Synthesis of substituted benzooxaborinin-1-ols via palladium-catalysed cyclisation of alkenyl- and alkynyl-boronic acids

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I. General methods

Reactions involving organometallic or moisture sensitive compounds were carried out under argon and glassware was dried in the oven overnight. Dry THF was purchased from Acros Organics (Tetrahydrofuran, 99.5%, Extra Dry over Molecular Sieves, Stabilised, AcroSeal®). *n*BuLi (1,6 mol:L in hexane) and triisopropyl borate was purchased from Acros Organics. $Pd(CH_3CN)_2Cl_2$, $Pd(PhCN)_2Cl_2$, anhydrous $CuCl_2$ and *tert*-butanol, 2-vinylbenzeneboronic acid were used as received. Flash column chromatography was carried out using normal phase silica gel (33-70 μm) supplied by VWR or a Biotage automated purification system using SNAP cartridges. Thin layer chromatography was carried out using Merck TLC Silica gel 60 F_{254} plates and products were visualised using combinations of UV light (254 nm).

Benzooxaborininol (**2**) were obtained by following the procedure already described by our group.[1]

^{1}H NMR spectra were recorded at 400, 500 or 600 MHz, on a Bruker Avance 400, 500 or 600 spectrometers using the residual protic solvent $CDCl_3$ (δ = 7.26 ppm, s) as the internal standard. Chemical shifts are quoted in ppm to the nearest 0.01 ppm using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet) defined as all multi-peak signals where overlap or complex coupling of signals make definitive descriptions of peaks difficult. ^{13}C NMR spectra were recorded at 100, 125 or 150 MHz on a Bruker Avance 400, 500 or 600 MHz spectrometers at 25°C (otherwise stated) in $CDCl_3$ as described below. All chemical shifts were referenced with $CDCl_3$ solvent (δ = 77.0 ppm, t) as the internal standard. Chemical shifts are reported to the nearest 0.1 ppm. The coupling constants are defined as *J* and quoted in Hz. Mass spectra were performed in the Department of Chemistry (University College London) and the EPSRC UK National Mass Spectrometry Service. ^{11}B NMR spectra were recorded at 128 MHz on a Bruker Avance 400 MHz spectrometer at 25°C in $CDCl_3$ using $BF_3.Et_2O$ (neat) as standard. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FT-IR Spectrometer operating in ATR mode. Melting points were measured with a Gallenkamp apparatus and were uncorrected.

II. Optimisations and general procedures

II.1. Synthesis of aryl bromides

II.1.1. Synthesis of 1-bromo-2-alkenyl-benzenes

1-bromo-2-(prop-1-en-2-yl)benzene,[2] 1-bromo-2-(prop-1-en-1-yl)benzene,[3] 1-bromo-2-(4-methylstyryl)benzene,[3] were obtained *via* a Wittig olefination by following procedures already described in the literature.

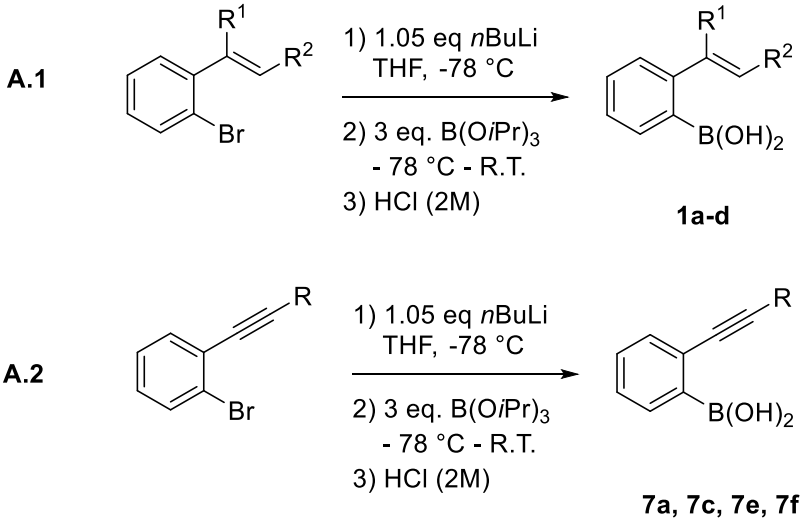
II.1.2. Synthesis of 1-bromo-2-alkynyl-benzenes

2-bromophenyl)ethynyl)trimethylsilane, 1-bromo-2-(phenylethynyl)benzene, 1-bromo-2-(p-tolylethynyl)benzene, were obtained *via* a Sonogashira coupling already described in our group.[1]

II.2. Synthesis of boronic acids (2, 7)

Boronic acids were obtained by a classical sequence of lithium bromine exchange followed by a borylation step (cf. General procedure A.1). *ortho*-Alkynylphenylboronic acids were also prepared according to this procedure (Cf. General procedure A.2) and spectroscopic data were consistent with those we have previously reported. [1]

Procedures A: General procedures for lithiation-borylation reaction



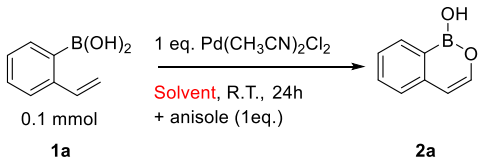
In a schlenk tube, *n*BuLi (1.6 M in hexane, 1.1 eq) was added dropwise at -78 °C to a solution of aryl bromide (1 eq) in THF(C ≈ 0.15 mol/L). After 1 hour at -78 °C, triisopropylborate (3

eq) was added and the solution was allowed to warm at room temperature overnight. The reaction mixture was then quenched with HCl (2M, 20 mL), extracted with Et_2O (3×20 mL) and dried on anhydrous Na_2SO_4. After filtration, solvent were removed under vacuum and the crude residue was purified by column chromatography on SiO_2 using Petrol:Et_2O (100:0 to 70:30) as eluent. Evaporation of the solvent gave the boronic acid.

II.3. Palladium catalysed Wacker-type oxidation

II.3.1. Optimisation of the reaction conditions

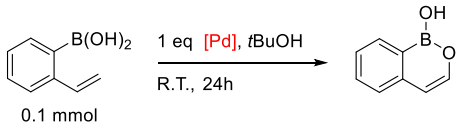
SOLVENT



0.1 mmol — **1a** — **2a**

Solvents	Solubility	Conversion
DMSO	+	x
CH_3CN	+	x
Dioxane	+	x
***t*BuOH**	+	+
$CHCl_3$	Partial	+
THF	+	+
CH_2Cl_2	Partial	+
Toluene	x	traces

PALLADIUM SOURCE

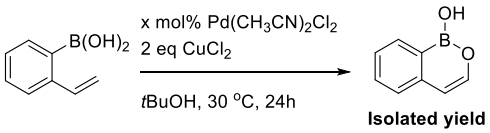


0.1 mmol — **1a** — **2a**

Yields were measured by ^{1}H NMR using an internal standard (anisole)

Pd source	Yield (%)
$PdCl_2$	-
$Pd(PPh_3)_2Cl_2$	-
$Pd(CH_3CN)_2Cl_2$	> 95
$Pd(PhCN)_2Cl_2$	60
$Pd(OAc)_2$	decomposition
$Pd(Py)_2Cl_2$	-

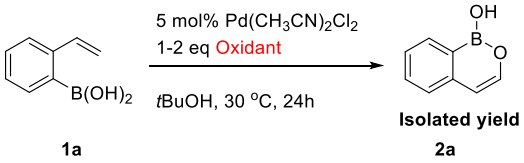
CATALYST LOADING



1a — **Isolated yield** — **2a**

Mol% Cat	Yield (%)
10	63
5	60
2	39

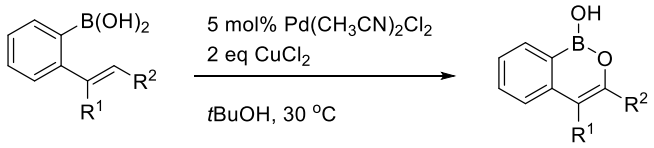
OXIDANT



Oxidants	Yield (%)
Benzoquinone	11
$CuCl_2$	63
$Cu(OAc)_2$	-
CuCl	10
$Cu(NO_3)_2.5:2H_2O$	-
$CuBr_2$	-
AgOTf	-

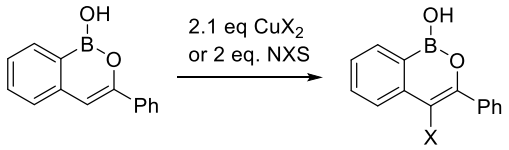
II.3.2. General procedure for the palladium catalysed Wacker-type oxidation

General procedure B



In a round bottom flask, $Pd(CH_3CN)_2Cl_2$ (5 or 10 mol%) and anhydrous $CuCl_2$ (2 eq) were added to a solution of boronic acid (1eq) in *tert*-butanol ([C] ≈ 0.04 mol:L). The resulting solution was stirred at 30 °C for 24 hours. The solution was then evaporated to dryness and the crude material was purified by column chromatography to afford the products.

II.4. Halogenation of benzooxaborininols



2e

3e (X = Cl)
6e (X = Br)

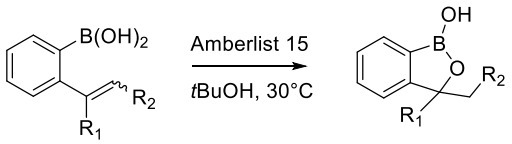
Procedure C.1: A solution of benzooxaborininol (1 eq) and NXS (2 eq) in acetonitrile ([C] ≈ 0.1 mol/L) was stirred at room temperature for 3 days. The reaction mixture was then concentrated and the crude material was filtered through SiO_2 using Petrol:EtOAc (95:5) as solvent. Evaporation of the solvents afforded the halo-benzooxaborininol.

Procedure C.2: A solution of benzooxaborininol (1 eq) and $CuCl_2$ or $CuBr_2$ (2.1 eq) in *t*BuOH ([C] ≈ 0.1 mol/L) was stirred at 30 °C overnight. The reaction mixture was then

concentrated and the crude material dissolved in Et_2O and filtered through silica gel to afford the halo-benzooxaborininol.

II.5. Acid mediated or platinium catalysed synthesis of benzooxaborole (4)

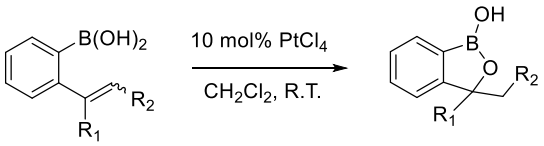
Procedure D.1: Acid mediated synthesis of benzooxaboroles



1c-d **4c-d**

Amberlist 15 resin (≈ 60 mg) was added to a solution of boronic acid in *t*BuOH (C ≈ 0.2 mol/L). The heterogeneous mixture was allowed to stir 24 hours at 30 °C before filtration through a pad of celite. Evaporation of the solvent afforded the benzooxaborole.

Procedure D.2: Pt-catalysed synthesis of benzooxaboroles



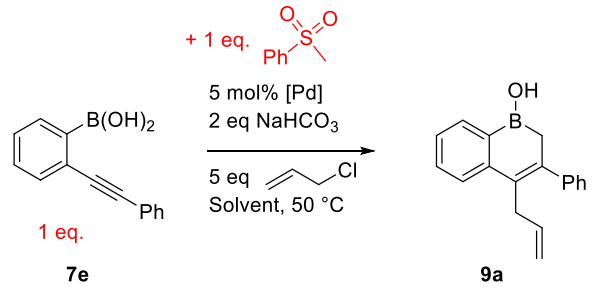
1c-d **4c-d**

Platinium tetrachloride (10 mol%) was added to a solution of boronic acid (1 eq) in CH_2Cl_2 (C ≈ 0.2 mol/L). The resulting solution was stirred at room temperature for 24 hours or 3 days depending on the substrate. The mixture was then pre-absorbed on silica and purified by column chromatography using Petrol:Et_2O (100:0 to 50:50) as eluent. Evaporation of the solvent gave the benzooxaborole.

II.6. Synthesis of allylated benzooxaborininols (9)

II.6.1. Optimisation of the reaction conditions

SOLVENT



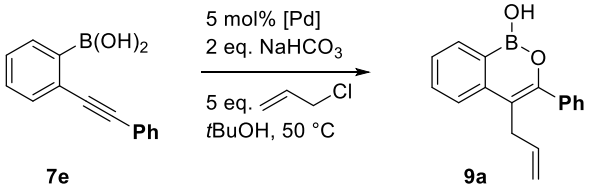
7e 9a

[Pd] = $Pd(CH_3CN)_2Cl_2$

The yields were determined by ^1H NMR using an internal standard (methylphenyl sulfone)

Solvents	Yield (%)
Toluene	11
CH_2Cl_2	25
CH_3CN	42
***t*BuOH**	55

PALLADIUM CATALYST

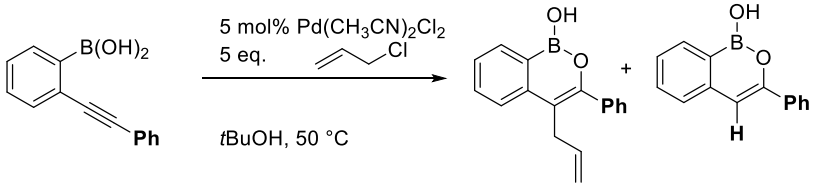


7e 9a

Isolated yield

[Pd]	Yields
$Pd(CH_3CN)_2Cl_2$	50
$Pd(hfacac)_2$	16
$Pd(PhCN)_2Cl_2$	70

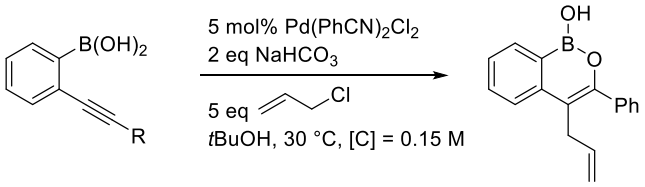
BASE



7e 9a 2e

Base (2 eq)	Ratio 9a:2e
$NaHCO_3$	1:traces
None	1:0.3

II.6.2. General procedure for the synthesis of allylated-benzooxaborininols



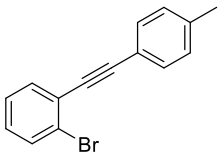
7a, 7c, 7e, 7f 9a - 9g

General procedure E: In a round-botton flask, the palladium catalyst (5 mol%) and sodium bicarbonate (2 eq) were added to a solution of boronic acid (1 eq) in *tert*-butanol ([C] ≈ 0.15 mol:L). The allyl chloride (5 eq) was then added *via* microsyringe. The solution was allowed to stir for 6 hours at 30°C before evaporation of the volatiles under vacuum. The residue was then purified by column chromatography on silica using Petrol:EtOAc as solvent (100:0 to 80:20) to give the allyl-benzooxaborininol.

III. Spectroscopic Data

III.1. 1-Bromo-2-alklynyl-benzenes

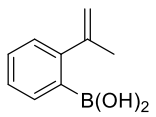
1-Bromo-2-(*p*-tolylethynyl)benzene



$Pd(PPh_3)_2Cl_2$ (140 mg, 0.2 mmol, 2 mol%) and CuI (40 mg, 0.2 mmol, 2 mol%) were added to a solution of 2-bromo-iodobenzene (1.3 mL, 10.0 mmol, 1 eq) in Et_2NH (C ≈ 0.3 mol/L). After 10 min a solution of tolylacetylene (1.7 mL, 13.0 mmol, 1.3 eq) in Et_2NH (C ≈ 15.3 mol/L) was added dropwise over 3 hours via syringe pump and the reaction mixture was left to stir overnight. The resulting mixture was then quenched with a saturated solution of NH_4Cl solution (50 mL) and extracted with Petrol (3×60 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude material was purified by flash chromatography using Petrol as eluent. After purification the product was obtained as a colourless oil (2.41 g, 91%); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.65 – 7.58 (m, 1H, CH_{Ar}), 7.54 (dd, *J* = 7.6, 1.6, 1H, CH_{Ar}), 7.52 – 7.45 (m, 2H, 2×CH_{tol}), 7.30 (td, *J* = 7.6, 1.2, 1H, CH_{Ar}), 7.18 – 7.10 (m, 3H, 2×CH_{tol}, CH_{Ar}), 2.37 (s, 3H, C$H_{3\text{-}tol}$); ^{13}C NMR (125 MHz, $CDCl_3$) δ = 138.9, 133.2, 132.5, 131.7, 129.3, 129.2, 127.1, 125.7, 125.6, 119.9, 94.3, 87.5, 21.6. ppm. These spectroscopic data are in agreement with those reported in the literature.[4]

III.2. Boronic acids (1, 7)

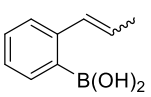
(2-(Prop-1-en-2-yl)phenyl)boronic acid (1d)



The desired product was prepared by following **procedure A.1** using 1-bromo-2-(prop-1-en-2-yl)benzene (500 mg, 2.5 mmol, 1 eq), *n*BuLi (1.8 mL, 2.8 mmol, 1.1 eq) and trimethylborate (0.85 mL, 7.6 mmol, 3.0 eq). After purification the boronic acid was obtained as a white solid (261 mg, 64%); mp = 66 °C; ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop D_2O) δ = 7.87 (d, *J* = 7.4, 1H, CH_{Ar}), 7.41 (td, *J* = 7.4, 1.1,

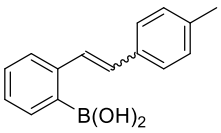
1H, CH_{Ar}), 7.32 (td, *J* = 7.4, 1.1, 1H, CH_{Ar}), 7.17 (d, *J* = 7.4, 1H, CH_{Ar}), 5.32 (d, *J* = 1.1, 1H, =C*H*), 5.06 (d, *J* = 1.1, 1H, =C*H*), 2.15 (s, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.8, 149.5, 135.2, 130.8, 127.4, 127.0, 115.7, 25.8. The carbon adjacent to the boron atom was not observed; FT-IR (ATR) υ = 3296, 3072, 2972, 1590, 1342, 1299, 1259, 1229, 1117, 1070, 1040, 1000, 945, 889, 777, 748, 707, 681, 668, 648, 598, 583, 563, 516, 494 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{14}O_2B$ [M + Ethyleneglycol + H]$^+$ 188.1118 found 188.1118. These spectroscopic data are in agreement with those reported in the literature.[5]

(2-(Prop-1-en-1-yl)phenyl)boronic acid (1b)



The desired product was prepared by following **procedure A.1** using 1-bromo-2-(prop-1-en-1-yl)benzene (792 mg, 4.0 mmol, 1eq), *n*BuLi (2.6 mL, 4.2 mmol, 1.1 eq) and triisopropylborate (2.8 mL, 12.0 mmol, 3.0 eq). After purification the boronic acid was obtained as a white solid (490 mg, 76%) as a mixture of *Z*:*E* isomers (ratio 0.3:1); mp = 71 °C; ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop D_2O) δ = 7.92 (d, *J* = 7.5, 1H, C$H_{Ar(E)}$), 7.68 (d, *J* = 7.3, 0.3H, C$H_{Ar(Z)}$), 7.44 (td, *J* = 7.5, 1.1, 1H, C$H_{Ar(E)}$), 7.41 – 7.36 (m, 0.6H, 2×C$H_{Ar(Z)}$), 7.31 (t, *J* = 7.5, 1H, C$H_{Ar(E)}$), 7.28 – 7.21 (m, 0.3H, C$H_{Ar(Z)}$), 7.16 (d, *J* = 7.5, 1H, C$H_{Ar(E)}$), 6.80 (m, 1.3H, =C$H_{(Z),}$ =C$H_{(E)}$), 6.17 – 6.02 (m, 1.3H, =C$H_{(Z),}$ =C$H_{(E)}$), 1.92 (dd, *J* = 6.6, 1.7, 0.9H, C$H_{3(Z)}$), 1.70 (dd, *J* = 6.9, 1.7, 3H, C$H_{3(E)}$); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 143.2, 142.6, 135.3, 134.1, 131.6, 131.4, 130.9, 130.8, 130.6, 130.2, 129.2, 126.7, 126.7, 126.6, 18.8, 14.3. The carbon adjacent to the boron atom was not observed. FT-IR (ATR) υ = 3324, 3015, 1559, 1440, 1334, 1185, 1152, 1083, 1059, 1035, 987, 965, 924, 882, 812, 754, 732, 715, 688, 638, 524, 490 cm^{-1}; HRMS (CI) calcd for $C_{11}H_{14}O_2B$ [M + Ethyleneglycol + H]$^+$ 188.1118 found 188.1116.

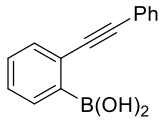
(2-(4-Methylstyryl)phenyl)boronic acid (1c)



The desired product was prepared by following **procedure A.1** using 1-bromo-2-(4-methylstyryl)benzene (1.00 g, 3.7 mmol, 1 eq), *n*BuLi (2.4 mL, 3.9 mmol, 1.1 eq) and triisopropylborate (2.6 mL, 11.0 mmol, 3.0 eq). After purification the boronic acid was obtained as a white solid (860 mg, 97%) as a mixture of *Z*:*E* isomers (ratio 1:0.6); mp = 148 °C; ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop D_2O); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 7.4, 1H, C$H_{Ar(Z)}$), 7.69 (d, *J* = 7.5, 0.6H, C$H_{Ar(E)}$), 7.60 (d, *J* = 7.5, 0.6H, C$H_{Ar(E)}$), 7.50 (d, *J* = 16.2, 0.6H, =CH_E), 7.42 (m, 2.6H, 2×C$H_{Ar(Z),}$ C$H_{Ar(E)}$), 7.33 (t, *J* = 7.4, 1H, C$H_{Ar(Z)}$), 7.30 (t, *J* = 7.4, 0.6H, C$H_{Ar(E)}$), 7.23 – 7.15 (m, 2.2H, 2×C$H_{Ar(Z),}$ 2×C$H_{Ar(E)}$), 6.98 (m, 4.6H, =C$H_{(E)}$, 3×C$H_{Ar(Z),}$ C$H_{Ar(E)}$), 6.89 (t, *J* = 13.0, 1H,

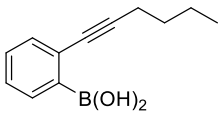
=C*H*$_{(Z)}$), 6.75 (d, *J* = 13.0, 1H, =C*H*$_{(Z)}$), 2.37 (s, 2H, C*H*$_{3(E)}$), 2.26 (s, 3H, C*H*$_{3(Z)}$); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 143.6, 142.6, 138.1, 137.9, 135.7, 134.4, 134.2, 133.2, 132.8, 132.1, 131.4, 130.8, 130.9, 129.6, 129.4, 129.1, 128.9, 128.1, 127.1, 126.7, 126.3, 21.4, 21.3. The carbon adjacent to the boron atom was not observed; FT-IR (ATR) υ = 3042, 3010, 2916, 1589, 1508, 1473, 1439, 1279, 1232, 1192, 1178, 971, 958, 803, 747, 705, 686, 587, 532 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{20}O_2B$ [M + 2 × OMe + H]$^+$ 267.1556 found 267.1556.

(2-(Phenylethynyl)phenyl)boronic acid (7e)



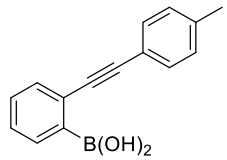
The desired product was prepared by following **procedure A.2** using 1-bromo-2-(phenylethynyl)benzene (1.08 g, 4.2 mmol, 1 eq), *n*BuLi (2.8 mL, 4.4 mmol, 1.1 eq) and triisopropylborate (2.9 mL, 12.6 mmol, 3.0 eq). After purification the boronic acid was obtained as a white solid (780 mg, 83 %); mp = 110 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ = 8.02 (d, *J* = 7.5, 1H, C*H*$_{Ar}$), 7.60 (d, *J* = 7.5, 1H, C*H*$_{Ar}$), 7.57-7.53 (m, 2H, 2×C*H*$_{Ar}$), 7.47 (td, *J* = 7.4, 1.4, 1H, C*H*$_{Ar}$), 7.43-7.37 (m, 4H, 4×C*H*$_{Ar}$), 6.04 (s, 2H, $B(OH)_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ = 135.8, 132.7, 131.7, 130.9, 129.2, 128.7, 128.4, 126.7, 122.0, 93.6, 89.8. The carbon adjacent to the boron atom was not observed; FT-IR (ATR) υ = 3341, 3080, 3054, 2959, 2928, 1590, 1491, 1474, 1440, 1333, 1011, 746, 684, 638, 584, 538, 516 cm^{-1}; LRMS (EI): [M]$^+$ 222, [M-OH]$^+$ 205. These spectroscopic data are in agreement with those reported in the literature.[1]

(2-(Hex-1-yn-1-yl)phenyl)boronic acid (7f)



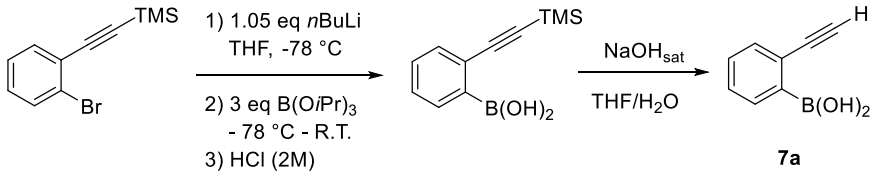
The desired product was prepared by following **procedure A.2** using 1-bromo-2-(hex-1-yn-1-yl)benzene (2.00 g, 8.4 mmol, 1 eq), *n*BuLi (5.8 mL, 9.3 mmol, 1.1 eq) and triisopropylborate (5.9 mL, 25.0 mmol, 3.0 eq). After purification the boronic acid was obtained as a colourless oil (1.40 mg, 82 %); NMR revealed a mixture of trimer and monomer (ratio 1:0.6). ^{1}H NMR ($CDCl_3$, 500 MHz, monomer) δ = 7.95 (dd, *J* = 7.4, 1.0, 1H, C*H*$_{Ar}$), 7.45 (dd, *J* = 7.6, 1.0, 1H, C*H*$_{Ar}$), 7.39 (td, *J* = 7.4, 1.4, 1H, C*H*$_{Ar}$), 7.34 (td, *J* = 7.6, 1.4, 1H, C*H*$_{Ar}$), 5.75 (br, 2H, B(O*H*)$_2$), 2.50 (t, *J* = 7.5, 2H, ≡CC*H*$_2$), 1.64 (qn, *J* = 7.5, 2H, C*H*$_2$(CH_2CH_3)), 1.50 (sext, *J* = 7.5, 2H, C*H*$_2$(CH_3)), 0.97 (t, *J* = 7.5, 3H, C*H*$_3$); ^{13}C NMR ($CDCl_3$, 500 MHz, monomer) δ = 135.5, 132.7, 130.8, 127.7, 127.6, 95.1, 81.8, 30.7, 22.1, 19.2, 13.6. The carbon adjacent to the boron atom was not observed; FT-IR (ATR) υ = 3423, 3087, 2959, 2873, 2220, 1642, 1593, 1478, 1443, 1341, 1262, 1237, 1074, 1018, 758, 539 cm^{-1}; LRMS (EI) m/z [M]$^+$ 202, [M-CH5]$^+$ 184, [M-BO_2H]$^+$ 159. These spectroscopic data are in agreement with those reported in the literature.[1]

(2-(*p*-Tolylethynyl)phenyl)boronic acid (7c)



The desired product was prepared by following **procedure A.2** using 1-bromo-2-(p-tolylethynyl)benzene (1.00 g, 3.7 mmol, 1 eq), *n*BuLi (2.5 mL, 4.0 mmol, 1.1 eq) and triisopropylborate (2.6 mL, 11.0 mmol, 3.0 eq). After purification the boronic acid was obtained as a white solid (680 mg, 78 %); mp = 159 - 161 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 7.5, 1H, C*H*$_{Ar}$), 7.58 (d, *J* = 7.0, 1H, C*H*$_{Ar}$), 7.48 – 7.42 (m, 3H, 3×C*H*$_{Ar}$), 7.39 (td, *J* = 7.5, 1.2, 1H, C*H*$_{Ar}$), 7.19 (d, *J* = 8.0, 2H, 2×C*H*$_{Ar}$), 5.69 (s, 2H, B(O*H*)$_2$), 2.39 (s, 3H, C*H*$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 139.5, 135.7, 132.6, 131.6, 131.0, 129.5, 128.3, 127.0, 118.9, 93.8, 89.3, 21.7. The carbon adjacent to the boron atom was not observed; FT-IR (ATR) υ = 3339, 3057, 3023, 1590, 1559, 1510, 1475, 1439, 1408, 1373, 1147, 1096, 1065, 1036, 1003, 953, 755,637, 508 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{13}BO_2$ $[M]^+$ 235.10394 found 235.10388.

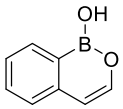
(2-Ethynylphenyl)boronic acid (7a)



(2-((Trimethylsilyl)ethynyl)phenyl)boronic acid was prepared by following **procedure A.2** using ((2-bromophenyl)ethynyl)trimethylsilane (1.00 g, 3.9 mmol, 1 eq), *n*BuLi (2.6 mL, 4.1 mmol, 1.1 eq) and triisopropylborate (2.7 mL, 11.8 mmol, 3.0 eq). After purification the TMS-proctected boronic acid was obtained as a white solid (560 mg, 65 %). This latter was dissolved in THF and stirred in presence of a saturated solution of sodium hydroxide for 30 minutes. The aqueous solution was then washed with Et_2O (3×10 mL) before addition of HCl (2M) and extraction with Et_2O (3×20 mL) dried on anhydrous Na_2SO_4. After filtration solvent were removed under vacuum and the crude residue was filtered through a small pad of SiO_2 using Petrol:Et_2O as eluent to afford the pure boronic acid as a white solid (250 mg, 44% over two steps); mp = 95 °C; ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop D_2O) δ = 8.00 (m, 1H, C*H*$_{Ar}$), 7.64 – 7.51 (m, 1H, C*H*$_{Ar}$), 7.53 – 7.37 (m, 2H, 2×C*H*$_{Ar}$), 5.82 (br s, 2H, B(O*H*)$_2$), 3.48 (s, 1H, ≡C*H*); ^{13}C NMR (151 MHz, $CDCl_3$ + 1 drop D_2O) δ = 135.8, 133.3, 131.0, 129.0, 125.5, 85.2, 81.4. The carbon adjacent to the boron atom was not observed; FT-IR (ATR) υ = 3491, 3353, 3288, 3262, 1437, 1389, 1362, 1335, 1256, 1164, 1151, 1069, 1043, 1017, 789, 757, 700, 687, 615, 576, 559, 537 cm^{-1}; HRMS (CI) calcd for $C_8H_7O_2B$ $[M + H]^+$ 146.0648 found 146.0647.

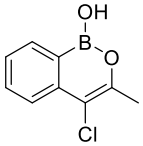
III.3. Benzooxaborininols and halo-benzooxaborininols (2, 3, 4, 6)

1*H*-Benzo[c][1,2]oxaborinin-1-ol (2a)



The desired product was prepared by following **procedure B** using 2-vinylbenzeneboronic acid (100 mg, 0.68 mmol, 1eq), $Pd(CH_3CN)_2Cl_2$ (9 mg, 0.03 mmol, 0.05 eq) and $CuCl_2$ (182 mg, 0.14 mmol, 2 eq.) in *tert*-butanol (12 mL). Purification by column chromatography on silica using Petrol:Et_2O (100:0 to 80:20) afforded the product as a colourless oil as a mixture of monomer and dimer (ratio M:D = 1:0.4) (72 mg, 71%); ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.09 (d, *J* = 7.6, 0.4H, C*H*$_{Ar(D)}$), 8.02 (d, *J* = 7.5, 1H, C*H*$_{Ar(M)}$), 7.65 (td, *J* = 7.6, 1.2, 0.4H, C*H*$_{Ar(D)}$), 7.61 (td, *J* = 7.5, 1.2, 1H, C*H*$_{Ar(M)}$), 7.47 (d, *J* = 7.6, 0.4H, C*H*$_{Ar(D)}$), 7.44 – 7.35 (m, 2.4H, C*H*$_{Ar(D)}$, 2×C*H*$_{Ar(M)}$), 7.20 (d, *J* = 5.4, 0.4H, =C*H*$_{Ar(D)}$), 7.04 (d, *J* = 5.4, 1H, =C*H*$_{(M)}$), 6.45 (d, *J* = 5.4, 0.4H, =CH$_{(D)}$), 6.31 (d, *J* = 5.5, 1H, =C*H*$_{(M)}$), 4.82 (s, 1H, BOH); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 143.0, 142.7, 142.5, 142.0, 133.7, 132.89, 132.84, 132.5, 126.5, 126.5, 125.6, 125.5, 110.6, 110.5; the carbon adjacent to the boron atom was not observed; ^{11}B NMR (128 MHz, $CDCl_3$ + 1 drop D_2O) δ = 27.8 ; FT-IR (ATR) υ = 3424, 3068, 2923, 1629, 1479, 1435, 1392, 1292, 1242, 1205, 1193, 1092, 1060, 960, 924, 883, 793, 763, 750, 685, 622, 560, 497, 460, 427 cm^{-1}; HRMS (EI) calcd for $C_8H_7BO_2$ $[M]^+$ 146.0539 found 146.0535.

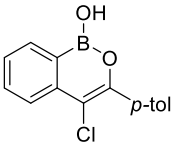
4-Chloro-3-methyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (3b)



The desired product was prepared by following **procedure B** using (2-(prop-1-en-1-yl)phenyl)boronic acid (100 mg, 0.62 mmol, 1eq), $Pd(CH_3CN)_2Cl_2$ (8 mg, 0.03 mmol, 0.05eq) and $CuCl_2$ (166 mg, 0.12 mmol, 2 eq) in *tert*-butanol (11 mL). Purification by column chromatography on silica using Petrol:Et_2O (100:0 to 80:20) afforded a mixture of monomeric and dimeric benzooxaborininol (84 mg) which was converted to the chloro-benzooxaborininol by stirring the mixture of benzooxaborininol in *tert*-butanol (5 mL) in the presence of $CuCl_2$ (83 mg, 0.06 mmol, 1eq) for 4 hours. After purification by column chromatography on SiO_2, a mixture of monomeric and dimeric (ratio M:D = 0.5:1) halo-benzooxaborininol was obtained as a white solid (70 mg, 58%); mp = 137 – 138 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.01 (d, *J* = 7.8, 1H, C*H*$_{Ar(D)}$), 7.97 (d, *J* = 7.8, 0.5H, C*H*$_{Ar(M)}$), 7.89 (d, *J* = 7.8, 1H, C*H*$_{Ar(D)}$), 7.82 (d, *J* = 7.8, 0.5H C*H*$_{Ar(M)}$ 7.74 (t, *J* = 7.8, 1H, C*H*$_{Ar(D)}$), 7.69 (t, *J* = 7.8, 0.5H, C*H*$_{Ar(M)}$), 7.42 (m, 1.5H, C*H*$_{Ar(D)}$, C*H*$_{Ar(M)}$), 4.59 (s, 0.5H, BO*H*), 2.45 (s, 3H, C*H*$_{3(D)}$), 2.39 (s, 1.5H, C*H*$_{3(M)}$); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 148.7, 148.1, 141.7, 141.0, 133.5, 133.4, 133.0, 132.7, 126.4, 126.4, 123.1, 123.0, 114.3, 113.7, 19.6,

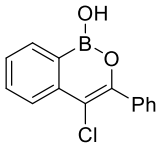
19.5; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 27.7 ; FT-IR (ATR) υ = 3304, 2917, 1620, 1366, 1307, 1291, 1242, 1210, 1099, 968, 762, 752, 640, 629, 602 cm^{-1}; HRMS (CI) calcd for $C_9H_9BClO_2$ $[M + H]^+$ 194.0415 found 194.0415.

4-Chloro-3-(*p*-tolyl)-1*H*-benzo[c][1,2]oxaborinin-1-ol (3c)



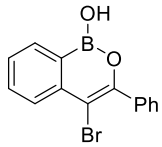
The desired product was prepared by following **procedure C.2** using 3-(*p*-tolyl)-1*H*-benzo[c][1,2]oxaborinin-1-ol (50 mg, 0.21 mmol, 1 eq), $CuCl_2$ (57 mg, 0.42 mmol, 2 eq) in *tert*-butanol (2 mL). Purification by column chromatography on silica using Petrol:EtOAc (100:0 to 80:20) afforded the chloro-benzooxaborininol (56 mg, 98%) as a white solid; mp = 194 - 195 °C; ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop D_2O) δ = 8.06 (dd, *J* = 7.4, 0.6, 1H, CH_{Ar}), 8.00 (d, *J* = 8.1, 1H, CH_{Ar}), 7.80 – 7.65 (m, 3H, CH_{Ar}, 2×CH_{ptol}), 7.47 (td, *J* = 7.4, 0.7, 1H, CH_{Ar}), 7.27 (d, *J* = 5.9, 2H, 2×CH_{ptol}), 2.43 (s, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$ + 1 drop D_2O) δ = 147.8, 141.4, 139.3, 133.0, 132.8, 132.4, 129.3, 128.8, 127.0, 124.0, 114.0, 21.5; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 27.8 ; FT-IR (ATR) υ = 3055, 3024, 2913, 2852, 1600, 1401, 1377, 1306, 1287, 1269, 1245, 1184, 1158, 1104, 1059, 873, 816, 763, 734, 719, 590, 534 cm^{-1}; HRMS (CI) calcd for $C_{15}H_{12}BClO_2$ $[M + H]^+$ 271.0697 found 271.0693.

4-Chloro-3-phenyl-1H-benzo[c][1,2]oxaborinin-1-ol (3e)



The desired product was prepared by following **procedure C.2** using 3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (87 mg, 0.39 mmol, 1eq), $CuCl_2$ (109 mg, 0.81 mmol, 2.1 eq) in *tert*-butanol (5 mL). Purification by filtration through a pad of silica using Et_2O as eluent afforded the chloro-benzooxaborininol (82 mg, 82% mmol) as a white solid; mp = 166 °C; ^{1}H NMR (500 MHz, $CDCl_3$ + 1 drop D_2O) δ = 8.06 (dd, *J* = 7.4, 0.6, 1H, CH_{Ar}), 8.00 (d, *J* = 8.2, 1H, CH_{Ar}), 7.82-7.78 (m, 2H, 2×CH_{Ar}), 7.75 (td, *J* = 7.4, 1.4, 1H, CH_{Ar}), 7.51-7.41(m, 4H, 4×CH_{Ar}), 4.81 (s, 1H, BO*H*); ^{13}C NMR (500 MHz, $CDCl_3$ + 1 drop D_2O) δ = 147.6, 141.2, 135.2, 133.0, 132.8, 129.4, 129.2, 128.0, 127.2, 124.0, 114.2. The carbon adjacent to the boron atom was not observed; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 27.8 ; FT-IR (ATR) υ = 3223, 3055, 2919, 1603, 1471, 1371, 1247, 1135, 1106, 1022, 967, 759, 692, 635, 594, 539 cm^{-1}; HRMS (CI) calcd for $C_{14}H_{11}BO_2Cl$ $[M+H]^+$ 257.0540 found 257.0541.

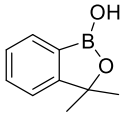
4-Bromo-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (6e)



The desired product was prepared by following **procedure C.2** using 3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (60 mg, 0.27 mmol, 1eq), $CuBr_2$ (121 mg, 0.54 mmol, 2.1 eq) in *tert*-butanol (mL). Purification by filtration through a pad of silica using Et_2O as solvent afforded the bromo-benzooxaborininol (21 mg, 26%) as a white solid; mp = 86 - 88 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.06 (d, *J* = 7.5, 1H, C*H*$_{Ar}$), 8.02 (d, *J* = 8.2, 1H, C*H*$_{Ar}$), 7.75 (td, *J* = 7.5, 1.3, 1H, C*H*$_{Ar}$), 7.73 (dd, *J* = 8.2, 1.3, 1H, C*H*$_{Ar}$), 7.50 - 7.44 (5H, m, C*H*$_{Ar}$); ^{13}C NMR (600 MHz, $CDCl_3$) δ = 149.2, 141.8, 136.7, 133.3, 132.8, 129.7, 129.3, 129.2, 128.1, 127.3, 126.7, 105.3; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 28.0 ; FT-IR (ATR) υ = 3059, 2952, 2921, 2852, 1693, 1595, 1579 cm^{-1}; HRMS (CI) calcd for $C_{14}H_{11}BO_2Cl$ $[M+H]^+$ 299.9951 found 299.9957.

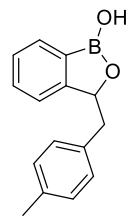
III.4. Benzoxaboroles (4)

3,3-Dimethylbenzo[c][1,2]oxaborol-1(3*H*)-ol (4d)



The desired product was prepared by following **procedure D.2** using (2-(prop-1-en-1-yl)phenyl)boronic acid (98 mg, 0.60 mmol, 1eq), $PtCl_4$ (20 mg, 0.06 mmol, 0.1 eq) in CH_2Cl_2 (2 mL). Purification by filtration column chromatography on silica using Petrol:Et_2O (100:0 to 50:50) as solvent afforded a mixture of monomeric and dimeric benzooxaborole (50 mg, 50%, ratio M:D = 1:0.2) as a white solid; mp = 82 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 (d, *J* = 7.3, 0.2H, C*H*$_{Ar(D)}$), 7.76 (d, *J* = 7.3, 1H, C*H*$_{Ar(M)}$), 7.54 – 7.45 (m, 1.2H, C*H*$_{Ar(D)}$, C*H*$_{Ar(M)}$), 7.37 (m, 1.2H, C*H*$_{Ar(D)}$, C*H*$_{Ar(M)}$), 7.33 (d, *J* = 7.7, 0.2H, C*H*$_{Ar(D)}$), 7.29 (d, *J* = 7.6, 1H, C*H*$_{Ar(M)}$), 7.03 (s, 1H, BO*H*), 1.65 (s, 1.2H, C*H*$_{3(D)}$), 1.62 (s, 6H, C*H*$_{3(M)}$).^{13}C NMR (151 MHz, $CDCl_3$) δ = 161.7, 131.4, 130.9, 127.5, 120.5, 85.2, 29.3. The carbon adjacent to the boron atom was not observed; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 31.3 ; FT-IR (ATR) υ = 3341, 2967, 1607, 1478, 1421, 1323, 1295, 1233, 1127, 1072, 945, 772, 728, 705, 653, 592 cm^{-1}; HRMS (EI) calcd for $C_9H_{11}BO_2$ $[M^+]$ 162.0852 found 162.0851. These spectroscopic data are in agreement with those reported in literature.[6]

3-(4-Methylbenzyl)benzo[c][1,2]oxaborol-1(3*H*)-ol (4c)

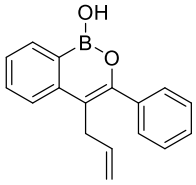


The desired product was prepared by following **procedure D.2** with slight modification using 2-(4-methylstyryl)phenyl)boronic acid (100 mg, 0.40 mmol, 1eq), $PtCl_4$ (15 mg, 0.04 mmol, 0.1 eq) in CH_2Cl_2 (2 mL). The solution was

allowed to stir for 3 days. Purification by filtration column chromatography on silica using Petrol:Et_2O (100:0 to 50:50) as solvent afforded the monomeric benzooxaborole (24 mg, 24%) as a white solid; mp = 95 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.81 (d, *J* = 7.5, 1H, C*H*$_{Ar}$), 7.44 (td, *J* = 7.5, 1.4, 1H, C*H*$_{Ar}$), 7.35 (d, *J* = 7.9, 2H, 2×C*H*$_{ptol}$), 7.32 (t, *J* = 7.5, 1H, C*H*$_{Ar}$), 7.21 (d, *J* = 7.9, 2H, 2×C*H*$_{ptol}$), 7.19 (d, *J* = 7.5, 1H, C*H*$_{Ar}$), 5.27 (dd, *J* = 11.8, 3.1, 1H, OC*H*), 4.46 (s, 1H, BO*H*), 3.18 (dd, *J* = 16.1, 11.8, 1H, CH*H*), 3.00 (dd, *J* = 16.1, 3.1, 1H, CH*H*), 2.38 (s, 3H, C*H*$_3$); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 145.4, 139.6, 137.6, 133.1, 131.9, 129.3, 127.0, 126.6, 125.9, 76.6, 40.7, 21.3. The carbon adjacent to the boron atom was not observed; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 28.3 ; FT-IR (ATR) υ = 3374, 3021, 2916, 1600, 1449, 1393, 1348, 1325, 1299, 1268, 1124, 973, 864, 808, 760, 734, 718, 655, 559, 476 cm^{-1}; HRMS (CI) calcd for $C_{15}H_{15}BO_2$ $[M+H]^+$ 239.1238 found 239.1237.

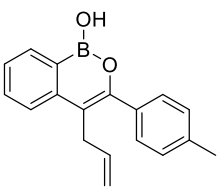
III.5. Allyl-benzooxaborininols (9)

4-Allyl-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9a)



The desired product was prepared by following **procedure E** using (2-(phenylethynyl)phenyl)boronic acid (100 mg, 0.45 mmol, 1eq), $Pd(PhCN)_2Cl_2$ (8.6 mg, 0.02 mmol, 5 mol%), $NaHCO_3$ (76 mg, 0.90 mmol, 2eq) and allyl chloride (185 µL, 2.25 mmol, 5 eq) in *tert*-butanol (3.5 mL). Purification by column chromatography on silica using Petrol:EtOAc (100:0 to 80:20) as solvent afforded the monomeric allyl-benzooxaborininol (90 mg, 76% mmol) as a colourless oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ = 8.07 (d, *J* = 6.7, 1H, C*H*$_{Ar}$), 7.65 (m, 1H, C*H*$_{Ar}$), 7.63 – 7.58 (m, 3H, 3×C*H*$_{Ar}$), 7.46 – 7.38 (m, 4H, 4×C*H*$_{Ar}$), 6.12 (ddt, *J* = 17.4, 10.2, 4.9, 1H, =C*H*), 5.17 (dd, *J* = 10.2, 1.8, 1H, =C*H*H), 5.06 (dd, *J* = 17.4, 1.9, 1H, =CH*H*), 4.54 (s, 1H, BO*H*), 3.47 – 3.34 (m, 2H, C*H*$_2$); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.7, 143.2, 137.3, 137.0, 132.8, 132.4, 128.8, 128.7, 128.2, 126.0, 124.3, 116.5, 112.9, 32.5. The carbon adjacent to the boron atom was not observed; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 28.2 ; FT-IR (ATR) υ = 3396, 3058, 2918, 2849, 1678, 1603, 1446, 1379, 1316, 1294, 1266, 1198, 993,910, 757, 732, 696, 635, 595 cm^{-1}; HRMS (CI) calcd for $C_{17}H_{15}BO_2$ $[M]^+$ 261.1196 found 261.1195.

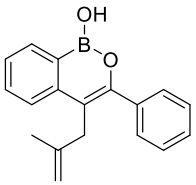
4-Allyl-3-(*p*-tolyl)-1*H*-benzo[c][1,2]oxaborinin-1-ol (9d)



The desired product was prepared by following **procedure E** using (2-(*p*-tolylethynyl)phenyl)boronic acid (126 mg, 0.53 mmol, 1eq), $Pd(PhCN)_2Cl_2$ (10.2 mg, 0.03 mmol, 5 mol%), $NaHCO_3$ (90 mg, 1.10 mmol, 2eq) and

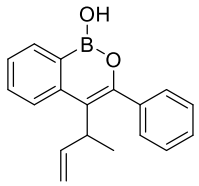
allyl chloride (220 µL, 2.70 mmol, 5eq) in *tert*-butanol (3.5 mL). Purification by column chromatography on silica using Petrol:EtOAc (100:0 to 80:20) as solvent afforded the allyl-benzooxaborininol (100 mg, 68% mmol) as a colourless oil. NMR revealed a mixture of monomer and dimer (ratio M:D = 1:0.4); ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 7.3, 0.4H, C*H*$_{Ar(D)}$), 8.07 (d, *J* = 7.3, 1H, C*H*$_{Ar(M)}$), 7.72 – 7.57 (m, 2.8H, 2×C*H*$_{Ar(D)}$, 2×C*H*$_{Ar(M)}$), 7.50 (m, 2.8H, 2×C*H*$_{ptol(D)}$, 2×C*H*$_{ptol(M)}$), 7.46 – 7.37 (m, 1.4H, C*H*$_{Ar(D)}$, C*H*$_{Ar(M)}$), 7.31 – 7.20 (m, 2H, 2×C*H*$_{ptol(M)}$), 7.13 (d, *J* = 7.8, 0.8H, 2×C*H*$_{ptol(D)}$), 6.24 – 6.02 (m, 1.4H, =C*H*$_{(D)}$, =C*H*$_{(M)}$), 5.23 – 5.02 (m, 2.8H, =C*H*$_{2(D)}$, =C*H*$_{2(M)}$), 4.60 (br s, 1H, BO*H*), 3.55 – 3.47 (m, 0.8H, C*H*$_{2(D)}$), 3.47 – 3.39 (m, 2H, C*H*$_{2(M)}$), 2.41 (s, 3H, C*H*$_{3(M)}$), 2.39 (s, 1.2H, C*H*$_{3(D)}$); ^{13}C NMR (126 MHz, $CDCl_3$) δ = 150.3, 149.8, 144.1, 143.3, 138.6, 138.3, 137.5, 137.4, 134.1, 133.6, 132.8, 132.5, 132.3, 128.8, 128.7, 128.6, 125.8, 125.7, 124.2, 116.2, 116.4, 112.9, 112.6, 32.7, 32.6, 21.4. Some signals of the dimer and monomer are overlapping; FT-IR (ATR) υ = 3388, 3057, 3026, 2976, 2918, 1972, 1606, 1477, 1440, 1378, 1317, 1294, 1267, 907, 824, 783, 756, 727 cm^{-1};HRMS (EI) calcd for $C_{18}H_{17}BO_2$ $[M]^+$ 275.1352 found 275.1353.

4-(2-Methylallyl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9b)



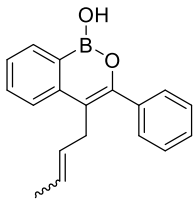
The desired product was prepared by following **procedure E** using (2-(phenylethynyl)phenyl)boronic acid (100 mg, 0.45 mmol, 1 eq), $Pd(PhCN)_2Cl_2$ (8.6 mg, 0.02 mmol, 5 mol%), $NaHCO_3$ (76 mg, 0.9 mmol, 2 eq) and 3-chloro-2-methylprop-1-ene (220 µL, 2.30 mmol, 5 eq) in *tert*-butanol (3.5 mL). Purification by column chromatography on silica using Petrol:EtOAc (100:0 to 80:20) as solvent afforded the allyl-benzooxaborininol (104 mg, 83% mmol) as a white solid; mp = 99 - 101 °C; NMR revealed a mixture of monomer and dimer (ratio M:D = 1:0.1); ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop D_2O) δ = 8.24 (dd, *J* = 7.4, 1.4, 0.1H, C*H*$_{Ar(D)}$), 8.10 – 8.04 (m, 1H, C*H*$_{Ar(M)}$), 7.72 – 7.60 (m, 3.2H, 2×C*H*$_{Ar(D)}$, 3×C*H*$_{Ar(M)}$), 7.56 (d, *J* = 8.1, 0.2H, 2×C*H*$_{Ar(D)}$), 7.50 (d, *J* = 8.1, 1H, C*H*$_{Ar(M)}$), 7.48 – 7.29 (m, 4.4H, 4×C*H*$_{Ar(D)}$, 4×C*H*$_{Ar(M)}$), 4.95 (m, 0.1H, =CH*H*$_{(D)}$), 4.93 (sept, *J* = 1.5, 1H, =CH*H*$_{(M)}$) 4.72 (br s, 0.1H, =CH*H*$_{(D)}$), 4.69 (m, 1H, =C*H*H$_{(M)}$), 4.57 (s, 1H, BO*H*), 3.38 (s, 0.3H, C*H*$_{2(D)}$), 3.31 (s, 2H, C*H*$_{2(M)}$), 1.91 (s, 0.6H, C*H*$_{3(D)}$), 1.88 (s, 3H, C*H*$_{3(M)}$); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 150.2, 149.7, 144.54, 144.52, 144.4, 143.6, 137.02, 137.00, 133.5, 132.7, 132.6, 132.4, 128.9, 128.7, 128.6, 128.5, 128.48, 128.45, 128.2, 128.0, 126.0, 125.9, 124.39, 124.36, 113.6, 113.3, 112.3, 112.1, 37.1, 36.9, 23.6, 23.5; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 28.2 ; FT-IR (ATR) υ = 3363, 3058, 3028, 2969, 2929, 2882, 1603, 1476, 1448, 1374, 1316, 1295, 1269,

1200, 1153, 1132, 930, 838, 822, 732, 697, 649, 632, 540, 449 cm^{-1}; HRMS (EI) calcd for $C_{18}H_{17}BO_2$ [M] $^+$ 275.13524 found 275.13530. **4-(But-3-en-2-yl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9e)**



The desired product was prepared by following **procedure E** slightly modified using (2-(phenylethynyl)phenyl)boronic acid (50 mg, 0.23 mmol, 1eq), $Pd(PhCN)_2Cl_2$ (4.3 mg, 0.01 mmol, 5 mol%), $NaHCO_3$ (38 mg, 0.45 mmol, 2eq) and crotyl chloride (108 µL, 1.15 mmol, 5eq) in *tert*-butanol (1.8 mL). The resulting mixture was heated at 50 °C for 7 hours. Purification by column chromatography on silica using Petrol:EtOAc (100:0 to 80:20) as solvent afforded the allyl-benzooxaborininol (25 mg, 40%) as pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop D_2O) δ = 8.08 (d, *J* = 7.2, 1H, CH_{Ar}), 7.83 (d, *J* = 8.2, 1H, CH_{Ar}), 7.62 – 7.56 (m, 1H, CH_{Ar}), 7.53 (m, 2H, 2×CH_{Ar}), 7.46 - 736 (m, 4H, 4×CH_{Ar}), 6.21 (ddd, *J* = 17.4, 10.6, 3.4, 1H, =C*H*), 5.14 (m, 2H, =CH_2), 3.85 – 3.78 (m, 1H, C*H*(CH_3)), 1.48 (d, *J* = 7.3, 3H, CH_3); ^{13}C NMR (151 MHz, $CDCl_3$) δ = 149.7, 143.2, 141.8, 137.7, 133.1, 131.4, 128.9, 128.7, 128.4, 127.3, 126.4, 125.8, 118.4, 114.1, 37.4, 18.8; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 28.0 ; FT-IR (ATR) υ = 3252, 3060, 2971, 2932, 2876, 1603, 1473, 1450, 1370, 1314, 1279, 1254, 1174, 1020, 904, 758, 696, 633 cm^{-1}; HRMS (CI) calcd for $C_{18}H_{17}BO_2$ [M] $^+$ 275.1350 found 275.1350.

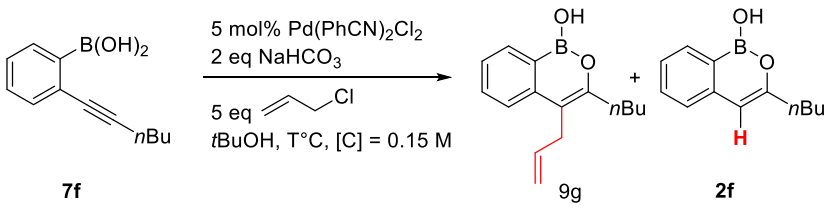
4-(But-2-en-1-yl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9c)



The desired product was prepared by following **procedure E** using (2-(phenylethynyl)phenyl)boronic acid (100 mg, 0.45 mmol, 1eq), $Pd(PhCN)_2Cl_2$ (8.6 mg, 0.02 mmol, 5 mol%), $NaHCO_3$ (76 mg, 0.9 mmol, 2 eq) and 3-chloro-2-methylprop-1-ene (230 µL, 2.30 mmol, 5 eq) in *tert*-butanol (3.5 mL). Purification by column chromatography on silica using Petrol: EtOAc (100:0 to 80:20) as solvent afforded the allyl-benzooxaborininol (104 mg, 83% mmol) as a colourless oil. The NMR revealed a mixture of two isomers cis:trans (ratio E:Z = 1:0.6) and traces of benzooxaborininol; ^{1}H NMR (600 MHz, $CDCl_3$ + 1 drop D_2O) δ = 8.13 – 8.08 (m, 1.6H, $CH_{Ar(Z),}$ $CH_{Ar(E)}$), 7.71 – 7.54 (m, 6.4H, 4×$CH_{Ar(E),}$ 4×$CH_{Ar(Z)}$), 7.50 – 7.36 (m, 6.4H, 4×$CH_{Ar(E),}$ 4×$CH_{Ar(Z)}$), 5.72 (dqt, *J* = 15.5, 6.5, 1.9, 1H, =C*H*(CH_3)$_{(E)}$), 5.60 (m, 1.2H, =C*H*(CH_3)$_{(Z)}$, =C*H*(CH_2)$_{(Z)}$), 5.38 (dqt, *J* = 15.4, 5.2, 1.9, 1H, =C*H*(CH_2)$_{(E)}$), 3.46 – 3.34 (m, 3.2H, $CH_{2(E/Z)}$), 1.71 (ddt, *J* = 6.5, 1.7, 1.4, 3H, $CH_{3(E)}$), 1.68 (br d, *J* = 4.5, 1.8H, $CH_{3(Z)}$); ^{13}C NMR (151 MHz, $CDCl_3$ + D_2O) δ = 149.3, 149.1, 143.34, 143.31, 137.1, 137.0, 133.0, 132.8,

132.5, 132.40, 130.2, 129.9, 129.2, 128.8, 128.7, 128.6, 128.5, 128.3, 128.1, 126.9, 126.1, 126.0, 125.2, 124.9, 124.4, 123.8, 114.8, 113.8, 31.4, 26.7, 18.3, 13.3; ^{11}B NMR (128 MHz, $CDCl_3$+ 1 drop D_2O) δ = 28.2 ; FT-IR (ATR) υ = 3410, 3055, 3019, 2969, 2912, 2850, 1602, 1548, 1446, 1375, 1314, 1291, 1150, 1000, 777, 760, 735, 696, 655 cm^{-1}; HRMS (CI) calcd for $C_{18}H_{17}BO_2$ $[M]^+$ 275.13524 found 275.13521.

Application of Procedure E to (2-(hex-1-yn-1-yl)phenyl)boronic acid

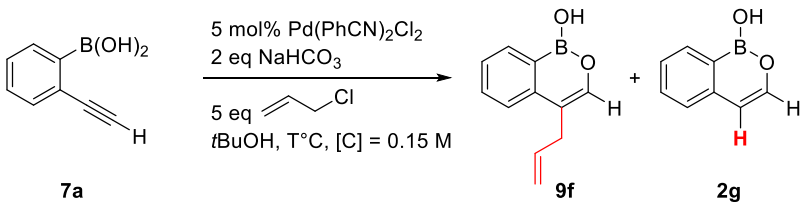


7f **9g** **2f**

Entry	T°C	Ratio 9g:2f
1	50 °C	1.1:1
2	30 °C	1:1.2

Procedure E was applied using (2-(hex-1-yn-1-yl)phenyl)boronic acid (115 mg, 0.47 mmol, 1eq), $Pd(PhCN)_2Cl_2$ (11.5 mg, 0.02 mmol, 5 mol%), $NaHCO_3$ (96 mg, 0.95 mmol, 2 eq) and allyl chloride (230 µL, 2.37 mmol, 5 eq) in *tert*-butanol (3.5 mL). Purification by column chromatography on silica using Petrol:EtOAc (100:0 to 80:20) as solvent afforded a mixture of allyl-benzooxaborininol and benzooxaborininol (77 mg, ratio = 1.1:1). Moreover, each benzooxaborininol was also present as a mixture of monomer and dimer (ratio M:D = 80:20); ^{1}H NMR (600 MHz, $CDCl_3$, monomer) δ = 7.98 (d, *J* = 7.4, 1.1H, C*H*$_{Ar}$), 7.94 (d, *J* = 7.4, 1H, C*H*$_{Ar}$), 7.62 – 7.53 (m, 3H, 3×C*H*$_{Ar}$), 7.50 (d, *J* = 8.1, 1.1H, C*H*$_{Ar}$), 7.36 – 7.28 (m, 3H, 3×C*H*$_{Ar}$), 6.10 (s, 1H, =C*H*(O)), 6.00 – 5.93 (m, 1.1H, =C*H*), 5.14 – 5.00 (m, 2H, =CH_2), 4.61 (s, 1H, BO*H*), 4.56 (s, 1.1H, BO*H*), 3.38 (dd, *J* = 3.7, 1.7, 2H, CH_{2allyl}), 2.51 (m, 2H, CH_2), 2.48 – 2.42 (m, 2H, CH_2), 1.65 (m, 4H, 2×CH_2), 1.39 (m, 4H, 2×CH_2), 1.00 – 0.89 (m, 6H, 2 ×CH_3).

Application of Procedure E to (2-ethynylphenyl)boronic acid



7a **9f** **2g**

Entry	T°C	Ratio 9f:2g
1	50°C	1:0.3
2	30°C	1:0

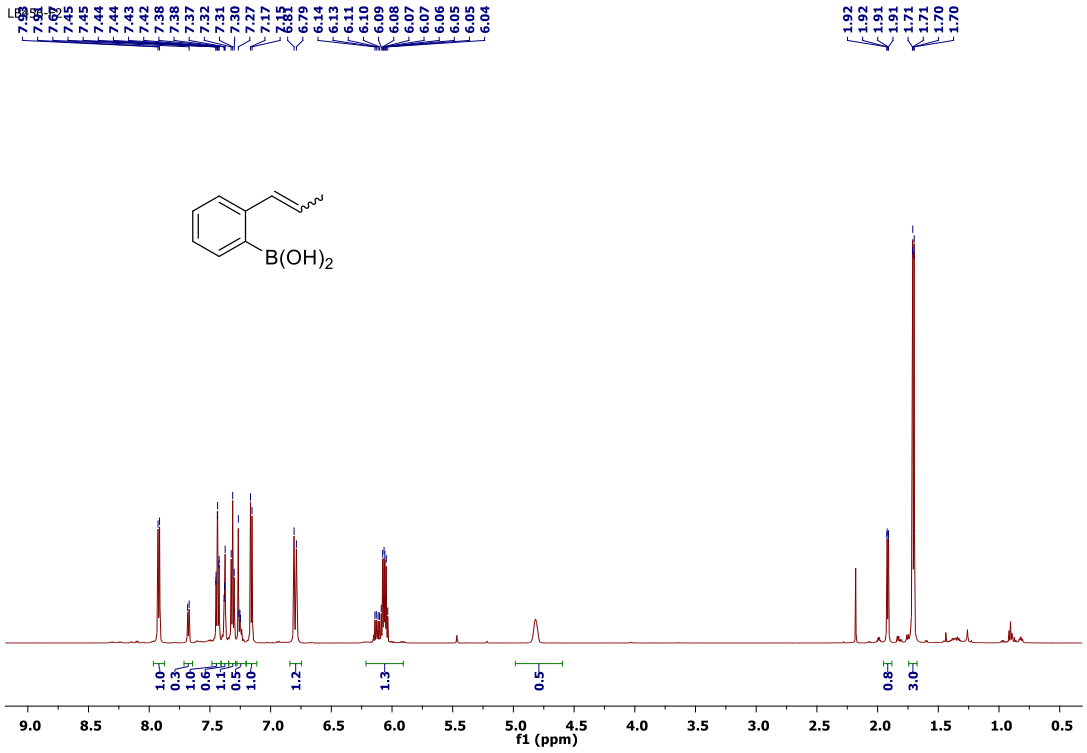
Procedure E was applied using (2-ethynylphenyl)boronic acid (88 mg, 0.60 mmol, 1 eq), $Pd(PhCN)_2Cl_2$ (11.5 mg, 0.03 mmol, 5 mol%), $NaHCO_3$ (101 mg, 1.20 mmol, 2 eq) and allyl

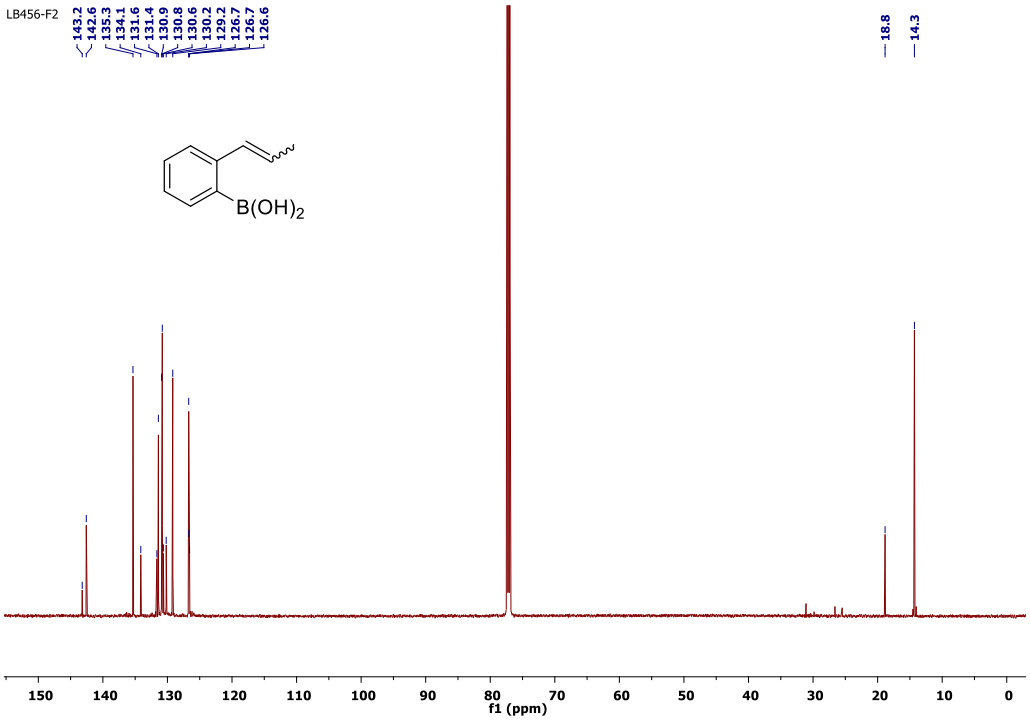
chloride (250 µL, 3.00 mmol, 5 eq) in *tert*-butanol (3.5 mL). Purification by column chromatography on silica using Petrol:EtOAc (100:0 to 80:20) as solvent afforded the allyl-benzooxaborininol (12 mg, 11%). Subsequent attempts to purify the final compounds remained unsuccessful; ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 7.4, 1H, C*H*$_{Ar}$), 7.70 – 7.59 (m, 1H, C*H*$_{Ar}$), 7.57 – 7.46 (m, 1H, C*H*$_{Ar}$), 7.38 (td, *J* = 7.4, 0.9, 1H, C*H*$_{Ar}$), 6.93 (s, 1H, =C*H*(O)), 5.99 (ddt, *J* = 16.3, 10.2, 6.1, 1H, =C*H*), 5.21 – 4.99 (m, 2H, =CH_2), 4.60 (s, 1H, BO*H*), 3.37 – 3.20 (m, 2H, CH_2).

IV. Spectra

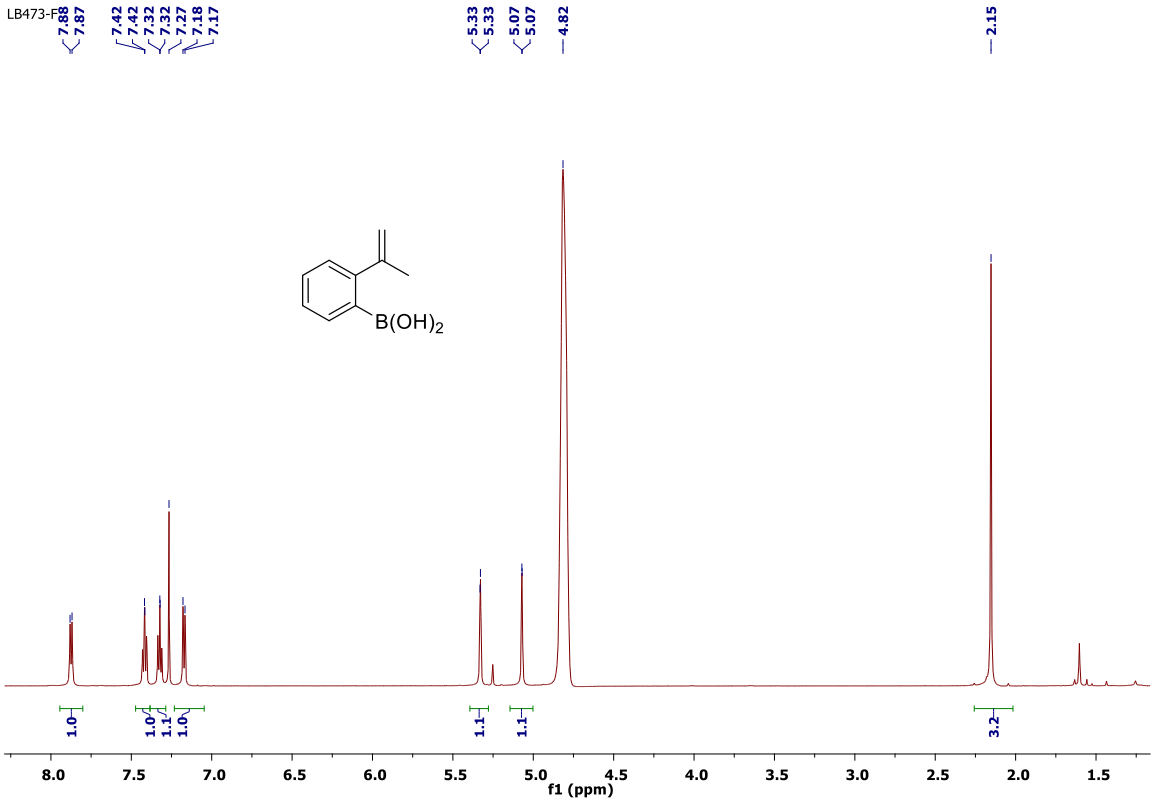
IV.1. Boronic acids (1,7)

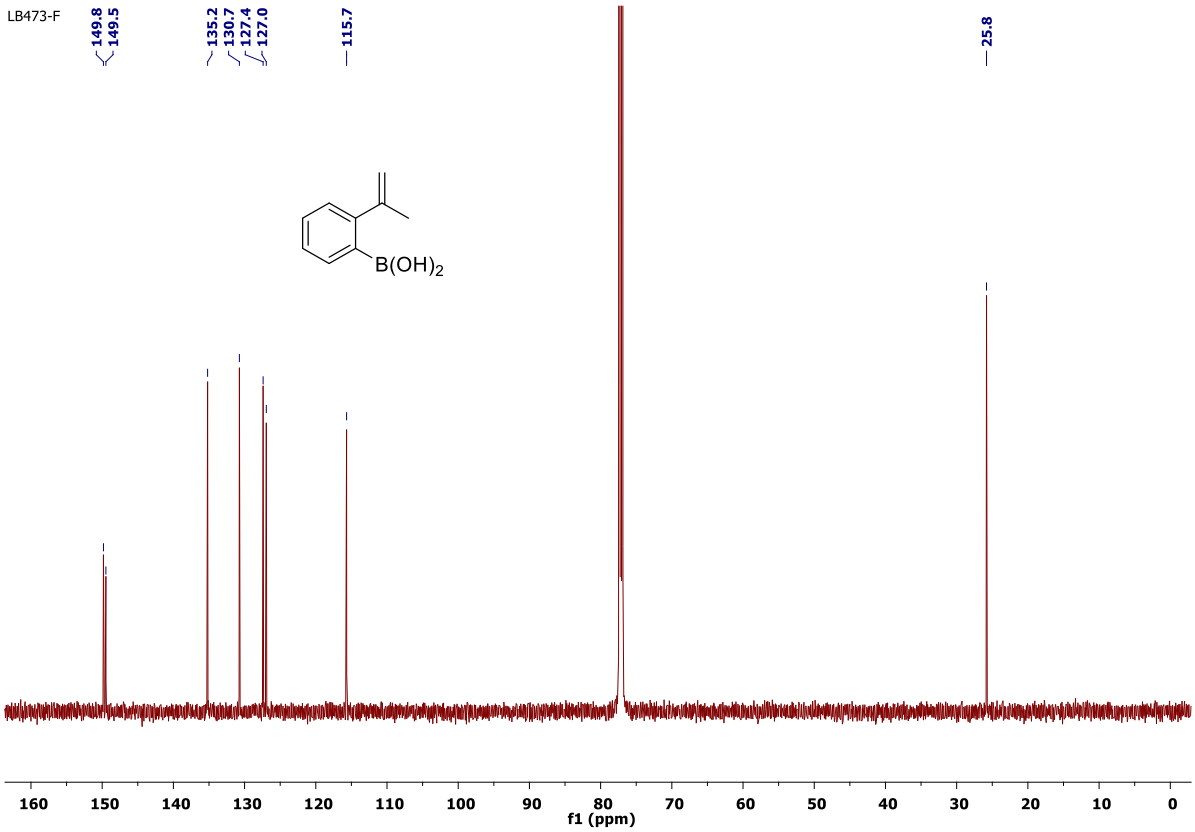
(2-(Prop-1-en-1-yl)phenyl)boronic acid (1b)



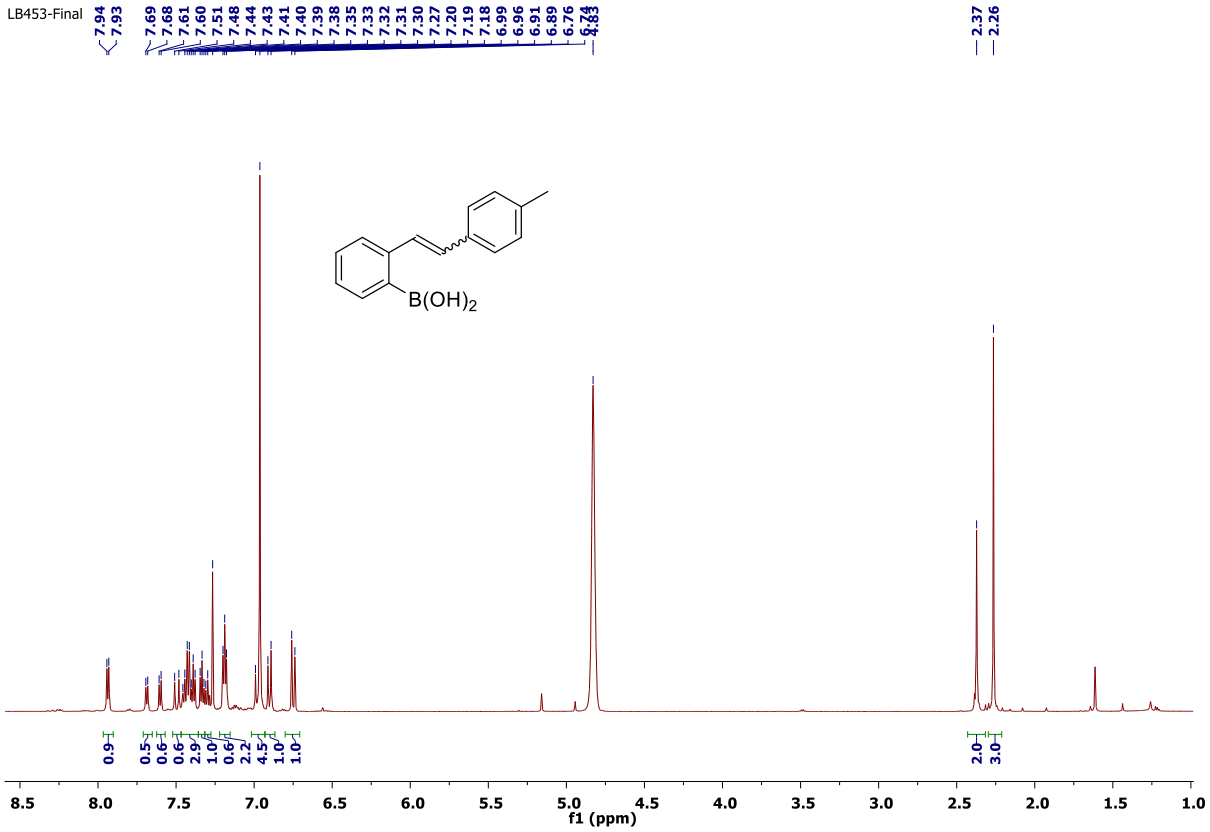


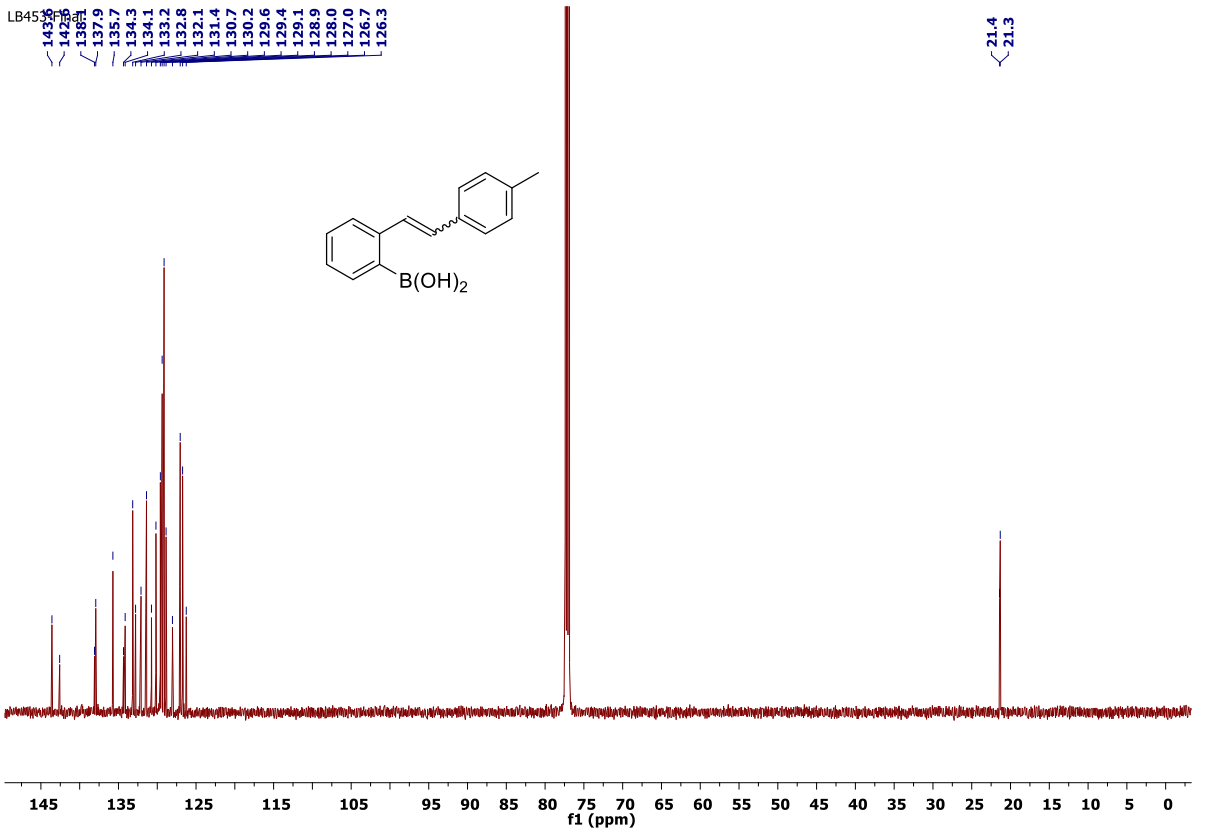
(2-(Prop-1-en-2-yl)phenyl)boronic acid (1d)



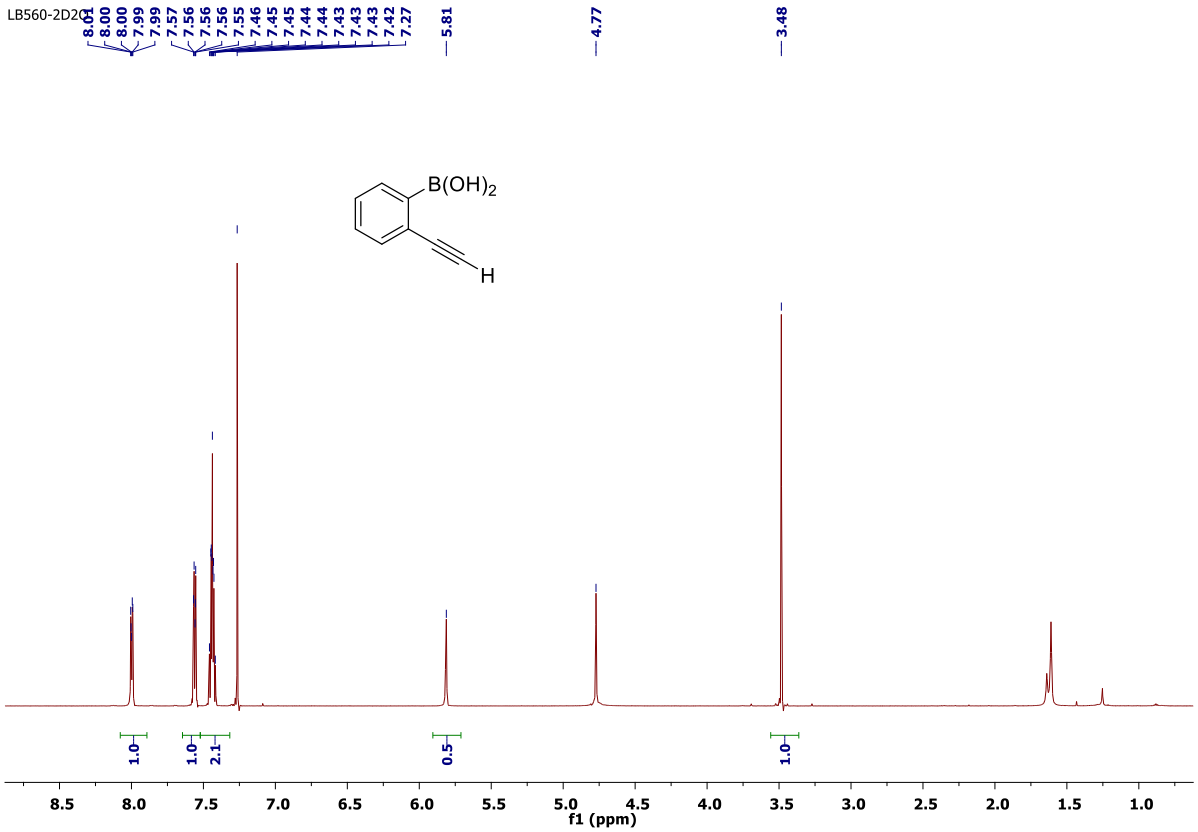


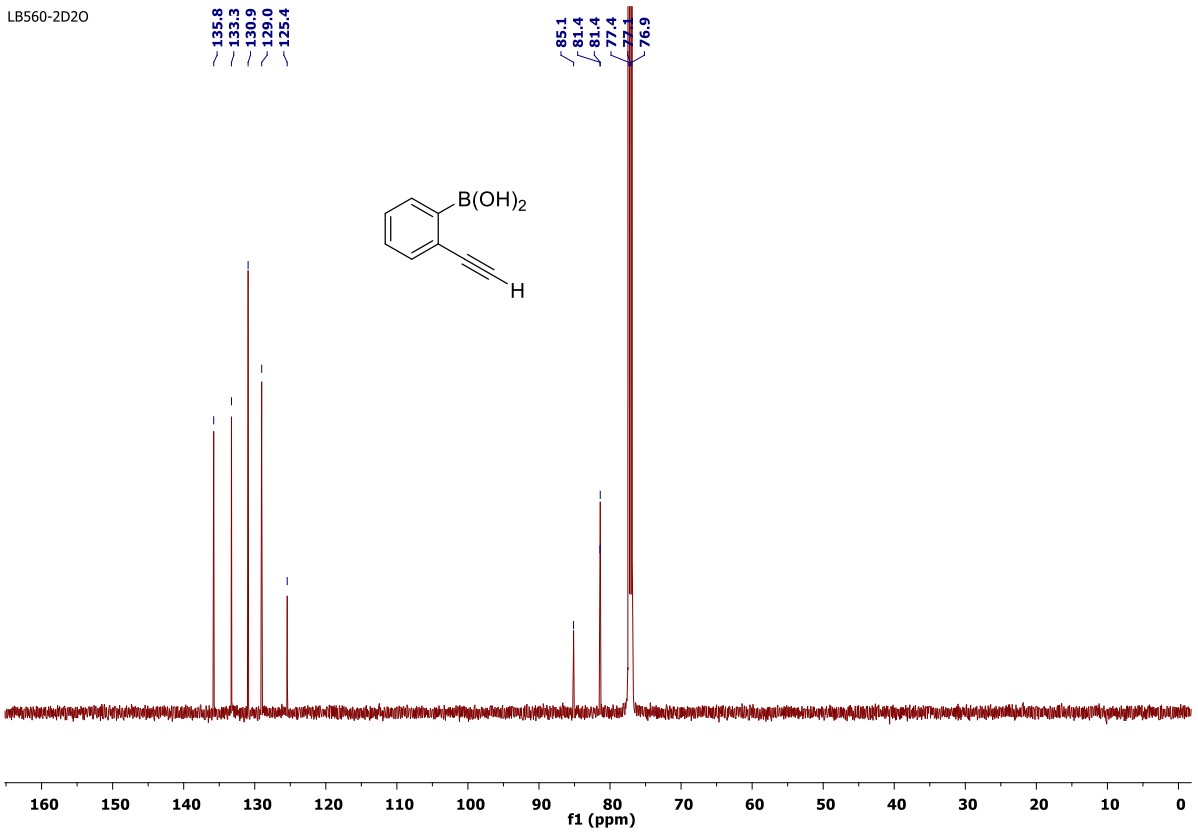
(2-(4-Methylstyryl)phenyl)boronic acid (1c)



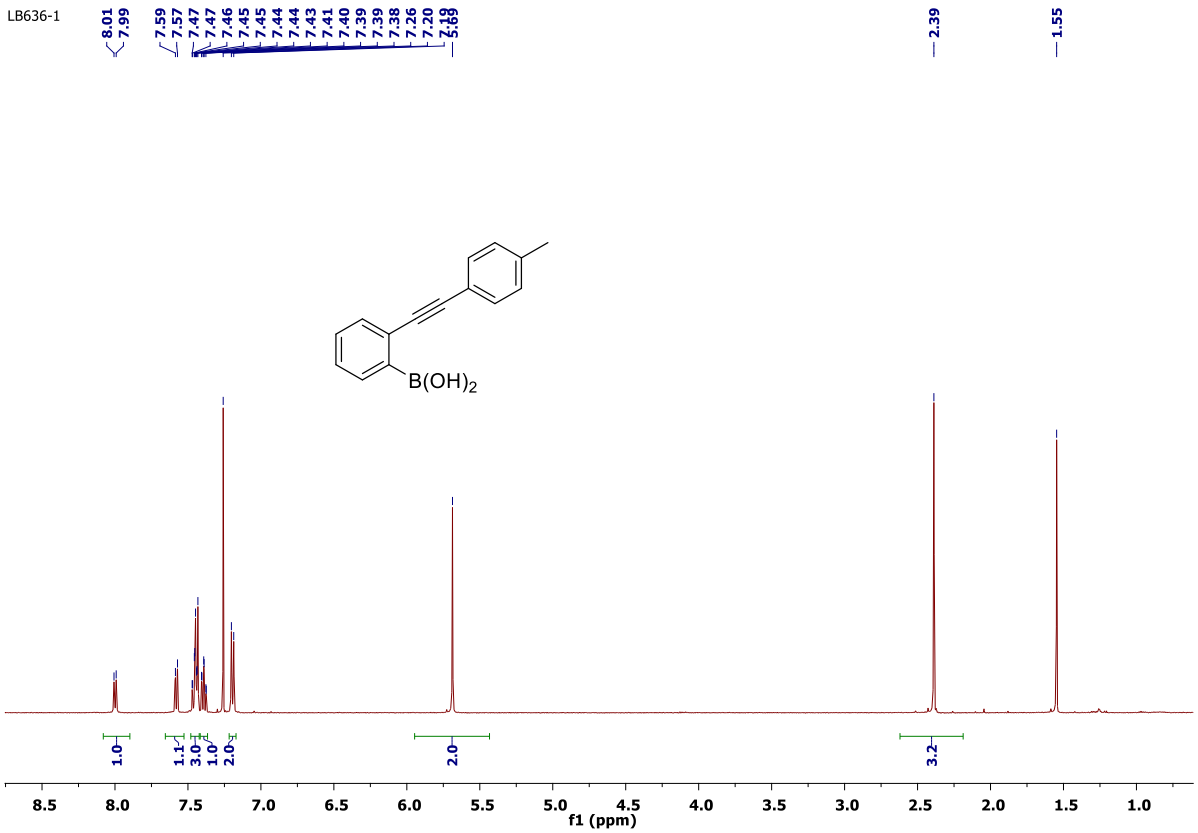


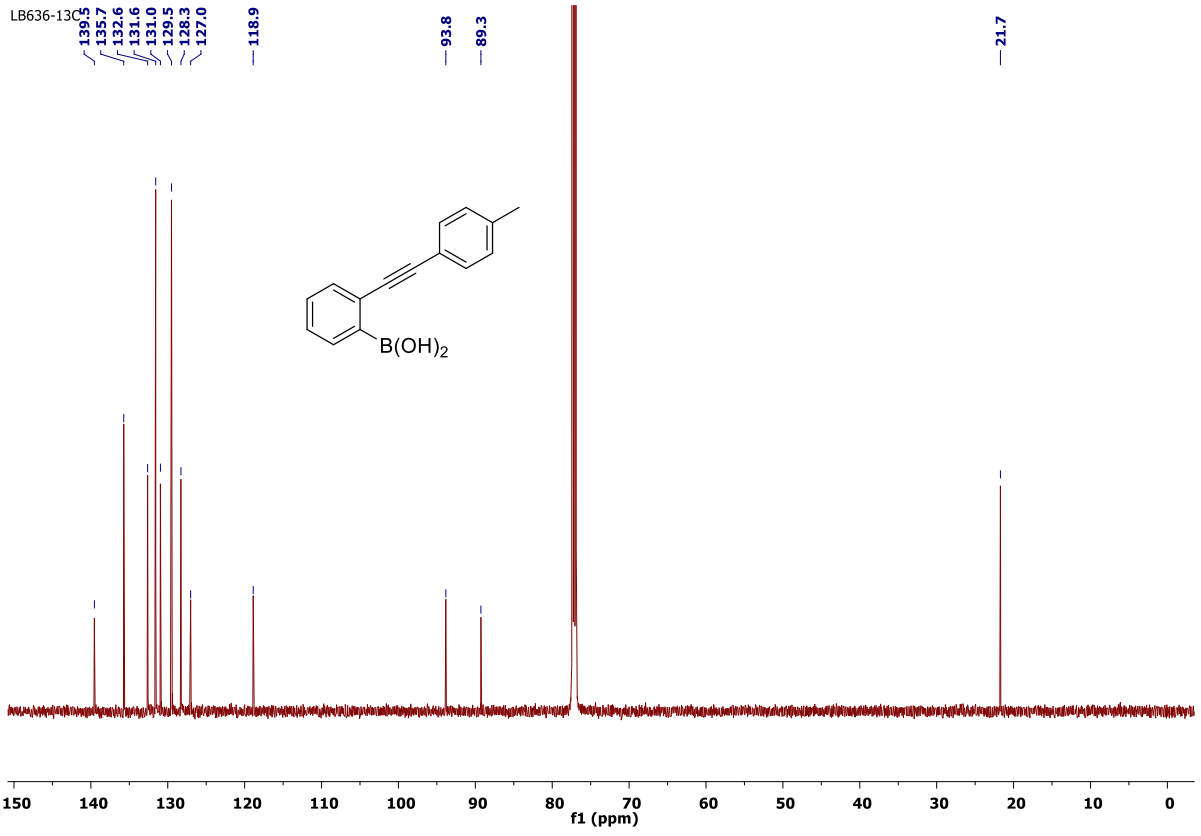
(2-Ethynylphenyl)boronic acid (7a)



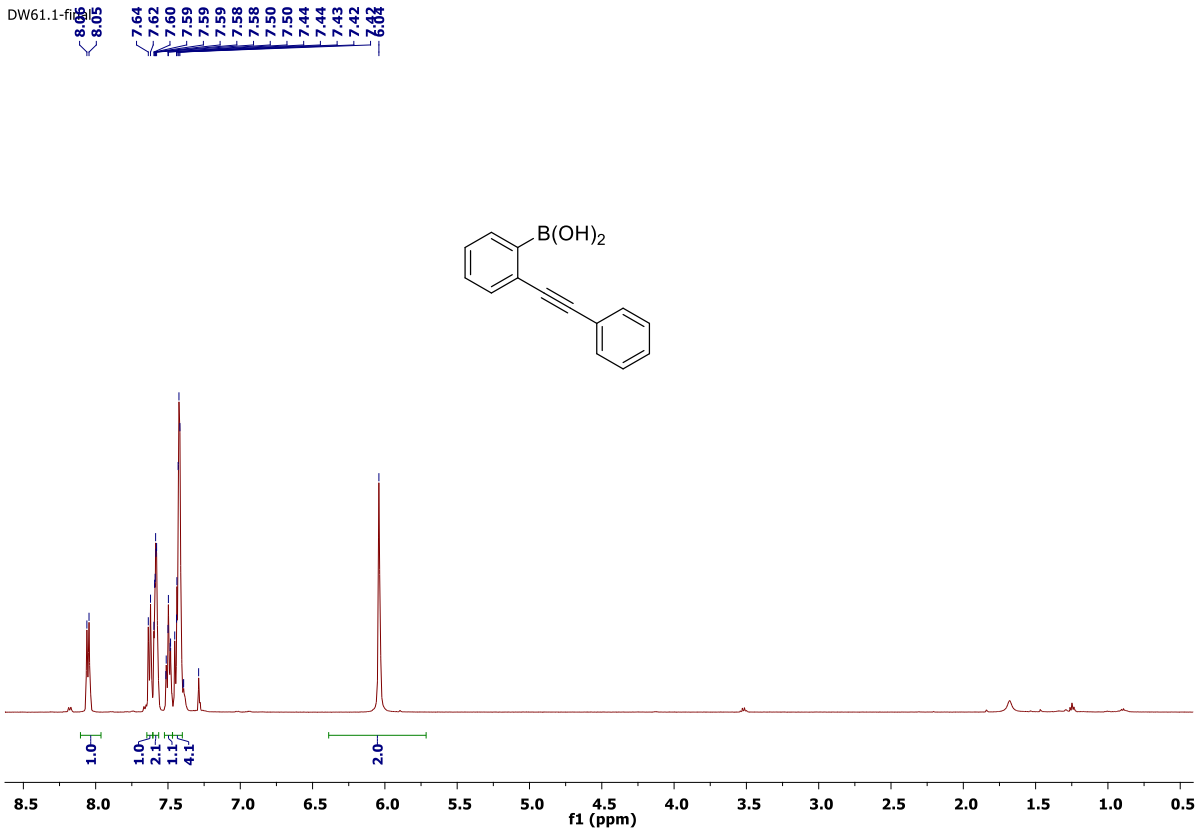


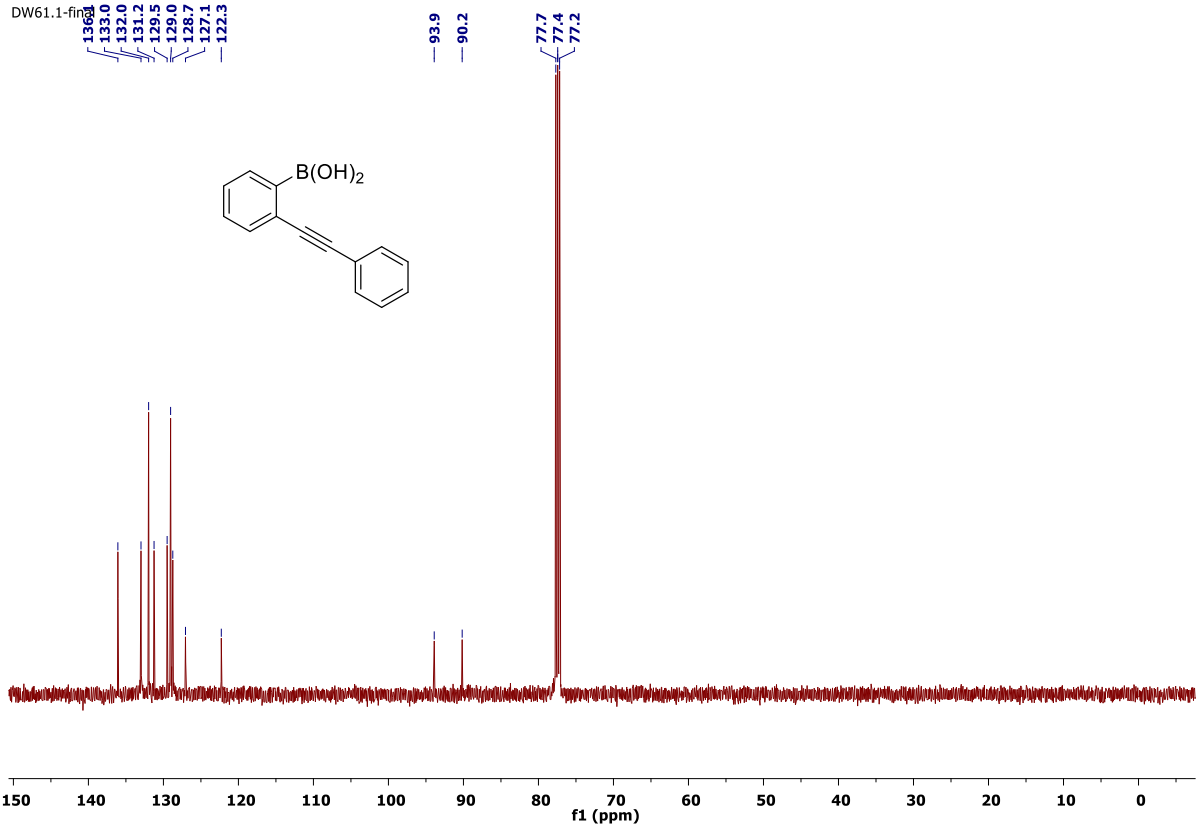
(2-(*p*-Tolylethynyl)phenyl)boronic acid (7c)



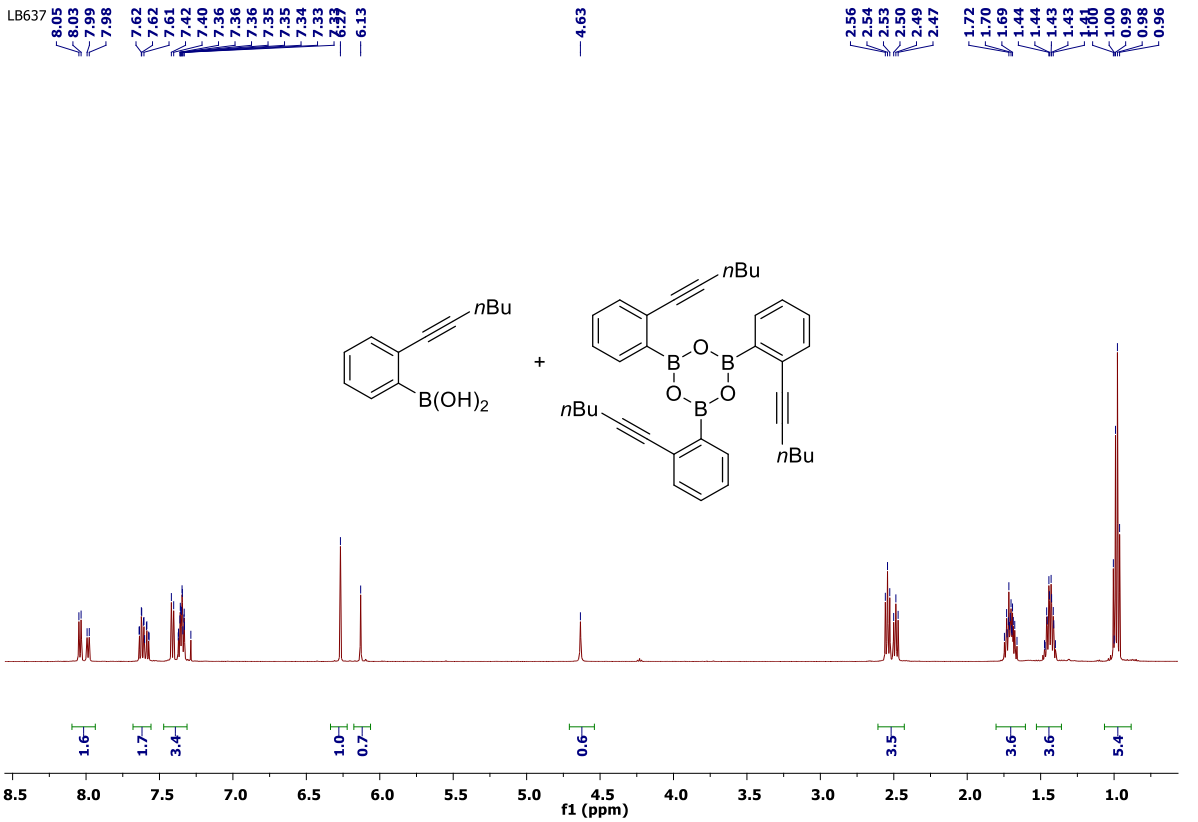


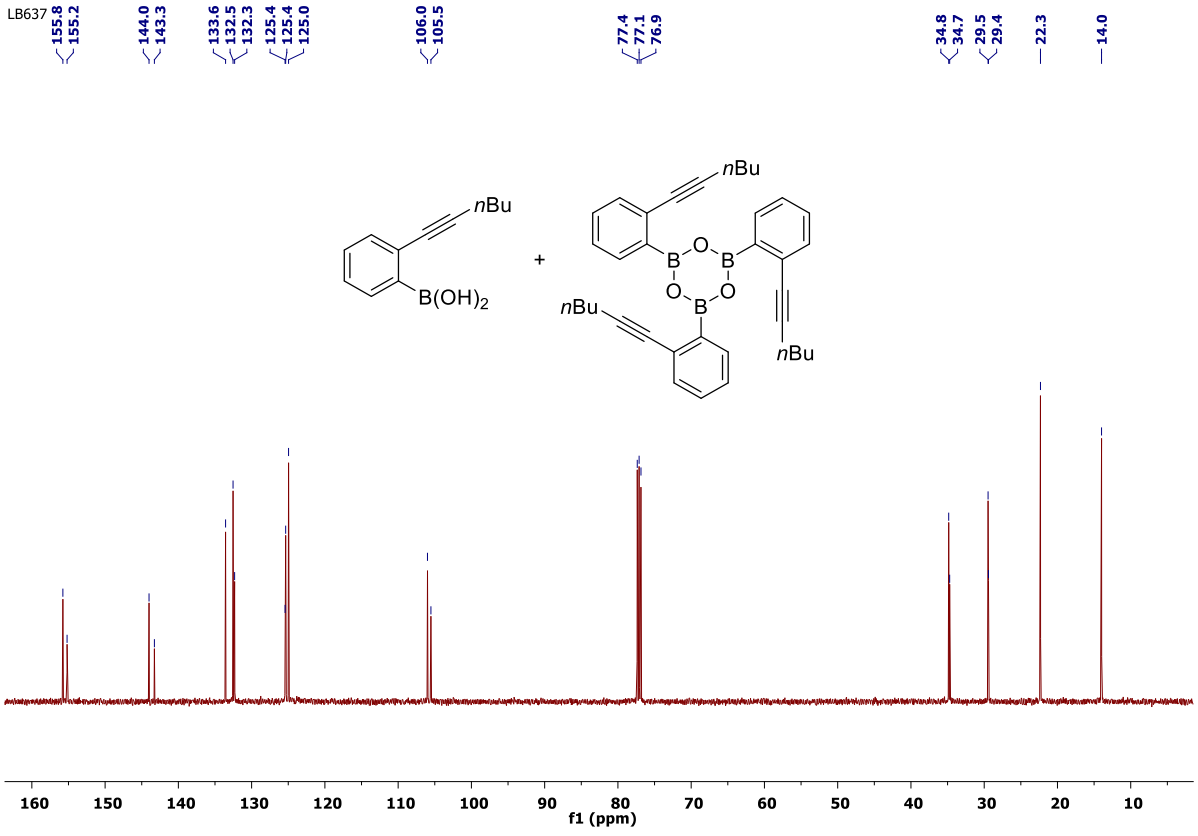
(2-(Phenylethynyl)phenyl)boronic acid (7e)





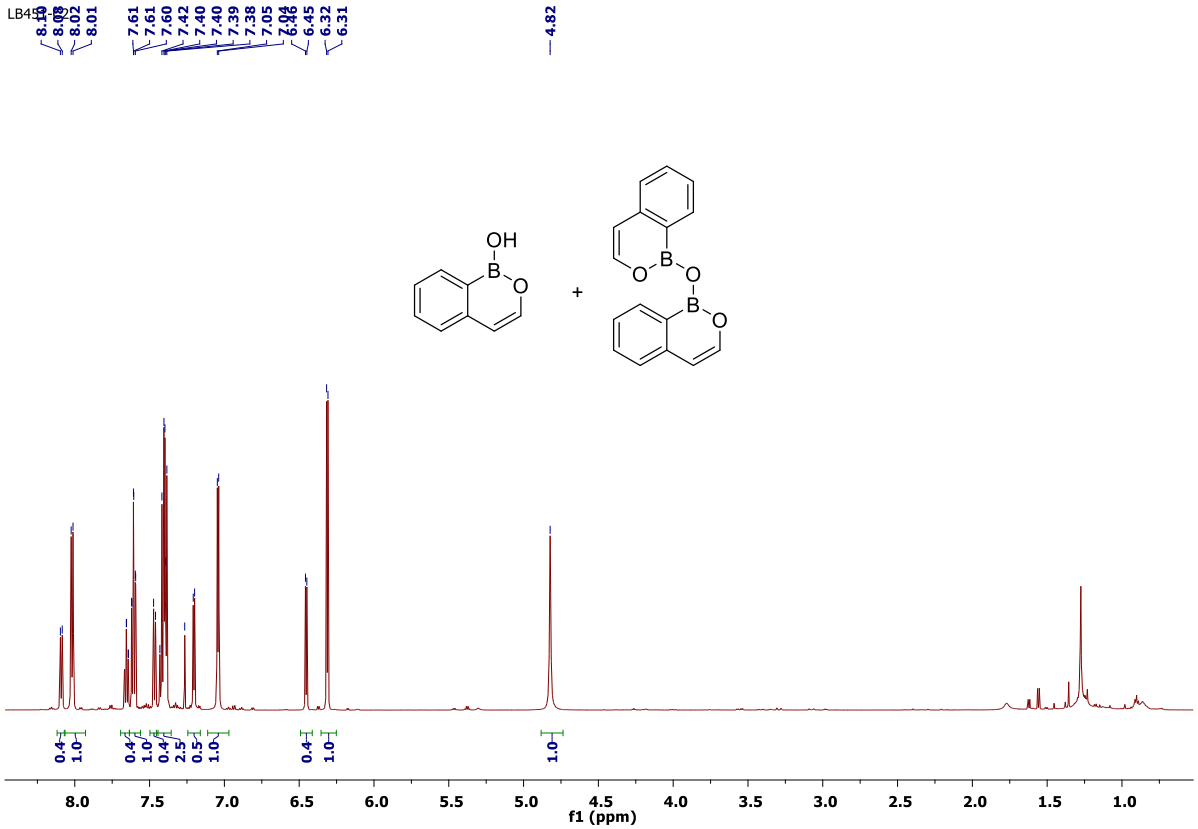
(2-(Hex-1-yn-1-yl)phenyl)boronic acid (7f)

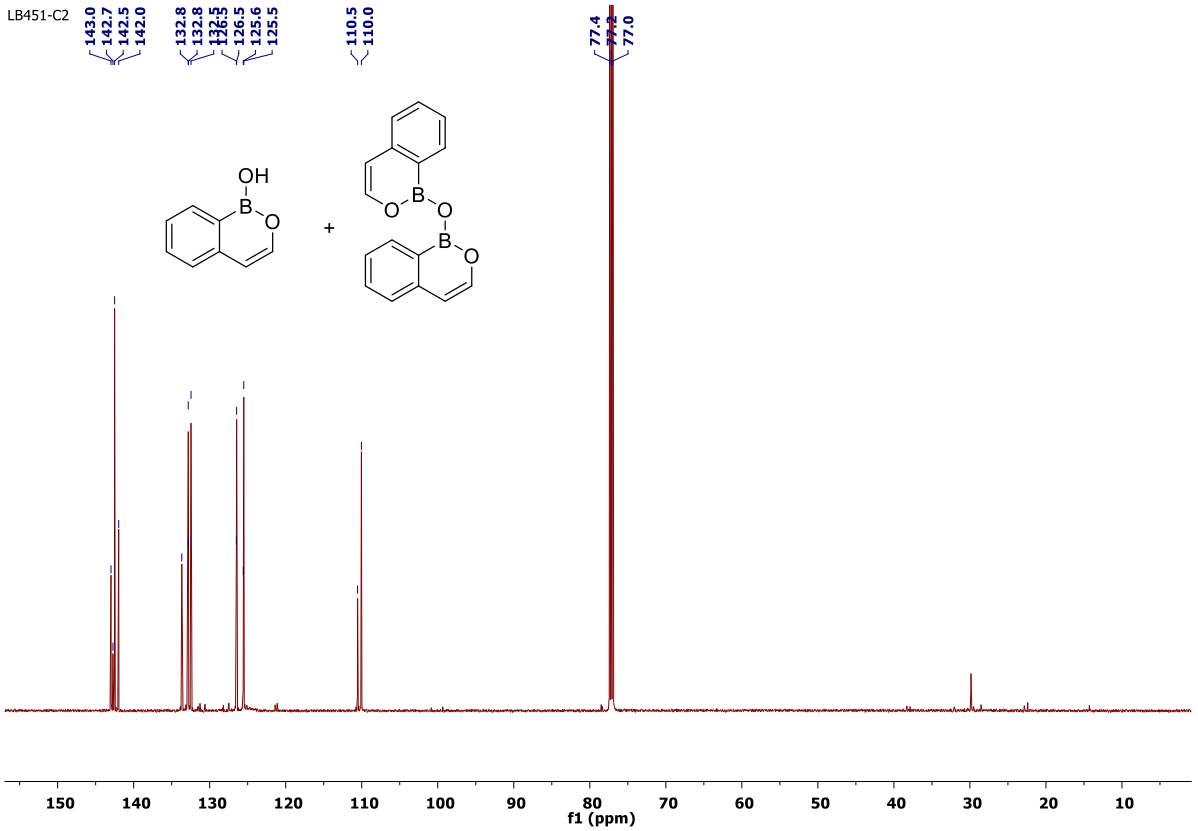




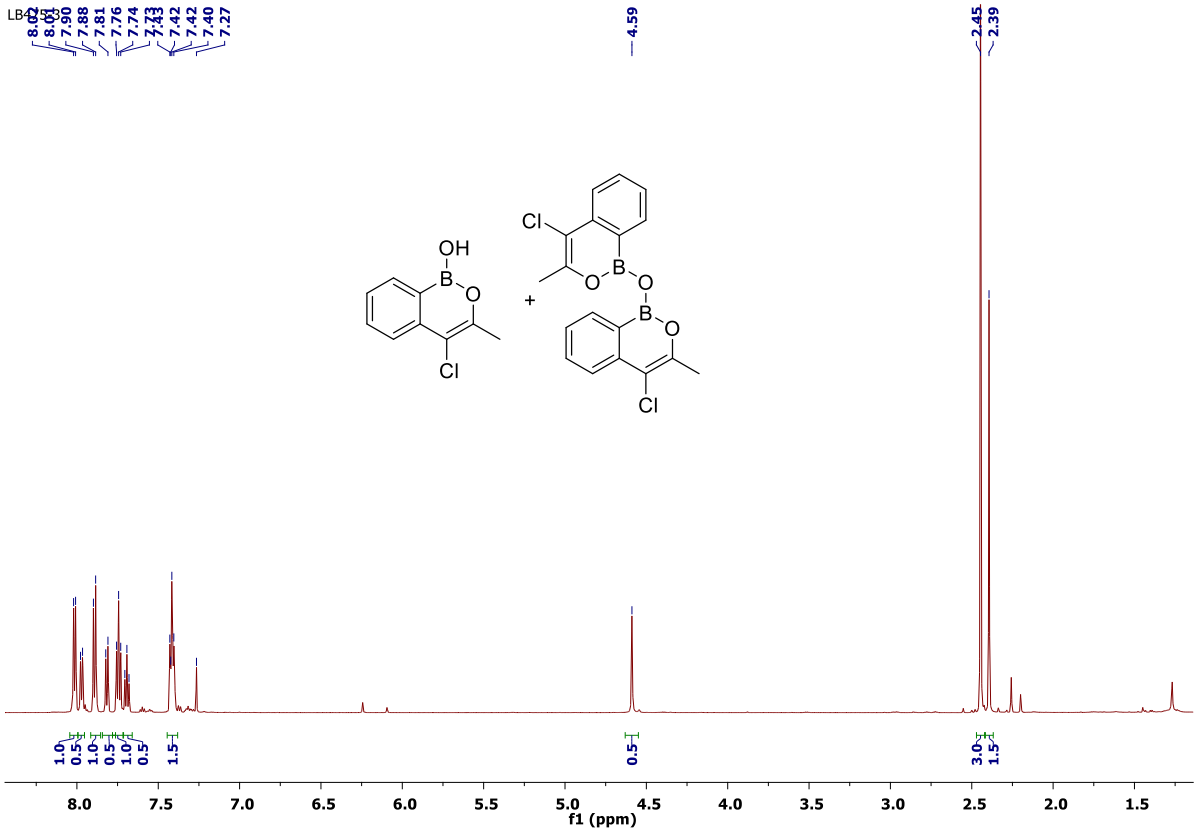
IV.2. Benzooxaborininols and halo-benzooxaborininols (2, 3, 4, 6)

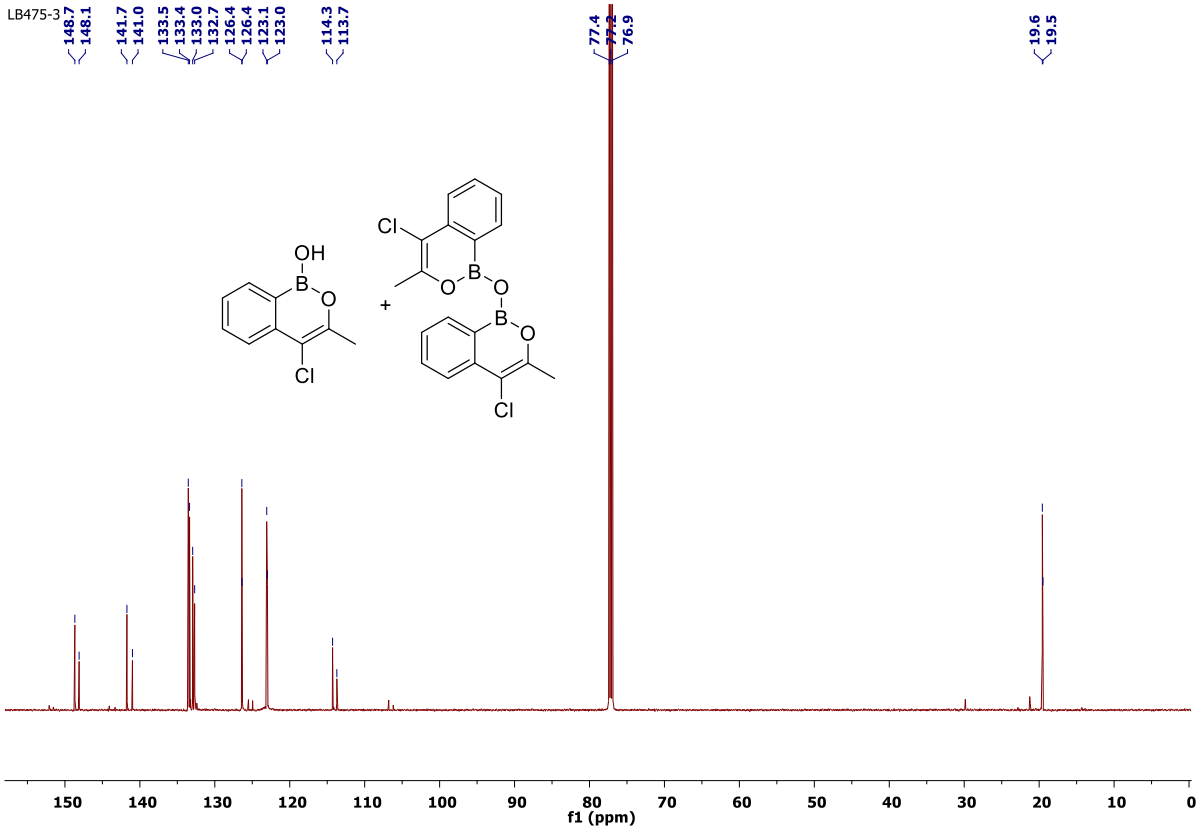
1*H*-Benzo[c][1,2]oxaborinin-1-ol (2a)



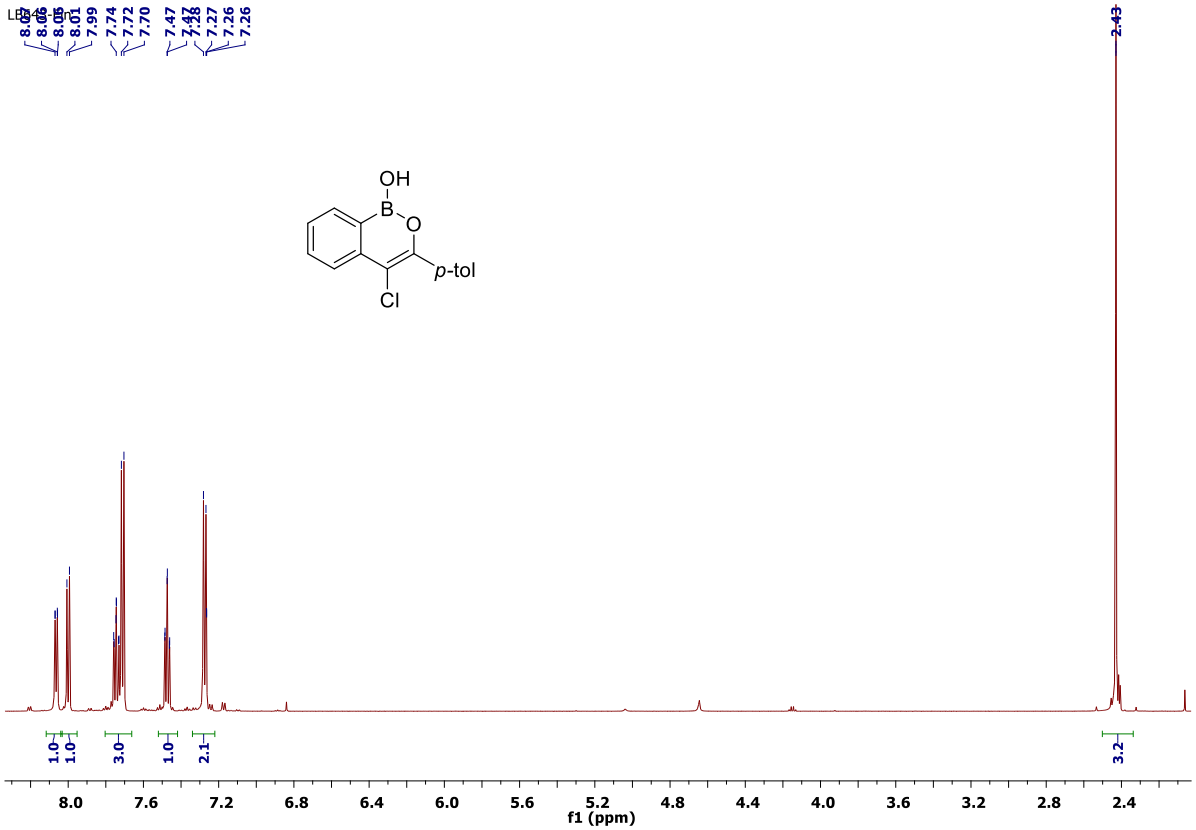


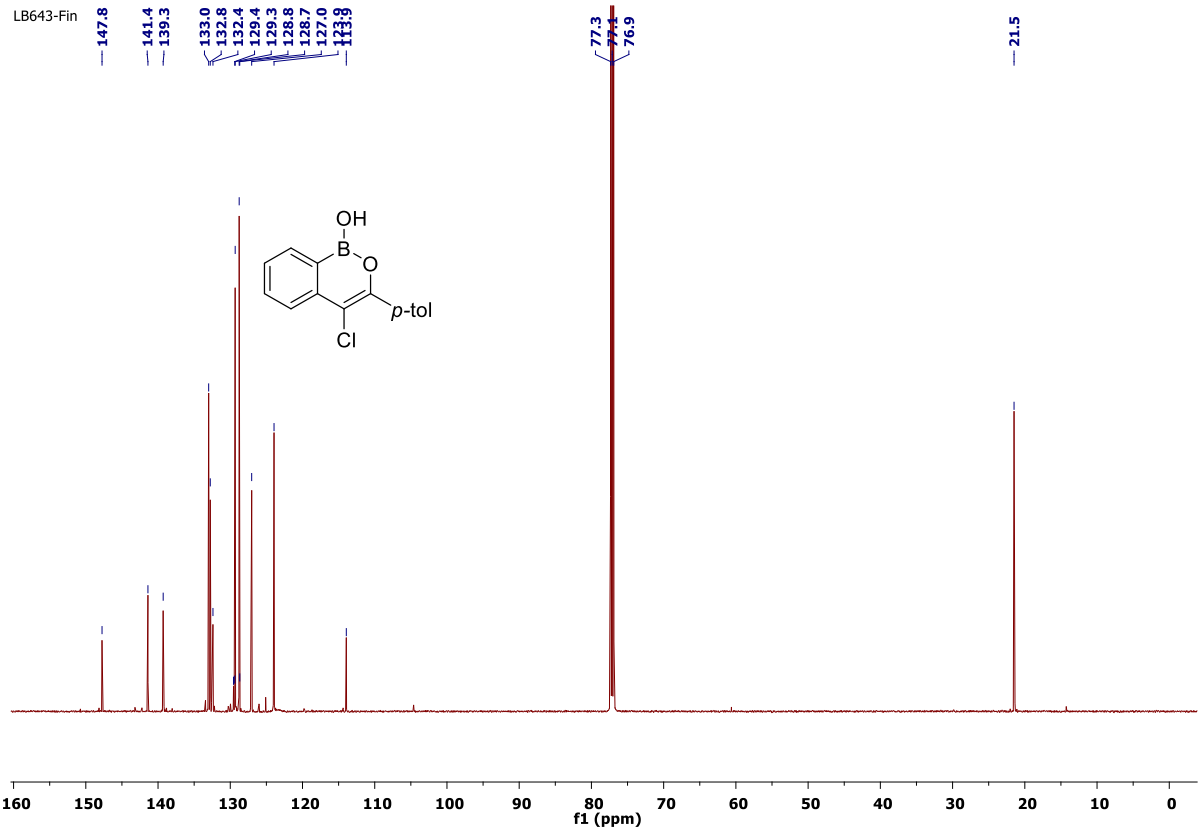
4-Chloro-3-methyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (3b)



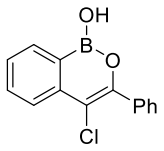


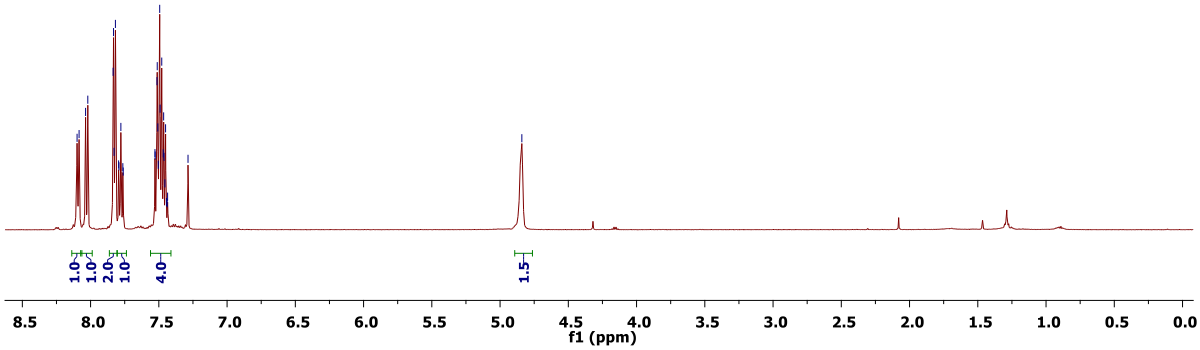
4-Chloro-3-(*p*-tolyl)-1*H*-benzo[c][1,2]oxaborinin-1-ol (3c)

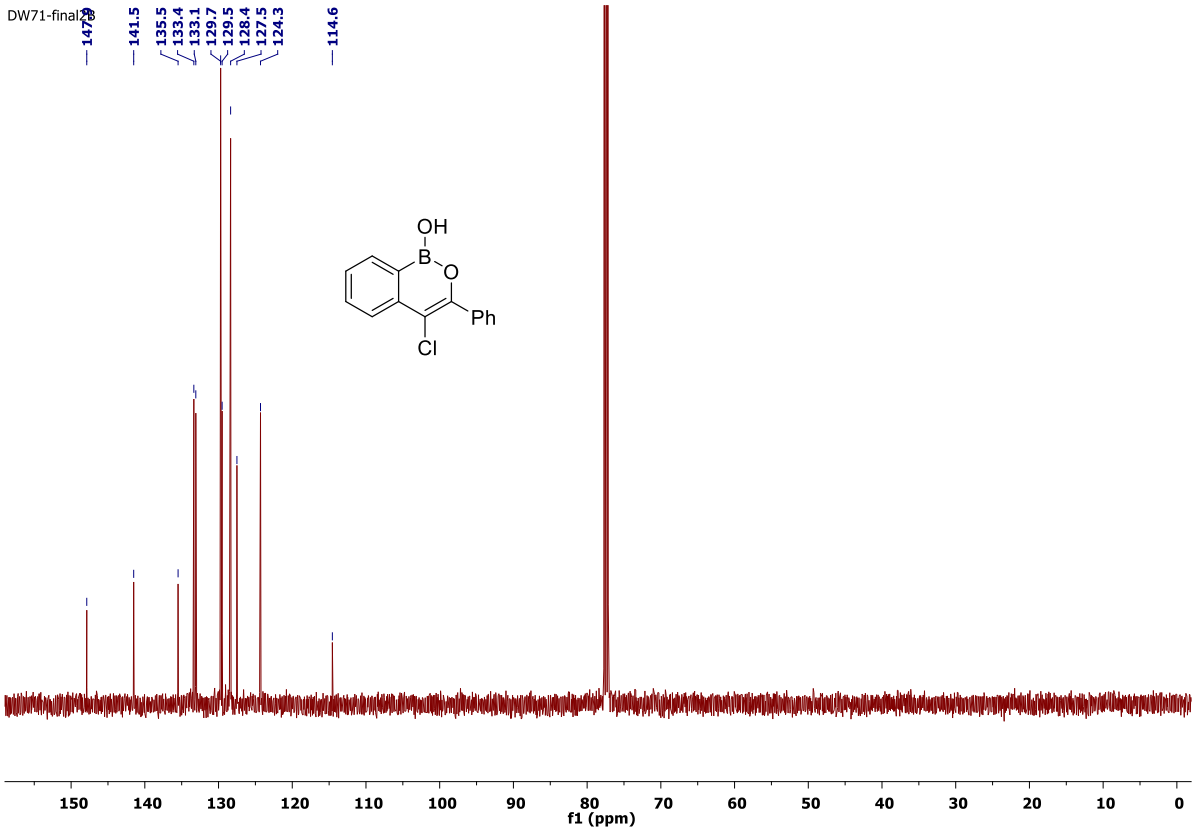




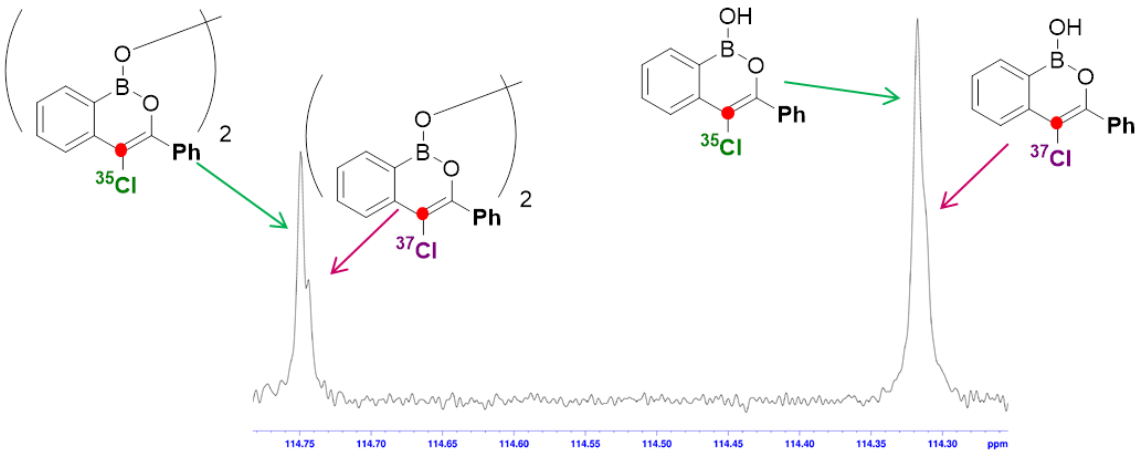
4-Chloro-3-phenyl-1H-benzo[c][1,2]oxaborinin-1-ol (3e)



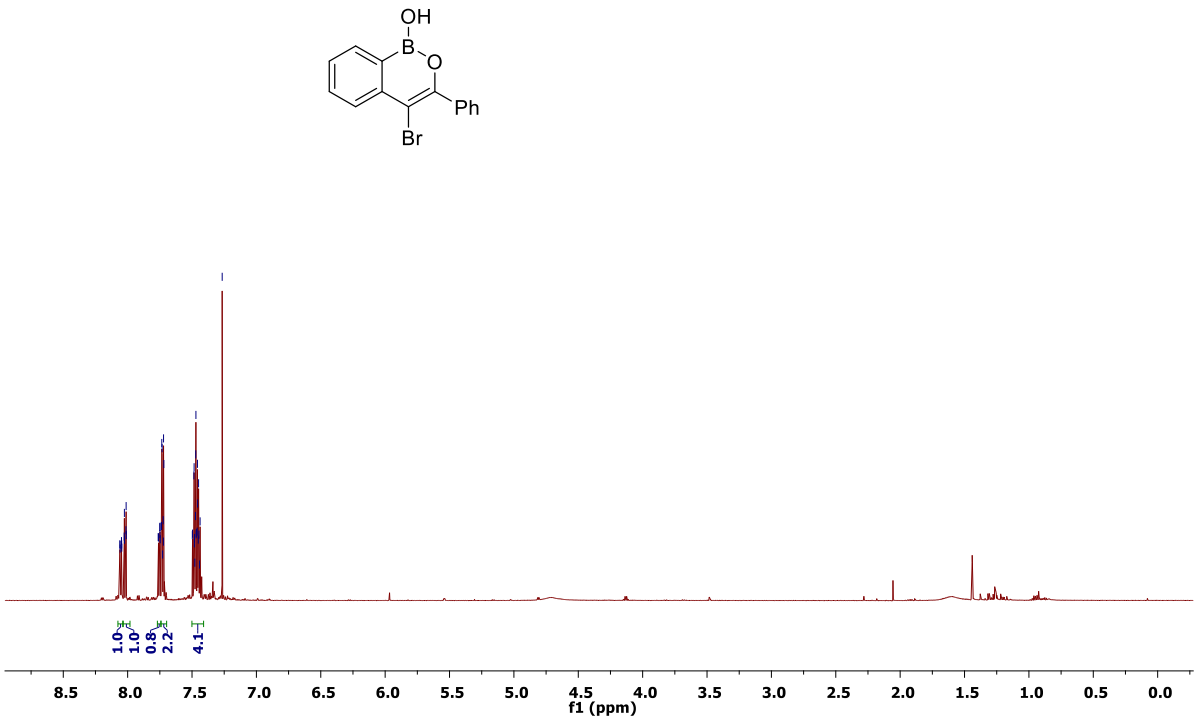


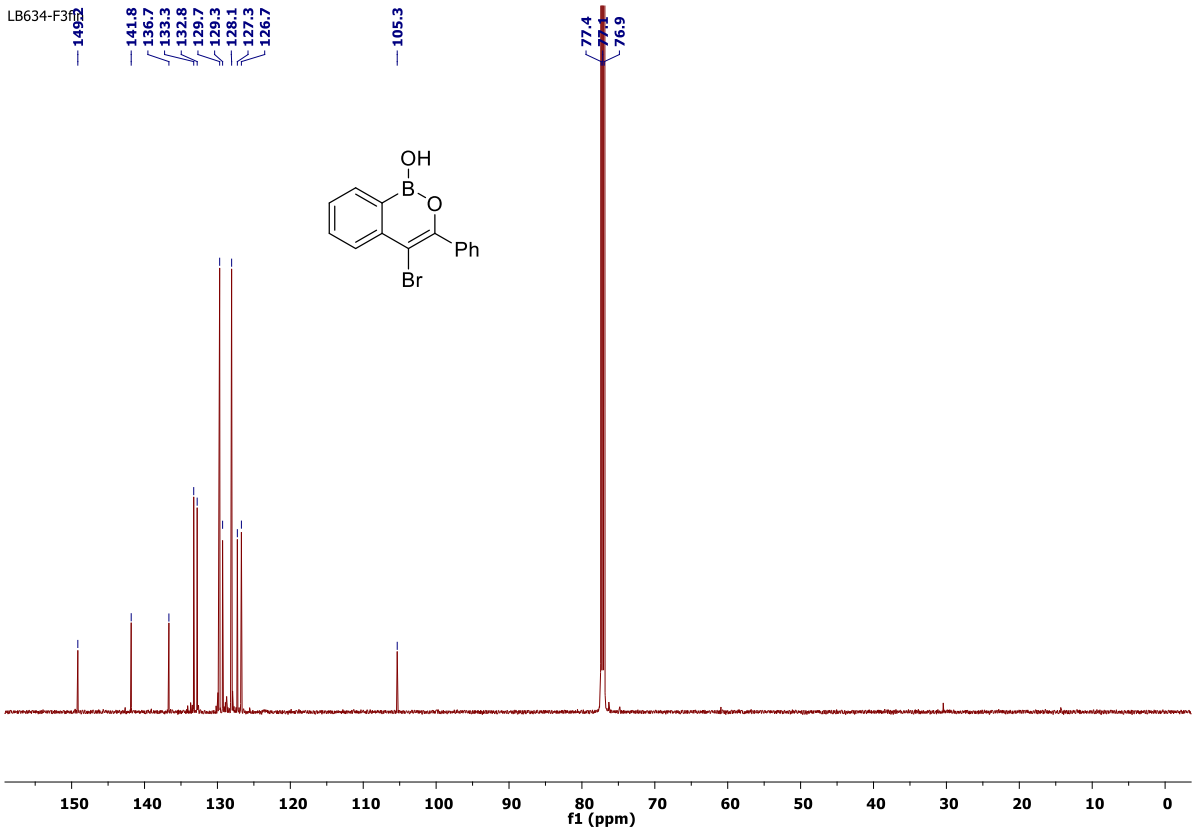


^{13}C NMR ($CDCl_3$, 150 MHz, R.T.): isotope effect [7]



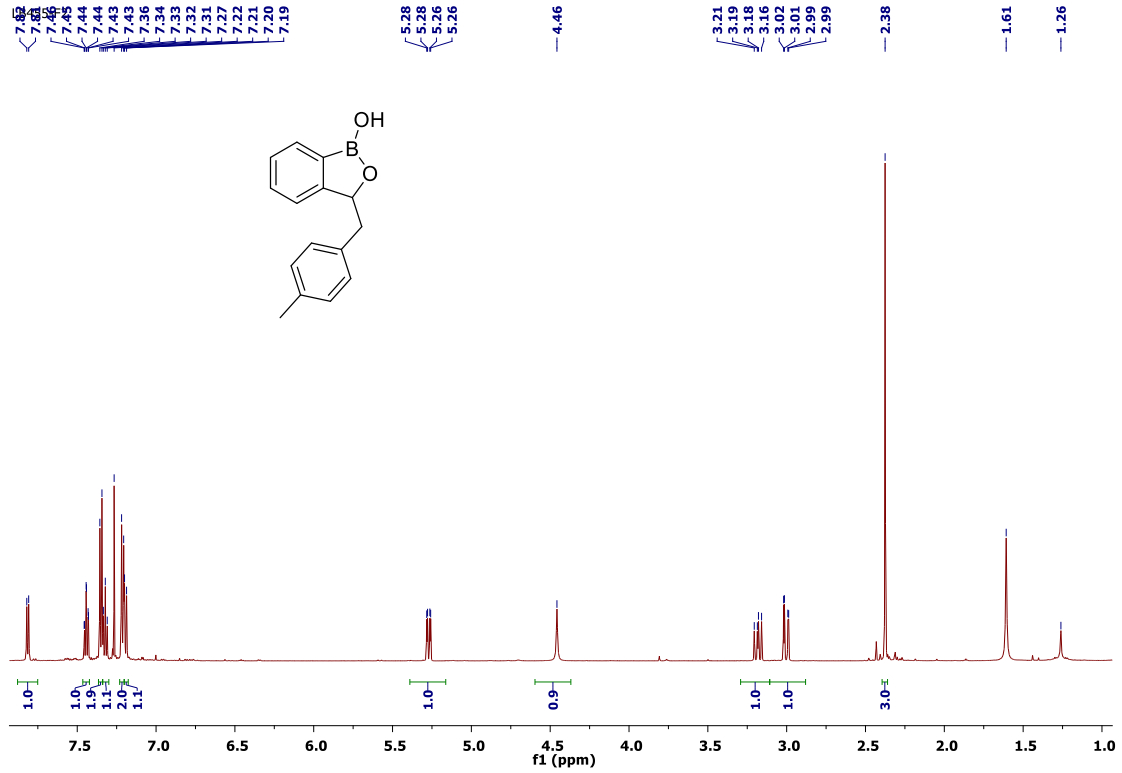
4-Bromo-3-phenyl-1H-benzo[c][1,2]oxaborinin-1-ol (6e)

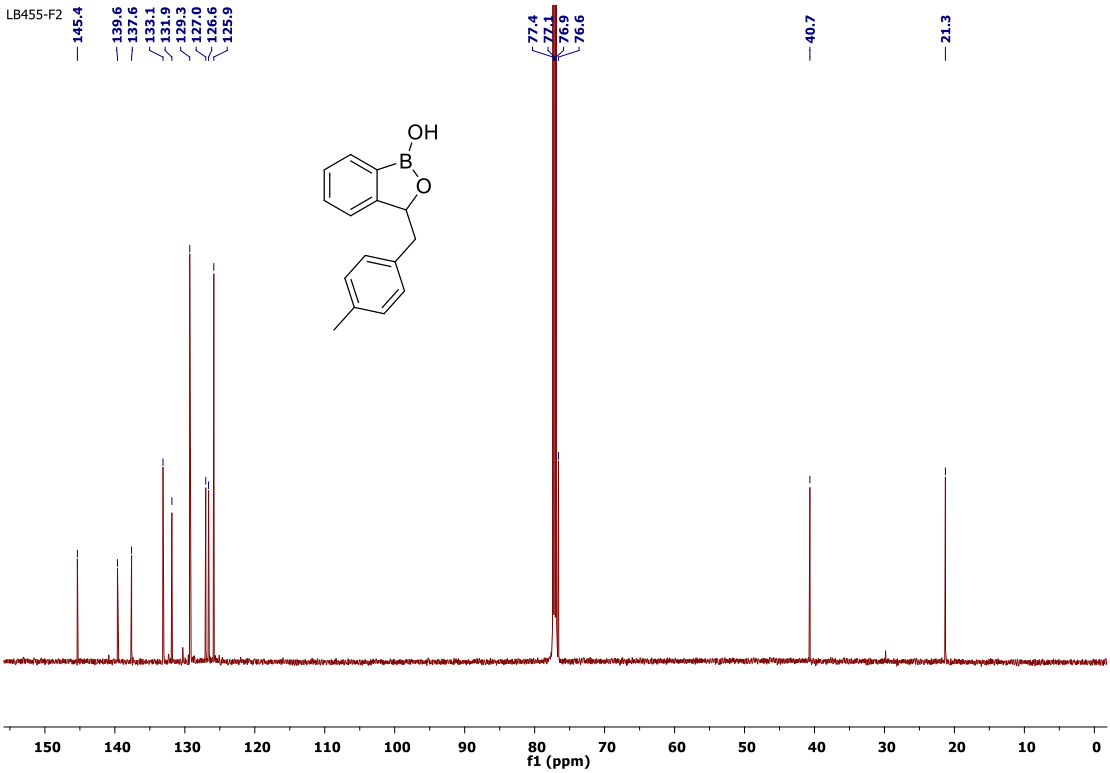




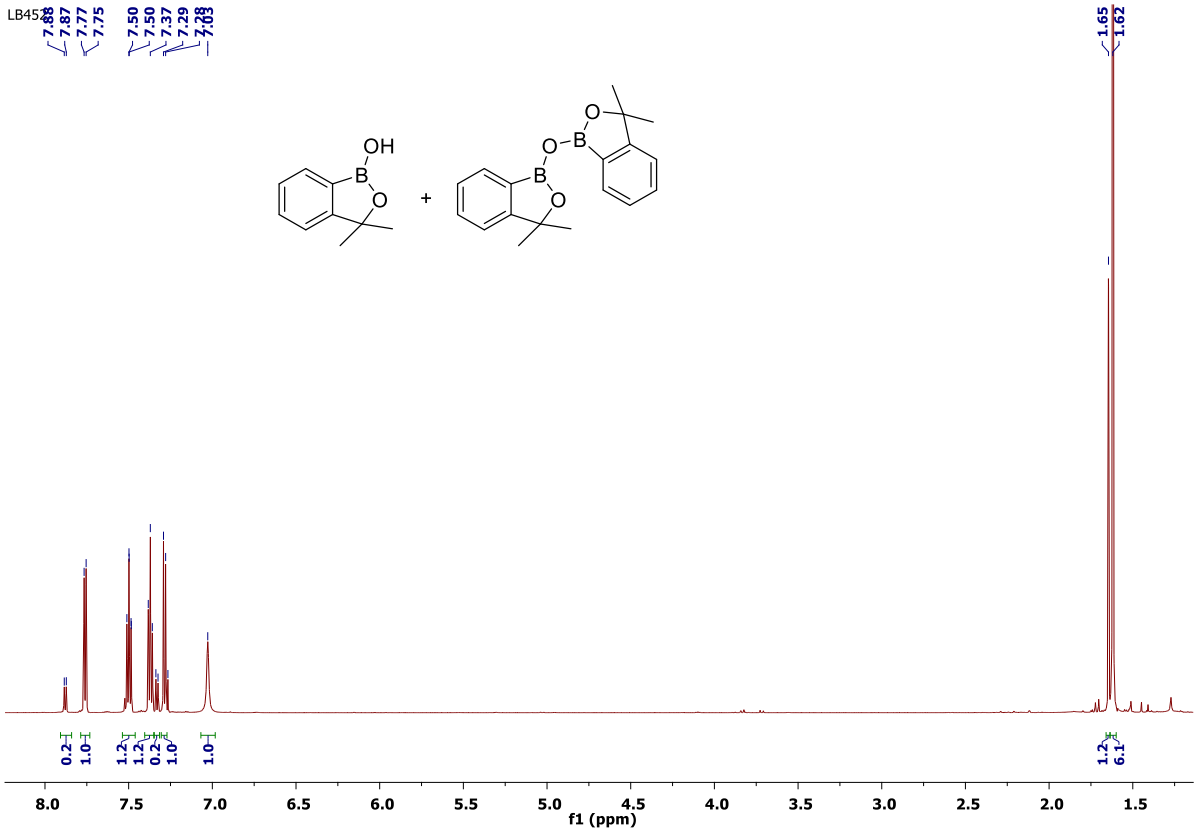
IV.3. Benzoxaboroles (4)

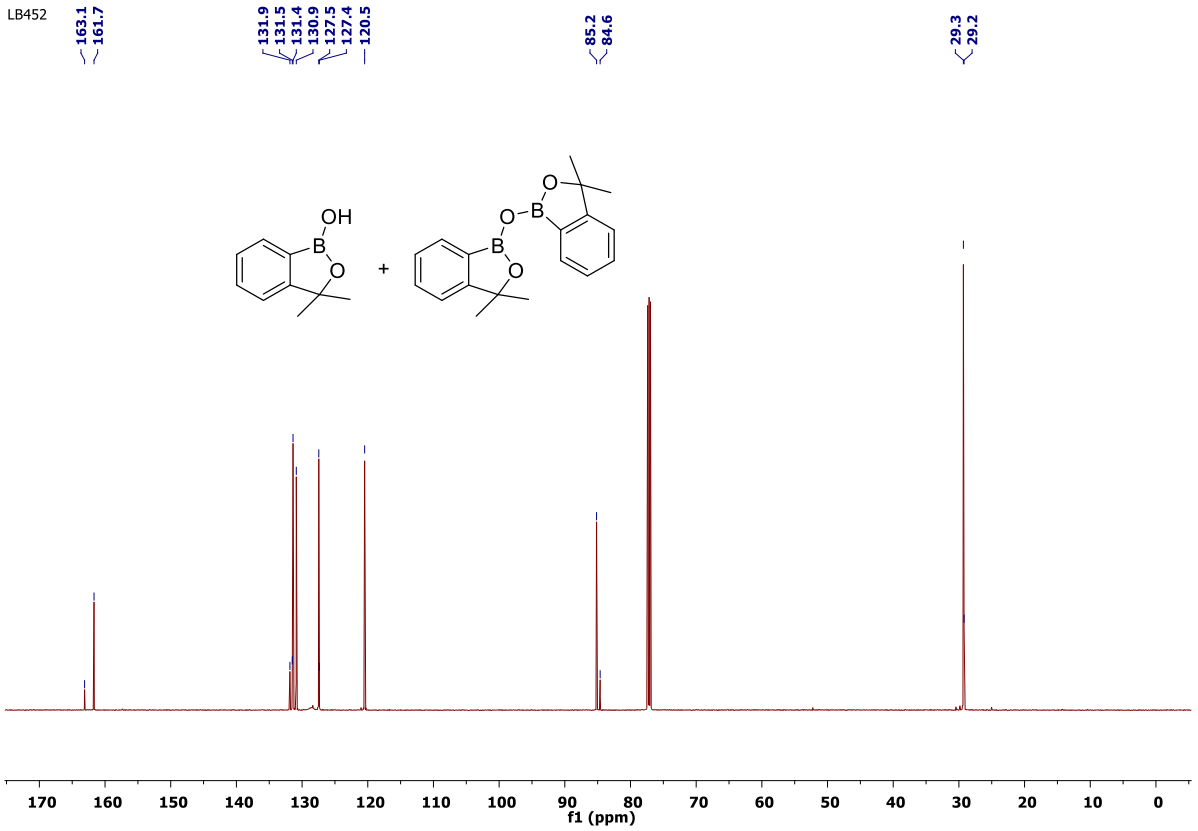
3-(4-Methylbenzyl)benzo[c][1,2]oxaborol-1(3*H*)-ol (4c)





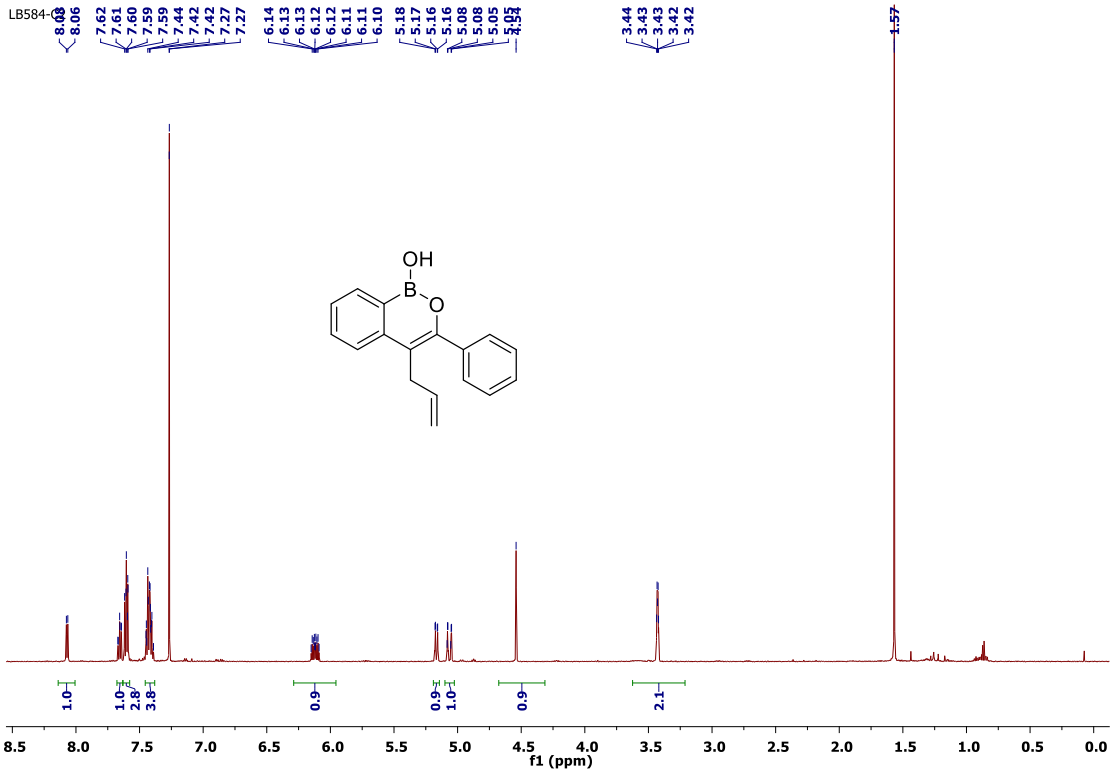
3,3-Dimethylbenzo[c][1,2]oxaborol-1(3*H*)-ol (4d)

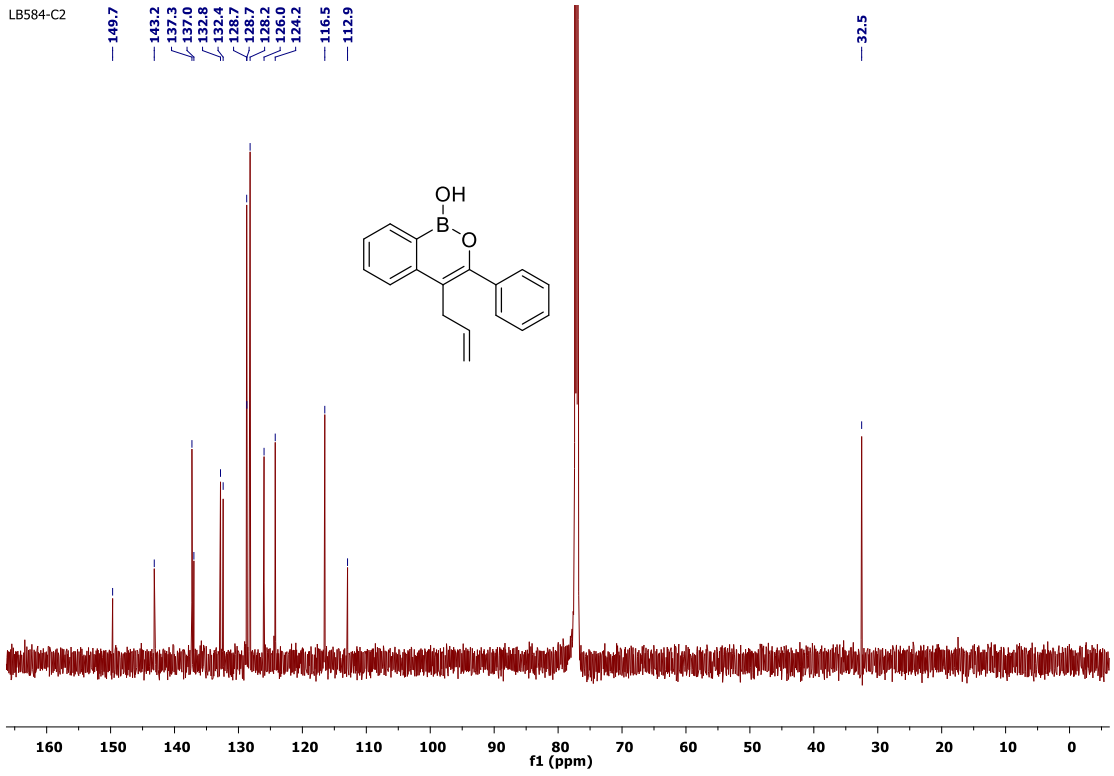




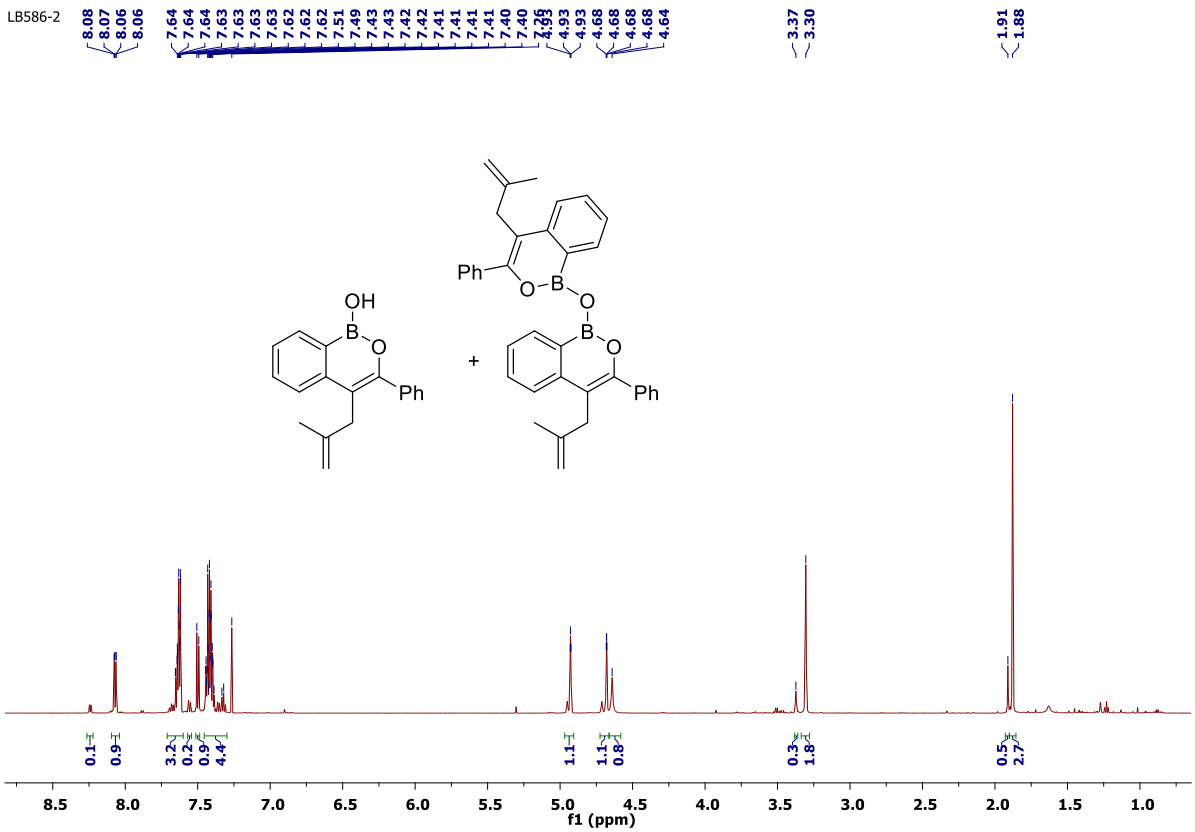
IV.4. Allyl-benzooxaborininols (9)

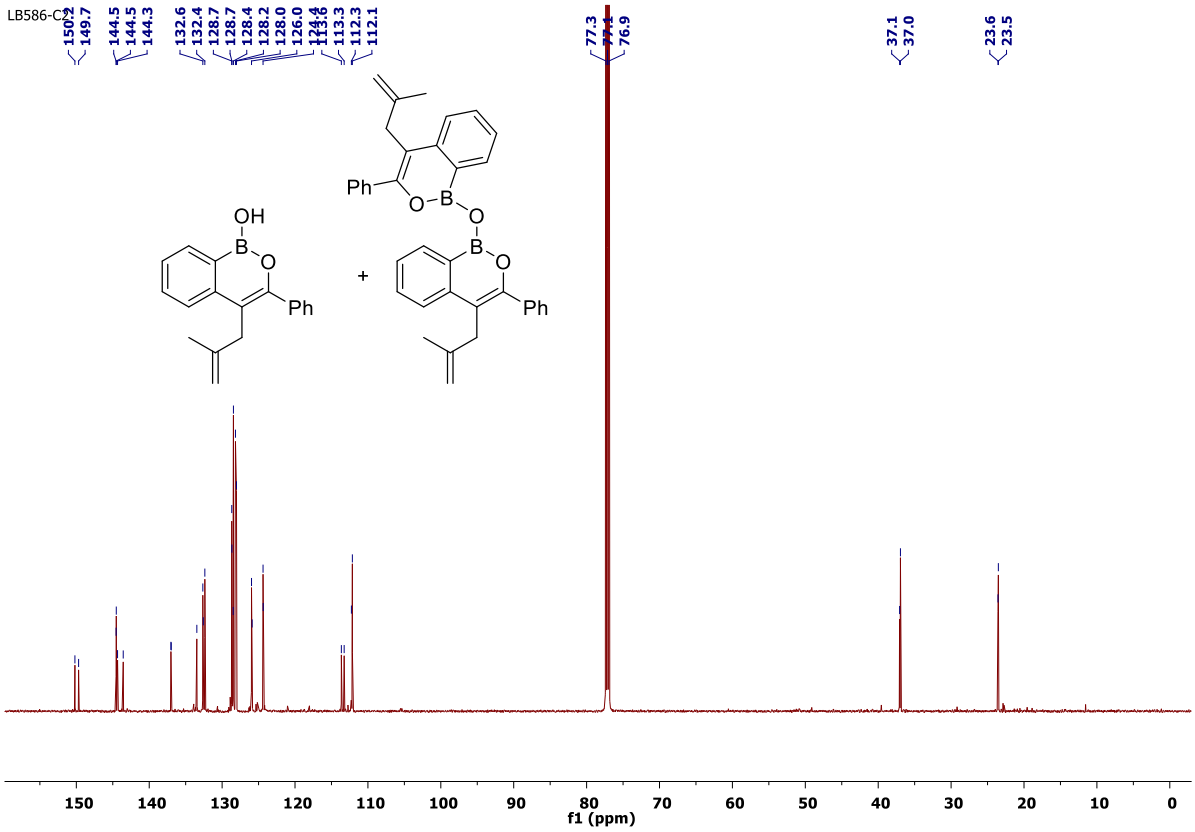
4-Allyl-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9a)



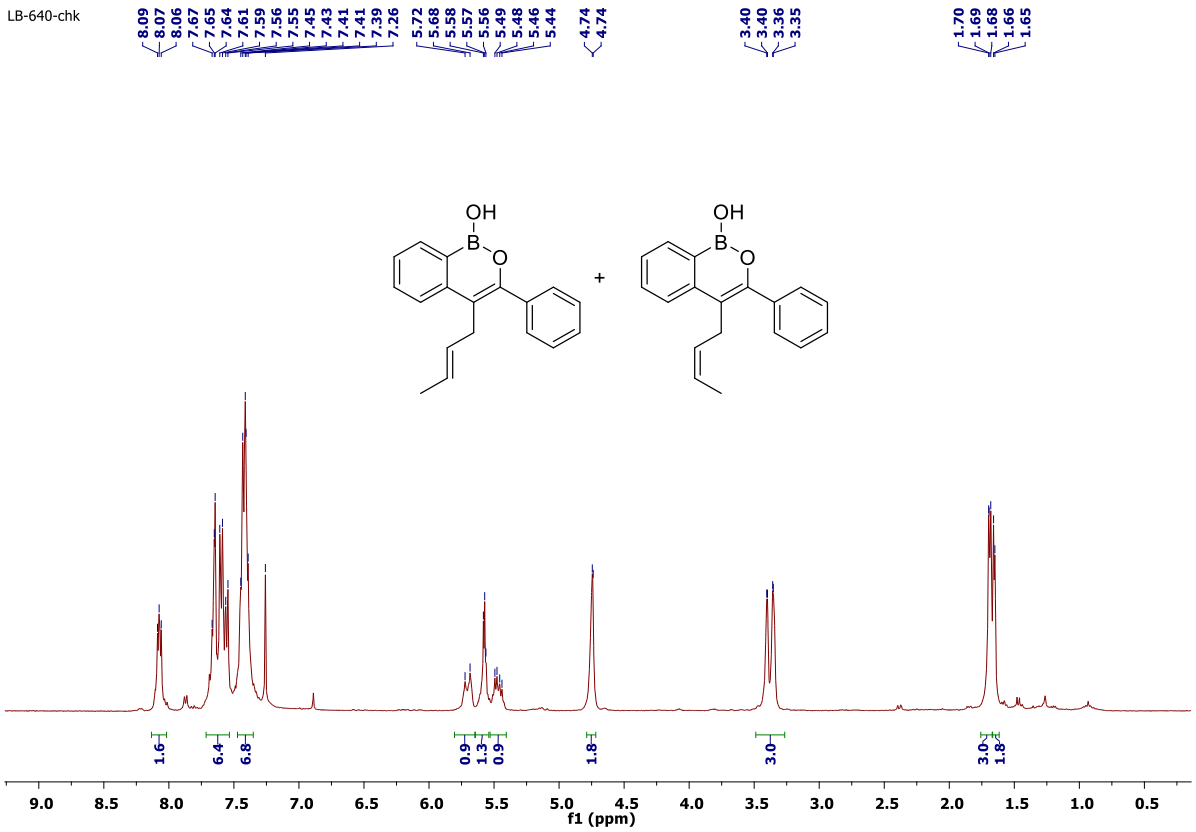


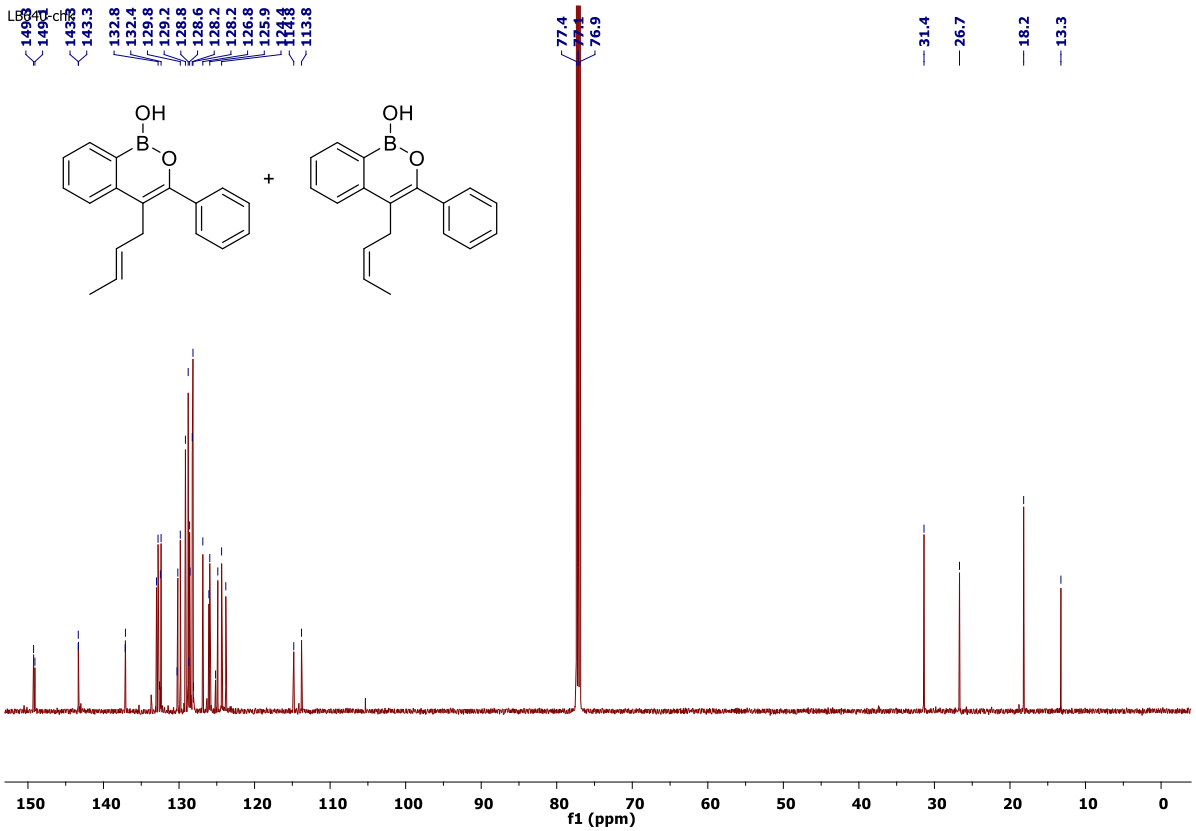
4-(2-Methylallyl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9b)



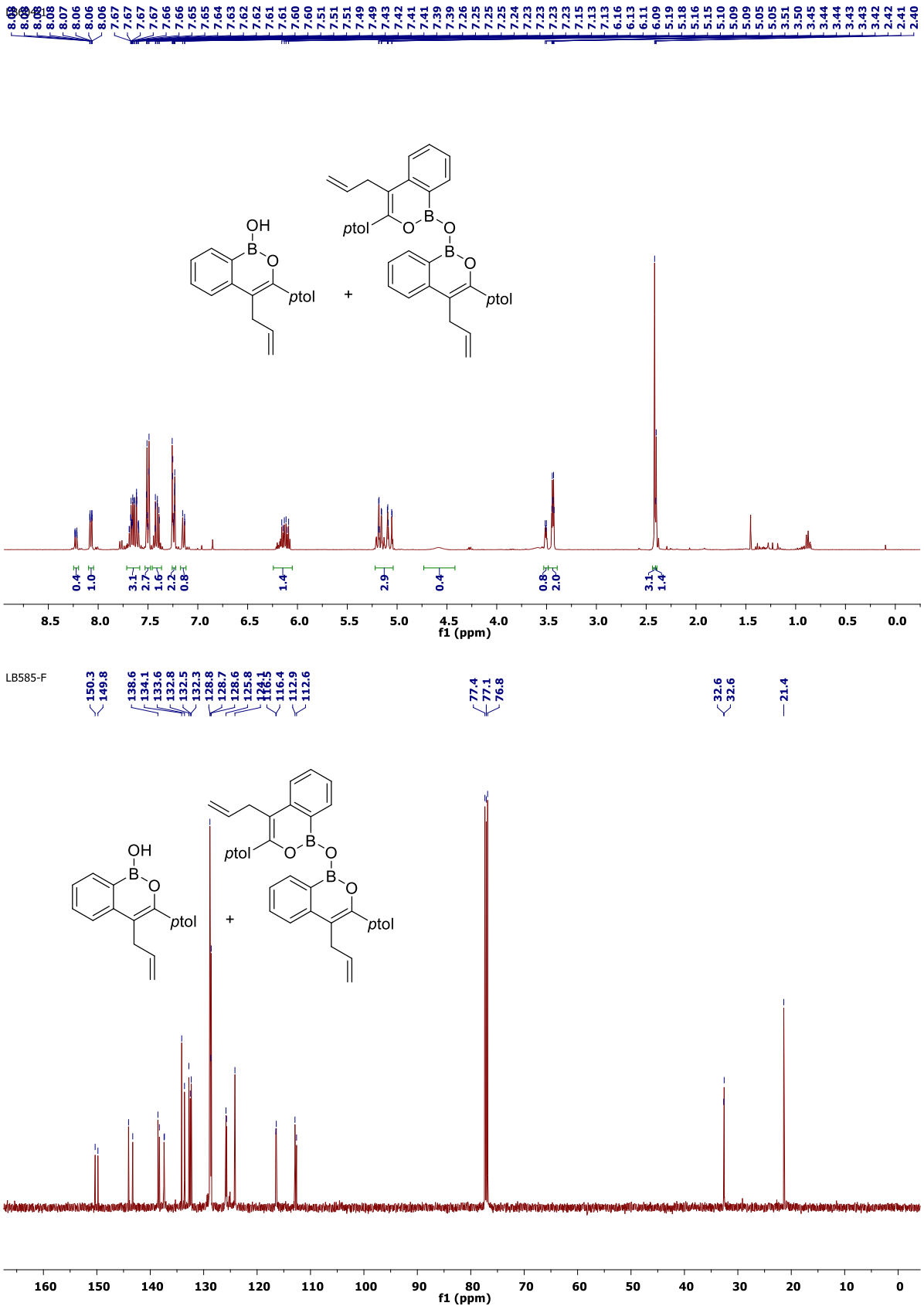


4-(But-2-en-1-yl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9c)

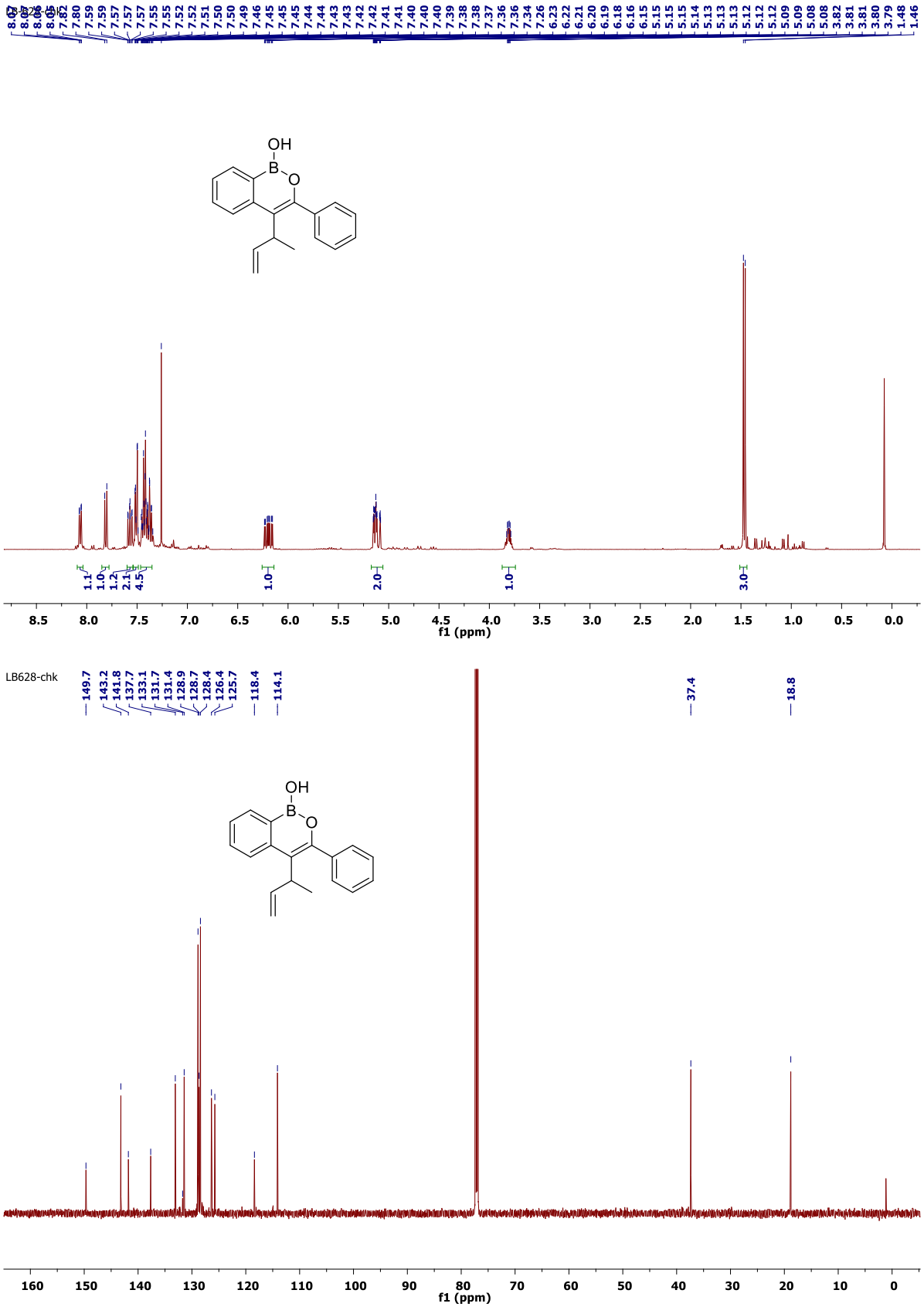




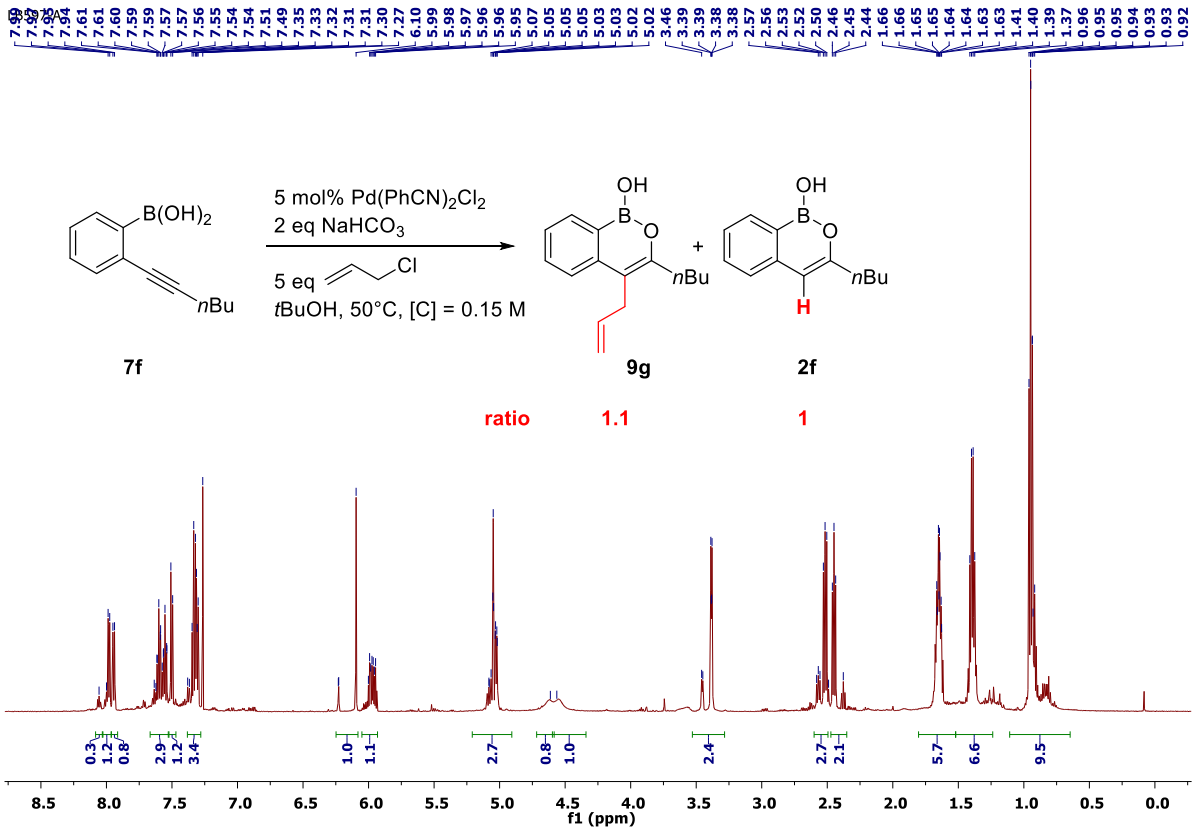
4-Allyl-3-(*p*-tolyl)-1*H*-benzo[c][1,2]oxaborinin-1-ol (9d)



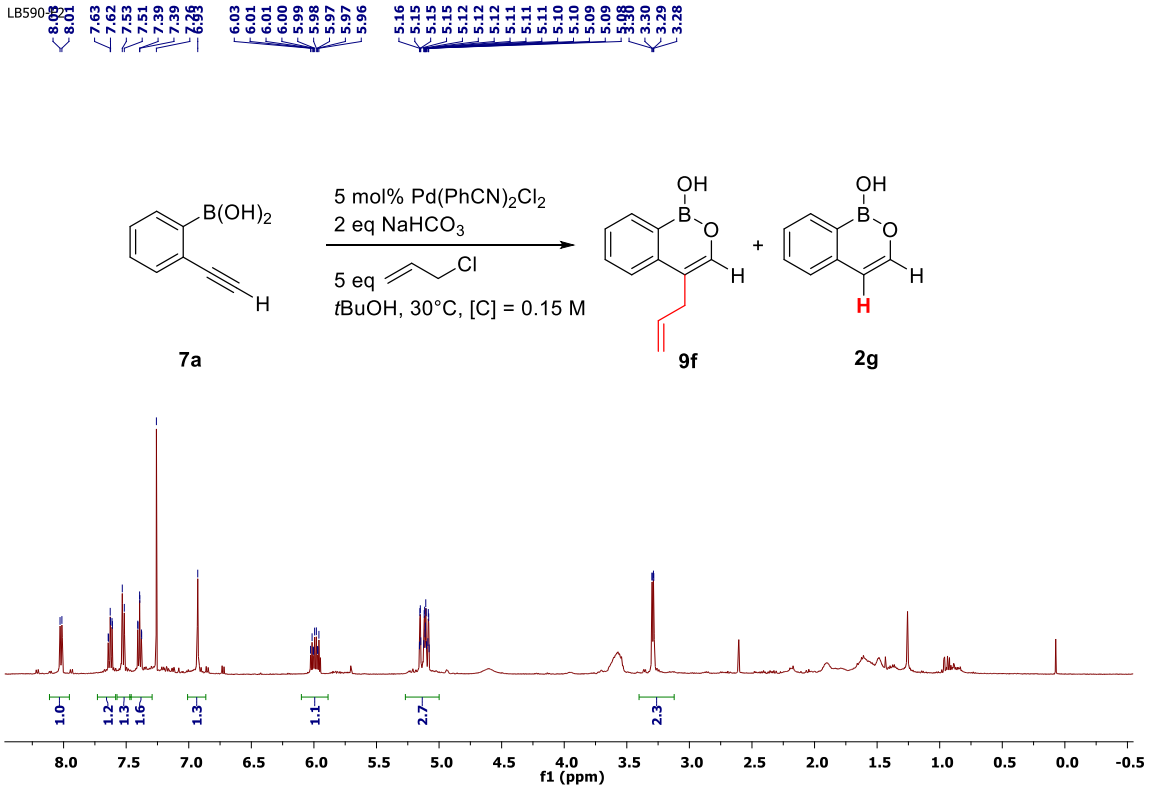
4-(But-3-en-2-yl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9e)



Application of Procedure E to (2-(Hex-1-yn-1-yl)phenyl)boronic acid

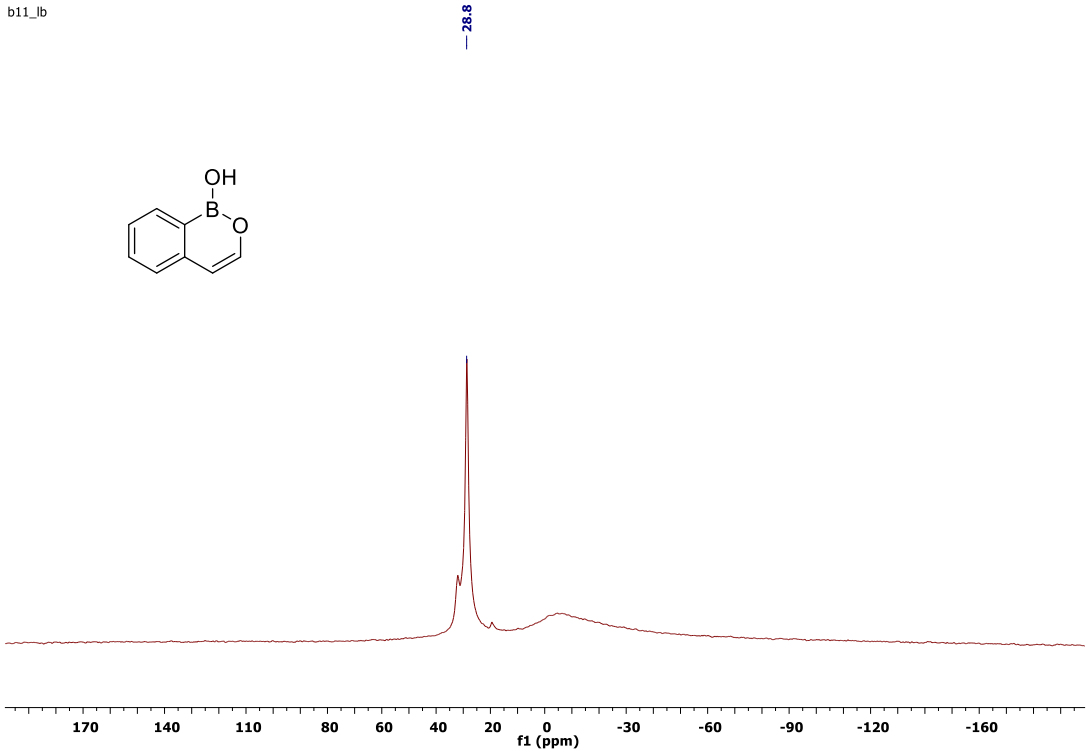


Application of Procedure E to (2-Ethynylphenyl)boronic acid

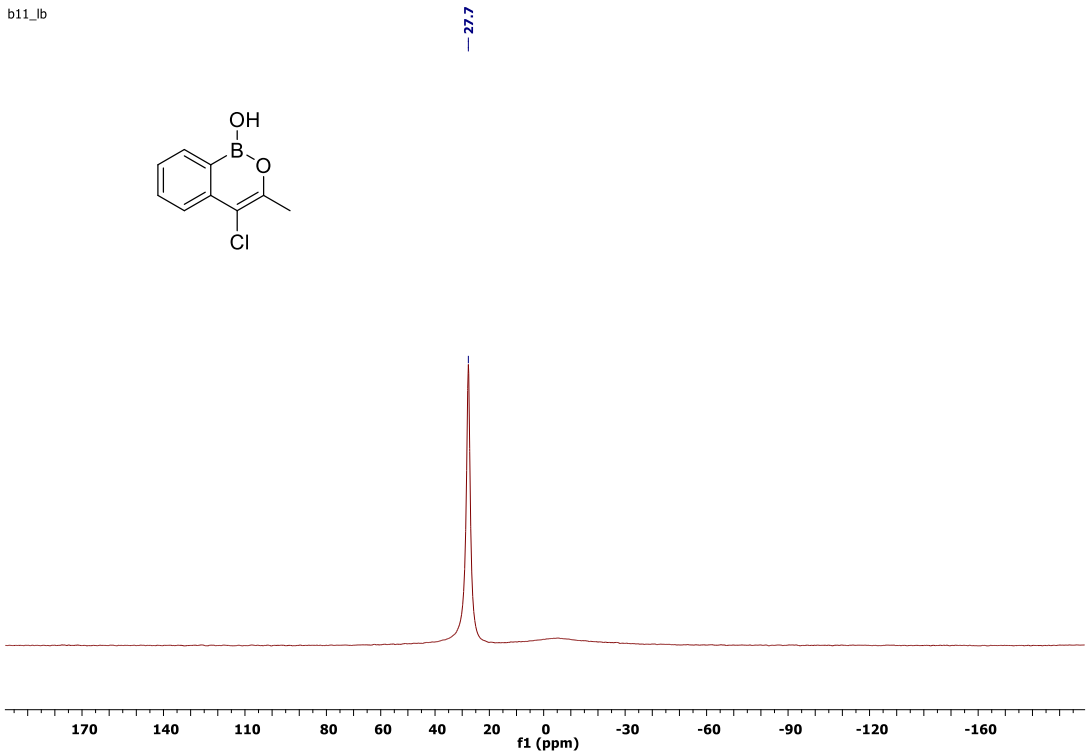


IV.5. Boron NMR spectra

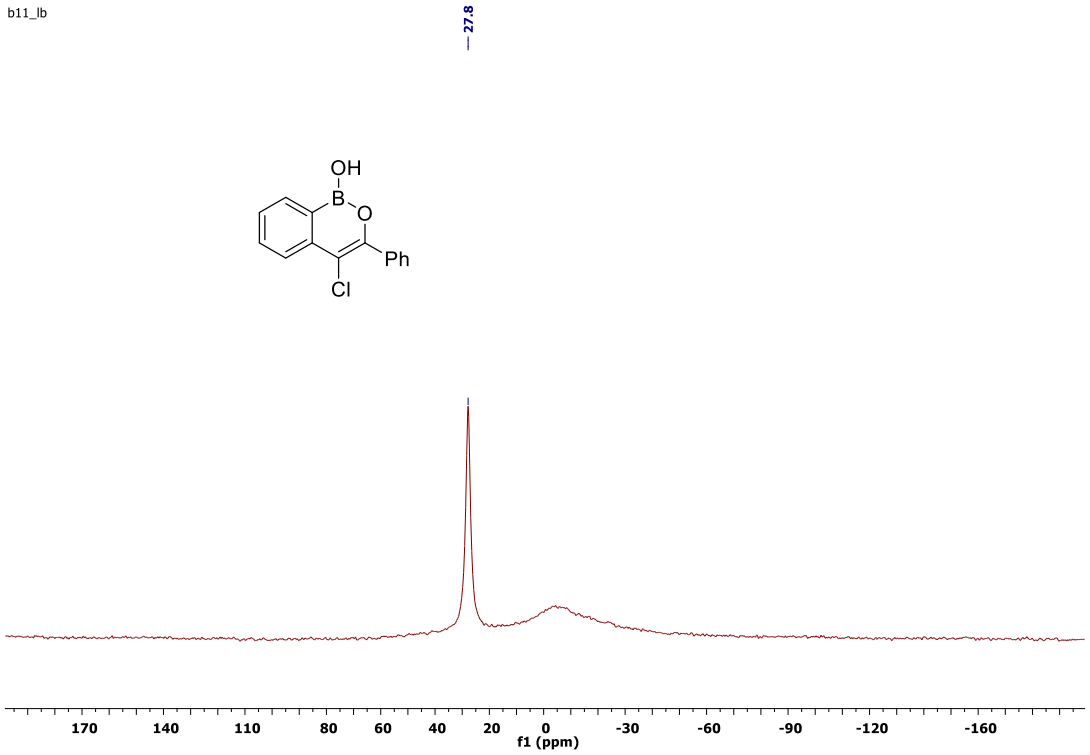
1*H*-Benzo[c][1,2]oxaborinin-1-ol (2a)



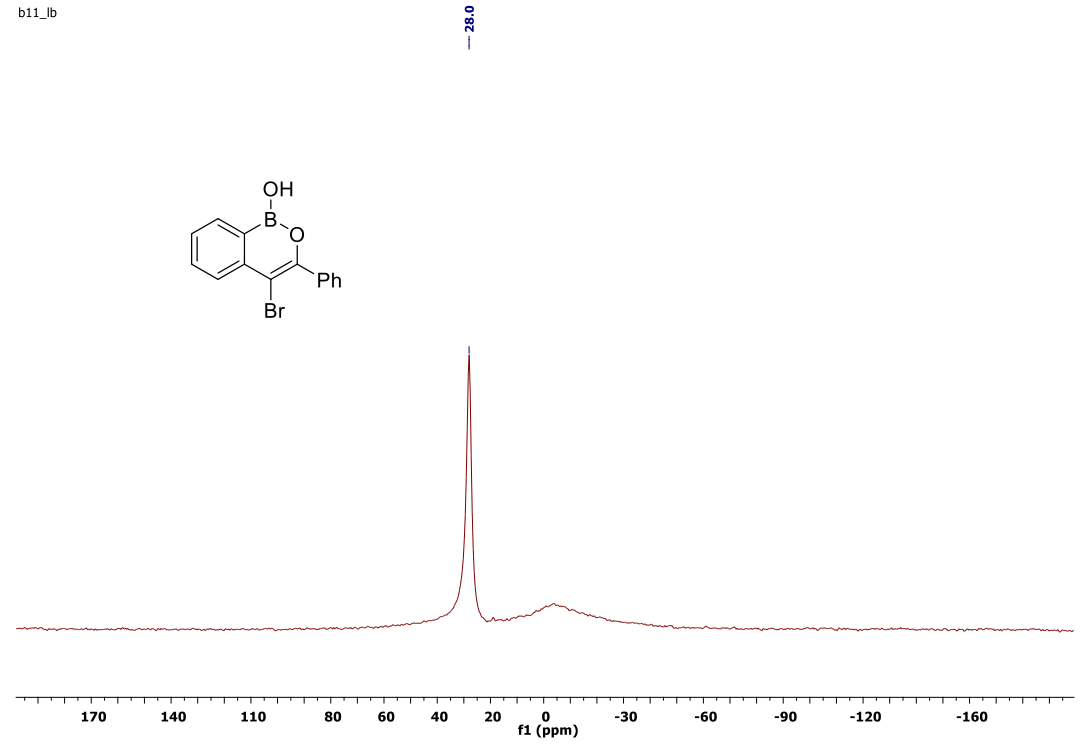
4-Chloro-3-methyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (3b)



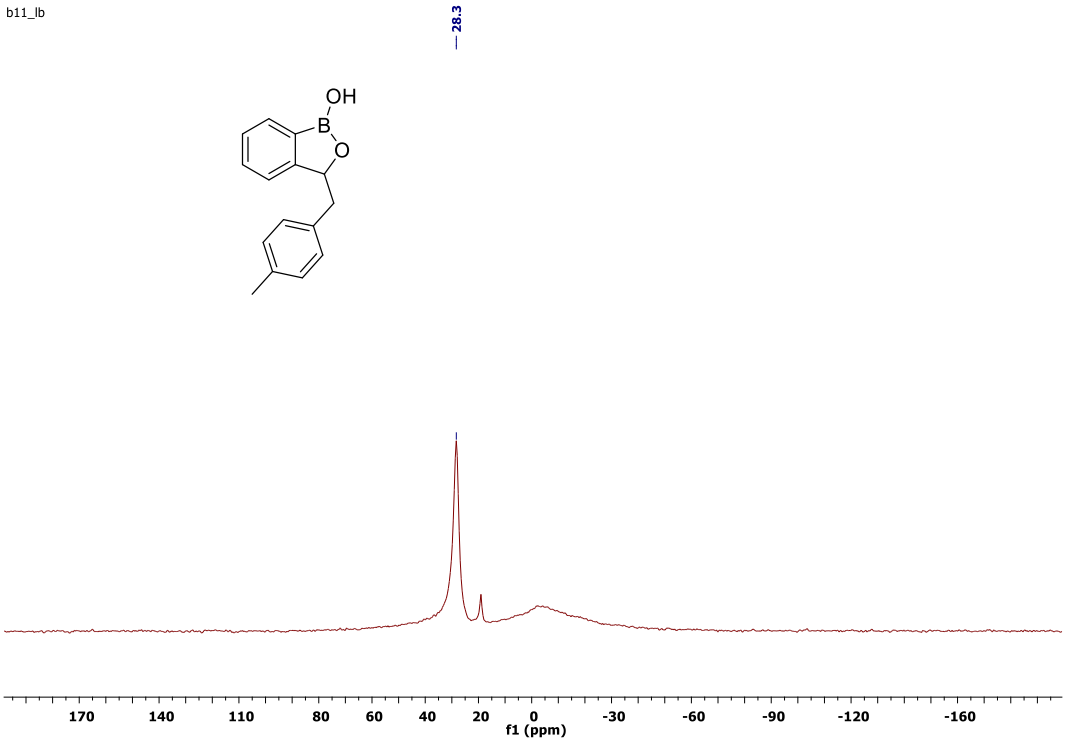
4-Chloro-3-phenyl-1H-benzo[c][1,2]oxaborinin-1-ol (3e)



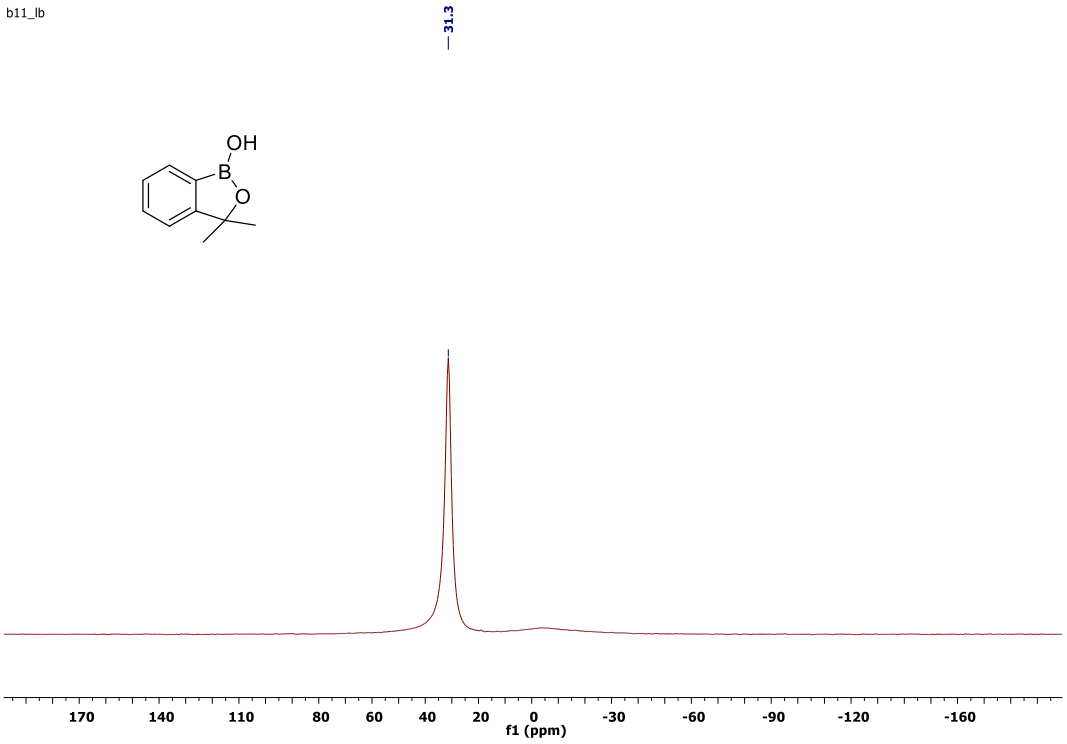
4-Bromo-3-phenyl-1H-benzo[c][1,2]oxaborinin-1-ol (6e)



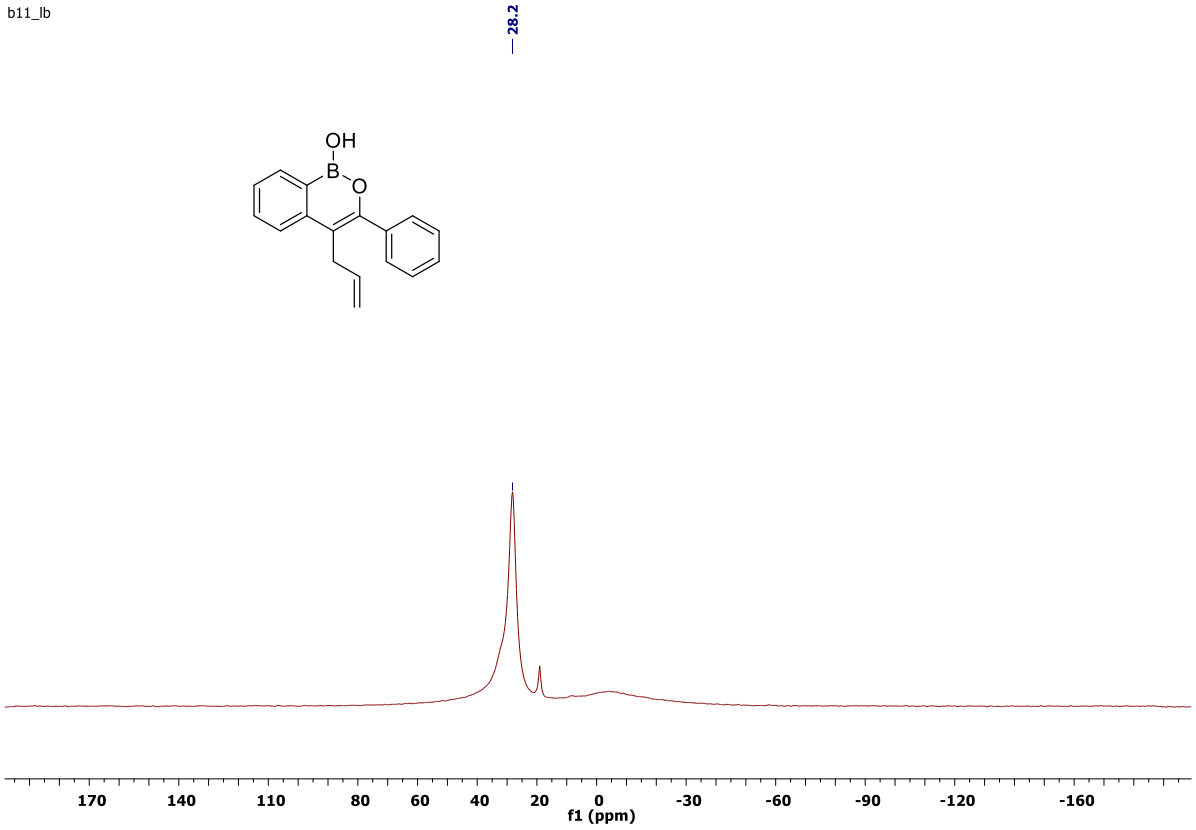
3-(4-Methylbenzyl)benzo[c][1,2]oxaborol-1(3*H*)-ol (4c)



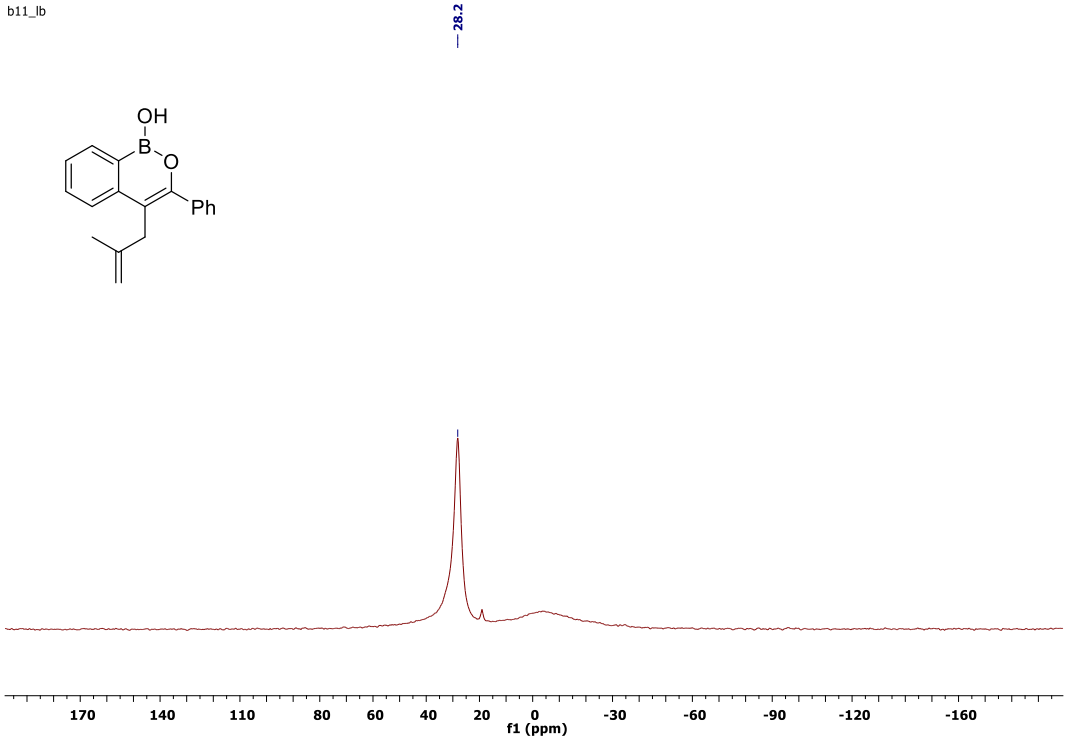
3,3-Dimethylbenzo[c][1,2]oxaborol-1(3*H*)-ol (4d)



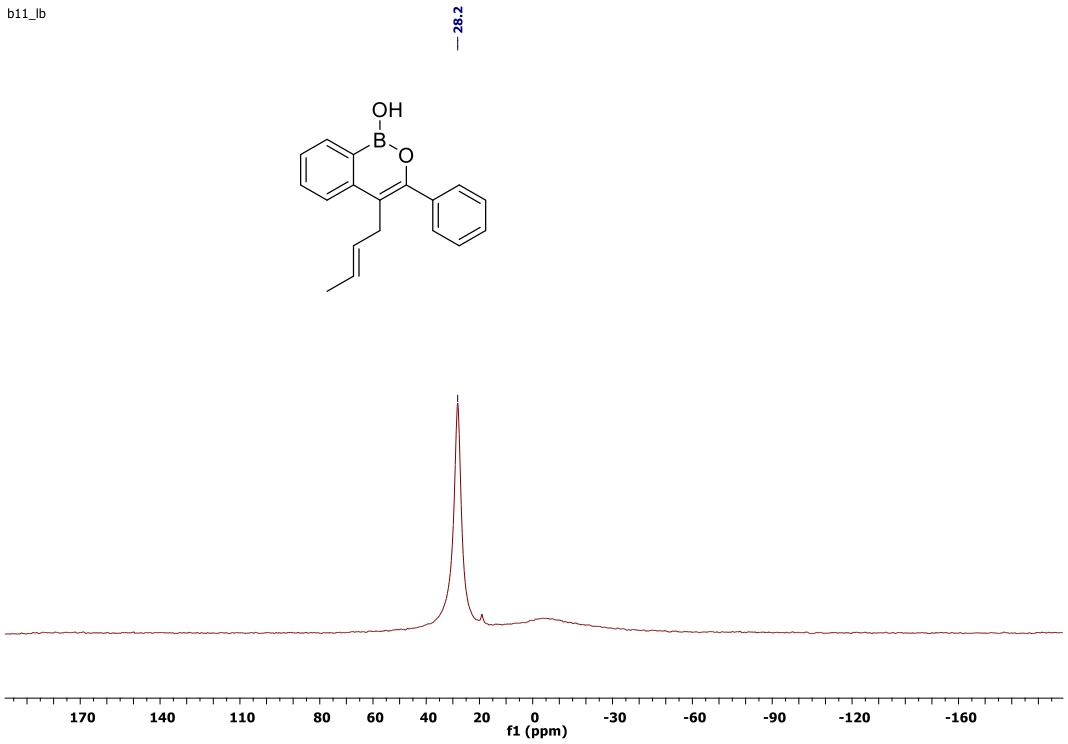
4-Allyl-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9a)



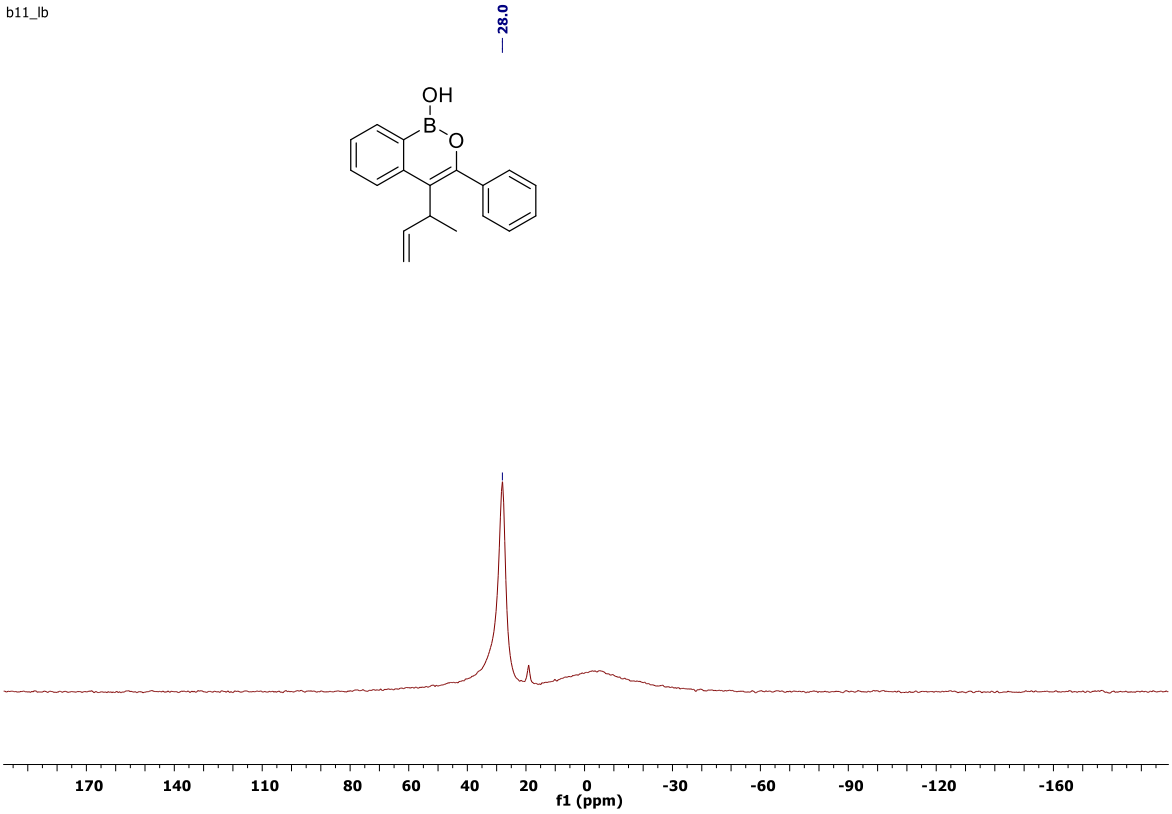
4-(2-Methylallyl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9b)



4-(But-2-en-1-yl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9c)



4-(But-3-en-2-yl)-3-phenyl-1*H*-benzo[c][1,2]oxaborinin-1-ol (9e)



V. Single crystal X-ray diffraction studies of compound 3e.

Single X-ray diffraction data was collected using an *Agilent SuperNova (Dual Source)* single crystal X-ray diffractometer equipped with an *Atlas CCD Detector*. The data were collected at 150 K using CuK_α radiation (λ = 1.54184 Å). The data were collected and processed using the *CrysAlisPro* program.[8] Empirical absorption correction was performed using spherical harmonics implemented in the *SCALE3 ABSPACK* scaling algorithm. Structure solution and refinement were accomplished using *SHELXS-97* and *SHELXL-97*, respectively.[9] The structure was solved using direct methods. All non-hydrogen atoms were refined anisotropically, while hydrogen atoms associated with carbon and oxygen atoms were refined isotropically in geometrically constrained positions.

Table 1. Crystallographic and refinement parameters for **3e**, as obtained by single crystal X-ray diffraction.

Empirical formula	$C_{14}H_{10}BClO_2$
M_r / g mol^{-1}	256.48
T / K	150.0(7)
Crystal system	triclinic
Space group	$P-1$
a / Å	7.1880(2)
b / Å	11.2966(3)
c / Å	15.7477(3)
α / °	84.309(2)
β / °	86.703(2)
γ / °	73.529(2)
V / Å^3	73.529(2)
Z	4
ρ_{calc} / g cm^{-3}	1.397
μ / mm^{-1}	2.674
F(000)	528.0
Crystal size / mm^3	0.20 × 0.14 × 0.08
Radiation	CuK_α (λ = 1.5418 Å)
Index ranges	$-8 \le h \le 8$, $-13 \le k \le 13$, $-18 \le l \le 18$
Reflections collected	17205
Independent reflections	4305 [R_{int} = 0.0221, R_{sigma} = 0.0173]
Data, restraints, parameters	4305, 0, 327
Goodness-of-fit on F^2	1.026
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0290, wR_2 = 0.0776
Final R indexes [all data]	R_1 = 0.0309, wR_2 = 0.0793
Largest diff. peak:hole : e Å^{-3}	0.234, −0.226

CCDC deposition number 1479176

VI. References

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[2] G. Chen, J. Gui, L. Li, and J. Liao, *Angew. Chem. Int. Ed*, 2011, **50**, 7681.

[3] K. Gerdes, P. Sagar, R. Fröhlich, B. Wibbeling, and E. U. Würthwein, *Eur. J. Org. Chem.*, 2004, 3465.

[4] I. Nakamura, T. Sato, M. Terada, and Y. Yamamoto, *Org. Lett.*, 2007, **9**, 4081.

[5] J. R. Falck, M. Bondlela, S. K. Venkataraman, and D. Srinivas, *J. Org. Chem.*, 2001, **8**, 7148.

[6] T. Glinka, R. Higuchi, H. Scott, B. Eastman, and O. Rodny, WO2012109164A1, 2012.

[7] The observed splitting in the ^{13}C spectrum is 5±1 ppb, which is in agreement with the magnitude of the one-bond $^{35}Cl/^{37}Cl$ effect reported previously in A.E. Aliev and K.D.M. Harris, *Magn. Reson. Chem.*, 1993, **31**, 54.

[8] CrysAlisPro, Agilent Technologies, Version 1.171.36.28 (release 01-02-2013 CrysAlis171 .NET).

[9] G. M. Sheldrick, *Acta Crystallogr. A.* **2008**, *64*, 112–122.