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Supplementary Information

Engineered Cytochrome *c*-Catalyzed Lactone-Carbene B–H Insertion

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I. General Information

Unless otherwise noted, all chemicals and reagents were obtained from commercial suppliers (Sigma-Aldrich, VWR, Alfa Aesar) and used without further purification. Silica gel chromatography was carried out using AMD Silica Gel 60, 230-400 mesh. ^{1}H, ^{13}C and ^{11}B NMR spectra were recorded on a Bruker Prodigy 400 MHz instrument (400 MHz for ^{1}H and 100 MHz for ^{13}C). Chemical shifts (δ) are reported in ppm downfield from tetramethylsilane, using the solvent resonance as the internal standard. Sonication was performed using a Qsonica Q500 sonicator. High-resolution mass spectra were obtained at the California Institute of Technology Mass Spectral Facility. Synthetic reactions were monitored using thin layer chromatography (Merck 60 gel plates) using a UV-lamp for visualization. Gas chromatography-mass spectrometry (GC-MS) analyses were carried out using Shimadzu GCMS-QP2010SE system and J&W HP-5ms column. Chiral normal-phase HPLC analyses were performed using an Agilent 1200 series instrument with isopropanol and hexanes as the mobile phase.

Plasmid pET22b(+) was used as a cloning vector, and cloning was performed using Gibson assembly (*1*). The cytochrome *c* maturation plasmid pEC86 (*2*) was used as part of a two-plasmid system to express prokaryotic cytochrome *c* proteins. Cells were grown using Luria-Bertani medium or HyperBroth (AthenaES) with 100 μg/mL ampicillin and 20 μg/mL chloramphenicol ($LB_{amp/chlor}$ or $HB_{amp/chlor}$). Cells without the pEC86 plasmid were grown with 100 μg/mL ampicillin (LB_{amp} or HB_{amp}). Primer sequences are available upon request. Electrocompetent *Escherichia coli* cells were prepared following the protocol of Sambrook *et al.* (*3*). T5 exonuclease, Phusion polymerase, and *Taq* ligase were purchased from New England Biolabs (NEB, Ipswich, MA). M9-N minimal medium (abbreviated as M9-N buffer; pH 7.4) was used as a buffering system for whole cells, unless otherwise specified. M9-N buffer was used without a carbon source; it contains 47.7 mM Na_2HPO_4, 22.0 mM KH_2PO_4, 8.6 mM NaCl, 2.0 mM $MgSO_4$, and 0.1 mM $CaCl_2$.

II. General Protocol

(A) Plasmid construction. All variants described in this paper were cloned and expressed using the pET22b(+) vector (Novagen). The gene encoding *Rma* cyt *c* (UNIPROT ID B3FQS5) was obtained as a single gBlock (IDT), codon-optimized for *E. coli*, and cloned using Gibson assembly (*1*) into pET22b(+) (Novagen) between restriction sites *Nde*I and *Xho*I in frame with an *N*-terminal pelB leader sequence (to ensure periplasmic localization and proper maturation; MKYLLPTAAAGLLLLAAQPAMA) and a *C*-terminal 6xHis-tag. This plasmid was co-transformed with the cytochrome *c* maturation plasmid pEC86 (*2*) into *E. cloni*® EXPRESS BL21(DE3) cells (Lucigen).

(B) Expression of cytochrome *c* variants. 25 mL $HB_{amp/chlor}$ in a 125 mL flask was inoculated with an overnight culture (0.5 mL, $LB_{amp/chlor}$) of recombinant *E.* cloni® EXPRESS BL21(DE3) cells containing a pET22b(+) plasmid encoding the cytochrome *c* variant, and the pEC86 plasmid. The culture was shaken at 37 °C and 230 rpm (no humidity control) until the OD_{600} was 0.7 (approximately 3 hours). The culture was placed on ice for 30 minutes, and isopropyl β-D-1-thiogalactopyranoside (IPTG) and 5-aminolevulinic acid (ALA) were added to final concentrations of 20 μM and 200 μM, respectively. The incubator temperature was reduced to 20 °C, and the culture was allowed to shake for 22 hours at 160 rpm. Cells were harvested by centrifugation (4 °C, 5 min, 4,000 × g). The cell pellet was resuspended in M9-N buffer.

(C) Hemochrome assay. A solution of 0.5 M sodium dithionite in 0.5 M NaOH was first prepared. Separately, a solution of 1 M NaOH (0.4 mL) was mixed with pyridine (1 mL), followed by centrifugation (10,000 × g, 30 seconds) to separate the excess aqueous layer and give a pyridine-NaOH solution. To a cuvette containing 400 μL protein solution (purified protein or heat-treated lysate) in M9-N buffer, 400 μL pyridine-NaOH solution was added and mixed thoroughly. 2 μL of sodium dithionite solution was added to the solution and the cuvette was sealed with Parafilm, and the UV-Vis spectrum was recorded immediately. Cytochrome *c* concentration was determined using $\varepsilon_{550} = 30.27\ mM^{-1}cm^{-1}$ (*4*). Protein concentrations determined by the hemochrome assay were in agreement with those determined by the bicinchoninic acid (BCA) assay (Thermo Fisher) using bovine serum albumin (BSA) for standard curve preparation.

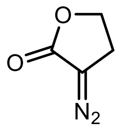
(D) Library construction. Cytochrome *c* site-saturation mutagenesis libraries were generated using a modified version of the 22-codon site-saturation method (*5*). For each site-saturation library, oligonucleotides were ordered such that the coding strand contained the degenerate codon NDT, VHG or TGG. The reverse complements of these primers were also ordered. The three forward primers were mixed together in a 12:9:1 ratio, (NDT:VHG:TGG) and the three reverse primers were mixed similarly. Two PCRs were performed, pairing the mixture of forward primers with a pET22b(+) internal reverse primer, and the mixture of reverse primers with a pET22b(+) internal forward primer. The two PCR products were gel purified, ligated together using Gibson assembly (*1*), and transformed into *E. cloni*® EXPRESS BL21(DE3) cells. Primer sequences are available upon request.

(E) Enzyme library screening. Single colonies were picked with toothpicks off of $LB_{amp/chlor}$ agar plates, and grown in deep-well (2 mL) 96-well plates containing $LB_{amp/chlor}$ (400 μL) at 37 °C, 250 rpm shaking, and 80% relative humidity overnight. After 16 hours, 30 μL aliquots of these overnight cultures were transferred to deep-well 96-well plates containing $HB_{amp/chlor}$ (1 mL) using a 12-channel EDP3-Plus 5-50 μL pipette (Rainin). Glycerol stocks of the libraries were prepared by mixing cells in $LB_{amp/chlor}$ (100 μL) with 50% v/v glycerol (100 μL).

Glycerol stocks were stored at −78 °C in 96-well microplates. Growth plates were allowed to shake for 3 hours at 37 °C, 250 rpm shaking, and 80% relative humidity. The plates were then placed on ice for 30 min. Cultures were induced by adding 10 μL of a solution, prepared in sterile deionized water, containing 2 mM IPTG and 20 mM ALA. The incubator temperature was reduced to 20 °C, and the induced cultures were allowed to shake for 20 hours (250 rpm, no humidity control). Cells were pelleted (4,000 × g, 5 min, 4 °C) and the plates containing the cell pellets were transferred into an anaerobic chamber and then resuspended in 380 μL M9-N buffer. To deep-well plates of cell suspensions were added the NHC-borane substrate (10 μL per well, 400 mM in MeCN) and the diazo compound (10 μL per well, 400 mM in MeCN). The plates were sealed with aluminum sealing tape and shaken at 480 rpm for 12 h in the anaerobic chamber. After quenching with hexanes/ethylacetate (4:6, 0.6 mL), internal standard was added (20 μL of 20 mM 1,3,5-trimethoxybenzene in toluene). The plates were then sealed with sealing mats and shaken vigorously to thoroughly mix the organic and aqueous layers. The plates were centrifuged (4,000 × g, 5 min) and the organic layer (300 μL) was transferred to autosampler vials with inserts for chiral HPLC analysis. Hits from library screening were confirmed by small-scale biocatalytic reactions, which were analyzed by GC-MS and chiral HPLC for accurate determination of turnovers and enantioselectivities.

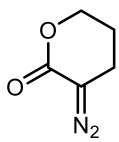
III. Synthesis of Lactone Diazos and NHC-Boranes

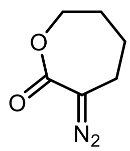
3-Diazodihydrofuran-2(3*H*)-one (1)



The preparation of the title compound **1** followed a modified procedure reported by Sattely *et al.* (*6*). Sodium azide (4.83 g, 74.3 mmol, 4 equiv.), sodium hydroxide (80 mL of 2 M in water, 160 mmol), tetrabutylammonium bromide (60.0 mg, 0.190 mmol, 0.01 equiv.), and hexane (80 mL) were combined in a 500-mL flask with magnetic stir bar open to the air and cooled to 0 °C. With vigorous stirring, triflic anhydride (6.20 mL, 37.1 mmol, 2 equiv.) was added dropwise. After 15 min, a solution of 2-acetyl-butyrolactone (2.00 mL, 18.6 mmol) in acetonitrile (70 mL) was poured into the vessel through a funnel, followed by an additional 10 mL of acetonitrile to complete the transfer. The initially colorless reaction mixture immediately turned yellow. After stirring for 20 min at 0 °C, the mixture was diluted with ice water (50 mL) and chilled EtOAc (50 mL) and transferred to a separatory funnel. After phase separation and removal of the organic fraction, the aqueous layer was washed with chilled EtOAc (50 mL × 5). The combined organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was purified through a silica column using hexane: ethyl acetate (3:1 to 2:1) as eluents. The yellow-colored fractions were concentrated to afford the product as a bright yellow crystalline solid (1.2 – 1.6 g, 60 – 75% yield).

3-Diazotetrahydro-2*H*-pyran-2-one (4) and 3-diazooxepan-2-one (6)

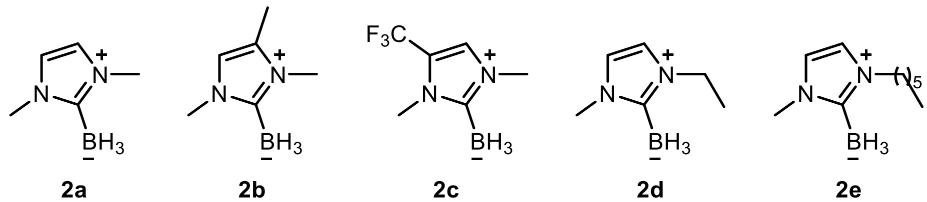




The preparation of the title compounds **4** and **6** followed a modified procedure reported by DeAngelis *et al.* (*7*). A flame-dried round-bottomed flask was charged with diisopropylamine (1.88 mL, 13.41 mmol) under a nitrogen atmosphere. Anhydrous THF (40mL) was added and the flask was cooled to 0 °C. A solution of *n*-butyllithium (5.36 mL, 13.4 mmol) (2.5M solution in hexanes) was added dropwise and the mixture was stirred for 30 min and subsequently cooled to −78 °C by a bath of dry ice/acetone. A solution of tetrahydro-2*H*-pyran-2-one or oxepan-2-one (11.2 mmol) in 27 mL of anhydrous THF was added dropwise and the reaction was stirred at −78 °C for 15 minutes. 2,2,2-Trifluoroethyl trifluoroacetate (TFEA) (2.24 mL, 16.8 mmol) was then added dropwise and the reaction was stirred at −78 °C for 30 minutes and then allowed to warm to room temperature over 1 hour. The reaction was quenched with 50 mL of 10% HCl and extracted with Et_2O (50 mL × 3). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The crude product 3-(2,2,2-trifluoroacetyl)tetrahydro-2*H*-pyran-2-one or 3-(2,2,2-trifluoroacetyl)oxepan-2-one was used for the next step without further purification.

The crude product was dissolved in anhydrous CH_2Cl_2 (110 mL), and *o*-nitrobenzenesulfonyl azide (*o*-NBSA) (3.21 g, 14.1 mmol) was added followed by dropwise addition of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU, 2.39 mL, 16 mmol) and the reaction was stirred at room temperature for 3 hours. The reaction was quenched by water (50 mL) and the product was extracted by ether (40 mL × 7). The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The resulting crude product was purified through a silica column using hexane: ethyl acetate (2:1 to 1:2) as eluents. The yellow-colored fractions were concentrated to afford product **4** as a bright yellow crystalline solid (1.06 g, 75% yield) and product **6** as an orange oil (1.28 g, 82% yield).

NHC-boranes were synthesized using the procedures reported in our previous paper (*8*).

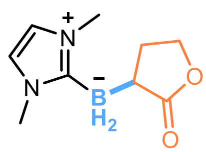


IV. Synthesis of Organoborane Standard Products

The preparation of racemic organoborane standard products follows the reported protocol using rhodium acetate (*9*) or iodine (*10*) as catalyst for carbene B–H insertion. Iodine (10 mol%) or $Rh_2(OAc)_4$ (2 mol%) was added to the solution of NHC-BH_3 (1.0 equiv) in dichloromethane. The mixture was allowed to stir for 5 min. A solution of diazo compound (1.2 equiv) in dichloromethane was then added through a syringe pump. The reaction mixture was allowed to stir for 10 h. Quick filtration and further purification through a silica column using hexane : ethyl acetate (2: 1 to 0: 1) or hexane : (ethyl acetate : acetone 5: 5) (2: 1 to 0: 1) elution system afforded the organoborane standard products.

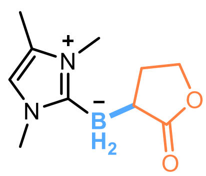
The ^{1}H NMR resonances of the B–H protons are broad (due to geminal coupling with boron) and generally in the range of 0.4–1.6 ppm. The ^{13}C NMR resonances of the boron-binding NHC quaternary carbons usually appear at around 170 ppm and are typically broad (due to germinal coupling with boron) and weak; these signals are sometimes not visible in the ^{13}C NMR spectra.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydrofuran-3-yl)dihydroborate (3a)



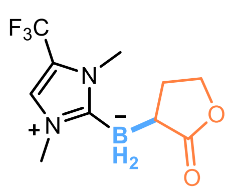
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 2H), 4.45 (dddd, *J* = 10.7, 8.1, 6.8, 1.0 Hz, 1H), 4.27 (tq, *J* = 9.0, 1.1 Hz, 1H), 3.83 – 3.69 (m, 6H), 2.53 – 2.25 (m, 1H), 2.01 – 1.93 (m, 1H), 1.88 – 1.80 (m, 1H), 1.79 – 1.16 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.91, 120.62, 67.86, 36.15, 30.86; ^{11}B NMR (128 MHz, $CDCl_3$) δ -27.08 (t, *J* = 89.6Hz). HRMS (FAB+) m/z: 193.1144 (($M+H^+$)–H_2); calc. for $C_9H_{14}O_2N_2B$: 193.1148.

(2-Oxotetrahydrofuran-3-yl)(1,3,5-trimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3b)



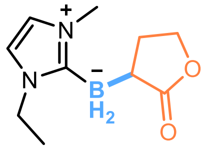
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.57 (q, *J* = 1.1 Hz, 1H), 4.47 (ddd, *J* = 10.8, 8.2, 6.8 Hz, 1H), 4.28 (ddd, *J* = 9.0, 8.2, 1.8 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 2.45 – 2.33 (m, 1H), 2.18 (d, *J* = 1.2 Hz, 3H), 2.00 – 1.92 (m, 1H), 1.89 – 1.59 (m, 2H), 1.49 – 1.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.20, 128.29, 117.79, 67.89, 35.77, 32.59, 30.95, 9.67; ^{11}B NMR (128 MHz, $CDCl_3$) δ -26.77 (t, *J* = 89.4 Hz). HRMS (FAB+) m/z: 207.1317 (($M+H^+$)–H_2); calc. for $C_{10}H_{16}O_2N_2B$: 207.1305.

(1,3-Dimethyl-5-(trifluoromethyl)-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydrofuran-3-yl)dihydroborate (3c)



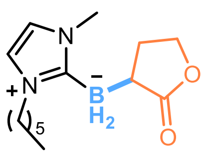
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (q, *J* = 1.3 Hz, 1H), 4.45 (ddd, *J* = 10.4, 8.3, 7.0 Hz, 1H), 4.29 (ddd, *J* = 8.9, 8.3, 2.2 Hz, 1H), 3.87 (d, *J* = 0.8 Hz, 3H), 3.81 (s, 3H), 2.51 – 2.32 (m, 1H), 2.07 – 1.65 (m, 3H), 1.59 – 1.10 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.70, 122.82 (q, *J* = 4.2 Hz), 122.52 (q, *J* = 41.1 Hz), 119.39 (q, *J* = 268.7 Hz), 68.00, 36.81, 34.25, 34.23, 34.21, 34.19, 30.65; ^{11}B NMR (128 MHz, $CDCl_3$) δ -27.15 (t, *J* = 90.7 Hz). HRMS (FAB+) m/z: 261.1030 (($M+H^+$)–H_2); calc. for $C_{10}H_{13}O_2N_2F_3B$: 261.1022.

(1-Ethyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydrofuran-3-yl)dihydroborate (3d)



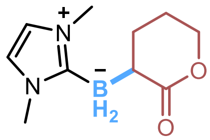
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 2.0 Hz, 1H), 6.84 (d, *J* = 2.0 Hz, 1H), 4.45 (ddd, *J* = 10.8, 8.2, 6.8 Hz, 1H), 4.27 (ddd, *J* = 8.9, 8.2, 1.8 Hz, 1H), 4.24 – 4.09 (m, 2H), 3.76 (s, 3H), 2.50 – 2.29 (m, 1H), 2.02 – 1.66 (m, 3H), 1.61 – 1.13 (m, 1H), 1.40 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.77, 121.00, 118.45, 67.82, 43.72, 36.07, 30.93, 15.90; ^{11}B NMR (128 MHz, $CDCl_3$) δ -27.10 (t, *J* = 89.6 Hz). HRMS (FAB+) m/z: 207.1296 ($(M+H^+)–H_2$); calc. for $C_{10}H_{16}O_2N_2B$: 207.1305.

(3-Hexyl-1-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydrofuran-3-yl)dihydroborate (3e)



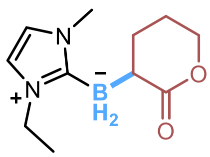
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 1.9 Hz, 1H), 6.83 (d, *J* = 1.9 Hz, 1H), 4.45 (ddd, *J* = 10.8, 8.2, 6.8 Hz, 1H), 4.27 (ddd, *J* = 8.9, 8.2, 1.8 Hz, 1H), 4.17 – 4.01 (m, 2H), 3.76 (s, 3H), 2.48 – 2.31 (m, 1H), 2.13 – 1.64 (m, 5H), 1.58 – 1.14 (m, 7H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.77, 120.82, 119.03, 67.82, 48.85, 36.12, 31.46, 30.95, 30.65, 26.36, 22.61, 14.12; ^{11}B NMR (128 MHz, $CDCl_3$) δ -27.09 (t, *J* = 90.3 Hz). HRMS (FAB+) m/z: 263.1927 ($(M+H^+)–H_2$); calc. for $C_{14}H_{24}O_2N_2B$: 263.1931.

(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydro-2*H*-pyran-3-yl)dihydroborate (5a)



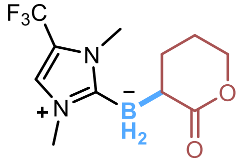
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.80 (s, 2H), 4.46 (dddd, *J* = 11.0, 7.4, 3.7, 1.0 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.74 (s, 6H), 2.14 – 1.95 (m, 3H), 1.89 – 1.75 (m, 1H), 1.71 – 1.55 (m, 2H), 1.51 – 1.15 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.58, 120.48, 69.44, 36.10, 27.17, 22.39; ^{11}B NMR (128 MHz, $CDCl_3$) δ -24.71 (t, *J* = 90.4 Hz). HRMS (FAB+) m/z: 207.1330 ($(M+H^+)–H_2$); calc. for $C_{10}H_{16}O_2N_2B$: 207.1305.

(1-Ethyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydro-2*H*-pyran-3-yl)dihydroborate (5b)



^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 1.9 Hz, 1H), 4.46 (dddd, *J* = 10.8, 7.4, 3.7, 1.0 Hz, 1H), 4.26 – 4.10 (m, 3H), 3.75 (s, 3H), 2.14 – 1.94 (m, 3H), 1.86 – 1.74 (m, 1H), 1.70 – 1.10 (m, 3H), 1.43 – 1.38 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.45, 120.88, 118.29, 69.42, 43.64, 36.02, 27.22, 22.40, 15.88; ^{11}B NMR (128 MHz, $CDCl_3$) δ -24.73 (t, *J* = 90.4 Hz). HRMS (FAB+) m/z: 221.1452 ($(M+H^+)–H_2$); calc. for $C_{11}H_{18}O_2N_2B$: 221.1461.

(1,3-Dimethyl-5-(trifluoromethyl)-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydro-2*H*-pyran-3-yl)dihydroborate (5c)



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 4.43 (dddd, *J* = 10.7, 7.1, 3.7, 1.1 Hz, 1H), 4.30 – 4.19 (m, 1H), 3.90 – 3.82 (m, 3H), 3.79 (s, 3H), 2.13 – 1.96 (m, 3H), 1.90 – 1.59 (m, 3H), 1.54 – 1.11 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 181.22, 122.70 (q, *J* = 4.1 Hz), 122.32 (q, *J* = 40.8 Hz), 119.44 (q, J = 267.6 Hz), 69.76, 36.71, 34.14, 34.12, 27.29, 22.32; ^{11}B NMR (128 MHz, $CDCl_3$) δ -24.93 (t, J = 91.3 Hz). HRMS (FAB+) m/z: 275.1170 (($M+H^+$)–H_2); calc. for $C_{11}H_{15}O_2N_2F_3B$: 275.1179.

V. Enzymatic Synthesis of Lactone-Based Organoboranes in Analytical and Preparative Scale

All enzymatic reactions for lactone-based organoborane formation in analytical scale were conducted following the general procedure described below and analyzed with gas chromatography-mass spectrometry (GC-MS). All TTNs for the different products were determined using the GC standard curve of the corresponding racemic standard product made with $Rh_2(OAc)_4$ or I_2.

General procedure for analytical-scale reactions:

To a 2 mL vial were added degassed suspension of *E. coli* expressing *Rma* cytochrome *c* variant in M9-N buffer (OD_{600} = 15, 400 μL), borane (10 μL of 400 mM stock solution in MeCN, 10 mM), and lactone-diazo (10 μL of 400 mM stock solution in MeCN, 10 mM) under anaerobic conditions. The vial was capped and shaken at 520 rpm at room temperature for 18 h. After the reaction was completed, internal standard 1,3,5-trimethoxybenzene (20 μL of 20 mM stock solution in toluene) was added to the reaction vial followed by mixed solvent (hexane / ethyl acetate = 3 : 7, 1 mL). The mixture was transferred to a 1.5 mL microcentrifuge, vortexed (15 seconds × 3) and centrifuged (14,000 rpm, 5 min) to completely separate the organic and aqueous layers. 0.8 mL of organic layer was taken for GC-MS analysis. TTN was calculated based on measured protein concentration. Enantiomeric excess was measured by chiral HPLC. Reactions for every substrate were set up in quadruplicate.

GC standard curve:

All data points represent the average of duplicate runs. The calibration curves depict product concentration in mM (y-axis) against the ratio of product area to internal standard area on the GC (x-axis).

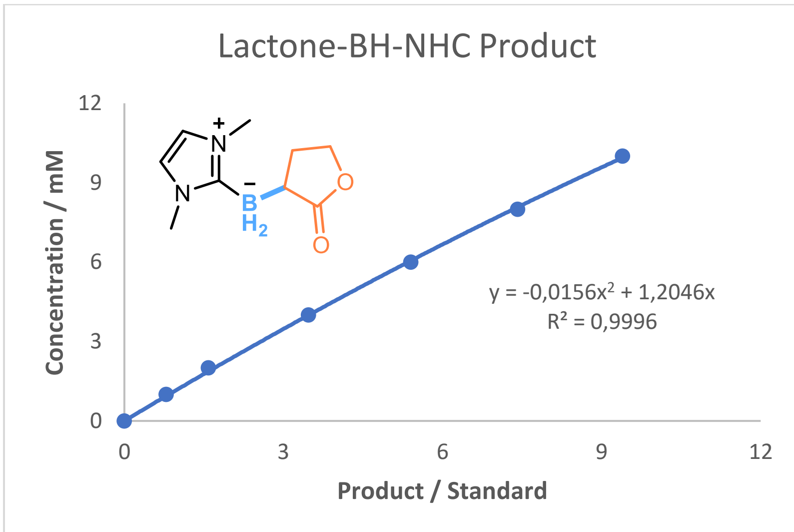
All enzymatic reactions for lactone-based organoborane formation in preparative scale were conducted following the general procedure described below, and the corresponding lactone-based organoborane products were isolated. Detailed conditions for preparative-scale reactions of different substrates are indicated separately.

General procedure for preparative-scale reactions:

To a 20 mL vial were added degassed suspension of *E. coli* expressing *Rma* cytochrome *c* (5 mL, OD_{600} = 15), borane (150 μL of 400 mM stock solution in MeCN, 0.06 mmol), lactone diazo (150 μL of 400 mM stock solution in MeCN, 0.06 mmol), *D*-glucose (50 mM), in M9-N buffer (pH 7.4) under anaerobic conditions. The vial was capped and shaken (480 rpm) at room temperature for 18 h. Reactions for each substrate were set up in quadruplicate.

After the reaction was completed, reactions in replicate were combined and transferred to 50 mL centrifuge tubes. The reaction vials were washed with water (2 mL × 2) followed by mixed organic solvent (hexane / ethyl acetate = 1 : 1, 2 mL × 3). The washing solution was combined with the reaction mixture in the centrifuge tubes. An additional 15 mL of hexane / ethyl acetate solvent was added to every tube. The tube was then vortexed (1 min × 3) and shaken vigorously, and centrifuged (5,000 × g, 5 min). The organic layer was separated and the aqueous layer was subjected to three more rounds of extraction. The organic layers were combined, dried over Na_2SO_4 and concentrated under reduced pressure. Purification by silica column chromatography with hexane / (ethyl acetate: acetone 7:3) as eluent afforded the desired lactone-based organoboranes. Enantiomeric excess (*ee*) was measured by chiral HPLC. TTNs were calculated based on measured protein concentration and isolated product yield.

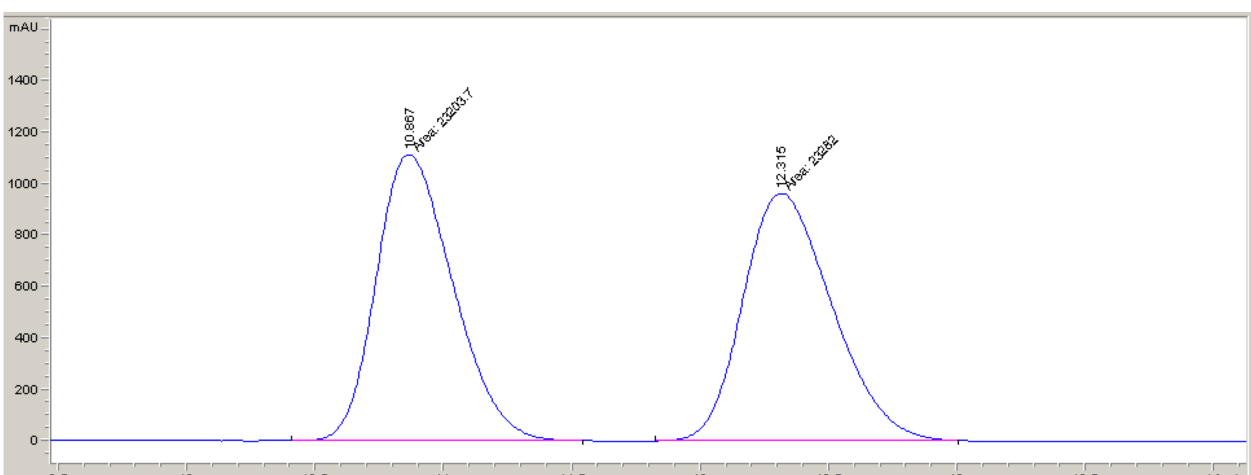
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydrofuran-3-yl)dihydroborate (3a)
GC calibration curve:

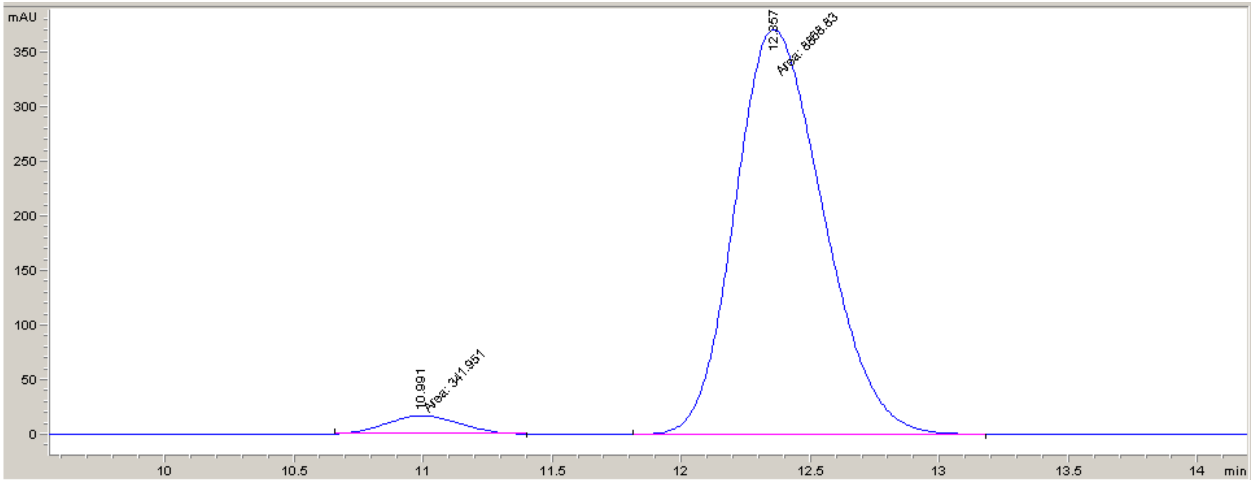


Analysis Data:

Pdt-Entries	Pdt	Std	Pdt/Std	[Pdt]/mM	[PC]/µM	TTN	Avg. TTN	Avg. yield
3a-(1)	38262	5643	6.780	7.45	8.30	898		
3a-(2)	40969	5630	7.277	7.94	8.30	957		
3a-(3)	43223	5984	7.223	7.89	8.30	950		
3a-(4)	49313	5559	8.871	9.46	8.30	1140	986	81.8%

Chiral HPLC trace:
Chiralpak IC, 40% *i*-PrOH in hexane, 1.5 mL/min, 32 °C, 235 nm

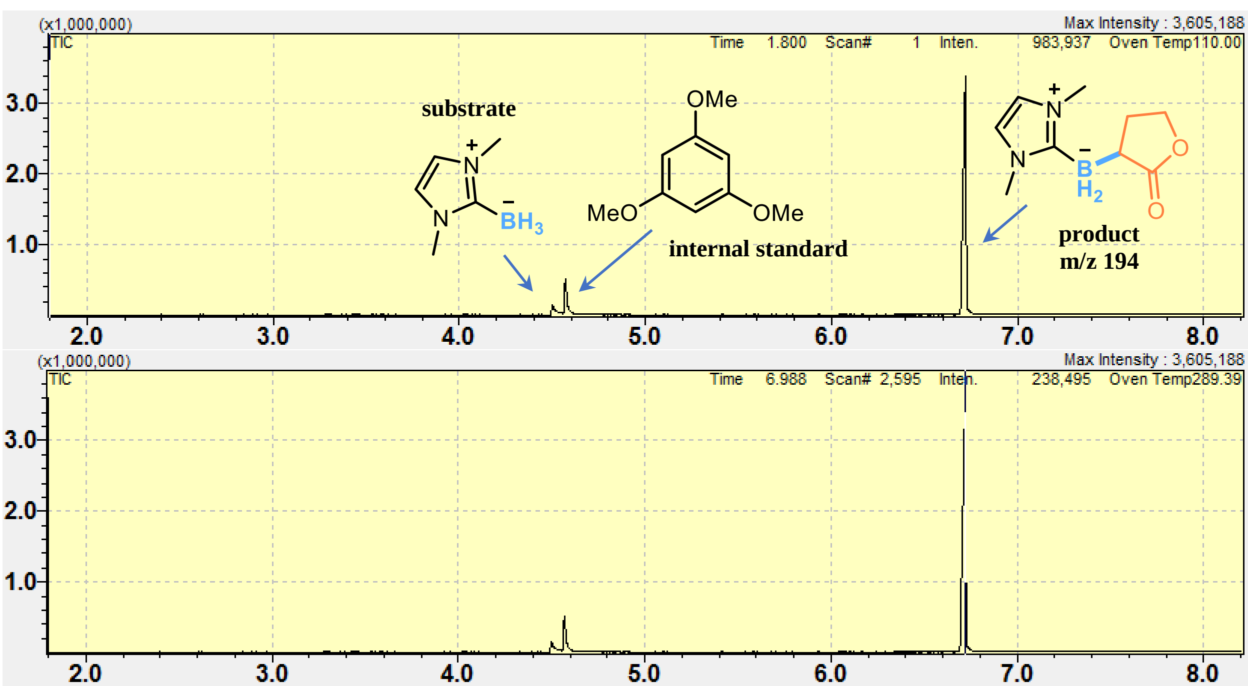


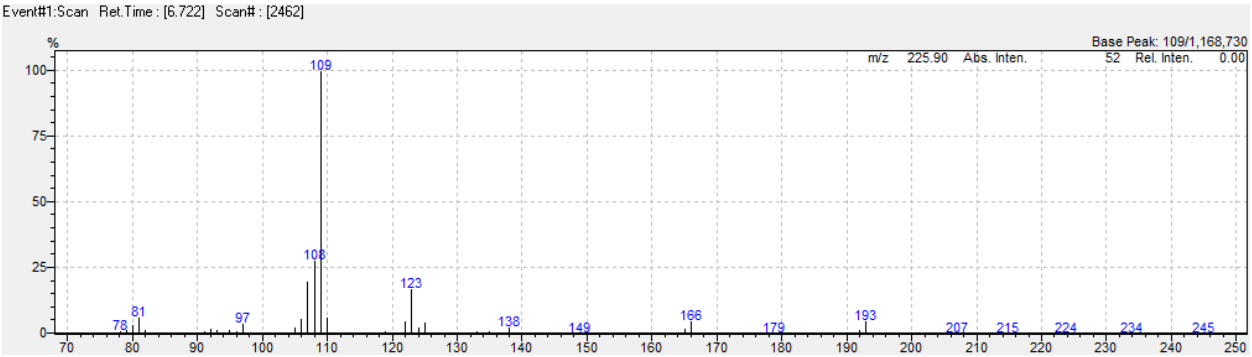


Area% report for **3a**:

***rac*-3a**			**Enzymatically produced 3a**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
10.867	23203.7	49.92	10.991	341.95	3.71
12.315	23282	50.08	12.857	8868.83	96.29
Total	46485.7	100.00	Total	9210.78	100.00

GC-MS trace:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 25 °C/min → 190 °C → 50 °C/min → 300 °C (isothermal, 1 min), total time: 8.2 min.

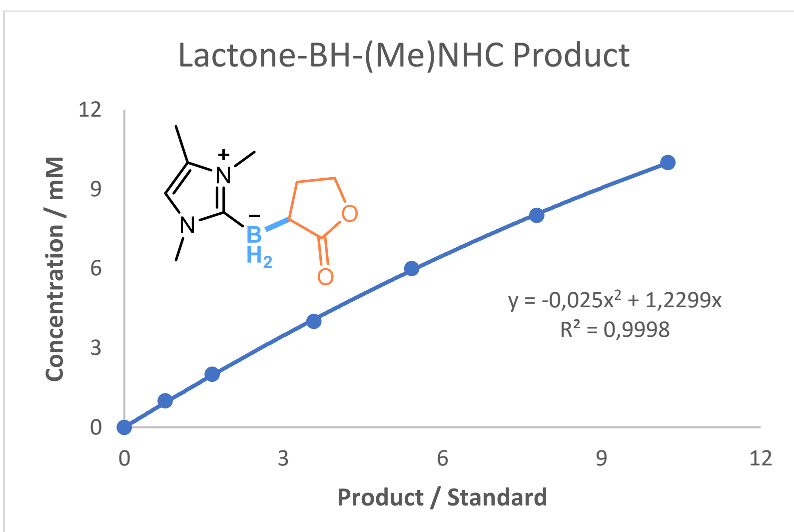




Preparative-scale reaction:

E. coli **suspension expressing BOR^{LAC} in M9-N**				***D*****-glucose**	
OD_{600}	volume/mL	[PC]/µM	n_pro/µmol	weight/mg	[Glu]/mM
15	20	8.30	0.166	180	50
borane (2a) stock in MeCN			**diazo (1) stock in MeCN**		
stock/mM	volume/µL	n_1/mmol	stock/mM	volume/µL	n_2/mmol
400	600	0.24	400	600	0.24
purification eluent		**Product**			
(ethyl acetate: acetone 7:3) in hexanes (30% to 100% gradient)		m[Pdt]/mg	n[Pdt]/mmol	yield	TTN
		41.4	0.213	89%	1290

(2-Oxotetrahydrofuran-3-yl)(1,3,5-trimethyl-1*H*-imidazol-3-ium-2-yl)dihydroborate (3b)
GC calibration curve:

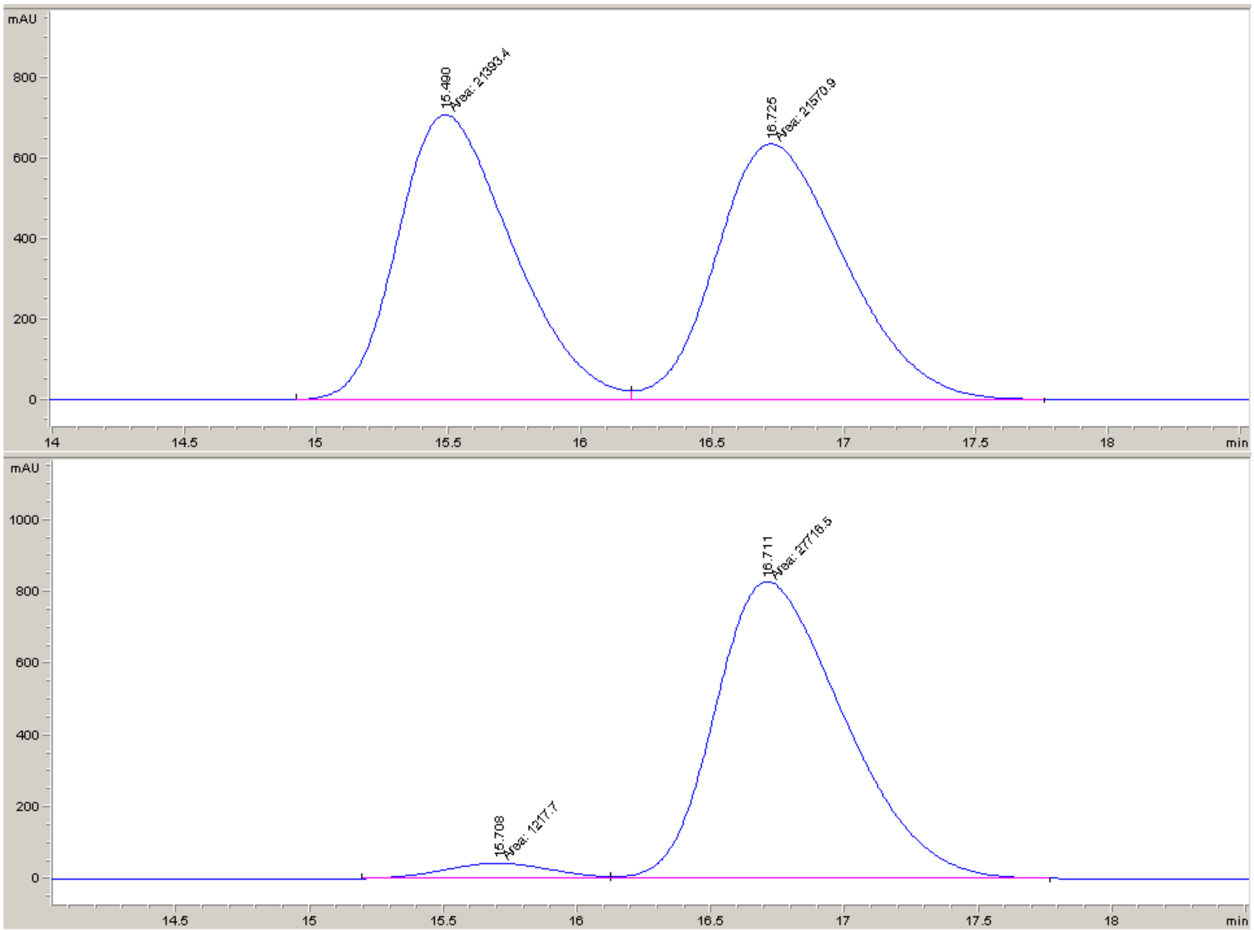


Analysis Data:

Pdt-Entries	Pdt	Std	Pdt/Std	[Pdt]/mM	[PC]/µM	TTN	Avg. TTN	Avg. yield

3b-(1)	53629	5587	9.599	9.50	8.20	1159		
3b-(2)	47943	4968	9.650	9.54	8.20	1164		
3b-(3)	50689	5641	8.986	9.03	8.20	1102		
3b-(4)	51778	5029	10.296	10.01	8.20	1221	1161	95.2%

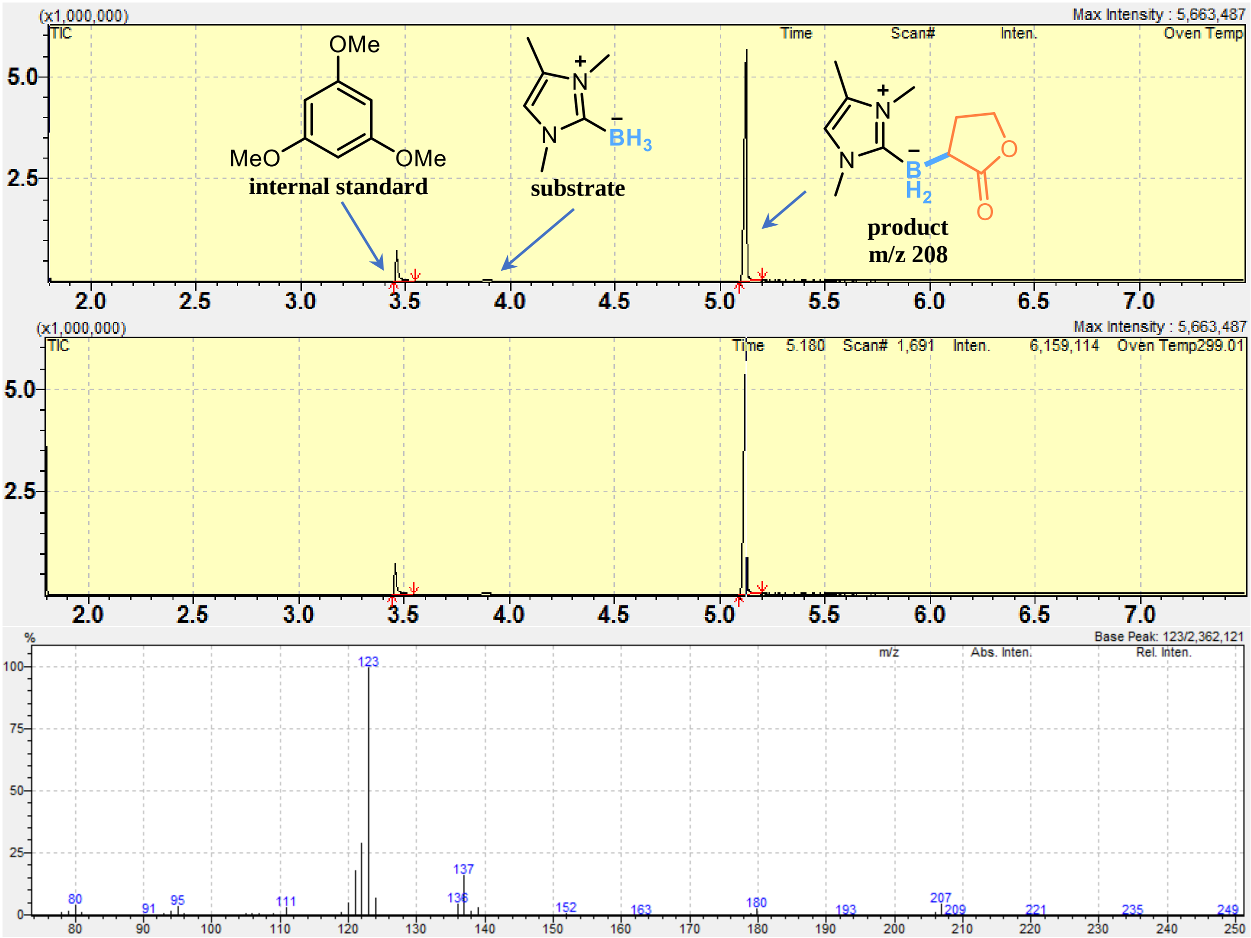
Chiral HPLC trace:
Chiralpak IC, 40% *i*-PrOH in hexane, 1.5 mL/min, 32 °C, 235 nm



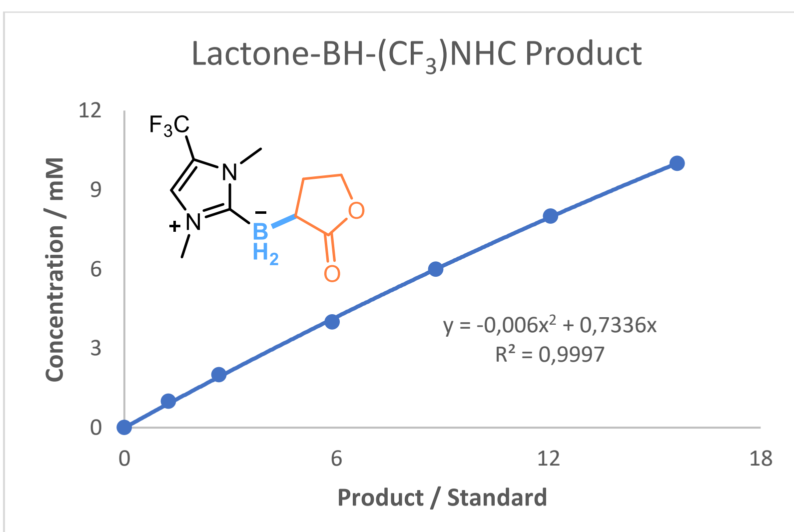
Area% report for **3b**:

***rac*-3b**			**Enzymatically produced 3b**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
15.490	21393.4	49.79	15.708	1217.7	4.21
16.725	21570.9	50.21	16.711	27716.5	95.79
Total	42964.3	100.00	Total	28934.2	100.00

GC-MS trace:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 60 °C/min → 300 °C (isothermal, 3 min), total time: 7.5 min.



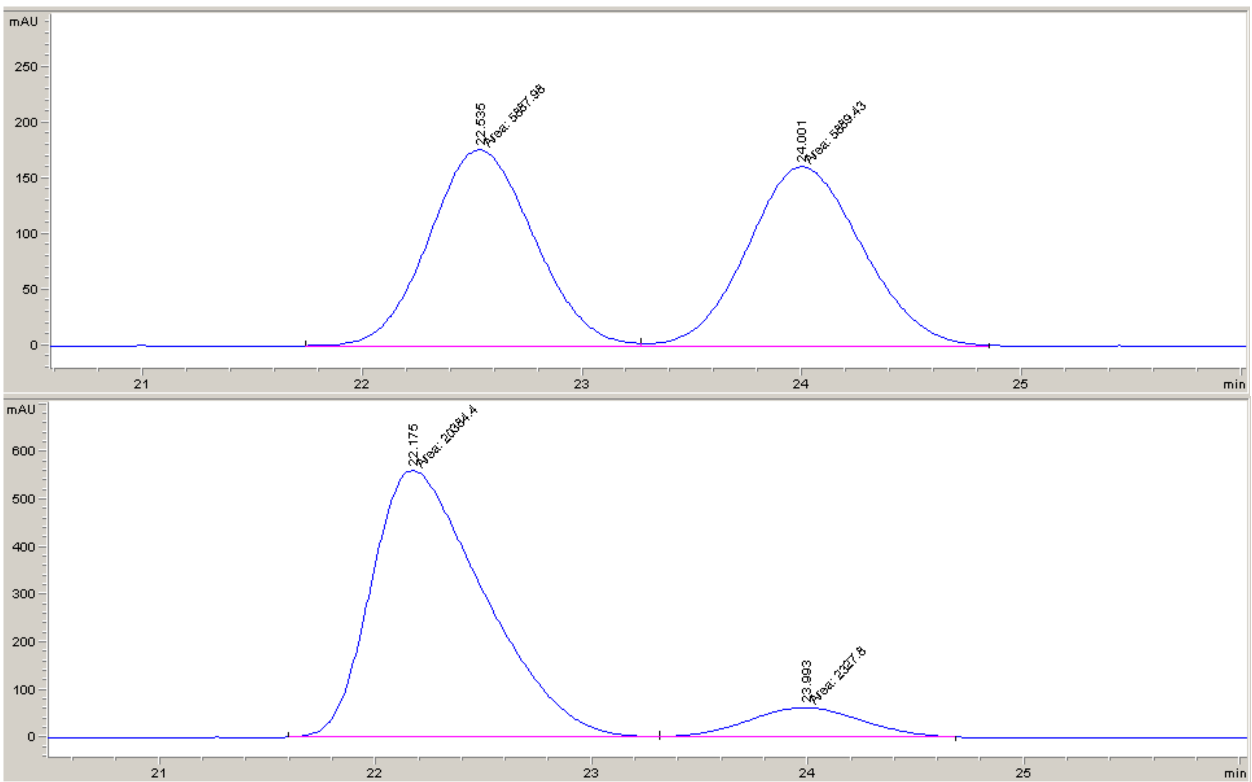
(1,3-Dimethyl-5-(trifluoromethyl)-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydrofuran-3-yl)dihydroborate (3c)
GC calibration curve:



Analysis Data:

Pdt-Entries	Pdt	Std	Pdt/Std	[Pdt]/mM	[PC]/µM	TTN	Avg. TTN	Avg. yield
3c-(1)	47111	4874	9.666	6.53	8.20	796		
3c-(2)	43029	5227	8.232	5.63	8.20	687		
3c-(3)	48256	5249	9.193	6.24	8.20	761		
3c-(4)	49190	5251	9.368	6.35	8.20	774	754	61.9%

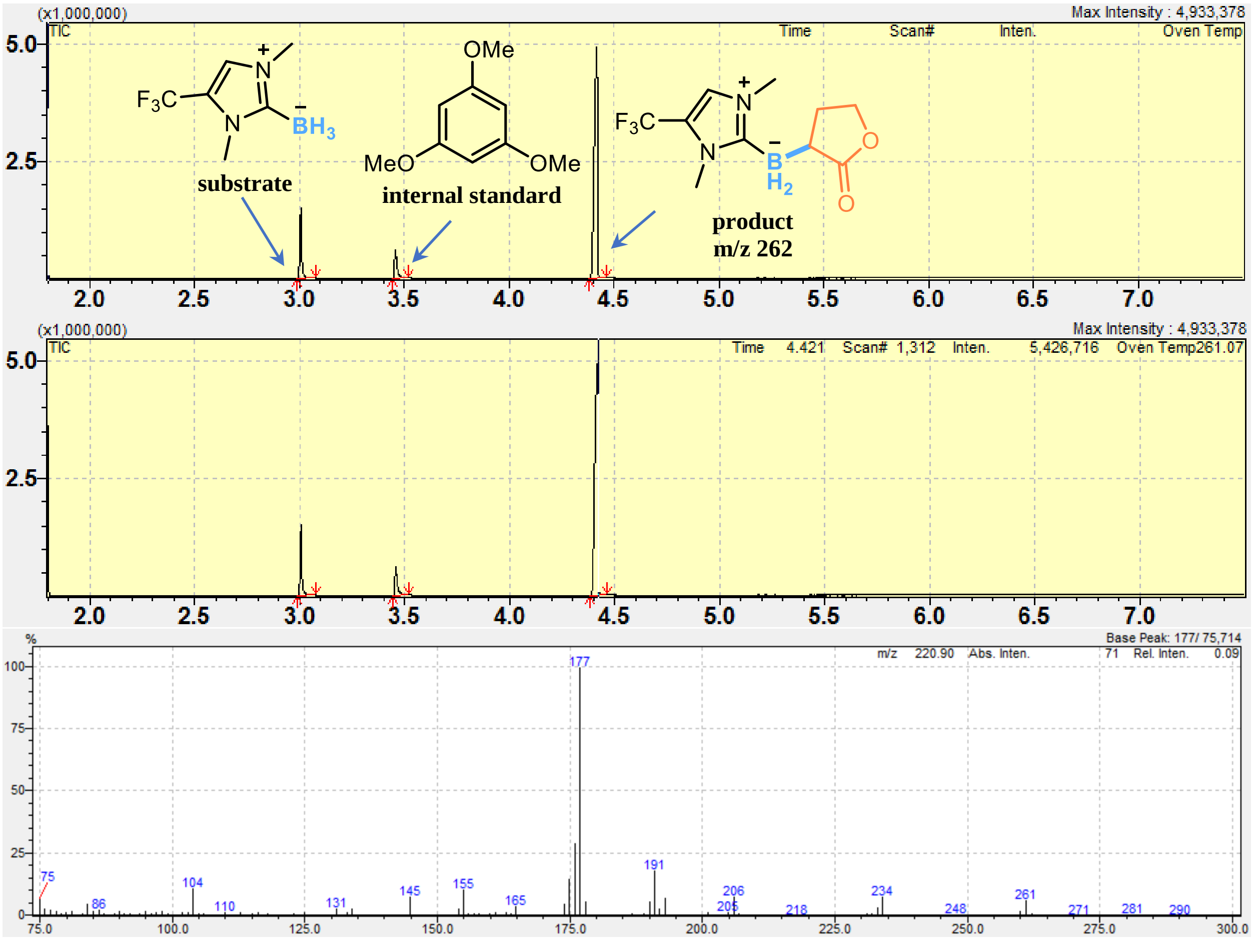
Chiral HPLC trace:
Chiralpak IC, 12% *i*-PrOH in hexane, 1 mL/min, 32 °C, 235 nm



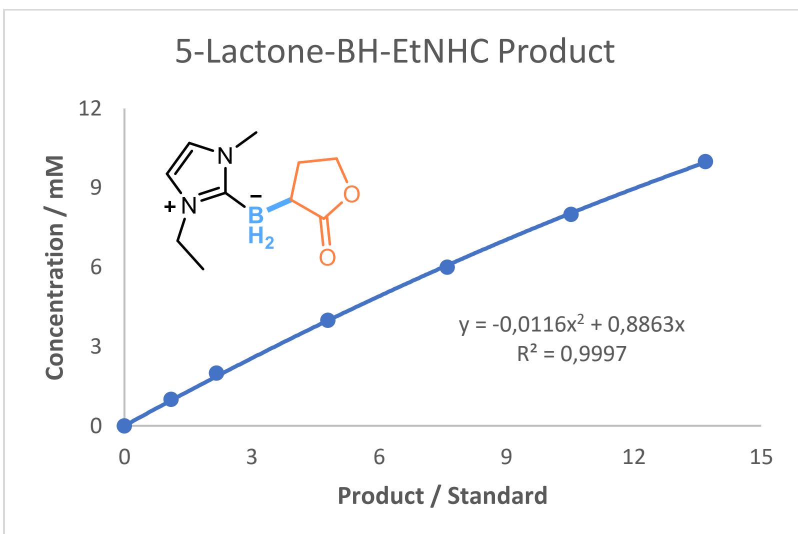
Area% report for **3c**:

***rac*-3c**			**Enzymatically produced 3c**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
22.535	5887.98	49.99	22.175	20384.4	89.75
24.001	5889.43	50.01	23.993	2327.8	10.25
Total	11777.41	100.00	Total	22712.2	100.00

GC-MS trace:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 60 °C/min → 300 °C (isothermal, 3 min), total time: 7.5 min.



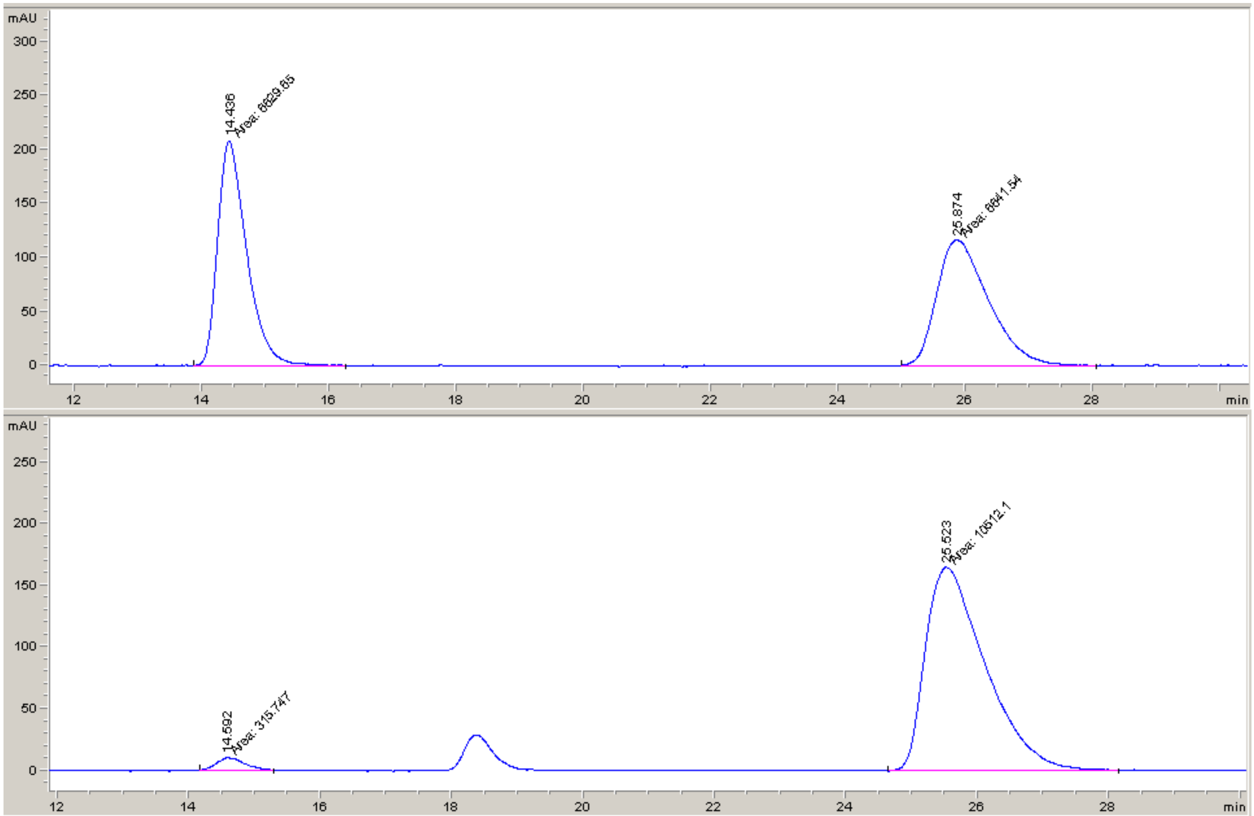
(1-Ethyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydrofuran-3-yl)dihydroborate (3d)
GC calibration curve:



Analysis Data:

Pdt-Entries	Pdt	Std	Pdt/Std	[Pdt]/mM	[PC]/µM	TTN	Avg. TTN	Avg. yield
3d-(1)	68768	6671	10.308	7.90	8.20	964		
3d-(2)	63101	6924	9.113	7.11	8.20	868		
3d-(3)	68256	6203	11.004	8.35	8.20	1018		
3d-(4)	68771	6607	10.409	7.97	8.20	972	955	78.3%

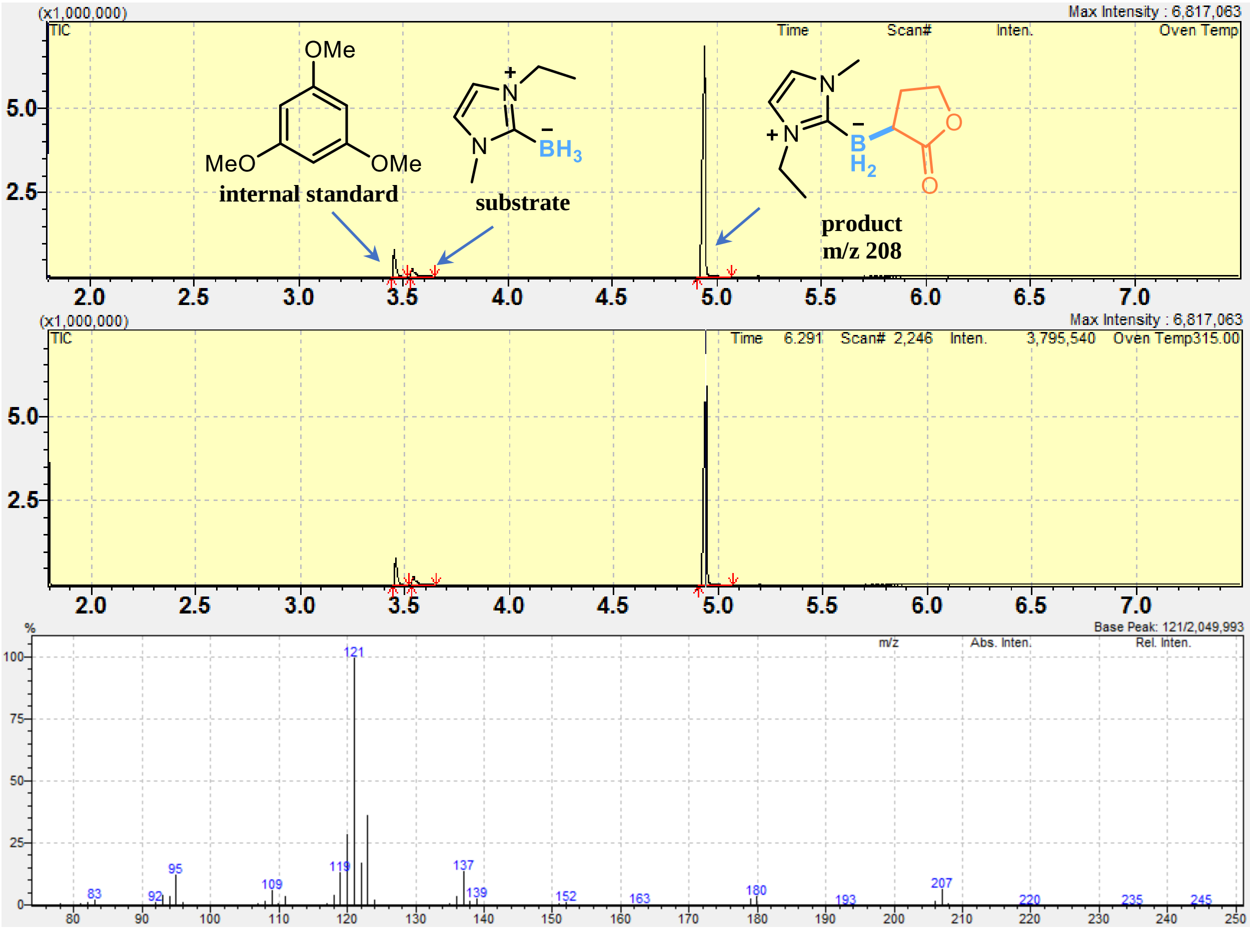
Chiral HPLC trace:
Chiralpak OD-H, 15% *i*-PrOH in hexane, 1.2 mL/min, 32 °C, 235 nm



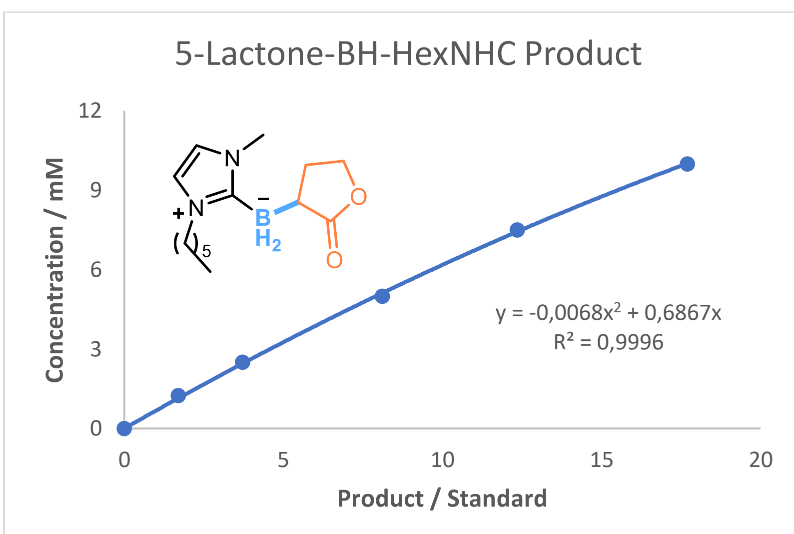
Area% report for **3d**:

***rac*-3d**			**Enzymatically produced 3d**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
14.436	6629.85	49.96	14.592	315.7	2.92
25.874	6641.54	50.04	25.523	10512.1	97.08
Total	13271.39	100.00	Total	10827.8	100.00

GC-MS trace:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 60 °C/min → 300 °C (isothermal, 3 min), total time: 7.5 min.



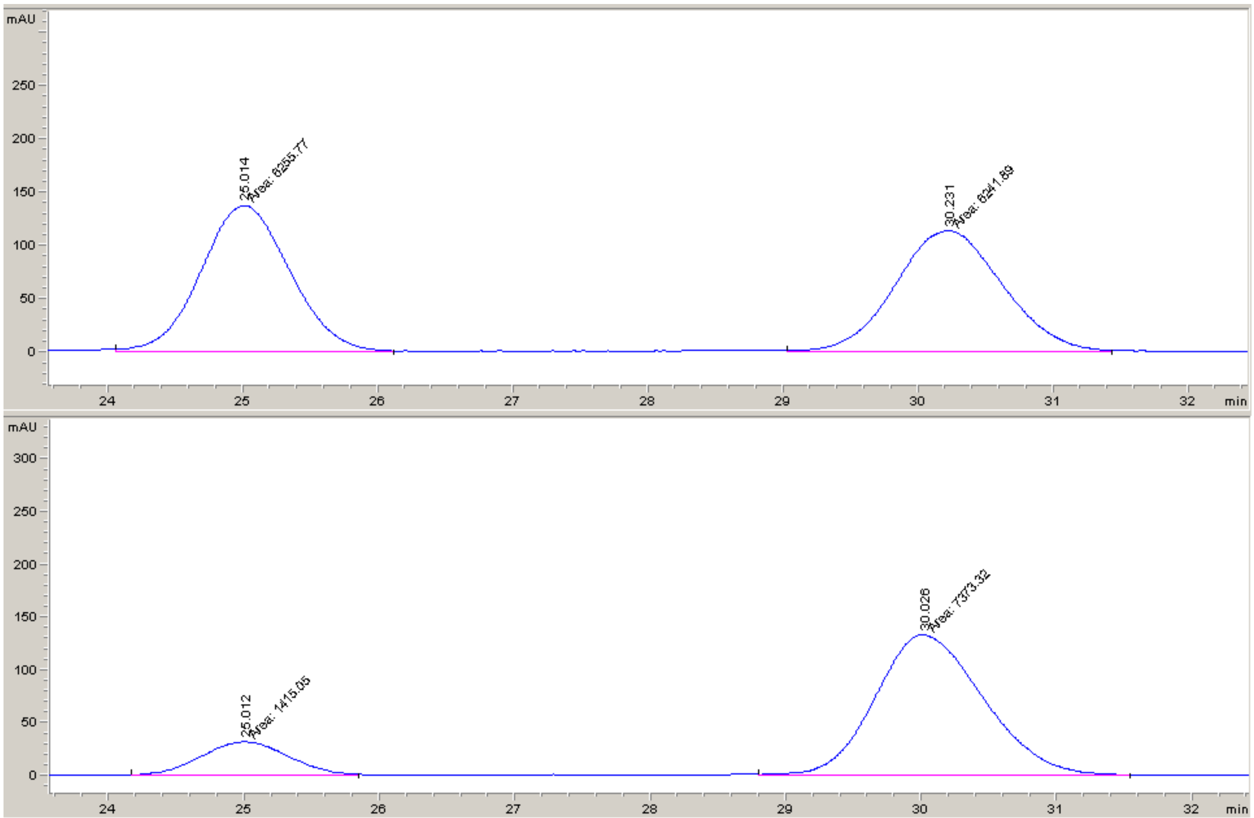
(3-Hexyl-1-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydrofuran-3-yl)dihydroborate (3e)
GC calibration curve:



Analysis Data:

Pdt-Entries	Pdt	Std	Pdt/Std	[Pdt]/mM	[PC]/µM	TTN	Avg. TTN	Avg. yield
3e-(1)	69850	6510	10.730	6.59	8.20	803		
3e-(2)	70694	6131	11.531	7.01	8.20	855		
3e-(3)	73353	5669	12.939	7.75	8.20	945		
3e-(4)	70012	5728	12.223	7.38	8.20	900	876	71.8%

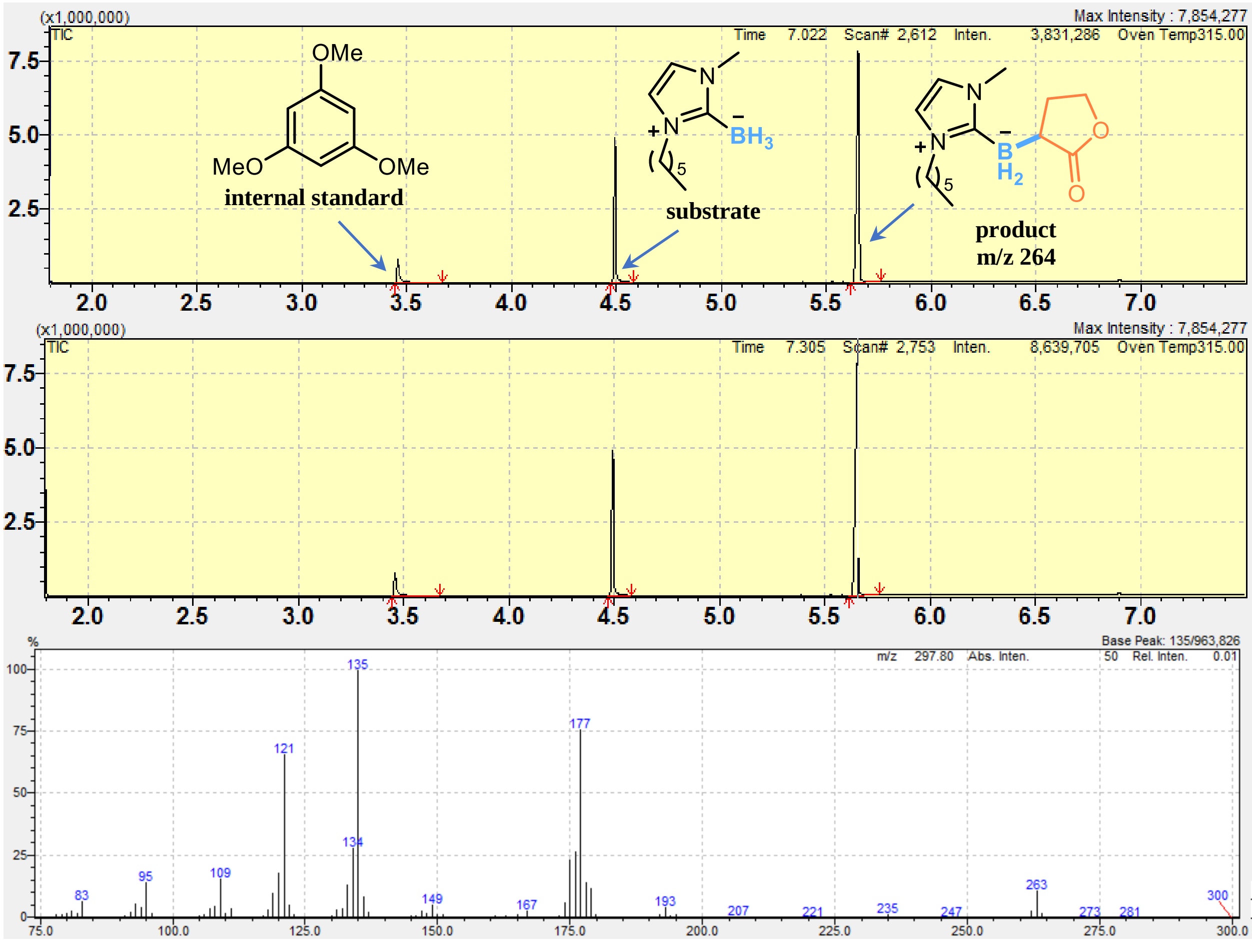
Chiral HPLC trace:
Chiralpak IC, 20% *i*-PrOH in hexane, 1.3 mL/min, 32 °C, 235 nm



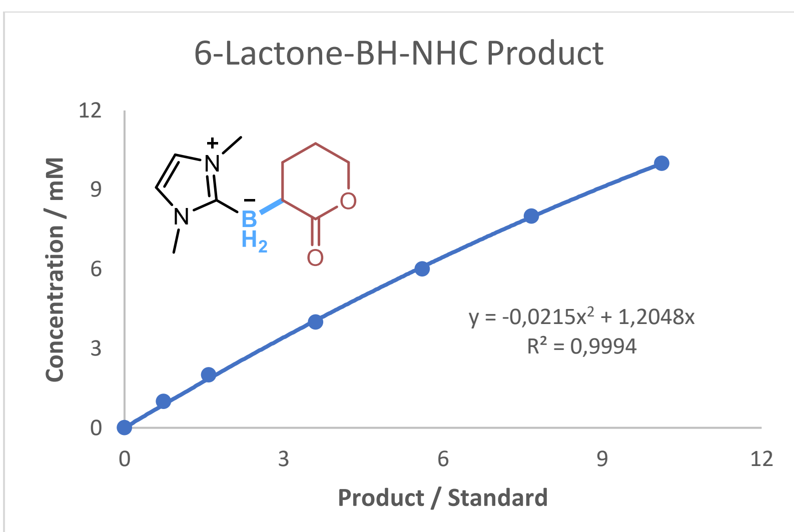
Area% report for **3e**:

***rac*-3e**			**Enzymatically produced 3e**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
25.014	6255.77	50.06	25.012	1415.05	16.10
30.231	6241.89	49.94	30.026	7373.32	83.90
Total	12497.66	100.00	Total	8788.37	100.00

GC-MS trace:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 60 °C/min → 300 °C (isothermal, 3 min), total time: 7.5 min.



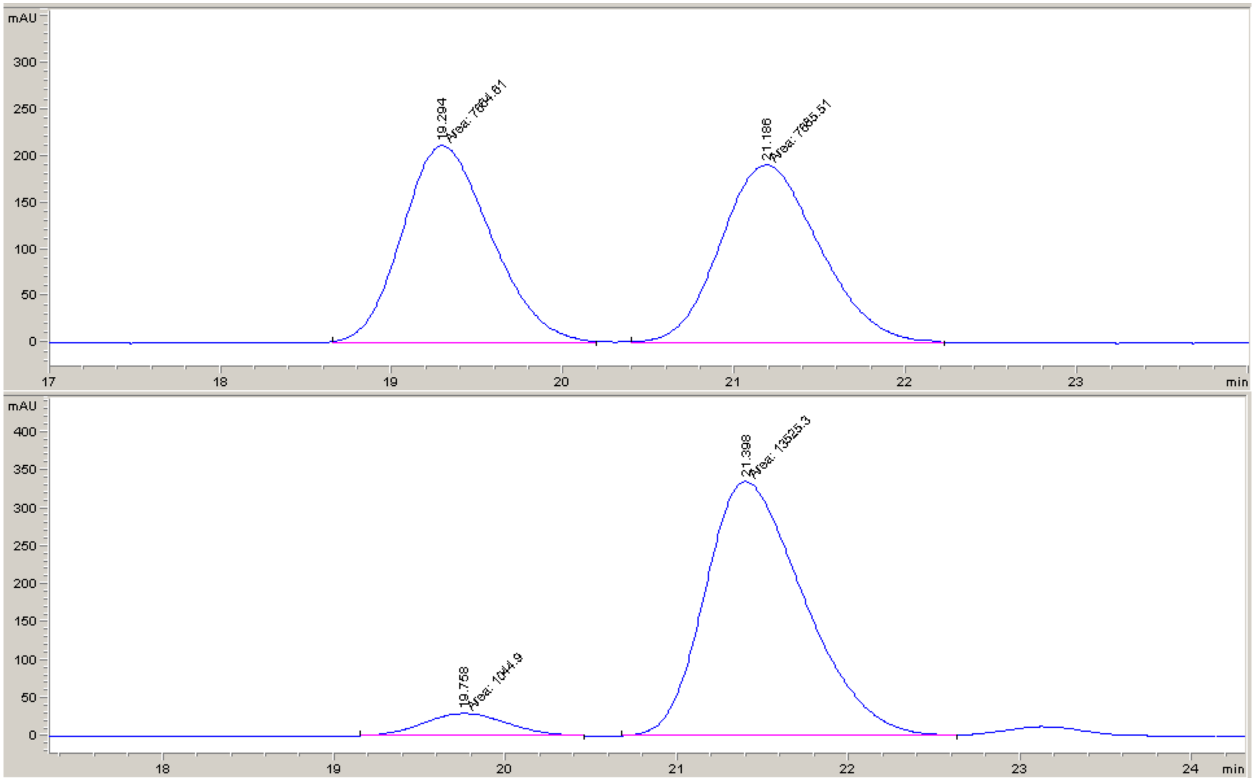
(1,3-Dimethyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydro-2*H*-pyran-3-yl)dihydroborate (5a)
GC calibration curve:



Analysis Data:

Pdt-Entries	Pdt	Std	Pdt/Std	[Pdt]/mM	[PC]/μM	TTN	Avg. TTN	Avg. yield
5a-(1)	41922	4513	9.289	9.34	8.30	1125		
5a-(2)	39155	4803	8.152	8.39	8.30	1011		
5a-(3)	46105	4530	10.178	10.04	8.30	1209		
5a-(4)	42958	4690	9.159	9.23	8.30	1112	1114	92.5%

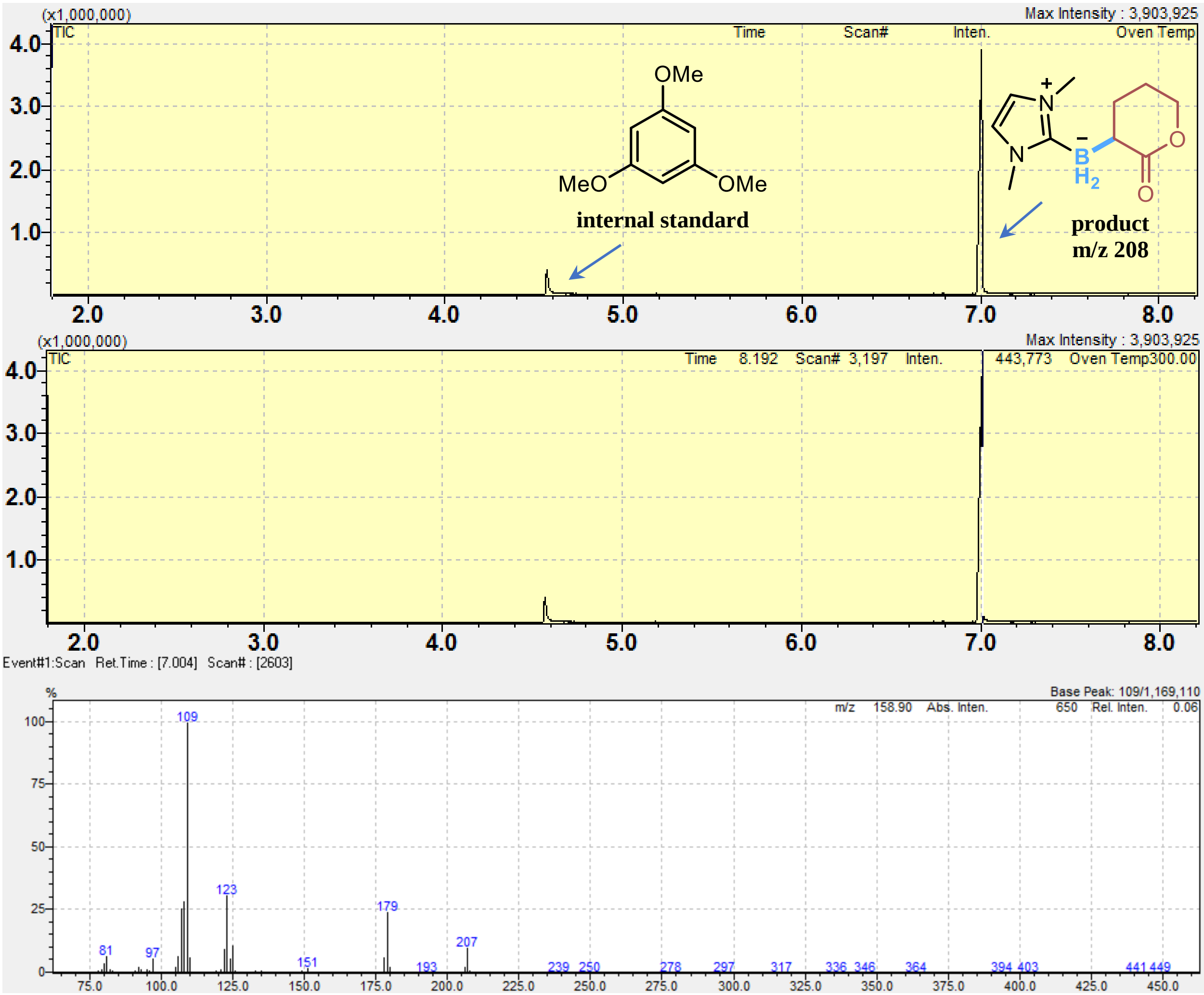
Chiral HPLC trace:
Chiralpak IC, 30% *i*-PrOH in hexane, 1.3 mL/min, 32 °C, 235 nm



Area% report for **5a**:

***rac*-5a**			**Enzymatically produced 5a**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
19.294	7664.61	49.93	19.758	1044.9	7.17
21.186	7685.51	50.07	21.398	13525.3	92.83
Total	15350.12	100.00	Total	14570.2	100.00

GC-MS trace:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 25 °C/min → 190 °C → 50 °C/min → 300 °C (isothermal, 1 min), total time: 8.2 min.

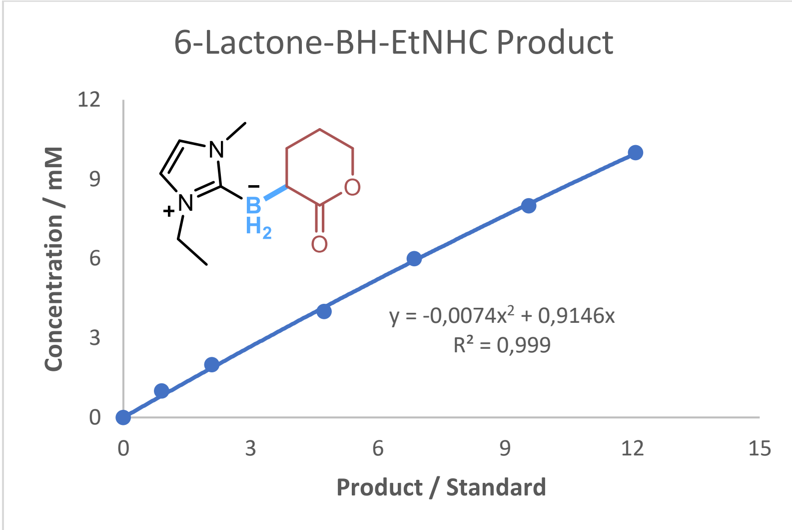


Preparative-scale reaction:

E. coli **suspension expressing BOR**$^{\mathbf{LAC}}$ **in M9-N**				***D*****-glucose**	
OD_{600}	volume/mL	[PC]/μM	n_pro/μmol	weight/mg	[Glu]/mM
15	20	8.30	0.166	180	50
borane (2a) stock in MeCN			**diazo (1) stock in MeCN**		
stock/mM	volume/μL	n_1/mmol	stock/mM	volume/μL	n_2/mmol
400	600	0.24	400	600	0.24
purification eluent		**Product**			
(ethyl acetate: acetone 7:3) in hexanes (30% to 100% gradient)		m[Pdt]/mg	n[Pdt]/mmol	yield	TTN
		41.3	0.198	83%	1200

(1-Ethyl-3-methyl-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydro-2*H*-pyran-3-yl)dihydroborate (5b)

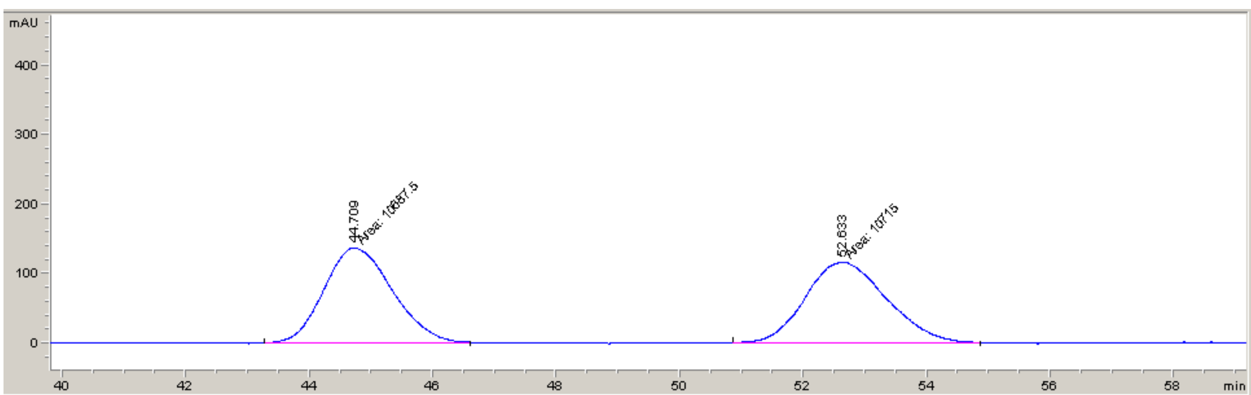
GC calibration curve:

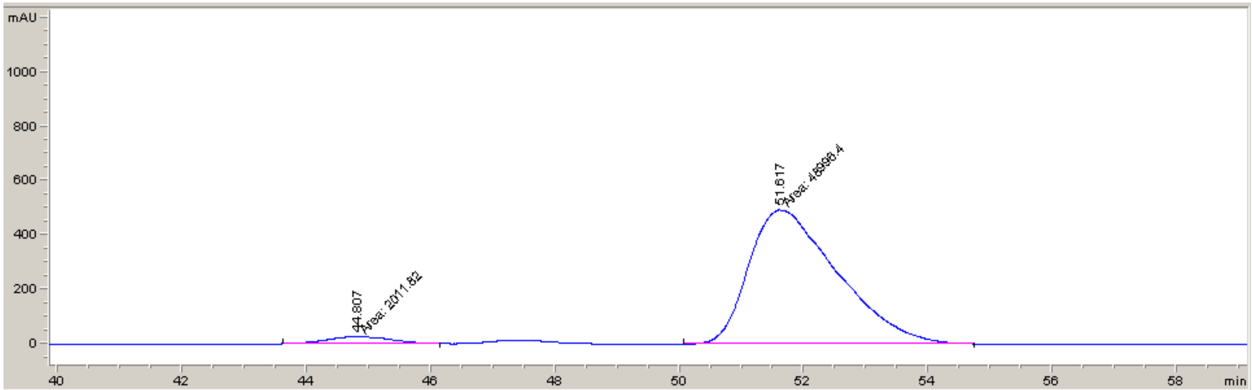


Analysis Data:

Pdt-Entries	Pdt	Std	Pdt/Std	[Pdt]/mM	[PC]/µM	TTN	Avg. TTN	Avg. yield
5b-(1)	45859	4230	10.841	9.05	8.30	1090		
5b-(2)	48114	4168	11.544	9.57	8.30	1153		
5b-(3)	49338	3648	13.525	11.02	8.30	1327		
5b-(4)	43728	3735	11.708	9.69	8.30	1168	1185	98.3%

Chiral HPLC trace:
Chiralpak IC, 18% *i*-PrOH in hexane, 1.2 mL/min, 32 °C, 235 nm

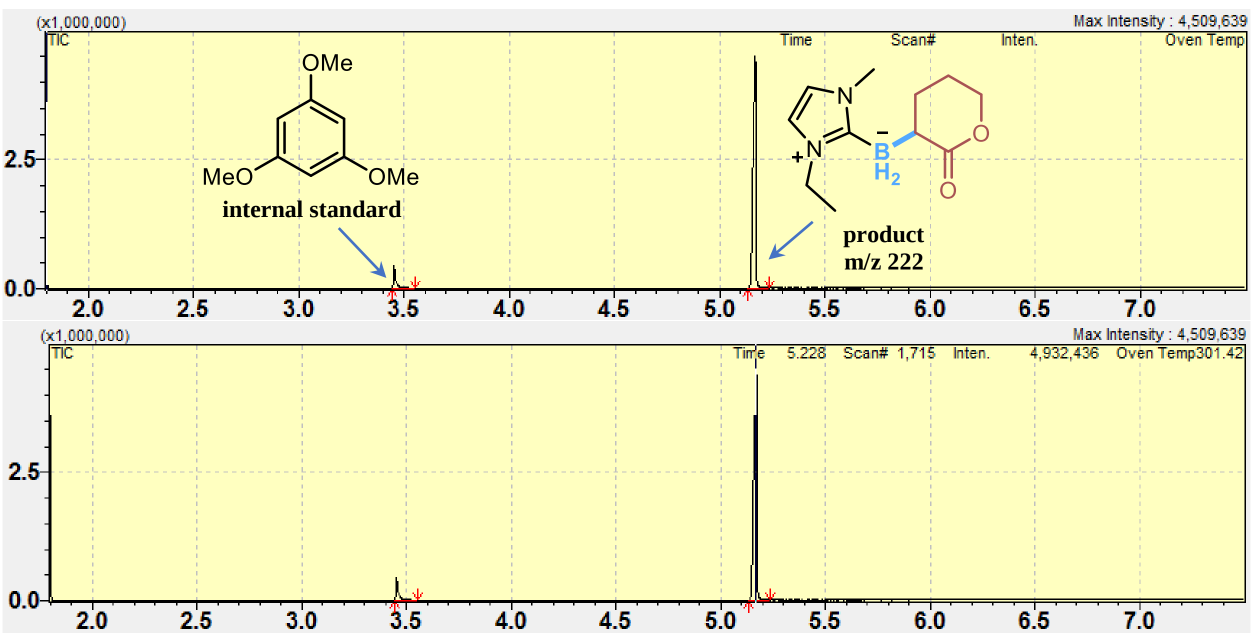


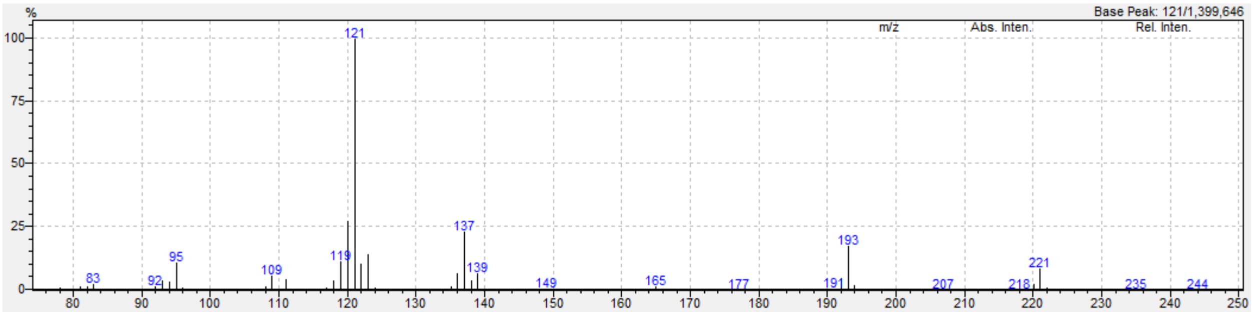


Area% report for **5b**:

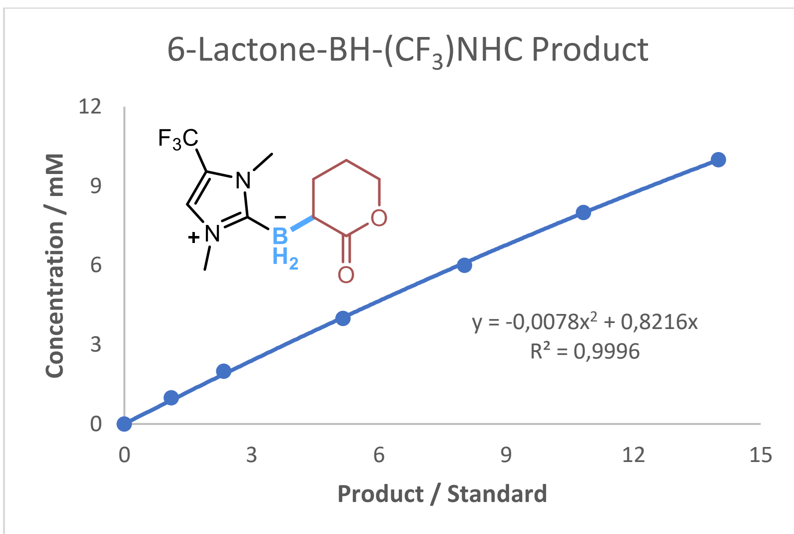
***rac*-5b**			**Enzymatically produced 5b**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
44.709	10687.5	49.94	44.807	2011.8	3.94
52.633	10715	50.06	51.617	48996.4	96.06
Total	21402.5	100.00	Total	51008.2	100.00

GC-MS trace:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 60 °C/min → 300 °C (isothermal, 3 min), total time: 7.5 min.





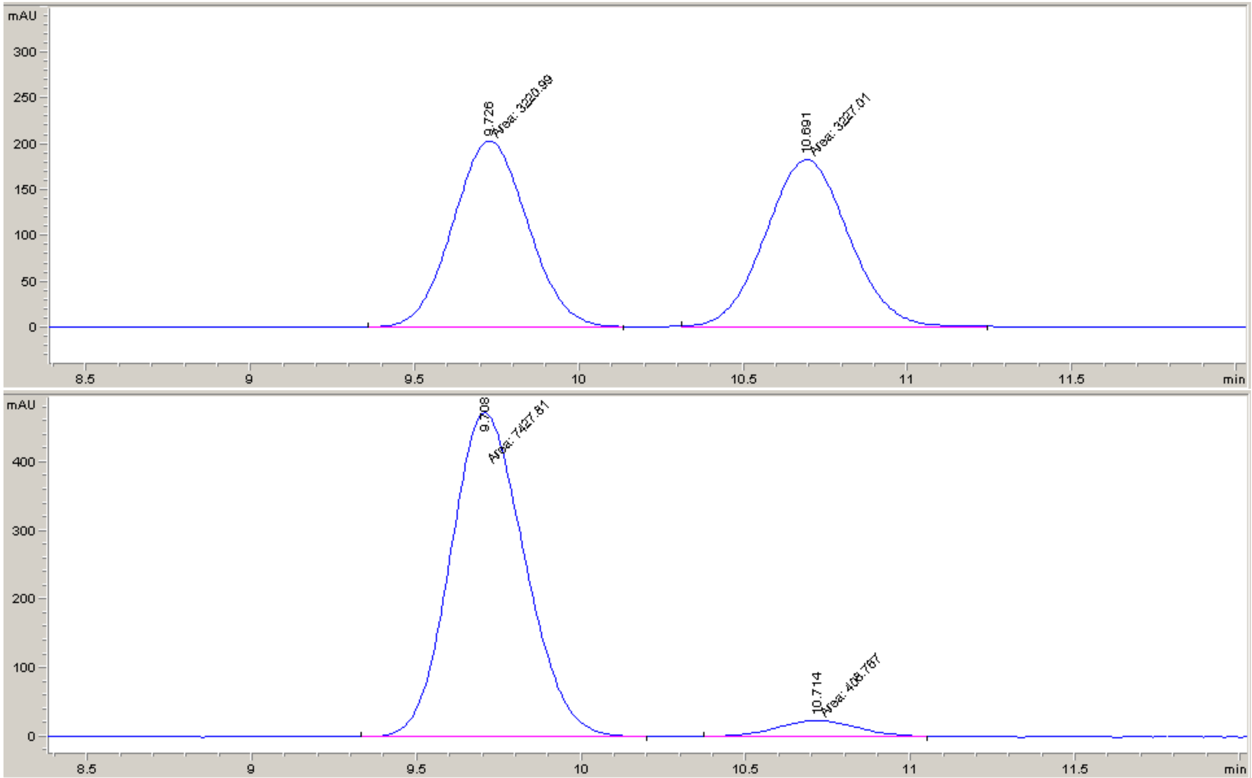
(1,3-Dimethyl-5-(trifluoromethyl)-1*H*-imidazol-3-ium-2-yl)(2-oxotetrahydro-2*H*-pyran-3-yl)dihydroborate (5c)
GC calibration curve:



Analysis Data:

Pdt-Entries	Pdt	Std	Pdt/Std	[Pdt]/mM	[PC]/µM	TTN	Avg. TTN	Avg. yield
5c-(1)	59591	4739	12.575	9.10	8.30	1096		
5c-(2)	60894	4605	13.223	9.50	8.30	1145		
5c-(3)	60528	4424	13.682	9.78	8.30	1178		
5c-(4)	63271	4501	14.057	10.01	8.30	1206	1156	96.0%

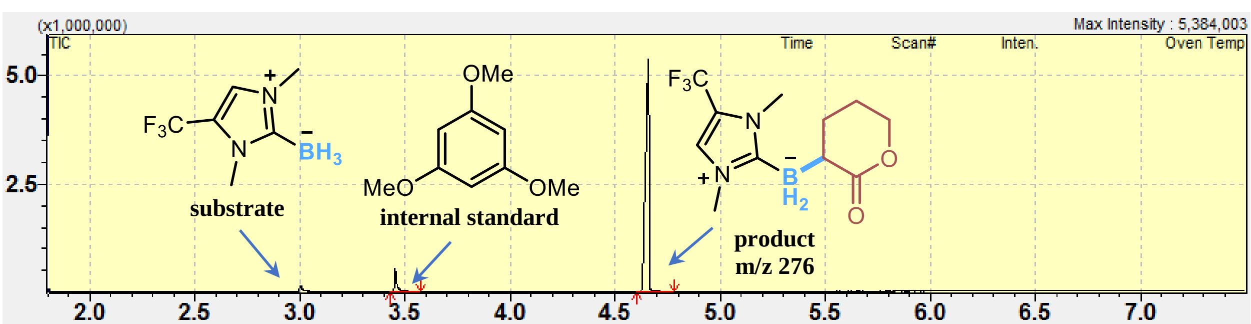
Chiral HPLC trace:
Chiralpak IC, 18% *i*-PrOH in hexane, 1.2 mL/min, 32 °C, 235 nm

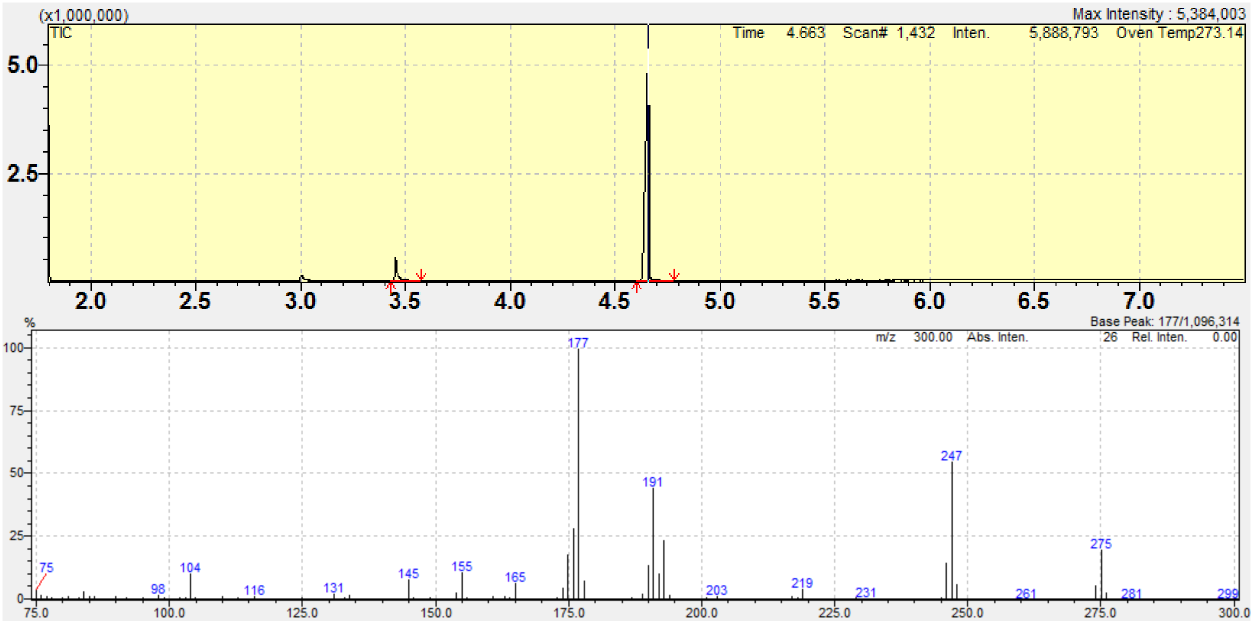


Area% report for **5c**:

***rac*-5c**			**Enzymatically produced 5c**		
Retention Time (min)	Area (mAU*s)	Area %	Retention Time (min)	Area (mAU*s)	Area %
9.726	3220.99	49.95	9.708	7427.81	94.78
10.691	3227.01	50.05	10.714	408.77	5.22
Total	6448	100.00	Total	7836.58	100.00

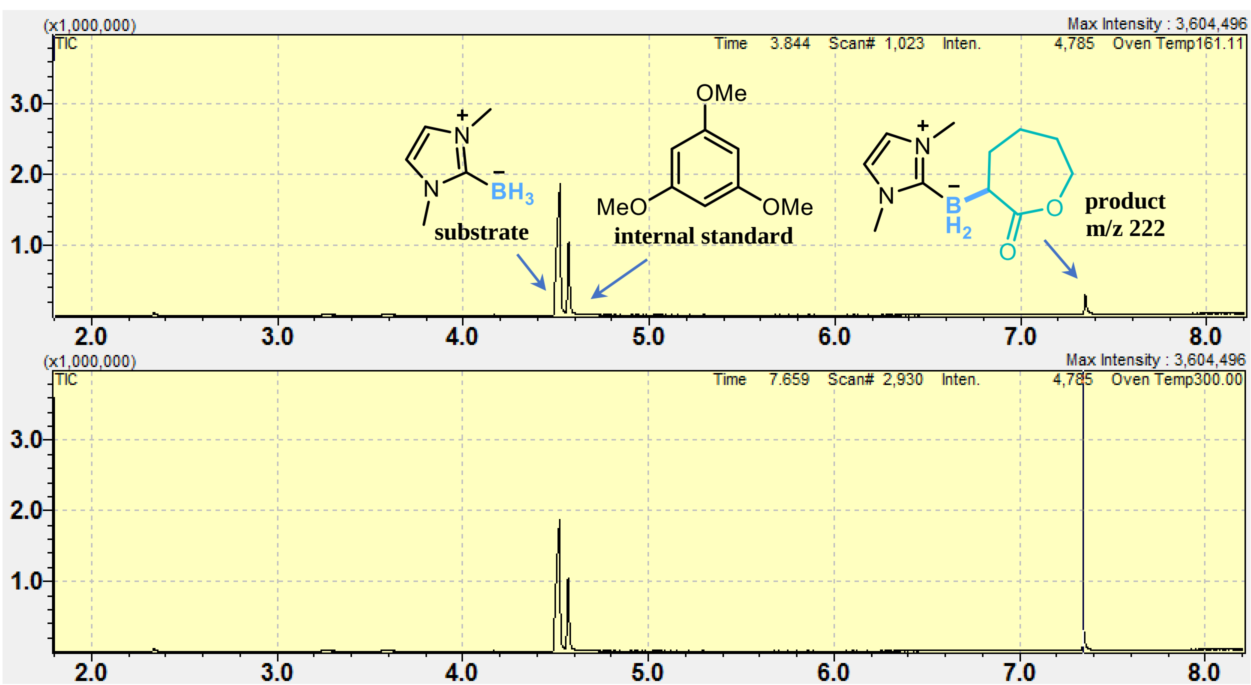
GC-MS trace:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 60 °C/min → 300 °C (isothermal, 3 min), total time: 7.5 min.

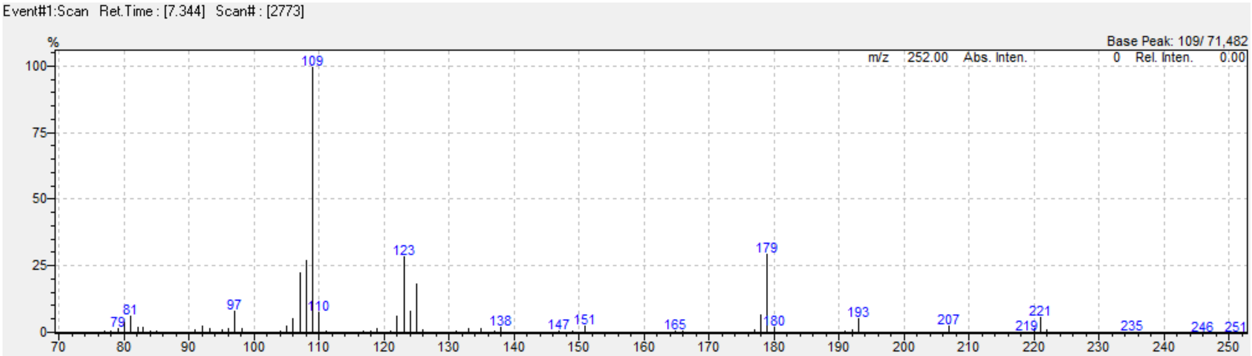




(1,3-Dimethyl-5-(trifluoromethyl)-1*H*-imidazol-3-ium-2-yl)(2-oxooxepan-3-yl)dihydroborate (7a)

GC-MS traces:
Shimadzu GCMS-QP2010SE system, J&W HP-5ms column, 90 °C (isothermal, 1 min) → 25 °C/min → 190 °C → 50 °C/min → 300 °C (isothermal, 1 min), total time: 8.2 min.





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207
219
221
235
246
251

VI. Computational Study of Carbene Intermediates

Computational Details

All DFT calculations were performed with the Gaussian 16 software package (*11*). Geometry optimizations of all the minima and transition states were carried out at the B3LYP (*12*) level of theory with the def2-SVP basis set (*13*). Vibrational frequencies were computed at the same level to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. The single-point energies were computed at the same level of theory with additional Grimme's D3 dispersion correction (Becke-Johnson damping) (*14*), combined with def2-TZVP (*13*) basis set using the optimized structures. The 3D diagrams of molecules were generated using CYLView (*15*). All the C–H bonds are omitted for clarity in the 3D diagrams.

Table S1. Zero-point correction (*ZPE*), thermal correction to enthalpy (*TCH*), thermal correction to Gibbs free energy (*TCG*), energies (*E*), enthalpies (*H*), and Gibbs free energies (*G*) (in Hartree) of the structures for all the figures calculated at the B3LYP-D3(BJ)/def2-TZVPP//B3LYP/def2-SVP level of theory. CSS is closed-shell singlet and OSS is open-shell singlet.

Structures	*ZPE*	*TCH*	*TCG*	*E*	*H*	*G*	Stability
IPC1-CSS	0.472807	0.505106	0.410124	-2824.951173	-2824.446067	-2824.541049	NO
IPC1-OSS	0.472424	0.504896	0.409028	-2824.952173	-2824.447277	-2824.543145	YES
IPC1-triplet	0.471812	0.504391	0.407192	-2824.934335	-2824.429944	-2824.527143	YES
IPC2-CSS	0.425091	0.453867	0.367495	-2784.397714	-2783.943847	-2784.030219	NO
IPC2-OSS	0.424626	0.453548	0.366794	-2784.403635	-2783.950087	-2784.036841	YES
IPC2-triplet	0.424041	0.453254	0.364435	-2784.392251	-2783.938997	-2784.027816	YES
IPC3-CSS	0.453876	0.483772	0.395051	-2823.730466	-2823.246694	-2823.335415	NO
IPC3-OSS	0.453437	0.483436	0.394091	-2823.733043	-2823.249607	-2823.338952	YES
IPC3-triplet	0.452846	0.483098	0.391584	-2823.720649	-2823.237551	-2823.329065	YES
IPC4-CSS	0.482730	0.513624	0.423250	-2863.068057	-2862.554433	-2862.644807	NO
IPC4-OSS	0.482434	0.513443	0.422540	-2863.069632	-2862.556189	-2862.647092	YES
IPC4-triplet	0.481543	0.512921	0.419578	-2863.050012	-2862.537091	-2862.630434	YES

Note: To have a consistent comparison of different **ICP**s, we recalculated the electronic states of **IPC1** using the method indicated here. The results are overall consistent with what we previously observed under a different calculation method (*16*).

Coordinates

IPC1-CSS

Fe	0.20024900	-0.13321800	0.00821700
N	-1.06356600	1.45240400	0.13773200
N	-1.35603900	-1.41862500	0.24009000
N	1.70986700	1.14639700	-0.43424400
N	1.42114100	-1.72146800	-0.32717000
C	-0.74970600	2.78034300	0.02806100
C	-1.32053100	-2.78715700	0.20754900
C	-2.40214600	1.39465700	0.41933200
C	-2.65512900	-1.07353700	0.50451800
C	1.66240100	2.51394600	-0.46945100
C	1.09195900	-3.05072000	-0.29214400
C	3.01098900	0.80235000	-0.68383900

C	2.76132900	-1.66516900	-0.60164000
C	-1.92916700	3.59394400	0.24178900
C	-2.63958100	-3.32931100	0.46403200
C	-2.95730400	2.73080600	0.48640800
C	-3.46904900	-2.26326700	0.65044500
C	2.97457800	3.05596600	-0.75916200
C	2.26304200	-3.86486300	-0.54910000
C	3.81378400	1.99108200	-0.89081200
C	3.30192700	-3.00268500	-0.73895300
C	0.52036100	3.28487700	-0.25692700
C	-0.18386300	-3.55735800	-0.04326000
C	3.50749100	-0.49761500	-0.75465900
C	-3.14429000	0.22822700	0.59872100
H	0.62969800	4.36998200	-0.31134800
H	-0.30193700	-4.64287900	-0.04040400
H	4.57261100	-0.61215900	-0.96641800
H	-4.20807100	0.34453100	0.81659600
C	0.55073000	-0.11275200	1.76749400
O	-0.29561200	1.63057800	3.12013400
C	0.81038700	1.15240600	2.52499500
O	1.90573200	1.65394500	2.63155000
H	4.88162900	1.99018800	-1.10584900
H	3.20512500	4.11741100	-0.84139000
H	-1.95129100	4.68243800	0.20022200
H	-4.00296200	2.96080000	0.68801900
H	-4.53748600	-2.26396500	0.86298700
H	-2.88190000	-4.39106900	0.49051400
H	2.26995300	-4.95381000	-0.57913800
H	4.34381000	-3.23316000	-0.95814300
N	-0.24734900	-0.16889000	-2.14090100
C	-0.28493600	0.88749600	-2.92966800
C	-0.53662300	-1.25656000	-2.93301800
H	-0.10104500	1.91487400	-2.62421800
C	-0.75249000	-0.84389800	-4.22492000
H	-0.57142700	-2.26370500	-2.52765800
H	-1.00138900	-1.38852600	-5.13139600
N	-0.58751700	0.52587000	-4.20244600
H	-0.67422300	1.15501500	-4.99109600
C	-0.15187500	2.84286400	3.88198600
C	-1.50198300	3.18327800	4.47755100
H	0.21514500	3.63825100	3.21364200
H	0.61693900	2.69004800	4.65704500
H	-1.42842400	4.10737600	5.07252200
H	-2.24968900	3.33668100	3.68472600
H	-1.85693400	2.37570700	5.13663900
C	0.67748200	-1.29061500	2.67979300

H	0.49459900	-2.25408100	2.19414800
H	1.69502800	-1.29231100	3.11615500
H	-0.01792600	-1.17061800	3.53253000

IPC1-OSS

Fe	0.25613400	0.17409900	-0.06070800
N	-0.97749200	1.78302200	-0.16692900
N	-1.30616500	-1.02090500	0.45059700
N	1.77231200	1.33344800	-0.74921000
N	1.43872900	-1.46782800	-0.14639300
C	-0.65430900	3.06190500	-0.53495200
C	-1.28666900	-2.37145200	0.67912000
C	-2.30657200	1.80175000	0.16479000
C	-2.58673700	-0.60567600	0.70152600
C	1.73656600	2.67096600	-1.04553100
C	1.10034400	-2.75989300	0.15410700
C	3.05975700	0.92493000	-0.97373500
C	2.77415600	-1.48207100	-0.44576200
C	-1.81542100	3.92138800	-0.43224500
C	-2.59915800	-2.82977100	1.08390900
C	-2.84234700	3.13791000	0.00512300
C	-3.40752200	-1.73019900	1.09888300
C	3.04485800	3.12583400	-1.46965700
C	2.25575100	-3.62425700	0.03046700
C	3.86846800	2.04020200	-1.42196900
C	3.29774500	-2.82901700	-0.34007600
C	0.60834600	3.48536700	-0.95157900
C	-0.16782300	-3.19288300	0.53581800
C	3.53422100	-0.37684300	-0.82215100
C	-3.05553900	0.70122400	0.57713400
H	0.72382800	4.53837600	-1.21609800
H	-0.29169500	-4.25535200	0.75458500
H	4.59138200	-0.54905600	-1.03432300
H	-4.10771800	0.87615900	0.81113600
C	0.66274100	0.51349700	1.69025700
O	-0.54190000	-0.48110700	3.45652600
C	0.59657700	-0.55257800	2.73489100
O	1.47010000	-1.36080400	2.95319200
H	4.92776800	1.98068700	-1.66891600
H	3.28366800	4.14725700	-1.76354700
H	-1.82569800	4.98447600	-0.66978200
H	-3.87527800	3.42162100	0.20327200
H	-4.46644900	-1.67028800	1.34787300
H	-2.85337100	-3.86288300	1.31839600
H	2.25191500	-4.69765400	0.21560100
H	4.33362900	-3.10938800	-0.52673400

N	-0.26424900	-0.21774000	-2.15936400
C	-0.63770700	-1.38523400	-2.64652900
C	-0.26619600	0.66444700	-3.21563800
H	-0.74015300	-2.30673000	-2.07814800
C	-0.64932300	0.01211500	-4.36162600
H	0.00736000	1.70780200	-3.08722800
H	-0.77338500	0.35185600	-5.38605700
N	-0.88147500	-1.29299400	-3.97820800
H	-1.18005300	-2.05188800	-4.57851800
C	-0.71343100	-1.45751000	4.49623300
C	-2.03970000	-1.18806900	5.17669800
H	0.13349000	-1.38834700	5.19878900
H	-0.67959300	-2.46392200	4.04844100
H	-2.20378400	-1.91685100	5.98626200
H	-2.06087200	-0.17701700	5.61256400
H	-2.86980200	-1.27185700	4.45881900
C	1.08551400	1.82291900	2.28058000
H	0.38292100	2.10792700	3.08700600
H	2.07597800	1.70972800	2.76298600
H	1.14161300	2.63955500	1.55342200

IPC1-triplet

Fe	-0.03289200	0.04538900	-0.18834100
N	-1.34863200	1.54644000	-0.39887500
N	-1.58943200	-1.24487300	-0.07104400
N	1.50644700	1.29804000	-0.47009000
N	1.27752500	-1.49409900	-0.14410100
C	-1.04524900	2.83930100	-0.72923000
C	-1.50861900	-2.61273500	-0.08635800
C	-2.70383700	1.50664200	-0.19311500
C	-2.91568800	-0.93591900	0.08506500
C	1.41480000	2.62470200	-0.79159200
C	0.96116400	-2.82710600	-0.14975000
C	2.84289000	1.02321600	-0.33589400
C	2.64321800	-1.41957600	-0.05792900
C	-2.24740400	3.64347000	-0.74301100
C	-2.82820800	-3.18847100	0.05481300
C	-3.27636700	2.82053000	-0.38908200
C	-3.70107400	-2.14603400	0.18064200
C	2.73596000	3.20882400	-0.87179000
C	2.16710100	-3.62284600	-0.07378400
C	3.62352800	2.21893600	-0.56760500
C	3.21183100	-2.74757400	0.00296400
C	0.23264800	3.33893400	-0.96330100
C	-0.32983600	-3.35495700	-0.16091400
C	3.38402300	-0.23953100	-0.10465100

C	-3.44284200	0.35492700	0.07012900
H	0.31837800	4.39586600	-1.22189900
H	-0.42421700	-4.44262600	-0.16327800
H	4.46952200	-0.31849100	-0.02089400
H	-4.51973300	0.46464900	0.21135700
C	0.03011400	0.18542700	1.76898200
O	0.20757200	1.32177900	3.81846000
C	0.16076500	1.46701800	2.44836000
O	0.22741200	2.58311500	1.95385200
H	4.71020000	2.27217400	-0.51617700
H	2.93965800	4.25123300	-1.11323400
H	-2.27957900	4.70705900	-0.97588500
H	-4.33295200	3.06161400	-0.27966700
H	-4.78187000	-2.17826800	0.31243100
H	-3.04206400	-4.25654100	0.06987000
H	2.19376500	-4.71183600	-0.06664300
H	4.27623300	-2.96629400	0.07787100
N	-0.10608100	-0.21257700	-2.36757700
C	-1.19968800	-0.18887500	-3.10400200
C	0.94620800	-0.41702800	-3.22909700
H	-2.21182600	-0.04391700	-2.73228000
C	0.47334400	-0.51860000	-4.51409900
H	1.97095200	-0.47717800	-2.87201100
H	0.97523000	-0.67800400	-5.46436200
N	-0.89551400	-0.37069300	-4.41291000
H	-1.55989000	-0.39177300	-5.17722800
C	0.33285100	2.52123400	4.57592900
H	-0.51108000	3.19498000	4.34683900
H	1.24785400	3.05862900	4.27170200
C	0.36675500	2.14834900	6.04598500
H	0.46402500	3.05266200	6.66786400
H	-0.55602700	1.62396000	6.34032200
H	1.21885200	1.48541600	6.26407700
C	-0.03328400	-1.02968900	2.64782600
H	0.88845300	-1.12061500	3.25273100
H	-0.85595400	-0.93796900	3.38034000
H	-0.16950900	-1.96450300	2.09624300

IPC2-CSS

Fe	-0.05123700	0.05082400	-0.12805700
N	-1.27955100	1.64235100	-0.39831000
N	-1.64412200	-1.19421300	-0.04636800
N	1.54242300	1.26909700	-0.44211900
N	1.17196200	-1.56559200	-0.06825700
C	-0.92355900	2.94760900	-0.62073600
C	-1.63447000	-2.56022800	0.04702800

C	-2.64825100	1.62378700	-0.33029200
C	-2.96095000	-0.81793500	-0.02794300
C	1.53017900	2.62260900	-0.65799300
C	0.81311800	-2.88273300	0.03199600
C	2.86093100	0.89695900	-0.40603900
C	2.54155900	-1.54157800	-0.08232400
C	-2.10407200	3.78229600	-0.69758900
C	-2.98879200	-3.06716900	0.12570000
C	-3.17630200	2.95950900	-0.51314800
C	-3.81402100	-1.98366500	0.08650100
C	2.88414500	3.12400100	-0.76728000
C	1.99218200	-3.72179600	0.08847400
C	3.71132900	2.05126900	-0.60684800
C	3.06785000	-2.88748700	0.02436100
C	0.38419100	3.41366700	-0.74938400
C	-0.49492300	-3.35955700	0.06742700
C	3.33150600	-0.40219100	-0.22294600
C	-3.43365800	0.48791400	-0.14091100
H	0.52332400	4.48260000	-0.92296600
H	-0.63687900	-4.43843400	0.15295500
H	4.41431800	-0.54301200	-0.21649300
H	-4.51576500	0.63043900	-0.10825700
C	-0.00103500	0.31915600	1.63014100
C	0.06867900	1.63141000	2.34750500
C	0.59678100	1.28036000	3.74477200
H	0.12579100	1.84863100	4.56072500
H	1.68979200	1.41842800	3.81220600
H	-0.96422300	2.02932500	2.40521500
H	0.66348500	2.39349600	1.82657900
O	0.29385500	-0.10290000	3.92747000
C	-0.02541700	-0.70857300	2.74190900
O	-0.28559600	-1.88074800	2.70007300
H	4.80020200	2.02553300	-0.62533300
H	3.14958700	4.16542600	-0.94526400
H	-2.09558100	4.85740100	-0.87304300
H	-4.23500200	3.21595400	-0.50609800
H	-4.90223800	-1.95599700	0.12588200
H	-3.25352400	-4.12047900	0.20843500
H	1.97846600	-4.80765300	0.17297800
H	4.12698800	-3.14149100	0.04101700
N	-0.10732900	-0.22041400	-2.32760500
C	-0.22751900	-1.37123300	-2.96099600
C	-0.02779000	0.75129200	-3.29924400
H	-0.31577700	-2.34819500	-2.49139200
C	-0.10169700	0.17116000	-4.54168600
H	0.07736500	1.80264900	-3.04728500

H	-0.07548200	0.59006500	-5.54373300
N	-0.22896800	-1.18212200	-4.30486400
H	-0.30944800	-1.91010900	-5.00419000

IPC2-OSS

Fe	-0.04388300	0.04350900	-0.17682400
N	-1.27054700	1.63993600	-0.41470900
N	-1.63524900	-1.19758800	-0.05822800
N	1.54762000	1.26686500	-0.46206400
N	1.17675700	-1.56913300	-0.09622500
C	-0.91501800	2.94725000	-0.62812600
C	-1.62661800	-2.56308400	0.04943700
C	-2.63820200	1.62209700	-0.33226800
C	-2.95100500	-0.81823100	-0.02366600
C	1.53651000	2.62244200	-0.67009500
C	0.81862500	-2.88613400	0.01742100
C	2.86584700	0.89447600	-0.42165600
C	2.54622200	-1.54381700	-0.10438400
C	-2.09464800	3.78271000	-0.68858700
C	-2.97950500	-3.06619400	0.15093200
C	-3.16603300	2.95905500	-0.50050100
C	-3.80337000	-1.98099000	0.11285100
C	2.88995700	3.12344300	-0.77119200
C	1.99749200	-3.72303900	0.08219400
C	3.71635300	2.04933500	-0.61231900
C	3.07259900	-2.88804300	0.01365100
C	0.39185000	3.41444700	-0.75831400
C	-0.48811200	-3.36357800	0.06461200
C	3.33680400	-0.40501400	-0.24261900
C	-3.42371200	0.48738900	-0.13676700
H	0.53094500	4.48450500	-0.92415500
H	-0.62942000	-4.44130500	0.16295800
H	4.41952000	-0.54531200	-0.23101000
H	-4.50499300	0.63166100	-0.09085000
C	0.01015000	0.31671800	1.66484300
C	0.06912900	1.63979500	2.36725500
C	0.52601800	1.28432700	3.79054300
H	0.01748600	1.85709200	4.58096800
H	1.61526300	1.42098800	3.91259300
H	-0.94661800	2.08250600	2.37695900
H	0.71958500	2.37631800	1.87471100
O	0.21240500	-0.09651400	3.96126300
C	-0.02839300	-0.70541700	2.75180700
O	-0.24095200	-1.89085900	2.70065200
H	4.80529500	2.02384700	-0.62447500
H	3.15647100	4.16596200	-0.94060800

H	-2.08666000	4.85940600	-0.85359300
H	-4.22424000	3.21667600	-0.47957600
H	-4.89077600	-1.95097000	0.16886400
H	-3.24494000	-4.11788900	0.24947000
H	1.98443900	-4.80783000	0.17861000
H	4.13189400	-3.14073100	0.03717900
N	-0.10970200	-0.22271700	-2.35824800
C	-0.23770600	-1.37411100	-2.98979600
C	-0.02818000	0.74906600	-3.32969100
H	-0.32906700	-2.35000100	-2.51835000
C	-0.10898200	0.16797100	-4.57096300
H	0.08299800	1.79982100	-3.07759700
H	-0.08388800	0.58589600	-5.57341700
N	-0.24232100	-1.18473400	-4.33279400
H	-0.32866300	-1.91256300	-5.03175200

IPC2-triplet

Fe	-0.02765300	0.03059800	-0.21939400
N	-1.33288000	1.56382000	-0.41800800
N	-1.58718300	-1.23421900	-0.06355700
N	1.53183200	1.29511200	-0.48503200
N	1.26727700	-1.50312000	-0.14065400
C	-1.01389100	2.86971500	-0.68822800
C	-1.51483300	-2.59974200	-0.00515700
C	-2.69468900	1.52444900	-0.25591400
C	-2.91503000	-0.91369600	0.06375600
C	1.45255600	2.63845400	-0.74313400
C	0.94298000	-2.83104100	-0.07583600
C	2.86710200	1.00002000	-0.38463800
C	2.63615800	-1.43821200	-0.08196700
C	-2.21189300	3.67816600	-0.71275600
C	-2.83772700	-3.16316300	0.15245800
C	-3.25594300	2.84400600	-0.43159300
C	-3.70774000	-2.11474800	0.20985200
C	2.77976700	3.20944900	-0.82143300
C	2.14251500	-3.63360500	0.01244900
C	3.65912700	2.19275800	-0.58568500
C	3.19543000	-2.76729100	0.02370300
C	0.27398700	3.37211500	-0.86686200
C	-0.34628700	-3.35306900	-0.04920400
C	3.39266500	-0.27254200	-0.17131500
C	-3.44089200	0.37409700	-0.00427100
H	0.36910700	4.43954300	-1.07520100
H	-0.44646600	-4.43815800	0.00911500
H	4.47816300	-0.36811200	-0.10813100
H	-4.52041600	0.48684300	0.11181100

C	0.04809900	0.30887600	1.69318700
C	0.01109600	1.64138500	2.38065500
C	0.42255300	1.28870600	3.82148800
H	-0.13279000	1.84692700	4.59139500
H	1.50263000	1.46344200	3.98208200
H	-1.01493700	2.06032500	2.35193600
H	0.66657700	2.40061900	1.92702800
O	0.14748400	-0.09866900	3.97771700
C	0.02443500	-0.71265800	2.73882200
O	-0.08924400	-1.91772800	2.67667900
H	4.74731900	2.22919100	-0.55637000
H	2.99411600	4.25853700	-1.02170400
H	-2.23438500	4.74930700	-0.90973700
H	-4.31536200	3.08491900	-0.35381100
H	-4.78955300	-2.13451800	0.33469800
H	-3.05281600	-4.22819400	0.22757900
H	2.15750500	-4.72069900	0.07650000
H	4.25930100	-2.99048000	0.09087800
N	-0.10371800	-0.22950600	-2.38208500
C	-1.20425500	-0.30967700	-3.10497300
C	0.95258100	-0.35066900	-3.25496300
H	-2.22077800	-0.25254300	-2.72167300
C	0.47489400	-0.50713800	-4.53246500
H	1.98283000	-0.31863800	-2.91062500
H	0.97759500	-0.63388400	-5.48717000
N	-0.90025000	-0.47785900	-4.41530100
H	-1.56923700	-0.56808800	-5.17058200

IPC3-CSS

Fe	-0.13287800	0.04600600	-0.07834300
N	1.47515100	1.27049800	-0.30540700
C	1.46841000	2.62448700	-0.51468000
C	2.79168300	0.89927000	-0.22008700
C	0.32465700	3.41288900	-0.66036400
C	2.82462800	3.12945100	-0.56323200
C	3.25694800	-0.40204700	-0.02888500
C	3.64726700	2.05688100	-0.37727100
C	-0.98763600	2.94444900	-0.60313800
H	0.47040200	4.48242600	-0.82498900
H	3.09522600	4.17234800	-0.72408200
C	2.46586500	-1.54540100	0.07345700
H	4.33919500	-0.54065200	0.01746100
H	4.73615600	2.03366400	-0.35336500
C	-2.16451000	3.77676600	-0.74646400
N	-1.35158700	1.63910300	-0.39660500
C	2.98840200	-2.89111300	0.19455600

N	1.09588800	-1.57168800	0.03207100
C	-3.24268200	2.95097500	-0.62217900
H	-2.14933500	4.85171300	-0.92257100
C	-2.72074000	1.61622800	-0.41070300
C	1.91181300	-3.72752700	0.21272600
H	4.04613800	-3.14507500	0.25222700
C	0.73462700	-2.89019300	0.10906400
H	-4.30087800	3.20396700	-0.67610200
C	-3.51078200	0.47505800	-0.27929500
H	1.89722600	-4.81386300	0.29096300
C	-0.57566600	-3.36470200	0.07544200
C	-3.03936500	-0.83036300	-0.15742000
H	-4.59369900	0.61297900	-0.30533800
C	-1.71376500	-2.56742400	-0.01808100
H	-0.72245000	-4.44359400	0.15303600
C	-3.89406000	-1.99973000	-0.09644500
N	-1.72300000	-1.20224300	-0.11031800
C	-3.06881900	-3.08015100	-0.01618600
H	-4.98288400	-1.97545700	-0.11610000
H	-3.33357000	-4.13467000	0.04914800
N	-0.06406200	-0.20002400	-2.27572100
C	-0.12021800	-1.34911300	-2.92103300
C	0.03882600	0.78016000	-3.23658600
N	-0.05792300	-1.15074200	-4.26226900
H	-0.20709900	-2.33133400	-2.46257500
C	0.04451800	0.20707600	-4.48452900
H	0.10243000	1.83208300	-2.97374600
H	-0.08312400	-1.87569000	-4.96881700
H	0.11066200	0.63366200	-5.48148000
C	-0.15120700	0.26779500	1.69910400
C	-0.17445600	1.59333600	2.41817400
C	-0.03872500	-0.87875800	2.66058400
C	0.62618000	1.56454500	3.74075200
H	0.19772900	2.38274800	1.75325100
H	-1.23719400	1.84392400	2.60424600
O	-0.80180200	-1.80792800	2.73257500
O	1.01131100	-0.80538500	3.52524100
H	-0.03000700	1.36137300	4.60330300
H	1.10906500	2.53804100	3.92269900
C	1.67203900	0.45995500	3.67030400
H	2.26164400	0.38132000	4.59494400
H	2.36897200	0.62093300	2.82880200

IPC3-OSS

Fe	-0.09651700	0.02314000	-0.12434100
N	1.50904100	1.24223700	-0.35894300

C	1.50739000	2.59707300	-0.57078800
C	2.82438900	0.86617000	-0.27690600
C	0.36714900	3.39180000	-0.69988500
C	2.86440100	3.09498500	-0.62761600
C	3.28663900	-0.43659600	-0.09217200
C	3.68310600	2.01935500	-0.43923600
C	-0.94479600	2.93006200	-0.60782500
H	0.51526400	4.46068300	-0.86572300
H	3.13883300	4.13642400	-0.79097600
C	2.49042500	-1.57640500	0.00084300
H	4.36824700	-0.57923400	-0.04725900
H	4.77188000	1.99178200	-0.41690400
C	-2.11933600	3.77008100	-0.70527600
N	-1.31075100	1.62513200	-0.39712300
C	3.00819700	-2.92511800	0.10627500
N	1.12076500	-1.59709100	-0.03759000
C	-3.19840900	2.95117600	-0.54402100
H	-2.10275300	4.84595400	-0.87509900
C	-2.67974900	1.61228500	-0.35846100
C	1.92882000	-3.75779600	0.11574300
H	4.06514700	-3.18283800	0.16084400
C	0.75492800	-2.91524500	0.02795000
H	-4.25591900	3.21228800	-0.55569000
C	-3.47384100	0.47764600	-0.20025500
H	1.90990100	-4.84468300	0.18371300
C	-0.55589200	-3.38605900	0.00755000
C	-3.00724000	-0.83135200	-0.10286500
H	-4.55573300	0.62394300	-0.18461300
C	-1.69027400	-2.58052500	-0.03669900
H	-0.70570800	-4.46525900	0.07217600
C	-3.86669000	-1.99495300	-0.02620100
N	-1.69265300	-1.21332500	-0.10737300
C	-3.04686700	-3.08289500	0.00547500
H	-4.95525700	-1.96296200	-0.00435100
H	-3.31718400	-4.13629600	0.06485800
N	-0.08035500	-0.21137300	-2.32433400
C	-0.13928300	-1.35758300	-2.97501000
C	-0.01168300	0.77637400	-3.28064400
N	-0.11171100	-1.14976100	-4.31532600
H	-0.20418300	-2.34325600	-2.52023100
C	-0.02964500	0.21055300	-4.53152700
H	0.04648700	1.82724900	-3.01241500
H	-0.14600100	-1.87061500	-5.02582300
H	0.00784400	0.64372400	-5.52710700
C	-0.08422400	0.25918600	1.73214500
C	-0.12851400	1.62121400	2.38344500

C	0.05012300	-0.88053200	2.68299100
C	0.40838900	1.62876200	3.82568600
H	0.44790500	2.32989700	1.76998900
H	-1.16842300	1.99717500	2.34797600
O	-0.55896400	-1.92224700	2.62749100
O	0.93732200	-0.71474000	3.71254800
H	-0.38528300	1.38090900	4.55094900
H	0.79485400	2.62535400	4.09526200
C	1.49986600	0.57822200	3.94260200
H	1.94077300	0.53622000	4.94957300
H	2.31468800	0.77292500	3.22025400

IPC3-triplet

Fe	-0.03238900	-0.01128400	-0.17640600
N	1.52773400	1.25017600	-0.45065000
C	1.44775400	2.58720500	-0.73991100
C	2.86119900	0.95916500	-0.32606200
C	0.26824500	3.31566500	-0.88785700
C	2.77470200	3.15923900	-0.81045800
C	3.38455400	-0.31427700	-0.10485800
C	3.65300800	2.15070900	-0.53518400
C	-1.02018200	2.81993400	-0.69135400
H	0.36362800	4.37796700	-1.12111100
H	2.99042800	4.20377700	-1.03202800
C	2.62724300	-1.48248600	-0.06301400
H	4.46882900	-0.40987300	-0.02293800
H	4.74061200	2.19117600	-0.49136100
C	-2.21673700	3.63140900	-0.70984200
N	-1.33838700	1.52171500	-0.38520200
C	3.18235000	-2.81710500	-0.01183000
N	1.26001300	-1.54260200	-0.15240400
C	-3.25654500	2.80759100	-0.38425300
H	-2.24120300	4.69780100	-0.93109900
C	-2.69597800	1.48893000	-0.19726100
C	2.12931900	-3.67922200	-0.10018700
H	4.24405600	-3.04667400	0.06756200
C	0.93187200	-2.87079600	-0.17216700
H	-4.31341300	3.05393600	-0.29018800
C	-3.44061700	0.33900100	0.06446800
H	2.14295900	-4.76828000	-0.09870500
C	-0.35977400	-3.38863700	-0.20107800
C	-2.91741100	-0.95163900	0.08284000
H	-4.51737500	0.45260300	0.20316300
C	-1.52583700	-2.63518900	-0.10861800
H	-0.46392400	-4.47495600	-0.21501900
C	-3.71306500	-2.15705700	0.17401100

N	-1.59395100	-1.26925900	-0.08143400
C	-2.84927600	-3.20264400	0.03353200
H	-4.79290100	-2.18080900	0.31450600
H	-3.06847300	-4.26948700	0.04489300
N	-0.10694000	-0.23322400	-2.35804700
C	-1.20591900	-0.30147300	-3.08385100
C	0.95044600	-0.34033700	-3.23101700
N	-0.90017300	-0.44845700	-4.39662300
H	-2.22305800	-0.25082500	-2.70137500
C	0.47518000	-0.47606400	-4.51193500
H	1.98012200	-0.31382700	-2.88444400
H	-1.56801900	-0.52650800	-5.15421900
H	0.97947100	-0.58733300	-5.46775400
C	0.07308500	0.27956200	1.77293400
C	0.16913200	1.68288300	2.31759600
C	0.10322100	-0.84917200	2.70151700
C	0.12939500	1.74867100	3.84758300
H	1.11316200	2.14161900	1.96551500
H	-0.62637000	2.31435100	1.89027600
O	-0.22078500	-1.99490200	2.44686000
O	0.51518300	-0.62438000	4.00308000
H	-0.89874200	1.59789200	4.21976800
H	0.46712900	2.73565900	4.20601100
C	1.00980900	0.64540900	4.39879500
H	1.02947400	0.63266700	5.49978800
H	2.05306000	0.77330900	4.04677400

IPC4-CSS

Fe	-0.10228500	0.06105500	-0.07359200
C	-0.16056200	0.29264100	1.71307000
C	-0.28922800	1.61750800	2.42264200
C	-0.14275700	-0.86323900	2.67499100
C	0.09622200	1.63878500	3.91230000
H	-1.35111200	1.91320700	2.31363100
H	0.26839000	2.38244400	1.85888000
O	0.97938800	-1.03211900	3.41538600
O	-1.08857000	-1.59178500	2.83989300
C	1.55430100	1.22683200	4.18087000
H	-0.57793700	0.96752700	4.47022800
H	-0.08137300	2.64754300	4.31945900
C	1.97596900	-0.00014400	3.36993600
H	1.68356300	1.03110800	5.25819000
H	2.24321800	2.04997700	3.92153800
H	2.89085300	-0.45518400	3.77454700
H	2.18080000	0.27018500	2.32263500
N	1.50504600	1.28541600	-0.30988900

C	1.49558900	2.64189300	-0.50452800
C	2.82339300	0.90978700	-0.28027100
C	0.35010000	3.43003000	-0.63539300
C	2.85088700	3.14494300	-0.58921500
C	3.29150300	-0.39408900	-0.11492600
C	3.67626800	2.06726600	-0.45229200
C	-0.96079600	2.95638900	-0.59861100
H	0.49368600	4.50147900	-0.78933700
H	3.11871400	4.18941100	-0.74448000
C	2.50190700	-1.53336100	0.03826600
H	4.37431400	-0.53631200	-0.11484700
H	4.76522000	2.04080200	-0.46912400
C	-2.13837400	3.78470800	-0.76042900
N	-1.32245000	1.64767000	-0.41172600
C	3.02527100	-2.87707400	0.17473900
N	1.13113300	-1.55462200	0.05702200
C	-3.21474800	2.95222800	-0.67067500
H	-2.12461400	4.86123700	-0.92674400
C	-2.69075900	1.61855100	-0.45584400
C	1.94799800	-3.70822500	0.26685300
H	4.08377900	-3.13404400	0.19212400
C	0.77009700	-2.87004700	0.18279200
H	-4.27271300	3.20031300	-0.74724900
C	-3.47900800	0.47508300	-0.33229000
H	1.93387000	-4.79184600	0.37671600
C	-0.54175300	-3.34343600	0.18558600
C	-3.00664300	-0.82576900	-0.17235600
H	-4.56165500	0.60890800	-0.38120500
C	-1.68086400	-2.55267200	0.05394100
H	-0.68780300	-4.41882100	0.30340500
C	-3.86026600	-1.99426800	-0.08217400
N	-1.69064600	-1.19217900	-0.09326600
C	-3.03510800	-3.06831300	0.05709100
H	-4.94867900	-1.97316600	-0.11966000
H	-3.29901700	-4.11988800	0.16136100
N	-0.03086900	-0.20823000	-2.25490900
C	-0.11056100	-1.36311400	-2.88708800
C	0.09347100	0.75910400	-3.22592700
N	-0.04264500	-1.18081700	-4.23034300
H	-0.21871600	-2.33802400	-2.41751600
C	0.08844500	0.17209900	-4.46742000
H	0.17841000	1.81230900	-2.97393200
H	-0.08262100	-1.91273300	-4.92897500
H	0.16426000	0.58608300	-5.46898100

IPC4-OSS

Fe	-0.09959700	0.05274900	-0.10053000
C	-0.15223800	0.28821400	1.73140900
C	-0.27636700	1.62609800	2.42232400
C	-0.11776000	-0.87547600	2.67549500
C	0.07627400	1.65265100	3.92007500
H	-1.32509600	1.95730300	2.29409500
H	0.31947700	2.37453900	1.87413300
O	0.99182100	-1.01066500	3.45161400
O	-1.02202600	-1.66318600	2.80660800
C	1.53032300	1.25352300	4.22270000
H	-0.60510000	0.97679700	4.46397700
H	-0.11828200	2.66072400	4.32200700
C	1.97765500	0.02788400	3.42387900
H	1.63799400	1.06055200	5.30307500
H	2.21788200	2.08229400	3.97718800
H	2.88805100	-0.41728000	3.85054600
H	2.20170800	0.29925500	2.38063000
N	1.50597200	1.27753100	-0.32614900
C	1.49918500	2.63451700	-0.52125700
C	2.82375600	0.90146600	-0.28184400
C	0.35577400	3.42424300	-0.65396800
C	2.85461600	3.13600000	-0.59448300
C	3.29091300	-0.40187200	-0.11173200
C	3.67811700	2.05793700	-0.44666200
C	-0.95471800	2.95176800	-0.60912800
H	0.50020700	4.49564500	-0.80669700
H	3.12450800	4.18023800	-0.74735000
C	2.49966900	-1.54085800	0.02994900
H	4.37359200	-0.54367500	-0.09896500
H	4.76714800	2.03107200	-0.45107300
C	-2.13198000	3.78219600	-0.75471000
N	-1.31690700	1.64269600	-0.42258100
C	3.02207900	-2.88435400	0.16830600
N	1.12880700	-1.56322100	0.03282500
C	-3.20895300	2.95177600	-0.65219800
H	-2.11788600	4.85923700	-0.91728800
C	-2.68568500	1.61684200	-0.44720400
C	1.94458000	-3.71663000	0.24601500
H	4.08053800	-3.14017700	0.19818300
C	0.76735600	-2.87944300	0.15375000
H	-4.26732600	3.20240700	-0.71269300
C	-3.47583300	0.47612000	-0.31372100
H	1.92984800	-4.80031700	0.35455000
C	-0.54368000	-3.35297900	0.15498000
C	-3.00445600	-0.82580700	-0.16205300
H	-4.55857900	0.61320200	-0.34641000

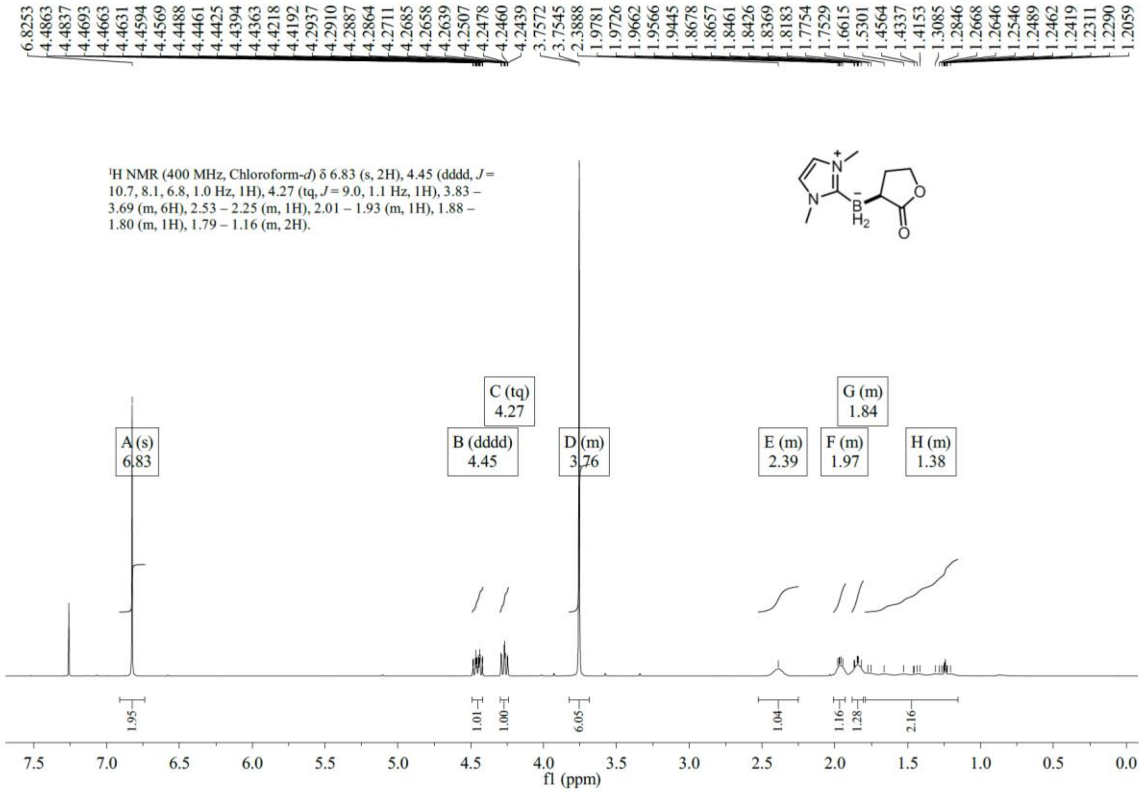
C	-1.68120600	-2.55846900	0.03813900
H	-0.69064600	-4.42839800	0.27013200
C	-3.85969600	-1.99150500	-0.06336200
N	-1.68851300	-1.19700200	-0.10406500
C	-3.03595200	-3.06917600	0.05832800
H	-4.94846700	-1.96659300	-0.08322000
H	-3.30174700	-4.12014900	0.16328900
N	-0.03718500	-0.21240200	-2.28520900
C	-0.11221500	-1.36718700	-2.91844000
C	0.07704500	0.75763200	-3.25475200
N	-0.05099000	-1.18199500	-4.26116100
H	-0.21232700	-2.34329200	-2.44945300
C	0.07060100	0.17217700	-4.49682100
H	0.15638100	1.81089200	-3.00105400
H	-0.08926500	-1.91300200	-4.96096900
H	0.13973700	0.58793100	-5.49812100

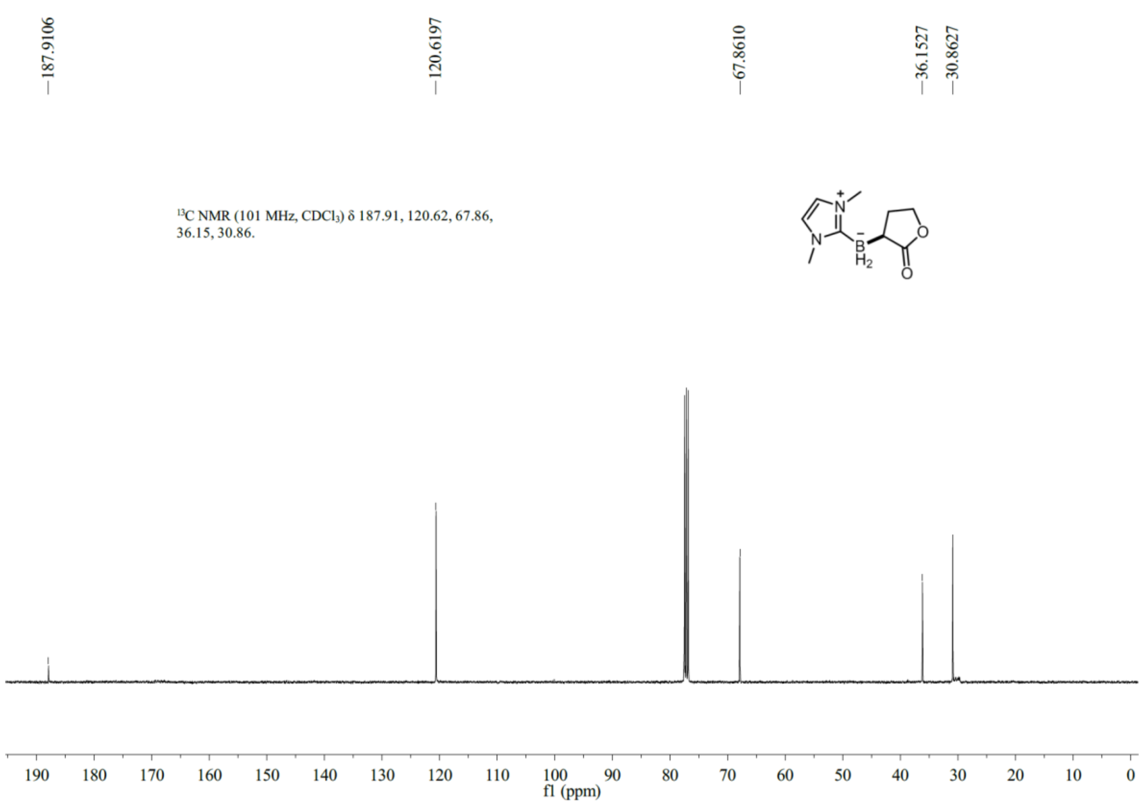
IPC4-triplet

Fe	-0.06981200	-0.00503300	-0.17237500
C	-0.02093600	0.24611500	1.78776300
C	-0.23003900	1.61678800	2.39149100
C	0.12939200	-0.92168100	2.66975900
C	-0.08627700	1.72620300	3.91987000
H	-1.24825000	1.95576200	2.12580600
H	0.44013400	2.35194600	1.90756200
O	1.05721600	-0.84197500	3.68783200
O	-0.49617900	-1.95804700	2.58872200
C	1.33784900	1.46830600	4.42870200
H	-0.77705800	1.01235300	4.39918500
H	-0.41582300	2.72928200	4.23970200
C	1.96200300	0.25527000	3.74134900
H	1.31921900	1.31758100	5.52135500
H	1.98392200	2.34427500	4.23884100
H	2.84286900	-0.10595900	4.29526200
H	2.29370800	0.51486900	2.72181500
N	1.51288400	1.25146700	-0.37934900
C	1.45377900	2.59505600	-0.63857400
C	2.84170700	0.94277500	-0.24631100
C	0.28456100	3.33439500	-0.81035700
C	2.78801400	3.15553600	-0.67376600
C	3.34922900	-0.33968000	-0.04256500
C	3.65090600	2.13016200	-0.41650200
C	-1.01247000	2.83920900	-0.68298600
H	0.39307000	4.40093000	-1.01688300
H	3.01776700	4.20304600	-0.86510700

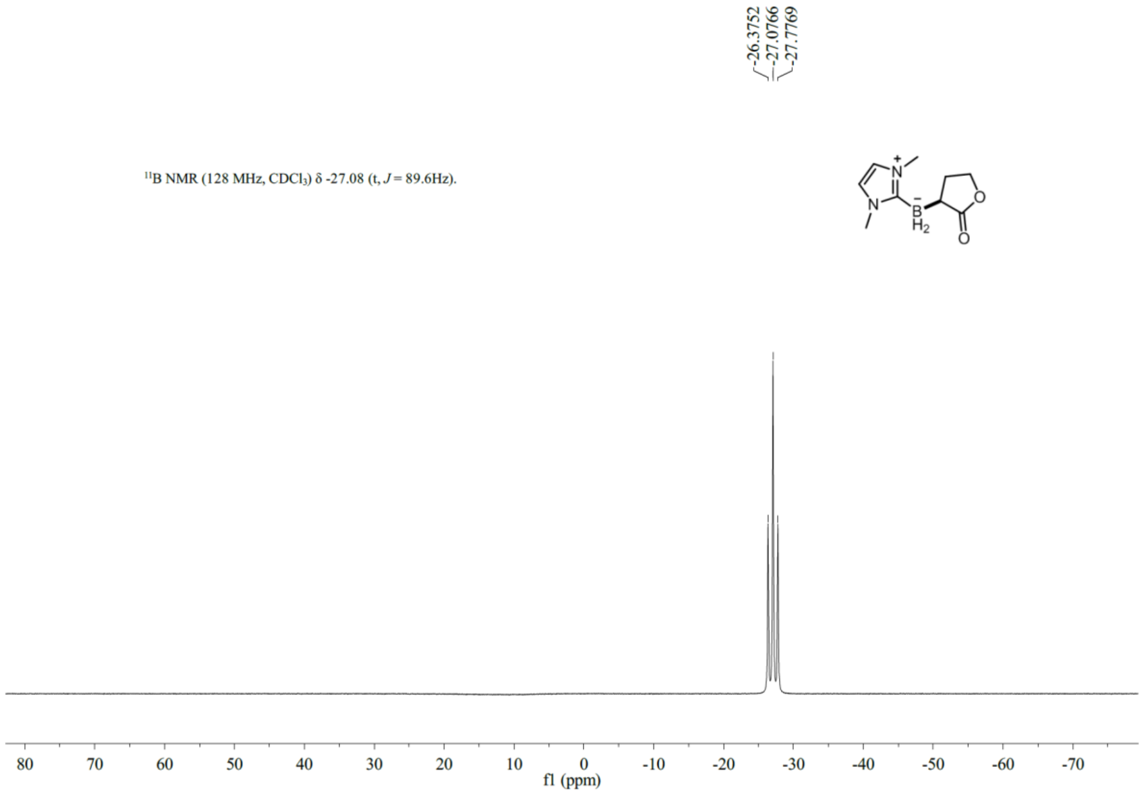
C	2.58113500	-1.50152500	-0.00512700
H	4.43201800	-0.44764000	0.04438100
H	4.73826900	2.15644300	-0.35792300
C	-2.20239100	3.65619500	-0.75111300
N	-1.35110700	1.53659900	-0.41950100
C	3.12498800	-2.83849400	0.07094900
N	1.21283800	-1.55260500	-0.09774100
C	-3.26194700	2.83123100	-0.50070600
H	-2.21021700	4.72669100	-0.95270000
C	-2.71755500	1.50808600	-0.30375100
C	2.06496500	-3.69479200	0.00266300
H	4.18469500	-3.07487800	0.15675300
C	0.87482300	-2.87953500	-0.09100500
H	-4.32141900	3.08081100	-0.45950700
C	-3.48114300	0.36349300	-0.07652800
H	2.07037500	-4.78359400	0.02834300
C	-0.42104400	-3.38767000	-0.12282100
C	-2.96878800	-0.92955600	-0.01152500
H	-4.56244200	0.48573800	0.00966500
C	-1.58363700	-2.62429600	-0.09236900
H	-0.53311200	-4.47307700	-0.10363800
C	-3.77708400	-2.12725600	0.08172600
N	-1.64231300	-1.25822900	-0.11265500
C	-2.91567900	-3.18095900	0.01437200
H	-4.86197800	-2.13985300	0.17744500
H	-3.14145700	-4.24577700	0.05206600
N	-0.07154400	-0.23401300	-2.35410200
C	-1.14458800	-0.38060400	-3.10673600
C	1.01184100	-0.26351200	-3.20106500
N	-0.79700000	-0.50321800	-4.41162300
H	-2.17172800	-0.40398400	-2.74926200
C	0.57907100	-0.43171000	-4.49318800
H	2.02809200	-0.16282600	-2.82956400
H	-1.43875400	-0.62810200	-5.18532800
H	1.11336700	-0.50553700	-5.43624500

VII. NMR Spectra

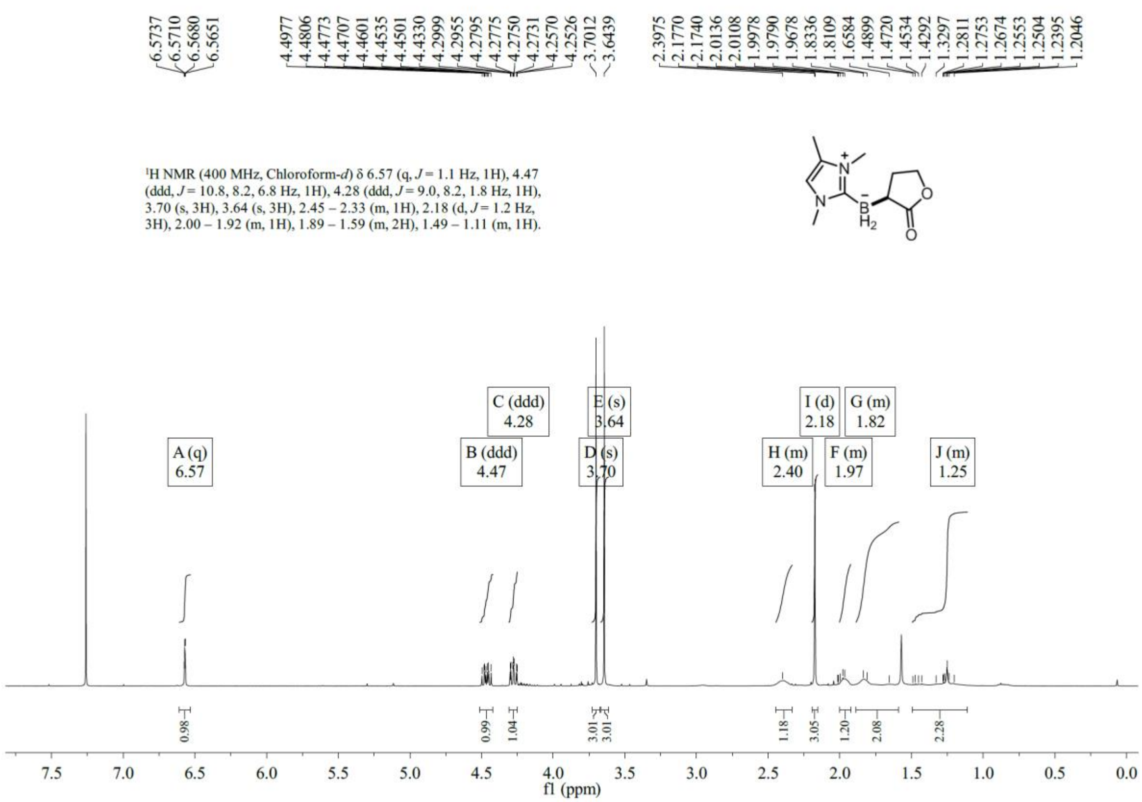


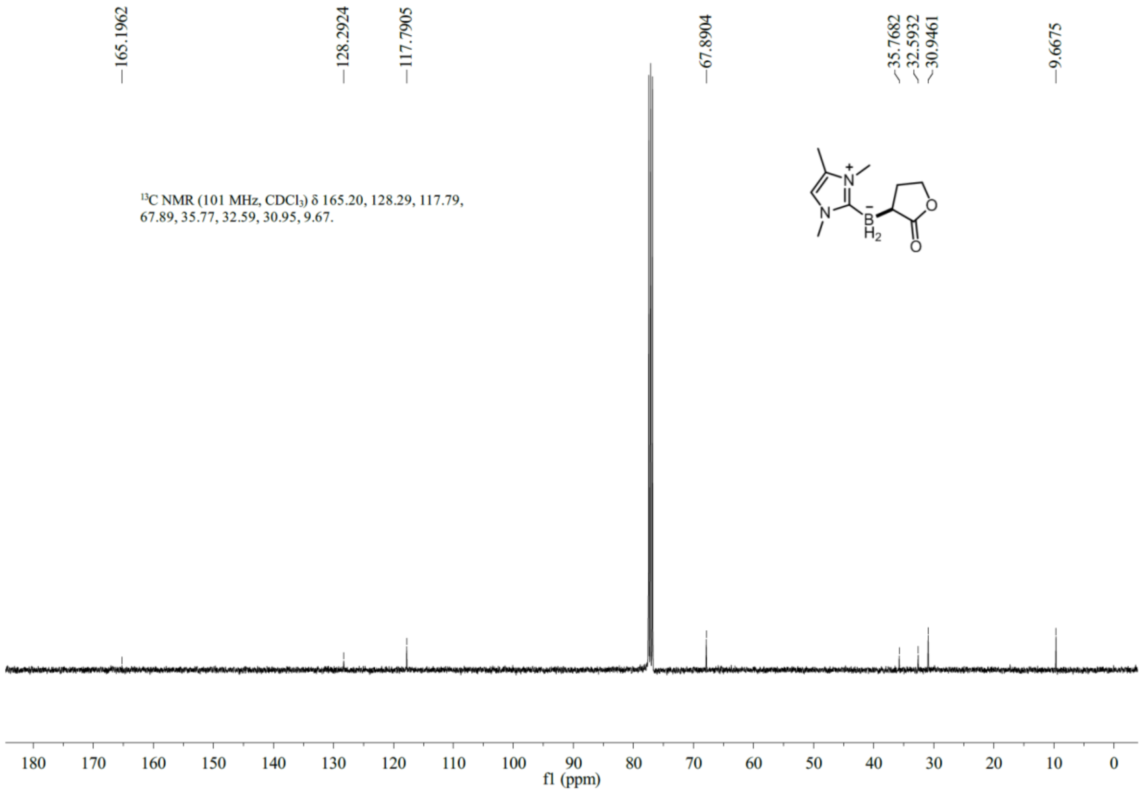


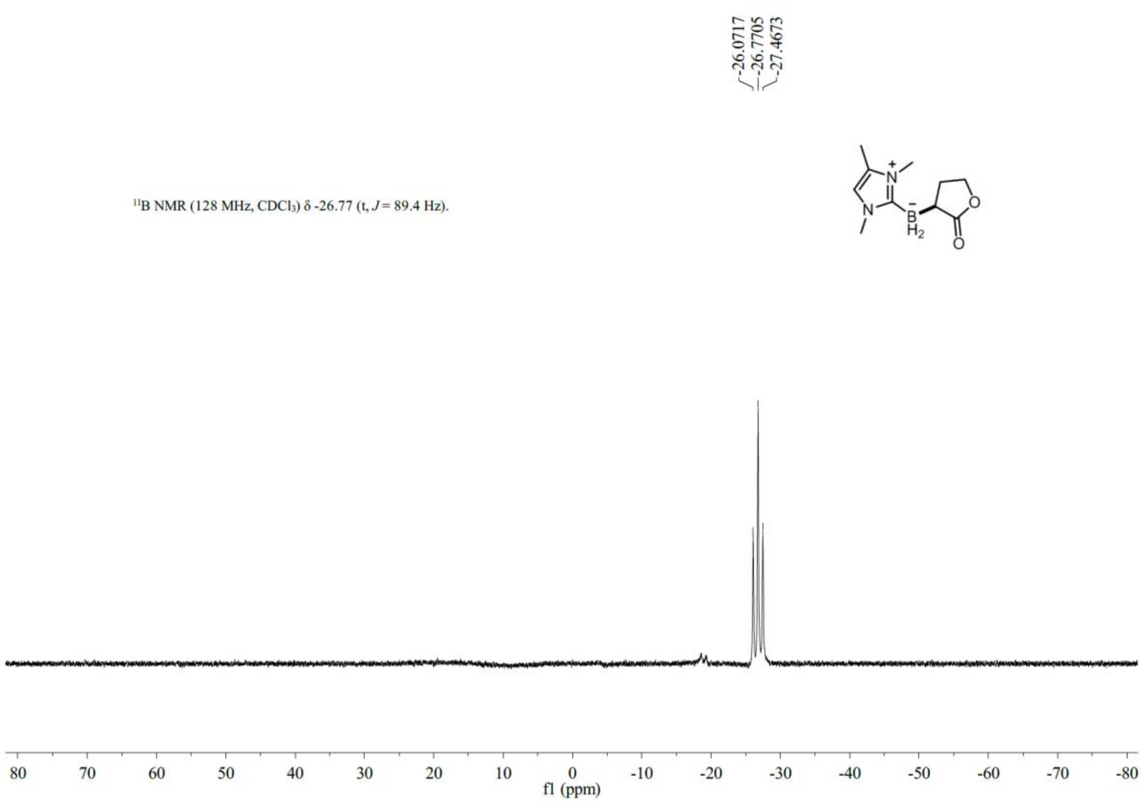
[11]B NMR (128 MHz, $CDCl_3$) δ -27.08 (t, *J* = 89.6Hz).

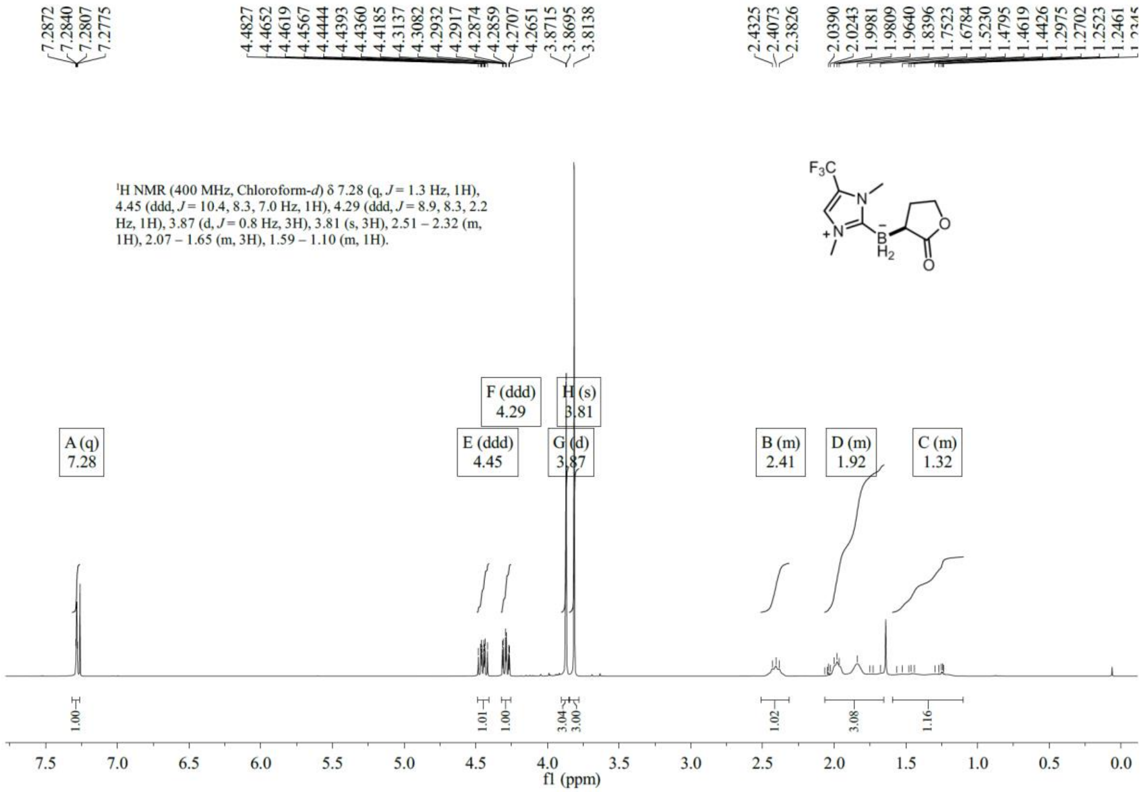


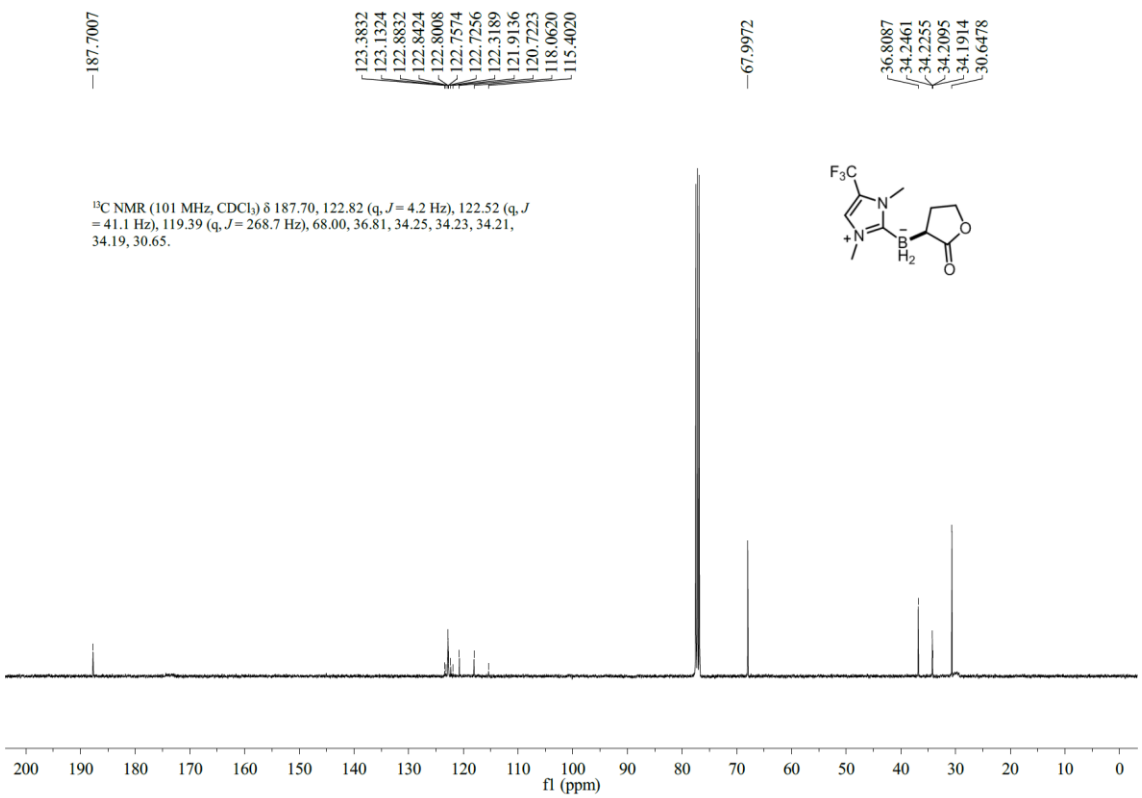
[1]H NMR (400 MHz, Chloroform-*d*) δ 6.57 (q, *J* = 1.1 Hz, 1H), 4.47 (ddd, *J* = 10.8, 8.2, 6.8 Hz, 1H), 4.28 (ddd, *J* = 9.0, 8.2, 1.8 Hz, 1H), 3.70 (s, 3H), 3.64 (s, 3H), 2.45 – 2.33 (m, 1H), 2.18 (d, *J* = 1.2 Hz, 3H), 2.00 – 1.92 (m, 1H), 1.89 – 1.59 (m, 2H), 1.49 – 1.11 (m, 1H).

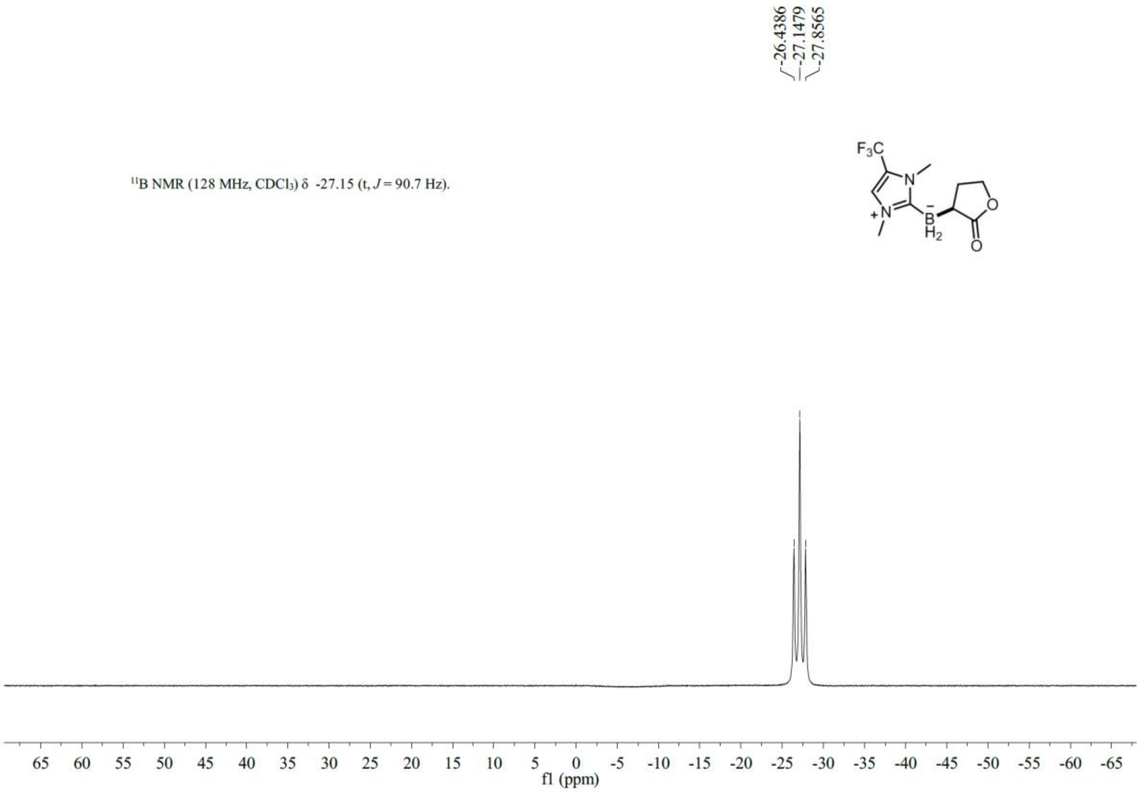



165.1962
128.2924
117.7905
67.8904
35.7682
32.5932
30.9461
9.6675
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.20, 128.29, 117.79, 67.89, 35.77, 32.59, 30.95, 9.67.
f1 (ppm)

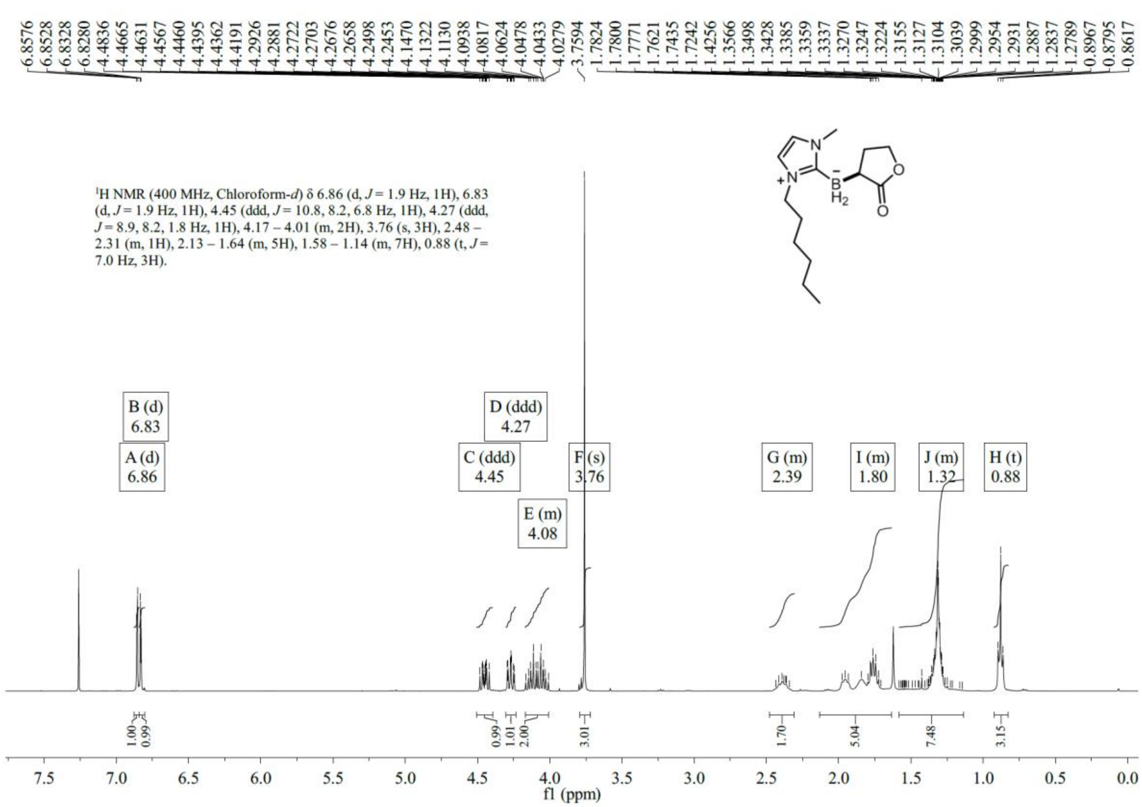

-26.0717
-26.7705
-27.4673
^{11}B NMR (128 MHz, $CDCl_3$) δ -26.77 (t, J = 89.4 Hz).
f1 (ppm)


1H NMR (400 MHz, Chloroform-d) δ 7.28 (q, J = 1.3 Hz, 1H), 4.45 (ddd, J = 10.4, 8.3, 7.0 Hz, 1H), 4.29 (ddd, J = 8.9, 8.3, 2.2 Hz, 1H), 3.87 (d, J = 0.8 Hz, 3H), 3.81 (s, 3H), 2.51 – 2.32 (m, 1H), 2.07 – 1.65 (m, 3H), 1.59 – 1.10 (m, 1H).
A (q) 7.28
E (ddd) 4.45
F (ddd) 4.29
G (d) 3.87
H (s) 3.81
B (m) 2.41
D (m) 1.92
C (m) 1.32
f1 (ppm)

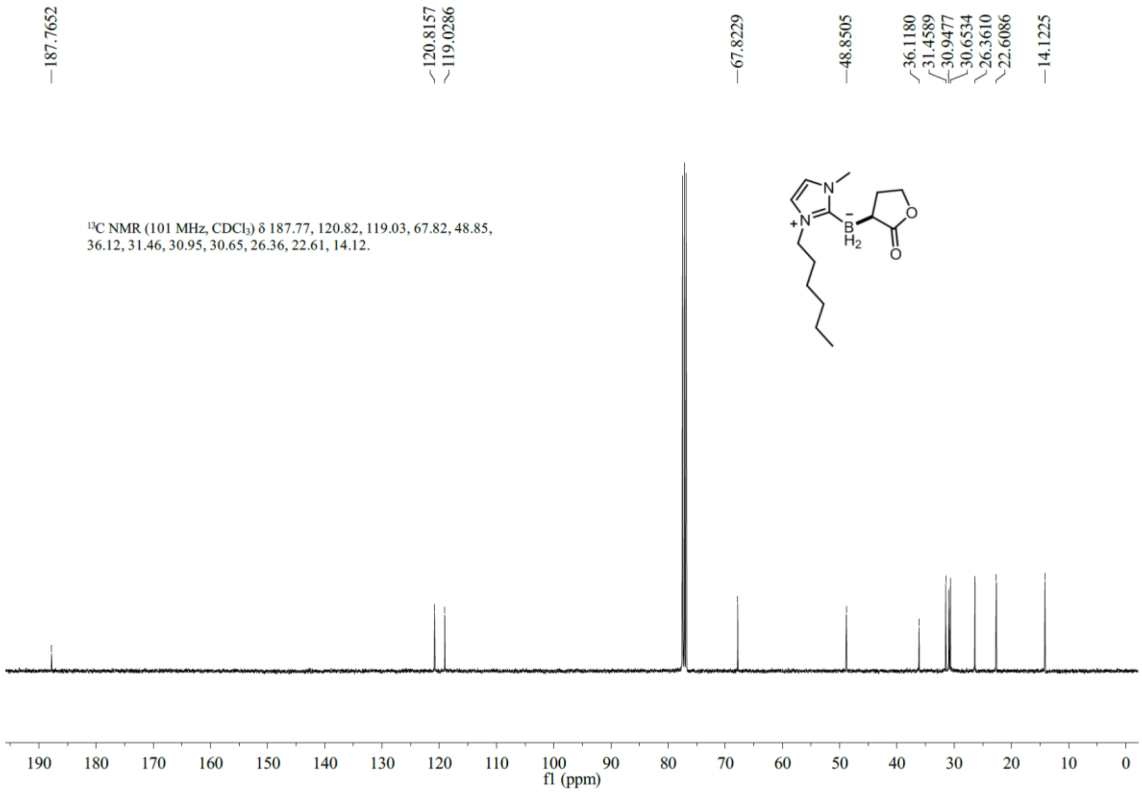

13C NMR (101 MHz, CDCl3) δ 187.70, 122.82 (q, J = 4.2 Hz), 122.52 (q, J = 41.1 Hz), 119.39 (q, J = 268.7 Hz), 68.00, 36.81, 34.25, 34.23, 34.21, 34.19, 30.65.
f1 (ppm)



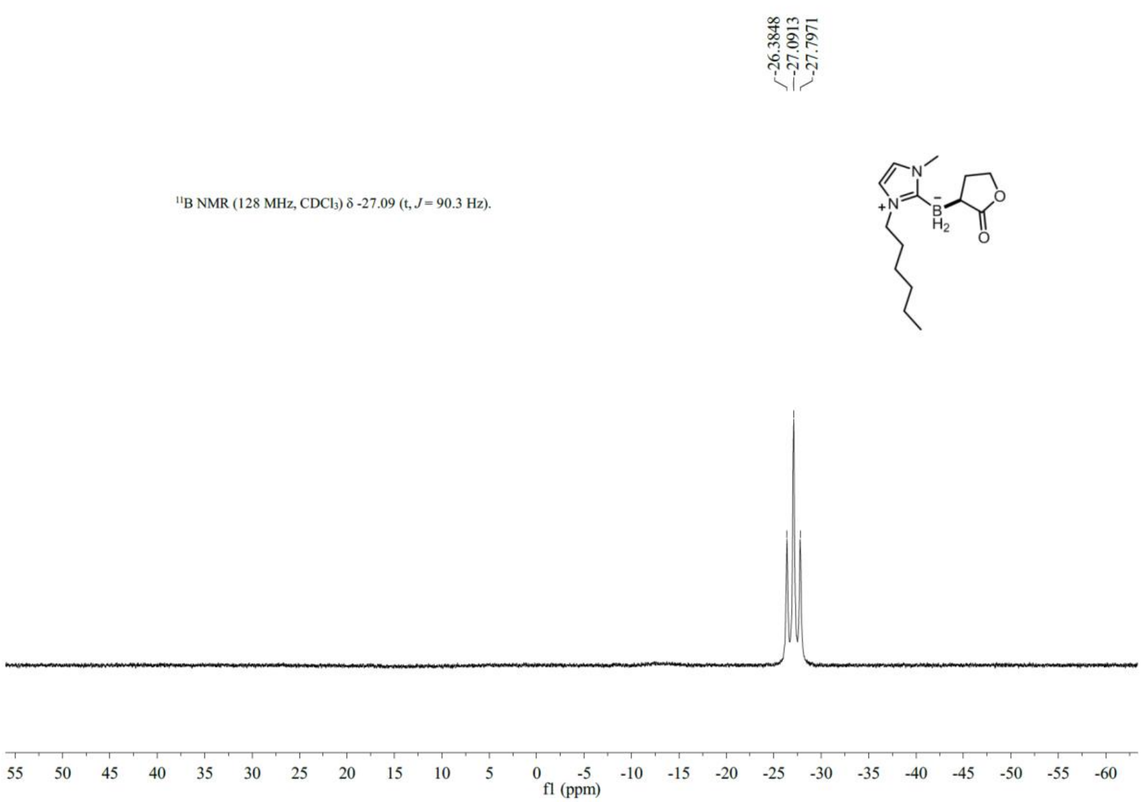
^{11}B NMR (128 MHz, CDCl$_3$) δ -27.15 (t, J = 90.7 Hz).



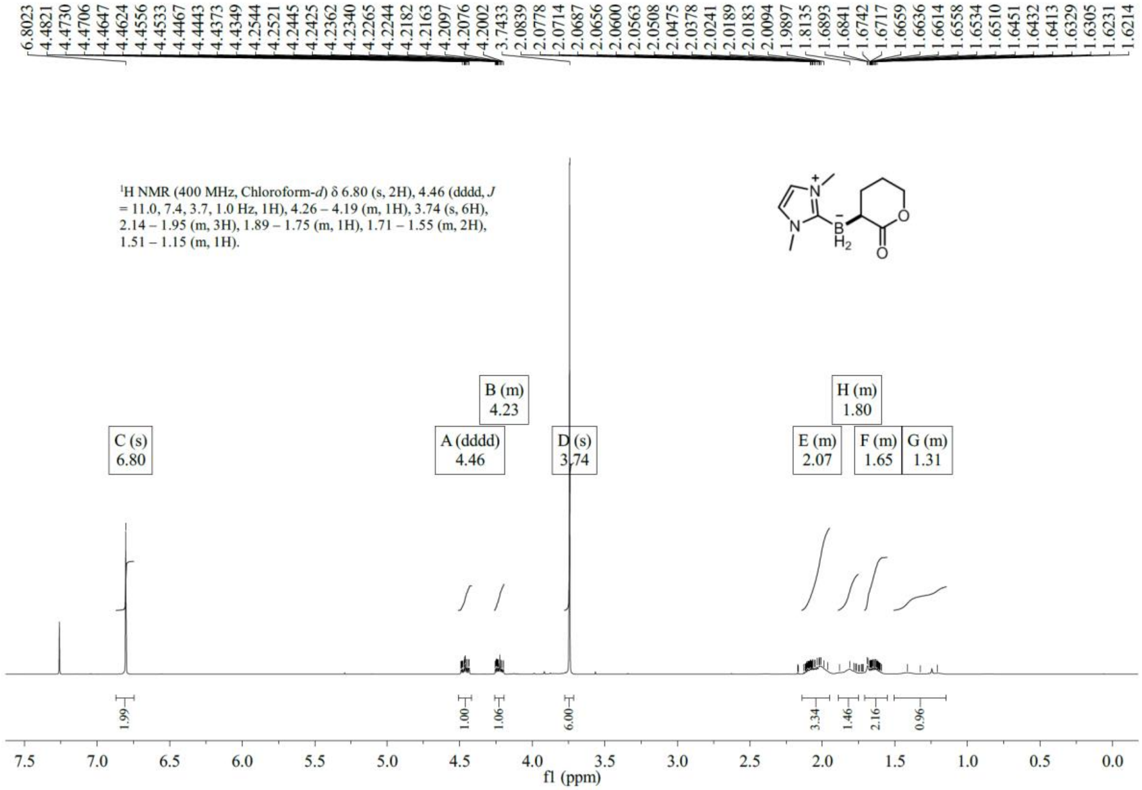
^{1}H NMR (400 MHz, Chloroform-d) δ 6.86 (d, J = 1.9 Hz, 1H), 6.83 (d, J = 1.9 Hz, 1H), 4.45 (ddd, J = 10.8, 8.2, 6.8 Hz, 1H), 4.27 (ddd, J = 8.9, 8.2, 1.8 Hz, 1H), 4.17 – 4.01 (m, 2H), 3.76 (s, 3H), 2.48 – 2.31 (m, 1H), 2.13 – 1.64 (m, 5H), 1.58 – 1.14 (m, 7H), 0.88 (t, J = 7.0 Hz, 3H).



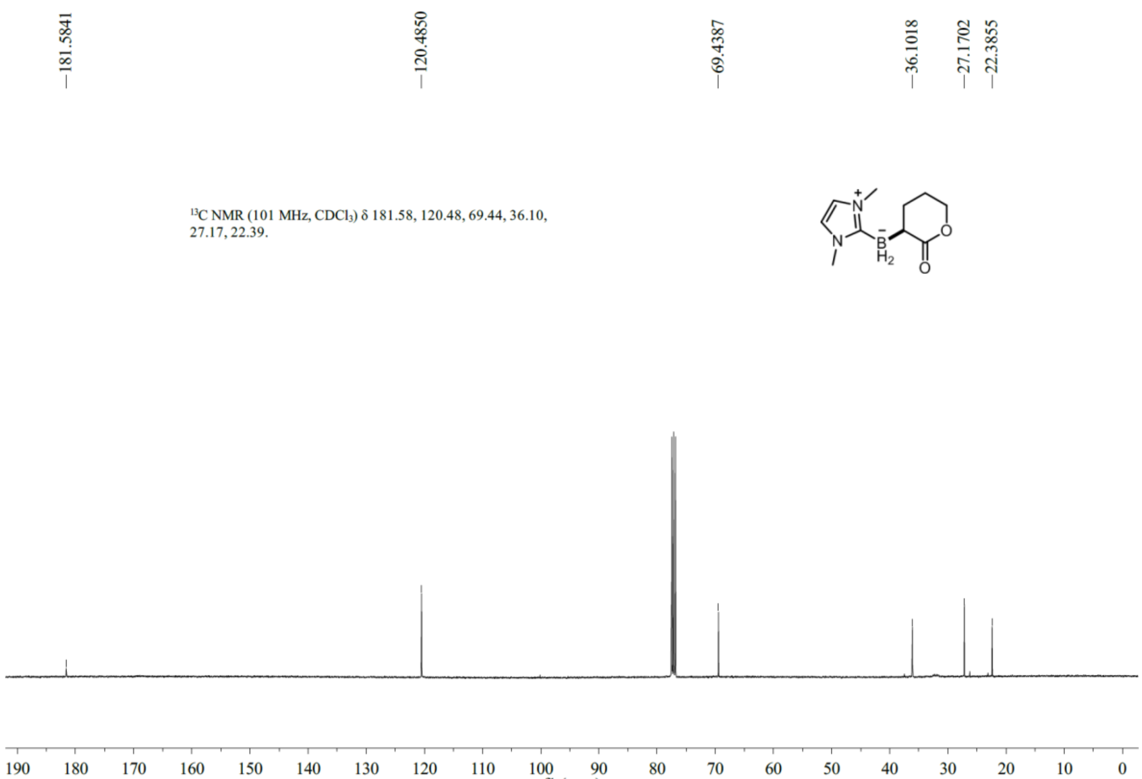
187.7652
120.8157
119.0286
67.8229
48.8505
36.1180
31.4589
30.9477
30.6534
26.3610
22.6086
14.1225
^{13}C NMR (101 MHz, CDCl$_3$) δ 187.77, 120.82, 119.03, 67.82, 48.85, 36.12, 31.46, 30.95, 30.65, 26.36, 22.61, 14.12.
N
N
B
H2
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



-26.3848
-27.0913
-27.7971
^{11}B NMR (128 MHz, CDCl$_3$) δ -27.09 (t, J = 90.3 Hz).
N
N
B
H2
O
O
55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60
f1 (ppm)

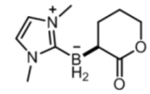


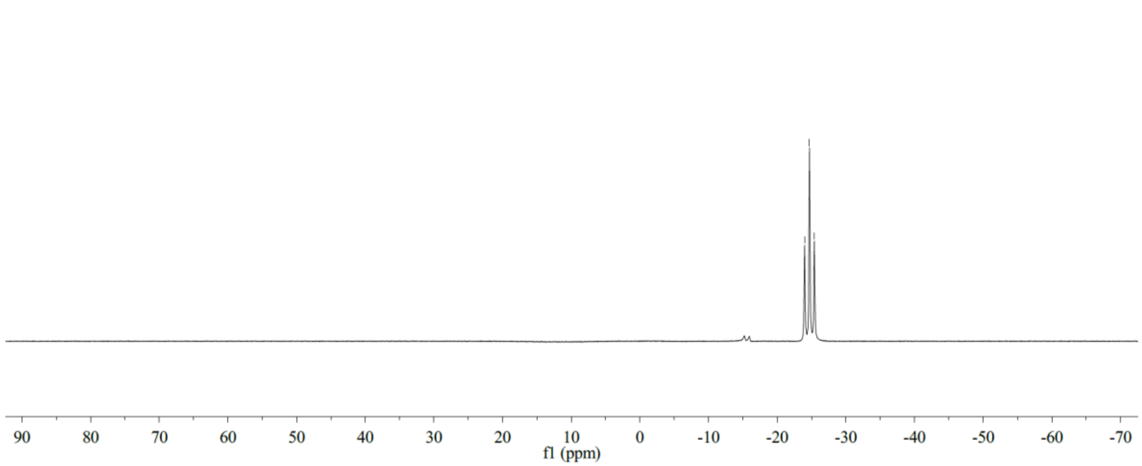
[1]H NMR (400 MHz, Chloroform-*d*) δ 6.80 (s, 2H), 4.46 (dddd, *J* = 11.0, 7.4, 3.7, 1.0 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.74 (s, 6H), 2.14 – 1.95 (m, 3H), 1.89 – 1.75 (m, 1H), 1.71 – 1.55 (m, 2H), 1.51 – 1.15 (m, 1H).
C (s) 6.80
A (dddd) 4.46
B (m) 4.23
D (s) 3.74
E (m) 2.07
H (m) 1.80
F (m) 1.65
G (m) 1.31
f1 (ppm)



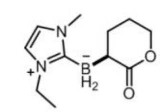
181.5841
120.4850
69.4387
36.1018
27.1702
22.3855
[13]C NMR (101 MHz, CDCl$_3$) δ 181.58, 120.48, 69.44, 36.10, 27.17, 22.39.
f1 (ppm)

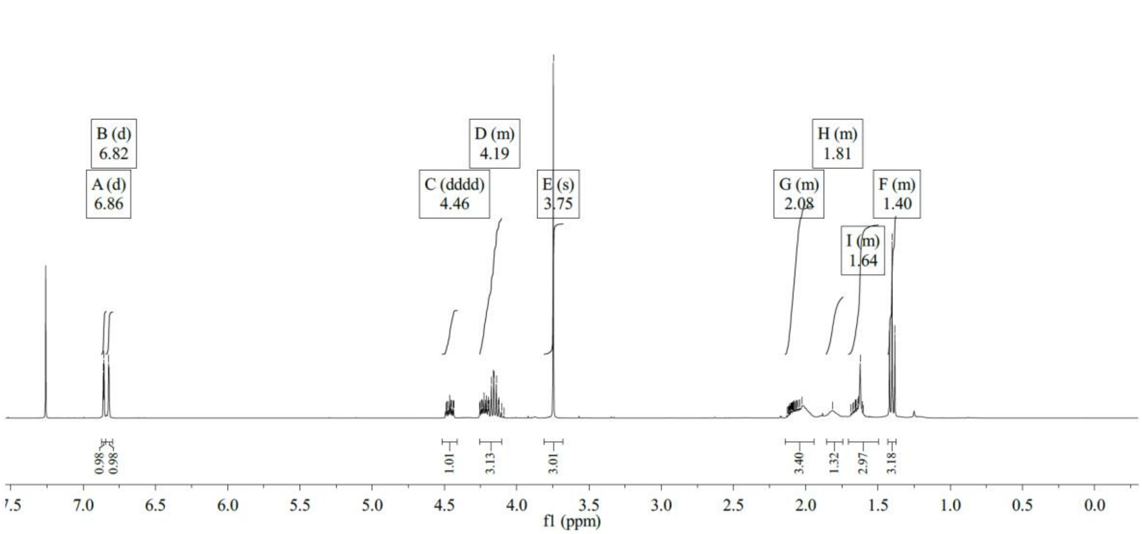
^{11}B NMR (128 MHz, $CDCl_3$) δ -24.71 (t, *J* = 90.4 Hz).

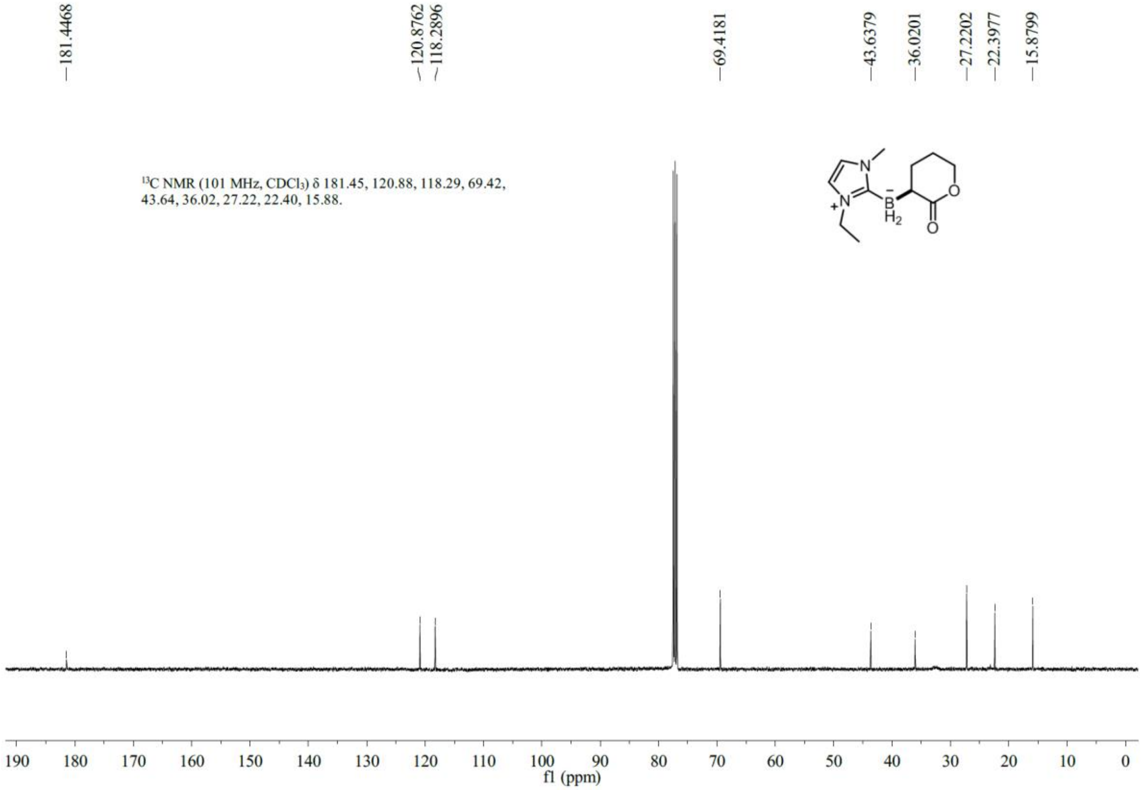


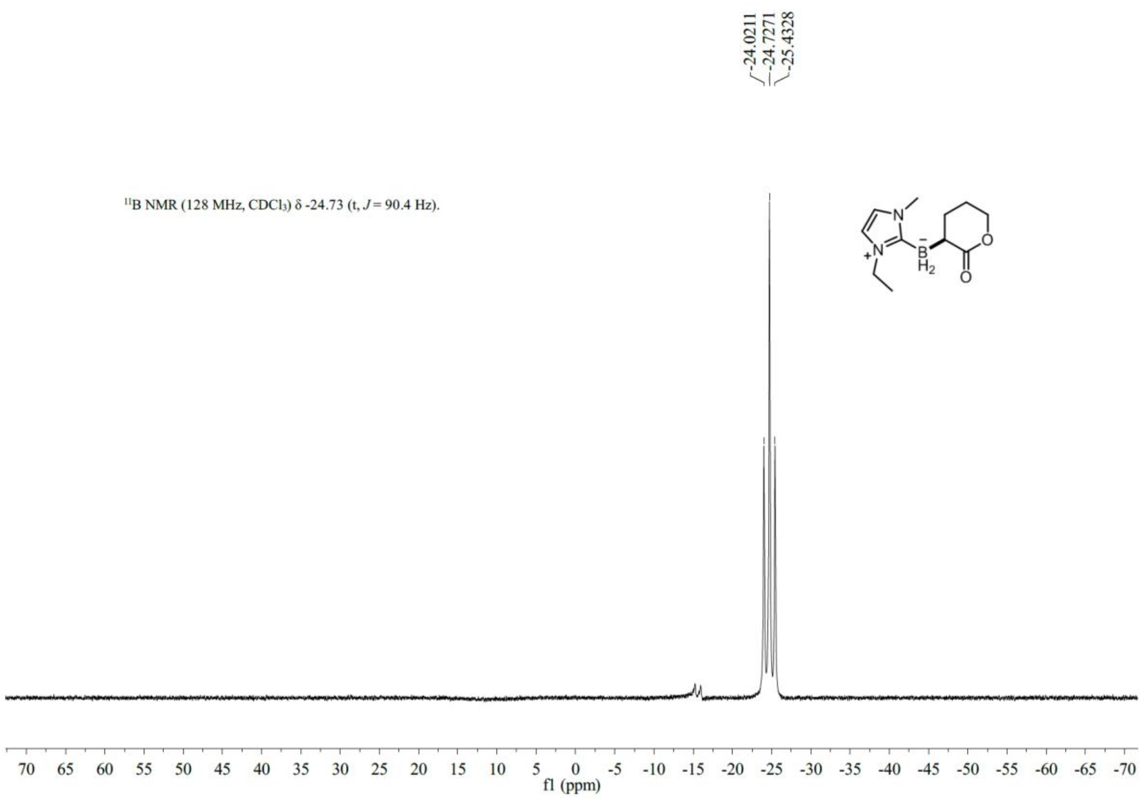


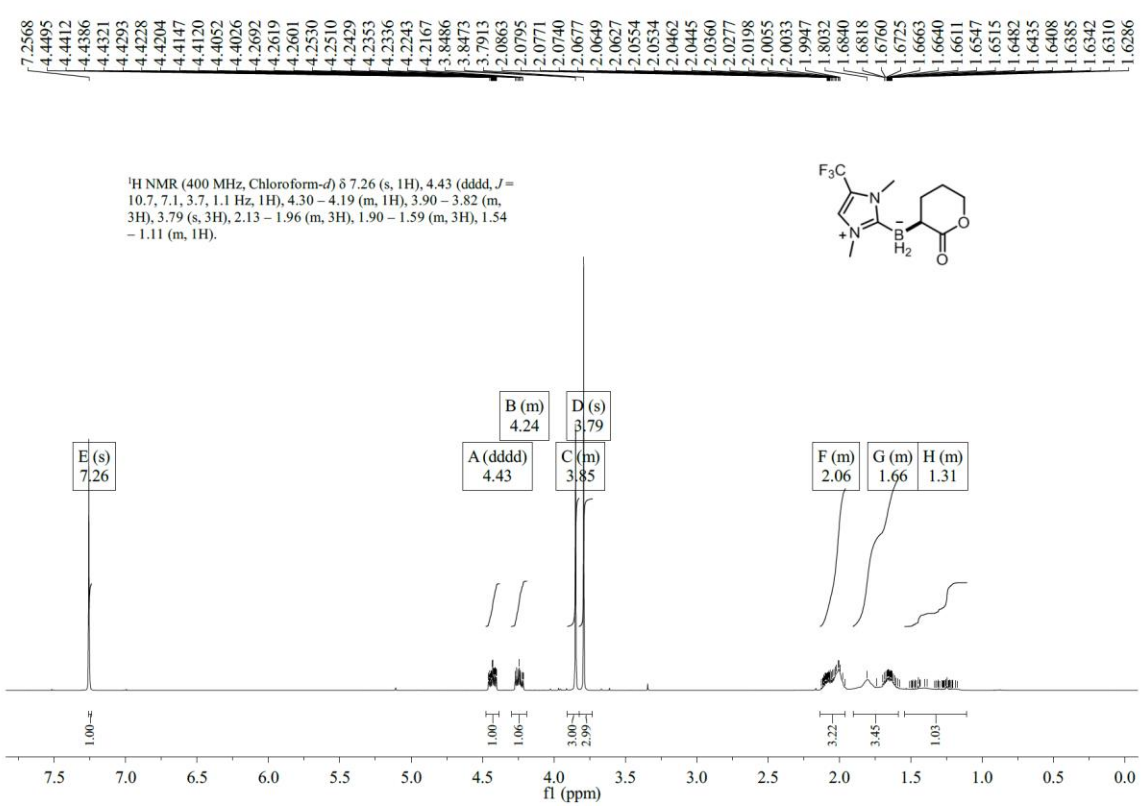
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.86 (d, *J* = 2.0 Hz, 1H), 6.82 (d, *J* = 1.9 Hz, 1H), 4.46 (dddd, *J* = 10.8, 7.4, 3.7, 1.0 Hz, 1H), 4.26 – 4.10 (m, 3H), 3.75 (s, 3H), 2.14 – 1.94 (m, 3H), 1.86 – 1.74 (m, 1H), 1.70 – 1.10 (m, 3H), 1.43 – 1.38 (m, 3H).

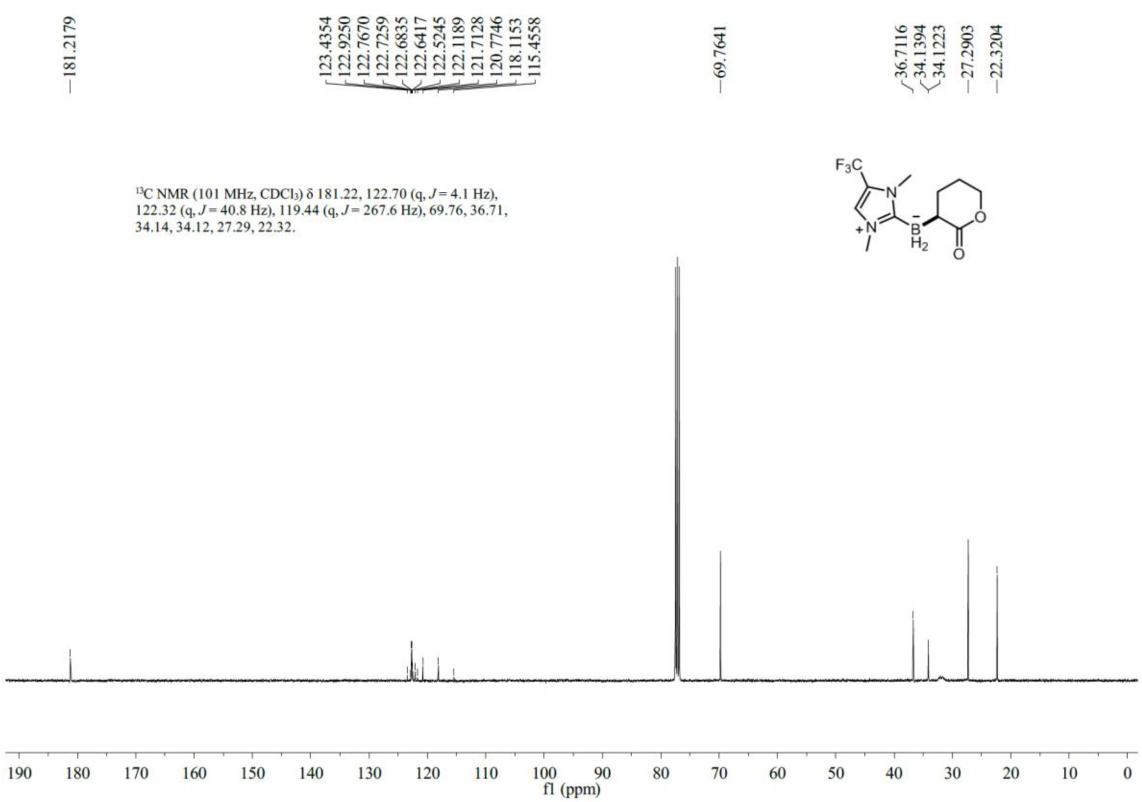


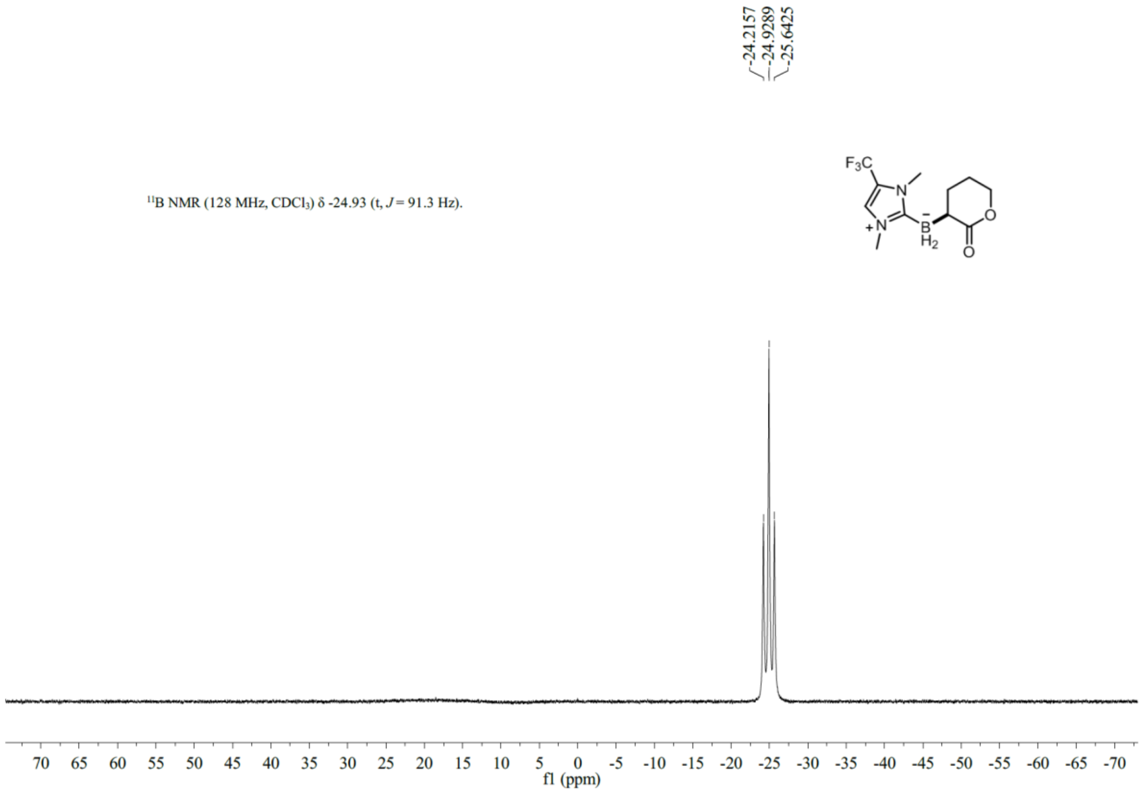



181.4468
120.8762
118.2896
69.4181
43.6379
36.0201
27.2202
22.3977
15.8799
13C NMR (101 MHz, CDCl3) δ 181.45, 120.88, 118.29, 69.42, 43.64, 36.02, 27.22, 22.40, 15.88.
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-24.0211
-24.7271
-25.4328
11B NMR (128 MHz, CDCl3) δ -24.73 (t, J = 90.4 Hz).
70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70
f1 (ppm)


1H NMR (400 MHz, Chloroform-d) δ 7.26 (s, 1H), 4.43 (dddd, J = 10.7, 7.1, 3.7, 1.1 Hz, 1H), 4.30 – 4.19 (m, 1H), 3.90 – 3.82 (m, 3H), 3.79 (s, 3H), 2.13 – 1.96 (m, 3H), 1.90 – 1.59 (m, 3H), 1.54 – 1.11 (m, 1H).
E (s) 7.26
A (dddd) 4.43
B (m) 4.24
C (m) 3.85
D (s) 3.79
F (m) 2.06
G (m) 1.66
H (m) 1.31
f1 (ppm)


13C NMR (101 MHz, CDCl3) δ 181.22, 122.70 (q, J = 4.1 Hz), 122.32 (q, J = 40.8 Hz), 119.44 (q, J = 267.6 Hz), 69.76, 36.71, 34.14, 34.12, 27.29, 22.32.
f1 (ppm)



^{11}B NMR (128 MHz, $CDCl_3$) δ -24.93 (t, J = 91.3 Hz).

VIII. Reference

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