SUPPORTING INFORMATION

Regioselective *trans*-Carboboration of Propargyl Alcohols

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SUPPORTING CRYSTALLOGRAPHIC DATA

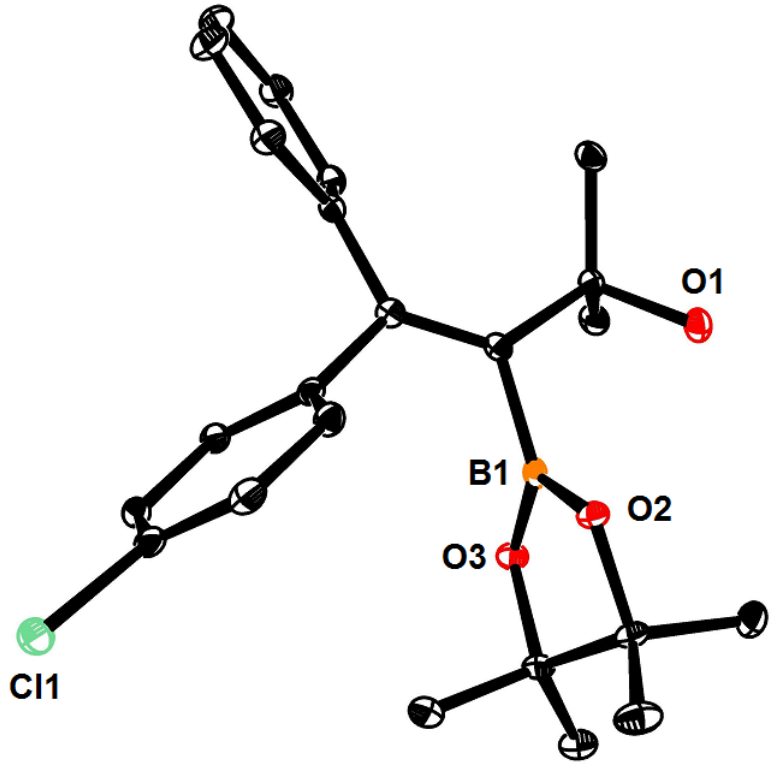


Figure S1. Structure of compound **5b** in the solid state; only one of two independent molecules present in the unit cell is shown for clarity

X-ray Crystal Structure Analysis of 5b: ($C_{23}H_{28}BClO_3$), M_r = 398.71 g·mol^{-1}, colorless plate, crystal size 0.327 x 0.298 x 0.050 mm^3, triclinic, space group $P\bar{1}$, a = 9.8066(2) Å, b = 10.5520(3) Å, c = 21.6009(6) Å, α = 103.3530(10)°, β = 92.0280(10)°, γ = 99.6610(10)°, V = 2137.56(10) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.239 g·cm^3, λ = 1.54178 Å, μ(*Cu-K*$_\alpha$) = 1.736 mm^{-1}, Gaussian absorption correction (T_{min} = 0.63, T_{max} = 0.93), Bruker AXS X8 Proteum diffractometer, 4.900 < θ < 72.472°, 40538 measured reflections, 7914 independent reflections, 6551 reflections with $I > 2\sigma(I)$, R_{int} = 0.0529.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.047 [$I > 2\sigma(I)$], wR_2 = 0.112, 561 parameters. Several low-angle reflections were shadowed by the beamstop and were omitted before the final refinement cycles.

The H atoms were refined using a rotational group riding model, S = 1.028, residual electron density 0.3/–0.5 e Å^{-3}. **CCDC 1895345**.

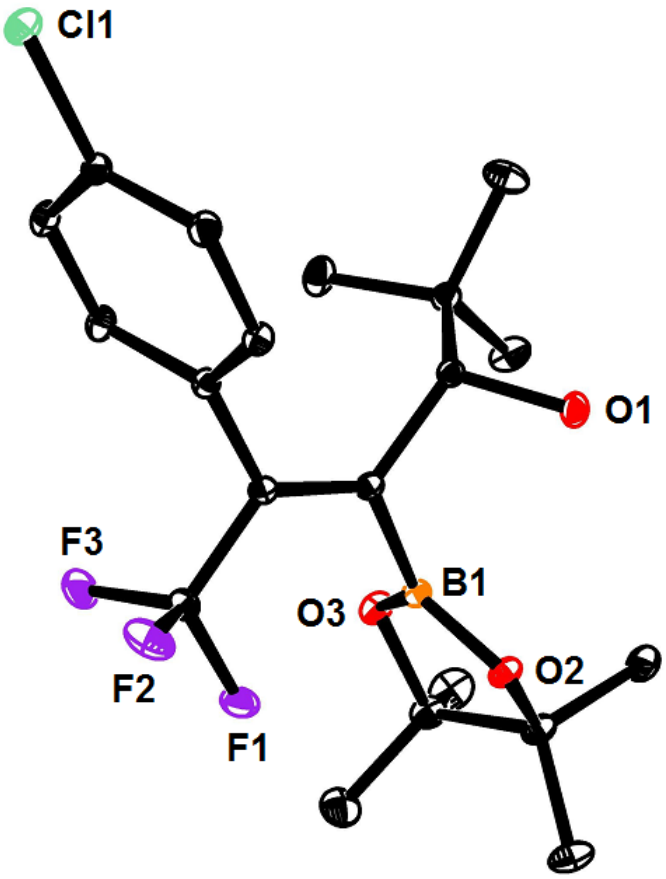


Figure S2. Structure of compound **5n** in the solid state; only one of the two antipodal molecules present in the unit cell is shown for clarity

X-ray Crystal Structure Analysis of 5n: ($C_{20}H_{27}BClF_3O_3$), M_r = 418.67 g·mol^{-1}, colorless prism, crystal size 0.144 x 0.111 x 0.092 mm^3, triclinic, space group $P\bar{1}$, a = 9.1295(10) Å, b = 11.2795(13) Å, c = 21.152(3) Å, α = 99.045(2)°, β = 95.674(5)°, γ = 91.865(2)°, V = 2138.0(5) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.301 g·cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.221 mm^{-1}, Gaussian absorption correction (T_{min} = 0.97, T_{max} = 0.98), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 1.961 < θ < 33.142°, 65114 measured reflections, 16259 independent reflections, 13805reflections with $I > 2\sigma(I)$, R_{int} = 0.0243.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.039 [$I > 2\sigma(I)$], wR_2 = 0.109, 527 parameters. Several low-angle reflections were shadowed by the beamstop and were omitted before the final refinement cycles.

Hydroxyl H atoms were found and refined. Otherwise, H atoms were refined using a riding model, S = 1.025, residual electron density 0.8/–0.5 e Å^{-3}. **CCDC 1895348**.

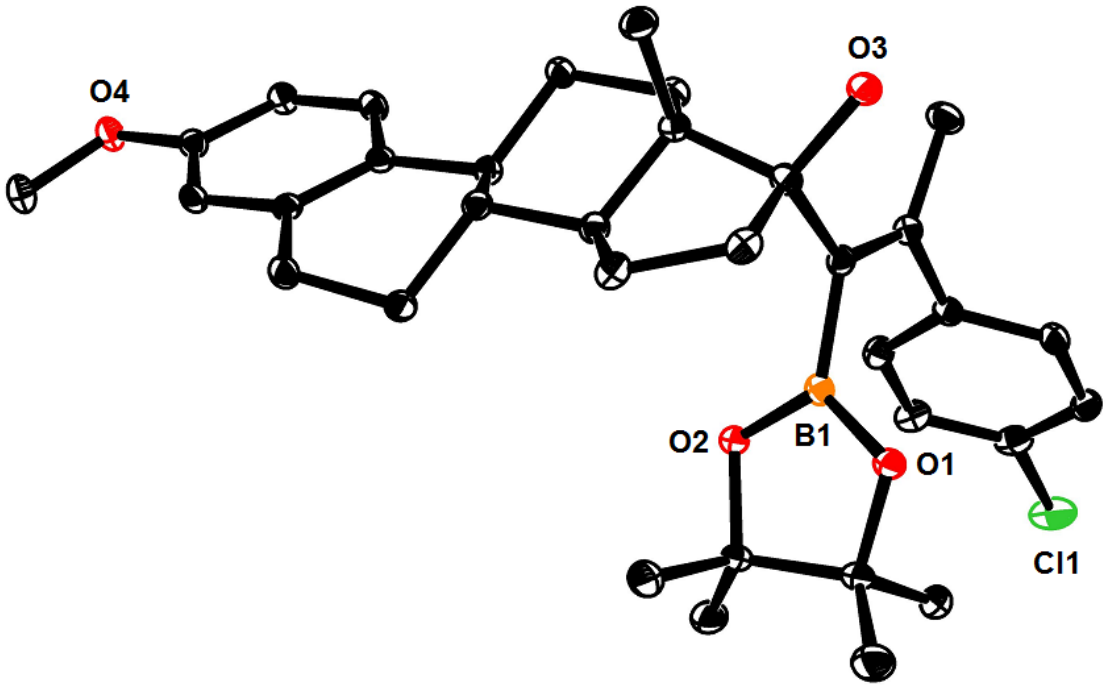


Figure S3. Structure of compound **10i** in the solid state; two co-crystallized [D_4]-MeOH molecules are not shown for clarity

X-ray Crystal Structure Analysis of 10i: ($C_{36}H_{44}D_8BClO_6$), M_r = 635.08 g·mol^{-1}, colorless prism, crystal size 0.260 x 0.169 x 0.103 mm^3, monoclinic, space group $P2_1$, a = 9.4553(4) Å, b = 11.9148(5) Å, c = 16.3010(6) Å, β = 106.060(2)°, V = 1764.77(12) Å^3, T = 100(2) K, Z = 2, D_{calc} = 1.195 g·cm^3, λ = 1.54178 Å, μ(*Cu-K*$_\alpha$) = 1.289 mm^{-1}, Gaussian absorption correction (T_{min} = 0.85, T_{max} = 0.91), Bruker AXS X8 Proteum diffractometer, 2.821 < θ < 72.228°, 68680 measured reflections, 6357 independent reflections, 5764 reflections with $I > 2\sigma(I)$, R_{int} = 0.0514, Absolute structure parameter = 0.014(15).

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.033 [$I > 2\sigma(I)$], wR_2 = 0.082, 419 parameters. Several low-angle reflections were shadowed by the beamstop and were omitted before the final refinement cycles.

Hydroxy-H atoms were found and refined. Otherwise, H atoms were refined using a riding model, S = 1.110, residual electron density 0.3/–0.3 e Å^{-3}. **CCDC 1895347**.

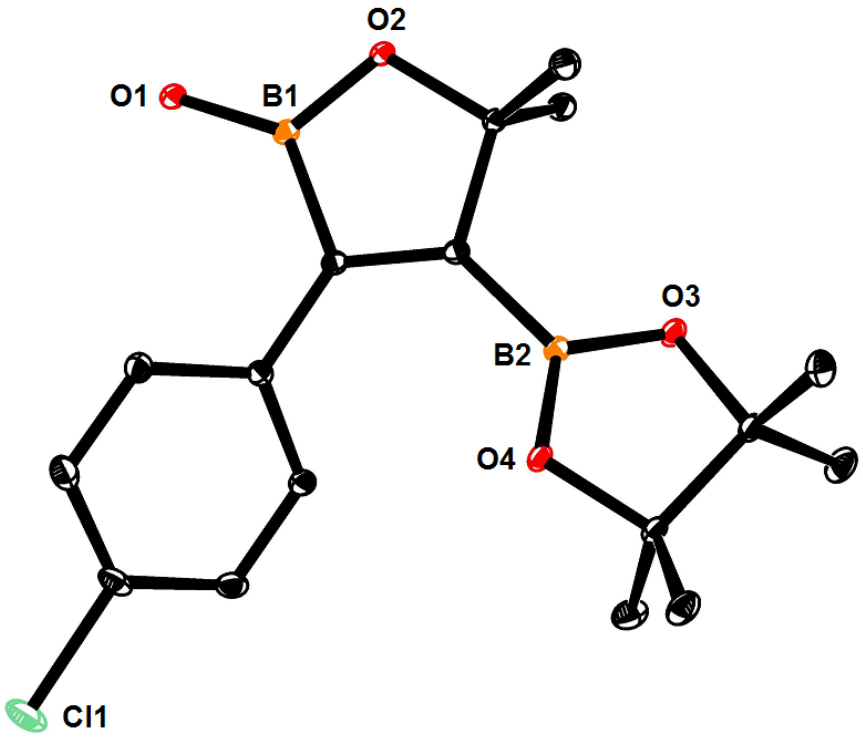


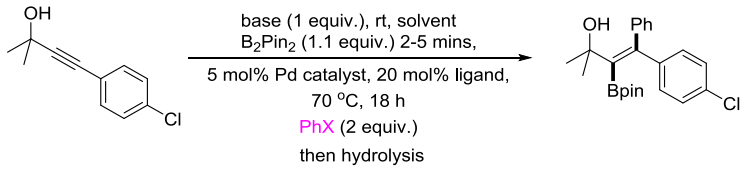
Figure S4. Structure of 1,2-oxaborolol derivative **3b** in the solid state

X-ray Crystal Structure Analysis of 3b: ($C_{17}H_{23}B_2ClO_4$), M_r = 348.42 g·mol^{-1}, colorless prism, crystal size 0.153 x 0.095 x 0.021 mm^3, monoclinic, space group $P2_1/n$, a = 6.4123(12) Å, b = 16.923(3) Å, c = 17.041(3) Å, β = 100.090(4)°, V = 1820.6(6) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.271 g·cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.227 mm^{-1}, Gaussian absorption correction (T_{min} = 0.43, T_{max} = 0.84), Bruker AXS Enraf-Nonius KappaCCD diffractometer, 2.407 < θ < 30.533°, 47844 measured reflections, 5551 independent reflections, 4565 reflections with $I > 2\sigma(I)$, R_{int} = 0.0545.

The structure was solved by direct methods and refined by full-matrix least-squares against F^2 to R_1 = 0.040 [$I > 2\sigma(I)$], wR_2 = 0.107, 224 parameters. Several low-angle reflections were shadowed by the beamstop and were omitted before the final refinement cycles.

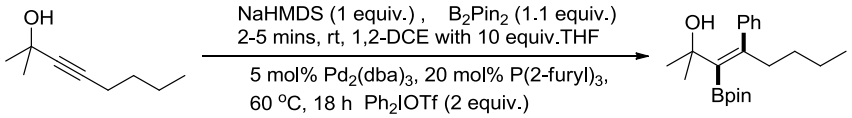
The H atoms were refined using a rotational group riding model, S = 1.032, residual electron density 0.5/–0.4 e Å^{-3}. **CCDC 1895346**.

REACTION OPTIMIZATION



Entry	Base	Pd catalyst	Ligand	PhX	Solvent	Yield (%)[a]
1	n-BuLi	$Pd(OAc)_2$	dppf[d]	PhOTf	THF	0
2	LiTMP	$Pd(OAc)_2$	dppf[d]	PhOTf	THF	0
3	LiHMDS	$Pd(OAc)_2$	dppf[d]	PhOTf	THF	10
4	LiHMDS	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	Ph_2I^+ OTf^-	THF	31
5	NaHMDS	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	Ph_2I^+ OTf^-	THF	37
6	NaOtBu	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	Ph_2I^+ OTf^-	THF	0
7	NaH	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	Ph_2I^+ OTf^-	THF	10
8	NaHMDS	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	$PhMesI^+$ OTf^-	THF	20
9	NaHMDS	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	PhI	1,4-dioxane	< 5
10	NaHMDS	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	Ph_2I^+ OTf^-	1,4-dioxane	62 (66)[b]
11	NaHMDS	$Pd_2(dba)_3$	XPhos	Ph_2I^+ OTf^-	1,4-dioxane	< 5[b]
12	NaHMDS	$Pd_2(dba)_3$	P(1-nap)$_3$	Ph_2I^+ OTf^-	1,4-dioxane	< 5[b]
13	NaHMDS	$Pd_2(dba)_3$	$P(tBu)_3$	Ph_2I^+ OTf^-	1,4-dioxane	< 5[b]
14	NaHMDS	$Pd_2(dba)_3$	DPEPhos[d]	Ph_2I^+ OTf^-	1,4-dioxane	33
15	NaHMDS	$Pd(dba)_2$	$P(2\text{-furyl})_3$	Ph_2I^+ OTf^-	1,4-dioxane	68
16	NaHMDS	$Pd(OAc)_2$	$P(2\text{-furyl})_3$	Ph_2I^+ OTf^-	1,4-dioxane	73
17	**NaHMDS**	**$Pd_2(dba)_3$**	**$P(2\text{-furyl})_3$**	**Ph_2I^+ OTf^-**	**1,4-dioxane**	**81[b]**

[a]isolated yields. [b]at 60 °C. [c]10 mol% of the ligand

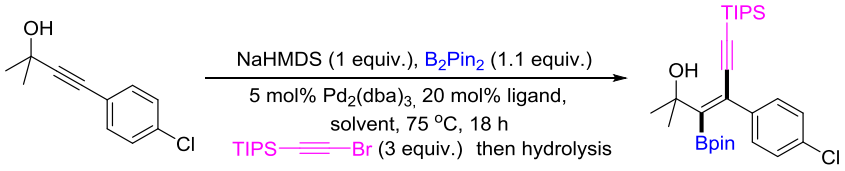


Entry	Variations on the standard condition	Yield (%)[a]
1	none	62
2	dioxane as solvent	15
3	without THF	0
4	LiHMDS instead of NaHMDS	0

[a]isolated yields.

Entry	Catalyst	Ligand	Solvent	Yield (%)[a]
1	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	THF	34 (25)[b]
2	$Pd_2(dba)_3$	$P(o\text{-}tol)_3$	1,4-dioxane	67
3	$Pd_2(dba)_3$	$P(2\text{-}furyl)_3$	1,4-dioxane	36
4	$Pd_2(dba)_3$	$P(1\text{-}nap)_3$	1,4-dioxane	77 (67)[c]
5	CuCl	Xantphos[d]	THF	0

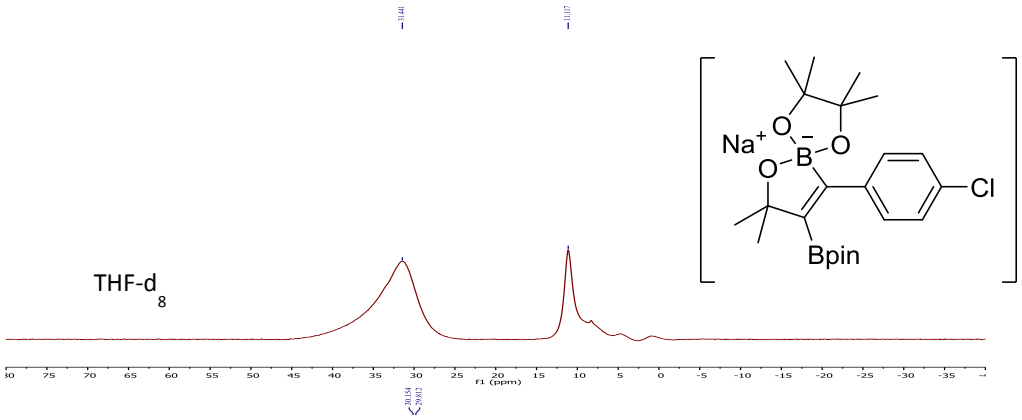
[a]isolated yields. [b]LiHMDS instead of NaHMDS. [C]1.5 equiv. MeI was used. [d]10 mol% of Xantphos

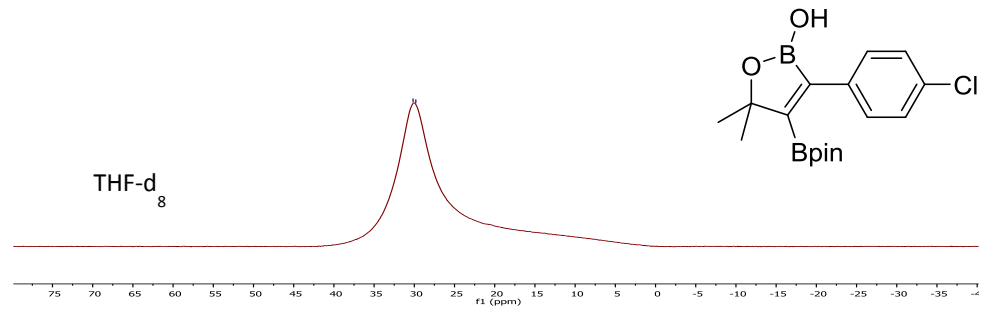


Entry	Catalyst	Ligand	Solvent	Yield (%)[a]
1	$Pd_2(dba)_3$	$P(2\text{-}furyl)_3$	1,4-dioxane	78
2	$Pd_2(dba)_3$	XPhos	1,4-dioxane	17
3	$Pd_2(dba)_3$	DPEPhos[b]	PhMe/THF (10 equiv.)	44
4	$Pd_2(dba)_3$	$P(2\text{-}furyl)_3$	PhMe/THF (10 equiv.)	90
5	$Pd_2(dba)_3$	$P(2\text{-}furyl)_3$	PhMe	68
5	CuCl	Xantphos[d]	THF	0

[a]isolated yields. [b]10 mol% of the ligand.

^{11}B NMR: Evidence that intermediate 2b is (largely) in the borate state





PROCEDURES AND CHARACTERIZATION DATA

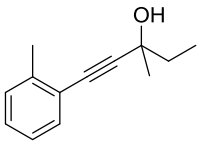
General Methods: Unless stated otherwise, all reactions were carried out under Argon atmosphere in flame-dried glassware. The solvents were purified by distillation over the indicated drying agents under Argon: THF, 1,4-dioxane, hexane, toluene (Na/K); CH_2Cl_2 (CaH_2) and 1,2-dichloroethane (CaH_2) were stored over molecular sieves and degassed via three freeze-pump-thaw cycles. If not mentioned otherwise, NMR spectra were recorded at room temperature using either a Bruker DPX 300, AMX 300 or AV 400 spectrometer in the solvents indicated. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz. The following abbreviations are used to indicate the signal multiplicity: s (singlet), brs (broad singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. Mass spectra (MS and HRMS) were determined using either a Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker), Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan) spectrometer. Infrared Spectroscopy (IR): Spectrum One Perkin Elmer, wavenumbers ($\tilde{\nu}$) in cm^{-1}. Flash chromatography was carried out using Merck silica gel 60 (40-63 μm) using the indicated eluents. Analytical Thin Layer Chromatography (TLC) was carried out on precoated Macherey-Nagel plates (POLYGRAM® SIL G/UV254). Preparative TLC: Macherey-Nagel precoated plates (SIL G-100 UV 254; silica gel layer: 1.0 mm); detection was accomplished using UV-light (254

nm), $KMnO_4$ (in 1.5M Na_2CO_3 (aq.)), molybdatophosphoric acid (5 % in ethanol), vanillin/H_2SO_4 (in ethanol) or anisaldehyde/HOAc (in ethanol).

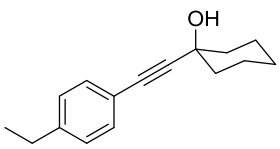
Starting Materials

Propargyl alcohols and diaryl iodonium triflates were purchased from Sigma-Aldrich, ABCR, or TCI, or were prepared in analogy to the literature procedures cited below:

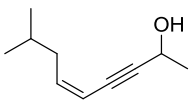
3-Methyl-1-(2-methylphenyl)pent-1-yn-3-ol (S1).[1] Colorless oil (344 mg, 91%); ^{1}H NMR (400 MHz, CD_3OD) δ = 7.37-7.29 (m, 1 H), 7.23-7.16 (m, 2 H), 7.15-7.07 (m, 1 H), 2.41 (s, 3 H), 1.88-1.66 (m, 2 H), 1.53 (s, 3 H), 1.11 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 139.6, 131.4, 129.0, 127.8, 125.2, 122.7, 96.8, 81.2, 68.3, 36.3, 28.3, 19.4, 8.2 ppm; IR (ATR): ṽ = 3363, 2972, 2934, 1485, 1456, 1370, 1155, 1125, 1033, 995, 906, 754, 716 cm^{-1}; HRMS (EI) *m/z* calcd for $[C_{13}H_{16}O]^+$: 188.1195; found: 188.1193.



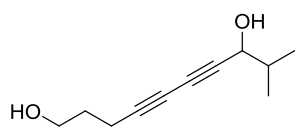
1-((4-Ethylphenyl)ethynyl)cyclohexan-1-ol (S2).[1] White solid (415 mg, 90%); mp: 89-90 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.34-7.26 (m, 2 H), 7.20-7.11 (m, 2 H), 2.63 (q, *J* = 7.6 Hz, 2 H), 2.04-1.87 (m, 2 H), 1.79-1.52 (m, 7 H), 1.36-1.25 (m, 1 H), 1.22 (t, *J* = 7:6 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 144.4, 131.1, 127.5, 120.3, 91.9, 83.6, 68.0, 39.6, 28.3, 25.0, 23.0, 14.5 ppm; IR (ATR): ṽ = 3197, 2927, 2854, 1510, 1448, 1345, 1297, 1186, 1071, 965, 827, 682, 548 cm^{-1}; HRMS (EI) *m/z* calcd for $[C_{16}H_{20}O]^+$: 228.1509; found: 228.1510.

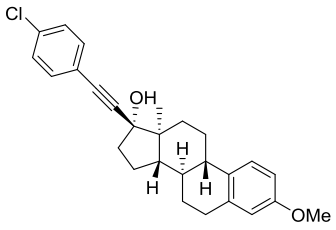


(*Z*)-8-Methylnon-5-en-3-yn-2-ol (S3).[2] Colorless oil (390 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 5.89-5.77 (m, 1 H), 5.45-5.36 (m, 1 H), 4.63-4.47 (m, 1 H), 2.14-2.03 (m, 2 H), 1.73 (brs, OH), 1.67-1.54 (m, 1 H), 1.38 (d, *J* = 6.4 Hz, 3 H), 0.82 (d, *J* = 6.8 Hz, 6 H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ = 143.3, 109.0, 94.9, 81.1, 58.9, 39.2, 28.3, 24.5, 22.4 ppm; IR (ATR): ṽ = 3318, 2956, 2929, 2871, 1464, 1368, 1330, 1278, 1154, 1121, 1073, 1015, 985, 884, 828, 729, 641 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{10}H_{16}O+Na]^+$: 175.1093; found: 175.1094.



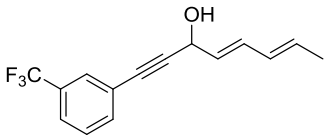
9-Methyldeca-4,6-diyne-1,8-diol (S4).[3] White solid (337 mg, 71%), mp: 32-33 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 4.05 (d, *J* = 6.0 Hz, 1 H), 3.56 (t, *J* = 6.4 Hz, 2 H), 2.41-2.25 (m, 2 H), 1.82-1.58 (m, 3 H), 0.99-0.83 (m, 6 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 79.4, 75.6, 69.2, 67.2, 64.3, 59.9, 34.6, 30.8, 17.2, 16.6, 14.9 ppm; IR (ATR): ṽ = 3301, 3217, 2958, 2874, 2255, 1463, 1317, 1166, 1057, 1025, 896, 684 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{11}H_{16}O_2+Na]^+$: 203.1042; found: 203.1043.



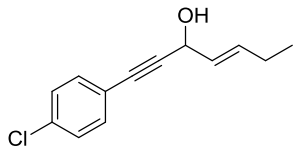
(8*R*,9*S*,13*S*,14*S*,17*S*)-17-((4-Chlorophenyl)ethynyl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-ol (S5).[4] 

Pale yellow solid (628 mg, 74%); mp: 73-74 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.38 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 7.17 (d, *J* = 8.4 Hz, 1 H), 6.65 (d, *J* = 8.4 Hz, 1 H), 6.58 (s, 1 H), 3.72 (s, 3 H), 2.94-2.68 (m, 2 H), 2.49-2.24 (m, 2 H), 2.23-1.69 (m, 7 H), 1.55-1.20 (m, 4 H), 0.91 (s, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 157.5, 137.4, 133.7, 132.5, 132.1, 128.3, 125.9, 121.9, 113.2, 111.0, 94.2, 83.8, 79.4, 54.1, 49.8, 47.4, 43.7, 39.7, 38.5, 33.0, 29.4, 27.2, 26.3, 22.4, 12.1 ppm; IR (ATR): $\tilde{\nu}$ = 3421, 2927, 2867, 1608, 1488, 1453, 1252, 1234, 1090, 1039, 1013, 826, 781, 527 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{27}H_{29}ClO_2+Na]^-$: 443.1748; found: 443.1749.

(4*E*,6*E*)-1-(3-(Trifluoromethyl)phenyl)octa-4,6-dien-1-yn-3-ol (S6).[1] Semi-solid (479 mg, 90%, contains ≈11 % *Z*,*Z*-isomer); ^{1}H NMR (400 MHz, CD_3OD) δ = 7.74-7.60 (m, 3 H), 7.57-7.49 (m, 1 H), 6.45-6.32 (m, 1 H), 6.18-6.01 (m, 1 H), 5.86-5.74 (m, 1 H), 5.74-5.64 (m, 1 H), 5.06 (d, *J* = 6.4 Hz, 1 H), 1.81-1.72 (m, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 134.7 (d, *J* = 0.8 Hz), 131.9, 130.7, 130.6 (q, *J* = 32 Hz), 130.3, 129.1, 128.8, 127.7 (q, *J* = 4.0 Hz), 124.6 (q, *J* = 3.8 Hz), 123.9, 123.8 (q, *J* =270 Hz), 90.4, 82.9, 62.0, 16.9 ppm; IR (ATR): $\tilde{\nu}$ = 3350, 2207, 1650, 1610, 1433, 1330, 1166, 1123, 1071, 985, 902, 801, 694, 659 cm^{-1}; HRMS (CI Ammonia) *m/z* calcd for $[C_{15}H_{12}F_3O+NH_3]^-$: 282.1111; found: 282.1102.

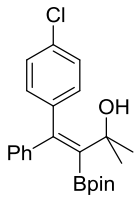


(*E*)-1-(4-Chlorophenyl)hept-4-en-1-yn-3-ol (S7).[1] White solid (620 mg, 87%); mp: 31-32 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.41 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 6.03-5.86 (m, 1 H), 5.70-5.57 (m, 1 H), 4.98 (d, *J* = 6.4 Hz, 1 H), 2.19-2.04 (m, 2 H), 1.05 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 134.4, 134.0, 132.6, 128.3, 128.2, 121.6, 89.9, 83.2, 62.3, 24.6, 12.2 ppm; IR (ATR): $\tilde{\nu}$ = 3223, 2964, 2874, 1669, 1487, 1296, 1251, 1089, 993, 962, 828, 766, 735, 521 cm^{-1}; HRMS (EI) *m/z* calcd for $[C_{13}H_{13}ClO]^+$: 220.0649; found: 220.0646.



trans-Carboboration Reactions

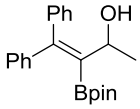
Representative Procedure for *trans*-Arylboration. Preparation of (*Z*)-4-(4-Chlorophenyl)-2-methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (5d). A flame-dried tube equipped with a magnetic stir bar was charged under Ar with THF (0.2 mL), 2-methyl-4-phenylbut-3-yn-2-ol (32 mg, 0.2 mmol,), and NaHMDS (36.7 mg, 0.2 mmol). B_2Pin_2 (55.8 mg, 0.22 mol,), 1,2-dichloroethane (2 mL), $Pd_2(dba)_3$ (9.1 mg, 0.01 mmol), tri(2-furyl)phosphine (9.2 mg, 0.04 mmol) and bis(4-chlorophenyl) iodonium triflate (200 mg, 0.4 mmol) were sequentially added. The tube was sealed and the mixture stirred at 60 °C (bath temperature) for 18 h. After cooling to room temperature, the reaction was quenched with aq. sat. NH_4Cl (2 mL), the aqueous phase was extracted by EtOAc (3 x 5 mL), and the combined organic



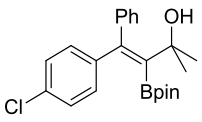
layer were dried ($NaSO_4$), filtered and evaporated. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc) or thin layer chromatography to provide the title compound as a white solid (55.8 mg, 70 %). mp: 119-120 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.33-7.26 (m, 4 H), 7.25-7.14 (m, 5 H), 1.26 (s, 6 H), 1.02 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 144.7, 144.2, 141.8, 132.1, 129.9, 128.7, 127.6, 127.5, 126.6, 83.3, 73.6, 30.1, 23.7 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.0 ppm; IR (ATR): ṽ = 2975, 2931, 1622, 1488, 1335, 1303, 1265, 1138, 1092, 1013, 962, 835, 760, 696, 637, 541 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{23}H_{28}ClBO_3+Na]^+$: 421.1712; found: 421.1715.

The following compounds were prepared analogously:

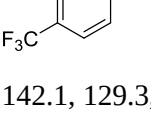
4,4-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (5a). White solid (51 mg, 72%); mp: 136-137 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.38-7.30 (m, 2 H), 7.30-7.14 (m, 8 H), 5.80-5.71 (m, 1 H), 4.53 (q, *J* = 6.4 Hz, 1 H), 1.31 (d, *J* = 6.4 Hz, 3 H), 1.19 (s, 6 H), 1.12 (s, 6 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 149.1, 143.9, 141.7, 128.7, 128.6, 127.9, 127.5, 126.9, 126.7, 83.4, 68.9, 23.9, 23.7, 21.9 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.9 ppm; IR (ATR): ṽ = 2977, 2927, 2559, 1614, 1491, 1443, 1358, 1291, 1142, 1126, 1069, 929, 851, 766, 704, 638, 596 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{22}H_{27}BO_3+Na]^+$: 373.1945; found: 373.1947.

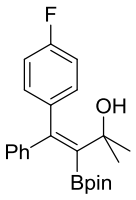


(*E*)-4-(4-Chlorophenyl)-2-methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (5b). White solid (65 mg, 81%); mp: 123-124 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.38-7.10 (m, 9 H), 1.21 (s, 6 H), 1.04 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 144.6, 143.2, 142.5, 132.3, 130.3, 128.3, 127.6, 127.4, 126.4, 83.3, 73.8, 29.9, 23.6 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.0 ppm; IR (ATR): ṽ = 3483, 2974, 2932, 1480, 1369, 1329, 1280, 1141, 1083, 1011, 940, 848, 801, 766, 702, 658, 598, 541 cm^{-1}; HRMS (EI) *m/z* calcd for $[C_{23}H_{27}BClO_3]^-$: 397.1747; found: 397.1747.



(*E*)-4-(4-Trifluoromethylphenyl)-2-methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (5c). White solid (70 mg, 90%); mp: 164-165 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.58-7.43 (m, 4 H), 7.36-7.26 (m, 2 H), 7.26-7.17 (m, 3 H), 1.23 (s, 6 H), 1.00 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 148.5, 144.5, 142.1, 129.3, 128.5 (q, *J* = 32 Hz), 128.3, 127.8, 126.6, 124.33 (q, *J* = 269 Hz), 124.34 (q, *J* = 3.9 Hz), 83.3, 73.8, 29.8, 23.6 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.9 ppm; IR (ATR): ṽ = 3571, 2980, 2931, 1612, 1382, 1326, 1300, 1161, 1138, 1107, 1065, 1029, 961, 849, 708, 675, 615, 546, 499 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{24}H_{28}BF_3O_3+Na]^+$: 455.1975; found: 455.1980.

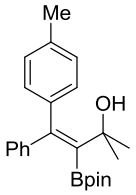




(*Z*)-4-(4-Fluorophenyl)-2-methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (5e). White solid (31.3 mg, 61%); mp: 186-187 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.32-7.26 (m, 2 H), 7.26-7.14 (m, 5 H), 7.08-6.99 (m, 2 H), 1.25 (s, 6 H), 1.02 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 162.9, 160.5, 144.7 (d, *J*

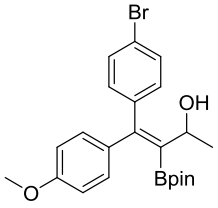
= 51.7 Hz), 139.1 (d, *J* = 3.7 Hz), 130.0 (d, *J* = 8.1 Hz), 128.7, 127.5, 126.5, 114.2 (d, *J* = 21.4 Hz), 83.3, 73.6, 30.0, 23.6 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.1 ppm; IR (ATR): ṽ = 2979, 2938, 2577, 1599, 1503, 1371, 1330, 1288, 1216, 1142, 1041, 964, 854, 736, 699, 639, 560, 529 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{23}H_{28}FBO_3+Na]^+$: 405.2007; found: 405.2011.

(*Z*)-2-Methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(p-tolyl)but-3-en-2-ol

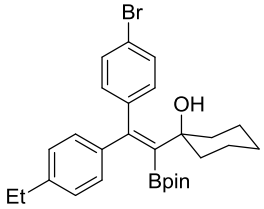


(5f). White solid (42 mg, 70%); mp: 143-144 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.19-7.14 (m, 2 H), 7.11-7.02 (m, 3 H), 7.01-6.95 (m, 4 H), 2.12 (s, 3 H), 1.11 (s, 6 H), 0.90 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 146.1, 144.8, 140.0, 135.9, 128.7, 128.2, 128.1, 127.3, 126.3, 83.2, 73.9, 30.0, 23.7, 19.8 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.3 ppm; IR (ATR): ṽ = 2978, 2928, 2547, 1508, 1371, 1339, 1299, 1144, 1109, 1044, 964, 849, 728, 694, 635, 560, 525 cm^{-1}; HRMS (ESI) m/z calcd for $[C_{24}H_{31}BO_3+Na]^+$: 401.2258; found: 401.2263.

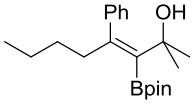
(Z)-4-(4-Bromophenyl)-4-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (5g). Pale yellow solid (320.6 mg, 70%); mp: 128-129 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.54-7.40 (m, 2 H), 7.16-6.98 (m, 4 H), 6.86-6.73 (m, 2 H), 4.44 (q, *J* = 6.4 Hz, 1 H), 3.75 (s, 3 H), 1.28 (d, *J* = 6.4 Hz, 3 H), 1.19 (s, 6 H), 1.13 (s, 6 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 159.4, 147.4, 141.1, 136.0, 130.9, 130.6, 129.9, 120.5, 112.9, 83.4, 68.9, 54.3, 23.9, 23.7, 21.9 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 31.1 ppm; IR (ATR): ṽ = 3482, 2976, 2931, 1737, 1606, 1509, 1300, 1243, 1132, 1034, 849, 829, 817, 758, 618 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{23}H_{28}BrBO_4+Na]^+$: 481.1156; found: 481.1158.



(1*E*,4*E*)-1-(4-Chlorophenyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-dien-3-ol (5h). Yellow solid (35 mg, 68%); mp: 157-158 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.36-7.29 (m, 2 H), 7.10-6.92 (m, 6 H), 2.47 (q, *J* = 7.6 Hz, 2 H), 1.63-1.27 (m, 11 H), 1.06 (t, *J* = 7.6 Hz, 3 H), 0.89 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 145.2, 143.4, 142.8, 141.8, 131.0, 130.1, 128.7, 127.4, 120.3, 83.4, 75.2, 38.0, 28.5, 25.3, 24.4, 21.5, 15.7 ppm; ^{11}B NMR (128 MHz, CD_2Cl_2) δ = 29.9 ppm; IR (ATR): ṽ = 2928, 2846, 1483, 1372, 1337, 1302, 1140, 1069, 1013, 969, 885, 850, 822, 751, 611 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{28}H_{36}BBrO_3+Na]^+$: 533.1833; found: 533.1840.



(*Z*)-2-Methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-3-en-2-ol (5i). White solid (33 mg, 62%); mp: 86-87 °C; ^{1}H NMR (400 MHz, C_6D_6) δ = 7.04-6.99 (m, 4 H), 6.98-6.91 (m, 1 H), 2.45 (t, *J* = 8 Hz, 2 H), 1.78 (brs, OH), 1.47-1.36 (m, 2 H), 1.33-1.21 (m, 8 H), 1.15 (s, 12 H), 0.81 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, C_6D_6) δ = 145.1, 143.3, 128.5, 126.2, 82.9, 74.1, 41.3, 31.2, 30.8, 24.8, 22.8, 14.0 ppm; ^{11}B NMR (128 MHz, C_6D_6) δ = 30.6 ppm; IR (ATR): ṽ = 2974, 2930, 2860, 1630, 1467, 1378, 1339, 1294,



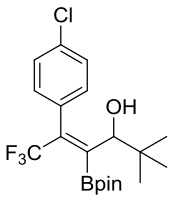
1141, 1060, 963, 845, 771, 716, 665, 528 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{21}H_{33}BO_3+Na]^+$: 367.2415; found: 367.2417.

(*Z*)-4-(Cyclohex-1-en-1-yl)-2-methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (5j). White solid (54 mg, 79%); mp: 141-142 ^oC; ^1H NMR (400 MHz, CD_3OD) δ = 7.32-7.16 (m, 3 H), 7.12-7.04 (m, 2 H), 5.80-5.70 (m, 1 H), 2.11-1.99 (m, 2 H), 1.95-1.84 (m, 2 H), 1.53-1.43 (m, 4 H), 1.29 (s, 12 H), 1.10 (s, 6 H), ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 149.0, 143.0, 141.2, 128.5, 127.1, 126.2, 123.9, 83.1, 73.5, 30.1, 26.7, 25.0, 24.2, 22.2, 21.6 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.3 ppm; IR (ATR): ṽ = 2974, 2938, 1724, 1447, 1365, 1201, 1144, 1081, 982, 850, 756, 699, 672 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{23}H_{33}BO_3+Na]^+$: 391.2415; found: 391.2416.

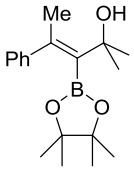
(*Z*)-1-(Cyclohex-1-en-1-yl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-3-ol (5k). Colorless oil (48 mg, 70%); ^1H NMR (400 MHz, CD_3OD) δ = 7.36-7.29 (m, 2 H), 7.28-7.21 (m, 1 H), 7.20-7.14 (m, 2 H), 5.80-5.71 (m, 1 H), 4.10 (t, *J* = 7.2 Hz, 1 H), 2.16-2.07 (m, 2 H), 1.97-1.70 (m, 2 H), 1.71-1.51 (m, 6 H), 1.31 (s, 6 H), 1.30 (s, 6 H), 0.70 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 154.0, 143.1, 140.0, 128.4, 127.6, 126.6, 124.7, 83.1, 73.6, 29.4, 26.9, 25.1, 24.2, 23.8, 22.3, 21.8, 9.5 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.9 ppm; IR (ATR): ṽ = 2975, 2928, 1443, 1354, 1295, 1134, 1083, 963, 853, 772, 703, 667, 608 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{23}H_{33}BO_3+Na]^+$: 391.2415; found: 391.2417.

(*E*)-2-Methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-3-en-5-yn-2-ol (5l). Colorless oil (34 mg, 51%); ^1H NMR (400 MHz, CD_3OD) δ = 7.34-7.21 (m, 3 H), 7.21-7.13 (m, 2 H), 2.23 (t, *J* = 6.8 Hz, 2 H), 1.52-1.39 (m, 2 H), 1.35 (s, 12 H), 1.32-1.27 (m, 4 H), 1.12 (s, 6 H), 0.86 (t, *J* = 7.2 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 140.7, 128.1, 127.6, 126.7, 126.6, 91.6, 83.6, 82.9, 73.5, 30.8, 29.6, 28.1, 23.9, 21.8, 18.9, 12.9 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.0 ppm; IR (ATR): ṽ = 2974, 2931, 2860, 1587, 1463, 1369, 1347, 1297, 1143, 1040, 964, 848, 725, 701, 669, 613 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{24}H_{35}BO_3+Na]^+$: 405.2571; found: 405.2573.

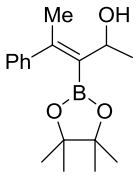
(1*E*,4*E*)-1-(4-chlorophenyl)-1-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-1,4-dien-3-ol (5m). The reaction was carried out in 1,4-dioxane instead of 1,2-dichloroethane/THF; white solid (36 mg, 56 %). mp: 120-121 ^oC; ^1H NMR (400 MHz, CD_2Cl_2) δ = 7.30-7.09 (m, 5 H), 7.08-6.97 (m, 4 H), 5.65-5.47 (m, 2 H), 4.56-4.45 (m, 1 H), 2.70 (d, *J* = 8.8 Hz, 1 H), 2.07-1.91 (m, 2 H), 1.09 (s, 6 H), 1.03 (s, 6 H), 0.92 (t, *J* = 7.6 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 149.1, 143.9, 141.7, 128.7, 128.6, 127.9, 127.5, 126.9, 126.7, 83.4, 68.9, 23.9, 23.7, 21.9 ppm; ^{11}B NMR (128 MHz, CD_2Cl_2) δ = 30.8 ppm; IR (ATR): ṽ = 2976, 2927, 1592, 1485, 1349, 1312, 1246, 1140, 1085, 1012, 962, 848, 765, 700, 608 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{25}H_{30}BClO_3+Na]^+$: 447.1869; found: 447.1872.

(*E*)-5-(4-Chlorophenyl)-trifluoro-2,2-dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-3-ol (5n). 

White solid (32 mg, 52%); mp: 140-141 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.36-7.24 (m, 2 H), 7.14-7.02 (m, 2 H), 3.87 (d, *J* = 6.4 Hz, 1 H), 2.30 (d, *J* = 6.4 Hz, 1 H), 1.26 (s, 6 H), 1.25 (s, 6 H), 0.71 (s, 9 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 137.4 (q, *J* = 29.4 Hz), 134.4, 132.5, 131.2, 128.6, 123.2 (q, *J* = 273 Hz), 84.9, 79.7, 36.4, 26.2, 25.2, 24.9 ppm; ^{11}B NMR (128 MHz, CD_2Cl_2) δ = 30.1 ppm; IR (ATR): ṽ = 3501, 2961, 1491, 1307, 1200, 1164, 1119, 1087, 1015, 961, 826, 736, 576 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{20}H_{27}F_3ClBO_3+Na]^+$: 441.1586; found: 441.1587.

Representative Procedure for *trans*-Methylboration. Preparation of (*E*)-2-Methyl-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-2-ol (10a). A flame-dried tube equipped with a magnetic stir bar was charged under Ar with 1,4-dioxane (2 mL), 2-methyl-4-phenylbut-3-yn-2-ol (32 mg, 0.2 mmol), NaHMDS (36.7 mg, 0.2 mmol), and B_2Pin_2 (55.8 mg, 0.22 mol). The mixture was stirred for 2-5 min at room temperature before $Pd_2(dba)_3$ (9.1 mg, 0.01 mmol), tri-1-naphthylphosphine (16.5 mg, 0.04 mmol) and MeI (37 μL, 0.6 mmol) were added. The tube was sealed and stirred at 60 °C (bath temperature) for 18 h. After cooling to room temperature, the reaction was quenched with aq. sat. NH_4Cl (2 mL), the aqueous phase was extracted with EtOAc (3 x 5 mL), the combined organic layers were dried over Na_2SO_4 and filtered, and the filtrate was evaporated under vacuum. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc) or thin layer chromatography to give the title compound as a colorless oil (42.3 mg, 70%). When carried out with KHMDS (39.8 mg, 0.2 mmol) instead of NaHMDS, the yield was 56%. 

^{1}H NMR (400 MHz, CD_3OD) δ = 7.29-7.15 (m, 5 H), 2.12 (s, 3 H), 1.50 (s, 6 H), 0.93 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 146.6, 143.3, 128.0, 127.5, 126.2, 83.0, 72.8, 29.2, 23.7, 21.3 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.6 ppm; IR (ATR): ṽ = 2976, 2931, 2067, 1441, 1371, 1343, 1293, 1142, 977, 849, 765, 700, 667, 553 cm^{-1}; HRMS (EI) *m/z* calcd for $[C_{18}H_{27}BO_3+Na]^+$: 325.1945; found: 325.1946.

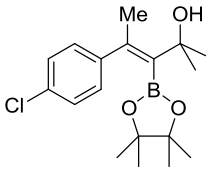
(*E*)-4-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-2-ol (10f) (Larger Scale). A flame-dried round bottom flask equipped with a magnetic stir bar was charged under Ar with 1,4-dioxane (25 mL), 4-phenylbut-3-yn-2-ol (730 mg, 5 mmol) and KHMDS (998 mg, 5 mmol), followed by slow addition of B_2Pin_2 (1.40 g, 5.5 mol) (*Attention*: *exothermic*!). $Pd_2(dba)_3$ (228 mg, 0.25 mmol), tri-1-naphthylphosphine (412 mg, 1.0 mmol) and MeI (935 μL, 15 mmol) were sequentially introduced and the resulting mixture was stirred at 60 °C (bath temperature) for 24 h. After cooling to room temperature, the reaction was quenched with aq. sat. NH_4Cl (10 mL), the aqueous phase was extracted with EtOAc (3 x 10mL), the combined organic layers were dried (Na_2SO_4), filtered and evaporated. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc) to provide the title compound as a pale yellow oil (972 mg, 67 %). 

^{1}H NMR (400 MHz, CD_3OD) δ = 7.33-7.15 (m, 5 H), 4.79 (q, *J* = 8 Hz, 1 H), 2.01 (s, 3 H), 1.37 (d, *J* = 8 Hz, 3 H), 1.08 (s, 6 H), 1.01 (s, 6 H) ppm; ^{13}C NMR (101 MHz,

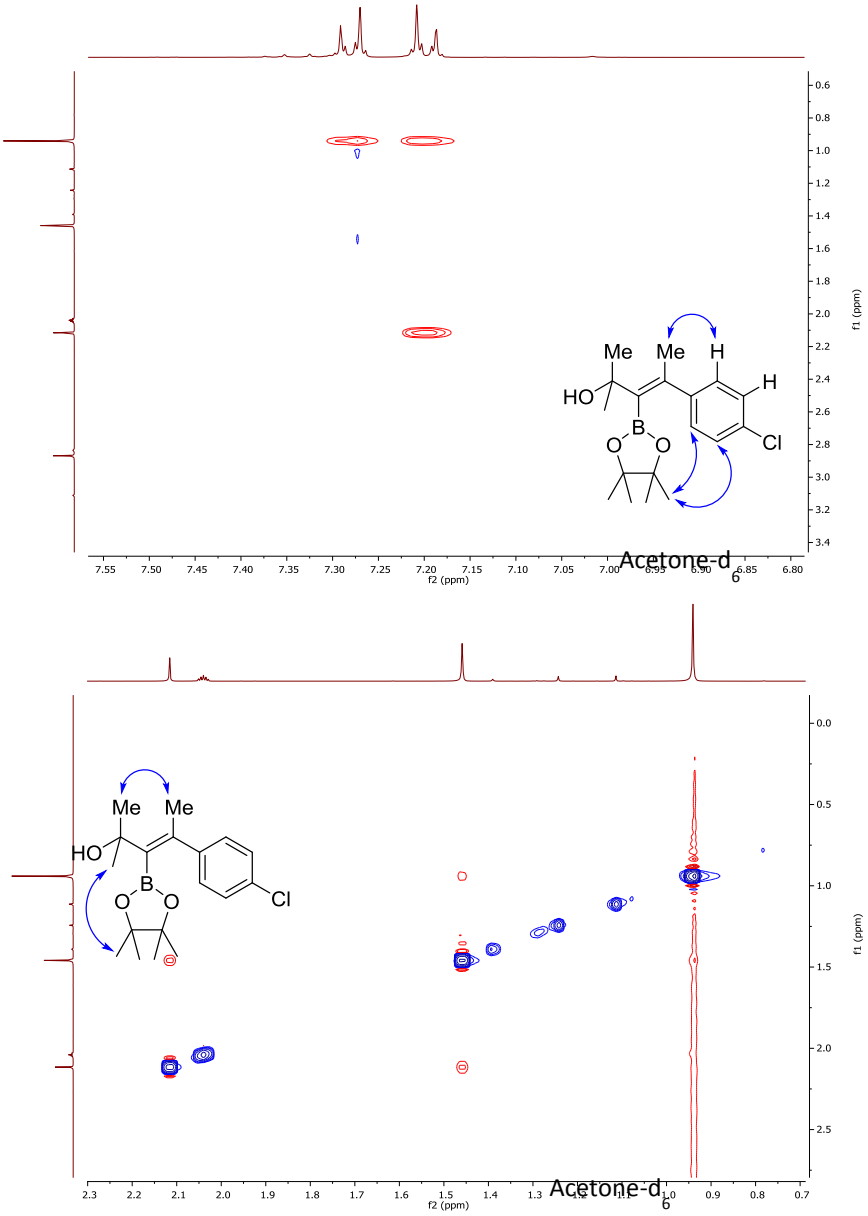
CD_3OD) δ = 145.7, 143.1, 127.6, 127.4, 126.5, 83.0, 67.9, 23.7, 23.6, 21.6, 18.8 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.9 ppm; IR (ATR): $\tilde{\nu}$ = 2976, 2928, 1629, 1372, 1354, 1293, 1140, 973, 855, 762, 700, 670, 533 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{17}H_{25}BO_3+Na]^+$: 311.1789; found: 311.1789.

The following compounds were prepared analogously:

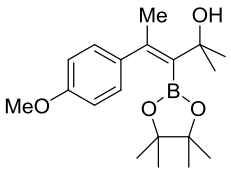
(*E*)-4-(4-Chlorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-2-ol



(10b). White solid (48 mg, 77%); mp: 68-70 °C; ^1H NMR (400 MHz, CD_3OD) δ = 7.30-7.24 (m, 2 H), 7.22-7.16 (m, 2 H), 2.13 (s, 3 H), 1.51 (s, 6 H), 0.98 (s, 12 H) ppm; ^{13}C NMR (125 MHz, CD_3OD) δ = 145.2, 141.9, 132.1, 129.7, 127.5, 83.1, 72.8, 29.1, 23.6, 21.1 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.8 ppm; IR (ATR): $\tilde{\nu}$ = 3451, 2975, 2930, 1619, 1481, 1372, 1335, 1288, 1214, 1164, 1141, 1086, 1012, 923, 847, 828, 688, 648, 550 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{18}H_{26}BClO_3+Na]^+$:359.1556; found: 359.1557.

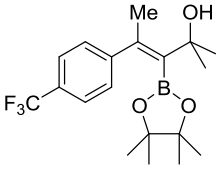


(*E*)-4-(4-Methoxyphenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-3-en-2-ol



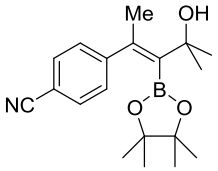
(10c). Colorless oil (52 mg, 85%); ^{1}H NMR (400 MHz, CD_3OD) δ = 7.17-7.09 (m, 2 H), 6.86-6.79 (m, 2 H), 3.77 (s, 3 H), 2.11 (s, 3 H), 1.51 (s, 6 H), 0.98 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 158.7, 143.0, 139.1, 129.1, 112.9, 83.0, 72.8, 54.4, 29.2, 23.7, 21.4 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.9 ppm; IR (ATR): $\tilde{\nu}$ = 2975, 2931, 1607, 1509, 1370, 1343, 1289, 1241, 1142, 1083, 1034, 980, 849, 831, 734, 666, 557 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{19}H_{29}BO_4+Na]^+$: 355.2051; found: 355.2052.

(*E*)-2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(4-(trifluoromethyl)phenyl)pent-



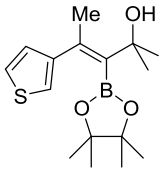
3-en-2-ol (10d). Yellow oil (65 mg, 82%); ^{1}H NMR (400 MHz, CD_3OD) δ = 7.62-7.50 (m, 2 H), 7.43-7.34 (m, 2 H), 2.16 (s, 3 H), 1.53 (s, 6 H), 0.95 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 150.6, 141.9, 128.7, 128.5 (q, *J* = 32 Hz), 124.5 (q, *J* = 4 Hz), 124.4 (q, *J* = 270 Hz), 83.1, 72.8, 29.1, 23.6, 21.0 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.7 ppm; IR (ATR): $\tilde{\nu}$ = 2977, 2933, 1614, 1372, 1323, 1297, 1162, 1123, 1107, 1063, 1016, 927, 844, 667, 608, 539 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{19}H_{26}BF_3O_3+Na]^+$: 393.1819; found: 393.1820.

(*E*)-4-(4-Hydroxy-4-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-2-en-2-



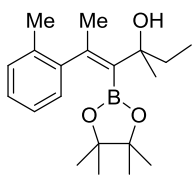
yl)benzonitrile (10e). White solid (45 mg, 62%); mp: 147-148 ^{o}C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.60-7.50 (m, 2 H), 7.33-7.21 (m, 2 H), 2.03 (s, 3 H), 1.40 (s, 6 H), 0.86 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 151.6, 141.5, 131.6, 129.2, 118.4, 109.9, 83.2, 72.9, 29.1, 23.7, 20.8 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.5 ppm; IR (ATR): $\tilde{\nu}$ = 2980, 2928, 2585, 2231, 1598, 1347, 1297, 1256, 1141, 1081, 975, 946, 843, 648, 577, 517 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{19}H_{26}NO3B+Na]^+$: 350.1898; found: 350.1899.

(*E*)-2-Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(thiophen-3-yl)pent-3-en-2-ol



(10g). Pale yellow solid (40 mg, 68%); mp: 77-78 ^{o}C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.19-7.14 (m, 1 H), 7.04-7.00 (m, 1 H), 6.90-6.87 (m, 1 H), 1.99 (s, 3 H), 1.39 (s, 6 H), 0.95 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 147.2, 137.7, 127.7, 124.5, 121.6, 83.2, 72.8, 29.2, 23.9, 20.8 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.6 ppm; IR (ATR): $\tilde{\nu}$ = 2972, 2929, 2557, 1619, 1370, 1340, 1290, 1142, 1086, 978, 852, 793, 664, 636, 521 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{16}H_{25}O_3BS+Na]^+$: 331.1510; found: 331.1511.

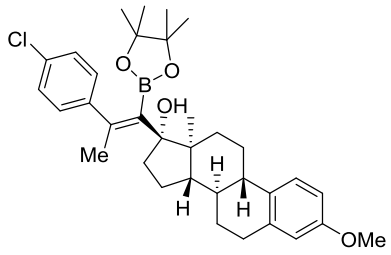
(*E*)-3-Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-5-(*o*-tolyl)hex-4-en-3-ol (10h).



Colorless oil (50 mg, 77%); ^{1}H NMR (400 MHz, CD_3OD) δ = 7.12-6.95 (m, 4 H), 2.29 (d, *J* = 2.8 Hz, 3 H), 2.02 (d, *J* = 3.2 Hz, 3 H), 1.97-1.82 (m, 1 H), 1.82-1.67 (m, 1 H), 1.48 (d, *J* = 4.0 Hz, 3 H), 1.06 (dt, *J* = 1.2, 7.6 Hz, 3 H), 0.87 (d, *J* = 2.5 Hz, 6 H), 0.83 (s, 6 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 145.65, 145.63, 142.5, 142.3, 135.42, 135.39, 129.34, 129.32, 128.96, 128.92, 126.3, 124.89, 124.88, 82.6, 75.57,

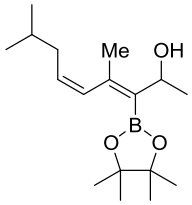
75.55, 34.84, 34.82, 27.36, 27.19, 23.58, 23.56, 23.34, 23.30, 20.84, 20.76, 18.27, 18.16, 7.56, 7.50 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.7 ppm; IR (ATR): $\tilde{\nu}$ = 2977, 2930, 2069, 1372, 1346, 1292, 1144, 1122, 1078, 976, 851, 769, 727, 668 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{20}H_{31}BO_3+Na]^+$: 353.2258; found: 353.2259.

(8*R*,9*S*,13*S*,14*S*,17*R*)-17-((*E*)-2-(4-Chlorophenyl)-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-en-1-yl)-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta-[a]phenanthren-17-ol (10i). White solid (85 mg, 72% using KHMDS); mp: 145-146 °C; ^{1}H NMR



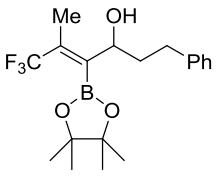
(400 MHz, CD_3OD) δ = 7.31-7.23 (m, 2 H), 7.23-7.13 (m, 3 H), 6.70-6.61 (m, 1 H), 6.61-6.54 (m, 1 H), 3.73 (s, 3 H), 2.9-2.71 (m, 2 H), 2.52-2.40 (m, 1 H), 2.39-2.28 (m, 1 H), 2.18 (s, 3 H), 2.16-2.07 (m, 1 H), 1.98-1.67 (m, 6 H), 1.52-1.22 (m, 4 H), 1.00 (s, 3 H), 0.96 (s, 6 H), 0.92 (s, 6 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 157.5, 148.0, 146.1, 137.4, 132.4, 132.2, 130.1, 127.6, 125.8, 113.2, 111.1, 86.4, 82.9, 54.1, 49.0, 48.4, 43.5, 40.0, 38.7, 33.7, 29.5, 27.3, 26.7, 24.8, 24.1, 23.7, 13.6 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.6 ppm; IR (ATR): $\tilde{\nu}$ = 2976, 2930, 1609, 1499, 1335, 1253, 1141, 1092, 1014, 982, 850, 830, 697, 548 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{34}H_{43}BClO_4]^-$: 561.2948; found: 561.2943.

(3*E*,5*Z*)-4,8-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)nona-3,5-dien-2-ol (10j).



Colorless oil (29 mg, 60%); ^{1}H NMR (400 MHz, CD_3OD) δ = 6.01 (d, *J* = 12 Hz, 1 H), 5.34-5.17 (m, 1 H), 4.57 (q, *J* = 8 Hz, 1 H), 2.00-1.80 (m, 2 H), 1.67 (s, 3 H), 1.56-1.42 (m, 1 H), 1.20 (d, *J* = 8 Hz, 3 H), 1.15 (s, 12 H), 0.79 (d, *J* = 8 Hz, 3 H), 0.78 (d, *J* = 8 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 139.9, 133.3, 129.8, 83.0, 67.4, 37.6, 28.5, 23.9, 23.6, 21.7, 21.6, 21.4, 17.4 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.6 ppm; IR (ATR): $\tilde{\nu}$ = 2956, 2929, 1465, 1371, 1352, 1291, 1143, 1107, 975, 855, 732, 672, 517 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{17}H_{31}BO_3+Na]^+$: 317.2258; found: 317.2259.

(*E*)-6,6,6-Trifluoro-5-methyl-1-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-3-ol (10k). Colorless oil (39 mg, 66%); ^{1}H NMR (400 MHz, CD_3OD) δ = 7.30-7.19



(m, 4 H), 7.19-7.12 (m, 1 H), 4.50-4.41 (m, 1 H), 2.84-2.73 (m, 1 H), 2.72-2.60 (m, 1 H), 2.09-1.96 (m, 1 H), 1.76-1.65 (m, 1 H), 1.60 (s, 3 H), 1.30 (s, 6 H), 1.29 (s, 6 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 141.7, 128.2, 128.0, 127.2 (q, *J* = 29 Hz), 125.4, 124.4 (q, *J* = 270 Hz), 84.0, 69.7, 37.3, 31.2, 23.9, 23.8, 10.9 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.1 ppm; IR (ATR): $\tilde{\nu}$ = 2979, 2930, 1661, 1454, 1357, 1313, 1165, 1137, 1102, 1021, 847, 748, 699, 531 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{19}H_{26}BF_3O_3+Na]^+$: 393.1819; found: 393.1819.

(*E*)-2,3-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)deca-1,3-dien-5-ol (10l). Colorless oil (49 mg, 63%); ^{1}H NMR (400 MHz, CD_3OD) δ = 4.67-4.63 (m, 1 H), 4.59-4.55 (m, 1 H), 4.31 (t, *J* = 8 Hz, 1 H), 1.73 (q, *J* = 0.8 Hz, 3 H), 1.65 (s, 3 H), 1.61-1.40 (m, 2 H), 1.33-1.18 (m, 6 H), 1.13 (s, 12 H), 0.81 (t, *J* = 8 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 150.4, 146.6, 111.7, 82.9, 71.1, 36.6, 31.7, 25.2, 23.8, 23.7, 22.3, 20.0, 15.7, 13.0 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.6 ppm; IR (ATR): $\tilde{\nu}$ = 2929, 2858, 1628, 1446, 1371, 1354, 1293, 1166, 1142, 1009, 964, 895, 859, 687, 669, 564 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{18}H_{33}BO_3+Na]^+$: 331.2415; found: 331.2412.

(*E*)-6,9-Dimethyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)dec-6-en-4-yne-1,8-diol (10m). Colorless oil (30 mg, 48 %, using 2 equiv. NaHMDS and 2.2 equiv. B_2Pin_2); ^{1}H NMR (400 MHz, CD_3OD) δ = 3.94 (d, *J* = 8.4 Hz, 1 H), 3.54 (t, *J* = 6.4 Hz, 2 H), 2.29 (t, *J* = 7.2 Hz, 2 H), 1.74 (s, 3 H), 1.72-1.67 (m, 1 H), 1.67-1.60 (m, 2 H), 1.20 (s, 12 H), 0.91 (d, *J* = 6.8 Hz, 3 H), 0.71 (d, *J* = 6.8 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 126.4, 89.6, 83.4, 83.2, 76.4, 60.4, 33.7, 31.3, 23.8, 23.7, 19.1, 18.4, 18.1, 15.4 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.6 ppm; IR (ATR): $\tilde{\nu}$ = 3439, 2974, 2932, 2872, 1607, 1442, 1379, 1324, 1304, 1139, 1008, 854, 672, 578 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{18}H_{31}BO_4+Na]^+$: 345.2208; found: 345.2209.

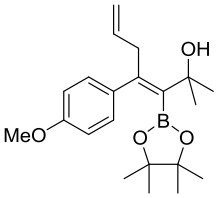
(*E*)-2,4-Dimethyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undec-3-en-5-yn-2-ol (10n). Colorless oil (39 mg, 60%); ^{1}H NMR (400 MHz, CD_3OD) δ = 2.26 (t, *J* = 8 Hz, 2 H), 1.96 (s, 3 H), 1.56-1.46 (m, 2 H), 1.44-1.32 (m, 10 H), 1.30 (s, 12 H), 0.92 (t, *J* = 8 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 123.5, 88.3, 84.0, 83.4, 72.6, 30.9, 28.9, 28.3, 23.9, 21.9, 20.1, 18.8, 12.9 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.9 ppm; IR (ATR): $\tilde{\nu}$ = 2975, 2931, 2860, 1592, 1465, 1371, 1348, 1294, 1165, 1143, 976, 928, 855, 668, 554 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{19}H_{33}BO_3+Na]^+$: 343.2415; found: 343.2415.

(*E*)-5-(Cyclohex-1-en-1-yl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-en-3-ol (10o). Colorless oil (33 mg, 69%); ^{1}H NMR (400 MHz, CD_3OD) δ = 5.47-5.38 (m, 1 H), 4.35 (t, *J* = 8 Hz, 1 H), 2.21-1.97 (m, 4 H), 1.74 (s, 3 H), 1.72-1.55 (m, 6 H), 1.26 (s, 12 H), 0.91 (t, *J* = 8 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 148.1, 144.2, 122.1, 82.8, 72.8, 29.5, 26.7, 24.8, 24.1, 23.9, 22.4, 21.8, 16.0, 9.4 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.5 ppm; IR (ATR): $\tilde{\nu}$ = 2977, 2929, 2876, 2068, 1623, 1378, 1353, 1291, 1131, 1081, 977, 918, 857, 699, 563 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{18}H_{31}BO_3+Na]^+$: 329.2258; found: 329.2261.

(2*E*,5*E*,7*E*)-3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(3-(trifluoromethyl)phenyl)nona-2,5,7-trien-4-ol (10p). Yellow oil (56 mg, 68%, contains ≈8 % of the 2*E*,5*Z*,7*Z*-isomer); ^{1}H NMR (400 MHz,

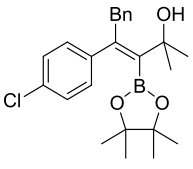
CD_3OD) δ = 7.62-7.42 (m, 4 H), 6.36-6.19 (m, 1 H), 6.19-6.02 (m, 1 H), 5.93-5.52 (m, 2 H), 5.08 (d, *J* = 8 Hz, 1 H), 2.06 (s, 3 H), 1.82-1.74 (m, 3 H), 1.06 (s, 6 H), 1.01 (s, 6 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 146.6, 143.7, 131.3, 131.2, 131.1, 130.4, 129.8 (q, *J* = 31 Hz), 129.1, 128.4, 124.4 (q, *J* = 270 Hz), 124.3 (q, *J* =4 Hz), 123.2 (q, *J* =4 Hz), 83.2, 72.6, 23.6, 23.5, 19.3, 16.9 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.2 ppm; IR (ATR): $\tilde{\nu}$ = 2977, 2931, 2058, 1575, 1361, 1329, 1309, 1119, 1076, 986, 850, 804, 696, 663 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{22}H_{28}BF_3O_3+Na]^+$: 431.1976; found: 431.1976.

Representative Procedure for *trans*-Allylboration. Preparation of (*E*)-4-(4-Methoxyphenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hepta-3,6-dien-2-ol (11). A flame-dried



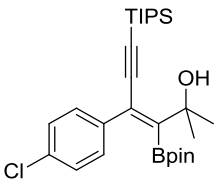
glass tube equipped with a magnetic stir bar was charged under Ar with 1,4-dioxane (2.5 mL), 2-methyl-4-(4-methoxyphenyl)but-3-yn-2-ol (48.2 mg, 0.253 mmol), NaHMDS (46.5 mg, 0.253 mmol), and B_2Pin_2 (71.1 mg, 0.28 mol). The mixture was stirred for 2-5 minutes at room temperature before $Pd(PtBu_3)_2$ (12.7 mg, 0.025 mmol) and allyl bromide (65 μL, 0.75 mmol) were added. The tube was sealed and the mixture stirred at 75 ^{o}C (bath temperature) for 18 h. After cooling to room temperature, the reaction was quenched with aq. sat. NH_4Cl (2 mL), the aqueous phase was extracted by EtOAc (3 x 5 mL), and the combined organic layer were dried ($NaSO_4$), filtered and evaporated. The residue was purified by flash chromatography (SiO_2, hexanes/acetone), affording the title compound as a colorless oil (60 mg, 66 %). ^{1}H NMR (400 MHz, CD_3OD) δ = 7.12-7.02 (m, 2 H), 6.83-6.74 (m, 2 H), 5.70-5.55 (m, 1 H), 4.90-4.85 (m, 1 H), 4.84-4.82 (m, 1 H), 3.75 (s, 3 H), 3.41-3.33 (m, 2 H), 1.50 (s, 6 H), 0.94 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 158.7, 144.9, 136.5, 135.7, 130.2, 114.8, 112.6, 83.0, 72.7, 54.3, 39.3, 29.9, 23.7 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 29.6 ppm; IR (ATR): $\tilde{\nu}$ = 2976, 2932, 1606, 1509, 1463, 1348, 1291, 1242, 1175, 1143, 1109, 1034, 909, 832, 808, 732, 666, 553, 512 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{21}H_{31}BO_4+Na]^+$: 381.2208; found: 381.2209.

(*E*)-4-(4-Chlorophenyl)-2-methyl-5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-

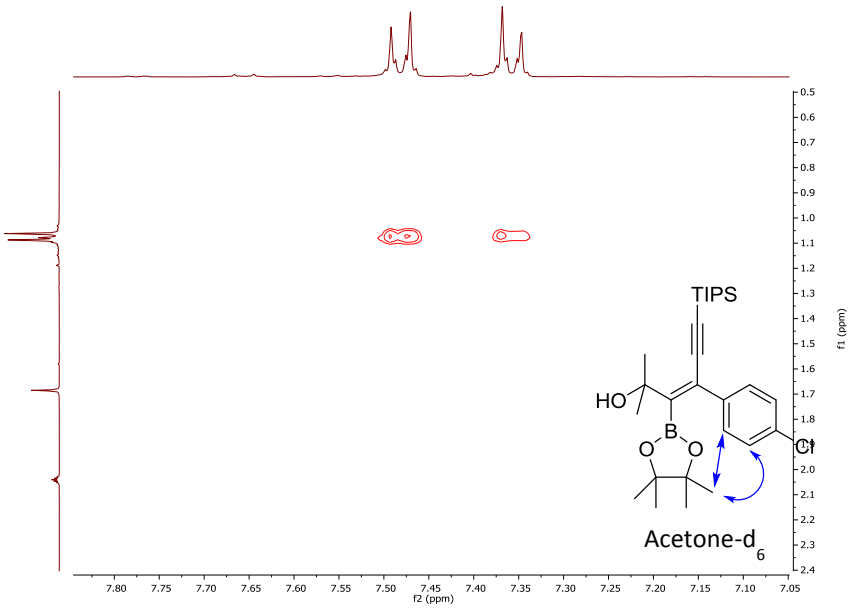


3-en-2-ol (12). Prepared according to the representative procedure using benzyl bromide instead of MeI; white solid (50 mg, 65%); mp: 133-134 ^{o}C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ = 7.18-6.99 (m, 9 H), 4.13 (s, 2 H), 3.86 (brs, OH), 1.57(s, 6 H), 0.94 (s, 12 H) ppm; ^{13}C NMR (101 MHz, $(CD_3)_2CO$) δ = 143.6, 143.0, 139.5, 131.6, 131.2, 129.2, 127.8, 127.1, 125.5, 82.8, 72.6, 39.9, 31.1, 24.2 ppm; ^{11}B NMR (128 MHz, $(CD_3)_2CO$) δ = 29.9 ppm; IR (ATR): $\tilde{\nu}$ = 2975, 2932, 1601, 1484, 1349, 1298, 1203, 1141, 1085, 1014, 980, 848, 724, 700, 548, 460 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{24}H_{30}BClO_3+Na]^+$: 435.1869; found: 435.1870.

Representative Procedure for *trans*-Alkynylboration. Preparation of (*Z*)-4-(4-chlorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-6-(triisopropylsilyl)hex-3-en-5-yn-2-ol

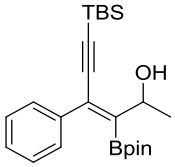


(13a). A flame-dried tube equipped with a magnetic stir bar was charged under Ar with THF (0.2 mL), toluene (2 mL), 2-methyl-4-(4-chlorophenyl)but-3-yn-2-ol (38.8 mg, 0.2 mmol,), NaHMDS (36.7 mg, 0.2 mmol,), and B_2Pin_2 (55.8mg, 0.22 mol). The mixture was stirred for 2 minutes at room temperature before $Pd_2(dba)_3$ (9.1 mg, 0.01 mmol), tri(2-furyl)phosphine (9.2 mg, 0.04 mmol) and (bromoethynyl)triisopropylsilane (156 mg, 0.6 mmol) were added. The flask was sealed and the mixture stirred at 75 ^{o}C (bath temperature) for 20 h. After cooling to room temperature, the reaction was quenched with aq. sat. NH_4Cl (2 mL), the aqueous phase was extracted by EtOAc (3 x 5 mL), and the combined organic layer were dried ($NaSO_4$), filtered and evaporated. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc) to provide the title compound as a white solid (90 mg, 90 % yield). mp: 79-80 ^{o}C; ^{1}H NMR (400 MHz, $(CD_3)_2CO$) δ = 7.39-7.33 (m, 2 H), 7.27-7.21 (m, 2 H), 3.93 (s, 1 H), 1.57 (s, 6 H), 0.98-0.93 (m, 33 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 140.3, 132.8, 130.2, 127.9, 124.0, 106.3, 99.9, 83.4, 74.1, 28.1, 24.2, 18.1, 11.3 ppm; ^{11}B NMR (128 MHz, CD_2Cl_2) δ = 29.5 ppm; IR (ATR): $\tilde{\nu}$ = 2943, 2865, 2129, 1584, 1463, 1360, 1326, 1303, 1142, 1086, 1014, 998, 939, 883, 806, 677, 663, 618, 560 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{28}H_{44}BSiClO_3+Na]^+$: 525.2733; found: 525.2734.



The following compound was prepared analogously:

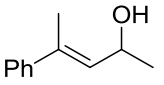
(*Z*)-6-(*tert*-Butyldimethylsilyl)-4-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-3-en-5-yn-2-ol (13b). White solid (65 mg, 55%); mp: 114-115 ^{o}C;; ^{1}H NMR (400 MHz, CD_3OH) δ = 7.46-7.36 (m, 2 H), 7.34-7.22 (m, 3 H), 5.09 (q, *J* = 6.4 Hz, 1 H), 1.43 (d, *J* = 6.8 Hz, 3 H), 1.19 (s, 6 H), 1.14 (s, 6 H), 0.98 (s, 9 H), 0.15 (s, 3 H), 0.14 (s, 3



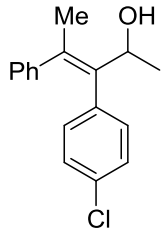
H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 139.9, 127.8, 127.76, 127.71, 127.5, 103.6, 99.8, 83.8, 71.1, 25.2, 23.8, 23.7, 21.2, 16.1, -5.81, -5.83 ppm; ^{11}B NMR (128 MHz, CD_3OH) δ = 30.6 ppm; IR (ATR): ṽ = 2977, 2929, 1590, 1354, 1305, 1250, 1141, 1058, 976, 824, 812, 769, 698, 672, 606 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{24}H_{37}BSiO_3+Na]^+$: 435.2497; found: 435.2499.

Downstream Functionalization

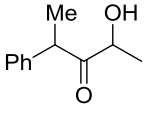
(*E*)-4-Phenylpent-3-en-2-ol (14).[5] Prepared by adaptation of a literature procedure:[6] A mixture of compound **10f** (34.8 mg, 0.12 mmol), $AgNO_3$ (2 mg, 0.012 mmol, 10 mol %), NEt_3 (16 mg, 0.16 mmol) in EtOH/H_2O (0.5 mL/0.5 mL) was stirred at 80 °C for 3 h under air. The reaction was quenched with brine (5 mL) and the aqueous phase extracted with ethyl acetate (5 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and evaporated under vacuum. The residue was purified by flash chromatography on silica gel to afford the product as a colorless oil (16.2 mg, 83%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.35-7.28 (m, 2 H), 7.26-7.19 (m, 2 H), 7.18-7.12 (m, 1 H), 5.69 (dq, *J* = 1.2 and 8.0 Hz, 1 H), 4.69-4.58 (m, 1 H), 1.99 (d, *J* = 1.2 Hz, 3 H), 1.21 (d, *J* = 6.0 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 143.0, 135.7, 132.2, 128.2, 127.1, 125.7, 65.0, 23.3, 15.8 ppm.



(*E*)-3-(4-Chlorophenyl)-4-phenylpent-3-en-2-ol (15). Prepared by adaptation of a literature procedure:[8] A flame-dried Schlenk flask was charged with compound **10f** (0.157 mmol, 45.2 mg) and THF (2 mL). Pd(P*t*-Bu_3)$_2$ (8 mg, 10 mol %), 1-chloro-4-iodobenzene (45.3 mg, 0.19 mmol), solid NaOH (18.8 mg, 0.47 mmol) and H_2O (8.5 µL) were added under Ar and the resulting mixture was stirred at 50 °C for 12 h. After evaporation of all volatile materials, the crude product was purified by flash chromatography on silica gel to offer the title compound as a pale yellow solid (28.4 mg, 66 %). mp: 99-100 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.03-6.97 (m, 4 H), 6.96-6.92 (m, 1 H), 6.92-6.83 (m, 4 H), 5.04 (q, *J* = 6.4 Hz, 1 H), 2.09 (s, 3 H), 1.13 (d, *J* = 6.4 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 144.0, 139.7, 137.5, 135.7, 132.5, 131.8, 128.5, 127.6, 127.3, 125.9, 66.8, 22.0, 20.1 ppm; IR (ATR): ṽ = 3273, 2926, 1488, 1442, 1129, 1069, 1015, 940, 835, 763, 699, 603, 508 cm^{-1}; HRMS (EI) *m/z* calcd for $[C_{17}H_{17}OCl]^+$: 272.0968; found: 272.0963.

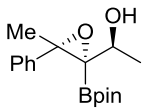


2-Hydroxy-4-phenylpentan-3-one (16). Prepared by adaptation of a literature procedure:[6]: A mixture of compound **10f** (46.2 mg, 0.16 mmol), $NaBO_3{\cdot}H_2O$ (128 mg, 0.64 mmol) and THF/H_2O (2 mL/2 mL) was stirred at room temperature for 3 h. The reaction was quenched with brine (5 mL) and the aqueous phase was extracted with ethyl acetate (3 x 5 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated under vacuum. The crude product was purified by flash chromatography on silica gel to afford the title compound as a colorless oil (20 mg, 70 %, dr = 3.3 :1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.28-7.21 (m, 2 H), 7.21-7.09 (m, 3 H), 4.31-4.04 (m, 1 H), 3.98-3.84 (m, 1 H), 3.18 (brs, OH), 1.37-1.30 (m, 3 H), 1.28-1.04 (m, 3 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 212.8, 140.0, 129.0, 128.7, 127.84, 127.82, 127.4,



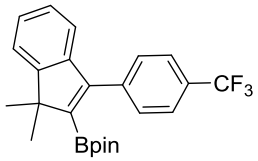
127.2, 72.7, 70.9, 47.8, 47.7, 19.9, 19.7, 19.2, 17.5 ppm; IR (ATR): ṽ = 3400, 2979, 2935, 1713, 1447, 1367, 1149, 1073, 1009, 899, 698 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{11}H_{14}O_2+Na]^+$: 201.0886; found: 201.0887.

(*S)-1-((*2S**,*3S**)-3-Methyl-3-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oxiran-2-yl)ethan-1-ol (17).** Prepared by adaptation of a literature procedure:[7] A flame-dried Schlenk flask



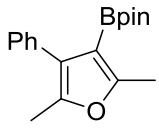
was charged with compound **10f** (40.5 mg, 0.14 mmol), CH_2Cl_2 (2 mL) and $VO(acac)_2$ (5.6 mg, 15 mol %) under Ar. The resulting greenish-blue solution was cooled to –20 ºC before a solution of *tert*-butyl hydroperoxide (5.0 M solution in decane, 84 µL, 0.42 mmol) was added dropwise at this temperature. The mixture was stirred at –20 ºC for 20 h before it was filtered through a pad of Celite. The filtrate was evaporated and the residue was *rapidly* purified by flash chromatography on silica gel to afford the title compound as a white solid (28.5 mg, 66 %). mp: 130-131 ºC; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.30-7.22 (m, 2 H), 7.22-7.16 (m, 2 H), 7.16-7.09 (m, 1 H), 3.66-3.55 (m, 1 H), 2.32-2.22 (m, 1 H), 1.62 (s, 3 H), 1.25 (d, *J* = 6.4 Hz, 3 H), 0.85 (s, 6 H), 0.76 (s, 6 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 142.4, 127.8, 127.1, 126.1, 84.2, 68.6, 65.2, 24.2, 24.1, 21.5, 19.8 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.5 ppm; IR (ATR): ṽ = 3473, 2977, 2921, 1449, 1316, 1276, 1141, 1086, 1057, 982, 851, 780, 703, 661, 551 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{17}H_{25}BO_4+Na]^+$: 327.1738; found: 327.1739.

2-(1,1-Dimethyl-3-(4-(trifluoromethyl)phenyl)-1*H*-inden-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18). Prepared by adaptation of a literature procedure:[9b]



$Sc(OTf)_3$ (2.46 mg, 5 mol%) was added to a solution of compound **5c** (43 mg, 0.1 mmol,) in 1,2-dichloroethane (2 mL) and the resulting mixture was stirred at 50 ^{o}C for 1 h. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel to afford the title compound as a white solid (38.1 mg, 92 %). mp: 124-125 ^{o}C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ = 7.62-7.56 (m, 2 H), 7.53-7.46 (m, 2 H), 7.36-7.30 (m, 1 H), 7.23-7.09 (m, 3 H), 1.36 (s, 6 H), 1.12 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_2Cl_2) δ = 156.9, 151.4, 142.3, 140.3 (d, *J* = 1.5 Hz), 129.7, 129.3 (q, *J* = 32 Hz), 126.6, 126.4, 124.6 (q, *J* = 3.9 Hz), 124.5 (q, *J* = 270 Hz), 121.5, 121.0, 83.1, 52.6, 24.4, 24.3 ppm; ^{11}B NMR (128 MHz, CD_2Cl_2) δ = 30.1 ppm; IR (ATR): ṽ = 2971, 2928, 1591, 1575, 1369, 1321, 1307, 1265, 1120, 1105, 1064, 1016, 852, 759, 719, 673, 634 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{24}H_{26}BF_3O_2+Na]^+$: 437.1870; found: 437.1874.

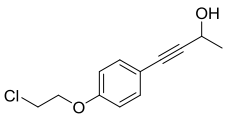
2-(2,5-Dimethyl-4-phenylfuran-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (19). Prepared by adaptation of a literature procedure:[9a]



$AuCl_3$ (1.5 mg, 5 mol%) was added to a solution of (Z)-enynol **13b** (0.11 mmol, 46 mg) in 1,2-dichloroethane (2 mL) and the resulting mixture was stirred at room temperature for 2 h. The solvent was removed in vacuo and the residue was purified by flash chromatography on silica gel to afford the title compound as a colorless oil (19.6 mg, 65 %). ^{1}H NMR (400 MHz, CD_3OD) δ = 7.48-7.26 (m, 5 H),

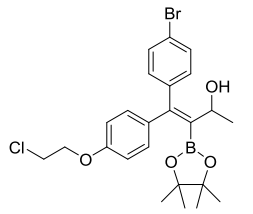
2.52 (s, 3 H), 2.32 (s, 3 H), 1.33 (s, 12 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 159.7, 146.1, 134.6, 129.4, 127.1, 125.8, 125.1, 82.7, 23.6, 12.6, 10.5 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 30.2 ppm; IR (ATR): ṽ = 2977, 2921, 1577, 1413, 1341, 1302, 1141, 1055, 994, 846, 758, 698, 663 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{18}H_{23}BO_3+Na]^+$: 321.1632; found: 321.1633.

4-(4-(2-Chloroethoxy)phenyl)but-3-yn-2-ol (20). Prepared according to a literature procedure.[4]

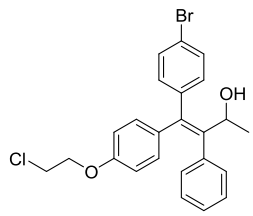


Yellow solid (487 mg, 94%); mp: 73-74 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.40-7.30 (m, 2 H), 6.96-6.86 (m, 2 H), 4.67 (q, *J* = 6.4 Hz, 1 H), 4.25 (t, *J* = 5.6 Hz, 2 H), 3.86 (t, *J* = 5.6 Hz, 2 H), 148 (d, *J* = 6.4 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 158.4, 132.6, 115.6, 114.3, 89.6, 82.5, 68.1, 57.6, 41.8, 23.4 ppm; IR (ATR): ṽ = 3393, 2981, 1609, 1510, 1453, 1289, 1254, 1179, 1110, 1036, 933, 827, 666 cm^{-1}; HRMS (EI) *m/z* calcd for $[C_{12}H_{13}O_2Cl+Na]^+$: 247.0496; found: 247.0495.

(*Z*)-4-(4-Bromophenyl)-4-(4-(2-chloroethoxy)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)but-3-en-2-ol (21). A flame-dried Schlenk-tube equipped with a magnetic stir bar was charged under Ar with THF (0.24 mL), 4-(4-(2-chloroethoxy)phenyl)but-3-yn-2-ol **20** (67.5 mg, 0.3 mmol), and NaHMDS (55.8 mg, 0.3 mmol). B_2Pin_2 (83.8 mg, 0.33 mmol), 1,2-dichloroethane (3 ml), $Pd_2(dba)_3$ (13.7 mg, 0.015 mmol), tri(2-furyl)phosphine (13.9 mg, 0.06 mmol) and bis(4-bromophenyl)iodonium triflate (352 mg, 0.6 mmol) were sequentially added, the tube was sealed and the mixture stirred at 60 °C (bath temperature) for 18 h. After cooling to room temperature, the reaction was quenched with aq. sat. NH_4Cl (2 mL), the aqueous phase was extracted with EtOAc (3 × 5mL), and the combined organic layers were dried ($NaSO_4$), filtered and evaporated. The residue was purified by flash chromatography (SiO_2, hexanes/EtOAc) to provide the title compound as a white solid (95 mg, 62%); mp: 160-161 °C; ^{1}H NMR (400 MHz, CD_3OD) δ = 7.53-7.43 (m, 2 H), 7.13-7.01 (m, 4 H), 6.87-6.80 (m, 2 H), 4.44 (q, *J* = 6.4 Hz, 1 H), 4.20 (t, *J* = 5.6 Hz, 2 H), 3.81 (t, *J* = 5.6 Hz, 2 H), 1.28 (d, *J* = 6.4 Hz, 3 H), 1.19 (s, 6 H), 1.13 (s, 6 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 158.1, 147.3, 141.0, 136.6, 131.0, 130.6, 130.0, 120.6, 113.8, 83.5, 68.9, 68.1, 41.8, 23.9, 23.7, 21.9 ppm; ^{11}B NMR (128 MHz, CD_3OD) δ = 32.0 ppm; IR (ATR): ṽ = 2975, 2924, 1605, 1508, 1484, 1352, 1299, 1242, 1132, 1069, 1010, 961, 882, 850, 828, 814, 757, 671, 617 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{24}H_{29}BBrClO_4+Na]^+$: 529.0923; found: 529.0932.

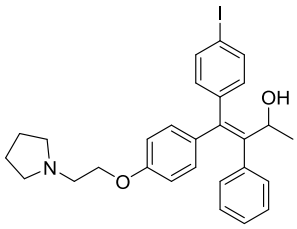


(*Z*)-4-(4-Bromophenyl)-4-(4-(2-chloroethoxy)phenyl)-3-phenylbut-3-en-2-ol (S8). A flame-dried Schlenk flask was charged with compound **21** (0.065 mmol, 33 mg) and THF (0.6 mL). Pd(dppf)Cl_2 (4.7 mg, 10 mol %), iodobenzene (15 µL, 0.134 mmol), aq. KOH (9 M, 29 µL, 0.26 mmol) were added under Ar atmosphere and the resulting mixture was stirred at room temperature for 6 h. After evaporation of all volatile materials, the crude product was purified by flash chromatography to give the title compound as a white solid (29 mg, 97%); mp: 50-51 °C; ^{1}H NMR (400 MHz, CD_3OD)



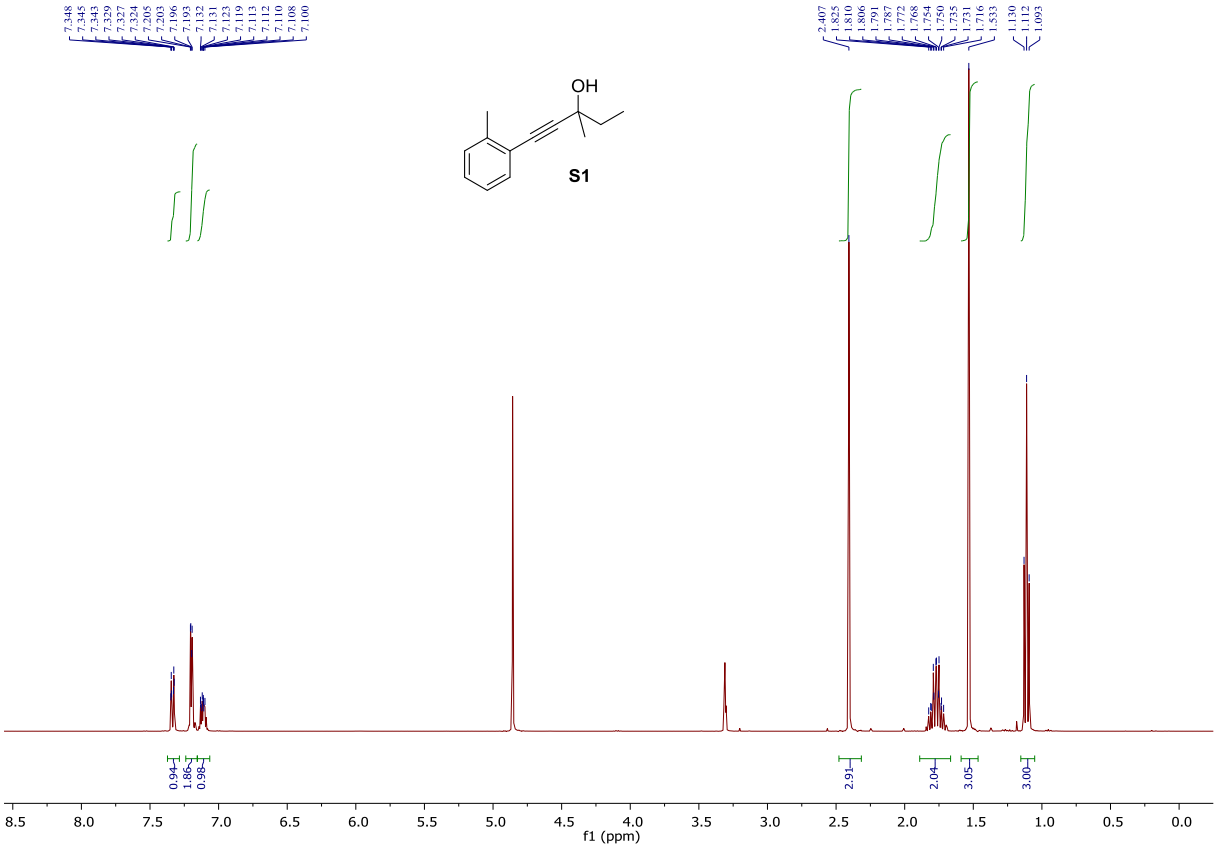
δ = 7.63-7.42 (m, 2 H), 7.30-7.06 (m, 7 H), 6.90-6.75 (m, 2 H), 6.63-6.50 (m, 2 H), 4.75 (q, *J* = 6.4 Hz, 1 H), 4.07 (t, *J* = 5.6 Hz, 2 H), 3.74 (t, *J* = 5.6 Hz, 2 H), 1.13 (d, *J* = 6.4 Hz, 3 H) ppm; ^{13}C NMR (101 MHz, CD_3OD) δ = 156.7, 142.6, 141.2, 139.3, 138.5, 134.8, 131.23, 131.21, 131.1, 130.9, 126.9, 126.0, 120.5, 113.2, 67.8, 67.0, 41.8, 20.5 ppm; IR (ATR): ṽ = 2966, 2925, 1604, 1507, 1485, 1238, 1173, 1070, 1010, 827, 759, 701, 666 cm^{-1}; HRMS (ESI) *m/z* calcd for $[C_{24}H_{22}BrClO_2+Na]^+$: 479.0384; found: 479.0387.

α-Hydroxyidoxifene (22).[11] A Schlenk flask was charged with compound **S1** (0.04 mmol, 18.3 mg),



EtOH (0.15 mL) and pyrrolidine (0.15 mL) and the resulting mixture was stirred at reflux temperature overnight. After reaching ambient temperature, all volatile materials were evaporated. CuI (1.5 mg, 0.008 mmol), NaI (30 mg, 0.2 mmol), 1,4-dioxane (0.3 mL) and *N*,*N*'-dimethylethane-1,2-diamine (1.8 µL, 0.016mmol) were added under Ar and the resulting mixture was stirred at 110 °C (bath temperature) for 18 h. The mixture was allowed to cool before it was filtered through a short plug of silica. The filtrate was concentrated and the residue purified by thin layer chromatography to give the title compound as a white solid (16.3 mg, 75%); mp: 148-149 °C; ^{1}H NMR (300 MHz, CD_3OD) δ = 7.80-7.64 (m, 2 H), 7.30-7.10 (m, 5 H), 7.10-6.99 (m, 2 H), 6.87-6.75 (m, 2 H), 6.64-6.48 (m, 2 H), 4.75 (q, *J* = 6.6 Hz, 1 H), 3.96 (t, *J* = 5.7 Hz, 2 H), 2.81 (t, *J* = 5.7 Hz, 2 H), 2.69-2.50 (m, 4 H), 1.87-1.69 (, m, 4 H), 1.13 (d, *J* = 6.6 Hz, 3 H) ppm; ^{13}C NMR (75 MHz, CD_3OD) δ = 158.5, 143.8, 143.2, 140.9, 139.9, 138.4, 135.8, 132.7, 132.6, 132.5, 128.3, 127.4, 114.4, 93.0, 68.4, 67.4, 55.9, 55.5, 24.1, 21.9 ppm; IR (ATR): ṽ = 2964, 2925, 2806, 1604, 1507, 1480, 1281, 1242, 1109, 1052, 1006, 911, 826, 759, 736, 700 cm^{-1}; HRMS (EI) *m/z* calcd for $[C_{28}H_{30}INO_2+H]^+$: 540.1394; found: 540.1396.

NMR SPECTRA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7.324
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7.203
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7.132
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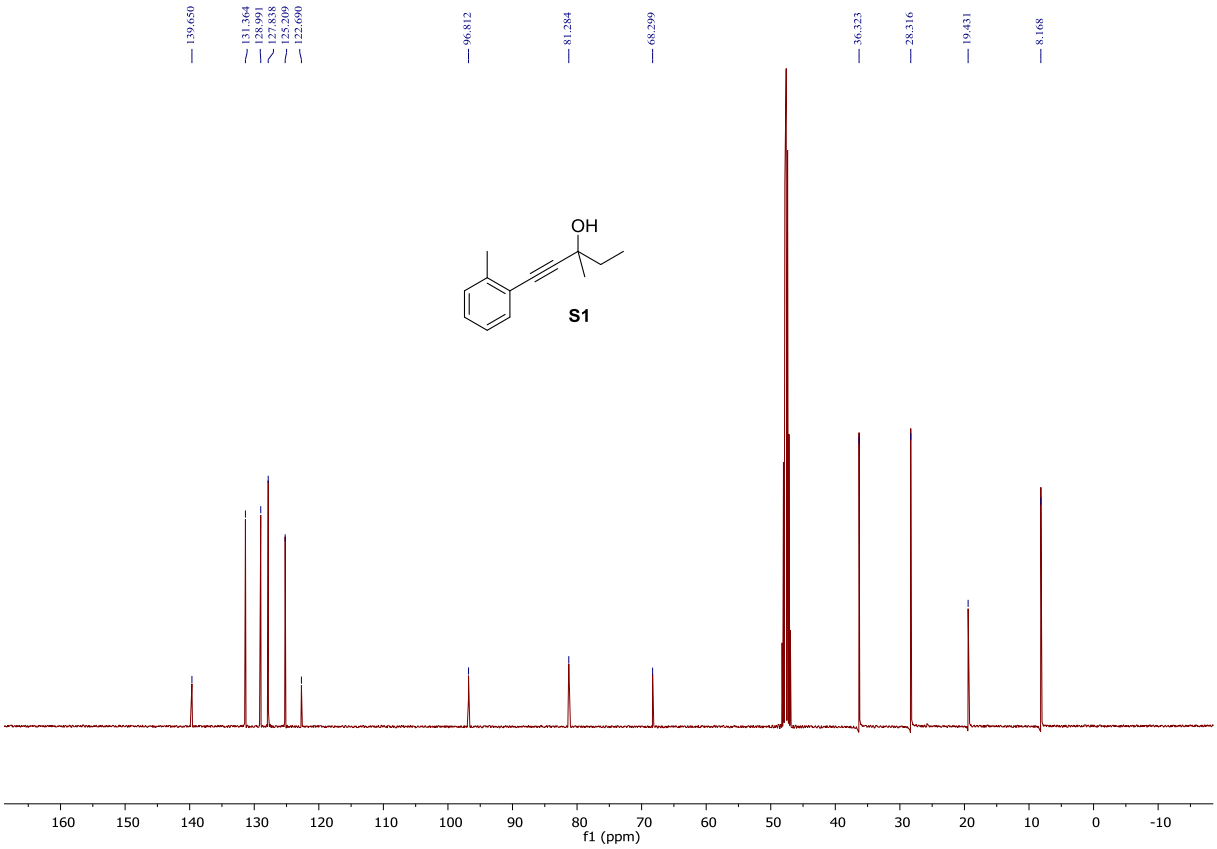
7.119
7.113
7.112
7.110
7.108
7.100
2.407
1.825
1.810
1.806
1.791
1.787
1.772
1.768
1.754
1.750
1.735
1.731
1.716
1.533
1.130
1.112
1.093
OH
S1
0.94
1.86
0.98
2.91
2.04
3.05
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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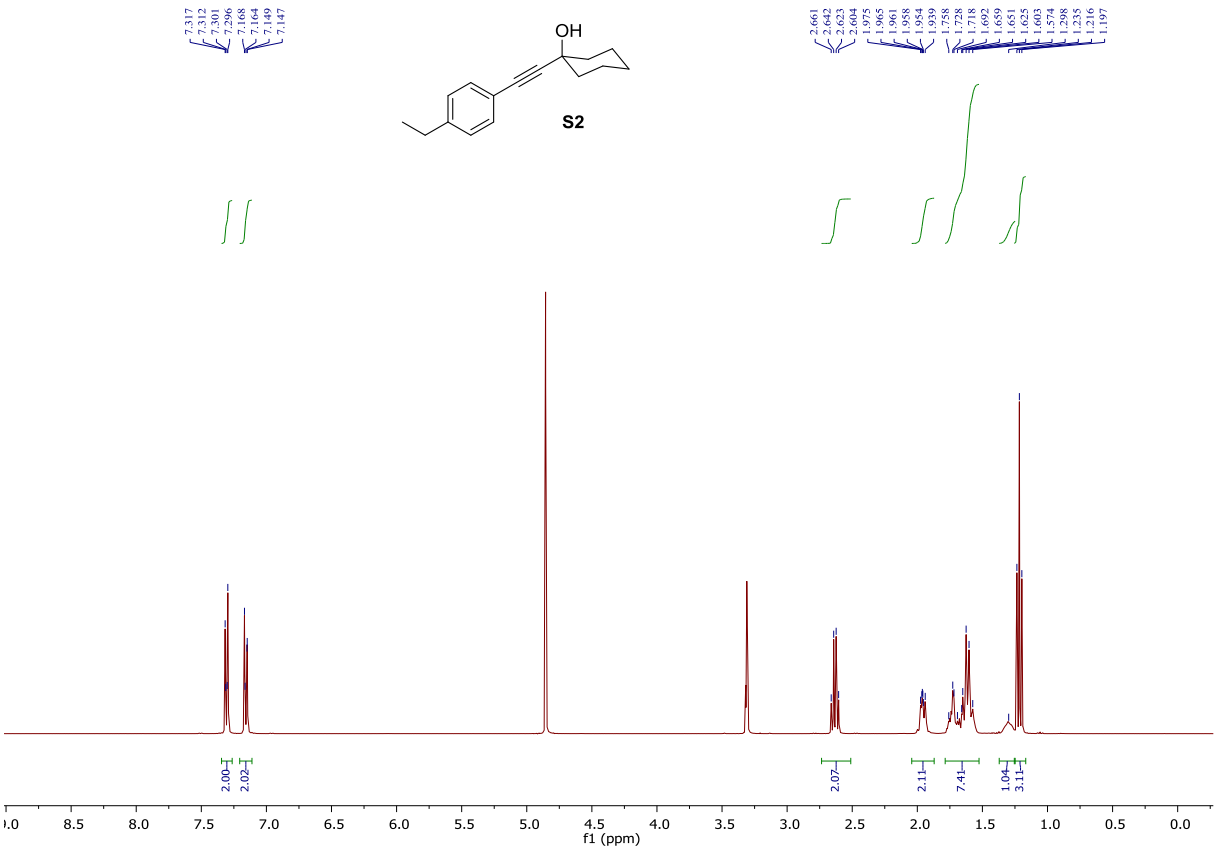
131.364
128.991
127.838
125.209
122.690
96.812
81.284
68.299
36.323
28.316
19.431
8.168
OH
S1
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.301
7.296
7.168
7.164
7.149
7.147
OH
S2
2.661
2.642
2.623
2.604
1.975
1.965
1.961
1.958
1.954
1.939
1.758
1.728
1.718
1.692
1.659
1.651
1.625
1.603
1.574
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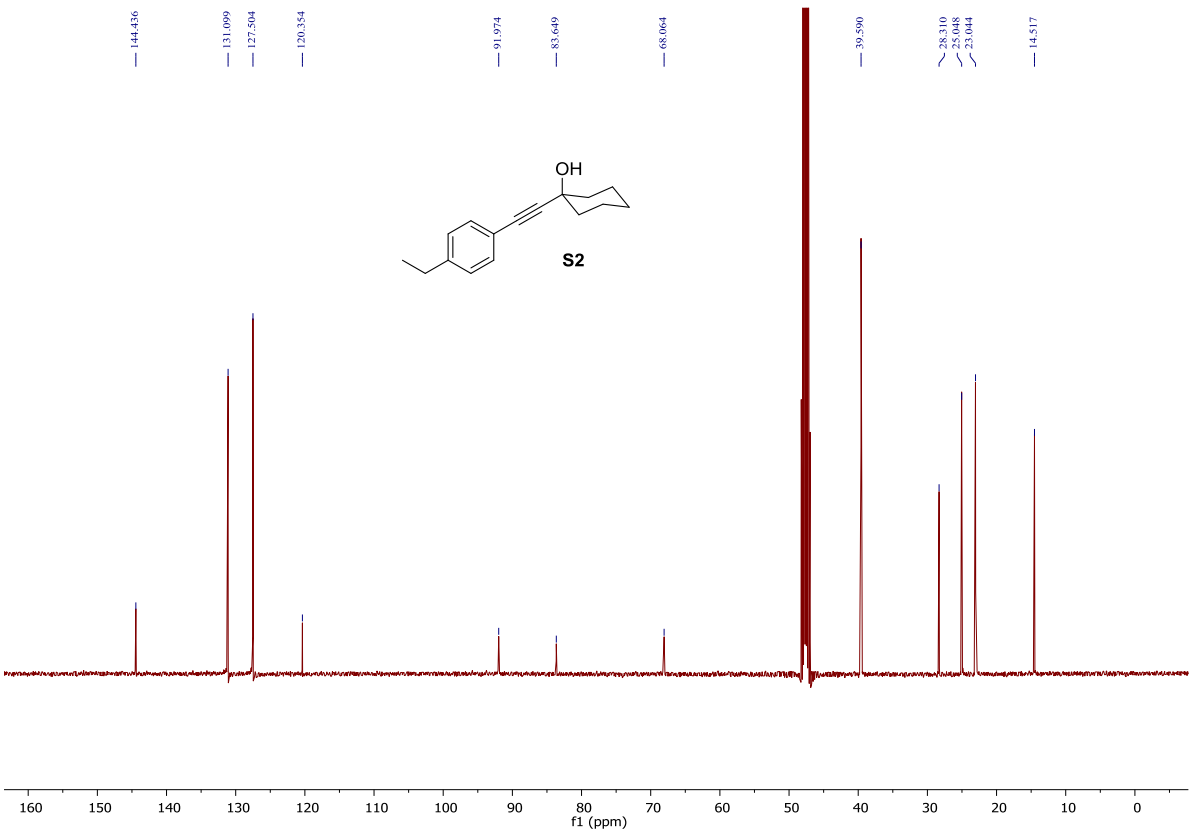
7.41
1.04
3.11
f1 (ppm)


144.436
131.099
127.504
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91.974
83.649
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39.590
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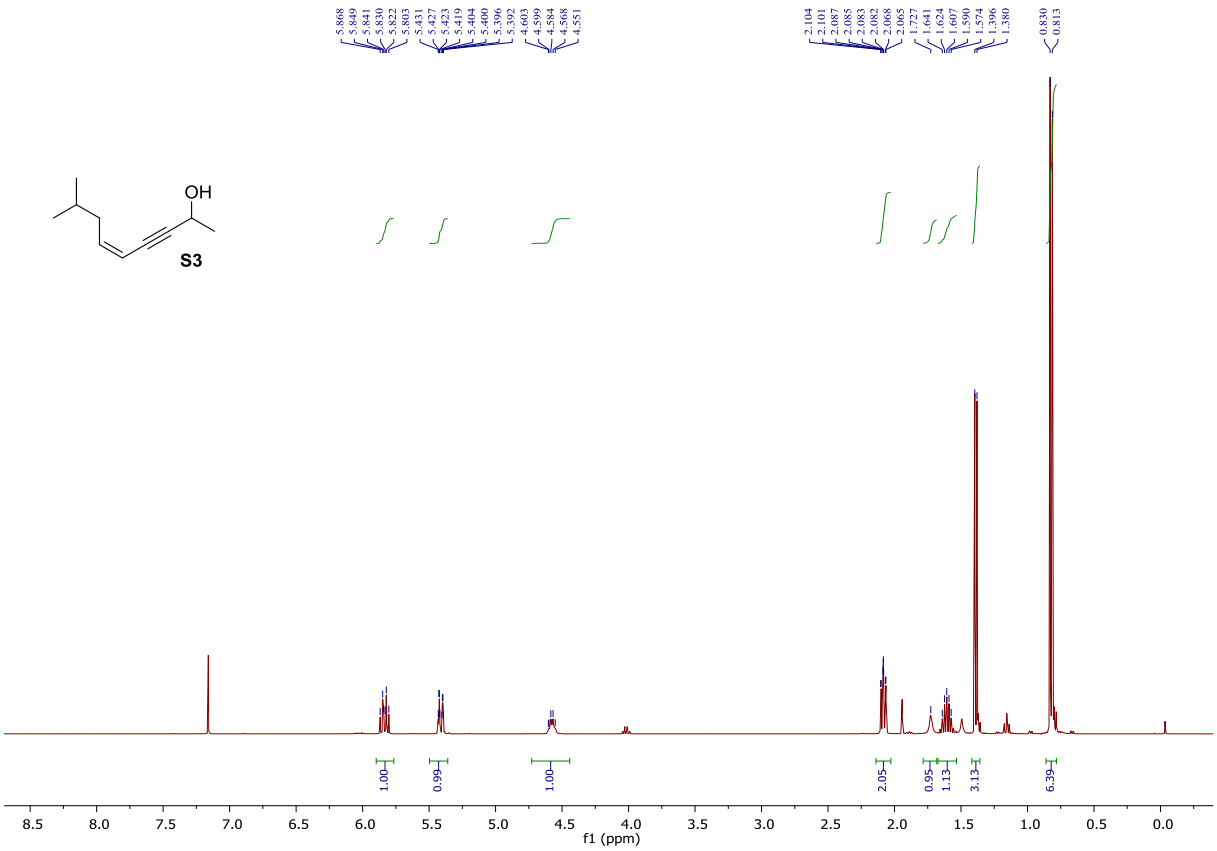
25.048
23.044
14.517
OH
S2
f1 (ppm)


OH
S3
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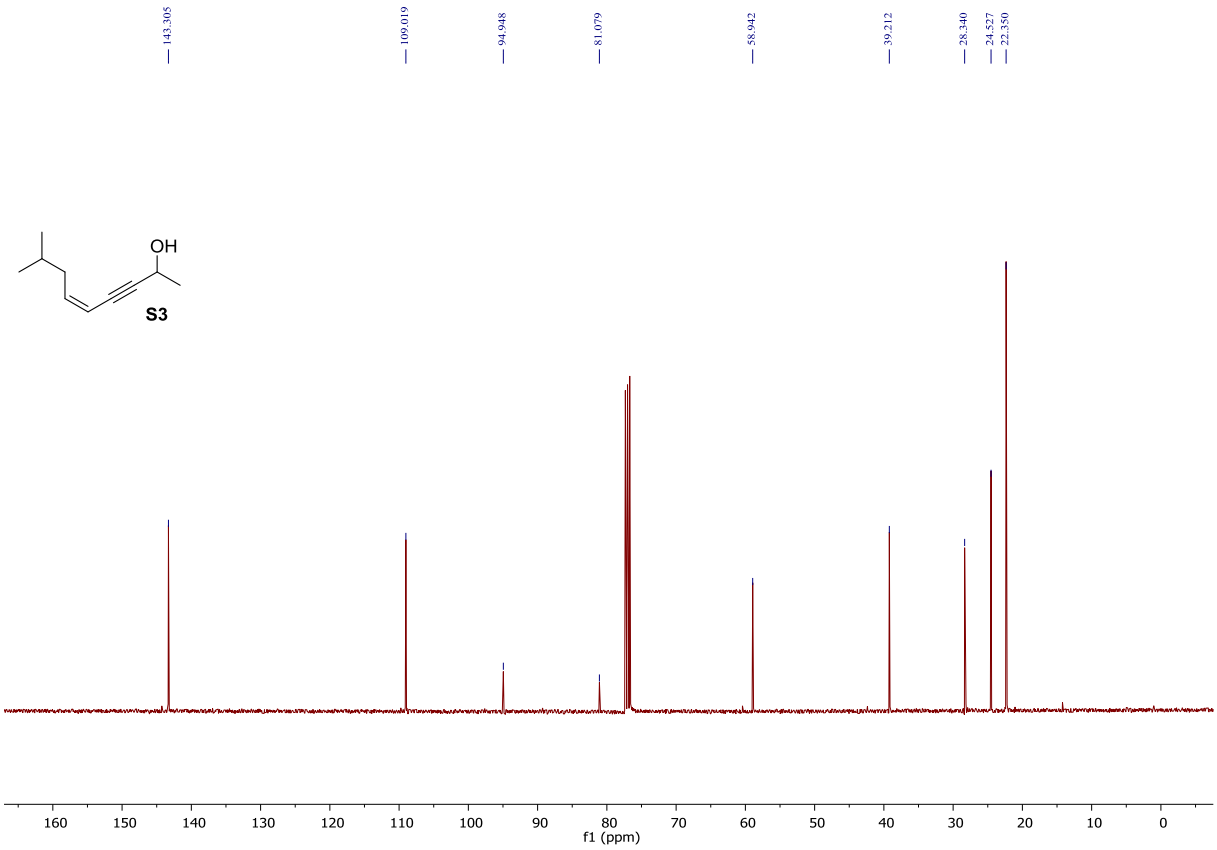
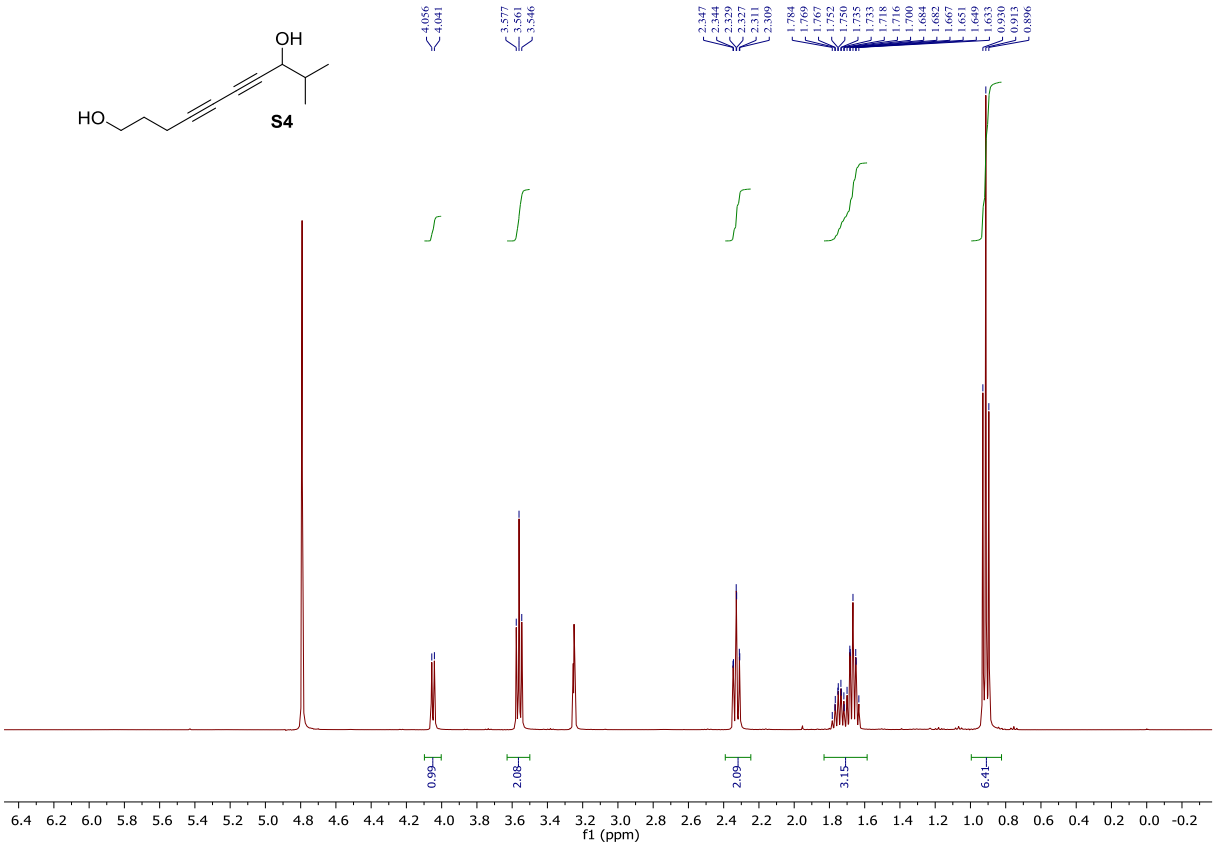
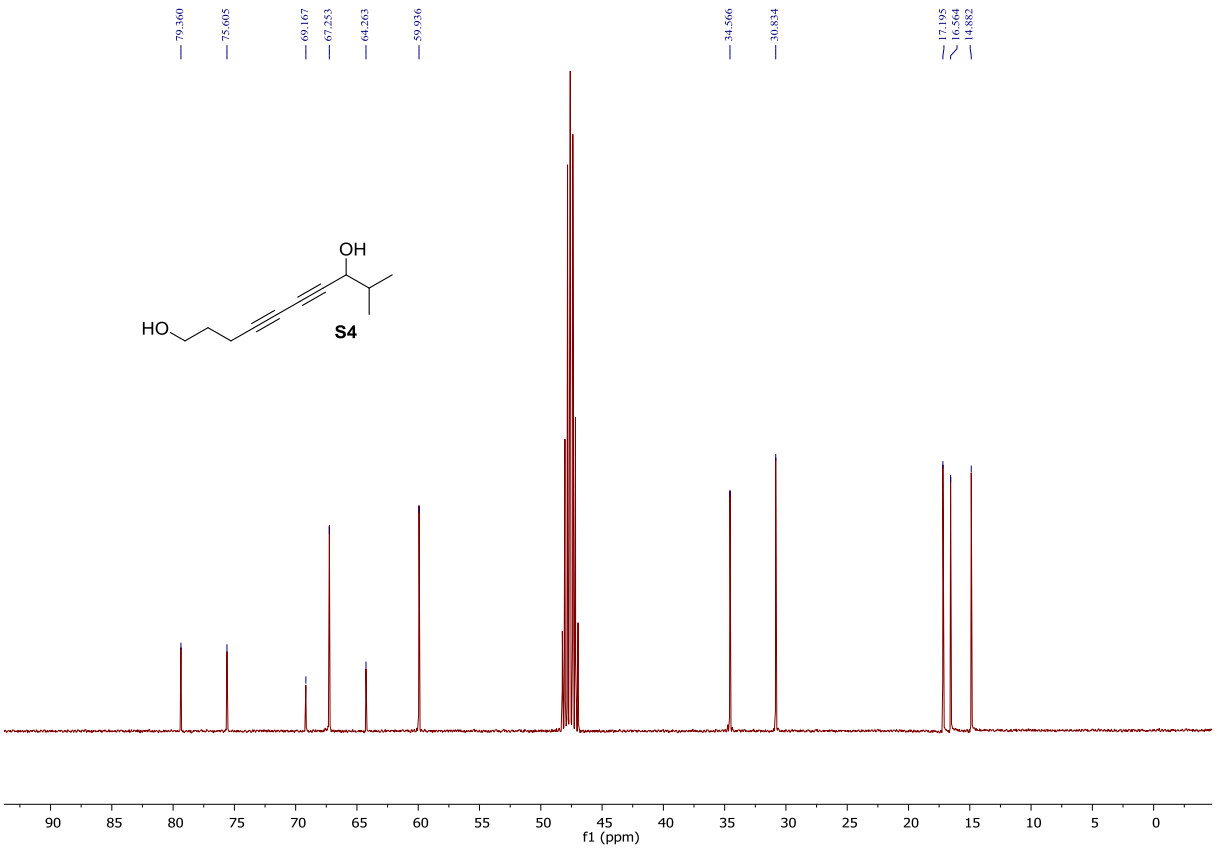
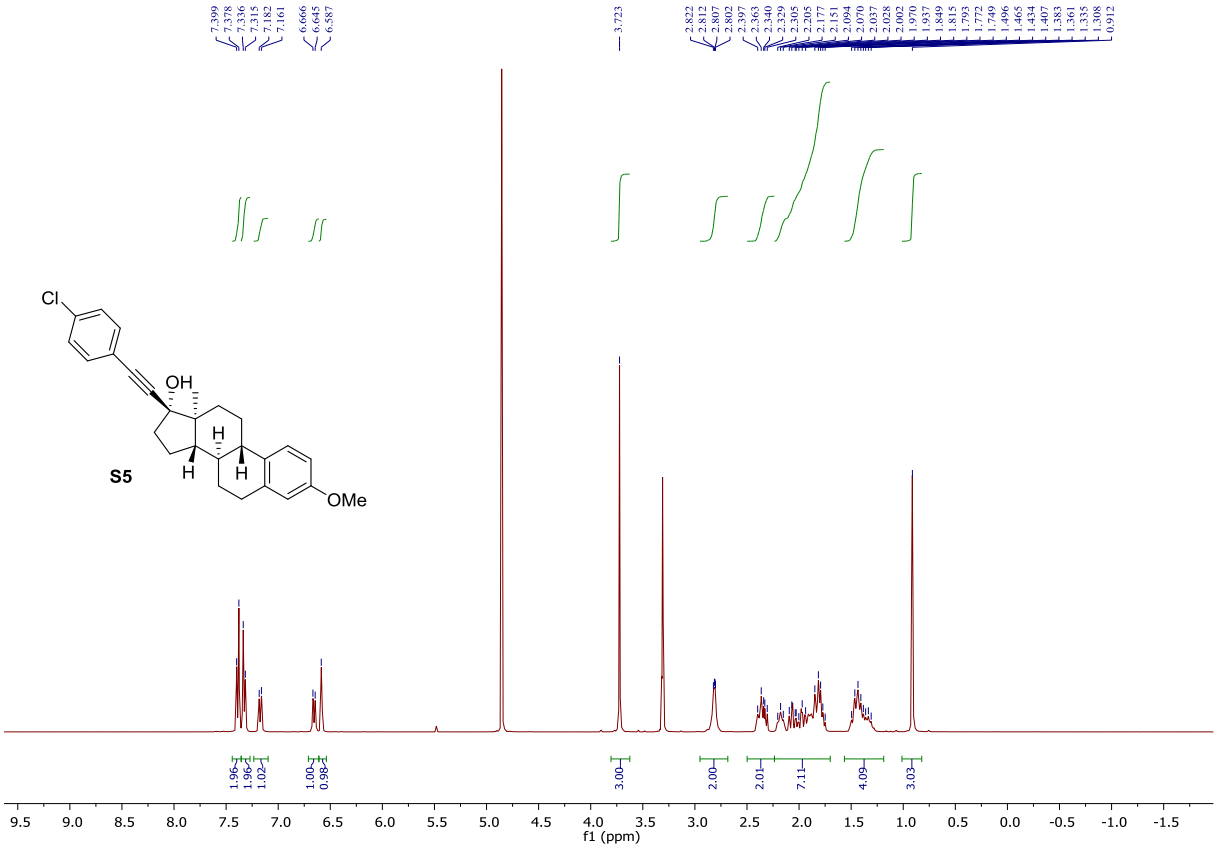
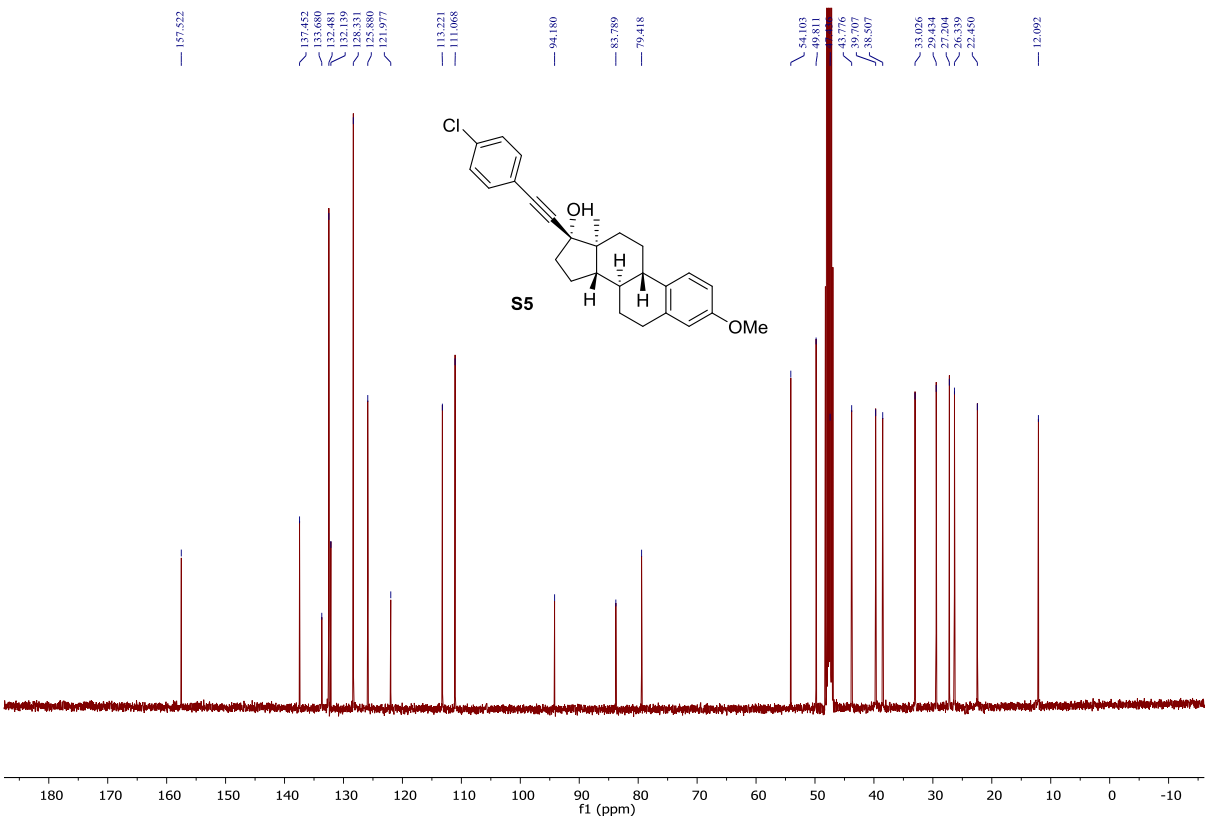
5.849
5.841
5.830
5.822
5.803
5.431
5.427
5.423
5.414
5.404
5.400
5.396
5.392
4.603
4.599
4.584
4.568
4.551
2.104
2.101
2.087
2.085
2.083
2.082
2.068
2.065
1.727
1.641
1.624
1.607
1.590
1.574
1.396
1.380
0.830
0.813
1.00
0.99
1.00
2.05
0.95
1.13
3.13
6.39
f1 (ppm)

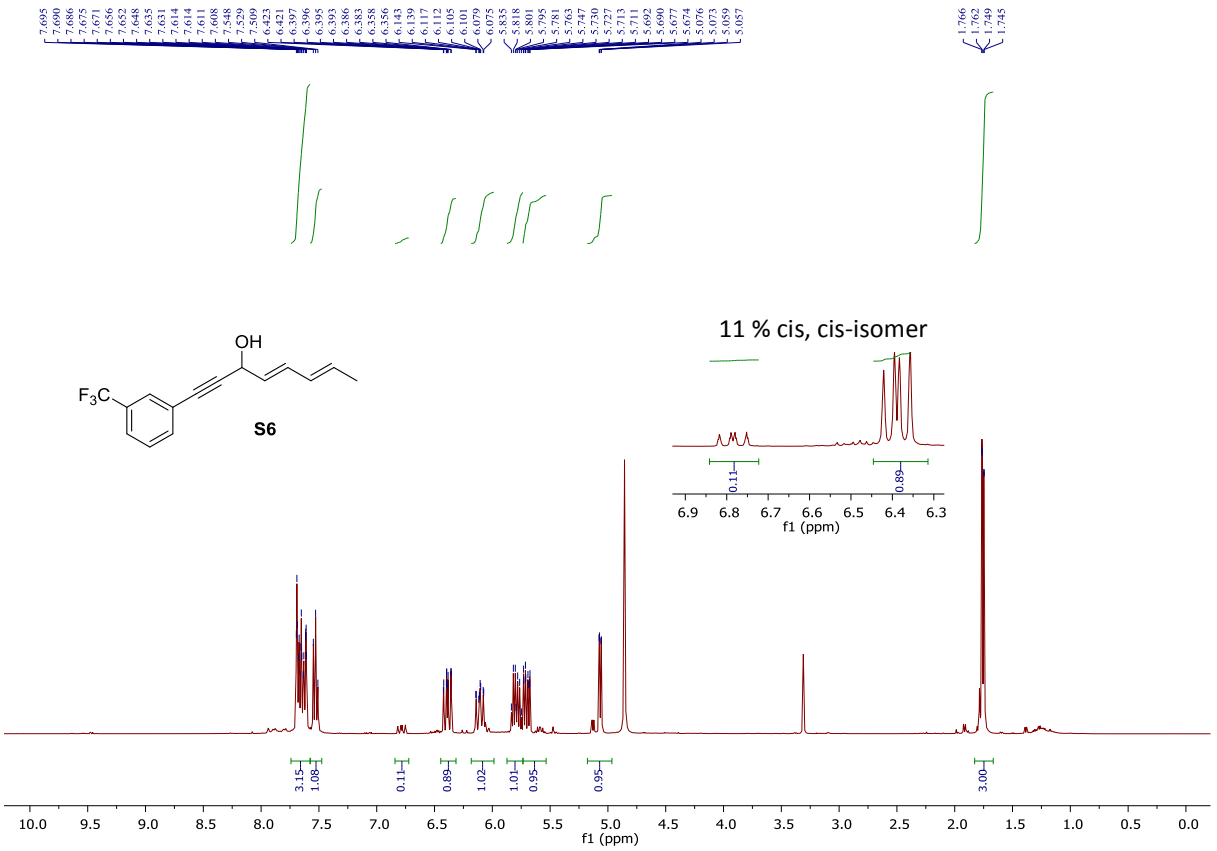

OH
S3
143.305
109.019
94.948
81.079
58.942
39.212
28.340
24.527
22.350
f1 (ppm)

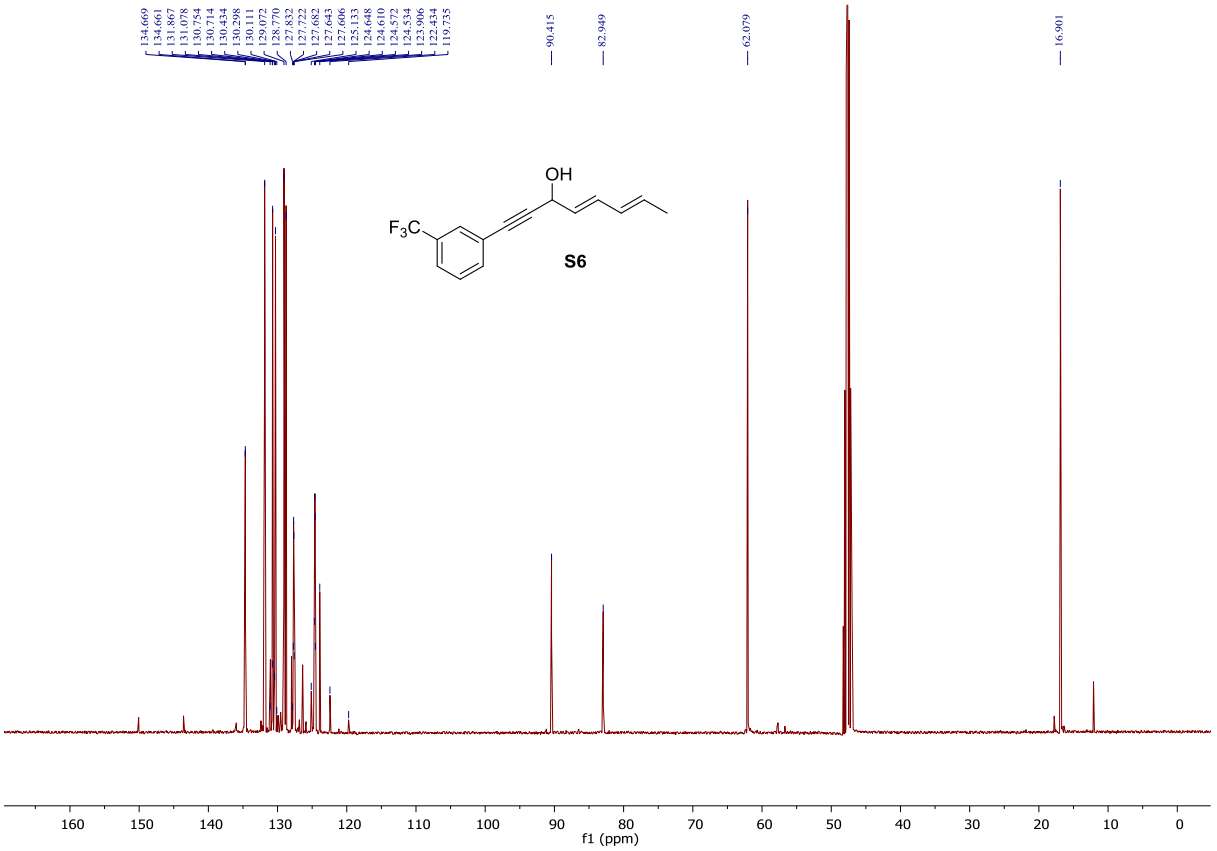

OH
HO
S4
4.056
4.041
3.577
3.561
3.546
2.347
2.344
2.329
2.327
2.311
2.309
1.784
1.769
1.767
1.752
1.750
1.735
1.733
1.718
1.716
1.700
1.684
1.682
1.667
1.651
1.649
1.633
0.930
0.913
0.896
0.99
2.08
2.09
3.15
6.41
f1 (ppm)

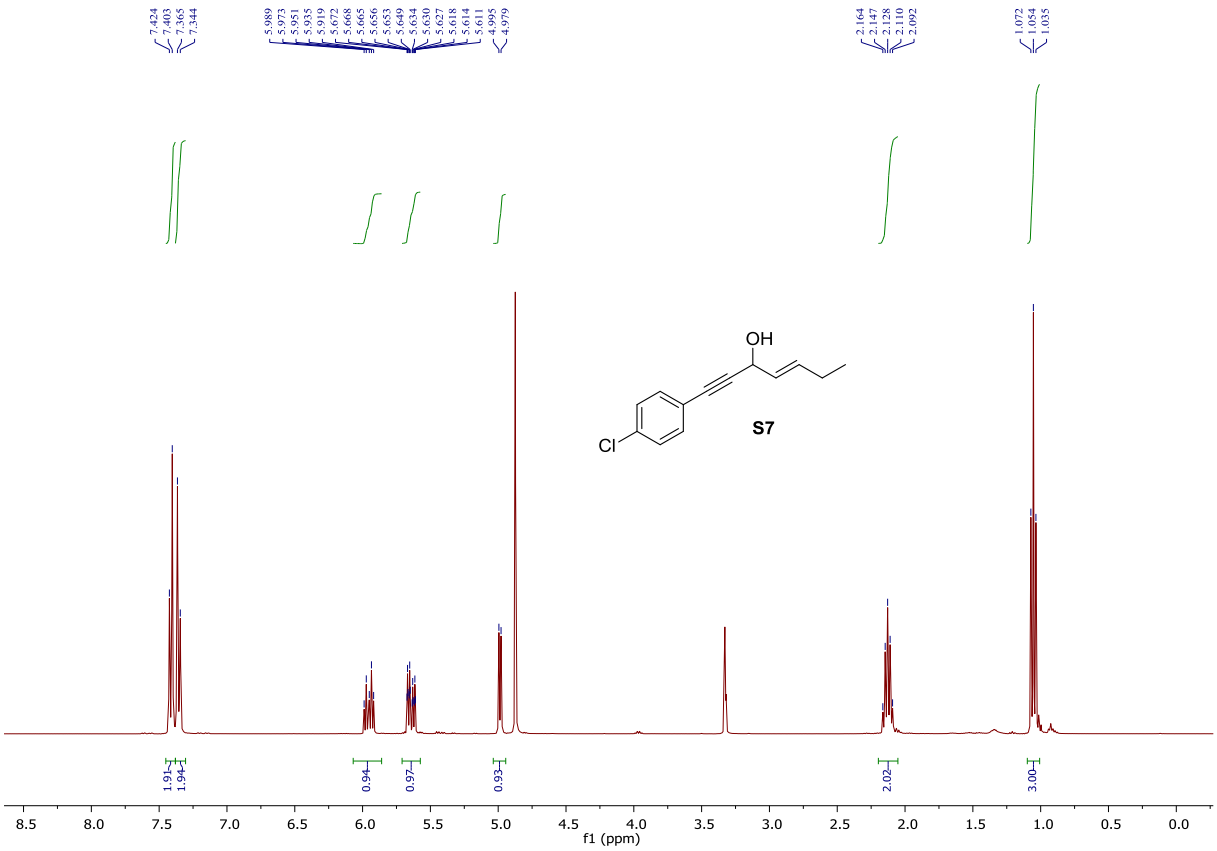

79.360
75.605
69.167
67.253
64.263
59.936
34.566
30.834
17.195
16.564
14.882
OH
HO
S4
f1 (ppm)


Cl
OH
H
H
H
S5
OMe
f1 (ppm)


Cl
OH
H
H
H
S5
OMe
f1 (ppm)


11 % cis, cis-isomer
OH
F3C
S6
f1 (ppm)


OH
F3C
S6
f1 (ppm)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5.973
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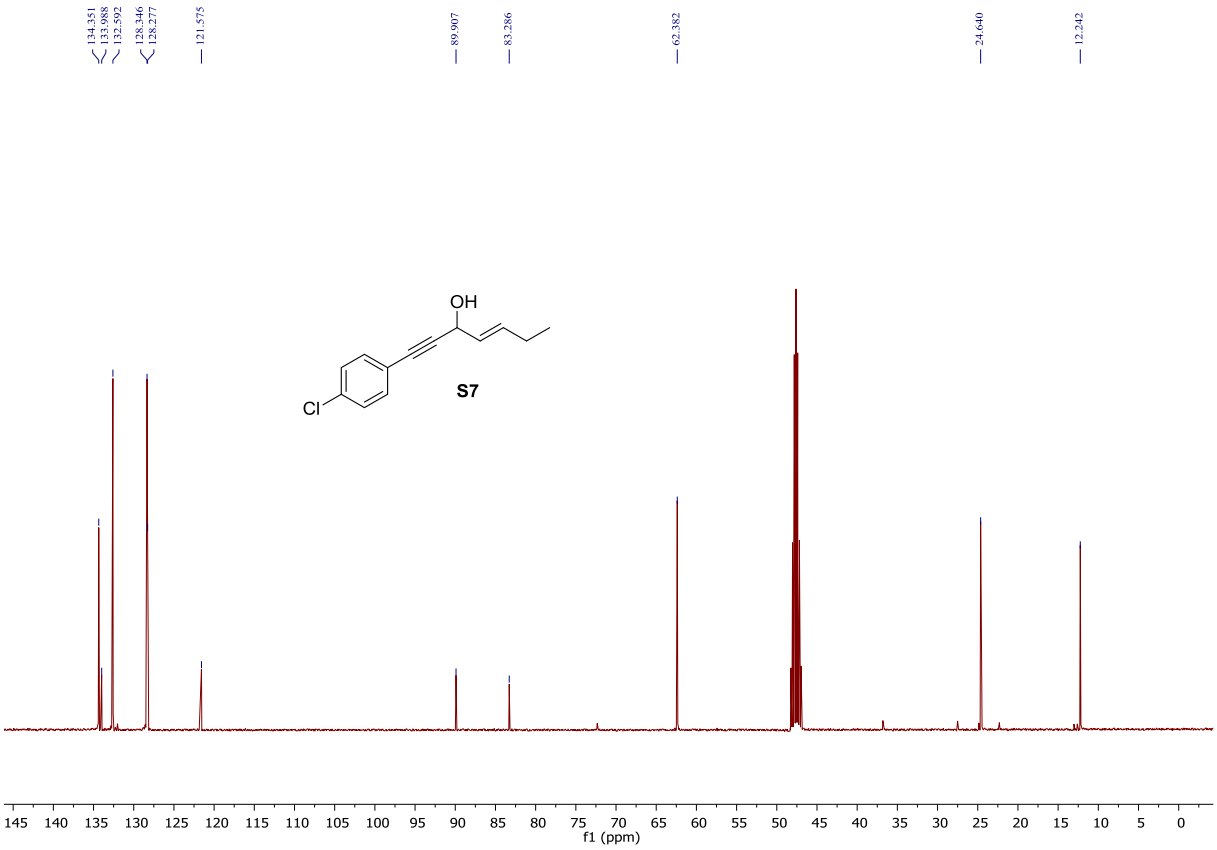
5.935
5.919
5.672
5.668
5.665
5.656
5.653
5.649
5.634
5.630
5.627
5.618
5.614
5.611
4.995
4.979
2.164
2.147
2.128
2.110
2.092
1.072
1.054
1.035
OH
Cl
S7
1.91
1.94
0.94
0.97
0.93
2.02
3.00
f1 (ppm)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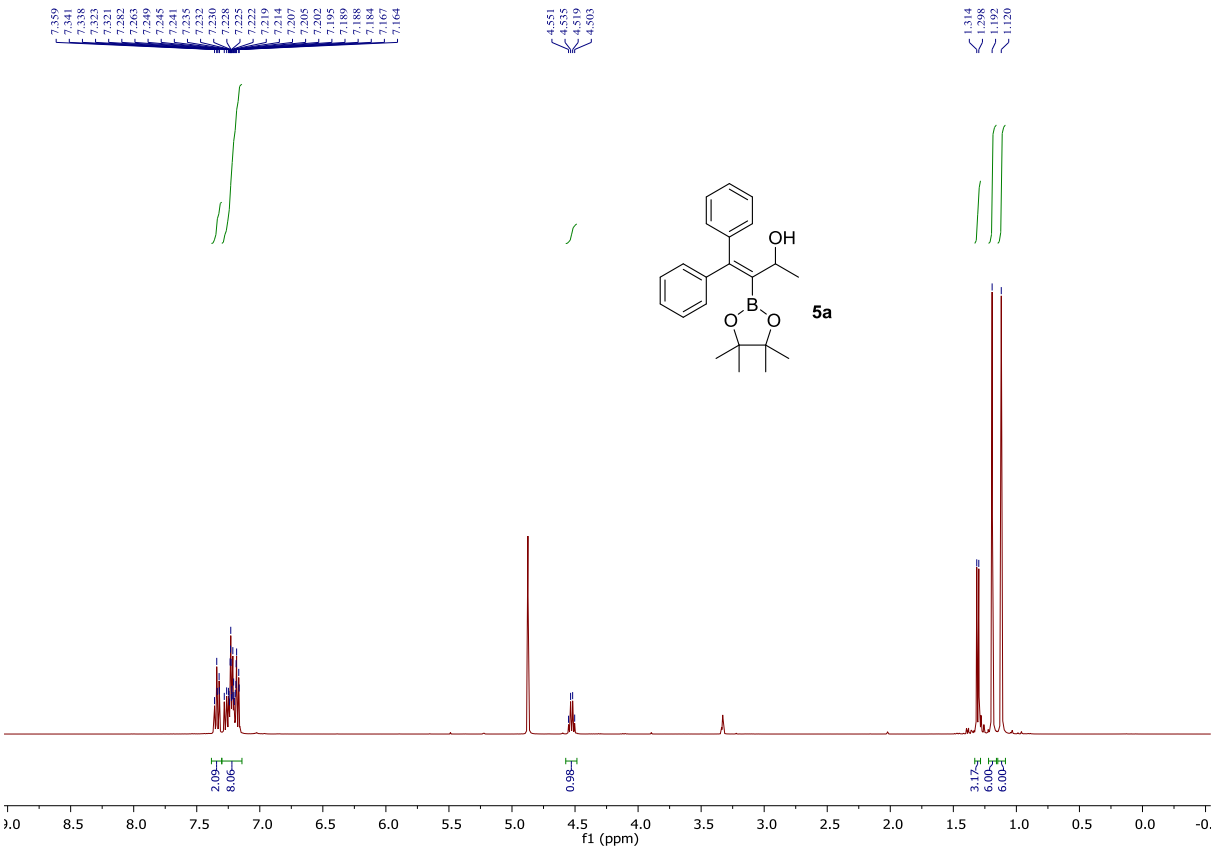
24.640
12.242
OH
Cl
S7
f1 (ppm)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7.321
7.282
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7.249
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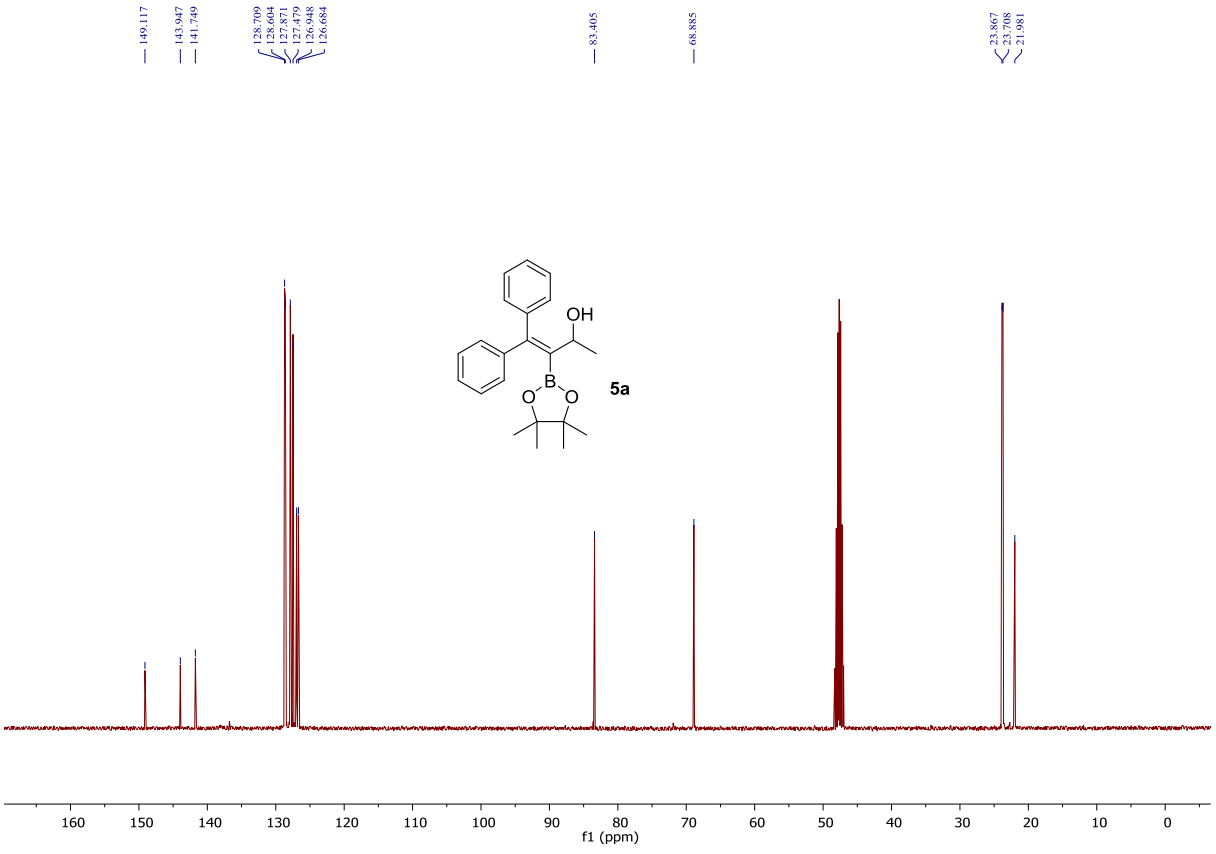
7.241
7.235
7.232
7.230
7.228
7.225
7.222
7.219
7.214
7.207
7.205
7.202
7.195
7.189
7.188
7.184
7.167
7.164
4.551
4.535
4.519
4.503
1.314
1.298
1.192
1.120
OH
B
O
O
5a
2.09
8.06
0.98
3.17
6.00
6.00
f1 (ppm)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128.604
127.871
127.479
126.948
126.684
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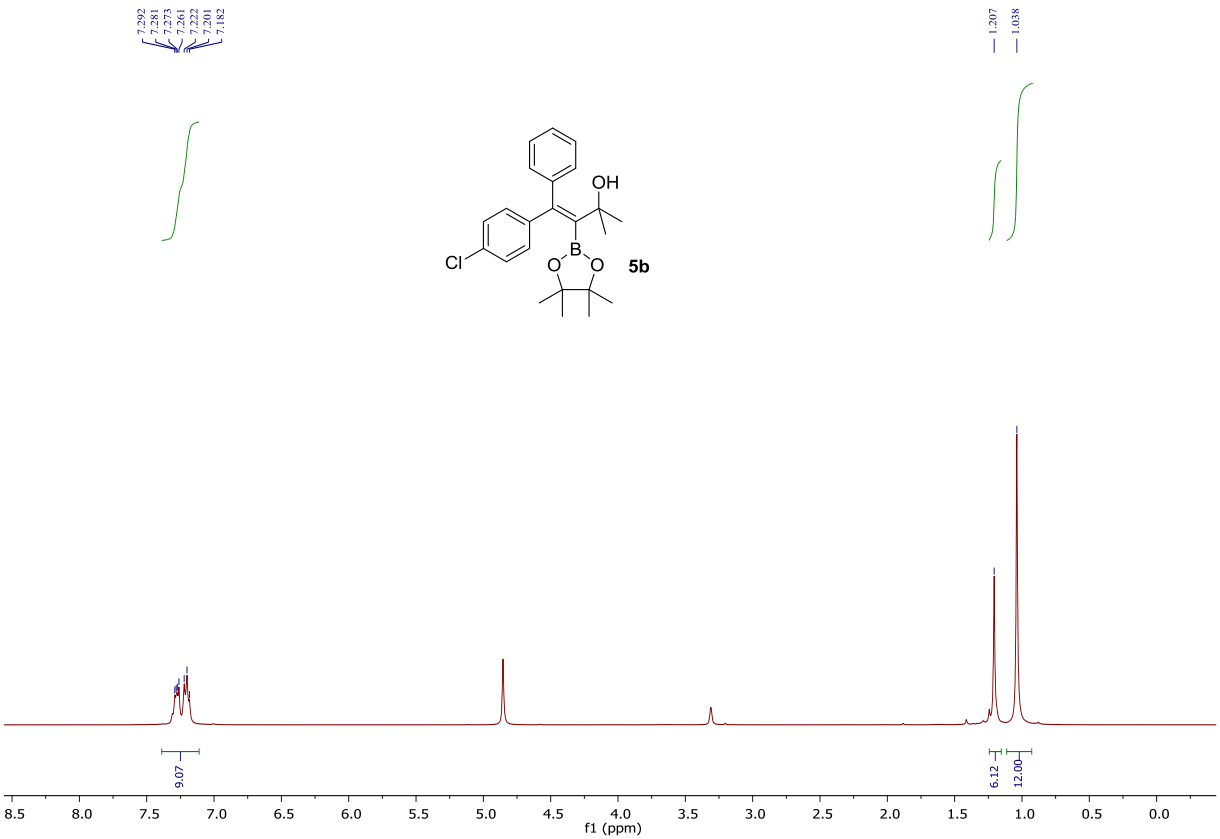
68.885
23.867
23.708
21.981
OH
B
O
O
5a
f1 (ppm)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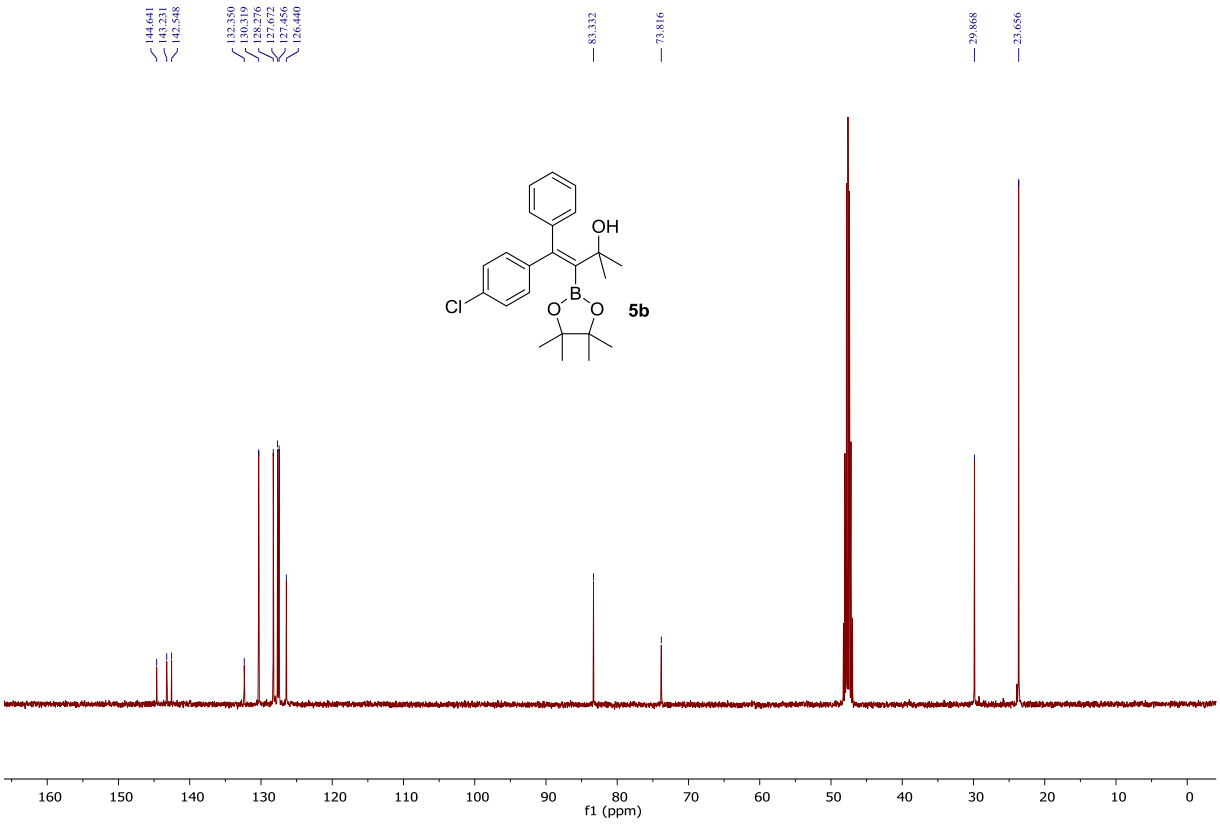
7.281
7.273
7.261
7.222
7.201
7.182
1.207
1.038
OH
Cl
B
O
O
5b
9.07
6.12
12.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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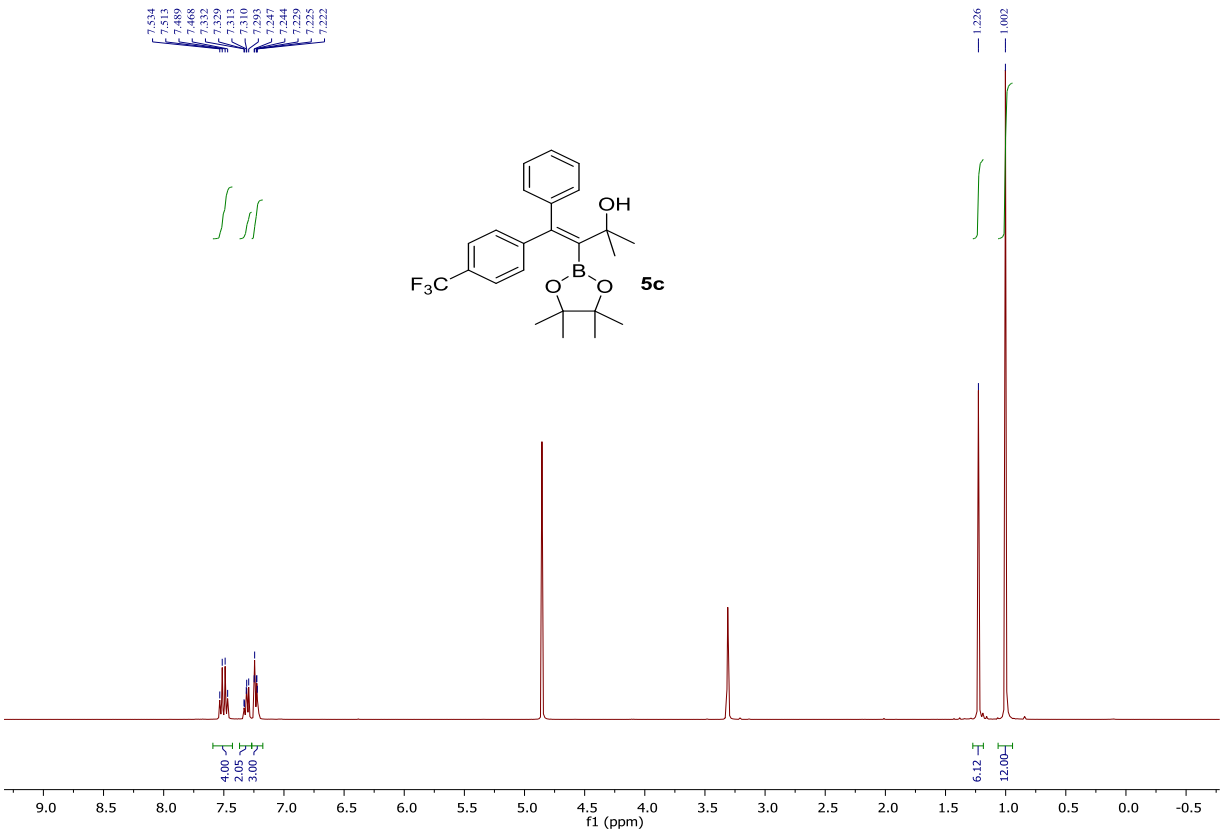
83.332
73.816
29.868
23.656
OH
Cl
B
O
O
5b
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.247
7.244
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7.222
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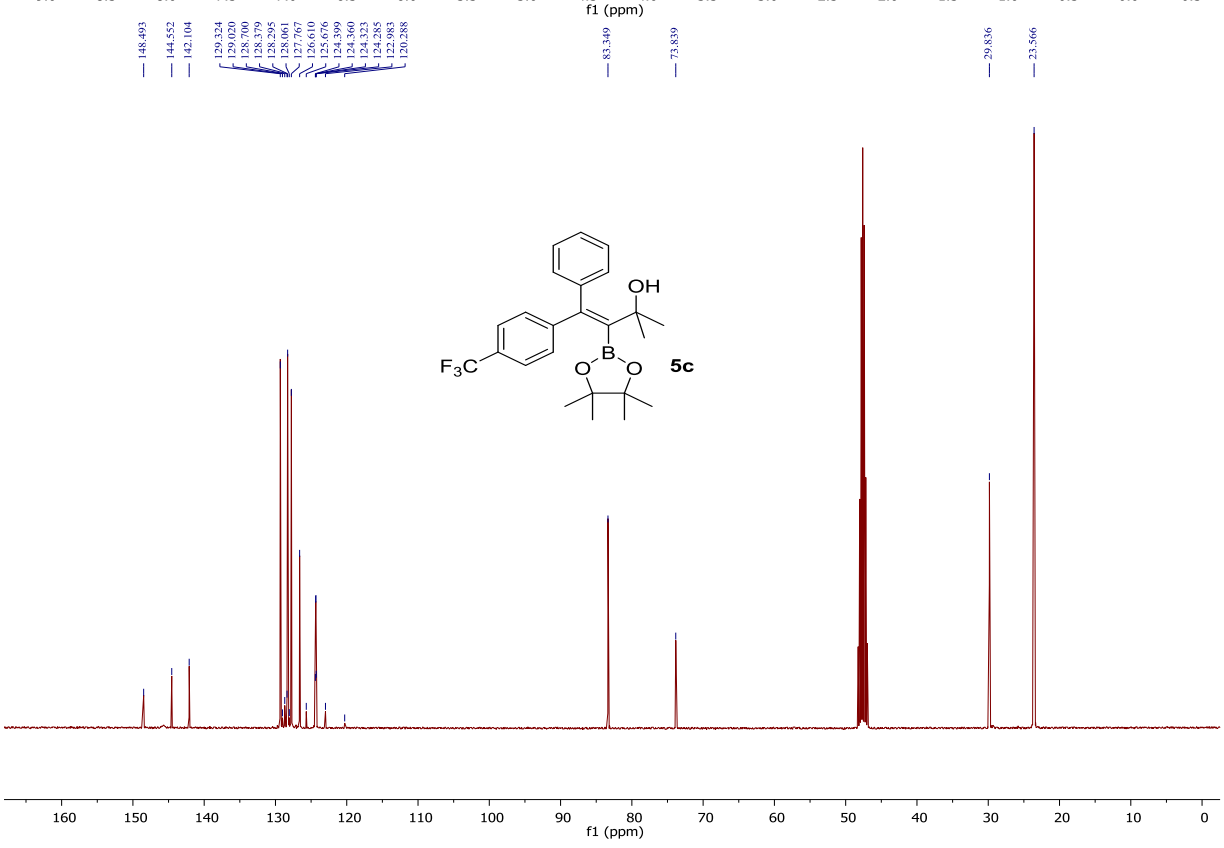
2.05
3.00
6.12
12.00
f1 (ppm)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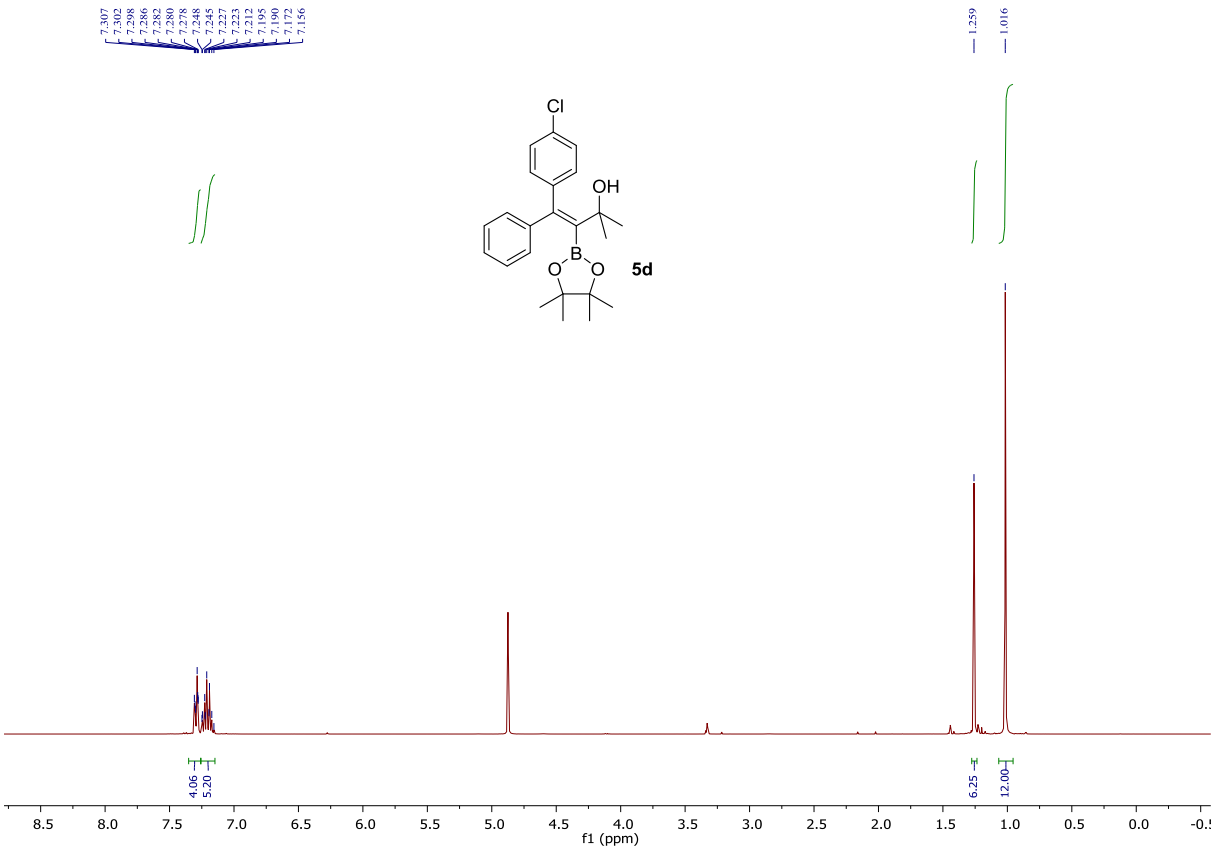
OH
F3C
B
O
O
5c
f1 (ppm)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7.298
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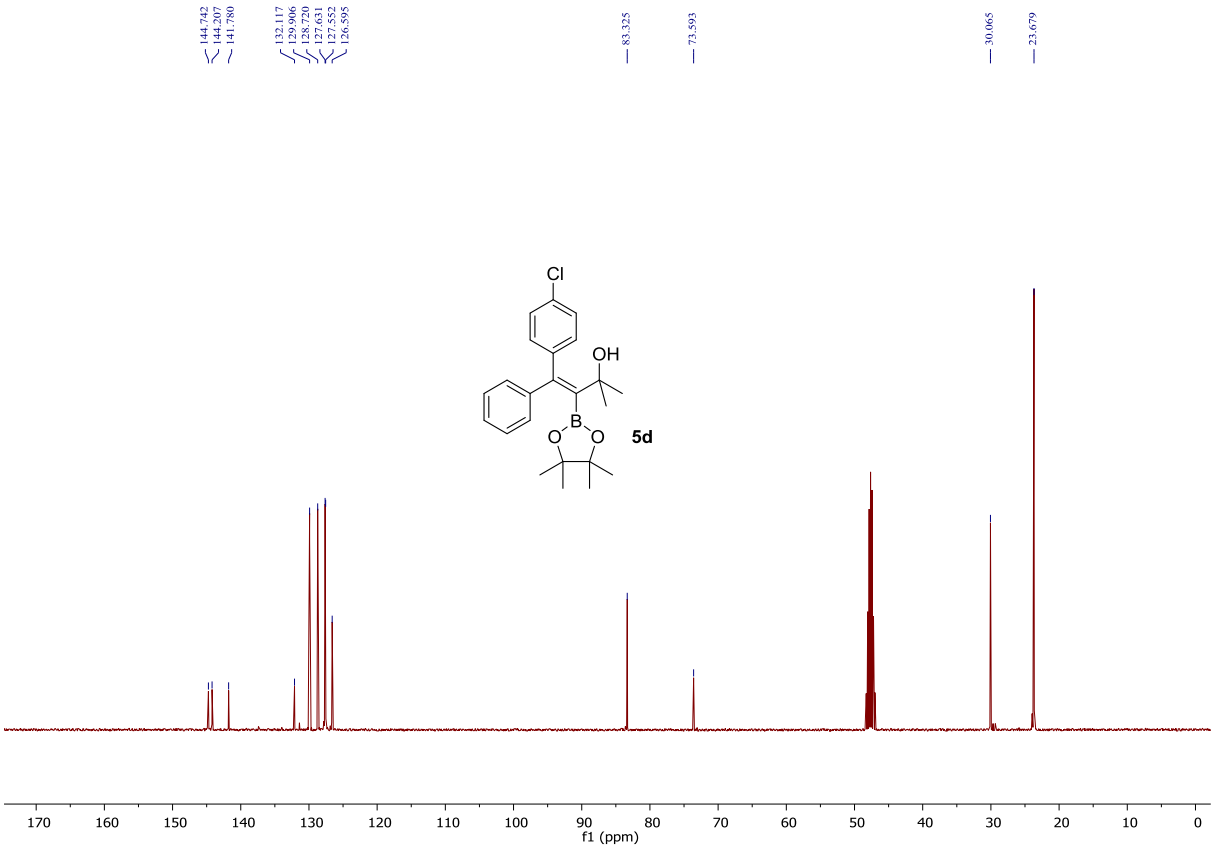
7.282
7.280
7.278
7.248
7.245
7.227
7.223
7.212
7.195
7.190
7.172
7.156
1.259
1.016
Cl
OH
B
O
O
5d
4.06
5.20
6.25
12.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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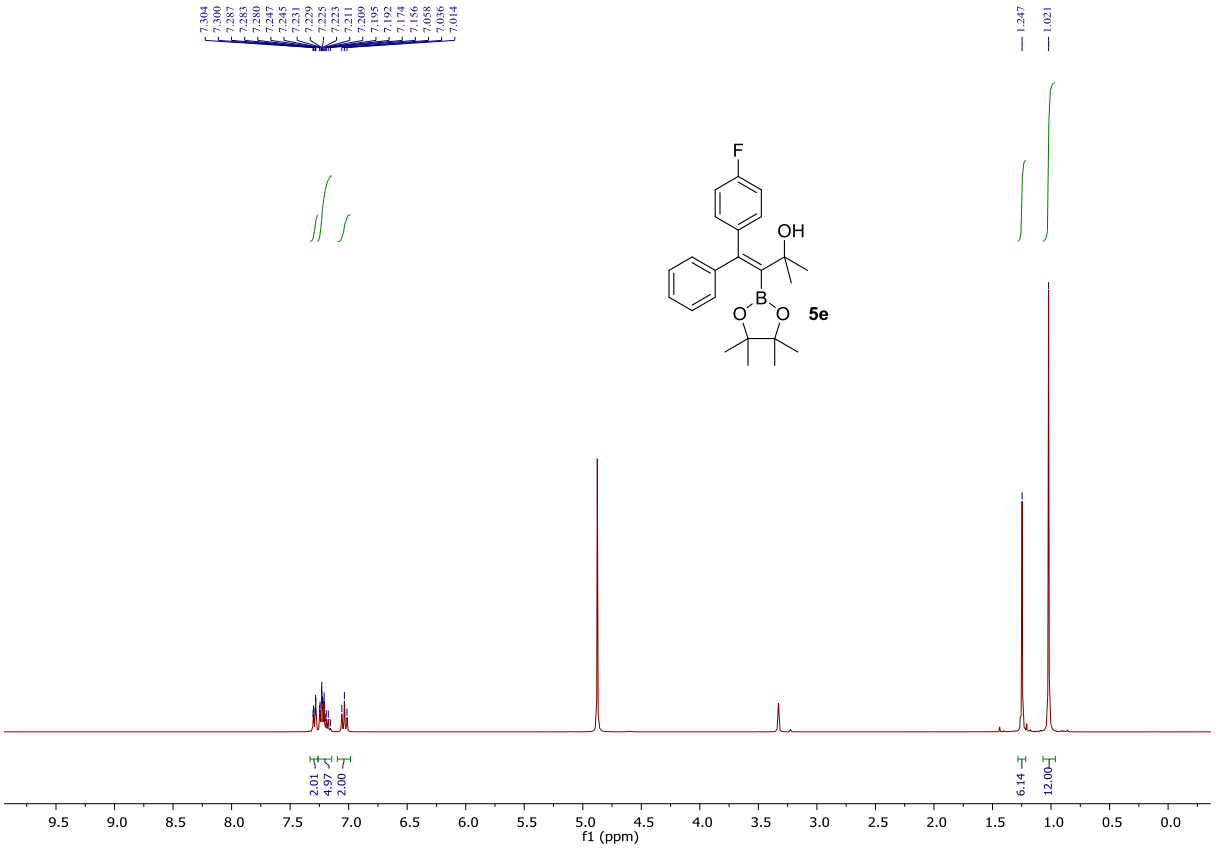
144.207
141.780
132.117
129.906
128.720
127.631
127.552
126.595
83.325
73.593
30.065
23.679
Cl
OH
B
O
O
5d
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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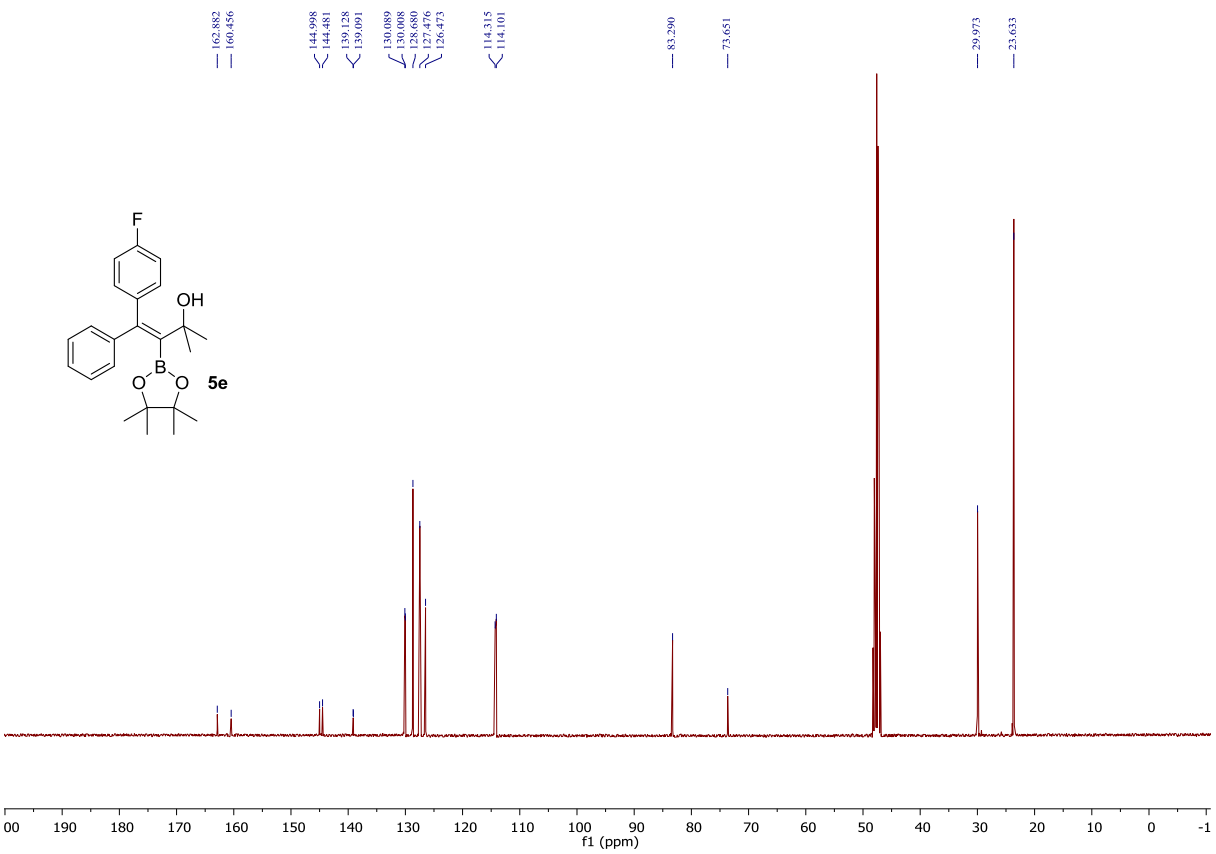
7.287
7.283
7.280
7.247
7.245
7.231
7.229
7.225
7.223
7.211
7.209
7.195
7.192
7.174
7.156
7.058
7.036
7.014
1.247
1.021
F
OH
B
O
O
5e
2.01
4.97
2.00
6.14
12.00
f1 (ppm)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160.456
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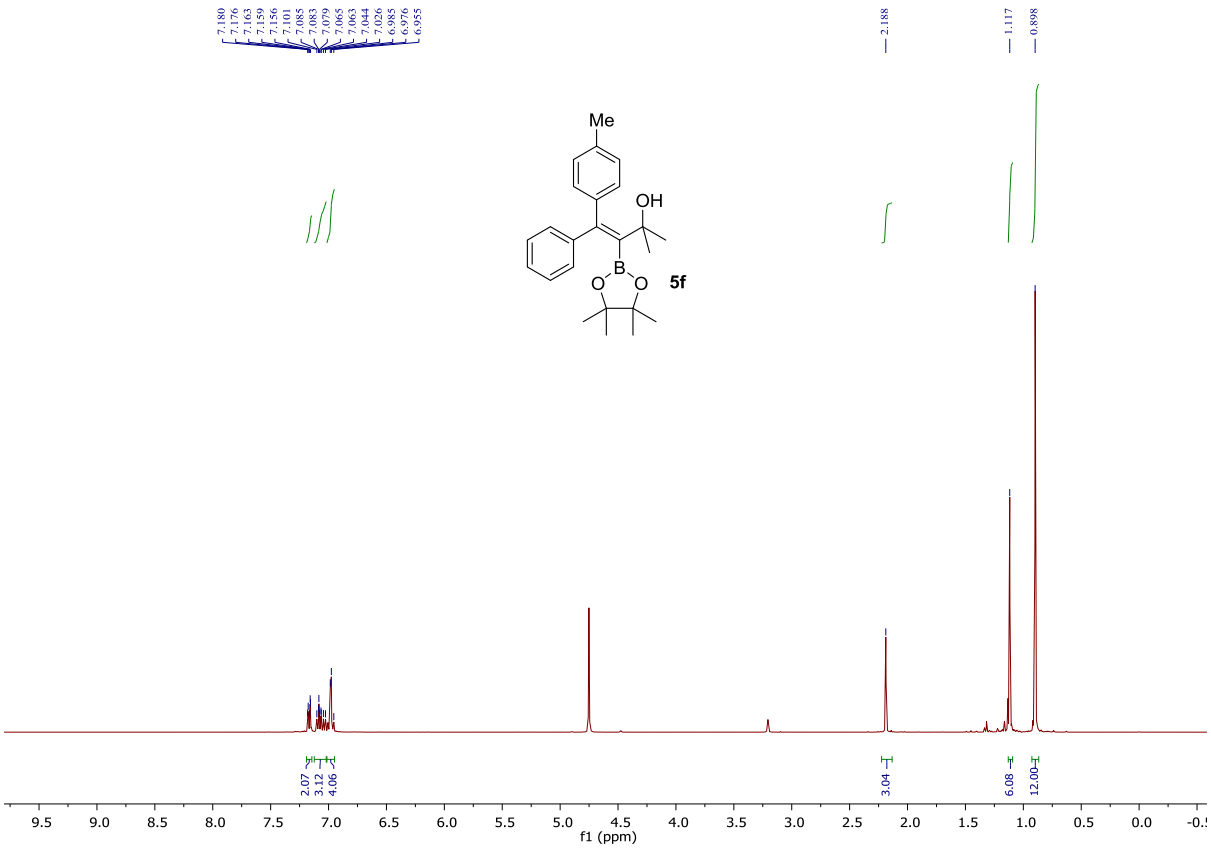
139.091
130.089
130.008
128.680
127.476
126.473
114.315
114.101
83.290
73.651
29.973
23.633
F
OH
B
O
O
5e
f1 (ppm)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7.176
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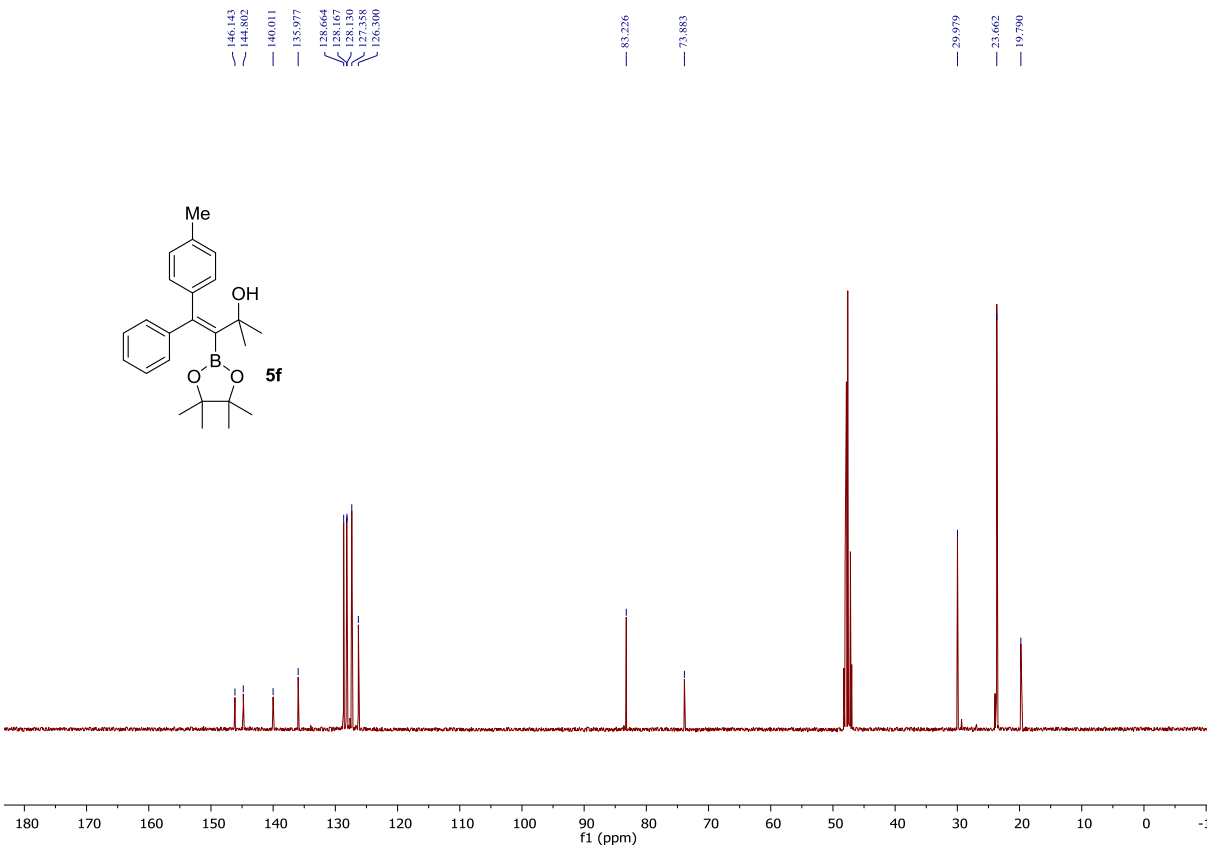
7.159
7.156
7.101
7.085
7.083
7.079
7.065
7.063
7.044
7.026
6.985
6.976
6.955
2.188
1.117
0.898
Me
OH
B
O
O
5f
2.07
3.12
4.06
3.04
6.08
12.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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144.802
140.011
135.977
128.664
128.167
128.130
127.358
126.300
83.226
73.883
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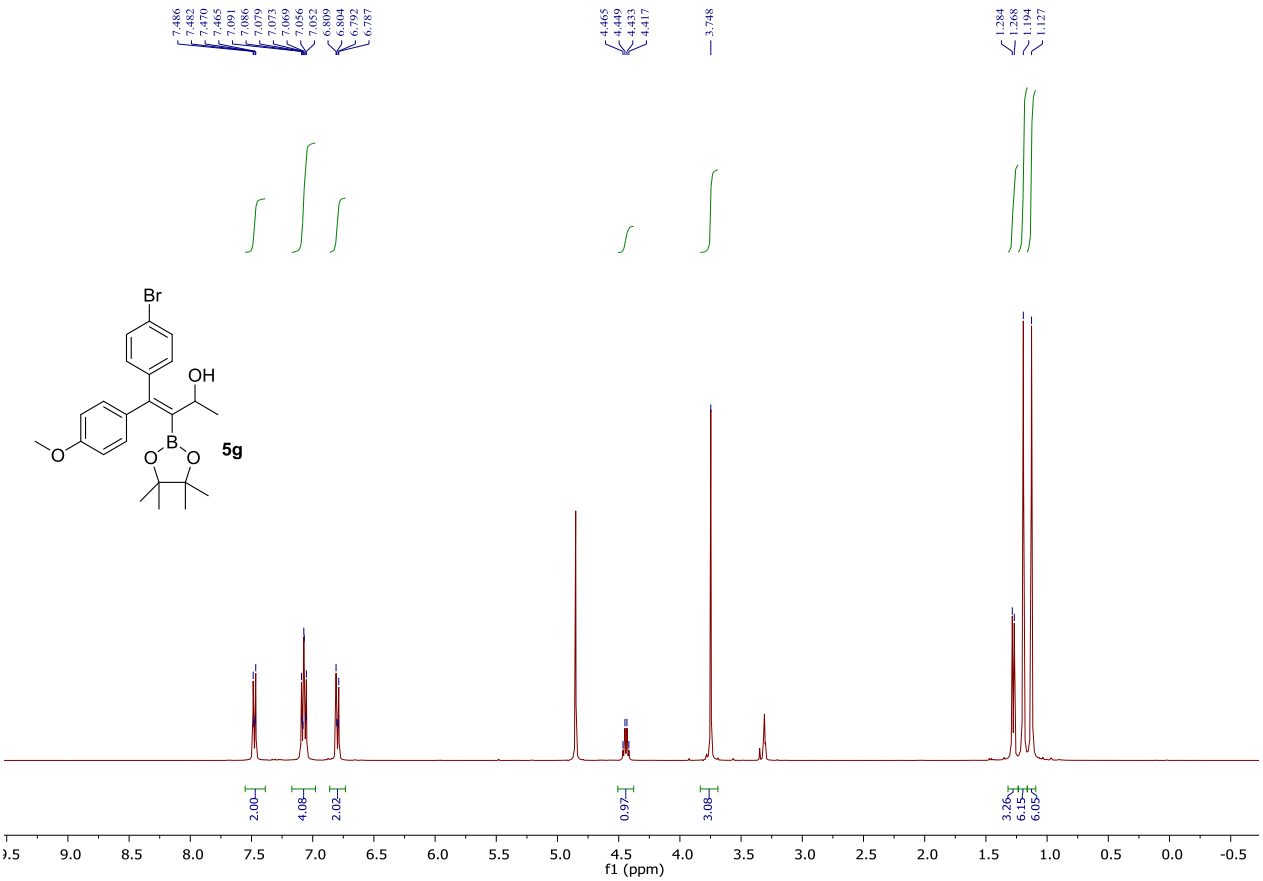
Me
OH
B
O
O
5f
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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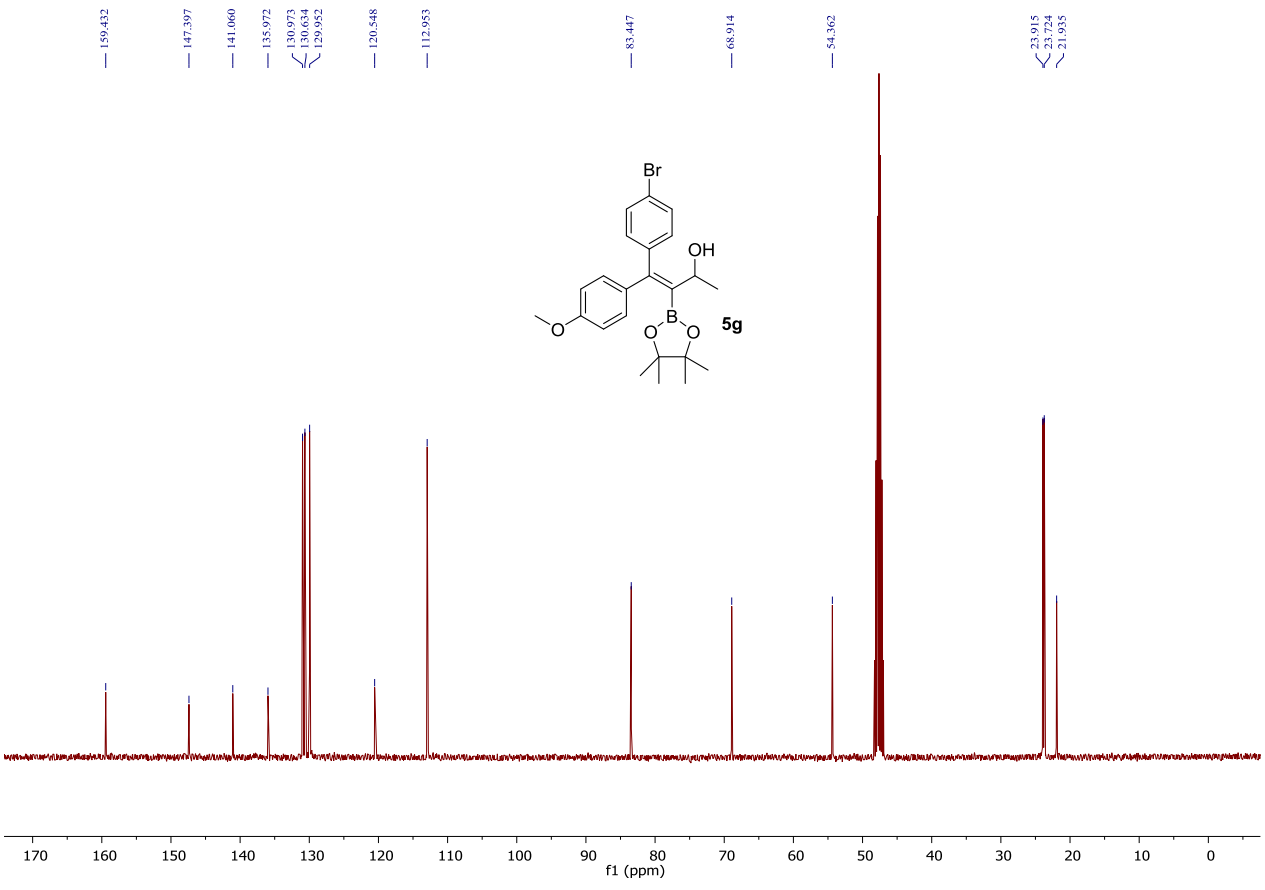
7.470
7.465
7.091
7.086
7.079
7.073
7.069
7.056
7.052
6.809
6.804
6.792
6.787
4.465
4.449
4.433
4.417
3.748
1.284
1.268
1.194
1.127
Br
OH
O
B
O
O
5g
2.00
4.08
2.02
0.97
3.08
3.26
6.15
6.05
f1 (ppm)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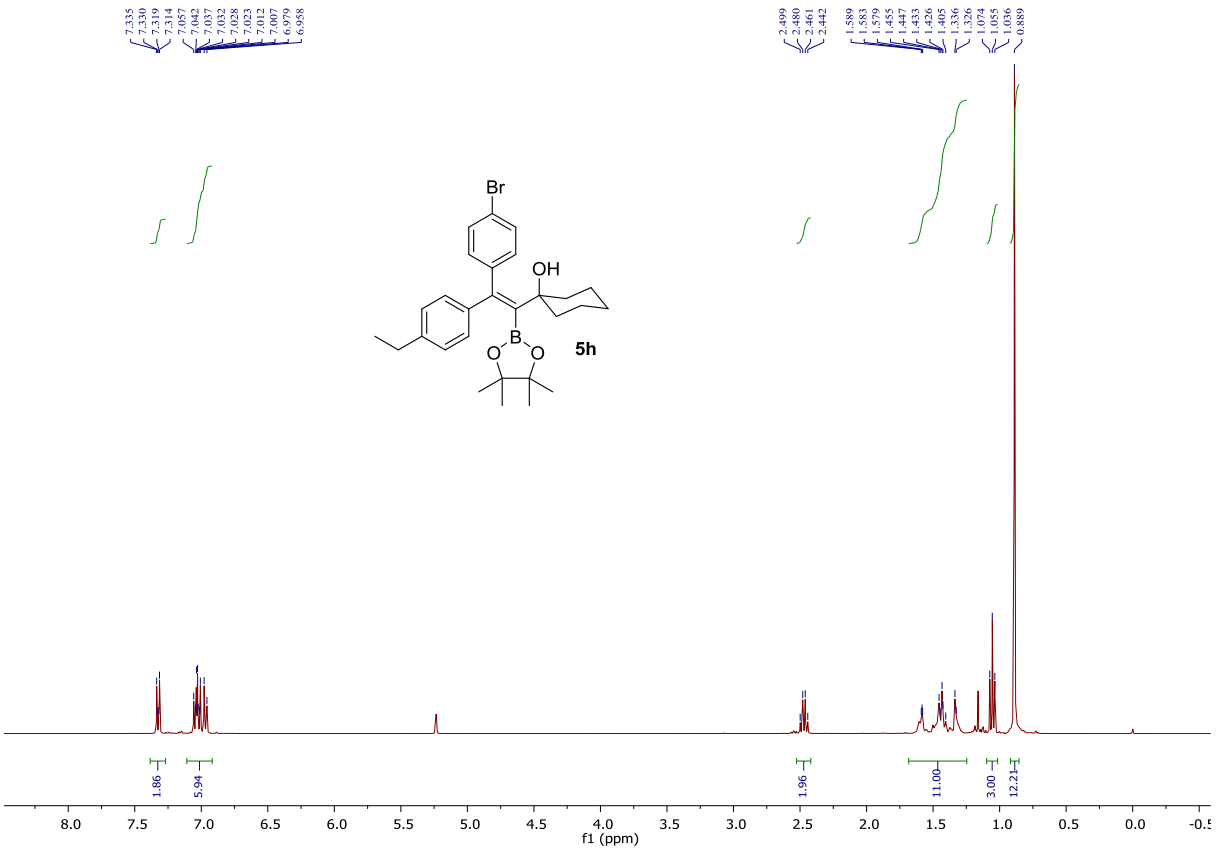
147.397
141.060
135.972
130.973
130.634
129.952
120.548
112.953
83.447
68.914
54.362
23.915
23.724
21.935
Br
OH
O
B
O
O
5g
f1 (ppm)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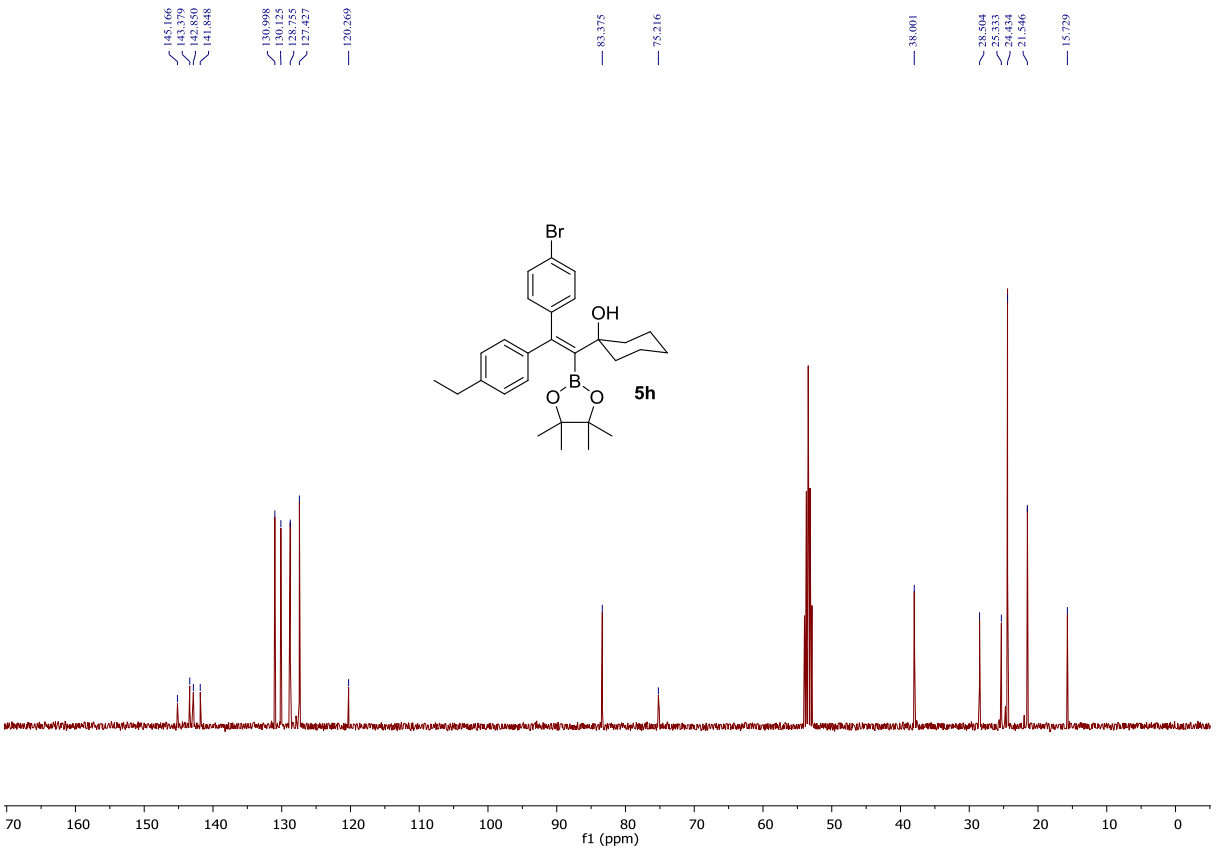
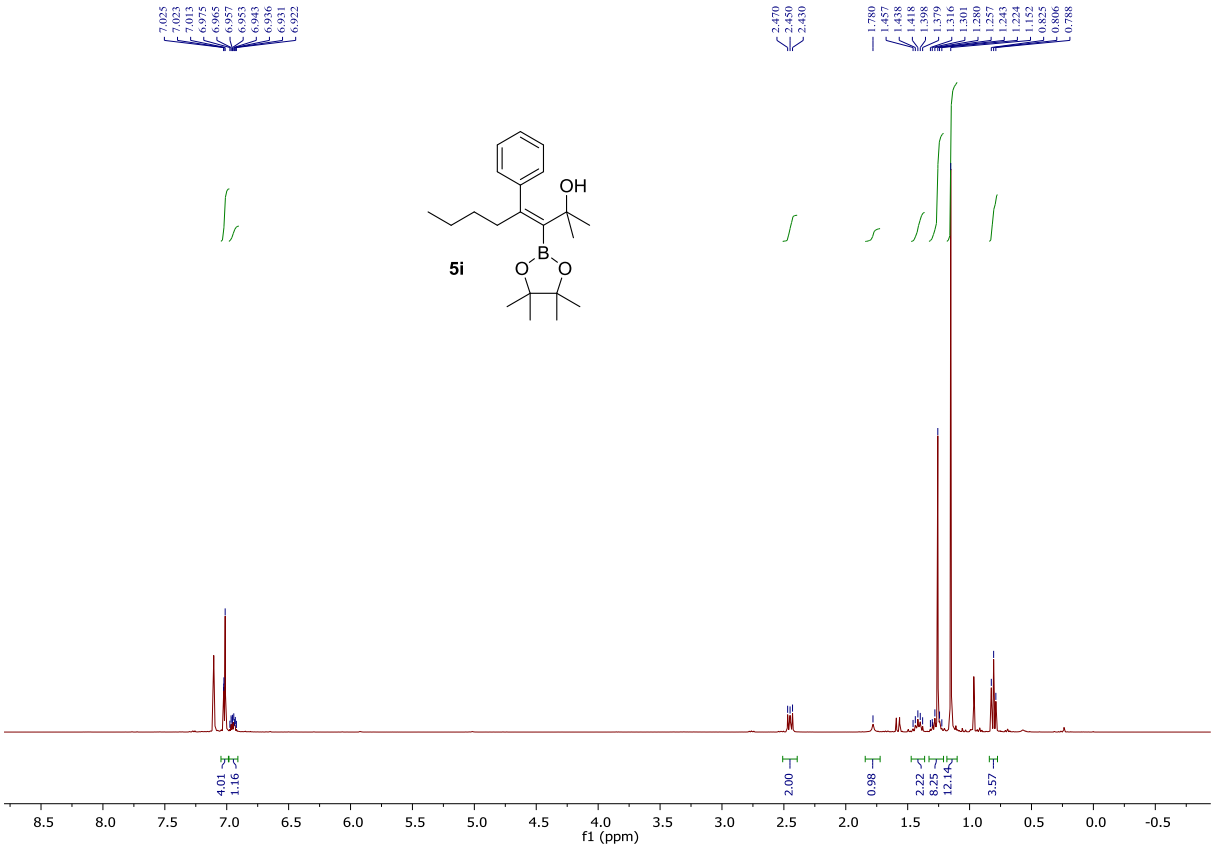
7.330
7.319
7.314
7.057
7.042
7.037
7.032
7.028
7.023
7.012
7.007
6.979
6.958
2.499
2.480
2.461
2.442
1.589
1.583
1.579
1.455
1.447
1.433
1.426
1.405
1.336
1.326
1.074
1.055
1.036
0.889
Br
OH
B
O
O
5h
1.86
5.94
1.96
11.00
3.00
12.21
f1 (ppm)


145.166
143.379
142.850
141.848
130.998
130.125
128.755
127.427
120.269
83.375
75.216
38.001
28.504
25.333
24.434
21.546
15.729
Br
OH
B
O
O
5h
f1 (ppm)


7.025
7.023
7.013
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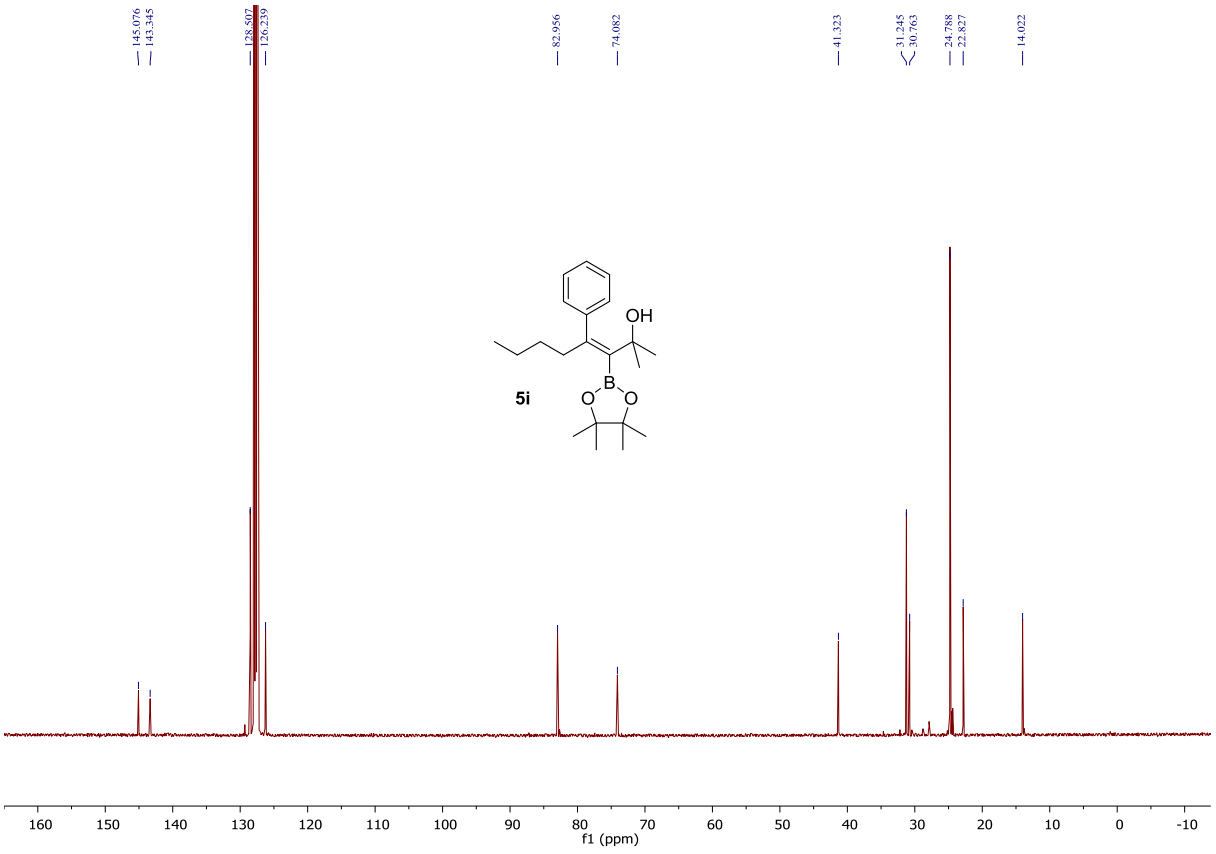
6.965
6.957
6.953
6.943
6.936
6.931
6.922
2.470
2.450
2.430
1.780
1.457
1.438
1.418
1.398
1.379
1.316
1.301
1.280
1.257
1.243
1.224
1.152
0.825
0.806
0.788
OH
B
O
O
5i
4.01
1.16
2.00
0.98
2.22
8.25
12.14
3.57
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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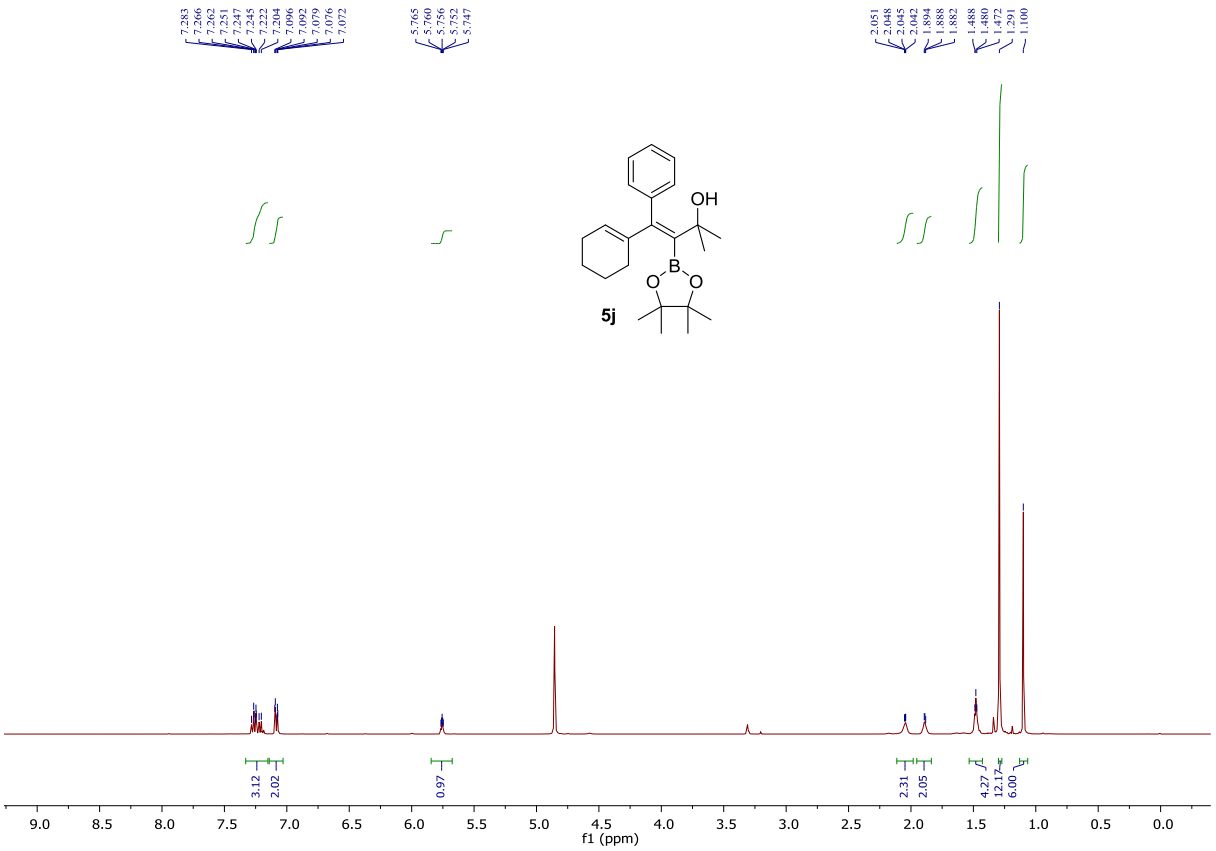
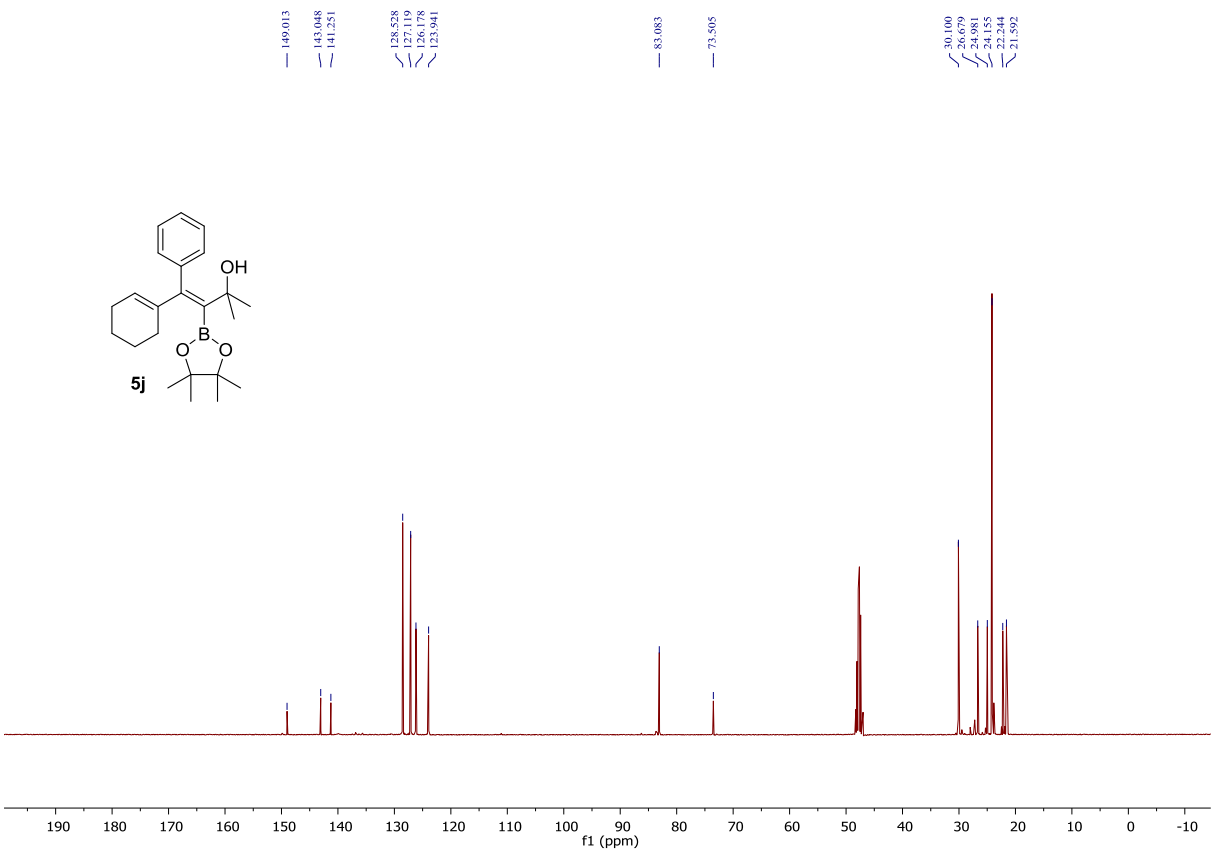
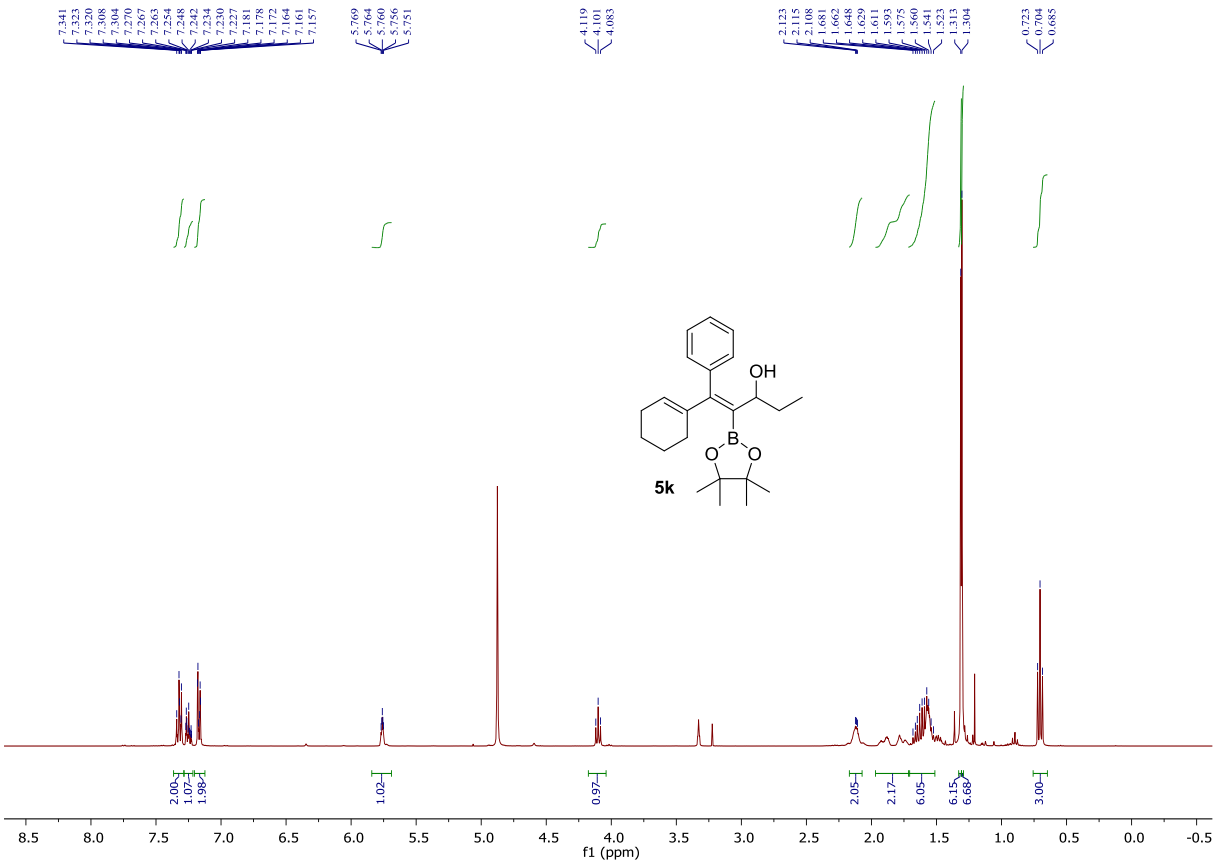
143.345
128.507
126.239
82.956
74.082
41.323
31.245
30.763
24.788
22.827
14.022
OH
B
O
O
5i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.283
7.266
7.262
7.251
7.247
7.245
7.232
7.204
7.096
7.092
7.079
7.076
7.072
5.765
5.760
5.756
5.752
5.747
2.051
2.048
2.045
2.042
1.894
1.888
1.882
1.488
1.480
1.472
1.291
1.100
OH
B
O
O
5j
3.12
2.02
0.97
2.31
2.05
4.27
12.17
6.00
f1 (ppm)


149.013
143.048
141.251
128.528
127.119
126.178
123.941
83.083
73.505
30.100
26.679
24.981
24.155
22.244
21.592
OH
B
O
O
5j
f1 (ppm)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7.323
7.320
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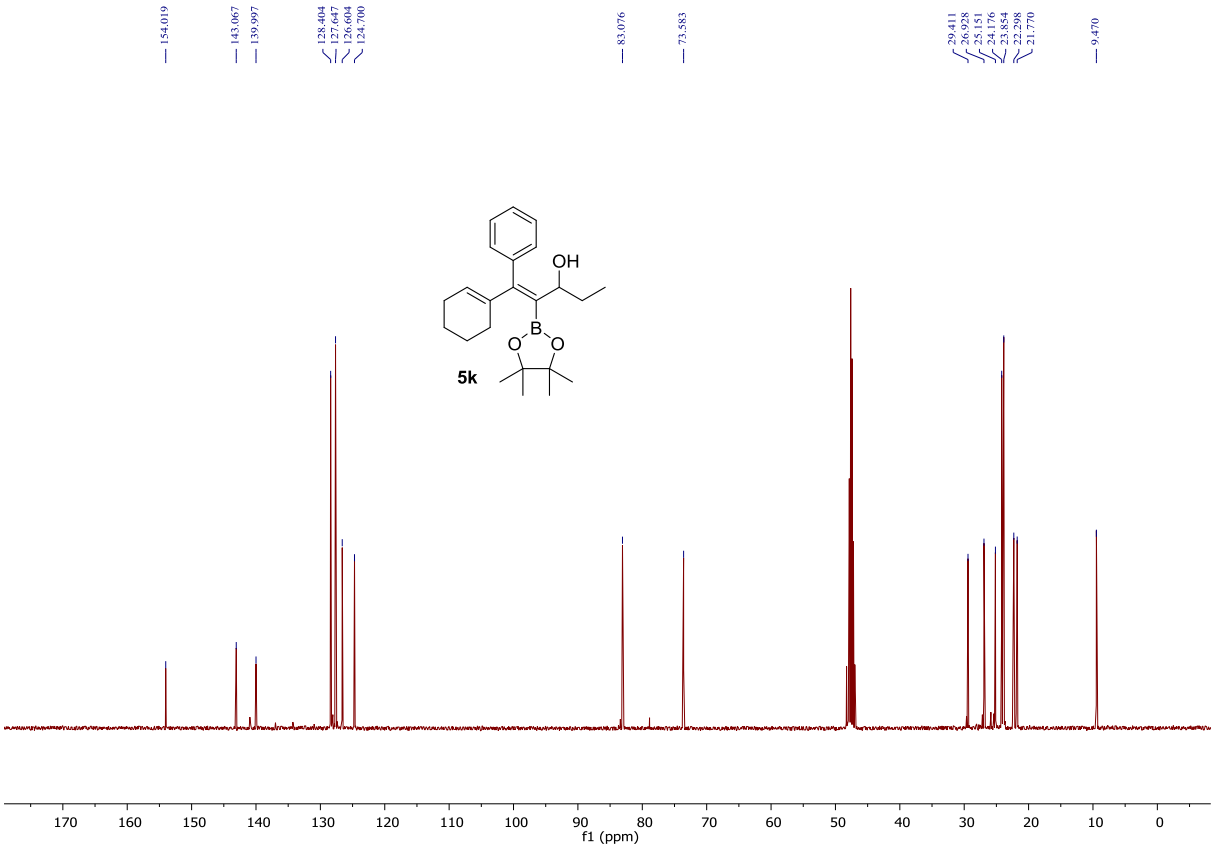
7.304
7.270
7.267
7.263
7.254
7.248
7.242
7.234
7.230
7.227
7.181
7.178
7.172
7.164
7.161
7.157
5.769
5.764
5.760
5.756
5.751
4.119
4.101
4.083
2.123
2.115
2.108
2.081
1.662
1.648
1.629
1.611
1.593
1.575
1.560
1.541
1.523
1.313
1.304
0.723
0.704
0.685
OH
B
O
O
5k
2.00
1.07
1.98
1.02
0.97
2.05
2.17
6.05
6.15
6.68
3.00
f1 (ppm)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139.997
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127.647
126.604
124.700
83.076
73.583
29.411
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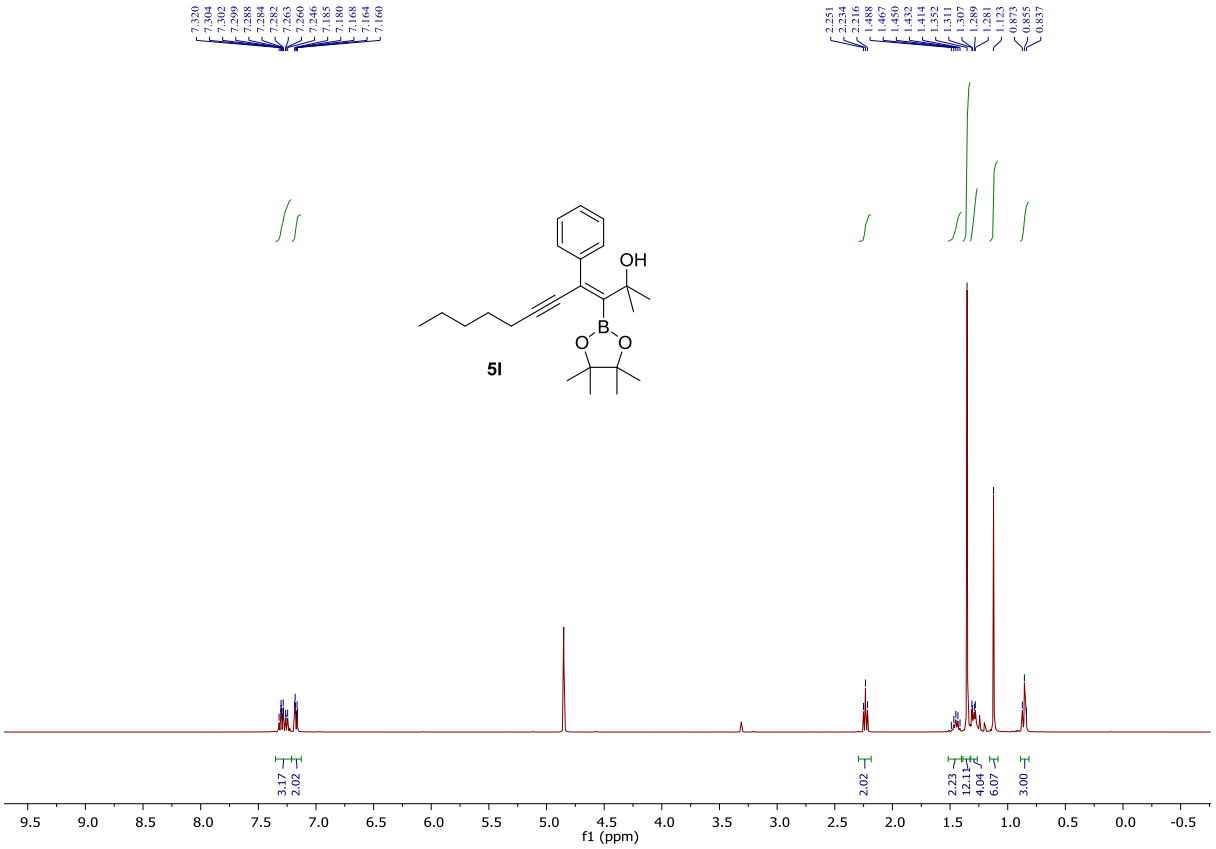
24.176
23.854
22.298
21.770
9.470
OH
B
O
O
5k
f1 (ppm)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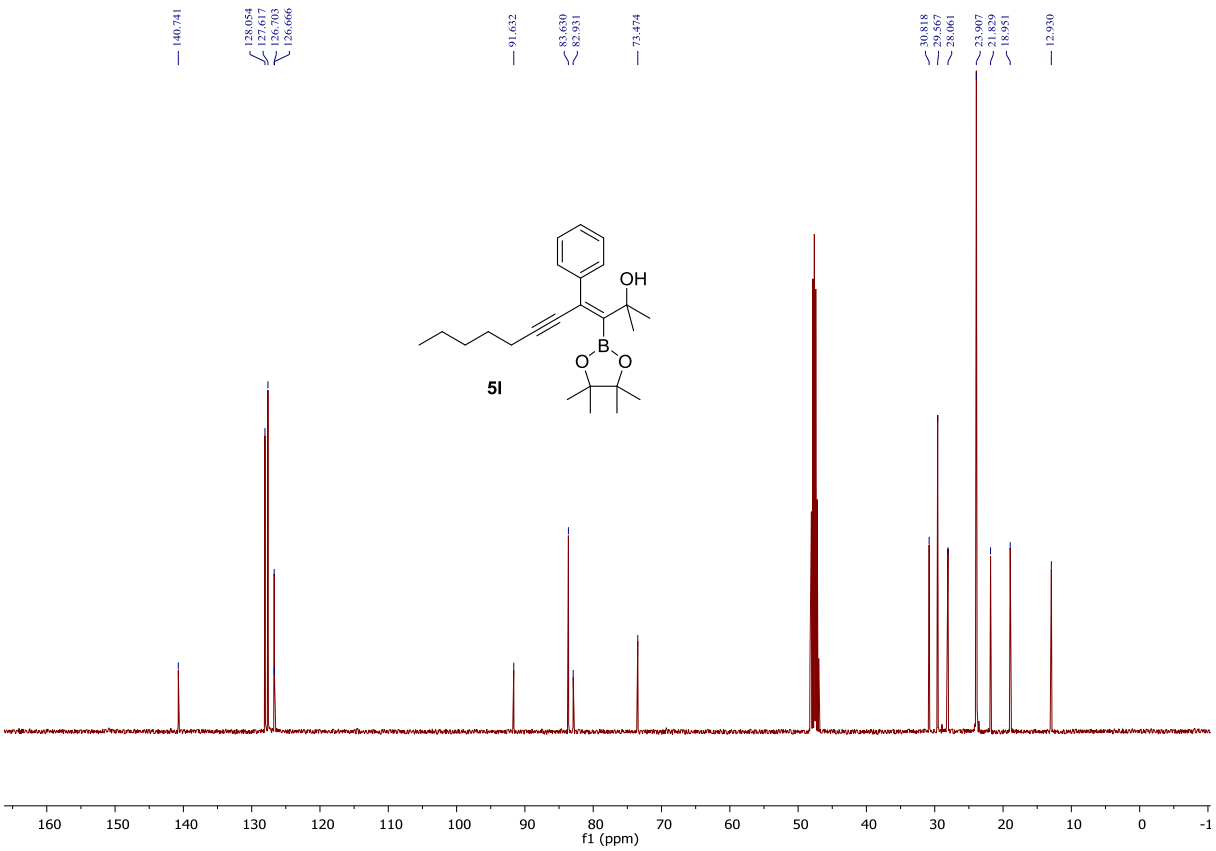
7.290
7.288
7.284
7.282
7.263
7.260
7.246
7.185
7.180
7.168
7.164
7.160
2.251
2.234
2.216
1.488
1.467
1.450
1.432
1.414
1.352
1.311
1.307
1.289
1.281
1.123
0.873
0.855
0.837
OH
B
O
O
5l
3.17
2.02
2.02
2.23
12.11
4.04
6.07
3.00
f1 (ppm)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127.617
126.703
126.666
91.632
83.630
82.931
73.474
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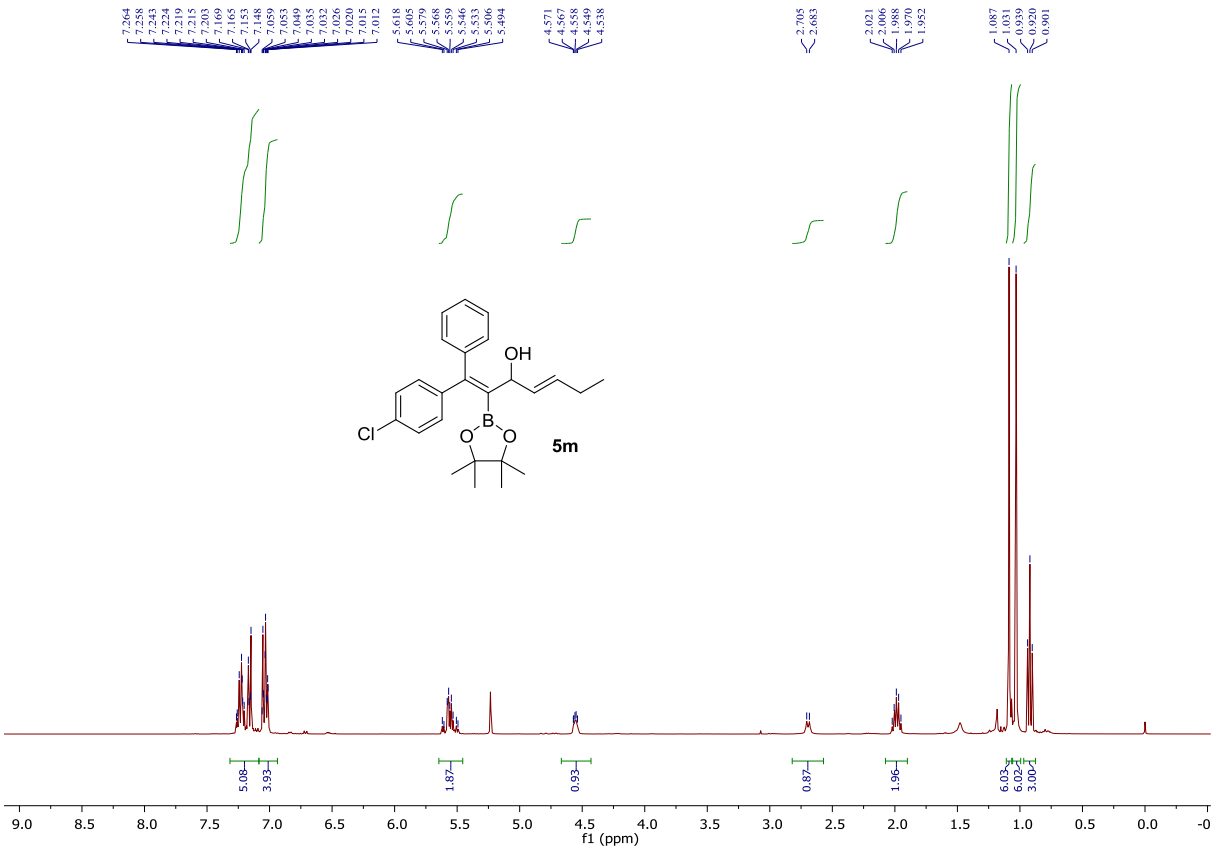
28.061
23.907
21.829
18.951
12.930
OH
B
O
O
5l
f1 (ppm)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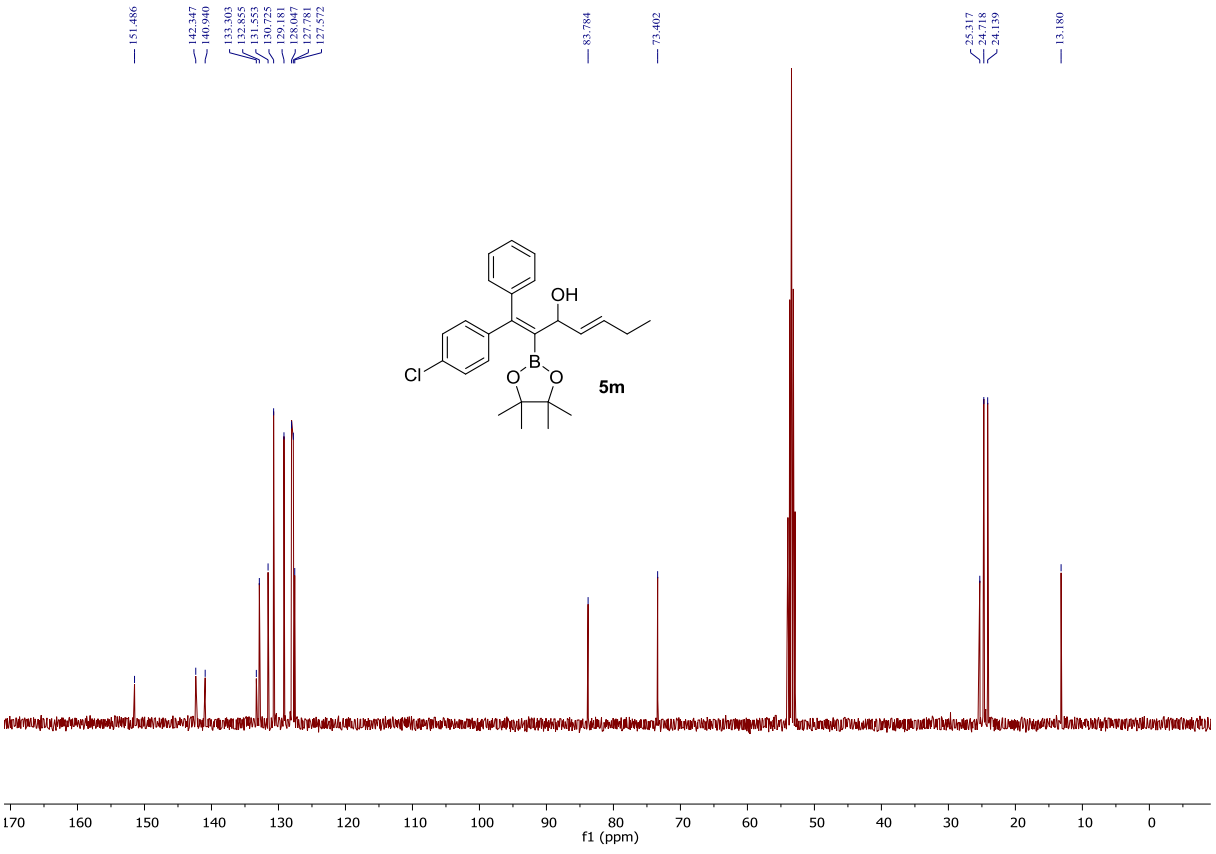
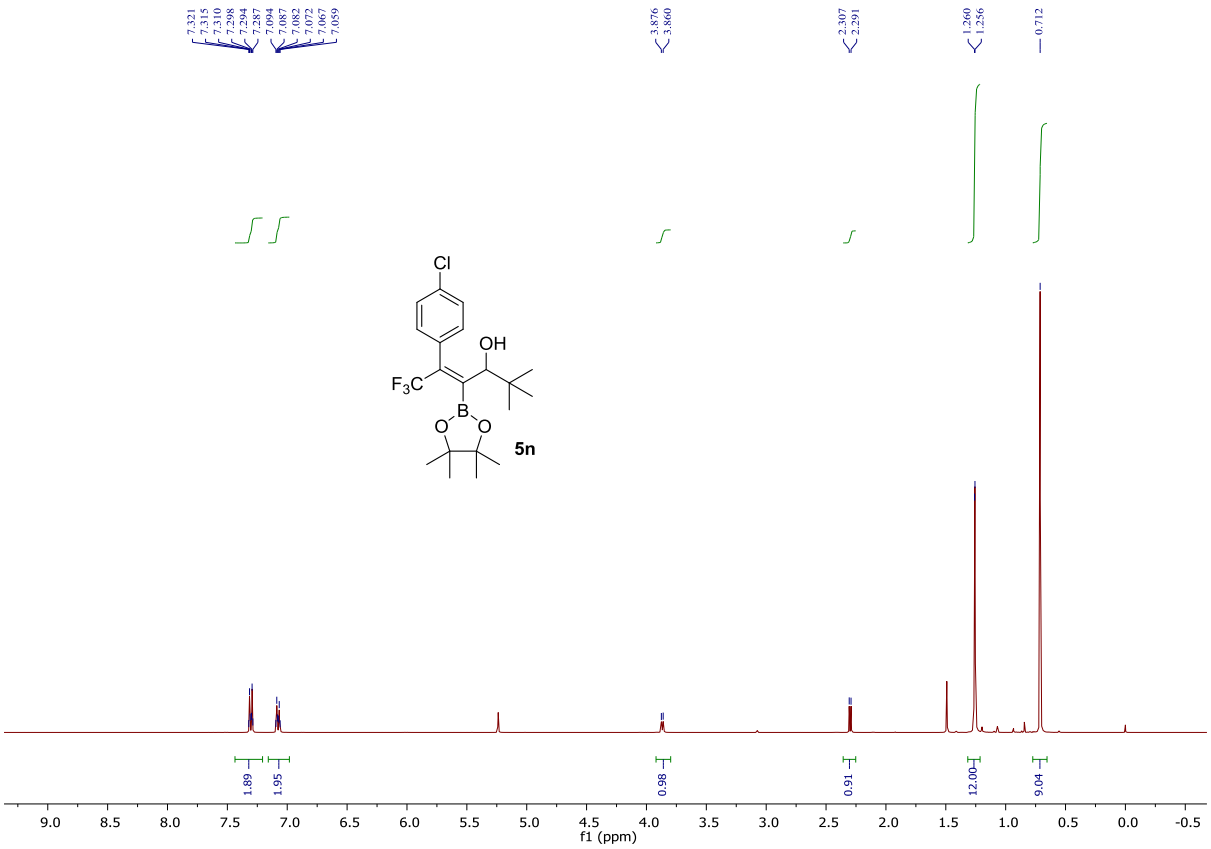
7.169
7.165
7.153
7.148
7.059
7.053
7.049
7.035
7.032
7.026
7.020
7.015
7.012
5.618
5.605
5.579
5.568
5.559
5.546
5.533
5.506
5.494
4.571
4.567
4.558
4.549
4.538
2.705
2.683
2.021
2.006
1.988
1.970
1.952
1.087
1.031
0.959
0.939
0.920
0.901
OH
Cl
B
O
O
5m
5.08
3.93
1.87
0.93
0.87
1.96
6.03
6.02
3.00
f1 (ppm)


151.486
142.347
140.940
133.303
132.855
131.553
130.725
129.181
128.047
127.781
127.572
83.784
73.402
25.317
24.718
24.139
13.180
OH
Cl
B
O
O
5m
f1 (ppm)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7.294
7.287
7.094
7.087
7.082
7.072
7.067
7.059
3.876
3.860
2.307
2.291
1.260
1.256
0.712
Cl
OH
F3C
B
O
O
5n
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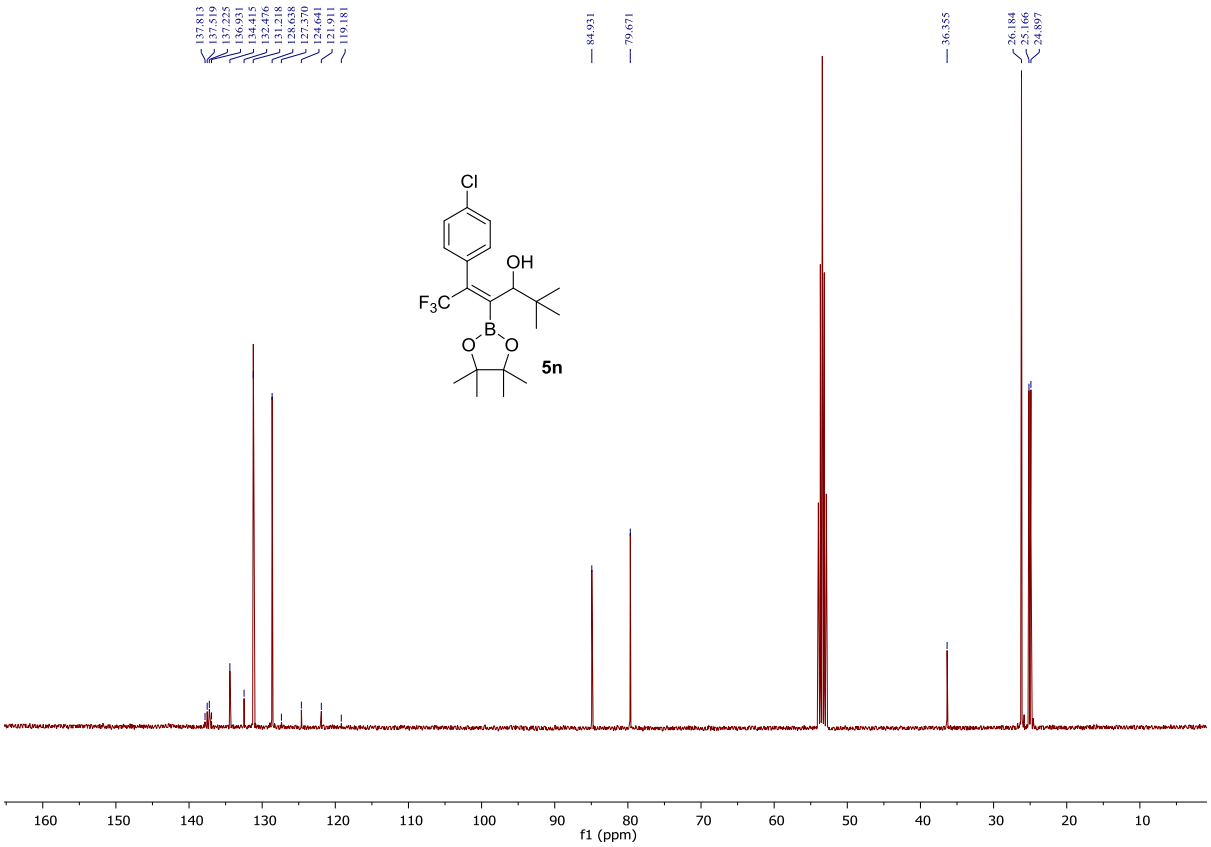
1.95
0.98
0.91
12.00
9.04
f1 (ppm)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128.458
127.750
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121.911
119.181
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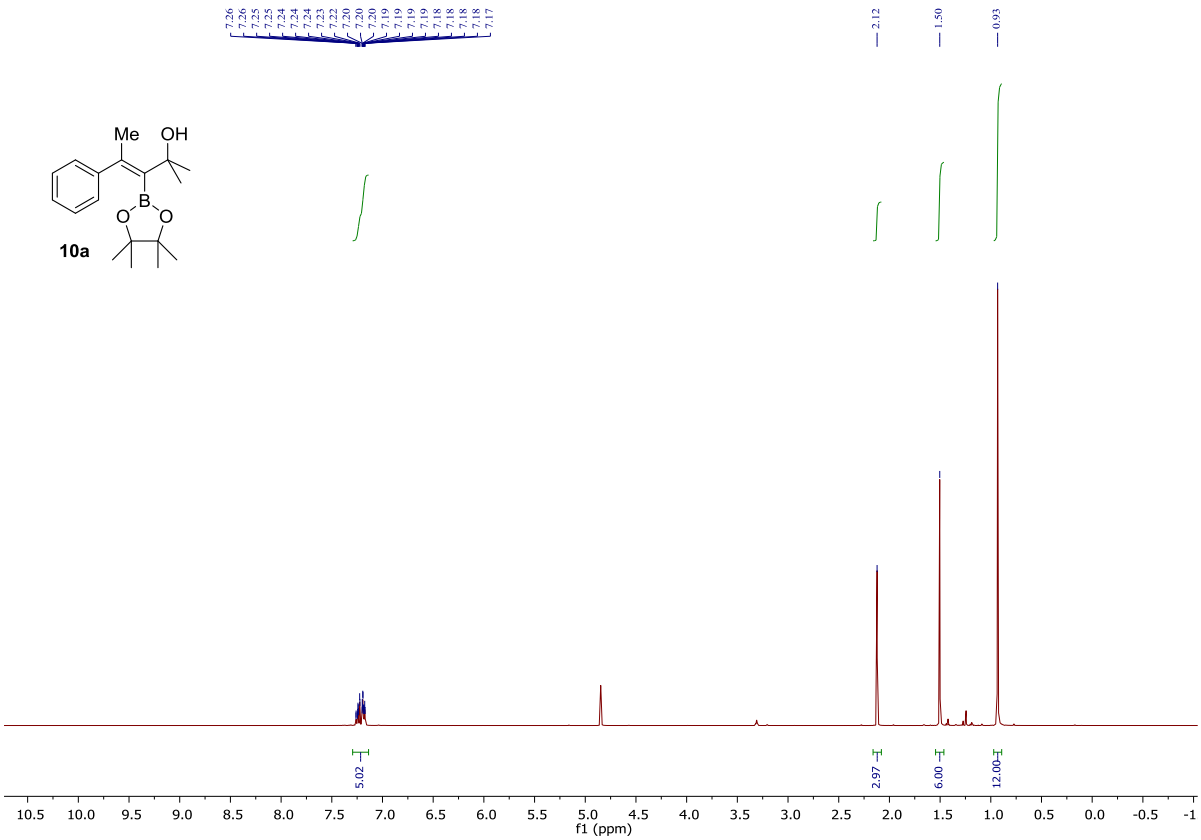
79.671
36.355
26.184
25.166
24.897
Cl
OH
F3C
B
O
O
5n
f1 (ppm)


Me
OH
B
O
O
10a
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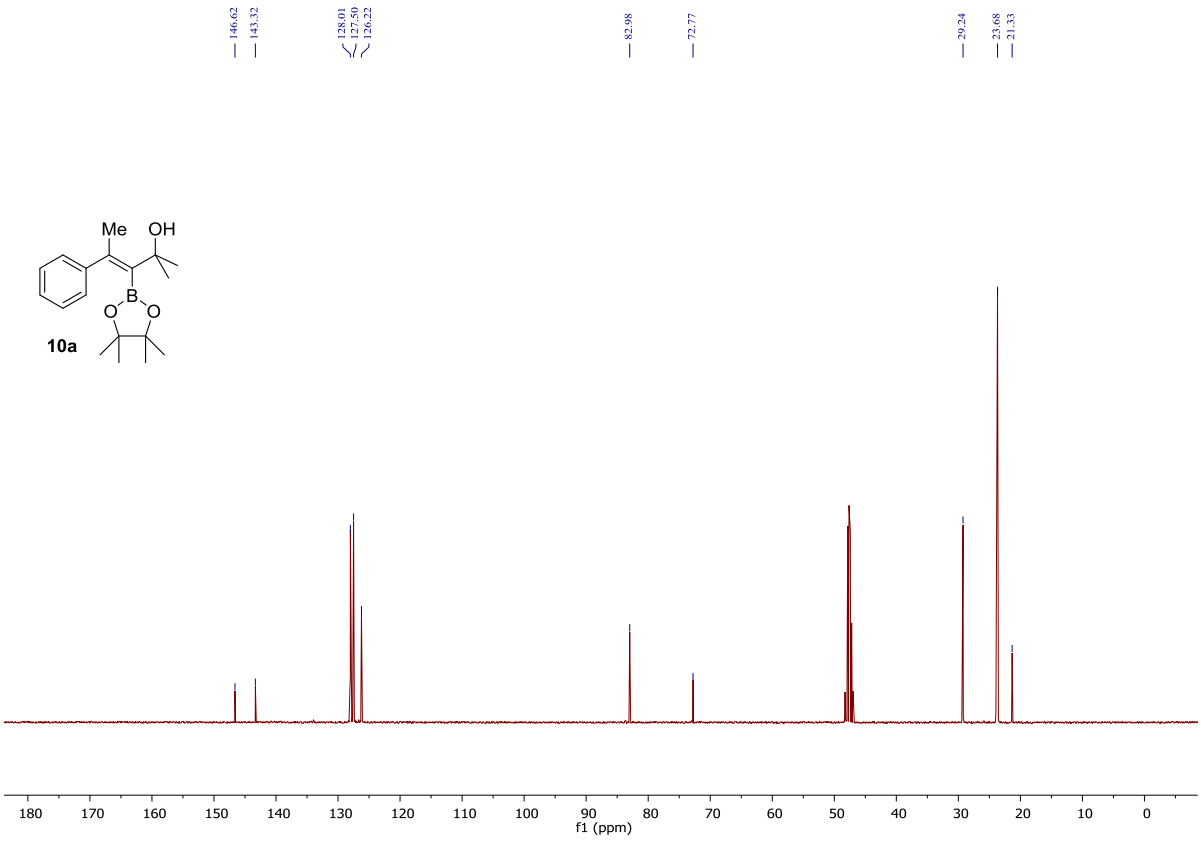
7.26
7.25
7.25
7.24
7.24
7.24
7.23
7.22
7.20
7.20
7.19
7.19
7.19
7.18
7.18
7.18
7.17
2.12
1.50
0.93
5.02
2.97
6.00
12.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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126.22
82.98
72.77
29.24
23.68
21.33
Me
OH
B
O
O
10a
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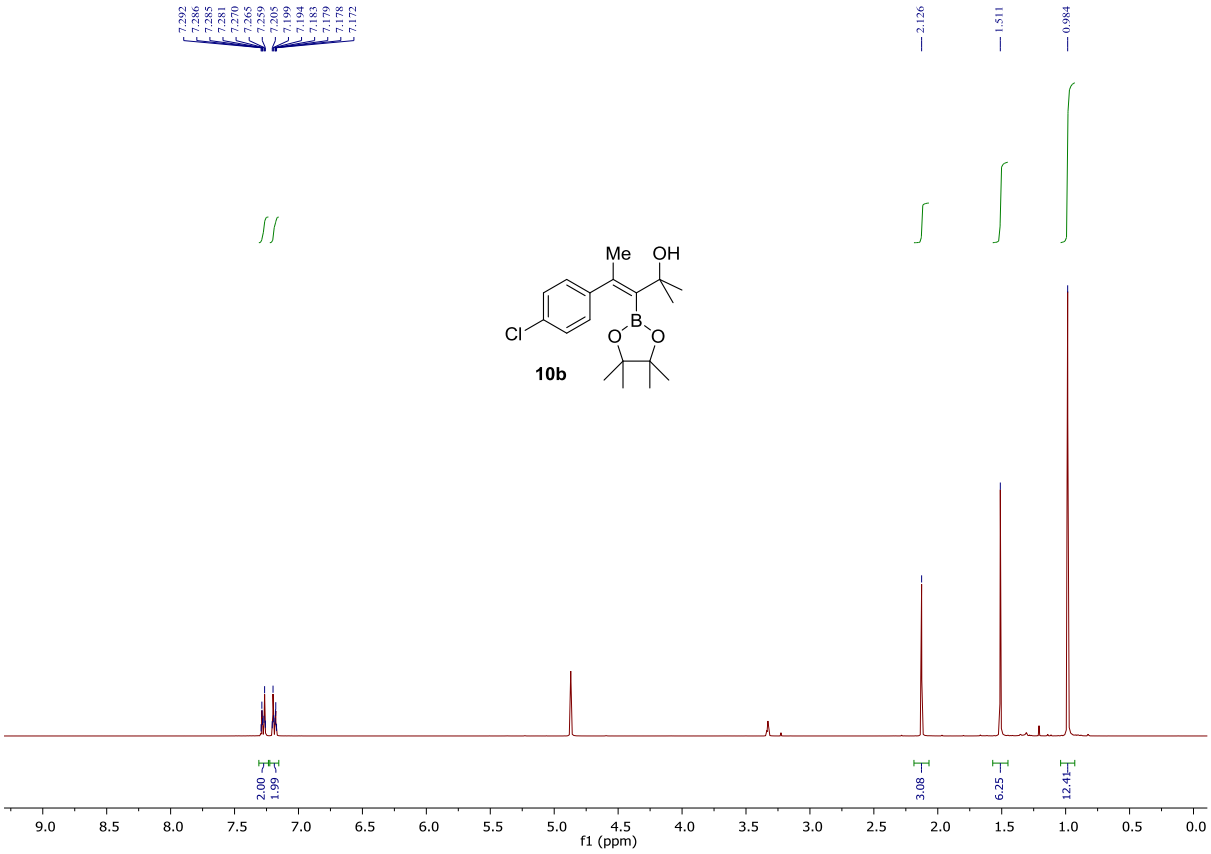
f1 (ppm)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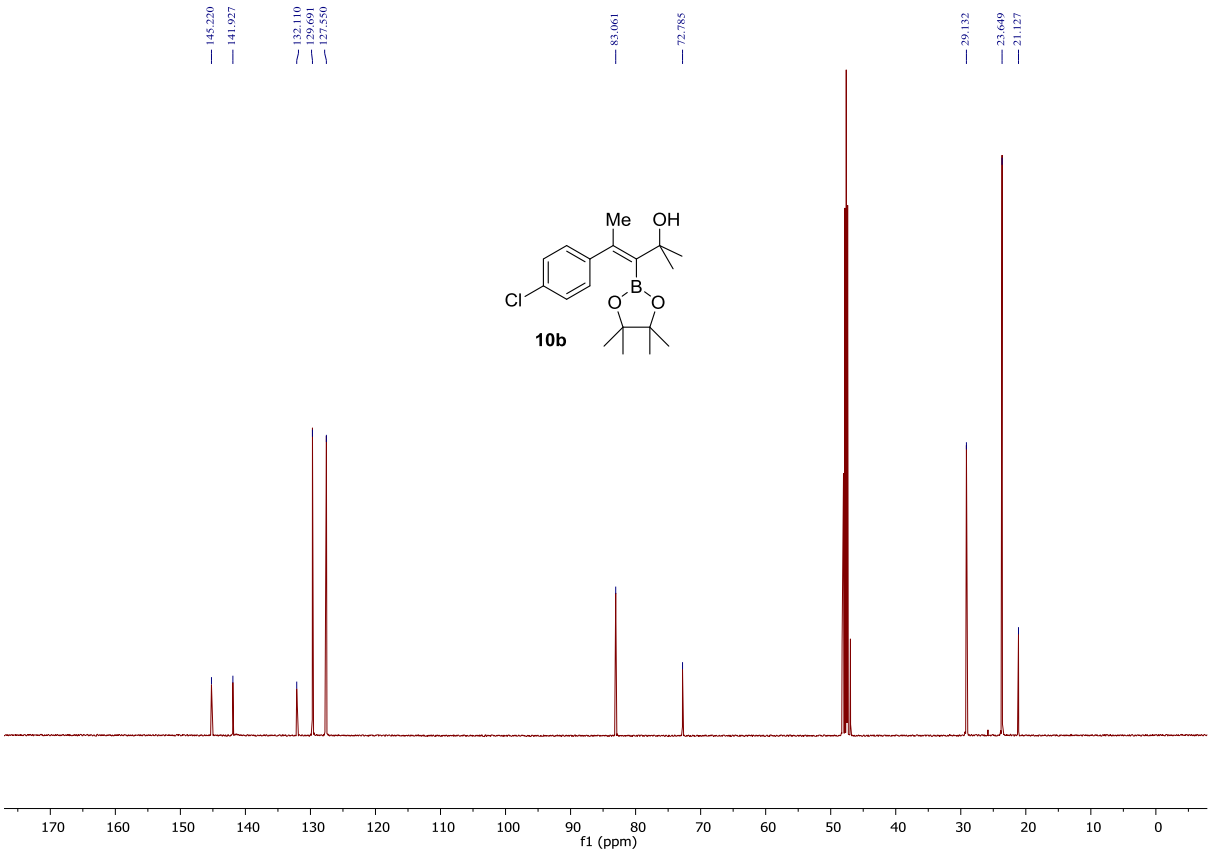
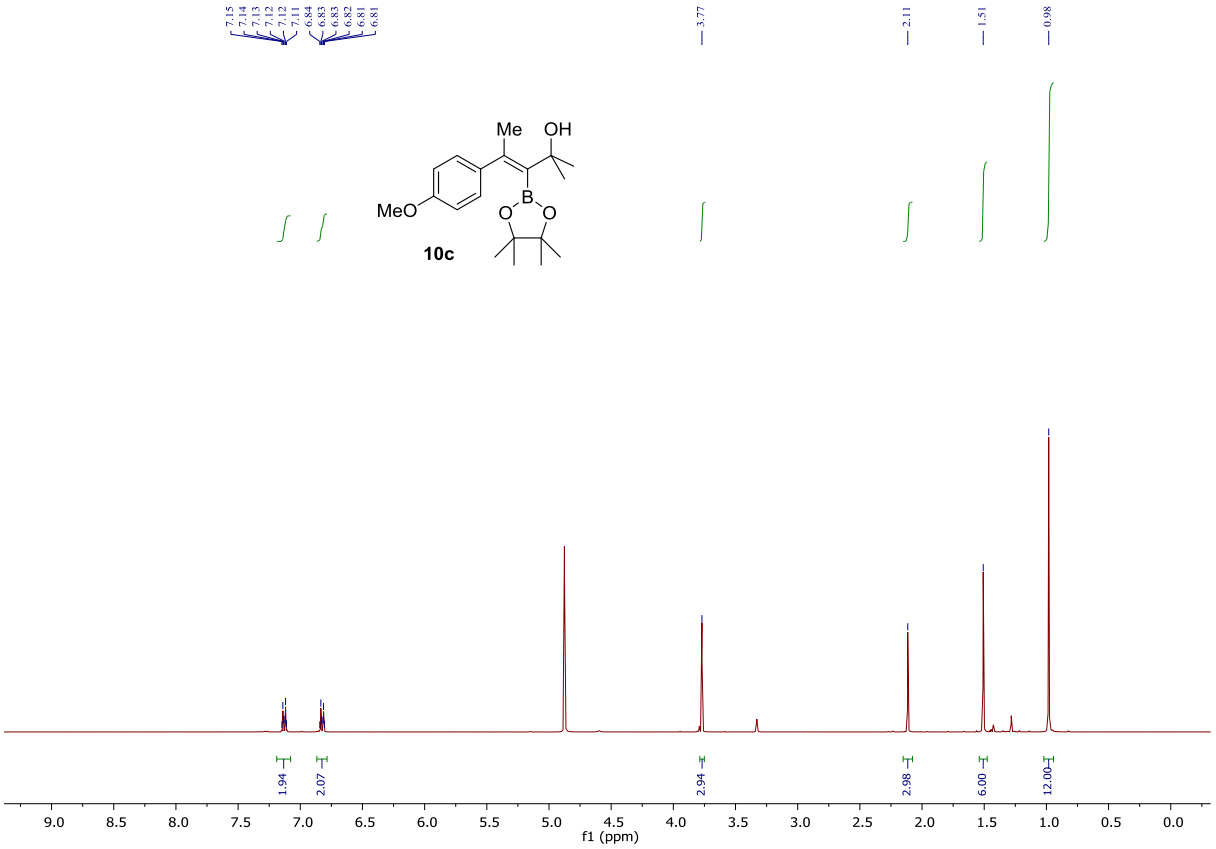
7.265
7.259
7.205
7.199
7.194
7.183
7.179
7.178
7.172
2.126
1.511
0.984
Me
OH
Cl
B
O
O
10b
2.00
1.99
3.08
6.25
12.41
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


145.220
141.927
132.110
129.691
127.550
83.061
72.785
29.132
23.649
21.127
Me
OH
Cl
B
O
O
10b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.15
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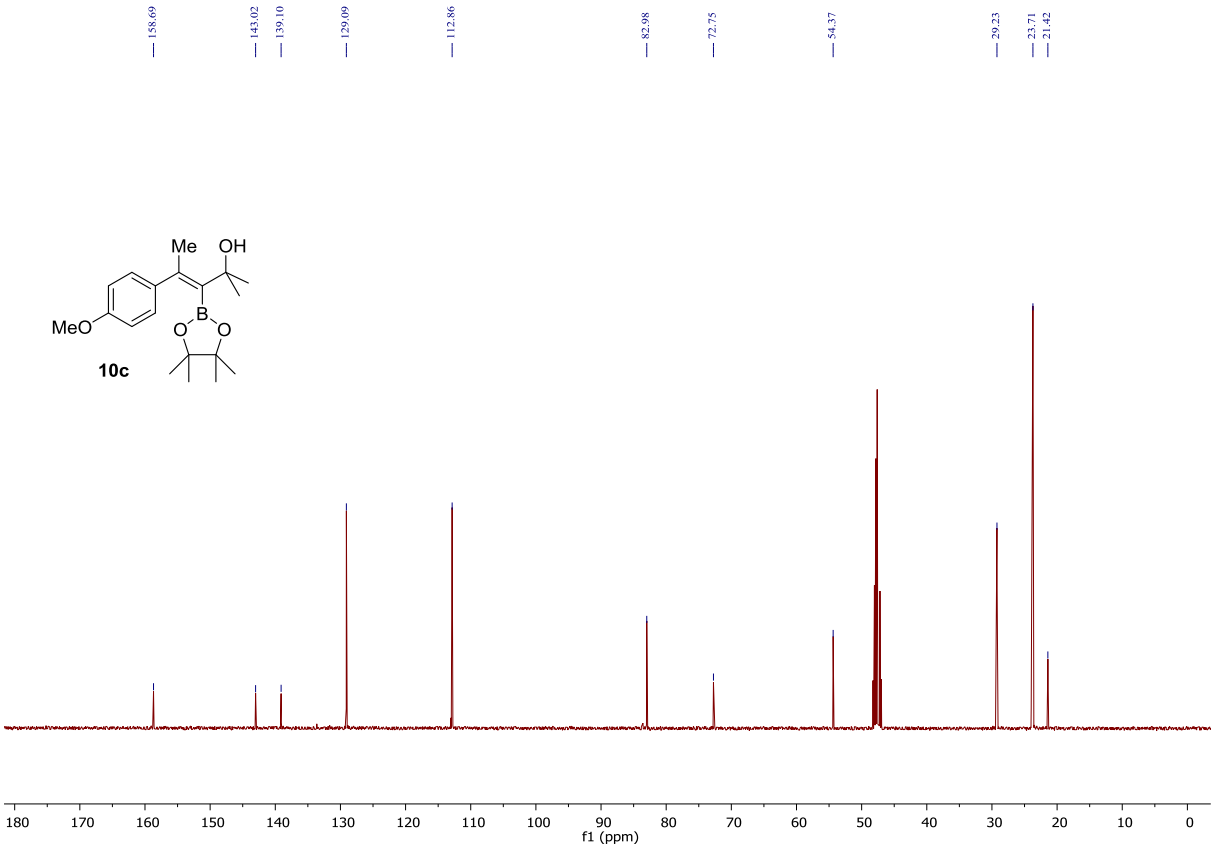
7.13
7.12
7.12
7.11
6.84
6.83
6.82
6.81
6.81
3.77
2.11
1.51
0.98
Me
OH
MeO
B
O
O
10c
1.94
2.07
2.94
2.98
6.00
12.00
f1 (ppm)


158.69
143.02
139.10
129.09
112.86
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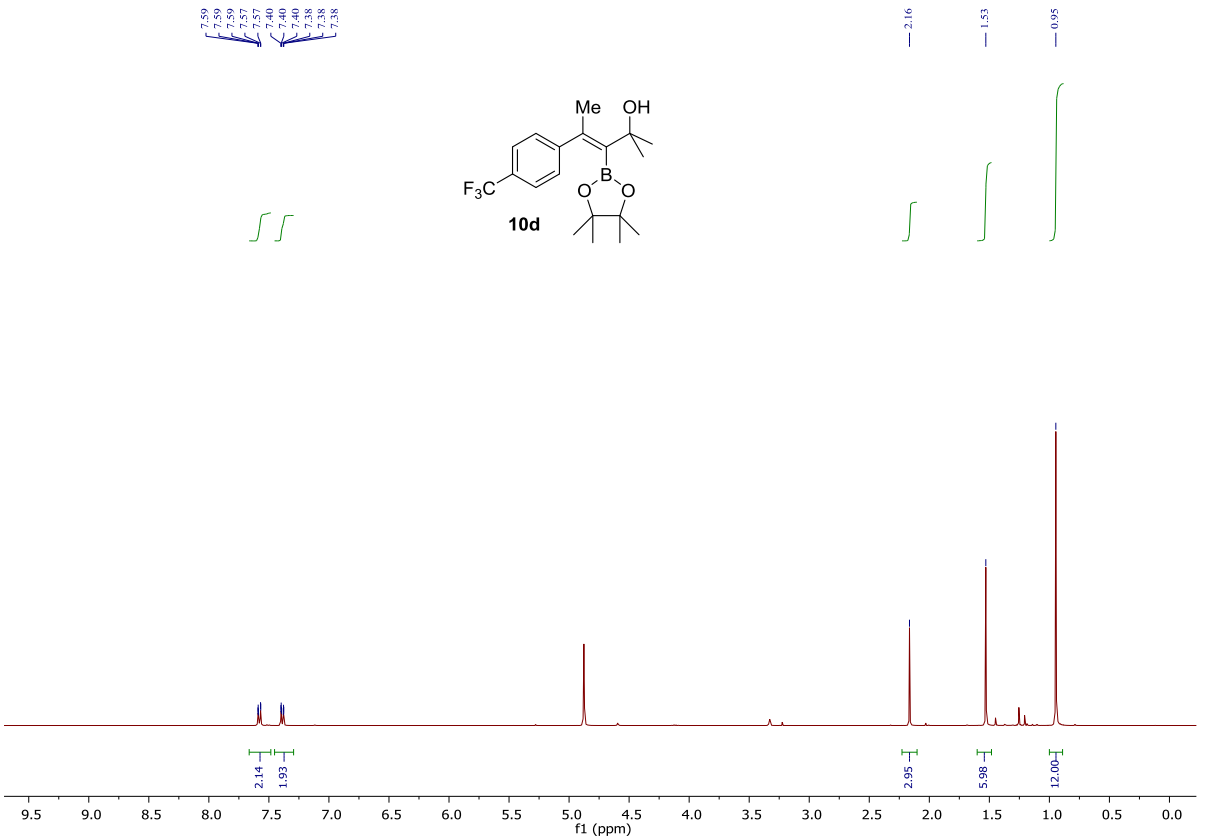
54.37
29.23
23.71
21.42
Me
OH
MeO
B
O
O
10c
f1 (ppm)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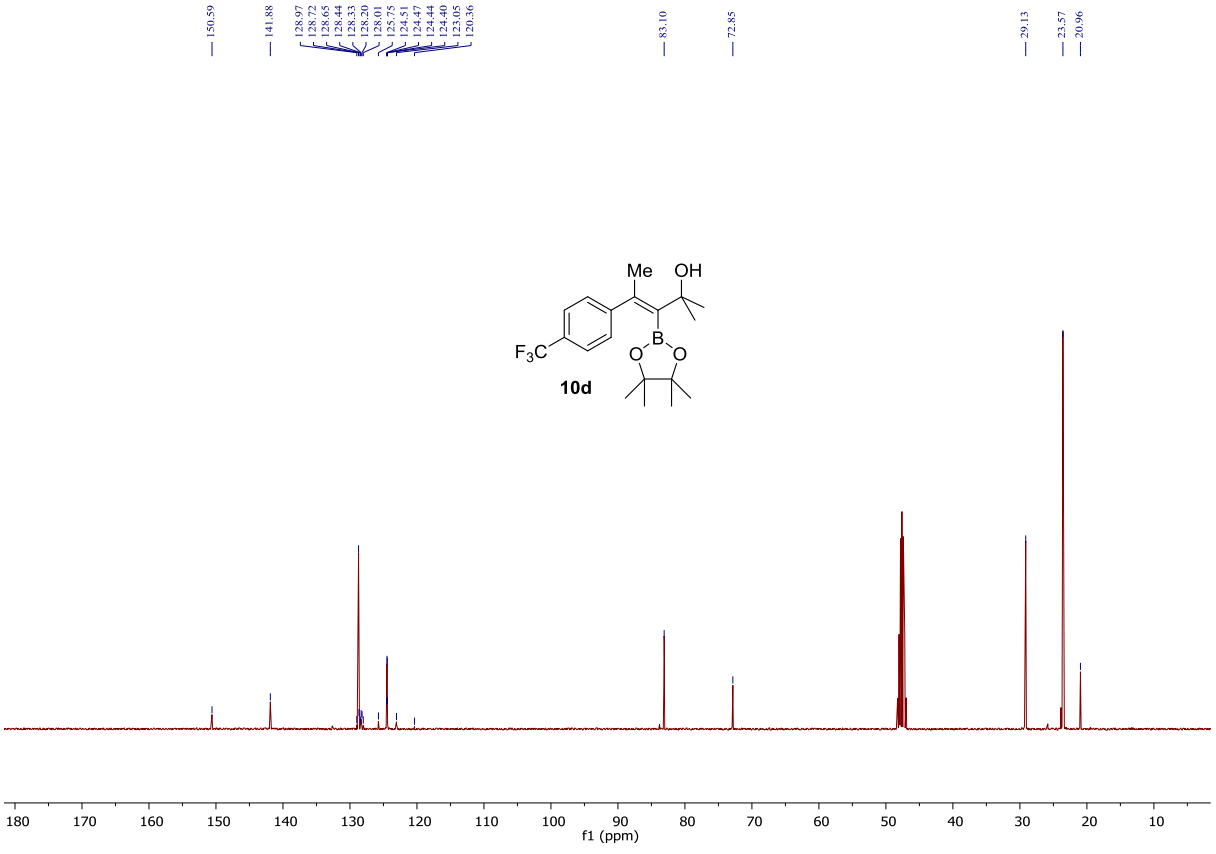
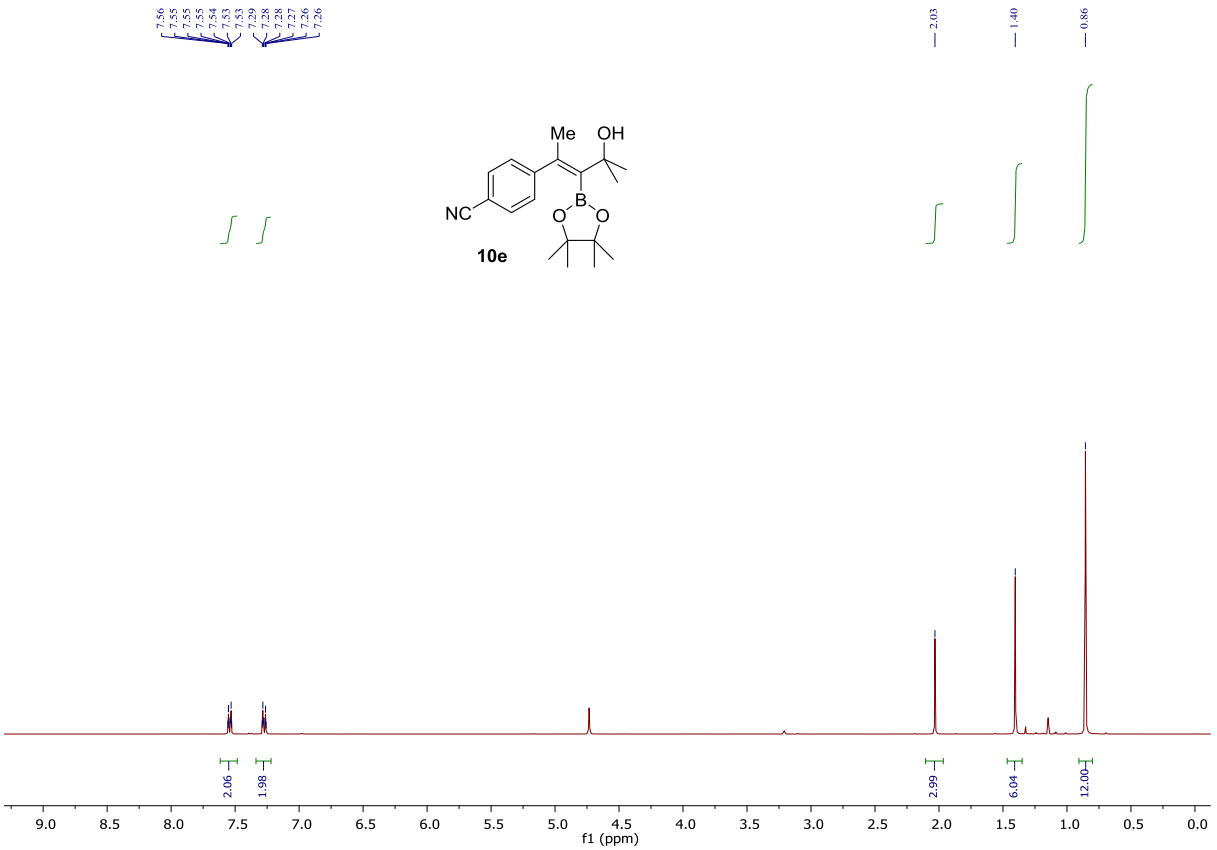
7.59
7.57
7.57
7.40
7.40
7.38
7.38
7.38
2.16
1.53
0.95
Me
OH
F3C
B
O
O
10d
2.14
1.93
2.95
5.98
12.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


150.59
141.88
128.97
128.72
128.65
128.44
128.33
128.20
128.01
125.75
124.51
124.47
124.44
124.40
123.05
120.36
83.10
72.85
29.13
23.57
20.96
Me
OH
F3C
B
O
O
10d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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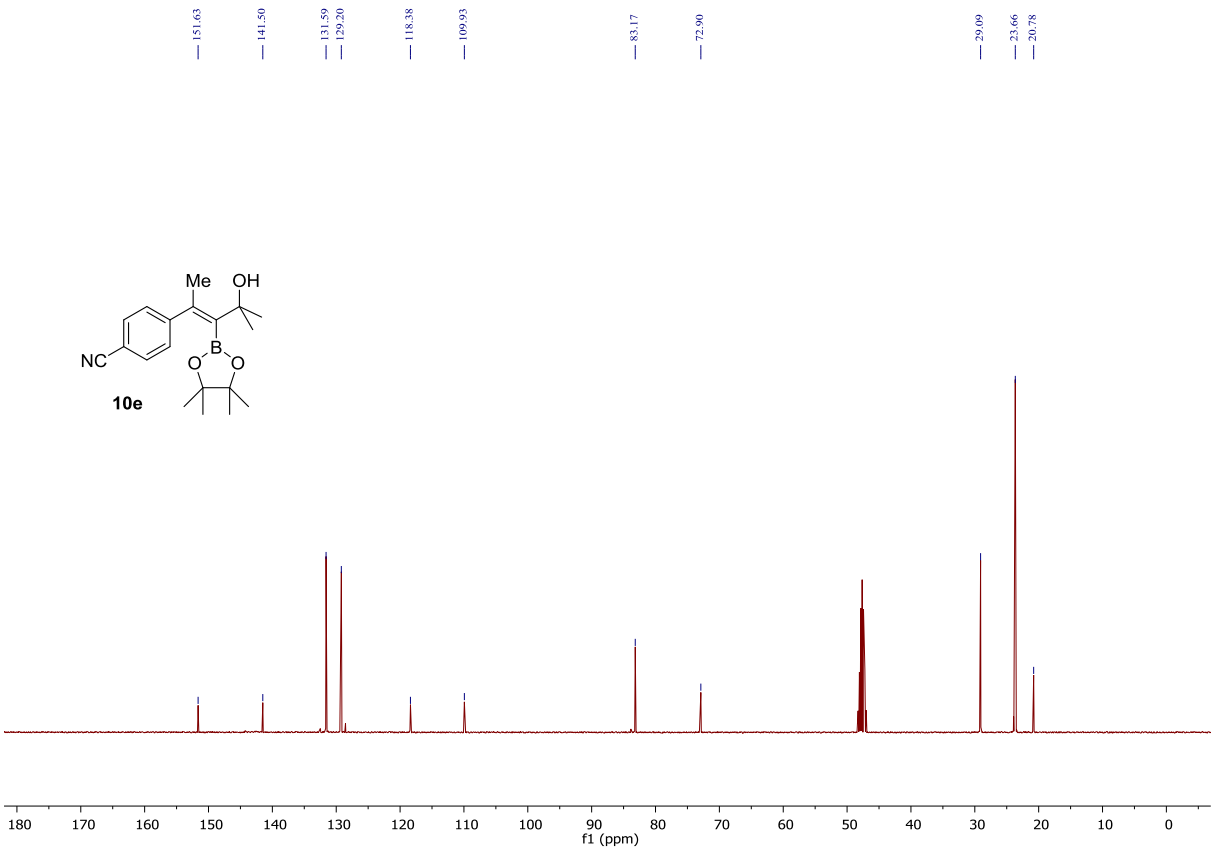
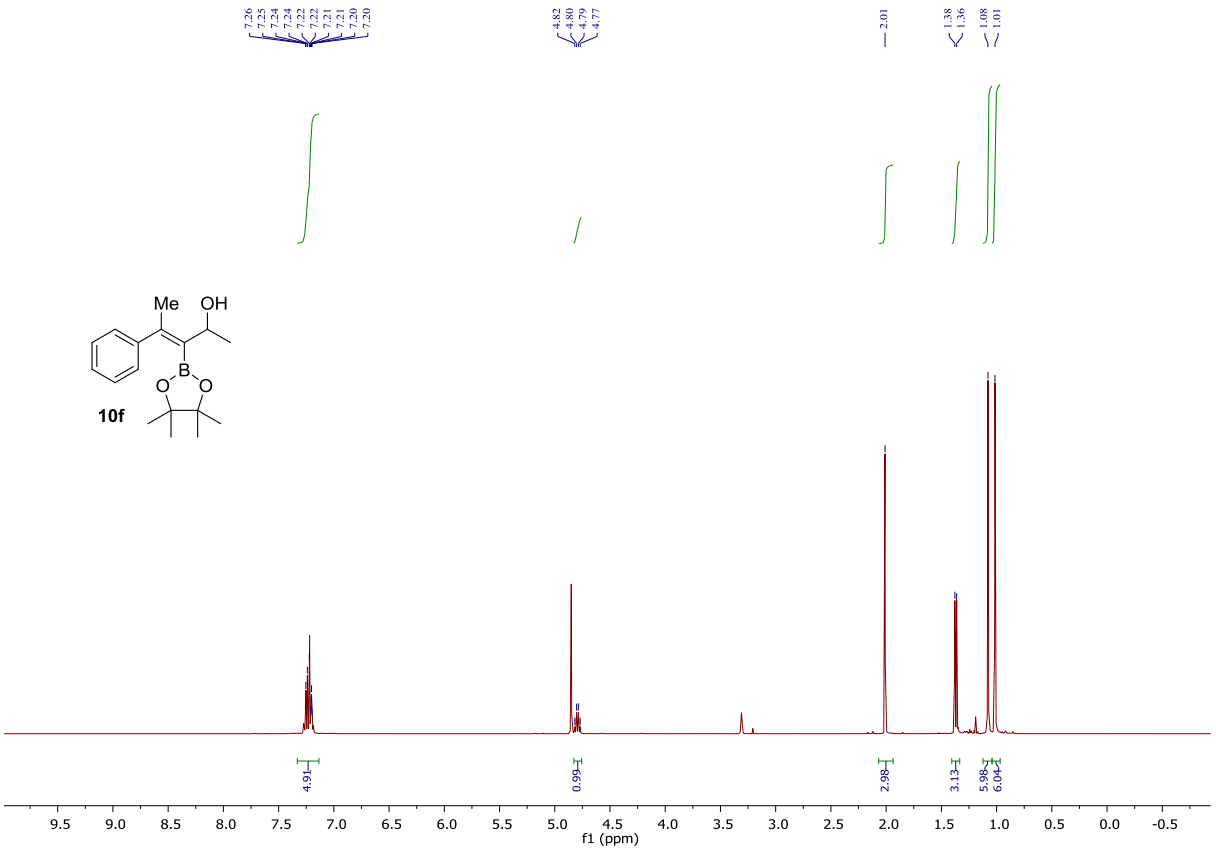
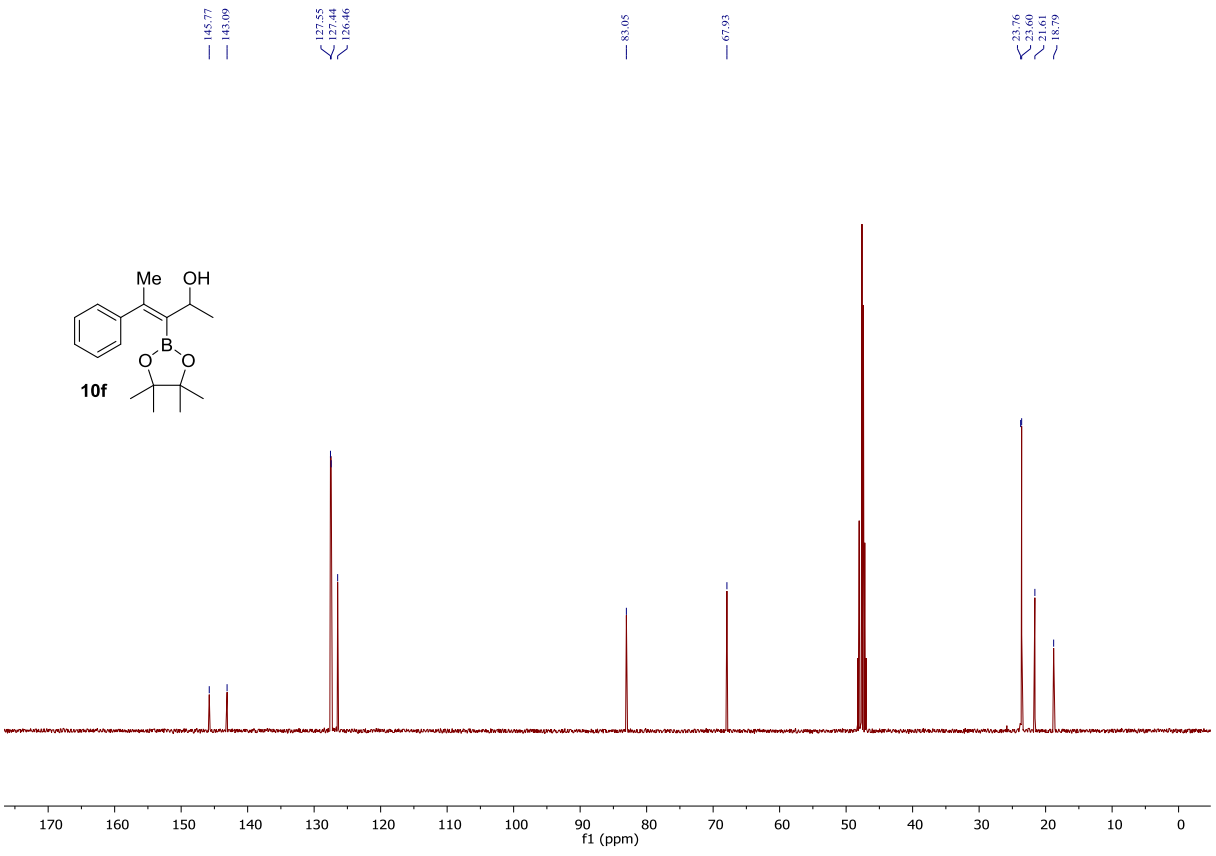
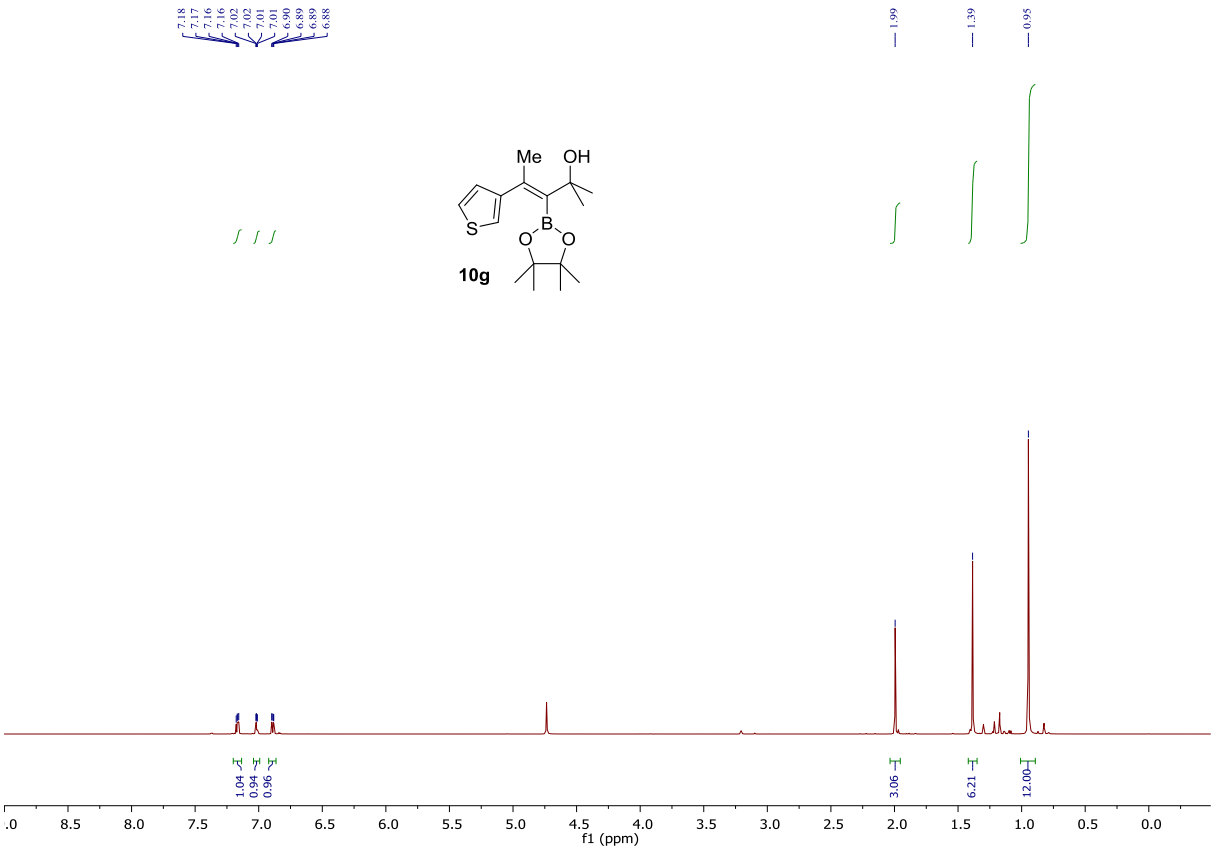
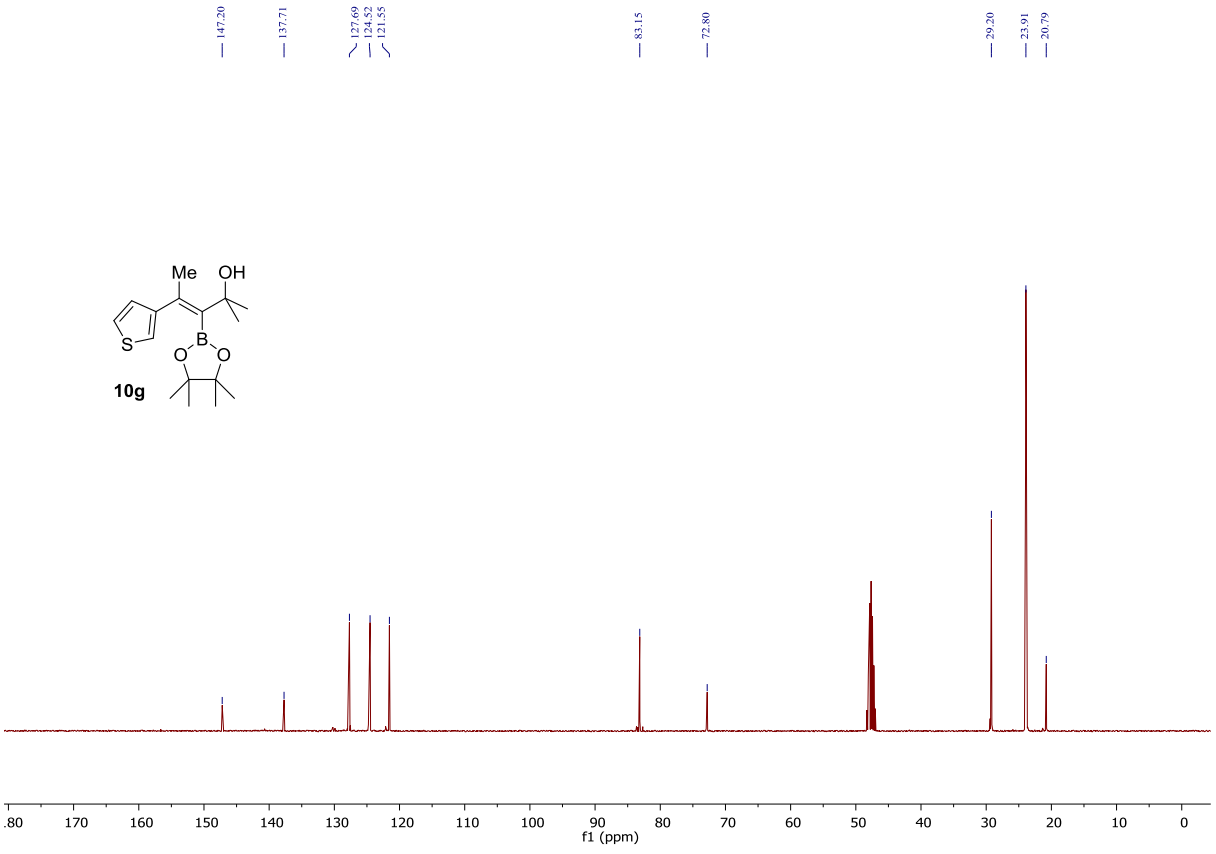
7.55
7.55
7.54
7.53
7.53
7.29
7.28
7.28
7.27
7.26
7.26
2.03
1.40
0.86
Me
OH
NC
B
O
O
10e
2.06
1.98
2.99
6.04
12.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

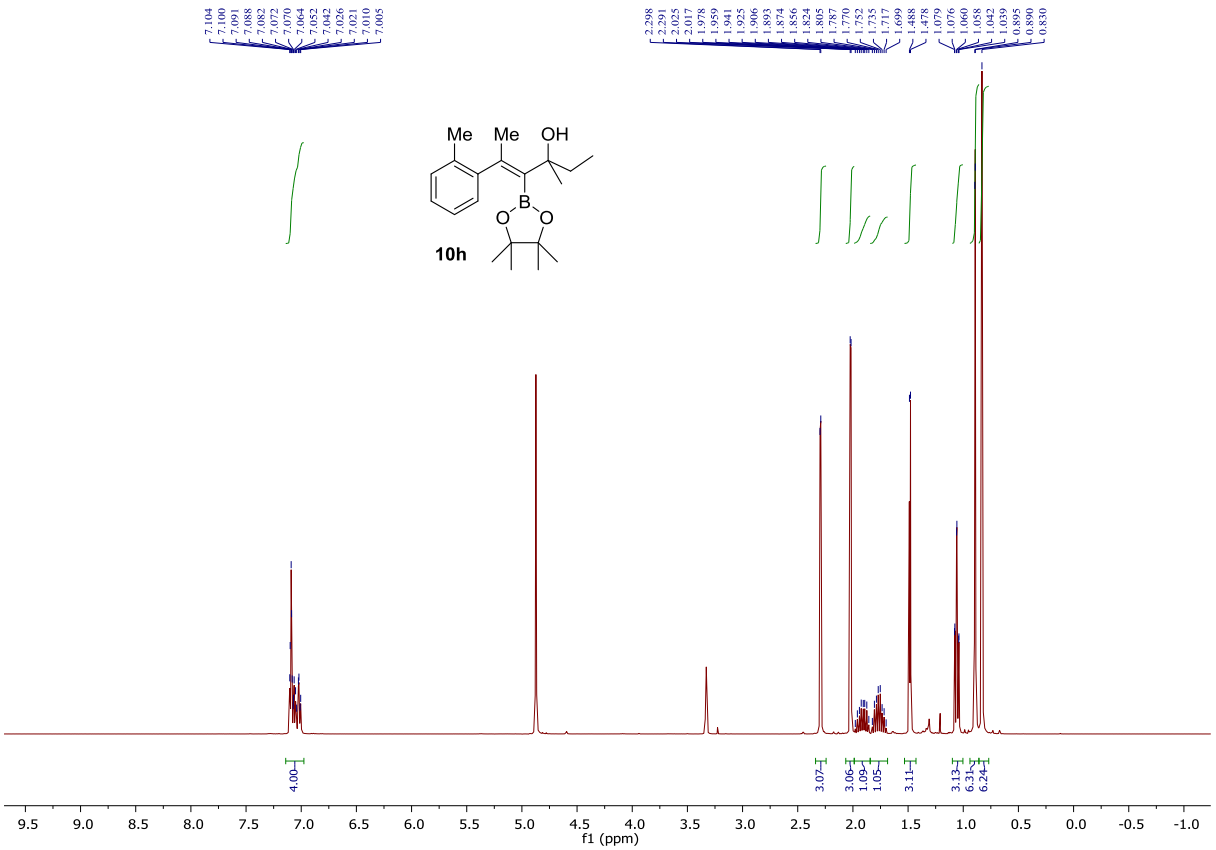

151.63
141.50
131.59
129.20
118.38
109.93
83.17
72.90
29.09
23.66
20.78
Me
OH
NC
B
O
O
10e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

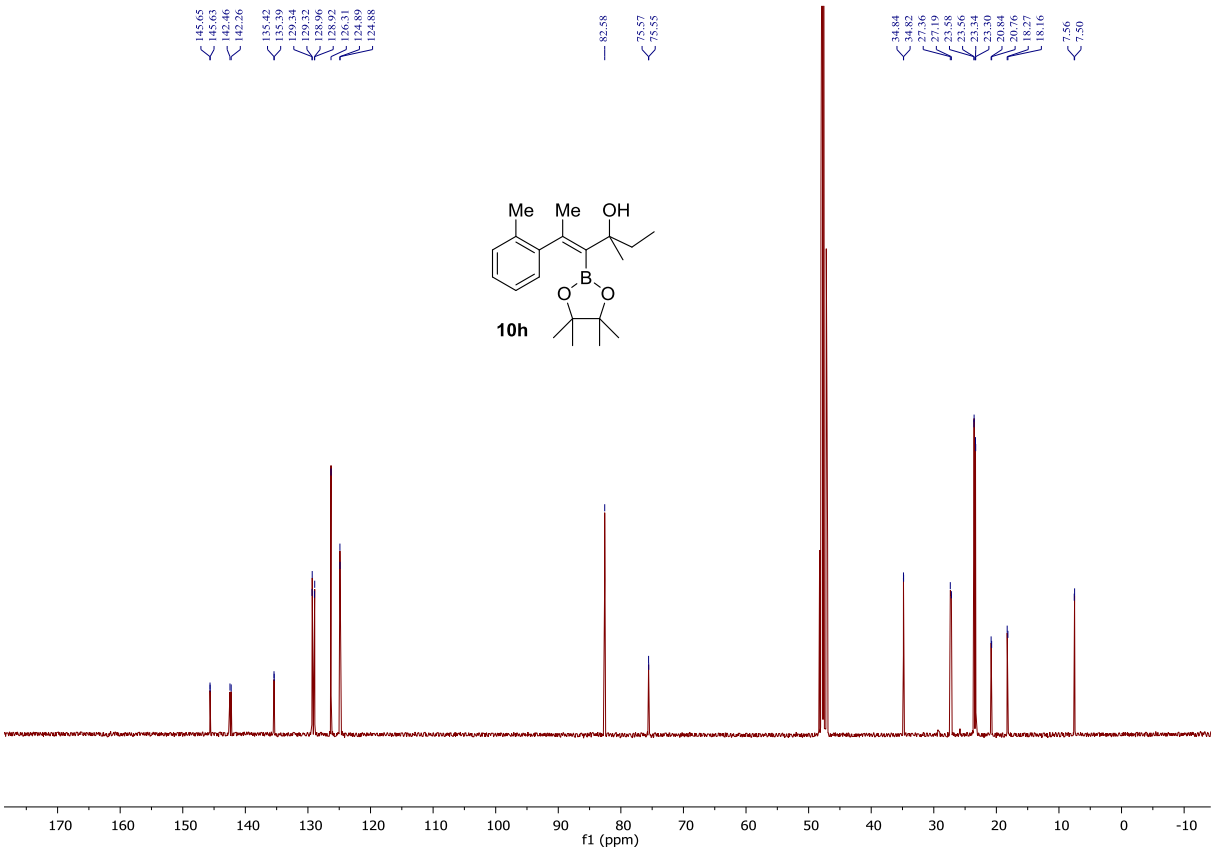

7.26
7.25
7.24
7.24
7.22
7.22
7.21
7.21
7.20
7.20
4.82
4.80
4.79
4.77
2.01
1.38
1.36
1.08
1.01
Me
OH
B
O
O
10f
4.91
0.99
2.98
3.13
5.98
6.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

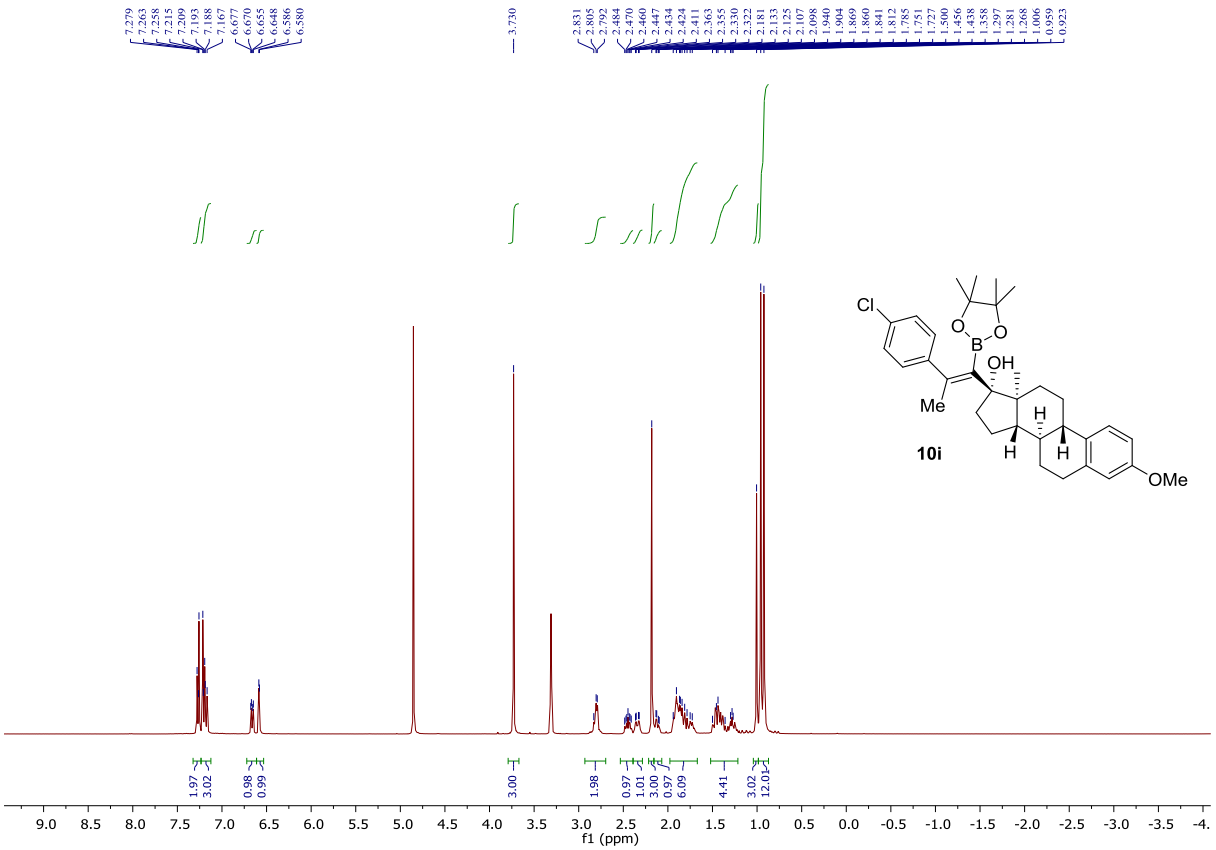

145.77
143.09
127.55
127.44
126.46
83.05
67.93
23.76
23.60
21.61
18.79
Me
OH
B
O
O
10f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

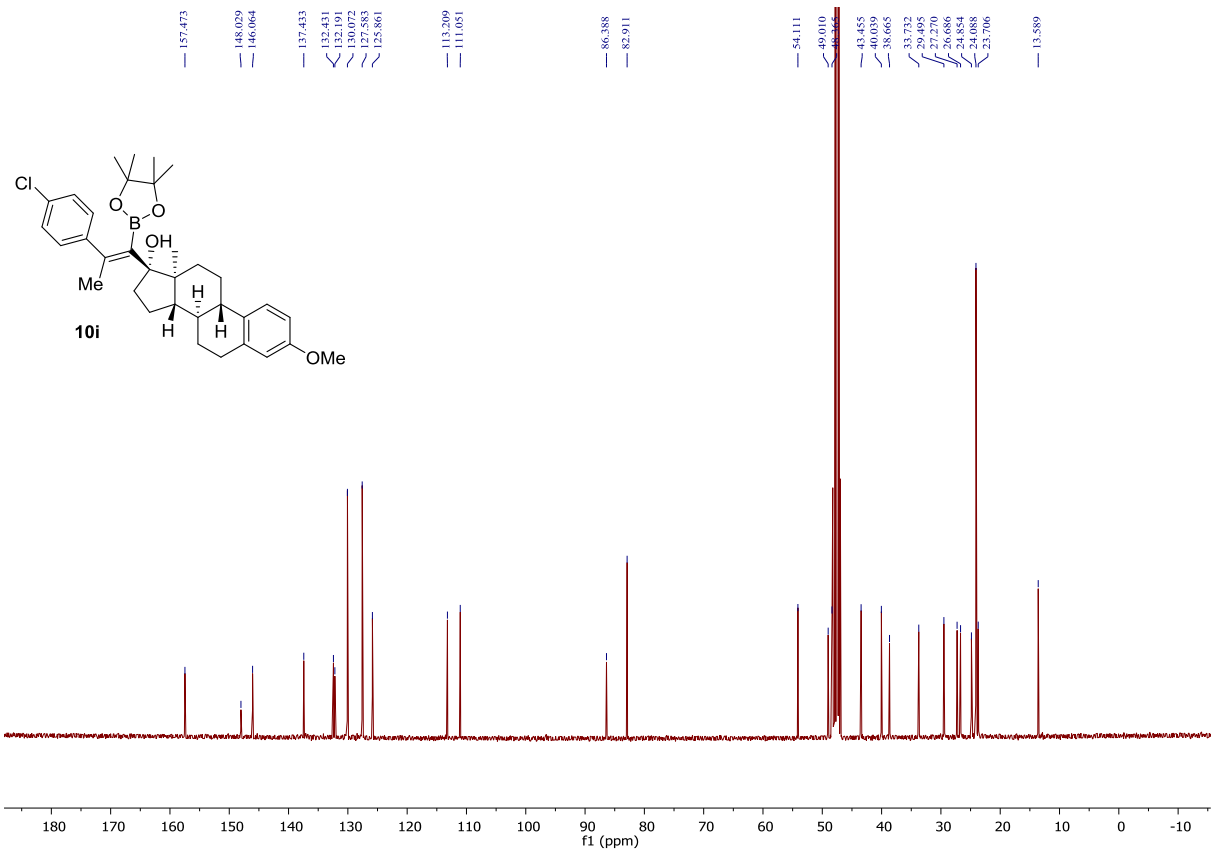

7.18
7.17
7.16
7.16
7.02
7.02
7.01
7.01
6.90
6.89
6.89
6.88
1.99
1.39
0.95
Me
OH
S
B
O
O
10g
1.04
0.94
0.96
3.06
6.21
12.00
f1 (ppm)


147.20
137.71
127.69
124.52
121.55
83.15
72.80
29.20
23.91
20.79
Me
OH
S
B
O
O
10g
f1 (ppm)


7.104
7.100
7.091
7.088
7.082
7.072
7.070
7.064
7.052
7.042
7.026
7.021
7.010
7.005
2.298
2.291
2.025
2.017
1.978
1.959
1.941
1.925
1.906
1.893
1.874
1.856
1.824
1.805
1.787
1.770
1.752
1.735
1.717
1.699
1.488
1.478
1.079
1.076
1.060
1.058
1.043
1.039
0.895
0.890
0.830
Me
Me
OH
B
O
O
10h
4.00
3.07
3.06
1.09
1.05
3.11
3.13
6.31
6.24
f1 (ppm)


145.65
145.63
142.46
142.26
135.42
135.39
129.34
129.32
128.96
128.92
126.31
124.89
124.88
82.58
75.57
75.55
34.84
34.82
27.36
27.19
23.58
23.56
23.34
23.30
20.84
20.76
18.27
18.16
7.56
7.50
Me
Me
OH
B
O
O
10h
f1 (ppm)


7.279
7.263
7.258
7.215
7.209
7.193
7.188
7.167
6.677
6.670
6.655
6.648
6.586
6.580
3.730
2.831
2.805
2.792
2.484
2.470
2.460
2.447
2.434
2.424
2.411
2.363
2.355
2.330
2.322
2.181
2.133
2.125
2.107
2.098
1.940
1.904
1.869
1.860
1.841
1.812
1.785
1.751
1.727
1.500
1.456
1.438
1.358
1.297
1.281
1.268
1.006
0.959
0.923
Cl
O
B
O
OH
Me
H
H
H
10i
OMe
1.97
3.02
0.98
0.99
3.00
1.98
0.97
1.01
3.00
0.97
6.09
4.41
3.02
12.01
f1 (ppm)


157.473
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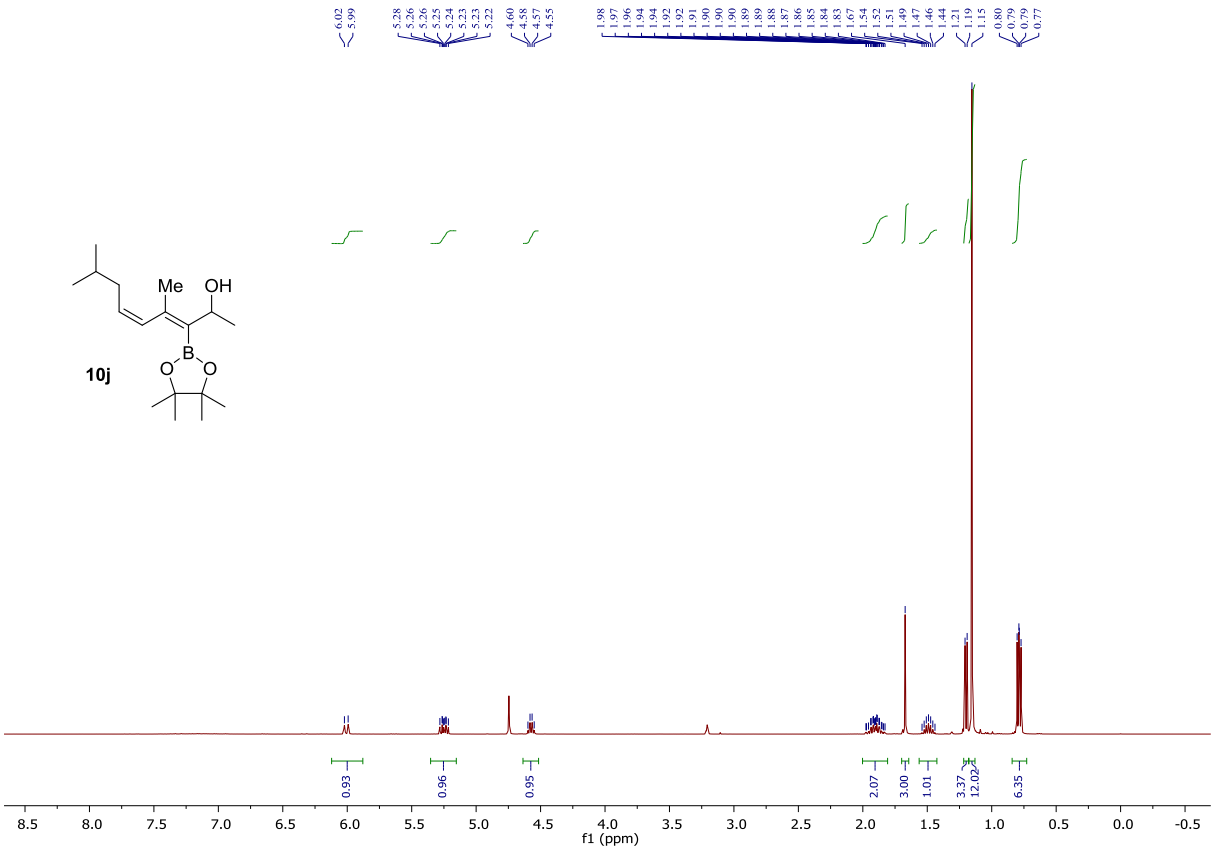
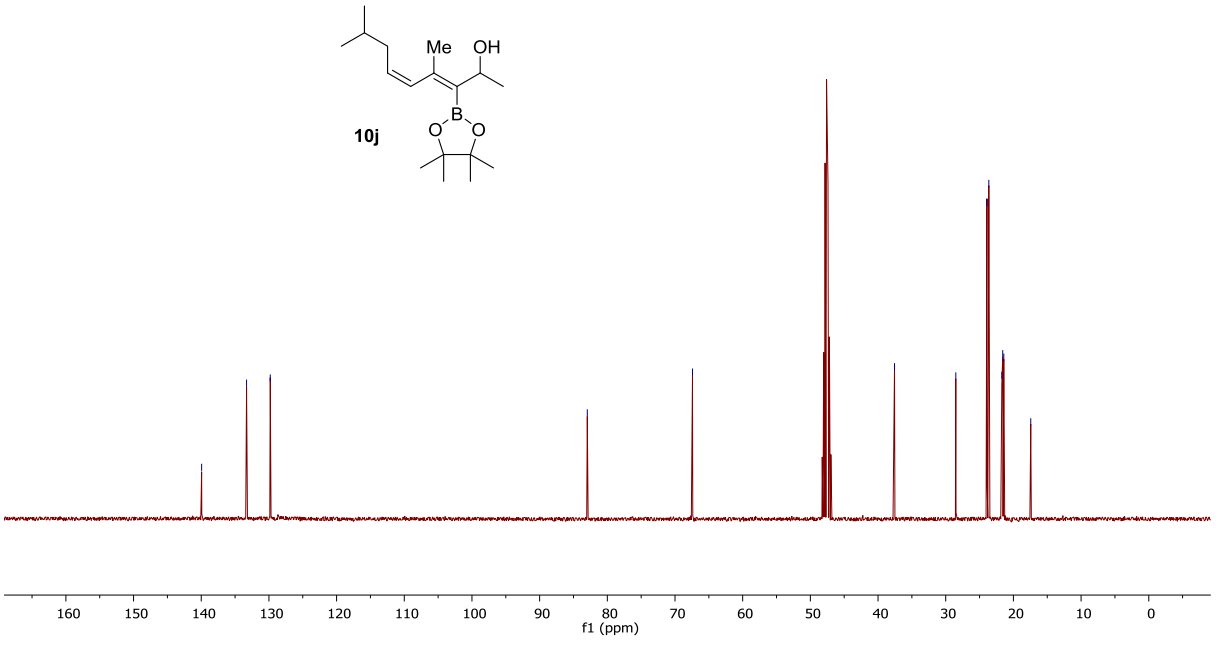
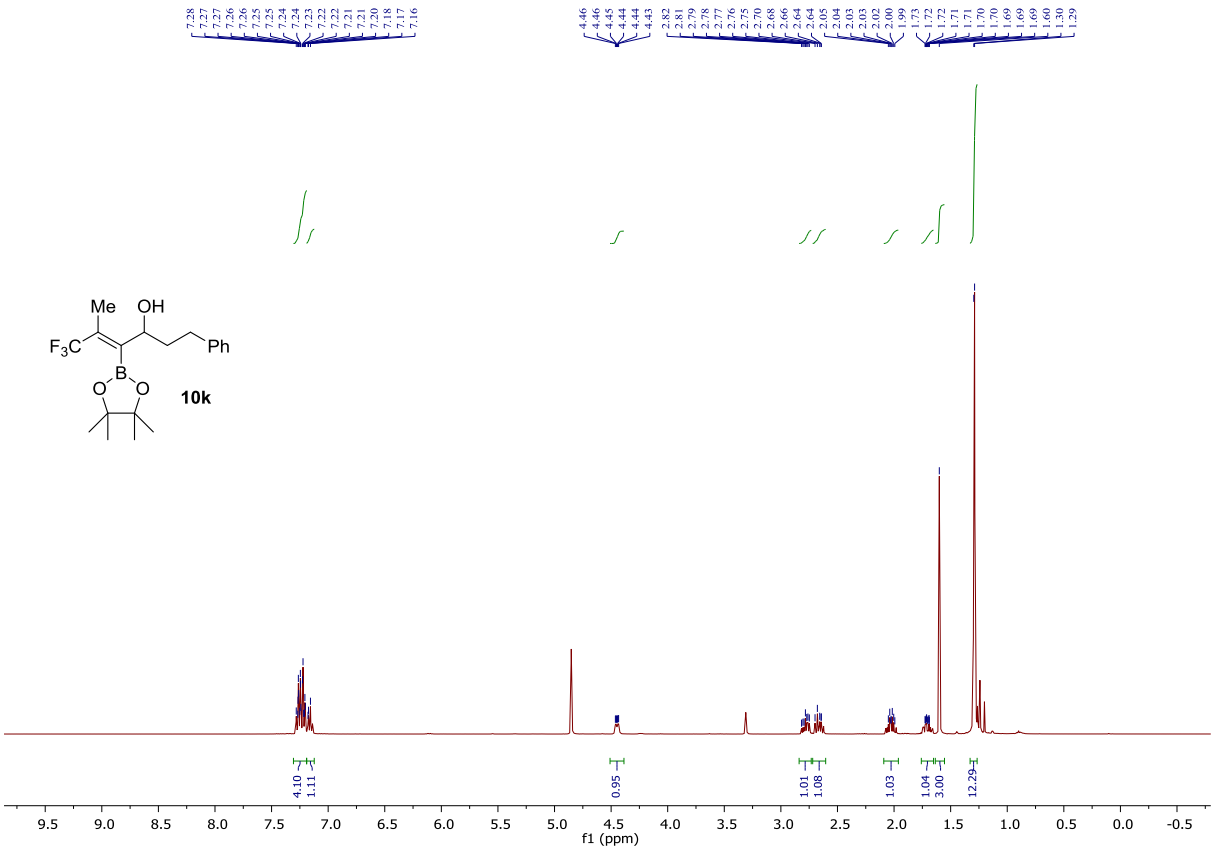
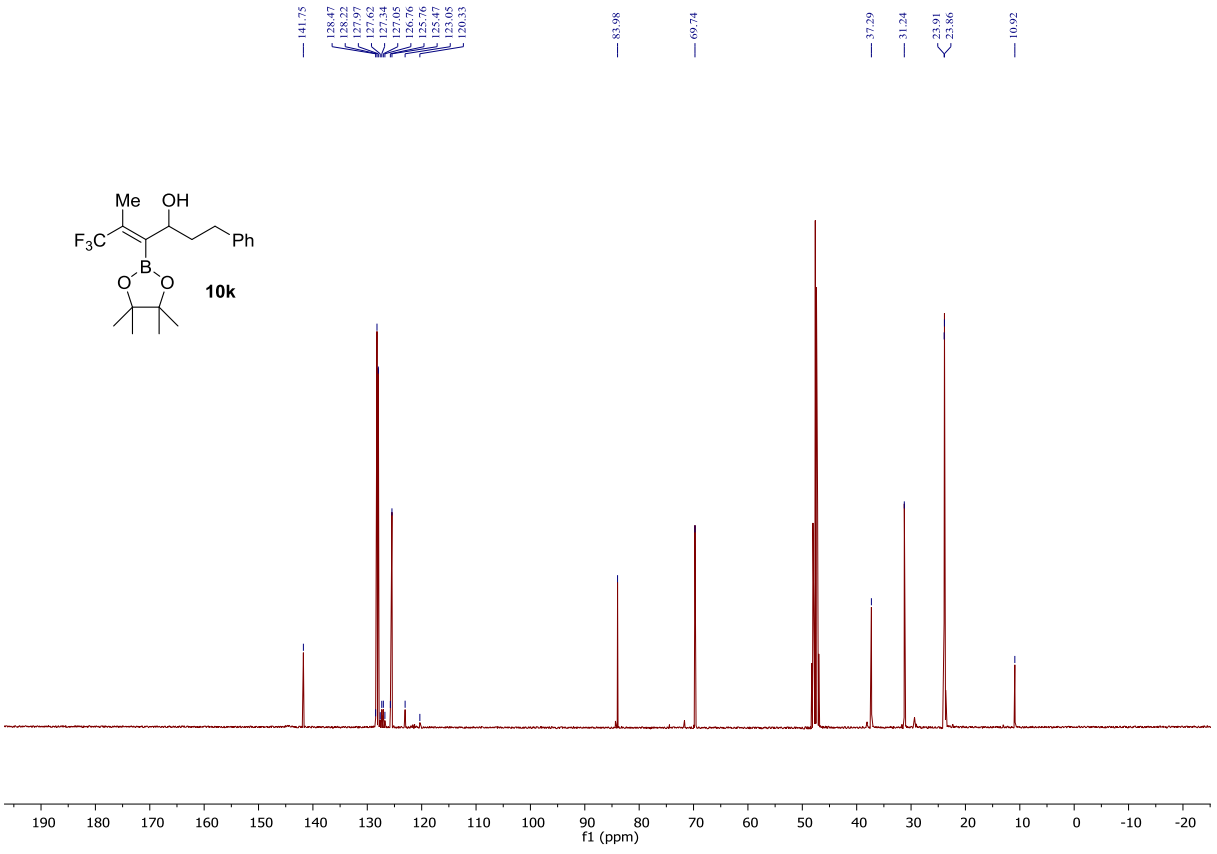
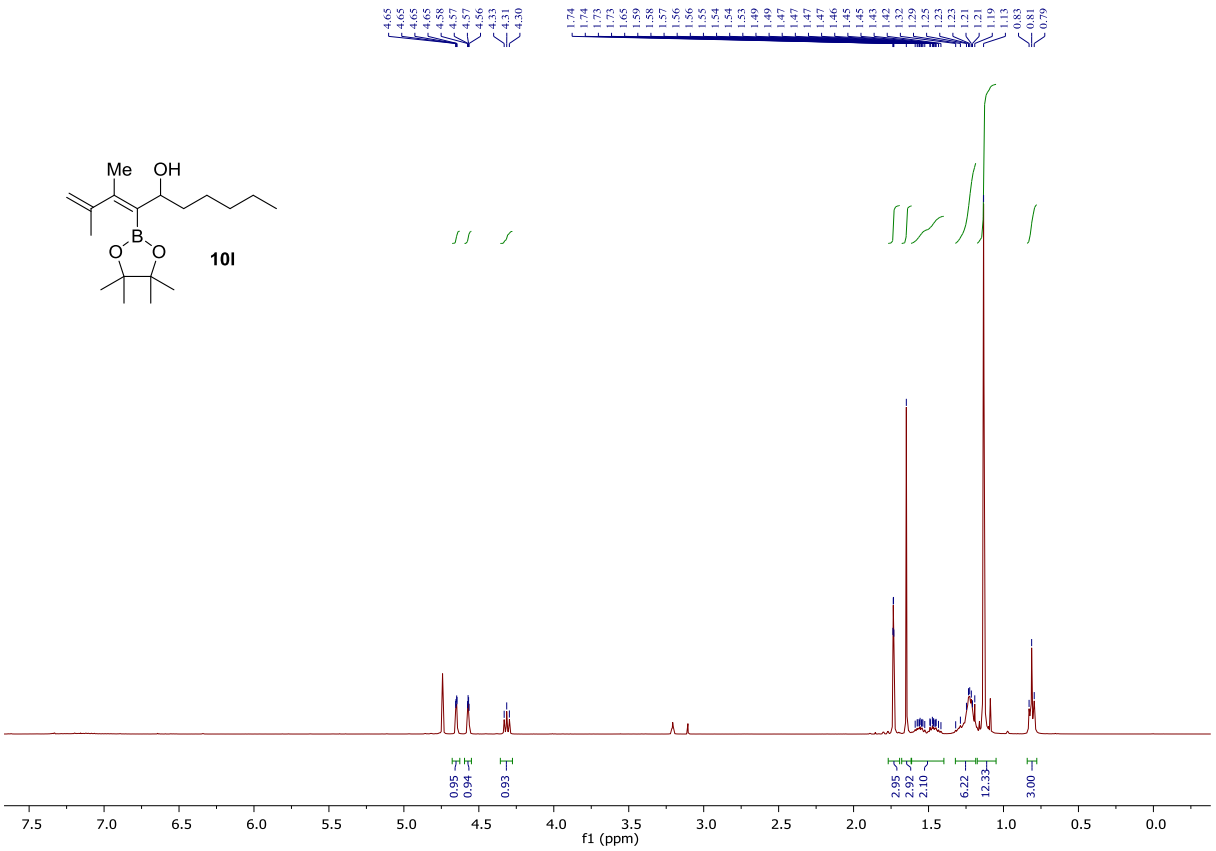
146.064
137.433
132.431
132.191
130.072
127.583
125.861
113.209
111.051
86.388
82.911
54.111
49.010
43.455
40.039
38.665
33.732
29.495
27.270
26.686
24.854
24.088
23.706
13.589
Cl
O
B
O
OH
Me
H
H
H
10i
OMe
f1 (ppm)

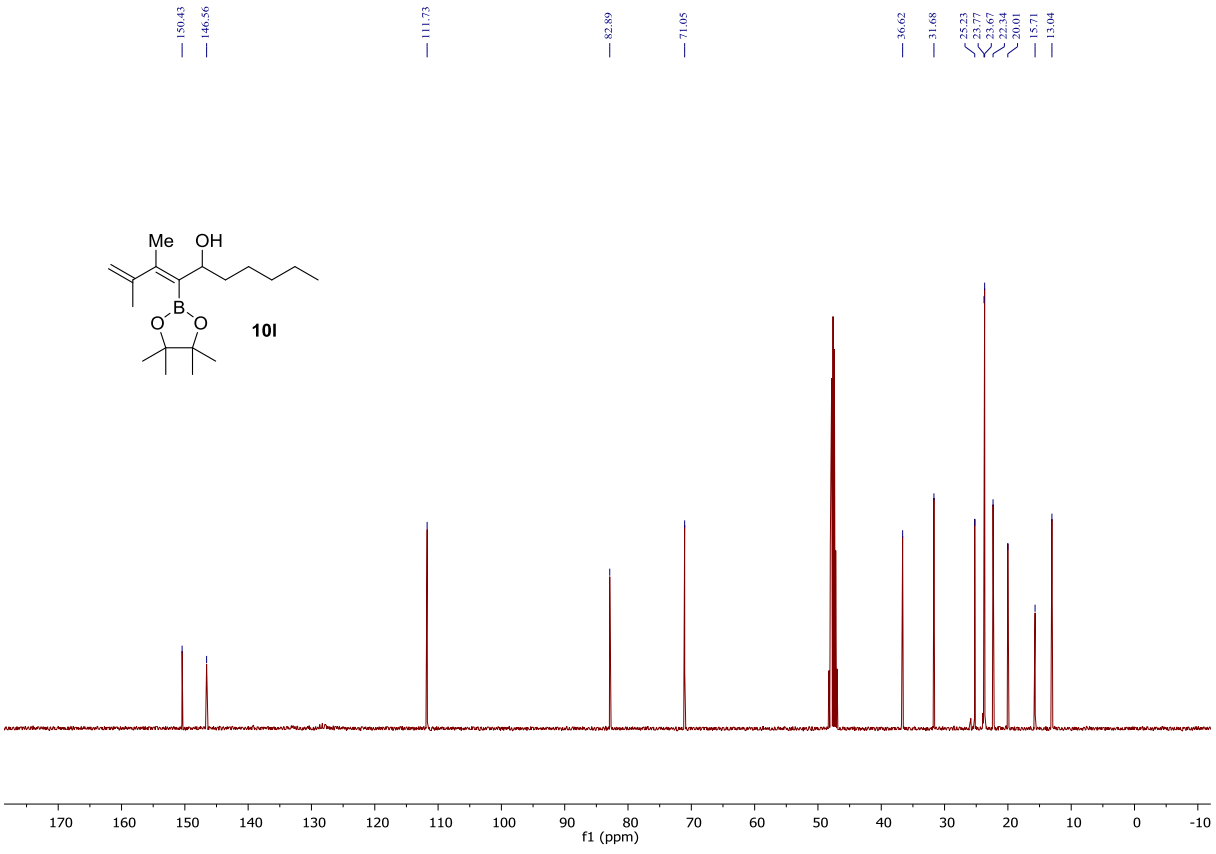

Me
OH
B
O
O
10j
f1 (ppm)

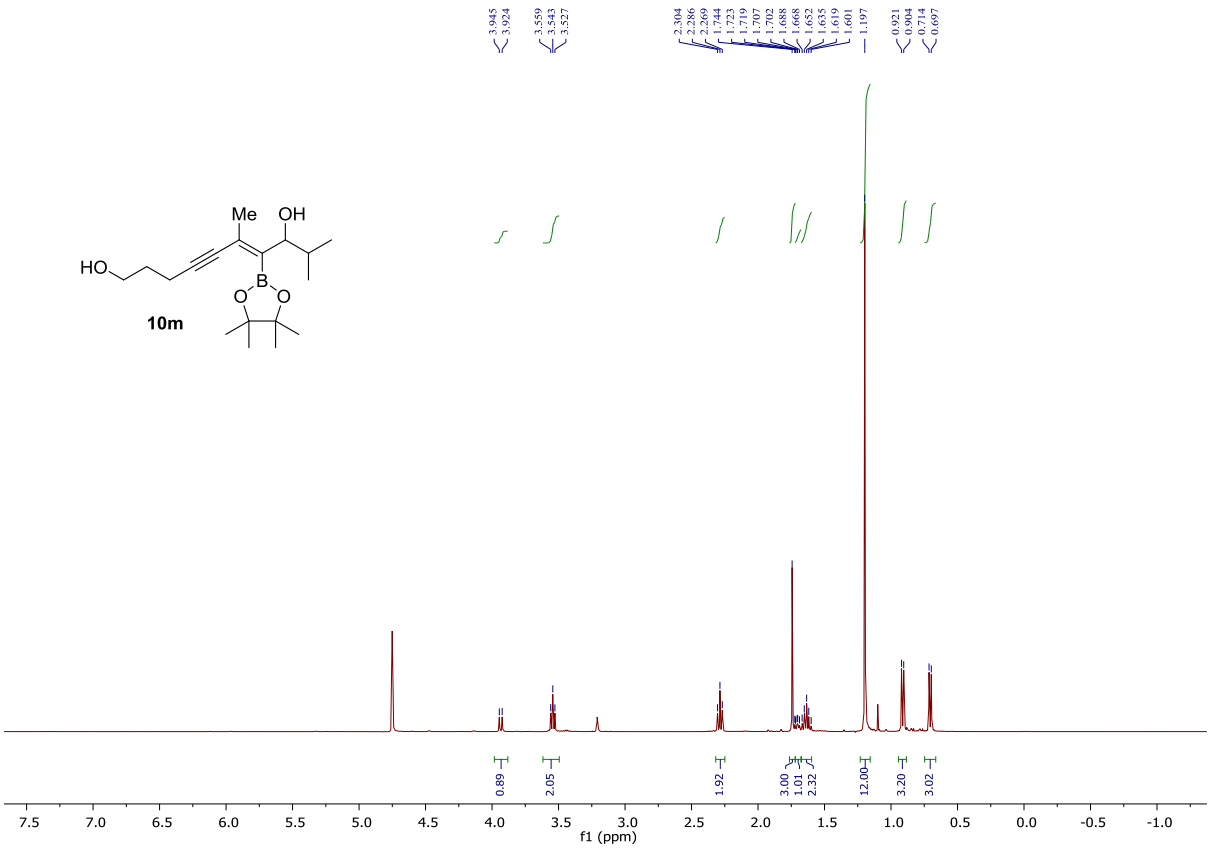

Me
OH
B
O
O
10j
f1 (ppm)

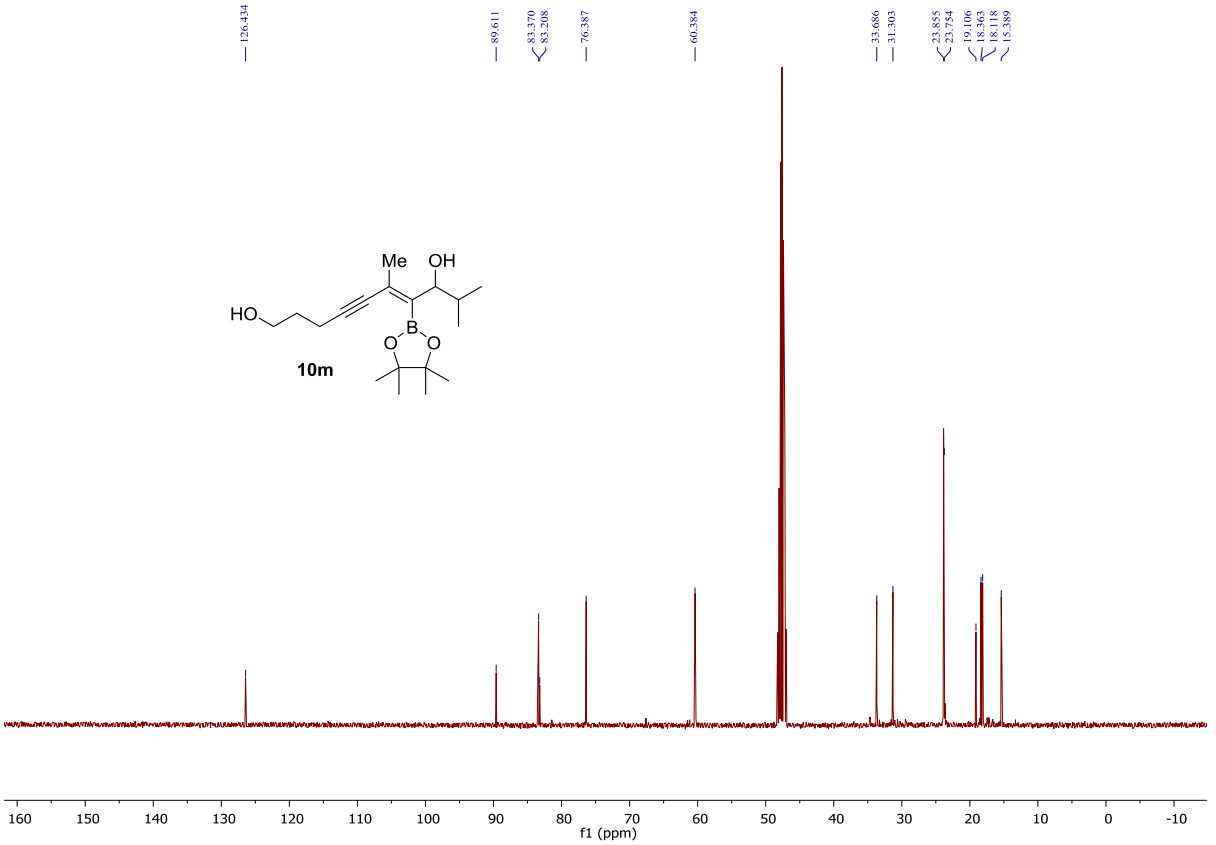

Me
OH
F3C
Ph
B
O
O
10k
4.10
1.11
0.95
1.01
1.08
1.03
1.04
3.00
12.29
f1 (ppm)

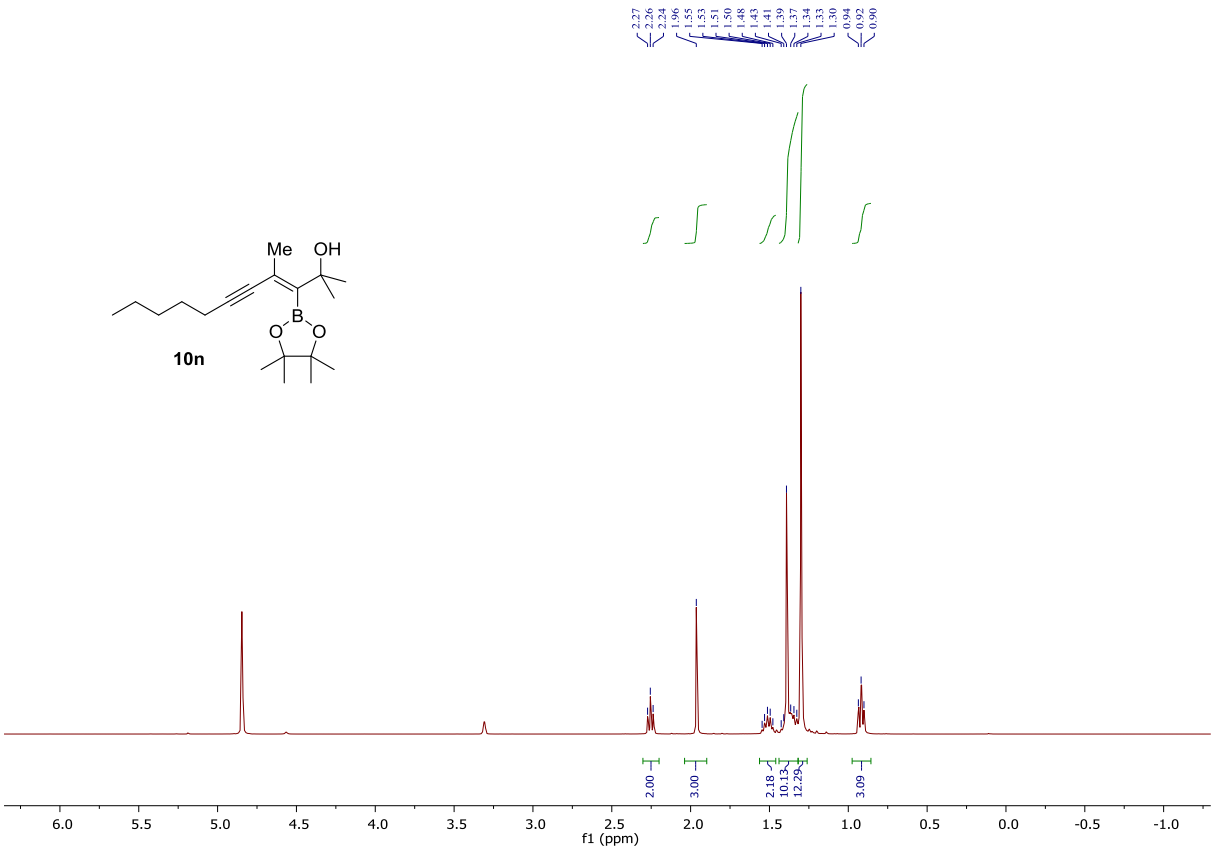

Me
OH
F3C
Ph
B
O
O
10k
141.75
128.47
128.22
127.97
127.62
127.34
127.05
126.76
125.76
125.47
123.05
120.33
83.98
69.74
37.29
31.24
23.91
23.86
10.92
f1 (ppm)

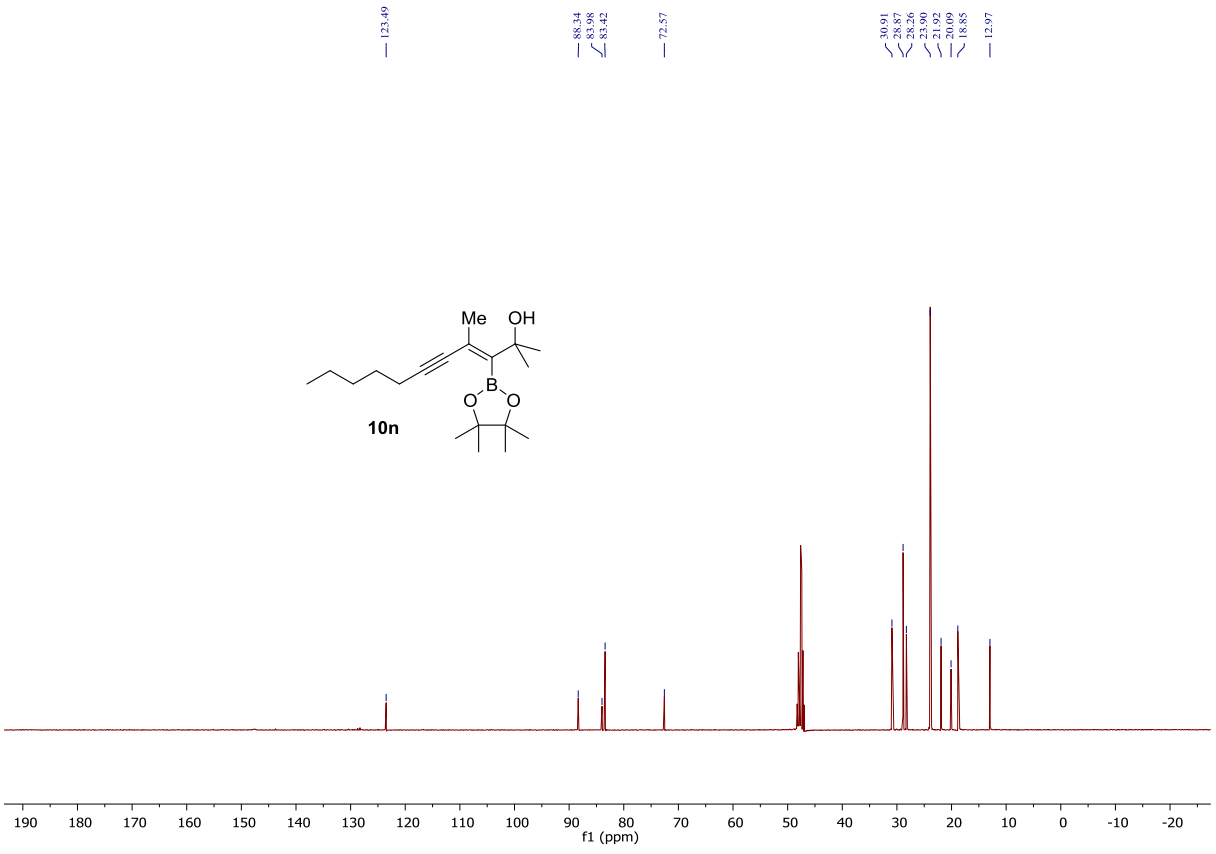

Me
OH
B
O
O
10l
4.65
4.65
4.65
4.58
4.57
4.57
4.56
4.33
4.31
4.30
1.74
1.74
1.73
1.73
1.65
1.59
1.58
1.57
1.56
1.56
1.55
1.54
1.54
1.53
1.49
1.49
1.48
1.47
1.47
1.47
1.46
1.45
1.45
1.43
1.42
1.32
1.29
1.25
1.23
1.23
1.21
1.21
1.19
1.13
0.83
0.81
0.79
0.95
0.94
0.93
2.95
2.92
2.10
6.22
12.33
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

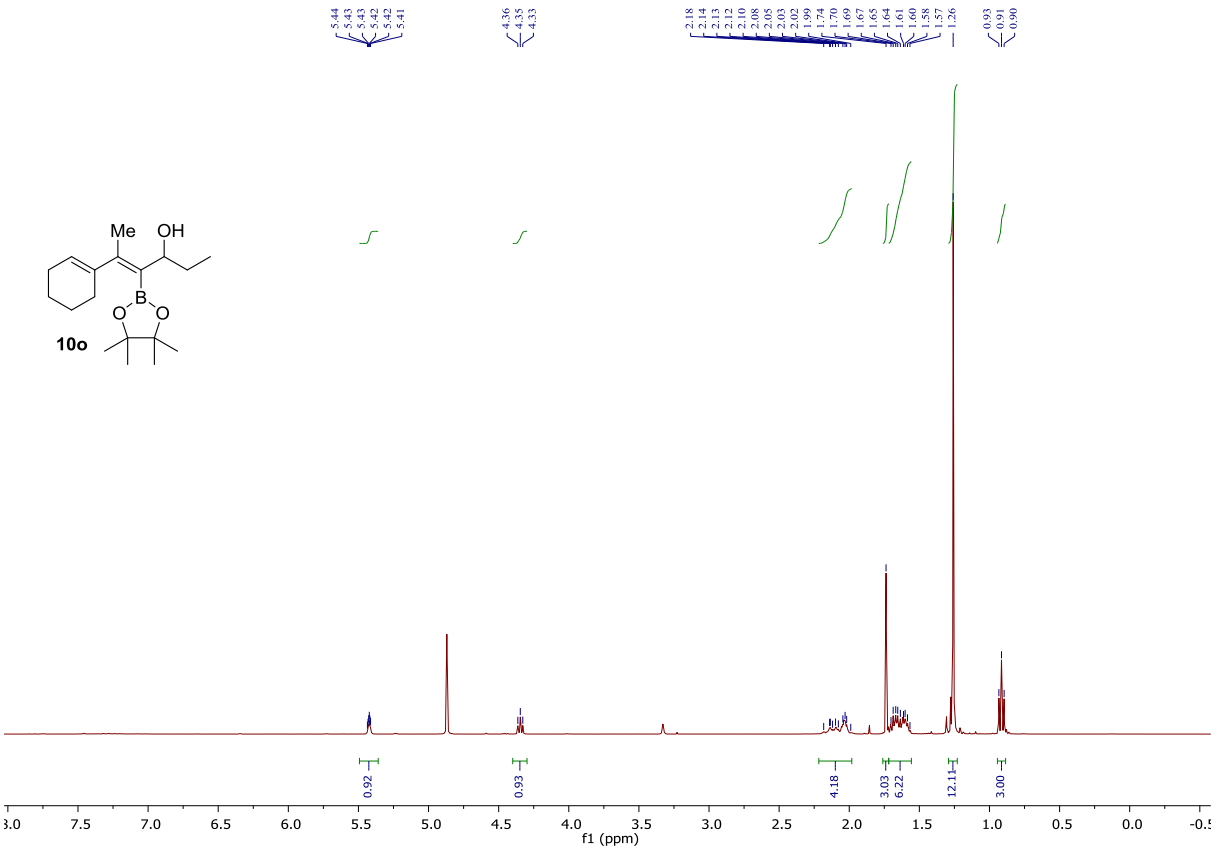

150.43
146.56
111.73
82.89
71.05
36.62
31.68
25.23
23.77
23.67
22.34
20.01
15.71
13.04
Me
OH
B
O
O
10l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

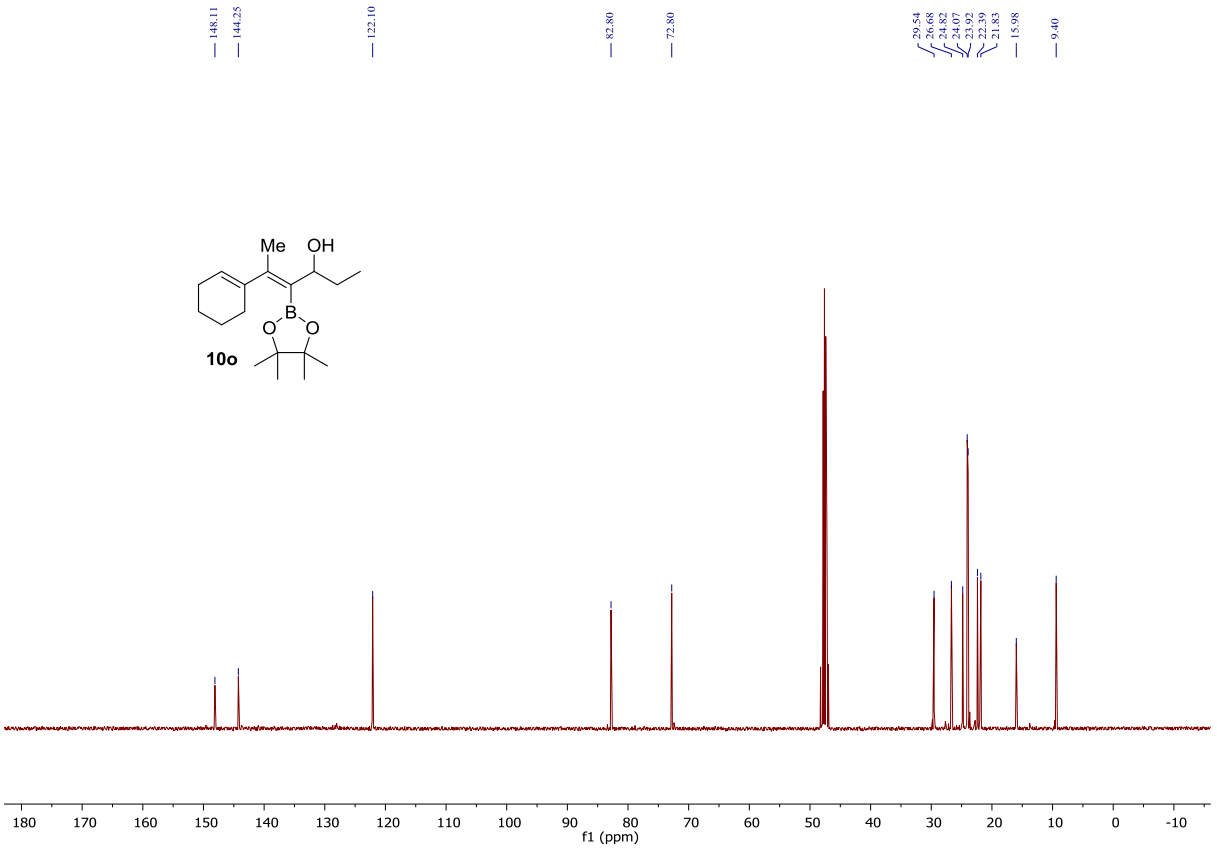

3.945
3.924
3.559
3.543
3.527
2.304
2.286
2.269
1.744
1.723
1.719
1.707
1.702
1.688
1.668
1.652
1.635
1.619
1.601
1.197
0.921
0.904
0.714
0.697
Me
OH
HO
B
O
O
10m
0.89
2.05
1.92
3.00
1.01
2.32
12.00
3.20
3.02
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

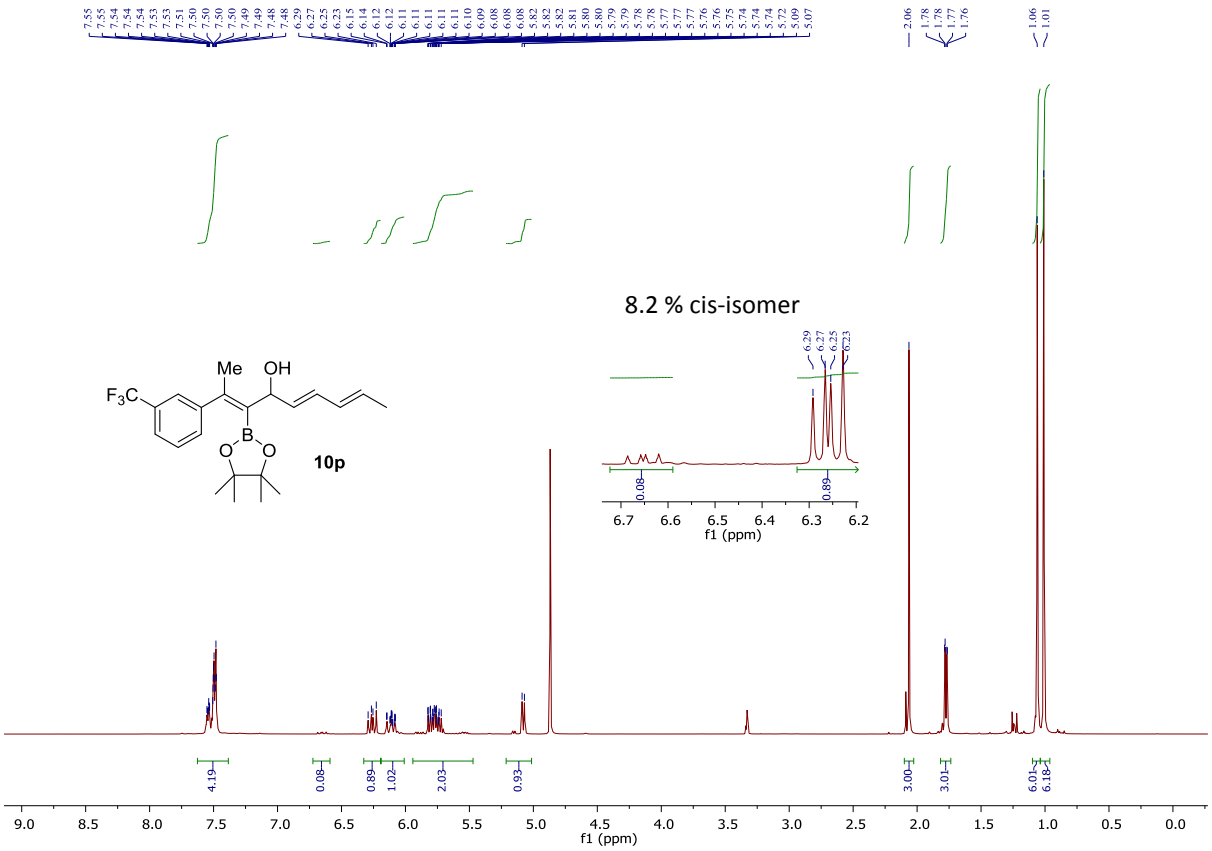

126.434
89.611
83.370
83.208
76.387
60.384
33.686
31.303
23.855
23.754
19.106
18.363
18.118
15.389
Me
OH
HO
B
O
O
10m
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

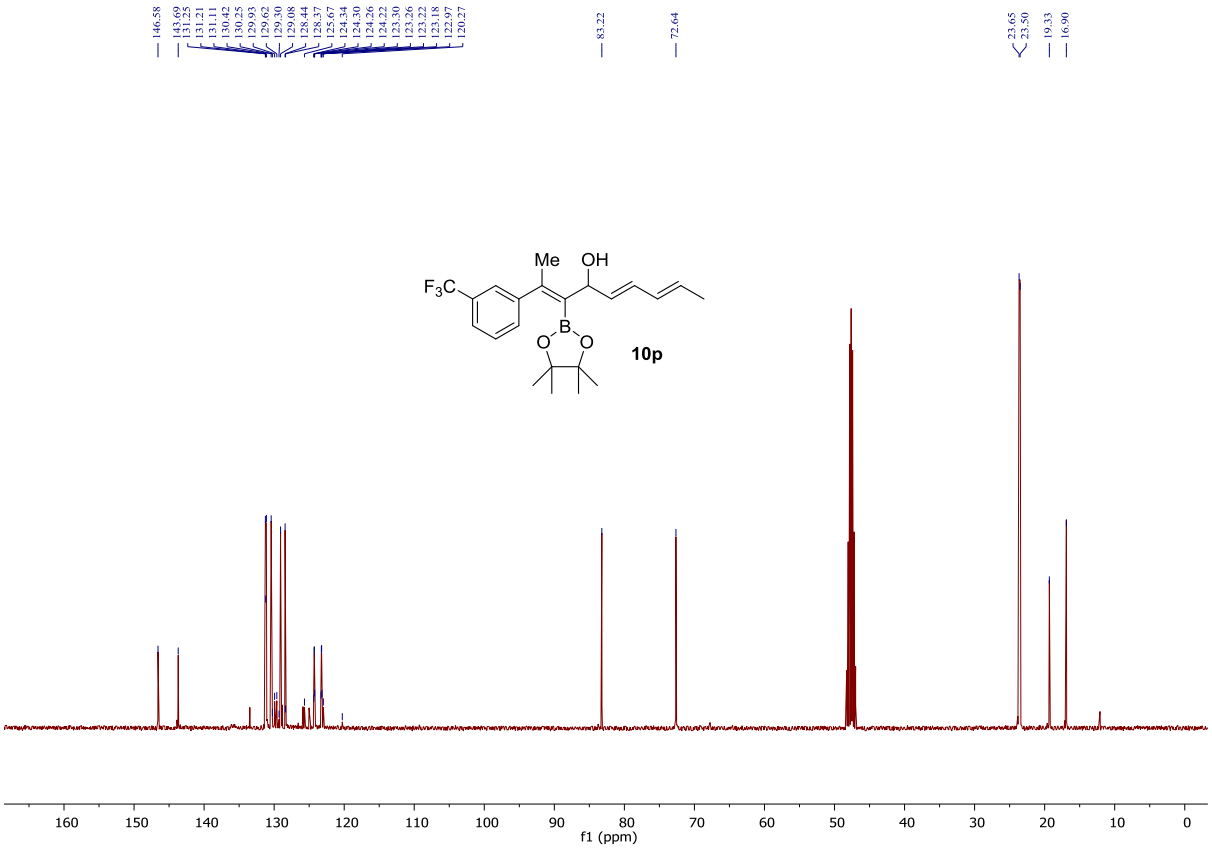

2.27
2.26
2.24
1.96
1.55
1.53
1.51
1.50
1.48
1.43
1.41
1.39
1.37
1.34
1.33
1.30
0.94
0.92
0.90
Me
OH
B
O
O
10n
2.00
3.00
2.18
10.13
12.29
3.09
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

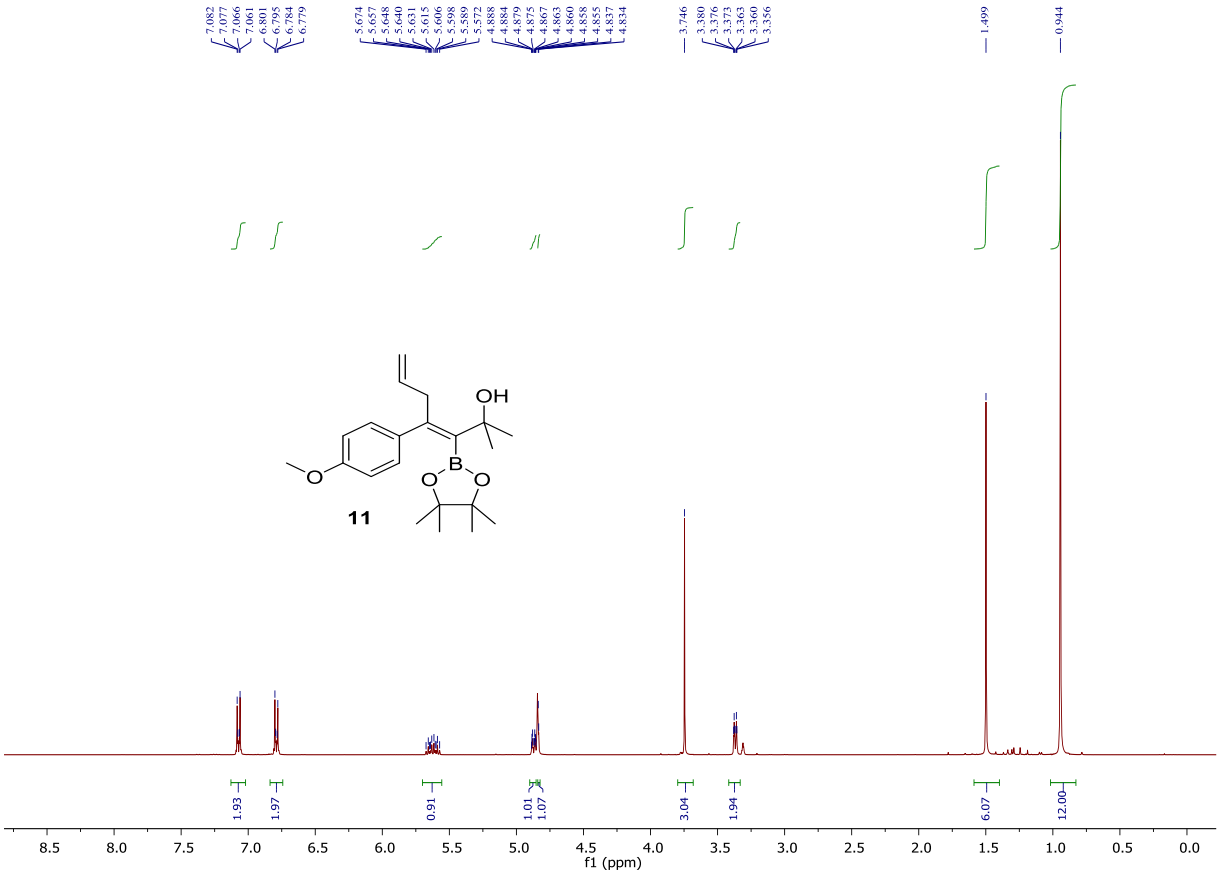

123.49
88.34
83.98
83.42
72.57
30.91
28.87
28.26
23.90
21.92
20.09
18.85
12.97
Me
OH
B
O
O
10n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)

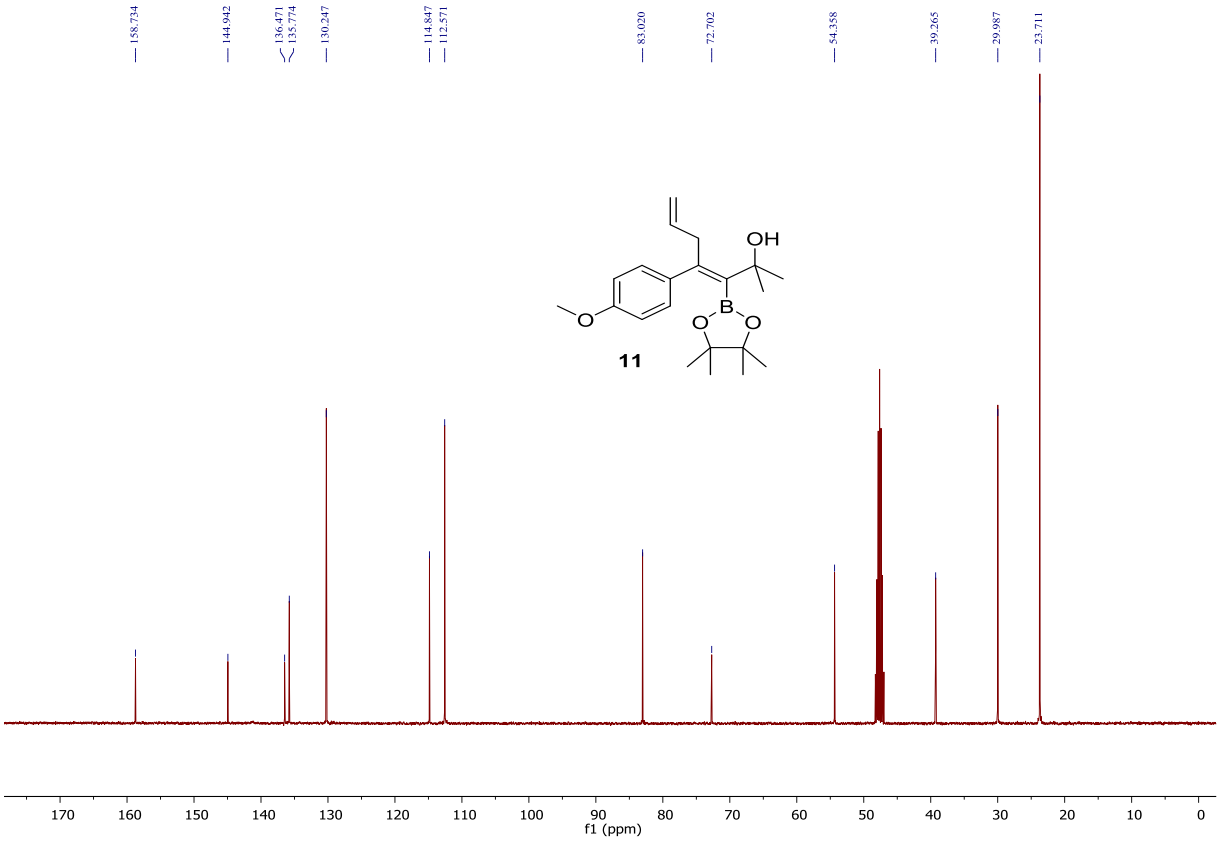

Me
OH
B
O
O
10o
f1 (ppm)

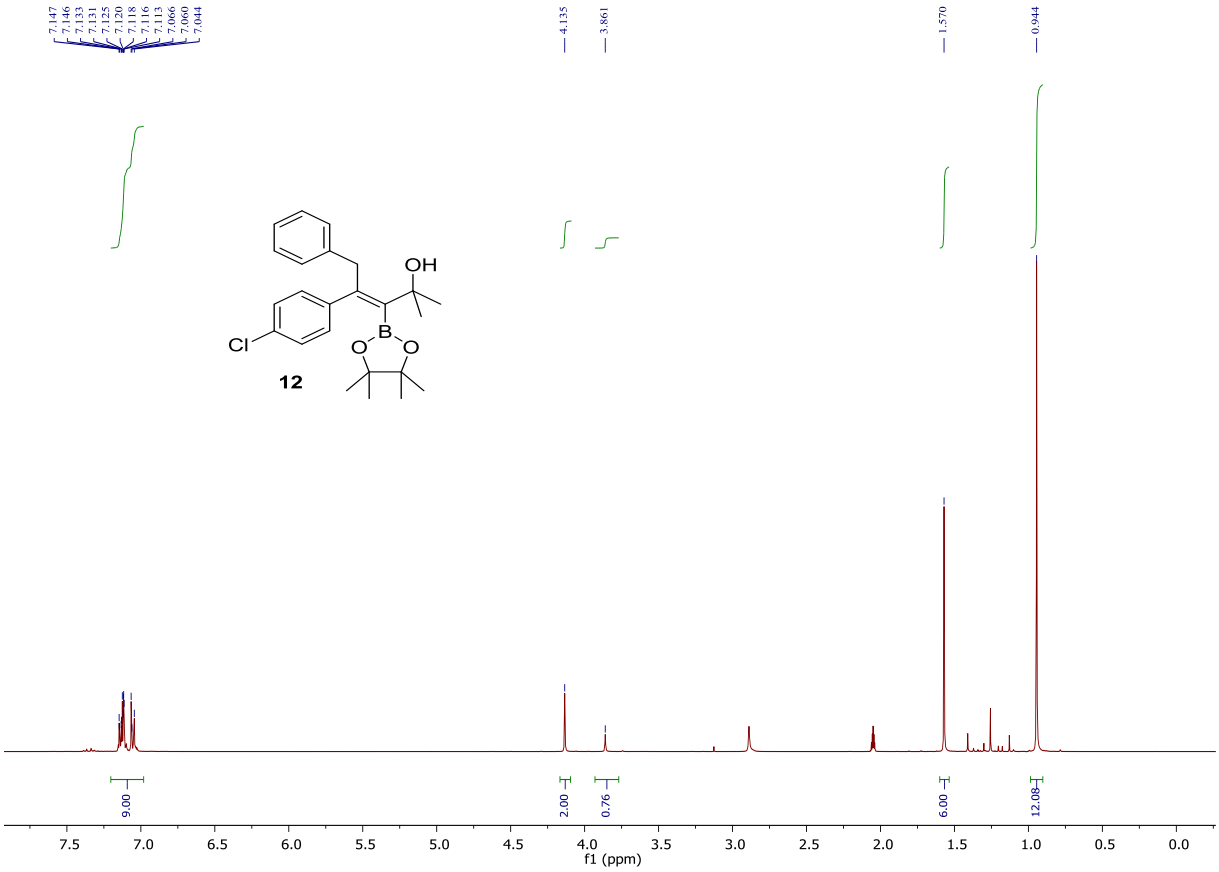

Me
OH
B
O
O
10o
f1 (ppm)


8.2 % cis-isomer
Me
OH
F3C
B
O
O
10p
f1 (ppm)


Me
OH
F3C
B
O
O
10p
f1 (ppm)


7.082
7.077
7.066
7.061
6.801
6.795
6.784
6.779
5.674
5.657
5.648
5.640
5.631
5.615
5.606
5.598
5.589
5.572
4.888
4.884
4.879
4.875
4.867
4.863
4.860
4.858
4.855
4.837
4.834
3.746
3.380
3.376
3.373
3.363
3.360
3.356
1.499
0.944
OH
O
B
O
O
11
1.93
1.97
0.91
1.01
1.07
3.04
1.94
6.07
12.00
f1 (ppm)


158.734
144.942
136.471
135.774
130.247
114.847
112.571
83.020
72.702
54.358
39.265
29.987
23.711
OH
O
B
O
O
11
f1 (ppm)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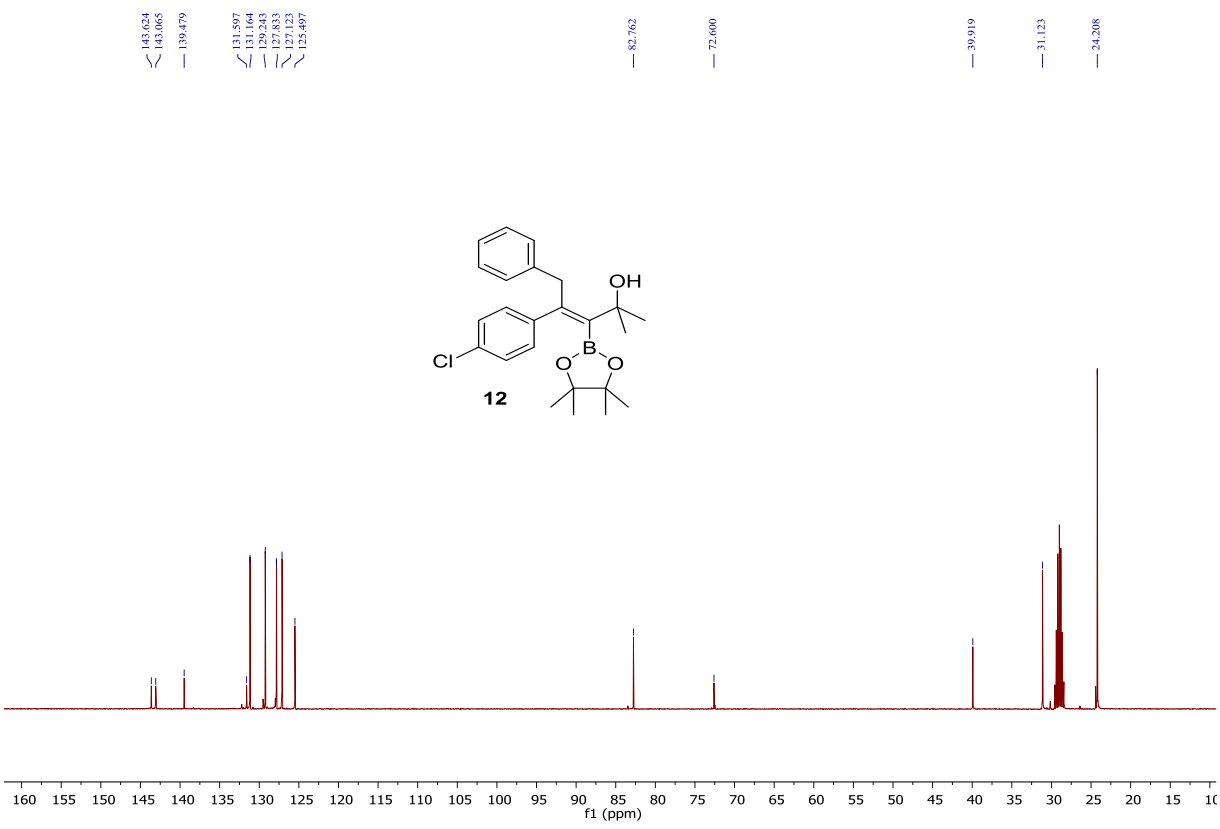
7.146
7.133
7.131
7.125
7.120
7.118
7.116
7.113
7.066
7.060
7.044
4.135
3.861
1.570
0.944
OH
Cl
B
O
O
12
9.00
2.00
0.76
6.00
12.08
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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139.479
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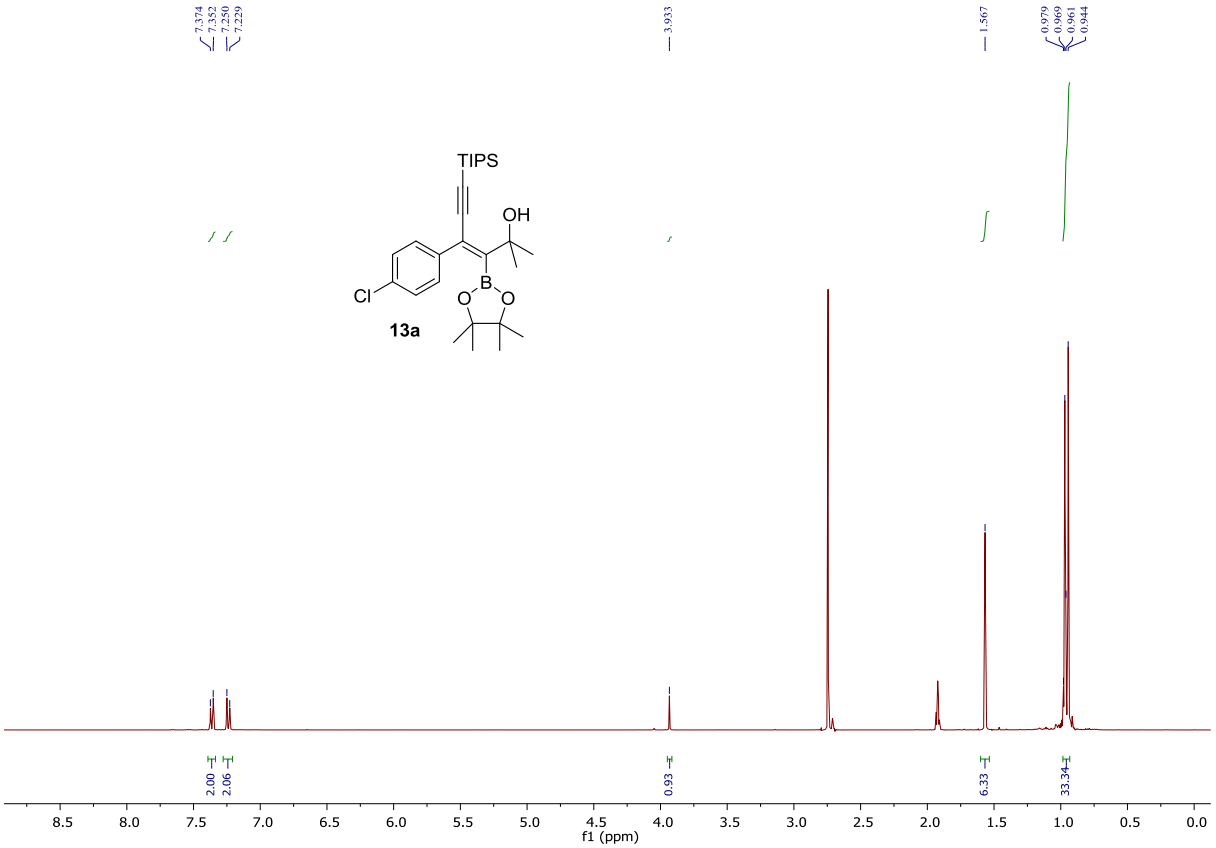
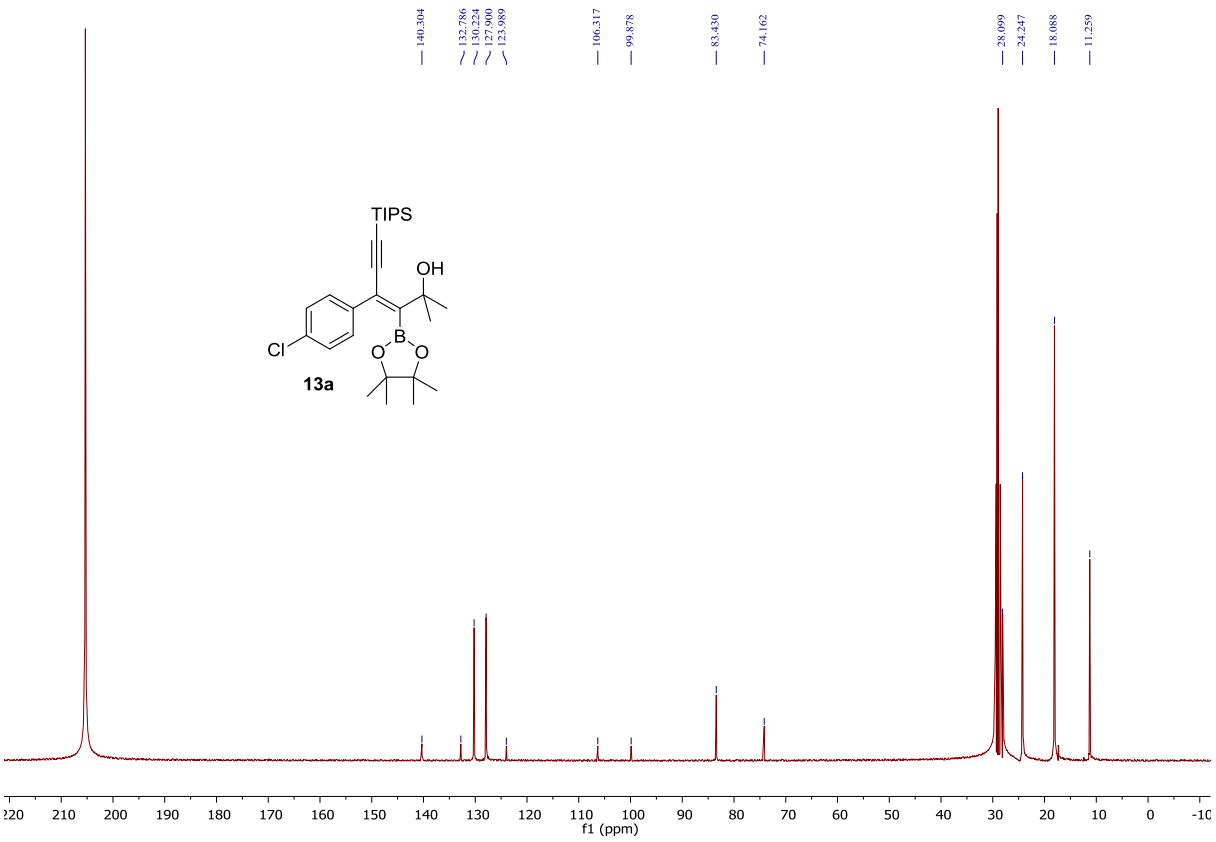
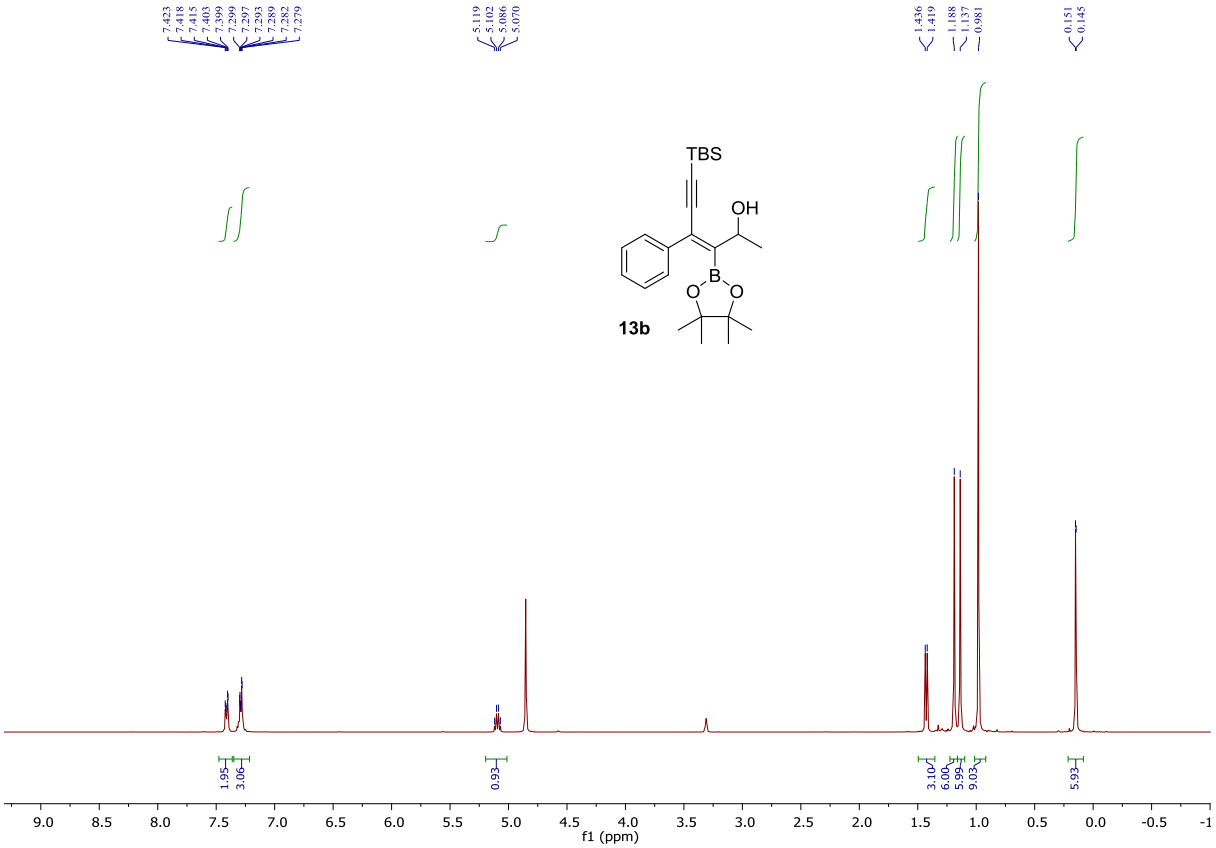
131.164
129.243
127.833
127.123
125.497
82.762
72.600
39.919
31.123
24.208
OH
Cl
B
O
O
12
160
155
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
f1 (ppm)


7.374
7.352
7.250
7.229
3.933
1.567
0.979
0.969
0.961
0.944
TIPS
OH
Cl
B
O
O
13a
2.00
2.06
0.93
6.33
33.34
f1 (ppm)


140.304
132.786
130.224
127.900
123.989
106.317
99.878
83.430
74.162
28.099
24.247
18.088
11.259
TIPS
OH
Cl
B
O
O
13a
f1 (ppm)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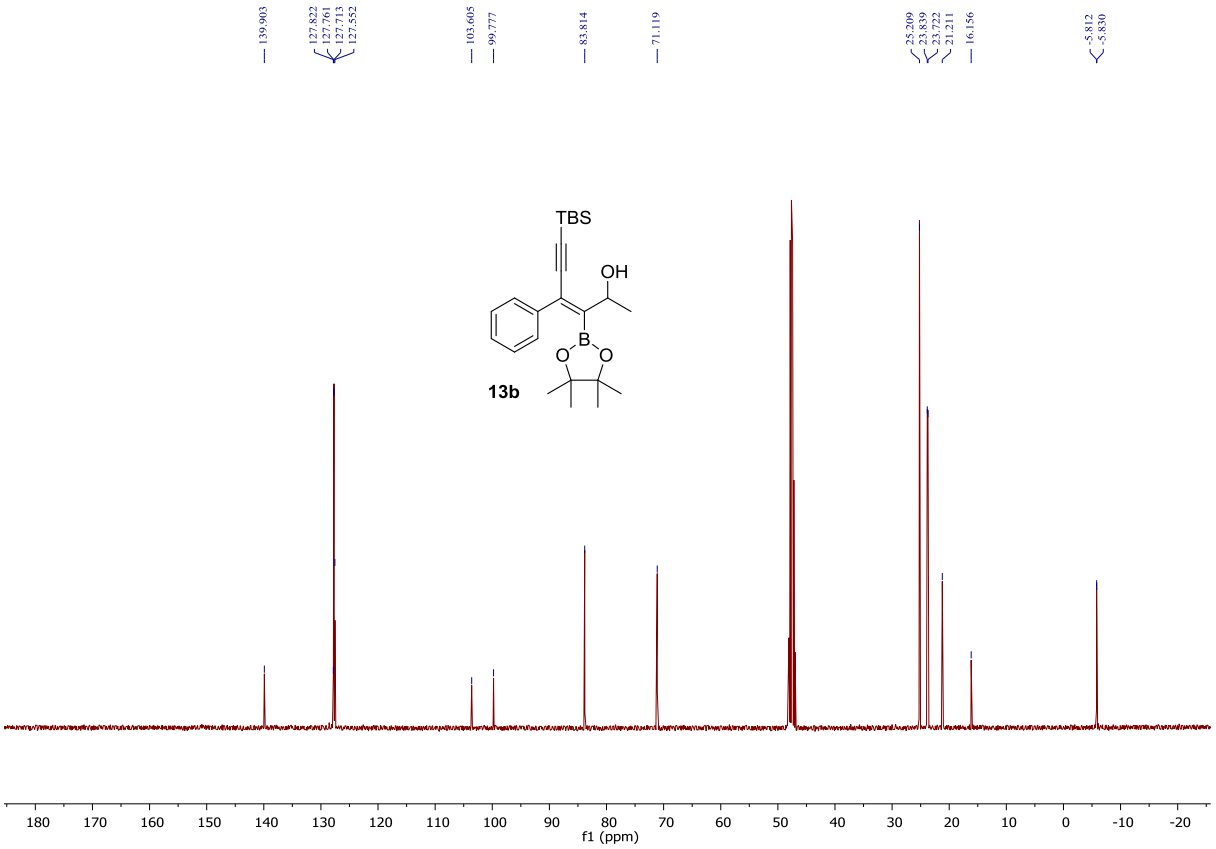
7.418
7.415
7.401
7.399
7.299
7.297
7.293
7.289
7.282
7.279
5.119
5.102
5.086
5.070
1.436
1.419
1.188
1.137
0.981
0.151
0.145
TBS
OH
B
O
O
13b
1.95
3.06
0.93
3.10
6.00
5.99
9.03
5.93
f1 (ppm)


139.903
127.822
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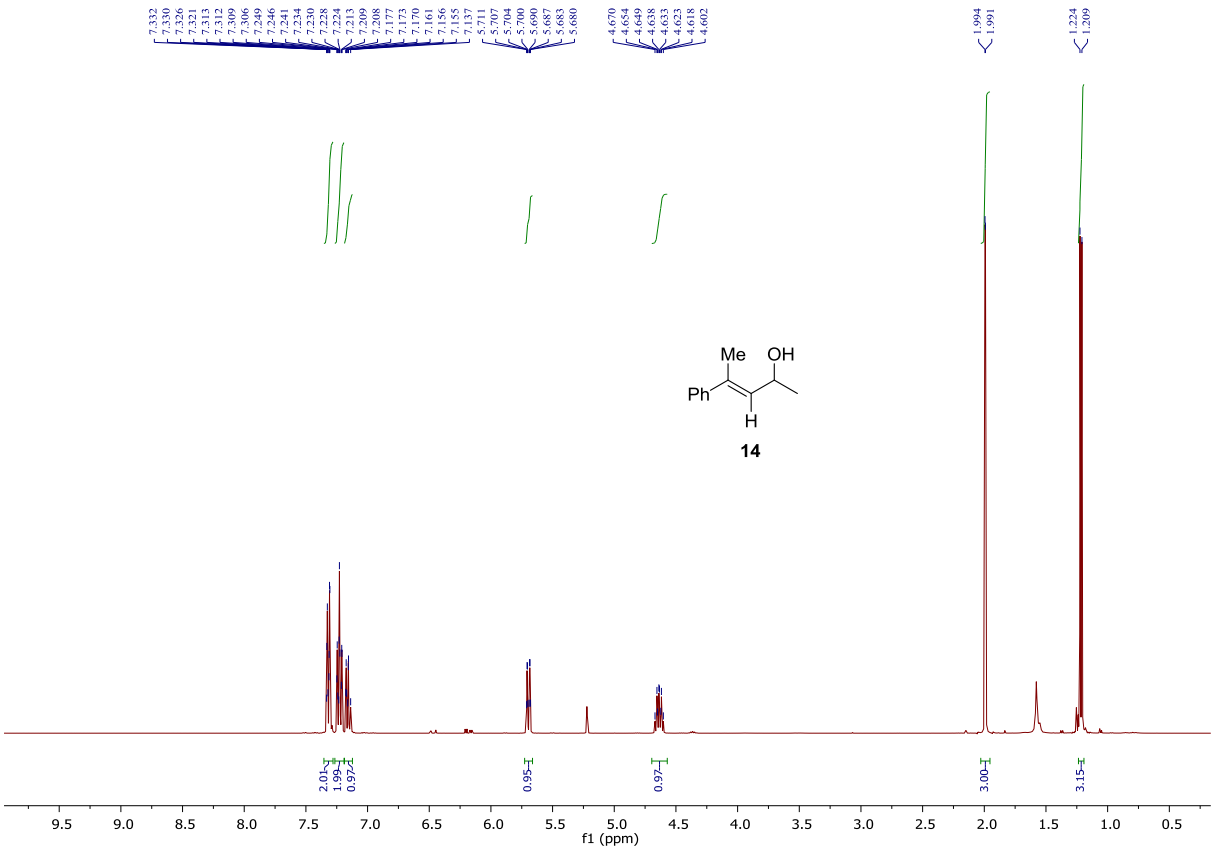
103.605
99.777
83.814
71.119
25.209
23.839
23.722
21.211
16.156
-5.812
-5.830
TBS
OH
B
O
O
13b
f1 (ppm)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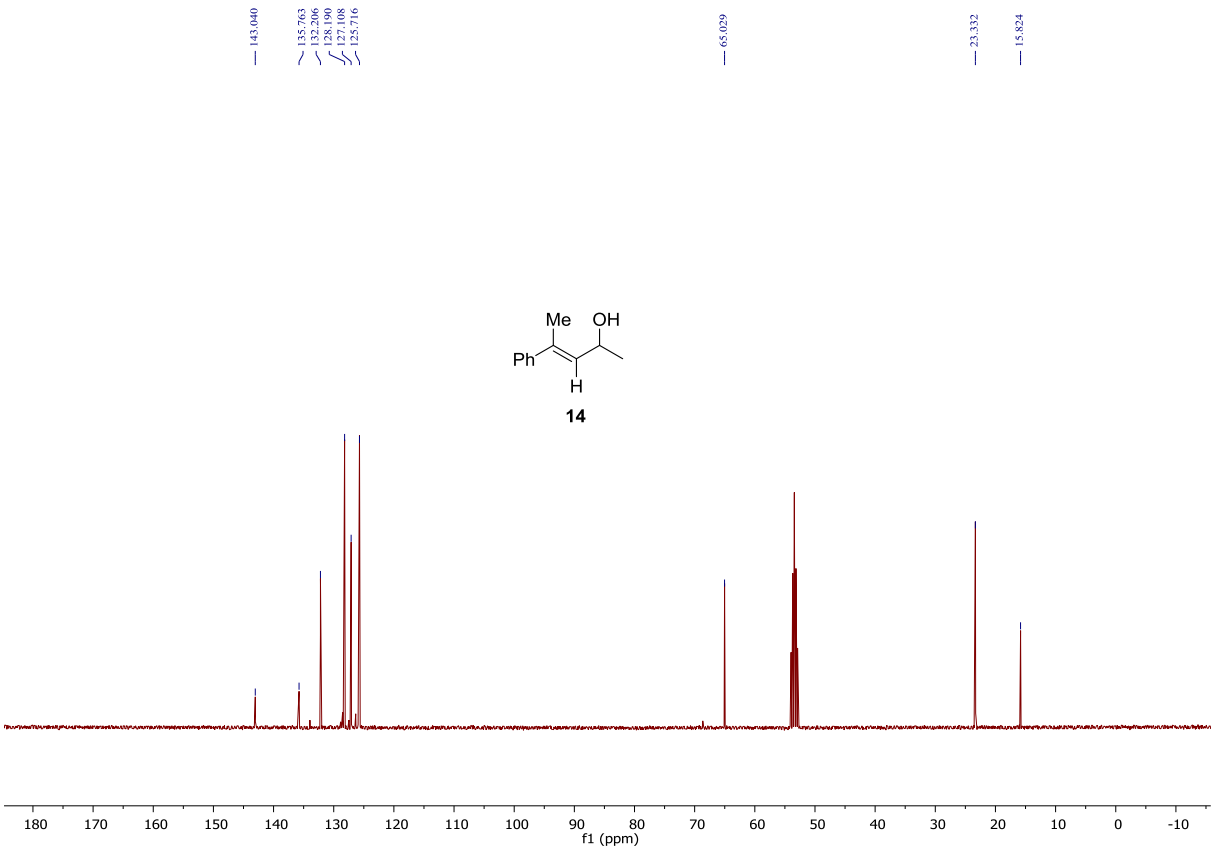
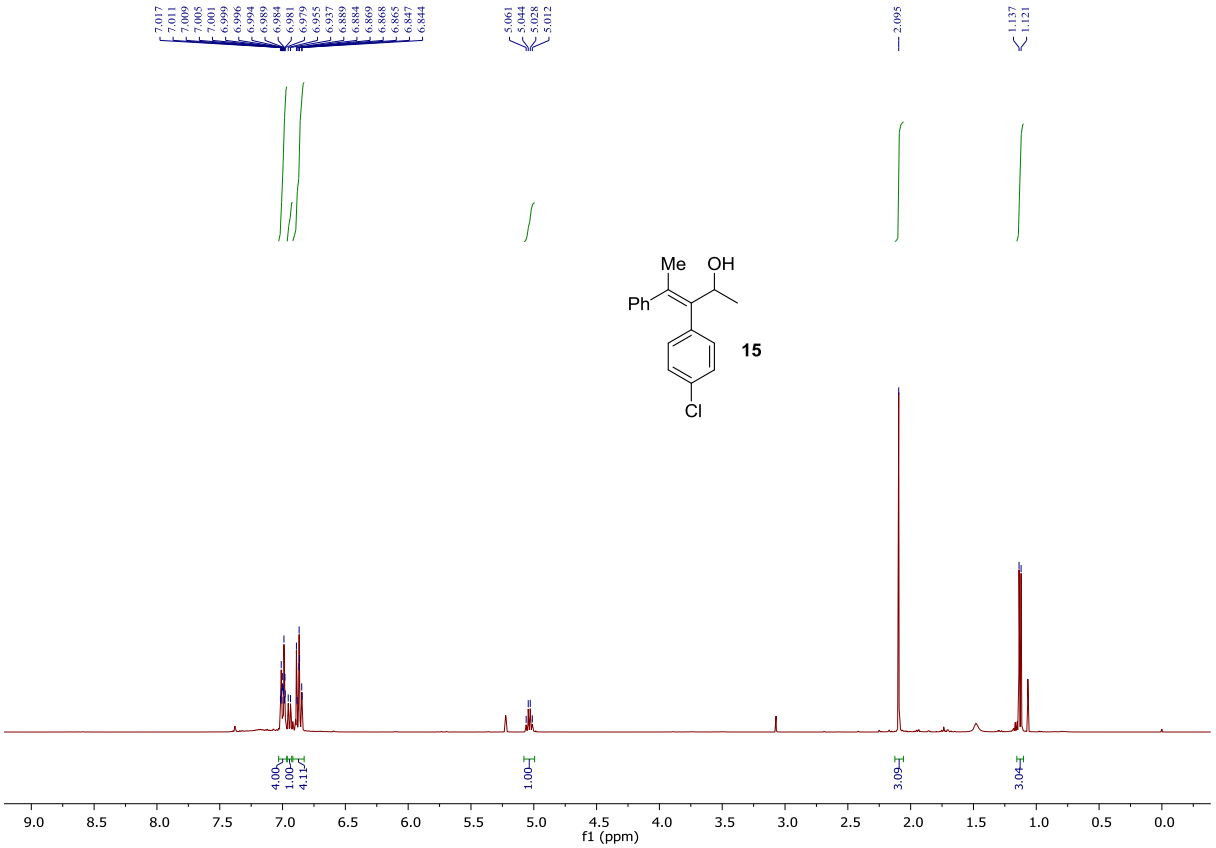
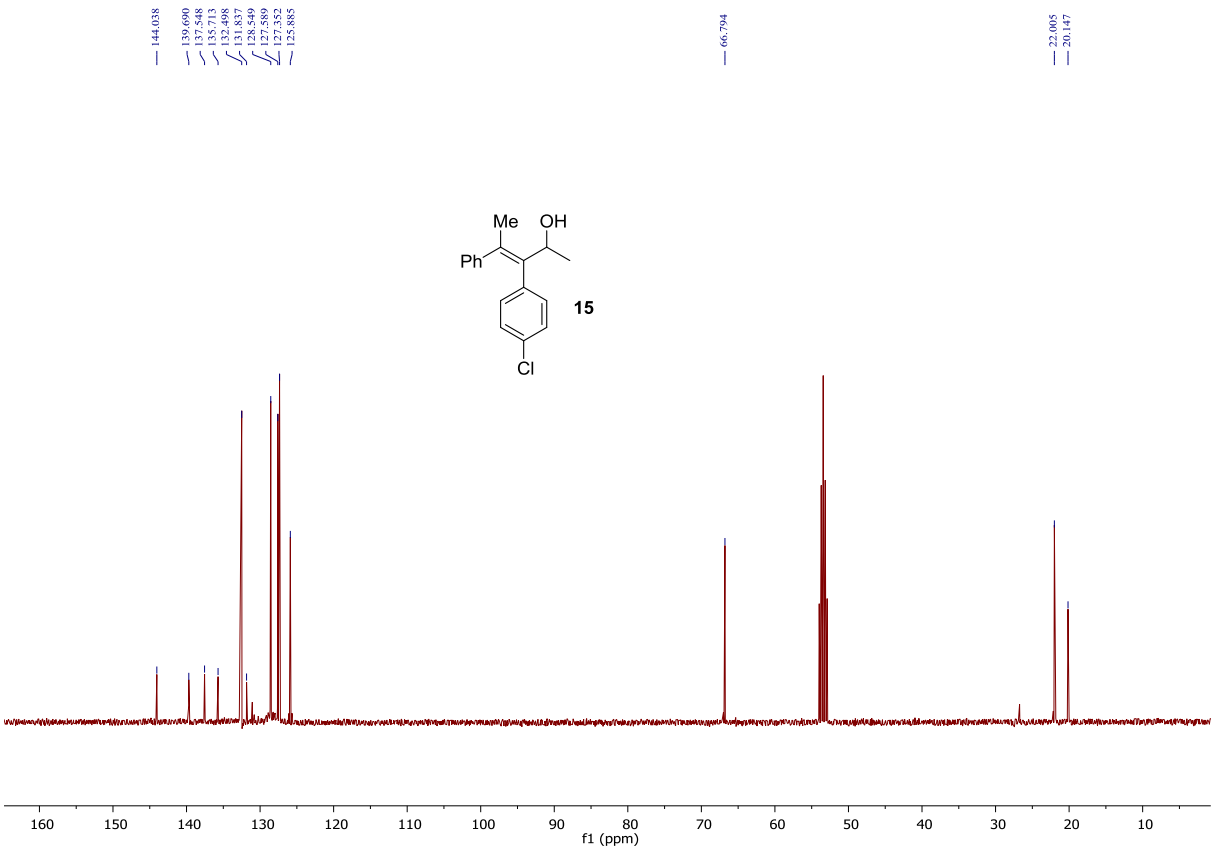
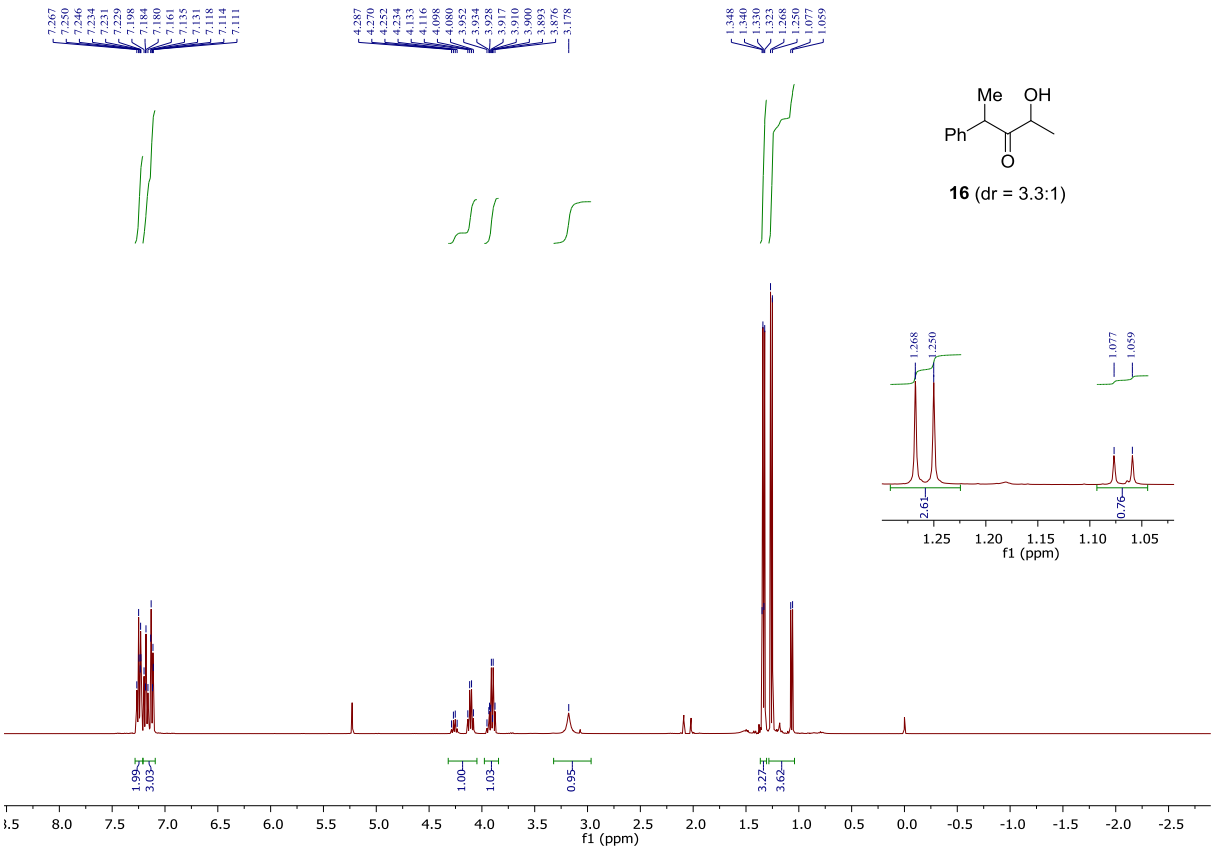
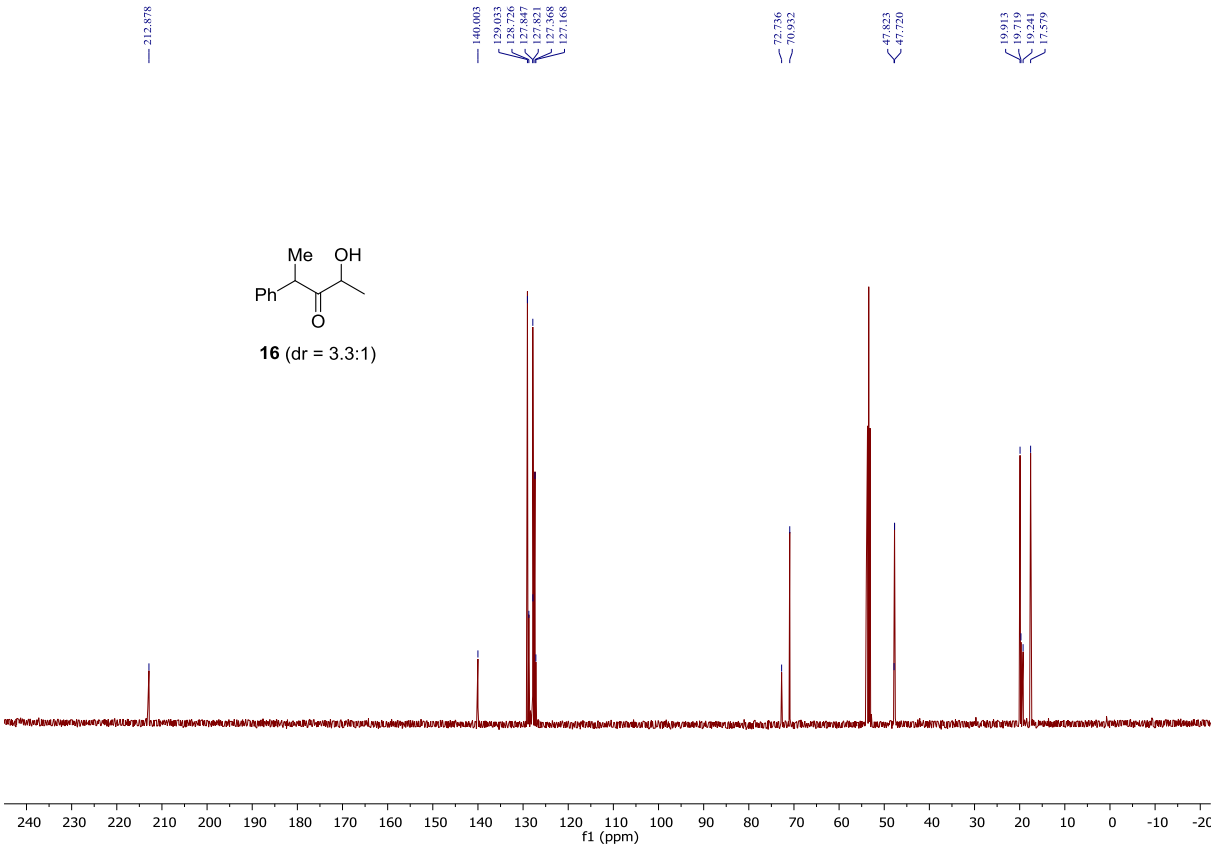
7.330
7.326
7.321
7.311
7.312
7.309
7.306
7.249
7.246
7.241
7.234
7.230
7.228
7.224
7.213
7.209
7.208
7.177
7.173
7.170
7.161
7.156
7.155
7.137
5.711
5.707
5.704
5.700
5.690
5.687
5.683
5.680
4.670
4.654
4.649
4.638
4.633
4.623
4.618
4.602
1.994
1.991
1.224
1.209
Me
OH
Ph
H
14
2.01
1.99
0.97
0.95
0.97
3.00
3.15
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

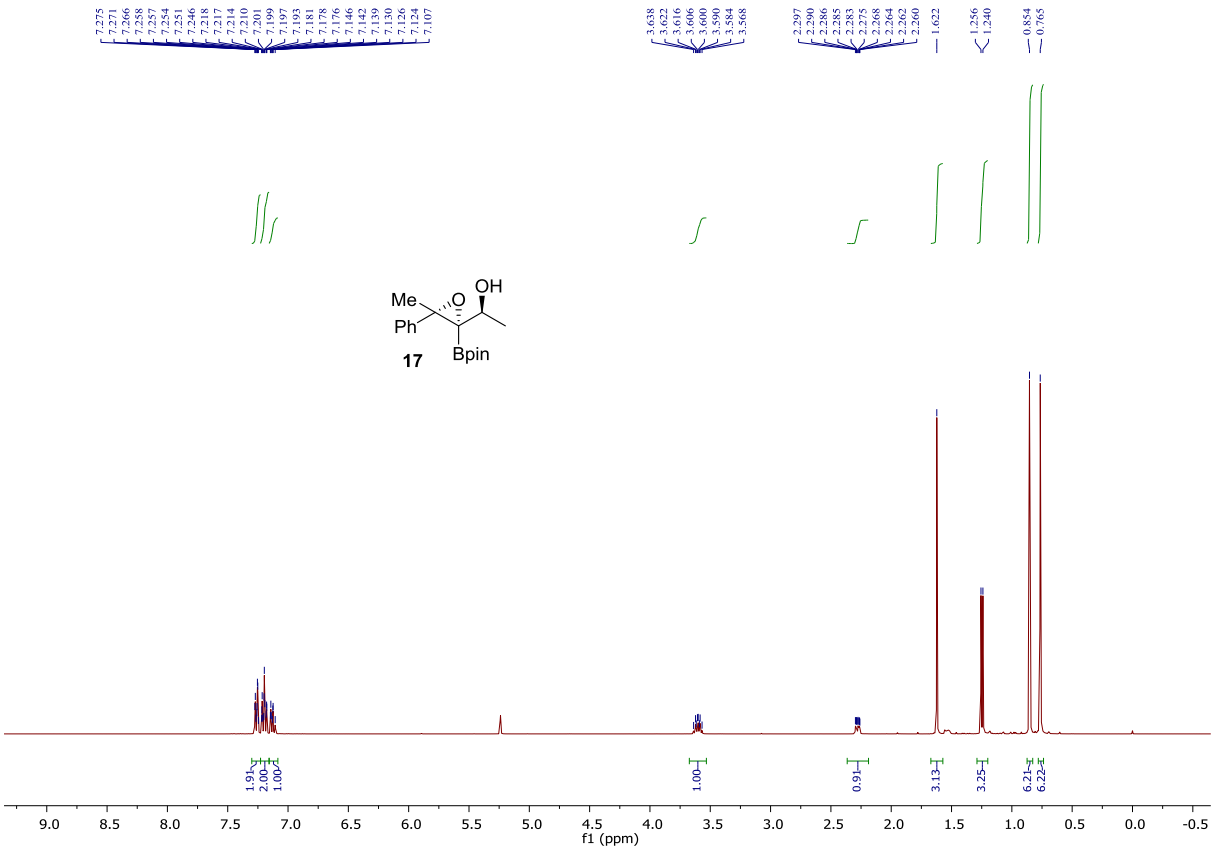

143.040
135.763
132.206
128.190
127.108
125.716
65.029
23.332
15.824
Me
OH
Ph
H
14
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.017
7.011
7.009
7.005
7.001
6.999
6.996
6.994
6.989
6.984
6.981
6.979
6.955
6.937
6.889
6.884
6.869
6.868
6.865
6.847
6.844
5.061
5.044
5.028
5.012
2.095
1.137
1.121
Me
OH
Ph
15
Cl
4.00
1.00
4.11
1.00
3.09
3.04
f1 (ppm)


144.038
139.690
137.548
135.713
132.498
131.837
128.549
127.589
127.352
125.885
66.794
22.005
20.147
Me
OH
Ph
15
Cl
f1 (ppm)


Me
OH
Ph
O
16 (dr = 3.3:1)
f1 (ppm)


Me
OH
Ph
O
16 (dr = 3.3:1)
f1 (ppm)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7.258
7.257
7.254
7.251
7.246
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7.217
7.214
7.210
7.201
7.199
7.197
7.193
7.181
7.178
7.176
7.146
7.142
7.139
7.130
7.126
7.124
7.107
3.638
3.622
3.616
3.606
3.600
3.590
3.584
3.568
2.297
2.290
2.286
2.283
2.275
2.268
2.264
2.262
2.260
1.622
1.256
1.240
0.854
0.765
Me
O
OH
Ph
Bpin
17
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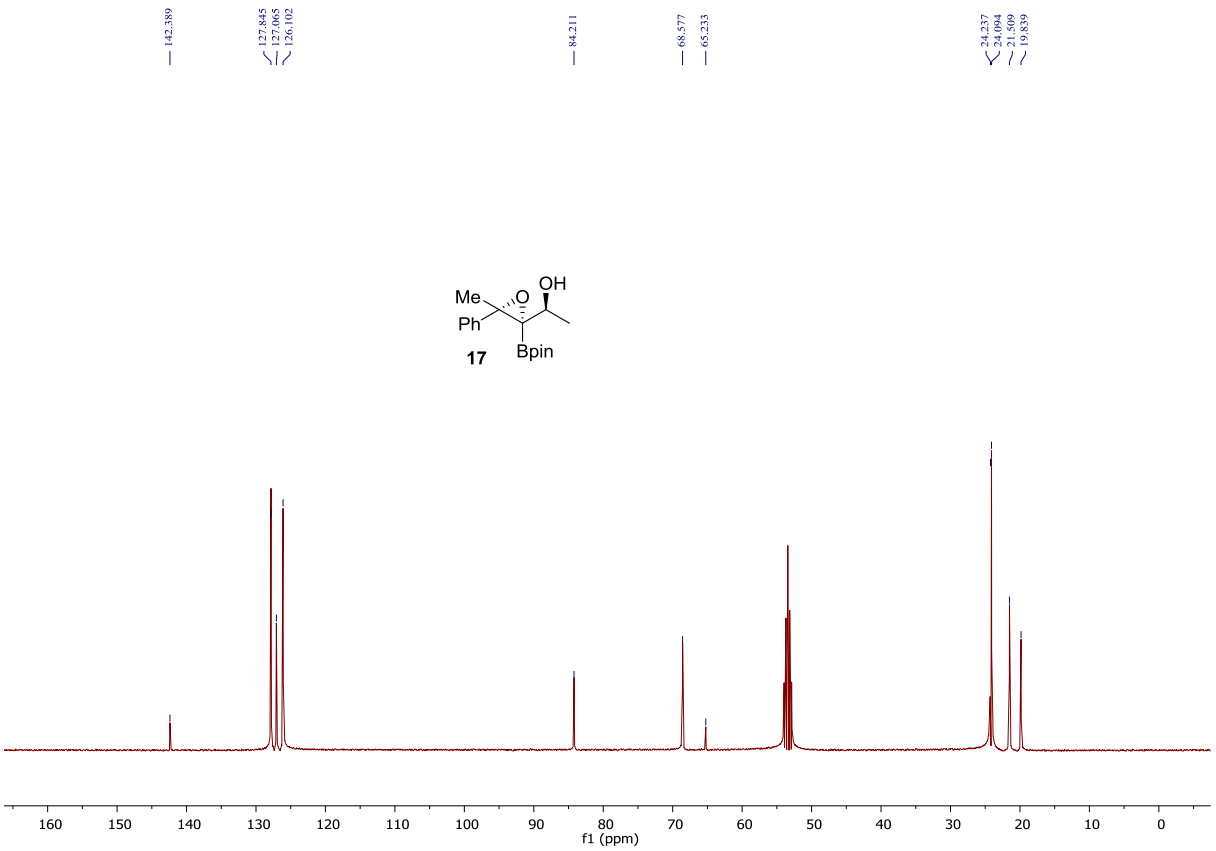
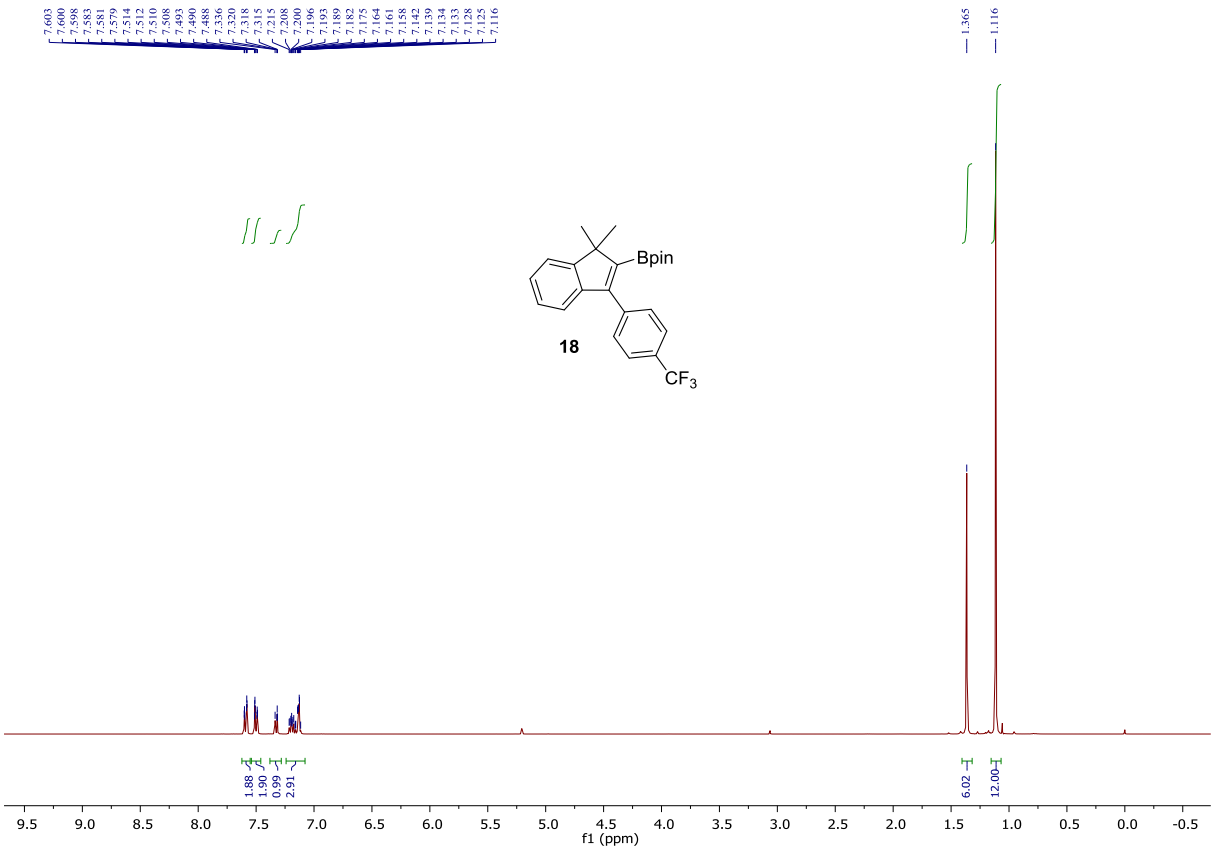
2.00
1.00
1.00
0.91
3.13
3.25
6.21
6.22
f1 (ppm)


142.389
127.845
127.065
126.102
84.211
68.577
65.233
24.237
24.094
21.509
19.839
Me
O
OH
Ph
Bpin
17
f1 (ppm)


7.603
7.600
7.598
7.583
7.581
7.579
7.514
7.512
7.510
7.508
7.493
7.490
7.488
7.336
7.320
7.318
7.315
7.215
7.208
7.200
7.196
7.193
7.189
7.182
7.175
7.164
7.161
7.158
7.142
7.139
7.134
7.133
7.128
7.125
7.116
1.365
1.116
Bpin
18
CF3
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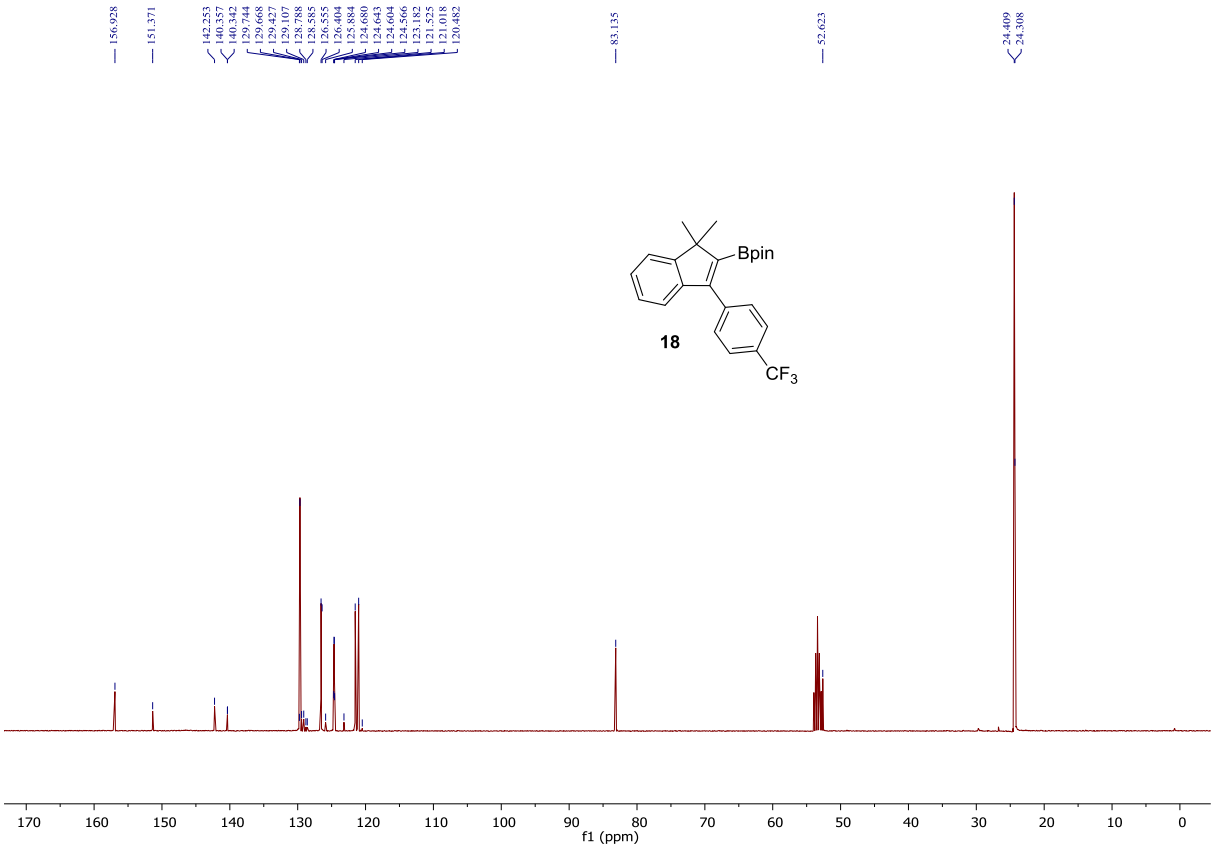
1.90
0.99
2.91
6.02
12.00
f1 (ppm)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129.427
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128.788
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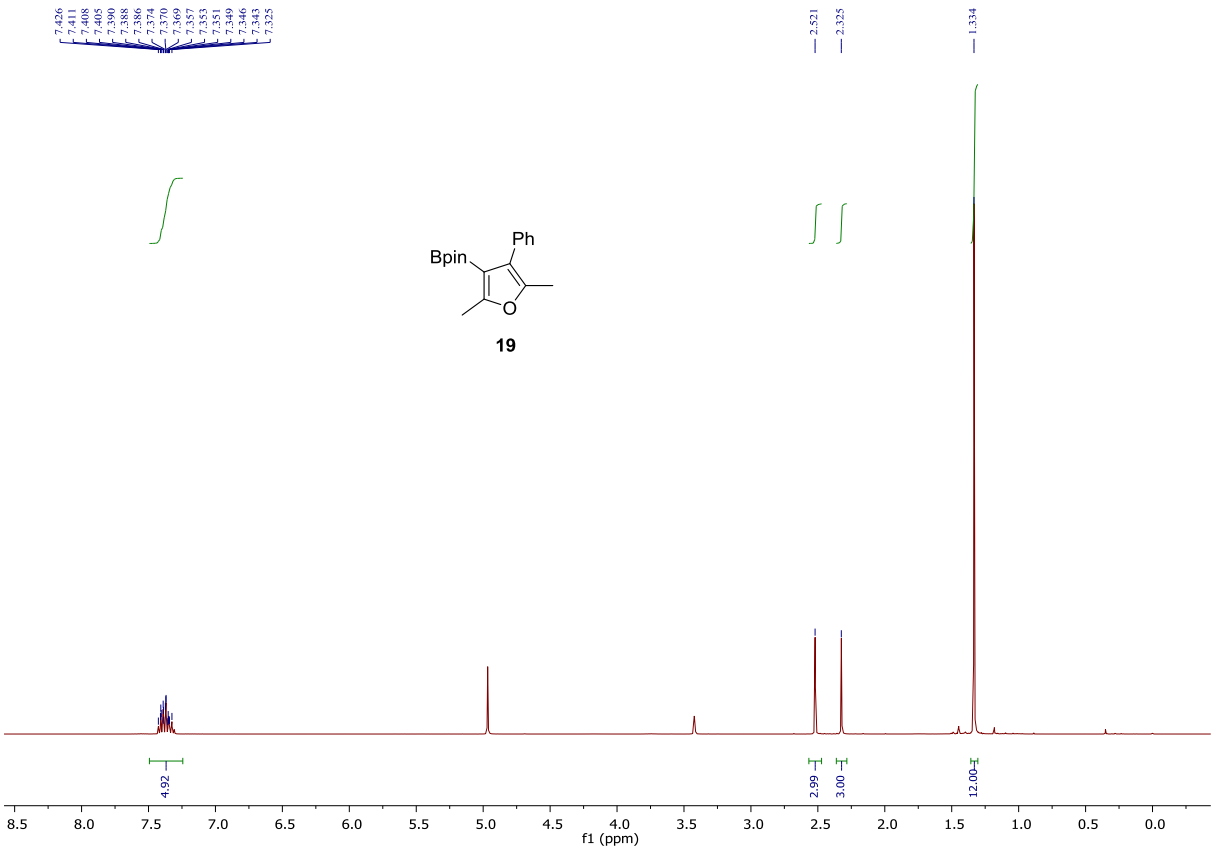
126.404
125.884
124.680
124.643
124.604
124.566
123.192
121.525
121.018
120.482
83.135
52.623
24.409
24.308
Bpin
18
CF3
f1 (ppm)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7.374
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7.369
7.357
7.353
7.351
7.349
7.346
7.343
7.325
2.521
2.325
1.334
Ph
Bpin
O
4.92
2.99
3.00
12.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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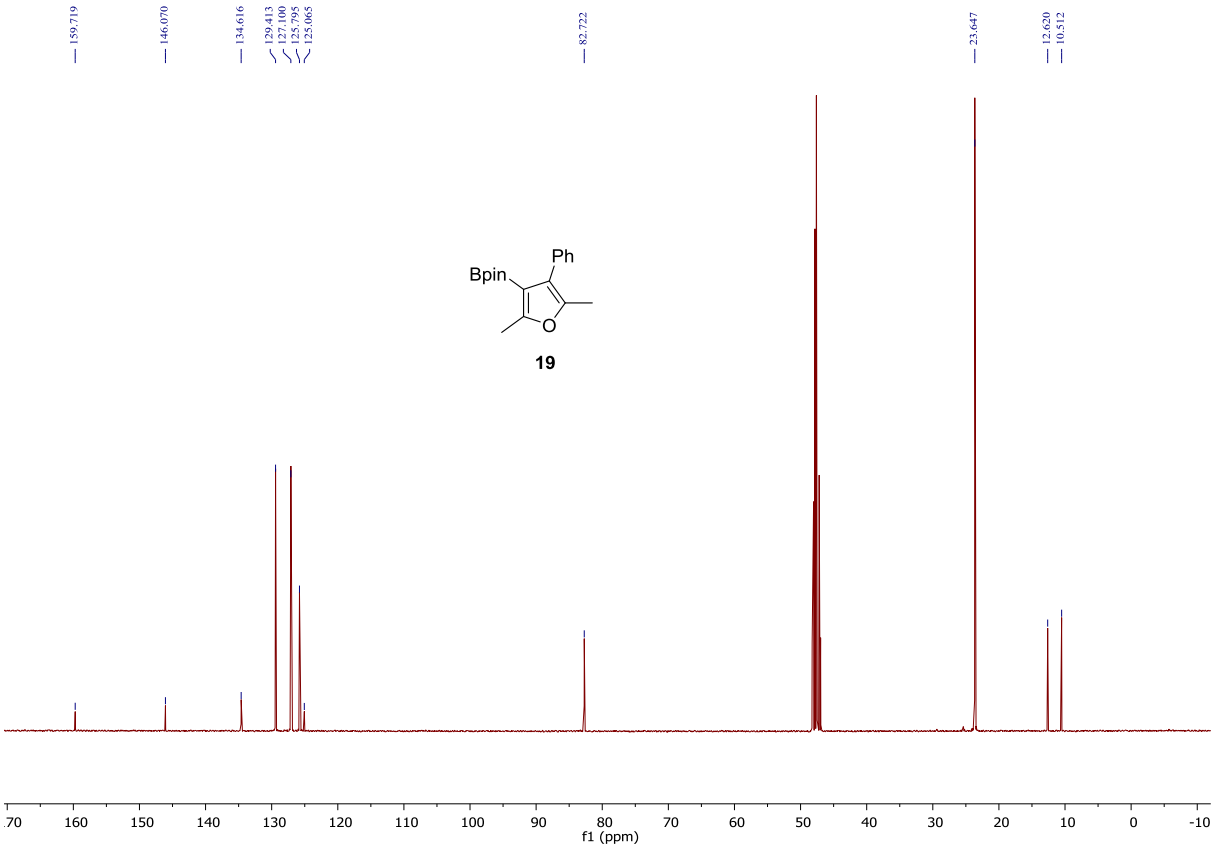
0.0
f1 (ppm)

19


159.719
146.070
134.616
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82.722
23.647
12.620
10.512
Ph
Bpin
O
70
160
150
140
130
120
110
100
90
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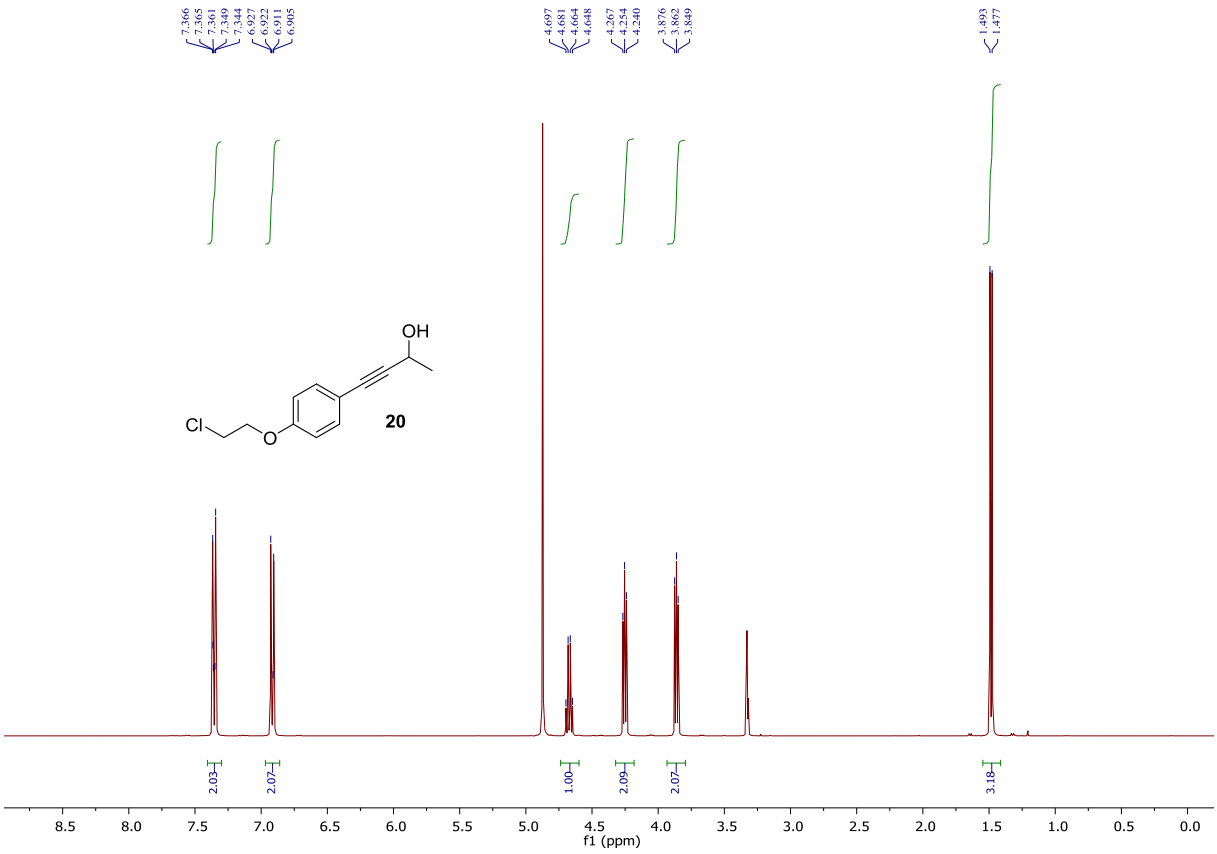
70
60
50
40
30
20
10
0
-10
f1 (ppm)

19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7.361
7.349
7.344
6.927
6.922
6.911
6.905
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4.681
4.664
4.648
4.267
4.254
4.240
3.876
3.862
3.849
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OH
Cl
O
20
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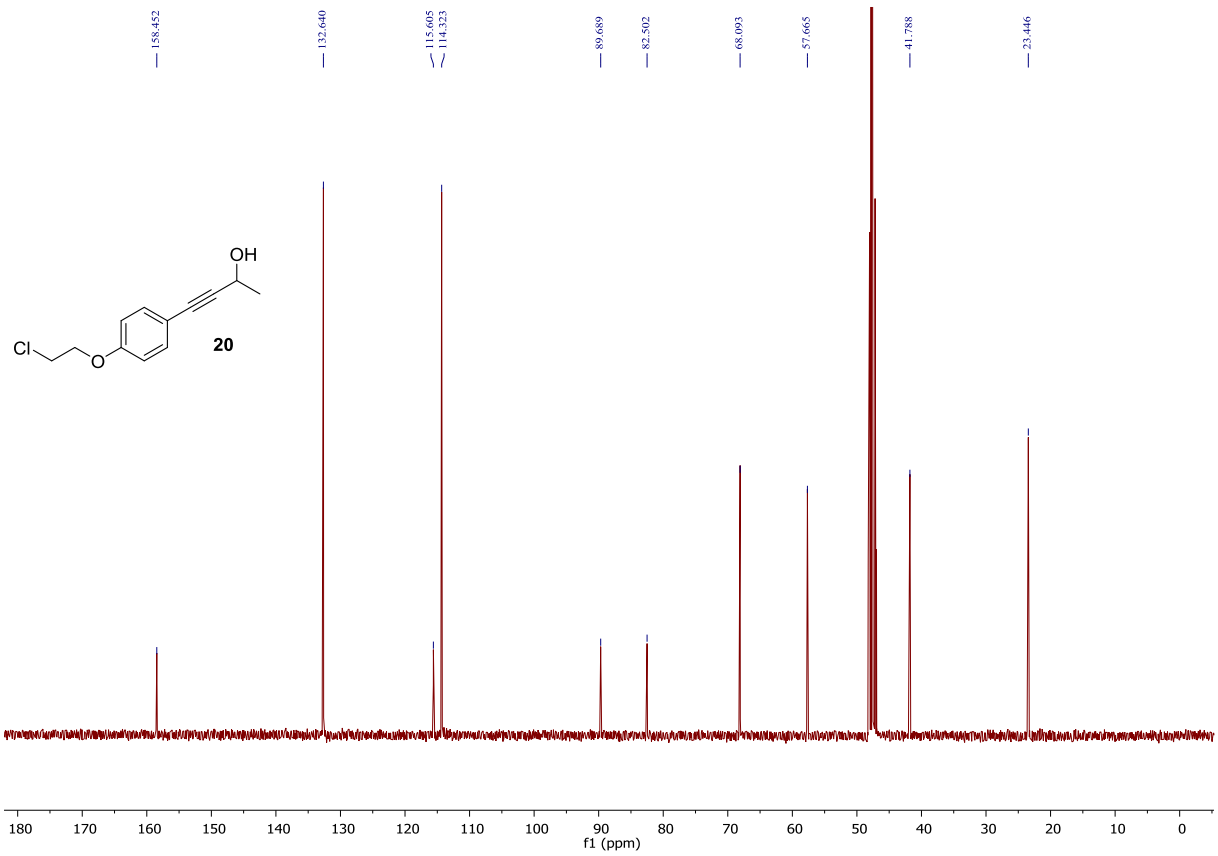
2.07
1.00
2.09
2.07
3.18
f1 (ppm)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82.502
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57.665
41.788
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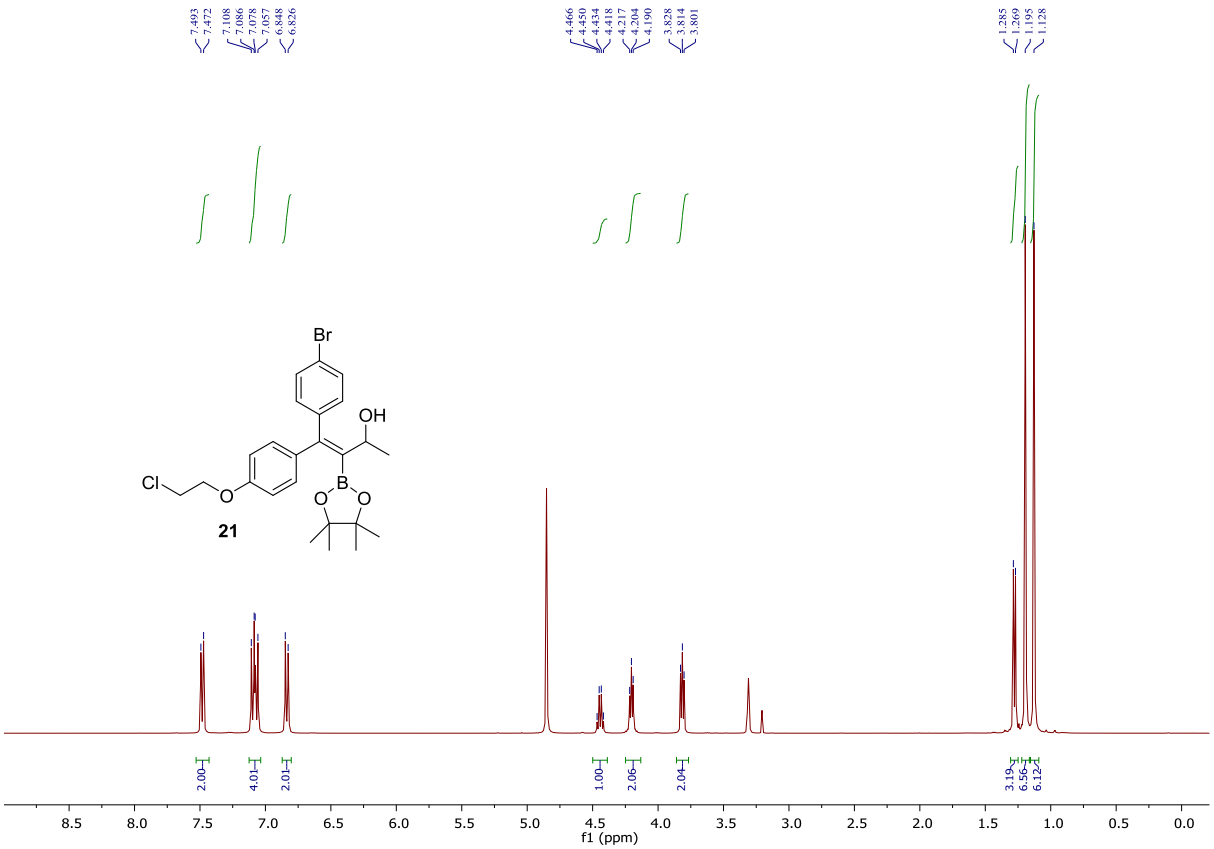
Cl
O
20
f1 (ppm)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6.826
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4.418
4.217
4.204
4.190
3.828
3.814
3.801
1.285
1.269
1.195
1.128
Br
OH
Cl
O
B
O
O
21
2.00
4.01
2.01
1.00
2.06
2.04
3.19
6.56
6.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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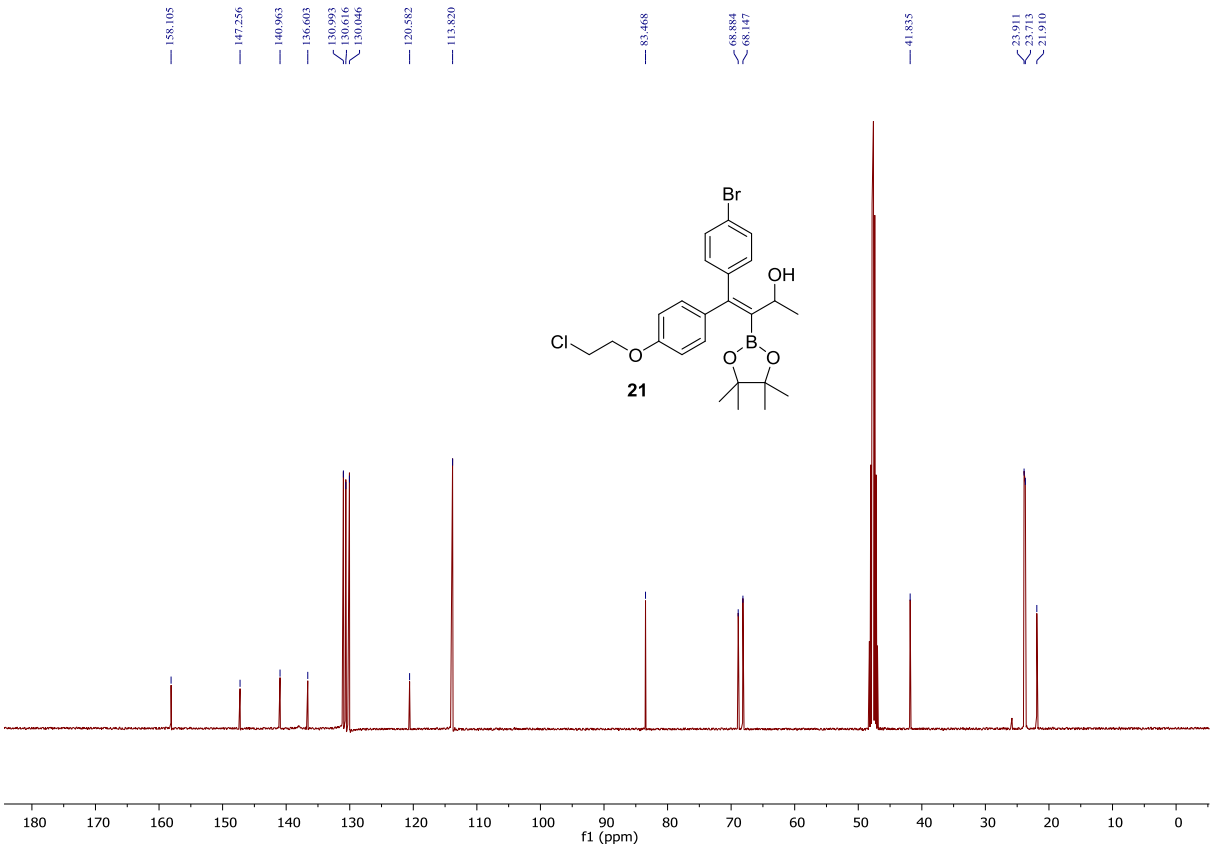
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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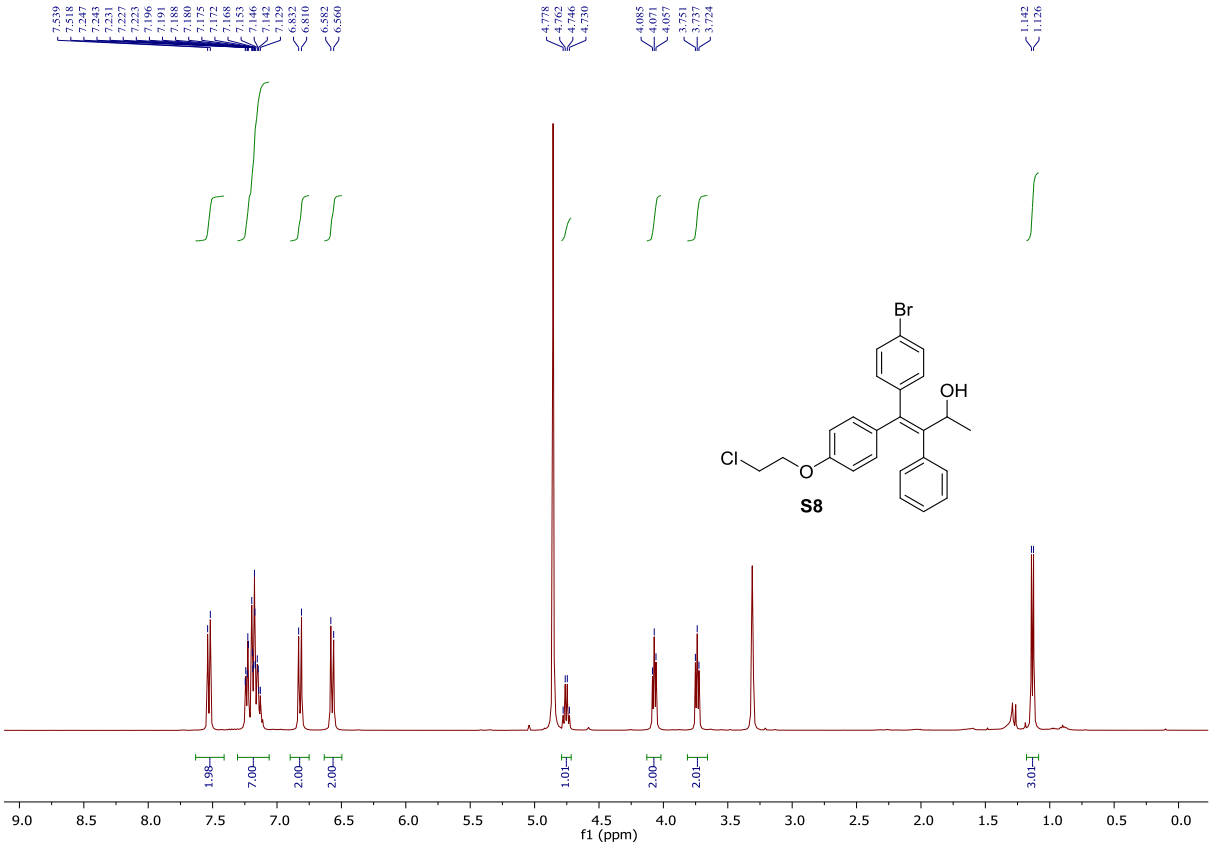
68.147
41.835
23.911
23.713
21.910
Br
OH
Cl
O
B
O
O
21
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.196
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7.188
7.180
7.175
7.172
7.168
7.153
7.146
7.142
7.129
6.832
6.810
6.582
6.560
4.778
4.762
4.746
4.730
4.085
4.071
4.057
3.751
3.737
3.724
1.142
1.126
Br
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Cl
O
S8
1.98
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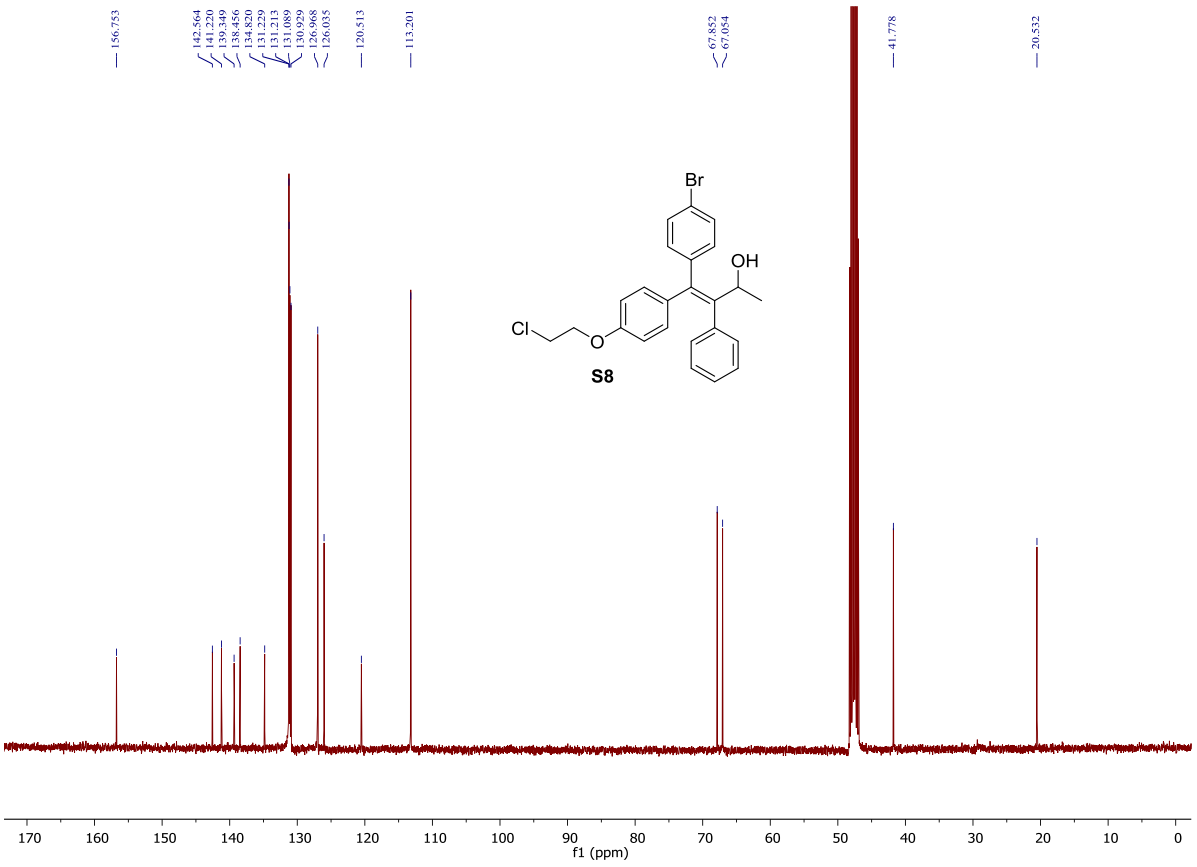
1.01
2.00
2.01
3.01
f1 (ppm)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126.968
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113.201
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67.654
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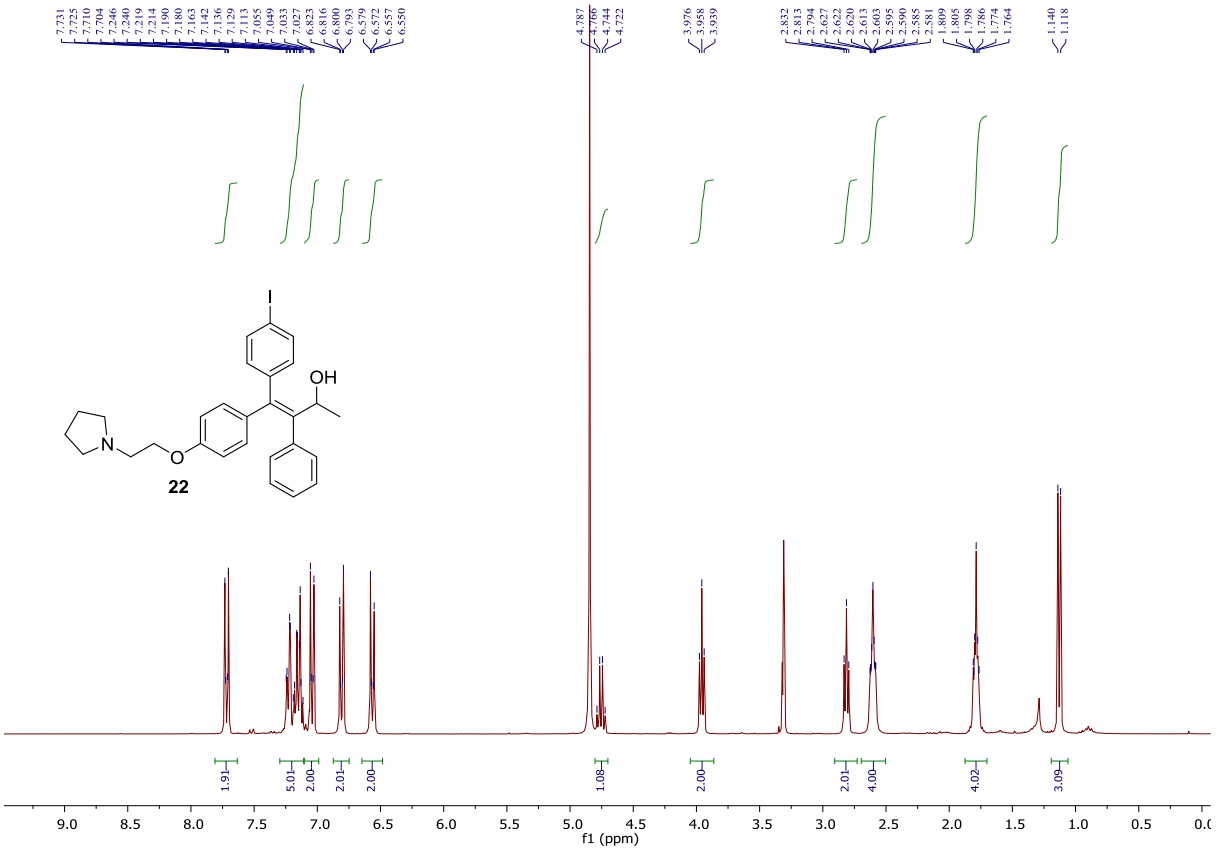
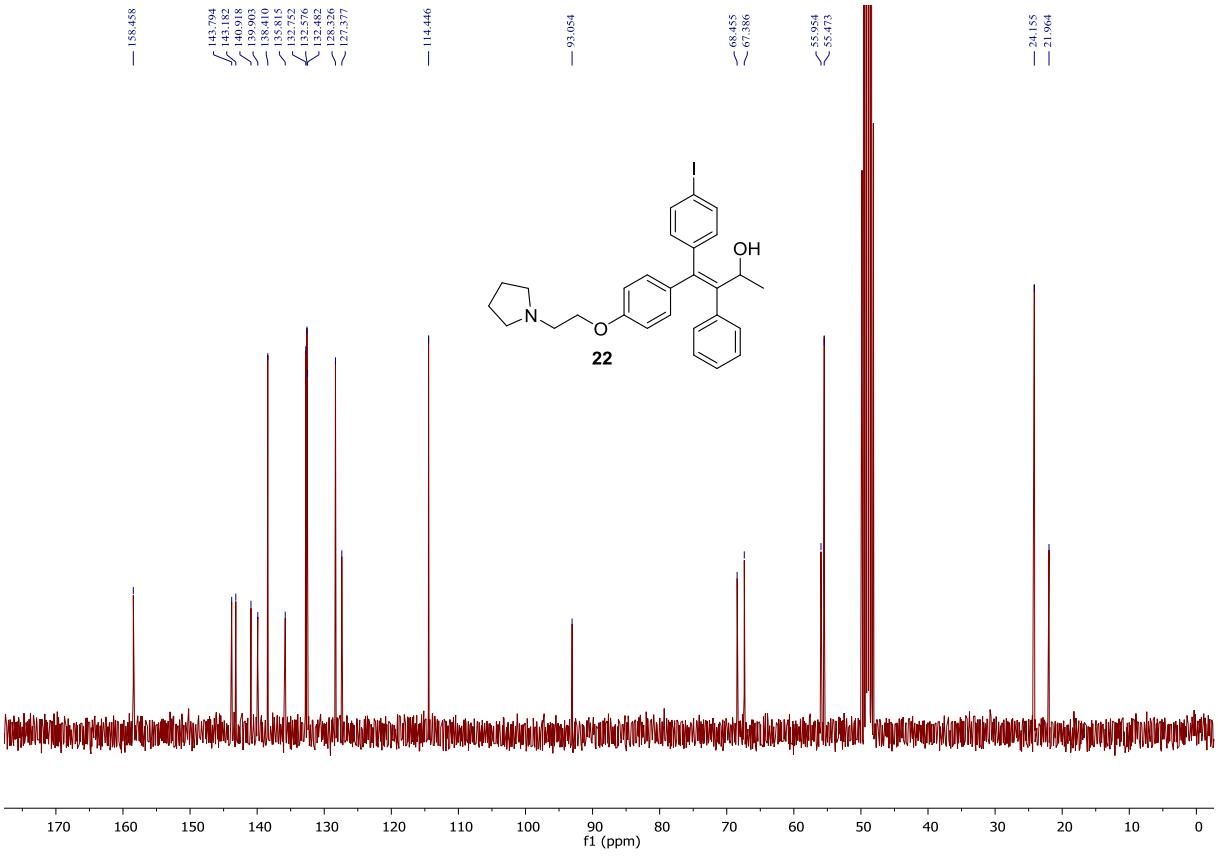
Br
OH
Cl
O
S8
f1 (ppm)


I
OH
N
O
22
f1 (ppm)


I
OH
N
O
22
f1 (ppm)

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