Evidence for a Boroxinate Based Brønsted Acid Derivative of VAPOL as the Active Catalyst in the Catalytic Asymmetric Aziridination Reaction.

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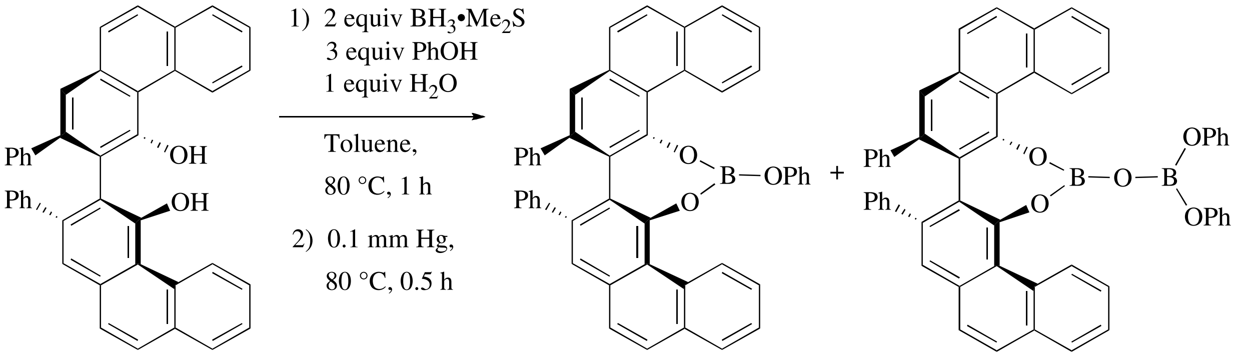
Supporting information

Table of Contents:

1. General information.

(*S*)-VAPOL (>99% ee) was prepared by our previously described procedure[1] and was dried over P_2O_5 overnight under reduced pressure (0.1 mm Hg) with refluxing hexane in a Abderhalden drying apparatus. $B(OPh)_3$ was used as purchased from Aldrich and was stored in a desiccator. Phenol was purified by distillation and stored in a desicator. Tetramethyl ammonium acetate, borane dimethylsulfide and 4-dimethylaminopyridine (DMAP) were purchased from Aldrich and used without purification. The tetramethylammonium acetate is highly hygroscopic and was opened in a dry box. Toluene and THF were dried over sodium and freshly distilled prior to use. Deuterium solvents as well as dichloromethane and pentane were dried over 3 Å molecular sieves and then distilled under argon and stored in a dry box. Melting points were determined on a Thomas Hoover capillary melting point apparatus. ^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz or VXR-500 MHz instrument in $CDCl_3$ unless otherwise noted. The residual peak of $CDCl_3$ was used as the internal standard for both ^1H NMR (δ = 7.24 ppm) and ^{13}C NMR (δ = 77.0 ppm). ^{11}B NMR spectra were recorded on a Varian 500 MHz instrument in $CDCl_3$ unless otherwise noted. Pure $BF_3 \bullet OEt_2$ (δ = 0 ppm) was used as the external standard for ^{11}B NMR spectra. Both low-resolution and high-resolution mass spectra (MALDI) were performed in the Michigan State University Mass Spectroscopy Facility. Analytical thin-layer chromatography (TLC) was performed on Silicycle silica gel plates with F-254 indicator. Visualization was by short wave (254 nm) and long wave (365nm) ultraviolet light, or by staining with phosphomolybdic acid in ethanol or with potassium permanganate. Flash column chromatography was performed with silica gel 60 (230 – 450 mesh).

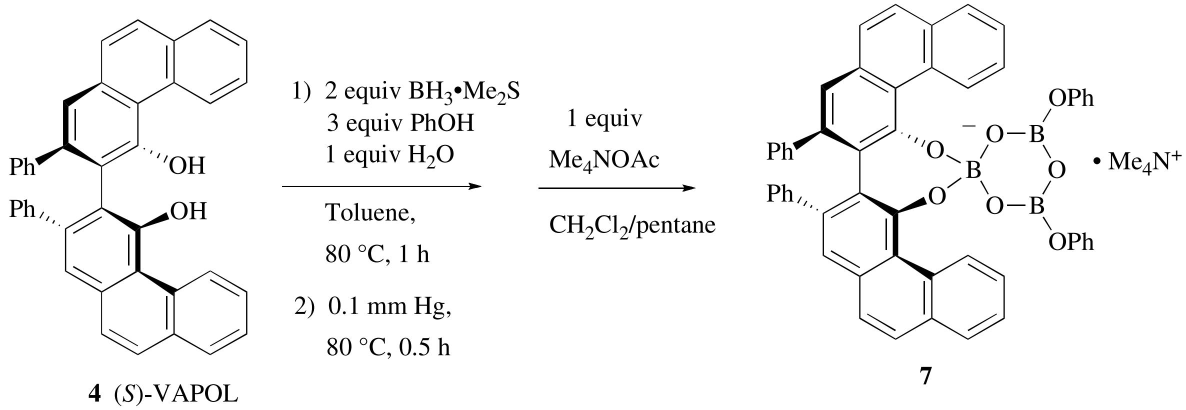
2. Preparation of Pyroborate 6 from Borane•Dimethyl Sulfide Complex and Phenol.



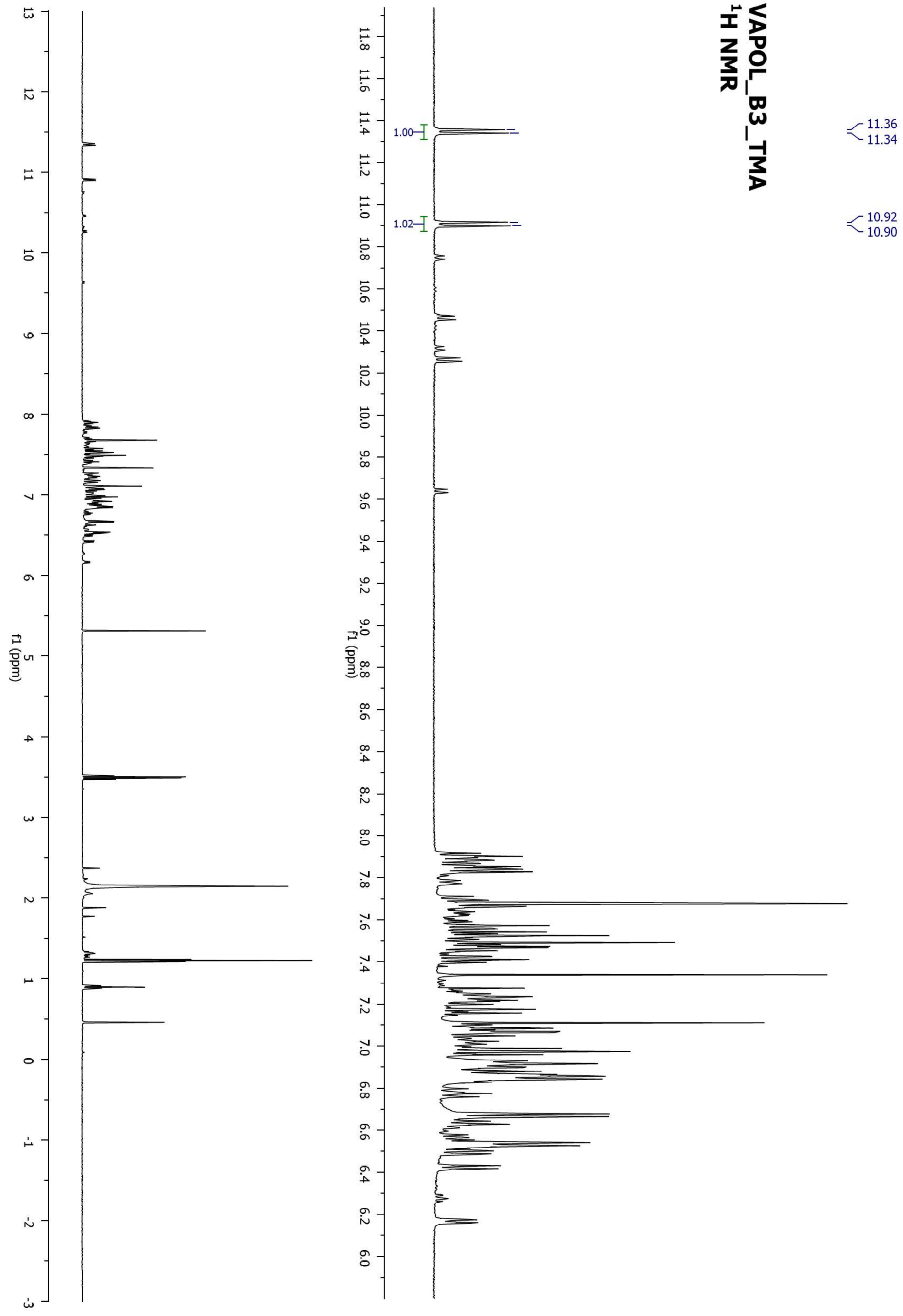
4 (*S*)-VAPOL **5** **6**

A 25 mL pear-shaped flask that had its 14/20 joint replaced by a high vacuum threaded T-shaped Teflon value and which was flame dried and cooled under argon to room temperature was equipped with a stir bar and charged (*S*)-VAPOL (54 mg, 0.1 mmol), phenol (28 mg, 0.3 mmol), 2 mL toluene and 100 μL BH_3Me_2S (2.0 M in toluene, 0.2 mmol). To this solution was added 1.8 μL H_2O (0.1 mmol). The Teflon valve was closed to seal the flask and the mixture was then heated to 80 °C for 1 h. The volatiles were removed by carefully opening the Teflon valve and applying high vacuum. When dry, the flask was heated at 80 °C for 0.5 h under high vacuum (0.1 mm Hg). After cooling, the flask with the catalyst was moved into a glove box and the catalyst was dissolved into approximately 0.75 mL $CDCl_3$ and analyzed by NMR. The catalyst prepared by this method typically gave a ratio of VAPOL:B1:B2 = 0.1:1.0:8.2 as determined by ^{1}H NMR.[2] These ratio are taken from the integration of the bay protons for each species which are: VAPOL **4** δ = 9.77 ppm in $CDCl_3$ (9.88 in toluene d8), mesoborate **5** δ = 9.51 ppm in $CDCl_3$ (9.74 in toluene d8), pyroborate **6** δ = 9.22 ppm in $CDCl_3$ (9.53 in toluene d8). The spectrum shown in Figure 3 in the text contains a small amount of VAPOL. The ^{11}B NMR spectrum was taken in $CDCl_3$ in a quartz NMR tube and, as indicated in Figure 3 in the text, shows two broad peaks at 18.25 ppm and 16.20 ppm (baseline separation not achieved) relative to BF_3•Et_2O.

3. Preparation of Tetramethylammonium VAPOL Boroxinate Complex 7.



A flame dried 25 mL pear-shaped flask that had its 14/20 joint replaced by a high vacuum threaded T-shaped Teflon value and which contained a stir bar was cooled under argon to room temperature and charged with (*S*)-VAPOL (108 mg, 0.2 mmol), PhOH (56.4 mg, 0.6 mol), BH_3Me_2S (200 μL, 0.4 mmol) and 4 mL toluene, consecutively. To the solution was added deionized water (3.6 μL, 0.2 mmol). The flask was sealed and heated to 80 °C for 1 h. The volatile materials were removed via high vacuum at 80 °C for 0.5 h yielding a mixture of mesoborate **5** and pyroborate **6** as described above. After cooling, the flask containing **5** and **6** was transferred into a glove box. To this mixture was added tetramethylammonium acetate (TMAA) (26.6 mg, 0.2 mmol) and 6 mL CH_2Cl_2. The solution was allowed to stir at room temperature for 24 h followed by addition of pentane until a permanent precipitate appeared. A small amount of CH_2Cl_2 was added to the mixture until a clear solution was obtained. The solution was then filtered through a plug of glass wool in a pipette. The colorless solution was collected in a 20 mL vial and capped. The vial was allowed to stand in the glove box overnight. Colorless crystals appeared inside the vial. These crystals were of X-ray quality and could be subjected to crystallographic study directly and the quality of the crystals quickly deteriorated in the absence of solvent. Decanting the mother liquor followed by two washes with a 1:1 mixture of CH_2Cl_2/pentane afforded complex **7** (39 mg, 22% yield) as colorless crystals. The mass spectrum of complex **7** was taken by negative ion MALDI and the parent peak was the boroxinate anion: mass spectrum (MALDI, negative), *m/z* (% rel intensity) 803 $M^+ - Me_4N$ (100), 727 (14), 407 (8); HRMS *m/z* calcd for $C_{52}H_{34}B_3O_7$ 803.2584, found 803.2588. The ^1H NMR spectrum of complex **11** is shown below and is labeled VAPOL_B3_TMA. The symmetry of this molecule is broken as indicated by the observation of two equal sized doublets for the bay region protons at 10.91 and 11.35 ppm. This is interpreted to mean that the migration of the tetramethyl ammonium cation from one face of the boroxinate core to the other face is slow on the NMR time scale. The x-ray structure of complex **7** was also determined and the results from this study are given below. The crystal structures presented in the text of this paper were visualized using the Mercury Program.


VAPOL_B3_TMA
^{1}H NMR
11.36
11.34
10.92
10.90
1.00
1.02
f1 (ppm)
f1 (ppm)

4. X-Ray Structure Determination of Tetramethyl Ammonium Boroxinate Complex 7.

Figure 1. **ORTEP Drawing of complex 7.**

QuickTime™ and a
decompressor
are needed to see this picture.

Figure 2. ORTEP Drawing of complex 7 with Tetramethylammonium Removed.

Table 1. Crystal data and structure refinement for complex **7**.

Identification code	wf081606
Empirical formula	C59 H49.25 B3 Cl3.25 N O7 S0.75
Formula weight	1055.93
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system	Ortho.
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 14.311(3) A
	b = 18.360(4) A
	c = 21.044(4) A
	alpha = 90 deg.
	beta = 90 deg.
	gamma = 90 deg.
Volume	5529.1(19) A^3
Z	4
Density (calculated)	1.269 Mg/m^3
Absorption coefficient	0.259 mm^-1
F(000)	2194
Crystal size	0.7 x 0.2 x 0.2 mm
Theta range for data collection	1.47 to 28.29 deg.
Index ranges	-19<=h<=19, -24<=k<=24, -28<=l<=28
Reflections collected / unique	64900 / 13458 [R(int) = 0.0660]
Completeness to theta = 28.29	99.1%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	13458 / 6 / 661
Goodness-of-fit on F^2	1.413
Final R indices [I>2sigma(I)]	R1 = 0.0895, wR2 = 0.2242
R indices (all data)	R1 = 0.1545, wR2 = 0.2450
Absolute structure parameter	0.14(14)
Largest diff. peak and hole	1.106 and -0.757 e.A^-3

Table 2. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters (A^2 x 10^3), and occupancies for complex **7**.

	x	y	z	U(eq)	Occ.
O(1)	1640(2)	7637(1)	9684(1)	33(1)	1
C(2)	1377(3)	6997(2)	9408(2)	34(1)	1
C(3)	943(3)	6475(2)	9786(2)	34(1)	1
C(4)	832(3)	6638(2)	10483(2)	31(1)	1
C(5)	361(3)	7296(2)	10646(2)	32(1)	1
O(6)	104(2)	7743(1)	10159(1)	32(1)	1
B(7)	856(3)	8146(2)	9834(2)	35(1)	1
O(8)	1261(2)	8704(1)	10258(1)	37(1)	1
B(9)	1174(4)	9419(3)	10129(3)	48(1)	1
O(10)	780(3)	9672(1)	9587(2)	78(1)	1
B(11)	431(4)	9167(3)	9145(3)	50(1)	1
O(12)	453(2)	8455(1)	9259(1)	36(1)	1
O(13)	1508(3)	9962(2)	10518(2)	75(1)	1
C(14)	1861(4)	9911(3)	11103(3)	55(1)	1
C(15)	1294(4)	9706(3)	11610(3)	64(2)	1
C(16)	1658(6)	9709(3)	12226(3)	77(2)	1
C(17)	2557(7)	9892(3)	12331(3)	88(2)	1
C(18)	3135(5)	10088(3)	11820(4)	85(2)	1
C(19)	2771(4)	10109(3)	11207(3)	72(2)	1
O(20)	57(3)	9496(2)	8626(2)	66(1)	1
C(21)	-252(4)	9135(2)	8084(2)	47(1)	1
C(22)	-1169(4)	9245(3)	7902(2)	54(1)	1
C(23)	-1476(4)	8935(3)	7339(3)	66(2)	1
C(24)	-901(4)	8524(3)	6972(2)	62(1)	1
C(25)	25(4)	8428(3)	7156(3)	64(1)	1
C(26)	353(4)	8725(3)	7723(2)	50(1)	1
C(27)	1560(3)	6863(2)	8753(2)	33(1)	1
C(28)	2068(3)	7373(2)	8335(2)	42(1)	1

C(29)	2594(3)	7981(3)	8547(2)	49(1)	1
C(30)	3056(4)	8413(3)	8124(2)	54(1)	1
C(31)	3028(4)	8281(3)	7480(3)	65(2)	1
C(32)	2546(4)	7714(3)	7262(3)	63(2)	1
C(33)	2071(4)	7232(3)	7674(2)	52(1)	1
C(34)	1626(4)	6581(3)	7432(2)	60(2)	1
C(35)	1229(4)	6088(3)	7808(2)	55(1)	1
C(36)	1198(3)	6214(2)	8496(2)	39(1)	1
C(37)	766(3)	5705(2)	8882(2)	42(1)	1
C(38)	624(3)	5805(2)	9524(2)	36(1)	1
C(39)	113(3)	5237(2)	9894(2)	46(1)	1
C(40)	330(4)	4494(3)	9784(3)	63(1)	1
C(41)	-146(6)	3950(3)	10105(4)	88(2)	1
C(42)	-810(6)	4117(4)	10519(4)	93(2)	1
C(43)	-1064(5)	4853(3)	10639(3)	75(2)	1
C(44)	-582(3)	5392(2)	10325(2)	47(1)	1
C(45)	1161(3)	6183(2)	10961(2)	34(1)	1
C(46)	1731(3)	5510(2)	10834(2)	40(1)	1
C(47)	1533(4)	4870(3)	11160(3)	56(1)	1
C(48)	2083(4)	4266(3)	11086(3)	74(2)	1
C(49)	2833(4)	4265(3)	10691(3)	68(2)	1
C(50)	3047(4)	4904(3)	10352(2)	54(1)	1
C(51)	2488(3)	5500(3)	10420(2)	44(1)	1
C(52)	1008(3)	6369(2)	11586(2)	39(1)	1
C(53)	529(3)	7006(3)	11752(2)	43(1)	1
C(54)	460(4)	7204(3)	12415(2)	53(1)	1
C(55)	67(5)	7823(3)	12591(2)	68(2)	1
C(56)	-393(4)	8307(3)	12133(2)	56(1)	1
C(57)	-865(5)	8912(3)	12342(3)	70(2)	1
C(58)	-1334(5)	9349(3)	11932(3)	77(2)	1
C(59)	-1348(4)	9182(3)	11296(3)	56(1)	1
C(60)	-860(3)	8581(2)	11066(2)	47(1)	1
C(61)	-356(3)	8132(2)	11478(2)	42(1)	1

C(62)	170(3)	7486(2)	11289(2)	36(1)	1
N(101)	-1651(2)	7163(2)	8792(2)	39(1)	1
C(102)	-834(3)	7215(3)	8357(2)	52(1)	1
C(103)	-1466(3)	6644(3)	9314(2)	48(1)	1
C(104)	-1810(3)	7894(2)	9081(2)	51(1)	1
C(105)	-2464(1)	6937(1)	8430(1)	50(1)	1
C(00)	556(1)	1189(1)	8694(1)	400(20)	0.914(5)
Cl(1)	-10(1)	1938(1)	9117(1)	113(1)	0.914(5)
Cl(2)	1933(1)	1553(1)	8451(1)	211(2)	0.914(5)
Cl(3)	5679(1)	3132(1)	9133(1)	198(3)	0.723(6)
Cl(4)	3515(1)	3527(1)	9016(1)	375(8)	0.723(6)
C(01)	4681(1)	3894(1)	9000(1)	168(8)	0.723(6)
S(1)	2846(1)	12217(1)	10425(1)	351(8)	0.783(12)
C(04)	1390(1)	12563(1)	10500(1)	204(11)	0.783(12)
C(05)	3210(1)	12753(1)	9755(1)	1790(150)	0.783(12)

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

Table 3. Bond lengths [A] and angles [deg] for complex **7**.

O(1)-C(2)	1.364(5)
O(1)-B(7)	1.494(5)
C(2)-C(3)	1.392(6)
C(2)-C(27)	1.425(6)
C(3)-C(38)	1.424(6)
C(3)-C(4)	1.506(6)
C(4)-C(45)	1.389(5)

C(4)-C(5)	1.425(6)
C(5)-O(6)	1.363(5)
C(5)-C(62)	1.425(6)
O(6)-B(7)	1.475(5)
B(7)-O(12)	1.455(5)
B(7)-O(8)	1.476(6)
O(8)-B(9)	1.346(6)
B(9)-O(10)	1.355(6)
B(9)-O(13)	1.375(6)
O(10)-B(11)	1.404(6)
B(11)-O(12)	1.330(6)
B(11)-O(20)	1.358(6)
O(13)-C(14)	1.333(6)
C(14)-C(19)	1.369(8)
C(14)-C(15)	1.392(8)
C(15)-C(16)	1.397(9)
C(16)-C(17)	1.348(11)
C(17)-C(18)	1.404(11)
C(18)-C(19)	1.392(9)
O(20)-C(21)	1.392(6)
C(21)-C(26)	1.376(7)
C(21)-C(22)	1.382(7)
C(22)-C(23)	1.388(8)
C(23)-C(24)	1.358(8)
C(24)-C(25)	1.391(8)
C(25)-C(26)	1.394(7)
C(27)-C(36)	1.407(6)
C(27)-C(28)	1.475(6)
C(28)-C(33)	1.417(7)
C(28)-C(29)	1.417(7)
C(29)-C(30)	1.363(7)
C(30)-C(31)	1.378(8)
C(31)-C(32)	1.331(8)

C(32)-C(33)	1.413(7)
C(33)-C(34)	1.447(8)
C(34)-C(35)	1.329(8)
C(35)-C(36)	1.468(6)
C(36)-C(37)	1.383(6)
C(37)-C(38)	1.379(6)
C(38)-C(39)	1.492(6)
C(39)-C(44)	1.377(7)
C(39)-C(40)	1.418(7)
C(40)-C(41)	1.385(8)
C(41)-C(42)	1.326(10)
C(42)-C(43)	1.422(10)
C(43)-C(44)	1.374(7)
C(45)-C(52)	1.376(6)
C(45)-C(46)	1.506(6)
C(46)-C(51)	1.390(6)
C(46)-C(47)	1.389(6)
C(47)-C(48)	1.369(8)
C(48)-C(49)	1.357(8)
C(49)-C(50)	1.407(8)
C(50)-C(51)	1.363(7)
C(52)-C(53)	1.400(6)
C(53)-C(62)	1.410(6)
C(53)-C(54)	1.444(6)
C(54)-C(55)	1.321(8)
C(55)-C(56)	1.468(8)
C(56)-C(57)	1.373(8)
C(56)-C(61)	1.415(7)
C(57)-C(58)	1.357(9)
C(58)-C(59)	1.373(8)
C(59)-C(60)	1.392(6)
C(60)-C(61)	1.397(7)
C(61)-C(62)	1.460(6)

N(101)-C(105)	1.452(4)
N(101)-C(103)	1.478(6)
N(101)-C(102)	1.488(6)
N(101)-C(104)	1.490(6)
C(00)-Cl(1)	1.8268
C(00)-Cl(2)	2.1437
Cl(3)-C(04)#1	1.805(3)
Cl(3)-C(01)	2.0188
Cl(4)-C(01)	1.7999
Cl(4)-C(05)#2	2.1514
S(1)-C(05)	1.7973
S(1)-C(04)	2.1840
C(04)-Cl(3)#3	1.805(3)
C(05)-Cl(4)#4	2.1513
C(2)-O(1)-B(7)	115.0(3)
O(1)-C(2)-C(3)	118.2(3)
O(1)-C(2)-C(27)	120.7(4)
C(3)-C(2)-C(27)	121.1(4)
C(2)-C(3)-C(38)	121.1(4)
C(2)-C(3)-C(4)	117.9(3)
C(38)-C(3)-C(4)	121.0(4)
C(45)-C(4)-C(5)	119.7(4)
C(45)-C(4)-C(3)	123.4(4)
C(5)-C(4)-C(3)	116.9(3)
O(6)-C(5)-C(4)	117.2(3)
O(6)-C(5)-C(62)	121.0(4)
C(4)-C(5)-C(62)	121.8(4)
C(5)-O(6)-B(7)	117.0(3)
O(12)-B(7)-O(8)	112.8(3)
O(12)-B(7)-O(6)	107.0(3)
O(8)-B(7)-O(6)	110.8(3)
O(12)-B(7)-O(1)	111.5(3)
O(8)-B(7)-O(1)	105.4(3)

O(6)-B(7)-O(1)	109.4(3)
B(9)-O(8)-B(7)	121.2(4)
O(8)-B(9)-O(10)	122.8(4)
O(8)-B(9)-O(13)	123.7(5)
O(10)-B(9)-O(13)	113.4(4)
B(9)-O(10)-B(11)	118.6(3)
O(12)-B(11)-O(20)	126.2(5)
O(12)-B(11)-O(10)	121.4(4)
O(20)-B(11)-O(10)	112.3(4)
B(11)-O(12)-B(7)	122.8(4)
C(14)-O(13)-B(9)	129.1(4)
O(13)-C(14)-C(19)	119.3(6)
O(13)-C(14)-C(15)	120.3(5)
C(19)-C(14)-C(15)	120.2(6)
C(14)-C(15)-C(16)	119.5(6)
C(17)-C(16)-C(15)	120.7(7)
C(16)-C(17)-C(18)	120.0(6)
C(19)-C(18)-C(17)	119.8(6)
C(14)-C(19)-C(18)	119.8(6)
B(11)-O(20)-C(21)	124.9(4)
C(26)-C(21)-C(22)	121.7(5)
C(26)-C(21)-O(20)	120.9(5)
C(22)-C(21)-O(20)	117.3(5)
C(21)-C(22)-C(23)	118.5(5)
C(24)-C(23)-C(22)	121.4(5)
C(23)-C(24)-C(25)	119.4(5)
C(26)-C(25)-C(24)	120.6(5)
C(21)-C(26)-C(25)	118.4(5)
C(36)-C(27)-C(2)	116.7(4)
C(36)-C(27)-C(28)	119.4(4)
C(2)-C(27)-C(28)	123.8(4)
C(33)-C(28)-C(29)	116.8(4)
C(33)-C(28)-C(27)	118.0(4)

C(29)-C(28)-C(27)	125.1(4)
C(30)-C(29)-C(28)	120.7(5)
C(29)-C(30)-C(31)	121.8(5)
C(32)-C(31)-C(30)	119.4(5)
C(31)-C(32)-C(33)	121.9(5)
C(32)-C(33)-C(28)	119.3(5)
C(32)-C(33)-C(34)	120.9(5)
C(28)-C(33)-C(34)	119.7(4)
C(35)-C(34)-C(33)	122.8(4)
C(34)-C(35)-C(36)	119.6(5)
C(37)-C(36)-C(27)	120.8(4)
C(37)-C(36)-C(35)	119.1(4)
C(27)-C(36)-C(35)	120.0(4)
C(38)-C(37)-C(36)	123.5(4)
C(37)-C(38)-C(3)	116.6(4)
C(37)-C(38)-C(39)	119.4(4)
C(3)-C(38)-C(39)	124.0(4)
C(44)-C(39)-C(40)	117.6(4)
C(44)-C(39)-C(38)	123.7(4)
C(40)-C(39)-C(38)	118.7(4)
C(41)-C(40)-C(39)	120.5(6)
C(42)-C(41)-C(40)	120.3(6)
C(41)-C(42)-C(43)	121.4(6)
C(44)-C(43)-C(42)	118.1(6)
C(39)-C(44)-C(43)	122.1(5)
C(52)-C(45)-C(4)	119.3(4)
C(52)-C(45)-C(46)	117.4(4)
C(4)-C(45)-C(46)	123.2(4)
C(51)-C(46)-C(47)	117.3(4)
C(51)-C(46)-C(45)	123.0(4)
C(47)-C(46)-C(45)	119.7(4)
C(48)-C(47)-C(46)	120.7(5)
C(49)-C(48)-C(47)	121.8(5)

C(48)-C(49)-C(50)	118.7(5)
C(51)-C(50)-C(49)	119.3(5)
C(50)-C(51)-C(46)	122.2(4)
C(45)-C(52)-C(53)	121.6(4)
C(52)-C(53)-C(62)	121.9(4)
C(52)-C(53)-C(54)	119.0(4)
C(62)-C(53)-C(54)	119.0(4)
C(55)-C(54)-C(53)	121.1(5)
C(54)-C(55)-C(56)	121.8(5)
C(57)-C(56)-C(61)	121.0(5)
C(57)-C(56)-C(55)	120.0(5)
C(61)-C(56)-C(55)	119.1(4)
C(58)-C(57)-C(56)	121.1(5)
C(57)-C(58)-C(59)	119.7(5)
C(58)-C(59)-C(60)	120.6(6)
C(59)-C(60)-C(61)	120.7(5)
C(60)-C(61)-C(56)	116.8(4)
C(60)-C(61)-C(62)	125.2(4)
C(56)-C(61)-C(62)	117.9(4)
C(53)-C(62)-C(5)	115.7(4)
C(53)-C(62)-C(61)	120.5(4)
C(5)-C(62)-C(61)	123.8(4)
C(105)-N(101)-C(103)	110.4(3)
C(105)-N(101)-C(102)	109.0(3)
C(103)-N(101)-C(102)	110.9(4)
C(105)-N(101)-C(104)	110.4(3)
C(103)-N(101)-C(104)	107.8(4)
C(102)-N(101)-C(104)	108.3(3)
Cl(1)-C(00)-Cl(2)	106.8
C(04)#1-Cl(3)-C(01)	161.38(8)
C(01)-Cl(4)-C(05)#2	116.7
Cl(4)-C(01)-Cl(3)	113.2
C(05)-S(1)-C(04)	100.0

Cl(3)#3-C(04)-S(1)	111.27(6)
S(1)-C(05)-Cl(4)#4	171.1

Symmetry transformations used to generate equivalent atoms:

#1 x+1/2,-y+3/2,-z+2 #2 x,y-1,z #3 x-1/2,-y+3/2,-z+2
#4 x,y+1,z

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for complex **7**.

	U11	U22	U33	U23	U13	U12
O(1)	32(2)	28(1)	37(2)	2(1)	0(1)	-2(1)
C(2)	33(2)	35(2)	35(2)	2(2)	1(2)	10(2)
C(3)	35(2)	32(2)	35(2)	-1(2)	-4(2)	6(2)
C(4)	28(2)	34(2)	32(2)	1(2)	4(2)	-3(2)
C(5)	28(2)	35(2)	32(2)	5(2)	-1(2)	-6(2)
O(6)	34(2)	29(1)	34(1)	0(1)	2(1)	3(1)
B(7)	37(3)	31(2)	37(3)	6(2)	7(2)	3(2)
O(8)	38(2)	31(2)	41(2)	-3(1)	1(1)	-4(1)
B(9)	59(3)	38(3)	46(3)	-7(2)	-7(3)	-6(3)
O(10)	136(3)	28(1)	71(2)	1(1)	-42(2)	-2(2)

B(11)	60(3)	31(3)	58(3)	6(3)	-10(3)	2(3)
O(12)	38(2)	31(1)	38(2)	1(1)	-1(1)	-1(1)
O(13)	116(3)	41(2)	69(2)	-7(2)	-29(2)	-19(2)
C(14)	63(3)	31(2)	71(3)	-10(2)	-8(3)	-3(2)
C(15)	62(3)	43(3)	85(4)	-11(3)	9(3)	5(3)
C(16)	121(6)	53(3)	56(4)	-13(2)	2(4)	21(3)
C(17)	133(7)	58(4)	72(4)	-28(3)	-41(5)	17(4)
C(18)	55(4)	60(4)	140(7)	-45(4)	-37(4)	5(3)
C(19)	73(4)	44(3)	98(5)	-28(3)	2(4)	-8(3)
O(20)	106(3)	39(2)	54(2)	4(2)	-25(2)	1(2)
C(21)	67(3)	34(2)	40(3)	11(2)	-6(2)	-2(2)
C(22)	56(3)	59(3)	46(3)	11(2)	-1(2)	5(3)
C(23)	64(4)	56(3)	78(4)	20(3)	-13(3)	5(3)
C(24)	80(4)	64(3)	41(3)	5(2)	-13(3)	1(3)
C(25)	63(4)	70(4)	57(3)	8(3)	20(3)	-1(3)
C(26)	48(3)	51(3)	52(3)	13(2)	3(2)	-6(2)
C(27)	32(2)	35(2)	33(2)	2(2)	4(2)	10(2)
C(28)	43(3)	39(2)	45(3)	9(2)	6(2)	15(2)
C(29)	49(3)	48(3)	49(3)	8(2)	12(2)	12(2)
C(30)	51(3)	44(3)	68(3)	13(2)	23(2)	4(2)
C(31)	79(4)	49(3)	67(4)	12(3)	38(3)	15(3)
C(32)	73(4)	65(4)	50(3)	13(3)	29(3)	19(3)
C(33)	54(3)	65(3)	38(3)	5(2)	14(2)	15(3)
C(34)	75(4)	78(4)	27(2)	1(3)	12(2)	28(3)
C(35)	62(3)	52(3)	50(3)	-15(2)	-8(3)	21(3)
C(36)	40(2)	40(2)	37(2)	0(2)	5(2)	12(2)
C(37)	41(2)	38(2)	45(3)	-7(2)	-4(2)	9(2)
C(38)	27(2)	32(2)	49(3)	-1(2)	-4(2)	6(2)
C(39)	51(3)	33(2)	55(3)	1(2)	-14(2)	-4(2)
C(40)	78(4)	36(3)	76(3)	8(3)	-1(3)	-1(3)
C(41)	105(6)	42(3)	118(5)	5(3)	8(5)	-12(3)
C(42)	110(6)	58(4)	112(5)	31(4)	22(5)	-25(4)
C(43)	81(4)	66(4)	80(4)	13(3)	12(3)	-24(3)

C(44)	49(3)	38(2)	54(3)	3(2)	-1(2)	-7(2)
C(45)	33(2)	33(2)	36(2)	5(2)	1(2)	-4(2)
C(46)	43(3)	39(2)	40(2)	4(2)	1(2)	1(2)
C(47)	59(3)	42(3)	65(3)	14(2)	-2(3)	5(2)
C(48)	77(4)	61(4)	84(4)	31(3)	12(4)	15(3)
C(49)	80(4)	57(3)	68(3)	9(3)	1(3)	31(3)
C(50)	49(3)	57(3)	56(3)	4(2)	5(2)	19(3)
C(51)	50(3)	43(3)	39(2)	4(2)	1(2)	4(2)
C(52)	38(2)	44(3)	35(2)	12(2)	2(2)	-6(2)
C(53)	31(2)	61(3)	35(2)	4(2)	7(2)	-14(2)
C(54)	57(3)	65(3)	36(2)	-2(2)	8(2)	-7(3)
C(55)	87(4)	77(4)	39(3)	-16(3)	20(3)	-13(3)
C(56)	58(3)	59(3)	51(3)	-15(3)	23(2)	-10(3)
C(57)	93(5)	63(3)	56(3)	-12(3)	29(3)	-3(3)
C(58)	83(4)	44(3)	105(5)	-19(3)	48(4)	-2(3)
C(59)	52(3)	45(3)	72(3)	-9(3)	15(3)	5(2)
C(60)	35(2)	46(3)	61(3)	-7(2)	13(2)	-2(2)
C(61)	35(2)	44(2)	46(3)	-9(2)	10(2)	-10(2)
C(62)	31(2)	37(2)	41(2)	-2(2)	7(2)	-3(2)
N(101)	28(2)	34(2)	55(2)	2(2)	1(2)	3(1)
C(102)	39(3)	56(3)	63(3)	-4(2)	8(2)	0(2)
C(103)	40(3)	44(3)	59(3)	6(2)	-2(2)	0(2)
C(104)	45(3)	42(3)	65(3)	-4(2)	-1(2)	3(2)
C(105)	38(3)	53(3)	58(3)	-4(2)	-2(2)	-5(2)
C(00)	530(40)	38(6)	620(40)	-2(12)	-420(40)	-15(12)
Cl(1)	132(2)	107(2)	99(2)	10(1)	-12(1)	-43(2)
Cl(2)	340(6)	156(3)	136(2)	-1(2)	26(3)	107(4)
Cl(3)	260(6)	230(6)	103(3)	-14(3)	49(3)	-41(5)
Cl(4)	437(14)	547(19)	140(5)	-188(8)	-8(7)	93(13)
C(01)	231(19)	96(9)	177(14)	-52(9)	102(14)	-87(11)
S(1)	446(14)	243(8)	364(12)	-191(8)	244(11)	-158(9)
C(04)	340(30)	80(8)	188(15)	-10(9)	-149(18)	12(11)
C(05)	2000(200)	2000(180)	1380(140)	-1000(150)	-1000(150)	2000(190)

The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

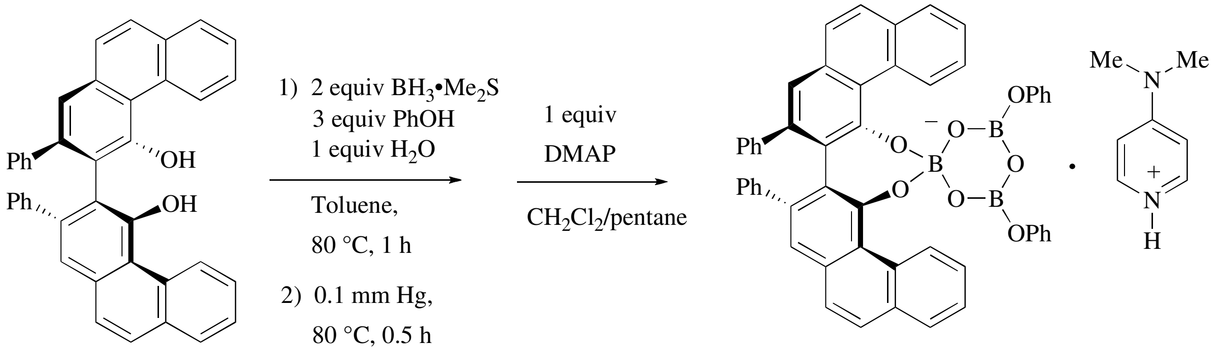
Table 5. Hydrogen coordinates (x 10^4), isotropic displacement parameters (A^2 x 10^3), and occupancies for complex **7**.

	x	y	z	U(eq)	Occ.
H(15A)	677	9569	11539	76	1
H(16A)	1277	9583	12566	92	1
H(17A)	2794	9889	12743	105	1
H(18A)	3759	10204	11891	102	1
H(19A)	3144	10257	10869	86	1
H(22A)	-1571	9521	8152	64	1
H(23A)	-2090	9011	7209	79	1
H(24A)	-1123	8309	6602	74	1
H(25A)	428	8162	6898	76	1
H(26A)	966	8649	7854	61	1
H(29A)	2624	8086	8979	59	1
H(30A)	3400	8806	8275	65	1

H(31A)	3344	8586	7200	78	1
H(32A)	2521	7633	6826	75	1
H(34A)	1618	6504	6995	72	1
H(35A)	972	5667	7636	65	1
H(37A)	561	5273	8699	50	1
H(40A)	795	4372	9495	76	1
H(41A)	1	3464	10029	106	1
H(42A)	-1117	3746	10735	112	1
H(43)	-1541	4967	10923	90	1
H(44A)	-731	5876	10407	56	1
H(47A)	1021	4852	11432	67	1
H(48A)	1939	3845	11312	89	1
H(49A)	3198	3849	10645	82	1
H(50A)	3564	4920	10085	65	1
H(51A)	2618	5915	10182	53	1
H(52A)	1228	6064	11906	47	1
H(54A)	697	6891	12722	63	1
H(55A)	83	7955	13018	81	1
H(57A)	-864	9024	12773	84	1
H(58A)	-1644	9761	12080	93	1
H(59A)	-1687	9472	11017	68	1
H(60A)	-869	8478	10633	57	1
H(10B)	-972	7550	8020	79	1
H(10C)	-703	6743	8181	79	1
H(10D)	-299	7383	8590	79	1
H(10E)	-1998	6625	9591	72	1
H(10F)	-928	6801	9550	72	1
H(10G)	-1352	6169	9140	72	1
H(10H)	-2348	7875	9353	76	1
H(10I)	-1914	8245	8750	76	1
H(10J)	-1272	8033	9324	76	1
H(10K)	-3001	6923	8703	75	1
H(10L)	-2357	6461	8255	75	1

H(10M)	-2573	7277	8091	75	1
H(00A)	207	1067	8314	477	0.914(5)
H(00B)	588	761	8963	477	0.914(5)
H(01A)	4738	4262	9329	201	0.723(6)
H(01B)	4784	4130	8594	201	0.723(6)

5. Preparation of Dimethylaminopyridinium VAPOL Boroxinate Complex 8.

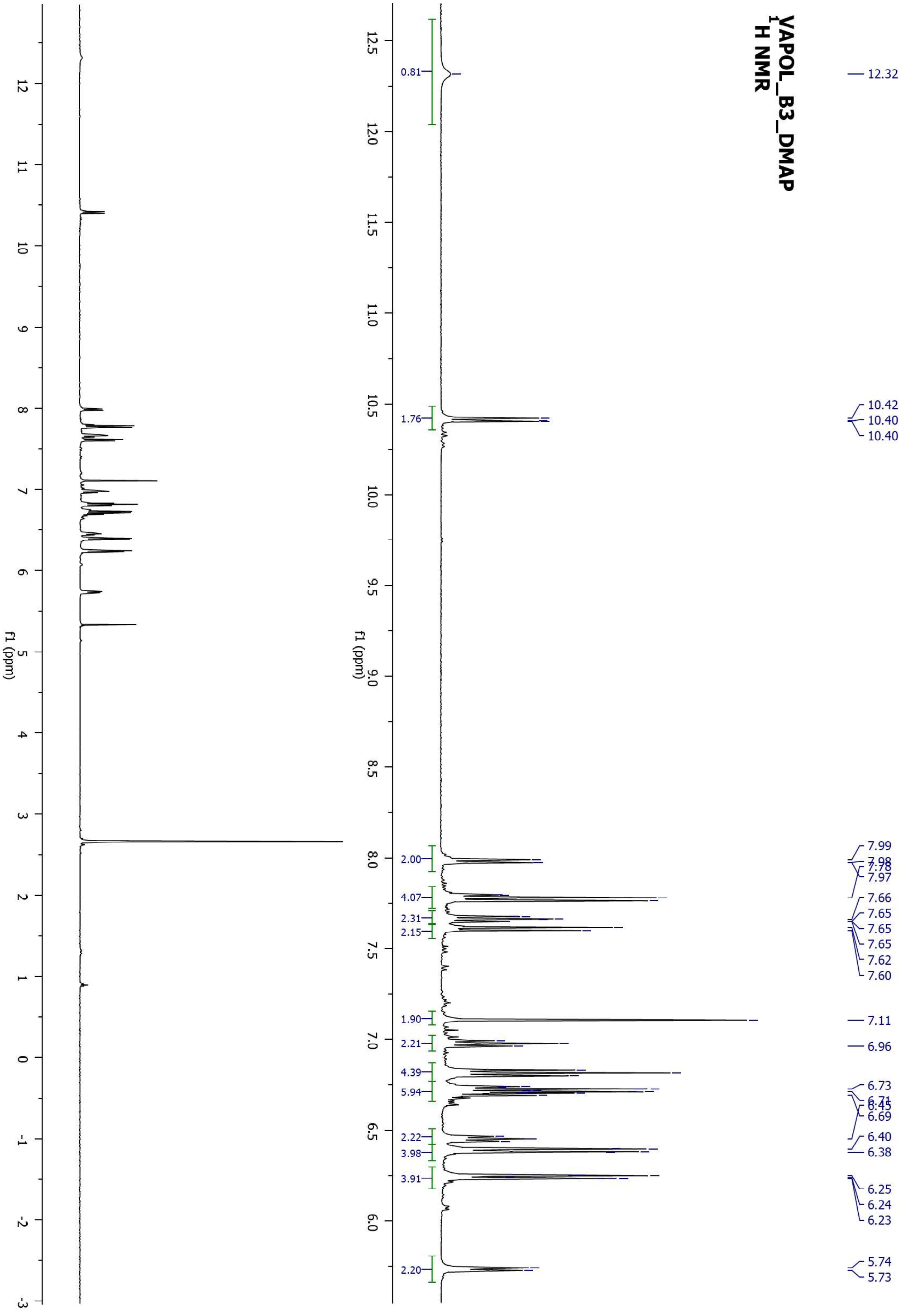


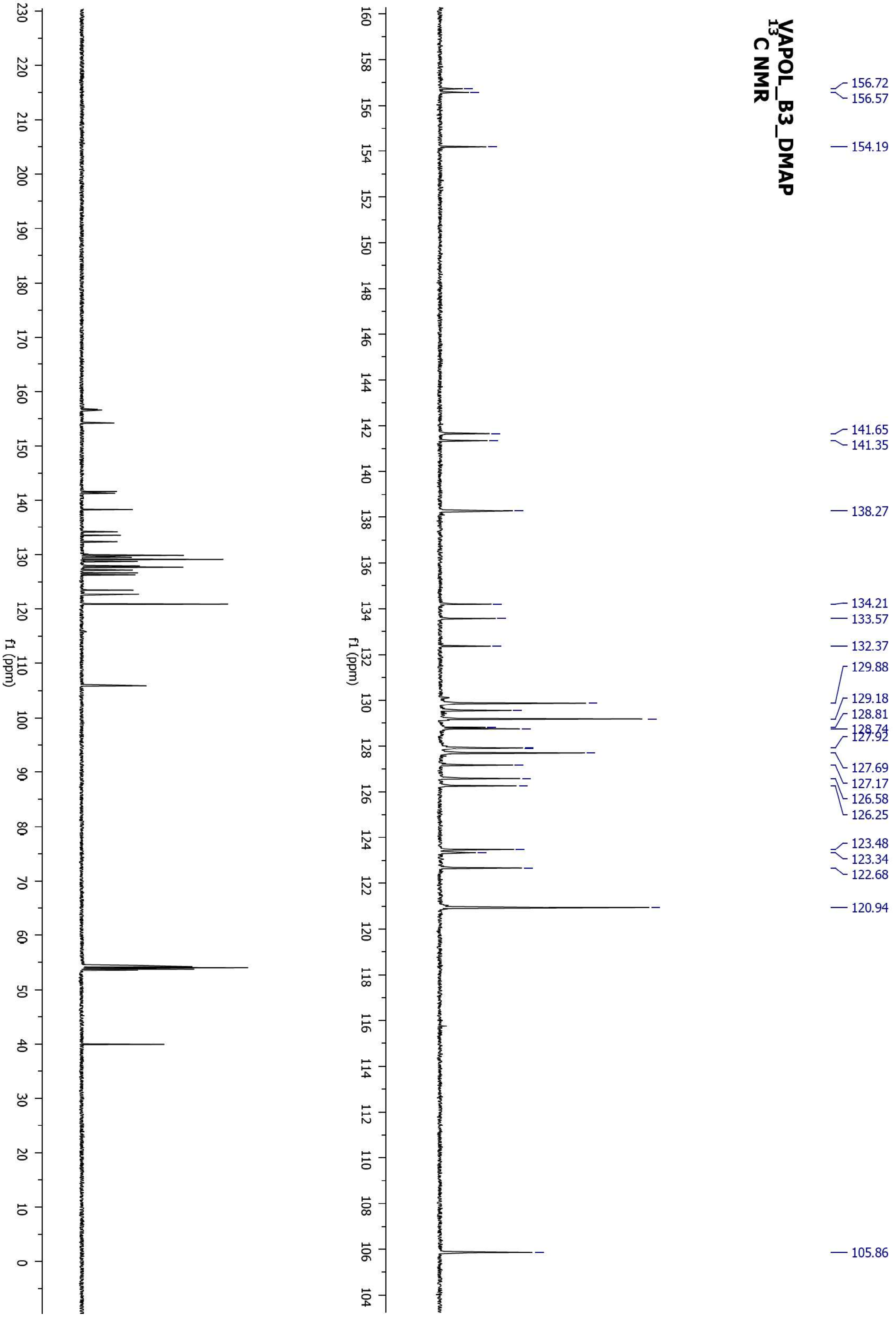
4 (*S*)-VAPOL

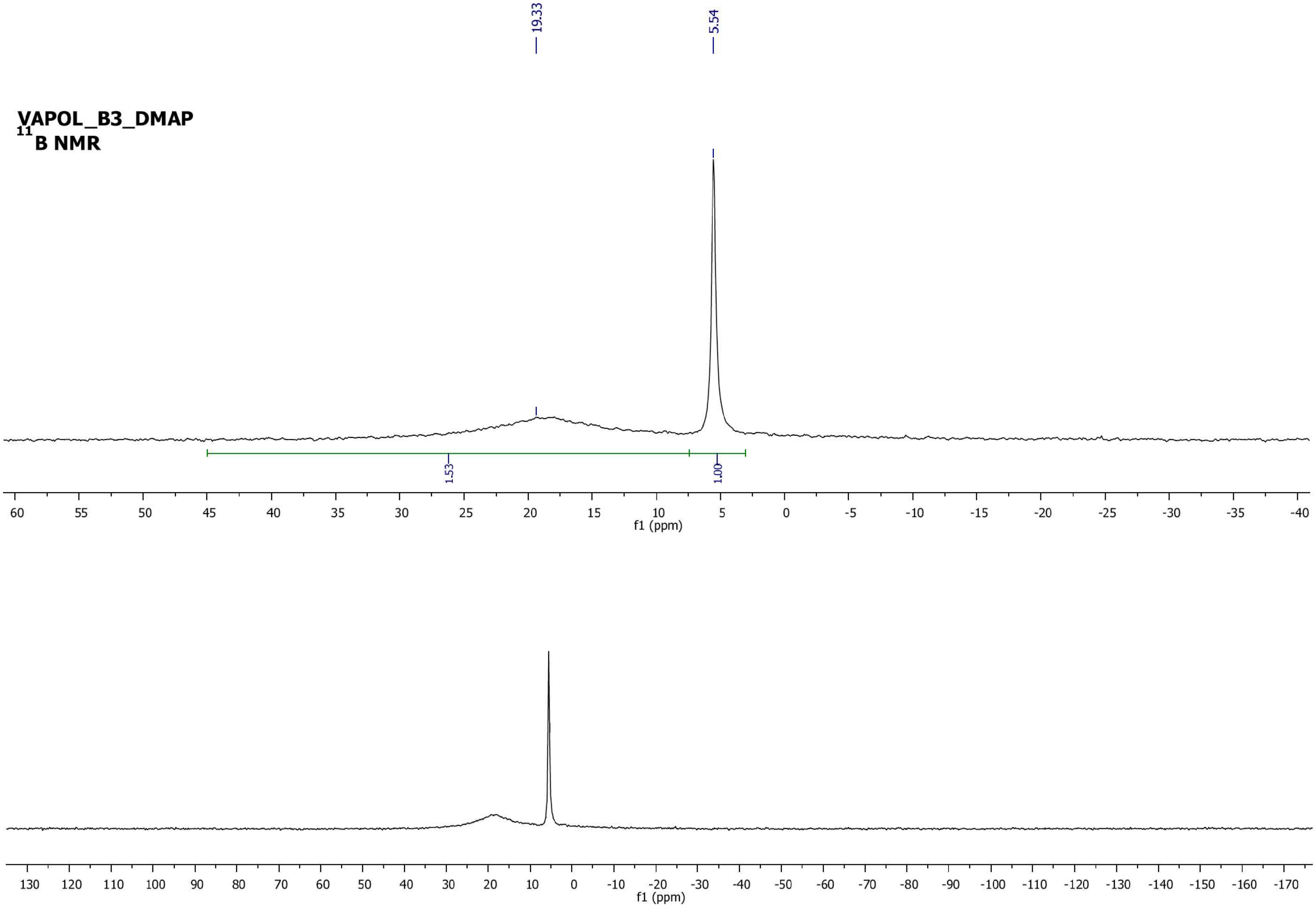
8

A flame dried 25 mL pear-shaped flask that had its 14/20 joint replaced by a high vacuum threaded T-shaped Teflon value and which contained a stir bar was cooled under argon to room temperature and charged with (*S*)-VAPOL (108 mg, 0.2 mmol), PhOH (56.4 mg, 0.6 mol), 200 μL BH_3Me_2S (0.4 mmol) and 4 mL toluene, consecutively. To the solution was added deionized water (3.6 μL, 0.2 mmol). The flask was sealed and heated to 80 °C for 1 h. The volatile materials were removed via high vacuum and left under high vacuum at 80 °C for 0.5 h yielding a mixture of mesoborate **5** and pyroborate **6** as described above. After cooling, the flask containing **5** and **6** was transferred into a glove box. To the catalyst was added dimethylaminopyridine (DMAP) (24.4 mg, 0.2 mmol) and 4 mL CH_2Cl_2. To the solution was added pentane until a permanent precipitate appeared. A small amount of CH_2Cl_2 was added to the mixture until a clear solution was obtained. The solution was then filtered through glass fiber in a pipette. The colorless solution was collected in a 20 mL vial and capped. The vial was allowed to stand in the glove box overnight. Colorless crystals appeared inside the vial. These crystals were of X-ray quality and could be subject to crystallographic study directly and the quality of the crystals rapidly deteriorated in the absence of solvent. Decanting the mother solution followed by two washes with a 1:1 mixture CH_2Cl_2/pentane afforded complex **8** (42 mg, 23% yield) as colorless crystals. Spectral data for complex **8**: ^1H NMR (CD_2Cl_2, 500 MHz) δ 2.66 (s, 6H), 5.73 (d, 2H, J = 7.0 Hz), 6.23-6.25 (m, 4H), 6.39 (d, 4H, J = 8.0 Hz), 6.45 (t, 2H, J

= 7.0 Hz), 6.70-6.74 (m, 6H), 6.82 (t, 4H, *J* = 8.0 Hz), 6.97 (t, 2H, *J* = 7.5 Hz), 7.11 (s, 2H), 7.60 (d, 2H, *J* = 9.0 Hz), 7.67 (t, 2H, *J* = 8.0 Hz), 7.76-7.78 (m, 4H), 7.98 (d, 2H, *J* = 8.0 Hz), 10.41 (d, 2H, *J* = 8.0 Hz), 12.32 (s, br, 1H); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 39.93, 105.87, 120.95, 122.69, 123.35, 123.49, 126.26, 126.59, 127.18, 127.70, 127.90, 127.93, 128.75, 128.82, 129.19, 129.58, 129.89, 132.39, 133.58, 134.23, 138.28, 141.36, 141.67, 154.20, 156.59, 156.74. ^{11}B NMR (CD_2Cl_2, 500 MHz) δ 5.54 (s, 1B), 19.31 (s, br, 2B). Mass spectrum (MALDI, negative), *m/z* (% rel intensity) 803 $M^+ - C_7H_{11}N_2$ (100), 727 (10), 407 (8); HRMS *m/z* calcd for $C_{52}H_{34}B_3O_7$ 803.2584; found 803.2554. The ^{1}H, ^{11}B, ^{13}C NMR spectra are given below and are labeled as VAPOL_B3_DMAP. The x-ray structural data is also given below.


VAPOL_B3_DMAP
1H NMR
12.32
10.42
10.40
10.40
7.99
7.98
7.78
7.97
7.66
7.65
7.65
7.65
7.62
7.60
7.11
6.96
6.73
6.71
6.45
6.69
6.40
6.38
6.25
6.24
6.23
5.74
5.73
0.81
1.76
2.00
4.07
2.31
2.15
1.90
2.21
4.39
5.94
2.22
3.98
3.91
2.20
12.5
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
f1 (ppm)
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)


VAPOL_B3_DMAP
^{13}C NMR
156.72
156.57
154.19
141.65
141.35
138.27
134.21
133.57
132.37
129.88
129.18
128.81
128.74
127.92
127.69
127.17
126.58
126.25
123.48
123.34
122.68
120.94
105.86
f1 (ppm)
f1 (ppm)
160
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
110
108
106
104
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


VAPOL_B3_DMAP
^{11}B NMR
19.33
5.54
1.53
1.00
60 55 50 45 40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -40
f1 (ppm)
130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170
f1 (ppm)

6. X-Ray Structure Determination of Dimethylpyridinium Boroxinate Complex 8.

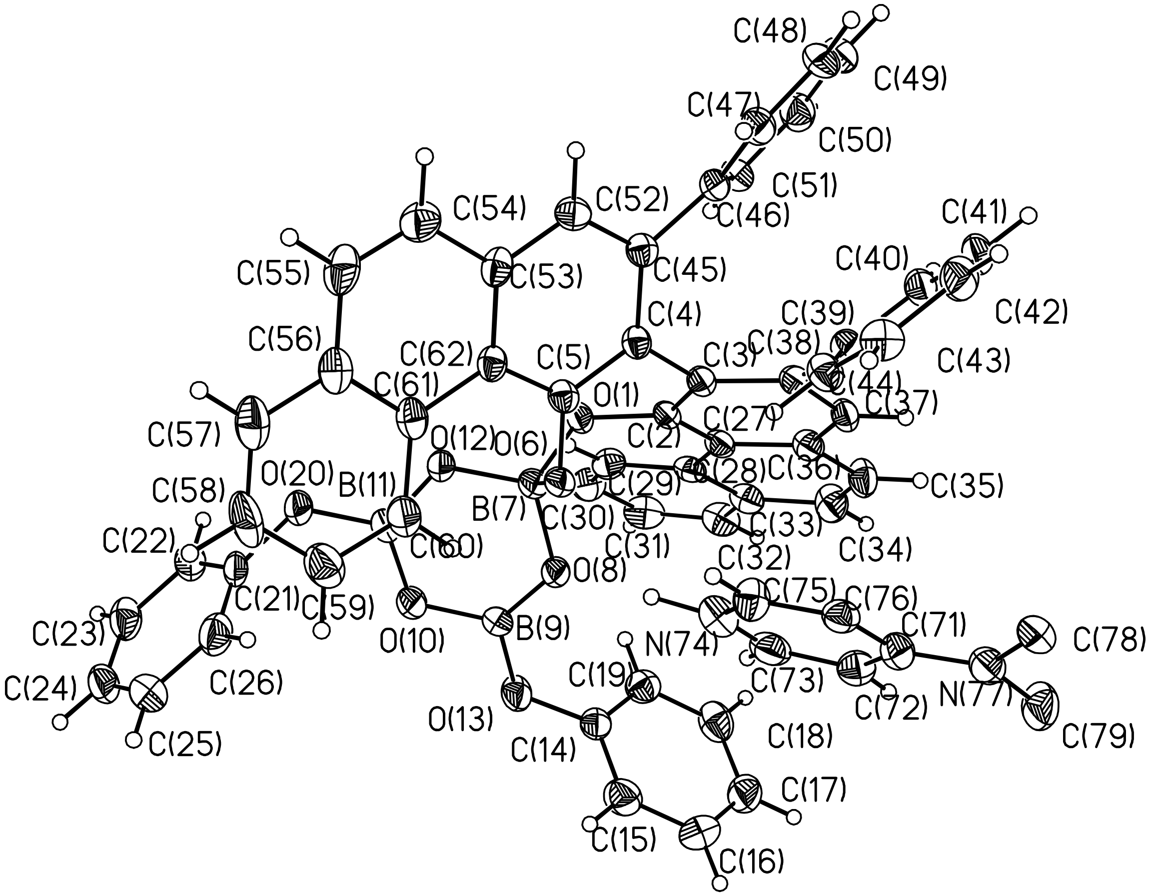


Figure 3. ORTEP Drawing of complex 8.

Table 1. Crystal data and structure refinement for complex **8**.

Identification code	wf090506
Empirical formula	C60 H47 B3 Cl2 N2 O7
Formula weight	1011.33
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system	Ortho.
Space group	P2(1)2(1)2(1)
Unit cell dimensions	a = 12.865(3) A
	b = 17.944(4) A
	c = 21.546(4) A
	alpha = 90 deg.
	beta = 90 deg.
	gamma = 90 deg.
Volume	4973.9(17) A^3
Z	4
Density (calculated)	1.351 Mg/m^3
Absorption coefficient	0.190 mm^-1
F(000)	2104
Crystal size	0.4 x 0.3 x 0.3 mm
Theta range for data collection	1.48 to 28.28 deg.
Index ranges	-16<=h<=17, -23<=k<=23, -28<=l<=28
Reflections collected / unique	59972 / 12068 [R(int) = 0.0573]
Completeness to theta = 28.28	99.1%
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12068 / 0 / 671
Goodness-of-fit on F^2	0.941
Final R indices [I>2sigma(I)]	R1 = 0.0497, wR2 = 0.1253
R indices (all data)	R1 = 0.0859, wR2 = 0.1455
Absolute structure parameter	-0.03(7)
Largest diff. peak and hole	0.524 and -0.400 e.A^-3

Table 2. Atomic coordinates (x 10^4), equivalent isotropic displacement parameters (A^2 x 10^3), and occupancies for complex **8**.

	x	y	z	U(eq)	Occ.
C(00)	5853(3)	6936(2)	9191(2)	55(1)	1
Cl(1)	4750(1)	7200(1)	8776(1)	76(1)	1
Cl(2)	6917(1)	7527(1)	9027(1)	66(1)	1
O(1)	2002(1)	1913(1)	10275(1)	23(1)	1
C(2)	1747(2)	2548(1)	10592(1)	22(1)	1
C(3)	1241(2)	3118(1)	10268(1)	23(1)	1
C(4)	1094(2)	3013(1)	9582(1)	22(1)	1
C(5)	606(2)	2361(1)	9372(1)	22(1)	1
O(6)	281(1)	1861(1)	9814(1)	24(1)	1
B(7)	1135(2)	1423(2)	10107(1)	24(1)	1
O(8)	662(1)	1077(1)	10671(1)	25(1)	1
B(9)	705(2)	336(2)	10770(1)	25(1)	1
O(10)	1024(2)	-164(1)	10320(1)	30(1)	1
B(11)	1387(2)	130(2)	9767(1)	27(1)	1
O(12)	1533(1)	860(1)	9682(1)	26(1)	1
O(13)	446(2)	-7(1)	11322(1)	32(1)	1
C(14)	170(2)	350(1)	11868(1)	27(1)	1
C(15)	-856(2)	331(2)	12050(1)	38(1)	1
C(16)	-1135(3)	634(2)	12624(2)	47(1)	1
C(17)	-390(3)	945(2)	13003(1)	42(1)	1
C(18)	634(3)	965(2)	12812(1)	38(1)	1
C(19)	919(2)	671(2)	12244(1)	32(1)	1
O(20)	1621(2)	-349(1)	9286(1)	39(1)	1
C(21)	1342(2)	-1093(1)	9281(1)	30(1)	1
C(22)	2115(3)	-1628(2)	9330(1)	35(1)	1
C(23)	1844(3)	-2379(2)	9291(1)	38(1)	1
C(24)	827(3)	-2592(2)	9201(1)	40(1)	1

C(25)	64(3)	-2050(2)	9149(2)	43(1)	1
C(26)	317(3)	-1297(2)	9185(1)	38(1)	1
C(27)	2014(2)	2613(1)	11238(1)	23(1)	1
C(28)	2627(2)	2074(1)	11594(1)	24(1)	1
C(29)	3116(2)	1441(1)	11339(1)	28(1)	1
C(30)	3725(2)	965(2)	11697(1)	34(1)	1
C(31)	3851(2)	1090(2)	12329(1)	36(1)	1
C(32)	3379(2)	1701(2)	12596(1)	35(1)	1
C(33)	2776(2)	2196(1)	12244(1)	29(1)	1
C(34)	2338(2)	2843(2)	12535(1)	36(1)	1
C(35)	1811(2)	3356(2)	12205(1)	33(1)	1
C(36)	1644(2)	3264(1)	11543(1)	26(1)	1
C(37)	1118(2)	3818(1)	11222(1)	26(1)	1
C(38)	922(2)	3774(1)	10589(1)	24(1)	1
C(39)	368(2)	4419(1)	10304(1)	25(1)	1
C(40)	715(2)	5144(1)	10432(1)	30(1)	1
C(41)	187(2)	5762(2)	10205(1)	35(1)	1
C(42)	-690(2)	5668(2)	9841(1)	36(1)	1
C(43)	-1051(2)	4956(2)	9719(1)	34(1)	1
C(44)	-524(2)	4332(2)	9942(1)	29(1)	1
C(45)	1478(2)	3532(1)	9138(1)	23(1)	1
C(46)	2031(2)	4241(1)	9294(1)	24(1)	1
C(47)	1751(2)	4898(1)	8982(1)	30(1)	1
C(48)	2285(2)	5554(2)	9080(1)	36(1)	1
C(49)	3112(2)	5574(2)	9491(2)	38(1)	1
C(50)	3399(2)	4930(2)	9803(1)	34(1)	1
C(51)	2868(2)	4271(1)	9705(1)	28(1)	1
C(52)	1388(2)	3369(1)	8515(1)	26(1)	1
C(53)	904(2)	2721(1)	8299(1)	26(1)	1
C(54)	893(2)	2570(2)	7642(1)	34(1)	1
C(55)	481(2)	1949(2)	7416(1)	38(1)	1
C(56)	-27(2)	1423(2)	7815(1)	32(1)	1
C(57)	-502(2)	783(2)	7561(2)	41(1)	1

C(58)	-1049(3)	294(2)	7919(2)	45(1)	1
C(59)	-1152(2)	436(2)	8553(2)	40(1)	1
C(60)	-678(2)	1047(2)	8823(1)	31(1)	1
C(61)	-75(2)	1552(1)	8469(1)	27(1)	1
C(62)	455(2)	2204(1)	8724(1)	23(1)	1
C(71)	3321(2)	1687(1)	8193(1)	30(1)	1
C(73)	4426(2)	2761(2)	8231(2)	39(1)	1
C(72)	3942(2)	2224(2)	7890(1)	36(1)	1
N(74)	4303(2)	2812(1)	8844(1)	36(1)	1
C(75)	3692(2)	2317(2)	9150(1)	34(1)	1
C(76)	3206(2)	1761(1)	8841(1)	29(1)	1
N(77)	2872(2)	1126(1)	7877(1)	34(1)	1
C(78)	2356(3)	516(2)	8209(2)	40(1)	1
C(79)	2939(3)	1083(2)	7201(1)	47(1)	1

U(eq) is defined as one third of the trace of the orthogonalized
Uij tensor.

Table 3. Bond lengths [A] and angles [deg] for complex **8**.

C(00)-Cl(1)	1.744(4)
C(00)-Cl(2)	1.766(4)
O(1)-C(2)	1.370(3)
O(1)-B(7)	1.466(3)

C(2)-C(3)	1.400(3)
C(2)-C(27)	1.438(3)
C(3)-C(38)	1.425(3)
C(3)-C(4)	1.501(3)
C(4)-C(5)	1.404(3)
C(4)-C(45)	1.424(3)
C(5)-O(6)	1.372(3)
C(5)-C(62)	1.437(3)
O(6)-B(7)	1.492(3)
B(7)-O(12)	1.455(3)
B(7)-O(8)	1.493(3)
O(8)-B(9)	1.348(3)
B(9)-O(13)	1.379(3)
B(9)-O(10)	1.384(3)
O(10)-B(11)	1.384(4)
B(11)-O(12)	1.336(3)
B(11)-O(20)	1.379(3)
O(13)-C(14)	1.386(3)
C(14)-C(15)	1.377(4)
C(14)-C(19)	1.384(4)
C(15)-C(16)	1.398(4)
C(16)-C(17)	1.378(5)
C(17)-C(18)	1.380(5)
C(18)-C(19)	1.383(4)
O(20)-C(21)	1.382(3)
C(21)-C(26)	1.384(4)
C(21)-C(22)	1.387(4)
C(22)-C(23)	1.394(4)
C(23)-C(24)	1.376(5)
C(24)-C(25)	1.386(5)
C(25)-C(26)	1.393(4)
C(27)-C(36)	1.422(3)
C(27)-C(28)	1.464(3)

C(28)-C(29)	1.409(4)
C(28)-C(33)	1.431(4)
C(29)-C(30)	1.392(4)
C(30)-C(31)	1.389(4)
C(31)-C(32)	1.380(4)
C(32)-C(33)	1.403(4)
C(33)-C(34)	1.435(4)
C(34)-C(35)	1.346(4)
C(35)-C(36)	1.451(4)
C(36)-C(37)	1.387(4)
C(37)-C(38)	1.389(4)
C(38)-C(39)	1.492(3)
C(39)-C(44)	1.396(4)
C(39)-C(40)	1.403(4)
C(40)-C(41)	1.389(4)
C(41)-C(42)	1.384(4)
C(42)-C(43)	1.385(4)
C(43)-C(44)	1.395(4)
C(45)-C(52)	1.377(4)
C(45)-C(46)	1.498(3)
C(46)-C(51)	1.395(4)
C(46)-C(47)	1.405(3)
C(47)-C(48)	1.379(4)
C(48)-C(49)	1.386(4)
C(49)-C(50)	1.386(4)
C(50)-C(51)	1.382(4)
C(52)-C(53)	1.398(4)
C(53)-C(62)	1.427(4)
C(53)-C(54)	1.440(4)
C(54)-C(55)	1.327(4)
C(55)-C(56)	1.435(4)
C(56)-C(57)	1.412(4)
C(56)-C(61)	1.430(4)

C(57)-C(58)	1.364(5)
C(58)-C(59)	1.396(5)
C(59)-C(60)	1.383(4)
C(60)-C(61)	1.415(4)
C(61)-C(62)	1.463(3)
C(71)-N(77)	1.346(4)
C(71)-C(76)	1.411(4)
C(71)-C(72)	1.412(4)
C(73)-N(74)	1.333(4)
C(73)-C(72)	1.362(4)
N(74)-C(75)	1.357(4)
C(75)-C(76)	1.352(4)
N(77)-C(79)	1.461(4)
N(77)-C(78)	1.465(4)
Cl(1)-C(00)-Cl(2)	111.37(19)
C(2)-O(1)-B(7)	116.13(19)
O(1)-C(2)-C(3)	118.1(2)
O(1)-C(2)-C(27)	119.5(2)
C(3)-C(2)-C(27)	122.4(2)
C(2)-C(3)-C(38)	119.6(2)
C(2)-C(3)-C(4)	117.3(2)
C(38)-C(3)-C(4)	123.0(2)
C(5)-C(4)-C(45)	118.9(2)
C(5)-C(4)-C(3)	118.6(2)
C(45)-C(4)-C(3)	122.4(2)
O(6)-C(5)-C(4)	117.1(2)
O(6)-C(5)-C(62)	120.4(2)
C(4)-C(5)-C(62)	122.5(2)
C(5)-O(6)-B(7)	114.49(19)
O(12)-B(7)-O(1)	107.7(2)
O(12)-B(7)-O(6)	111.0(2)
O(1)-B(7)-O(6)	110.39(19)
O(12)-B(7)-O(8)	111.5(2)

O(1)-B(7)-O(8)	111.0(2)
O(6)-B(7)-O(8)	105.3(2)
B(9)-O(8)-B(7)	121.5(2)
O(8)-B(9)-O(13)	124.6(2)
O(8)-B(9)-O(10)	122.6(2)
O(13)-B(9)-O(10)	112.7(2)
B(9)-O(10)-B(11)	117.2(2)
O(12)-B(11)-O(20)	118.5(3)
O(12)-B(11)-O(10)	122.6(2)
O(20)-B(11)-O(10)	118.9(2)
B(11)-O(12)-B(7)	123.0(2)
B(9)-O(13)-C(14)	126.0(2)
C(15)-C(14)-C(19)	120.8(3)
C(15)-C(14)-O(13)	118.4(2)
C(19)-C(14)-O(13)	120.7(3)
C(14)-C(15)-C(16)	119.2(3)
C(17)-C(16)-C(15)	120.3(3)
C(16)-C(17)-C(18)	119.8(3)
C(17)-C(18)-C(19)	120.5(3)
C(18)-C(19)-C(14)	119.5(3)
B(11)-O(20)-C(21)	123.5(2)
O(20)-C(21)-C(26)	120.3(3)
O(20)-C(21)-C(22)	118.8(3)
C(26)-C(21)-C(22)	120.8(3)
C(21)-C(22)-C(23)	119.0(3)
C(24)-C(23)-C(22)	121.0(3)
C(23)-C(24)-C(25)	119.3(3)
C(24)-C(25)-C(26)	120.7(3)
C(21)-C(26)-C(25)	119.2(3)
C(36)-C(27)-C(2)	115.7(2)
C(36)-C(27)-C(28)	118.8(2)
C(29)-C(28)-C(33)	116.4(2)
C(29)-C(28)-C(27)	124.7(2)

C(33)-C(28)-C(27)	118.9(2)
C(30)-C(29)-C(28)	122.0(2)
C(31)-C(30)-C(29)	120.7(3)
C(32)-C(31)-C(30)	119.0(3)
C(31)-C(32)-C(33)	121.4(3)
C(32)-C(33)-C(28)	120.4(3)
C(32)-C(33)-C(34)	119.6(2)
C(28)-C(33)-C(34)	120.0(2)
C(35)-C(34)-C(33)	121.3(2)
C(34)-C(35)-C(36)	121.1(3)
C(37)-C(36)-C(27)	121.4(2)
C(37)-C(36)-C(35)	118.8(2)
C(27)-C(36)-C(35)	119.8(2)
C(36)-C(37)-C(38)	122.6(2)
C(37)-C(38)-C(3)	118.1(2)
C(37)-C(38)-C(39)	116.6(2)
C(3)-C(38)-C(39)	125.3(2)
C(44)-C(39)-C(40)	118.4(2)
C(44)-C(39)-C(38)	122.4(2)
C(40)-C(39)-C(38)	119.1(2)
C(41)-C(40)-C(39)	121.0(3)
C(42)-C(41)-C(40)	120.1(3)
C(43)-C(42)-C(41)	119.6(3)
C(42)-C(43)-C(44)	120.8(3)
C(43)-C(44)-C(39)	120.1(2)
C(52)-C(45)-C(4)	119.2(2)
C(52)-C(45)-C(46)	116.1(2)
C(4)-C(45)-C(46)	124.7(2)
C(51)-C(46)-C(47)	118.1(2)
C(51)-C(46)-C(45)	122.8(2)
C(47)-C(46)-C(45)	118.9(2)
C(48)-C(47)-C(46)	121.0(3)
C(47)-C(48)-C(49)	120.1(3)

C(48)-C(49)-C(50)	119.5(3)
C(51)-C(50)-C(49)	120.6(3)
C(50)-C(51)-C(46)	120.7(2)
C(45)-C(52)-C(53)	122.6(2)
C(52)-C(53)-C(62)	120.4(2)
C(52)-C(53)-C(54)	119.3(2)
C(62)-C(53)-C(54)	120.3(2)
C(55)-C(54)-C(53)	121.6(3)
C(54)-C(55)-C(56)	121.0(3)
C(57)-C(56)-C(61)	119.7(3)
C(57)-C(56)-C(55)	120.1(3)
C(61)-C(56)-C(55)	120.3(2)
C(58)-C(57)-C(56)	121.8(3)
C(57)-C(58)-C(59)	119.0(3)
C(60)-C(59)-C(58)	120.9(3)
C(59)-C(60)-C(61)	121.5(3)
C(60)-C(61)-C(56)	116.9(2)
C(60)-C(61)-C(62)	124.4(2)
C(56)-C(61)-C(62)	118.7(2)
C(53)-C(62)-C(5)	116.3(2)
C(53)-C(62)-C(61)	117.9(2)
C(5)-C(62)-C(61)	125.8(2)
N(77)-C(71)-C(76)	121.8(2)
N(77)-C(71)-C(72)	121.4(3)
C(76)-C(71)-C(72)	116.8(3)
N(74)-C(73)-C(72)	122.0(3)
C(73)-C(72)-C(71)	119.5(3)
C(73)-N(74)-C(75)	120.3(3)
C(76)-C(75)-N(74)	120.8(3)
C(75)-C(76)-C(71)	120.6(3)
C(71)-N(77)-C(79)	121.2(2)
C(71)-N(77)-C(78)	120.4(2)
C(79)-N(77)-C(78)	118.3(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters (A^2 x 10^3) for complex **8**.

	U11	U22	U33	U23	U13	U12
C(00)	81(3)	51(2)	34(2)	8(2)	1(2)	2(2)
Cl(1)	66(1)	79(1)	82(1)	35(1)	-4(1)	-6(1)
Cl(2)	67(1)	74(1)	57(1)	-6(1)	0(1)	-2(1)
O(1)	29(1)	17(1)	23(1)	-1(1)	0(1)	0(1)
C(2)	26(1)	17(1)	22(1)	-1(1)	1(1)	-4(1)
C(3)	27(1)	19(1)	22(1)	-1(1)	0(1)	-2(1)
C(4)	24(1)	19(1)	23(1)	-1(1)	-1(1)	2(1)
C(5)	24(1)	19(1)	23(1)	1(1)	-2(1)	3(1)
O(6)	31(1)	20(1)	21(1)	1(1)	2(1)	-3(1)
B(7)	31(2)	18(1)	23(1)	2(1)	2(1)	0(1)

O(8)	33(1)	20(1)	22(1)	0(1)	4(1)	0(1)
B(9)	27(1)	20(1)	27(2)	1(1)	2(1)	-2(1)
O(10)	41(1)	18(1)	31(1)	1(1)	7(1)	0(1)
B(11)	32(2)	21(1)	29(2)	-3(1)	1(1)	-2(1)
O(12)	36(1)	20(1)	23(1)	-2(1)	6(1)	0(1)
O(13)	52(1)	21(1)	25(1)	2(1)	4(1)	1(1)
C(14)	38(2)	22(1)	22(1)	4(1)	3(1)	0(1)
C(15)	36(2)	40(2)	38(2)	-3(1)	-3(1)	-9(1)
C(16)	43(2)	50(2)	47(2)	-3(2)	17(2)	-7(2)
C(17)	62(2)	36(2)	29(2)	-2(1)	10(2)	-2(2)
C(18)	49(2)	34(2)	31(2)	-3(1)	-9(1)	-2(1)
C(19)	33(1)	30(1)	32(2)	5(1)	1(1)	2(1)
O(20)	62(1)	20(1)	34(1)	-5(1)	18(1)	-3(1)
C(21)	49(2)	19(1)	23(1)	-6(1)	8(1)	-1(1)
C(22)	48(2)	29(1)	30(2)	-4(1)	1(1)	0(1)
C(23)	56(2)	27(1)	31(2)	-2(1)	-2(1)	7(1)
C(24)	62(2)	23(1)	35(2)	-4(1)	6(2)	-6(1)
C(25)	43(2)	40(2)	46(2)	-7(1)	5(1)	-11(1)
C(26)	44(2)	33(2)	38(2)	-6(1)	6(1)	7(1)
C(27)	25(1)	21(1)	23(1)	0(1)	-1(1)	-6(1)
C(28)	27(1)	23(1)	23(1)	5(1)	-1(1)	-6(1)
C(29)	29(1)	31(1)	24(1)	3(1)	-1(1)	0(1)
C(30)	32(2)	32(1)	37(2)	4(1)	2(1)	4(1)
C(31)	30(1)	40(2)	37(2)	12(1)	-6(1)	1(1)
C(32)	39(2)	37(2)	28(1)	6(1)	-8(1)	-6(1)
C(33)	31(1)	27(1)	29(1)	4(1)	-3(1)	-5(1)
C(34)	51(2)	35(2)	21(1)	-3(1)	-5(1)	-2(1)
C(35)	48(2)	26(1)	26(1)	-5(1)	-2(1)	2(1)
C(36)	32(1)	24(1)	21(1)	0(1)	-3(1)	-4(1)
C(37)	35(1)	19(1)	24(1)	-4(1)	1(1)	-3(1)
C(38)	26(1)	21(1)	23(1)	0(1)	0(1)	-4(1)
C(39)	32(1)	22(1)	22(1)	0(1)	5(1)	1(1)
C(40)	40(2)	24(1)	27(1)	-3(1)	1(1)	-1(1)

C(41)	51(2)	20(1)	34(2)	-2(1)	6(1)	4(1)
C(42)	44(2)	28(1)	37(2)	5(1)	3(1)	12(1)
C(43)	31(1)	36(2)	34(2)	4(1)	-3(1)	1(1)
C(44)	34(1)	24(1)	29(1)	1(1)	-3(1)	0(1)
C(45)	24(1)	22(1)	24(1)	1(1)	-2(1)	2(1)
C(46)	28(1)	18(1)	25(1)	1(1)	3(1)	2(1)
C(47)	36(2)	25(1)	31(2)	2(1)	2(1)	5(1)
C(48)	45(2)	20(1)	44(2)	6(1)	10(1)	2(1)
C(49)	41(2)	25(1)	49(2)	-3(1)	11(1)	-6(1)
C(50)	30(1)	32(1)	40(2)	-6(1)	1(1)	-2(1)
C(51)	31(1)	22(1)	30(1)	1(1)	1(1)	-1(1)
C(52)	32(1)	24(1)	24(1)	5(1)	0(1)	1(1)
C(53)	32(1)	26(1)	19(1)	-1(1)	-2(1)	8(1)
C(54)	46(2)	35(2)	23(1)	5(1)	-1(1)	3(1)
C(55)	50(2)	43(2)	20(1)	-7(1)	-9(1)	6(1)
C(56)	33(1)	31(1)	31(1)	-7(1)	-7(1)	6(1)
C(57)	42(2)	40(2)	39(2)	-17(1)	-10(1)	2(1)
C(58)	42(2)	38(2)	56(2)	-24(2)	-13(2)	-4(1)
C(59)	32(2)	34(2)	52(2)	-8(1)	-3(1)	-3(1)
C(60)	30(1)	28(1)	35(2)	-6(1)	-1(1)	1(1)
C(61)	26(1)	25(1)	31(1)	-6(1)	-5(1)	5(1)
C(62)	26(1)	21(1)	22(1)	-1(1)	-1(1)	5(1)
C(71)	31(1)	26(1)	32(1)	0(1)	-1(1)	2(1)
C(73)	40(2)	28(1)	48(2)	8(1)	5(1)	-6(1)
C(72)	43(2)	33(1)	30(2)	4(1)	5(1)	-3(1)
N(74)	38(1)	30(1)	41(1)	1(1)	-7(1)	-1(1)
C(75)	38(2)	33(1)	31(2)	0(1)	-3(1)	6(1)
C(76)	31(1)	26(1)	31(1)	5(1)	2(1)	-2(1)
N(77)	44(1)	29(1)	29(1)	-1(1)	3(1)	-4(1)
C(78)	47(2)	29(2)	44(2)	-5(1)	9(1)	-10(1)
C(79)	69(2)	42(2)	31(2)	-9(1)	4(2)	1(2)

The anisotropic displacement factor exponent takes the form:

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

Table 5. Hydrogen coordinates (x 10^4), isotropic displacement parameters (A^2 x 10^3), and occupancies for complex **8**.

	x	y	z	U(eq)	Occ.
H(00A)	6035	6427	9085	66	1
H(00B)	5703	6953	9632	66	1
H(15A)	-1357	118	11794	46	1
H(16A)	-1826	625	12750	56	1
H(17A)	-577	1142	13387	51	1
H(18A)	1135	1177	13068	46	1
H(19A)	1608	689	12115	38	1
H(22A)	2804	-1488	9387	42	1
H(23A)	2357	-2741	9327	46	1
H(24A)	654	-3094	9175	48	1
H(25A)	-624	-2191	9090	51	1
H(26A)	-196	-935	9145	46	1
H(29A)	3030	1339	10919	34	1

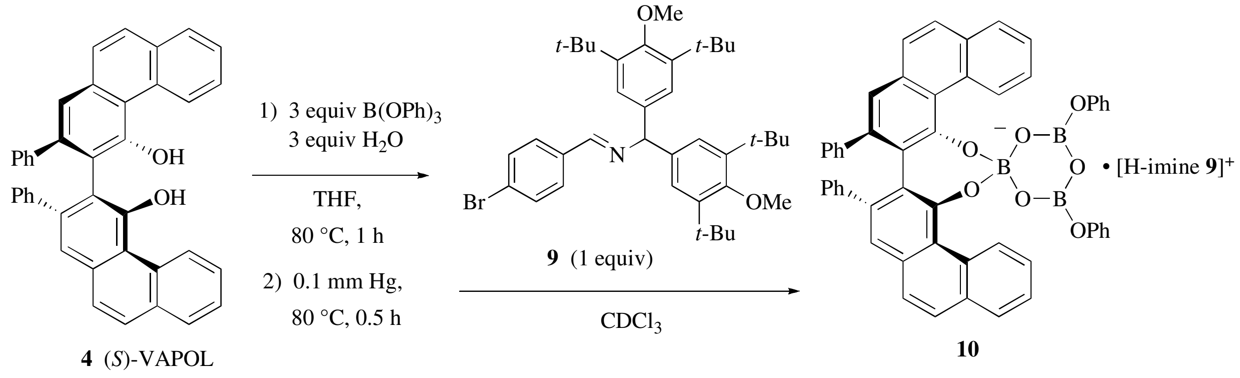
H(30A)	4050	560	11511	40	1
H(31A)	4248	766	12568	43	1
H(32A)	3464	1787	13019	42	1
H(34A)	2420	2910	12961	43	1
H(35A)	1550	3776	12404	40	1
H(37A)	887	4234	11438	31	1
H(40A)	1307	5212	10674	36	1
H(41A)	424	6239	10297	42	1
H(42A)	-1034	6080	9680	44	1
H(43A)	-1652	4893	9485	41	1
H(44A)	-767	3856	9849	35	1
H(47A)	1196	4891	8705	36	1
H(48A)	2089	5985	8869	43	1
H(49A)	3473	6016	9558	46	1
H(50A)	3953	4942	10079	41	1
H(51A)	3070	3843	9917	33	1
H(52A)	1660	3703	8228	32	1
H(54A)	1182	2916	7371	41	1
H(55A)	523	1854	6992	45	1
H(57A)	-440	692	7137	49	1
H(58A)	-1348	-128	7743	54	1
H(59A)	-1546	115	8797	47	1
H(60A)	-757	1128	9246	37	1
H(73A)	4855	3102	8031	46	1
H(72A)	4021	2212	7461	43	1
H(74)	4750(30)	3220(20)	9110(20)	84(13)	1
H(75A)	3607	2360	9577	41	1
H(76A)	2793	1425	9058	35	1
H(78A)	2370	615	8646	60	1
H(78B)	2712	57	8125	60	1
H(78C)	1648	478	8071	60	1
H(79A)	3289	1517	7046	71	1
H(79B)	2252	1059	7029	71	1

H(79C)	3322	645	7085	71	1

Table 6. Hydrogen-bonds [A and deg.] for complex **8**.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N74-H74…O8	1.091	1.787	2.850	163.58
N74-H74…O6	1.091	2.426	3.207	127.35

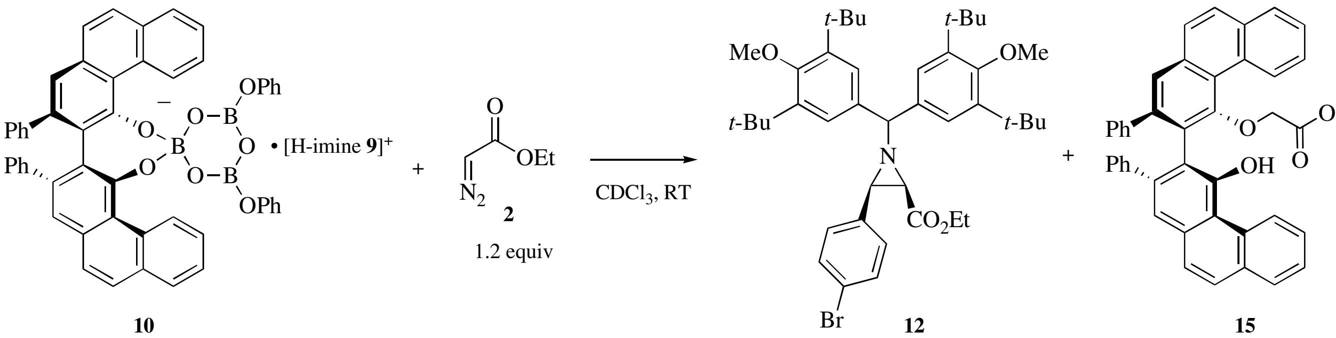
7. Preparation of the VAPOL Boroxinate Imine Complex 10 by using stoichiometric $B(OPh)_3$ and its reaction with ethyl diazoacetate (EDA).



A flame dried 25 mL pear-shaped flask that had its 14/20 joint replaced by a high vacuum threaded T-shaped Teflon value and which contained a stir bar was cooled under argon to room temperature and charged with (*S*)-VAPOL (54 mg, 0.1 mmol), commercial $B(OPh)_3$ (87 mg, 0.3 mmol), and 4 mL THF. To this solution was added deionized water (5.4 μL, 0.3 mmol). The flask was sealed and heated to 80 °C for 1 h. The volatile materials were removed via high vacuum at 80 °C for 0.5 h yielding a mixture of VAPOL **4**, mesoborate **5** and pyroborate **6** in a ratio of 0.9:0.09:1.0. After cooling, the flask containing the mixture of **4**, **5** and **6** was moved into a glove box. To the mixture of **4**, **5** and **6** was added imine **9**[3] (64 mg, 0.1 mmol) followed by

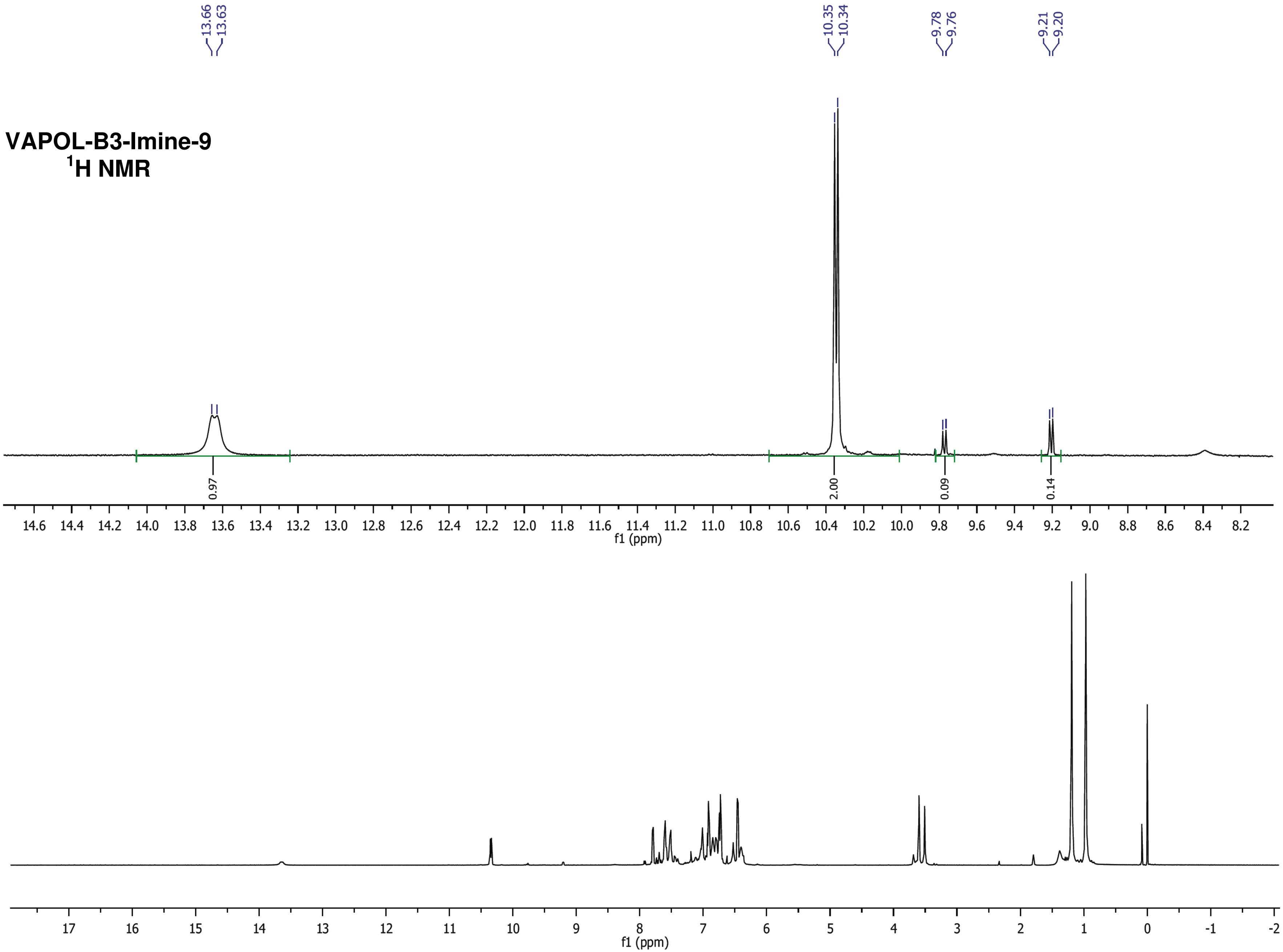
~0.75 mL of $CDCl_3$. A red solution formed immediately. The ^1H NMR spectrum of the solution indicated the clean formation of **10** containing 4% VAPOL **4**, <1% of **5**, and 6% of **6**. The ^1H and ^{11}B NMR spectra are given below and are labeled as VAPOL_B3_Imine _**9**.

It should be noted that the ratio of **10**, VAPOL, **5** and **6** may vary significantly depending on the nature and amount of hydrolyzed boron species present in commercial $B(OPh)_3$. Depending on the particular batch of $B(OPh)_3$, it may be necessary to adjust the amount of $B(OPh)_3$ or the amount of water or the amount of the imine to maximize the percentage of **10** present in the mixture. As an example, see Section 8 below.

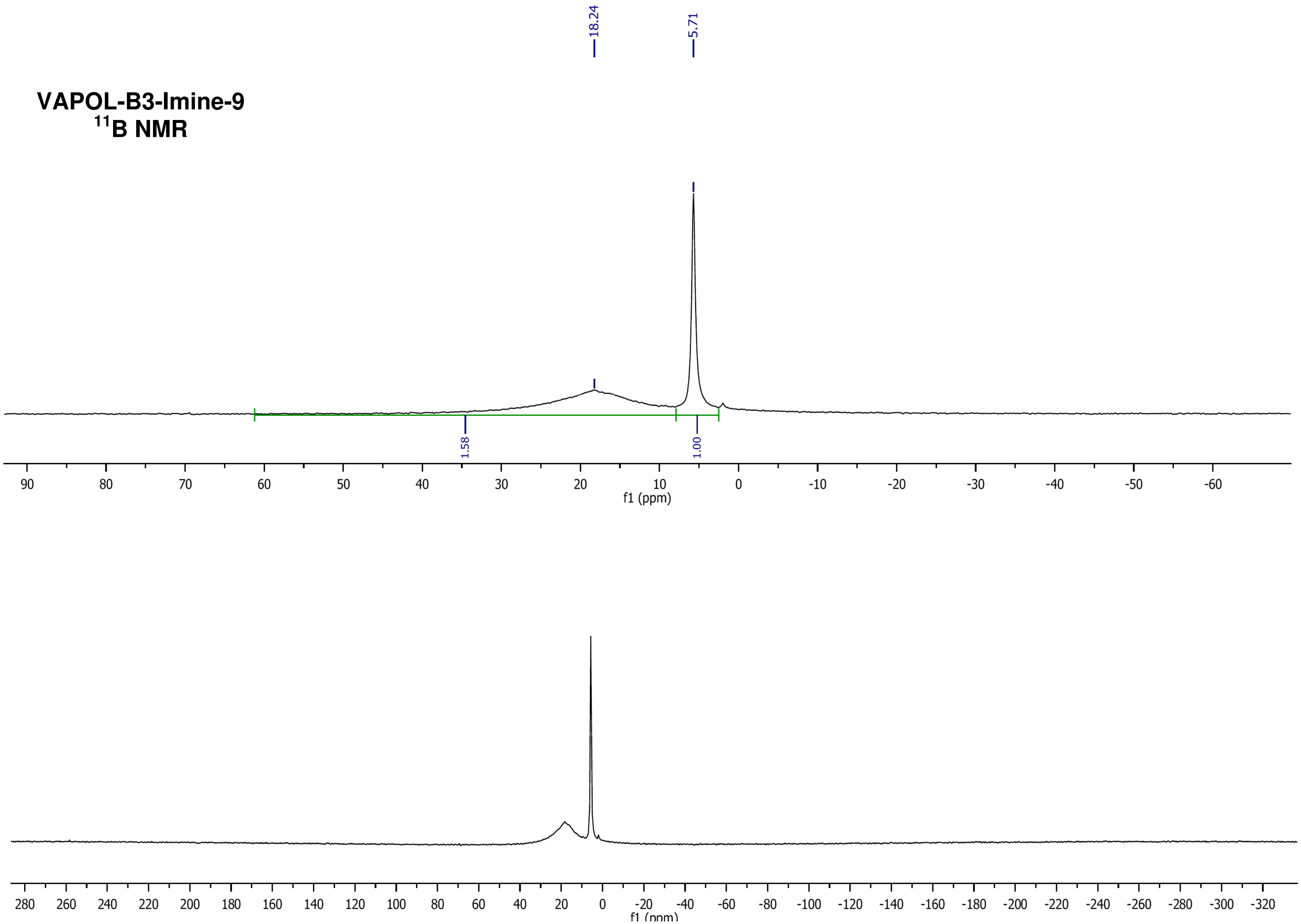


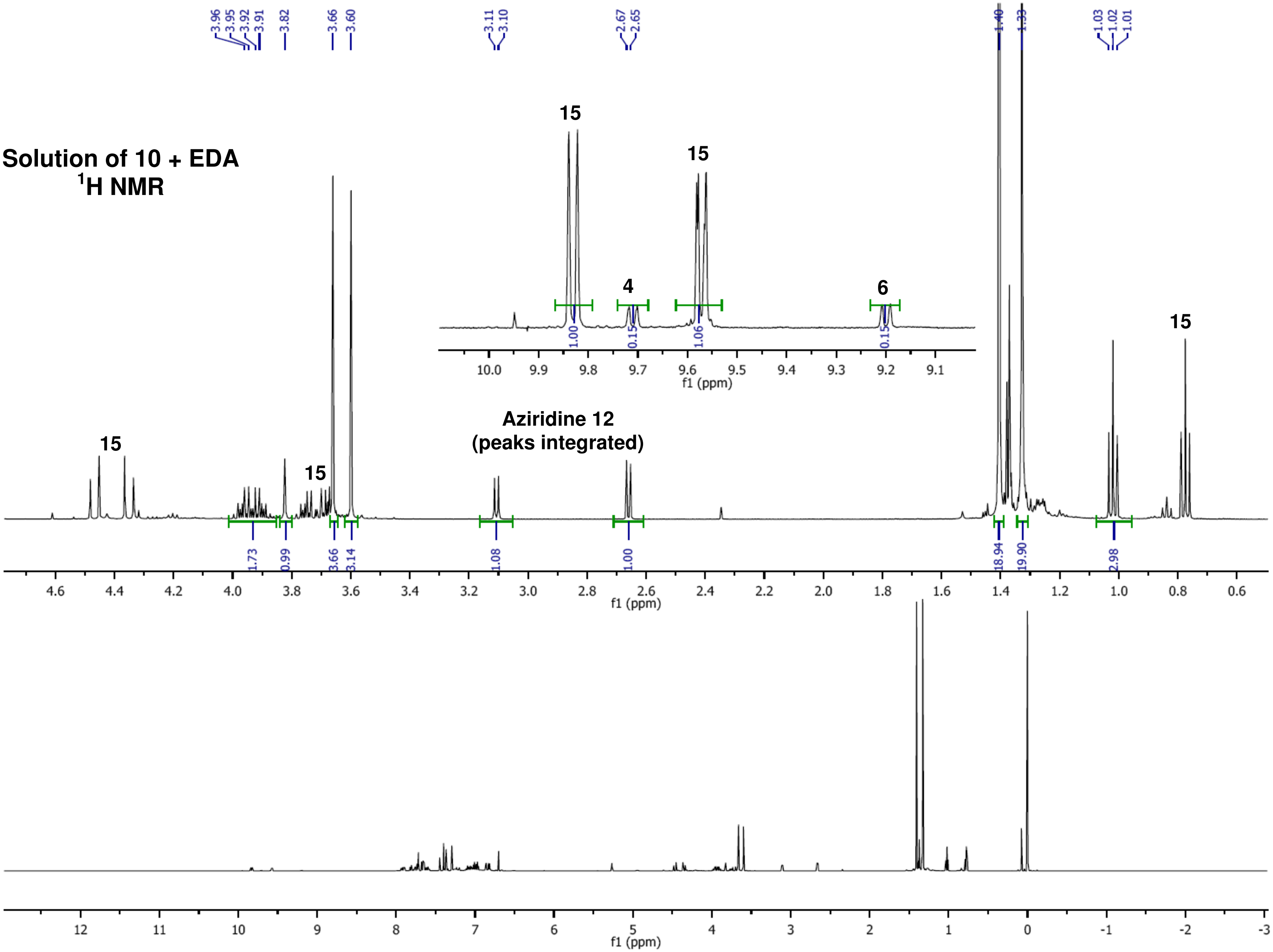
Following the NMR study on the solution of complex **10** prepared as described above, the solution was transferred to a Schlenk tube in a glove box. Ethyl diazoacetate (13 μL, 1.5 equiv) was added. A reaction occurred instantly upon shaking at room temperature as indicated by intense discharge of a gas and the fading of the color of the solution. The aziridination was completed in a few minutes as judged by the cessation of the bubbling (loss of N_2) and the initial red color completely disappearing to leave a colorless solution. The volatiles were removed under vacuum at room temperature and the residue was dissolved in $CDCl_3$. The ^1H NMR spectrum revealed a complete conversion of the imine **9** and a clean production of the aziridine **12** with the aid of a ^1H NMR spectrum of an authentic sample of **12**.[3] No significant amounts of enamine side-products were observed. As indicated by NMR analysis of the crude reaction mixture, the characteristic peaks for the boroxinate care (10.35 ppm in the ^{1}H NMR spectrum and 5.7 ppm in the ^{11}B NMR spectrum) are nearly gone. The peaks in the bay proton region suggest that the bulk of the VAPOL ligand was alkylated by EDA to give the ester **15** while only small amounts of free VAPOL **4** and pyroborate **6** are present as evidenced by their bay regions doublets. The ratio of **12** to **15** is 3.0:2.6. The observation of the alkylated VAPOL derivative **15** has been previously documented at the end of the AZ reaction.[2] The ^{1}H and ^{11}B NMR spectrum of the crude reaction mixture of the reaction of **10** with ethyl diazoacetate are presented below and labeled with Solution of **10**+EDA.

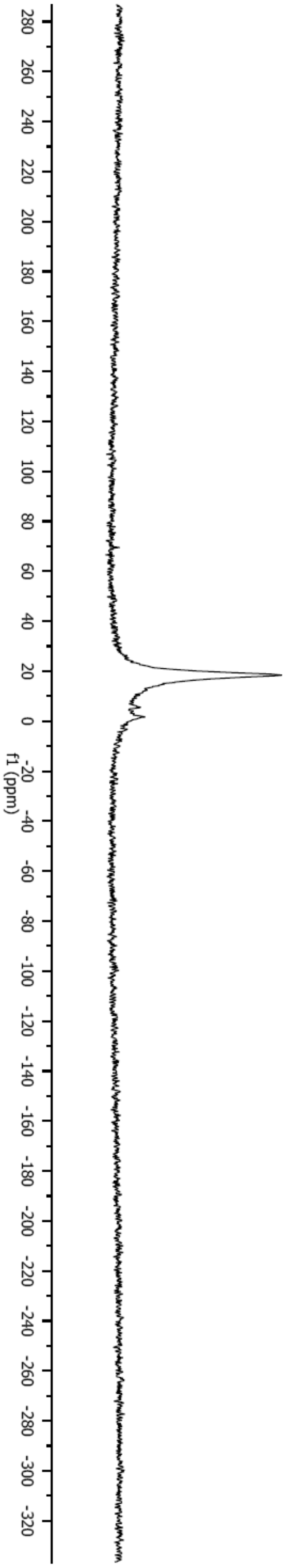
VAPOL-B3-Imine-9
^{1}H NMR



VAPOL-B3-Imine-9
^{11}B NMR







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220
200
180
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140
120
100
80
60
40
20
0
-20
-40
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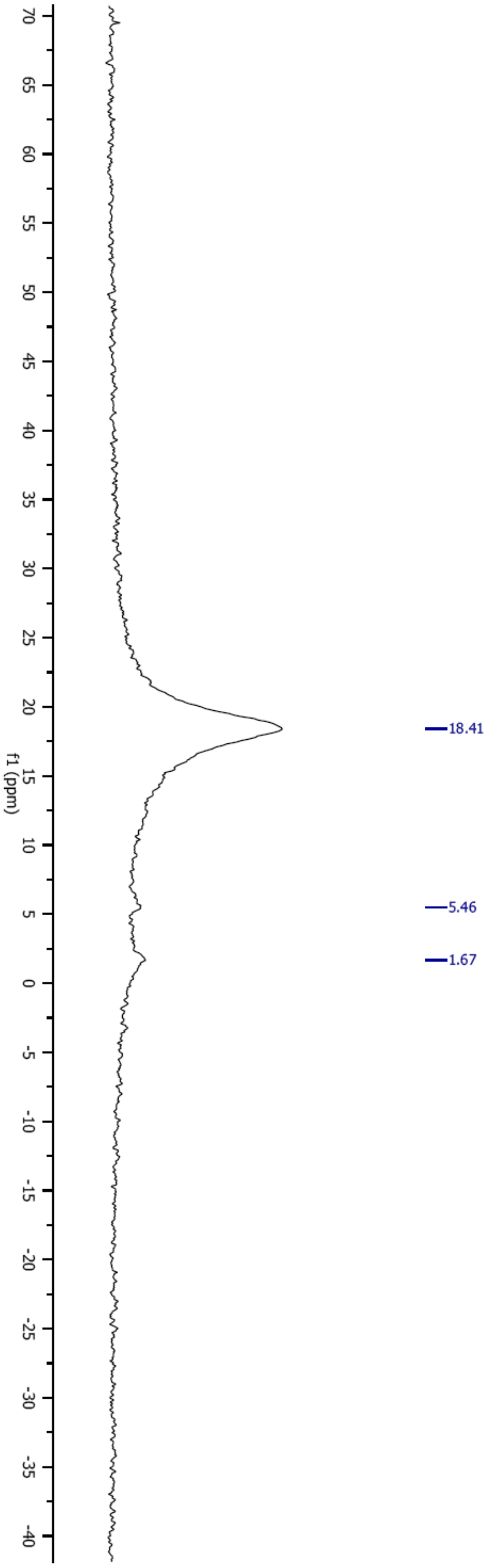
f1 (ppm)



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55
50
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35
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25
20
15
10
5
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-5
-10
-15
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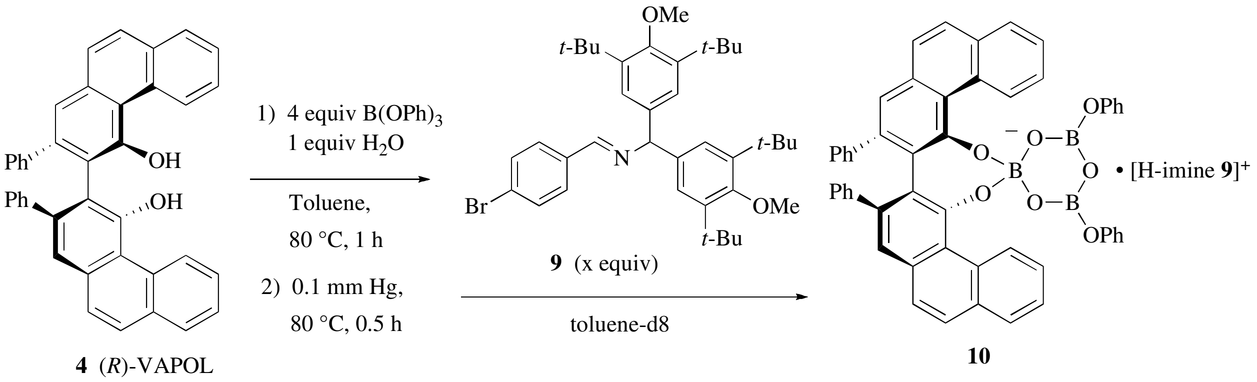
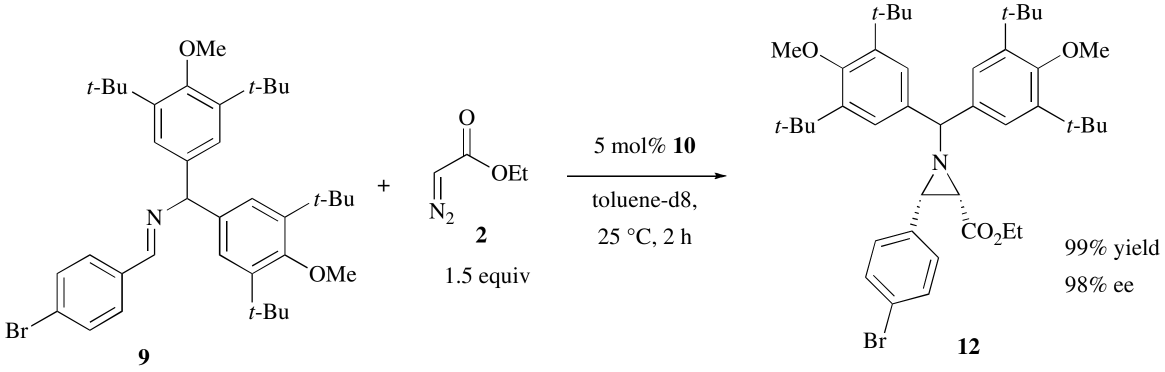
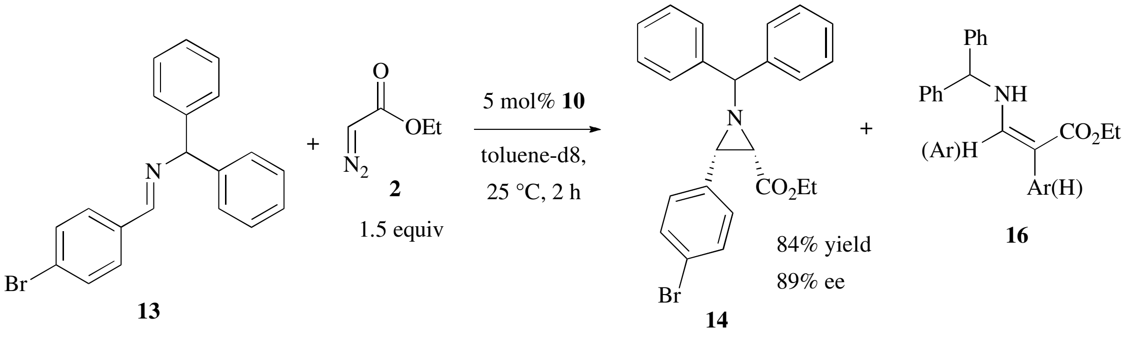
-30
-35
-40
f1 (ppm)

8. Preparation of the VAPOL Boroxinate Imine Complex 10 and its use as a Catalyst in the AZ Reaction.







A flame dried 25 mL pear-shaped flask that had its 14/20 joint replaced by a high vacuum threaded T-shaped Teflon value and which contained a stir bar was cooled under argon to room temperature and charged with (*R*)-VAPOL (54 mg, 0.1 mmol), commercial $B(OPh)_3$ (116 mg, 0.4 mmol), and 2 mL THF. To this solution was added deionized water (1.8 mg, 0.1 mmol). The flask was sealed and heated to 80 °C for 1 h. The volatile materials were removed via high vacuum (0.1 mm Hg) at 80 °C for 0.5 h. After cooling to room temperature, imine **9** (64 mg, 0.1

mmol) and toluene d8 (2 mL) were added to the flask under argon. The solution was split into two equal parts of 1 mL each.

The first 1 mL of the solution was transferring by syringe to an NMR tube under argon. The ^{1}H NMR spectrum revealed a mixture of **10**, VAPOL and pyroborate **6** in a ratio of 2.00:0.19:0.50. A few minutes later, a second equivalent of the solid imine **9** (32 mg, 0.05 mmol) was added to the NMR tube by removing the cap and quickly adding the imine and then replacing the cap and shaking the tube. This gave a 2.00:<0.02:0.33 ratio of **10**, VAPOL and pyroborate **6**. Finally, after a few minutes, a third equivalent of imine **9** (32 mg, 0.05 mmol) was added to the NMR tube in the same manner to give a 2.00:<0.02:0.10 ratio of **10**, VAPOL and pyroborate **6**. This solution of **10** in the NMR tube was poured under an argon stream into a flame dried 25 mL pear-shaped flask that had its 14/20 joint replaced by a high vacuum threaded T-shaped Teflon value and which contained a stir bar was cooled under argon to room temperature. To the flask was also added 1 mL of toluene d8 to rinse the NMR tube. The flask was then added imine **9** (544 mg, 0.85 mmol) followed by ethyl diazoacetate (155 μL, 1.5 mmol). Vigorous bubbling was observed upon addition of ethyl diazoacetate. The red color of the solution of **10** faded within 5 minutes. The mixture was stirred at room temperature for 2 h. After evaporation of the solvent, the residue was loaded onto a 30 mm diameter chromatography column packed to a depth of 300 mm with silica gel and eluted with a 19:1 mixture of hexane and ethyl acetate to give 715 mg (0.993 mmol, 99.3%) of the aziridine **12** as a white solid. The optical purity of **12** was determined to be 99% ee by HPLC analysis (Pirkle covalent (*R,R*) Whelk-O1 column, 225nm, 99:1 hexane/2-PrOH, flow-rate: 1 mL/min). Retention times: R_t = 5.43 min for (*2S,3S*)-**12** and R_t = 9.15 min for (*2R,3R*)-**12**. The cis/trans selectivity was >50:1. Spectral data for (2*S*,3*S*)-**12**: R_f = 0.32 (20:1 hexane/EtOAc); ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.02 (t, 3H, *J* = 6.9 Hz), 1.33 (s, 18H), 1.41 (s, 18H), 2.67 (d, 1H, *J* = 6.6 Hz), 3.12 (d, 1H, *J* = 6.6 Hz), 3.61 (s, 3H), 3.67 (s, 3H), 3.84 (s, 1H), 3.91-3.97 (m, 2H), 7.30 (s, 2H), 7.37 (s, 4H), 7.41 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 13.99, 32.03, 32.11, 35.69, 35.77, 46.33, 48.04, 60.61, 63.93, 63.98, 77.15, 121.21, 125.29, 125.38, 129.88, 130.68, 134.44, 136.40, 136.62, 143.11, 143.14, 158.29, 158.33, 167.88. The spectral data for **12** match those previously reported for this compound and the ^{1}H and ^{13}C NMR spectra are shown below.[3] The 99% yield and 98% ee is to be compared with the 98% yield and 99% ee reported for this compound from the AZ reaction.[3] The ^{1}H and ^{11}B NMR spectra of **10** prepared from 1, 2 and 3 equivalents of imine **9** are shown below and are labeled HL2-B3-BUDAMimine-xequiv. The stoichiometric reaction of **10** was also examined with ethyl diazoacetate. If a solution of **10** was generated as described above with 1 equivalent of imine **9** and reacted with 1.2 equivalents of ethyl diazoacetate for 24 h at 24 °C, the aziridine **12** could be isolated from the reaction in 100% yield in 99% ee.

To the flask containing the second 1 mL portion of the solution of **10** was added imine **9** (64 mg, 0.1 mmol) and toluene-d8 (1 mL). The addition was accomplished by removing the threaded Teflon stopcock while there was a flow of argon into the side-T of the Teflon value. The additional imine **9** was added to make a solution of **10** identical to that of the first portion. Then imine **13** (350 mg, 1.0 mmol) and ethyl diazoacetate (155 μL, 1.5 mmol) were added. Vigorous bubbling was observed and the initial red color of the solution faded within 30 minutes. The mixture was stirred at room temperature for 2 hours. After evaporation of the solvent, the residue was loaded onto a 35 mm diameter chromatography column packed to a depth of 350 mm with silica gel and eluted with a 19:1 mixture of hexane and ethyl acetate to give 365 mg (0.84 mmol, 84%) of the aziridine **14** as a white solid. The optical purity of **14** was determined to be 89% *ee* by HPLC (Chiralcel OD-H column, 98:2 hexanes/2-propanol, 222 nm, flow rate 1 mL/min); Retention times: R_t = 5.37 min (major enantiomer) and R_t = 13.48 min (minor enantiomer). Spectral data for (2*S*,3*S*)-**14**; R_f = 0.33 (1:9 ethyl acetate/hexanes). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.07 (t, J = 7 Hz, 3H), 2.74 (d, J = 7 Hz, 1H), 3.19 (d, J = 7 Hz, 1H), 4.00 (q, *J* = 7 Hz, 2H), 4.01 (s, 1H), 7.23 (t, *J* = 7 Hz, 1H), 7.29-7.45 (m, 9H), 7.50 (d, *J* = 7 Hz, 2H), 7.65 (d, *J* = 7 Hz, 2H); ^{13}C NMR (CDCl$_3$, 125 MHz) δ 13.96, 46.44, 47.31, 60.67, 77.55, 121.31, 127.11, 127.25, 127.40, 127.46, 128.49, 129.52, 130.86, 134.06, 142.12, 142.29, 167.37. These spectral data match those previously reported for this compound and the ^{1}H and ^{13}C NMR spectra are shown below.[2] The 84% yield and 89% ee is to be compared with the 78% yield and 90% ee reported for this compound from the AZ reaction.[2] The aziridine **12** was also isolated from this reaction but it was not pure since it co-eluted with the enamine side-products **16**. These side products are not formed in the reaction of imine **9**.

HL2-B3-BUDAMimine-1equiv07182009

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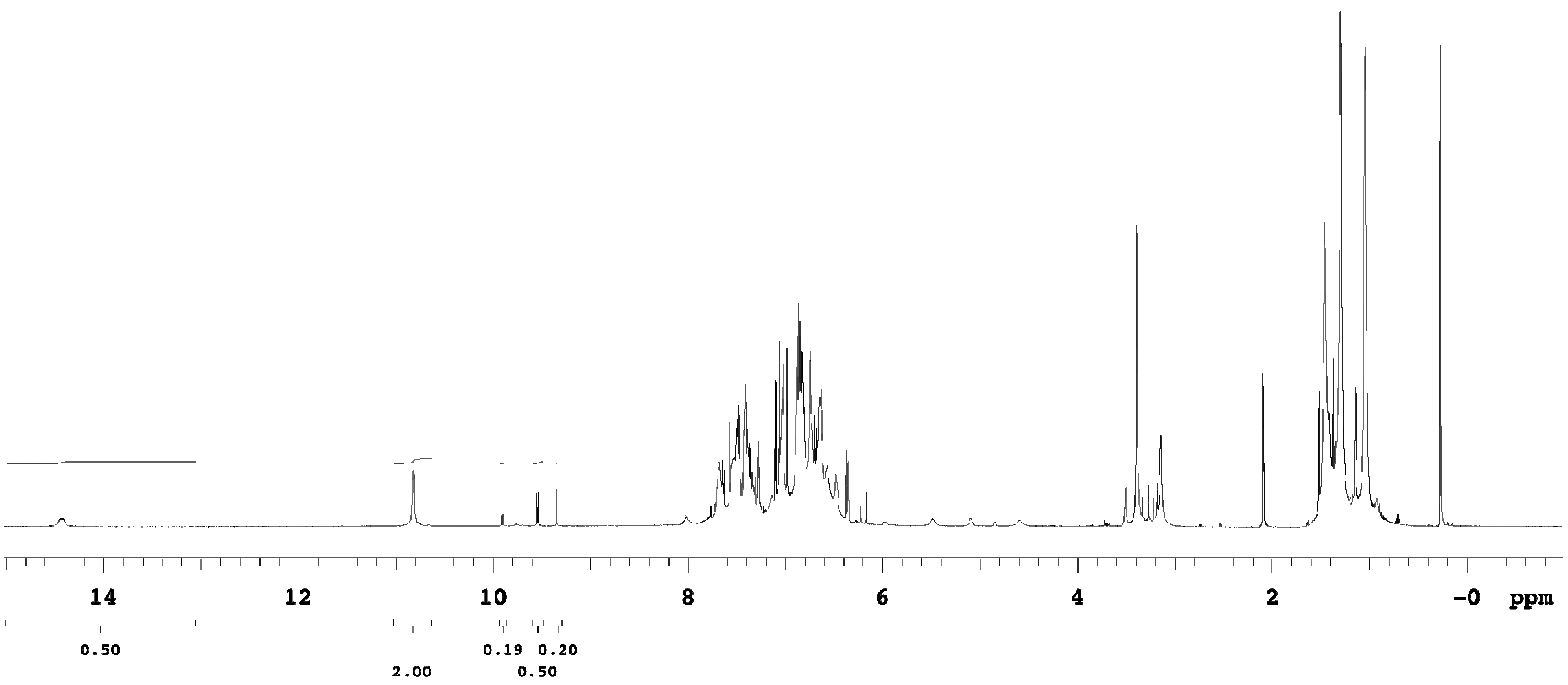

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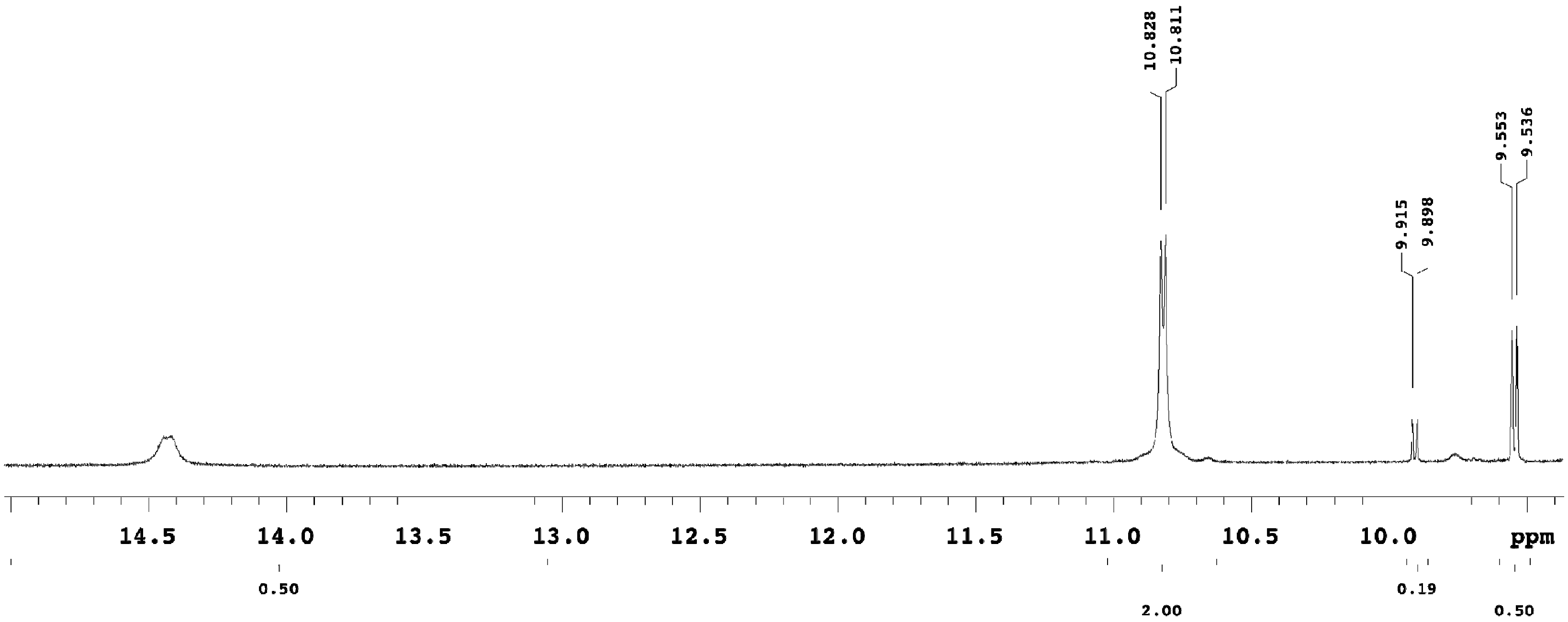

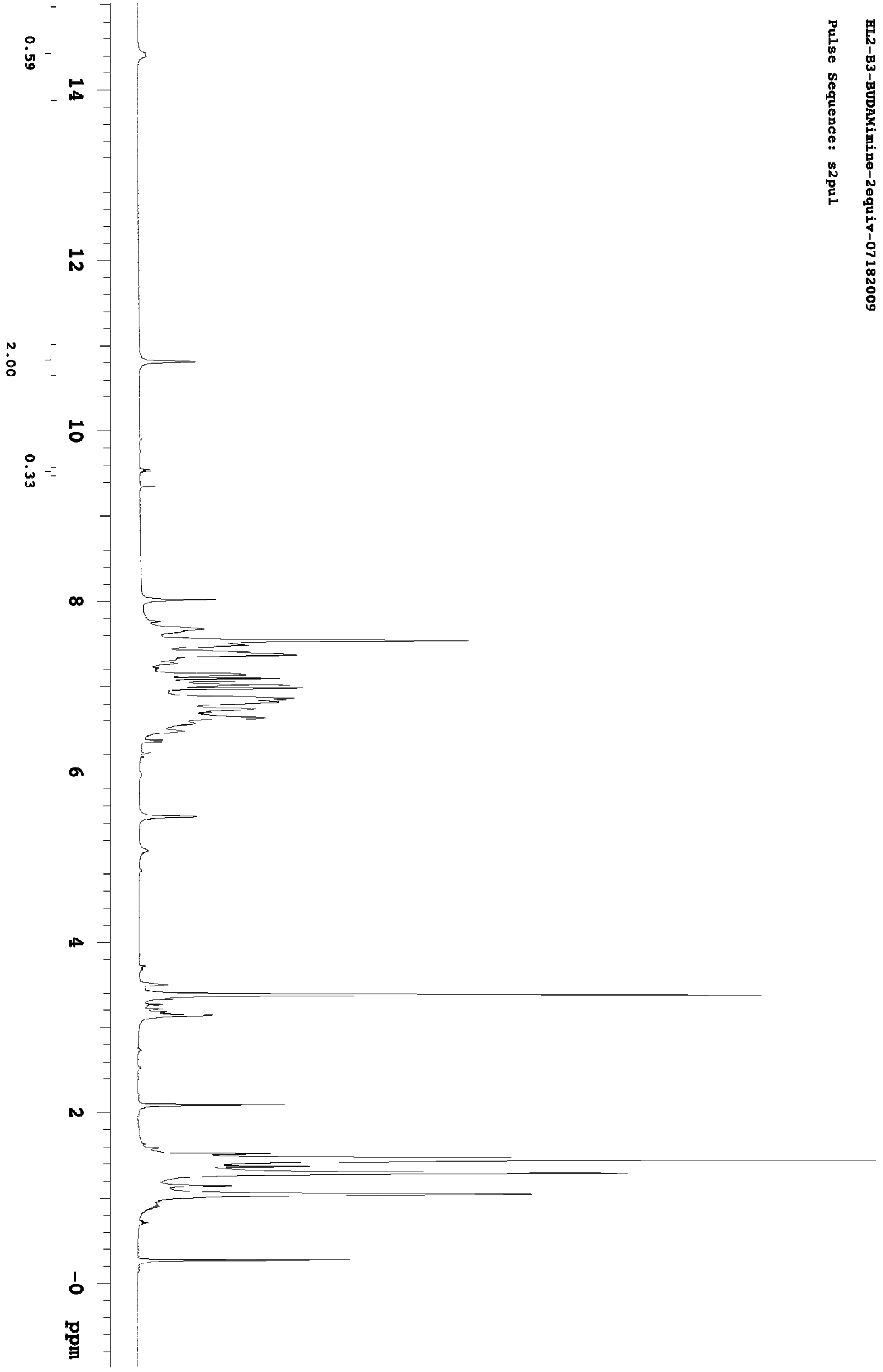
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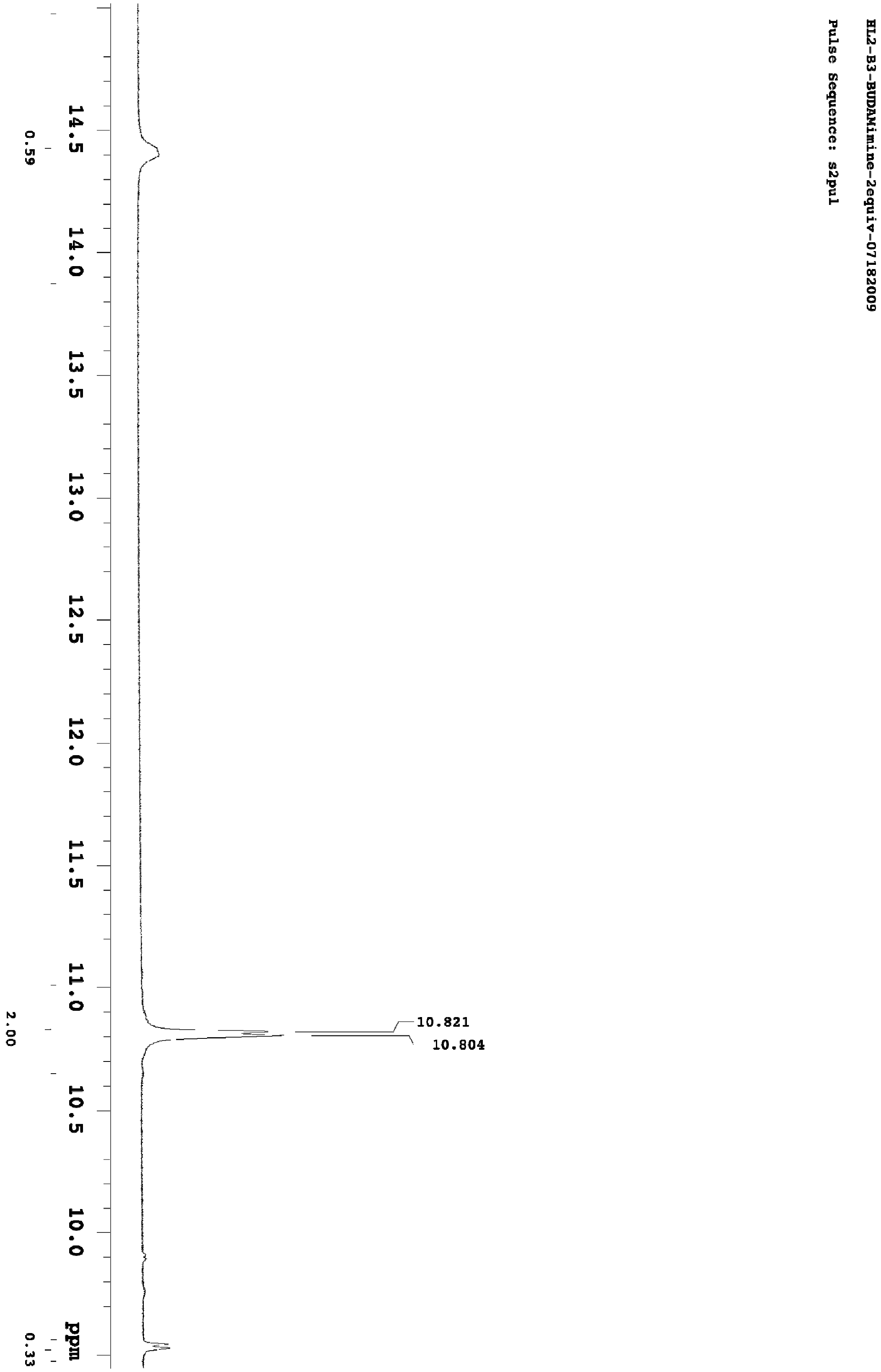
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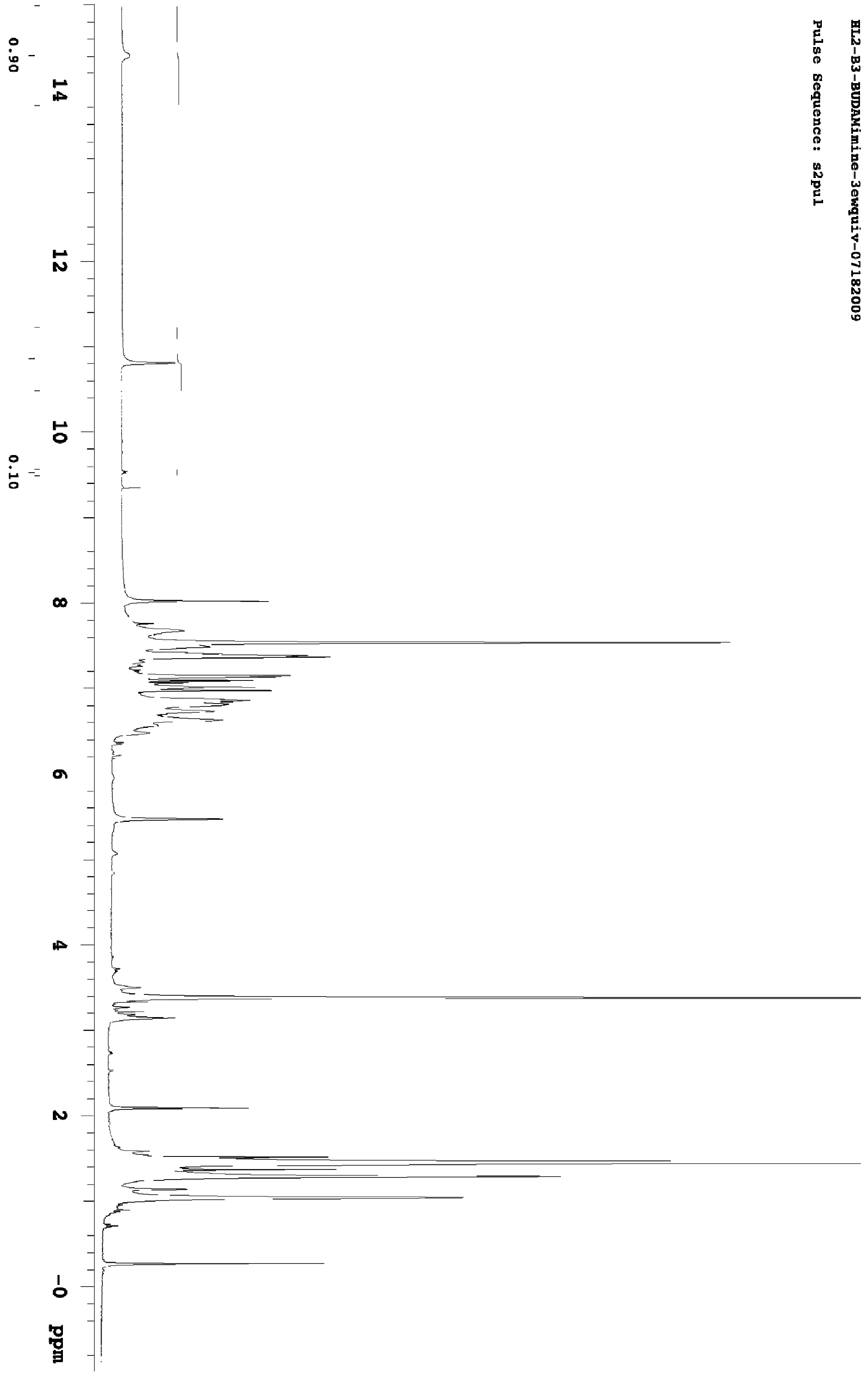
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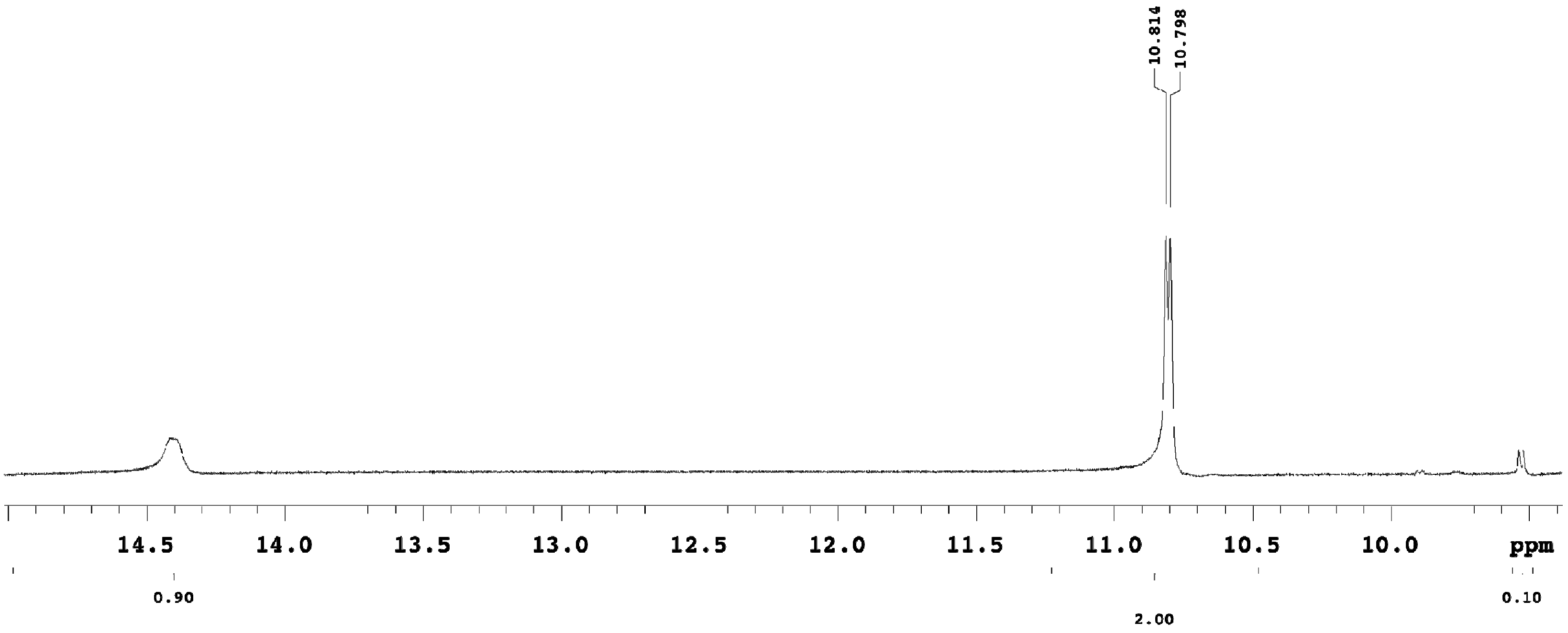

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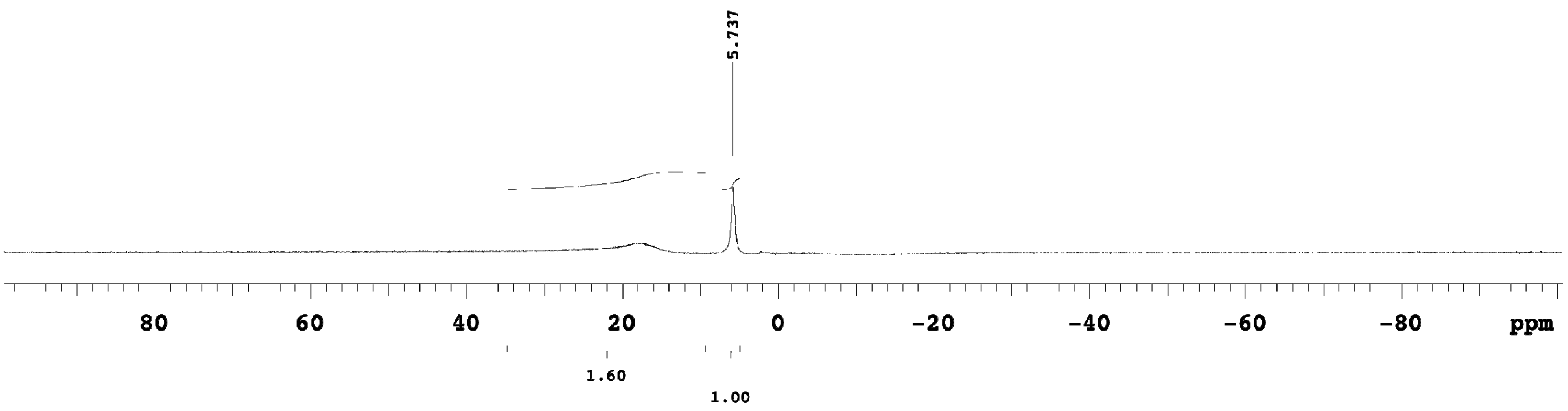

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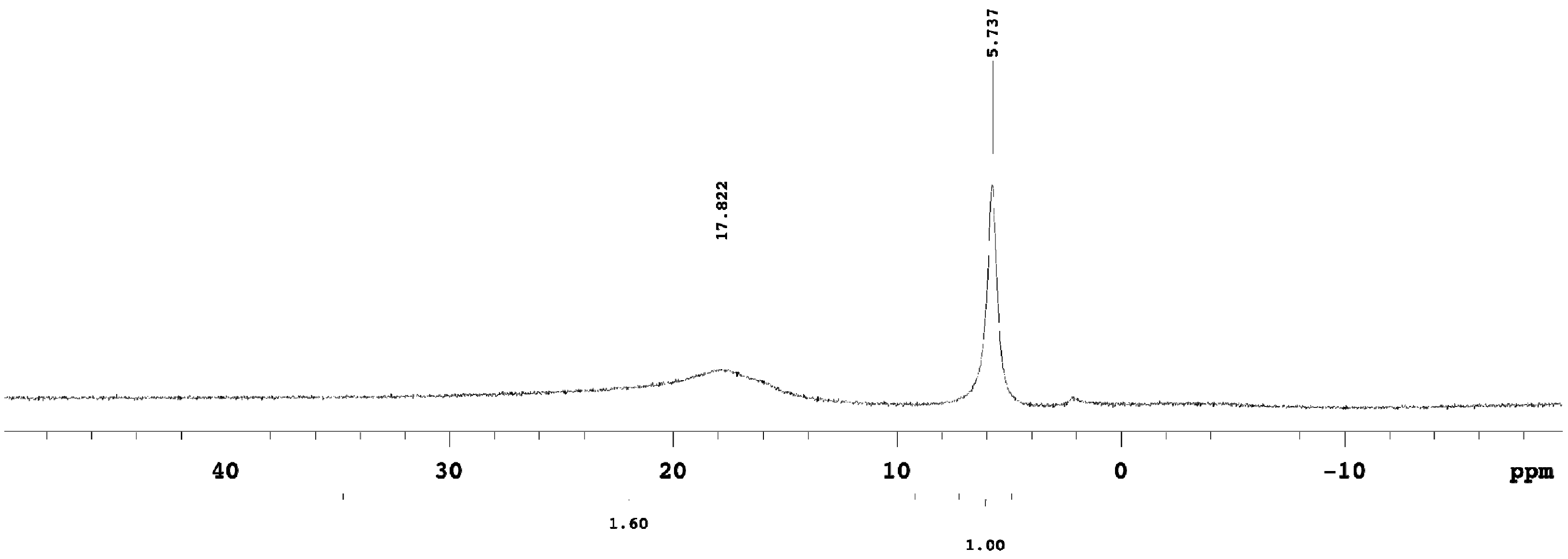

07182009-BUDAMazi

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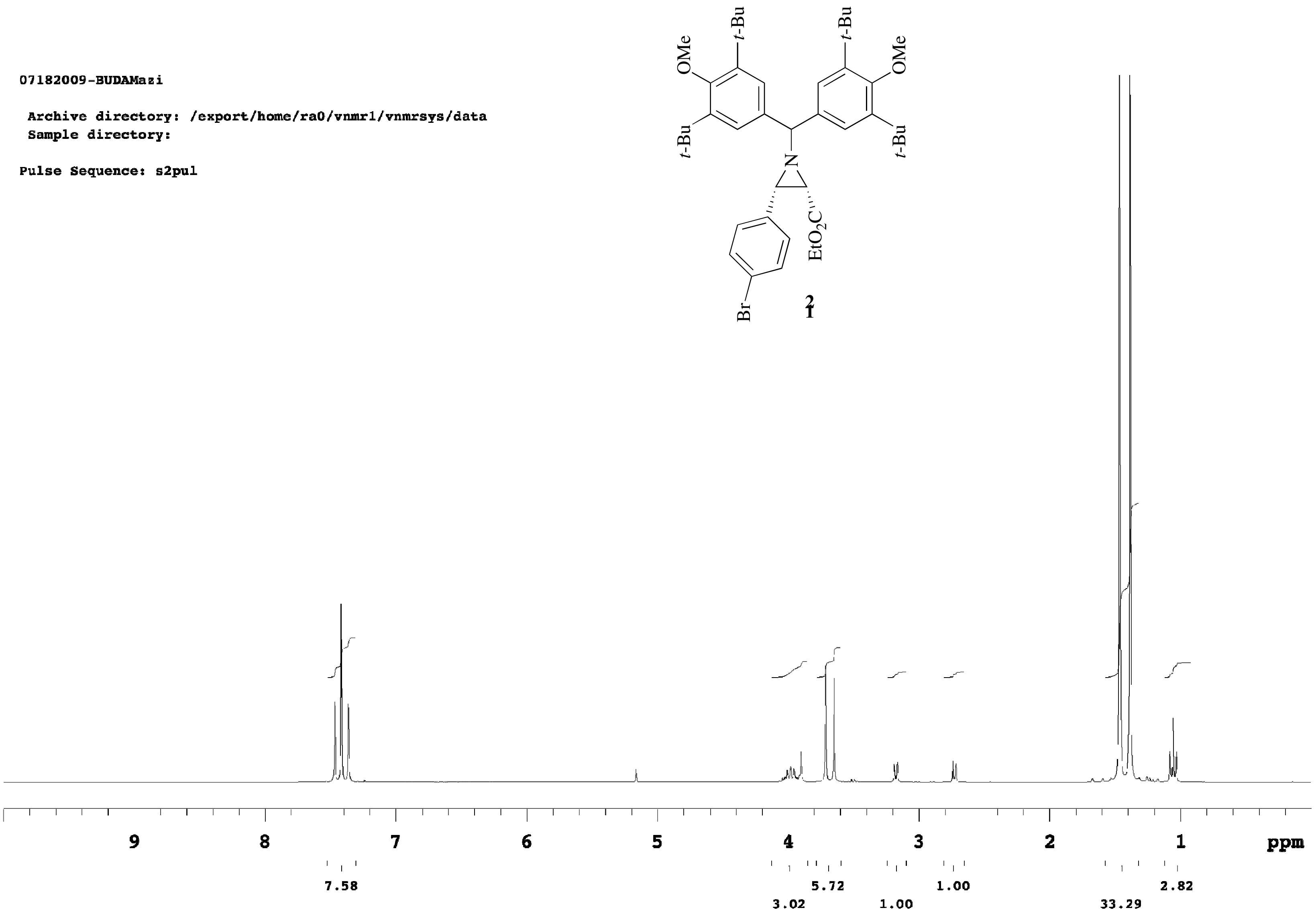
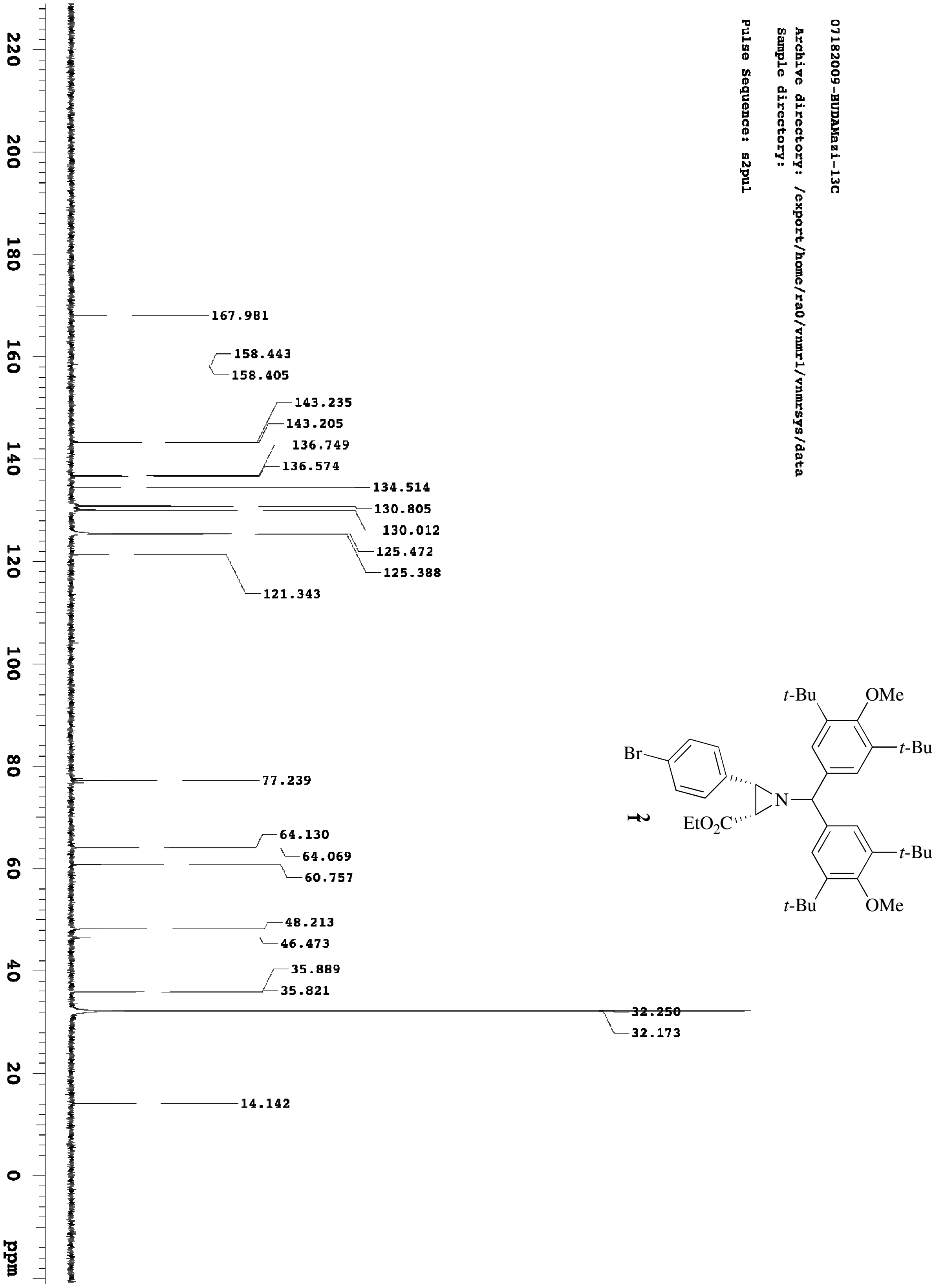


12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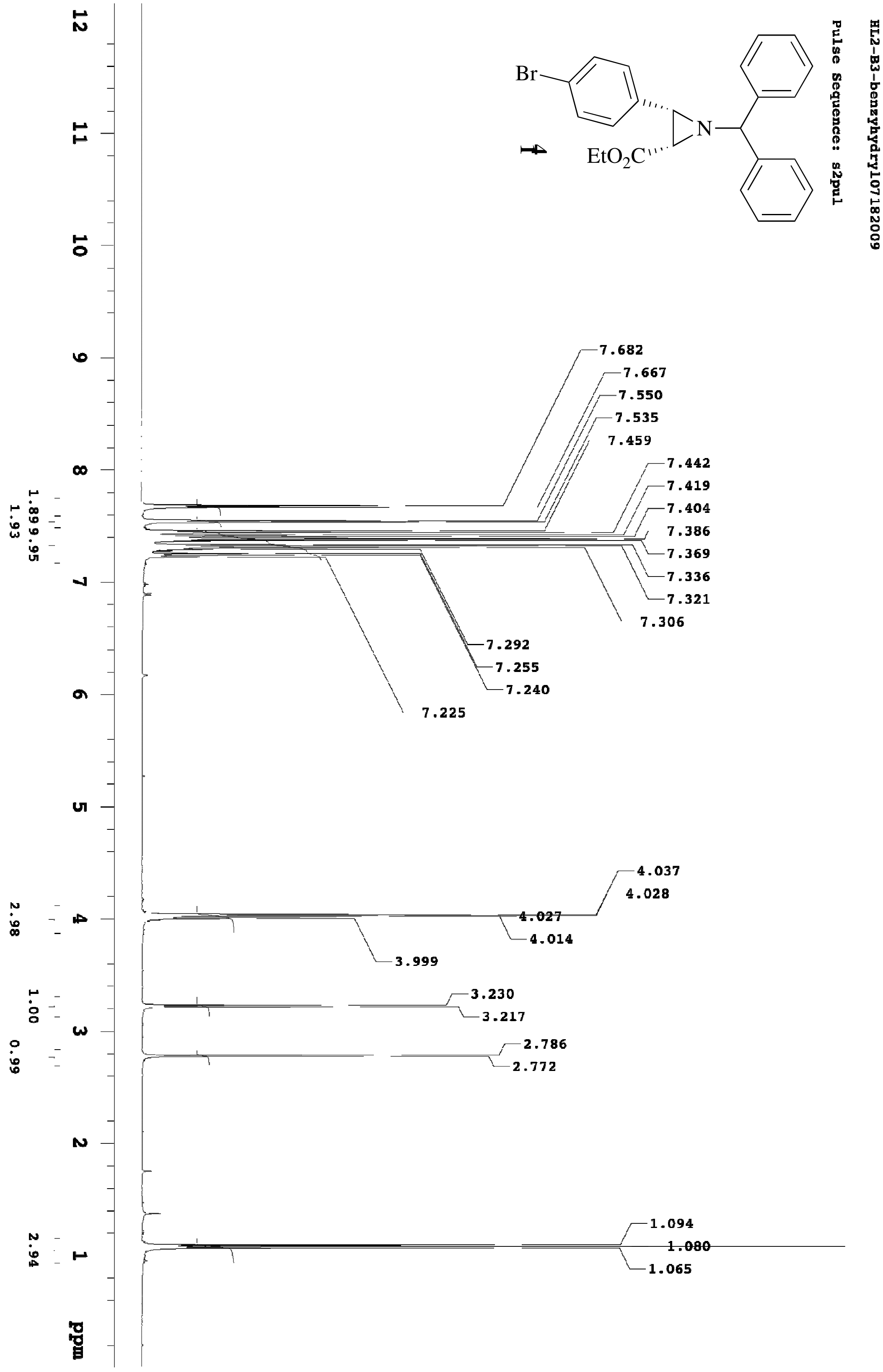
7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1.89
9.95
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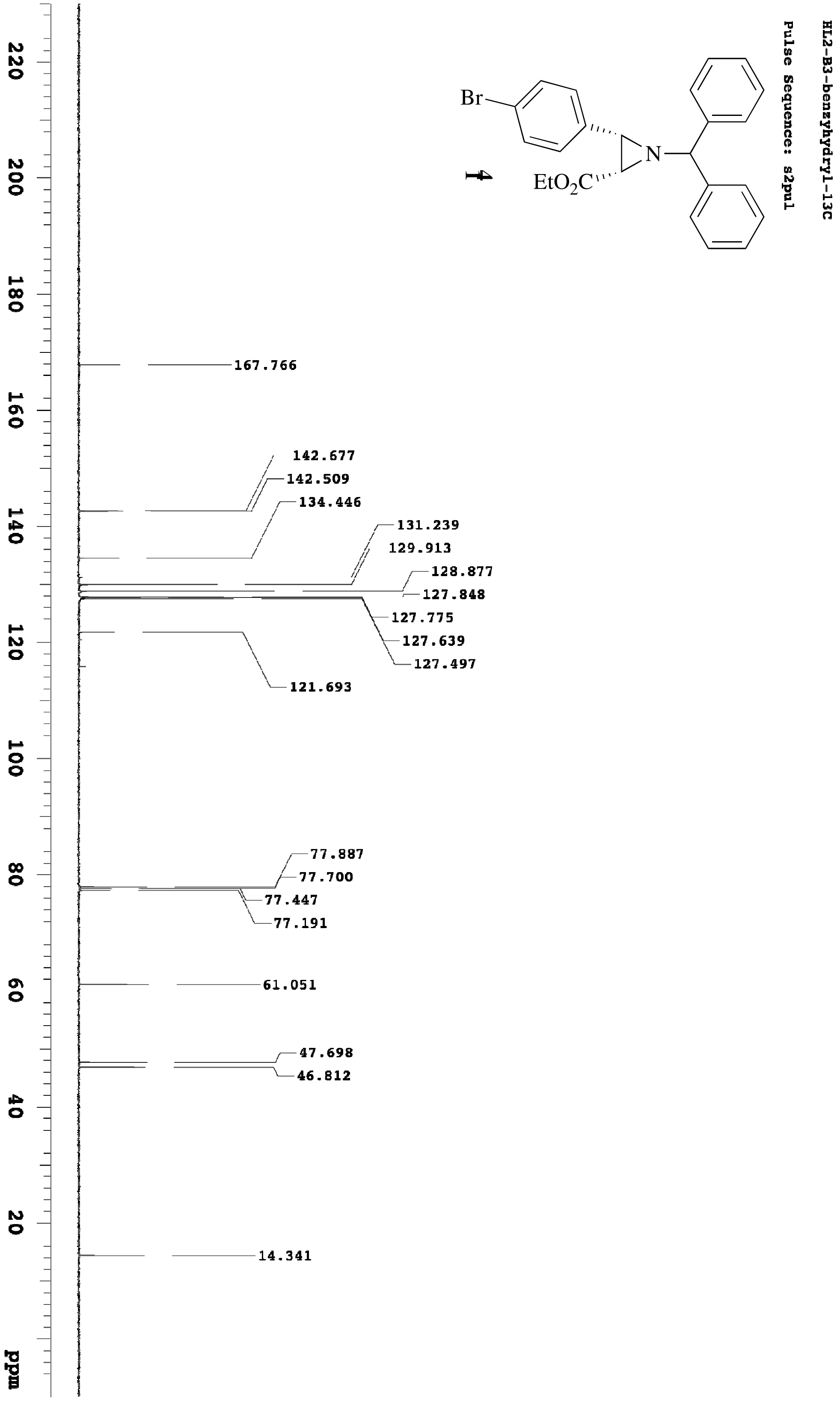
2.98
1.00
0.99
2.94
12
11
10
9
8
7
6
5
4
3
2
1
ppm


HL2-B3-benzyhdryl-13C
Pulse Sequence: s2pul
Br
N
EtO_2C
167.766
142.677
142.509
134.446
131.239
129.913
128.877
127.848
127.775
127.639
127.497
121.693
77.887
77.700
77.447
77.191
61.051
47.698
46.812
14.341
220
200
180
160
140
120
100
80
60
40
20
ppm

4

9. References:

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