Electronic Supplementary Information (ESI)

Pd-Catalyzed Coupling of Benzyl Bromides with BMIDA-substituted *N*-Tosylhydrazones: Synthesis of *trans*-Alkenyl MIDA Boronates

Shichao Li,[a] Muyao Li[a], Shu-Sen Li[a] and Jianbo Wang[ab]*

[a]*Beijing National Laboratory of Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China.*

[b]*The State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China*

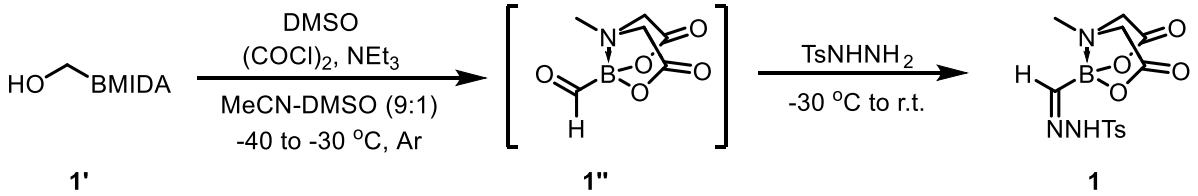
Email: wangjb@pku.edu.cn

CONTENTS

1. General

All the Pd-catalyzed reactions were performed under nitrogen atmosphere in an oven-dried reaction tube. THF, toluene, dioxane was dried over Na with benzophenone-ketyl intermediate as indicator; MeCN was dried over CaH_2. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Bruker ARX 400 spectrometer. Chemical shifts are reported in ppm using tetramethylsilane as internal standard when using $CDCl_3$, CD_3CN, $(CD_3)_2CO$ as the solvent, and coupling constants (*J*) were in Hertz (Hz). IR spectra were recorded on Nicolet 5MX–S infrared spectrometer and were reported in terms of frequency of absorption (cm^{-1}). High-resolution mass spectra (HRMS) were obtained on a Bruker APEX IV FTMS instrument and a Bruker Solarix XR FTMS instrument by ESI. Benzyl bromides were bought and used directly without further purification. Pd_2dba_3 was purchased from Adamas, Inc. and Cs_2CO_3 and $P(2\text{-furyl})_3$ were purchased from Energy Chemicals. These commercial chemicals were used without further purification. PE: petroleum ether; EA: ethyl acetate. S-Phos: 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet.

BMIDA substituted *N*-tosylhydrozone **1** was synthesized according to literature[1]



1' **1"** **1**

DMSO (0.23 mL, 3.21 mmol) was dissolved in CH_3CN (20 mL) under Ar atmosphere and the solution was cooled to -40 °C. $(COCl)_2$ (0.26 mL, 3.08 mmol) was added and the mixture was stirred for 15 min at -40 °C to -30 °C interval. A solution of hydroxymethyl MIDA boronate **1'** (500 mg, 2.67 mmol) in 1:1 mixture of DMSO-CH_3CN (5 mL) was added dropwise. The mixture was stirred at the same temperature interval for 30 min (Note: It is important to control specified temperature. Below –40 °C, the mixture starts to freeze, and above -30 °C, the yield decreases dramatically). NEt_3 (0.86 mL, 6.15 mmol) was added and the mixture was allowed to reach 0 °C during 40 min. At this point $TsNHNH_2$ (570 mg, 3.06 mmol) was added. The reaction mixture was stirred overnight at ambient temperature and evaporated. The residue was quenched with half-saturated NaCl/H_2O (30 mL) and extracted with EtOAc (3×30 mL). The product crystallized directly from reaction mixture after quenching with H_2O/EtOAc, BMIDA substituted *N*-tosylhydrozone **1** was obtained by recrystallization from CH_3CN/EtOAc.

2. General procedure for Pd-catalyzed synthesis of vinylboronates

N-tosylhydrozone **1** (35.3 mg, 0.1 mmol), Pd_2dba_3 (2.3 mg, 0.0025 mmol), P(2-furyl)$_3$ (4.6 mg, 0.02 mmol), Cs_2CO_3 (65.2 mg, 0.2 mmol) were weighed in a 10 mL oven-dried reaction flask. The flask was degassed in a vacuum and backfilled with N_2 three times, followed by the addition of dry degassed dioxane (1.5 mL). Then, benzyl bromides **2** (0.25 mmol, 2.5 equiv) was added using a micro-syringe successively. The reaction mixture was stirred at 80 °C with an oil bath under N_2 for 6 h. After the reaction, the mixture was allowed to cool to room temperature and filtered through flash column chromatography on silica gel (EA). Then, the solvent was evaporated in *vacuo* and the crude product was purified by preparative thin layer chromatography on silica gel (300−400 mesh) using ethyl acetate, which afforded product alkenyl boronates **3**-**31**.

3. General procedure for Suzuki-Miyaura coupling of aryl bromides with alkenyl MIDA boronate 2

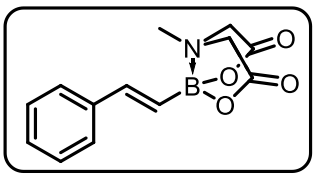
In a 10 mL oven-dried reaction flask equipped with a stirring bar were placed with alkenyl MIDA boronate **2** (31.1 mg, 0.12 mmol, 1.2 equiv), $Pd(OAc)_2$ (1.1 mg, 0.005 mmol, 5 mol%), S-Phos (4.1 mg, 0.01 mmol, 10 mol%). The flask was degassed in a vacuum and backfilled with N_2 three times, followed by the addition of dry degassed dioxane (1 mL) and aryl bromides (0.1 mmol, 1 equiv). The mixture was stirred at room temperature for 15 min. Then, aq. K_3PO_4 (3.0 M, 0.25 mL, 7.5 equiv) was added. The flask was placed in a 60 ^oC oil bath with stirring for 10 h. After cooling to room temperature the mixture was transferred to separatory funnel and was diluted with H_2O and ethyl acetate, the mixture was shaken and the phases were separated. The aqueous phase was extracted with ethyl acetate (3 × 5 mL). The combined organic fractions were dried over Na_2SO_4. The organic residue after filtration was concentrated and then purified by preparative thin layer chromatography on silica gel (300−400 mesh) using PE to give the corresponding product.

4. Other transformations of alkenyl MIDA boronate 3

The reaction of alkenyl MIDA boronate **3** with Olah's reagent,[2] *m*-CPBA,[3] KHF_2[4] was carried out according to the literature procedures.

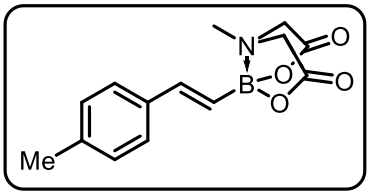
5. Characterization data of the products

(*E*)-4-methyl-8-styryldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**3**)[5]



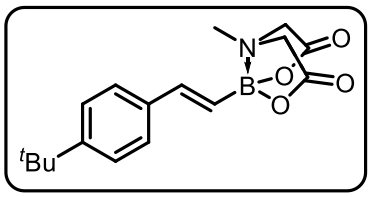
Yield: 19.7 mg (76%), white solid, R_f = 0.26 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.52 (d, J = 7.3 Hz, 2H), 7.35 (t, J = 7.3 Hz, 2H), 7.28 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 18.2 Hz, 1H), 6.28 (d, J = 18.2 Hz, 1H), 3.99 (d, J = 17.0 Hz, 2H), 3.84 (d, J = 17.0 Hz, 2H), 2.81 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 142.9, 138.7, 129.2, 128.6, 127.2, 62.0, 47.3.

(*E*)-4-methyl-8-(4-methylstyryl)dihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**4**)[5]



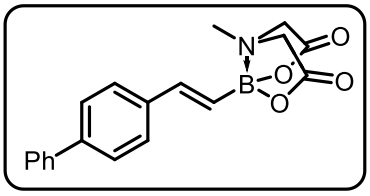
Yield: 12.1 mg (48%), white solid, R_f = 0.26 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.40 (d, J = 8.1 Hz, 2H), 7.17 (d, J = 8.0 Hz, 2H), 6.90 (d, J = 18.2 Hz, 1H), 6.20 (d, J = 18.2 Hz, 1H), 3.98 (d, J = 16.9 Hz, 2H), 3.83 (d, J = 16.9 Hz, 2H), 2.80 (s, 3H), 2.32 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.1, 142.8, 138.7, 136.0, 129.8, 127.2, 62.0, 47.3, 20.8.

(*E*)-8-(4-(*tert*-butyl)styryl)-4-methyldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**5**)[5]



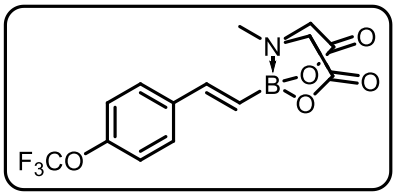
Yield: 18.4 mg (58%), white solid, R_f = 0.28 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.48-7.38 (m, 4H), 6.91 (d, J = 18.2 Hz, 1H), 6.23 (d, J = 18.2 Hz, 1H), 3.98 (d, J = 17.0 Hz, 2H), 3.83 (d, J = 17.0 Hz, 2H), 2.80 (s, 3H), 1.30 (s, 9H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.1, 151.8, 142.7, 136.0, 130.3, 127.0, 126.0, 61.9, 47.3, 34.8, 31.4.

(*E*)-8-(2-([1,1'-biphenyl]-4-yl)vinyl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**6**)[5]



Yield: 20.7 mg (62%), white solid, R_f = 0.23 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.67-7.59 (m, 6H), 7.46 (t, J = 7.5 Hz, 2H), 7.36 (t, J = 7.5 Hz, 1H), 7.00 (d, J = 18.3 Hz, 1H), 6.34 (d, J = 18.3 Hz, 1H), 4.01 (d, J = 17.0 Hz, 2H), 3.86 (d, J = 17.0 Hz, 2H), 2.83 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.1, 142.4, 141.0, 140.9, 137.9, 129.5, 128.1, 127.8, 127.6, 127.3, 62.0, 47.3.

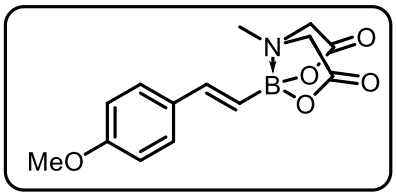
(*E*)-4-methyl-8-(4-(trifluoromethoxy)styryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (7)



Yield: 22.1 mg (64%), colorless oil, R_f = 0.29 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.60 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 18.2 Hz, 1H), 6.30 (d, J = 18.3 Hz, 1H), 4.00 (d, J = 17.0 Hz, 2H), 3.85 (d, J = 17.1 Hz, 2H), 2.82 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 149.1, 141.3, 137.9,

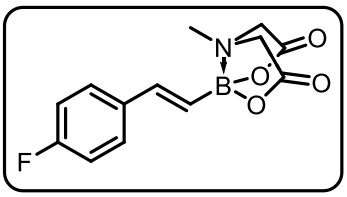
128.8, 121.7, 121.1(q, $^{1}J_{CF}$ = 255.6 Hz), 62.1, 47.3; ^{19}F NMR (471 MHz, CD_3CN) δ -58.6 (s, 3F); HRMS (ESI, *m/z*): calcd for $C_{14}H_{17}BF_3N_2O_5$ $[M+NH_4]^+$ 361.1183, found 361.1177; IR (film): 1260, 1288, 1292, 1735, 1744, 1765, 1778 cm^{-1}.

(*E*)-8-(4-methoxystyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**8**)[5]



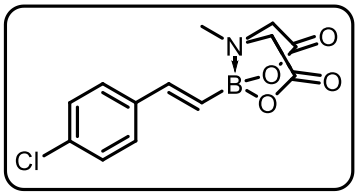
Yield: 11.0 mg (38%), white solid, R_f = 0.27 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.45 (d, *J* = 8.3 Hz, 2H), 7.13-6.80 (m, 3H), 6.10 (d, *J* = 18.2 Hz, 1H), 3.98 (d, *J* = 17.0 Hz, 2H), 3.83 (d, *J* = 17.2 Hz, 2H), 3.78 (s, 3H), 2.80 (s, 3H) ; ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.1, 160.3, 142.4, 131.5, 128.5, 114.5, 61.9, 55.5, 47.2.

(*E*)-8-(4-fluorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**9**)[6]



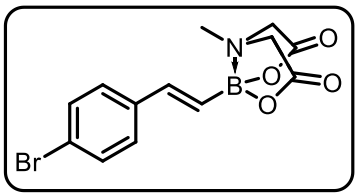
Yield: 16.7 mg (74%), colorless oil, R_f = 0.25 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.55-7.52 (m, 2H), 7.09 (t, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 18.3 Hz, 1H), 6.21 (d, *J* = 18.3 Hz, 1H), 3.99 (d, *J* = 17.0 Hz, 2H), 3.84 (d, *J* = 17.0 Hz, 2H), 2.81 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 163.1 (d, *J* = 244.8 Hz), 141.6, 129.0 (d, *J* = 8.0 Hz), 115.8 (d, *J* = 22.0 Hz), 62.0, 47.3; ^{19}F NMR (471 MHz, CD_3CN) δ -115.8 (m, 1F).

(*E*)-8-(4-chlorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**10**)[5]



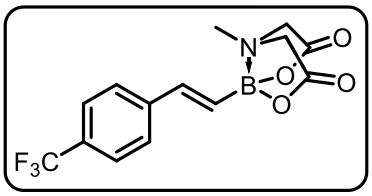
Yield: 20.9 mg (71%), colorless oil, R_f = 0.25 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 6.92 (d, *J* = 18.2 Hz, 1H), 6.29 (d, *J* = 18.2 Hz, 1H), 4.00 (d, *J* = 17.0 Hz, 2H), 3.85 (d, *J* = 17.0 Hz, 2H), 2.81 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 141.5, 137.5, 133.6, 129.1, 128.7, 62.0, 47.3.

(*E*)-8-(4-bromostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**11**)[5]



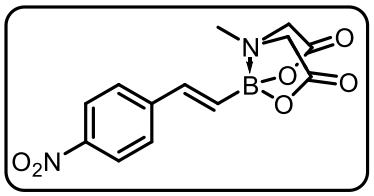
Yield: 23.0 mg (73%), white solid, R_f = 0.26 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.51 (d, J = 8.2 Hz, 2H), 7.43 (d, J = 8.2 Hz, 2H), 6.91 (d, J = 18.2 Hz, 1H), 6.30 (d, J = 18.2 Hz, 1H), 4.00 (d, J = 17.0 Hz, 2H), 3.84 (d, J = 17.0 Hz, 2H), 2.81 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 141.6, 137.9, 132.1, 129.0, 121.8, 62.0, 47.3.

(*E*)-4-methyl-8-(4-(trifluoromethyl)styryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**12**)[7]



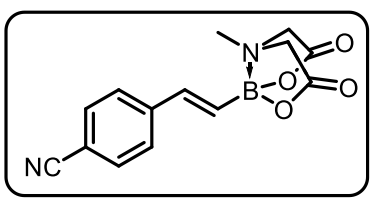
Yield: 20.6 mg (63%), white solid, R_f = 0.27 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.70-7.65 (m, 4H), 7.02 (d, J = 18.3 Hz, 1H), 6.45 (d, J = 18.3 Hz, 1H), 4.02 (d, J = 16.9 Hz, 2H), 3.86 (d, J = 17.0 Hz, 2H), 2.83 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 142.5, 141.4, 130.3, 129.5 (q, J = 32.0 Hz), 126.0 (q, J = 4.0 Hz), 125.1 (q, J = 271.7 Hz), 62.1, 47.4; ^{19}F NMR (471 MHz, CD_3CN) δ -63.0 (s, 3F).

(*E*)-4-methyl-8-(4-nitrostyryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**13**)



Yield: 20.3 mg (67%), white solid, m.p.= 142-145 ^{o}C, R_f = 0.22 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 8.19 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.5 Hz, 2H), 7.06 (d, J = 18.3 Hz, 1H), 6.54 (d, J = 18.3 Hz, 1H), 4.03 (d, J = 17.1 Hz, 2H), 3.87 (d, J = 17.1 Hz, 2H), 2.84 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.2, 148.1, 145.2, 141.0, 128.2, 124.6, 62.4, 47.6; HRMS (ESI, *m/z*): calcd for $C_{13}H_{14}BN_2O_6$ $[M+H]^+$ 305.0945, found 305.0939; IR (film): 1309, 1345, 1516, 1752, 1765, 1778 cm^{-1}.

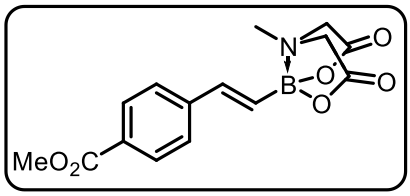
(*E*)-4-(2-(4-methyl-2,6-dioxotetrahydro-2*H*-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazabor ol-8-yl)vinyl)benzonitrile (**14**)[8]



Yield: 20.1 mg (71%), colorless oil, R_f = 0.21 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.71-7.64 (m, 4H), 7.00 (d, J = 18.2 Hz, 1H), 6.47 (d, J = 18.2 Hz, 1H), 4.02 (d, J = 17.0 Hz, 2H), 3.86 (d, J = 17.0 Hz, 2H), 2.82 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 143.0, 141.2, 133.1, 127.8, 119.4, 111.4, 62.1, 47.4.

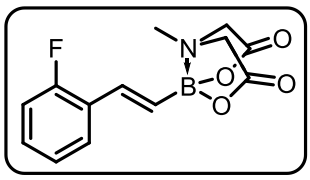
methyl (*E*)-4-(2-(4-methyl-2,6-dioxotetrahydro-2*H*-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]

oxazaborol-8-yl)vinyl)benzoate (**15**)[8]



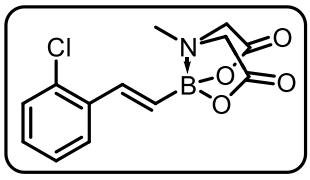
Yield: 20.2 mg (64%), white solid, R_f = 0.27 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.97 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H), 7.01 (d, J = 18.3 Hz, 1H), 6.44 (d, J = 18.2 Hz, 1H), 4.01 (d, J = 17.0 Hz, 2H), 3.87 (d, J =17.0 Hz, 2H), 3.86 (s, 3H), 2.83 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 167.0, 143.1, 141.80, 130.2, 130.1, 127.3, 62.1, 52.2, 47.3.

(*E*)-8-(2-fluorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**16**)



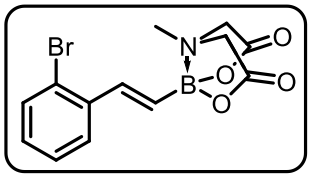
Yield: 18.1 mg (65%), white solid, m.p. = 139-142 ^{o}C, R_f = 0.29 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.66 (td, J = 7.8, 1.7 Hz, 1H), 7.34-7.26 (m, 1H), 7.21-7.15 (m, 1H), 7.14-7.06 (m, 2H), 6.37 (d, J = 18.4 Hz, 1H), 4.01 (d, J = 17.0 Hz, 2H), 3.85 (d, J = 17.0 Hz, 2H), 2.83 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 160.8 (d, J = 247.7 Hz), 134.4 (d, J = 4.4 Hz), 130.2 (d, J = 8.6 Hz), 128.0 (d, J = 3.5 Hz), 125.0 (d, J = 3.3 Hz), 116.2 (d, J = 22.3 Hz), 62.1, 47.4; ^{19}F NMR (471 MHz, CD_3CN) δ -120.8 (m, 1F); HRMS (ESI, *m/z*): calcd for $C_{13}H_{17}BFN_2O_4$ $[M+NH_4]^+$ 295.1265, found 295.1260; IR (film): 1032, 1763, 1779, 2035 cm^{-1}.

(*E*)-8-(2-chlorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**17**)[8]



Yield: 17.2 mg (59%), white solid, R_f = 0.27 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.73 (dd, J = 7.7, 1.7 Hz, 1H), 7.40 (dd, J = 7.8, 1.4 Hz, 1H), 7.35-7.23 (m, 3H), 6.32 (d, J = 18.1 Hz, 1H), 4.02 (d, J = 17.0 Hz, 2H), 3.86 (d, J = 17.0 Hz, 2H), 2.84 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 138.4, 136.5, 133.3, 130.1, 129.9, 127.8, 127.8, 62.1, 47.4.

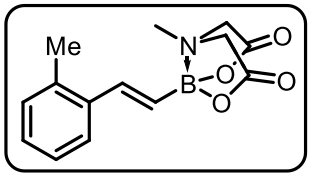
(*E*)-8-(2-bromostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**18**)[9]



Yield: 22.4 mg (66%), colorless oil, R_f = 0.28 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.71 (dd, J = 7.8, 1.7 Hz, 1H), 7.59 (dd, J = 8.0, 1.3 Hz, 1H), 7.41-7.33 (m, 1H), 7.28-7.15 (m, 2H), 6.27 (d, J =

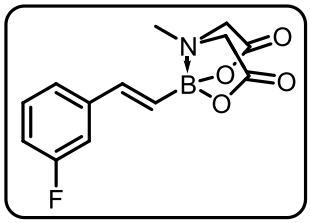
18.0 Hz, 1H), 4.02 (d, *J* = 17.0 Hz, 2H), 3.86 (d, *J* = 17.0 Hz, 2H), 2.84 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 141.1, 138.3, 133.4, 130.2, 128.4, 128.0, 123.8, 62.1, 47.4.

(*E*)-4-methyl-8-(2-methylstyryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**19**)[5]



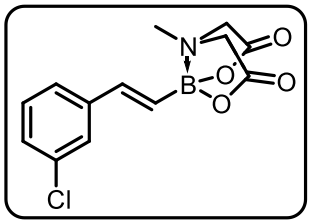
Yield: 8.4 mg (31%), white solid, R_f = 0.26 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.56 (d, *J* = 4.6 Hz, 1H), 7.21-7.17 (m, 4H), 6.15 (d, *J* = 18.1 Hz, 1H), 4.00 (d, *J* = 17.0 Hz, 2H), 3.85 (d, *J* = 17.0 Hz, 2H), 2.83 (s, 3H), 2.36 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 140.6, 137.9, 136.2, 130.8, 128.4, 126.7, 126.1, 62.0, 47.3, 19.4.

(*E*)-8-(3-fluorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**20**)[10]



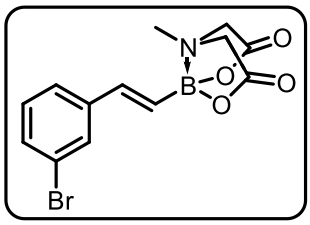
Yield: 14.8 mg (53%), white solid, R_f = 0.28 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.43-7.22 (m, 3H), 7.02 (td, *J* = 8.2, 7.8, 2.4 Hz, 1H), 6.94 (d, *J* = 18.2 Hz, 1H), 6.33 (d, *J* = 18.2 Hz, 1H), 4.01 (d, *J* = 17.0 Hz, 2H), 3.85 (d, *J* = 17.0 Hz, 2H), 2.82 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 163.7 (d, *J* = 243.1 Hz), 141. 6 (d, *J* = 2.2 Hz), 130.9 (d, *J* = 8.7 Hz), 123.4 (d, *J* = 2.9 Hz), 115.1 (d, *J* = 21.6 Hz), 113.3 (d, *J* = 22.1 Hz), 62.0, 47.3; ^{19}F NMR (471 MHz, CD_3CN) δ -115.4 (m, 1F).

(*E*)-8-(3-chlorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**21**)[5]



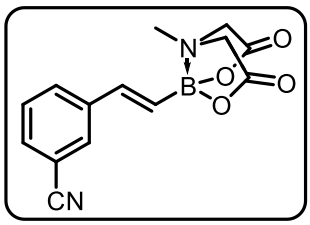
Yield: 19.6 mg (67%), white solid, R_f = 0.30 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.55 (t, *J* = 1.9 Hz, 1H), 7.49-7.41 (m, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.28 (ddd, *J* = 7.9, 2.1, 1.3 Hz, 1H), 6.92 (d, *J* = 18.2 Hz, 1H), 6.34 (d, *J* = 18.2 Hz, 1H), 4.00 (d, *J* = 17.0 Hz, 2H), 3.84 (d, *J* = 16.9 Hz, 2H), 2.81 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 141.3, 140.9, 134.6, 130.7, 128.3, 126.9, 125.8, 62.0, 47.3.

(*E*)-8-(3-bromostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**22**)[5]



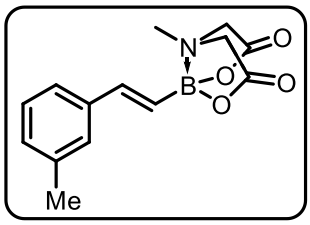
Yield: 25.1 mg (74%), white solid, R_f = 0.25 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.71 (t, J = 1.9 Hz, 1H), 7.48 (dt, J = 7.7, 1.4 Hz, 1H), 7.43 (ddd, J = 7.9, 2.0, 1.0 Hz, 1H), 7.27 (t, J = 7.8 Hz, 1H), 6.90 (d, J = 18.2 Hz, 1H), 6.33 (d, J = 18.2 Hz, 1H), 4.00 (d, J = 17.0 Hz, 2H), 3.84 (d, J = 17.0 Hz, 2H), 2.81 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 141.2, 141.1, 131.2, 131.0, 129.8, 126.2, 122.8, 62.0, 47.3.

(*E*)-3-(2-(4-methyl-2,6-dioxotetrahydro-2*H*-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)vinyl)benzonitrile (**23**)



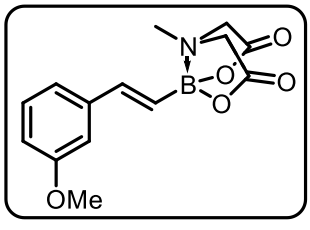
Yield: 17.9 mg (63%), colorless oil, R_f = 0.23 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.88 (s, 1H), 7.79 (d, J = 7.9 Hz, 1H), 7.62 (d, J = 7.6 Hz, 1H), 7.51 (t, J = 7.7 Hz, 1H), 6.96 (d, J = 18.2 Hz, 1H), 6.41 (d, J = 18.3 Hz, 1H), 4.02 (d, J = 17.0 Hz, 2H), 3.85 (d, J = 17.1 Hz, 2H), 2.82 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 140.6, 131.9, 131.6, 130.8, 130.2, 125.7, 119.3, 113.0, 62.1, 47.3; HRMS (ESI, *m/z*): calcd for $C_{14}H_{14}BN_2O_4$ $[M+H]^+$ 285.1047, found 285.1041; IR (film): 1121, 1292, 1459, 1754, 1765, 2232 cm^{-1}.

(*E*)-4-methyl-8-(3-methylstyryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**24**)[5]



Yield: 17.0 mg (62%), white solid, R_f = 0.30 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.37-7.28 (m, 2H), 7.23 (t, J = 7.5 Hz, 1H), 7.10 (d, J = 7.2 Hz, 1H), 6.91 (d, J = 18.2 Hz, 1H), 6.26 (d, J = 18.2 Hz, 1H), 3.99 (d, J = 17.0 Hz, 2H), 3.84 (d, J = 17.0 Hz, 2H), 2.81 (s, 3H), 2.33 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 143.0, 138.8, 138.7, 129.3, 129.0, 127.9, 124.3, 62.0, 47.3, 21.0.

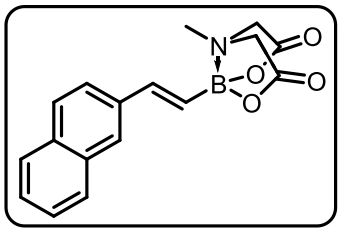
(*E*)-8-(3-methoxystyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**25**)[10]



Yield: 19.9 mg (69%), white solid, R_f = 0.26 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.26 (t, J = 7.9 Hz, 1H), 7.16-7.05 (m, 2H), 6.92 (d, J = 18.2 Hz, 1H), 6.85 (dd, J = 8.0, 2.5 Hz, 1H), 6.29 (d, J = 18.2 Hz, 1H), 4.00 (d, J = 17.0 Hz, 2H), 3.84 (d, J = 17.1 Hz, 2H),

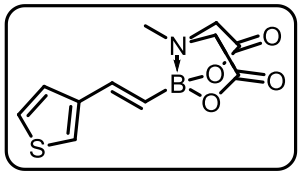
3.79 (s, 3H), 2.81 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 160.6, 142.8, 140.2, 130.2, 119.7, 114.2, 112.4, 62.0, 55.4, 47.3.

(*E*)-4-methyl-8-(2-(naphthalen-2-yl)vinyl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**26**)[10]



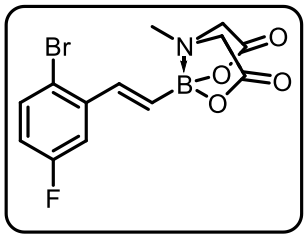
Yield: 19.2 mg (62%), white solid, R_f = 0.30 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.96-7.82 (m, 4H), 7.77 (d, J = 8.6 Hz, 1H), 7.49 (dq, J = 6.3, 4.2, 2.4 Hz, 2H), 7.12 (d, J = 18.2 Hz, 1H), 6.42 (d, J = 18.2 Hz, 1H), 4.02 (d, J = 17.0 Hz, 2H), 3.87 (d, J = 17.1 Hz, 2H), 2.85 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.1, 142.9, 136.2, 134.1, 133.8, 130.3, 128.7, 128.6, 128.2, 127.4, 127.0, 126.7, 124.2, 62.1, 47.3.

(*E*)-4-methyl-8-(2-(thiophen-3-yl)vinyl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**27**)



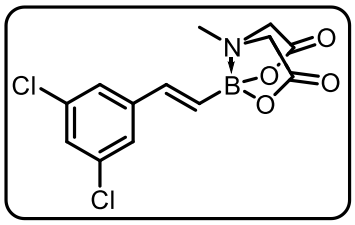
Yield: 13.1 mg (49%), colorless oil, R_f = 0.27 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.36-7.35 (m, 3H), 6.95 (d, J = 18.2 Hz, 1H), 6.07 (d, J = 18.2 Hz, 1H), 3.98 (d, J = 17.0 Hz, 2H), 3.83 (d, J = 16.9 Hz, 2H), 2.81 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.0, 142.33, 136.9, 130.3, 126.9, 125.8, 123.9, 61.9, 47.3; HRMS (ESI, *m/z*): calcd for $C_{11}H_{13}BNO_4S$ $[M+H]^+$ 266.0658, found 266.0653; IR (film): 1028, 1295, 1343, 1769 cm^{-1}.

(*E*)-8-(2-bromo-5-fluorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**28**)



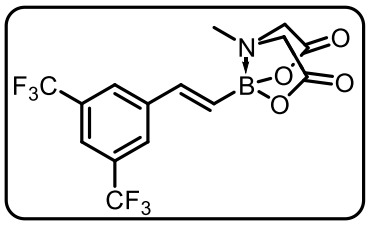
Yield: 22.1 mg (62%), colorless oil, R_f = 0.29 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.59 (dd, J = 8.8, 5.4 Hz, 1H), 7.47 (dd, J = 10.2, 3.1 Hz, 1H), 7.25-7.10 (m, 1H), 6.99 (td, J = 8.4, 3.0 Hz, 1H), 6.32 (d, J = 18.1 Hz, 1H), 4.03 (d, J = 17.0 Hz, 2H), 3.87 (d, J = 17.1 Hz, 2H), 2.84 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 168.9, 162.8 (d, J = 244.7 Hz), 150.2 (d, J = 8.3 Hz), 140.1, 134.9 (d, J = 8.3 Hz), 124.0 (d, J = 22.1 Hz), 117.1 (d, J = 23.1 Hz), 114.5 (d, J = 23.8 Hz), 62.1, 47.4; ^{19}F NMR (471 MHz, CD_3CN) δ -116.3 (m, 1F); HRMS (ESI, *m/z*): calcd for $C_{13}H_{13}BBrFNO_4$ $[M+H]^+$ 356.0105, found 356.0100; IR (film): 1298, 1460, 1338, 1467, 1754, 1765, 1777 cm^{-1}.

(*E*)-8-(3,5-dichlorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**29**)



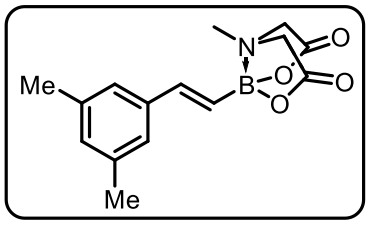
Yield: 24.4 mg (75%), colorless oil, R_f = 0.29 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.48 (d, J = 1.8 Hz, 2H), 7.35 (t, J = 1.9 Hz, 1H), 6.87 (d, J = 18.2 Hz, 1H), 6.39 (d, J = 18.2 Hz, 1H), 4.01 (d, J = 17.0 Hz, 2H), 3.85 (d, J = 17.1 Hz, 2H), 2.82 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 168.9, 150.3, 142.2, 139.9, 135.4, 127.8, 125.7, 62.1, 47.4; HRMS (ESI, *m/z*): calcd for $C_{13}H_{13}BCl_2NO_4$ $[M+H]^+$ 328.0315, found 328.0309; IR (film): 1034, 1113, 1292, 1295, 1562, 1748, 1766 cm^{-1}.

(*E*)-8-(3,5-bis(trifluoromethyl)styryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**30**)



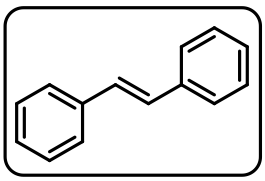
Yield: 27.7 mg (70%), colorless oil, R_f = 0.32 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 8.08 (s, 2H), 7.88 (s, 1H), 7.08 (d, J = 18.2 Hz, 1H), 6.56 (d, J = 18.2 Hz, 1H), 4.04 (d, J = 17.1 Hz, 2H), 3.87 (d, J = 17.0 Hz, 2H), 2.84 (s, 3H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 168.9, 150.3 (d, J = 8.1 Hz), 141.2, 139.7, 131.82 (q, J = 33.3 Hz), 127.51, 124.20 (q, J = 271.9 Hz), 121.74 (q, J = 3.8 Hz), 62.1, 47.4; ^{19}F NMR (471 MHz, CD_3CN) δ -63.4 (s, 6F); HRMS (ESI, *m/z*): calcd for $C_{15}H_{13}BF_6NO_4$ $[M+H]^+$ 396.0842, found 396.0836; IR (film): 1006, 1034, 1130, 1170, 1376, 1462, 1749, 1765 cm^{-1}.

(*E*)-8-(3,5-dimethylstyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**31**)



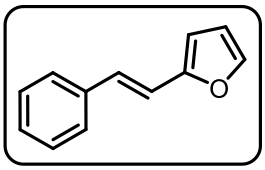
Yield: 12.1 mg (42%), colorless oil, R_f = 0.32 (EA); ^{1}H NMR (400 MHz, CD_3CN) δ 7.14-7.11 (m, 2H), 6.94 (s, 1H), 6.86 (d, J = 18.2 Hz, 1H), 6.23 (d, J = 18.3 Hz, 1H), 3.98 (d, J = 16.9 Hz, 2H), 3.83 (d, J = 16.9 Hz, 2H), 2.80 (s, 3H), 2.28 (s, 6H); ^{13}C{1H} NMR (100 MHz, CD_3CN) δ 169.1, 143.2, 138.6, 130.2, 125.1, 62.0, 47.3, 20.9; HRMS (ESI, *m/z*): calcd for $C_{15}H_{19}BNO_4$ $[M+H]^+$ 288.1407, found 288.1402; IR (film): 1044, 1400, 1510, 1624, 1772, 1777 cm^{-1}.

(*E*)-1,2-diphenylethene (**32**)[11]



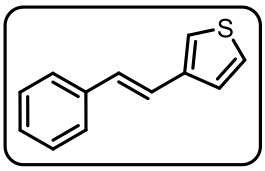
Yield: 18.0 mg (100%, 0.1 mmol scale), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 7.5 Hz, 4H), 7.35 (t, J = 7.5 Hz, 4H), 7.25 (t, J = 7.5 Hz, 2H), 7.11 (s, 2H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 137.4, 128.7, 127.7, 126.6.

(*E*)-2-styrylfuran (**33**)[12]



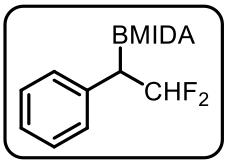
Yield: 9.5 mg (56%, 0.1 mmol scale), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 7.6 Hz, 2H), 7.40 (s, 1H), 7.34 (t, J = 7.5 Hz, 2H), 7.28-7.20 (m, 1H), 7.04 (d, J = 16.3 Hz, 1H), 6.90 (d, J = 16.3 Hz, 1H), 6.51-6.30 (m, 2H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 153.3, 142.2, 137.0, 128.7, 127.6, 127.2, 126.4, 116.6, 111.7, 108.6.

(*E*)-3-styrylthiophene (**34**)[13]



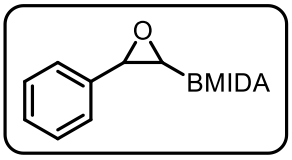
Yield: 15.7 mg (84%, 0.1 mmol scale), white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.7 Hz, 2H), 7.36-7.31 (m, 4H), 7.29-7.21 (m, 2H), 7.12 (d, J = 16.3 Hz, 1H), 6.95 (d, J = 16.2 Hz, 1H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 140.2, 137.4, 132.9, 128.7, 127.5, 126.3, 126.2, 125.0, 122.9, 122.4.

8-(2,2-difluoro-1-phenylethyl)-4-methyldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**35**)[14]



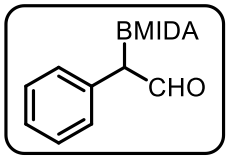
Yield: 18.5 mg (62%, 0.1 mmol scale), white solid; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.40 (d, J = 7.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 6.23 (td, J = 57.0, 4.7 Hz, 1H), 4.29 (d, J = 17.0 Hz, 1H), 4.22 (d, J = 17.0 Hz, 1H), 4.09 (d, J = 17.1 Hz, 1H), 3.57 (d, J = 17.0 Hz, 1H), 3.11 (s, 3H), 3.07-2.92 (m, 1H); ^{13}C{1H} NMR (100 MHz, Acetone-d_6) δ 168.2, 137.2 (d, J = 8.2 Hz), 131.2, 129.0, 127.1, 121.2 (d, J = 241.9, 239.9 Hz), 63.4, 63.0, 46.9 (d, J = 1.6 Hz).

4-methyl-8-(3-phenyloxiran-2-yl)dihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**36**)[3]



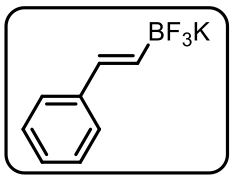
Yield: 64.4 mg (78%, 0.3 mmol scale), white solid; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.36-7.30 (m, 5H), 4.35 (d, J = 17.2 Hz, 1H), 4.28 (d, J = 16.8 Hz, 1H), 4.18 (d, J = 17.2 Hz, 1H), 4.04 (d, J = 16.7 Hz, 1H), 3.81 (s, 1H), 3.34 (s, 3H), 2.46 (s, 1H); ^{13}C{1H} NMR (100 MHz, acetone-d_6) δ 168.6, 167.5, 139.3, 128.4, 127.8, 125.6, 62.1, 62.0, 55.7, 46.2.

2-(4-methyl-2,6-dioxotetrahydro-2*H*-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)-2-phenylacetaldehyde (**37**)[3]



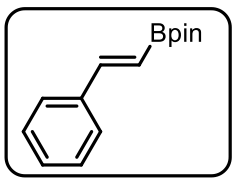
Yield: 27.0 mg (98%, 0.1 mmol scale), white solid; ^{1}H NMR (400 MHz, acetone-d_6) δ 9.82 (d, J = 2.3 Hz, 1H), 7.38-7.32 (m, 4H), 7.27-7.22 (m, 1H), 4.30 (d, J = 13.0 Hz, 1H), 4.26 (d, J = 13.1 Hz, 1H), 4.15 (d, J = 16.9 Hz, 1H), 3.75 (d, J = 5.6 Hz, 1H), 3.72 (s, 1H), 3.19 (s, 3H); ^{13}C{1H} NMR (100 MHz, acetone-d_6) δ 203.5, 167.5, 136.5, 129.8, 128.5, 126.2, 62.8, 62.5, 46.3.

(*E*)-trifluoro(styryl)-λ^4-borane, potassium salt (**38**)[4]



Yield: 60.4 mg (58%, 0.5 mmol scale), white solid; ^{1}H NMR (400 MHz, acetone-d_6) δ 7.36-7.07 (m, 5H), 6.67 (d, J = 18.2 Hz, 1H), 6.33 (d, J = 18.5 Hz, 1H); ^{13}C{1H} NMR (100 MHz, acetone-d_6) δ 141.0, 133.9, 128.1, 125.7, 125.6.

(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**39**)[4]



Yield: 9.1 mg (40%, 0.1 mmol scale), colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.46 (m, 2H), 7.40 (d, J = 18.4 Hz, 1H), 7.32 (dt, J = 12.3, 7.0 Hz, 3H), 6.17 (d, J = 18.4 Hz, 1H), 1.32 (s, 12H); ^{13}C{1H} NMR (100 MHz, $CDCl_3$) δ 149.5, 137.5, 128.9, 128.6, 127.1, 83.4, 24.8.

6. References

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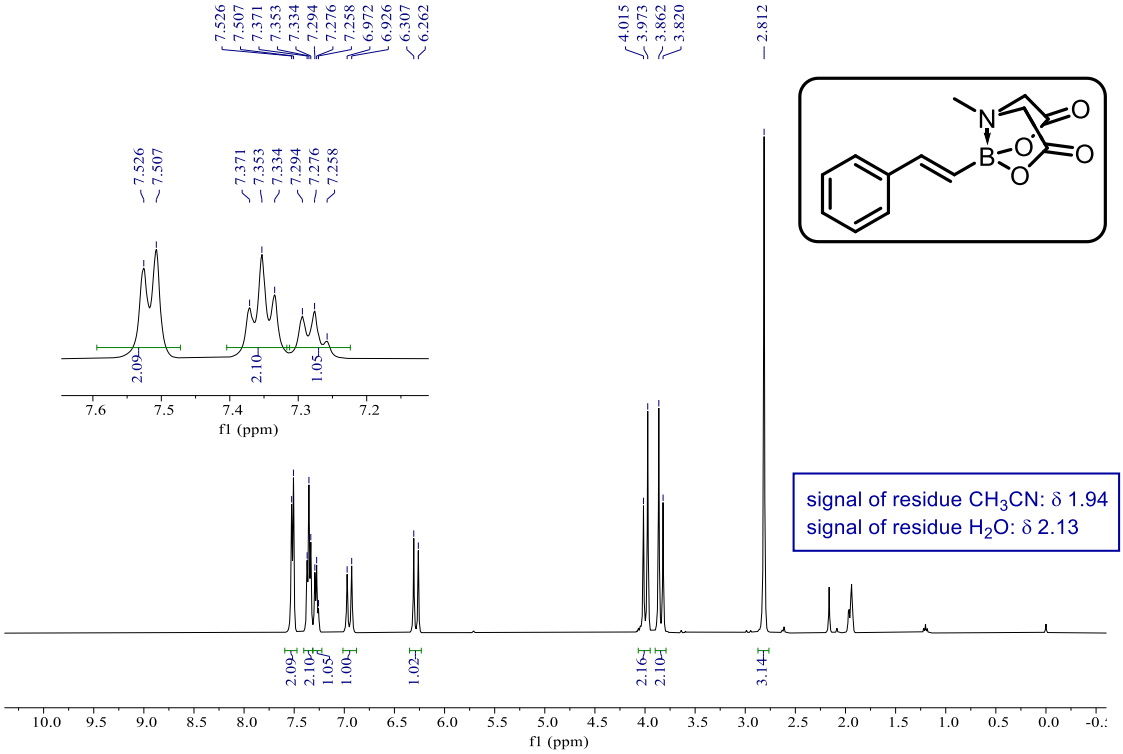
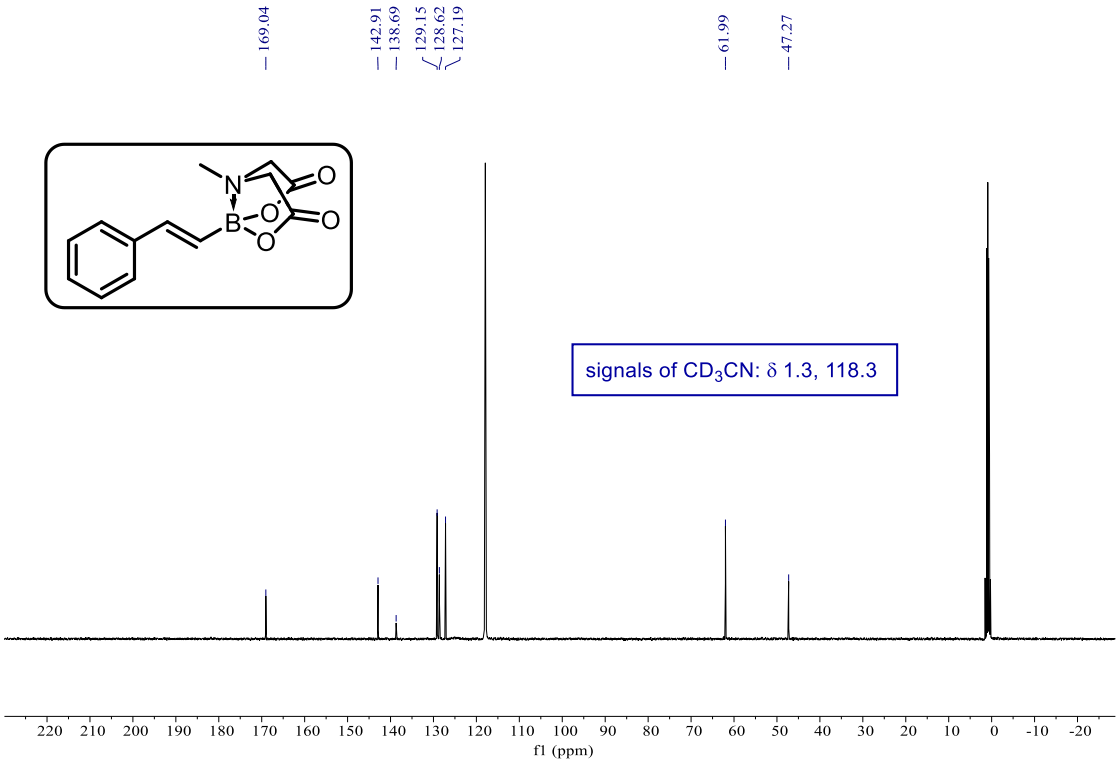
7. NMR spectra of the products

(*E*)-4-methyl-8-styryldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**3**)

^{1}H NMR (400 MHz, CD_3CN)

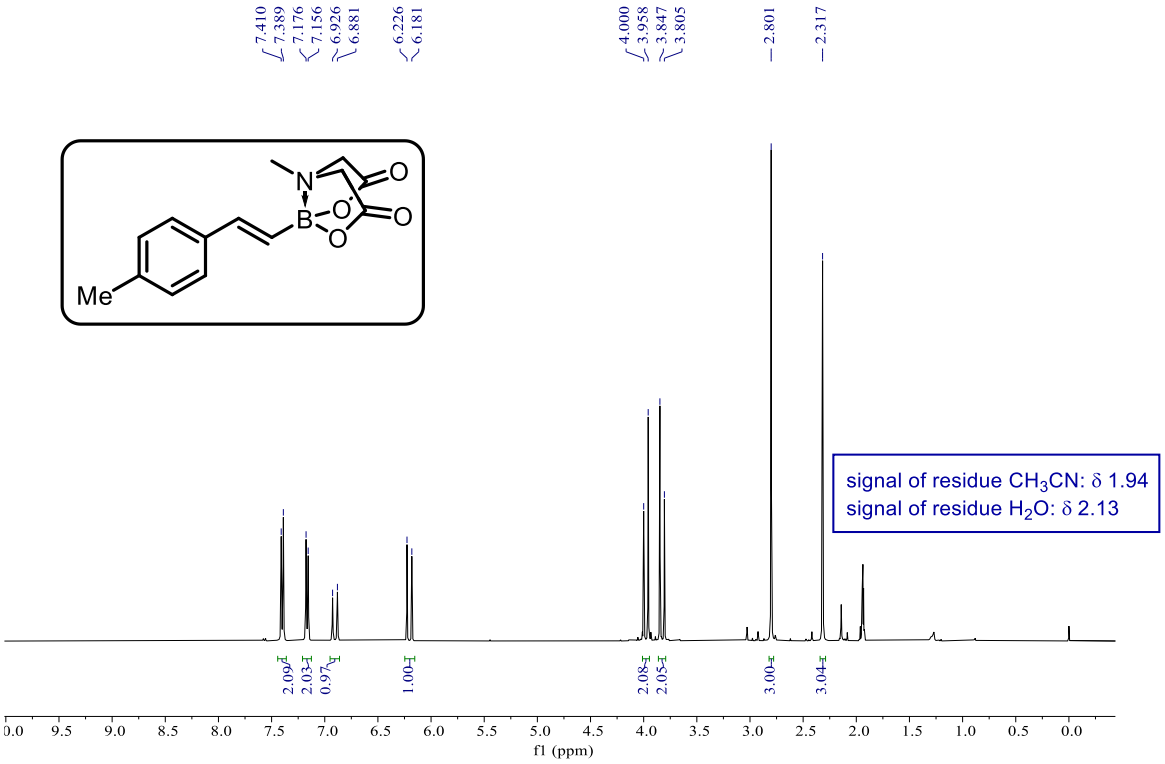


^{13}C{1H} NMR (100 MHz, CD_3CN)

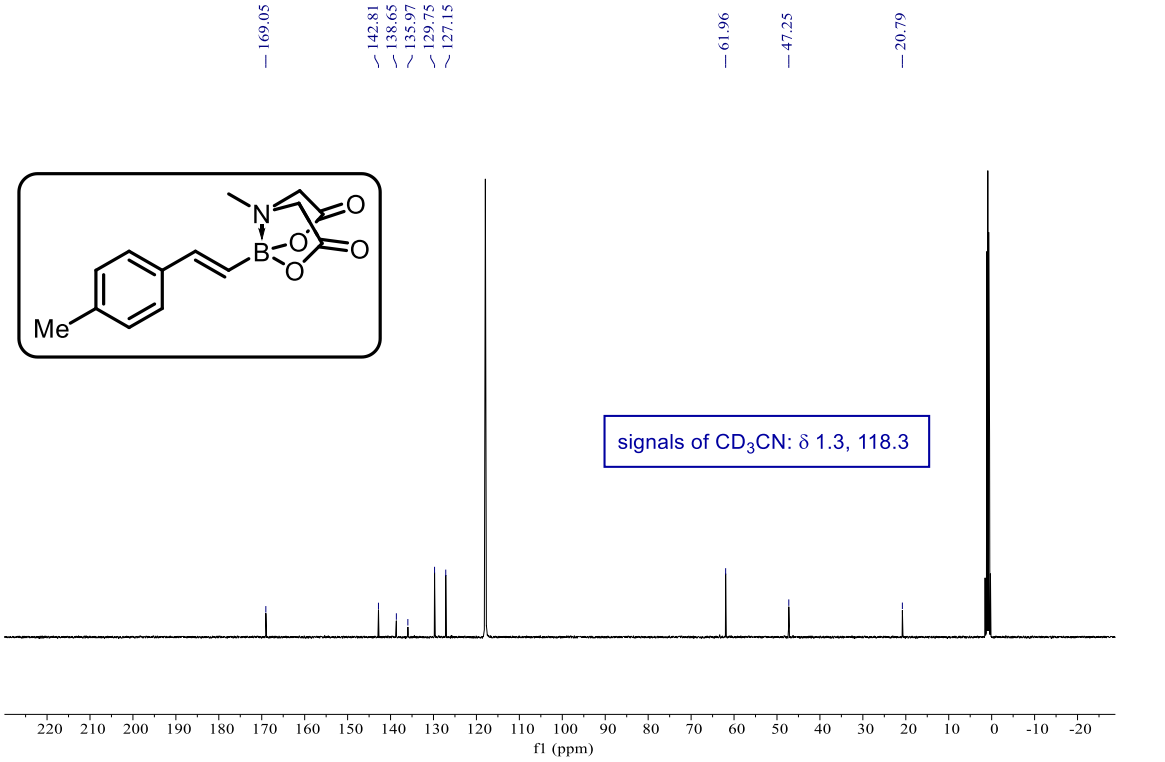


(*E*)-4-methyl-8-(4-methylstyryl)dihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**4**)

^{1}H NMR (400 MHz, CD_3CN)

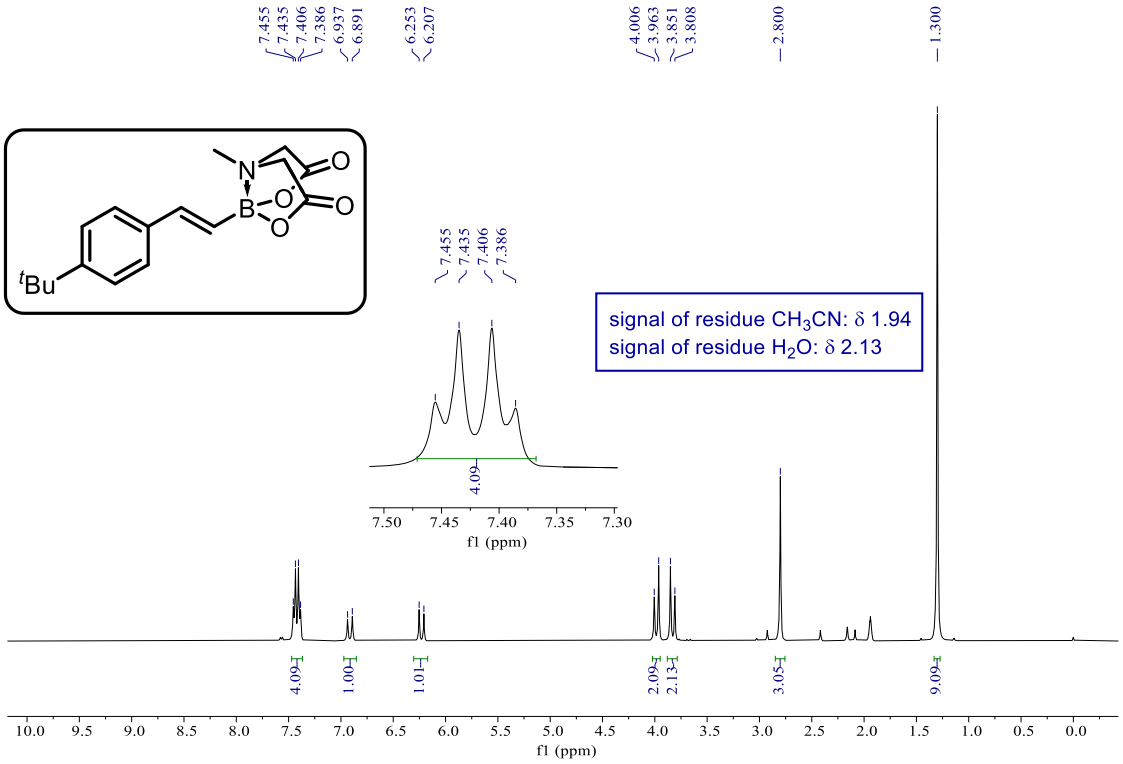


^{13}C{1H} NMR (100 MHz, CD_3CN)

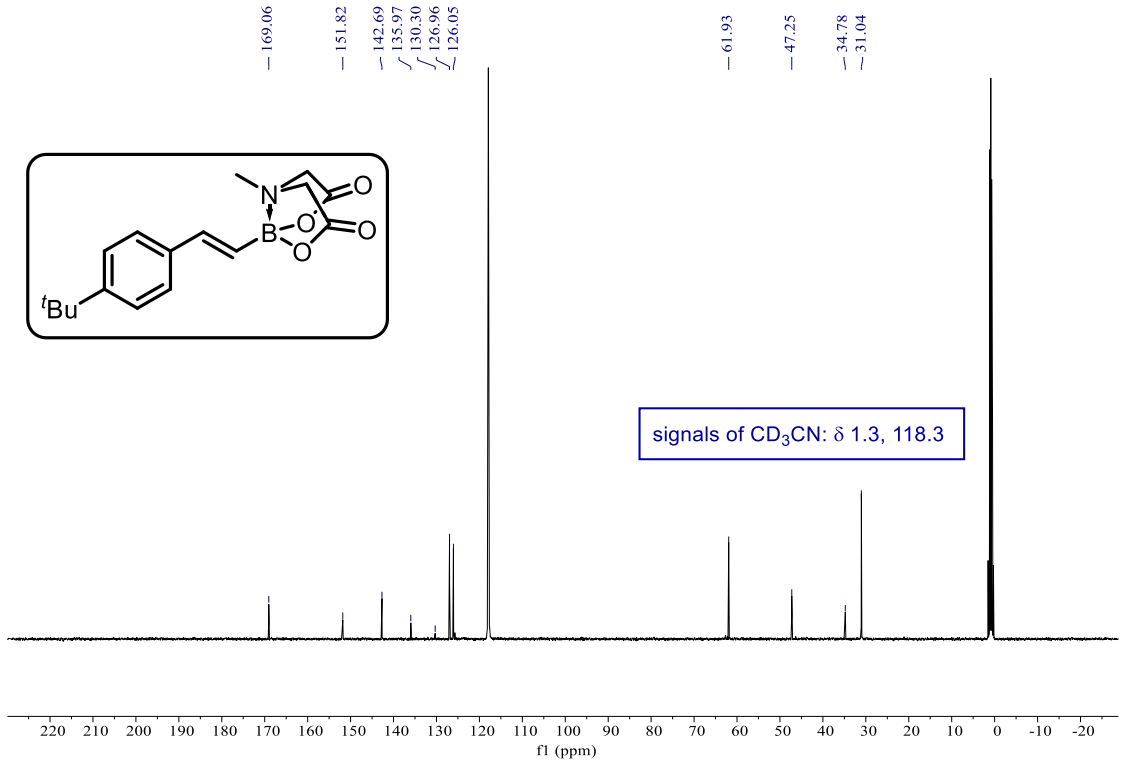


(*E*)-8-(4-(*tert*-butyl)styryl)-4-methyldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**5**)

^{1}H NMR (400 MHz, CD_3CN)

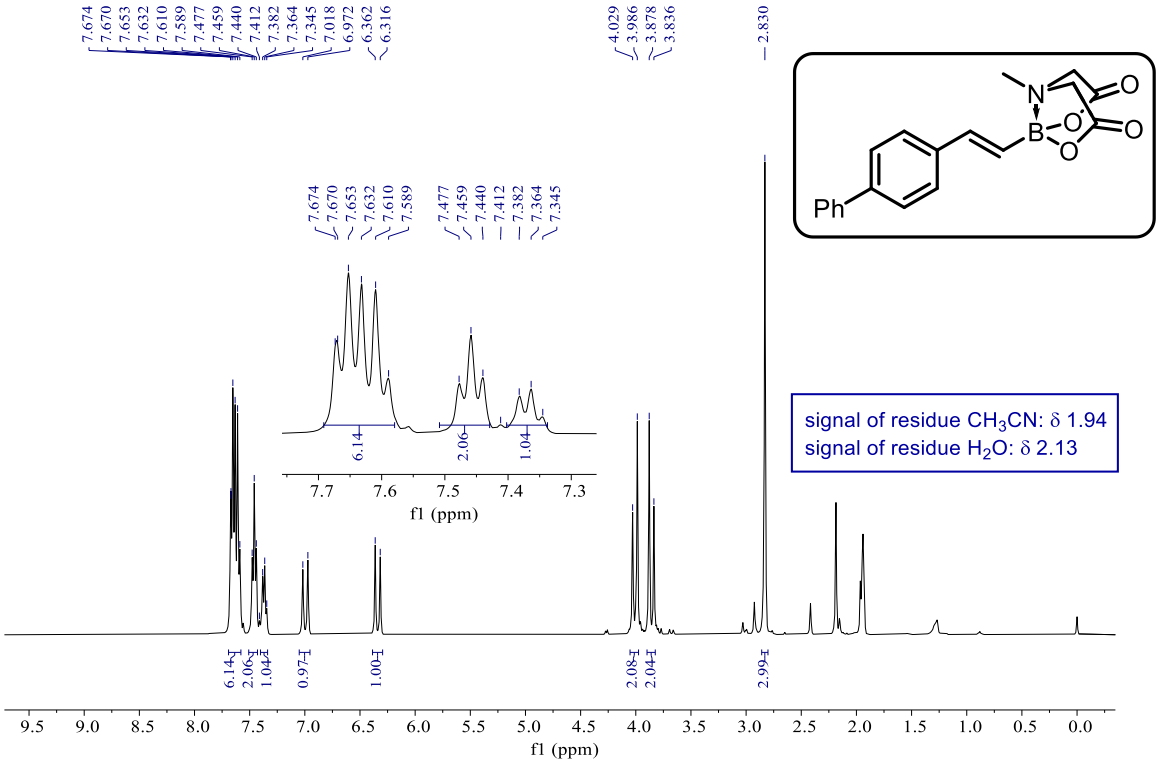


^{13}C{1H} NMR (100 MHz, CD_3CN)

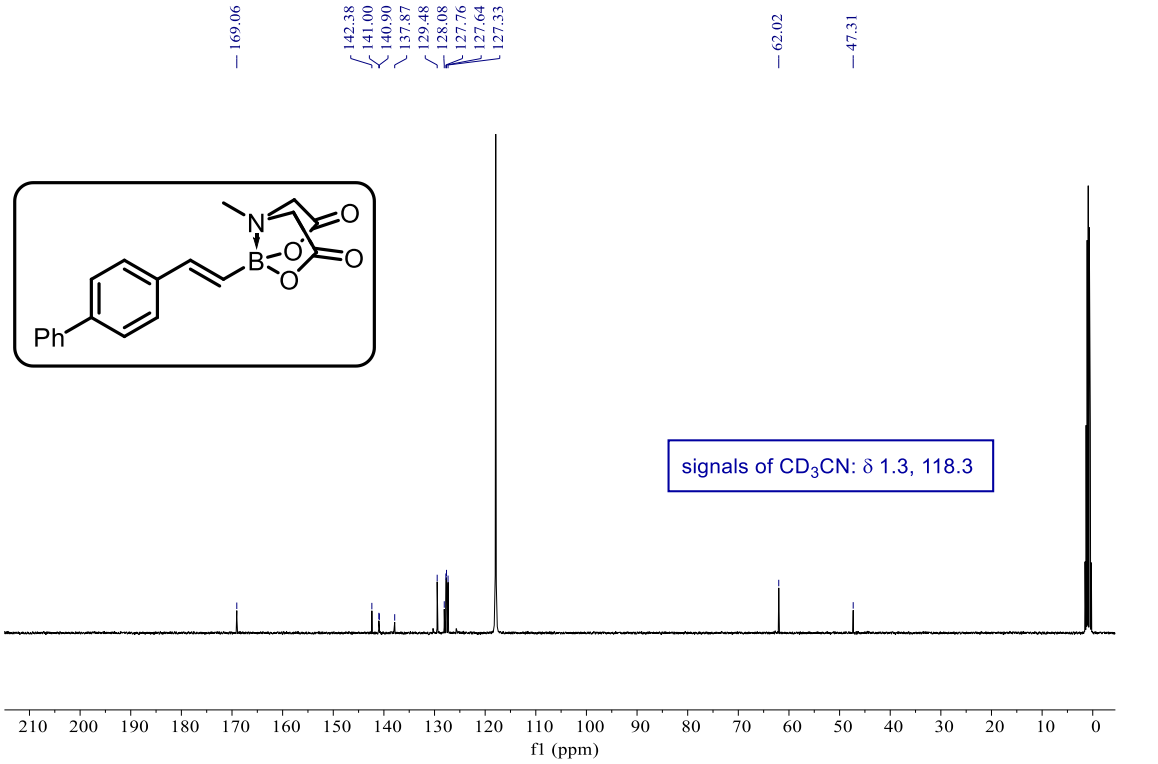


(*E*)-8-(2-([1,1'-biphenyl]-4-yl)vinyl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**6**)

^{1}H NMR (400 MHz, CD_3CN)

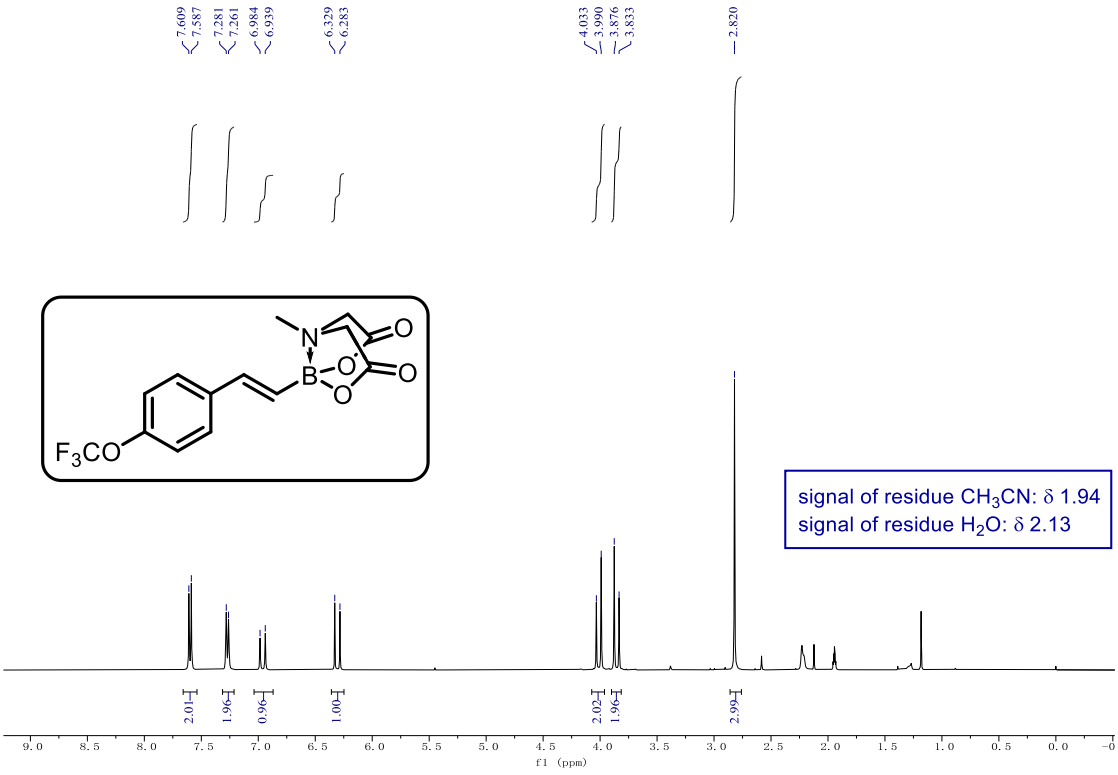


^{13}C{1H} NMR (100 MHz, CD_3CN)

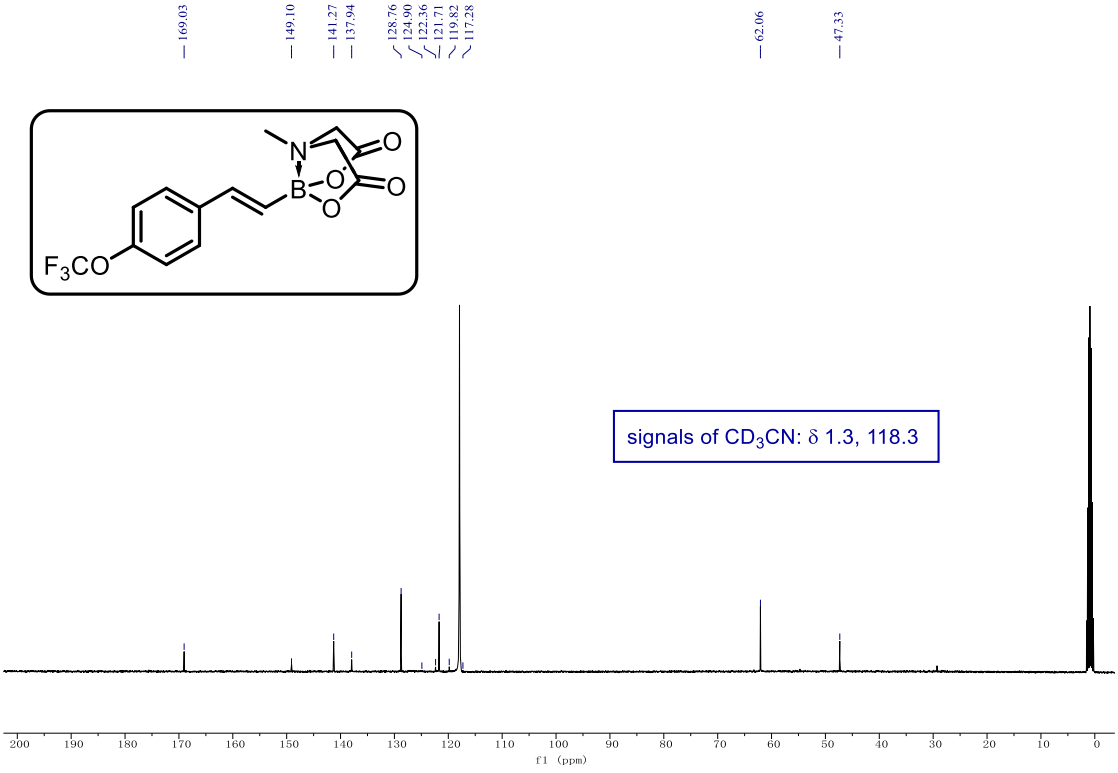


(*E*)-4-methyl-8-(4-(trifluoromethoxy)styryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**7**)

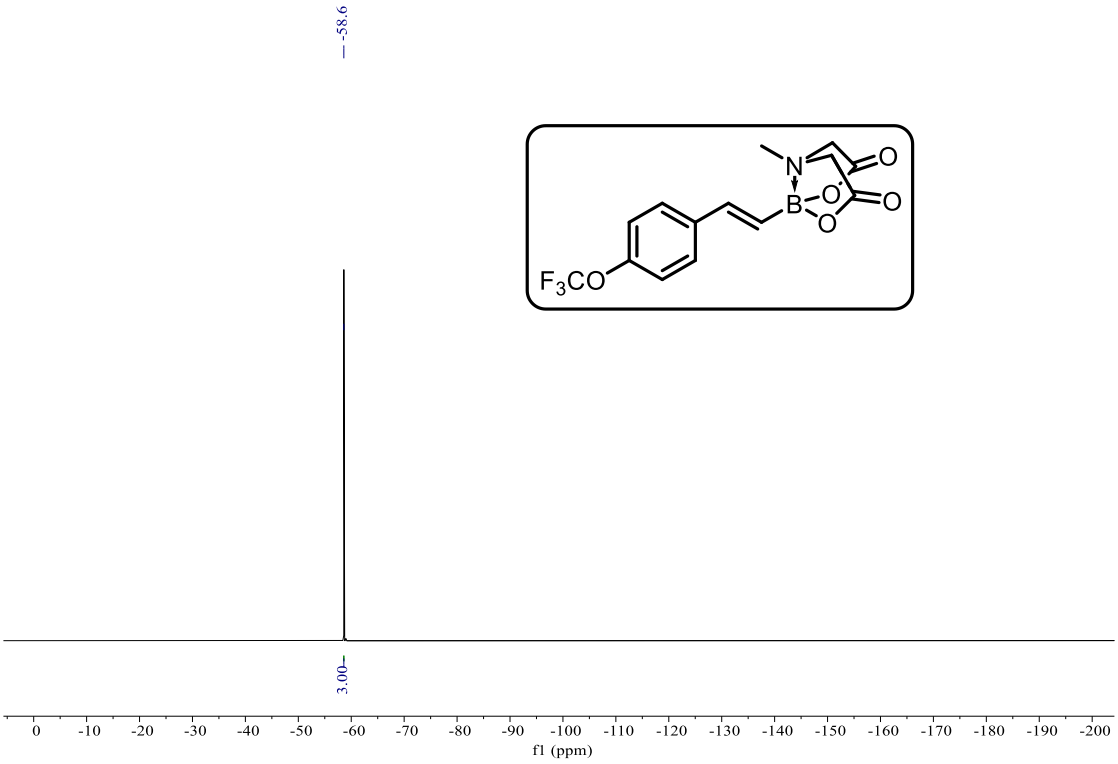
^{1}H NMR (400 MHz, CD_3CN)



^{13}C{1H} NMR (100 MHz, CD_3CN)

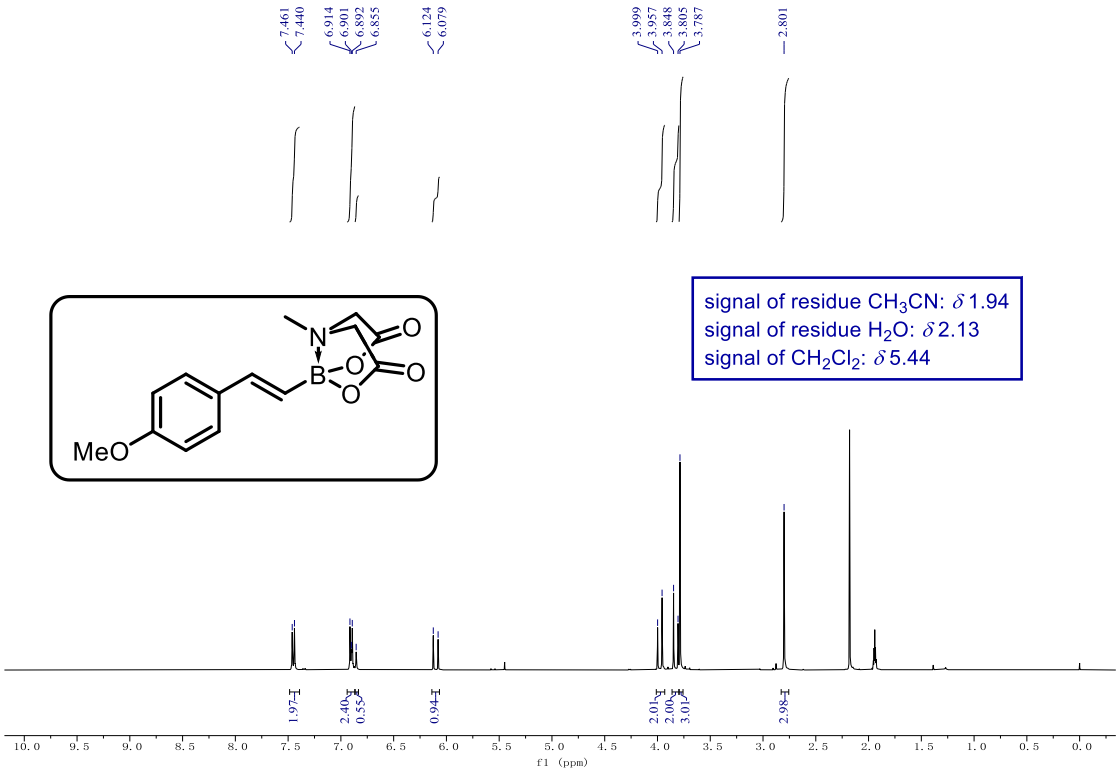


^{19}F NMR (471 MHz, CD_3CN)

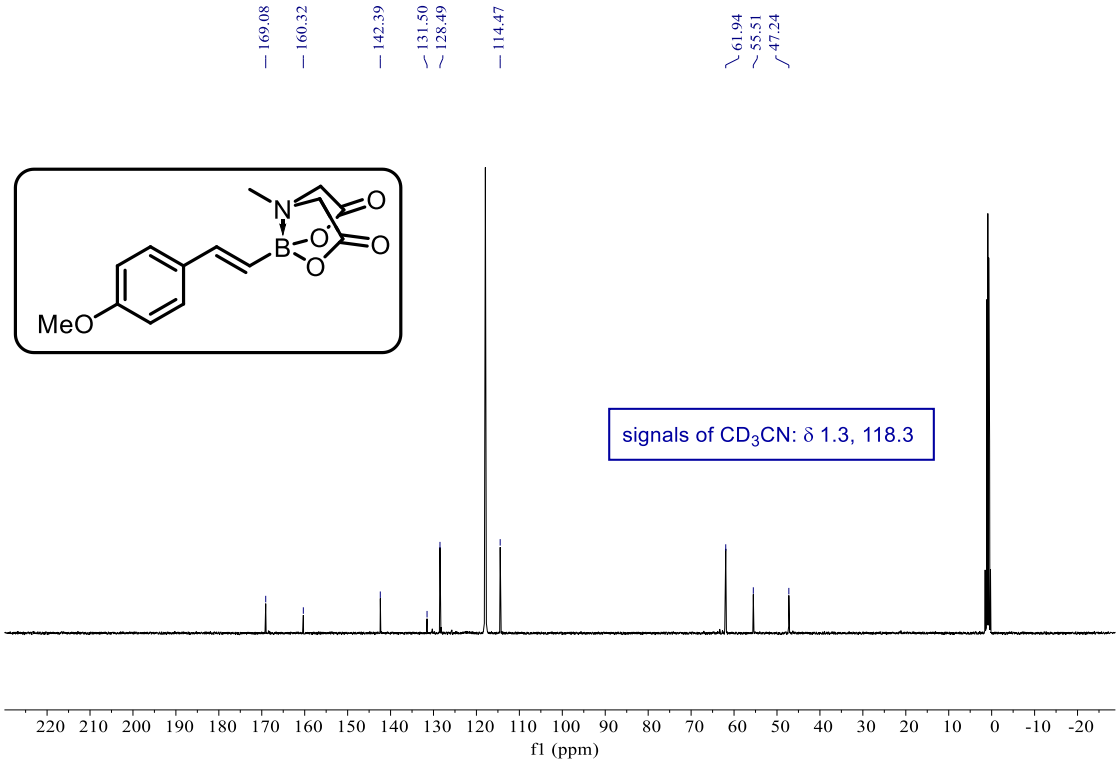


(*E*)-8-(4-methoxystyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**8**)

^{1}H NMR (400 MHz, CD_3CN)

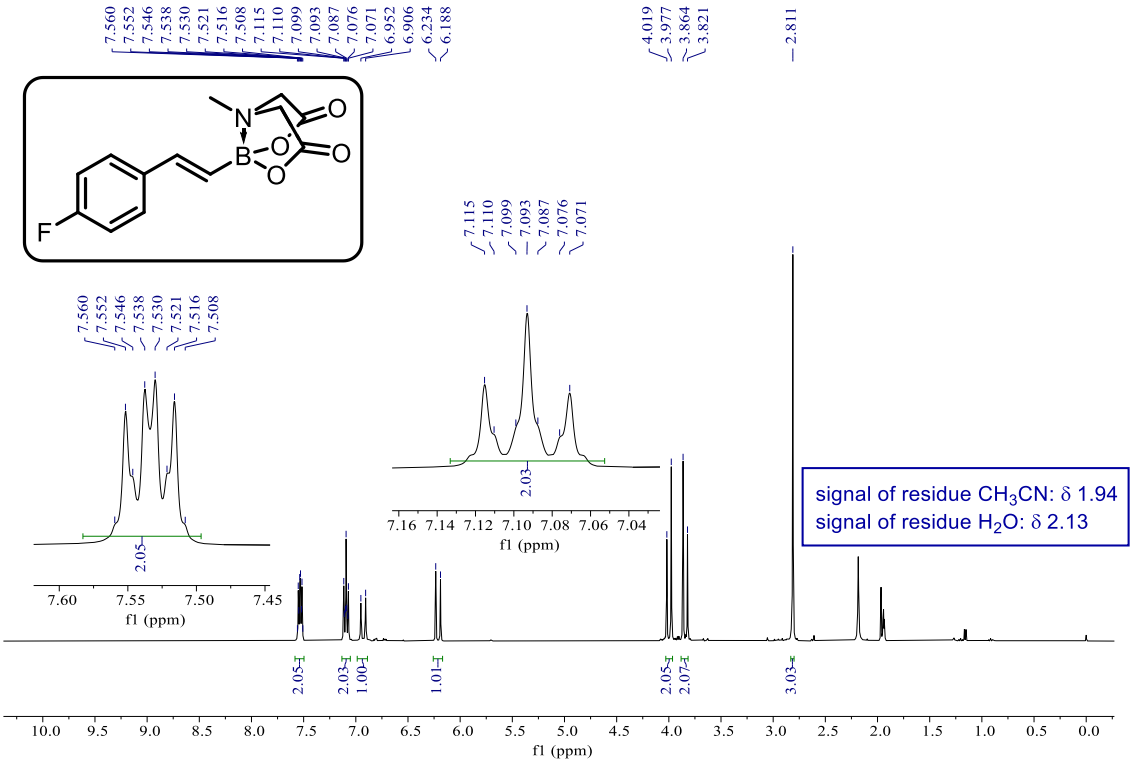


^{13}C{1H} NMR (100 MHz, CD_3CN)

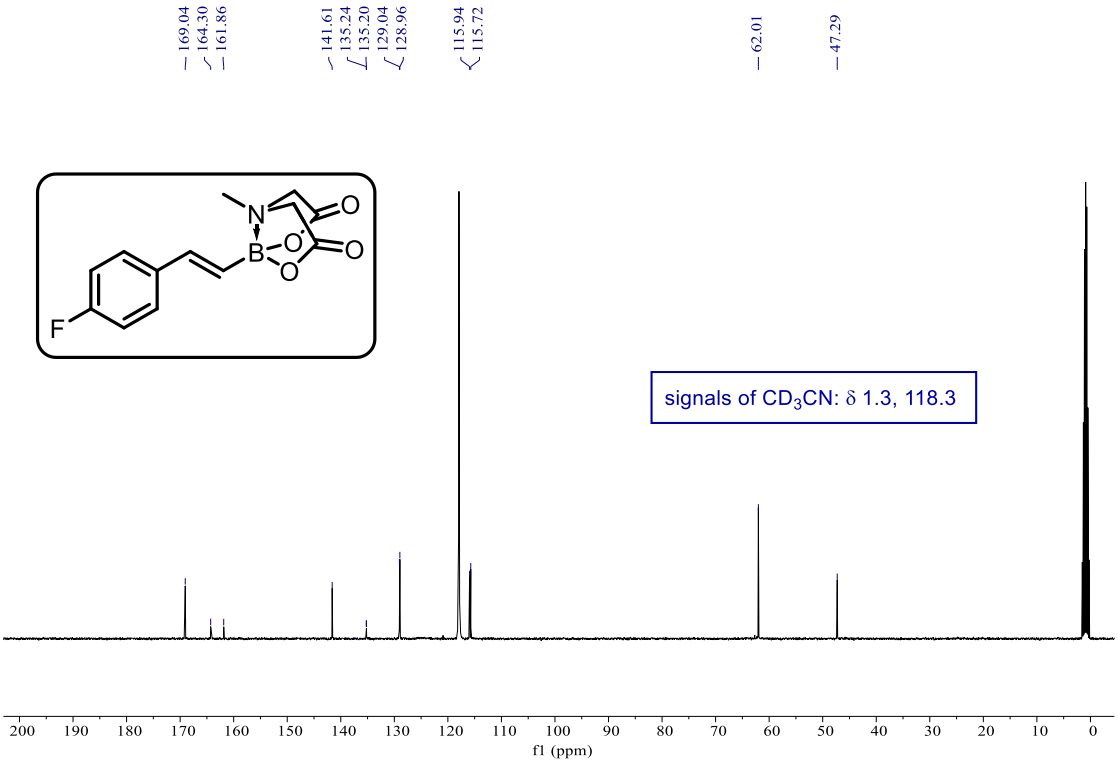


(*E*)-8-(4-fluorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**9**)

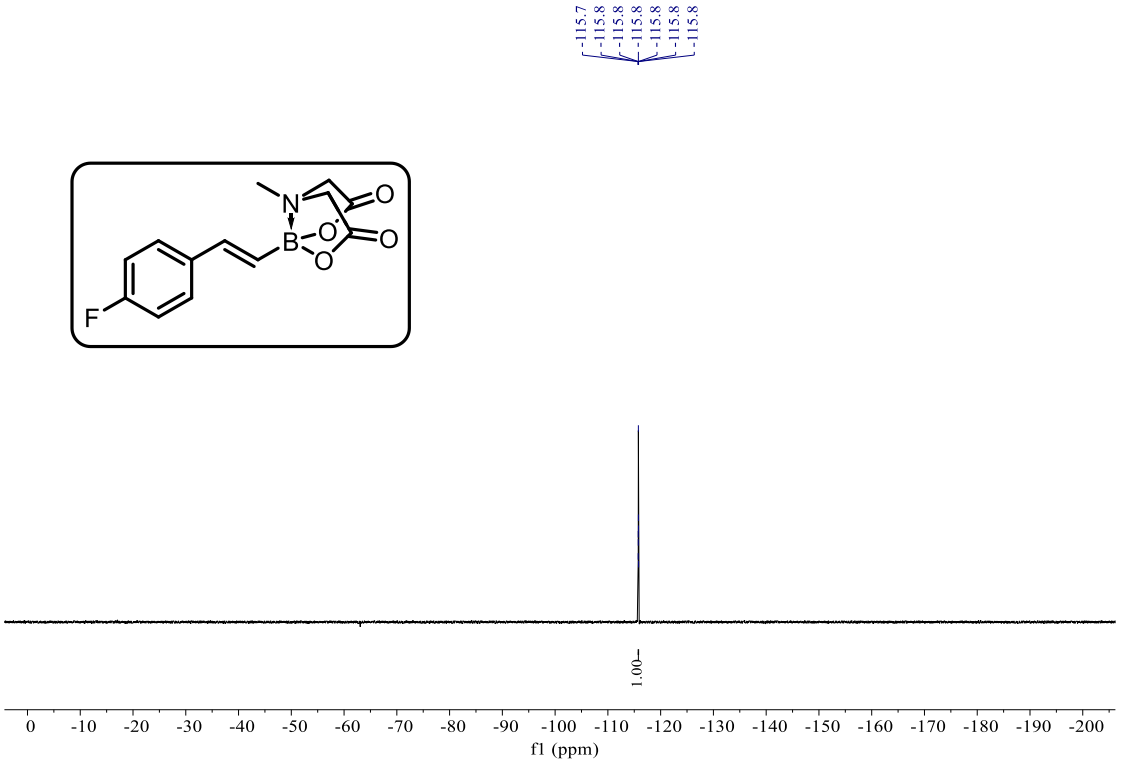
^{1}H NMR (400 MHz, CD_3CN)



^{13}C{1H} NMR (100 MHz, CD_3CN)

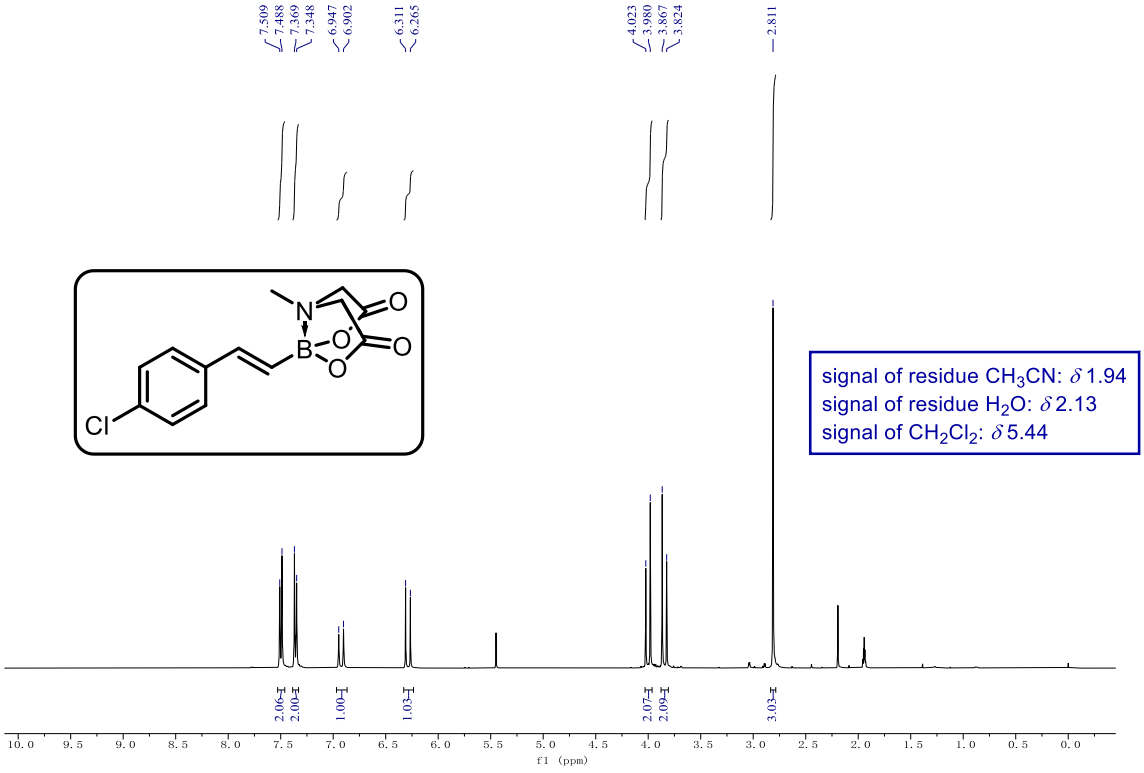


^{19}F NMR (471 MHz, CD_3CN)

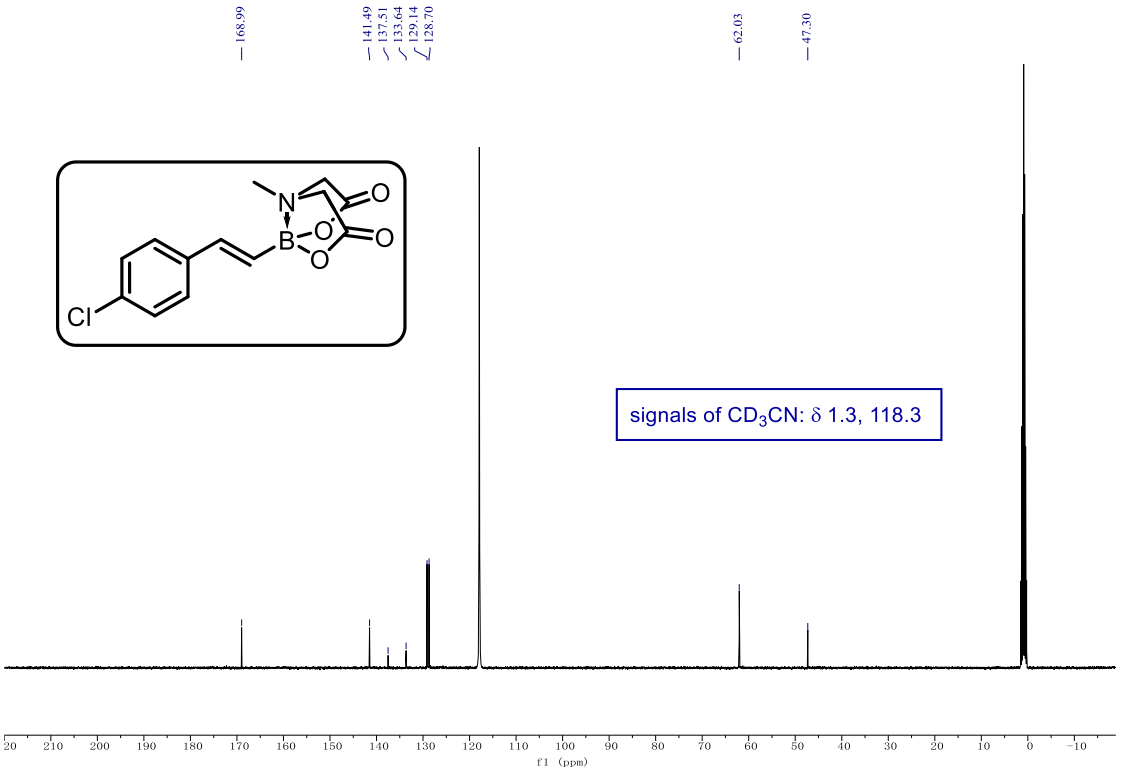


(*E*)-8-(4-chlorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**10**)

^{1}H NMR (400 MHz, CD_3CN)

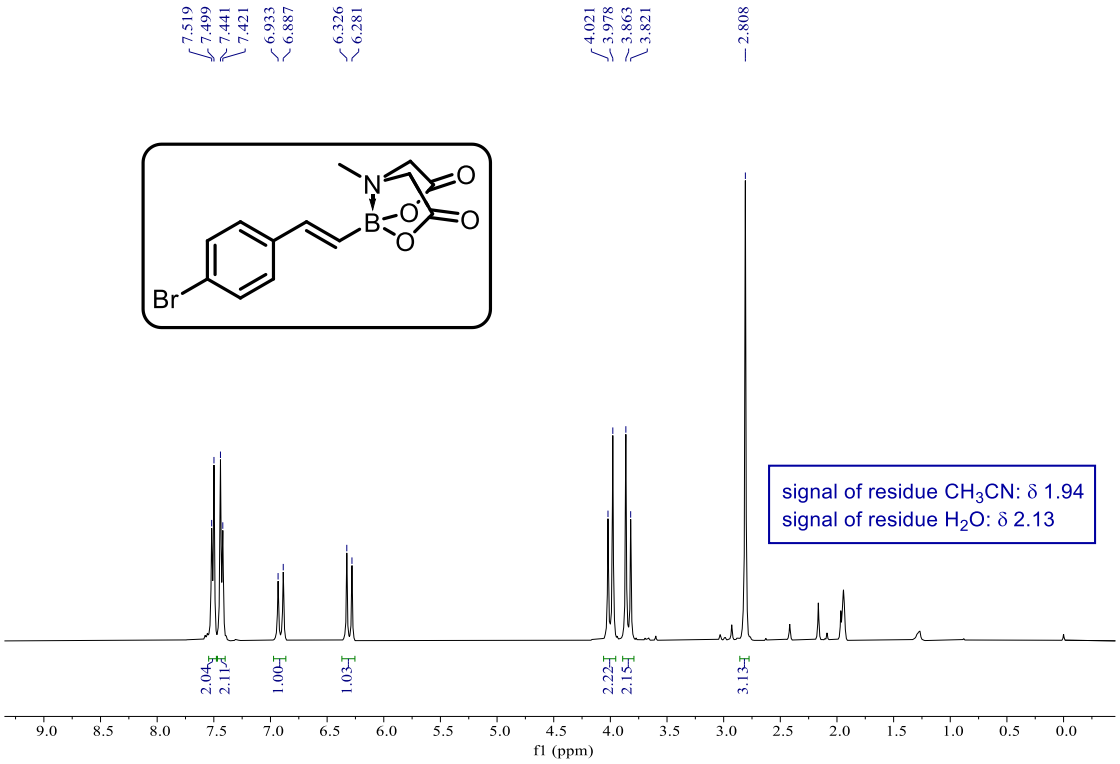


^{13}C{1H} NMR (100 MHz, CD_3CN)

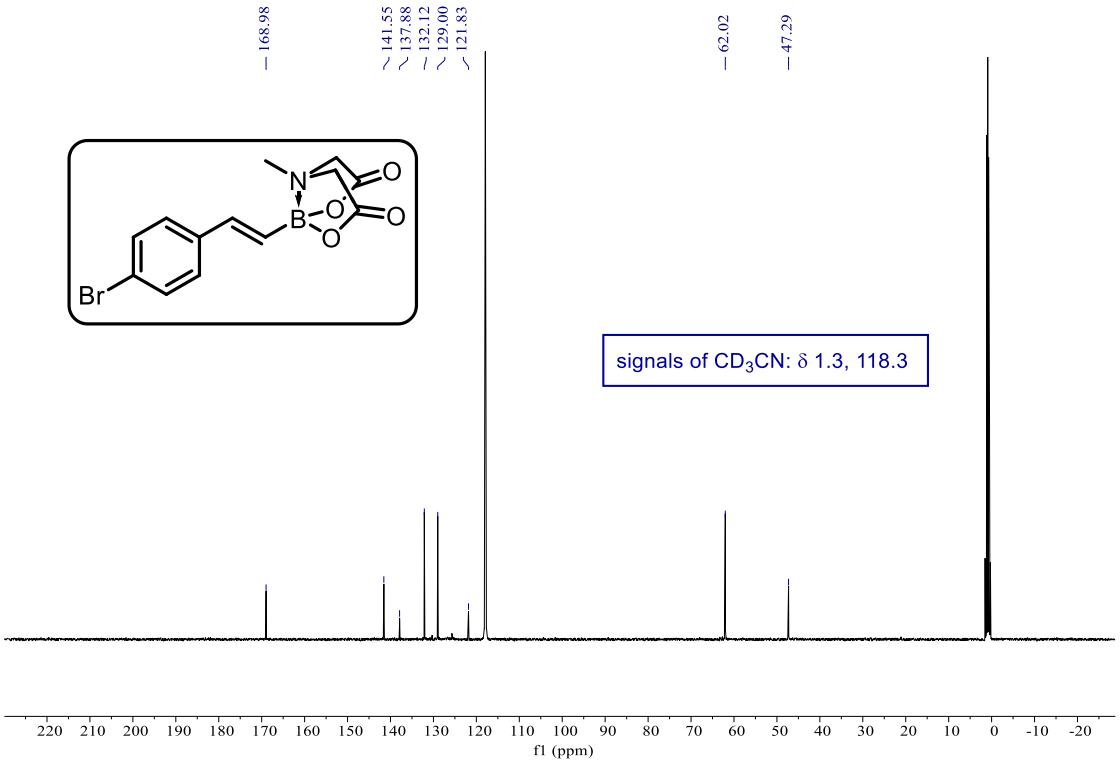


(*E*)-8-(4-bromostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**11**)

^{1}H NMR (400 MHz, CD_3CN)

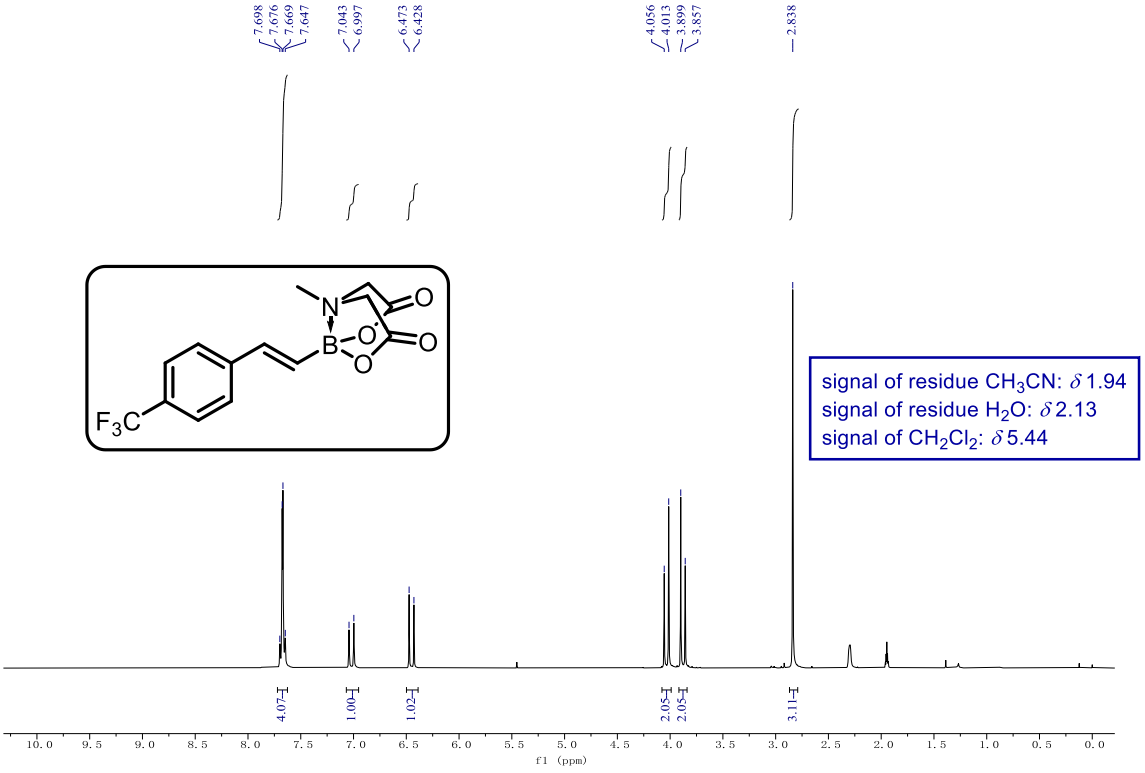


^{13}C{1H} NMR (100 MHz, CD_3CN)

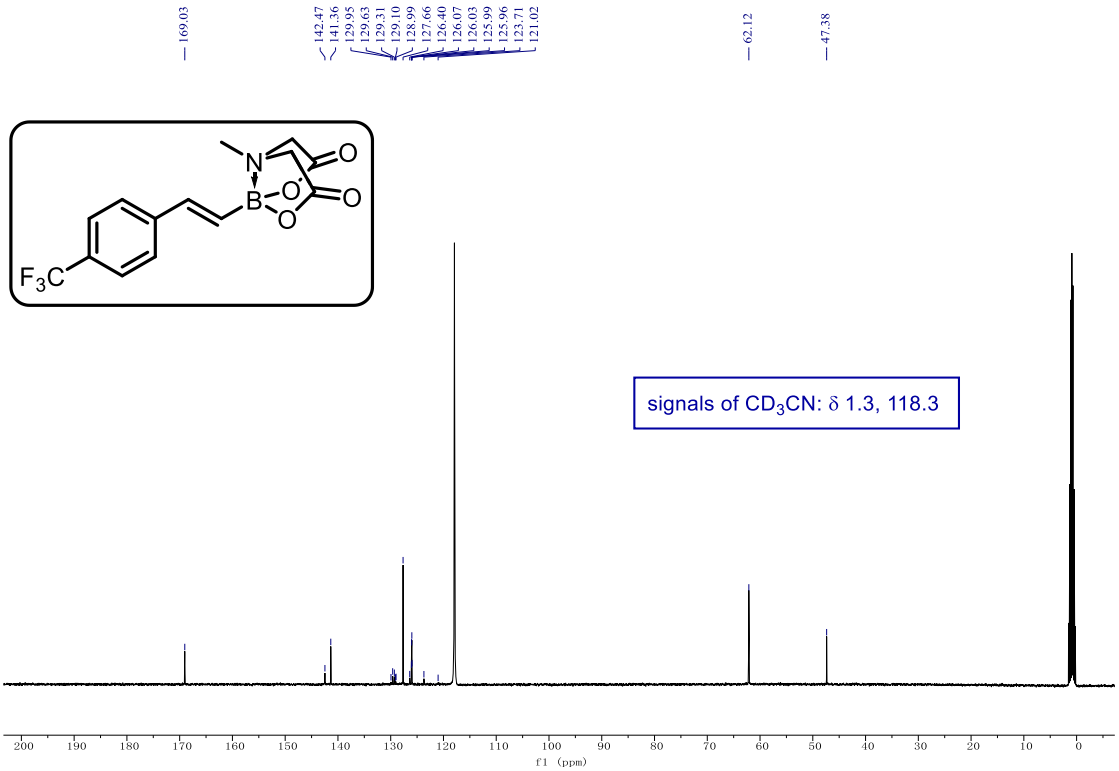


(*E*)-4-methyl-8-(4-(trifluoromethyl)styryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**12**)

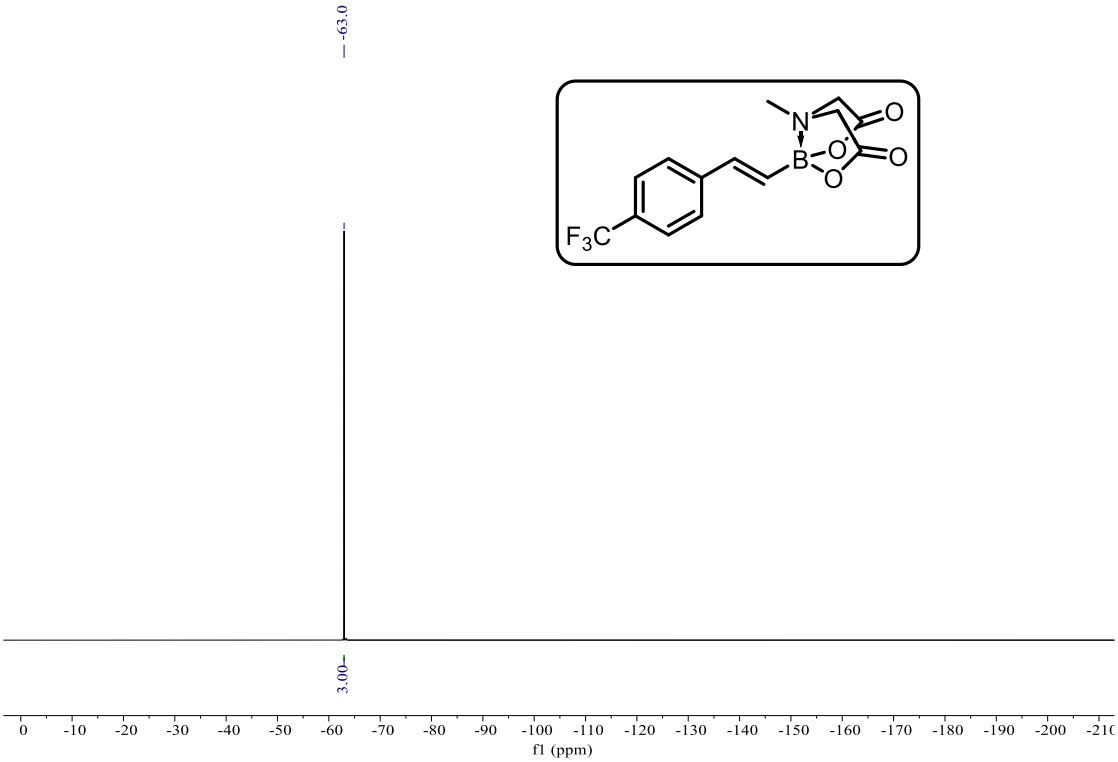
^{1}H NMR (400 MHz, CD_3CN)



^{13}C{1H} NMR (100 MHz, CD_3CN)

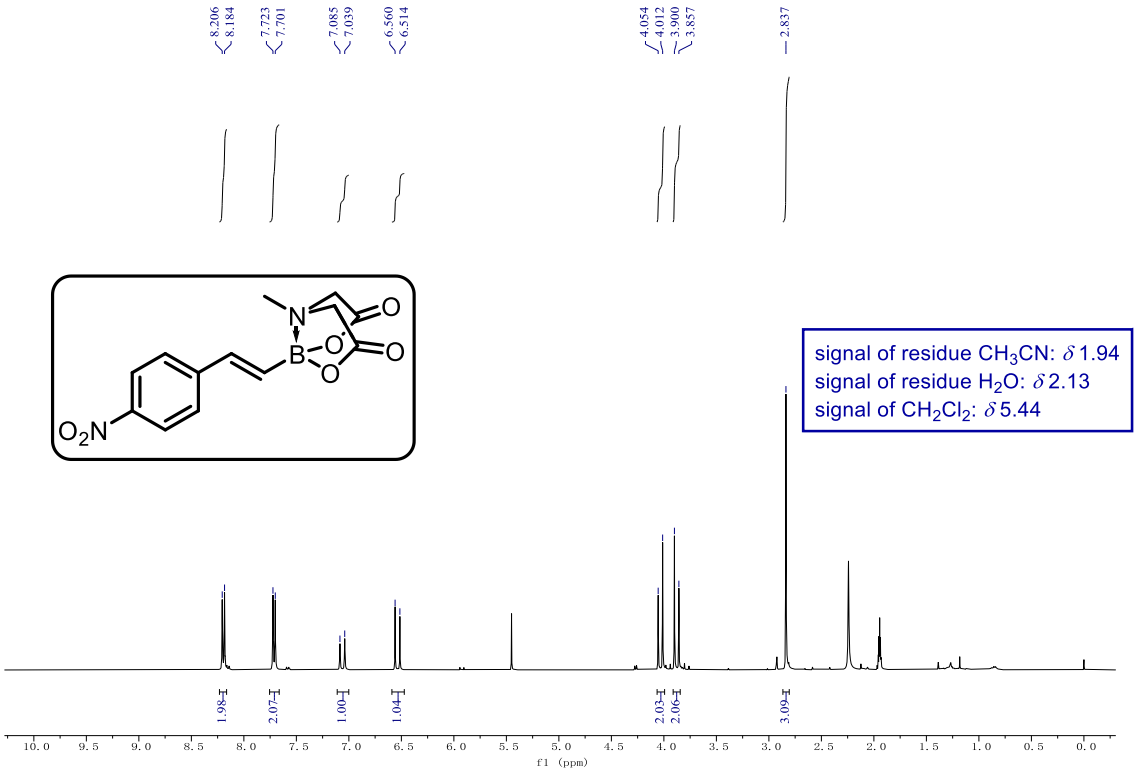


^{19}F NMR (471 MHz, CD_3CN)

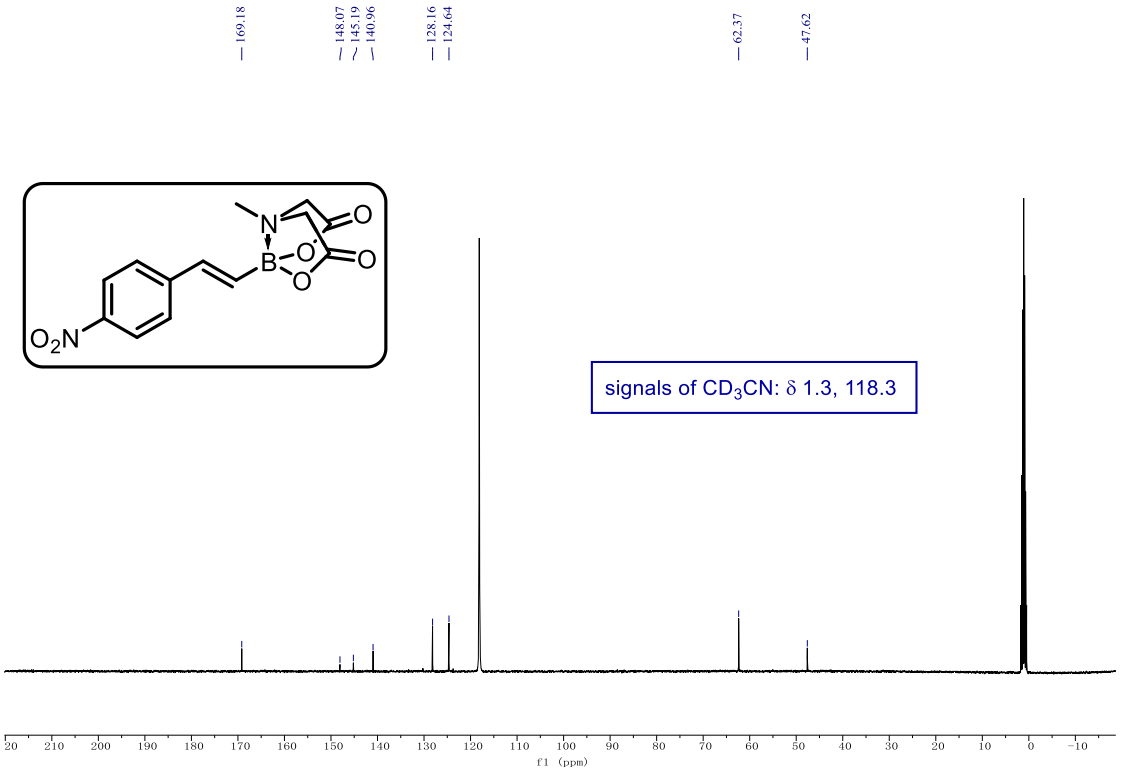


(*E*)-4-methyl-8-(4-nitrostyryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**13**)

^{1}H NMR (400 MHz, CD_3CN)

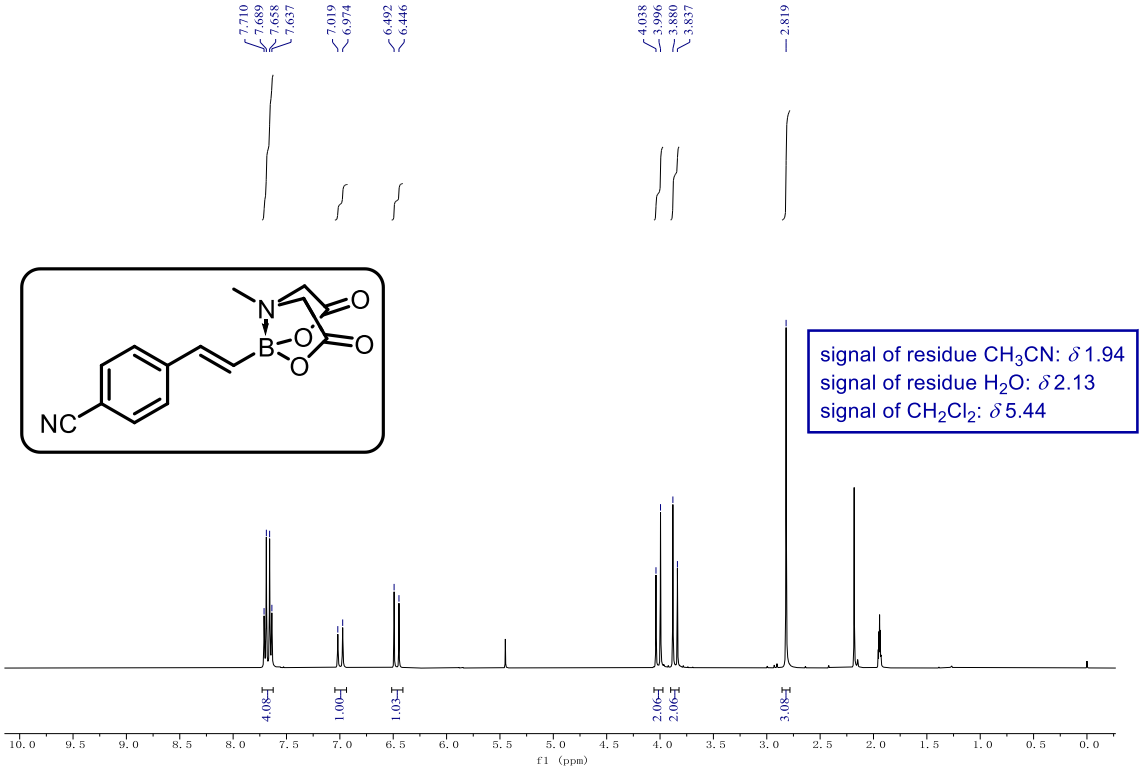


^{13}C{1H} NMR (100 MHz, CD_3CN)

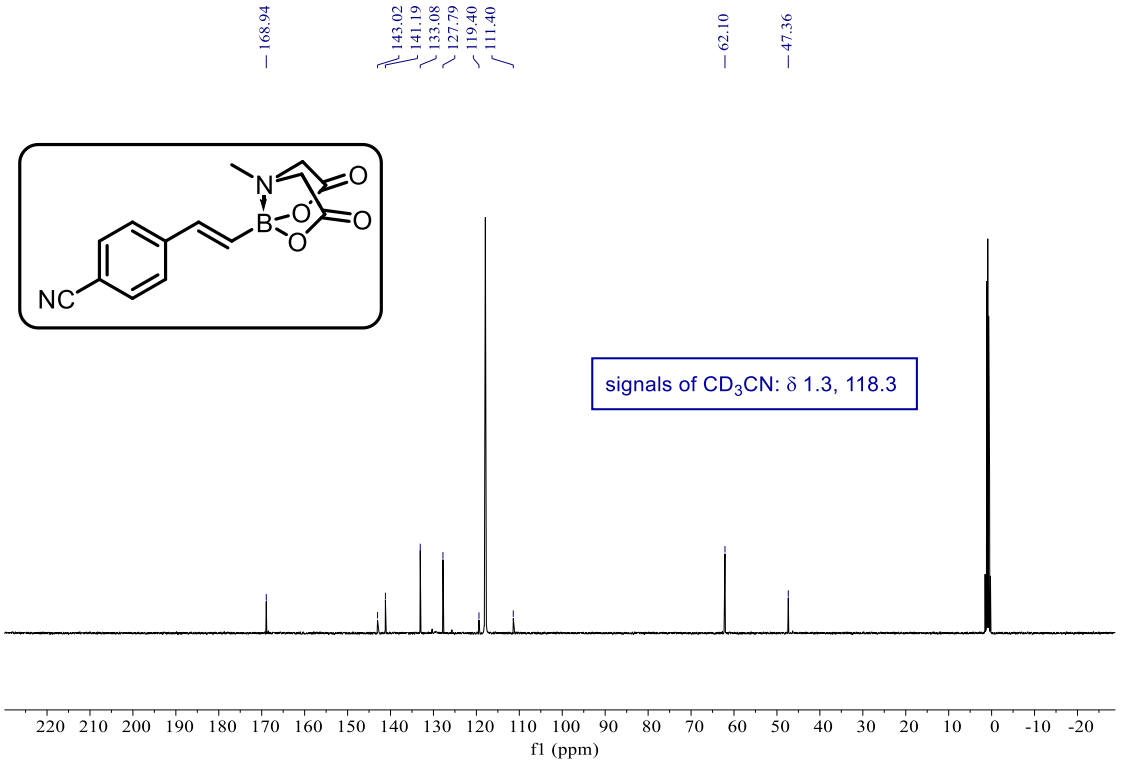


(*E*)-4-(2-(4-methyl-2,6-dioxotetrahydro-2*H*-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)vinyl)benzonitrile (**14**)

^{1}H NMR (400 MHz, CD_3CN)

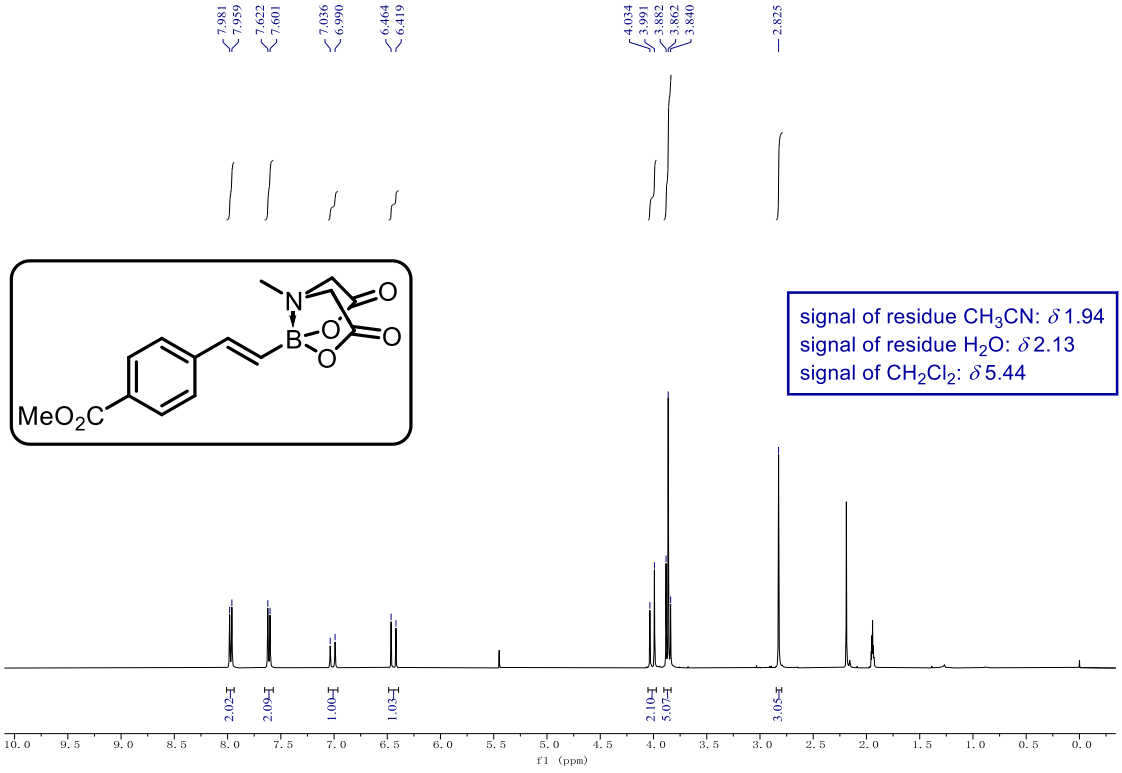


^{13}C{1H} NMR (100 MHz, CD_3CN)

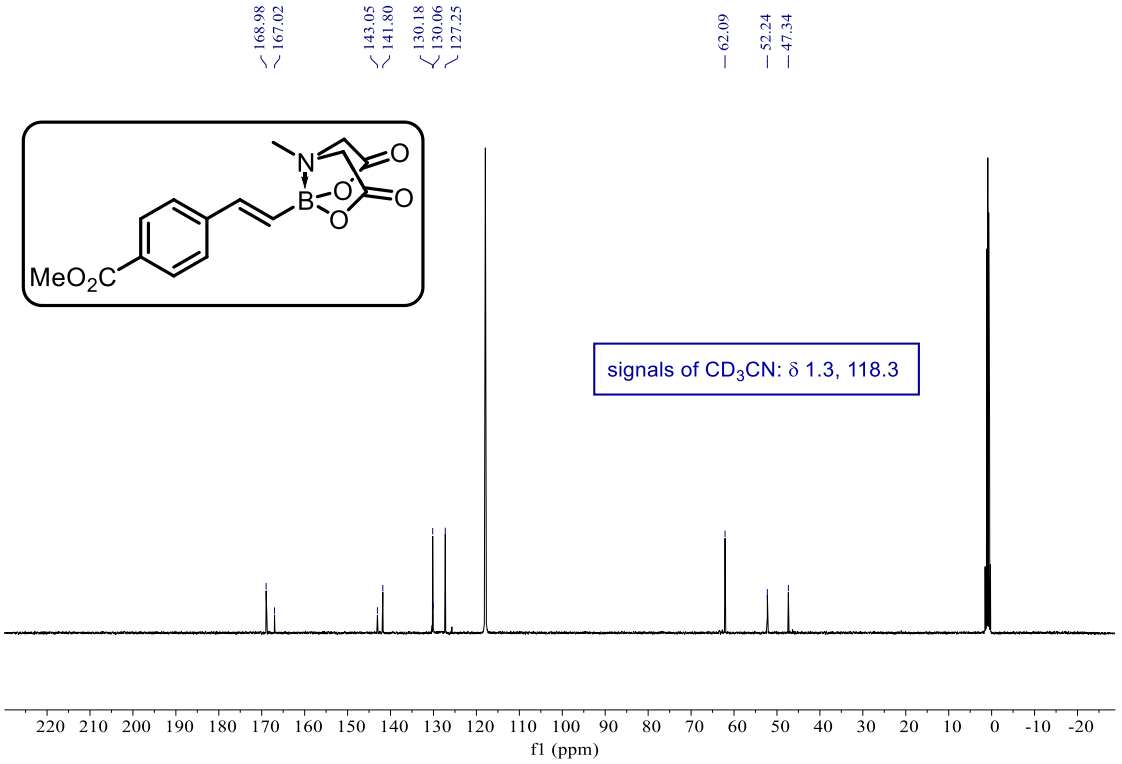


methyl (*E*)-4-(2-(4-methyl-2,6-dioxotetrahydro-2*H*-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)vinyl)benzoate (**15**)

^{1}H NMR (400 MHz, CD_3CN)

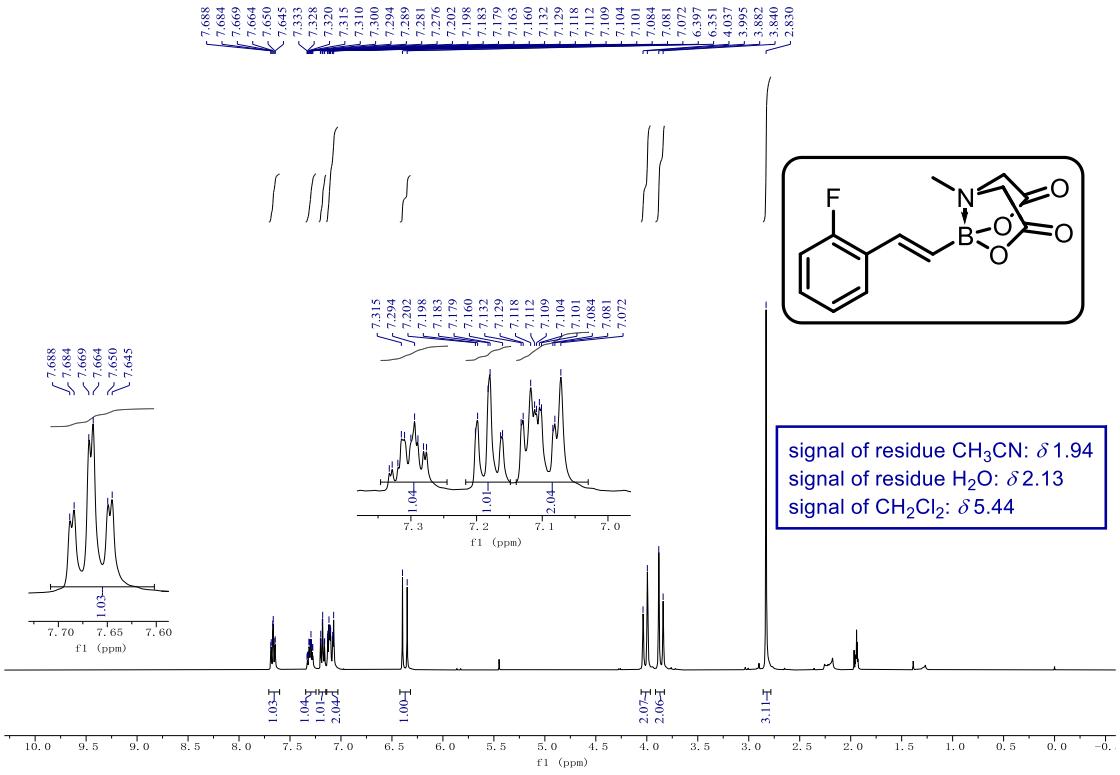


^{13}C{1H} NMR (100 MHz, CD_3CN)

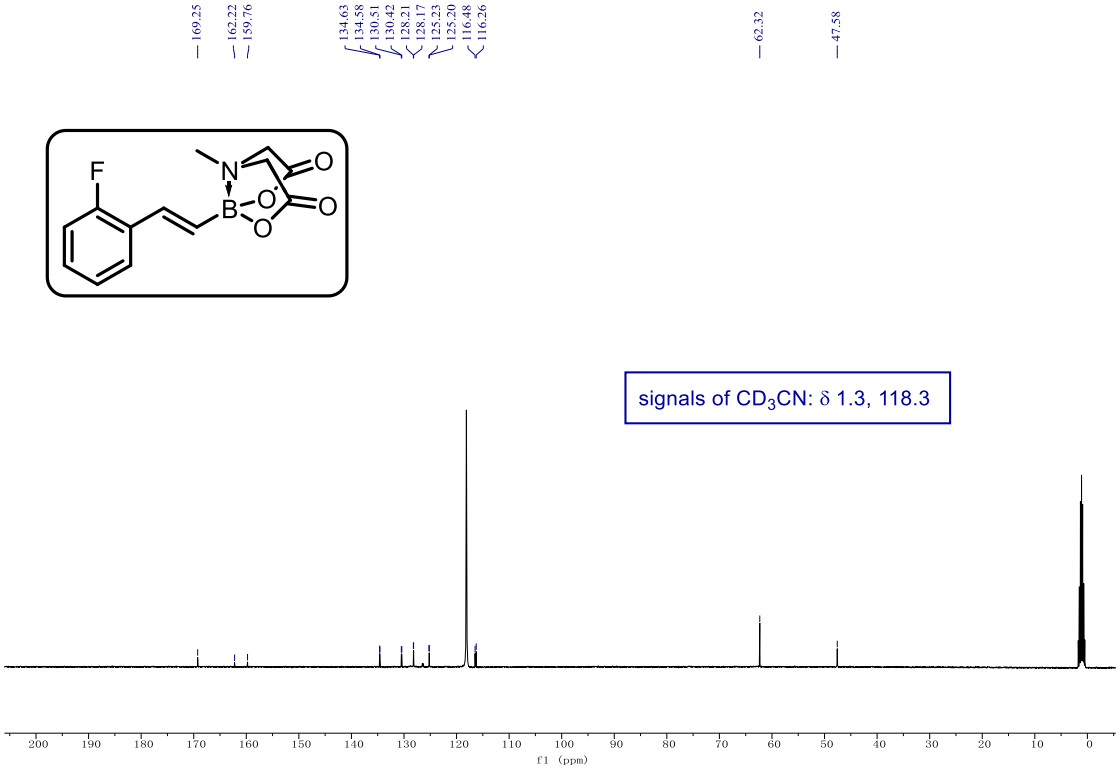


(*E*)-8-(2-fluorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**16**)

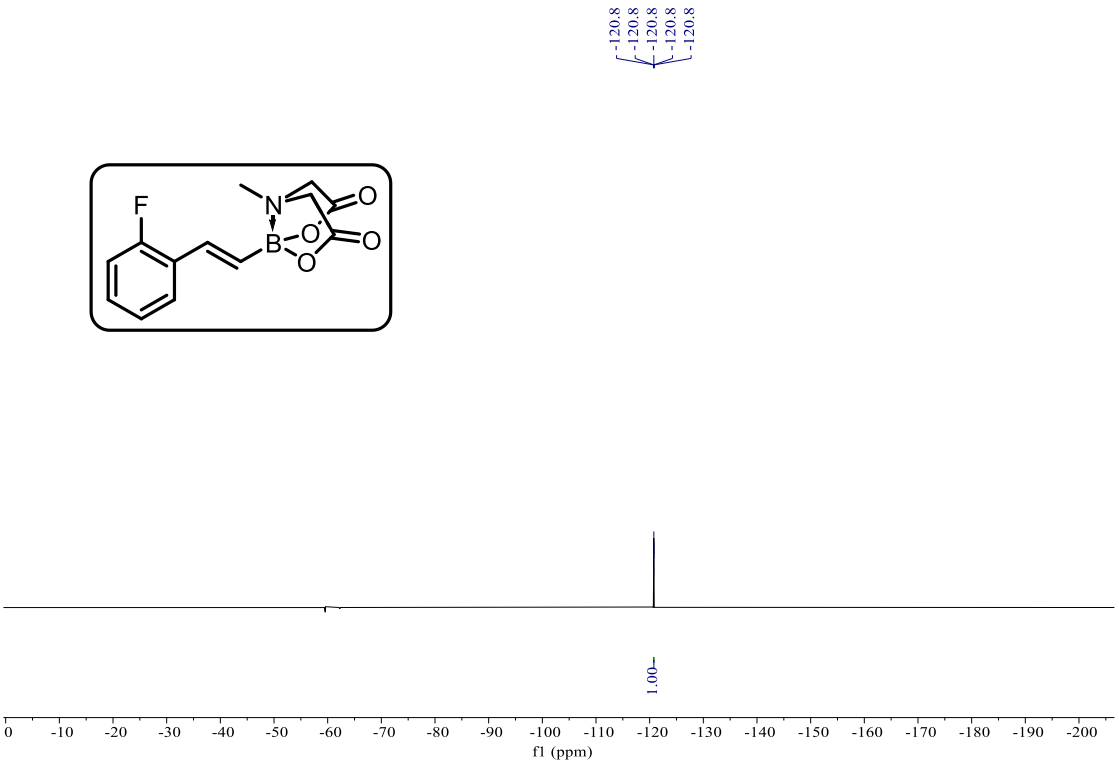
^{1}H NMR (400 MHz, CD_3CN)



^{13}C{1H} NMR (100 MHz, CD_3CN)

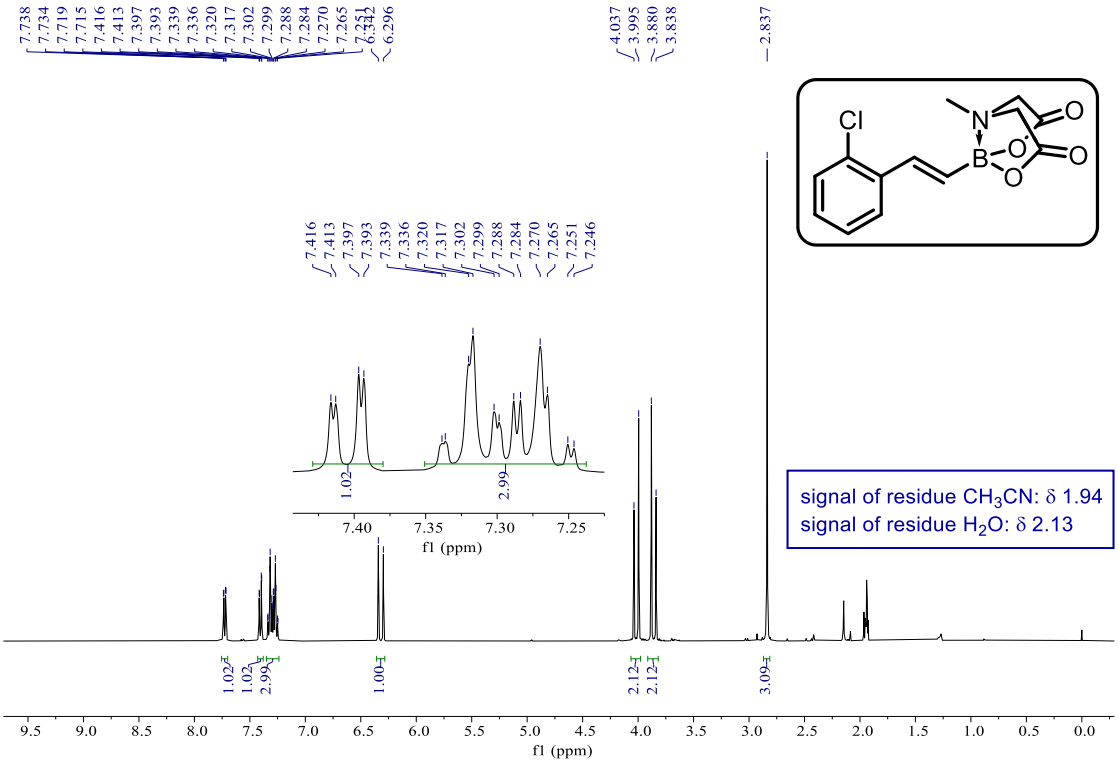


^{19}F NMR (471 MHz, CD_3CN)

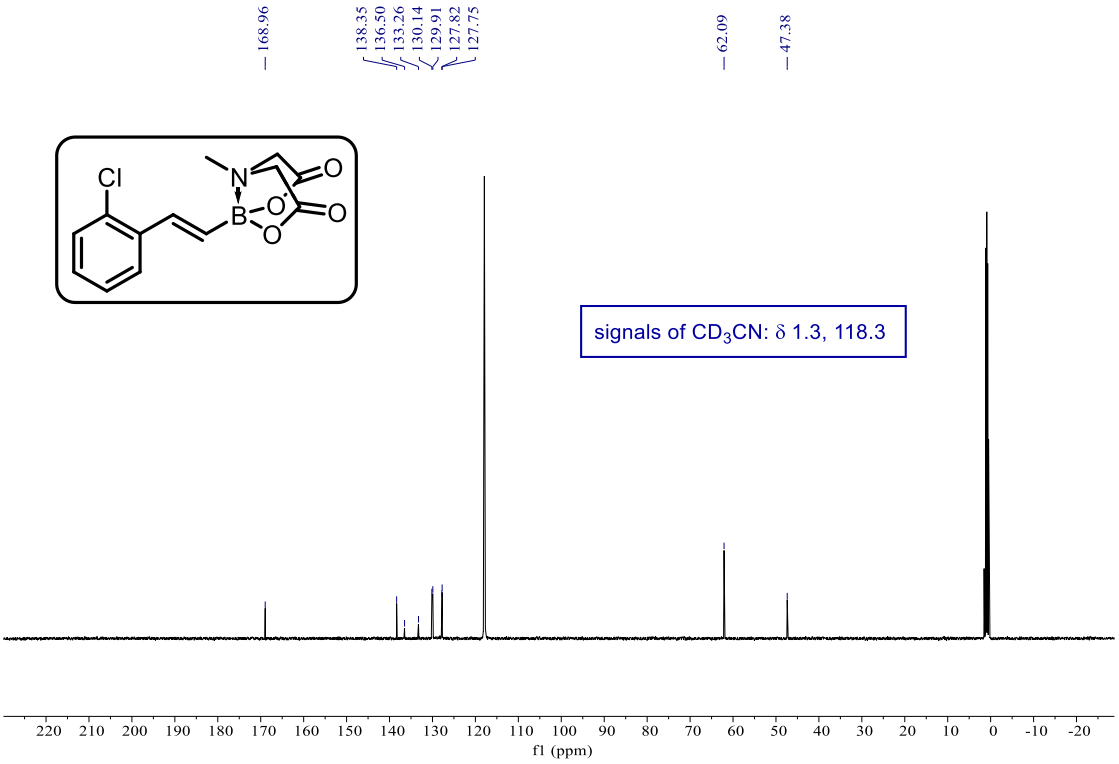


(*E*)-8-(2-chlorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**17**)

^{1}H NMR (400 MHz, CD_3CN)

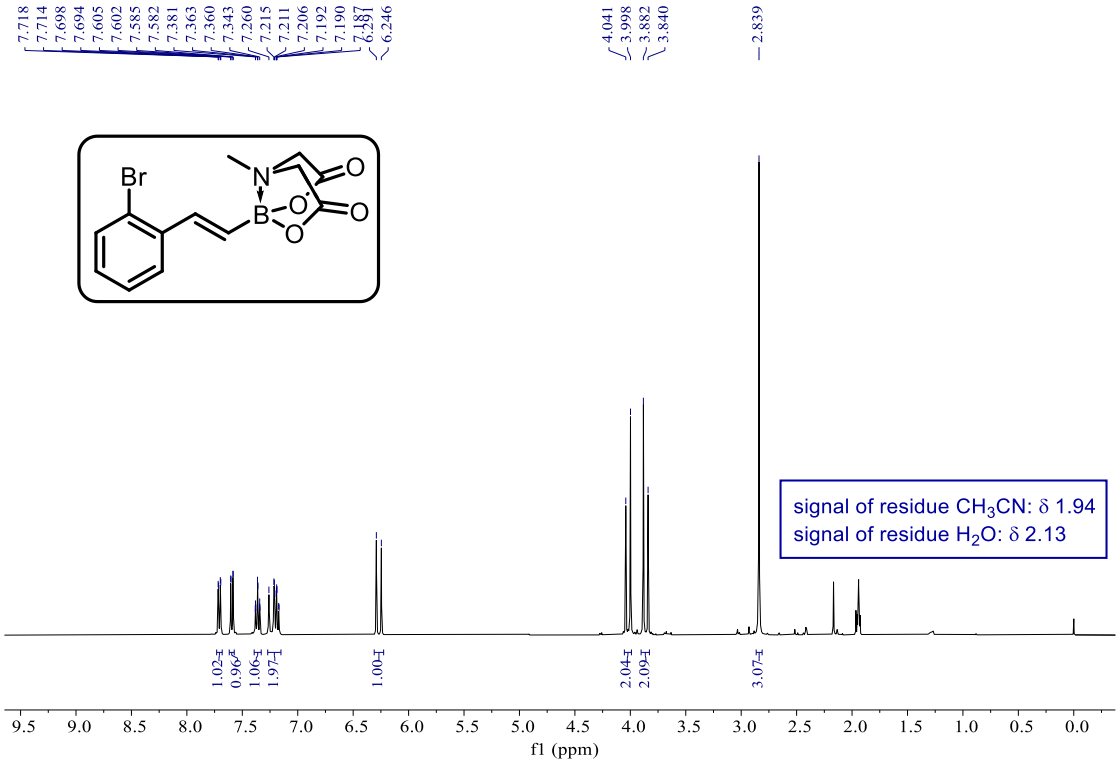


^{13}C{1H} NMR (100 MHz, CD_3CN)

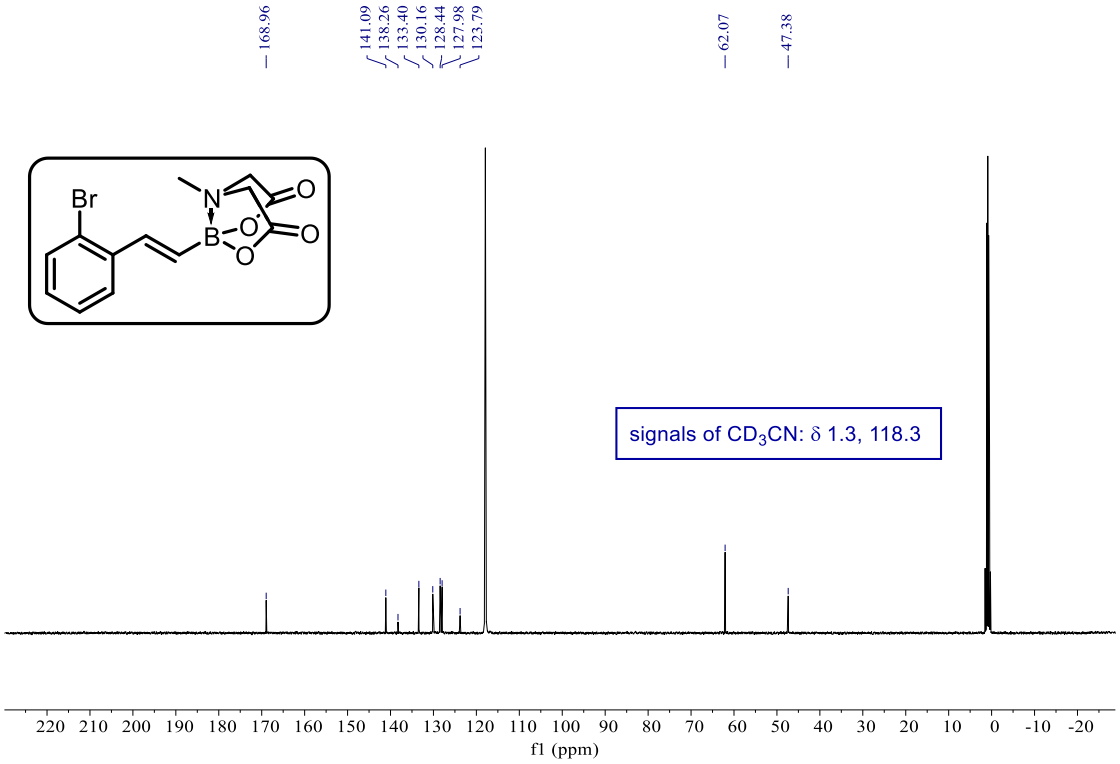


(*E*)-8-(2-bromostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**18**)

^{1}H NMR (400 MHz, CD_3CN)

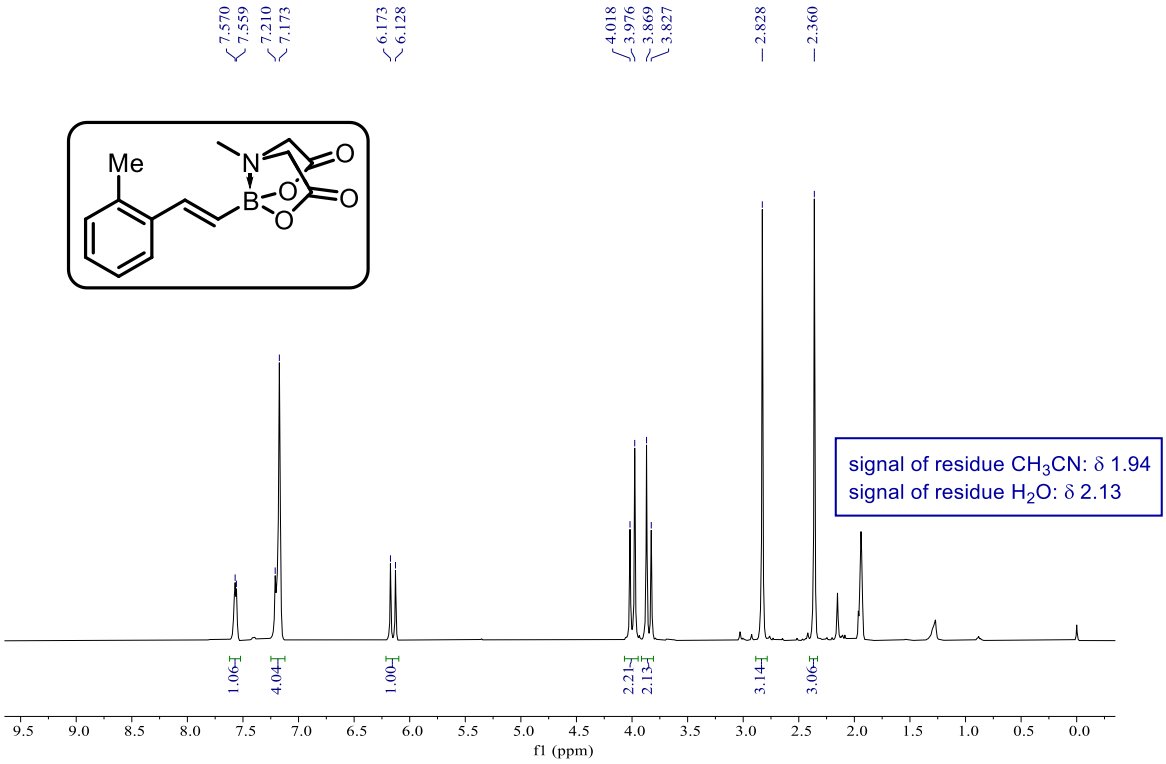


^{13}C{1H} NMR (100 MHz, CD_3CN)

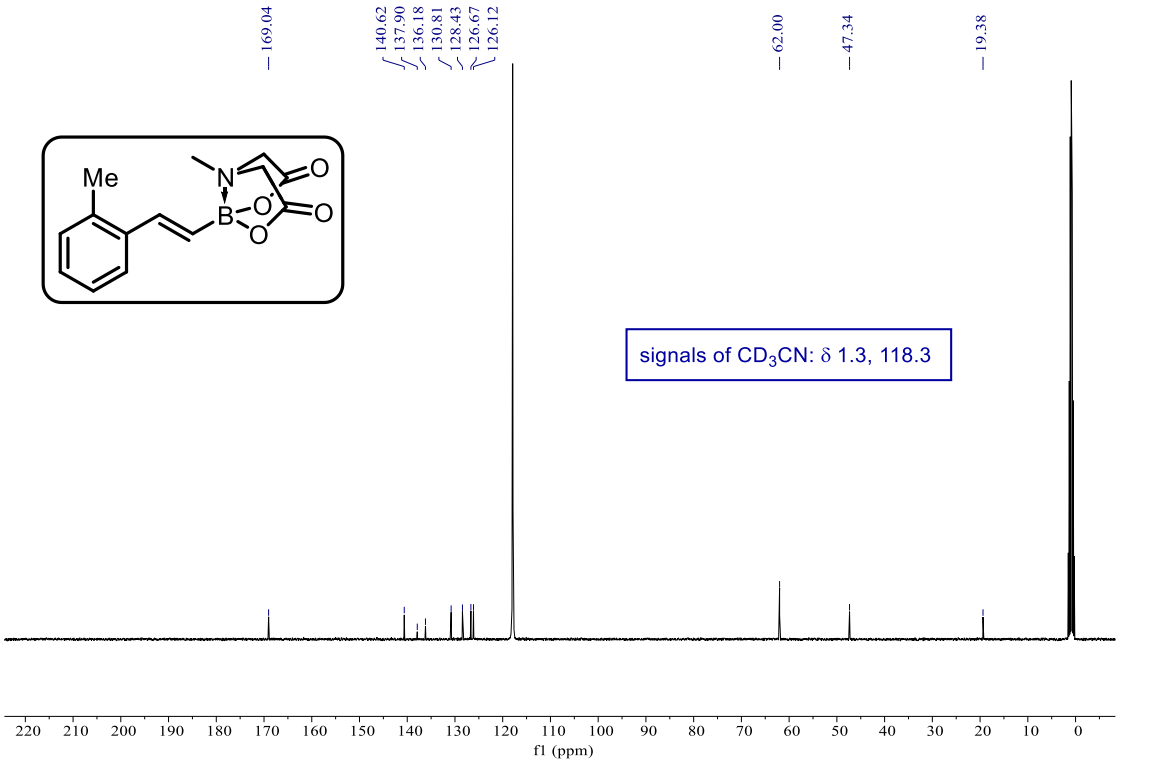


(*E*)-4-methyl-8-(2-methylstyryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**19**)

^{1}H NMR (400 MHz, CD_3CN)

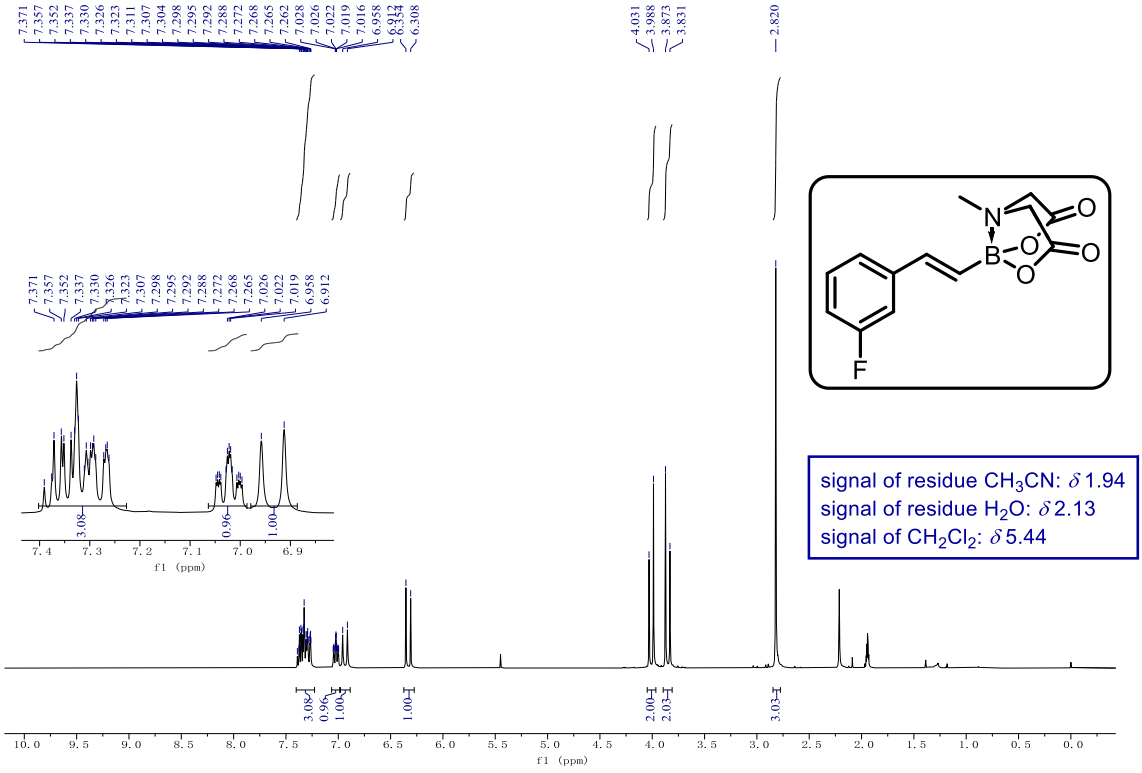


^{13}C{1H} NMR (100 MHz, CD_3CN)

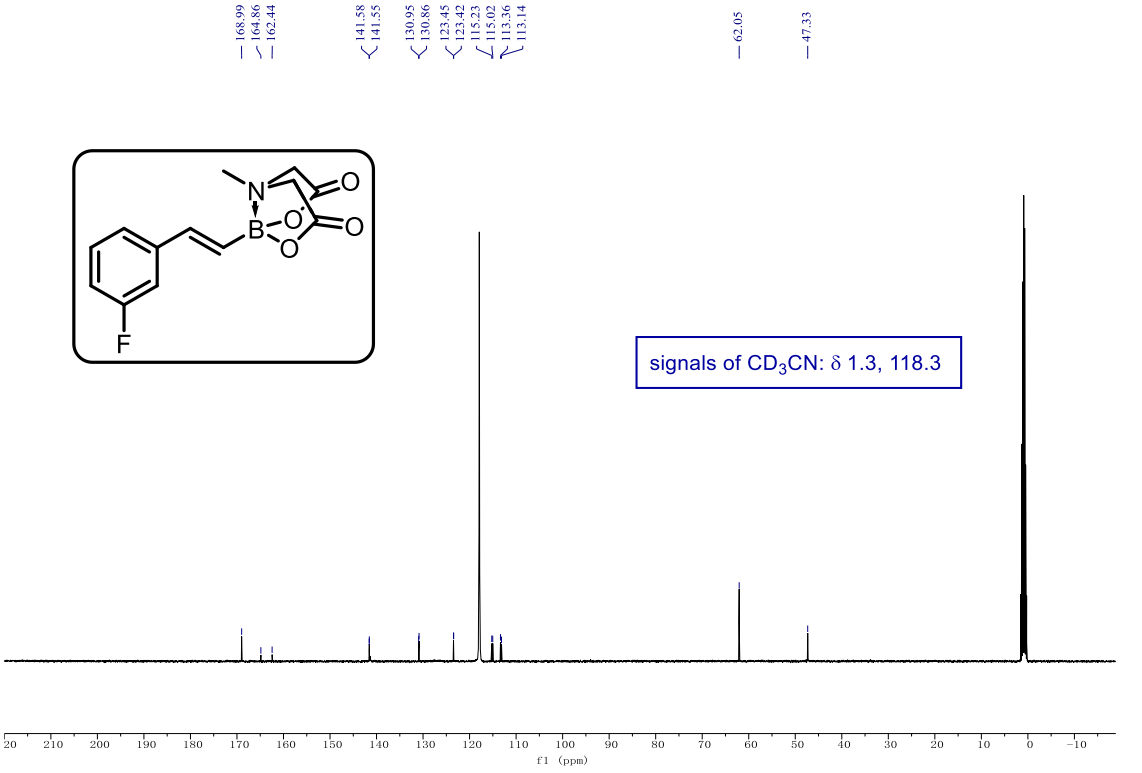


(*E*)-8-(3-fluorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**20**)

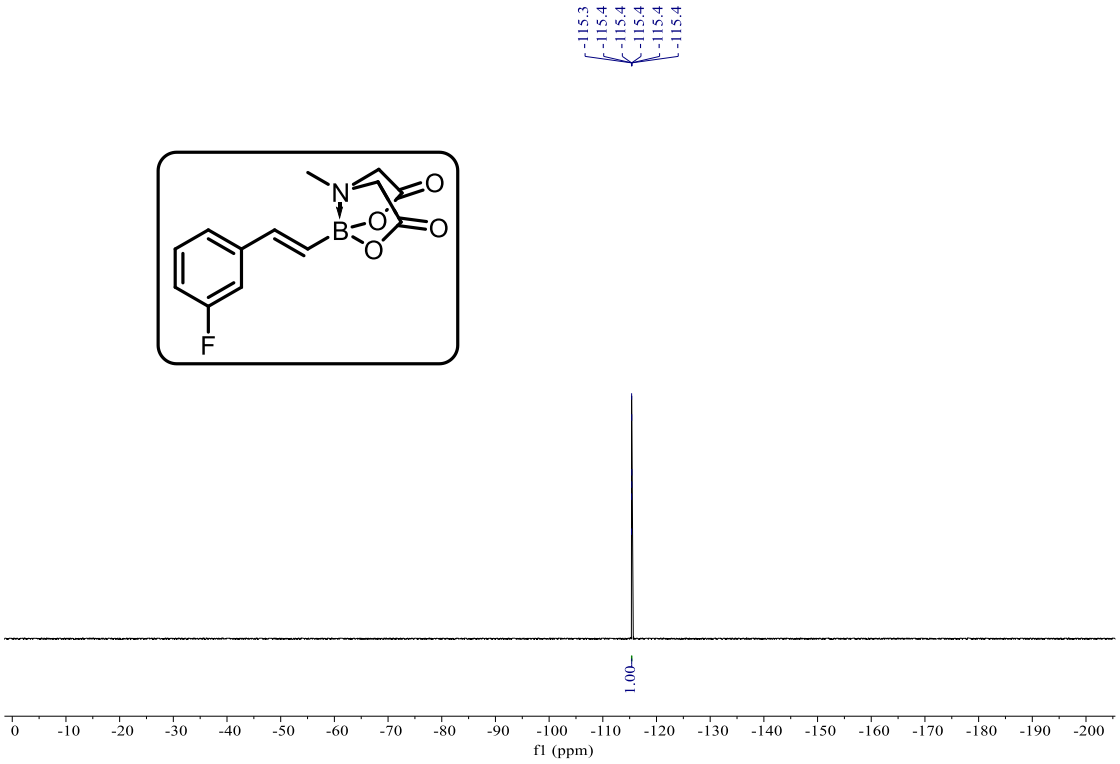
^{1}H NMR (400 MHz, CD_3CN)



^{13}C{1H} NMR (100 MHz, CD_3CN)

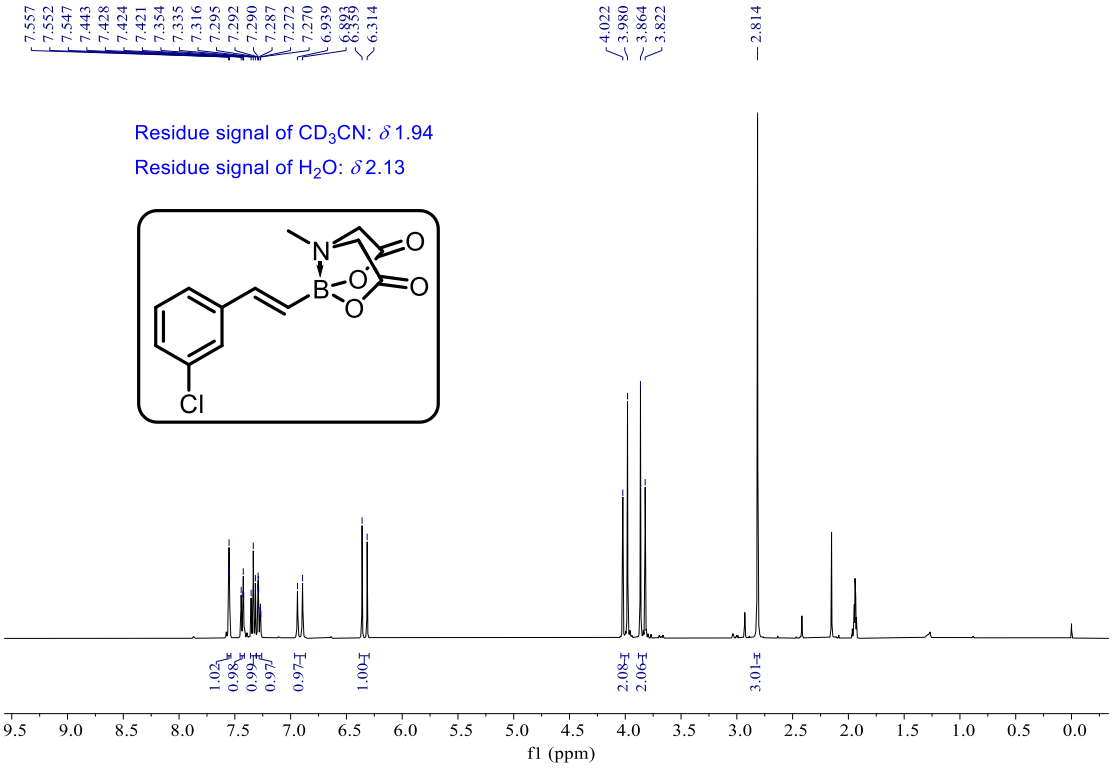


^{19}F NMR (471 MHz, CD_3CN)

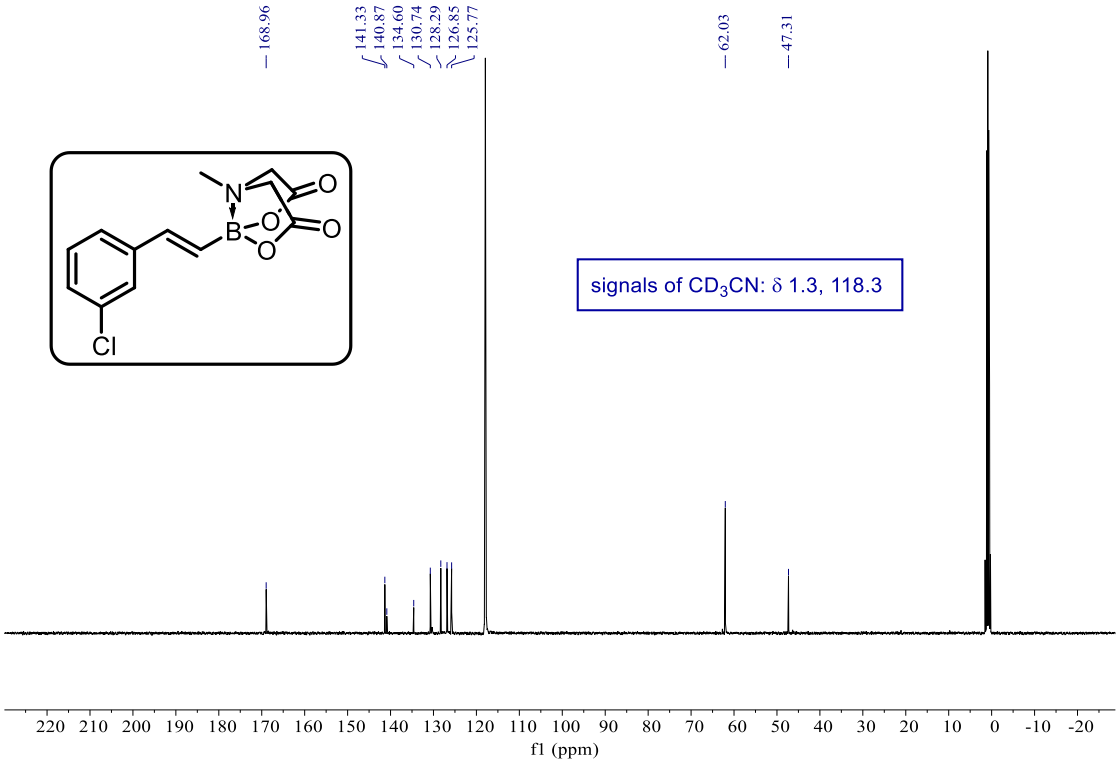


(*E*)-8-(3-chlorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**21**)

^{1}H NMR (400 MHz, CD_3CN)

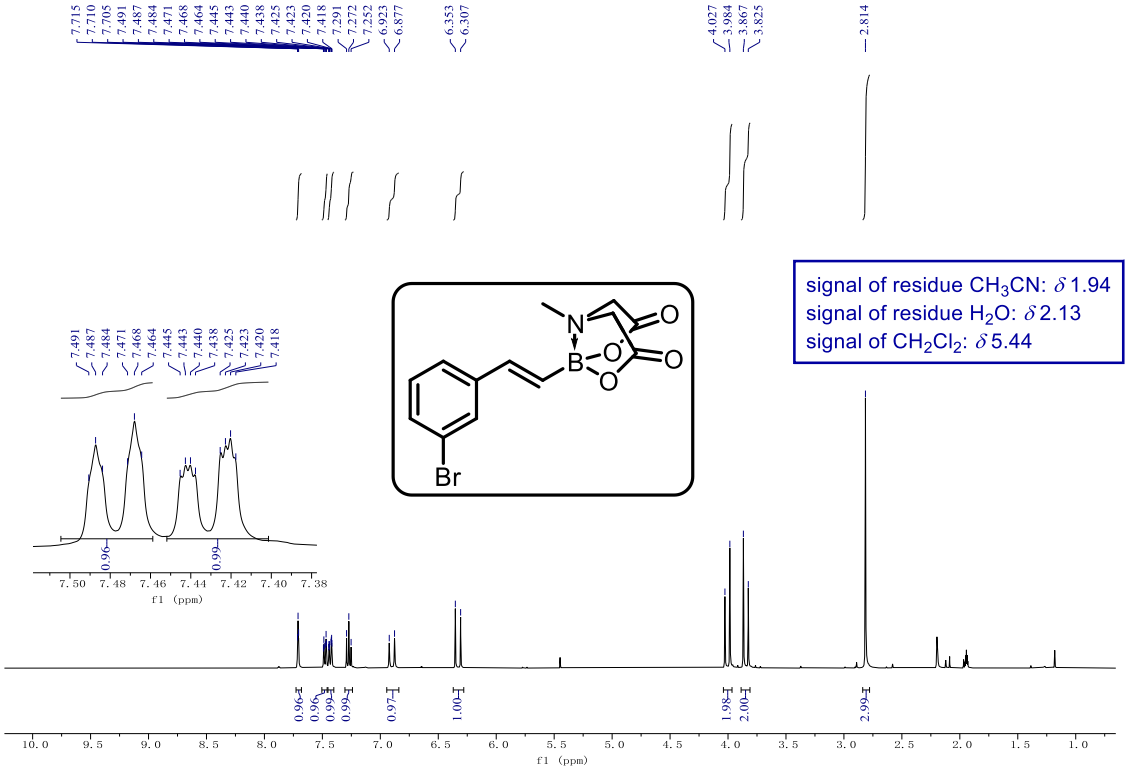


^{13}C{1H} NMR (100 MHz, CD_3CN)

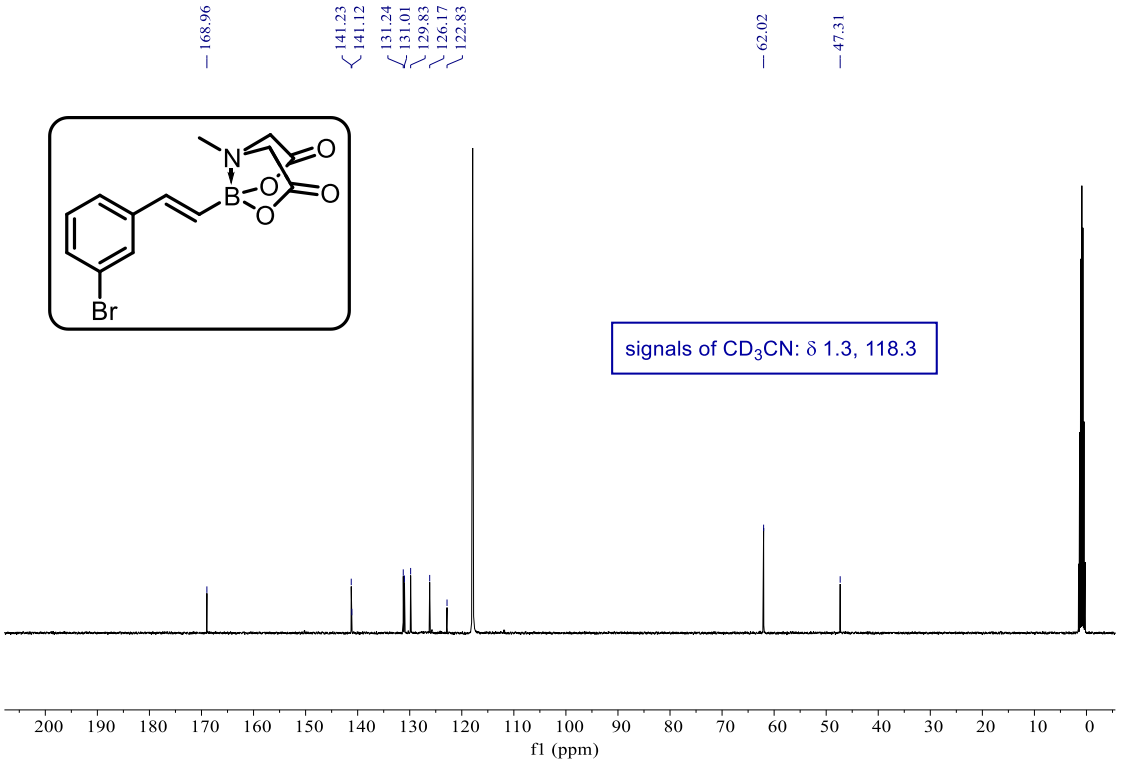


(*E*)-8-(3-bromostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**22**)

^{1}H NMR (400 MHz, CD_3CN)

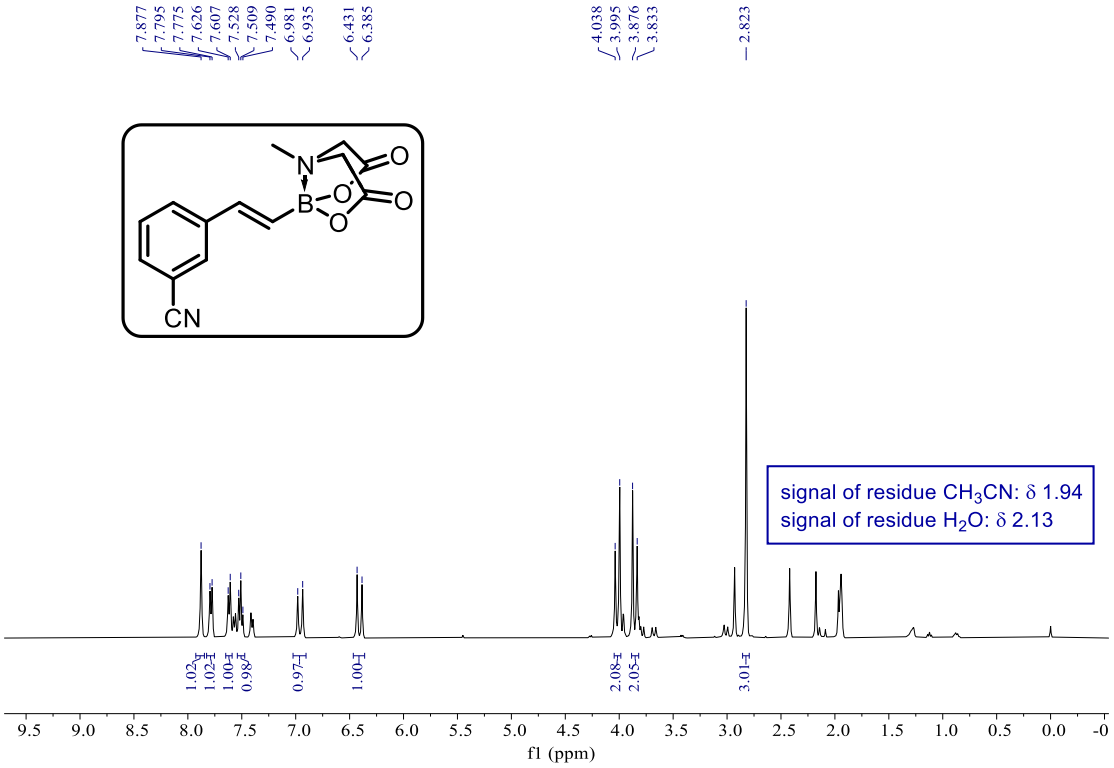


^{13}C{1H} NMR (100 MHz, CD_3CN)

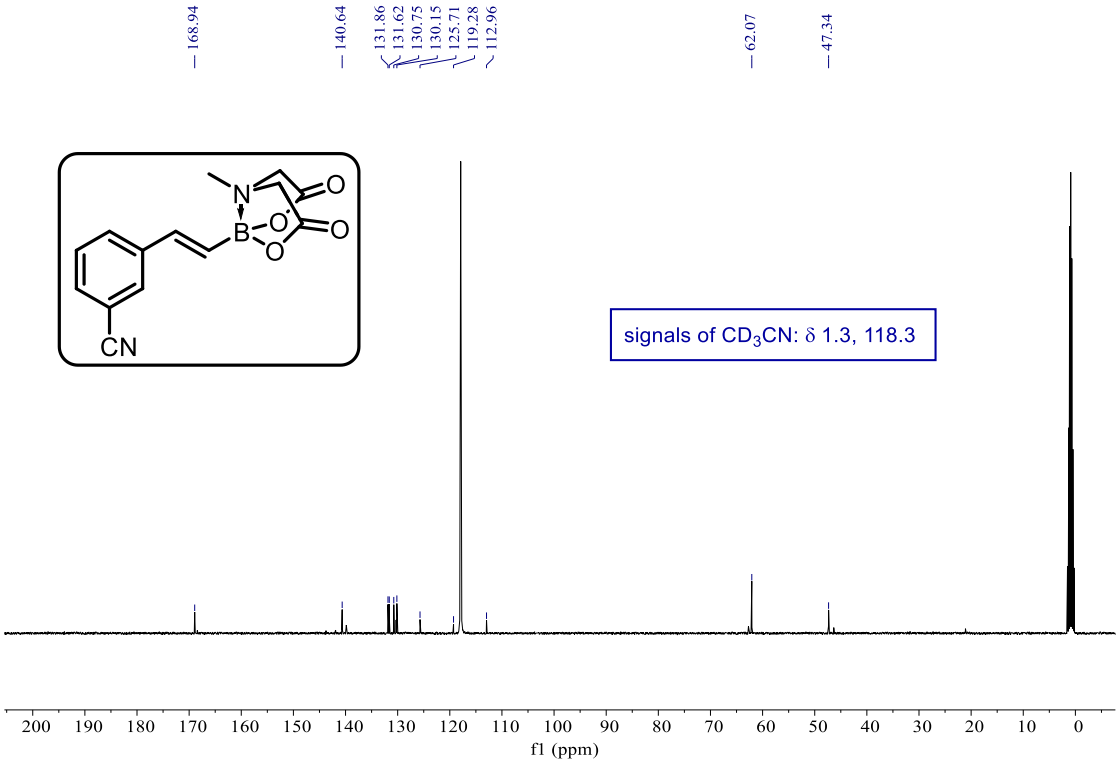


(*E*)-3-(2-(4-methyl-2,6-dioxotetrahydro-2*H*-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)vinyl)benzonitrile (**23**)

^{1}H NMR (400 MHz, CD_3CN)

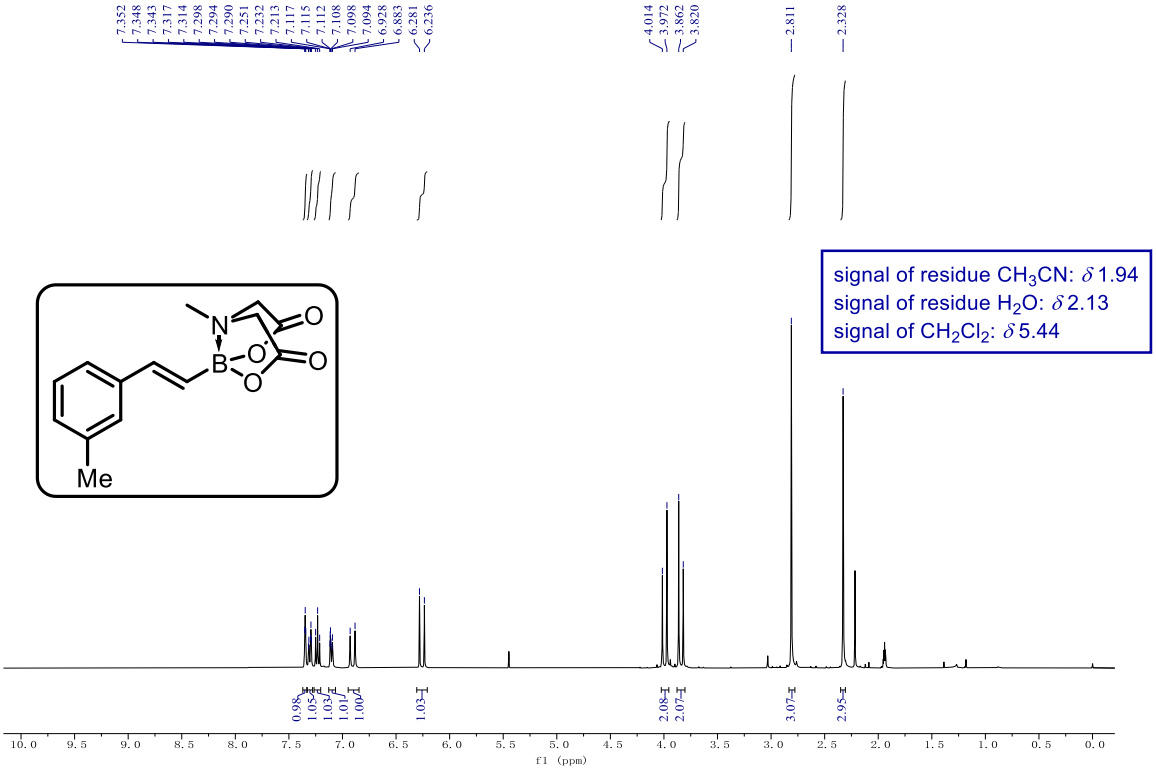


^{13}C{1H} NMR (100 MHz, CD_3CN)

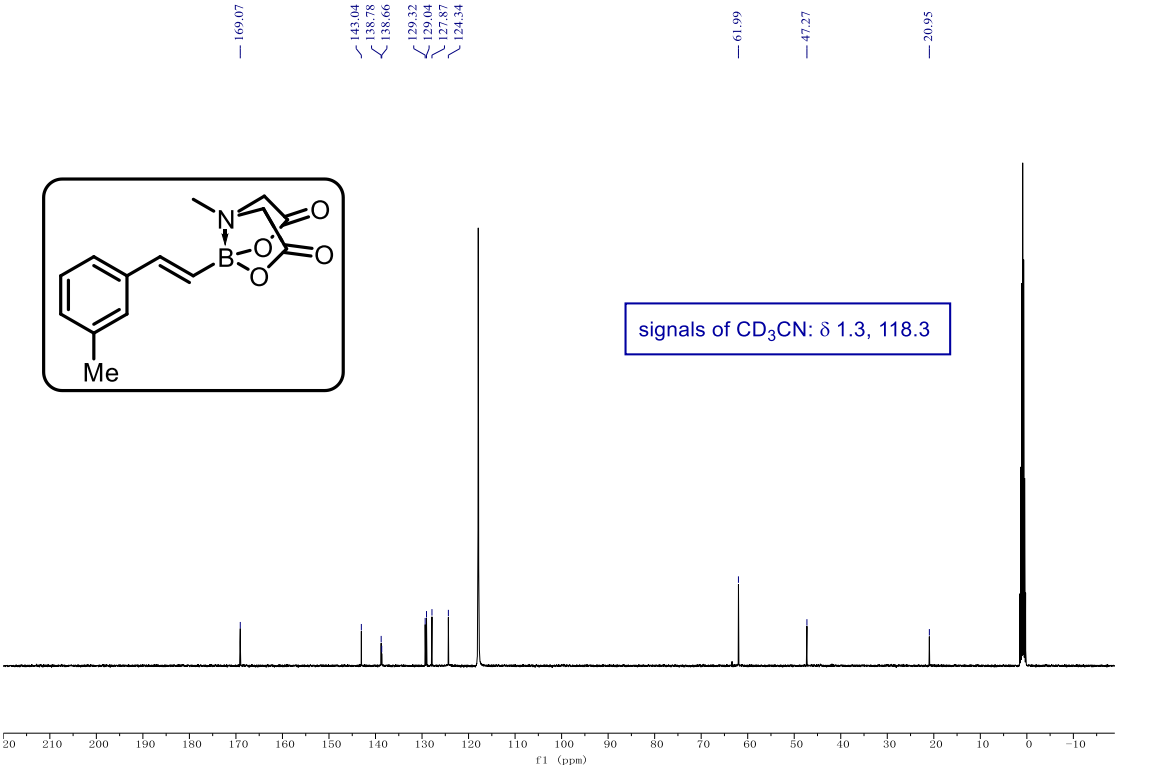


(*E*)-4-methyl-8-(3-methylstyryl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**24**)

^{1}H NMR (400 MHz, CD_3CN)

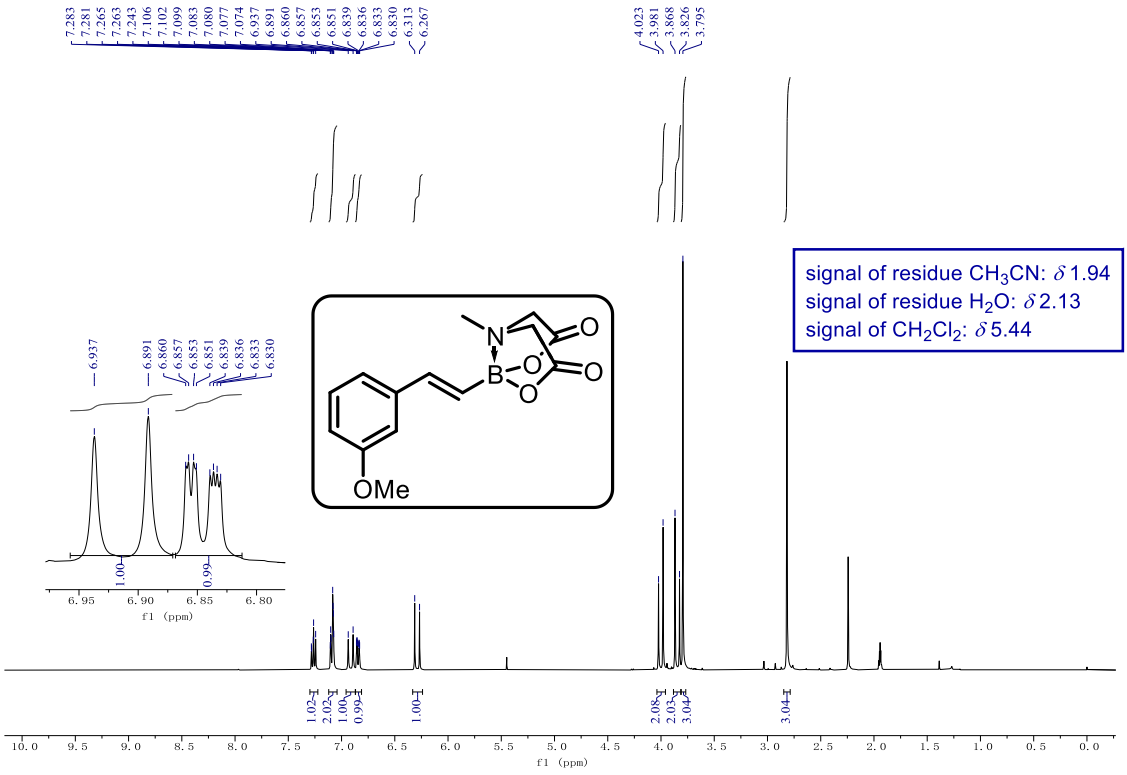


^{13}C{1H} NMR (100 MHz, CD_3CN)

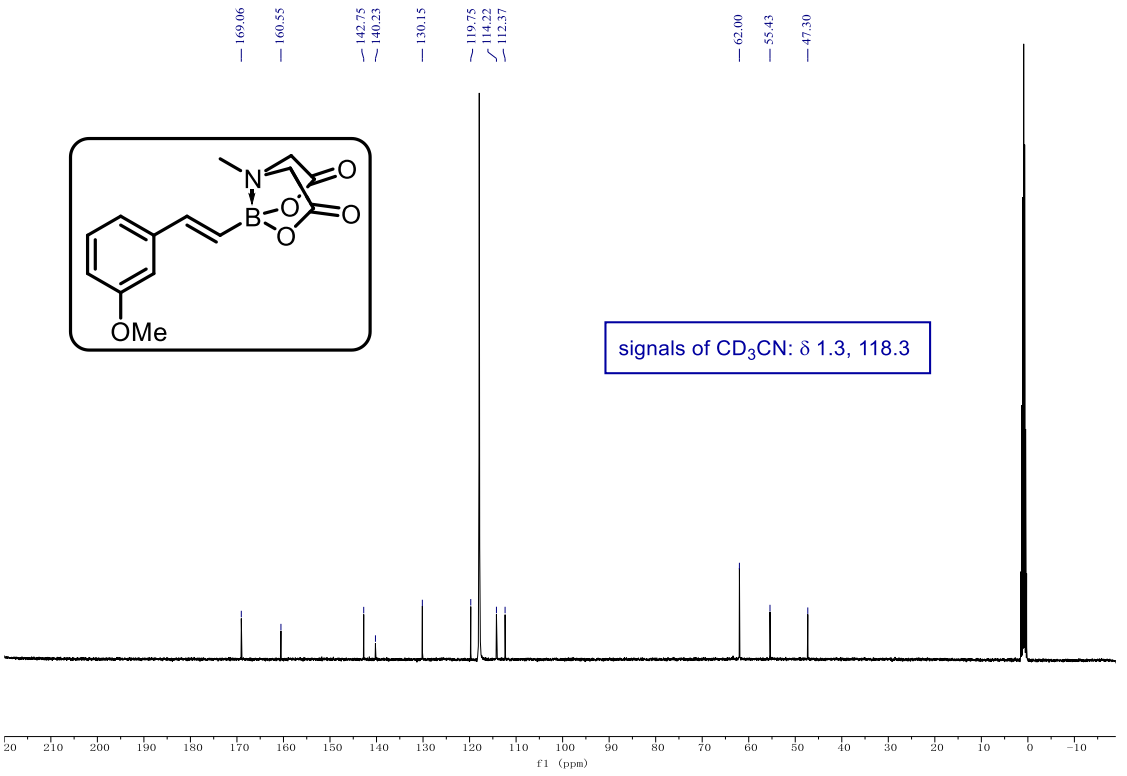


(*E*)-8-(3-methoxystyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**25**)

^{1}H NMR (400 MHz, CD_3CN)

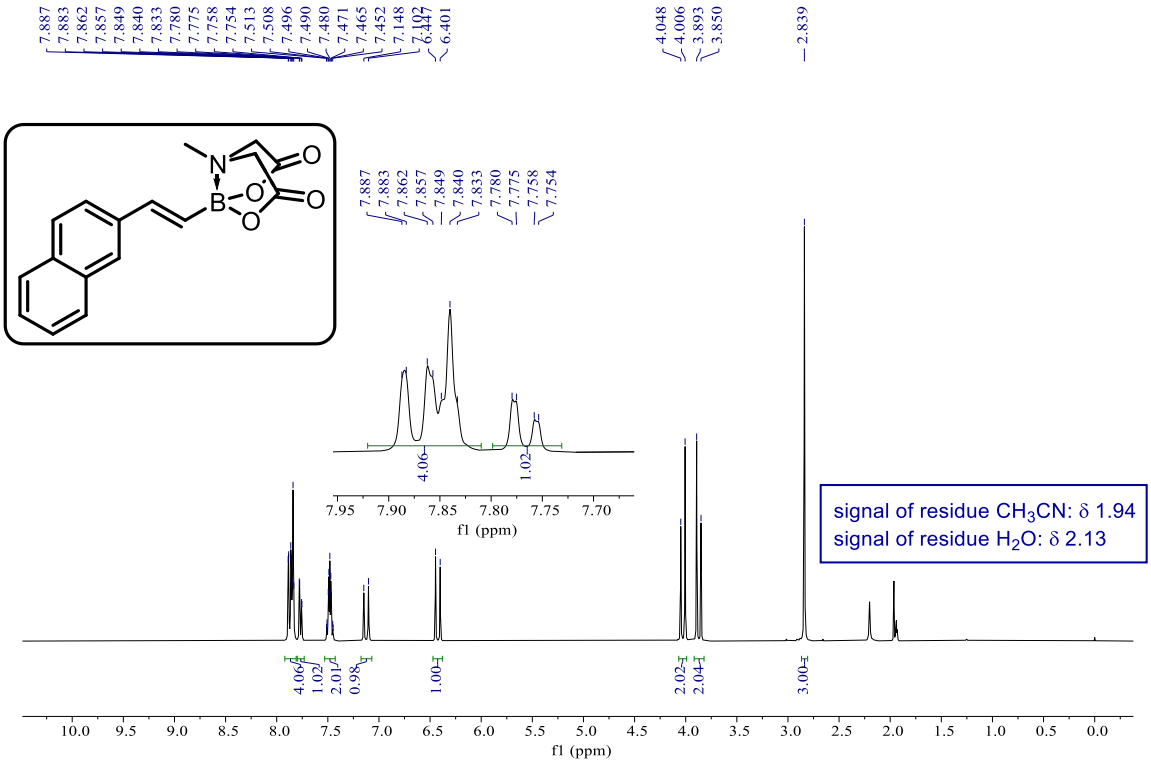


^{13}C{1H} NMR (100 MHz, CD_3CN)

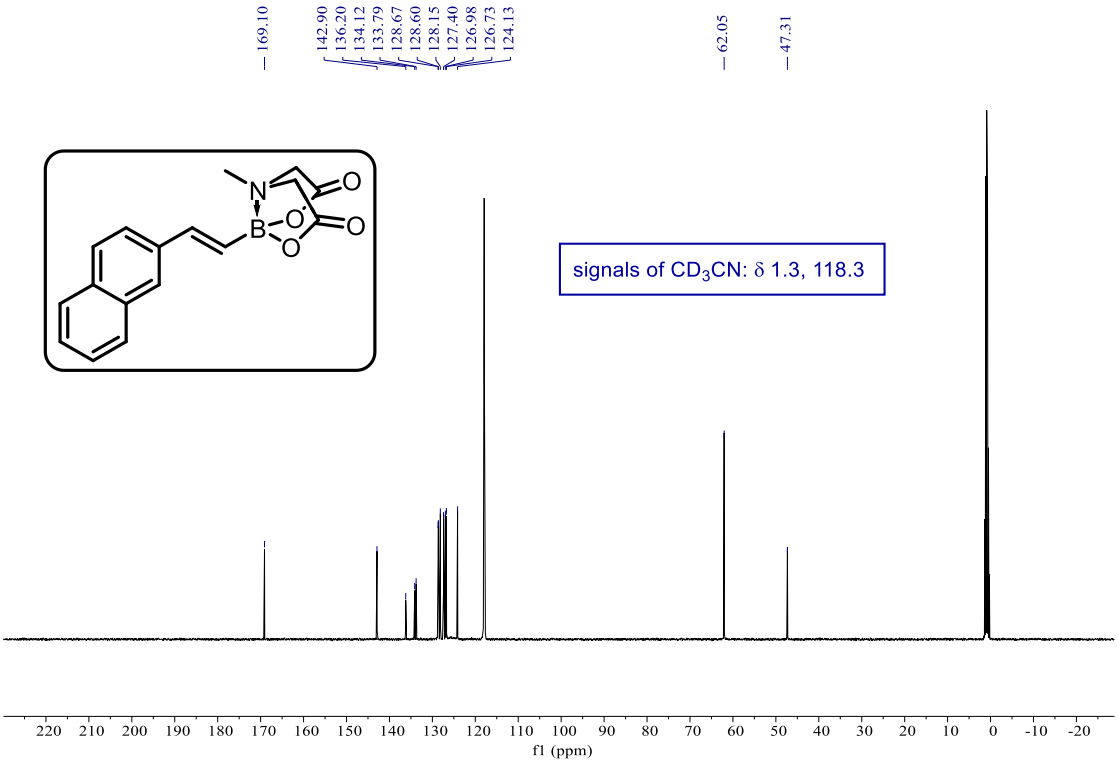


(*E*)-4-methyl-8-(2-(naphthalen-2-yl)vinyl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**26**)

^{1}H NMR (400 MHz, CD_3CN)

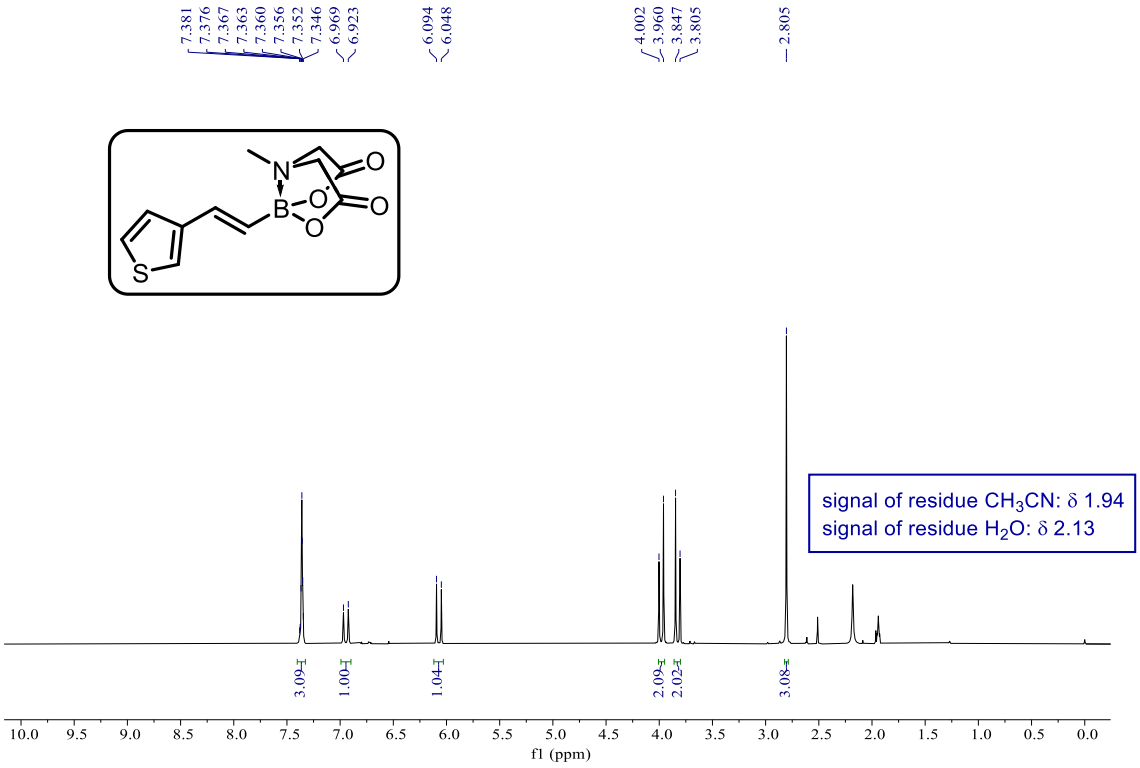


^{13}C{1H} NMR (100 MHz, CD_3CN)

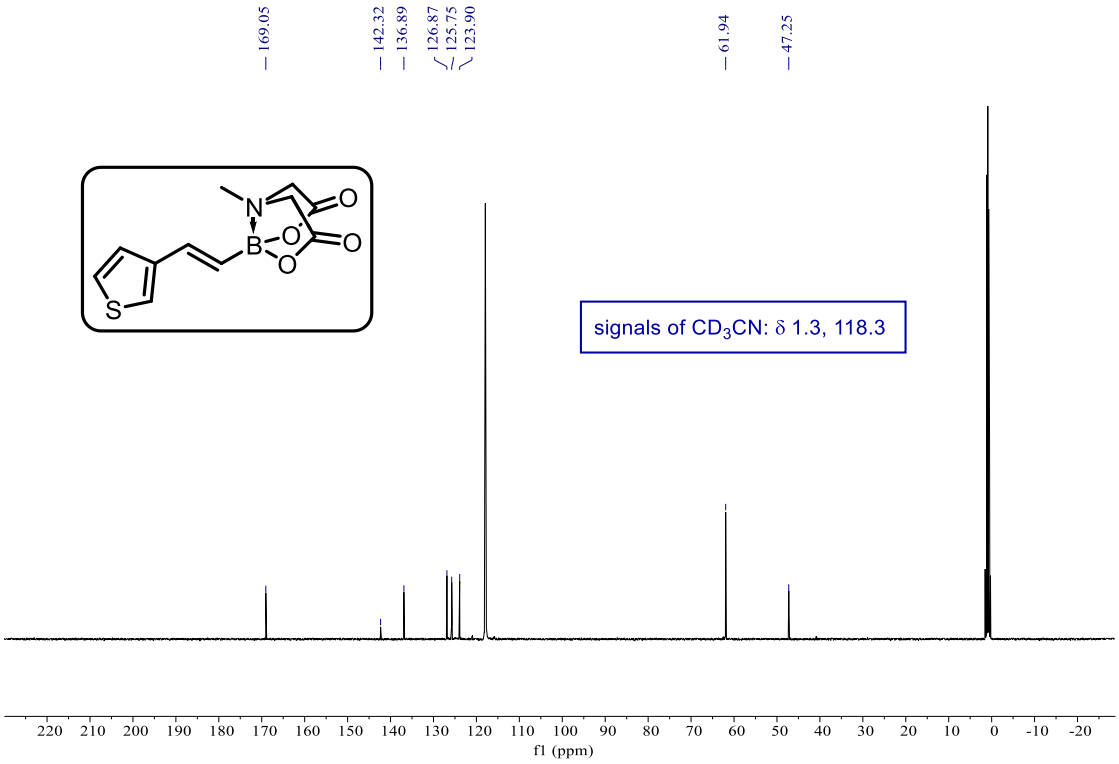


(*E*)-4-methyl-8-(2-(thiophen-3-yl)vinyl)dihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**27**)

^{1}H NMR (400 MHz, CD_3CN)

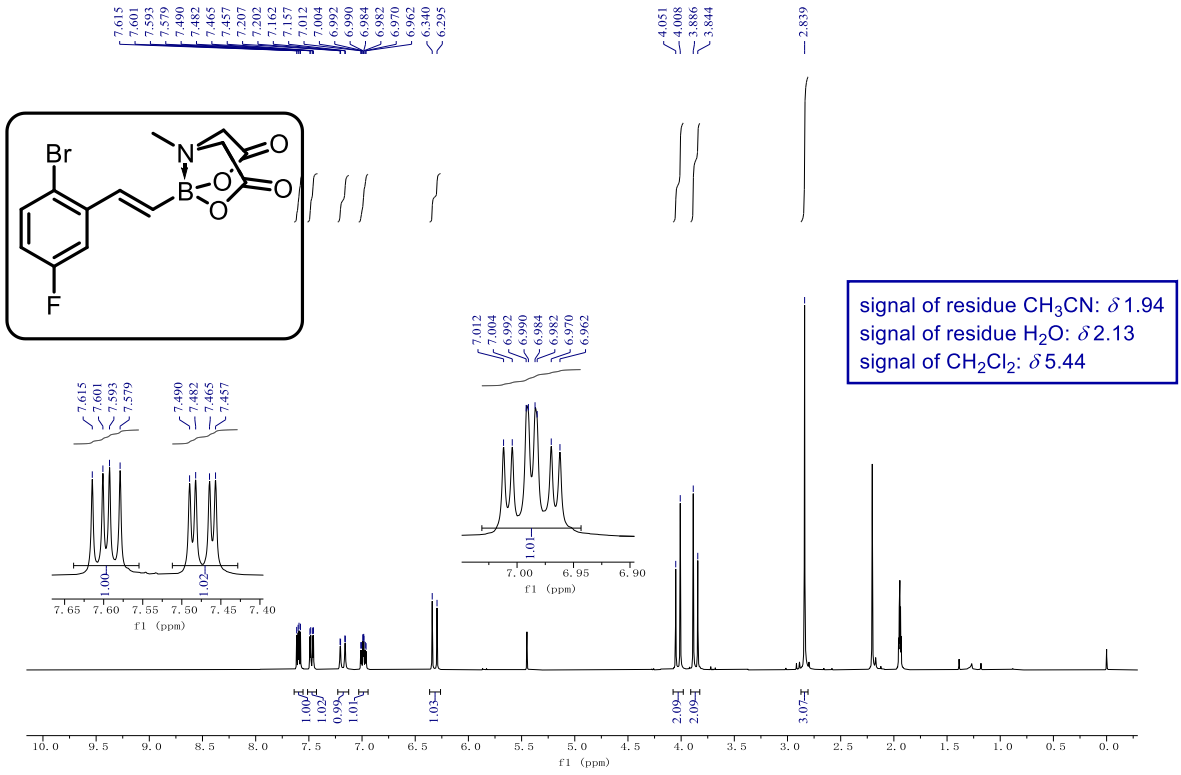


^{13}C{1H} NMR (100 MHz, CD_3CN)

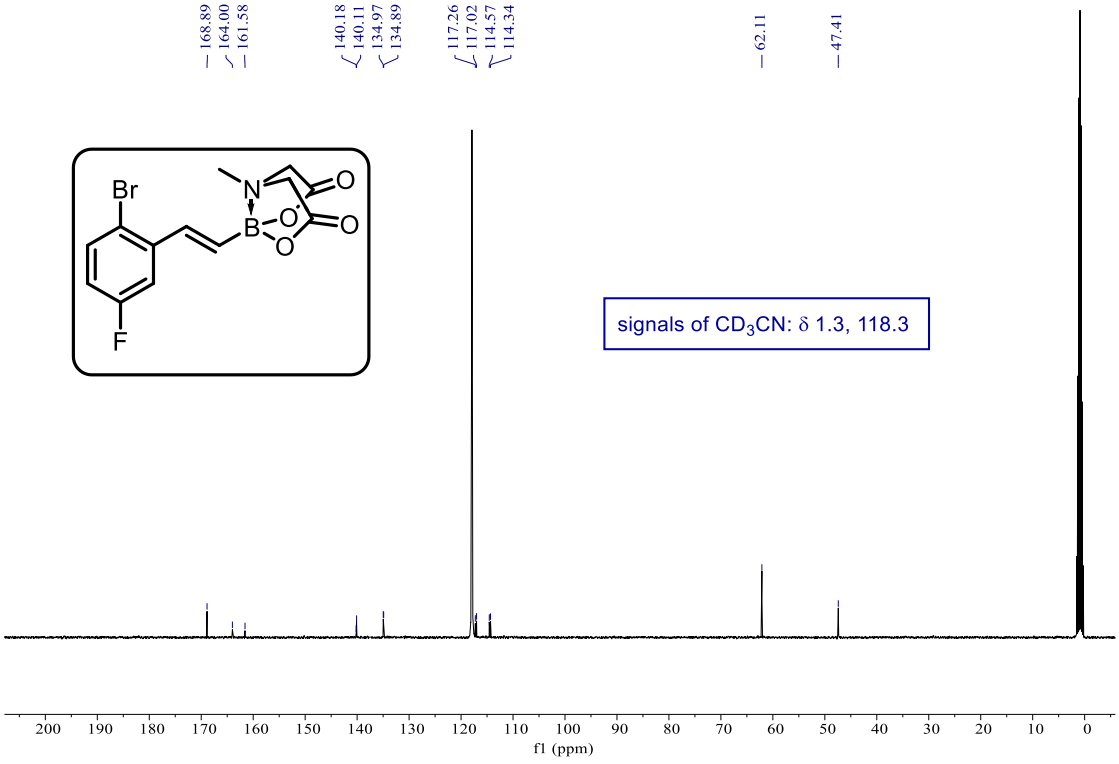


(*E*)-8-(2-bromo-5-fluorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**28**)

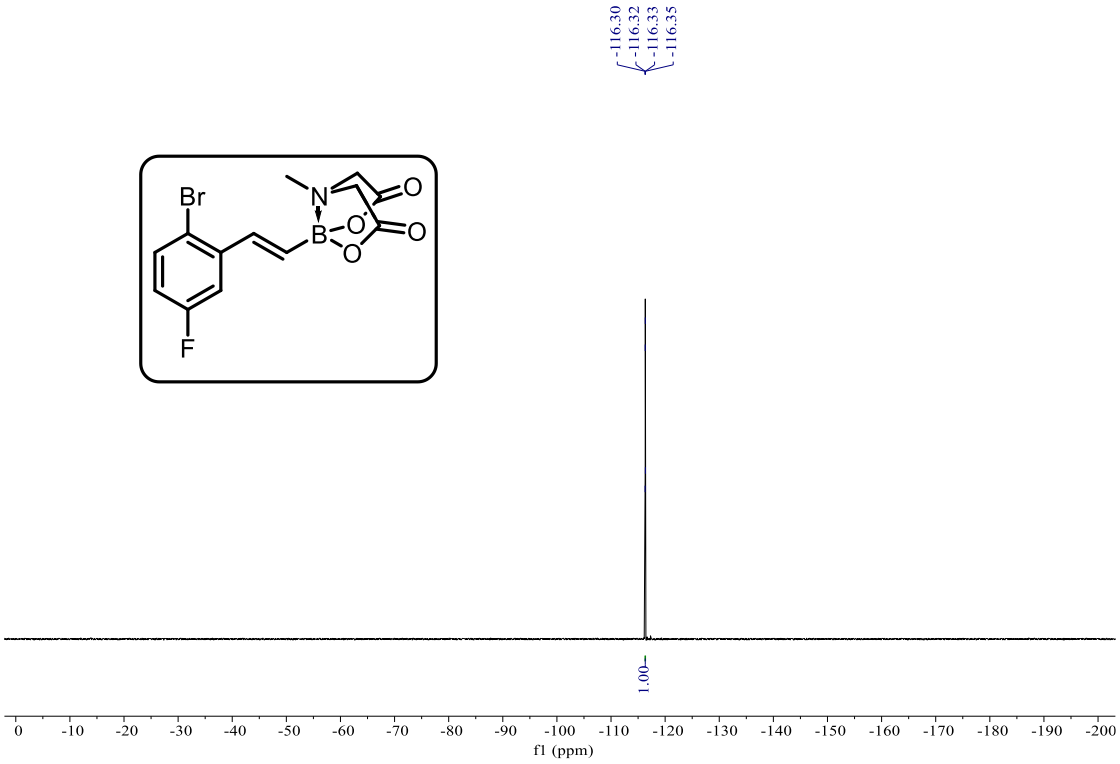
^{1}H NMR (400 MHz, CD_3CN)



^{13}C{1H} NMR (100 MHz, CD_3CN)

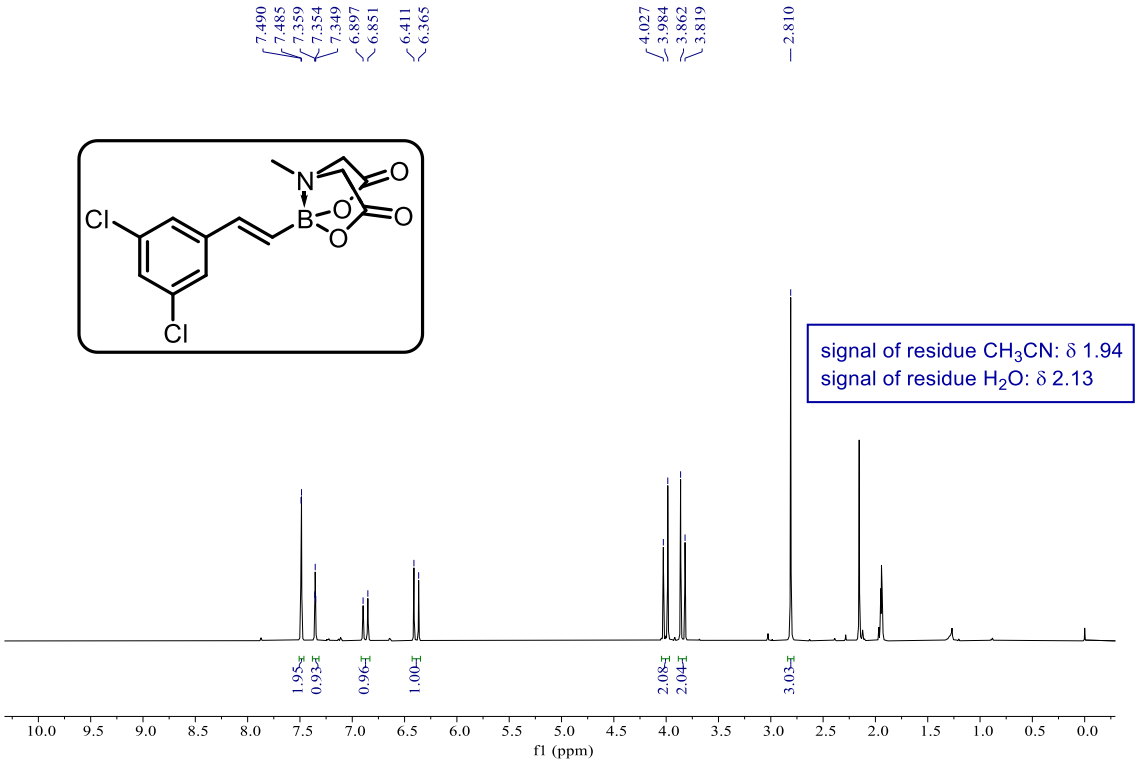


^{19}F NMR (471 MHz, CD_3CN)

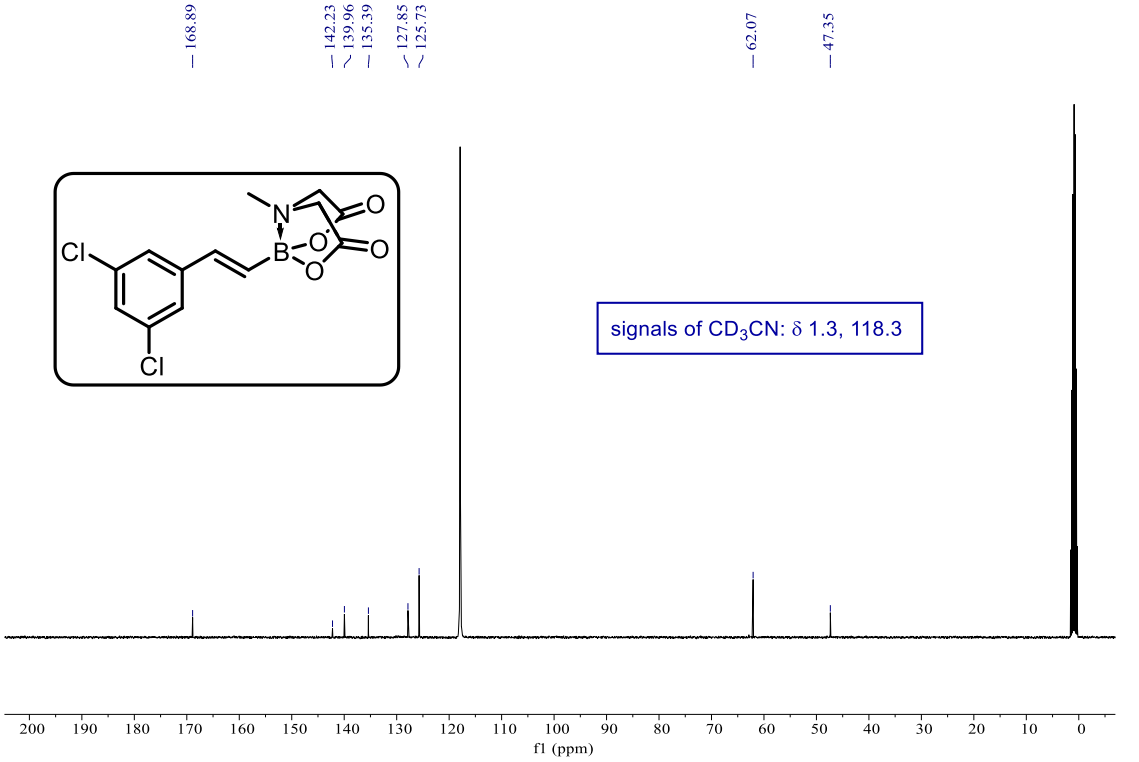


(*E*)-8-(3,5-dichlorostyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**29**)

^{1}H NMR (400 MHz, CD_3CN)

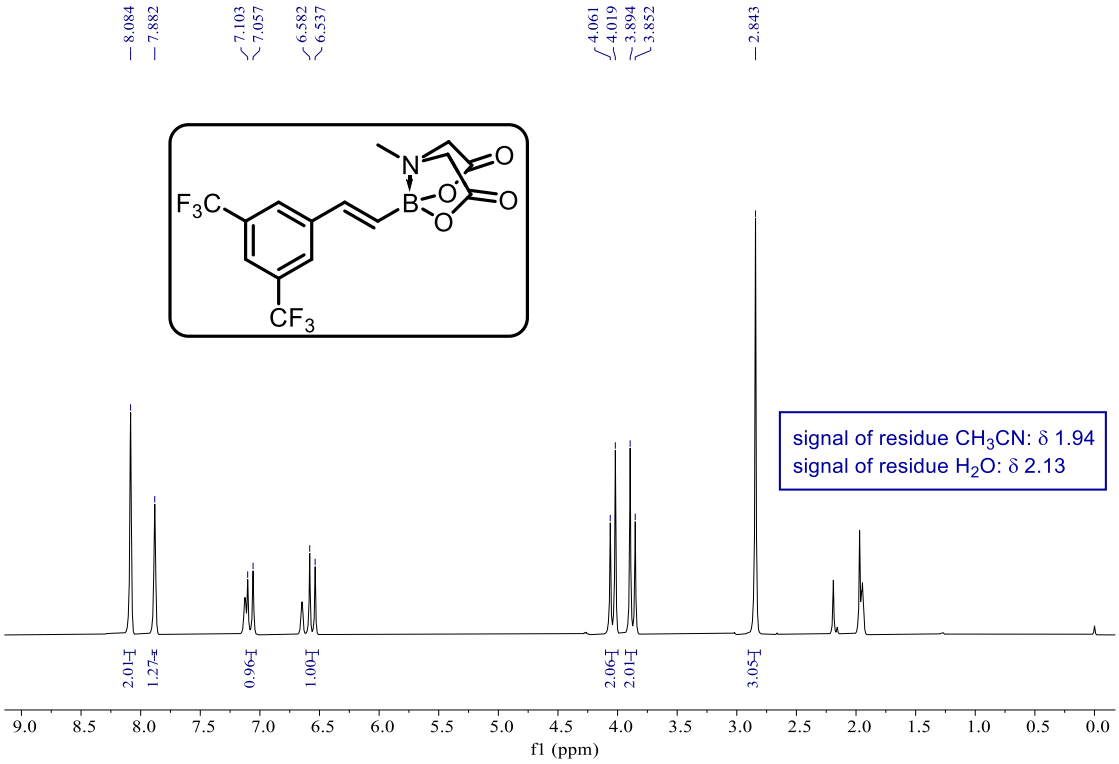


^{13}C{1H} NMR (100 MHz, CD_3CN)

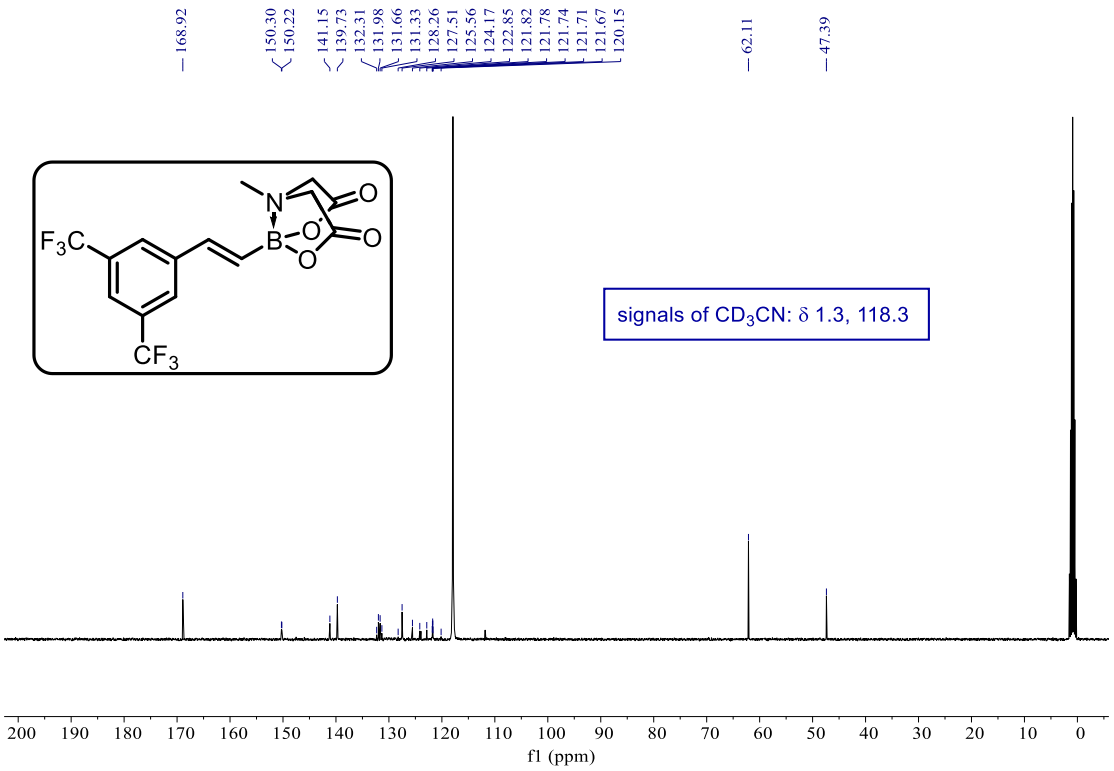


(*E*)-8-(3,5-bis(trifluoromethyl)styryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**30**)

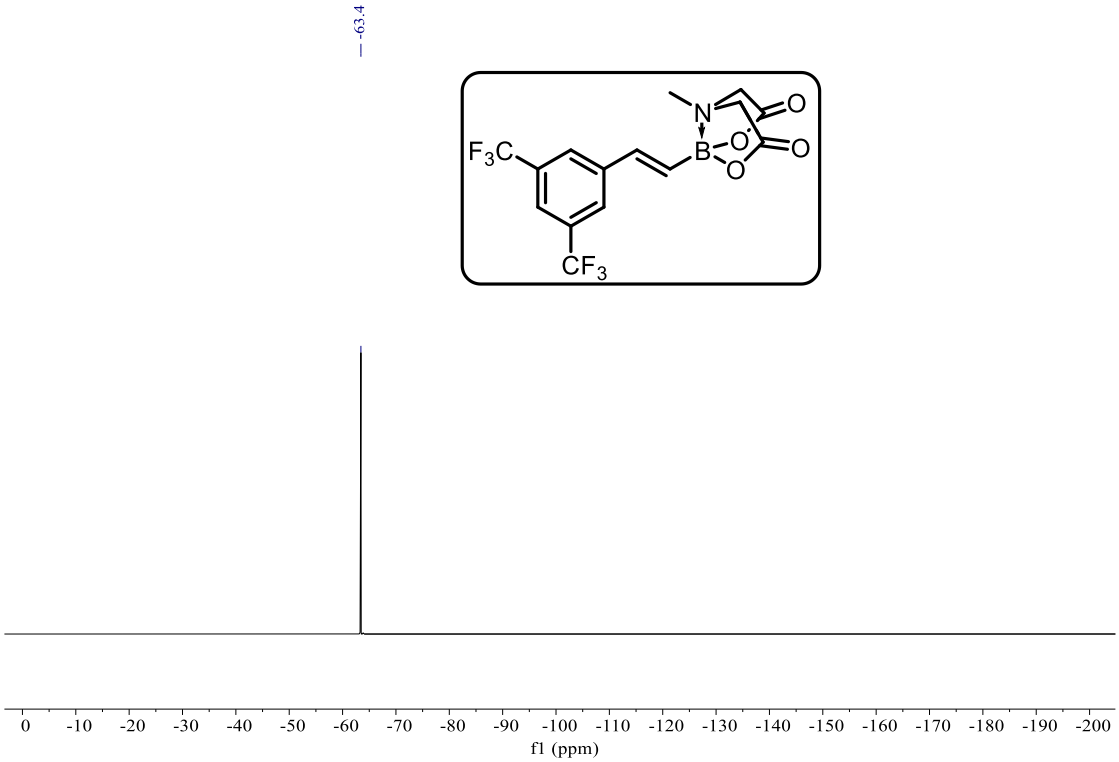
^{1}H NMR (400 MHz, CD_3CN)



^{13}C{1H} NMR (100 MHz, CD_3CN)

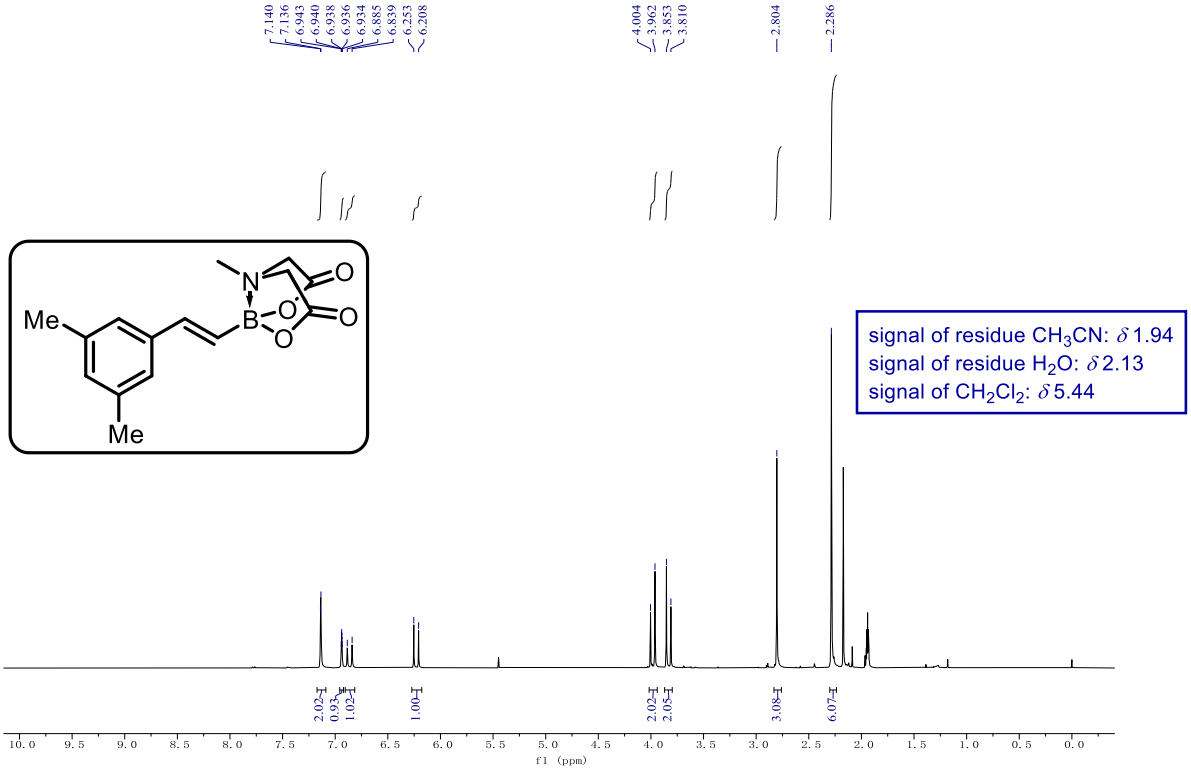


^{19}F NMR (471 MHz, CD_3CN)

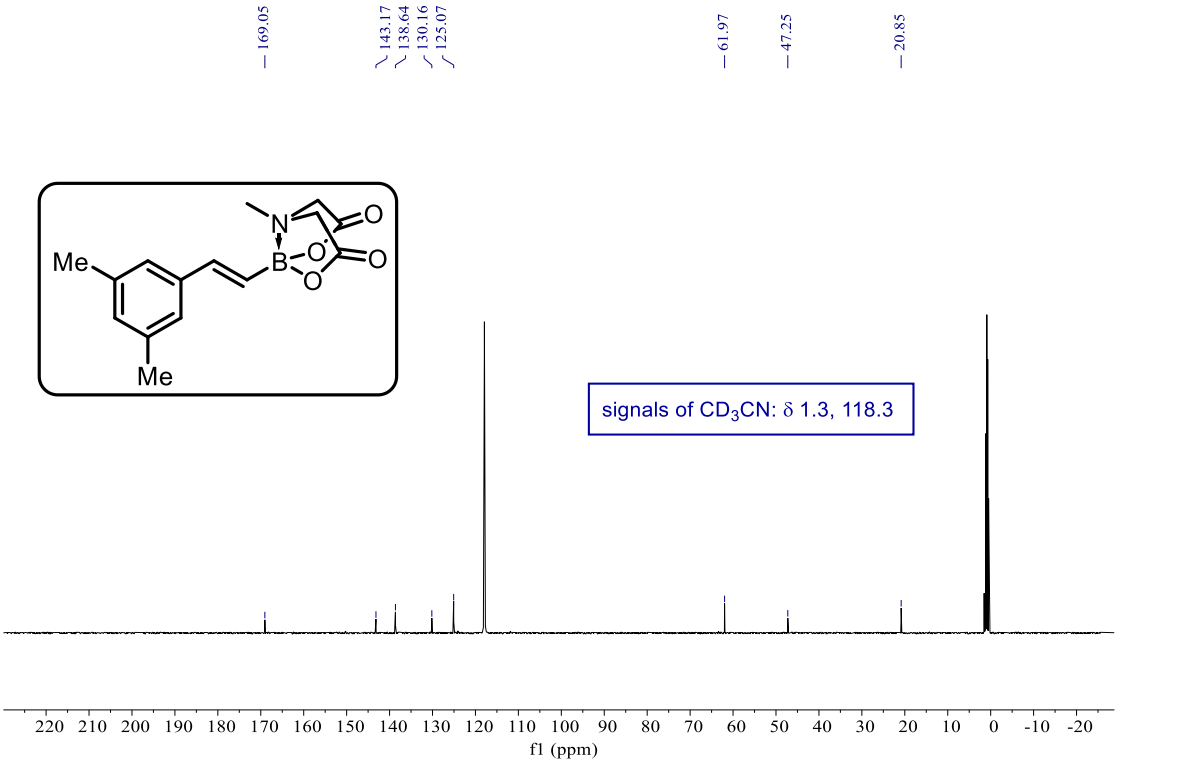


(*E*)-8-(3,5-dimethylstyryl)-4-methyldihydro-λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**31**)

^{1}H NMR (400 MHz, CD_3CN)

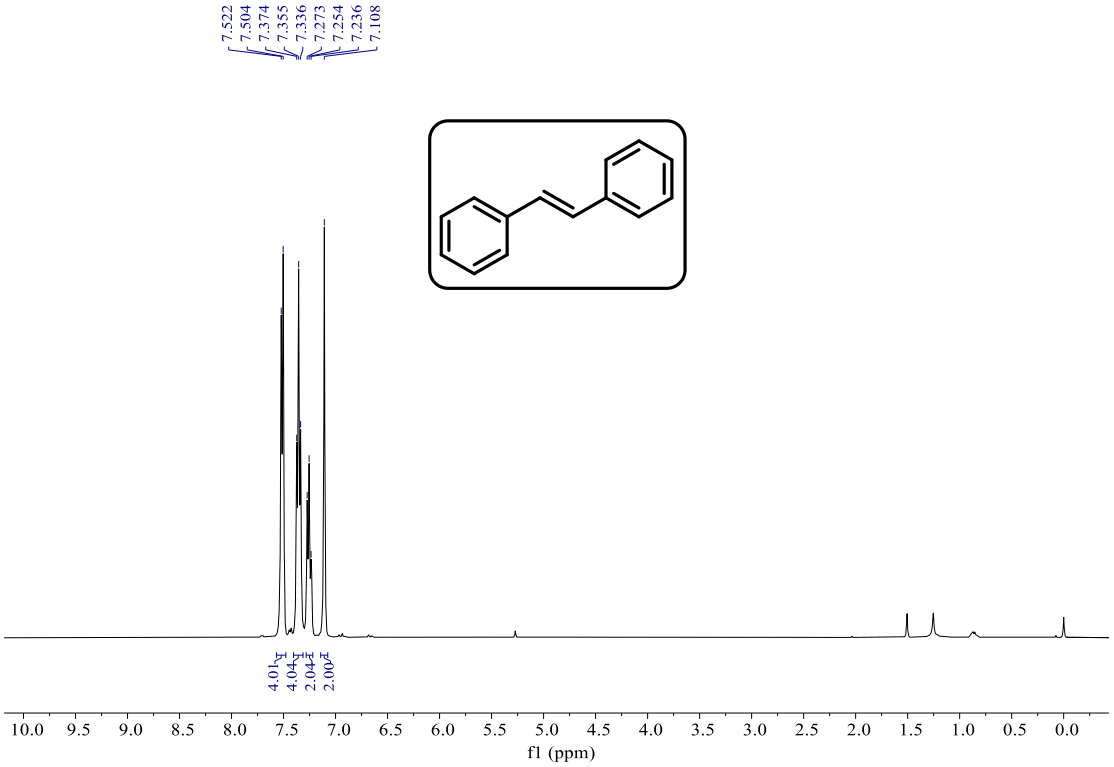


^{13}C{1H} NMR (100 MHz, CD_3CN)

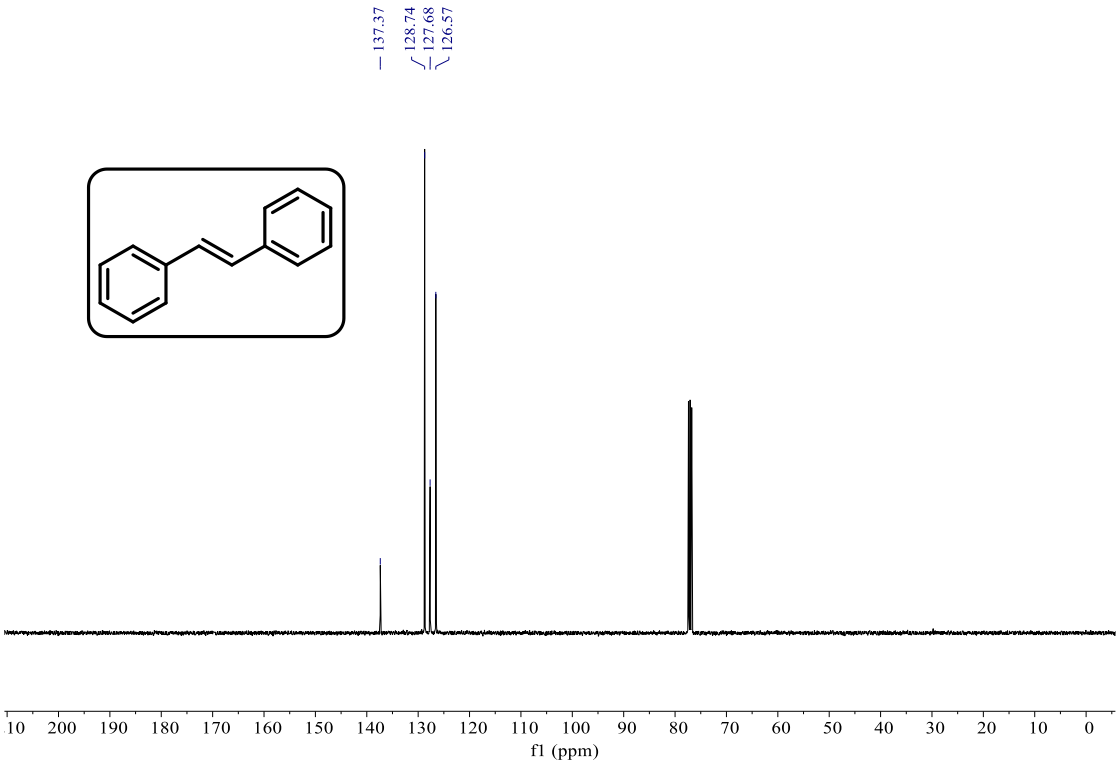


(*E*)-1,2-diphenylethene (**32**)

^{1}H NMR (400 MHz, $CDCl_3$)

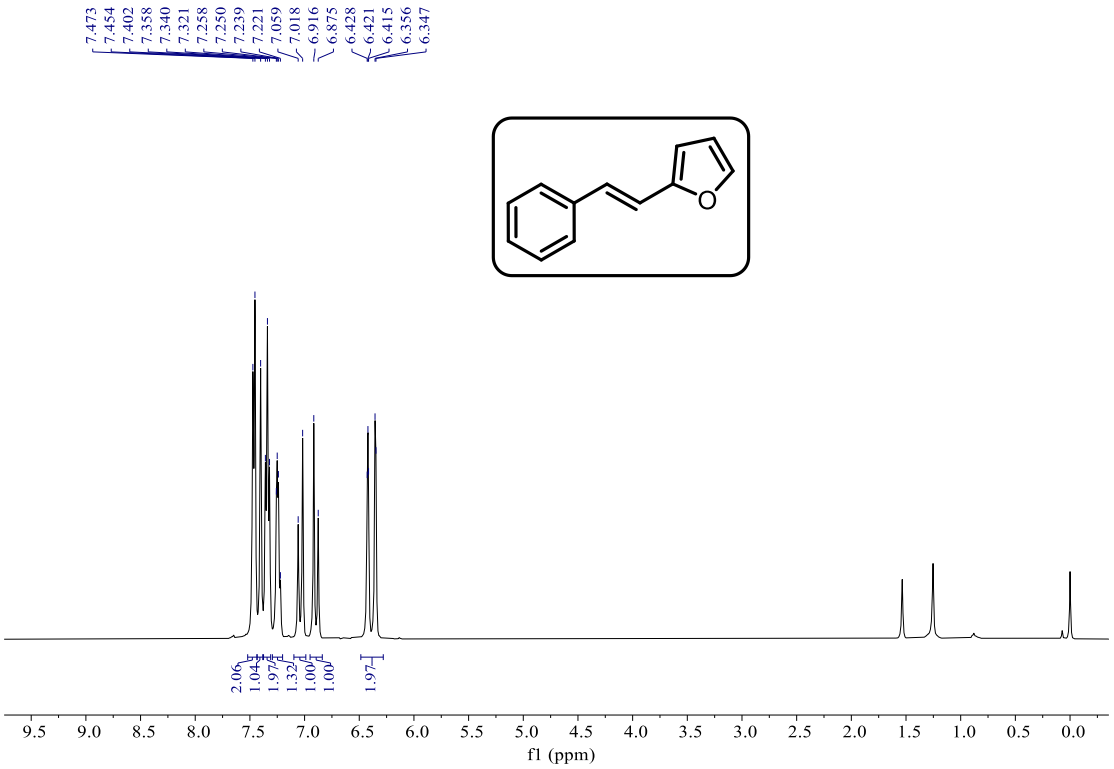


^{13}C{1H} NMR (100 MHz, $CDCl_3$)

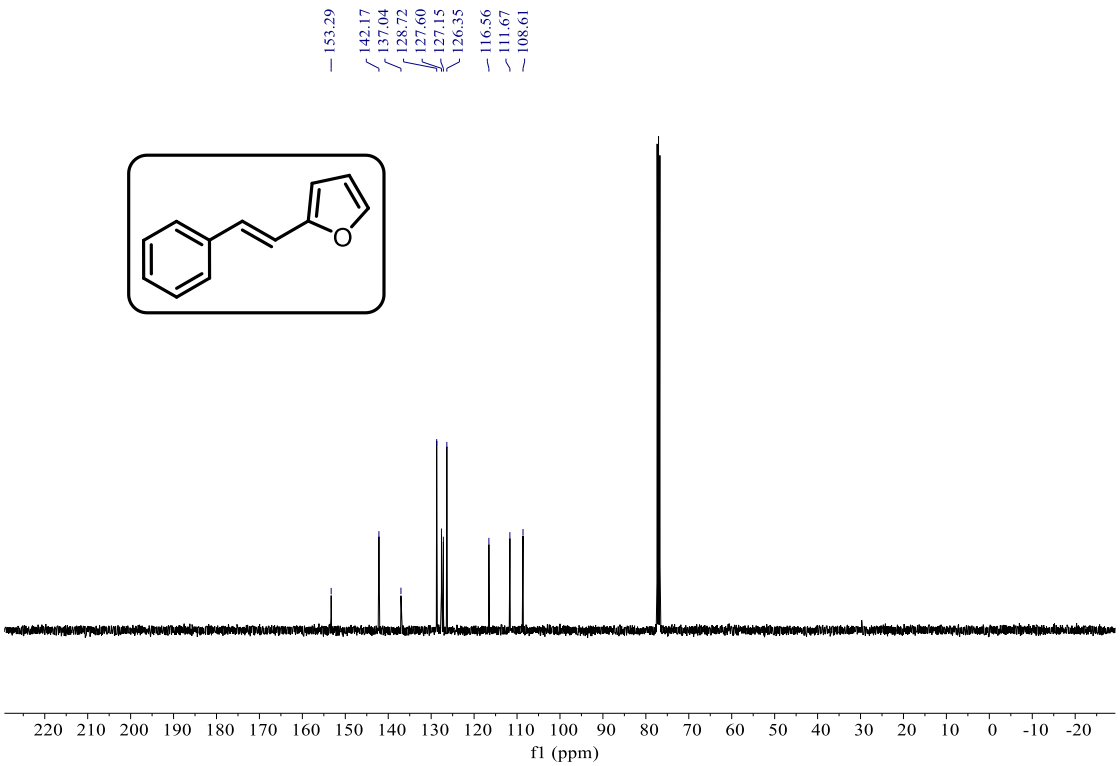


(*E*)-2-Styrylfuran (**33**)

^{1}H NMR (400 MHz, $CDCl_3$)

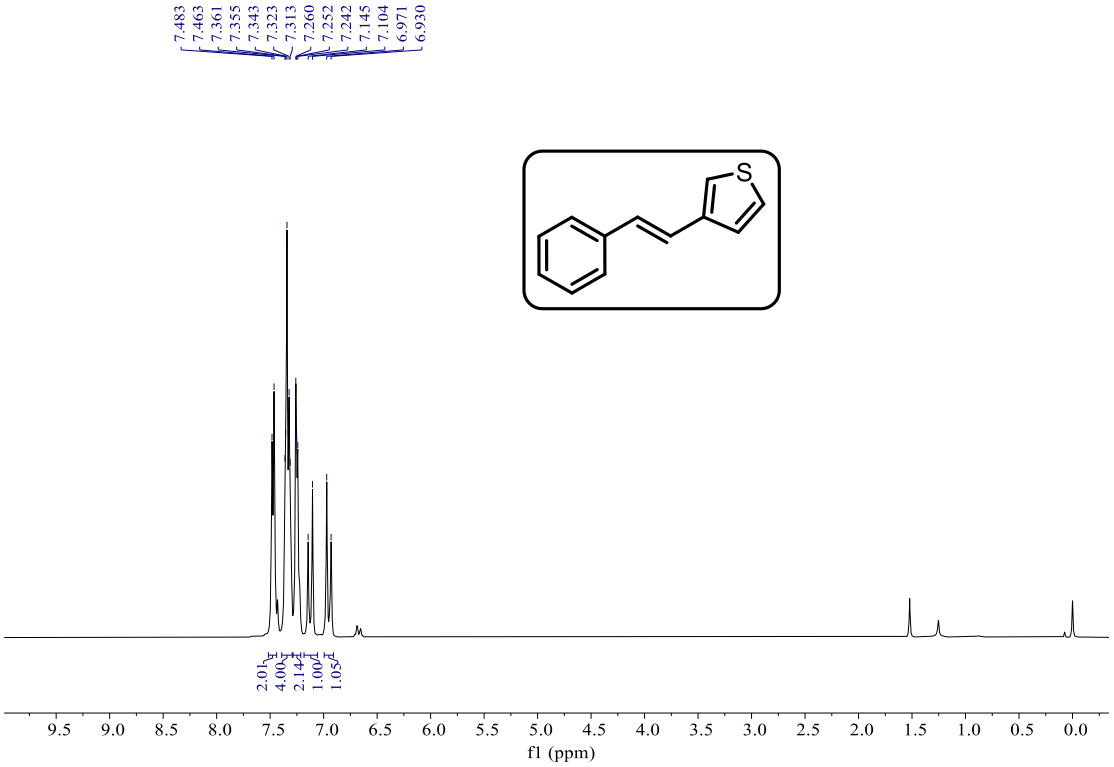


^{13}C{1H} NMR (100 MHz, $CDCl_3$)

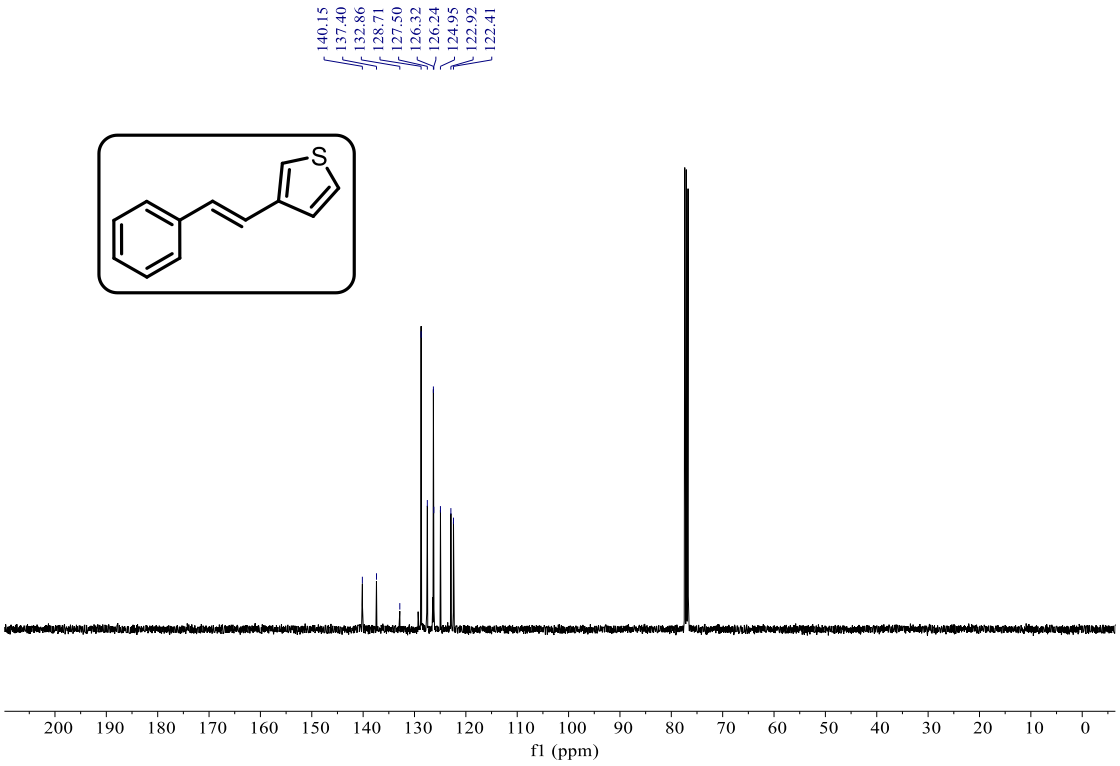


(*E*)-3-styrylthiophene (**34**)

^{1}H NMR (400 MHz, $CDCl_3$)

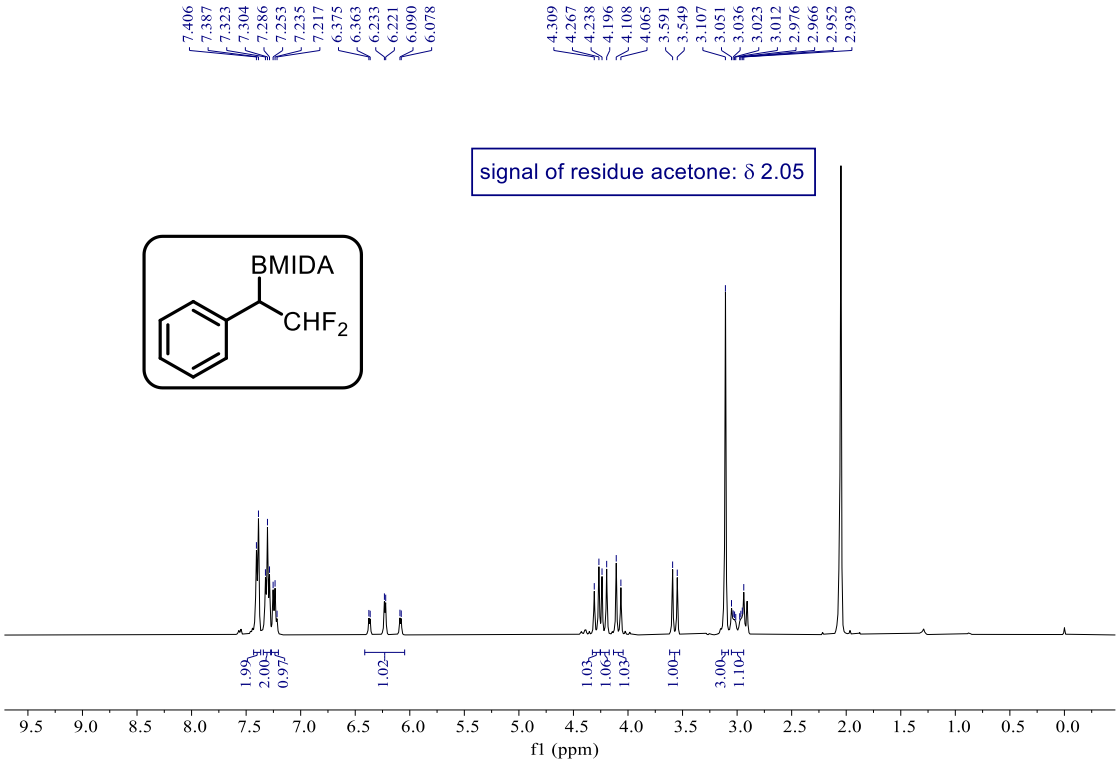


^{13}C{1H} NMR (100 MHz, $CDCl_3$)

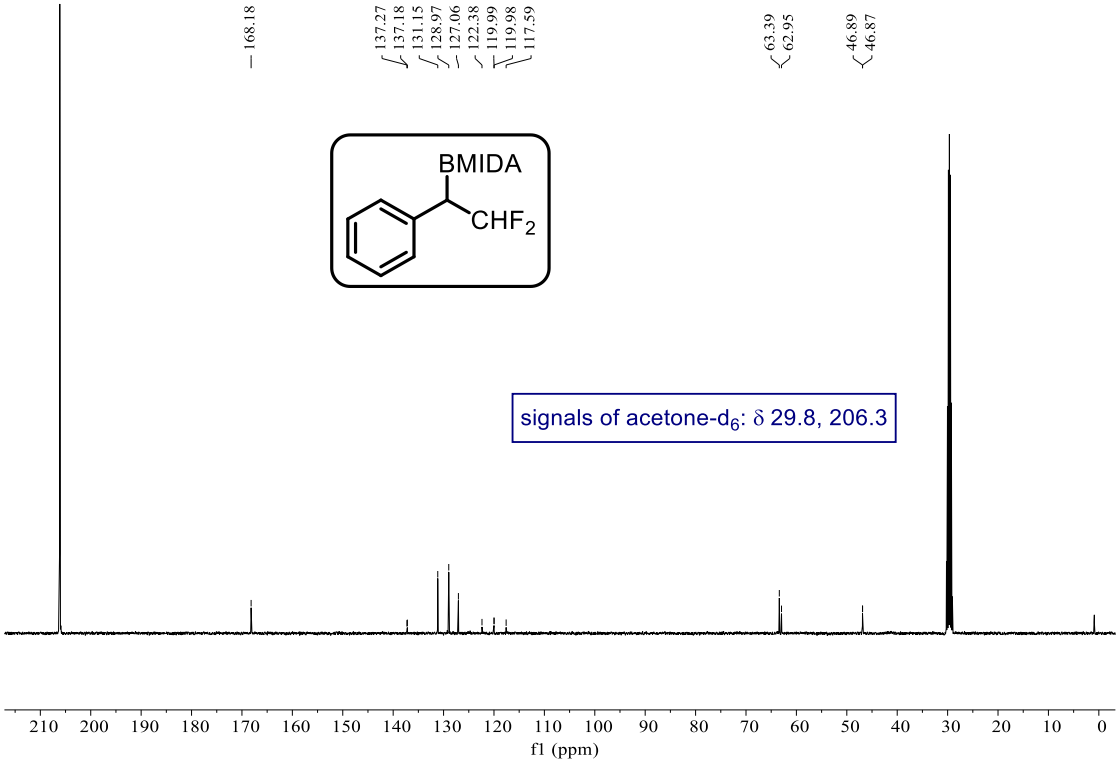


8-(2,2-difluoro-1-phenylethyl)-4-methyldihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**35**)

^{1}H NMR (400 MHz, acetone-d_6)

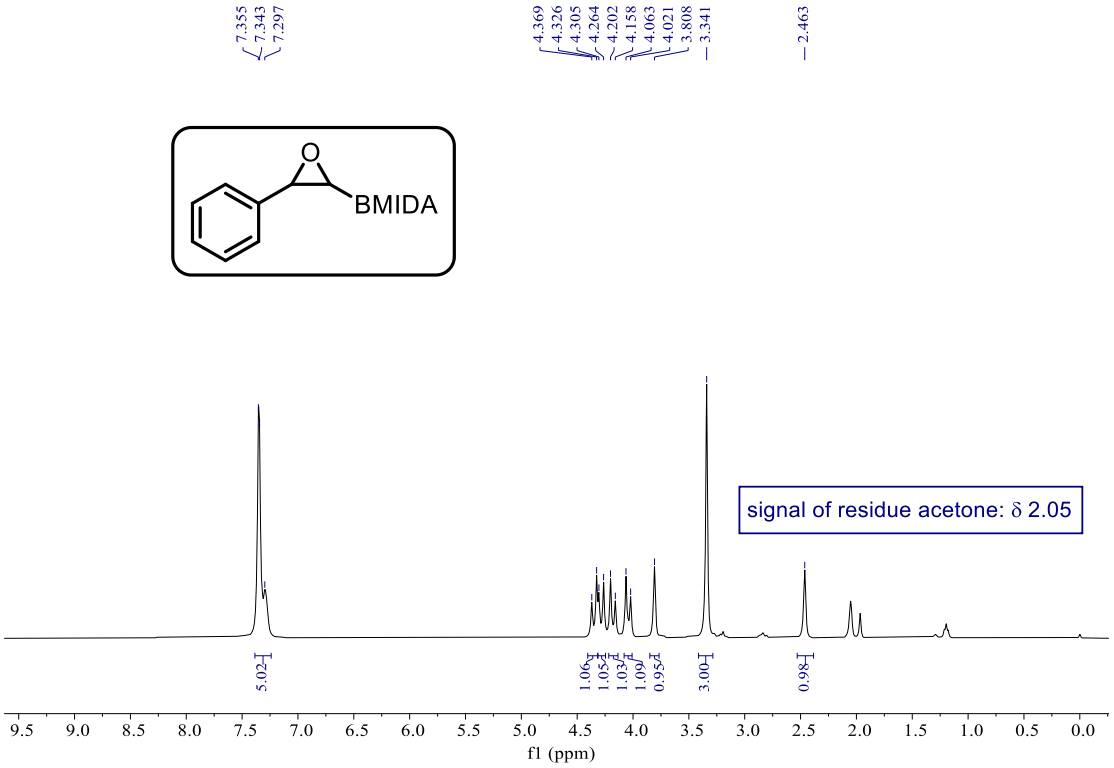


^{13}C{1H} NMR (100 MHz, acetone-d_6)

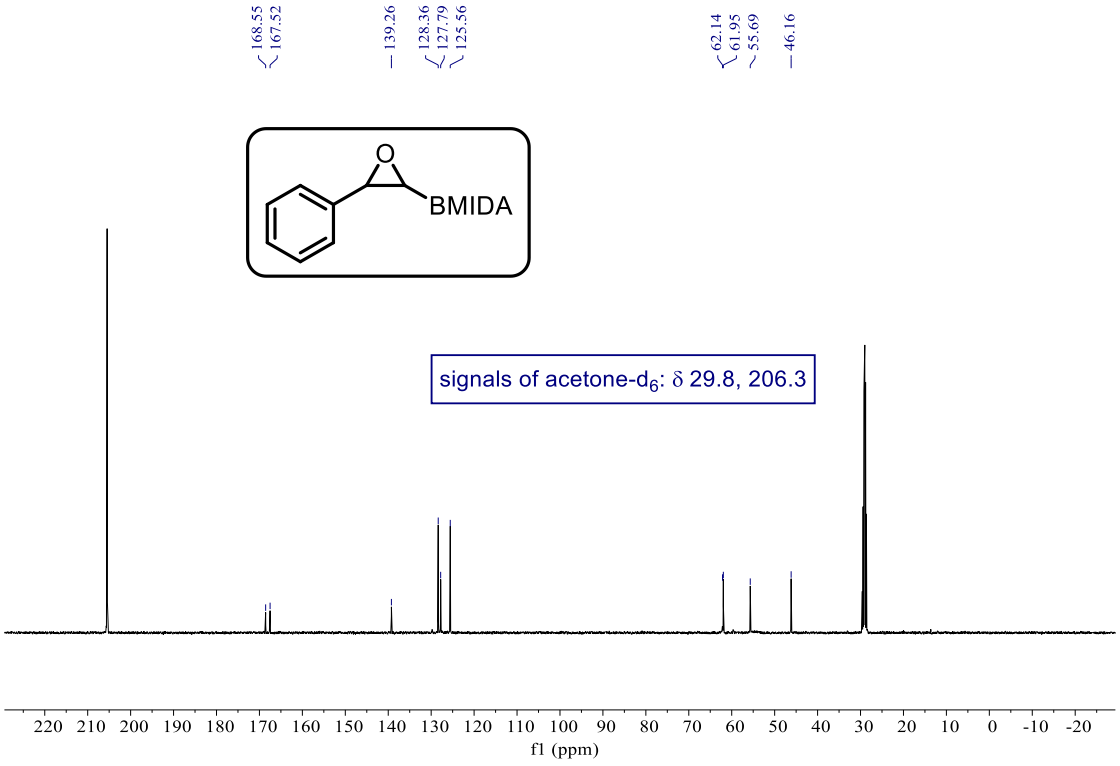


4-methyl-8-(3-phenyloxiran-2-yl)dihydro-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborole-2,6(3*H*,5*H*)-dione (**36**)

^{1}H NMR (400 MHz, acetone-d_6)

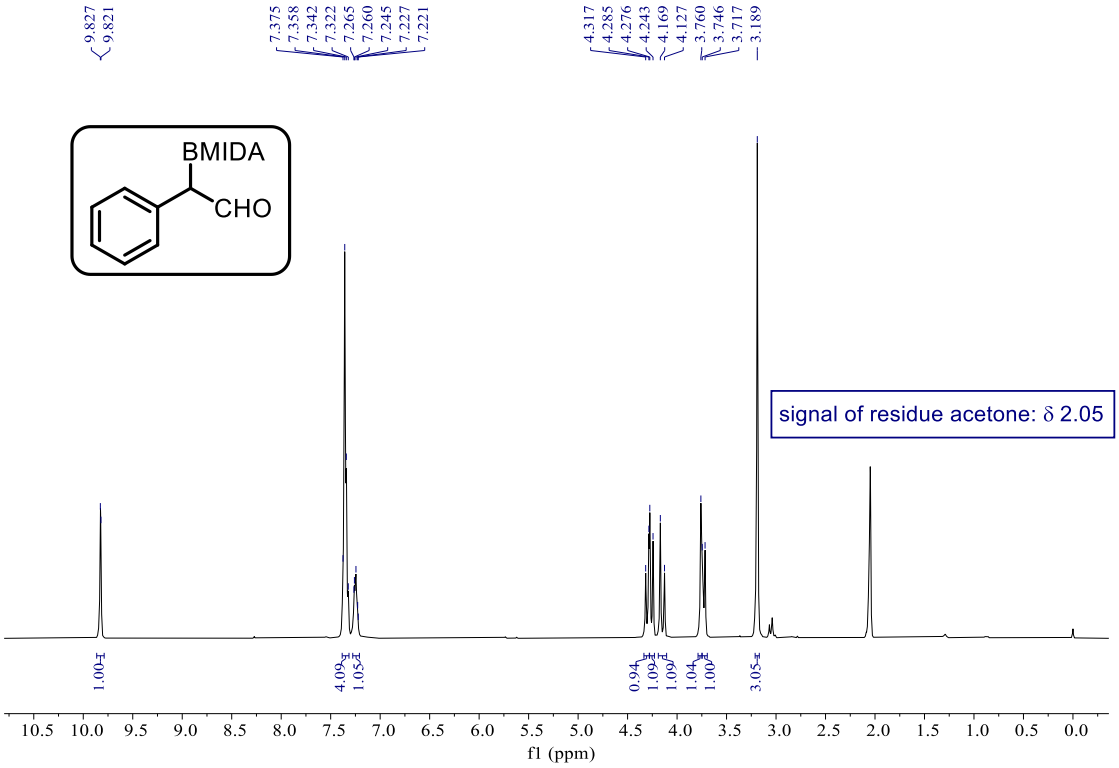


^{13}C{1H} NMR (100 MHz, acetone-d_6)

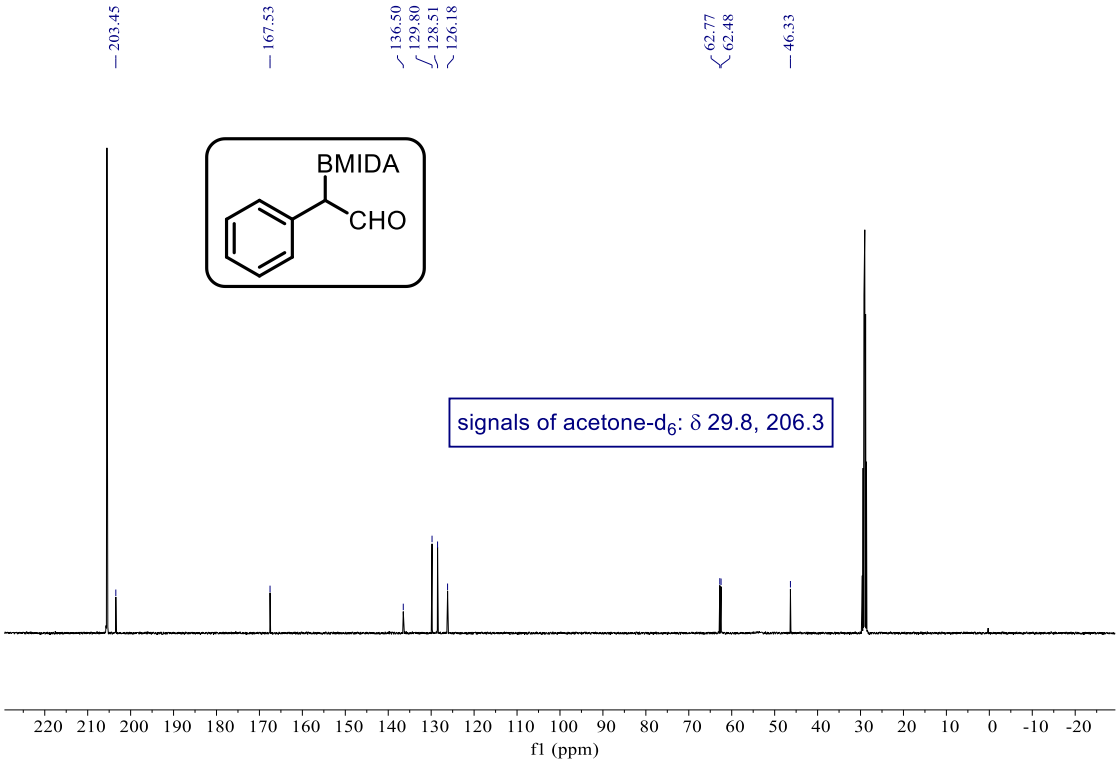


2-(4-methyl-2,6-dioxotetrahydro-2*H*-4λ^4,8λ^4-[1,3,2]oxazaborolo[2,3-*b*][1,3,2]oxazaborol-8-yl)-2-phenylacetaldehyde (**37**)

^{1}H NMR (400 MHz, acetone-d_6)

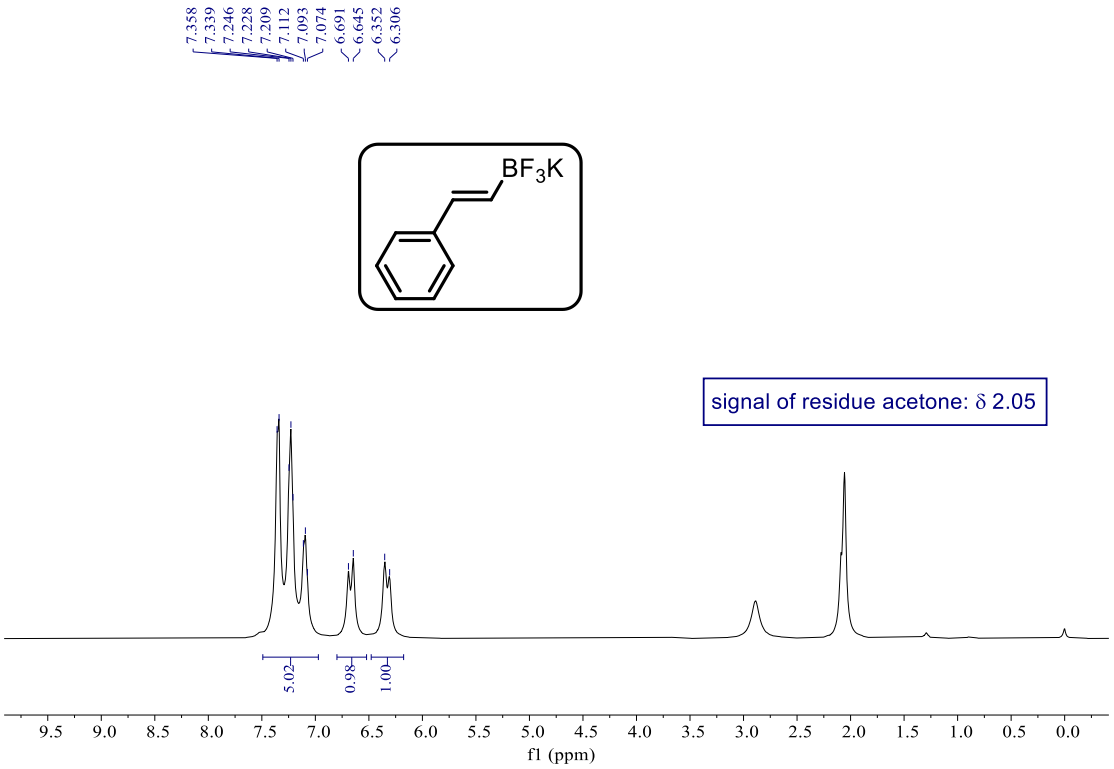


^{13}C{1H} NMR (100 MHz, acetone-d_6)

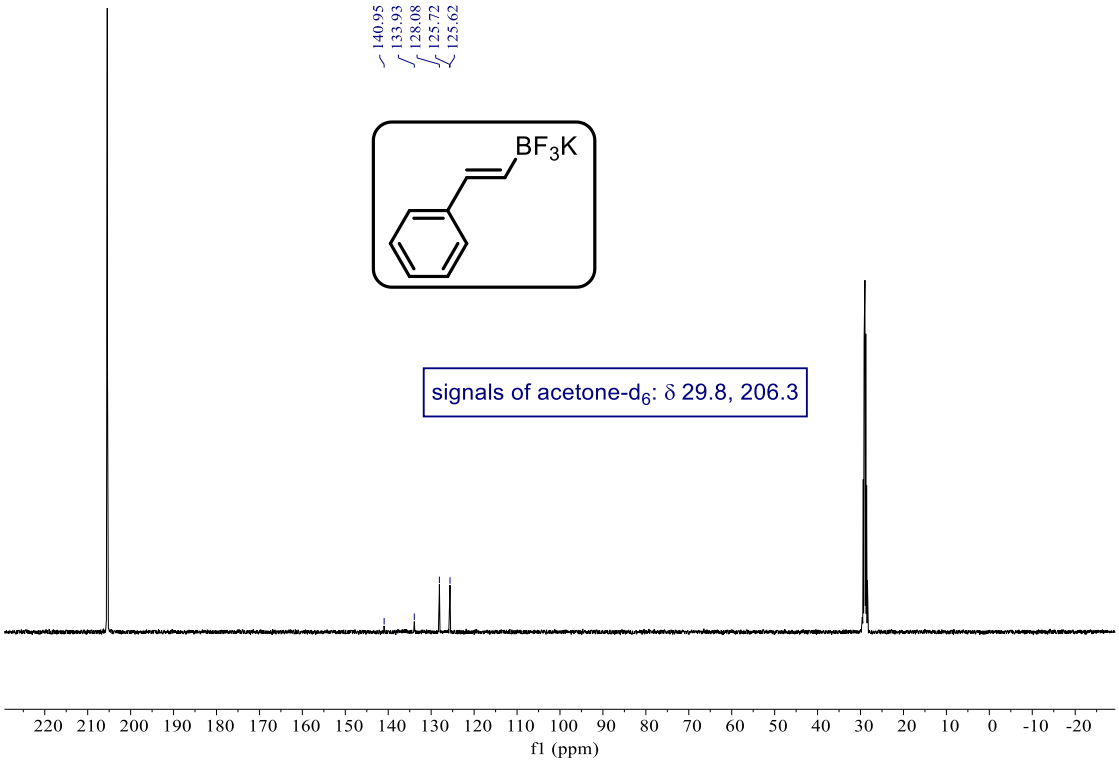


(*E*)-trifluoro(styryl)-λ^4-borane, potassium salt (**38**)

^{1}H NMR (400 MHz, acetone-d_6)

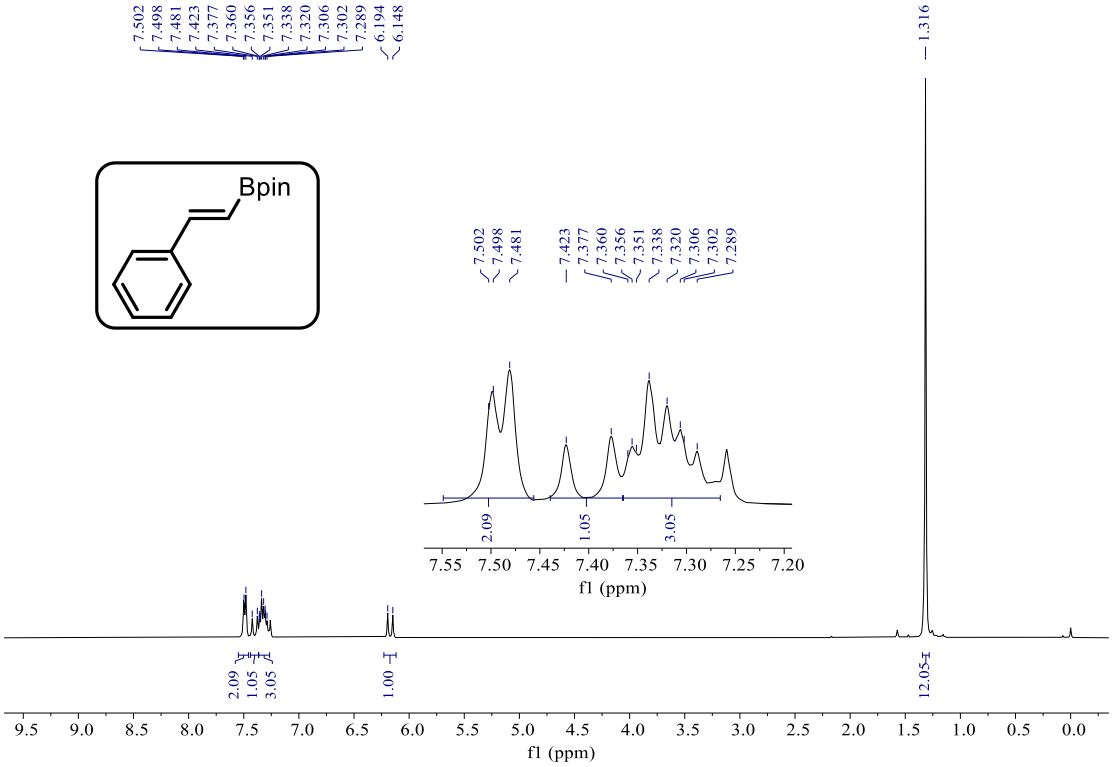


^{13}C{1H} NMR (100 MHz, acetone-d_6)



(*E*)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (**39**)

^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C{1H} NMR (100 MHz, $CDCl_3$)