Cu-Catalyzed Enantioselective Synthesis of Tertiary BenzylicCopper Complexes and Their in situ Addition to Carbonyl Compounds

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SUPPORTING INFORMATION

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■ **General.** Infrared (IR) spectra were recorded on a BRUKER TENSOR 27 FT-IR spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on an Agilent 400 MHz spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constant (Hz). ^{13}C NMR spectra were recorded on an Agilent 100 MHz spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.00 ppm). ^{11}B NMR spectra were recorded on Bruker 128 MHz spectrometers. Chemical shifts are reported in ppm from Boron fluoride ethyl ether as the external standard ($BF_3{\cdot}C_2H_5OC_2H_5$: δ 0.00 ppm). EI-HRMS and ESI-HRMS spectra were obtained on a Waters Micromass G1540N/GCT Premier and a Thermo Fisher Scientific LTQ FT Ultra or Agilent Technologies 6224 TOF LC/MS respectively. Enantiomeric ratios were determined by high-performance liquid chromatography (HPLC) with a Shimadzu LC-20AT chromatograph (Chiralcel IG (4.6 x 250 mm), Chiralcel AD-H (4.6 x 250 mm), Chiralcel OZ-H (4.6 x 250 mm), Chiralcel IC (4.6 x 250 mm)) in comparison with authentic racemic materials. Specific rotations were measured on a Rudolph Research Analytical Autopol VI Polarimeter and Autopol I Polarimeter. Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Anhydrous tetrahydrofuran (Energy Chemical Co., Ltd.) were used without further purification. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher Scientific) in air.

■ **Reagents and Ligands:**

Copper chloride: purchased from Strem Chemicals Inc. and used as received.

Copper iodide: purchased from Strem Chemicals Inc. and used as received.

Chial phosphine ligands (6): purchased from Strem Chemicals Inc. and used as received.

Tricyclohexylphosphine: purchased from Energy Chemical Co., Ltd. and used as received.

Bis(pinacolato)diboron: purchased from Dalian AllyChem Co., Ltd. and recrystallized from pentane.

1,1-disubstituted alkenes (1): prepared according to a previous reported procedure.[1]

Ketone (2): purchased from Tokyo Chemical Industry Co., Ltd. or Energy Chemical Co., Ltd. and used as received.

Phenol Ester (7, 8): prepared according to a previous reported procedure.[2, 3]

4Å molecular sieve: purchased from Energy Chemical Co., Ltd. and dried in Muffle at 400 °C for 12 hours.

Lithium *tert*-butoxide, potassium carbonate and sodium chloride: purchased from J&K Chemical Ltd. and used as received.

NHC copper chloride 6j: prepared according to a previous reported procedure.[4]

Sodium perborate tetrahydrate: purchased from Energy Chemical Co., Ltd. and used as received.

Potassium hydrogen fluoride: purchased from Tokyo Chemical Industry Co., Ltd. and used as received.

Palladium diacetate: purchased from Adamas Reagent, Ltd. and used as received.

RuPhos: purchased from Sinocompound Co., Ltd. and used as received.

4-Bromoanisole: purchased from Energy Chemical Co., Ltd. and used as received.

TetraMethylammonium triacetoxyborohydride: purchased from Energy Chemical Co., Ltd. and used as received.

■ **Representative Experimental Procedure for Phosphine–Cu-Catalyzed Reactions of $B_2(pin)_2$, 1,1-Disubstituted Alkene and Ketone:** In a N_2-filled glove-box, an oven-dried vial (4 mL, 17 × 38 mm) with a magnetic stir bar was charged with (*R*,*R*)-Ph-BPE (10.1 mg, 0.02 mmol, 10 mol %), CuCl (2.0 mg, 0.02 mmol, 10 mol%), LiO*t*-Bu (24.0 mg, 0.3 mmol, 1.5 equiv), 4Å molecular sieve (200 mg) and tetrahydrofuran (thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution

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(1) Maity, S; Naveen, T; Sharma, U. *Org. Lett.,* **2013**, 15, 3384.

(2) Gu, J. X.; Holland, H. L. *Synth. Commun.***1998**, *28*, 3305.

(3) Kankanala K, Reddy V R, Mukkanti K. *J. Fluorine Chem.*, **2009**, 130, 505.

(4) Park, J, Lackey, H, Rexford M. *Org. lett.*, **2010**, 12, 5008.

was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (76.2 mg, 0.30 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 30 min under an atmosphere of N_2. Alkene **1a** (63.3 mg, 0.40 mmol, 2.0 equiv) and acetophenone (24.0 mg, 0.20 mmol, 1.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 2 mL). The filtrate was concentrated in vacuo to provide yellow oil. The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate = 15:1) to afford **3a** as white solid (56.3 mg, 0.18 mmol, 92% yield).

■ Representative Experimental Procedure for Oxidative of 3a.

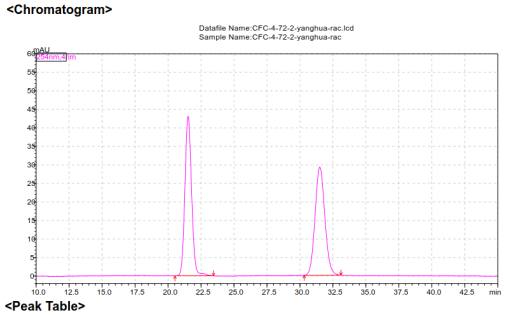
3a (48.0 mg, 0.15 mmol, 1 equiv) was dissolved in tetrahydrofuran (thf, 1.0 mL). $NaBO_3$•$4H_2O$ (92.3 mg, 0.60 mmol, 4.0 equiv) and H_2O (1 mL) were added. The resulting mixture was allowed to stir at 22 °C for three hours. The aqueous layer was washed with Et_2O (3 × 2 mL). The combined organic layers were concentrated *in vacuo* to provide colorless oil, which was purified by silica gel chromatography (petroleum ether : ethyl acetate = 5:1) to afford **7** as white solid (42.1 mg, 0.14 mmol, 95% yield).

■ Characterization of product of 3a-3s and 7a-7r.

(*4S,5S*)-4-(Benzofuran-2-yl)-4,5-dimethyl-5-phenyl-1,2-oxaborolan-2-ol (3a). Yield: (56.3 mg, 92%); **IR (neat):** 3323 (m), 2968 (w), 1598 (w), 1437 (s), 1311 (m), 1287 (s), 1252 (s), 1172 (m), 1120 (s), 1062 (s), 1004 (m), 946 (m), 933 (s), 850 (m), 762 (s), 702 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 - 7.29 (m , 2H), 7.20 - 7.05 (m, 4H), 7.04 - 6.95 (m, 3H), 6.08 (s, 1H), 5.91 (s, 1H), 1.86 (s, 3H), 1.69 - 1.58 (m, 4H), 1.28 (d, J = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.1, 154.2, 143.7, 128.1, 127.3, 126.6, 124.4, 123.3, 122.2, 120.3, 110.6, 102.5, 89.5, 50.4, 24.9, 22.9; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{19}H_{20}O_3B$: 306.1536, found: 306.1533; Specific rotation: $[\alpha]_D^{20}$ –34.0 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-2-methyl-3-phenylbutane-1,3-diol (3a-oxi). Yield: (41.2 mg, 95%); **IR (neat):** 3172 (br), 2974 (w), 2920 (w), 1476 (w), 1431 (s), 1375 (m), 1243 (m), 1137 (m), 1109 (m), 1032 (s), 997 (m), 919 (s), 824 (s), 758 (s), 697 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, J = 7.4 Hz, 1H), 7.41 (d, J = 7.8 Hz, 1H), 7.29 - 7.06 (m, 7H), 6.27 (s, 1H), 3.98 - 3.84 (m, 2H), 3.71 (s, 1H), 1.72 (s, 3H), 1.53 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.9, 154.0, 144.5, 128.0, 127.2, 126.9, 126.4, 123.8, 122.7, 120.7, 111.0, 104.9, 79.6, 67.6, 48.8, 26.1, 17.9; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{19}H_{24}O_3N$: 314.1751, found: 314.1747; Specific rotation: $[\alpha]_D^{20}$ -41.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3a-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

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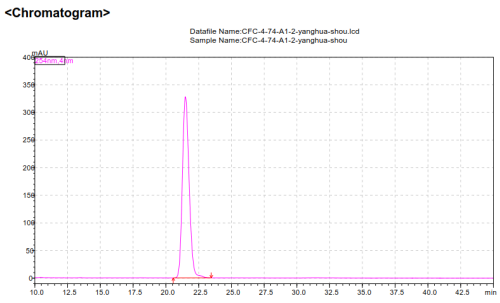
2	31.505	1507053	29182	49.742	49.742
Total		3029725	72198	100.000	



<Peak Table>
PDA Ch1 254nm

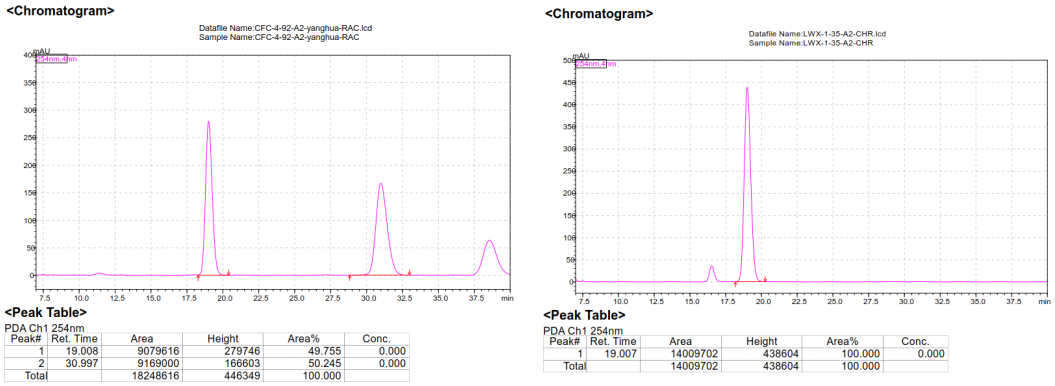
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	21.493	11779467	327858	100.000	0.000
Total		11779467	327858	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	21.522	50.258	1	21.493	>99.000
2	31.505	49.742	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-4,5-dimethyl-5-(4-(trifluoromethyl)phenyl)-1,2-oxaborolan-2-ol (3b). Yield: (41.9 mg, 56%); **IR (neat):** 3302 (m), 2945 (w), 1556 (w), 1447 (s), 1323 (m), 1236 (s), 1221 (s), 1112 (m), 1060 (s), 967 (m), 921 (s), 820 (m), 760 (s), 699 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 (d, *J* = 7.4 Hz, 1H), 7.26 - 7.03 (m, 7H), 6.11 (s, 1H), 5.51 (s, 1H), 1.79 (s, 3H), 1.68 - 1.56 (m, 4H), 1.33 (d, *J* = 16.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.4, 154.2, 148.0, 128.8 (q, *J* = 32.4 Hz), 127.8, 124.8, 124.3 (q, *J* = 3.8 Hz), 123.6, 121.2 (q, *J* = 271.0 Hz), 122.4, 110.5, 102.8, 89.1, 50.6, 24.8, 22.7; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -63.6; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{20}H_{19}BF_3O_3$: 374.1410 m/z, found: 374.1405 m/z; Specific rotation: $[\alpha]_D^{20}$ -10.9 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-2-methyl-3-(4-(trifluoromethyl)phenyl)butane-1,3-diol (3b-oxi). Yield: (31.5 mg, 95%); **IR (neat):** 3165 (br), 2945 (w), 2910 (w), 1498 (w), 1425 (s), 1367 (m), 1242 (m), 1120 (m), 1099 (m), 1025 (s), 956 (m), 910 (s), 816 (s), 778 (s), 654 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.46 - 7.36 (m, 3H), 7.30 - 7.19 (m, 4H), 6.30 (s, 1H), 4.00 - 3.82 (m, 3H), 2.83 (s, 1H), 1.74 (s, 3H), 1.51 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.3, 154.0, 148.7, 129.1 (q, *J* = 32.6 Hz), 127.7, 126.9, 124.2 (q, *J* = 271.0 Hz), 124.1 (q, *J* = 3.4 Hz), 122.9, 120.8, 111.0, 105.1, 79.5, 67.6, 48.6, 26.1, 18.0; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.4; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{20}H_{23}O_3NF_3$: 382.1625 m/z, found: 382.1622 m/z; Specific rotation: $[\alpha]_D^{20}$ -43.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3b-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 98:2 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).

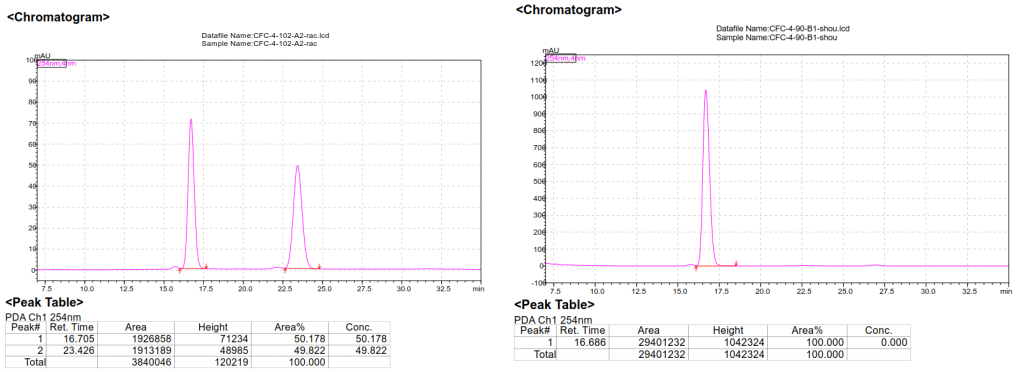


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	19.008	49.755	1	19.007	>99.000
2	30.997	50.245	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-5-(4-chlorophenyl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3c). Yield: (53.7 mg, 79%); **IR (neat):** 3369 (br), 2965 (m), 2931 (m), 1490 (m), 1453 (s), 1424 (s), 1396 (s), 1306 (m), 1257 (s), 1170 (m), 1093 (s), 1051 (m), 1021 (s), 916 (w), 802 (s), 739 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 - 7.25 (m, 2H), 7.21 - 7.07 (m, 2H), 7.04 - 6.91 (m, 4H), 6.10 (s, 1H), 5.95 (s, 1H), 1.79 (s, 3H), 1.65 - 1.55 (m, 4H), 1.29 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.7, 154.2, 142.5, 132.5, 127.9, 127.4, 125.9, 123.5, 122.4, 120.4, 110.6, 102.7, 89.1, 50.4, 24.9, 22.8; **HRMS (ESI$^+$) $[M+H]^+$:** Calcd for: $C_{19}H_{19}BClO_3$: 340.1147 m/z, found: 340.1143 m/z; Specific rotation: $[\alpha]_D^{20}$ -16.1 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-3-(4-chlorophenyl)-2-methylbutane-1,3-diol (3c-oxi). Yield: (48.0 mg, 92%); **IR (neat):** 3181 (br), 2919 (w), 2849 (w), 1488 (s), 1451 (s), 1270 (m), 1162 (w), 1096 (s), 1028 (s), 938 (m), 843 (m), 811 (s), 735 (s), 647 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.29 - 7.17 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 2H), 7.02 (d, *J* = 7.6 Hz, 2H), 6.27 (s, 1H), 3.99 - 3.77 (m, 3H), 3.02 (s, 1H), 1.69 (s, 3H), 1.49 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.5, 153.9, 143.1, 132.7, 128.0, 127.8,127.2, 123.9, 122.8, 120.7, 111.0, 105.0, 79.4, 67.6, 48.6, 26.0, 17.9; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for $C_{19}H_{23}ClNO_3$: 348.1361 m/z, found: 348.1363 m/z; Specific rotation: $[\alpha]_D^{20}$ -39.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3c-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).

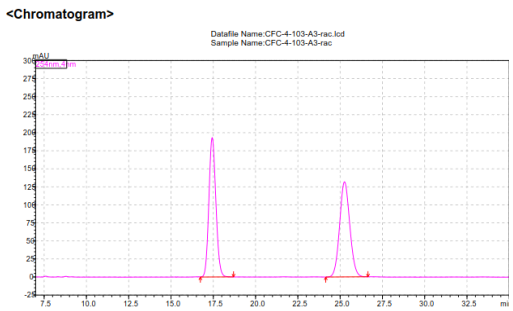


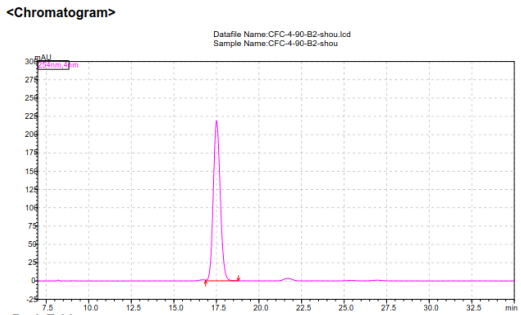
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	16.705	50.178	1	16.686	>99.000
2	23.426	49.822	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-5-(4-bromophenyl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3d). Yield: (55.3 mg, 72%); **IR (neat):** 3361 (br), 2965 (m), 2931 (m), 1575 (w), 1486 (m), 1453 (s), 1392 (s), 1303(m), 1256 (s), 1170 (w), 1079 (s), 1050 (m), 1008 (s), 915 (m), 802 (s), 737 (s), 698 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 - 7.26 (m, 2H), 7.22 - 7.07 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 2H), 6.11 (s, 1H), 5.87 (s, 1H), 1.78 (s, 1H), 1.68 - 1.52 (m, 4H), 1.29 (d, *J* = 16.2 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.7, 154.3, 143.1, 130.4, 128.0, 126.3, 123.6, 122.4, 120.7, 120.5, 110.7, 102.8, 89.1, 50.4, 24.9, 22.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{19}H_{19}BBrO_3$: 384.0641 m/z, found: 384.0637 m/z; Specific rotation: $[\alpha]_D^{20}$ -15.5 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-3-(4-bromophenyl)-2-methylbutane-1,3-diol (3d-oxi). Yield: (50.0 mg, 93%); **IR (neat):** 3194 (br), 2920 (m), 2849 (w), 1588 (w), 1484 (m), 1450 (s), 1396 (m), 1254 (m), 1198 (m), 1137 (m), 1053 (m), 1021 (s), 1007 (s), 914 (s), 840 (s), 808 (s), 733 (s), 676 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.33 - 7.18 (m, 4H), 6.99 (d, *J* = 7.8 Hz, 2H), 6.29 (s, 1H), 4.01 - 3.84 (m, 2H), 3.69 (s, 1H), 2.73 (s, 1H), 1.70 (s, 3H), 1.48 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.5, 143.6, 130.2, 128.4, 127.8, 124.0, 122.8, 121.0, 120.8, 111.0, 105.1, 79.3, 67.7, 48.7, 26.1, 18.0; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{19}H_{23}BrNO_3$: 392.0856 m/z, found: 392.0857 m/z; Specific rotation: $[\alpha]_D^{20}$ -41.1 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3d-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



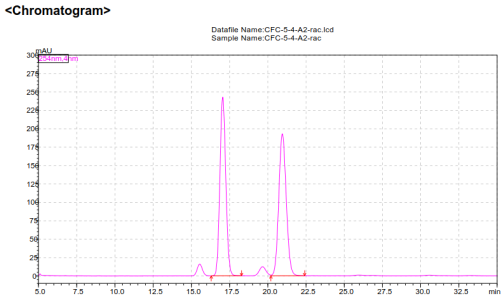


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	17.436	50.124	1	17.509	>99.000
2	25.258	49.876	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-5-(3-chlorophenyl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3e). Yield: (53.7 mg, 79%); **IR (neat):** 3340 (br), 2975 (m), 2930 (w), 1593 (m), 1570 (m), 1453 (s), 1429 (s), 1351 (m), 1253 (s), 1169 (m), 1110 (m), 996 (m), 882 (m), 828 (m), 804 (s), 740 (s), 692 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 - 7.26 (m, 2H), 7.21 - 7.05 (m, 3H), 7.00 - 6.86 (m, 3H), 6.11 (s, 1H), 5.62 (s, 1H), 1.78 (s, 3H), 1.66 - 1.58 (m, 4H), 1.31 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.7, 154.2, 146.0, 133.5, 128.6, 127.9, 126.6, 124.8, 123.5, 122.6, 122.3, 120.3, 110.6, 102.7, 89.1, 50.5, 24.9, 22.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{19}H_{19}BClO_3$: 340.1147 m/z, found: 340.1143 m/z; Specific rotation: $[\alpha]_D^{20}$ -10.0 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

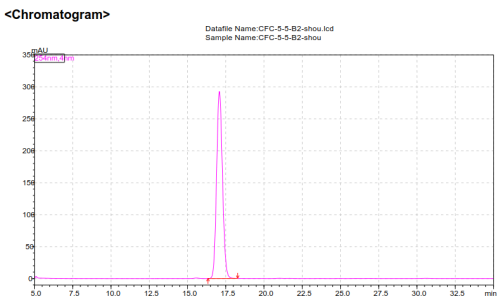
(*2S,3S*)-2-(Benzofuran-2-yl)-3-(3-chlorophenyl)-2-methylbutane-1,3-diol (3e-oxi). Yield: (46.9 mg, 90%); **IR (neat):** 3161 (br), 2978 (m), 2948 (m), 1590 (m), 1567 (m), 1451 (s), 1407 (m), 1252 (m), 1196 (m), 1161 (m), 1088 (m), 1031 (s), 953 (m), 898 (m), 809 (s), 742 (s), 685 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 7.6 Hz, 1H), 7.40 (d, *J* = 7.8 Hz, 1H), 7.29 - 7.13 (m, 4H), 7.07 (t, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.31 (s, 1H), 3.98 - 3.80 (m, 3H), 2.89 (s, 1H), 1.68 (s, 3H), 1.50 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.4, 154.0, 146.8, 133.3, 128.3, 127.8, 127.0, 126.8, 124.7, 123.9, 122.8, 120.7, 111.0, 105.1, 79.3, 67.5, 48.7, 26.0, 17.9; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{19}H_{23}ClNO_3$: 348.1361 m/z, found: 348.1360 m/z; Specific rotation: $[\alpha]_D^{20}$ -41.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3e-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	17.051	6532049	242574	49.922	0.000
2	20.952	6552371	192798	50.078	0.000
Total		13084421	435372	100.000	



<Peak Table>
PDA Ch1 254nm

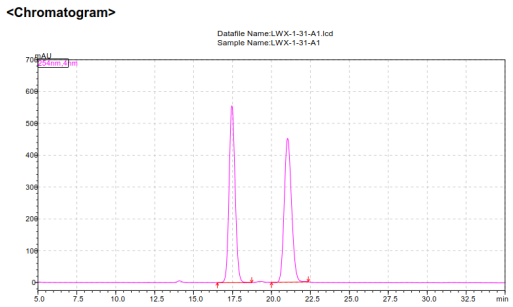
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	17.088	7808147	292389	100.000	0.000
Total		7808147	292389	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	17.051	49.922	1	17.088	>99.000
2	20.952	50.078	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-5-(3-fluorophenyl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3f). Yield: (43.4 mg, 67%); **IR (neat):** 3372 (br), 2926 (m), 2854 (m), 1614 (w), 1587 (m), 1483 (m), 1453 (s), 1426 (s), 1292 (m), 1255 (s), 1185 (m), 1102 (m), 1057 (m), 939 (m), 880 (m), 789 (m), 739 (s), 700 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 - 7.24 (m, 2H), 7.18 - 7.06 (m, 2H), 6.97 - 6.89 (m, 1H), 6.83 (t, *J* = 8.8 Hz, 2H), 6.74 - 6.64 (m, 1H), 6.10 (s, 1H), 5.59 (s, 1H), 1.78 (s, 3H), 1.66 - 1.58 (m, 4H), 1.31 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.5, 161.8, 161.0, 154.2, 146.7 (d, *J* = 6.8 Hz), 128.8 (d, *J* = 8.0 Hz), 128.0, 123.5, 122.3, 120.3, 120.2 (d, *J* = 2.6 Hz), 113.3 (d, *J* = 21.0 Hz), 111.8 (d, *J* = 23.2 Hz), 110.6, 102.6, 89.0, 50.5, 25.0, 22.8; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -114.1; **HRMS (ESI^+) $[M+H]^+$:** Calcd for: $C_{19}H_{19}BFO_3$: 324.1442 m/z, found: 324.1440 m/z; Specific rotation: $[\alpha]_D^{20}$ -5.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

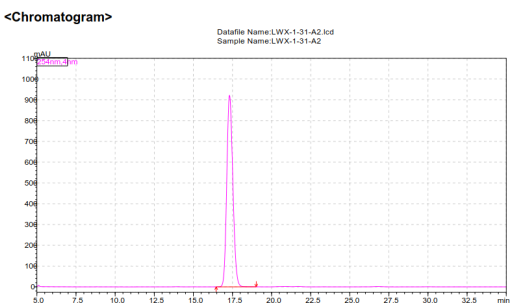
(*2S,3S*)-2-(Benzofuran-2-yl)-3-(3-fluorophenyl)-2-methylbutane-1,3-diol (3f-oxi). Yield: (37.4 mg, 89%); **IR (neat):** 3300 (br), 2918 (w), 2848 (m), 1645 (w), 1586 (s), 1453 (m), 1375 (m), 1253 (s), 1197 (s), 1066 (m), 1033 (s), 932 (m), 883 (m), 827 (m), 739 (s), 700 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 (d, *J* = 7.4 Hz, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.30 - 7.17 (m, 2H), 7.16 - 7.08 (m, 1H), 6.98 - 6.86 (m, 2H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.32 (s, 1H), 3.98 - 3.85 (m, 2H), 3.81 (s, 1H), 2.87 (s, 1H), 1.70 (s, 3H), 1.51 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.3, 160.9, 159.5, 154.0, 147.4 (d, *J* = 6.4 Hz), 128.5 (d, *J* = 8.2 Hz), 127.8, 123.9, 122.8, 122.2 (d, *J* = 2.6 Hz), 120.7, 113.9, 113.7 (d, *J* = 7.8 Hz), 113.5, 111.0, 105.0, 79.3, 67.5, 48.7, 26.1, 18.0; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -113.9; **HRMS (ESI^+) $[M+NH_4]^+$:** Calcd for: $C_{19}H_{23}FNO_3$: 332.1656 m/z, found: 332.1656 m/z; Specific rotation: $[\alpha]_D^{20}$ -37.5 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3f-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	17.460	14939066	555495	50.374	0.000
2	21.036	14717464	451473	49.626	0.000
Total		29656530	1006969	100.000	



<Peak Table>
PDA Ch1 254nm

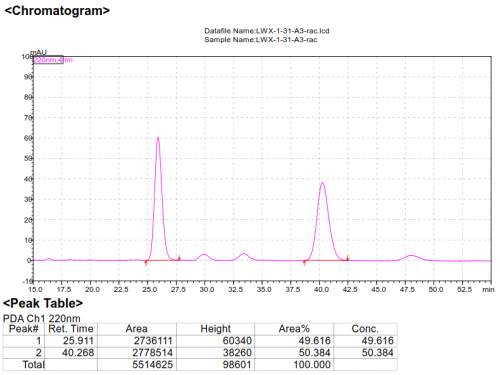
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	17.314	24886490	921726	100.000	0.000
Total		24886490	921726	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	17.460	50.374	1	17.314	>99.000
2	21.036	49.626	2		<1.000

Methyl 4-((*4S,5S*)-4-(benzofuran-2-yl)-2-hydroxy-4,5-dimethyl-1,2-oxaborolan-5-yl)benzoate (3g). Yield: (48.0 mg, 66%); **IR (neat):** 3419 (br), 2952 (m), 2924 (m), 1722 (m), 1454 (m), 1403 (m), 1280 (s), 1191 (m), 1114 (m), 968 (m), 818 (m), 802 (m), 772 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 (d, *J* = 7.8 Hz, 2H), 7.33 - 7.21 (m, 2H), 7.19 - 7.00 (m, 4H), 6.05 (s, 1H), 5.58 (s, 1H), 3.81 (s, 3H), 1.78 (s, 3H), 1.64 (s, 3H), 1.58 (d, *J* = 16.2 Hz, 1H), 1.30 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 166.9, 161.7, 154.2, 149.3, 128.7, 128.2, 127.9, 124.6, 123.5, 122.3, 120.4, 110.6, 102.6, 89.1, 51.9, 50.6, 25.1, 22.8; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for : $C_{21}H_{25}BNO_5$: 381.1857 m/z, found: 381.1853 m/z; Specific rotation: $[\alpha]_D^{20}$ -0.5 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Methyl 4-((*2S,3S*)-3-(benzofuran-2-yl)-2,4-dihydroxy-3-methylbutan-2-yl)benzoate (3g-oxi). Yield: (44.4 mg, 95%); **IR (neat):** 3344 (br), 2983 (w), 2920 (m), 1702 (s), 1608 (s), 1452 (m), 1375 (m), 1279 (s), 1254 (s), 1190 (m), 1100 (m), 1016 (s), 919 (m), 884 (m), 863 (m), 799 (s), 748 (s), 683 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.30 - 7.13 (m, 4H), 6.25 (s, 1H), 4.00 (s, 1H), 3.95 - 3.82 (m, 5H), 2.96 (s, 1H), 1.73 (s, 3H), 1.52 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 167.1, 159.4, 153.9, 149.9, 128.6, 128.4, 127.7, 126.6, 123.9, 122.8, 120.7, 111.0, 105.0, 79.6, 67.6, 52.0, 48.6, 25.9, 18.0; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for: $C_{21}H_{26}NO_5$: 372.1805 m/z, found: 372.1800 m/z; Specific rotation: $[\alpha]_D^{20}$ -45.9 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3g-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 220nm

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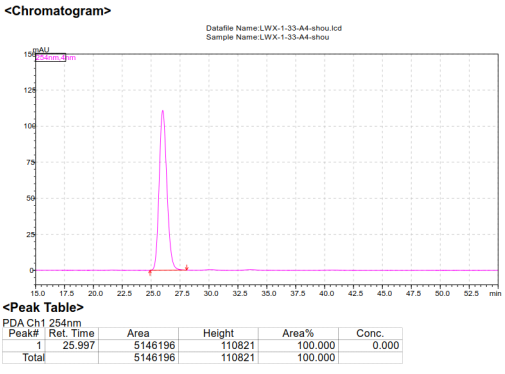
2	40.268	2778514	38260	50.384	50.384
Total		5514625	98601	100.000	



<Peak Table>
PDA Ch1 254nm

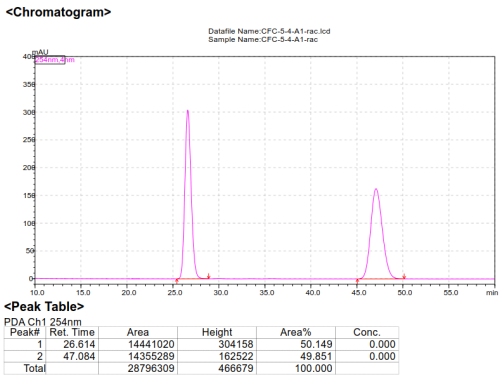
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	25.997	5146196	110821	100.000	0.000
Total		5146196	110821	100.000	

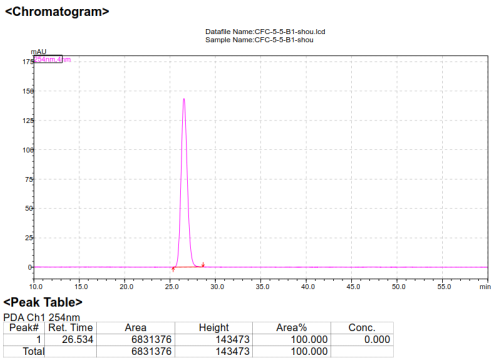
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	25.911	49.616	1	25.997	>99.000
2	40.268	50.384	2		<1.000

(*4S,5S*)-5-([1,1'-Biphenyl]-4-yl)-4-(benzofuran-2-yl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3h). Yield: (66.5 mg, 87%); **IR (neat):** 3378 (br), 3030 (w), 2978 (w), 1575 (w), 1519 (m), 1452 (s), 1423 (s), 1397 (s), 1302 (m), 1255 (s), 1170 (m), 1078 (m), 1051 (m), 1007 (m), 914 (m), 803 (m), 750 (s), 738 (s), 695 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.34 - 7.27 (m, 3H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.19 - 7.06 (m, 4H), 6.14 (s, 1H), 5.89 (s, 1H), 1.89 (s, 1H), 1.73 (d, *J* = 16.4 Hz, 1H), 1.67 (s, 2H), 1.31 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.0, 154.3, 143.0, 140.7, 139.3, 128.6, 128.2, 127.1, 126.9, 126.1, 124.9, 123.4, 122.3, 120.4, 110.7, 102.8, 89.4, 50.6, 24.9, 23.0; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{25}H_{24}BO_3$: 382.1849 m/z, found: 382.1853 m/z; Specific rotation: $[\alpha]_D^{20}$ -35.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-3-([1,1'-Biphenyl]-4-yl)-2-(benzofuran-2-yl)-2-methylbutane-1,3-diol (3h-oxi). Yield: (58.9 mg, 91%); **IR (neat):** 3237 (br), 2977 (w), 2920 (w), 1573 (m), 1485 (m), 1451 (s), 1369 (m), 1253 (s), 1158 (s), 1103 (s), 1067 (s), 1023 (s), 940 (m), 842 (m), 768 (m), 748 (s), 698 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 5H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.28 - 7.15 (m, 4H), 6.32 (s, 1H), 4.03 - 3.86 (m, 2H), 3.58 (s, 1H), 2.83 (s, 1H), 1.76 (s, 3H), 1.55 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.9, 154.0, 143.6, 140.6, 139.5, 128.7, 127.9, 127.2, 126.9, 126.9, 125.8, 123.8, 122.7, 120.7, 111.0, 105.0, 79.5, 67.7, 49.0, 26.2, 18.0; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{25}H_{28}NO_3$: 390.2064 m/z, found: 390.2064 m/z; Specific rotation: $[\alpha]_D^{20}$ -57.1 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3h-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



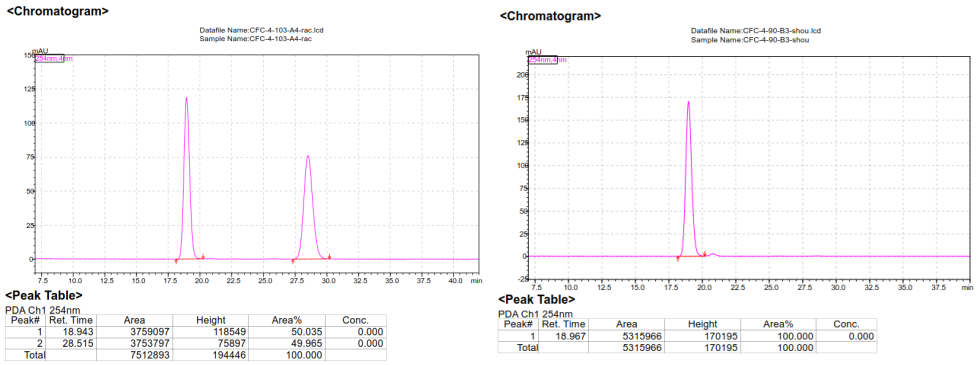


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	26.614	50.149	1	26.534	>99.000
2	47.084	49.851	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-5-(4-methoxyphenyl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3i). Yield: (59.8 mg, 89%); **IR (neat):** 3361 (br), 2935 (m), 2835 (w), 1581 (m), 1507 (m), 1425 (m), 1377 (m), 1288 (s), 1245 (s), 1177 (s), 1068 (s), 1031 (s), 907 (m), 854 (m), 749 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 - 7.28 (m, 2H), 7.20 - 7.07 (m, 2H), 6.96 (d, *J* = 8.2 Hz, 2H), 6.53 (d, *J* = 8.2 Hz, 2H), 6.25 - 5.95 (m, 2H), 3.63 (s, 3H), 1.82 (s, 3H), 1.63 - 1.55 (m, 4H), 1.24 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.7, 154.3, 143.1, 130.4, 128.0, 126.3, 123.6, 122.4, 120.7, 120.5, 110.7, 102.8, 89.1, 50.4, 24.9, 22.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{20}H_{22}BO_4$: 336.1642 m/z, found: 336.1646 m/z; Specific rotation: $[\alpha]_D^{20}$ -37.5 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-3-(4-methoxyphenyl)-2-methylbutane-1,3-diol (3i-oxi). Yield: (55.0 mg, 93%); **IR (neat):** 3242 (br), 2993 (w), 2838 (w), 1610 (m), 1574 (m), 1511 (s), 1452 (s), 1301 (m), 1248 (s), 1177 (m), 1024 (s), 940 (m), 884 (m), 801 (m), 735 (s), 683 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29 - 7.16 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.72 (d, *J* = 8.5 Hz, 2H), 6.28 (s, 1H), 3.98 - 3.84 (m, 2H), 3.77 (s, 3H), 3.47 (s, 1H), 2.88 (s, 1H), 1.70 (s, 3H), 1.50 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.1, 158.3, 154.0, 136.7, 128.0, 127.6, 123.7, 122.7, 120.6, 112.4, 111.0, 104.9, 79.3, 67.7, 55.1, 49.0, 26.3, 17.9; **HRMS (ESI$^+$) [M-OH]$^+$:** Calcd for $C_{20}H_{21}O_3$: 309.1485 m/z, found: 309.1483 m/z; Specific rotation: $[\alpha]_D^{20}$ -32.9 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3i-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).

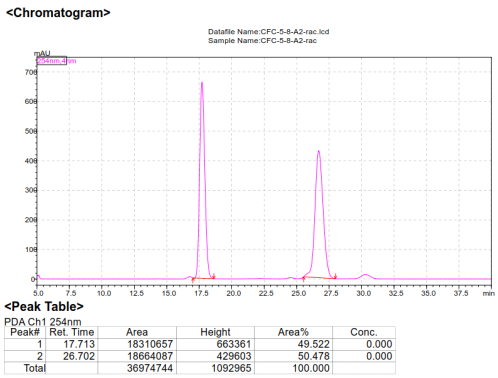


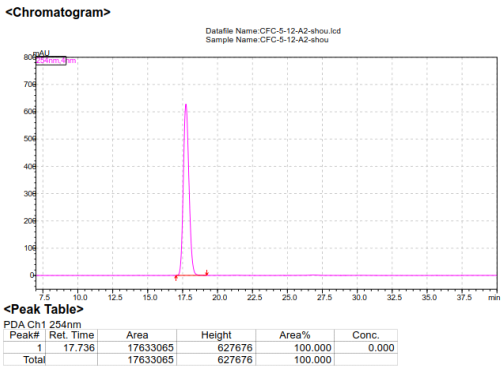
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	18.943	50.035	1	18.967	>99.000
2	28.515	49.965	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-4,5-dimethyl-5-(o-tolyl)-1,2-oxaborolan-2-ol (3j). Yield: (53.8 mg, 84%);**IR (neat):** 3360 (br), 2961 (m), 2854 (m), 1453 (s), 1423 (m), 1307 (m), 1257 (s), 1170 (w), 1095 (m), 1048 (m), 923 (w), 802 (s), 752 (s), 690 (w) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.29 (d, *J* = 7.4 Hz, 1H), 7.18 (t, *J* = 8.2 Hz, 2H), 7.14 - 7.03 (m, 2H), 7.00 - 6.88 (m, 2H), 6.75 (d, *J* = 7.4 Hz, 1H), 6.04 (s, 1H), 5.39 (s, 1H), 2.22 (s, 3H), 1.82 (s, 3H), 1.71 (s, 3H), 1.63 (d, *J* = 16.6 Hz, 1H), 1.37 (d, *J* = 16.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.8, 154.1, 141.3, 135.4, 132.5, 128.1, 126.5, 126.3, 124.8, 123.2, 122.1, 120.2, 110.5, 102.3, 92.1, 51.4, 27.1, 23.1, 23.0; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{20}H_{22}BO_3$: 320.1693 m/z, found: 320.1690 m/z; Specific rotation: $[\alpha]_D^{20}$ 69.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-2-methyl-3-(o-tolyl)butane-1,3-diol (3j-oxi). Yield: (47.9 mg, 92%); **IR (neat):** 3188 (br), 2953 (w), 1565 (w), 1447 (s), 1371 (m), 1271 (m), 1170 (m), 1084 (m), 1023 (s), 936 (m), 832 (m), 815 (m), 748 (s), 656 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 1H), 7.28 - 7.17 (m, 2H), 7.14 - 7.05 (m, 2H), 7.02 (t, *J* = 7.6 Hz, 2H), 6.33 (s, 1H), 4.06 - 3.94 (m, 2H), 3.36 (s, 1H), 2.94 (s, 1H), 2.06 (s, 3H), 1.83 (s, 3H), 1.50 (s, 3H).; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.3, 154.0, 141.9, 137.0, 132.5, 128.9, 128.1, 127.0, 124.6, 123.8, 122.7, 120.6, 111.0, 105.0, 82.3, 67.8, 49.6, 28.5, 23.1, 18.3; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{20}H_{26}NO_3$: 328.1907 m/z, found: 328.1910 m/z; Specific rotation: $[\alpha]_D^{20}$ -33.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3j-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



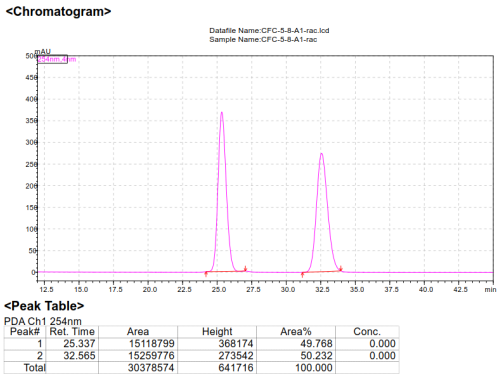


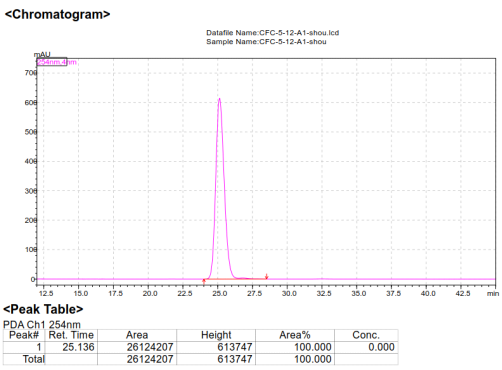
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	17.713	49.522	1	17.736	>99.000
2	26.702	50.478	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-4,5-dimethyl-5-(naphthalen-2-yl)-1,2-oxaborolan-2-ol (3k). Yield: (60.9 mg, 88%); **IR (neat):** 3344 (br), 2926 (w), 2930 (w), 1573 (w), 1439 (s), 1408 (m), 1381 (m), 1283 (s), 1254 (s), 1168 (m), 1087 (m), 1040 (m), 942 (m), 878 (m), 799 (s), 738 (s), 714 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.67 - 7.56 (m, 3H), 7.39 - 7.31 (m, 3H), 7.29 - 7.19 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 7.07 (t, *J* = 7.4 Hz, 1H), 7.00 (d, *J* = 8.8 Hz, 1H), 6.04 (s, 1H), 5.86 (s, 1H), 1.94 (s, 1H), 1.72 - 1.62 (m, 1H), 1.26 (d, *J* = 16.6, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.8, 154.3, 141.6, 132.6, 132.1, 128.1, 127.1, 126.8, 125.7, 125.5, 123.3, 123.2, 123.1, 122.2, 120.4, 110.6, 102.9, 89.5, 50.4, 25.0, 23.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{23}H_{22}BO_3$: 356.1693 m/z, found: 356.1703 m/z; Specific rotation: $[\alpha]_D^{20}$ -114.0 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-2-methyl-3-(naphthalen-2-yl)butane-1,3-diol (3k-oxi). Yield: (56.6 mg, 93%); **IR (neat):** 3326 (br), 2980 (m), 2939 (m), 1711 (m), 1571 (m), 1452 (s), 1374 (s), 1273 (s), 1194 (m), 1126 (m), 1027 (s), 938 (m), 856 (m), 819 (s), 741 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.73 - 7.65 (m, 2H), 7.59 (d, *J* = 8.8 Hz, 1H), 7.49 - 7.36 (m, 4H), 7.31 - 7.18 (m, 2H), 7.10 (d, *J* = 8.8 Hz, 1H), 6.24 (s, 1H), 3.97 (d, *J* = 10.8 Hz, 1H), 3.89 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 1H), 3.01 (s, 1H), 1.82 (s, 3H), 1.58 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.8, 154.0, 142.1, 132.5, 132.2, 128.2, 127.9, 127.2, 126.4, 125.8, 125.8, 125.38, 124.9, 123.8, 122.7, 120.7, 111.0, 105.0, 79.8, 67.6, 48.8, 26.3, 18.0; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{23}H_{26}NO_3$: 364.1907 m/z, found: 364.1906 m/z; Specific rotation: $[\alpha]_D^{20}$ -71.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3k-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



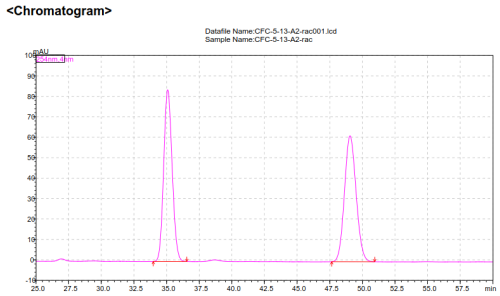


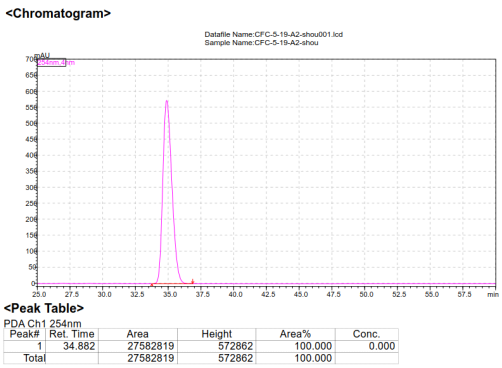
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	25.337	49.768	1	25.136	>99.000
2	32.565	50.232	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-5-(furan-2-yl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3l). Yield: (26.0 mg, 44%); **IR (neat):** 3366 (br), 2963 (m), 2926 (m), 1452 (s), 1400 (s), 1337 (m), 1257 (s), 1169 (m), 1094 (m), 1057 (m), 933 (w), 797 (s), 739 (s), 698 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.20 - 7.08 (m, 2H), 7.05 (s, 1H), 6.24 (s, 1H), 6.02 - 5.96 (m, 1H), 5.88 (d, *J* = 3.2 Hz, 1H), 5.39 (s, 1H), 2.01 (d, *J* = 16.4 Hz, 1H), 1.80 (s, 3H), 1.54 (s, 3H), 1.20 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ161.9, 156.6, 154.7, 141.3, 128.3, 123.3, 122.2, 120.3, 110.7, 109.9, 105.4, 101.7, 85.8, 49.8, 23.4, 21.9; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{17}H_{18}BO_4$: 296.1329 m/z, found: 296.1324 m/z; Specific rotation: $[\alpha]_D^{20}$ –108.6 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-3-(furan-2-yl)-2-methylbutane-1,3-diol (3l-oxi). Yield: (24.2 mg, 96%); **IR (neat):** 3305 (br), 2921 (m), 2851 (w), 1490 (w), 1444 (m), 1430 (m), 1373 (m), 1236 (m), 1157 (m), 1089 (m), 1041 (s), 999 (m), 921 (m), 824 (m), 742 (s), 699 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.29 - 7.13 (m, 3H), 6.45 (s, 1H), 6.27 (s, 1H), 6.09 (d, *J* = 2.4 Hz, 1H), 4.12 - 3.97 (m, 2H), 3.53 (s, 1H), 2.40 (s, 1H), 1.60 (s, 3H), 1.52 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.8, 157.5, 141.2, 128.1, 123.8, 122.7, 120.7, 110.9, 110.1, 106.5, 104.7, 76.9, 67.5, 49.3, 23.7, 17.5; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{17}H_{22}NO_4$: 304.1543 m/z, found: 304.1543 m/z; Specific rotation: $[\alpha]_D^{20}$ –0.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3l-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel IC column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



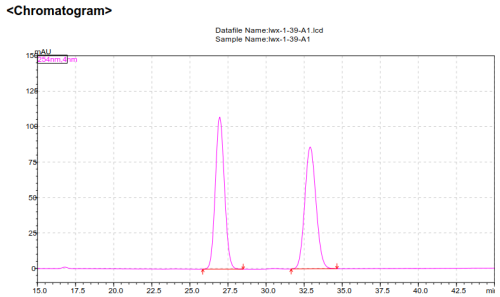


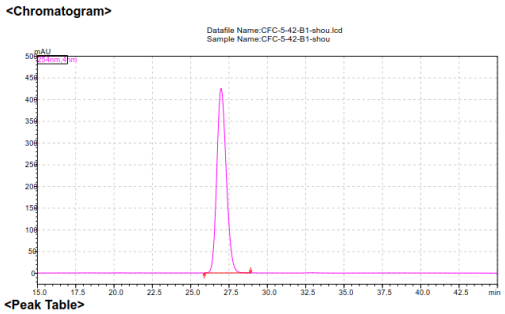
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	35.086	49.969	1	34.882	>99.000
2	49.056	50.031	2		<1.000

(*4S,5S*)-4,5-Di(benzofuran-2-yl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3m). Yield: (44.3 mg, 64%); **IR (neat):** 3340 (br), 3020 (w), 2978 (m), 1430 (m), 1356 (m), 1287 (m), 1155 (m), 1078 (s), 1002 (m), 946 (s), 845 (m), 814 (m), 730 (s), 716 (m), 686 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.34 - 7.22 (m, 2H), 7.15 - 6.96 (m, 6H), 6.34 (s, 1H), 6.24 (s, 1H), 5.50 (s, 1H), 2.02 (d, *J* = 16.4 Hz, 1H), 1.88 (s, 3H), 1.62 (s, 3H), 1.25 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.5, 159.6, 154.6, 154.5, 128.1, 127.8, 123.6, 123.3, 122.3, 122.1, 120.6, 120.4, 110.7, 110.6, 102.2, 102.1 , 86.1, 49.8, 23.3, 22.0; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{21}H_{20}BO_4$: 346.1485 m/z, found: 346.1492 m/z; Specific rotation: $[\alpha]_D^{20}$ –85.5 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2,3-Di(benzofuran-2-yl)-2-methylbutane-1,3-diol (3m-oxi). Yield: (40.0 mg, 93%); **IR (neat):** 3284 (br), 3122 (w), 3063 (w), 1577 (w), 1472 (s), 1419 (m), 1288 (m), 1252 (s), 1205 (m), 1160 (m), 1082 (m), 1023 (s), 957 (m), 883 (m), 809 (s), 750 (s), 732 (s), 669 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** 7.48 (d, *J* = 5.6 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.26 - 7.14 (m, 5H), 6.52 (s, 1H), 6.48 (s, 1H), 4.18 - 4.04 (m, 2H), 3.84 (s, 1H), 2.46 (s, 1H), 1.70 (s, 3H), 1.59 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** 160.5, 159.4, 154.3, 154.3, 128.0, 123.8, 123.8, 122.7, 122.7, 120.9, 120.7, 111.0, 110.9, 105.0, 103.5, 77.1, 67.4, 49.2, 23.8, 17.5; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{21}H_{24}NO_4$: 354.1700 m/z, found: 354.1697 m/z; Specific rotation: $[\alpha]_D^{20}$ 7.8 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3m-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



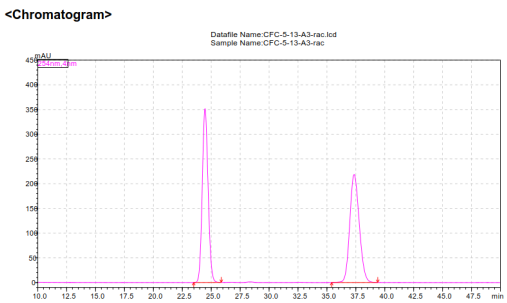


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	26.959	50.247	1	26.981	>99.000
2	32.896	49.753	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-4,5-dimethyl-5-(thiophen-3-yl)-1,2-oxaborolan-2-ol (3n). Yield: (46.2 mg, 74%); **IR (neat):** 3385 (br), 2972 (w), 2926 (w), 1481 (m), 1453 (s), 1431 (s), 1406 (m), 1284 (m), 1219 (m), 1151 (m), 1092 (m), 1030 (m), 940 (m), 883 (m), 783 (m), 745 (s), 632 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 - 7.31 (m, 2H), 7.23 - 7.09 (m, 2H), 6.93 - 6.82 (m, 2H), 6.43 (d, *J* = 4.8 Hz, 1H), 6.21 - 6.09 (m, 2H), 1.84 (s, 3H), 1.70 (d, *J* = 16.4 Hz, 1H), 1.59 (s, 1H), 1.23 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ162.1, 154.4, 145.9, 128.2, 125.2, 124.7, 123.4, 122.3, 120.4, 119.3, 110.7, 102.5, 88.6, 49.8, 24.8, 23.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{17}H_{18}BO_3S$: 312.1101 m/z, found: 312.1097 m/z; Specific rotation: $[\alpha]_D^{20}$ –108.6 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1

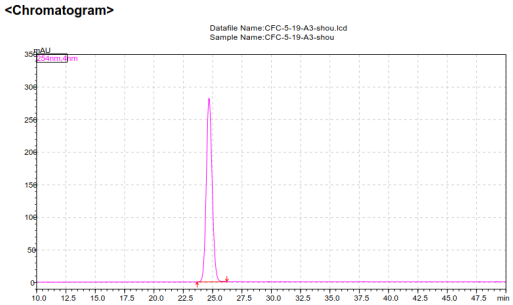
(*2S,3S*)-2-(Benzofuran-2-yl)-2-methyl-3-(thiophen-3-yl)butane-1,3-diol (3n-oxi). Yield: (40.7 mg, 90%); **IR (neat):** 3207 (br), 2940 (w), 1567 (m), 1470 (s), 1407 (m), 1253 (m), 1237 (m), 1174 (m), 1136 (m), 1025 (s), 1006 (m), 954 (m), 891 (m), 828 (s), 812 (s), 747 (s), 696 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.29 - 7.16 (m, 2H), 7.14 - 7.06 (m, 1H), 6.97 (s, 1H), 6.66 (d, *J* = 5.0 Hz, 1H), 6.33 (s, 1H), 4.04 - 3.85 (m, 2H), 3.74 (s, 1H), 3.01 (s, 1H), 1.66 (s, 3H), 1.53 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.9, 154.0, 146.8, 127.9, 126.9, 124.1, 123.8, 122.7, 121.3, 120.7, 111.0, 104.7, 78.8, 67.6, 48.8, 26.4, 17.7; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{17}H_{22}NO_3S$: 320.1315 m/z, found: 320.1315 m/z; Specific rotation: $[\alpha]_D^{20}$ –30.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3n-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	24.458	12396605	351406	49.800	0.000
2	37.352	12496211	218408	50.200	0.000
Total		24892815	569814	100.000	



<Peak Table>
PDA Ch1 254nm

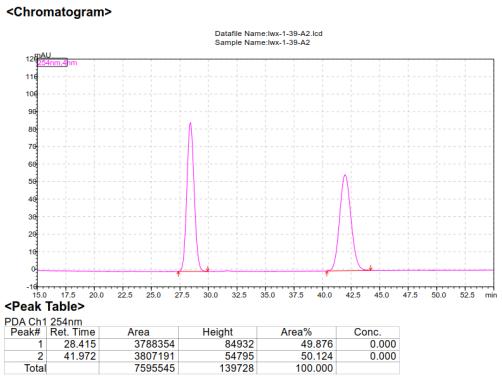
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	24.697	9778811	281856	100.000	0.000
Total		9778811	281856	100.000	

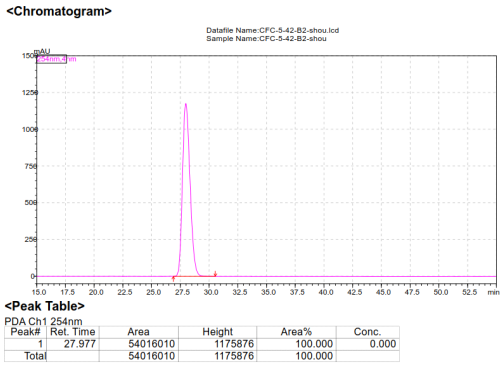
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	24.458	49.800	1	24.697	>99.000
2	37.352	50.200	2		<1.000

(*4S,5S*)-5-(Benzo[b]thiophen-2-yl)-4-(benzofuran-2-yl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3o). Yield: (52.8 mg, 73%); **IR (neat):** 3387 (br), 2956 (w), 2876 (m), 1476 (m), 1407 (s), 1376 (m), 1301 (m), 1230 (m), 1145 (m), 1067 (m), 956 (s), 021 (m), 845 (m), 801 (m), 745 (s), 667 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 7.3 Hz, 1H), 7.47 - 7.31 (m, 3H), 7.23 - 7.07 (m, 4H), 6.73 (s, 1H), 6.25 (s, 1H), 5.50 (s, 1H), 1.95 (s, 3H), 1.83 (d, *J* = 16.4 Hz, 1H), 1.65 (s, 4H), 1.30 (d, *J* = 16.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.6, 154.5, 149.7, 139.5, 139.0, 128.2, 123.8, 123.5, 123.1, 122.34, 121.8, 120.6, 119.4, 110.8, 103.2, 88.6, 50.5, 26.0, 23.5; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{21}H_{22}BO_3S$: 362.1257 m/z, found: 362.1254 m/z; Specific rotation: $[\alpha]_D^{20}$ -89.1 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-3-(Benzo[b]thiophen-2-yl)-2-(benzofuran-2-yl)-2-methylbutane-1,3-diol (3o-oxi). Yield: (45.2 mg, 88%); **IR (neat):** 3333 (br), 2983 (w), 2937 (m), 1597 (w), 1452 (s), 1372 (m), 1305 (m), 1253 (s), 1169 (m), 1129 (m), 1028 (s), 936 (m), 883 (m), 830 (m), 742 (s), 689 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** 7.72 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.44 (d, *J* = 8.2 Hz, 1H), 7.32 - 7.18 (m, 4H), 6.85 (s, 1H), 6.44 (s, 1H), 4.16 - 3.99 (m, 3H), 2.56 (s, 1H), 1.79 (s, 3H), 1.63 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.2, 154.2, 151.2, 139.6, 139.2, 127.9, 124.0, 123.9, 123.8, 123.3, 122.8, 121.9, 120.8, 120.8, 111.1, 105.4, 79.4, 67.7, 49.1, 27.5, 18.1; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{21}H_{24}NO_3S$: 370.1471 m/z, found: 370.1469 m/z; Specific rotation: $[\alpha]_D^{20}$ -12.0 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3o-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



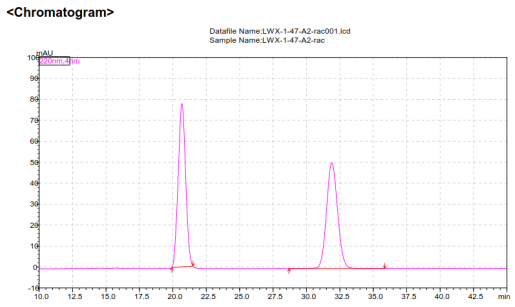


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	28.415	49.876	1	27.977	>99.000
2	41.972	50.124	2		<1.000

(*1S,4'S*)-4'-(Benzofuran-2-yl)-4'-methyl-3,4-dihydro-2H-spiro[naphthalene-1,5'-[1,2]oxaborolan]-2'-ol (3p). Yield: (54.4 mg, 82%); **IR (neat):** 3368 (br), 2955 (w), 2920 (m), 1488 (m), 1452 (m), 1414 (s), 1328 (m), 1288 (s), 1171 (m), 1079 (m), 1016 (m), 923 (m), 871 (m), 808 (s), 750 (s), 739 (s), 687 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.31 (d, *J* = 7.2 Hz, 1H), 7.23 (d, *J* = 7.2 Hz, 1H), 7.17 - 6.92 (m, 5H), 6.79 (d, *J* = 6.8 Hz, 2H), 6.10 (s, 1H), 5.92 (s, 1H), 2.74 - 2.60 (m, 1H), 2.57 - 2.46 (m, 1H), 2.46 - 2.35 (m, 1H), 2.34 - 2.21 (m, 1H), 2.18 - 2.01 (m, 2H), 1.94 - 1.82 (m, 1H), 1.65 (s, 3H), 1.26 (d, *J* = 17.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.3, 154.1, 138.9, 136.9, 128.6, 128.2, 127.0, 125.1, 124.8, 123.1, 122.1, 120.2, 110.4, 102.9, 87.6, 50.3, 33.1, 27.8, 24.3, 18.5; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{21}H_{22}BO_3$: 332.1693 m/z, found: 332.1693 m/z; Specific rotation: $[\alpha]_D^{20}$ -85.6 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*S*)-1-((*S*)-2-(Benzofuran-2-yl)-1-hydroxypropan-2-yl)-1,2,3,4-tetrahydronaphthalen-1-ol (3p-oxi). Yield: (46.3 mg, 85%); **IR (neat):** 3163 (br), 2932 (m), 2860 (w), 1556 (w), 1448 (s), 1338 (m), 1252 (s), 1168 (m), 1122 (m), 1039 (s), 1005 (s), 953 (m), 920 (m), 880 (m), 818 (m), 762 (s), 683 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 7.2 Hz, 1H), 7.38 (d, *J* = 7.6 Hz, 1H), 7.28 - 7.13 (m, 4H), 7.11 - 6.98 (m, 2H), 6.20 (s, 1H), 4.06 (d, *J* = 11.2 Hz, 1H), 3.89 (d, *J* = 11.2 Hz, 1H), 3.68 (s, 1H), 3.28 (s, 1H), 2.67 - 2.50 (m, 1H), 2.37 - 2.26 (m, 1H), 2.24 - 2.14 (m, 1H), 2.01 - 1.90 (m, 1H), 1.68 - 1.42 (m, 5H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.1, 153.8, 139.4, 139.1, 128.2, 128.1, 127.7, 127.1, 125.4, 123.7, 122.7, 120.6, 111.0, 105.1, 77.9, 68.6, 49.4, 36.1, 30.0, 19.9, 17.0; **HRMS (ESI$^+$) [M-OH]$^+$:** Calcd for: $C_{21}H_{21}O_2$: 305.1536 m/z, found: 305.1530 m/z; Specific rotation: $[\alpha]_D^{20}$ 13.6 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3p-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
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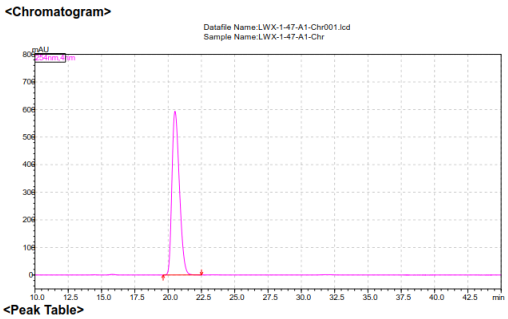
2	31.900	2909402	50512	48.988	0.000
Total		5938988	128400	100.000	



<Peak Table>
PDA Ch1 254nm

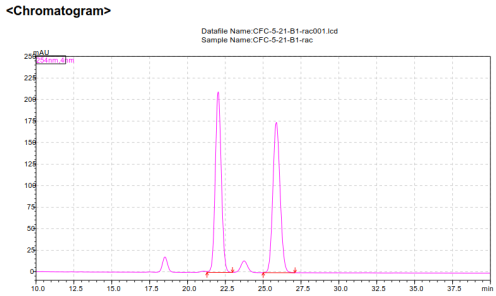
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	20.516	23201958	593517	100.000	0.000
Total		23201958	593517	100.000	

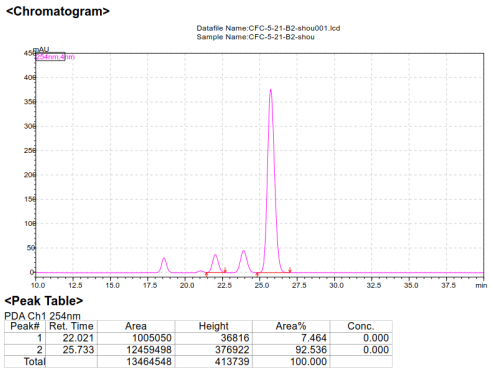
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	20.682	51.012	1	20.516	>99.000
2	31.900	48.988	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-5-cyclohexyl-4,5-dimethyl-1,2-oxaborolan-2-ol (3q). Yield: (39.3 mg, 88%); **IR (neat):** 3350 (br), 2917 (m), 2840 (m), 1579 (m), 1448 (m), 1400 (m), 1267 (m), 1230 (s), 1156 (m), 1120 (m), 1020 (m), 910 (s), 884 (m), 831 (s), 745 (s), 684 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.4 Hz, 1H), 7.28 - 7.13 (m, 3H), 6.49 (s, 1H), 5.50 (s, 1H), 1.72 - 1.58 (m, 2H), 1.55 - 1.38 (m, 6H), 1.36 - 1.17 (m, 6H), 1.09 - 0.94 (m, 3H), 0.87 - 0.66 (m, 2H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.3, 154.4, 128.3, 123.4, 122.5, 120.4, 111.0, 102.6, 90.2, 49.0, 45.6, 28.7, 27.9, 26.9, 26.6, 26.4, 26.3, 24.4, 18.4; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{19}H_{26}BO_3$: 312.2006 m/z, found: 312.2002 m/z; Specific rotation: $[\alpha]_D^{20}$ –30.8 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzofuran-2-yl)-3-cyclohexyl-2-methylbutane-1,3-diol (3q-oxi). Yield: (34.6 mg, 91%); **IR (neat):** 3248 (br), 2978 (m), 2954 (m), 2931 (m), 1567 (m), 1450 (s), 1429 (m), 1358 (m), 1284 (m), 1249 (m), 1146 (m), 1021 (s), 954 (m), 920 (m), 875 (m), 812 (m), 747 (s), 687 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.28 - 7.16 (m, 2H), 6.64 (s, 1H), 4.12-4.06 (m, 2H), 2.81 (s, 1H), 2.57 (s, 1H), 1.82 - 1.51 (m, 7H), 1.48 (s, 3H), 1.26 (s, 3H), 1.10 - 0.91 (m, 4H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.3, 154.1, 128.1, 123.7, 122.7, 120.6, 111.0, 104.5, 79.6, 68.2, 49.0, 46.0, 29.7, 27.4, 26.9, 26.8, 26.4, 19.7, 18.8; **HRMS (ESI$^+$) [M+Na]$^+$:** Calcd for: $C_{19}H_{26}O_3Na$: 325.1774 m/z, found: 325.1771 m/z; Specific rotation: $[\alpha]_D^{20}$ –2.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3q-oxi** was determined by HPLC analysis in comparison with authentic racemic material (93:7 e.r. shown; Chiralcel IC column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



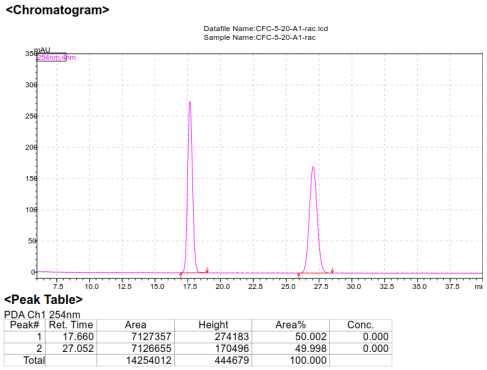


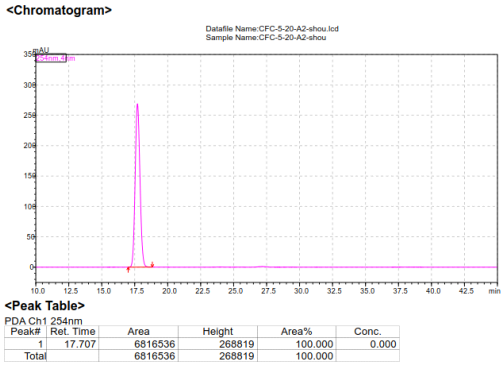
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	22.028	50.064	1	22.021	7.464
2	25.866	49.936	2	25.733	92.536

(*S*)-4-(Benzofuran-2-yl)-4-methyl-1-oxa-2-boraspiro[4,5]decan-2-ol (3r). Yield: (54.5 mg, 96%); **IR (neat):** 3357 (br), 2930 (m), 2857 (w), 1579 (w), 1452 (m), 1402 (m), 1350 (m), 1287 (m), 1249 (s), 1134 (m), 1007 (m), 926 (m), 842 (m), 798 (s), 739 (s), 693 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 7.4 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.29 - 7.16 (m, 2H), 6.51 (s, 1H), 6.00 (s, 1H), 2.03 - 1.92 (m, 1H), 1.84 (d, *J* = 16.4 Hz, 1H), 1.78 - 1.61 (m, 4H), 1.59 - 1.37 (m, 6H), 1.20 (d, *J* = 16.4 Hz, 1H), 1.14 - 1.00 (m, 1H), 0.98 - 0.85 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 163.4, 154.7, 128.4, 123.4, 122.5, 120.4, 111.0, 102.4, 87.2, 48.4, 34.0, 32.1, 25.2, 22.8, 22.4, 22.0; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{17}H_{22}BO_3$: 284.1693 m/z, found: 284.1690 m/z; Specific rotation: $[\alpha]_D^{20}$ –41.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*S*)-1-(2-(Benzofuran-2-yl)-1-hydroxypropan-2-yl)cyclohexan-1-ol (3r-oxi). Yield: (48.9 mg, 93%); **IR (neat):** 3192 (br), 2978 (w), 2932 (m), 2849 (m), 1574 (w), 1450 (s), 1370 (m), 1279 (s), 1202 (m), 1129 (m), 1099 (m), 1034 (s), 929 (m), 844 (m), 747 (s), 733 (s), 676 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 (d, *J* = 7.2 Hz, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.29 - 7.13 (m, 2H), 6.66 (s, 1H), 4.10 - 3.98 (m, 2H), 2.99 (s, 1H), 2.53 (s, 1H), 1.90 - 1.72 (m, 2H), 1.67 - 1.47 (m, 7H), 1.45 (s, 3H), 1.40 - 1.31 (m, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.0, 154.2, 128.1, 123.6, 122.7, 120.6, 111.0, 104.8, 76.3, 67.4, 48.9, 32.9, 31.9, 25.5, 21.5, 17.2; **HRMS (ESI$^+$) [M+Na]$^+$:** Calcd for: $C_{17}H_{22}O_3Na$: 297.1461 m/z, found: 297.1459 m/z; Specific rotation: $[\alpha]_D^{20}$ –3.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3r-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



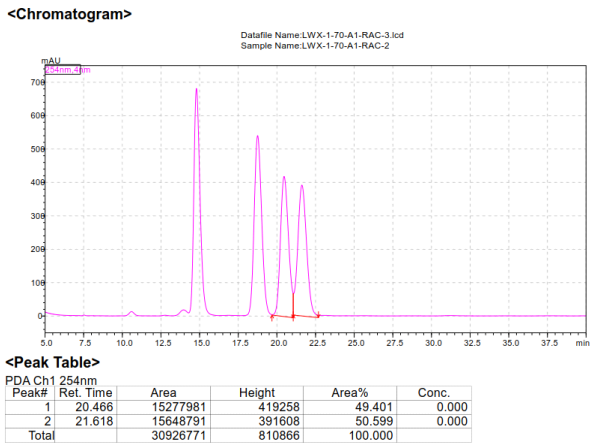


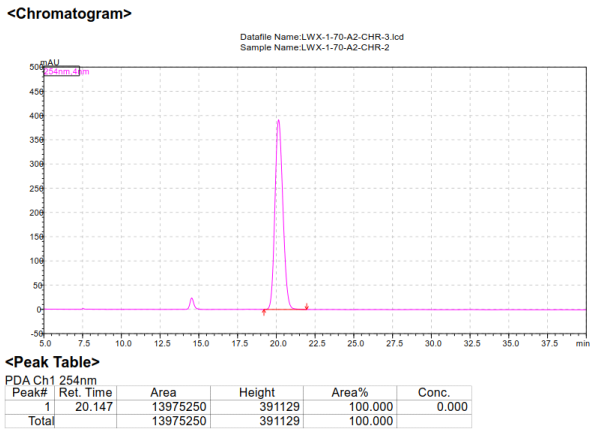
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	17.660	50.002	1	17.707	>99.000
2	27.052	49.998	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-4,5-dimethyl-5-((*E*)-2-(2,6,6-trimethylcyclohex-1-en-1-yl)vinyl)-1,2-oxaborolan-2-ol (3s). Yield: (49.1 mg, 65%); **IR (neat):** 3364 (br), 2960 (w), 2926 (m), 1579 (w), 1452 (s), 1426 (m), 1401 (m), 1288 (m), 1254 (s), 1167 (m), 1077 (m), 1007 (m), 946 (m), 883 (s), 799 (s), 738 (s), 691 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 - 7.46 (m, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 7.24 - 7.15 (m, 2H), 6.46 (s, 1H), 6.05 - 5.93 (m, 2H), 5.02 (d, *J* = 15.8 Hz, 1H), 1.83 - 1.77 (m, 3H), 1.63 (s, 3H), 1.49 - 1.45 (m, 4H), 1.36 (s, 3H), 1.34 - 1.27 (m, 3H), 1.17 (d, *J* = 16.2 Hz, 1H), 0.80 (s, 3H), 0.79 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.9, 154.8, 136.7, 136.3, 128.5, 127.8, 125.6, 123.4, 122.4, 120.5, 111.0, 102.5, 87.6, 48.2, 39.1, 33.9, 32.3, 28.4, 28.3, 23.5, 23.2, 21.0, 19.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{24}H_{32}BO_3$: 378.2475 m/z, found: 378.2468 m/z.

(*2S,3S,E*)-2-(benzofuran-2-yl)-2,3-dimethyl-5-(2,6,6-trimethylcyclohex-1-en-1-yl)pent-4-ene-1,3-diol (3s-oxi). Yield: (33.7 mg, 72%); **IR (neat):** 3335 (br), 2862 (m), 2826(w), 1572 (w), 1453 (s), 1374 (m), 1254 (s), 1165 (m), 1109 (m), 1030 (s), 977 (s), 938 (m), 911 (m), 847 (m), 810 (m), 739 (s), 661 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 8.0 Hz, 1H), 7.28 - 7.15 (m, 2H), 6.61 (s, 1H), 6.15 (d, *J* = 16.0 Hz, 1H), 5.58 (d, *J* = 16.0 Hz, 1H), 4.19 (d, *J* = 11.0 Hz, 1H), 4.00 (d, *J* = 11.0 Hz, 1H), 2.97 (s, 1H), 2.68 (s, 1H), 1.93 (t, *J* = 6.2 Hz, 2H), 1.66 - 1.48 (m, 8H), 1.46 - 1.38 (m, 2H), 1.35 (s, 3H), 0.98 - 0.86 (m, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.5, 154.3, 137.6, 137.0, 128.1, 128.0, 126.2, 123.7, 122.7, 120.6, 111.0, 104.5, 78.2, 67.9, 48.2, 39.3, 34.0, 32.6, 28.7, 28.5, 25.1, 21.3, 19.2, 17.2; **HRMS (ESI$^+$) [M-OH]$^+$:** Calcd for : $C_{24}H_{31}O_2$: 351.2319 m/z, found: 351.2311 m/z; Specific rotation: $[\alpha]_D^{20}$ -33.1 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3s-oxi** was determined by HPLC analysis in comparison with authentic racemic material (97:3 e.r. shown; Chiralcel OZ-H column, 98:2 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



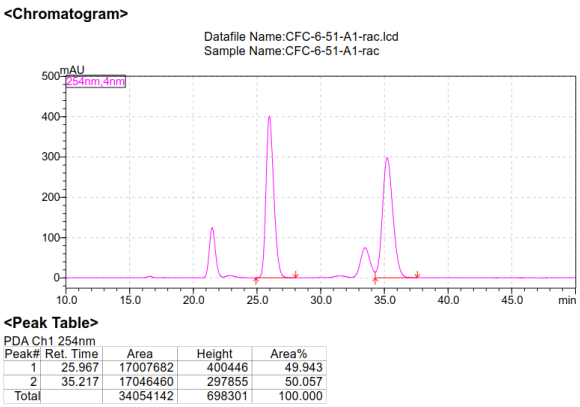


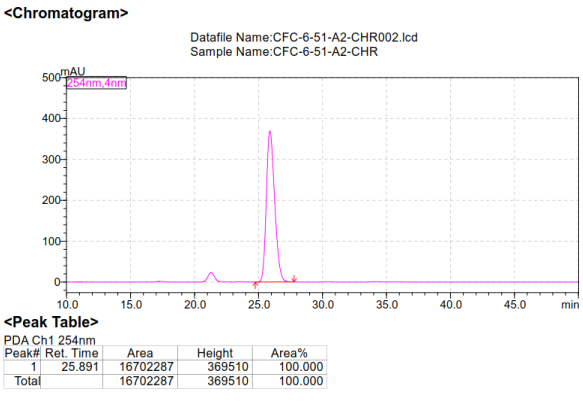
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	20.466	49.401	1	20.147	>99.000
2	21.618	50.599	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-5-(2-bromophenyl)-4,5-dimethyl-1,2-oxaborolan-2-ol (3t). Yield: (73.7 mg, 96%); **IR (neat):** 3359 (br), 3062 (w), 2973 (m), 2935 (w), 1575 (w), 1452 (m), 1419 (m), 1396 (s), 1304 (m), 1254 (s), 1169 (m), 1053 (m), 1039 (s), 912 (m), 883 (m), 802 (m), 748 (s), 680 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.37 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 7.11 - 7.01 (m, 2H), 6.83 - 6.71 (m, 2H), 6.19 (s, 1H), 2.05 (s, 3H), 1.85 (s, 3H), 1.69 (d, *J* = 16.6 Hz, 1H), 1.38 (d, *J* = 16.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 162.2, 154.1, 142.3, 134.9, 128.8, 128.1, 128.0, 126.2, 123.2, 122.1, 120.2, 119.3, 110.5, 102.4, 91.0, 51.7, 25.0, 24.1; **HRMS (ESI$^+$) $[M+H]^+$:** Calcd for: $C_{19}H_{19}BBrO_3$: 384.0641 m/z, found: 384.0635 m/z.

(*2S,3S*)-2-(benzofuran-2-yl)-3-(2-bromophenyl)-2-methylbutane-1,3-diol (3t-oxi). Yield: (68.8 mg, 92%); **IR (neat):** 3317 (br), 3060 (w), 2983 (w), 2930 (w), 1674 (m), 1572 (m), 1452 (s), 1419 (m), 1376 (m), 1254 (s), 1208 (m), 1169 (m), 1109 (m), 1015 (s), 908 (m), 800 (m), 745 (s), 676 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.45 (t, *J* = 7.0 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 1H), 7.25 - 7.14 (m, 3H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.38 (s, 1H), 4.20 (s, 1H), 4.11 (d, *J* = 11.2 Hz, 1H), 4.00 (d, *J* = 11.2 Hz, 1H), 2.80 (s, 1H), 1.91 (s, 3H), 1.49 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.2, 154.3, 142.1, 135.2, 131.3, 128.5, 128.3, 126.1, 123.8, 122.6, 121.0, 120.6, 111.0, 105.7, 81.5, 67.4, 50.0, 27.2, 18.4; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for $C_{19}H_{23}BrNO_3$: 392.0856 m/z, found: 392.0857 m/z; Specific rotation: $[\alpha]_D^{20}$ -2.9 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **3t-oxi** was determined by HPLC analysis in comparison with authentic racemic material (95:5 d.r., >99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



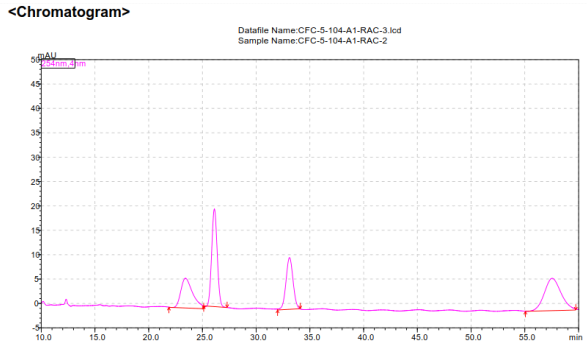


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	25.967	49.943	1	25.891	>99.000
2	35.217	50.057	2		<1.000

(*4S,5S*)-4-(Benzofuran-2-yl)-4-ethyl-5-methyl-5-phenyl-1,2-oxaborolan-2-ol (7a). Yield: (61.4 mg, 96%); **IR (neat):** 3366 (br), 3058 (w), 2963 (m), 1452 (m), 1400 (m), 1376 (m), 1257 (s), 1169 (m), 1094 (m), 1057 (m), 954 (m), 880 (m), 797 (s), 749 (s), 698 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 (d, *J* = 6.4 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.16 - 7.08 (m, 2H), 7.06 - 6.95 (m, 5H), 6.13 (s, 1H), 5.98 (s, 1H), 2.40 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.85 (s, 3H), 1.81 - 1.77 (m, 1H), 1.53 (d, *J* = 16.5 Hz, 1H), 1.33 (d, *J* = 16.6 Hz, 1H), 0.77 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.3, 154.4, 143.9, 128.1, 127.3, 126.5, 124.5, 123.2, 122.1, 120.2, 110.5, 104.8, 89.8, 55.6, 26.8, 24.5, 9.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{20}H_{22}BO_3$: 320.1693 m/z, found: 320.1694 m/z.

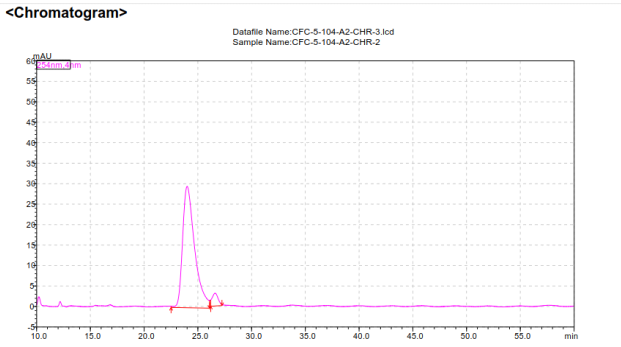
(*2S,3S*)-2-(benzofuran-2-yl)-2-ethyl-3-phenylbutane-1,3-diol (7a-oxi). Yield: (54.2 mg, 91%); **IR (neat):** 3298 (br), 2977 (m), 2879 (w), 1491 (s), 1451 (s), 1377 (m), 1255 (m), 1171 (m), 1156 (m), 1073 (m), 1037 (s), 953 (s), 909 (m), 860 (m), 803 (s), 749 (s), 701 (s), 664 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.33 (d, *J* = 6.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.16 - 7.08 (m, 2H), 7.06 - 6.95 (m, 5H), 6.13 (s, 1H), 5.98 (s, 1H), 2.40 (dq, *J* = 14.4, 7.2 Hz, 1H), 1.85 (s, 3H), 1.81 - 1.77 (m, 1H), 1.53 (d, *J* = 16.6 Hz, 1H), 1.33 (d, *J* = 16.6 Hz, 1H), 0.77 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.7, 153.8, 145.1, 127.8, 127.1, 126.7, 126.1, 123.6, 122.6, 120.6, 110.9, 105.3, 81.5, 62.8, 51.3, 26.3, 21.4, 9.0; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{20}H_{26}NO_3$: 328.1907 m/z, found: 328.1909 m/z.

Enantiomeric purity of **7a-oxi** was determined by HPLC analysis in comparison with authentic racemic material (95:5 d.r., >99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	23.423	467217	6085	19.584	0.000
2	26.112	717018	20046	30.054	0.000
3	33.103	485702	10608	20.358	0.000
4	57.537	715819	6622	30.004	0.000
Total		2385755	43361	100.000	



<Peak Table>
PDA Ch1 254nm

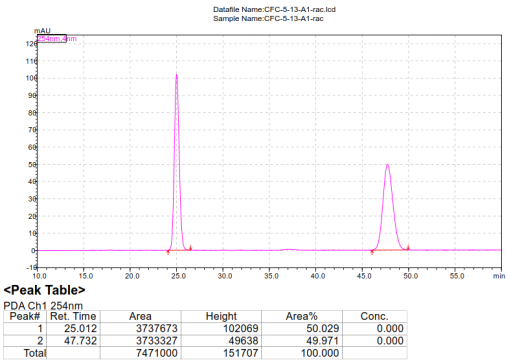
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	24.001	2310230	29651	95.054	0.000
2	26.604	120199	3112	4.946	0.000
Total		2430430	32763	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	23.423	19.584	1	24.001	95.054
2	26.112	30.054	2	26.604	4.946
3	33.103	20.358	3		
4	57.537	30.004	4		

(*4S,5S*)-4-(Benzo[b]thiophen-2-yl)-4,5-dimethyl-5-phenyl-1,2-oxaborolan-2-ol (7b). Yield: (58.0 mg, 90%); **IR (neat):** 3338 (br), 2973 (w), 2932 (m), 1427 (m), 1396 (m), 1271 (s), 1189 (m), 1097 (m), 1061 (s), 901 (m), 854 (m), 823 (s), 743 (s), 724 (s), 696 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.29 - 7.15 (m, 2H), 7.08 - 6.98 (m, 5H), 6.70 (s, 1H), 6.07 (s, 1H), 1.85 (s, 3H), 1.79 - 1.69 (m, 4H), 1.37 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.3, 143.3, 139.4, 139.0, 127.3, 126.6, 124.9, 123.8, 123.5, 122.9, 121.7, 121.0, 89.8, 51.8, 26.4, 24.6; **HRMS (ESI$^+$) $[M+H]^+$:** Calcd for: $C_{19}H_{20}BO_2S$: 322.1308 m/z, found: 322.1311 m/z; Specific rotation: $[\alpha]_D^{20}$ 32.0 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

(*2S,3S*)-2-(Benzo[b]thiophen-2-yl)-2-methyl-3-phenylbutane-1,3-diol (7b-oxi). Yield: (52.8 mg, 94%); **IR (neat):** 3171 (br), 2974 (m), 2849(w), 1476 (s), 1430 (s), 1375 (m), 1270 (m), 1154 (m), 1089 (m), 1031 (s), 945 (s), 907 (m), 858 (m), 824 (s), 758 (m), 741 (s), 697 (s), 661 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 6.8 Hz, 1H), 7.35 - 7.25 (m, 2H), 7.23 - 7.10 (m, 5H), 6.72 (s, 1H), 4.02 - 3.90 (m, 2H), 3.36 (s, 1H), 2.98 (s, 1H), 1.76 (s, 3H), 1.57 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.1, 144.2, 139.1, 139.0, 127.1, 124.0, 123.9, 123.1, 123.0, 121.7, 79.6, 69.4, 49.8, 25.9, 20.8; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for: $C_{19}H_{24}NO_2S$: 330.1522 m/z, found: 330.1518 m/z; Specific rotation: $[\alpha]_D^{20}$ 11.0 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **7b-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	25.012	3737673	102069	50.029	0.000
2	47.732	3733327	49638	49.971	0.000
Total		7471000	151707	100.000	

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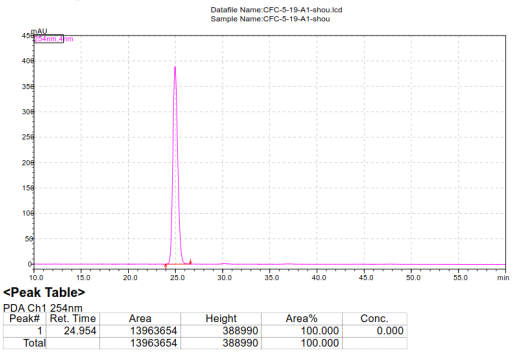


<Peak Table>
PDA Ch1 254nm

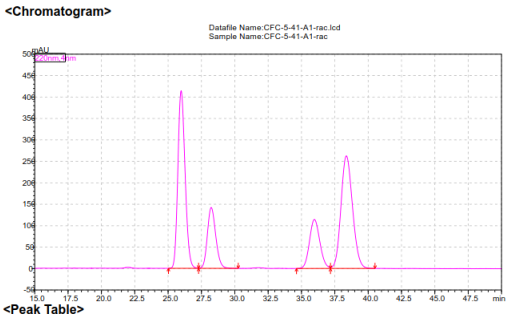
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	24.954	13963654	388990	100.000	0.000
Total		13963654	388990	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	25.012	50.029	1	24.954	>99.000
2	47.732	49.971	2		<1.000

(*4S,5S*)-4-(Benzofuran-3-yl)-4,5-dimethyl-5-phenyl-1,2-oxaborolan-2-ol (7c). Yield: (48.3 mg, 79%); **IR (neat):** 3342 (br), 2975 (m), 1467 (m), 1412 (m), 1396 (s), 1296 (s), 1246 (m), 1169 (m), 1111 (m), 1054 (m), 1057 (m), 904 (m), 855 (m), 742 (s), 698 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.39 - 7.27 (m, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.09 (s, 1H), 7.06 - 6.91 (m, 6H), 6.10 (s, 1H), 1.87 (s, 3H), 1.74 - 1.66 (m, 4H), 1.23 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.4, 143.7, 142.3, 127.2, 127.1, 126.7, 125.6, 125.3, 123.4, 121.9, 121.6, 111.4, 89.6, 48.8, 25.1, 24.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{19}H_{20}O_3B$: 306.1536 m/z, found: 306.1533 m/z.

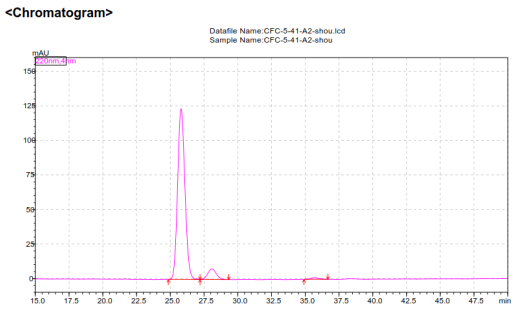
(*2S,3S*)-2-(Benzofuran-3-yl)-2-methyl-3-phenylbutane-1,3-diol (7c-oxi). Yield: (43.0 mg, 92%); **IR (neat):** 3234 (br), 3003 (m), 2949(w), 1492 (m), 1448 (s), 1338 (m), 1286 (m), 1231 (m), 1171 (m), 1079 (m), 1022 (s), 1013 (s), 913 (s), 856 (m), 804 (m), 765 (m), 739 (s), 702 (s), 638 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43 (d, *J* = 8.4 Hz, 1H), 7.29 - 7.08 (m, 8H), 7.02 (t, *J* = 7.6 Hz, 1H), 4.11 - 3.91 (m, 2H), 3.15 (s, 1H), 2.83 (s, 1H), 1.72 (s, 3H), 1.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.0, 144.8, 143.9, 127.4, 127.2, 126.9, 123.7, 122.7, 122.2, 122.0, 111.4, 79.9, 68.5, 47.5, 26.1, 19.2; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for : $C_{19}H_{24}NO_3$: 314.1751 m/z, found: 314.1749 m/z;

Enantiomeric purity of **7c-oxi** was determined by HPLC analysis in comparison with authentic racemic material (92:8 d.r., >99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	25.978	15576885	414022	35.581	35.581
2	28.232	6212180	141938	14.190	14.190
3	35.968	6176425	114274	14.108	14.108
4	38.364	15812581	262485	36.120	36.120
Total		43778071	932719	100.000	



<Peak Table>
PDA Ch1 220nm

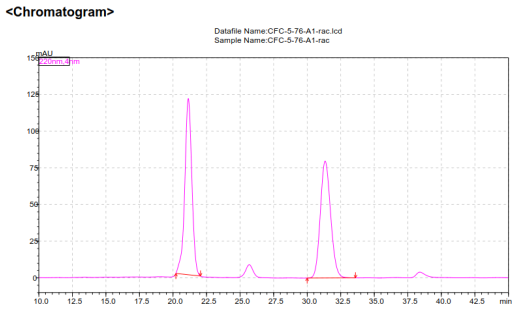
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	25.798	4653148	123591	91.959	0.000
2	28.082	349455	7736	6.906	0.000
3	35.715	57439	1143	1.135	0.000
Total		5060042	132470	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	25.978	35.581	1	25.798	91.959
2	28.232	14.190	2	28.082	6.906
3	35.968	14.108	3	35.715	1.135
4	38.364	36.120	4		

(*4S,5S*)-4,5-Dimethyl-5-phenyl-4-(5-phenylfuran-2-yl)-1,2-oxaborolan-2-ol (7d). Yield: (65.1 mg, 98%); **IR (neat):** 3363 (br), 2962 (m), 2926 (m), 1539 (w), 1445 (m), 1425 (m), 1399 (s), 1260 (s), 1209 (m), 1088 (m), 1067 (m), 1022 (s), 958 (m), 904 (m), 855 (m), 797 (s), 757 (s), 693 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 - 7.45 (m, 2H), 7.36 - 7.27 (m, 3H), 7.24 - 7.18 (m, 1H), 7.15 - 7.09 (m, 4H), 6.31 (d, *J* = 3.4 Hz, 1H), 5.76 (d, *J* = 3.4 Hz, 1H), 1.83 (s, 3H), 1.61 (s, 3H), 1.61 (d, *J* = 16.4 Hz, 1H), 1.28 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 158.6, 151.9, 144.0, 130.9, 128.4, 127.4, 126.8, 126.5, 124.4, 123.3, 107.5, 105.1, 89.6, 50.2, 24.7, 22.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{21}H_{22}BO_3$: 332.1693 m/z, found: 332.1698 m/z.

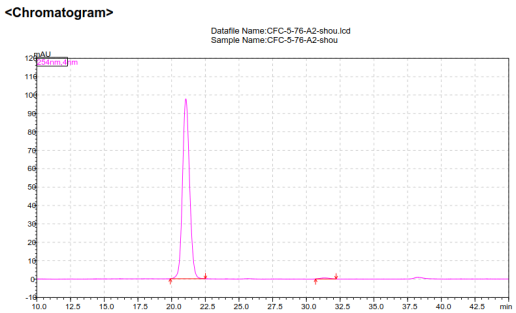
(*2S,3S*)-2-Methyl-3-phenyl-2-(5-phenylfuran-2-yl)butane-1,3-diol (7d-oxi). Yield: (49.2 mg, 78%); **IR (neat):** 3246(br), 2983 (w), 2935 (w), 1587 (w), 1478 (m), 1441 (s), 1374 (m), 1277 (m), 1244 (m), 1143 (m), 1059 (m), 1022 (s), 962 (s), 914 (m), 790 (m), 757 (s), 691 (s), 655 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.17 (m, 4H), 7.15 – 7.09 (m, 2H), 6.55 (d, *J* = 3.4 Hz, 1H), 6.00 (d, *J* = 3.4 Hz, 1H), 3.94 (d, *J* = 11.0 Hz, 1H), 3.81 (d, *J* = 11.0 Hz, 1H), 3.49 (s, 1H), 2.85 (s, 1H), 1.72 (s, 3H), 1.53 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.1, 152.4, 144.9, 130.7, 128.6, 127.1, 127.0, 126.8, 126.4, 123.5, 109.8, 105.4, 79.8, 67.7, 48.4, 26.0, 17.7; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{21}H_{26}NO_3$: 340.1907 m/z, found: 340.1901 m/z; Specific rotation: $[\alpha]_D^{20}$ -46.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **7d-oxi** was determined by HPLC analysis in comparison with authentic racemic material (99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	21.140	4407718	120093	50.772	0.000
2	31.339	4273746	79671	49.228	0.000
Total		8681464	199764	100.000	



<Peak Table>
PDA Ch1 254nm

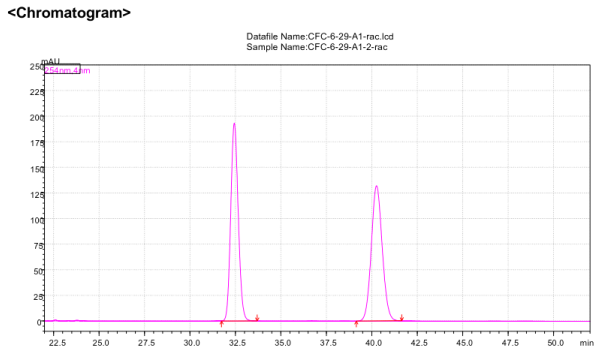
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	21.054	3572157	97721	99.284	0.000
2	31.316	25762	548	0.716	0.000
Total		3597919	98270	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	21.140	50.772	1	21.054	99.284
2	31.339	49.228	2	31.316	0.716

(*4S,5S*)-4-(5-(3,4-Dimethoxyphenyl)furan-2-yl)-4,5-dimethyl-5-phenyl-1,2-oxaborolan-2-ol (7e). Yield: (56.4 mg, 72%); **IR (neat):** 3343 (br), 2963 (w), 2922 (w), 1578 (w), 1432 (m), 1402 (m), 1376 (s), 1243 (s), 1201 (m), 1088 (m), 1034 (m), 1004 (m), 934 (m), 904 (s), 846 (m), 803 (m), 750 (s), 696 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.13 - 6.97 (m, 6H), 6.90 (d, *J* = 1.6 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.17 (d, *J* = 3.2 Hz, 1H), 5.88 (s, 1H), 5.74 (d, *J* = 3.2 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 1.76 (s, 3H), 1.63 - 1.53 (m, 4H), 1.26 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 158.0, 151.8, 148.9, 148.1, 144.2, 127.3, 126.4, 124.4, 124.3, 116.0, 111.2, 107.3, 106.8, 103.7, 89.4, 55.9, 55.8, 50.3, 24.6, 22.5; **HRMS (ESI$^+$) [M+NH$_4$]$^+$:** Calcd for: $C_{23}H_{29}BNO_2$: 409.2170 m/z, found: 409.2164 m/z. Specific rotation: $[\alpha]_D^{20}$ 32.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

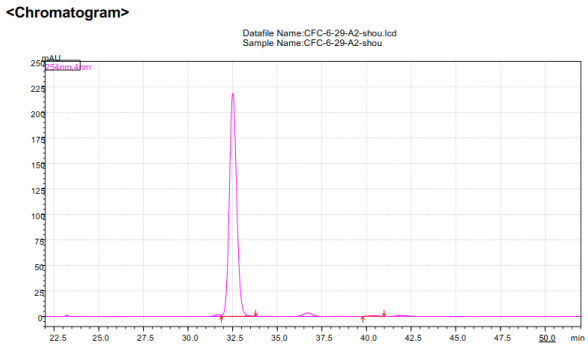
(*2S,3S*)-2-(5-(3,4-Dimethoxyphenyl)furan-2-yl)-2-methyl-3-phenylbutane-1,3-diol (7e-oxi). Yield: (48.4 mg, 88%); **IR (neat):** 3334 (br), 2934 (w), 2835 (w), 1596 (w), 1539 (m), 1501 (s), 1442 (m), 1379 (m), 1270 (m), 1247 (s), 1217 (s), 1172 (m), 1138 (s), 1069 (m), 1021 (s), 955 (m), 908 (m), 847 (m), 783 (m), 701 (m), 664 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.22 - 7.14 (m, 3H), 7.12 - 7.06 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 1H), 6.87 - 6.78 (m, 2H), 6.40 (d, *J* = 3.2 Hz, 1H), 6.02 (d, *J* = 3.2 Hz, 1H), 3.95 (d, *J* = 10.8 Hz, 1H), 3.86 (s, 4H), 3.84 (s, 3H), 3.75 (d, *J* = 10.8 Hz, 1H), 3.65 (s, 1H), 3.03 (s, 1H), 1.67 (s, 3H), 1.51 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 155.4, 152.2, 148.9, 148.4, 145.1, 127.1, 126.6, 126.4, 124.0, 116.2, 111.2, 109.7, 106.9, 104.0, 79.8, 67.6, 55.9, 48.2, 25.8, 17.7; **HRMS (ESI$^+$) [M+NH$_4$]$^+$:** Calcd for: $C_{23}H_{30}NO_5$: 400.2118 m/z, found: 400.2112 m/z; Specific rotation: $[\alpha]_D^{20}$ -10.6 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **7e-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel IC column, 90:10 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	32.436	5546061	193159	50.123	0.000
2	40.258	5518658	131919	49.874	0.000
Total		11064718	325078	100.000	



<Peak Table>
PDA Ch1 254nm

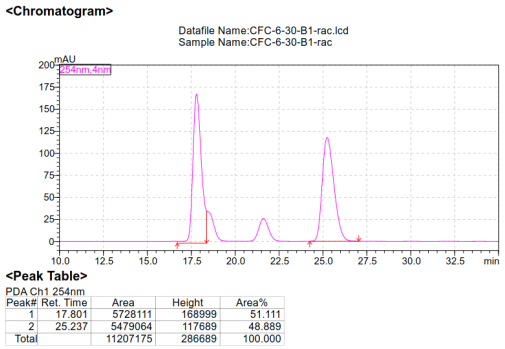
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	32.509	6212210	218464	99.600	0.000
2	40.432	21779	570	0.400	0.000
Total		6233989	219034	100.000	

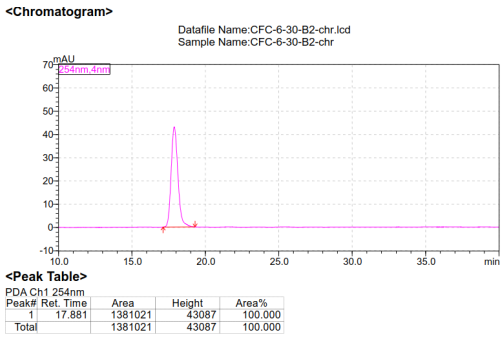
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	32.436	50.123	1	32.509	99.600
2	40.258	49.874	2	40.432	0.400

(*4S,5S*)-4,5-Dimethyl-5-phenyl-4-(5-(4-(trifluoromethyl)phenyl)furan-2-yl)-1,2-oxaborolan-2-ol (7f). Yield: (63.2 mg, 79%); **IR (neat):** 3347 (br), 2979 (w), 2922 (w), 1617 (m), 1544 (w), 1424 (m), 1399 (m), 1320 (s), 1276 (s), 1163 (m), 1107 (s), 1070 (s), 1025 (m), 1014 (m), 955 (m), 903 (m), 880 (m), 839 (m), 757 (s), 697 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.49 (q, *J* = 8.6 Hz, 4H), 7.40 - 7.34 (m, 1H), 7.16 - 7.07 (m, 4H), 6.39 (d, *J* = 3.4 Hz, 1H), 6.14 (s, 1H), 5.80 (d, *J* = 3.4 Hz, 1H), 1.79 (s, 3H), 1.60 (d, *J* = 16.4 Hz, 4H), 1.60 (s, 3H), 1.31 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.9, 150.5, 143.9, 133.9, 132.8 (q, *J* = 32.0 Hz), 127.5, 126.7, 125.5 (q, *J* = 3.8 Hz), 124.3, 123.5 (q, *J* = 271.6 Hz), 123.2, 107.9, 107.2, 89.7, 50.4, 24.7, 22.5; **^{19}F NMR (376 MHz, $CDCl_3$): δ** -62.4; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{22}H_{21}BF_3O_3$: 400.1567 m/z, found: 400.1560 m/z.

(*2S,3S*)-2-Methyl-3-phenyl-2-(5-(4-(trifluoromethyl)phenyl)furan-2-yl)butane-1,3-diol (7f-oxi). Yield: (34.5 mg, 56%); **IR (neat):** 3342 (br), 2982 (w), 2943 (w), 1617 (m), 1539 (m), 1495 (s), 1447 (m), 1377 (m), 1321 (s), 1211 (m), 1163 (s), 1108 (s), 1071 (m), 1024 (m), 947 (m), 908 (m), 839 (m), 788 (m), 701 (m), 652 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.24 - 7.16 (m, 3H), 7.15 - 7.06 (m, 2H), 6.66 (d, *J* = 3.2 Hz, 1H), 6.09 (d, *J* = 3.2 Hz, 1H), 3.99 (d, *J* = 10.8 Hz, 1H), 3.79 (d, *J* = 11.0 Hz, 1H), 3.58 (s, 1H), 3.06 (s, 1H), 1.71 (s, 3H), 1.54 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.4, 140.8, 134.9, 123.7, 118.7 (q, *J* = 32.2 Hz), 117.2, 116.9, 116.3, 115.6 (q, *J* = 3.8 Hz), 115.5, 114.4 (q, *J* = 272.0 Hz), 113.4, 100.1, 97.4, 69.8, 57.7, 38.3, 15.9, 7.7; **^{19}F NMR (376 MHz, $CDCl_3$): δ** -62.5; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for : $C_{22}H_{25}F_3NO_3$: 408.1781 m/z, found: 408.1781 m/z; Specific rotation: $[\alpha]_D^{20}$ -33.5 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **7f-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



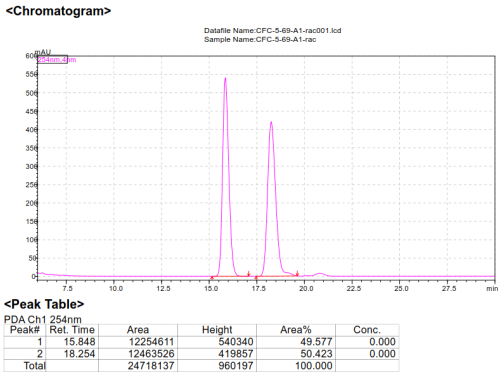


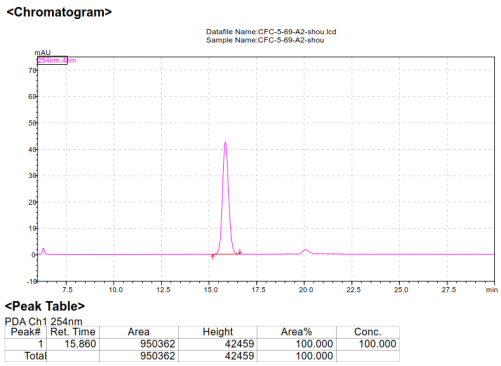
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	17.801	51.111	1	17.881	>99.000
2	25.237	48.889	2		<1.000

(*4S,5S*)-4,5-Dimethyl-5-phenyl-4-(5-phenylthiophen-2-yl)-1,2-oxaborolan-2-ol (7g). Yield: (68.2 mg, 98%); **IR (neat):** 3339 (br), 2972 (w), 2930 (w), 1598 (w), 1444 (m), 1421 (m), 1396 (s), 1265 (s), 1211 (m), 1096 (m), 1056 (m), 1027 (m), 952 (m), 904 (s), 848 (m), 803 (m), 752 (s), 694 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 7.0 Hz, 1H), 7.16 - 7.09 (m, 3H), 7.08 - 7.01 (m, 2H), 6.94 (d, *J* = 3.6 Hz, 1H), 6.42 (d, *J* = 3.6 Hz, 1H), 1.82 (s, 3H), 1.74 - 1.66 (m, 4H), 1.34 (d, *J* = 16.6 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.2, 143.6, 142.2, 134.4, 128.7, 127.3, 127.0, 126.6, 125.4, 125.2, 124.9, 122.1, 89.9, 51.5, 26.2, 24.3; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{21}H_{22}BO_2S$: 348.1464 m/z, found: 348.1467 m/z.

(*2S,3S*)-2-Methyl-3-phenyl-2-(5-phenylthiophen-2-yl)butane-1,3-diol (7g-oxi). Yield: (55.6 mg, 84%); **IR (neat):** 3175 (br), 2942 (w), 2881 (w), 1595 (w), 1491 (m), 1460 (s), 1376 (m), 1272 (m), 1236 (m), 1161 (m), 1092 (m), 1059 (m), 1032 (s), 954 (m), 910 (m), 820 (m), 753 (s), 700 (s), 687 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.29 - 7.20 (m, 4H), 7.19 - 7.13 (m, 2H), 7.08 (d, *J* = 3.8 Hz, 1H), 6.41 (d, *J* = 3.8 Hz, 1H), 3.93 (d, *J* = 10.8 Hz, 1H), 3.87 (d, *J* = 10.8 Hz, 1H), 3.66 (s, 1H), 3.34 (s, 1H), 1.73 (s, 3H), 1.54 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 145.6, 144.4, 142.7, 134.3, 128.8, 127.3, 127.1, 127.1, 127.0, 127.0, 125.5, 121.8, 79.9, 69.5, 49.3, 25.7, 20.8; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for : $C_{21}H_{26}NO_2S$: 356.1679 m/z, found: 356.1676 m/z; Specific rotation: $[\alpha]_D^{20}$ 6.27 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **7g-oxi** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel OZ-H column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



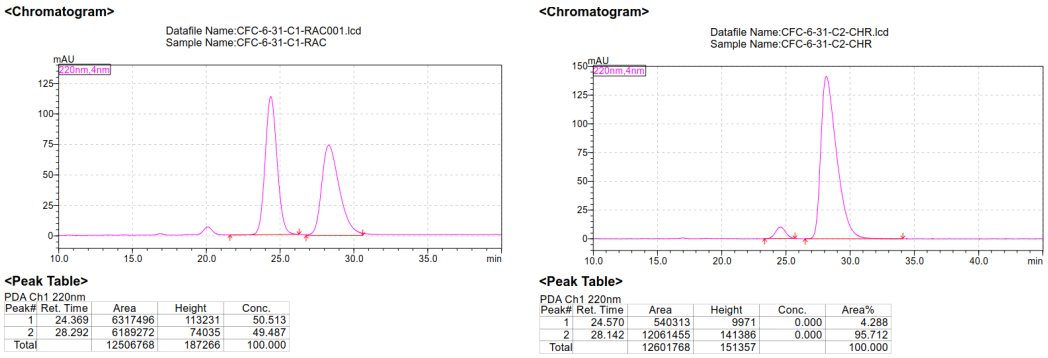


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	15.848	49.577	1	15.860	>99.000
2	18.254	50.423	2		<1.000

***tert*-Butyl 3-((*4R,5S*)-2-hydroxy-4,5-dimethyl-5-phenyl-1,2-oxaborolan-4-yl)-1H-indole-1-carboxylate (7h). Yield:** (66.4 mg, 82%); **IR (neat):** 3343 (br), 2966 (w), 2910 (w), 1723 (s), 1545 (w), 1456 (m), 1434 (m), 1406 (s), 1345 (m), 1301 (s), 1267 (m), 1130 (s), 1102 (m), 1038 (m), 1010 (m), 945 (w), 902 (m), 843 (m), 732 (s), 689 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.20 (d, *J* = 8.2 Hz, 1H), 7.49 (s, 1H), 7.38 - 7.28 (m, 6H), 7.13 - 7.05 (m, 1H), 6.99 - 6.91 (m, 1H), 5.89 (s, 1H), 2.26 (d, *J* = 16.4 Hz, 1H), 1.70 (s, 9H), 1.63 (s, 3H), 1.54 (s, 3H), 1.26 (d, *J* = 16.4 Hz, 1H);**^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.7, 143.4, 129.6, 127.4, 127.0, 126.3, 125.3, 125.0, 124.9, 123.8, 123.2, 121.7, 115.1, 89.5, 83.8, 49.4, 28.2, 27.4, 26.8; **HRMS (ESI^+) $[M+NH_4]^+$:** Calcd for: $C_{24}H_{32}BN_2O_4$: 422.2486 m/z, found: 422.2481 m/z.

***tert*-Butyl 3-((*2S,3S*)-1,3-dihydroxy-2-methyl-3-phenylbutan-2-yl)-1H-indole-1-carboxylate (7h-oxi). Yield:** (38.9 mg, 60%); **IR (neat):** 3378 (br), 2965 (m), 2913 (m), 1714 (s), 1565 (m), 1433 (m), 1401 (m), 1356 (s), 1326 (s), 1245 (m), 1136 (m), 1102 (s), 1031 (m), 1001 (s), 941 (m), 875 (m), 837 (m), 743 (s), 688 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.16 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.35 (d, *J* = 6.4 Hz, 2H), 7.27 - 7.19 (m, 4H), 7.11 (t, *J* = 7.8 Hz, 1H), 4.27 (d, *J* = 11.0 Hz, 1H), 3.91 (d, *J* = 11.0 Hz, 1H), 2.61 (s, 1H), 2.02 (s, 1H), 1.66 (s, 9H), 1.62 (s, 3H), 1.47 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.6, 144.6, 135.6, 130.2, 127.3, 126.9, 126.9, 126.1, 123.9, 122.6, 122.4, 121.9, 115.1, 83.9, 79.3, 67.8, 49.1, 28.2, 26.9, 20.2; **HRMS (ESI^+) $[M+NH_4]^+$:** Calcd for: $C_{24}H_{33}N_2O_4$: 413.2435 m/z, found: 413.2431 m/z. Specific rotation: $[\alpha]_D^{20}$ -3.7 (*c* 0.50, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

Enantiomeric purity of **7h-oxi** was determined by HPLC analysis in comparison with authentic racemic material (96:4 e.r. shown; Chiralcel OZ-H column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).

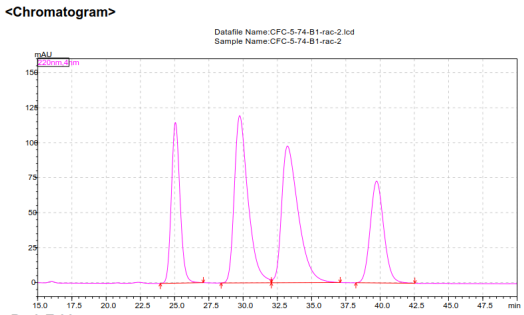


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	24.369	50.513	1	24.570	4.288
2	28.292	49.487	2	28.142	95.712

***tert*-Butyl 4-((*4R,5S*)-2-hydroxy-4,5-dimethyl-5-phenyl-1,2-oxaborolan-4-yl)-1H-indole-1-carboxylate (7i). Yield:** (66.5 mg, 82%); **IR (neat):** 3357 (br), 2977 (w), 2933 (w), 1731 (s), 1542 (w), 1477 (m), 1452 (m), 1412 (s), 1372 (m), 1345 (s), 1283 (m), 1149 (s), 1118 (m), 1048 (m), 1030 (m), 945 (w), 900 (m), 850 (m), 755 (s), 699 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07 (d, *J* = 8.0 Hz, 1H), 7.56 - 7.47 (m, 1H), 7.30 (s, 1H), 7.05 - 6.95 (m, 2H), 6.95 - 6.81 (m, 3H), 6.74 - 6.66 (m, 2H), 6.13 (s, 1H), 1.97 (d, *J* = 16.0 Hz, 1H), 1.91 (s, 3H), 1.83 (s, 3H), 1.68 (s, 9H), 1.13 (d, *J* = 16.0 Hz, 1H);**^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.6, 143.8, 137.4, 129.1, 126.9, 126.2, 125.3, 124.6, 123.5, 122.7, 113.8, 108.6, 90.0, 83.6, 54.4, 28.2, 26.3, 25.7; **HRMS (ESI^+) $[M+H]^+$:** Calcd for: $C_{24}H_{29}BNO_4$: 405.2220 m/z, found: 405.2215 m/z.

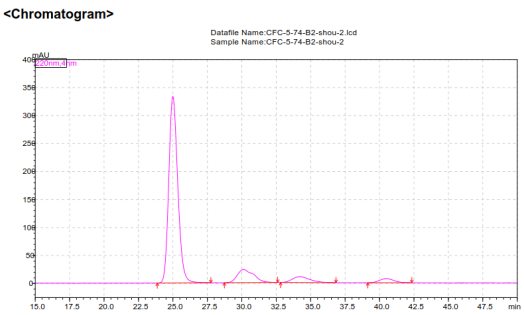
***tert*-Butyl 4-((*2S,3S*)-1,3-dihydroxy-2-methyl-3-phenylbutan-2-yl)-1H-indole-1-carboxylate (7i-oxi). Yield:** (53.1 mg, 82%); **IR (neat):** 3368 (br), 2977 (m), 2929 (m), 1728 (s), 1598 (m), 1477 (m), 1448 (m), 1413 (s), 1344 (s), 1316 (s), 1283 (m), 1154 (m), 1128 (s), 1048 (m), 1026 (s), 921 (m), 886 (m), 851 (m), 755 (s), 701 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.19 (d, *J* = 8.4 Hz, 1H), 7.47 (d, *J* = 3.8 Hz, 1H), 7.20 - 7.09 (m, 4H), 7.01 (d, *J* = 7.0 Hz, 2H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.42 (d, *J* = 3.8 Hz, 1H), 4.30 (d, *J* = 11.0 Hz, 1H), 4.05 (d, *J* = 8.0 Hz, 1H), 2.85 (s, 1H), 2.31 (s, 1H), 1.73 (s, 3H), 1.67 (s, 9H), 1.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 149.5, 144.8, 136.0, 134.6, 130.4, 127.0, 126.9, 126.7, 125.0, 124.3, 123.5, 114.2, 108.9, 83.6, 79.7, 68.7, 52.6, 28.1, 26.2, 21.2; **HRMS (ESI^+) $[M+NH_4]^+$:** Calcd for: $C_{24}H_{33}N_2O_4$: 413.2435 m/z, found: 413.2431 m/z.

Enantiomeric purity of **7i-oxi** was determined by HPLC analysis in comparison with authentic racemic material (84.5:15.5 d.r. , 97:3 e.r. shown; Chiralcel IC column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	25.057	5045155	114805	18.917	0.000
2	29.748	8324547	119521	31.214	0.000
3	33.239	8284761	97718	31.065	0.000
4	39.743	5014958	72756	18.804	0.000
Total		26669421	404801	100.000	



<Peak Table>
PDA Ch1 220nm

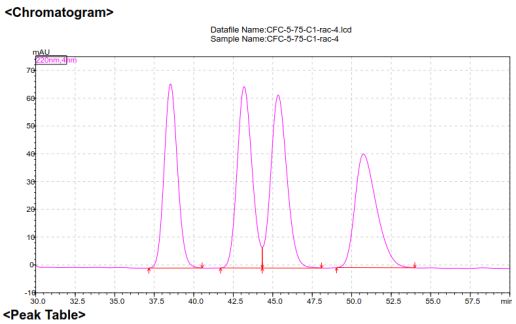
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	24.995	15133174	333044	81.592	81.592
2	30.127	1945142	23443	10.487	10.487
3	34.201	927985	10484	5.003	5.003
4	40.473	540975	7421	2.917	2.917
Total		18547277	374393	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	25.057	18.917	1	24.995	81.592
2	29.748	31.214	2	30.127	10.487
3	33.239	31.065	3	34.201	5.003
4	39.743	18.804	4	40.473	2.917

(*4S,5S*)-4-(Dibenzo[*b,d*]furan-3-yl)-4,5-dimethyl-5-phenyl-1,2-oxaborolan-2-ol (7j). Yield: (49.8 mg, 70%); **IR (neat):** 3355 (br), 3058 (w), 2975 (w), 1600 (w), 1479 (m), 1448 (m), 1422 (m), 1398 (s), 1378 (m), 1302 (m), 1283 (m), 1199 (s), 1129 (m), 1061 (m), 1022 (m), 903 (m), 842 (m), 748 (s), 699 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.83 (d, *J* = 7.6 Hz, 1H), 7.59 (s, 1H), 7.52 - 7.44 (m, 2H), 7.35 - 7.27 (m, 2H), 7.22 (d, *J* = 8.8 Hz, 1H), 6.99 - 6.91 (m, 3H), 6.85 - 6.77 (m, 2H), 1.85 (d, *J* = 16.4 Hz, 1H), 1.85 (s, 3H), 1.75 (s, 3H), 1.30 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.4, 154.5, 143.7, 139.4, 127.1, 126.8, 126.4, 126.3, 125.2, 124.3, 123.2, 122.5, 120.4, 118.8, 111.5, 110.1, 90.1, 52.5, 26.0, 24.7; **HRMS (ESI^+) $[M+H]^+$:** Calcd for: $C_{23}H_{22}BO_3$: 356.1693 m/z, found: 356.1695 m/z.

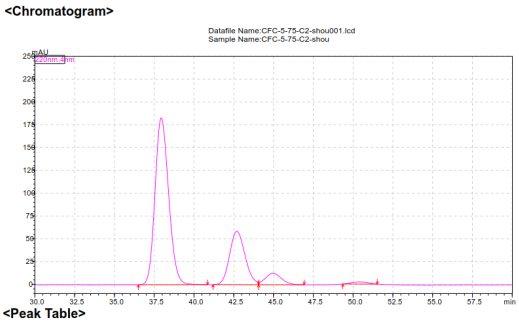
(*2S,3S*)-2-(Dibenzo[*b,d*]furan-3-yl)-2-methyl-3-phenylbutane-1,3-diol (7j-oxi). Yield: (41.4 mg, 83%); **IR (neat):** 3215 (br), 2978 (w), 2923 (w), 1589 (w), 1475 (m), 1447 (s), 1372 (m), 1313 (m), 1249 (m), 1198 (s), 1128 (m), 1063 (m), 1019 (s), 922 (m), 842 (m), 810 (m), 747 (s), 701 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.85 - 7.79 (m, 1H), 7.60 - 7.55 (m, 2H), 7.47 - 7.41 (m, 2H), 7.36 - 7.31 (m, 2H), 7.21 - 7.14 (m, 3H), 6.99 (d, *J* = 7.4 Hz, 2H), 4.21 - 4.16 (m, 1H), 3.94 (d, *J* = 11.0 Hz, 1H), 3.30 (s, 1H), 3.03 (s, 1H), 1.68 (s, 3H), 1.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.4, 154.8, 144.7, 136.1, 127.8, 127.2, 127.1, 127.0, 126.9, 124.3, 123.2, 122.6, 120.8, 120.4, 111.6, 110.1, 79.9, 68.9, 49.6, 25.8, 19.6; **HRMS (ESI^+) $[M+NH_4]^+$:** Calcd for: $C_{23}H_{26}NO_3$: 364.1907 m/z, found: 364.1906 m/z.

Enantiomeric purity of **7j-oxi** was determined by HPLC analysis in comparison with authentic racemic material (69.5:30.5 d.r. , 97.5:2.5 e.r. shown; Chiralcel IG column, 96:4 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	38.530	3895951	66268	23.583	23.583
2	43.190	4296826	65256	26.010	26.010
3	45.343	4412943	62262	26.712	26.712
4	50.748	3914469	40944	23.695	23.695
Total		16520190	234730	100.000	



<Peak Table>
PDA Ch1 220nm

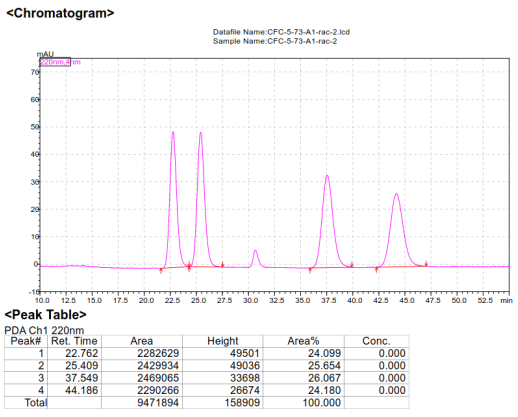
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	37.943	10909842	182902	68.391	0.000
2	42.693	3969362	58679	24.883	0.000
3	44.970	899800	12639	5.641	0.000
4	50.400	173077	2307	1.085	0.000
Total		15952082	256526	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	38.530	23.583	1	37.943	68.391
2	43.190	26.010	2	42.693	24.883
3	45.343	26.712	3	44.970	5.641
4	50.748	23.695	4	50.400	1.085

***tert*-Butyl 2-((*4S,5S*)-2-hydroxy-4,5-dimethyl-5-phenyl-1,2-oxaborolan-4-yl)-9H-carbazole-9-carboxylate (7k). Yield:** (67.3 mg, 74%); **IR (neat):** 3399 (br), 2974 (w), 2932 (w), 1722 (s), 1622 (w), 1496 (m), 1458 (m), 1422 (m), 1396 (s), 1356 (s), 1334 (s), 1285 (m), 1225 (m), 1142 (s), 1117 (m), 1047 (m), 1006 (m), 903 (m), 840 (m), 758 (s), 747 (s), 699 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.38 - 8.32 (m, 1H), 8.03 - 7.92 (m, 2H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.47 - 7.30 (m, 4H), 7.00 - 6.92 (m, 2H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.27 (s, 1H), 1.86 (d, *J* = 16.4 Hz, 1H), 1.86 (s, 3H), 1.76 (s, 3H), 1.73 (s, 9H), 1.24 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.0, 143.8, 138.9, 138.1, 127.4, 127.0, 126.7, 126.4, 126.2, 125.3, 123.7, 122.8, 122.1, 119.4, 118.2, 116.2, 115.2, 90.0, 83.5, 53.2, 28.3, 25.9, 24.5; **HRMS (ESI^+) $[M+H]^+$:** Calcd for: $C_{28}H_{31}BNO_4$: 455.2377 m/z, found: 455.2373 m/z.

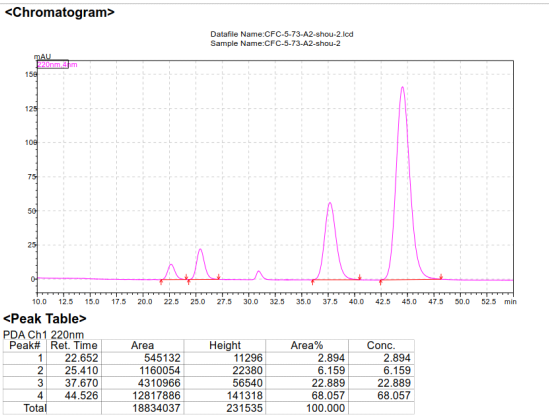
***tert*-Butyl 2-((*2S,3S*)-1,3-dihydroxy-2-methyl-3-phenylbutan-2-yl)-9H-carbazole-9-carboxylate (7k-oxi). Yield:** (52.7 mg, 80%); **IR (neat):** 3339 (br), 2977 (w), 2930 (w), 1722 (s), 1623 (w), 1496 (m), 1457 (s), 1421 (m), 1355 (s), 1335 (s), 1309 (m), 1255 (m), 1154 (s), 1141 (s), 1118 (m), 1046 (m), 1025 (s), 938 (m), 836 (m), 820 (m), 747 (s), 702 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.40 (d, *J* = 8.4 Hz, 1H), 8.00 - 7.91 (m, 2H), 7.80 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.23 - 7.10 (m, 4H), 6.96 (d, *J* = 7.4 Hz, 2H), 4.19 (d, *J* = 11.0 Hz, 1H), 3.95 (d, *J* = 11.0 Hz, 1H), 3.45 (s, 1H), 3.06 (s, 1H), 1.72 (s, 3H), 1.70 (s, 3H), 1.67 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 150.9, 144.7, 140.8, 139.0, 137.7, 127.1, 127.0, 126.9, 126.7, 125.3, 124.2, 123.6, 123.0, 119.4, 118.2, 116.8, 116.3, 83.6, 80.0, 68.6, 50.1, 28.2, 25.9, 19.4; **HRMS (ESI^+) $[M+NH_4]^+$:** Calcd for: $C_{28}H_{35}N_2O_4$: 463.2591 m/z, found: 463.2585 m/z.

Enantiomeric purity of **7k-oxi** was determined by HPLC analysis in comparison with authentic racemic material (71:29 d.r., 96:4 e.r. shown; Chiralcel IC column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	22.762	2282629	49501	24.099	0.000
2	25.409	2429934	49036	25.654	0.000
3	37.549	2469065	33698	26.067	0.000
4	44.186	2290266	26674	24.180	0.000
Total		9471894	158909	100.000	



<Peak Table>
PDA Ch1 220nm

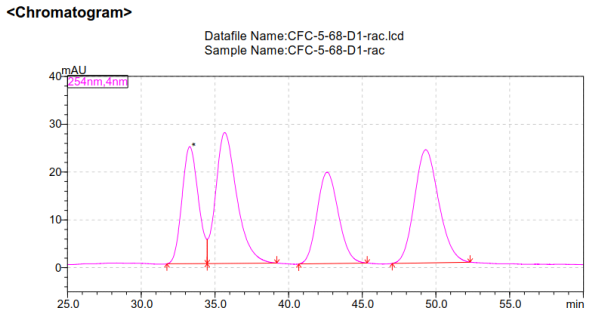
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	22.652	545132	11296	2.894	2.894
2	25.410	1160054	22380	6.159	6.159
3	37.670	4310966	56540	22.889	22.889
4	44.526	12817886	141318	68.057	68.057
Total		18834037	231535	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	22.762	24.099	1	22.652	2.894
2	25.409	25.654	2	25.410	6.159
3	37.549	26.067	3	37.670	22.899
4	44.186	24.180	4	44.526	68.057

***tert*-Butyl 3-((*4S,5S*)-2-hydroxy-4,5-dimethyl-5-phenyl-1,2-oxaborolan-4-yl)-9H-carbazole-9-carboxylate (7l). Yield:** (62.8 mg, 69%); **IR (neat):** 3378 (br), 2954 (w), 2912 (w), 1710 (s), 1598 (m), 1478 (m), 1446 (m), 1421 (m), 1367 (s), 1321 (s), 1267 (m), 1212 (m), 1130 (s), 1110 (m), 1041 (m), 903 (m), 843 (m), 756 (s), 678 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.28 (d, *J* = 8.4 Hz, 1H), 8.01 - 7.88 (m, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.55 - 7.40 (m, 1H), 7.40 - 7.25 (m, 3H), 7.14 (d, *J* = 7.4 Hz, 1H), 6.99 - 6.90 (m, 2H), 6.90 - 6.78 (m, 2H), 5.96 (s, 1H), 1.85 (s, 3H), 1.82 - 1.78 (m, 4H), 1.74 (s, 9H), 1.28 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.1, 143.8, 139.7, 138.7, 136.7, 127.1, 126.8, 126.4, 125.3, 122.8, 119.3, 118.0, 116.2, 114.9, 90.1, 83.8, 52.5, 28.4, 26.0, 24.8; **HRMS (ESI$^+$) $[M+H]^+$:** Calcd for: $C_{28}H_{31}BNO_4$: 455.2377 m/z, found: 455.2373 m/z.

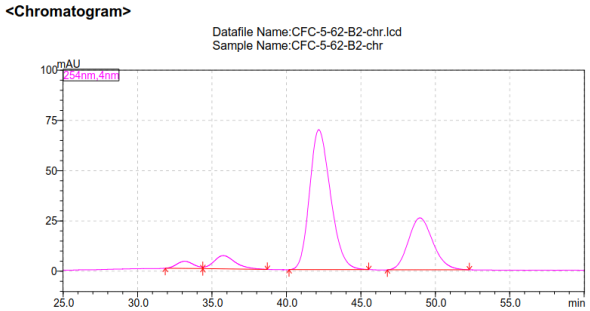
***tert*-Butyl 3-((2S,3S)-1,3-dihydroxy-2-methyl-3-phenylbutan-2-yl)-9H-carbazole-9-carboxylate (7l-oxi). Yield:** (52.2 mg, 85%); **IR (neat):** 3324 (br), 3013 (w), 2956 (w), 1734 (s), 1587 (w), 1478 (m), 1445 (s), 1412 (m), 1336 (s), 1306 (m), 1251 (m), 1154 (s), 1124 (m), 1078 (m), 1025 (s), 910 (m), 824 (m), 756 (s), 698 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.30 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H), 7.51 – 7.44 (m, 2H), 7.40 – 7.29 (m, 2H), 7.20 – 7.13 (m, 3H), 7.01 (d, *J* = 7.4 Hz, 2H), 4.24 – 4.20 (m, 1H), 3.94 – 3.92 (m, 1H), 3.34 (s, 1H), 3.01 (s, 1H), 1.76 (s, 9H), 1.69 (s, 3H), 1.62 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 151.1, 143.8, 139.7, 138.7, 136.7, 127.1, 126.8, 126.4, 125.3, 122.8, 119.3, 118.0, 116.2, 114.9, 90.1, 83.8, 52.5, 28.4, 26.0, 24.8; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for: $C_{28}H_{35}N_2O_4$: 463.2591 m/z, found: 463.2585 m/z.

Enantiomeric purity of **7l-oxi** was determined by HPLC analysis in comparison with authentic racemic material (66:34 d.r., 96:4 e.r. shown; Chiralcel OZ-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	33.289	1892681	24480	20.408
2	35.663	2732673	27382	29.465
3	42.607	1920504	19112	20.708
4	49.310	2728566	23682	29.420
Total		9274424	94656	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	33.152	282962	3574	2.639
2	35.775	667886	6637	6.229
3	42.174	6814230	69628	63.550
4	48.961	2957579	25848	27.583
Total		10722657	105687	100.000

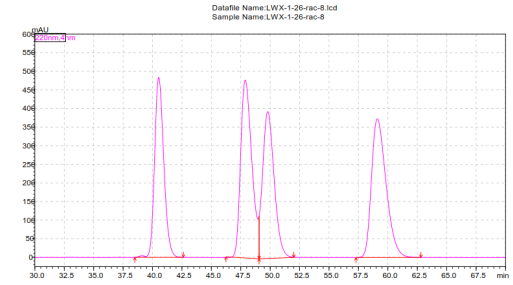
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	33.289	20.408	1	33.152	2.639
2	35.663	29.465	2	35.775	6.229
3	42.607	20.708	3	42.174	63.550
4	49.310	29.420	4	48.961	27.583

(*4S,5S*)-4,5-Dimethyl-4-(naphthalen-2-yl)-5-phenyl-1,2-oxaborolan-2-ol (7m). Yield: (57.5 mg, 91%); **IR (neat):** 3347 (br), 3056 (w), 2976 (m), 1423 (m), 1396 (m), 1298 (m), 1193 (m), 1059 (m), 1029 (m), 949 (m), 855 (m), 813 (s), 745 (s), 697 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.78 - 7.63 (m, 2H), 7.56 - 7.48 (m, 2H), 7.46 - 7.37 (m, 2H), 7.08 (d, *J* = 8.6 Hz, 1H), 7.05 - 6.90 (m, 3H), 6.87 (d, *J* = 7.4 Hz, 2H), 6.20 (s, 1H), 1.90 - 1.82 (m, 4H), 1.78 (s, 3H), 1.31 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.7, 142.3, 132.7, 131.5, 128.0, 127.1, 127.1, 126.5, 126.3, 125.6, 125.4, 125.2, 90.1, 52.6, 25.6, 24.9; **HRMS (ESI^+) $[M+H]^+$:** Calcd for: $C_{21}H_{22}BO_2$: 316.1744 m/z, found: 316.1740 m/z.

(*2S,3S*)-2-Methyl-2-(naphthalen-2-yl)-3-phenylbutane-1,3-diol (7m-oxi). Yield: (50.1 mg, 90%); **IR (neat):** 3320 (br), 2980 (m), 2934(m), 1597 (m), 1492 (s), 1444 (s), 1373 (s), 1275 (m), 1109 (m), 1022 (s), 919 (m), 868 (m), 853 (m), 758 (m), 747 (s), 701 (s), 626 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 (d, *J* = 8.4 Hz, 1H), 7.70 - 7.61 (m, 2H), 7.49 - 7.41 (m, 3H), 7.24 - 7.11 (m, 4H), 6.98 (d, *J* = 7.6 Hz, 2H), 4.18 (d, *J* = 10.8 Hz, 1H), 3.93 (d, *J* = 10.8 Hz, 1H), 3.37 (s, 1H), 3.00 (s, 1H), 1.68 (s, 3H), 1.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.7, 139.2, 132.6, 132.0, 128.1, 127.8, 127.1, 126.9, 126.8, 126.8, 126.5, 125.9, 125.8, 79.9, 68.6, 49.7, 25.9, 19.2; **HRMS (ESI^+) $[M+NH_4]^+$:** Calcd for: $C_{21}H_{26}NO_2$: 324.1958 m/z, found: 324.1955 m/z;

Enantiomeric purity of **7m-oxi** was determined by HPLC analysis in comparison with authentic racemic material (91:9 d.r., 99:1 e.r. shown; Chiralcel AD-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).

<Chromatogram>



<Peak Table>

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	40.528	26262509	483714	22.386	0.000
2	47.879	31830829	478230	27.132	0.000
3	49.792	27004253	395025	23.018	0.000
4	59.104	32219143	372818	27.463	0.000
Total		117316734	1729787	100.000	

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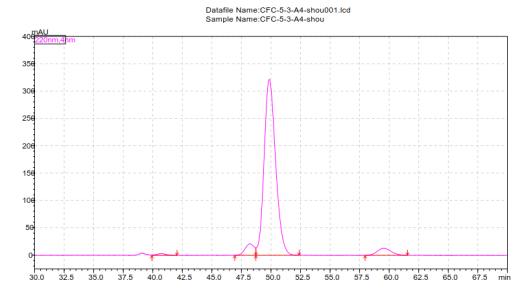


<Peak Table>

PDA Ch1 220nm

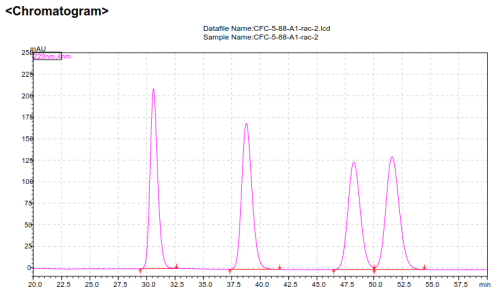
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	40.700	174493	3135	0.722	0.000
2	48.216	1139019	20866	4.716	0.000
3	49.855	21770152	321621	90.139	0.000
4	59.550	1068206	12980	4.423	0.000
Total		24151869	358603	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	40.528	23.386	1	40.700	0.722
2	47.879	27.132	2	48.216	4.716
3	49.792	23.018	3	49.855	90.139
4	59.104	27.463	4	59.550	4.423

(*4S,5S*)-4-(6-Methoxynaphthalen-2-yl)-4,5-dimethyl-5-phenyl-1,2-oxaborolan-2-ol (7n). Yield: (51.2 mg, 74%); **IR (neat):** 3337 (br), 3058 (w), 2957 (w), 1631 (w), 1603 (m), 1422 (m), 1391 (s), 1302 (m), 1264 (s), 1206 (s), 1163 (m), 1096 (m), 1029 (s), 902 (s), 887 (m), 850 (m), 758 (s), 700 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 (d, *J* = 8.8 Hz, 1H), 7.40 - 7.33 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 1H), 7.01 - 6.87 (m, 5H), 6.81 (d, *J* = 7.8 Hz, 2H), 5.88 (s, 1H), 3.87 (s, 3H), 1.81 (s, 1H), 1.81 (d, *J* = 16.4 Hz, 1H), 1.70 (s, 3H), 1.23 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.3, 143.8, 140.0, 132.6, 129.5, 128.2, 127.0, 126.3, 126.2, 126.1, 125.4, 125.4, 125.3, 118.3, 105.1, 90.0, 55.2, 52.5, 25.6, 24.9; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{22}H_{24}BO_3$: 346.1849 m/z, found: 346.1851 m/z.

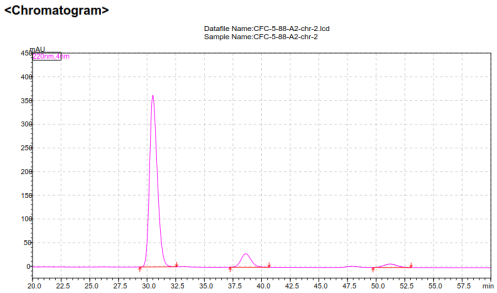
(*2S,3S*)-2-(6-Methoxynaphthalen-2-yl)-2-methyl-3-phenylbutane-1,3-diol (7n-oxi). Yield: (43.8 mg, 88%); **IR (neat):** 3292 (br), 3057 (w), 2932 (m), 2835 (w), 1630 (m), 1601 (s), 1483 (m), 1446 (m), 1391 (m), 1263 (m), 1231 (s), 1200 (m), 1164 (m), 1110 (m), 1062 (m), 1024 (s), 926 (m), 907 (m), 848 (s), 762 (m), 704 (s), 678 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 - 7.53 (m, 2H), 7.24 - 7.18 (m, 2H), 7.18 - 7.06 (m, 5H), 6.99 (d, *J* = 7.4 Hz, 2H), 4.16 (d, *J* = 11.0 Hz, 1H), 3.98 - 3.88 (m, 4H), 3.16 (s, 1H), 2.78 (s, 1H), 1.67 (s, 3H), 1.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.7, 144.7, 136.7, 133.1, 129.6, 128.1, 127.6, 127.3, 127.1, 126.9, 126.8, 125.5, 118.7, 105.0, 79.9, 68.7, 55.3, 49.6, 25.9, 19.2; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for: $C_{22}H_{28}NO_3$: 354.2064 m/z, found: 354.2061 m/z.

Enantiomeric purity of **7n-oxi** was determined by HPLC analysis in comparison with authentic racemic material (88:12 d.r., >99:1 e.r. shown; Chiralcel IC column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	30.603	9725822	209238	23.780	23.780
2	38.780	10787790	169449	26.377	26.377
3	48.247	9547221	124755	23.344	23.344
4	51.620	10837513	131197	26.499	26.499
Total		40898345	634638	100.000	



<Peak Table>
PDA Ch1 220nm

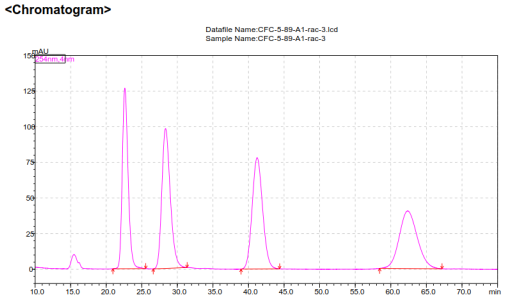
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	30.503	17121949	362171	87.889	0.000
2	38.615	1774333	28549	9.108	0.000
3	51.220	584974	7469	3.003	0.000
Total		19481257	398190	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	30.603	23.780	1	30.503	87.889
2	38.780	26.377	2	38.615	9.108
3	48.247	23.344	3		
4	51.620	26.499	4	51.220	3.003

(*4S,5S*)-4-(6-(Dibenzylamino)naphthalen-2-yl)-4,5-dimethyl-5-phenyl-1,2-oxaborolan-2-ol (7o). Yield: (83.8 mg, 82%); **IR (neat):** 3355 (br), 3058 (w), 2928 (w), 1629 (w), 1599 (m), 1495 (m), 1450 (m), 1396 (s), 1298 (m), 1272 (m), 1206 (m), 1177 (m), 1097 (m), 1047 (m), 962 (m), 900 (m), 844 (m), 758 (s), 697 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.51 (d, *J* = 9.0 Hz, 1H), 7.42 - 7.33 (m, 6H), 7.32 - 7.26 (m, 6H), 7.23 (d, *J* = 9.2 Hz, 1H), 7.05 - 6.95 (m, 3H), 6.93 - 6.83 (m, 3H), 6.19 (s, 1H), 4.74 (s, 4H), 1.89 - 1.77 (m, 4H), 1.71 (s, 3H), 1.21 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 146.9, 143.9, 138.5, 138.2, 133.1, 129.1, 128.6, 127.0, 126.9, 126.7, 126.7, 126.2, 126.0, 125.4, 125.2, 124.9, 115.7, 105.7, 90.0, 54.1, 52.3, 26.9, 25.7, 24.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{35}H_{35}BNO_2$: 512.2756 m/z, found: 512.2758 m/z.

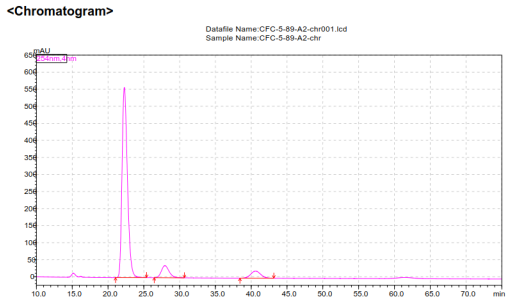
(*2S,3S*)-2-(6-(Dibenzylamino)naphthalen-2-yl)-2-methyl-3-phenylbutane-1,3-diol (7o-oxi). Yield: (65.7 mg, 80%); **IR (neat):** 3332 (br), 3026 (w), 2924 (m), 2851 (w), 1629 (m), 1598 (s), 1493 (s), 1449 (m), 1398 (m), 1357 (m), 1296 (m), 1200 (m), 1176 (m), 1110 (m), 1025 (s), 961 (m), 921 (m), 843 (m), 757 (m), 731 (s), 697 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 (d, *J* = 9.0 Hz, 1H), 7.41 - 7.36 (m, 5H), 7.36 - 7.29 (m, 7H), 7.28 - 7.19 (m, 4H), 7.07 (d, *J* = 7.0 Hz, 2H), 7.02 - 6.95 (m, 2H), 4.79 (s, 4H), 4.14 (d, *J* = 10.8 Hz, 1H), 3.90 (d, *J* = 10.8 Hz, 1H), 3.39 (s, 1H), 2.90 (s, 1H), 1.68 (s, 3H), 1.61 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 147.2, 144.8, 138.3, 134.9, 133.5, 129.3, 128.6, 127.3, 127.2, 127.1, 126.9, 126.8, 126.6, 126.0, 124.9, 115.8, 105.3, 79.8, 68.6, 54.1, 49.5, 26.9, 25.9, 19.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{35}H_{36}NO_2$: 502.2741 m/z, found: 502.2734 m/z.

Enantiomeric purity of **7o-oxi** was determined by HPLC analysis in comparison with authentic racemic material (86:14 d.r., >99:1 e.r. shown; Chiralcel OZ-H column, 94:6 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	22.616	7236834	126628	23.746	23.746
2	28.337	8115281	98124	26.628	26.628
3	41.205	7995241	78085	26.235	26.235
4	62.363	7128615	40418	23.391	23.391
Total		30475970	343254	100.000	



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	22.277	29215971	557748	86.199	0.000
2	27.946	2663841	35524	7.859	0.000
3	40.597	2013871	20934	5.942	0.000
Total		33893683	614206	100.000	

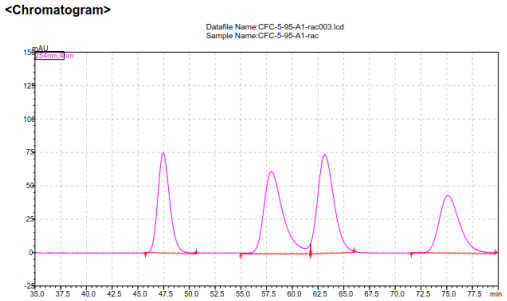
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	22.616	23.746	1	22.277	86.199
2	28.337	26.628	2	27.946	7.859
3	41.205	26.235	3	40.597	5.942
4	62.363	23.391	4		

***tert*-Butyl 4-(6-((*4S,5S*)-2-hydroxy-4,5-dimethyl-5-phenyl-1,2-oxaborolan-4-yl)naphthalen-2-yl)piperazine-1-carboxylate (7p). Yield:** (85.0 mg, 85%); **IR (neat):** 3386 (br), 2975 (m), 2931 (w), 1672 (m), 1600 (m), 1449 (s), 1392 (m), 1321 (m), 1248 (s), 1204 (m), 1161 (s), 1127 (s), 1043 (m), 981 (m), 945 (m), 882 (m), 851 (m), 758 (s), 700 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 9.0 Hz, 1H), 7.32 - 7.27 (m, 2H), 7.22 - 7.14 (m, 3H), 6.93 - 6.85 (m, 3H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.45 (s, 1H), 3.67 - 3.61 (m, 4H), 3.21 - 3.14 (m, 4H), 1.78 (s, 3H), 1.78 (d, *J* = 16.2 Hz, 1H), 1.69 (s, 3H), 1.50 (s, 9H), 1.27 (d, *J* = 16.4 Hz, 1H);**^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.7, 148.7, 144.9, 144.0, 140.5, 140.4, 132.7, 132.4, 129.0, 127.9, 127.0, 126.7, 125.3, 119.4, 110.2, 89.6, 79.9, 52.5, 49.8, 49.7, 28.4, 24.5, 24.2; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{30}H_{38}BN_2O_4$: 501.2919 m/z, found: 501.2916 m/z.

***tert*-Butyl 4-(6-((*2S,3S*)-1,3-dihydroxy-2-methyl-3-phenylbutan-2-yl)naphthalen-2-yl)piperazine-1-carboxylate (7p-oxi). Yield:** (62.5 mg, 75%); **IR (neat):** 3369 (br), 2975 (m), 2931 (m), 2818 (w), 1673 (s), 1630 (m), 1599 (m), 1479 (m), 1421 (s), 1391 (s), 1366 (s), 1284 (m), 1249 (s), 1162 (s), 1124 (s), 1067 (m), 1028 (m), 965 (m), 920 (m), 859 (m), 760 (m), 703 (s), 684 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.60 - 7.55 (m, 1H), 7.51 (d, *J* = 8.8 Hz, 1H), 7.33 (s, 1H), 7.24 – 7.18 (m, 2H), 7.17 - 7.12 (m, 2H), 7.10 - 7.04 (m, 2H), 6.99 (d, *J* = 7.6 Hz, 2H), 4.18 - 4.14 (m, 1H), 3.90 (d, *J* = 9.4 Hz, 1H), 3.67 - 3.57 (m, 4H), 3.41 (s, 1H), 3.26 - 3.16 (m, 4H), 3.00 (s, 1H), 1.66 (s, 3H), 1.59 (s, 3H), 1.50 (s, 9H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 154.7, 149.1, 144.8, 136.8, 133.0, 129.1, 127.8, 127.3, 127.2, 127.2,

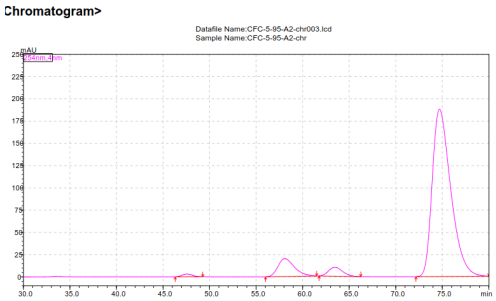
127.0, 126.8, 126.7, 125.5, 119.7, 110.0, 80.0, 79.9, 68.6, 49.6, 49.5, 28.4, 25.9, 19.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{30}H_{39}N_2O_4$: 491.2904 m/z, found: 491.2894 m/z.

Enantiomeric purity of **7p-oxi** was determined by HPLC analysis in comparison with authentic racemic material (88:12 d.r., 99:1 e.r. shown; Chiralcel OD-H column, 93:7 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	47.457	6065245	74873	21.446	0.000
2	57.967	8099312	61753	28.639	0.000
3	63.156	8127905	74171	28.740	0.000
4	75.099	5988603	43236	21.175	0.000
Total		28281065	254033	100.000	



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	47.565	244043	3197	0.821	0.000
2	58.098	2470785	20117	8.309	0.000
3	63.467	1061457	10108	3.570	0.000
4	74.701	25959366	187814	87.300	0.000
Total		29735652	221236	100.000	

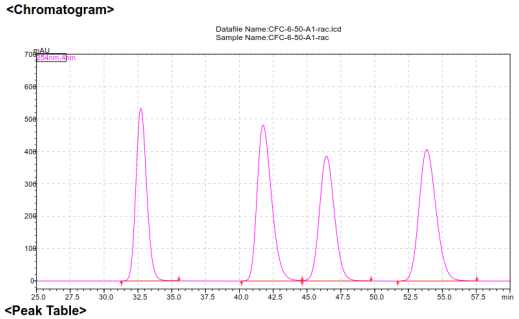
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	47.457	21.446	1	47.565	0.821
2	57.967	28.639	2	58.098	8.309
3	63.156	28.740	3	63.467	3.570
4	75.099	21.175	4	74.701	87.300

(*4S,5S*)-4-(6-(1H-pyrrol-1-yl)naphthalen-2-yl)-4,5-dimethyl-5-phenyl-1,2-oxaborolan-2-ol (7q). Yield: (75.4 mg, 99%); **IR (neat):** 3350 (br), 3058 (w), 2977 (w), 1603 (w), 1499 (m), 1424 (m), 1398 (m), 1322 (s), 1274 (m), 1142 (m), 1114 (m), 1065 (s), 1021 (m), 981 (w), 876 (m), 807 (m), 758 (m), 724 (s), 699 (s) cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.72 - 7.63 (m, 2H), 7.54 - 7.46 (m, 3H), 7.22 - 7.17 (m, 2H), 7.13 - 7.06 (m, 1H), 7.03 - 6.93 (m, 3H), 6.88 (d, *J* = 7.2 Hz, 2H), 6.42 (t, *J* = 2.0 Hz, 2H), 6.26 (s, 1H), 1.88 (s, 3H), 1.87 (d, *J* = 16.4 Hz, 1H), 1.77 (s, 1H), 1.32 (d, *J* = 16.4 Hz, 1H);**^{13}C NMR (100 MHz, CDCl$_3$):** δ 143.6, 142.2, 137.8, 131.8, 130.7, 129.6, 127.1, 126.6, 126.3, 126.2, 125.4, 125.2, 119.8, 119.4, 116.6, 110.4, 90.0, 52.6, 25.5, 24.9; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{25}H_{25}BNO_2$: 382.1973 m/z, found: 382.1970 m/z.

(*2S,3S*)-2-(6-(1H-pyrrol-1-yl)naphthalen-2-yl)-2-methyl-3-phenylbutane-1,3-diol (7q-oxi). Yield: (66.1 mg, 90%); **IR (neat):** 3331 (br), 3057 (w), 2980 (m), 1633 (m), 1602 (m), 1497 (s), 1469 (m), 1445 (m), 1370 (m), 1322 (s), 1276 (w), 1112 (m), 1065 (s), 1020 (s), 870 (m), 808 (m), 759 (m), 723 (s), 702 (s), 668 (m) cm^{-1}; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.75 - 7.69 (m, 2H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.54 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.44 (s, 1H), 7.25 - 7.12 (m, 6H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.41 (t, *J* = 2.2 Hz, 2H), 4.20 (d, *J* = 10.8 Hz, 1H), 3.93 (d, *J* = 10.8 Hz, 1H), 3.54 (s, 1H), 3.20 (s, 1H), 1.68 (s, 3H), 1.63 (s, 3H); **^{13}C NMR (100 MHz, CDCl$_3$):** δ 144.6, 139.2, 138.1, 132.3, 130.5, 129.8, 127.9, 127.6, 127.1, 126.9, 126.8, 126.1, 120.0, 119.4, 116.6,

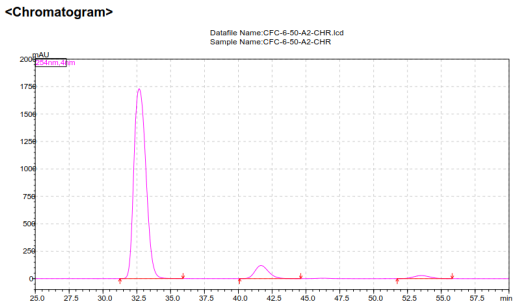
110.5, 79.9, 68.6, 49.6, 24.7, 19.2; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{25}H_{26}NO_2$: 372.1958 m/z, found: 372.1953 m/z.

Enantiomeric purity of **7q-oxi** was determined by HPLC analysis in comparison with authentic racemic material (91:9 d.r., >99:1 e.r. shown; Chiralcel IC column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	32.720	29660497	533088	22.562	0.000
2	41.757	36116584	481449	27.473	0.000
3	46.439	29825815	385579	22.687	0.000
4	53.847	35861299	406199	27.278	0.000
Total		131464195	1806315	100.000	



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	32.671	106949274	1730301	90.874	0.000
2	41.678	8404250	119537	7.141	0.000
3	53.528	2335707	27501	1.985	0.000
Total		117689230	1877338	100.000	

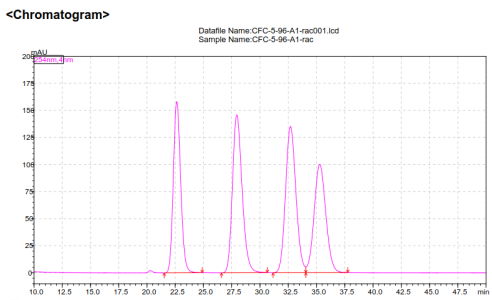
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	32.720	22.562	1	32.671	90.874
2	41.757	27.473	2	41.678	7.141
3	46.439	22.687	3		
4	53.847	27.278	4	53.528	1.985

(*4S,5S*)-4,5-Dimethyl-5-phenyl-4-(6-phenylnaphthalen-2-yl)-1,2-oxaborolan-2-ol (7r). Yield: (76.0 mg, 97%); **IR (neat):** 3349 (br), 3055 (w), 2975 (w), 1598 (w), 1493 (s), 1445 (m), 1397 (m), 1302 (m), 1266 (m), 1179 (m), 1134 (m), 1097 (m), 1063 (m), 956 (w), 898 (m), 847 (m), 755 (s), 697 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.92 (s, 1H), 7.77 - 7.65 (m, 4H), 7.58 - 7.45 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.11 - 7.05 (m, 1H), 7.04 - 6.93 (m, 3H), 6.91 - 6.85 (m, 2H), 6.08 (s, 1H), 1.93 - 1.83 (m, 4H), 1.77 (s, 3H), 1.31 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 143.8, 142.6, 141.1, 138.1, 132.0, 131.8, 128.8, 128.6, 127.3, 127.2, 127.2, 126.9, 126.4, 126.1, 125.4, 125.3, 125.0, 90.1, 52.7, 25.7, 25.0; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{27}H_{26}BO_2$: 392.2057 m/z, found: 392.2060 m/z.

(*2S,3S*)-2-Methyl-3-phenyl-2-(6-phenylnaphthalen-2-yl)butane-1,3-diol (7r-oxi). Yield: (63.0 mg, 85%); **IR (neat):** 3315 (br), 2980 (m), 2931 (w), 1597 (m), 1492 (m), 1445 (m), 1424 (m), 1373 (m), 1278 (w), 1110 (m), 1065 (m), 1021 (s), 893 (m), 816 (m), 756 (s), 699 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.01 (s, 1H), 7.79 - 7.69 (m, 5H), 7.54 - 7.47 (m, 3H), 7.41 (t, *J* = 7.4 Hz, 1H), 7.28 - 7.15 (m, 4H), 7.03 (d, *J* = 7.4 Hz, 2H), 4.21 (d, *J* = 10.8 Hz, 1H), 3.95 (d, *J* = 10.8 Hz, 1H), 3.44 (s, 1H), 3.07 (s, 1H), 1.71 (s, 3H), 1.65 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 144.7, 141.1, 139.5, 138.6, 132.3, 131.8, 128.9, 128.7, 127.6, 127.4, 127.3,

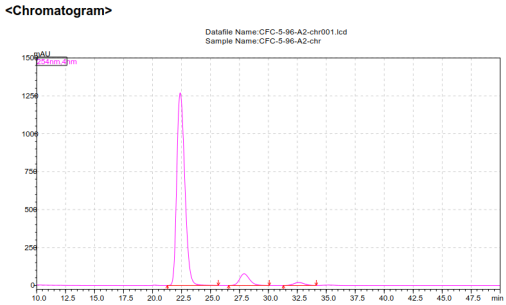
127.2, 127.1, 127.0, 126.9, 126.9, 125.6, 125.1, 80.0, 68.7, 49.8, 26.0, 19.3; **HRMS (ESI$^+$) [M+NH$_4$]$^+$:** Calcd for: $C_{27}H_{30}NO_2$: 400.2271 m/z, found: 400.2269 m/z.

Enantiomeric purity of **7r-oxi** was determined by HPLC analysis in comparison with authentic racemic material (91:9 d.r., >99:1 e.r. shown; Chiralcel OZ-H column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	22.633	7200106	158229	22.656	22.656
2	27.945	8685202	145848	27.328	27.328
3	32.698	8666753	135018	27.270	27.270
4	35.284	7228753	100150	22.746	22.746
Total		31780814	539244	100.000	



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	22.389	61039921	1268815	91.345	0.000
2	27.906	4540987	76516	6.796	0.000
3	32.626	1242233	19418	1.859	0.000
Total		66823142	1364749	100.000	

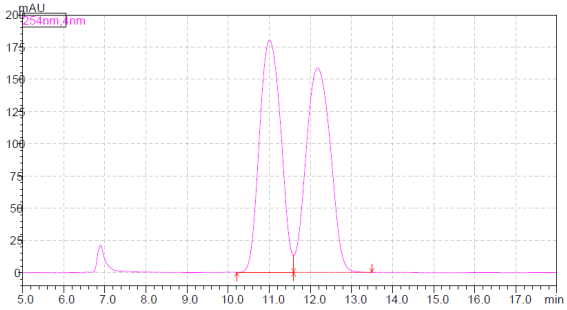
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	22.633	22.656	1	22.389	91.345
2	27.945	27.328	2	27.906	6.796
3	32.698	27.270	3	32.626	1.859
4	35.284	22.746	4		

■ **Representative Experimental Procedure for Phosphine–Cu-Catalyzed Reactions of B$_2$(pin)$_2$, Alkene and Phenol Esters:** In a N_2-filled glove-box, an oven-dried vial (4 mL, 17 × 38 mm) with a magnetic stir bar was charged with tricyclohexylphosphine (5.6 mg, 0.02 mmol, 10 mol %) or (*R*,*R*)-Ph-BPE (10.1 mg, 0.02 mmol, 10 mol %), CuCl (2.0 mg, 0.02 mmol, 10 mol%), LiO*t*-Bu (24.0 mg, 0.3 mmol, 1.5 equiv), 4Å molecular sieve (200 mg) and tetrahydrofuran (thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (76.2 mg, 0.30 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 30 min under an atmosphere of N_2. Alkene **1a** (63.3 mg, 0.40 mmol, 2.0 equiv) and phenol esters (39.7 mg, 0.20 mmol, 1.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 2 mL). The filtrate was concentrated in vacuo to provide yellow oil. The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate = 60:1) to afford **3a** as white solid (74.1 mg, 0.19 mmol, 95% yield).

■ **Characterization of product of 4a-4n.**

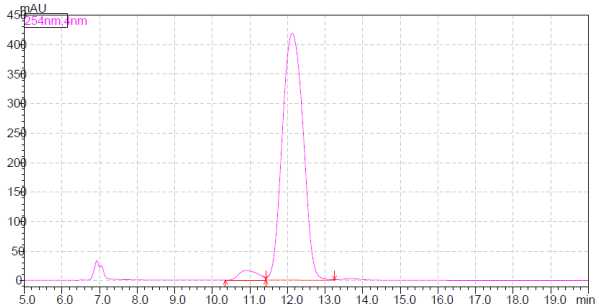
(*R*)-2-(Benzofuran-2-yl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4a). Yield: (60.8 mg, 78%); **IR (neat):** 2994 (w), 2972 (m), 2935 (m), 2886 (w), 1675 (s), 1577 (m), 1455 (m), 1390 (m), 1357 (s), 1315 (s), 1272 (m), 1252 (m), 1140 (s), 1109 (m), 1080 (m), 971 (s), 863 (m), 802 (m), 753 (s), 716 (s), 673 (m), 543 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.62 - 7.52 (m, 3H), 7.37 (dd, *J* = 12.8, 5.6 Hz, 2H), 7.23 (dd, *J* = 10.6, 5.6 Hz, 4H), 6.68 (s, 1H), 1.87 (s, 3H), 1.78 (d, *J* = 15.4 Hz, 1H), 1.37 (d, *J* = 15.4 Hz, 1H), 1.24 (s, 6H), 1.23 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.3, 162.2, 154.6, 136.7, 131.7, 128.8, 128.5, 128.0, 123.8, 122.7, 120.7, 111.3, 101.8, 83.1, 50.7, 24.8, 24.7, 24.1; **^{11}B NMR (128 MHz, $CDCl_3$):** 32.2; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{24}H_{28}O_4B$: 390.2111 m/z, found: 390.2111 m/z; Specific rotation: $[\alpha]_D^{20}$ –37.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 96.5:3.5 e.r.

Enantiomeric purity of **4a** was determined by HPLC analysis in comparison with authentic racemic material (96.5:3.5 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	11.006	6504904	179849	49.827	0.000
2	12.176	6538665	158453	50.173	0.000



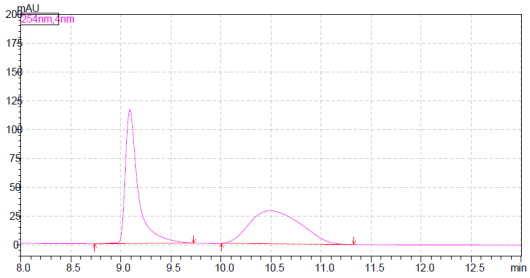
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	10.899	576782	16292	3.438	0.000
2	12.125	16199394	418239	96.562	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	11.006	49.827	1	10.899	3.438
2	12.176	50.173	2	12.125	96.562

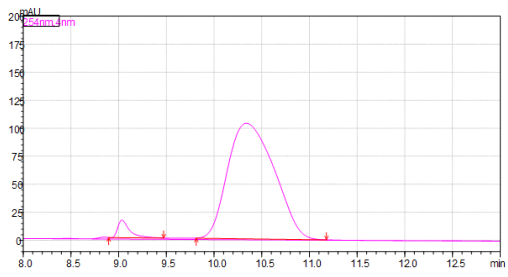
(*R*)-2-(Benzofuran-2-yl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethyl)phenyl)propan-1-one (4b). Yield: (60.4 mg, 66%); **IR (neat):** 2976 (m), 2936 (m), 1685 (m), 1576 (m), 1455 (m), 1359 (s), 1319 (s), 1271 (m), 1251 (m), 1216 (m), 1125 (s), 1065 (s), 1014 (m), 971 (s), 844 (s), 805 (m), 749 (s), 675 (m), 595 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.58 - 7.53 (m, 1H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.42 - 7.36 (m, 1H), 7.27 - 7.20 (m, 2H), 6.69 (s, 1H), 1.84 (s, 3H), 1.77 (d, *J* = 15.4 Hz, 1H), 1.41 (d, *J* = 15.4 Hz, 1H), 1.23 (s, 6H), 1.22 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.8, 161.2, 154.7, 140.0, 132.8 (q, *J* =32.0 Hz), 128.8, 128.3, 125.1 (q, *J* = 4.0 Hz), 124.1, 123.5 (q, *J* = 271.0 Hz) 122.9, 120.8, 111.3, 102.3, 83.2, 50.7, 24.7, 23.9; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -63.2; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{25}H_{27}O_4BF_3$:459.1943 m/z, found: 459.1949 m/z; Specific rotation: $[\alpha]_D^{20}$ –32.6 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

Enantiomeric purity of **4b** was determined by HPLC analysis in comparison with authentic racemic material (96:4 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	9.088	1028526	116573	50.252	0.000
2	10.488	1018205	28701	49.748	0.000



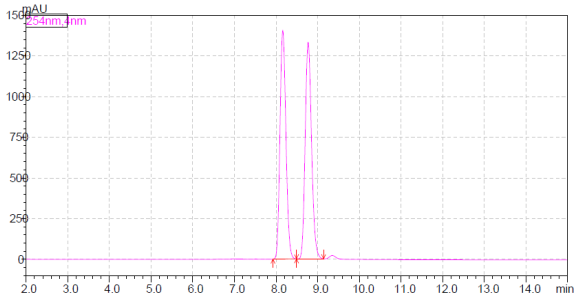
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	9.035	134322	15709	3.700	0.000
2	10.339	3495860	103121	96.300	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	9.088	50.252	1	9.035	3.700
2	10.488	49.748	2	10.339	96.300

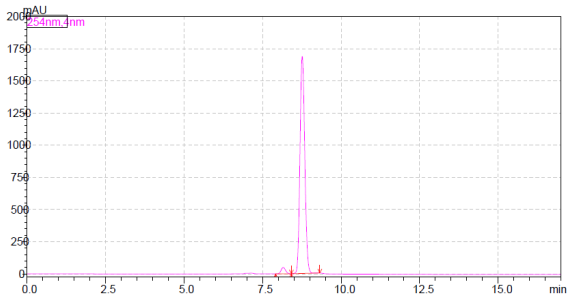
(*R*)-2-(Benzofuran-2-yl)-1-(4-bromophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4c). Yield: (72.1 mg, 77%); **IR (neat):** 2977 (m), 2927 (m), 1675 (m), 1582 (m), 1453 (m), 1351 (s), 1333 (s), 1270 (m), 1225 (m), 1195 (m), 1140 (s), 1071 (m), 1007 (w), 925 (m), 872 (m), 801 (m), 740 (s), 674 (m), 543 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 - 7.52 (m, 1H), 7.50 - 7.42 (m, 2H), 7.38 - 7.36 (m, 3H), 7.26 - 7.19 (m, 2H), 6.67 (s, 1H), 1.85 (s, 3H), 1.75 (d, J = 15.4 Hz, 1H), 1.37 (d, J = 15.4 Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.2, 161.8, 154.6, 135.3, 131.3, 130.4, 128.4, 126.7, 124.0, 122.8, 120.8, 111.3, 102.0, 83.1, 50.6, 24.8, 24.7, 24.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{24}H_{27}O_4BBr$: 468.1212 m/z, found: 468.1217 m/z; Specific rotation: $[\alpha]_D^{20}$ –15.5 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity of **4c** was determined by HPLC analysis in comparison with authentic racemic material (97:3 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	8.161	13960275	1407495	49.573	0.000
2	8.771	14200676	1332103	50.427	0.000



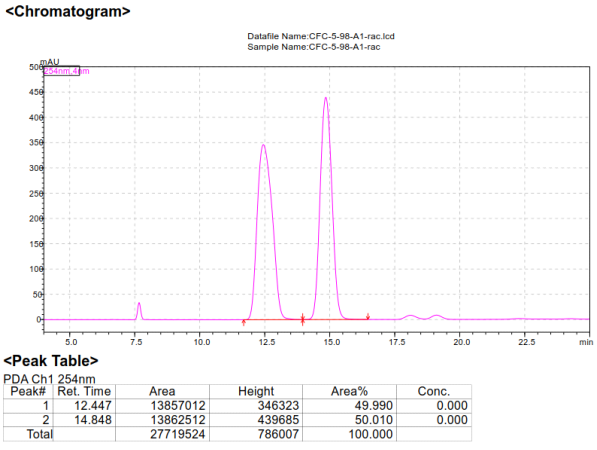
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	8.155	500919	50014	2.707	0.000
2	8.762	18006719	1687850	97.293	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	8.161	49.573	1	8.155	2.707
2	8.771	50.427	2	8.762	97.293

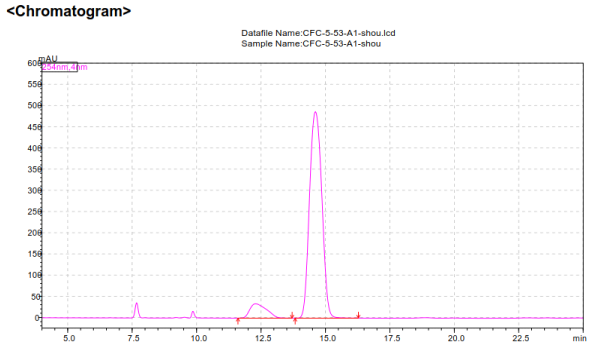
2-(Benzofuran-2-yl)-1-(4-chlorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4d). Yield: (56.8 mg, 67%); **IR (neat):** 2978 (m), 2938 (m), 2896 (w), 1678 (s), 1581 (m), 1453 (m), 1388 (m), 1360 (s), 1312 (s), 1270 (m), 1248 (m), 1214 (m), 1139 (s), 1092 (m), 1046 (m), 971 (s), 938 (m), 865 (m), 802 (m), 746 (s), 675 (m), 543 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.59 - 7.50 (m, 3H), 7.40 - 7.34 (m, 1H), 7.23 - 7.19 (m, 4H), 6.67 (s, 1H), 1.84 (s, 3H), 1.74 (d, *J* = 15.4 Hz, 1H), 1.36 (d, *J* = 15.5 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.0, 161.9, 154.6, 138.1, 134.9, 130.3, 128.4,128.3, 124.0, 122.8, 120.8, 111.3, 101.9, 83.1, 50.6, 24.8, 24.7, 24.1; **^{11}B NMR (128 MHz, $CDCl_3$):** 32.3; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{24}H_{27}O_4BCl$: 425.1682 m/z, found: 425.1685 m/z. Specific rotation: $[\alpha]_D^{20}$ –21.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 91:9 e.r.

Enantiomeric purity of **4d** was determined by HPLC analysis in comparison with authentic racemic material (91:9 e.r. shown; Chiralcel IC column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	12.447	13857012	346323	49.990	0.000
2	14.848	13862512	439685	50.010	0.000
Total		27719524	786007	100.000	



<Peak Table>
PDA Ch1 254nm

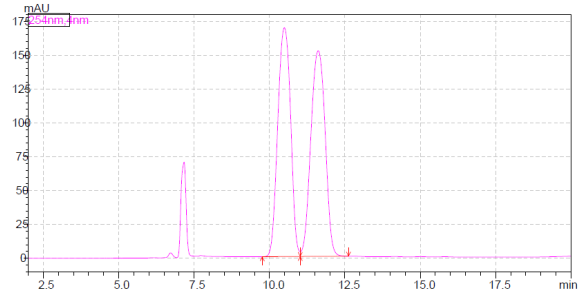
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	12.290	1532505	33905	8.656	0.000
2	14.611	16171741	467077	91.344	0.000
Total		17704246	520983	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	12.447	49.990	1	12.290	8.656
2	14.848	50.010	2	14.611	91.344

(*R*)-2-(Benzofuran-2-yl)-1-(4-fluorophenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4e). Yield: (62.0 mg, 78%); **IR (neat):** 2978 (m), 2927 (m), 1678 (s), 1596 (s), 1503 (m), 1453 (m), 1355 (s), 1312 (s), 1237 (s), 1140 (s), 1039 (w), 971 (s), 945 (m), 844 (s), 802 (s), 747 (s), 678 (m), 613 (m), 578 (m), 504 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.65 (dd, *J* = 8.8, 5.6 Hz, 2H), 7.55 (dd, *J* = 5.0, 4.0 Hz, 1H), 7.41 - 7.32 (m, 1H), 7.25 - 7.18 (m, 2H), 6.90 (t, *J* = 8.6 Hz, 2H), 6.68 (s, 1H), 1.86 (s, 3H), 1.75 (d, *J* =

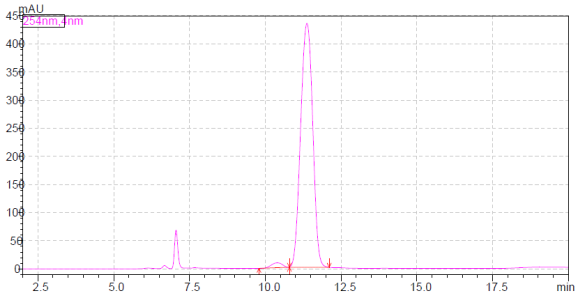
15.4 Hz, 1H), 1.35 (d, *J* = 15.4 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.5, 164.7(d, *J*=254.4 Hz), 162.1, 154.6, 132.73 (d, *J* = 3.2 Hz), 131.54 (d, *J* = 9.0 Hz), 128.4, 123.9, 122.8, 120.8, 115.2 (d, *J* = 21.0 Hz), 111.3, 101.8, 83.1, 50.6, 24.8, 24.7, 24.2; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -106.8; **HRMS (ESI^+) $[M+H]^+$**: Calcd for $C_{24}H_{27}O_4BF$: 409.1984 m/z, found: 409.1981 m/z; Specific rotation: $[\alpha]_D^{20}$ –29.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 e.r.

Enantiomeric purity of **4e** was determined by HPLC analysis in comparison with authentic racemic material (98:2 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	10.492	5008007	169039	49.892	49.892
2	11.613	5029708	151943	50.108	50.108



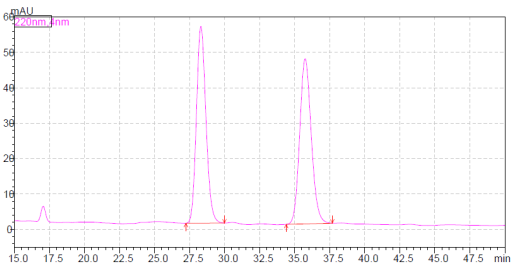
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	10.395	209776	8578	1.716	0.000
2	11.373	12017539	433631	98.284	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	10.492	49.892	1	10.395	1.716
2	11.613	50.108	2	11.373	98.284

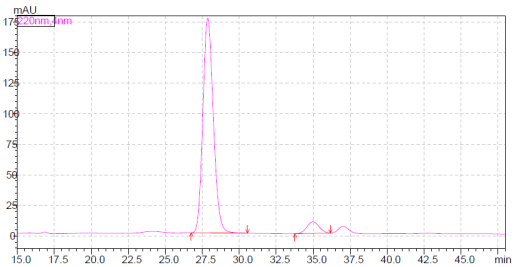
(*R*)-Methyl 3-(2-(benzofuran-2-yl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoyl)benzoate (4f). Yield: (61.8 mg, 69%); **IR (neat):** 2977 (m), 2933 (m), 1725 (s), 1682 (s), 1599 (m), 1452 (m), 1357 (s), 1300 (s), 1232 (s), 1140 (s), 1108 (m), 1045 (m), 966 (m), 881 (m), 805 (m), 733 (s), 543 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.21 (t, *J* = 1.6 Hz, 1H), 8.05 - 7.99 (m, 1H), 7.69 - 7.63 (m, 1H), 7.57 - 7.51 (m, 1H), 7.39 - 7.37 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.25 - 7.18 (m, 2H), 6.69 (s, 1H), 3.78 (s, 3H), 1.84 (s, 3H), 1.76 (d, *J* = 15.4 Hz, 1H), 1.40 (d, *J* = 15.4 Hz, 1H), 1.22 (s, 6H), 1.21 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.0, 166.2, 161.5, 154.6, 137.2, 132.6, 132.4, 130.1 ,130.0, 128.5, 128.2, 123.9, 122.8, 120.8, 111.3, 102.4, 83.2, 52.1, 50.7, 24.8, 24.0; **HRMS (ESI^+) $[M+H]^+$:** Calcd for: $C_{26}H_{30}O_6B$: 448.2161 m/z, found: 448.2166 m/z; Specific rotation: $[\alpha]_D^{20}$ –26.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 94:6 e.r.

Enantiomeric purity of **4f** was determined by HPLC analysis in comparison with authentic racemic material (94:6 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	28.303	2627456	55621	49.557	49.557
2	35.743	2674423	46637	50.443	50.443



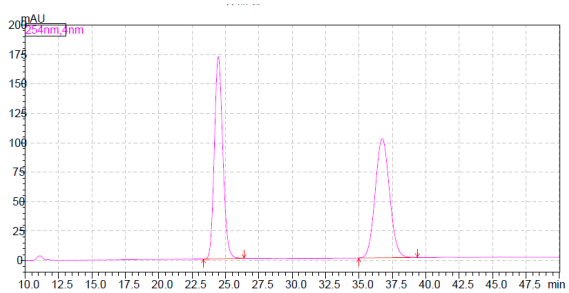
<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	27.871	8680467	175926	94.043	94.043
2	34.984	549834	9506	5.957	5.957

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	28.303	49.557	1	27.871	94.043
2	35.743	50.443	2	34.984	5.957

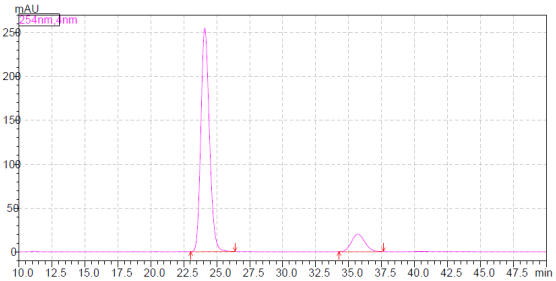
(*R*)-2-(Benzofuran-2-yl)-1-(4-methoxyphenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4g). Yield: (69.7 mg, 83%);**IR (neat):** 2975 (m), 2931 (m), 2844 (w), 1668 (s), 1598 (s), 1574 (m), 1509 (m), 1454 (m), 1417 (s), 1355 (s), 1312 (s), 1251 (s), 1219 (m), 1170 (s), 1141 (s), 1031 (m), 971 (s), 878 (m), 842 (s), 802 (m), 747 (s), 675 (m), 616 (m), 539 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.69 (d, *J* = 8.8 Hz, 2H), 7.53 (dd, *J* = 8.2, 4.4 Hz, 1H), 7.37 (dd, *J* = 8.2, 4.6 Hz, 1H), 7.24 - 7.17 (m, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.66 (s, 1H), 3.74 (s, 3H), 1.89 (s, 3H), 1.74 (d, *J* = 15.4 Hz, 1H), 1.30 (d, *J* = 15.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 199.1, 162.9, 162.5, 154.6, 131.5, 128.7, 128.6, 123.7, 122.6, 120.7, 113.3, 111.3, 101.4, 82.9 55.3, 50.7, 24.9, 24.8, 24.4; **HRMS (ESI^+) $[M+H]^+$:** Calcd for $C_{25}H_{30}O_5B$: 420.2214 m/z, found: 420.2217 m/z; Specific rotation: $[\alpha]_D^{20}$ – 8.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 89:11 e.r.

Enantiomeric purity of **4g** was determined by HPLC analysis in comparison with authentic racemic material (89:11 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	24.465	7528695	171605	49.814	49.814
2	36.731	7584994	101251	50.186	50.186



<Peak Table>
PDA Ch1 254nm

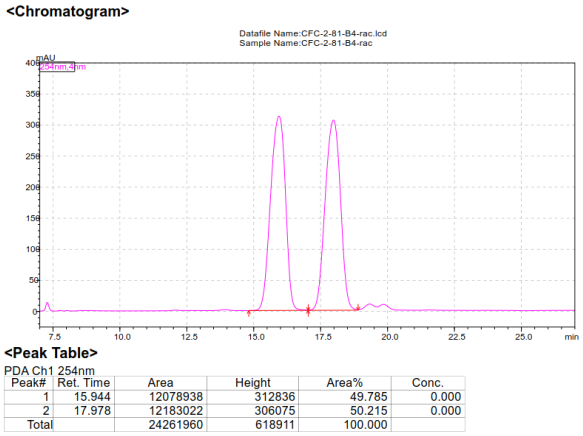
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	24.093	11443522	254119	89.077	0.000
2	35.700	1403289	19939	10.923	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	24.465	49.814	1	24.093	89.077

2	36.731	50.186	2	35.700	10.923

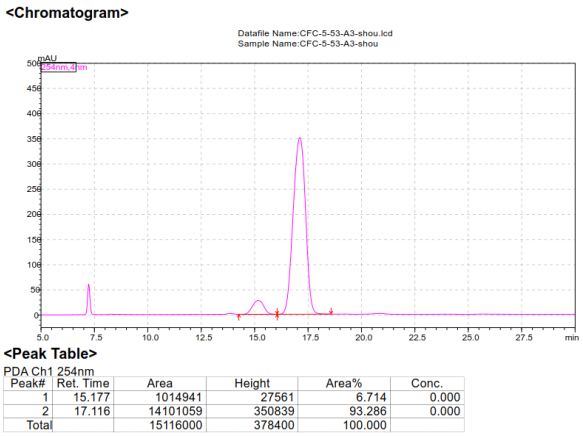
2-(Benzofuran-2-yl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(*p*-tolyl)propan-1-one (4h). Yield: (53.3 mg, 66%); **IR (neat):** 2973 (m), 2927 (w), 1672 (s), 1606 (m), 1453 (m), 1352 (s), 1309 (s), 1251 (m), 1214 (m), 1176 (m), 1139 (s), 1038 (m), 978 (m), 845 (m), 804 (m), 738 (s), 679 (m), 542(m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.59 - 7.51 (m, 3H), 7.40 - 7.34 (m, 1H), 7.24 - 7.17 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.67 (s, 1H), 2.28 (s, 3H), 1.89 (s, 3H), 1.77 (d, *J* = 15.4 Hz, 1H), 1.34 (d, *J* = 15.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 200.5, 162.6, 154.6, 142.5, 133.7, 129.1, 128.8, 128.6 123.7, 122.7, 120.7, 111.3, 101.6, 82.9, 50.7, 24.9, 24.7, 24.2, 21.5; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{25}H_{30}O_4B$: 404.2260 m/z, found: 404.2268 m/z. Specific rotation: $[\alpha]_D^{20}$ –39.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 93:7 e.r.

Enantiomeric purity of **4h** was determined by HPLC analysis in comparison with authentic racemic material (93:7 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	15.944	12078938	312836	49.785	0.000
2	17.978	12183022	306075	50.215	0.000
Total		24261960	618911	100.000	



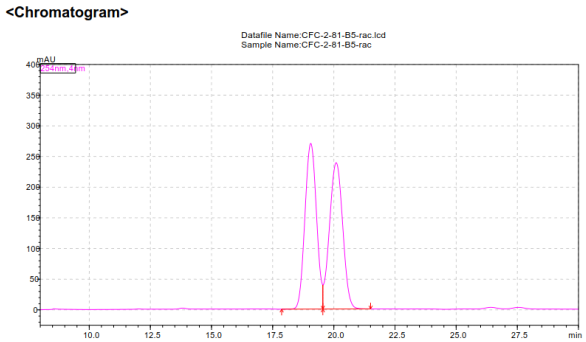
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	15.177	1014941	27561	6.714	0.000
2	17.116	14101059	350839	93.286	0.000
Total		15116000	378400	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	15.944	49.785	1	15.177	6.714
2	17.978	50.215	2	17.116	93.286

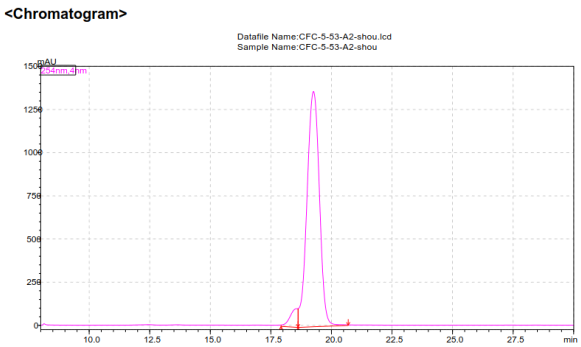
2-(Benzofuran-2-yl)-1-(3-methoxyphenyl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4i). Yield: (42.8 mg, 51%); **IR (neat):** 2977 (m), 2934 (m), 1672 (s), 1575 (m), 1433 (m), 1351 (m), 1315 (s), 1258 (s), 1218 (s), 1140 (s), 1053 (m), 999 (s), 886 (m), 823 (m), 793 (m), 741 (s), 691 (m), 550 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.56 - 7.51 (m, 1H), 7.39 -7.37 (m, 1H), 7.25 - 7.18 (m, 2H), 7.16 - 7.09 (m, 3H), 6.93 - 6.89 (m, 1H), 6.68 (s, 1H), 3.59 (s, 3H), 1.87 (s, 3H), 1.78 (d, *J* = 15.4 Hz, 1H), 1.37 (d, *J* = 15.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.2, 162.2, 159.1, 154.6, 137.9, 129.0, 128.5, 123.8, 122.7, 121.2, 120.7, 118.3, 113.1, 111.3, 101.9, 83.0, 55.0, 50.8, 24.8, 24.7, 24.0; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{25}H_{30}O_5B$: 421.2175 m/z, found: 421.2181 m/z. Specific rotation: $[\alpha]_D^{20}$ –42.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

Enantiomeric purity of **4i** was determined by HPLC analysis in comparison with authentic racemic material (96:4 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	19.056	8884739	270001	49.719	0.000
2	20.096	8985224	238450	50.281	0.000
Total		17869963	508451	100.000	



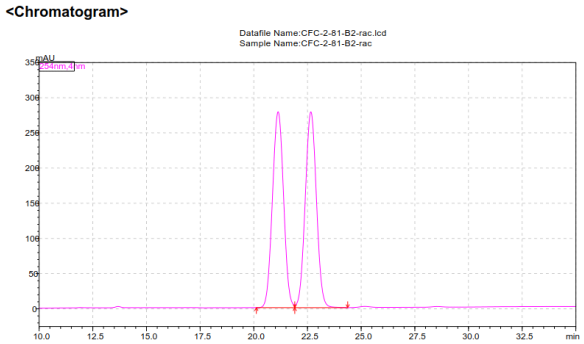
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	18.619	2456975	108487	4.818	0.000
2	19.259	48538790	1362409	95.182	0.000
Total		50995765	1470896	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	19.056	49.719	1	18.619	4.818
2	20.096	50.281	2	19.259	95.182

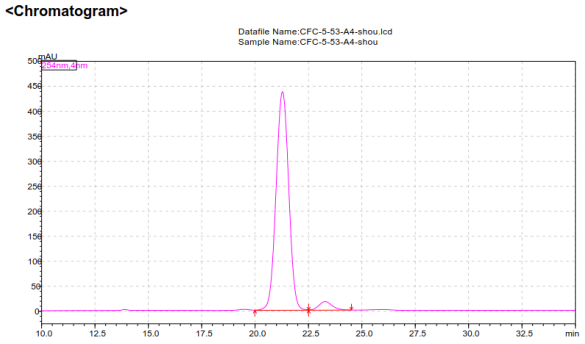
2-(Benzofuran-2-yl)-2-methyl-1-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4j). Yield: (44.9 mg, 51%); **IR (neat):** 2970 (m), 2921 (m), 2851 (w), 1677 (m), 1625 (w), 1576 (w), 1453 (m), 1351 (s), 1310 (s), 1254 (m), 1140 (s), 1002 (m), 845 (m), 824 (m), 744 (s), 688 (m), 542 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12 (s, 1H), 7.79 - 7.64 (m, 4H), 7.60 - 7.55 (m, 1H), 7.47 - 7.51 (m, 1H), 7.45 - 7.35 (m, 2H), 7.25 - 7.20 (m, 2H), 6.75 (s 1H), 1.95 (s, 3H), 1.85 (d, J = 15.4 Hz, 1H), 1.44 (d, J = 15.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.2, 162.3, 154.6, 134.6, 133.9, 132.2, 130.0, 129.4, 128.5, 127.9, 127.6, 127.4, 126.3, 125.1, 123.8, 122.7, 120.7, 111.3, 101.9, 83.0, 50.9, 24.8, 24.7, 24.3; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{28}H_{30}O_4B$: 441.2227 m/z, found: 441.2232 m/z. Specific rotation: $[\alpha]_D^{20}$ –2.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 96:4 e.r.

Enantiomeric purity of **4j** was determined by HPLC analysis in comparison with authentic racemic material (96:4 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	21.131	10039224	278334	49.837	0.000
2	22.656	10104778	278266	50.163	0.000
Total		20144002	556600	100.000	



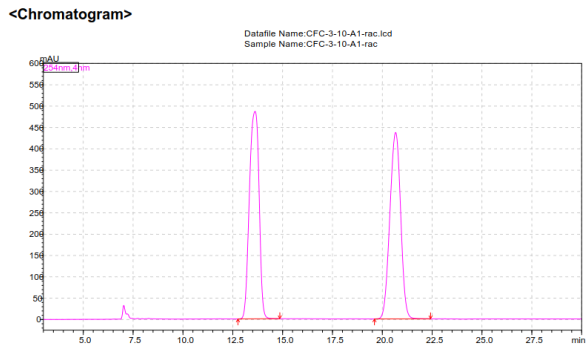
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	21.282	17984969	437086	96.005	0.000
2	23.282	748334	17092	3.995	0.000
Total		18733303	454178	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	21.131	49.837	1	21.282	96.005
2	22.656	50.163	2	23.282	3.995

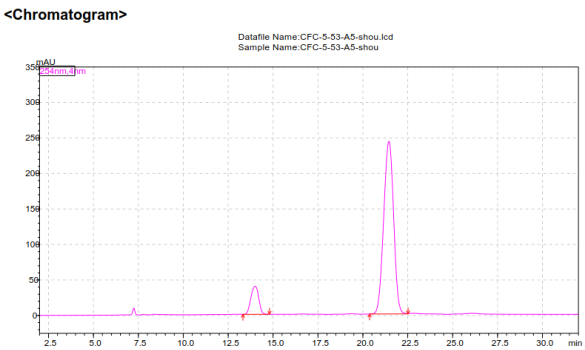
2-(Benzofuran-2-yl)-1-(furan-3-yl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4k). Yield: (41.8 mg, 55%); **IR (neat):** 2974 (m), 2920 (m), 2870 (w), 1669 (m), 1553 (w), 1502 (m), 1455 (m), 1355 (s), 1315 (s), 1214 (m), 1142 (s), 1080 (w), 1025 (m), 968 (m), 862 (s), 800 (m), 740 (s), 694 (m), 540 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 - 7.52 (m, 1H), 7.48 (m, 1H), 7.39 - 7.37 (m, 1H), 7.26 - 7.18 (m, 3H), 6.72 (s, 1H), 6.61 (dd, *J* = 1.8, 0.8 Hz, 1H), 1.84 (s, 3H), 1.68 (d, *J* = 15.4 Hz, 1H), 1.33 (d, *J* = 15.4 Hz, 1H), 1.24 (s, 6H), 1.21 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 195.3, 161.8, 154.5, 147.0, 142.8, 128.2, 124.4, 124.0, 122.8, 120.7, 111.3, 110.1, 102.6, 83.0, 51.0, 24.8, 24.7, 23.7; **HRMS (ESI$^+$) [M+H]$^+$**: Calcd for $C_{22}H_{26}O_5B$: 381.1863 m/z, found: 381.1868 m/z. Specific rotation: $[\alpha]_D^{20}$ –42.8 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 89:11 e.r.

Enantiomeric purity of **4k** was determined by HPLC analysis in comparison with authentic racemic material (89:11 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	13.616	16442470	485964	50.012	0.000
2	20.667	16434604	436745	49.988	0.000
Total		32877075	922709	100.000	



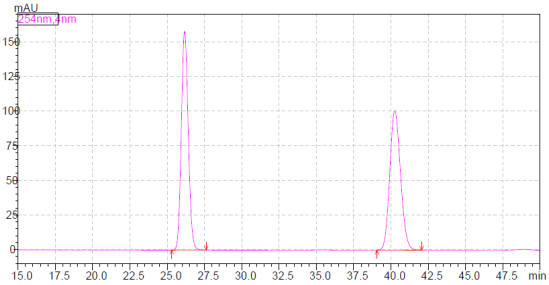
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	14.002	1192111	39452	11.337	0.000
2	21.450	9323284	243093	88.663	0.000
Total		10515395	282545	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	13.616	50.012	1	21.282	11.337
2	20.667	49.988	2	23.282	88.663

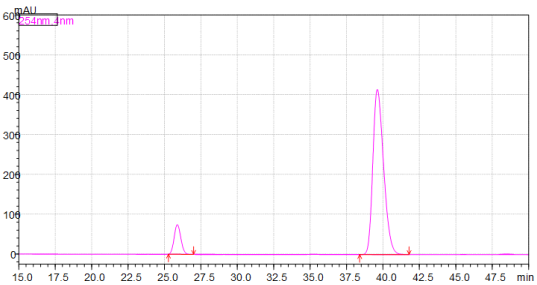
(*R*)-2-(Benzofuran-2-yl)-1-(furan-2-yl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4l). Yield: (57.8 mg, 76%); **IR (neat):** 2974 (m), 2932 (m), 2902 (w), 1669 (s), 1582 (m), 1457 (s), 1354 (s), 1316 (s), 1280 (m), 1140 (s), 1082 (m), 1010 (m), 967 (m), 942 (m), 862 (s), 800 (m), 695 (m), 540 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.55 - 7.50 (m, 1H), 7.41 (dd, *J* = 1.8, 0.8 Hz, 1H), 7.38 - 7.33 (m, 1H), 7.23 - 7.16 (m, 2H), 6.78 (dd, *J* = 3.6, 0.6 Hz, 1H), 6.68 (s, 1H), 6.28 (dd, *J* = 3.6, 1.8 Hz, 1H), 1.89 (s, 3H), 1.77 (d, *J* = 15.4 Hz, 1H), 1.37 (d, *J* = 15.4 Hz, 1H), 1.22 (s, 6H), 1.20 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 188.8, 161.9, 154.6, 150.5, 145.9, 128.4, 123.7, 122.62, 120.7, 118.7, 111.7, 111.2, 102.1, 83.0, 49.8, 24.8, 24.7, 23.6; **^{11}B NMR (128 MHz, $CDCl_3$):** 32.2; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{22}H_{26}O_5B$: 381.1865 m/z, found: 381.1868 m/z. Specific rotation: $[\alpha]_D^{20}$ –40.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 90:10 e.r.

Enantiomeric purity of **4l** was determined by HPLC analysis in comparison with authentic racemic material (90:10 e.r. shown; Chiralcel IC column, 98:2 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	26.166	5106646	157998	50.177	50.177
2	40.257	5070666	100520	49.823	49.823



<Peak Table>
PDA Ch1 254nm

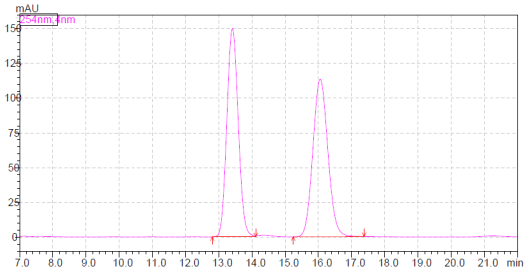
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	25.882	2360145	74286	9.992	0.000
2	39.608	21260833	414440	90.008	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	26.166	50.177	1	25.882	9.992
2	40.257	49.823	2	39.608	90.008

(*R*)-2-(Benzofuran-2-yl)-1-(furan-3-yl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4m). Yield: (40.4 mg, 51%); **IR (neat):** 2995 (m), 2973 (w), 2933 (w), 2888 (w), 1665 (s), 1579 (m), 1454 (m), 1355 (s), 1314 (s), 1253 (m), 1216 (m), 1139 (s), 1073 (m), 968 (m), 853 (s), 809 (s), 753 (s), 694 (m), 538 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.66 (dd, *J* = 2.8, 1.2 Hz, 1H), 7.57 - 7.52 (m, 1H), 7.39 - 7.33 (m, 2H), 7.25 - 7.18 (m, 2H), 7.10 (dd, *J* = 5.0, 2.8 Hz, 1H), 6.71 (d, *J* = 0.8 Hz, 1H), 1.87 (s, 3H), 1.71 (d, *J* = 15.4 Hz, 1H), 1.33 (d, *J* = 15.4 Hz, 1H), 1.24 (s, 6H), 1.22 (s, 6H); **^{13}C NMR (100MHz, $CDCl_3$):** δ 194.7, 162.3, 154.5, 139.2, 132.2, 128.5, 128.4, 125.0, 123.9, 122.7, 120.7, 111.3, 102.2, 82.9, 50.4, 24.7, 24.8, 23.8; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{22}H_{26}O_4BS$: 396.1674 m/z, found:396.1676 m/z.

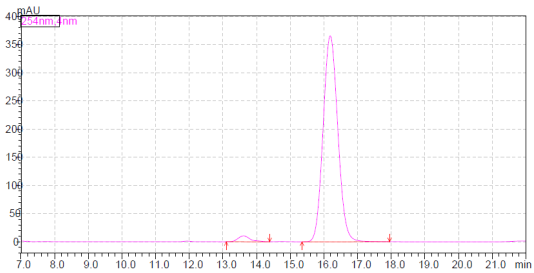
Specific rotation: $[\alpha]_D^{20}$ –49.5 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 e.r.

Enantiomeric purity of **4m** was determined by HPLC analysis in comparison with authentic racemic material (98:2 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	13.409	3580409	149935	50.098	0.000
2	16.053	3566346	113459	49.902	0.000



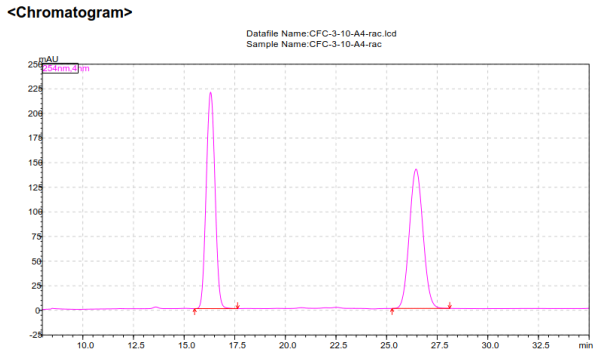
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	13.611	261819	10442	2.307	0.000
2	16.187	11086170	365031	97.693	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	13.409	50.098	1	13.611	2.307
2	16.053	49.902	2	16.187	97.693

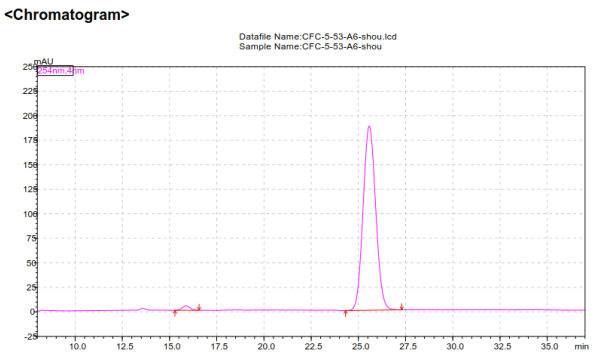
2-(Benzofuran-2-yl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(thiophen-2-yl)propan-1-one (4n). Yield: (41.2 mg, 52%); **IR (neat):** 3108 (w), 2972 (m), 2928 (m), 1654 (s), 1579 (m), 1455 (m), 1410 (m), 1388 (s), 1353 (s), 1254 (m), 1214 (m), 1139 (s), 1038 (m), 939 (m), 843 (s), 798 (m), 749 (s), 726 (s), 696 (m), 534 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 (dd, *J* = 4.8, 4.0 Hz, 1H), 7.42 (d, *J* = 5.0 Hz, 1H), 7.37 - 7.29 (m, 2H), 7.22 - 7.18 (m, 2H), 6.84 (t, *J* = 4.4 Hz, 1H), 6.73 (s, 1H), 1.90 (s, 3H), 1.74 (d, *J* = 15.4 Hz, 1H), 1.35 (d, *J* = 15.4 Hz, 1H), 1.22 (s, 6H), 1.19 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 193.2, 161.9, 154.6, 141.5, 133.1, 132.7, 128.4, 127.8, 123.9, 122.7, 120.7, 111.3, 102.6, 83.0, 50.7, 24.8, 24.7, 24.2; **HRMS (ESI$^+$) $[M+H]^+$:** Calcd for $C_{22}H_{26}O_4BS$: 396.1671 m/z, found: 396.1676 m/z. Specific rotation: $[\alpha]_D^{20}$ –63.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98.5:1.5 e.r.

Enantiomeric purity of **4n** was determined by HPLC analysis in comparison with authentic racemic material (98.5:1.5 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	16.310	6660696	219873	50.122	0.000
2	26.455	6628388	141519	49.878	0.000
Total		13289084	361392	100.000	



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	15.878	128000	4282	1.444	0.000
2	25.575	8733802	187674	98.556	0.000
Total		8861802	191955	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	16.310	50.122	1	15.878	1.444
2	26.455	49.878	2	25.575	98.556

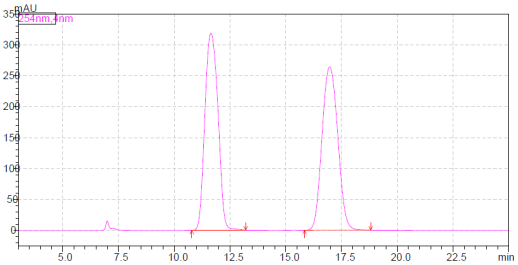
■ **Representative Experimental Procedure for Phosphine–Cu-Catalyzed Reactions of $B_2(pin)_2$, 1,1-Disubstituted Alkene and 4-chlorophenol ester:** In a N_2-filled glove-box, an oven-dried vial (4 mL, 17 × 38 mm) with a magnetic stir bar was charged with NHC-Cu complex (10.8 mg, 0.02 mmol, 10 mol %), CuCl (2.0 mg, 0.02 mmol, 10 mol%), LiO*t*-Bu (24 mg, 0.3 mmol, 1.5 equiv), 4Å molecular sieve (200 mg) and tetrahydrofuran (thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (76.2 mg, 0.30 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 30 min under an atmosphere of N_2. Alkene (34.8 mg, 0.20 mmol, 1 equiv) and 4-chlorophenol ester (46.2 mg, 0.20 mmol, 2.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 2 mL). The filtrate was concentrated *in vacuo* to provide colorless oil. The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate = 60:1) to afford **9a** as white solid (60.9 mg, 0.15 mmol, 75% yield).

■ **Characterization of product of 9a-9k.**

(*R*)-2-(Benzo[b]thiophen-2-yl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9a). Yield: (60.9 mg, 75%); **IR (neat):** 2971 (m), 2926 (m), 2884 (w), 1671 (s), 1593 (w), 1454 (m), 1388 (m), 1355 (s), 1317 (s), 1246 (m), 1184 (w), 1138 (s), 1004 (m), 969 (s), 847 (m), 796 (m), 611 (m), 539 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.80 (d, *J* = 7.8 Hz, 1H), 7.71 - 7.66 (m, 1H), 7.61 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.40 - 7.28 (m, 3H), 7.25 (dd, *J* = 10.8, 4.8 Hz, 2H), 7.17 (s, 1H), 1.92 (s, 3H), 1.85 (d, *J* = 15.4 Hz, 1H), 1.52 (d, *J* = 15.4 Hz, 1H), 1.21 (s, 6H), 1.20 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.4, 152.2, 139.9,

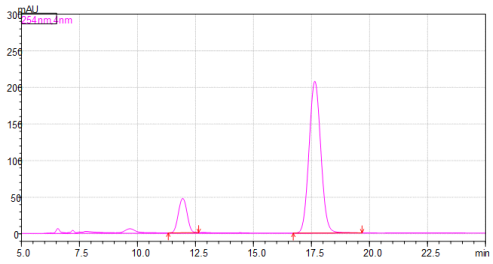
139.1, 136.5, 131.5, 129.2, 127.8, 124.2, 124.0, 123.3, 122.2, 120.4, 83.0, 52.0, 27.1, 24.7, 24.6; **HRMS (EI$^+$) [M]$^+$:** Calcd for $C_{24}H_{27}O_3SB$: 405.1815 m/z, found: 405.1810 m/z. Specific rotation: $[\alpha]_D^{20}$ –30.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 86:14 e.r.

Enantiomeric purity of **9a** was determined by HPLC analysis in comparison with authentic racemic material (86:14 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	11.645	13042777	318562	50.153	0.000
2	16.967	12963426	263936	49.847	0.000



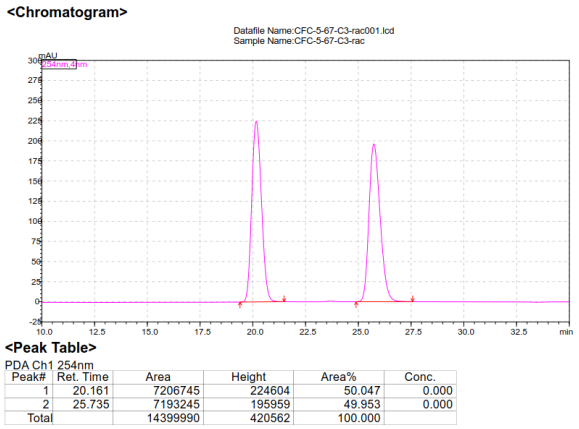
<Peak Table>
PDA Ch1 254nm

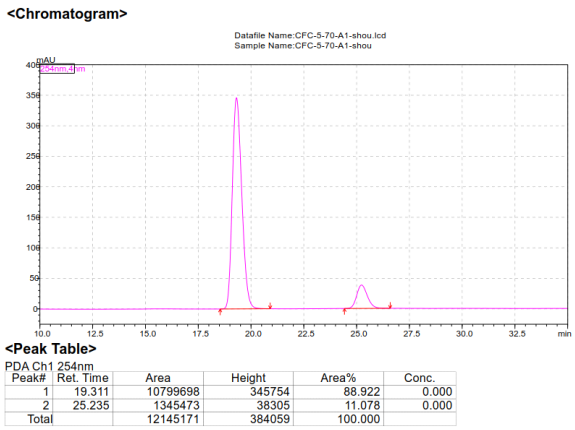
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	11.949	1220651	46817	14.267	14.267
2	17.641	7335034	207330	85.733	85.733

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	11.645	50.153	1	11.949	14.267
2	16.967	49.847	2	17.641	85.733

(*R*)-2-Methyl-1-phenyl-2-(5-phenylthiophen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9b). Yield: (53.6 mg, 62%); **IR (neat):** 2972 (m), 2931 (w), 1668 (s), 1595 (m), 1495 (m), 1445 (m), 1387 (m), 1356 (s), 1317 (s), 1253 (m), 1139 (s), 1074 (m), 1036 (m), 969 (s), 871 (m), 847 (m), 798 (m), 757 (s), 720 (s), 686 (s), 644 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 (t, *J* = 7.0 Hz, 3H), 7.42 - 7.32 (m, 3H), 7.30 - 7.22 (m, 3H), 7.19 (d, *J* = 3.8 Hz, 1H), 6.88 (d, *J* = 3.8 Hz, 1H), 1.86 (s, 3H), 1.78 (d, *J* = 15.6 Hz, 1H), 1.50 (d, *J* = 15.6 Hz, 1H), 1.21 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.9, 150.69, 142.9, 136.9, 134.3, 131.3, 129.1, 128.8, 127.8, 127.3, 125.4, 125.1, 123.1, 83.0, 51.7, 27.2, 24.7, 24.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{26}H_{30}O_3BS$: 432.2040 m/z, found: 432.2036 m/z; Specific rotation: $[\alpha]_D^{20}$ –49.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 89:11 e.r.

Enantiomeric purity of **9b** was determined by HPLC analysis in comparison with authentic racemic material (89:11 e.r. shown; Chiralcel IC column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).

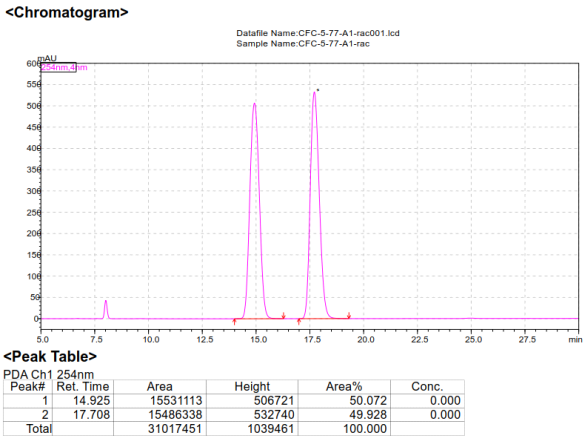


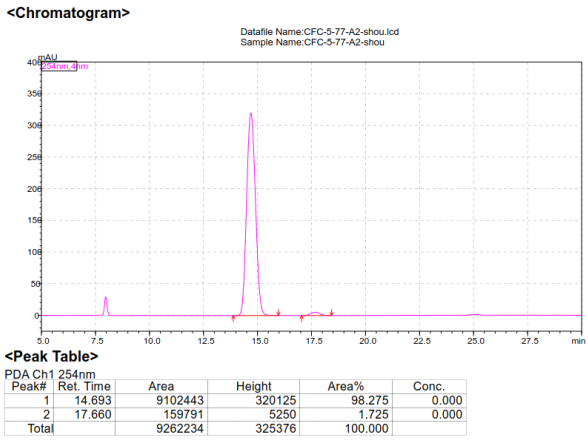


Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	20.161	50.047	1	19.311	88.922
2	25.735	49.953	2	25.235	11.078

(*R*)-2-Methyl-1-phenyl-2-(5-phenylfuran-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9c). Yield: (55.7 mg, 67%); **IR (neat):** 2975 (m), 2922 (m), 1675 (s), 1593 (m), 1475 (m), 1446 (m), 1388 (m), 1353 (s), 1311 (s), 1257 (m), 1184 (m), 1141 (s), 1062 (m), 1046 (m), 970 (s), 874 (m), 848 (m), 790 (m), 755 (s), 715 (m), 688 (s), 652 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.39 - 7.27 (m, 3H), 7.21 (dt, *J* = 19.9, 7.2 Hz, 3H), 6.67 - 6.56 (m, 3H), 6.34 - 6.30 (m, 1H), 1.80 (s, 2H), 1.72 (d, *J* = 15.4 Hz, 1H), 1.35 - 1.11 (m, 13H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.2, 158.2, 152.8, 136.9, 131.4, 130.6, 128.6, 128.5, 127.9, 127.1, 123.5, 107.3, 106.0, 82.9, 50.6, 24.8, 24.7, 23.9; **^{11}B NMR (128 MHz, $CDCl_3$):** 32.6; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{26}H_{30}O_4B$: 416.2268 m/z, found: 416.2262 m/z; Specific rotation: $[\alpha]_D^{20}$ –30.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 e.r.

Enantiomeric purity of **9c** was determined by HPLC analysis in comparison with authentic racemic material (98:2 e.r. shown; Chiralcel IC column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).

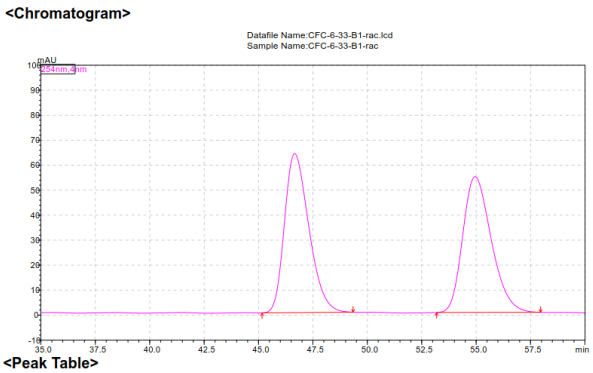




Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	14.925	50.072	1	14.693	98.275
2	17.708	49.928	2	17.660	1.725

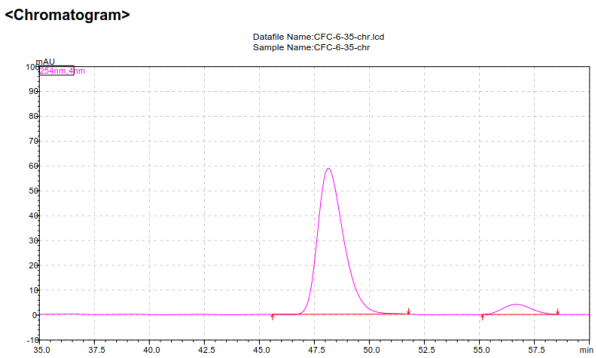
(*R*)-2-(5-(3,4-Dimethoxyphenyl)furan-2-yl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9d). Yield: (62.8 mg, 66%); **IR (neat):** 2972 (m), 2929 (m), 2854 (w), 1677 (s), 1597 (m), 1503 (m), 1462 (m), 1357 (s), 1318 (m), 1251 (m), 1142 (s), 1094 (m), 1024 (s), 970 (m), 876 (m), 792 (m), 763 (s), 719 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.52 - 7.45 (m, 2H), 7.36 (t, *J* = 7.4 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 2H), 7.13 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 6.50 (d, *J* = 3.3 Hz, 1H), 6.31 (d, *J* = 3.3 Hz, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 1.79 (s, 3H), 1.72 (d, *J* = 15.4 Hz, 1H), 1.32 - 1.15 (m, 13H).; **^{13}C NMR (100 MHz, $CDCl_3$):** δ 202.4, 157.7, 152.9, 149.0, 148.4, 137.0, 131.4, 128.6, 127.9, 124.0, 116.3, 111.2, 107.3, 106.9, 104.7, 82.9, 55.9, 50.6, 24.8, 24.7, 23.9; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{28}H_{34}O_6B$: 476.2479 m/z, found: 476.2474 m/z; Specific rotation: $[\alpha]_D^{20}$ – 12.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 93:7 e.r.

Enantiomeric purity of **9d** was determined by HPLC analysis in comparison with authentic racemic material (93:7 e.r. shown; Chiralcel IC column, 98:2 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	46.662	4965244	63655	50.046	0.000
2	54.953	4956043	54332	49.954	0.000
Total		9921288	117987	100.000	



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	48.138	4799369	58784	92.789	0.000
2	56.689	372952	4123	7.211	0.000
Total		5172321	62907	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	46.662	50.046	1	48.138	92.789
2	54.953	49.954	2	56.689	7.211

(*R*)-2-Methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-(5-(4-(trifluoromethyl)phenyl)furan-2-yl)propan-1-one (9e). Yield: (70.7 mg, 73%); **IR (neat):** 2990 (m), 2921 (w), 1678 (s), 1595 (m), 1497 (w), 1446 (w), 1383 (m), 1353 (m), 1319 (s), 1256 (m), 1215 (m), 1182 (m), 1124 (s), 1108 (s), 1071 (m), 970 (m), 872 (m), 858 (s), 788 (s), 714 (m), 693 (m), 652 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.58 - 7.47 (m, 4H), 7.43 - 7.30 (m, 1H), 7.25 (dd, *J* = 11.2, 3.8 Hz, 2H), 6.75 (d, *J* = 3.2 Hz, 1H), 6.42 - 6.35 (m, 1H), 1.82 (s, 3H), 1.72 (d, *J* = 15.4 Hz, 1H), 1.32 (d, *J* = 15.4 Hz, 1H), 1.25 (s, 6H), 1.24 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.9, 159.6, 151.4, 136.8, 133.7, 131.6, 128.7 (q, *J* = 32.6 Hz), 128.6, 128.0, 125.6 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 271.8 Hz), 123.5, 108.1, 107.7, 83.0, 50.7, 24.8, 24.7, 24.0; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.5; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{27}H_{29}BF_3O_4$: 484.2142 m/z, found: 484.2139 m/z; Specific rotation: $[\alpha]_D^{20}$ –14.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 87:13 e.r.

Enantiomeric purity of **9e** was determined by HPLC analysis in comparison with authentic racemic material (87:13 e.r. shown; Chiralcel IC column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).

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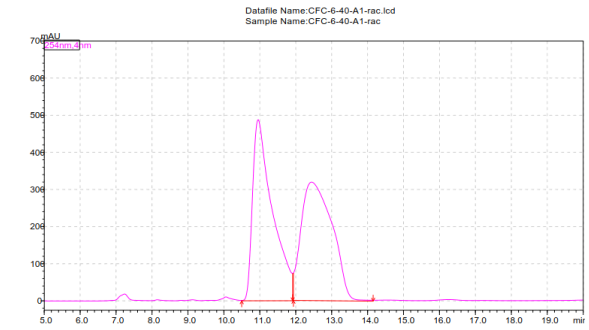

<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	10.953	18739463	487610	49.375	0.000
2	12.441	19213636	319151	50.625	0.000
Total		37953099	806761	100.000	

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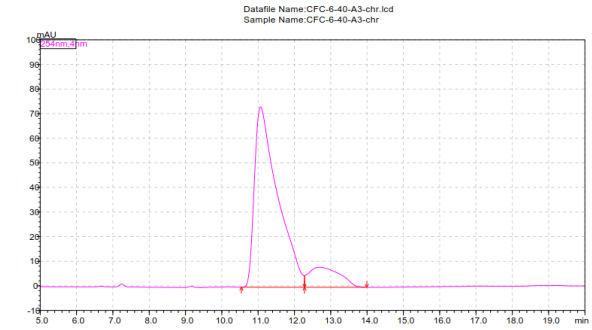


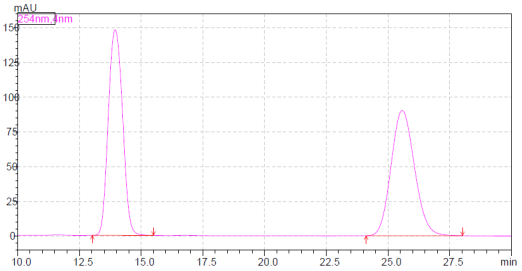
<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	11.068	3249295	73288	87.009	0.000
2	12.695	485123	8155	12.991	0.000
Total		3734418	81443	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	10.953	49.375	1	11.068	87.009
2	12.441	50.625	2	12.695	12.991

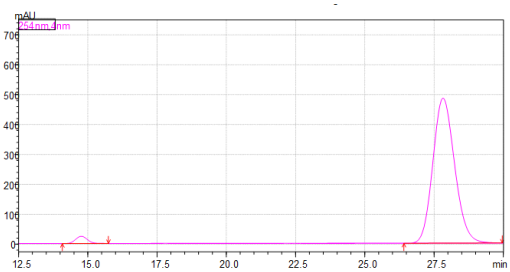
(*R*)-2-Methyl-2-(naphthalen-2-yl)-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9f). Yield: (57.6 mg, 72%); **IR (neat):** 2970 (m), 2925 (w), 1668 (s), 1632 (m), 1451 (m), 1353 (s), 1314 (s), 1266 (m), 1216 (m), 1140 (s), 1041 (m), 972 (s), 849 (m), 819 (s), 748 (s), 709 (m), 685 (m), 539 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.93 (s, 1H), 7.86 - 7.79 (m, 3H), 7.54 - 7.41 (m, 5H), 7.32 (t, J = 7.4 Hz, 1H), 7.17 (t, J = 7.8 Hz, 2H), 1.92 (s, 3H), 1.71 (d, J = 15.4 Hz, 1H), 1.44 (d, J = 15.4 Hz, 1H), 1.23 (s, 6H), 1.20 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.0, 143.8, 136.5, 133.5, 132.1, 131.4, 129.6, 128.5, 128.0, 127.8, 127.5, 126.1, 125.7, 124.9, 123.8, 82.8, 53.8, 25.5, 24.8, 24.7; **^{11}B NMR (128 MHz, $CDCl_3$):** 33.0; **HRMS (EI$^+$) [M]$^+$:** Calcd for: $C_{26}H_{29}O_3B$: 399.2252 m/z, found: 399.2246 m/z; Specific rotation: $[\alpha]_D^{20}$ –122.2 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity of **9f** was determined by HPLC analysis in comparison with authentic racemic material (97:3 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	13.950	5946747	148004	49.967	0.000
2	25.579	5954568	90183	50.033	0.000



<Peak Table>
PDA Ch1 254nm

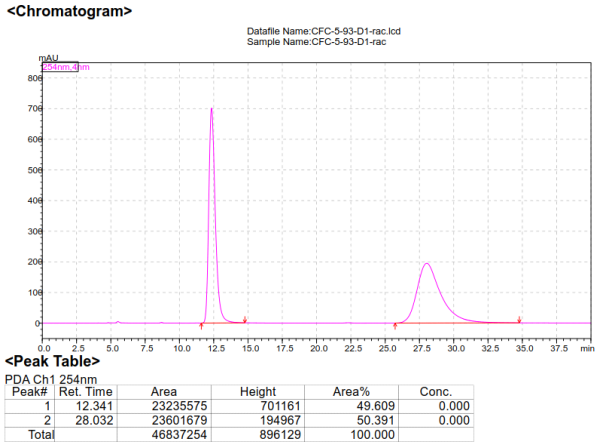
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	14.767	728002	24261	2.668	2.668
2	27.823	26555843	485038	97.332	97.332

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	13.950	49.967	1	14.767	2.668

2	25.579	50.033	2	27.823	97.332

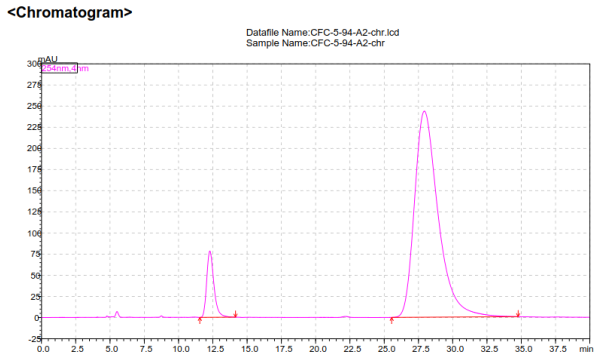
(*R*)-2-Methyl-1-phenyl-2-(6-phenylnaphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9g). Yield: (80.9 mg, 85%); **IR (neat):** 2971 (m), 2928 (w), 1668 (s), 1595 (m), 1494 (m), 1445 (m), 1383 (m), 1353 (s), 1310 (s), 1261 (m), 1211 (m), 1164 (m), 1139 (s), 1039 (w), 968 (m), 871 (m), 846 (m), 755 (s), 712 (m), 689 (s), 643 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.04 (s, 1H), 7.96 - 7.91 (m, 2H), 7.87 (d, *J* = 8.8 Hz, 1H), 7.81 - 7.76 (m, 1H), 7.74 (dd, *J* = 8.1, 0.9 Hz, 2H), 7.57 - 7.47 (m, 4H), 7.43 - 7.29 (m, 2H), 7.23 - 7.13 (m, 2H), 6.88 - 6.78 (m, 1H), 1.95 (s, 3H), 1.74 (d, *J* = 15.4 Hz, 1H), 1.48 (d, *J* = 15.4 Hz, 1H), 1.25 (s, 6H), 1.23 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.3, 154.8, 143.9, 140.9, 138.5, 136.5, 132.7, 132.4, 131.6, 129.6, 129.3, 128.8, 128.5, 127.8, 127.3, 125.9, 125.3, 123.6, 116.7, 83.0, 53.9, 25.6, 24.8, 24.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{32}H_{34}BO_3$: 476.2632 m/z, found: 476.2629 m/z; Specific rotation: $[\alpha]_D^{20}$ –89.4 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 91:9 e.r.

Enantiomeric purity of **9g** was determined by HPLC analysis in comparison with authentic racemic material (91:9 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	12.341	23235575	701161	49.609	0.000
2	28.032	23601679	194967	50.391	0.000
Total		46837254	896129	100.000	



<Peak Table>
PDA Ch1 254nm

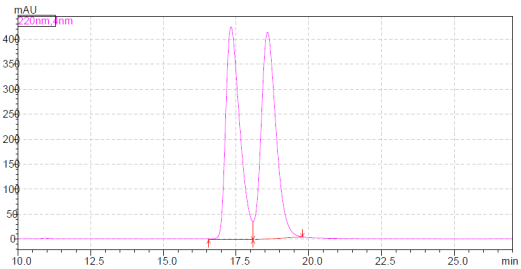
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	12.283	2858778	78448	8.882	0.000
2	27.932	29327847	243716	91.118	0.000
Total		32186625	322164	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	12.341	49.609	1	12.283	8.882
2	28.032	50.391	2	27.932	91.118

(*R*)-2-(6-Methoxynaphthalen-2-yl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9h). IR (neat): 2976 (m), 2926 (w), 1667 (m), 1602 (m), 1481 (m), 1386 (m), 1311 (s), 1278 (s), 1235 (s), 1168 (m), 1124 (s), 1031 (m), 973 (m), 911 (m), 848 (s), 811 (m), 760 (s), 687 (m), 578 (m), 541 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.82 (d, *J* = 1.8 Hz, 1H), 7.70 (dd, *J* = 14.6, 8.8 Hz, 2H), 7.48 - 7.44 (m, 2H), 7.38 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.33 - 7.28 (m, 1H), 7.18 - 7.14 (m, 3H), 7.11 (d, *J* = 2.4 Hz, 1H), 3.91 (s, 3H), 1.87 (s, 3H), 1.66 (d, *J* = 15.4 Hz, 1H), 1.41 (d, *J* = 15.4 Hz, 1H), 1.20 (s, 6H), 1.18 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.3, 157.6, 141.4, 136.7, 133.3, 131.4, 129.7,129.5, 129.0, 127.8, 127.4,

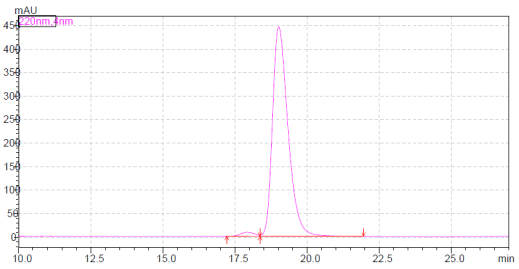
125.5, 123.8, 119.0, 105.5, 82.9, 55.3, 53.7, 25.6, 24.8, 24.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{27}H_{32}O_4B$: 431.2383 m/z, found: 431.2388 m/z. Specific rotation: $[\alpha]_D^{20}$ –97.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 e.r.

Enantiomeric purity of **9h** was determined by HPLC analysis in comparison with authentic racemic material (98:2 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	17.324	14382926	426107	49.481	0.000
2	18.579	14684541	413494	50.519	0.000



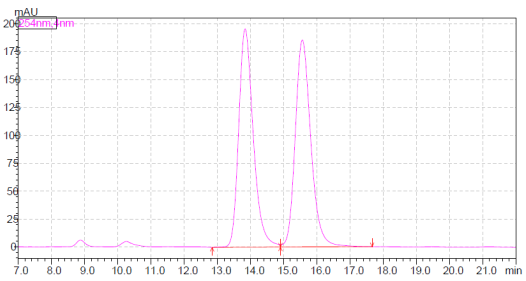
<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	17.926	289760	8712	1.714	1.714
2	19.023	16612597	445137	98.286	98.286

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	17.324	49.481	1	17.926	1.714
2	18.579	50.519	2	19.023	98.286

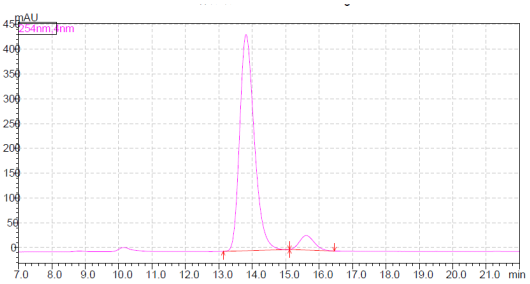
(*R*)-2-(6-(Dibenzylamino)naphthalen-2-yl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9i). Yield: (84.5 mg, 71%); **IR (neat):** 3356 (m), 3060 (w), 2974 (m), 2918 (m), 1667 (m), 1629 (s), 1599 (s), 1498 (m), 1450 (m), 1352 (s), 1317 (s), 1208 (m), 1141 (s), 1027 (m), 966 (s), 845 (s), 728 (s), 693 (s), 533 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.74 (s, 1H), 7.66 (d, *J* = 9.0 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 3H), 7.40 - 7.24 (m, 12H), 7.17 (t, *J* = 7.8 Hz, 3H), 6.97 (d, *J* = 1.8 Hz, 1H), 4.76 (s, 4H), 1.85 (s, 3H), 1.68 (d, *J* = 15.4 Hz, 1H), 1.37 (d, *J* = 15.4 Hz, 1H), 1.23 (s, 6H), 1.21 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.5, 147.1, 139.8, 138.4, 136.9, 133.7, 131.3, 129.7, 129.2, 128.7, 127.8, 127.0, 126.9, 126.8, 126.7, 125.3, 123.5, 116.1, 105.9, 82.8, 54.3, 53.6, 25.7, 24.8, 24.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{40}H_{43}NO_3$: 595.3367 m/z, found: 595.3363 m/z. Specific rotation: $[\alpha]_D^{20}$ –33.1 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 94:6 e.r.

Enantiomeric purity of **9i** was determined by HPLC analysis in comparison with authentic racemic material (94:6 e.r. shown; Chiralcel OZ–H column, 99:1 hexanes/ *i*PrOH, 0.5 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	13.836	5961784	195548	49.665	0.000
2	15.560	6042280	185440	50.335	0.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	13.813	13229993	435977	93.623	0.000
2	15.615	901136	29320	6.377	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	13.836	49.665	1	13.813	93.623
2	15.560	50.335	2	15.615	6.377

(*R*)-2-(6-(1H-pyrrol-1-yl)naphthalen-2-yl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (9j). Yield: (69.7 mg, 75%); **IR (neat):** 2977 (m), 2926 (m), 1666 (s), 1602 (m), 1494 (s), 1468 (m), 1379 (s), 1352 (s), 1312 (m), 1262 (m), 1139 (s), 1077 (m), 1036 (m), 972 (m), 870 (m), 848 (m), 792 (m), 760 (m), 720 (s), 686 (m), 642 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.91 - 7.82 (m, 2H), 7.75 (dd, *J* = 13.8, 5.2 Hz, 2H), 7.57 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.49 - 7.39 (m, 3H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.17 (dt, *J* = 15.6, 4.8 Hz, 4H), 6.38 (t, *J* = 2.0 Hz, 1H), 1.88 (s, 3H), 1.68 (d, *J* = 10.5 Hz, 1H), 1.42 (d, *J* = 15.4 Hz, 1H), 1.19 (s, 6H), 1.17 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 203.9, 143.6, 138.2, 136.5, 132.5, 131.5, 131.5, 129.6, 129.6, 128.2, 127.8, 126.0, 123.8, 120.4, 119.5, 117.1, 110.6, 82.9, 53.8, 25.6, 24.8, 24.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{30}H_{33}O_3BN$: 465.2584 m/z, found: 465.2584 m/z; Specific rotation: $[\alpha]_D^{20}$ –66.3 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 93:7 e.r.

Enantiomeric purity of **9j** was determined by HPLC analysis in comparison with authentic racemic material (93:7 e.r. shown; Chiralcel OZ–H column, 98:2 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).

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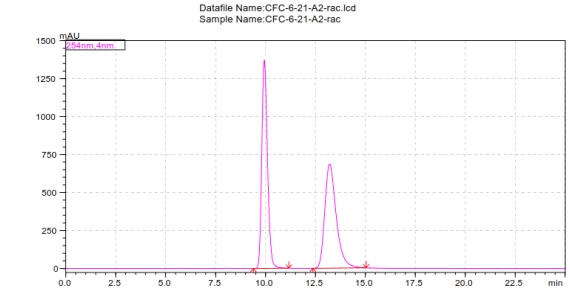

<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.940	1369121	66.616	27305267	50.027
2	13.211	686115	33.384	27275392	49.973
Total		2055236	100.000	54580659	100.000

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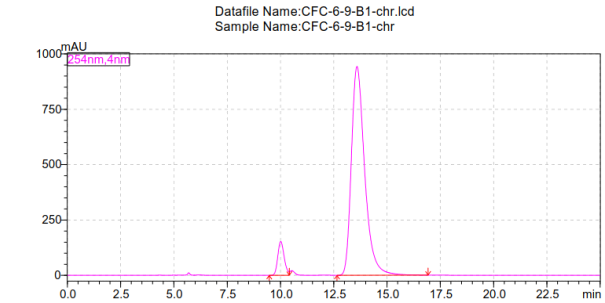


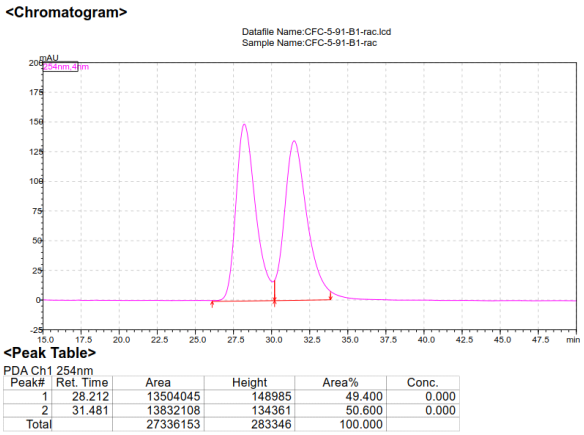
<Peak Table>
PDA Ch1 254nm

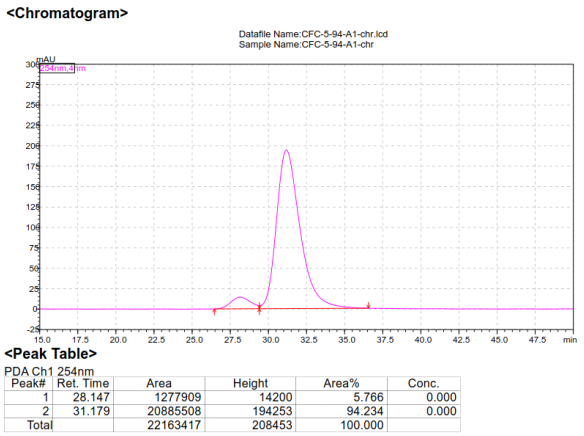
Peak#	Ret. Time	Area	Height	Area%
1	10.011	3217185	152858	7.265
2	13.590	41067999	942984	92.735
Total		44285184	1095843	100.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	9.940	50.027	1	10.011	7.265
2	13.211	49.973	2	13.590	92.735

***tert*-Butyl (*R*)-4-(6-(2-methyl-1-oxo-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-2-yl)naphthalen-2-yl)piperazine-1-carboxylate (9k). Yield:** (93.4 mg, 80%); **IR (neat):** 2973 (m), 2935 (w), 1691 (m), 1598 (m), 1498 (m), 1450 (m), 1388 (m), 1354 (s), 1314 (s), 1246 (m), 1164 (s), 1142 (m), 1041 (m), 968 (m), 870 (m), 847 (m), 757 (m), 715 (m), 689 (s), 647 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.77 (s, 1H), 7.72 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 8.8 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 – 7.23 (m, 3H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 2.2 Hz, 1H), 3.69 – 3.55 (m, 4H), 3.29 – 2.99 (m, 4H), 1.85 (s, 4H), 1.65 (d, *J* = 15.6 Hz, 1H), 1.50 (s, 9H), 1.39 (d, *J* = 15.6 Hz, 1H), 1.20 (s, 6H), 1.17 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 204.2, 154.7, 149.0, 141.4, 136.7, 133.2, 131.3, 129.6, 128.9, 128.8, 127.7, 127.4, 125.4, 123.5, 119.9, 110.5, 82.8, 79.9, 53.6, 49.6, 28.4, 25.5, 24.8, 24.7; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{35}H_{46}BN_2O_5$: 584.3531 m/z, found: 584.3527 m/z; Specific rotation: $[\alpha]_D^{20}$ –75.9 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 94:6 e.r.

Enantiomeric purity of **9k** was determined by HPLC analysis in comparison with authentic racemic material (94:6 e.r. shown; Chiralcel OZ–H column, 98:2 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).





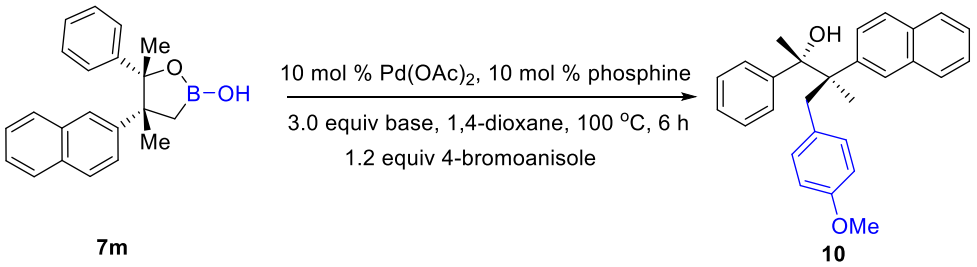
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	28.212	49.400	1	28.147	5.766
2	31.481	50.600	2	31.179	94.234

■ **Experimental Procedure for Gram Scale Synthesis of Phosphine–Cu-Catalyzed Reactions of $B_2(pin)_2$, 2-(prop-1-en-2-yl)naphthalene and Acetophenone:** In a N_2-filled glove-box, an oven-dried flask (100 mL) with a magnetic stir bar was charged with (*R*,*R*)-Ph-BPE **6i** (0.15 g, 0.3 mmol, 3 mol%), LiO*t*-Bu (1.20 g, 15 mmol, 1.5 equiv) and tetrahydrofuran (thf, 30 mL). The solution was allowed to stir at 22 °C for one hour.

Bis(pinacolato)diboron (3.81 g, 15 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The mixture was allowed to stir at 22 °C for 30 min under an atmosphere of N_2. 2-(prop-1-en-2-yl)naphthalene (2.52 g, 15 mmol, 1.5 equiv) and acetophenone (1.20 g, 10 mmol, 1.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 30 mL). The filtrate was concentrated *in vacuo* to provide yellow oil. The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate = 15:1) to afford **7m** as white solid (2.64 g, 85% yield).

■ **Experimental Procedure for Gram Scale Synthesis of Phosphine–Cu-Catalyzed Reactions of $B_2(pin)_2$, 2-(prop-1-en-2-yl)naphthalene and 4-chlorophenol ester:** In a N_2-filled glove-box, an oven-dried flask (50 mL) with a magnetic stir bar was charged with NHC–Cu complex **6j** (0.43 g, 0.8 mmol, 10 mol%), LiO*t*-Bu (0.96 g, 12 mmol, 1.5 equiv) and tetrahydrofuran (thf, 20 mL). The solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (3.05 g, 12 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The mixture was allowed to stir at 22 °C for 30 min under an atmosphere of N_2. 2-(prop-1-en-2-yl)naphthalene (1.34 g, 8 mmol, 1 equiv) and *p*-Cl-phenyl benzoate (2.78 g, 12 mmol, 1.5 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 20 mL). The filtrate was concentrated *in vacuo* to provide yellow oil. The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate = 60:1) to afford **9f** as white solid (1.95 g, 67% yield).

■ **Representative Experimental Procedure for Pd-Catalyzed Cross Coupling of 7m.**

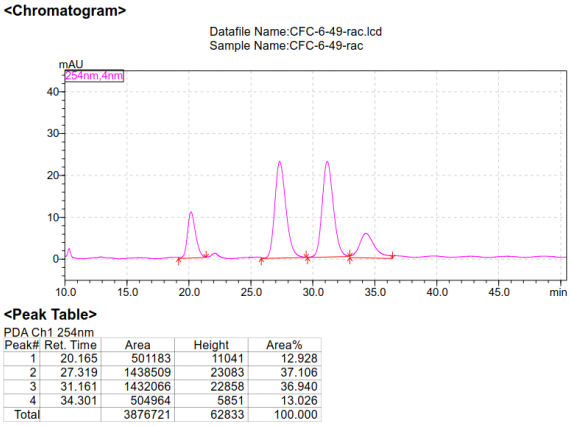


7m **10**

In a 15-mL Schlenk flask, Cs_2CO_3 (195.5 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (4.5 mg, 0.02 mmol, 10 mol%), RuPhos (9.2 mg, 10 mol%) and **7m** (63.2 mg, 0.2 mmol, 1.0 equiv) were dissolved in 1 mL of 1,4-dioxane were added followed by addition of 4-bromoanisole (46.6 mg, 0.24 mmol, 1.2 equiv). The tube was sealed and the reaction was allowed to stir at 100°C for 6 h. The reaction mixture was cooled down to room temperature, quenched with 1.5 mL of a 1/1 (v:v) $Na_2S_2O_3$ (sat.)/$NaHCO_3$ (sat.) solution, washed with EtOAc (3 x 2 mL). The organic phases were dried over $MgSO_4$ and concentrated under vacuum. The resulting solid was purification by silica gel chromatography (petroleum ether : ethyl acetate = 10:1) as colorless oil (49.5 mg, 0.13 mmol, 64% yield).

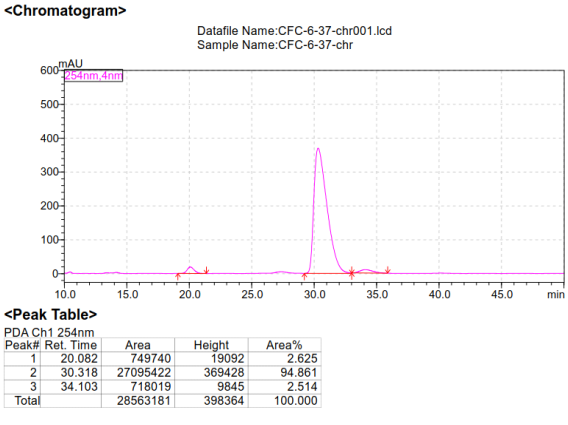
(*2S,3S*)-4-(4-Methoxyphenyl)-3-methyl-3-(naphthalen-2-yl)-2-phenylbutan-2-ol (10). Yield: (49.5 mg, 64%); **IR (neat):** 3317 (br), 2923 (w), 2885 (w), 1548 (m), 1488 (m), 1432 (m), 1387 (m), 1378 (s), 1325 (s), 1242 (m), 1143 (s), 1121 (m), 1015 (m), 957 (m), 860 (m), 831 (m), 765 (m), 700 (m), 670 (s), 645 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.71 (t, *J* = 6.4 Hz, 2H), 7.60 (s, 1H), 7.53 - 7.38 (m, 3H), 7.23 - 7.17 (m, 5H), 6.72 (d, *J* = 8.2 Hz, 2H), 6.49 (d, *J* = 7.6 Hz, 2H), 3.67 (d, *J* = 13.8 Hz, 1H), 3.60 (s, 3H), 3.07 (d, *J* = 13.8 Hz, 1H), 1.80 (s, 1H), 1.66 (s, 3H), 1.35 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 157.5, 145.0, 140.0, 132.6, 131.9, 131.4, 130.9, 128.8, 128.3, 128.2, 127.7, 127.2, 126.7, 126.6, 125.9, 125.7, 125.6, 112.9, 78.9, 54.9, 50.4, 39.8, 26.3, 21.2; **HRMS (ESI$^+$) [M+NH_4]$^+$:** Calcd for $C_{28}H_{32}NO_2$: 414.2428 m/z, found: 414.2416 m/z.

Enantiomeric purity of **10** was determined by HPLC analysis in comparison with authentic racemic material (95:5 d.r., >99:1 e.r. shown; Chiralcel OZ–H column, 98:2 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.165	501183	11041	12.928
2	27.319	1438509	23083	37.106
3	31.161	1432066	22858	36.940
4	34.301	504964	5851	13.026
Total		3876721	62833	100.000

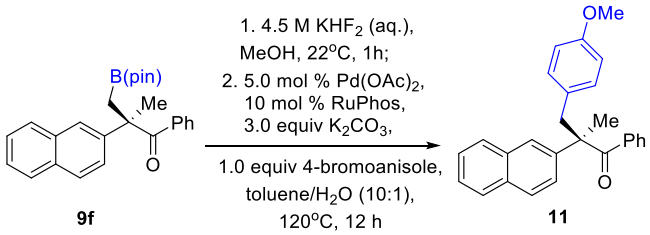


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	20.082	749740	19092	2.625
2	30.318	27095422	369428	94.861
3	34.103	718019	9845	2.514
Total		28563181	398364	100.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	20.165	12.928	1	20.082	2.625
2	27.319	37.106	2		
3	31.161	36.940	3	30.318	94.861
4	34.301	13.026	4	34.103	2.514

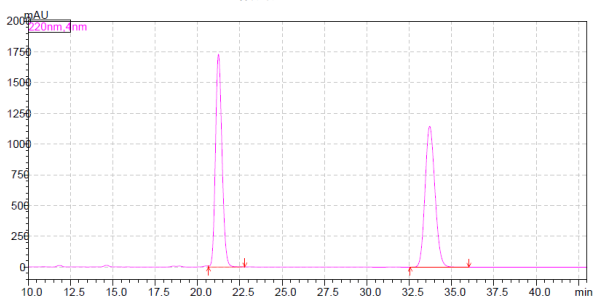
■ Representative Experimental Procedure for Pd-Catalyzed Suzuki Coupling of 9f.



To a stirred solution of boronic ester **9f** (80.0 mg, 0.2 mmol, 1.0 equiv) in methanol (2 mL) was added KHF_2 (0.2 mL of 4.5 M saturated aqueous solution, 0.9 mmol, 4.5 equiv) dropwise at ambient temperature and the reaction mixture was allowed to stir for 1 hour. The reaction mixture was concentrated in vacuo to provide white soild, which was used in the next step without further purification. In a 15-mL Schlenk flask, K_2CO_3 (82.8 mg, 0.6 mmol, 3.0 equiv), $Pd(OAc)_2$ (2.2 mg, 0.01 mmol, 5.0 mol%), RuPhos (9.2 mg, 10 mol%) and the potassium trifluoroborate were dissolved in 1 mL of toluene and 0.10 mL of water were added followed by addition of 4-bromoanisole (37.2 mg, 0.2 mmol, 1.0 equiv). The tube was sealed and the reaction was allowed to stir at 120°C for 12 h. The reaction mixture was cooled down to room temperature, quenched with 1.5 mL of a 1/1 (v:v) $Na_2S_2O_3$ (sat.)/$NaHCO_3$ (sat.) solution, washed with EtOAc (3 x 2 mL). The organic phases were dried over $MgSO_4$ and concentrated under vacuum. The resulting solid was purification by silica gel chromatography (petroleum ether : ethyl acetate = 20:1) as white solid (69.0 mg, 0.17 mmol, 86% yield).

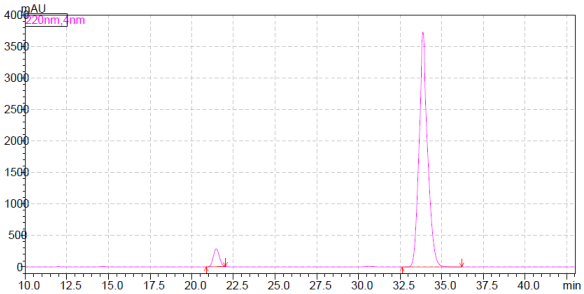
(*R*)-3-(4-Methoxyphenyl)-2-methyl-2-(naphthalen-2-yl)-1-phenylpropan-1-one 11. Yield: (69.0 mg, 86%); **IR (neat):** 3055 (m), 2973 (m), 2931 (m), 2833 (m), 1672 (s), 1608 (m), 1579 (m), 1509 (s), 1456 (m), 1356 (m), 1243 (s), 1177 (s), 1127 (m), 1033 (s), 966 (s), 847 (m), 747 (m), 664 (m), 628 (s), 542 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.88 - 7.76 (m, 3H), 7.67 (d, *J* = 1.4 Hz, 1H), 7.54 - 7.50 (m, 4H), 7.37 - 7.29 (m, 2H), 7.19 (t, *J* = 7.8 Hz, 2H), 6.67 - 6.51 (m, 4H), 3.71 (s, 3H), 3.49 - 3.37 (m, 2H), 1.67 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$)**: δ 204.0, 143.8, 136.5, 133.5, 132.1, 131.4, 129.6, 128.5, 127.9 , 127.8, 127.5, 126.1, 125.7, 124.9, 123.7, 82.8, 53.8, 25.5, 24.7, 24.6; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for $C_{27}H_{25}O_2$: 381.1844 m/z, found: 381.1849 m/z; Specific rotation: $[\alpha]_D^{20}$ –244.8 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95:5 e.r.

Enantiomeric purity of **11** was determined by HPLC analysis in comparison with authentic racemic material (95:5 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	21.237	46294215	1730747	49.822	49.822
2	33.707	46624332	1146234	50.178	50.178



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	21.467	7313433	285466	5.243	0.000
2	33.872	132189093	3730422	94.757	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	21.237	49.822	1	21.467	5.243

2	33.707	50.178	2	33.872	94.757

■ Representative Experimental Procedure for Oxidative of 3t.

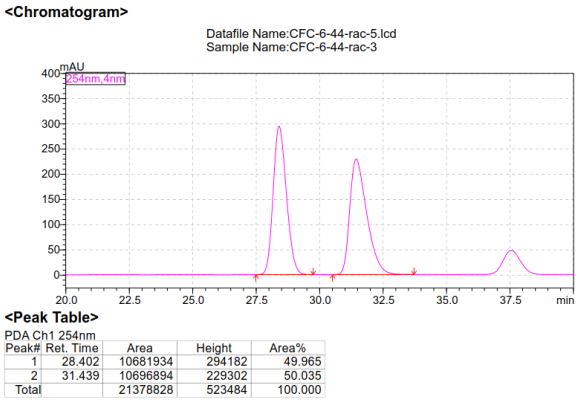
3t (109.6 mg, 0.29 mmol, 1 equiv) was dissolved in tetrahydrofuran (thf, 1.0 mL). $NaBO_3 \bullet 4H_2O$ (178.5 mg, 1.16 mmol, 4.0 equiv) and H_2O (1 mL) were added. The resulting mixture was allowed to stir at 22 °C for three hours. The reaction mixture quenched with 5 mL 20 % NaOH solution. The aqueous layer was washed with Et_2O (3 × 2 mL). The combined organic layers were concentrated *in vacuo* to provide colorless oil, which was purified by silica gel chromatography (petroleum ether : ethyl acetate = 5:1) to afford **12** as white solid (98.2 mg, 0.26 mmol, 92% yield).

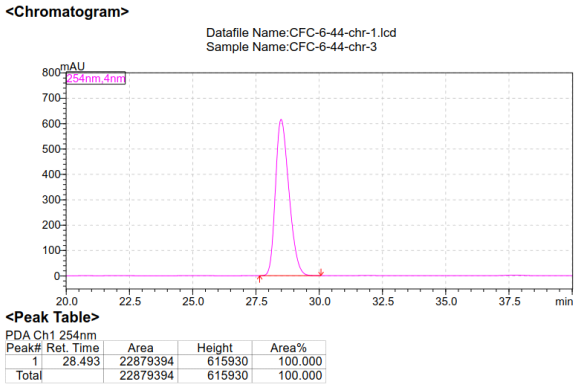
■ Cu-catalyzed Intramolecular Oxygenation of 12.

An oven-dried Schlenk flask was charged with CuI (3.8 mg, 0.02 mmol), ligand (4.3 mg, 0.03 mmol), Cs_2CO_3 (65.2 mg, 0.20 mmol), **12** (37.4 mg, 0.10 mmol) and a magnetic stir bar. Anhydrous MeCN (1 mL) were then added. The reaction mixture was heated in oil bath and stirred vigorously for 12 h at 60 ^oC. The reaction mixture was allowed to cool to room temperature, diluted with ethyl acetate (5 mL), filtered through a plug of silica gel, and further eluted with additional ethyl acetate (5 mL). The filtrate was concentrated and the resulting residue was purified by flash chromatography (petroleum ether : ethyl acetate = 15:1) to provide the desired product. (29.0 mg colourless oil, 0.1 mmol, 98 % yield).

(*3S,4S*)-3-(Benzofuran-2-yl)-3,4-dimethylchroman-4-ol (14). Yield: (29.0 mg, 98%); **IR (neat):** 3353 (br), 2921 (m), 2867 (w), 1580 (w), 1434 (m), 1400 (m), 1334 (m), 1267 (m), 1234 (s), 1123 (m), 1002 (m), 924 (m), 840 (m), 794 (s), 735 (s), 691 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.57 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 1H), 7.30 - 7.17 (m, 3H), 6.99 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 6.55 (s, 1H), 4.59 (d, *J* = 11.2 Hz, 1H), 4.35 (d, *J* = 11.2 Hz, 1H), 2.31 (s, 1H), 1.54 (s, 3H), 1.42 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.3, 154.2, 152.4, 128.9, 128.0, 127.9, 126.9, 123.9, 122.9, 121.3, 120.7, 116.2, 111.1, 103.1, 72.6, 70.1, 42.4, 29.1, 18.1; **HRMS (ESI$^+$) [M+H]$^+$:** Calcd for: $C_{19}H_{19}O_3$: 294.1365 m/z, found: 294.1360 m/z; Specific rotation: $[\alpha]_D^{20}$ -93.7 (*c*, $CHCl_3$) for an enantiomerically enriched sample of >99:1 e.r.

Enantiomeric purity of **14** was determined by HPLC analysis in comparison with authentic racemic material (>99:1 e.r. shown; Chiralcel IG column, 98:2 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).





Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	28.402	49.965	1	28.493	>99.000
2	31.439	50.035	2		<1.000

■ **Representative Experimental Procedure for Oxidative of 4a and Reduction of 4a-oxi with $Me_4NHB(OAc)_3$.** **4a** (78.0 mg, 0.2 mmol, 1.0 equiv) was dissolved in tetrahydrofuran (thf, 1.0 mL). $NaBO_3 \bullet 4H_2O$ (123.1 mg, 0.80 mmol, 4.0 equiv) and H_2O (1 mL) were added. The resulting mixture was allowed to stir at 22 °C for three hours. The aqueous layer was washed with Et_2O (3 × 2 mL). The combined organic layers were concentrated *in vacuo* to provide colorless oil, which was purified by silica gel chromatography (petroleum ether : ethyl acetate = 5:1) to afford **4a-oxi** as white solid (47.6 mg, 0.17 mmol, 85% yield).

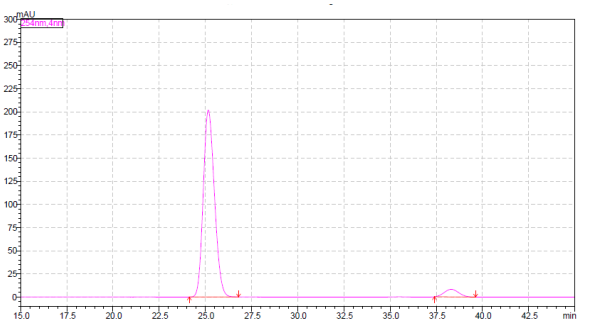
To a solution of $Me_4NHB(OAc)_3$ (328 mg, 1.25 mmol, 5 equiv) in 0.5 mL of acetonitrile and 1 mL of acetic acid at room temperature was added a solution of 70 mg of **4a-oxi** in 0.5 mL of acetonitrile. The mixture was allowed to stirr for 5 minutes at 22 °C. The mixture was poured into 4 mL of saturated sodium bicarbonate solution. The mixture was washed with CH_2Cl_2 (3 x 2 mL), the organic solution was concentrated in vacuo. HPLC analysis revealed the presence of a 4:1 ratio of diastereomers. The mixture was purified by silica gel chromatography (petroleum ether : ethyl acetate = 3:1) to afford **15** as white solid (46.6 mg, 0.165 mmol, 66% yield).

(*R*)-2-(Benzofuran-2-yl)-3-hydroxy-2-methyl-1-phenylpropan-1-one (4a-oxi). Yield: (47.6 mg, 85%); **IR (neat):** 3540 (w), 3405 (br, m), 3064 (w), 2993 (m), 2936 (m), 1678 (s), 1660 (s), 1594 (m), 1577 (m), 1451 (s), 1380 (m), 1249 (s), 1222 (s), 1167 (m), 1038 (w), 1003 (s), 950 (s), 855 (s), 750 (s), 682 (s), 565 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.71 - 7.64 (m, 2H), 7.60 - 7.55 (m, 1H), 7.47 - 7.38 (m, 2H), 7.31 - 7.21 (m, 4H), 6.74 (s, 1H), 4.29 (d, J = 11.4 Hz, 1H), 3.78 (d, J = 11.4 Hz, 1H), 2.76 (s, 1H), 1.85 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 201.7, 157.6, 154.8, 135.7, 132.8, 129.0, 128.4, 128.2, 124.3, 123.0, 121.0, 111.4, 103.7, 69.3, 53.5, 19.4; **HRMS (ESI^+) $[M+H]^+$:** Calcd for $C_{18}H_{17}O_3$: 281.1171 m/z, found: 281.1172 m/z; Specific rotation: $[\alpha]_D^{20}$ –114.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 95:5 e.r.

Enantiomeric purity of **4a-oxi** was determined by HPLC analysis in comparison with authentic racemic material (95:5 e.r. shown; Chiralcel OZ–H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).

<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	24.587	127753696	2545654	49.431	0.000
2	37.011	130696223	1740854	50.569	0.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	25.159	8525086	201859	95.010	0.000
2	38.305	447753	8213	4.990	0.000

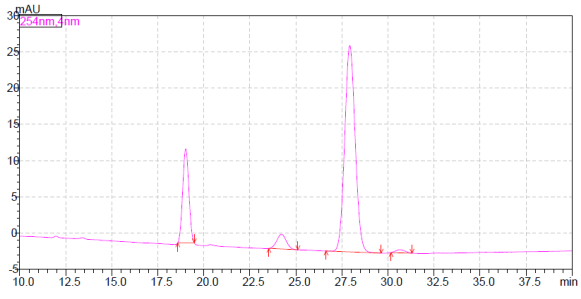
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	24.587	49.431	1	25.159	95.010
2	37.011	50.569	2	38.305	4.990

(*1R,2S*)-2-(Benzofuran-2-yl)-2-methyl-1-phenylpropane-1,3-diol 15. Yield: (46.6 mg, 66%); **IR (neat):** 3383 (br, m), 3061 (w), 2921 (s), 2851 (m), 1718 (m), 1578 (m), 1453 (s), 1374 (m), 1303 (m), 1253 (s), 1169 (m), 1024 (s), 957 (m), 914 (m), 850 (w), 749 (s), 702 (s), 627 (m), 548 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (dd, *J* = 13.6, 7.8 Hz, 2H), 7.31 - 7.20 (m, 5H), 7.17 - 7.14 (m, 2H), 6.49 (s, 1H), 5.15 (d, *J* = 3.4 Hz, 1H), 3.90 - 3.87 (m, 1H), 3.85 - 3.76 (m, 1H), 2.82 (d, *J* = 4.2 Hz, 1H), 2.30 (s, 1H), 1.32 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.9, 154.5, 140.0, 128.1, 127.9, 127.8, 127.34, 123.9, 122.8, 120.8, 111.1, 104.9, 78.0, 68.1, 47.2, 17.0; **HRMS (ESI$^+$) $[M+NH_4]^+$:** Calcd for $C_{18}H_{22}NO_3$: 300.1594 m/z, found: 300.1594 m/z; Specific rotation: $[\alpha]_D^{20}$ 58.6 (*c* 0.50, $CHCl_3$) for an enantiomerically enriched sample of 94:6 e.r.

Enantiomeric purity of **15** was determined by HPLC analysis in comparison with authentic racemic material (94:6 e.r. shown; Chiralcel IC column, 95:5 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).

<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	19.079	3110561	123642	9.836	0.000
2	24.585	12703801	356807	40.170	0.000
3	28.389	12702748	314614	40.167	0.000
4	31.264	3107821	70964	9.827	0.000

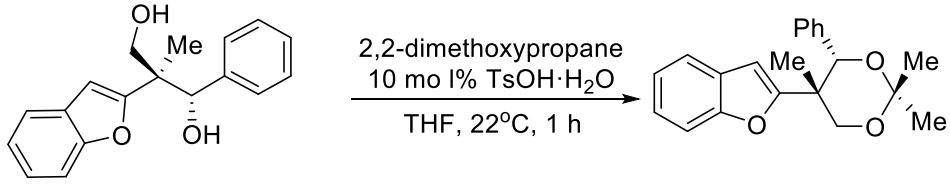


<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	19.014	302002	12968	19.910	0.000
2	24.215	73092	2030	4.819	0.000
3	27.926	1126620	28505	74.274	0.000
4	30.639	15139	431	0.997	0.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	19.079	9.836	1	19.014	19.910
2	24.585	40.170	2	24.215	4.819
3	28.389	40.167	3	27.926	74.274
4	31.264	9.827	4	30.639	0.997

Relative stereochemistry of **15** was determined through NOESY experimental study after protecting 1,3-diol **15** with 2,2-dimethoxypropane. The experimental procedure for protecting 1,3-diol as follow:

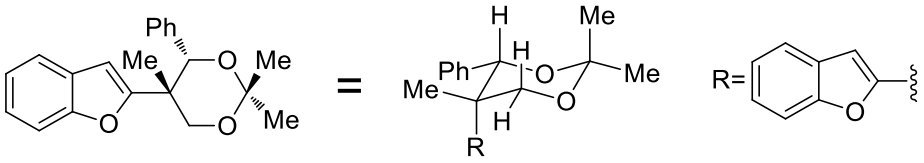


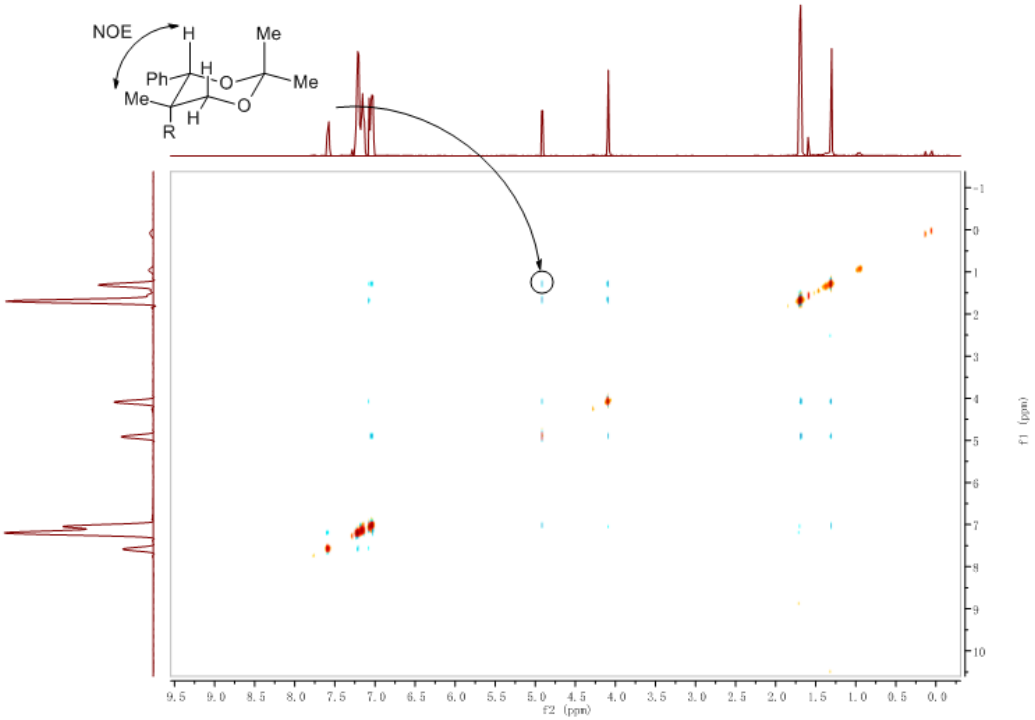
15 **15-a**

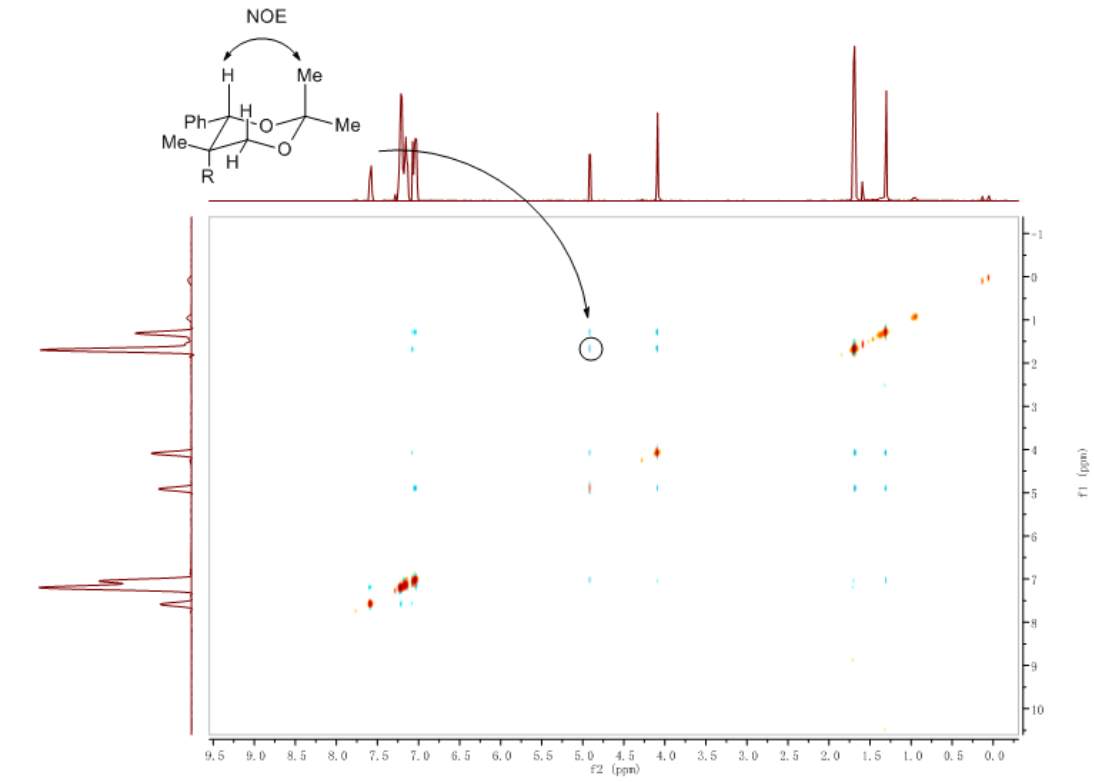
2,2-Dimethoxy propane (1 mL, 8 mmol) and *p*-toluene sulfonic acid monohydrate (3.0 mg, 0.016 mmol) were added to a solution of **15** (45 mg, 0.16 mmol) in THF (1 mL). The resulting solution was allowed to stir for 1 h at room temperature. The mixture was poured into 4 mL of 10% sodium hydroxide solution. The mixture was washed with Et_2O (3 x 2 mL), the organic solution was concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether : ethyl acetate = 50:1) to give **15-a** as white soild (43.9 mg, 0.137 mmol, 86% yield).

2-((*4R,5R*)-2,2,5-Trimethyl-4-phenyl-1,3-dioxan-5-yl)benzofuran 15-a. Yield: (43.9 mg, 86%); **IR (neat):** 2992 (m), 2965 (m), 2940 (m), 1572 (m), 1452 (s), 1378 (s), 1359 (m), 1328 (m), 1249 (s), 1196 (s), 1110 (s), 1069 (s), 1027 (s), 927 (m), 866 (m), 814 (m), 749 (s), 706 (s), 620 (m), 561 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.58 - 7.53 (m, 1H), 7.23 - 7.09 (m, 6H), 7.06 - 6.98 (m, 3H), 4.89 (s, 1H), 4.07 (s, 2H), 1.68 (s, 3H), 1.66 (s, 3H), 1.28 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 158.5, 153.6, 137.6, 128.7, 127.8, 127.5, 127.3, 123.1,

122.2, 120.5, 110.7, 105.5, 99.5, 79.7, 69.9, 40.4, 29.5, 18.7, 18.6; Specific rotation: $[\alpha]_D^{20}$ 162.8 (*c* 0.20, $CHCl_3$).



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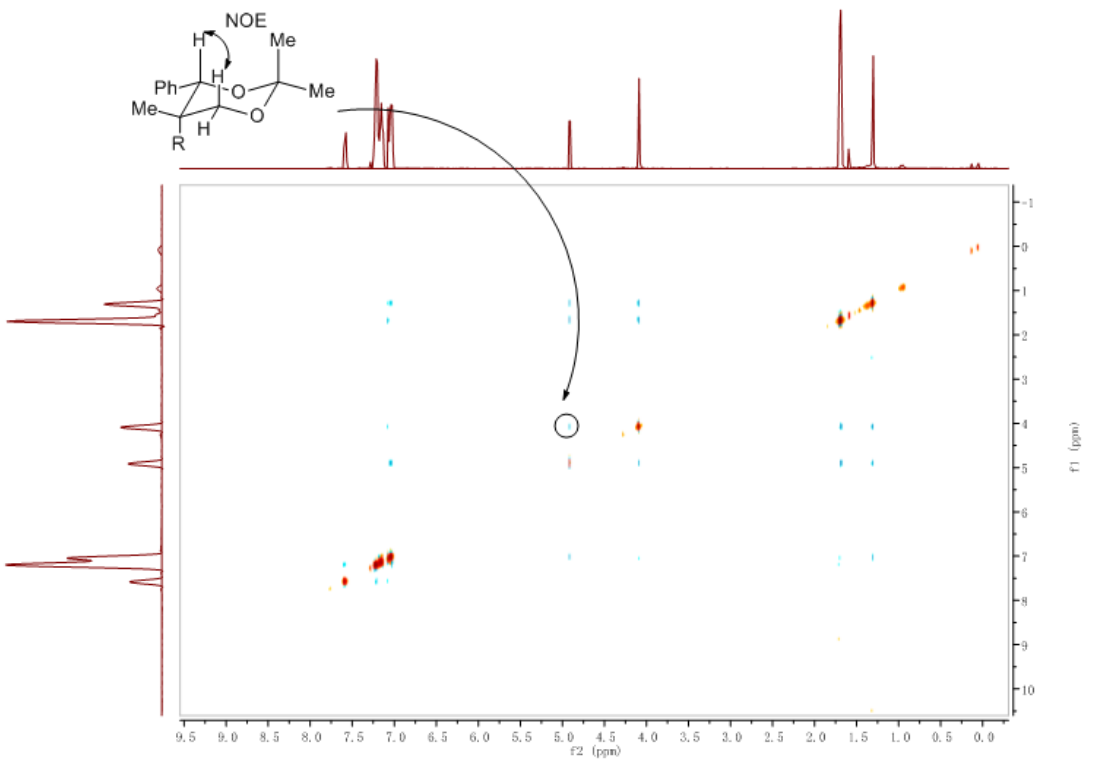
H
Me
Ph
H
O
Me
Me
O
H
R
f2 (ppm)
f1 (ppm)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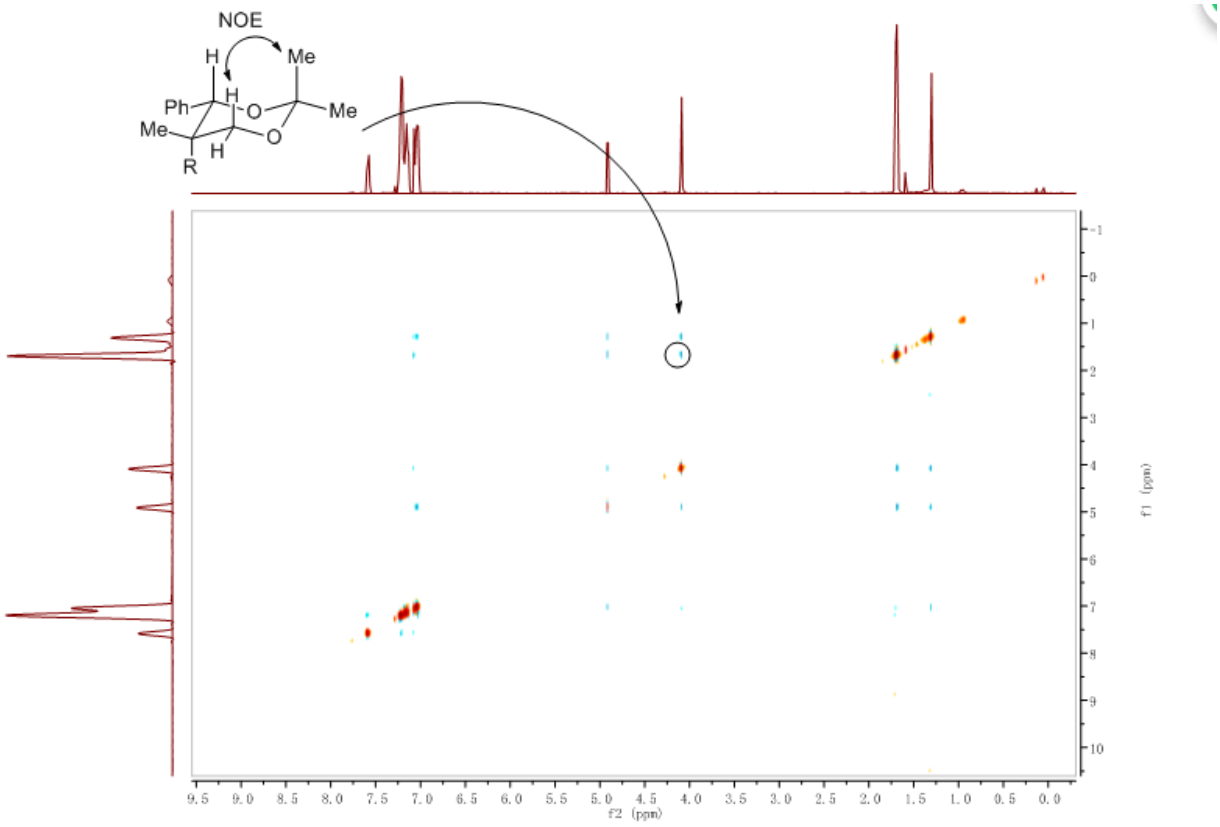
H
Me
Ph
H
O
Me
Me
O
H
R
f2 (ppm)
f1 (ppm)



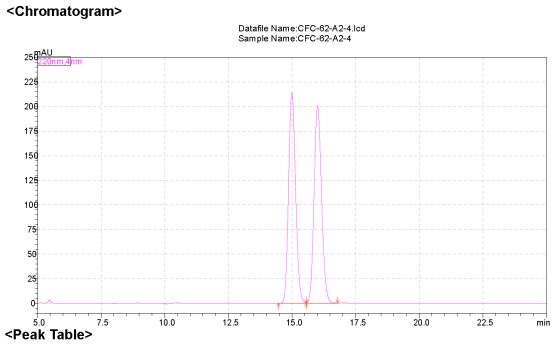
■ **Representative Experimental Procedure for Phosphine–Cu-Catalyzed Reactions of $B_2(pin)_2$, Alkene and MeOH.** In a N_2-filled glove-box, an oven-dried vial (4 mL, 17 × 38 mm) with a magnetic stir bar was charged with phosphine ligand **6i** (0.01 mmol, 5 mol %), CuCl (1.0 mg, 0.01 mmol, 5 mol%), NaO*t*-Bu (3.8 mg, 0.04 mmol, 0.2 equiv) and tetrahydrofuran (thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (60.9 mg, 0.24 mmol, 1.2 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 20 min under an atmosphere of N_2. Alkene **1a** (31.6 mg, 0.20 mmol, 1.0 equiv) and MeOH (25.6 mg, 0.80 mmol, 4.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 2 mL). The filtrate was concentrated in vacuo to provide yellow oil. The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate = 80:1) to afford **16** as colorless oil (56.3 mg, 0.19 mmol, 98% yield).

(*S*)-2-(2-(benzofuran-2-yl)propyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (16). Yield: (56.3 mg, 98%); **IR (neat):** 2977 (m), 2922 (m), 2851 (w), 1633 (w), 1455 (m), 1371 (s), 1324 (m), 1256 (m), 1144 (s), 968 (w), 847 (w), 797 (w), 750 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.47 (d, *J* = 7.2 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.21 - 7.13 (m, 2H), 6.36 (s, 1H), 3.26 - 3.18

(m, 1H), 1.37 (d, J = 6.8 Hz, 3H), 1.33 (dd, J = 15.2, 6.4 Hz, 1H), 1.24 (s, 12H), 1.12 (dd, J = 15.2, 8.0 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 165.2, 154.5, 128.9, 122.9, 122.2, 120.2, 110.7, 99.8, 83.2, 29.6, 24.8, 24.7, 21.3; **HRMS (EI$^+$) [M]$^+$** Calcd for $C_{17}H_{23}O_3B$: 285.1777 m/z, Found: 285.1782 m/z; Specific rotation: $[\alpha]_D^{20}$ 12.8 (*c* 0.50, $CHCl_3$) for an enantiomerically enriched sample of 98:2 e.r.

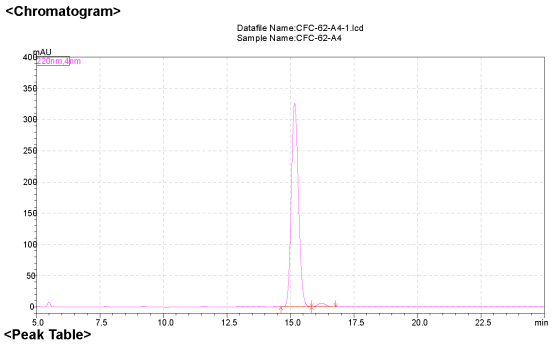
(*S*)-2-(Benzofuran-2-yl)propan-1-ol (16-oxi). Yield: (52.1 mg, 93%);**IR (neat):** 3344 (br), 2969 (w), 2878 (w), 1585 (w), 1454 (s), 1253 (s), 1168 (m), 1043 (s), 1025 (s), 938 (m), 882 (w), 801 (m), 742 (s) cm^{-1}; **1H NMR (400 MHz, $CDCl_3$):** δ 7.51 (d, J = 7.6 Hz, 1H), 7.43 (d, J = 8.0 Hz, 1H), 7.26 - 7.18 (m, 2H), 6.50 (s, 1H), 3.90 - 3.81 (m, 2H), 3.23 - 3.15 (m, 1H), 1.62 (s, 1H), 1.38 (d, J = 6.8 Hz, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.4, 154.6, 128.4, 123.5, 122.5, 120.4, 110.8, 102.3, 66.1, 36.5, 15.0; **HRMS (EI$^+$) [M]$^+$** Calcd for $C_{11}H_{12}O_2$: 176.0837 m/z, Found: 176.0842 m/z. Specific rotation: $[\alpha]_D^{20}$ 18.9 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 e.r.

Enantiomeric purity of **16-oxi** was determined by HPLC analysis in comparison with authentic racemic material (98:2 e.r. shown; Chiralcel AS-H column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	14.999	4099643	214113	50.026	0.000
2	16.009	4095398	200514	49.974	0.000
Total		8195041	414627	100.000	



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	15.167	6396899	325911	98.107	0.000
2	16.227	123453	5884	1.893	0.000
Total		6520352	331795	100.000	

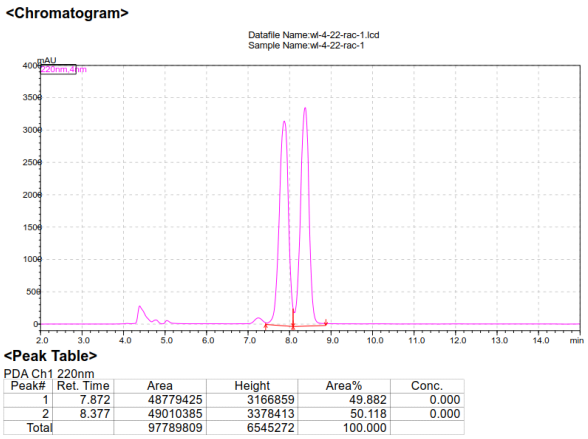
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	14.999	50.026	1	15.167	98.107
2	16.009	49.974	2	16.227	1.893

■ **Representative Experimental Procedure for Phosphine–Cu-Catalyzed Reactions of $B_2(pin)_2$, 1,1-Disubstituted Alkene and Cyanation reagent:** In a N_2-filled glove-box, an oven-dried vial (4 mL, 17 × 38 mm) with a magnetic stir bar was charged with (*R*,*R*)-Ph-BPE (10.1 mg, 0.02 mmol, 10 mol %), CuCl (2.0 mg, 0.02 mmol, 10 mol%), LiO*t*-Bu (24.0 mg, 0.3 mmol, 1.5 equiv), 4Å molecular sieve (200 mg) and tetrahydrofuran (thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (76.2

mg, 0.30 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 30 min under an atmosphere of N_2. Alkene **1a** (47.5 mg, 0.30 mmol, 1.5 equiv) and **17** (54.4 mg, 0.20 mmol, 1.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 2 mL). The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate =30:1) to afford **18** as colorless oil (28.0 mg, 0.09 mmol, 45 % yield).

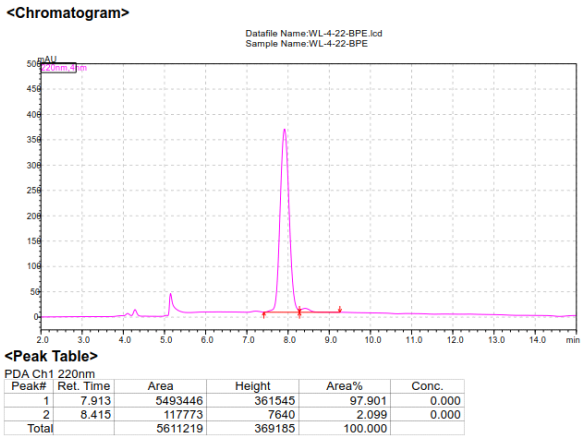
2-(Benzofuran-2-yl)-2-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanenitrile (18). Yield: (28.0 mg, 45%); **IR (neat):** 2979 (m), 2159 (w), 1581 (w), 1454 (m), 1366 (s), 1339 (m), 1259 (s), 1141 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.28 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 6.69 (s, 1H), 1.90 (s, 3H), 1.75 (d, *J* = 15.6 Hz, 1H), 1.68 (d, *J* = 15.6 Hz, 1H), 1.22 (s, 12H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 156.6, 154.8, 127.7, 124.4, 122.9, 122.2, 121.0, 111.2, 102.5, 83.8, 34.3, 25.9, 24.6, 24.6; **HRMS (EI$^+$) [M+NH$_4$]$^+$** Calcd for $C_{18}H_{26}BN_2O_3$: 328.2067 m/z, Found: 328.2076 m/z; Specific rotation: $[\alpha]_D^{20}$ 6.8 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 98:2 e.r.

Enantiomeric purity of **18** was determined by HPLC analysis in comparison with authentic racemic material (98:2 e.r. shown; Chiralcel OZ-H column, 99:1 hexanes/ *i*PrOH, 0.8 mL/min, 220 nm).



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	7.872	48779425	3166859	49.882	0.000
2	8.377	49010385	3378413	50.118	0.000
Total		97789809	6545272	100.000	



<Peak Table>
PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Area%	Conc.
1	7.913	5493446	361545	97.901	0.000
2	8.415	117773	7640	2.099	0.000
Total		5611219	369185	100.000	

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	7.872	49.882	1	7.913	97.901
2	8.377	50.118	2	8.415	2.099

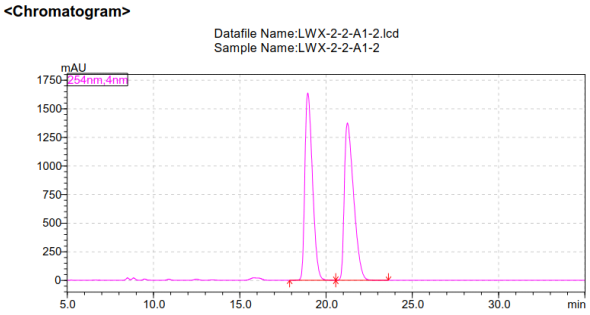
■ **Representative Experimental Procedure for Phosphine–Cu-Catalyzed Reactions of $B_2(pin)_2$, 1,1-Disubstituted Alkene and Benzaldehyde:** In a N_2-filled glove-box, an oven-dried vial (4 mL, 17 × 38 mm) with a magnetic stir bar was charged with

(*R*,*R*)-Ph-BPE (10.1 mg, 0.02 mmol, 10 mol %), CuCl (2.0 mg, 0.02 mmol, 10 mol%), LiO*t*-Bu (24.0 mg, 0.3 mmol, 1.5 equiv), 4Å molecular sieve (200 mg) and tetrahydrofuran (thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (76.2 mg, 0.30 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 30 min under an atmosphere of N_2. Alkene **1a** (63.3 mg, 0.40 mmol, 2.0 equiv) and **20** (21.2 mg, 0.20 mmol, 1.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 2 mL). The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate =15:1) to afford **21a** as colorless oil (22.5 mg, 0.08 mmol, 38 % yield).

4-(Benzofuran-2-yl)-4-methyl-5-phenyl-1,2-oxaborolan-2-ol (21a). Yield: (22.5 mg, 38%); **IR (neat):** 2962 (m), 2925 (w), 2856 (w), 1453 (w), 1425 (w), 1260 (s), 1091 (m), 1019 (s), 873 (w), 799 (s), 750 (w), 701 (m) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 - 7.30 (m, 1H), 7.28 - 7.22 (m, 1H), 7.18 - 7.09 (m, 2H), 7.09 - 7.02 (m, 3H), 7.02 - 6.94 (m, 2H), 6.11 (s, 1H), 5.32 (s, 1H), 5.16 (s, 1H), 1.73 (d, *J* = 16.4 Hz, 1H), 1.64 (s, 3H), 1.32 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 161.1, 154.4, 138.4, 128.0, 127.6, 127.5, 125.5, 123.3, 122.2, 120.3, 110.7, 102.6, 89.9, 49.1, 24.7; **HRMS (EI$^+$) [M+H]$^+$** Calcd for $C_{18}H_{18}BO_3$: 292.1380 m/z, Found: 292.1378 m/z; Specific rotation: $[\alpha]_D^{20}$ 83.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

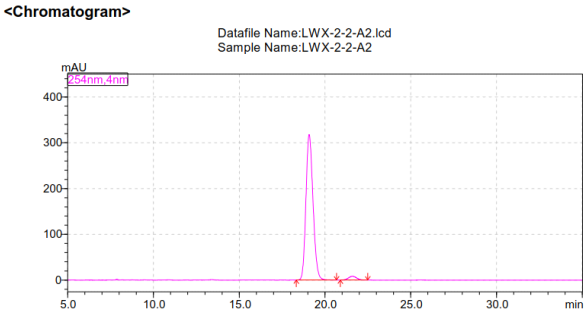
2-(Benzofuran-2-yl)-2-methyl-1-phenylpropane-1,3-diol (21a-oxi). Yield: (19.3 mg, 90%); **IR (neat):** 3356 (br), 3034 (w), 2921 (s), 2867 (m), 1575 (m), 1445 (s), 1356 (m), 1301 (m), 1223 (s), 1189 (m), 1024 (s), 934 (m), 852 (m), 732 (s), 625 (m) ; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.53 - 7.45 (m, 2H), 7.31 - 7.19 (m, 5H), 7.16 - 7.10 (m, 2H), 6.47 (s, 1H), 5.12 (s, 1H), 3.88 (d, *J* = 11.2 Hz, 1H), 3.79 (d, *J* = 11.2 Hz, 1H), 2.99 (s, 1H), 2.49 (s, 1H), 1.32 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 159.8, 154.4, 140.0, 128.0, 127.8, 127.7, 127.3, 123.8, 122.8, 120.7, 111.0, 104.8, 78.0, 67.9, 47.1, 17.1; **HRMS (EI$^+$) [M+NH_4]$^+$** Calcd for $C_{18}H_{22}NO_3$: 300.1594 m/z, Found: 300.1596 m/z; Specific rotation: $[\alpha]_D^{20}$ 50.7 (*c* 1.00, $CHCl_3$) for an enantiomerically enriched sample of 97:3 e.r.

Enantiomeric purity of **21a-oxi** was determined by HPLC analysis in comparison with authentic racemic material (97:3 e.r. shown; Chiralcel IG column, 97:3 hexanes/ *i*PrOH, 0.8 mL/min, 254 nm).



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	18.941	50426005	1637465	49.435
2	21.239	51578042	1376194	50.565
Total		102004047	3013660	100.000



<Peak Table>
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	19.078	9114398	317654	97.118
2	21.603	270457	8285	2.882
Total		9384856	325939	100.000

Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	18.941	49.435	1	19.078	97.118
2	21.239	50.565	2	21.603	2.882

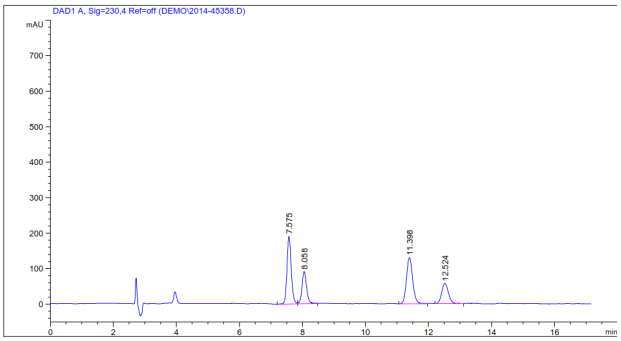
■ **Representative Experimental Procedure for Phosphine–Cu-Catalyzed Reactions of $B_2(pin)_2$, 1,1-Disubstituted Alkene and Aldimine:** In a N_2-filled glove-box, an oven-dried vial (4 mL, 17 × 38 mm) with a magnetic stir bar was charged with (*R*,*R*)-Ph-BPE (10.1 mg, 0.02 mmol, 10 mol %), CuCl (2.0 mg, 0.02 mmol, 10 mol%), LiO*t*-Bu (24.0 mg, 0.3 mmol, 1.5 equiv), 4Å molecular sieve (200 mg) and tetrahydrofuran (thf, 1 mL). The vessel was sealed with a cap (phenolic open top cap with red PTFE/white silicone septum) and the solution was allowed to stir at 22 °C for one hour. Bis(pinacolato)diboron (76.2 mg, 0.30 mmol, 1.5 equiv) was added to the solution, causing it to turn dark brown immediately. The vial was re-sealed with a cap (phenolic open top cap with red PTFE/white silicone septum). The mixture was allowed to stir at 22 °C for 30 min under an atmosphere of N_2. Alkene **1a** (63.3 mg, 0.40 mmol, 2.0 equiv) and aldimine **22** (54.2 mg, 0.20 mmol, 1.0 equiv) were added. The resulting solution was allowed to stir at 22 °C for 16 h before the reaction was quenched by passing the mixture through a short plug of celite and silica gel and eluted with Et_2O (3 × 2 mL). The crude was purified by silica gel chromatography (petroleum ether : ethyl acetate =60:1) to afford **23a** as colorless oil (65.8 mg, 0.12 mmol, 59 % yield).

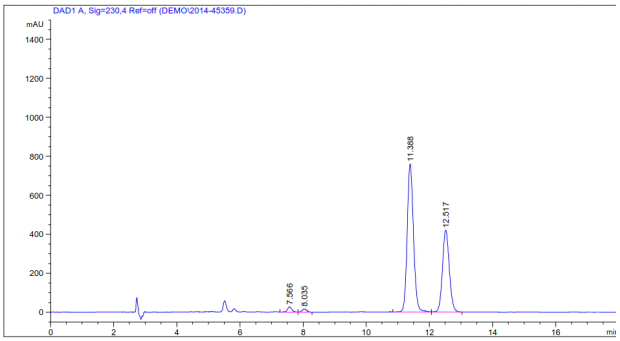
***N*-benzhydryl-2-(benzofuran-2-yl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-amine (23a). Yield:** (65.8 mg, 59%); **IR (neat):** 3060 (w), 3026 (w), 2976 (m), 1660 (w), 1491 (w), 1452 (s), 1355 (s), 1322 (m), 1253 (m), 1166 (m), 1108 (s), 1004 (m), 941 (m), 883 (m), 802 (m), 731 (s), 698 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.54 (d, *J* = 7.4 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.32 – 7.24 (m, 9H), 7.22 – 7.15 (m, 6H), 6.98 (d, *J* = 7.0 Hz, 2H), 6.52 (s, 1H), 4.46 (s, 1H), 3.88 (s, 1H), 1.53 (s, 3H), 1.16 (s, 6H), 1.12 (s, 6H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 164.1, 154.3, 144.9, 143.1, 140.0, 130.0, 128.5, 128.1, 128.0, 127.7, 127.5, 127.1, 127.0, 126.7, 126.5, 123.1, 122.2, 120.3, 110.9, 103.0, 82.8, 67.8, 63.3, 42.7,

24.7, 24.4, 24.1; **HRMS (ESI$^+$) [M+H]$^+$** Calcd for $C_{37}H_{41}BNO_3$: 557.3210 m/z, Found: 557.3206 m/z.

3-(Benzhydrylamino)-2-(benzofuran-2-yl)-2-methyl-3-phenylpropan-1-ol (23a-oxi). IR (neat): 3344 (br), 3059 (w), 2973 (w), 2925 (w), 1579 (w), 1491 (m), 1451 (s), 1348 (w), 1253 (s), 1167 (m), 1029 (m), 883 (m), 801 (m), 741 (s), 697 (s) cm^{-1}; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.35 - 7.27 (m, 10H), 7.24 - 7.18 (m, 6H), 6.66 (s, 1H), 4.52 (s, 1H), 4.31 (s, 1H), 4.13 (d, *J* = 11.4 Hz, 1H), 3.91 (s, 1H), 3.87 (d, *J* = 11.4 Hz, 1H), 1.17 (s, 3H); **^{13}C NMR (100 MHz, $CDCl_3$):** δ 160.8, 154.3, 143.3, 141.4, 137.7, 128.7, 128.5, 128.2, 128.1 127.8, 127.6, 127.4, 126.8, 123.7, 122.6, 120.8, 110.9, 104.0, 68.8, 66.9, 63.6, 45.3, 18.6; **HRMS (ESI$^+$) [M+H]$^+$** Calcd for $C_{31}H_{30}NO_2$: 448.2271 m/z, Found: 448.2263 m/z.

Enantiomeric purity of **23a-oxi** was determined by SFC analysis in comparison with authentic racemic material (62:38 d.r., 97.5:2.5 e.r. shown for both diastereomers; Chiralcel AD-H column, 80:20 CO_2/ *i*PrOH, 1.3 mL/min, 230 nm).





Signal 1: DAD1 A, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.575	BV	0.1436	1793.20618	190.88422	33.4471
2	8.058	VV	0.1579	933.63306	90.83450	17.4143
3	11.398	BV	0.2141	1786.41846	130.19733	33.3205
4	12.524	BB	0.2251	848.05688	57.14259	15.8181

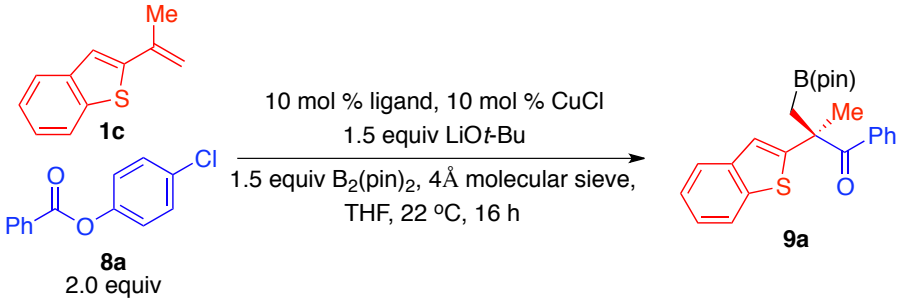
Signal 1: DAD1 A, Sig=230,4 Ref=off

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.566	VV	0.1514	274.99893	27.33329	1.6026
2	8.035	VB	0.1550	164.30467	16.11070	0.9575
3	11.388	VB	0.2124	1.04465e4	759.59180	60.8790
4	12.517	BV	0.2301	6273.62207	420.33893	36.5609

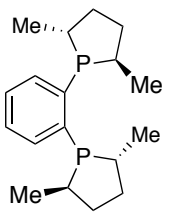
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	7.575	33.447	1	7.566	1.603
2	8.058	17.414	2	8.035	0.957
3	11.398	33.321	3	11.388	60.879
4	12.524	15.818	4	12.517	36.561

■ Additional Data for Ligand Screen

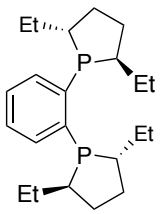
Table S1. Ligand Screen for Enantioselective Coupling of 1,1-Disubstituted Alkene, Phenol Ester and $B_2(pin)_2$



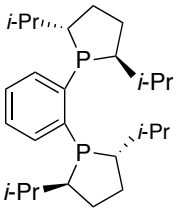
Entry	Ligand	Yield (%)[a]	e.r.[b]
1	**6d**	28	33:67
2	6e	32	34:66
3	6f	18	52:48
4	6k	32	75:25
5	6l	75	86:14
6	6m	85	83:17
7	6n	28	88:12
8	6o	<5%	na
9[c]	(*R*,*R*)-Ph-BPE	15	54:46



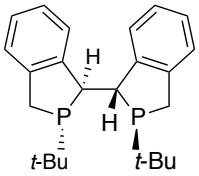
6d



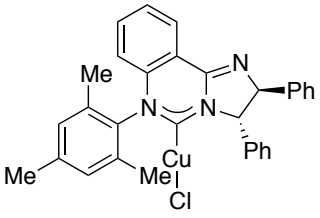
6e



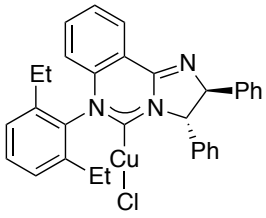
6f



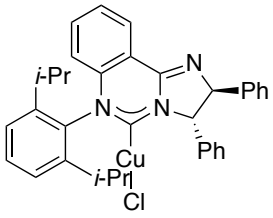
6k



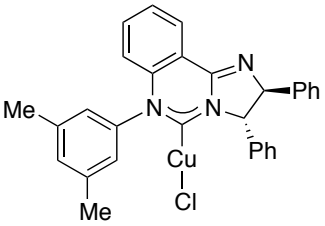
6l



6m



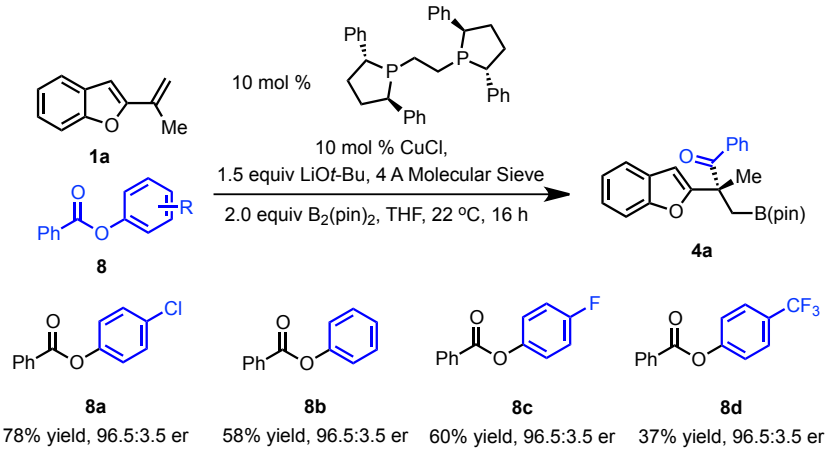
6n



6o

[a]Yields of purified product. [b]Enantiomeric ratios (e.r.) were determined by HPLC analysis. [c]The reaction was conducted at 60 °C for 12 h.

Scheme S1. Optimization of Electrophiles for Enantioselective Coupling of 1,1-Disubstituted Alkene, Phenol Ester and $B_2(pin)_2$



■ Proof of Stereochemistry: X-ray Characterization Data

1. (*R*)-2-(Benzofuran-2-yl)-2-methyl-1-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one (4a) (CCDC number: 1579294)

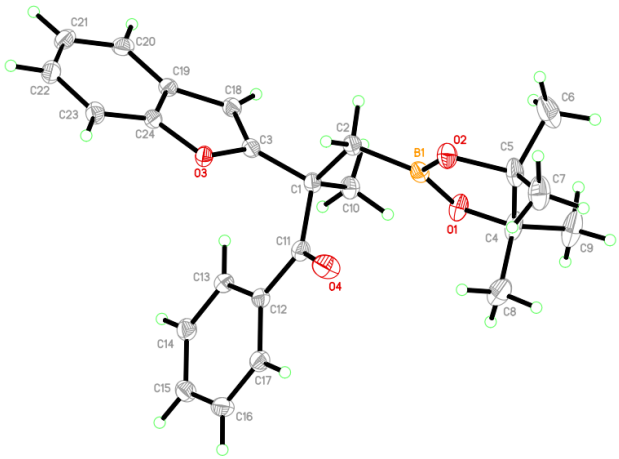


Table S2. Crystal data and structure refinement for A.

Identification code	A
Empirical formula	C24 H27 B O4
Formula weight	390.27

Temperature	173(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 12.5495(6) A alpha = 90 deg. b = 6.3424(3) A beta = 92.671(2) deg. c = 13.2506(6) A gamma = 90 deg.
Volume	1053.52(9) A^3
Z, Calculated density	2, 1.230 Mg/m^3
Absorption coefficient	0.652 mm^-1
F(000)	567
Crystal size	0.05 x 0.04 x 0.03 mm
Theta range for data collection	3.339 to 66.732 deg.
Limiting indices	-14<=h<=14, -7<=k<=7, -15<=l<=15
Reflections collected / unique	13476 / 3646 [R(int) = 0.0218]
Completeness to theta = 66.732	99.2 %

Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3646 / 1 / 267
Goodness-of-fit on F^2	1.057
Final R indices [I>2sigma(I)]	R1 = 0.0260, wR2 = 0.0676
R indices (all data)	R1 = 0.0267, wR2 = 0.0682
Absolute structure parameter	0.06(5)
Extinction coefficient	n/a
Largest diff. peak and hole	0.122 and -0.136 e.A^-3

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for A.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
B(1)	2193(2)	3931(3)	9132(1)	31(1)
C(1)	2704(1)	6288(3)	7550(1)	28(1)
C(2)	1859(1)	4981(3)	8090(1)	31(1)
C(3)	2208(1)	7140(3)	6583(1)	27(1)
C(4)	3052(2)	3158(3)	10636(1)	42(1)
C(5)	1948(2)	2056(3)	10562(1)	43(1)
C(6)	1089(2)	3247(5)	11106(2)	65(1)
C(7)	1951(2)	-257(4)	10861(2)	57(1)
C(8)	3975(2)	1710(4)	10392(2)	53(1)
C(9)	3315(2)	4351(4)	11614(2)	64(1)
C(10)	3092(2)	8131(3)	8226(1)	33(1)
C(11)	3661(1)	4848(3)	7349(1)	30(1)
C(12)	4594(1)	5630(3)	6786(1)	28(1)
C(13)	4617(1)	7561(3)	6278(1)	31(1)
C(14)	5502(1)	8127(3)	5747(1)	35(1)
C(15)	6367(1)	6792(3)	5719(1)	39(1)
C(16)	6363(1)	4892(3)	6231(1)	39(1)

C(17)	5485(1)	4308(3)	6760(1)	35(1)
C(18)	1783(1)	9022(3)	6334(1)	29(1)
C(19)	1385(1)	8874(3)	5299(1)	28(1)
C(20)	869(1)	10250(3)	4612(1)	34(1)
C(21)	605(1)	9507(3)	3654(1)	38(1)
C(22)	844(2)	7433(3)	3367(1)	39(1)
C(23)	1362(1)	6047(3)	4038(1)	34(1)
C(24)	1611(1)	6821(3)	4994(1)	28(1)
O(1)	2948(1)	4691(2)	9814(1)	39(1)
O(2)	1655(1)	2224(2)	9481(1)	39(1)
O(3)	2113(1)	5725(2)	5781(1)	28(1)
O(4)	3671(1)	3064(2)	7683(1)	47(1)

Table S4. Selected bond lengths [A] and angles [deg] for A.

Symmetry transformations used to generate equivalent atoms:

Table S5. Bond lengths [A] and angles [deg] for A.

B(1)-O(1)	1.365(2)
B(1)-O(2)	1.368(2)
B(1)-C(2)	1.573(2)

C(1)-C(3)	1.499(2)
C(1)-C(10)	1.537(2)
C(1)-C(11)	1.541(2)
C(1)-C(2)	1.548(2)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(18)	1.343(2)
C(3)-O(3)	1.391(2)
C(4)-O(1)	1.462(2)
C(4)-C(9)	1.523(3)
C(4)-C(8)	1.524(3)
C(4)-C(5)	1.551(3)
C(5)-O(2)	1.466(2)
C(5)-C(7)	1.520(3)
C(5)-C(6)	1.525(3)
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800

C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-O(4)	1.215(2)
C(11)-C(12)	1.502(2)
C(12)-C(13)	1.398(2)
C(12)-C(17)	1.399(2)
C(13)-C(14)	1.389(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.378(3)
C(14)-H(14)	0.9500
C(15)-C(16)	1.384(3)
C(15)-H(15)	0.9500
C(16)-C(17)	1.384(3)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(19)	1.441(2)
C(18)-H(18)	0.9500
C(19)-C(24)	1.397(3)
C(19)-C(20)	1.398(2)
C(20)-C(21)	1.380(3)
C(20)-H(20)	0.9500
C(21)-C(22)	1.405(3)
C(21)-H(21)	0.9500
C(22)-C(23)	1.390(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.381(2)
C(23)-H(23)	0.9500
C(24)-O(3)	1.3810(19)

O(1)-B(1)-O(2)	113.22(15)
O(1)-B(1)-C(2)	125.42(16)
O(2)-B(1)-C(2)	121.08(16)
C(3)-C(1)-C(10)	109.38(14)
C(3)-C(1)-C(11)	111.19(13)
C(10)-C(1)-C(11)	108.90(13)
C(3)-C(1)-C(2)	108.76(13)
C(10)-C(1)-C(2)	110.04(13)
C(11)-C(1)-C(2)	108.57(13)
C(1)-C(2)-B(1)	118.19(14)
C(1)-C(2)-H(2A)	107.8
B(1)-C(2)-H(2A)	107.8
C(1)-C(2)-H(2B)	107.8
B(1)-C(2)-H(2B)	107.8
H(2A)-C(2)-H(2B)	107.1
C(18)-C(3)-O(3)	111.52(14)
C(18)-C(3)-C(1)	132.45(16)
O(3)-C(3)-C(1)	115.96(14)
O(1)-C(4)-C(9)	108.18(17)
O(1)-C(4)-C(8)	106.58(16)
C(9)-C(4)-C(8)	110.11(18)
O(1)-C(4)-C(5)	101.71(15)
C(9)-C(4)-C(5)	115.76(19)
C(8)-C(4)-C(5)	113.62(18)
O(2)-C(5)-C(7)	108.84(17)
O(2)-C(5)-C(6)	106.02(17)
C(7)-C(5)-C(6)	110.3(2)

O(2)-C(5)-C(4)	102.24(14)
C(7)-C(5)-C(4)	115.3(2)
C(6)-C(5)-C(4)	113.3(2)
C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(4)-C(8)-H(8A)	109.5
C(4)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(4)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(4)-C(9)-H(9A)	109.5
C(4)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(4)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(1)-C(10)-H(10A)	109.5

C(1)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(1)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(4)-C(11)-C(12)	119.55(16)
O(4)-C(11)-C(1)	118.96(15)
C(12)-C(11)-C(1)	121.44(14)
C(13)-C(12)-C(17)	118.59(15)
C(13)-C(12)-C(11)	124.24(15)
C(17)-C(12)-C(11)	117.16(16)
C(14)-C(13)-C(12)	120.37(16)
C(14)-C(13)-H(13)	119.8
C(12)-C(13)-H(13)	119.8
C(15)-C(14)-C(13)	120.25(18)
C(15)-C(14)-H(14)	119.9
C(13)-C(14)-H(14)	119.9
C(14)-C(15)-C(16)	120.07(17)
C(14)-C(15)-H(15)	120.0
C(16)-C(15)-H(15)	120.0
C(17)-C(16)-C(15)	120.18(17)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(12)	120.53(17)
C(16)-C(17)-H(17)	119.7
C(12)-C(17)-H(17)	119.7
C(3)-C(18)-C(19)	106.98(15)
C(3)-C(18)-H(18)	126.5

C(19)-C(18)-H(18)	126.5
C(24)-C(19)-C(20)	119.21(16)
C(24)-C(19)-C(18)	105.70(14)
C(20)-C(19)-C(18)	135.10(17)
C(21)-C(20)-C(19)	117.99(18)
C(21)-C(20)-H(20)	121.0
C(19)-C(20)-H(20)	121.0
C(20)-C(21)-C(22)	121.61(17)
C(20)-C(21)-H(21)	119.2
C(22)-C(21)-H(21)	119.2
C(23)-C(22)-C(21)	121.20(17)
C(23)-C(22)-H(22)	119.4
C(21)-C(22)-H(22)	119.4
C(24)-C(23)-C(22)	116.18(18)
C(24)-C(23)-H(23)	121.9
C(22)-C(23)-H(23)	121.9
C(23)-C(24)-O(3)	126.19(17)
C(23)-C(24)-C(19)	123.82(16)
O(3)-C(24)-C(19)	109.99(14)
B(1)-O(1)-C(4)	107.08(15)
B(1)-O(2)-C(5)	106.40(14)
C(24)-O(3)-C(3)	105.81(13)

Symmetry transformations used to generate equivalent atoms:

Table S6. Anisotropic displacement parameters (A^2 x 10^3) for A.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
B(1)	35(1)	31(1)	28(1)	-1(1)	6(1)	2(1)
C(1)	31(1)	29(1)	23(1)	1(1)	2(1)	1(1)
C(2)	31(1)	35(1)	26(1)	0(1)	3(1)	-1(1)
C(3)	27(1)	29(1)	25(1)	-1(1)	4(1)	-1(1)
C(4)	68(1)	32(1)	25(1)	5(1)	-6(1)	2(1)
C(5)	69(1)	36(1)	25(1)	6(1)	10(1)	2(1)
C(6)	88(2)	60(2)	49(1)	10(1)	32(1)	10(1)
C(7)	93(2)	38(1)	39(1)	10(1)	5(1)	-5(1)
C(8)	61(1)	52(1)	45(1)	1(1)	-13(1)	7(1)
C(9)	113(2)	44(1)	31(1)	0(1)	-16(1)	4(1)
C(10)	40(1)	30(1)	29(1)	-2(1)	2(1)	-2(1)
C(11)	34(1)	28(1)	27(1)	2(1)	0(1)	1(1)
C(12)	30(1)	31(1)	25(1)	-2(1)	0(1)	3(1)
C(13)	30(1)	34(1)	30(1)	3(1)	1(1)	3(1)
C(14)	34(1)	41(1)	30(1)	4(1)	2(1)	-4(1)
C(15)	32(1)	52(1)	33(1)	-4(1)	4(1)	-4(1)
C(16)	31(1)	47(1)	40(1)	-6(1)	1(1)	7(1)
C(17)	38(1)	35(1)	31(1)	0(1)	-1(1)	6(1)
C(18)	30(1)	29(1)	28(1)	0(1)	4(1)	3(1)
C(19)	23(1)	33(1)	28(1)	5(1)	4(1)	-1(1)
C(20)	25(1)	37(1)	40(1)	10(1)	5(1)	2(1)

C(21)	28(1)	51(1)	36(1)	17(1)	-3(1)	-1(1)
C(22)	35(1)	52(1)	29(1)	5(1)	-1(1)	-7(1)
C(23)	34(1)	39(1)	28(1)	1(1)	3(1)	-5(1)
C(24)	25(1)	34(1)	26(1)	5(1)	3(1)	-2(1)
O(1)	54(1)	35(1)	28(1)	5(1)	-6(1)	-4(1)
O(2)	46(1)	39(1)	32(1)	6(1)	4(1)	-5(1)
O(3)	34(1)	27(1)	23(1)	1(1)	1(1)	2(1)
O(4)	50(1)	30(1)	63(1)	16(1)	16(1)	9(1)

Table S7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for A.

	x	y	z	U(eq)
H(2A)	1609	3847	7623	37
H(2B)	1241	5912	8197	37
H(6A)	1110	4742	10921	97
H(6B)	1219	3102	11838	97
H(6C)	387	2663	10909	97
H(7A)	1224	-818	10788	85
H(7B)	2215	-398	11566	85
H(7C)	2416	-1047	10423	85
H(8A)	3798	949	9763	80
H(8B)	4100	698	10943	80

H(8C)	4620	2554	10313	80
H(9A)	3996	5089	11563	95
H(9B)	3367	3354	12179	95
H(9C)	2749	5378	11729	95
H(10A)	3557	9050	7847	49
H(10B)	3489	7578	8823	49
H(10C)	2476	8939	8439	49
H(13)	4025	8490	6296	37
H(14)	5511	9440	5402	42
H(15)	6966	7178	5346	46
H(16)	6965	3986	6220	47
H(17)	5487	2999	7108	42
H(18)	1751	10224	6759	34
H(20)	705	11655	4799	41
H(21)	254	10419	3177	46
H(22)	647	6971	2702	46
H(23)	1534	4647	3849	40

Table S8. Selected torsion angles [deg] for A.

2. (*2S,3S*)-2-(benzo[b]thiophen-2-yl)-2-methyl-3-phenylbutane-1,3-diol (7b-oxi). (CCDC number: 1579300)

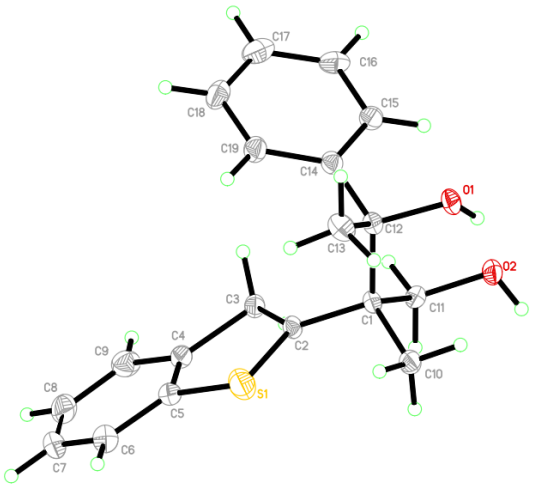


Table S9. Crystal data and structure refinement for a.

Identification code	a
Empirical formula	C19 H21 O2 S
Formula weight	313.42
Temperature	173(2) K
Wavelength	1.54178 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 6.6120(6) A alpha = 90 deg. b = 7.8997(7) A beta = 92.455(3) deg. c = 15.4119(13) A gamma = 90 deg.
Volume	804.27(12) A^3
Z, Calculated density	2, 1.294 Mg/m^3
Absorption coefficient	1.815 mm^-1

F(000)	608
Crystal size	0.05 x 0.04 x 0.03 mm
Theta range for data collection	2.870 to 66.577 deg.
Limiting indices	-7<=h<=7, -9<=k<=9, -18<=l<=18
Reflections collected / unique	10232 / 2796 [R(int) = 0.0340]
Completeness to theta = 66.577	99.2 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2796 / 193 / 203
Goodness-of-fit on F^2	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0824, wR2 = 0.2256
R indices (all data)	R1 = 0.0840, wR2 = 0.2279
Absolute structure parameter	0.123(9)
Extinction coefficient	n/a
Largest diff. peak and hole	1.824 and -0.411 e.A^-3

Table S10. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for a.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
S(1)	255(3)	2085(3)	7258(1)	50(1)
O(1)	3499(7)	5300(6)	9675(3)	33(1)
C(1)	3269(10)	3234(8)	8490(4)	27(1)
O(2)	6426(7)	3204(6)	9443(3)	34(1)
C(2)	2683(9)	2922(8)	7534(4)	25(1)
C(3)	4302(10)	3259(9)	6766(4)	30(1)
C(5)	888(11)	1930(9)	6185(4)	34(1)
C(4)	2813(12)	2479(8)	6019(4)	34(2)
C(6)	-396(14)	1237(11)	5523(6)	46(2)
C(7)	341(15)	1103(11)	4708(5)	50(2)
C(9)	3500(12)	2350(10)	5156(5)	42(2)
C(8)	2224(15)	1642(11)	4524(5)	51(2)
C(10)	2234(10)	1936(10)	9050(4)	35(2)
C(11)	5584(10)	2927(9)	8579(4)	29(1)
C(12)	2726(9)	5091(9)	8782(4)	28(1)
C(13)	473(10)	5386(11)	8836(5)	38(2)
C(14)	3661(10)	6423(8)	8204(4)	28(1)
C(15)	5581(10)	7079(10)	8413(4)	32(1)
C(16)	6447(12)	8296(9)	7889(5)	40(2)
C(17)	5399(14)	8870(10)	7155(5)	47(2)
C(18)	3504(13)	8235(10)	6933(5)	42(2)
C(19)	2659(11)	7033(10)	7458(4)	36(2)

Table S11. Selected bond lengths [A] and angles [deg] for a.

Symmetry transformations used to generate equivalent atoms:

Table S12. Bond lengths [A] and angles [deg] for a.

S(1)-C(5)	1.726(7)
S(1)-C(2)	1.771(7)
O(1)-C(12)	1.457(8)
O(1)-H(1)	0.8400
C(1)-C(10)	1.522(9)
C(1)-C(2)	1.526(8)
C(1)-C(11)	1.550(9)
C(1)-C(12)	1.580(9)
O(2)-C(11)	1.438(8)
O(2)-H(2)	0.8400
C(2)-C(3)	1.652(9)
C(3)-C(4)	1.605(9)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(5)-C(4)	1.379(11)
C(5)-C(6)	1.410(11)
C(4)-C(9)	1.427(10)
C(6)-C(7)	1.371(12)
C(6)-H(6)	0.9500
C(7)-C(8)	1.357(13)
C(7)-H(7)	0.9500
C(9)-C(8)	1.380(12)
C(9)-H(9)	0.9500
C(8)-H(8)	0.9500

C(10)-H(10A)	0.9800
C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.514(9)
C(12)-C(14)	1.526(9)
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-C(19)	1.388(9)
C(14)-C(15)	1.396(9)
C(15)-C(16)	1.394(10)
C(15)-H(15)	0.9500
C(16)-C(17)	1.378(12)
C(16)-H(16)	0.9500
C(17)-C(18)	1.380(13)
C(17)-H(17)	0.9500
C(18)-C(19)	1.381(11)
C(18)-H(18)	0.9500
C(19)-H(19)	0.9500

C(5)-S(1)-C(2)	90.1(3)
C(12)-O(1)-H(1)	109.5
C(10)-C(1)-C(2)	109.7(5)
C(10)-C(1)-C(11)	108.1(5)
C(2)-C(1)-C(11)	105.6(5)
C(10)-C(1)-C(12)	110.5(6)
C(2)-C(1)-C(12)	111.9(5)
C(11)-C(1)-C(12)	110.8(5)
C(11)-O(2)-H(2)	109.5
C(1)-C(2)-C(3)	121.3(5)
C(1)-C(2)-S(1)	118.9(4)
C(3)-C(2)-S(1)	119.7(4)
C(4)-C(3)-C(2)	93.2(5)
C(4)-C(3)-H(3A)	113.1

C(2)-C(3)-H(3A)	113.1
C(4)-C(3)-H(3B)	113.1
C(2)-C(3)-H(3B)	113.1
H(3A)-C(3)-H(3B)	110.5
C(4)-C(5)-C(6)	121.3(7)
C(4)-C(5)-S(1)	114.8(5)
C(6)-C(5)-S(1)	123.9(6)
C(5)-C(4)-C(9)	118.9(7)
C(5)-C(4)-C(3)	122.0(6)
C(9)-C(4)-C(3)	119.1(7)
C(7)-C(6)-C(5)	117.8(8)
C(7)-C(6)-H(6)	121.1
C(5)-C(6)-H(6)	121.1
C(8)-C(7)-C(6)	122.2(8)
C(8)-C(7)-H(7)	118.9
C(6)-C(7)-H(7)	118.9
C(8)-C(9)-C(4)	118.6(7)
C(8)-C(9)-H(9)	120.7
C(4)-C(9)-H(9)	120.7
C(7)-C(8)-C(9)	121.2(7)
C(7)-C(8)-H(8)	119.4
C(9)-C(8)-H(8)	119.4
C(1)-C(10)-H(10A)	109.5
C(1)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(1)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
O(2)-C(11)-C(1)	113.6(5)
O(2)-C(11)-H(11A)	108.8
C(1)-C(11)-H(11A)	108.8
O(2)-C(11)-H(11B)	108.8
C(1)-C(11)-H(11B)	108.8
H(11A)-C(11)-H(11B)	107.7
O(1)-C(12)-C(13)	103.7(5)
O(1)-C(12)-C(14)	109.8(5)

C(13)-C(12)-C(14)	110.5(6)
O(1)-C(12)-C(1)	107.4(5)
C(13)-C(12)-C(1)	113.2(5)
C(14)-C(12)-C(1)	111.8(5)
C(12)-C(13)-H(13A)	109.5
C(12)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(12)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(19)-C(14)-C(15)	117.3(7)
C(19)-C(14)-C(12)	122.1(6)
C(15)-C(14)-C(12)	120.6(6)
C(16)-C(15)-C(14)	121.0(6)
C(16)-C(15)-H(15)	119.5
C(14)-C(15)-H(15)	119.5
C(17)-C(16)-C(15)	119.9(7)
C(17)-C(16)-H(16)	120.1
C(15)-C(16)-H(16)	120.1
C(16)-C(17)-C(18)	120.3(7)
C(16)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	119.3(7)
C(17)-C(18)-H(18)	120.3
C(19)-C(18)-H(18)	120.3
C(18)-C(19)-C(14)	122.3(7)
C(18)-C(19)-H(19)	118.9
C(14)-C(19)-H(19)	118.9

Symmetry transformations used to generate equivalent atoms:

Table S13. Anisotropic displacement parameters (A^2 x 10^3) for a.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

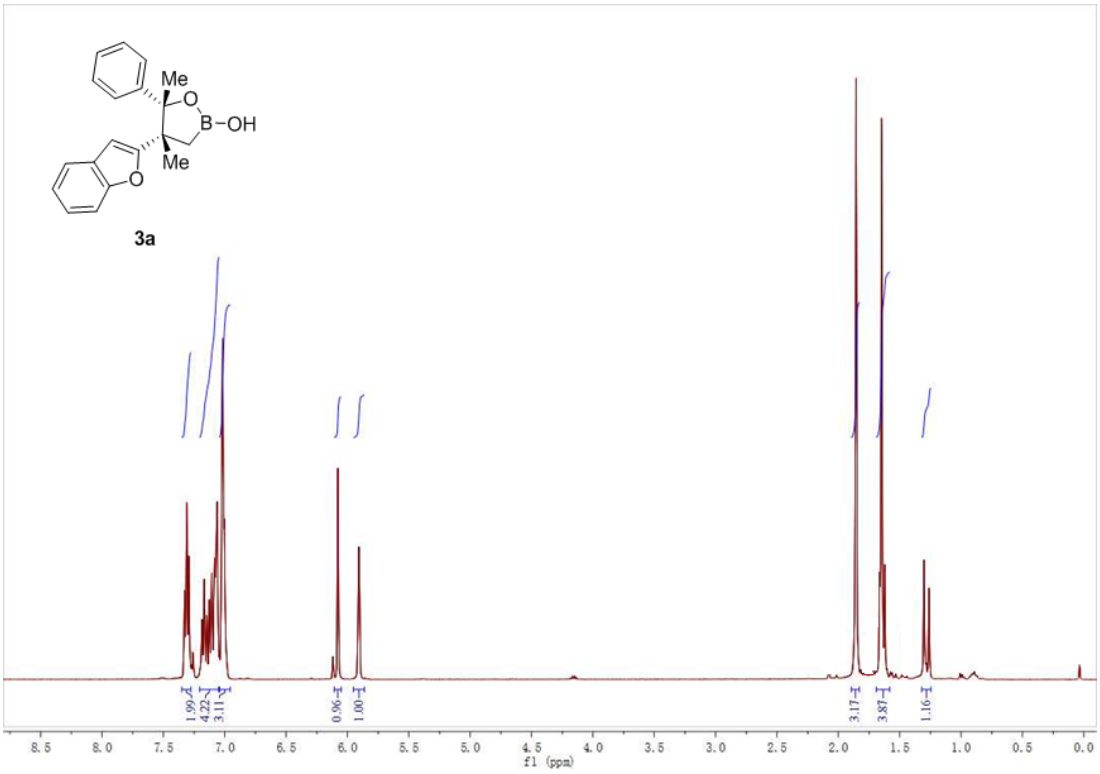
	U11	U22	U33	U23	U13	U12
S(1)	53(1)	57(1)	40(1)	-3(1)	-4(1)	-8(1)
O(1)	42(3)	37(3)	19(2)	-5(2)	-4(2)	0(2)
C(1)	31(3)	29(3)	21(3)	-1(2)	-4(2)	-3(3)
O(2)	34(2)	37(3)	29(2)	5(2)	-10(2)	-5(2)
C(2)	28(3)	29(3)	17(3)	-1(2)	2(2)	-1(2)
C(3)	37(2)	28(2)	24(2)	-2(1)	-4(1)	8(1)
C(5)	46(3)	27(3)	30(3)	0(3)	-4(3)	-1(3)
C(4)	48(4)	26(3)	28(3)	0(2)	-6(3)	4(3)
C(6)	53(4)	44(4)	41(4)	3(3)	-8(3)	-4(3)
C(7)	74(5)	44(5)	32(4)	1(3)	-17(4)	-12(4)
C(9)	49(4)	38(4)	40(4)	2(3)	8(3)	-3(3)
C(8)	85(5)	43(4)	25(3)	-1(3)	3(3)	5(4)
C(10)	41(3)	37(4)	27(3)	6(3)	-3(3)	-13(3)
C(11)	32(3)	27(3)	27(3)	4(3)	-3(2)	0(2)
C(12)	31(3)	28(3)	24(3)	-2(2)	-3(2)	0(3)
C(13)	32(3)	45(4)	39(4)	-8(3)	3(3)	-2(3)
C(14)	30(3)	28(3)	26(3)	-3(2)	-1(2)	3(2)
C(15)	35(3)	30(3)	30(3)	-2(3)	1(2)	1(3)
C(16)	44(4)	29(4)	49(4)	-1(3)	8(3)	-8(3)
C(17)	67(5)	31(4)	44(4)	3(3)	19(4)	3(3)
C(18)	60(4)	39(4)	28(3)	5(3)	4(3)	13(3)
C(19)	39(3)	35(3)	33(3)	0(3)	-5(3)	7(3)

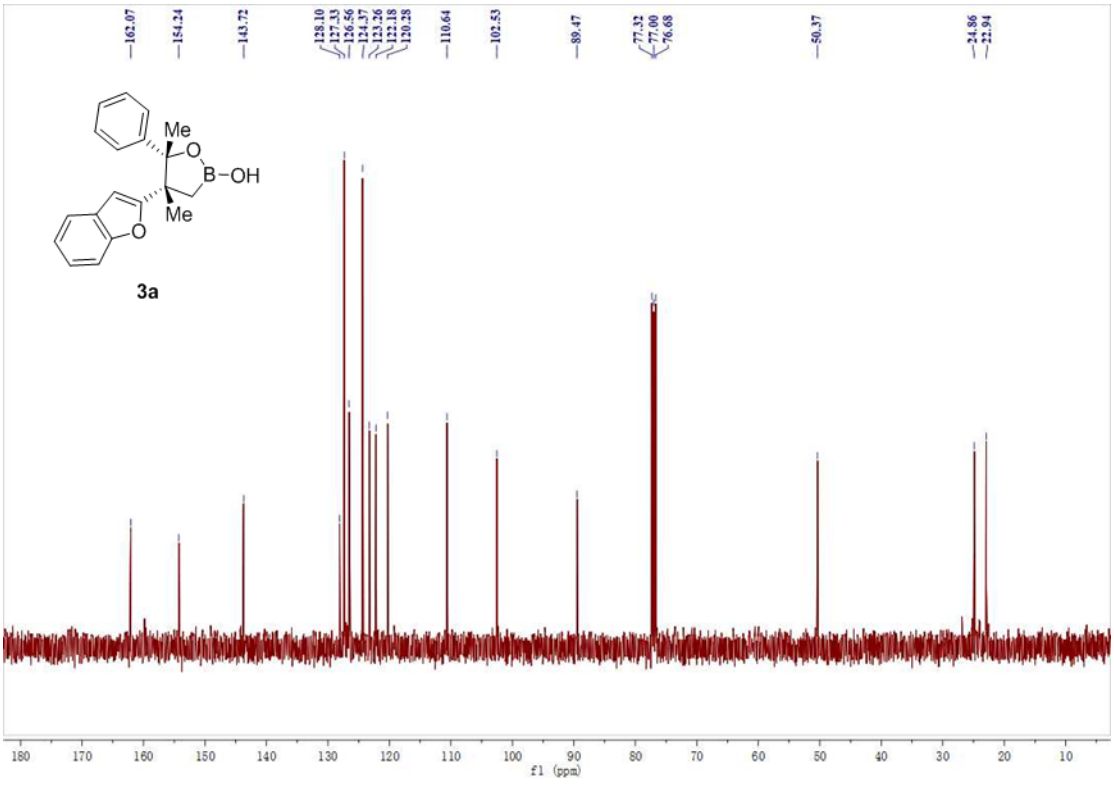
Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for a.

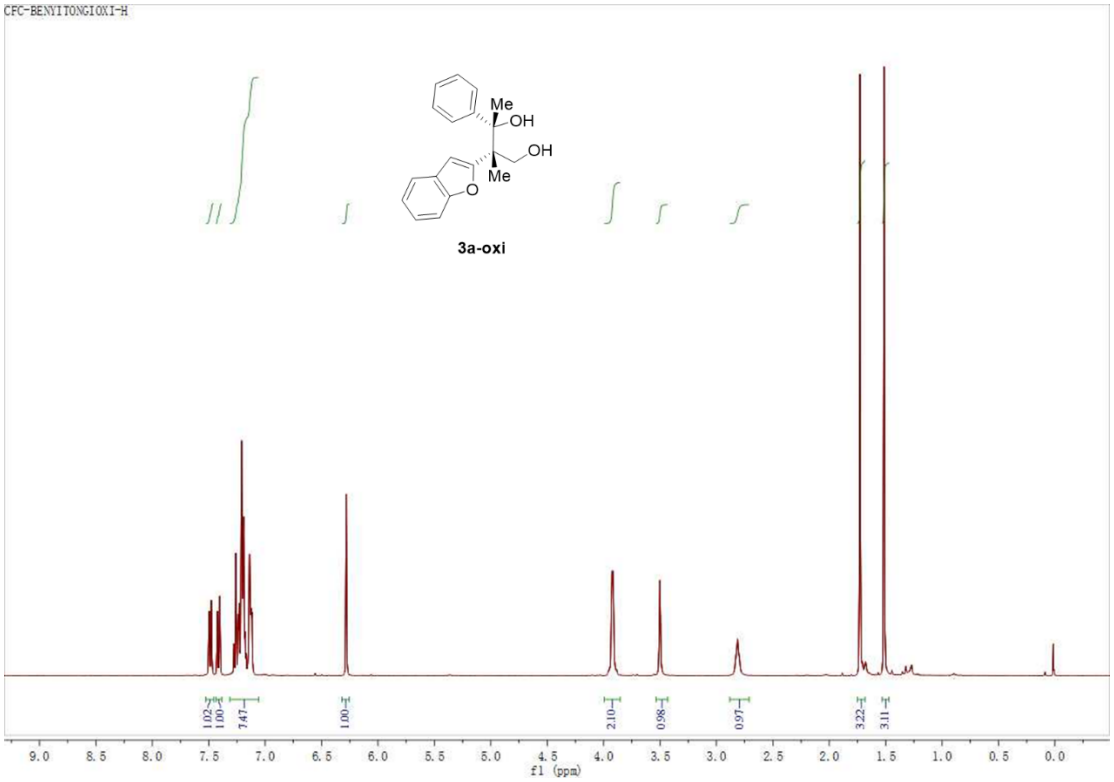
	x	y	z	U(eq)

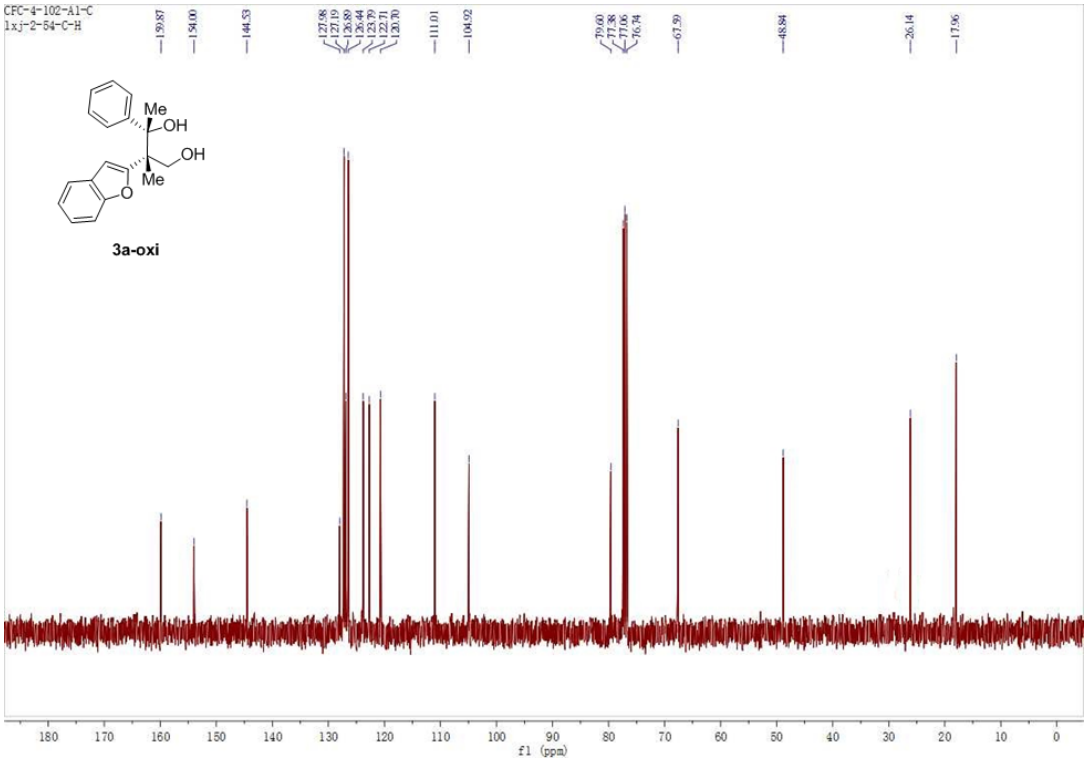
H(1)	4558	4723	9754	49
H(2)	6706	2268	9677	51
H(3A)	4597	4474	6678	35
H(3B)	5576	2610	6854	35
H(6)	-1729	875	5638	55
H(7)	-494	616	4257	61
H(9)	4806	2743	5020	51
H(8)	2672	1529	3949	61
H(10A)	2710	799	8906	53
H(10B)	765	1999	8939	53
H(10C)	2560	2173	9664	53
H(11A)	5870	1748	8405	35
H(11B)	6265	3689	8174	35
H(13A)	-63	4648	9283	58
H(13B)	-205	5129	8273	58
H(13C)	227	6571	8987	58
H(15)	6308	6691	8920	38
H(16)	7757	8728	8038	48
H(17)	5984	9707	6801	56
H(18)	2787	8619	6423	51
H(19)	1348	6610	7304	43

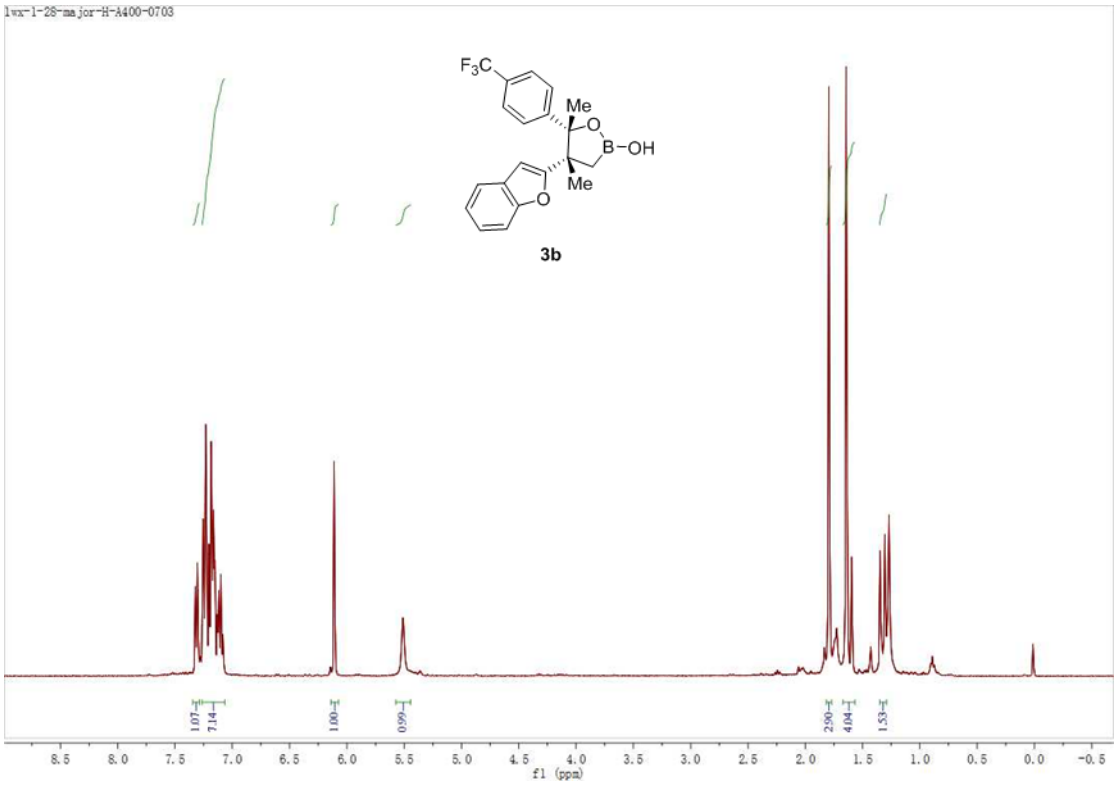
Table S15. Selected torsion angles [deg] for a.

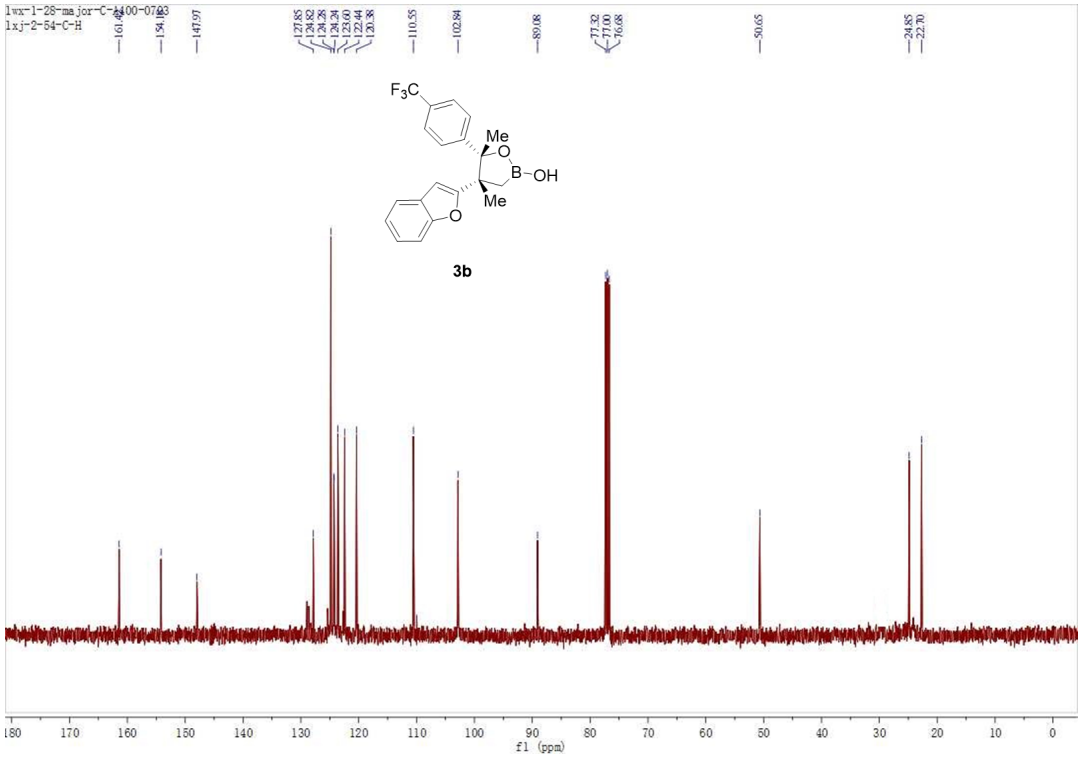

Me
O
B–OH
Me
O
3a
1.99
4.22
3.11
0.96
1.00
3.17
3.87
1.16
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

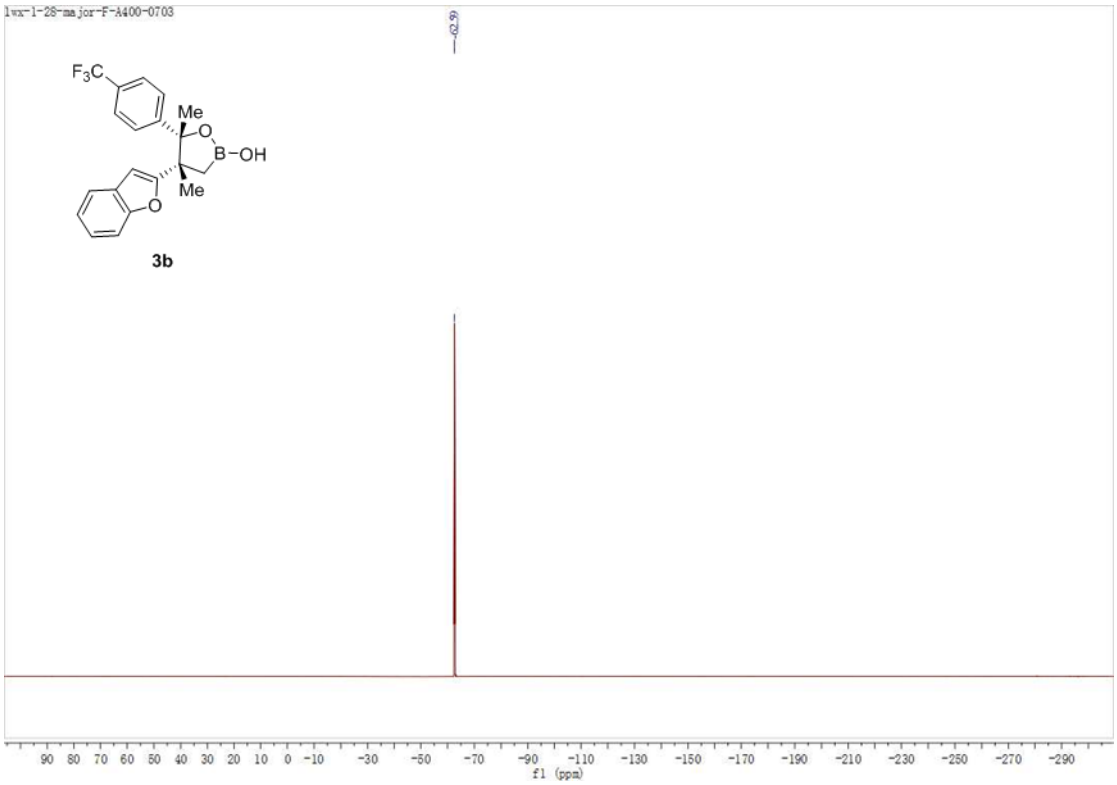

162.07
154.24
143.72
128.10
127.33
126.56
124.37
123.26
122.18
120.28
110.64
102.53
89.47
77.32
77.00
76.68
50.37
24.86
22.94
Me
O
B–OH
Me
O
3a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

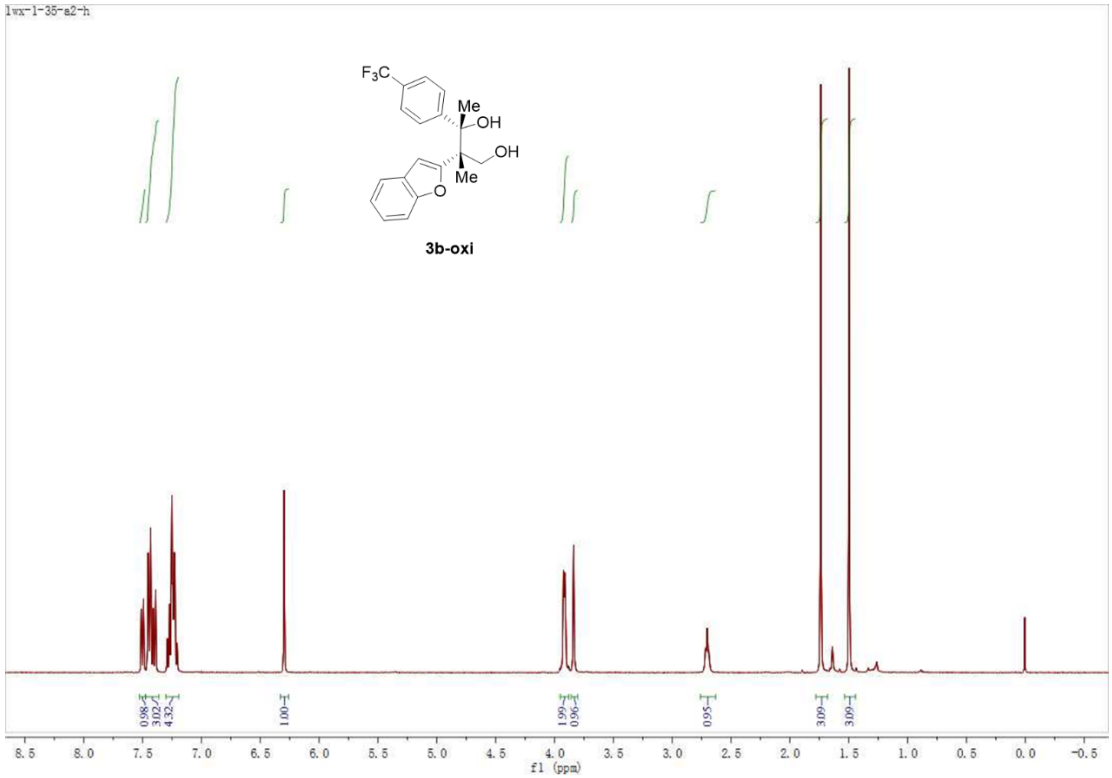

CFC-BENYITONGIOXI-H
Me
OH
OH
Me
O
3a-oxi
1.02
1.00
7.47
1.00
2.10
0.98
0.97
3.22
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

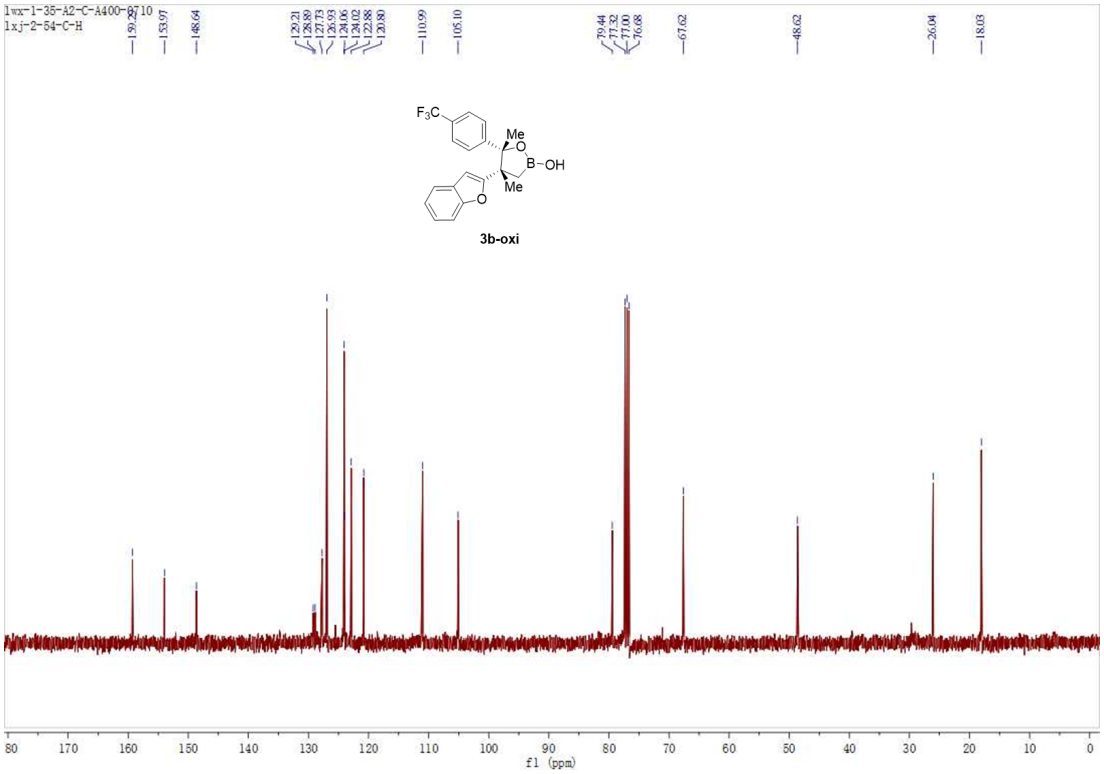

CFC-4-102-A1-C
lxj-2-54-C-H
159.87
154.00
144.53
127.98
127.19
126.89
126.44
123.79
122.71
120.70
111.01
104.92
79.60
77.38
77.06
76.74
67.59
48.84
26.14
17.96
Me
OH
OH
Me
O
3a-oxi
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

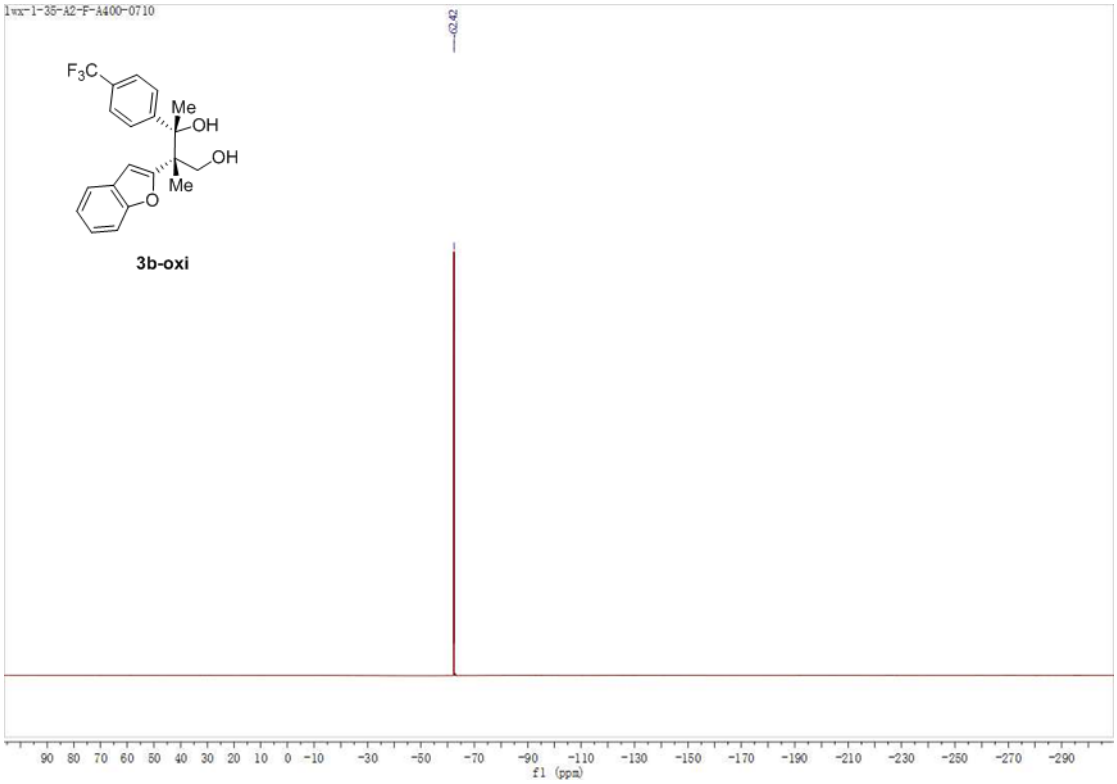

lwx-1-28-major-H-A400-0703
F3C
Me
O
B–OH
Me
O
3b
1.07
7.14
1.00
0.99
2.90
4.04
1.53
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

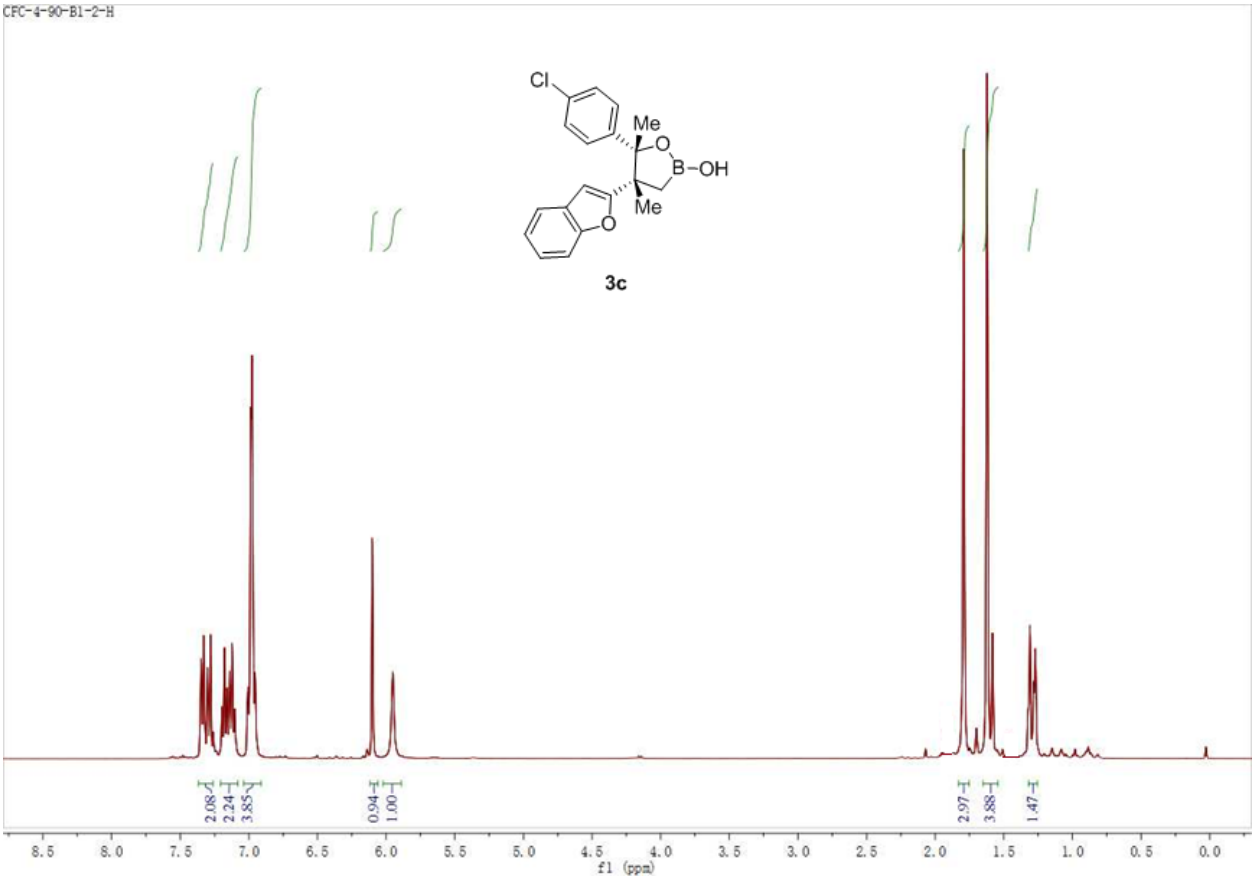

lwx-1-28-major-C-A400-0703
lxj-2-54-C-H
161.42
154.10
147.97
127.85
124.82
124.24
123.60
122.44
120.38
110.55
102.84
89.08
77.32
77.00
76.68
50.65
24.85
22.70
F3C
Me
O
B–OH
Me
O
3b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

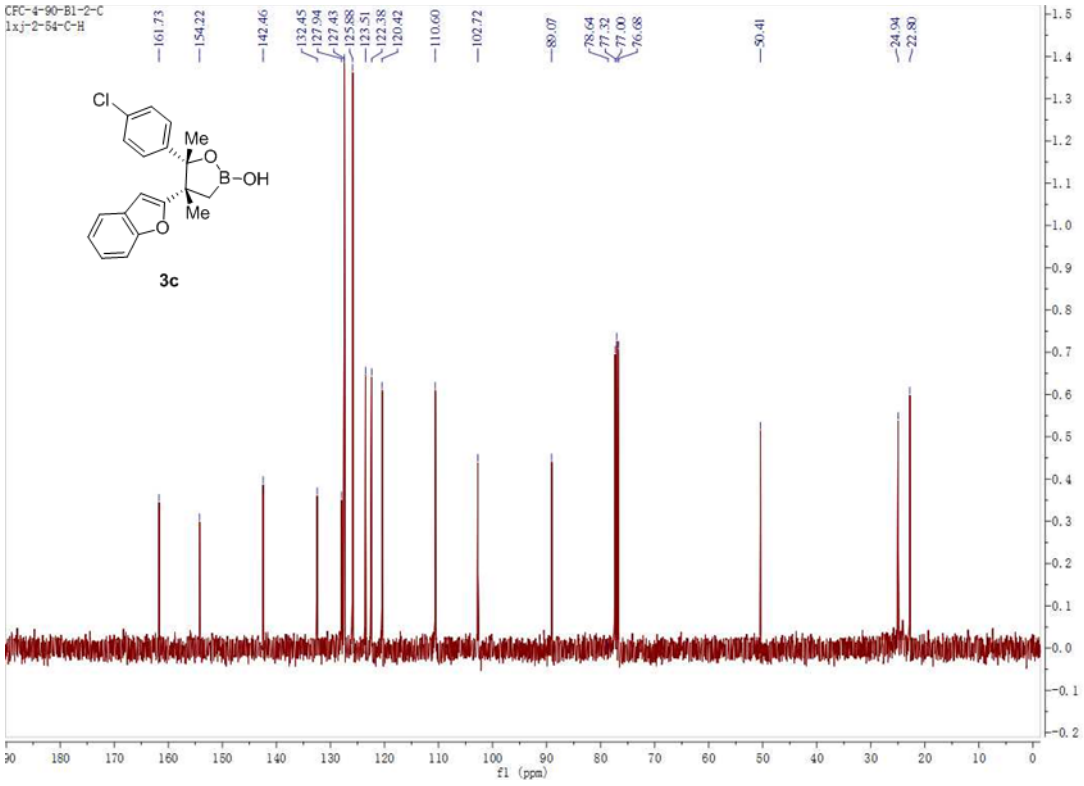

lwx-1-28-major-F-A400-0703
F3C
Me
O
B–OH
Me
O
3b
f1 (ppm)

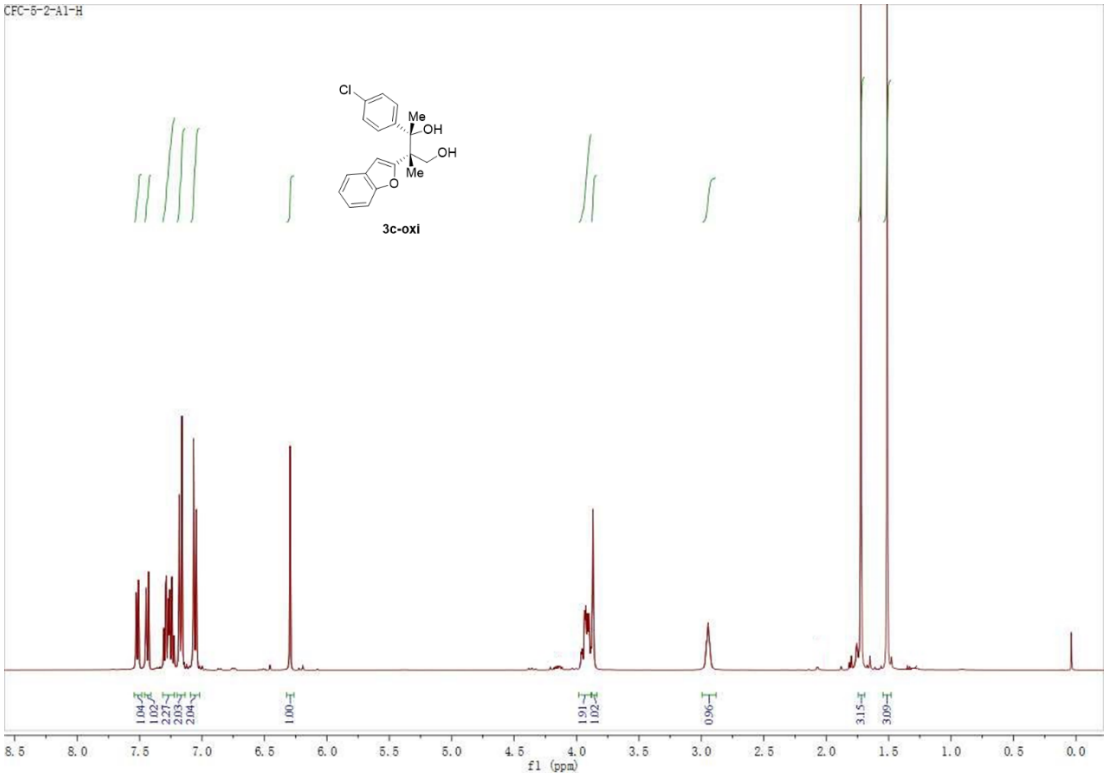

lwx-1-36-a2-h
F3C
Me
OH
OH
Me
O
3b-oxi
0.98
3.02
4.32
1.00
1.99
0.96
0.95
3.09
3.09
f1 (ppm)

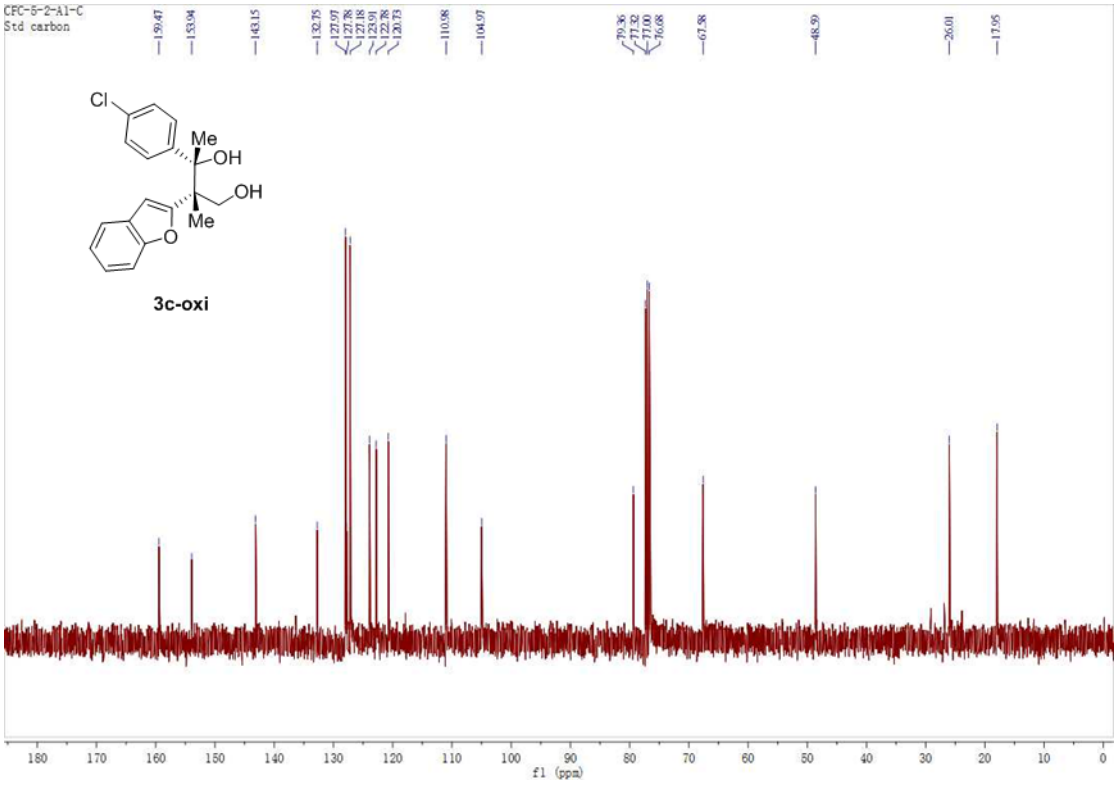

1wx-1-35-A2-C-A400-0710
1xj-2-54-C-H
159.27
153.97
148.64
130.21
128.89
127.73
126.93
124.06
124.02
122.88
120.80
110.99
105.10
79.44
77.32
77.00
76.68
67.62
48.62
26.04
18.03
F3C
Me
O
B–OH
Me
O
3b-oxi
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

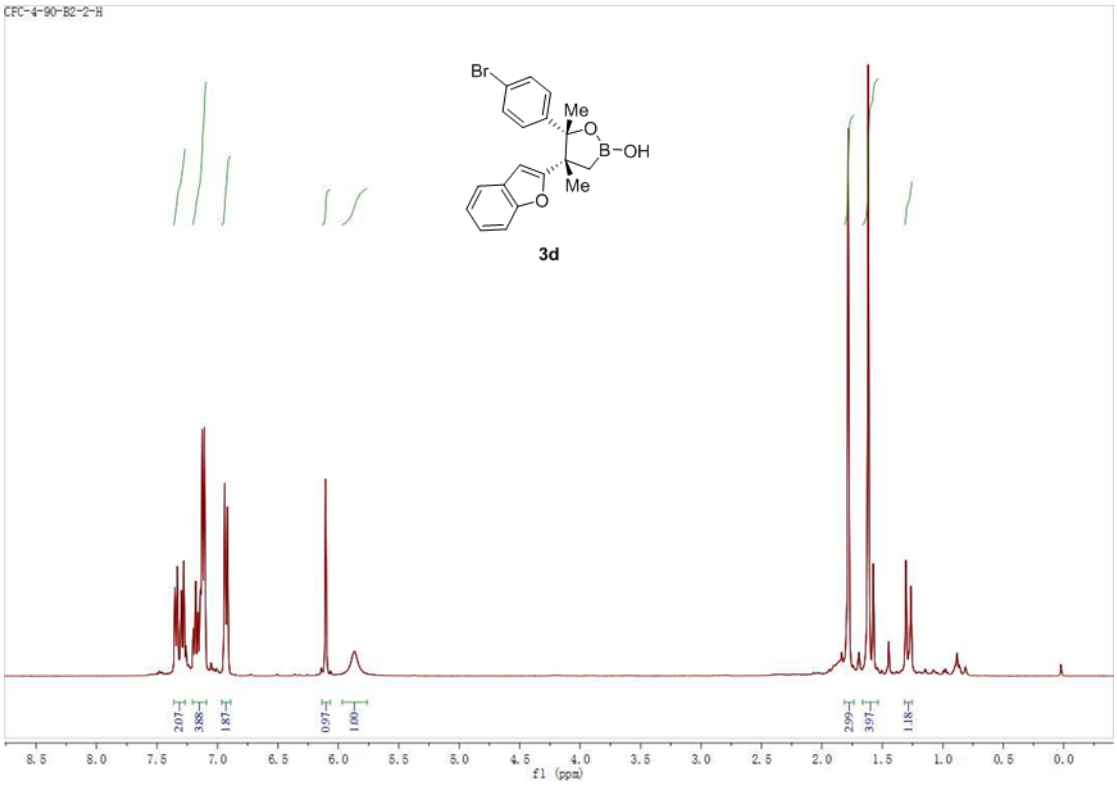

1wx-1-35-A2-F-A400-0710
-62.42
F3C
Me
OH
OH
Me
O
3b-oxi
90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250 -270 -290
f1 (ppm)

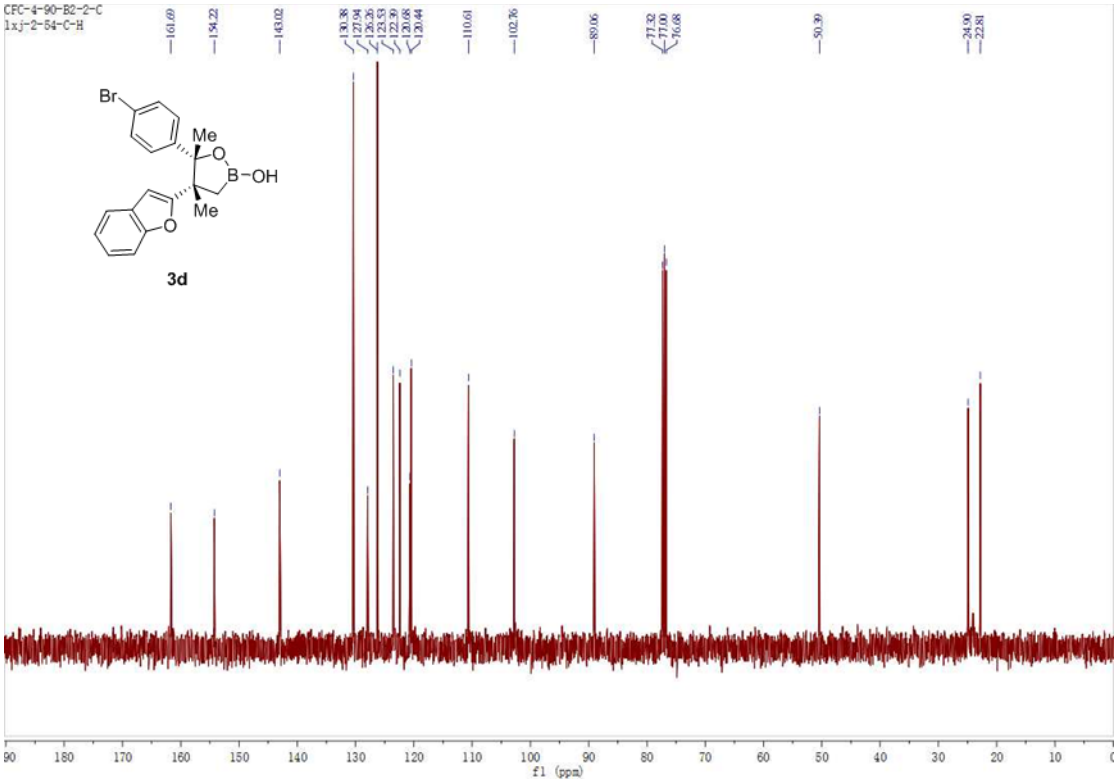

CFC-4-90-B1-2-H
Cl
Me
O
B–OH
Me
O
3c
2.08
2.24
3.85
0.94
1.00
2.97
3.88
1.47
f1 (ppm)

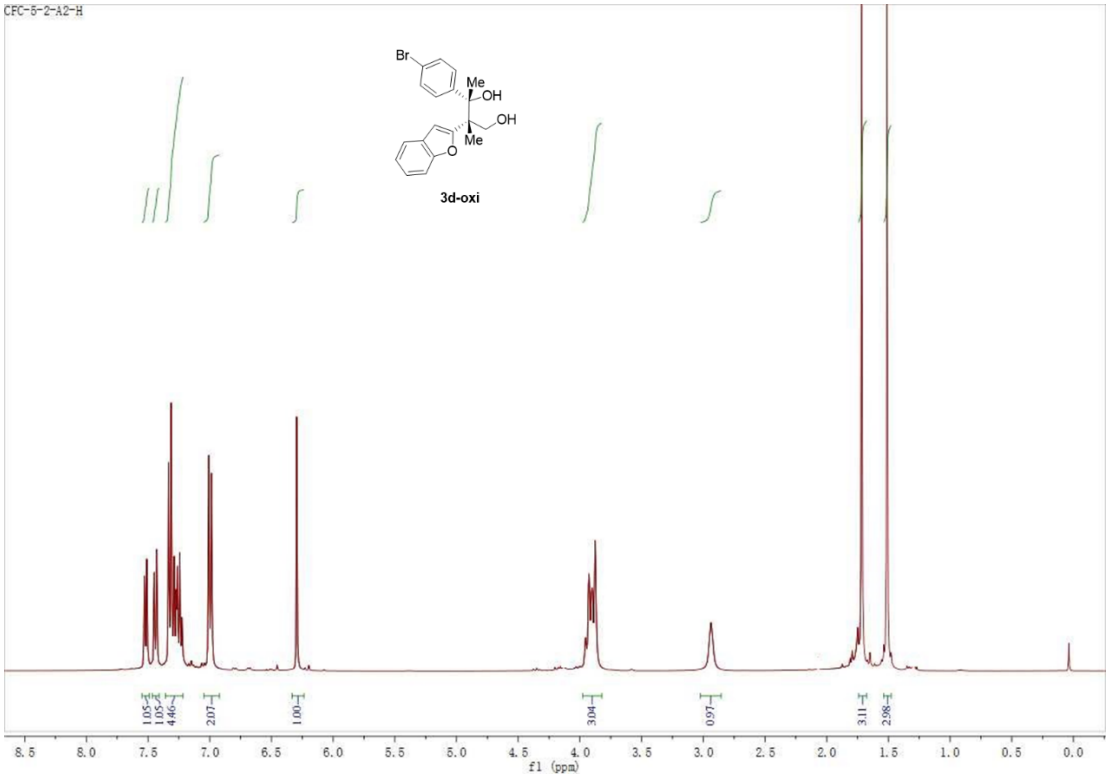

CFC-4-90-B1-2-C
lxj-2-54-C-H
161.73
154.22
142.46
132.45
127.94
127.43
125.88
123.51
122.38
120.42
110.60
102.72
89.07
78.64
77.32
77.00
76.68
50.41
24.94
22.80
Cl
Me
O
B–OH
Me
O
3c
f1 (ppm)

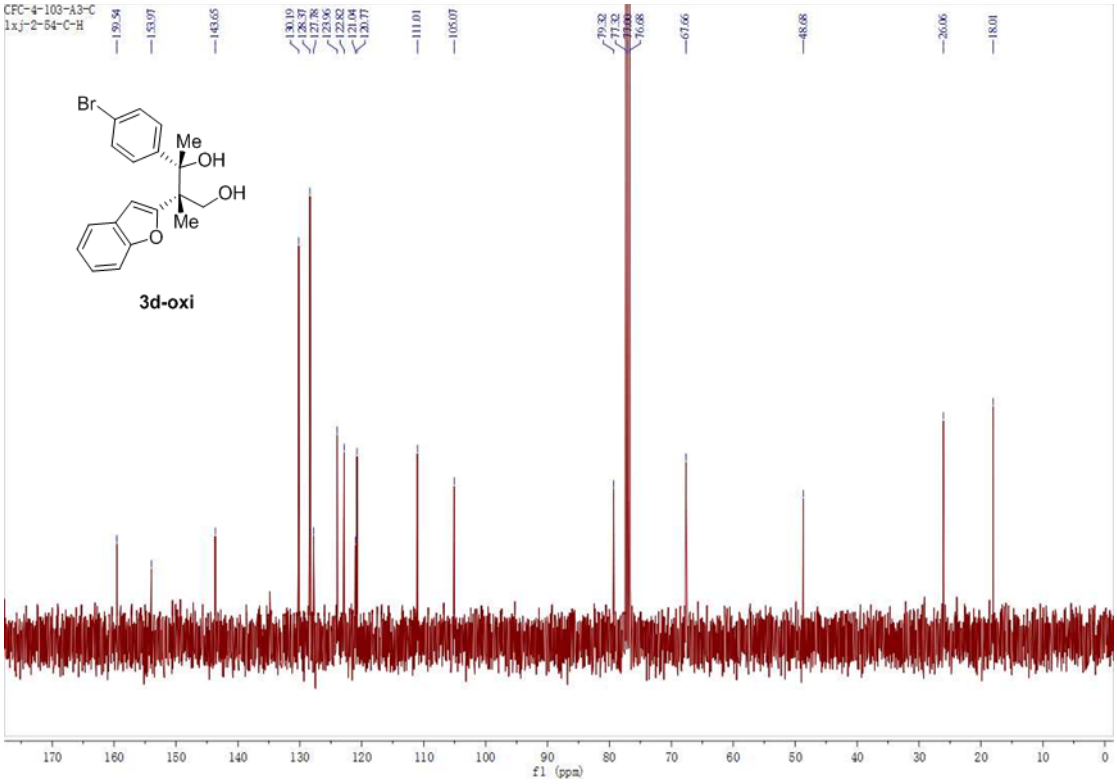

CFC-5-2-A1-H
Cl
Me
OH
OH
Me
O
3c-oxi
1.04
1.02
2.27
2.03
2.04
1.00
1.91
1.02
0.96
3.15
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

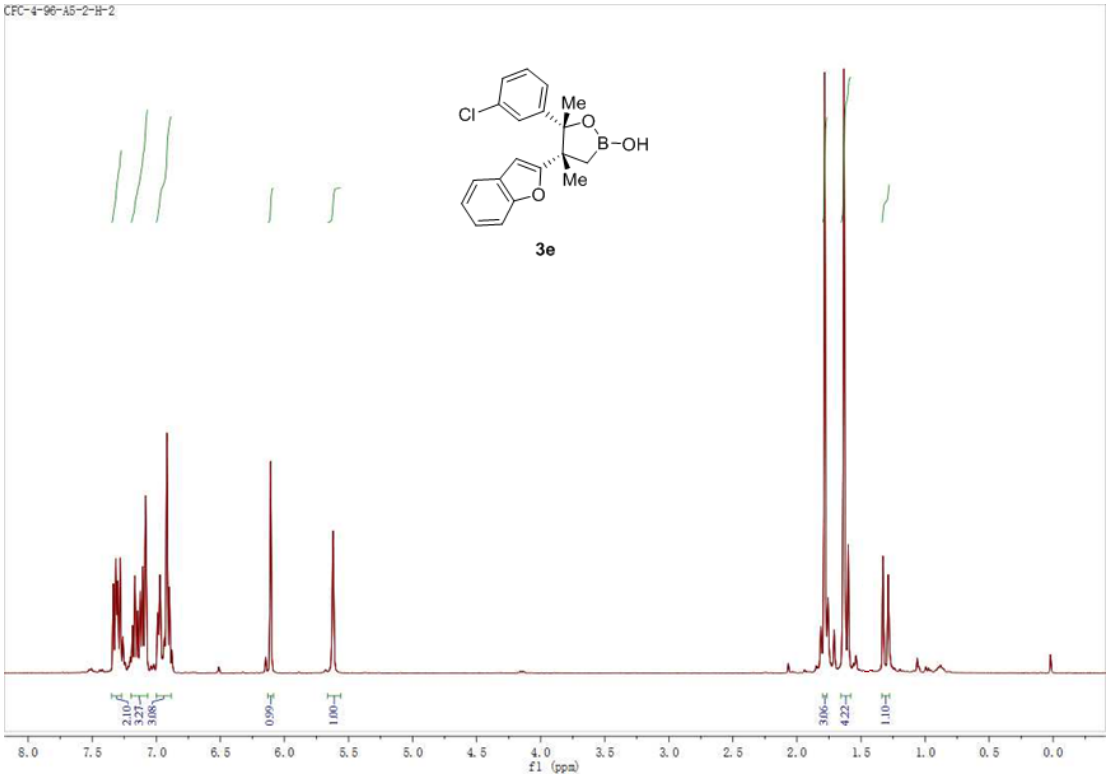

CFC-5-2-A1-C
Std carbon
159.47
153.04
143.15
132.75
127.97
127.78
127.18
123.91
122.78
120.73
110.98
104.97
79.36
77.32
77.00
76.68
67.58
48.59
26.01
17.95
Cl
Me
OH
OH
Me
O
3c-oxi
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

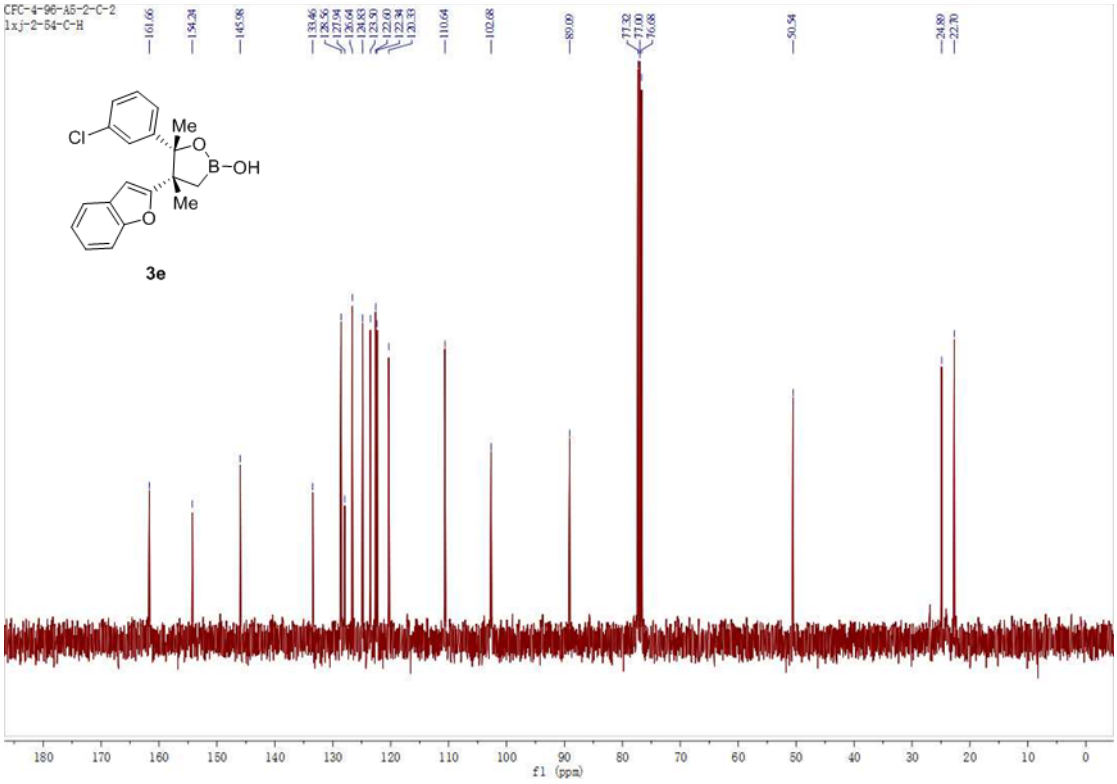

CFC-4-90-B2-2-H
Br
Me
O
B–OH
Me
O
3d
2.07
3.88
1.87
0.97
1.00
2.99
3.97
1.18
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

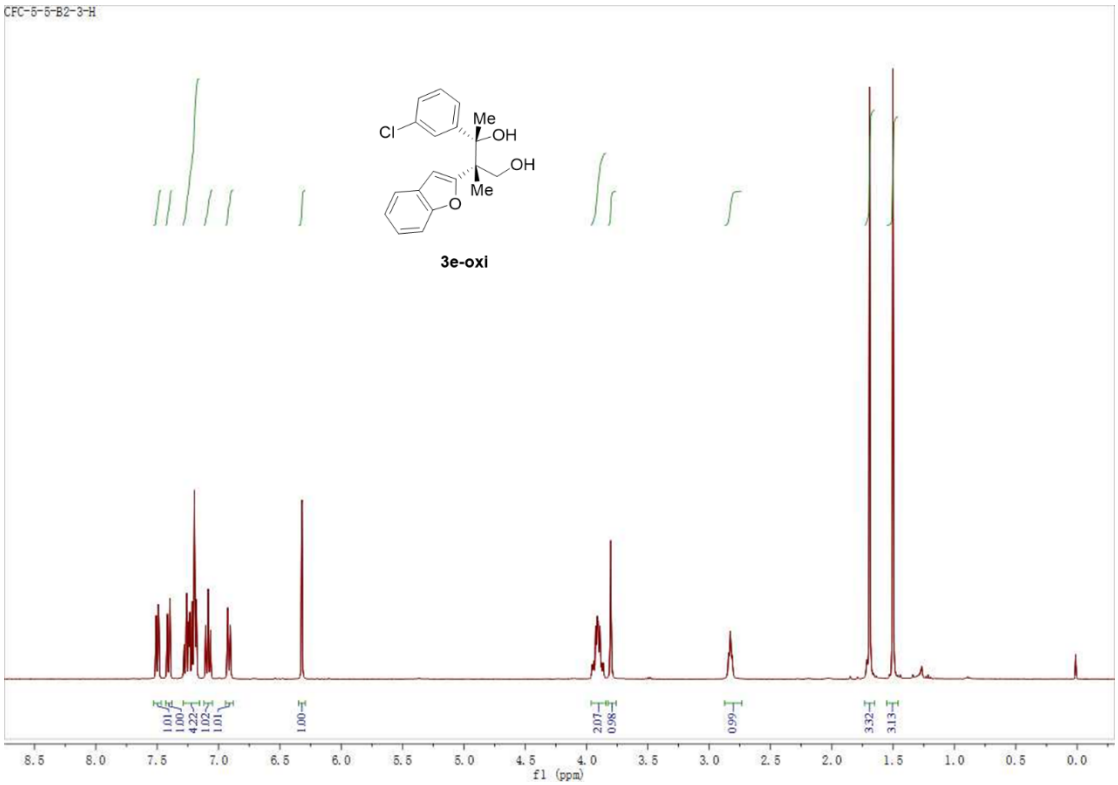

CFC-4-90-B2-2-C
lxj-2-54-C-H
161.69
154.22
143.02
130.38
127.94
126.26
123.53
122.39
120.68
120.44
110.61
102.76
89.06
77.32
77.00
76.68
50.39
24.90
22.81
Br
Me
O
B–OH
Me
O
3d
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

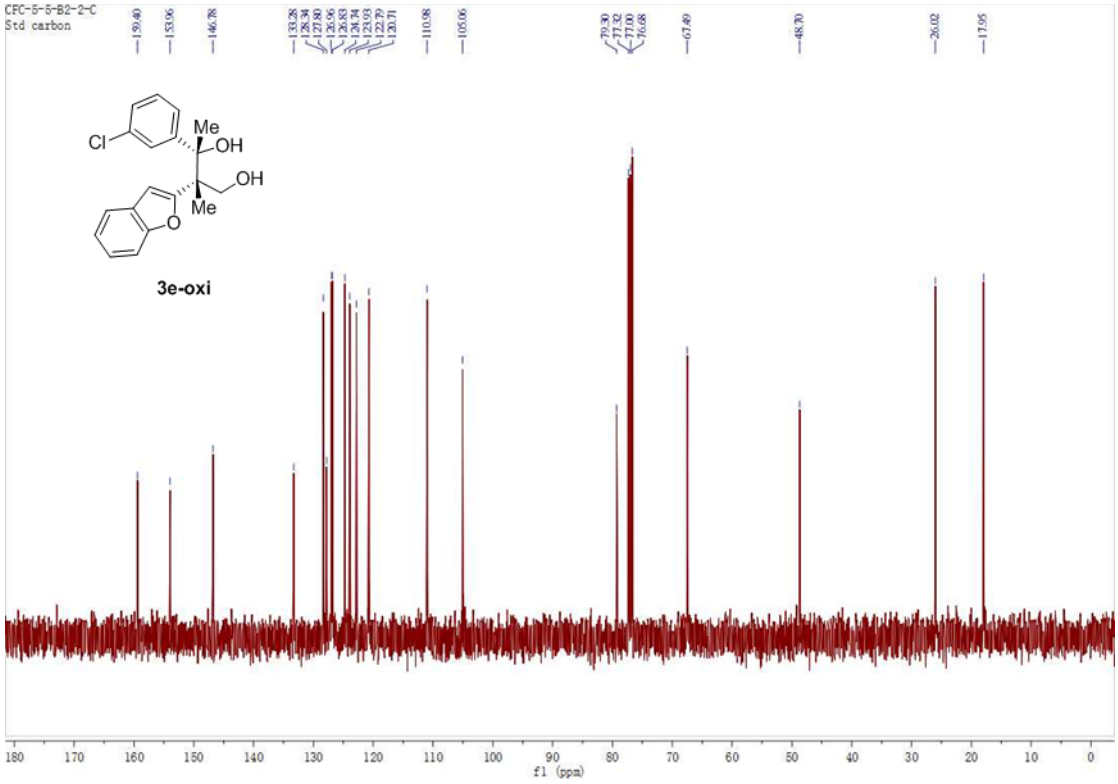

CFC-5-2-A2-H
Br
Me
OH
OH
Me
O
3d-oxi
1.05
1.05
4.46
2.07
1.00
3.04
0.97
3.11
2.98
f1 (ppm)

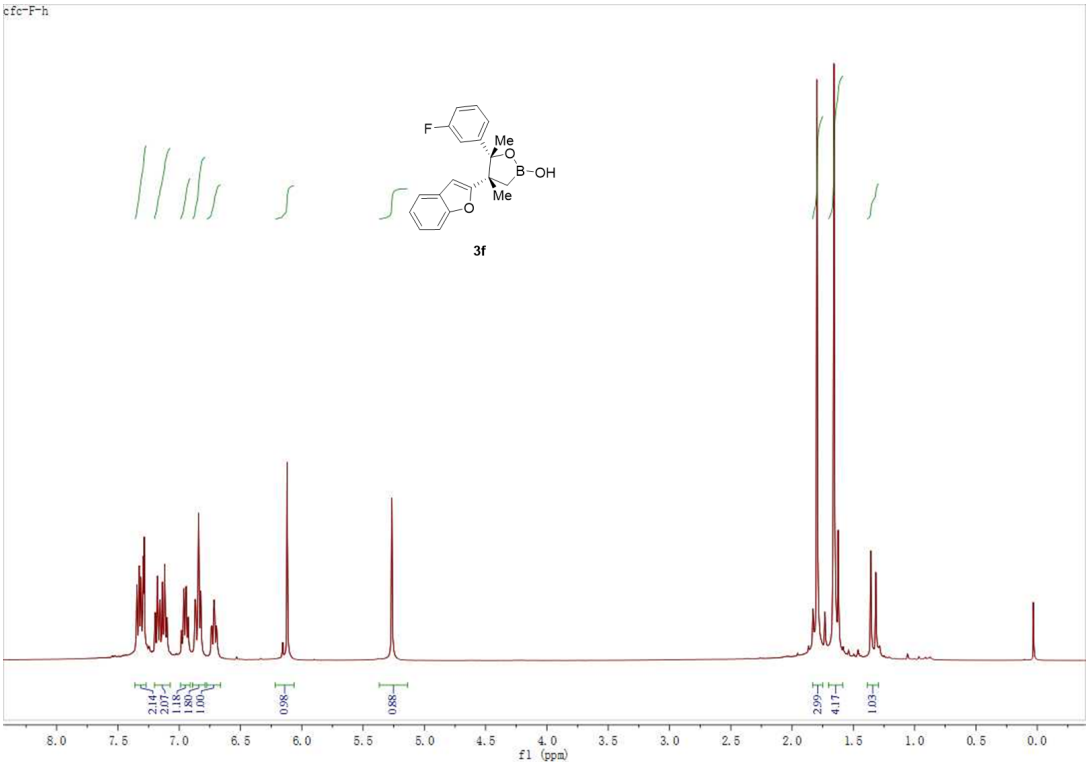

CFC-4-103-A3-C
lxj-2-54-C-H
Br
Me
OH
OH
Me
O
3d-oxi
f1 (ppm)

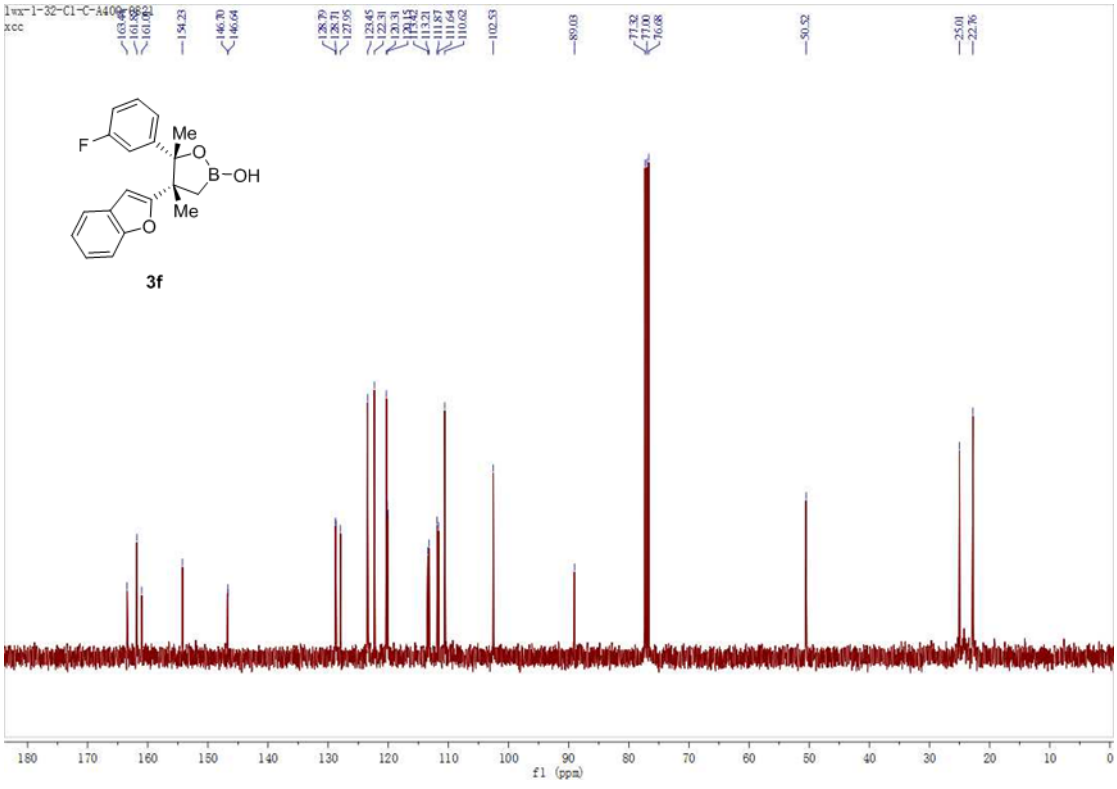

CFC-4-96-A5-2-H-2
Cl
Me
O
B–OH
Me
O
3e
2.10
3.27
3.08
0.99
1.00
3.06
4.22
1.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

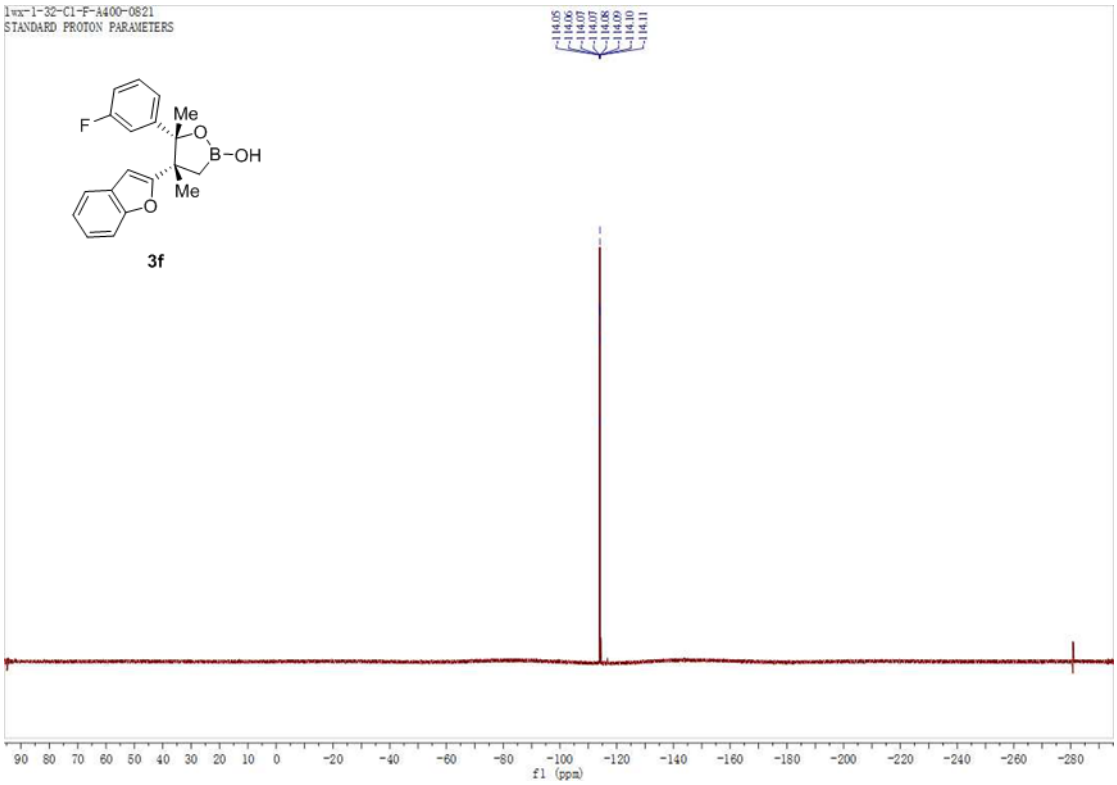

CFC-4-96-A5-2-C-2
lxj-2-54-C-H
161.66
154.24
145.98
133.46
128.56
127.94
126.64
124.83
123.50
123.00
122.34
120.33
110.64
102.68
89.09
77.32
77.10
76.88
50.54
24.89
22.70
Cl
Me
O
B–OH
Me
O
3e
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

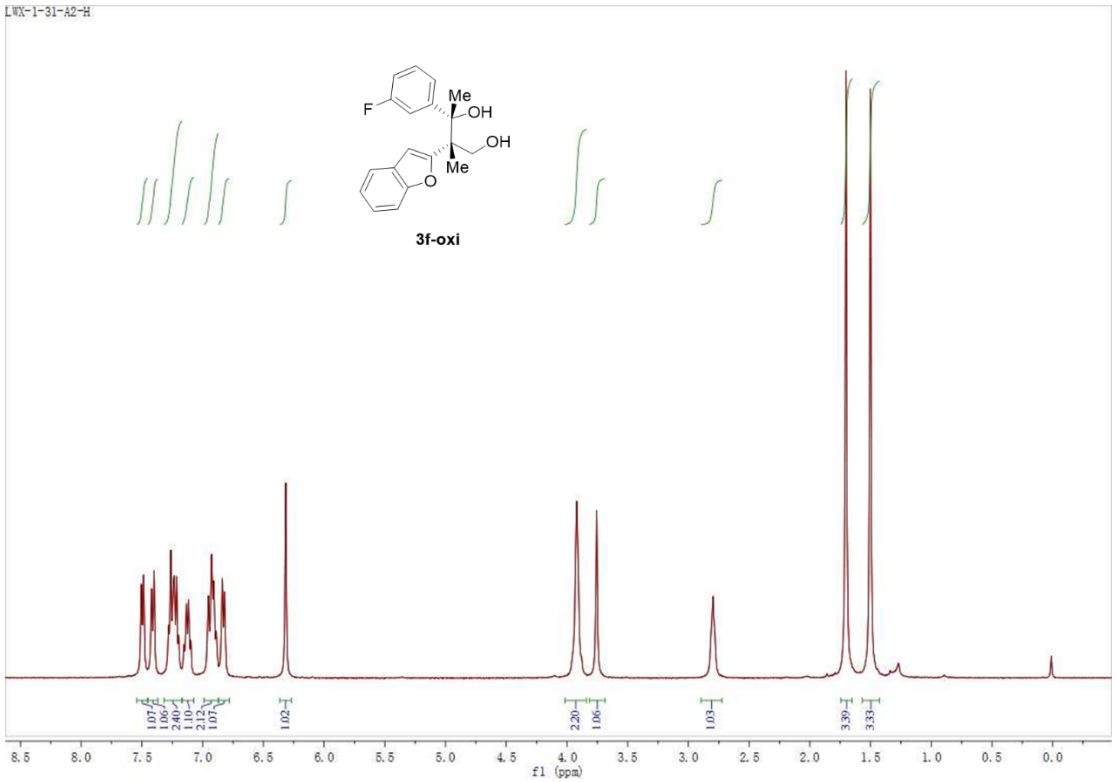

CFC-5-5-B2-3-H
Cl
Me
OH
OH
Me
O
3e-oxi
f1 (ppm)

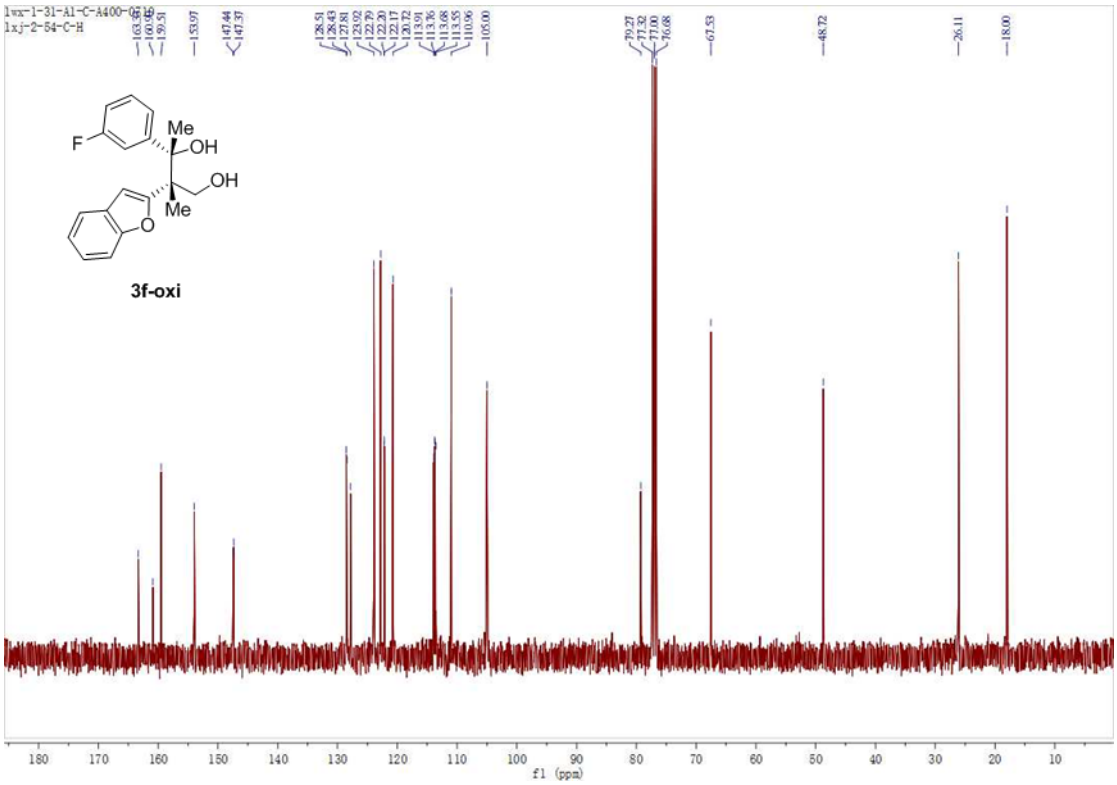

CFC-5-5-B2-2-C
Std carbon
Cl
Me
OH
OH
Me
O
3e-oxi
f1 (ppm)

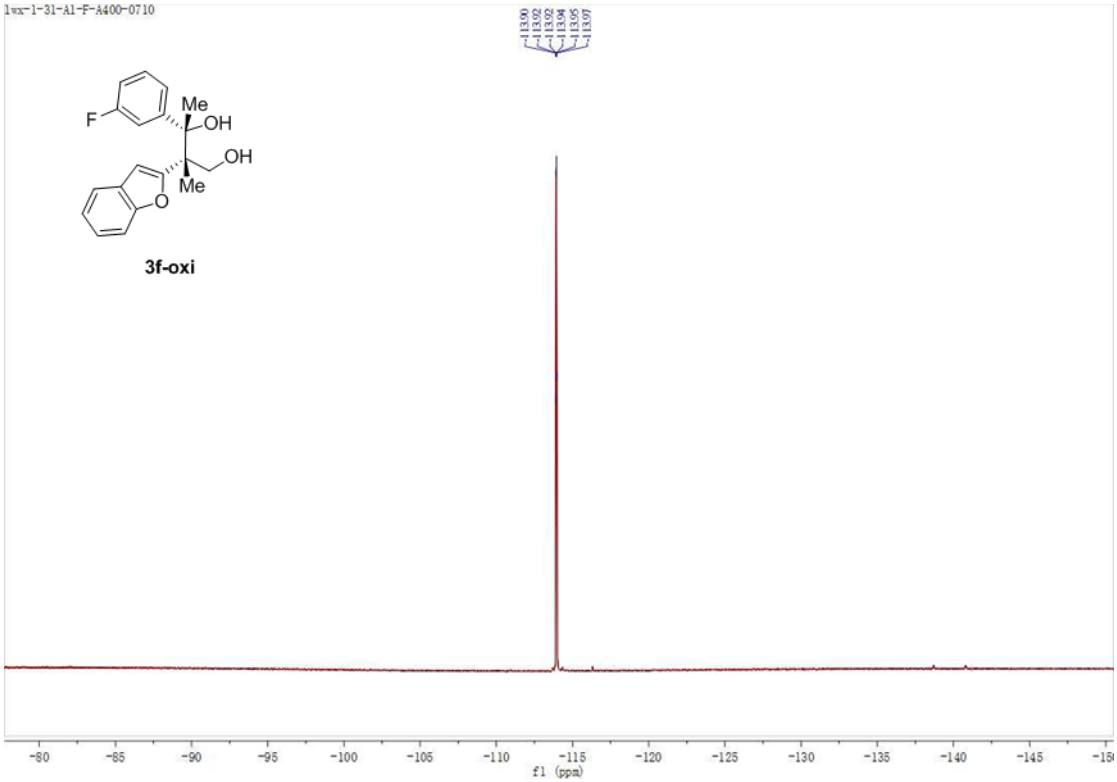

cfc-F-h
F
Me
O
B–OH
Me
O
3f
2.14
2.07
1.85
1.86
1.00
0.98
0.88
2.99
4.17
1.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

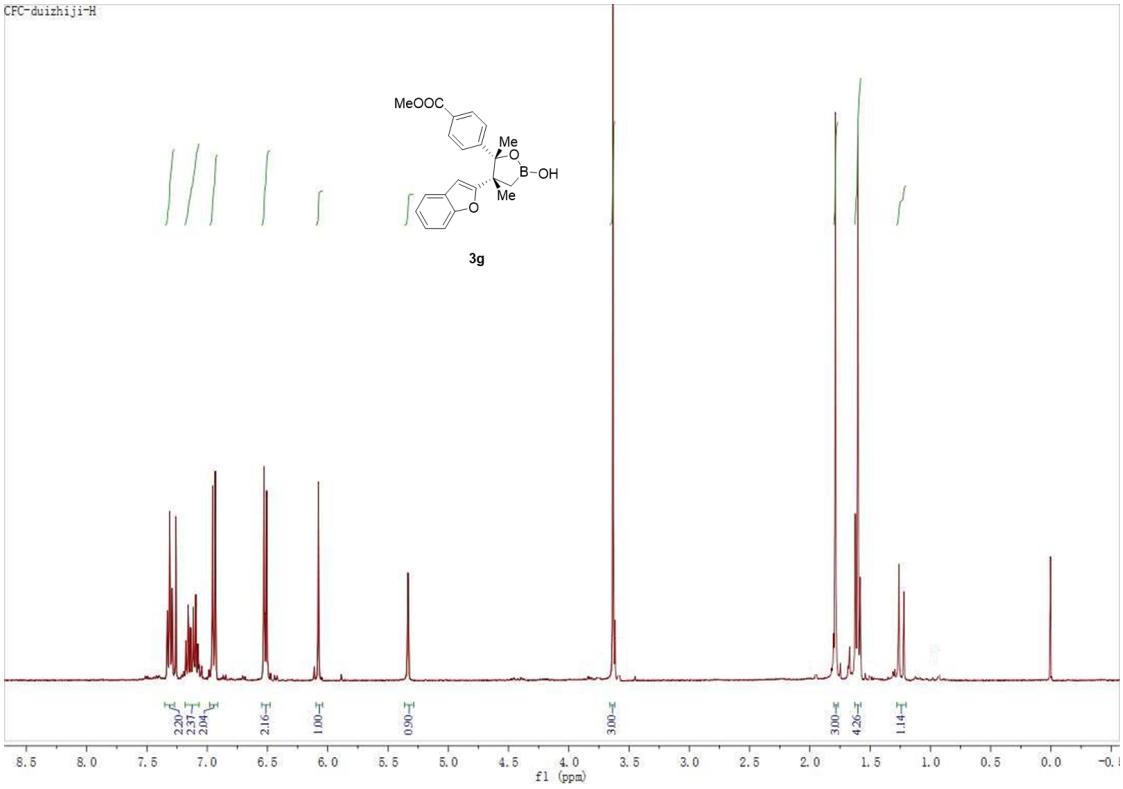

lwx-1-32-C1-C-A400
xcc
154.23
146.70
146.64
128.79
128.71
127.95
123.45
122.31
120.31
113.21
111.87
111.64
110.62
102.53
89.03
77.32
77.00
76.68
50.52
25.01
22.76
F
Me
O
B–OH
Me
O
3f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

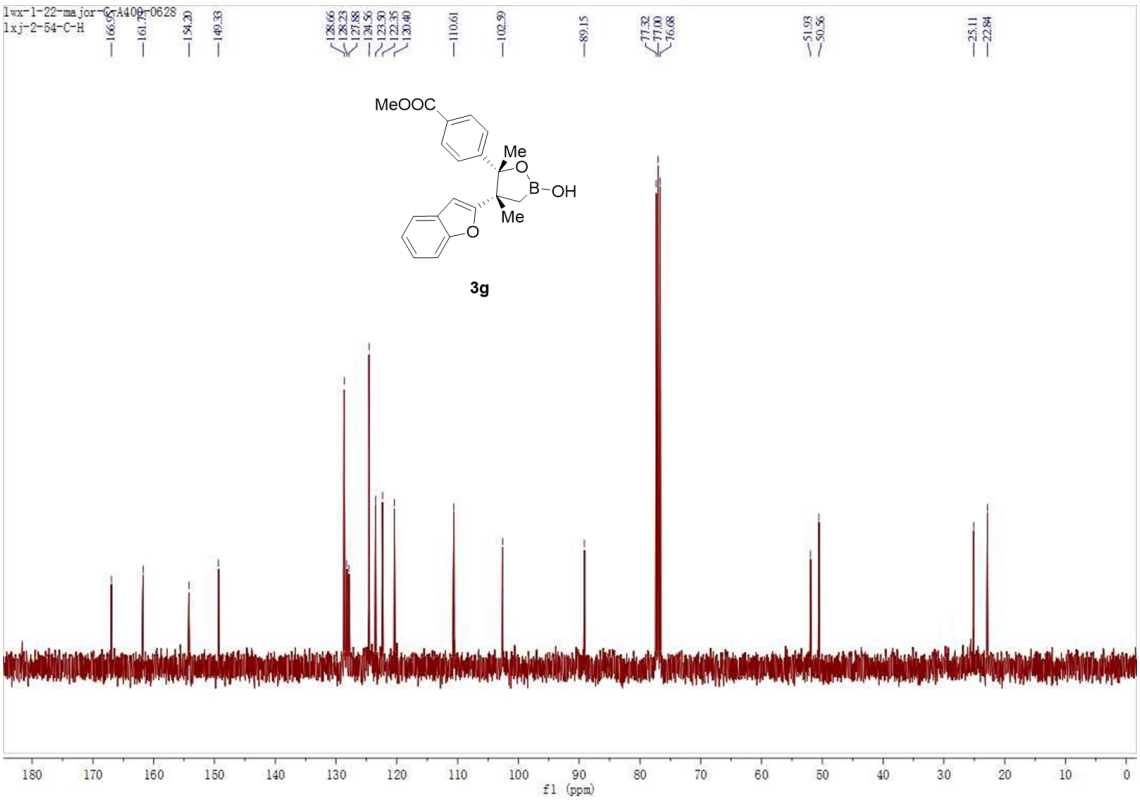

lwx-1-32-C1-F-A400-0821
STANDARD PROTON PARAMETERS
F
Me
O
B–OH
Me
O
3f
f1 (ppm)

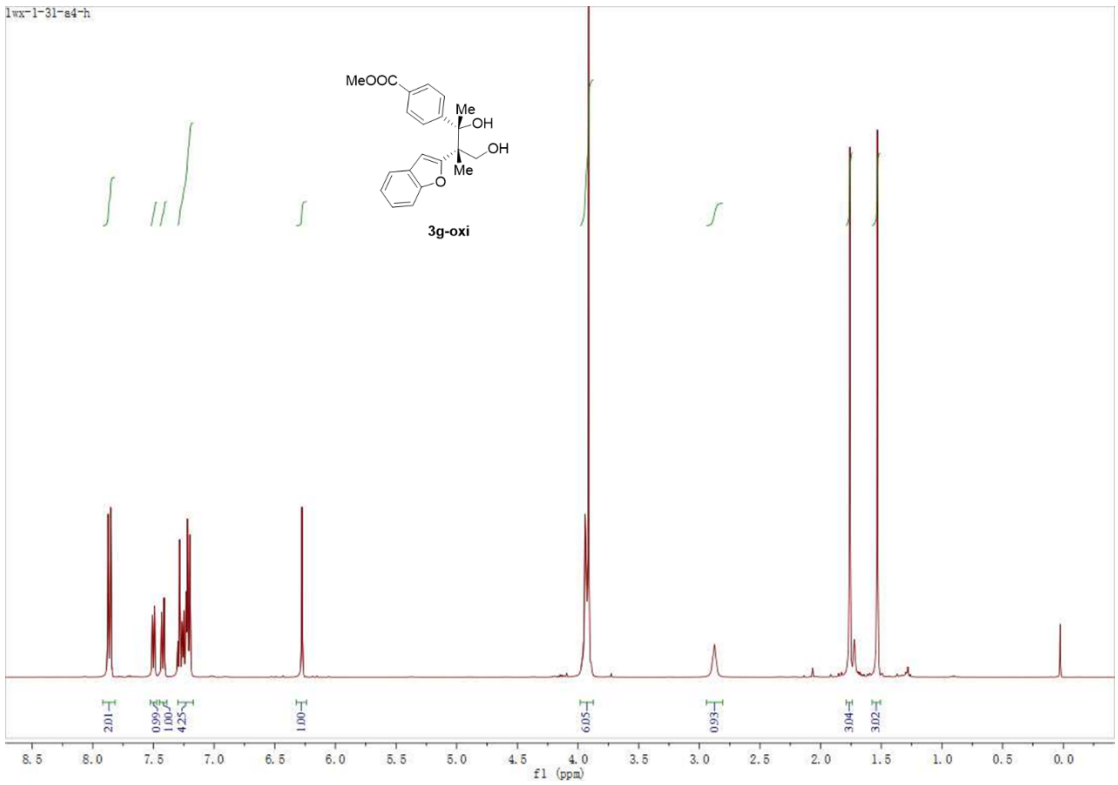

LWX-1-31-A2-H
F
Me
OH
OH
Me
O
3f-oxi
f1 (ppm)

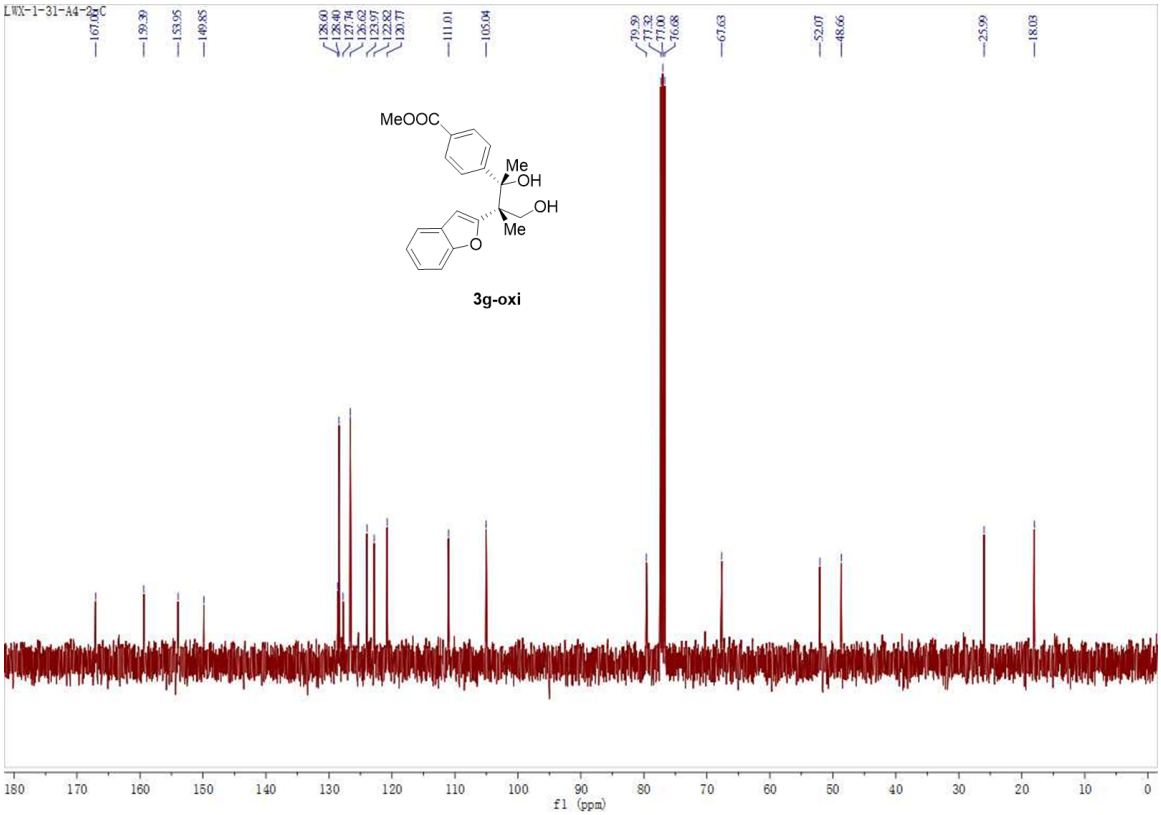

lwx-1-31-A1-C-A400-0
lxj-2-84-C-H
163.61
160.15
159.51
153.97
147.44
147.37
128.51
128.43
127.91
123.02
122.79
122.20
122.17
120.72
113.91
113.76
113.68
113.55
110.96
105.00
79.27
77.32
77.00
76.68
67.53
48.72
26.11
18.00
Me
OH
OH
Me
F
O
3f-oxi
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

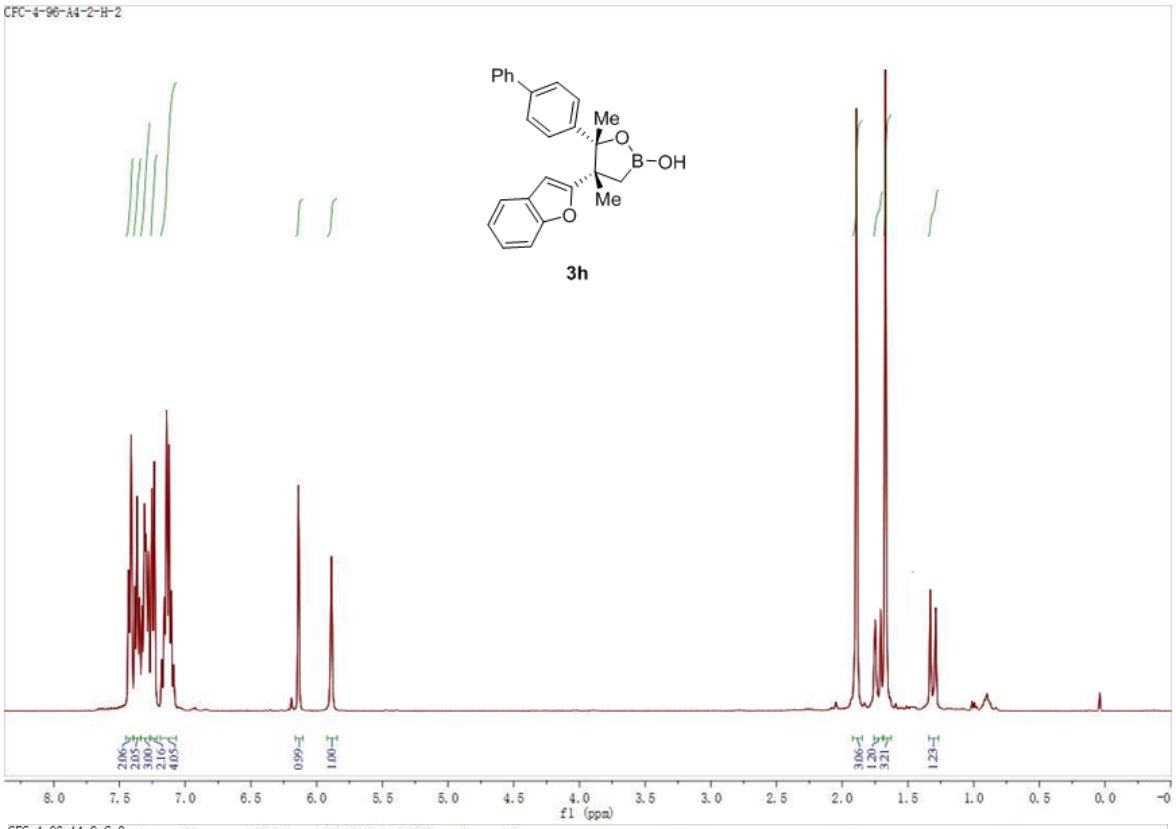

lwx-1-31-A1-F-A400-0710
-113.90
-113.92
-113.92
-113.94
-113.95
-113.97
Me
OH
OH
Me
F
O
3f-oxi
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)

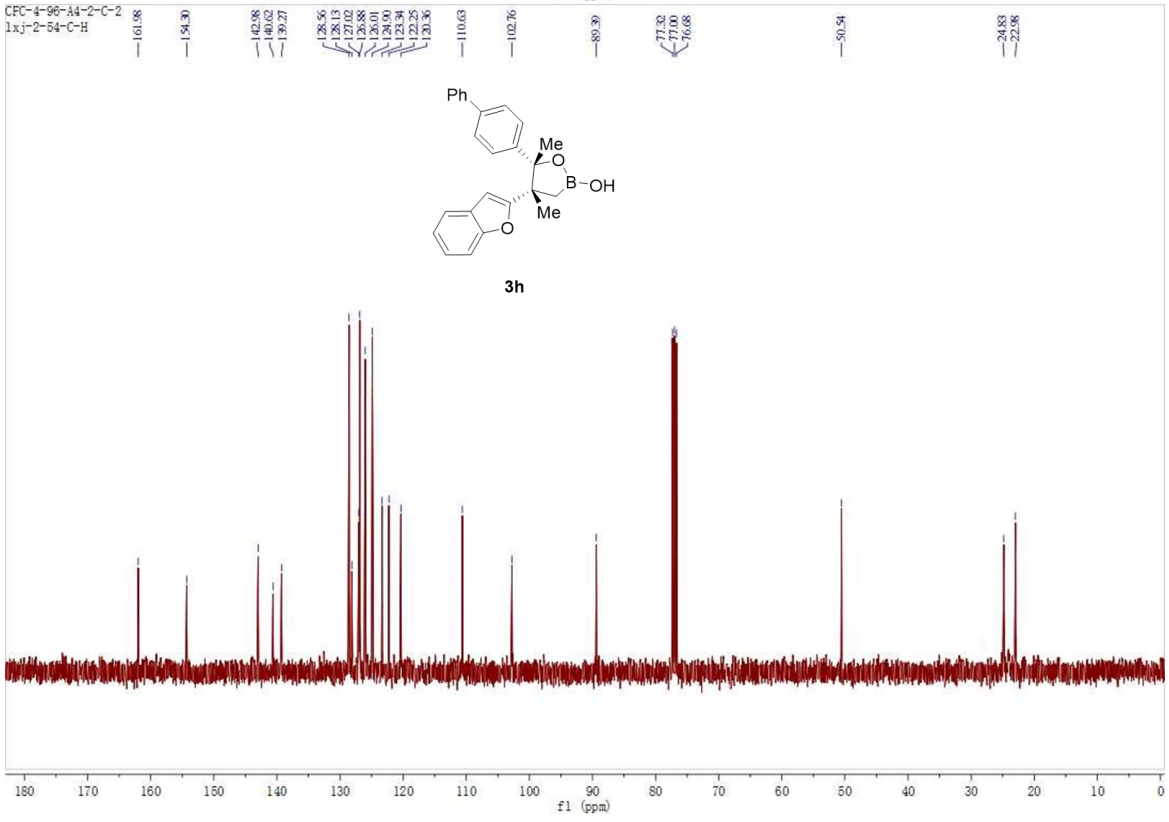

CFC-duizhiji-H
MeOOC
Me
O
B–OH
Me
O
3g
2.20
2.37
2.04
2.16
1.00
0.90
3.00
3.00
4.26
1.14
f1 (ppm)

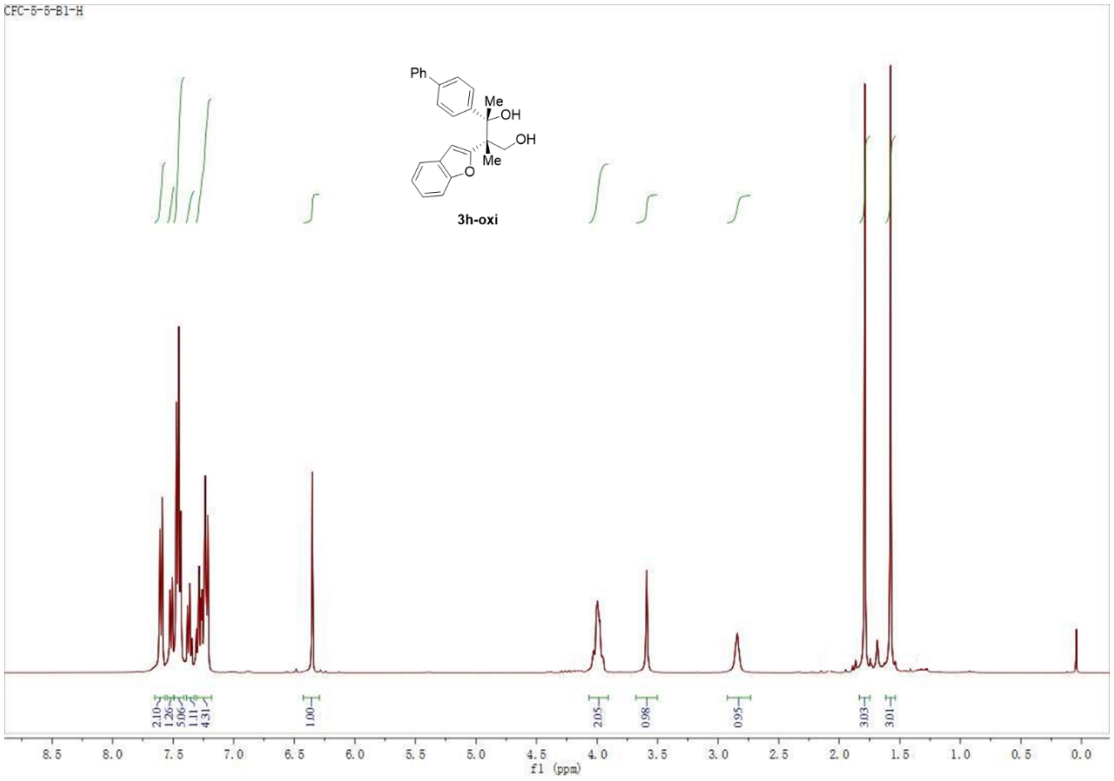

lwx-1-22-major-CrA400-0628
lxj-2-54-C-H
166.67
161.72
154.20
149.33
128.66
128.23
127.98
124.56
123.30
122.35
120.40
110.61
102.59
89.15
77.32
77.00
76.68
51.93
50.56
25.11
22.84
MeOOC
Me
O
B–OH
Me
O
3g
f1 (ppm)

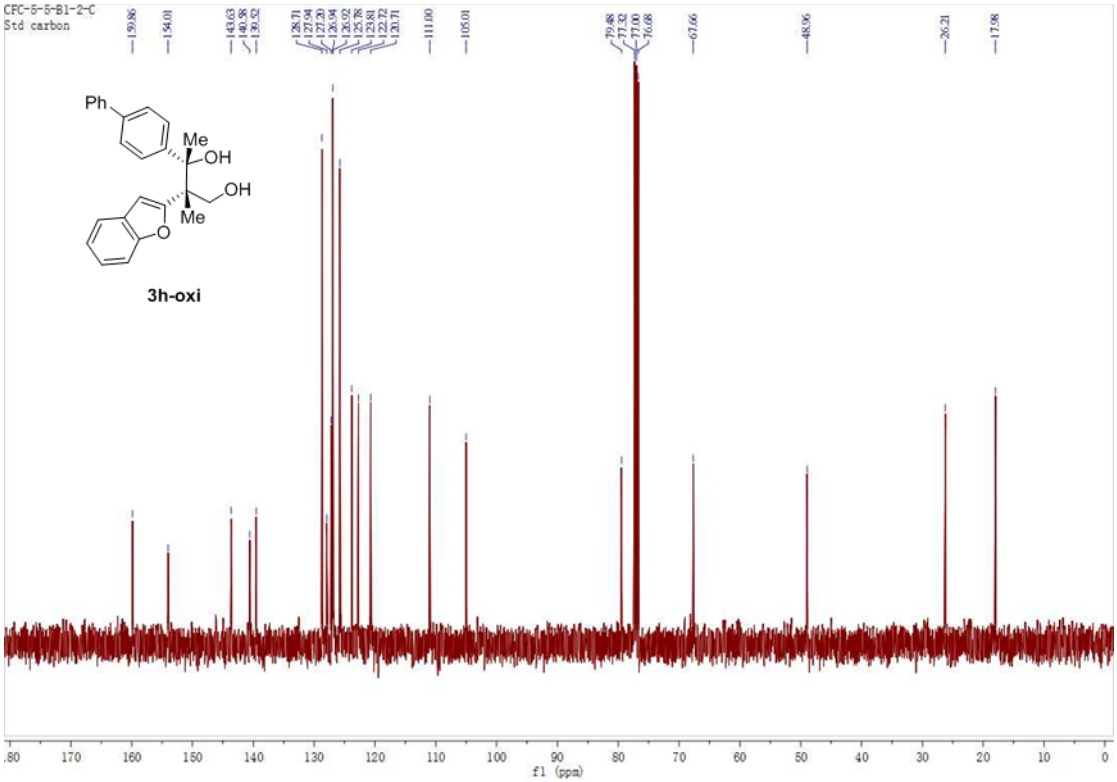

lwx-1-31-a4-h
MeOOC
Me
OH
OH
Me
O
3g-oxi
2.01
0.99
1.00
4.25
1.00
6.05
0.93
3.04
3.02
f1 (ppm)

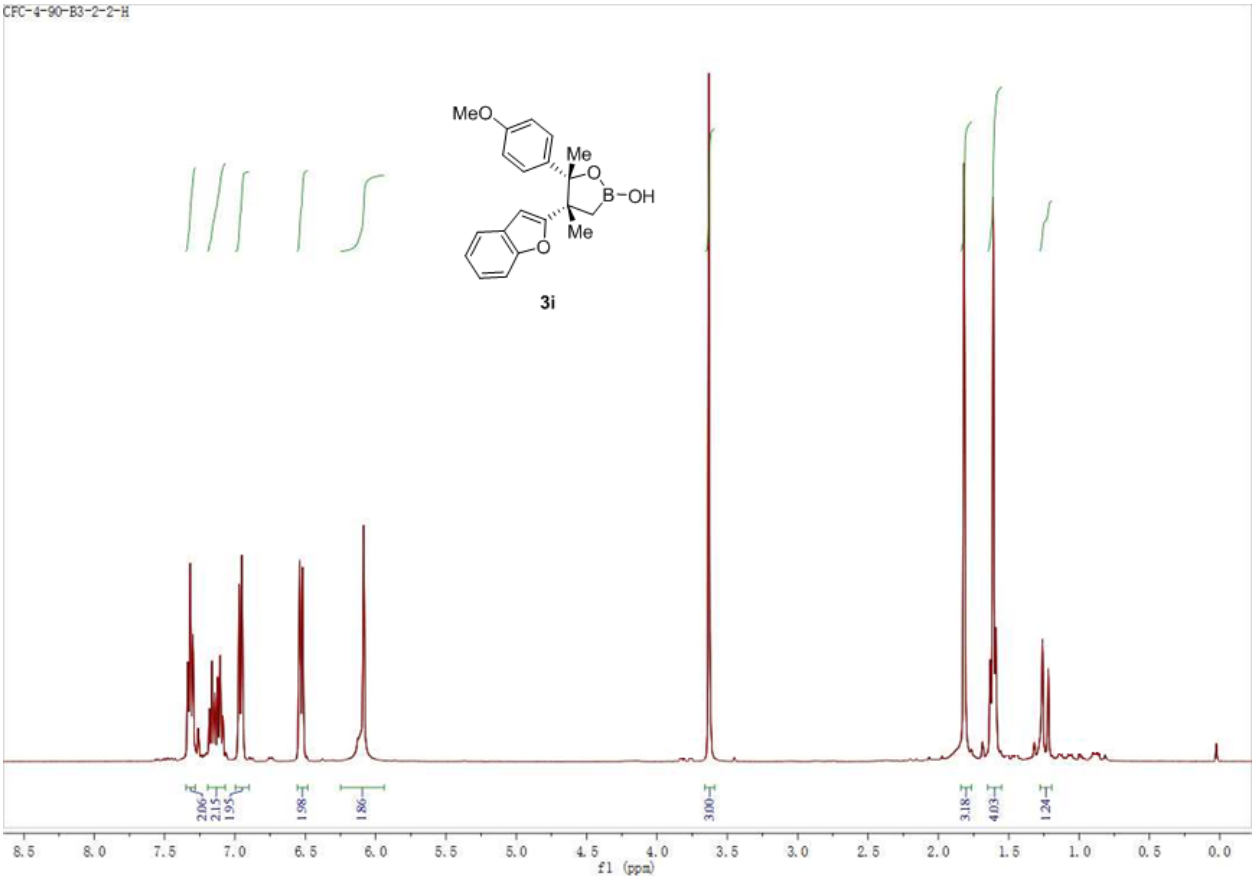

LWX-1-31-A4-2-C
167.02
159.39
153.95
149.85
128.60
128.40
127.74
126.62
123.97
122.82
120.77
111.01
105.04
79.99
77.32
77.00
76.68
67.63
52.07
48.66
25.99
18.03
MeOOC
Me
OH
OH
Me
O
3g-oxi
f1 (ppm)

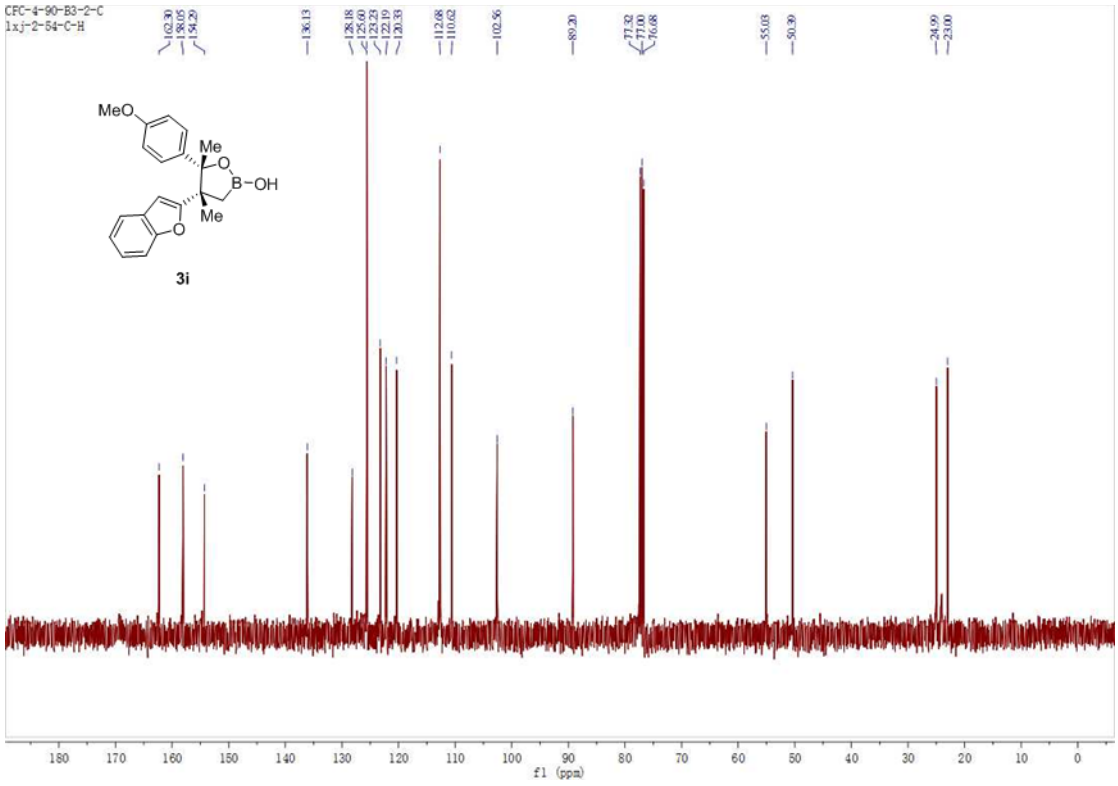

CFC-4-96-A4-2-H-2
Ph
Me
O
B–OH
Me
O
3h
f1 (ppm)

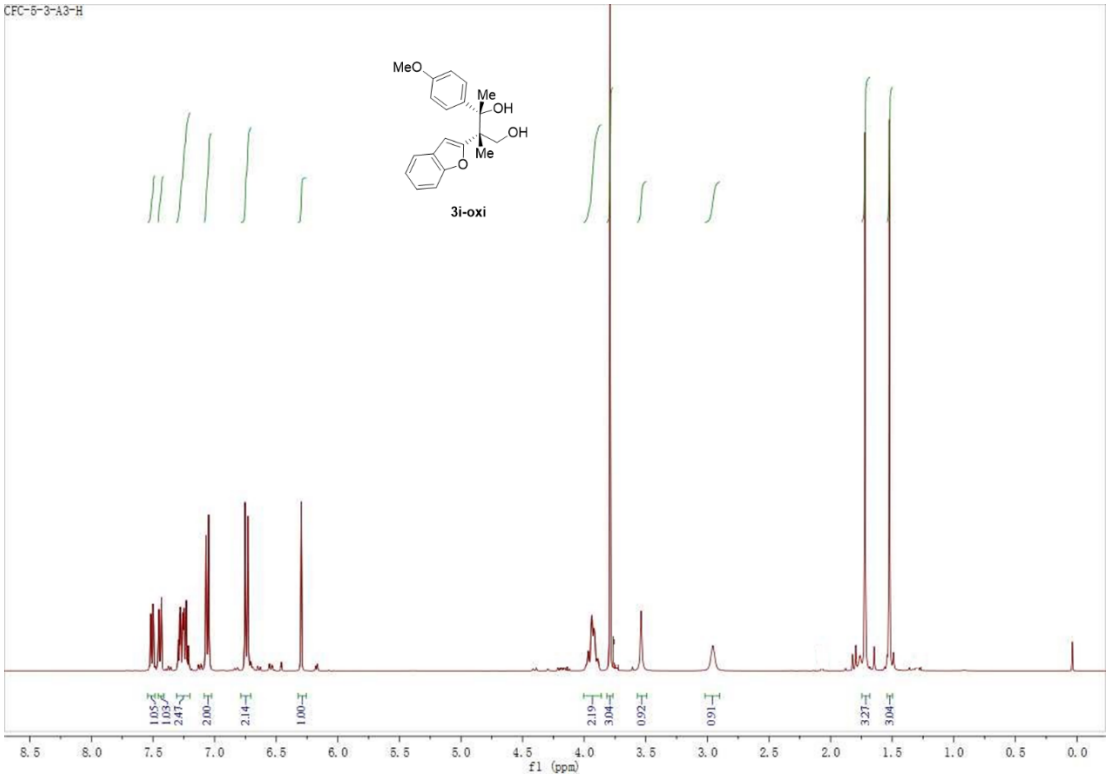

CFC-4-96-A4-2-C-2
1xj-2-54-C-H
Ph
Me
O
B–OH
Me
O
3h
f1 (ppm)

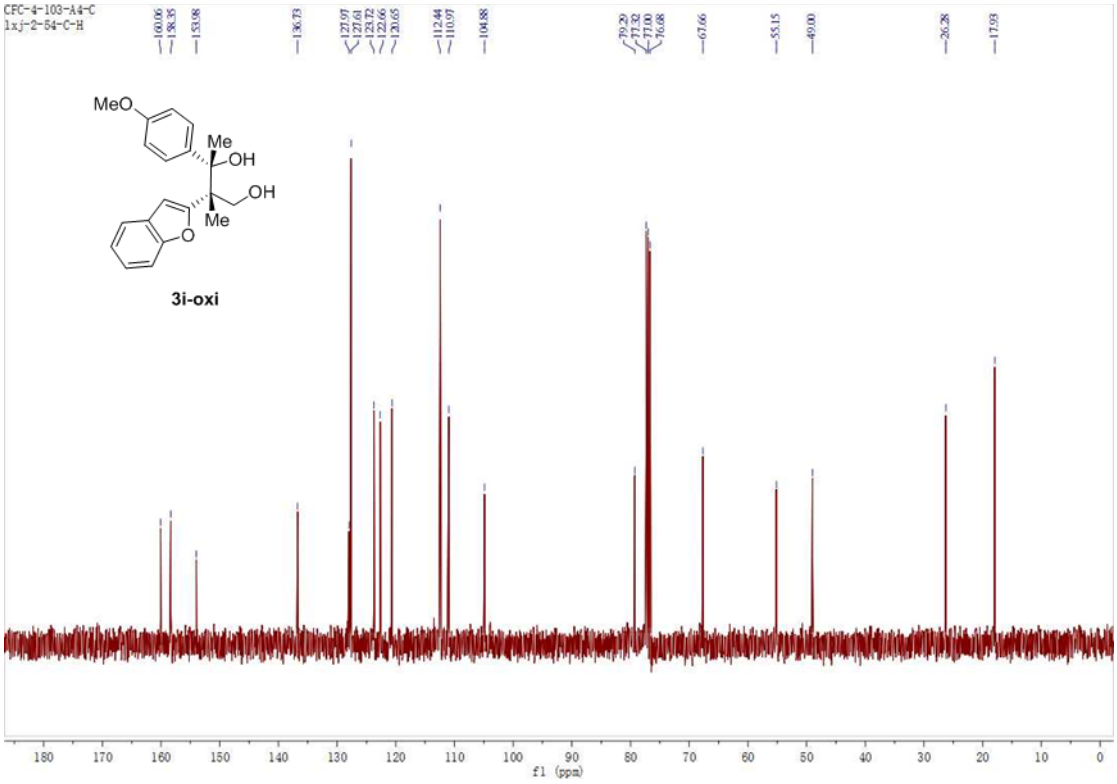

CFC-5-5-B1-H
Ph
Me
OH
OH
Me
O
3h-oxi
2.10
1.26
5.06
1.11
4.31
1.00
2.05
0.98
0.95
3.03
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

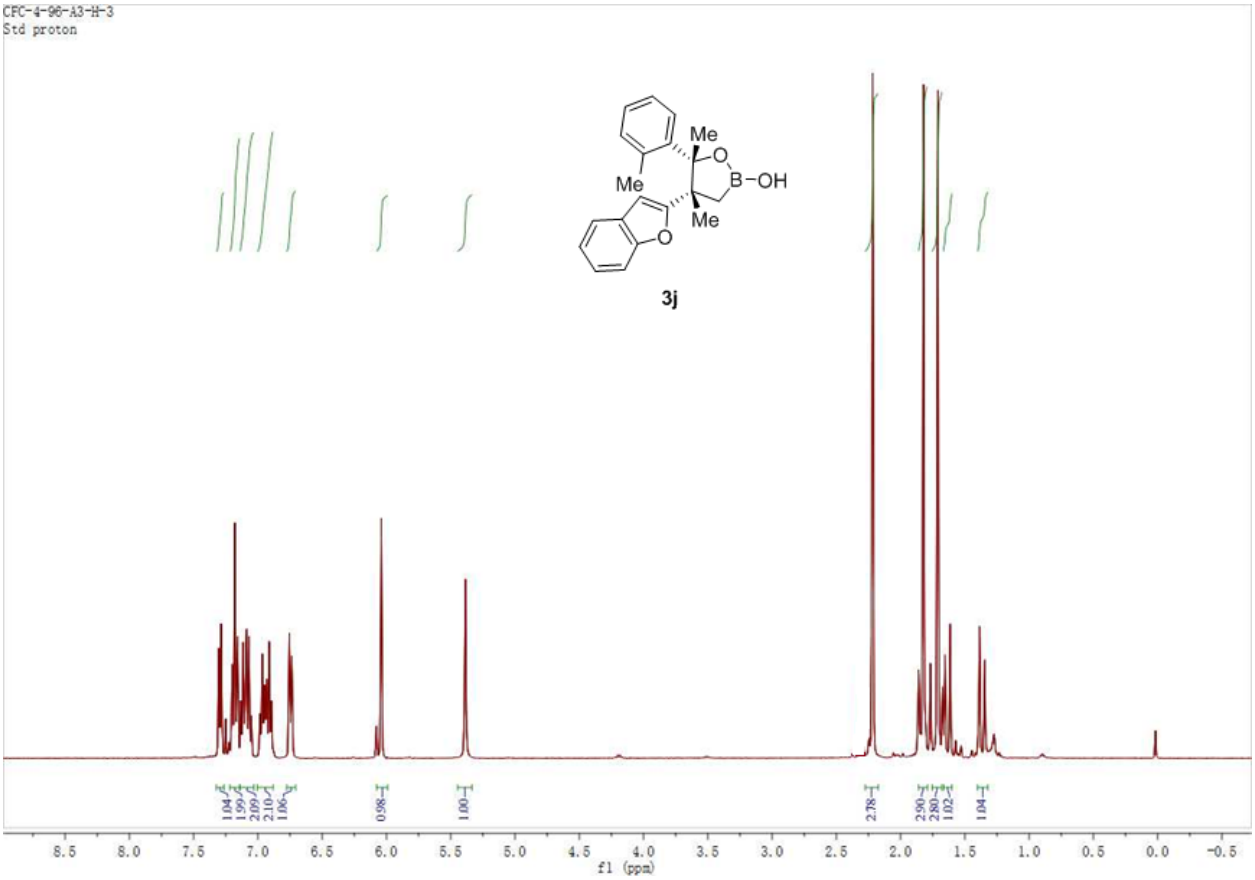

CFC-5-5-B1-2-C
Std carbon
139.86
154.01
143.63
140.98
139.52
128.71
127.94
127.20
126.94
126.92
125.78
123.81
122.72
120.71
111.00
105.01
79.48
77.32
77.00
76.68
67.66
48.96
26.21
17.98
Ph
Me
OH
OH
Me
O
3h-oxi
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

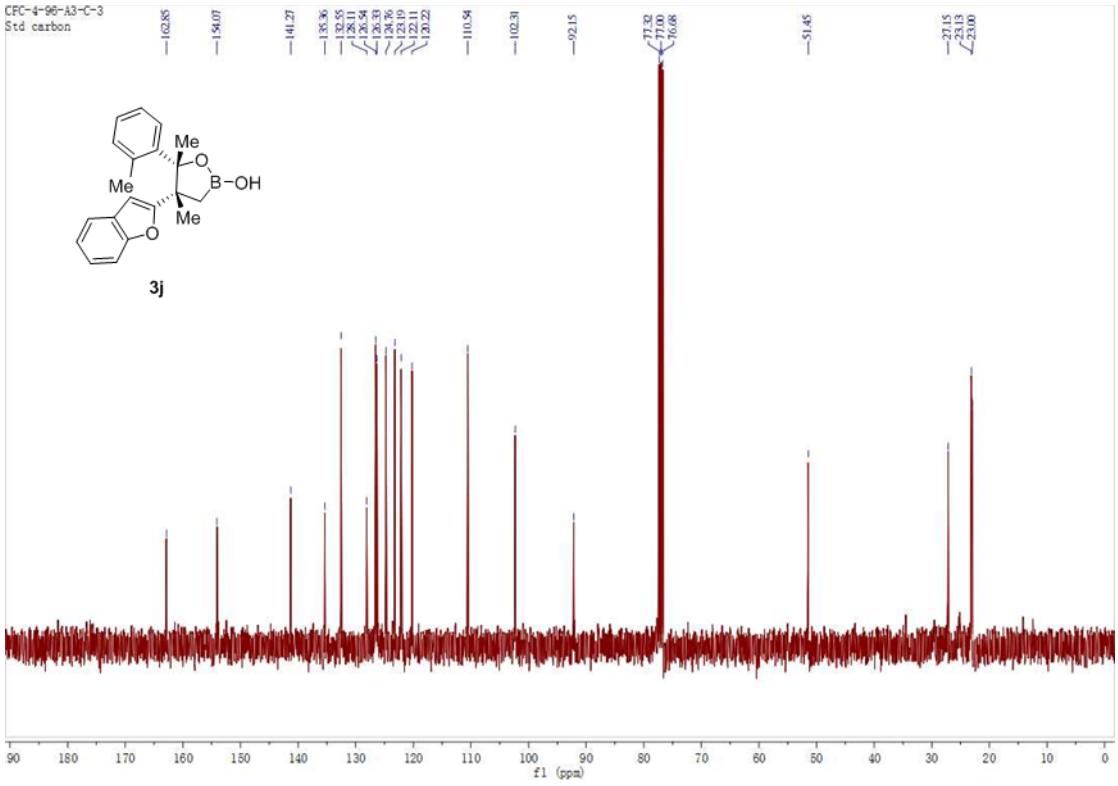

CFC-4-90-B3-2-2-H
MeO
Me
O
B-OH
Me
O
3i
2.06
2.15
1.95
1.98
1.86
3.00
3.18
4.03
1.24
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

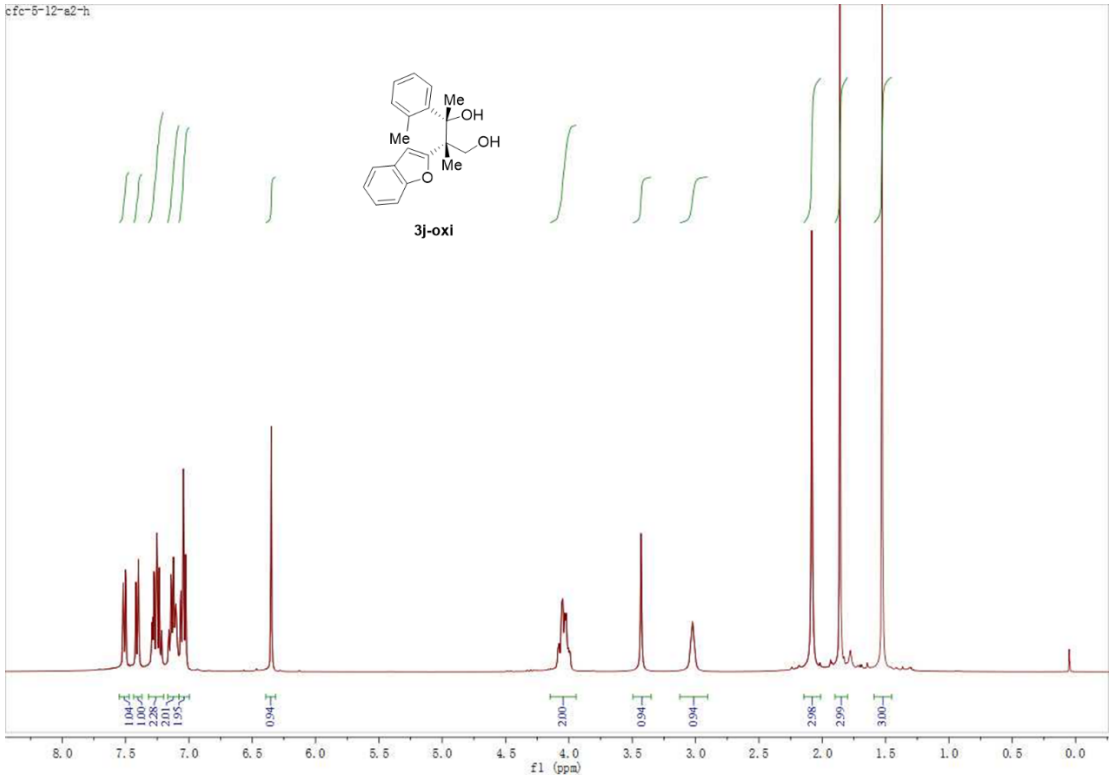

CFC-4-90-B3-2-C
lxj-2-54-C-H
162.30
158.05
154.29
136.13
128.18
125.60
123.23
122.19
120.33
112.68
110.62
102.56
89.20
77.32
77.00
76.68
55.03
50.30
24.99
23.00
MeO
Me
O
B-OH
Me
O
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

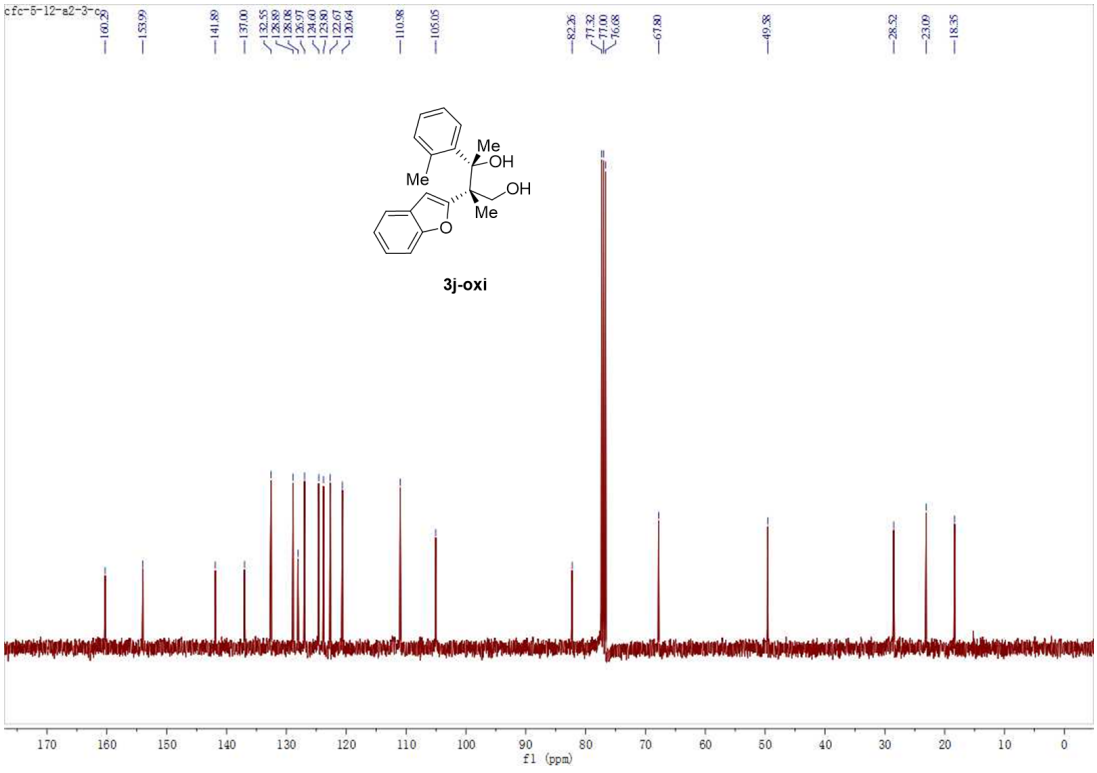

CFC-5-3-A3-H
MeO
Me
OH
OH
Me
O
3i-oxi
1.05
1.03
2.47
2.00
2.14
1.00
2.19
3.04
0.92
0.91
3.27
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

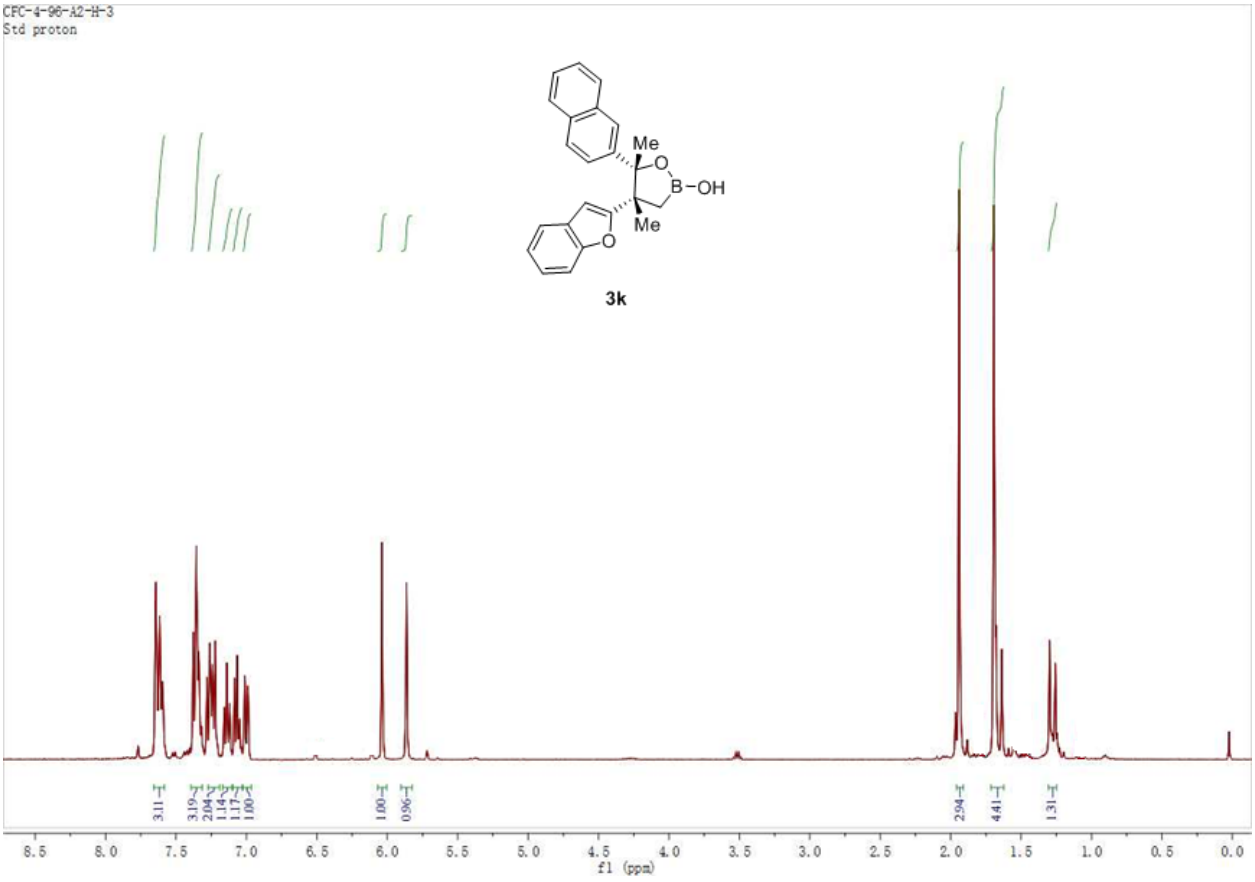

CFC-4-103-A4-C
lxj-2-54-C-H
160.06
158.35
153.98
136.73
127.97
127.61
123.72
122.66
120.65
112.44
110.97
104.88
79.29
77.32
77.00
76.68
67.66
55.15
49.00
26.28
17.93
MeO
Me
OH
OH
Me
O
3i-oxi
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

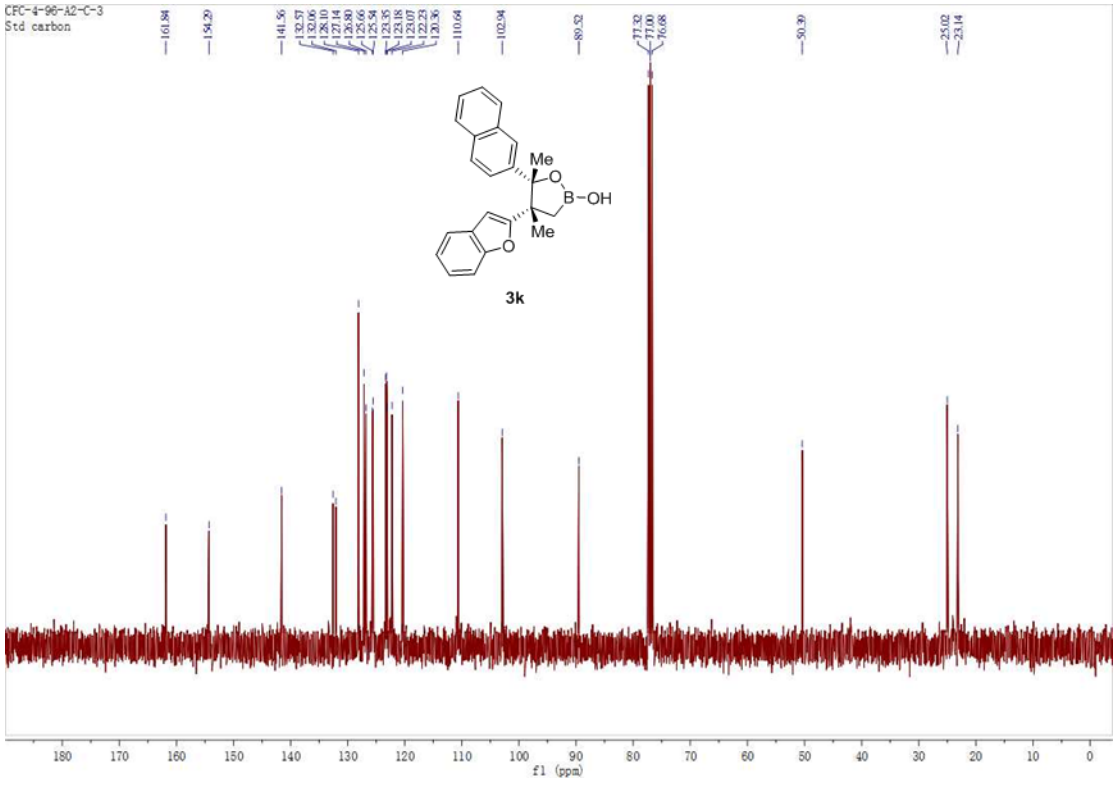

CFC-4-96-A3-H-3
Std proton
Me
O
B–OH
Me
Me
O
3j
1.04
1.99
2.09
2.10
1.06
0.98
1.00
2.78
2.90
2.80
1.02
1.04
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

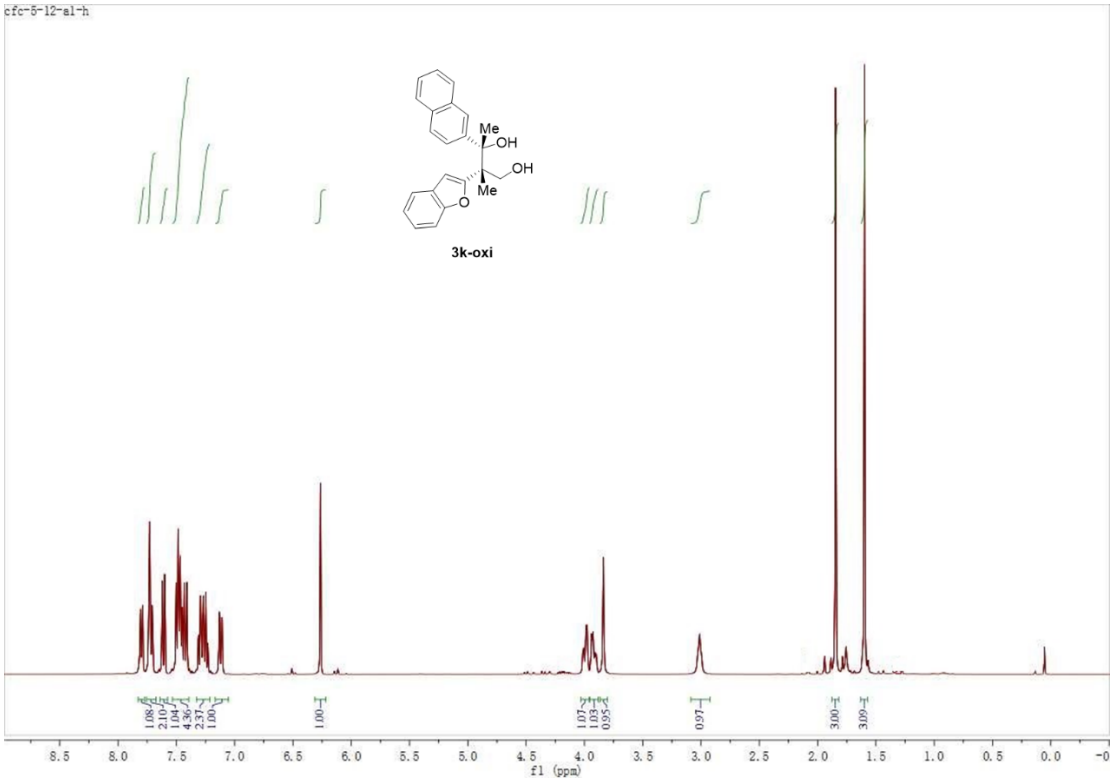

CFC-4-96-A3-C-3
Std carbon
162.85
154.07
141.27
135.36
132.55
128.11
126.54
126.33
124.76
123.10
122.11
120.22
110.54
102.31
92.15
77.32
77.00
76.68
51.45
27.15
23.13
23.00
Me
O
B–OH
Me
Me
O
3j
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

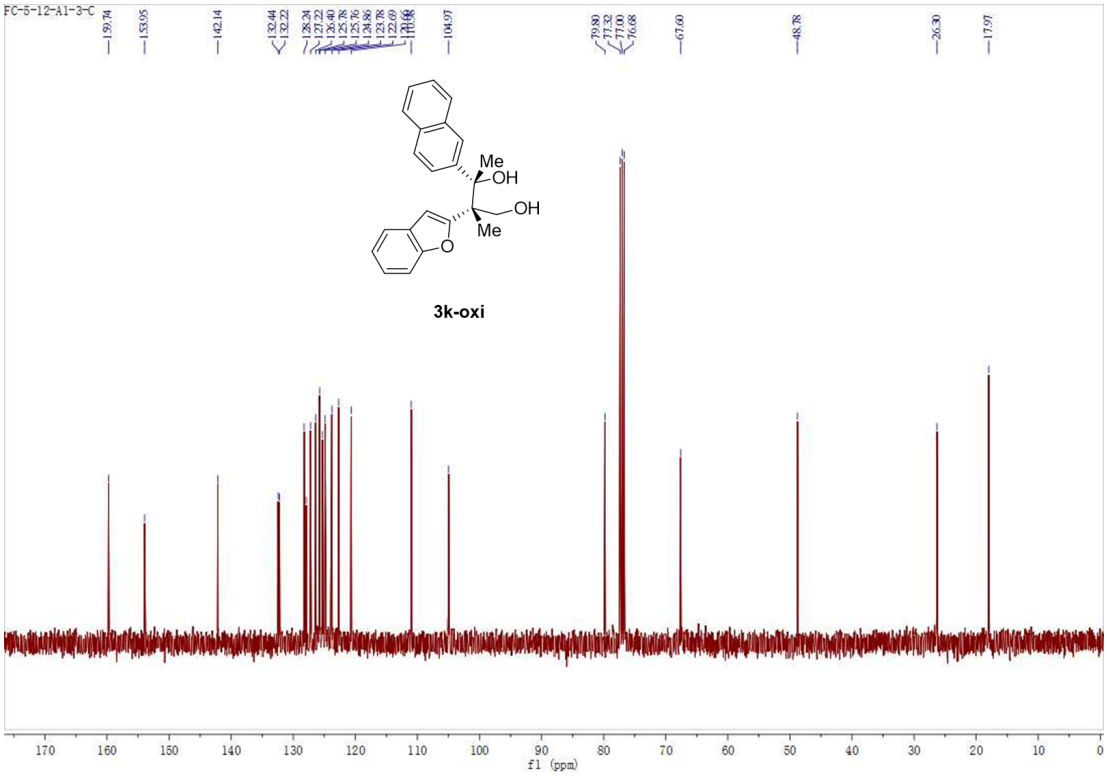

cfc-5-12-a2-h
Me
OH
Me
OH
Me
O
3j-oxi
1.04
1.00
2.28
2.01
1.95
0.94
2.00
0.94
0.94
2.98
2.99
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

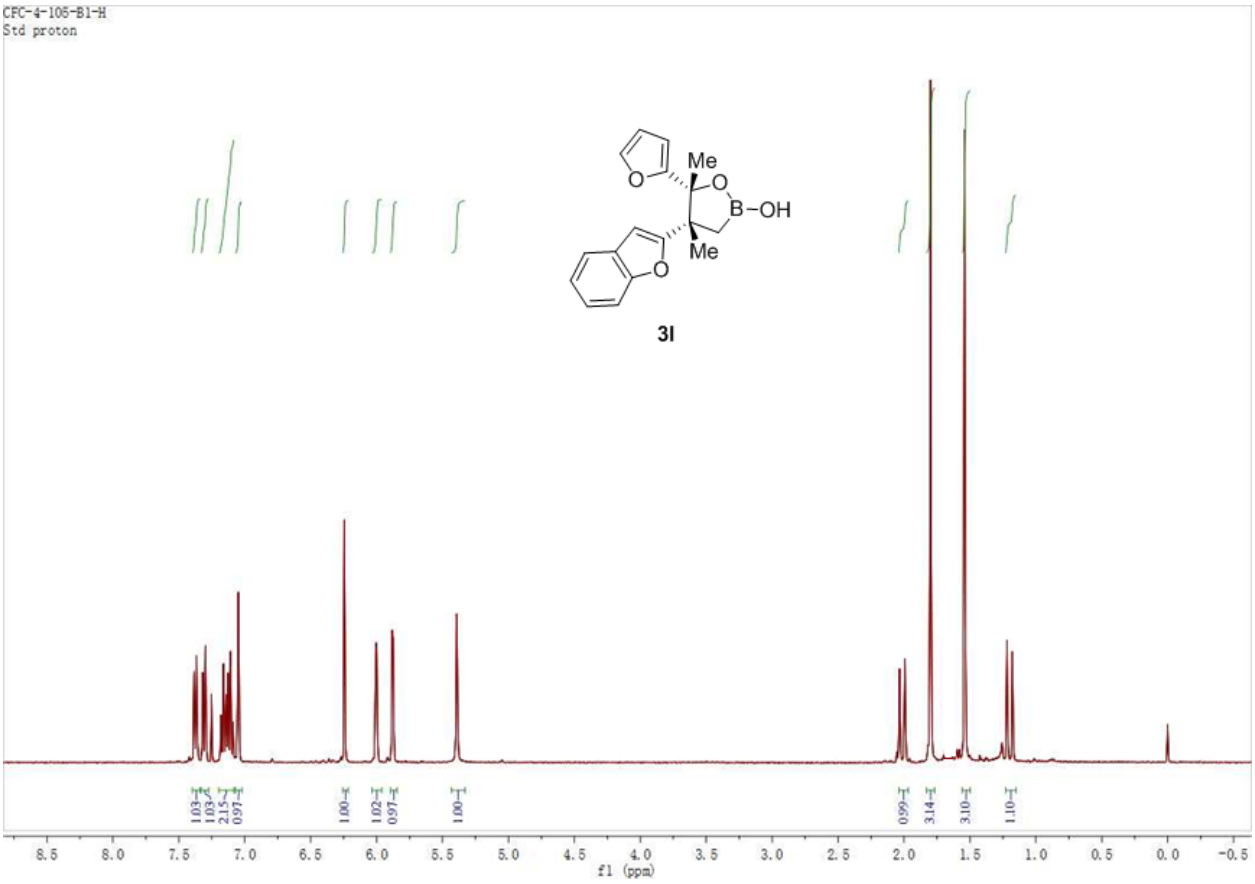

cfc-5-12-a2-3-c
160.28
153.99
141.89
137.00
132.55
128.89
128.08
126.97
124.60
123.80
122.67
120.64
110.98
105.05
82.26
77.32
77.00
76.68
67.80
49.88
28.52
23.09
18.35
Me
OH
Me
OH
Me
O
3j-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

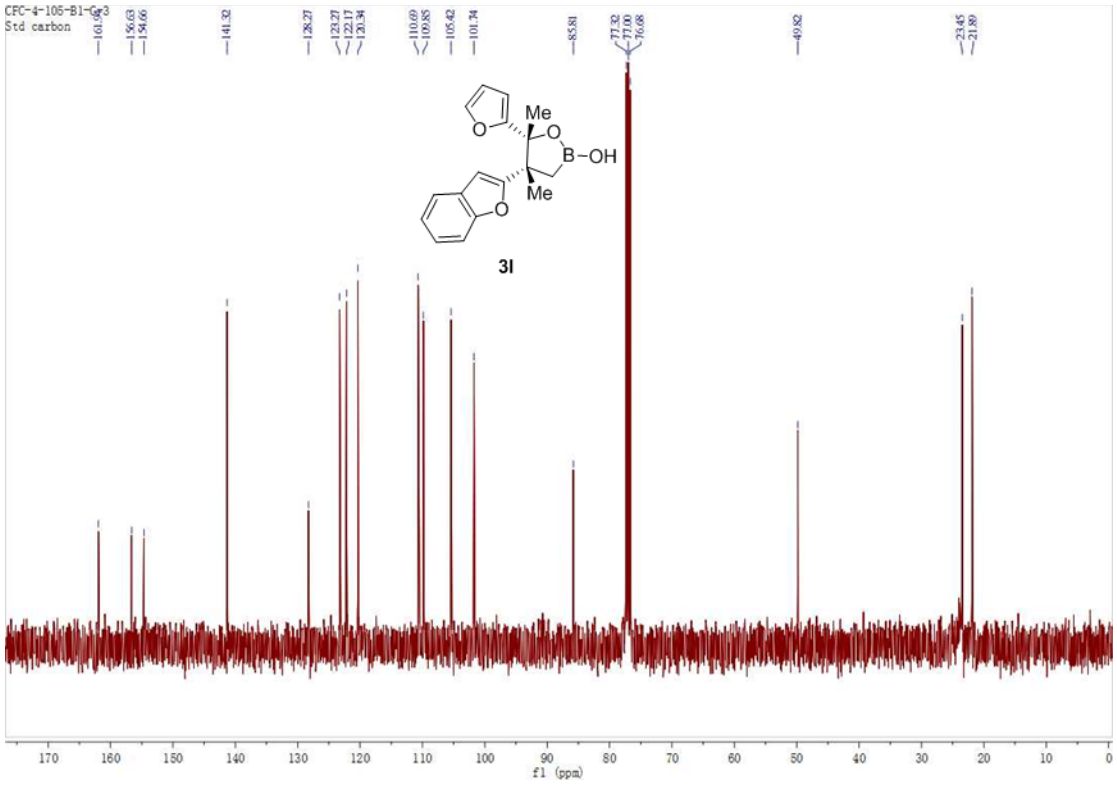

CFC-4-96-A2-H-3
Std proton
Me
O
B–OH
Me
O
3k
3.11
3.19
2.04
1.14
1.17
1.00
1.00
0.96
2.94
4.41
1.31
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

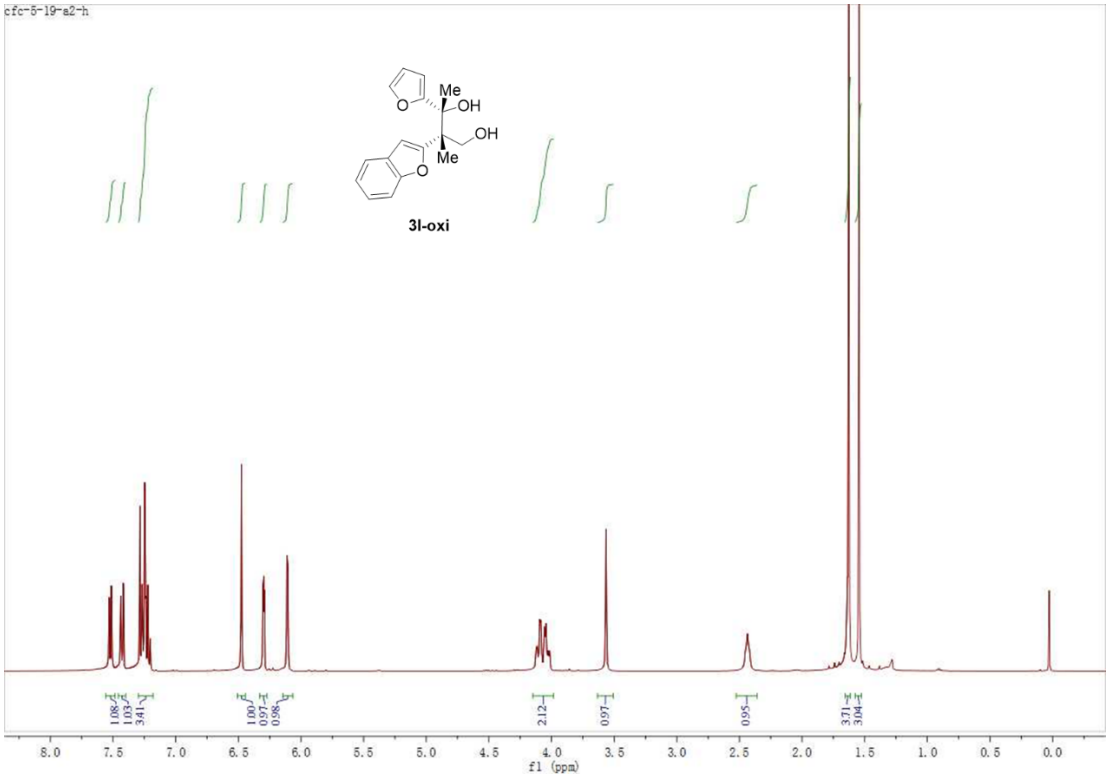

CFC-4-96-A2-C-3
Std carbon
161.84
154.29
141.56
132.57
132.06
128.10
127.14
126.80
125.66
125.54
123.35
123.18
123.07
122.23
120.36
110.64
102.94
89.52
77.32
77.00
76.68
50.39
25.02
23.14
Me
O
B–OH
Me
O
3k
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

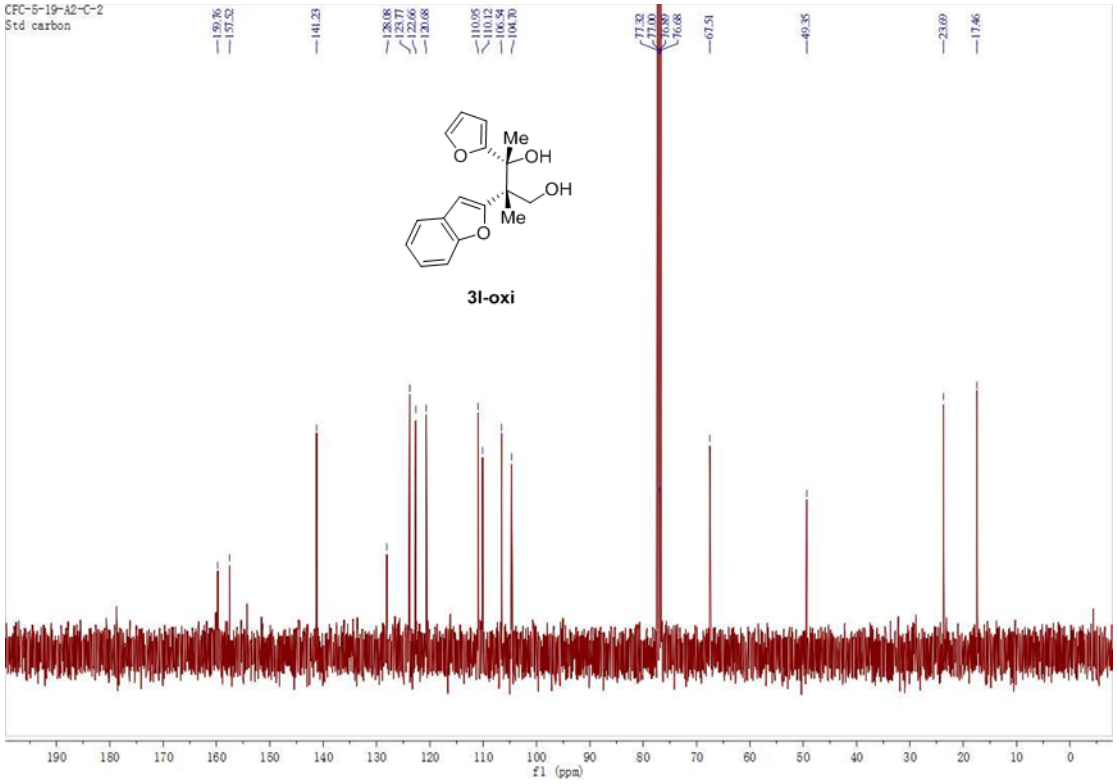

cfc-5-12-a1-h
Me
OH
OH
Me
O
3k-oxi
1.08
2.10
1.04
4.36
2.37
1.00
1.00
1.03
1.03
0.95
0.97
3.00
3.09
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

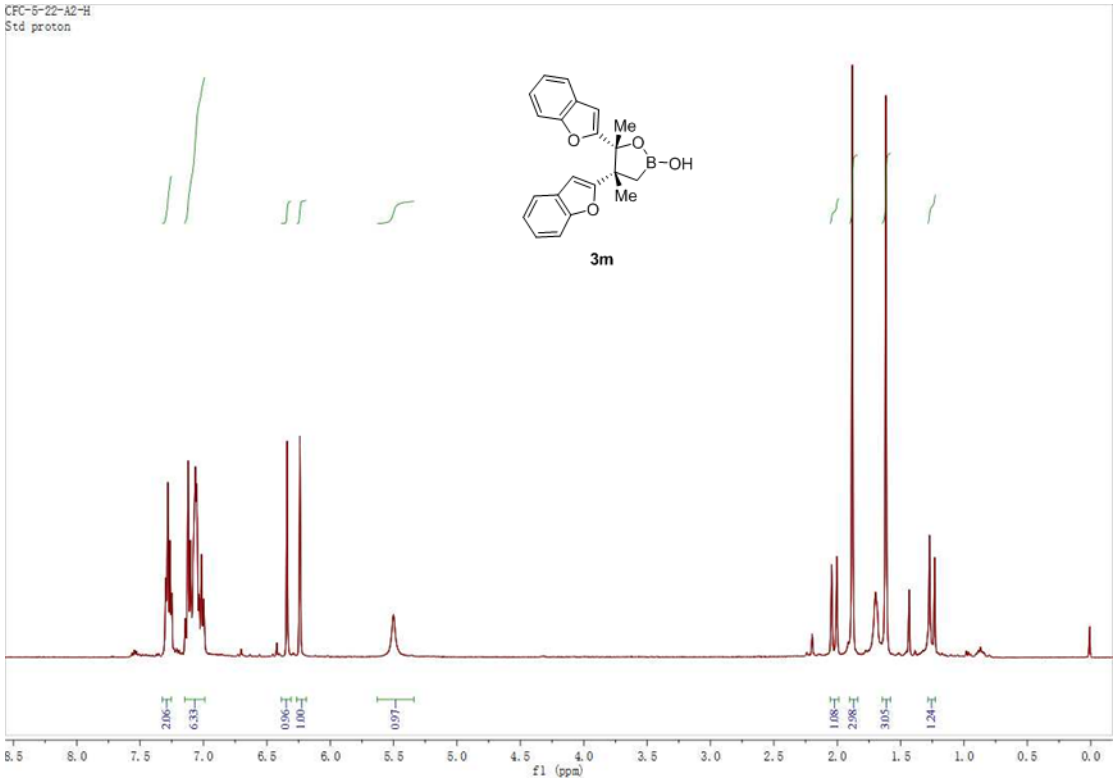

FC-5-12-A1-3-C
159.74
153.05
142.14
132.44
132.22
128.24
127.22
126.40
125.78
125.36
124.96
123.78
122.69
110.66
104.97
79.80
77.32
77.00
76.68
67.60
48.78
26.30
17.97
Me
OH
OH
Me
O
3k-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

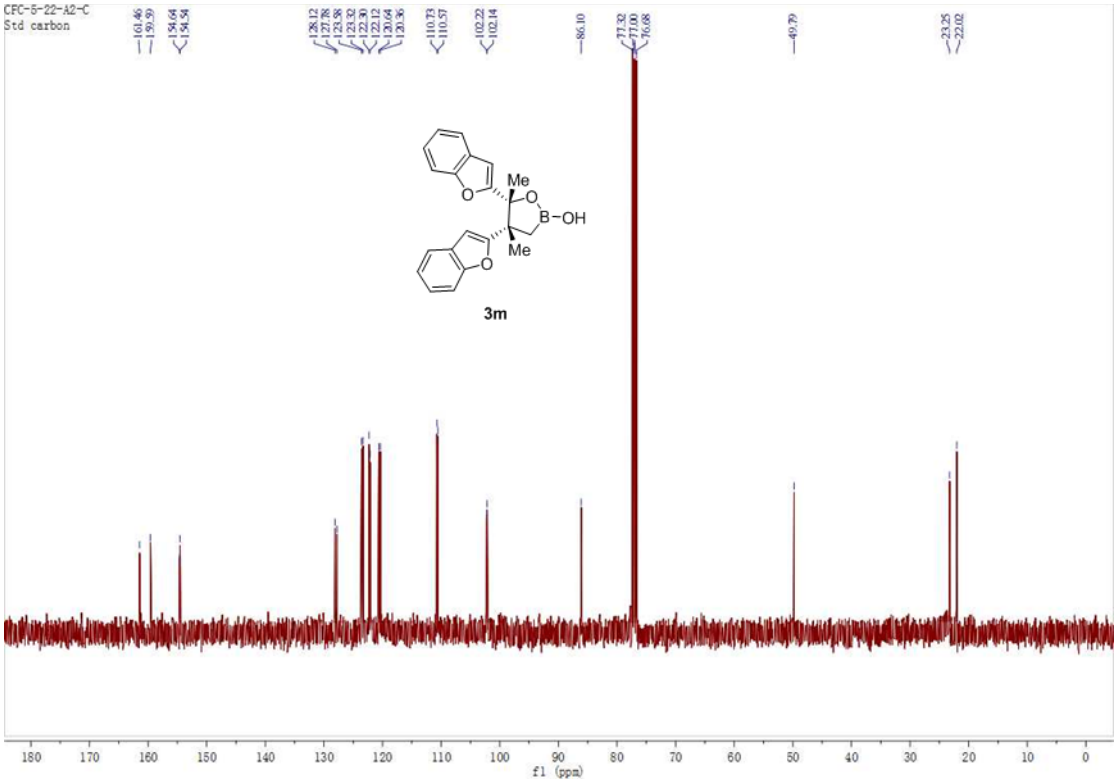

CFC-4-105-B1-H
Std proton
Me
O
B–OH
Me
O
O
3l
1.03
1.03
2.15
0.97
1.00
1.02
0.97
1.00
0.99
3.14
3.10
1.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

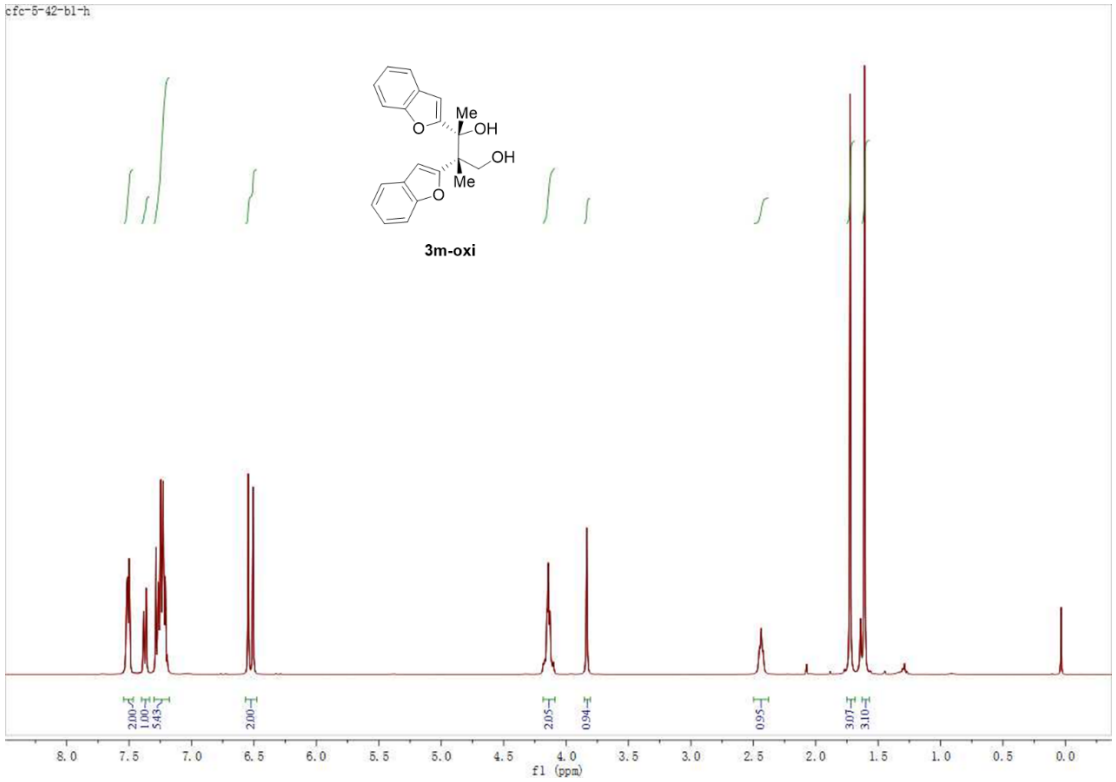

CFC-4-105-B1-C
Std carbon
160.98
156.63
154.66
141.32
128.27
123.27
122.17
120.34
110.69
109.85
105.42
101.74
85.81
77.32
77.00
76.68
49.82
23.45
21.89
Me
O
B–OH
Me
O
3l
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

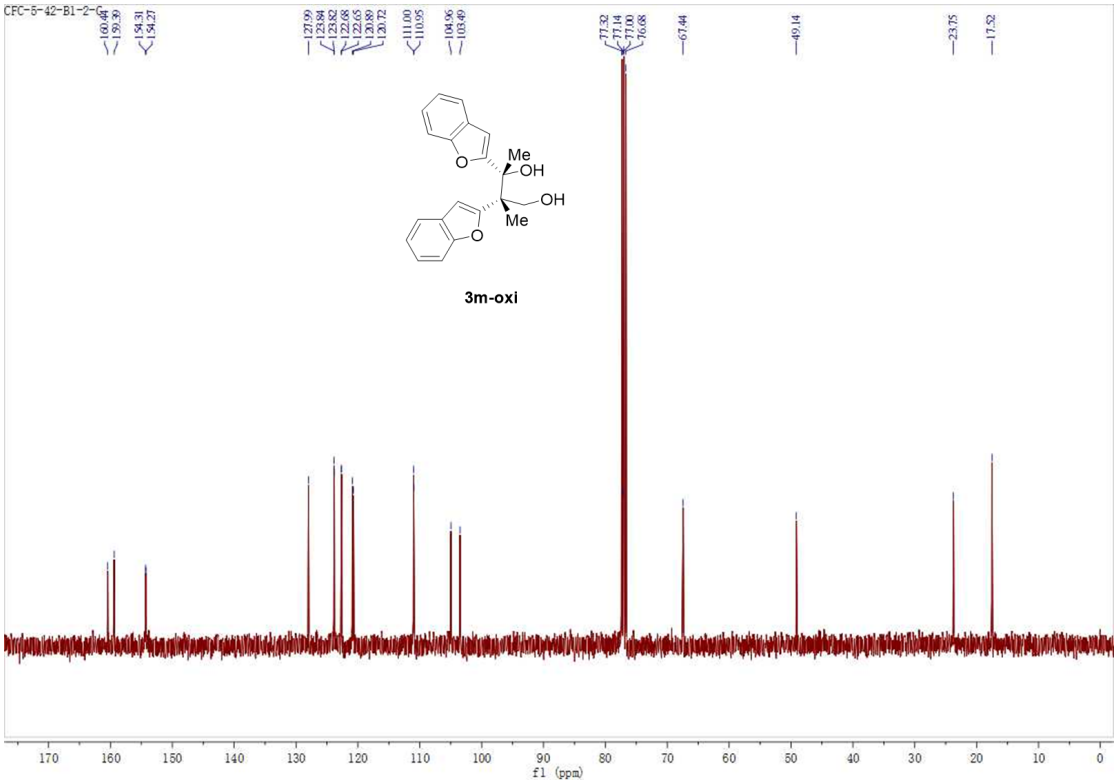

cfc-5-19-a2-h
Me
OH
OH
Me
O
O
3l-oxi
1.08
1.03
3.41
1.00
0.97
0.98
2.12
0.97
0.95
3.71
3.04
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

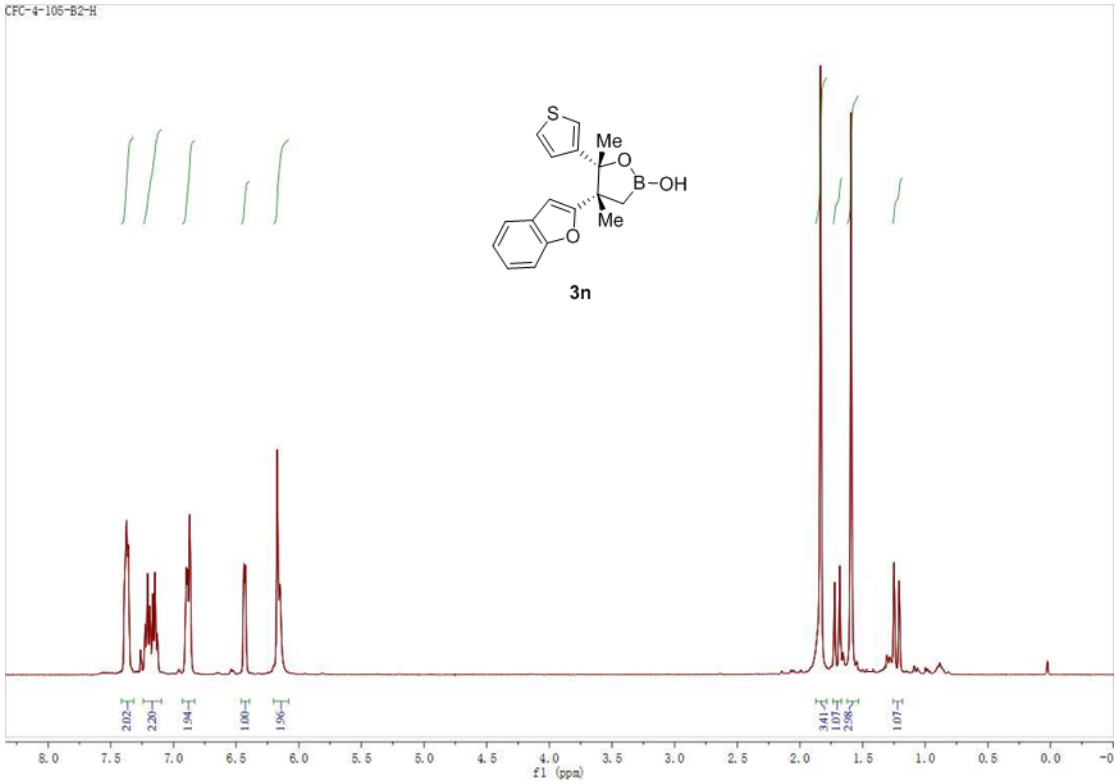

CFC-5-19-A2-C-2
Std carbon
190.76
157.52
141.23
126.08
123.77
122.66
120.68
110.95
110.12
106.54
104.30
77.32
77.00
76.69
76.68
67.51
49.35
23.69
17.46
Me
OH
OH
Me
O
O
3l-oxi
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

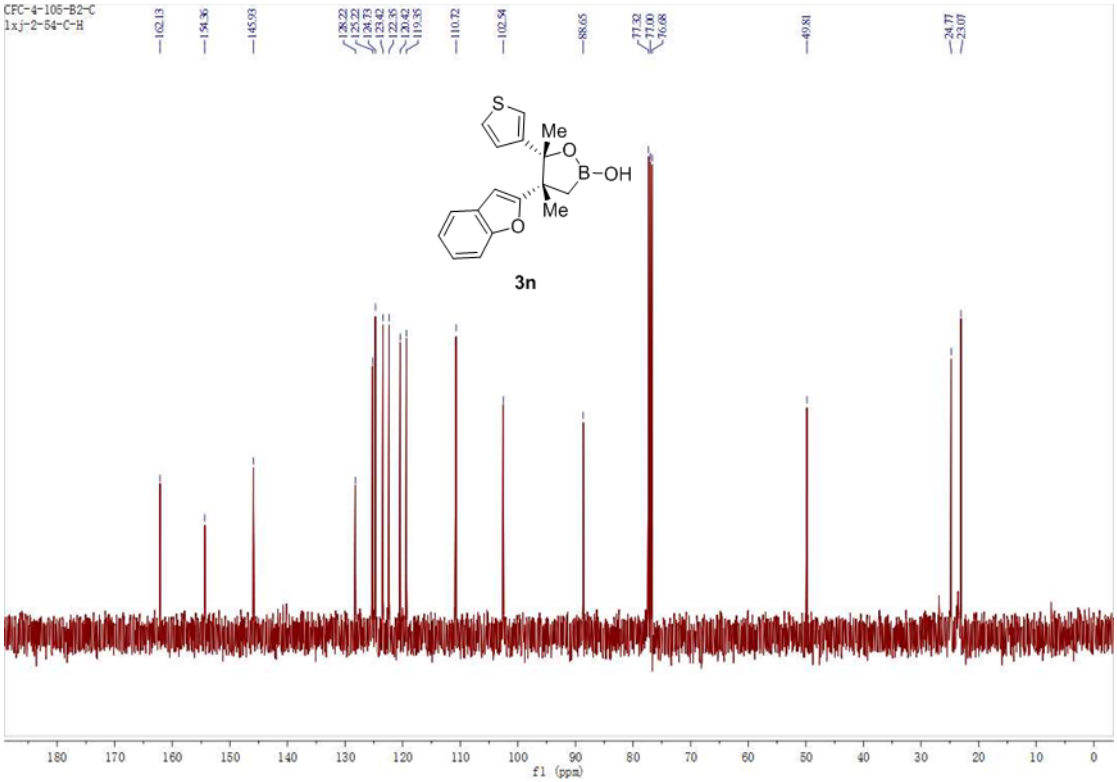

CFC-5-22-A2-H
Std proton
Me
O
B–OH
Me
O
3m
2.06
6.33
0.96
1.00
0.97
1.08
2.98
3.05
1.24
f1 (ppm)

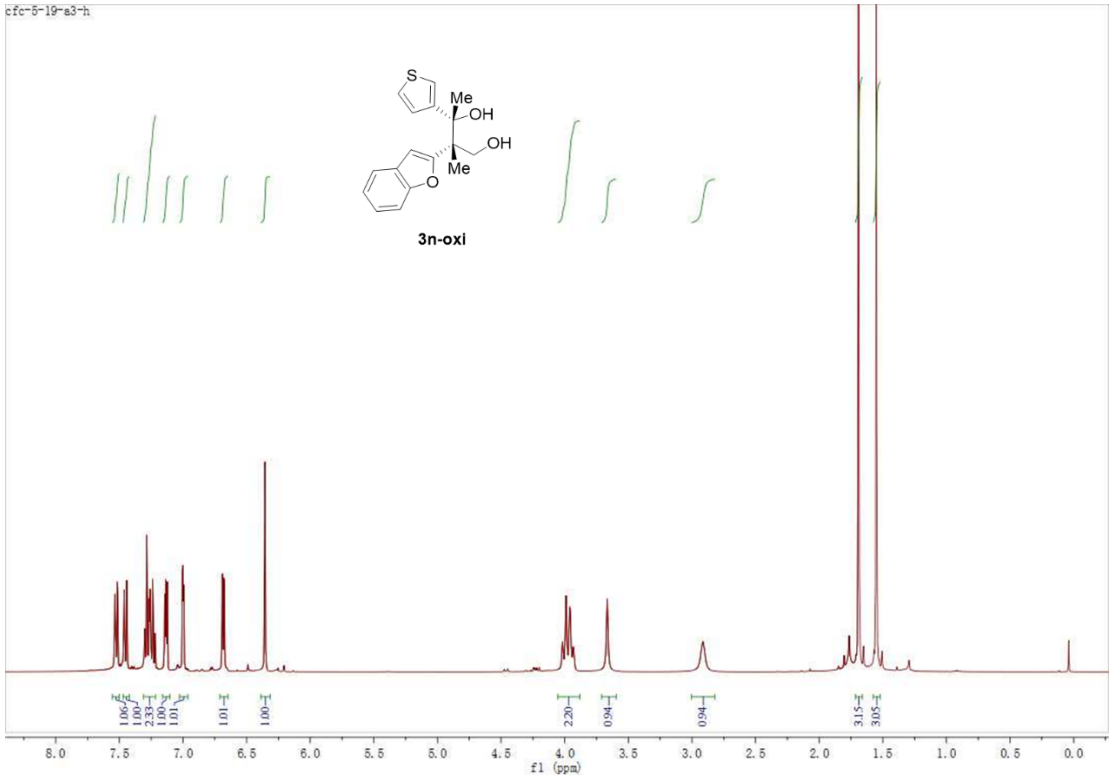

CFC-5-22-A2-C
Std carbon
161.46
159.59
154.64
154.54
128.12
127.78
123.98
123.32
122.30
122.12
120.64
120.36
110.73
110.57
102.22
102.14
86.10
77.32
77.00
76.68
49.79
23.25
22.02
Me
O
B–OH
Me
O
3m
f1 (ppm)

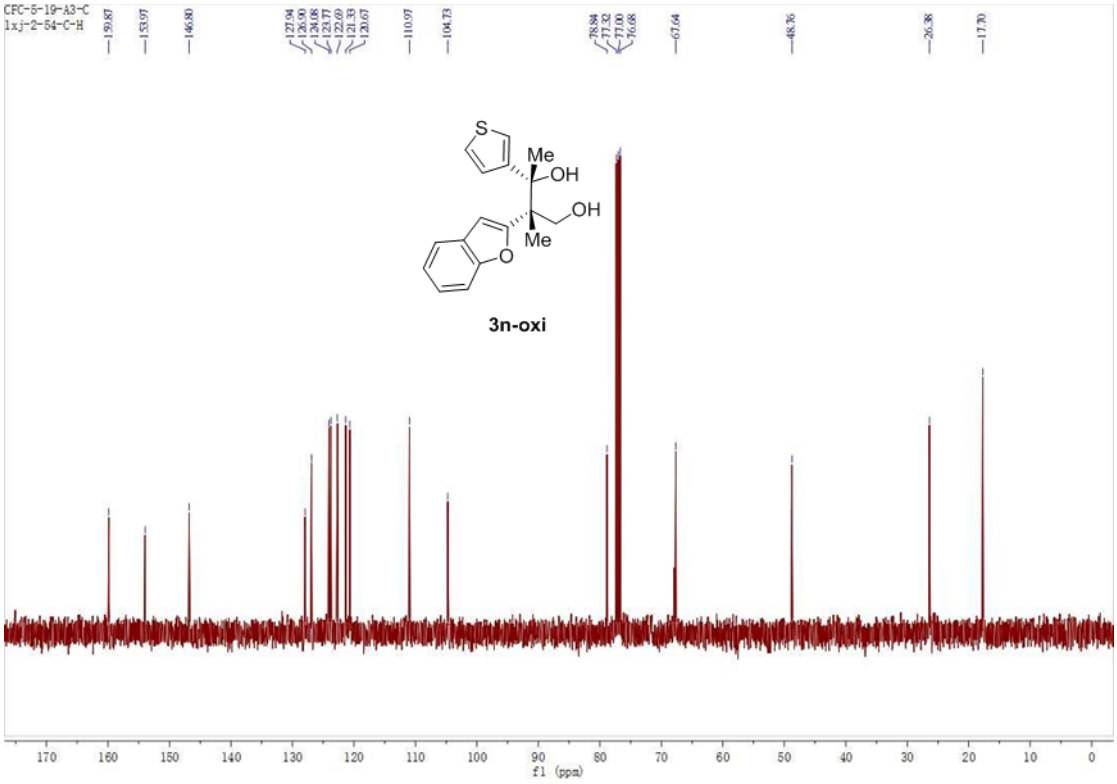

cfc-5-42-b1-h
Me
OH
OH
Me
O
O
3m-oxi
2.00
1.00
5.43
2.00
2.05
0.94
0.95
3.07
3.10
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

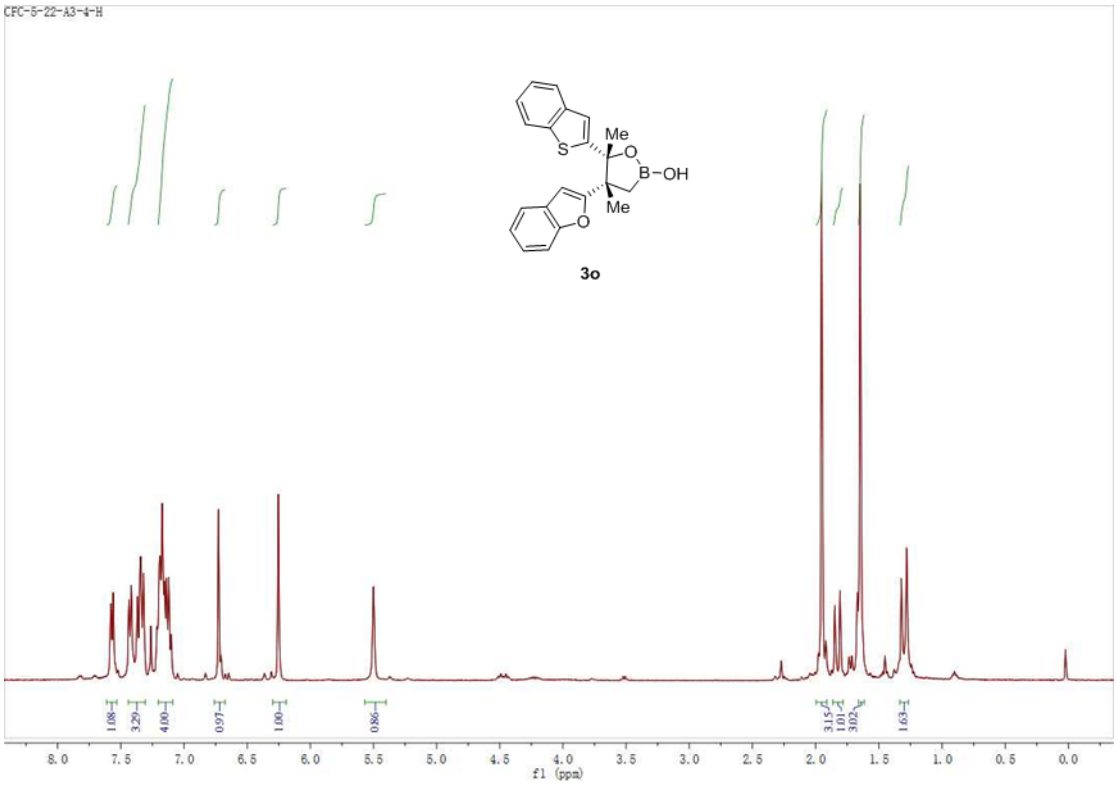

CFC-5-42-B1-2-C
160.44
159.39
154.31
154.27
127.99
123.84
123.82
122.66
122.65
120.89
120.72
111.00
110.95
104.96
103.49
77.32
77.14
77.00
76.68
67.44
49.14
23.75
17.52
Me
OH
OH
Me
O
O
3m-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

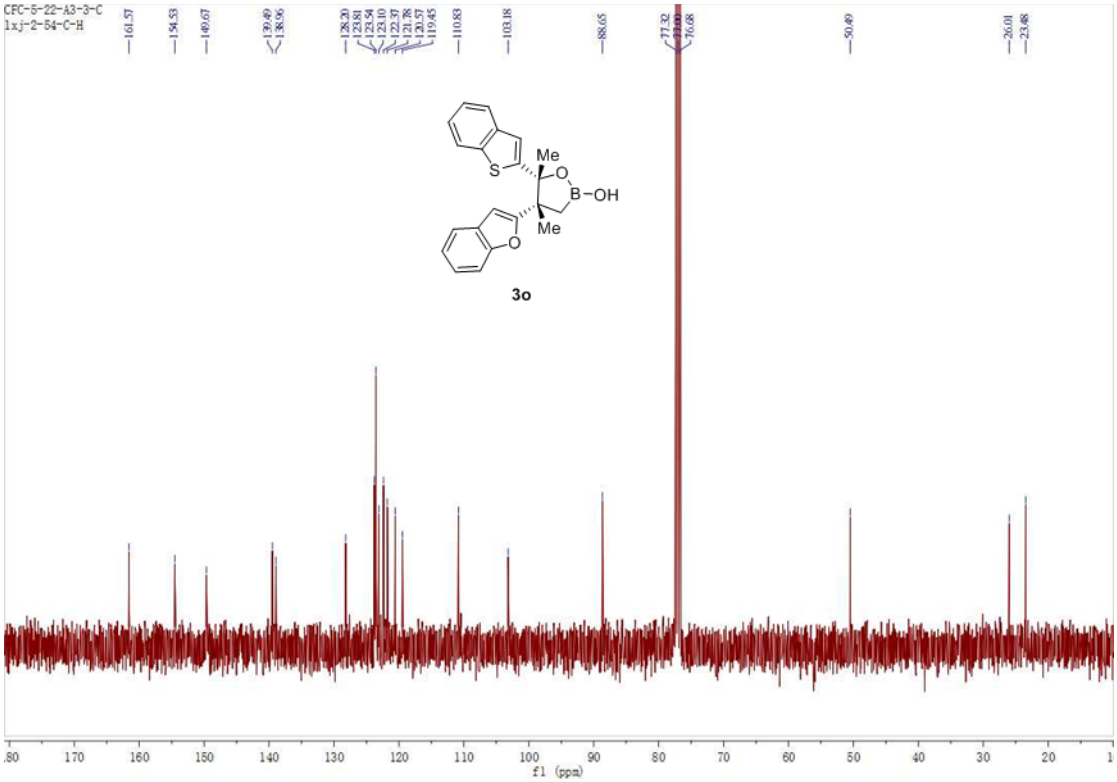

CFC-4-105-B2-H
S
Me
O
B–OH
Me
O
3n
2.02
2.20
1.94
1.00
1.96
3.41
1.07
2.98
1.07
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

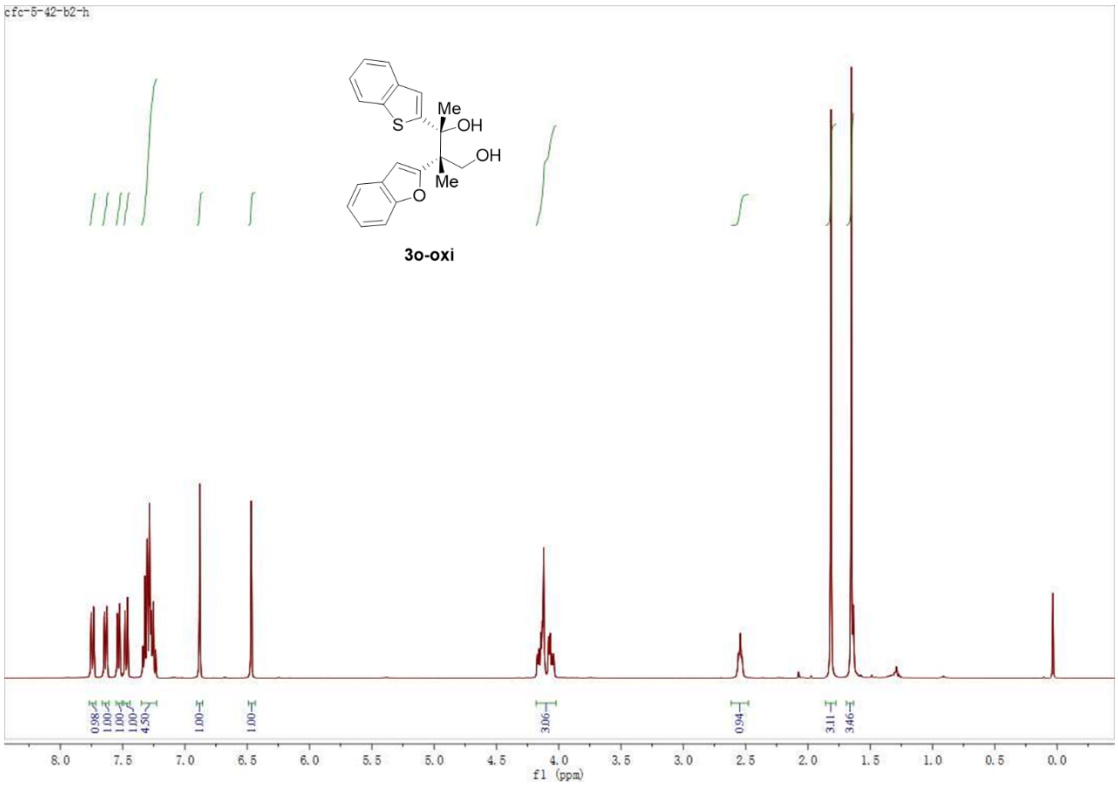

CFC-4-105-B2-C
lxj-2-54-C-H
162.13
154.36
145.93
128.22
125.22
124.73
123.42
122.35
120.42
119.35
110.72
102.54
88.65
77.32
77.00
76.68
49.81
24.77
23.07
S
Me
O
B–OH
Me
O
3n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

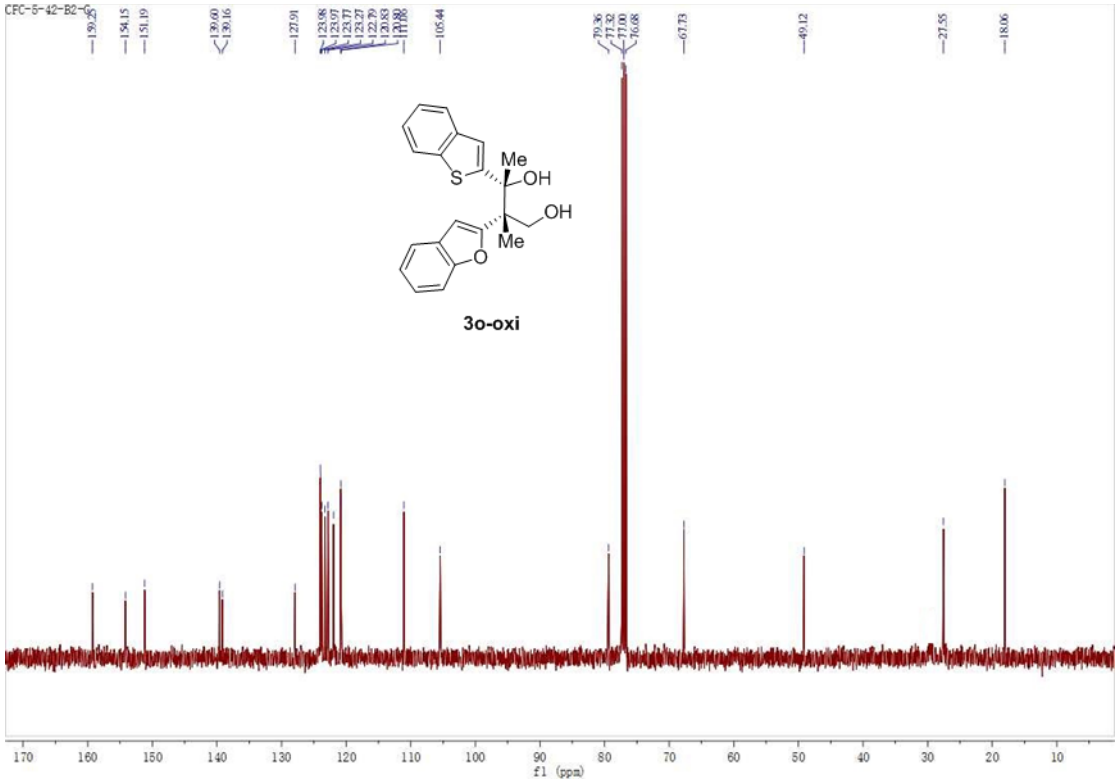

cfc-5-19-a3-h
S
Me
OH
OH
Me
O
3n-oxi
1.06
1.00
2.33
1.00
1.01
1.01
1.00
2.20
0.94
0.94
3.15
3.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

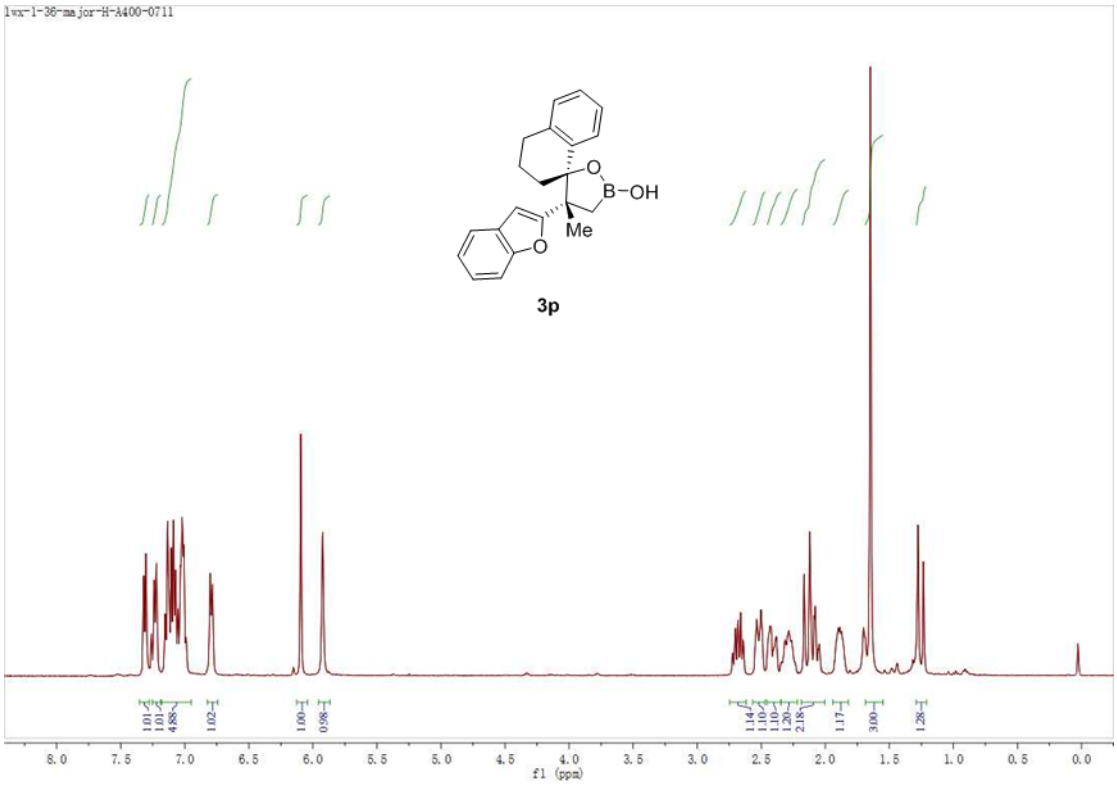

CFC-5-19-A3-C
lxj-2-54-C-H
159.87
153.97
146.80
127.94
126.00
124.08
123.77
122.60
121.33
120.67
110.97
104.73
78.84
77.32
77.00
76.68
67.64
48.36
26.38
17.70
S
Me
OH
OH
Me
O
3n-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

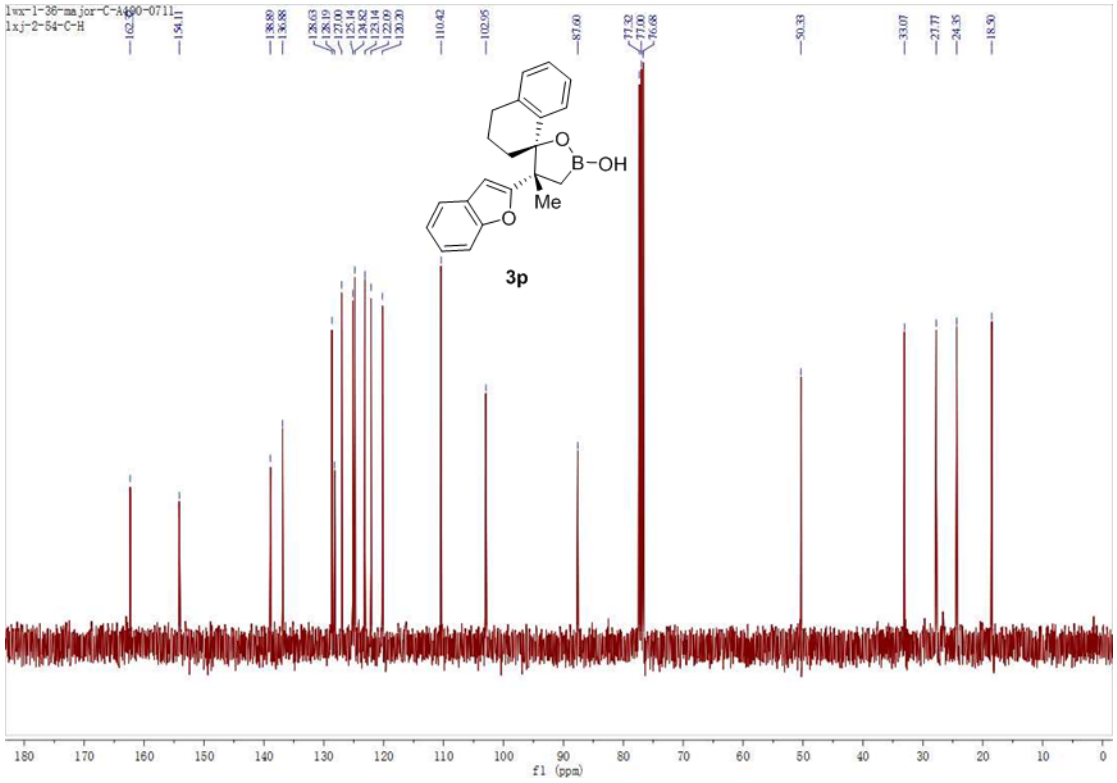

CFC-5-22-A3-4-H
Me
S
O
B–OH
Me
O
3o
1.08
3.29
4.00
0.97
1.00
0.86
3.15
1.01
3.02
1.63
f1 (ppm)

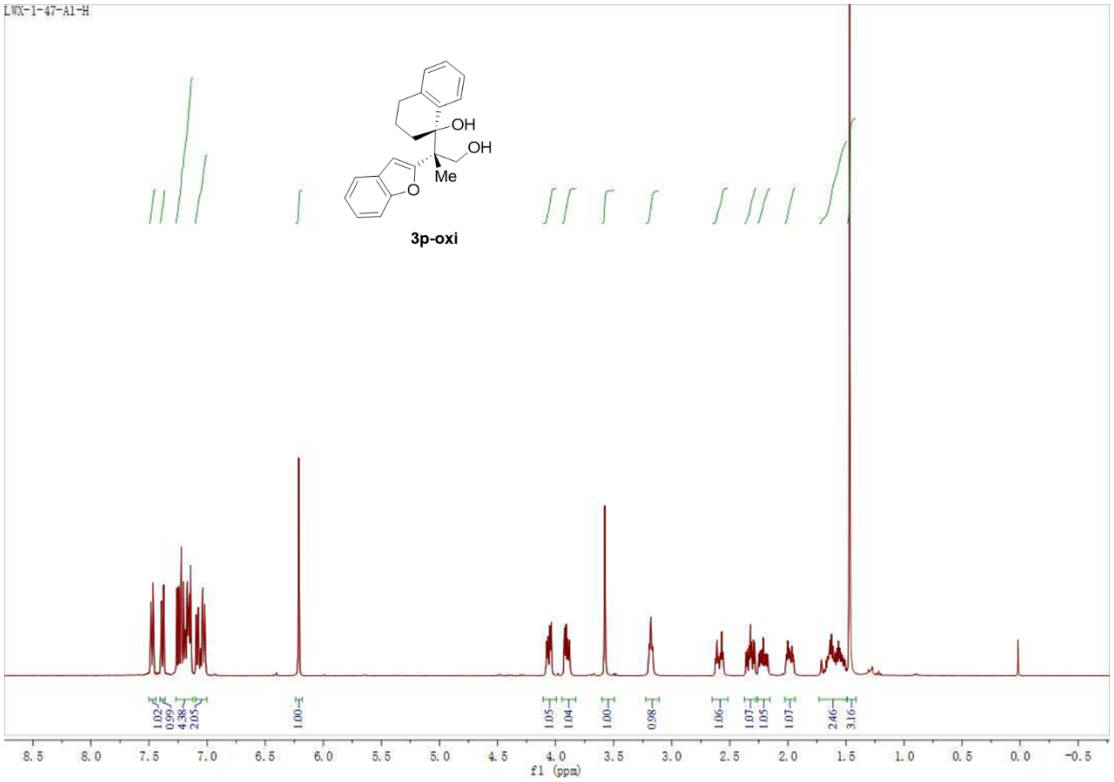

CFC-5-22-A3-3-C
lxj-2-54-C-H
161.57
154.53
149.67
130.49
128.96
128.20
123.81
123.54
123.10
122.37
121.78
120.57
119.45
110.83
103.18
88.65
77.32
77.00
76.68
50.49
26.01
23.48
Me
S
O
B–OH
Me
O
3o
f1 (ppm)

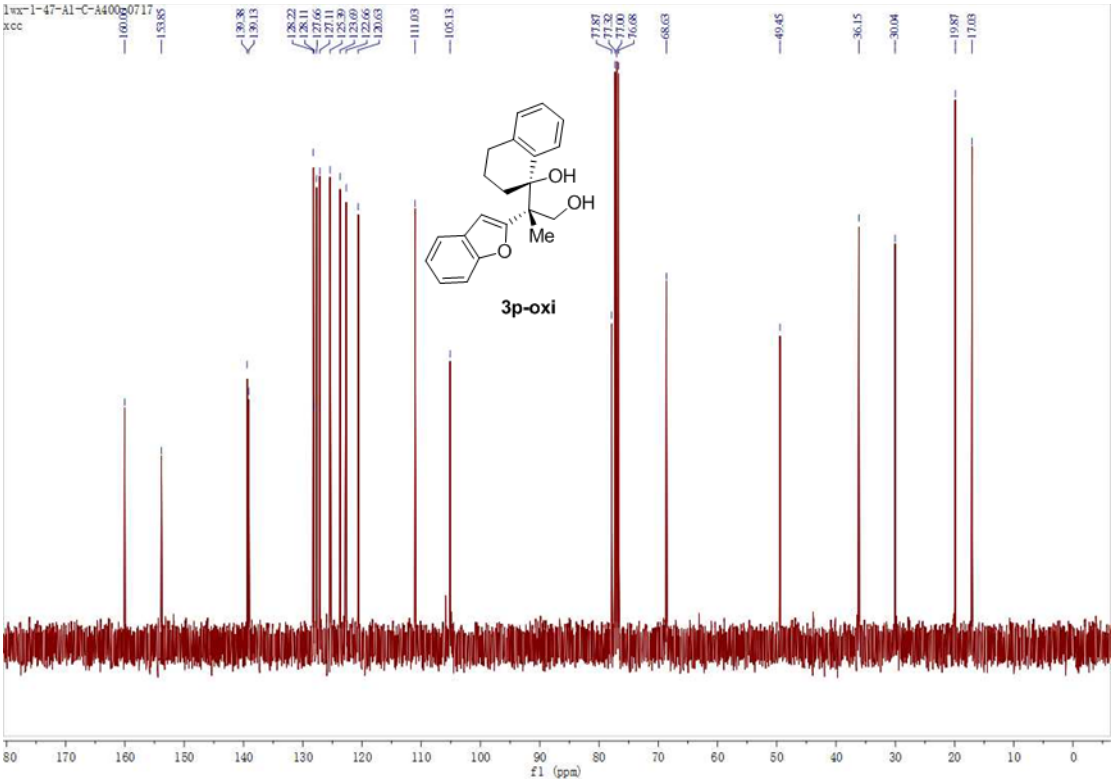

cfc-5-42-b2-h
Me
OH
OH
Me
S
O
3o-oxi
0.98
1.00
1.00
1.00
4.50
1.00
1.00
3.06
0.94
3.11
3.46
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

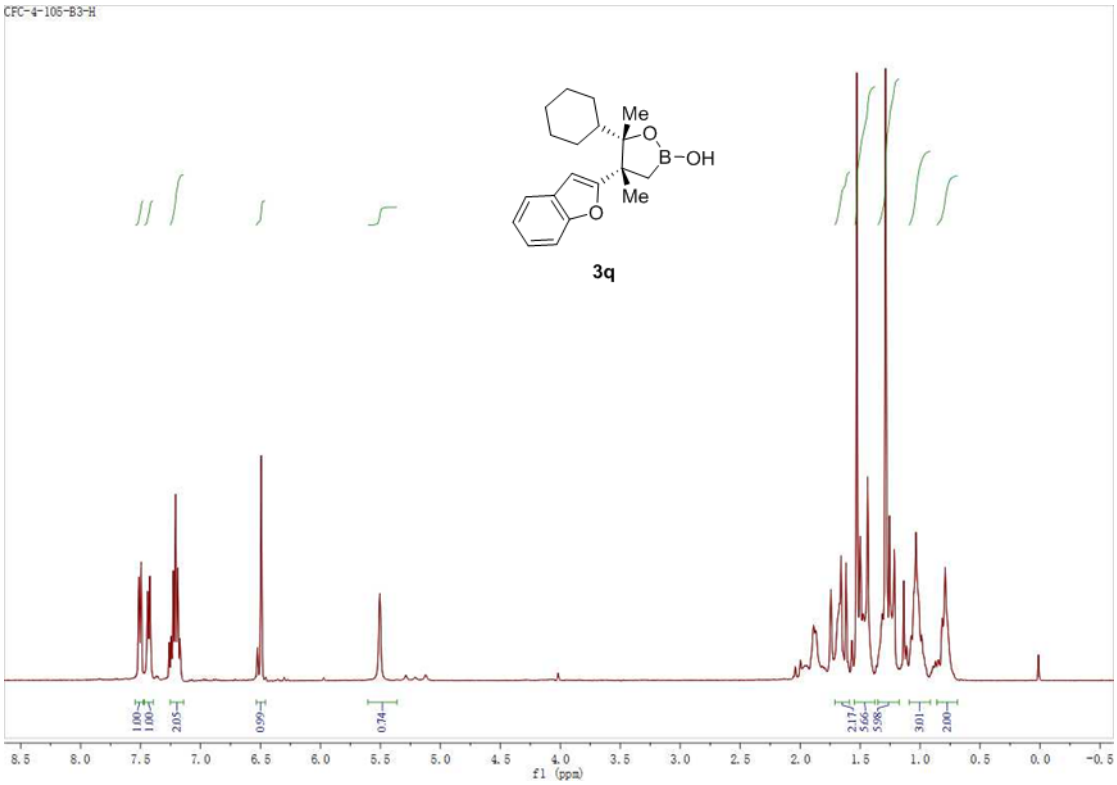

CFC-5-42-B2-C
159.25
154.15
151.19
130.60
130.16
127.91
123.98
123.97
123.77
123.37
122.79
120.83
120.80
111.88
111.08
105.44
79.36
77.32
77.00
76.68
67.73
49.12
27.55
18.06
Me
OH
OH
Me
S
O
3o-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

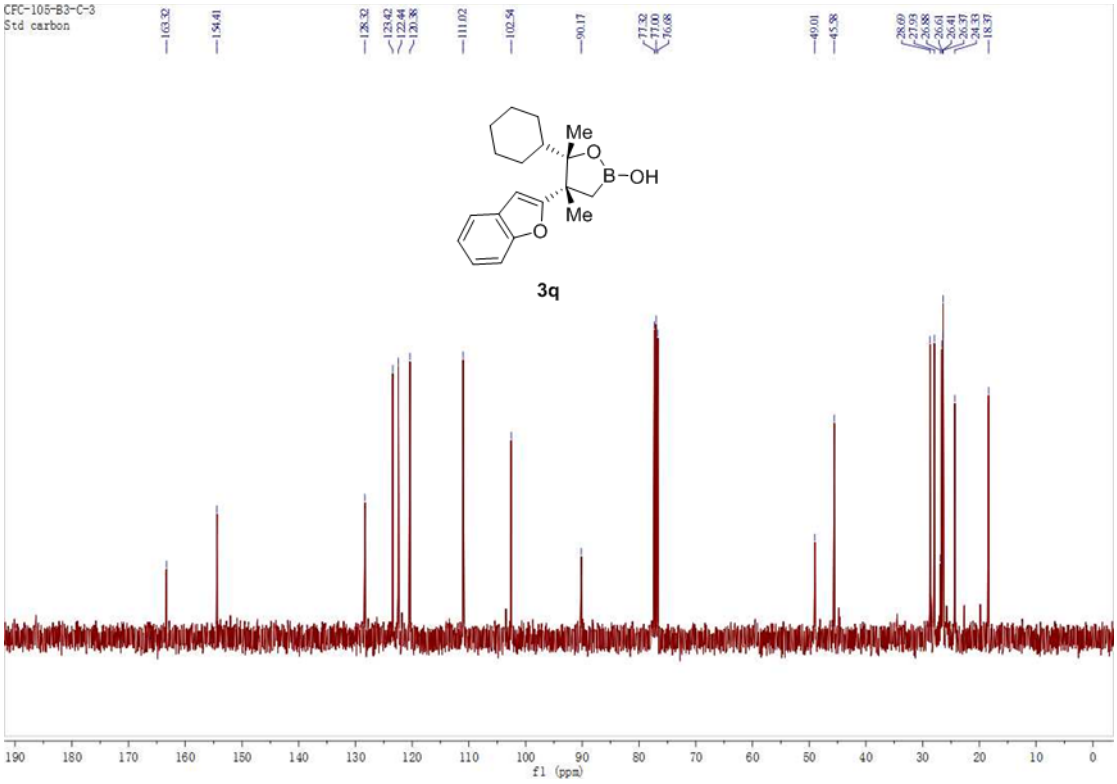

lwx-1-36-major-H-A400-0711
B–OH
Me
O
O
3p
f1 (ppm)

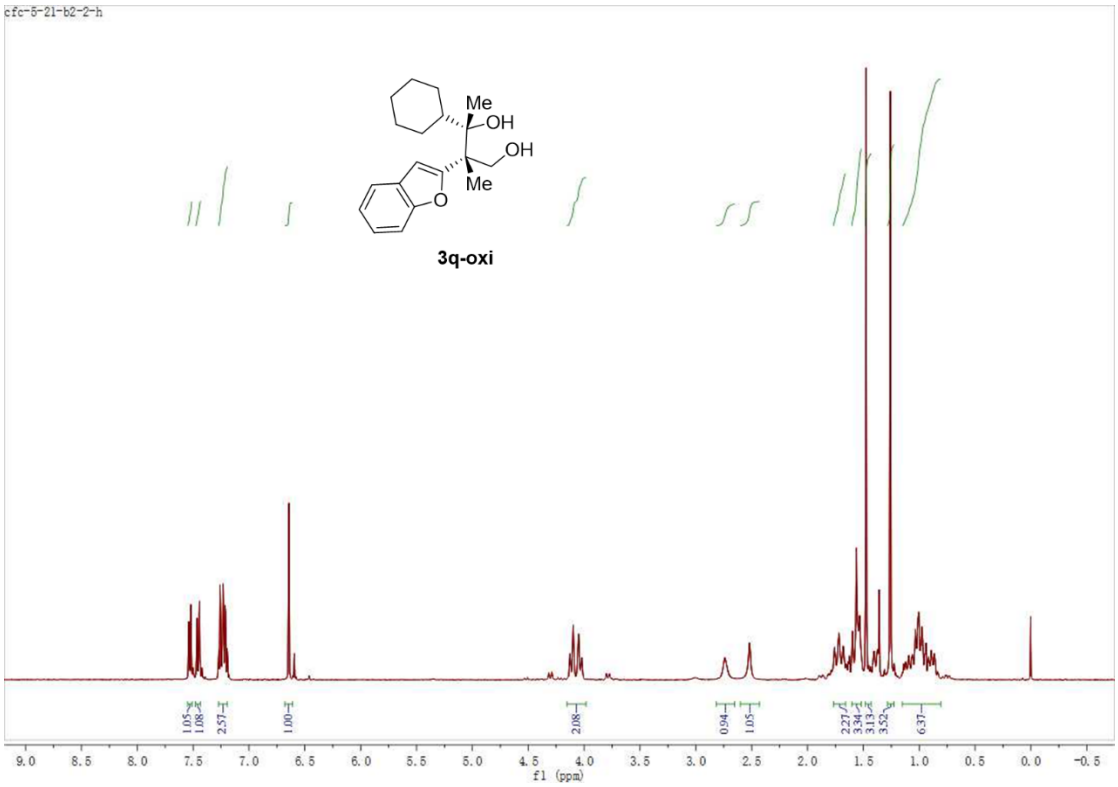

lwx-1-36-major-C-A400-0711
lxj-2-54-C-H
B–OH
Me
O
O
3p
f1 (ppm)

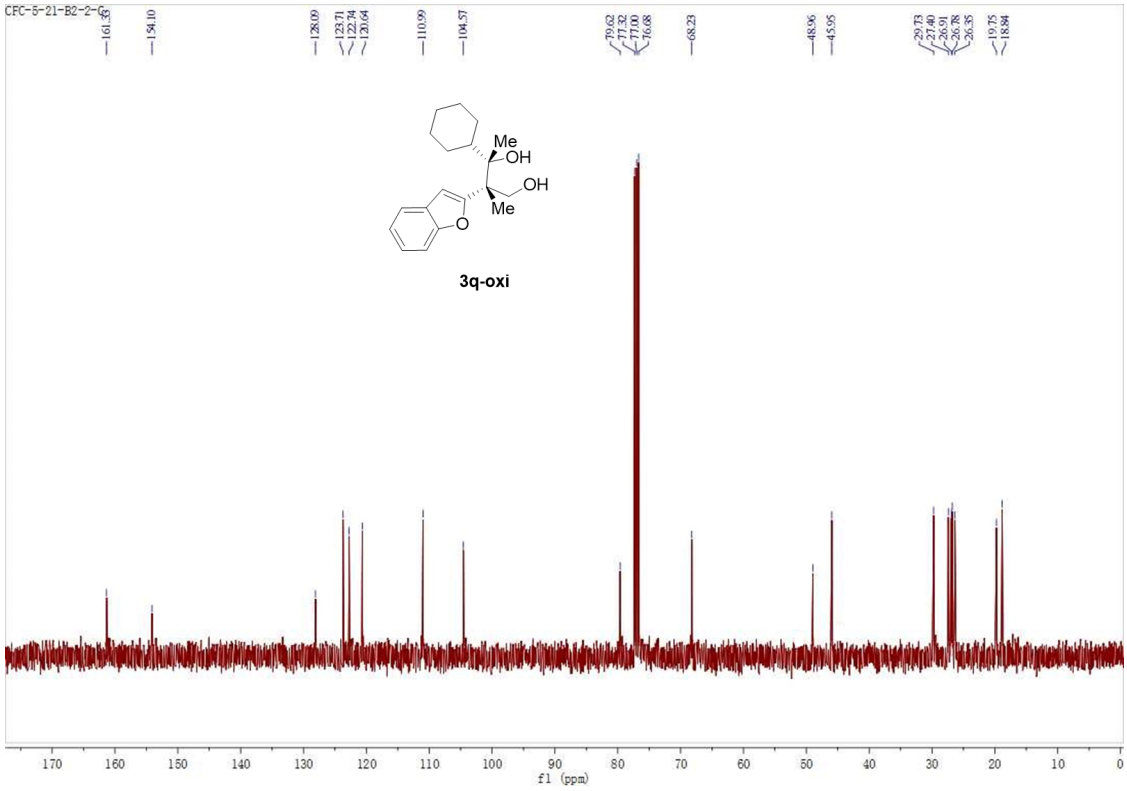

LWX-1-47-A1-H
OH
OH
Me
O
3p-oxi
f1 (ppm)

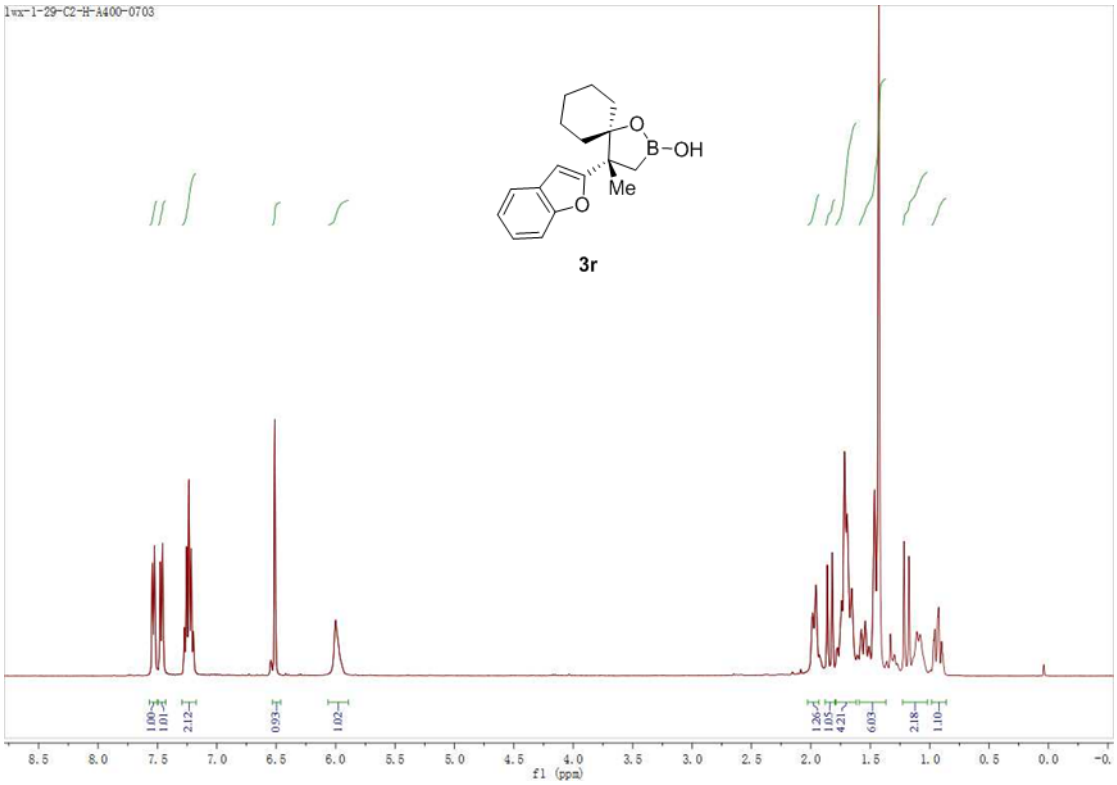

lwx-1-47-A1-C-A400g0717
xcc
OH
OH
Me
O
3p-oxi
f1 (ppm)

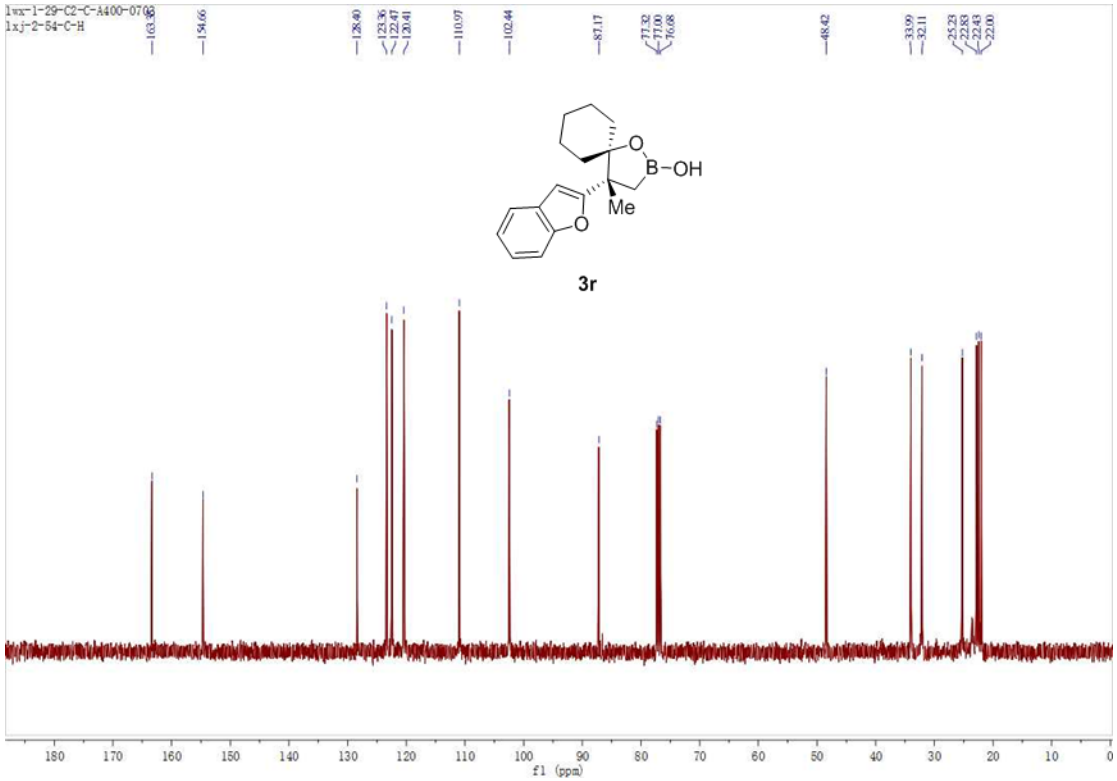

CFC-4-105-B3-H
Me
O
B–OH
Me
O
3q
f1 (ppm)

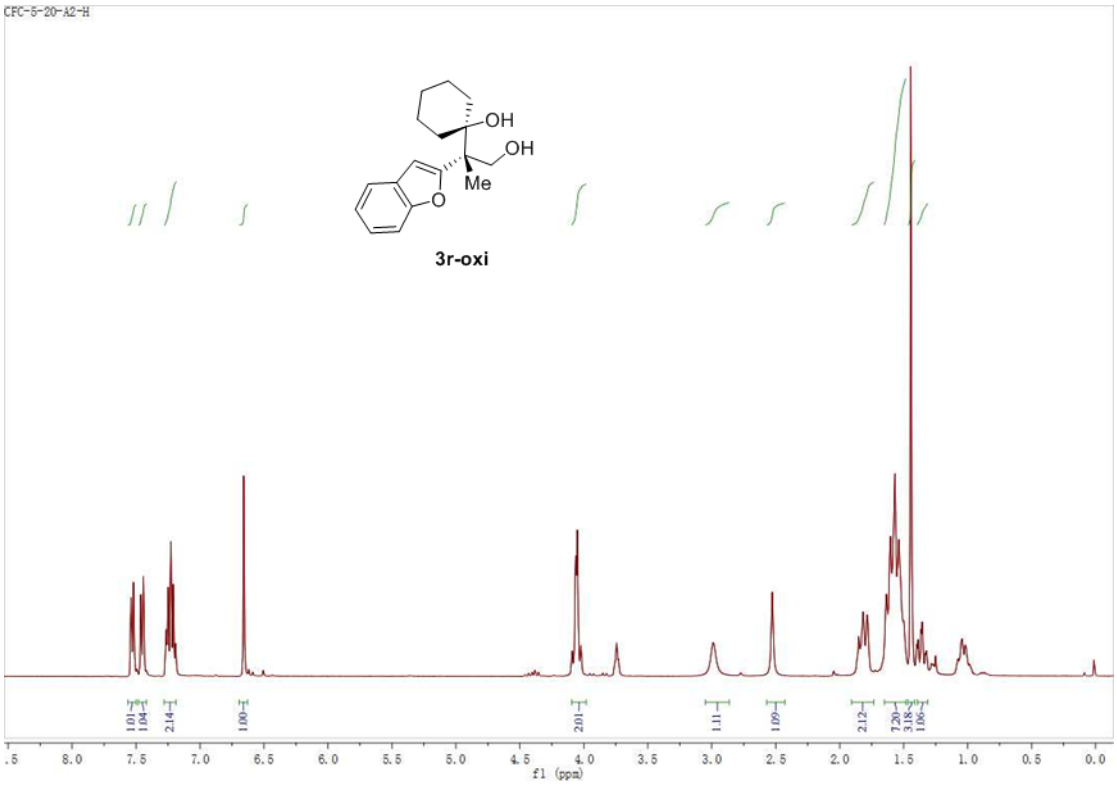

CFC-105-B3-C-3
Std carbon
Me
O
B–OH
Me
O
3q
f1 (ppm)

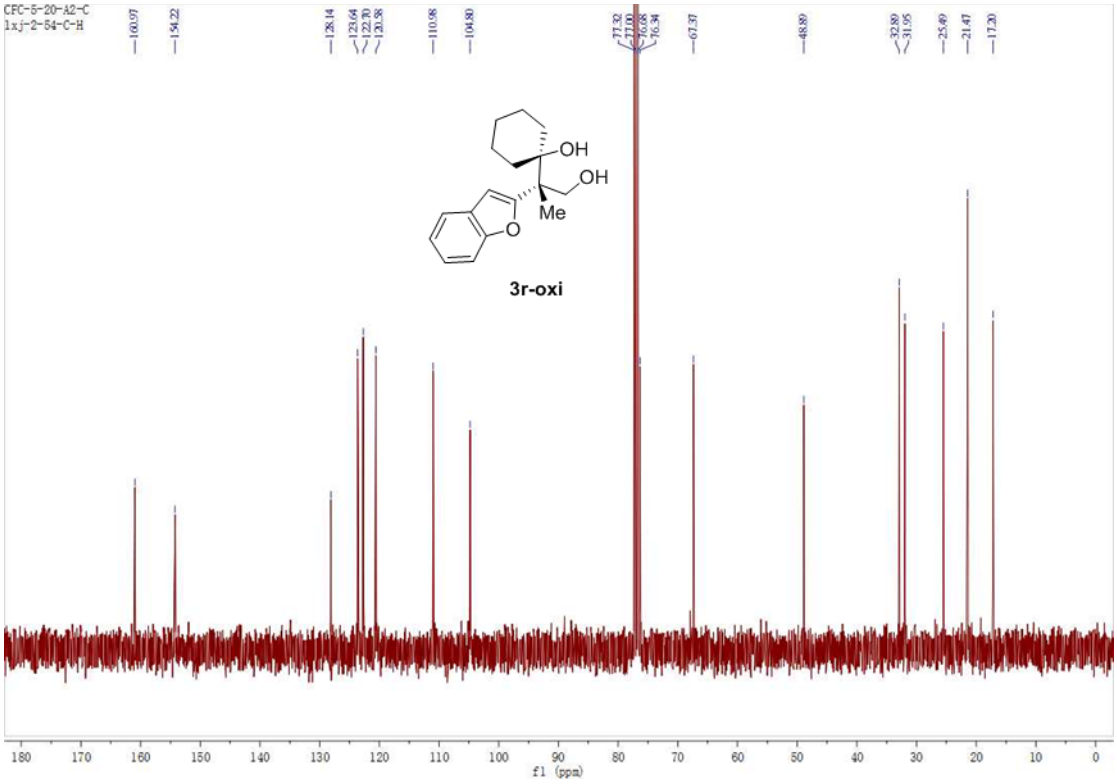

cfc-5-21-b2-2-h
Me
OH
OH
Me
O
3q-oxi
1.05
1.08
2.57
1.00
2.08
0.94
1.05
2.27
3.34
3.13
3.52
6.37
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

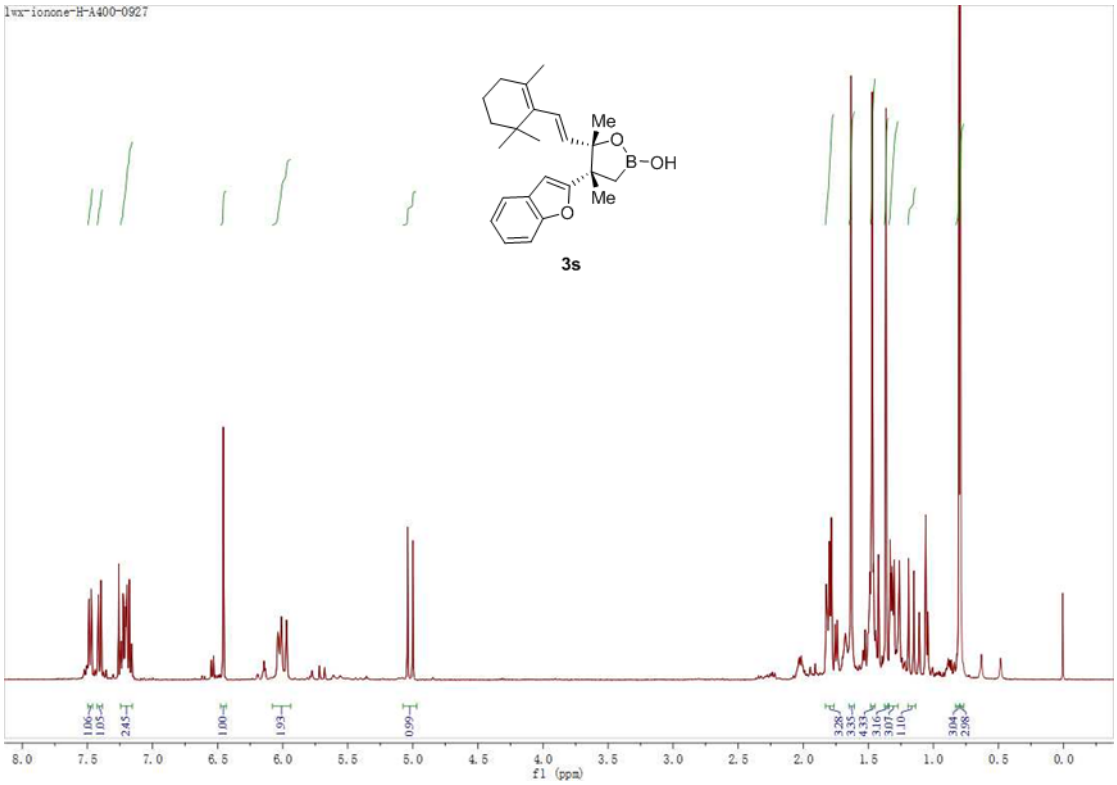

CFC-5-21-B2-2-C
161.55
154.10
128.09
123.71
122.34
120.64
110.99
104.57
79.62
77.32
77.00
76.68
68.23
48.06
45.95
29.73
27.40
26.91
26.78
26.35
19.75
18.84
Me
OH
OH
Me
O
3q-oxi
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

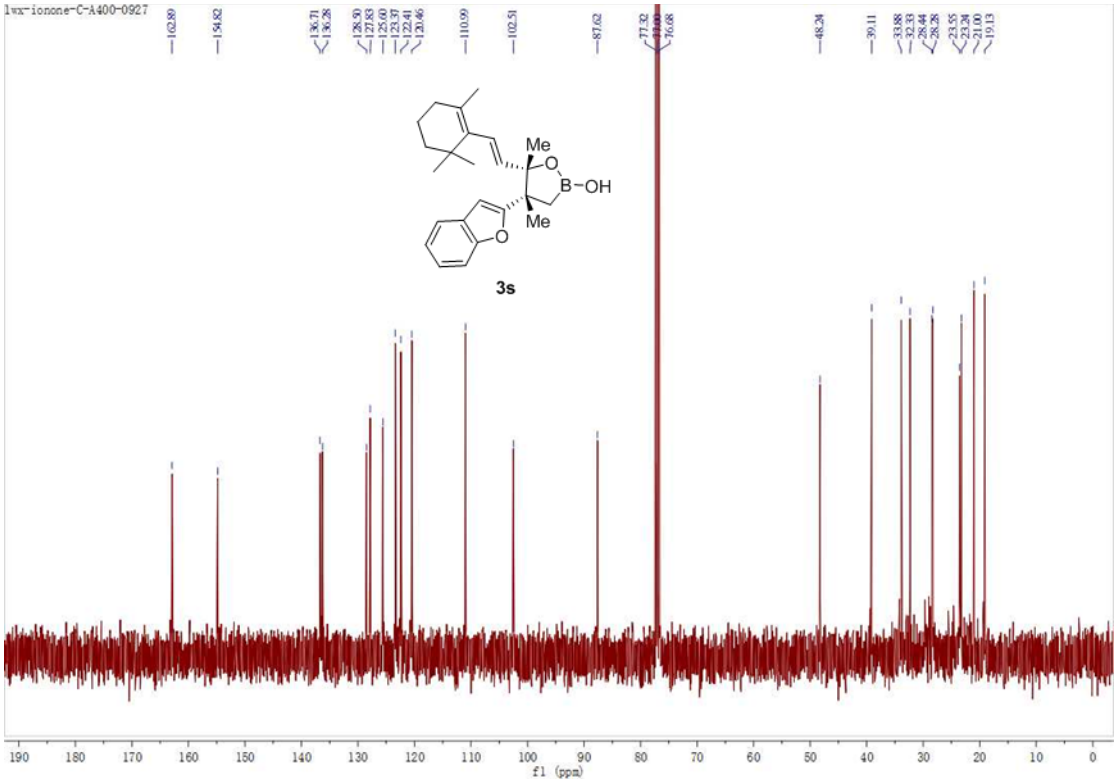

lwx-1-29-C2-H-A400-0703
B–OH
Me
O
O
3r
f1 (ppm)

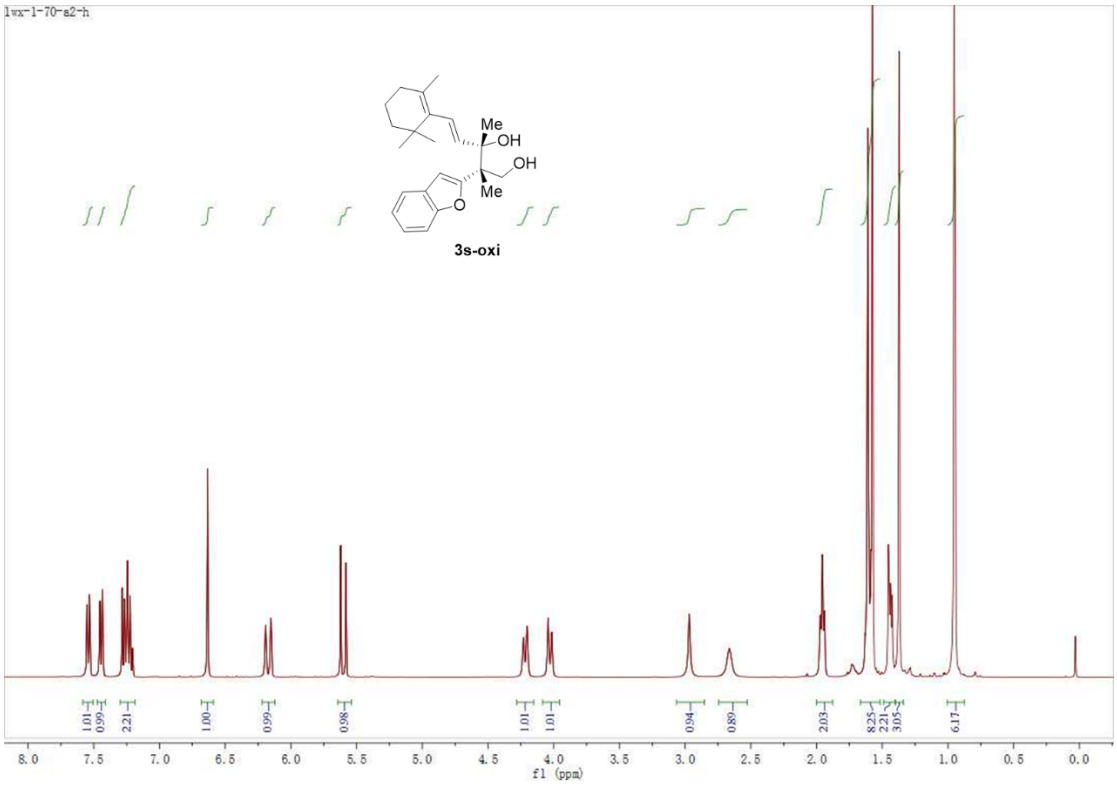

lwx-1-29-C2-C-A400-0703
lxj-2-54-C-H
B–OH
Me
O
O
3r
f1 (ppm)

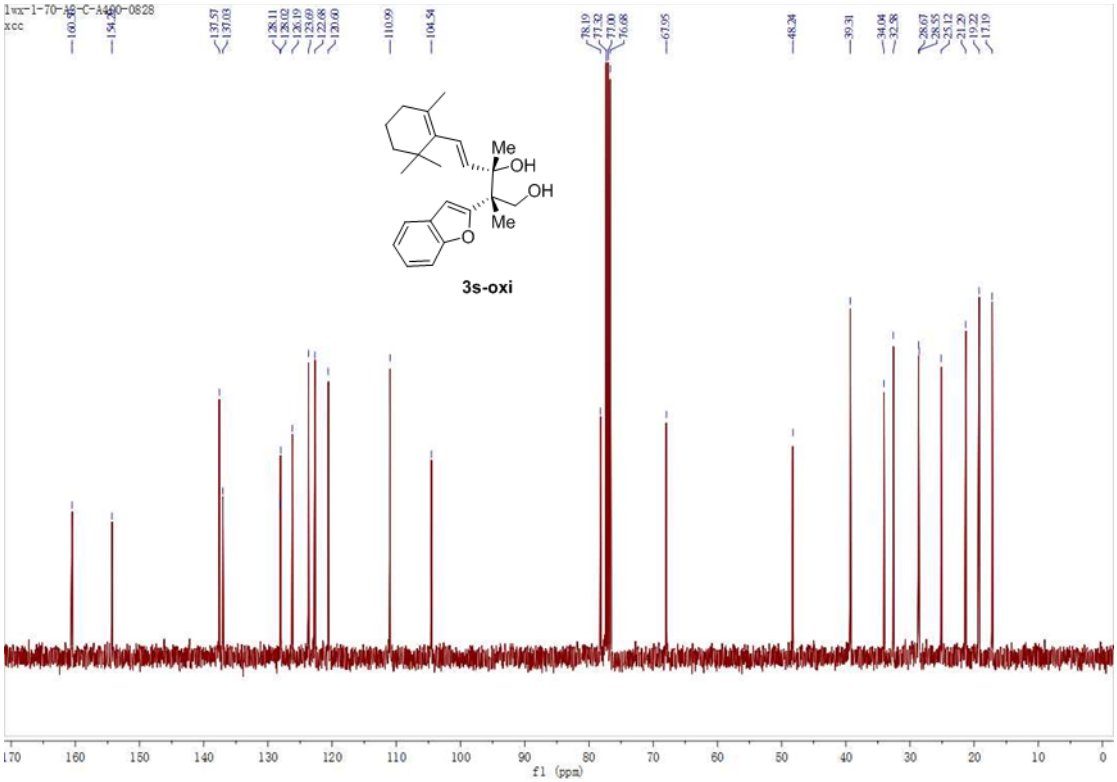

CFC-5-20-A2-H
OH
OH
Me
O
3r-oxi
f1 (ppm)

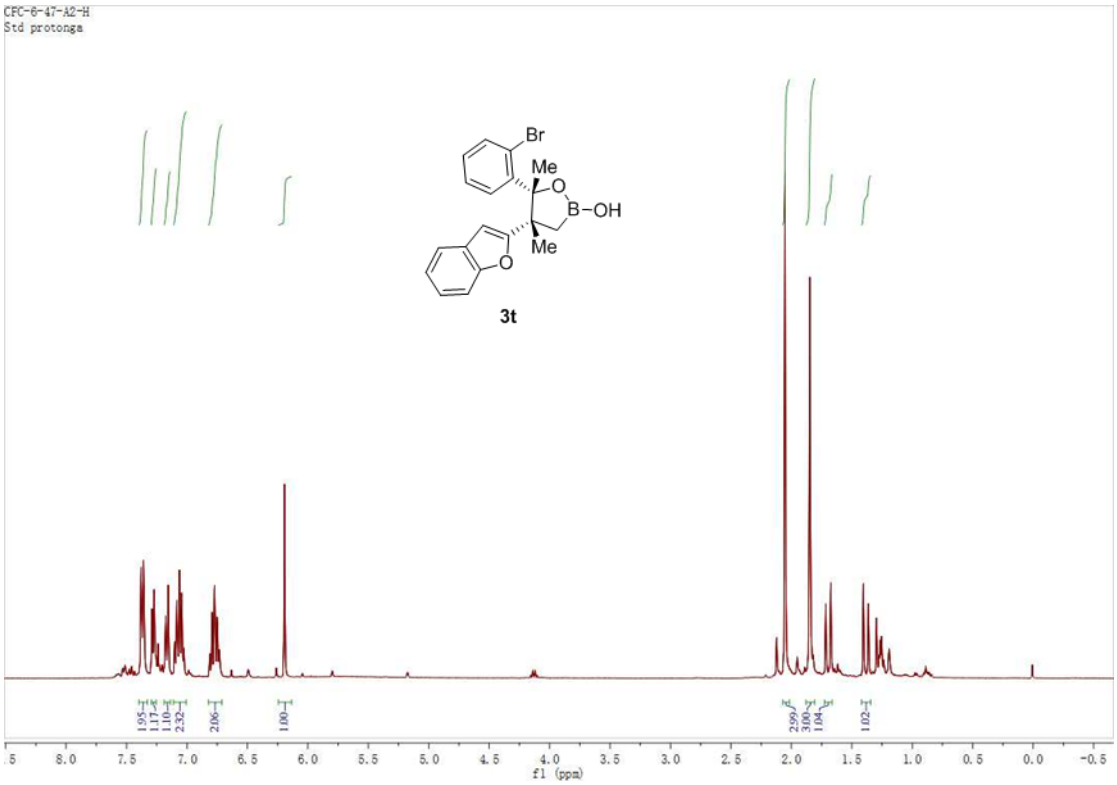

CFC-5-20-A2-C
lxj-2-54-C-H
160.97
154.22
128.14
123.64
122.80
120.58
110.98
104.80
77.32
77.00
76.68
76.34
67.37
48.89
32.89
31.95
25.49
21.47
17.20
OH
OH
Me
O
3r-oxi
f1 (ppm)

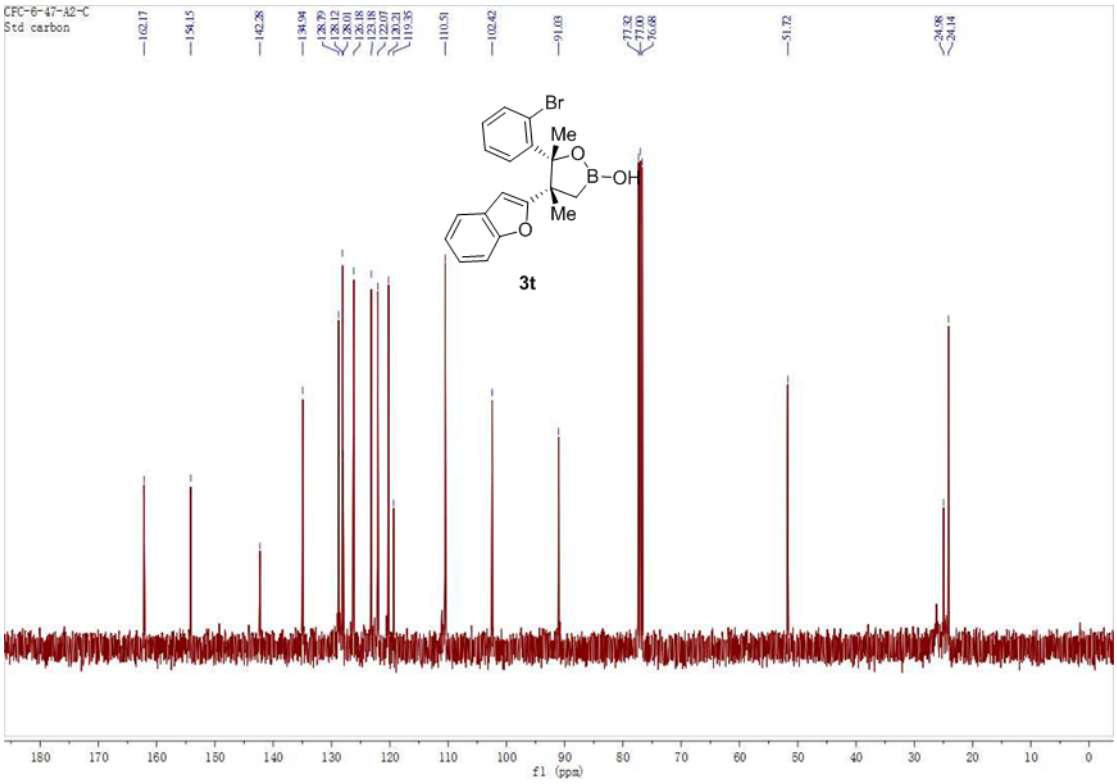

lwx-ionone-H-A400-0927
Me
O
B–OH
Me
O
3s
f1 (ppm)

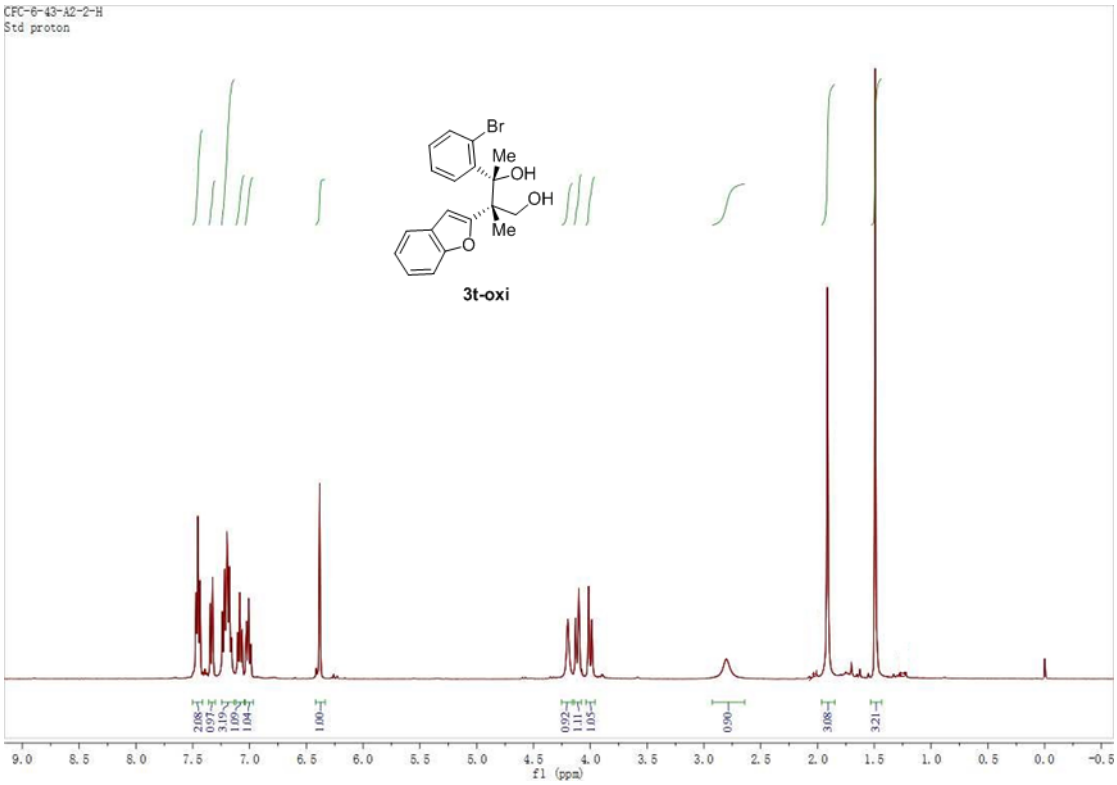

lwx-ionone-C-A400-0927
Me
O
B–OH
Me
O
3s
f1 (ppm)

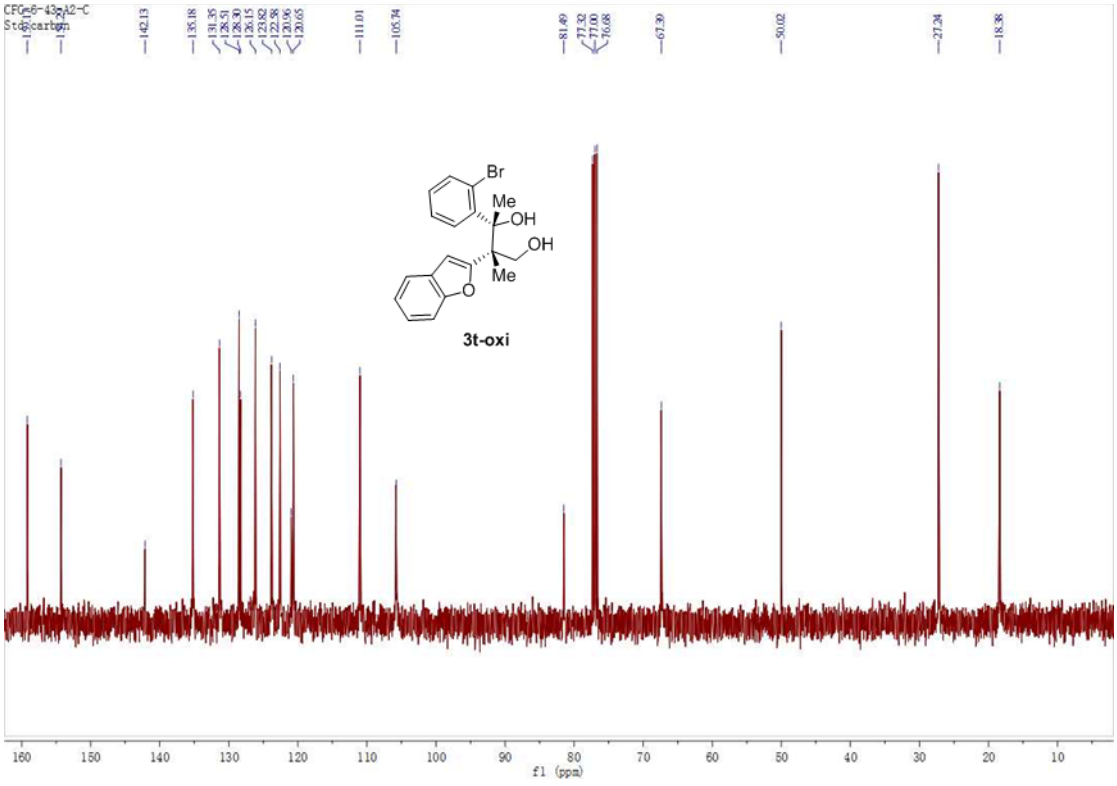

lwx-1-70-a2-h
Me
OH
OH
Me
O
3s-oxi
1.01
0.99
2.21
1.00
0.99
0.98
1.01
1.01
0.94
0.89
2.03
8.25
2.21
3.05
6.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

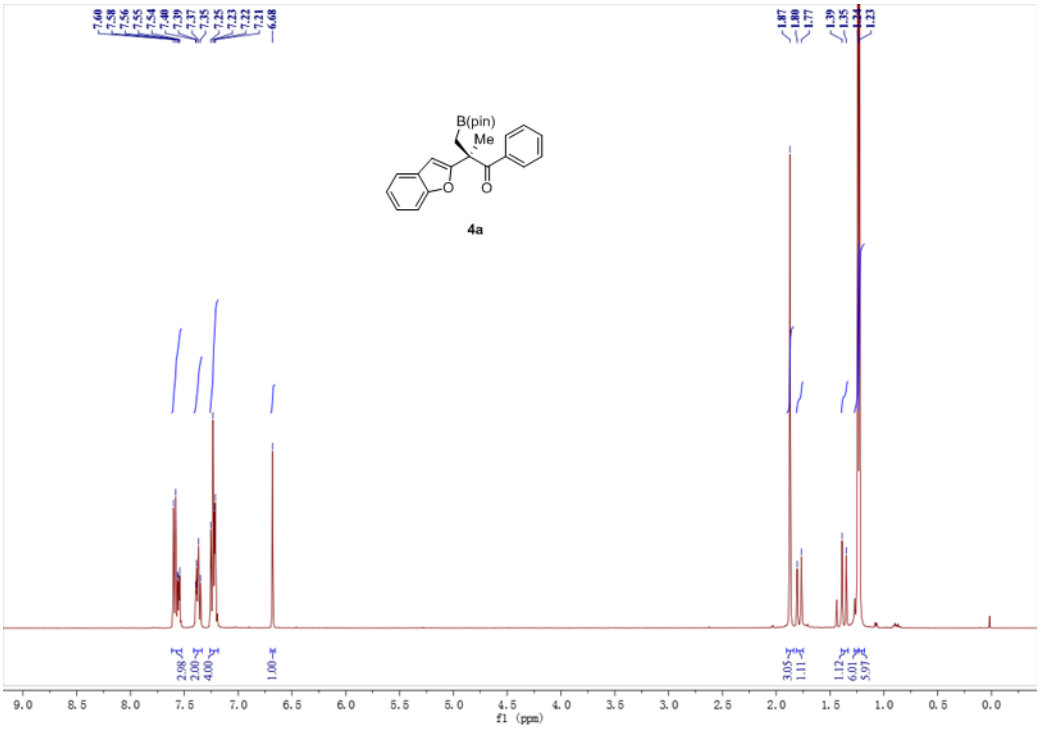

lwx-1-70-A2-C-A400-0828
xcc
160.50
154.25
137.57
137.03
128.11
128.02
126.19
123.69
122.68
120.60
110.99
104.54
78.19
77.32
77.00
76.68
67.95
48.24
39.31
34.04
32.58
28.67
28.55
25.12
21.29
19.22
17.19
Me
OH
OH
Me
O
3s-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

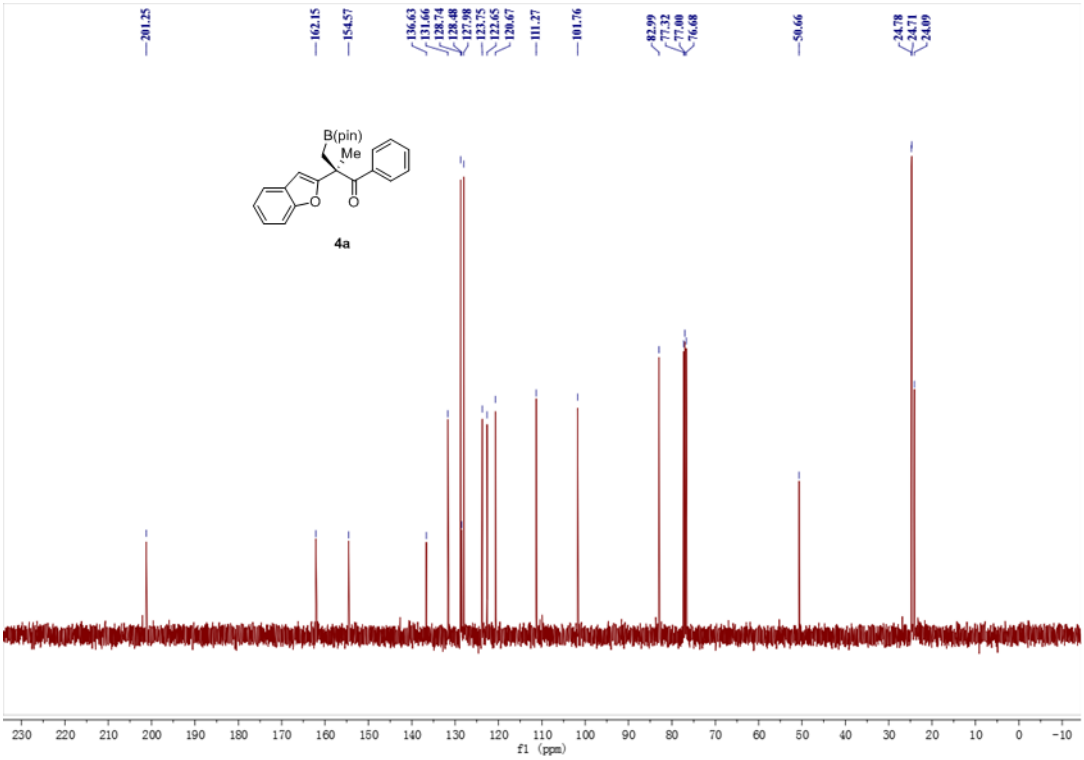

CFC-6-47-A2-H
Std protonga
Br
Me
O
B–OH
Me
O
3t
1.95
1.17
1.10
2.52
2.06
1.00
2.99
3.00
1.04
1.02
f1 (ppm)

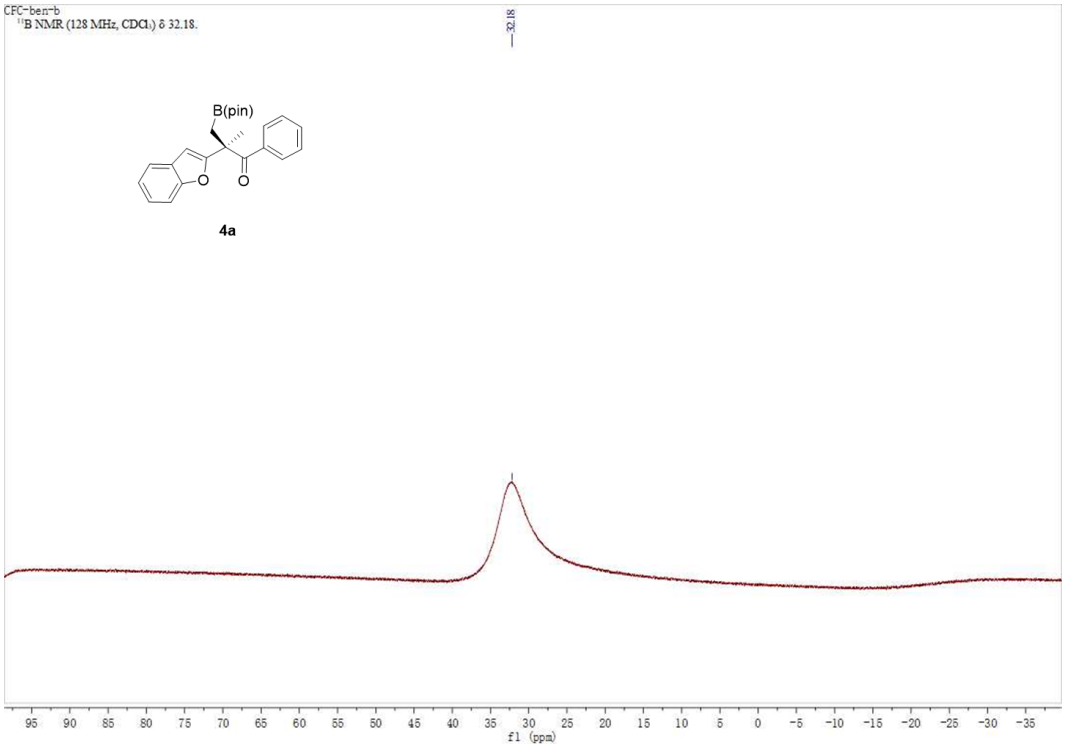

CFC-6-47-A2-C
Std carbon
162.17
154.15
142.28
134.94
128.79
128.12
126.01
125.18
123.38
122.07
120.21
119.35
110.51
102.42
91.03
77.32
77.00
76.68
51.72
24.58
24.14
Br
Me
O
B–OH
Me
O
3t
f1 (ppm)

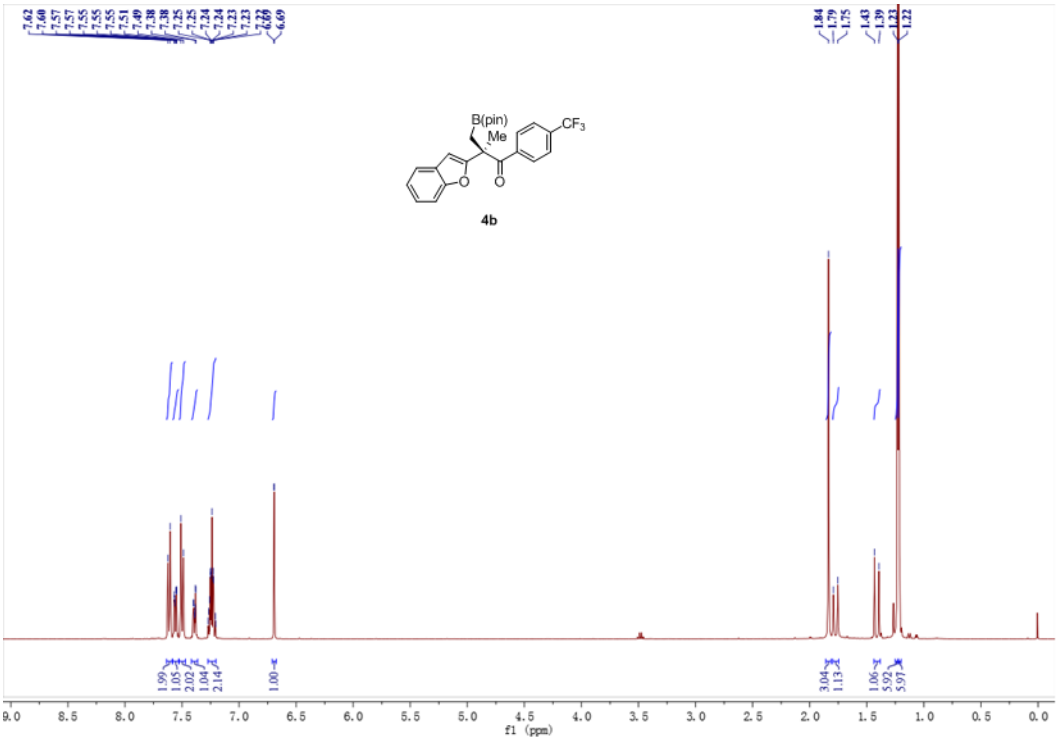

CFC-6-43-A2-2-H
Std proton
Br
Me
OH
OH
Me
O
3t-oxi
2.08
0.97
3.19
1.09
1.04
1.00
0.92
1.11
1.05
0.90
3.08
3.21
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

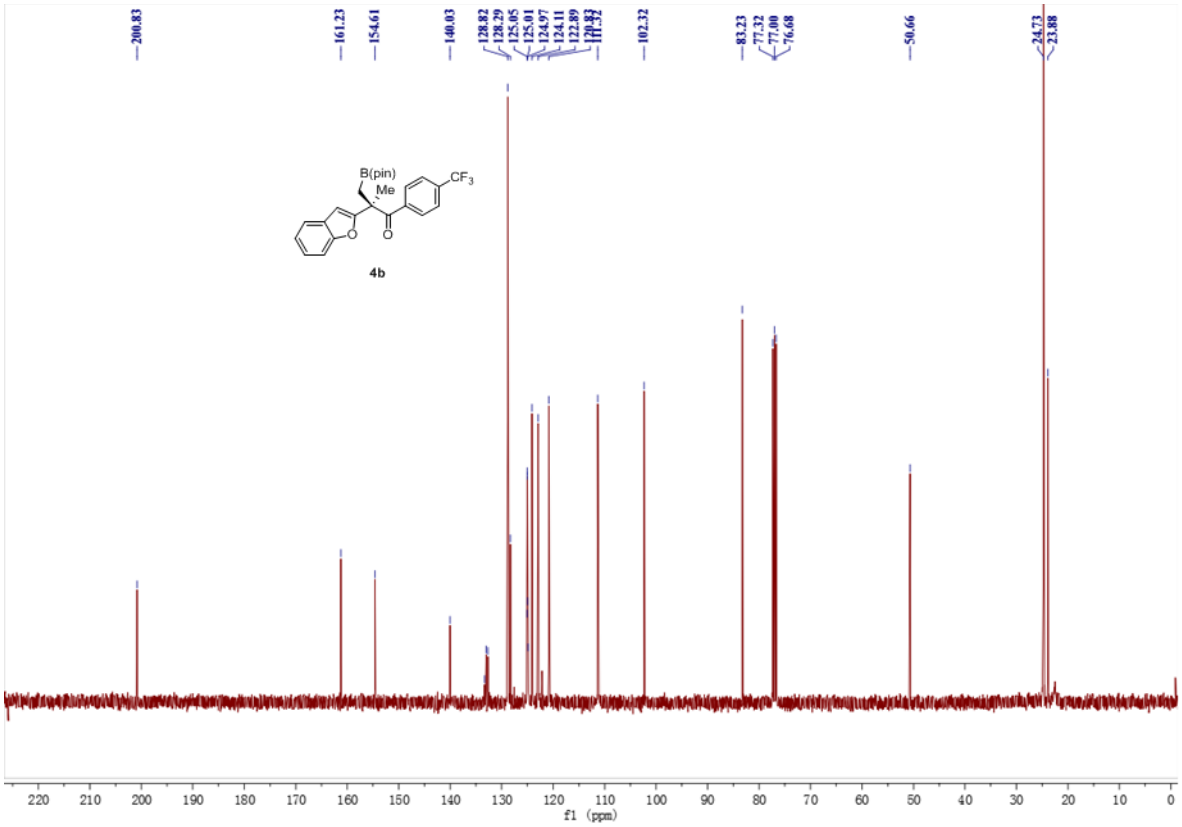

CFC-6-43-A2-C
Std carbon
142.13
135.18
131.35
128.51
126.30
126.15
123.82
121.98
120.96
120.65
111.01
105.74
81.49
77.32
77.00
76.68
67.39
50.02
27.24
18.38
Br
Me
OH
OH
Me
O
3t-oxi
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

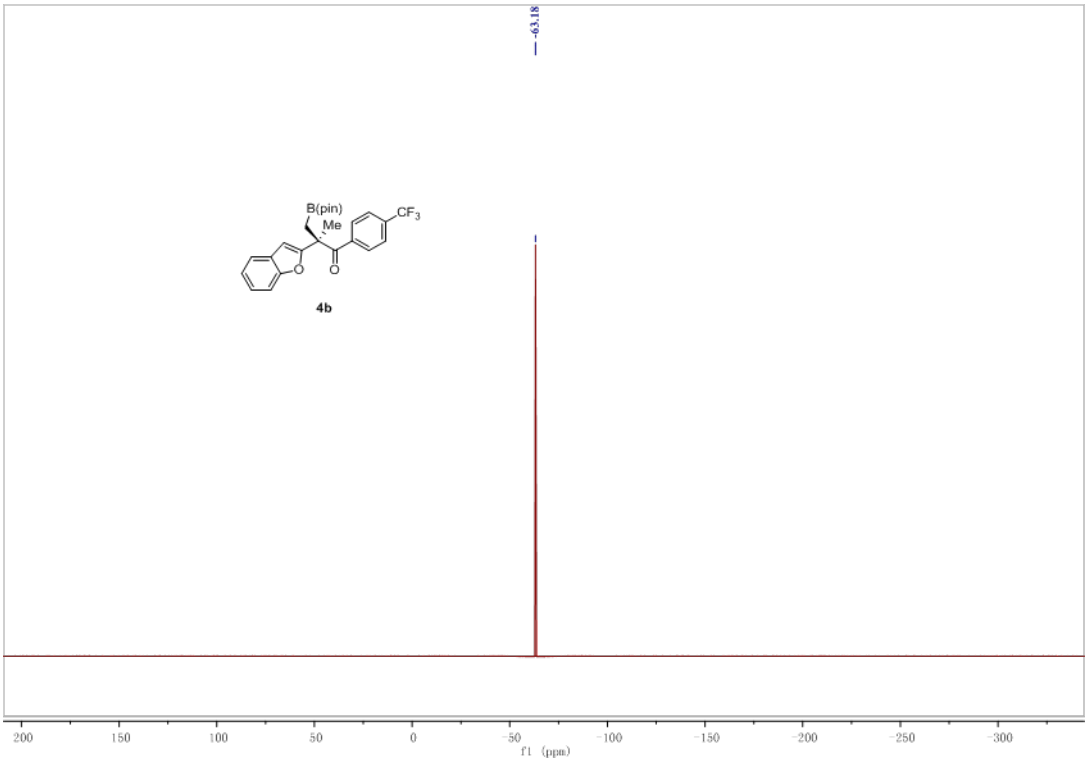

B(pin)
Me
O
O
4a
f1 (ppm)

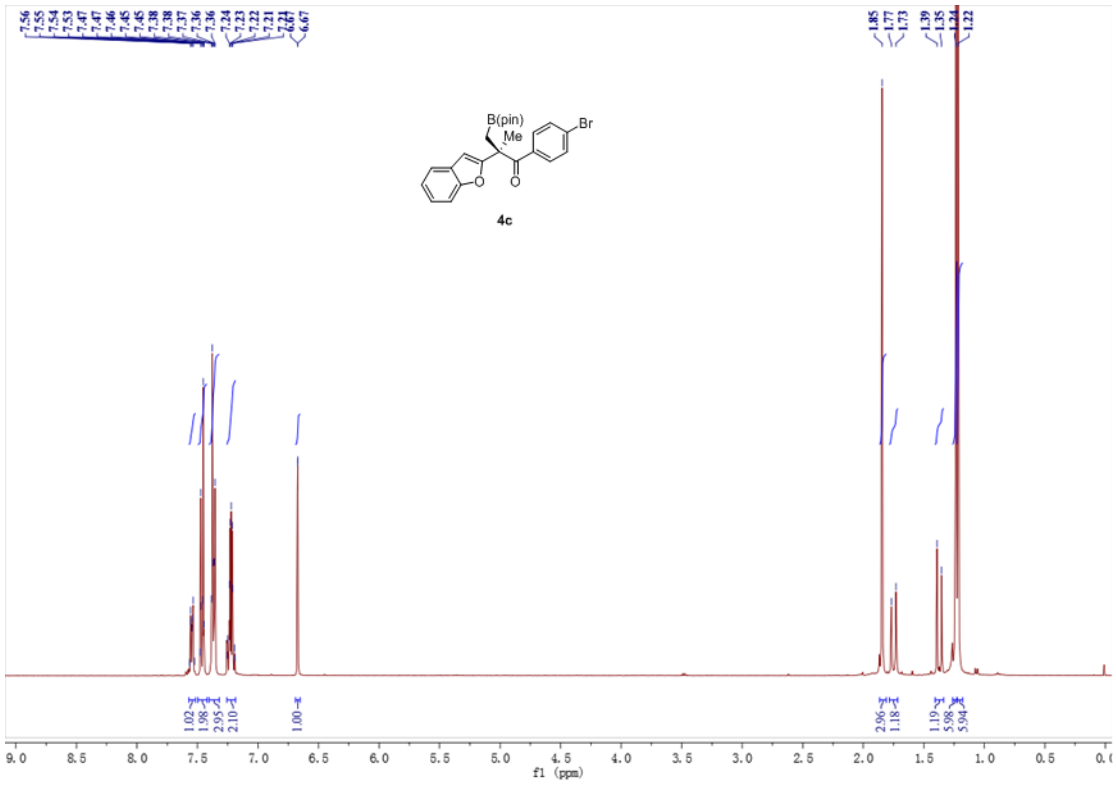

B(pin)
Me
O
O
4a
f1 (ppm)

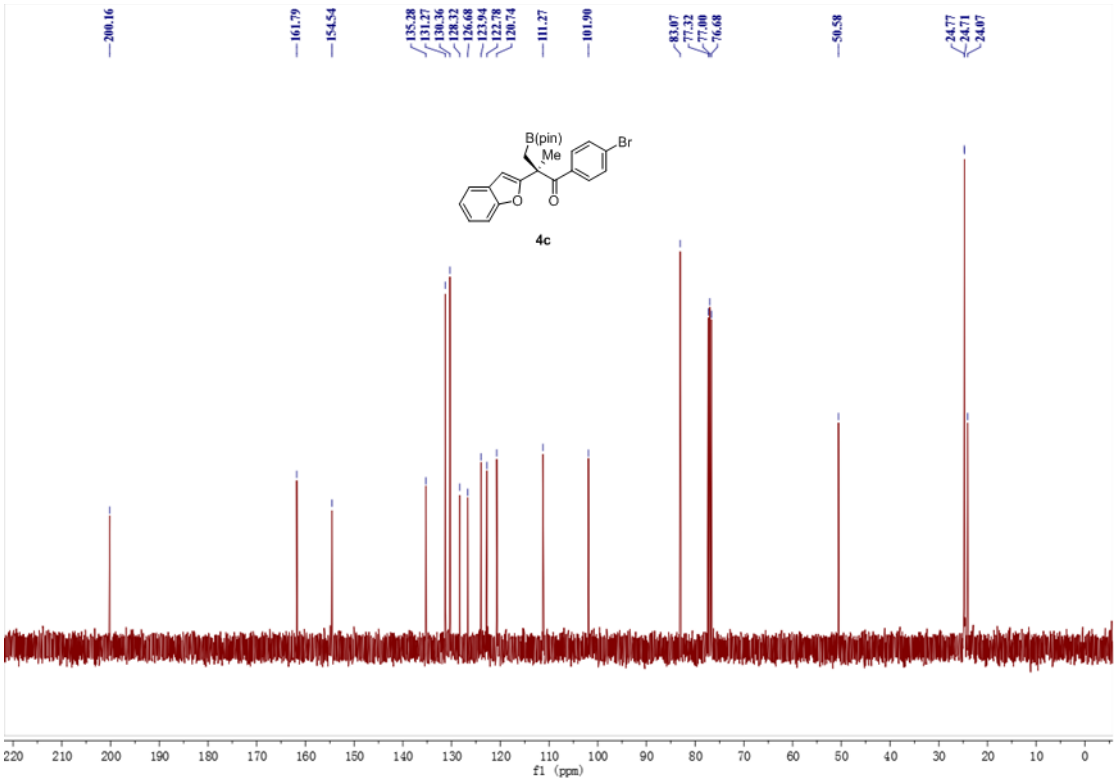

CFC-ben-b
^{11}B NMR (128 MHz, CDCl$_3$) δ 32.18.
32.18
B(pin)
O
O
4a
f1 (ppm)

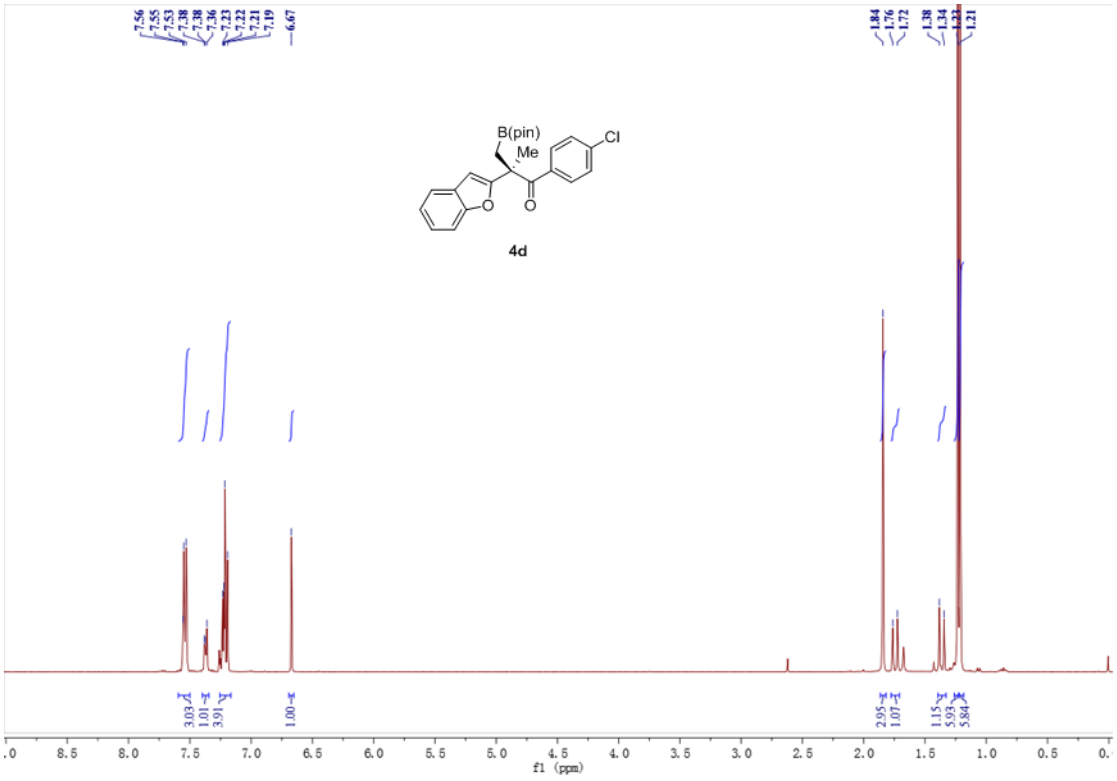

7.62
7.60
7.57
7.57
7.55
7.55
7.51
7.49
7.38
7.25
7.24
7.24
7.23
6.69
1.84
1.79
1.75
1.43
1.39
1.22
B(pin)
Me
CF$_3$
O
O
4b
1.99
1.05
2.02
1.04
2.14
1.00
3.04
1.13
1.06
5.92
5.97
f1 (ppm)

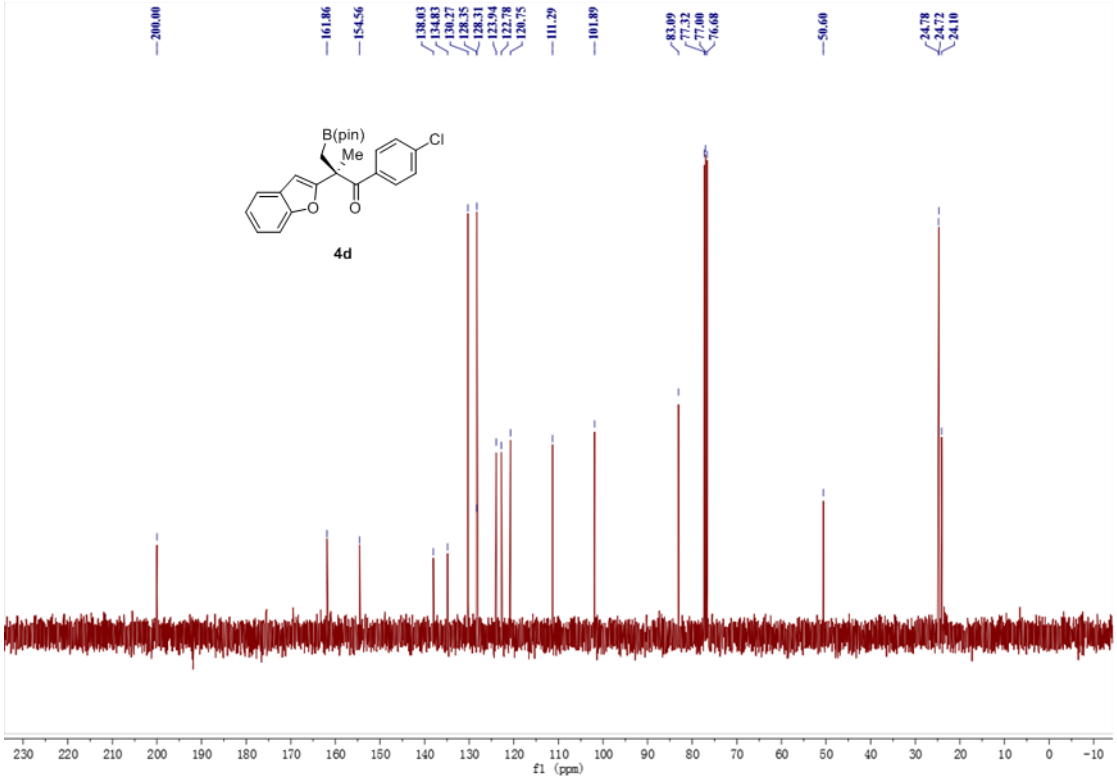

200.83
161.23
154.61
140.03
128.82
128.29
125.05
125.01
124.97
124.11
122.89
111.42
102.32
83.23
77.32
77.00
76.68
50.66
24.73
23.88
B(pin)
Me
CF3
O
O
4b
f1 (ppm)

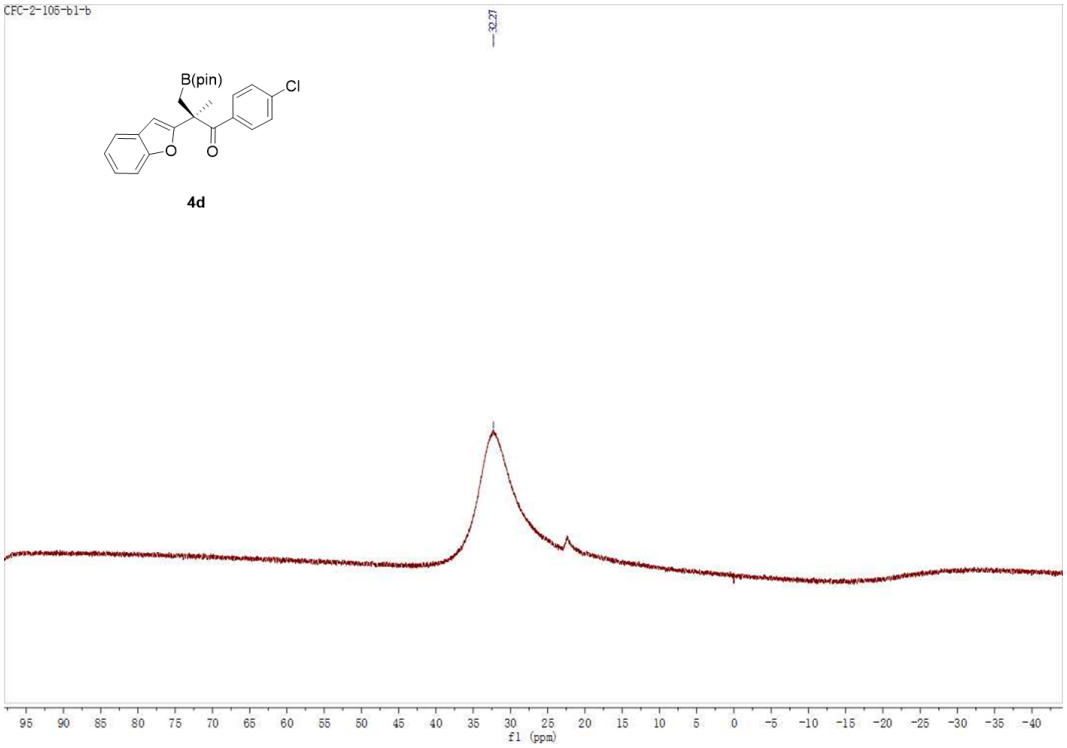

-63.18
B(pin)
Me
CF3
O
O
4b
f1 (ppm)

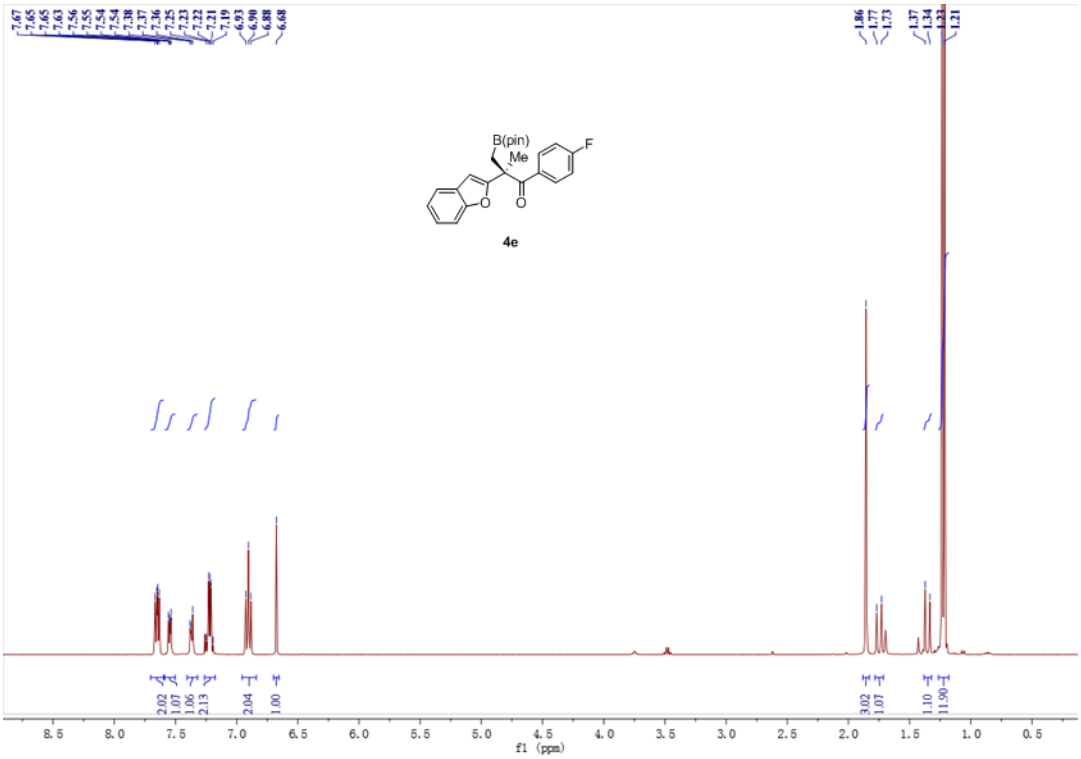

B(pin)
Me
Br
O
O
4c
f1 (ppm)

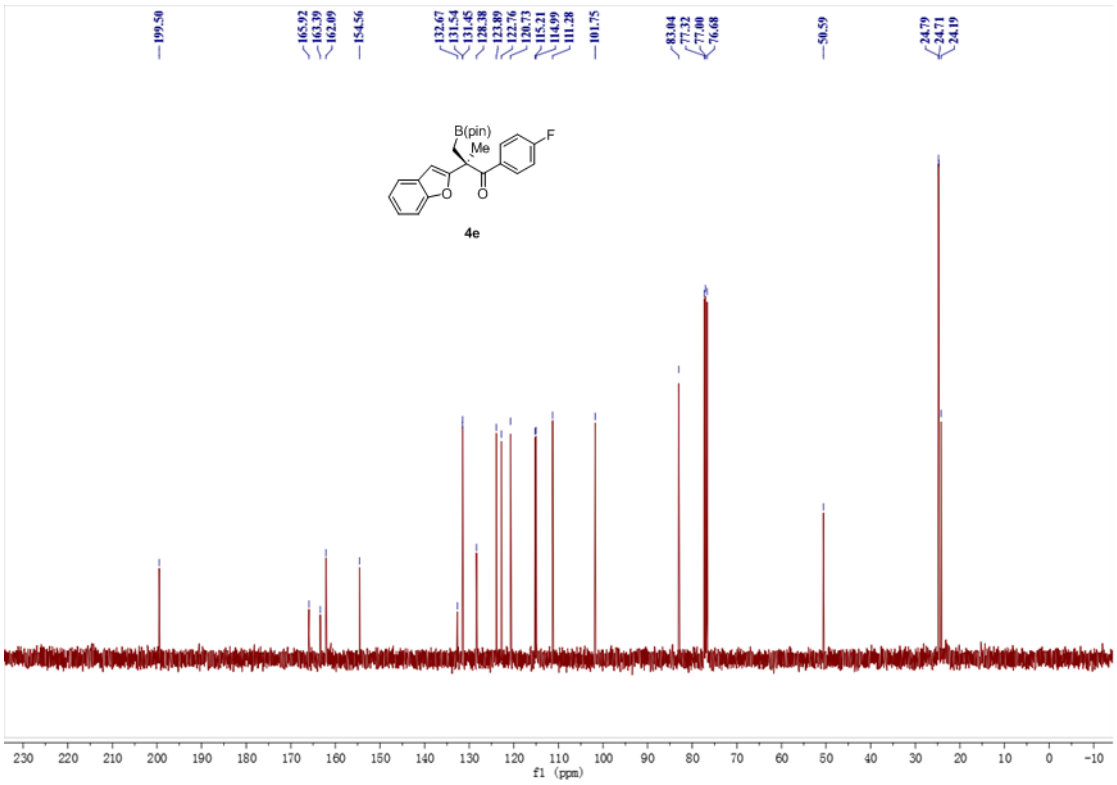

B(pin)
Me
Br
O
O
4c
f1 (ppm)

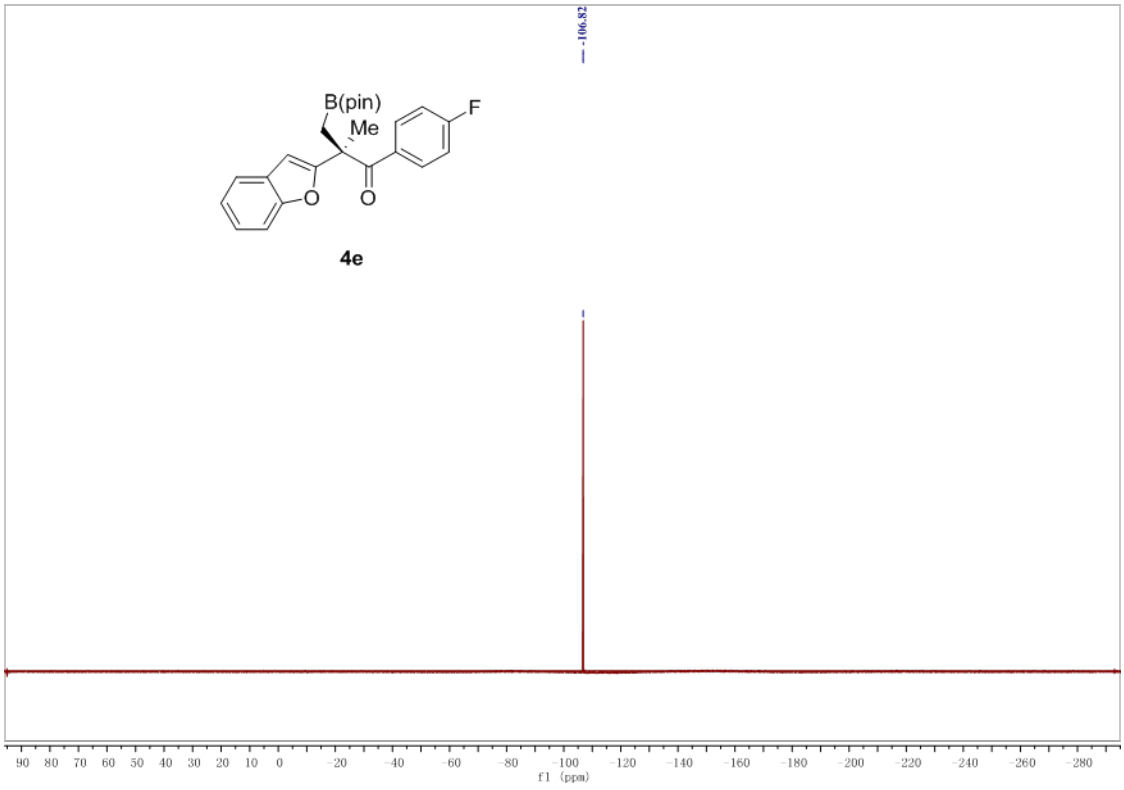

7.56
7.55
7.53
7.38
7.38
7.36
7.23
7.22
7.21
7.19
6.67
1.84
1.76
1.72
1.38
1.34
1.21
B(pin)
Me
Cl
O
O
4d
3.03
1.01
3.91
1.00
2.95
1.07
1.15
5.93
5.84
f1 (ppm)

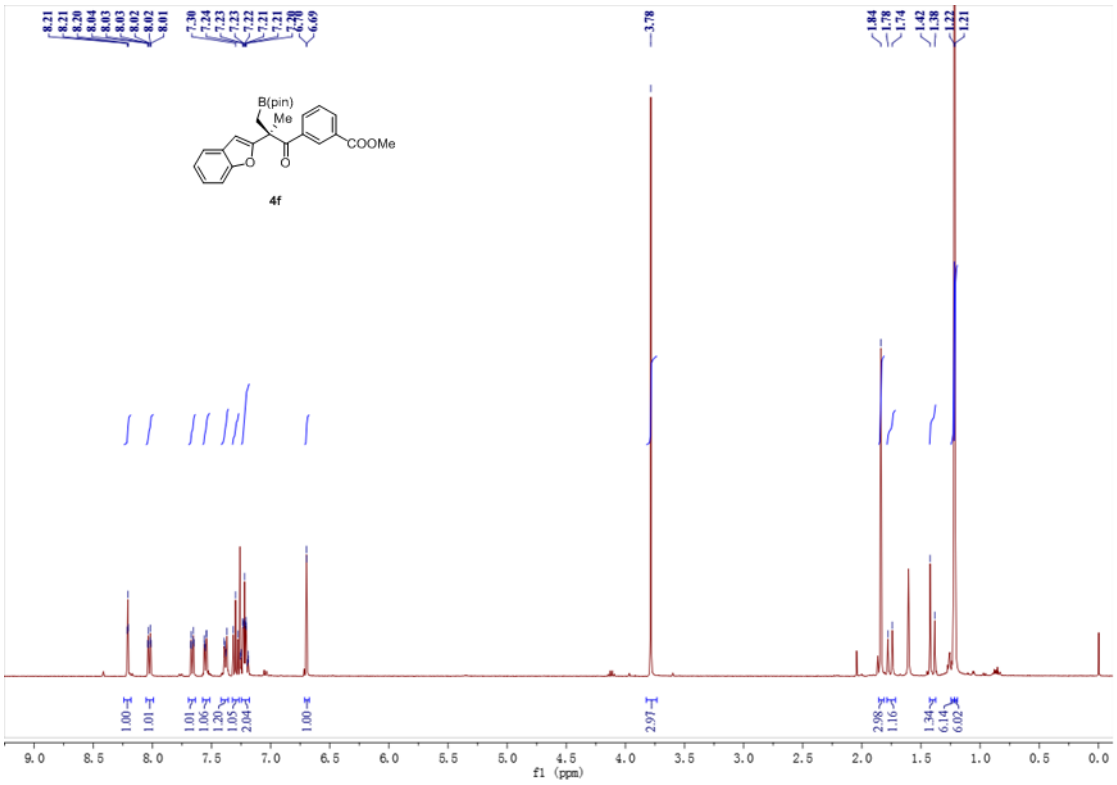

200.00
161.86
154.56
138.03
134.83
130.27
128.35
128.31
123.94
122.78
120.75
111.29
101.89
83.09
77.32
77.00
76.68
50.60
24.78
24.72
24.10
B(pin)
Me
Cl
O
O
4d
f1 (ppm)

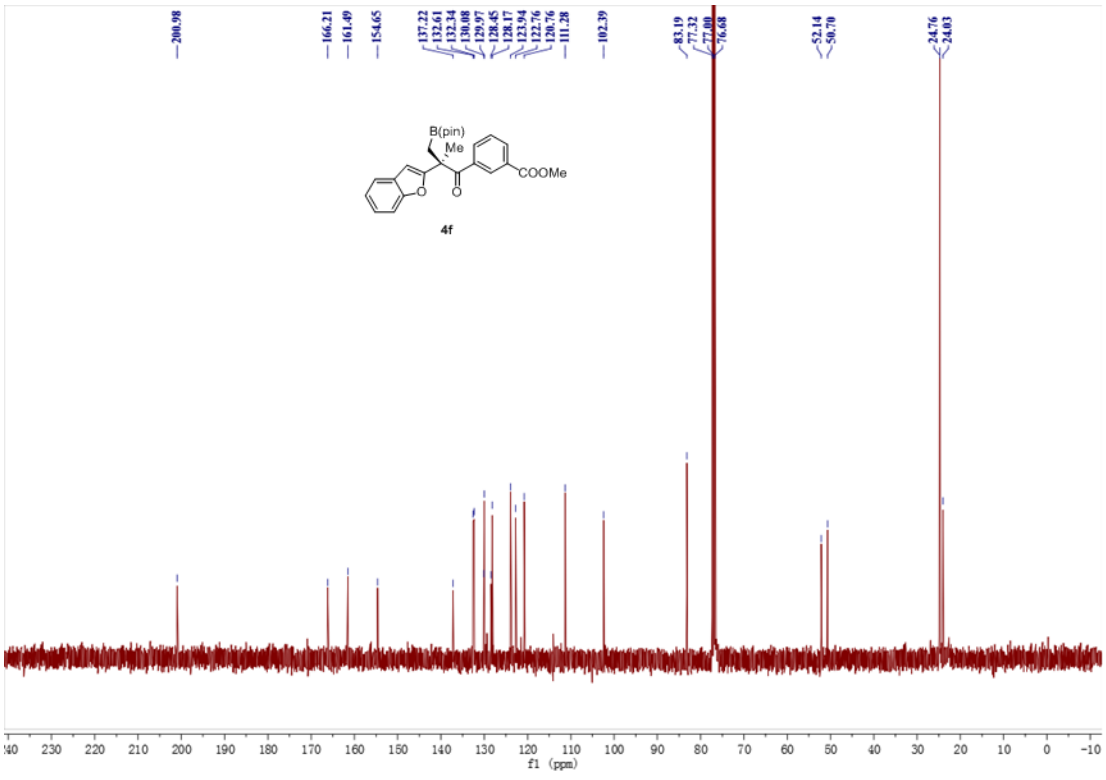

CFC-2-105-b1-b
32.27
B(pin)
Cl
O
O
4d
f1 (ppm)

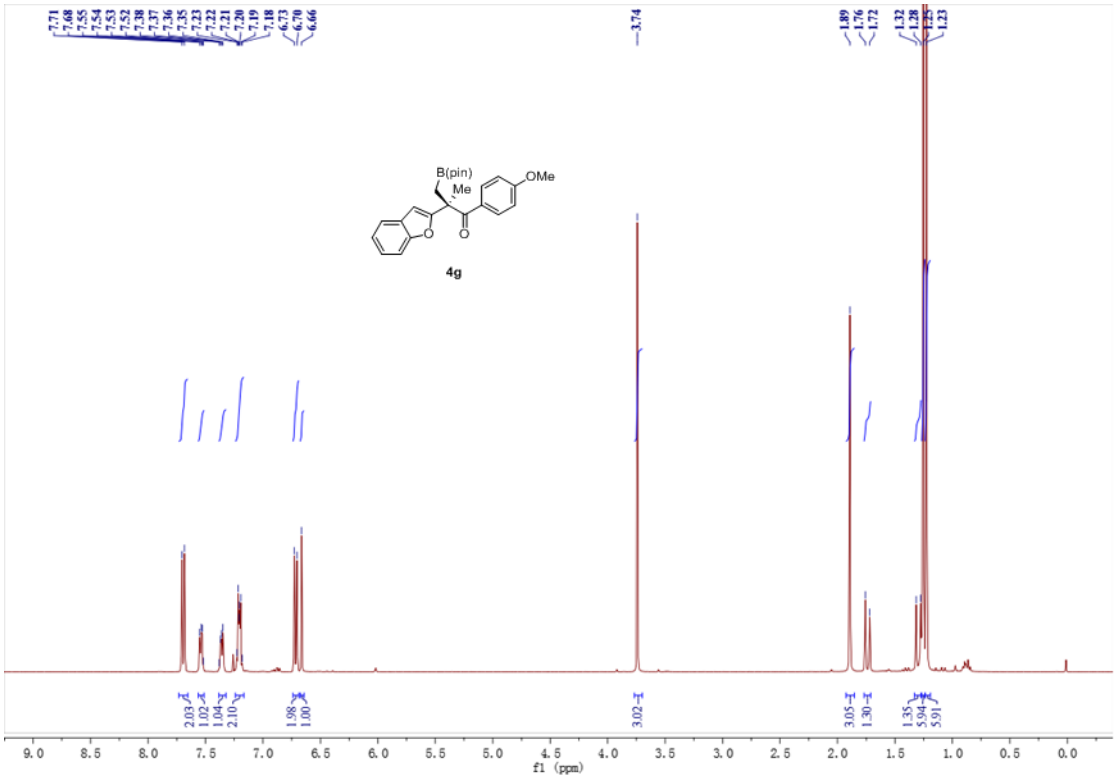

B(pin)
Me
F
O
O
4e
f1 (ppm)

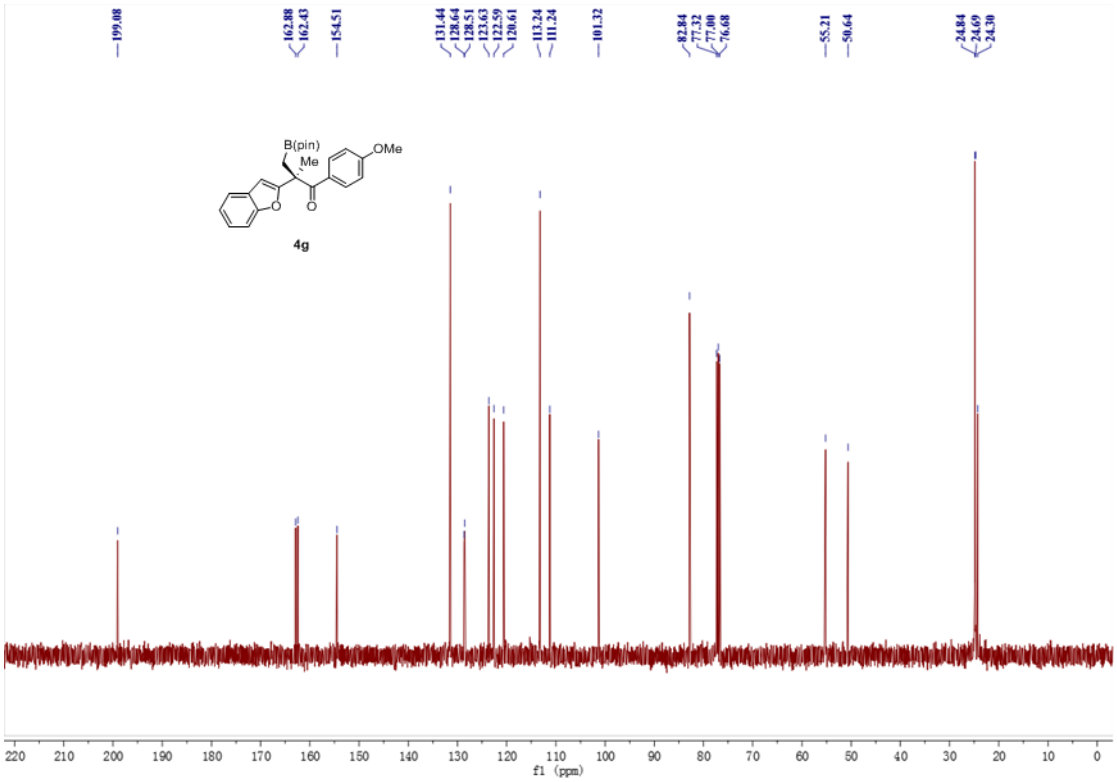

199.50
165.92
163.39
162.09
154.56
132.67
131.54
131.45
128.38
123.89
122.76
120.73
115.21
114.99
111.28
101.75
83.04
77.32
77.00
76.68
50.59
24.79
24.71
24.19
B(pin)
Me
F
O
O
4e
f1 (ppm)

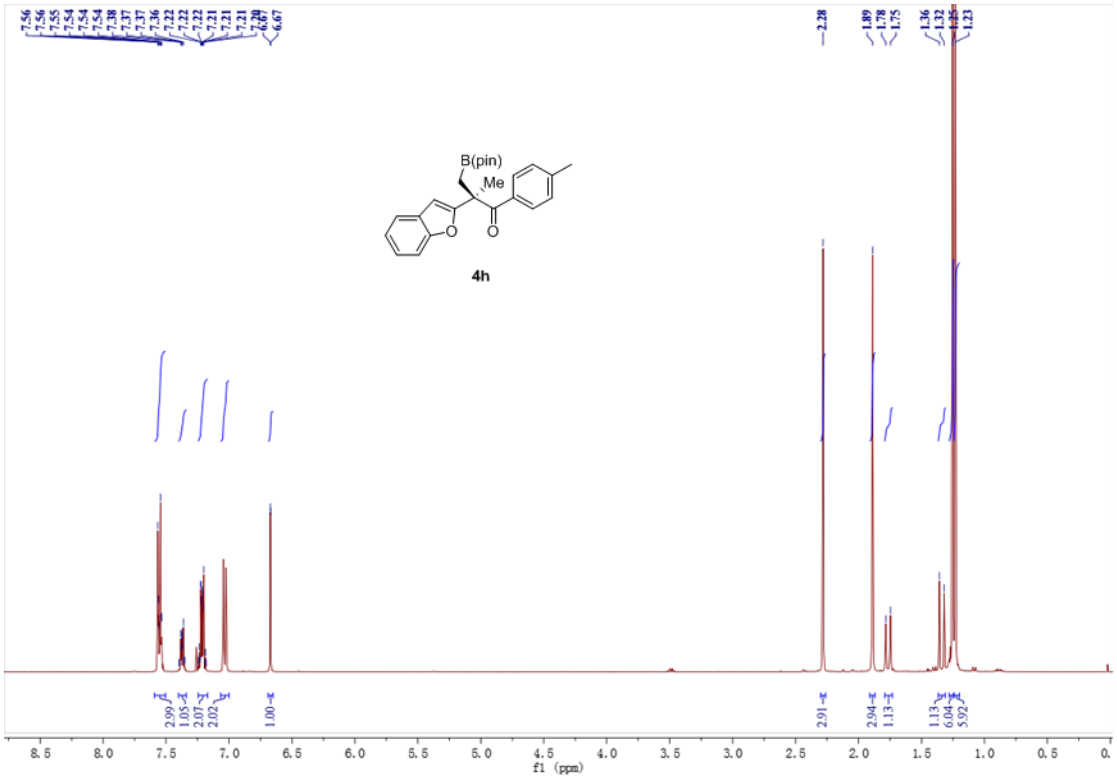

-106.82
B(pin)
Me
F
O
O
4e
f1 (ppm)

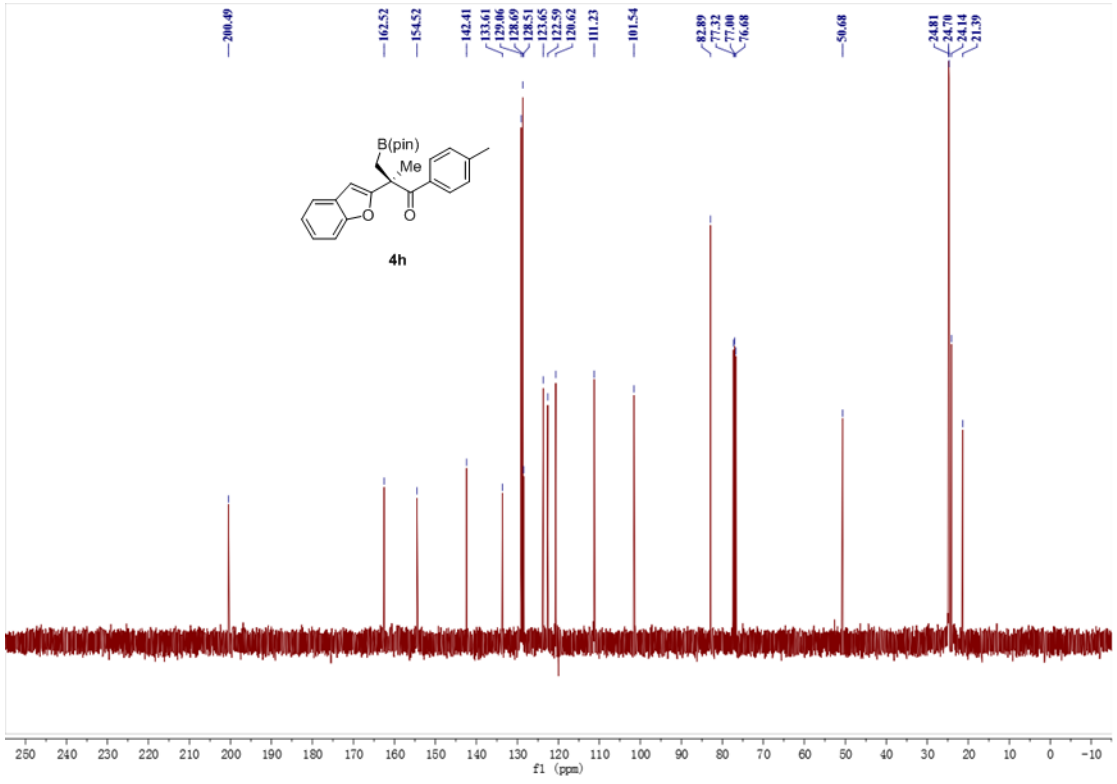

B(pin)
Me
COOMe
4f
f1 (ppm)

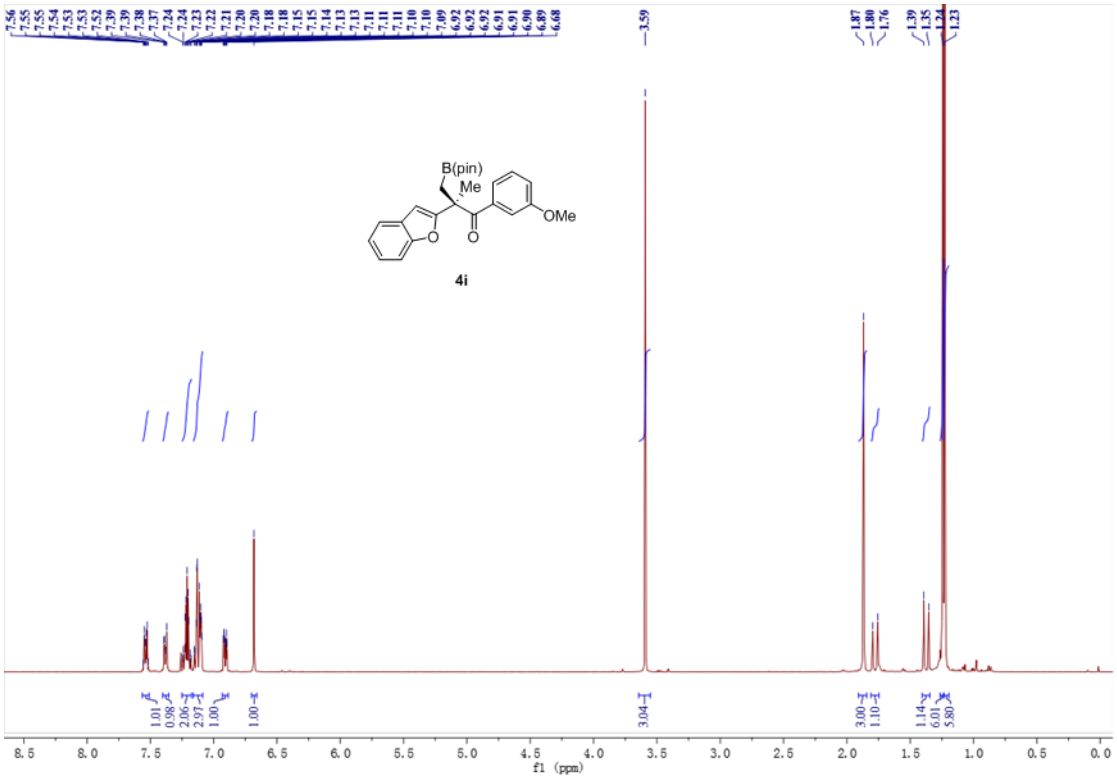

B(pin)
Me
COOMe
4f
f1 (ppm)

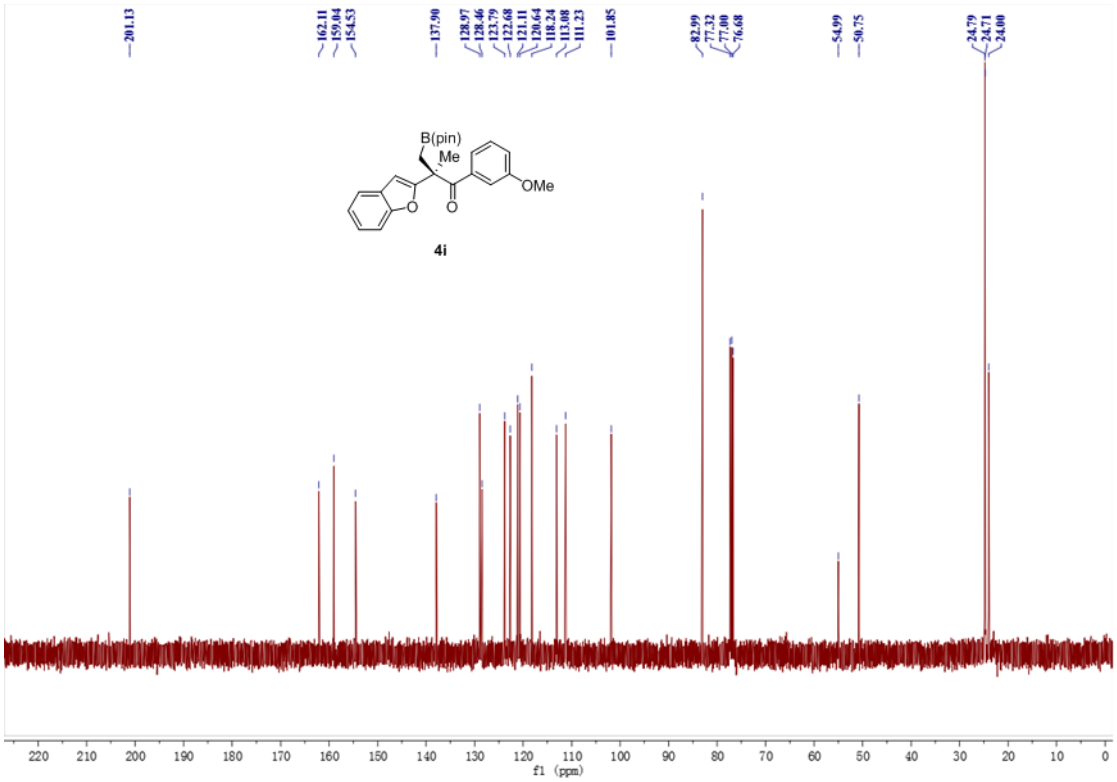

7.71
7.68
7.55
7.54
7.53
7.52
7.38
7.37
7.36
7.35
7.23
7.22
7.21
7.20
7.19
7.18
6.73
6.70
6.66
3.74
1.89
1.76
1.72
1.32
1.28
1.25
1.23
B(pin)
Me
OMe
O
O
4g
2.03
1.02
1.04
2.10
1.98
1.00
3.02
3.05
1.30
1.35
5.94
5.91
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

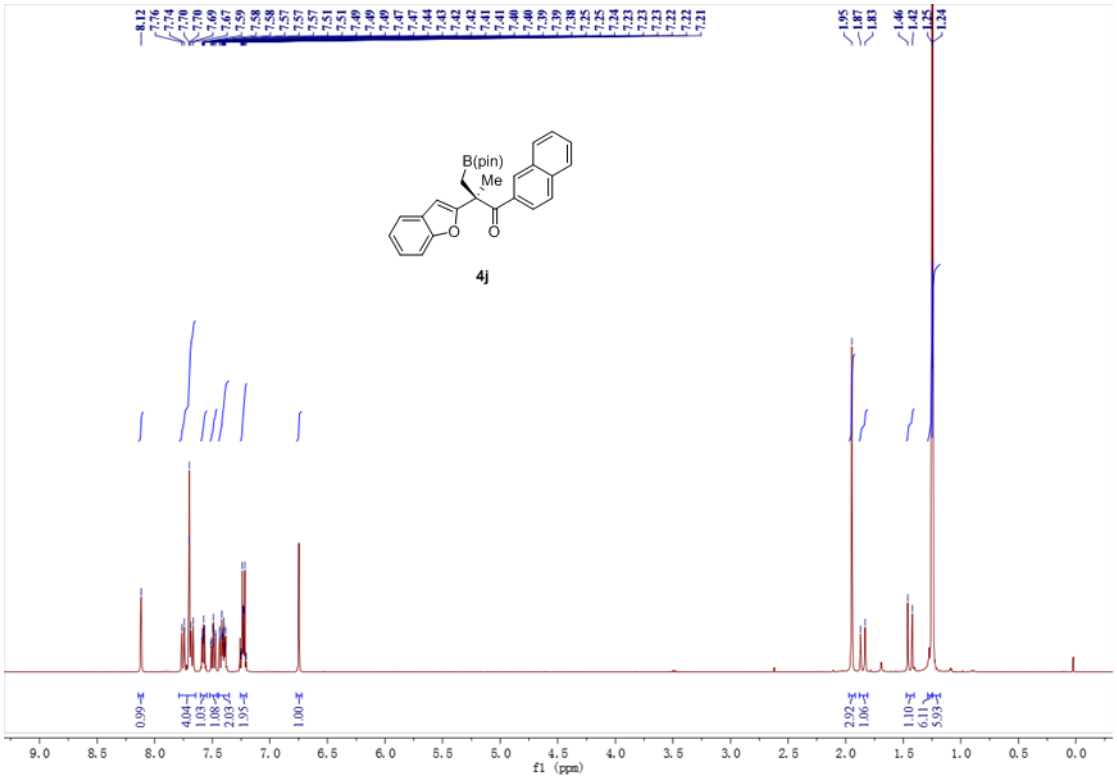

199.08
162.88
162.43
154.51
131.44
128.64
128.51
123.63
122.59
120.61
113.24
111.24
101.32
82.84
77.32
77.00
76.68
55.21
50.64
24.84
24.69
24.30
B(pin)
Me
OMe
O
O
4g
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

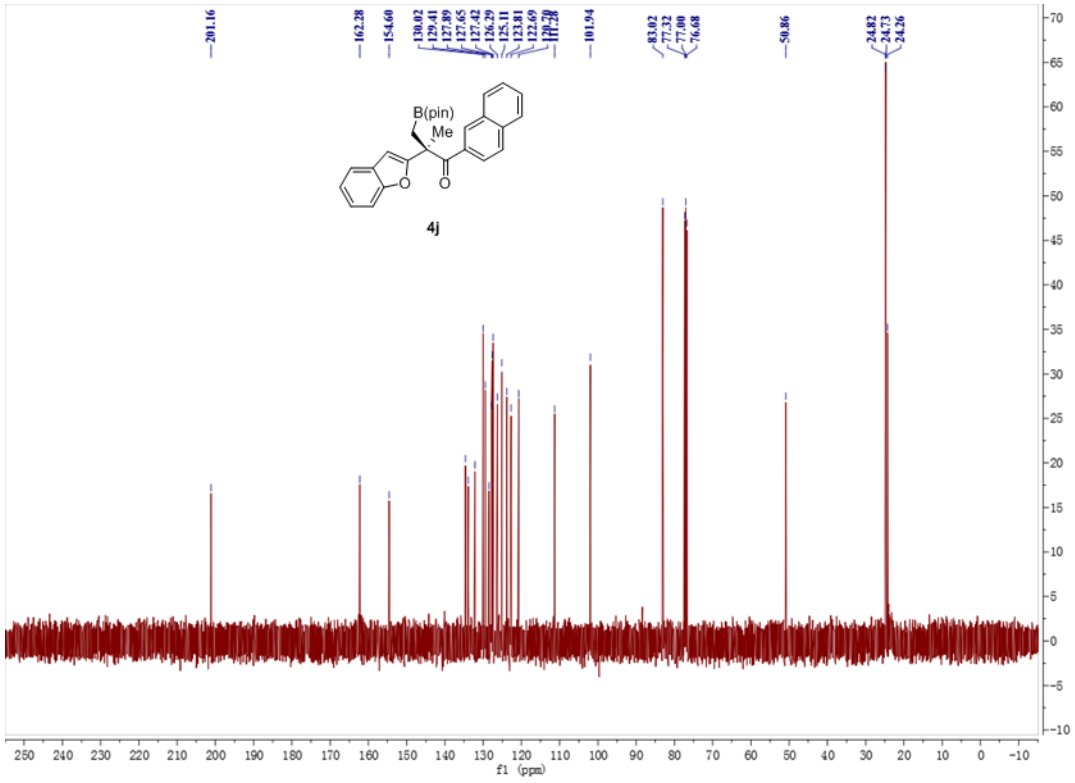

B(pin)
Me
O
O
4h
f1 (ppm)

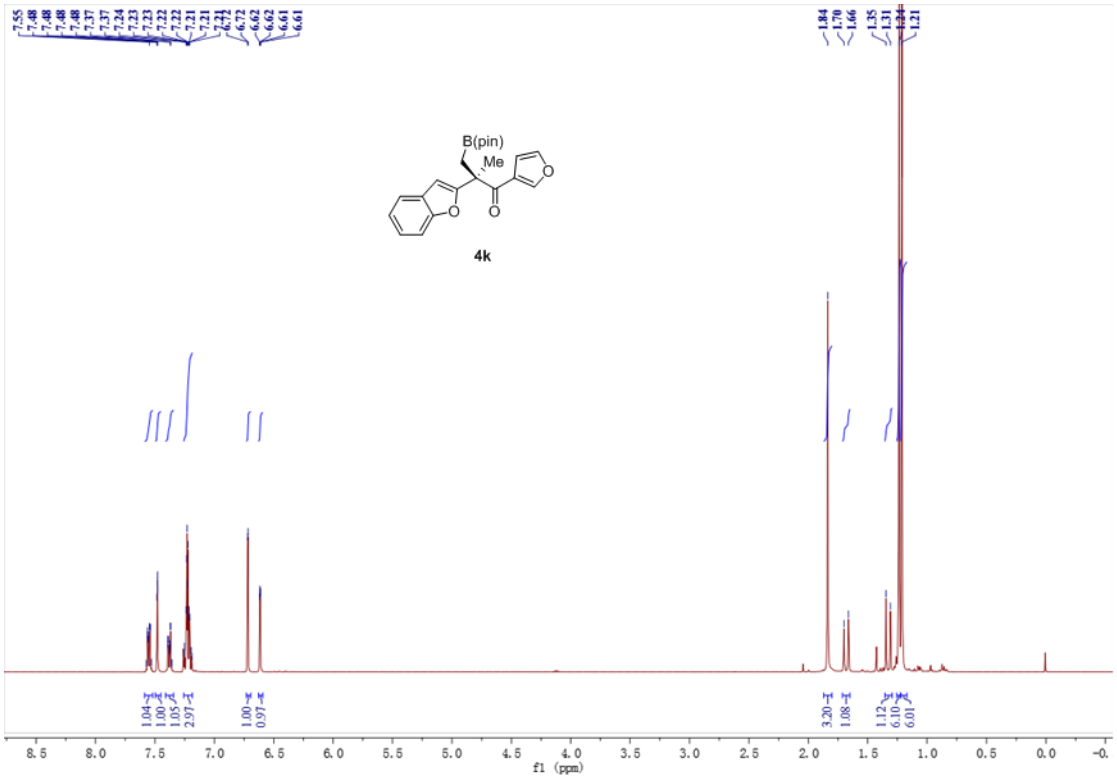

B(pin)
Me
O
O
4h
f1 (ppm)

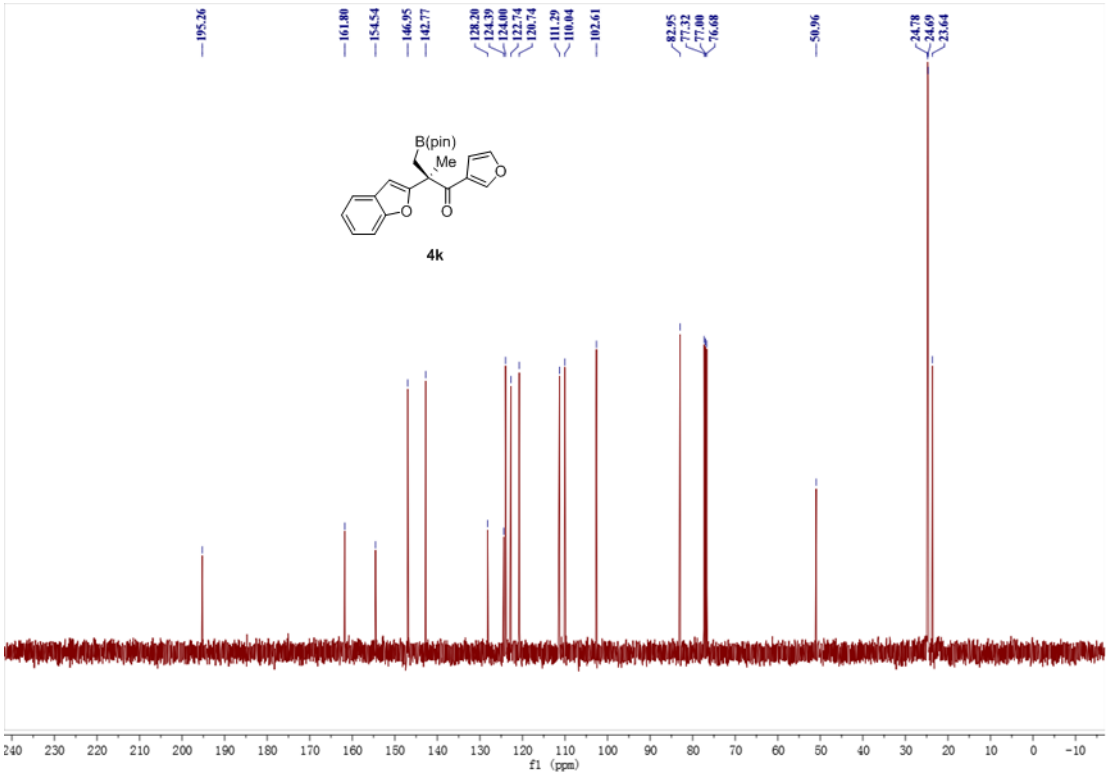

B(pin)
Me
OMe
O
4i
f1 (ppm)

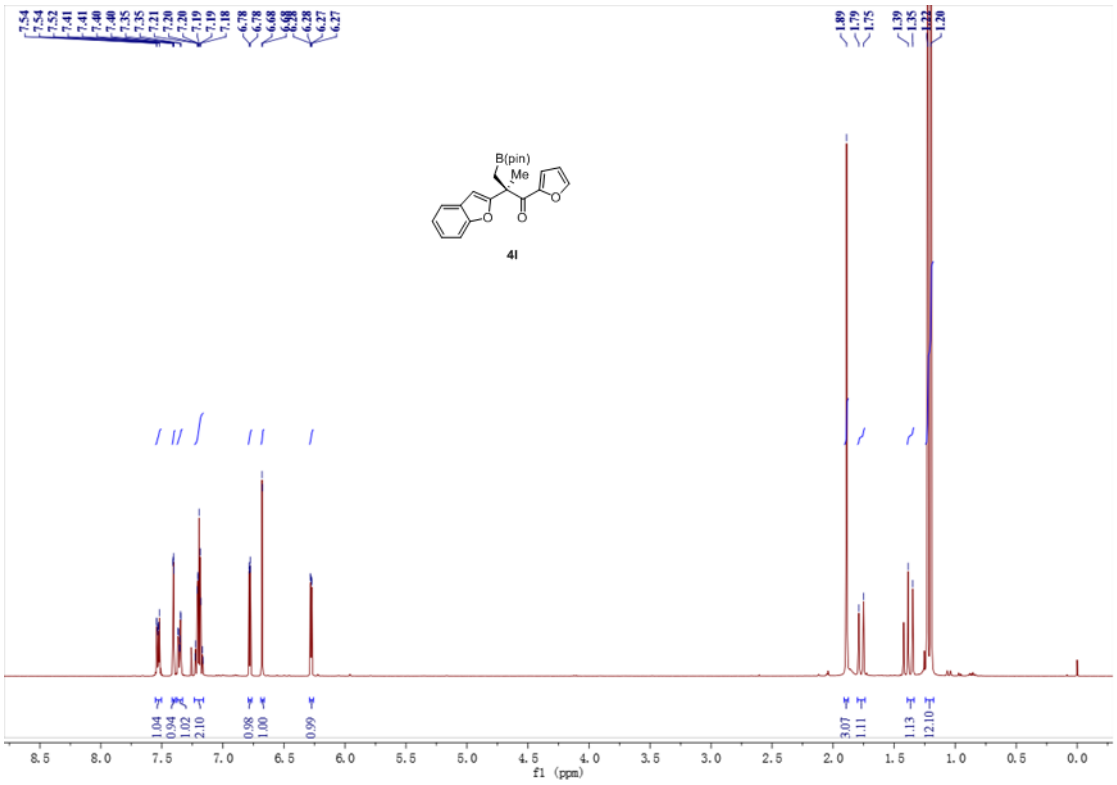

B(pin)
Me
OMe
O
4i
f1 (ppm)

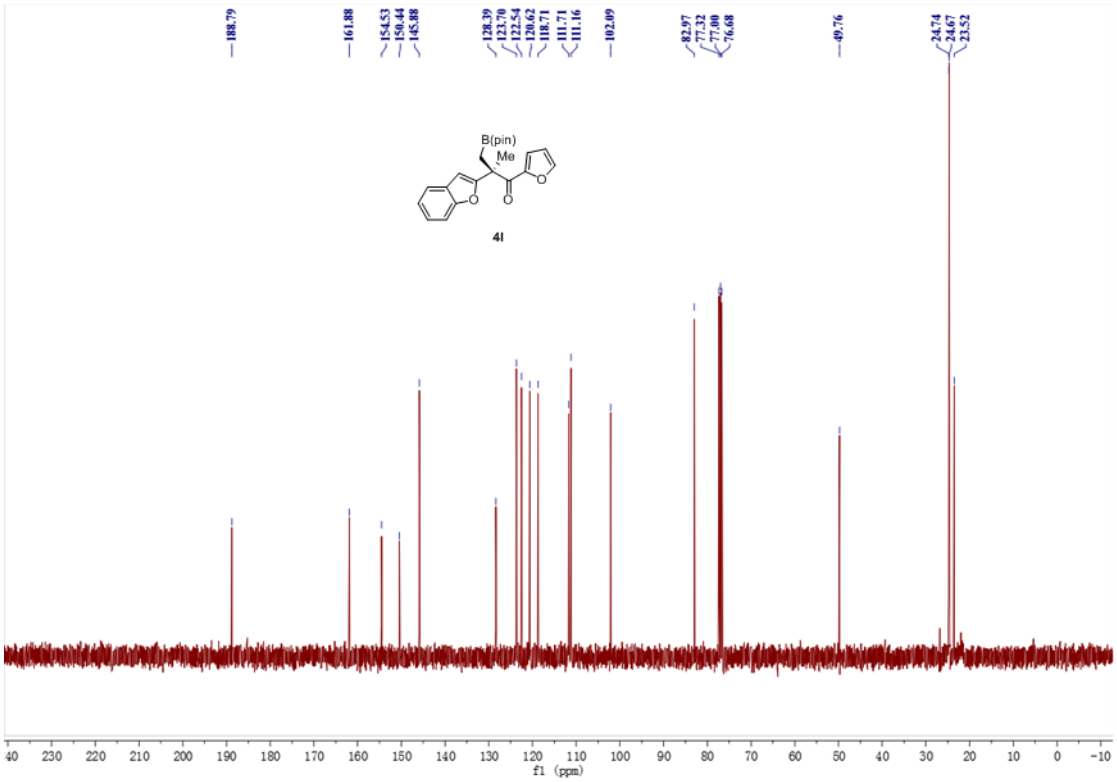

B(pin)
Me
O
O
4j
f1 (ppm)

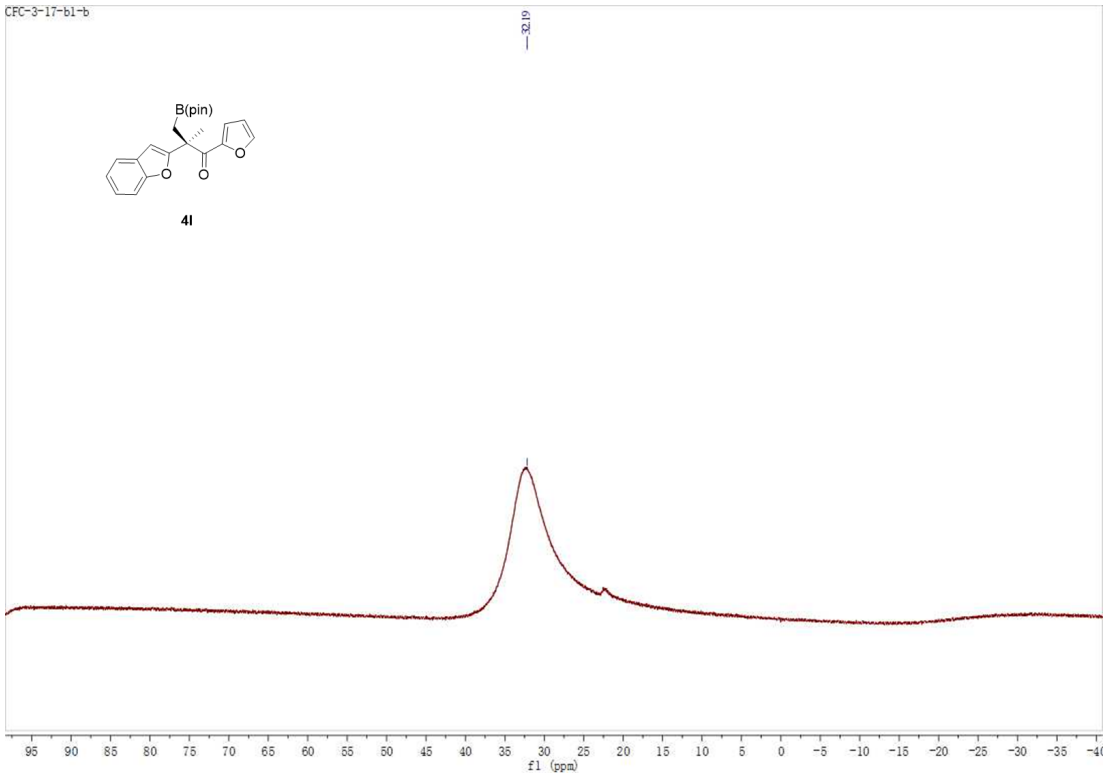

B(pin)
Me
O
O
4j
f1 (ppm)

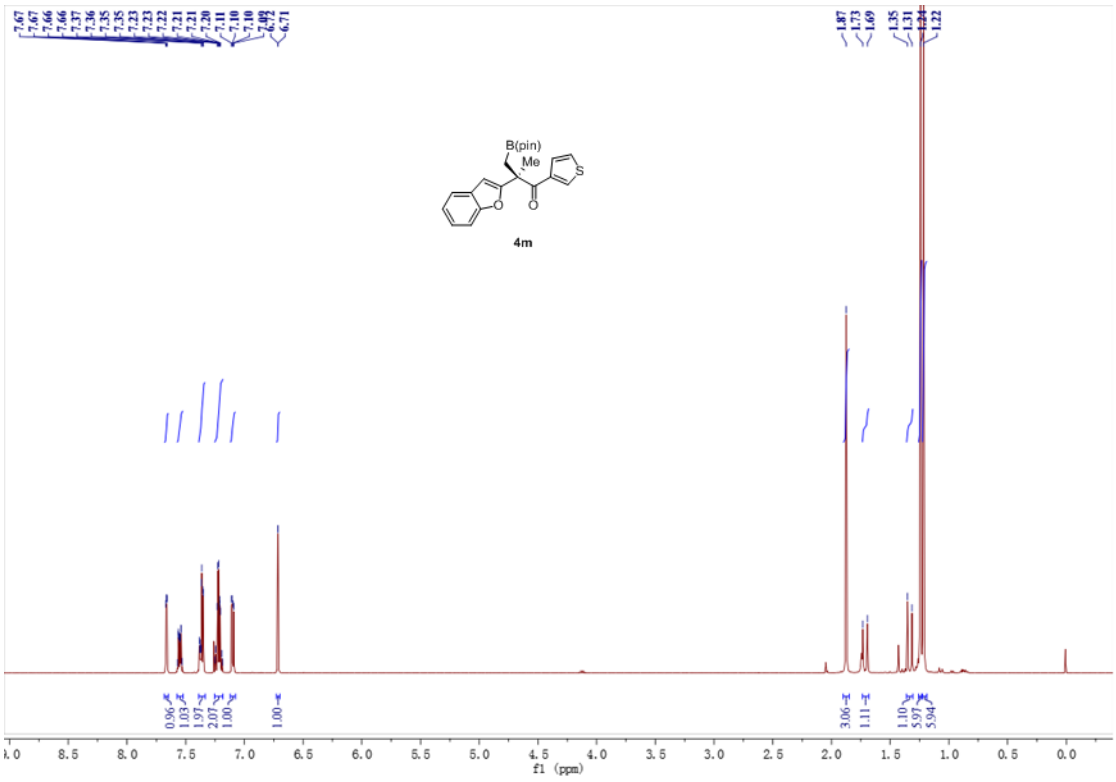

B(pin)
Me
O
O
4k
f1 (ppm)

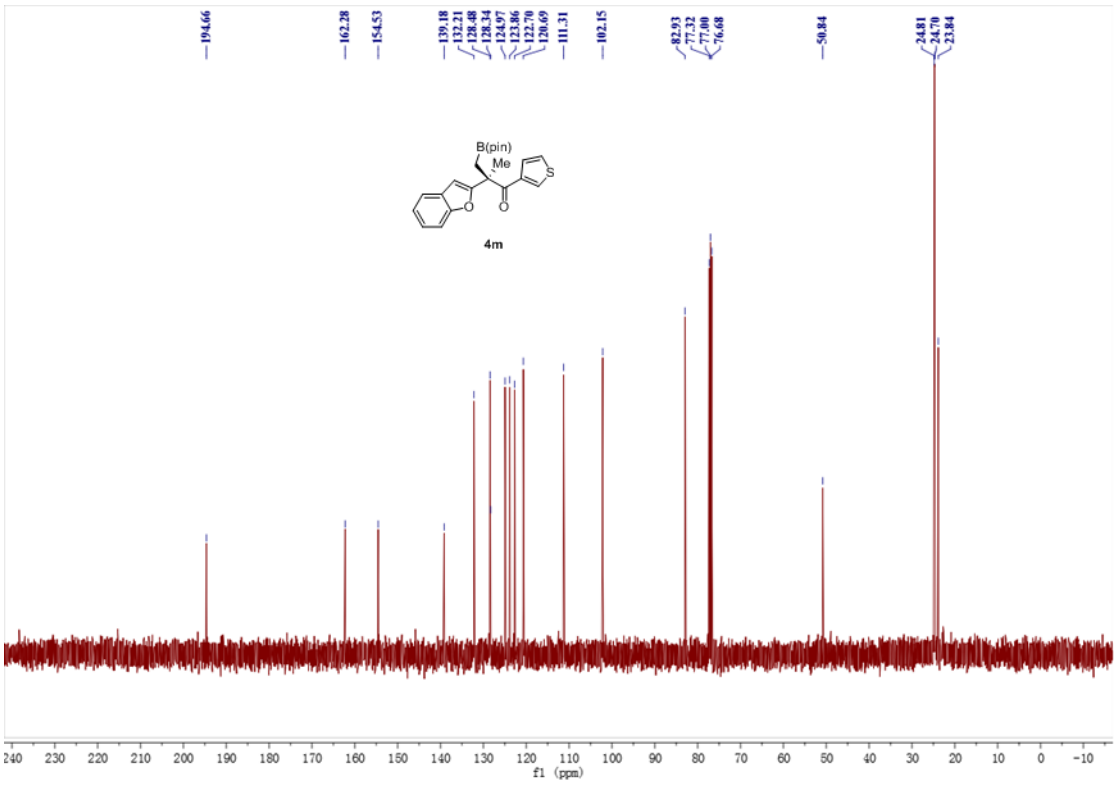

B(pin)
Me
O
O
4k
f1 (ppm)


B(pin)
Me
4l
f1 (ppm)


B(pin)
Me
4l
f1 (ppm)


CFC-3-17-b1-b
32.19
B(pin)
O
O
O
4l
95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35
f1 (ppm)


7.67
7.67
7.66
7.66
7.37
7.36
7.35
7.35
7.23
7.23
7.22
7.21
7.21
7.20
7.11
7.10
7.10
6.72
6.71
1.87
1.73
1.69
1.35
1.31
1.24
1.22
B(pin)
Me
S
O
O
4m
0.96
1.03
1.97
2.07
1.00
1.00
3.06
1.11
1.10
5.97
5.94
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)


194.66
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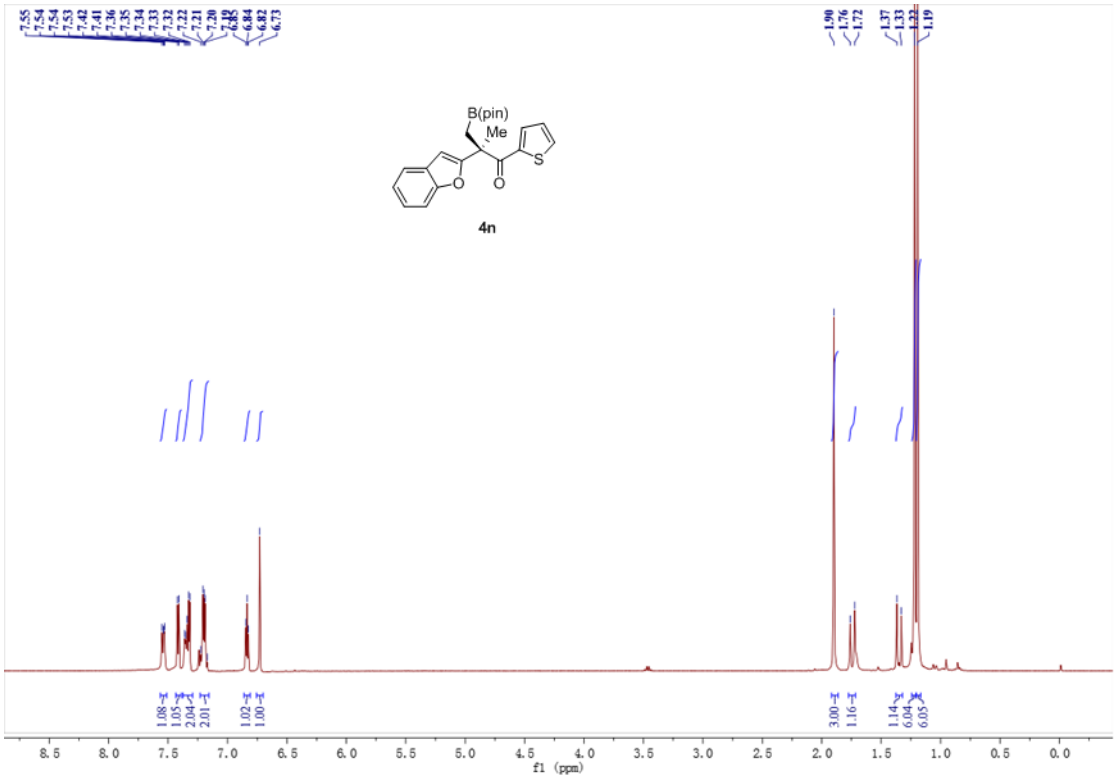
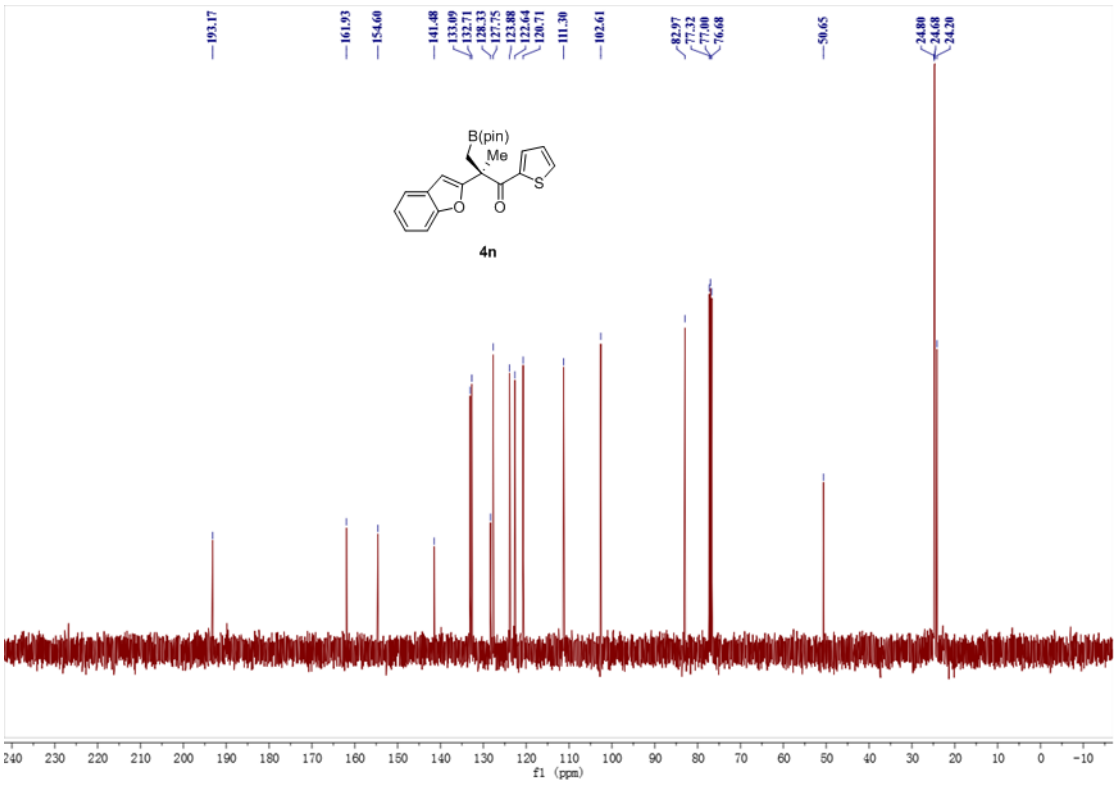
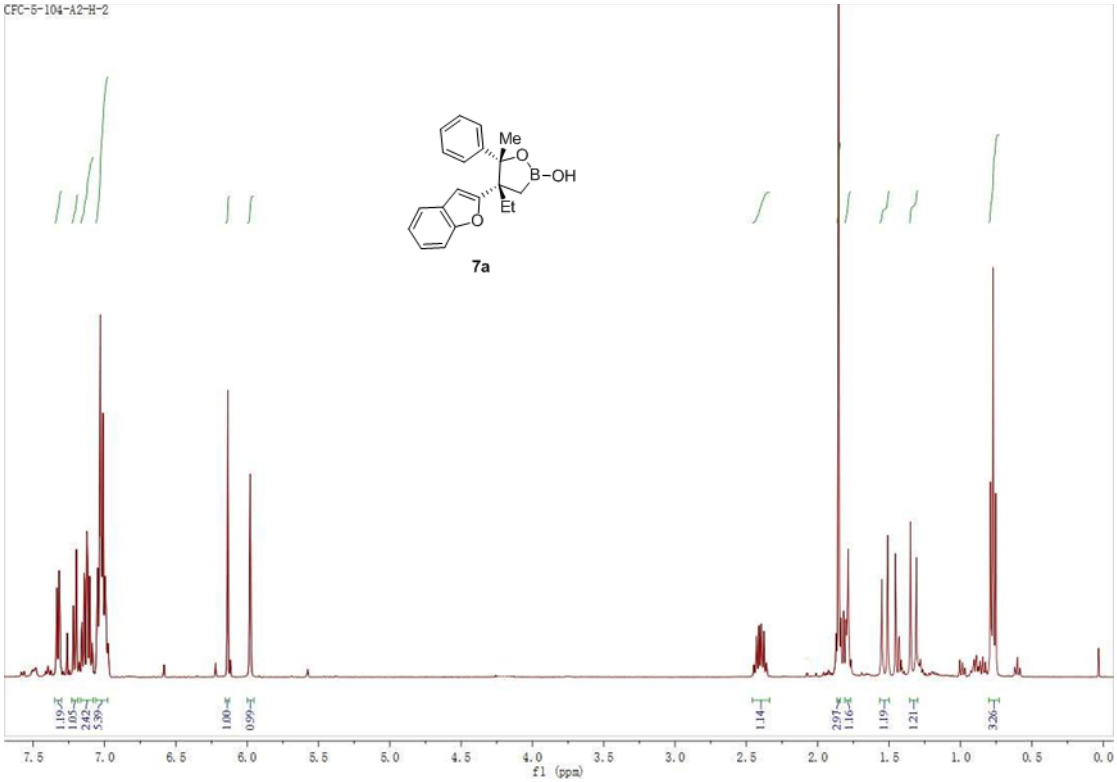
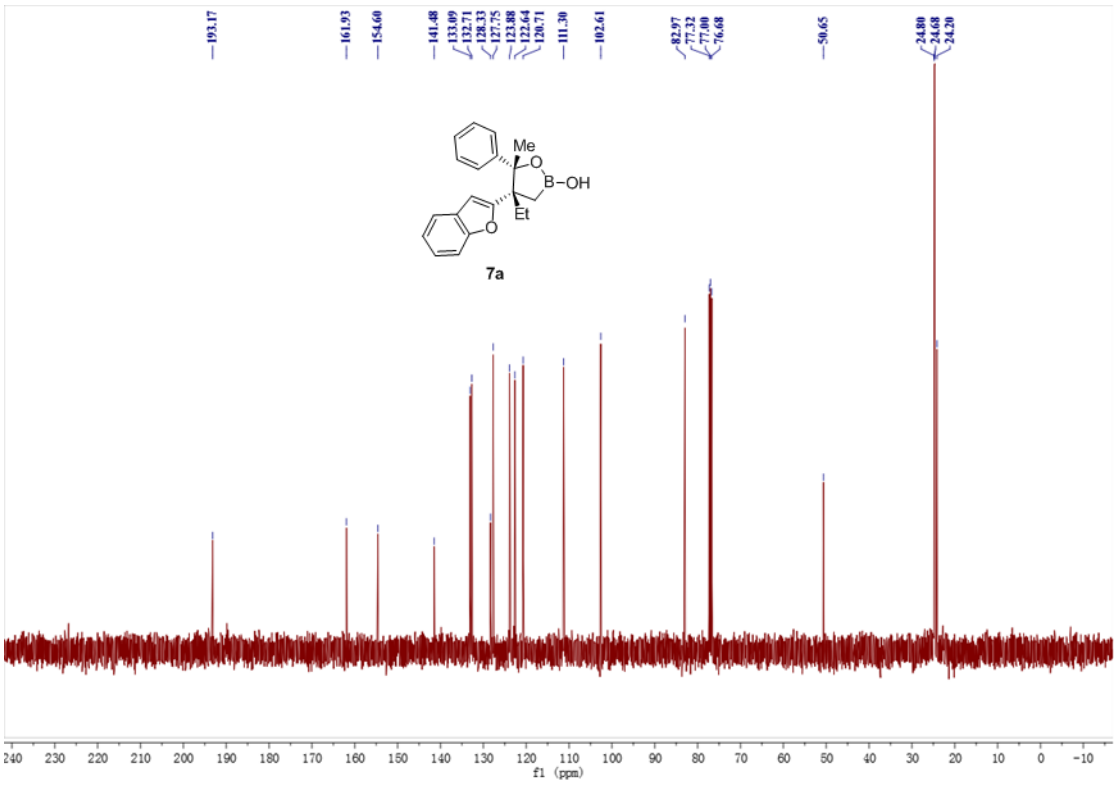
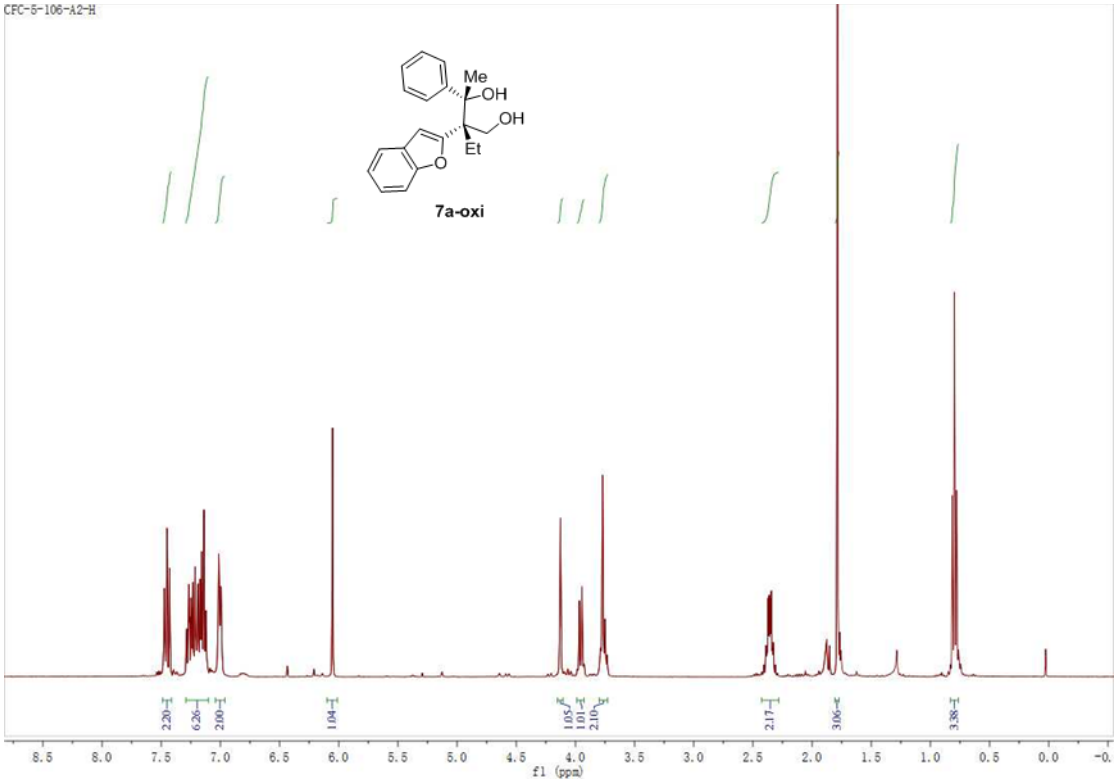
154.53
139.18
132.21
128.48
128.34
124.97
123.86
122.70
120.69
111.31
102.15
82.93
77.32
77.00
76.68
50.84
24.81
24.70
23.84
B(pin)
Me
S
O
O
4m
f1 (ppm)

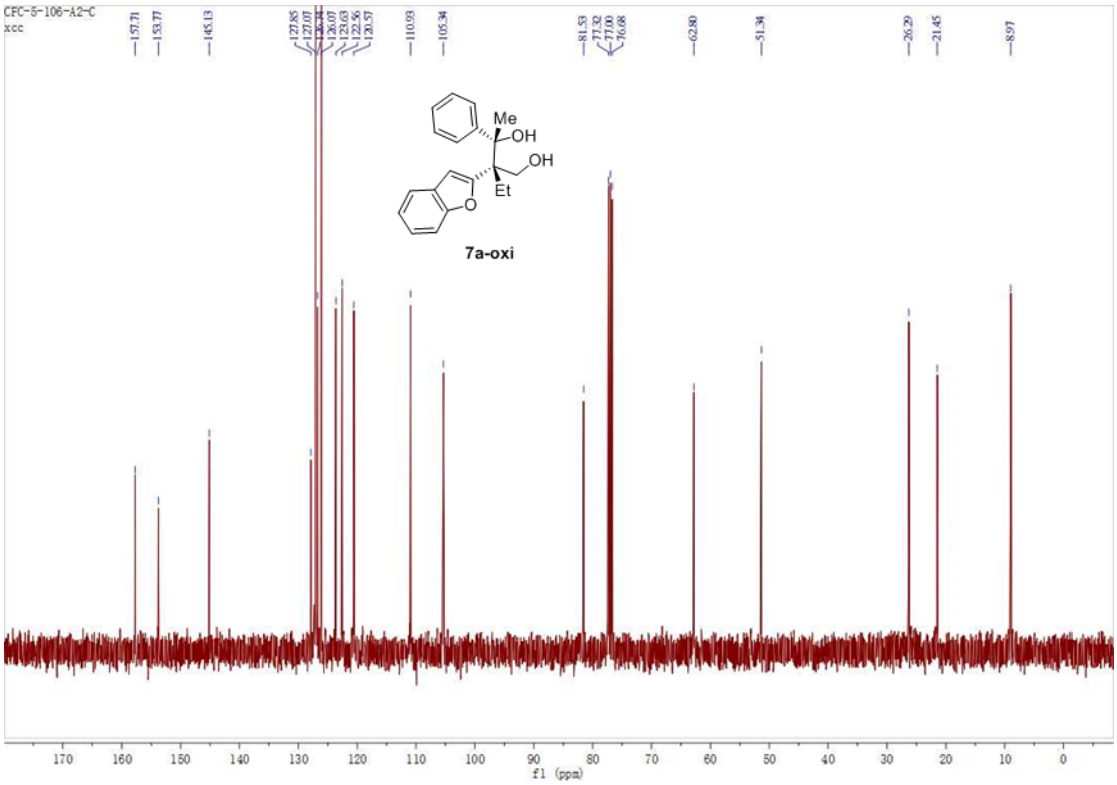

7.55
7.54
7.54
7.54
7.53
7.42
7.41
7.36
7.35
7.34
7.33
7.32
7.22
7.21
7.20
6.85
6.84
6.82
6.73
1.90
1.76
1.72
1.37
1.33
1.22
1.19
B(pin)
Me
S
O
O
4n
1.08
1.05
2.04
2.01
1.02
1.00
3.00
1.16
1.14
6.04
6.05
f1 (ppm)

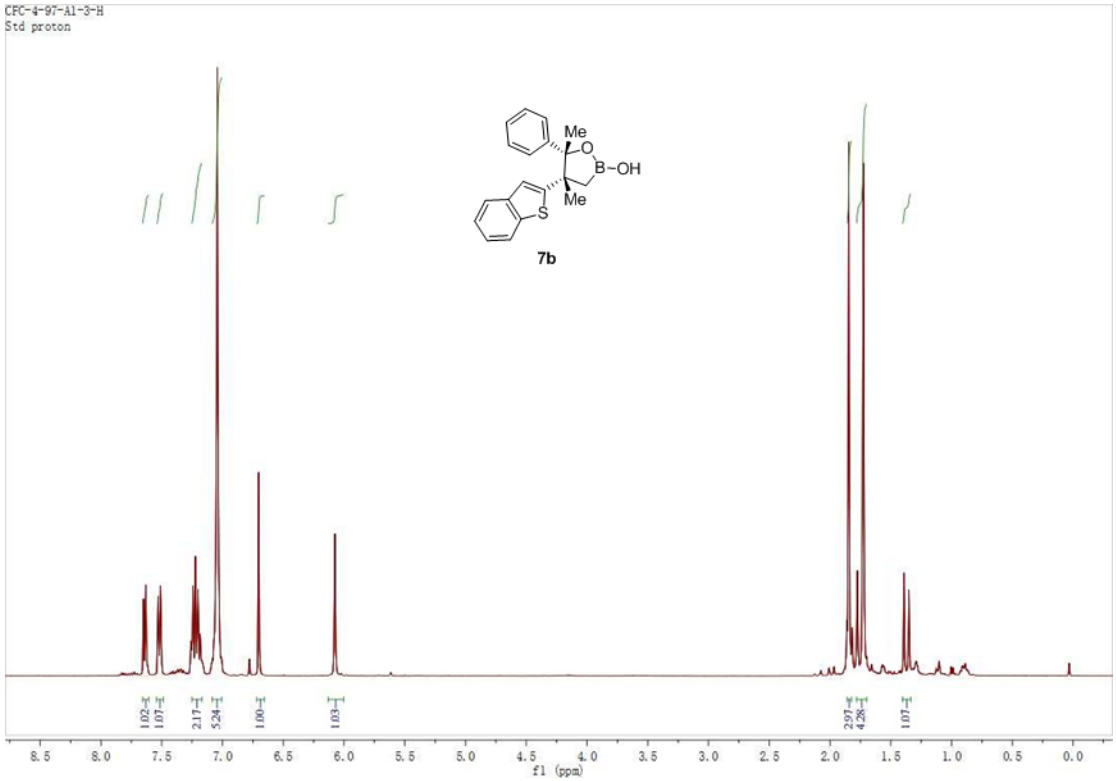

193.17
161.93
154.60
141.48
133.09
132.71
128.33
127.75
123.88
122.64
120.71
111.30
102.61
82.97
77.32
77.00
76.68
50.65
24.80
24.68
24.20
B(pin)
Me
O
S
O
4n
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

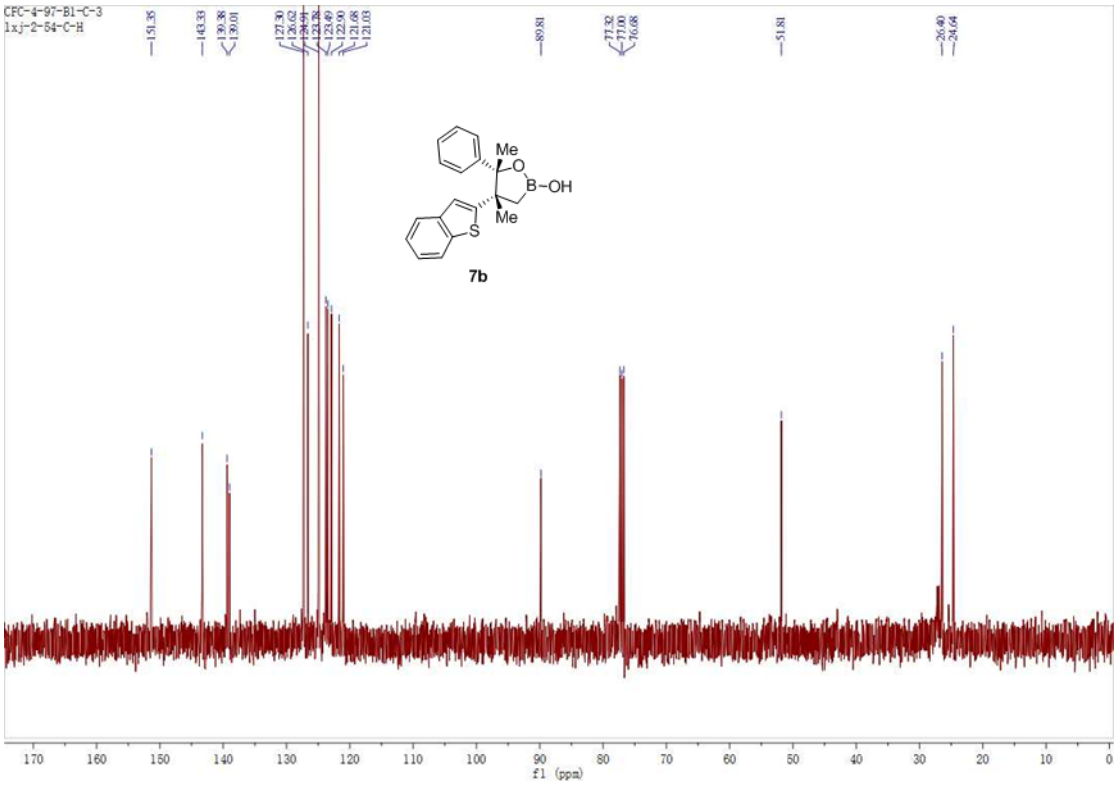

CFC-5-104-A2-H-2
Me
O
B–OH
Et
O
7a
1.19
1.05
2.42
5.39
1.00
0.99
1.14
2.97
1.16
1.19
1.21
3.26
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

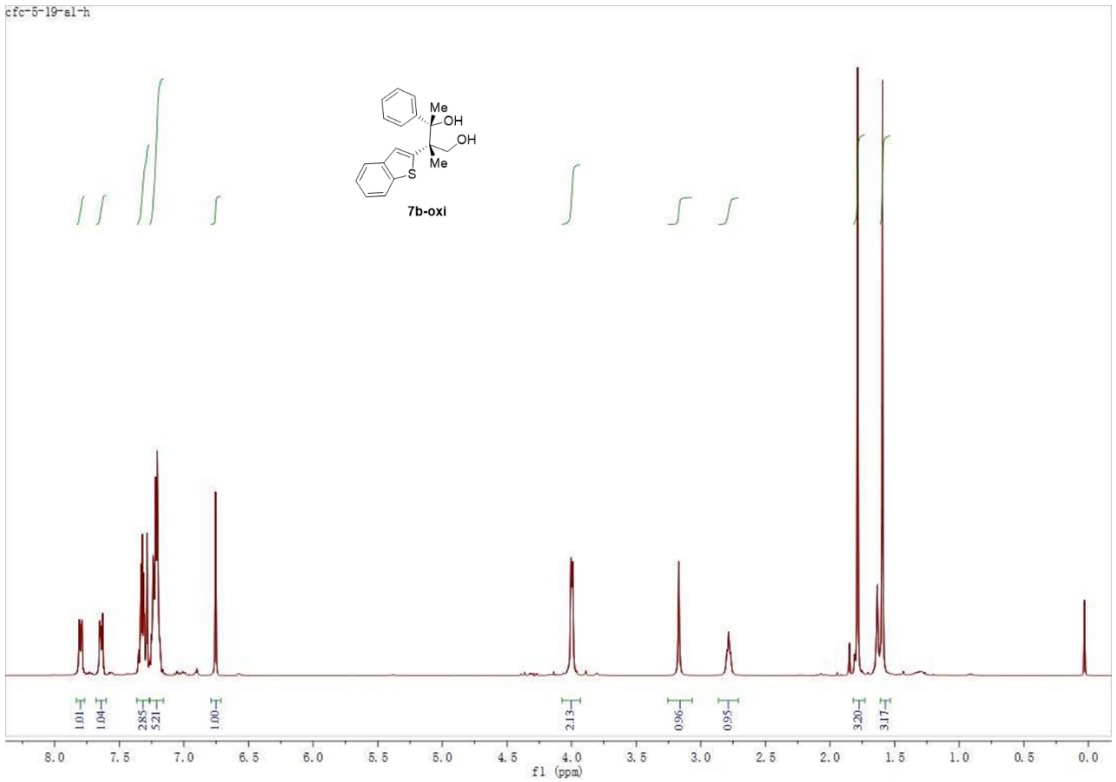

193.17
161.93
154.60
141.48
133.09
132.71
128.33
127.75
123.88
122.64
120.71
111.30
102.61
82.97
77.32
77.00
76.68
50.65
24.80
24.68
24.20
Me
O
B–OH
Et
O
7a
f1 (ppm)

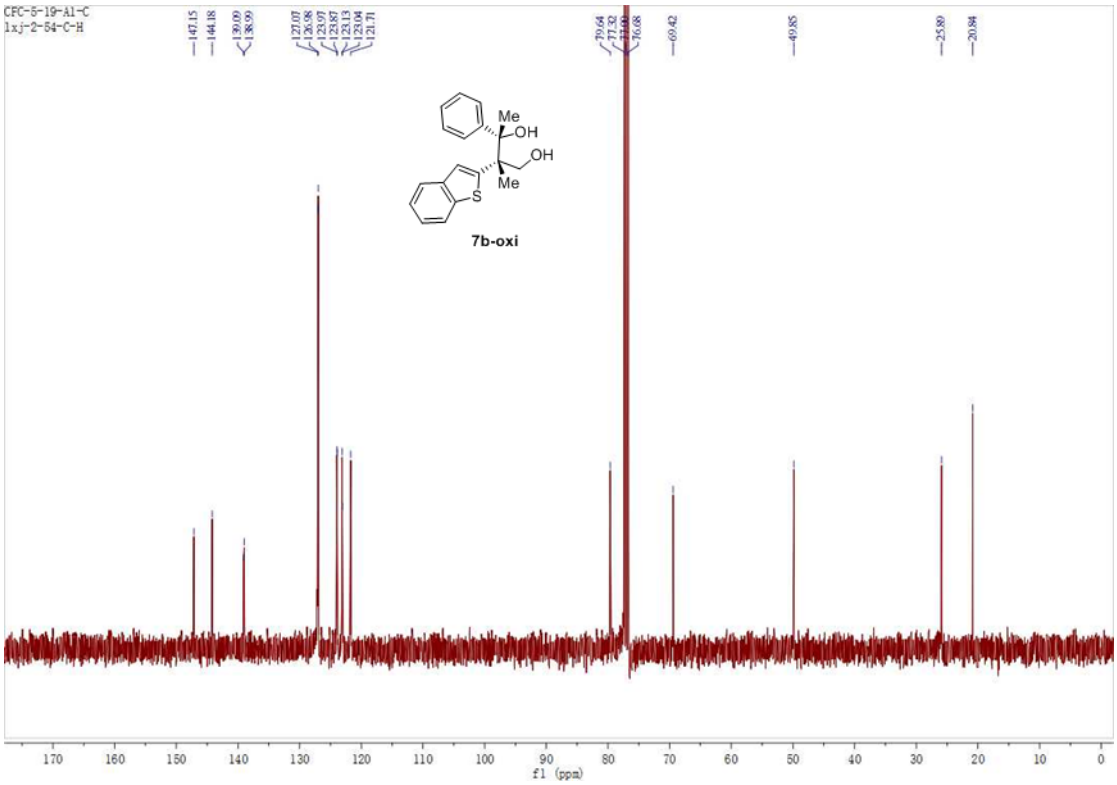

CFC-5-106-A2-H
Me
OH
OH
Et
O
7a-oxi
2.20
6.26
2.00
1.04
1.05
1.01
2.10
2.17
3.06
3.38
f1 (ppm)

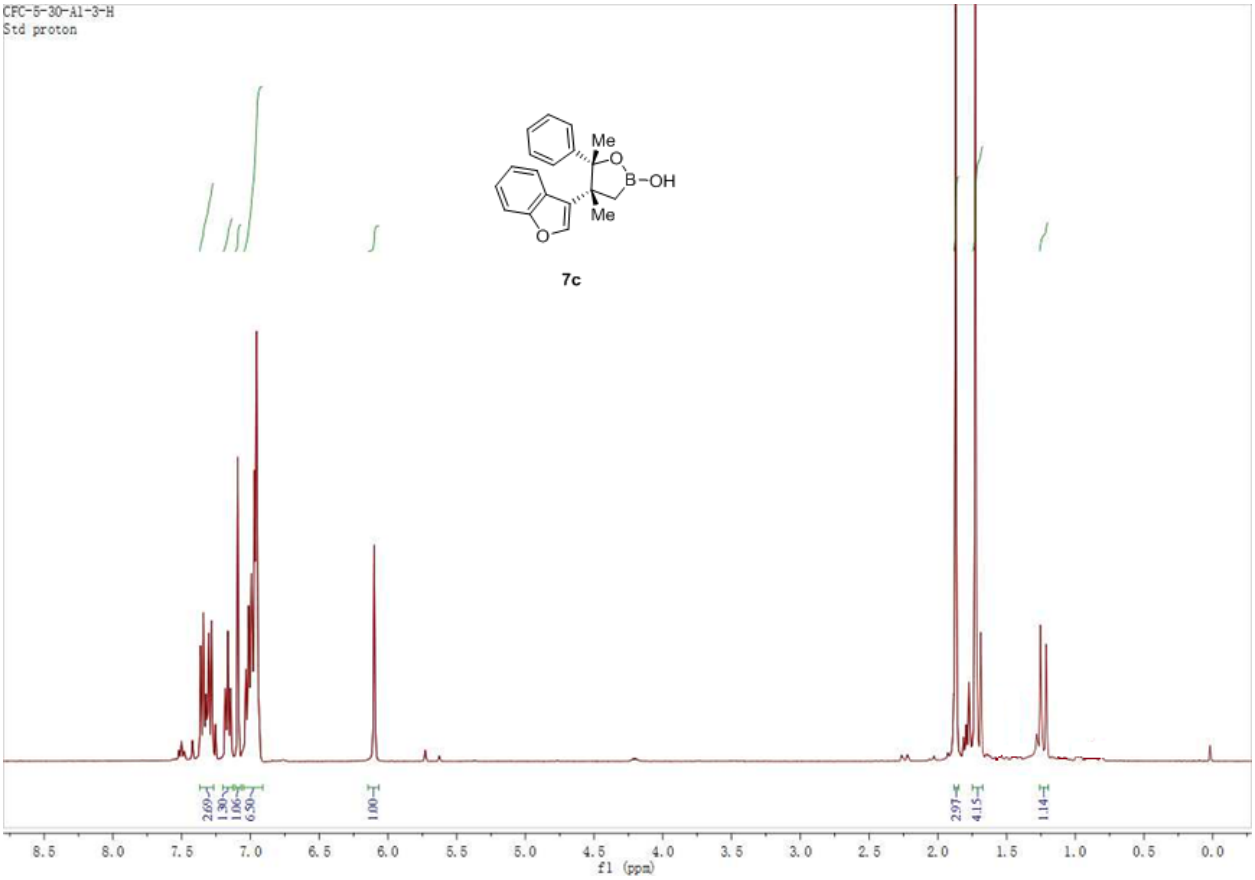

CFC-5-106-A2-C
xcc
157.71
153.77
145.13
127.85
127.07
126.44
126.07
125.63
122.96
120.57
110.93
105.34
81.53
77.32
77.00
76.68
62.80
51.34
26.29
21.45
8.97
Me
OH
OH
Et
O
7a-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

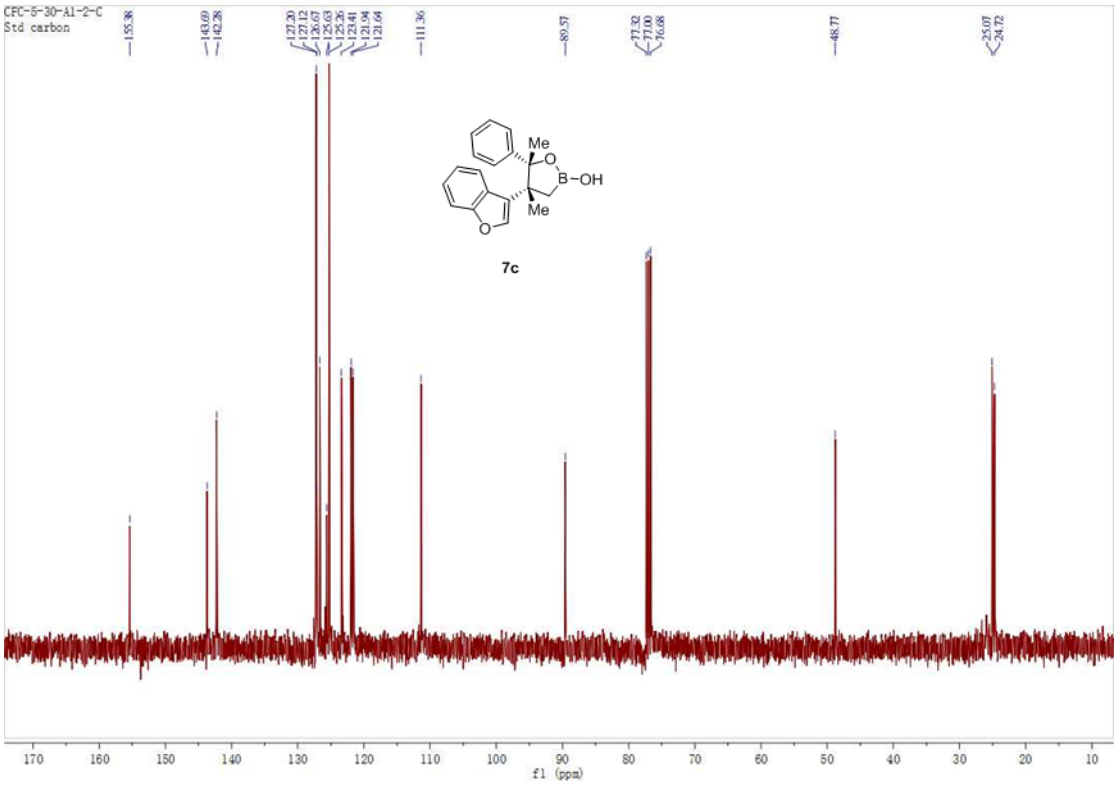

CFC-4-97-A1-3-H
Std proton
Me
O
B–OH
Me
S
7b
1.02
1.07
2.17
5.24
1.00
1.03
2.97
4.28
1.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

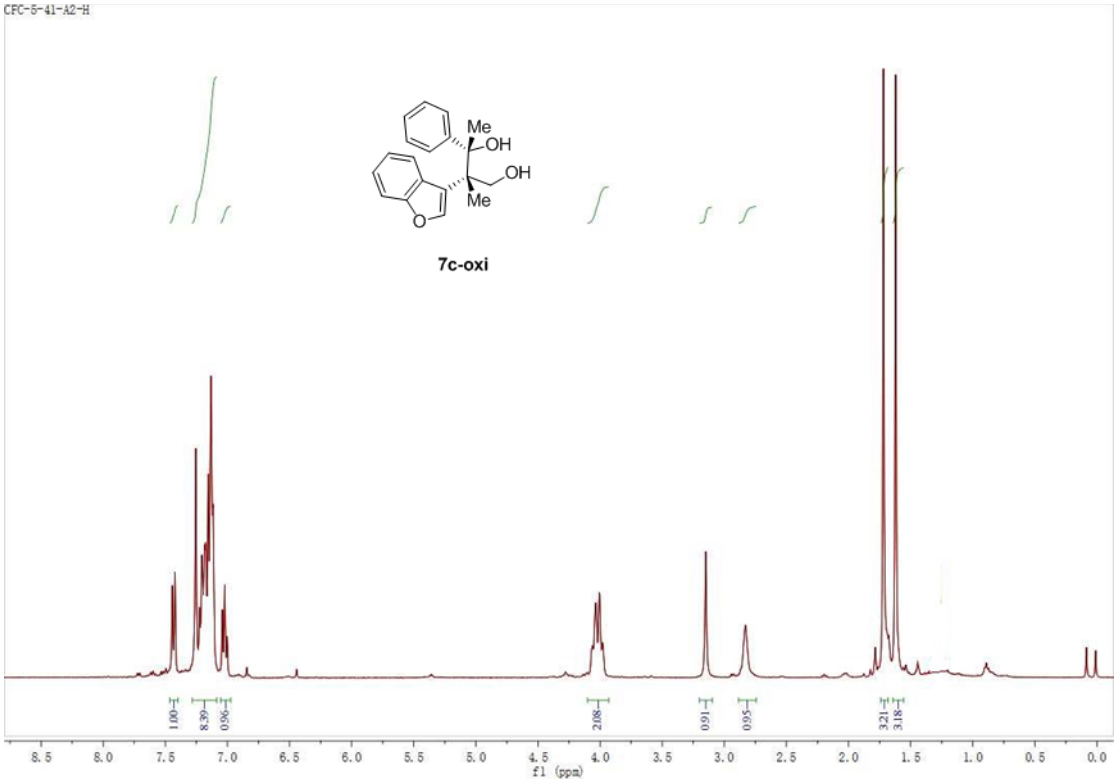

CFC-4-97-B1-C-3
lxj-2-54-C-H
151.35
143.33
139.38
139.01
127.30
126.02
124.54
123.78
123.40
122.90
121.68
121.03
89.81
77.32
77.00
76.68
51.81
26.40
24.64
Me
O
B–OH
Me
S
7b
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

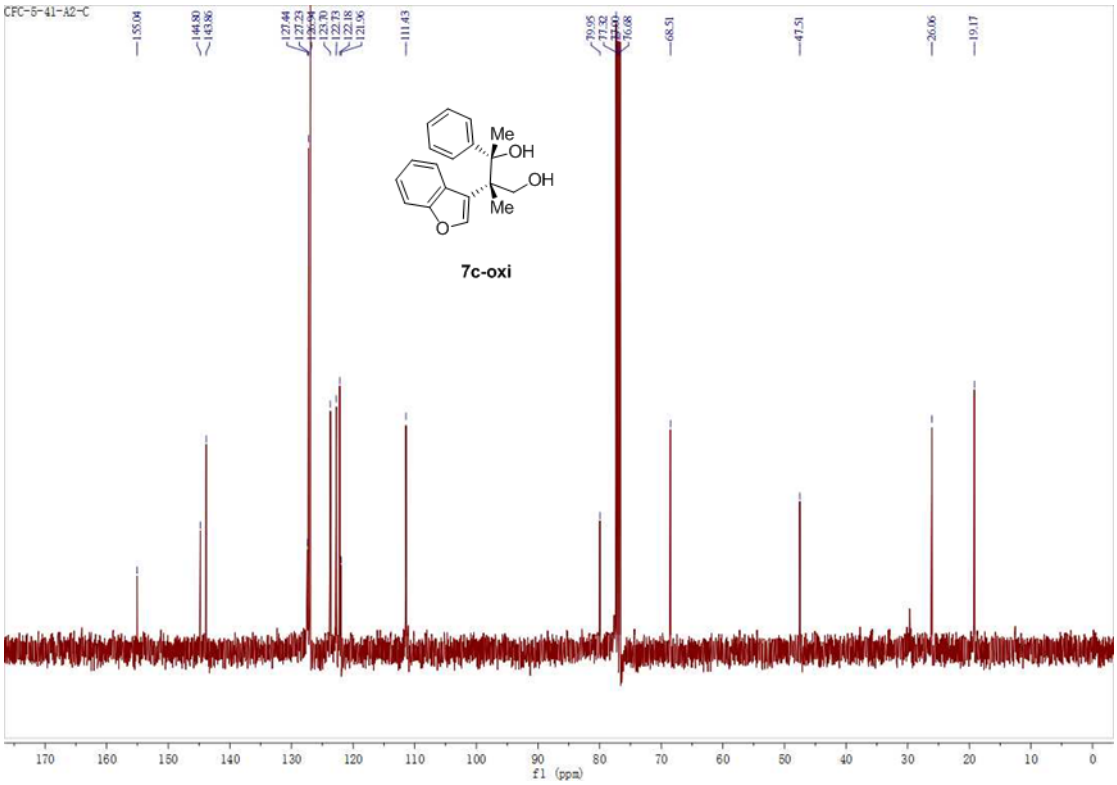

cfc-5-19-a1-h
Me
OH
OH
Me
S
7b-oxi
1.01
1.04
2.85
5.21
1.00
2.13
0.96
0.95
3.20
3.17
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

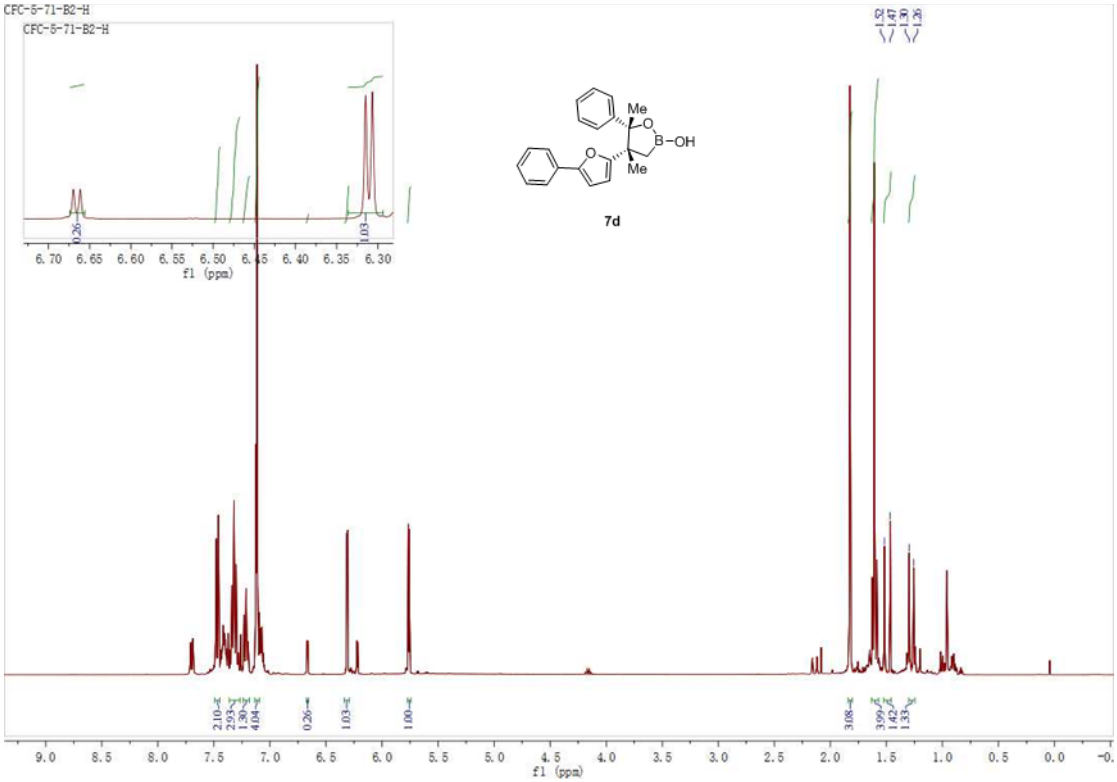

CPC-5-19-A1-C
lxj-2-84-C-H
147.15
144.18
139.09
138.99
127.07
126.98
123.97
123.87
123.13
123.04
121.71
79.64
77.32
77.00
76.68
69.42
49.85
25.89
20.84
Me
OH
OH
Me
S
7b-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

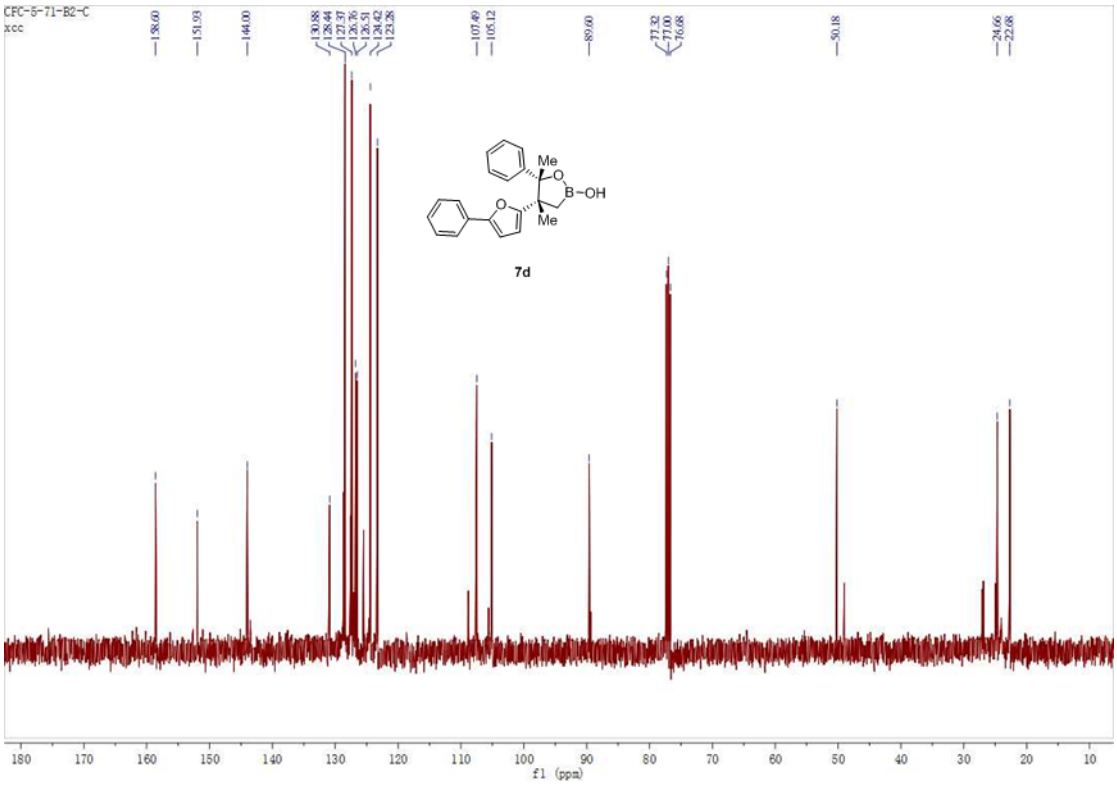

CPC-5-30-A1-3-H
Std proton
Me
O
B–OH
Me
O
7c
2.69
1.30
1.06
6.50
1.00
2.97
4.15
1.14
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

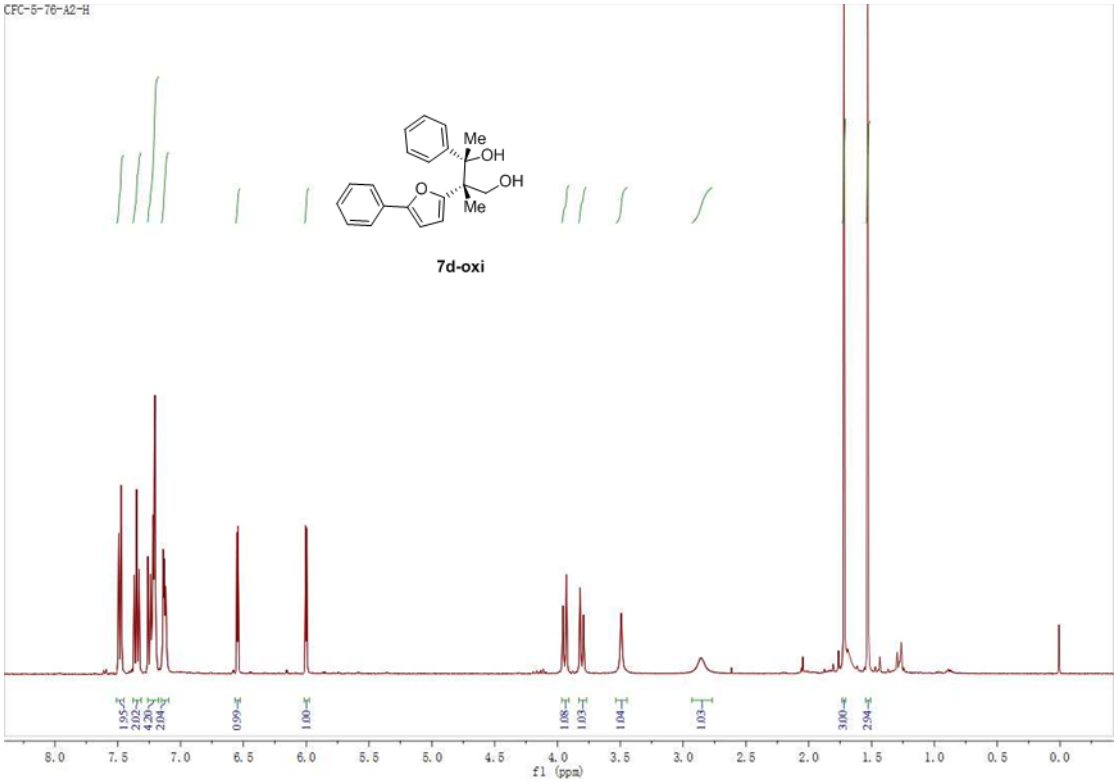

CFC-5-30-A1-2-C
Std carbon
155.38
143.69
142.28
127.20
127.12
126.67
125.63
125.26
123.41
121.94
121.64
111.36
89.57
77.32
77.00
76.68
48.77
25.07
24.72
Me
O
B–OH
Me
O
7c
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

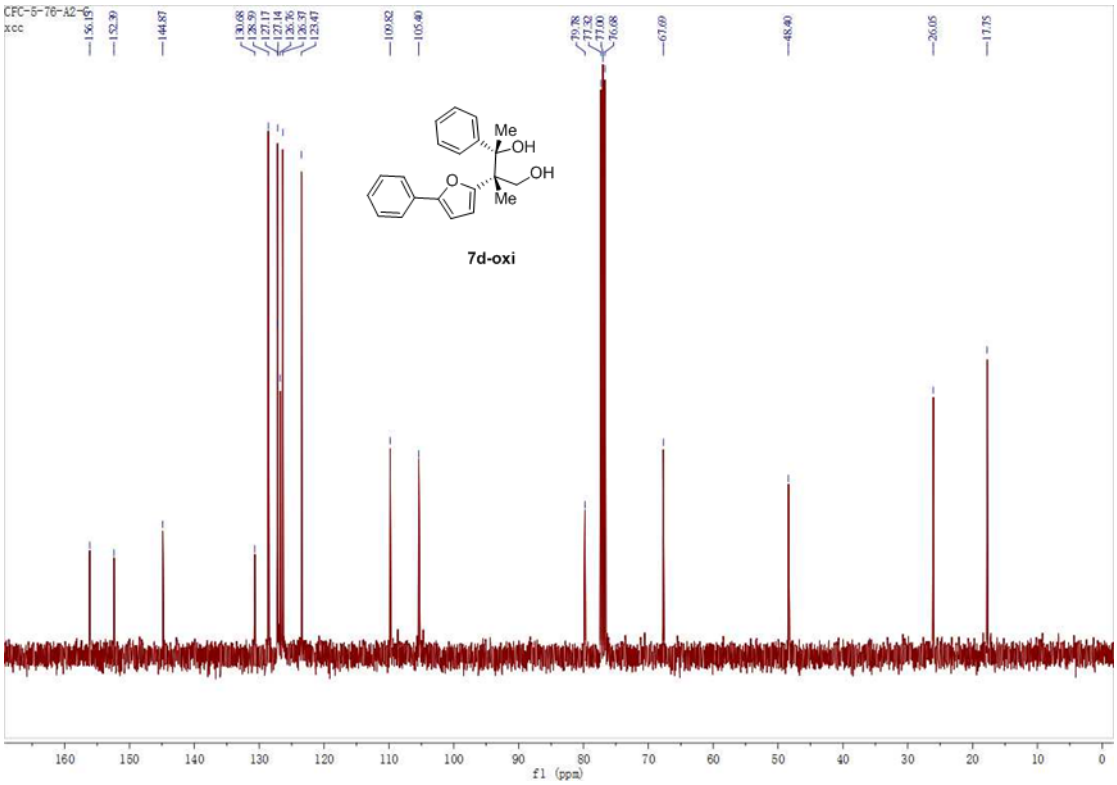

CFC-5-41-A2-H
Me
OH
OH
Me
O
7c-oxi
1.00
8.39
0.96
2.08
0.91
0.95
3.21
3.18
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

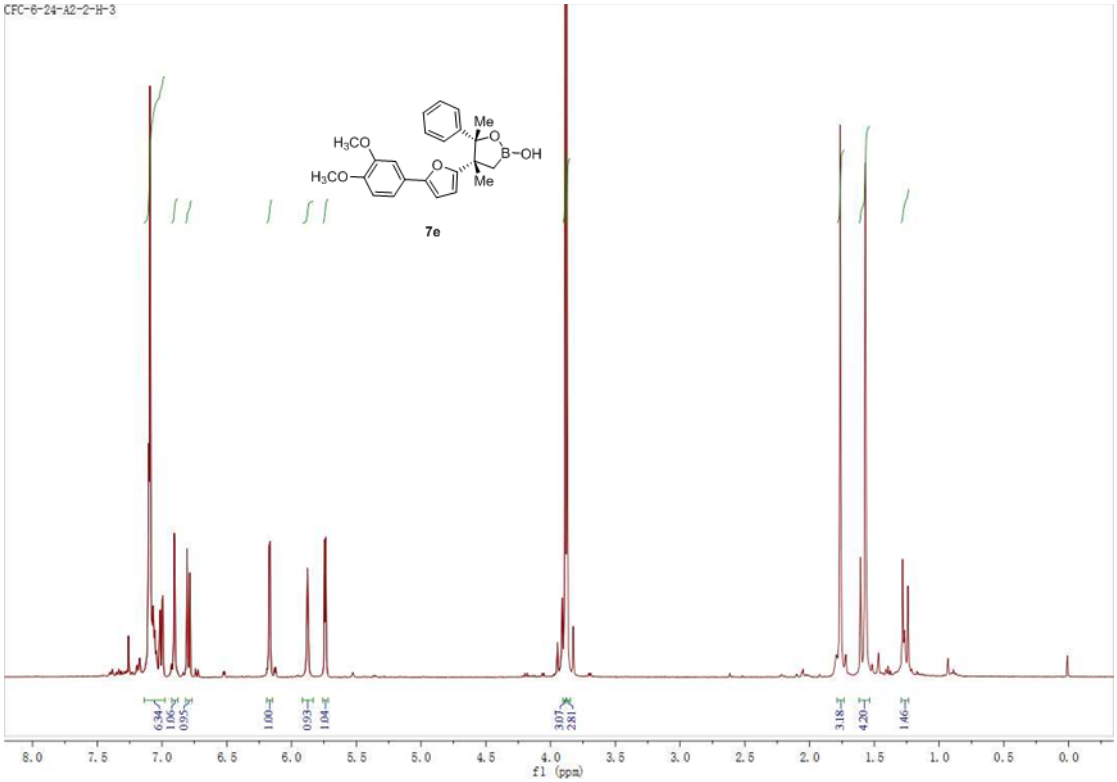

CFC-5-41-A2-C
155.04
144.80
143.86
127.44
127.23
126.94
123.70
122.73
122.18
121.96
111.43
79.95
77.32
77.00
76.68
68.51
47.51
26.06
19.17
Me
OH
OH
Me
O
7c-oxi
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

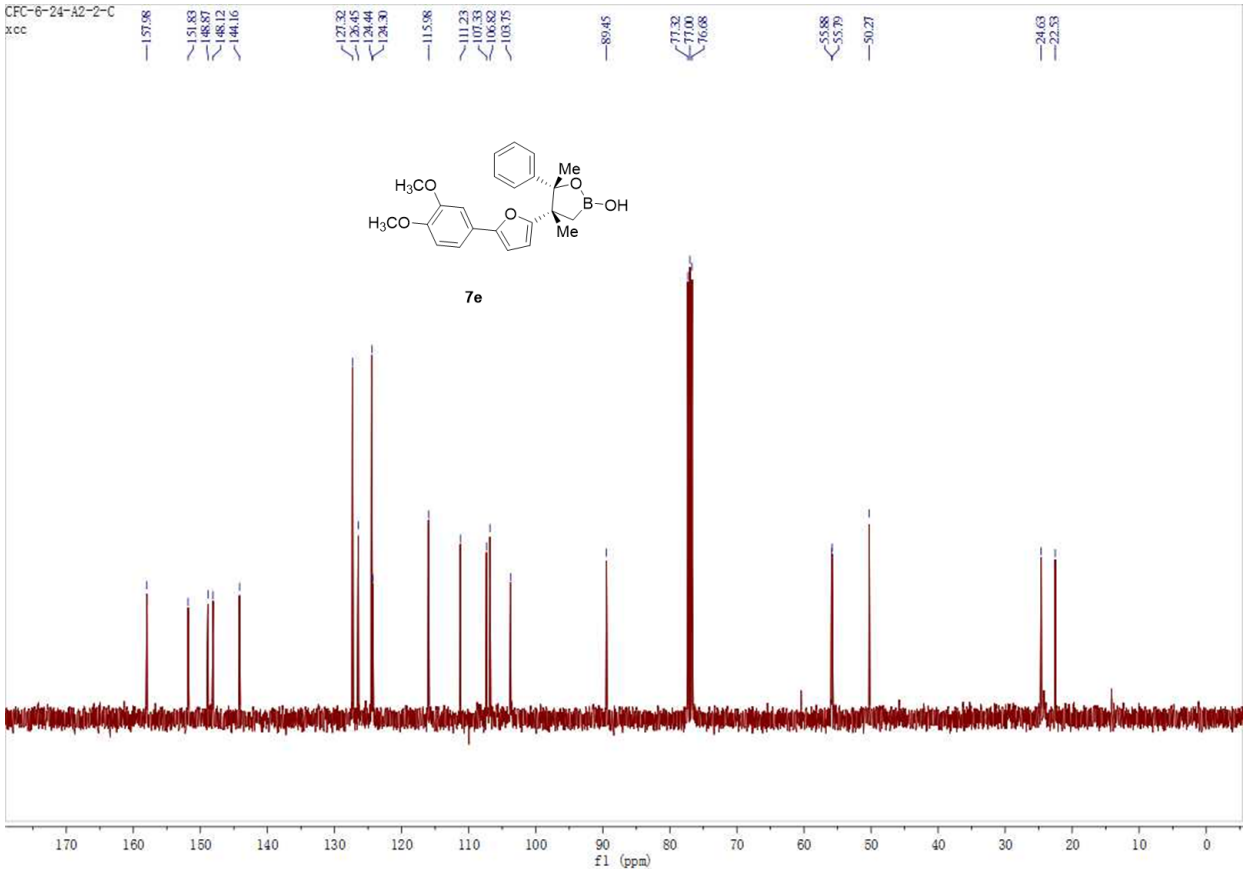

CFC-5-71-B2-H
CFC-5-71-B2-H
0.26
1.03
6.70 6.65 6.60 6.55 6.50 6.45 6.40 6.35 6.30
f1 (ppm)
Me
O
B–OH
O
Me
7d
1.92
1.47
1.43
1.26
2.10
2.93
1.30
4.04
0.26
1.03
1.00
3.08
3.99
1.42
1.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

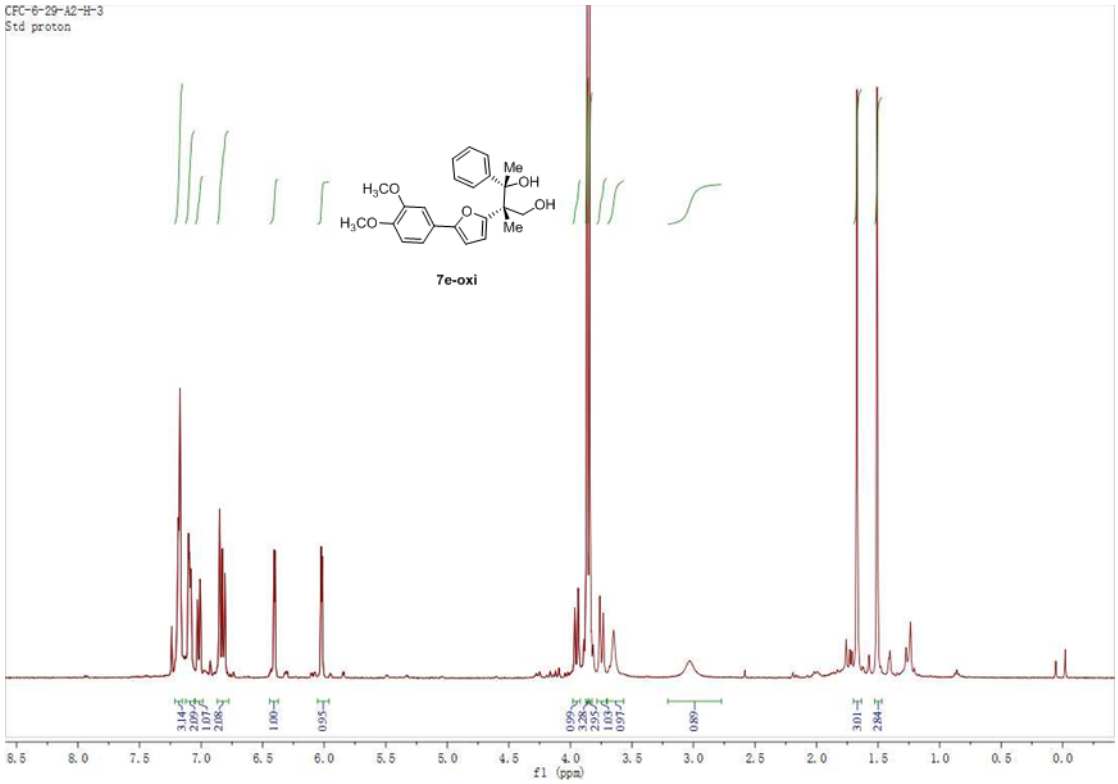

CFC-5-71-B2-C
xcc
138.60
151.93
144.00
130.88
128.44
127.37
126.76
126.51
124.42
123.28
107.49
105.12
89.60
77.32
77.00
76.68
50.18
24.66
22.68
Me
O
B–OH
O
Me
7d
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

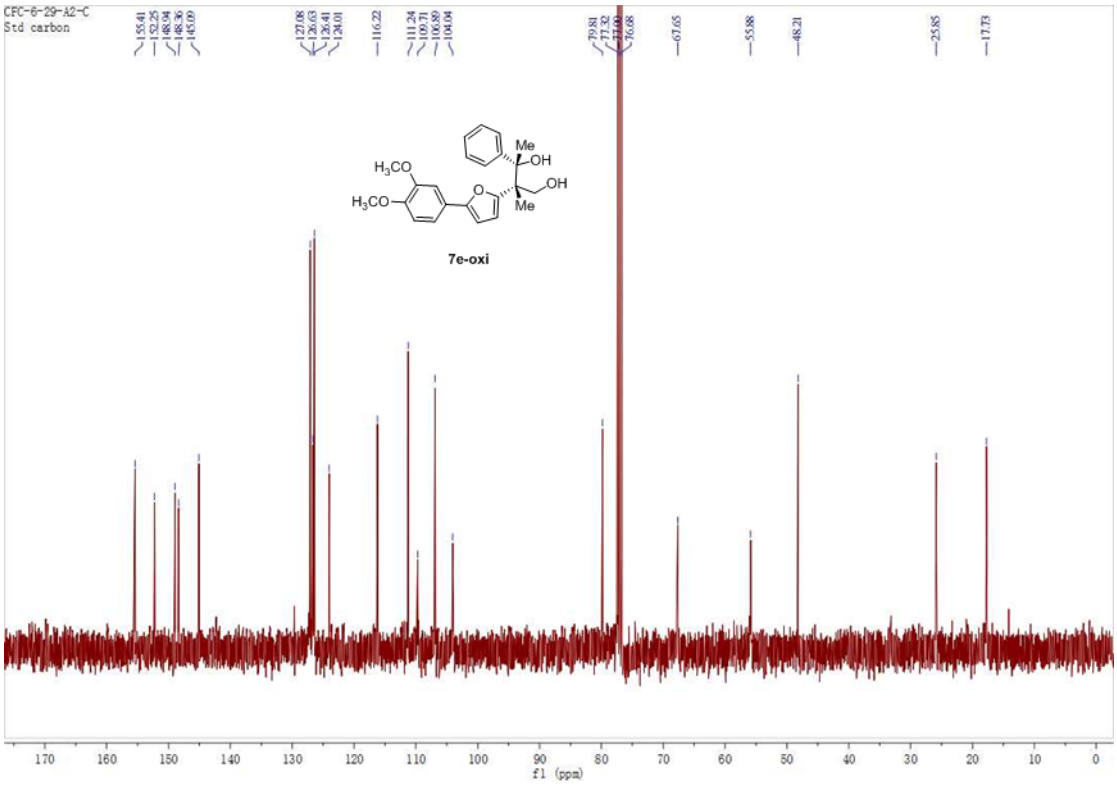

CFC-5-76-A2-H
Me
OH
OH
O
Me
7d-oxi
1.95
2.02
4.00
2.04
0.99
1.00
1.08
1.03
1.04
1.03
3.00
2.94
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

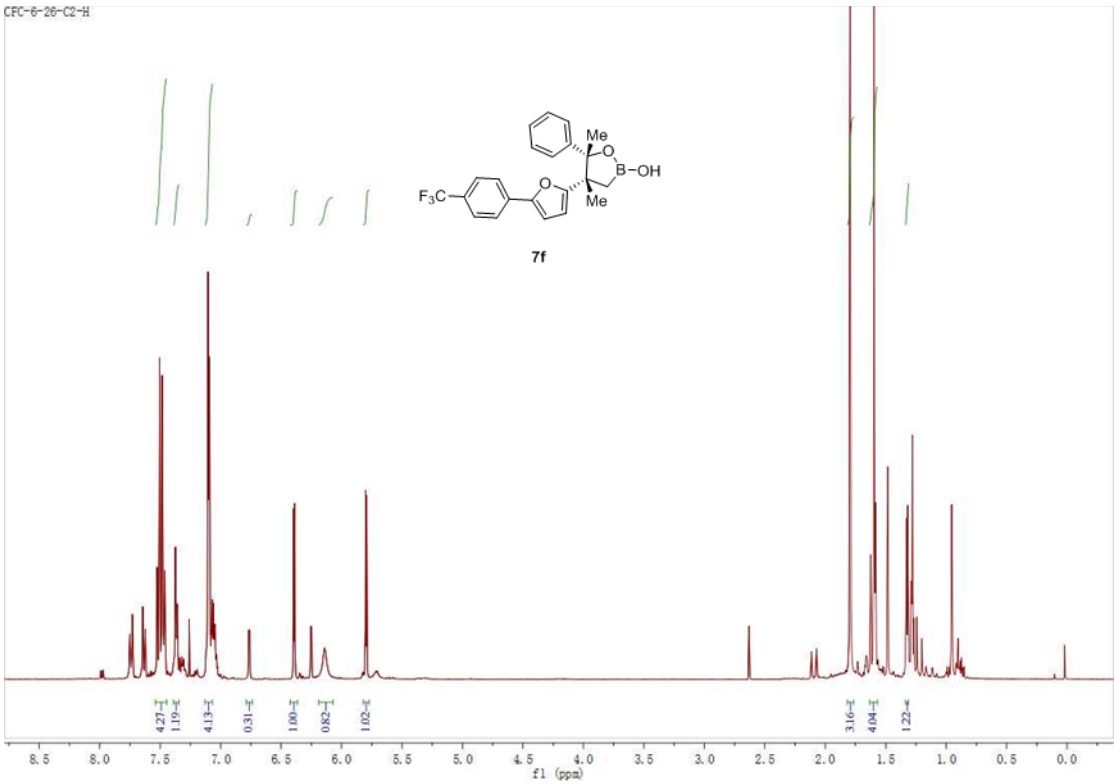

CFC-5-76-A2-C
xcc
156.15
152.39
144.87
130.68
128.59
127.17
127.14
126.76
126.57
123.47
109.82
105.40
79.78
77.32
77.00
76.68
67.69
48.40
26.05
17.75
Me
OH
OH
O
Me
7d-oxi
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

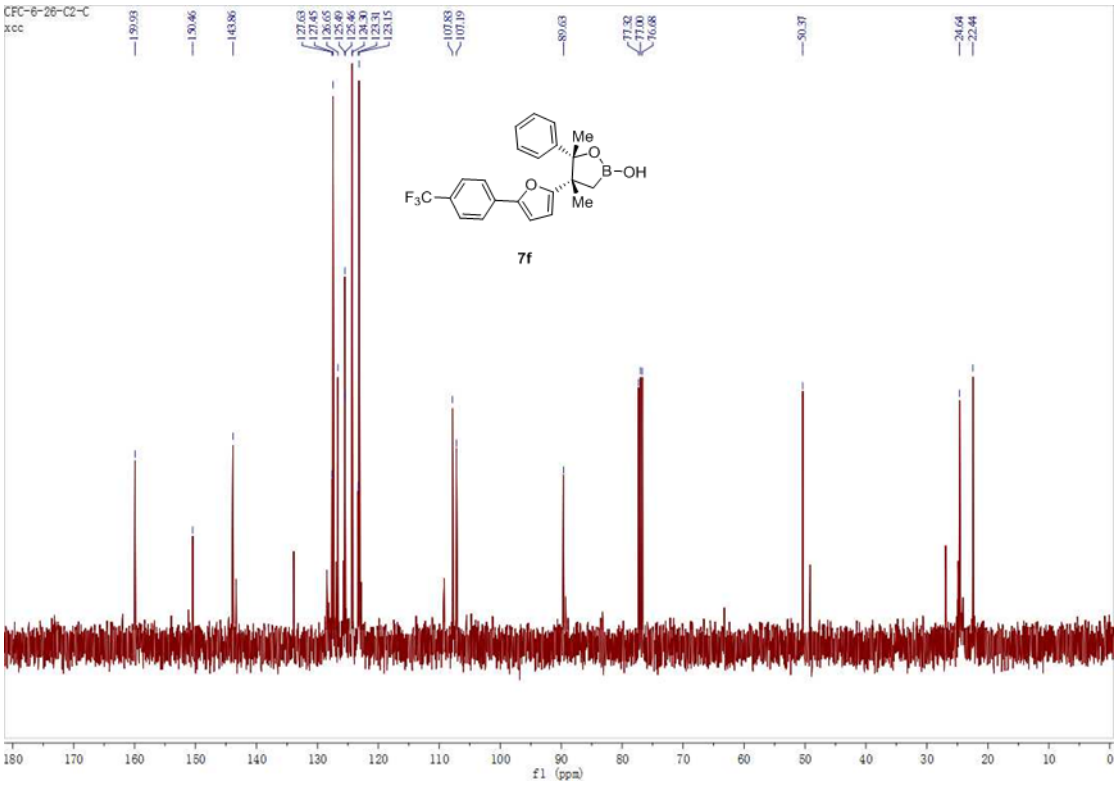

CFC-6-24-A2-2-H-3
Me
H3CO
H3CO
O
B–OH
O
Me
7e
6.34
1.06
0.95
1.00
0.93
1.04
3.07
2.81
3.18
4.20
1.46
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

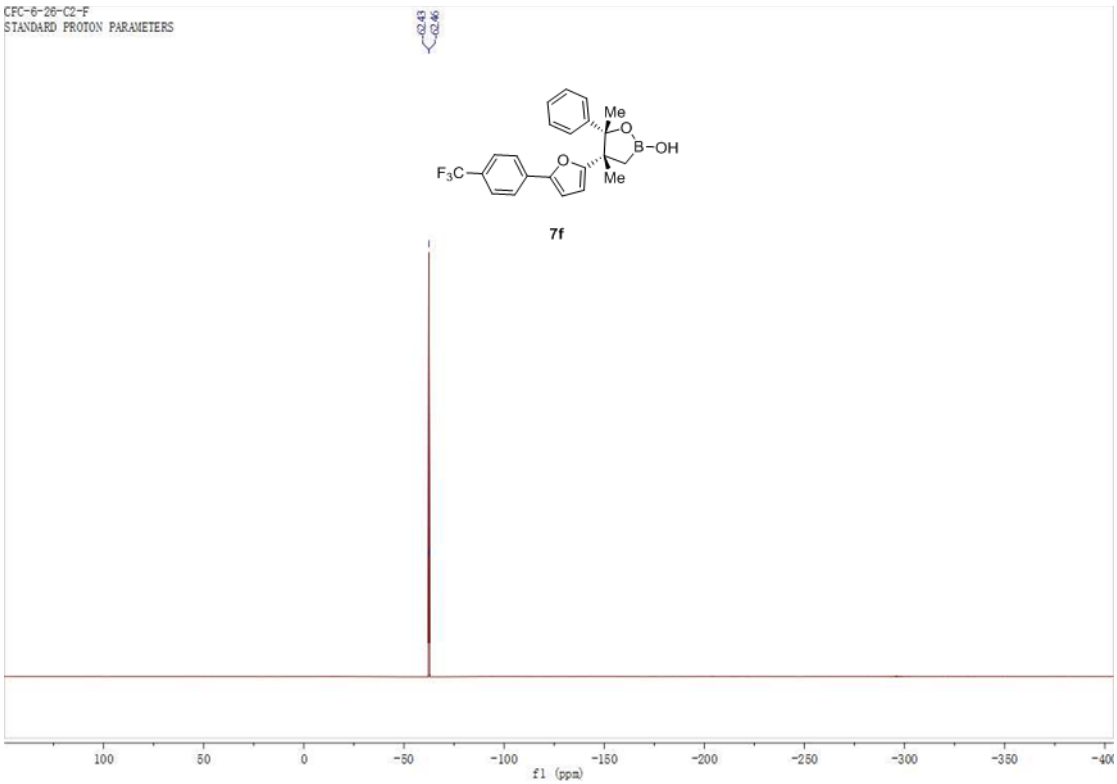

CFC-6-24-A2-2-C
xcc
157.98
151.83
148.87
148.12
144.16
127.32
126.45
124.44
124.30
115.98
111.23
107.33
106.82
103.75
89.45
77.32
77.00
76.68
55.88
55.79
50.27
24.63
22.53
H3CO
H3CO
Me
O
B-OH
O
Me
7e
f1 (ppm)

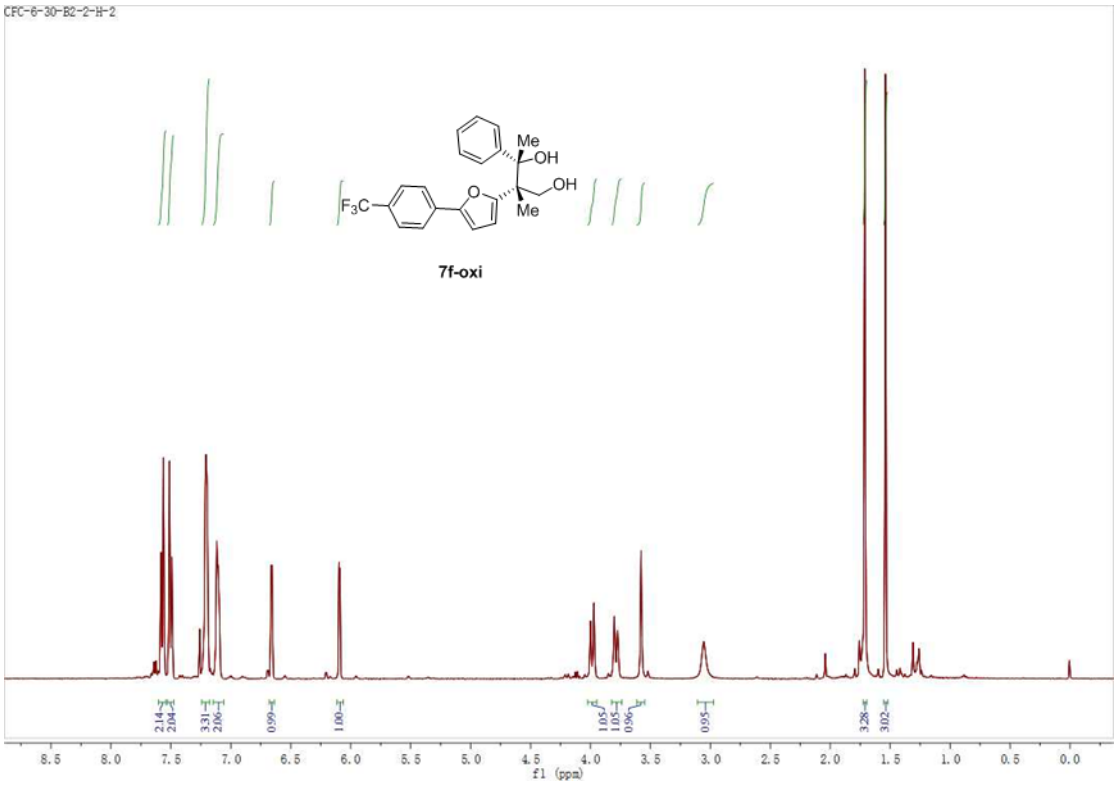

CFC-6-29-A2-H-3
Std proton
H3CO
H3CO
Me
OH
OH
Me
7e-oxi
3.14
2.09
1.07
2.08
1.00
0.93
0.99
3.28
2.95
1.03
0.97
0.89
3.01
2.84
f1 (ppm)

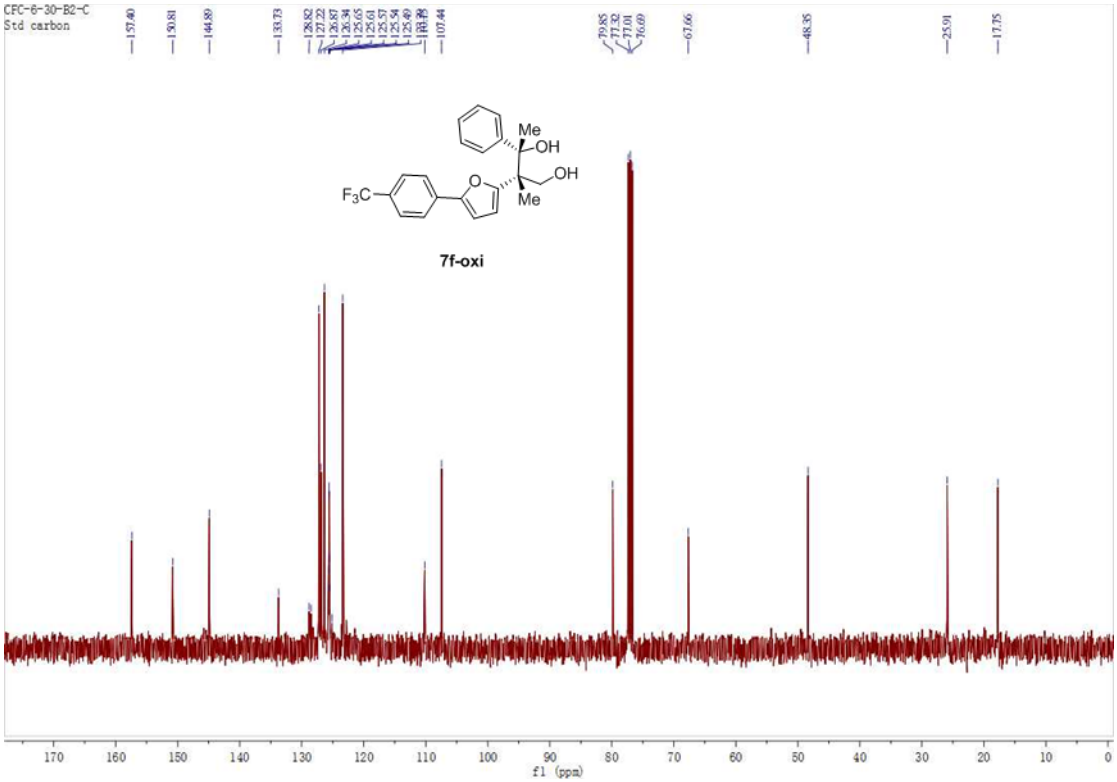

CFC-6-29-A2-C
Std carbon
155.41
152.25
148.94
148.36
145.69
127.08
126.63
126.41
124.01
116.22
111.24
109.71
106.89
104.04
79.81
77.32
77.00
76.68
67.65
55.88
48.21
25.85
17.73
Me
OH
OH
Me
H3CO
H3CO
O
7e-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

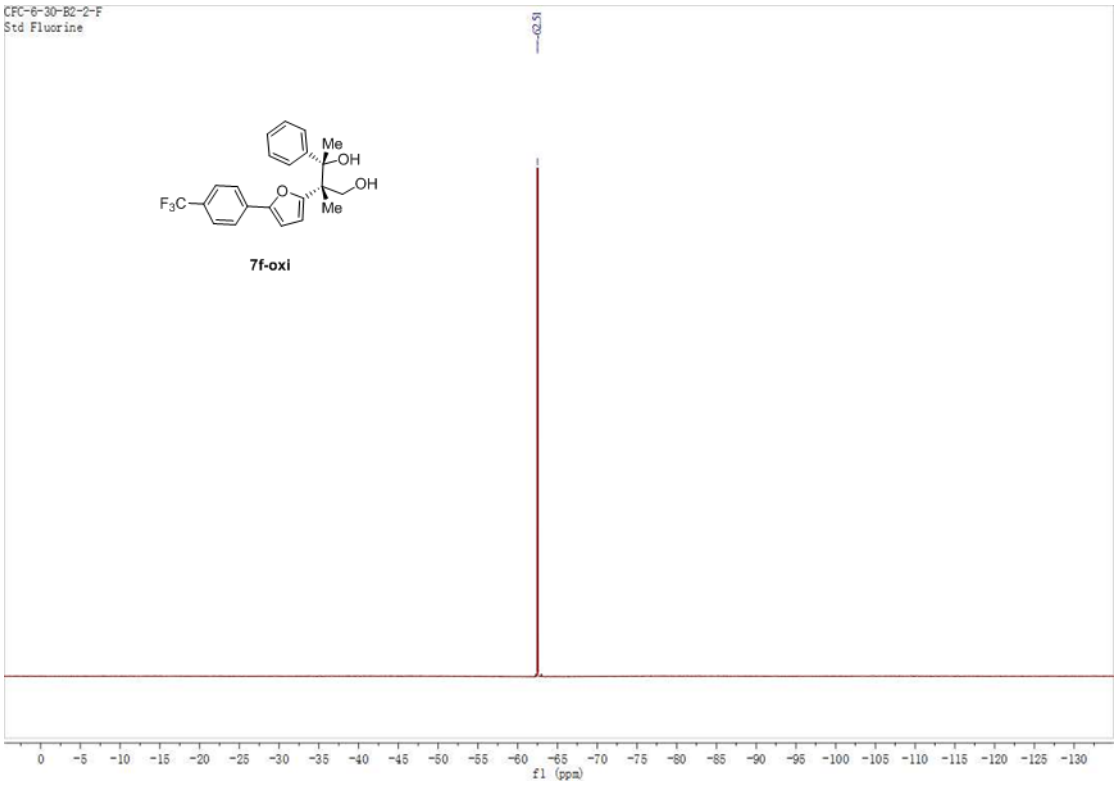

CFC-6-26-C2-H
Me
O
B-OH
F3C
O
Me
7f
4.27
1.19
4.13
0.31
1.00
0.82
1.02
3.16
4.04
1.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

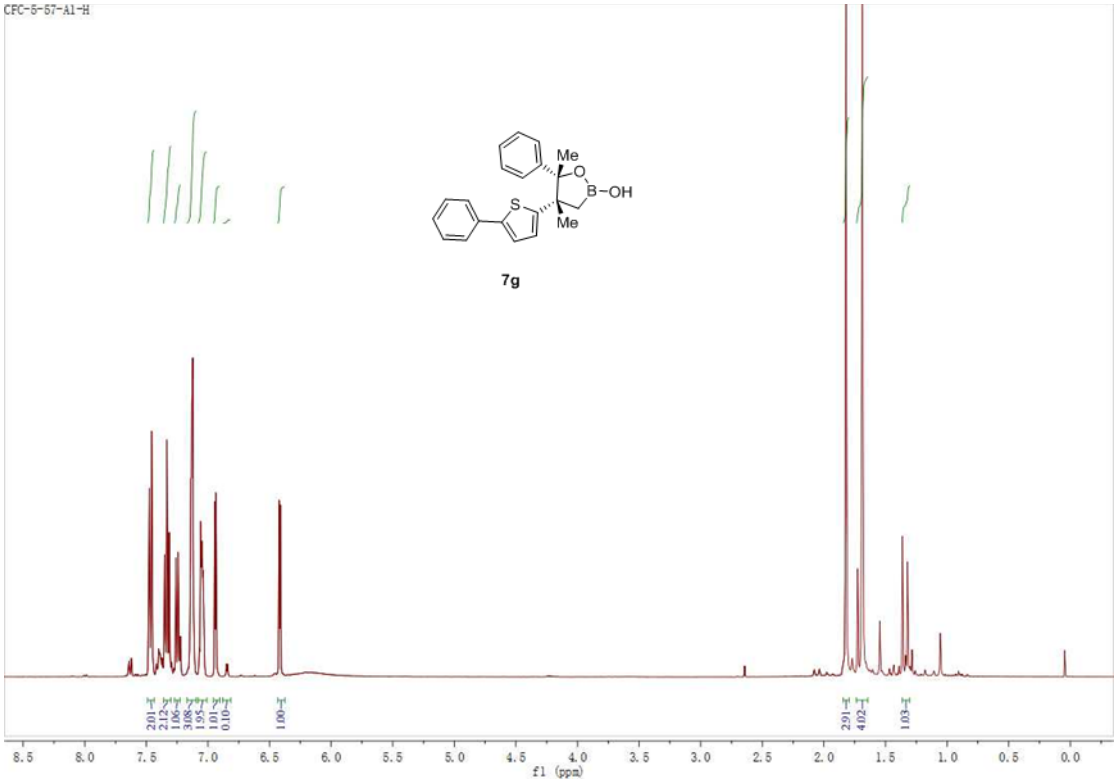

CFC-6-26-C2-C
xcc
159.93
150.46
143.86
127.63
127.45
126.65
125.49
125.46
124.30
123.31
123.15
107.83
107.19
89.63
77.32
77.00
76.68
50.37
24.64
22.44
Me
O
B–OH
F3C
O
Me
7f
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

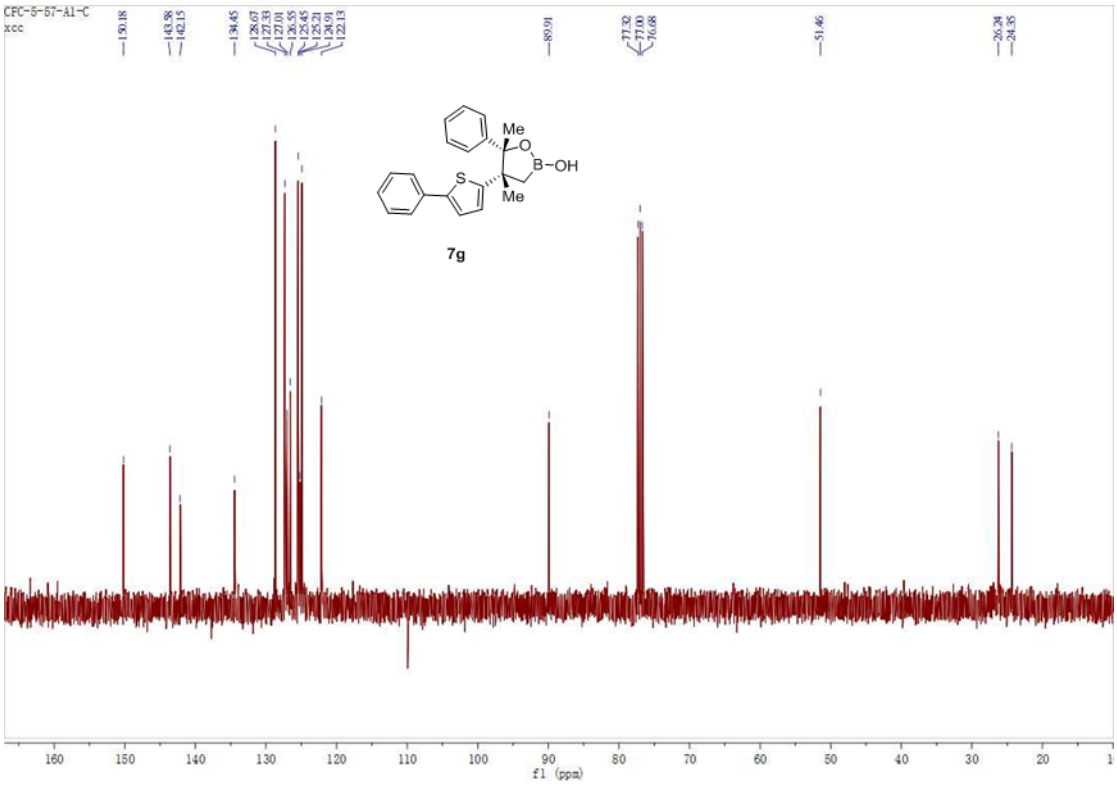

CFC-6-26-C2-F
STANDARD PROTON PARAMETERS
62.43
62.46
Me
O
B–OH
F3C
O
Me
7f
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
f1 (ppm)

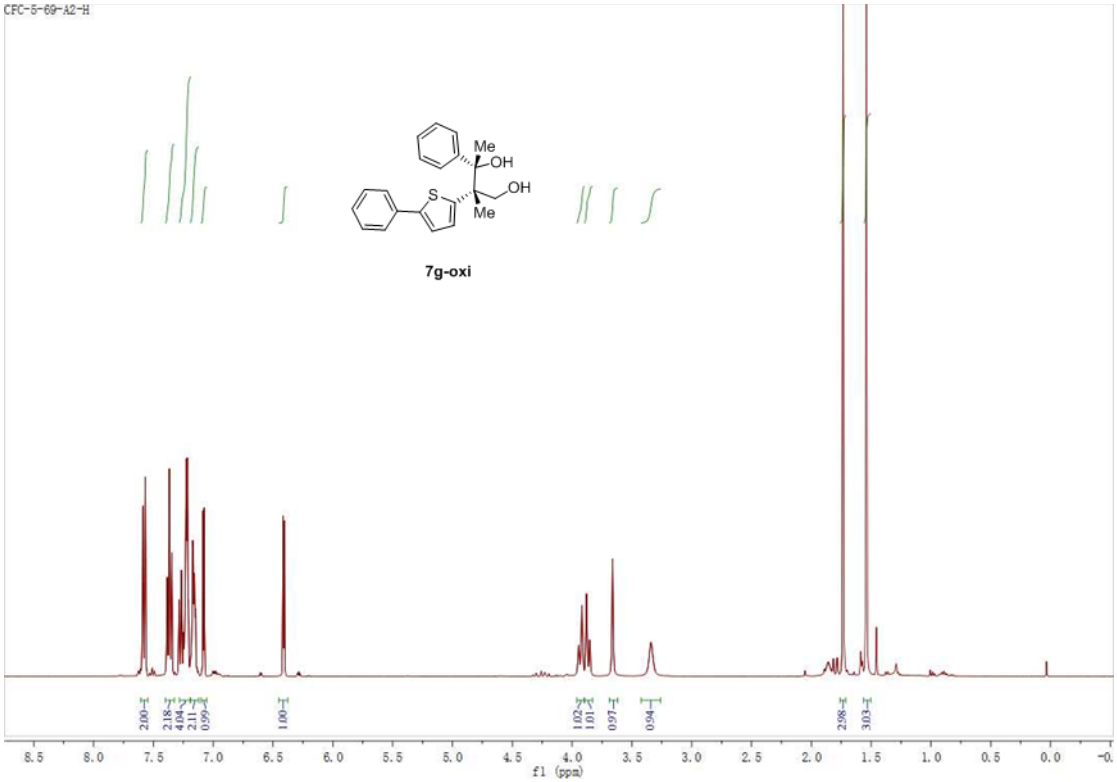

CFC-6-30-B2-2-H-2
Me
OH
OH
F3C
O
Me
7f-oxi
2.14
2.04
3.31
2.06
0.99
1.00
1.05
1.05
0.96
0.95
3.28
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

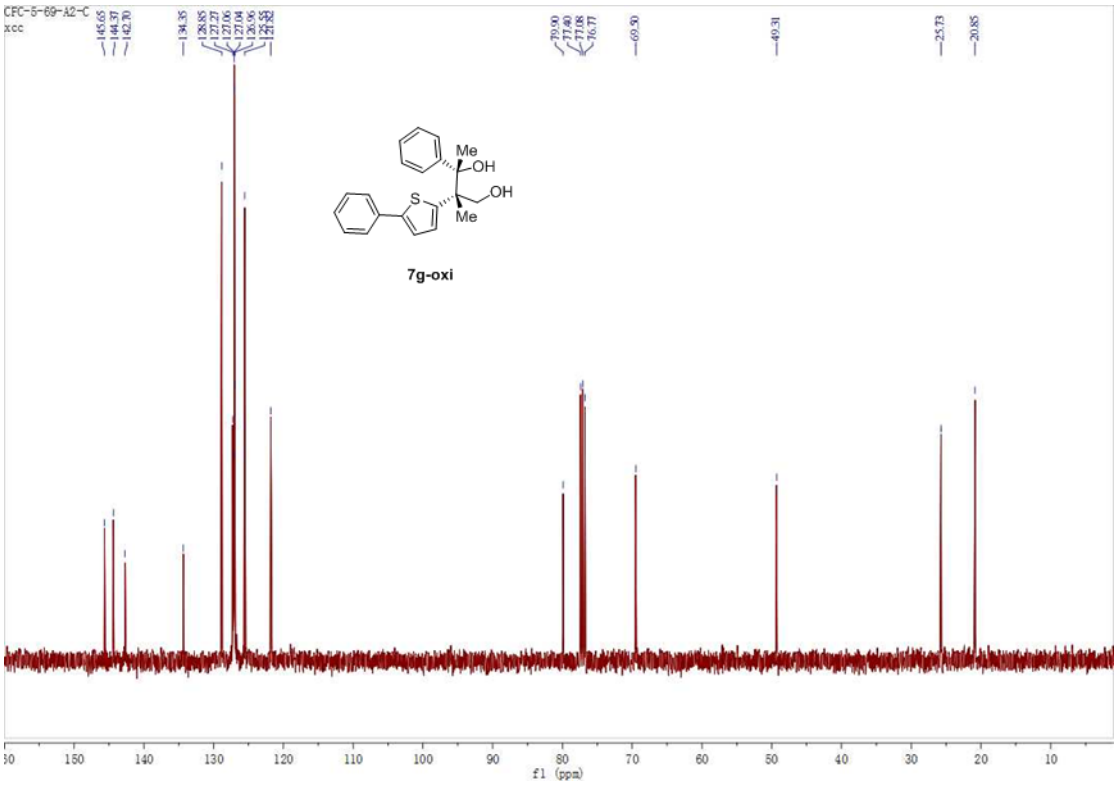

CFC-6-30-B2-C
Std carbon
157.40
150.81
144.89
133.73
126.82
127.22
126.87
126.34
125.65
125.61
125.57
125.54
125.49
107.44
79.85
77.32
77.01
76.69
67.66
48.35
25.91
17.75
Me
OH
OH
F3C
O
Me
7f-oxi
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

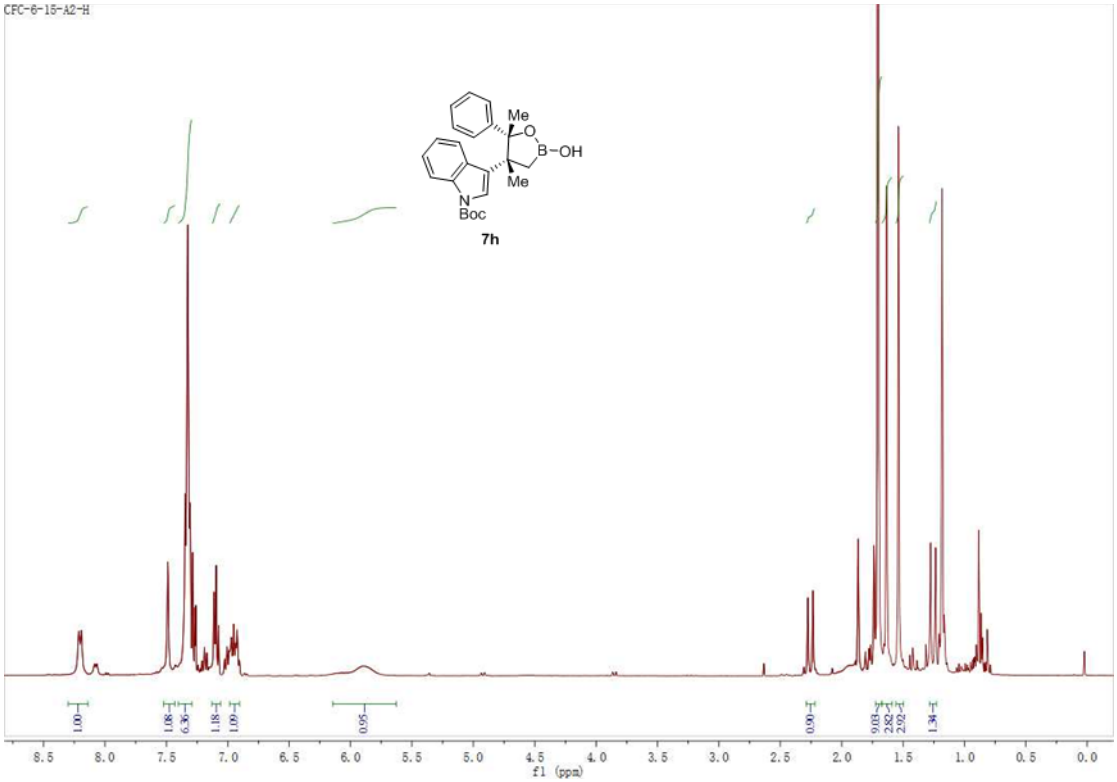

CFC-6-30-B2-2-F
Std Fluorine
-62.51
Me
OH
OH
Me
F3C
O
7f-oxi
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130
f1 (ppm)

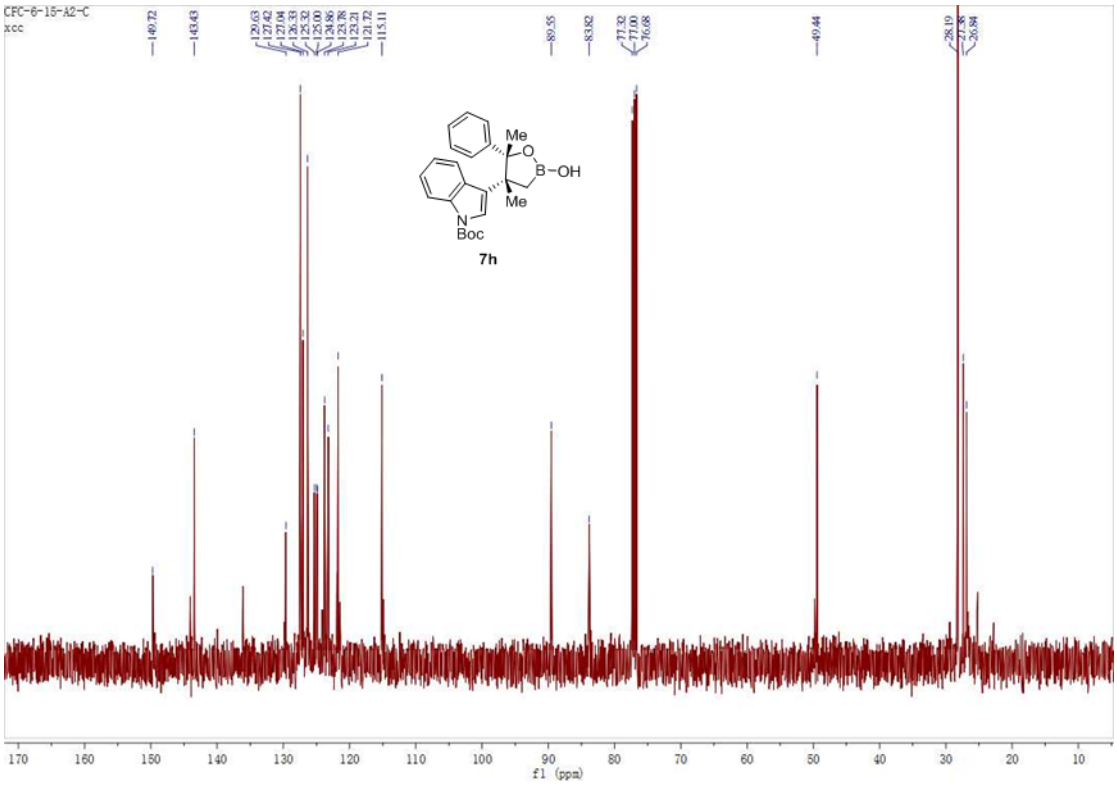

CFC-5-57-A1-H
Me
O
B–OH
S
Me
7g
2.01
2.12
2.06
3.08
1.95
1.01
0.10
1.00
2.91
4.02
1.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

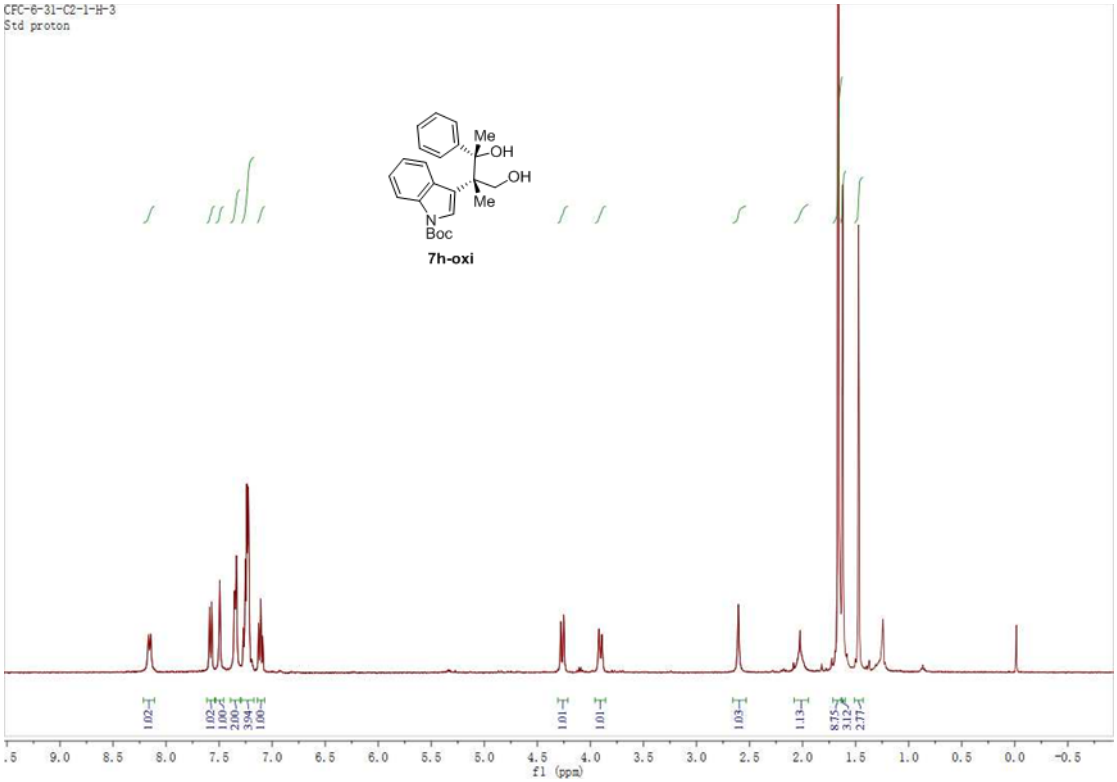

CFC-5-57-A1-C
xcc
150.18
143.58
142.15
134.45
126.67
127.33
127.01
126.55
125.45
125.31
124.91
122.13
89.91
77.32
77.00
76.68
51.46
26.24
24.35
Me
O
B–OH
S
Me
7g
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

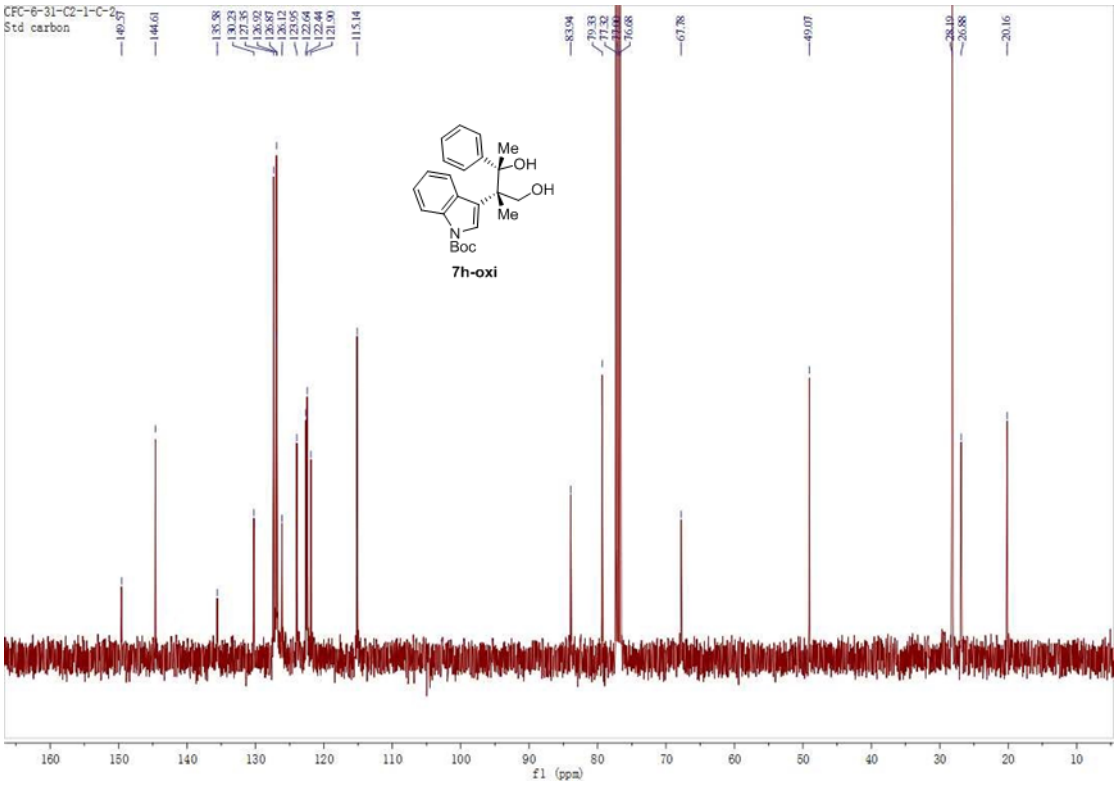

CFC-5-69-A2-H
Me
OH
OH
S
Me
7g-oxi
2.00
2.18
4.04
2.11
0.99
1.00
1.02
1.01
0.97
0.94
2.98
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

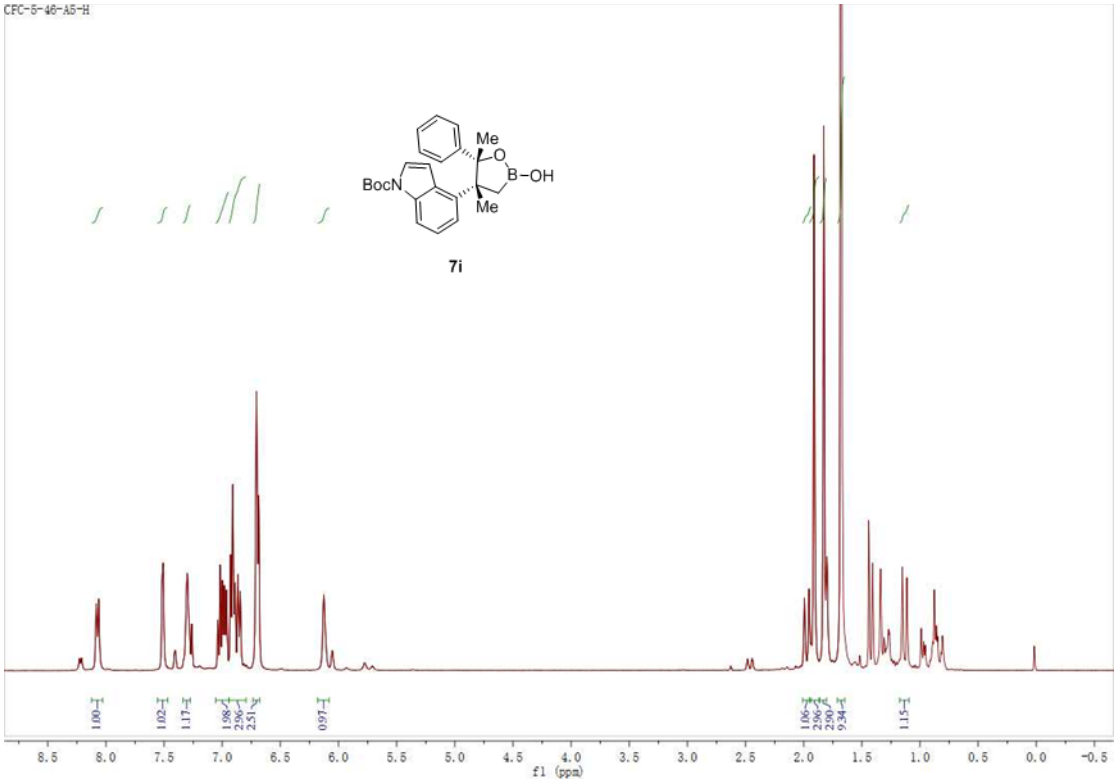

CFC-5-69-A2-C
xcc
145.65
144.37
142.70
134.35
128.85
127.27
127.06
127.04
126.06
79.90
77.40
77.08
76.77
69.50
49.31
25.73
20.85
Me
OH
OH
S
Me
7g-oxi
f1 (ppm)

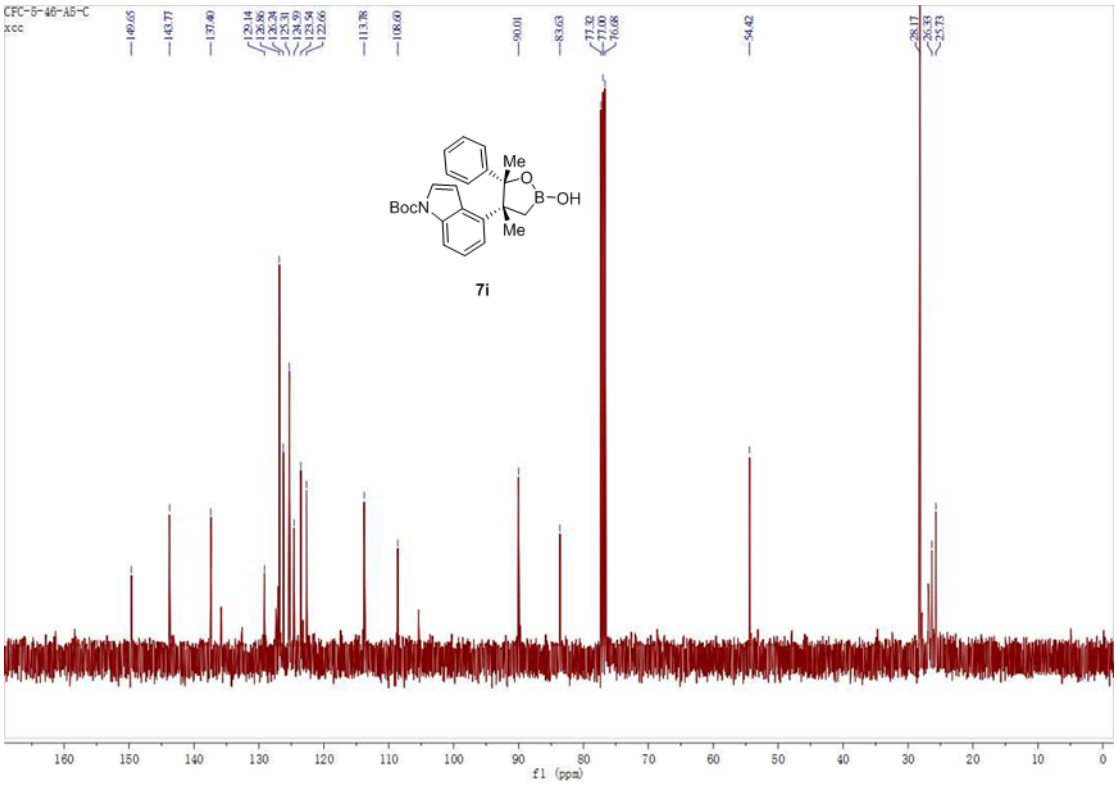

CFC-6-15-A2-H
Me
O
B–OH
Me
N
Boc
7h
1.00
1.08
6.30
1.18
1.09
0.95
0.90
9.03
2.82
2.92
1.34
f1 (ppm)

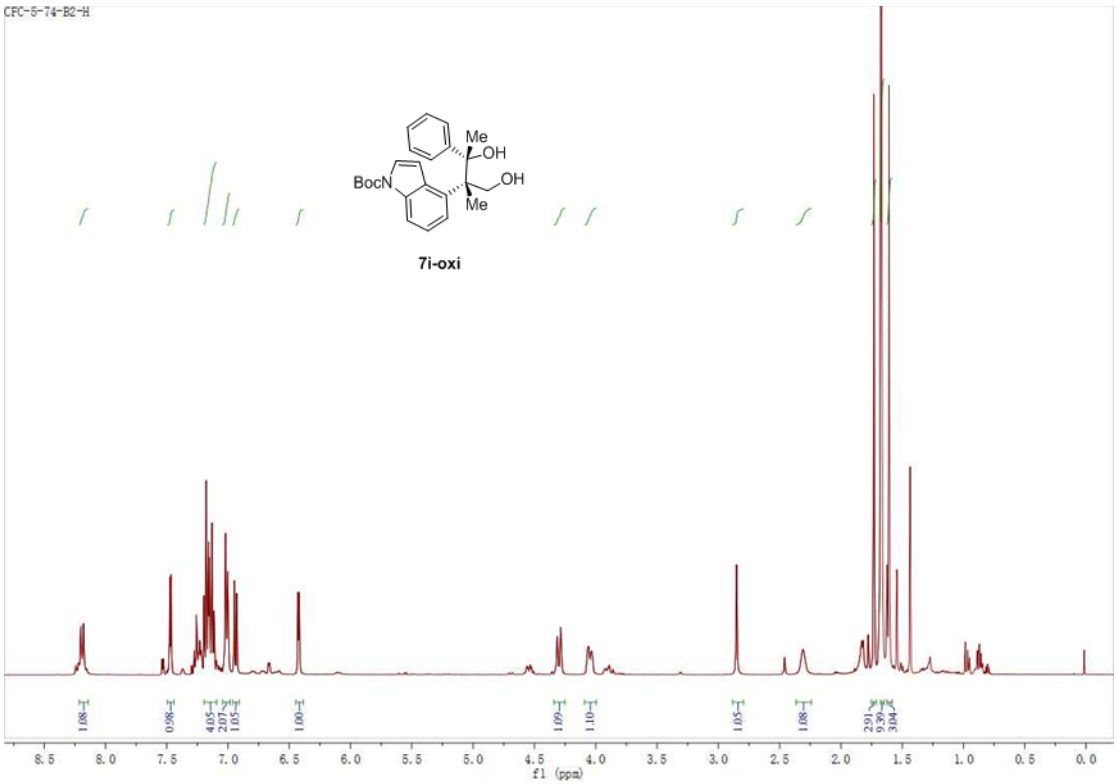

CFC-6-15-A2-C
xcc
Me
O
B–OH
Me
N
Boc
7h
f1 (ppm)

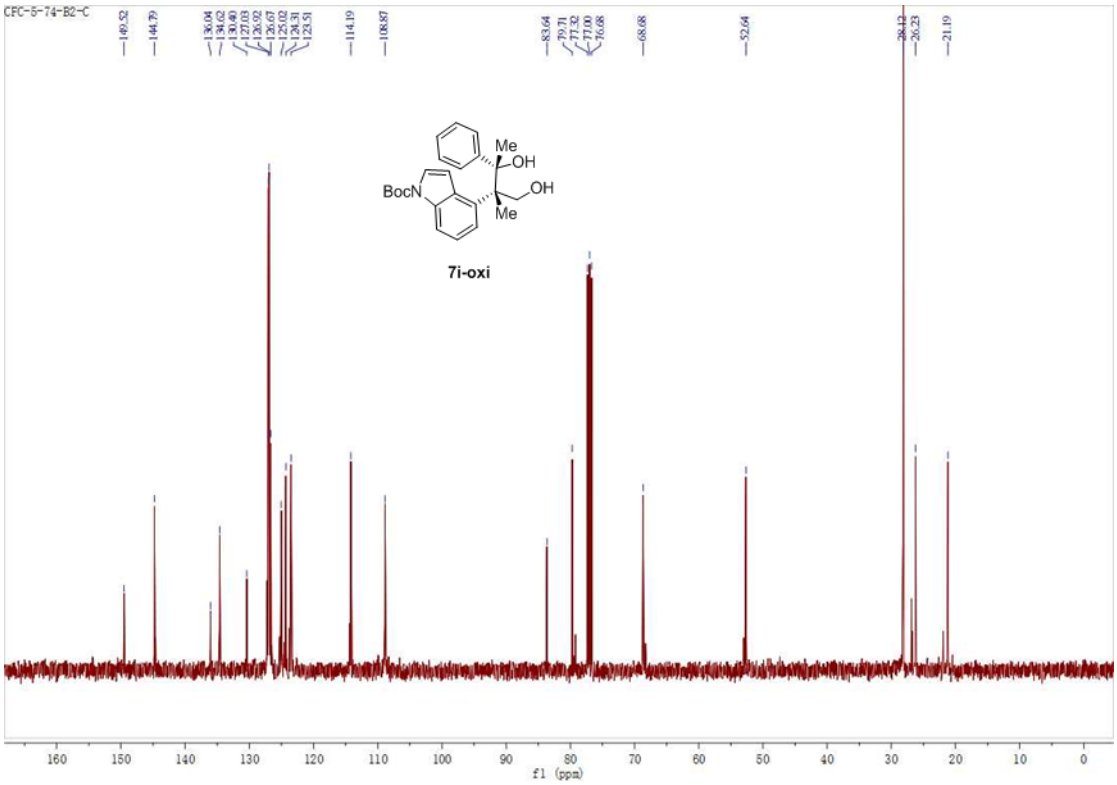

CFC-6-31-C2-1-H-3
Std proton
Me
OH
OH
Me
N
Boc
7h-oxi
f1 (ppm)

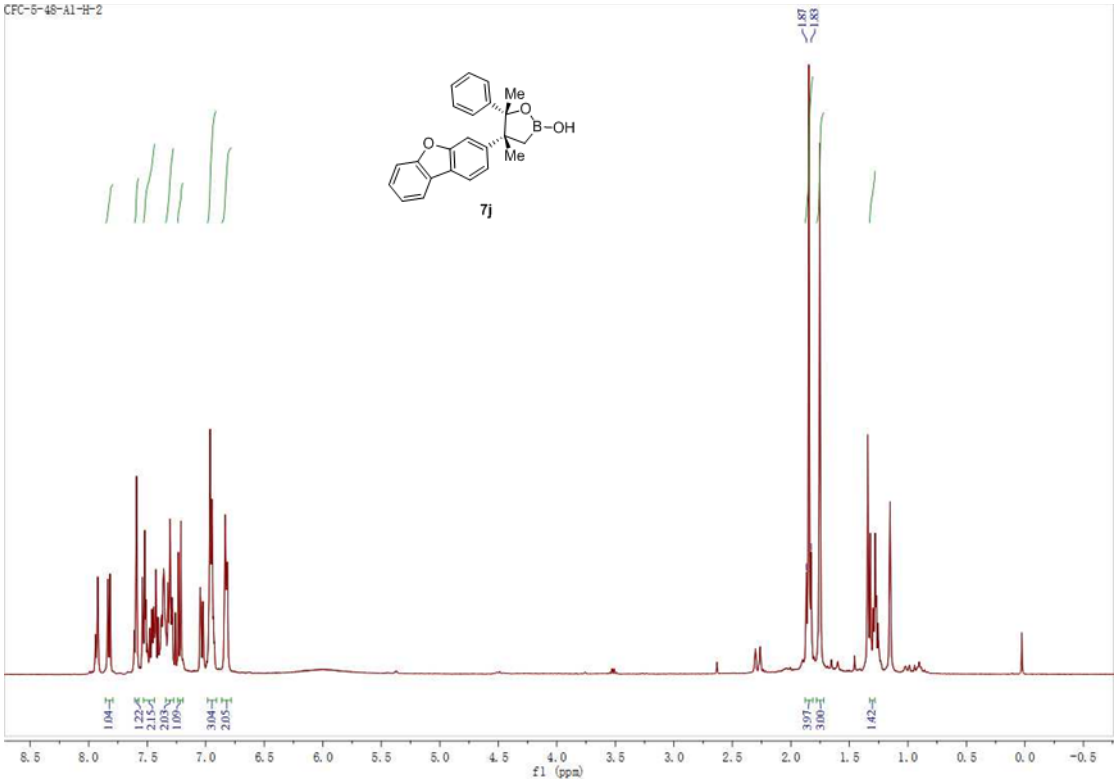

CFC-6-31-C2-1-C-2
Std carbon
Me
OH
OH
Me
N
Boc
7h-oxi
f1 (ppm)

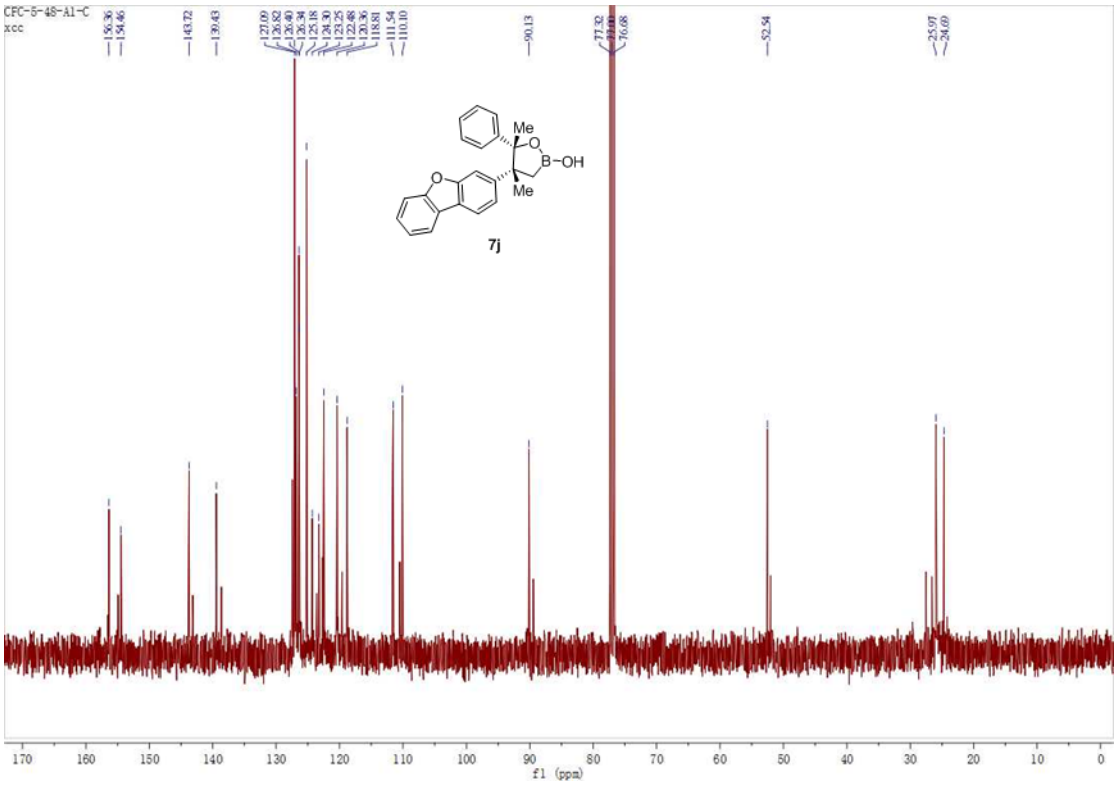

CFC-5-46-A5-H
Me
O
B–OH
BocN
Me
7i
f1 (ppm)

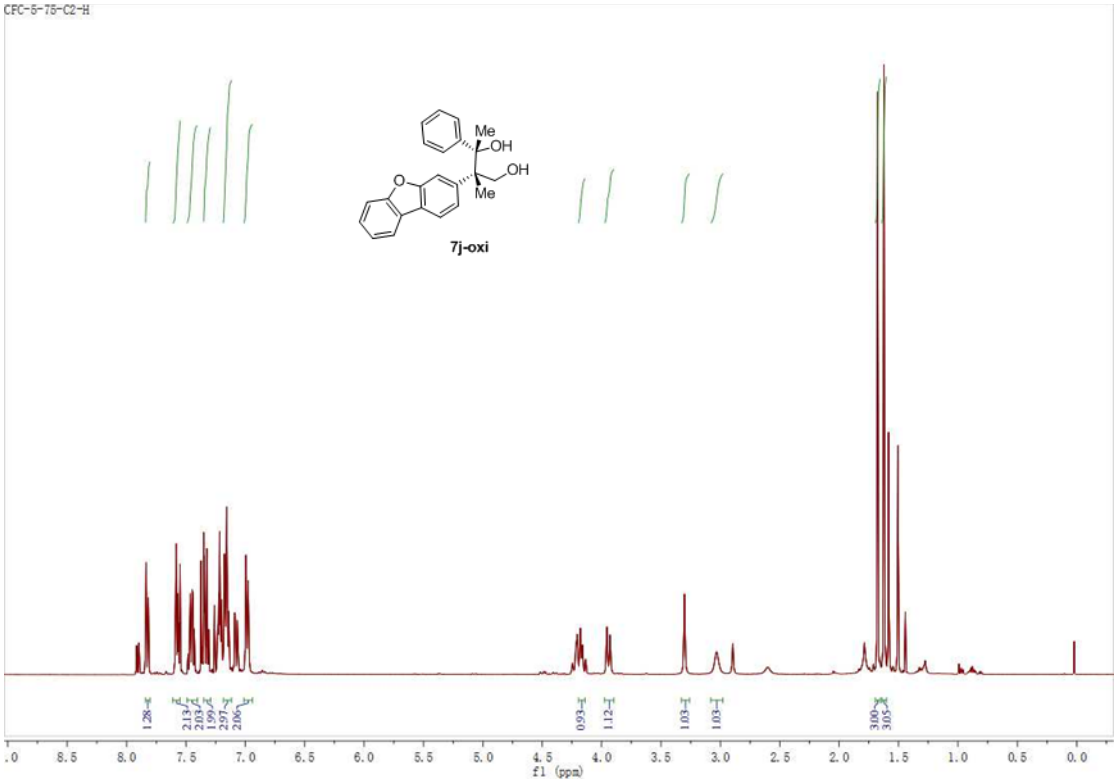

CFC-5-46-A5-C
xcc
149.65
143.77
137.40
129.14
126.96
126.34
125.31
124.59
123.54
122.66
113.78
108.60
90.01
83.63
77.32
77.00
76.68
54.42
28.17
26.33
25.73
Me
O
B–OH
BocN
Me
7i
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

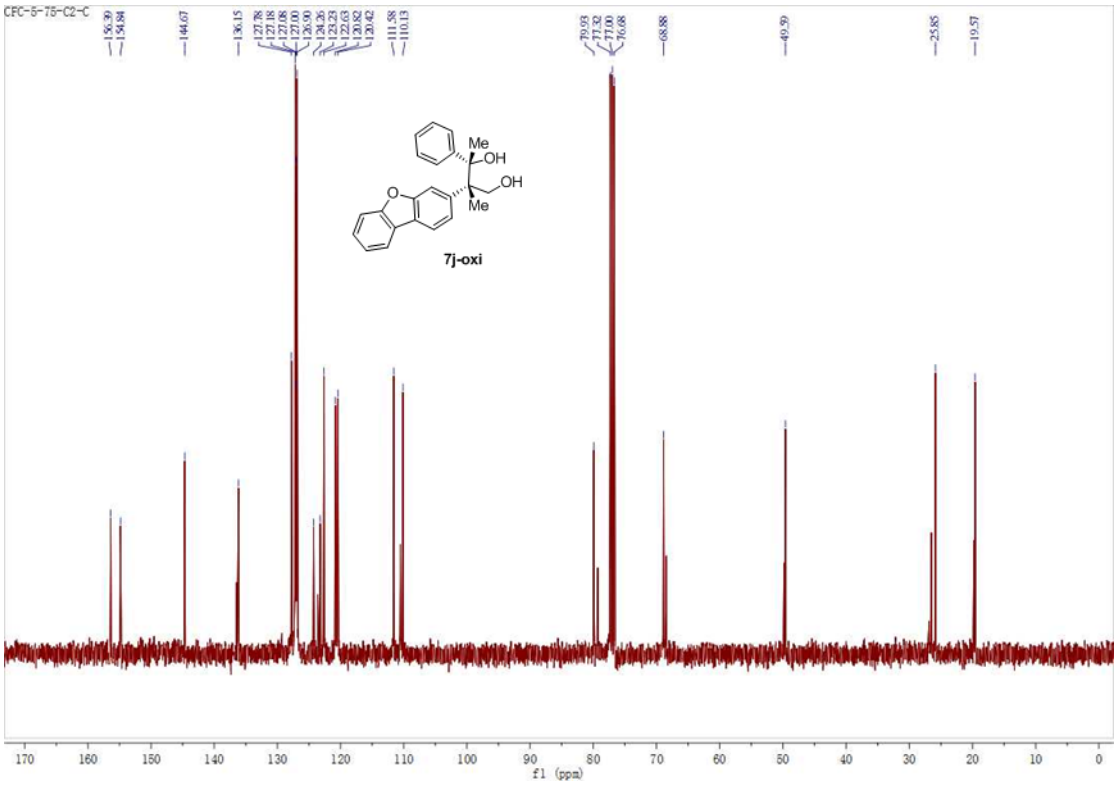

CFC-5-74-B2-H
Me
OH
OH
BocN
Me
7i-oxi
1.08
0.58
4.05
2.07
1.05
1.00
1.09
1.10
1.05
1.08
2.91
9.39
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

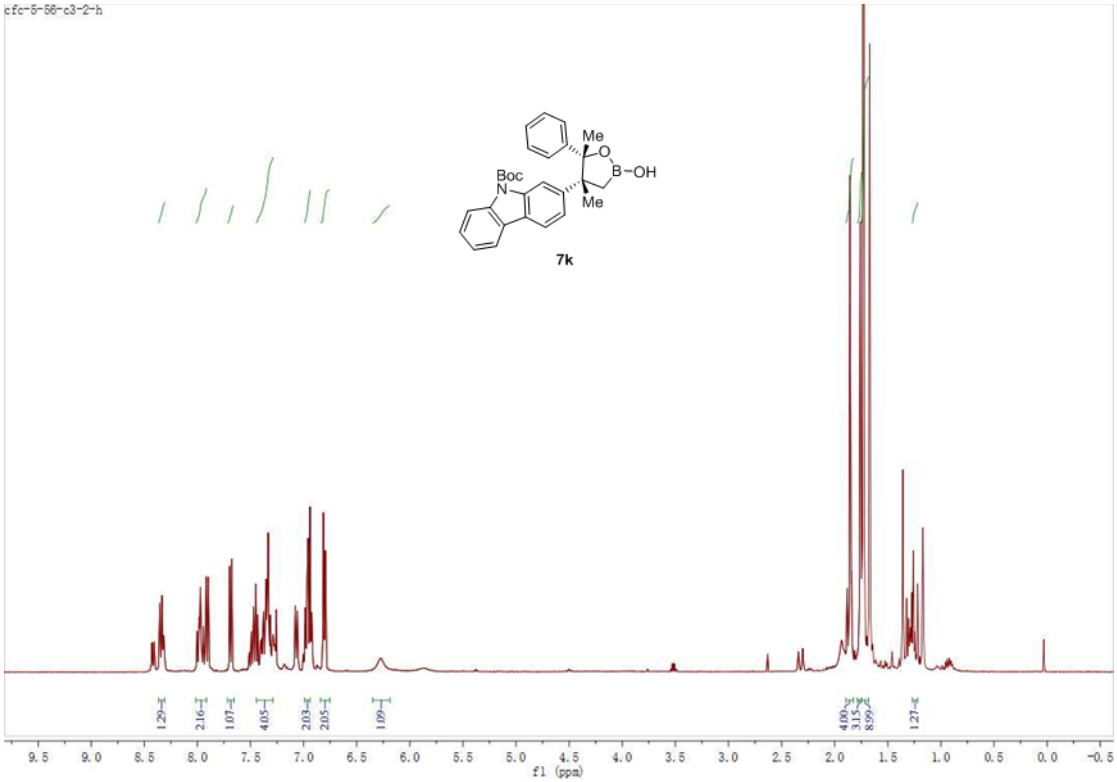

CFC-5-74-B2-C
149.52
144.79
136.04
134.62
130.60
127.03
126.92
126.67
125.02
124.31
123.51
114.19
108.87
83.64
79.71
77.32
77.00
76.68
68.68
52.64
28.12
26.23
21.19
Me
OH
OH
BocN
Me
7i-oxi
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

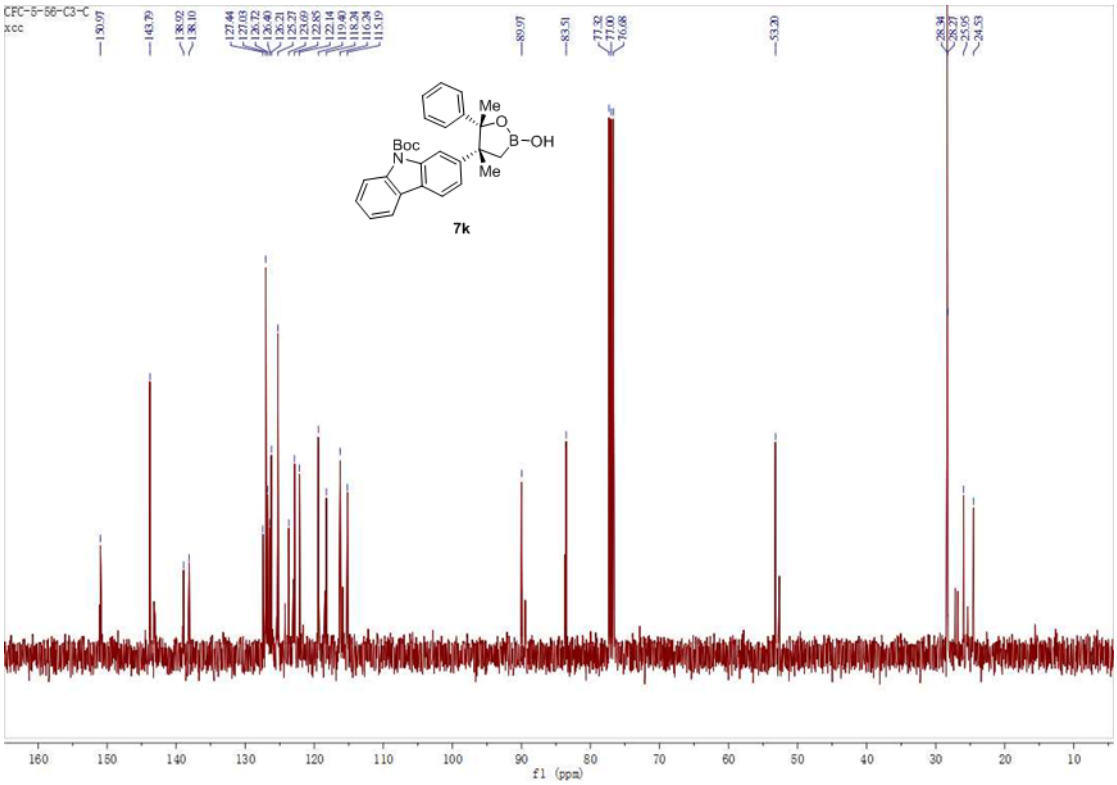

CFC-5-48-A1-H-2
1.87
1.83
Me
O
B–OH
Me
O
7j
1.04
1.22
2.15
2.03
1.09
3.04
2.05
3.97
3.00
1.42
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

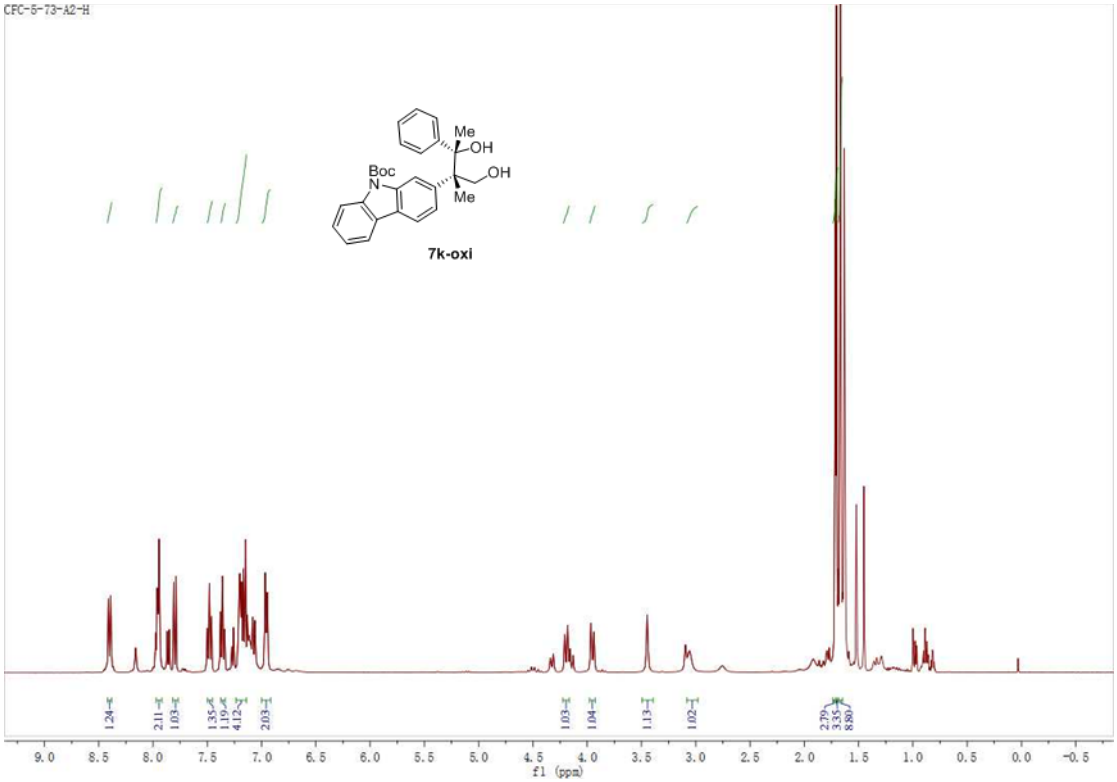

CFC-5-48-A1-C
xcc
Me
O
B–OH
Me
O
7j
f1 (ppm)

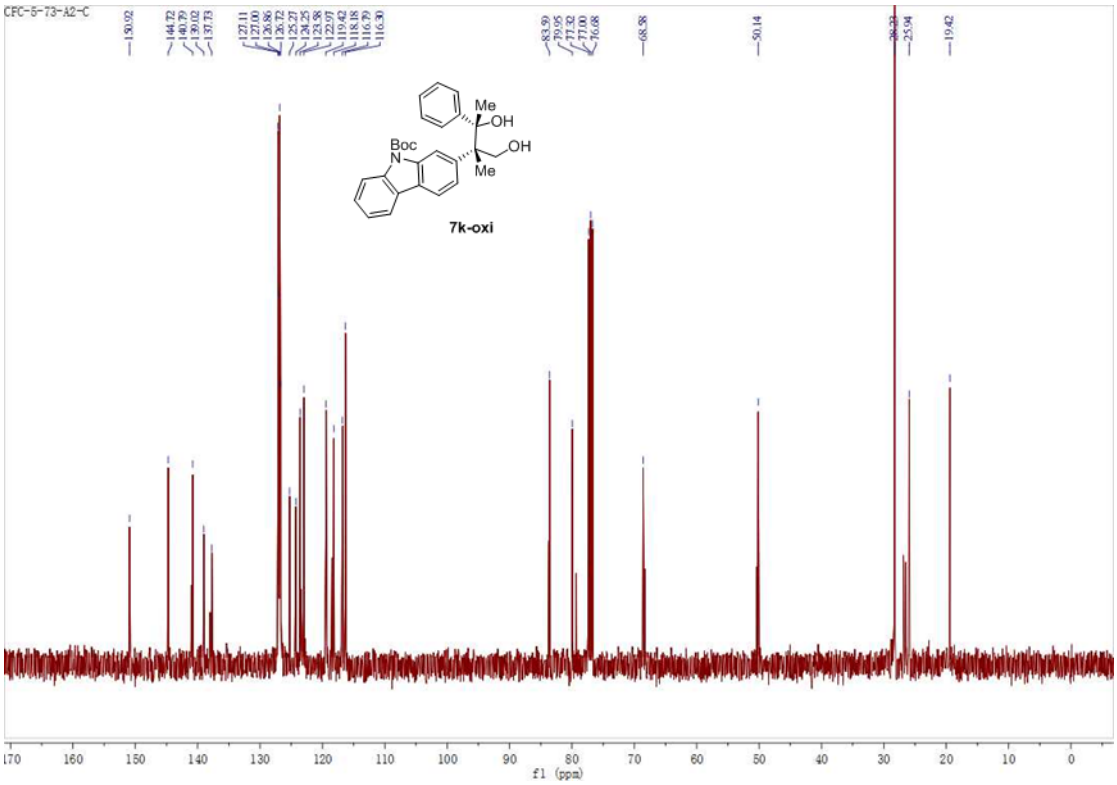

CFC-5-75-C2-H
Me
OH
OH
Me
O
7j-oxi
f1 (ppm)

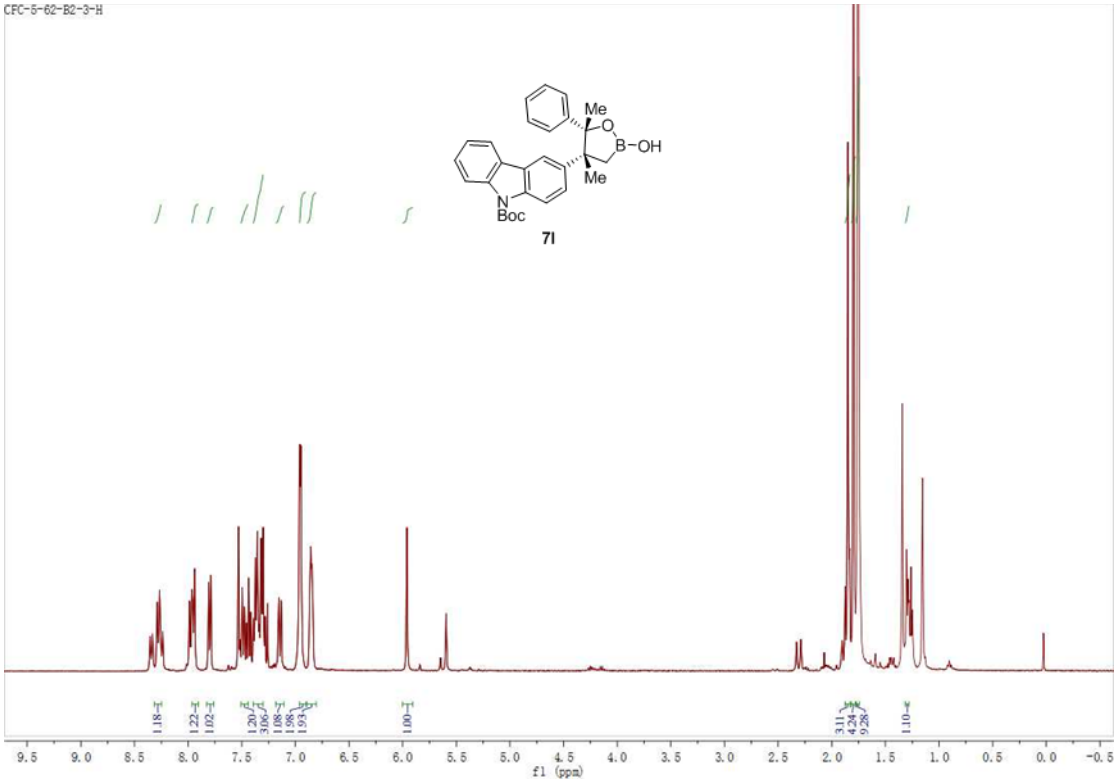

CFC-5-75-C2-C
156.39
154.84
144.67
136.15
127.28
127.18
127.08
127.00
126.90
124.26
123.23
120.63
120.42
111.58
110.13
79.93
77.32
77.00
76.68
68.88
49.59
25.85
19.57
Me
OH
OH
Me
O
7j-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

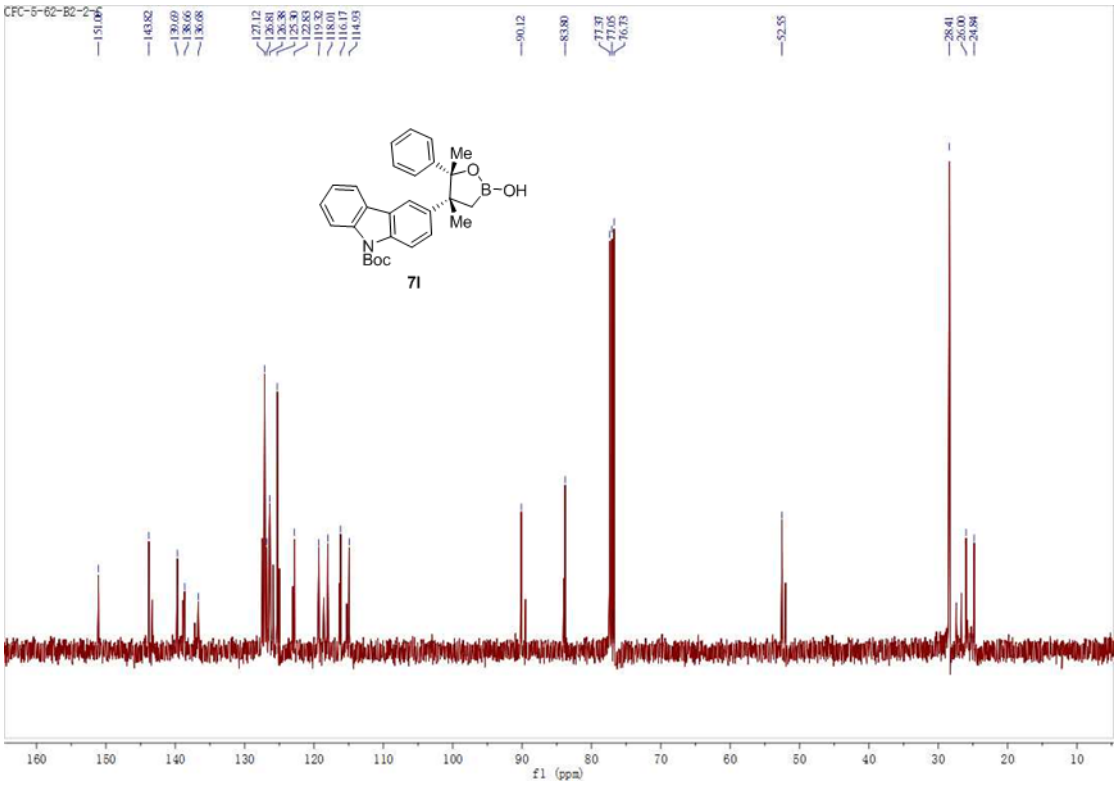

cfc-5-56-c3-2-h
Me
O
B–OH
Boc
N
Me
7k
1.29
2.16
1.07
4.05
2.03
2.05
1.09
4.00
3.15
8.99
1.27
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

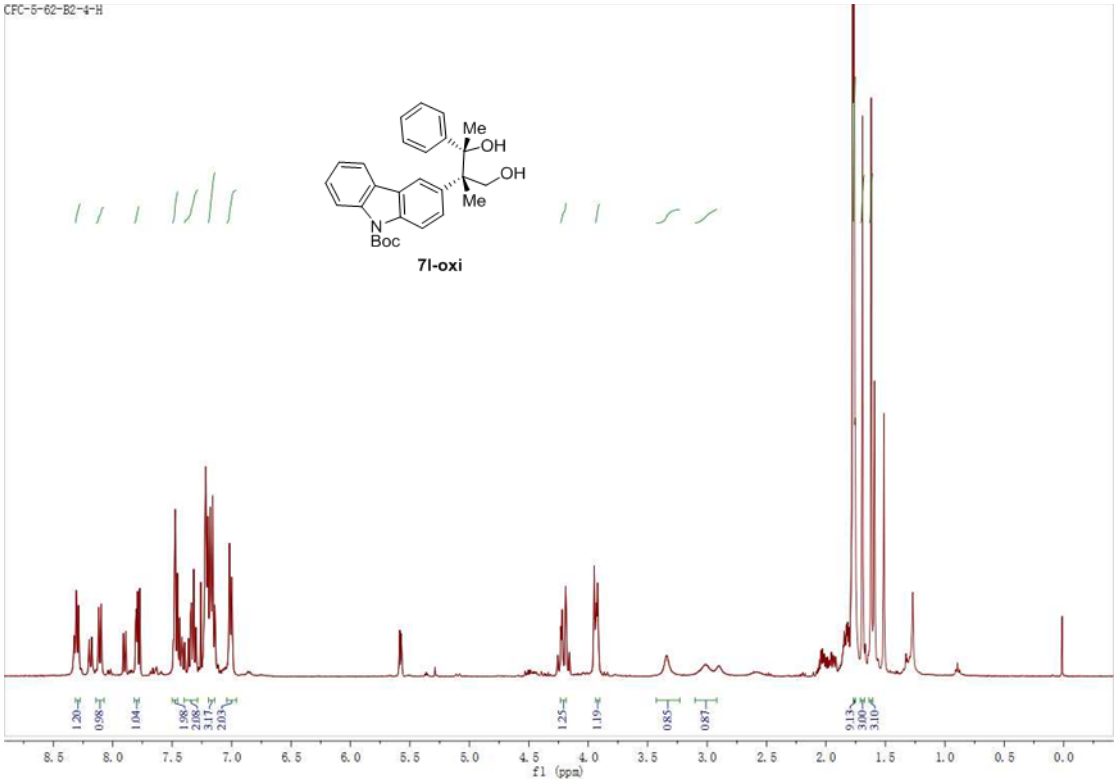

CFC-5-56-C3-C
xcc
Me
O
B–OH
Boc
N
Me
7k
f1 (ppm)

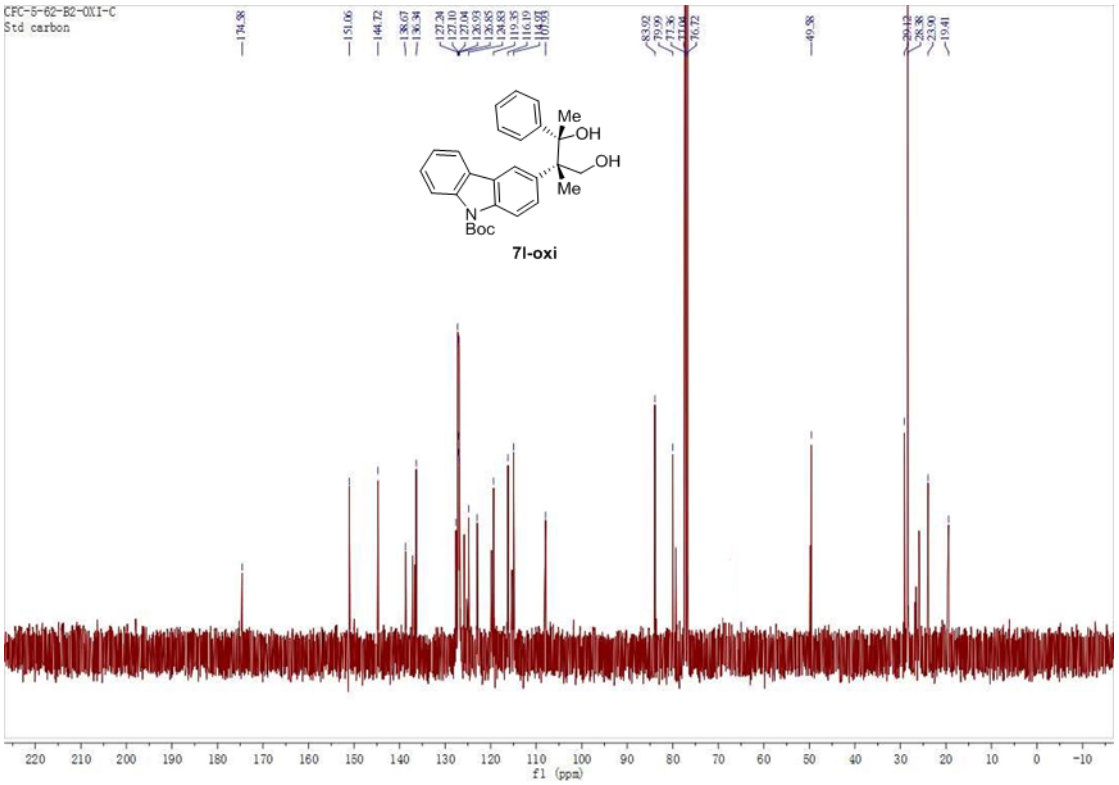

CFC-5-73-A2-H
Me
OH
OH
Boc
N
Me
7k-oxi
f1 (ppm)


CFC-5-73-A2-C
Me
OH
OH
Boc
N
Me
7k-oxi
f1 (ppm)

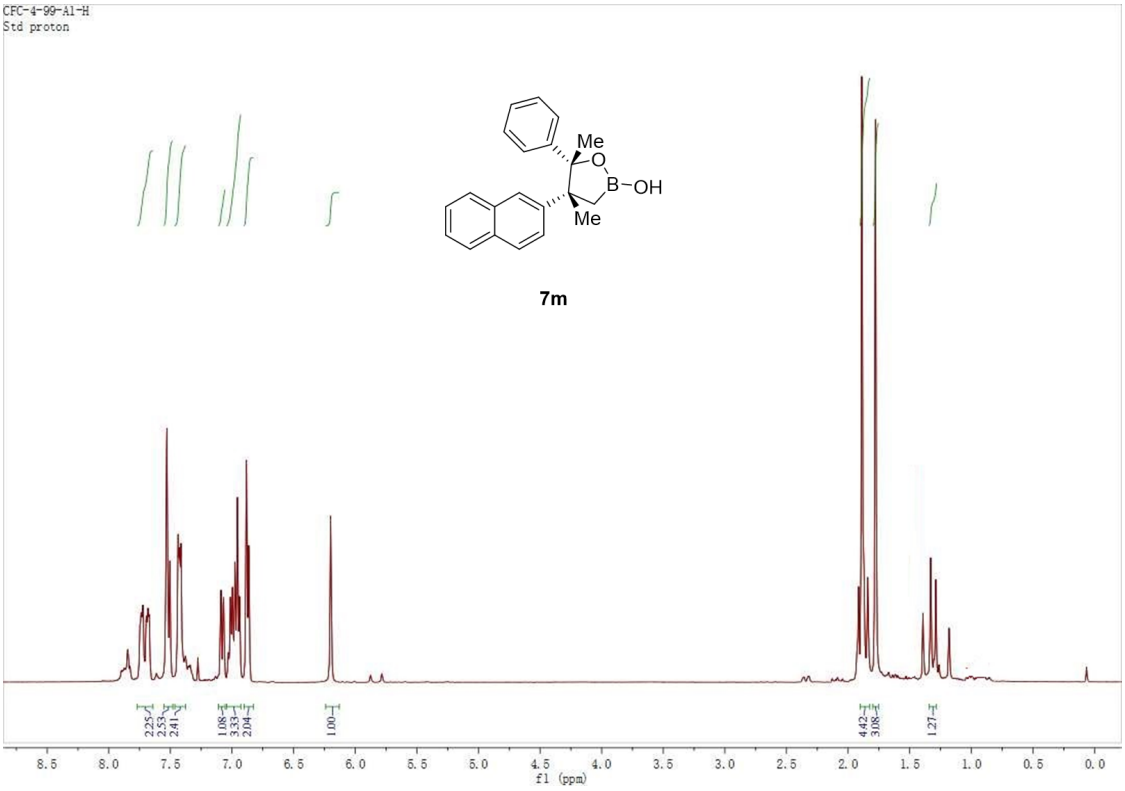

CFC-5-62-B2-3-H
Me
O
B–OH
Me
N
Boc
7l
f1 (ppm)


CFC-5-62-B2-2-C
151.09
143.82
139.69
138.66
136.68
127.12
126.81
126.38
125.30
122.93
119.32
118.91
116.17
114.93
90.12
83.80
77.37
77.05
76.73
52.55
28.41
24.00
20.84
Me
O
B–OH
Me
N
Boc
7l
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

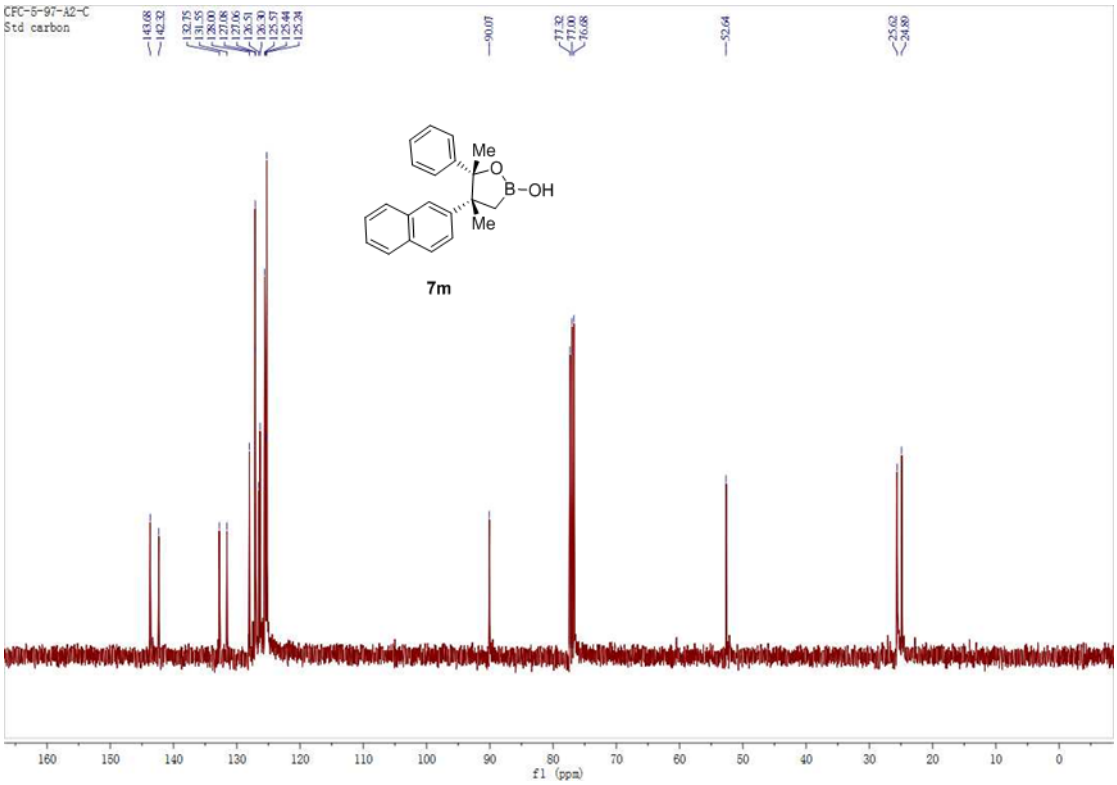

CFC-5-62-B2-4-H
Me
OH
OH
Me
N
Boc
7l-oxi
1.20
0.98
1.04
1.98
2.08
3.17
2.03
1.25
1.19
0.85
0.87
9.13
3.00
3.10
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

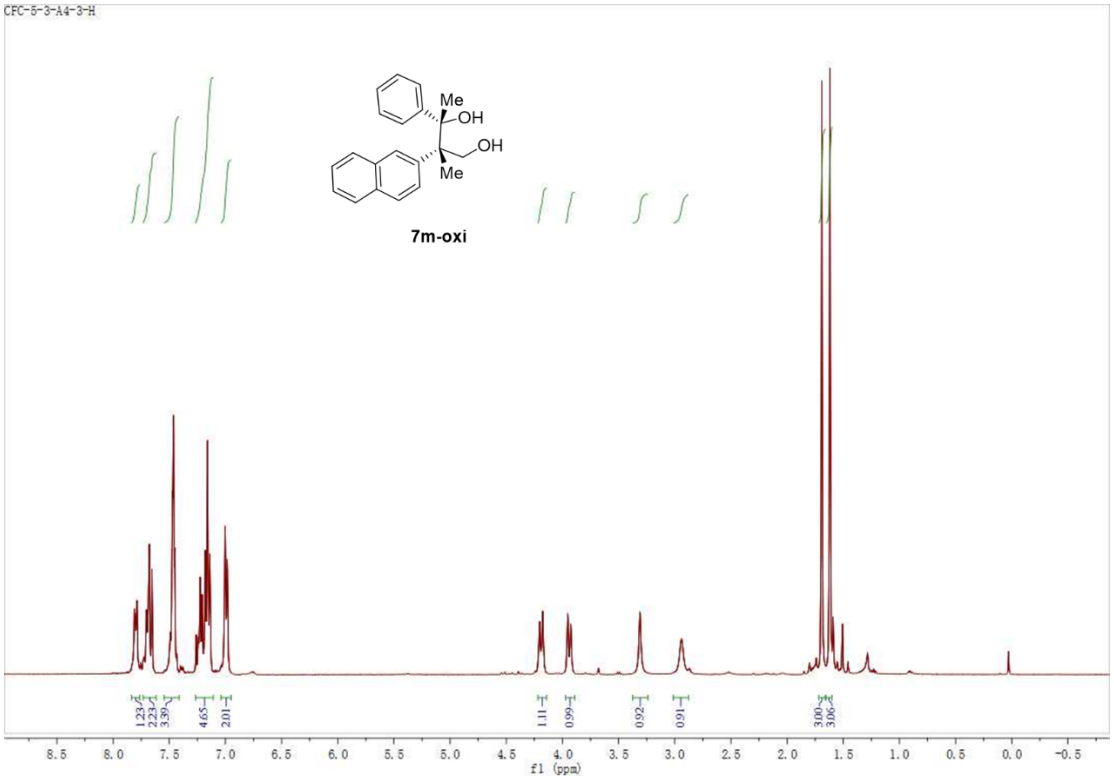

CFC-5-62-B2-OXI-C
Std carbon
Me
OH
OH
Me
N
Boc
f1 (ppm)

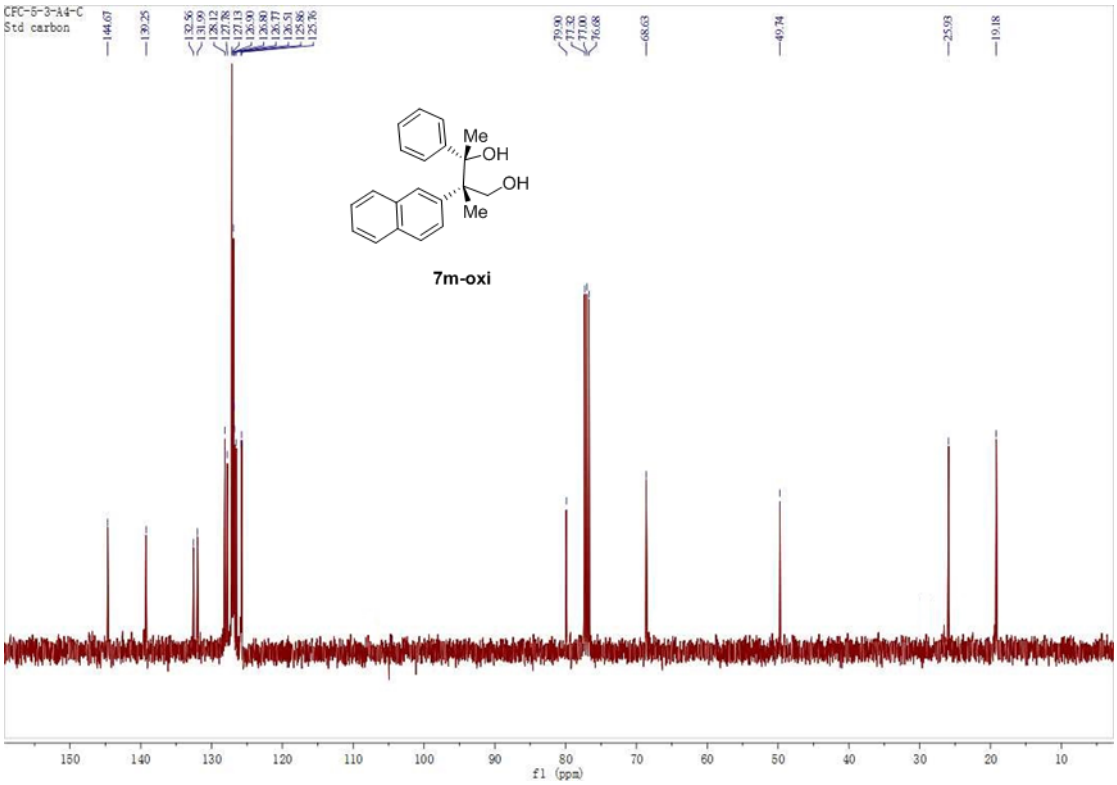
7l-oxi

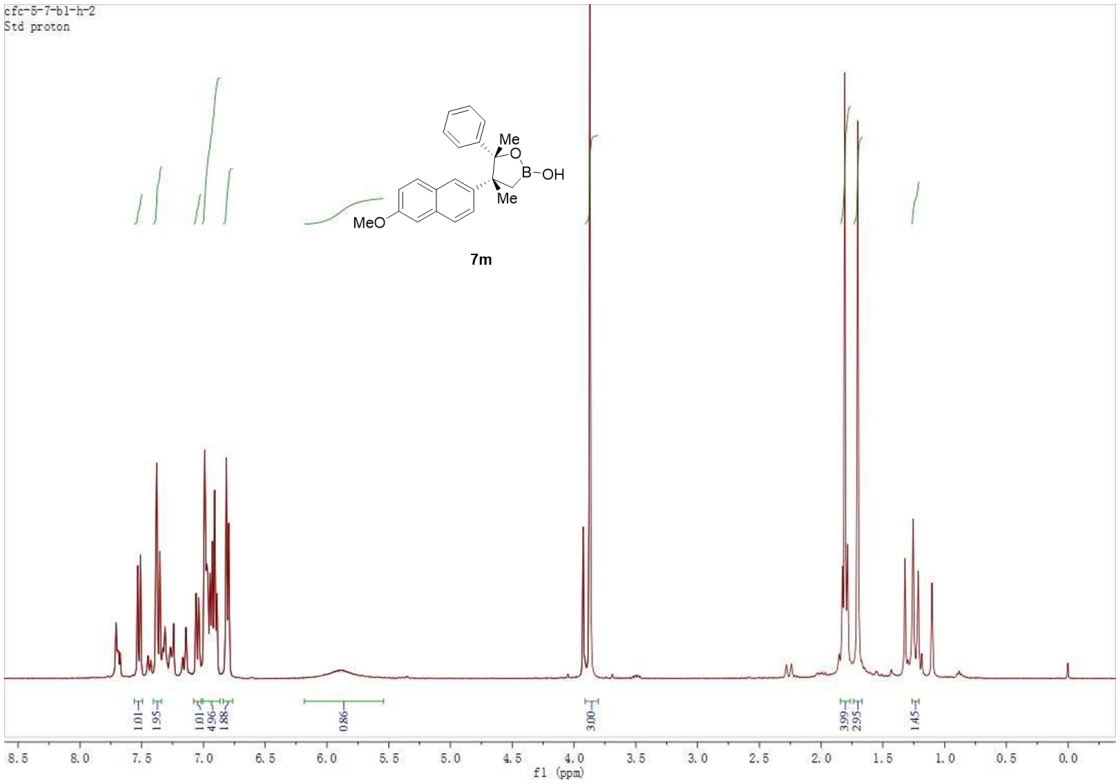

CFC-4-99-A1-H
Std proton
Me
O
B–OH
Me
f1 (ppm)

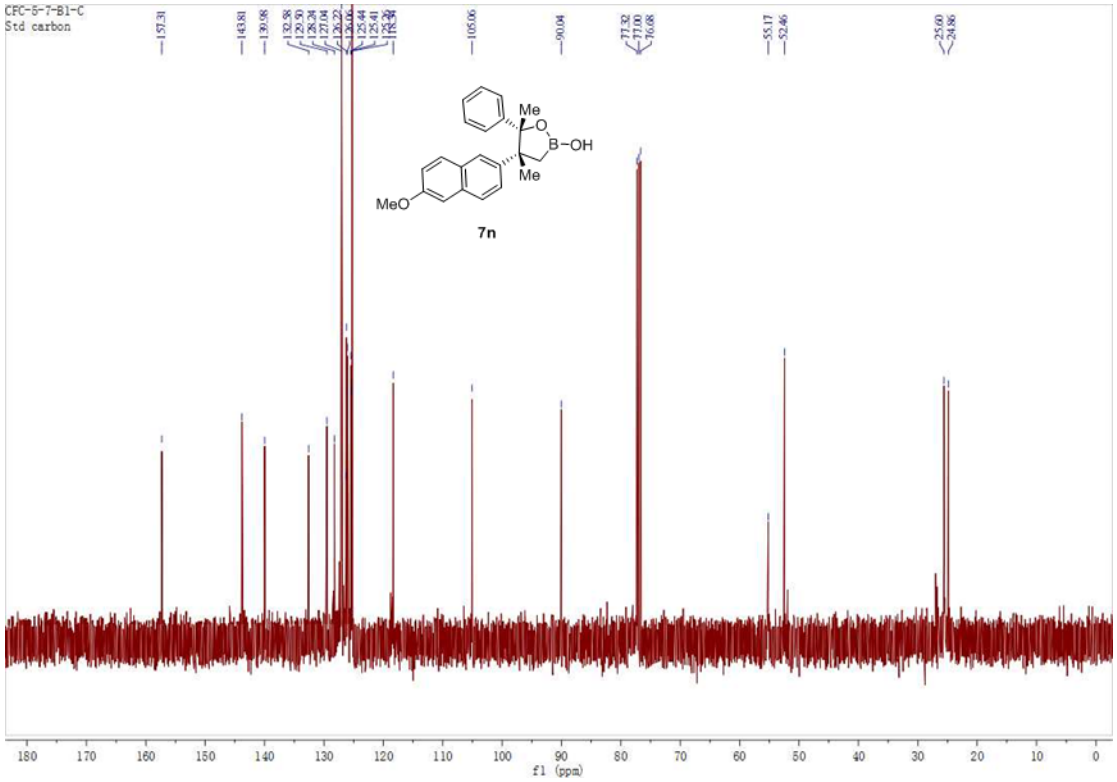
7m

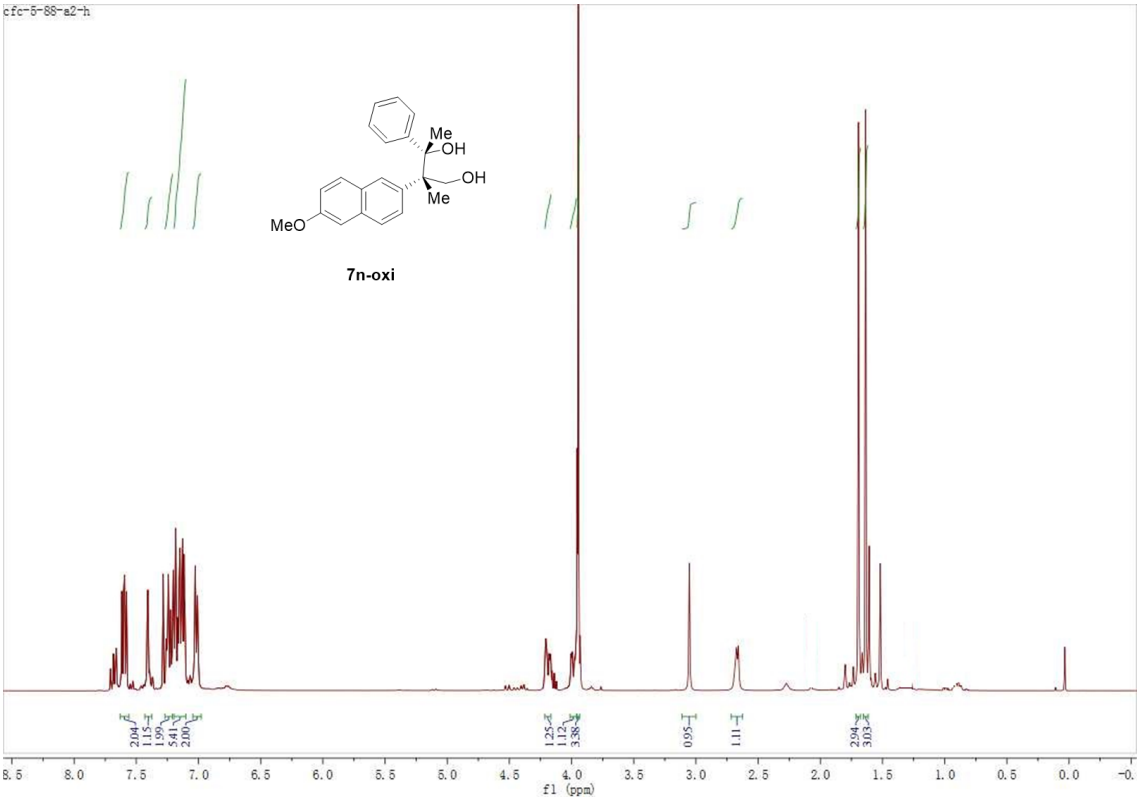

CFC-5-97-A2-C
Std carbon
Me
O
B–OH
Me
7m
f1 (ppm)

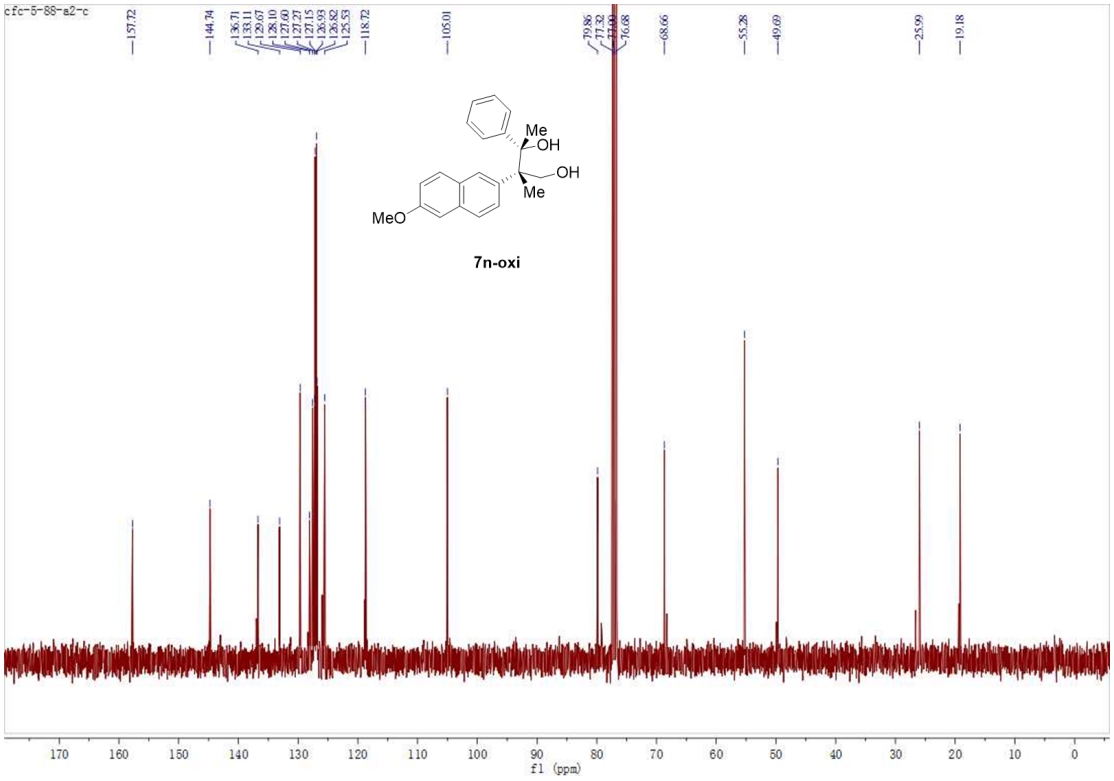

CFC-5-3-A4-3-H
Me
OH
OH
Me
7m-oxi
f1 (ppm)

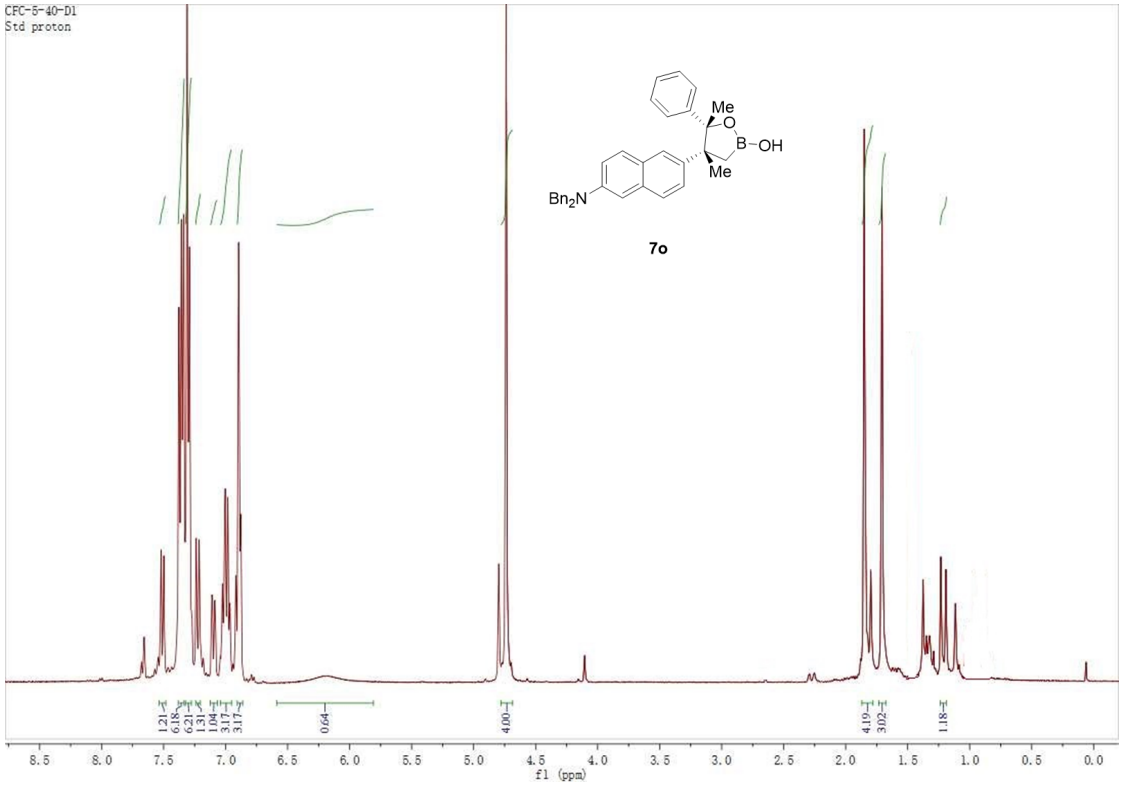

CFC-5-3-A4-C
Std carbon
144.67
139.25
132.56
131.99
128.12
127.78
127.13
126.90
126.80
126.77
126.71
125.86
125.76
79.00
77.32
77.10
76.68
68.63
49.74
25.93
19.18
Me
OH
OH
Me
7m-oxi
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

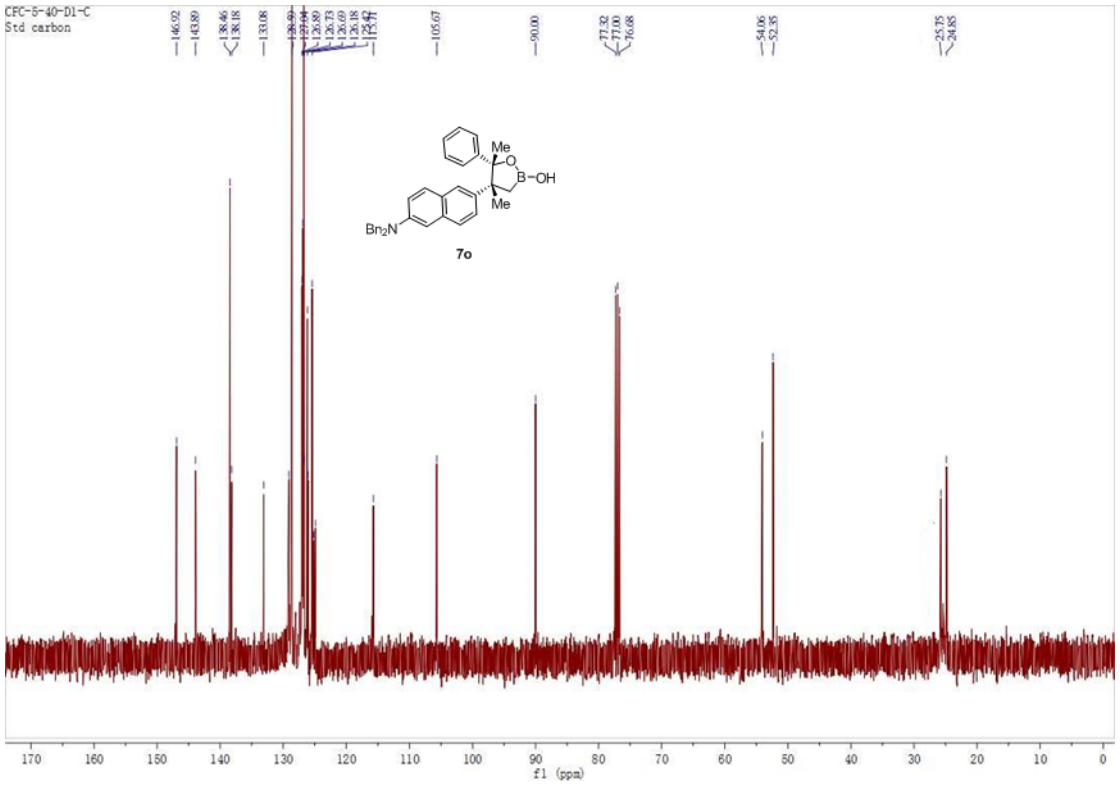

cfc-5-7-b1-h-2
Std proton
Me
O
B
OH
Me
MeO
7m
1.01
1.95
1.01
4.96
1.88
0.86
3.00
3.99
2.95
1.45
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

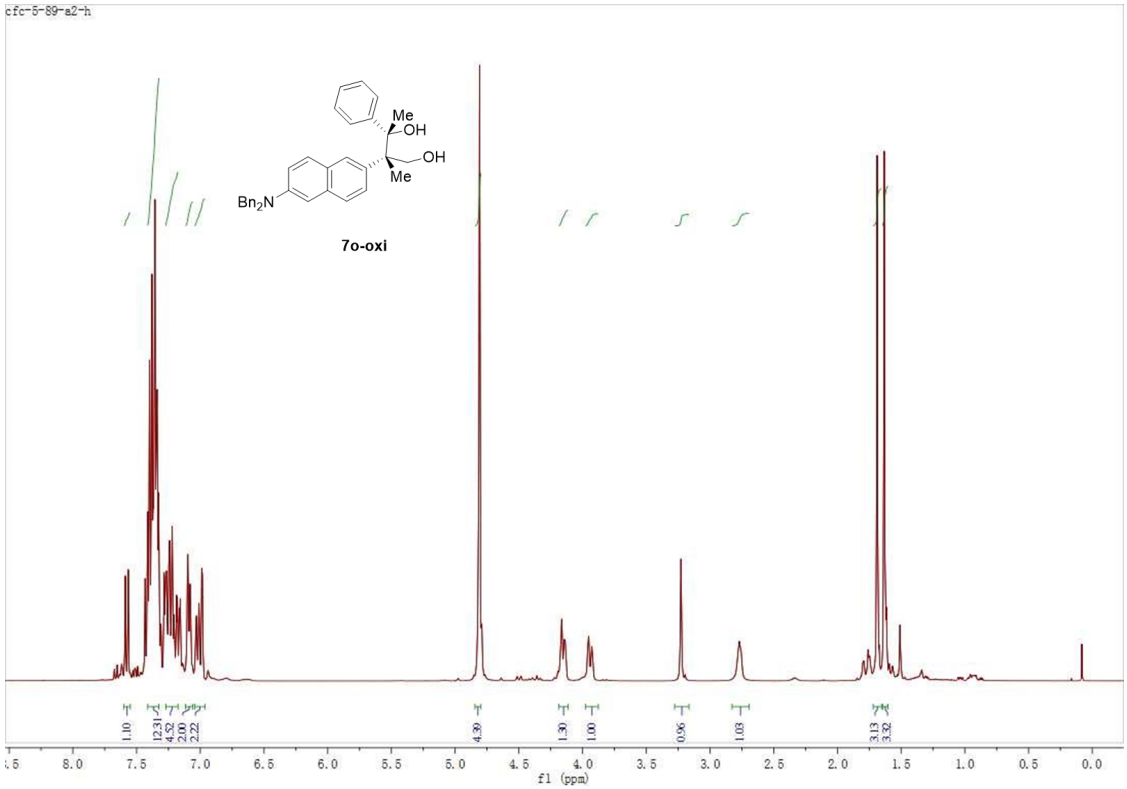

CFC-5-7-B1-C
Std carbon
Me
O
B–OH
Me
MeO
7n
f1 (ppm)

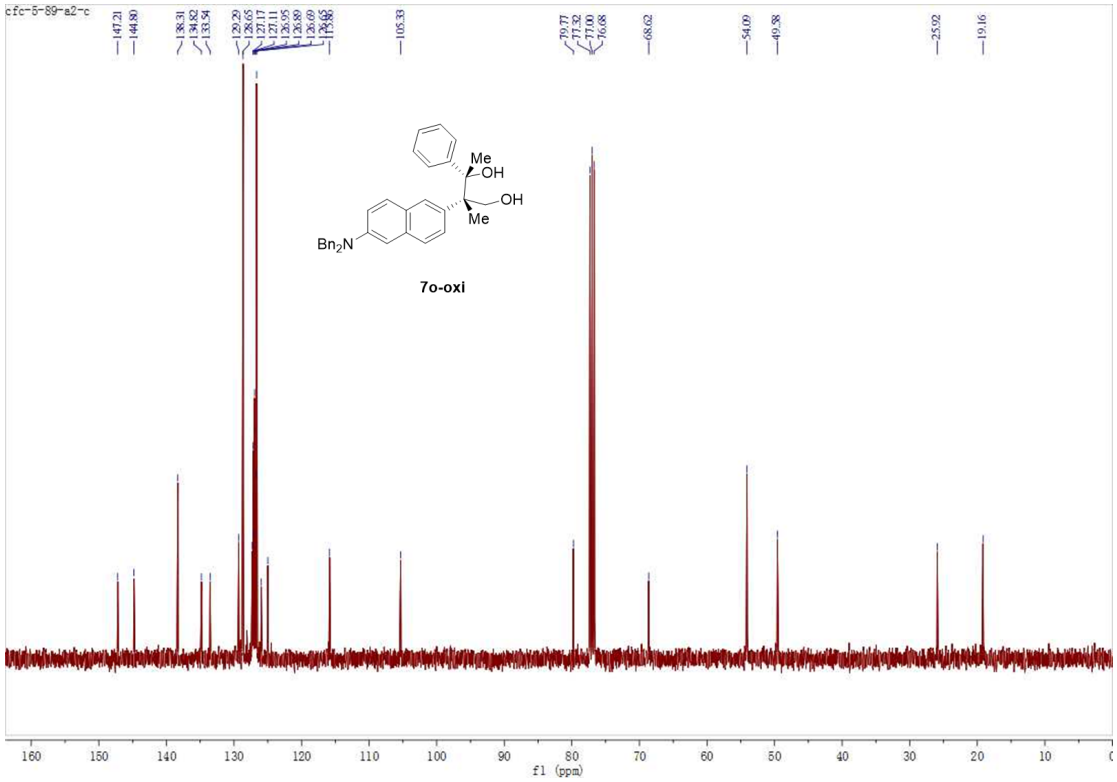

cfc-5-88-a2-h
Me
OH
OH
Me
MeO
7n-oxi
f1 (ppm)

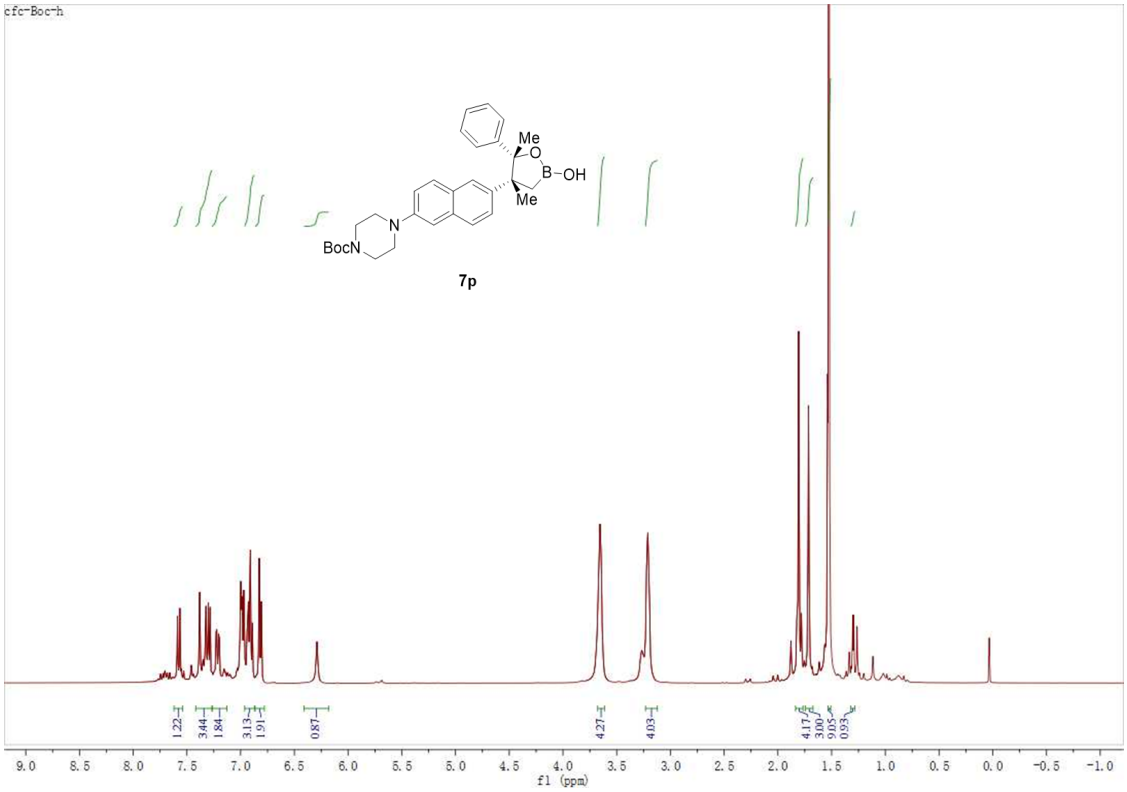

cfc-5-88-a2-c
157.72
144.74
136.71
133.11
129.07
128.10
127.60
127.27
127.15
126.93
126.82
125.53
118.72
105.01
79.86
77.32
77.00
76.68
68.66
55.28
49.69
25.99
19.18
Me
OH
OH
Me
MeO
7n-oxi
f1 (ppm)

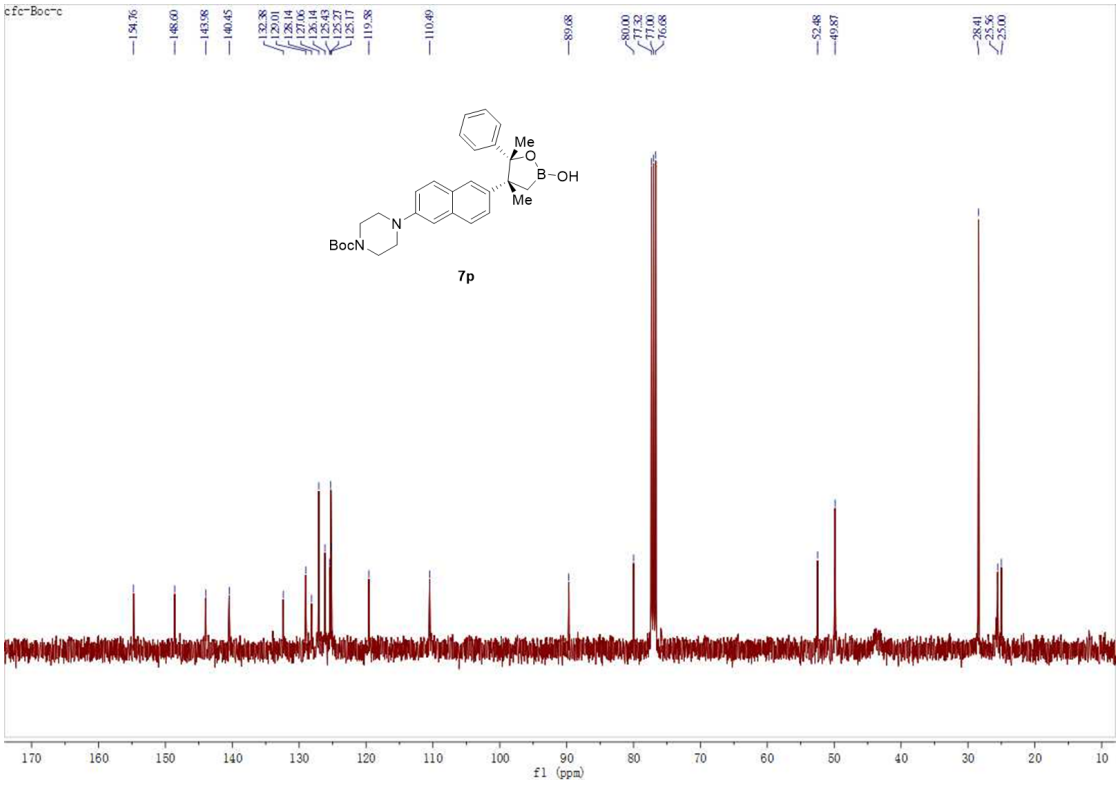

CFC-5-40-D1
Std proton
Me
O
B
OH
Me
Bn2N
7o
1.21
6.18
6.21
1.31
1.04
3.17
3.17
0.64
4.00
4.19
3.02
1.18
f1 (ppm)

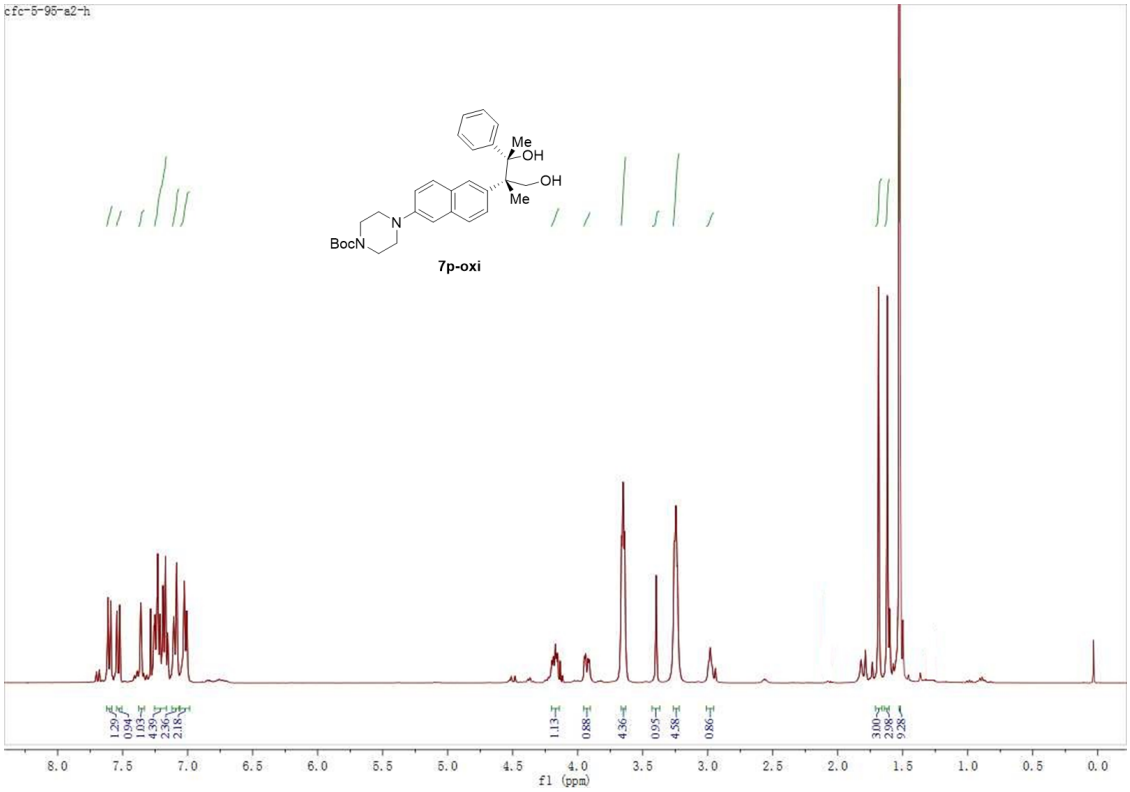

CFC-5-40-D1-C
Std carbon
Me
O
B–OH
Me
Bn2N
7o
f1 (ppm)

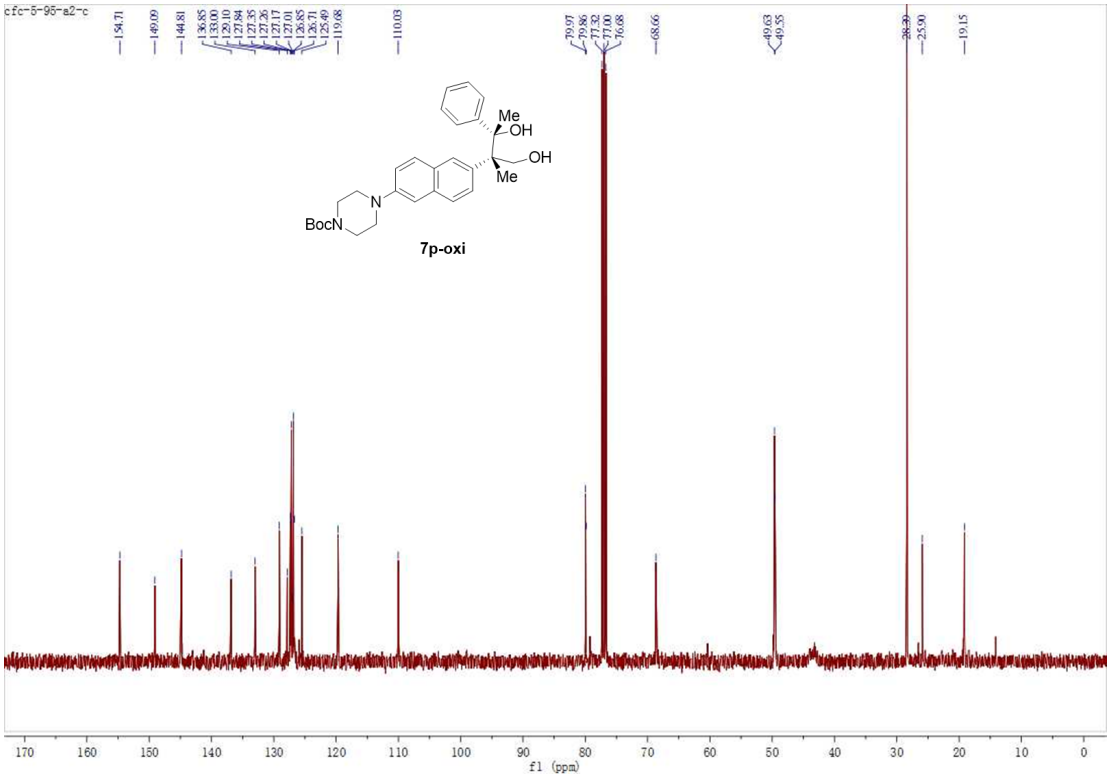

cfc-5-89-a2-h
Me
OH
OH
Me
Bn2N
7o-oxi
f1 (ppm)

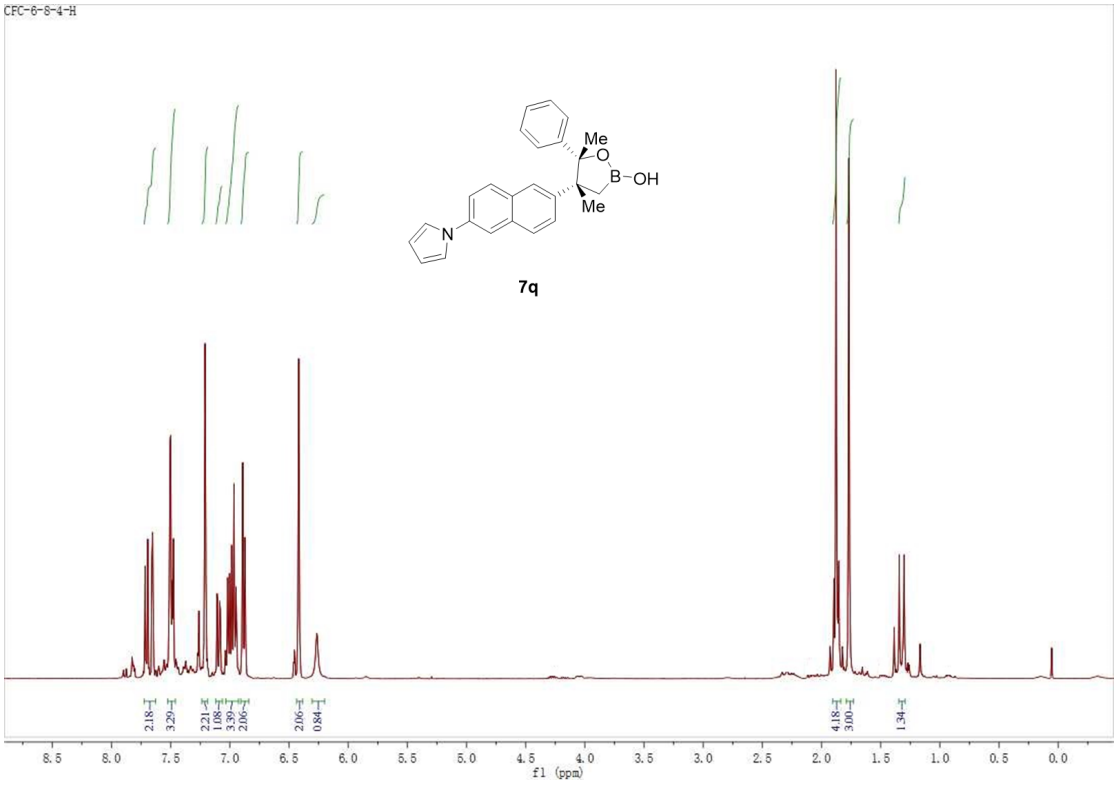

cfc-5-89-a2-c
147.21
144.80
138.31
134.82
133.54
129.29
128.65
127.17
127.11
126.95
126.89
126.69
125.85
125.68
105.33
79.77
77.32
77.00
76.68
68.62
54.09
49.38
25.92
19.16
Me
OH
OH
Me
Bn2N
7o-oxi
f1 (ppm)

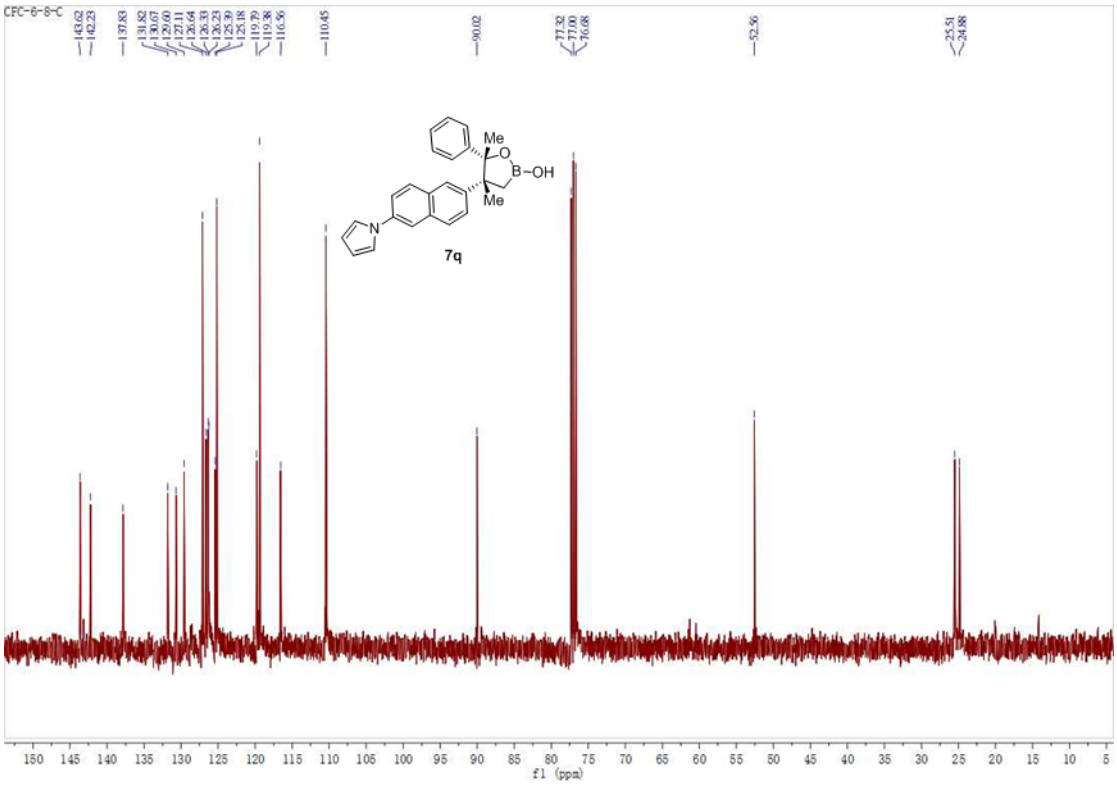

cfc-Boc-h
Me
O
B–OH
Me
N
BocN
7p
1.22
3.44
1.84
3.13
1.91
0.87
4.27
4.03
4.17
3.00
9.05
0.93
f1 (ppm)

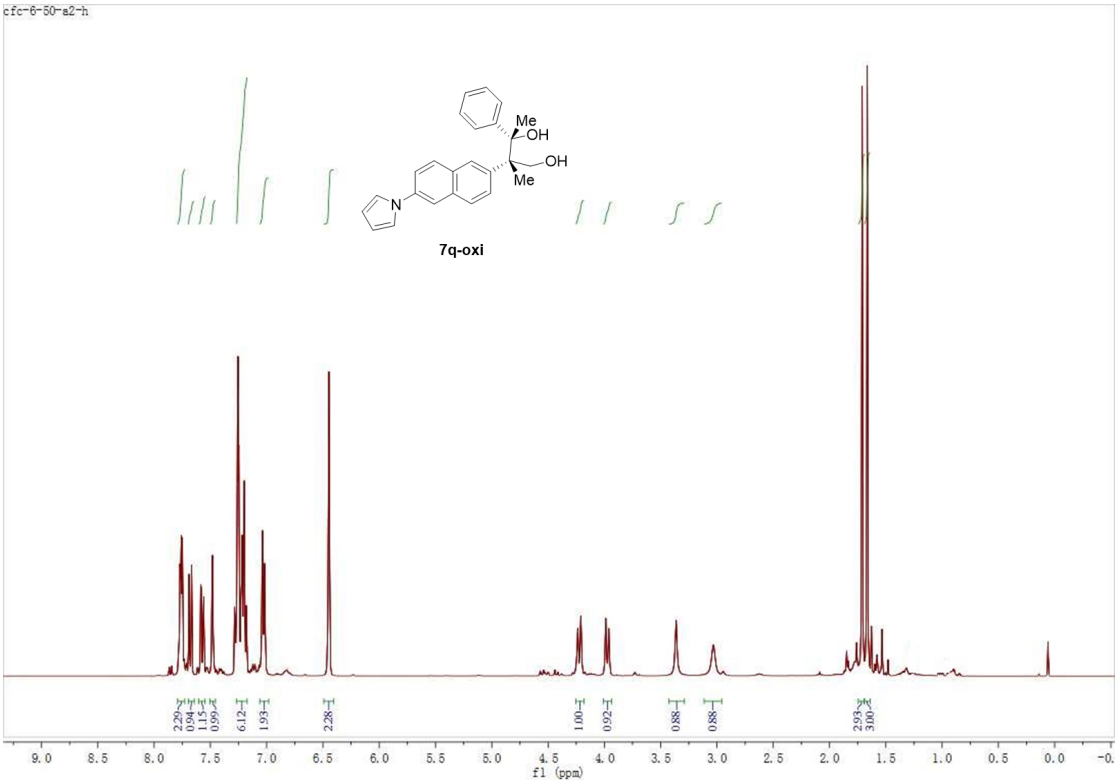

cfc-Boc-c
154.76
148.60
143.98
140.45
132.38
129.01
128.14
127.06
126.14
125.43
125.27
125.17
119.58
110.49
89.68
80.00
77.32
77.00
76.68
52.48
49.87
28.41
25.56
25.00
Me
O
B–OH
Me
N
BocN
7p
f1 (ppm)

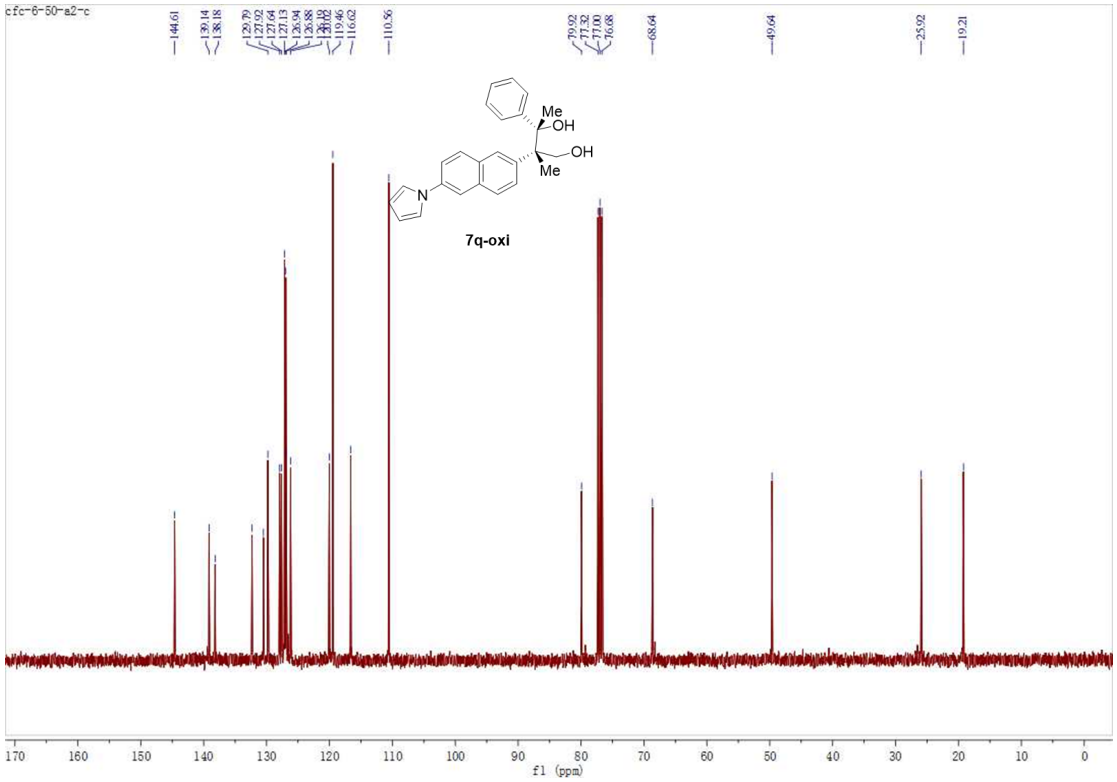

cfc-5-95-a2-h
Me
OH
OH
Me
N
BocN
7p-oxi
1.29
0.94
1.19
4.39
2.36
2.18
1.13
0.88
4.36
0.95
4.58
0.86
3.00
2.98
9.28
f1 (ppm)

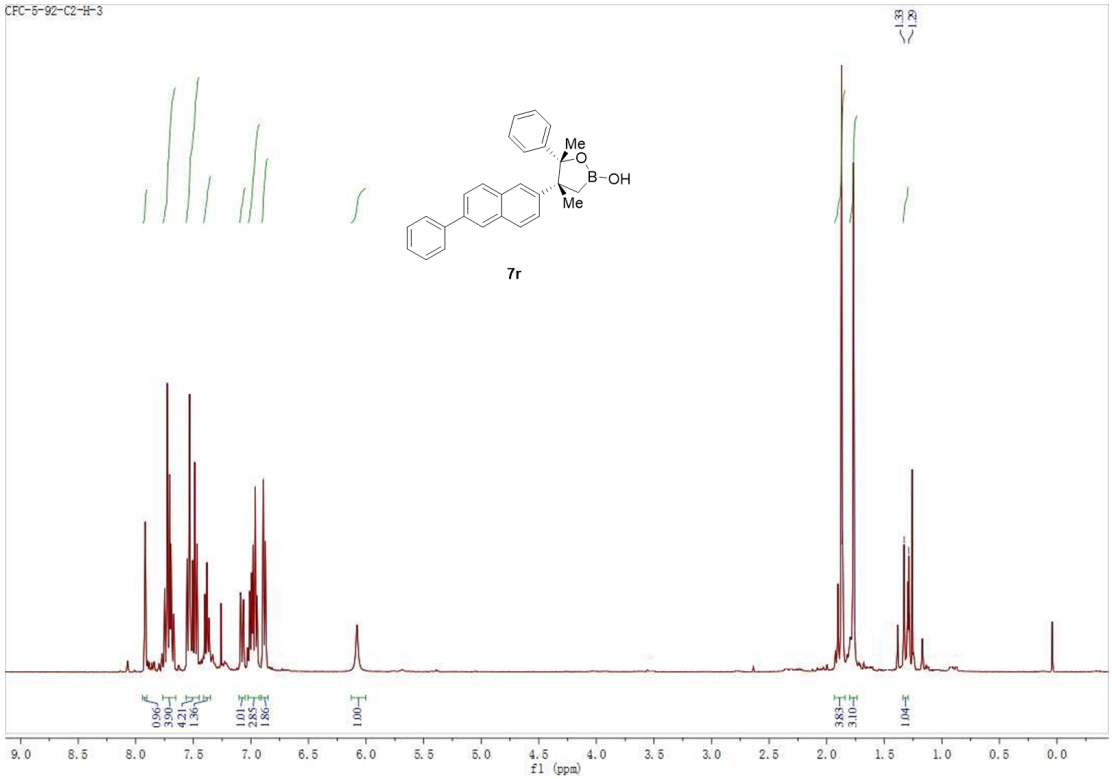

cfc-5-95-a2-c
154.71
149.09
144.81
136.85
135.00
129.10
127.84
127.35
127.26
127.17
127.01
126.85
126.71
125.40
119.68
110.03
79.97
79.86
77.32
77.00
76.68
68.66
49.63
49.55
28.39
25.90
19.15
Me
OH
OH
Me
N
BocN
7p-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

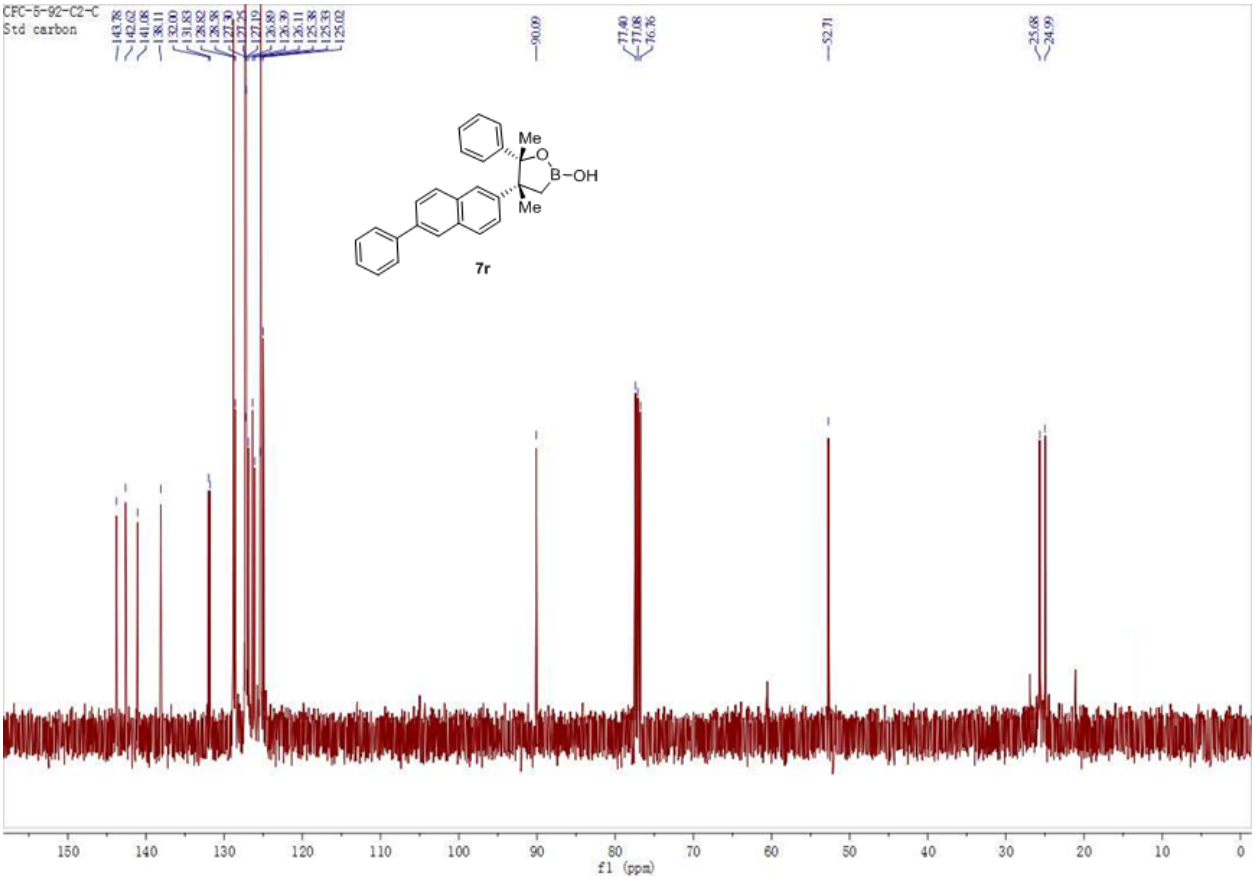

CFC-6-8-4-H
Me
O
B–OH
Me
N
7q
2.18
3.29
2.21
1.08
3.39
2.06
2.06
0.84
4.18
3.00
1.34
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

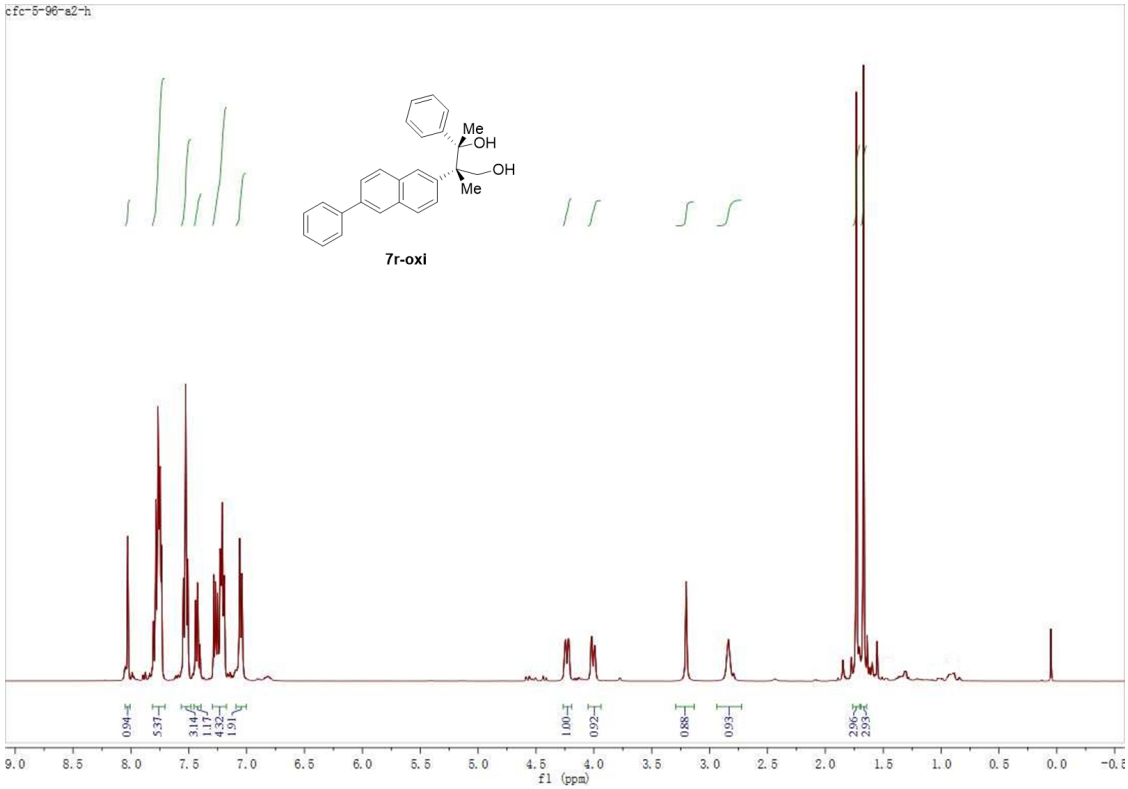

CFC-6-8-C
143.62
142.23
137.83
131.82
130.07
129.60
127.11
126.64
126.51
126.23
125.39
125.18
119.79
119.38
116.56
110.45
90.02
77.32
77.00
76.68
52.56
25.51
24.88
Me
O
B–OH
Me
N
7q
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

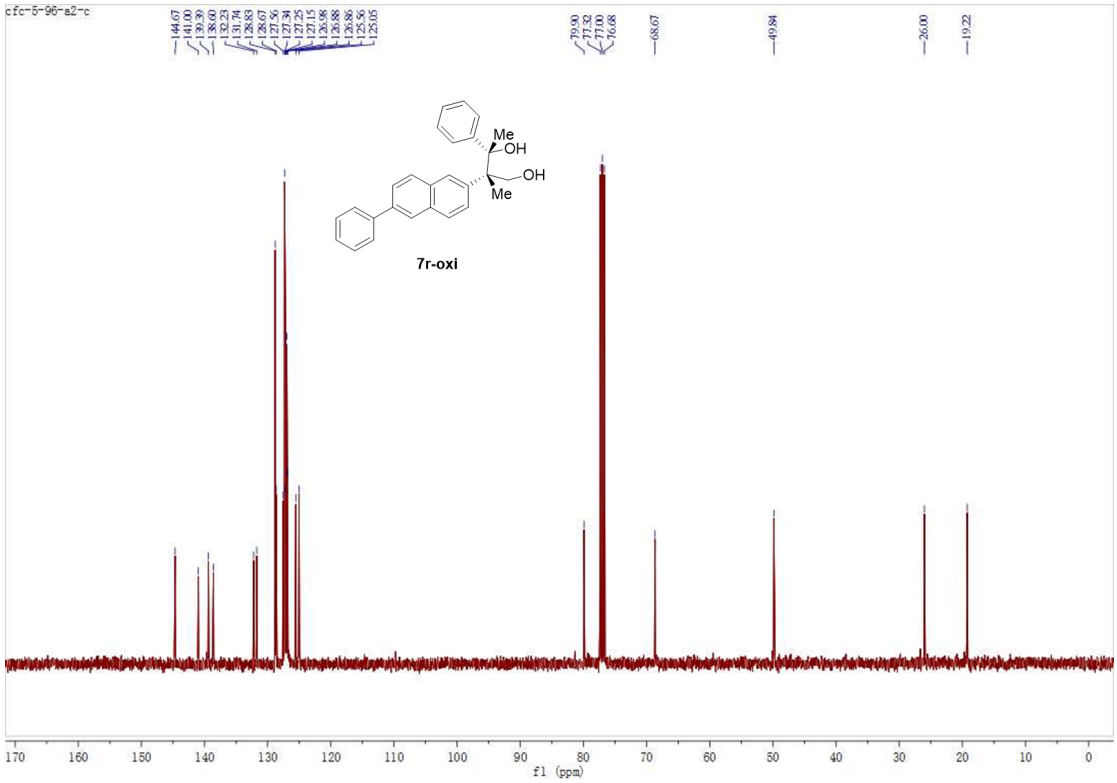

cfc-6-50-a2-h
Me
OH
OH
Me
N
7q-oxi
2.29
0.94
1.15
0.99
6.12
1.93
2.28
1.00
0.92
0.88
0.88
2.93
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

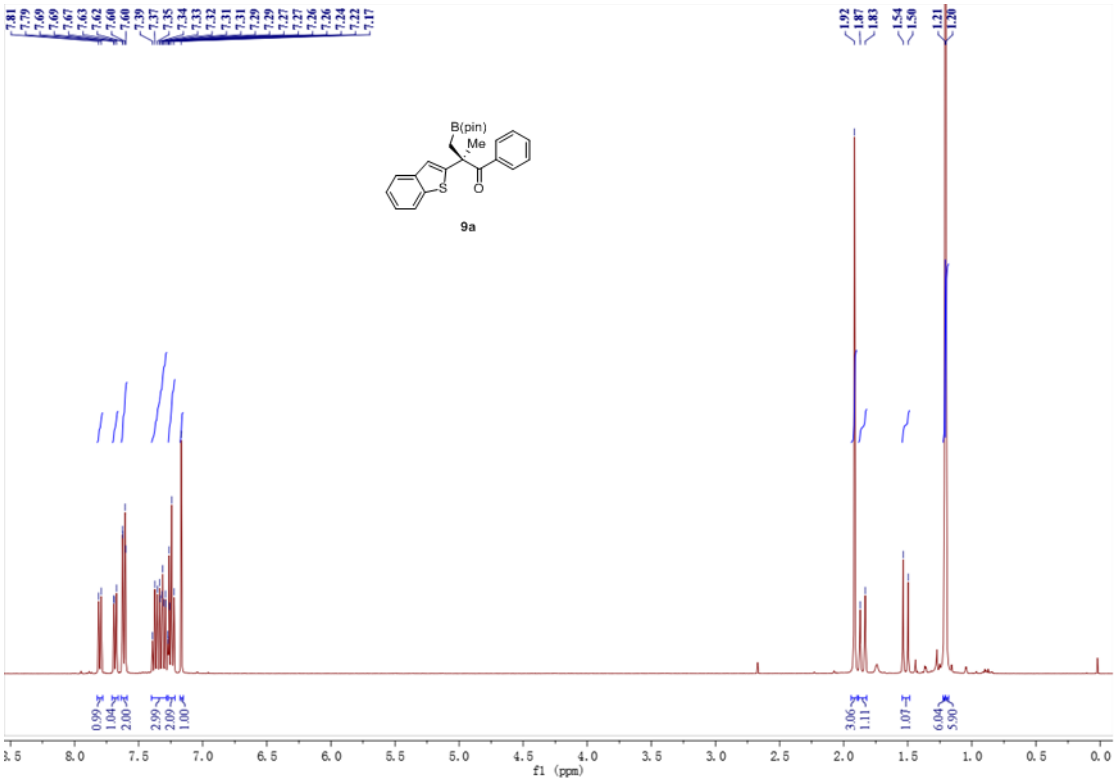

cfc-6-50-a2-c
144.61
139.14
138.18
129.79
127.92
127.64
127.13
126.94
126.88
120.02
119.46
116.62
110.56
79.92
77.32
77.00
76.68
68.64
49.64
25.92
19.21
Me
OH
OH
Me
N
7q-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

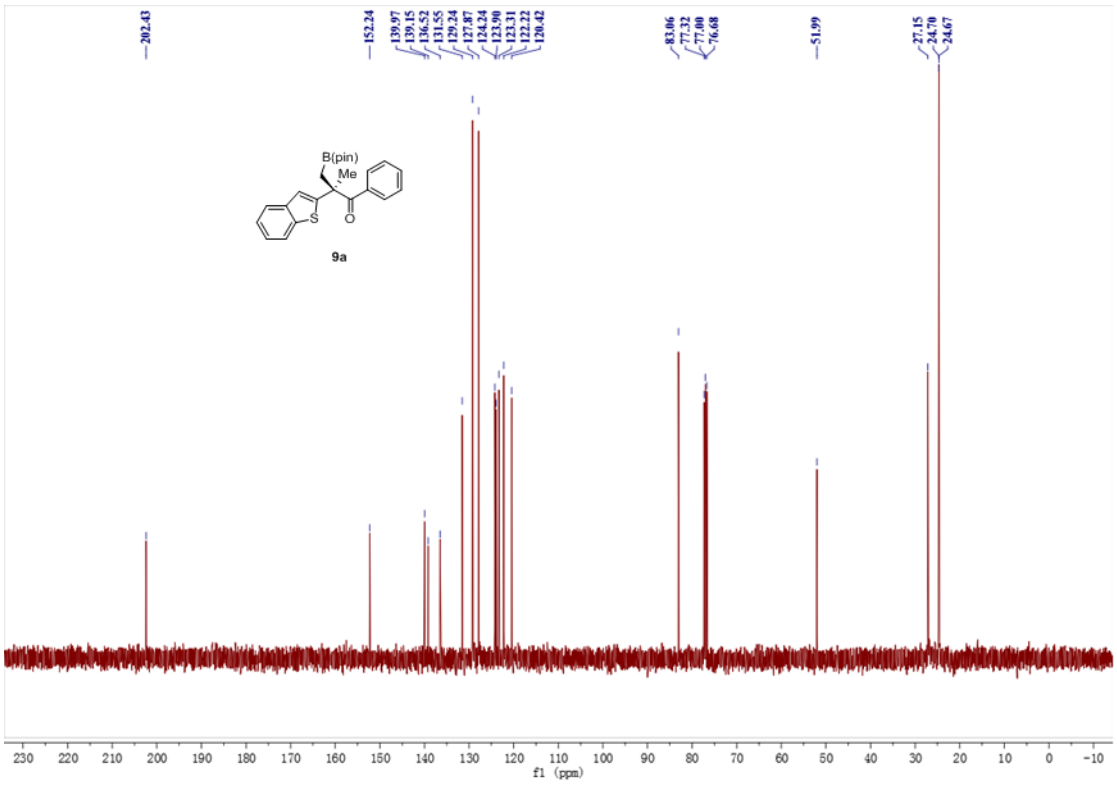

CFC-5-92-C2-H-3
1.33
1.29
Me
O
B–OH
Me
7r
0.96
3.90
4.21
1.36
1.01
2.85
1.86
1.00
3.83
3.10
1.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

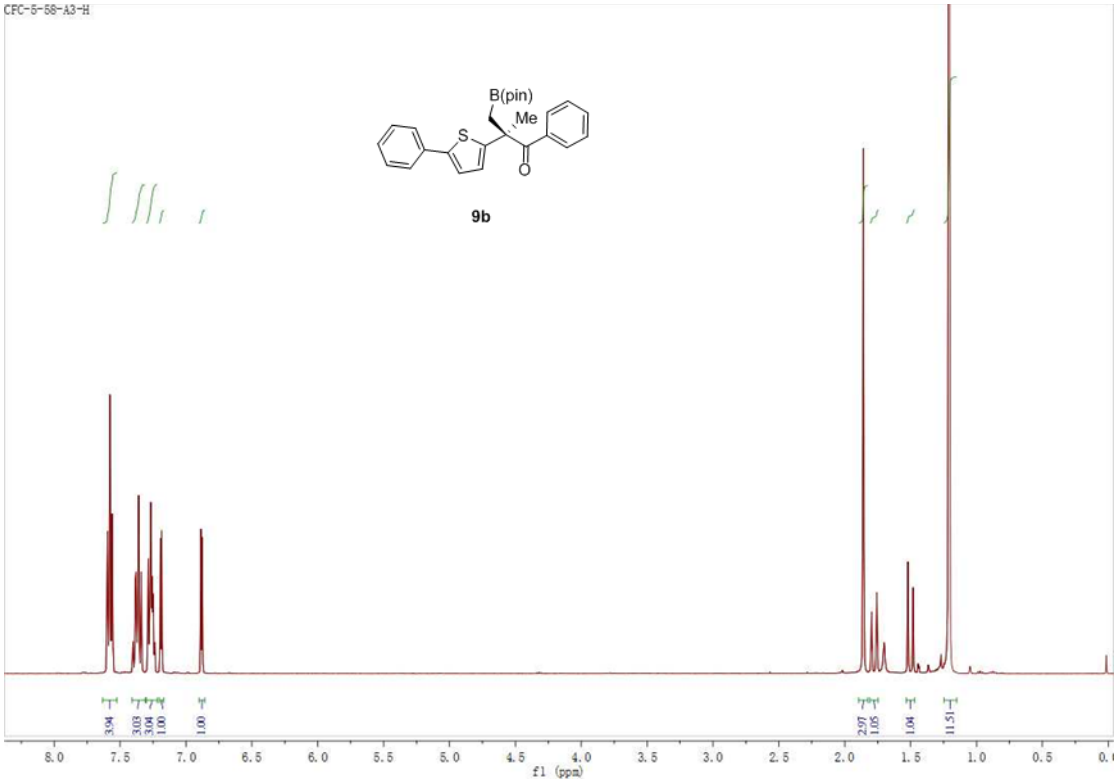

CFC-5-92-C2-C
Std carbon
Me
O
B–OH
Me
7r
f1 (ppm)

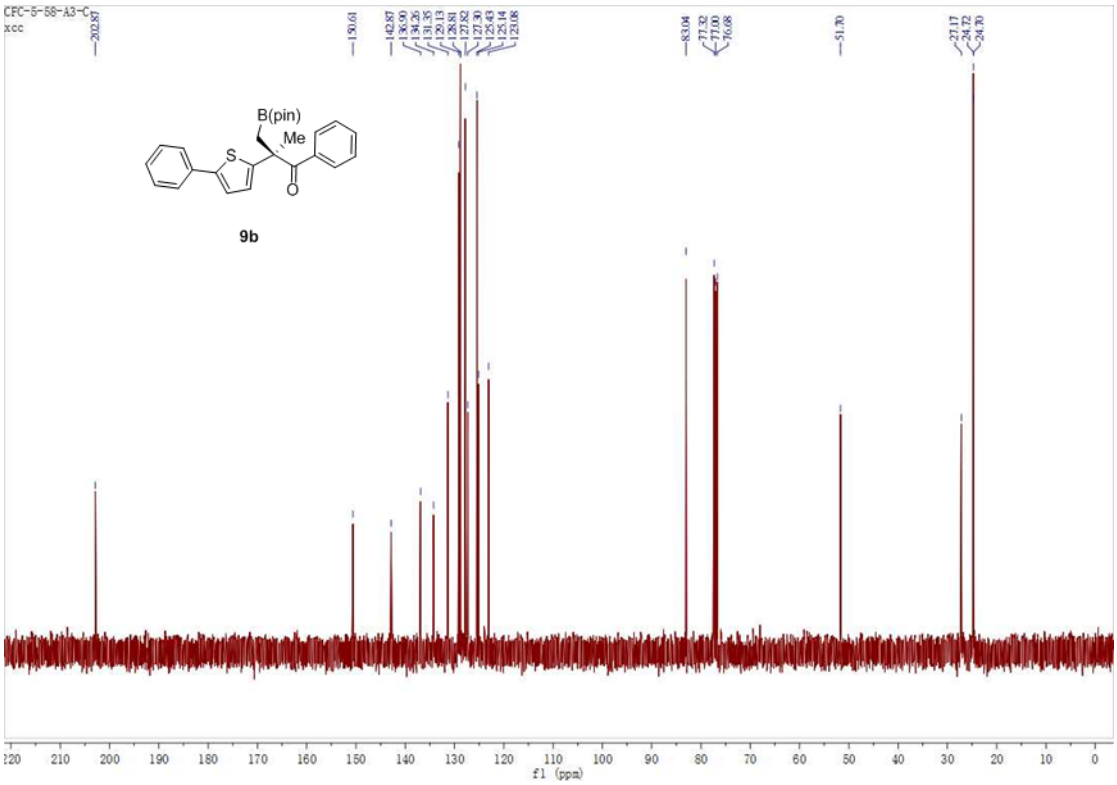

cfc-5-96-a2-h
Me
OH
OH
Me
7r-oxi
f1 (ppm)

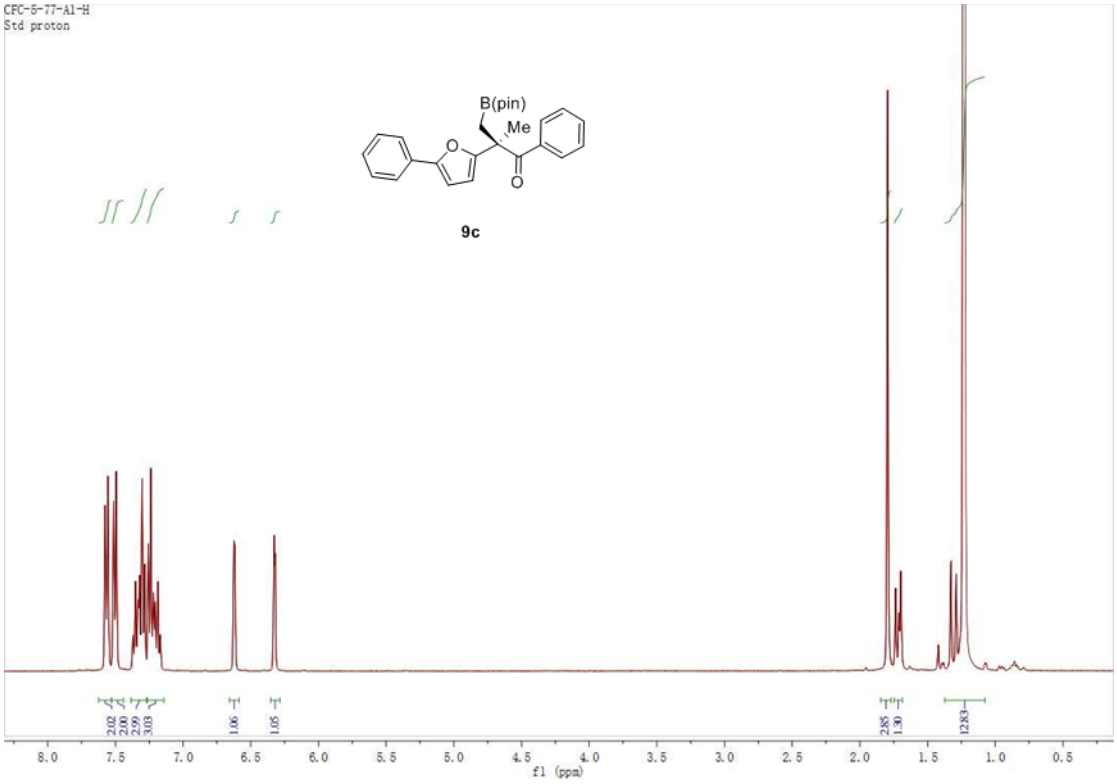

cfc-5-96-a2-c
144.67
141.00
139.39
138.60
132.23
131.74
128.83
128.67
127.56
127.34
127.25
127.15
126.98
126.88
126.86
125.56
125.05
79.90
77.32
77.00
76.68
68.67
49.84
26.00
19.22
Me
OH
OH
Me
7r-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

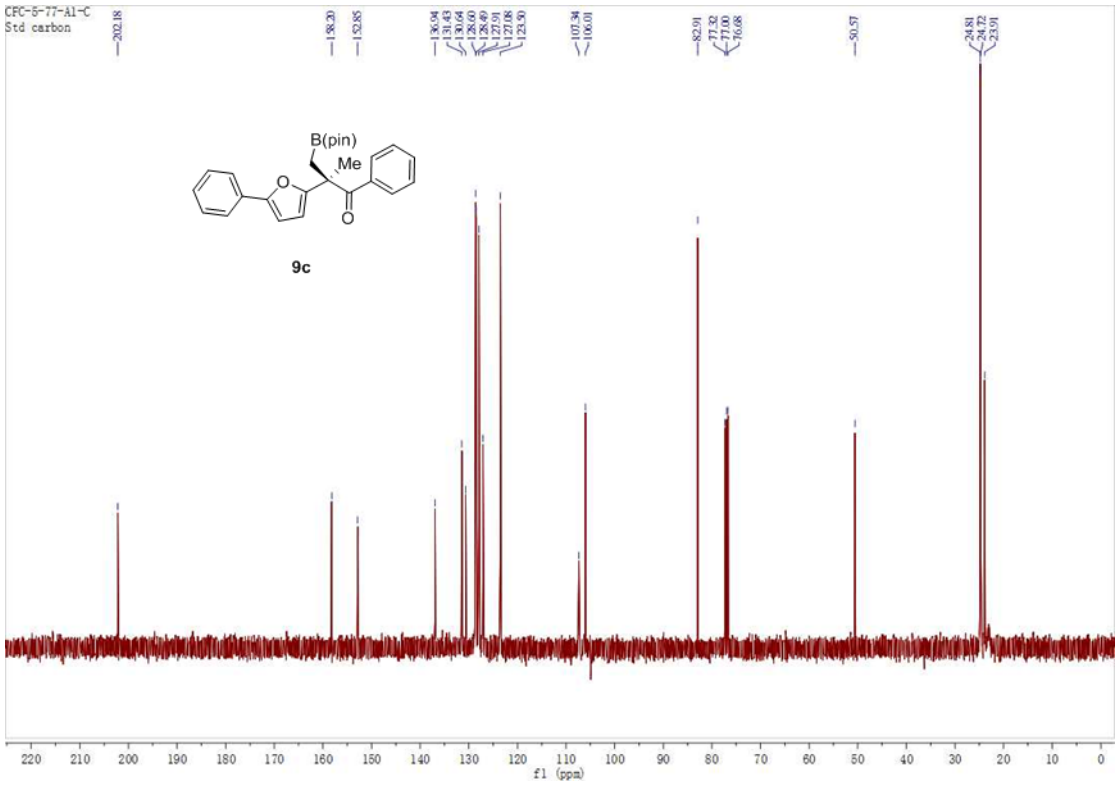

7.81
7.79
7.69
7.69
7.67
7.63
7.62
7.60
7.60
7.39
7.37
7.35
7.34
7.33
7.32
7.31
7.31
7.29
7.29
7.27
7.27
7.26
7.26
7.24
7.22
7.17
1.92
1.87
1.83
1.54
1.50
1.21
1.20
B(pin)
Me
S
O
9a
0.99
1.04
2.00
2.99
2.09
1.00
3.06
1.11
1.07
6.04
5.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

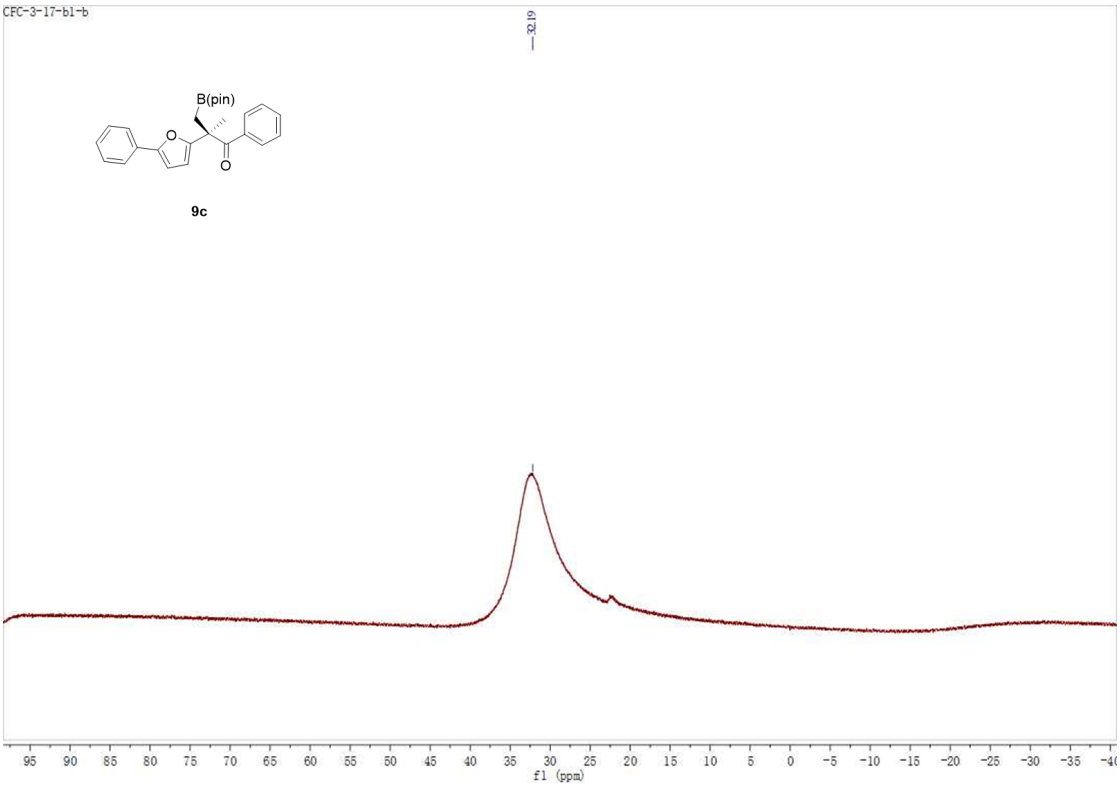

202.43
152.24
139.97
139.15
136.52
131.55
129.24
127.87
124.24
123.90
123.31
122.22
120.42
83.06
77.32
77.00
76.68
51.99
27.15
24.70
24.67
B(pin)
Me
S
O
9a
f1 (ppm)

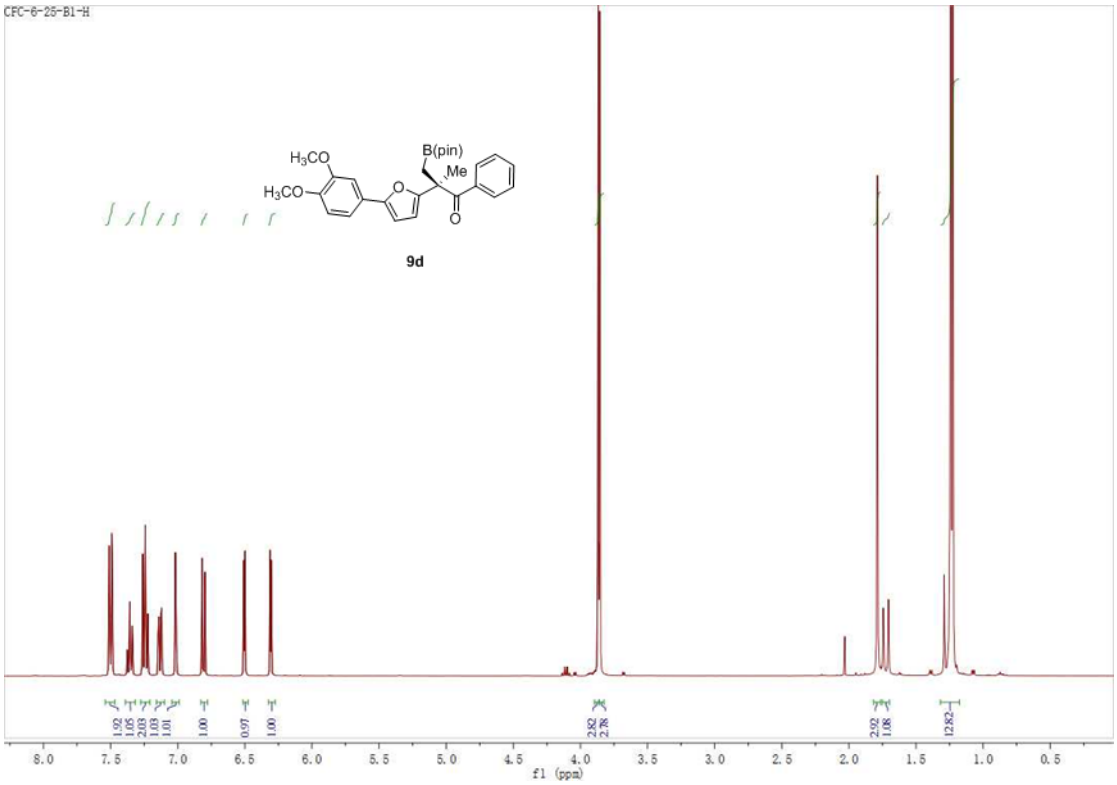

CFC-5-58-A3-H
B(pin)
Me
S
O
9b
3.94
3.03
3.04
1.00
1.00
2.97
1.05
1.04
11.51
f1 (ppm)

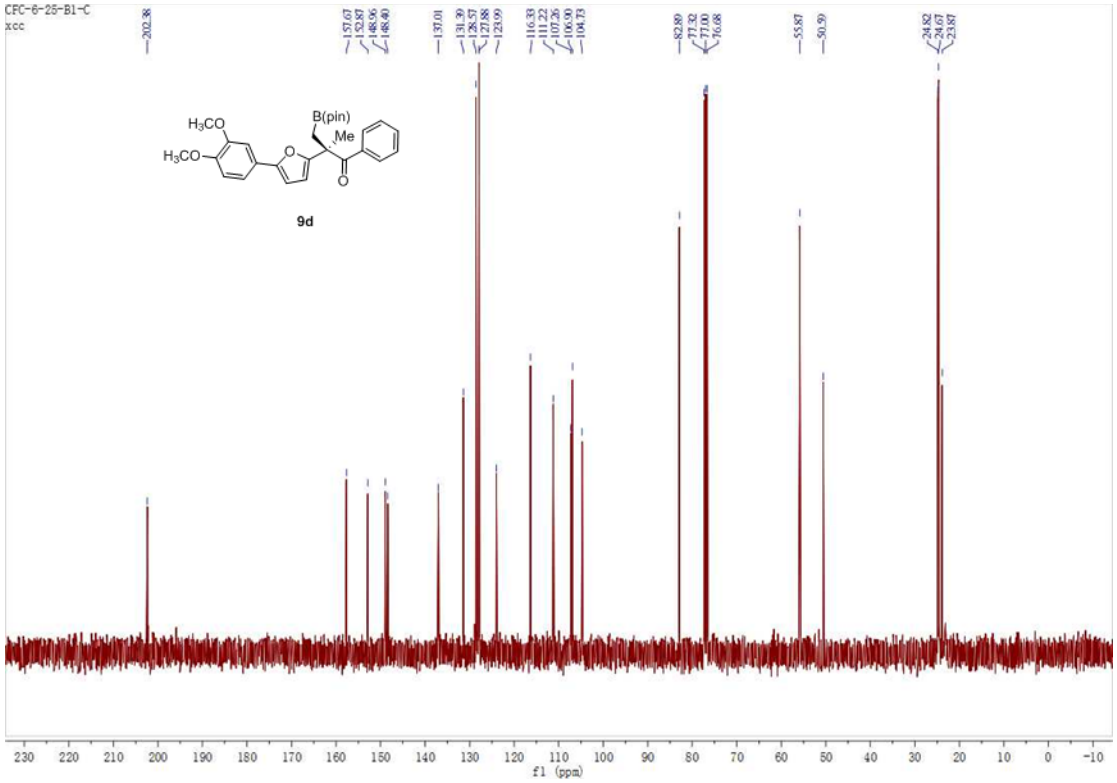

B(pin)
Me
S
O
9b
f1 (ppm)

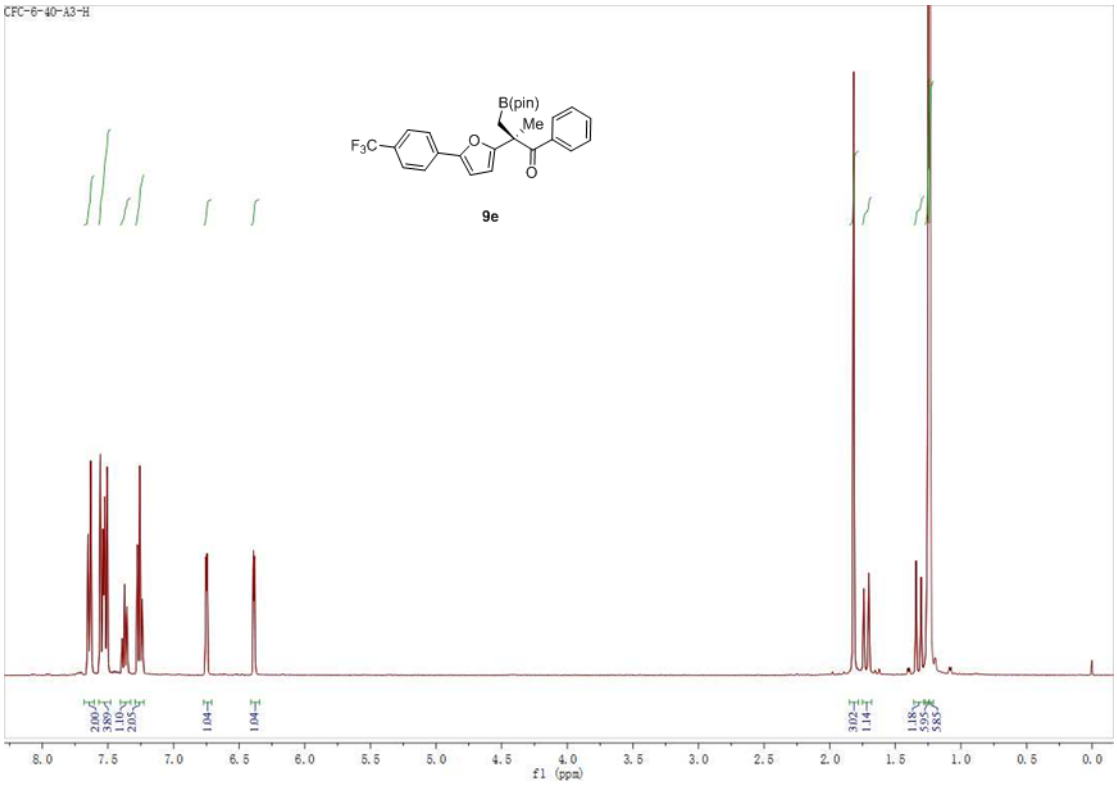

B(pin)
Me
O
O
9c
f1 (ppm)

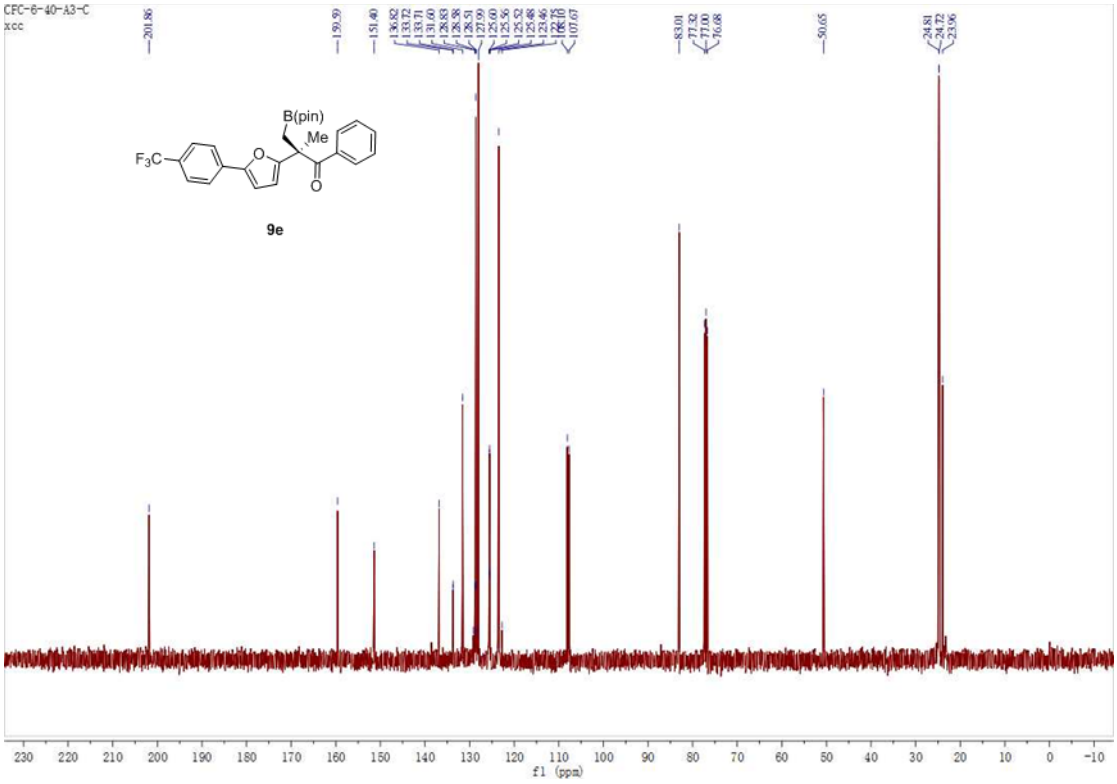

CFC-5-77-A1-C
Std carbon
B(pin)
Me
O
O
9c
f1 (ppm)

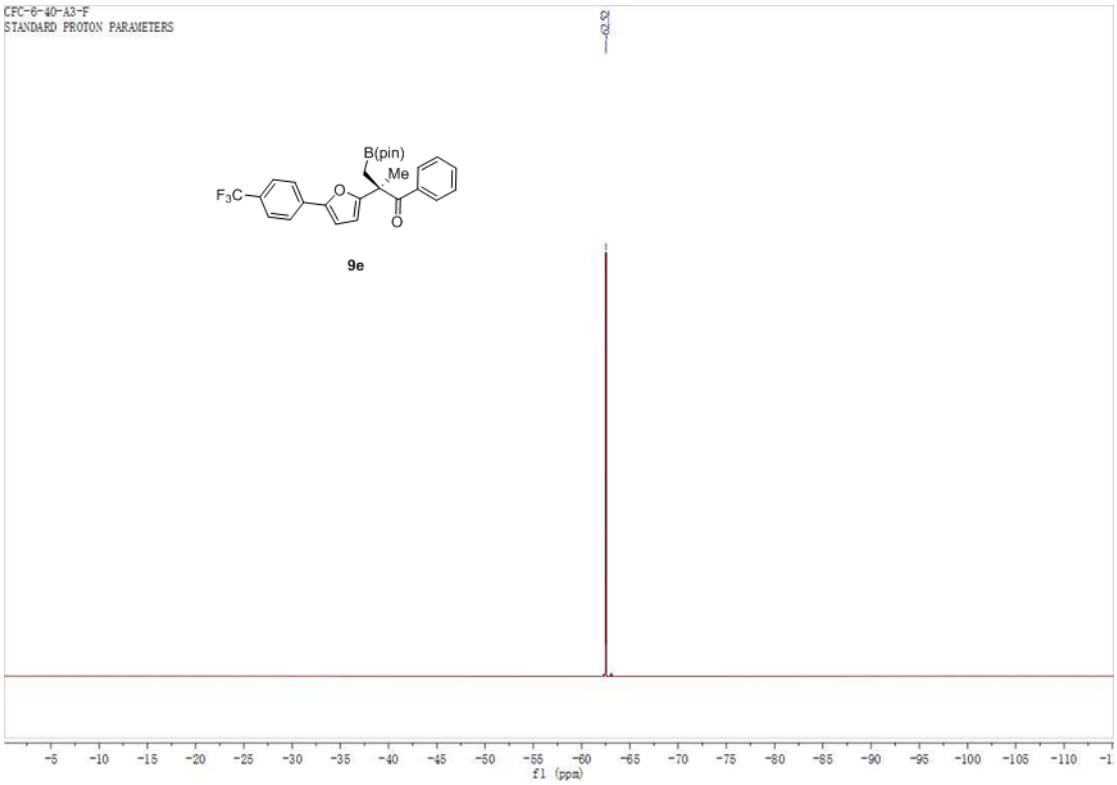

CFC-3-17-b1-b
B(pin)
O
O
9c
f1 (ppm)

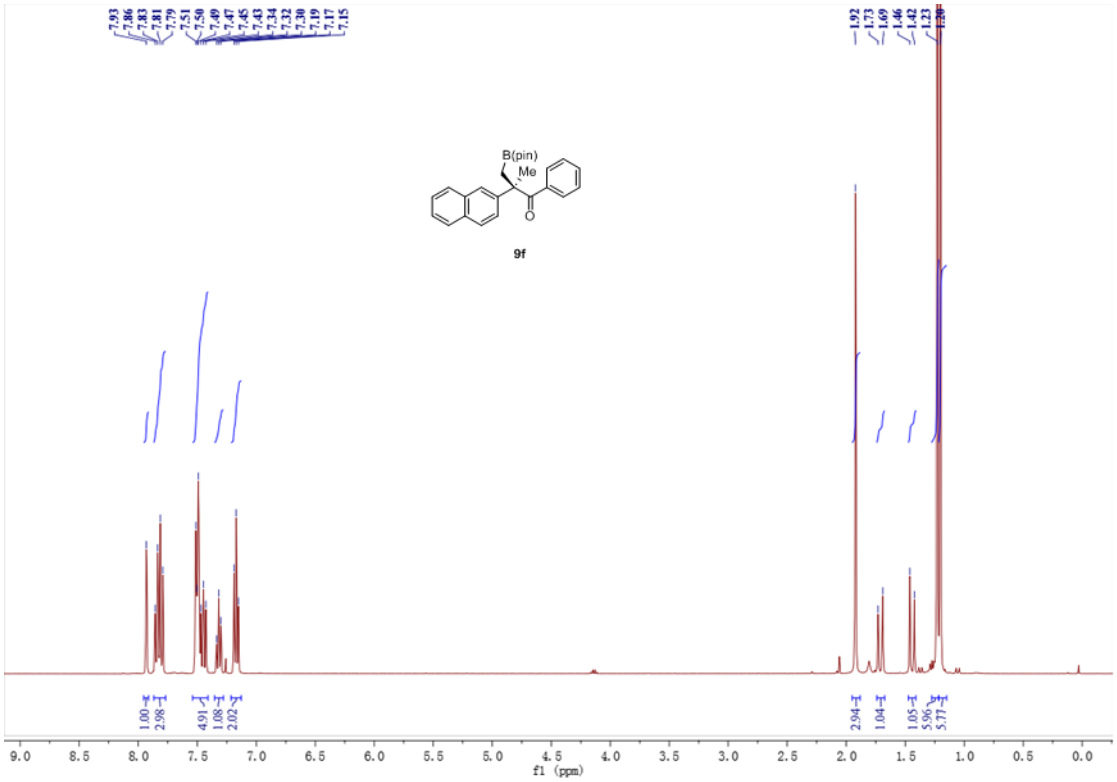

CFC-6-25-B1-H
H3CO
H3CO
B(pin)
Me
O
9d
1.92
1.05
2.03
1.03
1.01
1.00
0.97
1.00
2.82
2.78
2.92
1.08
12.82
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

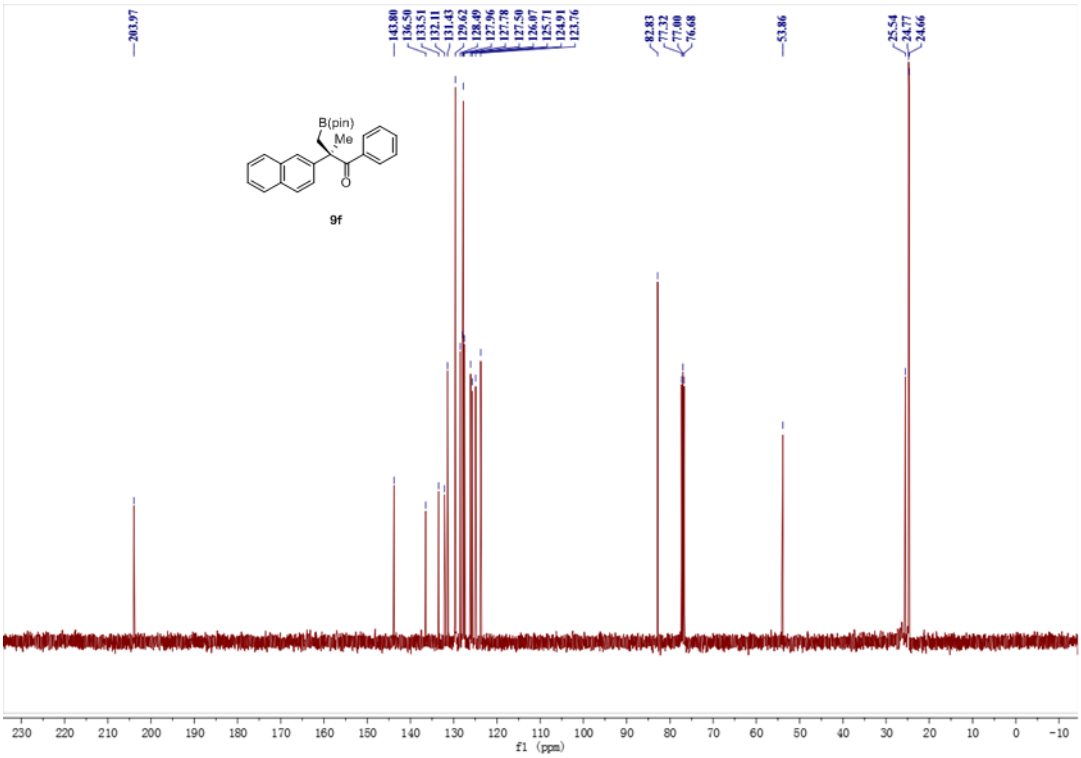

CFC-6-25-B1-C
xcc
202.38
157.67
152.87
148.95
148.40
137.01
131.39
128.57
127.98
123.09
116.33
111.22
107.26
106.60
104.73
82.89
77.32
77.00
76.68
55.87
50.99
24.82
24.67
23.87
H3CO
H3CO
B(pin)
Me
O
9d
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

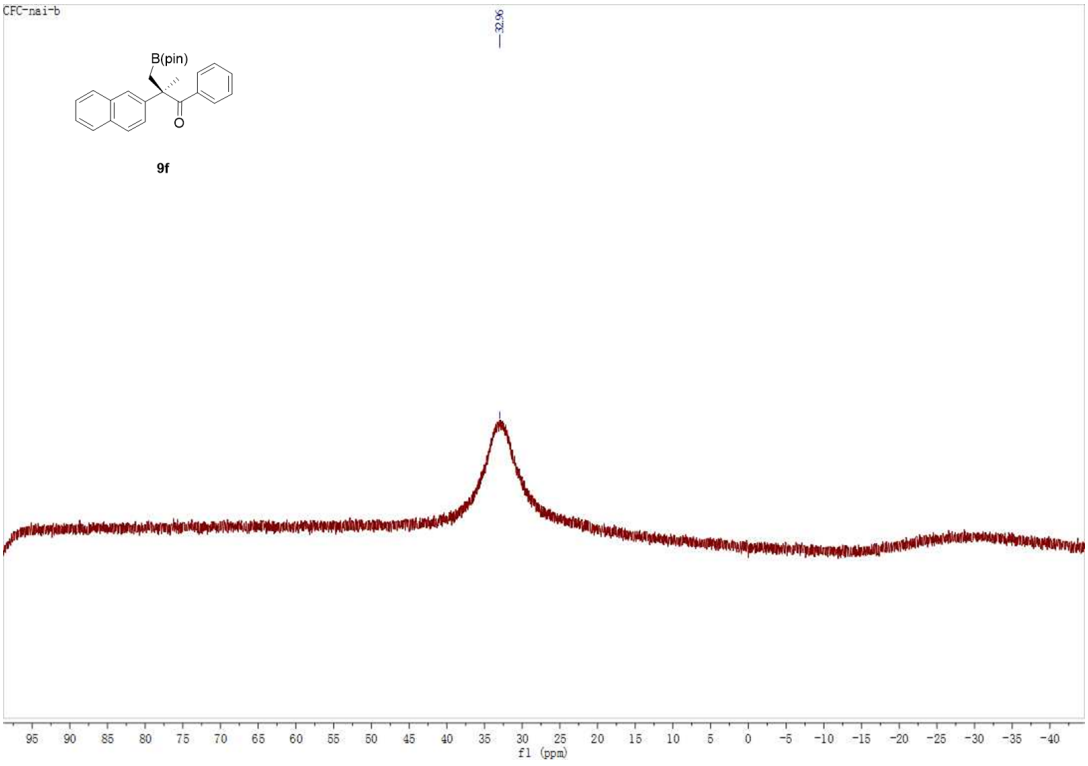

CFC-6-40-A3-H
B(pin)
Me
F3C
O
O
9e
f1 (ppm)

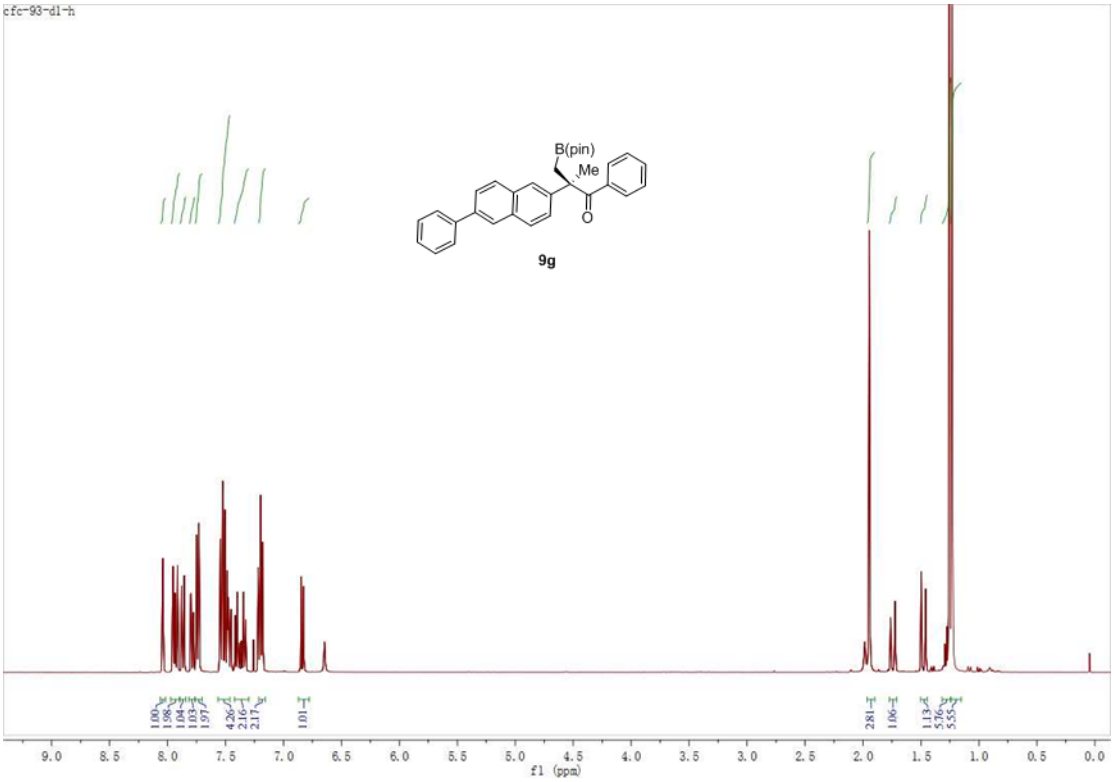

CFC-6-40-A3-C
xcc
B(pin)
Me
F3C
O
O
9e
f1 (ppm)

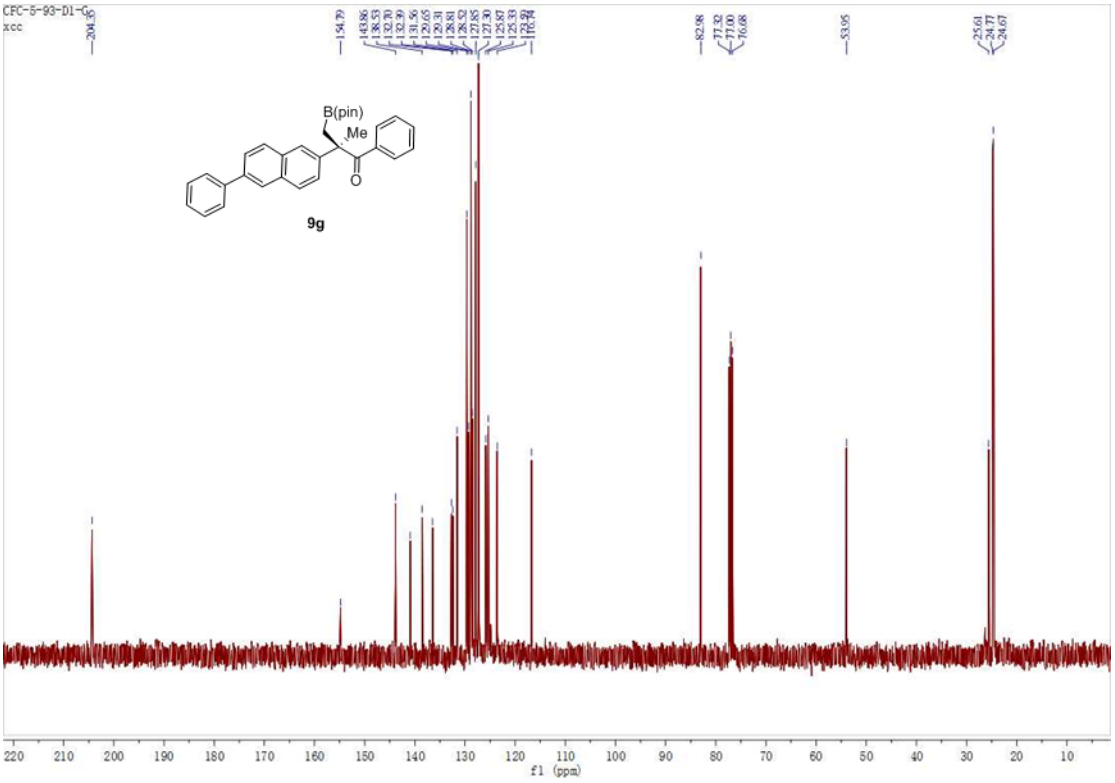

CFC-8-40-A3-F
STANDARD PROTON PARAMETERS
B(pin)
Me
F3C
O
O
9e
f1 (ppm)

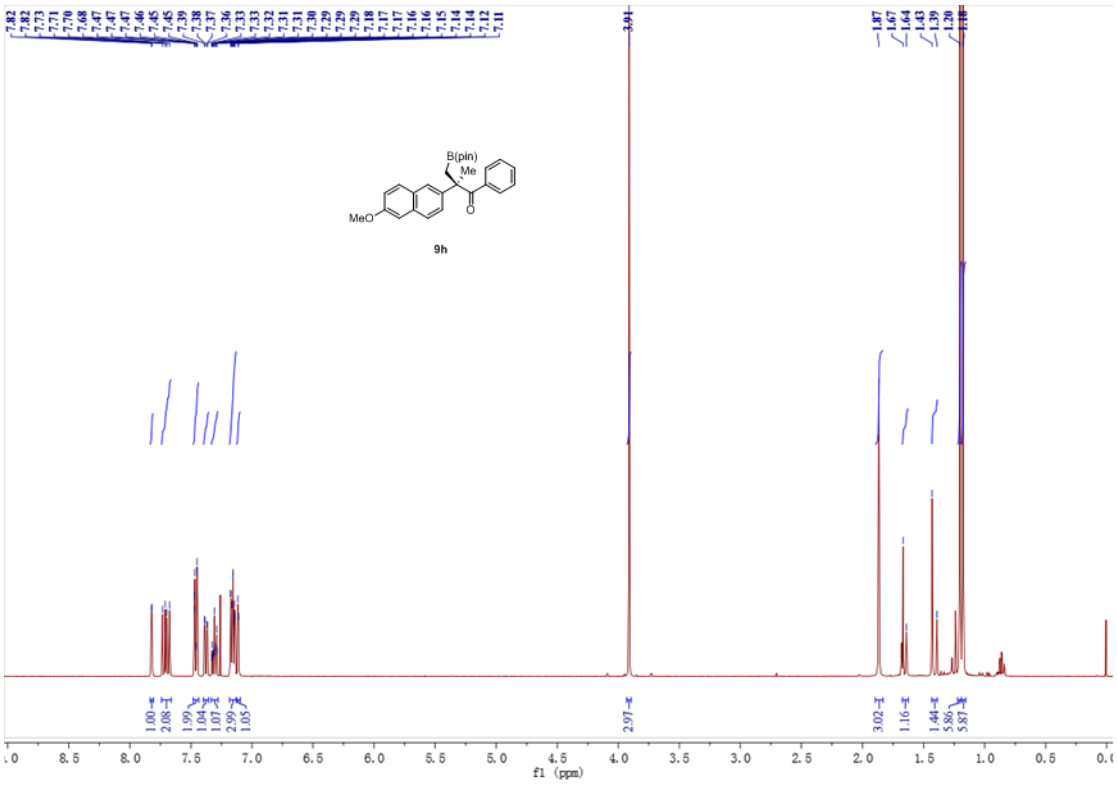

7.93
7.86
7.83
7.81
7.79
7.51
7.50
7.49
7.47
7.45
7.43
7.34
7.32
7.30
7.19
7.17
7.15
1.92
1.73
1.69
1.46
1.42
1.23
1.20
B(pin)
Me
O
9f
1.00
2.98
4.91
1.08
2.02
2.94
1.04
1.05
5.96
5.77
f1 (ppm)

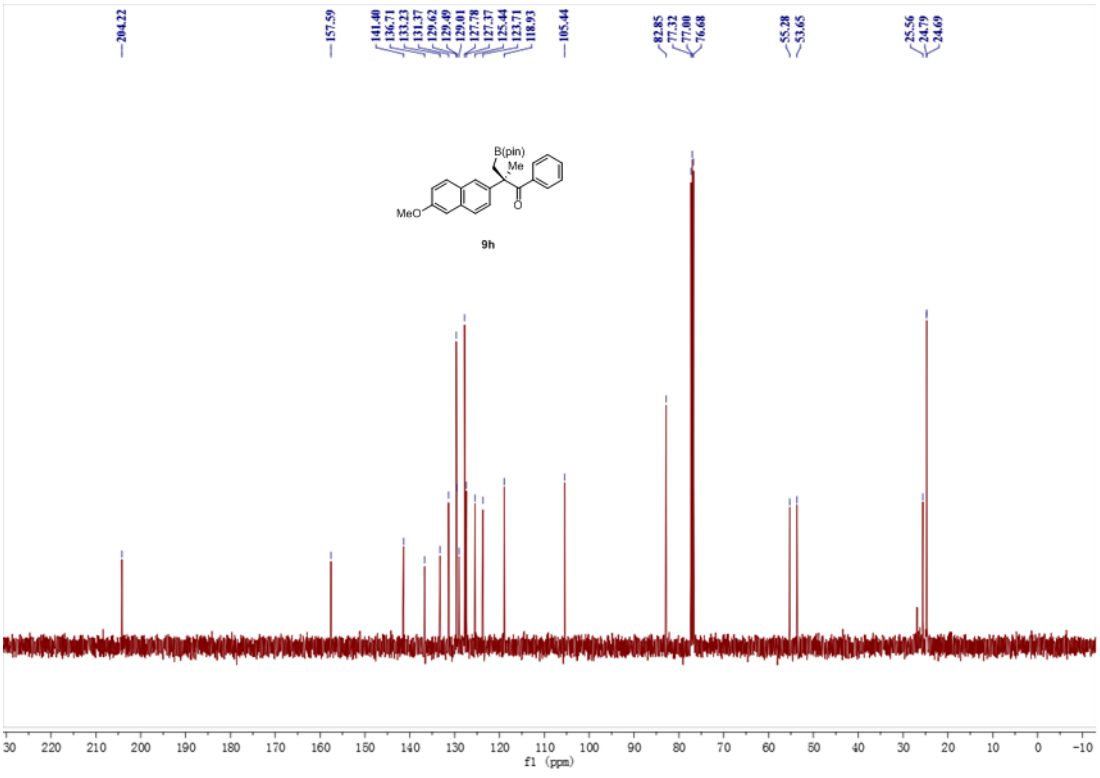

203.97
143.80
136.50
133.51
132.11
131.43
129.62
128.49
127.96
127.78
127.50
126.07
125.71
124.91
123.76
82.83
77.32
77.00
76.68
53.86
25.54
24.77
24.66
B(pin)
Me
O
9f
f1 (ppm)

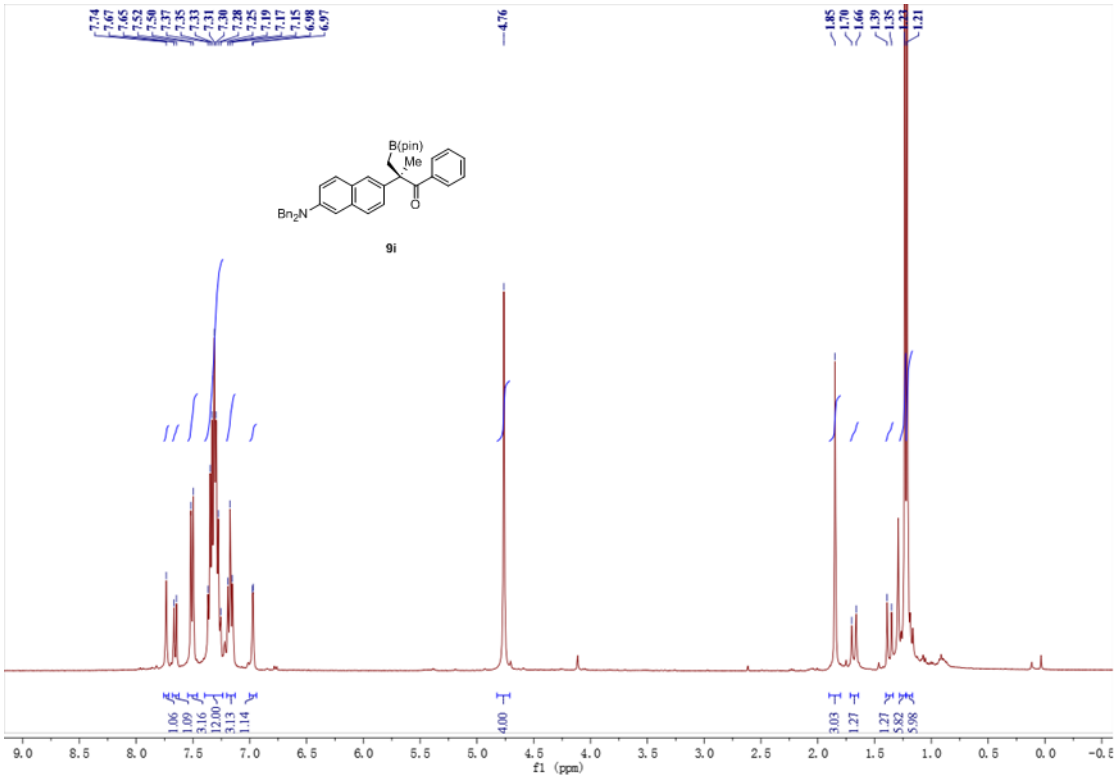

CFC-nai-b
32.96
B(pin)
O
9f
f1 (ppm)

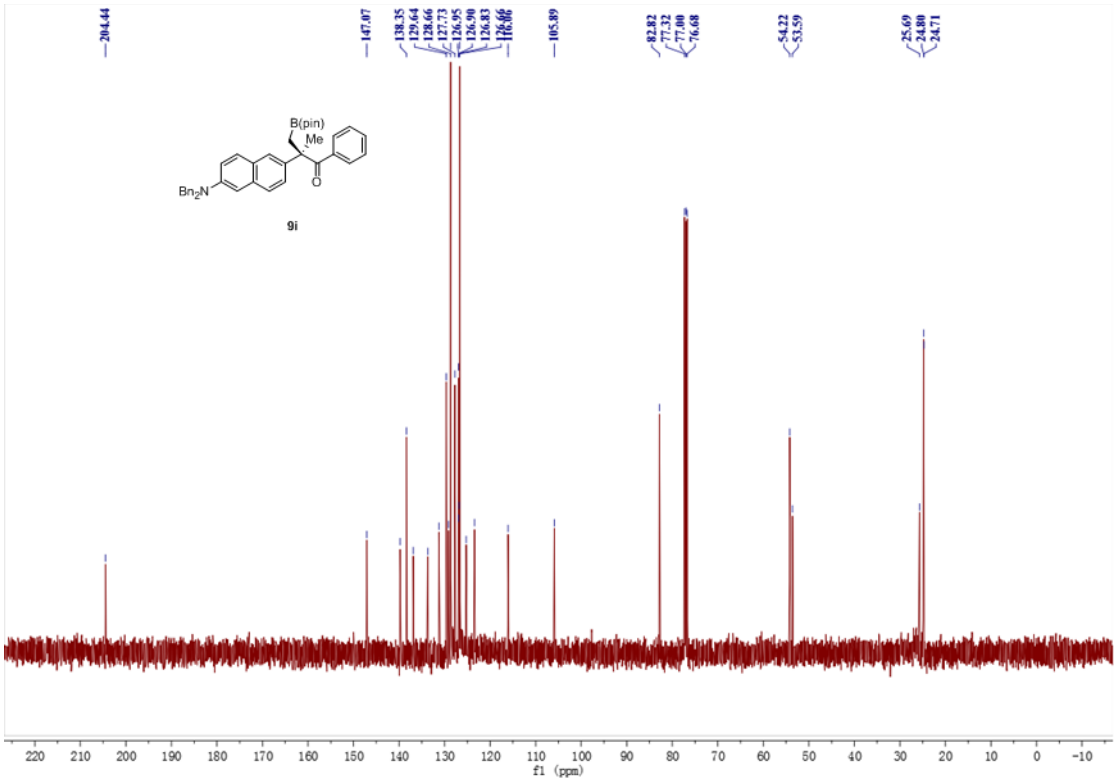

cfc-93-d1-h
B(pin)
Me
O
9g
f1 (ppm)

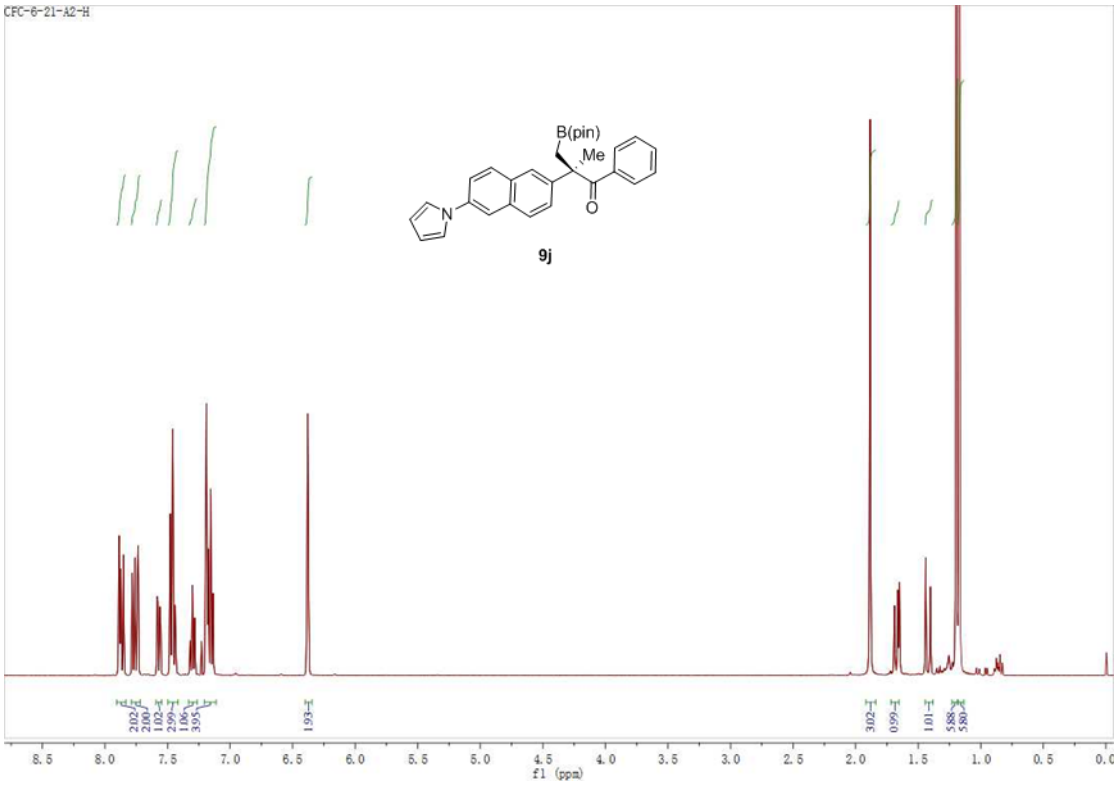

CFC-5-93-D1-C
xcc
B(pin)
Me
O
9g
f1 (ppm)

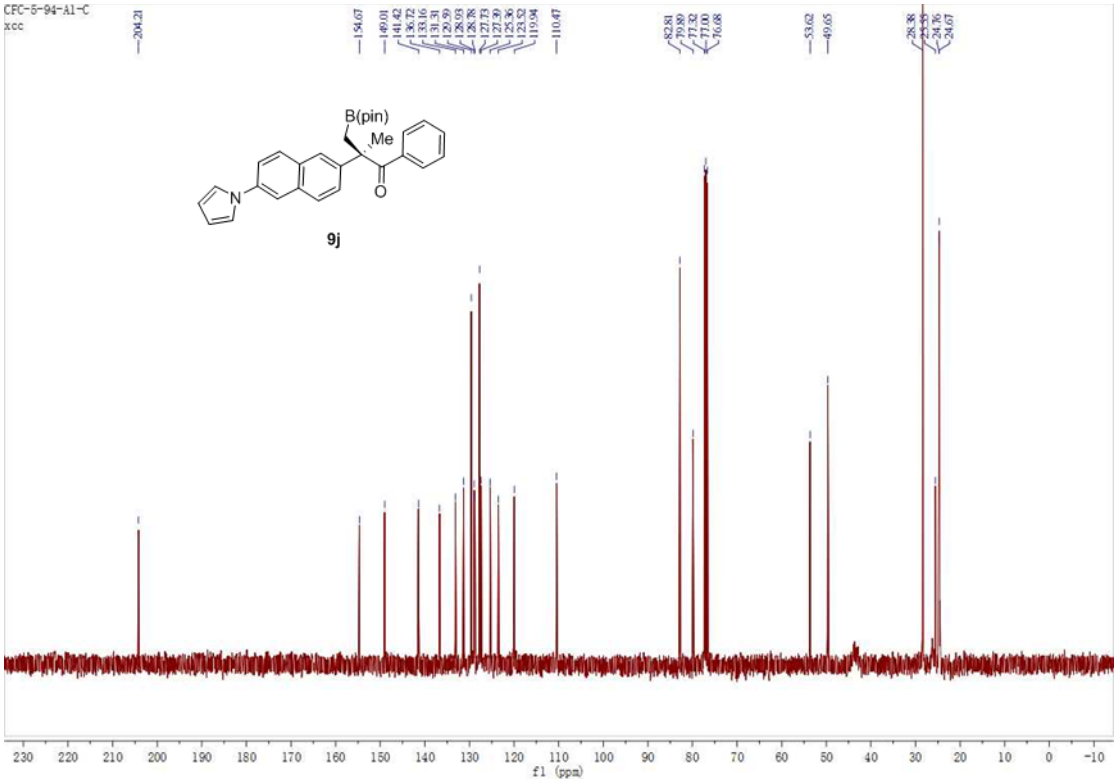

B(pin)
Me
MeO
O
9h
f1 (ppm)

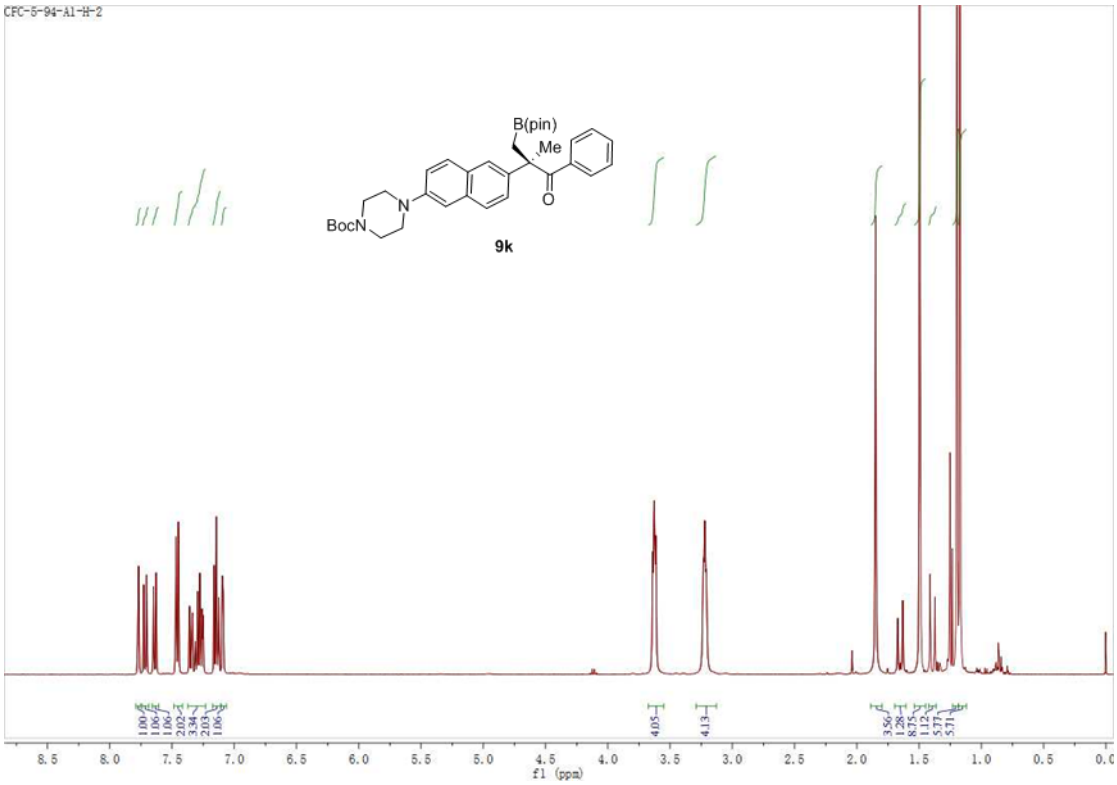

B(pin)
Me
MeO
O
9h
f1 (ppm)

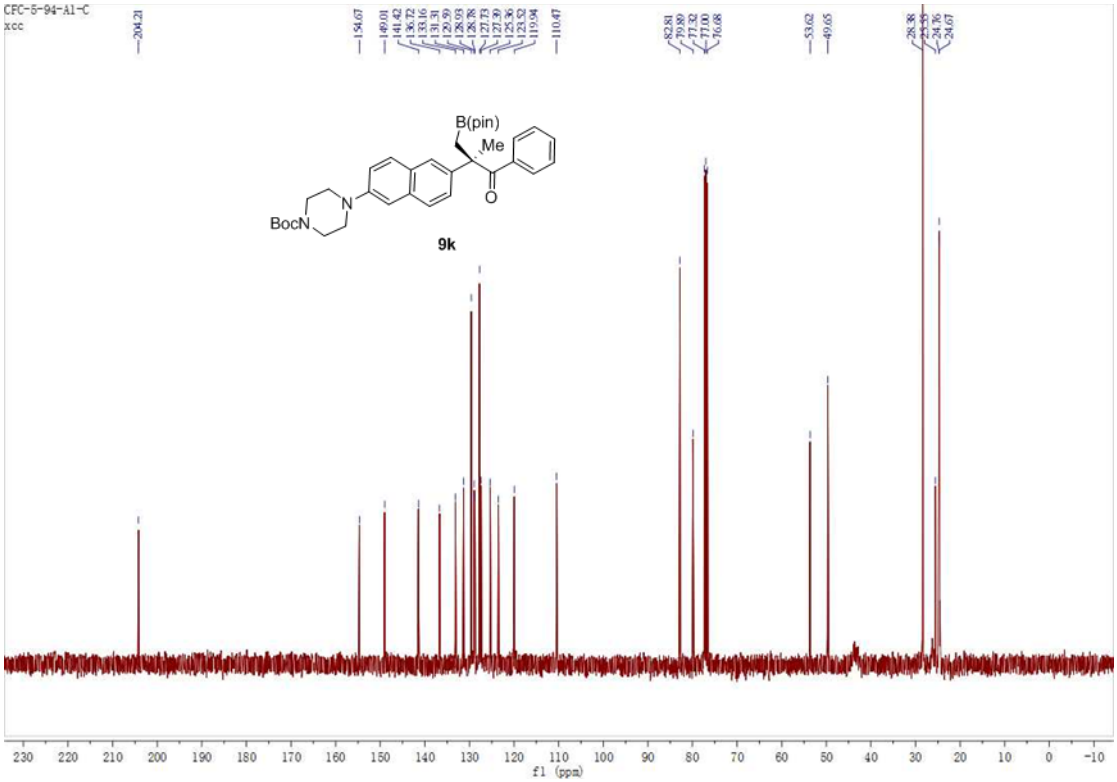

B(pin)
Me
Bn2N
O
9i
f1 (ppm)

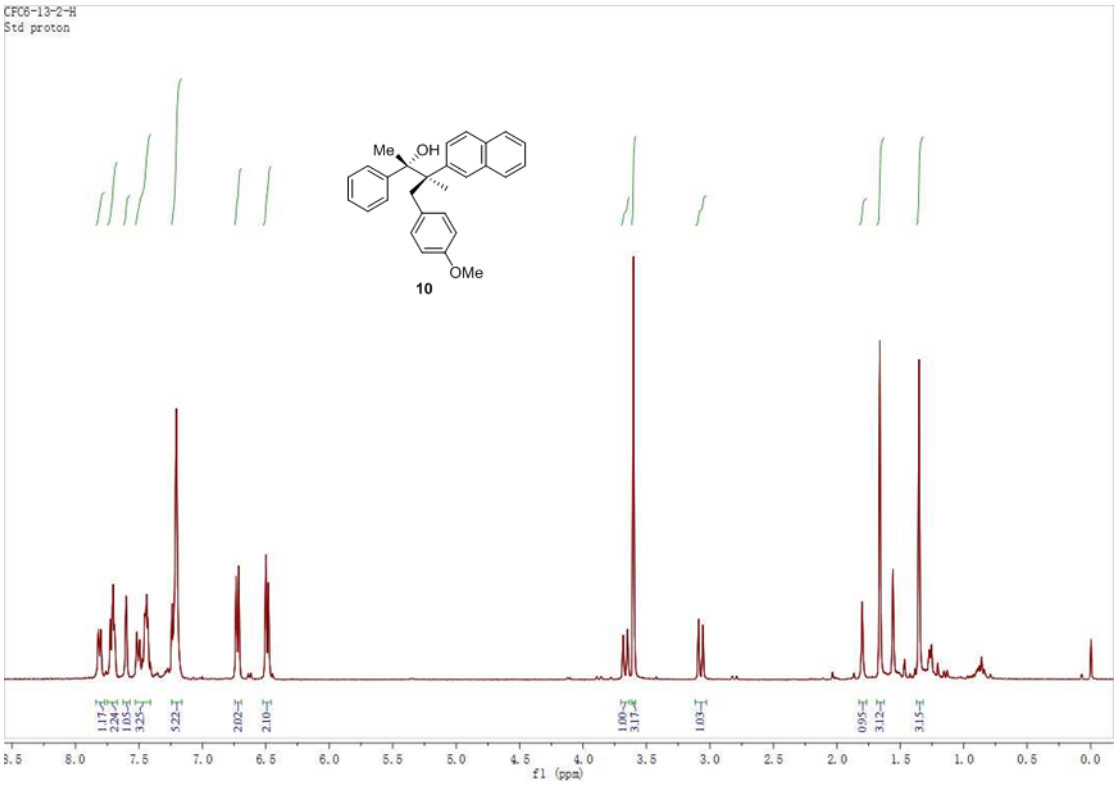

B(pin)
Me
Bn2N
O
9i
f1 (ppm)

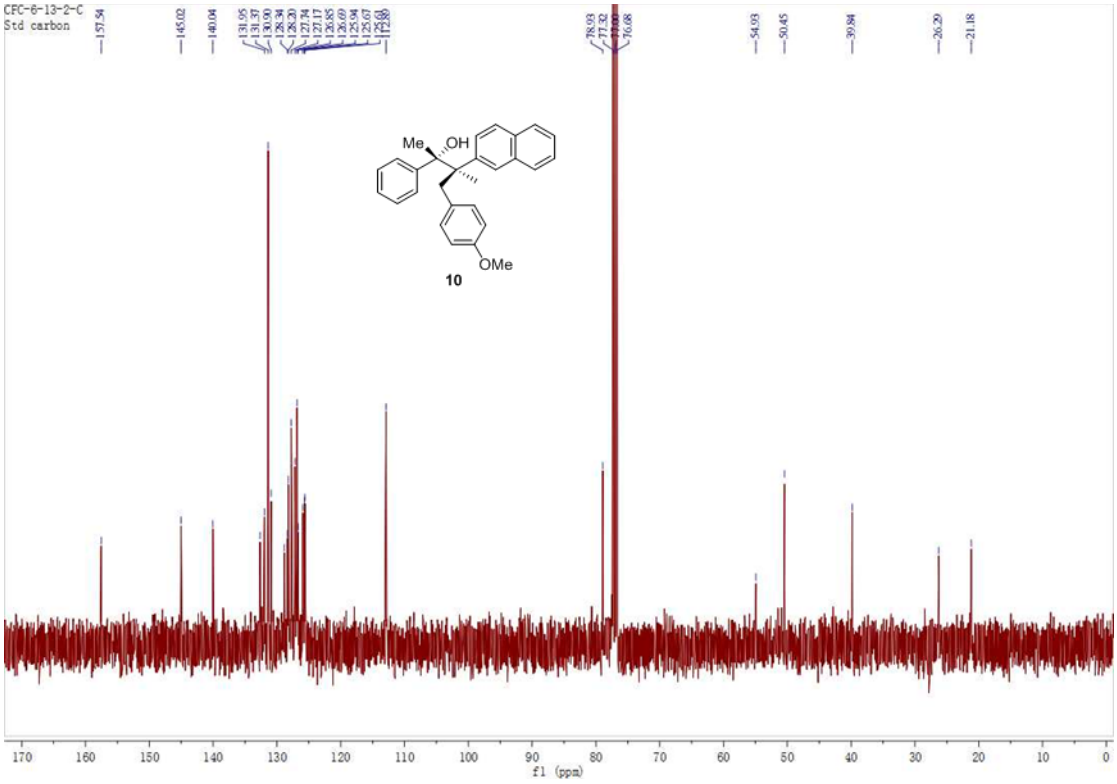

CFC-6-21-A2-H
B(pin)
Me
O
N
9j
f1 (ppm)

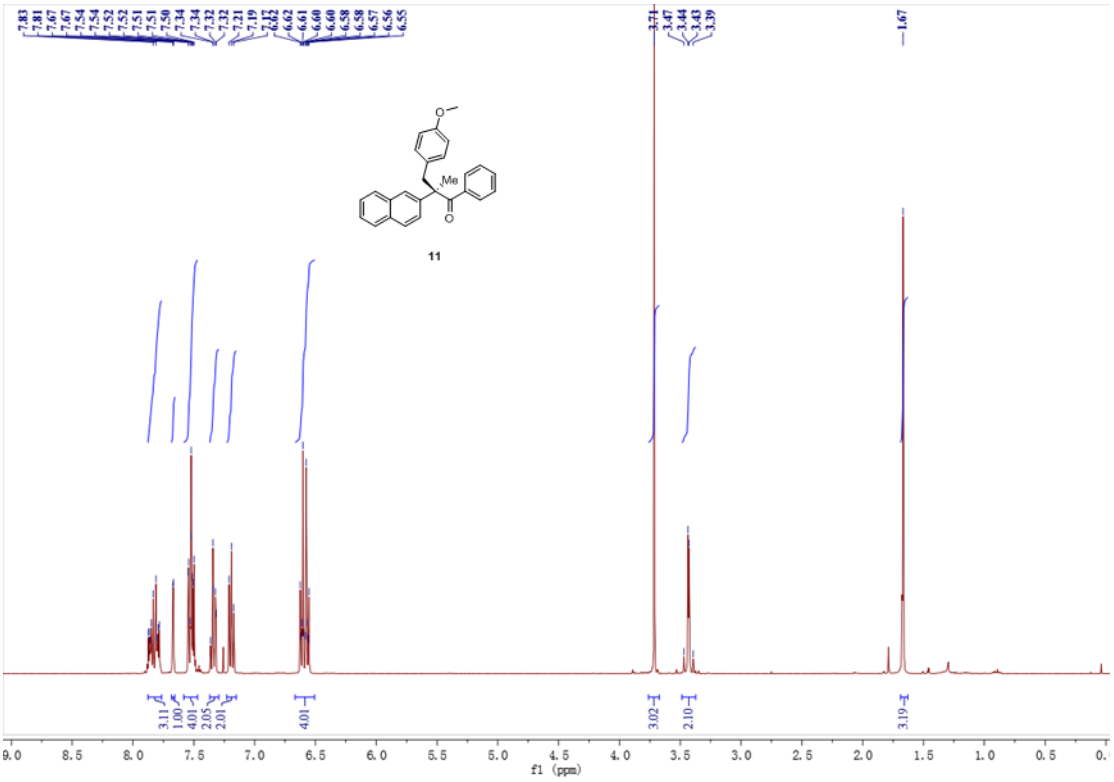

CFC-5-94-A1-C
xcc
B(pin)
Me
O
N
9j
f1 (ppm)

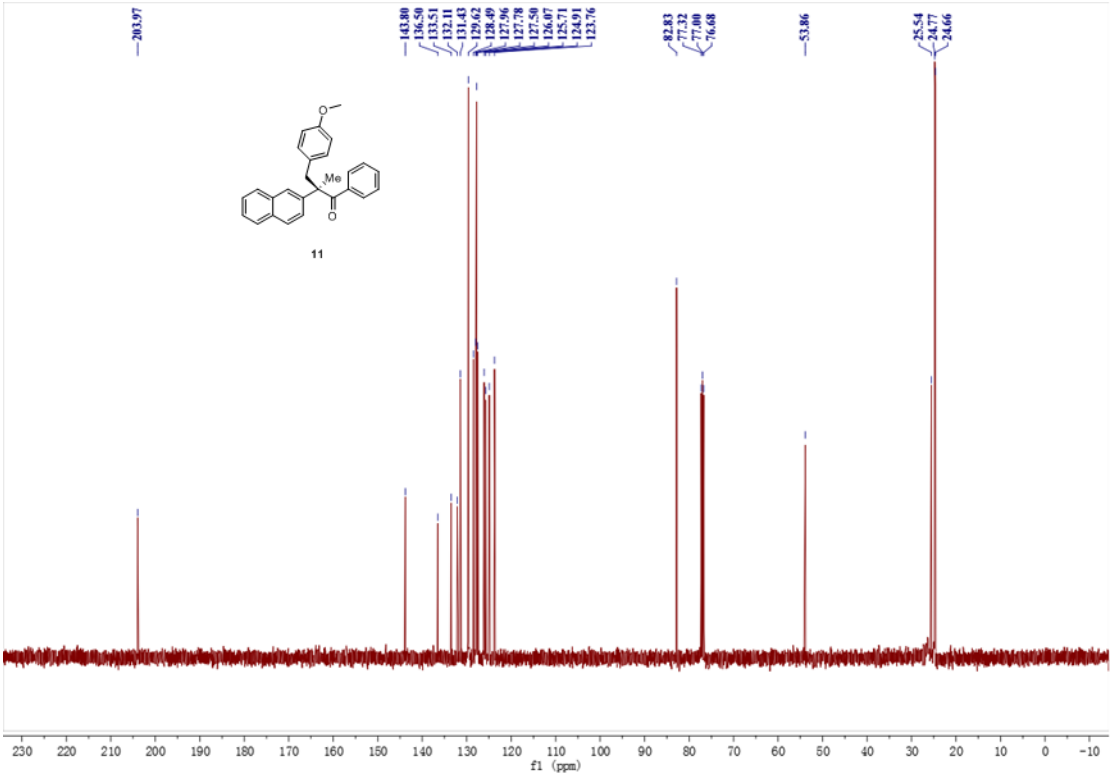

CFC-5-94-A1-H-2
B(pin)
Me
O
N
BocN
9k
f1 (ppm)

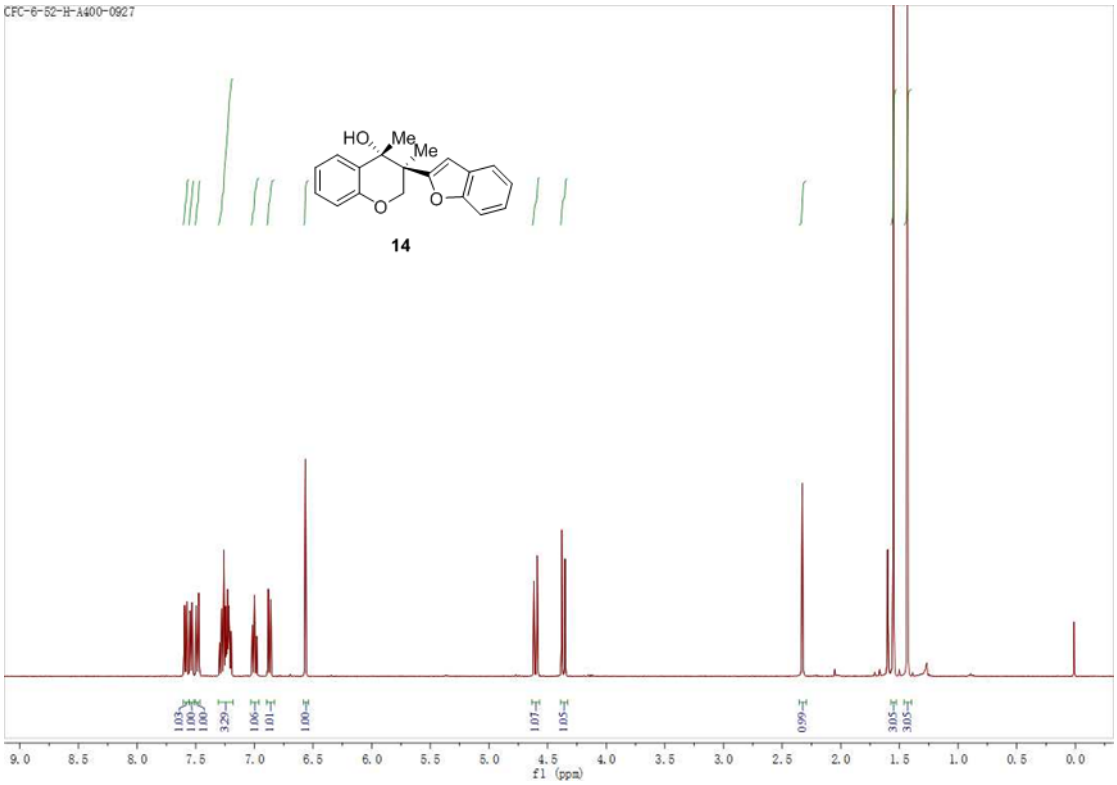

CFC-5-94-A1-C
xcc
B(pin)
Me
O
N
BocN
9k
f1 (ppm)

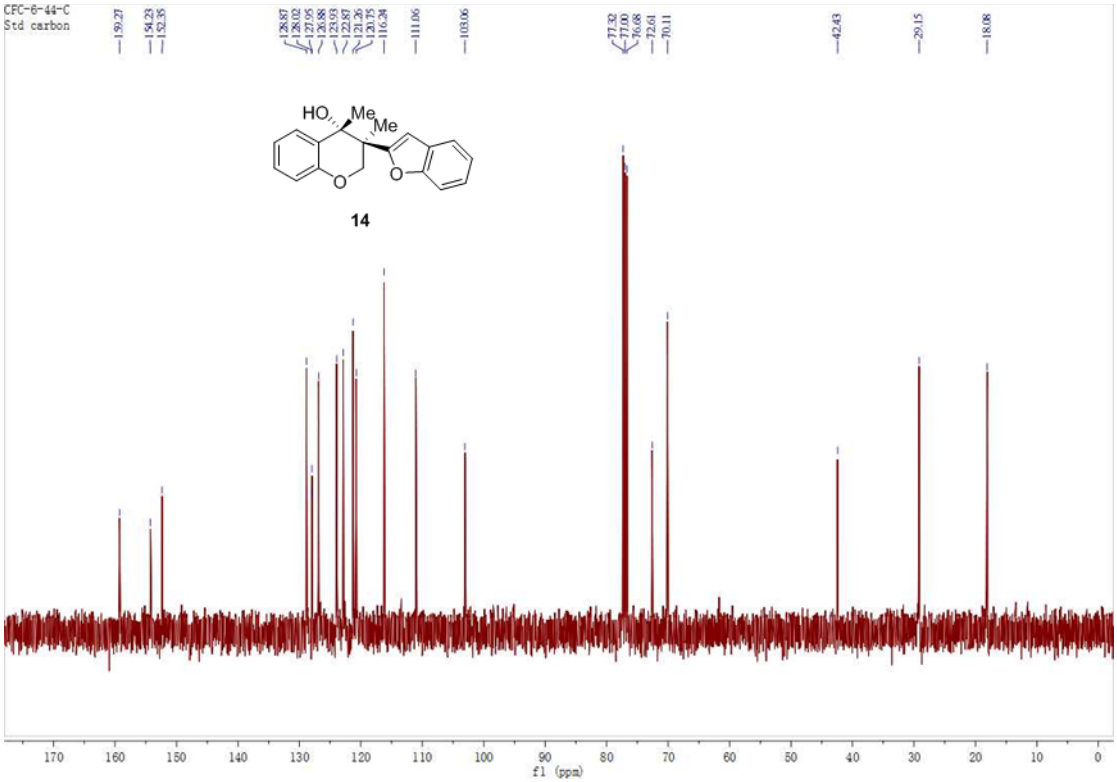

CFC6-13-2-H
Std proton
Me
OH
OMe
10
f1 (ppm)

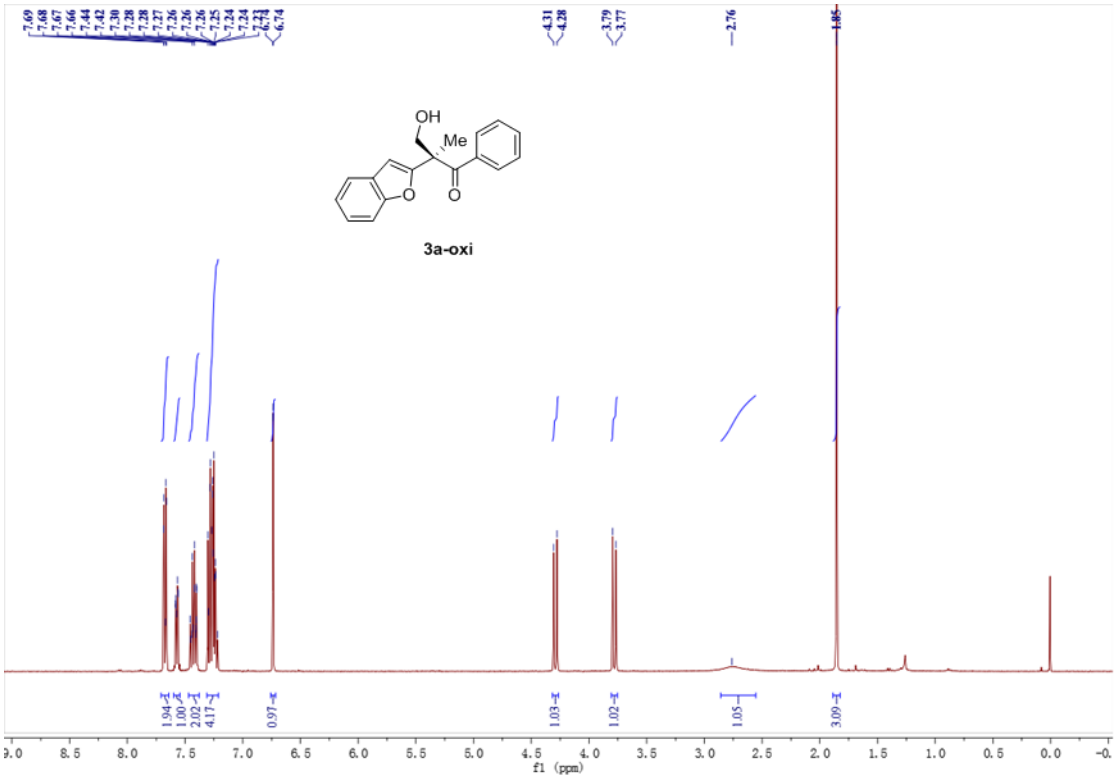

CFC-6-13-2-C
Std carbon
Me
OH
OMe
10
f1 (ppm)

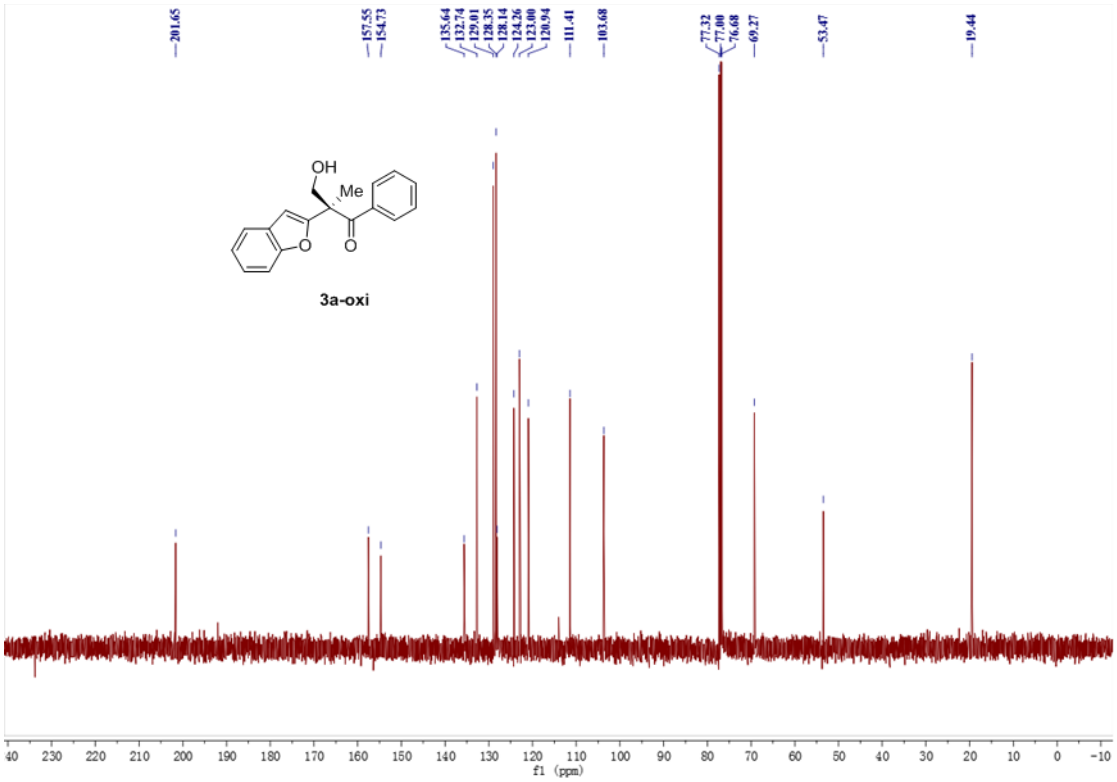

7.83
7.81
7.67
7.67
7.54
7.54
7.52
7.52
7.51
7.51
7.50
7.34
7.34
7.32
7.32
7.21
7.19
6.62
6.61
6.60
6.60
6.58
6.58
6.57
6.56
6.55
3.71
3.47
3.44
3.43
3.39
1.67
Me
O
11
3.11
1.00
4.01
2.05
2.01
4.01
3.02
2.10
3.19
f1 (ppm)

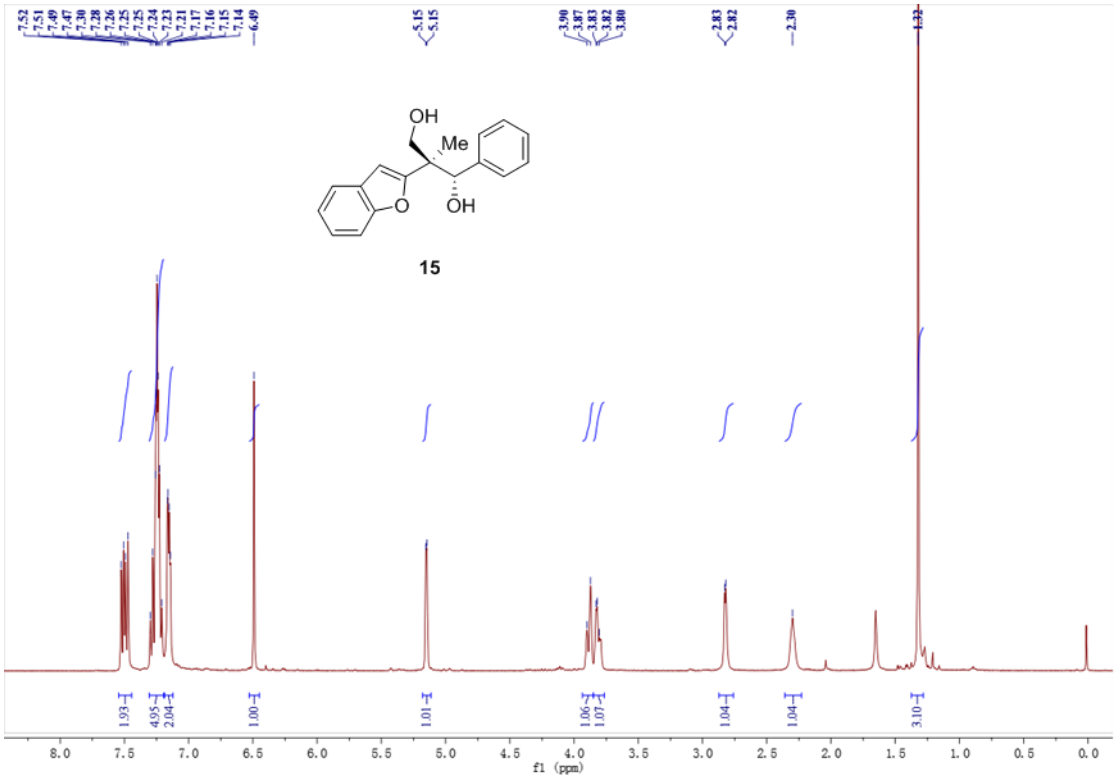

203.97
143.80
136.50
133.51
132.11
131.43
129.62
128.49
127.96
127.78
127.50
126.07
125.71
124.91
123.76
82.83
77.32
77.00
76.68
53.86
25.54
24.77
24.66
Me
O
11
f1 (ppm)

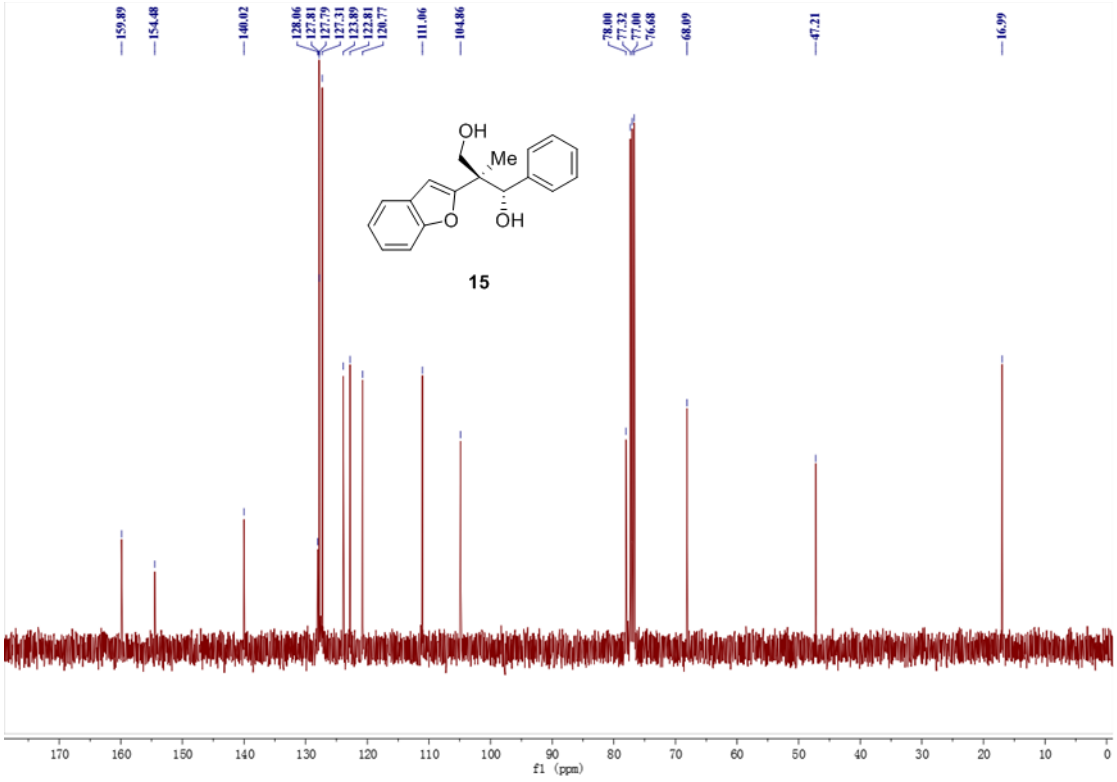

CFC-6-52-H-A400-0927
HO
Me
Me
O
O
14
1.03
1.04
1.02
3.29
1.06
1.01
1.00
1.07
1.05
0.99
3.05
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

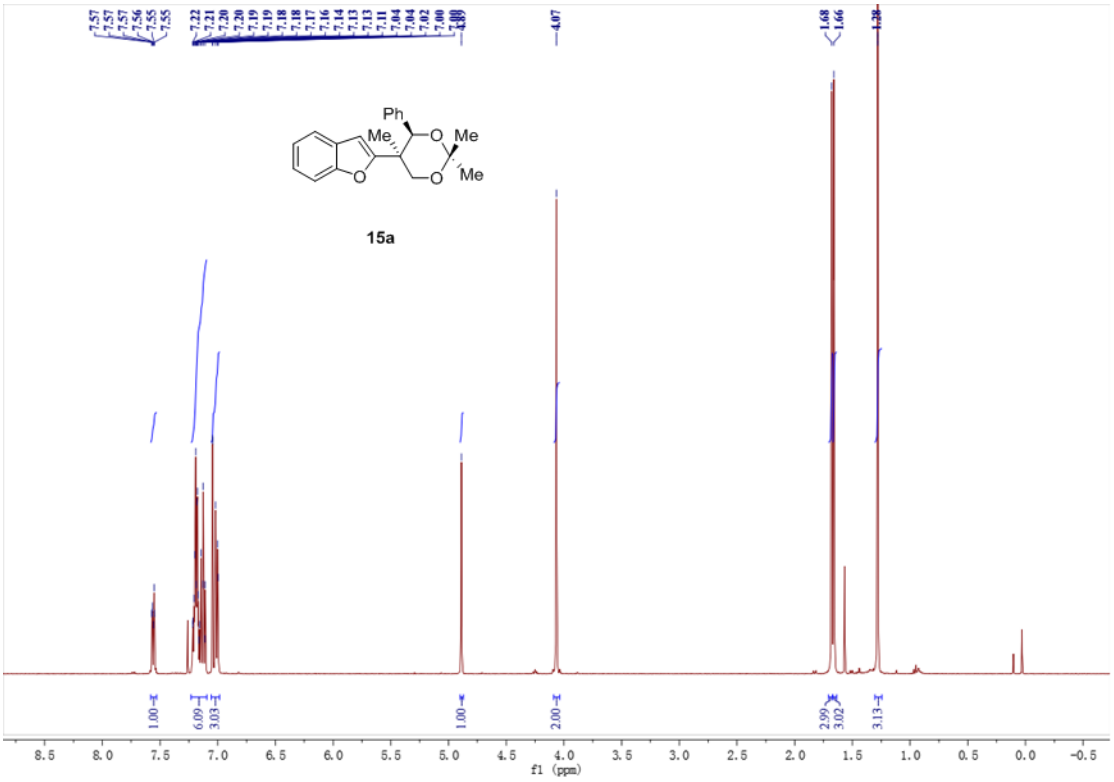

CFC-6-44-C
Std carbon
159.27
154.23
152.35
128.87
128.02
127.95
120.88
123.93
122.87
121.45
120.75
116.24
111.06
103.06
77.32
77.00
76.68
72.61
70.11
42.43
29.15
18.08
HO
Me
Me
O
O
14
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

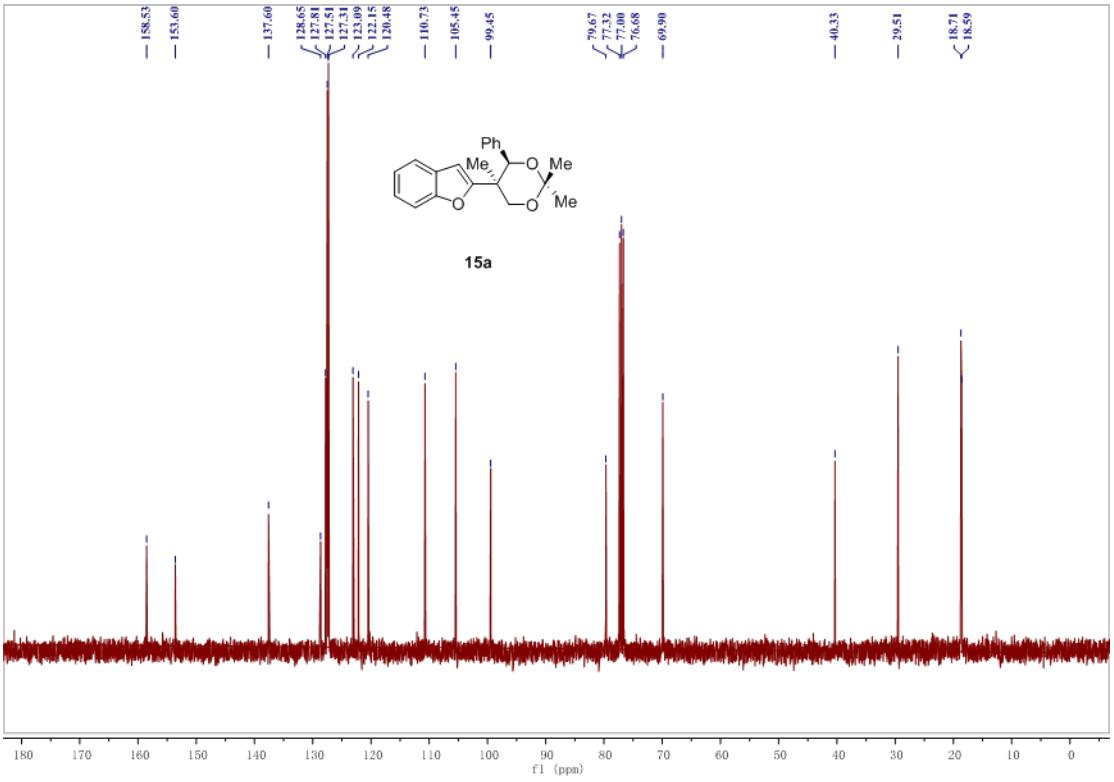

OH
Me
O
O
3a-oxi
f1 (ppm)

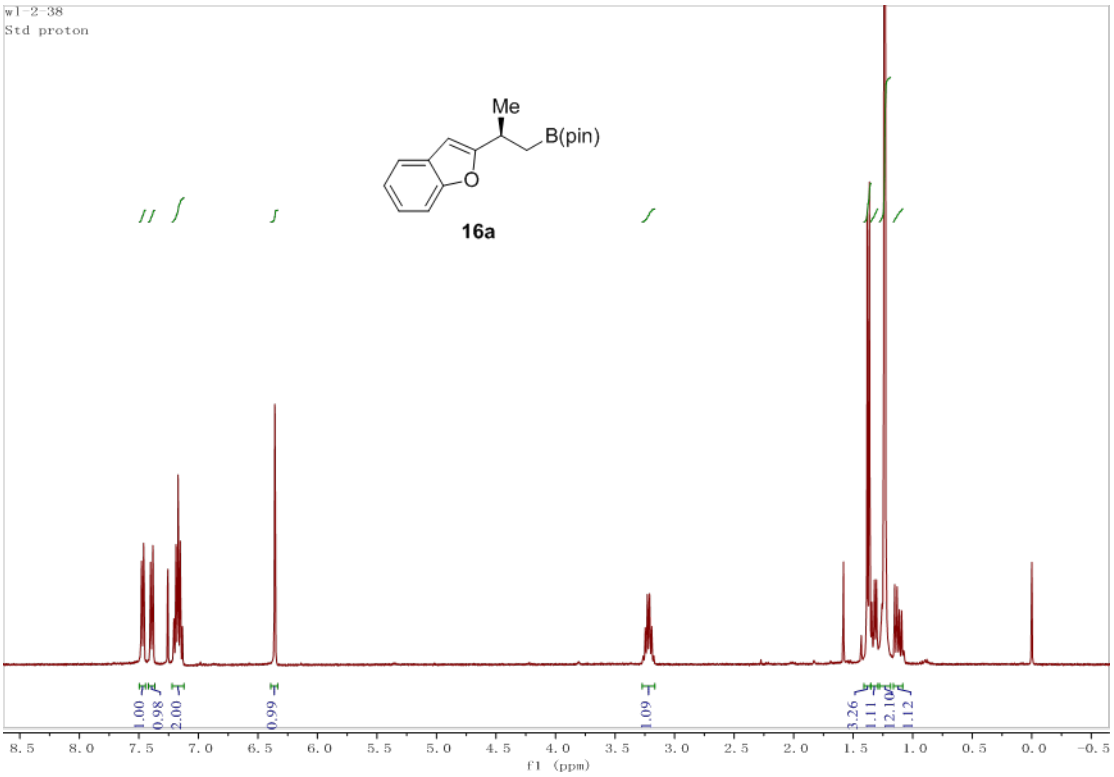

OH
Me
O
O
3a-oxi
f1 (ppm)

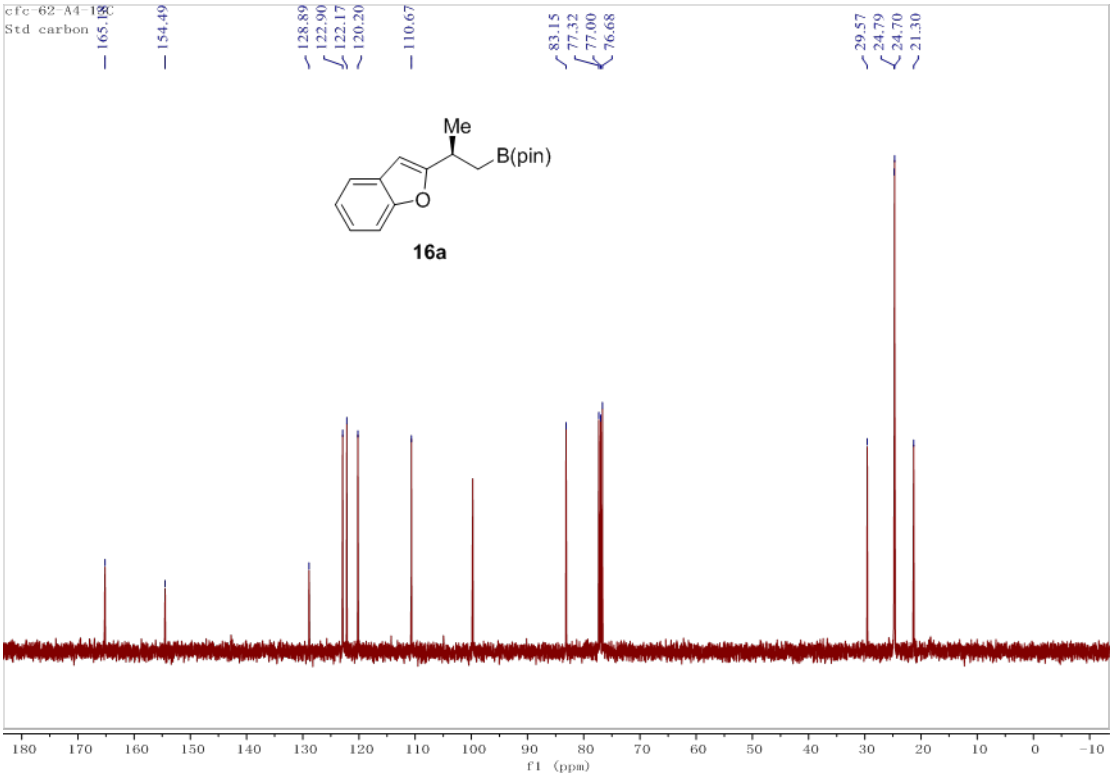

OH
Me
O
OH
15
f1 (ppm)

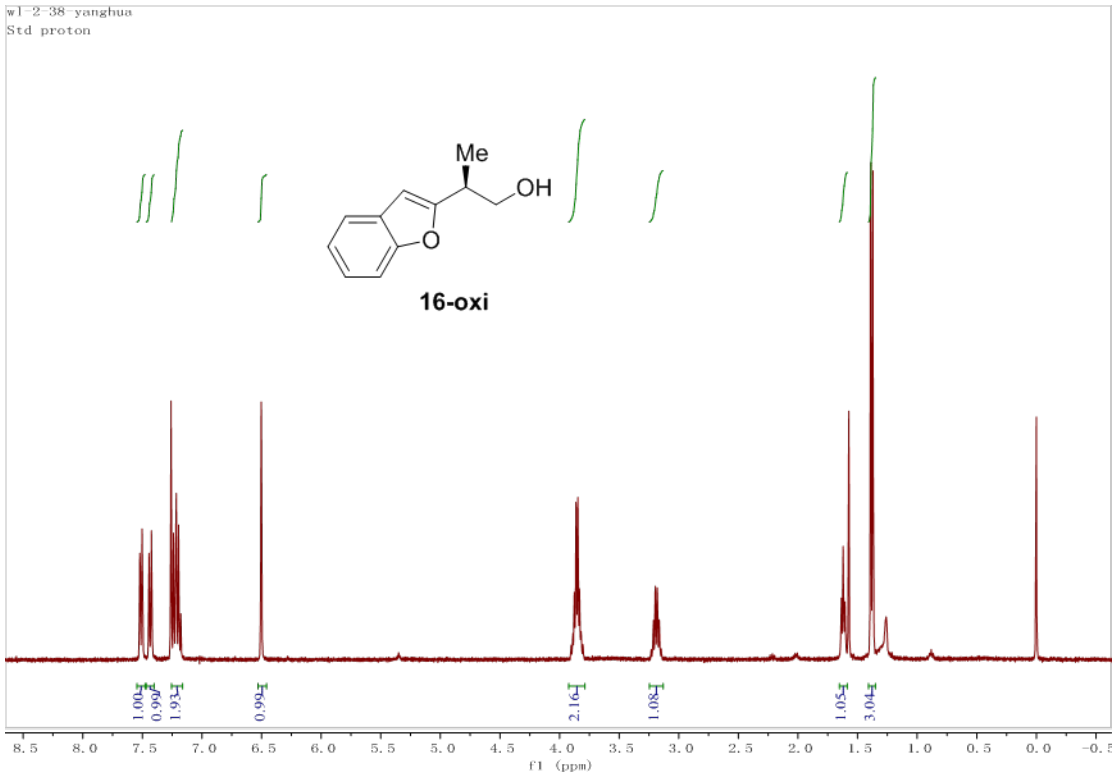

OH
Me
O
OH
15
f1 (ppm)

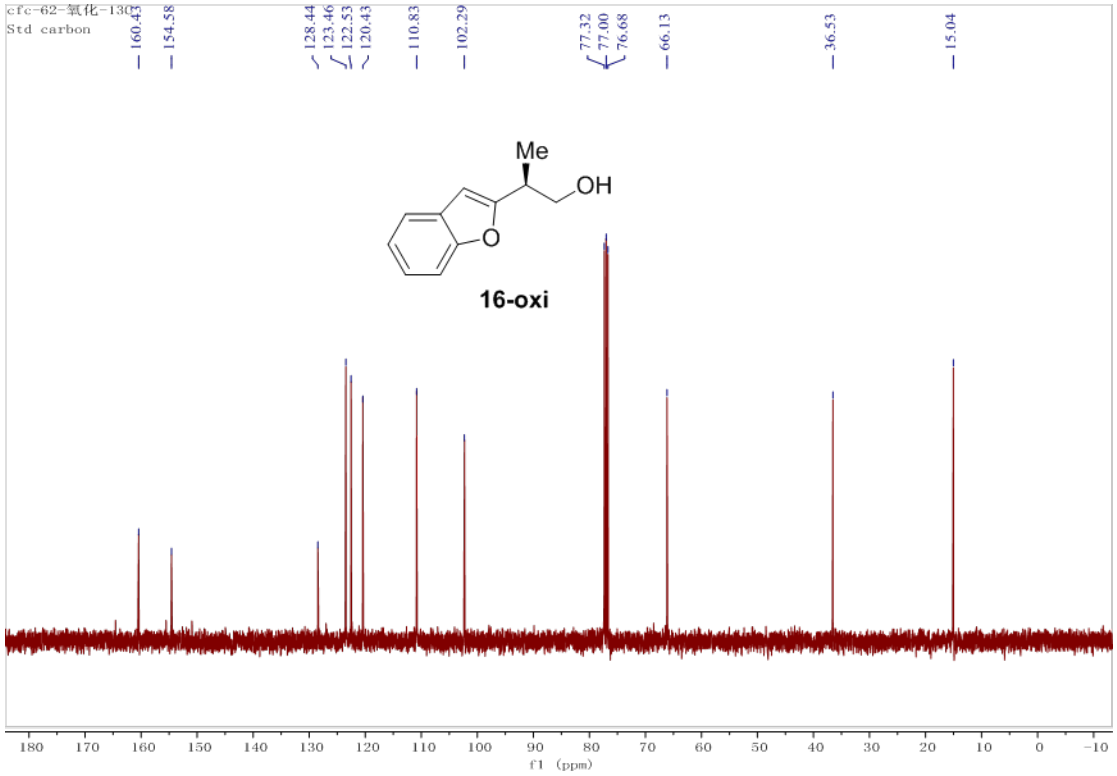

Ph
Me
O
Me
O
Me
15a
f1 (ppm)

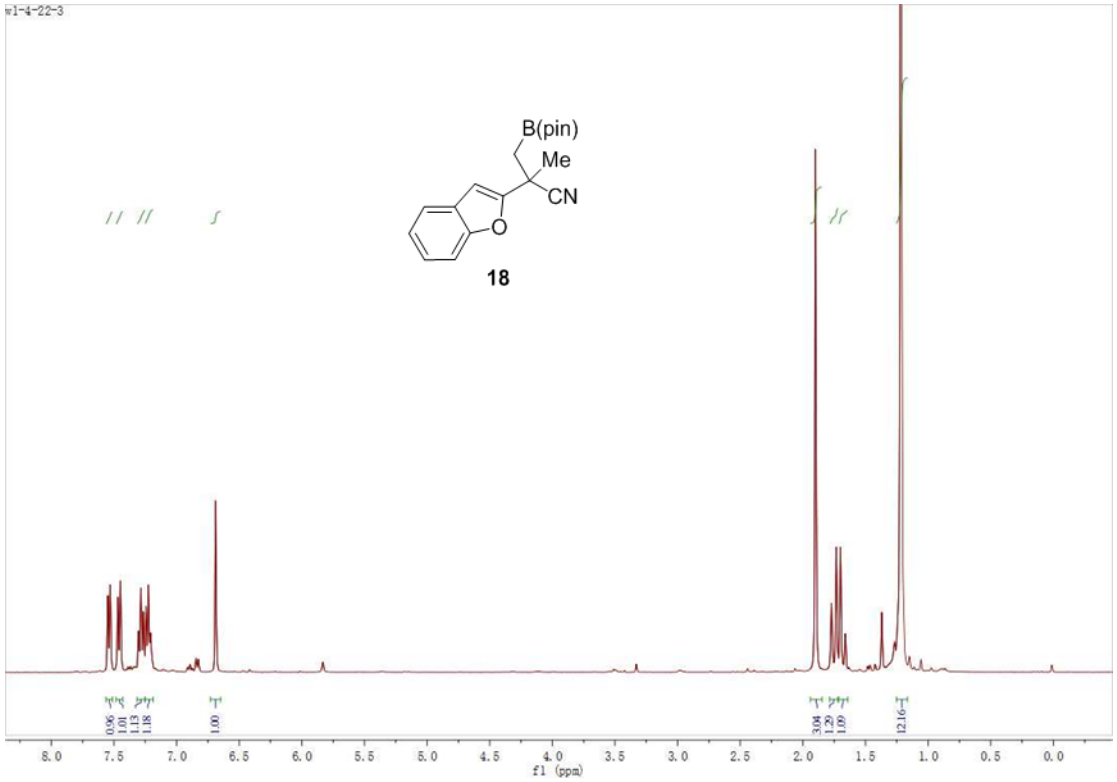

Ph
Me
O
Me
O
Me
15a
f1 (ppm)

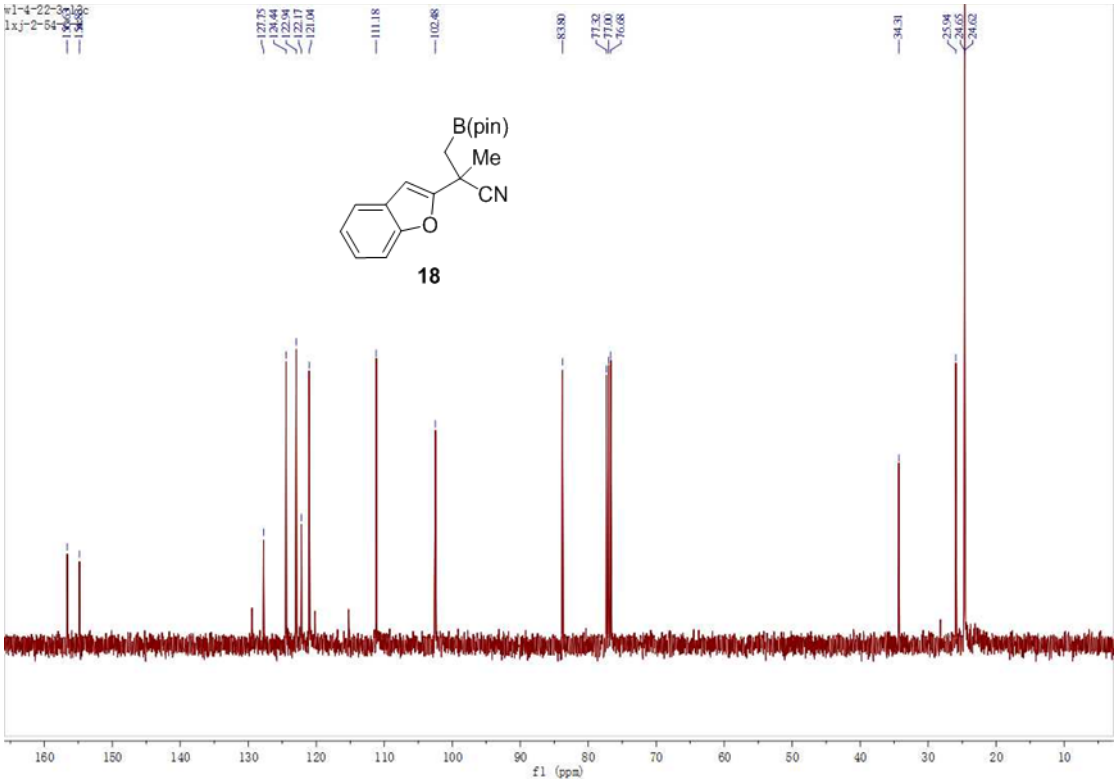

wl-2-38
Std proton
Me
B(pin)
O
16a
1.00
0.98
2.00
0.99
1.09
3.26
1.11
12.10
1.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

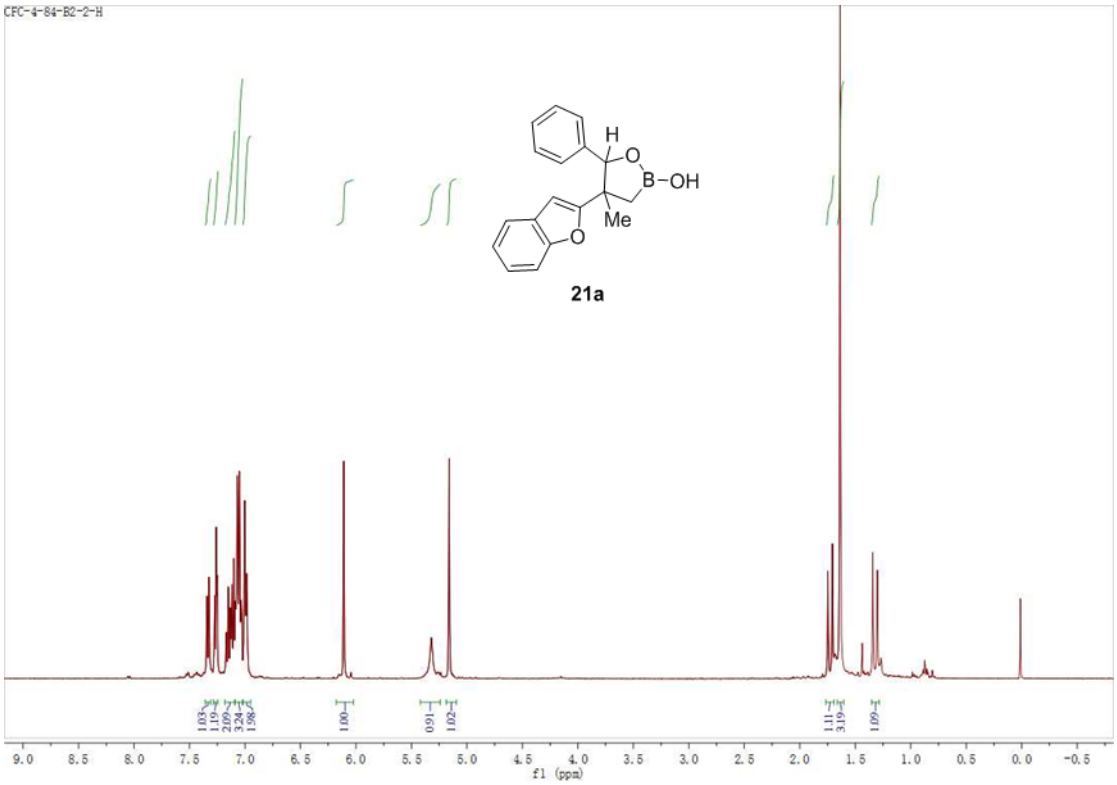

cfc-62-A4-13C
Std carbon
165.13
154.49
128.89
122.90
122.17
120.20
110.67
83.15
77.32
77.00
76.68
29.57
24.79
24.70
21.30
Me
B(pin)
O
16a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

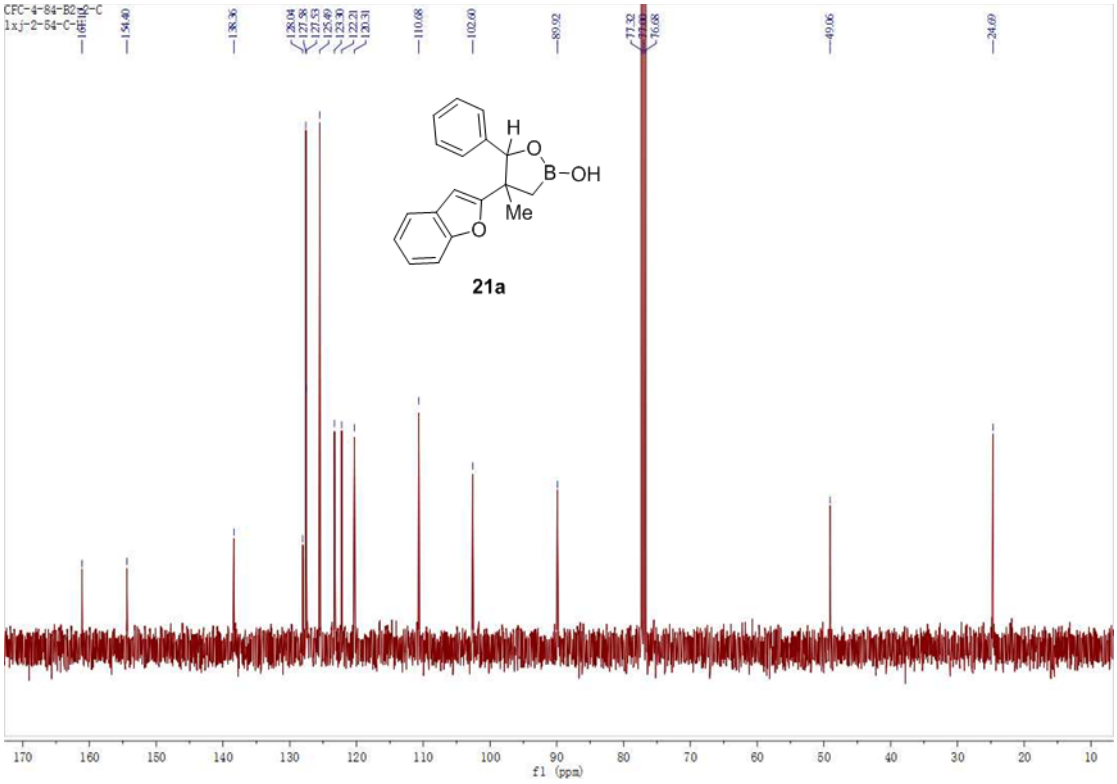

wl-2-38-yanghua
Std proton
Me
OH
O
16-oxi
1.00
0.99
1.93
0.99
2.16
1.08
1.05
3.04
f1 (ppm)

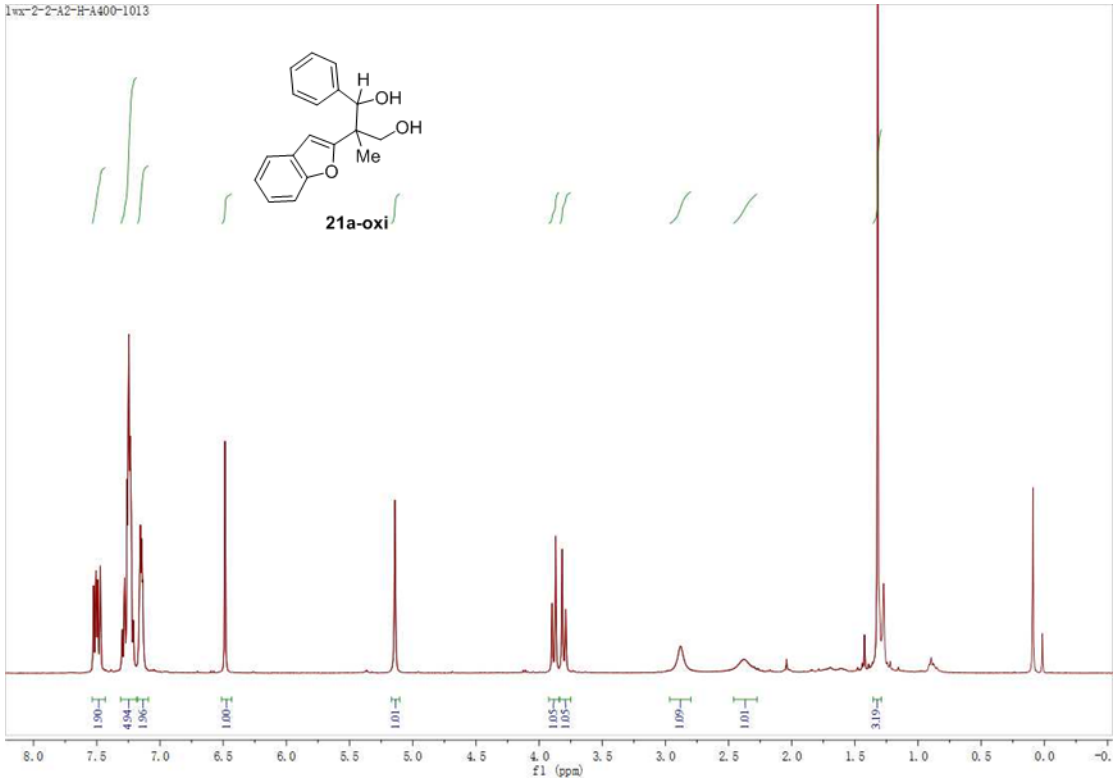

cfc-62-氧化-13C
Std carbon
160.43
154.58
128.44
123.46
122.53
120.43
110.83
102.29
77.32
77.00
76.68
66.13
36.53
15.04
Me
OH
O
16-oxi
f1 (ppm)

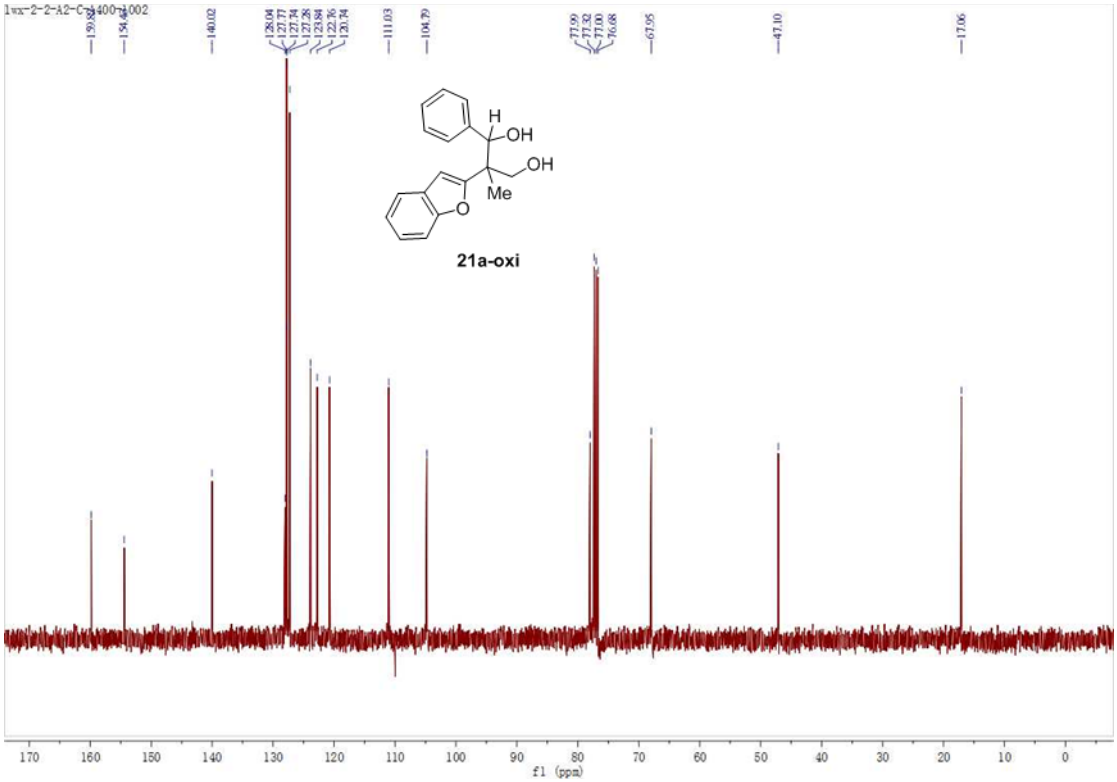

B(pin)
Me
CN
O
18
f1 (ppm)

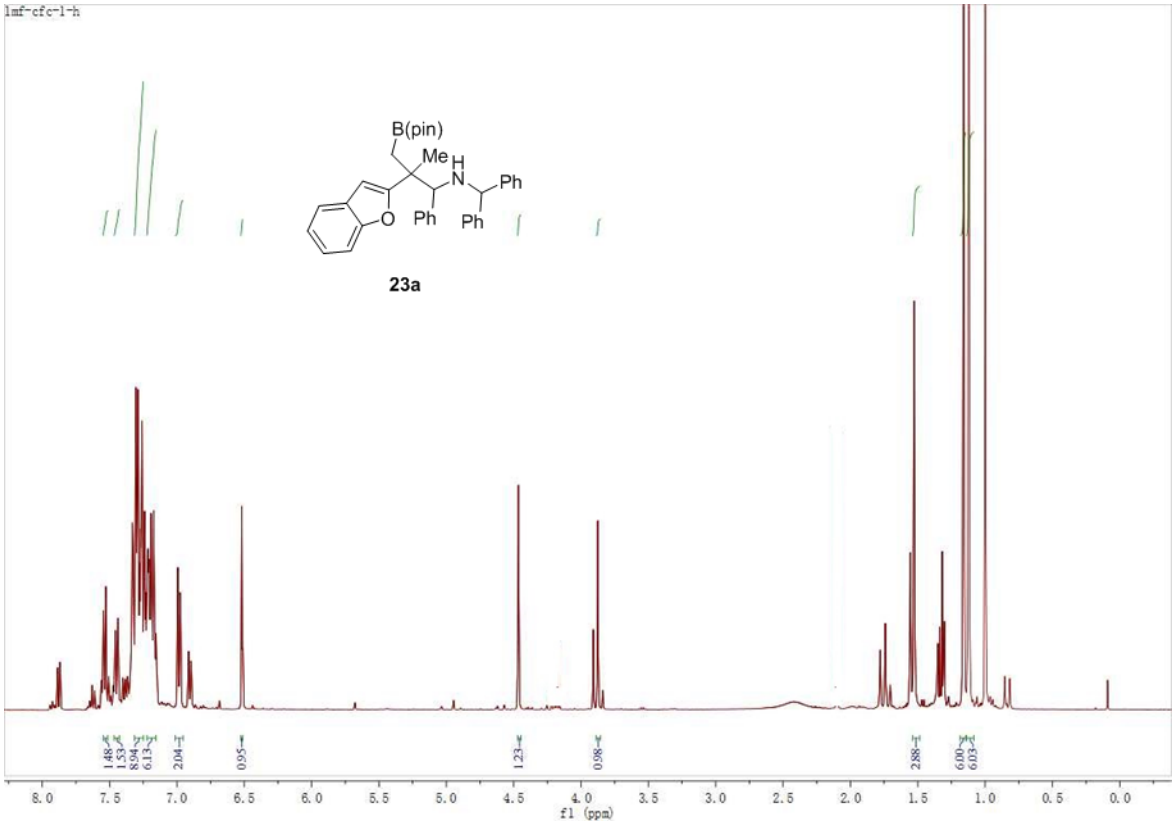

B(pin)
Me
CN
O
18
f1 (ppm)

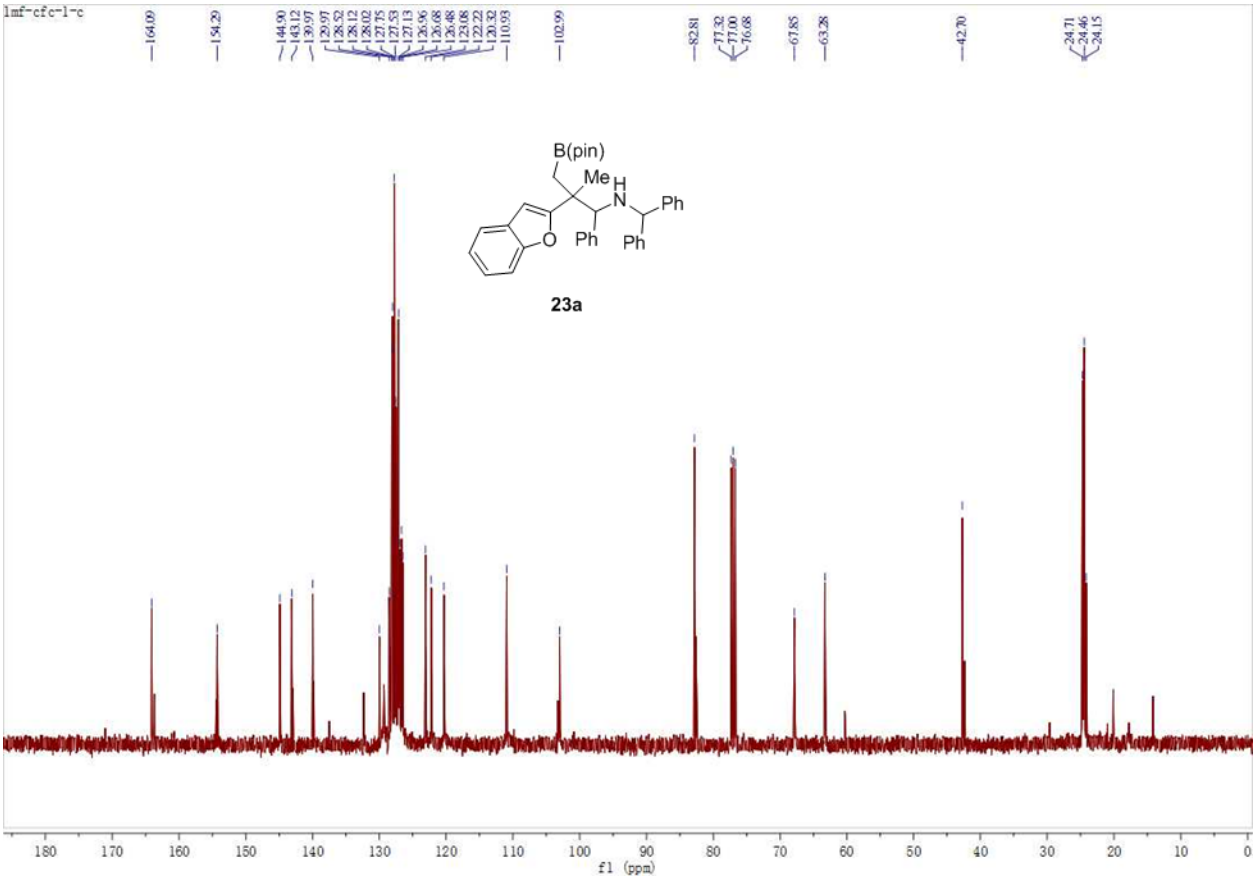

CFC-4-84-B2-2-H
H
O
B–OH
Me
O
21a
1.03
1.19
2.09
3.24
1.98
1.00
0.91
1.02
1.11
3.19
1.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

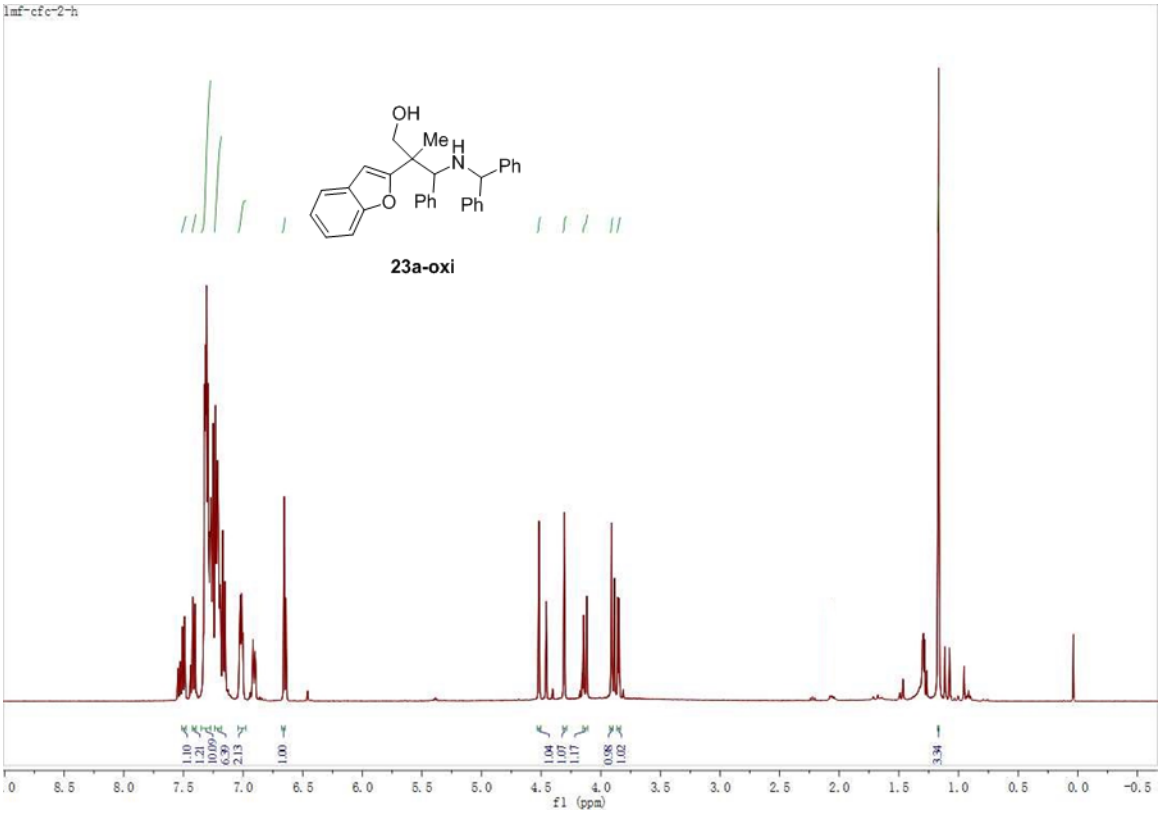

CFC-4-84-B2-C
lxj-2-54-C-DMSO
154.40
138.36
128.04
127.98
127.53
125.40
123.30
122.21
120.31
110.68
102.60
89.92
77.32
77.00
76.68
49.06
24.69
H
O
B–OH
Me
O
21a
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

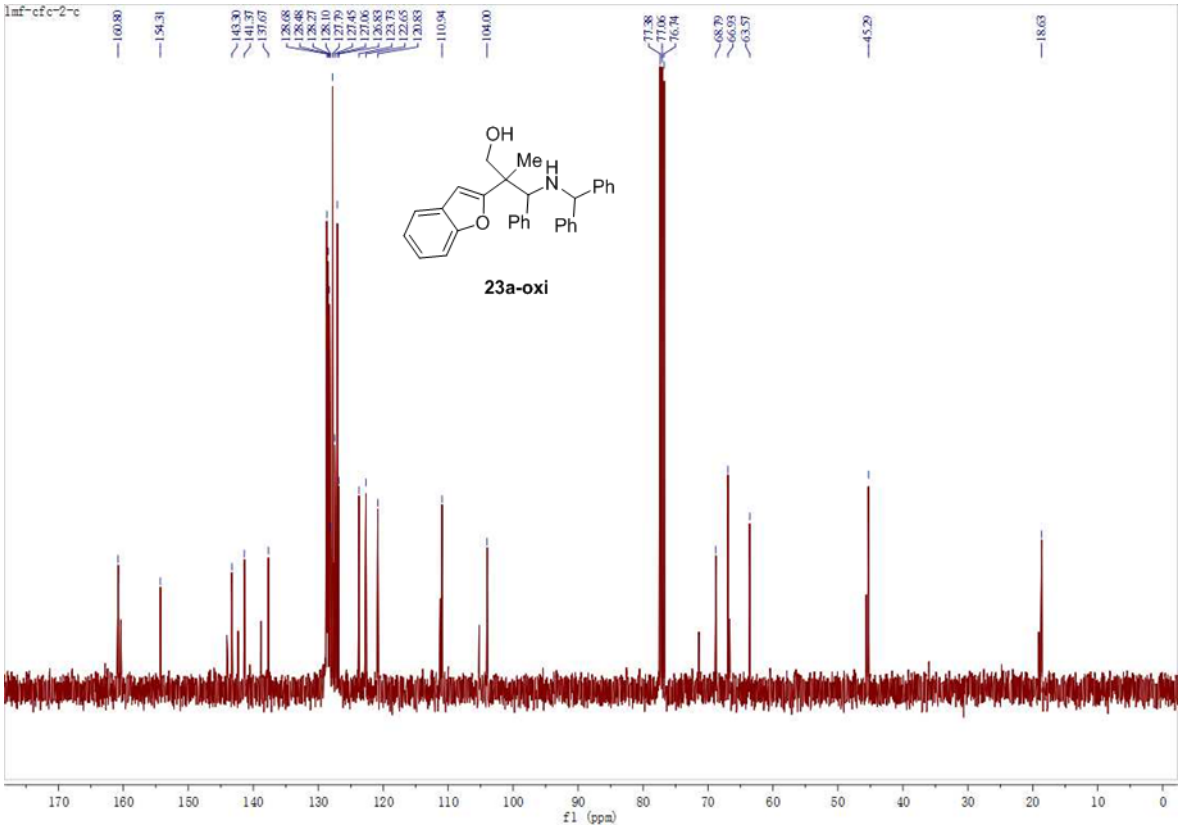

lwx-2-2-A2-H-A400-1013
H
OH
OH
Me
O
21a-oxi
1.90
4.94
1.96
1.00
1.01
1.05
1.05
1.09
1.01
3.19
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


lwx-2-2-A2-C-A400-1002
159.38
158.40
140.02
128.04
127.77
127.74
127.28
123.84
122.76
120.34
111.03
104.79
77.99
77.32
77.00
76.68
67.95
47.10
17.06
H
OH
OH
Me
O
21a-oxi
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


lmf-cfc-1-h
B(pin)
Me
H
N
Ph
Ph
O
Ph
Ph
23a
f1 (ppm)


lmf-cfc-1-c
B(pin)
Me
H
N
Ph
Ph
O
Ph
Ph
23a
f1 (ppm)


lmf-cfc-2-h
OH
Me
H
N
Ph
Ph
Ph
O
23a-oxi
1.10
1.21
10.00
6.39
2.13
1.00
1.04
1.07
1.17
0.98
1.02
3.34
f1 (ppm)


lmf-cfc-2-c
160.80
154.31
143.30
141.37
137.67
128.68
128.48
128.27
128.10
127.79
127.45
127.06
126.83
123.73
122.65
120.83
110.94
104.00
77.38
77.06
76.74
68.79
66.93
63.57
45.29
18.63
OH
Me
H
N
Ph
Ph
Ph
O
23a-oxi
f1 (ppm)