Supporting Information (67 pages)

Synthesis of Isoxazoloazaborines via Gold(I)-Catalyzed Propargyl Aza-Claisen Rearrangement/Borylative Cyclization Cascade

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1. General techniques

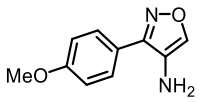
NMR spectra were recorded on a Bruker biospin AVANCE II (400 MHz for ^{1}H, 100 MHz for ^{13}C, 128 MHz for ^{11}B) or a Bruker biospin AVANCE III (500 MHz for ^{1}H, 125 MHz for ^{13}C, 160 MHz for ^{11}B) instrument in the indicated solvent. Chemical shifts are reported in units parts per million (ppm) relative to the signal (0.00 ppm) for internal tetramethylsilane for solutions in $CDCl_3$ (7.26 ppm for 1H, 77.16 ppm for ^{13}C). ^{11}B NMR chemical shifts are externally referenced to BF_3•Et_2O (0.00 ppm). Multiplicities are reported using the following abbreviations: s; singlet, d; doublet, dd; doublet of doublets, t; triplet, dt; doublet of triplets q; quartet, quint; quintet, m; multiplet, br; broad, *J*; coupling constants in Hertz. IR spectra were recorded on a JASCO FT/IR-4200 spectrometer. Only the strongest and/or structurally important peaks are reported as IR data given in cm^{-1}. Mass spectra were measured using a JMS-700 Mstation and Bruker micrOTOF II. HRMS (EI, 70 eV) was calibrated as perfluorokerosene and HRMS (ESI-TOF) was calibrated as sodium formate. All reactions were monitored by thin-layer chromatography carried out on 0.2 mm E. Merck silica gel plates (60F-254) with UV light (254 nm), and were visualized using an aqueous alkaline $KMnO_4$ solution. Gel permeation chromatography (GPC) for purification was performed on Japan Analytical Industry Model LC- 9225 NEXT (recycling preparative HPLC) and a Japan Analytical Industry Model UV-600 NEXT ultraviolet detector with a polystyrene gel column (JAIGEL-1H, 20 mm × 600 mm), using chloroform as solvent (3.5 mL/min). Column chromatography was performed on Silica Gel 60 N, purchased from Fuji Silysia Chemical Ltd. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (1.0 mm) prepared in our laboratory. 4-*N*-Propargylaminoisoxazoles such as 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a**, 3-phenyl-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1b**, 3-(*p*-tolyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1c**, 3-(*tert*-butyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1e**, 3-(4-chlorophenyl)-*N*-(1-(trimethylsilyl)hept-1-yn-3-yl)isoxazol-4-amine **1g**, and 3-(4-chlorophenyl)-*N*-(4-(dimethyl(phenyl)silyl)but-3-yn-2-yl)isoxazol-4-amine **1i**[1] and potassium organotrifluoroborates[2] were synthesized according to the literatures.

2. Synthesis of 3-substituted-4-aminoisoxazoles

Synthesis of 3-(4-methoxyphenyl)isoxazol-4-amine

To a mixture of (*Z*)-*N*-hydroxy-4-methoxybenzimidoyl chloride[3] (3.71 g, 20.0 mmol) and ethyl (*E*)-3-(pyrrolidin-1-yl)acrylate[4] (3.38 g, 20.0 mmol) in MeCN (2 mL/mmol of 3-(pyrrolidin-1-yl)acrylate), triethylamine (3.3 mL, 24 mmol) was added dropwise at 0 °C under an argon atmosphere. After being stirred at room temperature for 3 h, the residue was poured into diethyl ether and water. The aqueous layer was extracted with diethyl ether. The combined extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved in acetic acid (4 mL/mmol of 3-(pyrrolidin-1-yl)acrylate), 6 M HCl (10 mL/mmol of 3-(pyrrolidin-1-yl)acrylate) was added under an argon atmosphere. After being refluxed for 6 h, the residue was poured into ethyl acetate and water. The aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was dissolved in *tert*-butyl alcohol (3 mL/mmol of 3-(pyrrolidin-1-yl)acrylate), diphenyl phosphoryl azide (4.3 mL, 20 mmol) and triethylamine (2.8 mL, 20 mmol) were added. After being stirred at 85 °C for 12 h, the residue was passed through a pad of silica gel and concentrated *in vacuo*. Then, 4 M HCl in dioxane (10 mL/mmol of 3-(pyrrolidin-1-yl)acrylate) was added to the residue. After being stirred at room

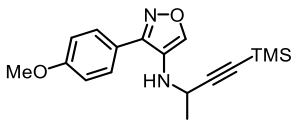
temperature for 3 h, saturated aq. $NaHCO_3$ was added. The mixture was poured into ethyl acetate, the aqueous layer was extracted with two portions of ethyl acetate. The combined extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo* to afford 3-(4-methoxyphenyl)isoxazol-4-amine (983 mg, 5.12 mmol, 26 % in 4 steps) as a white solid. Mp 73-74 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.73 (d, J = 7.9 Hz, 2H), 7.46-7.41 (m, 3H), 3.13 (brs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 144.1, 129.6, 129.0, 128.4, 127.6, 125.6; FT-IR (neat): 3400, 3333, 3222, 3124, 3124, 3065, 1633, 1454, 1396, 895, 698 cm^{-1}; HRMS (ESI-TOF): calcd. for $[C_{10}H_{10}N_2O_2+Na]^+$, 213.0634: found 213.0634.



3. *N*-Propargylation of 4-aminoisoxazoles

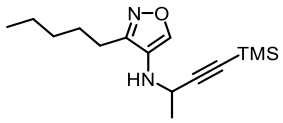
Representative procedure for the synthesis of 3-(4-methoxyphenyl)-*N*-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1d)

A mixture of 4-(trimethylsilyl)but-3-yn-2-one (743 µL, 4.5 mmol, 1.5 equiv.), 3-(4-methoxyphenyl)isoxazol-4-amine (570 mg, 3.0 mmol, 1.0 equiv.) and acetic acid (360 µL, 6.0 mmol, 2.0 equiv.) in MeOH (4 mL/1 mmol of 4-aminoisoxazoles) was stirred at 0 ºC for 10 min. To the solution was added $NaBH_3CN$ (566 mg, 9.0 mmol, 3.0 equiv.) at 0 ºC. After addition, the mixture was stirred at room temperature for 2 h. The reaction was quenched by addition of water. The resultant mixture was extracted with CH_2Cl_2 and the combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*, and the residue was purified silica gel column chromatography with hexane : ethyl acetate (19 : 1) to give the desired compound **1d** (380 mg, 0.962 mmol, 32%) as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 7.73 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 8.8, 2H), 3.89-3.84 (m, 4H), 3.00 (brs, 1H), 1.49 (d, J = 6.8 Hz, 3H), 0.14 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 155.2, 143.5, 129.3, 127.6, 121.2, 114.6, 106.5, 88.1, 55.5, 45.2, 22.4, 0.04; FT-IR (neat): 2972, 2842, 1635, 1611, 1463, 1251, 1051, 1032, 894, 837 cm^{-1}; HRMS (ESI-TOF): calcd. for $[C_{17}H_{22}N_2O_2Si+Na]^+$, 337.1343: found 337.1343.



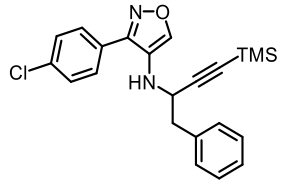
3-Pentyl-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1f)

Following the representative procedure using 4-(trimethylsilyl)but-3-yn-2-one (619 µL, 3.8 mmol) and 3-pentylisoxazol-4-amine (392 mg, 2.5 mmol),[1] purification by silica gel column chromatography with hexane : ethyl acetate (19 : 1) afforded the desired compound **1f** (380 mg, 0.962 mmol, 32%) as a yellow solid. Mp 120-122 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 3.84 (brs, 1H), 2.69 (brs, 1H), 2.57 (t, J = 7.6 Hz, 2H), 1.73-1.69 (m, 2H), 1.48 (d, J = 6.8 Hz, 3H), 1.38-1.35 (m, 4H), 0.90 (t, J = 6.8 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 142.7, 127.7, 106.7, 88.0, 45.2, 31.7, 26.8, 24.3, 22.3, 14.1, 0.03; FT-IR (neat): 2957, 2867, 1732, 1698, 1558, 1541, 1507, 1457, 1052, 1032, 838, 762 cm^{-1}; HRMS (ESI-TOF): calcd. for $[C_{15}H_{26}N_2OSi+Na]^+$, 310.1707: found 301.1703.



3-(4-Chlorophenyl)-*N*-(1-phenyl-4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1h)

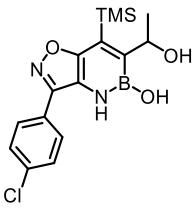
Following the representative procedure using 3-(4-chlorophenyl)isoxazol-4-amine (584 mg, 3.0 mmol)[5] and 1-phenyl-4-(trimethylsilyl)but-3-yn-2-one (631 mg, 4.5 mmol),[6] purification by silica gel column chromatography with hexane : ethyl acetate (19 : 1) afforded the desired compound **1h** (380 mg, 0.962 mmol, 32%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.58 (d, *J* = 8.5 Hz, 2H), 7.38 (d, *J* = 8.5, 2H), 7.34-7.25 (m, 5H), 3.97 (t, *J* = 6.0 Hz, 1H), 3.08 (dd, *J* = 16.5, 6.5 Hz, 2H), 2.97 (brs, 1H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 144.4, 136.5, 135.8, 129.8, 129.3, 129.0, 128.7, 127.3, 127.2, 104.8, 90.3, 50.9, 41.6, -0.05; FT-IR (neat): 3338, 2958, 2898, 2167, 1618, 1494, 1413, 1249, 1093, 878, 843 cm^{-1}; HRMS (ESI-TOF): m/z $[C_{22}H_{23}ClN_2OSi + Na]^+$ calcd. for, 417.1160: found 417.1160.



4. Synthesis of isoxazoloazaborines 3

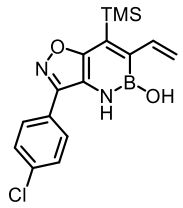
3-(4-Chlorophenyl)-6-(1-hydroxyethyl)-7-(trimethylsilyl)isoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-ol (3a)

To a mixture of RuPhosAuCl (7.0 mg, 0.010 mmol) and AgOTf (2.6 mg, 0.010 mmol) in a sealed vial, 4-propargylaminoisoxazole **1a** (31.9 mg, 0.10 mmol) in acetonitorile (1 mL) was added at room temperature under an argon atmosphere. After stirred at room temperature for 2 h, the mixture was passed through a pad of celite and concentrated *in vacuo*. The allene residue **2a** was dissolved in dichloromethane (3 mL). After the mixture was cooled at - 40 ºC, boron trichloride solution (1.0 M in heptane, 400 μL, 0.40 mmol) was added. The reaction mixture was stirred at 80 ºC for 16 h. The reaction was quenched with H_2O. The resultants mixture was extracted with ethyl acetate and the combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*, and the residue was purified by PTLC with hexane : ethyl acetate (19 : 1) to give 3-(4-chlorophenyl)-6-(1-hydroxyethyl)-7-(trimethylsilyl)isoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-ol **3a** (18.2 mg, 0.050 mmol, 50%) as a yellow solid. Mp 169-170 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 6.75 (brs, 1H), 6.56 (brs, 1H), 5.36 (q, *J* = 6.5 Hz, 1H), 1.48 (d, *J* = 6.5 Hz, 3H), 0.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 151.3, 139.6, 136.2, 129.8, 128.7, 127.2, 120.7, 72.6, 29.4, 25.4, 1.8; ^{11}B NMR (160 MHz, $CDCl_3$) δ 28.39; FT-IR (neat): 3345, 3270, 1410, 1275, 1046, 840 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{16}H_{20}ClN_2O_3SiB]^+$, 362.1025: found 362.1020.



3-(4-Chlorophenyl)-7-(trimethylsilyl)-6-vinylisoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-ol (3b)

To a mixture of RuPhosAuCl (7.0 mg, 0.010 mmol) and AgOTf (2.6 mg, 0.010 mmol) in a sealed vial, 4-propargylaminoisoxazole **1a** (31.9 mg, 0.100 mmol) in acetonitorile (1 mL) was added at room temperature under an argon atmosphere. After stirred at room temperature for 2 h, the mixture was cooled at - 40 ºC, then boron trichloride solution (1.0 M in heptane, 400 μL, 0.400 mmol) was added. The reaction mixture was warmed to 100 ºC, and stirred for 16 h. The reaction was quenched with H_2O. The resultants mixture was extracted with ethyl acetate and the combined organic layers were dried over $MgSO_4$ and filtered. The solvent was removed *in vacuo*, and the residue was purified by PTLC with hexane : ethyl acetate (19 : 1) to give 3-(4-chlorophenyl)-7-(trimethylsilyl)-6-vinylisoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-ol **3b** (17.5 mg, 0.051 mmol, 51%) as a yellow solid. Mp 135-136 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.0 Hz, 2H), 7.52 (d, *J* = 9.0 Hz, 2H), 7.03 (dd, *J* = 18.0, 11.5 Hz, 1H), 6.29 (brs, 1H), 5.51 (dd, *J* = 11.0, 1.5 Hz, 1H), 5,37 (dd, *J* = 18.0, 1.5 Hz, 1H), 4.54 (brs, 1H), 0.47 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 151.3, 142.5, 140.2, 136.2, 129.9, 128.7, 127.2, 120.4, 118.0, 1.2; ^{11}B NMR (160 MHz, $CDCl_3$) δ 27.78; FT-IR (neat): 3318, 2923, 1410, 1251, 1015, 834 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{16}H_{18}BClN_2O_2Si]^+$, 345.0995: found 345.0985.



5. Synthesis of isoxazoloazaborines 5 via gold-catalyzed propargyl aza-Claisen rearrangement/borylative cyclization cascade

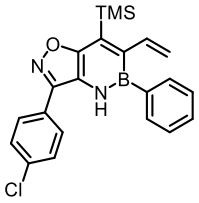
General procedure of isoxazoloazaborines 5 synthesis

To a mixture of RuPhosAuCl (0.10 equiv.) and AgOTf (0.10 equiv.) in a Biotage microwave vial, 4-propargylaminoisoxazole **1** (1.0 equiv.) in acetonitrile (10 mL/mmol of **1**) was added at room temperature under an argon atmosphere. After stirred at room temperature for 2 h, potassium organotrifluoroborate (2.0 equiv.), silicon tetrachloride (2.0 equiv.) and triethylamine (2.5 equiv.) were added to the mixture in the glovebox. The reaction mixture was stirred at 100 ºC for 1 h. After cooling the reaction mixture to room temperature, the mixture was passed through a pad of celite and concentrated *in vacuo*. The residue was purified by PTLC to afford the desired products **5**.

3-(4-Chlorophenyl)-5-phenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5a)

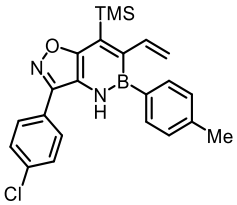
Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (319 mg, 1.0 mmol) and potassium phenyltrifluoroborate (368 mg, 2.0 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5a** (317 mg, 0.783 mmol, 78%) as a yellow solid. Mp 103-104 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.61-7.59 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 3H), 7.14 (dd, *J* = 17.5, 11 Hz, 1H), 5.26 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.03 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.3, 140.5, 136.4, 133.1, 130.0,

128.9, 128.5, 128.0, 127.0, 120.8, 120.2, 1.83; ^{11}B NMR (128 MHz, $CDCl_3$) δ 33.90; FT-IR (neat): 3404, 2955, 2924, 1600, 1502, 1408, 1251, 869, 834 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{22}H_{22}BClN_2OSi]^+$, 404.1283: found 404.1283



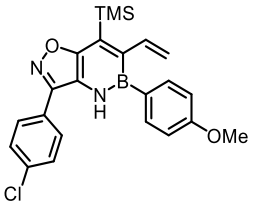
3-(4-Chlorophenyl)-5-(*p*-tolyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5b)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.8 mg, 0.10 mmol) and potassium *p*-tolyltrifluoroborate (39.6 mg, 0.20 mmol),[2] purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5b** (35.4 mg, 0.0845 mmol, 85%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (brs, 1H), 7.71 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.13 (dd, *J* = 17.5, 11 Hz, 1H), 5.26 (dd, *J* = 11.0, 1.5 Hz, 1H), 5.05 (dd, *J* = 17.5, 2.0 Hz, 1H), 2.40 (s, 3H) 0.53 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.1, 140.7, 138.4, 136.4, 133.2, 130.0, 128.9, 128.8, 127.0, 120.1, 21.6, 1.86; ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.08; FT-IR (neat): 3404, 2954, 2920, 1606, 1500, 1408, 1250, 869, 834 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{23}H_{24}BClN_2OSi]^+$, 418.1439: found 418.1451.



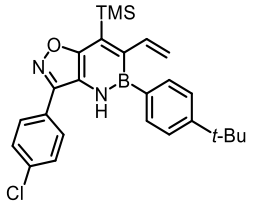
3-(4-Chlorophenyl)-5-(4-methoxyphenyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5c)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium trifluoro(4-methoxyphenyl)borate (42.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5c** (34.4 mg, 0.0791 mmol, 79%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73-7.70 (m, 3H), 7.56-7.53 (m, 4H), 7.13 (dd, *J* = 17.5, 11.5 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 2H), 5.27 (dd, *J* = 11.0, 1.5 Hz, 1H), 5.06 (dd, *J* = 17.5, 2.0 Hz, 1H), 3.85 (s, 3H), 0.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.3, 160.2, 154.9, 151.2, 141.0, 140.8, 136.4, 134.7, 131.7, 130.0, 128.9, 127.1, 120.9, 119.9, 113.7, 55.2, 1.88; ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.13; FT-IR (neat): 3403, 2954, 2898, 1601, 1499, 1407, 1234, 1179, 868, 832 cm^{-1}; HRMS (EI, 70 eV): calcd. for$[C_{23}H_{24}BClN_2O_2Si]^+$, 434.1389: found 434.1387.



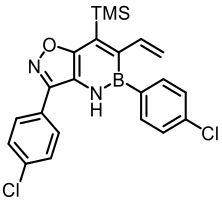
5-(4-(*tert*-Butyl)phenyl)-3-(4-chlorophenyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5d)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium (4-(*tert*-butyl)phenyl)trifluoroborate (48.0 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5d** (18.1 mg, 0.0393 mmol, 39%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.61-7.59 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 3H), 7.14 (dd, *J* = 17.5, 11 Hz, 1H), 5.26 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.03 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.3, 140.5, 136.4, 133.1, 130.0, 128.9, 128.5, 128.0, 127.0, 120.8, 120.2, 1.83; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.41; FT-IR (neat): 3400, 2961, 2865, 1603, 1541, 1249, 1092, 869, 831 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{26}H_{30}BClN_2OSi]^+$, 460.1909: found 460.1914.



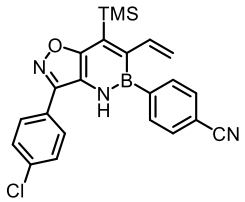
3,5-Bis(4-chlorophenyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5e)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium (4-chlorophenyl)trifluoroborate (43.7 mg, 0.20 mmol),[2] purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5e** (19.1 mg, 0.0434 mmol, 43%) as a brown solid. Mp 123-124 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (brs, 1H), 7.70 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.09 (dd, *J* = 17.5, 11.5 Hz, 1H), 5.25 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.99 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.3, 140.5, 136.4, 133.1, 130.0, 128.9, 128.5, 128.0, 127.0, 120.8, 120.2, 1.83; ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.26; FT-IR (neat): 3398, 2954, 2927, 1588, 1433, 1409, 1250, 1091, 869, 834 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{22}H_{21}BCl_2N_2OSi]^+$, 438.0893: found 438.0883.



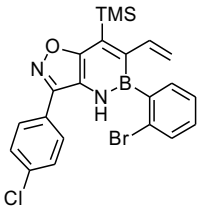
4-(3-(4-Chlorophenyl)-7-(trimethylsilyl)-6-vinylisoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-yl)benzonitrile (5f)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium (4-cyanophenyl)trifluoroborate (41.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5f** (27.8 mg, 0.0647 mmol, 65%) as a yellow solid. Mp 229-230 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.61-7.59 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 3H), 7.14 (dd, *J* = 17.5, 11 Hz, 1H), 5.26 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.03 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.3, 140.5, 136.4, 133.1, 130.0, 128.9, 128.5, 128.0, 127.0, 120.8, 120.2, 1.83; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.59; FT-IR (neat): 2956, 2921, 2849, 1716, 1698, 1540, 1507, 1014, 832 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{23}H_{21}BClN_3OSi]^+$, 429.1235: found 429.1224.



5-(2-Bromophenyl)-3-(4-chlorophenyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5g)

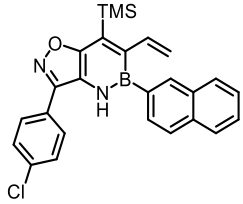
Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium (2-bromophenyl)trifluoroborate (52.6 mg, 0.20 mmol),[2] purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5g** (13.0 mg, 0.0269 mmol, 27%) as a yellow solid. Mp 145-146 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (brs, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.57-7.53 (m, 1H), 7.33-7.31 (m, 2H), 7.25-7.21 (m, 2H), 7.08 (dd, *J* = 17.5, 11 Hz, 1H), 5.12 (dd, *J* = 11.0, 1.5 Hz, 1H), 4.91 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.3, 141.6, 139.9, 136.5, 134.2, 132.1, 130.0, 129.9, 128.9, 126.9, 126.72, 126.65, 120.3, 119.6, 1.67; ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.10; FT-IR (neat): 3400, 2955, 2925, 1716, 1600, 1503, 1251, 1092, 1337, 1250, 869, 833 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{22}H_{21}BBrClN_2OSi]^+$, 482.0388: found 482.0380.



3-(4-Chlorophenyl)-5-(naphthalen-2-yl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5h)

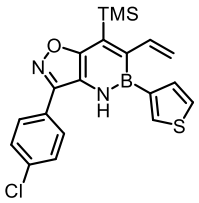
Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium 2-naphthalenyltrifluoroborate (46.8 mg, 0.20 mmol),[2] purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5h** (25.0 mg, 0.0549 mmol, 55%) as a brown

oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (brs, 1H), 7.89-7.84 (m, 4H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.68 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.54 (d, *J* = 8.5, 2H), 7.51-7.49 (m, 2H), 8.18 (dd, *J* = 17.5, 11.5 Hz, 1H), 5.24 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.04 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.56 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 151.3, 141.5, 140.3, 136.4, 133.4, 133.3, 132.9, 130.4, 130.0, 128.9, 128.2, 127.9, 127.04, 127.01, 126.4, 126.1, 120.9, 120.6, 1.82; ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.37; FT-IR (neat): 3400, 3052, 2956, 1598, 1545, 1467, 1250, 1092, 869, 833 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{26}H_{24}BClN_2OSi]^+$, 454.1439: found 454.1484.



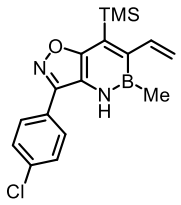
3-(4-Chlorophenyl)-5-(thiophen-3-yl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5i)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium 3-thienyltrifluoroborate (38.0 mg, 0.20 mmol),[2] purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5i** (18.8 mg, 0.0458 mmol, 46%) as a yellow solid. Mp 97-98 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.64 (dd, *J* = 2.5, 1.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.41 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.35 (dd, *J* = 4.5, 1.0 Hz, 1H), 7.15 (dd, *J* = 17.5, 11 Hz, 1H), 5.26 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.03 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 151.2, 141.2, 141.0, 136.5, 131.7, 131.1, 130.0, 128.9, 127.0, 125.6, 120.8, 119.6, 1.88; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.51; FT-IR (neat): 3404, 2954, 2897, 1600, 1542, 1434, 1249, 1091, 869, 833 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{20}H_{20}BClN_2OSSi]^+$, 410.0847: found 410.0848.



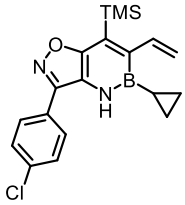
3-(4-Chlorophenyl)-5-methyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5j)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium trifluoro(methyl)borate (24.3 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5j** (17.3 mg, 0.0504 mmol, 50%) as a brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.57-7.55 (m, 3H), 7.08 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.39 (dd, *J* = 11.6, 2.0 Hz, 1H), 5.25 (dd, *J* = 18.0, 2.0 Hz, 1H), 0.79 (s, 3H), 0.49 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 150.9, 141.2, 139.5, 136.3, 129.9, 128.9, 127.3, 120.5, 118.3, 1.69; ^{11}B NMR (128 MHz, $CDCl_3$) δ 37.26; FT-IR (neat): 3410, 2955, 2898, 1601, 1548, 1409, 1251, 1093, 920, 833cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{17}H_{20}BClN_2OSi]^+$, 342.1126: found 342.1118.



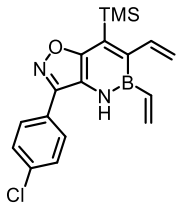
3-(4-Chlorophenyl)-5-cyclopropyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5k)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium cyclopropyltrifluoroborate (29.6 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5k** (12.8 mg, 0.0347 mmol, 35%) as a yellow solid. Mp 119-120 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 9.0 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.15 (dd, *J* = 18.0, 11.5 Hz, 1H), 7.04 (brs, 1H), 5.48 (dd, *J* = 18.0, 2.0 Hz, 1H), 5.44 (dd, *J* = 11.0, 2.0 Hz, 1H), 0.88-0.84 (m, 2H), 0.63-0.58 (m, 1H), 0.49 (s, 9H), 0.45-0.42 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.0, 150.9, 140.7, 139.3, 136.3, 120.3, 118.9, 6.86, 1.68; ^{11}B NMR (160 MHz, $CDCl_3$) δ 36.90; FT-IR (neat): 3412, 3071, 2957, 1600, 1541, 1500, 1409, 1251, 1093, 867, 833 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{19}H_{22}BClN_2OSi]^+$, 368.1283: found 368.1274.



3-(4-Chlorophenyl)-7-(trimethylsilyl)-5,6-divinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5l)

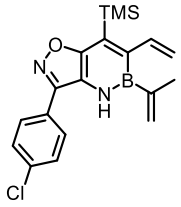
Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium trifluoro(vinyl)borate (26.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5l** (25.8 mg, 0.0727 mmol, 73%) as a brown solid. Mp 110-111 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (brs, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.13 (dd, *J* = 17.5, 11.5 Hz, 1H), 6.73-6.66 (m, 1H), 5.85-5.81 (m, 2H), 5.44 (dd, *J* = 11.0, 1.5 Hz, 1H), 5.31 (dd, *J* = 18.0, 2.0 Hz, 1H), 0.502 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 140.8, 140.2, 139.2, 136.4, 130.0, 128.9, 128.2, 127.1, 120.5, 119.6, 1.60; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.28; FT-IR (neat): 3406, 3049, 2953, 1601, 1541, 1499, 1404, 1250, 1092, 1011, 868, 832 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{18}H_{20}BClN_2OSi]^+$, 354.1126: found 354.1132.



3-(4-Chlorophenyl)-5-(prop-1-en-2-yl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine

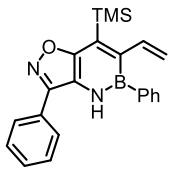
(5m)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1a** (31.9 mg, 0.10 mmol) and potassium trifluoro(prop-1-en-2-yl)borate (29.6 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5m** (29.1 mg, 0.0790 mmol, 79%) as a brown solid. Mp 105-106 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.5 Hz, 2H), 7.67 (brs, 1H), 7.55 (d, *J* = 8.5 Hz, 2H), 7.14 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.46-5.45 (m, 1H), 5.42 (dd, *J* = 17.5, 2.0 Hz, 1H), 5.33 (dd, *J* = 11.0, 1.5 Hz, 1H), 5.28-5.27 (m, 1H), 1.98 (t, *J* = 1.5 Hz, 3H), 0.50 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4, 151.1, 140.8, 140.7, 136.4, 130.0, 128.9, 127.1, 122.6, 120.3, 119.1, 23.2, 1.77; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.43; FT-IR (neat): 3410, 2953, 2899, 1601, 1541, 1500, 1408, 1251, 1093, 870, 834 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{19}H_{22}BClN_2OSi]^+$, 368.1283: found 468.1274.



3,5-Diphenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5n)

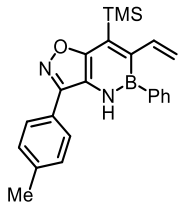
Following the general procedure using 3-phenyl-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1b** (28.4 mg, 0.10 mmol) and potassium phenyltrifluoroborate (36.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5n** (29.3 mg, 0.0791 mmol, 79%) as an brown solid. Mp 95-96 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.61-7.59 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 3H), 7.14 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.26 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.03 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.3, 140.5, 136.4, 133.1, 130.0, 128.9, 128.5, 128.0, 127.0, 120.8, 120.2, 1.83; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.45; FT-IR (neat): 3403, 2954, 2897, 1541, 1458, 1395, 1250, 1234, 868, 841 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{22}H_{23}BN_2OSi]^+$, 370.1673: found 370.1674.



5-Phenyl-3-(*p*-tolyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5o)

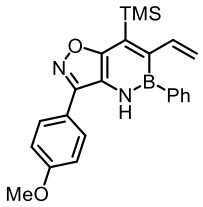
Following the general procedure using 3-(*p*-tolyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1c** (29.8 mg, 0.10 mmol) and potassium phenyltrifluoroborate (36.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5o** (26.0 mg, 0.0725 mmol, 73%) as an brown solid. Mp 75-76 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.61-7.59 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 3H), 7.14 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.26 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.03 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.3, 140.5, 136.4, 133.1, 130.0, 128.9, 128.5, 128.0, 127.0, 120.8, 120.2, 1.83; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.71; FT-IR (neat): 3406, 2954, 2898, 1556, 1519, 1436,

1250, 1235, 869, 841 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{23}H_{25}BN_2OSi]^+$, 384.1829: found 384.1839.



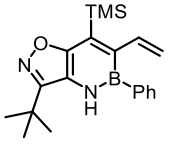
3-(4-Methoxyphenyl)-5-phenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5p)

Following the general procedure using 3-(4-methoxyphenyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1d** (31.4 mg, 0.10 mmol) and potassium phenyltrifluoroborate (36.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5p** (29.4 mg, 0.0785 mmol, 79%) as an orange oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (brs, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.61-7.59 (m, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 7.41-7.38 (m, 3H), 7.14 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.26 (dd, *J* = 11.5, 2.0 Hz, 1H), 5.03 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.54 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.3, 140.5, 136.4, 133.1, 130.0, 128.9, 128.5, 128.0, 127.0, 120.8, 120.2, 1.83; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.83; FT-IR (neat): 3404, 2955, 2898, 1613, 1518, 1434, 1252, 1175, 868, 835 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{23}H_{25}BClN_2O_2Si]^+$, 400.1778: found 400.1786.



3-(*tert*-Butyl)-5-phenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5q)

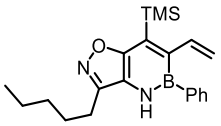
Following the general procedure using 3-(*tert*-butyl)-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1e** (26.4 mg, 0.10 mmol) and potassium phenyltrifluoroborate (36.8 mg, 0.20 mmol) , purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5q** (30.0 mg, 0.0856 mmol, 86%) as a yellow solid. Mp 125-126 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (brs, 1H), 7.60-7.59 (m, 2H), 7.42-7.40 (m, 3H), 7.10 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.21 (d, *J* = 11. 0 Hz, 1H), 4.98 (d, *J* = 17.5, 1H), 1.52 (s, 9H), 0.49 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.4, 141.3, 140.6, 133.2, 128.3, 128.0, 120.9, 119.8, 32.9, 28.9, 1.87; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.11; FT-IR (neat): 3429, 2961, 2902, 1538, 1395, 1250, 1238, 869, 840 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{20}H_{27}BClN_2OSi]^+$, 350.1986: found 350.1981.



3-Pentyl-5-phenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5r)

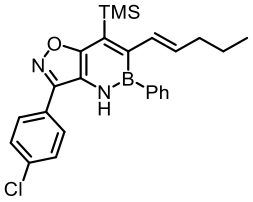
Following the general procedure using 3-pentyl-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1f** (27.8 mg, 0.10 mmol) and potassium phenyltrifluoroborate (36.8 mg, 0.20 mmol), purification by PTLC (hexane :

acetone = 39 : 1) afforded the desired product **5r** (11.7 mg, 0.0321 mmol, 32%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59-7.55 (m, 3H), 7.42-7.37 (m, 3H), 7.10 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.20 (dd, *J* = 11.0, 2.0 Hz, 1H), 4.98 (dd, *J* = 17.5, 2.0 Hz, 1H), 2.84 (t, *J* = 7.5 Hz, 2H), 1.80 (quint, *J* = 7.5 Hz, 2H), 1.45-1.34 (m, 4H), 0.91 (t, *J* = 7.0 Hz, 3H), 0.48 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.2, 153.0, 141.2, 140.7, 133.1, 128.3, 128.0, 121.8, 119.9, 31.7, 27.4, 24.5, 22.5, 14.1, 1.82; ^{11}B NMR (160 MHz, $CDCl_3$) δ 34.62; FT-IR (neat): 3254, 2955, 2929, 1541, 1507, 1435, 1405, 1249, 867, 842 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{21}H_{29}BClN_2OSi]^+$, 364.2142: found 364.2131.



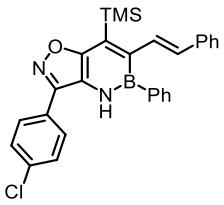
(*E*)-3-(4-Chlorophenyl)-6-(pent-1-en-1-yl)-5-phenyl-7-(trimethylsilyl)-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5s)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(1-(trimethylsilyl)hept-1-yn-3-yl)isoxazol-4-amine **1g** (36.1 mg, 0.10 mmol) and potassium phenyltrifluoroborate (36.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5s** (28.1 mg, 0.0628 mmol, 63%) as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (brs, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.58-7.53 (m, 4H), 7.41-7.35 (m, 3H), 6.74 (d, *J* = 15.5 Hz, 1H), 5.43 (dt, *J* = 15.5, 7.0 Hz, 1H), 2.06-2.02 (m, 2H), 1.35-1.31 (m, 2H), 0.84 (t, *J* = 7.5 Hz, 3H), 0.52 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 151.2, 141.3, 140.5, 136.4, 133.1, 130.0, 128.9, 128.5, 128.0, 127.0, 120.8, 120.2, 1.83; ^{11}B NMR (160 MHz, $CDCl_3$) δ 35.04; FT-IR (neat): 2956, 2925, 1716, 1698, 1541, 1507, 1456, 1338, 1249, 835cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{25}H_{28}BClN_2OSi]^+$, 446.1752: found 446.1750.



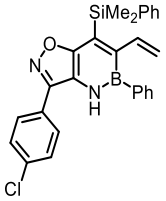
(*E*)-3-(4-Chlorophenyl)-5-phenyl-6-styryl-7-(trimethylsilyl)-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5t)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(1-phenyl-4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine **1h** (39.5 mg, 0.10 mmol) and potassium phenyltrifluoroborate (36.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5t** (31.3 mg, 0.0651 mmol, 65%) as a yellow solid. Mp 158-160 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (brs, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.63-7.60 (m, 2H), 7.56-7.52 (m, 3H), 7.41-7.39 (m, 3H), 7.32-7.23 (m, 6H), 6.38 (d, *J* = 16.4 Hz, 1H), 0.57 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.7, 151.2, 141.2, 137.6, 136.4, 135.1, 133.1, 132.6, 130.0, 129.0, 128.89, 128.84, 128.65, 128.58, 128.2, 127.7, 127.0, 126.5, 120.8, 1.88; ^{11}B (160 MHz, $CDCl_3$) δ 35.26; FT-IR (neat): 2954, 2923, 1748, 1716, 1540, 1507, 1456, 1338, 1092, 835 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{28}H_{26}BClN_2OSi]^+$, 480.1596: found 480.1590.



3-(4-Chlorophenyl)-7-(dimethyl(phenyl)silyl)-5-phenyl-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5u)

Following the general procedure using 3-(4-chlorophenyl)-*N*-(4-(dimethyl(phenyl)silyl)but-3-yn-2-yl)isoxazol-4-amine **1i** (38.1 mg, 0.10 mmol) and potassium phenyltrifluoroborate (36.8 mg, 0.20 mmol), purification by PTLC (hexane : acetone = 39 : 1) afforded the desired product **5u** (19.3 mg, 0.0411 mmol, 41%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (brs, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.65-7.63 (m, 2H), 7.56-7.53 (m, 4H), 7.38-7.35 (m, 6H), 6.90 (dd, *J* = 17.5, 11.0 Hz, 1H), 5.06 (dd, *J* = 11.3, 2.0 Hz, 1H), 4.90 (dd, *J* = 17.5, 2.0 Hz, 1H), 0.80 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 151.3, 140.3, 139.1, 138.7, 136.5, 134.0, 133.1, 130.0, 129.3, 128.9, 128.5, 128.1, 128.0, 127.0, 121.0, 120.6, 0.75; ^{11}B (160 MHz, $CDCl_3$) δ 35.35; FT-IR (neat): 3013, 2956, 2927, 1716, 1683, 1540, 1507, 1260, 913, 813 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{27}H_{24}BClN_2OSi]^+$, 466.1439: found 466.1444.

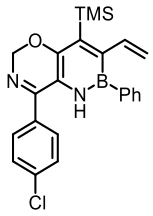


6. Synthesis of oxazine-fused azaborine 6 via methylene insertion into N-O bond of isoxazoloazaborine 5a

8-(4-Chlorophenyl)-2-phenyl-4-(trimethylsilyl)-3-vinyl-2,6-dihydro-1*H*-[1,2]azaborinino[6,5-*e*][1,3]oxazine (6)

To a stirred solution of isoxazoloazaborine **5a** (40.5 mg, 0.10 mmol, 1.0 equiv.) in CH_2Cl_2 (1 mL), diethylzinc (500 μL, 0.50 mmol, 5 equiv.) was added under an argon atmosphere at 0 ºC. After being stirred at 0 ºC for 15 min, diiodemethane (80.4 μL, 1.0 mmol, 10 equiv.) was added in dropwise under 0 ºC, then the reaction mixture was warmed to room temperature. After being stirred at room temperature for 24 h, saturated aq. $NHCl_4$ was added to the reaction mixture. The aqueous layer was extracted with two portions of CH_2Cl_2. The combined extract was washed with brine, dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel with hexane : ethyl acetate = 8 : 2 to give the desired compound **6** (20.0 mg, 0.048 mmol, 48%) as a yellow solid. Mp 168-169 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.5 Hz, 2H), 7.48-7.47 (m, 4H), 7.42 (brs, 1H), 7.35-7.31 (m, 3H), 7.08 (dd, *J* = 17.5, 11.5 Hz, 1H), 5.42 (s, 2H), 5.17 (dd, *J* = 11.0, 1.5 Hz, 1H), 4.96 (dd, *J* = 17.5, 1.5 Hz, 1H), 0.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.6, 151.6, 147.1, 141.0, 137.1, 133.2, 133.1, 130.2, 129.5, 128.2, 127.9, 119.3, 119.0, 78.6, 2.69; ^{11}B NMR (160 MHz, $CDCl_3$) δ 32.36; FT-IR (neat): 3390, 3003, 2954, 1617, 1508, 1387, 1246, 1015, 916, 835 cm^{-1}; HRMS (EI, 70 eV): calcd. for $[C_{27}H_{24}BClN_2OSi]^+$, 418.1439:

found 418.1445.



7. References

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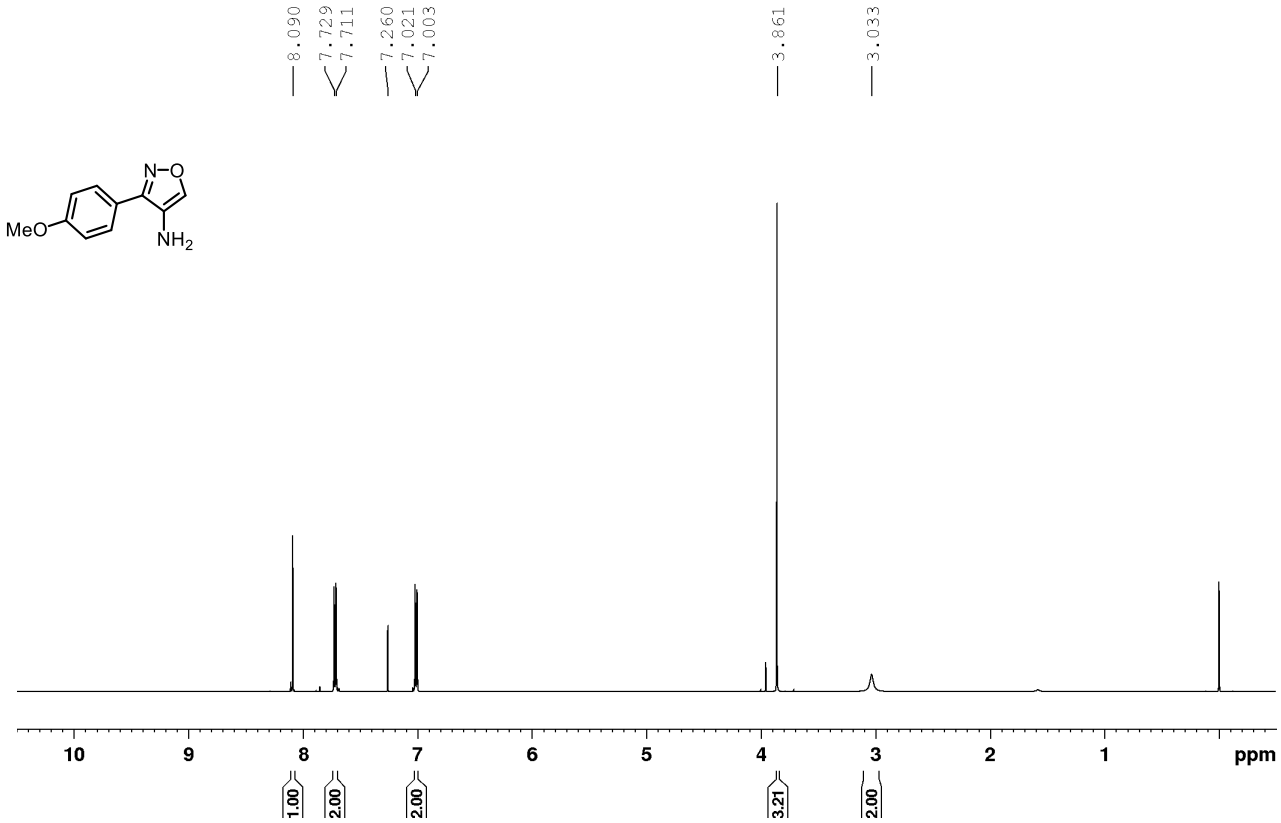
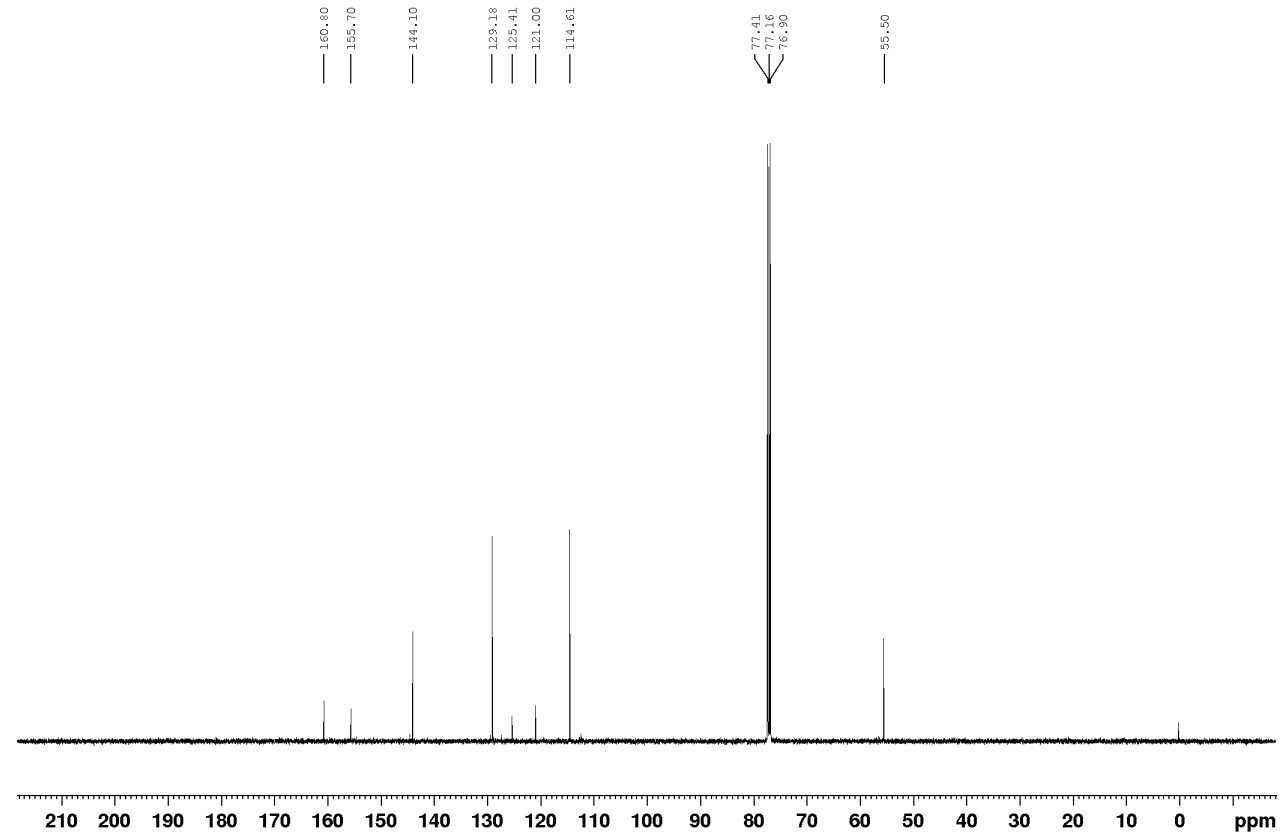
8. NMR spectra

3-(4-Methoxyphenyl)isoxazol-4-amine

^{1}H NMR (500 MHz, $CDCl_3$)

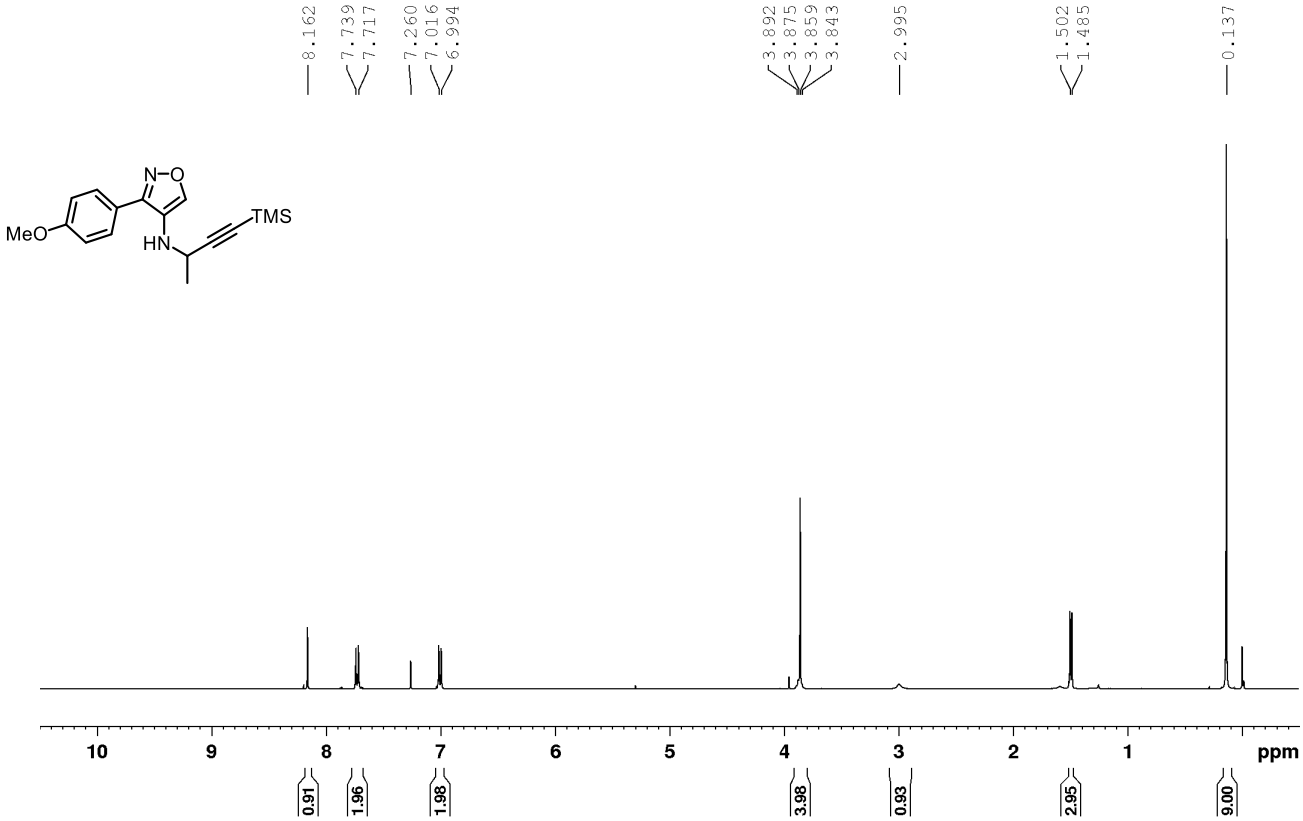


^{13}C NMR (125 MHz, $CDCl_3$)

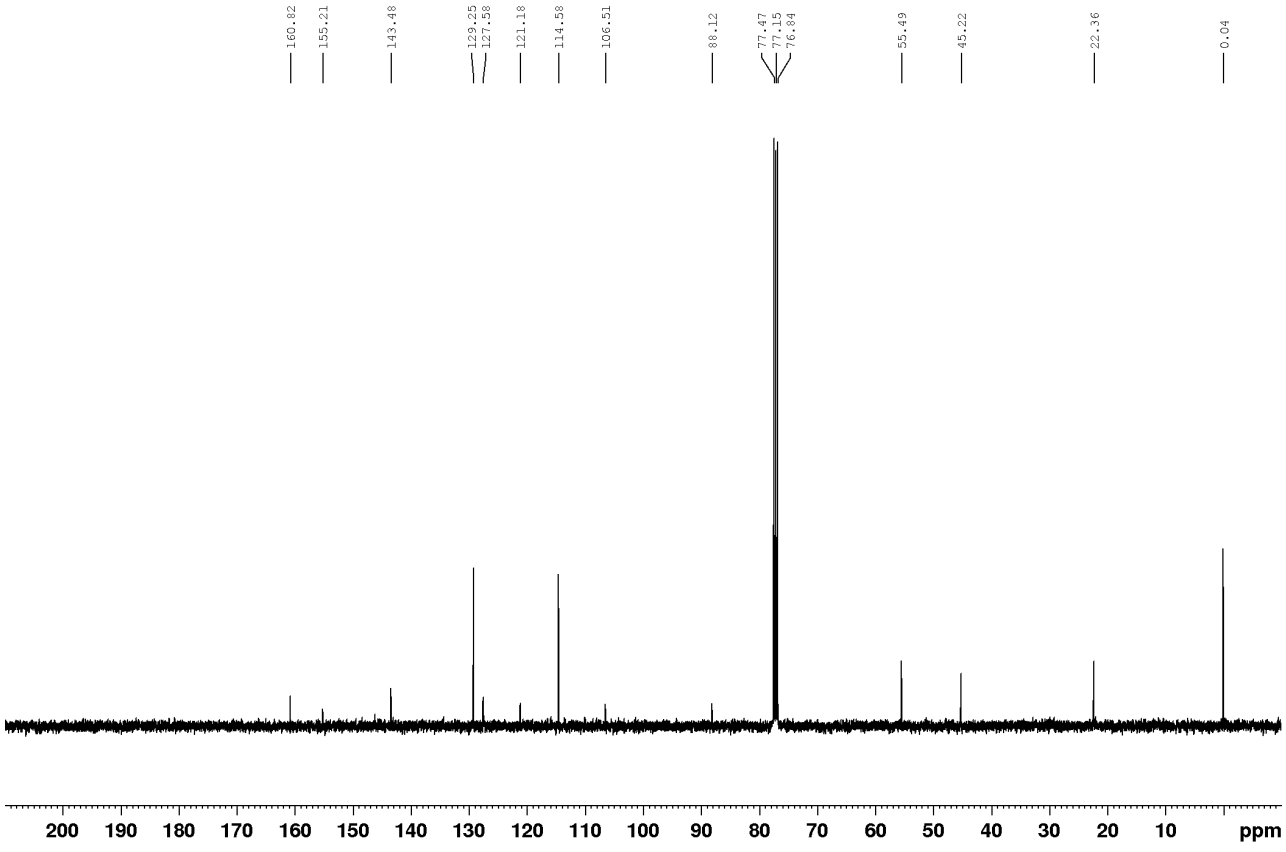


3-(4-Methoxyphenyl)-*N*-(1-phenyl-3-(trimethylsilyl)prop-2-yn-1-yl)isoxazol-4-amine (1d)

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

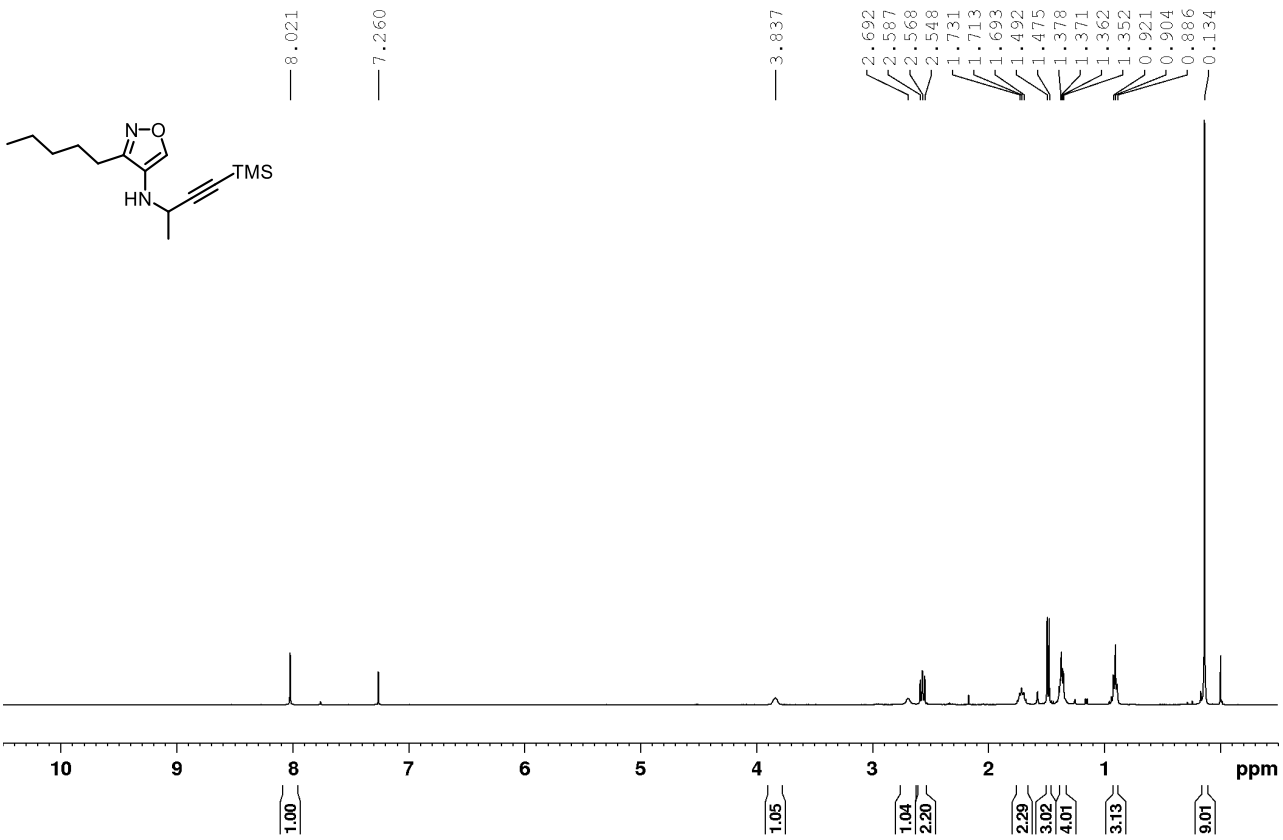


^{13}C NMR (100 MHz, $CDCl_3$)

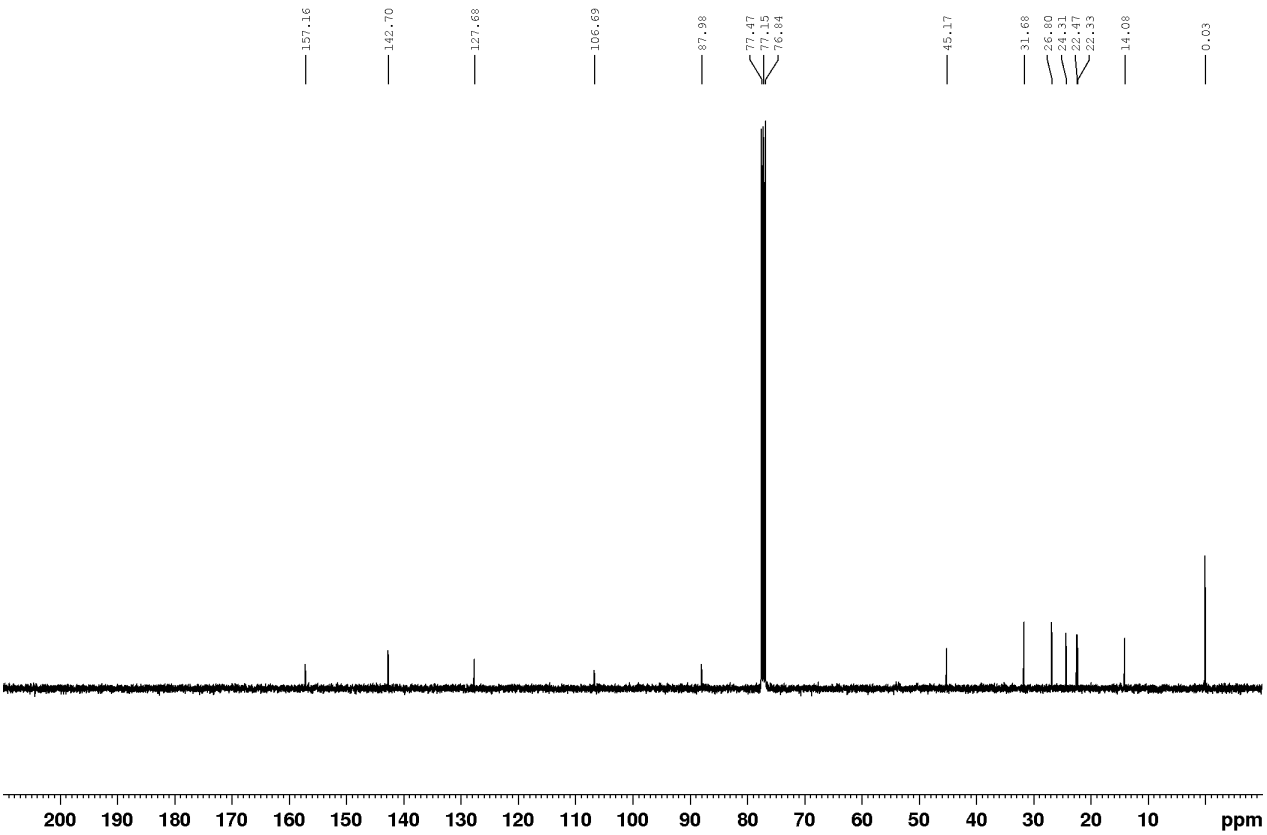


3-Pentyl-*N*-(4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1f)

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

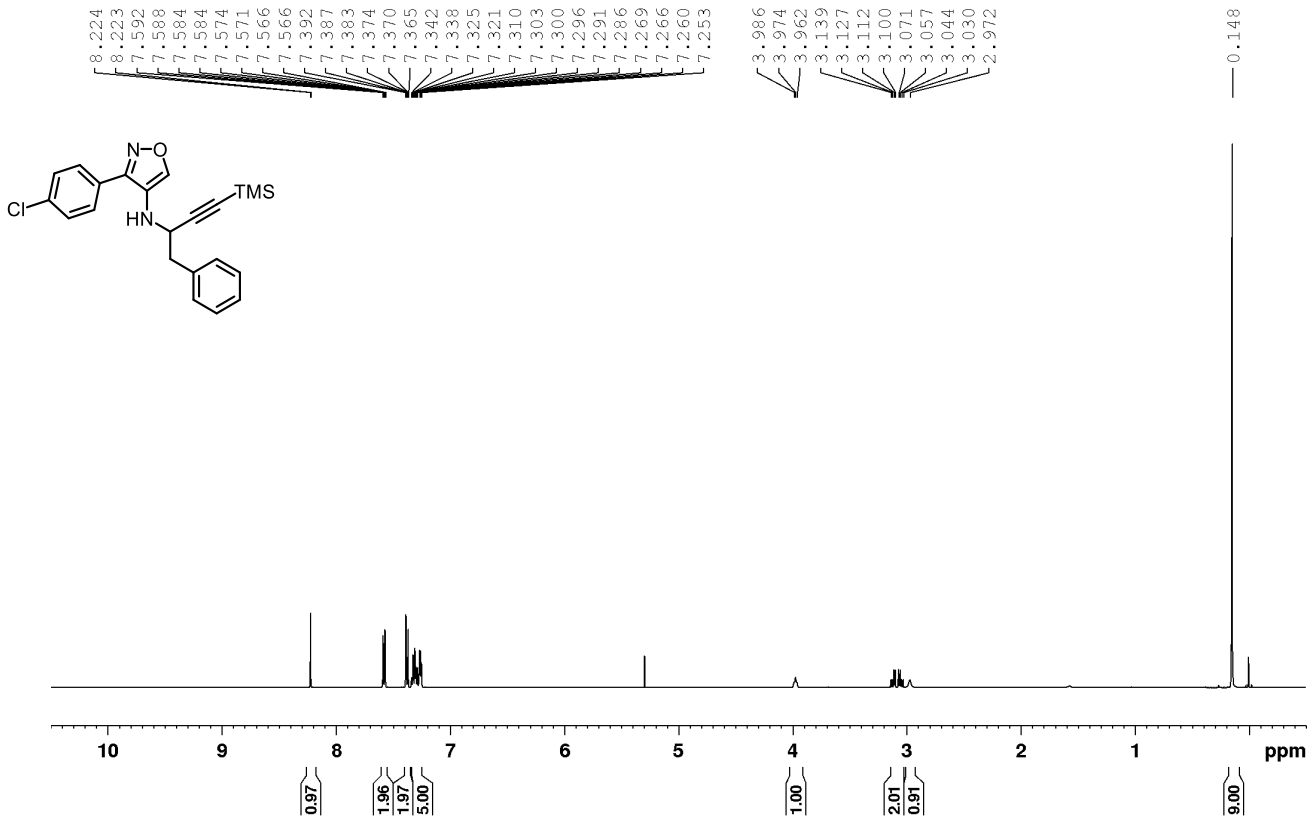


^{13}C NMR (100 MHz, $CDCl_3$)

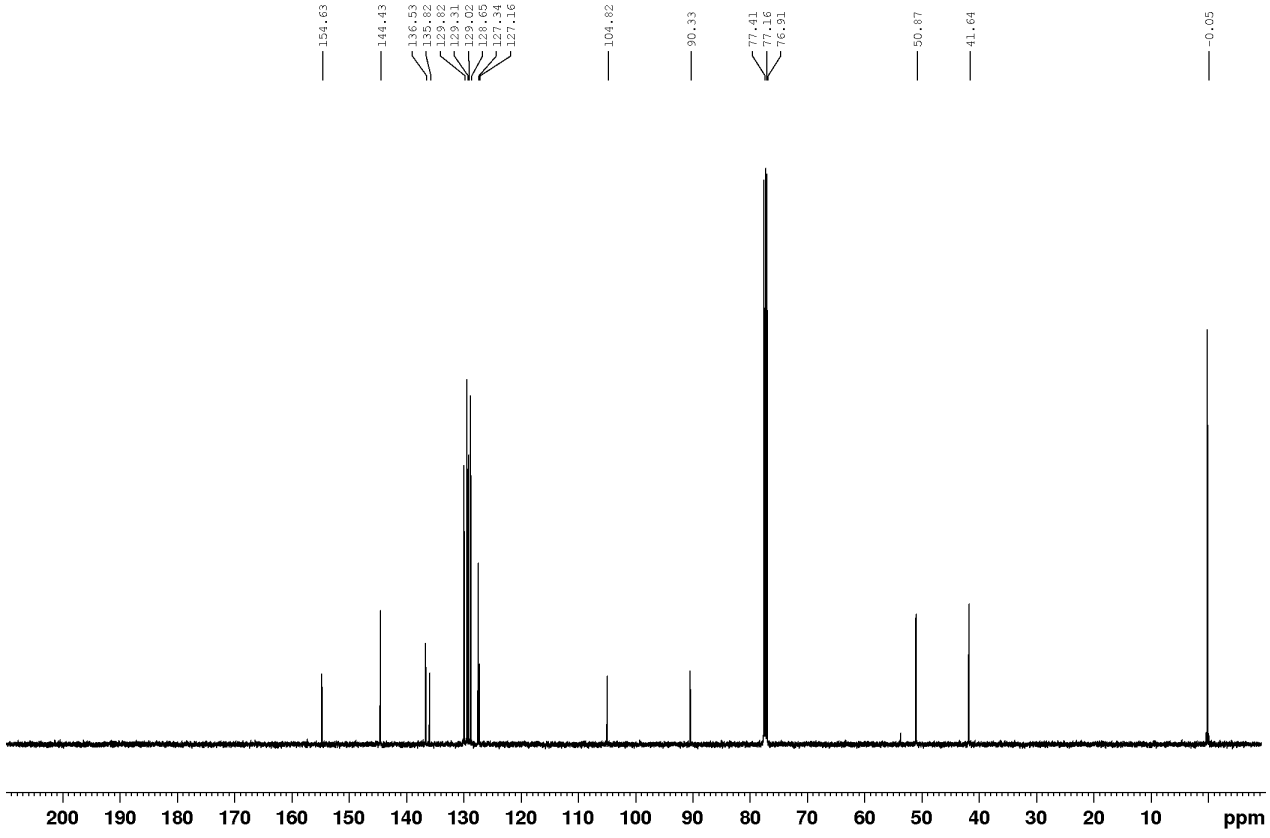


3-(4-Chlorophenyl)-*N*-(1-phenyl-4-(trimethylsilyl)but-3-yn-2-yl)isoxazol-4-amine (1h)

^{1}H NMR (500 MHz, $CDCl_3$)

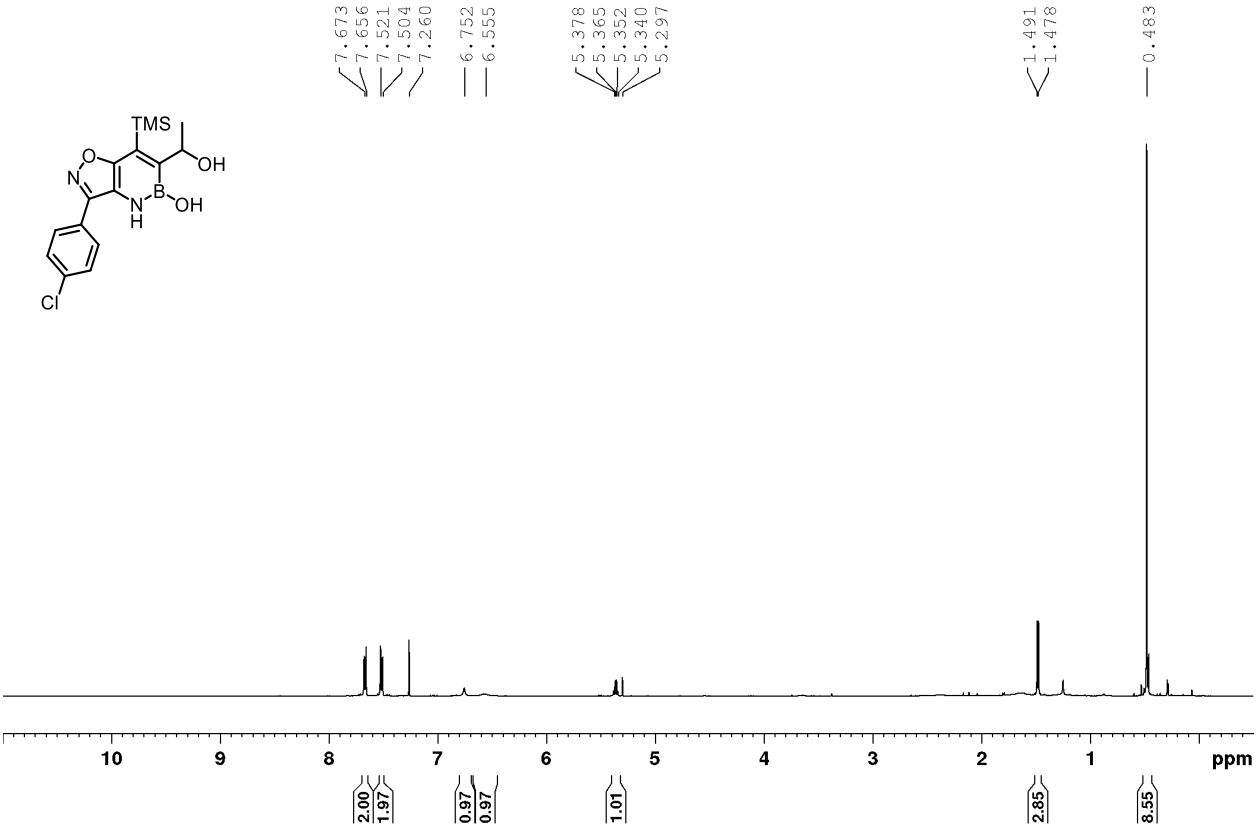


^{13}C NMR (125 MHz, $CDCl_3$)

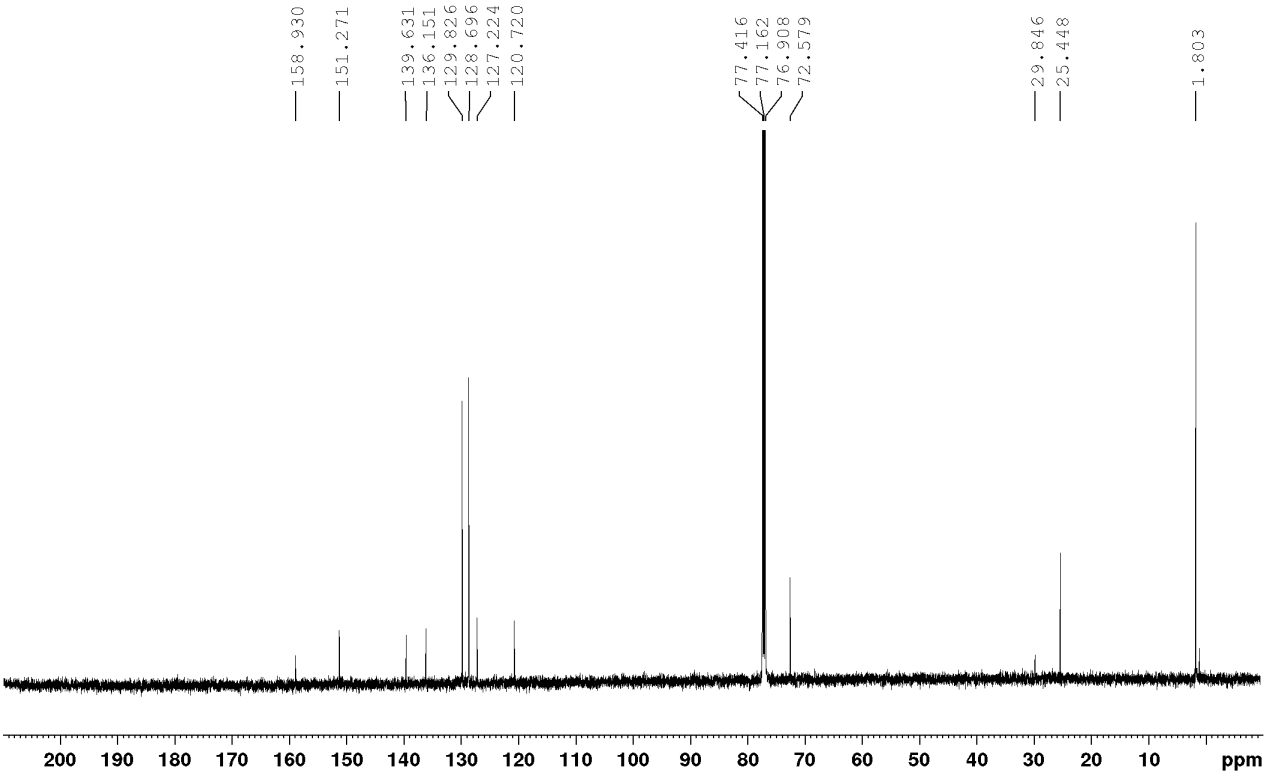


3-(4-Chlorophenyl)-6-(1-hydroxyethyl)-7-(trimethylsilyl)isoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-ol (3a)

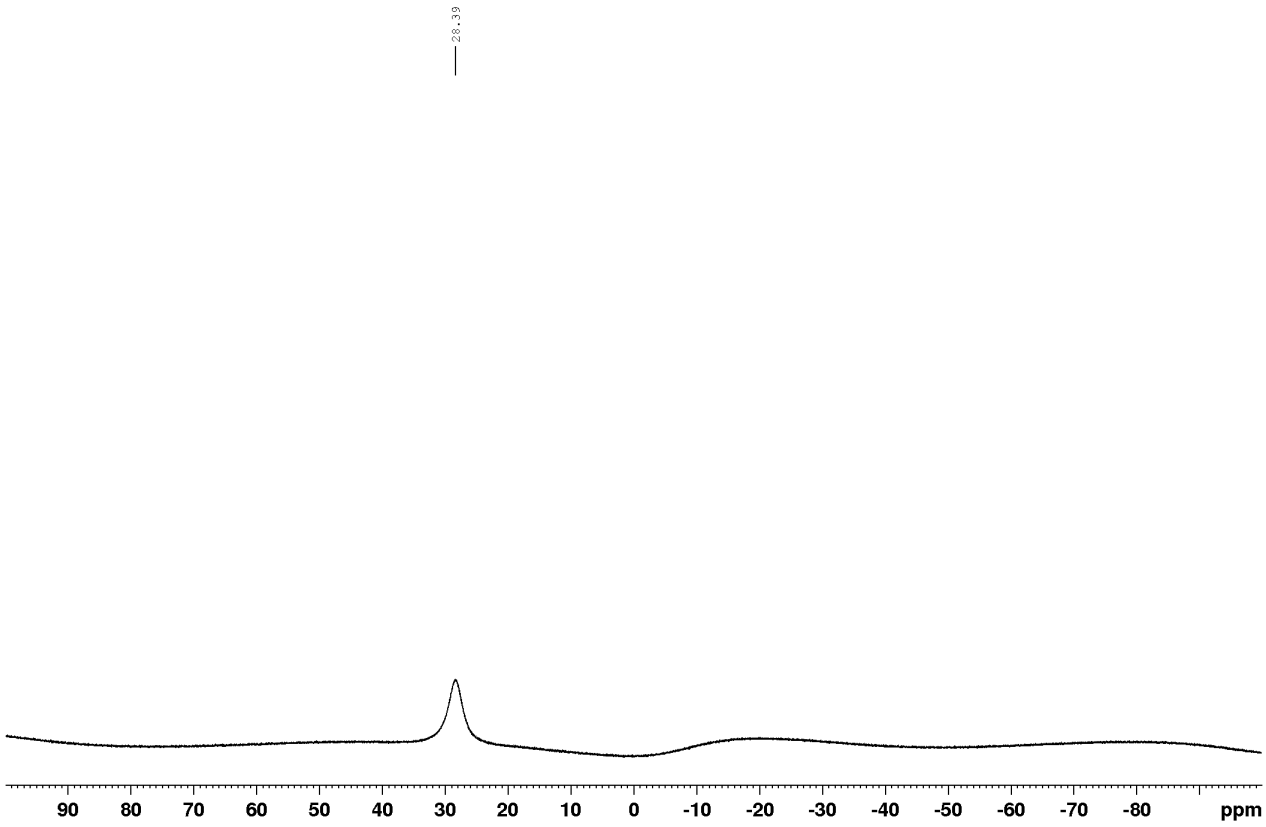
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

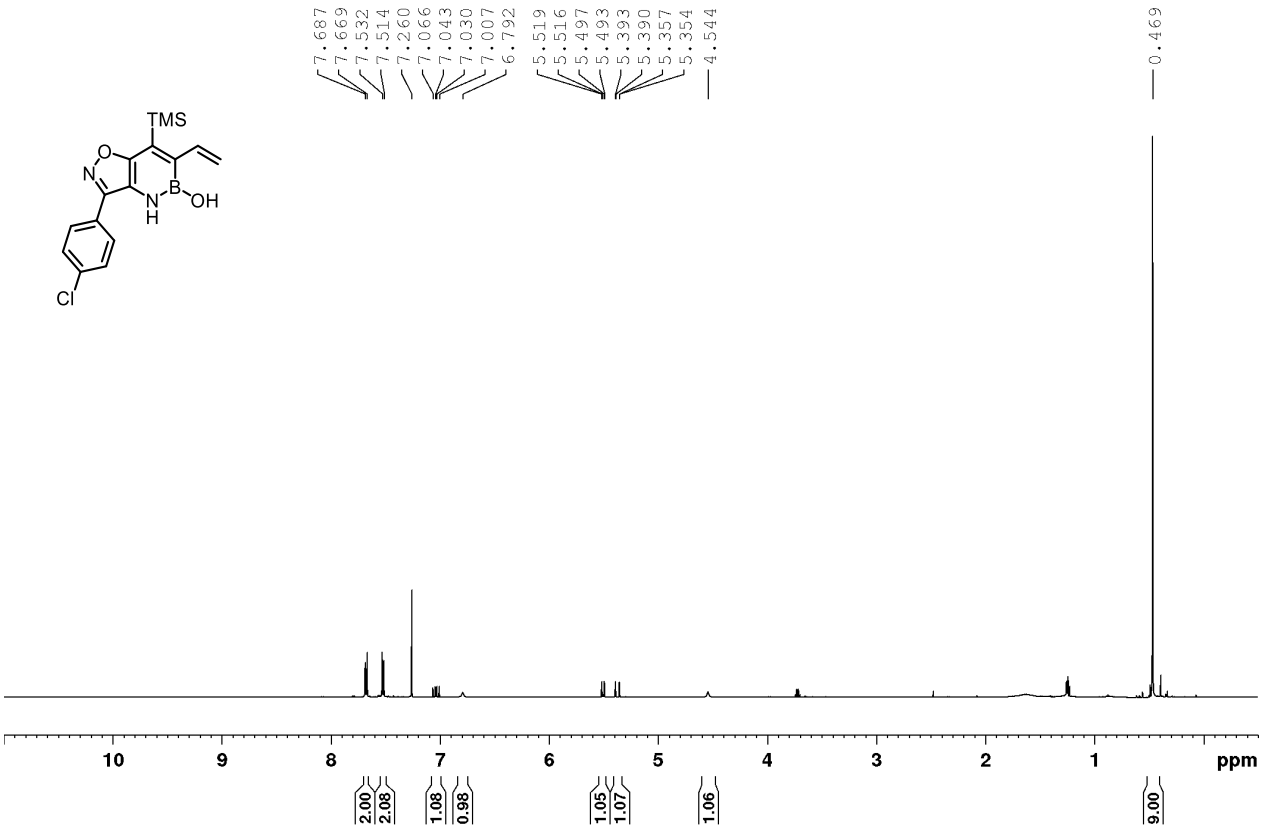


^{11}B NMR (160 MHz, $CDCl_3$)

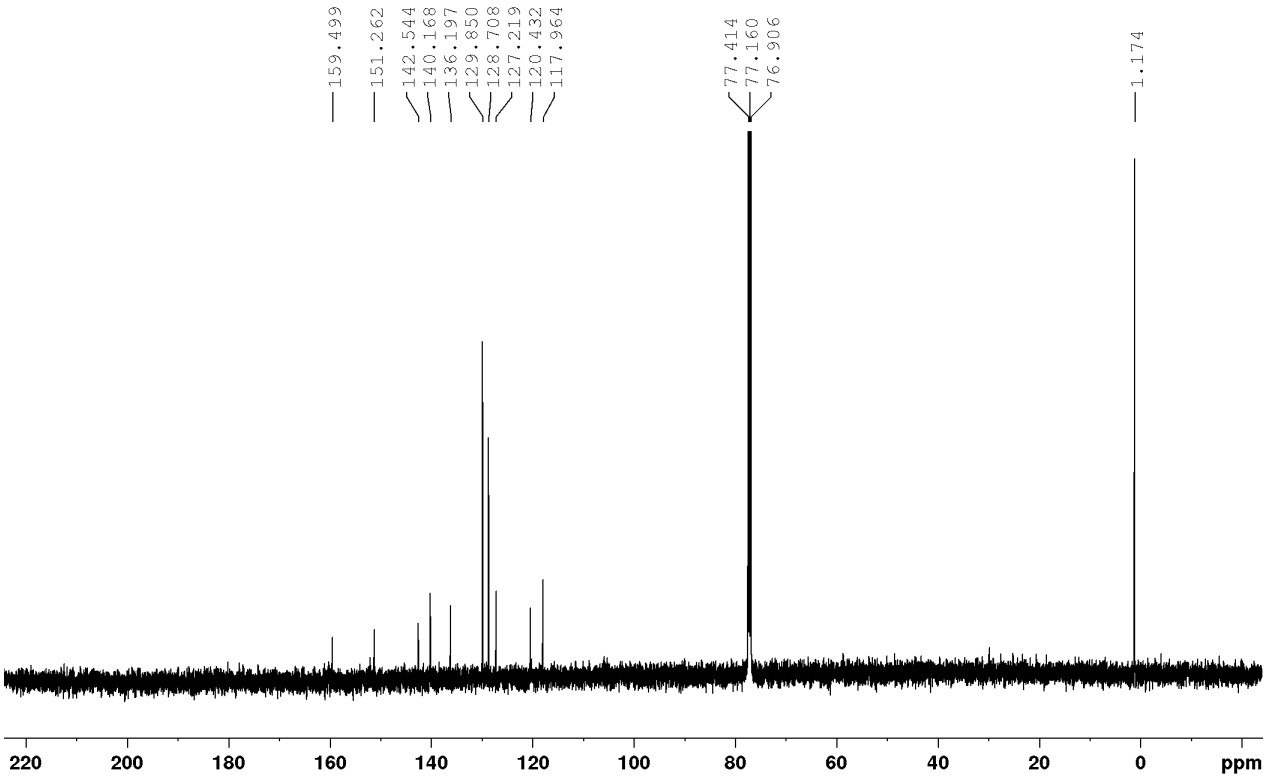


3-(4-Chlorophenyl)-7-(trimethylsilyl)-6-vinylisoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-ol (3b)

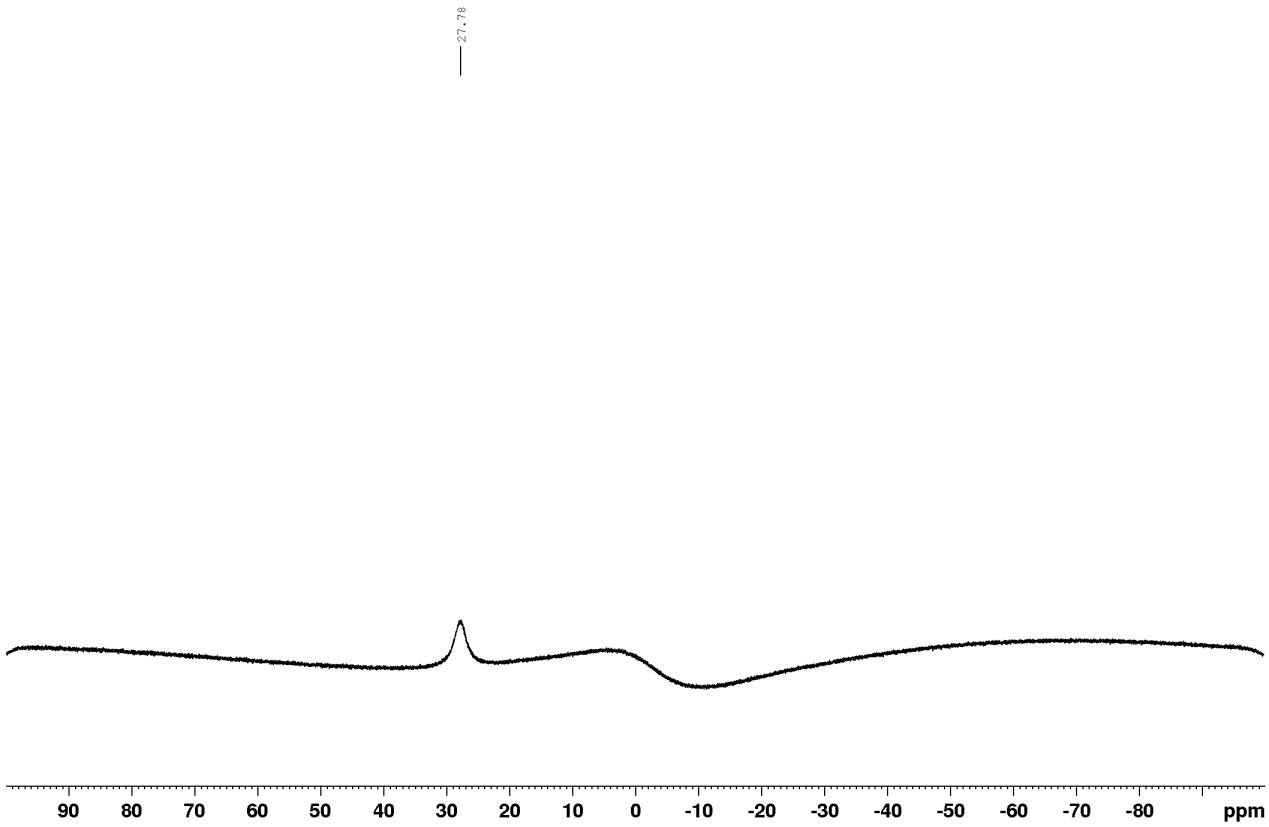
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

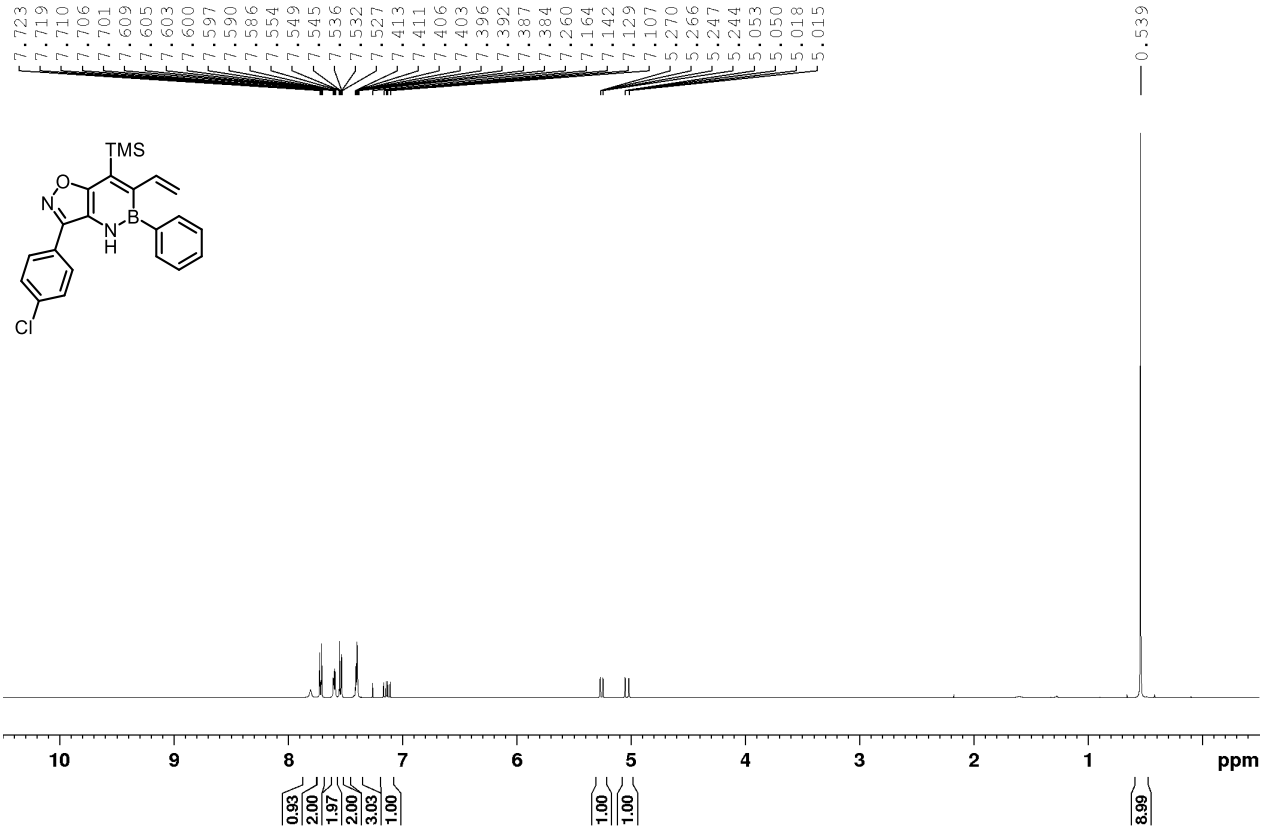


^{11}B NMR (160 MHz, $CDCl_3$)

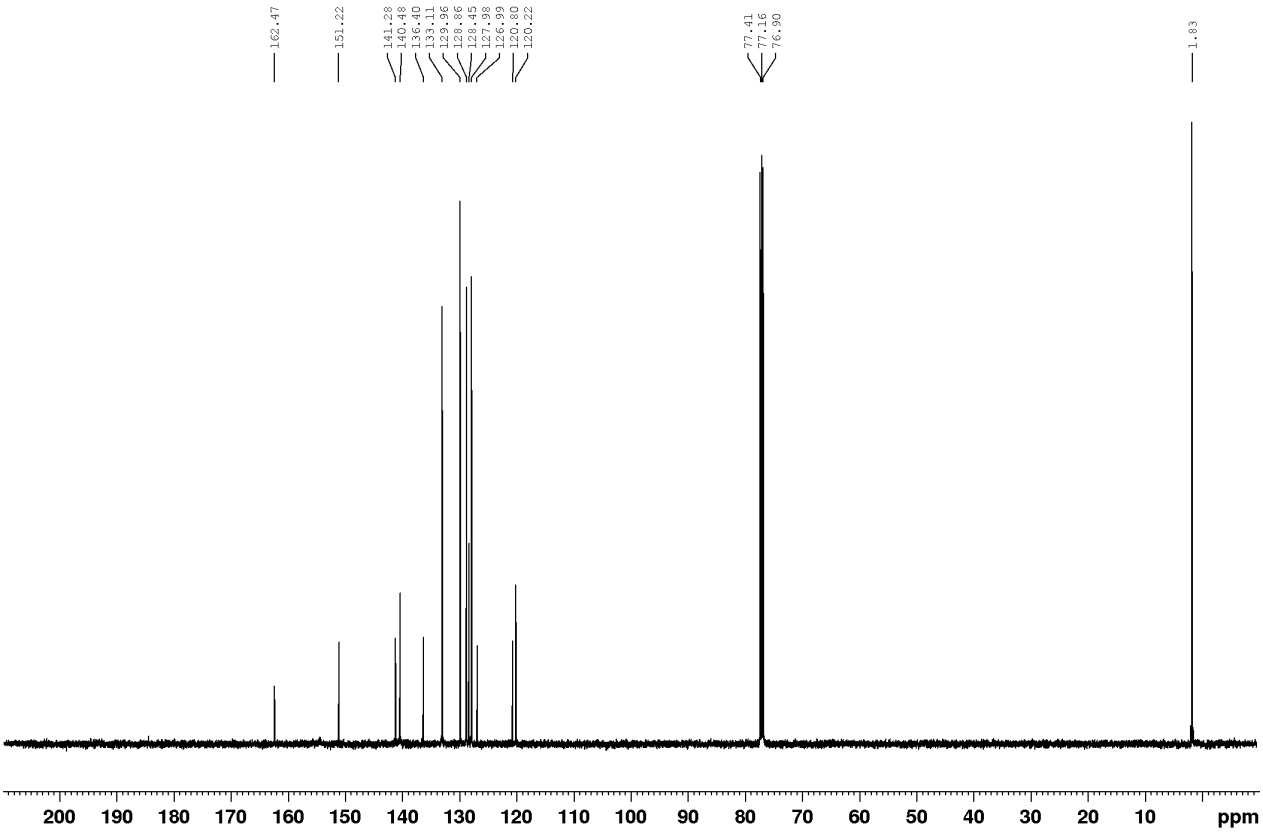


3-(4-Chlorophenyl)-6-(1-methoxyethyl)-7-(trimethylsilyl)isoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-ol (5a)

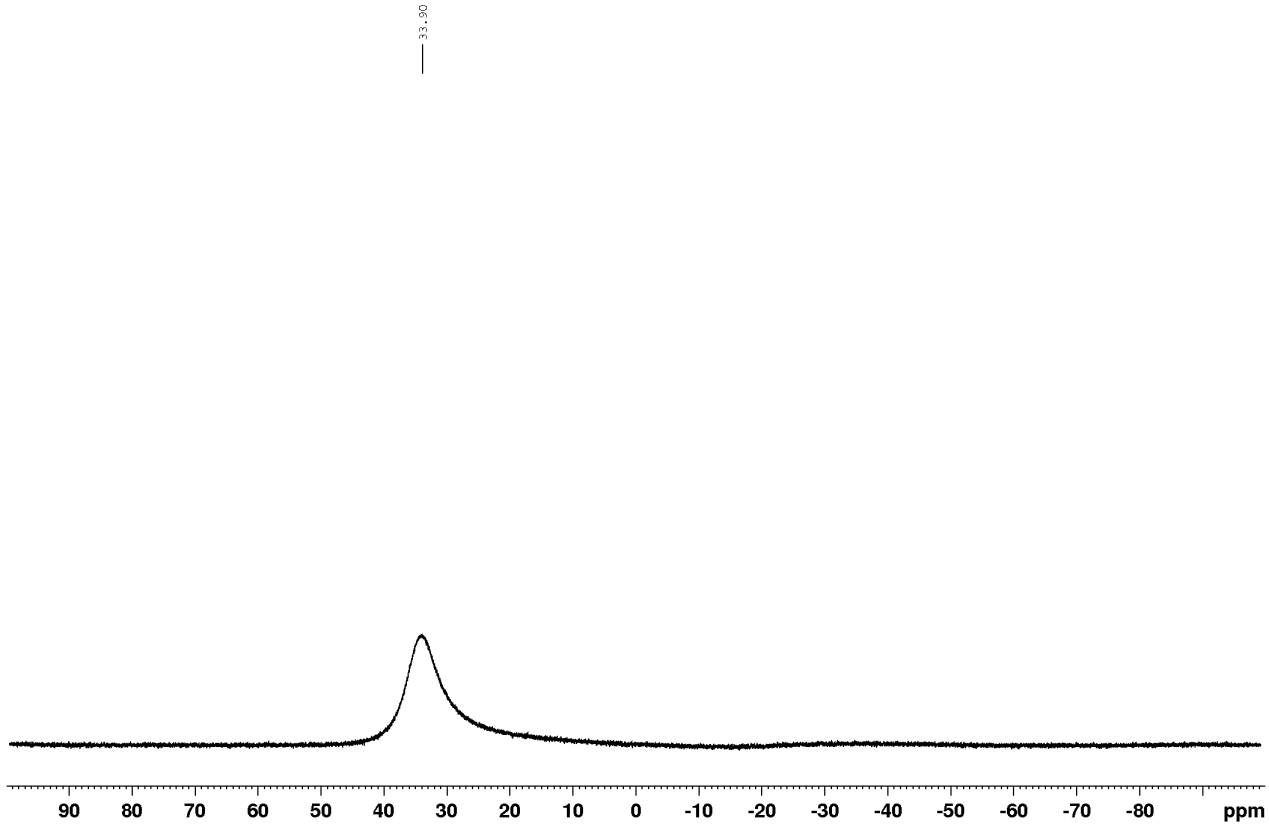
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

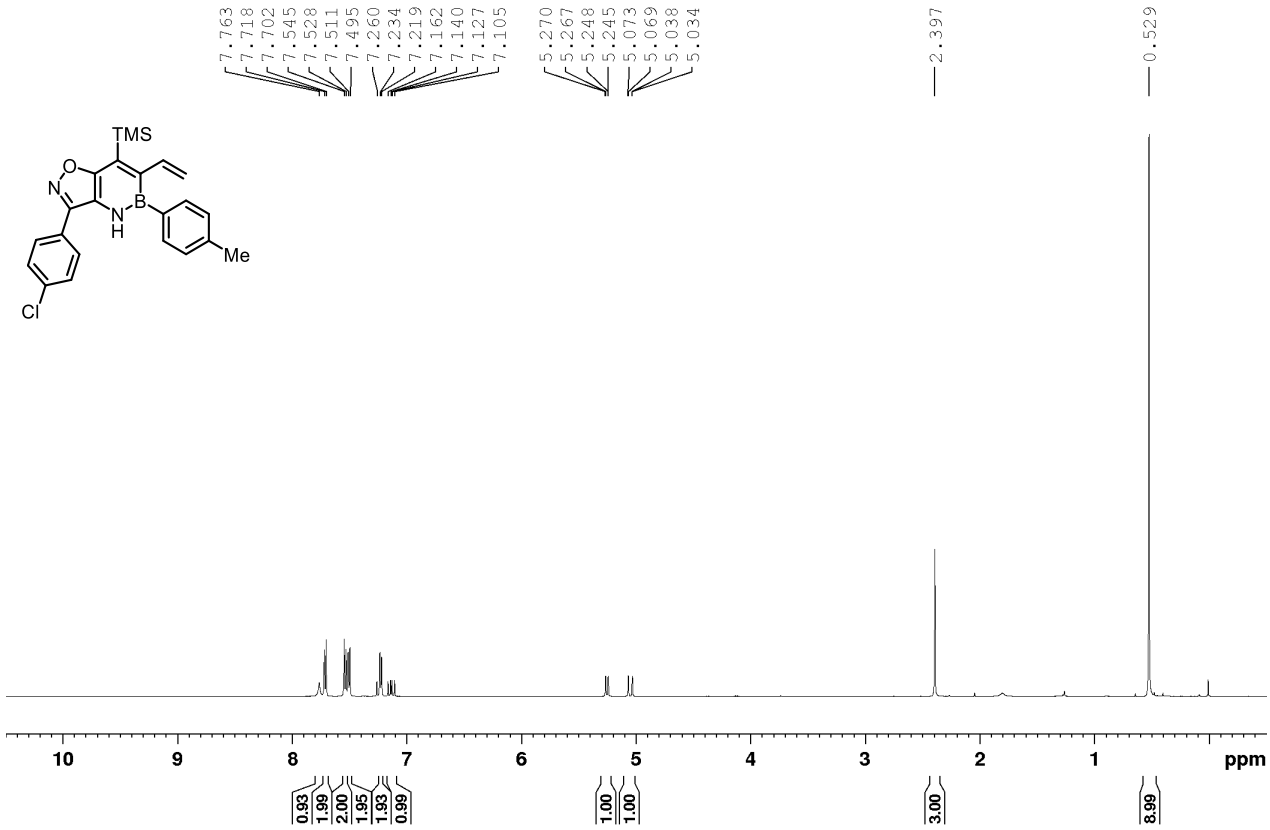


^{11}B NMR (128 MHz, $CDCl_3$)

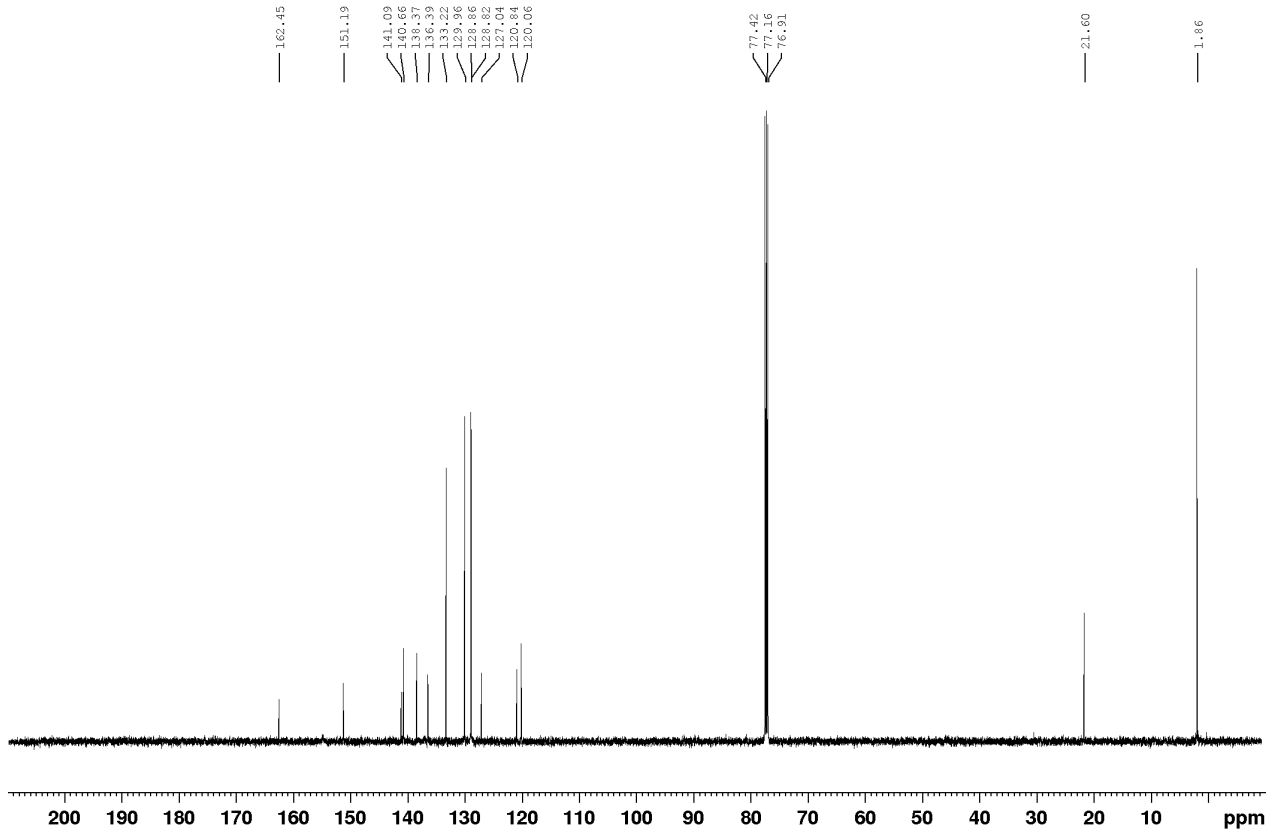


3-(4-Chlorophenyl)-5-(*p*-tolyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5b)

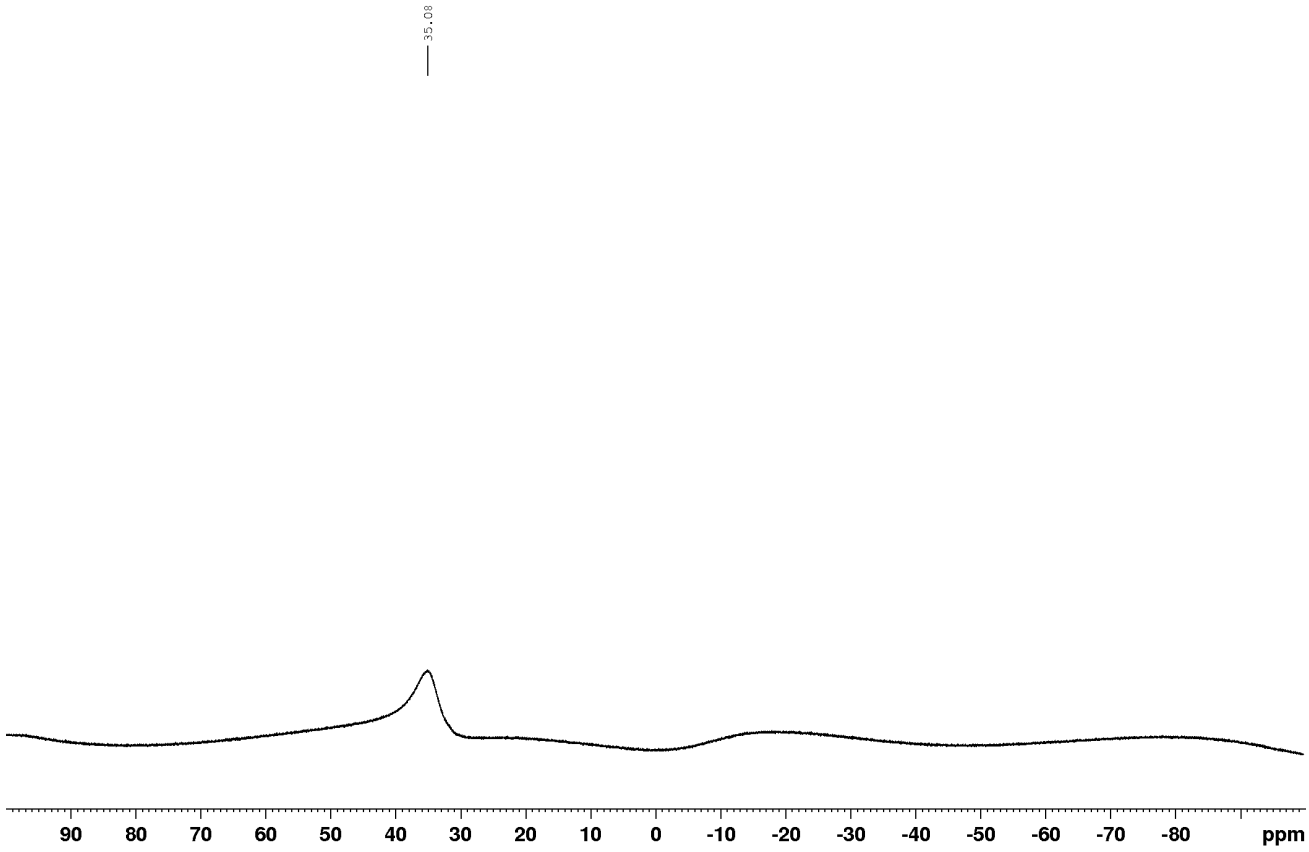
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

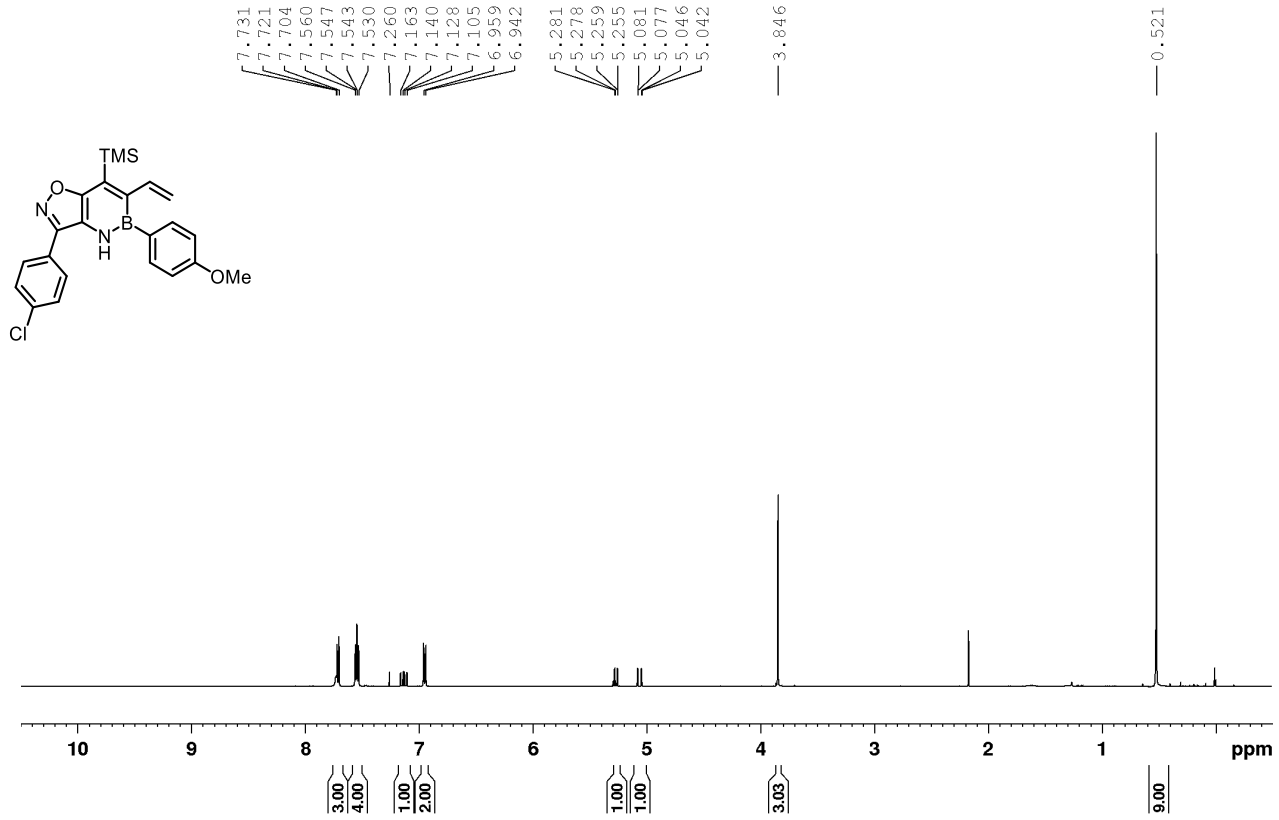


^{11}B NMR (160 MHz, $CDCl_3$)

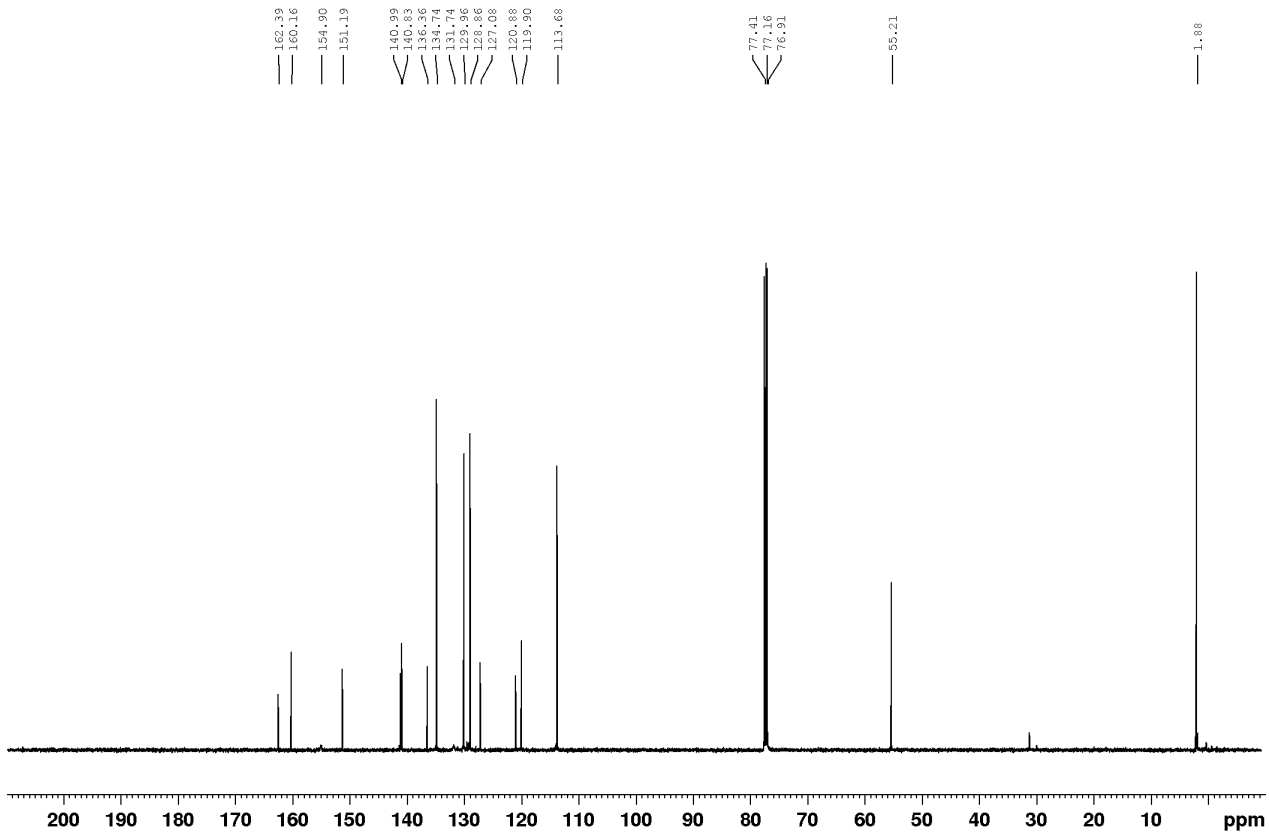


3-(4-Chlorophenyl)-5-(4-methoxyphenyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5c)

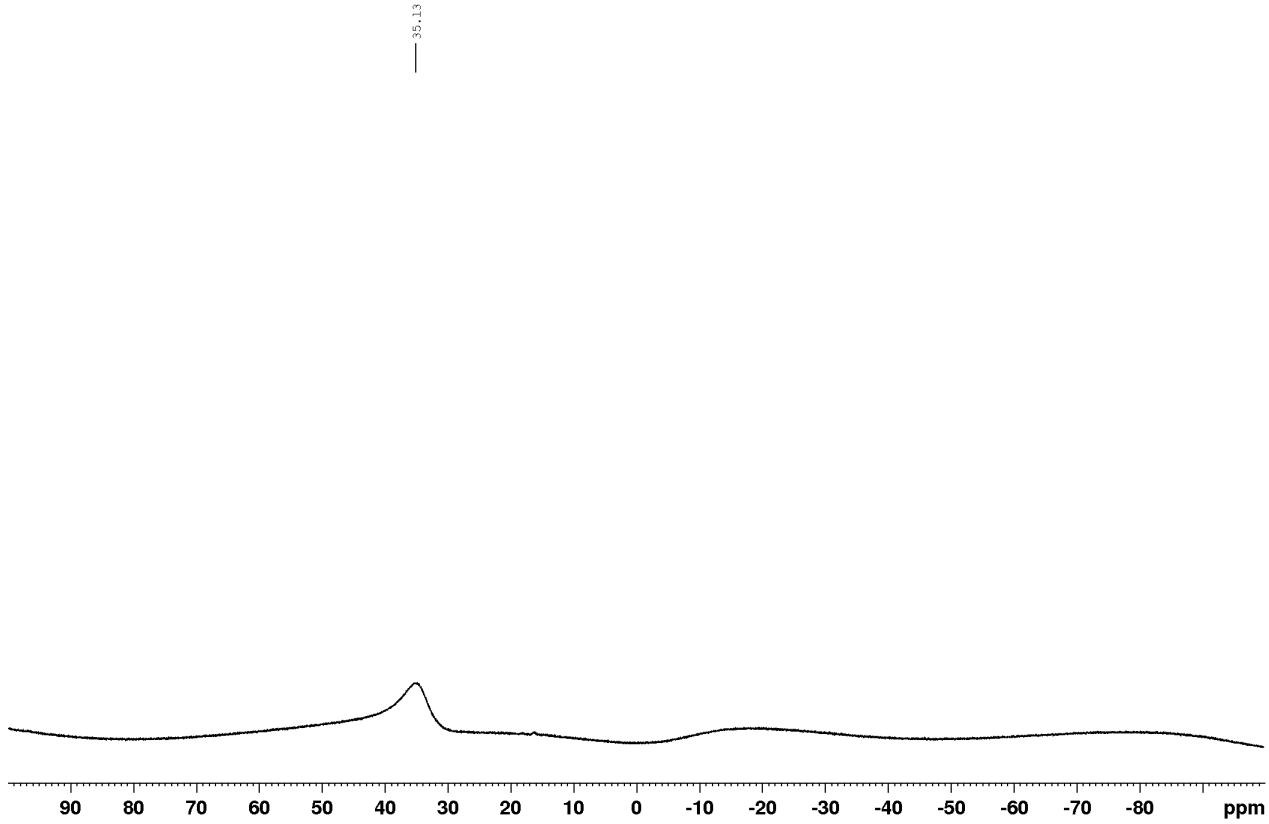
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

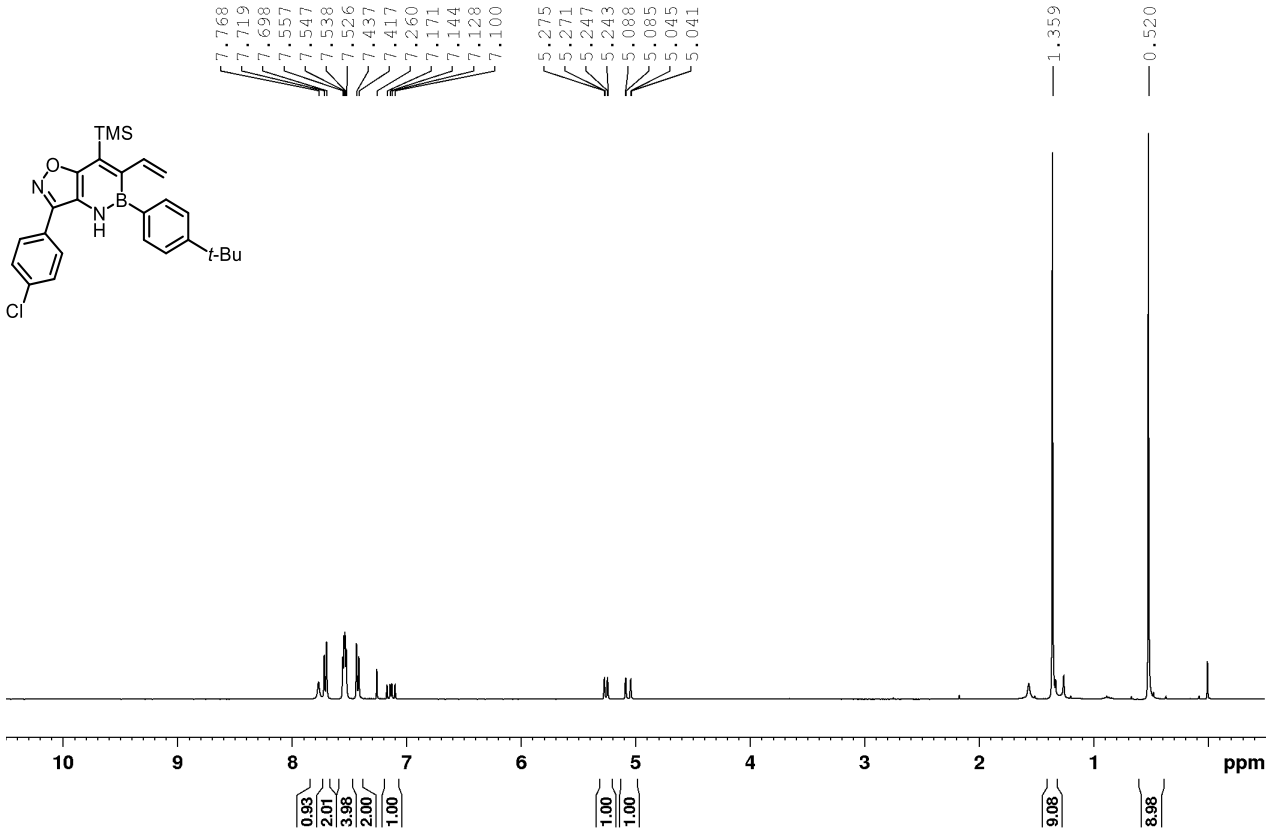


^{11}B NMR (160 MHz, $CDCl_3$)

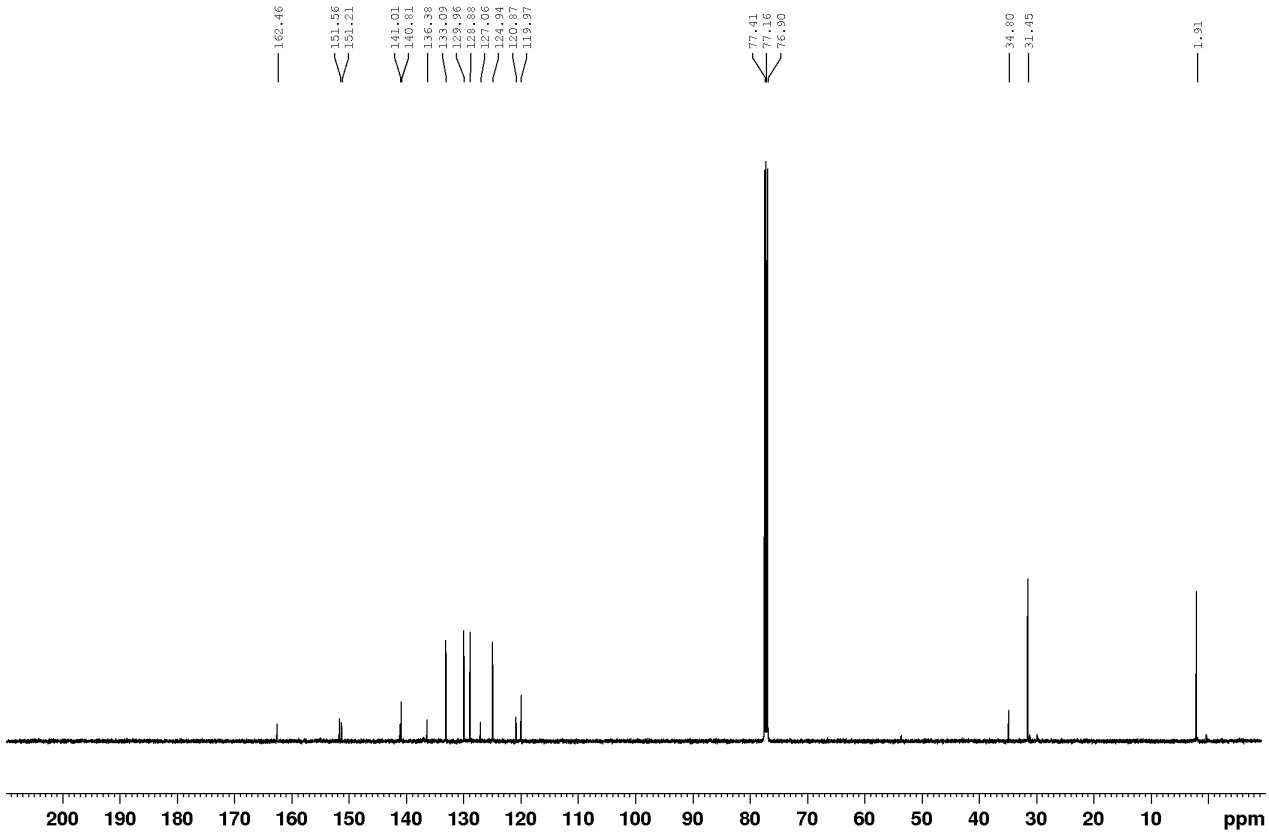


5-(4-(*tert*-Butyl)phenyl)-3-(4-chlorophenyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5d)

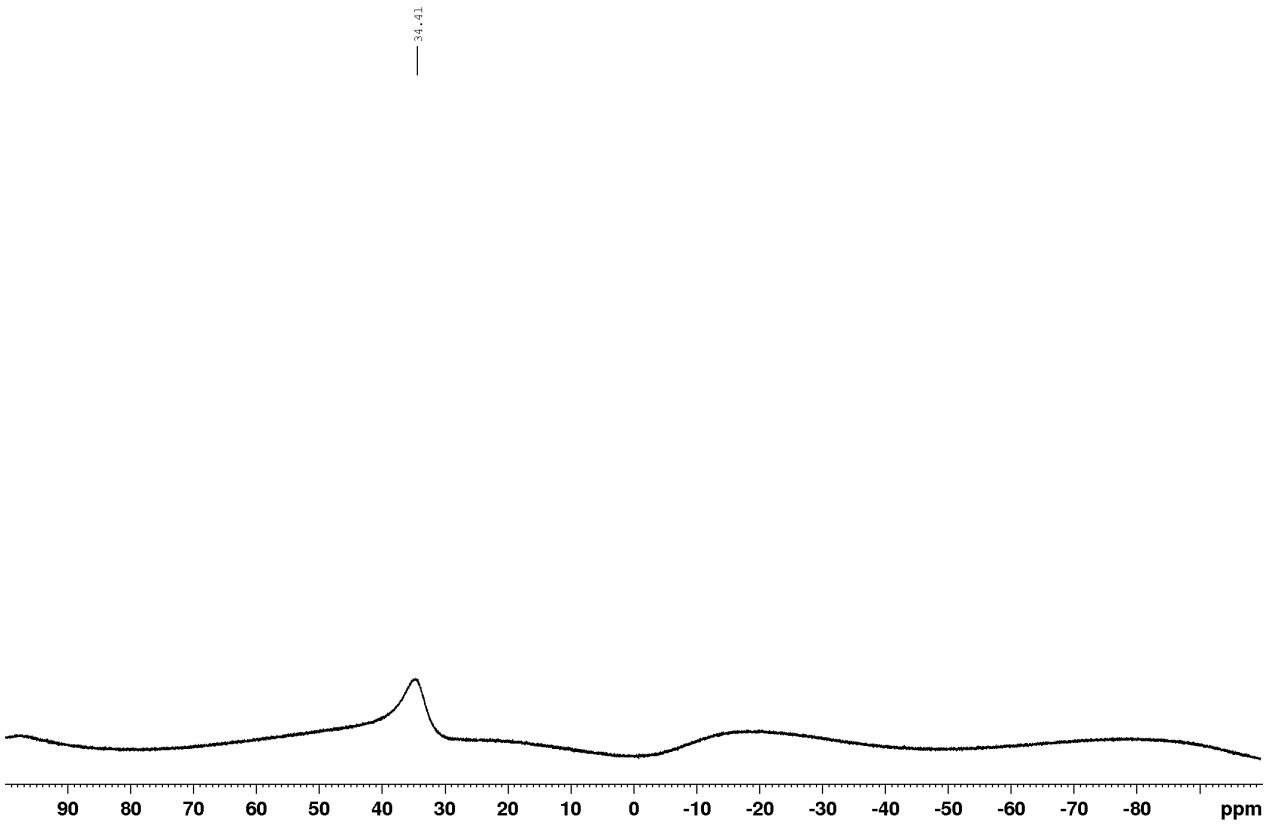
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

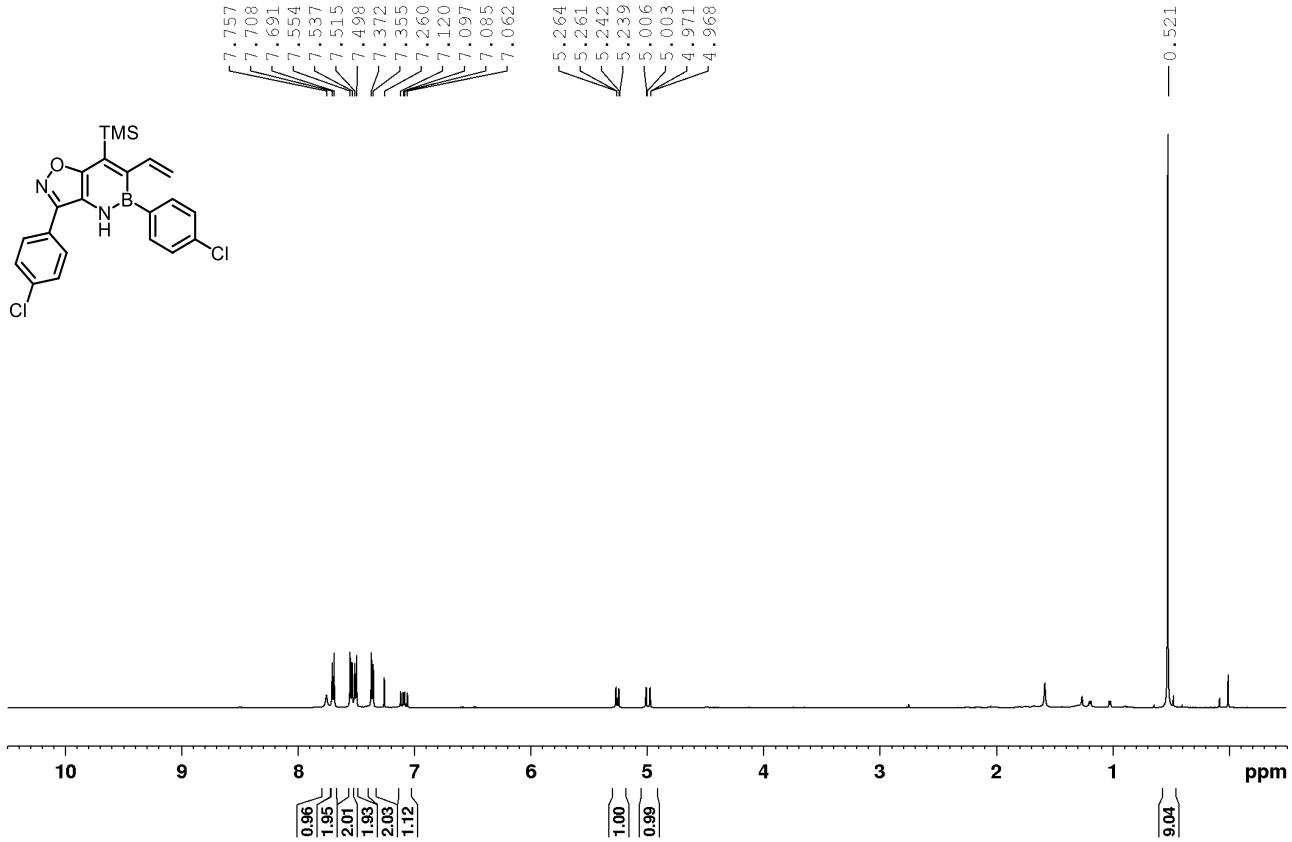


^{11}B NMR (160 MHz, $CDCl_3$)

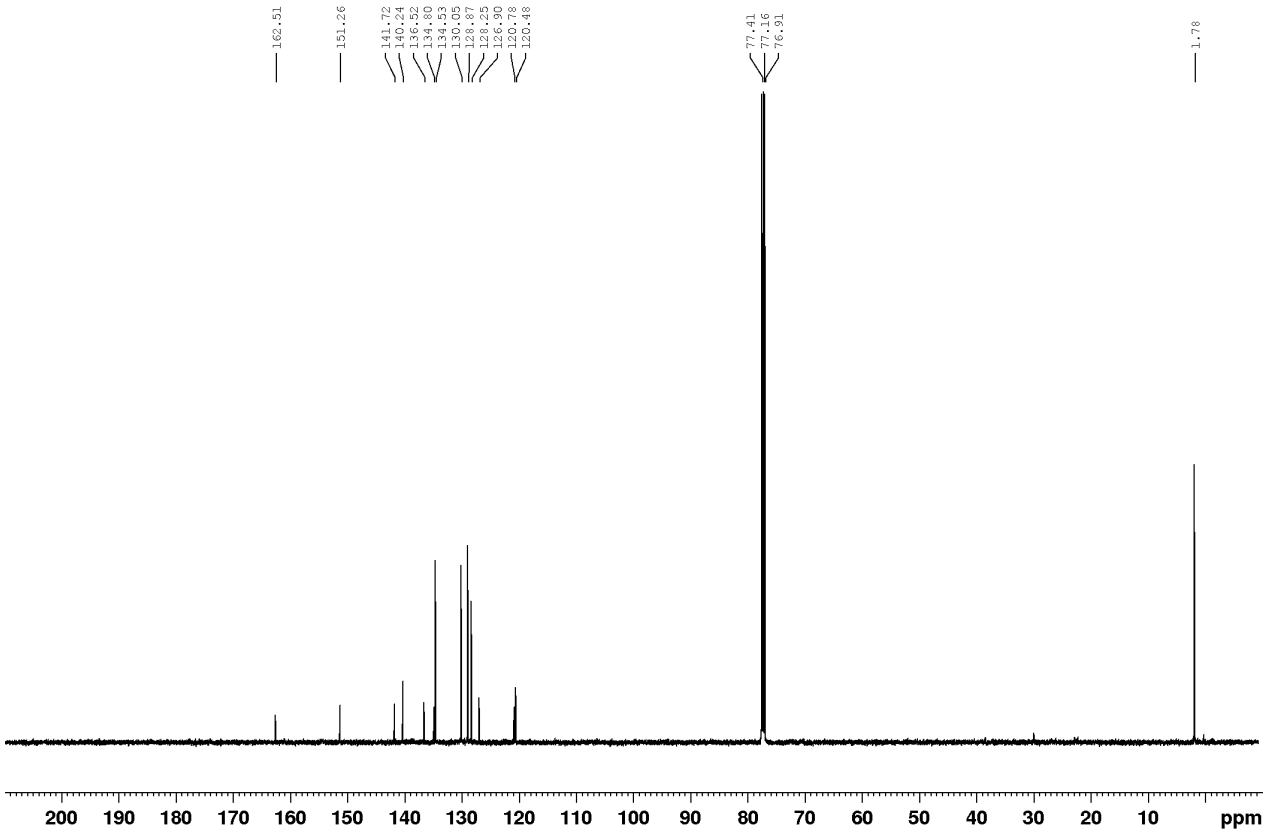


3,5-Bis(4-chlorophenyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5e)

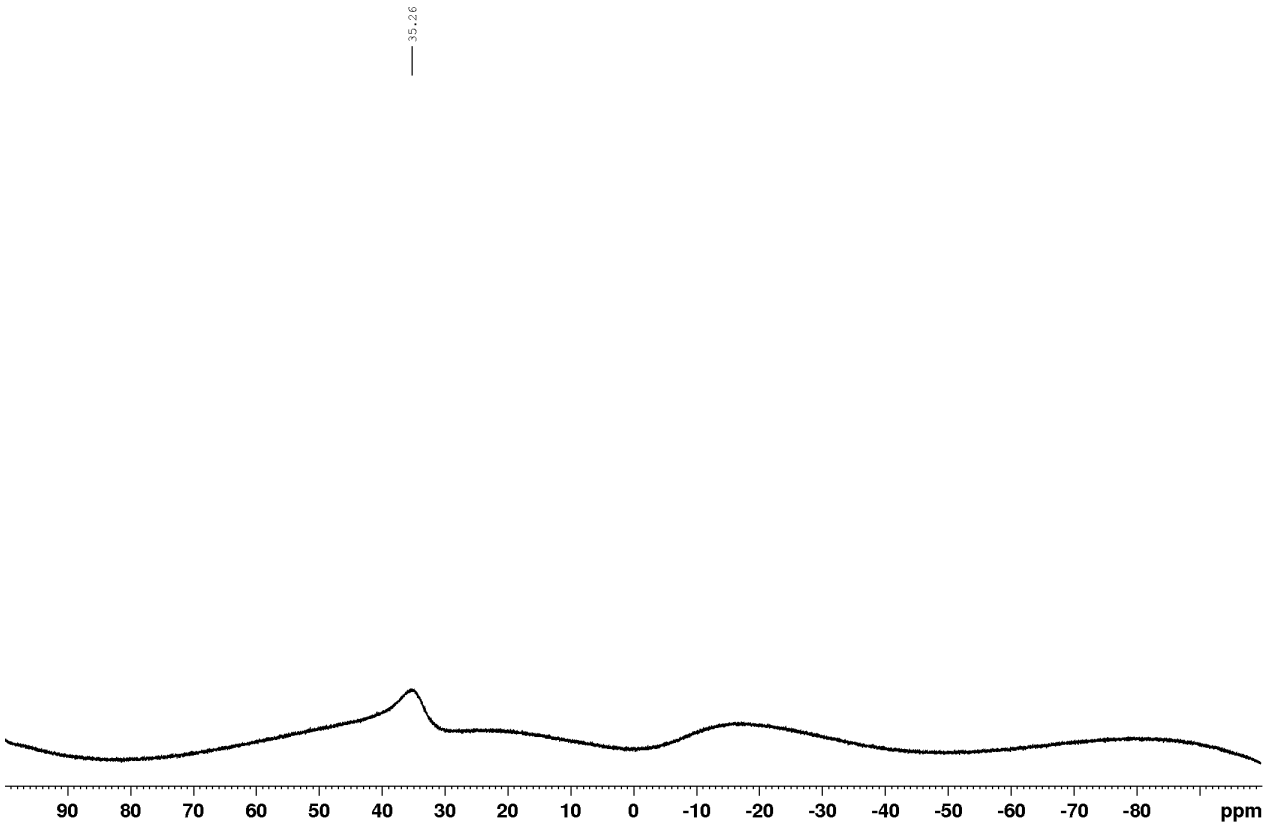
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

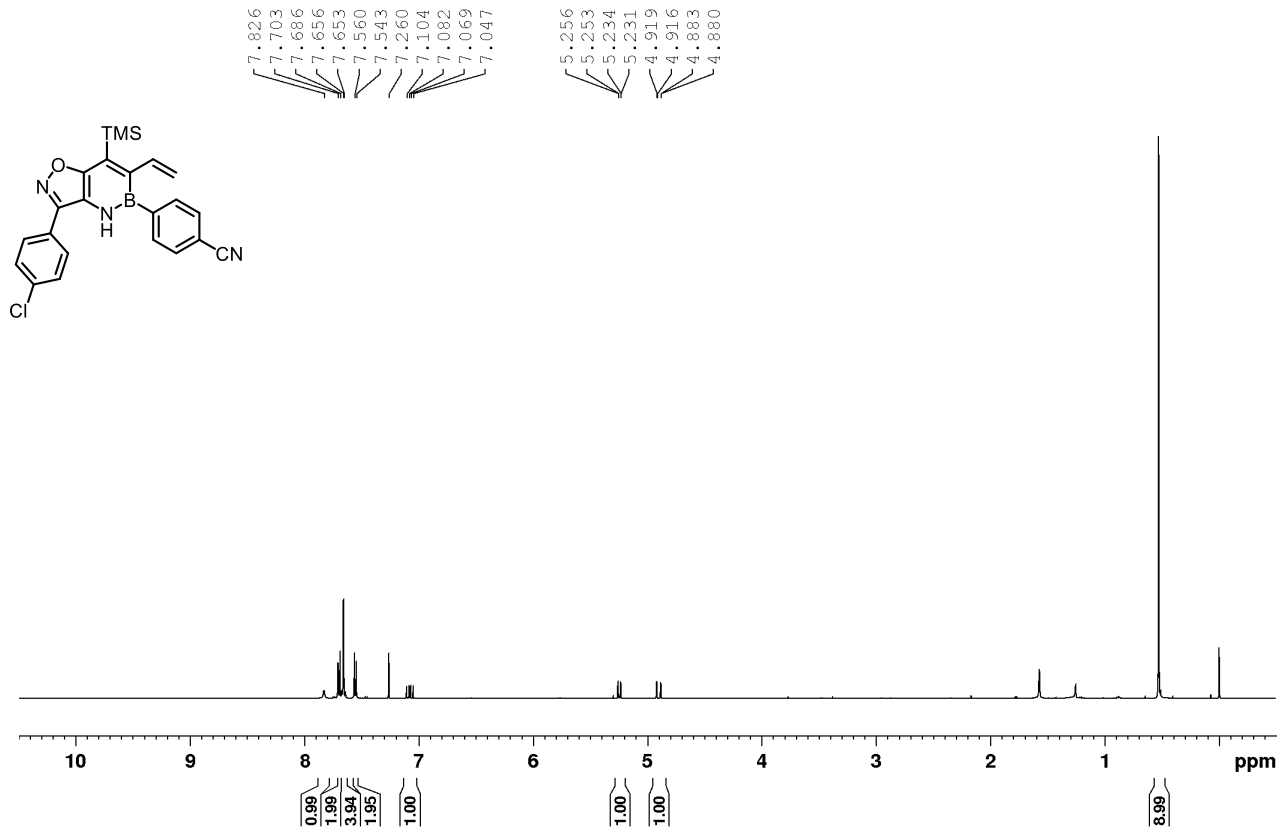


^{11}B NMR (160 MHz, $CDCl_3$)

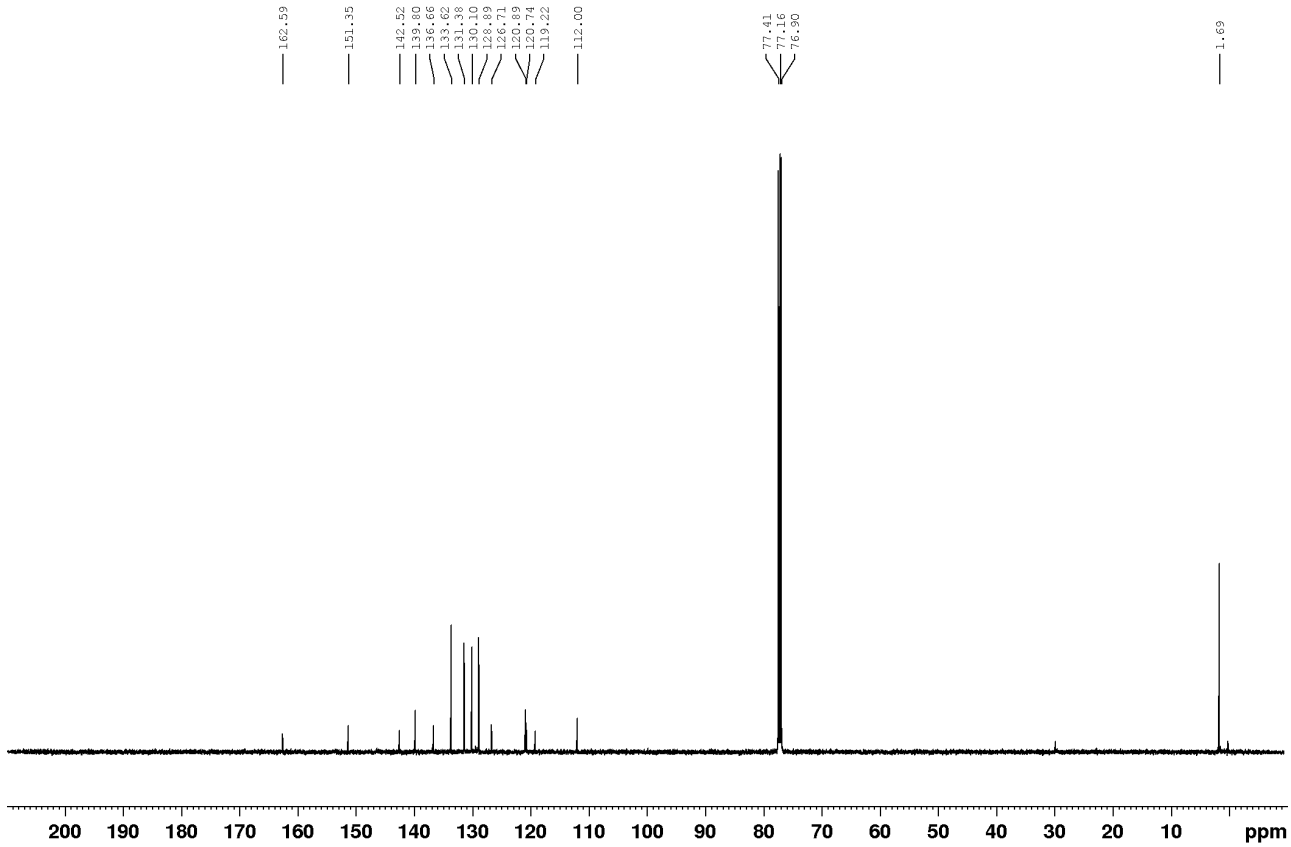


4-(3-(4-Chlorophenyl)-7-(trimethylsilyl)-6-vinylisoxazolo[5,4-*e*][1,2]azaborinin-5(4*H*)-yl)benzonitrile (5f)

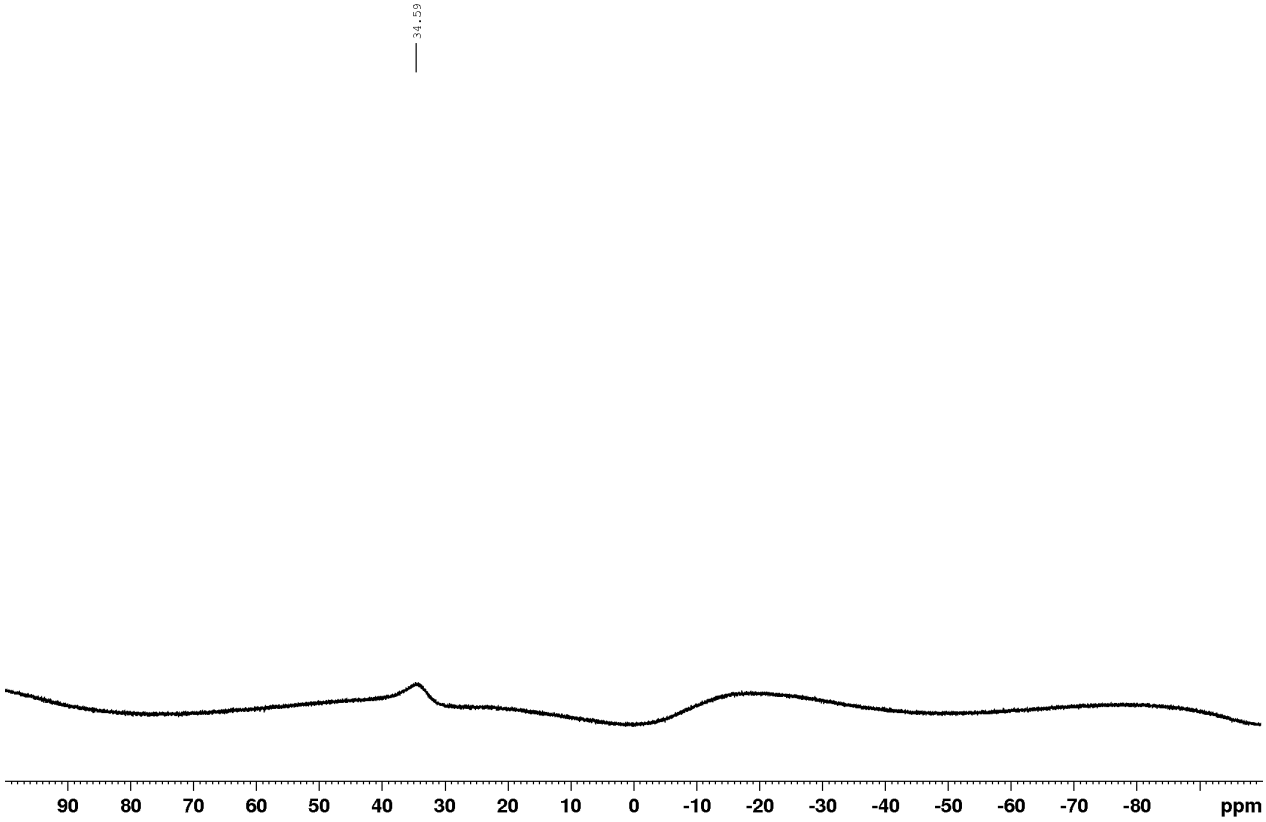
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

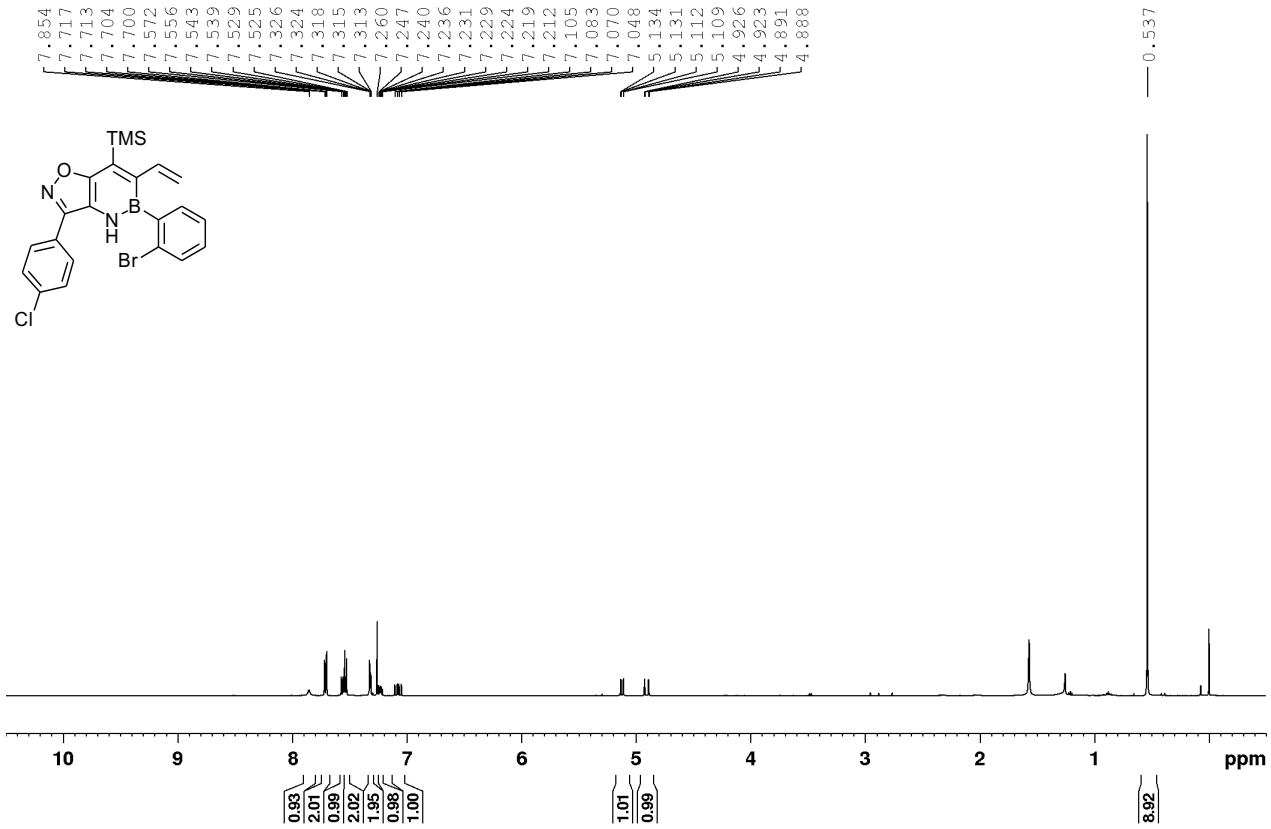


^{11}B NMR (160 MHz, $CDCl_3$)

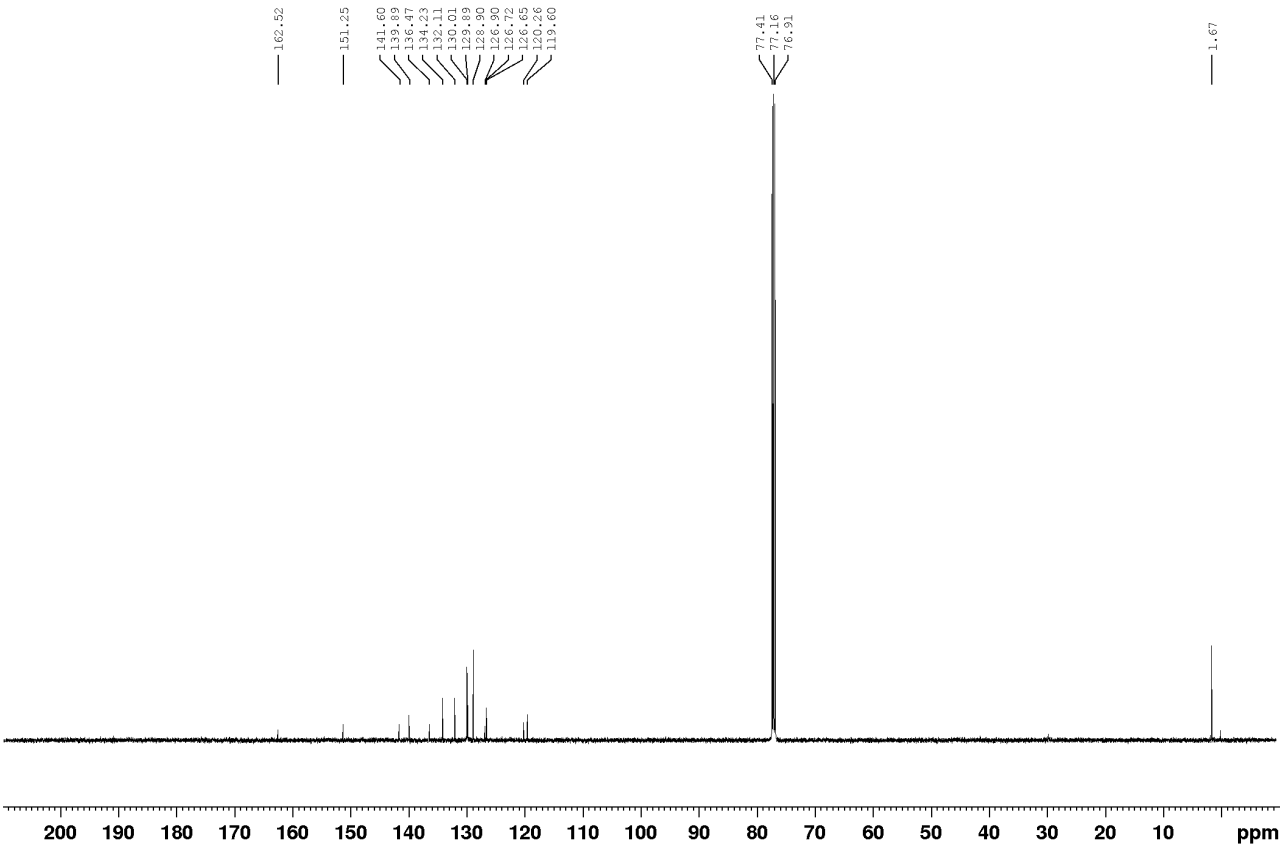


5-(2-Bromophenyl)-3-(4-chlorophenyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5g)

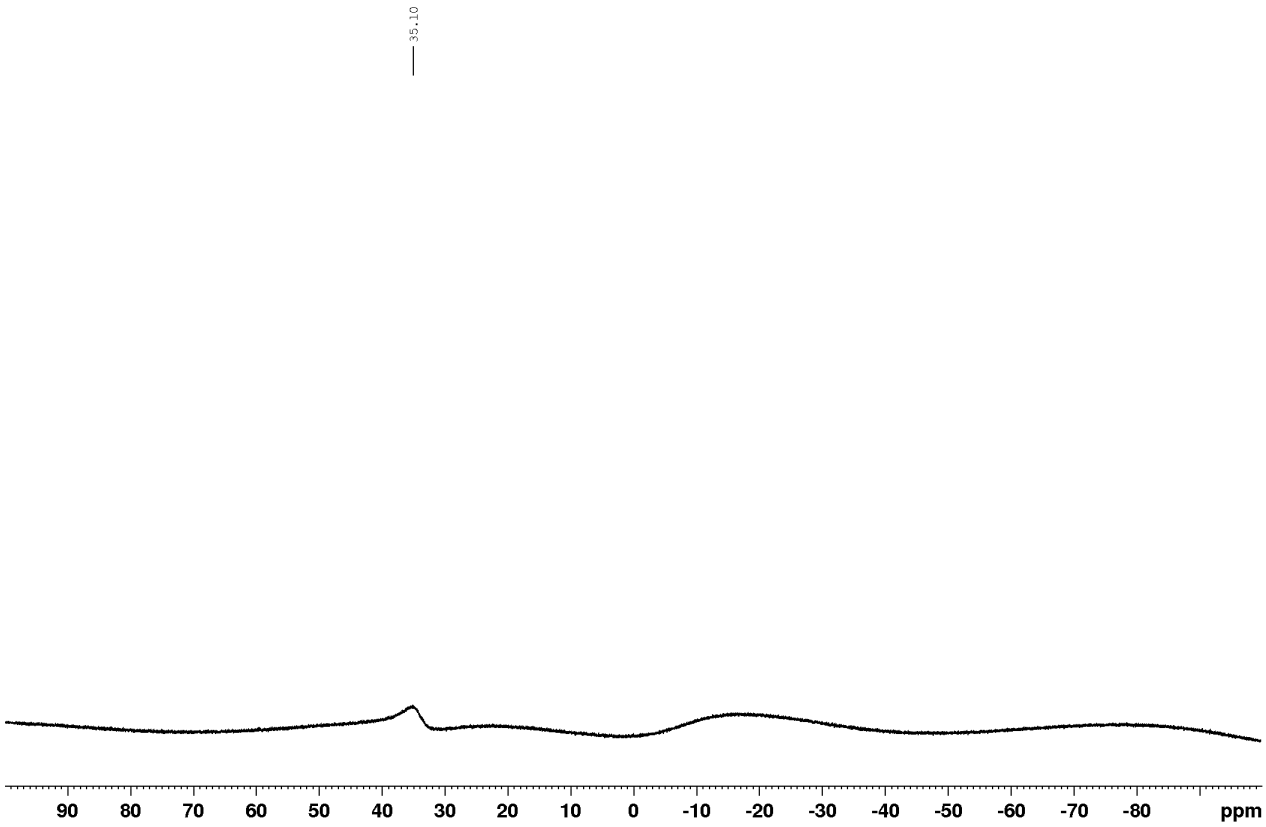
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

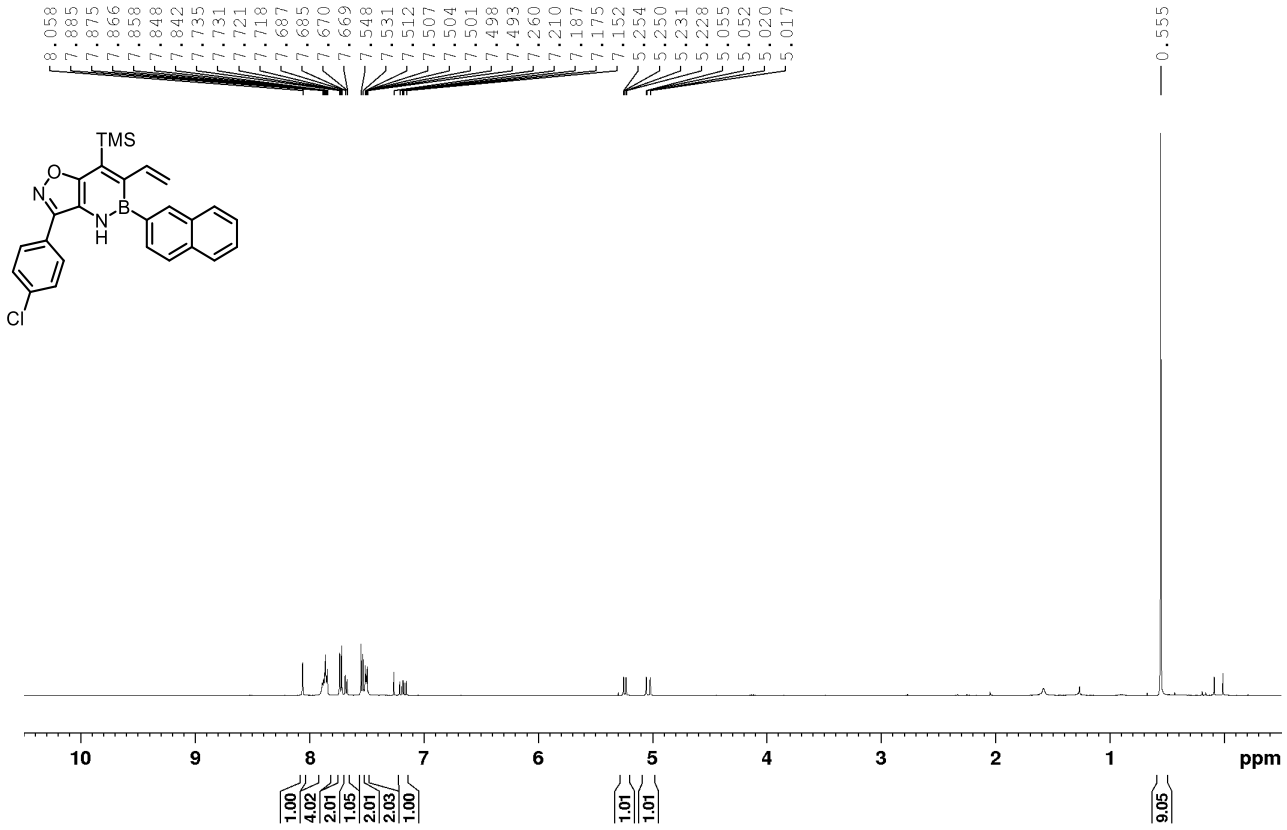


^{11}B NMR (160 MHz, $CDCl_3$)

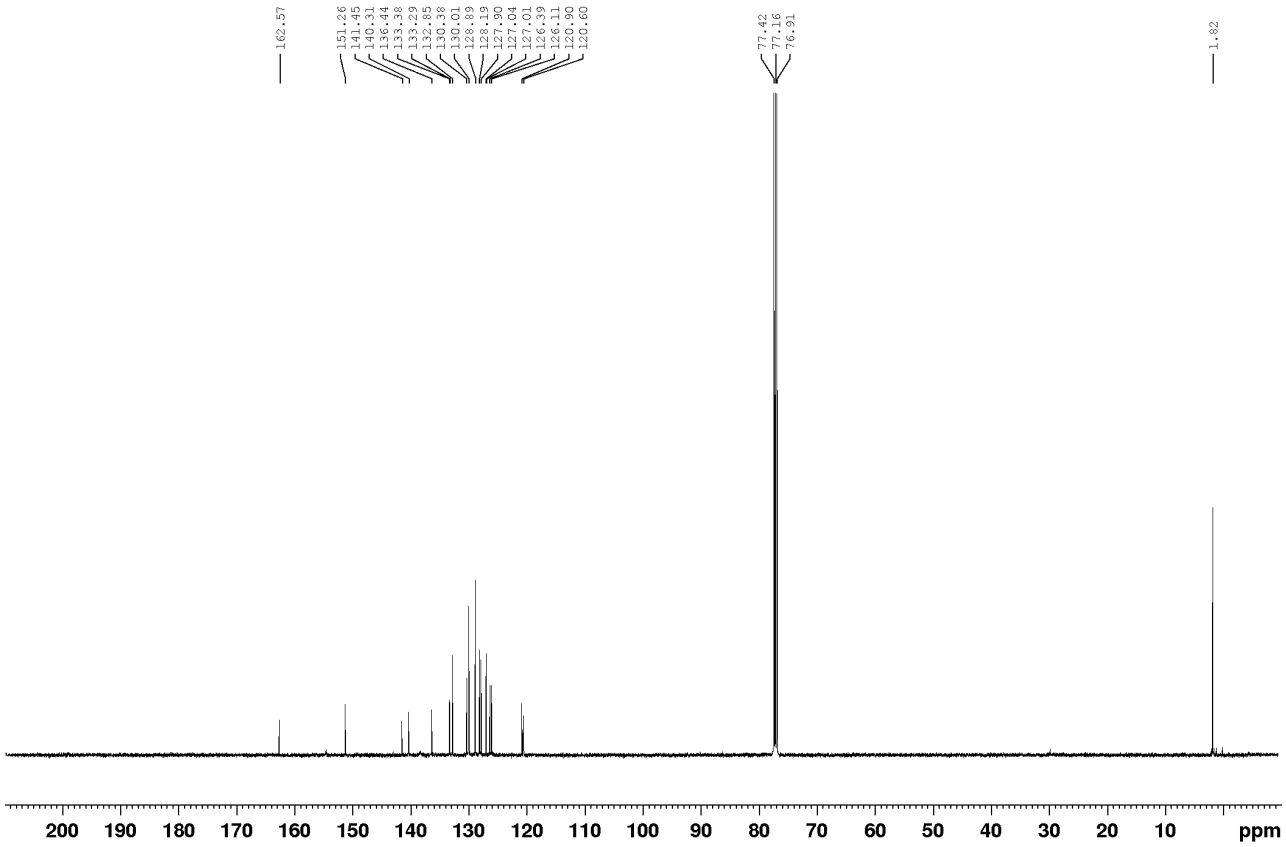


3-(4-Chlorophenyl)-5-(naphthalen-2-yl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5h)

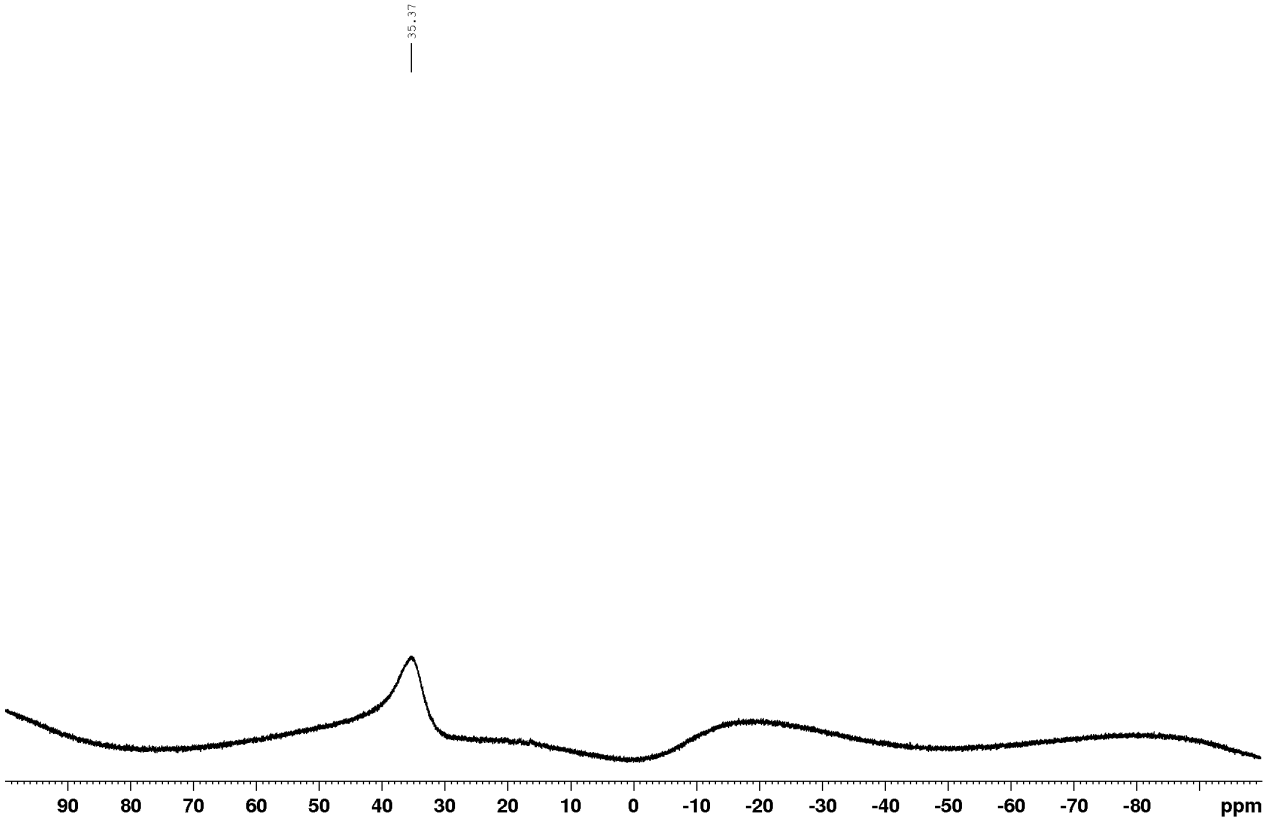
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

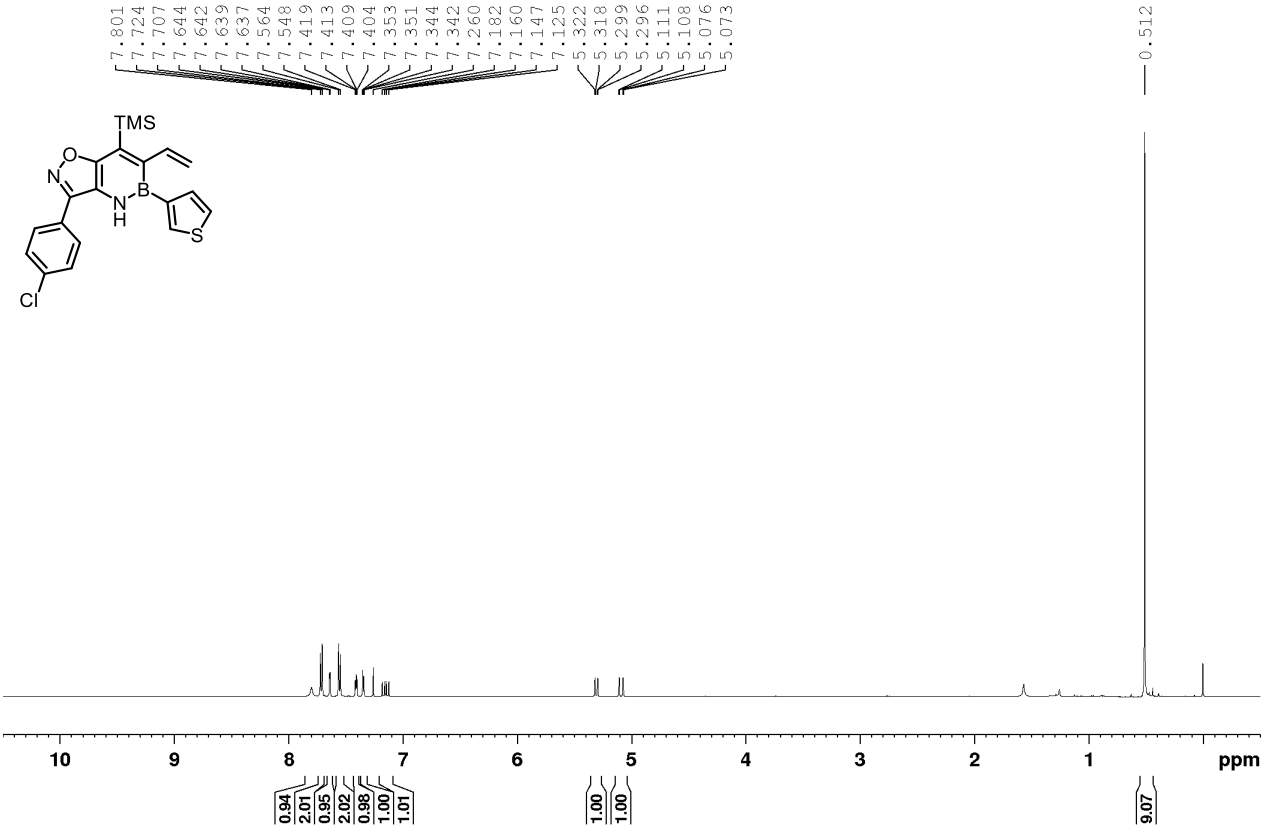


^{11}B NMR (160 MHz, $CDCl_3$)

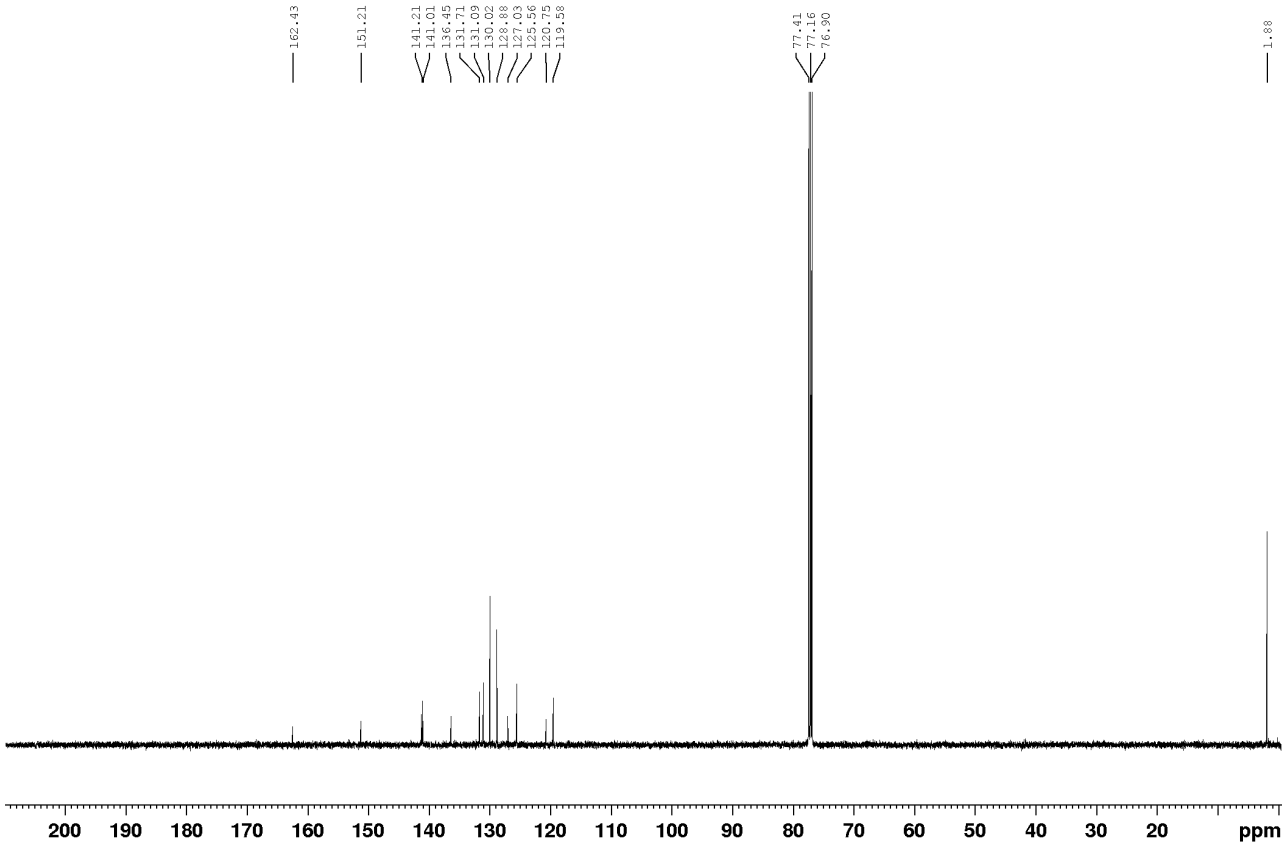


3-(4-Chlorophenyl)-5-(thiophen-3-yl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5i)

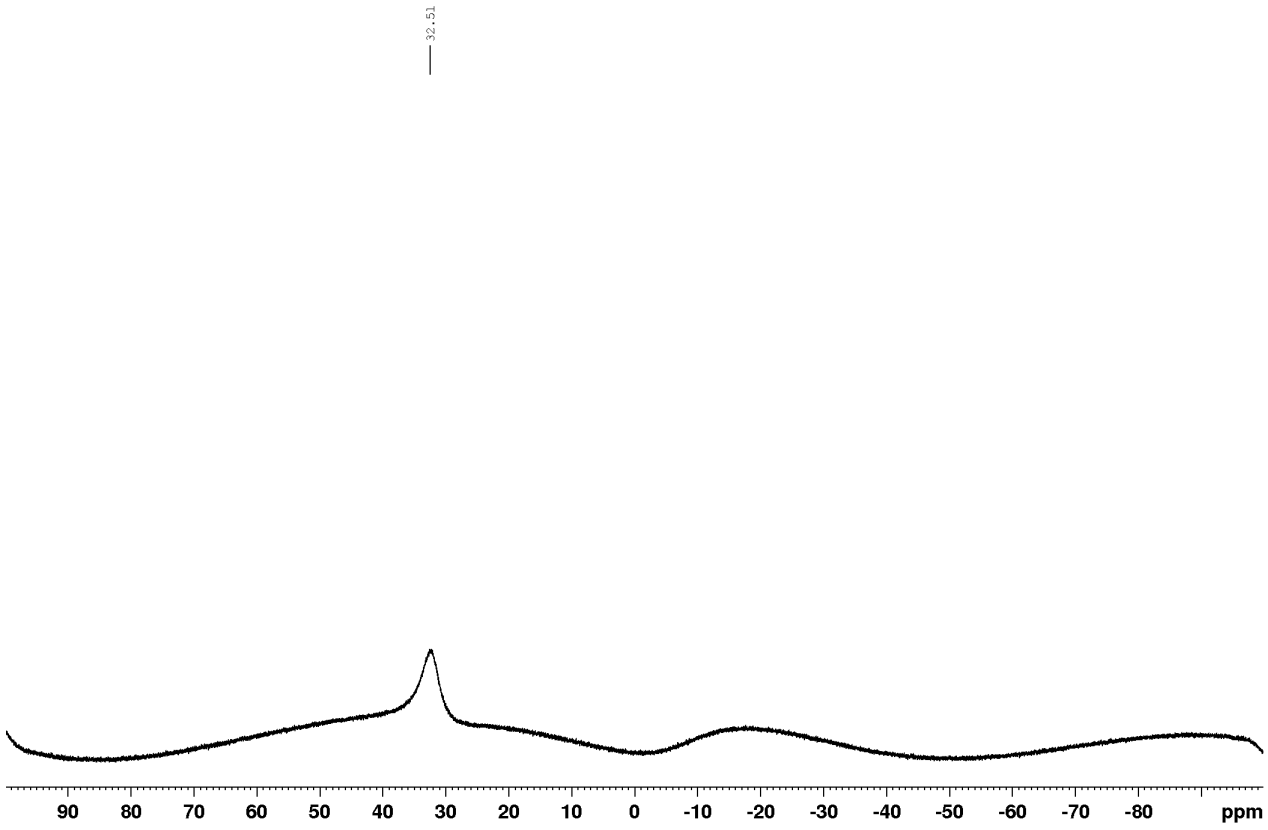
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

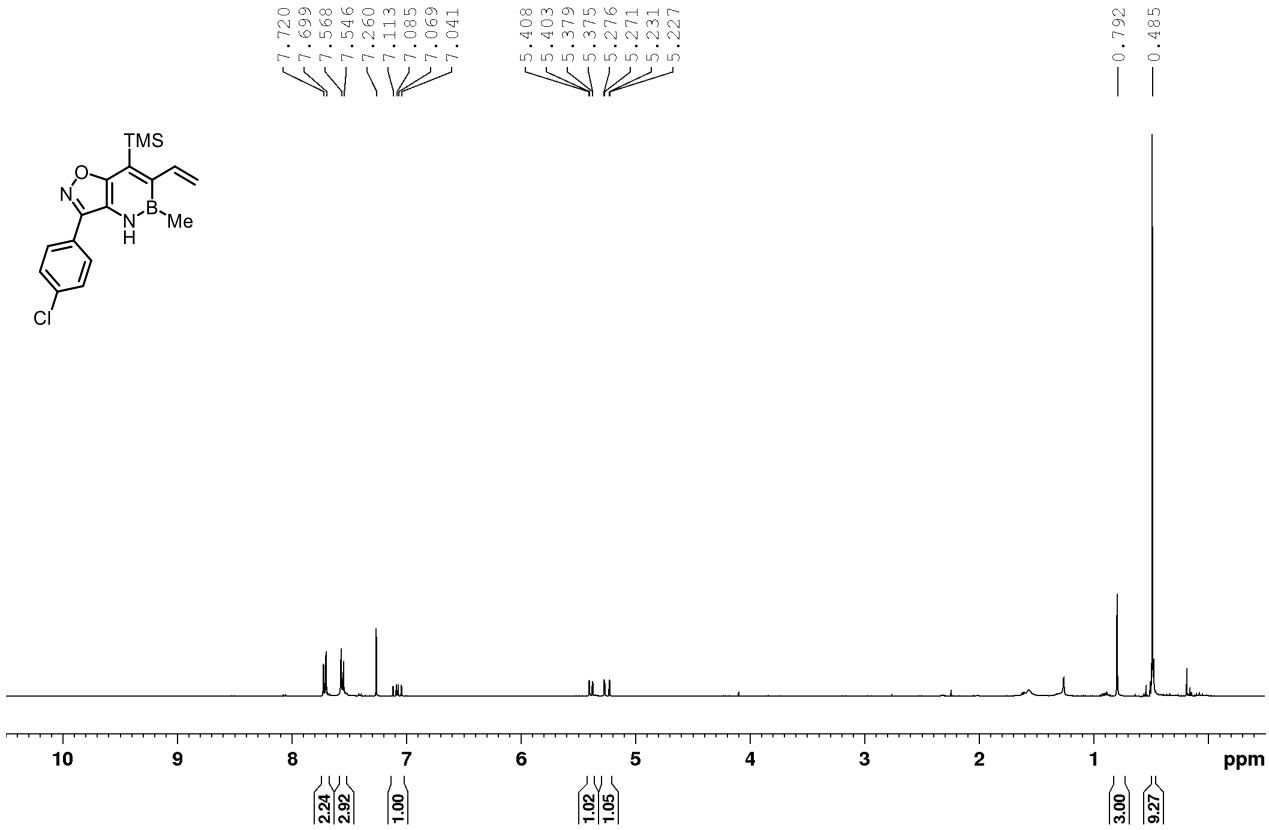


^{11}B NMR (160 MHz, $CDCl_3$)

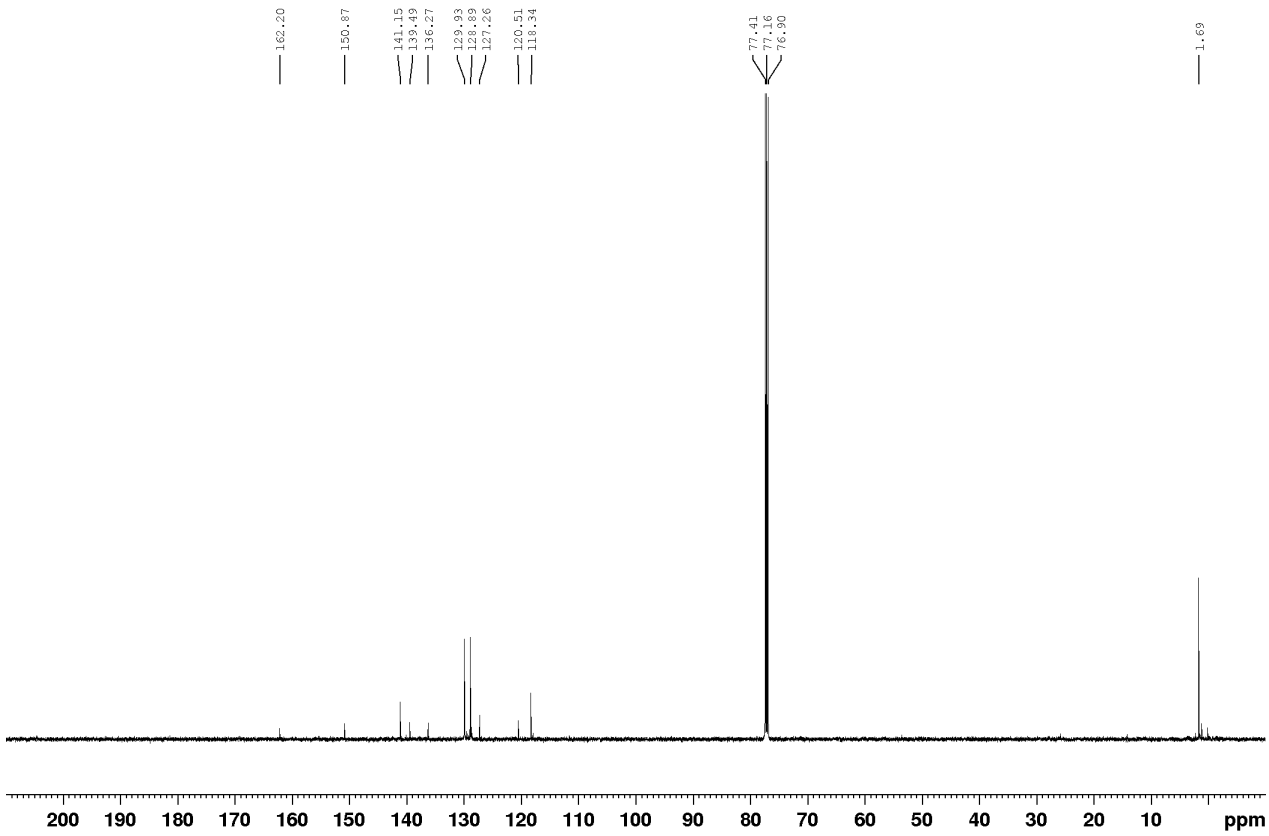


3-(4-Chlorophenyl)-5-methyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5j)

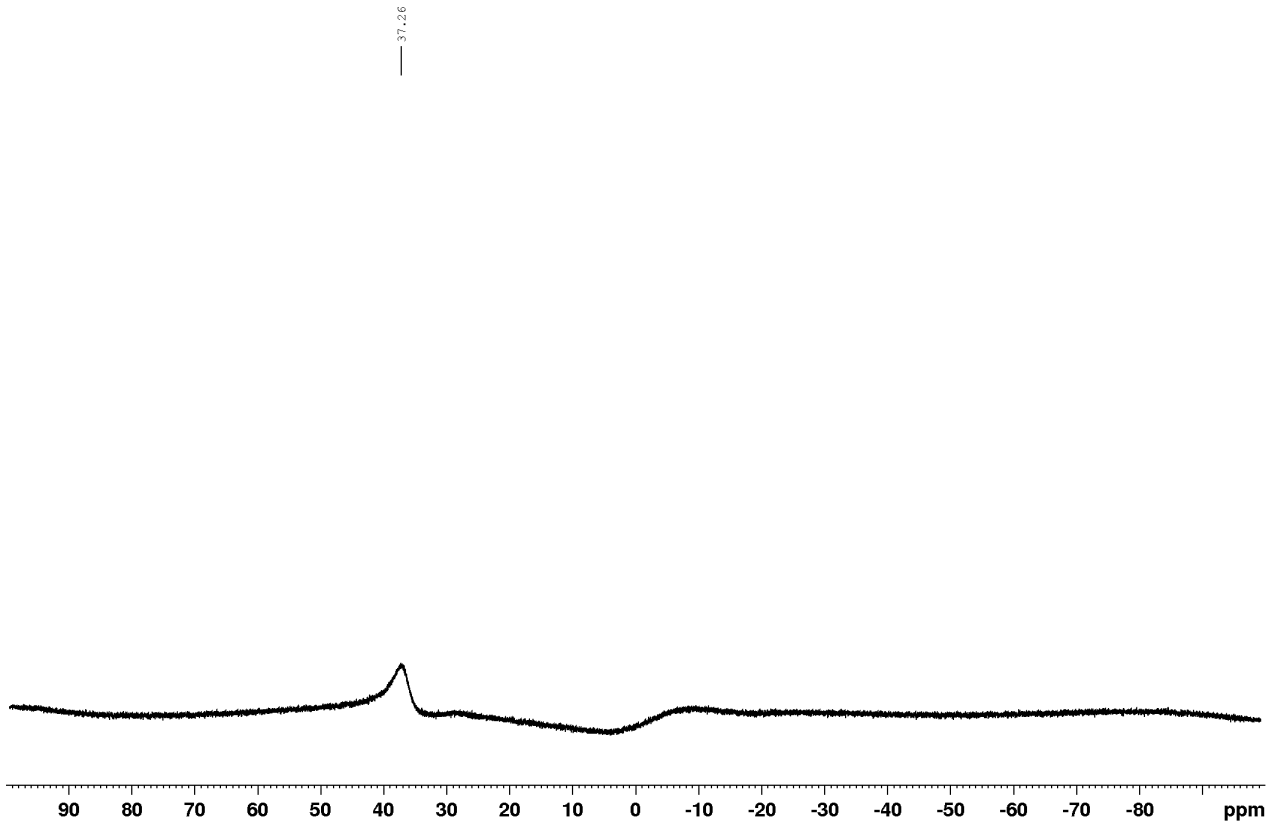
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

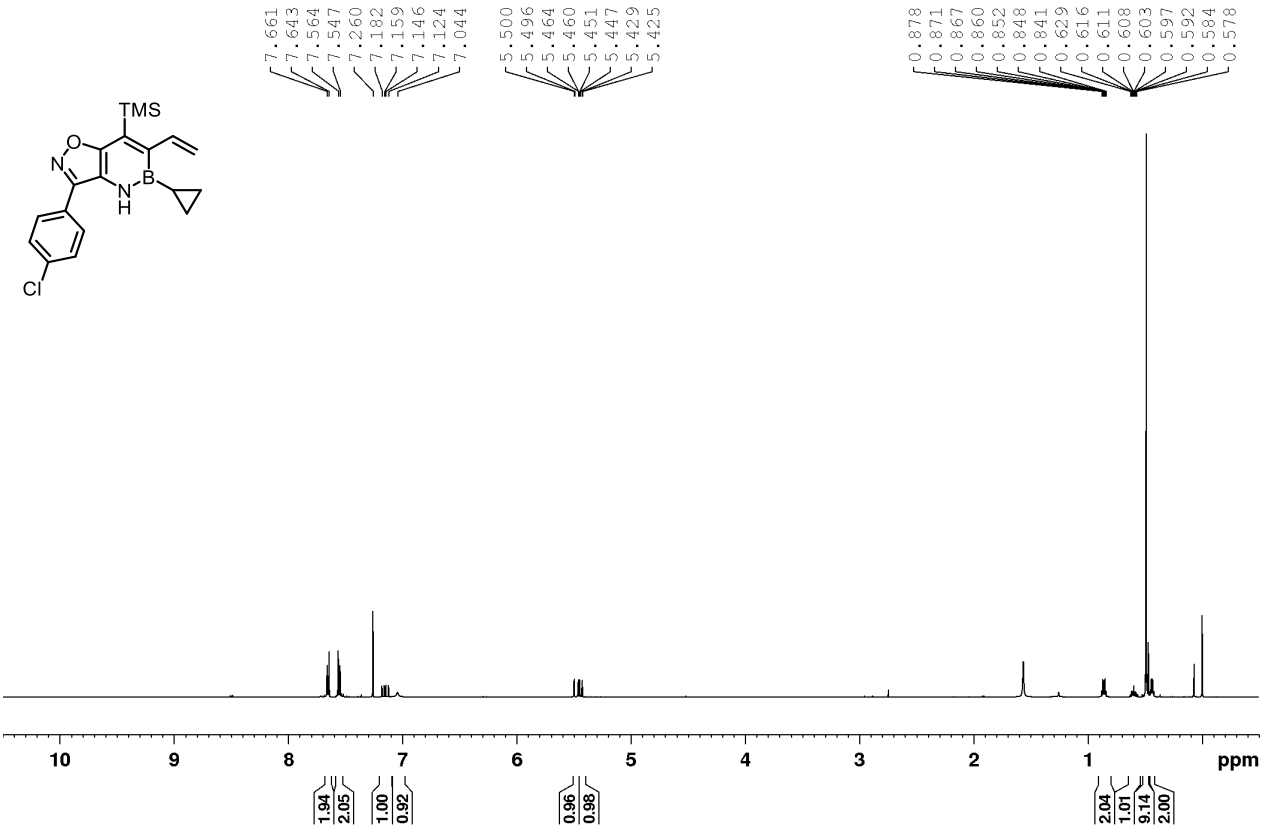


^{11}B NMR (128 MHz, $CDCl_3$)

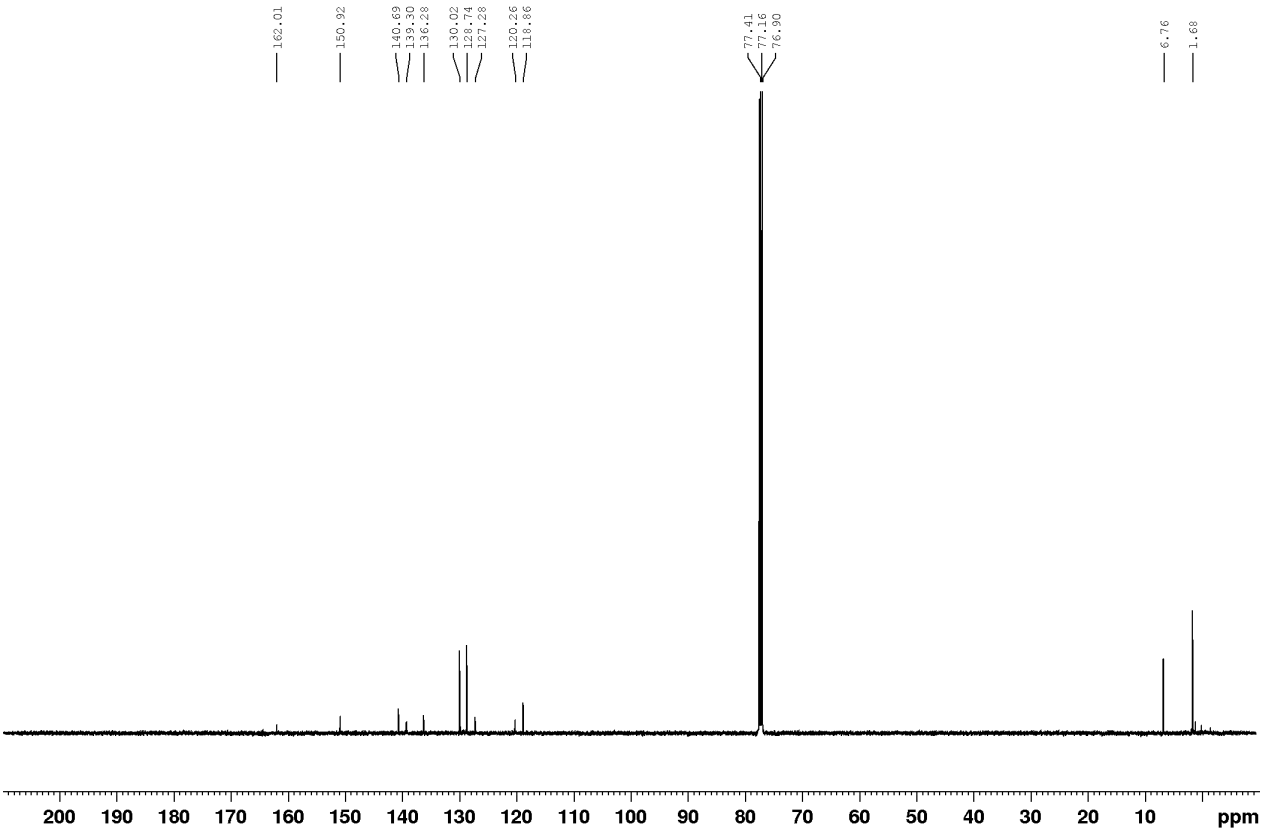


3-(4-Chlorophenyl)-5-cyclopropyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5k)

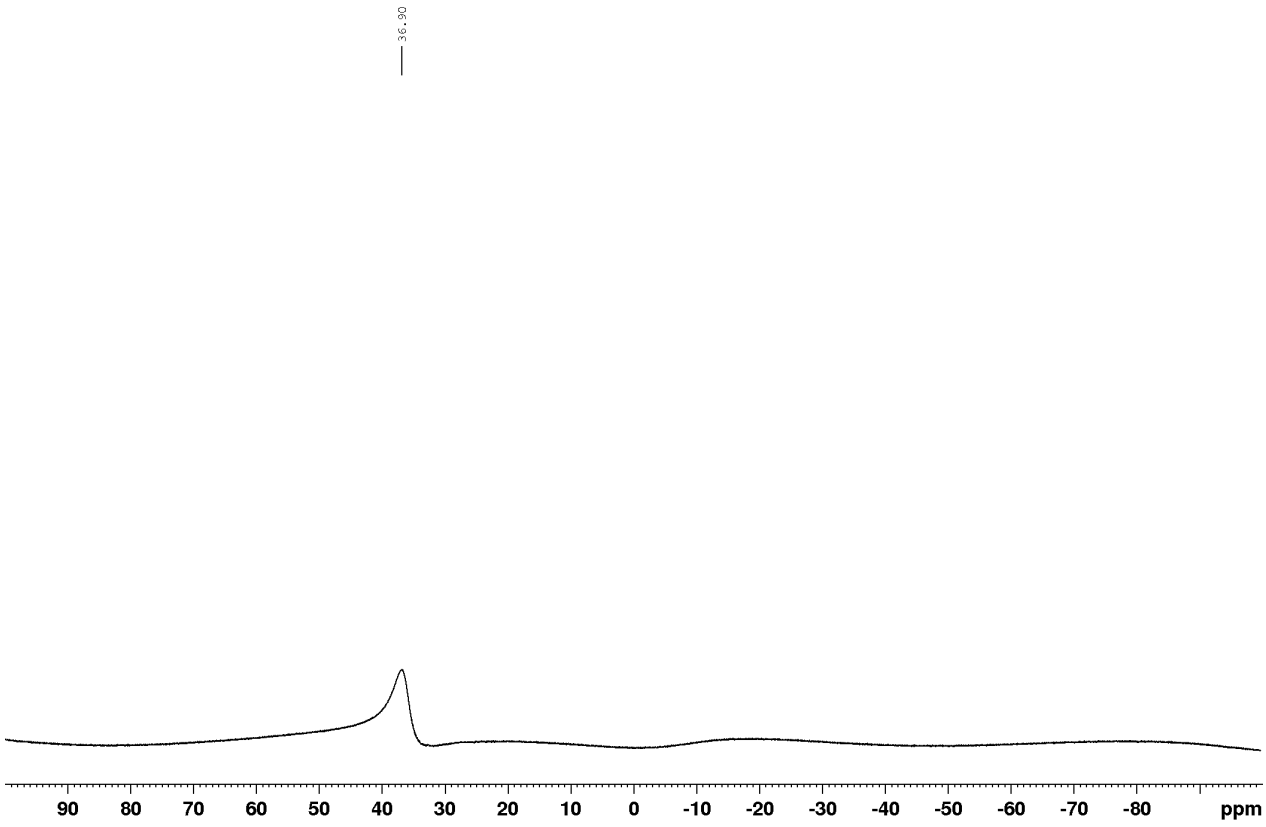
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

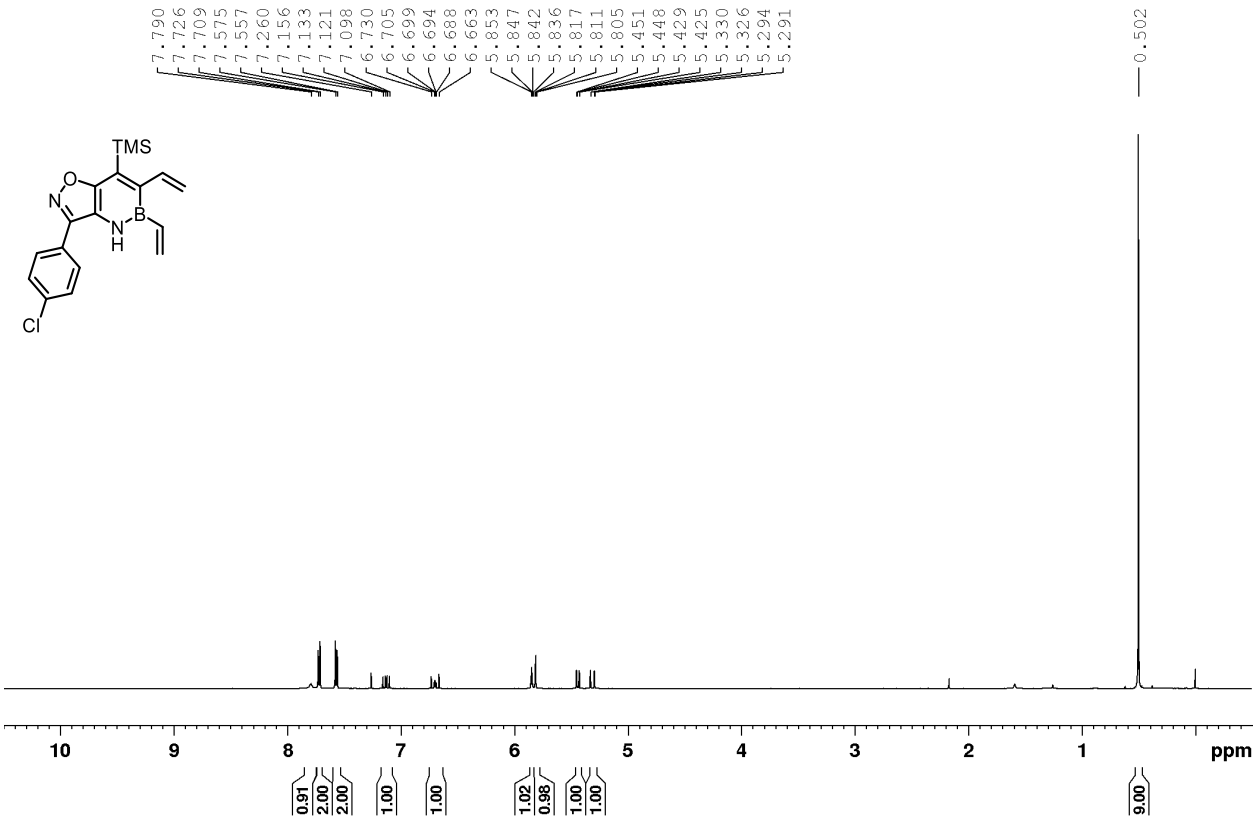


^{11}B NMR (160 MHz, $CDCl_3$)

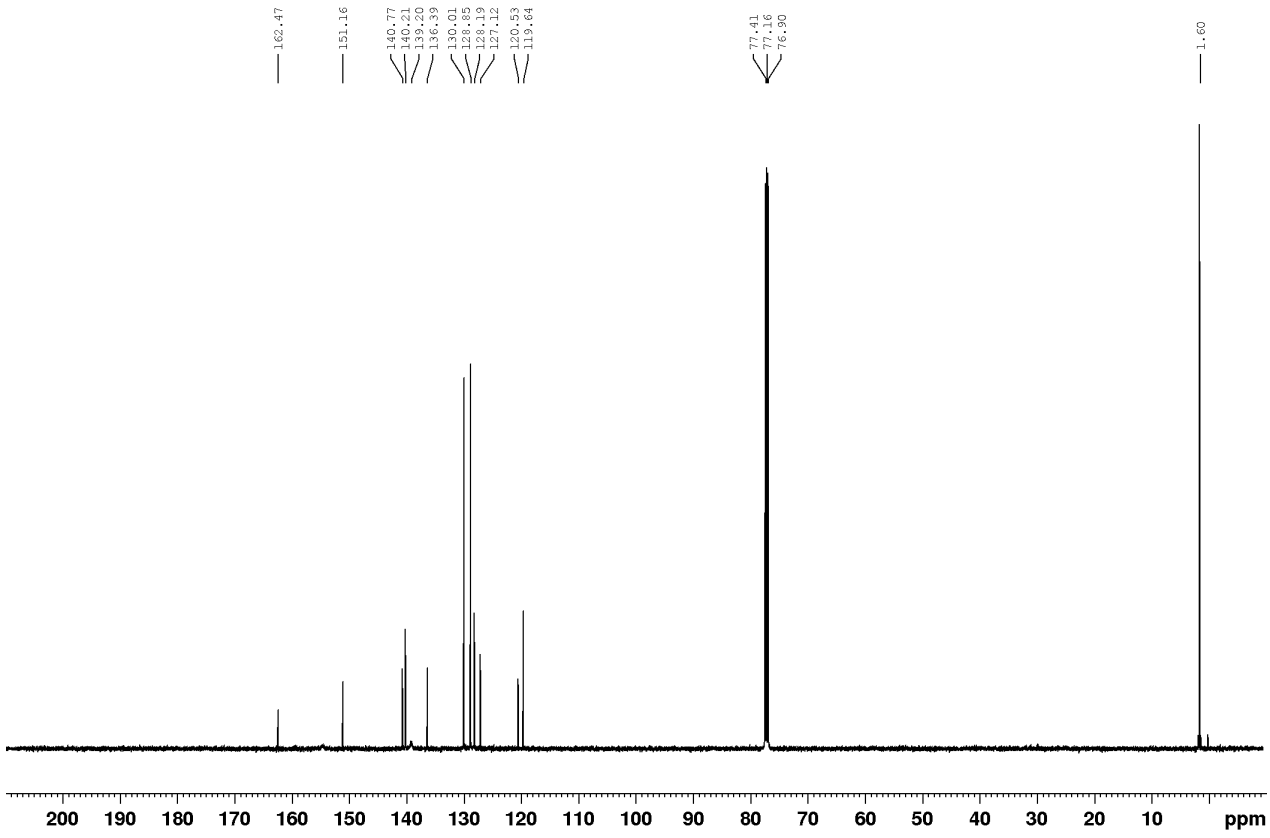


3-(4-Chlorophenyl)-7-(trimethylsilyl)-5,6-divinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5l)

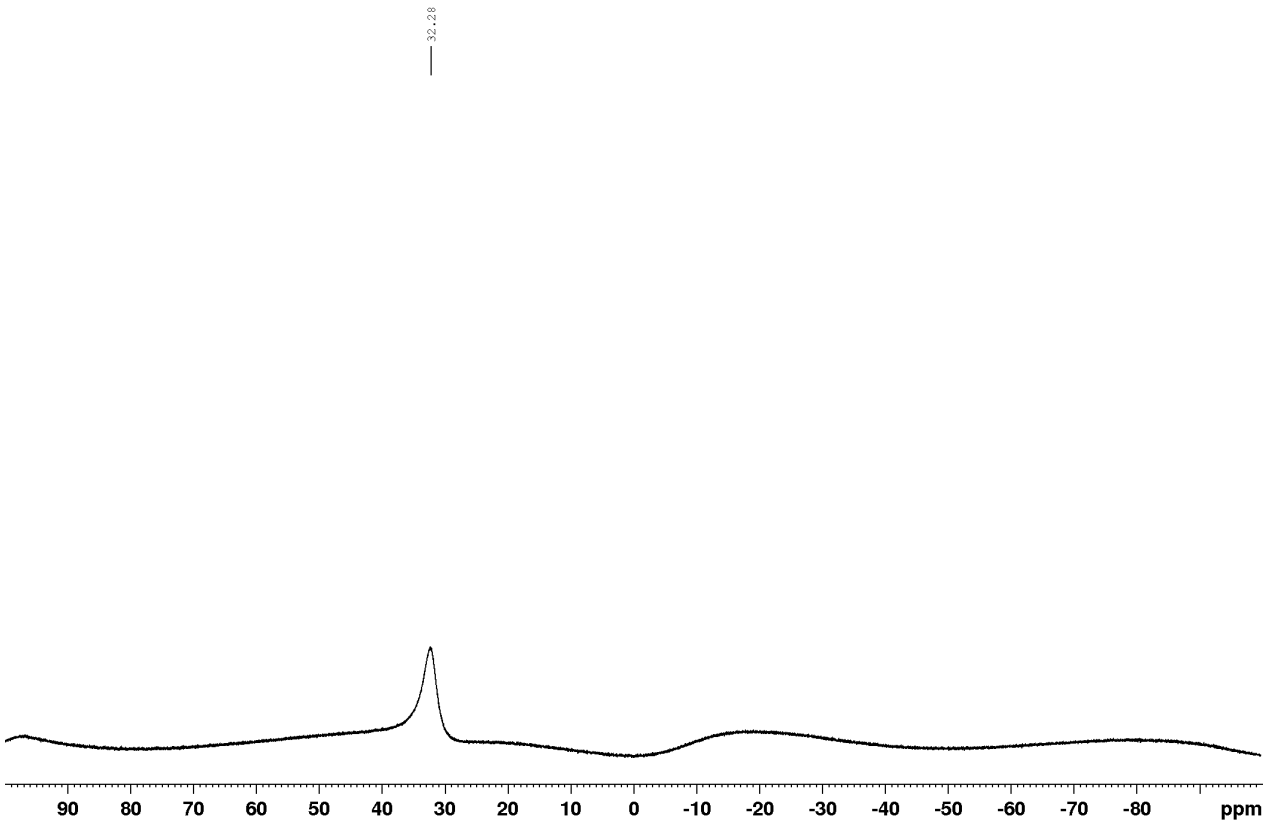
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

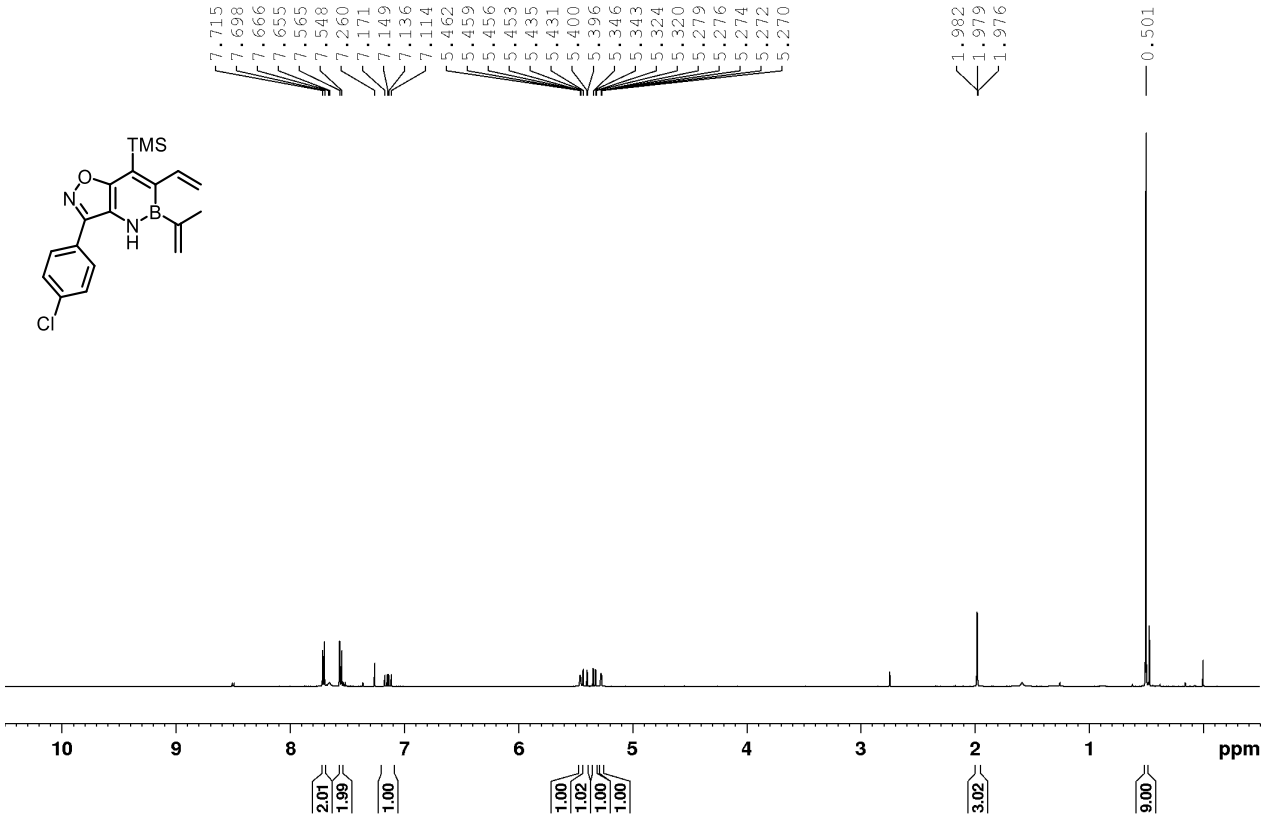


^{11}B NMR (160 MHz, $CDCl_3$)

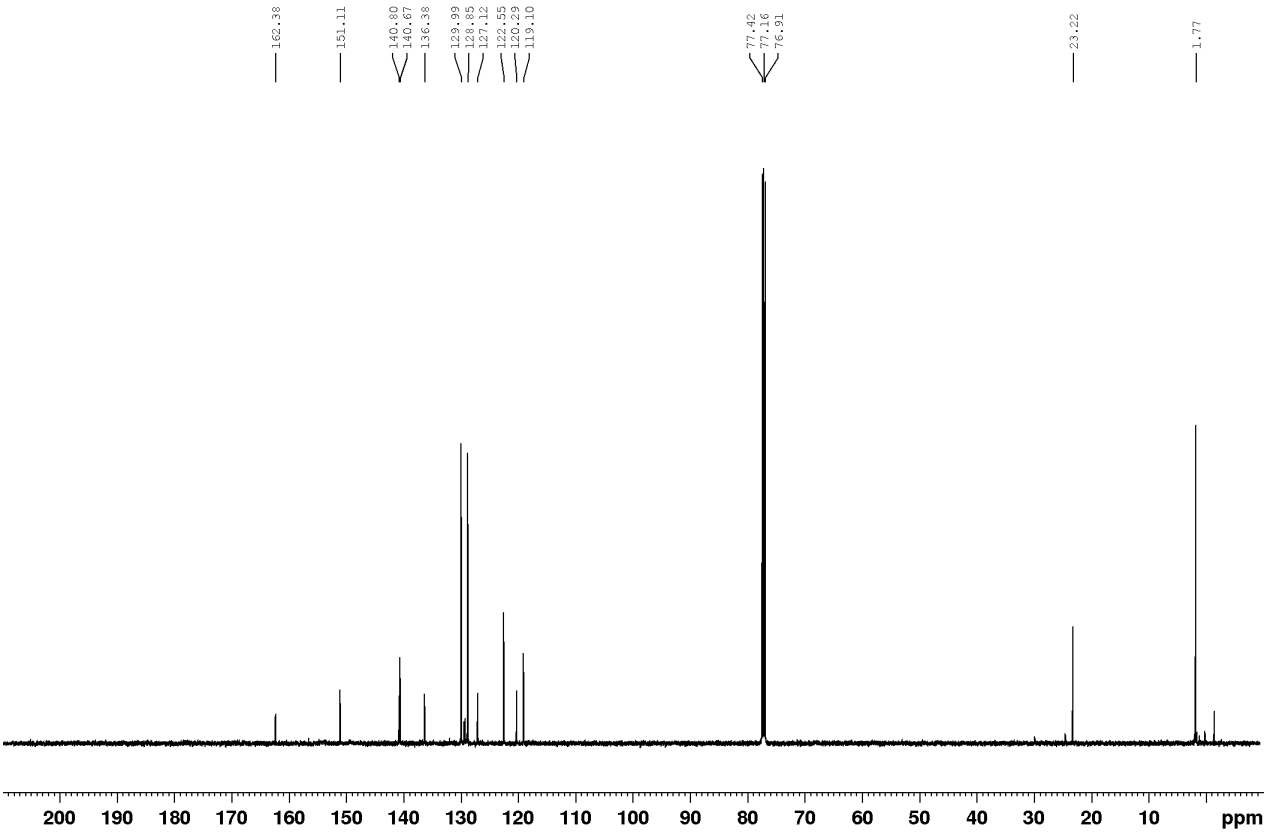


3-(4-Chlorophenyl)-5-(prop-1-en-2-yl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5m)

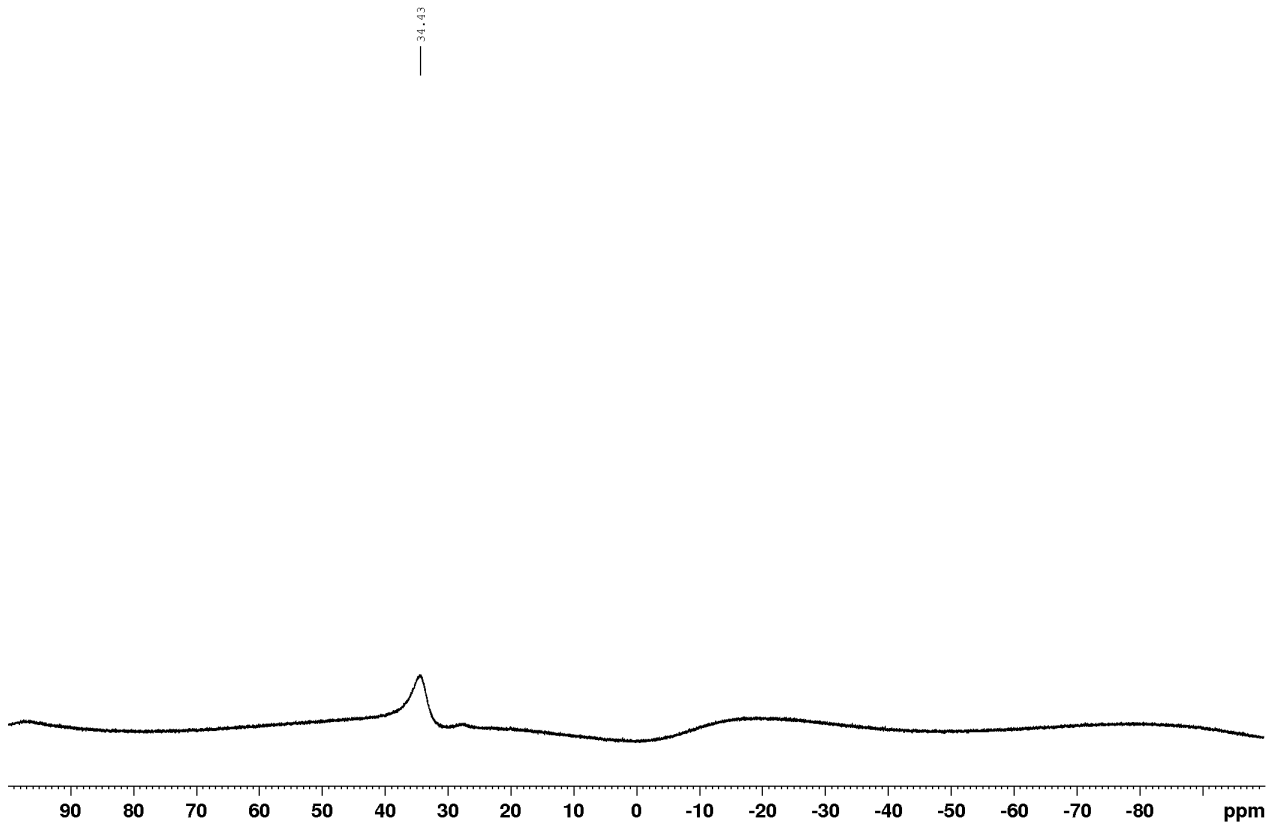
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

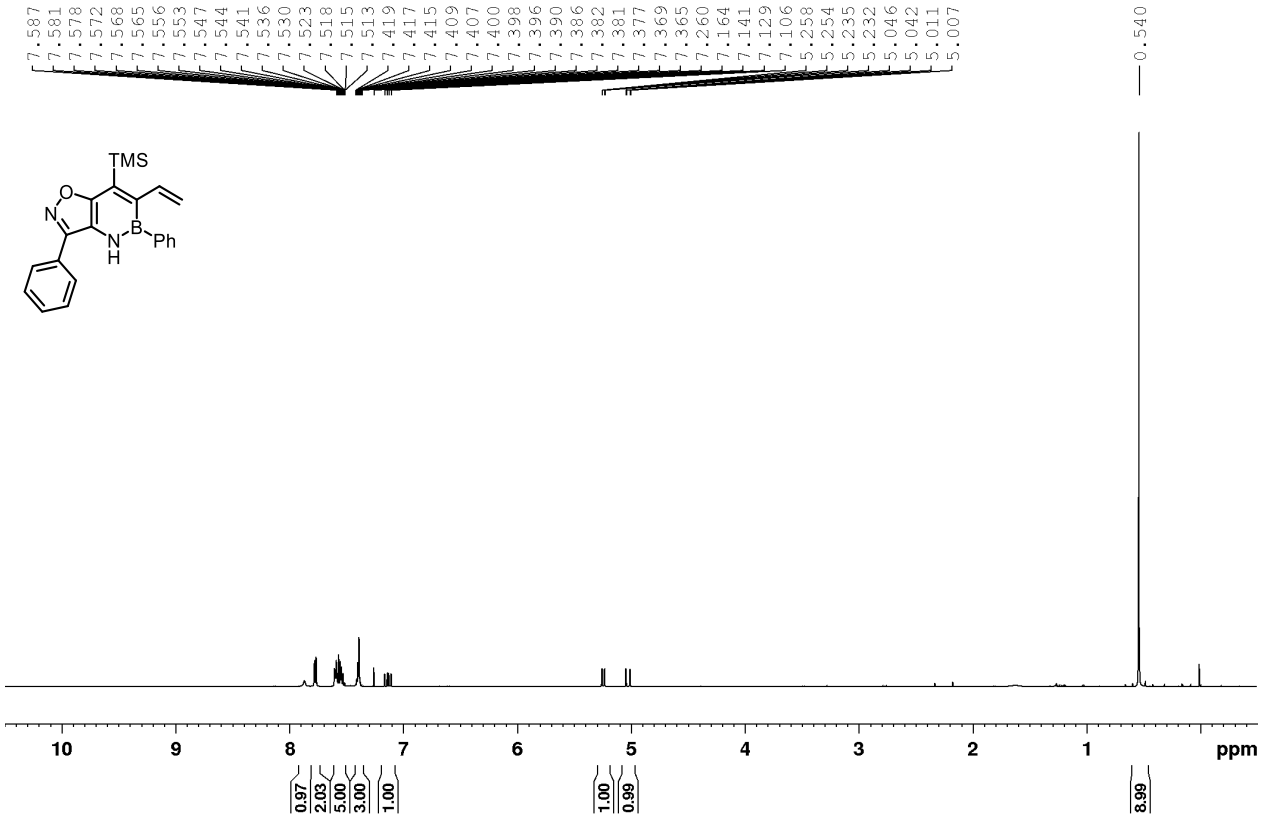


^{11}B NMR (160 MHz, $CDCl_3$)

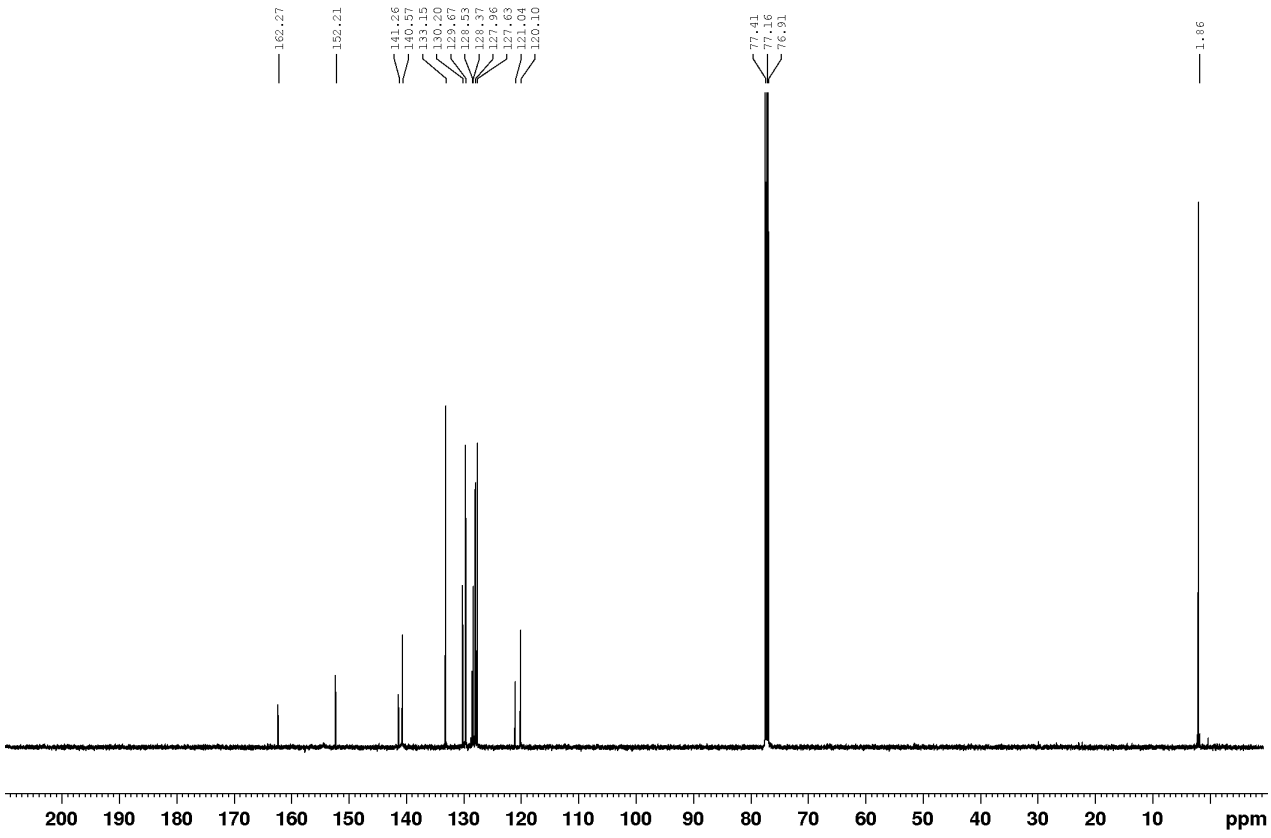


3,5-Diphenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5n)

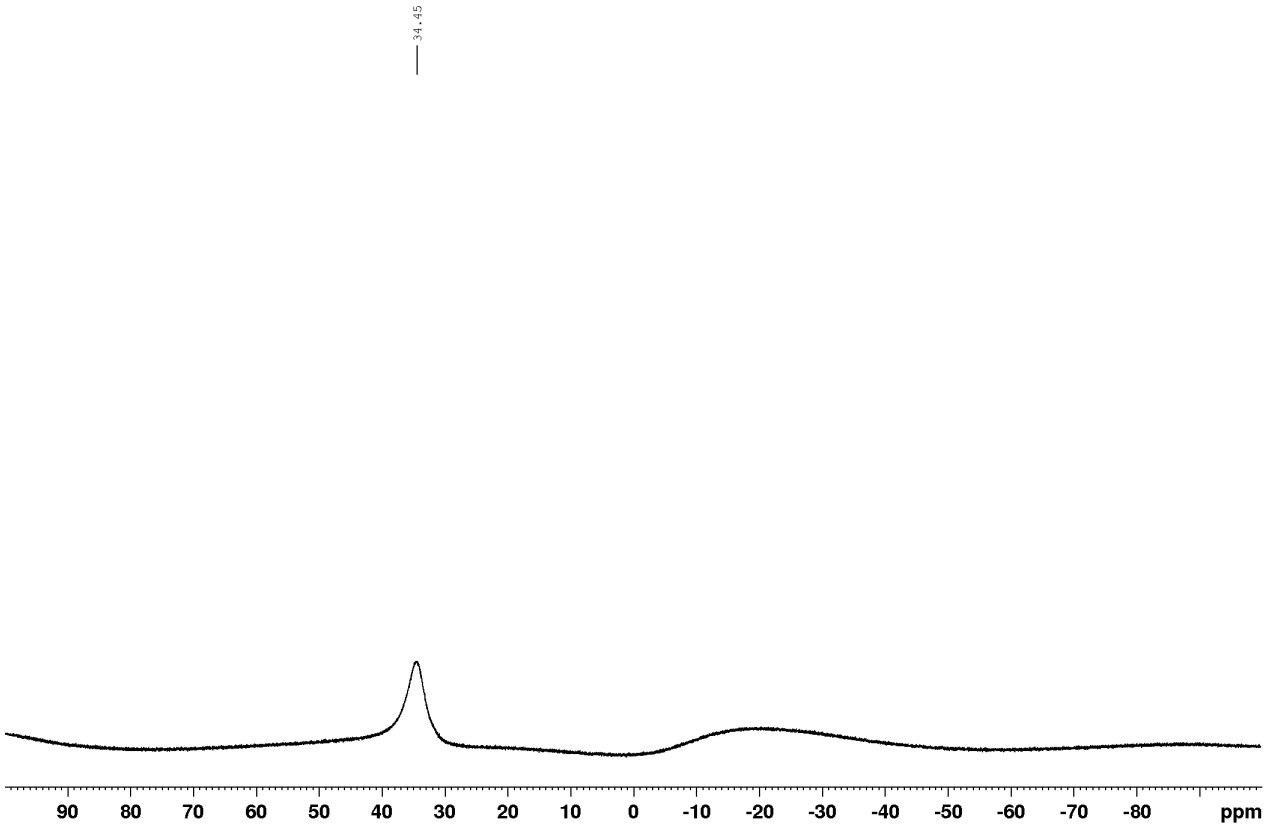
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

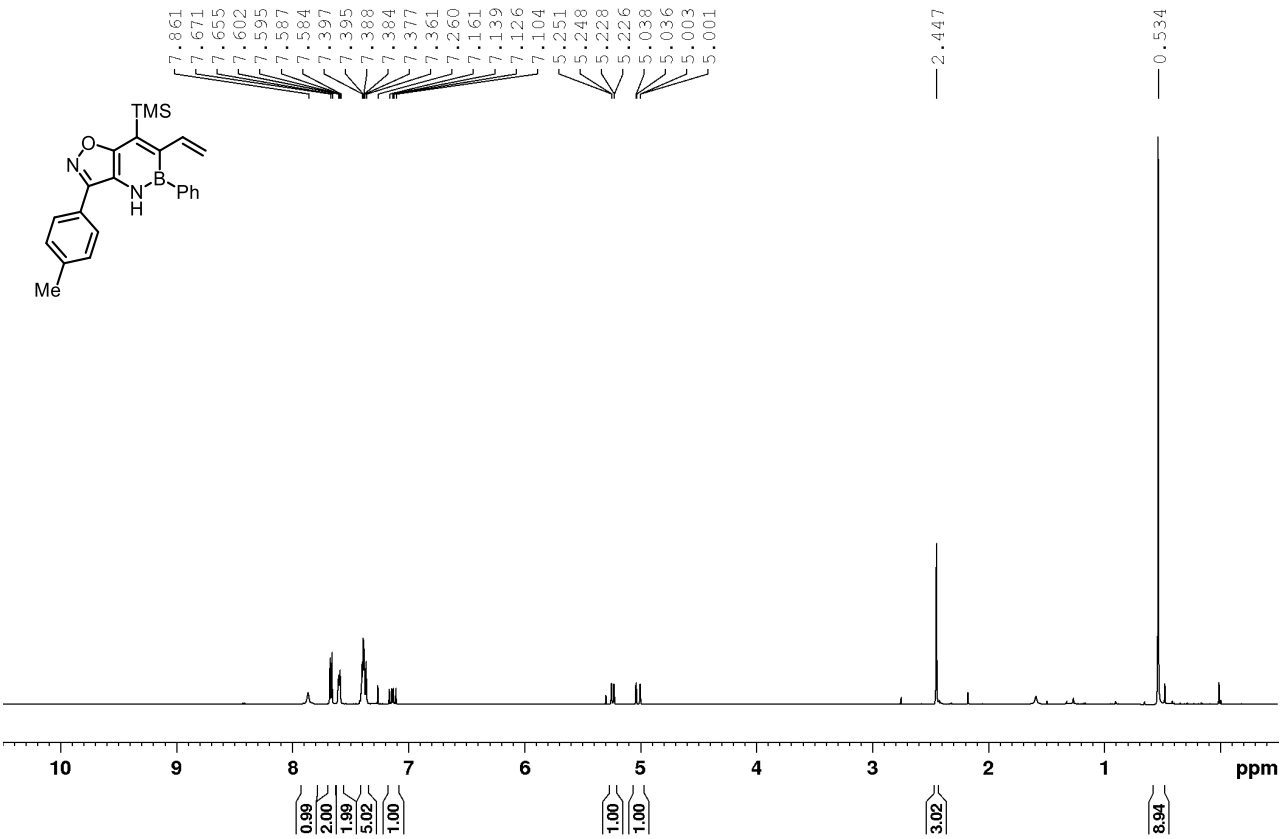


^{11}B NMR (160 MHz, $CDCl_3$)

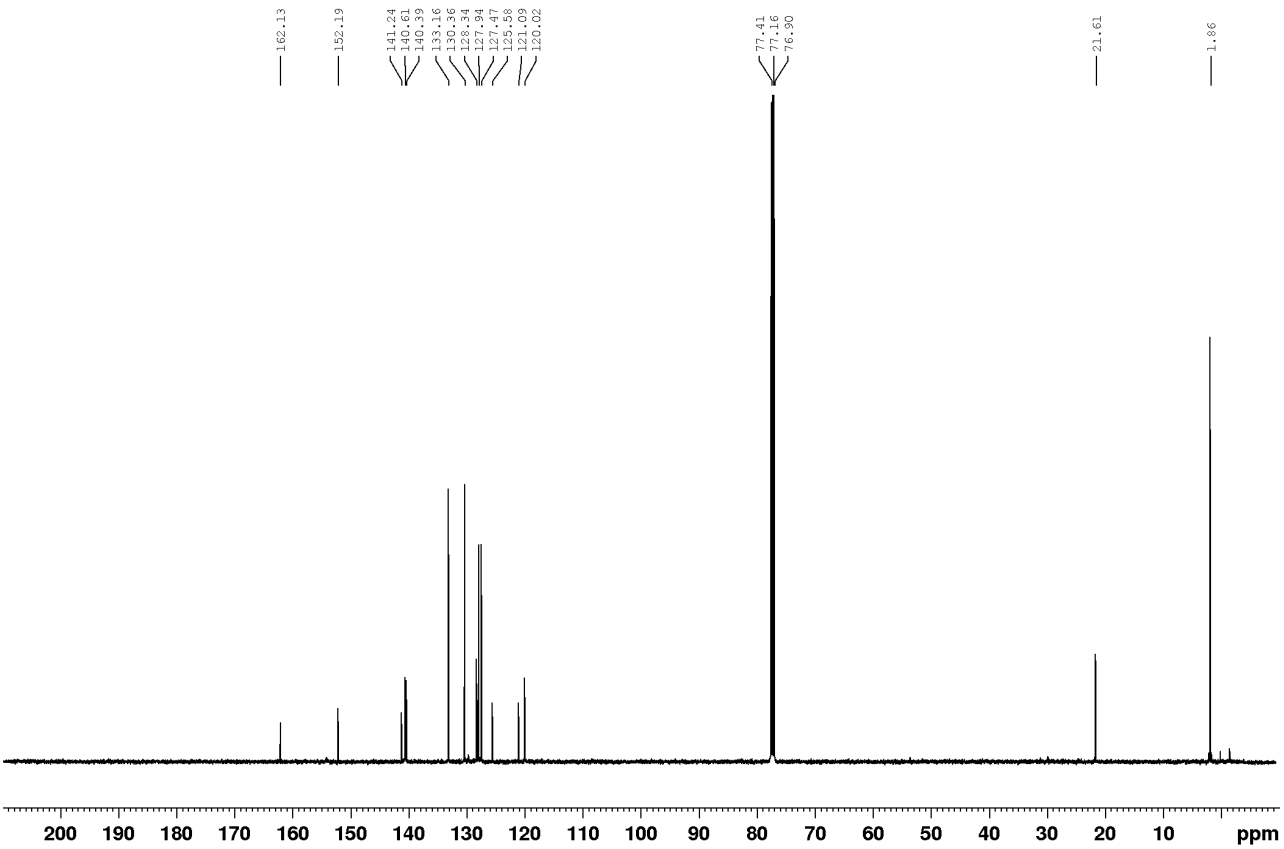


5-Phenyl-3-(*p*-tolyl)-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5o)

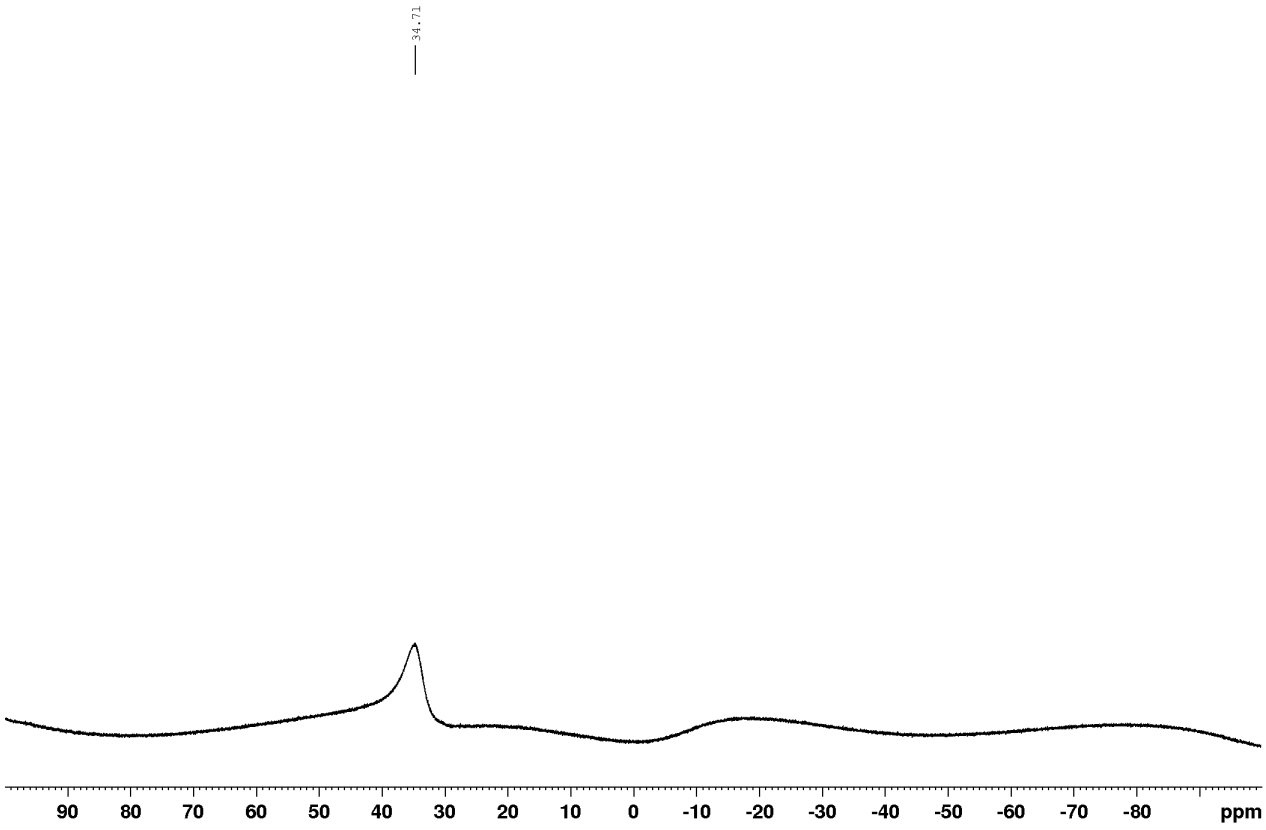
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

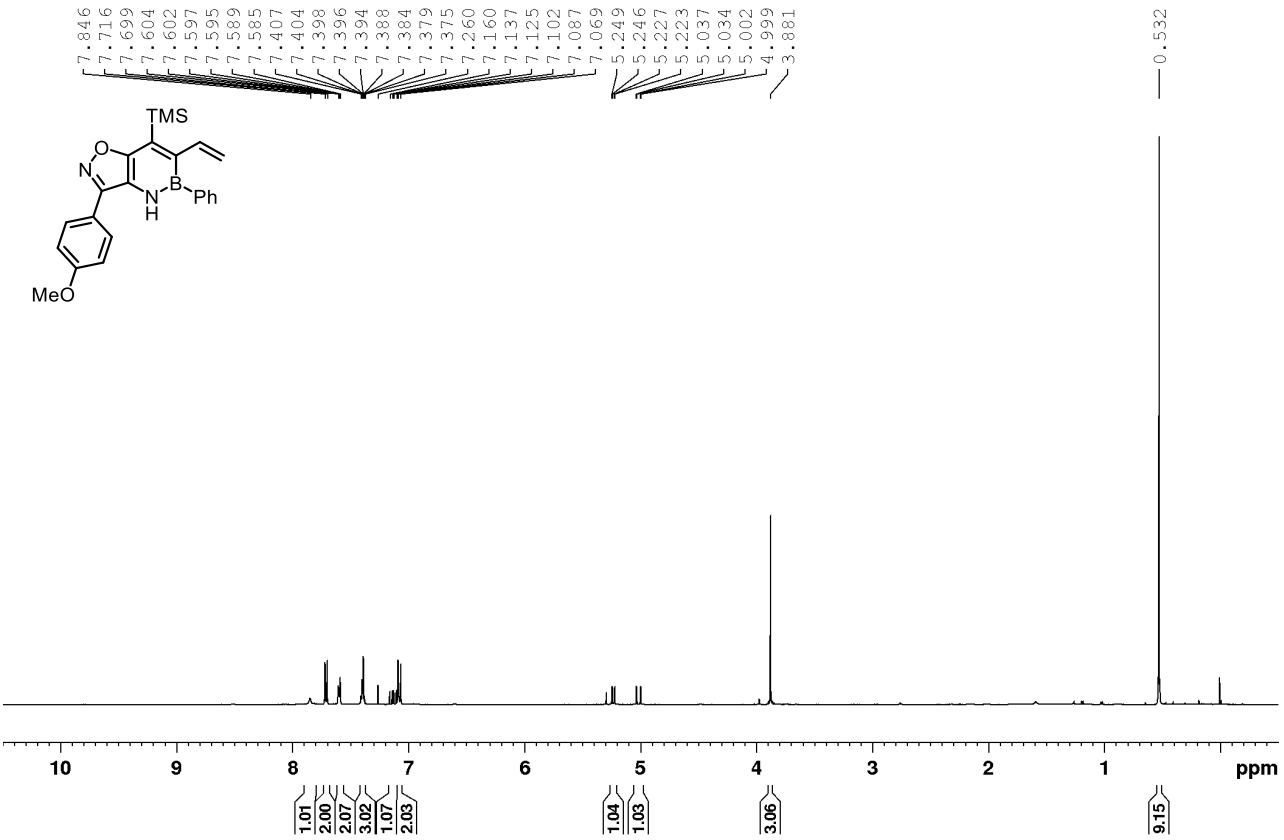


^{11}B NMR (160 MHz, $CDCl_3$)

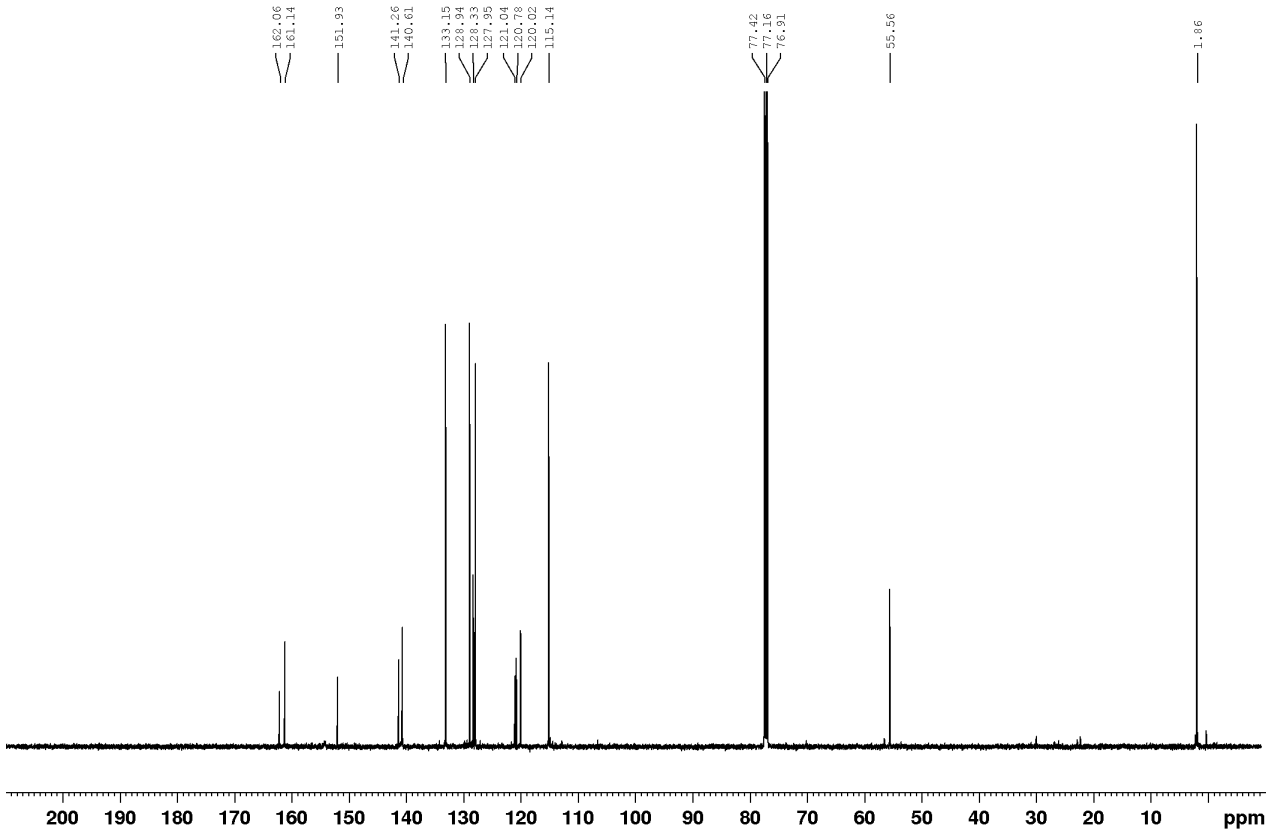


3-(4-Methoxyphenyl)-5-phenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5p)

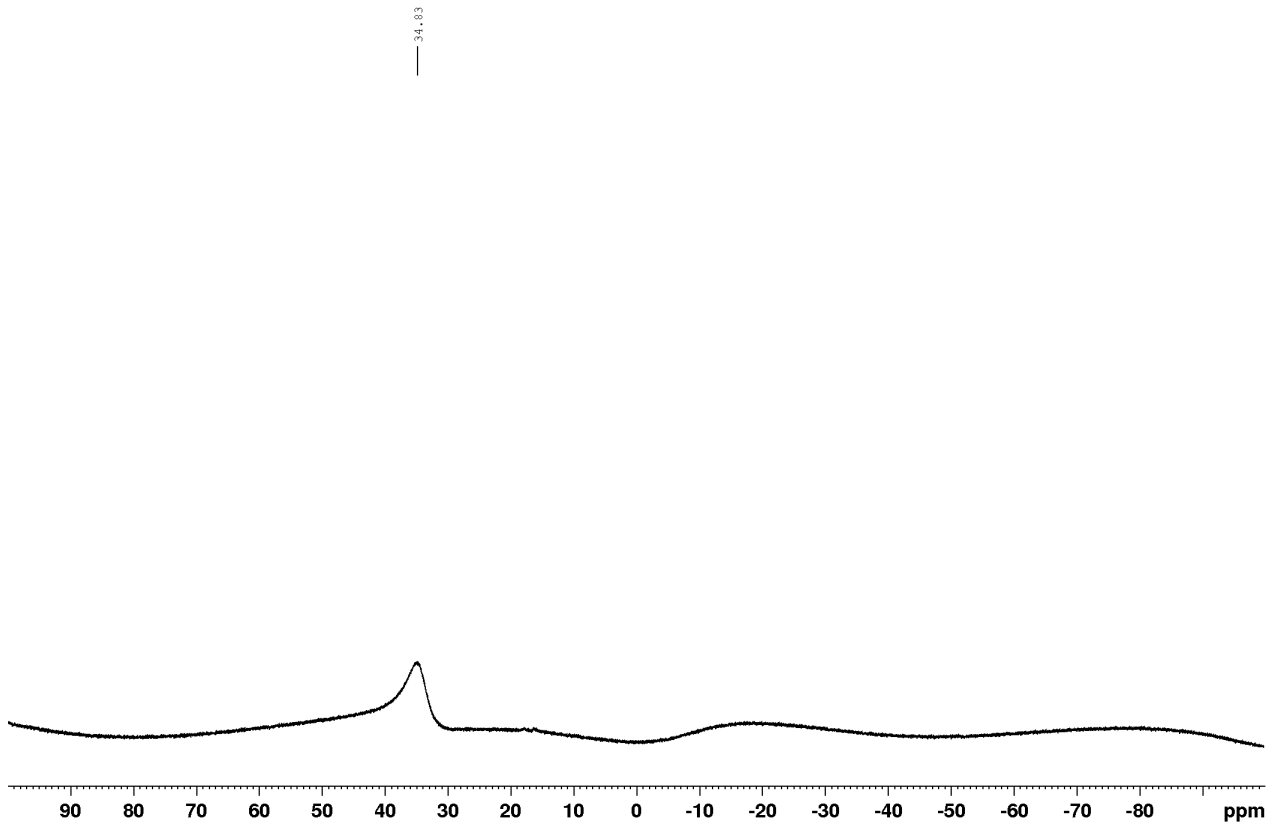
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

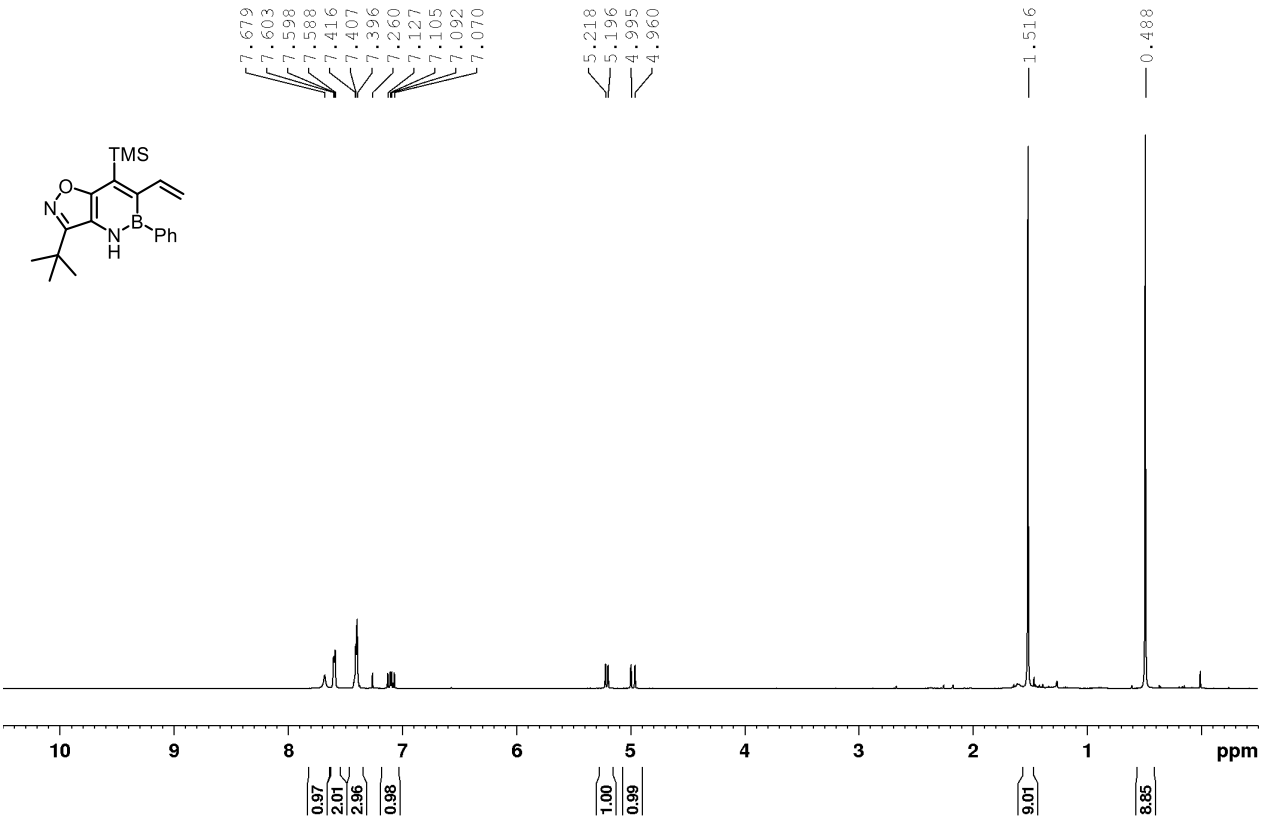


^{11}B NMR (160 MHz, $CDCl_3$)

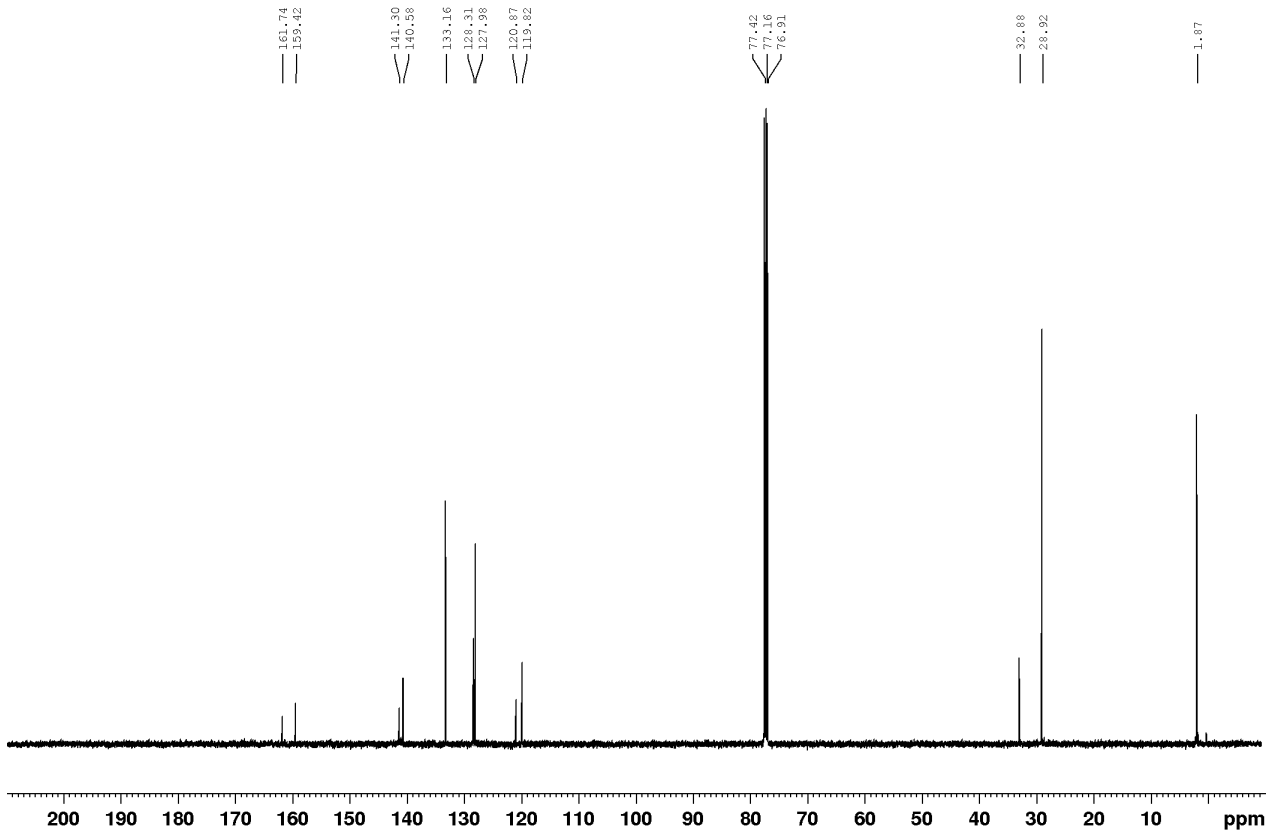


3-(*tert*-Butyl)-5-phenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5q)

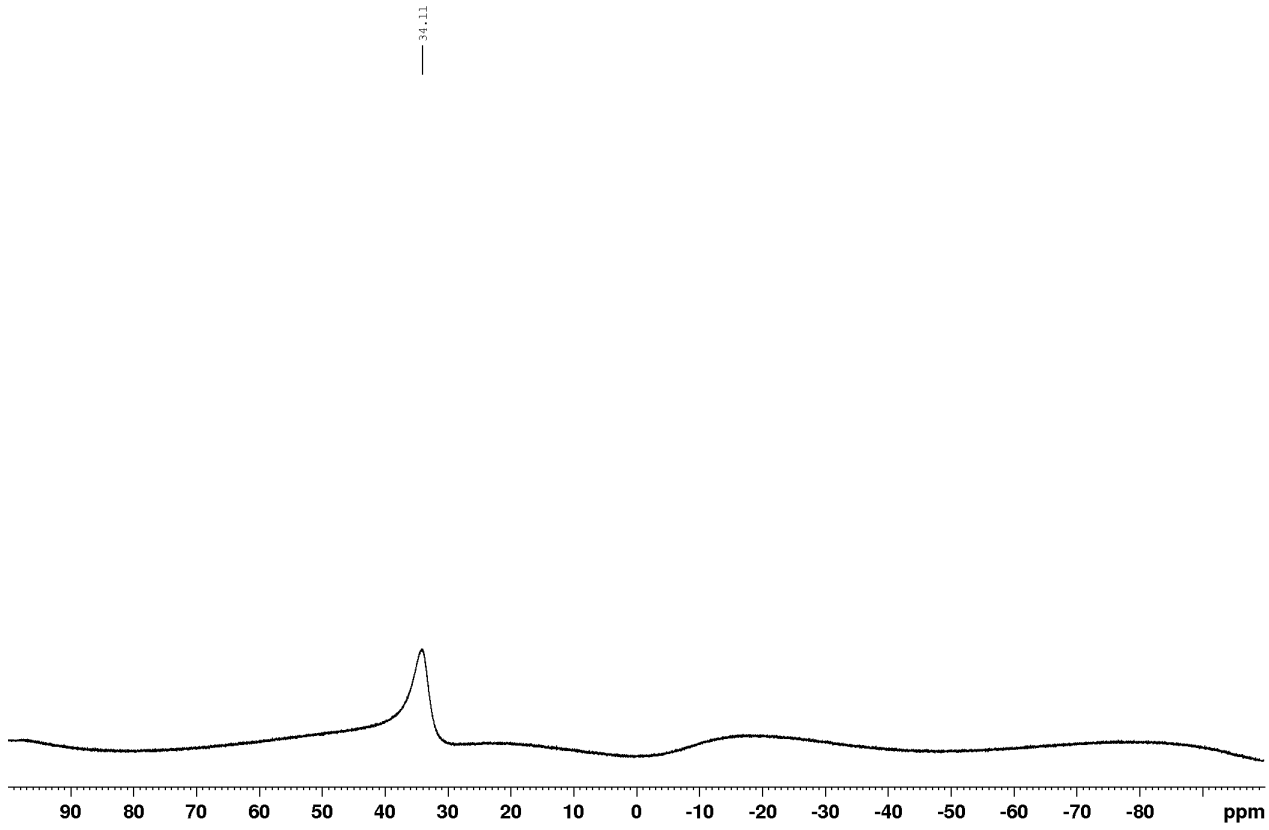
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

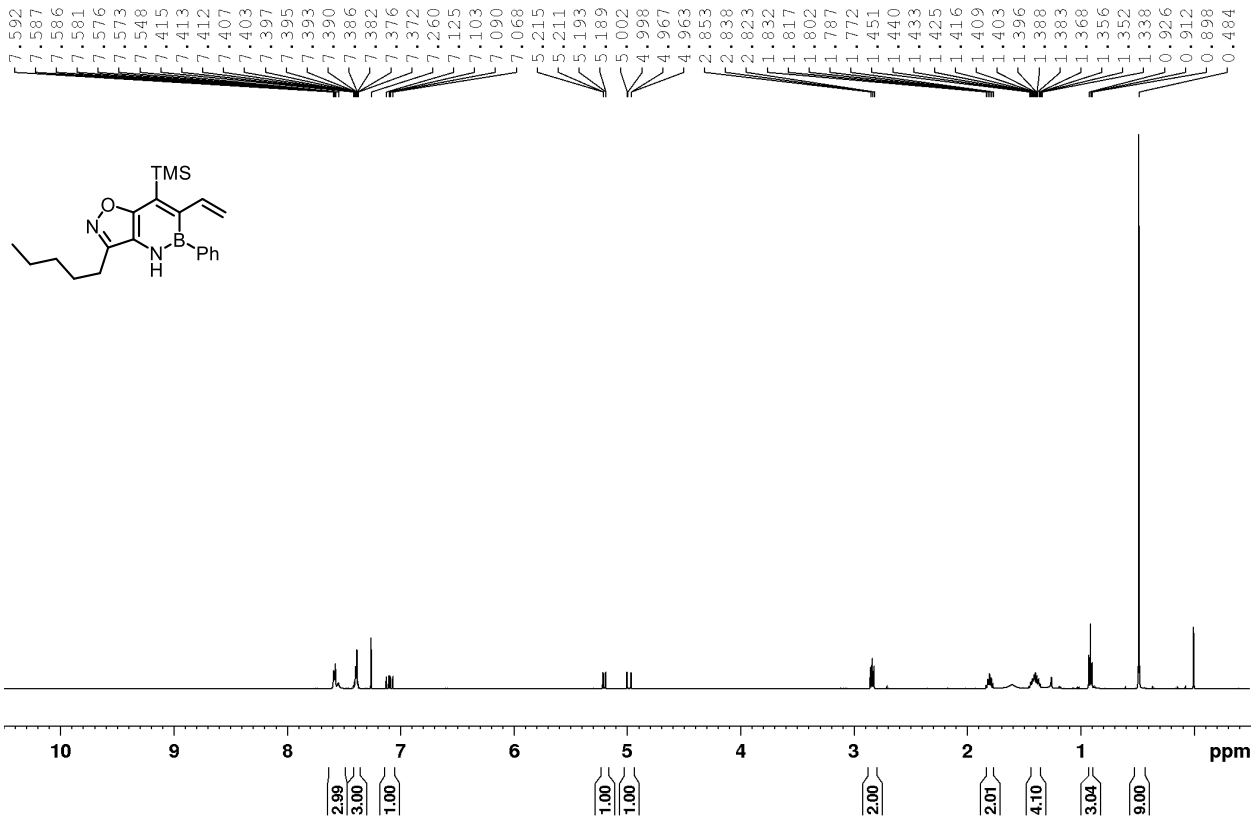


^{11}B NMR (160 MHz, $CDCl_3$)

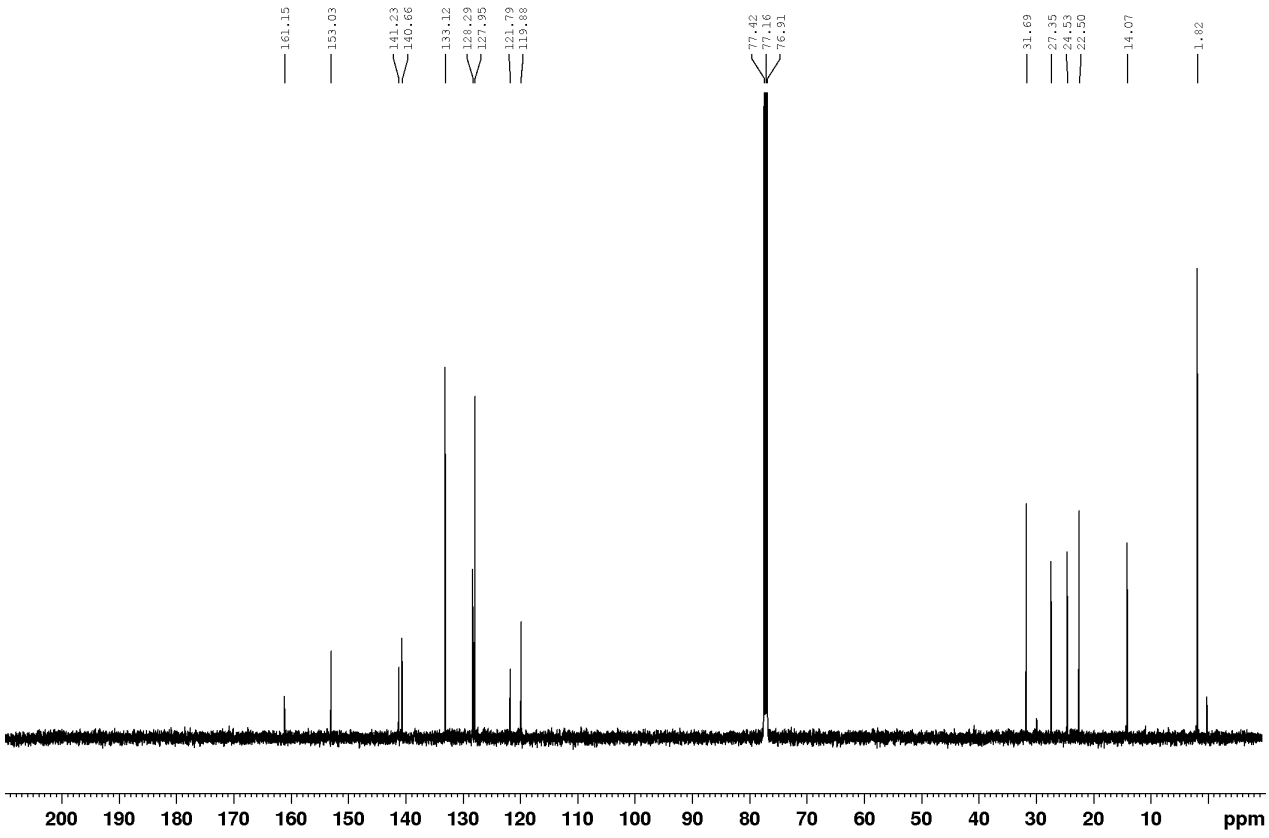


3-Pentyl-5-phenyl-7-(trimethylsilyl)-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5r)

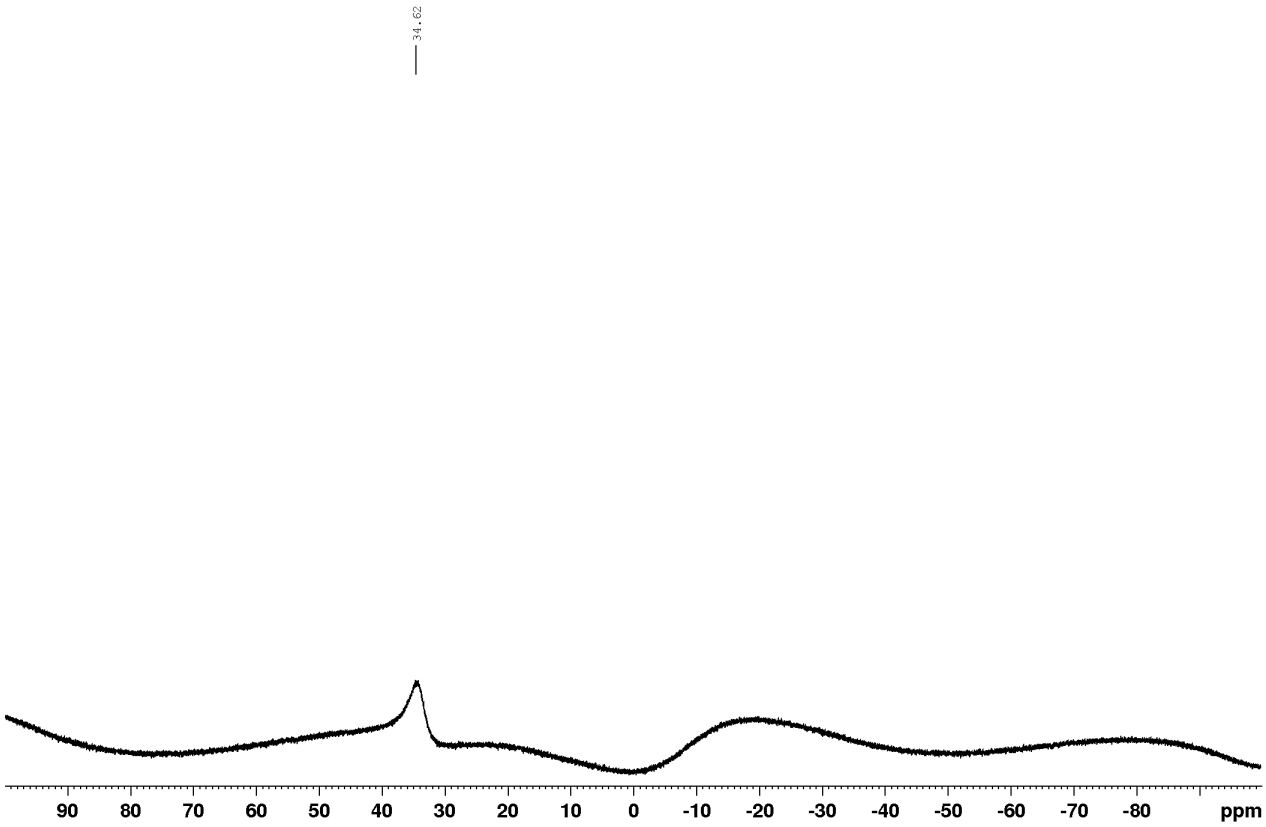
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

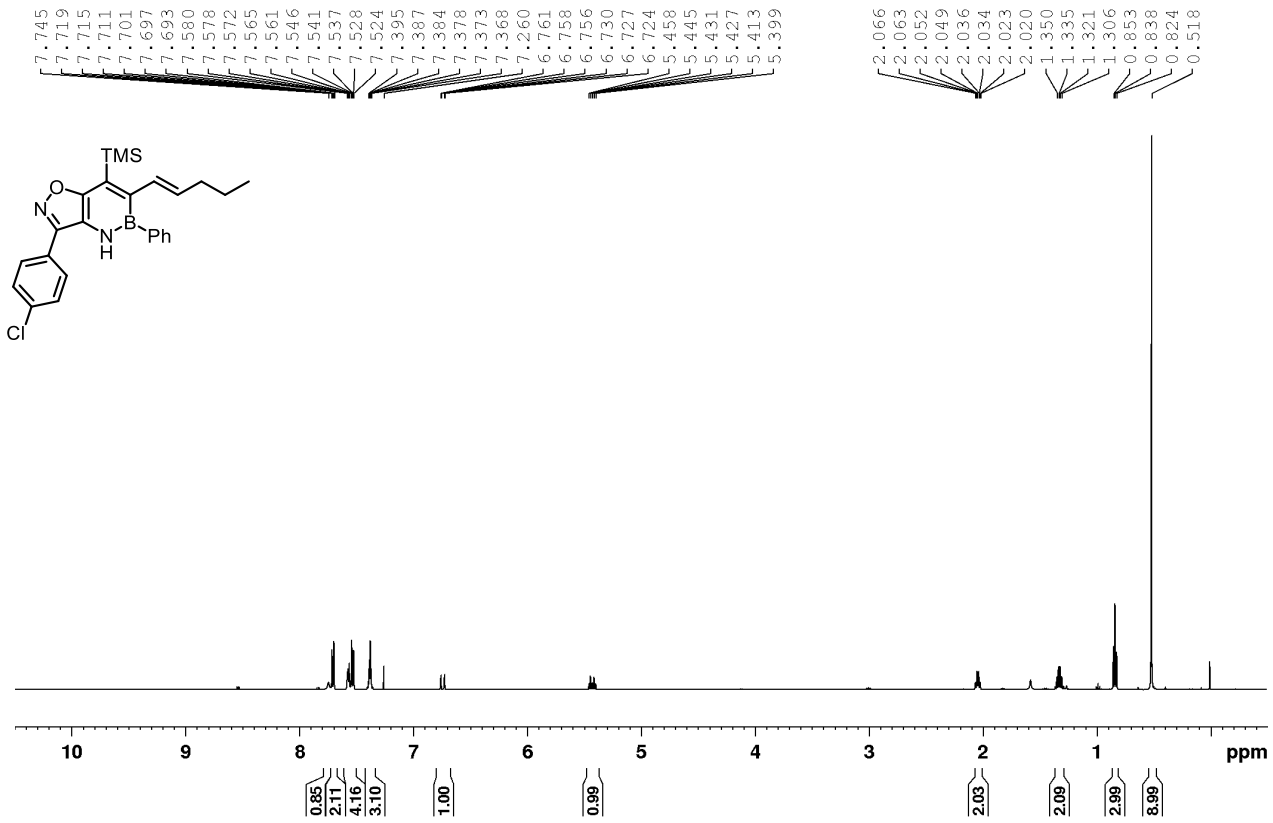


^{11}B NMR (160 MHz, $CDCl_3$)

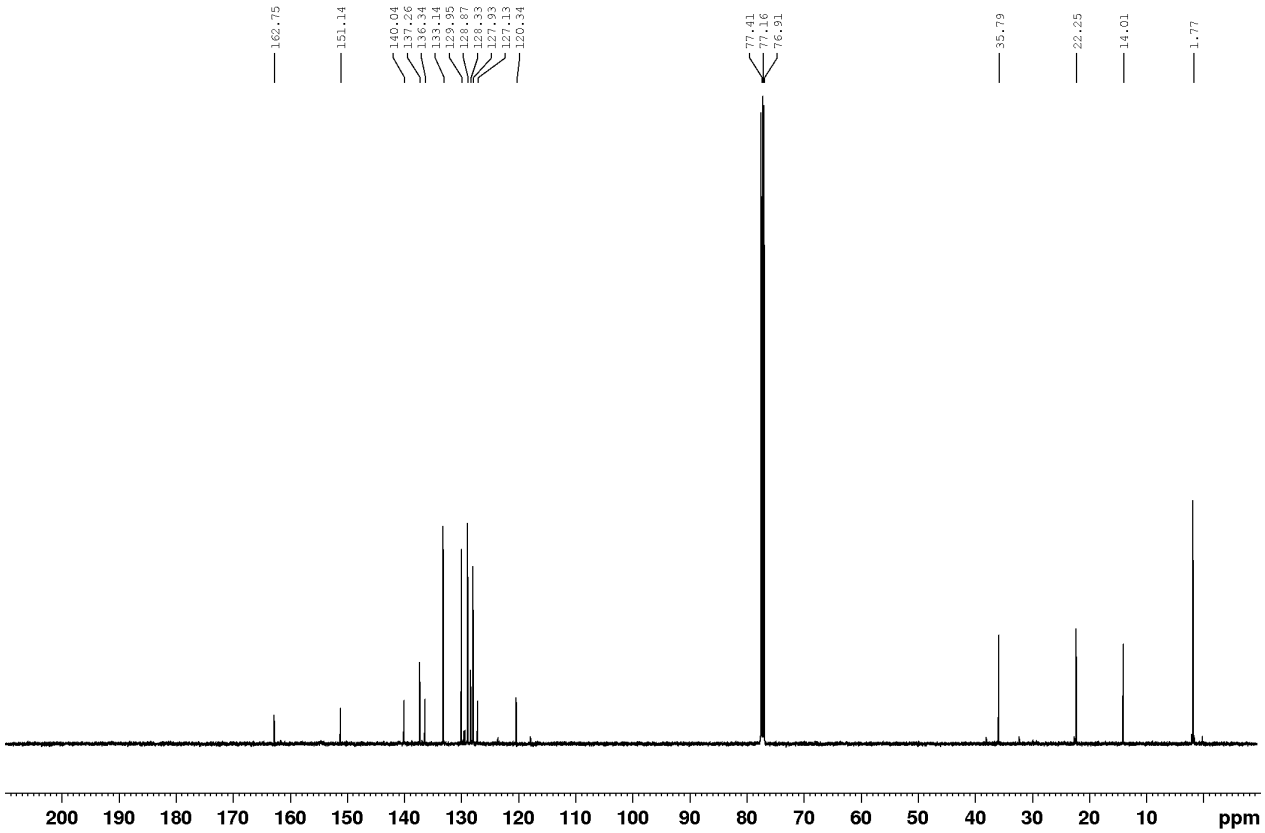


(*E*)-3-(4-Chlorophenyl)-6-(pent-1-en-1-yl)-5-phenyl-7-(trimethylsilyl)-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5s)

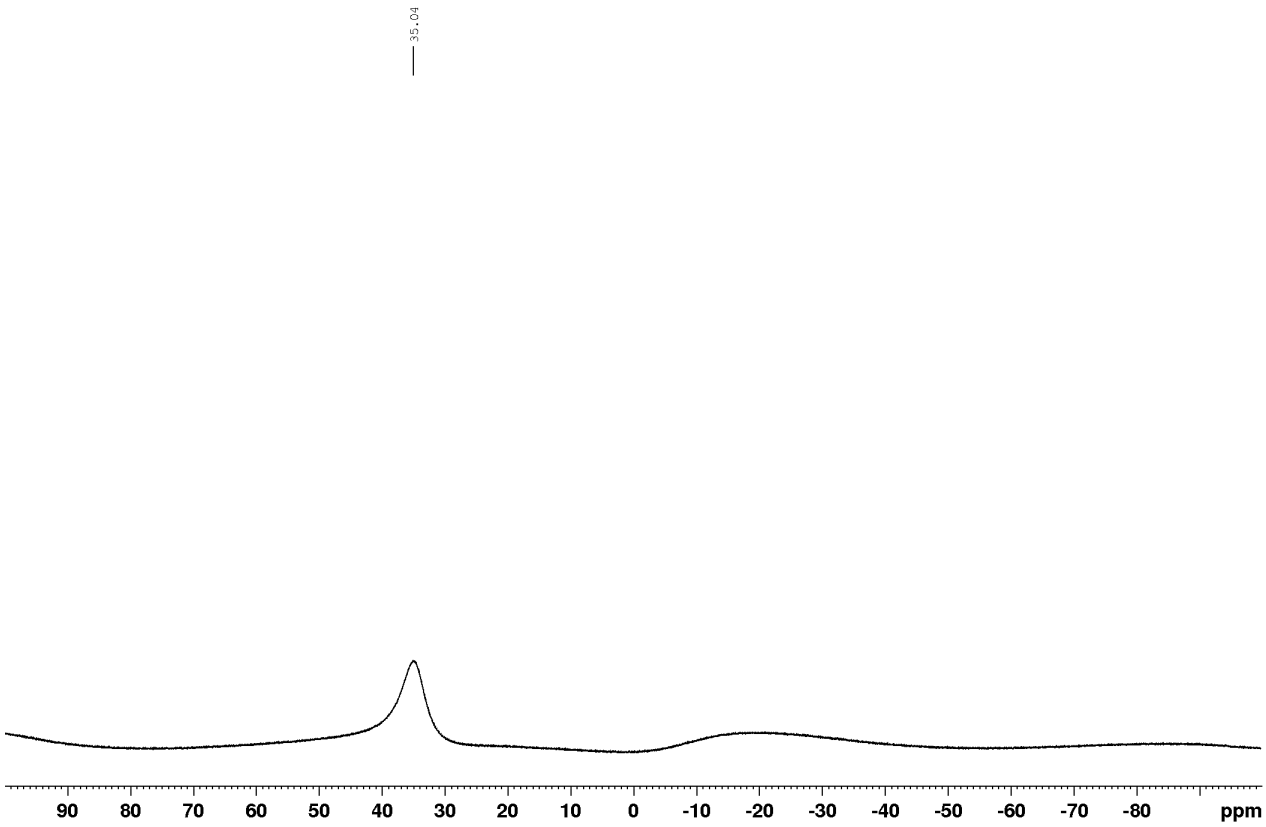
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

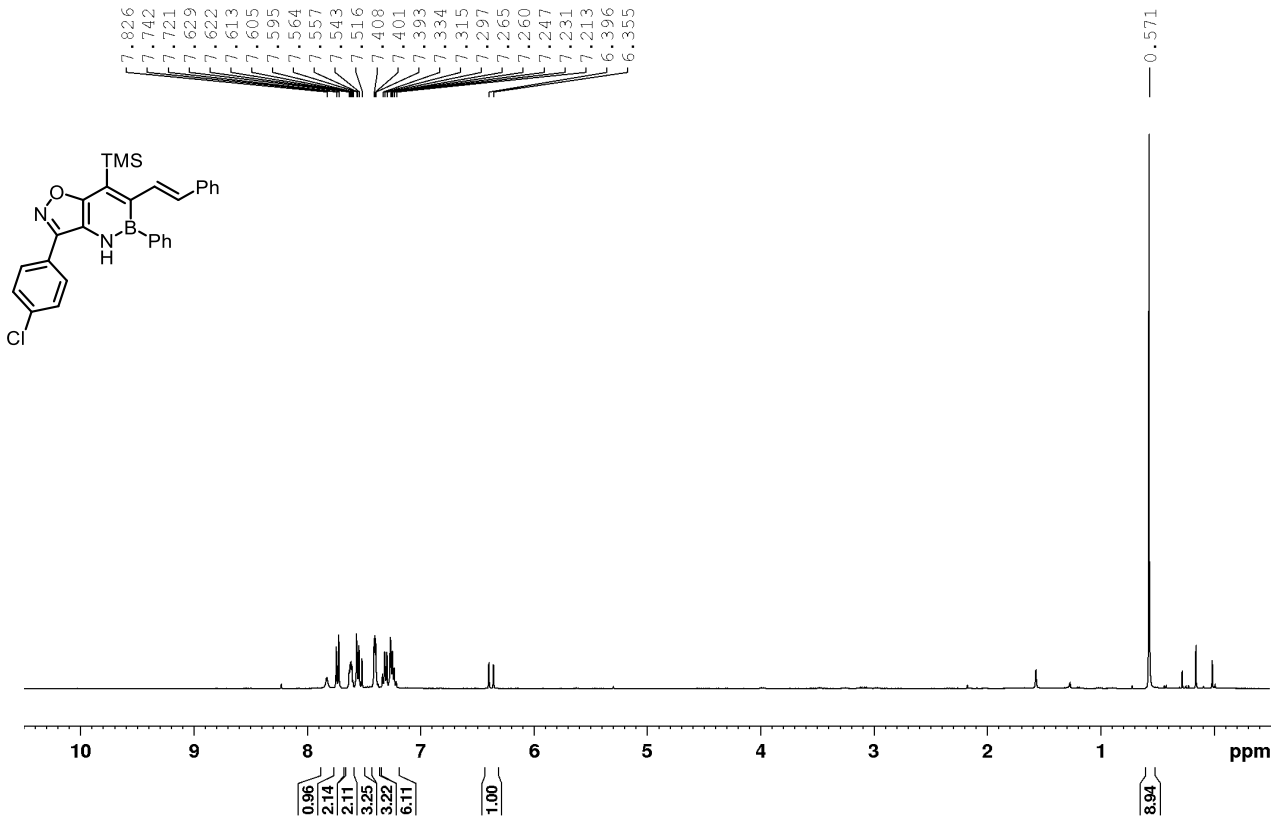


^{11}B NMR (160 MHz, $CDCl_3$)

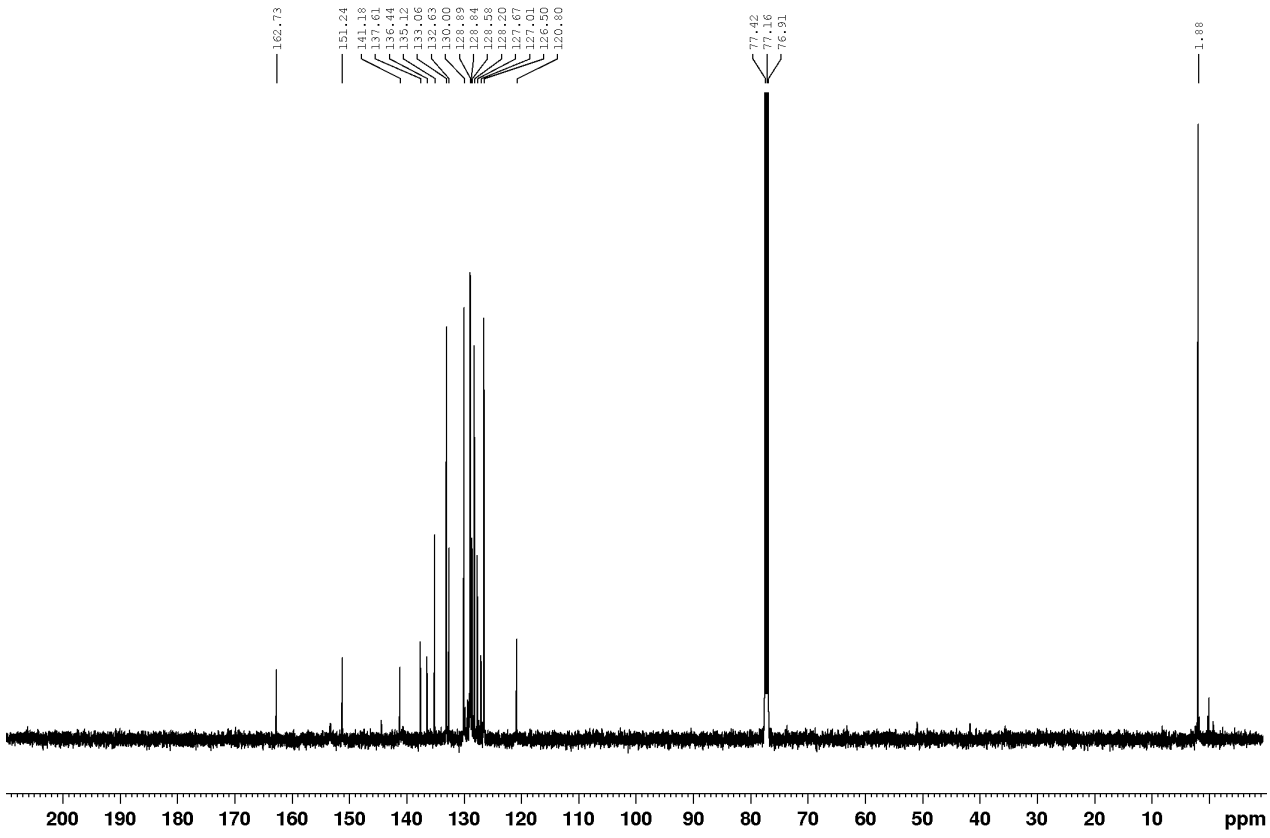


(*E*)-3-(4-Chlorophenyl)-5-phenyl-6-styryl-7-(trimethylsilyl)-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5t)

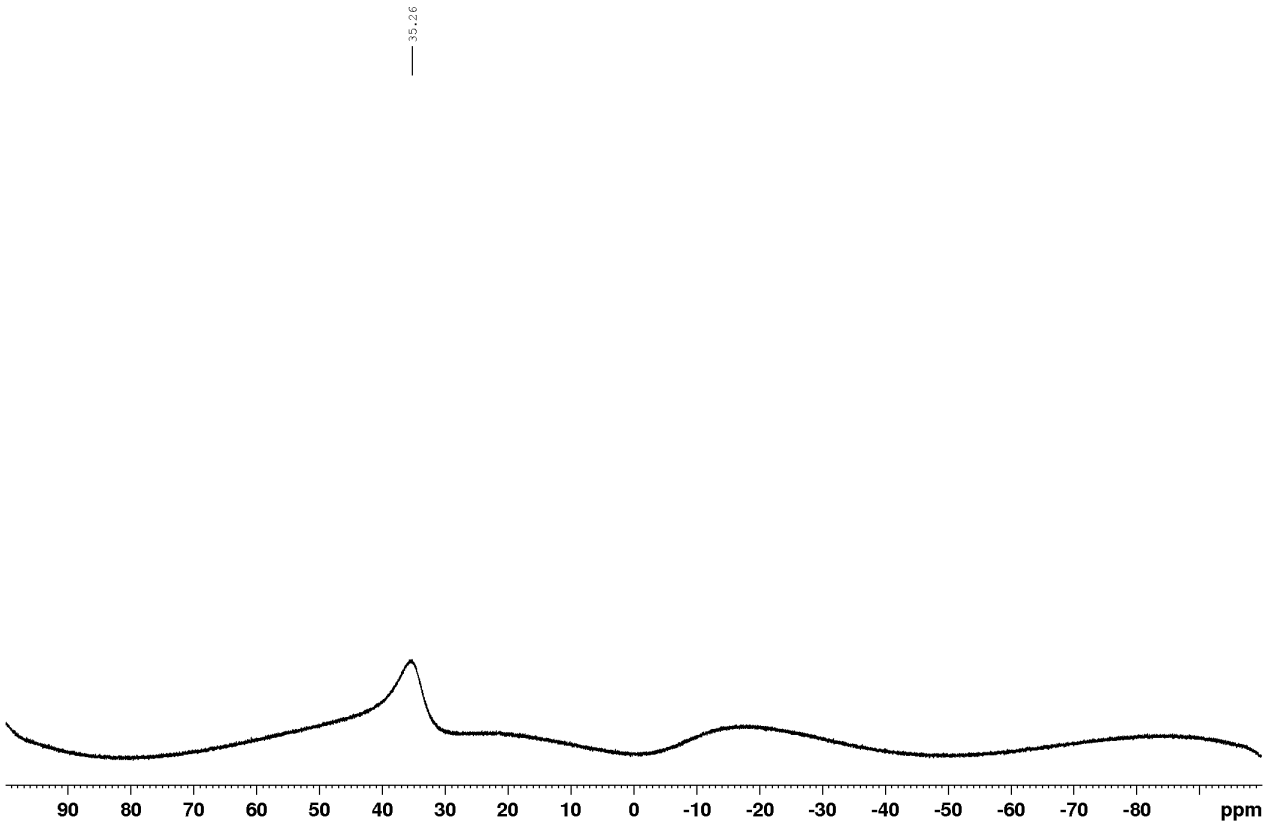
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

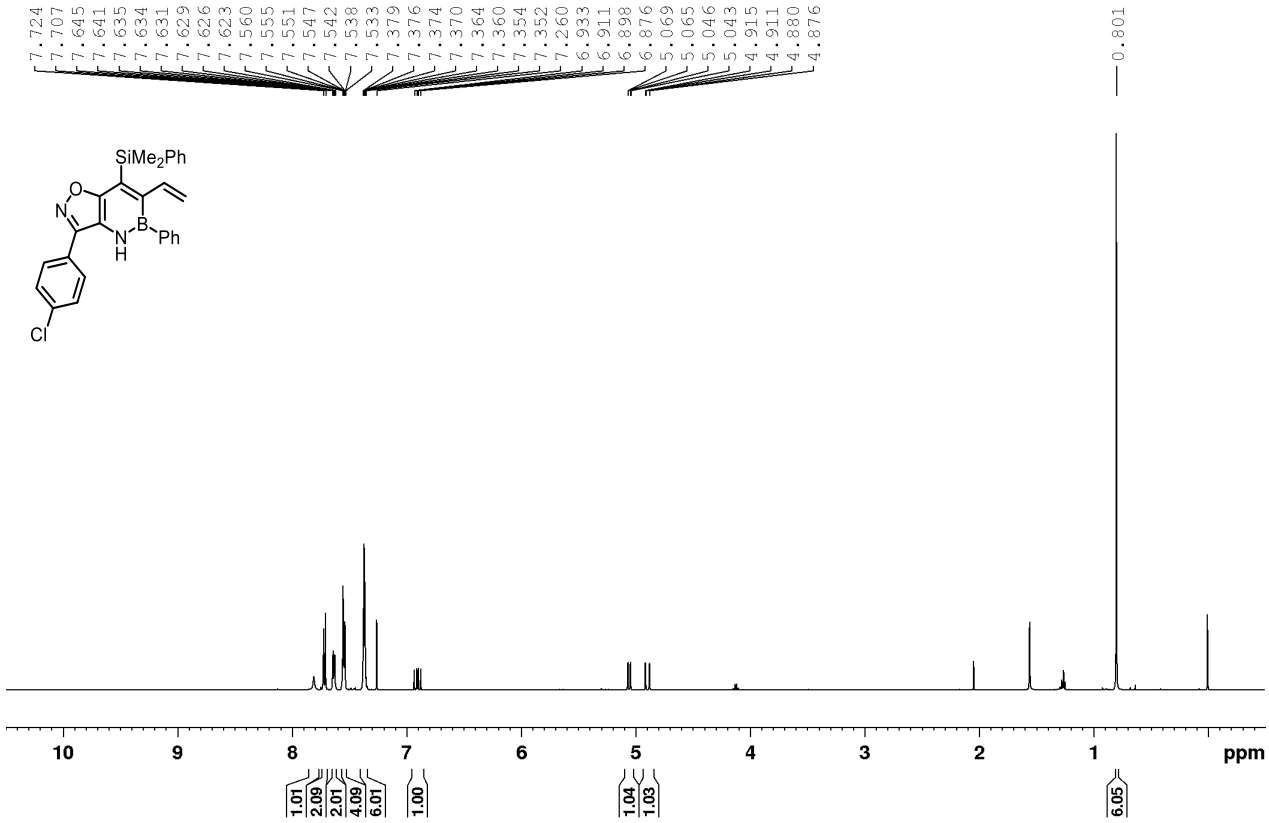


^{11}B NMR (160 MHz, $CDCl_3$)

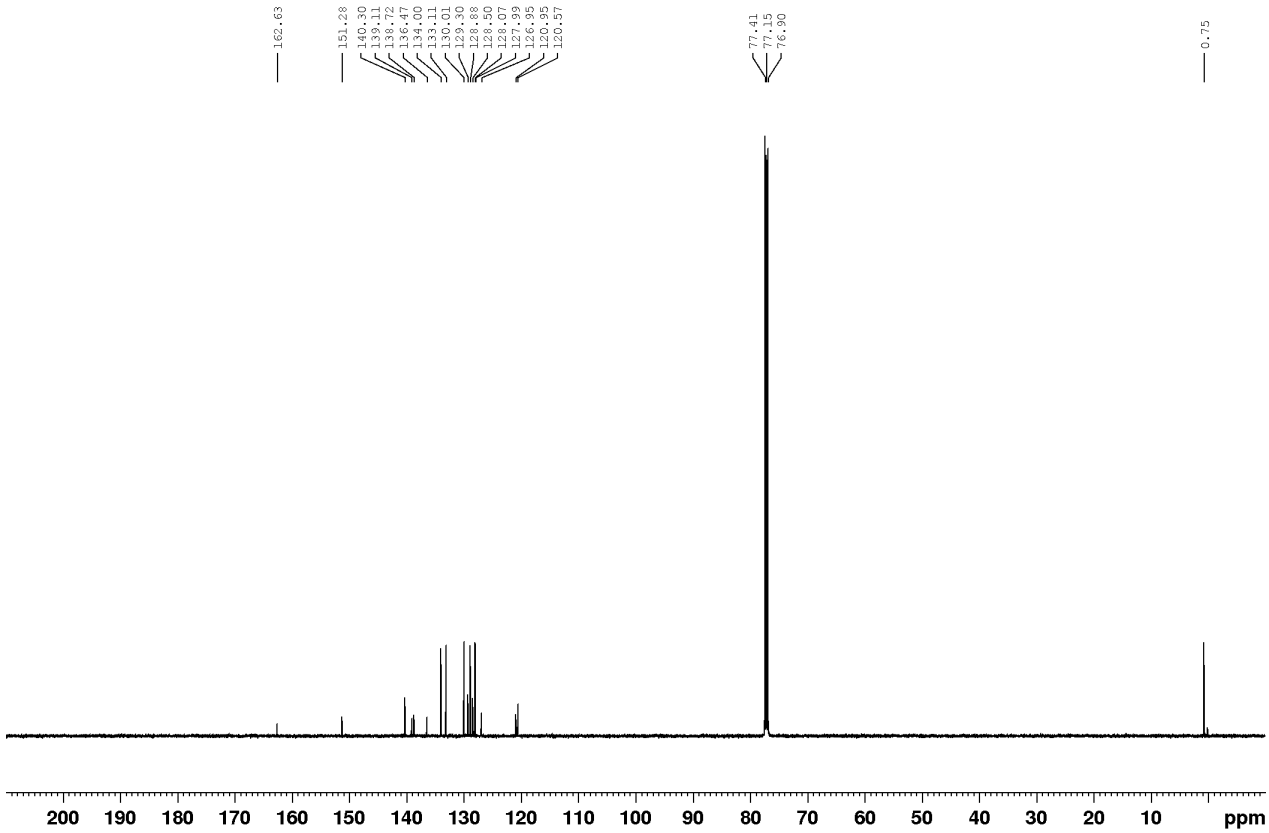


3-(4-Chlorophenyl)-7-(dimethyl(phenyl)silyl)-5-phenyl-6-vinyl-4,5-dihydroisoxazolo[5,4-*e*][1,2]azaborinine (5u)

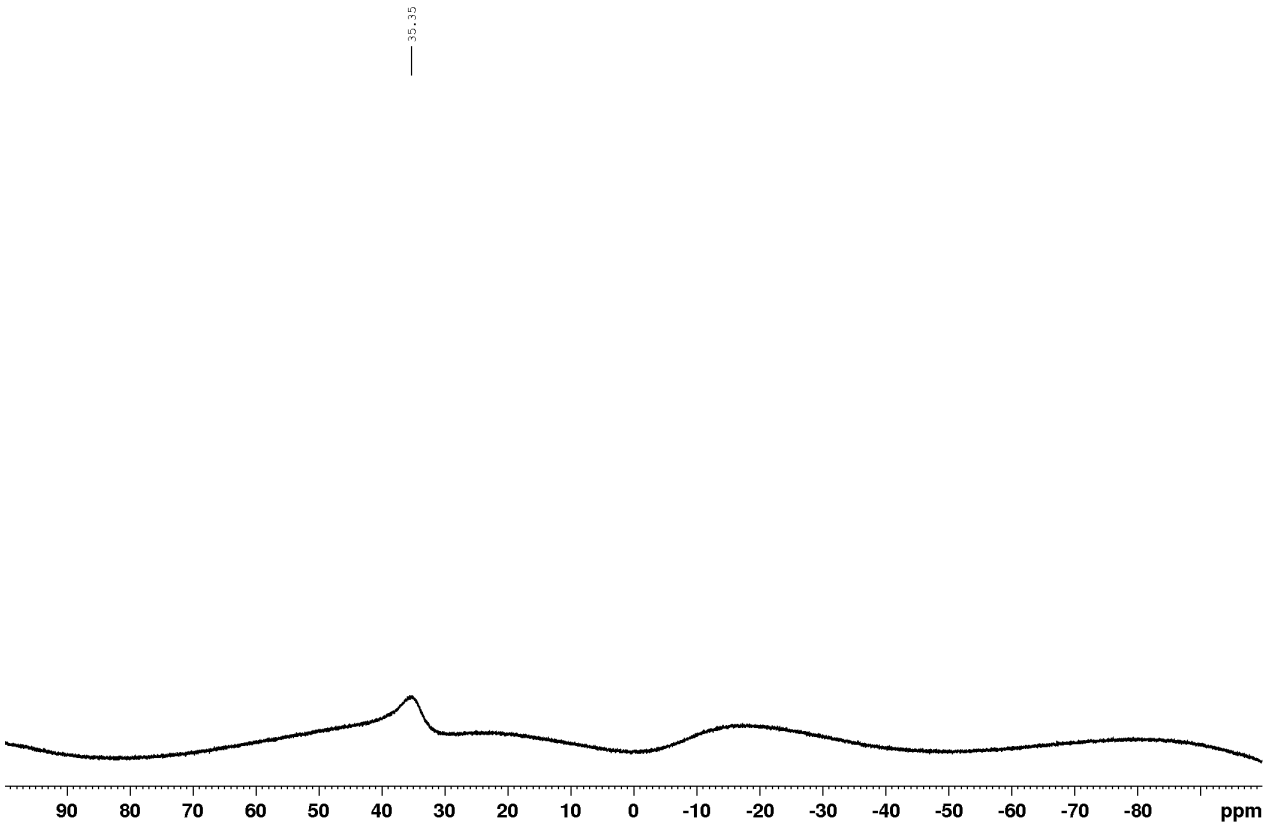
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

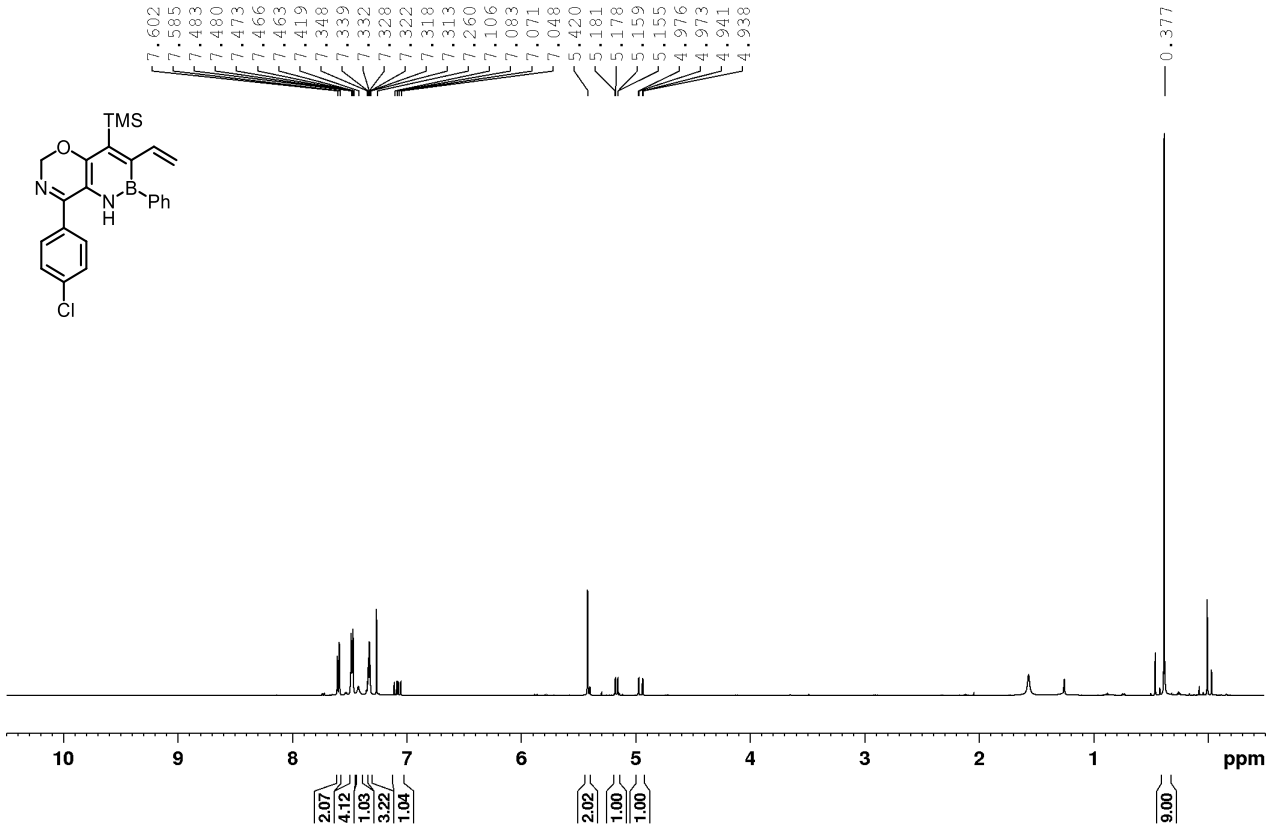


^{11}B NMR (160 MHz, $CDCl_3$)

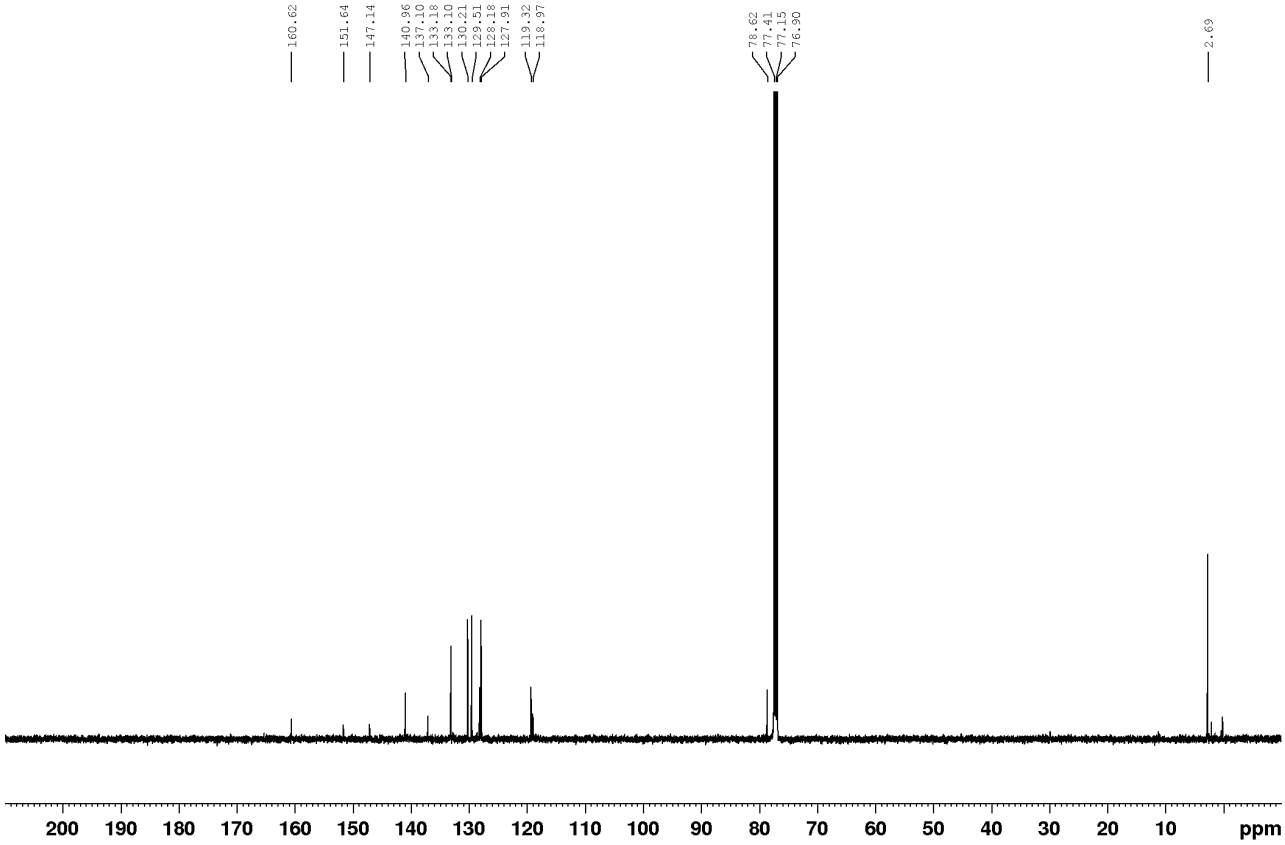


8-(4-Chlorophenyl)-2-phenyl-4-(trimethylsilyl)-3-vinyl-2,6-dihydro-1*H*-[1,2]azaborinino[6,5-*e*][1,3]oxazine (6)

^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



^{11}B NMR (160 MHz, $CDCl_3$)