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SUPPORTING INFORMATION

Title: Stereocontrolled Synthesis of 2-Fluorinated *C*-Glycosides
Author(s): Anna Sadurní, Ryan Gilmour*

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I. General Information

All chemicals were reagent grade and used without further purification. Dry solvents were dried by a Grubbs purification system including columns packed with molecular sieves and aluminium oxide. Solvents for extractions and chromatography were technical grade and distilled prior to use. Extracts were dried over technical grade $MgSO_4$. Analytical thin layer chromatography (TLC) was performed on aluminium foil pre-coated with SiO_2-60 F254 (*Merck*) and visualised with a UV-lamp (254 nm) and CAM solution. Flash column chromatography was carried out on SiO_2-60 (230-400 mesh ASTM; *Fluka*). Concentration *in vacuo* was performed at ~10 mbar and 45 °C, drying at ~10-2 mbar and room temperature. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra were recorded by the NMR service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster on a *Bruker AV300*, *Agilent DD2 500* or an *Agilent DD2 600* spectrometer at room temperature. The multiplicities are reported as: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, sept. = septet and m = multiplet. The assignment of the resonances of the new compounds was supported by additional 1D and 2D NMR experiments (e.g., 1H{19F}, DEPT, COSY, HMBC, HSQC and NOESY). Melting points were measured on a *Büchi B-545* melting-point apparatus in open capillaries. IR spectra were recorded on a *Perkin-Elmer 100 FT-IR* (ATR) spectrometer, selected adsorption bands are reported in wavenumbers (cm–1) and intensities are reported as: w = weak, m = medium, s =strong and br = broad. High-resolution mass spectra (HR ESI) were measured by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster. The optical rotations were measured on a *JASCO P2000* polarimeter.

Starting materials for the preparation of lactones L-X were prepared according to the following:

- C. Bucher, R. Gilmour, *Angew. Chem. Int. Ed.* **2010**, *49*, 8724-8728.
- E. Durantie, C. Bucher, R. Gilmour, *Chem. Eur. J.* **2012**, *18*, 8208-8215.

The lactones were prepared according to:

- **L1**, **L2**, **L3** were prepared as described by A. Sadurní, G. Kehr, M. Ahlqvist, H. Peilot Sjögren, C. Kankkonen, L. Knerr, R. Gilmour, *Chem. Eur. J.* **2018**, *24*, 2832-2836.
- **L4** was prepared as described by D. Waschke, Y. Leshch, J. Thimm, U. Himmelreich, J. Thiem, *Eur. J. Org. Chem.* **2012**, 948-959.

Compound **S10** was prepared according to A. P. Kale, G. G. Pawar, M. Kapur, *Org. Lett.* **2012**, *14*, 1808-1811.

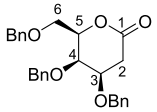
Determination of α:β ratios was achieved by coupling constant analysis and nOesy experiments.

Abbreviations: *tert*-BPPTS (*tert*-butylpyridinium *p*-toluensulfonate); CSA (Camphorsulfonic acid)

II. Experimental Section

II.1 Synthesis of lactones

Compound L5:



Ac_2O (5.4 mL) was added to a solution of *tri*-benzylated-2-deoxy-galactose (1.0 g, 2.3 mmol, 1.0 eq.) in DMSO (14.0 mL). The reaction mixture was stirred overnight at room temperature. The reaction mixture was then diluted with CH_2Cl_2 (15.0 mL) and H_2O (15.0 mL), the phases were separated, and the water phase was extracted with CH_2Cl_2 (3 x 10.0 mL). The combined organic layers were washed with H_2O (3 x 10.0 mL) and brine (1 x 10.0 mL). The solution was then dried over $MgSO_4$, filtered and dried *in vacuo*. The residue obtained was purified by flash column chromatography (SiO_2, CyH: EtOAc 3:1) to give compound **L5** (400 mg, 40%) as a colourless oil.

R_f 0.26 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 455.1828 $(M + Na)^+$, $C_{27}H_{28}O_5Na^+$ calculated 455.1829;

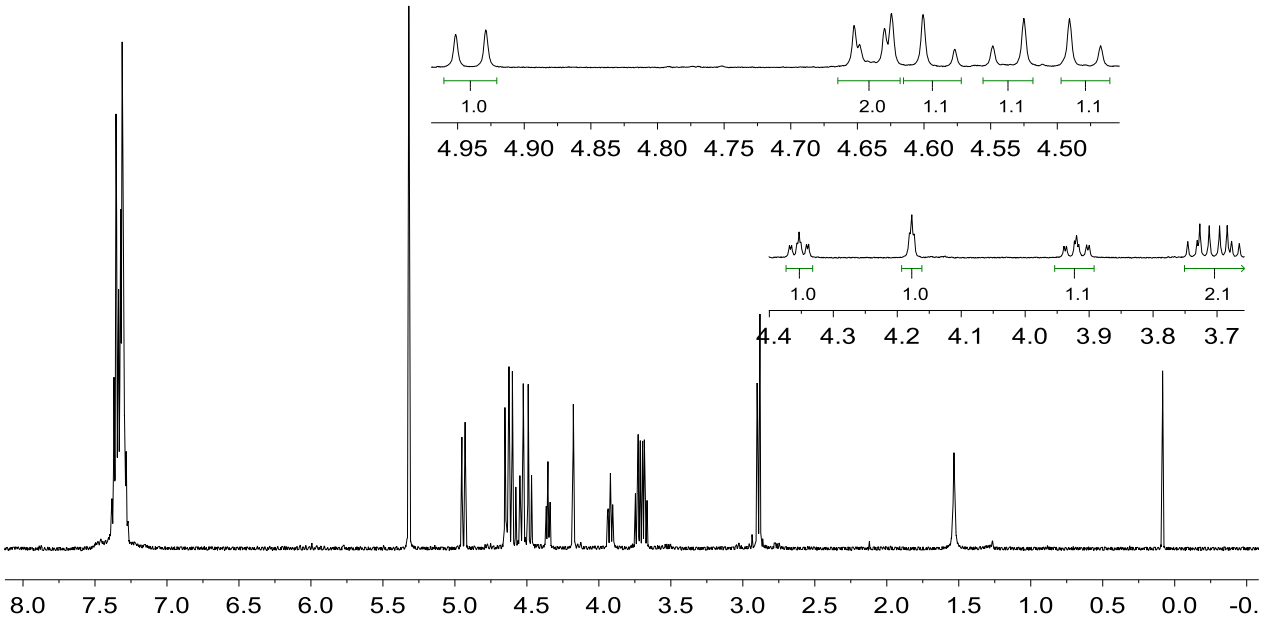
$[\alpha]_D^{25}$ +7.6 (*c* 1.00 in DCM);

ν_{max} (neat)/cm^{-1} 3676w, 2972m, 2901m, 1734s, 1497m, 1454m, 1362m, 1329w, 1227s, 1162m, 1136m, 1090s, 1058s, 1027s, 912m, 816m, 733s, 695s;

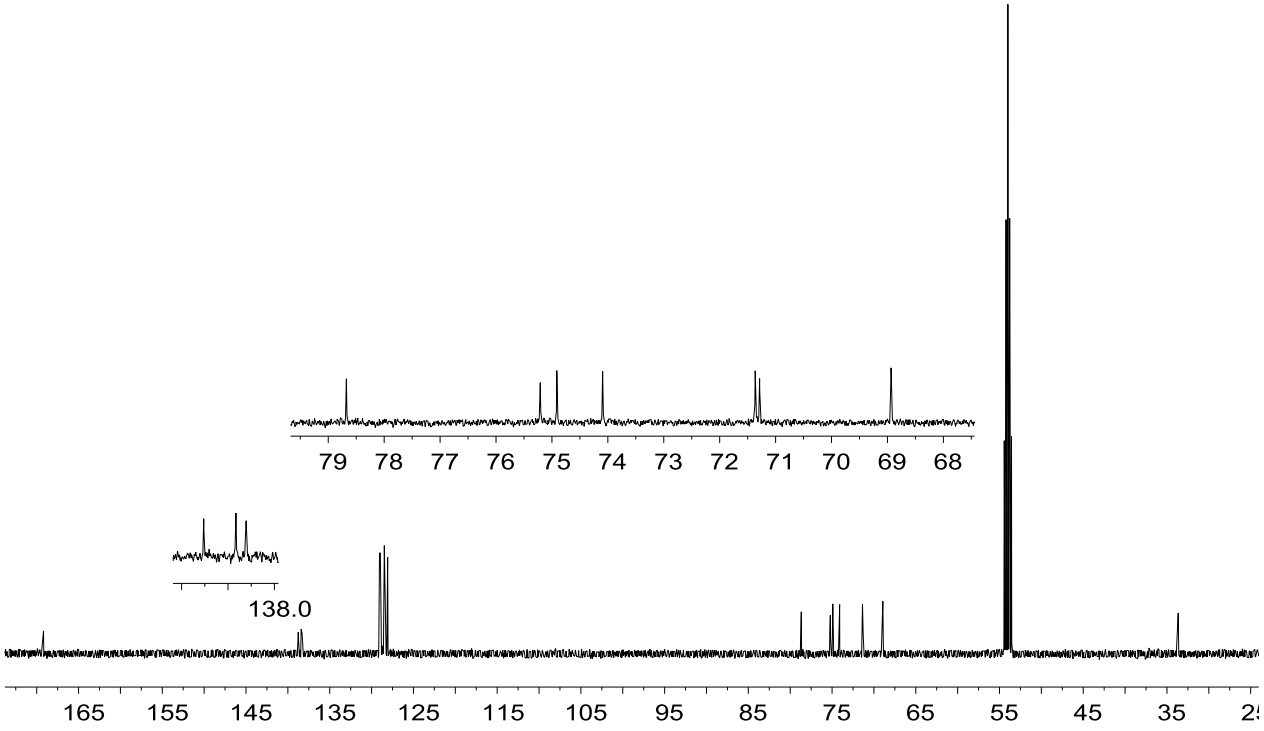
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.39 – 7.26 (m, 15H, H-Ph), 4.94 (d, *J* = 11.3 Hz, 1H, H-C$\underline{H}_2$Ph), 4.64 (d, *J* = 11.3 Hz, 1H, H-C$\underline{H}_2$Ph), 4.64 (d, *J* = 12.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.59 (d, *J* = 12.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.54 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.48 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.35 (ddd, *J* = 7.5, 5.9, 1.7 Hz, 1H, H-C5), 4.18 (t, *J* = 1.8 Hz, 1H, H-C4), 3.92 (ddd, *J* = 9.9, 8.1, 2.0 Hz, 1H, H-C3), 3.77 – 3.66 (m, 2H, H-C6), 2.91 – 2.88 (m, 2H, H-C2);

^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 169.2 (C1), 138.8 (*i*-Ph), 138.4 (*i*-Ph), 138.3 (*i*-Ph), 129.1 (*o*,*m*,*p*-Ph), 129.0 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 78.7 (C5), 75.2 (C3), 74.9 (C$\underline{H}_2$Ph), 74.1 (C$\underline{H}_2$Ph), 71.4 (C$\underline{H}_2$Ph), 71.3 (C4), 68.9 (C6), 33.7 (C2).

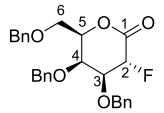
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound L6:



Ac_2O (5.4 mL) was added to a solution of *tri*-benzylated-2-deoxy-2-fluoro-galactose (900 mg, 1.6 mmol, 1.0 eq.) in DMSO (9.0 mL). The reaction mixture was stirred overnight at room temperature. The reaction mixture was diluted with CH_2Cl_2 (27.0 mL) and H_2O (27.0 mL), the phases were separated, and the water phase was extracted with CH_2Cl_2 (3 x 18.0 mL). The combined organic layers were washed with H_2O (3 x 18.0 mL) and brine (1 x 18.0 mL). The subsequent solution was dried over $MgSO_4$, filtered and dried *in vacuo*. The residue obtained was purified by flash column chromatography (SiO_2, CyH: EtOAc 3:1) to give compound **L6** (630 mg, 70%) as a white solid.

R_f 0.40 (SiO_2, CyH:EtOAc 3:1);

Mp 84 – 88 °C;

m/*z* (ESI) found: 473.1734 $(M + Na)^+$, $C_{27}H_{27}O_5FNa^+$ calculated 473.1735;

$[\alpha]_D^{25}$ +35.3 (*c* 1.00 in DCM);

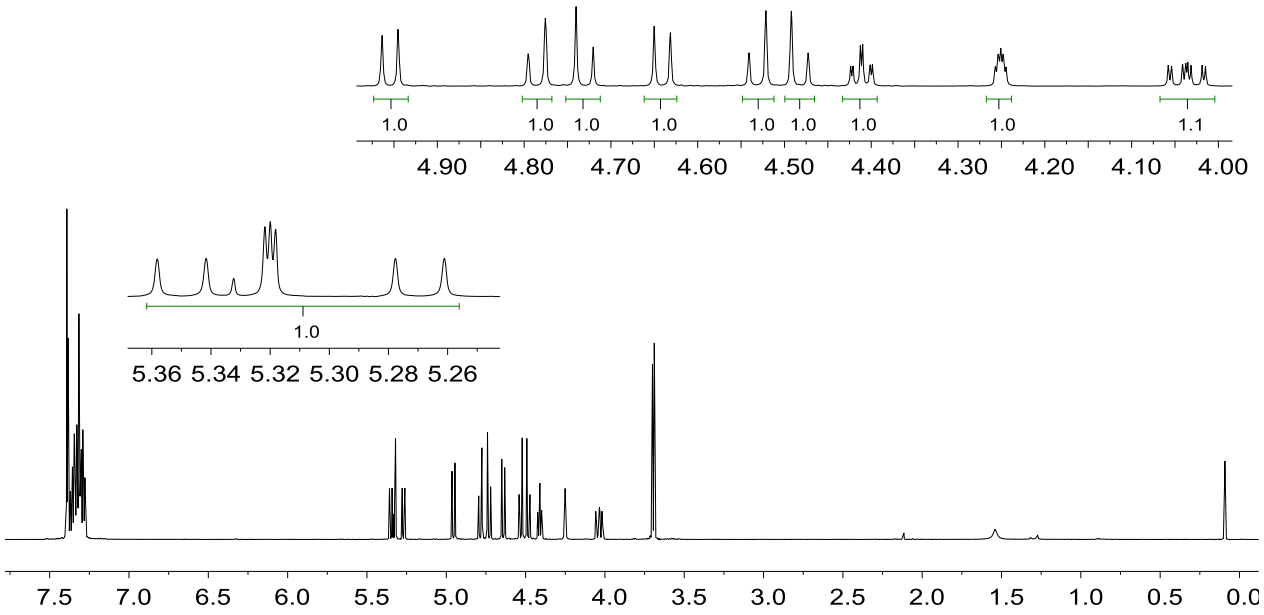
ν_{max} (neat)/cm^{-1} 3676w, 2969m, 2918m, 2877m, 1750s, 1498w, 1456m, 1394w, 1369m, 1346w, 1301w, 1252m, 1204s, 1144s, 1090s, 1056s, 1026s, 1003m, 990m, 973m, 94m3, 921m, 868m, 826w, 793m, 763s, 742s, 710m, 697s, 670m;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.40 – 7.26 (m, 15H, H-Ph), 5.31 (dd, J_{FH} = 48.4, J_{FH} = 9.9 Hz, 1H, H-C2), 4.95 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.79 (d, *J* = 11.8, 1H, H-C$\underline{H}_2$Ph), 4.73 (d, *J* = 11.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.64 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.53 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.48 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.41 (td, *J* = 6.8, 1.6 Hz, 1H, H-C5), 4.25 (m, 1H, H-C4), 4.04 (ddd, J_{FH} = 13.5, *J* = 9.9, 2.3 Hz, 1H, H-C3), 3.69 (d, *J* = 6.8 Hz, 2H, H-C6);

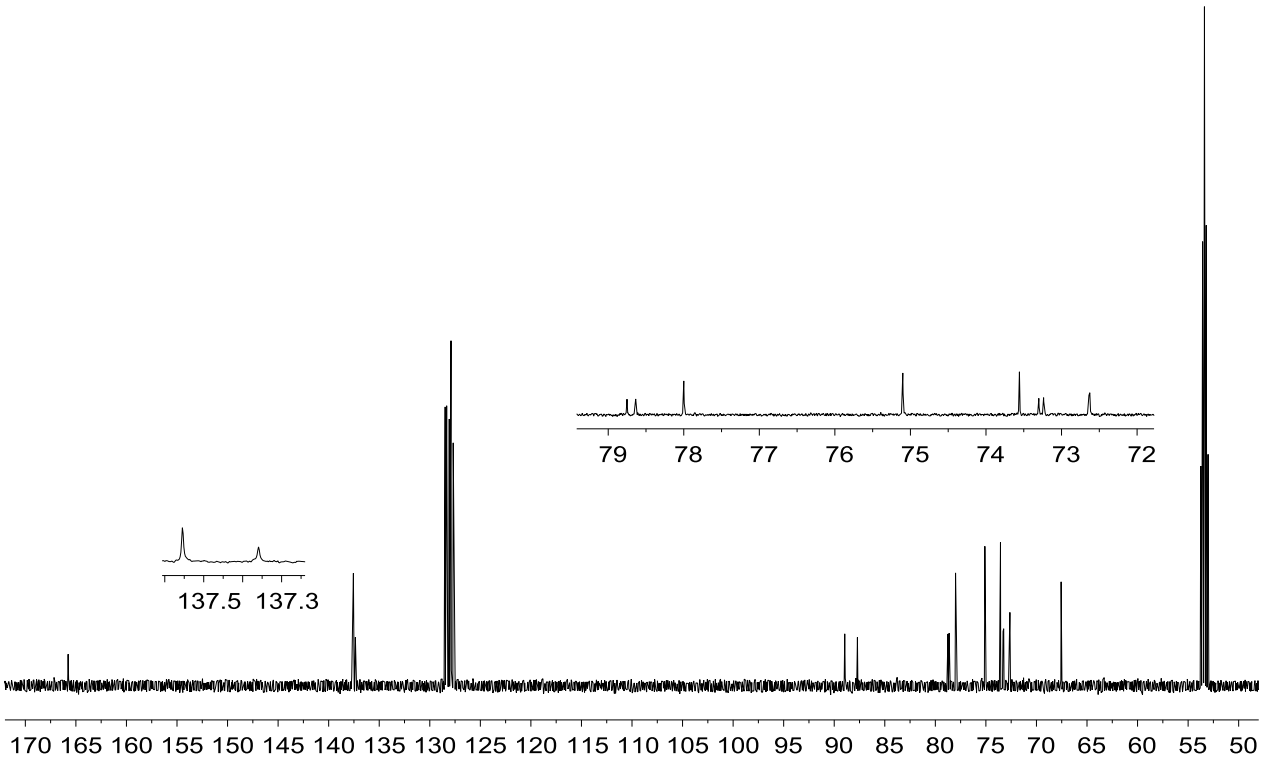
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 166.5 (d, J_{FC} = 19.9 Hz, C1), 138.2 (*i*-Ph), 138.0 (*i*-Ph), 129.1 (*o*,*m*,*p*-Ph), 129.0 (*o*,*m*,*p*-Ph), 129.0 (*o*,*m*,*p*-Ph), 128.7 (*o*,*m*,*p*-Ph), 128.6 (*o*,*m*,*p*-Ph), 128.6 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 89.0 (d, J_{FC} = 188.9 Hz, C2), 79.3 (d, J_{FC} = 17.4 Hz, H-C3), 78.6 (C5), 75.7 (C$\underline{H}_2$Ph), 74.2 (C$\underline{H}_2$Ph), 73.9 (d, J_{FC} = 9.6 Hz, C4), 73.24 (d, J_{FC} = 1.7 Hz, C$\underline{H}_2$Ph), 68.2 (C6);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -203.96 (ddd, *J* = 48.4, 13.5, 3.5 Hz).

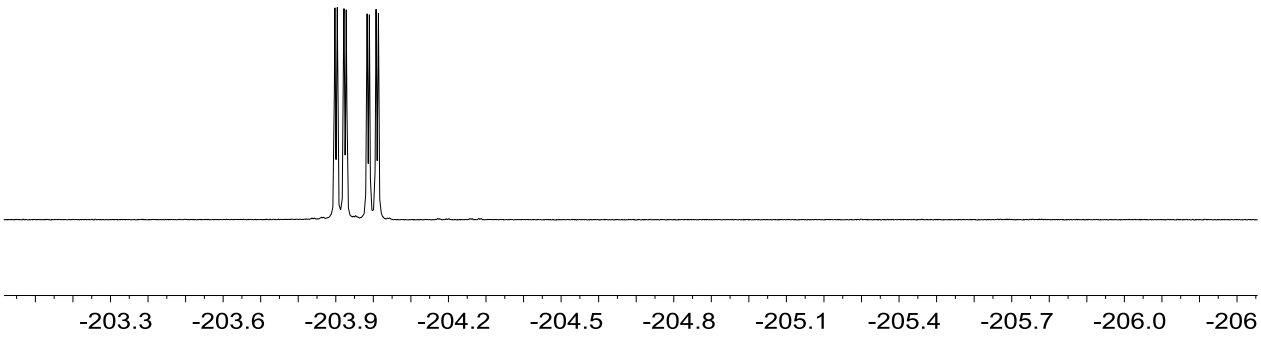
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



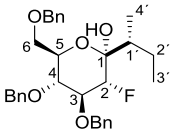
^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)

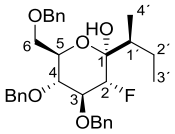


General Procedure A: *C*-glycosylations with MeLi, *n*-BuLi, *s*-BuLi.

The lithium reagent (MeLi: 1.6 M in Et_2O, 0.07 mL, 0.1 mmol, 1.1 eq. / *n*-BuLi: 2.5 M in Hexanes, 45 µL, 0.1 mmol, 1.1 eq. / *s*-BuLi: 1.4 M in CyH, 0.08 mL, 0.1 mmol, 1.1 eq.) was added slowly to a solution of the corresponding lactone (0.1 mmol, 1.0 eq.) in dry THF (0.58 mL, 0.17 M) at -78 °C. The reaction mixture was stirred for 30 min and quenched by addition of MeOH (5.0 mL). H_2O (5.0 mL) and EtOAc (5.0 mL) were then added. The aqueous layer was extracted with EtOAc (3 x 3 mL) and the combined organic layers were washed with H_2O (2 x 7.0 mL) and brine (1 x 7.0 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue obtained was purified by column chromatography CyH: EtOAc (SiO_2, specified combination of CyH: EtOAc).

Compound Table 1 Entry 1:





Prepared according to the general procedure A. Starting with **L1** (46 mg, 0.1 mmol) compound **Table 1 Entry 1** was obtained (30 mg, 59%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.50 (SiO_2, CyH:EtOAc 3:1);

m/z (ESI) found: 531.2520 $(M + Na)^+$, $C_{31}H_{37}O_5FNa^+$ calculated 531.2517;

ν_{max} (neat)/cm^{-1} 3443w, 3064w, 3031w, 2964m, 2928m, 2875m, 1954w, 1726w, 1497m, 1454m, 1367m, 1265m, 1207m, 1072s, 1026s, 909m, 820m, 732s, 696s;

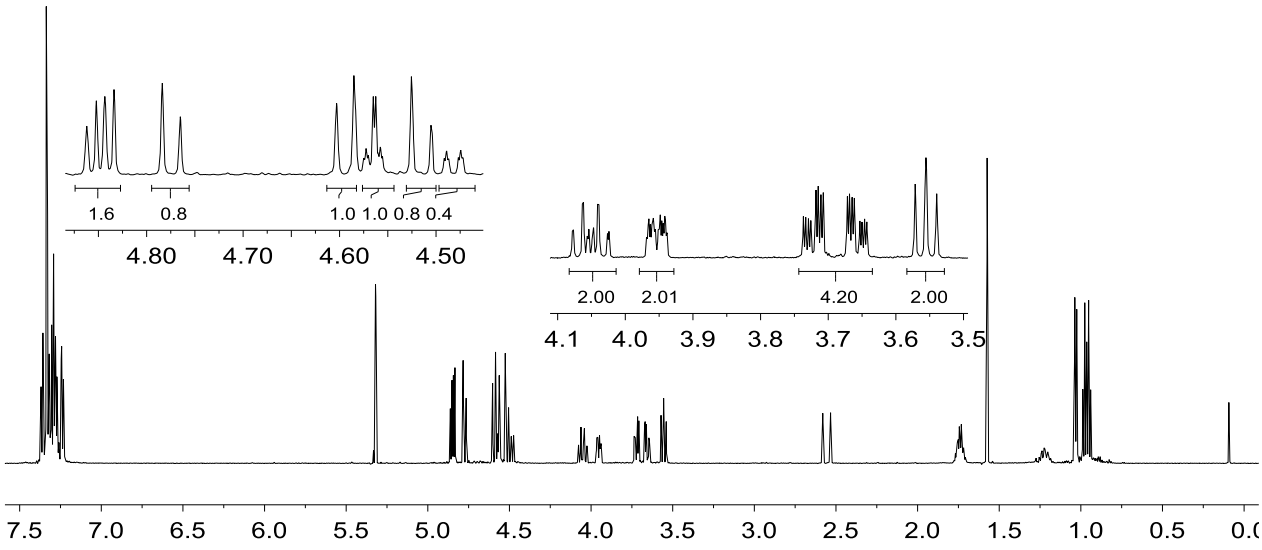
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.38 – 7.26 (m, 27H, H-Ph), 7.25 – 7.23 (m, 3H, H-Ph), 4.85 (d, *J* = 11.2 Hz, 2H, H-C$\underline{H}_2$Ph), 4.84 (d, *J* = 10.9 Hz, 2H, H-C$\underline{H}_2$Ph), 4.77 (d, *J* = 11.2 Hz, 2H, H-C$\underline{H}_2$Ph), 4.59 (d, *J* = 10.7 Hz, 2H, H-C$\underline{H}_2$Ph), 4.58 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.57 (d, *J* = 12.3 Hz, 1H, H-C$\underline{H}_2$Ph), 4.53 (m, 1H, H-C2), 4.52 (m, 1H, H-C2), 4.52 (d, *J* = 12.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.51 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.05 (m, 2H, H-C3), 3.95 (m, 2H, H-C5), 3.69 (m, 4H, H-C6), 3.58 – 3.54 (m, 2H, H-C4), 2.58 (d, *J* = 1.2 Hz, 1H, H-OH), 2.53 (d, *J* = 1.1 Hz, 1H, H-OH), 1.79 – 1.69 (m, 4H, H-C1´ + H-C2´),

1.30 – 1.17 (m, 2H, H-C2´), 1.05 – 1.02 (m, 6H, H-C4´), 0.98 (t, *J* = 7.2 Hz, 3H, H-C3´), 0.95 (t, *J* = 7.2 Hz, 3H, H-C3´);

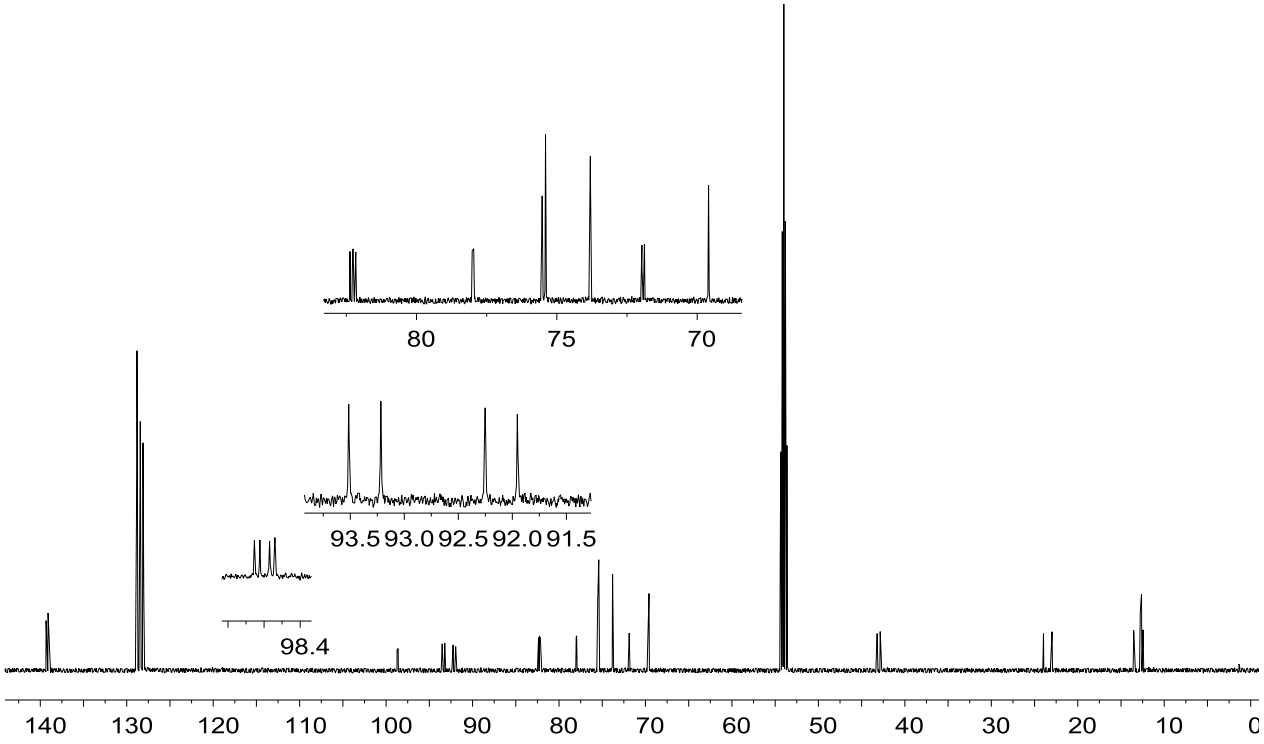
$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.3 (*i*-Ph), 139.2 (*i*-Ph), 139.2 (*i*-Ph), 139.1 (*i*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 98.8 (d, J_{FC} = 6.8 Hz, C1), 98.6 (d, J_{FC} = 6.6 Hz, C1), 92.9 (d, J_{FC} = 190.3 Hz, C2), 92.6 (d, J_{FC} = 190.5 Hz, C2), 82.3 (d, J_{FC} = 14.5 Hz, C3), 82.2 (d, J_{FC} = 14.4 Hz, C3), 78.0 (d, J_{FC} = 1.9 Hz, C4), 78.0 (d, J_{FC} = 1.9 Hz, C4), 75.5 (CH_2Ph), 75.5 (CH_2Ph), 75.5 (CH_2Ph), 75.4 (CH_2Ph), 73.8 (CH_2Ph), 72.0 (d, J_{FC} = 1.4 Hz, C5), 71.9 (d, J_{FC} = 1.3 Hz, C5), 69.6 (C6), 43.2 (d, J_{FC} = 1.6 Hz, C1´), 42.9 (d, J_{FC} = 1.5 Hz, C1´), 24.0 (d, J_{FC} = 2.0 Hz, C2´), 23.0 (d, J_{FC} = 1.3 Hz, C2´), 13.5 (d, J_{FC} = 2.0 Hz, C4´), 12.8 (C3´), 12.6 (C3´), 12.4 (d, J_{FC} = 1.8 Hz, C4´);

^{19}F NMR (564 MHz, Dichloromethane-d_2) δ -195.4 (dd, *J* = 49.9, 13.6 Hz), -196.3 (dd, *J* = 50.0, 13.5 Hz).

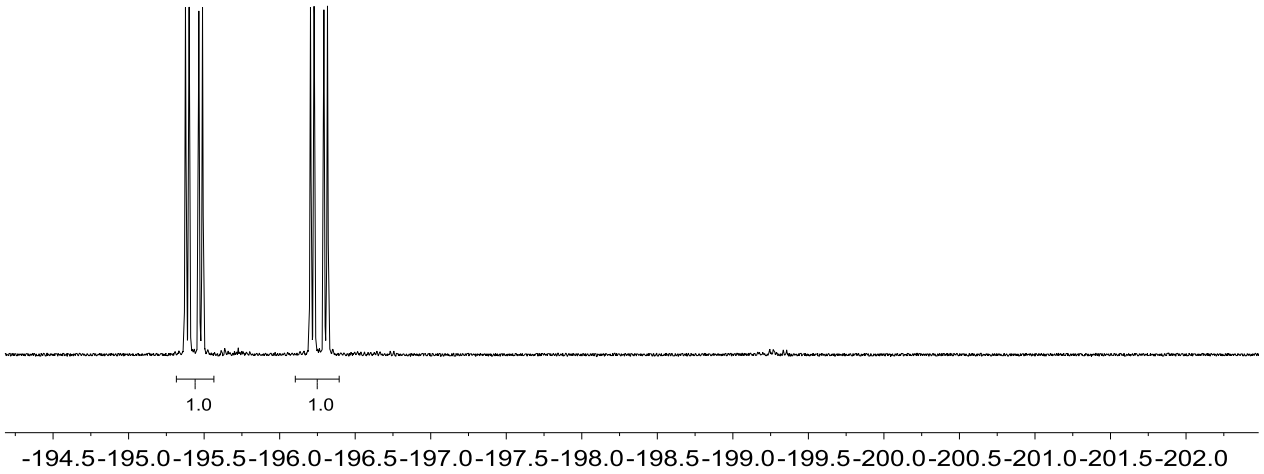
^{1}H (600 MHz, Dichloromethane-d_2, 299 K, 299 K)



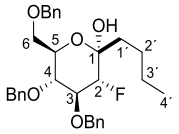
$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound Table 1 Entry 2:



Prepared according to the general procedure A. Starting with **L1** (46 mg, 0.1 mmol) compound **Table 1 Entry 2** was obtained (35 mg, 69%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.54 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 531.2539 $(M + Na)^+$, $C_{31}H_{37}O_5FNa^+$ calculated 531.2517;

$[\alpha]_D^{25}$ +31.2 (*c* 1.00 in DCM);

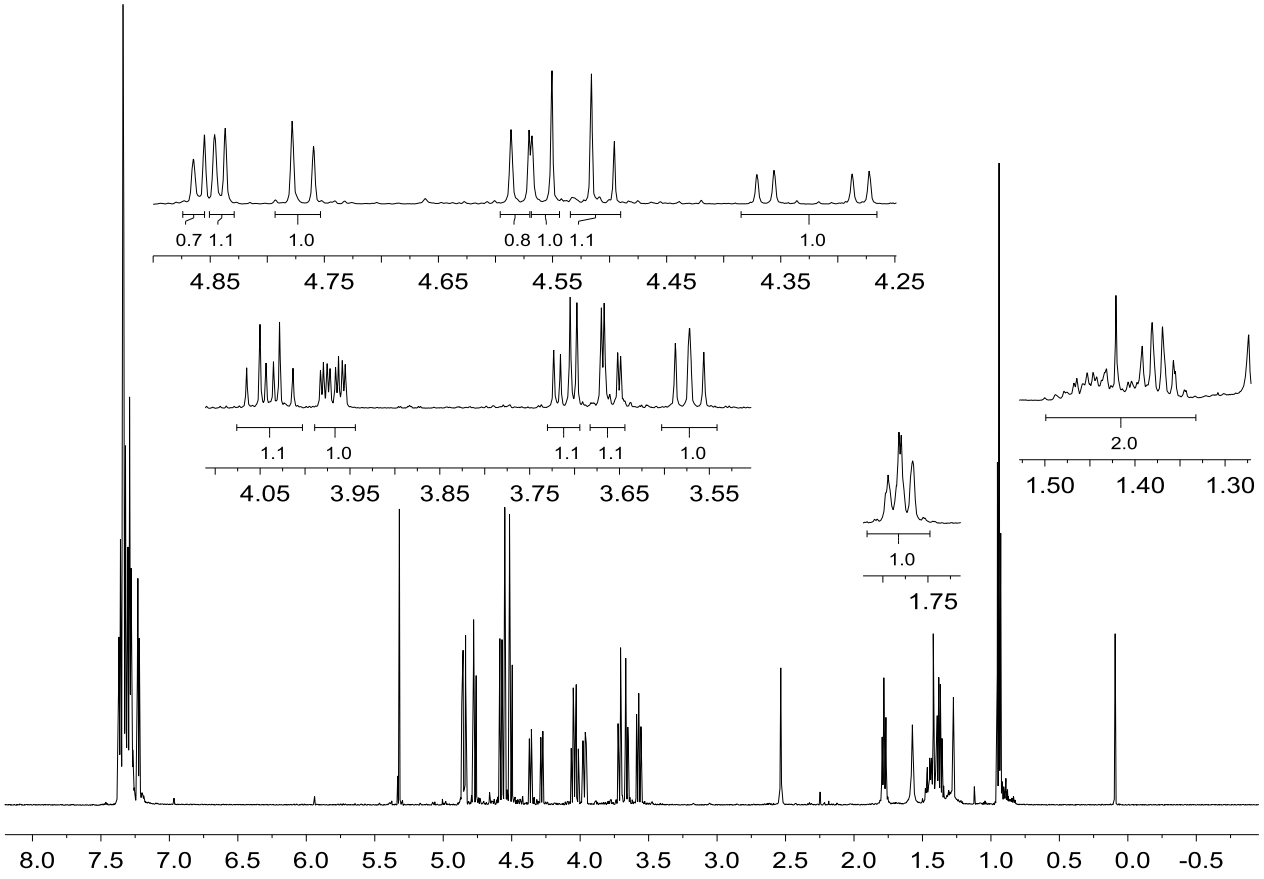
ν_{max} (neat)/cm^{-1} 3444w, 3090w, 3064w, 3030w, 2956m, 2928m, 2870m, 1497m, 1454m, 1406w, 1366m, 1309w, 1261w, 1210w, 1100s, 1067s, 1026s, 947m, 908m, 883w, 837m, 733s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.38 – 7.25 (m, 13H, H-Ph), 7.24 – 7.21 (m, 2H, H-Ph), 4.86 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.85 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.77 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.58 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.56 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.51 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.32 (dd, J_{FH} = 50.0, *J* = 9.0 Hz, 1H, H-C2), 4.04 (dt, J_{FH} = 13.0, *J* = 9.0 Hz, 1H, H-C3), 3.97 (ddd, *J* = 10.1, 4.5, 2.0 Hz, 1H, H-C5), 3.71 (dd, *J* = 10.9, 4.5 Hz, 1H, H-C6), 3.66 (dd, *J* = 10.9, 2.0 Hz, 1H, H-C6), 3.60 – 3.55 (m, 1H, H-C4), 2.53 (s, 1H, H-OH), 1.78 (m, 2H, H-C1´), 1.50 – 1.41 (m, 2H, H-C2´), 1.41 – 1.34 (m, 2H, H-C3´), 0.94 (t, *J* = 7.2 Hz, 3H, H-C4´);

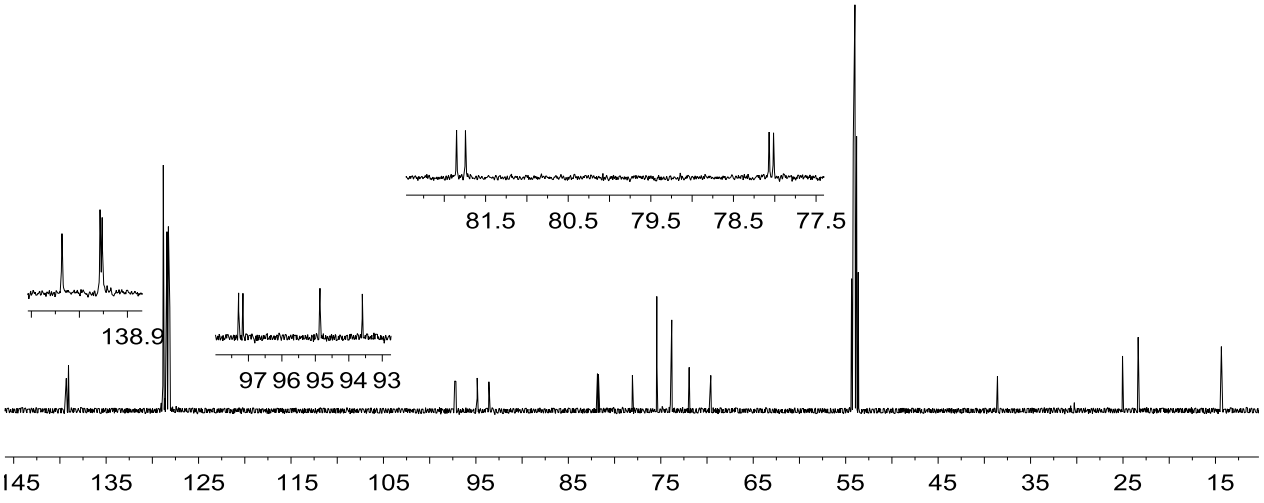
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.3 (*i*-Ph), 139.1 (*i*-Ph), 139.1 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 97.2 (d, J_{FC} = 19.4 Hz, C1), 94.2 (d, J_{FC} = 191.0 Hz, C2), 81.8 (d, J_{FC} = 16.3 Hz, C3), 78.0 (d, J_{FC} = 8.2 Hz, C4), 75.4 (C$\underline{H}_2$Ph), 75.4 (C$\underline{H}_2$Ph), 73.8 (C$\underline{H}_2$Ph), 71.9 (d, J_{FC} = 1.4 Hz, C5), 69.6 (C6), 38.6 (d, J_{FC} = 0.7 Hz, C1´), 25.1 (C2´), 23.4 (C3´), 14.4 (C4´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.7 (dd, *J* = 50.0, 13.0 Hz).

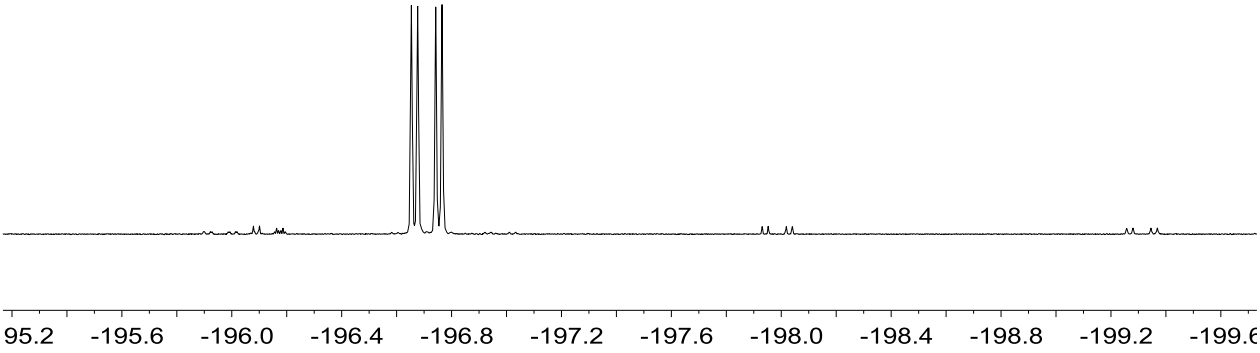
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



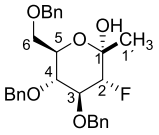
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound Table 1 Entry 3:



Prepared according to the general procedure A. Starting with **L1** (46 mg, 0.1 mmol) compound **Table 1 Entry 3** was obtained (45 mg, 95%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.30 (SiO_2, CyH:EtOAc 3:1);

m/z (ESI) found: 489.2074 $(M + Na)^+$, $C_{28}H_{31}O_5FNa^+$ calculated 489.2048;

$[\alpha]_D^{25}$ +38.4 (*c* 0.5 in DCM);

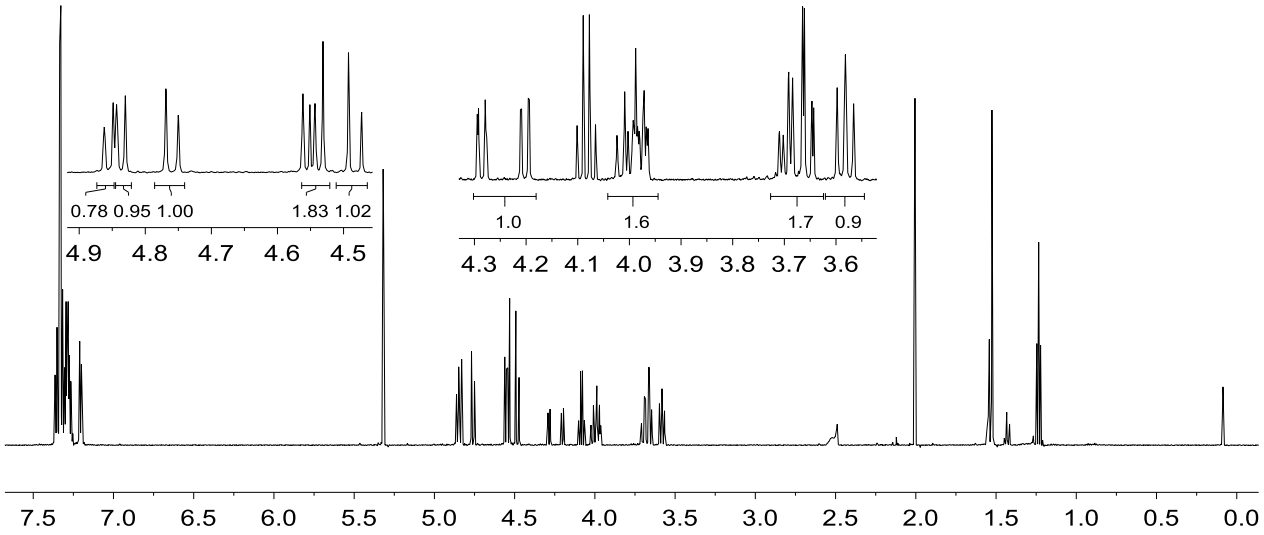
ν_{max} (neat)/cm^{-1} 3657w, 3406m, 3088w, 3064w, 3031w, 2924m, 2869m, 2317w, 2203w, 2165w, 2155w, 2054w, 2010w, 1970w, 1884w, 1813w, 1606w, 1587w, 1497m, 1454m, 1367m, 1315w, 1264w, 1207m, 1148m, 1121m, 1066s, 1026s, 986m, 910m, 871m, 836m, 734s, 695s, 655w;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.37 – 7.25 (m, 13H, H-Ph), 7.22 – 7.19 (m, 2H, H-Ph), 4.85 (d, *J* = 11.2 Hz, 1H, H-CH_2Ph), 4.84 (d, *J* = 11.0 Hz, 1H, H-CH_2Ph), 4.76 (d, *J* = 11.2 Hz, 1H, H-CH_2Ph), 4.55 (d, *J* = 11.0 Hz, 1H, H-CH_2Ph), 4.54 (d, *J* = 11.9 Hz, 1H, H-CH_2Ph), 4.48 (d, *J* = 11.9 Hz, 1H, H-CH_2Ph), 4.24 (ddd, J_{FH} = 50.0, *J* = 9.1, 1.3 Hz, 1H, H-C2), 4.03 – 3.96 (m, 2H, H-C3 + H-C5), 3.70 (dd, *J* = 10.8, 4.4, 1H, H-C6), 3.65 (dd, *J* = 10.8, 2.1 Hz, 1H, H-C6), 3.58 (t, *J* = 9.6, 1H, H-C4), 2.49 (br, 1H, OH), 1.52 (d, *J* = 1.2 Hz, 3H, H-C1´);

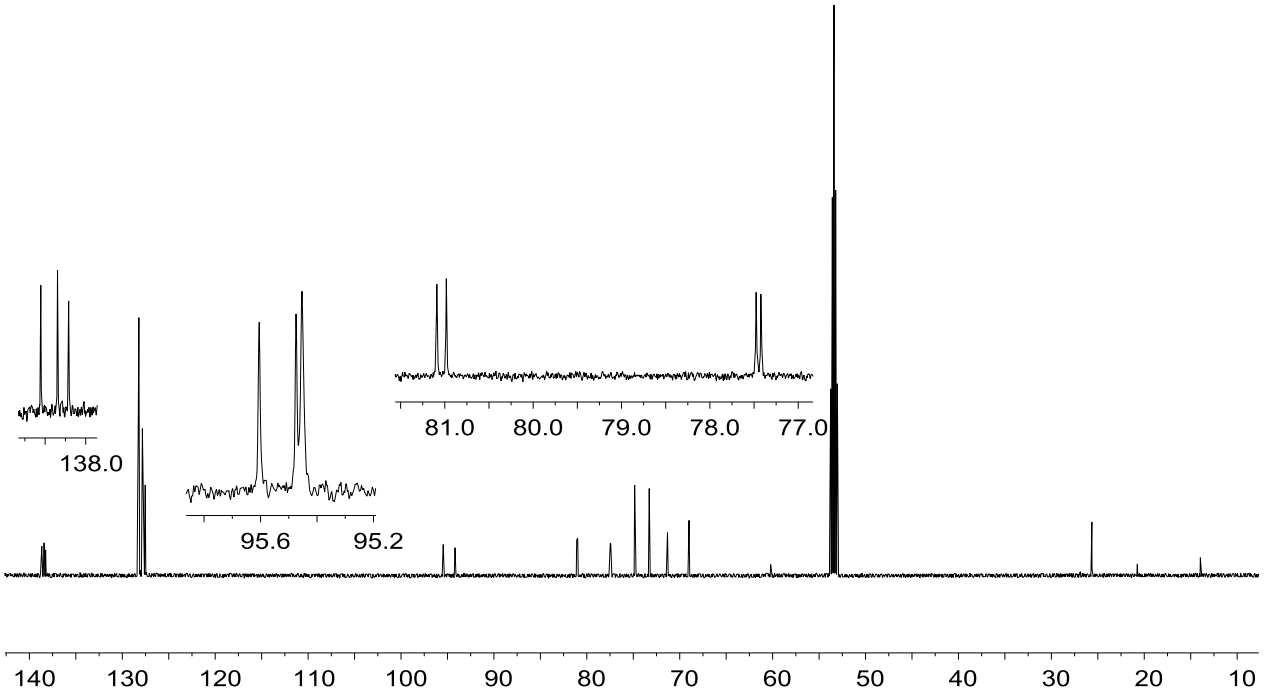
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.3 (*i*-Ph), 139.0 (*i*-Ph), 138.9 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 96.1 (d, J_{FC} = 19.7 Hz, C1), 95.4 (d, J_{FC} = 191.6 Hz, C2), 81.6 (d, J_{FC} = 16.2 Hz, C3), 78.1 (d, J_{FC} = 8.2 Hz, C4), 75.5 (CH_2Ph), 75.4 (d, J_{FC} = 2.7 Hz, CH_2Ph), 73.9 (CH_2Ph), 71.9 (d, J_{FC} = 1.5 Hz, C5), 69.6 (C6), 26.24 (C1´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.1 (dd, *J* = 49.9, 12.8 Hz).

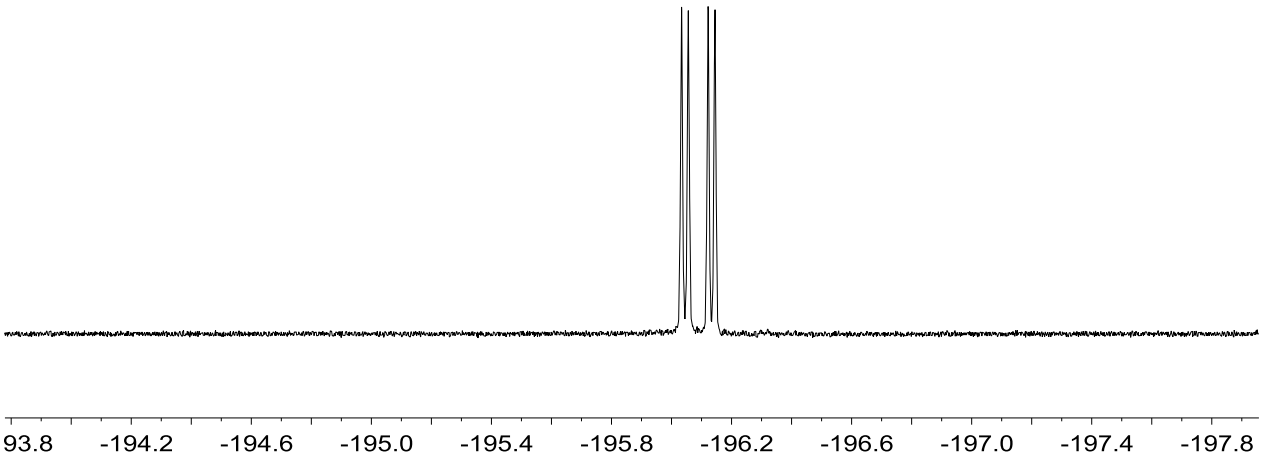
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



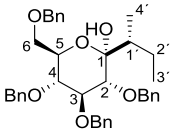
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)

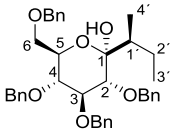


^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound Table 1 Entry 4:





Prepared according to the general procedure A. Starting with **L2** (55 mg, 0.1 mmol) compound **Table 1 Entry 4** was obtained (52 mg, 85%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.50 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 619.3033 $(M + Na)^+$, $C_{38}H_{44}O_6Na^+$ calculated 619.3030;

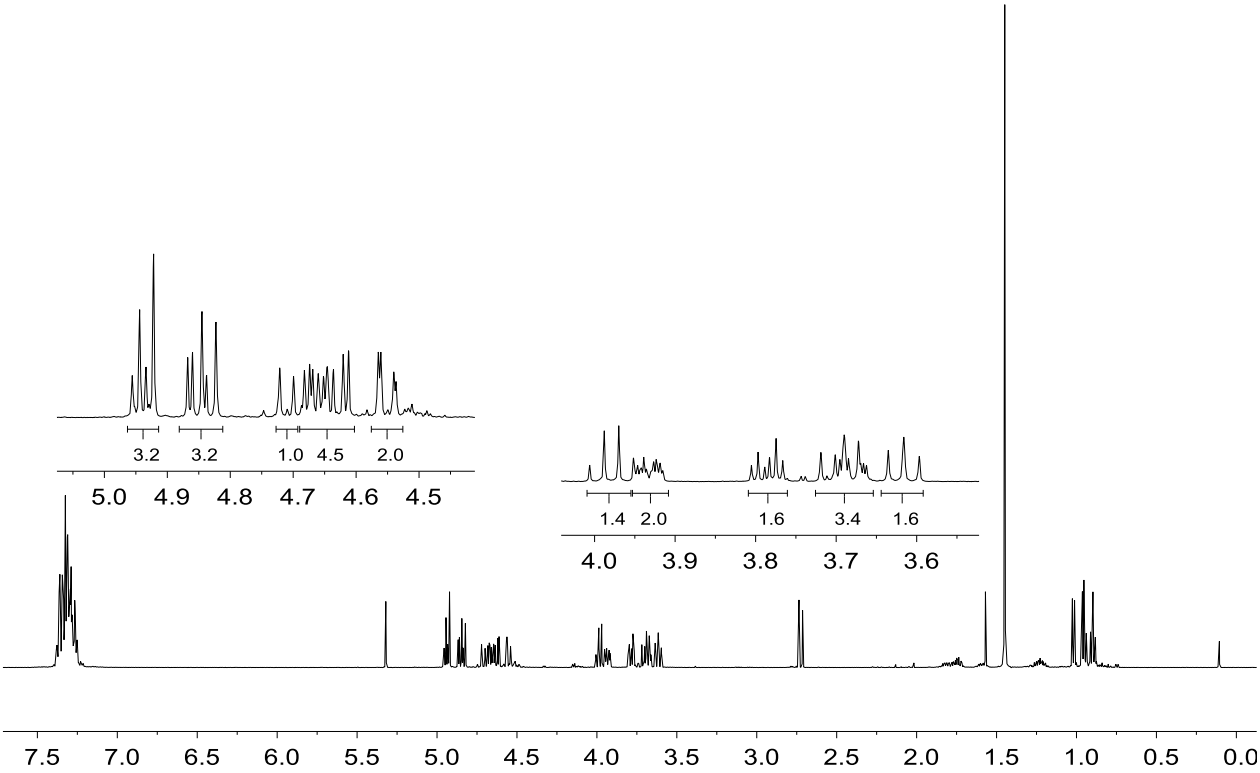
ν_{max} (neat)/cm^{-1} 3559w, 3064w, 3031w, 2965m, 2932m, 2873w, 1955w, 1756m, 1605m, 1497m, 1454m, 1362m, 1265m, 1209m, 1084s, 1027s, 908m, 811m, 732s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.39 – 7.24 (m, 40H, H-Ph), 4.94 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.93 (d, *J* = 11.0 Hz, 2H, H-C$\underline{H}_2$Ph), 4.86 (d, *J* = 11.4 Hz, 2H, H-C$\underline{H}_2$Ph), 4.85 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.83 (d, *J* = 11.1 Hz, 2H, H-C$\underline{H}_2$Ph), 4.71 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.67 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.66 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.65 – 4.60 (m, 3H, H-C$\underline{H}_2$Ph), 4.55 (d, *J* = 12.4 Hz, 1H, H-C$\underline{H}_2$Ph), 4.55 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 3.98 (m, 2H, H-C3), 3.95 – 3.91 (m, 2H, H-C5), 3.79 (m, 2H, H-C6), 3.71 (m, 1H, H-C2), 3.68 (m, 1H, H-C2), 3.70 – 3.68 (m, 1H, H-C6), 3.68 – 3.66 (m, 1H, H-C6), 3.62 (m, 2H, H-C4), 2.74 (s, 1H, H-OH), 2.71 (s, 1H, H-OH), 1.85 – 1.78 (m, 1H, H-C2´), 1.78 – 1.70 (m, 2H, H-C1´), 1.63 – 1.58 (m, 1H, H-C2´), 1.27 – 1.18 (m, 2H, H-C2´), 1.02 (d, *J* = 6.8 Hz, 3H, H-C4´), 0.96 (d, *J* = 6.9 Hz, 3H, H-C4´), 0.95 (t, *J* = 7.5 Hz, 3H, H-C3´), 0.90 (t, *J* = 7.5 Hz, 3H, H-C3´);

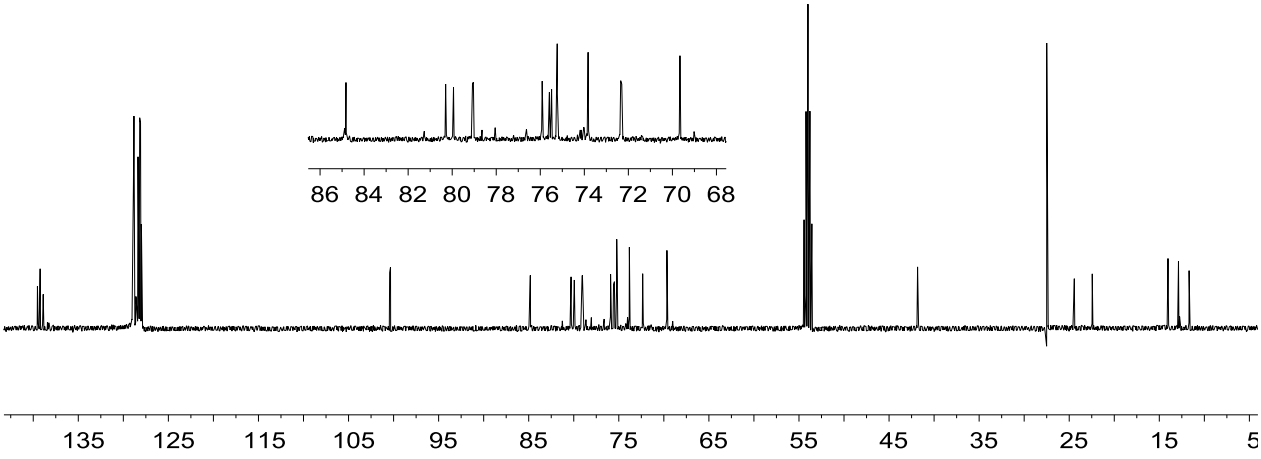
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.5 (*i*-Ph), 139.5 (*i*-Ph), 139.5 (*i*-Ph), 139.5 (*i*-Ph), 139.2 (*i*-Ph), 138.9 (*i*-Ph), 138.9 (*i*-Ph), 129.0 (*o*,*m*,*p*-Ph), 129.0 (*o*,*m*,*p*-Ph), 129.0 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.6 (*o*,*m*,*p*-Ph), 128.6 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 127.9 (*o*,*m*,*p*-Ph), 127.9 (*o*,*m*,*p*-Ph), 100.4 (C1), 100.3 (C1), 84.9 (C3), 84.8 (C3), 80.3 (C2),

79.9 (C2), 79.1 (C4), 79.0 (C4), 75.9 (<u>C</u>H$_2$Ph), 75.9 (<u>C</u>H$_2$Ph), 75.6 (<u>C</u>H$_2$Ph), 75.5 (<u>C</u>H$_2$Ph), 75.2 (<u>C</u>H$_2$Ph), 73.8 (<u>C</u>H$_2$Ph), 72.4 (C5), 72.3 (C5), 69.7 (C6), 41.8 (C1´), 41.8 (C1´), 24.4 (C2´), 22.4 (C2´), 14.0 (C4´), 12.9 (C3´), 12.8 (C3´), 11.7 (C4´).

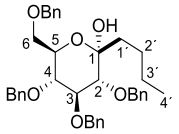
^{1}H (600 MHz, Dichloromethane-d_2, 299 K) (with water)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound Table 1 Entry 5:[1]



Prepared according to the general procedure A. Starting with **L2** (55 mg, 0.1 mmol) compound **Table 1 Entry 5** was obtained (56 mg, 92%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.45 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 619.3044 $(M + Na)^+$, $C_{38}H_{44}O_6Na^+$ calculated 619.3030;

$[\alpha]_D^{25}$ +30.3 (*c* 0.4 in DCM);

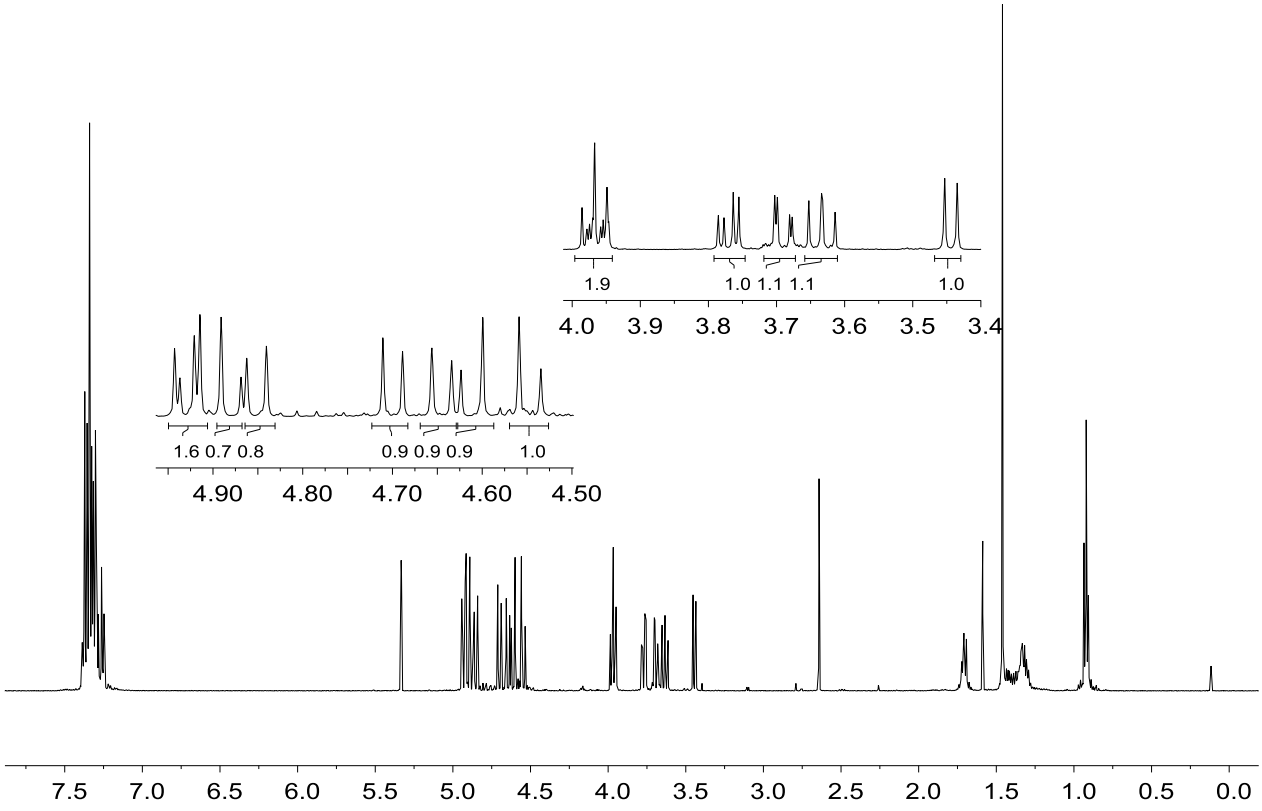
ν_{max} (neat)/cm^{-1} 3428w, 3064w, 3031w, 2955m, 2928m, 2865m, 2328w, 1948w, 1875w, 1755w, 1606w, 1497m, 1454m, 1361m, 1265w, 1209w, 1070s, 1027s, 999s, 954w, 907w, 848w, 820w, 732s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.38 – 7.25 (m, 18H, H-Ph), 7.23 (m, 2H, H-Ph), 4.91 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.90 (d, *J* = 11.4 Hz, 1H, H-C$\underline{H}_2$Ph), 4.85 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.82 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.67 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.62 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.59 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.52 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 3.96 – 3.91 (m, 2H, H-C3 + H-C5), 3.75 (dd, *J* = 10.9, 4.2 Hz, 1H, H-C6), 3.66 (dd, *J* = 11.0, 1.8 Hz, 1H, H-C6), 3.61 (t, *J* = 9.6 Hz, 1H, H-C4), 3.42 (d, *J* = 9.2 Hz, 1H, H-C2), 2.58 (d, *J* = 2.2 Hz, 1H, H-OH), 1.73 – 1.65 (m, 2H, H-C1´), 1.47 – 1.22 (m, 4H, H-C2´ + H-C3´), 0.94 – 0.84 (m, 3H, H-C4´);

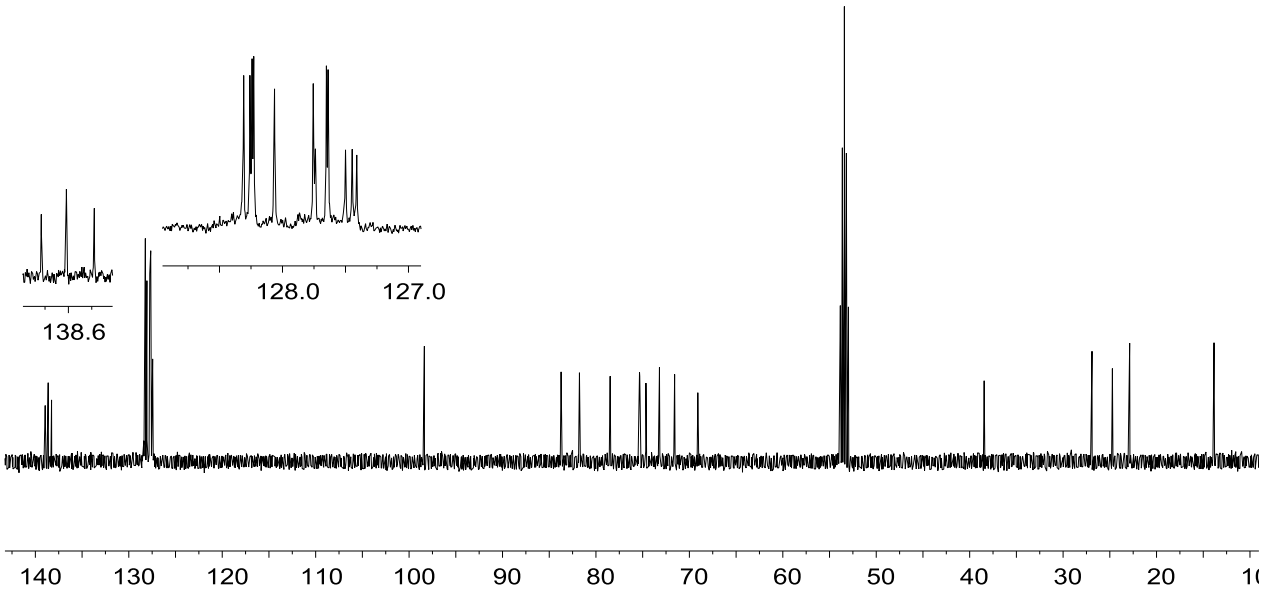
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.5 (*i*-Ph), 139.2 (*i*-Ph), 139.2 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.6 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 99.0 (C1), 84.3 (C3), 82.4 (C2), 79.1 (C4), 75.9 (C$\underline{H}_2$Ph), 75.9 (C$\underline{H}_2$Ph), 75.2 (C$\underline{H}_2$Ph), 73.8 (C$\underline{H}_2$Ph), 72.2 (C5), 69.7 (C6), 39.0 (C1´), 25.3 (C2´), 23.5 (C3´), 14.4 (C4´).

[1] Y. Oda, T. Yamanoi, *Synthesis* **2007**, *19*, 3021-3031.

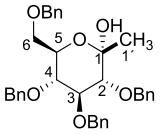
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-*d*2, 299 K)



Compound Table 1 Entry 6:[2]



Prepared according to the general procedure A. Starting with **L2** (55 mg, 0.1 mmol) compound **Table 1 Entry 6** was obtained (53 mg, 94%) as a white solid after purification by column chromatography (SiO_2, CyH: EtOAC 3:1).

R_f 0.30 (SiO_2, CyH:EtOAc 3:1);

Mp 96 – 97 °C;

m/*z* (ESI) found: 577.2569 $(M + Na)^+$, $C_{35}H_{38}O_6Na^+$ calculated 577.2561;

$[\alpha]_D^{25}$ +32.5 (*c* 1.00 in DCM);

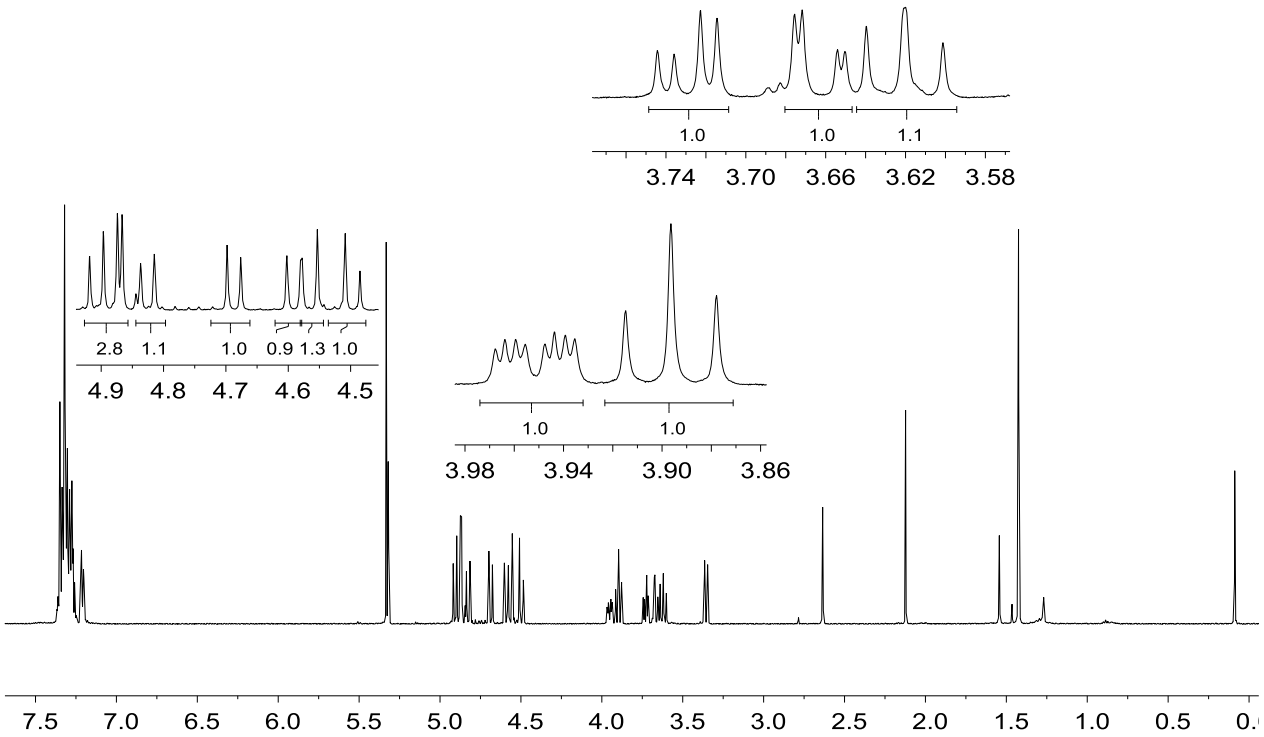
ν_{max} (neat)/cm^{-1} 3677w, 3441m, 3089w, 3063w, 3030w, 2920m, 2866m, 2180w, 2037w, 1952w, 1876w, 1811w, 1606w, 1586w, 1497m, 1454m, 1361m, 1265w, 1209m, 1149w, 1068s, 1027s, 958w, 908w, 871m, 845w, 820w, 732s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.37 – 7.25 (m, 18H, H-Ph), 7.21 (dd, *J* = 7.7, 1.8 Hz, 2H, H-Ph), 4.91 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.89 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.86 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.83 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.69 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.59 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.57 (d, *J* = 12.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.50 (d, *J* = 12.2 Hz, 1H, H-C$\underline{H}_2$Ph), 3.95 (ddd, *J* = 10.1, 4.2, 2.0 Hz, 1H, H-C5), 3.90 (t, *J* = 9.2 Hz, 1H, H-C3), 3.73 (dd, *J* = 10.7, 4.2 Hz, 1H, H-C6), 3.66 (dd, *J* = 10.7, 2.0 Hz, 1H, H-C6), 3.62 (dd, *J* = 10.1, 9.1 Hz, 1H, H-C4), 3.36 (d, *J* = 9.1 Hz, 1H, H-C2), 2.64 (s, 1H, H-OH), 1.42 (s, 3H, H-C1´);

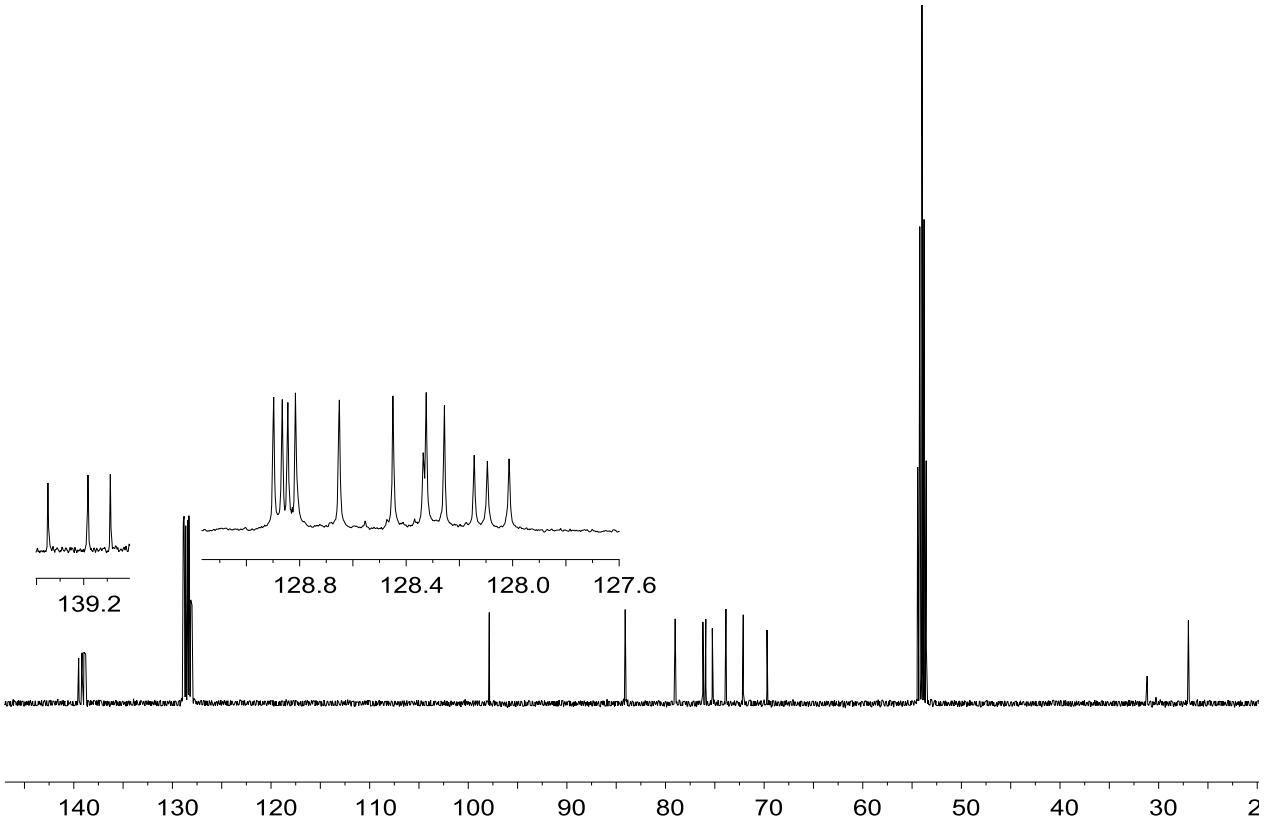
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.5 (*i*-Ph), 139.2 (*i*-Ph), 139.0 (*i*-Ph), 138.8 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.7 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 97.9 (C1), 84.1 (C2), 84.1 (C3), 79.0 (C4), 76.2 (C$\underline{H}_2$Ph), 75.9 (C$\underline{H}_2$Ph), 75.3 (C$\underline{H}_2$Ph), 73.9 (C$\underline{H}_2$Ph), 72.1 (C5), 69.7 (C6), 27.0 (C1´).

[2] L. Lay, F. Nicotra, L. Panza, G. Russo, and E. Caneva, *JOC* **1992**, *57*, 1304-1306.

^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



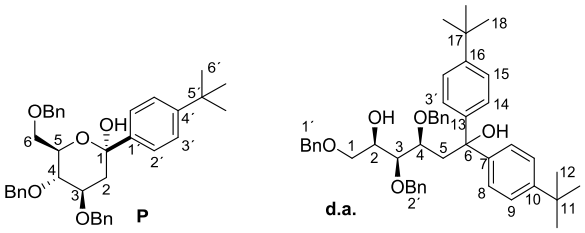
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



General Procedure B for *C*-glycosylations with *p*-bromo-4-*tert*-Butylbenzene.

n-BuLi (20 µL, 2.5 M in hexanes, 0.1 mmol, 1.1 eq.) was added to a solution of *p*-bromo-4-*tert*-butylbenzene (45 µL, 0.1 mmol, 1.1 eq.) in a mixture of toluene:THF (2:1; 0.15 mL:75 µL, 0.5 M), the mixture was stirred under argon at -78 °C for 30 min. This mixture was transferred slowly to a solution of the corresponding lactone (0.1 mmol, 1.0 eq.) in dry THF (0.35 mL, 0.3 M) at -78 °C under an argon atmosphere. After stirring for 30 min the reaction was quenched by addition of MeOH (5 mL). H_2O (5 mL) and EtOAc (5 mL) were added and the water phase was extracted with EtOAc (3 x 3 mL). The combined organic layers were washed H_2O (2 x 7 mL) and brine (1 x 7 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuum*. The residue was purified by column chromatography CyH: EtOAc (SiO_2, specified combination of CyH: EtOAc).

Compound Table 2 Entry 1 (mixture of the desired product P and the double addition product d.a.)



Prepared according to the general procedure B. Starting with **L3** (44 mg, 0.1 mmol) an inseparable mixture of **Table 2 Entry 1** and **d.a** was obtained (40mg, 69% as an inseparable mixture of **P*α*** + **P*β*** + **d.a.** (1:1:3) after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

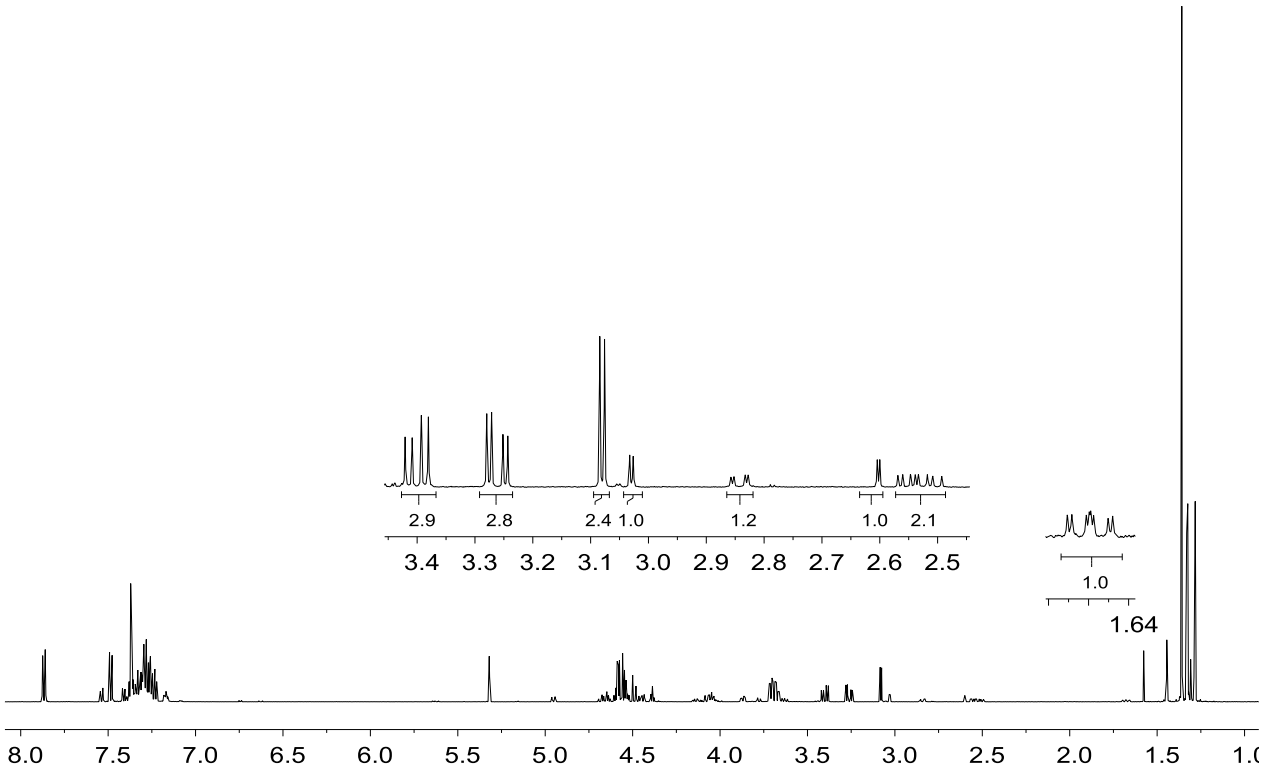
R_f 0.6 and 0.59 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 589.2974 $(M + Na)^+$ and 723.4049 (double addition), $C_{37}H_{42}O_5Na^+$ calculated 589.2924;

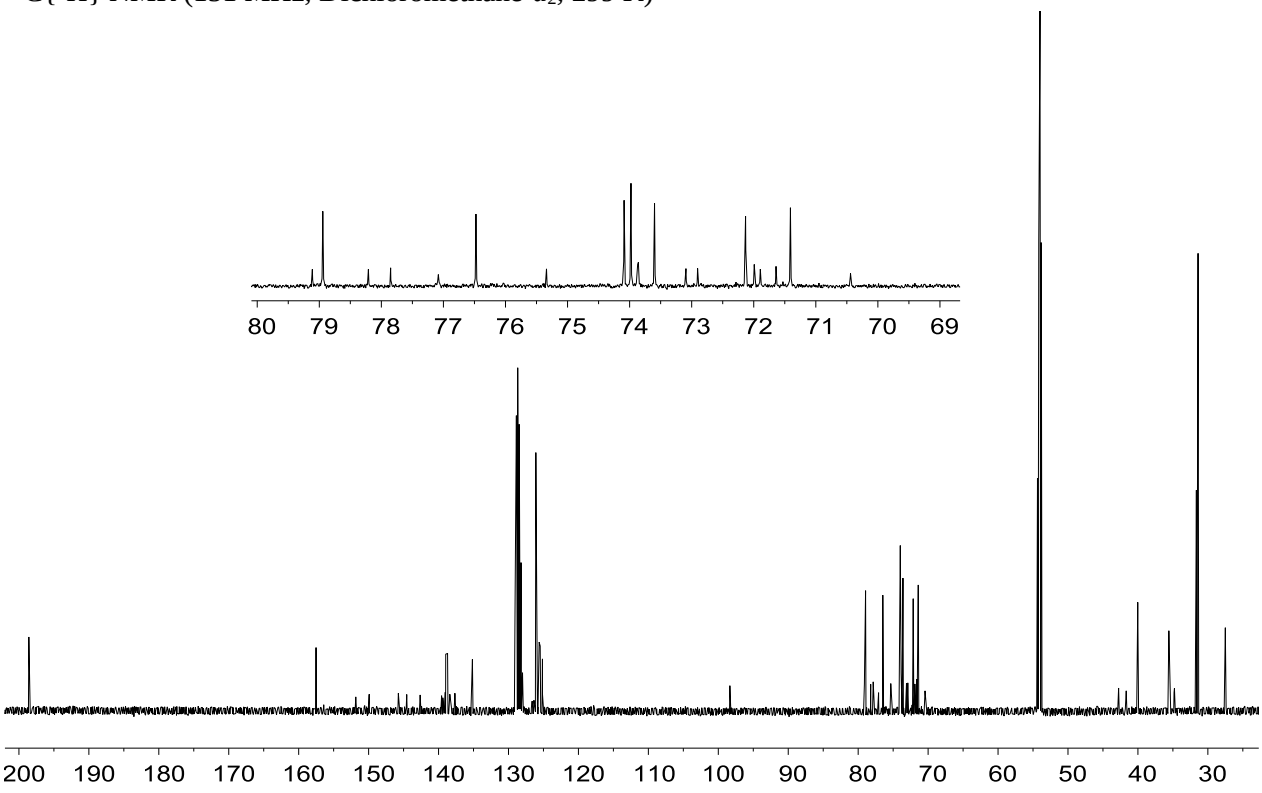
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) [key resonances] δ 3.03 (d, *J* = 3.6 Hz, 1H, H-OH), 2.84 (dd, *J* = 14.8, 3.0 Hz, 1H, H-C2), 2.60 (d, *J* = 2.6 Hz, 1H, H-OH), 2.58 – 2.48 (m, 2H, H-C2), 1.71 – 1.64 (m, 1H, H-C2);

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) [key resonances - d.a.] δ 3.40 (dd, *J* = 16.8, 7.3 Hz, 3H, H-C5), 3.26 (dd, *J* = 16.8, 5.0 Hz, 3H, H-C5), 3.08 (d, *J* = 4.9 Hz, 3H, H-OH).

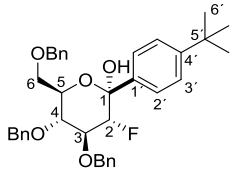
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 4:



Prepared according to the general procedure B. Starting with **L1** (46 mg, 0.1 mmol) compound **Table 2 Entry 4** was obtained (58 mg, 97%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.54 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 607.2847 $(M + Na)^+$, $C_{37}H_{41}O_5FNa^+$ requires 607.2830;

$[\alpha]_D^{25}$ +16.8 (*c* 2.29 in DCM);

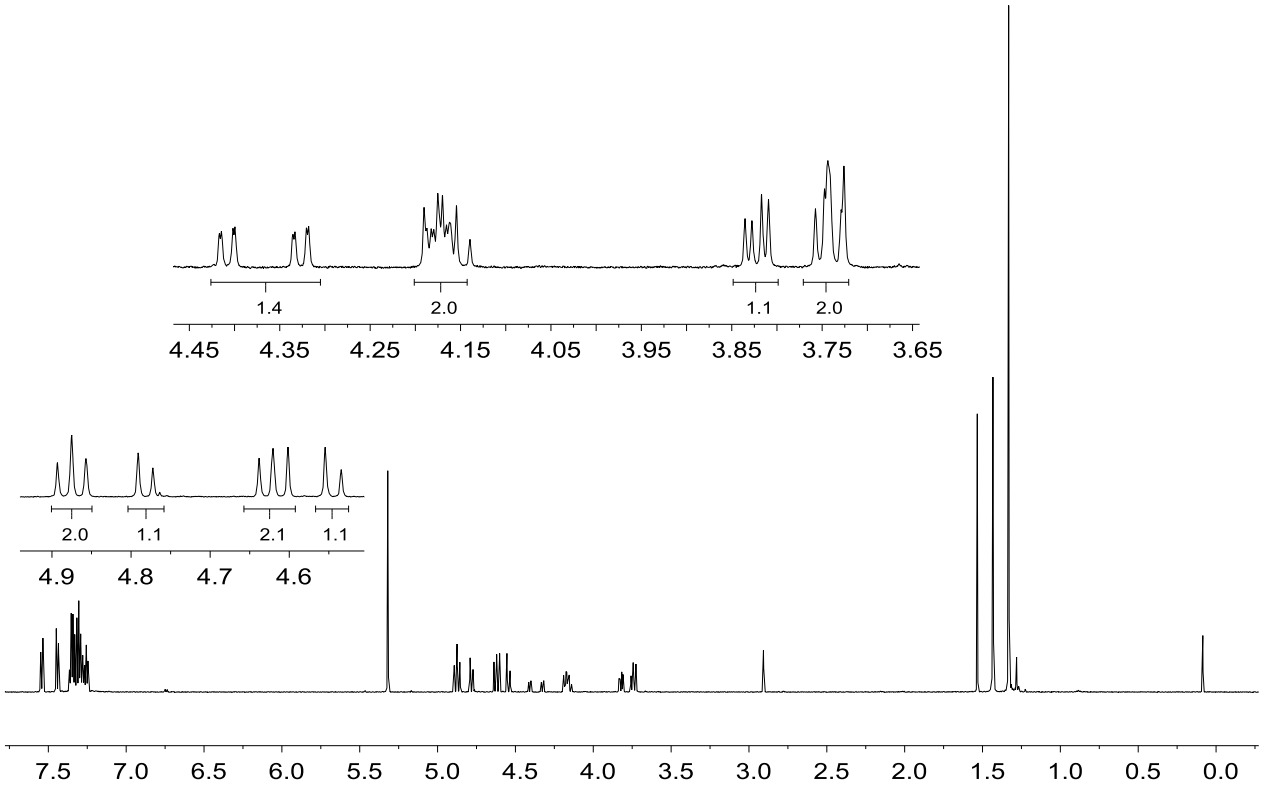
ν_{max} (neat)/cm^{-1} 3385m, 3063w, 3031w, 2961m, 2867w, 2038w, 1948w, 1808w, 1608w, 1514w, 1497m, 1454m, 1404m, 1365m, 1311w, 1268m, 1241w, 1208m, 1130s, 1086s, 1054s, 1026s, 910w, 838m, 815m, 733s, 715m, 696s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.56 – 7.52 (m, 2H, H-C2´), 7.46 – 7.43 (m, 2H, H-C3´), 7.37 – 7.23 (m, 15H, H-Ph), 4.88 (d, *J* = 10.8 Hz, 1H, H-CH_2Ph), 4.87 (d, *J* = 10.8 Hz, 1H, H-CH_2Ph), 4.78 (d, *J* = 11.2 Hz, 1H, H-CH_2Ph), 4.63 (d, *J* = 10.5 Hz, 1H, H-CH_2Ph), 4.78 (d, *J* = 11.2 Hz, 1H, H-CH_2Ph), 4.54 (d, *J* = 12.1 Hz, 1H, H-CH_2Ph), 4.37 (ddd, J_{FH} = 48.7, *J* = 8.9, 1.6 Hz, 1H, H-C2), 4.20 – 4.13 (m, 2H, H-C3 + H-C5), 3.82 (dd, *J* = 11.0, 4.6 Hz, 1H, H-C6), 3.76 – 3.72 (m, 2H, H-C6 + H-C4), 2.91 (d, *J* = 1.0 Hz, 1H, H-OH), 1.33 (s, 9H, H-C6´);

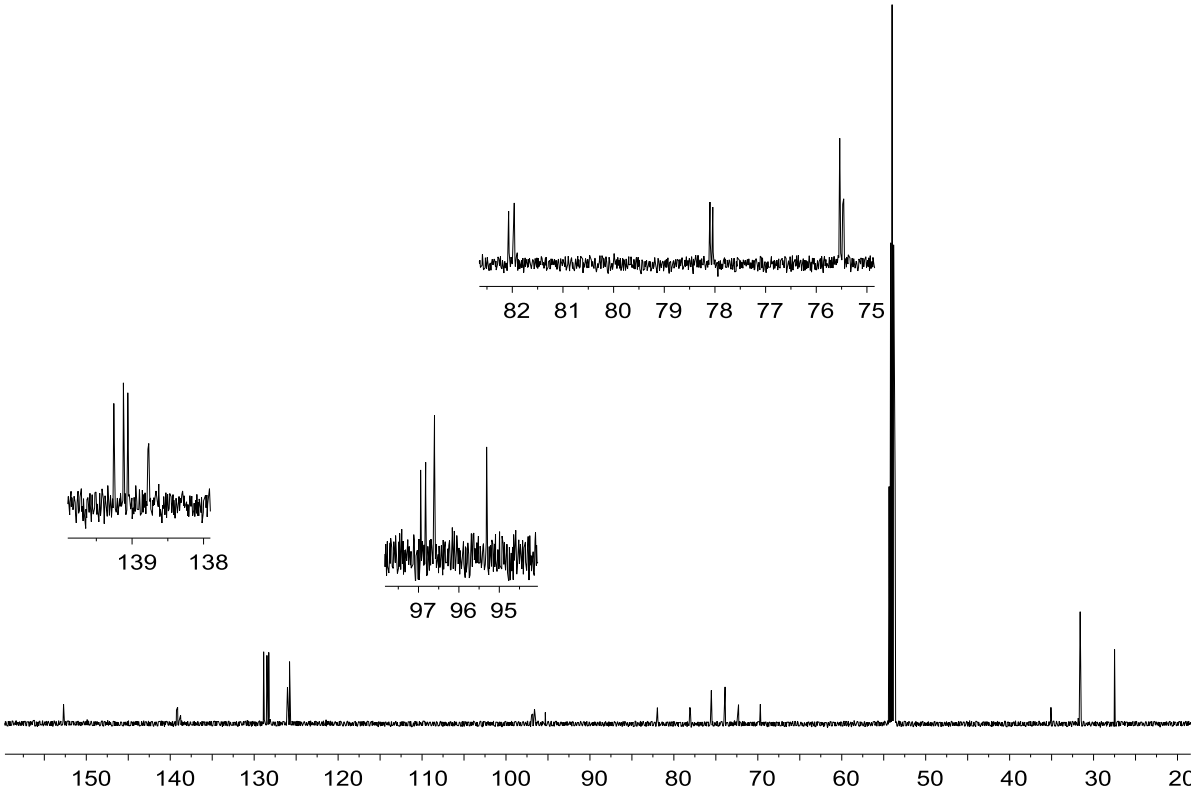
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 152.7 (C4´), 139.3 (*i*-Ph), 139.1 (*i*-Ph), 139.1 (*i*-Ph), 138.77 (d, J_{FC} = 1.4 Hz, C1´), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 126.0 (d, J_{FC} = 1.3 Hz, C2´), 125.8 (C3´), 96.9 (d, J_{FC} = 18.7 Hz, C1), 96.0 (d, J_{FC} = 194.4 Hz, C2), 82.0 (d, J_{FC} = 16.7 Hz, C3), 78.1 (d, J_{FC} = 8.3 Hz, C4), 75.5 ($\underline{C}H_2$Ph), 75.5 (d, J_{FC} = 2.9 Hz, $\underline{C}H_2$Ph), 73.9 ($\underline{C}H_2$Ph), 72.3 (d, J_{FC} = 1.4 Hz, C5), 69.7 (C6), 35.1 (C5´), 31.6 (C6´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.3 (dd, *J* = 48.9, 12.3 Hz).

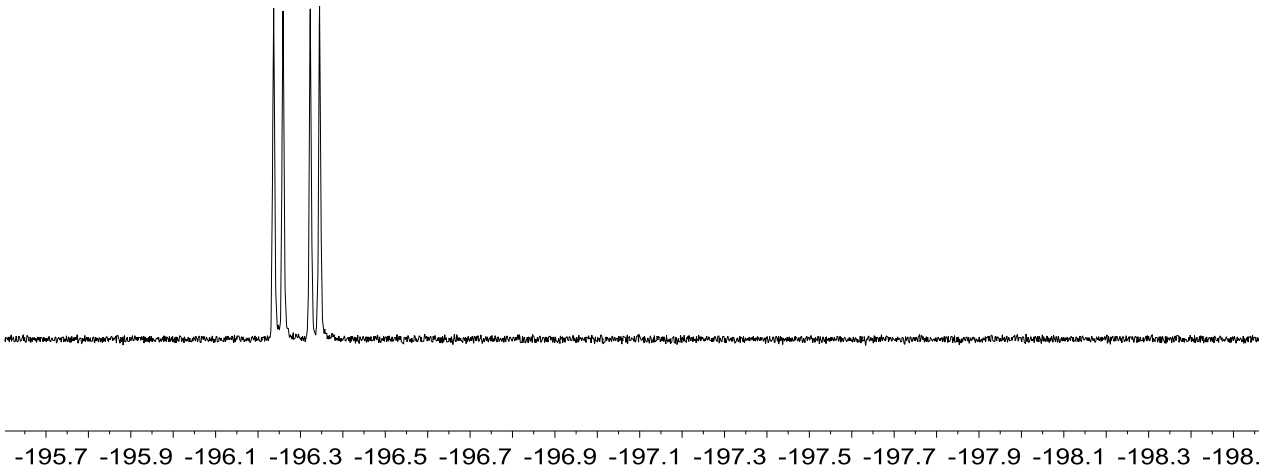
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



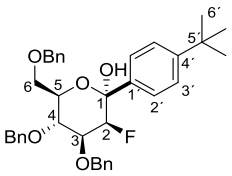
$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 7:



Prepared according to the general procedure B. Starting with **L4** (46 mg, 0.1 mmol) compound **Table 2 Entry 7** was obtained (59 mg, 99%) as a white solid after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.58 (SiO_2, CyH:EtOAc 3:1);

Mp 120 – 125 °C;

m/z (ESI) found: 607.2843 $(M + Na)^+$, $C_{37}H_{41}O_5FNa^+$ calculated 607.2830;

$[\alpha]_D^{25}$ +17.3 (*c* 0.5 in DCM);

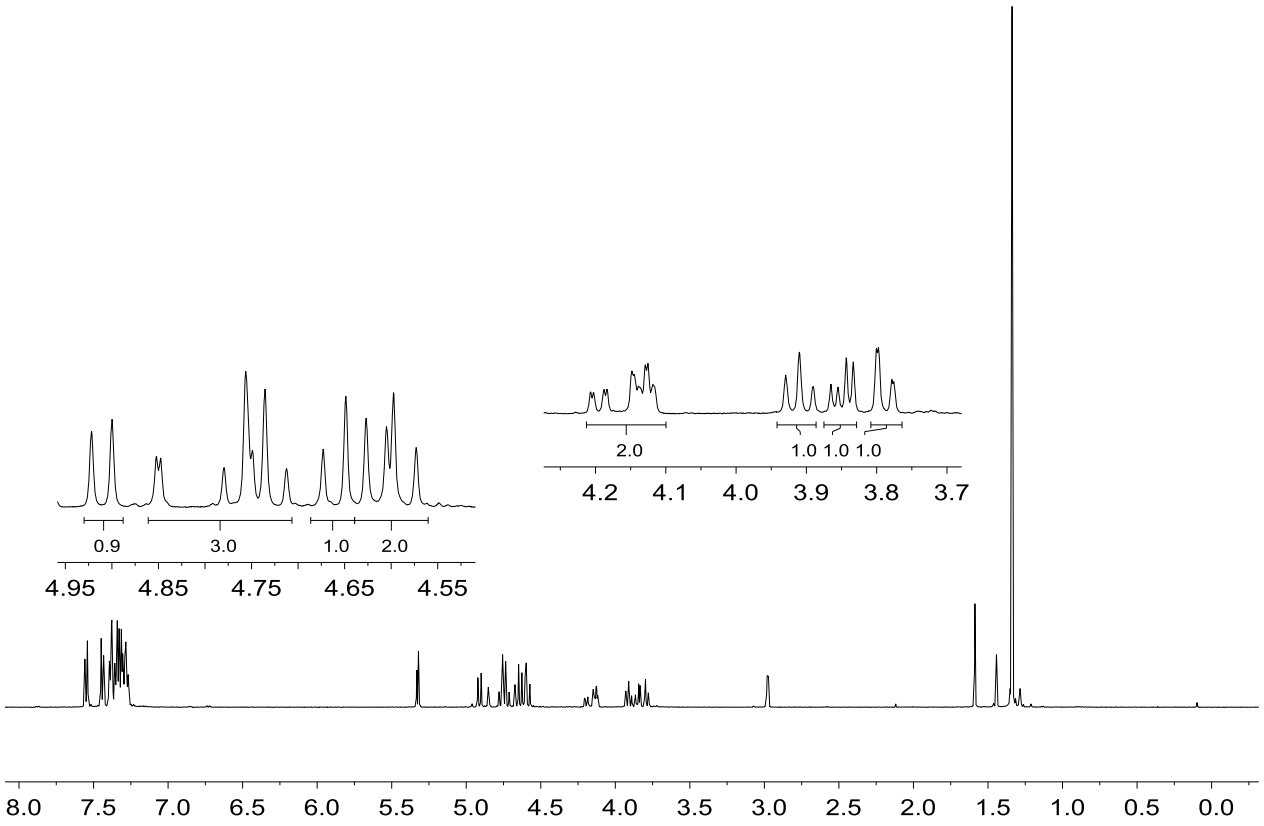
ν_{max} (neat)/cm^{-1} 3256m, 2966m, 2880m, 1613w, 1516w, 1497w, 1455m, 1393m, 1366m, 1295m, 1267m, 1250m, 1207m, 1147m, 1128m, 1086s, 1064s, 1013s, 995s, 974s, 946m, 907m, 894m, 861m, 848m, 833s, 733s, 694s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.55 (d, *J* = 8.4 Hz, 2H, H-C2´), 7.44 (d, *J* = 8.3 Hz, 2H, H-C3´), 7.41 – 7.25 (m, 15H, H-Ph), 4.91 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.80 (dd, J_{FC} = 49.4, *J* = 2.3 Hz, 1H, H-C$\underline{2}$), 4.77 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.72 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.66 (d, *J* = 12.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.62 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.59 (d, *J* = 12.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.17 (ddd, J_{FC} = 29.2, *J* = 9.6, 2.0 Hz, 1H, H-C3), 4.13 (dd, *J* = 9.9, 1.6 Hz, 1H, H-C5), 3.91 (t, *J* = 9.8 Hz, 1H, H-C4), 3.85 (dd, *J* = 10.9, 5.1 Hz, 1H, H-C6), 3.79 (dd, *J* = 10.9, 1.5 Hz, 2H, H-C6), 2.98 (d, *J* = 4.2 Hz, 1H, H-OH), 1.34 (s, 9H, H-C6´);

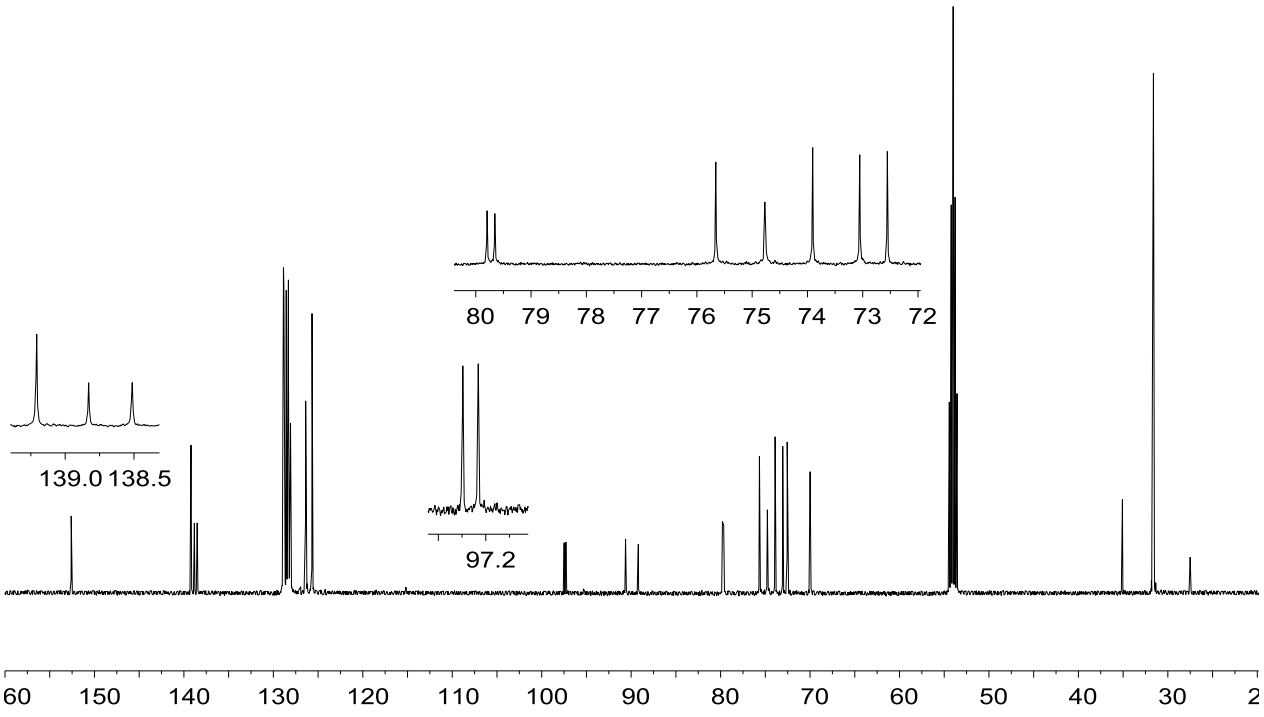
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 152.6 (C4´), 139.2 (*i*-Ph), 138.8 (*i*-Ph), 138.5 (C1´), 129.0 (*o,m,p*-Ph), 128.9 (*o,m,p*-Ph), 128.8 (*o,m,p*-Ph), 128.6 (*o,m,p*-Ph), 128.4 (*o,m,p*-Ph), 128.3 (*o,m,p*-Ph), 128.3 (*o,m,p*-Ph), 128.2 (*o,m,p*-Ph), 128.1 (*o,m,p*-Ph), 126.4 (d, J_{FC} = 1.2 Hz, C2´), 125.7 (C3´), 97.4 (d, J_{FC} = 24.6 Hz, C1), 89.9 (d, J_{FC} = 179.5 Hz, C2), 79.7 (d, J_{FC} = 17.6 Hz, C3), 75.7 (C$\underline{H}_2$Ph), 74.8 (d, J_{FC} = 1.7 Hz, C4), 73.9 (C$\underline{H}_2$Ph), 73.1 (C5), 72.6 (C$\underline{H}_2$Ph), 70.0 (C6), 35.1 (C5´), 31.6 (C6´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -204.0 (ddd, *J* = 49.4, 29.3, 4.2 Hz).

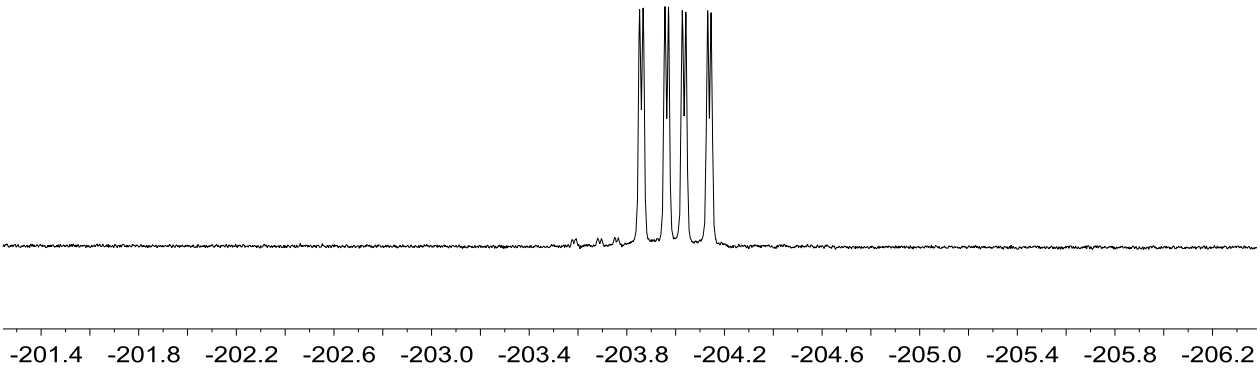
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



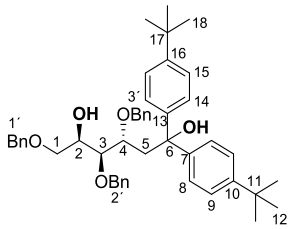
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 10:



Prepared according to the general procedure B. Starting with **L5** (44 mg, 0.1 mmol) compound **Table 2 Entry 10** was obtained (14 mg, 20%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.61 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 723.4035 $(M + Na)^+$, $C_{47}H_{56}O_5Na^+$ calculated 723,4025;

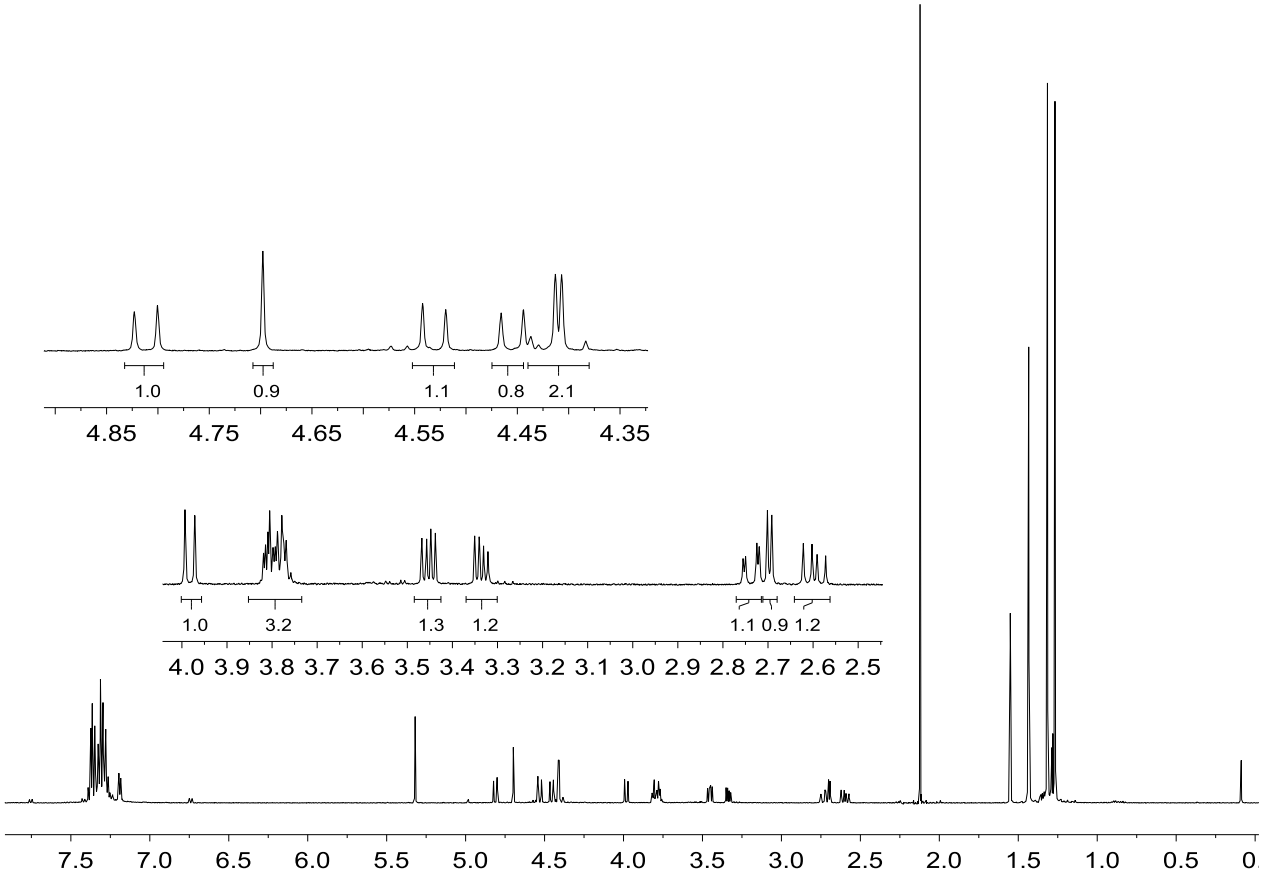
$[\alpha]_D^{25}$ +1.2 (*c* 0.25 in DCM);

ν_{max} (neat)/cm^{-1} 3455m, 3030w, 2962m, 2903w, 2867w, 2038w, 1946w, 1676w, 1605w, 1508m, 1497m, 1454m, 1404m, 1362m, 1265m, 1205w, 1176w, 1090s, 1027s, 912w, 824m, 734s, 696s;

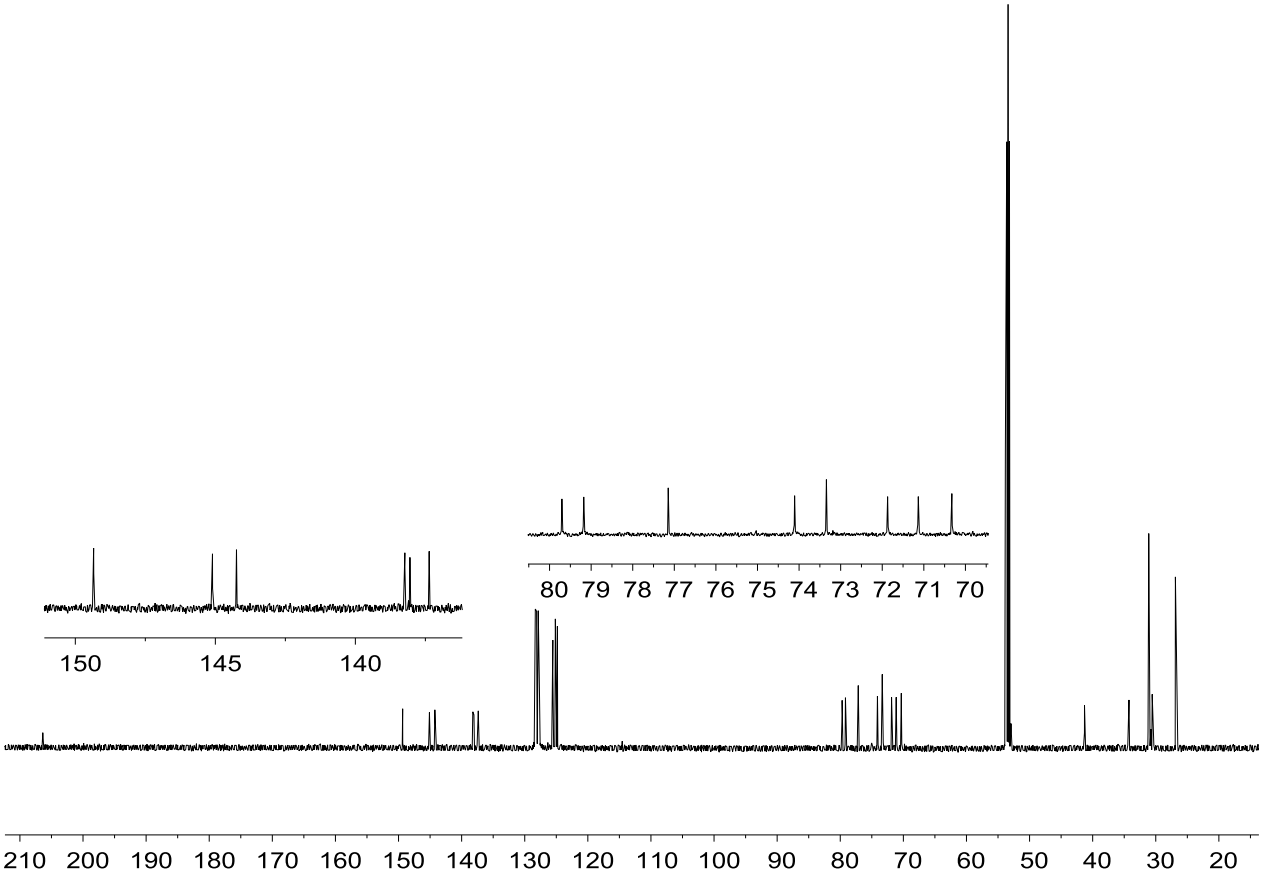
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.41 – 7.24 (m, 21H, H-Ph), 7.19 (dd, *J* = 7.7, 1.9 Hz, 2H, H-Ar), 4.81 (d, *J* = 11.3 Hz, 1H, H-C$\underline{H}_2$Ph3´), 4.70 (s, 1H, H-OH (tertiary)), 4.53 (d, *J* = 11.3 Hz, 1H, H-C$\underline{H}_2$Ph3´), 4.45 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph2´), 4.41 (m, 2H, H-C$\underline{H}_2$Ph1´), 3.98 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph2´), 3.84 – 3.75 (m, 3H, H-C2+H-C3+H-C4), 3.45 (dd, *J* = 9.8, 5.2 Hz, 1H, H-C1), 3.34 (dd, *J* = 9.8, 4.9 Hz, 1H, H-C1), 2.74 (dd, *J* = 15.2, 2.7 Hz, 1H, H-C5), 2.70 (d, *J* = 4.8 Hz, 1H, H-OH (secondary)), 2.60 (dd, *J* = 15.2, 9.5 Hz, 1H, H-C5), 1.32 (s, 9H, H-C12 or H-C18), 1.27 (s, 9H, H-C12 or H-C18);

^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 149.4 (C10/C16), 149.3 (C10/C16), 145.1 (C6 or C13), 144.2 1 (C6 or C13), 138.2 (*i*-Ph3´), 138.1 (*i*-Ph1´), 137.4 (*i*-Ph2´), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 127.9 (*o*,*m*,*p*-Ph), 127.9 (*o*,*m*,*p*-Ph), 127.8 (*o*,*m*,*p*-Ph), 127.7 (*o*,*m*,*p*-Ph), 125.6 (C8/C9/C14/C15), 125.2 (C8/C9/C14/C15), 125.1 (C8/C9/C14/C15), 124.8 (C8/C9/C14/C15), 79.7 (C3), 79.2 (C4), 77.2 (C6), 74.1 (CH_2Ph3´), 73.3 (CH_2Ph1´), 71.9 (CH_2Ph2´), 71.1 (C1), 70.3 (C2), 41.3 (C5), 34.3 (C11 or C17), 34.2 (C11 or C17), 31.1 (C12 or C18), 31.0 (C12 or C18).

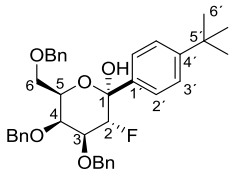
^{1}H (600 MHz, Dichloromethane-d_2, 299 K) (with acetone)



$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 13:



Prepared according to the general procedure B. Starting with **L6** (46 mg, 0.1 mmol) compound **Table 2 Entry 13** was obtained (53 mg, 89%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.60 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 607.2818 $(M + Na)^+$, $C_{37}H_{41}O_5FNa^+$ calculated 607.2830;

$[\alpha]_D^{25}$ +17.5 (*c* 2.0 in DCM);

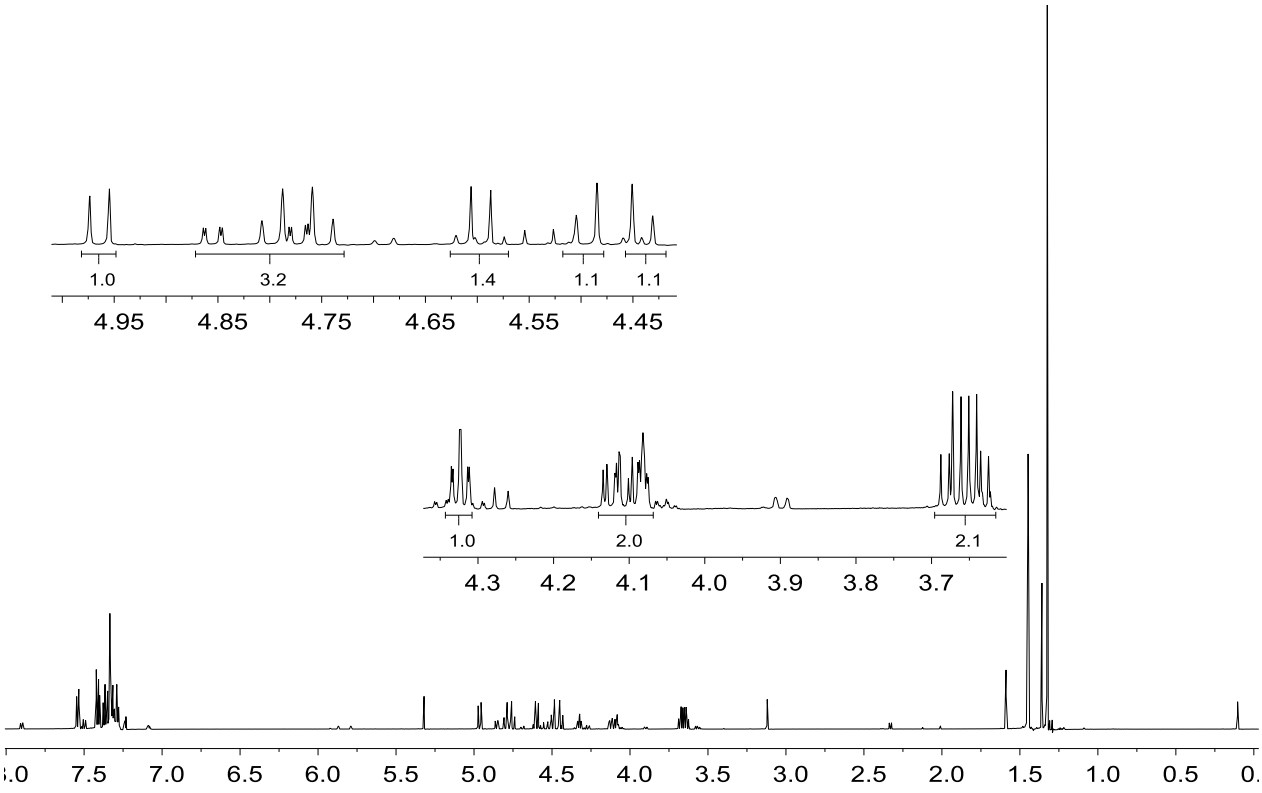
ν_{max} (neat)/cm^{-1} 3410w, 3032w, 2962m, 2868m, 2163w, 1607w, 1497m, 1454m, 1402m, 1366m, 1270m, 1234w, 1208m, 1148m, 1099s, 1067s, 1025s, 914w, 838m, 811m, 733s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.56 – 7.52 (m, 2H, H-C2´), 7.43 – 7.41 (m, 2H, H-C3´), 7.40 (m, 2H, H-Ph), 7.38 – 7.26 (m, 13H, H-Ph), 4.96 (d, J = 11.3 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.81 (ddd, J_{FH} = 49.6, J = 9.6, 1.5 Hz, 1H, H-C2), 4.80 (d, J = 11.9 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.75 (d, J = 12.0 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.60 (d, J = 11.3 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.49 (d, J = 11.9 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.44 (d, J = 11.9 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.32 (td, J = 6.5, 1.3 Hz, 1H, H-C5), 4.14 – 4.07 (m, 2H, H-C3 + H-C4), 3.69 – 3.62 (m, 2H, H-C6), 3.12 (dd, J = 1.5, 0.5 Hz, 1H, H-OH), 1.32 (s, 9H, H-C6´);

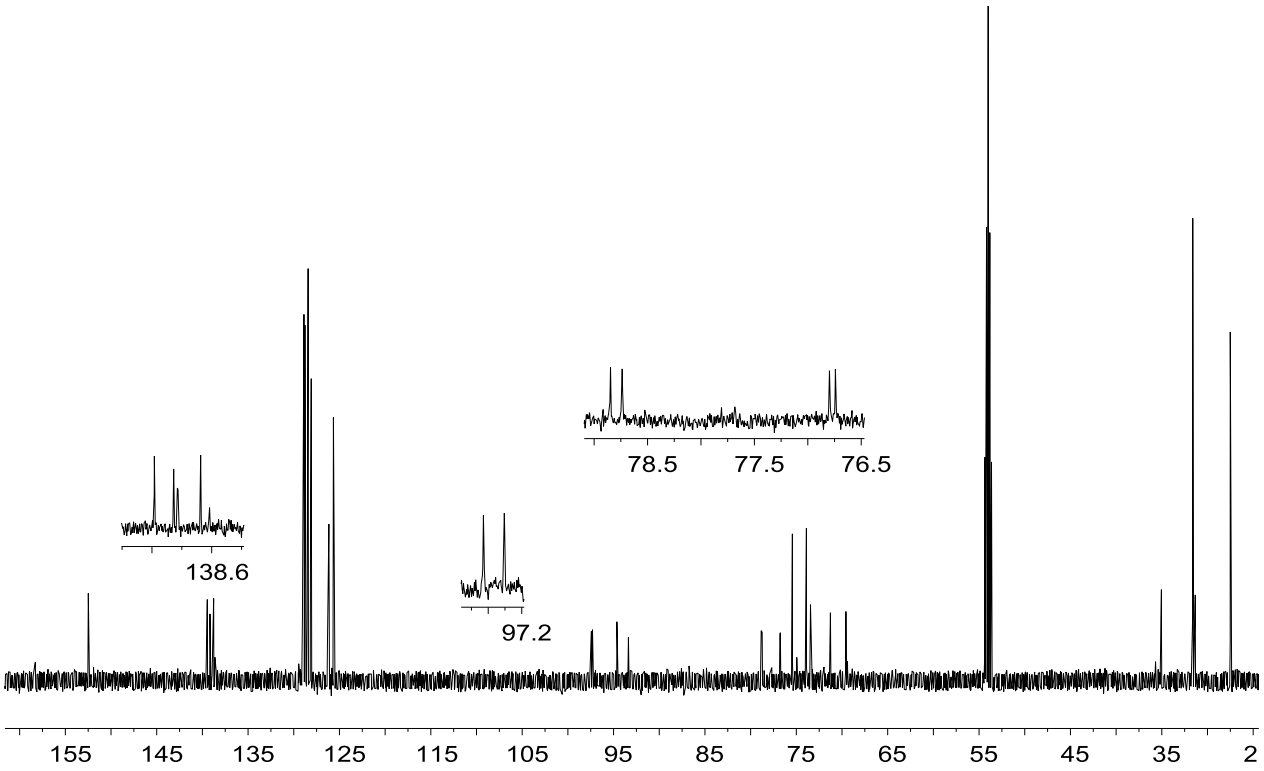
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 152.5 (C4´), 139.5 (*i*-Ph), 139.2 (*i*-Ph), 139.1 (d, J_{FC} = 1.5 Hz, C1´), 138.8 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 126.2 (d, J_{FC} = 1.2 Hz, C2´), 125.7 (C3´), 97.4 (d, J_{FC} = 18.7 Hz, C1), 94.0 (d, J_{FC} = 190.1 Hz, C2), 78.8 (d, J_{FC} = 16.6 Hz, H-C3), 76.8 (d, J_{FC} = 8.4 Hz, H-C4), 75.4 (<u>C</u>H$_2$Ph), 73.9 (<u>C</u>H$_2$Ph), 73.4 (d, J_{FC} = 2.1 Hz, <u>C</u>H$_2$Ph), 71.3 (C5), 69.6 (C6), 35.0 (C5´), 31.6 (C6´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -207.24 (ddd, J = 49.6, 10.6, 3.8 Hz).

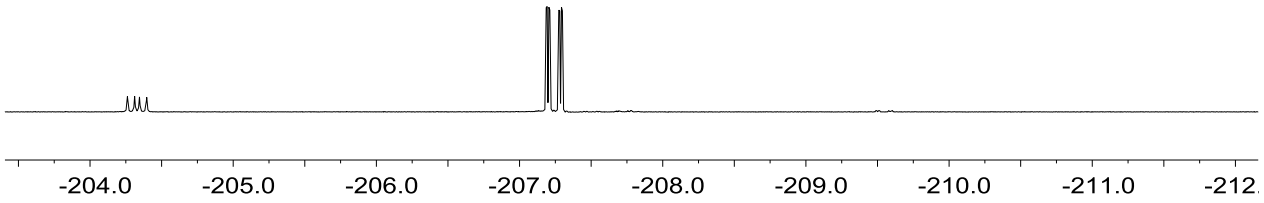
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



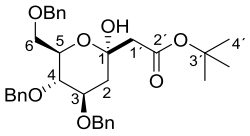
^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



General Procedure C for *C*-glycosylations with *enolate*s.

LiHMDS (27 mg, 0.2 mmol, 1.6 eq.) was added to a solution of *tert*-butyl acetate (22 µL, 0.2 mmol, 1.6 eq.) in toluene:THF (2:1, 0.15:75µL, 0.5 M) under an argon atmosphere and at -78 °C. The mixture was stirred for 30 min. The organolithium reagent was then transferred slowly to a solution of the corresponding lactone (0.1 mmol, 1.0 eq.) in dry THF (0.35 mL, 0.3 M) under argon and at -78 °C. The reaction mixture was stirred for 30 min and then quenched by addition of MeOH (5.0 mL). H_2O (5.0 mL) and EtOAc (5.0 mL) were added and the water phase was extracted with EtOAc (3 x 3 mL). The combined organic layers were washed with H_2O (2 x 7 mL) and brine (1 x 7 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue obtained was purified by filtration through celite (EtOAc).

Compound Table 2 Entry 2:



Prepared according to the general procedure C. Starting with **L3** (44 mg, 0.1 mmol) compound **Table 2 Entry 2** was obtained (55 mg, 99%) as a white solid after filtration through celite (EtOAc).

R_f 0.58 (SiO_2, CyH:EtOAc(3:1));

Mp 78 – 81 °C;

m/*z* (ESI) found: 571.2706 $(M + Na)^+$, $C_{33}H_{39}O_7FNa^+$ calculated 571.2666;

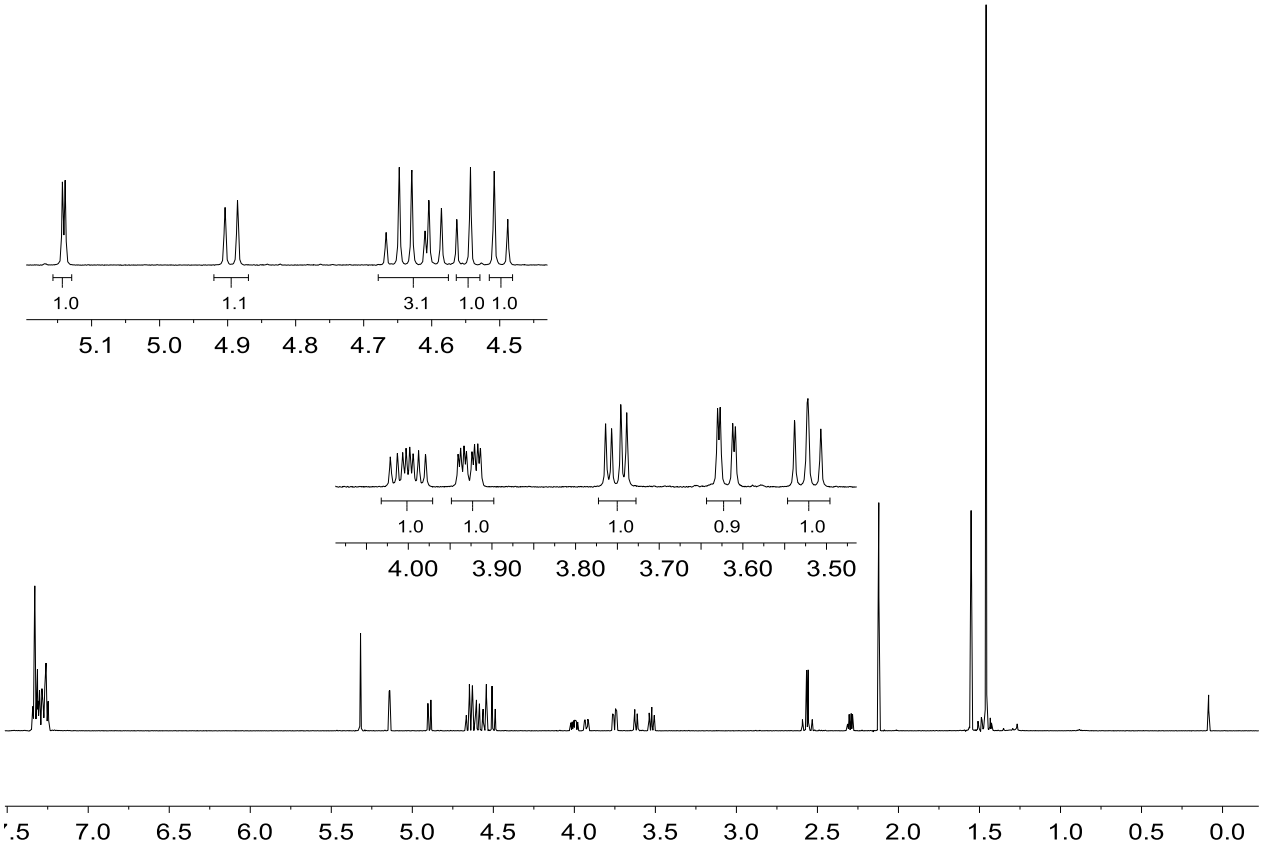
$[\alpha]_D^{25}$ +20.9 (*c* 0.25 in DCM);

ν_{max} (neat)/cm^{-1} 3427m, 3064w, 3031w, 2977w, 2928m, 2864m, 2168w, 2030w, 2009w, 1994w, 1951w, 1701m, 1607w, 1497w, 1454m, 1394w, 1367m, 1341w, 1246m, 1223m, 1152s, 1074s, 1027m, 1005s, 960w, 893w, 870w, 838w, 819w, 733s, 696s;

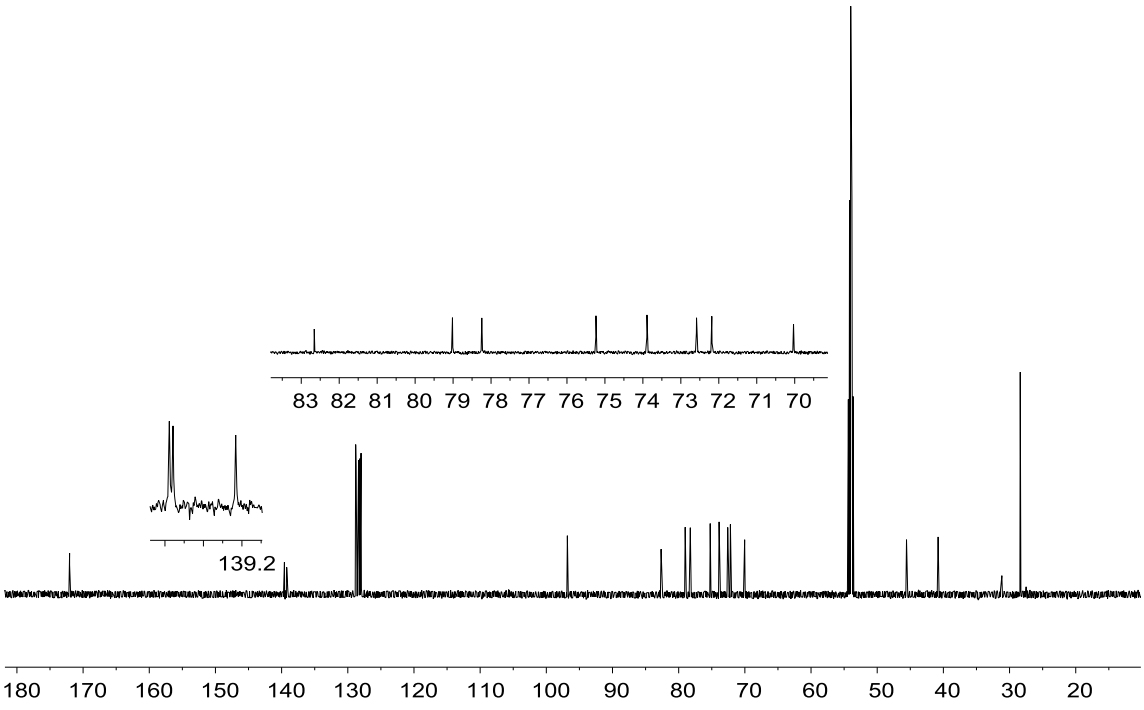
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.35 – 7.24 (m, 15H, H-Ph), 5.14 (d, *J* = 2.4 Hz, 1H, H-OH), 4.89 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.66 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.62 (d, *J* = 11.7 Hz, 1H, H-C$\underline{H}_2$Ph), 4.60 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.55 (d, *J* = 12.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.50 (d, *J* = 12.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.00 (ddd, *J* = 11.3, 8.9, 5.0 Hz, 1H, H-C3), 3.93 (ddd, *J* = 9.9, 4.3, 1.9 Hz, 1H, H-C5), 3.75 (dd, *J* = 10.9, 4.2 Hz, 1H, H-C6), 3.62 (dd, *J* = 10.9, 1.9 Hz, 1H, H-C6), 3.52 (dd, *J* = 9.9, 8.9 Hz, 1H, H-C4), 2.60 – 2.52 (m, 2H, H-C1´), 2.30 (dd, *J* = 12.5, 5.0 Hz, 1H, H-C2), 1.52 – 1.47 (m, 1H, H-C2), 1.46 (d, *J* = 0.6 Hz, 9H, H-C4´);

^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 172.0 (C2´), 139.6 (*i*-Ph), 139.6 (*i*-Ph), 139.2 (*i*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 96.8 (C1), 82.7 (C3´), 79.0 (C4), 78.2 (C3), 75.2 (C$\underline{H}_2$Ph), 73.9 (C$\underline{H}_2$Ph), 72.6 (C5), 72.2 (C$\underline{H}_2$Ph), 70.0 (C6), 45.6 (C1´), 40.8 (C2), 28.4 (C4´).

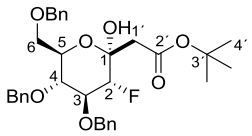
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 5:



Prepared according to the general procedure C. Starting with **L1** (46 mg, 0.1 mmol) compound **Table 2 Entry 5** was obtained (52 mg, 90%) as a colourless oil after filtration through celite (EtOAc).

R_f 0.55 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 589.2585 $(M + Na)^+$, $C_{33}H_{39}O_7FNa^+$ calculated 589.2572;

$[\alpha]_D^{25}$ +11.3 (*c* 0.42 in DCM);

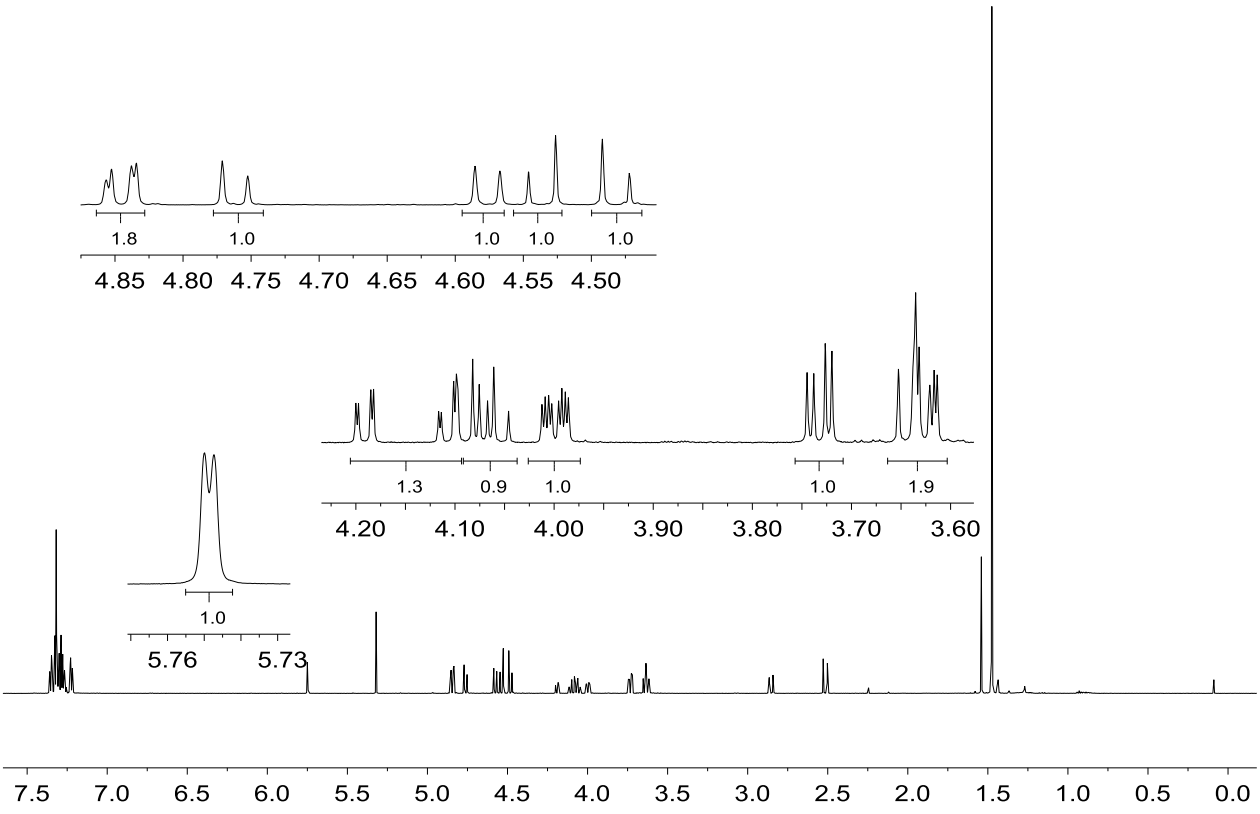
ν_{max} (neat)/cm^{-1} 3413w, 3032w, 2983w, 1696m/s, 1497m, 1454m, 1395m/s, 1366m, 1251m, 1225m, 1204m, 1152s, 1091s, 1051s, 1026s, 977m, 897w, 838m, 731s, 696s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.38 – 7.24 (m, 13H, H-Ph), 7.24 – 7.21 (m, 2H, H-Ph), 5.75 (d, *J* = 1.6 Hz, 1H, H-OH), 4.85 (dd, *J* = 11.1, 2.4 Hz, 2H, H-CH_2Ph), 4.76 (d, *J* = 11.2 Hz, 1H, H-CH_2Ph), 4.58 (d, *J* = 11.0 Hz, 1H, H-CH_2Ph), 4.54 (d, *J* = 11.9 Hz, 1H, H-CH_2Ph), 4.48 (d, *J* = 11.9 Hz, 1H, H-CH_2Ph), 4.15 (ddd, J_{FH} = 50.1, *J* = 9.1, 1.7 Hz, 1H, H-C2), 4.07 (dt, J_{FH} = 12.7, *J* = 9.0 Hz, 1H, H-C3), 4.00 (ddd, *J* = 10.1, 4.0, 1.9 Hz, 1H, H-C5), 3.73 (dd, *J* = 11.0, 4.0 Hz, 1H, H-C6), 3.63 (dd, *J* = 10.6, 4.2 Hz, 1H, H-C6), 3.63 (t, *J* = 10.8 Hz, 1H, H-C4), 2.85 (dd, *J* = 15.6, 1.7 Hz, 1H, H-C1´), 2.52 (d, *J* = 15.6 Hz, 1H, H-C1´), 1.48 (s, 9H, H-C4´);

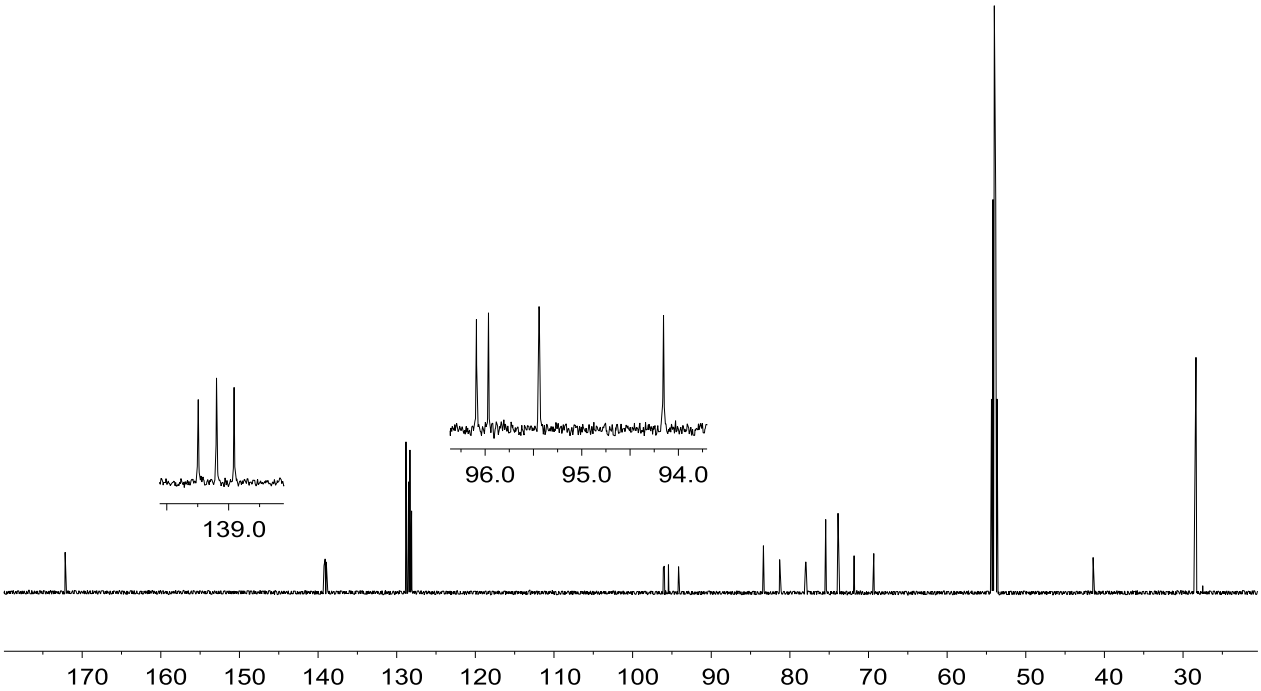
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 172.2 (C2´), 139.3 (*i*-Ph), 139.1 (*i*-Ph), 139.0 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 96.0 (d, J_{FC} = 18.9 Hz, C1), 94.8 (d, J_{FC} = 194.0 Hz, H-C2), 83.4 (C3´), 81.3 (d, J_{FC} = 16.0 Hz, C3), 78.0 (d, J_{FC} = 7.9 Hz, C4), 75.49 (d, J_{FC} = 2.6 Hz, H-C$\underline{H}_2$Ph), 75.4 (H-C$\underline{H}_2$Ph), 73.9 (H-C$\underline{H}_2$Ph), 72.0 (d, J_{FC} = 1.4 Hz, C5), 69.3 (C6), 41.4 (d, J_{FC} = 1.3 Hz, C1´), 28.4 (C4´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.1 (dd, *J* = 50.2, 12.9 Hz).

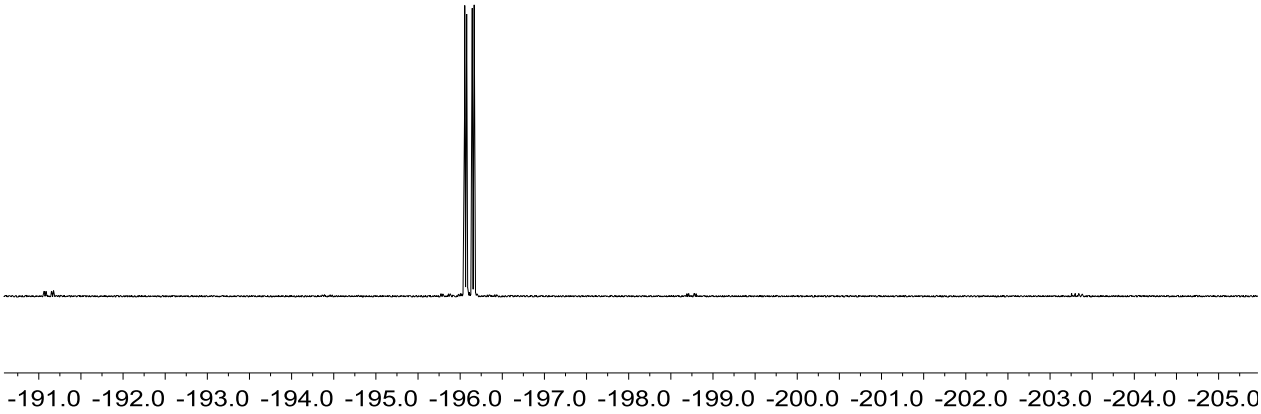
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



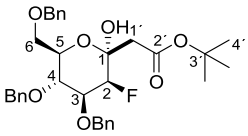
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 8:



Prepared according to the general procedure C. Starting with **L4** (46 mg, 0.1 mmol) compound **Table 2 Entry 8** was obtained (55 mg, 95%) as a colourless oil after filtration through celite (EtOAc).

R_f 0.59 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 589.2581 $(M + Na)^+$, $C_{33}H_{39}O_7FNa^+$ calculated 589.2572;

$[\alpha]_D^{25}$ +22.8 (*c* 0.25 in DCM);

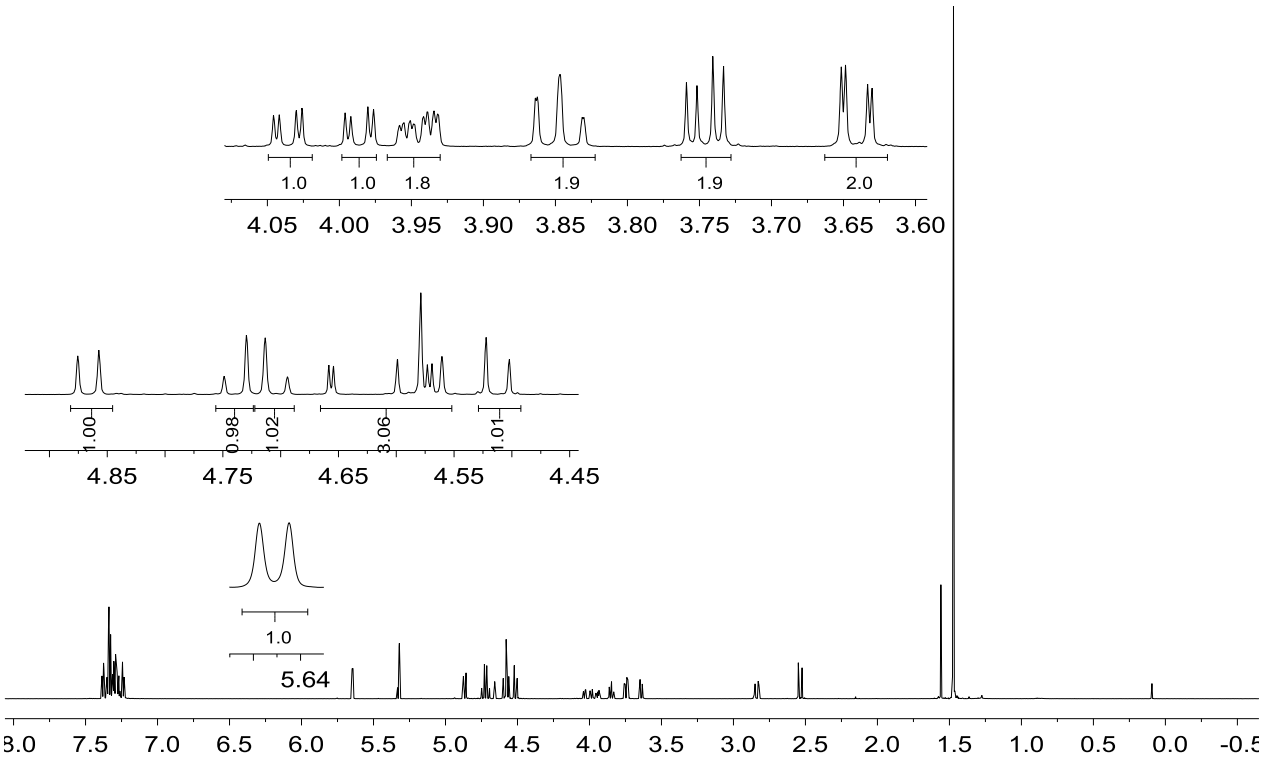
ν_{max} (neat)/cm^{-1} 3391w, 2927w, 1699m/s, 1497m, 1454m, 1394w, 1368m, 1254m, 1210m, 1150s, 1075s, 1027s, 961w, 903m, 845m, 734s, 696s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.40 – 7.22 (m, 15H, H-Ph), 5.65 (d, *J* = 3.8 Hz, 1H, H-OH), 4.87 (d, *J* = 10.9 Hz, 1H, H-CH_2Ph), 4.74 (d, *J* = 11.6 Hz, 1H, H-CH_2Ph), 4.70 (d, *J* = 11.6 Hz, 1H, H-CH_2Ph), 4.61 (dd, J_{FC} = 51.1, *J* = 2.4 Hz, 1H, H-C2), 4.59 (d, *J* = 12.1 Hz, 1H, H-CH_2Ph), 4.57 (d, *J* = 11.0 Hz, 1H, H-CH_2Ph), 4.51 (d, *J* = 12.4 Hz, 1H, H-CH_2Ph), 4.01 (ddd, J_{FC} = 29.8, *J* = 9.4, 2.4 Hz, 1H, H-C3), 3.95 (dddd, *J* = 10.0, 4.4, 1.9, 0.7 Hz, 1H, H-C5), 3.85 (td, *J* = 9.6, 1.0 Hz, 1H, H-C4), 3.75 (dd, *J* = 11.0, 4.4 Hz, 1H, H-C6), 3.64 (dd, *J* = 11.0, 1.8 Hz, 1H, H-C6), 2.84 (dd, *J* = 15.6, 2.9 Hz, 1H, H-C1´), 2.54 (d, *J* = 15.6 Hz, 1H, H-C1´), 1.47 (s, 9H, H-C4´);

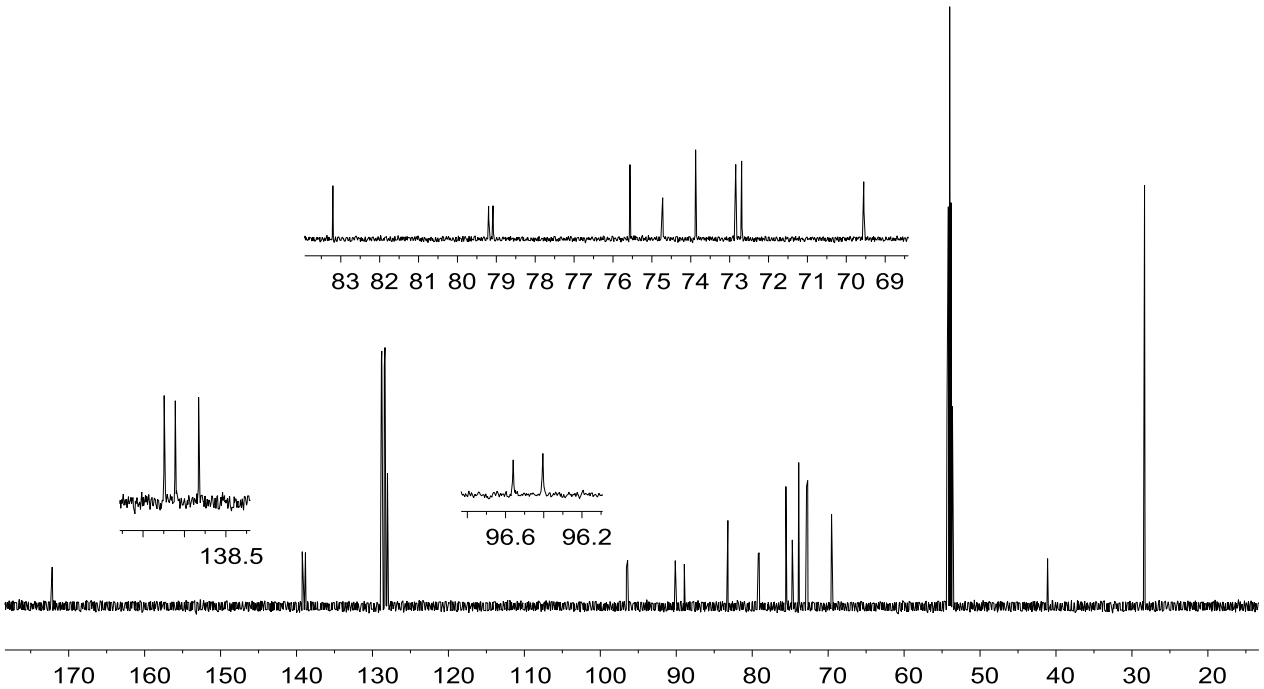
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 172.2 (C2´), 139.3 (*i*-Ph), 139.1 (*i*-Ph), 138.8 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 96.5 (d, J_{FC} = 23.4 Hz, C1), 89.5 (d, J_{FC} = 179.9 Hz, C2), 83.2 (C3´), 79.2 (d, J_{FC} = 17.1 Hz, C3), 75.6 (<u>C</u>H_2Ph), 74.7 (d, J_{FC} = 1.4 Hz, C4), 73.9 (<u>C</u>H_2Ph), 72.9 (C5), 72.7 (<u>C</u>H_2Ph), 69.6 (C6), 41.1 (d, J_{FC} = 3.9 Hz, C1´), 28.4 (C4´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -207.0 (ddt, *J* = 51.1, 29.7, 3.4 Hz).

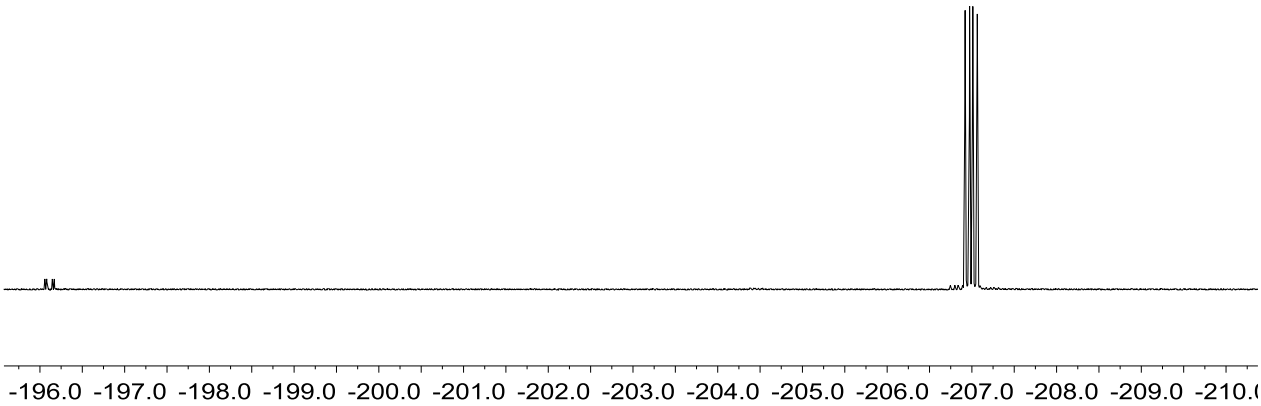
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



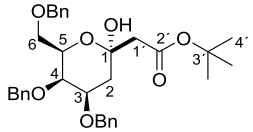
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 11:



Prepared according to the general procedure C. Starting with **L5** (44 mg, 0.1 mmol) compound **Table 2 Entry 11** was obtained (25 mg, 45%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.52 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 571.2685 $(M + Na)^+$, $C_{33}H_{39}O_7FNa^+$ calculated 571.2666;

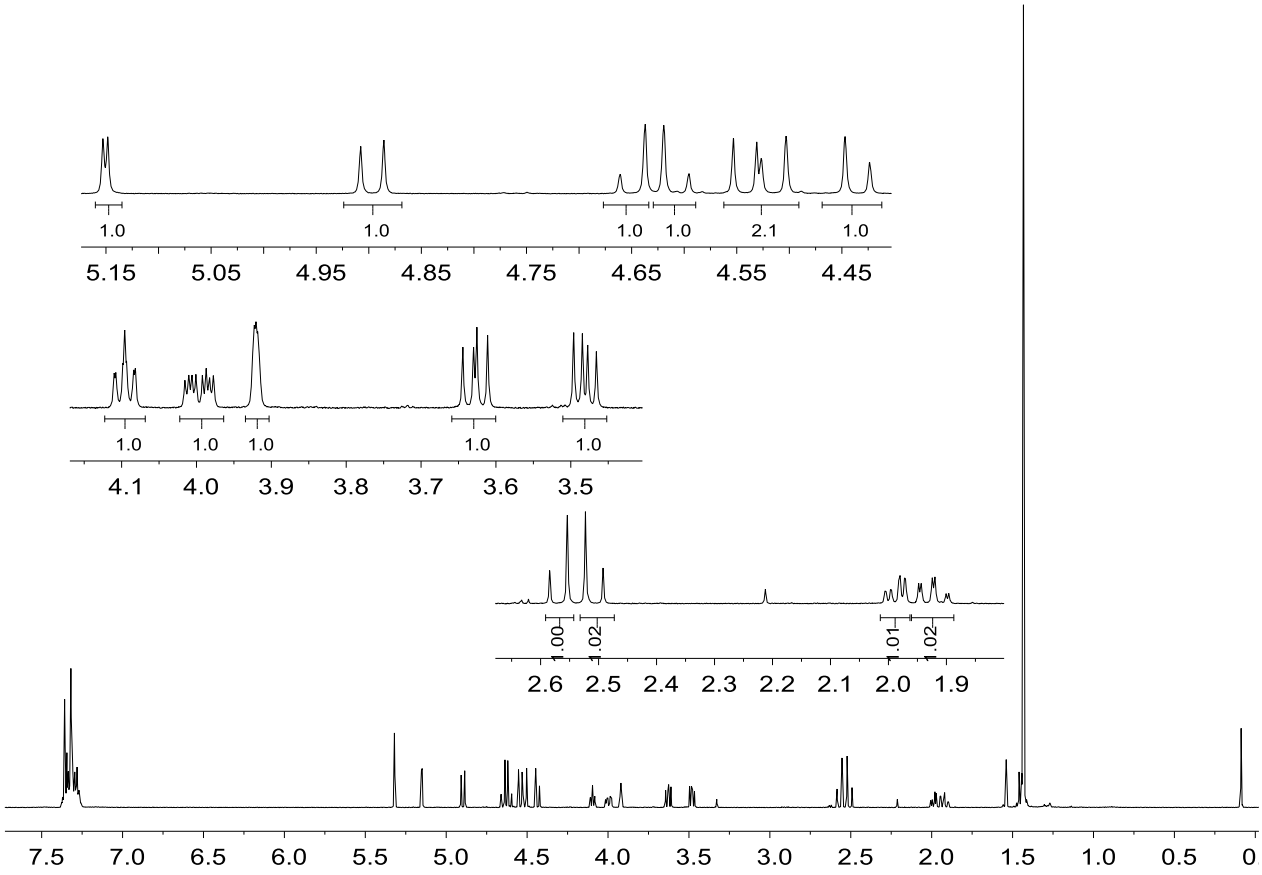
$[\alpha]_D^{25}$ +11.2 (*c* 0.25 in DCM);

ν_{max} (neat)/cm-1 3428m, 3064w, 3031w, 2978w, 2921m, 2869m, 2185w, 1947w, 1701m/s, 1607w, 1497w, 1454m, 1431w, 1394w, 1367m, 1351m, 1288w, 1233m, 1149s, 1084s, 1062s, 1040s, 1028s, 954w, 907w, 878m, 839w, 819w, 805w, 733s, 695s;

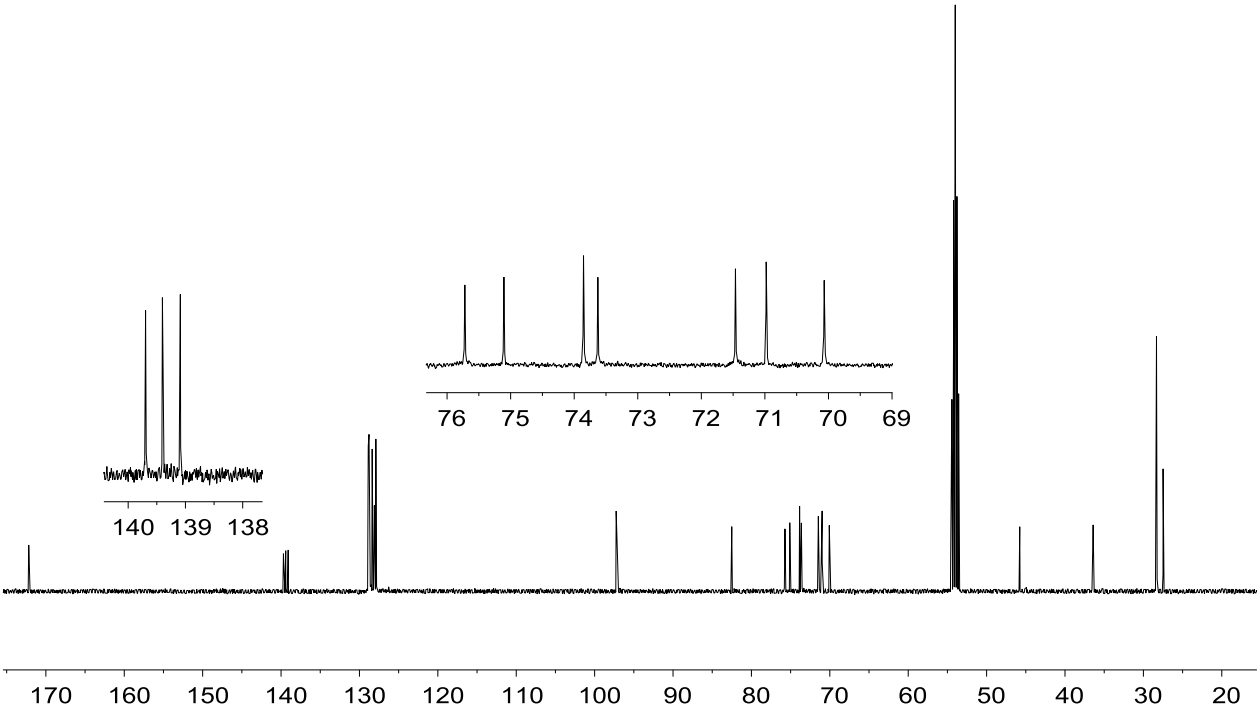
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.39 – 7.24 (m, 15H, H-Ph), 5.15 (d, *J* = 2.3 Hz, 1H, H-OH), 4.90 (d, *J* = 11.0 Hz, 1H, H-CH_2Ph), 4.65 (d, *J* = 11.9 Hz, 1H, H-CH_2Ph), 4.61 (d, *J* = 12.0 Hz, 1H, H-CH_2Ph), 4.54 (d, *J* = 11.1 Hz, 1H, H-CH_2Ph), 4.51 (d, *J* = 11.8 Hz, 1H, H-CH_2Ph), 4.44 (d, *J* = 11.6 Hz, 1H, H-CH_2Ph), 4.10 (m, 1H, H-C5), 4.00 (ddd, *J* = 11.7, 4.8, 2.6 Hz, 1H, H-C3), 3.94 – 3.90 (m, 1H, H-C4), 3.63 (dd, *J* = 9.4, 7.2 Hz, 1H, H-C6), 3.48 (dd, *J* = 9.4, 5.8 Hz, 1H, H-C6), 2.57 (d, *J* = 15.3 Hz, 1H, C1´), 2.51 (d, *J* = 15.2 Hz, 1H, C1´), 2.02 – 1.95 (m, 1H, H-C2), 1.92 (m, 1H, H-C2), 1.43 (s, 9H, H-C4´);

^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 172.2 (C2´), 139.7 (*i*-Ph), 139.4 (*i*-Ph), 139.1 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.7 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 127.9 (*o*,*m*,*p*-Ph), 97.3 (C1), 82.5 (C3´), 75.7 (C3), 75.1 (<u>C</u>H_2Ph), 73.9 (<u>C</u>H_2Ph), 73.6 (C4), 71.5 (C5), 71.0 (<u>C</u>H_2Ph), 70.1 (C6), 45.8 (C1´), 36.4 (C2), 28.3 (C4´).

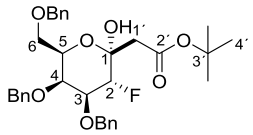
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 14:



Prepared according to the general procedure C. Starting with **L6** (46 mg, 0.1 mmol) compound **Table 2 Entry 14** was obtained (58 mg, quant.) as a colourless oil after filtration through celite (EtOAc).

R_f 0.58 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 589.2590 $(M + Na)^+$, $C_{33}H_{39}O_7FNa^+$ requires 589.2572;

$[\alpha]_D^{25}$ +23.3 (*c* 0.33 in DCM);

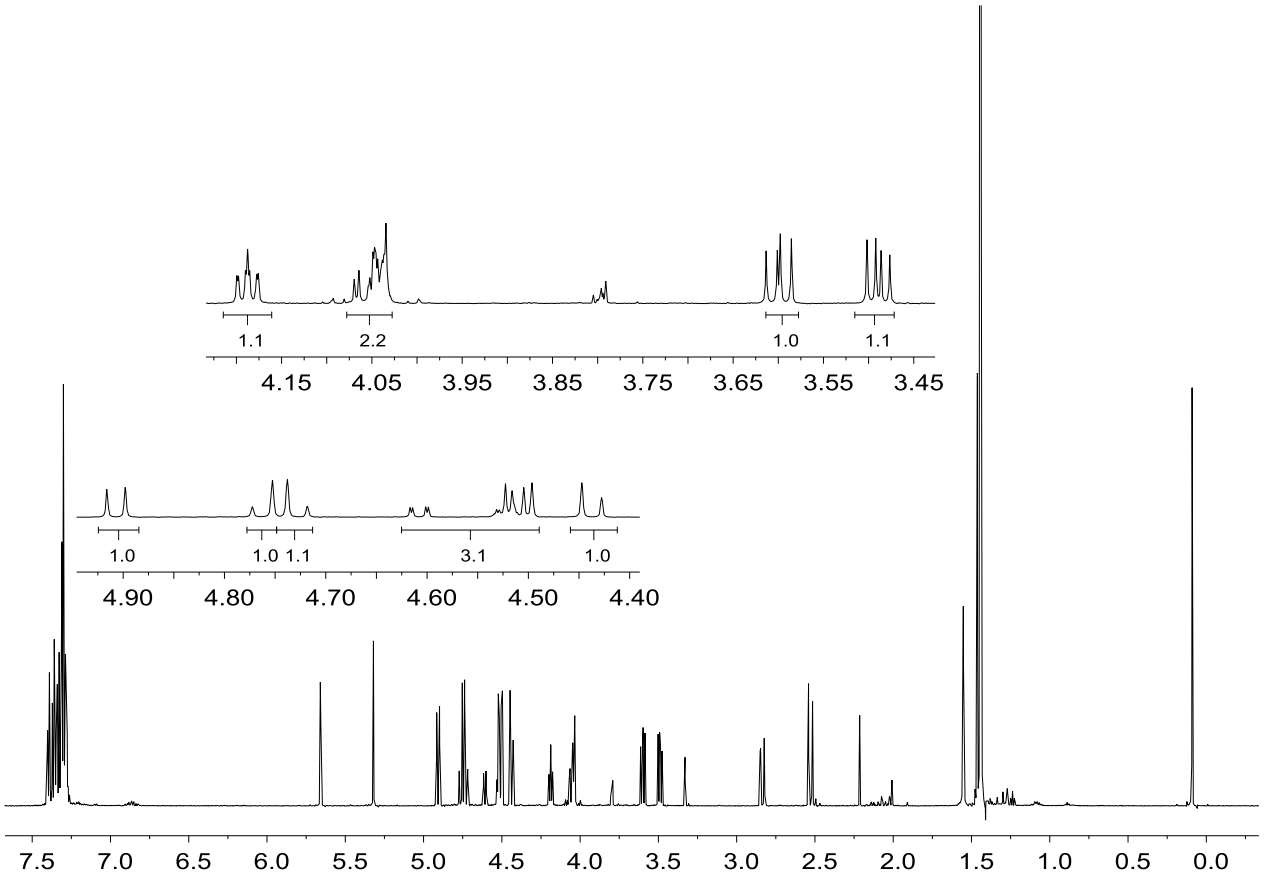
ν_{max} (neat)/cm^{-1} 3405w, 2923w, 1699m, 1497w, 1455m, 1394w, 1368m, 1249m, 1209m, 1148s, 1103s, 1069s, 1028s, 956w, 909w, 835m, 733s, 696s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.42 – 7.26 (m, 15H), 5.66 (d, *J* = 1.6 Hz, 1H, H-OH), 4.91 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.76 (d, *J* = 11.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.73 (d, *J* = 11.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.6 (dd, J_{FC} = 51.3, *J* = 9.3 Hz, 1H, H-C2), 4.51 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.51 (d, *J* = 11.7 Hz, 1H, H-C$\underline{H}_2$Ph), 4.44 (d, *J* = 11.7 Hz, 1H, H-C$\underline{H}_2$Ph), 4.19 (ddd, *J* = 7.2, 5.8, 1.3 Hz, 1H, H-C5), 4.08 – 4.02 (m, 2H, H-C3 + H-C4), 3.60 (dd, *J* = 9.4, 7.4 Hz, 1H, H-C6), 3.49 (dd, *J* = 9.3, 5.8 Hz, 1H, H-C6), 2.84 (dd, *J* = 15.5, 1.6 Hz, 1H, H-C1´), 2.53 (d, *J* = 15.5 Hz, 1H, H-C1´), 1.44 (s, 9H, H-C4´);

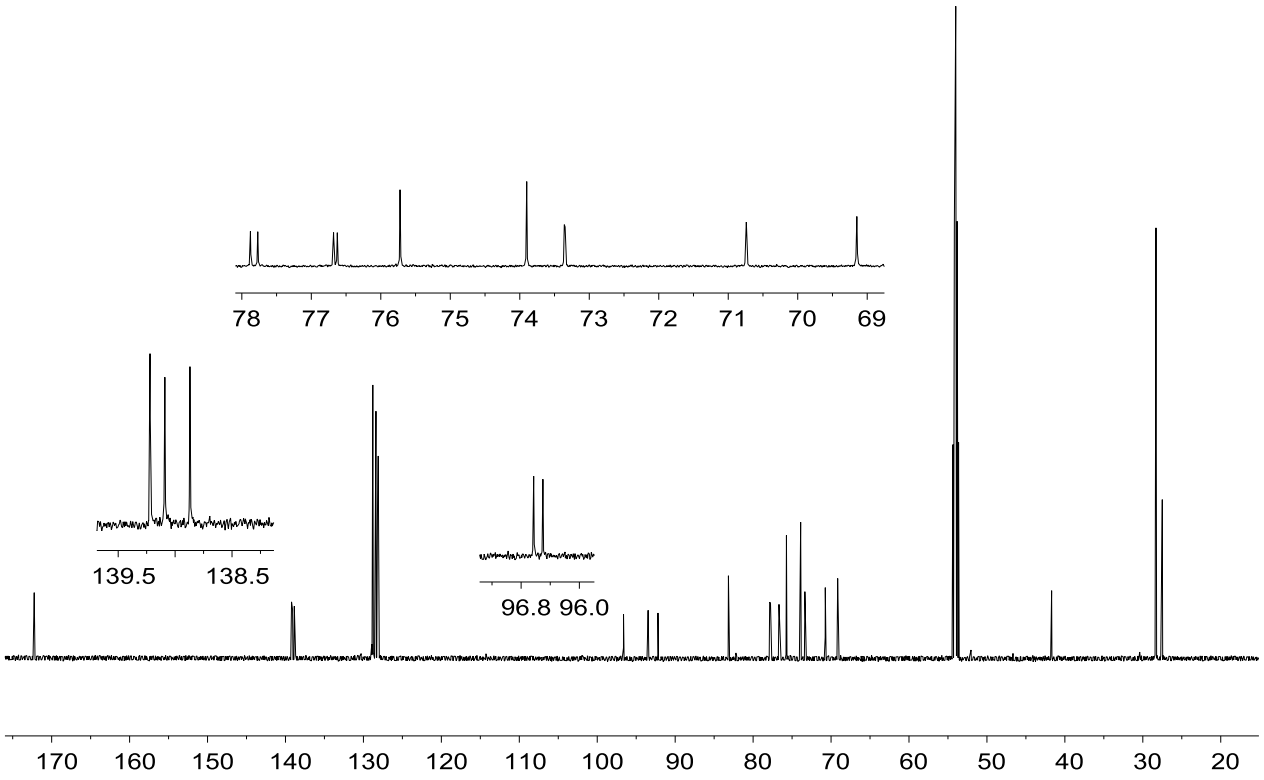
$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 172.2 (C2´), 139.2 (*i*-Ph), 139.1 (*i*-Ph), 138.9 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 96.6 (d, J_{FC} = 19.0 Hz, C1), 92.8 (d, J_{FC} = 190.1 Hz, C2), 83.2 (C3´), 77.8 (d, J_{FC} = 15.9 Hz, C3), 76.7 (d, J_{FC} = 8.1 Hz, C4), 75.7 ($\underline{C}H_2Ph$), 73.9 ($\underline{C}H_2Ph$), 73.4 (d, J_{FC} = 1.8 Hz, $\underline{C}H_2Ph$), 70.7 (d, J_{FC} = 1.2 Hz, C5), 69.2 (C6), 41.7 (C1´), 28.3 (C4´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -206.6 – -206.7 (m).

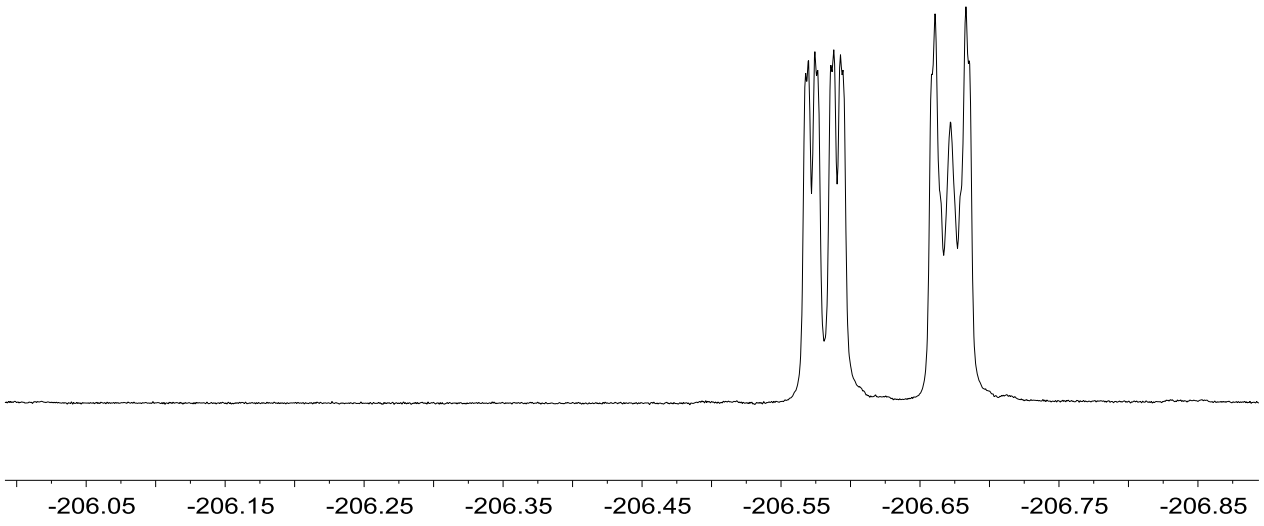
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



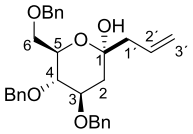
^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



General Procedure D: *C*-glycosylations with allyl magnesium bromide.

Allyl magnesium bromide (1.0 M in THF, 0.10 mL, 0.1 mmol, 1.1 eq.) was added slowly to a solution of the corresponding lactone (0.1 mmol, 1.0 eq.) in dry THF (0.58 mL, 0.2 M) at -78 °C. The reaction mixture was stirred for 30 min and then quenched by addition of MeOH (5.0 mL). H_2O (5.0 mL) and EtOAc (5.0 mL) were added and the aqueous phase was extracted with EtOAc (3 x 3 mL). The combined organic layers were washed H_2O (2 x 7.0 mL) and brine (1 x 7.0 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuum*. The residue obtained was purified by column chromatography CyH: EtOAc (SiO_2, specified combination of CyH: EtOAc).

Compound Table 2 Entry 3:



Prepared according to the general procedure D. Starting with **L3** (44 mg, 0.1 mmol) compound **Table 2 Entry 3** was obtained (30 mg, 62%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.42 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 497.2306 $(M + Na)^+$ and 539.2785 (double addition), $C_{30}H_{34}O_5Na^+$ calculated 497.2298;

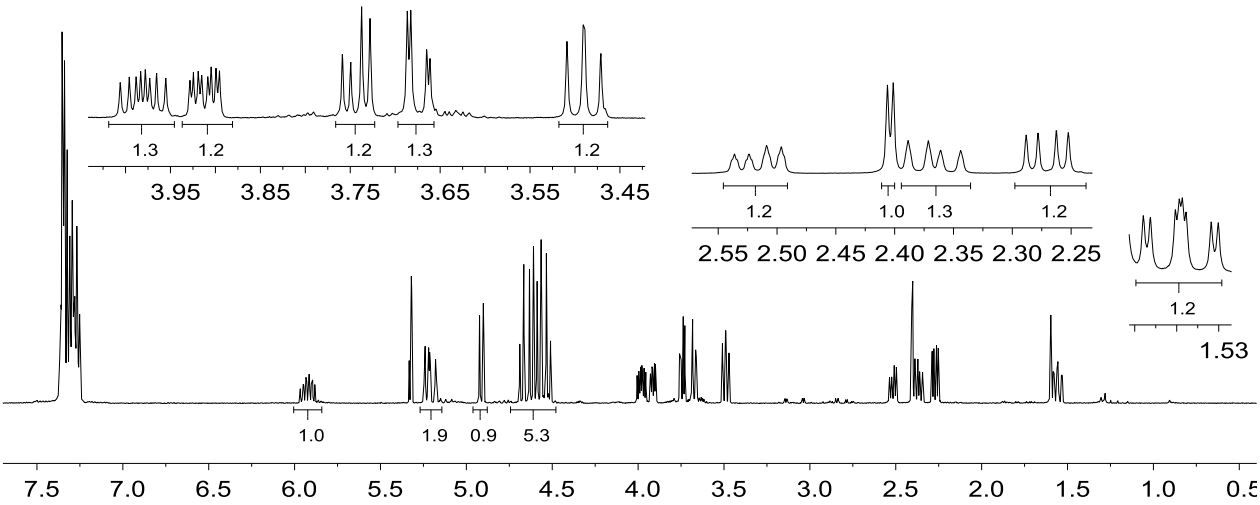
$[\alpha]_D^{25}$ +11.7 (*c* 0.67 in DCM);

ν_{max} (neat)/cm^{-1} 3412w, 3030w, 2908w, 1641w, 1497m, 1454m, 1365m, 1206w, 1071s, 1027m, 985s, 916m, 861w, 814w, 733s, 695s;

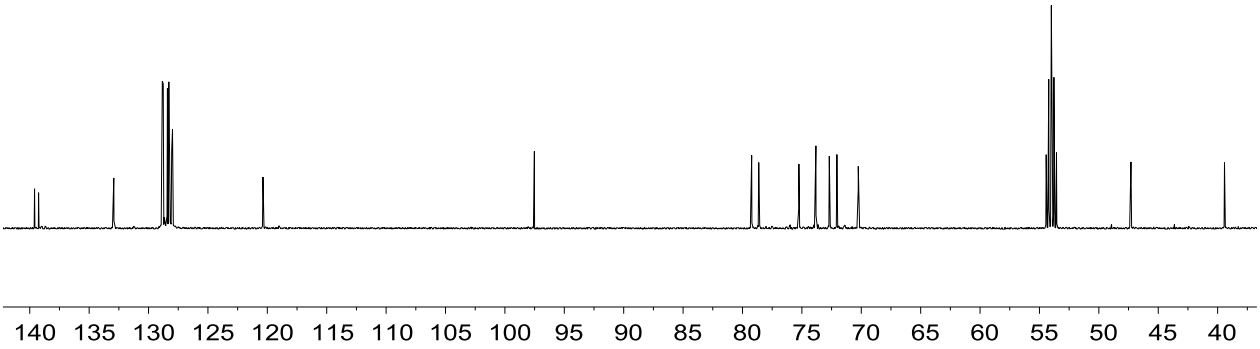
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.40 – 7.22 (m, 15H, H-Ph), 5.92 (dddd, *J* = 17.3, 10.3, 8.6, 6.2 Hz, 1H, H-C2´), 5.26 – 5.17 (m, 2H, H-C3´), 4.91 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.68 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.62 (d, *J* = 11.7 Hz, 1H, H-C$\underline{H}_2$Ph), 4.60 (d, *J* = 10.7 Hz, 1H, H-C$\underline{H}_2$Ph), 4.58 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.52 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 3.98 (ddd, *J* = 11.4, 8.9, 5.1 Hz, 1H, H-C3), 3.91 (ddd, *J* = 9.9, 4.6, 1.9 Hz, 1H, H-C5), 3.74 (dd, *J* = 10.7, 4.7 Hz, 1H, H-C6), 3.67 (dd, *J* = 10.7, 1.9 Hz, 1H, H-C6), 3.49 (dd, *J* = 9.9, 8.9 Hz, 1H, H-C4), 2.52 (ddt, *J* = 13.7, 6.2, 1.3 Hz, 1H, H-C3´), 2.40 (d, *J* = 2.5 Hz, 1H, H-OH), 2.39 – 2.34 (m, 1H, H-C1´), 2.27 (dd, *J* = 12.8, 5.1 Hz, 1H, H-C2), 1.56 (ddd, *J* = 12.8, 11.4, 2.5 Hz, 1H, H-C2);

^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.6 (*i*-Ph), 139.5 (*i*-Ph), 139.3 (*i*-Ph), 132.9 (C2´), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 120.4 (C3´), 97.5 (C1), 79.2 (C4), 78.6 (C3), 75.3 (C$\underline{H}_2$Ph), 73.8 (C$\underline{H}_2$Ph), 72.7 (C5), 72.1 (C$\underline{H}_2$Ph), 70.3 (C6), 47.3 (C1´), 39.4 (C2).

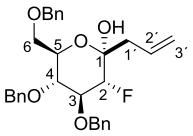
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 6:



Prepared according to the general procedure D. Starting with **L1** (46 mg, 0.1 mmol) compound **Table 2 Entry 6** was obtained (50 mg, 99%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.45 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 515.2222 $(M + Na)^+$, $C_{30}H_{33}O_5FNa^+$ requires 515.2204;

$[\alpha]_D^{25}$ +24.4 (*c* 1.00 in DCM);

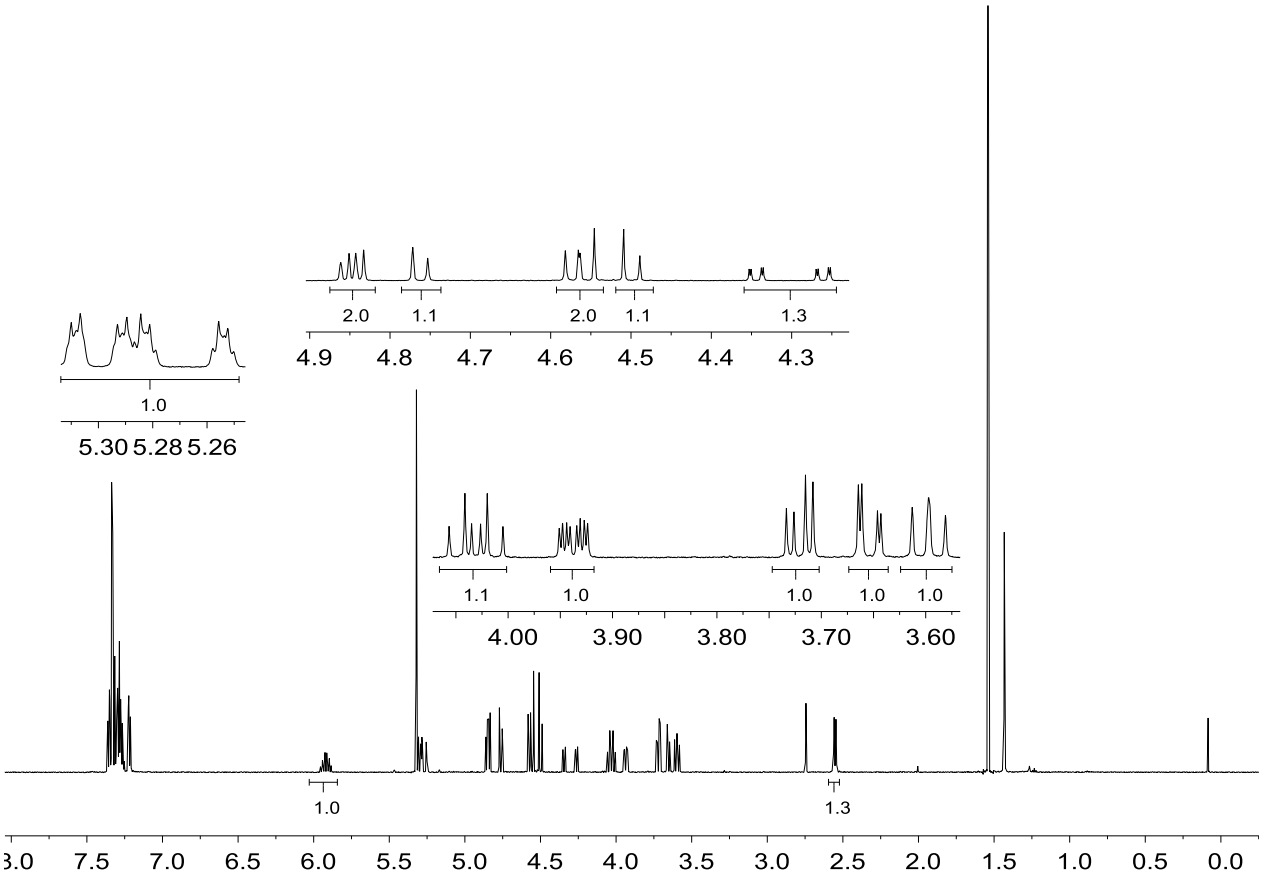
ν_{max} (neat)/cm^{-1} 3413w, 3030w, 2917w, 1641w, 1497w, 1454m, 1367m, 1209w, 1072s, 1026s, 922m, 872w, 824w, 734s, 696s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.37 – 7.25 (m, 13H, H-Ph), 7.22 (ddt, J = 7.3, 1.5, 0.7 Hz, 2H, H-Ph), 5.96 – 5.87 (m, 1H, H-C2´), 5.31 – 5.25 (m, 2H, H-C3´), 4.85 (d, J = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.84 (d, J = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.76 (d, J = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4 4.57 (d, J = 10.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.56 (d, J = 11.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.50 (d, J = 12.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.30 (ddd, J_{FH} = 50.1, J = 9.1, 1.5 Hz, 1H, H-C2), 4.03 (dt, J_{FH} = 12.9, J = 9.0 Hz, 1H, H-C3), 3.94 (ddd, J = 10.1, 4.3, 2.0 Hz, 1H, H-C5), 3.72 (dd, J = 10.9, 4.3 Hz, 1H, H-C6), 3.65 (dd, J = 11.0, 1.9 Hz, 1H, H-C6), 3.60 (dd, J = 10.0, 9.0 Hz, 1H, H-C4), 2.74 (dd, J = 1.6, 0.7 Hz, 1H, H-OH), 2.58 – 2.53 (m, 2H, H-C1´);

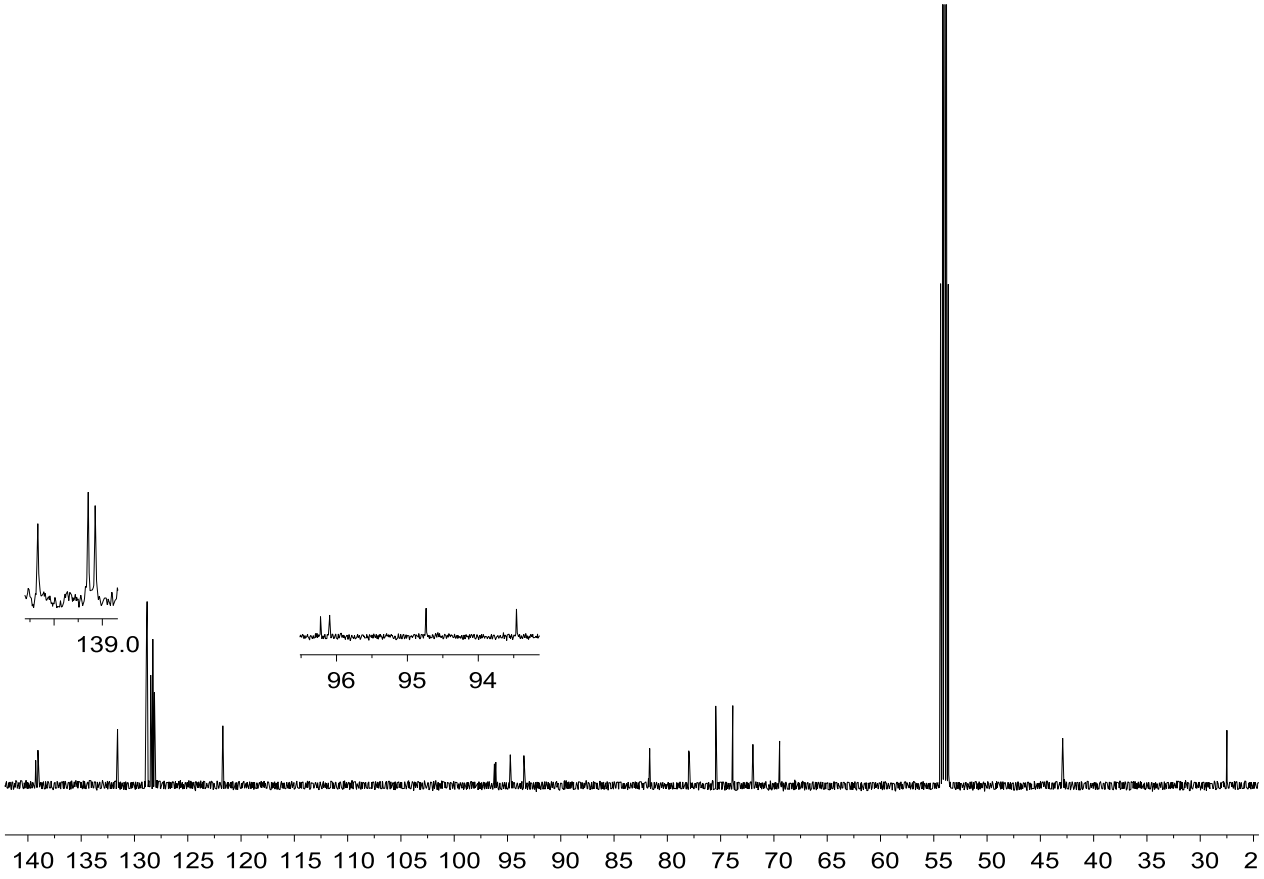
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.3 (*i*-Ph), 139.1 (*i*-Ph), 139.0 (*i*-Ph), 131.6 (C2´), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 121.7 (C3´), 96.2 (d, J_{FC} = 19.3 Hz, C1), 94.1 (d, J_{FC} = 192.3 Hz, C2), 81.7 (d, J_{FC} = 16.2 Hz, C3), 78.0 (d, J_{FC} = 8.2 Hz, C4), 75.5 (C$\underline{H}_2$Ph), 75.4 (d, J_{FC} = 2.7 Hz, C$\underline{H}_2$Ph), 73.9 (C$\underline{H}_2$Ph), 72.0 (d, J_{FC} = 1.4 Hz, C5), 69.5 (C6), 42.9 (C1´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -197.0 (dd, J = 50.1, 12.9 Hz).

^{1}H (600 MHz, Dichloromethane-d_2, 299 K) (with *cyclo*hexane)

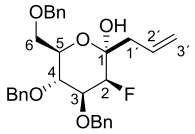


$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)

Compound Table 2 Entry 9:



Prepared according to the general procedure D. Starting with **L4** (46 mg, 0.1 mmol) compound **Table 2 Entry 9** was obtained (46 mg, 91%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.42 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 515.2203 $(M + Na)^+$, $C_{30}H_{33}O_5FNa^+$ calculated 515.2204;

$[\alpha]_D^{25}$ -1.1 (*c* 1.00 in DCM);

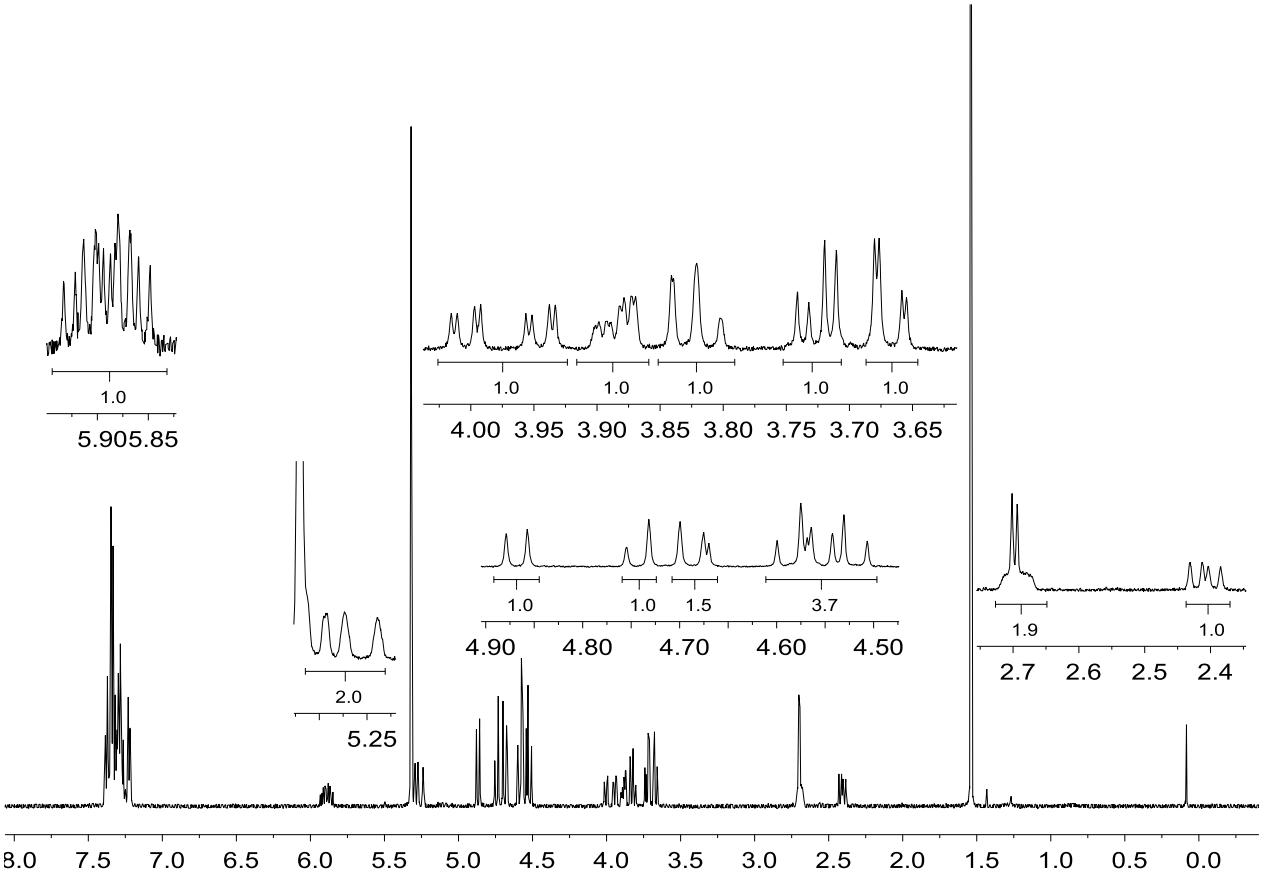
ν_{max} (neat)/cm^{-1} 3376m, 3065w, 3030w, 2913m, 2866m, 2197w, 2169w, 1950w, 1879w, 1643w, 1606w, 1587w, 1497m, 1454m, 1398w, 1367m, 1330w, 1310w, 1262w, 1208w, 1189w, 1073s, 1026s, 994s, 919m, 878m, 843m, 734s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.40 – 7.25 (m, 13H, H-Ph), 7.24 – 7.21 (m, 2H, H-Ph), 5.94 – 5.83 (m, 1H, H-C2´), 5.32 – 5.22 (m, 2H, H-C3´), 4.87 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.74 (d, *J* = 11.6 Hz, 1H, H-C$\underline{H}_2$Ph), 4.69 (d, *J* = 12.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.62 (dd, J_{FH} = 50.5, *J* = 2.4 Hz, 1H, H-C2), 4.59 (d, *J* = 12.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.55 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.52 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 3.97 (ddd, J_{FH} = 29.6, *J* = 9.2, 2.4 Hz, 1H, H-C3), 3.89 (ddd, *J* = 9.8, 4.9, 2.1 Hz, 1H, H-C5), 3.82 (m, 1H, H-C4), 3.73 (dd, *J* = 10.8, 4.6 Hz, 1H, H-C6), 3.67 (dd, *J* = 10.8, 1.9 Hz, 1H, H-C6), 2.70 (m, 1H, H-C1´), 2.69 (d, *J* = 3.9 Hz, 1H, H-OH), 2.41 (dd, *J* = 14.0, 9.3 Hz, 1H, H-C1´);

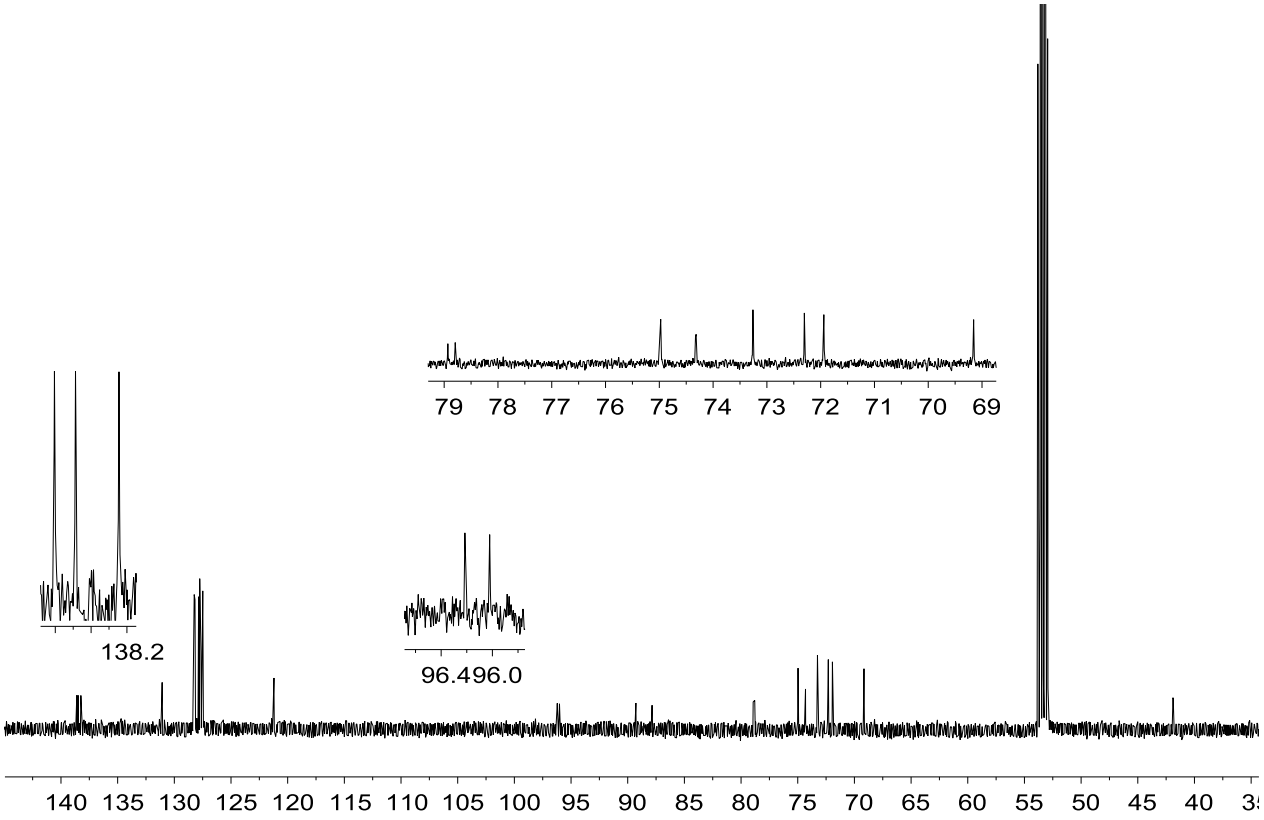
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.2 (*i*-Ph), 139.1 (*i*-Ph), 138.9 (*i*-Ph), 131.7 (C2´), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 121.8 (C3´), 96.7 (d, J_{FC} = 24.3 Hz, C1), 89.2 (d, J_{FC} = 179.3 Hz, C2), 79.5 (d, J_{FC} = 17.3 Hz, C3), 75.6 (C$\underline{H}_2$Ph), 74.9 (d, J_{FC} = 1.5 Hz, C4), 73.9 (C$\underline{H}_2$Ph), 72.9 (C5), 72.6 (C$\underline{H}_2$Ph), 69.8 (C6), 42.5 (d, J_{FC} = 3.3 Hz, C1´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -207.00 (ddt, *J* = 50.5, 29.7, 2.8 Hz).

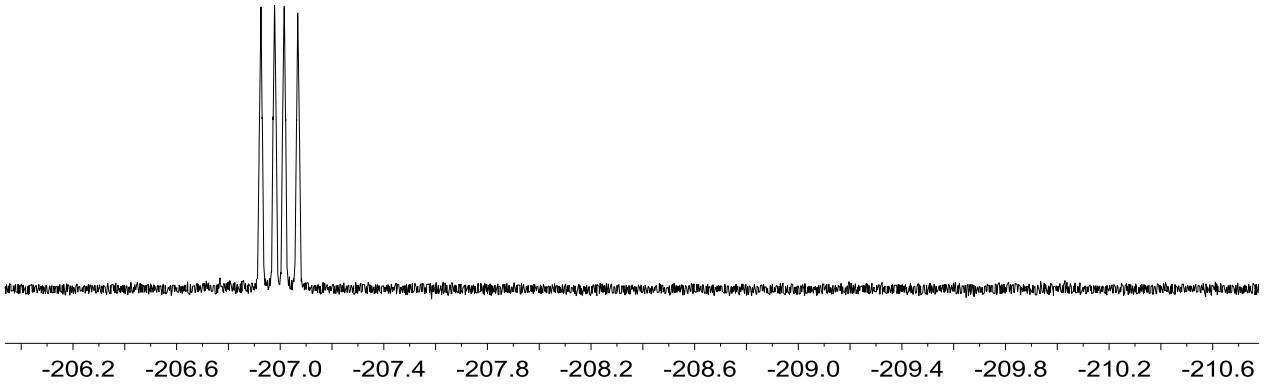
^{1}H (600 MHz, Dichloromethane-d_2, 299 K) (with H_2O)



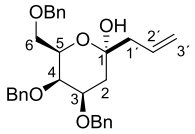
$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 12:



Prepared according to the general procedure D. Starting with **L5** (44 mg, 0.1 mmol) compound **Table 2 Entry 12** was obtained (31 mg, 65% / 18 mg, 37%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1). The compound was obtained as a mixture of the desired product and the open form. The two compounds were inseparable by column chromatography.

R_f 0.40 (SiO_2, CyH:EtOAc 3:1);

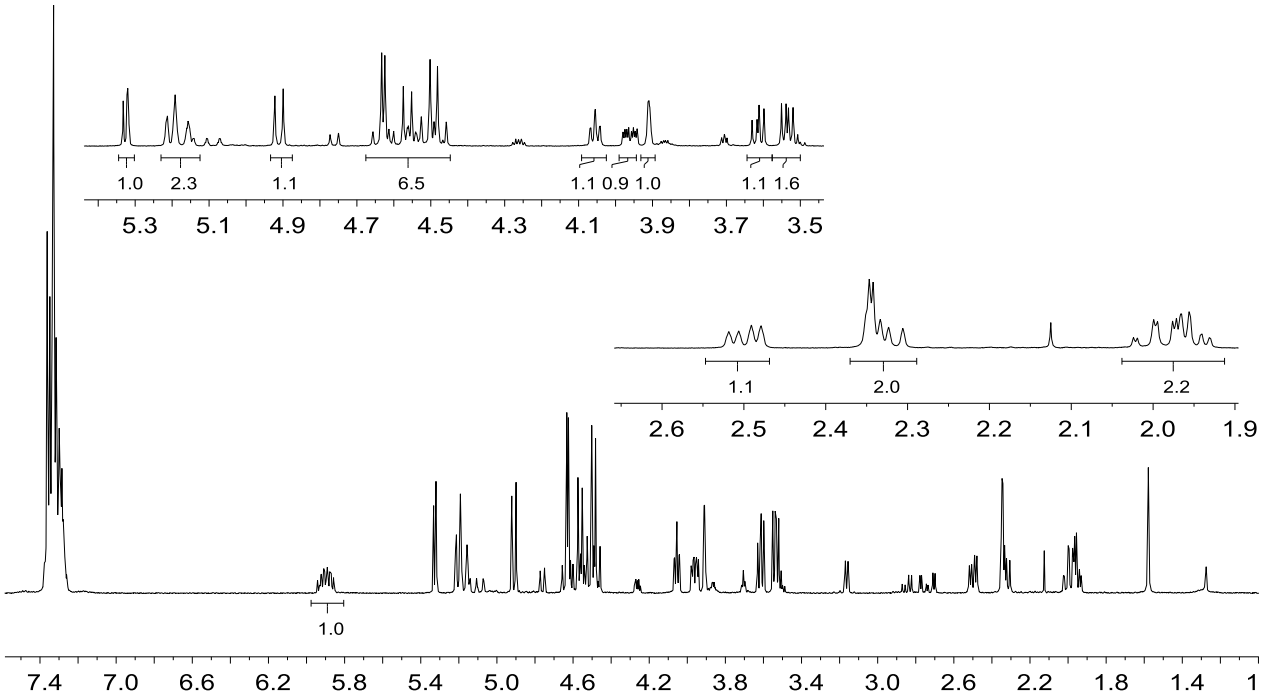
m/*z* (ESI) found: 497.2288 $(M + Na)^+$, $C_{30}H_{34}O_5Na^+$ calculated 497.2298;

Only the major product was characterised (compound **Table 2 Entry 12**)

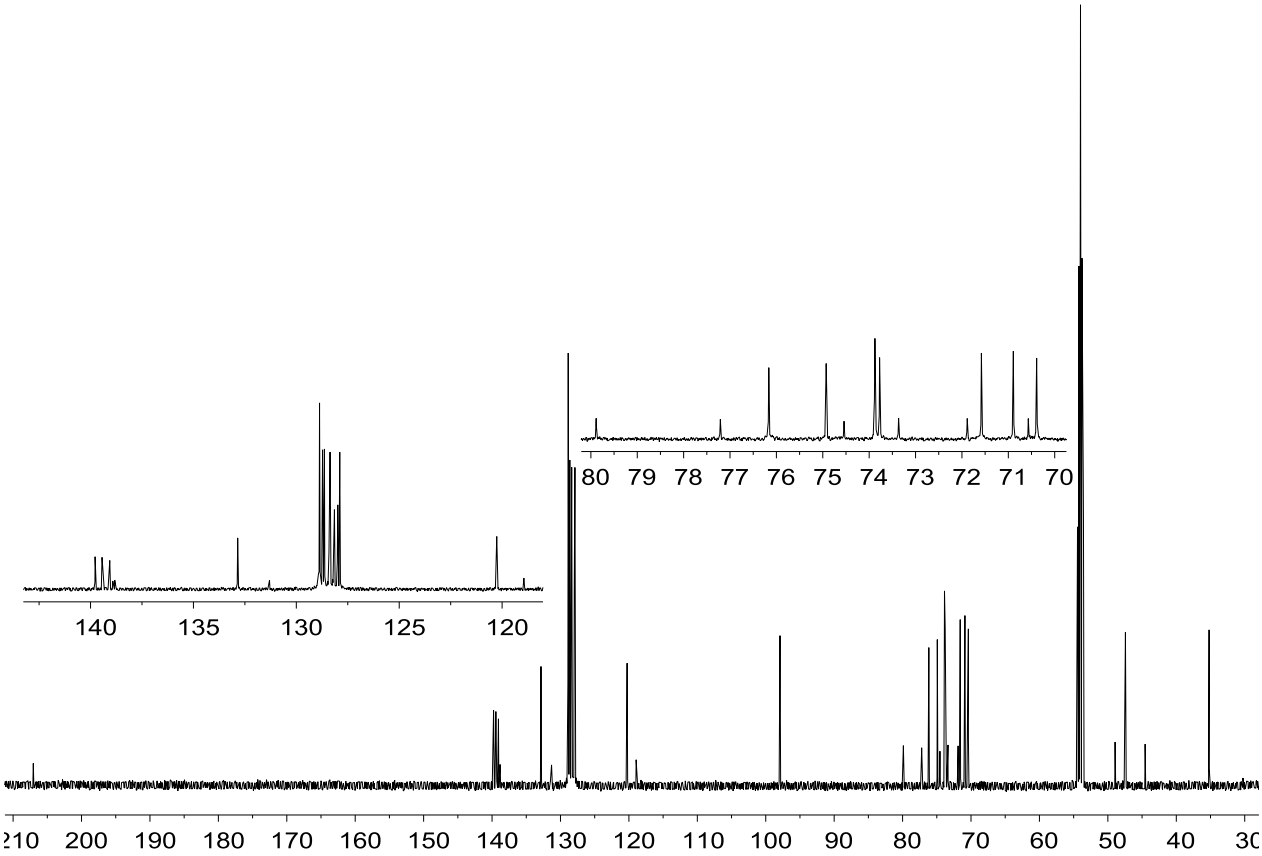
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.40 – 7.24 (m, 15H, H-Ph), 5.96 – 5.83 (m, 1H, H-C2´), 5.23 – 5.14 (m, 2H, H-C3´), 4.91 (d, *J* = 11.3 Hz, 1H, H-C$\underline{H}_2$Ph), 4.63 (m, 2H, H-C$\underline{H}_2$Ph), 4.56 (d, *J* = 11.3 Hz, 1H, H-C$\underline{H}_2$Ph), 4.51 (d, *J* = 11.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.47 (d, *J* = 11.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.09 – 4.02 (m, 1H, H-C5), 3.96 (ddd, *J* = 11.4, 5.1, 2.5 Hz, 1H, H-C3), 3.93 – 3.89 (m, 1H, H-C4), 3.61 (dd, *J* = 9.3, 6.7 Hz, 1H, H-C6), 3.54 (dd, *J* = 9.5, 6.2 Hz, 1H, H-C6), 2.50 (dd, *J* = 13.7, 6.0 Hz, 1H, H-C1´), 2.34 (d, *J* = 2.3 Hz, 1H, H-OH), 2.34 – 2.29 (m, 1H, H-C1´), 2.00 (td, *J* = 12.0, 2.3 Hz, 1H, H-C2), 1.95 (dd, *J* = 12.3, 5.1 Hz, 1H, H-C2);

^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.8 (*i*-Ph), 139.4 (*i*-Ph), 139.1 (*i*-Ph), 132.9 (C2´), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.7 (*o*,*m*,*p*-Ph), 128.6 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 127.9 (*o*,*m*,*p*-Ph), 120.3 (C3´), 97.9 (C1), 76.2 (C3), 74.9 (C$\underline{H}_2$Ph), 73.9 (C$\underline{H}_2$Ph), 73.8 (C4), 71.6 (C5), 70.9 (C$\underline{H}_2$Ph), 70.4 (C6), 47.4 (C1´), 35.2 (C2).

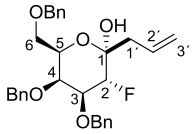
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound Table 2 Entry 15:



Prepared according to the general procedure D. Starting with **L6** (46 mg, 0.1 mmol) compound **Table 2 Entry 15** was obtained (47 mg, 94%) as a colourless oil after purification by column chromatography (SiO_2, CyH: EtOAC 6:1).

R_f 0.39 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 515.2212 $(M + Na)^+$, $C_{30}H_{33}O_5FNa^+$ calculated 515.2204;

$[\alpha]_D^{25}$ +25.0 (*c* 0.50 in DCM);

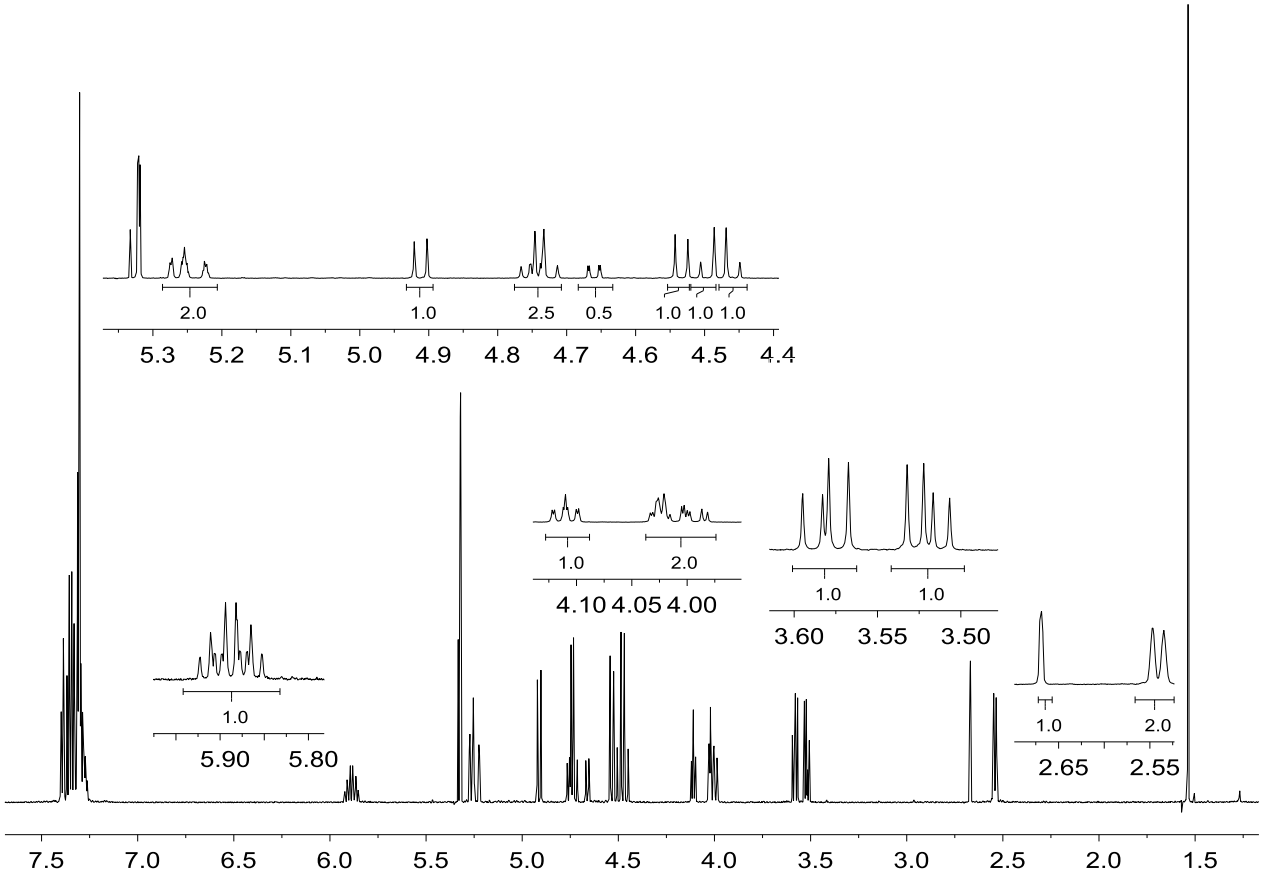
ν_{max} (neat)/cm^{-1} 3412w, 3030w, 2919w, 1641w, 1497w, 1454m, 1371w, 1208w, 1181w, 1067s, 1027s, 917m, 818m, 733s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.41 – 7.26 (m, 15H, H-Ph), 5.93 – 5.84 (m, 1H, H-C2´), 5.28 – 5.21 (m, 2H, H-C3´), 4.91 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.76 (d, *J* = 11.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.72 (d, *J* = 11.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.70 (ddd, J_{FH} = 50.8, *J* = 9.5, 1.3 Hz, 1H, H-C2) 4.53 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.50 (d, *J* = 11.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.46 (d, *J* = 11.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.11 (ddd, *J* = 7.2, 5.9, 1.3 Hz, 1H, H-C5), 4.04 – 3.97 (m, 2H, H-C3 + H-C4), 3.58 (dd, *J* = 9.4, 7.2 Hz, 1H, H-C6), 3.52 (dd, *J* = 9.4, 6.0 Hz, 1H, H-C6), 2.67 (dd, *J* = 1.4, 0.7 Hz, 1H, H-OH), 2.54 (dt, *J* = 7.0, 1.2 Hz, 2H, H-C1´);

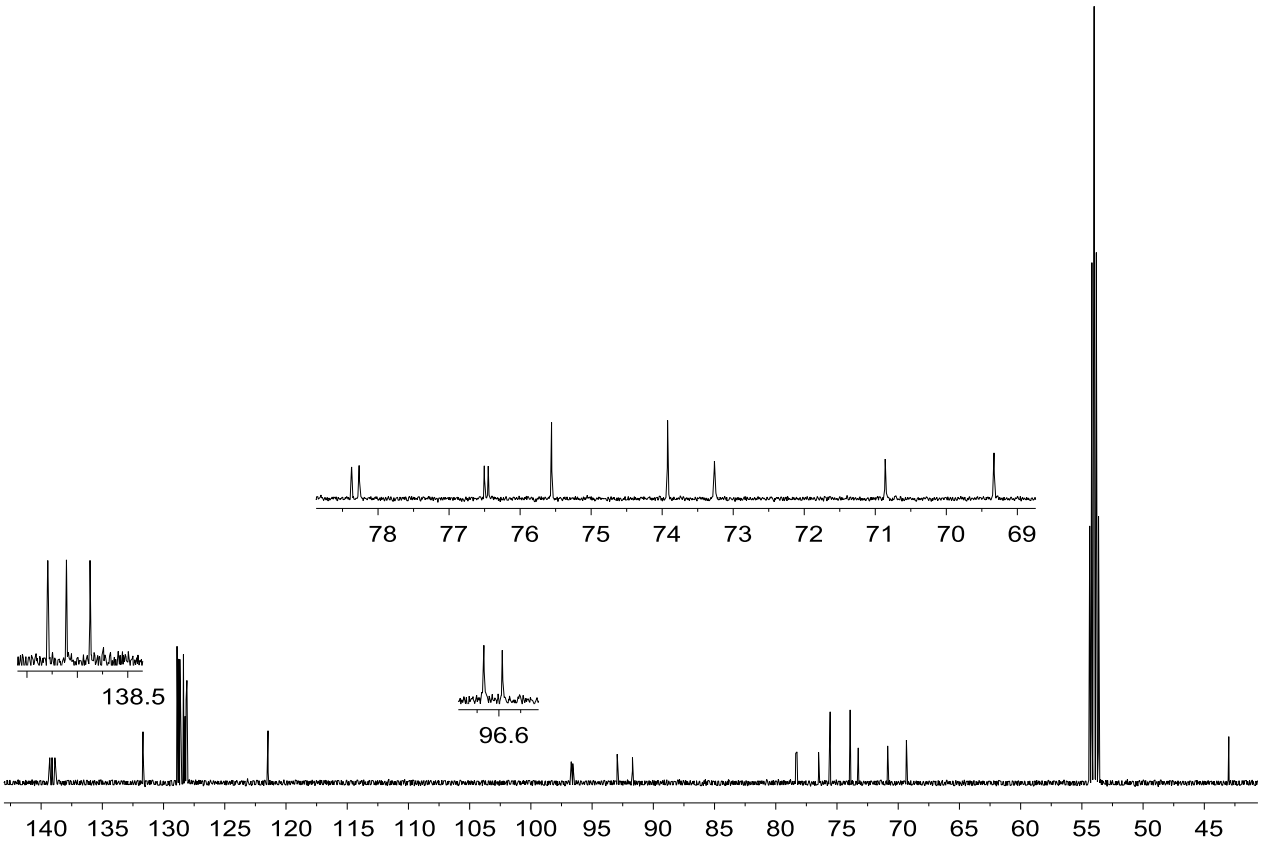
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.3 (*i*-Ph), 139.1 (*i*-Ph), 138.9 (*i*-Ph), 131.7 (C2´), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.7 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 121.5 (C3´), 96.6 (d, J_{FC} = 19.2 Hz, C1), 92.3 (d, J_{FC} = 188.2 Hz, C2), 78.3 (d, J_{FC} = 16.1 Hz, C3), 76.5 (d, J_{FC} = 8.4 Hz, C4), 75.6 ($\underline{C}H_2$Ph), 73.9 ($\underline{C}H_2$Ph), 73.3 (d, J_{FC} = 1.9 Hz, $\underline{C}H_2$Ph), 70.9 (d, J_{FC} = 1.2 Hz, C5), 69.3 (C6), 43.0 (C1´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -207.3 (ddd, *J* = 50.9, 10.9, 3.8 Hz).

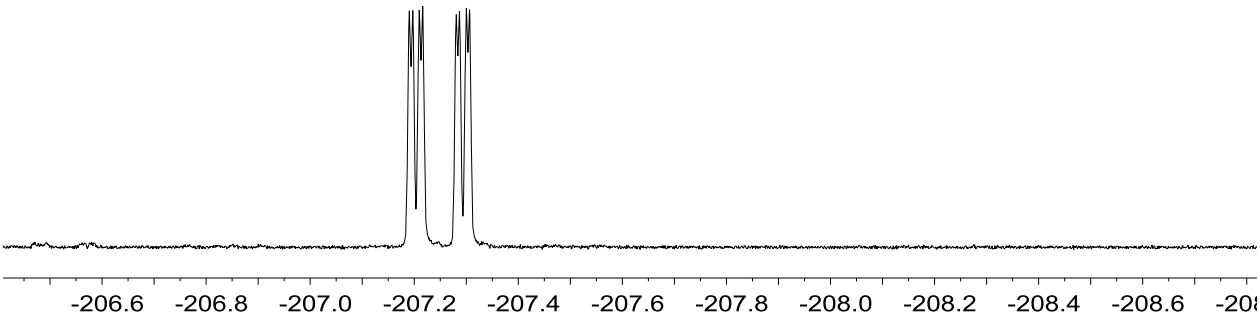
^{1}H (600 MHz, Dichloromethane-d_2, 299 K) (with H_2O)



$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)

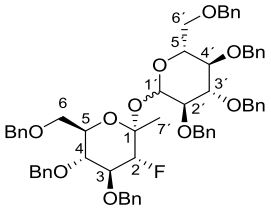


^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



***C*-glycosylations**

Compound 6:



tert-BPPTS (64 mg, 0.2 mmol, 3.0 eq.) was added to a mixture of TCA donor **5** (40 mg, 58.0 µmol, 1.0 eq.) and compound **4** (Table 1 Entry 3) (33 mg, 70.0 µmol, 1.2 eq.) under Argon at room temperature. The mixture was stirred overnight, filtered through celite and the volatiles evaporated in *vacuum*. The residue was purified by column chromatography CyH: EtOAc (SiO_2, 3:1). Compound **6** was obtained (17 mg, 30%, *αα*: *αβ* 1.8:1) as a colourless oil.

R_f 0.50 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 1011.4455 $(M + Na)^+$, $C_{62}H_{65}FO_{10}Na^+$ calculated 1011,4459;

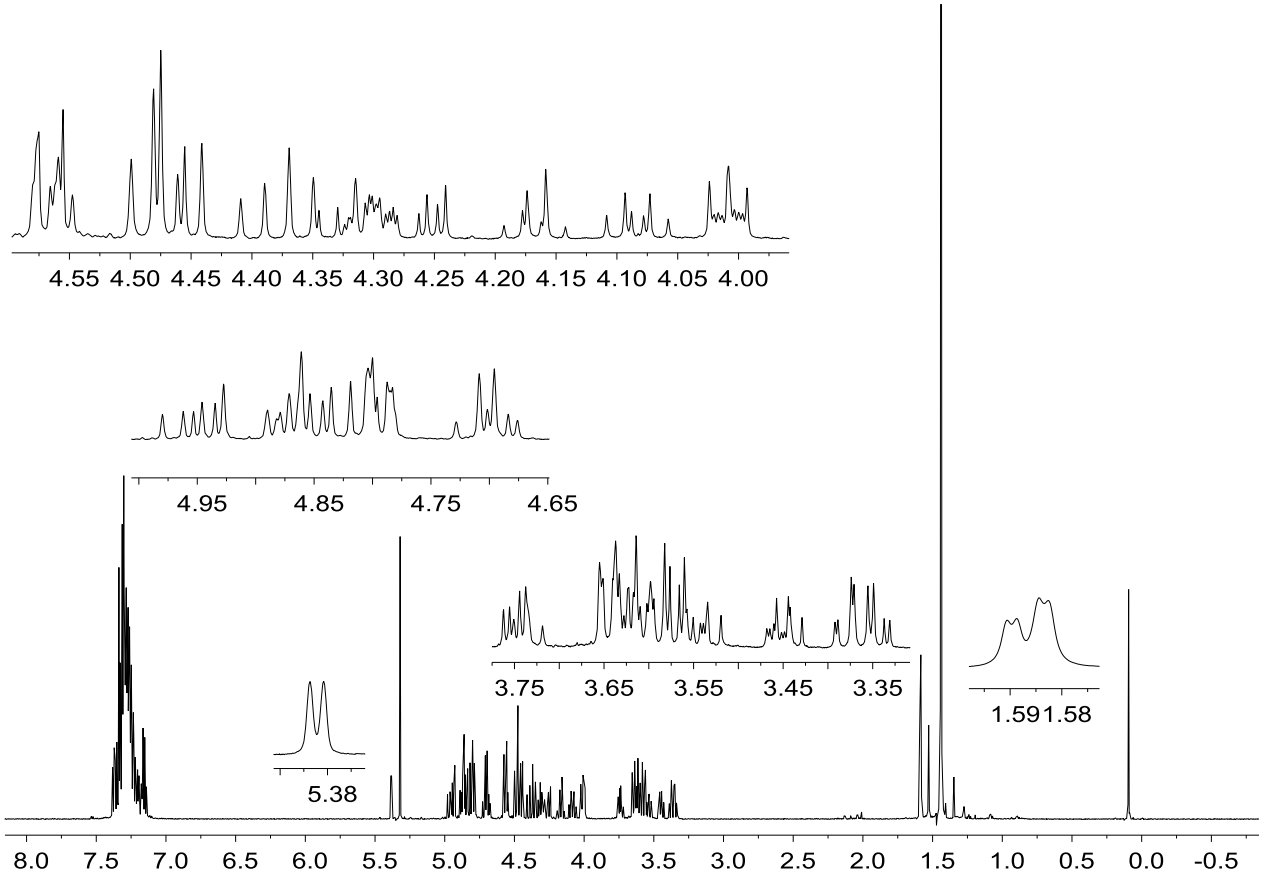
ν_{max} (neat)/cm^{-1} 3089w, 3063w, 3030w, 2915m, 2867m, 1497m, 1454m, 1362m, 1328w, 1265w, 1241w, 1209w, 1187w, 1066s, 1027s, 947m, 908w, 878w, 845w, 820w, 732s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.40 – 7.13 (m, 98H, H-Ph), 5.38 (d, *J* = 3.5 Hz, 2H, H-C1´), 4.97 (d, *J* = 10.7 Hz, 1H), 4.94 (d, *J* = 11.1 Hz, 1H), 4.94 (d, *J* = 11.0 Hz, 2H), 4.93 (s, 1H), 4.90 – 4.77 (m, 12H), 4.74 – 4.67 (m, 5H), 4.60 – 4.53 (m, 5H), 4.49 (d, *J* = 11.0 Hz, 3H), 4.47 (d, *J* = 8.3 Hz, 3H), 4.45 (d, *J* = 8.4 Hz, 2H), 4.40 (d, *J* = 11.7 Hz, 1H), 4.36 (d, *J* = 11.9 Hz, 2H), 4.34 (d, *J* = 9.3 Hz, 1H), 4.31 (d, *J* = 6.8 Hz, 1H), 4.25 (dd, *J* = 9.1, 4.0 Hz, 1H), 4.17 (dt, *J* = 11.9, 9.4 Hz, 2H), 4.08 (dt, *J* = 12.2, 9.1 Hz, 2H), 4.04 – 3.98 (m, 2H), 3.75 (dd, *J* = 10.7, 4.1 Hz, 3H), 3.67 – 3.51 (m, 9H), 3.48 – 3.42 (m, 1H), 3.38 (dd, *J* = 10.8, 1.9 Hz, 2H), 3.34 (dd, *J* = 10.9, 3.8 Hz, 2H), 1.59 (d, *J* = 1.1 Hz, 4H, C7´*αβ*), 1.58 (d, *J* = 1.1 Hz, 6H, C7´*αα*);

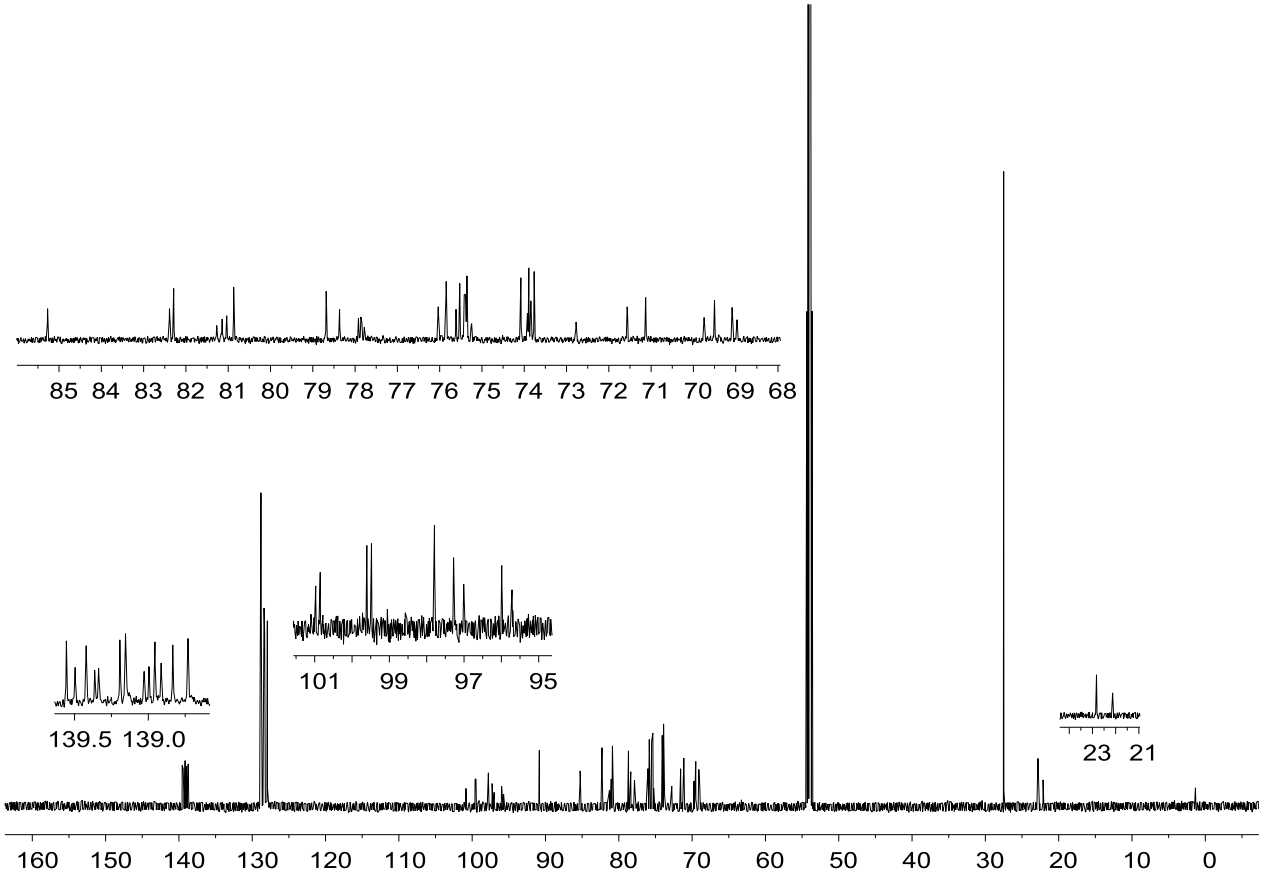
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.6 (*i*-Ph), 139.5 (*i*-Ph), 139.4 (*i*-Ph), 139.4 (*i*-Ph), 139.3 (*i*-Ph), 139.2 (*i*-Ph), 139.2 (*i*-Ph), 139.0 (*i*-Ph), 139.0 (*i*-Ph), 139.0 (*i*-Ph), 138.9 (*i*-Ph), 138.8 (*i*-Ph), 138.7 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 127.9 (*o*,*m*,*p*-Ph), 101.0, 100.9, 99.6, 99.5, 97.8 (C1´αβ), 96.63 (d, *J* = 194.3 Hz, C2*αα*), 96.36 (d, *J* = 195.1 Hz, C2*αβ*), 90.8 (C1´*αα*), 85.3, 82.4, 82.3, 81.3, 81.1, 81.0, 80.9, 78.7, 78.4, 77.9, 77.9, 77.8, 77.8, 76.0, 75.9, 75.6, 75.5, 75.4, 75.4, 75.4, 75.4, 75.4, 75.3, 74.1, 73.9, 73.9, 73.8, 73.8, 72.8, 71.6, 71.1, 69.8, 69.5, 69.1, 69.0, 22.8 (C7´*αα*), 22.1 (C7´*αβ*);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.77 (dd, *J* = 49.3, 12.2 Hz), -197.15 (dd, *J* = 49.2, 12.0 Hz).

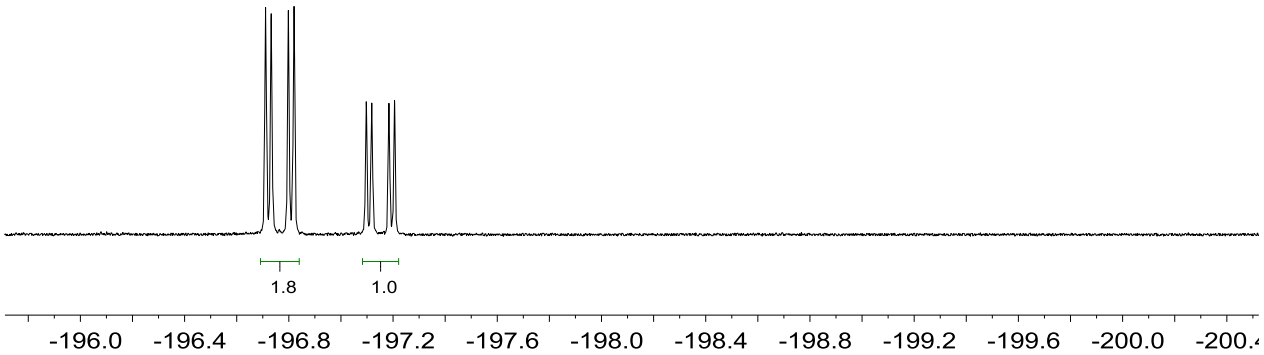
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K)



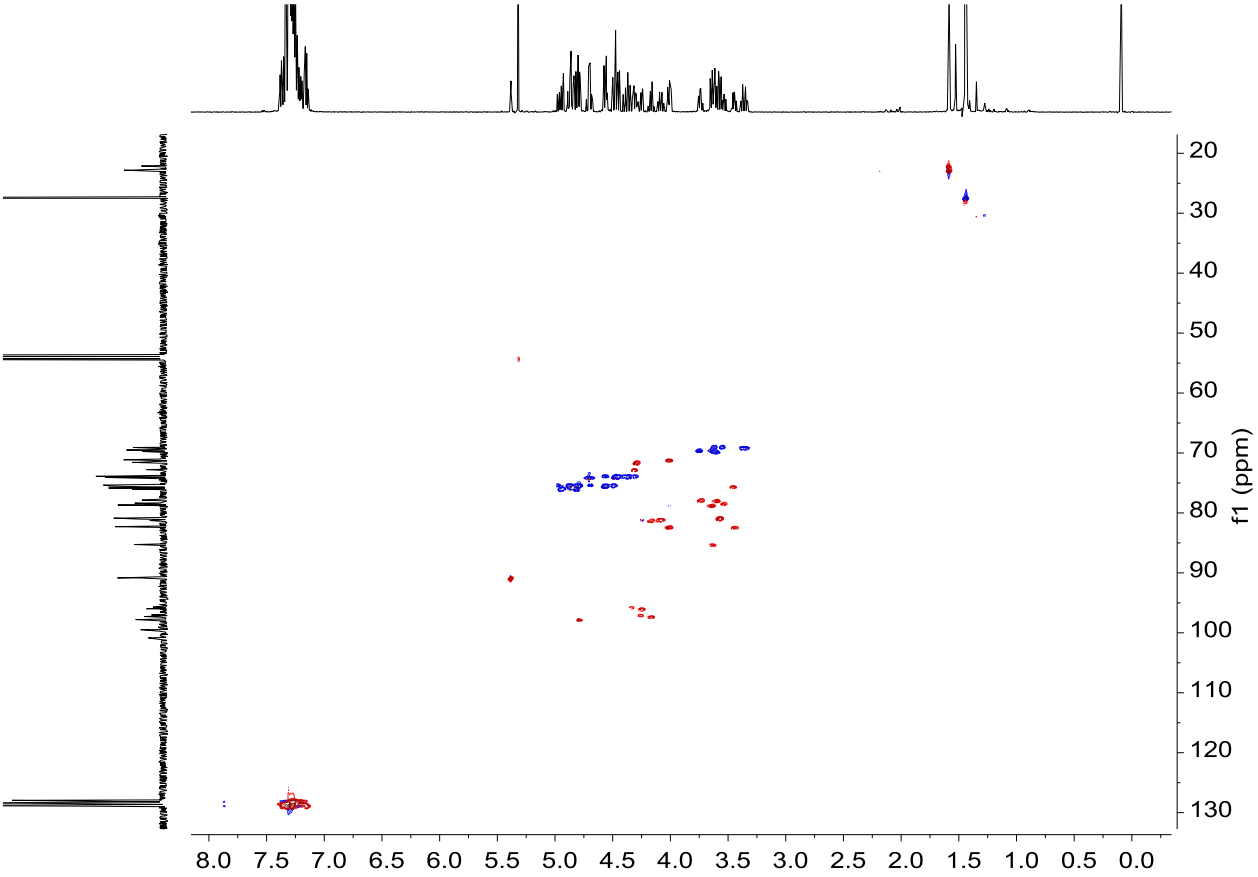
$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



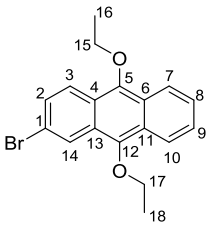
^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



HSQC



Compound S8:



2-Bromoanthraquinone (200 mg, 0.7 mmol, 1.0 eq.), TBAI (231 mg, 0.6 mmol, 0.9 eq.) and $Na_2S_2O_4$ (242 mg, 1.4 mmol, 2.0 eq.) in H_2O (7.0 mL) were stirred under an argon atmosphere for 10 min. CH_2Cl_2 (7.8 mL) was then was added. The mixture was stirred until the solution turned dark green and then NaOH (139 mg, 3.5 mmol, 5.0 eq. 20% in H_2O) was added. The solution then turned dark red and was stirred for and additional 1.5 h. After this time EtBr (0.52 mL, 7.0 mmol, 10.0 eq.) was added and the mixture was stirred overnight. The reaction was quenched by addition of $NaHCO_3$ (aq., sat. 7.0 mL). The organic layer was separated and the water layer was extracted with CH_2Cl_2 (2 x 7.0 mL). The combined organic layers were washed with H_2O (2 x 10.0 mL) and brine (1 x 10.0 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue was purified by column chromatography CyH: CH_2Cl_2 (SiO_2, 5:1). Compound **S8** was obtained (110 mg, 46%) as a bright yellow solid.

R_f 0.69 (SiO_2, CyH:EtOAc 3:1);

Mp 89 – 93 °C;

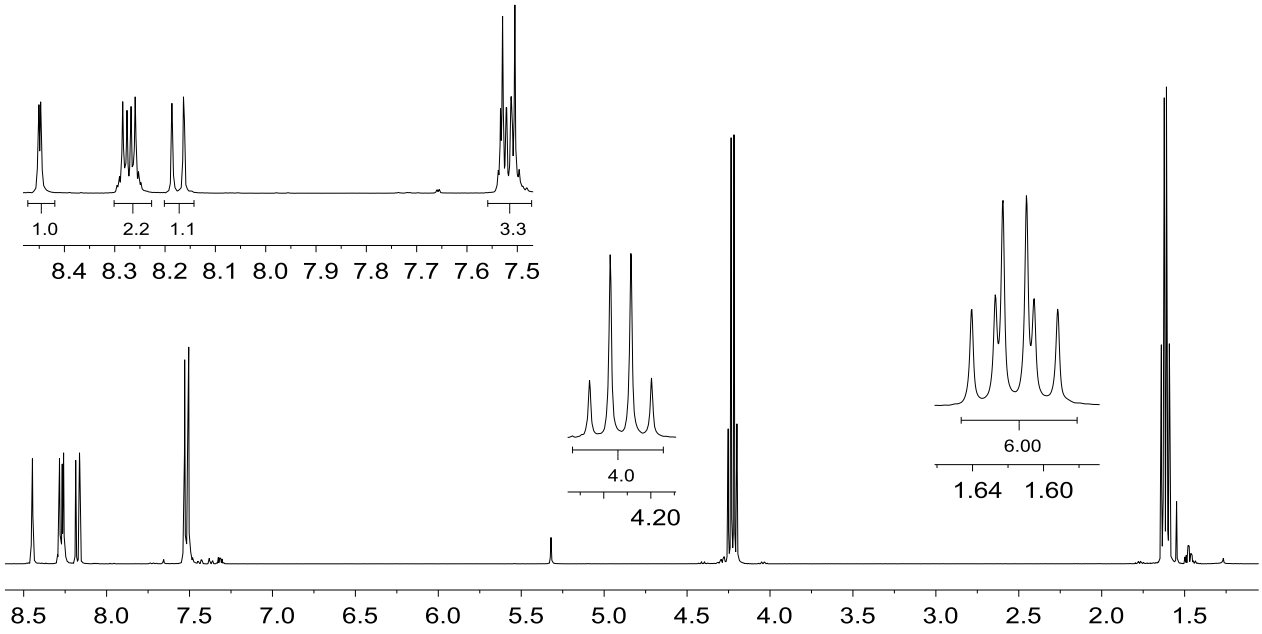
m/*z* (ESI) found: 367.0310 and 369.0287 $(M + Na)^+$, $C_{18}H_{17}BrO_2Na^+$ calculated 367.0310 and 269.0289;

ν_{max} (neat)/cm^{-1} 3676w, 3067w, 2974s, 2926m, 2883m, 1911w, 1737w, 1673w, 1622w, 1610m, 1558w, 1520w, 1487w, 1444m, 1424w, 1407m, 1374s, 1352s, 1336s, 1292m, 1266m, 1168m, 1156m, 1119w, 1106m, 1067s, 1051s, 1022s, 943s, 887m, 867s, 855m, 811s, 796m, 759s, 691s, 660m;

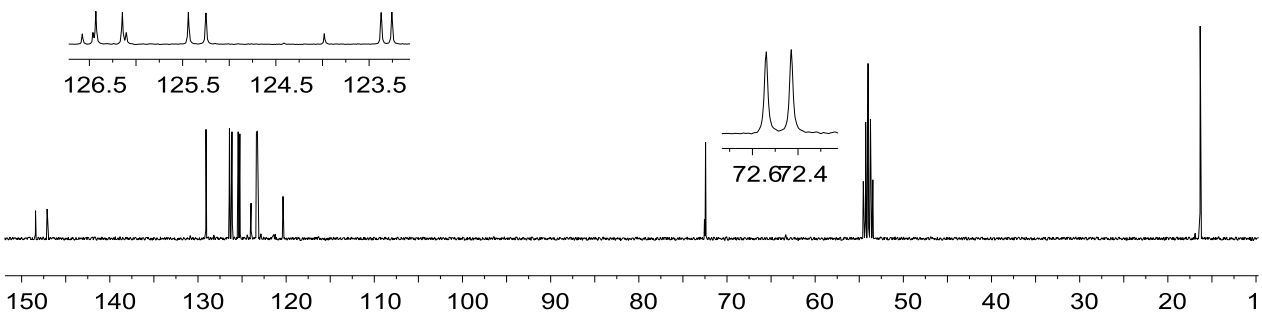
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 8.45 (dd, *J* = 2.0, 0.6 Hz, 1H, H-C14), 8.31 – 8.24 (m, 2H, H-Ar), 8.17 (dd, *J* = 9.2, 0.6 Hz, 1H, H-Ar), 7.55 – 7.48 (m, 3H, H-Ar), 4.23 (q, *J* = 7.0 Hz, 4H, H-15 + H-C17), 1.62 (t, *J* = 7.1 Hz, 3H, H-C16 or H-C18), 1.61 (t, *J* = 7.0 Hz, 3H, H-C16 or H-C18);

^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) 148.4 (C5), 147.1 (C12), 129.1 (CHAr), 126.6 (CAr), 126.5 (CAr), 126.4 (CHAr), 126.2 (CHAr), 126.1 (CAr), 125.4 (CHAr), 125.3 (C14), 124.0 (CAr), 123.4 (CHAr), 123.3 (CHAr), 120.4 (CAr), 72.5 (C15 or C17), 72.4 (C15 or C17) , 16.3 (C16 + C18).

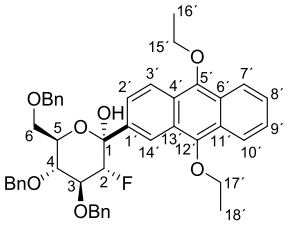
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



Compound 8:



n-BuLi (45 µL, 2.5 M in hexanes, 0.1 mmol, 0.1 eq.) was added to a solution of compound **S8** in THF (225 µL mL, 0.5 M), the mixture was stirred under argon at -78 °C for 30 min. This mixture was transferred slowly to a solution of the corresponding lactone (46 mg, 0.1 mmol, 1.0 eq.) in dry THF (350 µL, 0.3 M) at -78 °C under an argon atmosphere. The reaction mixture was stirred for 30 min and quenched by addition of MeOH (5.0 mL). H_2O (5.0 mL) and EtOAc (5.0 mL) were added and the water phase was extracted with EtOAc (3 x 3.0 mL). The combined organic layers were washed H_2O (2 x 7.0 mL) and brine (1 x 7.0 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue obtained was purified by column chromatography CyH: EtOAc (SiO_2, 6:1). Compound **8** was obtained (53 mg, 73%) as a bright yellow solid.

R_f 0.44 (SiO_2, CyH:EtOAc 3:1);

Mp 53 – 56 °C;

m/*z* (ESI) found: 739.3026 $(M + Na)^+$, $C_{45}H_{45}O_7FNa^+$ calculated 739.3042

$[\alpha]_D^{25}$ +12.7 (*c* 1.28 in DCM);

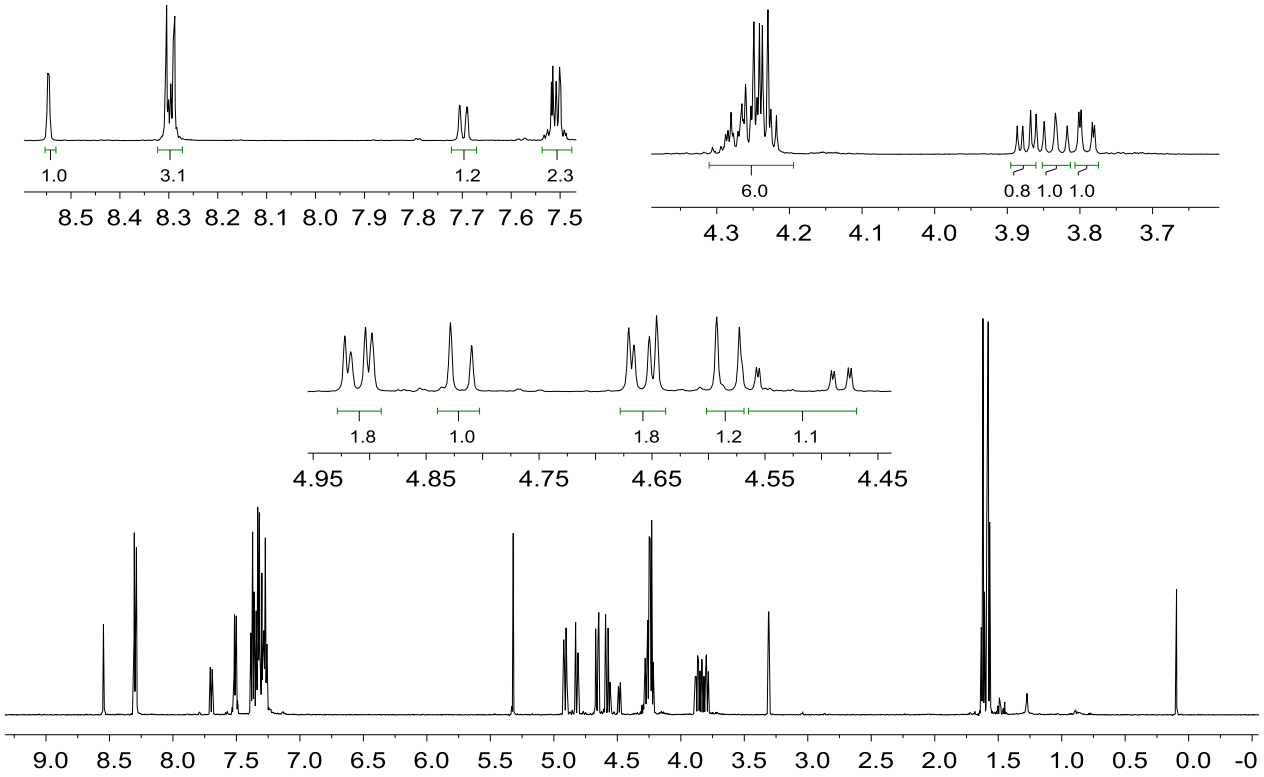
ν_{max} (neat)/cm^{-1} 3374w, 3031w, 2926w, 1623w, 1497w, 1454m, 1403m, 1375s, 1341s, 1208m, 1059s, 1025s, 907m, 887m, 819m, 734s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 8.55 (m, 1H, H-C14´), 8.32 – 8.27 (m, 3H, H-C3´, H-C7´, H-C10´), 7.70 (m, 1H, H-C2´), 7.54 – 7.48 (m, 2H, H-C8´, H-C9´), 7.40 – 7.23 (m, 15H, H-Ph), 4.91 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.91 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.82 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.66 (d, *J* = 10.9 Hz, 1H, H-C$\underline{H}_2$Ph), 4.66 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.58 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.53 (ddd, J_{FH} = 48.8, *J* = 9.0, 1.6 Hz, 1H, H-C2), 4.30 – 4.21 (m, 6H, H-C3, H-C5, H-C15´, H-C17´), 3.87 (dd, *J* = 11.1, 4.5 Hz, 1H, H-C6), 3.83 (dd, *J* = 10.1, 9.0 Hz, 1H, H-C4), 3.79 (dd, *J* = 11.1, 1.9 Hz, 1H, H-C6), 3.31 (d, *J* = 1.5 Hz, 1H, H-OH), 1.62 (t, *J* = 7.0 Hz, 3H, H-C16´ or H-C18´), 1.58 (t, *J* = 7.1 Hz, 3H, H-C16´ or H-C18´);

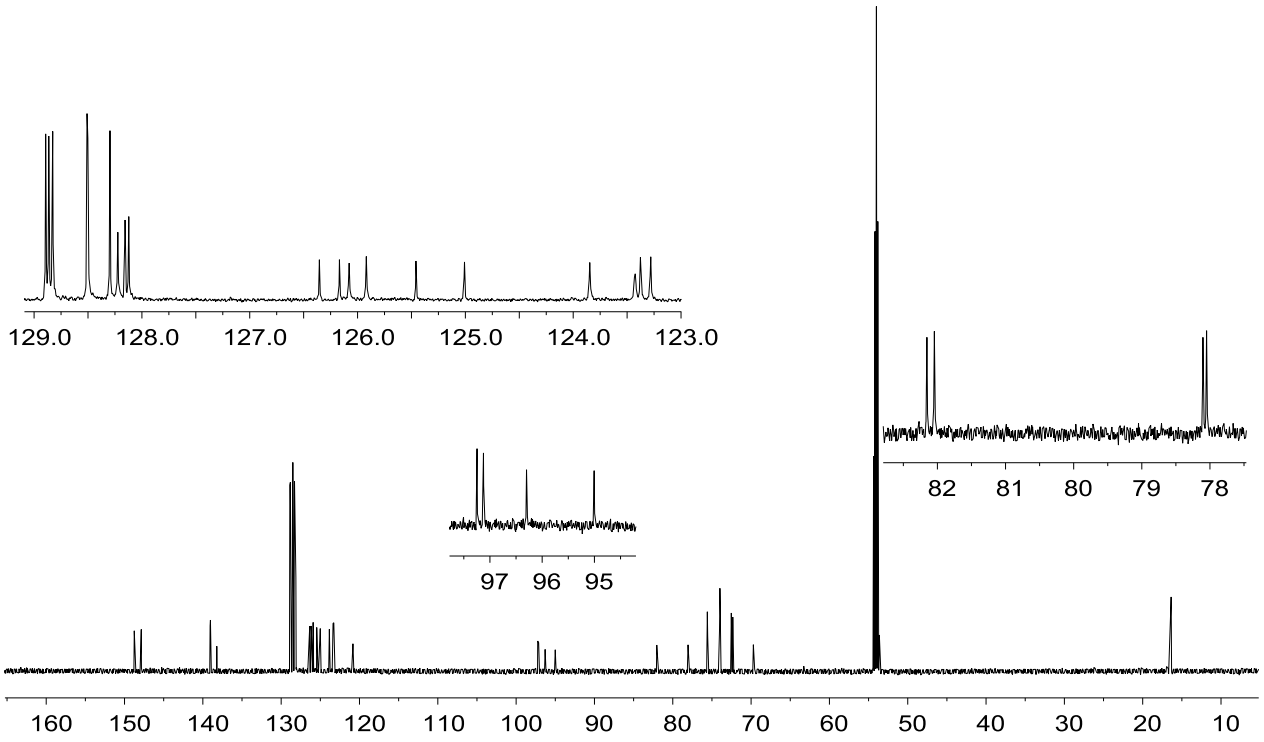
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 148.8 (12´), 147.9 (C5´), 139.2 (*i*-Ph), 139.1 (*i*-Ph), 139.0 (*i*-Ph), 138.23 (d, J_{FC} = 1.5 Hz, C1´), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 126.4 (C6´ or C11´), 126.2 (C6´ or C11´), 126.1 (C8´ or C9´), 125.9 (C8´ or C9´), 125.5 (C4´), 125.0 (C13´), 123.9 (C7´ or C10´), 123.4 (C2´), 123.4 (C7´ or C10´), 123.3 (C3´), 120.84 (d, J_{FC} = 1.1 Hz, C14´), 97.2 (d, J_{FC} = 18.6 Hz, C1), 95.65 (d, J_{FC} = 195.0 Hz, C2), 82.10 (d, J_{FC} = 16.5 Hz, H-C3), 78.08 (d, J_{FC} = 8.2 Hz, H-C4), 75.6 (C$\underline{H}_2$Ph), 75.6 (d, J_{FC} = 2.8 Hz, C$\underline{H}_2$Ph), 74.0 (C$\underline{H}_2$Ph), 72.5 (C15´ or C17´), 72.5 (d, J_{FC} = 1.3 Hz, C5), 72.3 (C15´ or C17´), 69.7 (C6), 16.4 (C16´ or C18´), 16.4 (C16´ or C18´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.13 (dd, *J* = 48.8, 12.5 Hz).

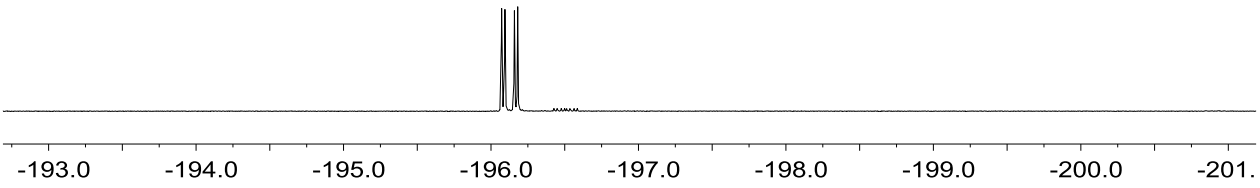
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



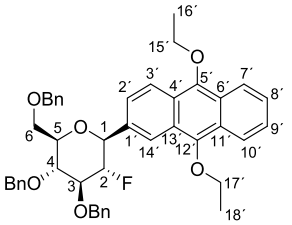
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound 9:



BF_3•Et_2O (15 µL, 0.1 mmol, 2.0 eq.) and Et_3SiH (19 µL, 0.1 mmol, 2.0 eq.) were added to a solution of compound **8** (44 mg, 61.0 µmol, 1.0 eq.) in CH_2Cl_2:MeCN (1:1; 0.12 mL:0.12 mL, 0.25 M) at -10 °C. The mixture was stirred at this temperature for 3 h. Then the reaction mixture was quenched by addition of saturated $NaHCO_3$ (aq., 5.0 mL) followed by extractions with EtOAc (3 x 5.0 mL). The combined organic phases were washed with H_2O (2 x 7.0 mL) and brine (1 x 7.0 mL).The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuum*. The residue obtained was purified by column chromatography CyH: EtOAc (SiO_2, 8:1). Compound **9** was obtained (35 mg, 82%) as a bright yellow oil.

R_f 0.63 (SiO_2, CyH:EtOAc 3:1);

m/z (ESI) found: 723.30934 $(M + Na)^+$, $C_{45}H_{45}O_6FNa^+$ calculated 723.30924

$[\alpha]_D^{25}$ +10.4 (*c* 1.1 in DCM);

νmax (neat)/cm^{-1} 3064w, 3031w, 2975w, 2927m, 2869m, 1623w, 1497w, 1454m, 1403w, 1375s, 1340s, 1305w, 1271w, 1207w, 1062s, 1024s, 905m, 887m, 823m, 790w, 733s, 695s;

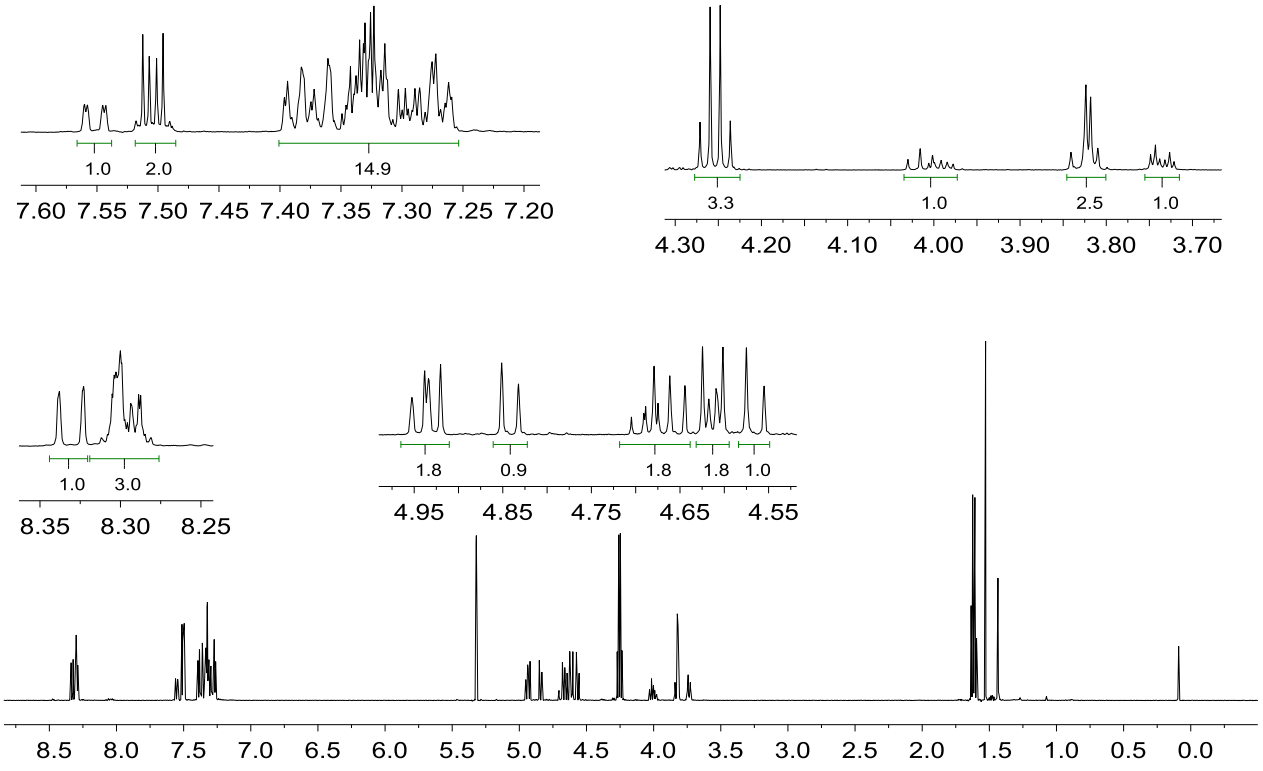
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 8.33 (mz, 1H, H-C14´), 8.32 – 8.27 (m, 3H, H-C3´+ H-C7´ + H-C10´), 7.55 (m, 1H, H-C2´), 7.53 – 7.48 (m, 2H, H-C8´ + H-C9´), 7.41 – 7.25 (m, 15H, H-Ph), 4.94 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.84 (d, *J* = 11.4 Hz, 1H, H-C$\underline{H}_2$Ph), 4.93 (d, *J* = 10.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.69 (m, C2), 4.67 (d, *J* = 10.7 Hz, 1H, H-C$\underline{H}_2$Ph), 4.63 (d, *J* = 12.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.60 (m, C1), 4.57 (d, *J* = 12.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.25 (q, *J* = 7.0 Hz, 4H, H-C15´ + H-C17´), 4.05 – 3.96 (m, 1H, H-C3), 3.85 – 3.80 (m, 3H, H-C4, H-C6), 3.73 (dt, *J* = 10.0, 3.2 Hz, 1H, H-C5), 1.62 (t, *J* = 7.0 Hz, 3H, H-C16´ or H-C18´), 1.61 (t, *J* = 7.0 Hz, 3H, H-C16´ or H-C18´);

^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 148.3 (C5´), 148.0 (C12´), 139.1 (*i*-Ph), 139.0 (*i*-Ph), 134.89 (d, *J* = 1.1 Hz, C1´), 128.9 (*o,m,p*-Ph), 128.9 (*o,m,p*-Ph), 128.6 (*o,m,p*-Ph), 128.5 (*o,m,p*-Ph), 128.4 (*o,m,p*-Ph), 128.3 (*o,m,p*-Ph), 128.2 (*o,m,p*-Ph), 128.1 (*o,m,p*-Ph), 126.2 (C6´ or C11´), 126.1 (C6´ or C11´), 125.9 (C8´ or C9´), 125.9 (C8´ or C9´), 125.6 (C4´), 125.3 (C4´), 124.3 (C2´), 124.0 (C14´), 123.3 (C3´), 122.4 (C7´ or C10´), 122.4 (C7´ or C10´), 95.13 (d, *J* = 185.2 Hz, C2), 85.27 (d, *J* = 16.3 Hz, C3), 80.32 (d, *J* = 23.5 Hz, C1), 80.03 (d, *J* = 1.4 Hz, C5), 78.05 (d, *J* = 8.8 Hz, C4), 75.7 (C$\underline{H}_2$Ph), 75.35 (d, *J*

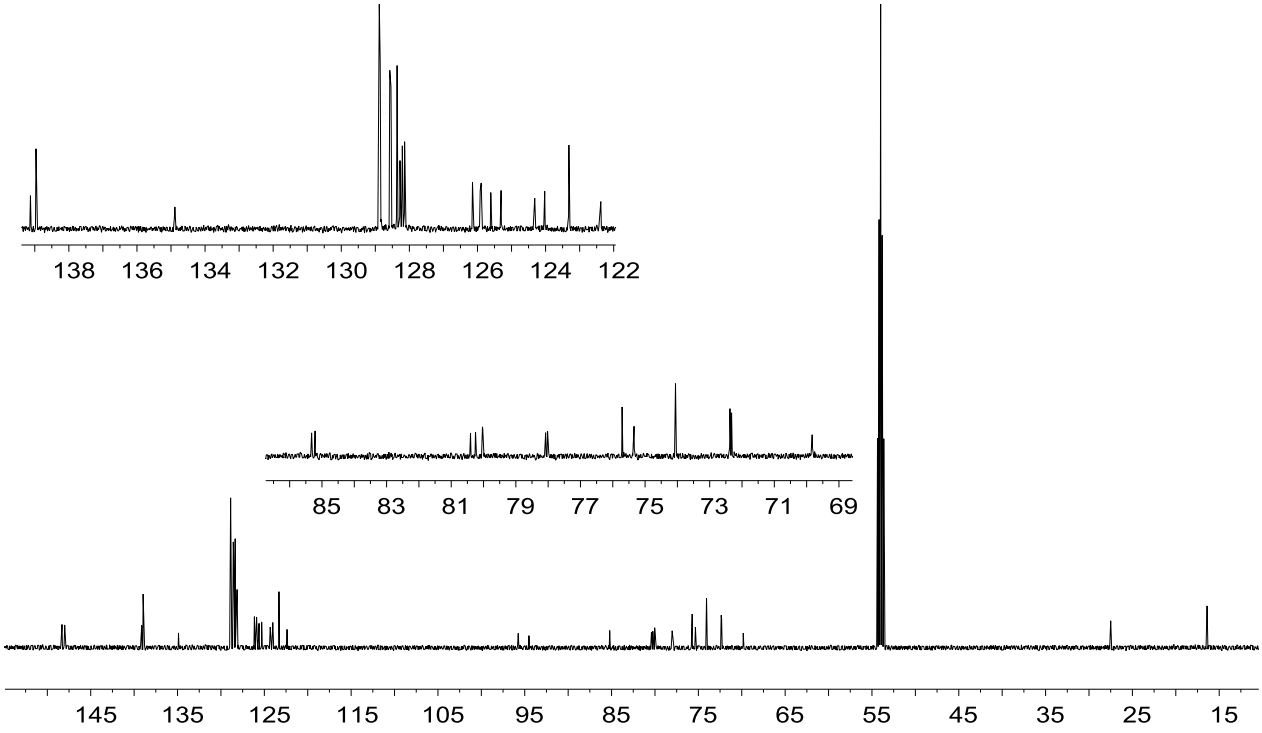
= 2.8 Hz, $\underline{C}H_2Ph$), 74.1 ($\underline{C}H_2Ph$), 72.4 (C15´ or C17´), 72.3 (C15´ or C17´, 69.8 (C6), 16.4 (C16´ or C18´), 16.4 (C16´ or C18´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -192.00 – -192.60 (m)

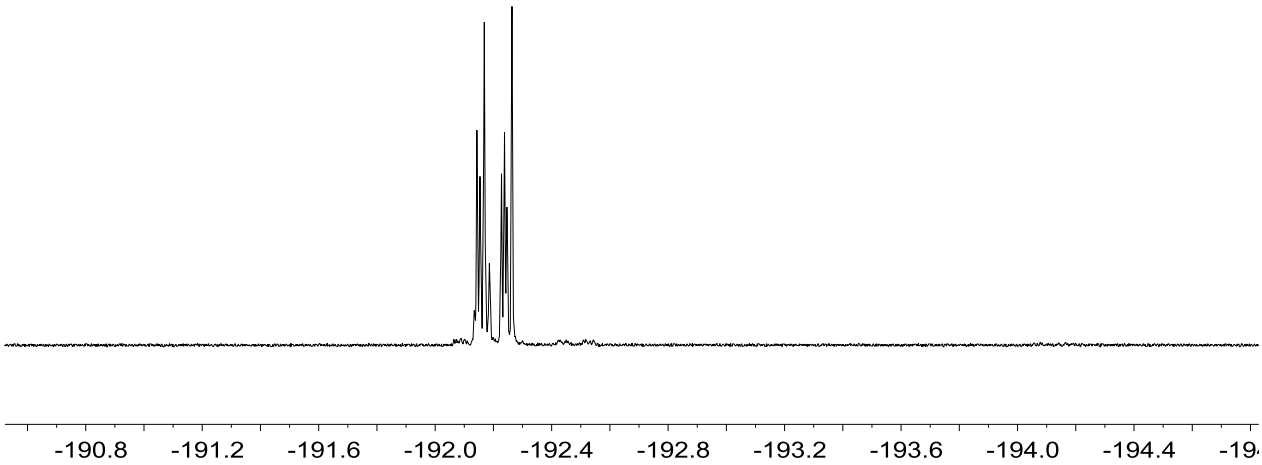
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)

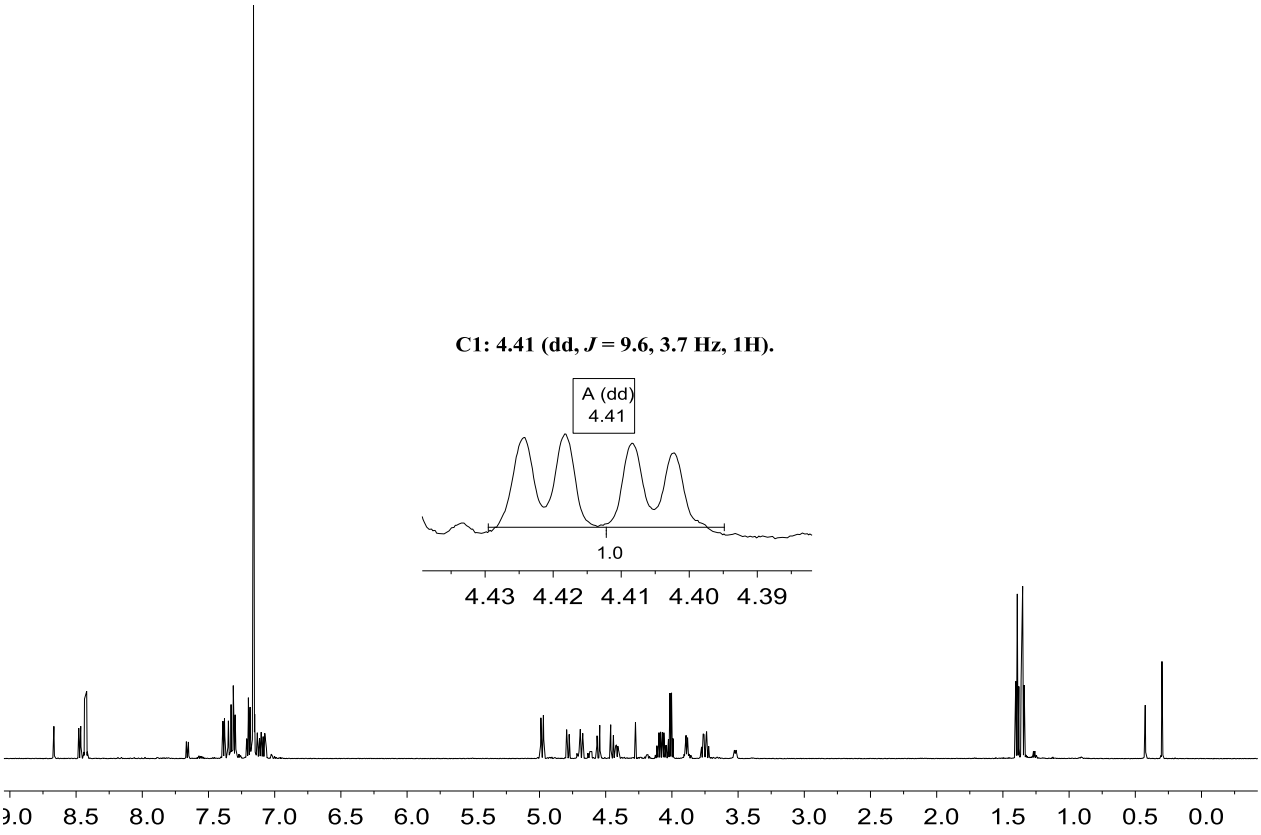


^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)

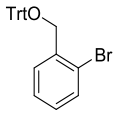


By changing the solvent for NMR it is possible to observe the coupling constant of C1 and determine the configuration of this stereocenter. (Found: dd, J = 9.6, 3.7Hz indicating β configuration)

^{1}H (600 MHz, Benzene-d_2, 299 K): β configuration.

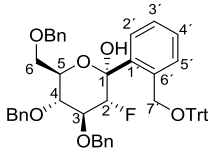


Compound S10:



See General Information.

Compound 10:



n-BuLi (97.0 µL, 2.5 M in hexanes, 0.2 mmol, 1.1 eq.) was added to a solution of compound **S10** (105 mg, 0.2 mmol, 1.1 eq.) in a mixture of toluene:THF (2:1; 0.33 mL:0.16 mL, 0.5 M), the mixture was stirred

under argon at -78 °C for 30 min. This mixture was transferred slowly to a solution of the corresponding lactone (100 mg, 0.2 mmol, 1.0 eq.) in dry THF (0.76 mL, 0.3 M) at -78 °C under argon. The reaction mixture was stirred for 30 min and quenched by addition of MeOH (5.0 mL). H_2O (5.0 mL) and EtOAc (5.0 mL) were added and the aqueous layer was extracted with EtOAc (3 x 3.0 mL). The combined organic layers were washed with H_2O (2 x 7.0 mL) and brine (1 x 7.0 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuum*. The residue obtained was purified by column chromatography CyH: EtOAc (SiO_2, 8:1). Compound **10** was obtained (130 mg, 73%) as a white solid.

R_f 0.58 (SiO_2, CyH:EtOAc 3:1);

Mp 58 – 64 °C;

m/*z* (ESI) found: 823.3417 $(M + Na)^+$, $C_{53}H_{49}O_6FNa^+$ calculated 823.3405

$[\alpha]_D^{25}$ -19.0 (*c* 1.00 in DCM);

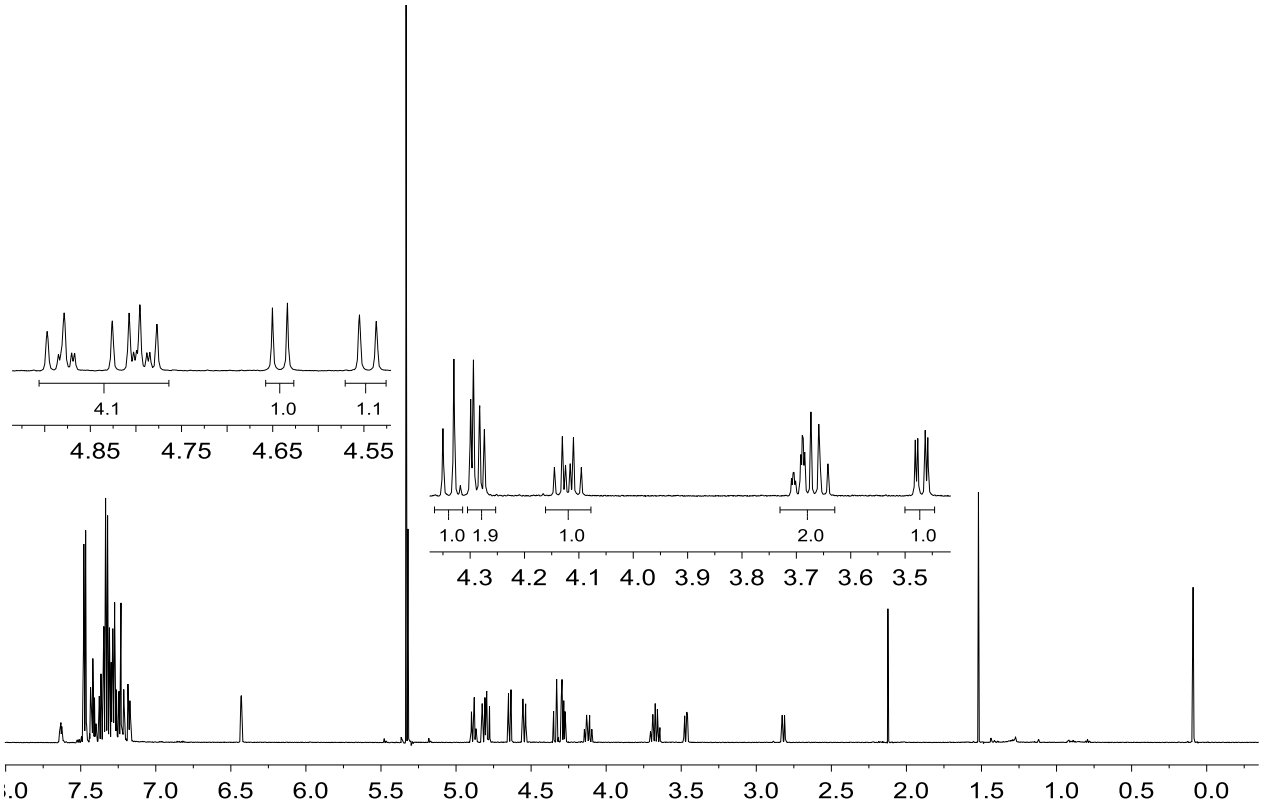
ν_{max} (neat)/cm^{-1} 3314m, 3061m, 3030m, 2925m, 2851m, 2341w, 2165w, 1965w, 1813w, 1597w, 1493m, 1449m, 1366m, 1309w, 1210w, 1154m, 1085m, 1020s, 976m, 942w, 899w, 846w, 809w, 765m, 744m, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.66 – 7.60 (m, 1H, H-Ph), 7.50 – 7.13 (m, 33H, H-Ph), 6.43 (d, *J* = 1.9 Hz, 1H, H-OH), 4.89 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.83 (ddd, J_{FH} = 49.6, *J* = 8.8, 2.0 Hz, 1H, H-C2), 4.82 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.79 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.64 (d, *J* = 9.8 Hz, 1H, H-C$\underline{H}_2$Ph7´), 4.55 (d, *J* = 11.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.34 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.29 (d, *J* = 9.9 Hz, 1H, H-C$\underline{H}_2$Ph7´), 4.28 (d, *J* = 12.1 Hz, 1H, H-C$\underline{H}_2$Ph), 4.12 (dt, J_{FH} = 12.3, *J* = 8.7 Hz, 1H, H-C3), 3.70 (ddd, *J* = 10.0, 2.7, 1.7 Hz, 1H, H-C5), 3.66 (dd, *J* = 10.0, 8.7 Hz, 1H, H-C4), 3.47 (dd, *J* = 11.0, 2.8 Hz, 1H, H-C6), 2.82 (dd, *J* = 11.1, 1.8 Hz, 1H, H-C6);

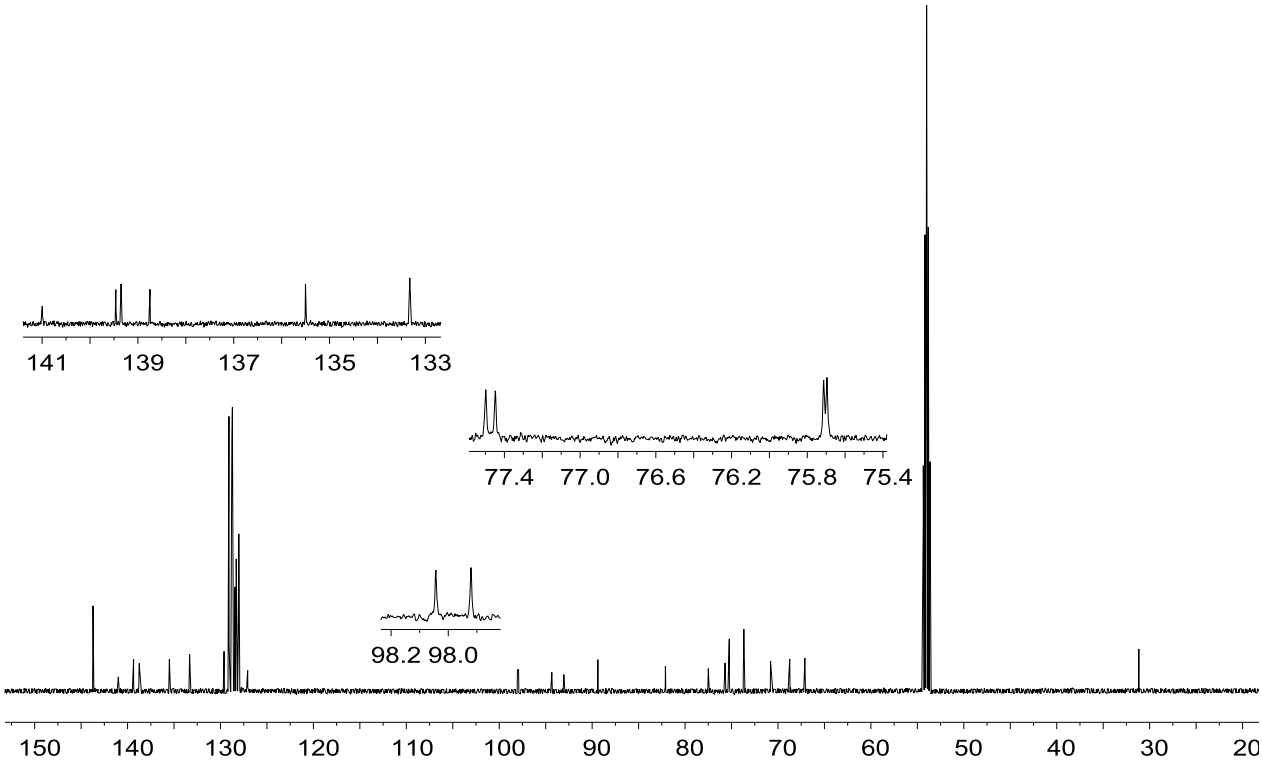
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) 143.7 (*i*-PhTrt), 141.0 (d, J_{FC} = 2.3 Hz, C1´)139.5 (*i*-Ph), 139.4 (*i*-Ph), 138.8 (*i*-Ph), 135.5 (C6´), 133.3 (C5´), 129.6 (C3´/C4´), 129.1 (C3´/C4´), 129.1 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.7 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.0 (*o*,*m*,*p*-Ph), 127.1 (d, J_{FC} = 4.9 Hz, (C2´), 98.0 (d, J_{FC} = 18.5 Hz, C1), 93.7 (d, J_{FC} = 194.9 Hz, C2), 89.4 (C$\underline{C}$Trt), 82.1 (d, J_{FC} = 16.8 Hz, C3), 77.5 (d, J_{FC} = 7.7 Hz, C4), 75.7 (d, J_{FC} = 2.7 Hz, $\underline{C}H_2$Ph), 75.2 ($\underline{C}H_2$Ph), 73.7 ($\underline{C}H_2$Ph), 70.8 (d, J_{FC} = 1.4 Hz, C5), 68.7 (C6), 67.1 ($\underline{C}H_2$Ph7´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -191.5 (ddd, *J* = 49.6, 12.3, 2.3 Hz).

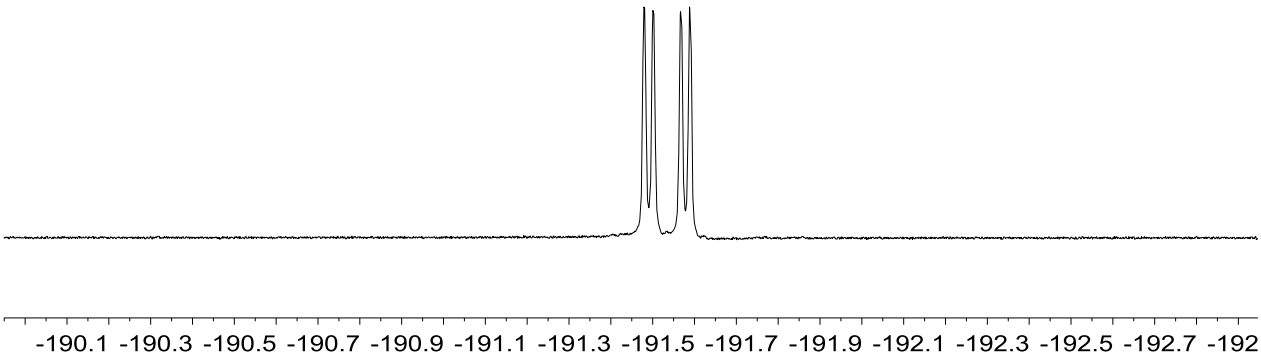
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



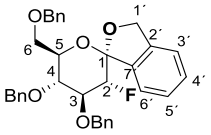
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound 11:



BF_3•Et_2O (17 µL, 0.14 mmol, 1.1 eq.) and Et_3SiH (22 µL, 0.14 mmol, 1.1 eq.) were added to a mixture of compound **10** (100 mg, 0.12 mmol, 1.0 eq.) in MeCN (1.8 mL, 0.1 M) under an argon atmosphere at -40 °C. The mixture was stirred for 1 h and then was warmed to 0 °C and stirred at this temperature an additional hour. The reaction mixture was quenched with $NaHCO_3$ (sat. aq., 1.0 mL), the aqueous layer was extracted with CH_2Cl_2 (3 x 1.0 mL), and the combined organic layers were washed H_2O (3 x 1.0 mL) and brine (1 x 1.0 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue obtained was purified by column chromatography CyH: EtOAc (SiO_2, 4:1). Compound **11** was obtained (47 mg, 69%) as a colourless oil.

R_f 0.58 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 563.2245 $(M + Na)^+$, $C_{34}H_{33}O_5FNa^+$ calculated 563.2215;

$[\alpha]_D^{25}$ +28.7 (*c* 1.00 in DCM);

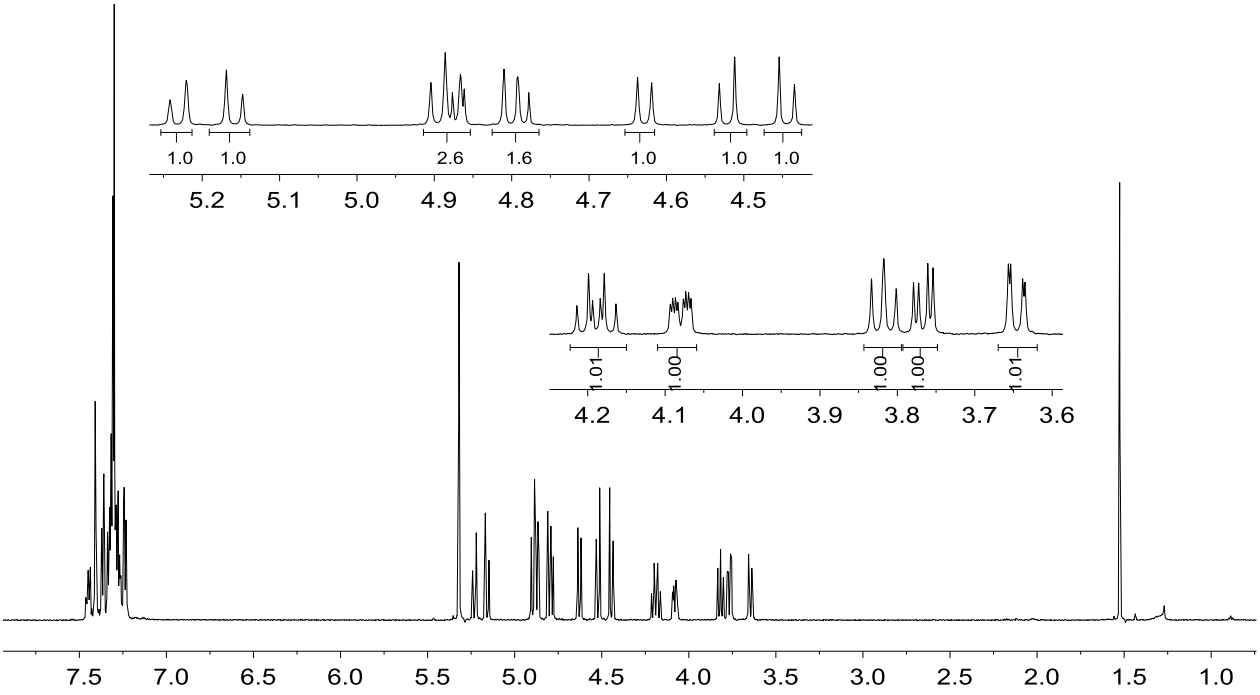
ν_{max} (neat)/cm^{-1} 3671w, 3063w, 3031w, 2925m, 2851m, 2206w, 2167w, 2027w, 1951w, 1879w, 1812w, 1607w, 1497m, 1463m, 1453m, 1364m, 1312w, 1263w, 1208w, 1154m, 1130w, 1110w, 1086s, 1048s, 1026s, 1010s, 904m, 862w, 848w, 821w, 786,m 764w, 730s, 695s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.47 – 7.42 (m, 1H H-(C3´/C4´/C5´/C6´)), 7.42 – 7.39 (m, 2H, H-(C3´/C4´/C5´/C6´)), 7.38 – 7.35 (m, 2H, H-Ph), 7.35 – 7.22 (m, 14H, H-Ph + H-(C3´/C4´/C5´/C6´)), 5.23 (d, *J* = 12.6 Hz, 1H, H-C1´), 5.16 (d, *J* = 12.6, 1.0 Hz, 1H, H-C1´), 4.90 (d, *J* = 11.1 Hz, 1H, H-CH_2Ph), 4.88 (d, *J* = 11.8 Hz, 1H, H-CH_2Ph) 4.83 (dd, J_{FH} = 50.4, *J* = 8.8 Hz, 1H, H-C2), 4.80 (d, *J* = 10.1 Hz, 1H, H-CH_2Ph), 4.63 (d, *J* = 10.9 Hz, 1H, H-CH_2Ph), 4.52 (d, *J* = 11.9 Hz, 1H, H-CH_2Ph), 4.44 (d, *J* = 11.9 Hz, 1H, H-CH_2Ph), 4.19 (dt, J_{FH} = 12.2, *J* = 9.0 Hz, 1H, H-C3), 4.08 (ddd, *J* = 10.1, 4.1, 2.0 Hz, 1H, H-C5), 3.82 (t, *J* = 9.5, 1H, H-C4), 3.77 (dd, *J* = 11.1, 4.1 Hz, 1H, H-C6), 3.65 (dd, *J* = 11.1, 1.9 Hz, 1H, H-C6);

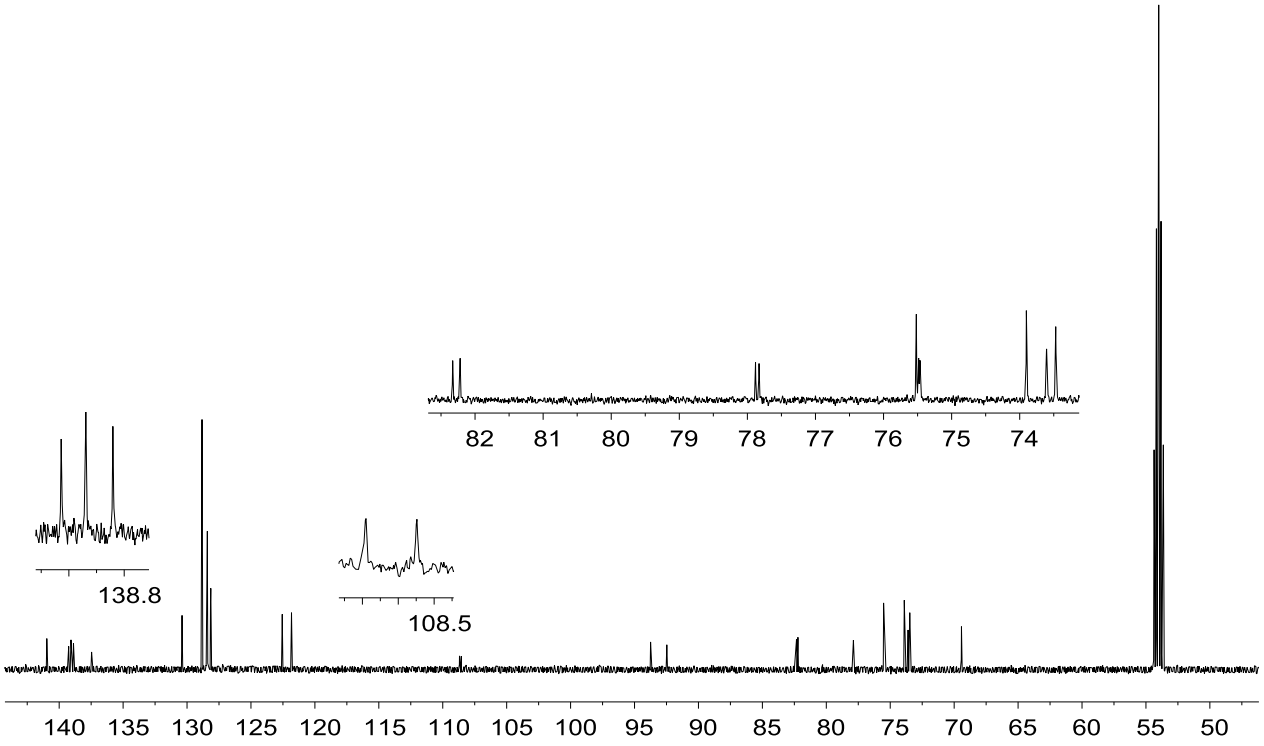
$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 141.0 (C7), 139.3 (*i*-Ph), 139.1 (*i*-Ph), 138.9 (*i*-Ph), 137.5 (C2), 130.4 (C3´/C4´/C5´/C6´), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (C3´/C4´/C5´/C6´), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 122.6 (C3´/C4´/C5´/C6´), 121.8 (C3´/C4´/C5´/C6´), 108.6 (d, J_{FC} = 21.5 Hz, C1), 93.1 (d, J_{FC} = 191.3 Hz, C2), 82.3 (d, J_{FC} = 16.4 Hz, C3), 77.9 (d, J_{FC} = 8.1 Hz, C4), 75.5 (C1´), 75.5 (d, J_{FC} = 2.7 Hz, $\underline{C}H_2Ph$), 73.9 ($\underline{C}H_2Ph$), 73.6 (d, J_{FC} = 1.4 Hz, C5), 73.5 ($\underline{C}H_2Ph$), 69.4 (C6);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.0 (dd, J = 50.0, 12.2 Hz).

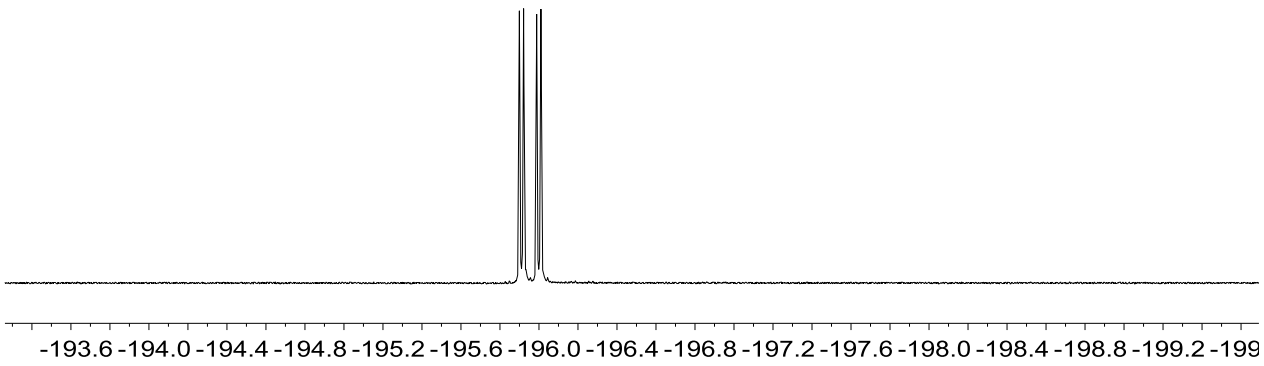
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



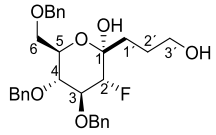
$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound 14:



9-BBN (3.6 mL, 13.2 mmol, 26.0 eq.) was added to a mixture of compound **13** (Table 2 Entry 6) (250 mg, 0.5 mmol, 1.0 eq.) in THF (3.6 mL, 0.1 M) under an argon atmosphere. The reaction was stirred for 2 h and then NaOH (aq. 3.0 M, 3.3 mL, 9.6 mmol, 19.0 eq.) and H_2O_2 (30%, 1.8 mL, 22.3 mmol, 44.0 eq.) were added to the reaction. The mixture was stirred at room temperature overnight. The reaction was quenched by addition of H_2O (15 mL) then Et_2O (15 mL) was added. The aqueous layer was extracted with Et_2O (3 x

7.0 mL). The combined organic layers were washed with $Na_2S_2O_3$ (aq. Sat.) (peroxide test was negative). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuo*. The residue obtained was purified by column chromatography CyH: EtOAc (SiO_2, 6:1). Product **14** was obtained (130 mg, 50%) as a colourless oil.

R_f 0.16 (SiO_2, CyH:EtOAc 2:1);

m/*z* (ESI) found: 533.2314 $(M + Na)^+$, $C_{30}H_{35}O_6FNa^+$ calculated 533.2310;

$[\alpha]_D^{25}$ +28.1 (*c* 0.33 in DCM);

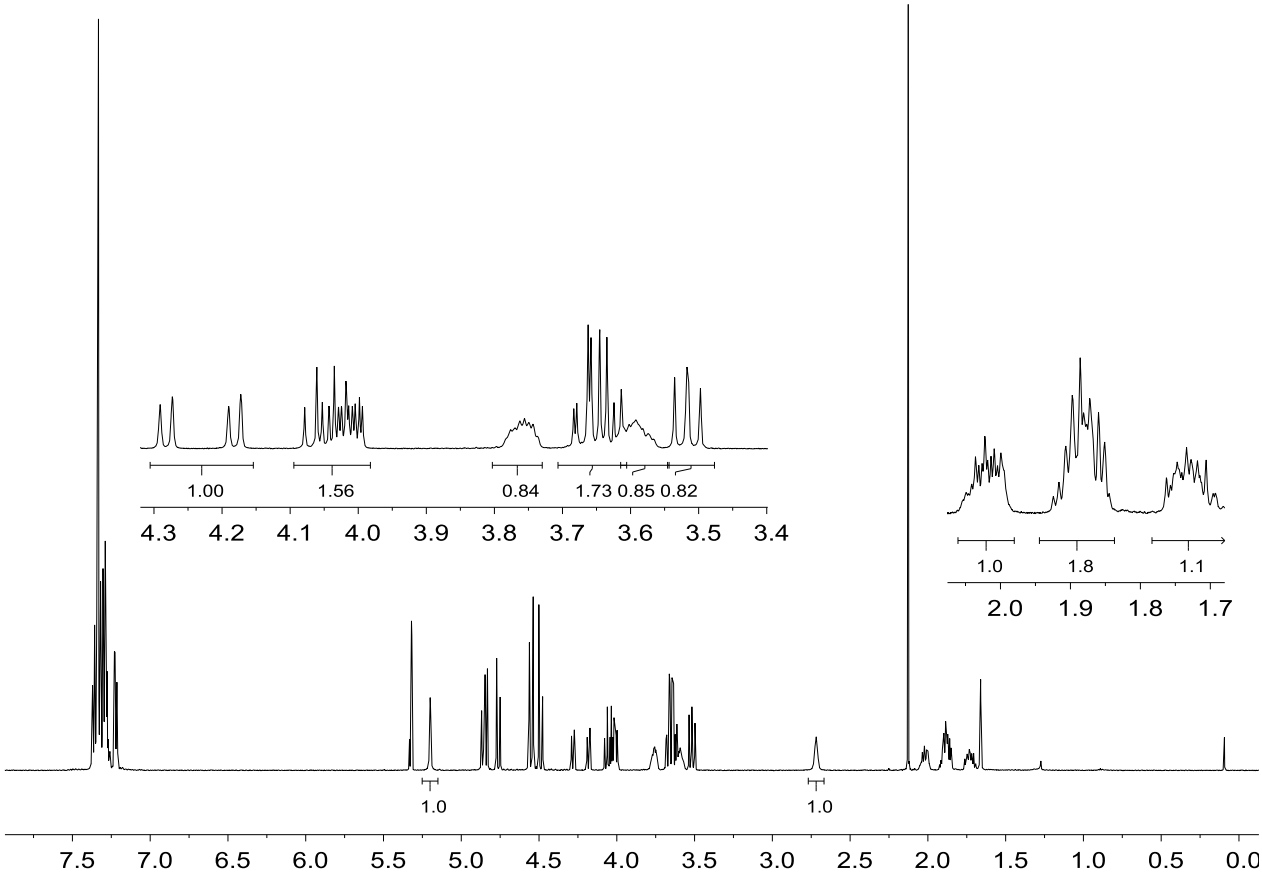
ν_{max} (neat)/cm^{-1} 3376m, 3088w, 3064w, 3032w, 2922m, 2866m, 2226w, 2160w, 2138w, 2007w, 1958w, 1877w, 1738w, 1606w, 1497m, 1454m, 1366m, 1310w, 1263w, 1208w, 1148m, 1057s, 1025s, 912w, 842w, 734s, 696s;

^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.38 – 7.25 (m, 13H, H-Ph), 7.22 (m, 2H, H-Ph), 5.20 (s, 1H, H-OH tertiary), 4.86 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.84 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.76 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.55 (d, *J* = 10.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.55 (d, *J* = 12.5 Hz, 1H, H-C$\underline{H}_2$Ph), 4.49 (d, *J* = 12.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.23 (dd, J_{FH} = 50.3, *J* = 9.0 Hz, 1H, H-C2), 4.05 (dt, J_{FH} = 13.2, *J* = 8.7 Hz, 1H, H-C3), 4.01 (ddd, *J* = 10.2, 5.3, 2.2 Hz, 1H, H-C5), 3.76 (m, 1H, H-C3´), 3.67 (dd, *J* = 10.5, 2.2 Hz, 1H, H-C6), 3.63 (dd, *J* = 10.5, 5.3 Hz, 1H, H-C6), 3.60 (m, 1H, C3´), 3.54 – 3.49 (m, 1H, H-C4), 2.72 (s, 1H, H-OH secondary), 2.07 – 1.98 (m, 1H, H-C1´), 1.93 – 1.84 (m, 2H, H-C1´ + H-C2´), 1.78 – 1.68 (m, 1H, H-C2´);

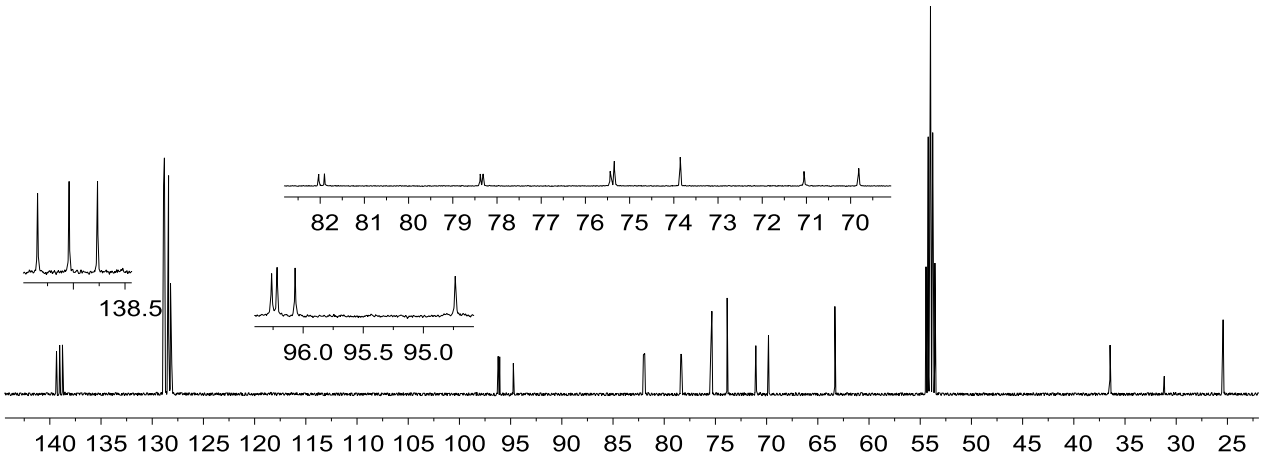
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.4 (*i*-Ph), 139.0 (*i*-Ph), 138.8 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 96.1 (d, J_{FC} = 19.0 Hz, C1), 95.5 (d, J_{FC} = 192.1 Hz, C2), 82.0 (d, J_{FC} = 16.3 Hz, C3), 78.4 (d, J_{FC} = 8.0 Hz, C4), 75.4 (d, J_{FC} = 2.7 Hz, $\underline{C}H_2$Ph), 75.4 ($\underline{C}H_2$Ph), 73.9 ($\underline{C}H_2$Ph), 71.1 (d, J_{FC} = 1.0 Hz, C5), 69.8 (C6), 63.3 (C3´), 36.5 (C1´), 25.4 (C2´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.66 (dd, *J* = 50.0, 13.2 Hz).

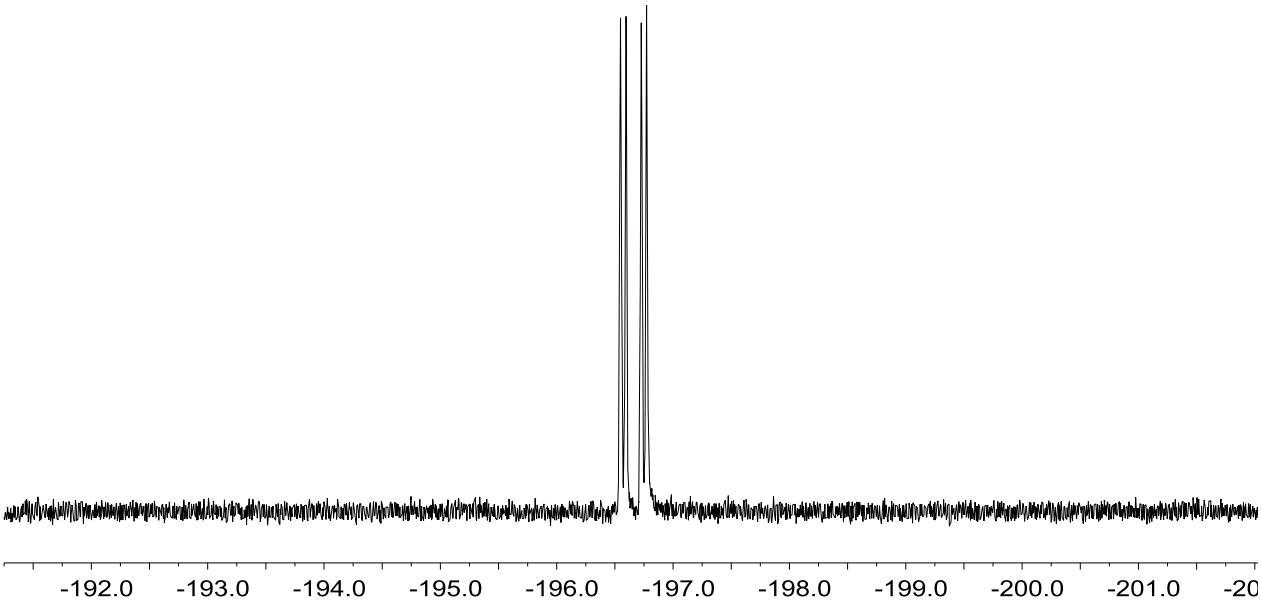
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



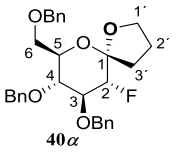
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K)



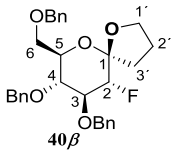
^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Compound 15*α* and 15*β*:



40*α*



40*β*

CSA (15 mg, 66.0 µmol, 0.8 eq.) was added to a mixture of compound **14** (45 mg, 88.0 µmol, 1.0 eq.) in THF (1.5 mL, 0.06 M). The mixture was stirred at 80 °C for 8 h, then it was cooled at room temperature and quenched by addition of $NaHCO_3$ (sat. aq., 1.0 mL). The aqueous layer was extracted EtOAc (3 x 1.0 mL). The combined organic layers were washed with H_2O (2 x 2 mL) and brine (1 x 2 mL). The organic layer was dried over $MgSO_4$, filtered and evaporated *in vacuum*. The residue obtained was purified by column chromatography CyH: EtOAc (SiO_2, 5:1). Compound **15*α*** was obtained (10 mg, 23%, *α*) as a colourless oil, **15*β*** (12 mg, 28%, *β*) as a white solid.

Characterisation for 15*α*:

R_f 0.64 (SiO_2, CyH:EtOAc 3:1);

m/*z* (ESI) found: 515.2195 $(M + Na)^+$, $C_{30}H_{33}O_5FNa^+$ calculated 515.2204;

$[\alpha]_D^{25}$ +56.8 (*c* 0.75 in DCM);

ν_{max} (neat)/cm^{-1} 3090w, 3064w, 3030w, 2901m, 1497m, 1454m, 1365m, 1316w, 1261w, 1240w, 1207w, 1144m, 1119m, 1067s, 1026s, 999s, 925m, 911m, 866m, 801m, 733s, 695s;

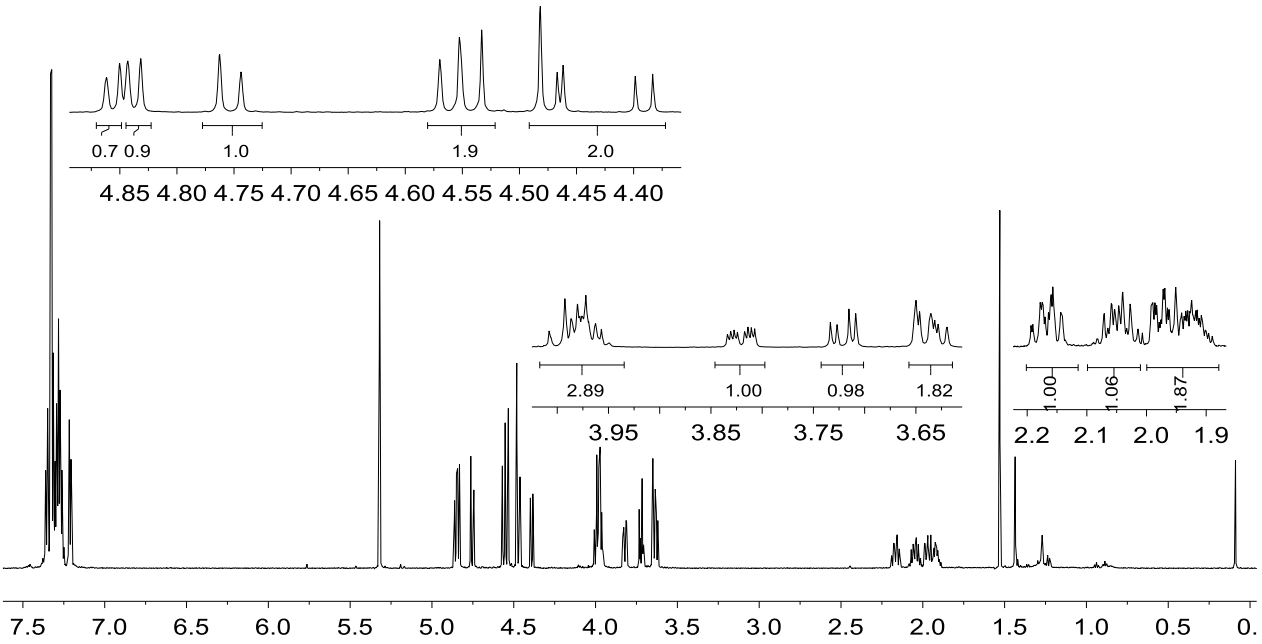
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.38 – 7.26 (m, 13H, H-Ph), 7.24 – 7.19 (m, 2H, H-Ph), 4.85 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.84 (d, *J* = 11.0 Hz, 1H, H-C$\underline{H}_2$Ph), 4.75 (d, *J* = 11.2 Hz, 1H, H-

C<u>H</u>$_2$Ph), 4.56 (d, J = 10.1 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.54 (d, J = 10.9 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.47 (d, J = 12.0 Hz, 1H), 4.43 (dd, J_{FH} = 50.2, J = 9.1, 1H, H-C2), 4.01 – 3.95 (m, 3H, H-C3 + H-C1´), 3.82 (dddd, J = 10.1, 4.0, 2.0, 0.8 Hz, 1H, H-C5), 3.72 (dd, J = 10.9, 3.9 Hz, 1H, H-C6), 3.65 – 3.62 (m, 2H, H-C4 + H-C6), 2.20 – 2.14 (m, 1H, H-C3´), 2.09 – 2.02 (m, 1H, H-C2´), 2.01 – 1.96 (m, 1H, H-C3´) 1.96 – 1.90 (m, 1H, H-C2´);

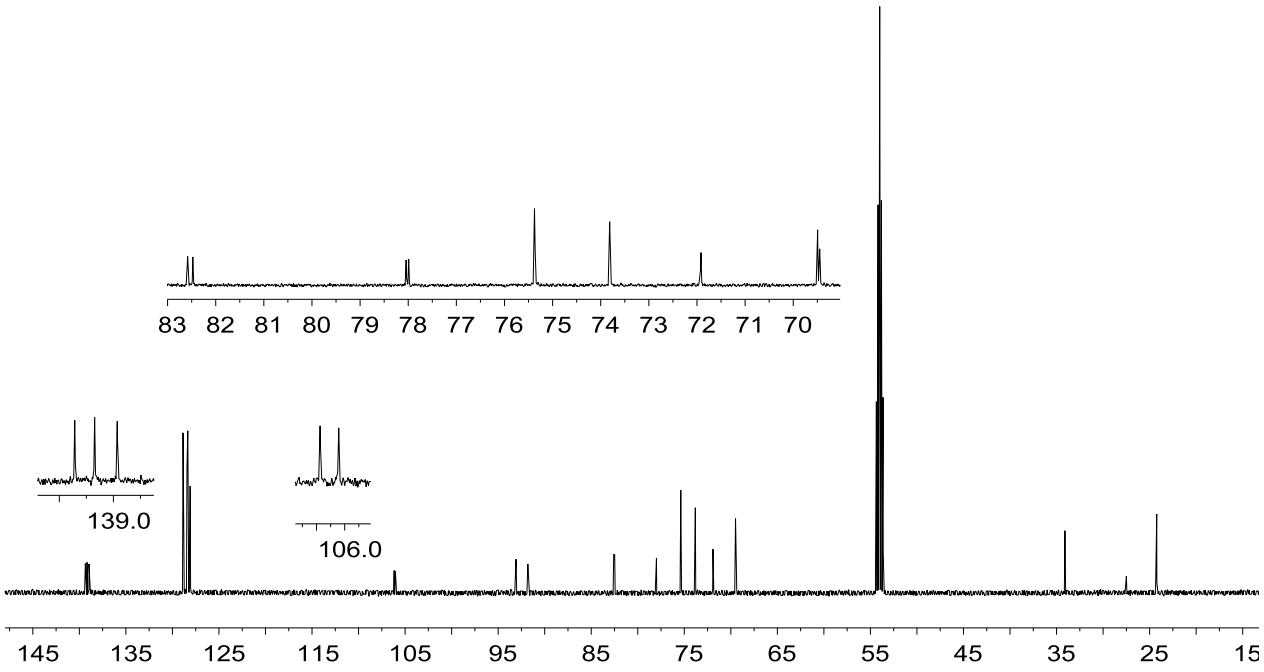
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.4 (*i*-Ph), 139.2 (*i*-Ph), 139.0 (*i*-Ph), 129.0 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.3 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 128.1 (*o*,*m*,*p*-Ph), 106.1 (d, J_{FC} = 20.0 Hz, C1), 92.4 (d, J_{FC} = 191.4 Hz, C2), 82.5 (d, J_{FC} = 16.1 Hz, C3), 78.0 (d, J_{FC} = 8.1 Hz, C4), 75.4 (<u>C</u>H$_2$Ph), 75.4 (<u>C</u>H$_2$Ph), 73.8 (<u>C</u>H$_2$Ph), 71.9 (d, J_{FC} = 1.4 Hz, C5), 69.5 (C1´), 69.5 (C6), 34.1 (C3´), 24.2 (C2´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -197.8 (dd, J = 50.2, 12.5 Hz).

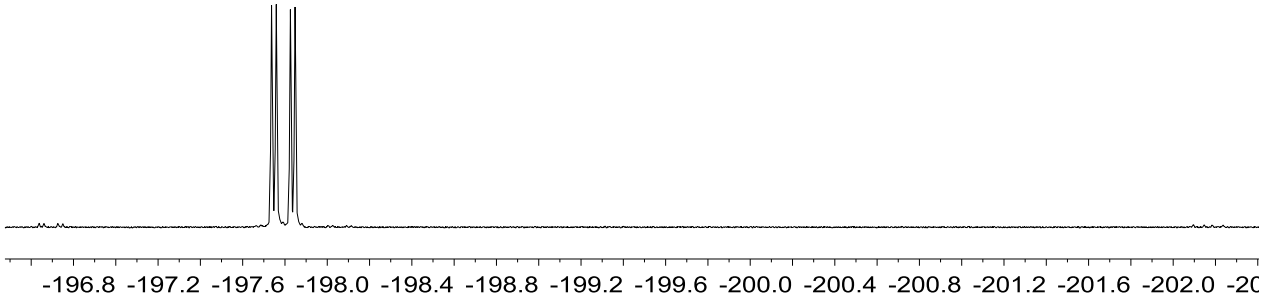
^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)



Characterisation for 15*β*:

R_f 0.42 (SiO_2, CyH:EtOAc 3:1);

Mp 67 °C;

m/*z* (ESI) found: 515.2195 $(M + Na)^+$, $C_{30}H_{33}O_5FNa^+$ calculated 515.2204;

$[\alpha]_D^{25}$ +26.1 (*c* 0.48 in DCM);

ν_{max} (neat)/cm^{-1} 3673w, 3063w, 3031w, 2890m, 2347w, 2153w, 2075w, 1966w, 1879w, 1812w, 1753w, 1587w, 1497m, 1454m, 1403w, 1366m, 1318w, 1262w, 1209w, 1150m, 1068s, 1025s, 999s, 951m, 912m, 889m, 820w, 787w, 739s, 696s;

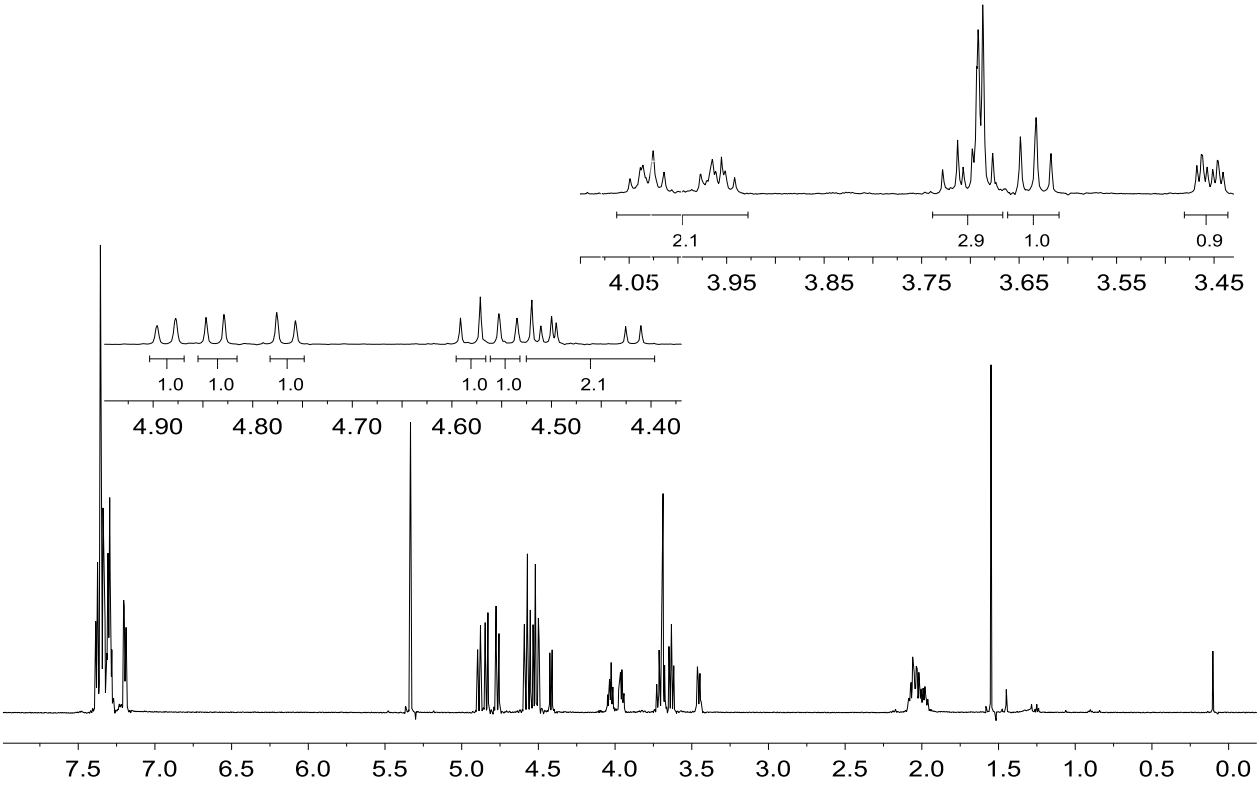
^{1}H NMR (600 MHz, Dichloromethane-d_2, 299 K) δ 7.38 – 7.26 (m, 13H, H-Ph), 7.20 – 7.17 (m, 2H, H-Ph), 4.87 (d, *J* = 11.2 Hz, 1H, H-C$\underline{H}_2$Ph), 4.82 (d, *J* = 10.8 Hz, 1H, H-C$\underline{H}_2$Ph), 4.75 (d, *J* = 11.2 Hz, 1H, H-

C<u>H</u>$_2$Ph), 4.57 (d, J = 11.9 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.53 (d, J = 10.8 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.50 (d, J = 12.0 Hz, 1H, H-C<u>H</u>$_2$Ph), 4.45 (dd, J_{FH} = 51.0, J = 9.2 Hz, 1H, H-C2), 4.04 – 3.92 (m, 2H, H-C1´), 3.72 – 3.65 (m, 3H, H-C3 + H-C6), 3.62 (t, J = 9.4 Hz, 1H, H-C4), 3.44 (ddd, J = 9.8, 3.7, 2.7 Hz, 1H, H-C5), 2.10 – 1.93 (m, 4H, H-C2´ + H-C3´);

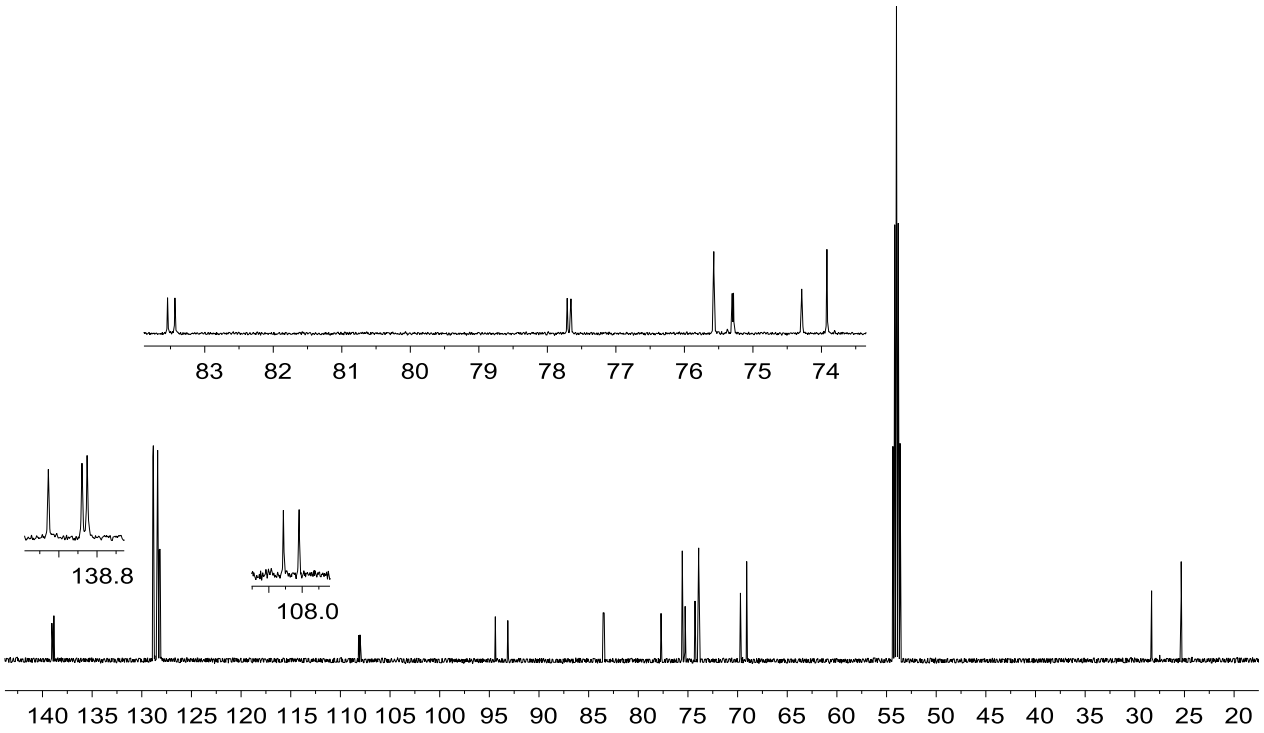
^{13}C{^{1}H} NMR (151 MHz, Dichloromethane-d_2, 299 K) δ 139.1 (*i*-Ph), 138.9 (*i*-Ph), 138.9 (*i*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.9 (*o*,*m*,*p*-Ph), 128.8 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.5 (*o*,*m*,*p*-Ph), 128.4 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 128.2 (*o*,*m*,*p*-Ph), 108.1 (d, J_{FC} = 21.2 Hz, C1), 93.8 (d, J_{FC} = 189.6 Hz, C2), 83.5 (d, J_{FC} = 16.1 Hz, C3), 77.7 (d, J_{FC} = 8.2 Hz, C4), 75.6 (CH_2Ph), 75.3 (d, J_{FC} = 2.9 Hz, CH_2Ph), 74.3 (d, J_{FC} = 1.3 Hz, C5), 73.9 (CH_2Ph), 69.7 (C6), 69.1 (C1´), 28.3 (C3´), 25.3 (C2´);

^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K) δ -196.3 (dd, J = 51.1, 12.6 Hz).

^{1}H (600 MHz, Dichloromethane-d_2, 299 K)



$^{13}C\{^{1}H\}$ NMR (151 MHz, Dichloromethane-d_2, 299 K)



^{19}F NMR (564 MHz, Dichloromethane-d_2, 299 K)