Electronic Supplementary Information

Selective Electrochemiluminescent Sensing of Saccharides using Boronic Acid-Modified Coreactant

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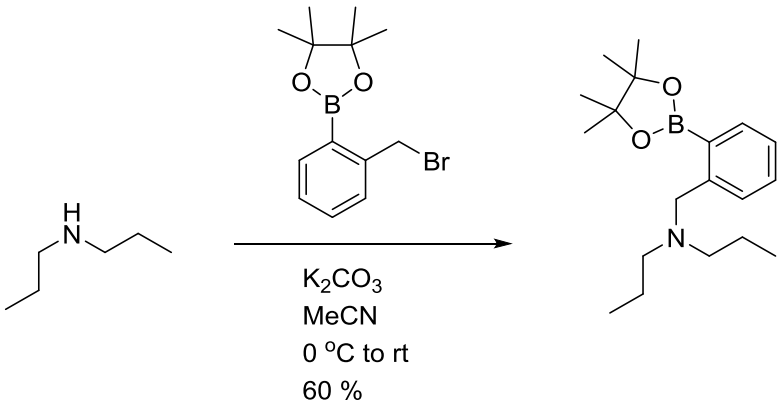
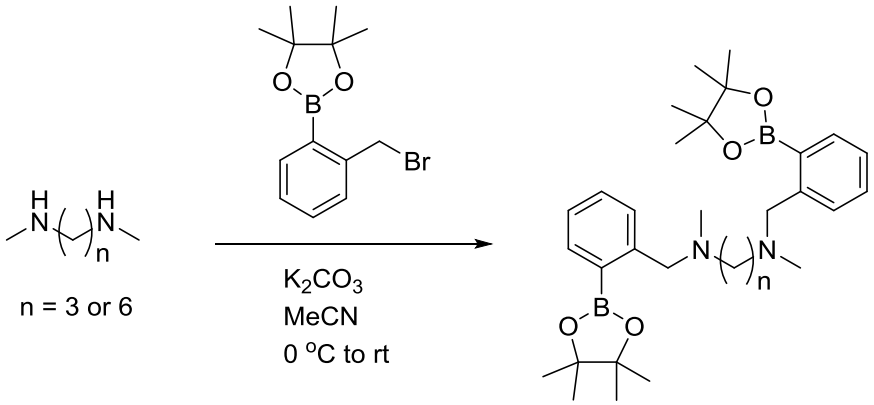
Contents

A. Additional schemes



Scheme S1 Synthesis of the boronic acid based coreactant **E0**. Reaction conditions – K_2CO_3 (3 eq), BPinBnBr (1 eq), amine, MeCN, 0 °C to rt, 16 h, 60 %.



Scheme S2 Synthesis of the boronic acid based coreactants **E3** and **E6**. Reaction conditions – K_2CO_3 (3 eq), BPinBnBr (2 eq), amine, MeCN, 0 °C to rt, 16 h, n = 3 (92 %), n = 6 (16 %).

B. Additional figures

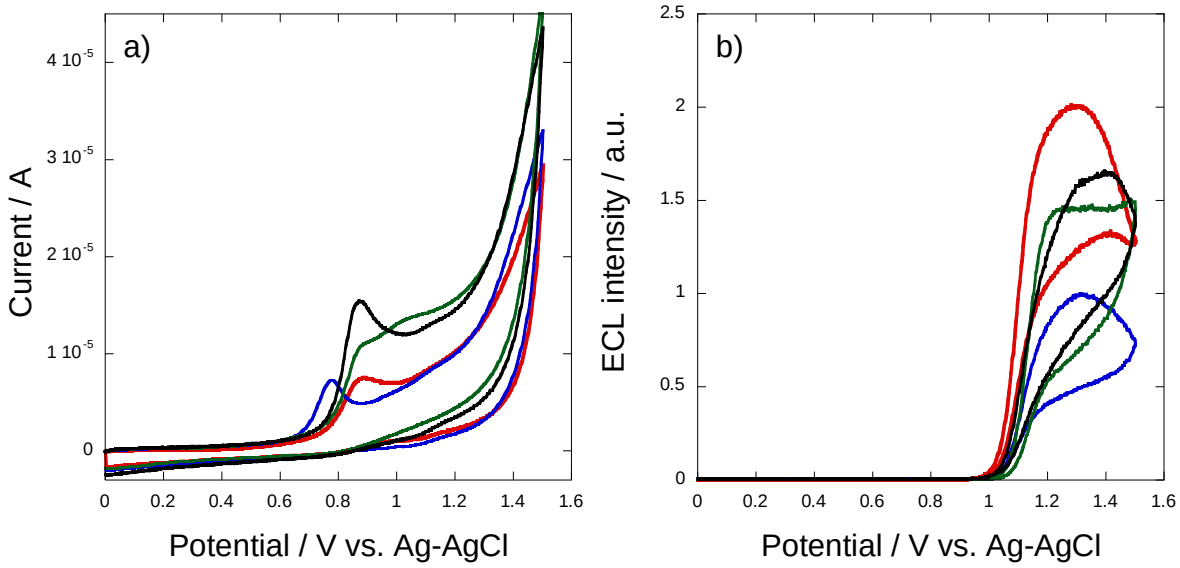


Figure S1. Comparison of the (a) voltammetric and (b) ECL signals of $Ru(bpy)_3^{2+}$ with either the coreactants TPrA (red line), **E0** (blue line), **E6** (black line) or **E3** (green line). Experiments were performed in 100 mM PBS solution (pH 7.4) containing 10 µM $Ru(bpy)_3^{2+}$ and 0.1 mM coreactant with a GC electrode as a working electrode. Scan rate 0.1 V s^{-1}.

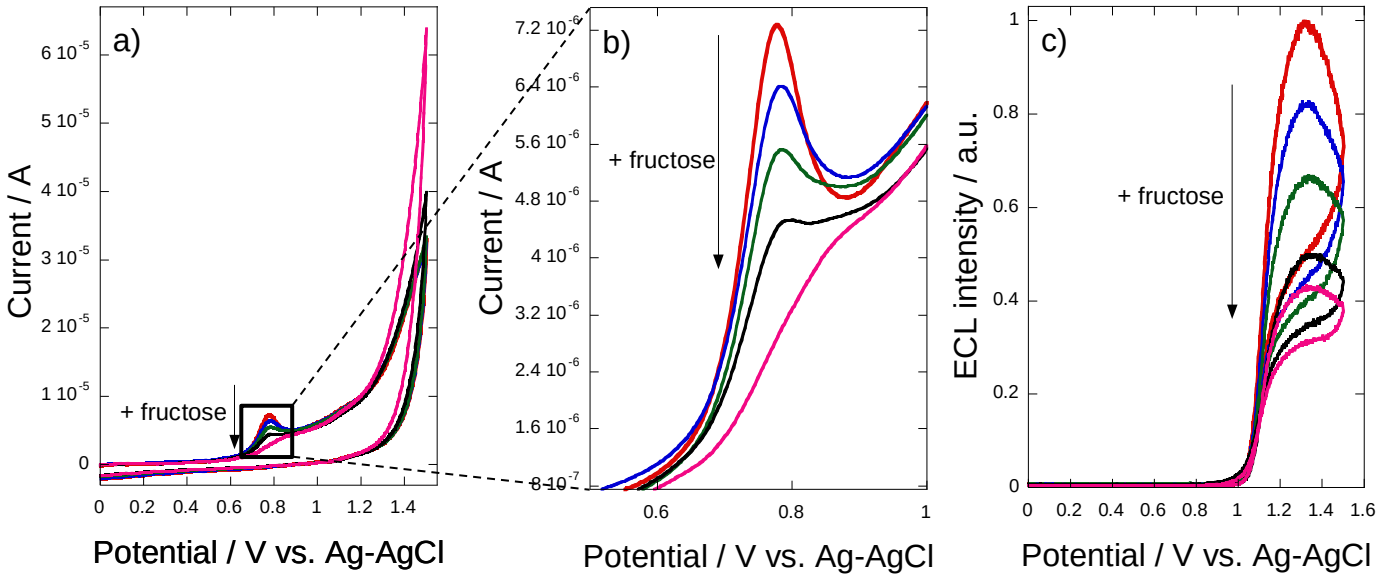


Figure S2. Effect of D-fructose addition on voltammetric and ECL responses. (a-b) Cyclic voltammetry and (c) ECL signal of a PBS solution (pH 7.4) containing 10 µM $Ru(bpy)_3^{2+}$, 0.1 mM **E0** and different concentrations of D-fructose. The arrow indicates increasing concentrations of D-fructose (0, 0.5, 1, 10, 50 mM). Experiments were performed on GC electrode at a scan rate of 0.1 V s^{-1}.

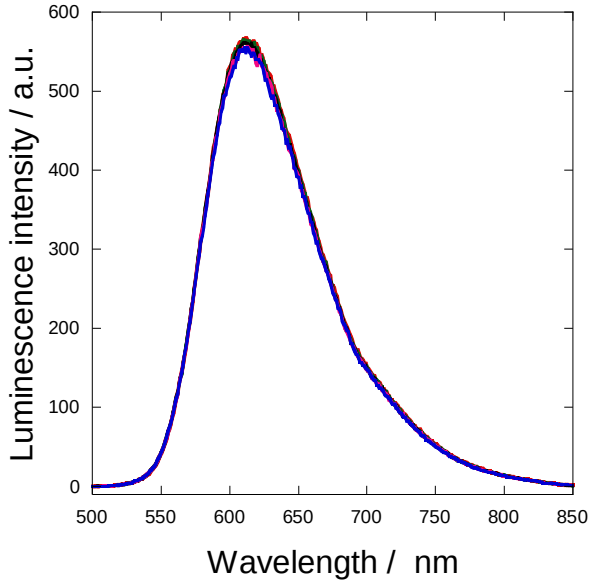


Figure S3. Comparison of the PL and ECL spectra recorded in presence of increasing concentrations of D-fructose. Spectra were recorded in PBS (pH 7.4) solution with 10 µM $Ru(bpy)_3^{2+}$, 0.1mM **E0** and different concentrations of D-fructose (0, 0.5, 1, 10 and 50 mM). λ_{exc}= 452 nm.

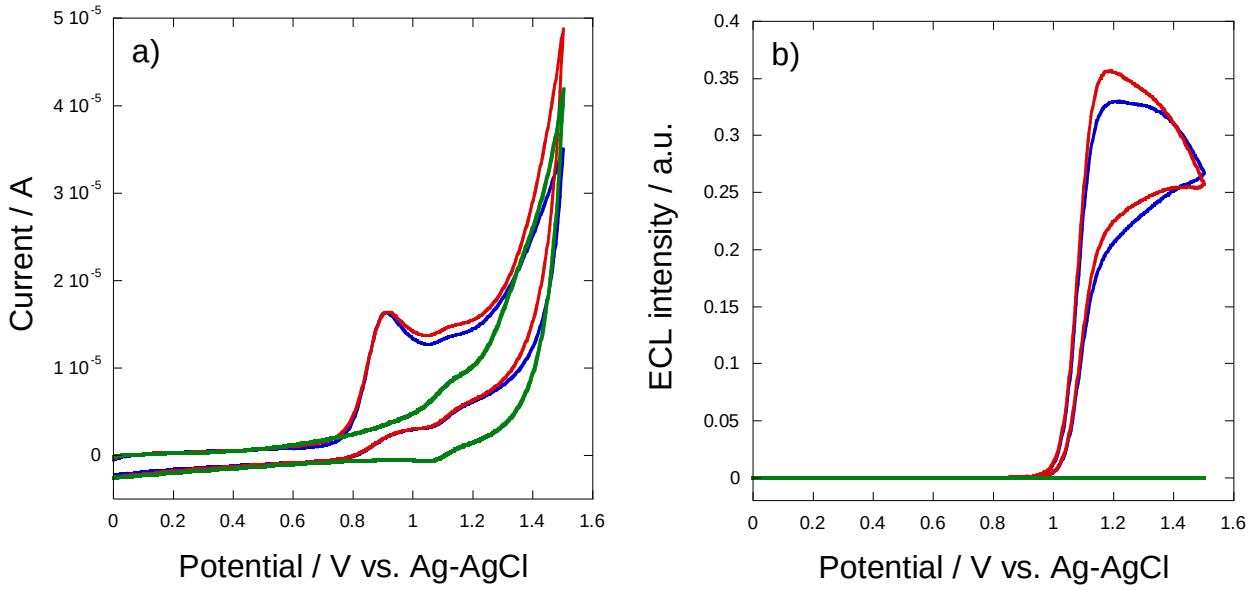
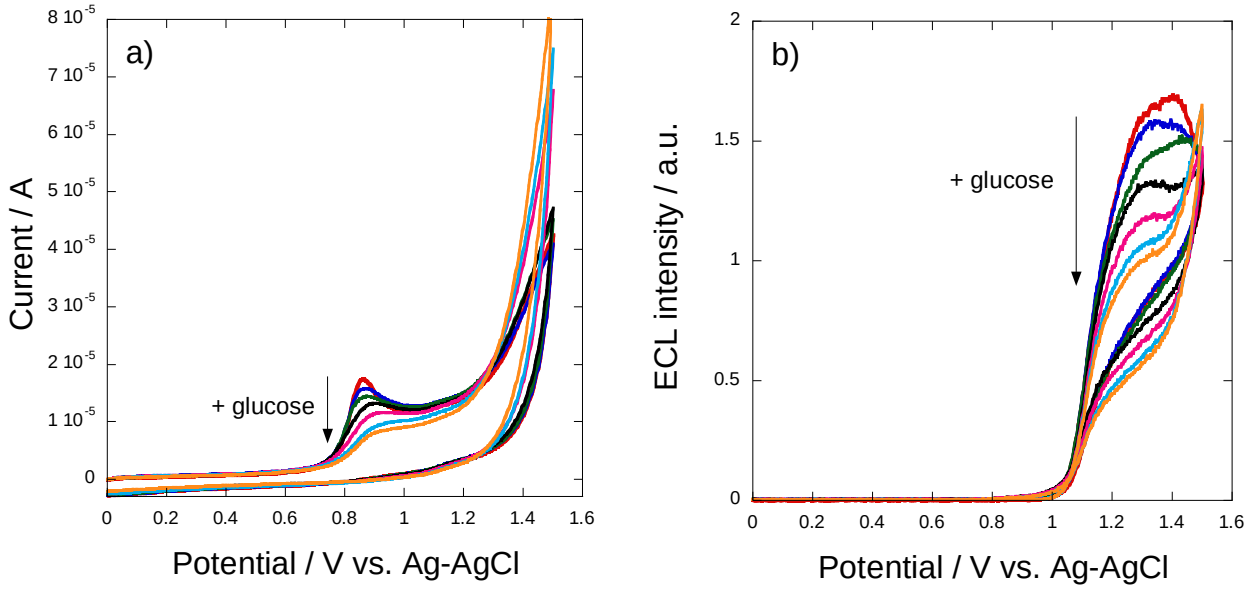


Figure S4. Effect of D-fructose on voltammetric and ECL signals of the model tandem system $Ru(bpy)_3^{2+}$/TPrA. (a) Cyclic voltammograms and (b) ECL signals of a PBS solution (pH 7.4) containing 10 µM $Ru(bpy)_3^{2+}$, 0.1 mM TPrA before (red line) and after the addition of 10 mM D-fructose (blue line). Green line corresponds to the PBS solution containing 10 µM $Ru(bpy)_3^{2+}$ and only 10 mM D-fructose (i.e. without TPrA or **E0**). Experiments were performed on GC electrode at a scan rate of 0.1 V s^{-1}.



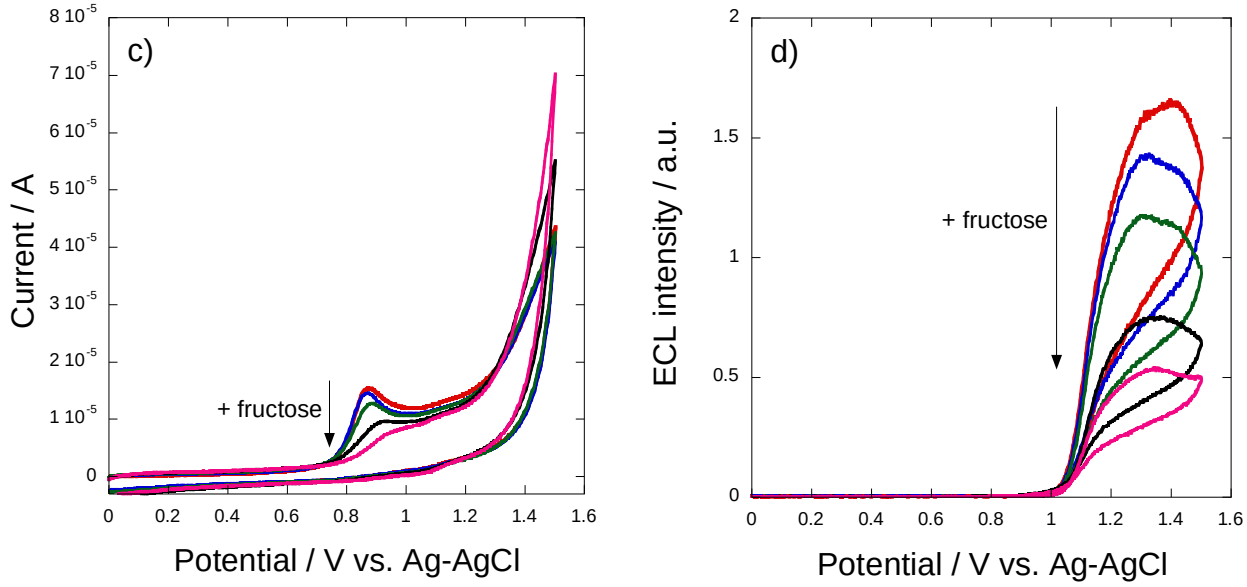


Figure S5. Effect of (a-b) D-glucose or (c-d) D-fructose addition on electrochemical oxidation of **E6** and on the corresponding ECL responses. Cyclic voltammograms and ECL signals of a PBS solution (pH 7.4) containing 10 µM $Ru(bpy)_3^{2+}$, 0.1 mM **E6** and different concentrations of D-glucose or of D-fructose. The arrow indicates increasing concentrations of D-glucose (0, 0.5, 1, 10, 50, 100 and 200 mM) or of D-fructose (0, 0.5, 1, 10 and 50 mM). Experiments were performed on glassy carbon (GC) electrode at a scan rate of 0.1 V s^{-1}.

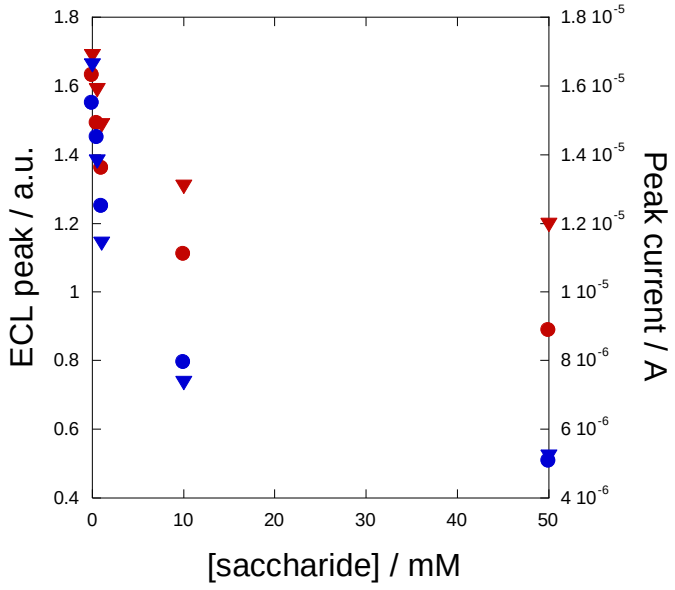


Figure S6. Variation of the ECL peak intensity (triangles) and of the oxidation peak current (dots) for the system $Ru(bpy)_3^{2+}$/**E6** as a function of the concentration of D-glucose (red markers) or of D-fructose (blue markers). Values are extracted from Figure S5.

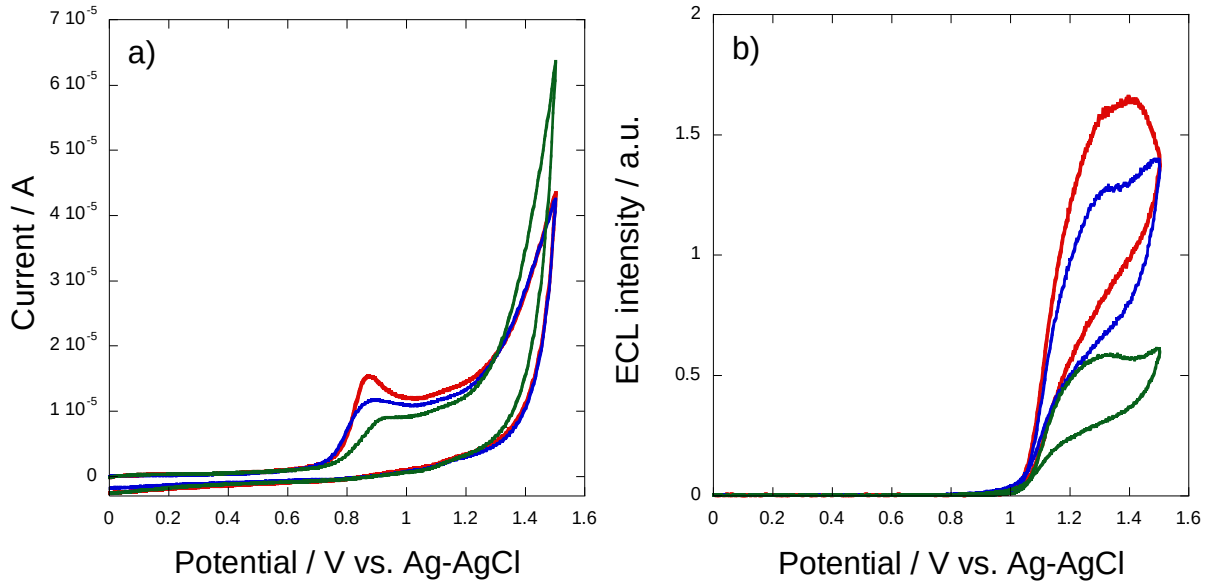


Figure S7. Variation of the (a) voltammetric response and (b) ECL peak intensity for the system $Ru(bpy)_3^{2+}$/**E6** in a competitive assay. Cyclic voltammograms and ECL signals of a PBS solution (pH 7.4) containing 10 µM $Ru(bpy)_3^{2+}$, 0.1 mM **E6** (red curve) after adding first 10 mM D-glucose (blue curve) and then 10 mM D-fructose (green curve). Experiments were performed on glassy carbon (GC) electrode at a scan rate of 0.1 V s^{-1}.

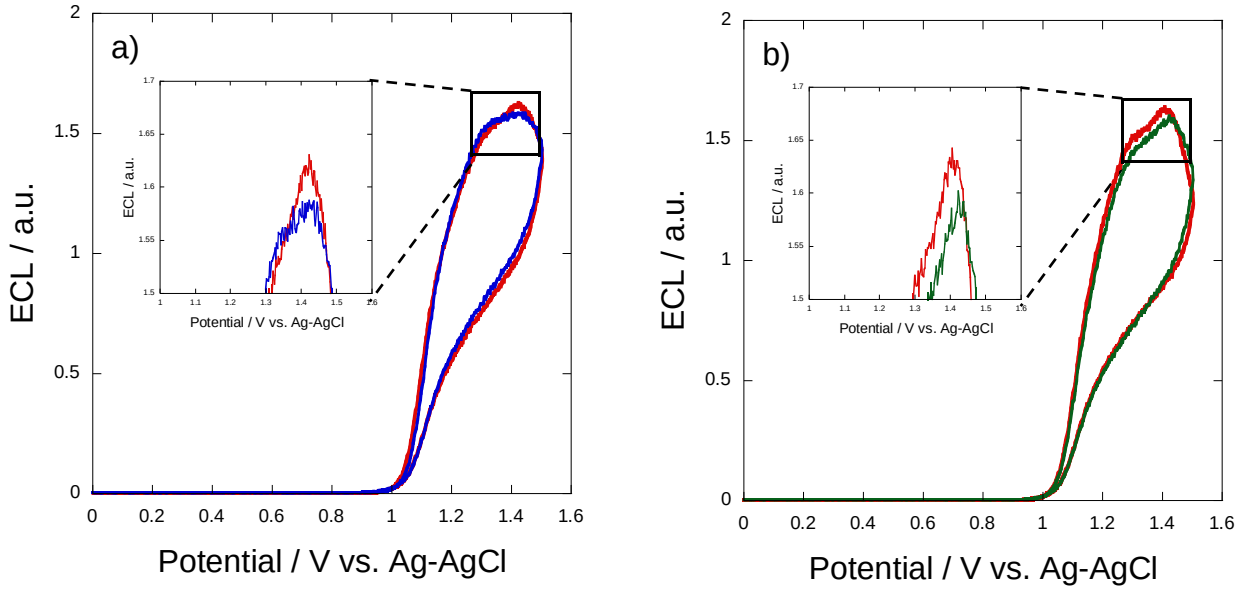


Figure S8. Variation of the ECL intensity for the system $Ru(bpy)_3^{2+}$/**E6** after the addition of (a) 20 µM D-glucose or (b) 10 µM D-fructose. ECL signals were recorded in a PBS solution (pH 7.4) containing 10 µM $Ru(bpy)_3^{2+}$, 0.1 mM **E6** (red curve) after adding either (a) 20 µM D-glucose (blue curve) or (b) 10 µM D-fructose (green curve). Experiments were performed on glassy carbon (GC) electrode at a scan rate of 0.1 V s^{-1}.

B. Experimental

1. Materials

The chemicals were analytical reagent grade and used as received. Tris(2,2'-bipyridyl) dichlororuthenium(II) hexahydrate, sodium phosphate dibasic heptahydrate, sodium phosphate monobasic monohydrate, tri-*n*-propylamine, D-fructose and D-glucose were purchased from Sigma-Aldrich. Solutions used in the experiments were prepared with water purified by Milli-Q station. Phosphate buffer solution (PBS, 100 mM, pH7.4) was prepared from sodium phosphate dibasic heptahydrate and sodium phosphate monobasic monohydrate. A conventional three-electrode system was applied for this study with a glassy carbon electrode (GCE) (d=3 mm) as working electrode, a Ag/AgCl/KCL (3 M) as reference and a Pt wire as counter-electrode. Prior to each measurement, GCE was polished with alumina slurry, rinsed thoroughly with water after each polishing step, and sonicated in ethanol/water.

2. Electrochemistry, ECL and Photoluminescence

Cyclic voltammetry was performed with a µ-Autolab Type III potentiostat connected to a home-made spectroelectrochemical cell. ECL intensity was measured simultaneously at the bottom of the cell by a Hamamatsu photomultiplier tube R5070. The PMT detector was held at -750 V powered by Hamamatsu C9525 high-voltage power supply. The ECL output signal was amplified by a Keithley 6485 Picoammeter before acquisition via the second input channel of the potentiostat. A stock solution of PBS containing 1M D-glucose or 1M D-fructose was prepared and used for the voltammetric and ECL experiments. After adding the D-fructose to the PBS solution which contains already the luminophore and the coreactant, we stirred it for 30 s and perform the voltammetric and ECL measurements. If we stirred for 5 or 10 min., the same values of the voltammetric and ECL signals were obtained indicating that the recognition of the saccharide by the synthesized coreactants is very fast. Experiments were performed on glassy carbon (GC) electrode at a scan rate of 0.1 V s^{-1}.

ECL spectra were recorded using a Princeton Instruments Acton SpectraPro 2300i after the CCD camera cooled to –115°C with liquid N_2. The electrochemical cell is built with a glass slide on the bottom in order to record the ECL signal. The optical fiber connected to the device is placed close to this glass slide in front of the working electrode.Photoluminescence spectra were collected on a Cary Eclipse spectrophotometer, using a 1 cm-path length quartz cuvette.

3. Solvents and reagents

Solvents and reagents were reagent grade unless stated otherwise and were purchased from Fisher Scientific UK, Frontier Scientific Europe Ltd, TCI UK, Alfa Aesar and Sigma-Aldrich Company Ltd and were used without further purification

4. Mass spectra

A micrOTOF electrospray time-of-flight (ESI-TOF) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) was used; this was coupled to an Agilent 1200 LC system (Agilent Technologies, Waldbronn, Germany) as an autosampler. 10 μL of sample was injected into a 30:70 flow of water: methanol at 0.4 mL/min to the mass spectrometer 10 μL of 5 mM sodium formate was injected after the sample. This acted as a calibrant over the mass range 50-1500 m/z. The observed mass and isotope pattern matched the corresponding theoretical values as calculated from the expected elemental formula.

5. Nuclear magnetic resonance (NMR) spectra

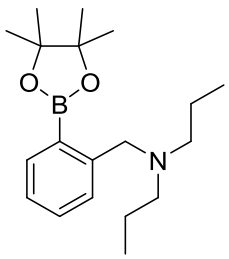
Nuclear magnetic resonance (NMR) spectra were run in chloroform-*D*, methanol-d_4, and dimethyl sulfoxide-d_6. Where a Bruker AVANCE 300 was used, ^{1}H spectra were recorded at 300 MHz, ^{11}B spectra at 96 MHz and ^{13}C at 75 MHz where a Bruker AVANCE 250 was used. Chemical shifts (δ) are expressed in parts per million and are reported relative to the residual solvent peak as an internal standard in ^{1}H and ^{13}C spectra. The multiplicities and general assignments of the spectroscopic data are denoted as: singlet (s), doublet (d), triplet (t), double of doublets (dd), unresolved multiplet (m), broad (br) and aryl (Ar).

6. Melting points (MP)

Capillary melting points were determined using Stuart MDP10. Compounds were purified and dried before melting points were determined

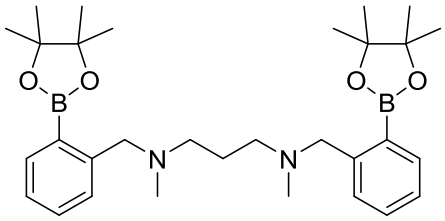
C. Synthesis and characterization

N-propyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propan-1-amine



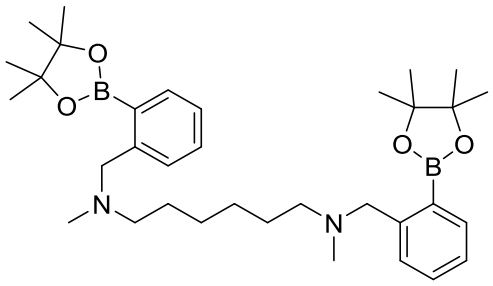
Dipropylamine (0.055 mL, 0.40 mmol) was added to a solution of 2-(2-(bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.10 g, 0.34 mmol) and K_2CO_3 (0.203 g, 1.01 mmol) in MeCN (25 mL) at 0 °C. The reaction was allowed to warm to rt and stir for 16 h before being filtered and concentrated *in-vacuo* to afford the title compound as a clear oil (0.065 g, 0.20 mmol, 60 %). ^{1}H NMR (300MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.8 Hz, 1 H, Ar*H*), 7.43 - 7.17 (m, 3 H, Ar*H*), 3.81 (s, 2 H, ArCH_2N), 2.55 - 2.42 (m, 4 H, NCH_2CH_2CH_3), 1.60 - 1.42 (m, 4 H, NCH_2CH_2CH_3), 1.35 (s, 12 H, BPin), 0.83 (t, *J* = 7.3 Hz, 6 H, NCH_2CH_2*CH_3*); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ = 134.2, 129.7, 128.1, 126.1, 83.0, 58.3, 55.4, 25.2, 19.0, 12.0; HRMS (ESI): m/z calculated for $C_{19}H_{32}BNO_2$: requires 318.2604 for $[M+H]^+$, found 318.2622

N^1,N^3-dimethyl-N^1,N^3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propane-1,3-diamine



N,N'-Dimethyl-1,3-propanediamine (0.061 mL, 0.49 mmol) was added to a solution of 2-(2-(bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.305 g, 1.03 mmol) and K_2CO_3 (0.203 g, 1.47 mmol) in MeCN (5 mL) at 0 °C. The reaction was allowed to warm to rt and stir for 16 h before being filtered and concentrated *in-vacuo* to afford the title compound as a clear oil (0.24 g, 0.45 mmol, 92 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 6.8 Hz, 2 H, Ar*H*), 7.26 - 7.18 (m, 4 H, Ar*H*), 7.14 (d, *J* = 7.3 Hz, 2 H, Ar*H*), 3.72 (s, 4 H, CH_2Ar), 2.59 - 2.51 (m, 4 H, N(CH_2CH_2), 2.32 (s, 6 H, CH_3N), 1.81 - 1.68 (m, 2H, N(CH_2CH_2CH_2)N), 1.31 (s, 24 H, BPin); ^{13}C NMR (125.5 MHz, $CDCl_3$) δ 142.6, 133.1, 128.8, 126.6, 126.1, 82.0, 61.1, 54.5, 42.1, 25.7; I.R (thinfilm) ν max (cm^{-1}): 2981.95 (C-H Sp^3); HRMS (ESI): m/z calculated for $C_{31}H_{49}B_2N_2O_4$: requires 535.3878 for $[M+H]^+$, found 535.3869

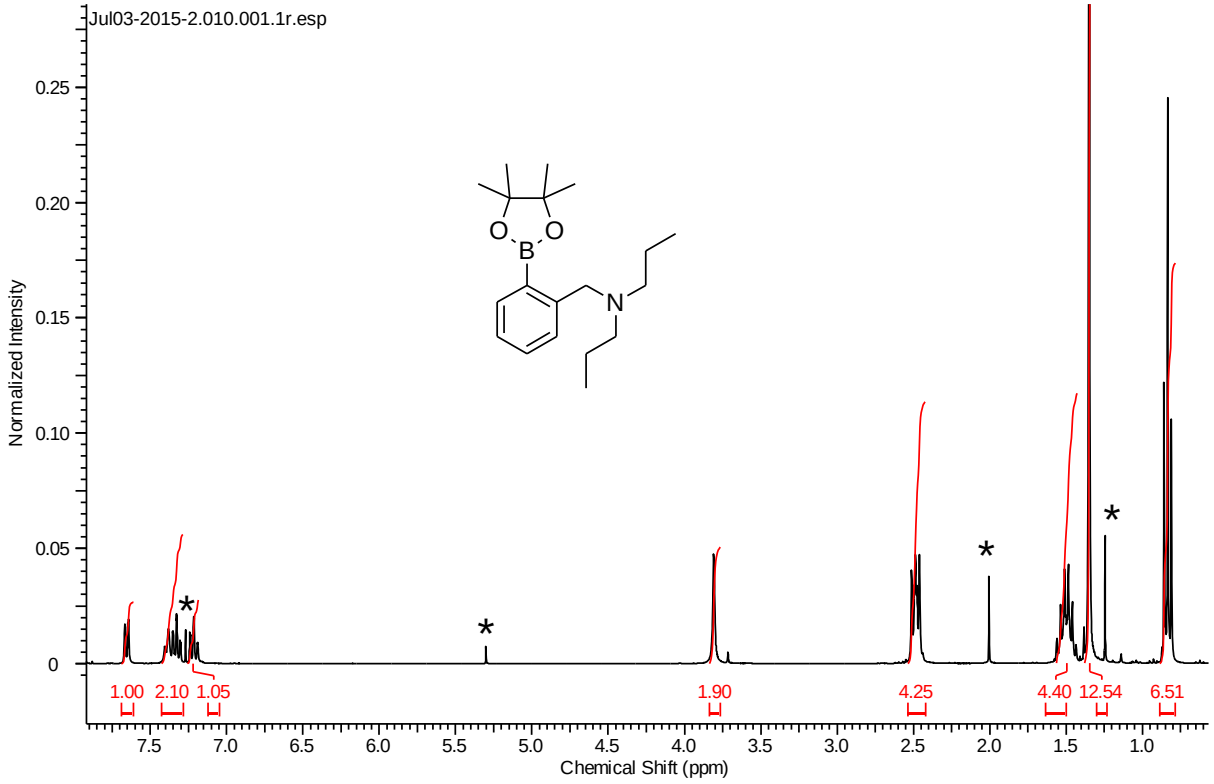
N^1, N^6-dimethyl-N^1, N^6-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzyl)hexane-1,6-diamine



N^1, N^6-Dimethylhexane-1,6-diamine (0.25 mL, 1.40 mmol) was added dropwise to a solution of 2-(2-(bromomethyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (0.873 g, 2.94 mmol) and K_2CO_3 (0.580 g, 4.20 mmol) in MeCN (10 mL) at 0 °C. The reaction was allowed to warm to rt and stir for 16 h before being filtered and concentrated *in-vacuo* to afford the crude material. The crude material was triturated with EtOAc to afford the title compound as a white solid (0.128 g, 0.22 mmol, 16 %). Mp 100-103 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (m, 2 H, Ar*H*), 7.25 - 7.18 (m, 4 H, Ar*H*), 7.08 (m, 2 H, Ar*H*), 3.76 (s, 4 H, C*H*$_2$Ar), 2.71 - 2.58 (m, 4 H, N(C*H*$_2$CH$_2$)), 2.40 (s, 6 H, C*H*$_3$N), 1.63 - 1.45 (m, 4 H, N(CH$_2$C*H*$_2$)), 1.32 (s, 24 H, BPin), 1.25 (s, 4 H, N(CH$_2$C*H*$_2$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 132.3, 128.2, 126.9, 124.8, 81.3, 60.9, 55.6, 41.9, 27.3, 26.2, 24.9, 24.0; I.R (thinfilm) ν max (cm^{-1}): 3039.8 (C-H sp^2), 2962.07 (C-H Sp^3); HRMS (ESI): m/z calculated for $C_{34}H_{55}B_2N_2O_4$: requires 577.4348 for $[M+H]^+$, found 577.4350

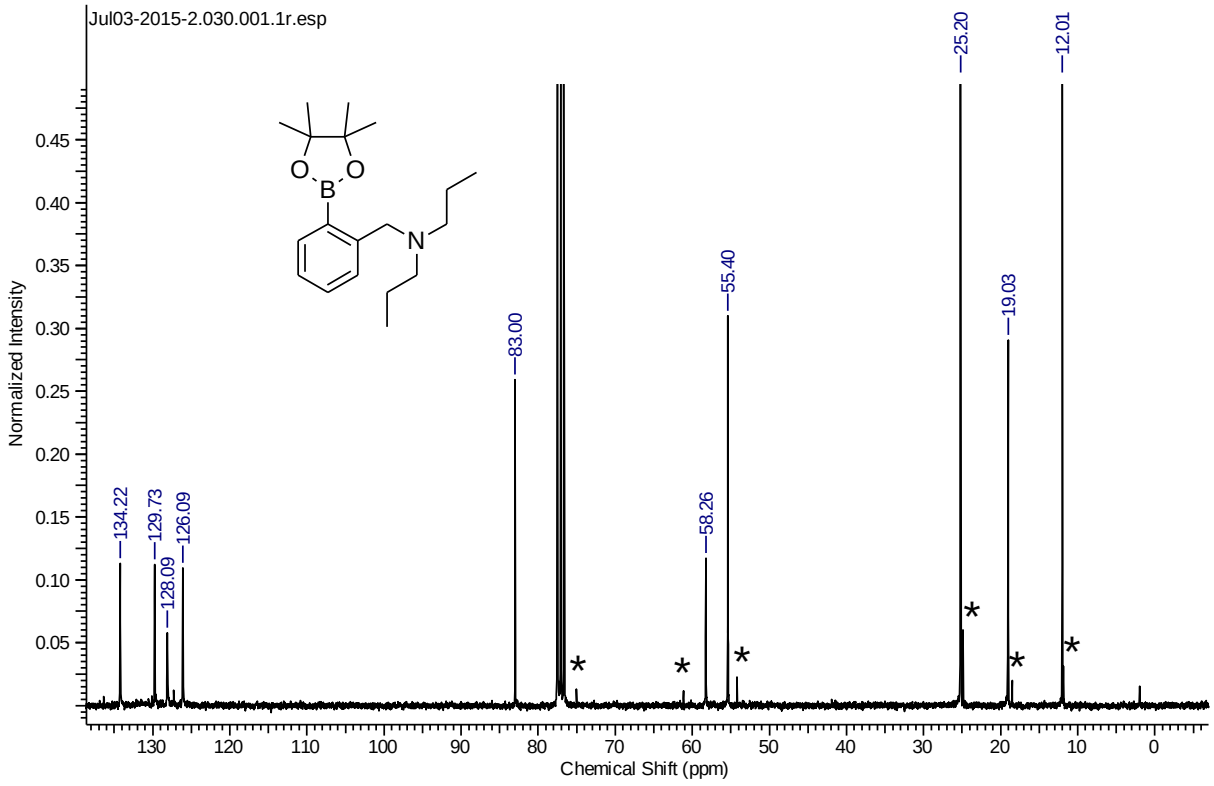
D. Spectra

N-propyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propan-1-amine (300 MHz, $CDCl_3$)



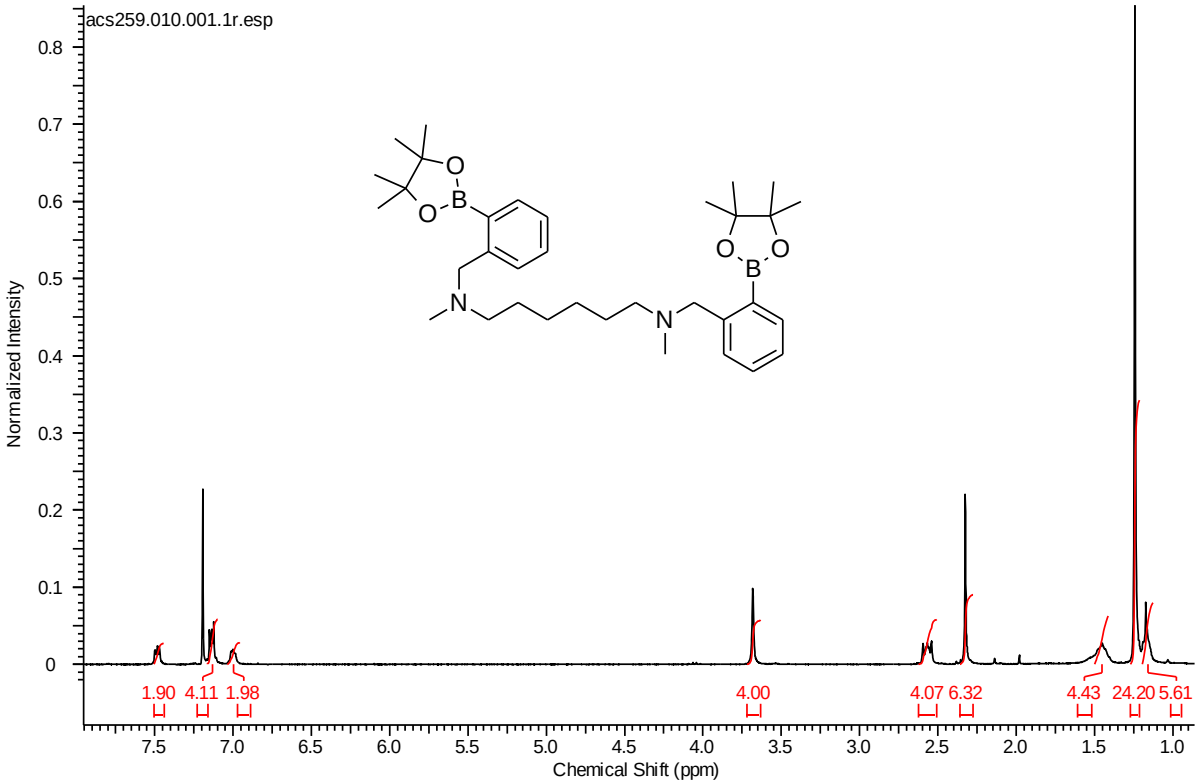
*Peak at 7.27 ppm = $CDCl_3$, Peak at 5.30 ppm = DCM, Peak at 2.00 ppm = MeCN, Peak at 1.24 ppm = H_2O

N-propyl-N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propan-1-amine (75.5 MHz, $CDCl_3$)

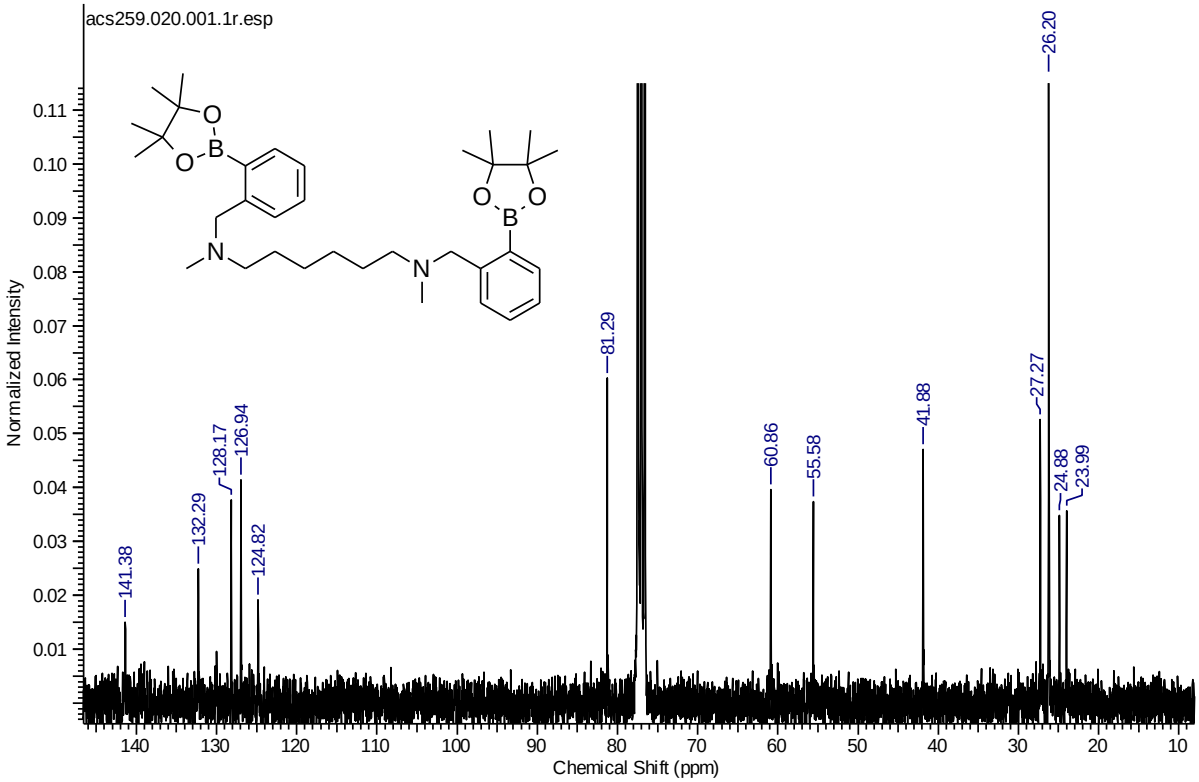


*Partial hydrolysis to **E0** to the free boronic acid under NMR measurement conditions. Starred signals are due to the boronic acid and free pinacol.

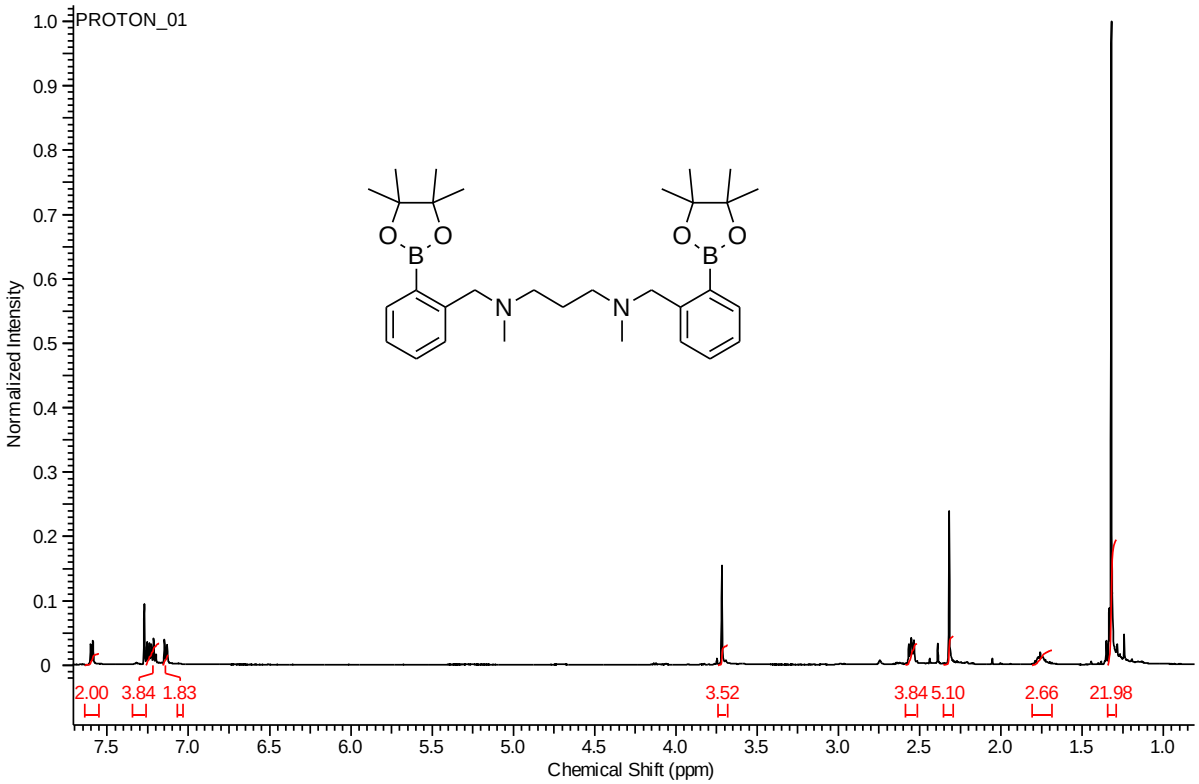
N^1, N^6-dimethyl-N^1, N^6-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzyl)hexane-1,6-diamine (300 MHz, $CDCl_3$)



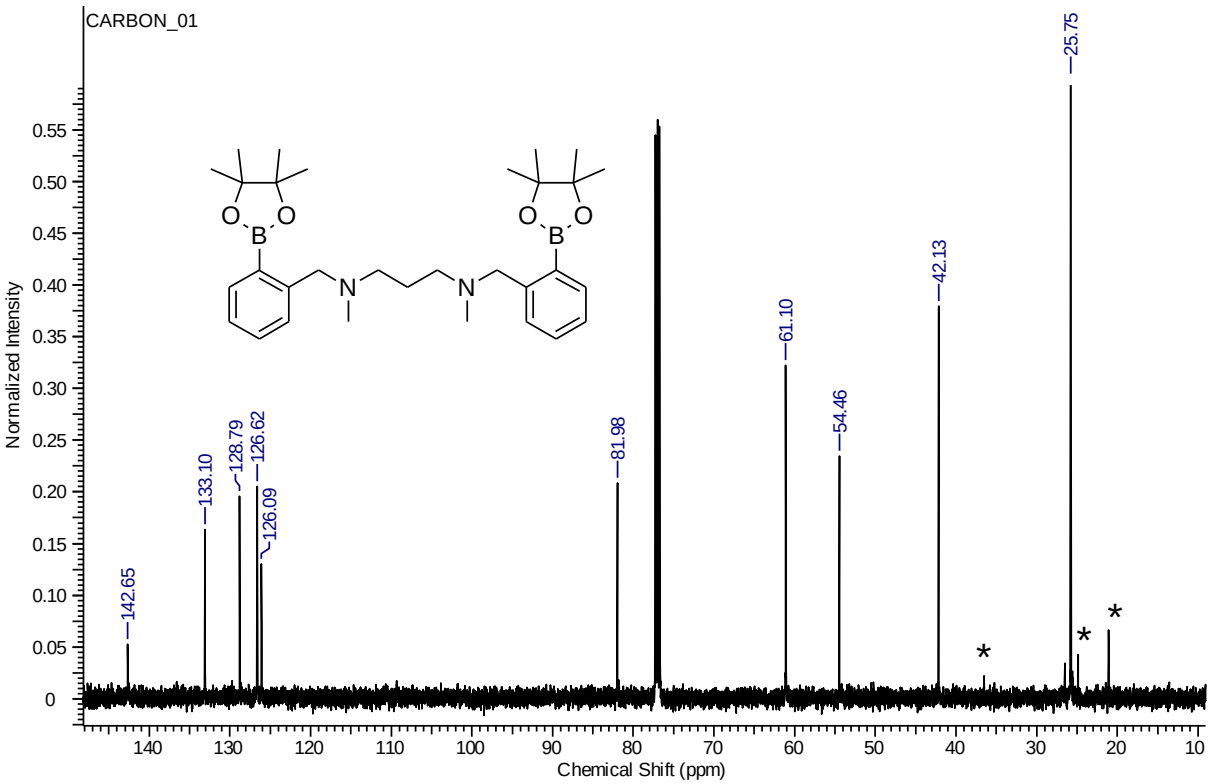
N^1, N^6-dimethyl-N^1, N^6-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzyl)hexane-1,6-diamine (75.5 MHz, $CDCl_3$)



N^1,N^3-dimethyl-N^1,N^3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propane-1,3-diamine (500 MHz, $CDCl_3$)



N^1,N^3-dimethyl-N^1,N^3-bis(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)propane-1,3-diamine (125.75 MHz, $CDCl_3$)



*Impurities

E. References

(1) Arimori, S.; Bell, M. L.; Oh, C. S.; Frimat, K. A.; James, T. D. *J. Chem. Soc. Perkin Trans 1* **2002**, 803.