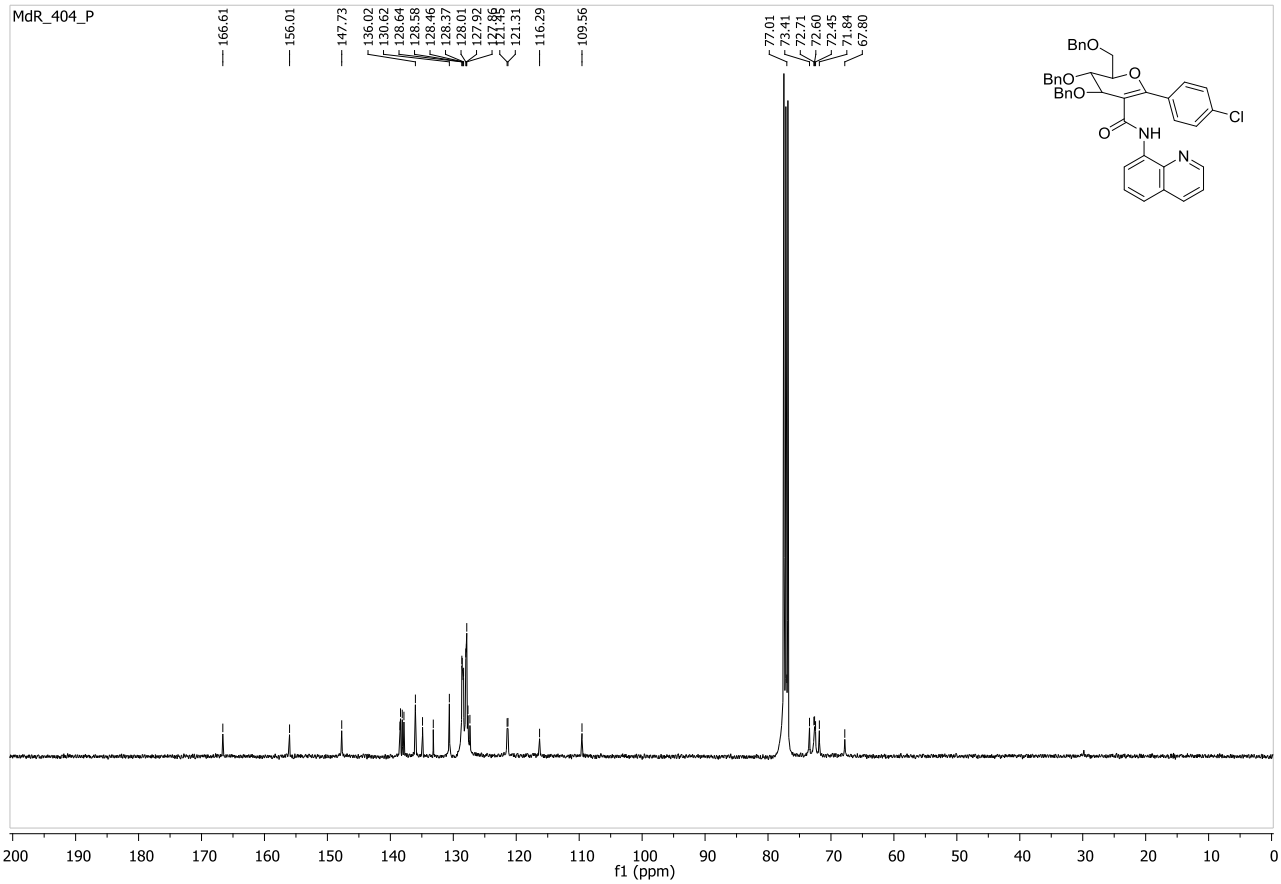
^{19}F-NMR spectrum of **2g**



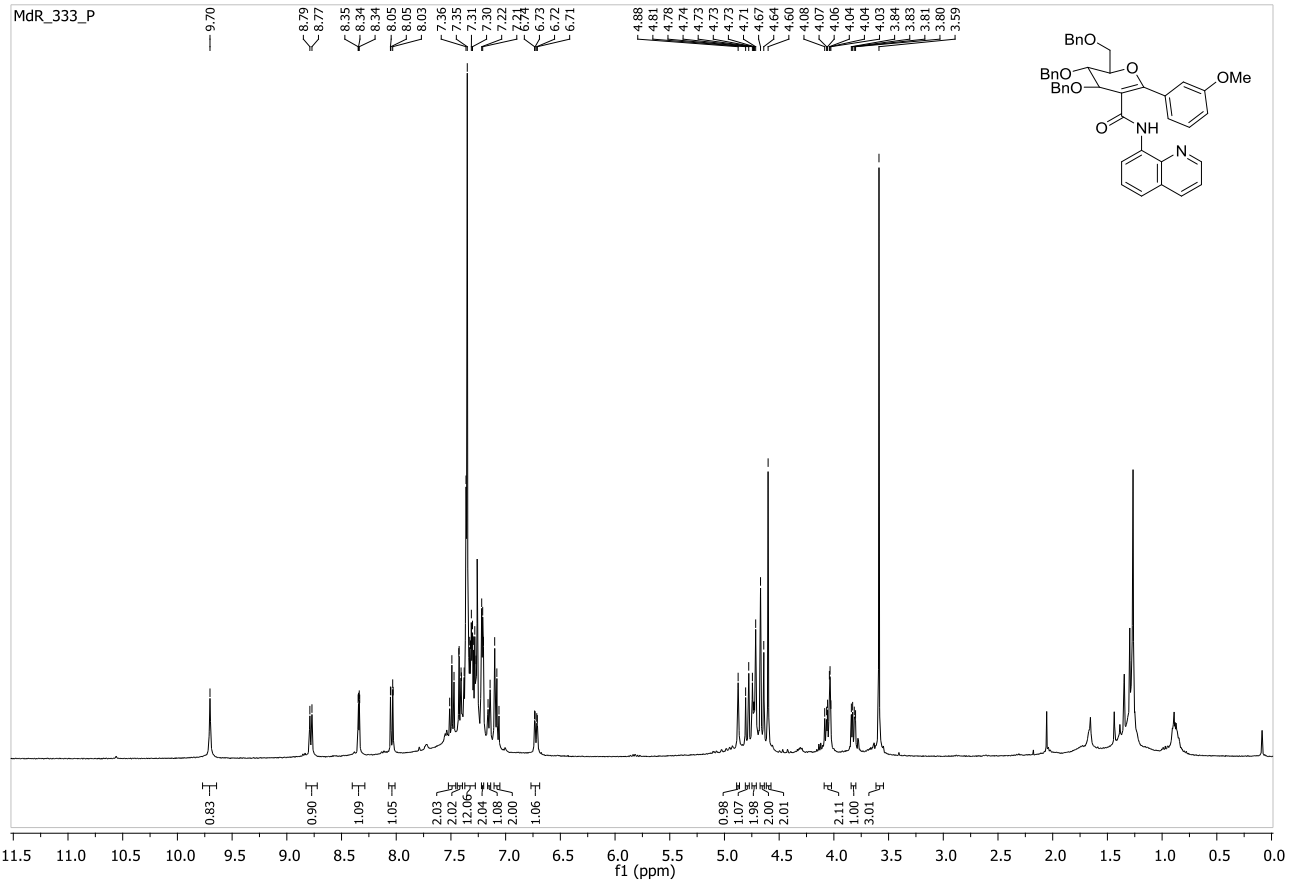
^{1}H-NMR spectrum of **2h**



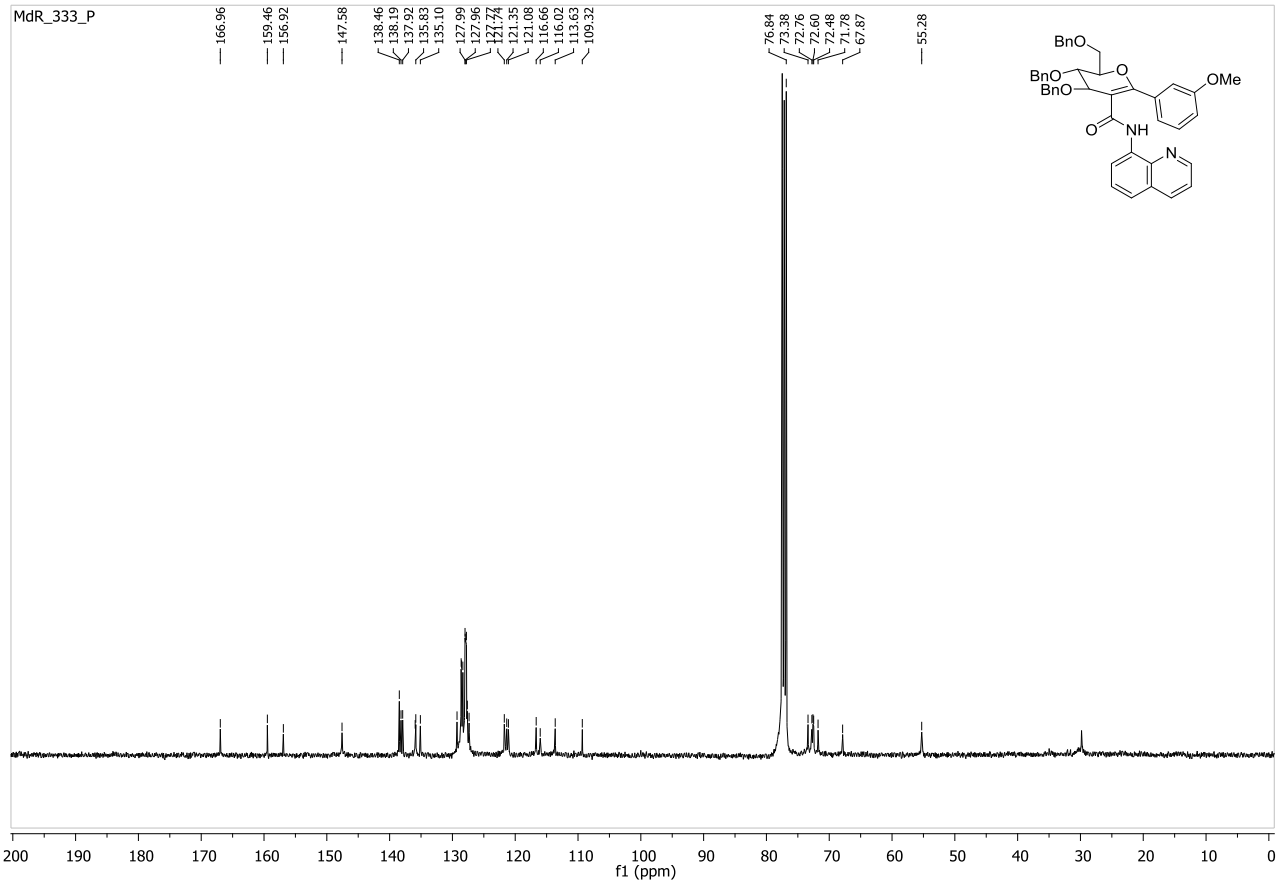
^{13}C-NMR spectrum of **2h**



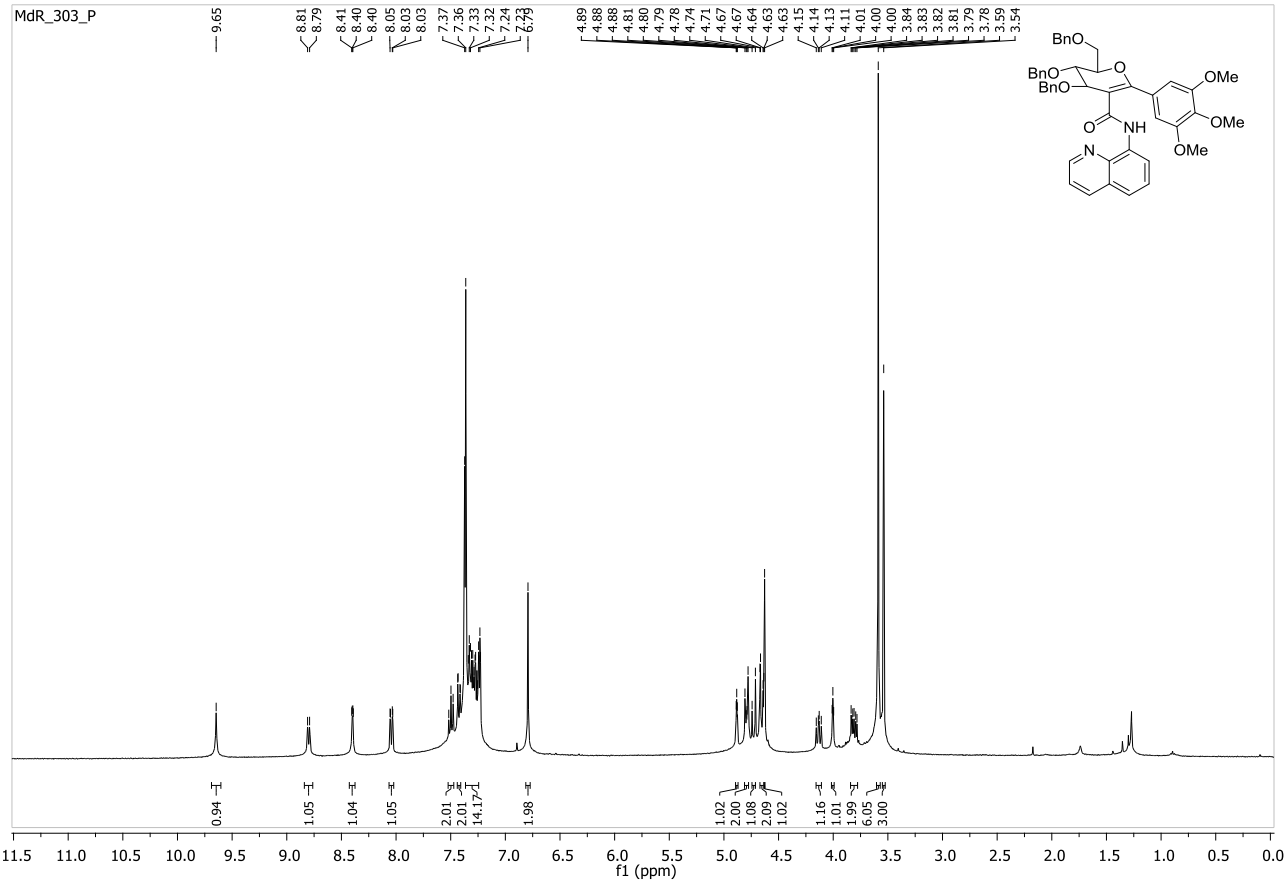
^{1}H-NMR spectrum of **2i**



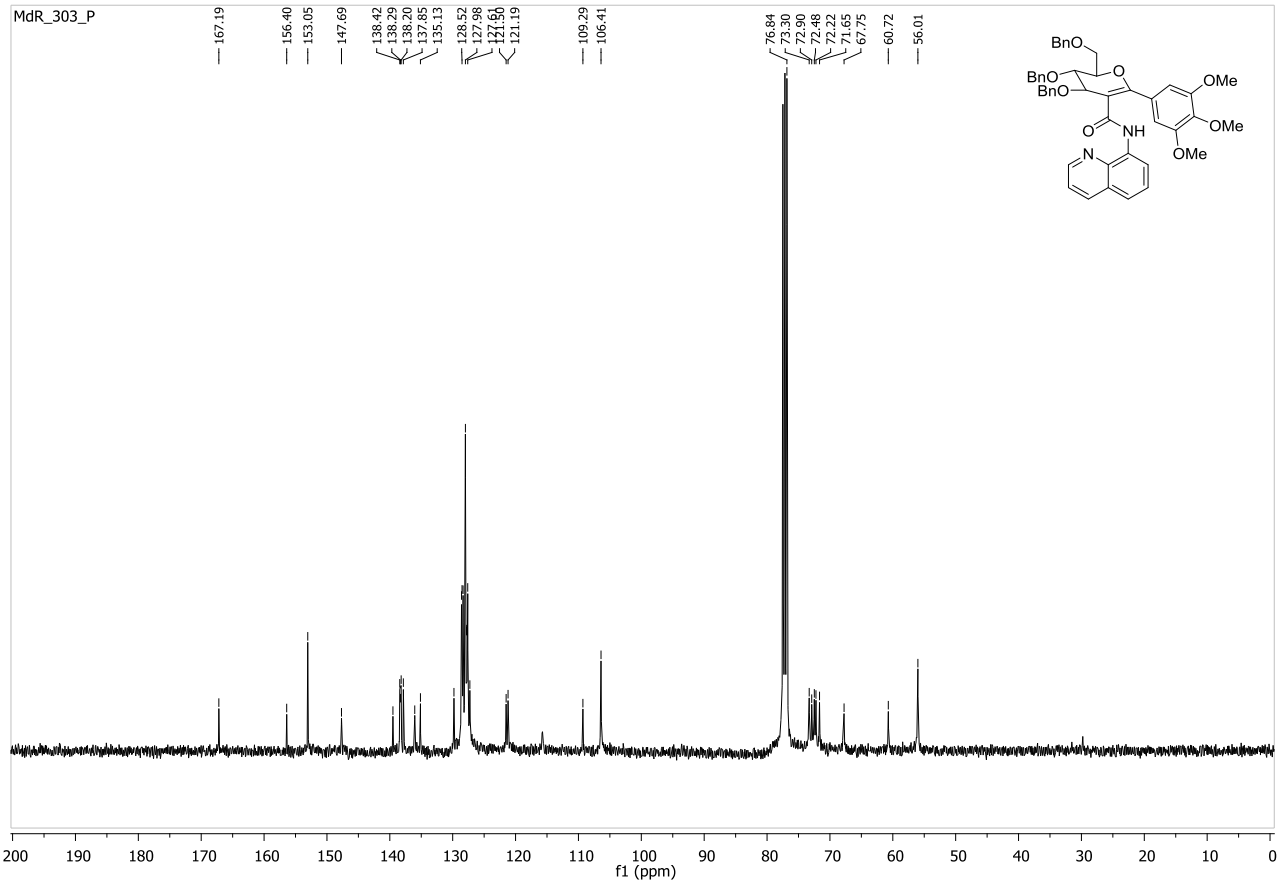
^{13}C-NMR spectrum of **2i**



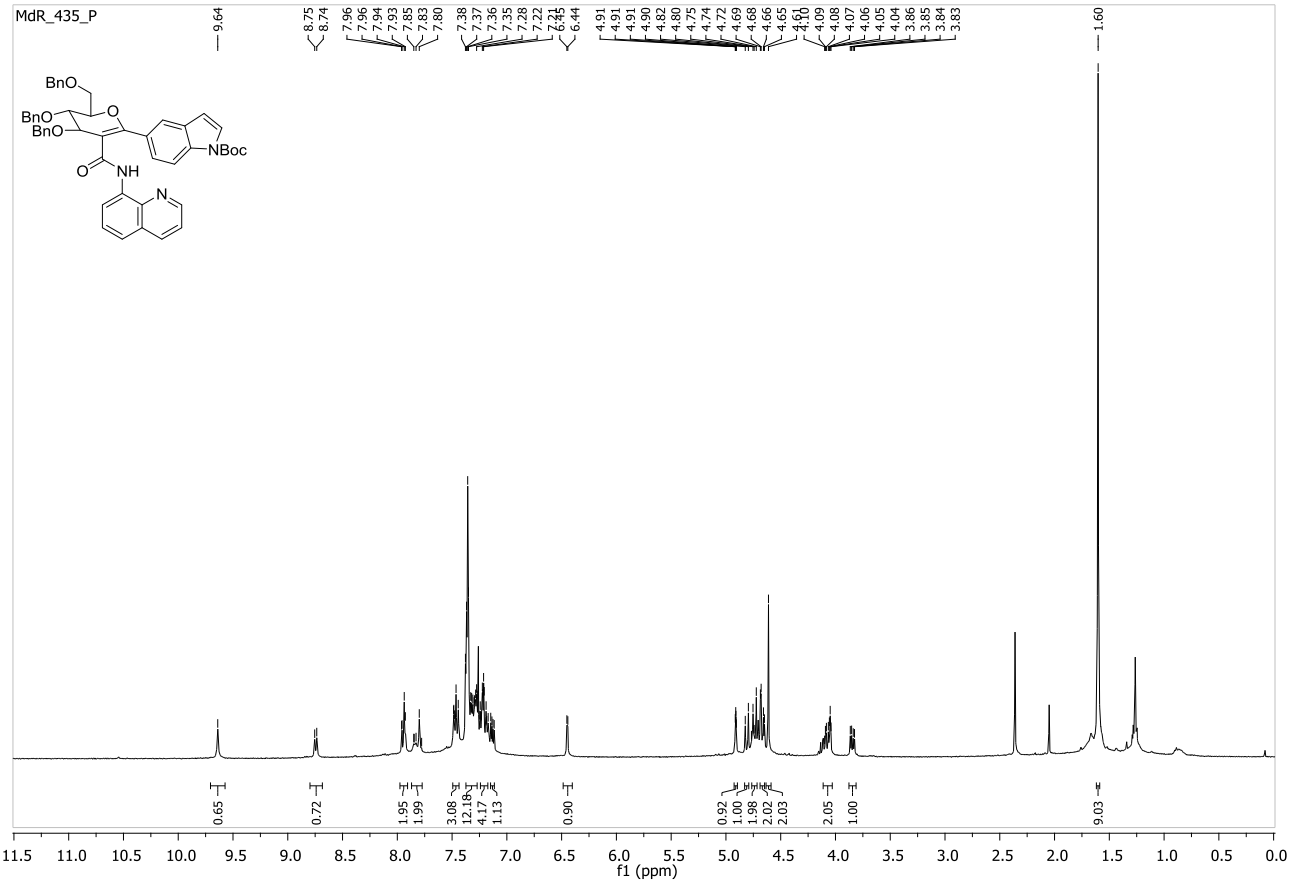
^{1}H-NMR spectrum of **2j**



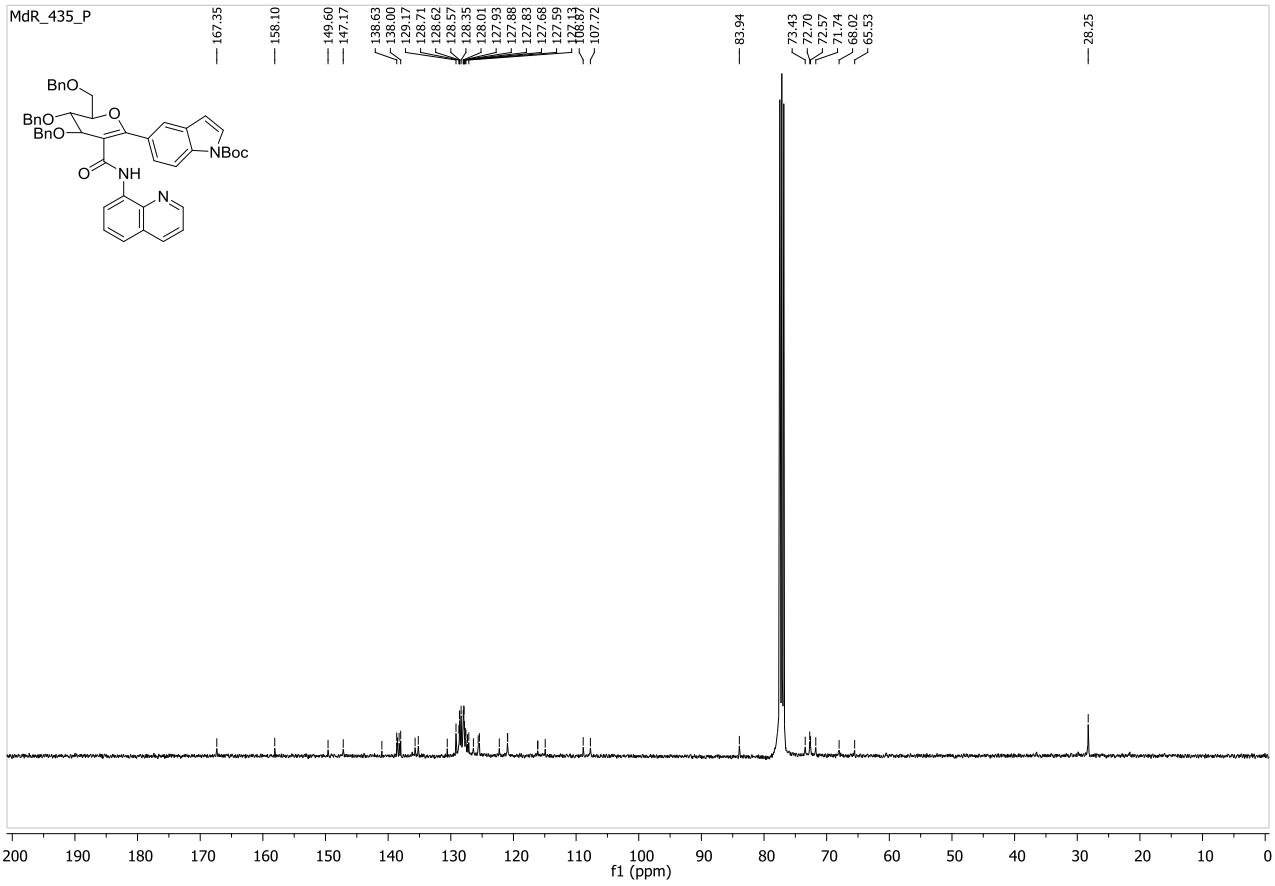
^{13}C-NMR spectrum of **2j**



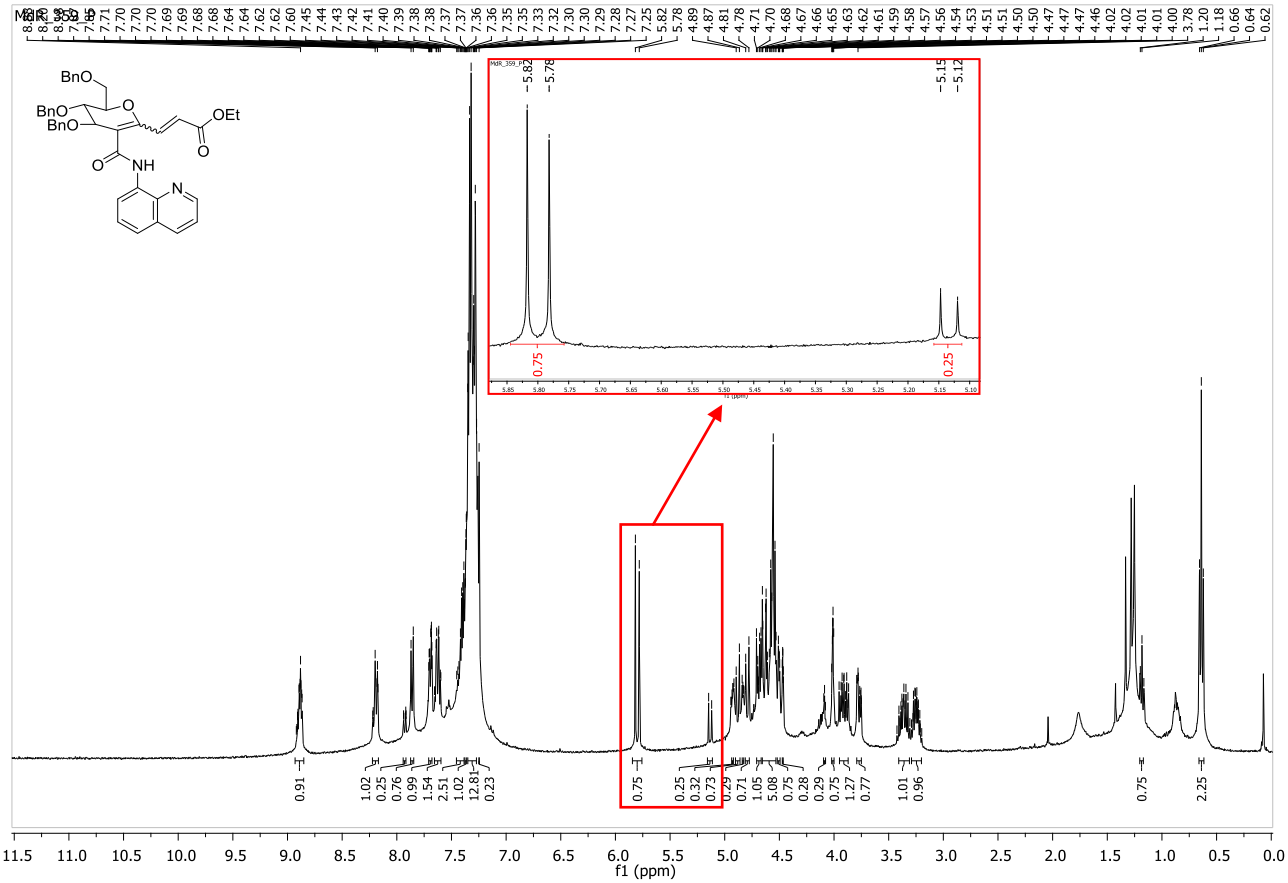
^{1}H-NMR spectrum of **2k**



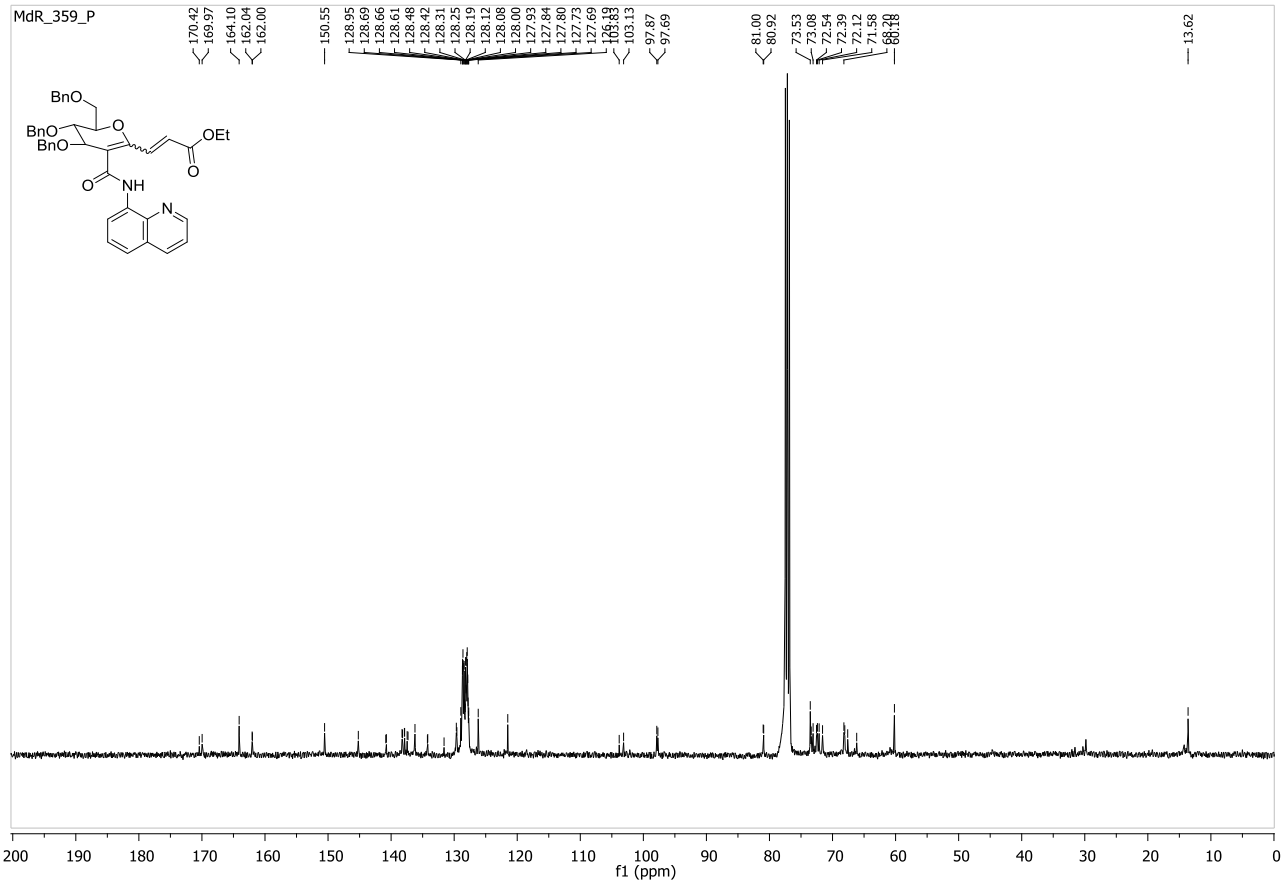
^{13}C-NMR spectrum of **2k**



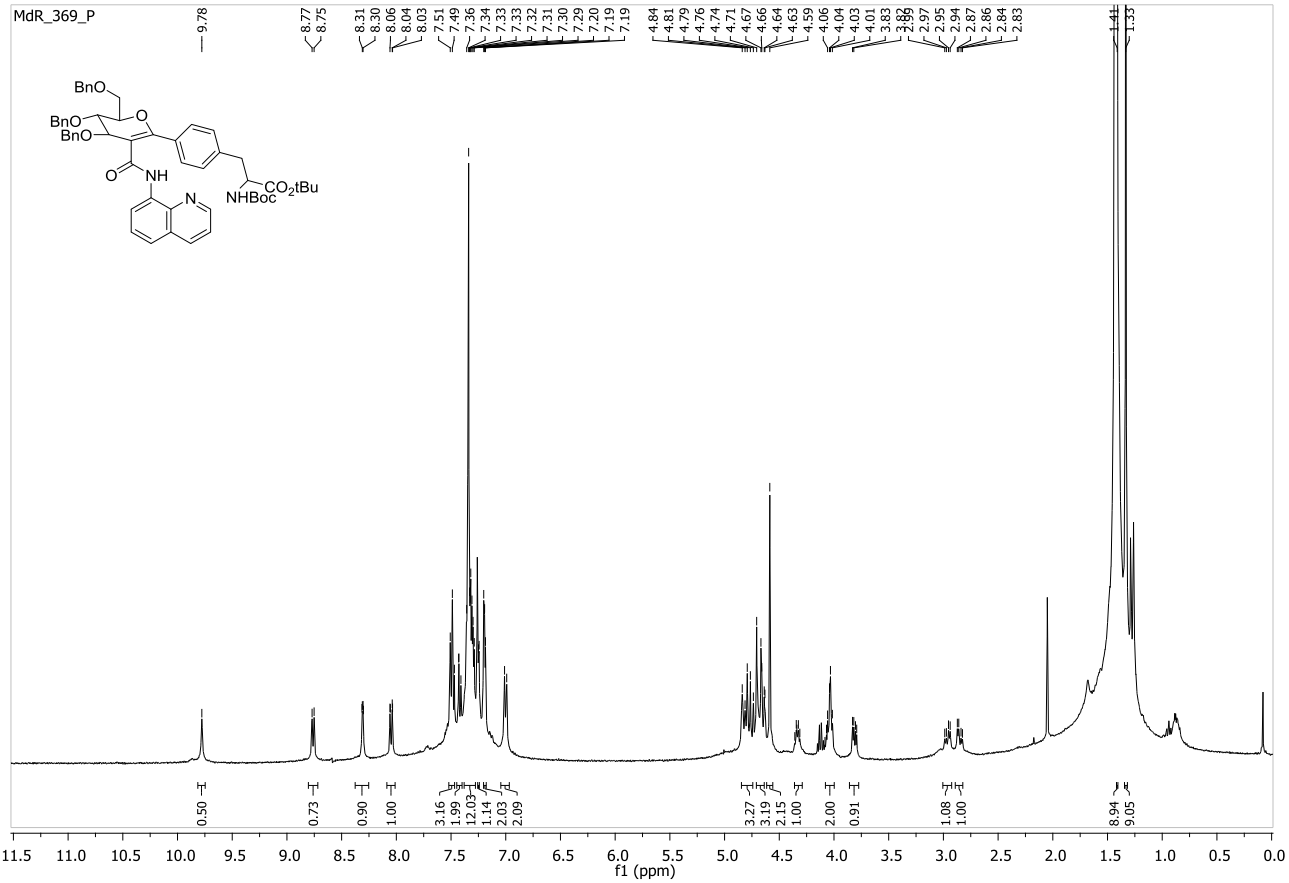
[1]H-NMR spectrum of **2l**



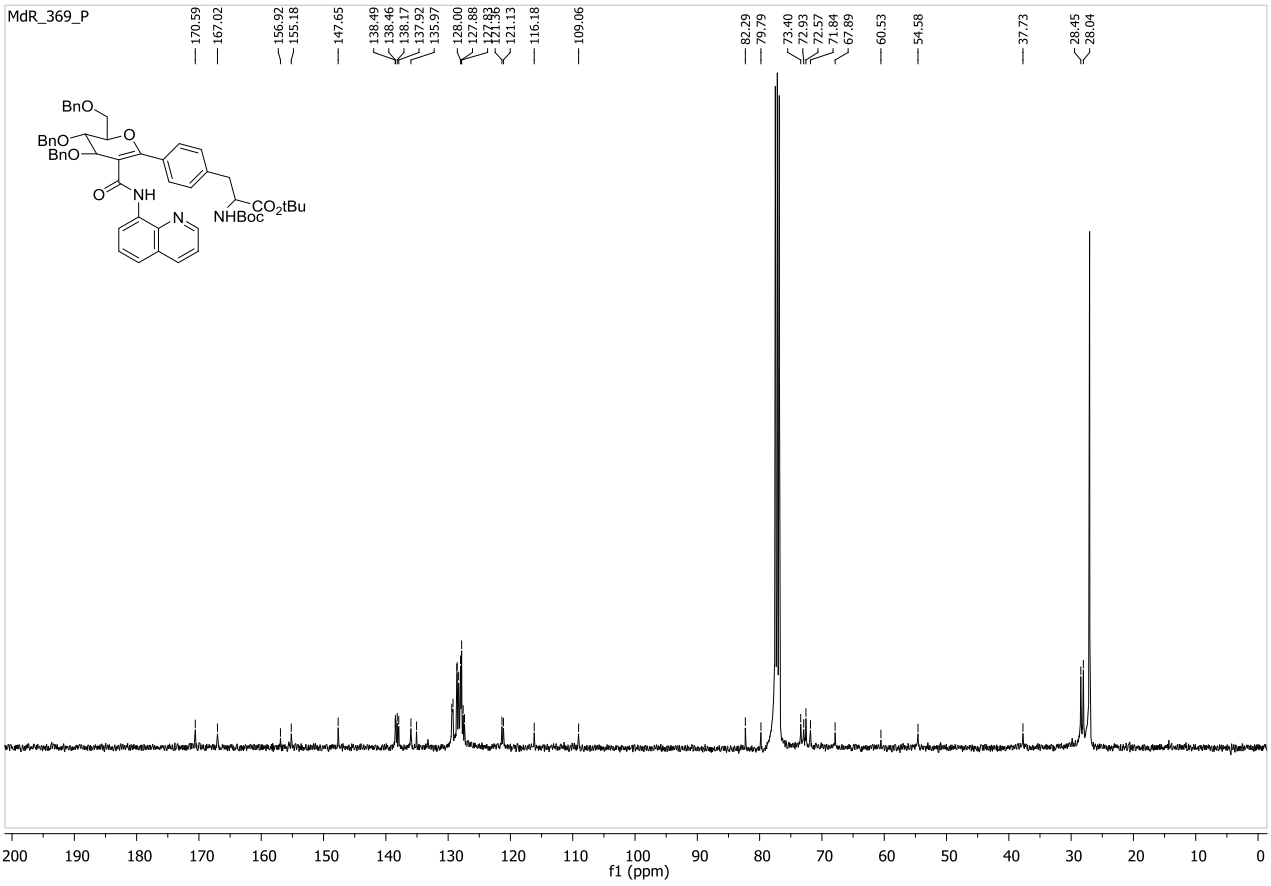
[13]C-NMR spectrum of **2l**



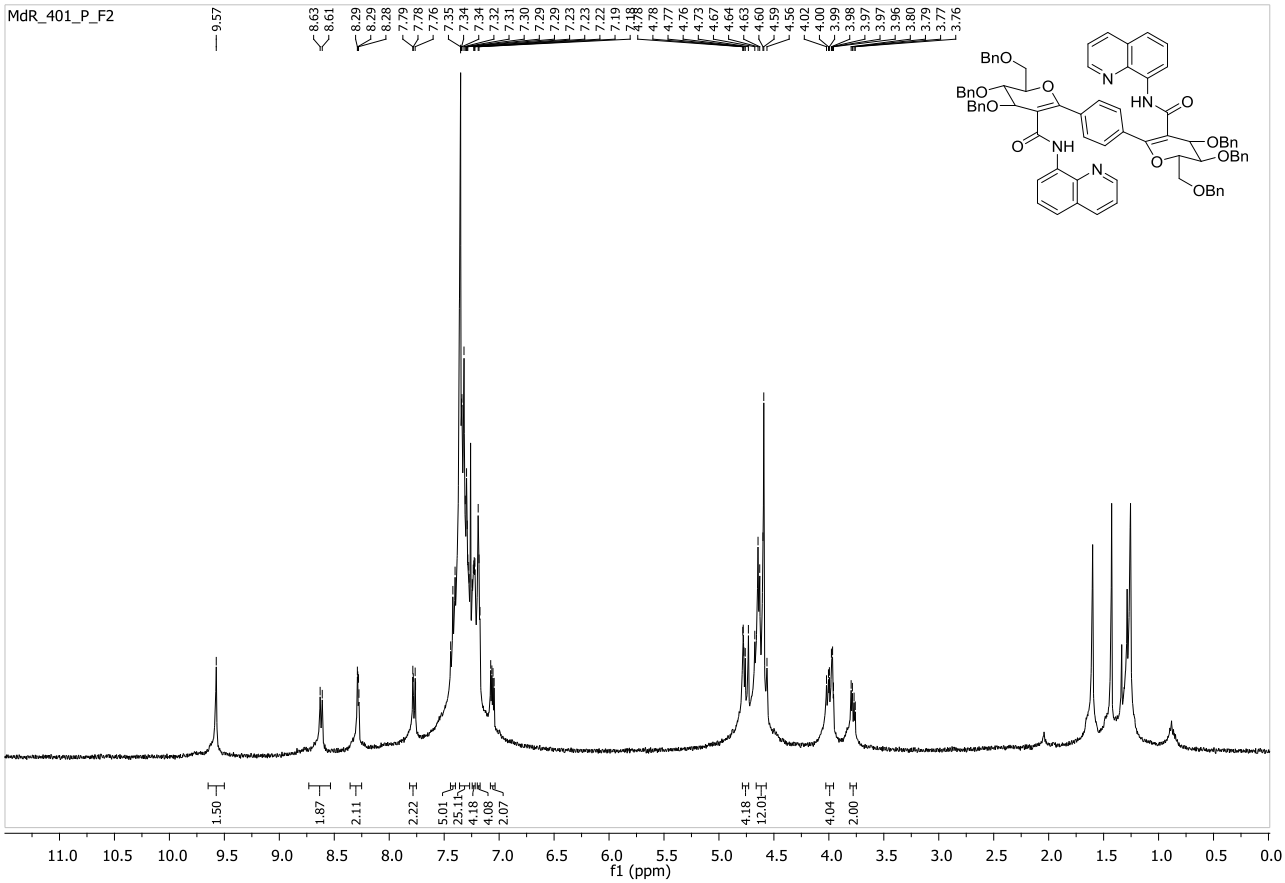
^{1}H-NMR spectrum of **2m**



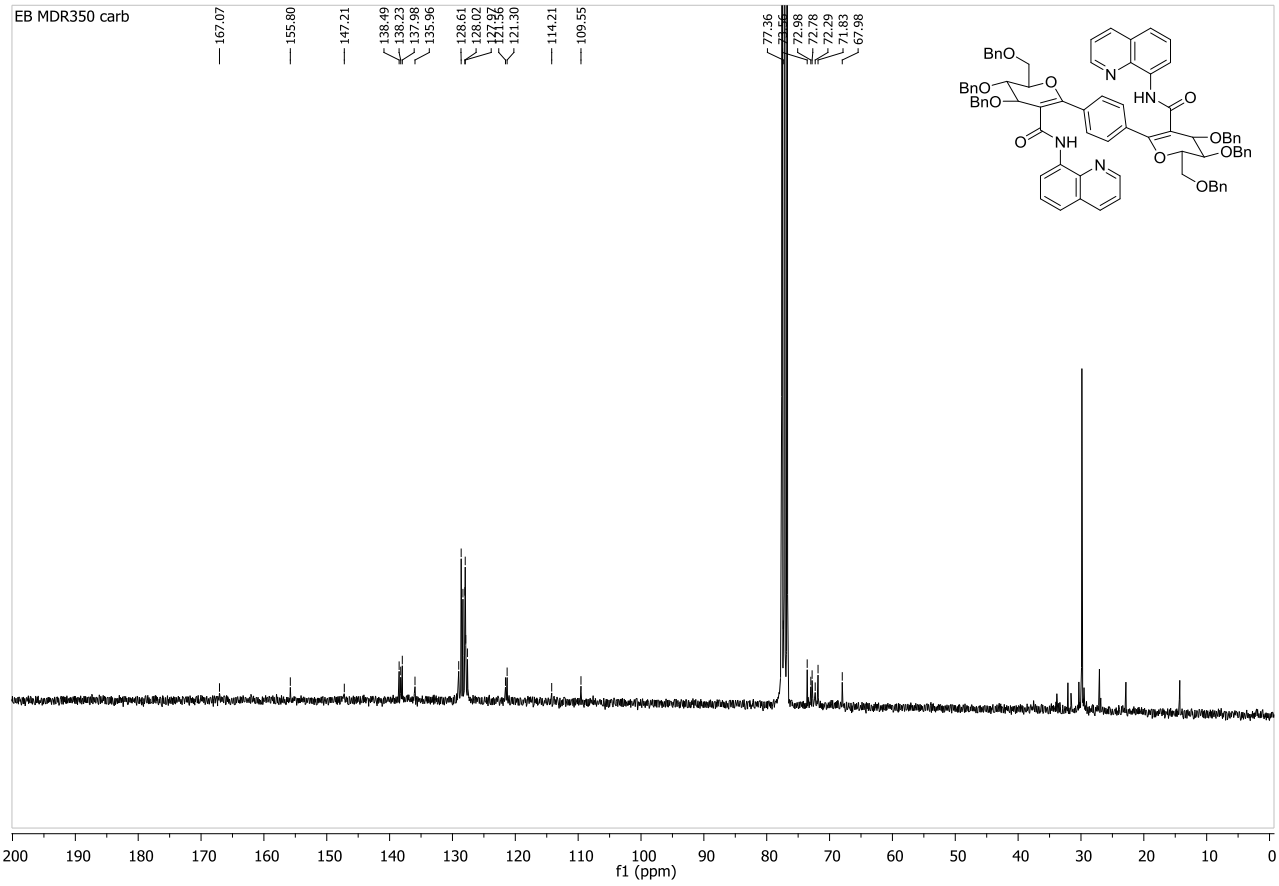
^{13}C-NMR spectrum of **2m**



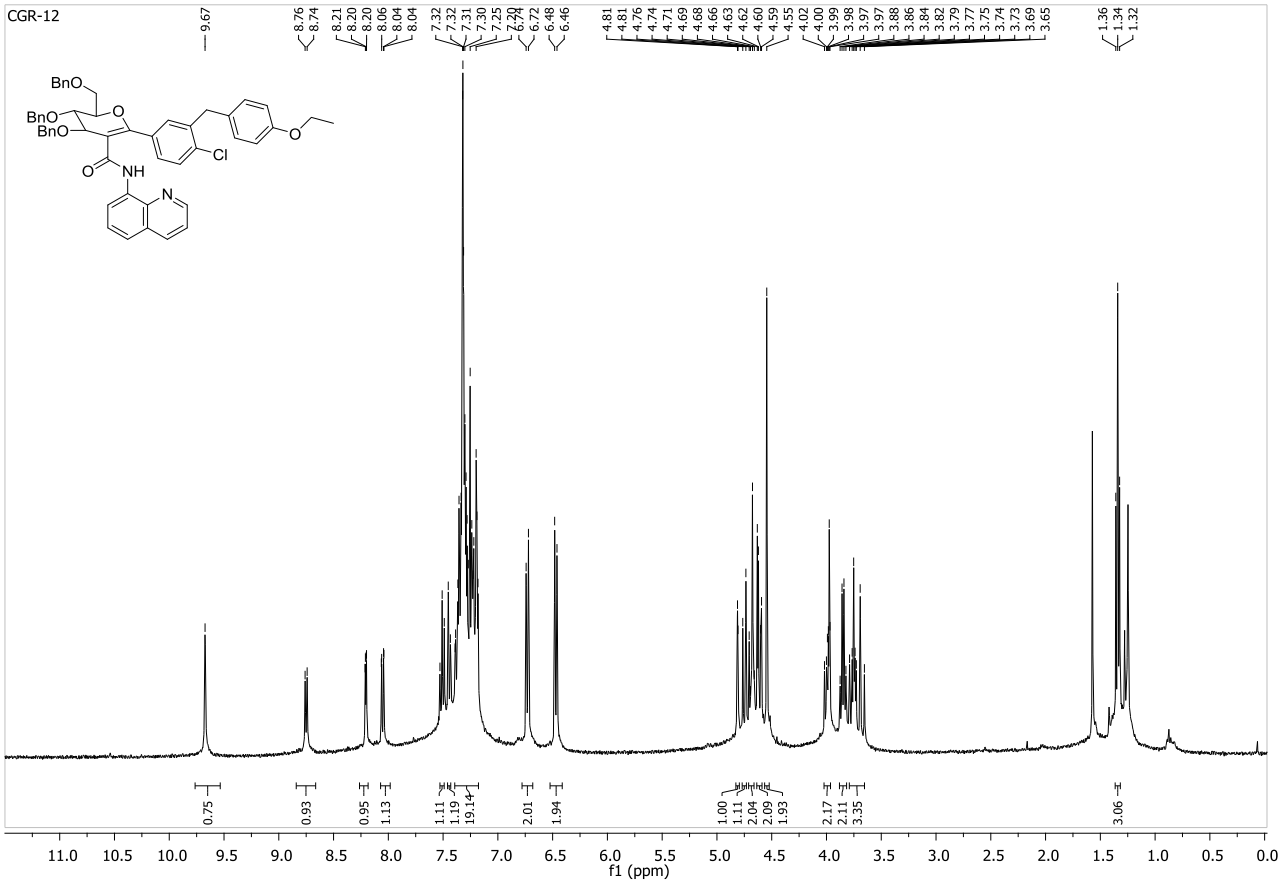
^{1}H-NMR spectrum of **2n**



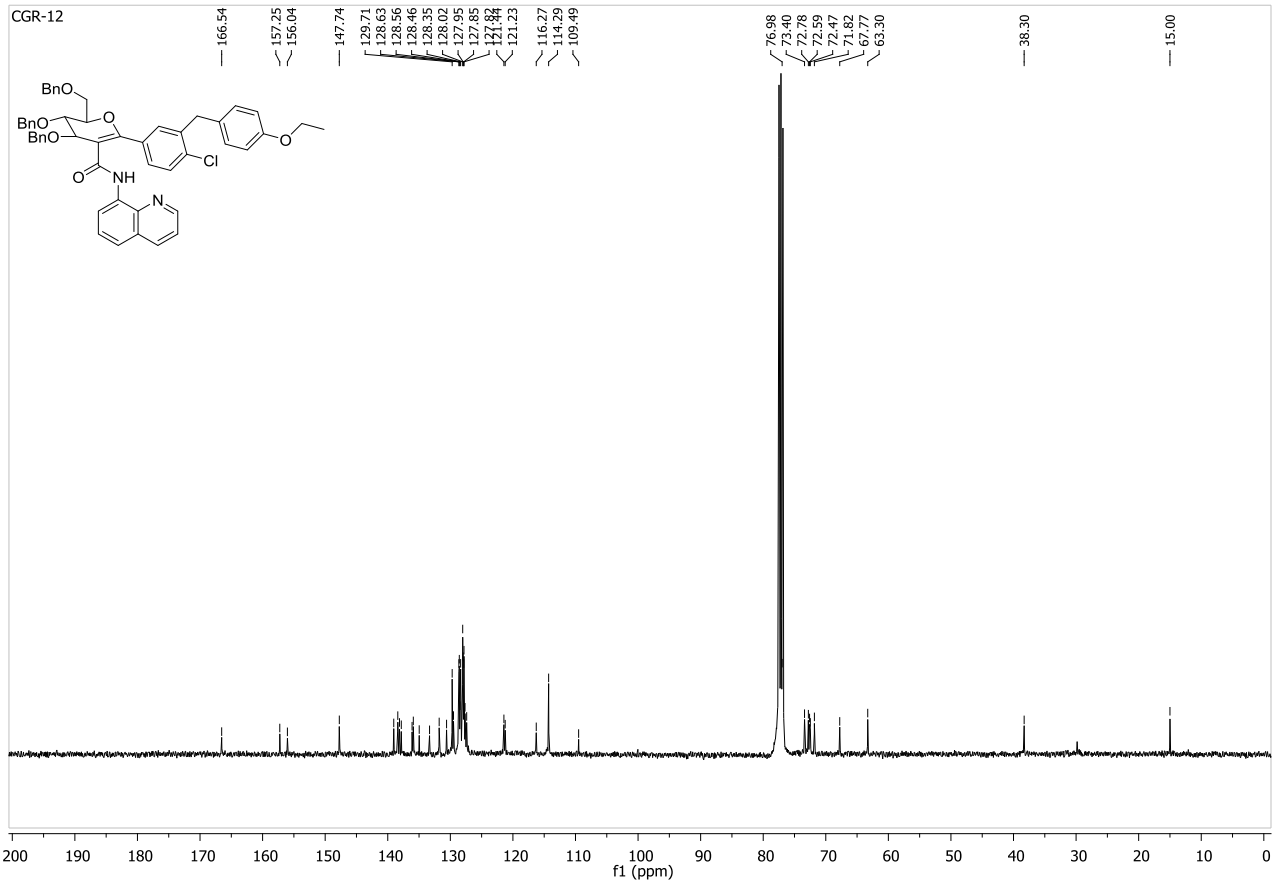
^{13}C-NMR spectrum of **2n**



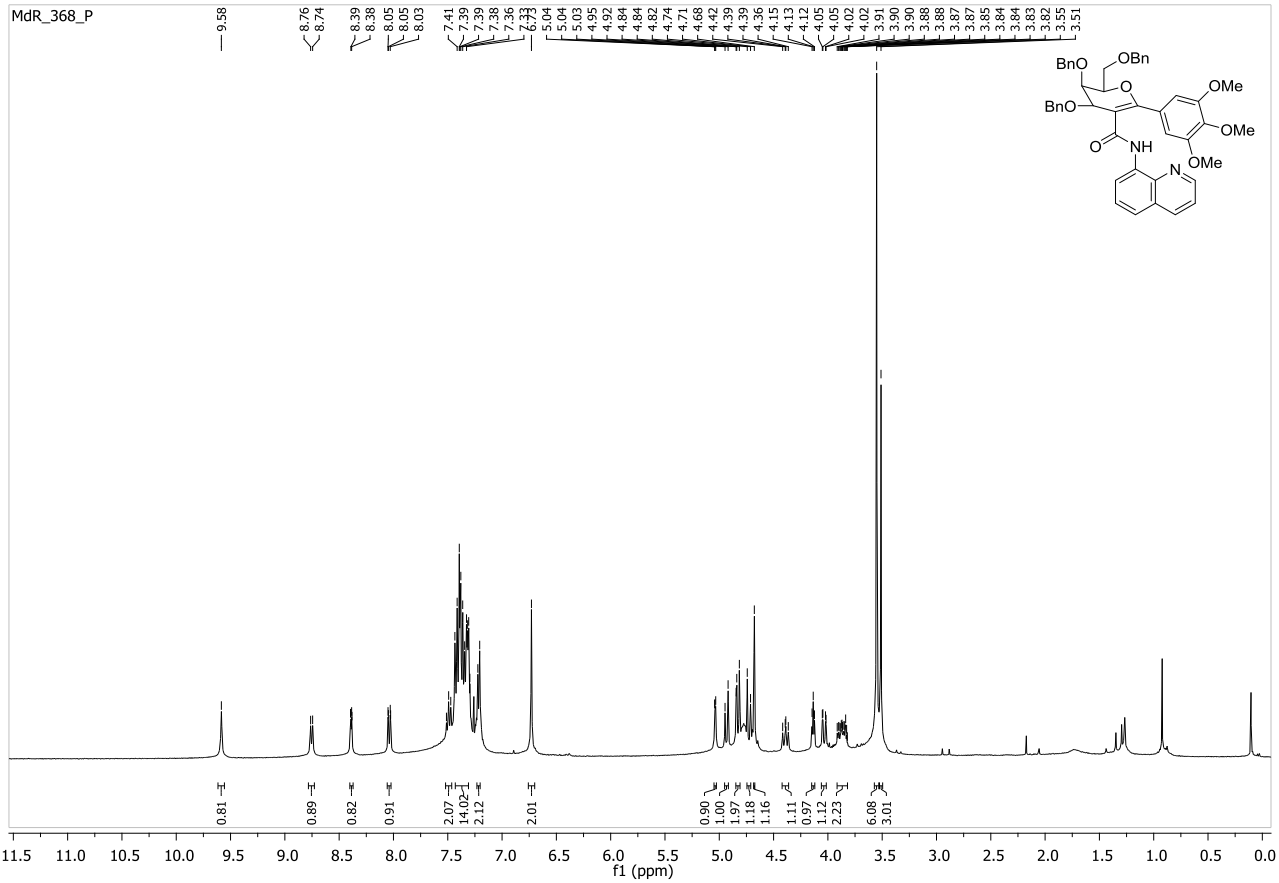
^{1}H-NMR spectrum of **2o**



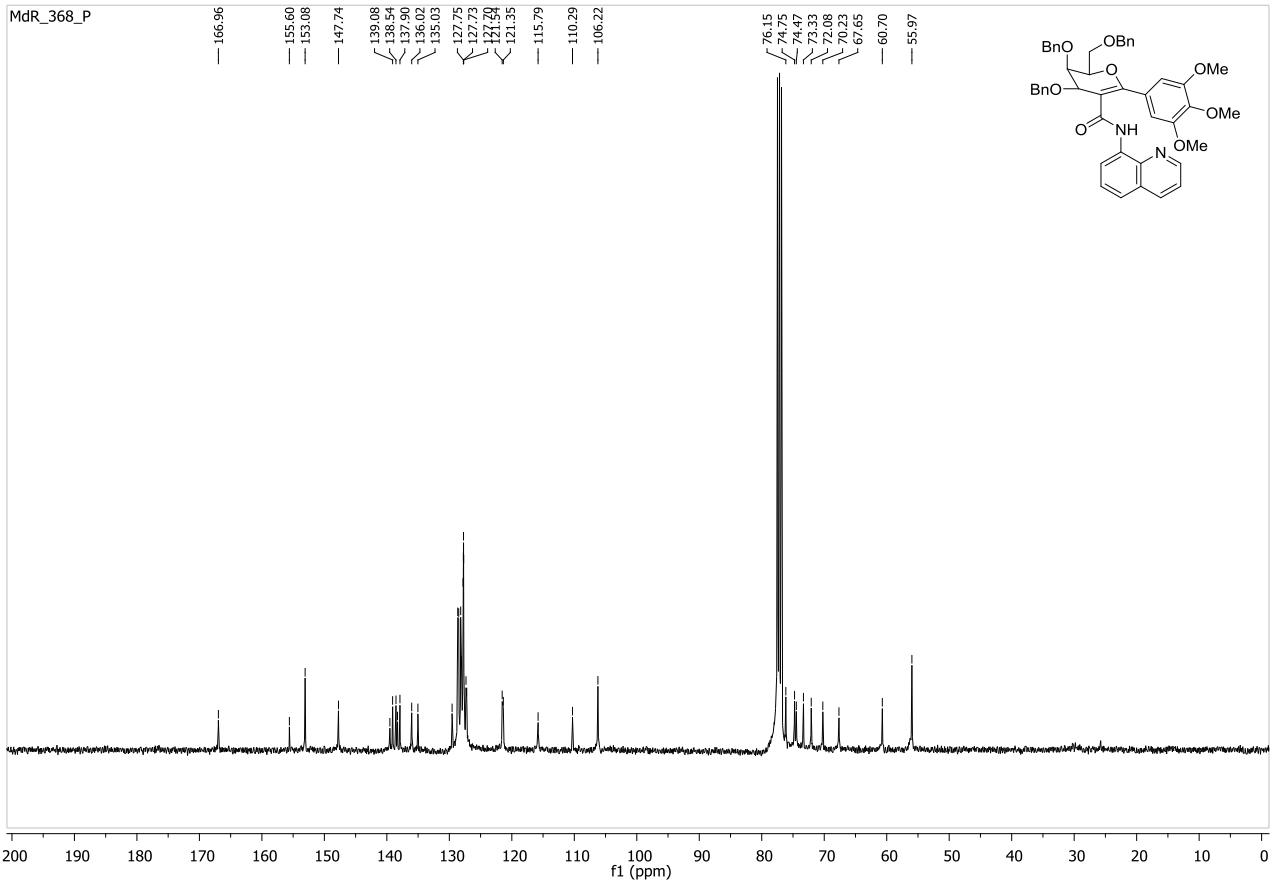
^{13}C-NMR spectrum of **2o**



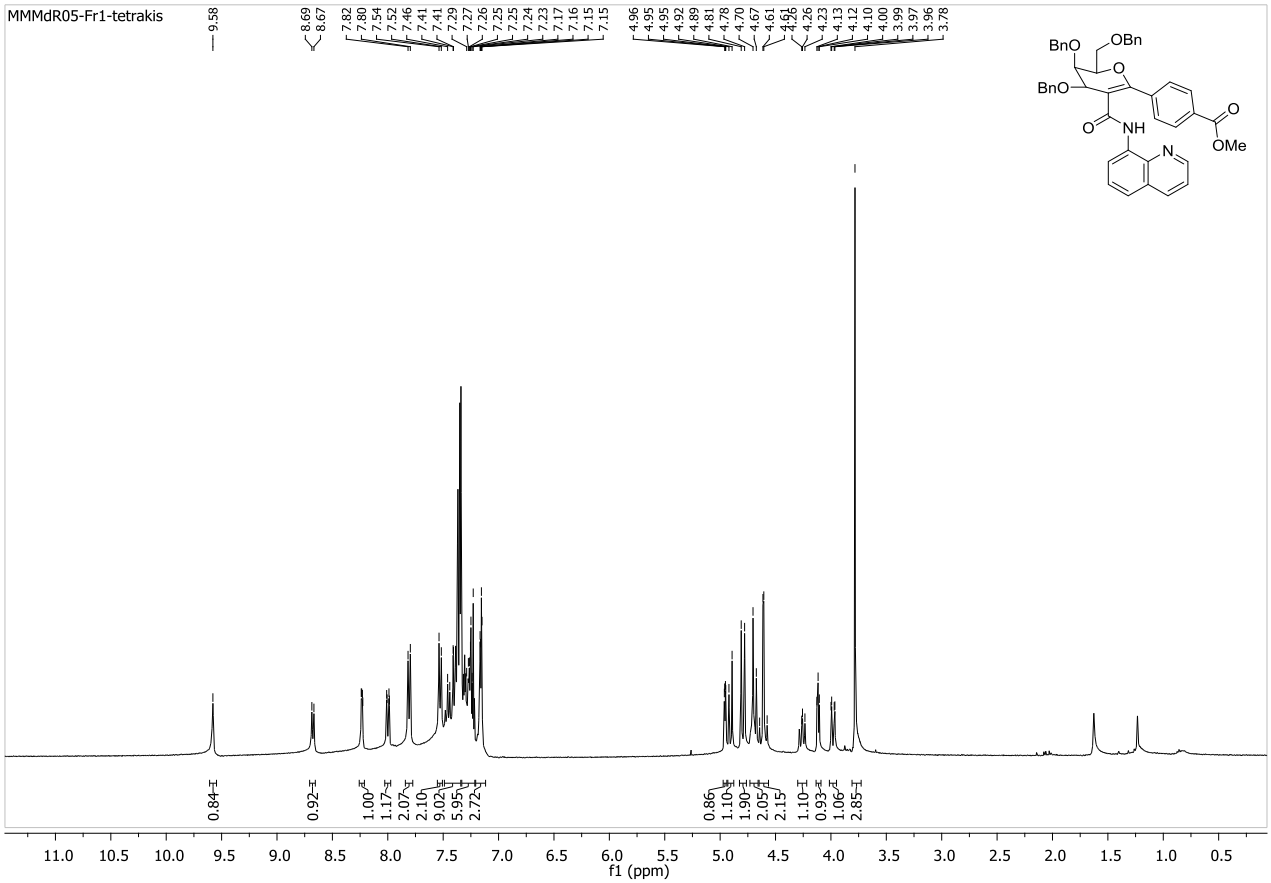
^{1}H-NMR spectrum of **3a**



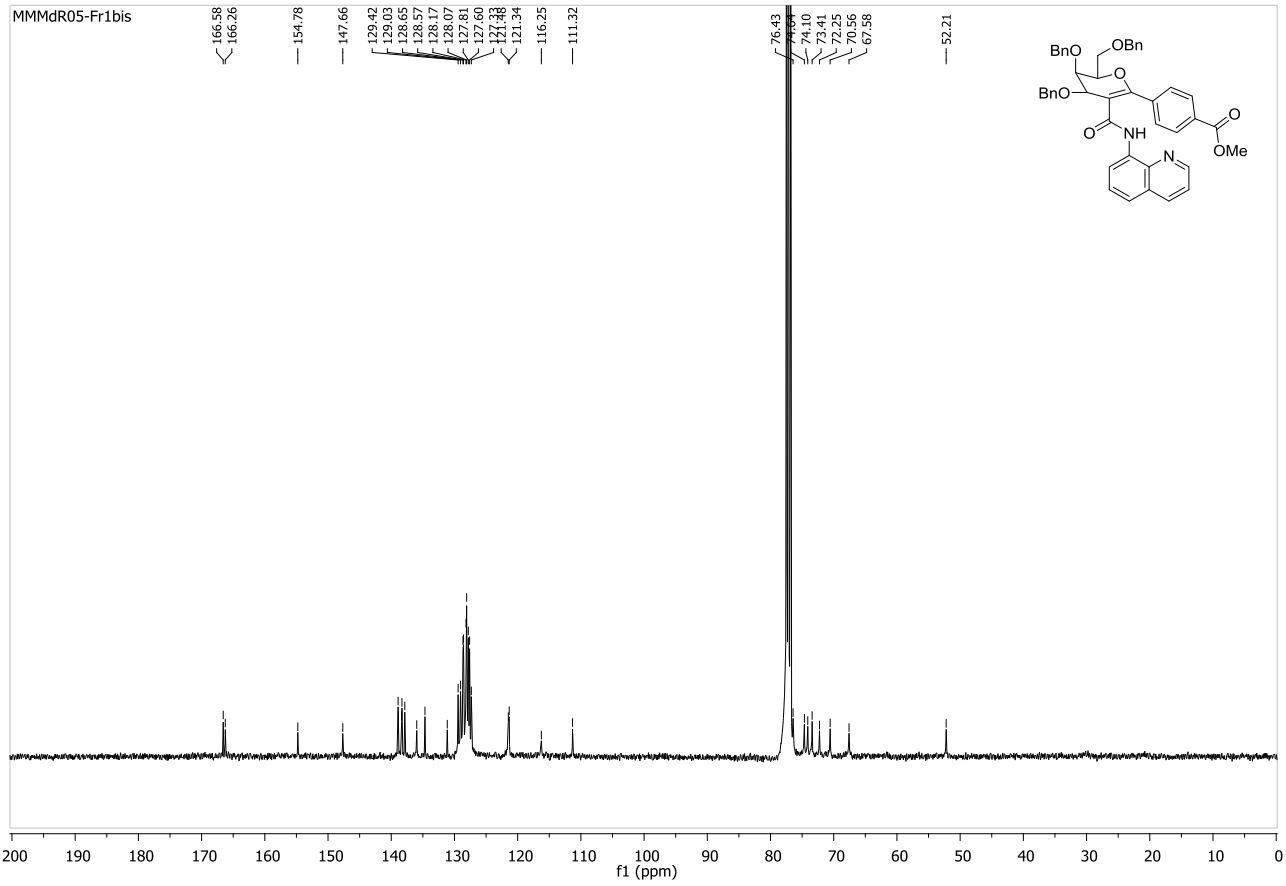
^{13}C-NMR spectrum of **3a**



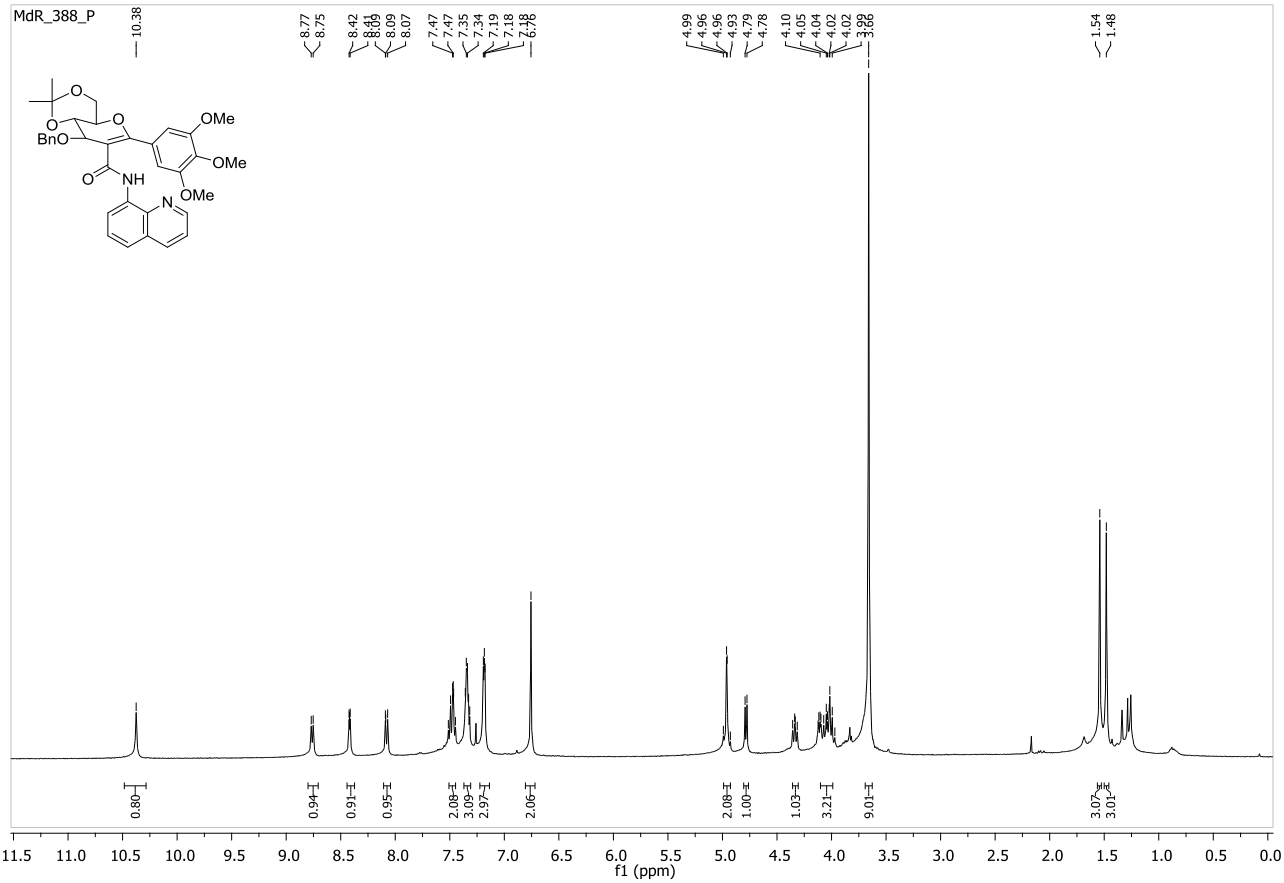
^{1}H-NMR spectrum of **3b**



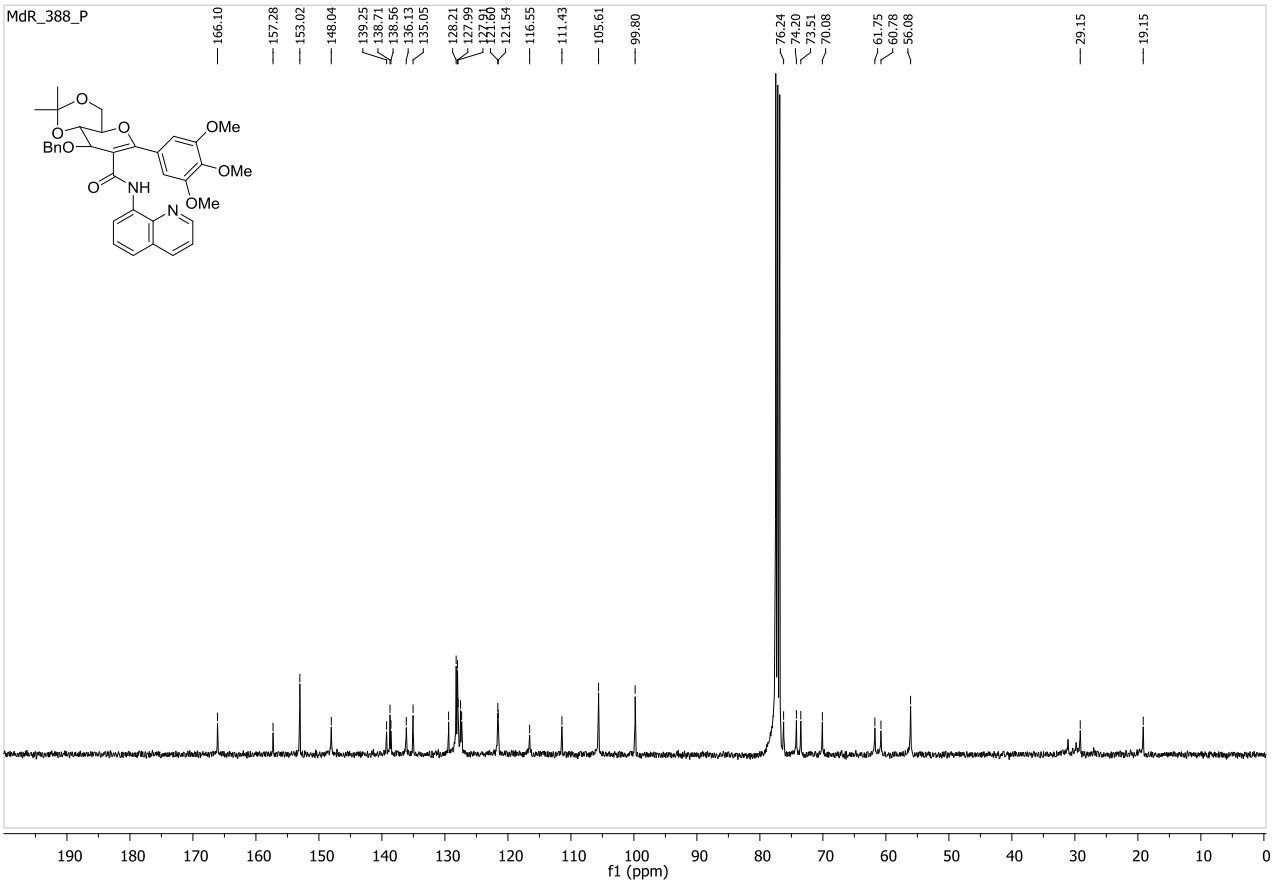
^{13}C-NMR spectrum of **3b**



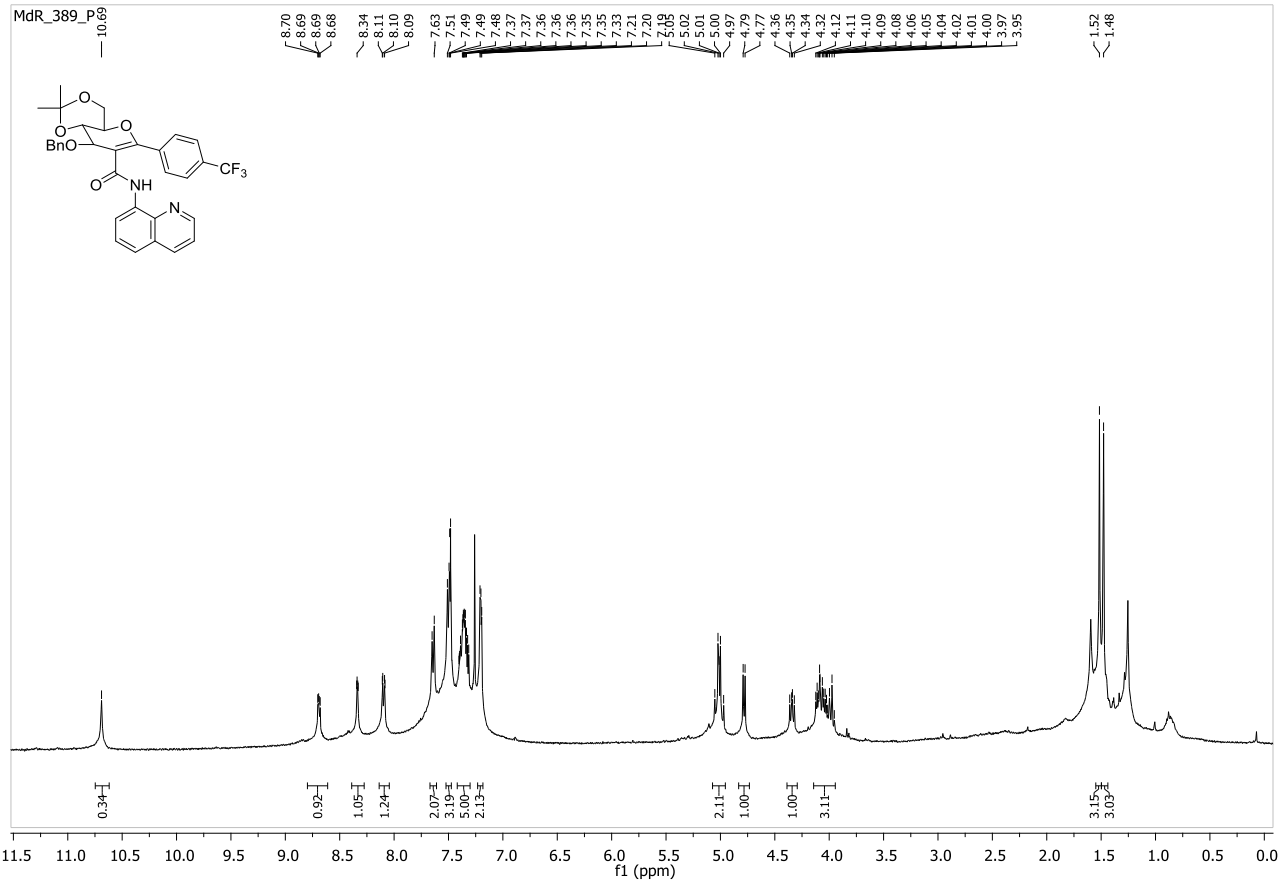
^{1}H-NMR spectrum of **4a**



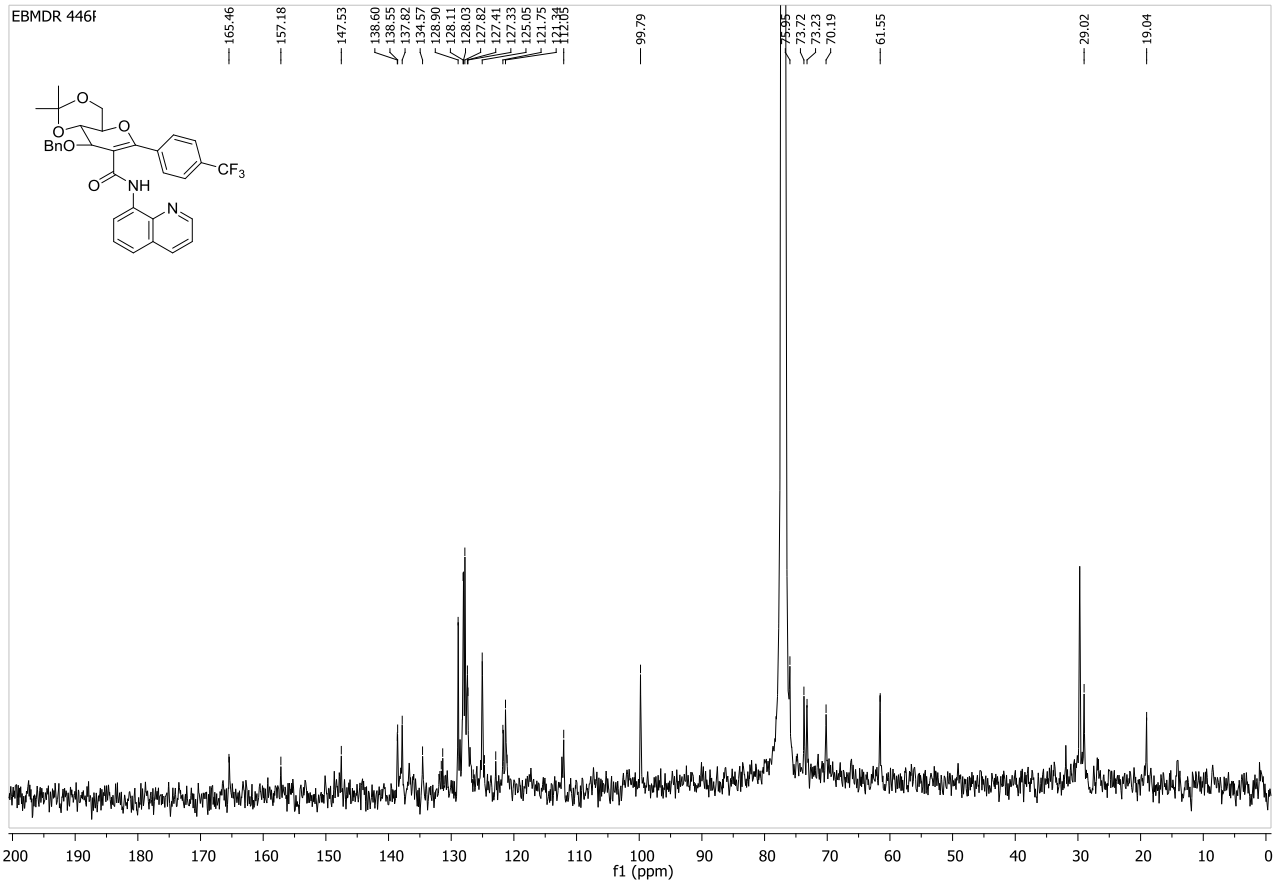
^{13}C-NMR spectrum of **4a**



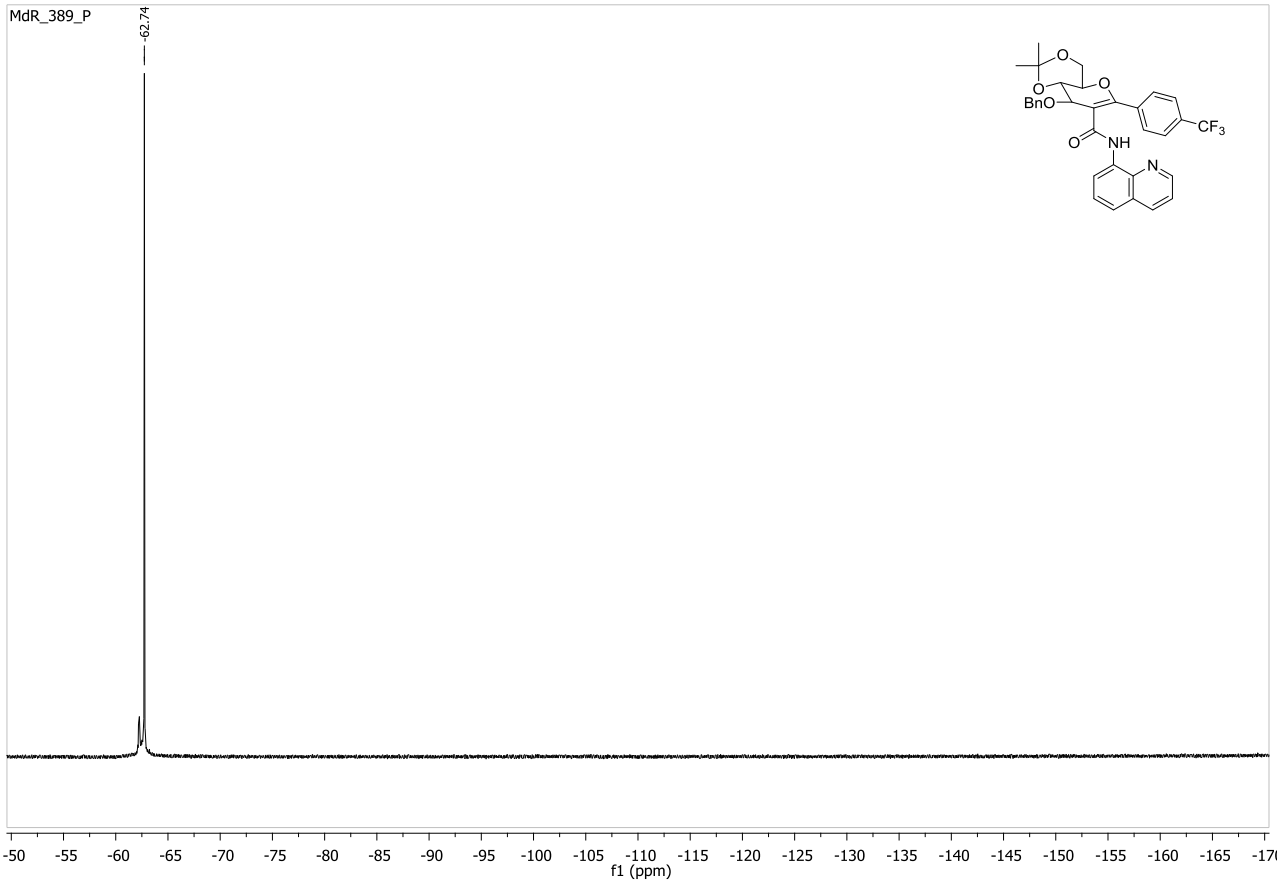
^{1}H-NMR spectrum of **4b**



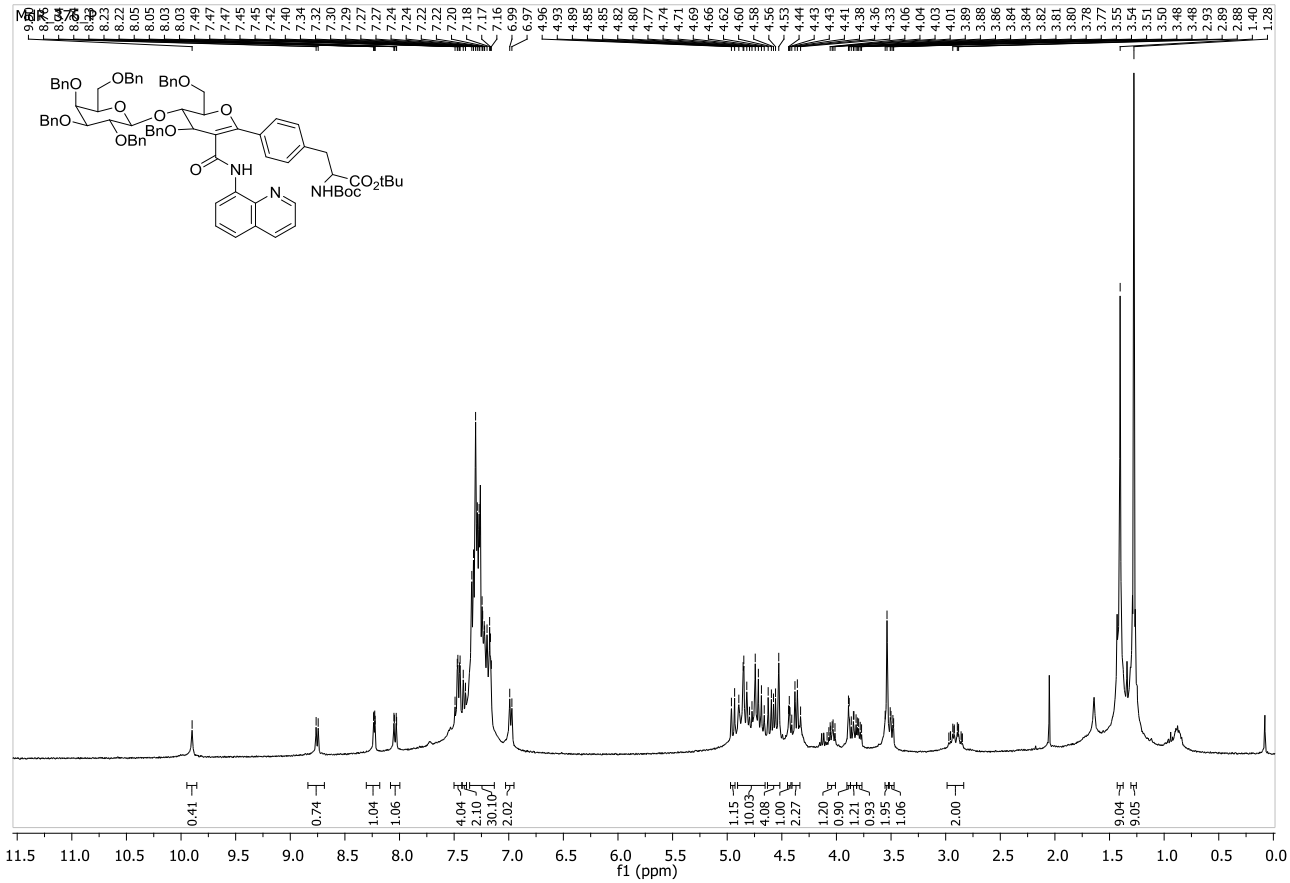
^{13}C-NMR spectrum of **4b**



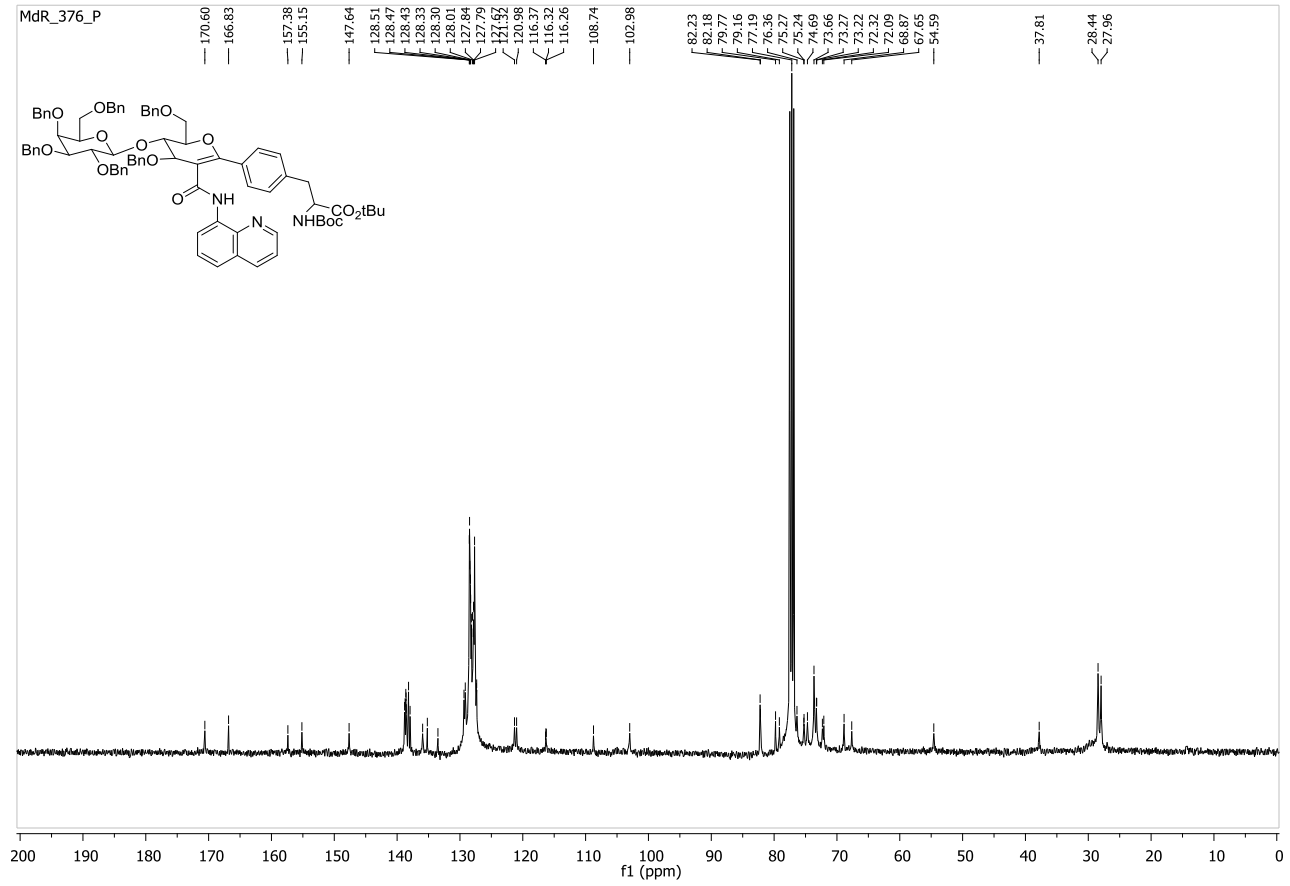
^{19}F-NMR spectrum of **4b**



^{1}H-NMR spectrum of **5**



^{13}C-NMR spectrum of **5**



^{1}H-NMR spectrum of **7**