

Synthesis and characterization of new boron compounds using reaction of diazonium tetraphenylborate with enaminoamides

Markéta Svobodová ^{1*}, Jan Svoboda ¹, Bing-Han Li ², Valerio Bertolasi ³, Luboš Socha ¹, Miloš Sedlák ¹, Lukáš Marek ¹

¹ Faculty of Chemical Technology, Institute of Organic Chemistry and Technology, University of Pardubice, Studentská 573, 532 10 Pardubice, Czech Republic; jan.svoboda@upce.cz (J.S.); st46953@upce.cz (L.S.); milos.sedlak@upce.cz (M.S.); lukas.marek3@student.upce.cz (L.M.)

² Department of Chemistry, National Tsing Hua University, Hsinchu 30013, Taiwan; w6520325@hotmail.com

³ Department of Chemical and Pharmaceutical Sciences, University of Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy; m38@unife.it

* Correspondence: marketa.svobodova@upce.cz

Summary

1. Experimental	7
1. 1 General Information.....	7
Scheme S1. Preparation of starting compounds.	8
2. NMR spectra.....	9
2.1 Triazaborinone 5a	9
Figure S1. 400 MHz ¹ H NMR of compound 5a in DMSO- <i>d</i> ₆	9
Figure S2. 400 MHz 1D-NOESY (mixing time d8 = 800 ms, relaxation delay d1 = 2s) of compound 5a in DMSO- <i>d</i> ₆	10
Figure S3. 100 MHz ¹³ C NMR of compound 5a in DMSO- <i>d</i> ₆	10
Figure S4. 160 MHz ¹¹ B NMR of compound 5a in CDCl ₃	11
Figure S5. 500 MHz ¹ H– ¹⁵ N HMBC NMR of compound 5a in DMSO- <i>d</i> ₆	11
2.2 Triazaborinone 5b	12
Figure S6. 500 MHz ¹ H NMR of compound 5b in CDCl ₃	12
Figure S7. 400 MHz 1D-NOESY (mixing time d8 = 800 ms, relaxation delay d1 = 2s) of compound 5b in CDCl ₃ ...	13
Figure S8. 125 MHz ¹³ C NMR of compound 5b in CDCl ₃	13
Figure S9. 128 MHz ¹¹ B NMR of compound 5a in CDCl ₃	14
Figure S10. 50 MHz ¹⁵ N NMR of compound 5a in DMSO- <i>d</i> ₆	14
Figure S11. 500 MHz ¹ H– ¹⁵ N HMBC NMR of compound 5b in CDCl ₃	15
2.3 Triazaborinone 5c.....	16
Figure S12. 500 MHz ¹ H NMR of compound 5c in CDCl ₃	16
Figure S13. 125 MHz ¹³ C NMR of compound 5c in CDCl ₃	17
Figure S14. 160 MHz ¹¹ B NMR of compound 5c in CDCl ₃	17
Figure S15. 500 MHz ¹ H– ¹⁵ N HMBC NMR of compound 5c in CDCl ₃	18
2.4 Triazaborinone 5d	19

Figure S16. 500 MHz ^1H NMR of compound 5d in CDCl_3	19
Figure S17. 125 MHz ^{13}C APT NMR of compound 5d in CDCl_3	20
Figure S18. 160 MHz ^{11}B NMR of compound 5c in CDCl_3	20
Figure S19. 50 MHz ^{15}N NMR of compound 5d in CDCl_3	21
Figure S20. 500 MHz ^1H – ^{15}N HMBC NMR of compound 5d in CDCl_3	21
2.5 Triazaborinone 5g	22
Figure S21. 500 MHz ^1H NMR of compound 5g in CDCl_3	22
Figure S22. 400 MHz 1D-NOESY (mixing time $d_8 = 800$ ms, relaxation delay $d_1 = 2$ s) of compound 5g in CDCl_3	23
Figure S23. 125 MHz ^{13}C NMR of compound 5g in CDCl_3	23
Figure S24. 160 MHz ^{11}B NMR of compound 5g in CDCl_3	24
Figure S25. 50 MHz ^{15}N NMR of compound 5g in CDCl_3	24
Figure S26. 500 MHz ^1H – ^{15}N HMBC NMR of compound 5g in CDCl_3	25
2.6 Triazaborinone 5h	26
Figure S27. 500 MHz ^1H NMR of compound 5h in CDCl_3	26
Figure S28. 125 MHz ^{13}C NMR of compound 5h in CDCl_3	27
Figure S29. 160 MHz ^{11}B NMR of compound 5h in CDCl_3	27
Figure S30. 50 MHz ^{15}N NMR of compound 5h in CDCl_3	28
Figure S31. 500 MHz ^1H – ^{15}N HMBC NMR of compound 5h in CDCl_3	28
2.7 Oxazaborine 6a	29
Figure S32. 500 MHz ^1H NMR of compound 6a in CDCl_3	29
Figure S33. 125 MHz ^{13}C NMR of compound 6a in CDCl_3	30
Figure S34. 160 MHz ^{11}B NMR of compound 6a in CDCl_3	30
Figure S35. 500 MHz ^1H – ^{15}N HMBC NMR of compound 6a in CDCl_3	31
2.8 Oxazaborine 6e	32
Figure S36. 500 MHz ^1H NMR of compound 6e in CDCl_3	32
Figure S37. 100 MHz ^{13}C NMR of compound 6e in CDCl_3	33
Figure S38. 100 MHz ^1H – ^{13}C HSQC NMR of compound 6e in CDCl_3	33
Figure S39. 160 MHz ^{11}B NMR of compound 6e in CDCl_3	34
Figure S40. 500 MHz ^1H – ^{15}N HMBC NMR of compound 6e in CDCl_3	34
2.9 Oxazaborine 6f	35
Figure S41. 500 MHz ^1H NMR of compound 6f in CDCl_3 (Signal with asterix is $-\text{CH}_3$ from toluene.)	35
Figure S42. 125 MHz ^{13}C NMR of compound 6f in CDCl_3	36
Figure S43. 160 MHz ^{11}B NMR of compound 6f in CDCl_3	36
Figure S44. 50 MHz ^{15}N NMR of compound 6f in CDCl_3	37
Figure S45. 500 MHz ^1H – ^{15}N HMBC NMR of compound 6f in CDCl_3	37
2.10 Oxazaborine 6g	38

Figure S46. 500 MHz ^1H NMR of compound 6g in CDCl_3	38
Figure S47. 125 MHz ^{13}C NMR of compound 6g in CDCl_3	39
Figure S48. 160 MHz ^{11}B NMR of compound 6g in CDCl_3	39
Figure S49. 400 MHz ^1H – ^{15}N HMBC NMR of compound 6g in CDCl_3	40
2.11 Oxazaborine 6h	41
Figure S50. 500 MHz ^1H NMR of compound 6h in CDCl_3	41
Figure S51. 125 MHz ^{13}C NMR of compound 6h in CDCl_3 (*Cyclohexane)	42
Figure S52. 160 MHz ^{11}B NMR of compound 6h in CDCl_3	42
Figure S53. 50 MHz ^{15}N NMR of compound 6h in CDCl_3	43
Figure S54. 500 MHz ^1H – ^{15}N HMBC NMR of compound 6h in CDCl_3	43
2.12 Diazaborinone 7a	44
Figure S55. 500 MHz ^1H NMR of compound 7a in CDCl_3	44
Figure S56. 125 MHz ^{13}C NMR of compound 7a in CDCl_3	45
Figure S57. 160 MHz ^{11}B NMR of compound 7a in CDCl_3	45
Figure S58. 500 MHz ^1H – ^{15}N HMBC NMR of compound 7a in CDCl_3	46
2.13 Diazaborinone 7b	47
Figure S59. 500 MHz ^1H NMR of compound 7b in CDCl_3	47
Figure S60. 125 MHz ^{13}C NMR of compound 7b in CDCl_3	48
Figure S61. 160 MHz ^{11}B NMR of compound 7b in CDCl_3	48
Figure S62. 50 MHz ^{15}N NMR of compound 7b in CDCl_3	49
Figure S63. 500 MHz ^1H – ^{15}N HMBC NMR of compound 7b in CDCl_3	49
2.14 Diazaborinone 7c	50
Figure S64. 400 MHz ^1H NMR of compound 7c in CDCl_3	50
Figure S65. 125 MHz ^{13}C NMR of compound 7c in CDCl_3	51
Figure S66. 160 MHz ^{11}B NMR of compound 7c in CDCl_3	51
Figure S67. 500 MHz ^1H – ^{15}N HMBC NMR of compound 7c in CDCl_3	52
2.15 Diazaborinone 7d	53
Figure S68. 500 MHz ^1H NMR of compound 7d in CDCl_3	53
Figure S69. 125 MHz ^{13}C NMR of compound 7d in CDCl_3	54
Figure S70. 160 MHz ^{11}B NMR of compound 7d in CDCl_3	54
Figure S71. 50 MHz ^{15}N NMR of compound 7d in CDCl_3	55
Figure S72. 500 MHz ^1H – ^{15}N HMBC NMR of compound 7d in CDCl_3	55
2.16 Diazaborinone 7e	56
Figure S73. 500 MHz ^1H NMR of compound 7e in CDCl_3	56
Figure S74. 125 MHz ^{13}C NMR of compound 7e in CDCl_3	57
Figure S75. 160 MHz ^{11}B NMR of compound 7e in CDCl_3	57

Figure S76. 400 MHz ^1H – ^{15}N HMBC NMR of compound 7e in CDCl_3 (* CH_2 from ethanol).....	58
2.17 Diazaborinone 7f	59
Figure S77. 500 MHz ^1H NMR of compound 7f in CDCl_3	59
Figure S78. 125 MHz ^{13}C NMR of compound 7f in CDCl_3	60
Figure S79. 160 MHz ^{11}B NMR of compound 7f in CDCl_3	60
Figure S80. 400 MHz ^1H – ^{15}N HMBC NMR of compound 7f in CDCl_3	61
2.18 Diazaborinone 7g	62
Figure S81. 500 MHz ^1H NMR of compound 7g in CDCl_3	62
Figure S82. 125 MHz ^{13}C NMR of compound 7g in CDCl_3	63
Figure S83. 160 MHz ^{11}B NMR of compound 7g in CDCl_3	63
Figure S84. 500 MHz ^1H – ^{15}N HMBC NMR of compound 7g in CDCl_3	64
2.19 Diazaborinone 7h	65
Figure S85. 500 MHz ^1H NMR of compound 7h in CDCl_3	65
Figure S86. 125 MHz ^{13}C NMR of compound 7h in CDCl_3	66
Figure S87. 160 MHz ^{11}B NMR of compound 7h in CDCl_3	66
Figure S88. 500 MHz ^1H – ^{15}N HMBC NMR of compound 7h in CDCl_3	67
2.20 Triazaborine 8e	68
Figure S89. 500 MHz ^1H NMR of compound 8e in CDCl_3	68
Figure S90. 125 MHz ^{13}C NMR of compound 8e in CDCl_3	69
Figure S91. 160 MHz ^{11}B NMR of compound 8e in CDCl_3	69
Figure S92. 50 MHz ^{15}N NMR of compound 8e in CDCl_3	70
Figure S93. 500 MHz ^1H – ^{15}N HMBC NMR of compound 8e in CDCl_3 (* CH_2 from ethanol).....	70
2.21 Triazaborine 8g	71
Figure S94. 500 MHz ^1H NMR of compound 8g in CDCl_3	71
Figure S95. 100 MHz ^{13}C NMR of compound 8g in CDCl_3	72
Figure S96. 128 MHz ^{11}B NMR of compound 8g in CDCl_3	72
2.22 Triazaborine 8h	73
Figure S97. 500 MHz ^1H NMR of compound 8h in CDCl_3	73
Figure S98. 125 MHz ^{13}C NMR of compound 8h in CDCl_3	74
Figure S99. 160 MHz ^{11}B NMR of compound 8h in CDCl_3	74
Figure S100. 50 MHz ^{15}N NMR of compound 8h in CDCl_3	75
Figure S101. 500 MHz ^1H – ^{15}N HMBC NMR of compound 8h in CDCl_3 (* CH_2 from ethanol).....	75
2.23 Oxazaborine–Triazaborine 9g	76
Figure S102. 400 MHz ^1H NMR of compound 9g in CDCl_3	76
Figure S103. 125 MHz ^{13}C NMR of compound 9g in CDCl_3	77
Figure S104. 160 MHz ^{11}B NMR of compound 9g in CDCl_3	77

Figure S105. 50 MHz ^{15}N NMR of compound 9g in CDCl_3	78
Figure S106. 500 MHz ^1H – ^{15}N HMBC NMR of compound 9g in CDCl_3	78
2.24 Oxazaborine–Triazaborine 9h	79
Figure S107. 500 MHz ^1H NMR of compound 9h in CDCl_3	79
Figure S108. 125 MHz ^{13}C NMR of compound 9h in CDCl_3	80
Figure S109. 160 MHz ^{11}B NMR of compound 9h in CDCl_3	80
Figure S110. 50 MHz ^{15}N NMR of compound 9h in CDCl_3	81
Figure S111. 500 MHz ^1H – ^{15}N HMBC NMR of compound 9h in CDCl_3	81
3. UV–Vis spectra	82
Figure S112. Normalized UV–VIS spectrum of oxazaborine 6g	82
Figure S113. UV–Vis spectrum in CH_2Cl_2 . (a) triazaborinone 5a and (b) triazaborinone 5b	82
Figure S114. UV–Vis spectrum in CH_2Cl_2 . (a) triazaborinone 5c and (b) triazaborinone 5d	82
Figure S115. UV–Vis spectrum in CH_2Cl_2 . (a) triazaborinone 5g and (b) triazaborinone 5h	83
Figure S116. UV–Vis spectrum in CH_2Cl_2 oxazaborine 6a	83
Figure S117. UV–Vis spectrum in CH_2Cl_2 . (a) oxazaborine 6e and (b) oxazaborine 6f	83
Figure S118. UV–Vis spectrum in CH_2Cl_2 . (a) oxazaborine 6g and (b) oxazaborine 6h	84
Figure S119. UV–Vis spectrum in CH_2Cl_2 . (a) diazaborine 7a and (b) diazaborinone 7b	84
Figure S120. UV–Vis spectrum in CH_2Cl_2 . (a) diazaborine 7c and (b) diazaborinone 7d	84
Figure S121. UV–Vis spectrum in CH_2Cl_2 . (a) diazaborine 7e and (b) diazaborinone 7f	85
Figure S122. UV–Vis spectrum in CH_2Cl_2 . (a) diazaborine 7g and (b) diazaborinone 7h	85
Figure S123. UV–Vis spectrum in CH_2Cl_2 . (a) triazaborine 8e and (b) triazaborine 8h	85
Figure S124. UV–Vis spectrum in CH_2Cl_2 . (a) oxazaborine–triazaborine 9g and (b) oxazaborine–triazaborine 9h	86
Table S1. UV–Vis parameters of prepared heterocyclic compounds in CH_2Cl_2	87
Table S2. UV–Vis parameters of triazaborine 5g . λ_{max} (nm), ϵ ($\text{l}\cdot\text{cm}^{-1}\text{mol}^{-1}$)	88
Table S3. UV–Vis parameters of oxazaborine 6g . λ_{max} (nm), ϵ ($\text{l}\cdot\text{cm}^{-1}\text{mol}^{-1}$)	88
Table S4. UV–Vis parameters of diazaborinone 7a . λ_{max} (nm), ϵ ($\text{l}\cdot\text{cm}^{-1}\text{mol}^{-1}$)	88
4. Crystallographic data	89
Table S5. Crystal data.	89
Figure S125. ORTEP view of the crystal structure of 5c in the direction of the crystallographic axis <i>a</i>	90
Figure S126. ORTEP view of the crystal structure of 5c in the direction of the crystallographic axis <i>c</i>	91
Figure S127. ORTEP view of the crystal structure of 5c in the direction of the reciprocal cell axis <i>b</i> [*]	92
Figure S128. Triazaborine 5c . The planes on which the double bonds C=N, C=N, and C=O lie.	93
Figure S129. ORTEP view of the crystal packing of triazaborinone 5d in the direction of the crystallographic axis <i>a</i>	94
Figure S130. ORTEP view of the crystal packing of triazaborinone 5d in the direction of the crystallographic axis <i>b</i>	95

Figure S131. ORTEP view of the crystal structure of 5g in the direction of the crystallographic axis <i>b</i> .	96
Figure S132. ORTEP diagram of the oxazaborine 6a asymmetric unit.	97
Figure S133. ORTEP view of the π – π stacking chain of 6e in the direction of the crystallographic axis <i>c</i> .	98
Figure S134. ORTEP view of the crystal structure of 6e in the direction of the crystallographic axis <i>b</i> .	99
Figure S135. ORTEP view of the crystal packing of diazaborinone 7f in the direction of the crystallographic axis <i>a</i> .	100
Figure S136. ORTEP view of the crystal packing of diazaborinone 7f in the direction of the crystallographic axis <i>b</i> .	101
5. Fluorescence	102
Figure S137. Triazaborinone 5g . (a) Absorption spectrum and (b) Emission spectrum.	102
Figure S138. Triazaborinone 5h . (a) Absorption spectrum and (b) Emission spectrum.	102
Figure S139. Diazaborinone 7a . (a) Absorption spectrum and (b) Emission spectrum.	102

1. Experimental

1.1 General Information

All chemicals and dried dichloromethane except those mentioned below were purchased from commercial suppliers (Acros Organics, Sigma-Aldrich, or Fluorochem). Toluene and diethylether were dried over sodium.

NMR spectra were measured in CDCl₃ or in DMSO-*d*₆ using a Bruker AVANCE III 400 spectrometer operating at 400 MHz (¹H) and 100 MHz (¹³C) or using a Bruker Ascend 500 spectrometer operating at 500 MHz (¹H), 125 MHz (¹³C), 160 MHz (¹¹B), and 50 MHz (¹⁵N). All of the pulse sequences were taken from the Bruker software library. The ¹³C NMR spectra were measured in a standard way and by means of the APT pulse sequence. The data are reported as follows. chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, q = quartet, m = multiplet, br s = broad singlet, br q = broad quartet). The coupling constants *J* are reported in Hertz (Hz). TMS was used as an internal standard for ¹H NMR in CDCl₃ (δ 0.00). CDCl₃ was used as an internal standard for ¹³C NMR (the middle signal, δ 77.16). B(OMe)₃ was used as an external standard for ¹¹B NMR (δ 18.1). Nitromethane was used as an external standard for ¹⁵N NMR (δ 0.00). DMSO-*d*₆ was used as an internal standard for both ¹H NMR (the middle signal δ 2.55) and ¹³C NMR (the middle signal δ 39.6).

Elemental analyses were performed on a Flash 2000 CHNS Elemental Analyzer.

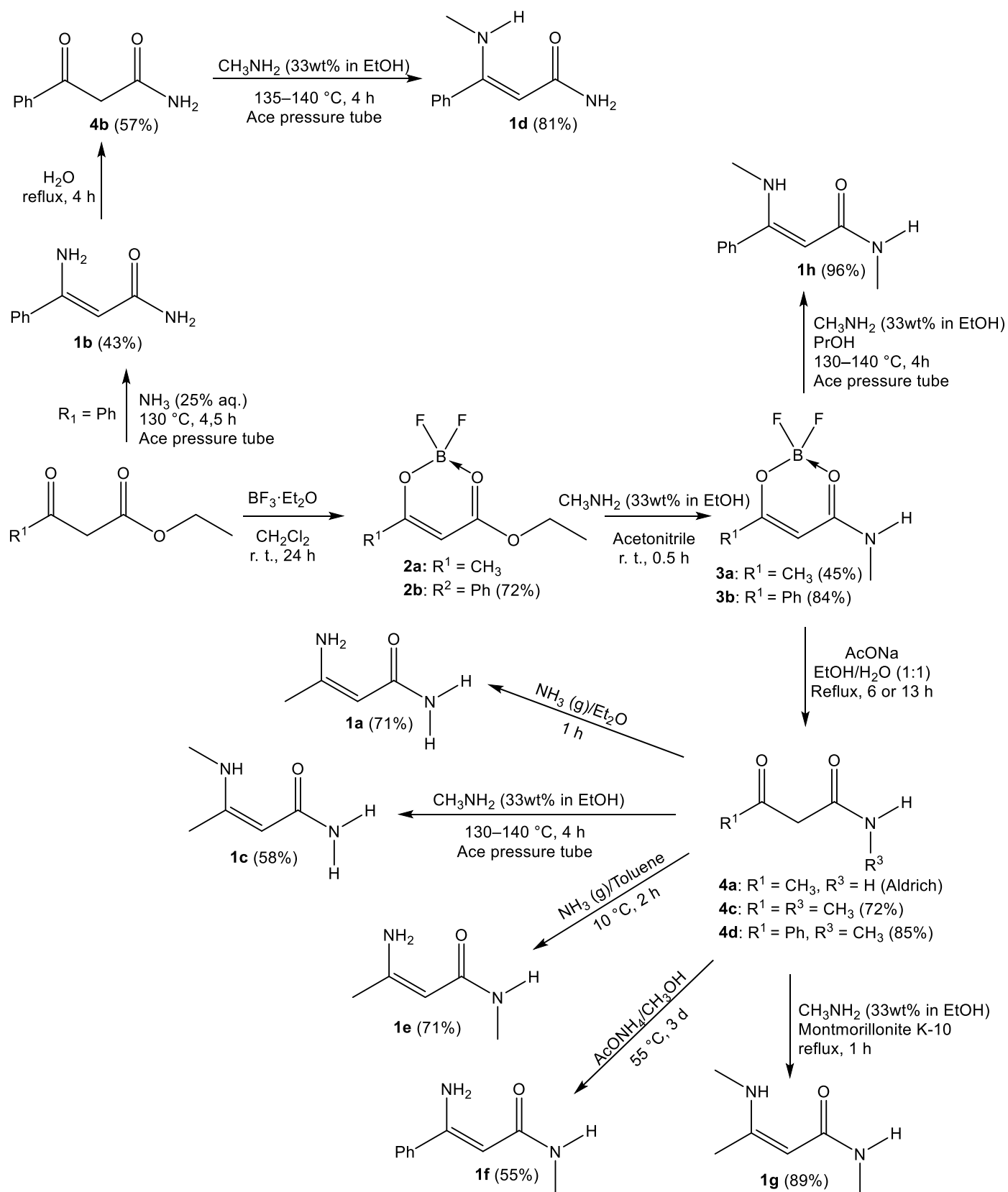
Melting points were measured on a Kofler Boetius PHMK 80/2644 hot-stage microscope and were not corrected.

High-resolution mass spectra were recorded on a MALDI LTQ Orbitrap XL (Thermo Fisher Scientific) equipped with a nitrogen UV laser (337 nm, 60 Hz, 8–20 μ J) in the positive ion mode. For the CID experiment using the linear trap quadrupole (LTQ) helium was used as the collision gas and 2,5-dihydroxybenzoic acid (DHB) as the MALDI matrix.

UV-Vis spectra were recorded on a UV-Vis spectrophotometer Hewlett-Packard 8453. IR spectra were recorded on a Nicolet iS50 equipped with an ATR diamond crystal (neat solid samples). The wavenumber range 2500–1700 cm⁻¹ is excluded due to diamond absorption.

Steady-state and time-resolved PL measurements were performed based on a multifunctional spectrometer with L-geometry of excitation-detection pathways (FluoTime 300, PicoQuant). A Xenon arc lamp and a PMT were used as the excitation sources and detectors for PL experiments. The PL-QY value can be obtained based on the spectrometer incorporated with an integrating sphere. Excitation wavelength. 360 nm. Range. 340–700 nm.

Crystal data for all compounds were collected at 295 K using a Nonius Kappa CCD diffractometer with graphite monochromated Mo-K α radiation (λ = 0.71073 Å). The data sets were integrated with the Denzo SMN package and corrected for Lorentz, polarization, and absorption effects (SORTAV). Structures were solved by direct methods using the SIR97 system of programs and refined anisotropically by using full-matrix least-squares for all non-hydrogen atoms and hydrogen atoms included on their calculated positions, riding on their carrier atoms; except the N–H hydrogens forming intramolecular hydrogen bonds, which were refined isotropically. All calculations were performed by using SHELXL 2014/6, PARST and PLATON implemented in WINGX system of programs. Visualisation of structures was done with MERCURY 2020.2.0.



Scheme S1. Preparation of starting compounds.

2. NMR spectra

2.1 Triazaborinone 5a

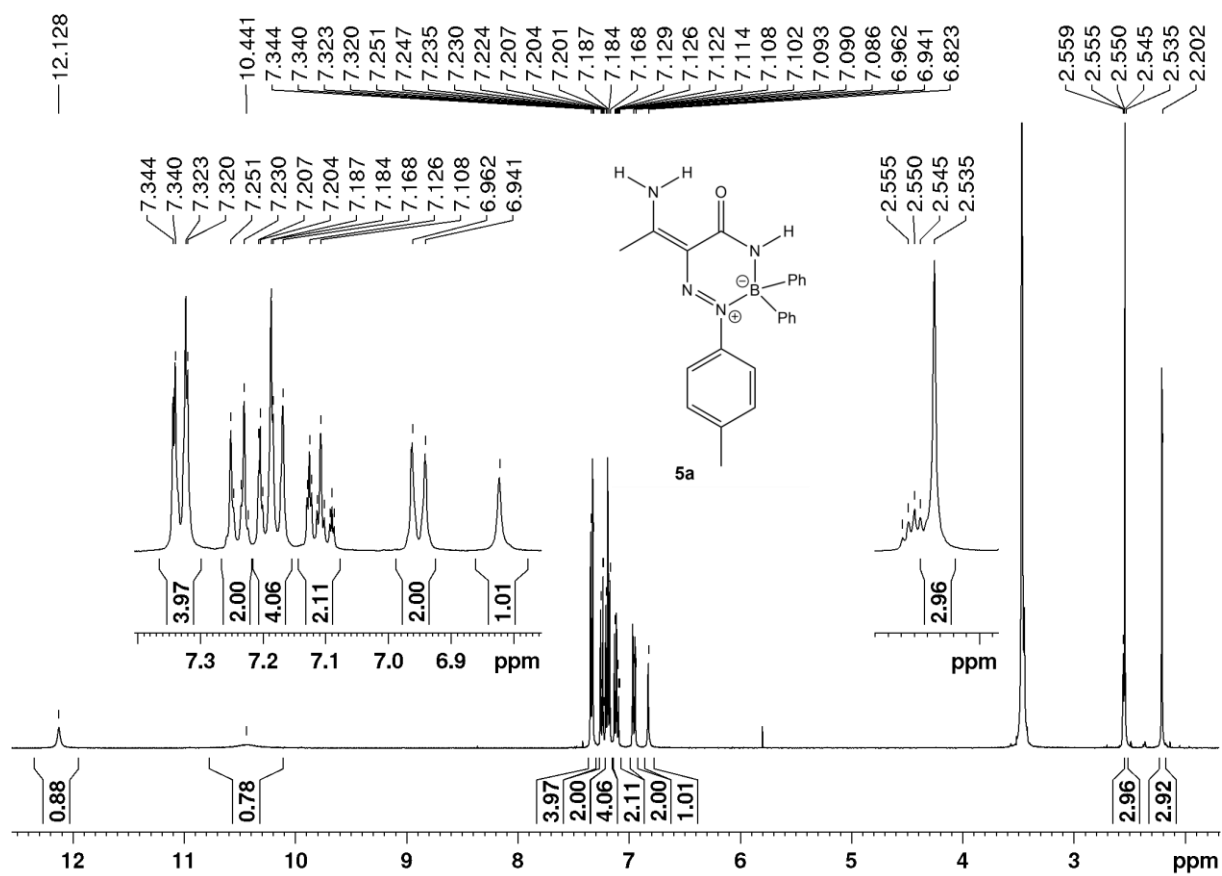
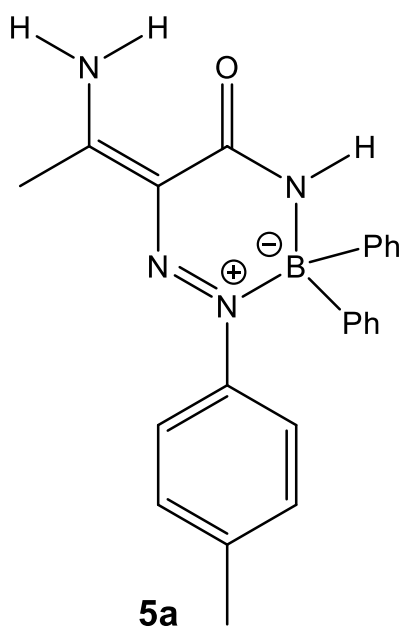


Figure S1. 400 MHz ^1H NMR of compound 5a in $\text{DMSO}-d_6$

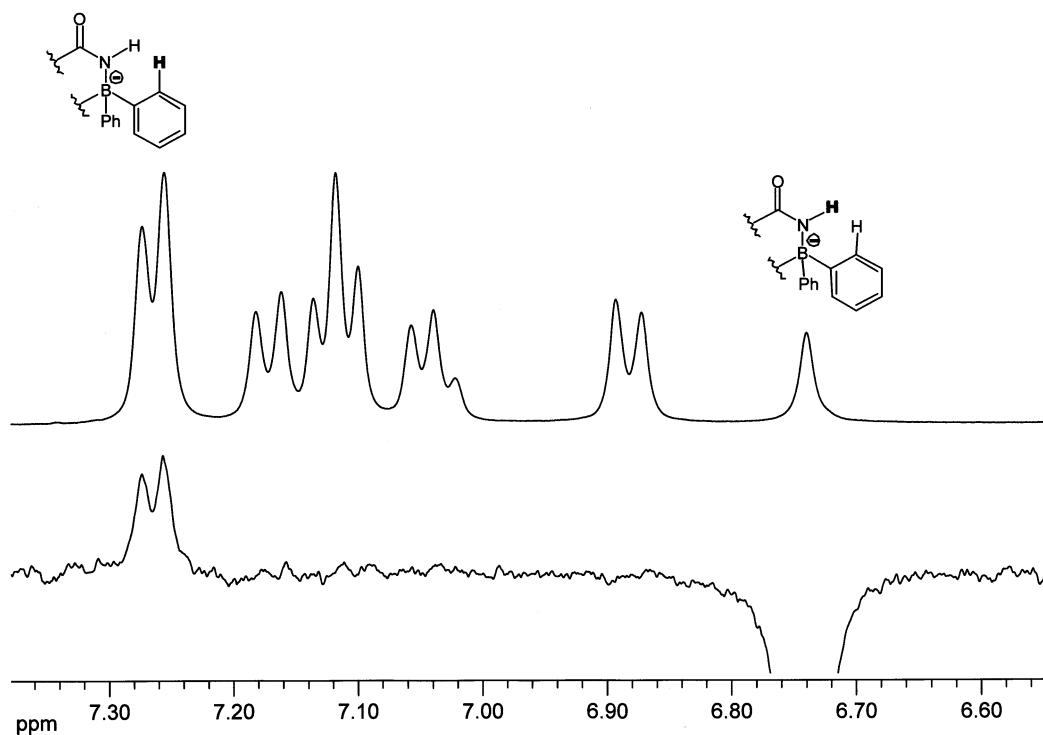


Figure S2. 400 MHz 1D-NOESY (mixing time d8 = 800 ms, relaxation delay d1 = 2s) of compound **5a** in DMSO- d_6

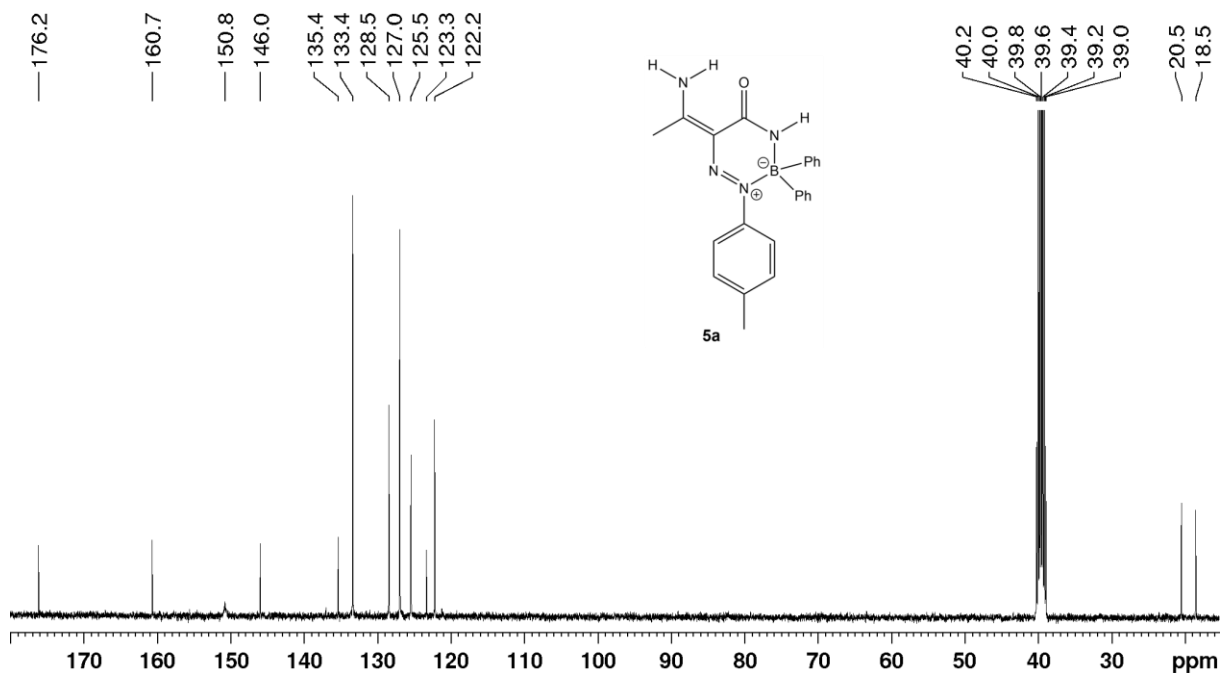


Figure S3. 100 MHz ^{13}C NMR of compound **5a** in DMSO- d_6

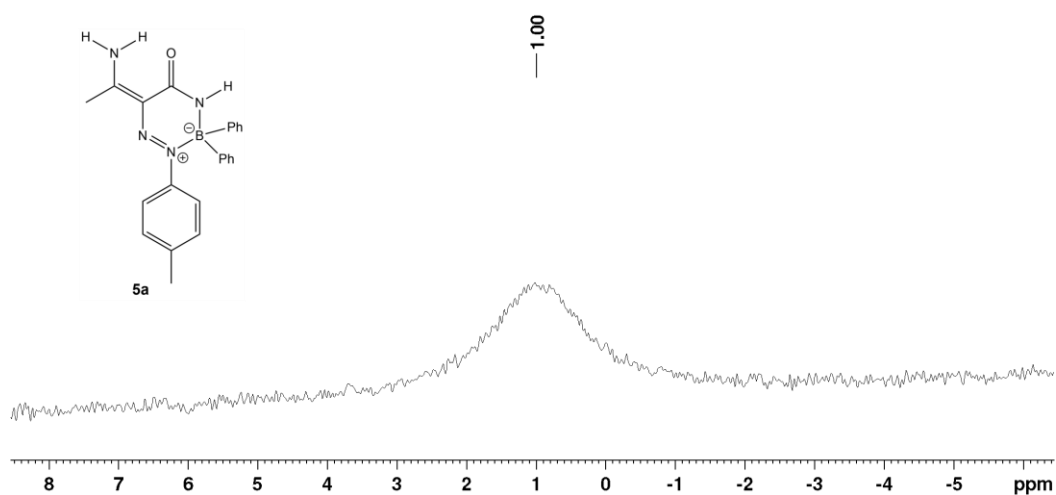


Figure S4. 160 MHz ^{11}B NMR of compound 5a in CDCl_3

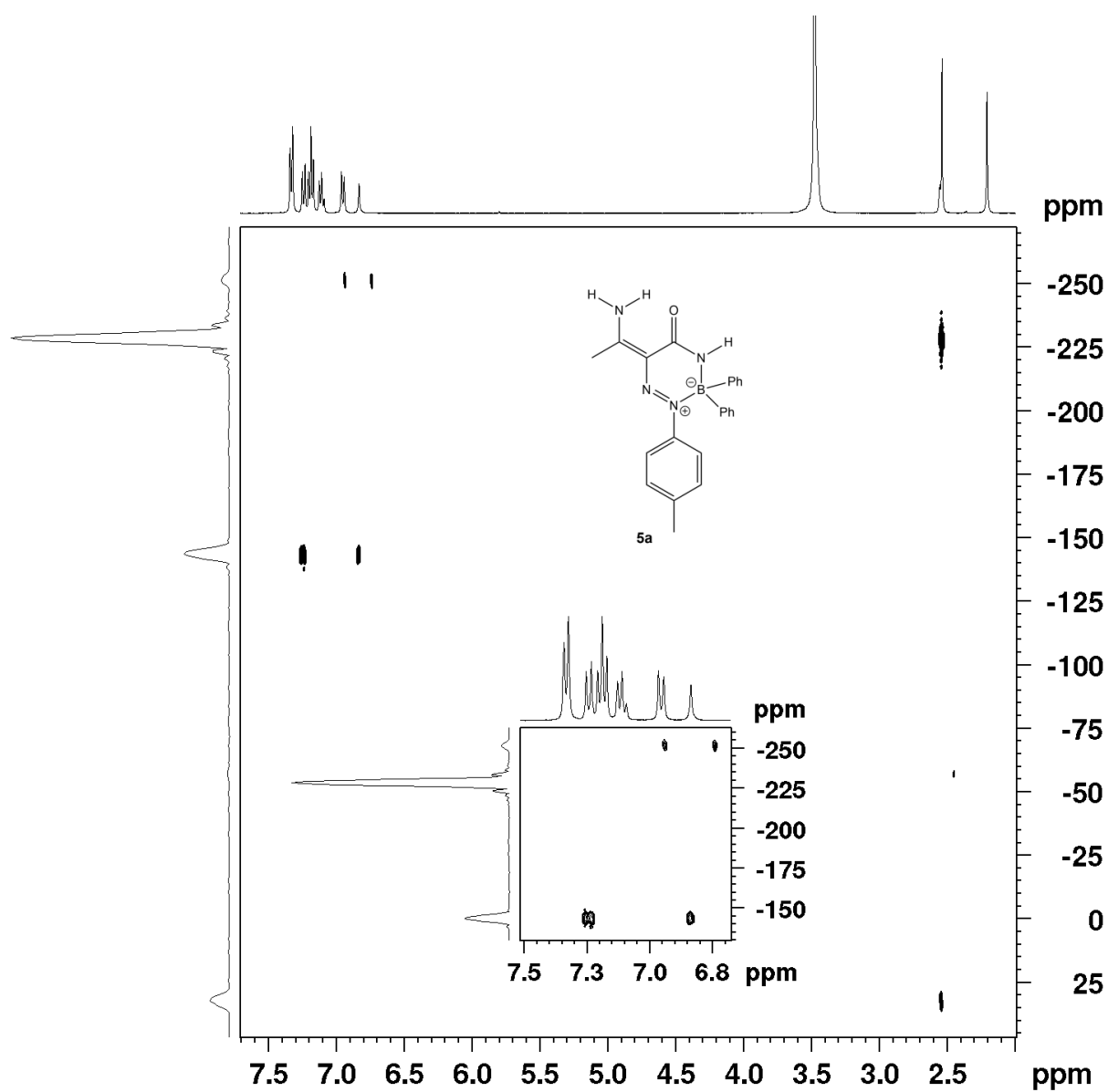


Figure S5. 500 MHz ^1H - ^{15}N HMBC NMR of compound 5a in $\text{DMSO}-d_6$

2.2 Triazaborinone 5b

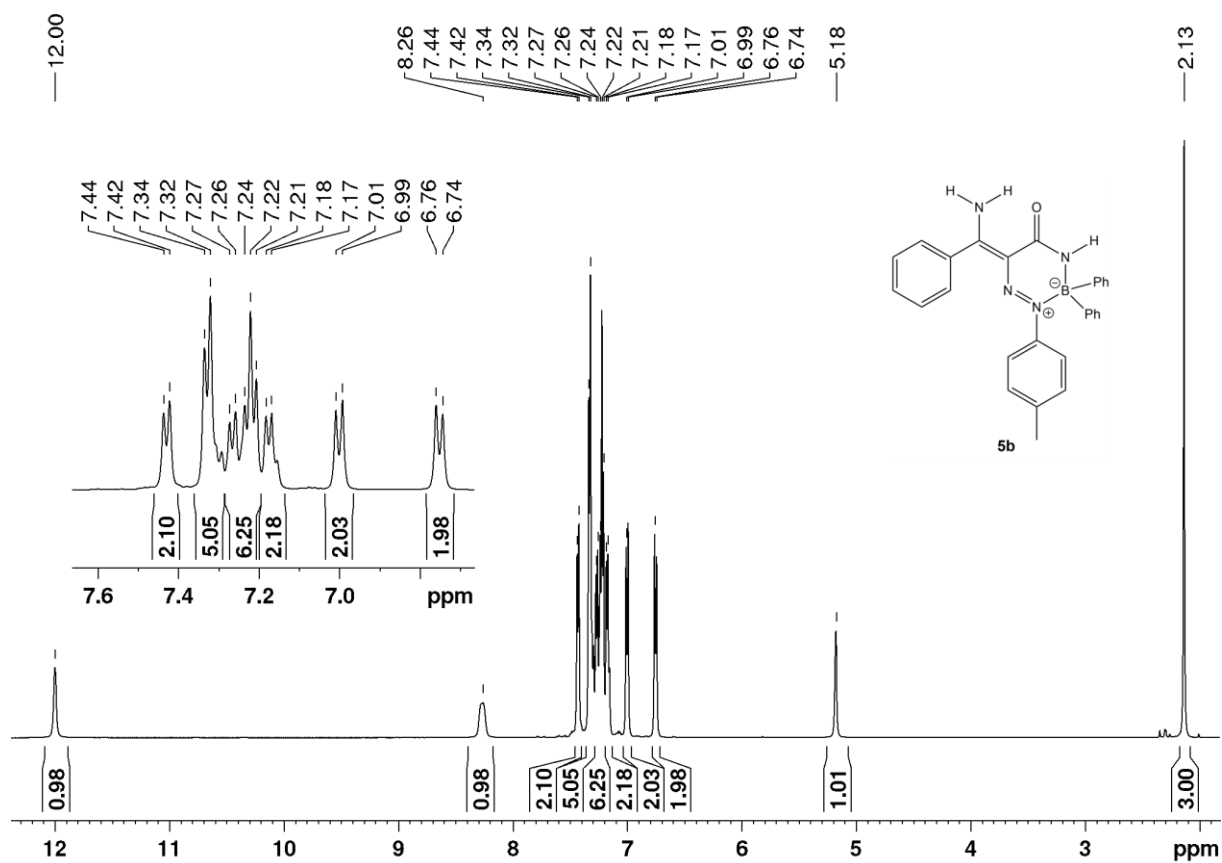
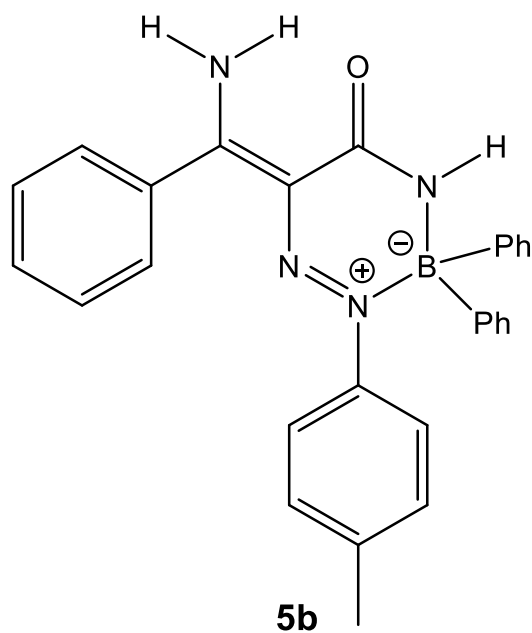


Figure S6. 500 MHz ^1H NMR of compound **5b** in CDCl_3

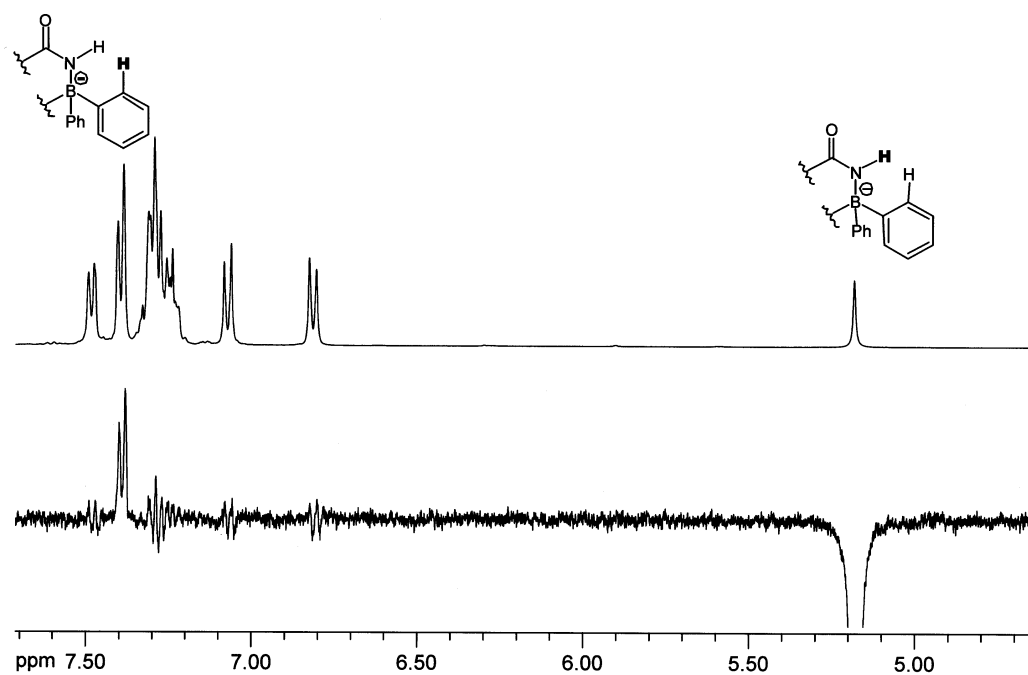


Figure S7. 400 MHz 1D-NOESY (mixing time d8 = 800 ms, relaxation delay d1 = 2s) of compound **5b** in CDCl₃

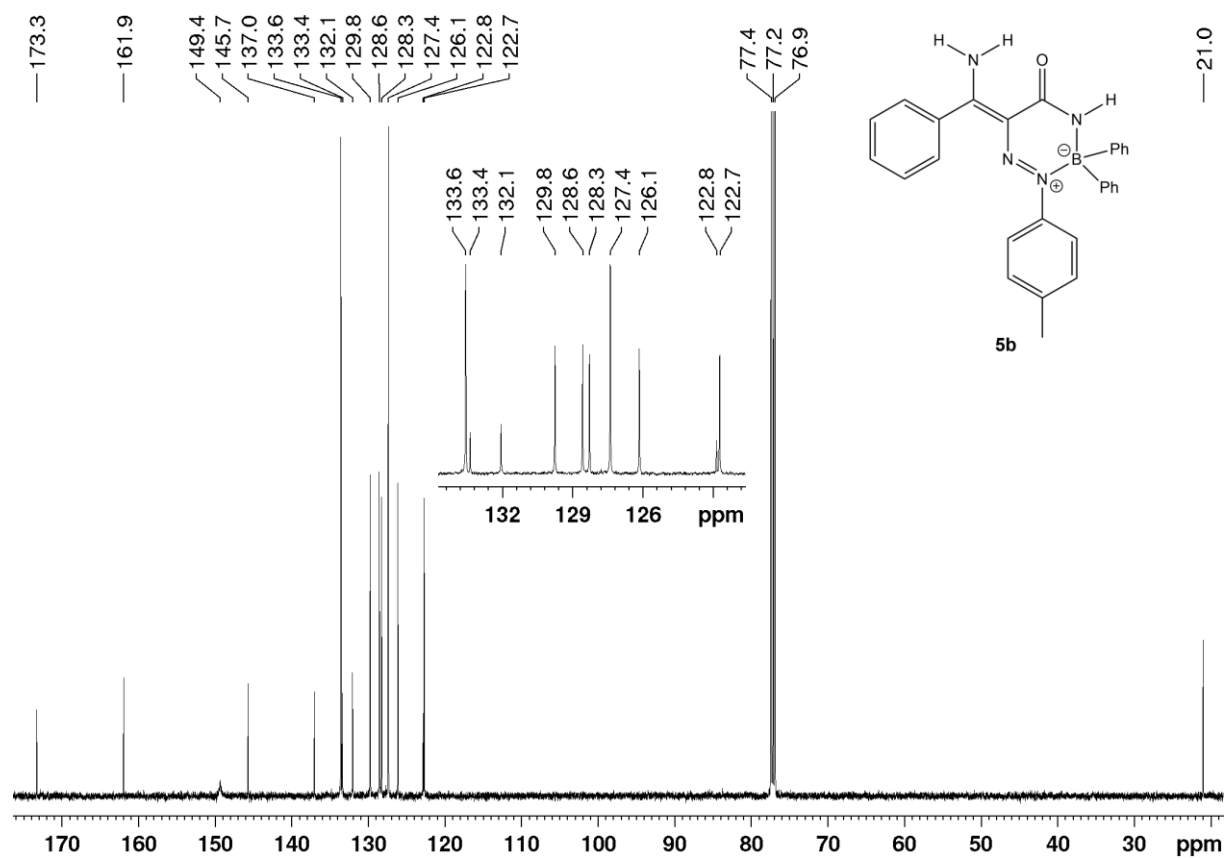


Figure S8. 125 MHz ¹³C NMR of compound **5b** in CDCl₃

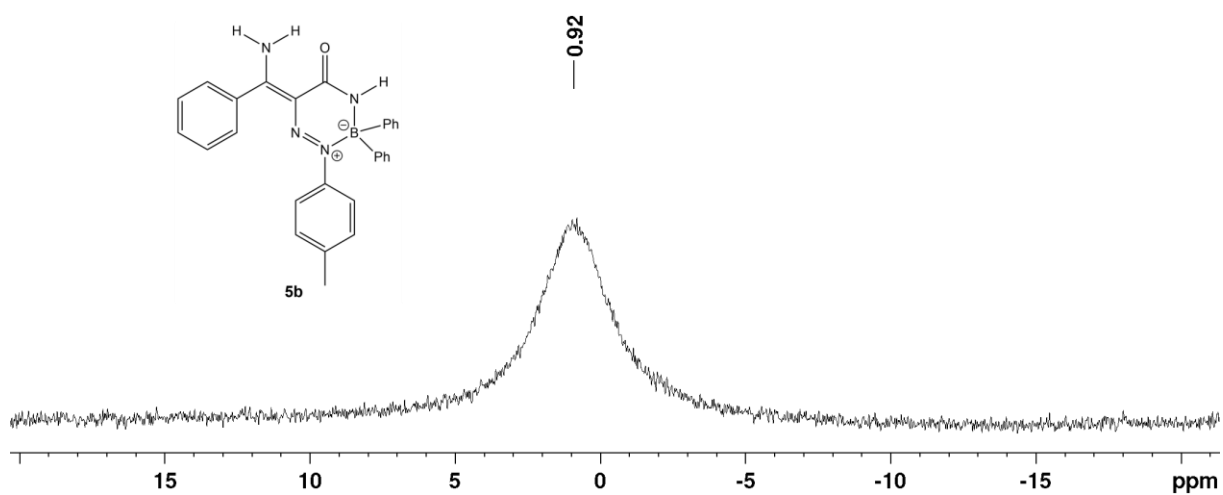


Figure S9. 128 MHz ^{11}B NMR of compound 5a in CDCl_3

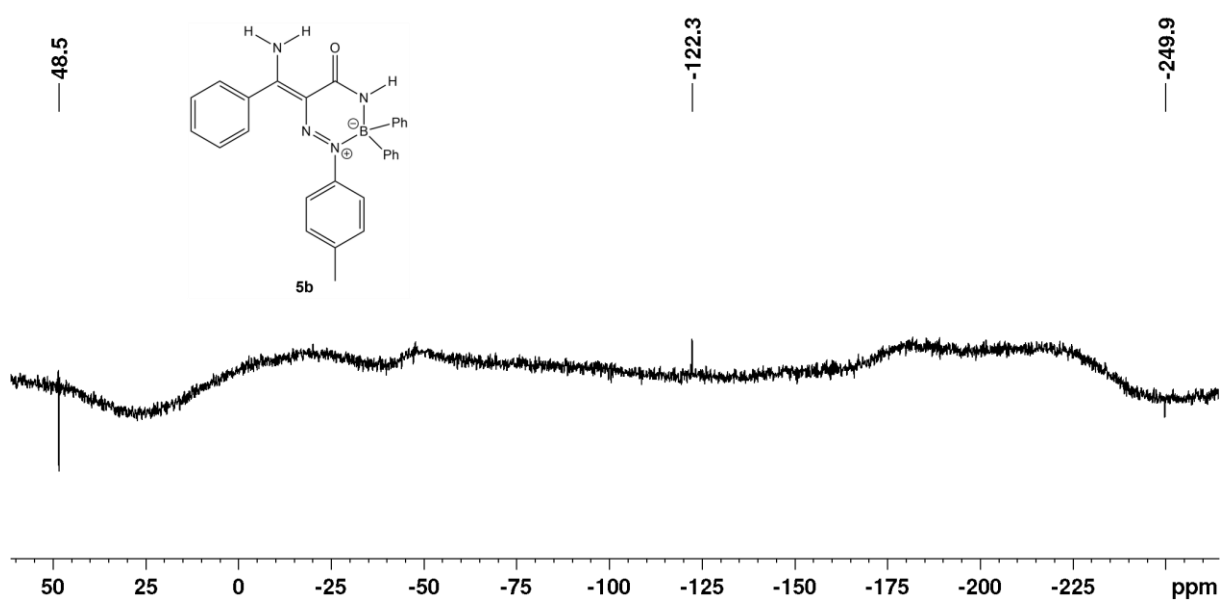


Figure S10. 50 MHz ^{15}N NMR of compound 5a in $\text{DMSO}-d_6$

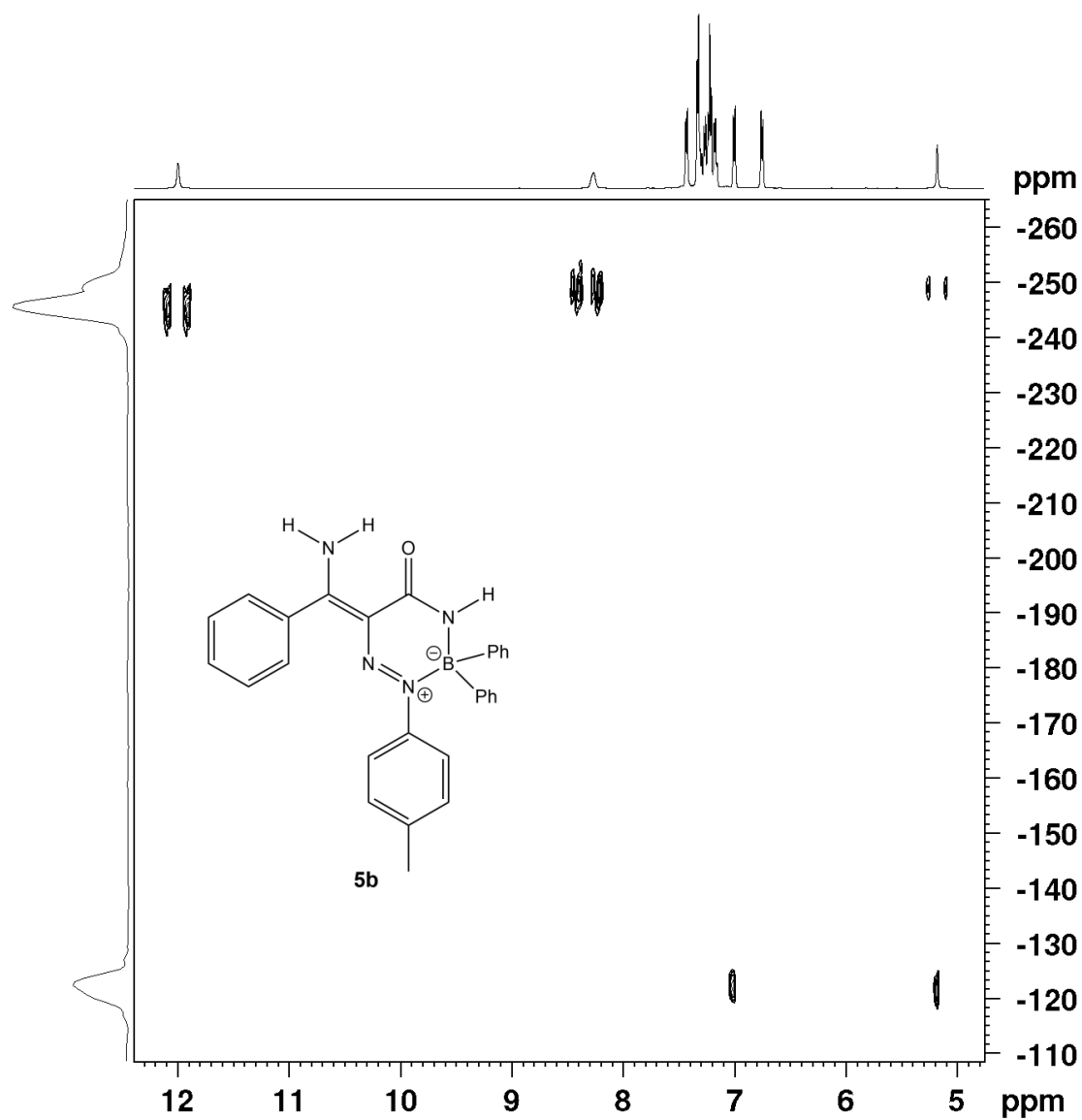


Figure S11. 500 MHz ^1H - ^{15}N HMBC NMR of compound **5b** in CDCl_3

2.3 Triazaborinone 5c

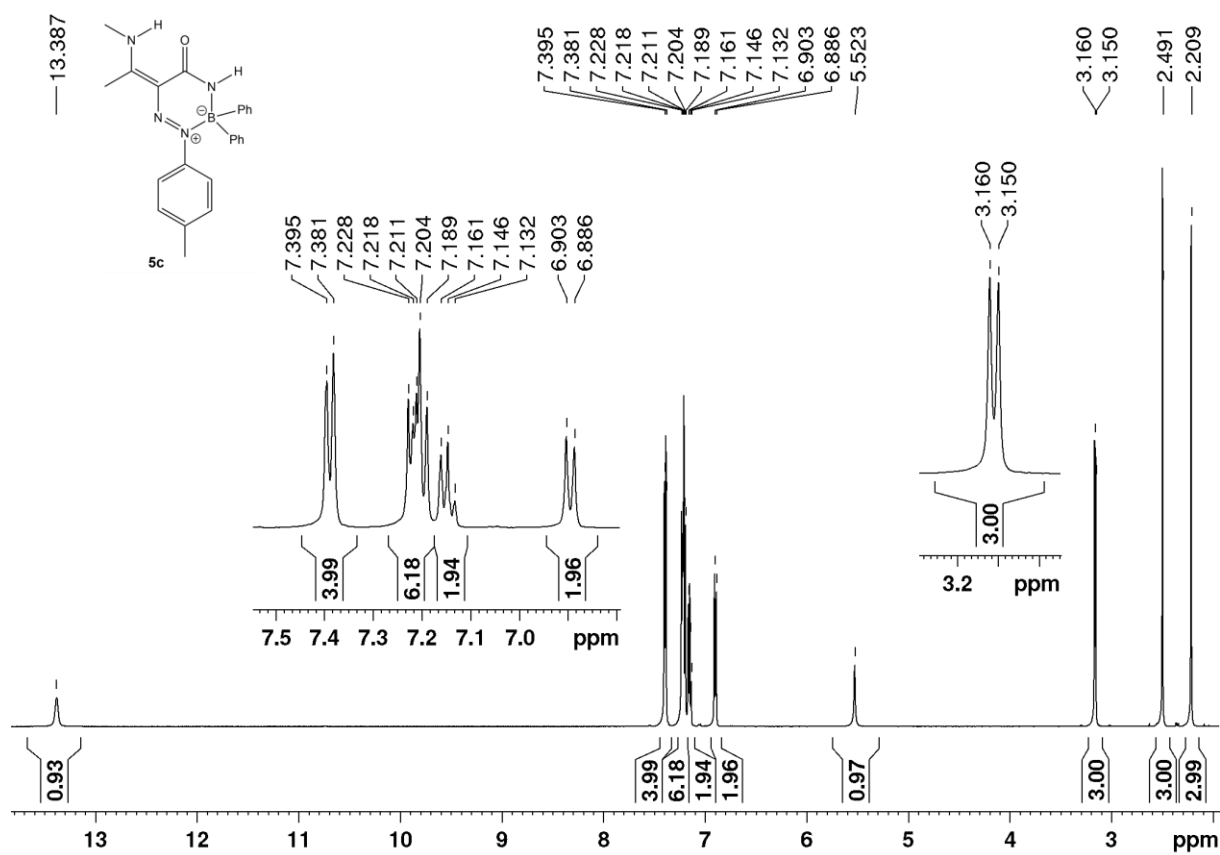
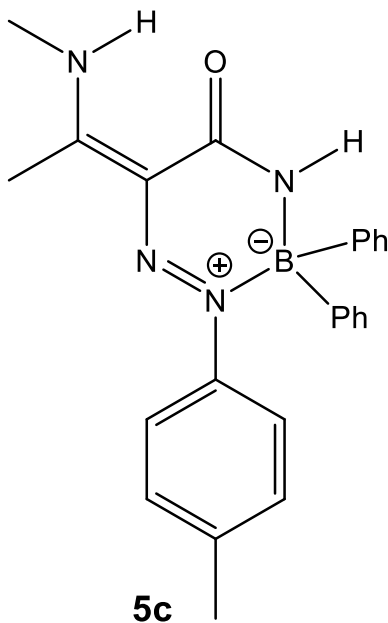


Figure S12. 500 MHz ^1H NMR of compound 5c in CDCl_3

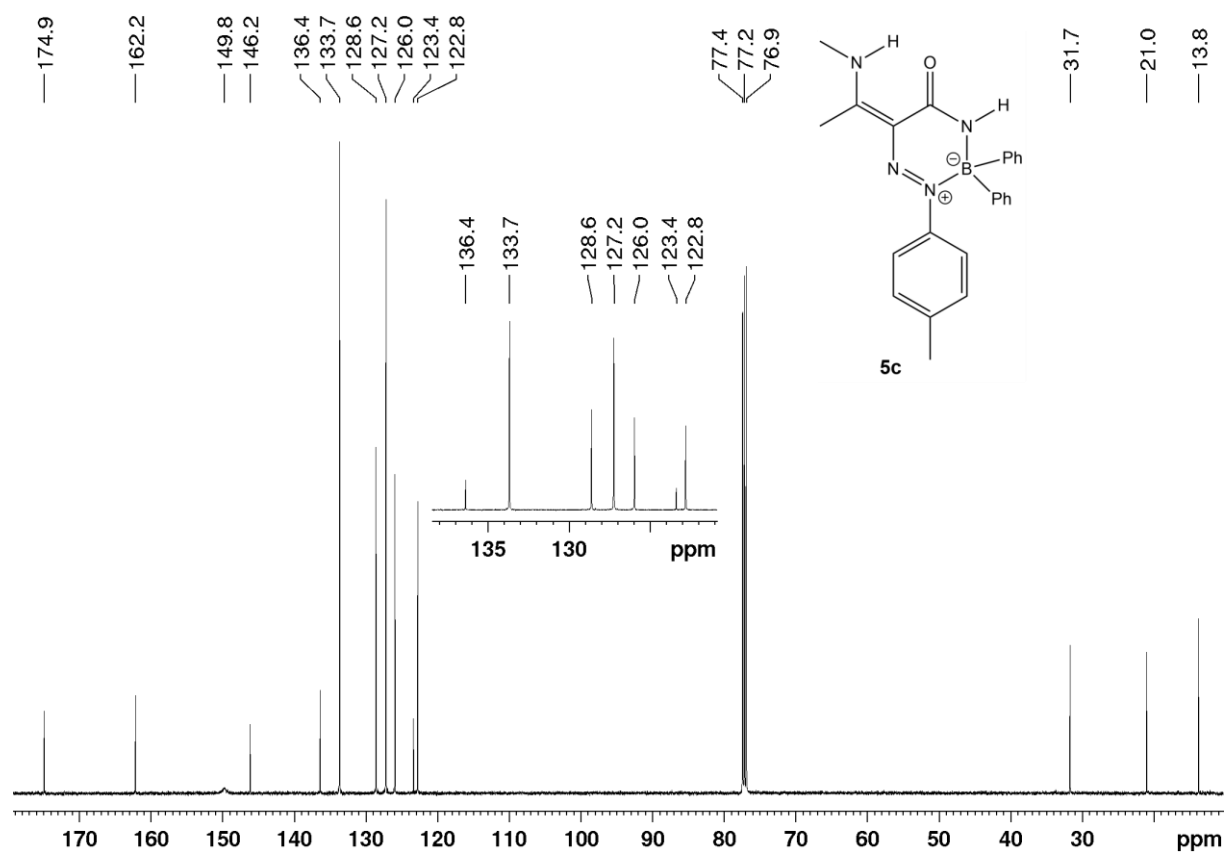


Figure S13. 125 MHz ^{13}C NMR of compound **5c** in CDCl_3

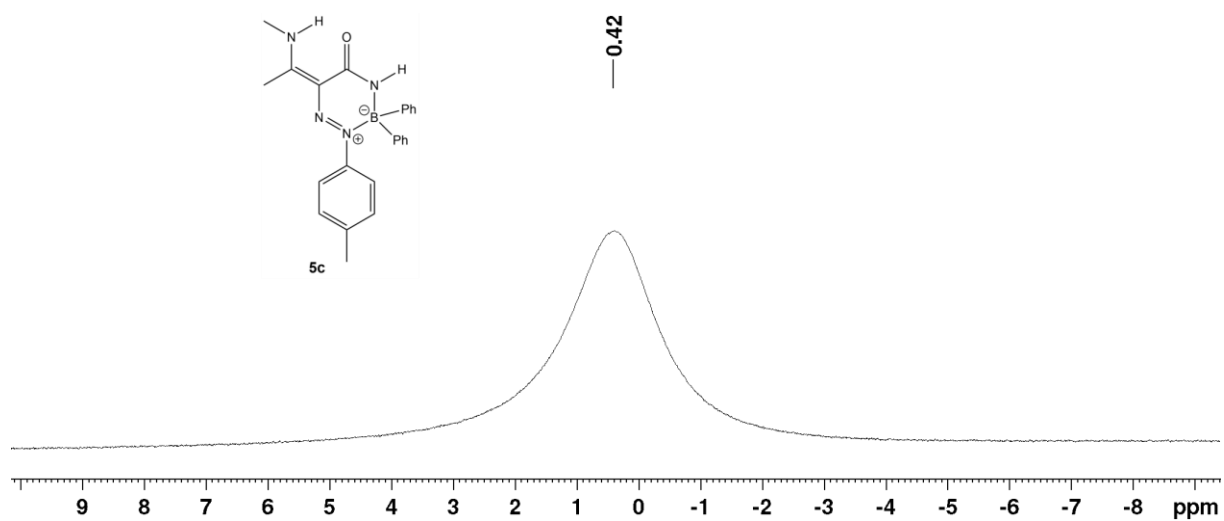


Figure S14. 160 MHz ^{11}B NMR of compound **5c** in CDCl_3

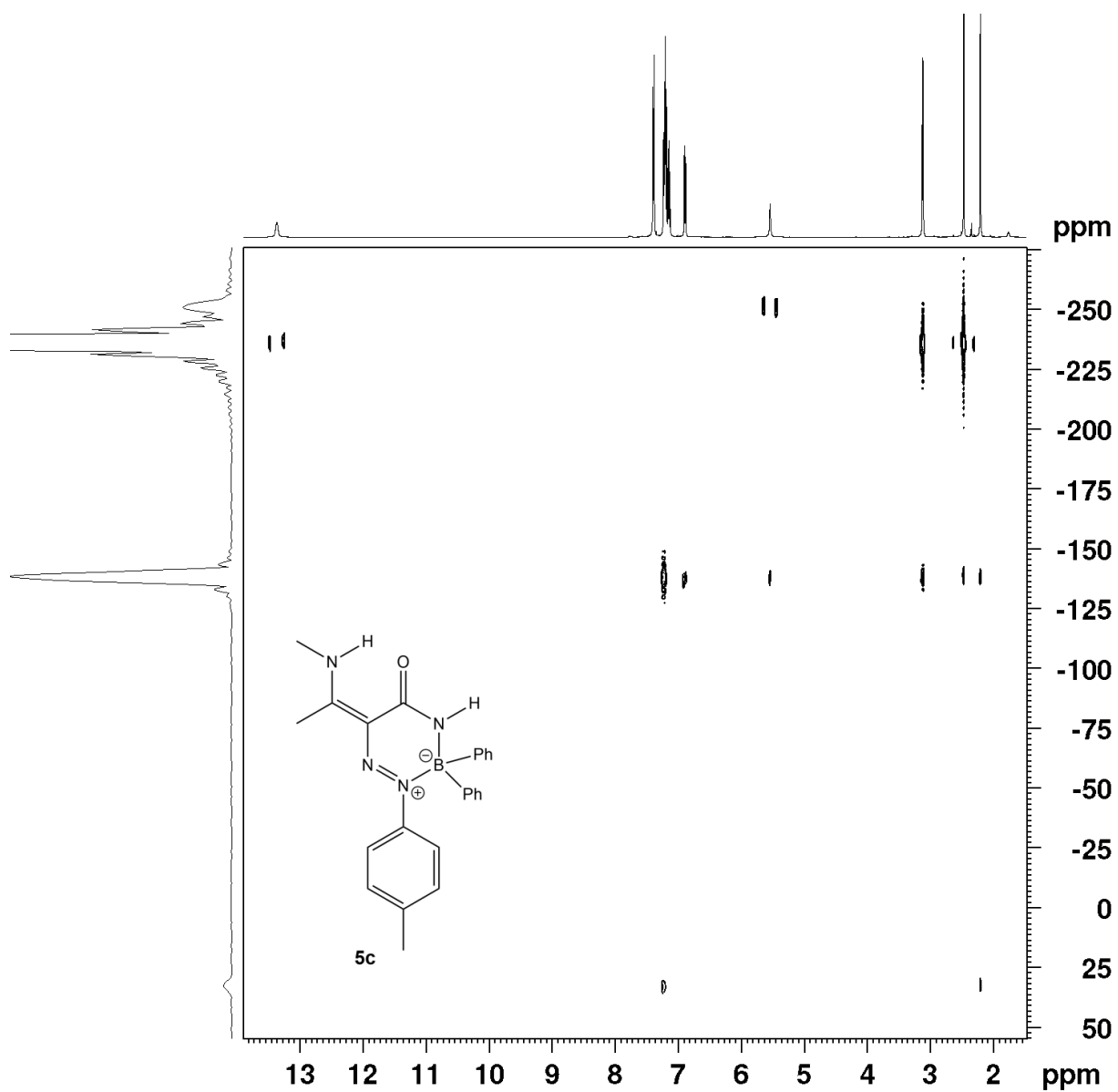


Figure S15. 500 MHz ^1H - ^{15}N HMBC NMR of compound **5c** in CDCl_3

2.4 Triazaborinone 5d

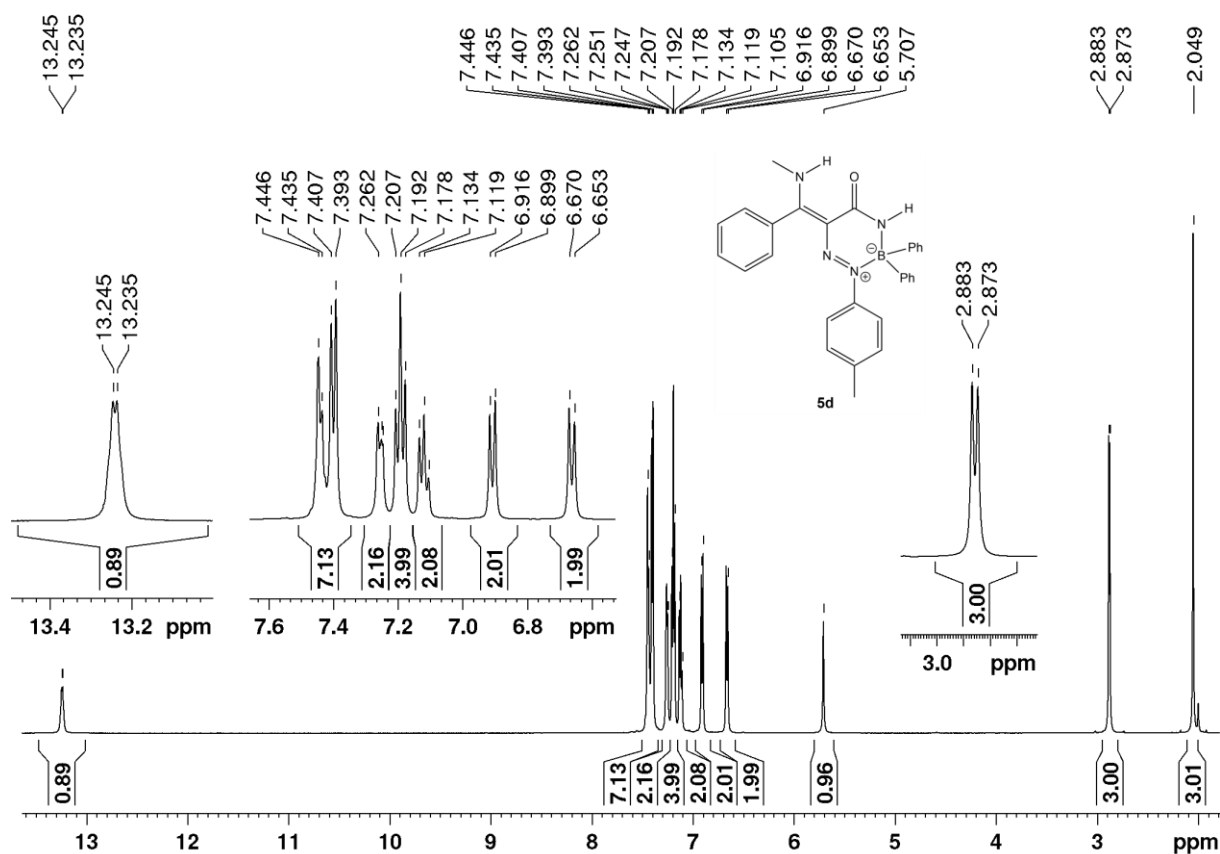
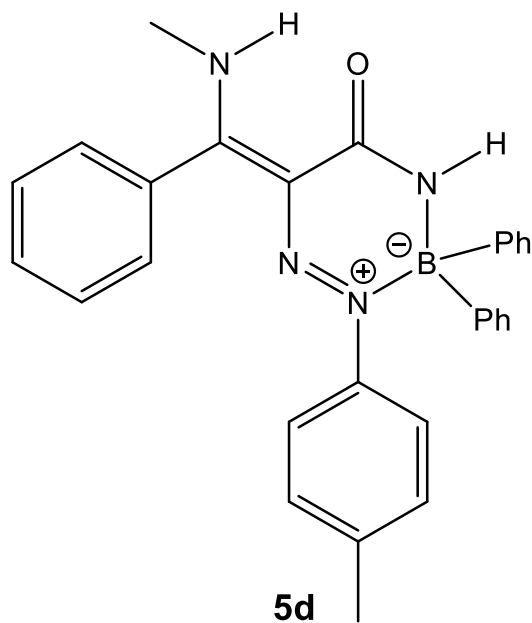


Figure S16. 500 MHz ^1H NMR of compound **5d** in CDCl_3

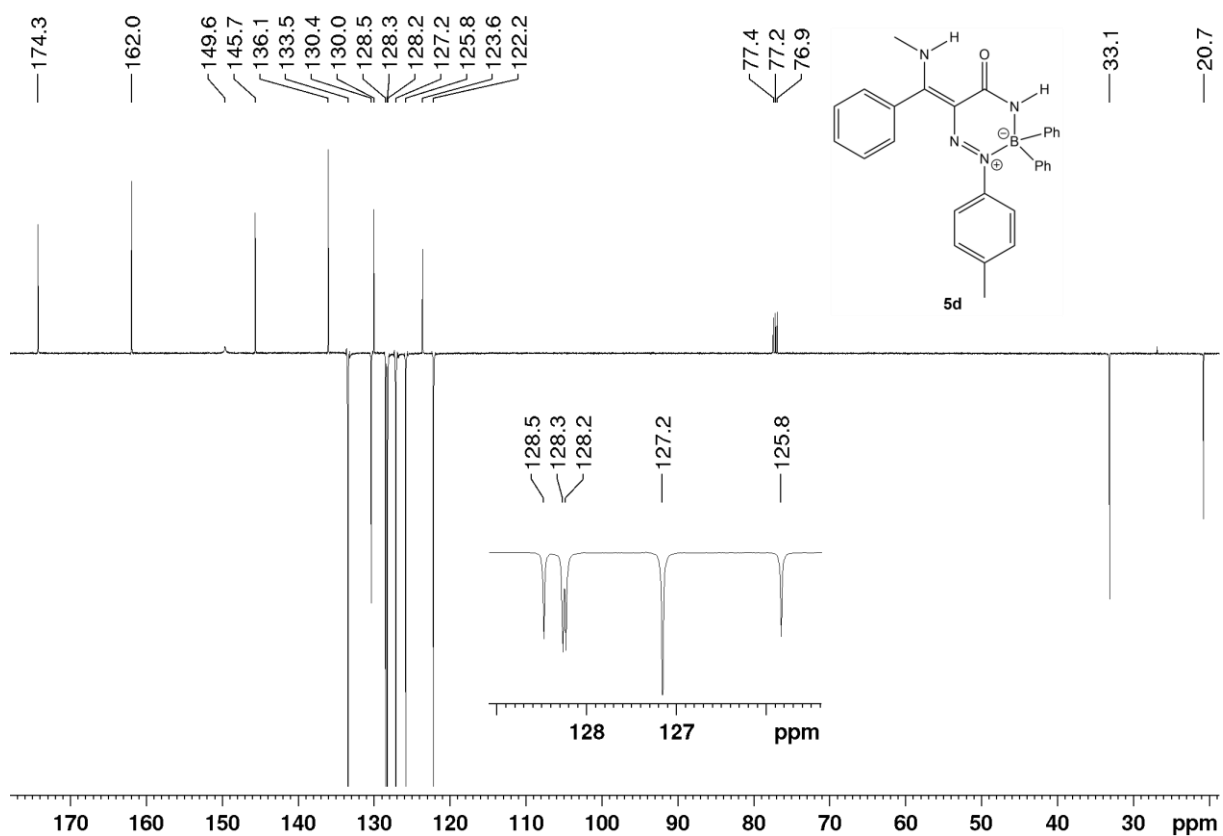


Figure S17. 125 MHz ¹³C APT NMR of compound **5d** in CDCl₃

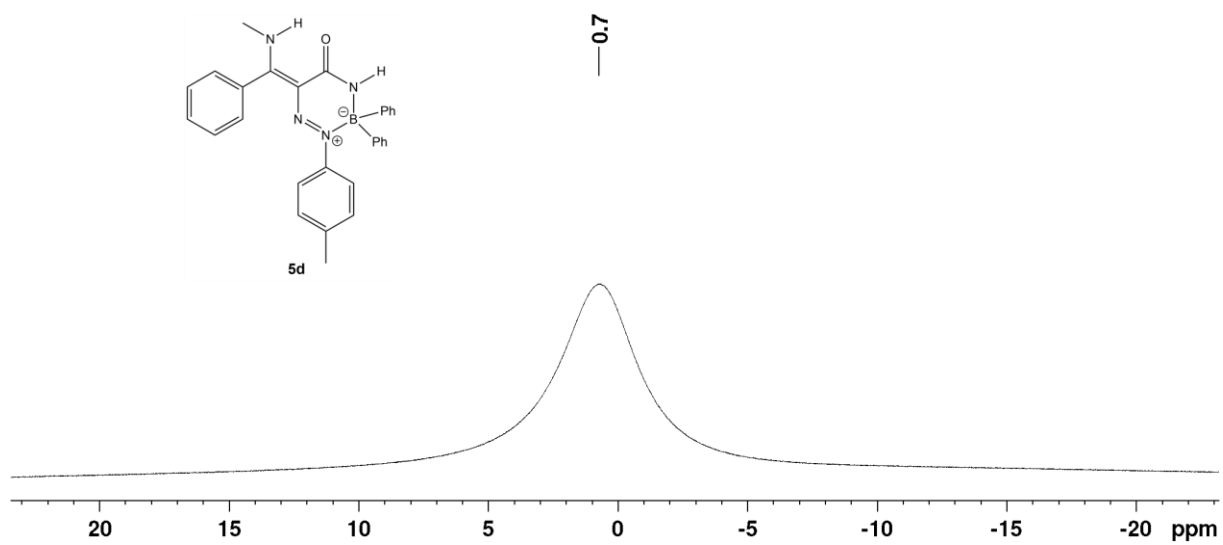


Figure S18. 160 MHz ¹¹B NMR of compound **5c** in CDCl₃

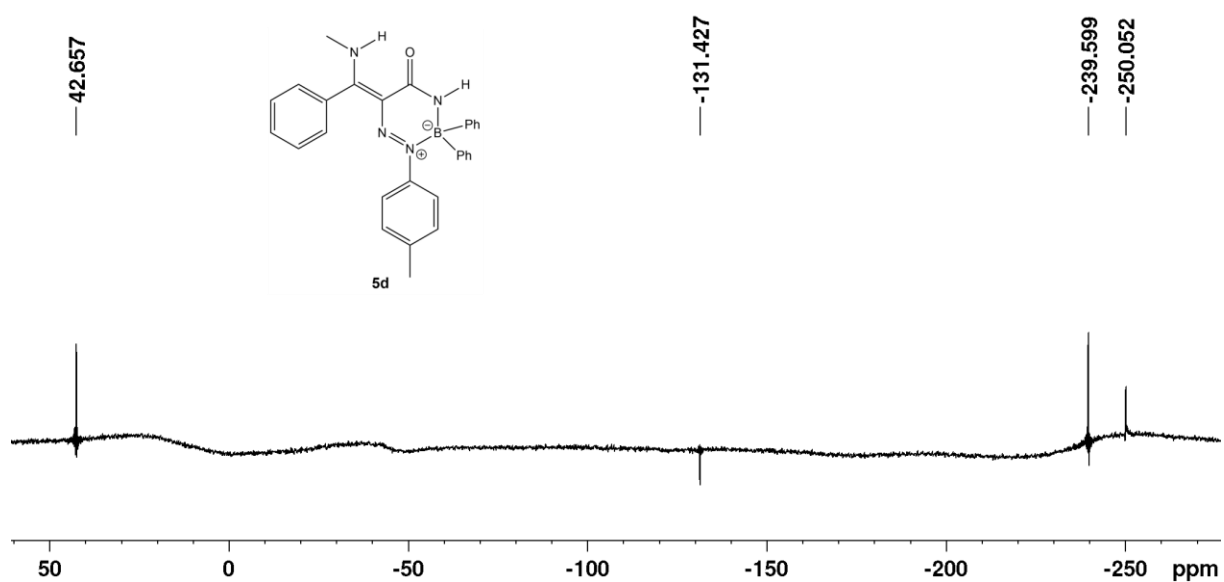


Figure S19. 50 MHz ^{15}N NMR of compound **5d** in CDCl_3

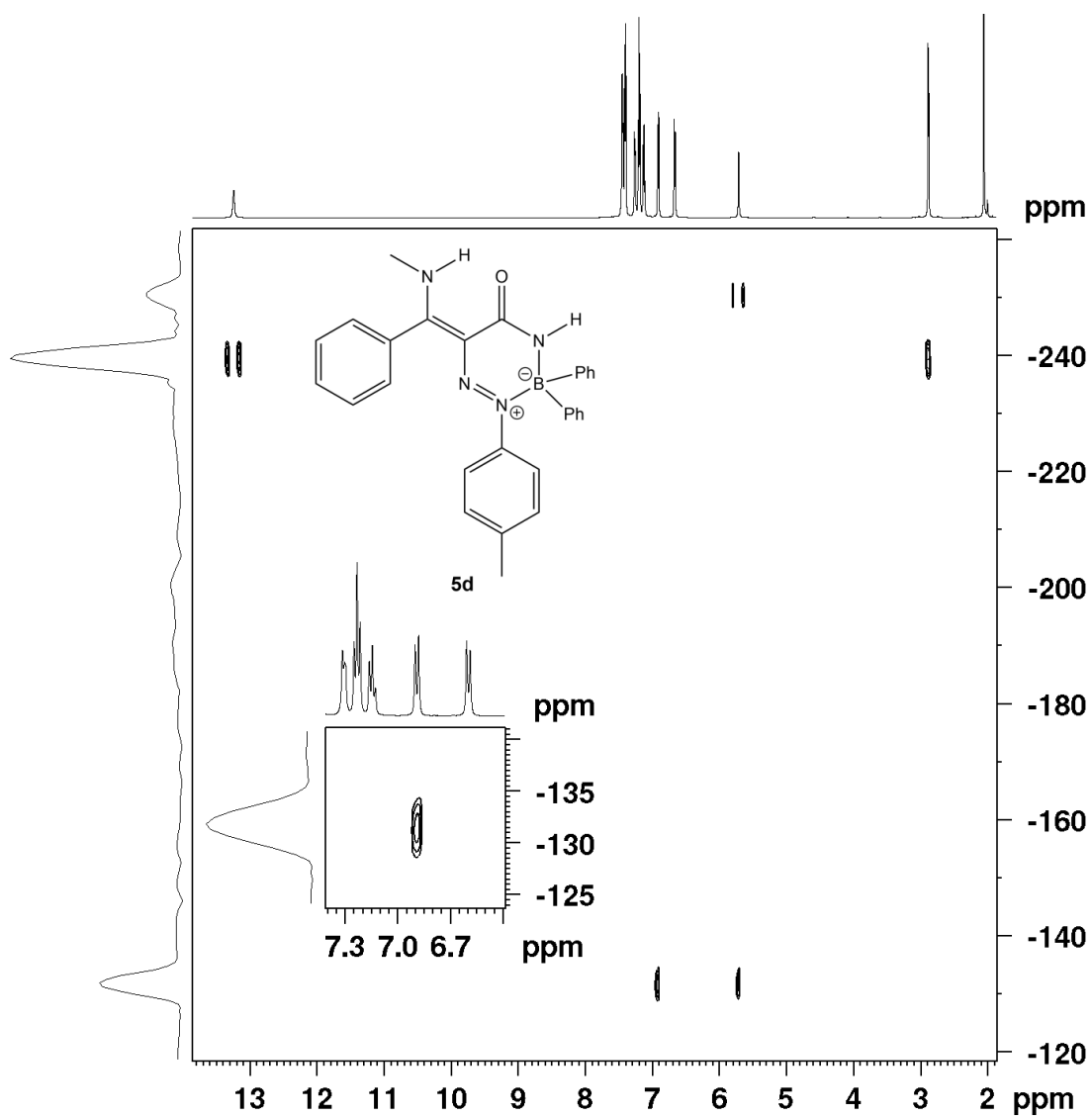


Figure S20. 500 MHz ^1H - ^{15}N HMBC NMR of compound **5d** in CDCl_3

2.5 Triazaborinone 5g

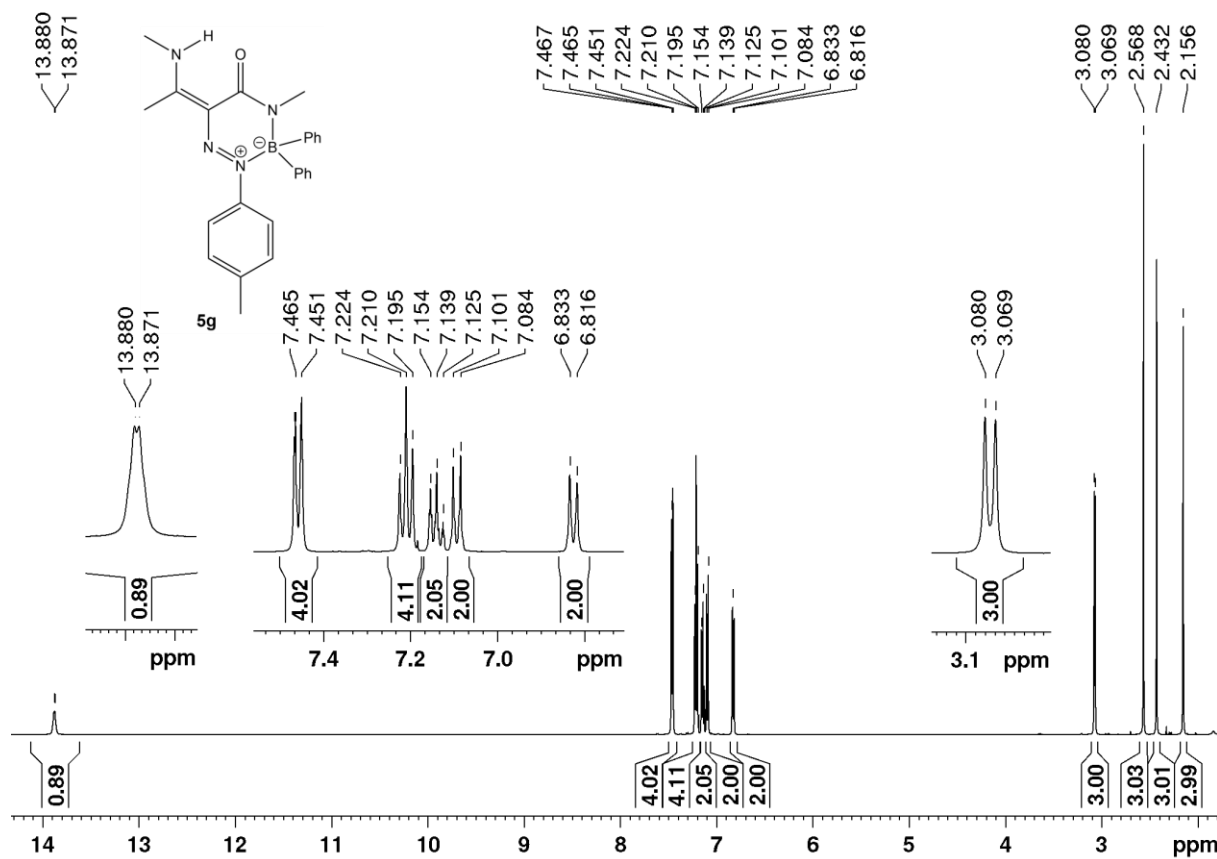
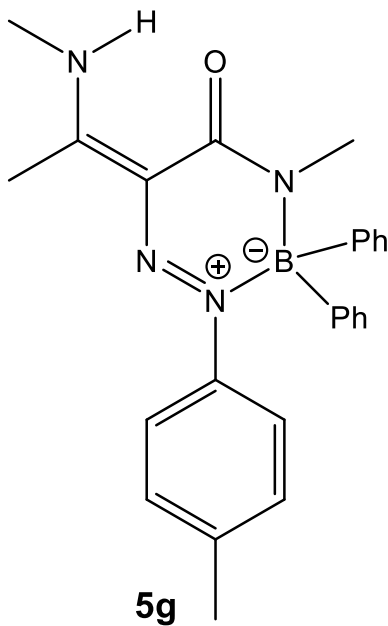


Figure S21. 500 MHz ^1H NMR of compound **5g** in CDCl_3

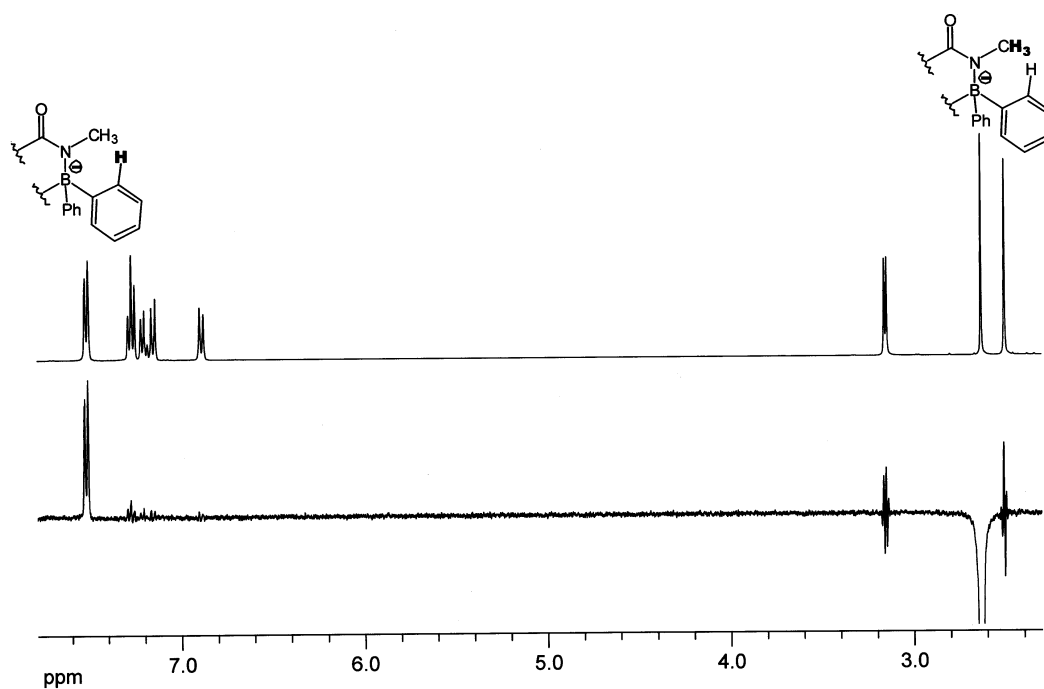


Figure S22. 400 MHz 1D-NOESY (mixing time d8 = 800 ms, relaxation delay d1 = 2s) of compound **5g** in CDCl₃

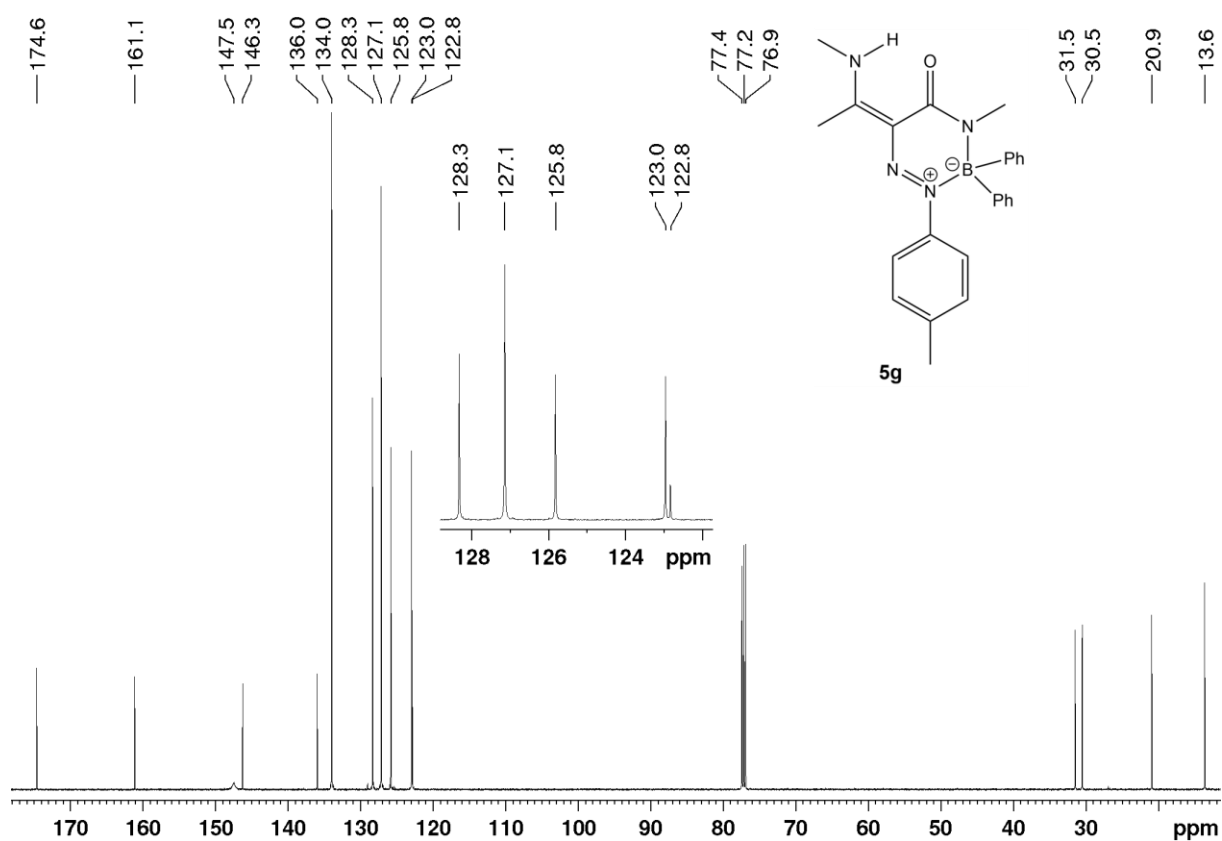


Figure S23. 125 MHz ¹³C NMR of compound **5g** in CDCl₃

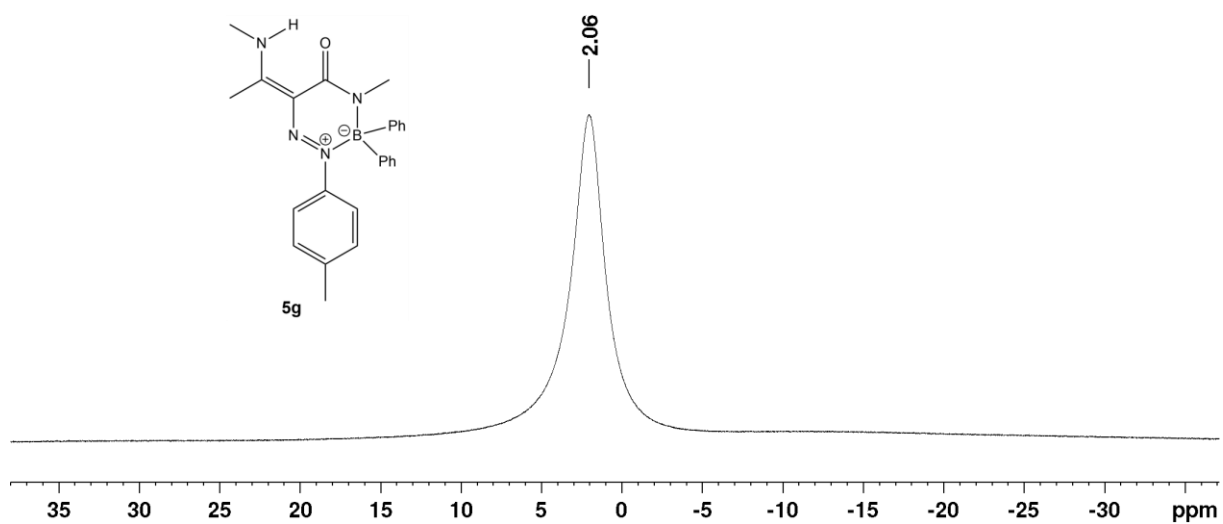


Figure S24. 160 MHz ^{11}B NMR of compound **5g** in CDCl_3

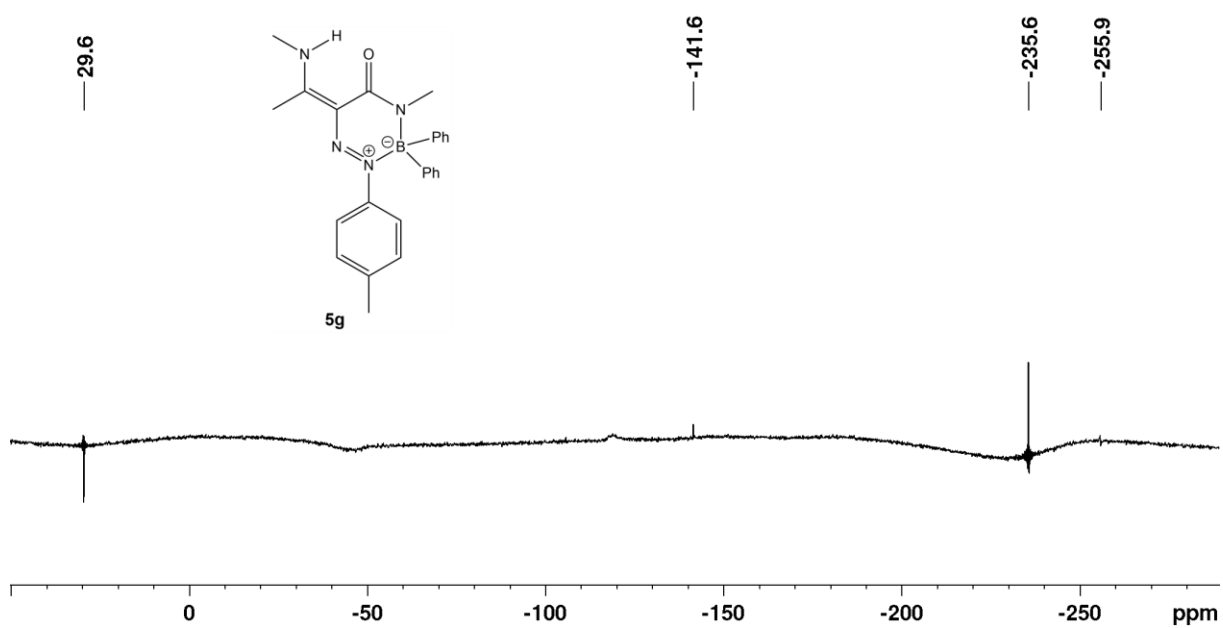


Figure S25. 50 MHz ^{15}N NMR of compound **5g** in CDCl_3

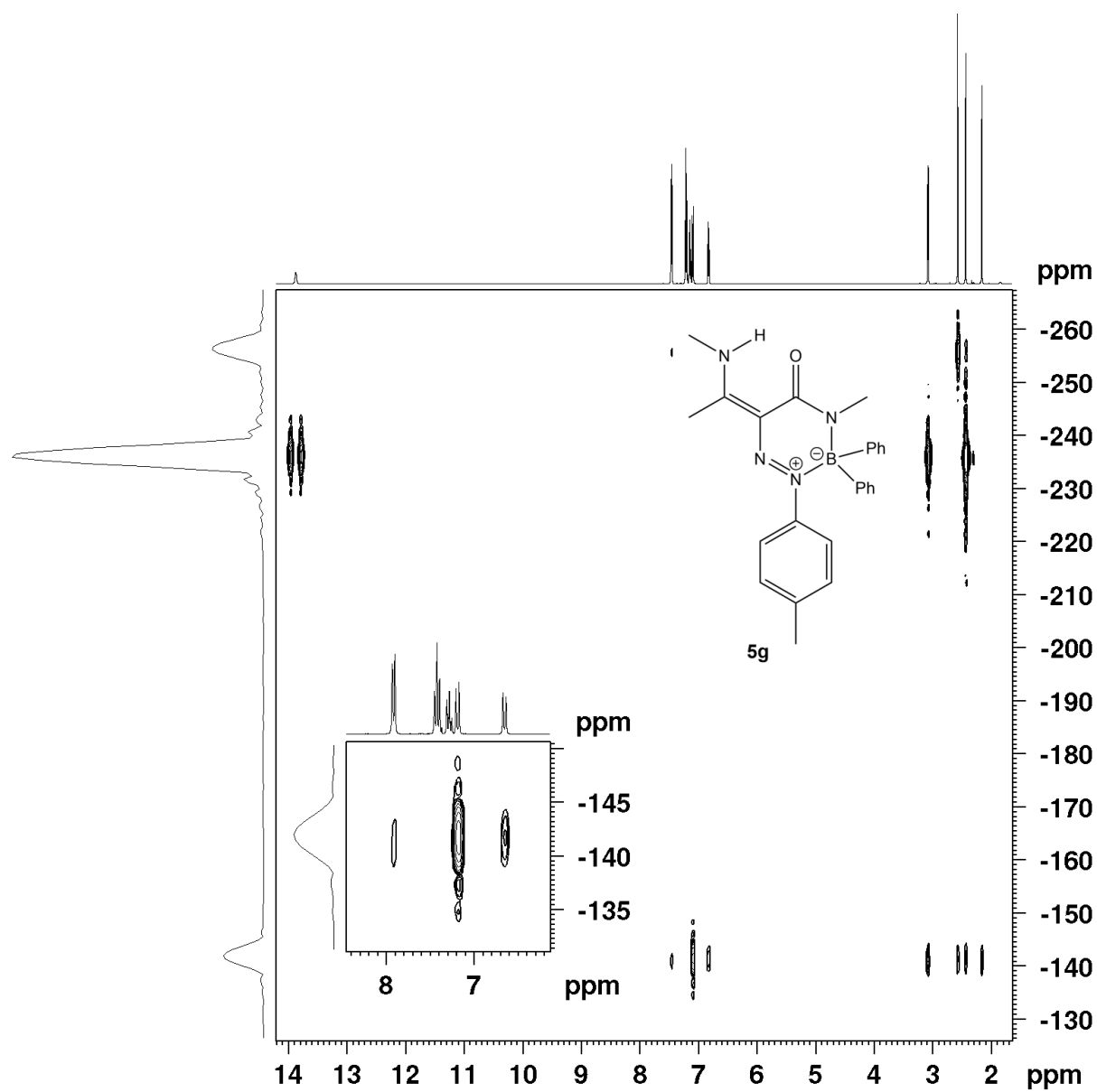


Figure S26. 500 MHz ^1H - ^{15}N HMBC NMR of compound **5g** in CDCl_3

2.6 Triazaborinone 5h

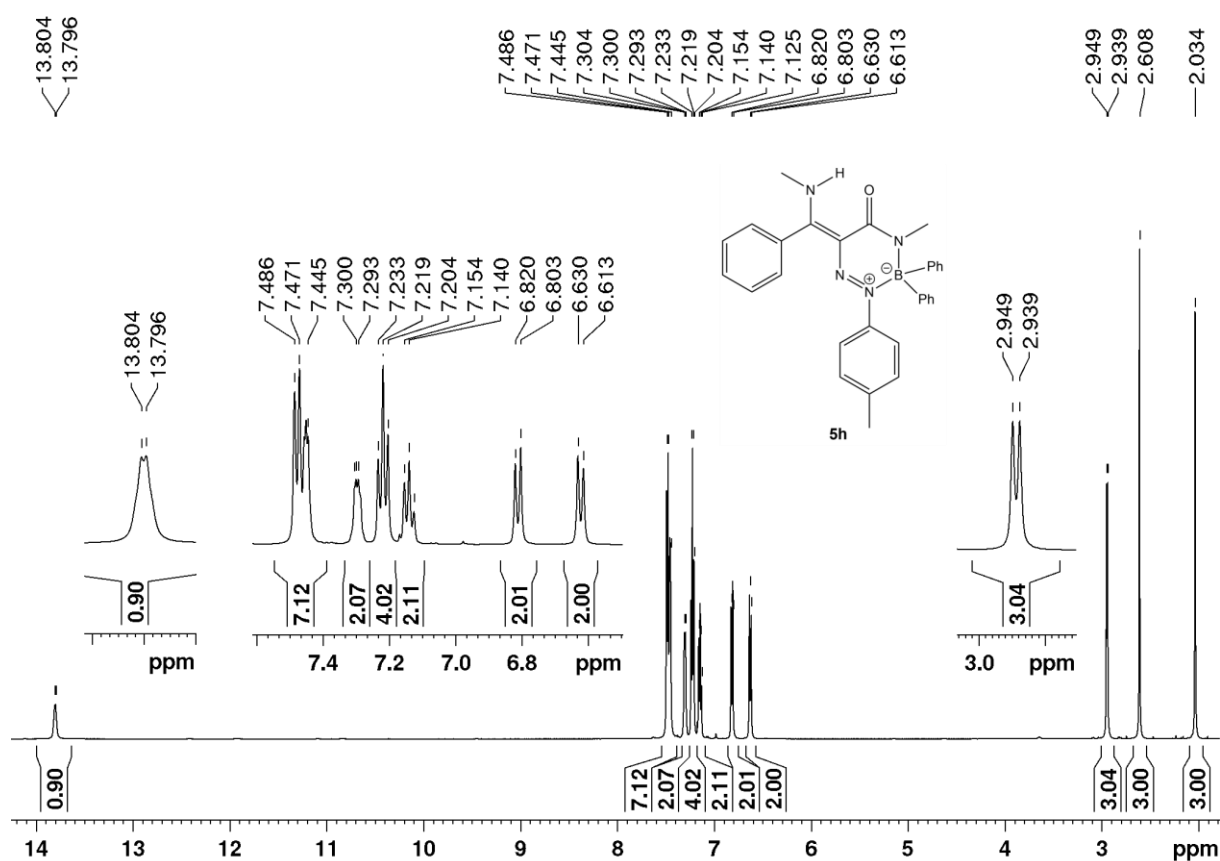
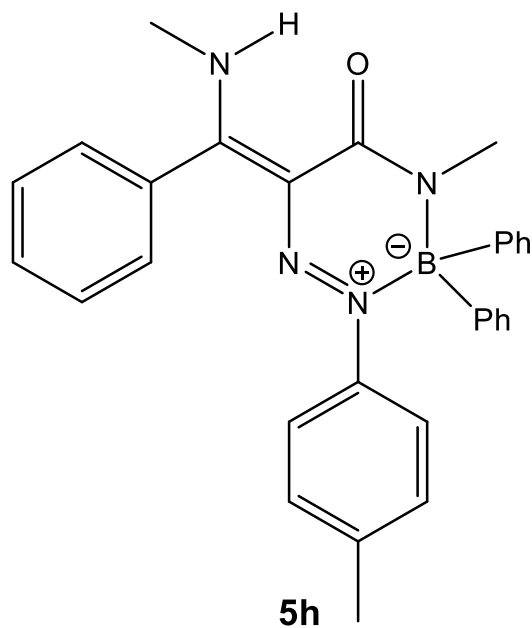


Figure S27. 500 MHz ^1H NMR of compound **5h** in CDCl_3

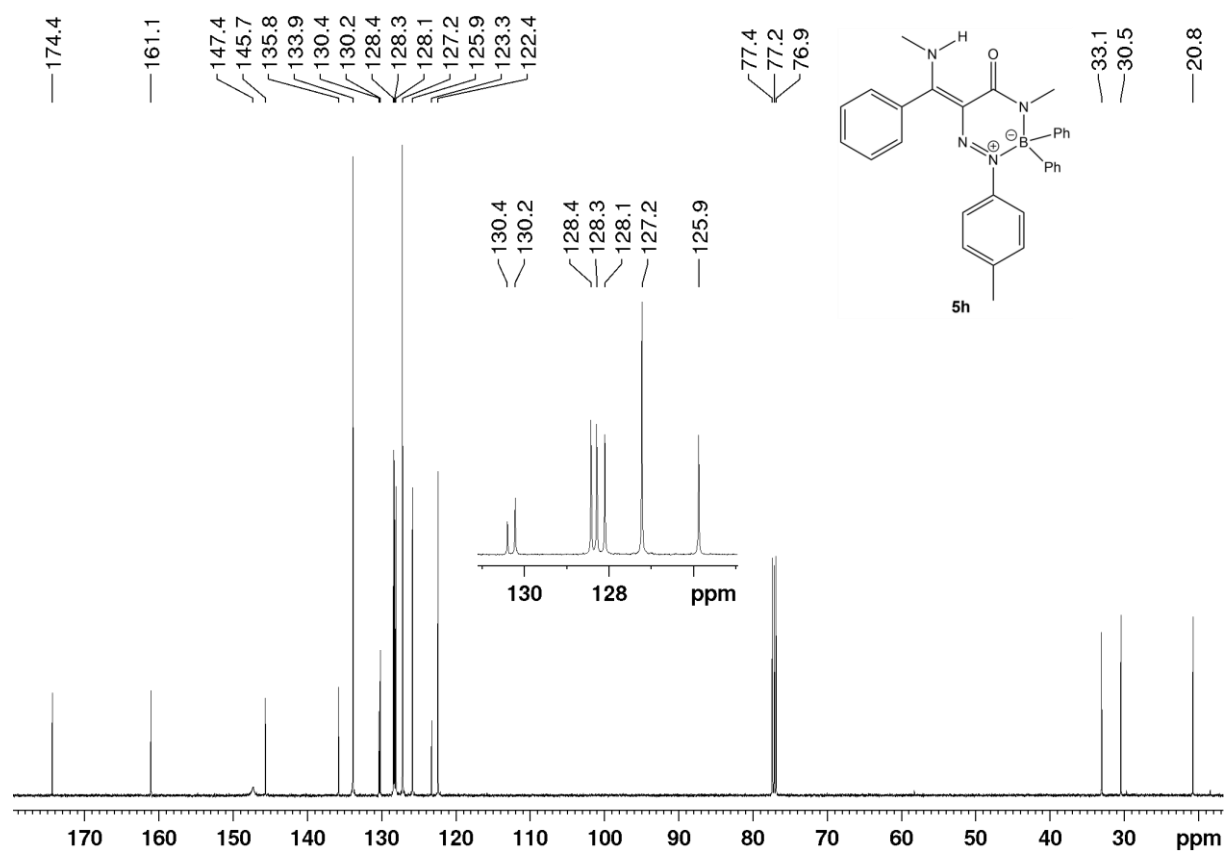


Figure S28. 125 MHz ^{13}C NMR of compound **5h** in CDCl_3

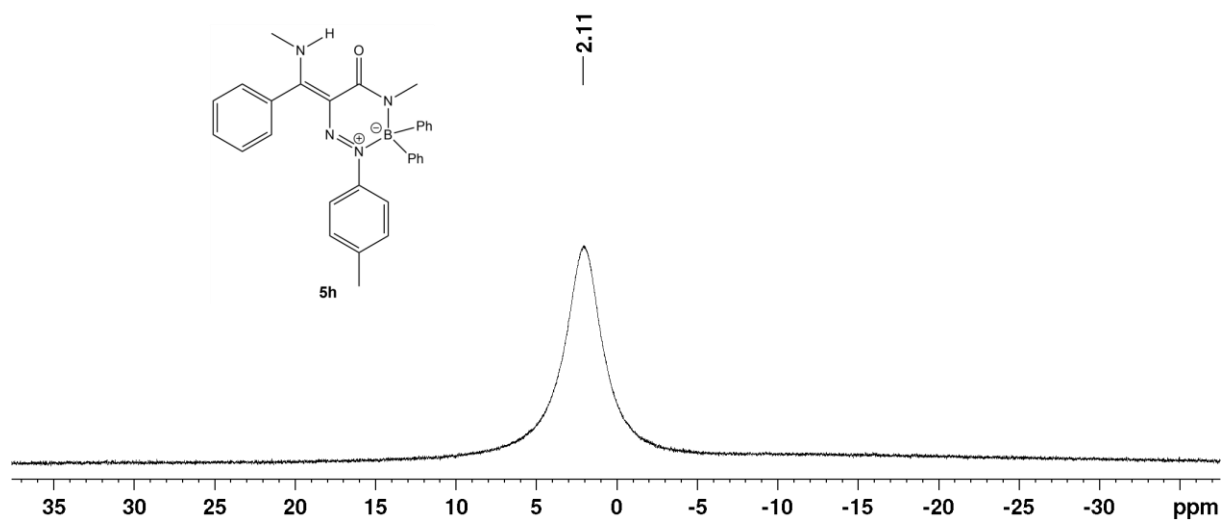


Figure S29. 160 MHz ^{11}B NMR of compound **5h** in CDCl_3

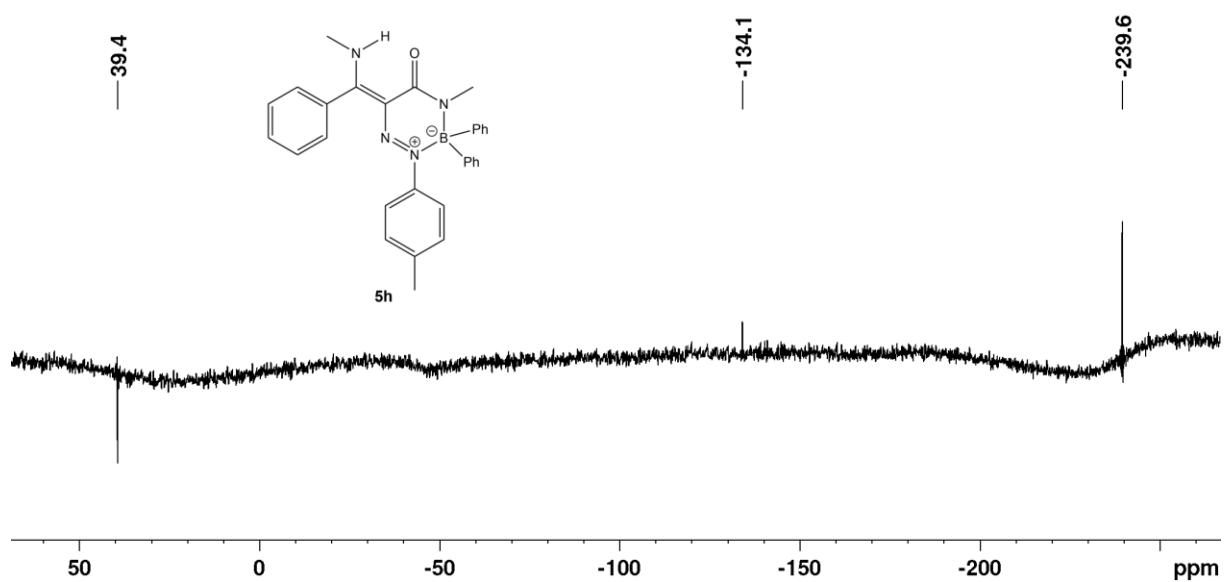


Figure S30. 50 MHz ^{15}N NMR of compound **5h** in CDCl_3

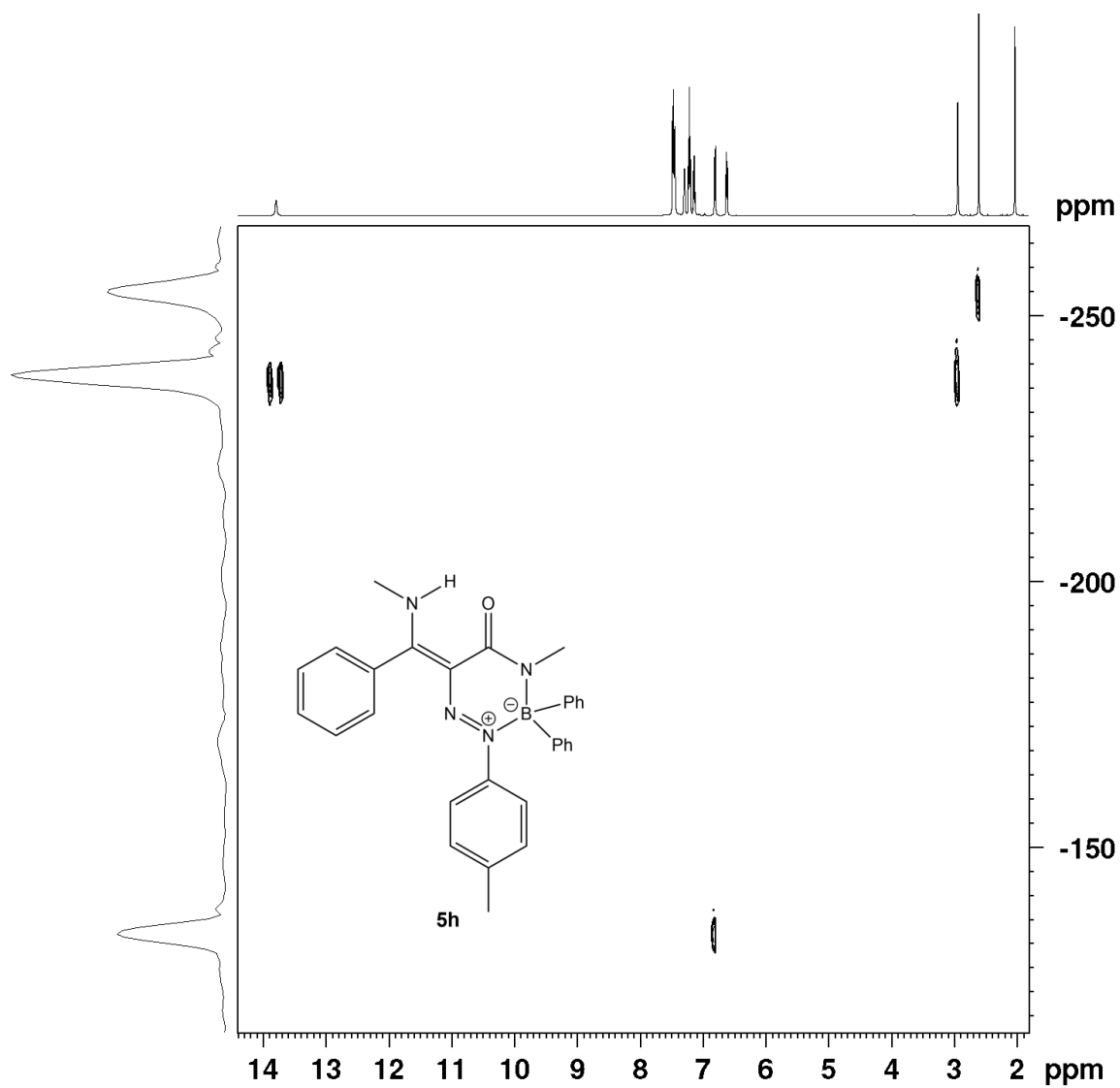


Figure S31. 500 MHz ^1H - ^{15}N HMBC NMR of compound **5h** in CDCl_3

2.7 Oxazaborine 6a

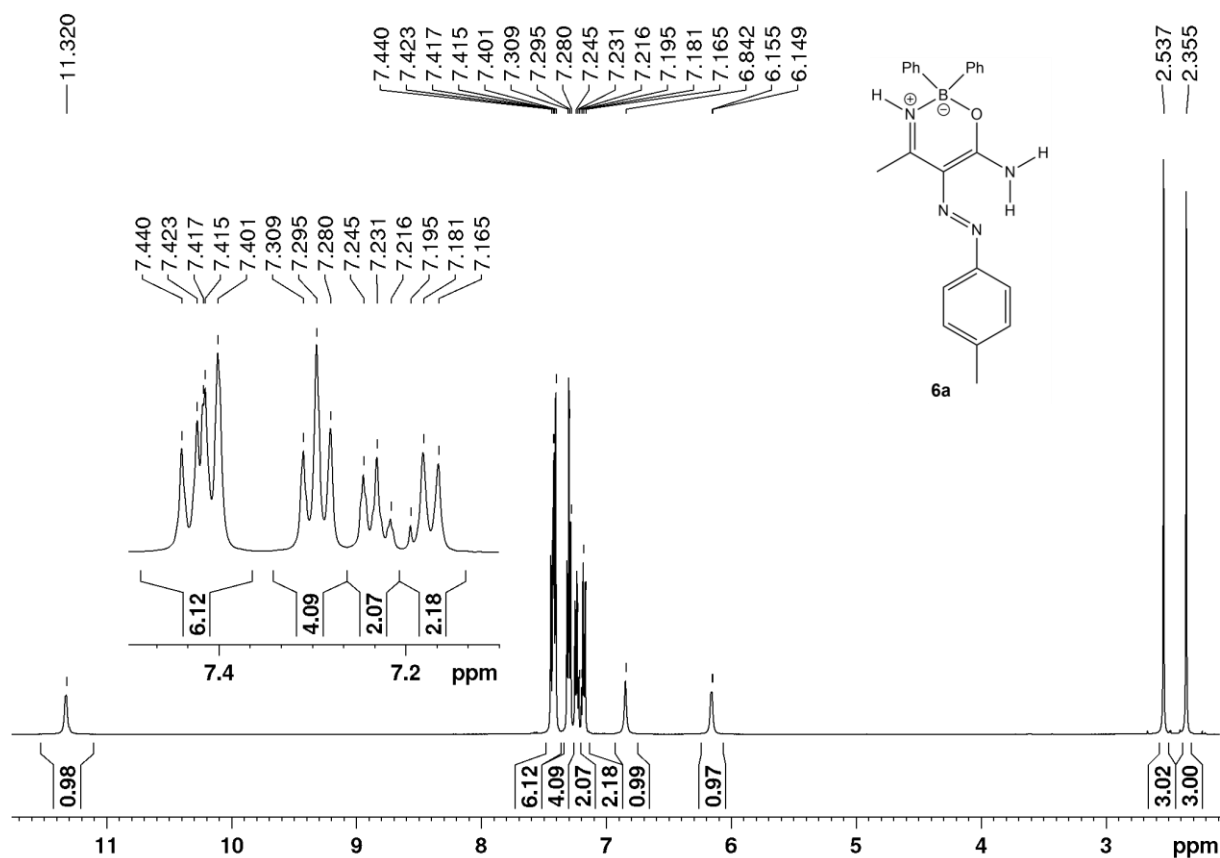
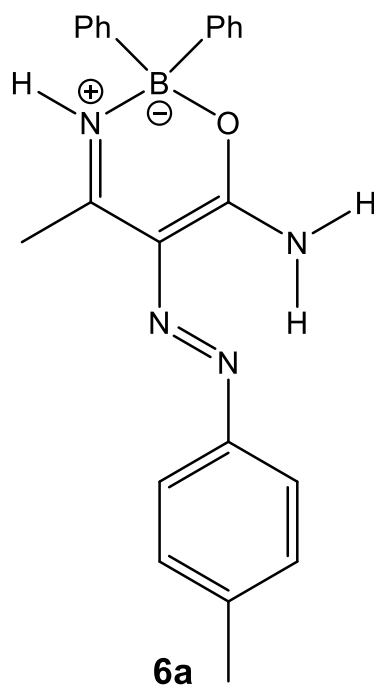


Figure S32. 500 MHz ^1H NMR of compound **6a** in CDCl_3

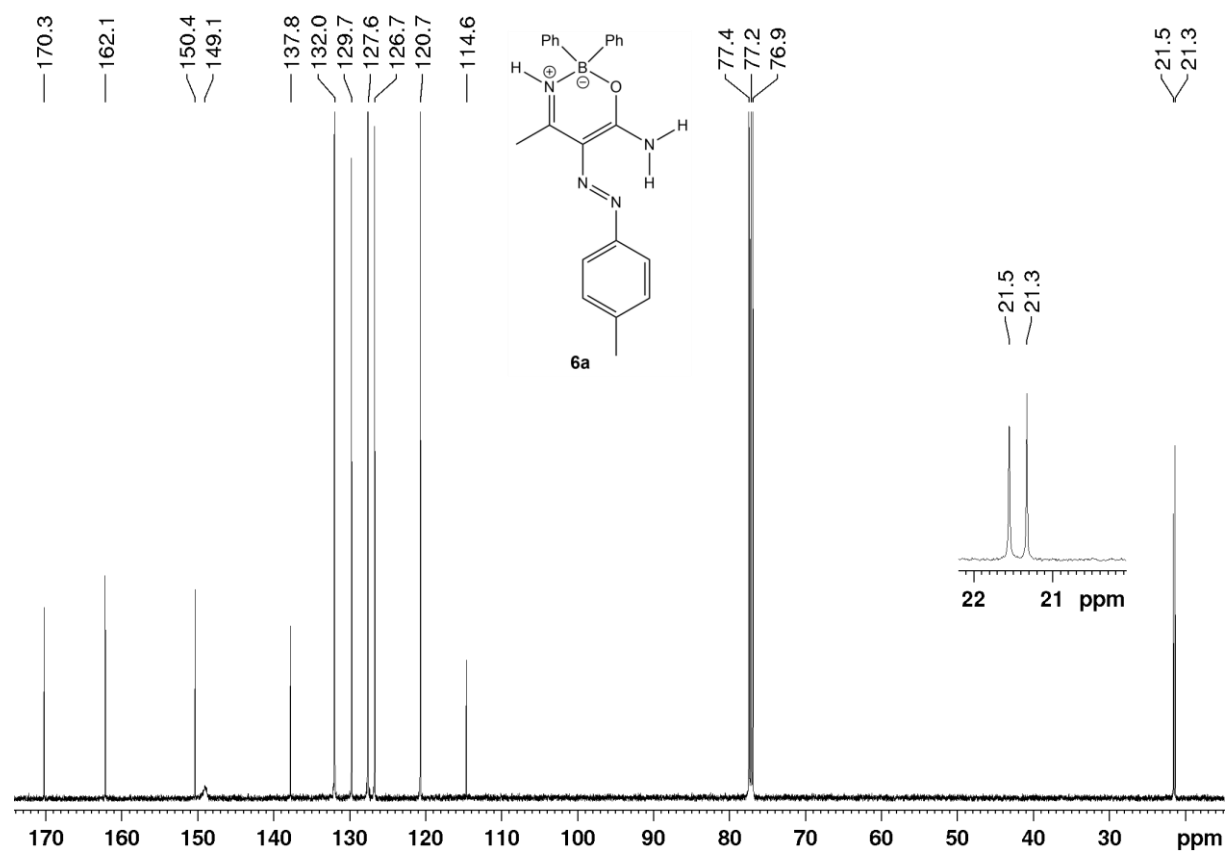


Figure S33. 125 MHz ^{13}C NMR of compound **6a** in CDCl_3

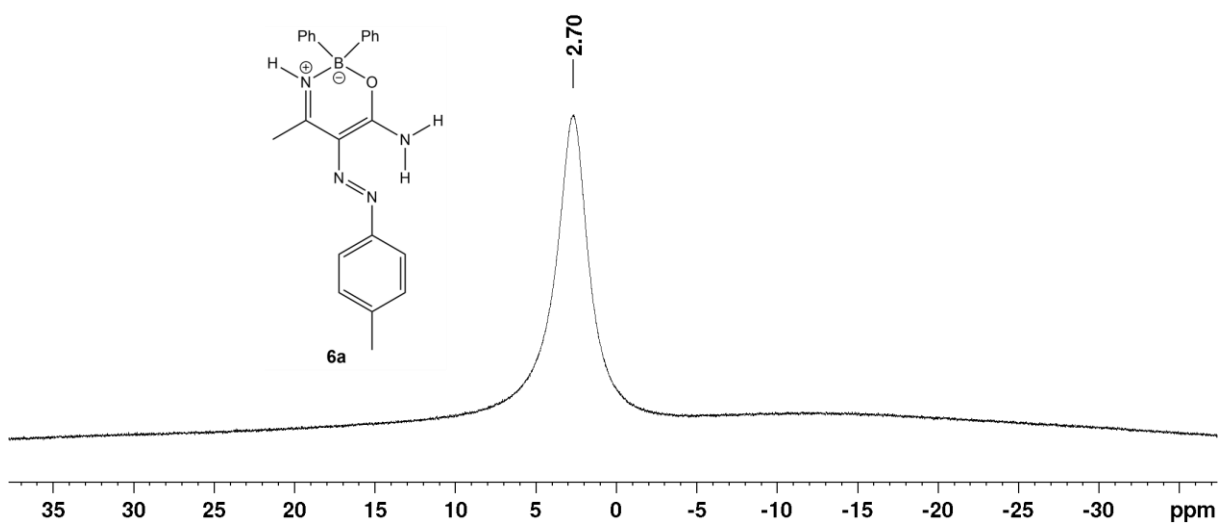


Figure S34. 160 MHz ^{11}B NMR of compound **6a** in CDCl_3

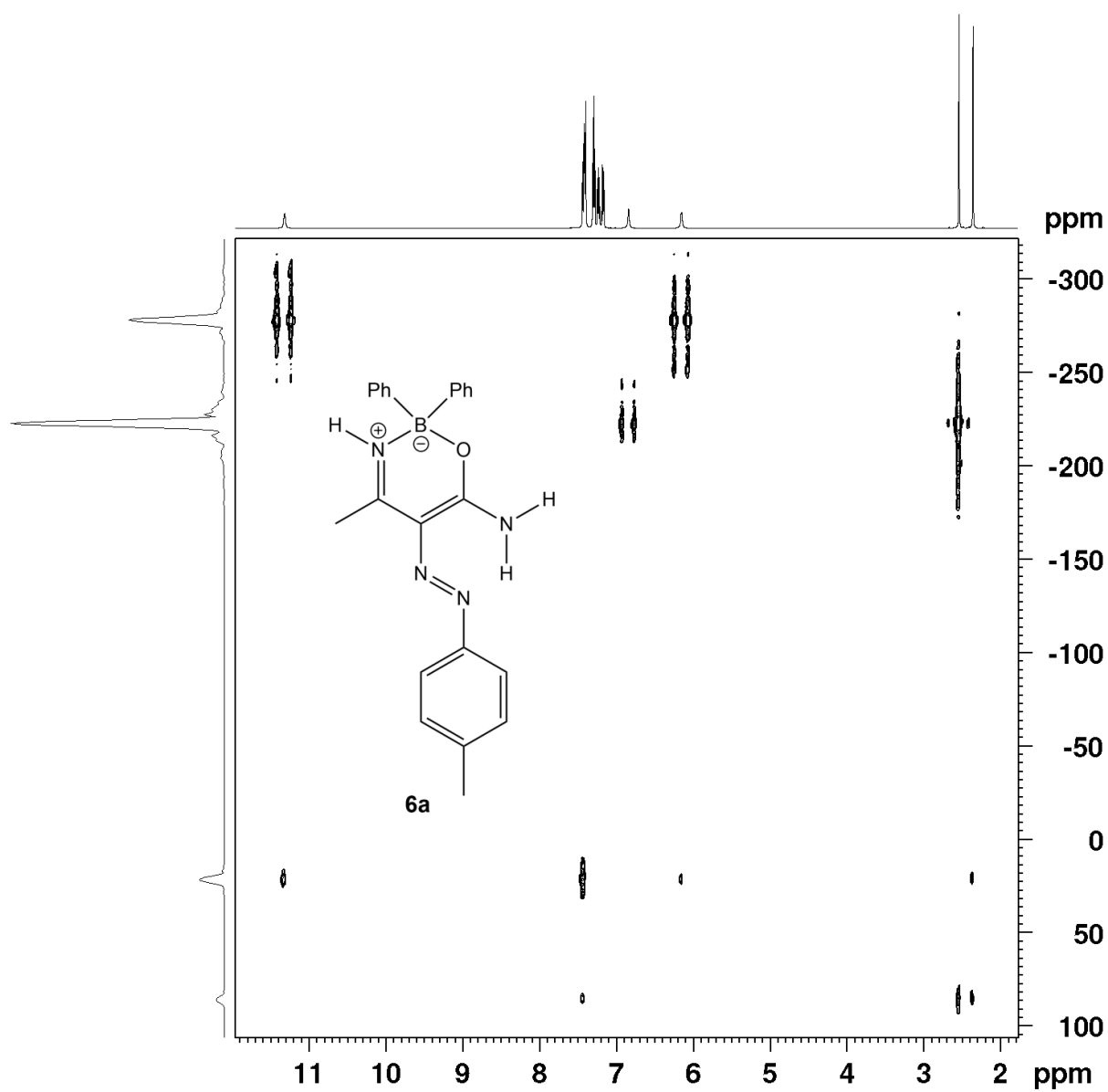


Figure S35. 500 MHz ^1H - ^{15}N HMBC NMR of compound **6a** in CDCl_3

2.8 Oxazaborine 6e

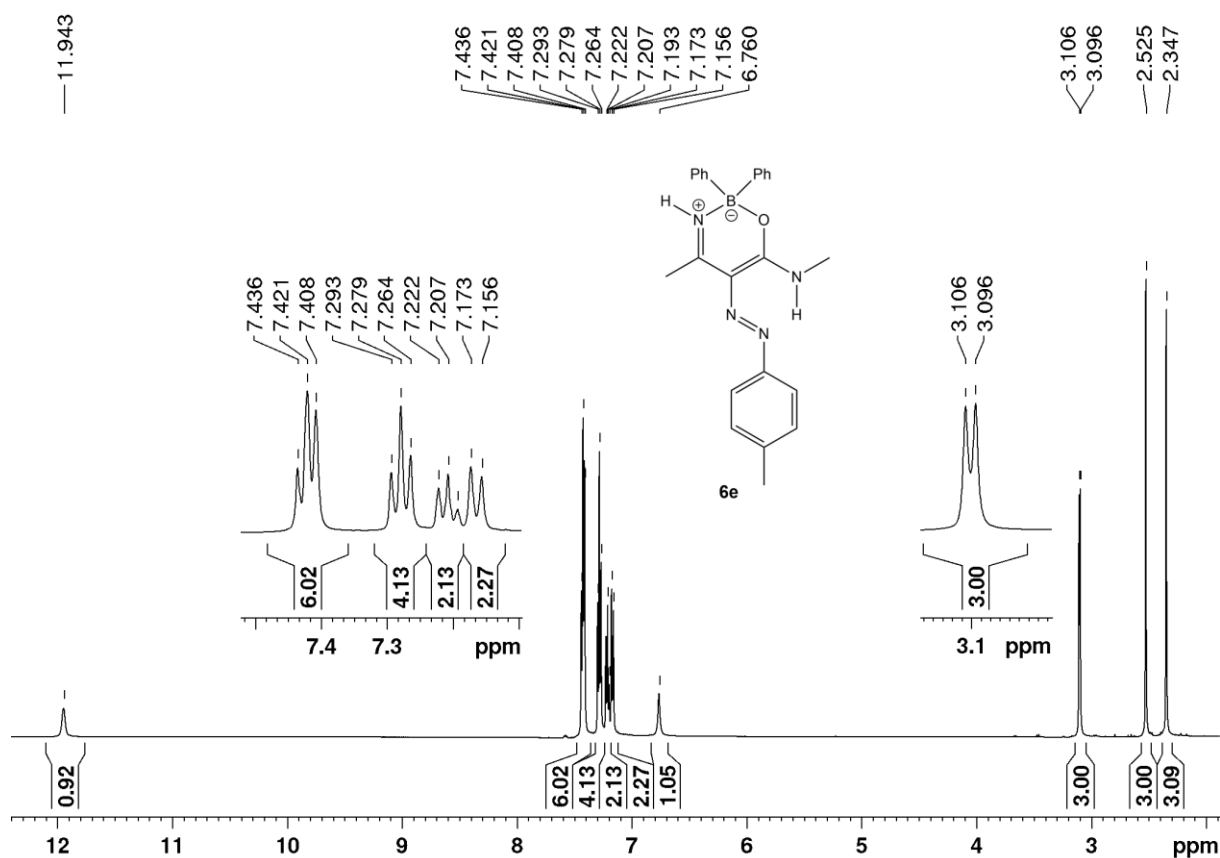
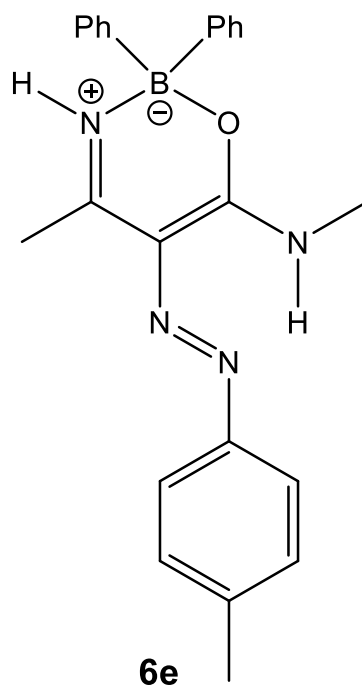


Figure S36. 500 MHz ^1H NMR of compound **6e** in CDCl_3

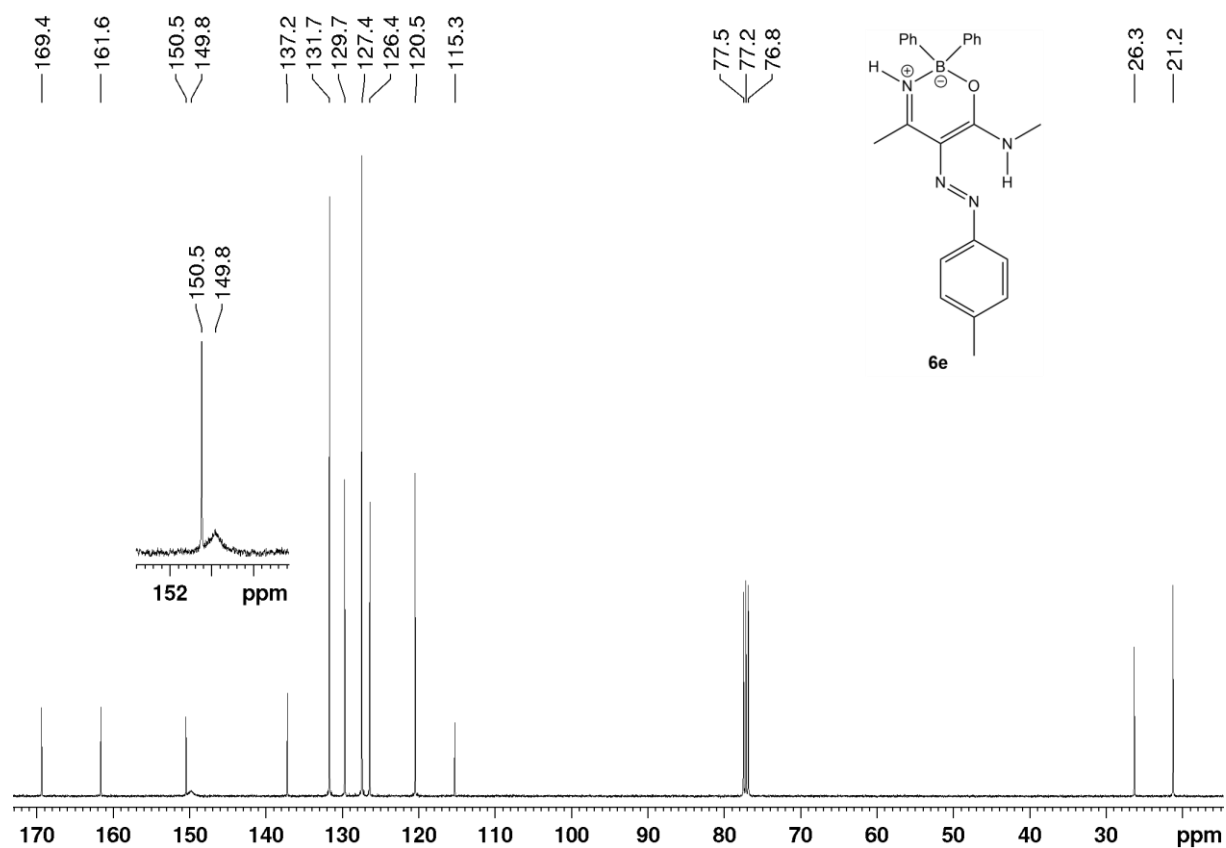


Figure S37. 100 MHz ^{13}C NMR of compound **6e** in CDCl_3

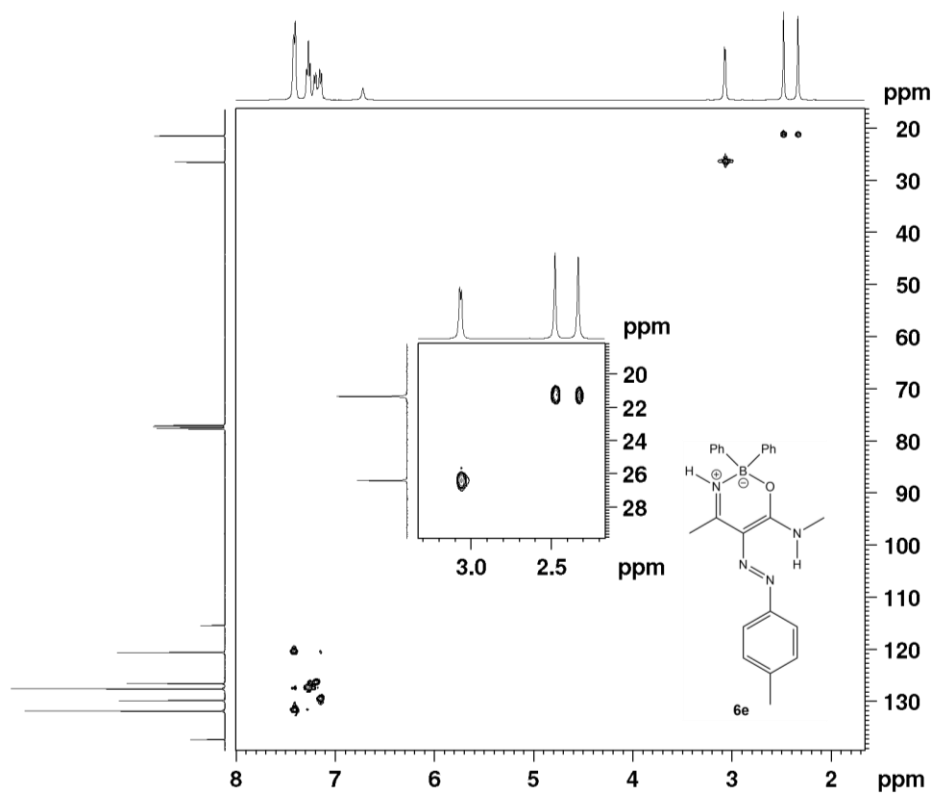


Figure S38. 100 MHz ^1H - ^{13}C HSQC NMR of compound **6e** in CDCl_3

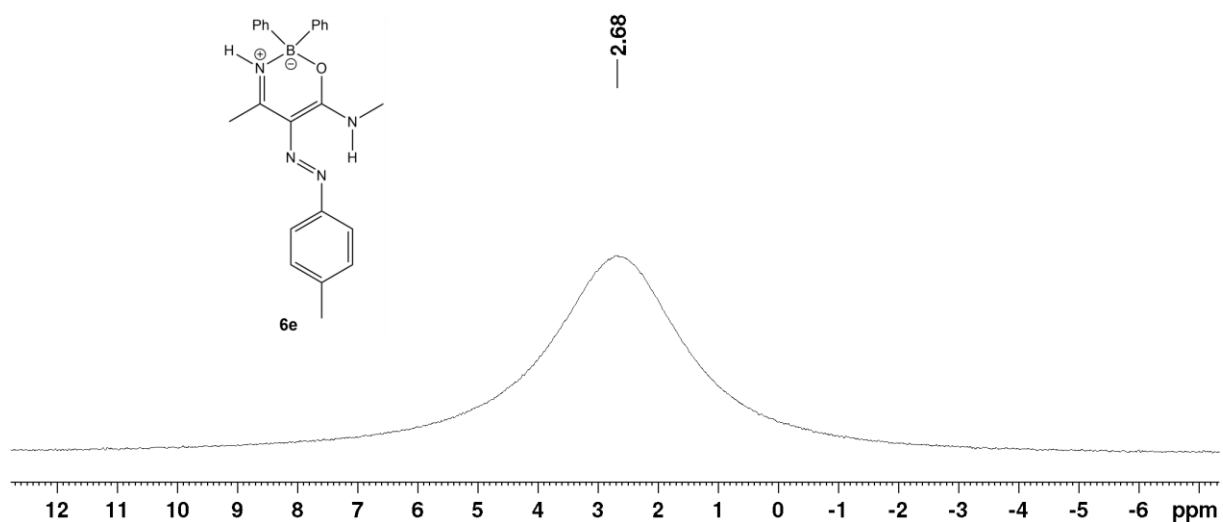


Figure S39. 160 MHz ^{11}B NMR of compound 6e in CDCl_3

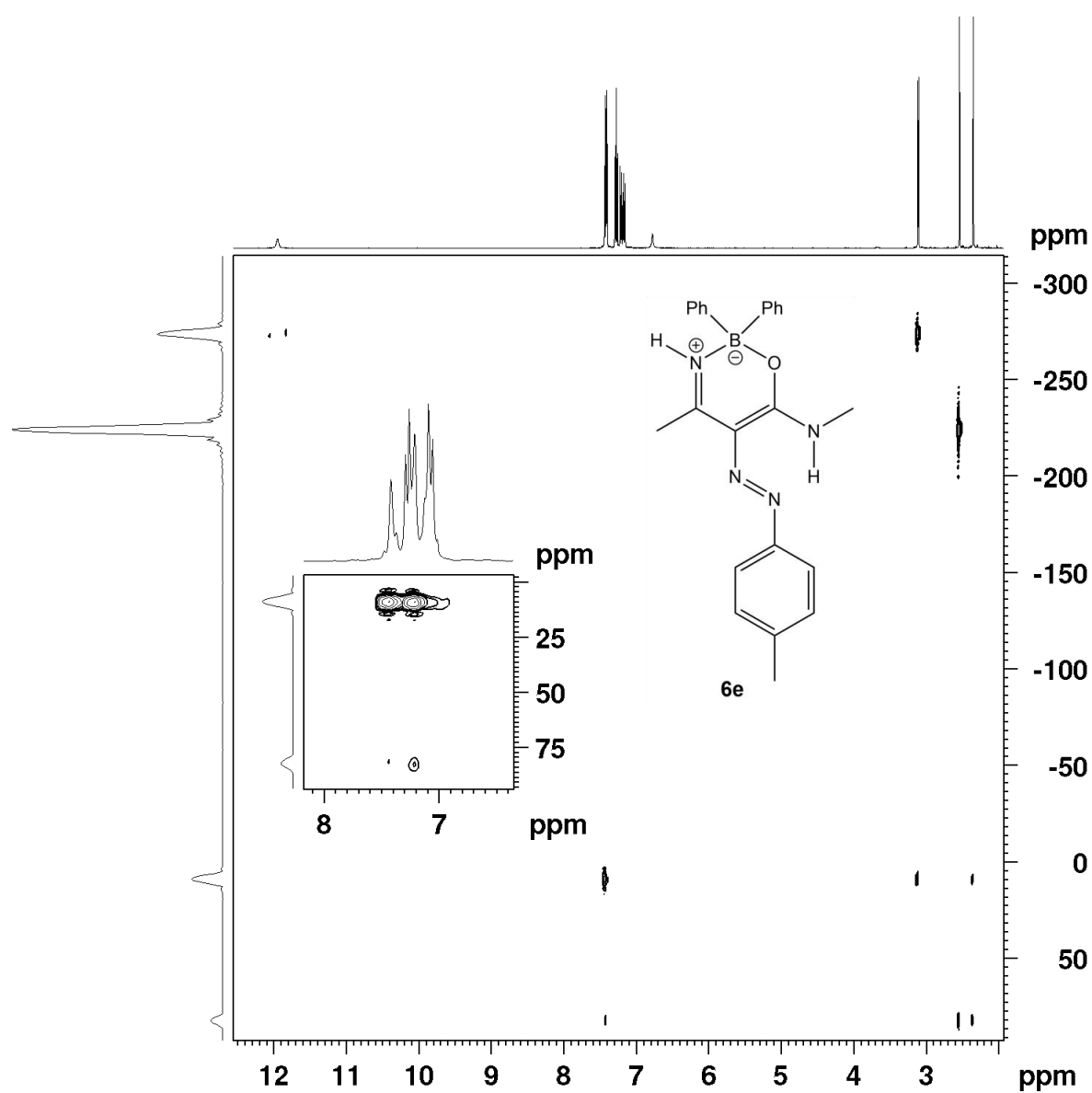


Figure S40. 500 MHz ^1H - ^{15}N HMBC NMR of compound 6e in CDCl_3

2.9 Oxazaborine 6f

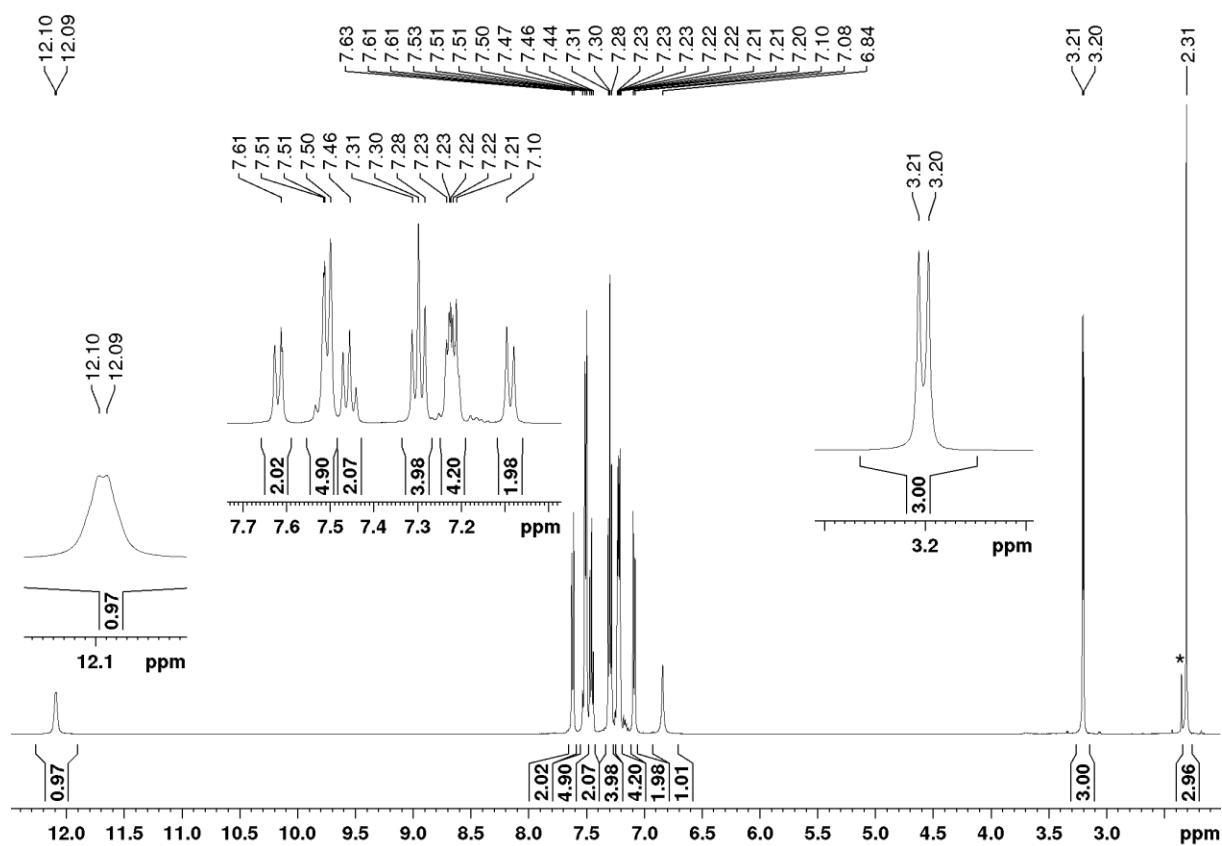
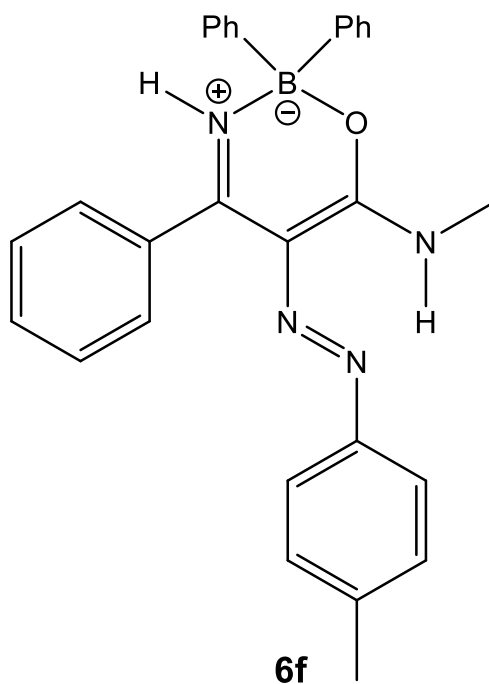


Figure S41. 500 MHz ^1H NMR of compound **6f** in CDCl_3 (Signal with asterisk is $-\text{CH}_3$ from toluene.)

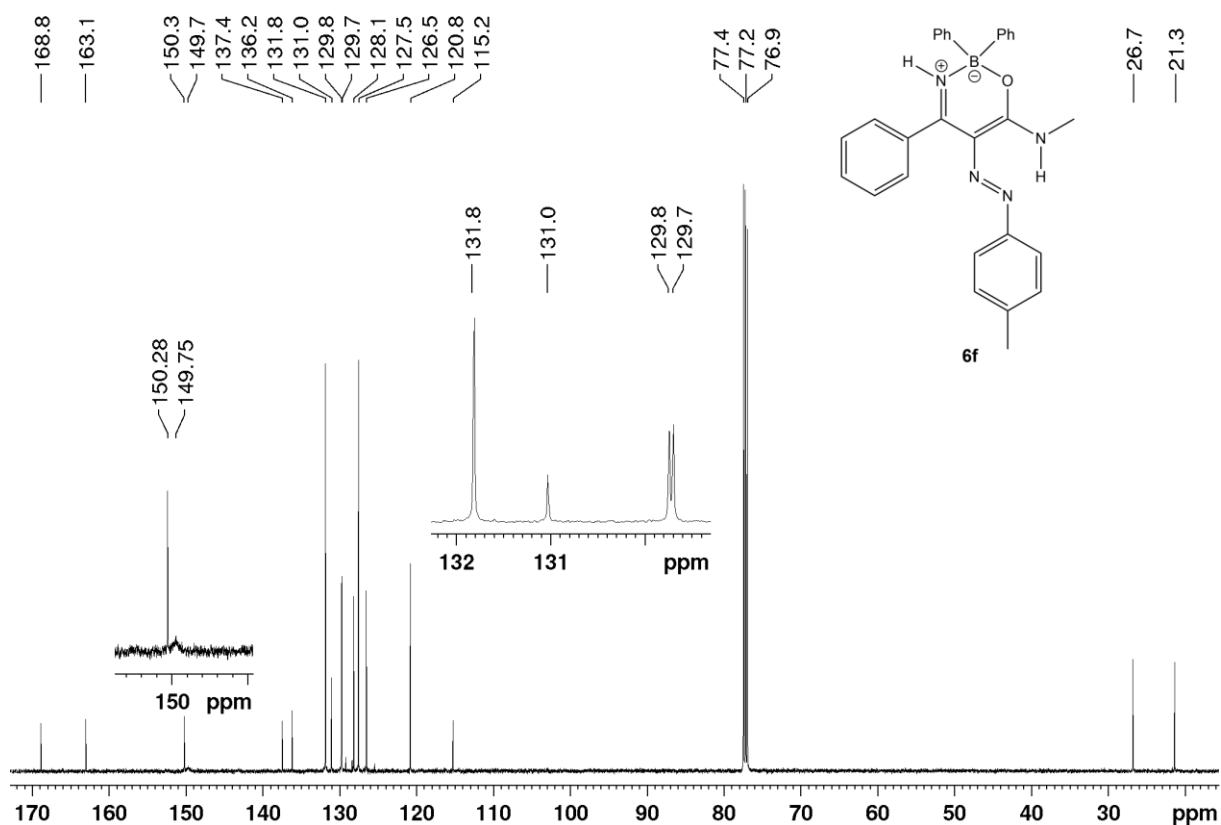


Figure S42. 125 MHz ^{13}C NMR of compound **6f** in CDCl_3

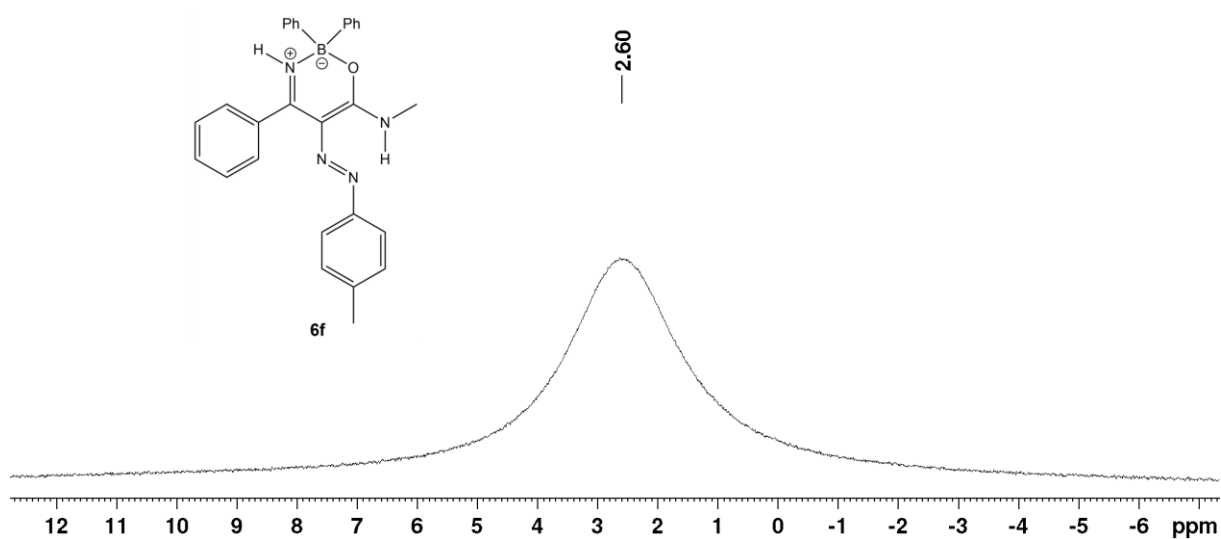


Figure S43. 160 MHz ^{11}B NMR of compound **6f** in CDCl_3

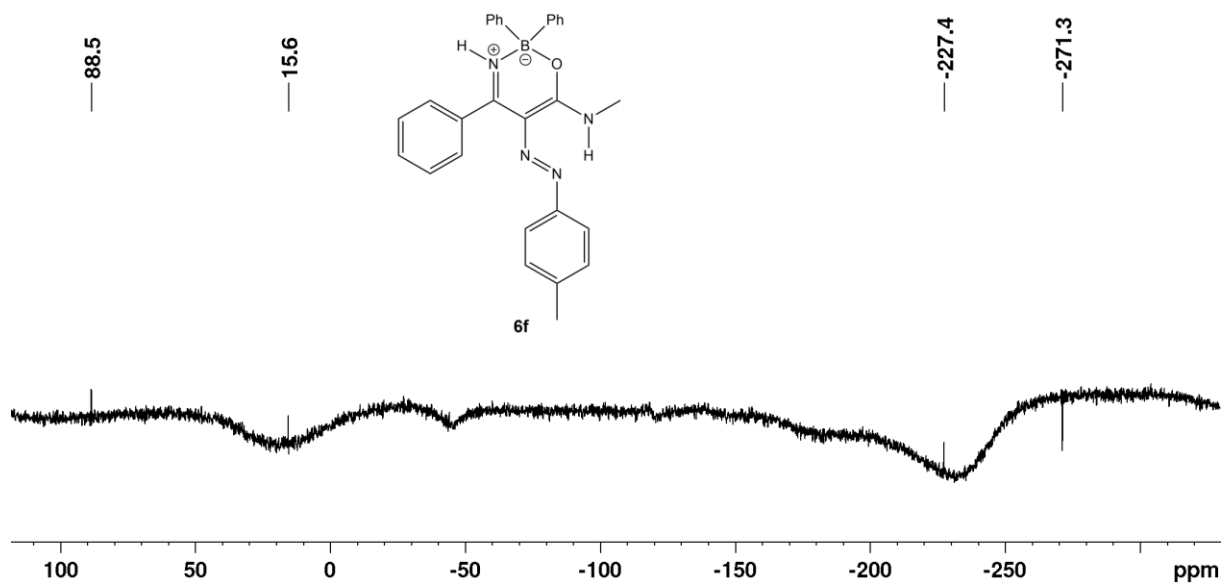


Figure S44. 50 MHz ¹⁵N NMR of compound **6f** in CDCl₃

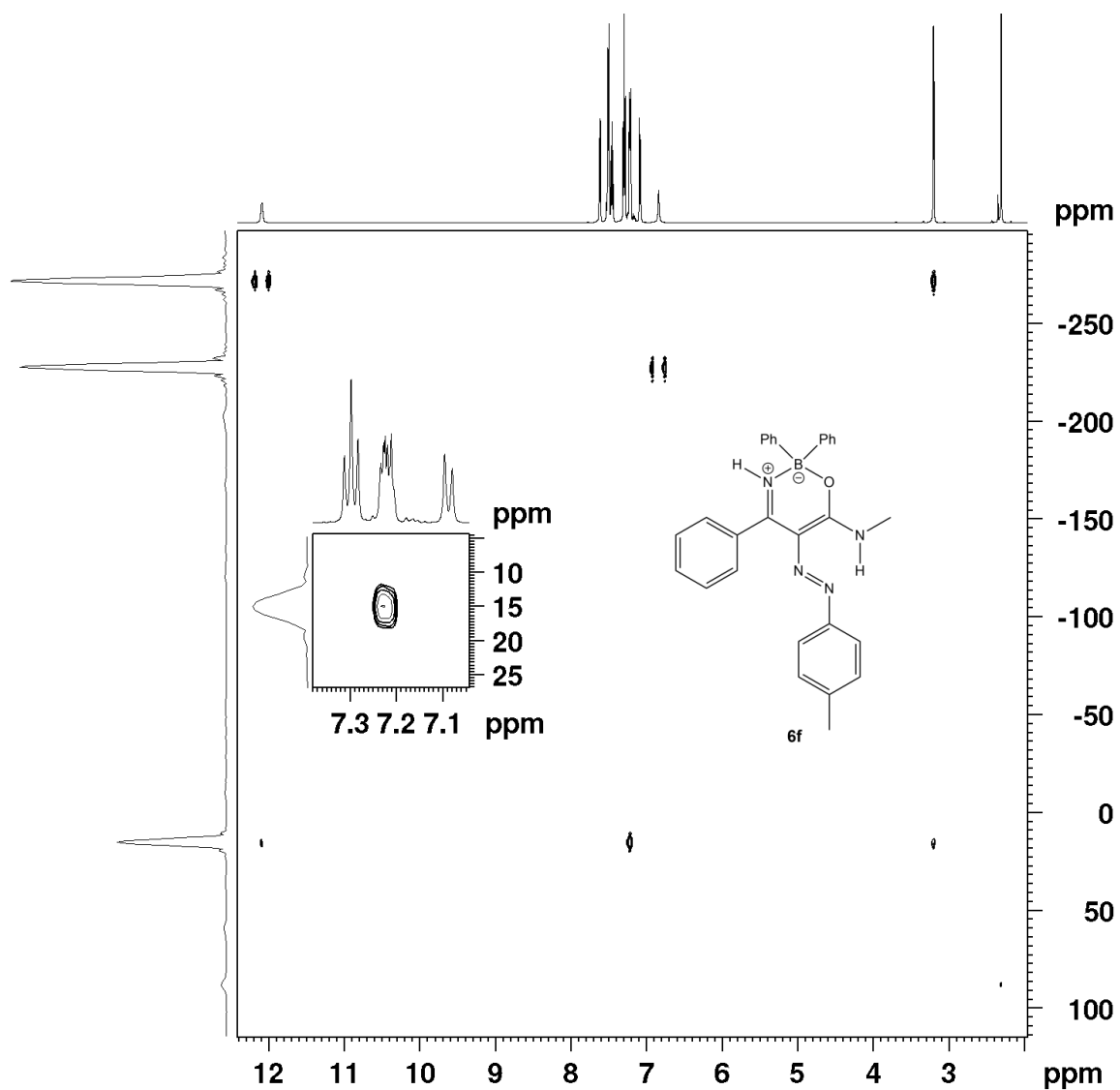


Figure S45. 500 MHz ¹H-¹⁵N HMBC NMR of compound **6f** in CDCl₃

2.10 Oxazaborine 6g

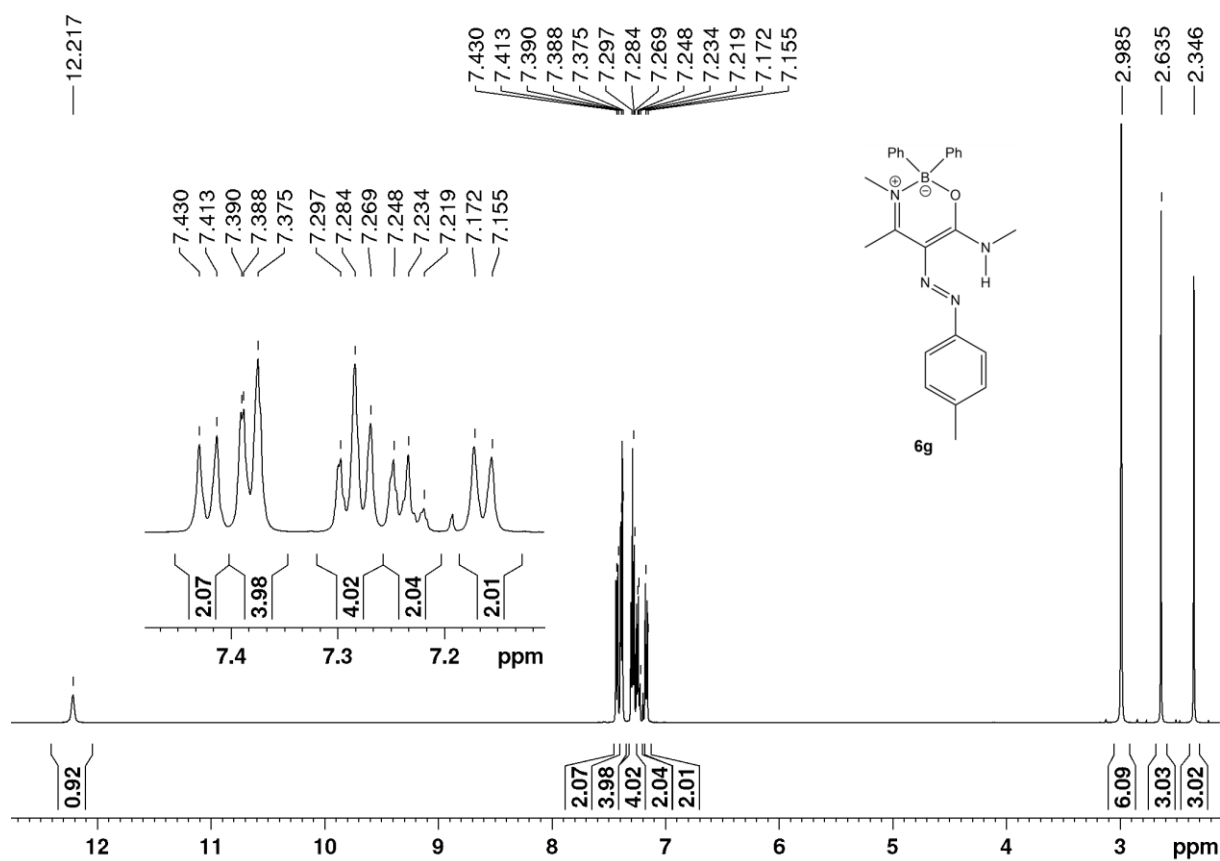
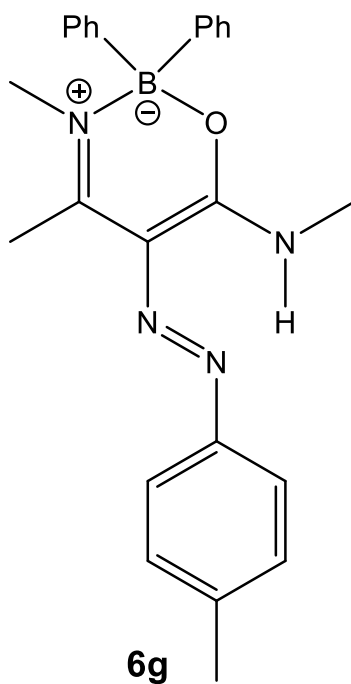


Figure S46. 500 MHz ^1H NMR of compound **6g** in CDCl_3

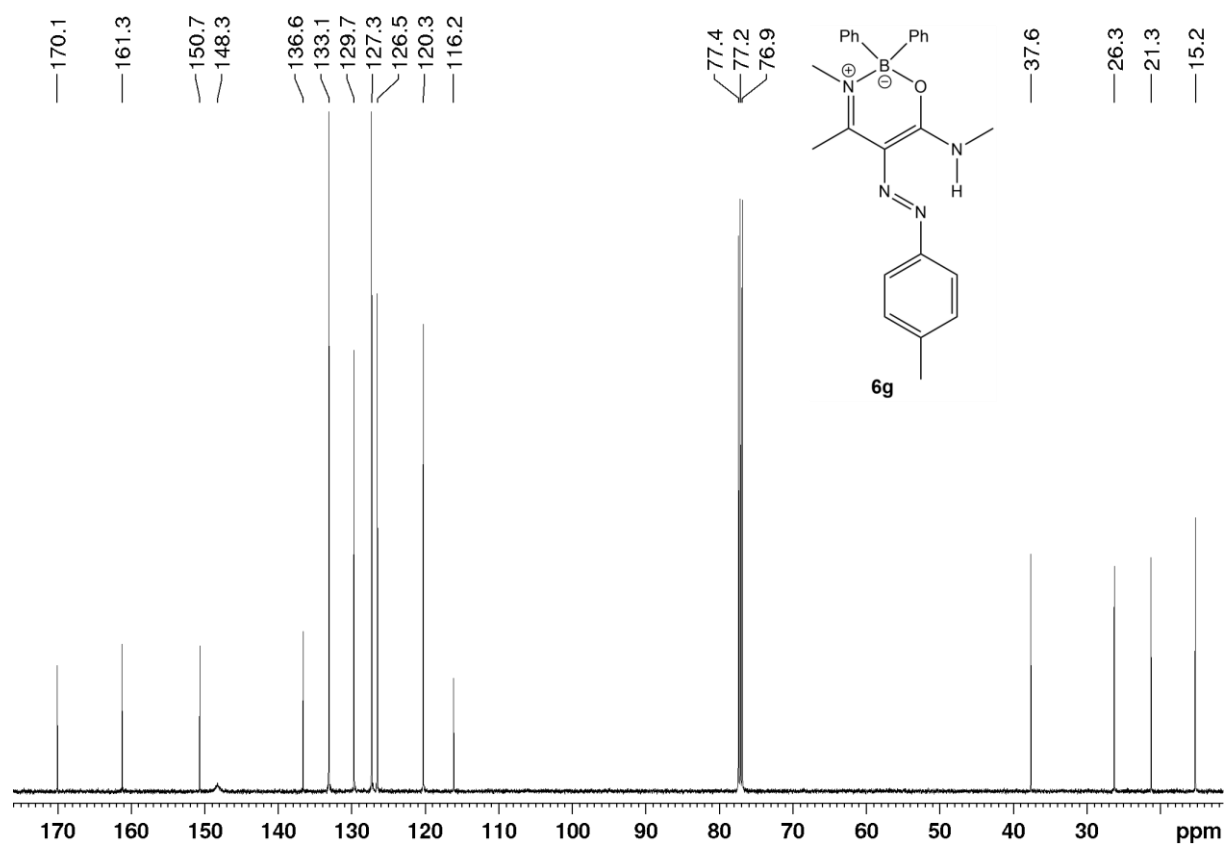


Figure S47. 125 MHz ¹³C NMR of compound **6g** in CDCl₃

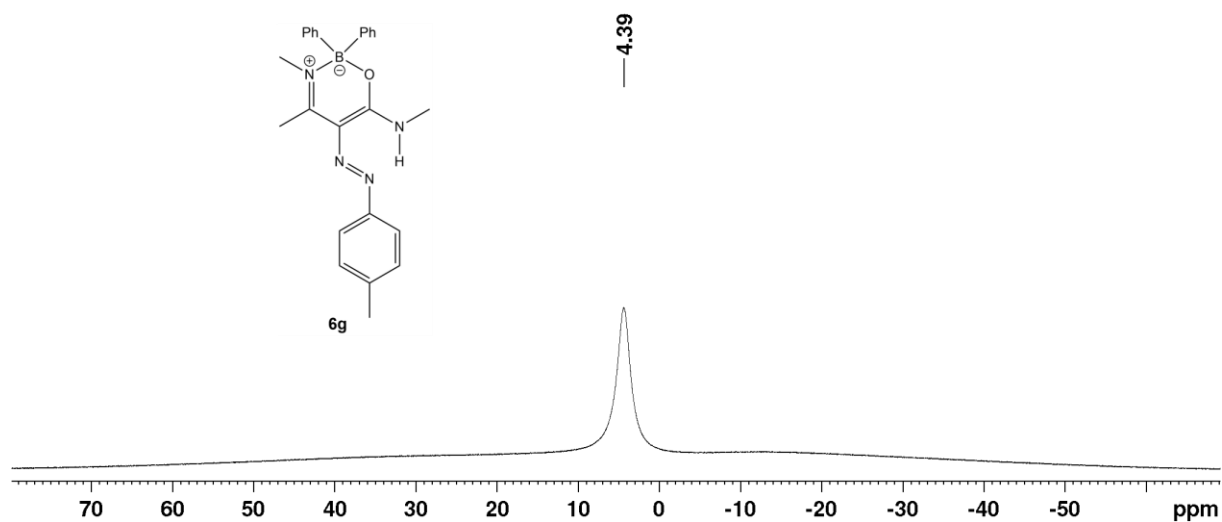


Figure S48. 160 MHz ¹¹B NMR of compound **6g** in CDCl₃

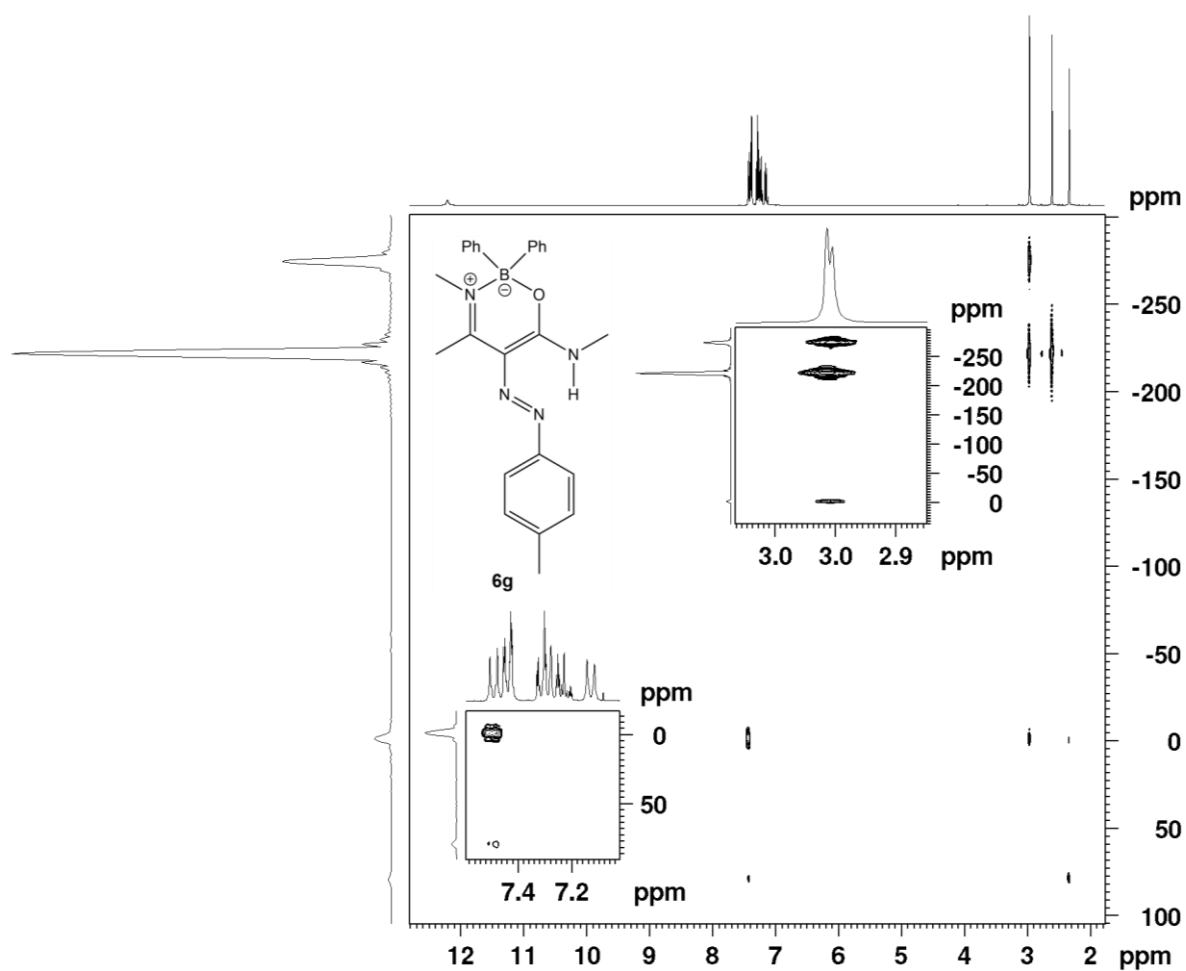


Figure S49. 400 MHz ^1H - ^{15}N HMBC NMR of compound **6g** in CDCl_3

2.11 Oxazaborine 6h

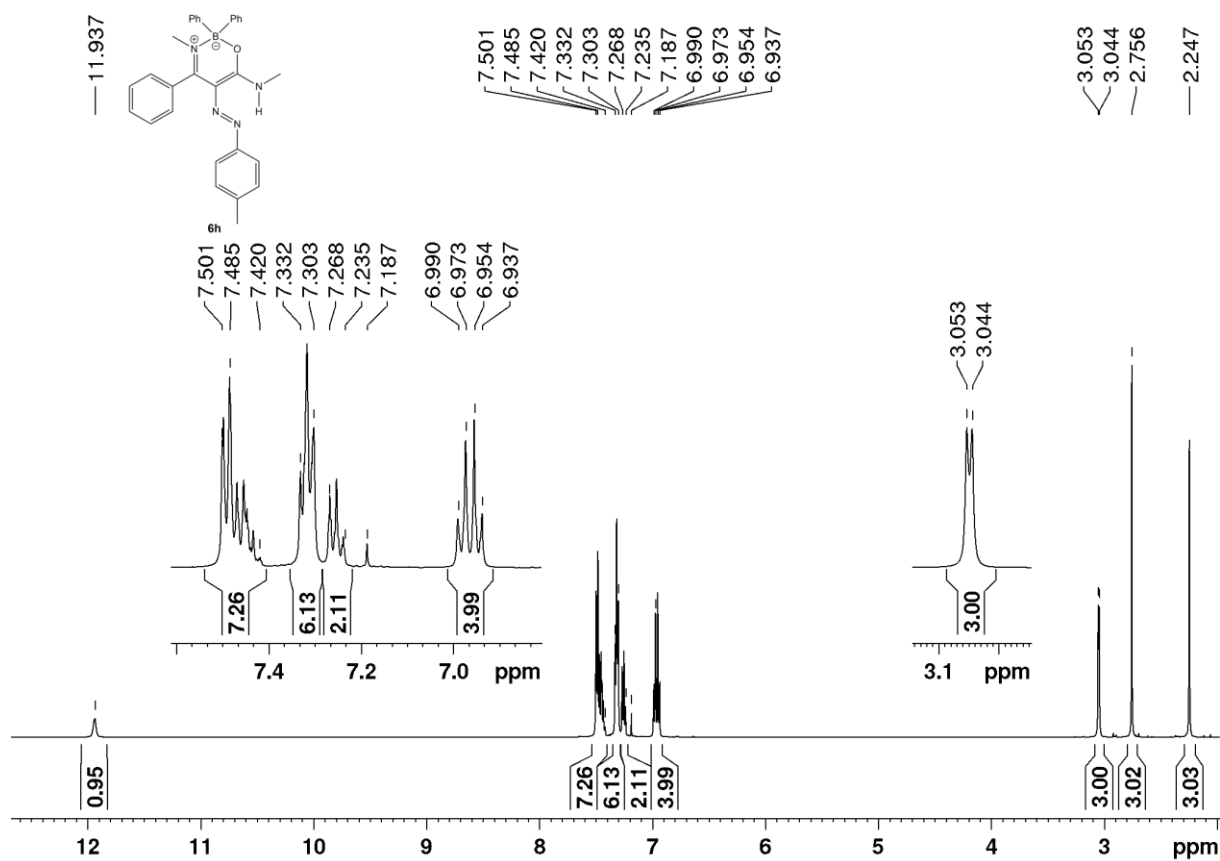
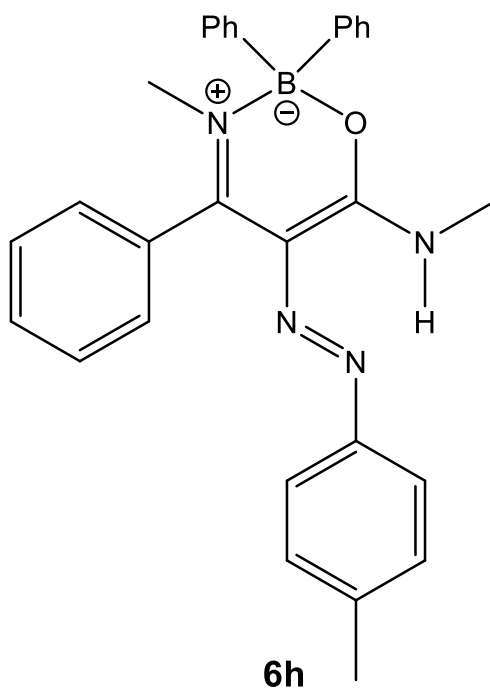


Figure S50. 500 MHz ^1H NMR of compound **6h** in CDCl_3

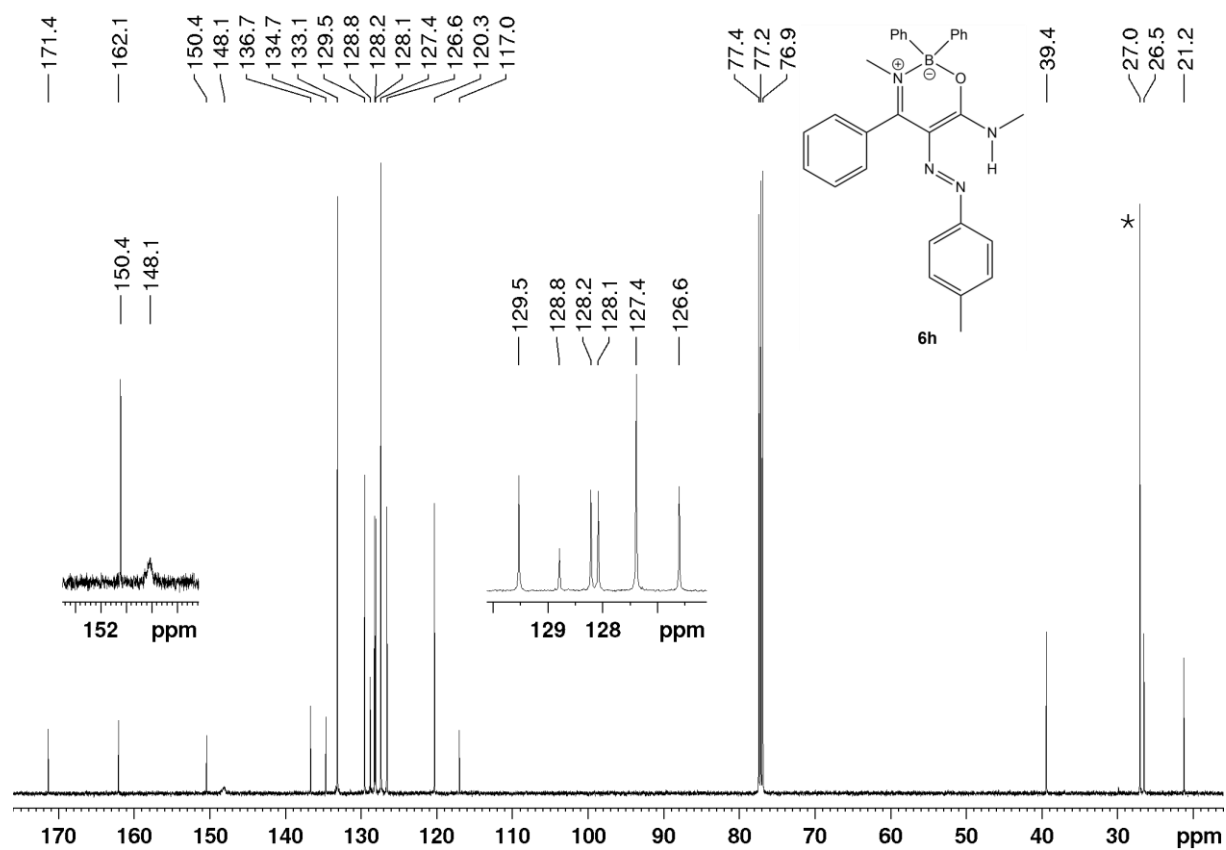


Figure S51. 125 MHz ^{13}C NMR of compound **6h** in CDCl_3 (*Cyclohexane)

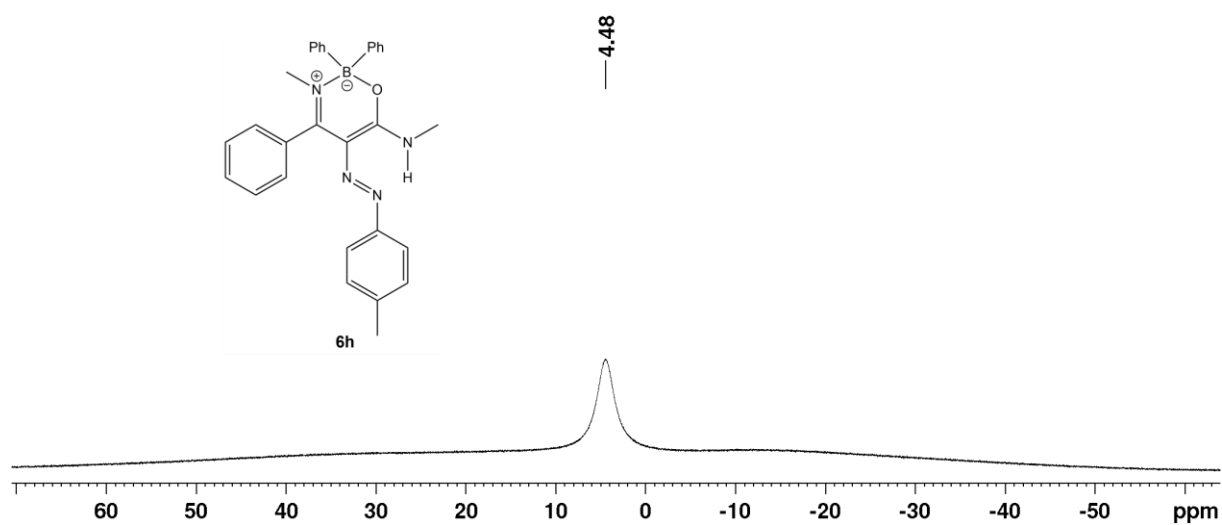


Figure S52. 160 MHz ^{11}B NMR of compound **6h** in CDCl_3

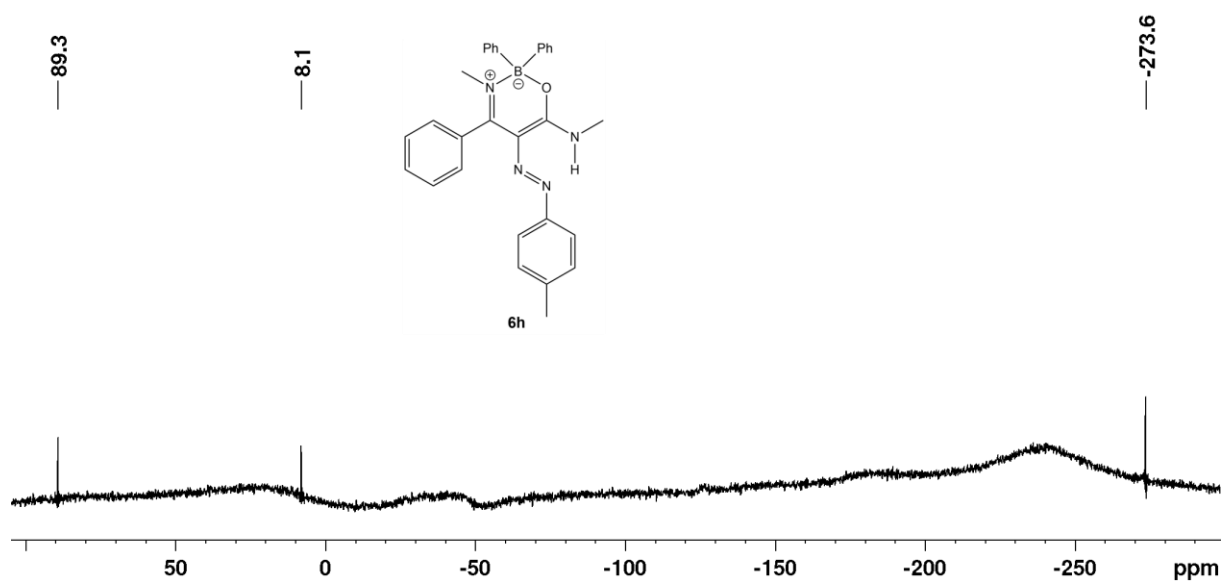


Figure S53. 50 MHz ^{15}N NMR of compound **6h** in CDCl_3

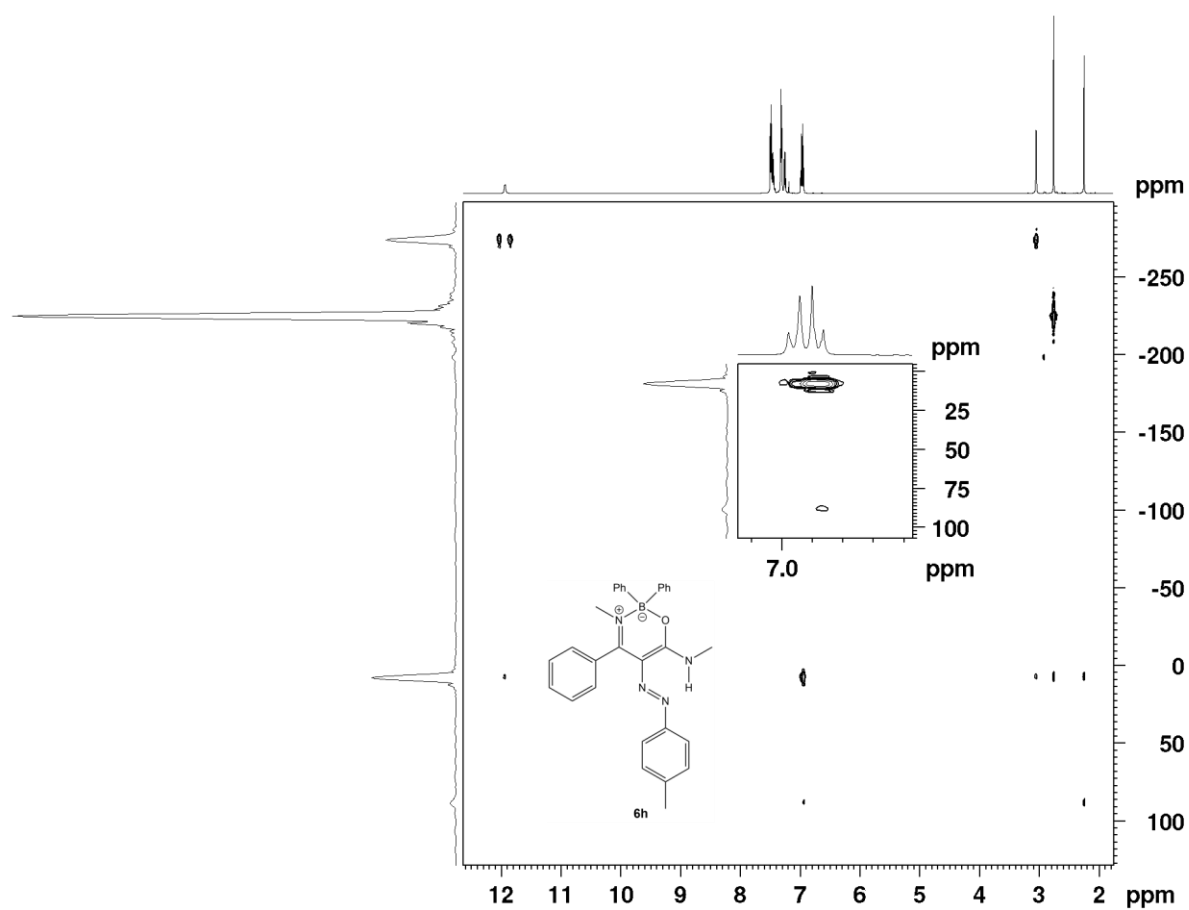


Figure S54. 500 MHz ^1H - ^{15}N HMBC NMR of compound **6h** in CDCl_3

2.12 Diazaborinone 7a

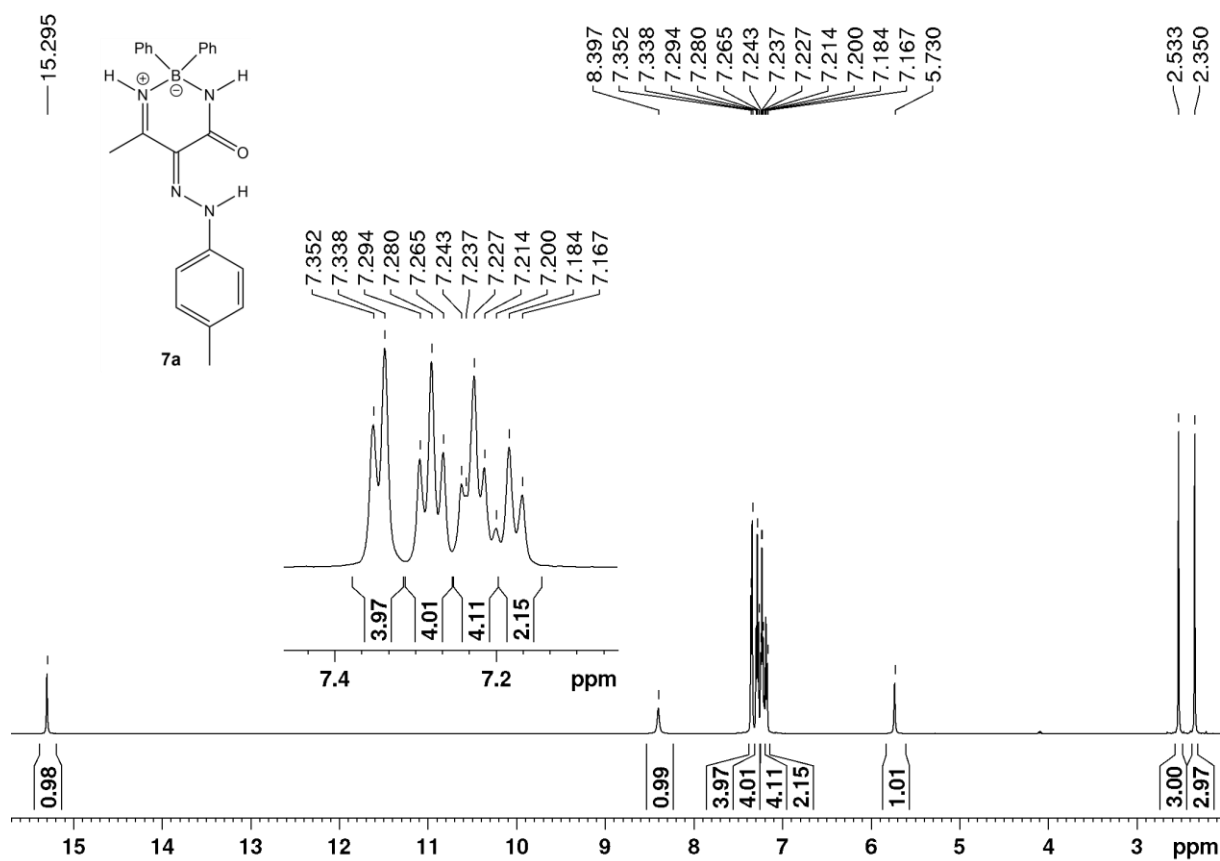
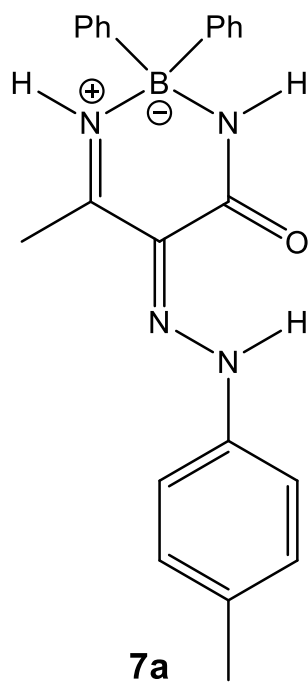


Figure S55. 500 MHz ^1H NMR of compound **7a** in CDCl_3

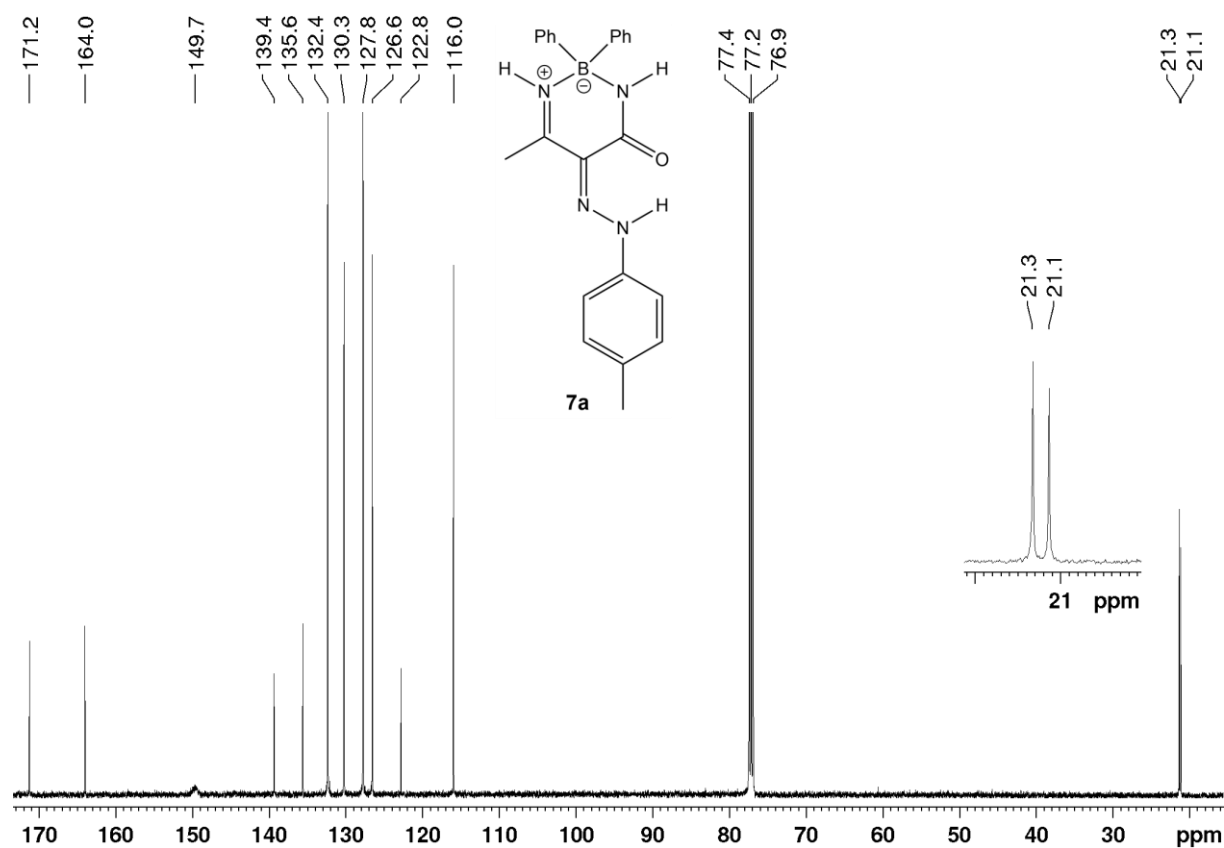


Figure S56. 125 MHz ^{13}C NMR of compound **7a** in CDCl_3

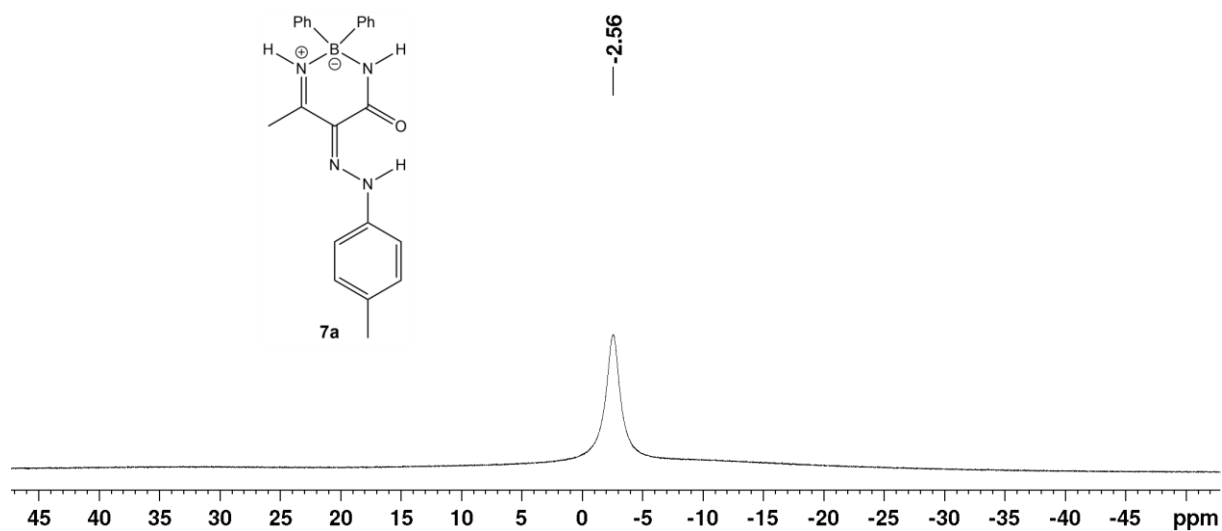


Figure S57. 160 MHz ^{11}B NMR of compound **7a** in CDCl_3

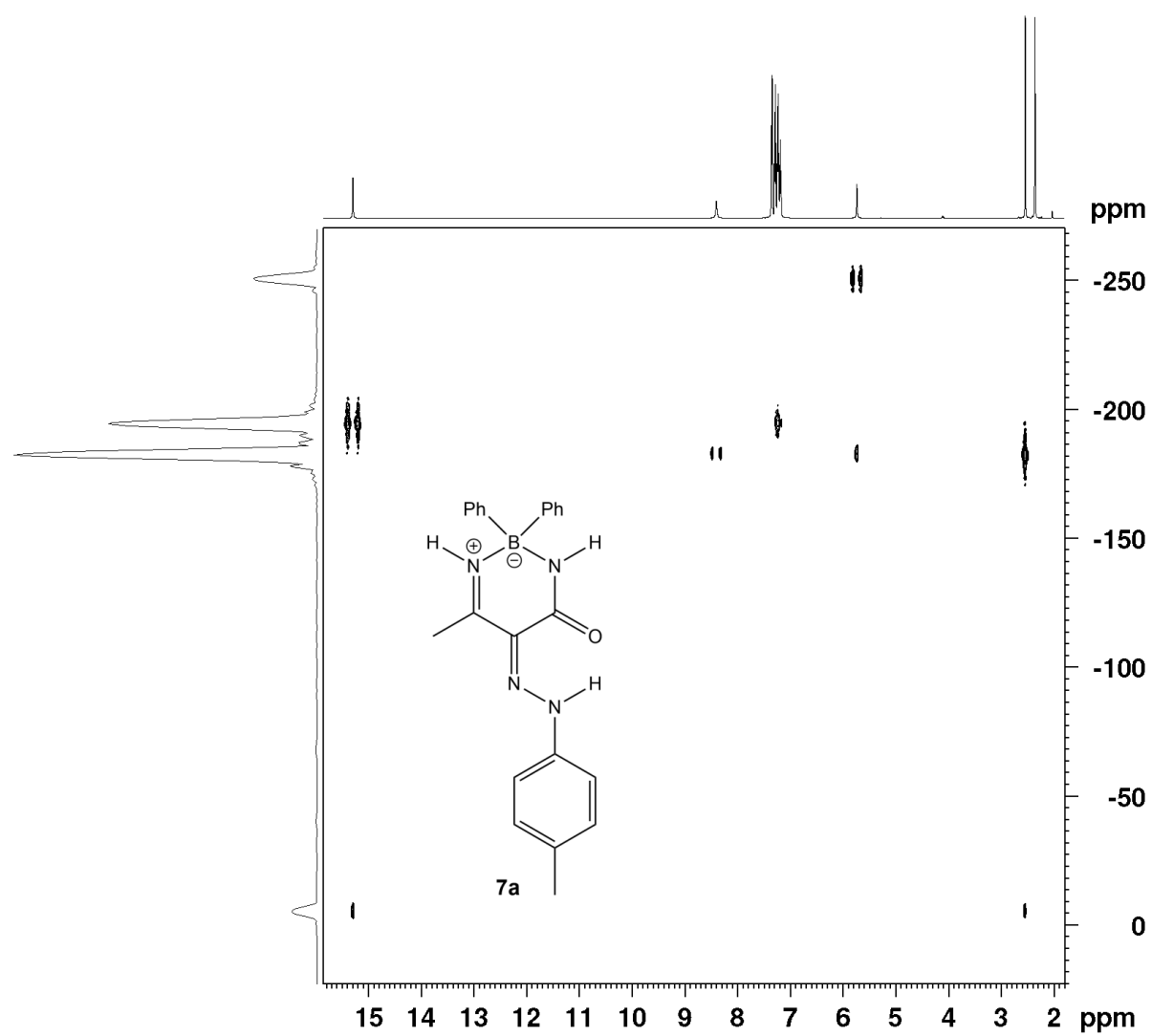


Figure S58. 500 MHz ^1H - ^{15}N HMBC NMR of compound **7a** in CDCl_3

2.13 Diazaborinone 7b

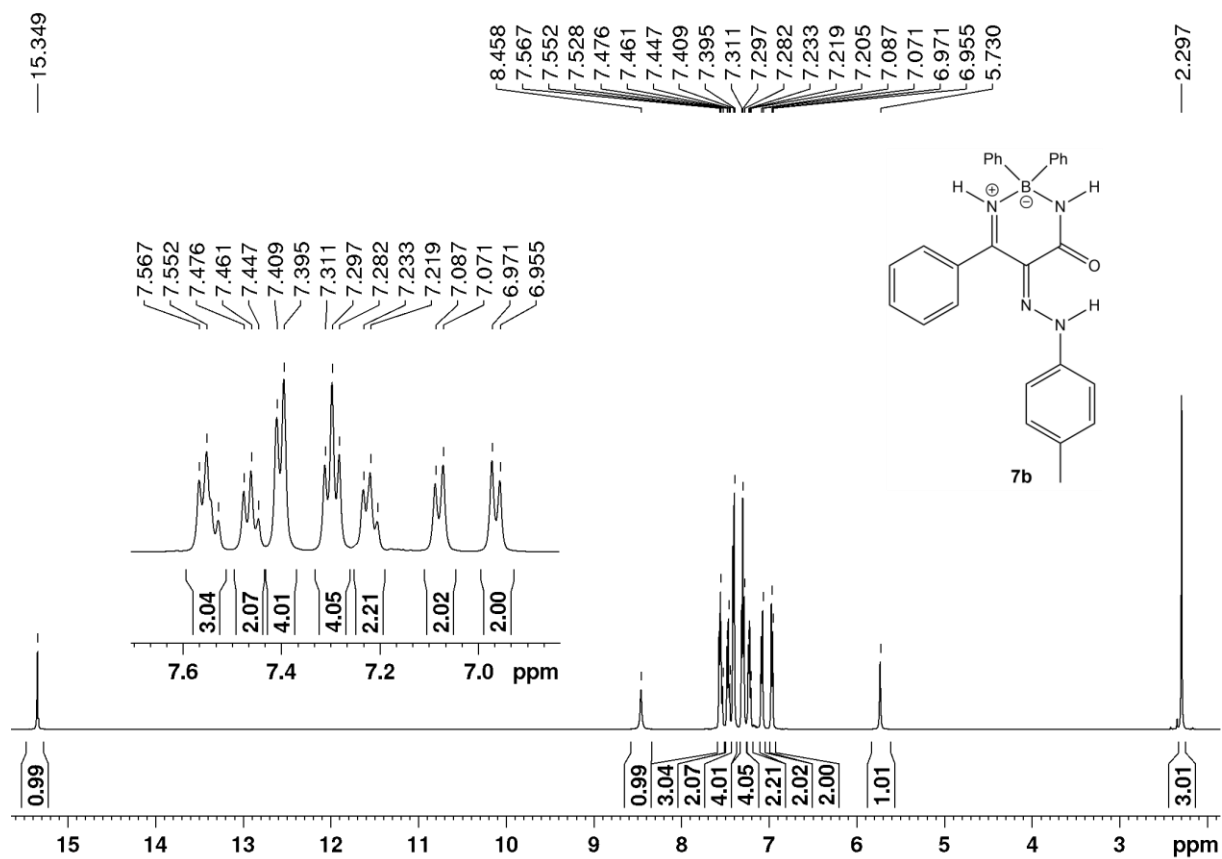
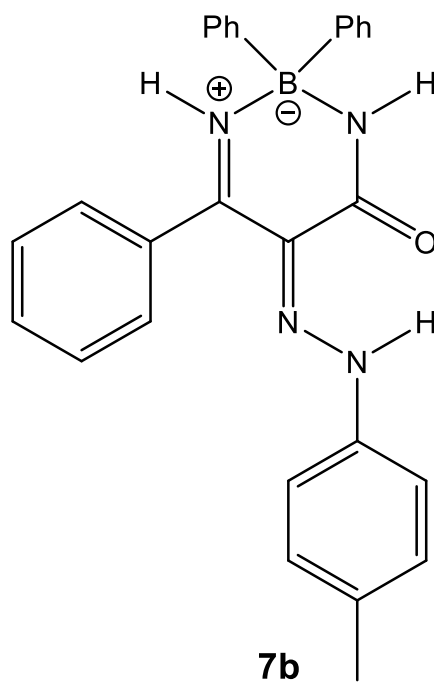


Figure S59. 500 MHz ^1H NMR of compound **7b** in CDCl_3

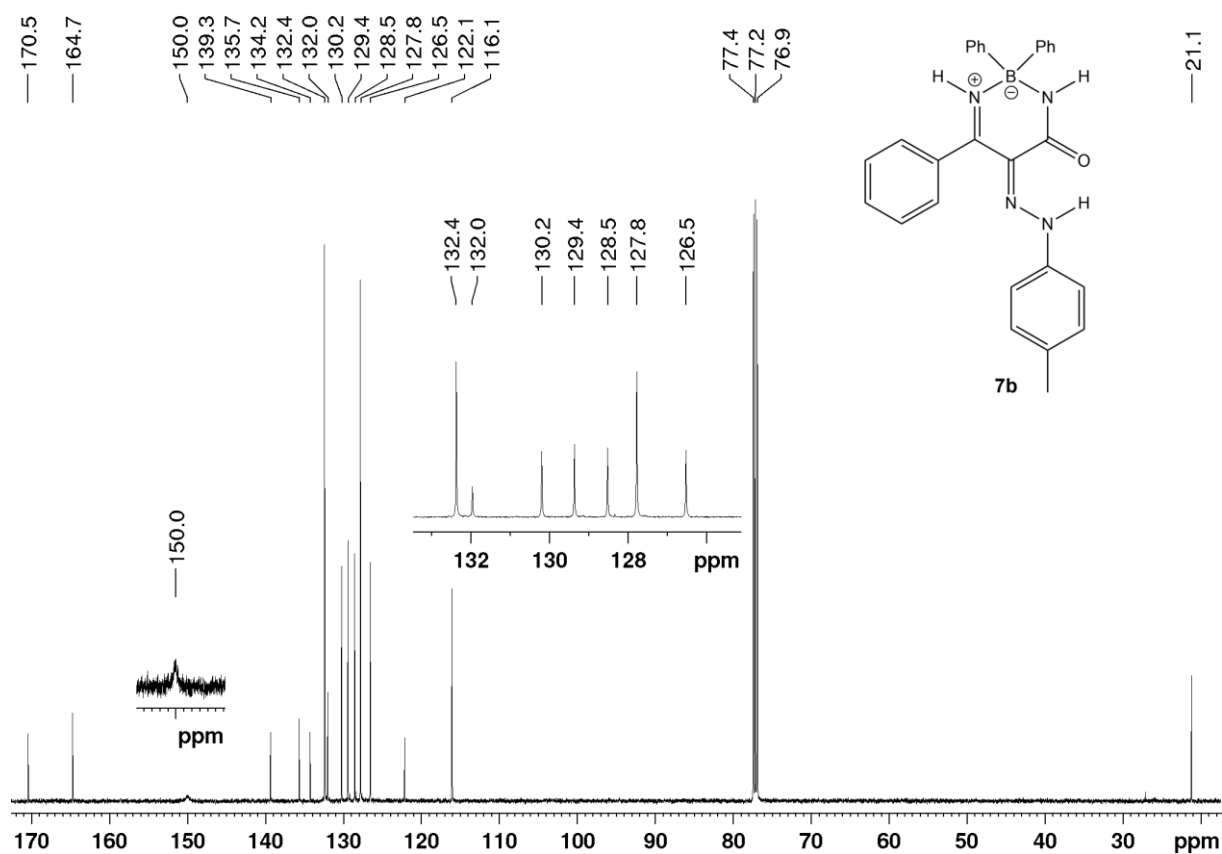


Figure S60. 125 MHz ^{13}C NMR of compound **7b** in CDCl_3

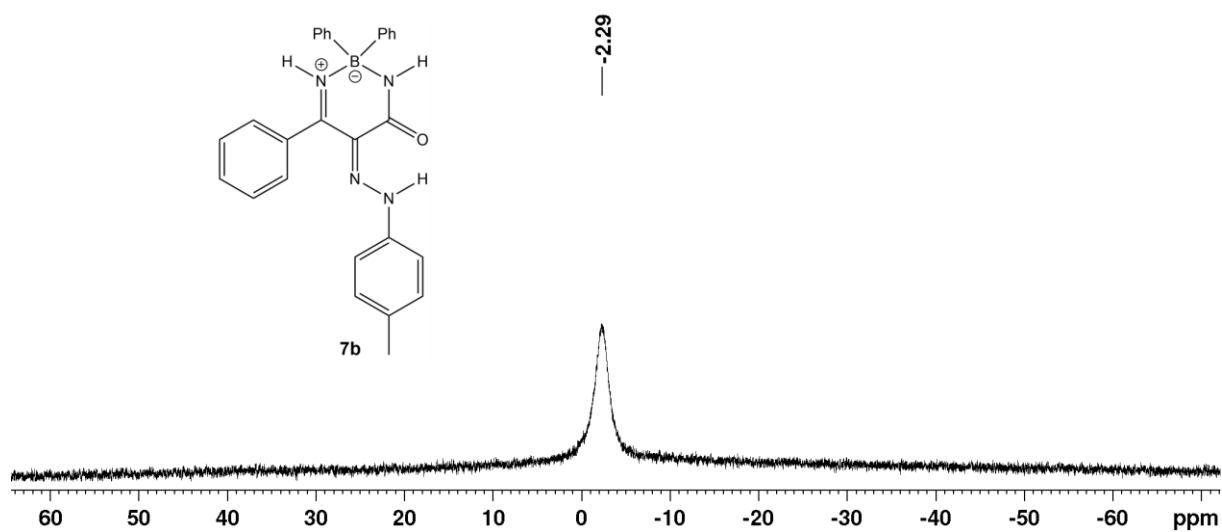


Figure S61. 160 MHz ^{11}B NMR of compound **7b** in CDCl_3

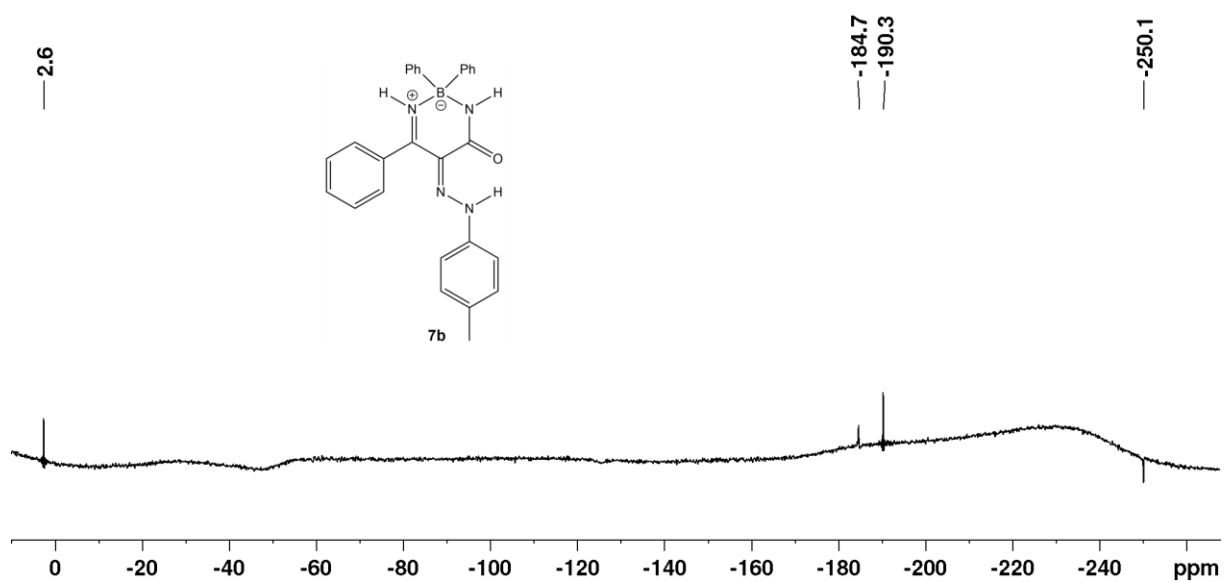
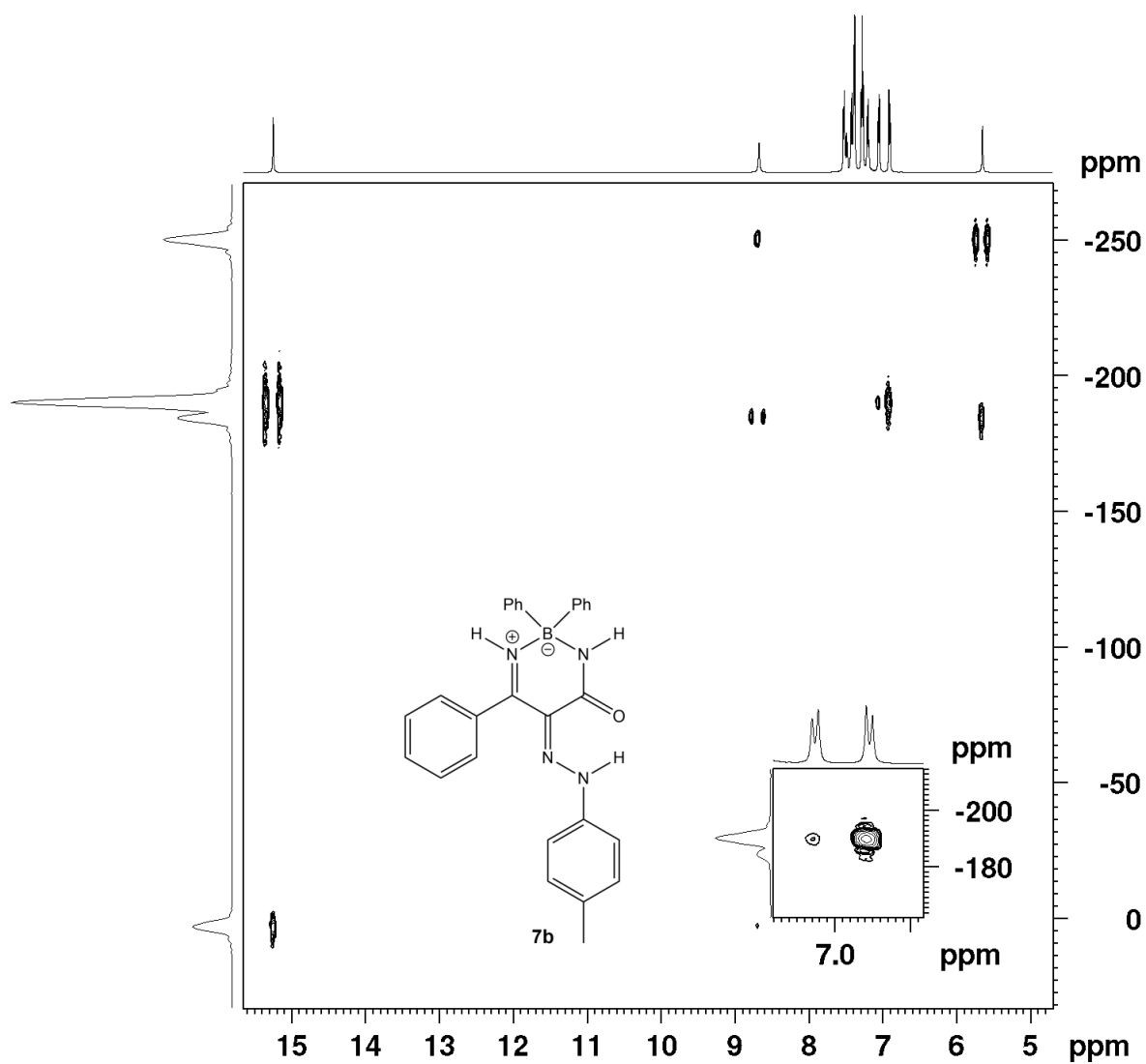


Figure S62. 50 MHz ^{15}N NMR of compound **7b** in CDCl_3



2.14 Diazaborinone 7c

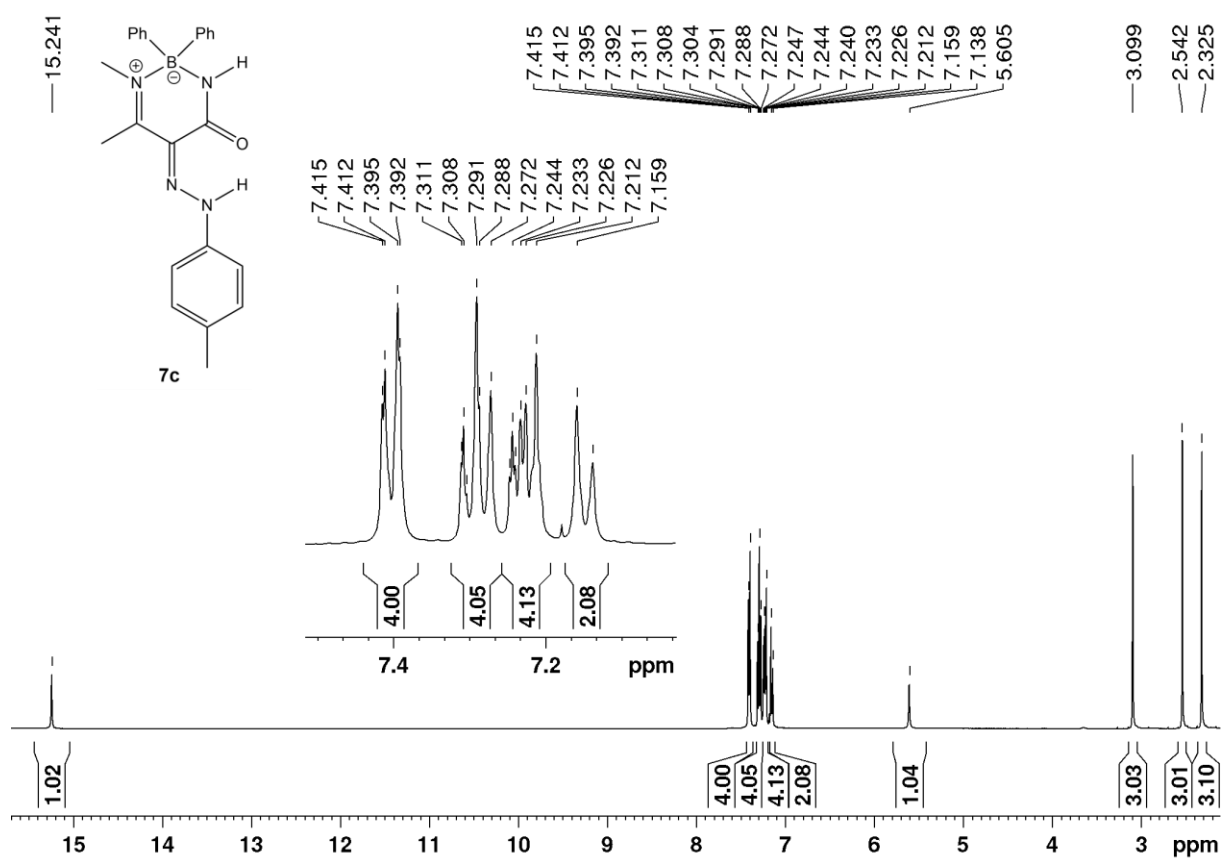
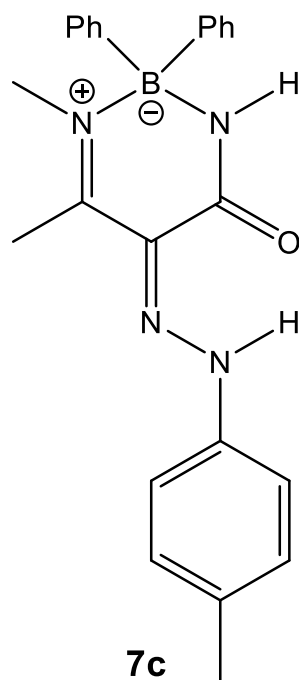
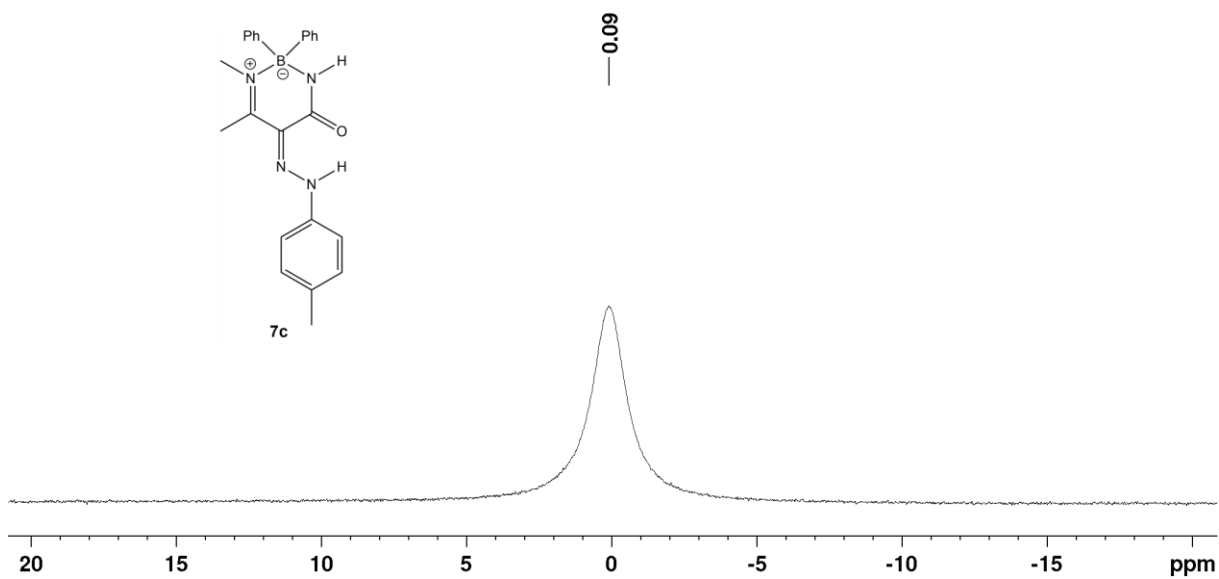
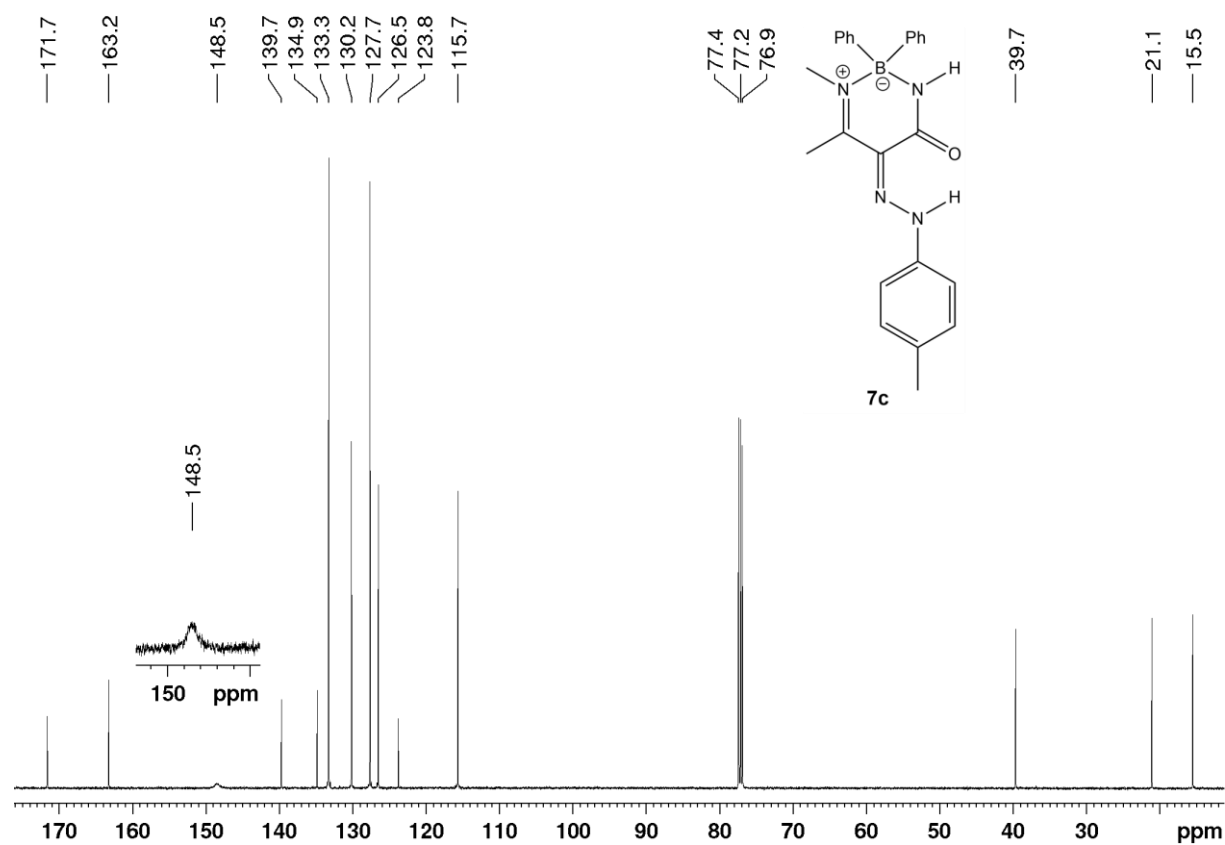


Figure S64. 400 MHz ^1H NMR of compound **7c** in CDCl_3



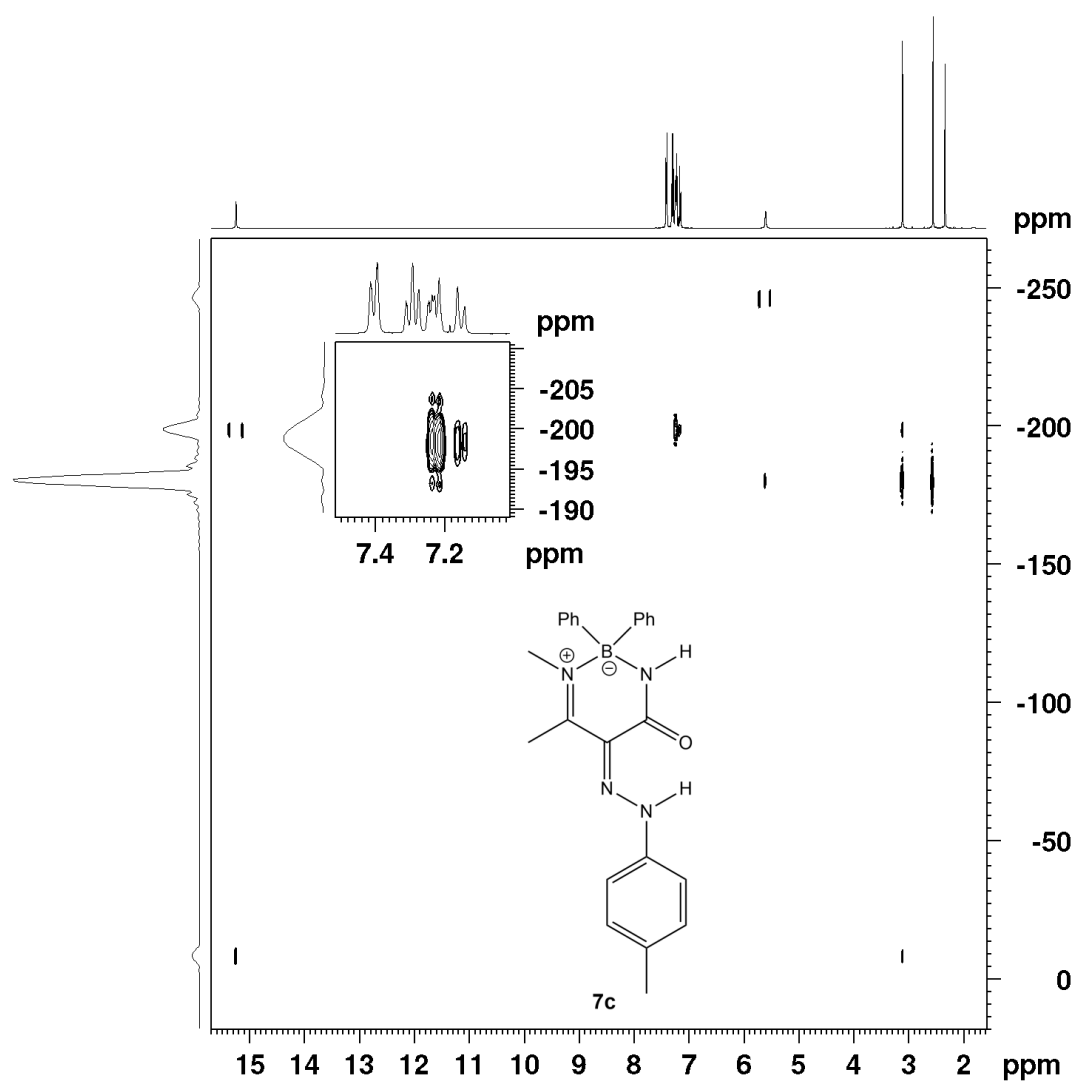


Figure S67. 500 MHz ^1H - ^{15}N HMBC NMR of compound **7c** in CDCl_3

2.15 Diazaborinone 7d

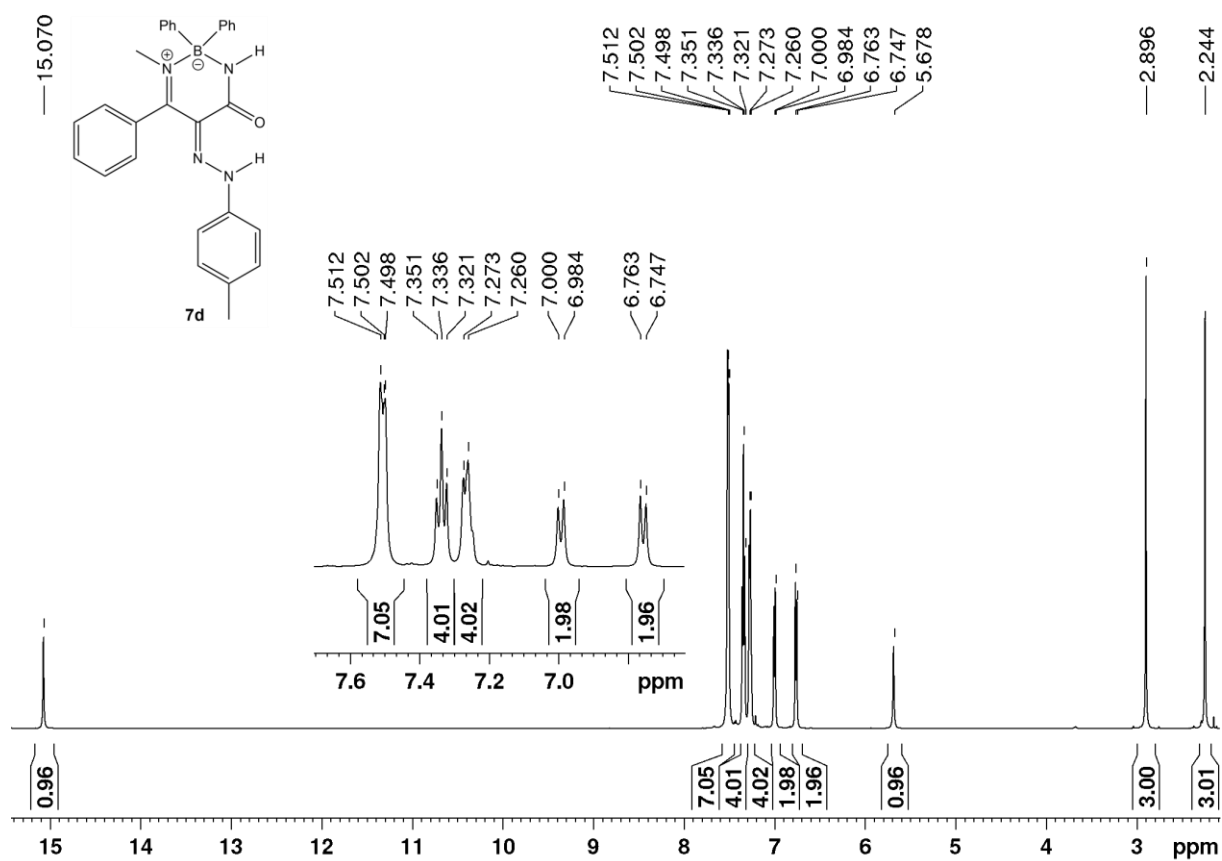
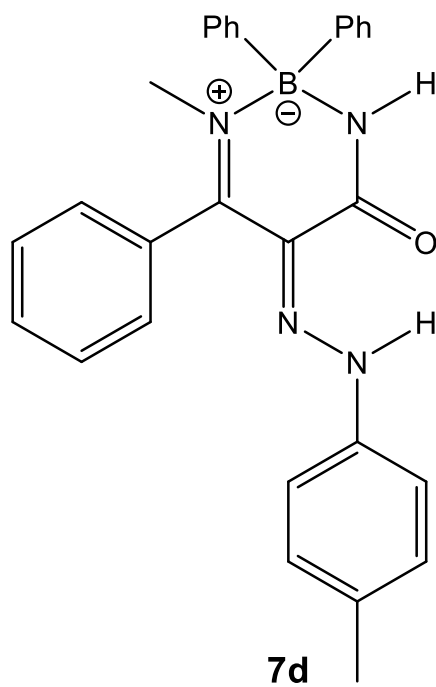


Figure S68. 500 MHz ^1H NMR of compound **7d** in CDCl_3

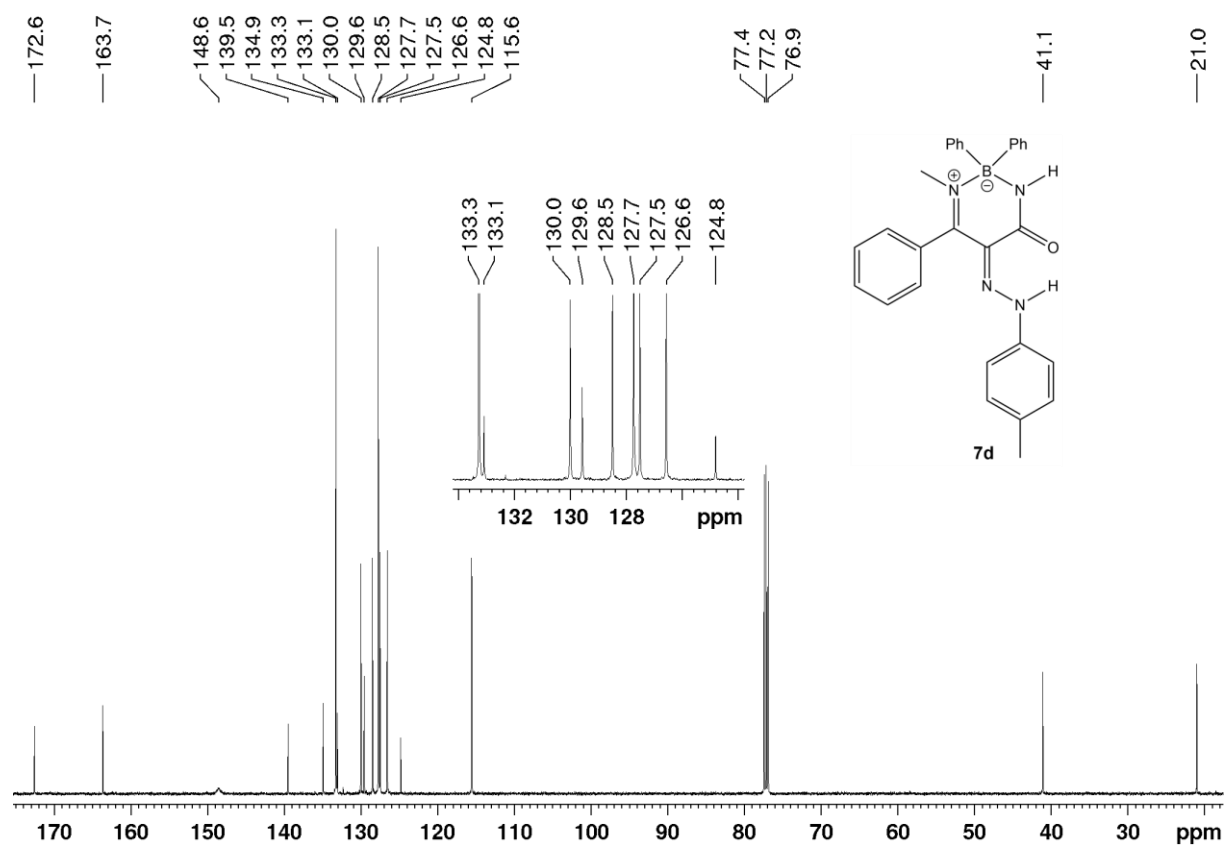


Figure S69. 125 MHz ^{13}C NMR of compound **7d** in CDCl_3

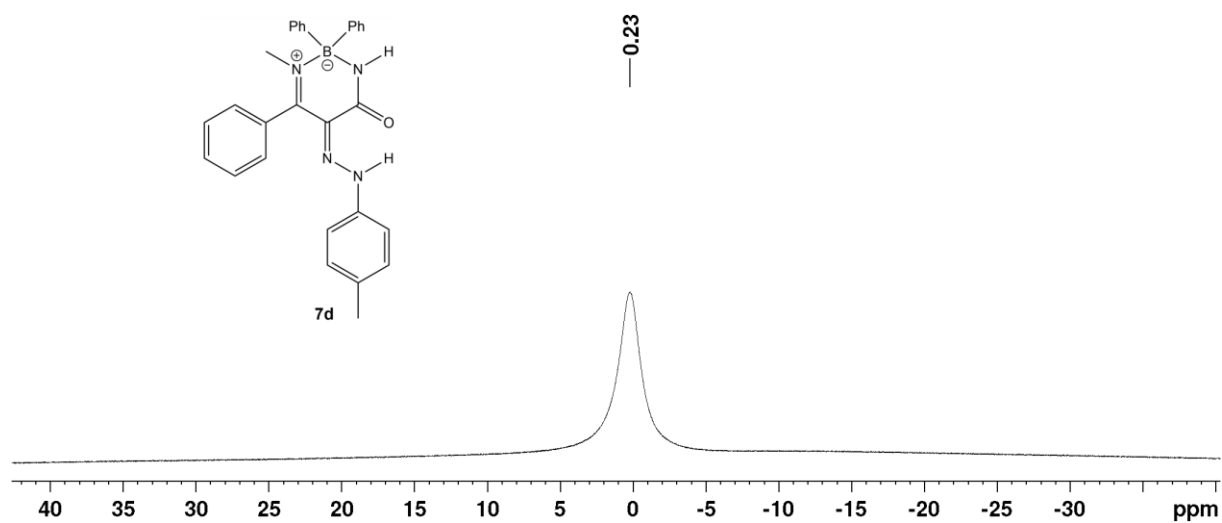
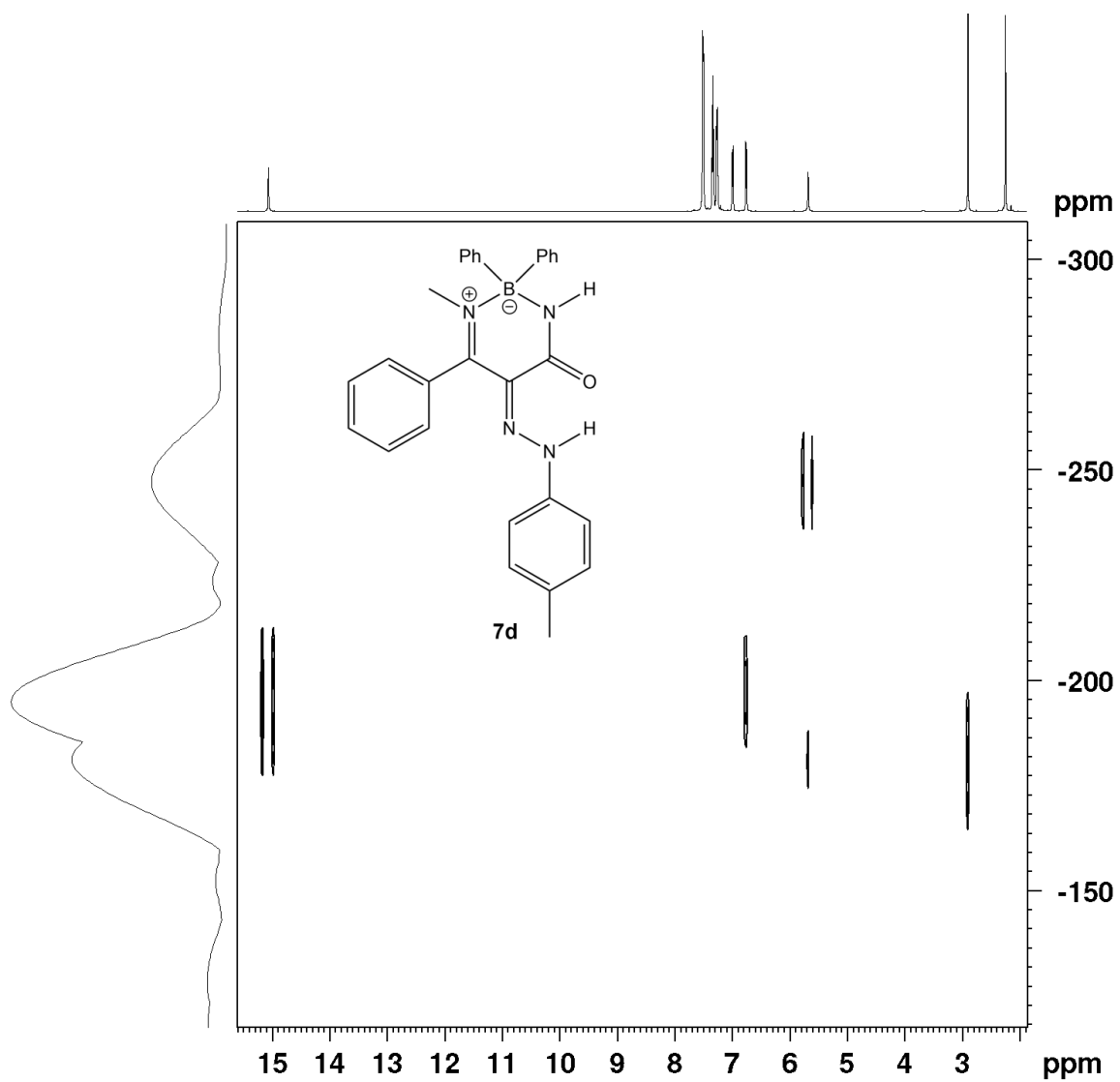
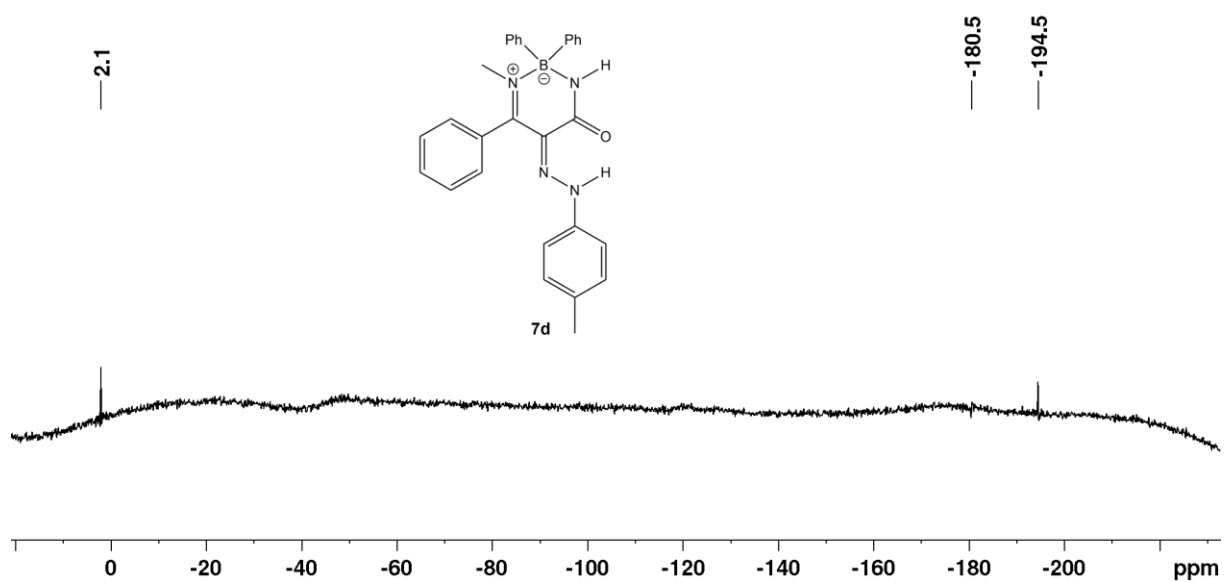


Figure S70. 160 MHz ^{11}B NMR of compound **7d** in CDCl_3



2.16 Diazaborinone 7e

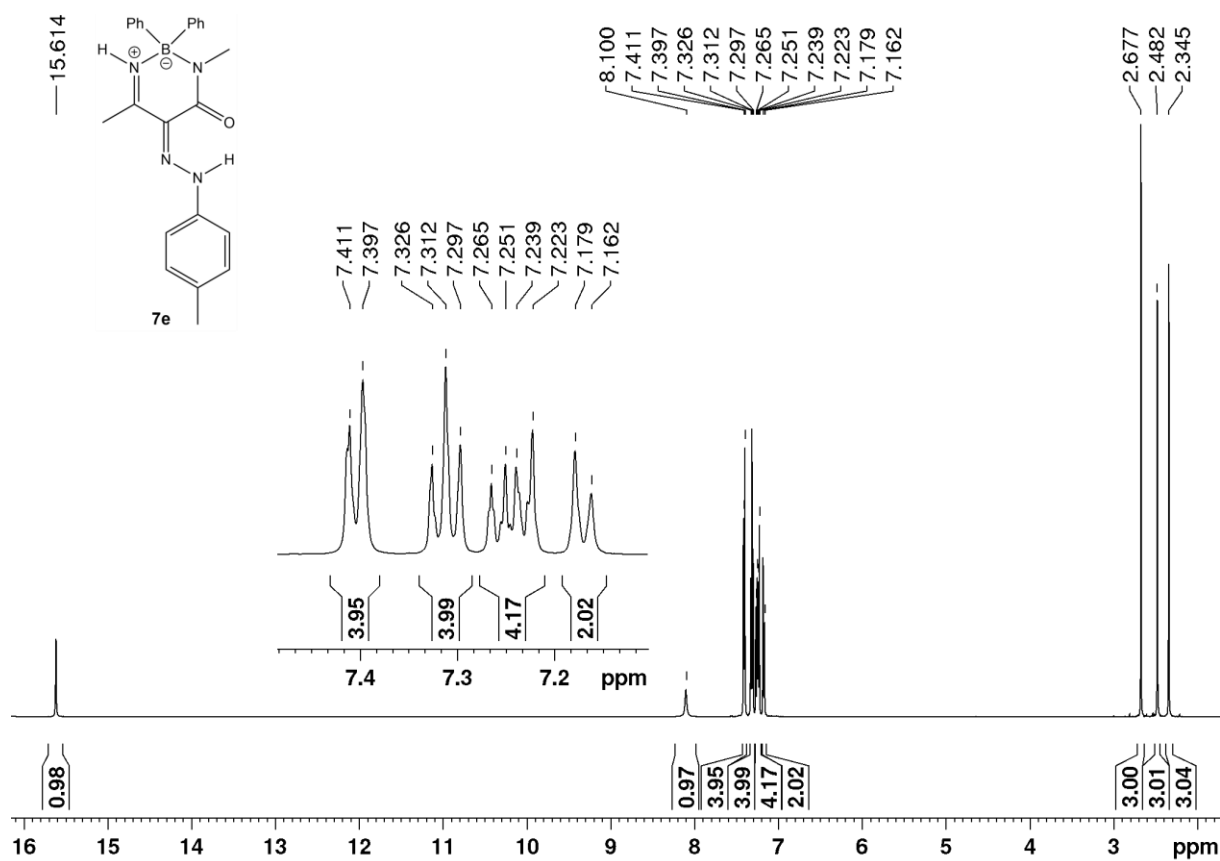
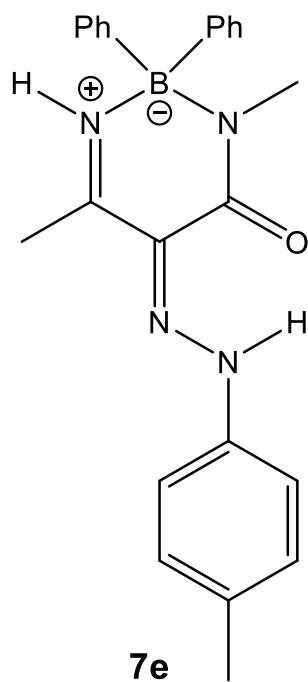


Figure S73. 500 MHz ^1H NMR of compound **7e** in CDCl_3

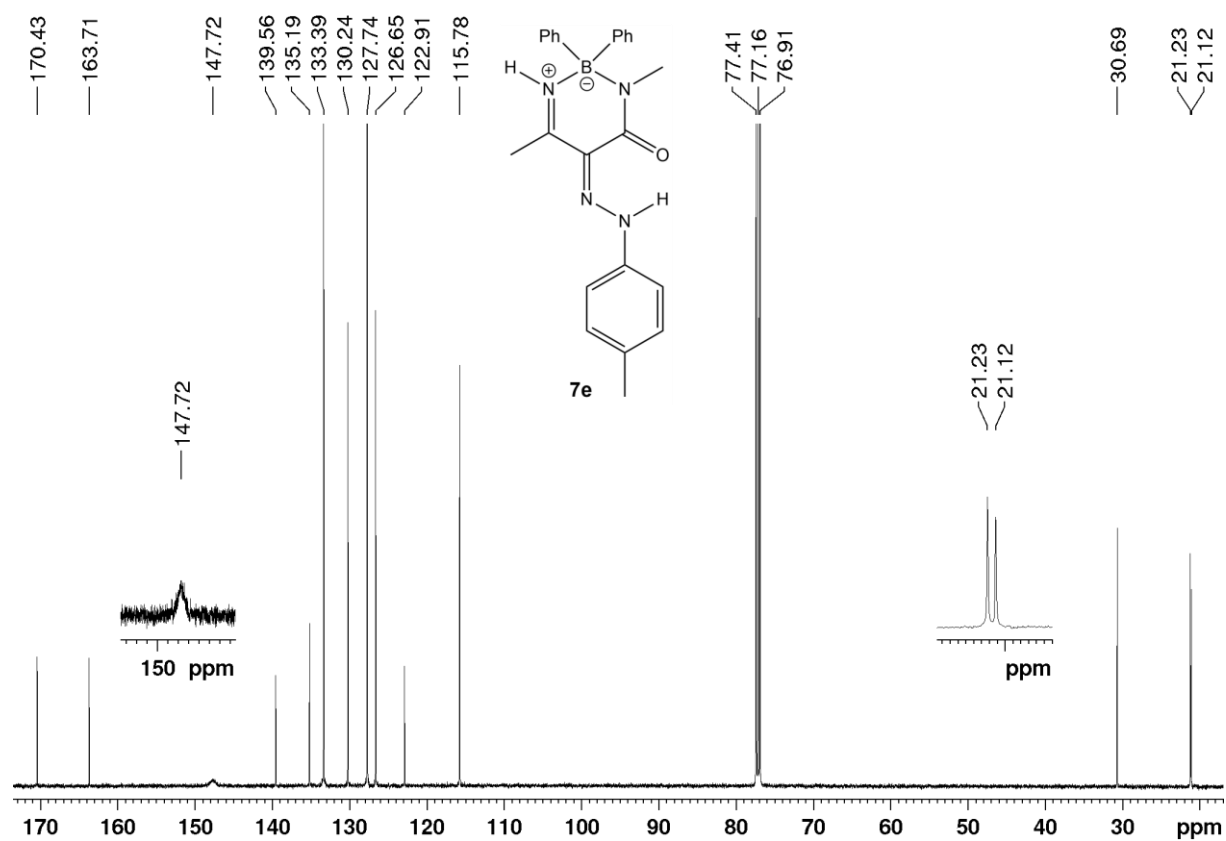


Figure S74. 125 MHz ^{13}C NMR of compound **7e** in CDCl_3

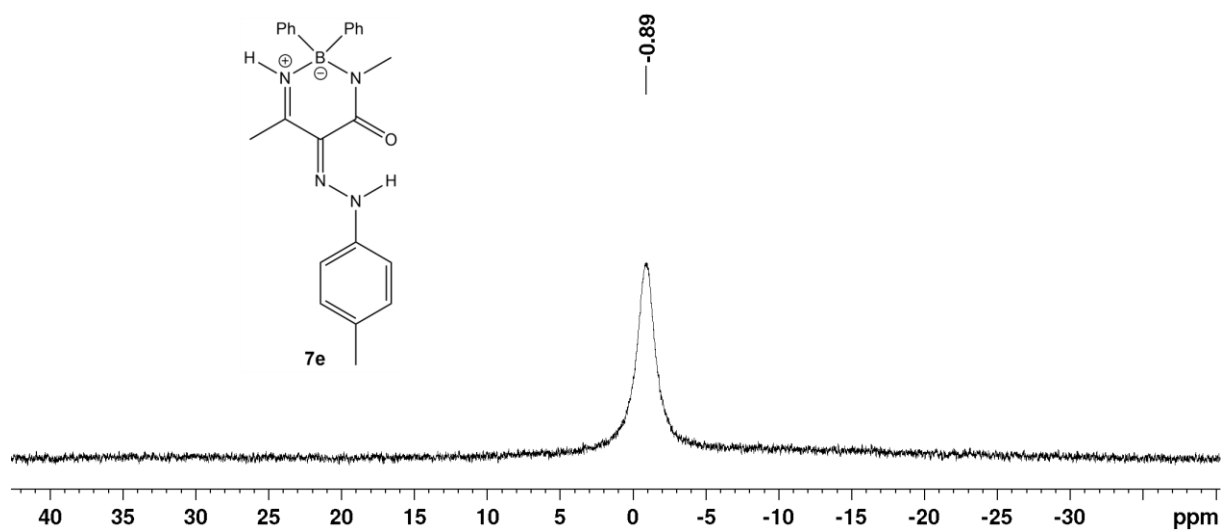


Figure S75. 160 MHz ^{11}B NMR of compound **7e** in CDCl_3

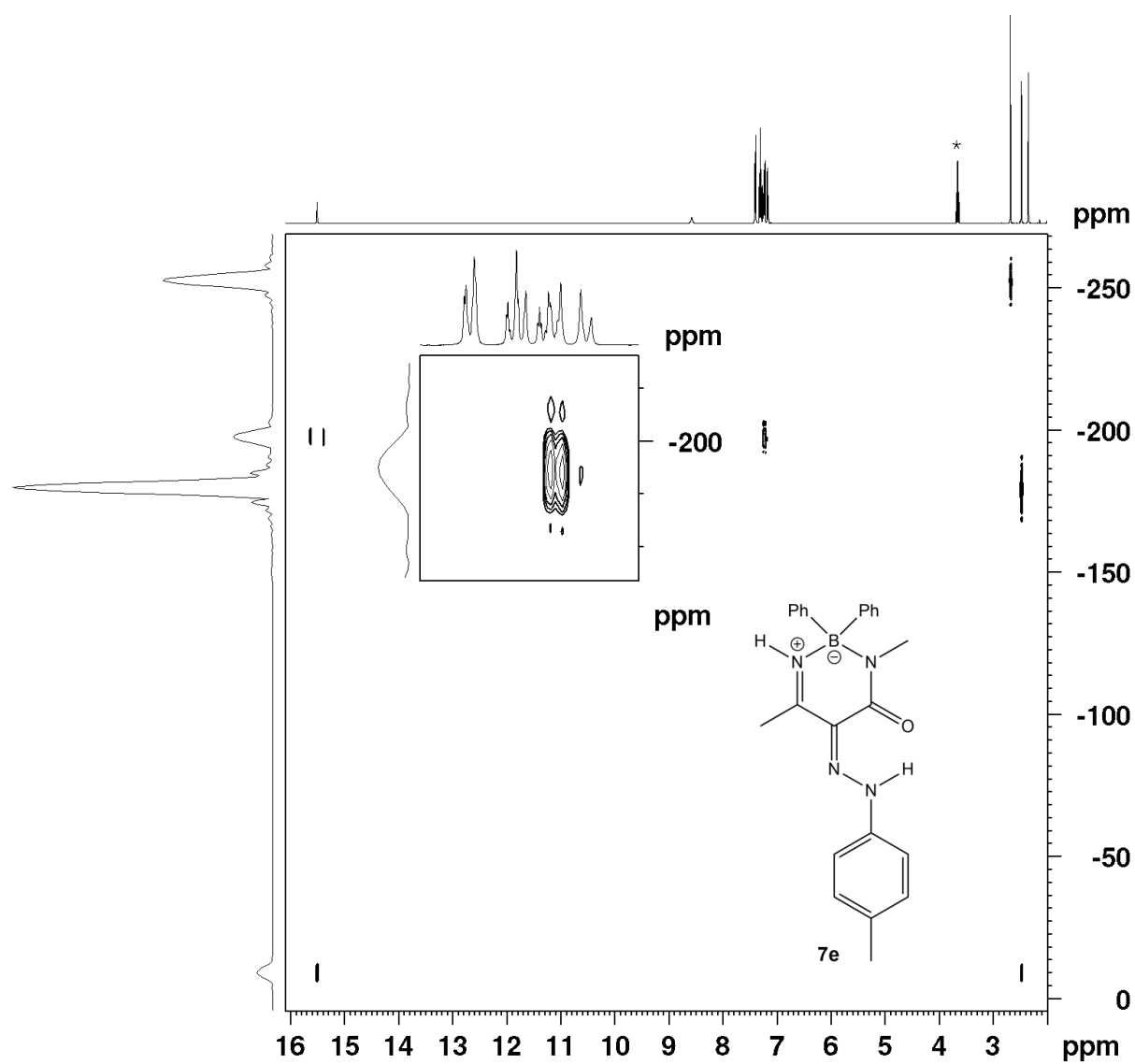


Figure S76. 400 MHz ^1H - ^{15}N HMBC NMR of compound **7e** in CDCl_3 (* CH_2 from ethanol)

2.17 Diazaborinone 7f

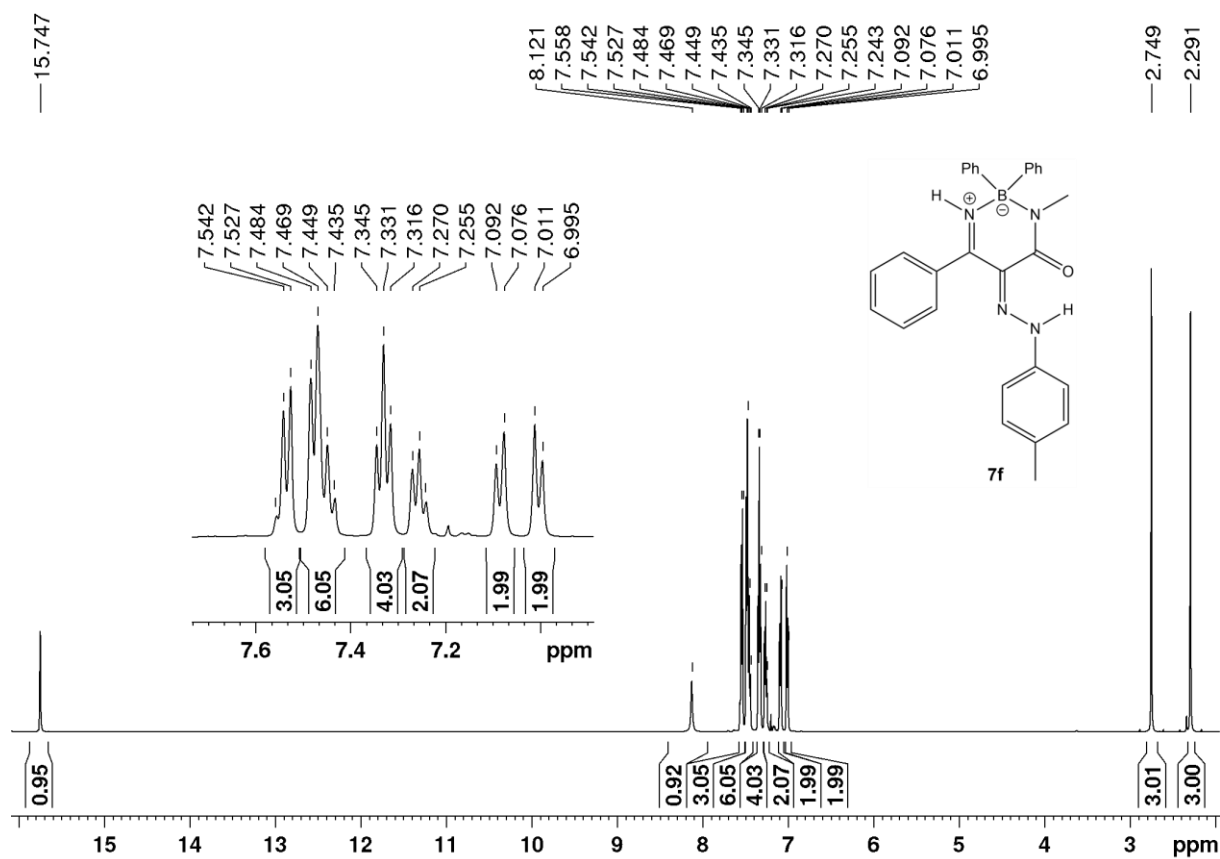
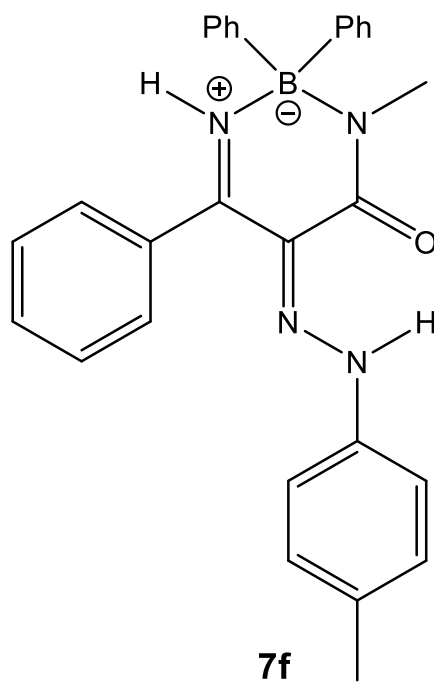


Figure S77. 500 MHz ^1H NMR of compound 7f in CDCl_3

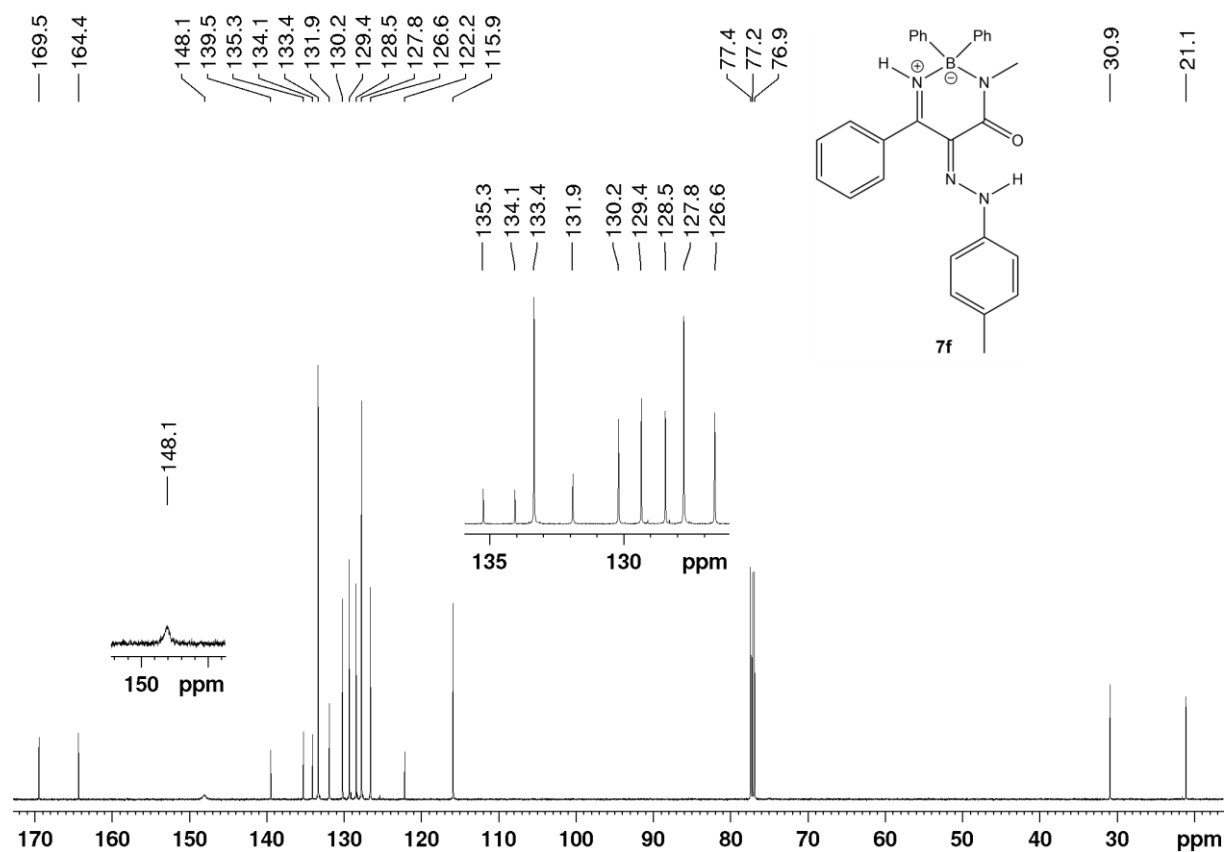


Figure S78. 125 MHz ^{13}C NMR of compound **7f** in CDCl_3

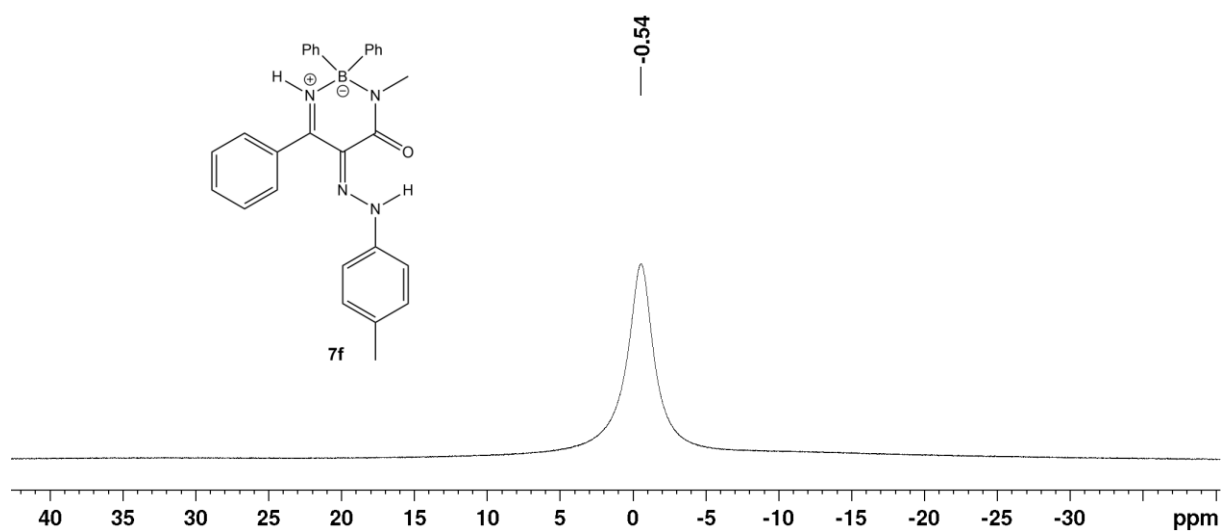


Figure S79. 160 MHz ^{11}B NMR of compound **7f** in CDCl_3

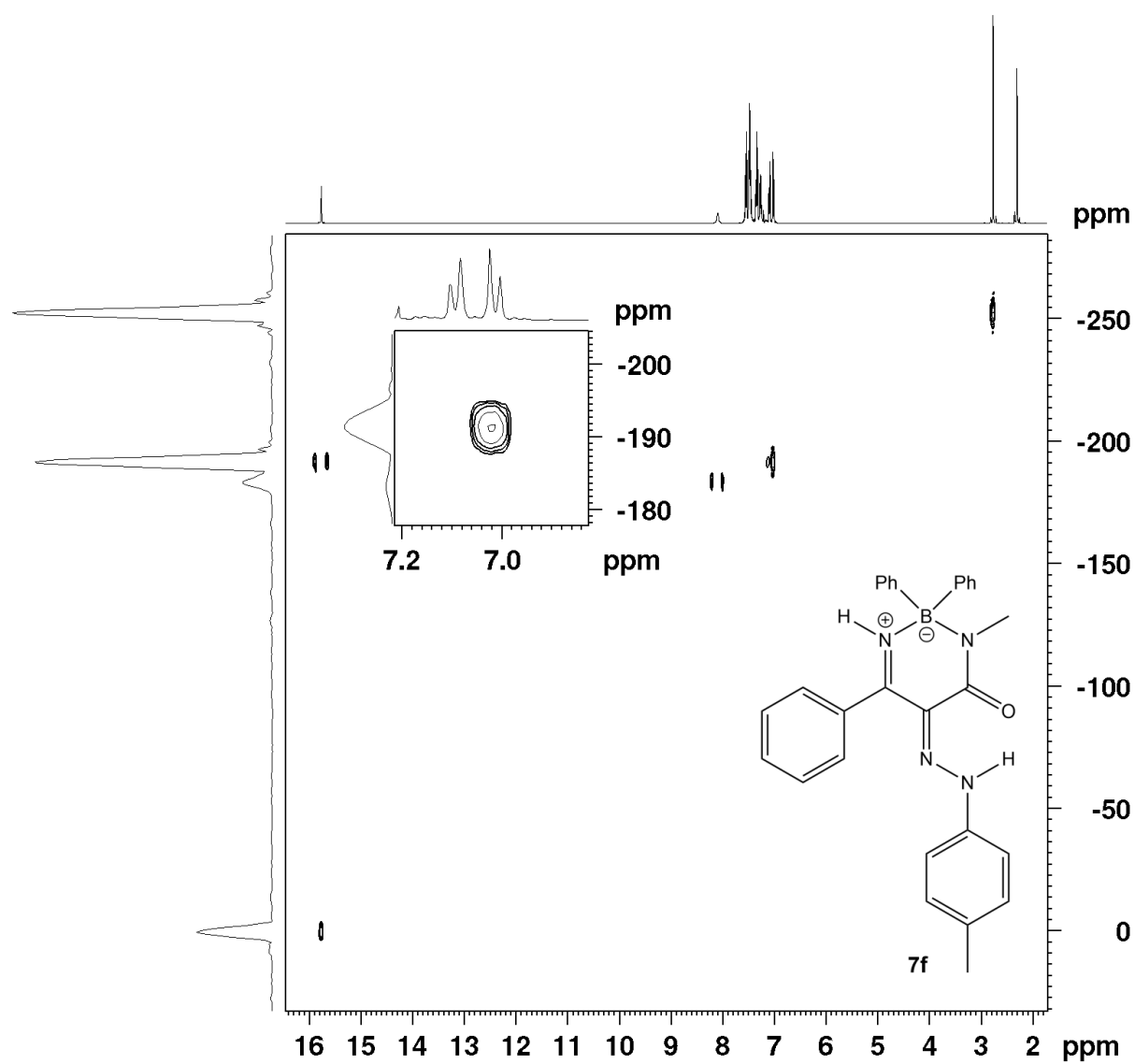


Figure S80. 400 MHz ^1H - ^{15}N HMBC NMR of compound **7f** in CDCl_3

2.18 Diazaborinone 7g

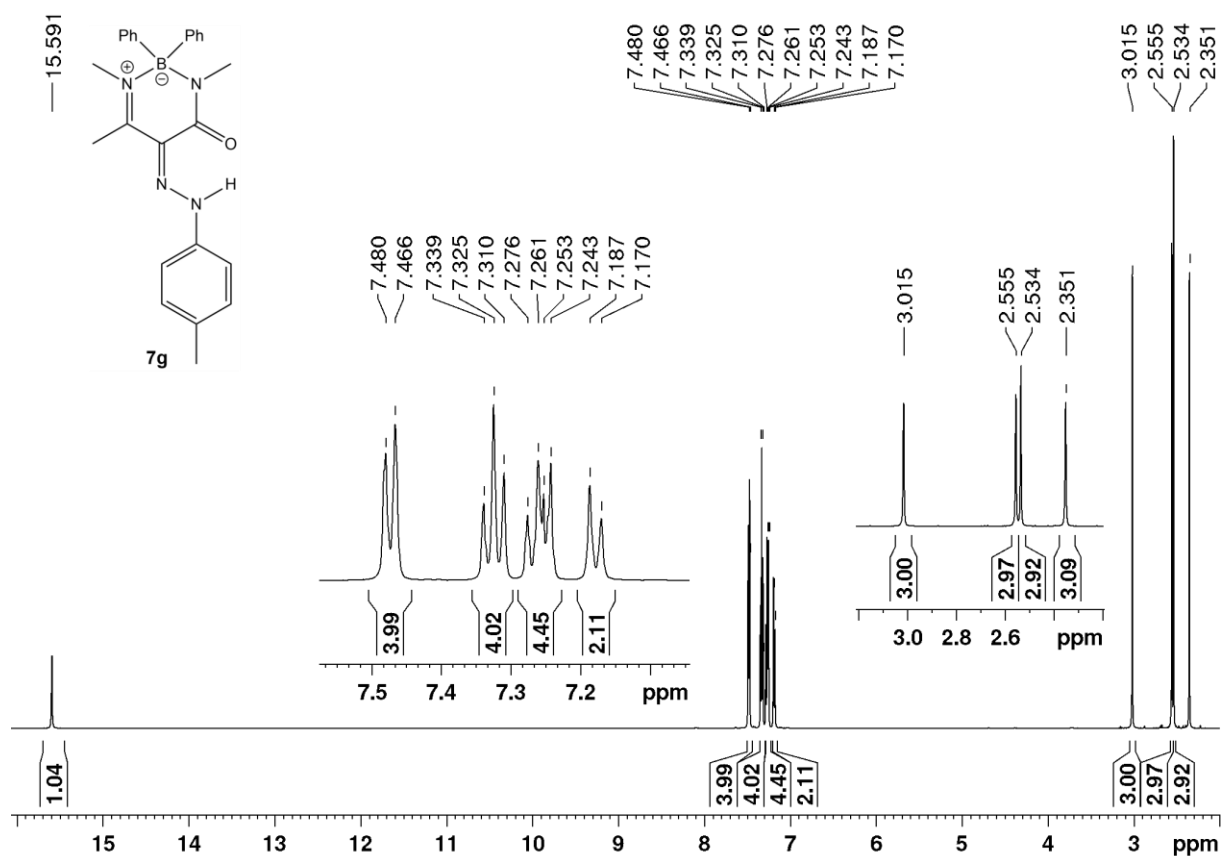
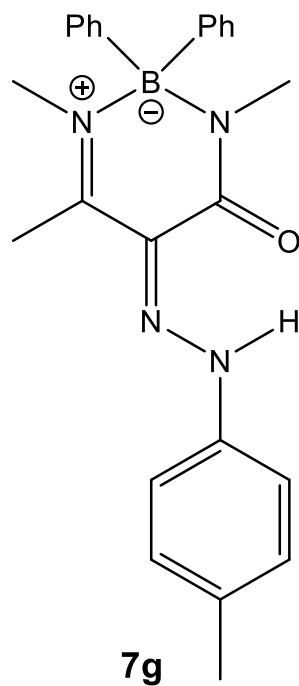


Figure S81. 500 MHz ^1H NMR of compound **7g** in CDCl_3

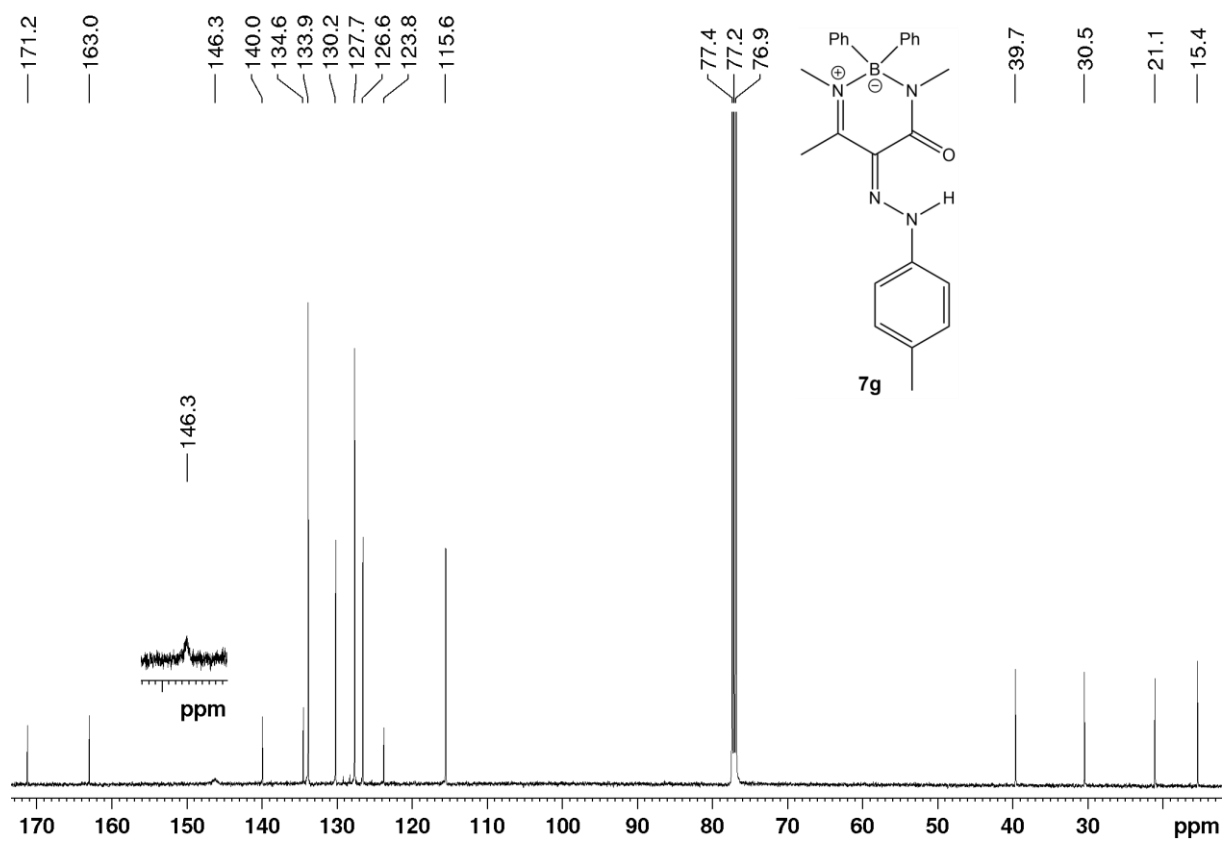


Figure S82. 125 MHz ^{13}C NMR of compound **7g** in CDCl_3

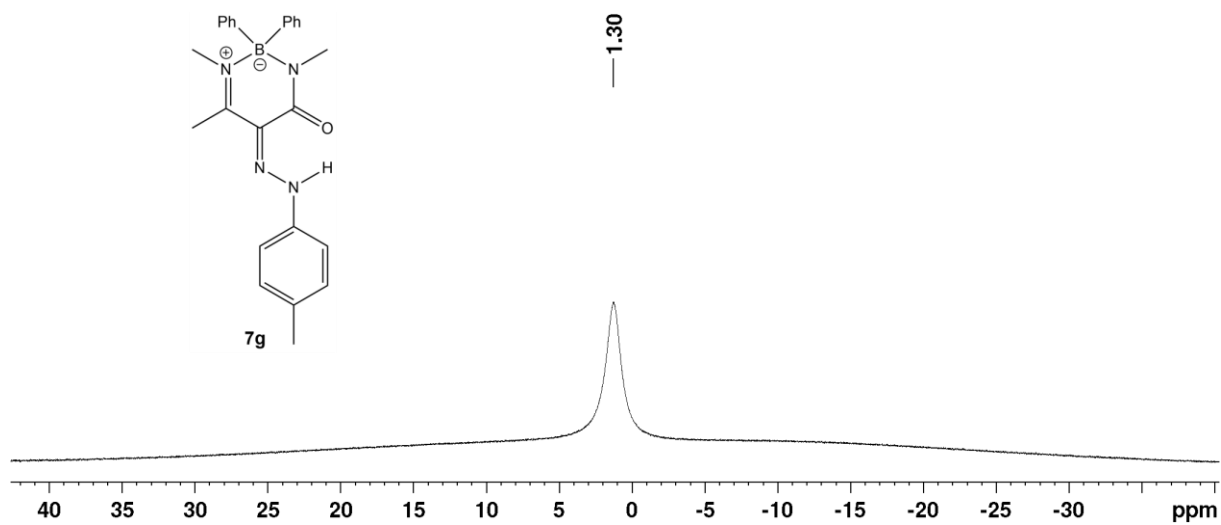


Figure S83. 160 MHz ^{11}B NMR of compound **7g** in CDCl_3

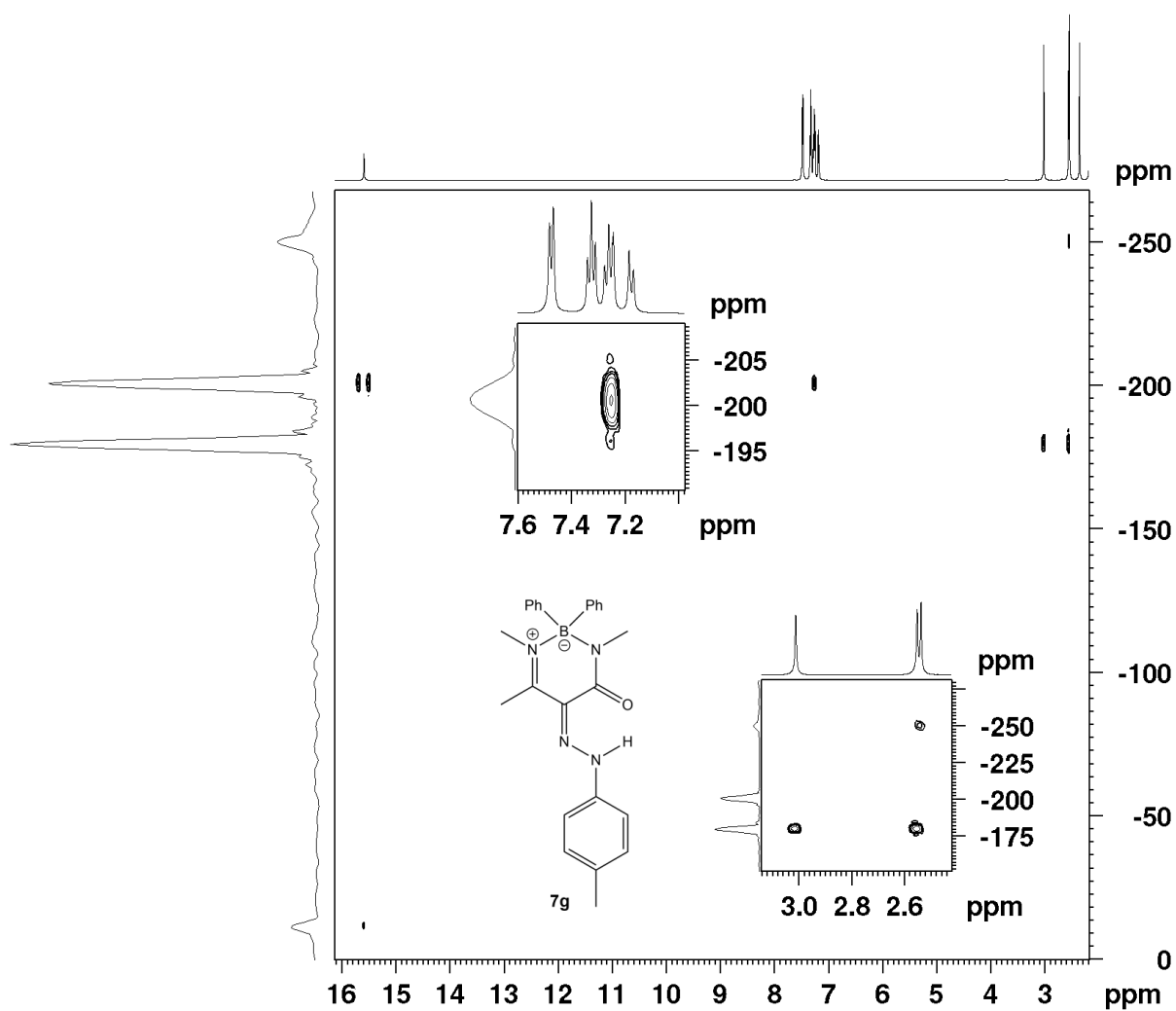


Figure S84. 500 MHz ^1H - ^{15}N HMBC NMR of compound **7g** in CDCl_3

2.19 Diazaborinone 7h

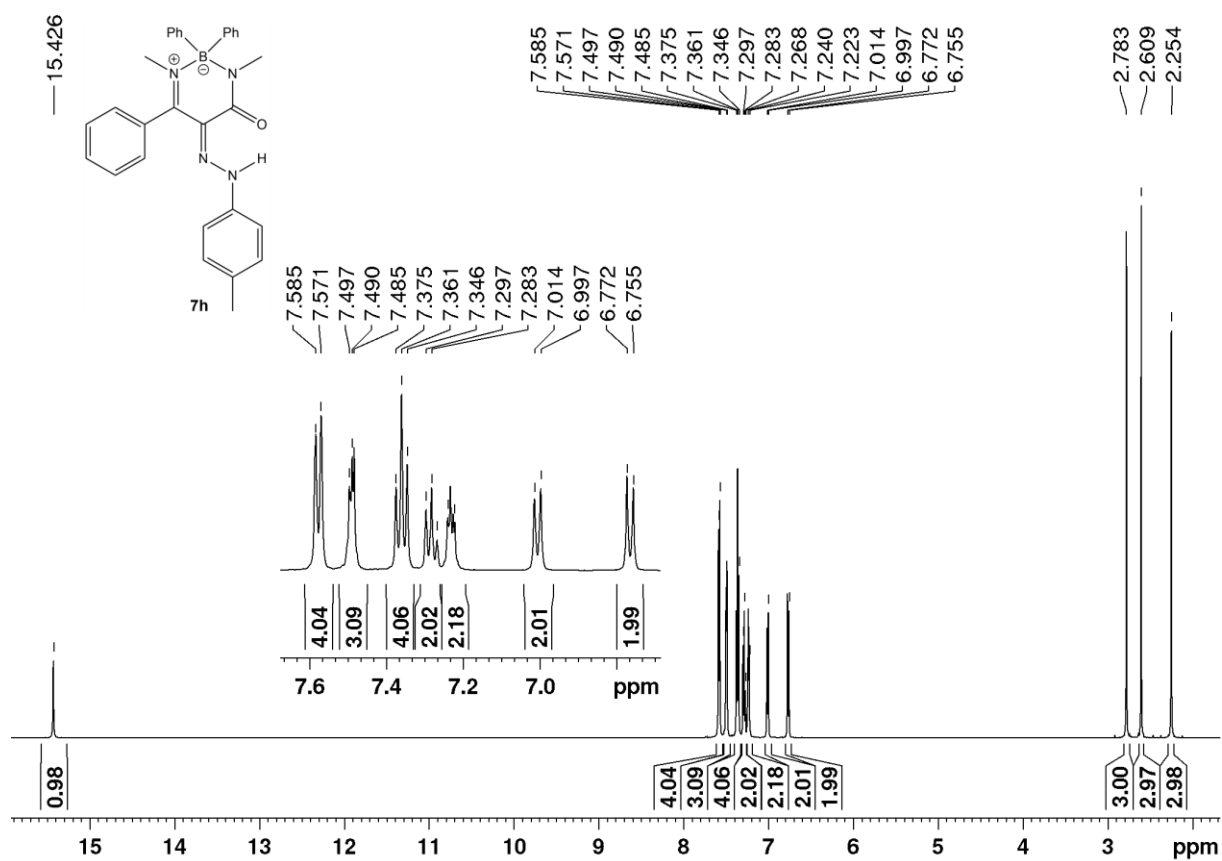
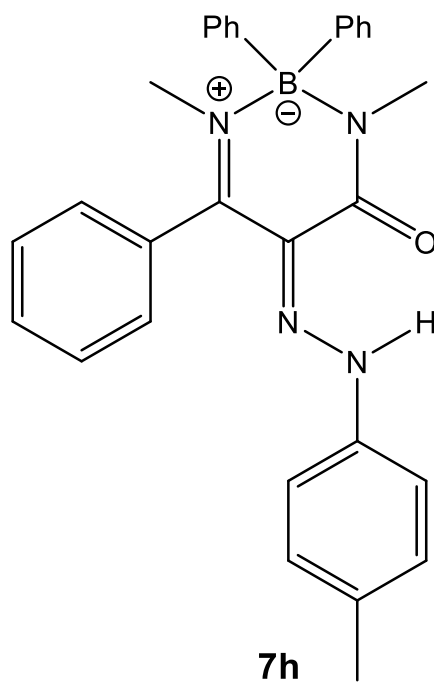


Figure S85. 500 MHz ^1H NMR of compound **7h** in CDCl_3

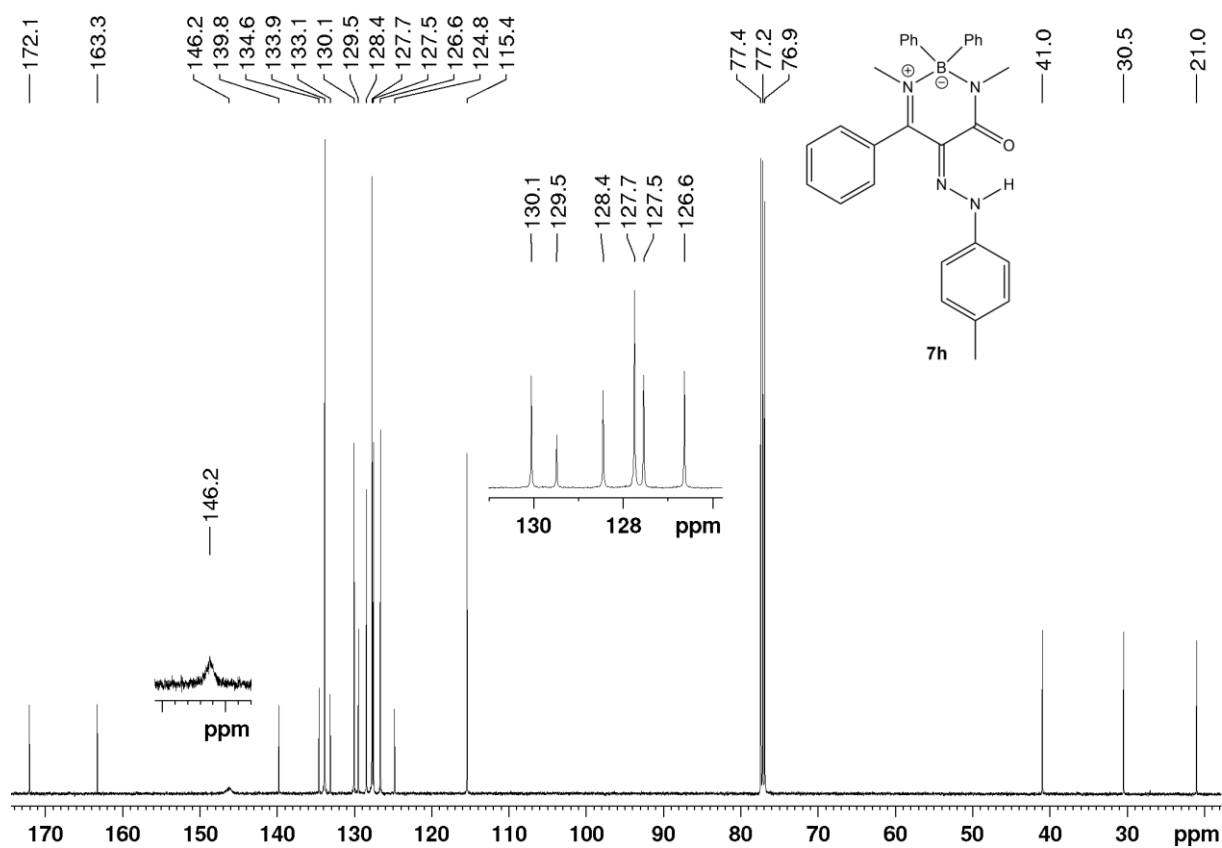


Figure S86. 125 MHz ^{13}C NMR of compound **7h** in CDCl_3

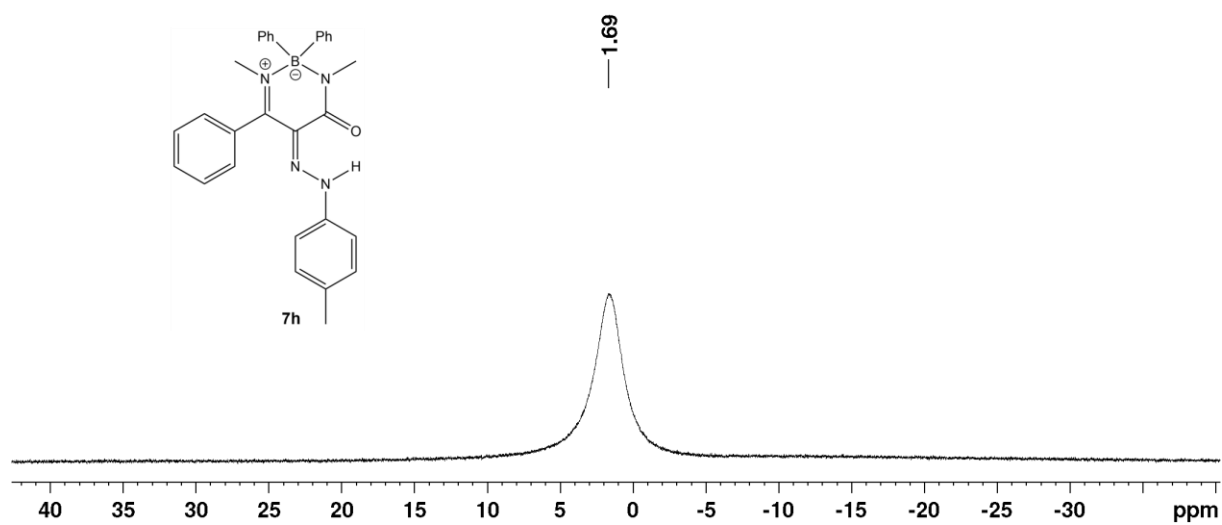


Figure S87. 160 MHz ^{11}B NMR of compound **7h** in CDCl_3

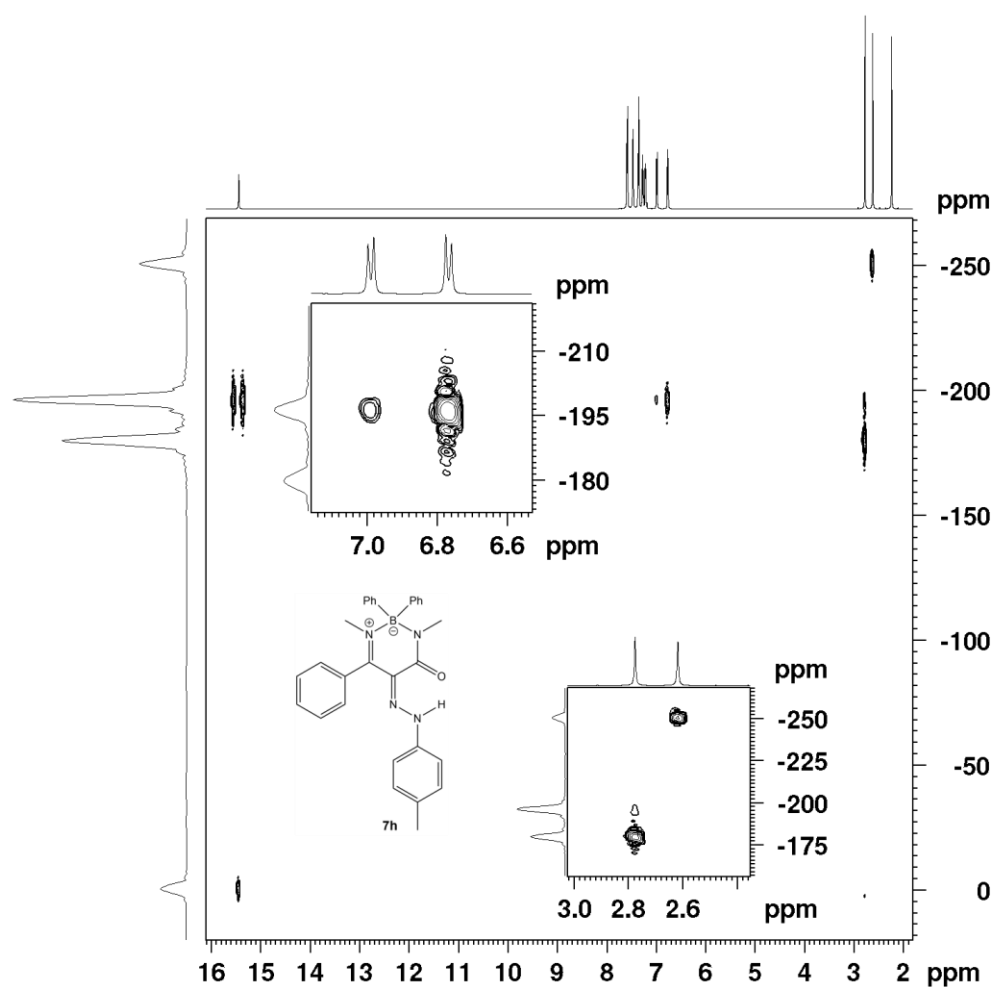


Figure S88. 500 MHz ^1H - ^{15}N HMBC NMR of compound **7h** in CDCl_3

2.20 Triazaborine 8e

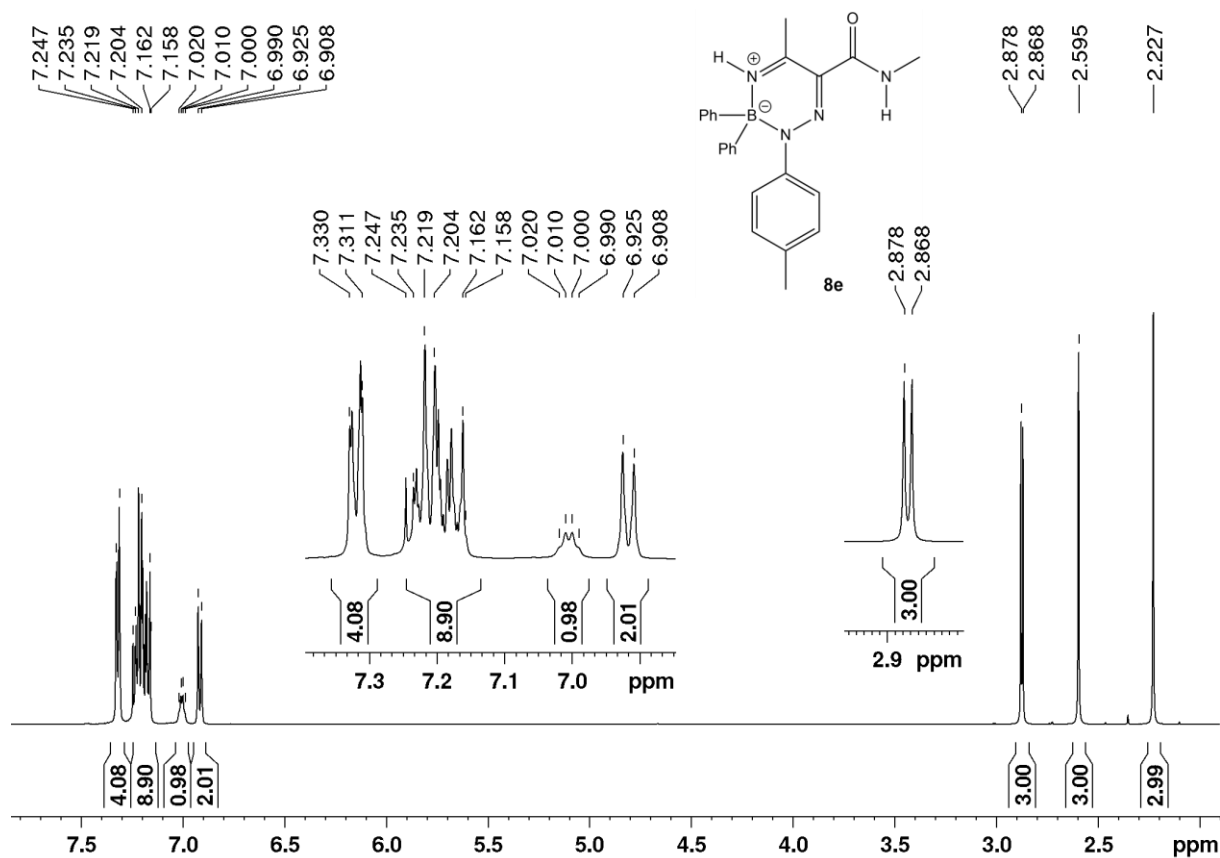
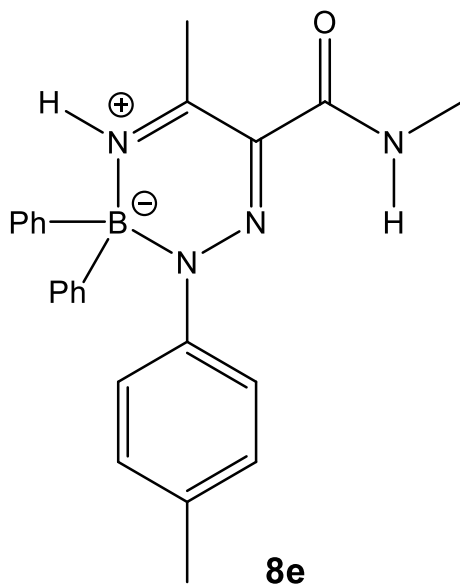


Figure S89. 500 MHz ^1H NMR of compound **8e** in CDCl_3

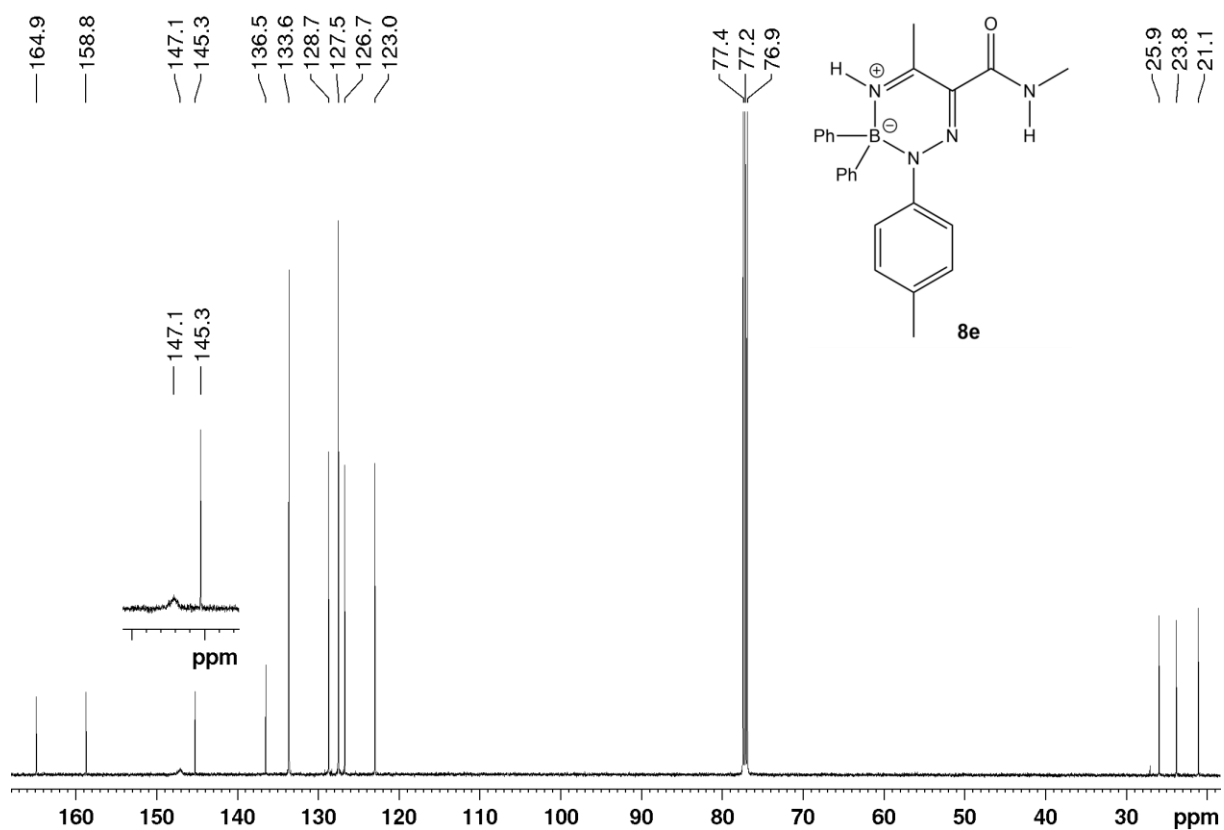


Figure S90. 125 MHz ^{13}C NMR of compound **8e** in CDCl_3

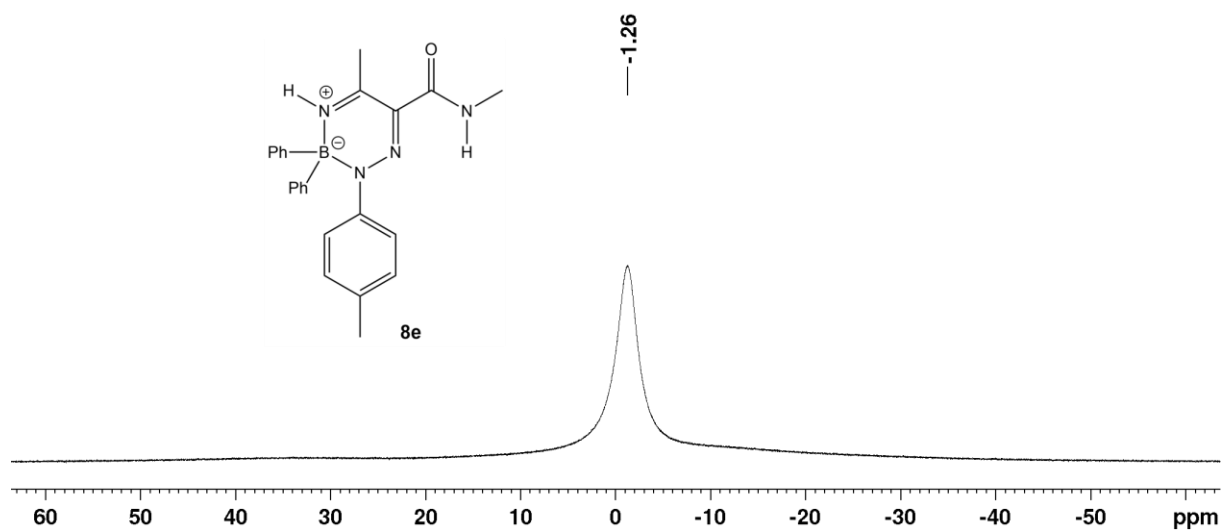


Figure S91. 160 MHz ^{11}B NMR of compound **8e** in CDCl_3

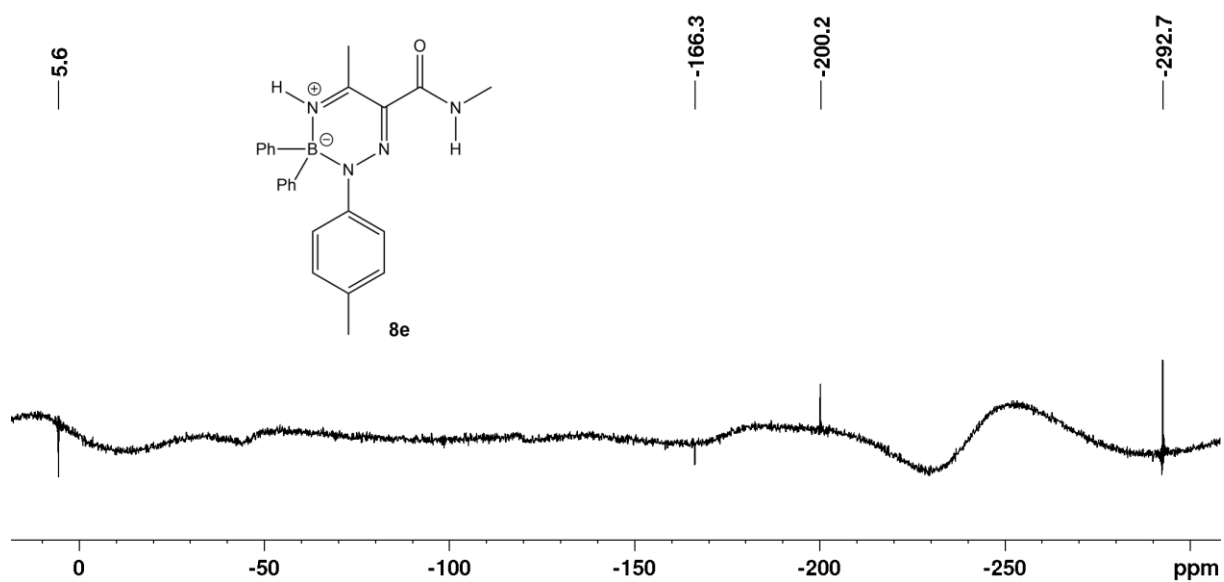


Figure S92. 50 MHz ^{15}N NMR of compound **8e** in CDCl_3

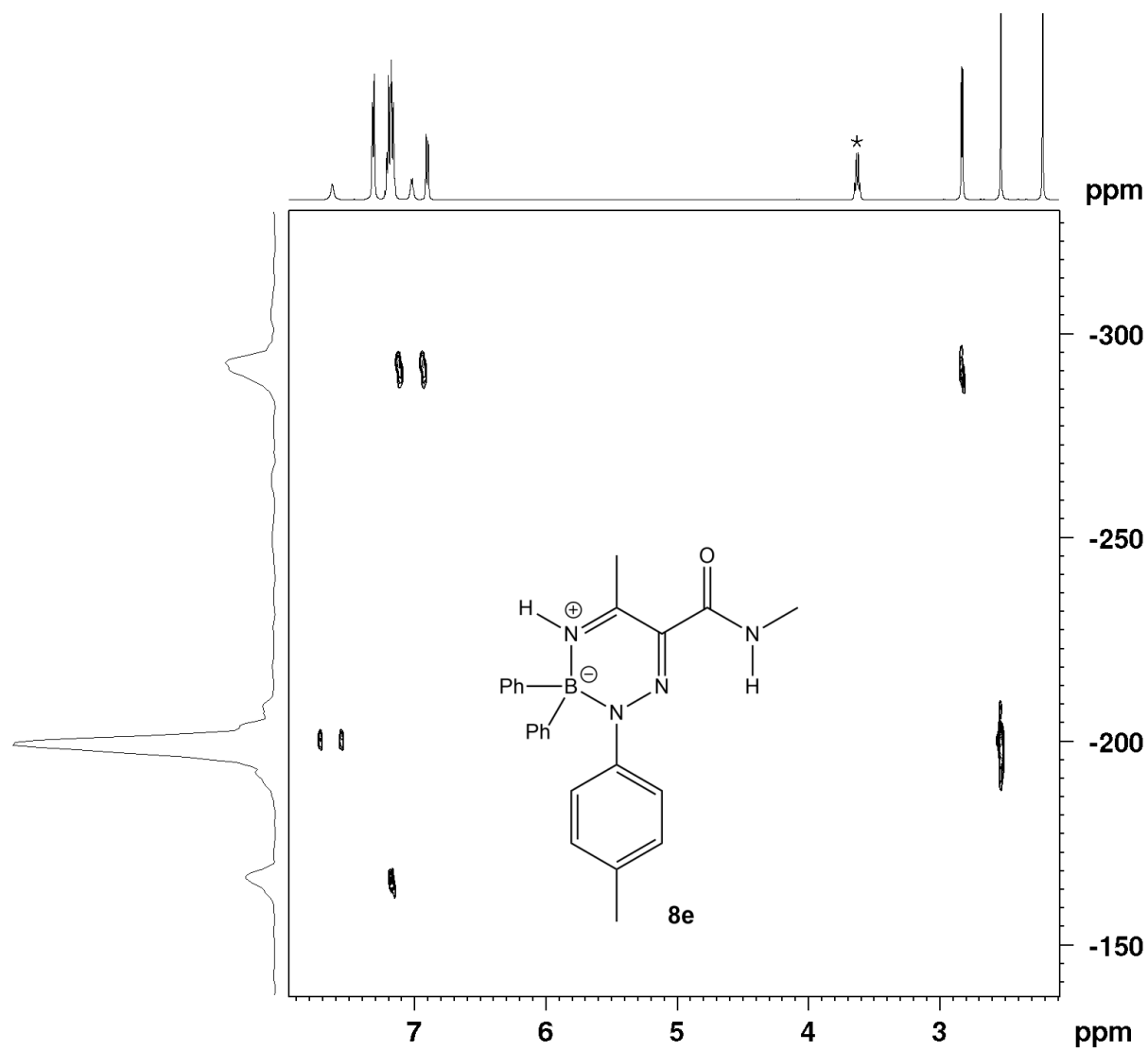


Figure S93. 500 MHz ^1H - ^{15}N HMBC NMR of compound **8e** in CDCl_3 (* CH_2 from ethanol)

2.21 Triazaborine 8g

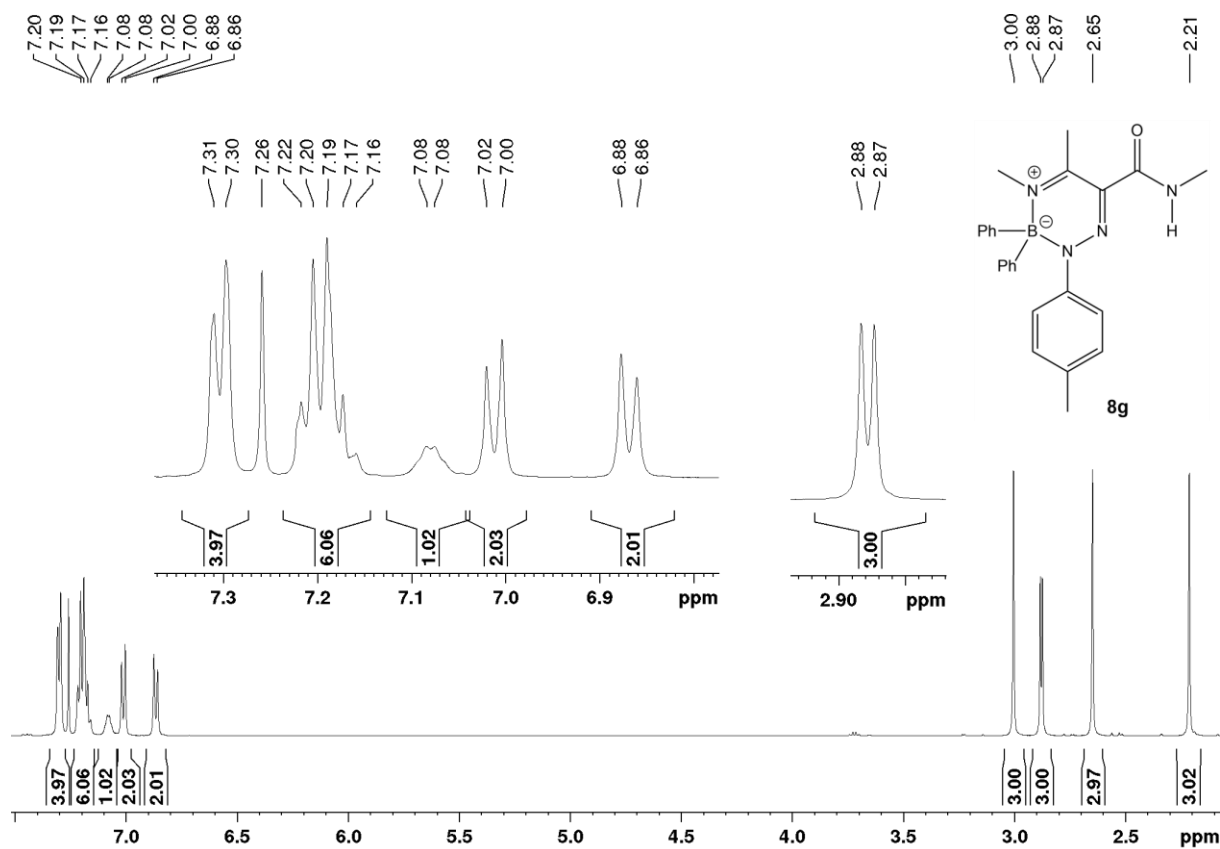
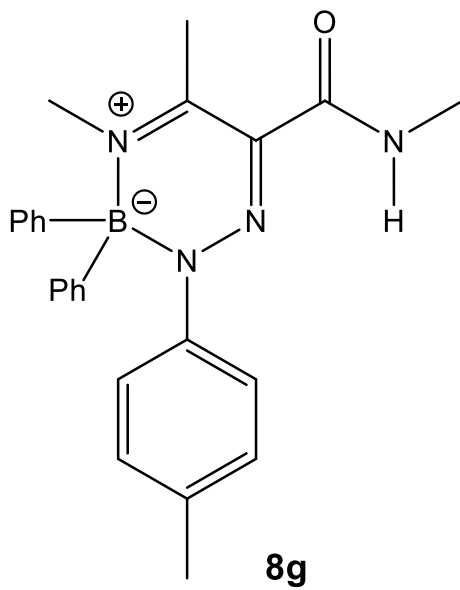


Figure S94. 500 MHz ^1H NMR of compound **8g** in CDCl_3

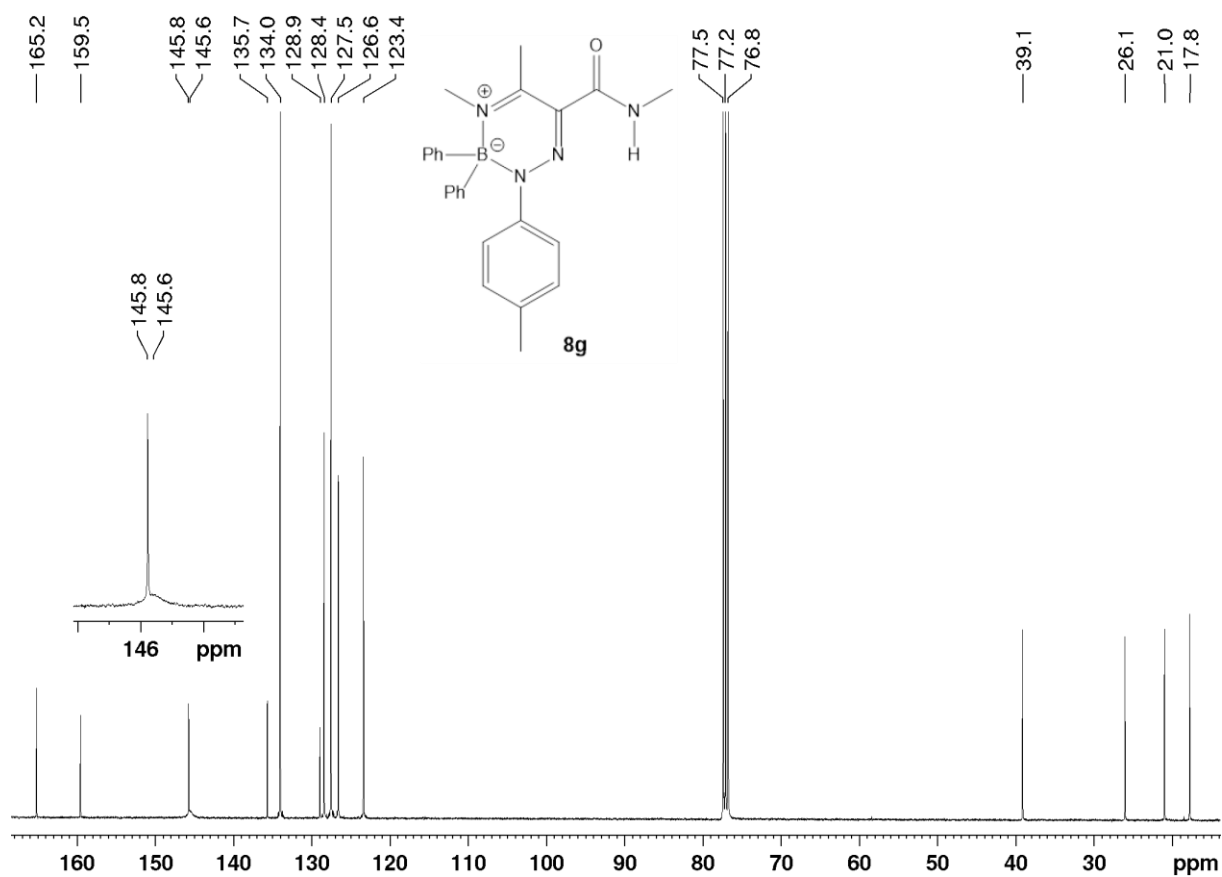


Figure S95. 100 MHz ^{13}C NMR of compound **8g** in CDCl_3

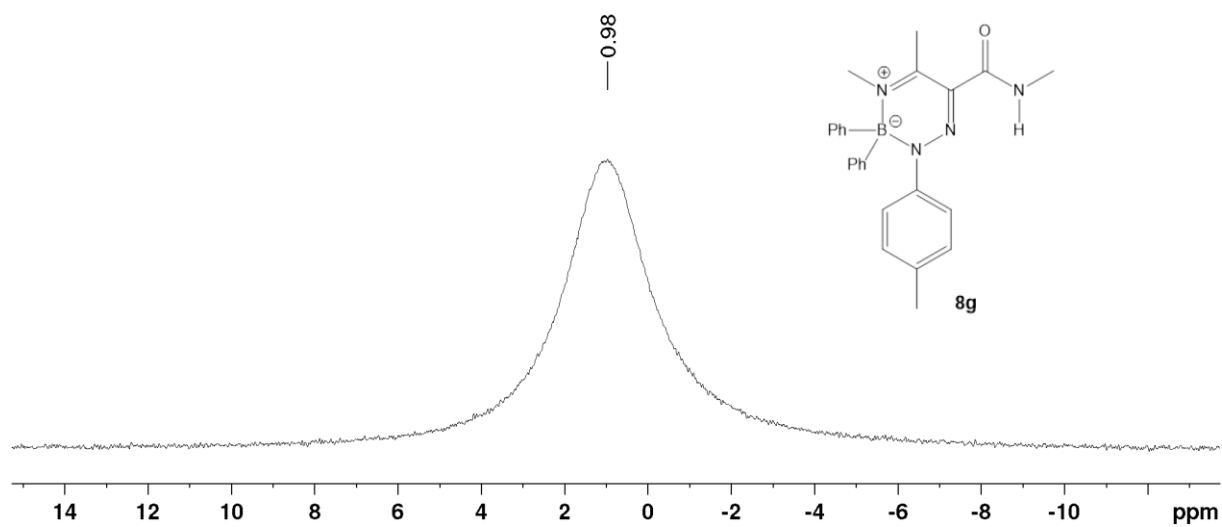


Figure S96. 128 MHz ^{11}B NMR of compound **8g** in CDCl_3

2.22 Triazaborine 8h

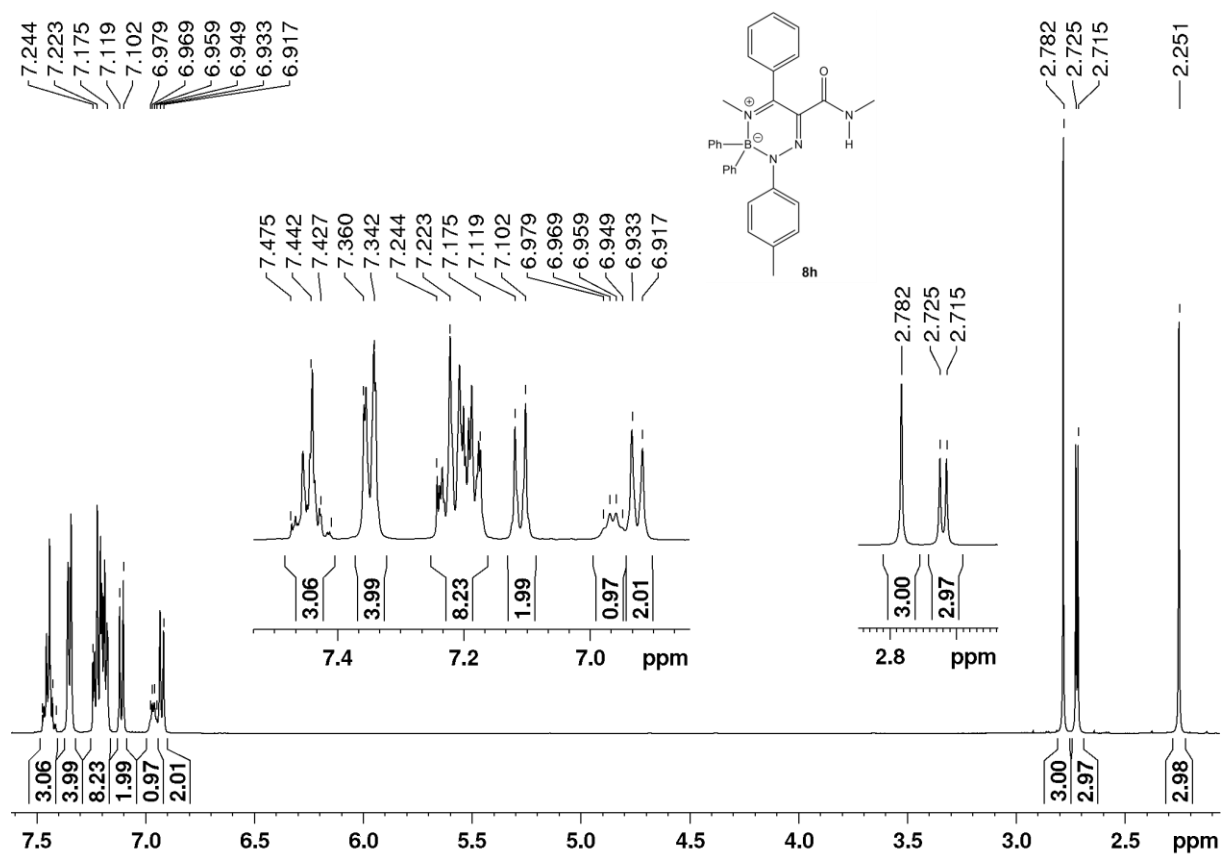
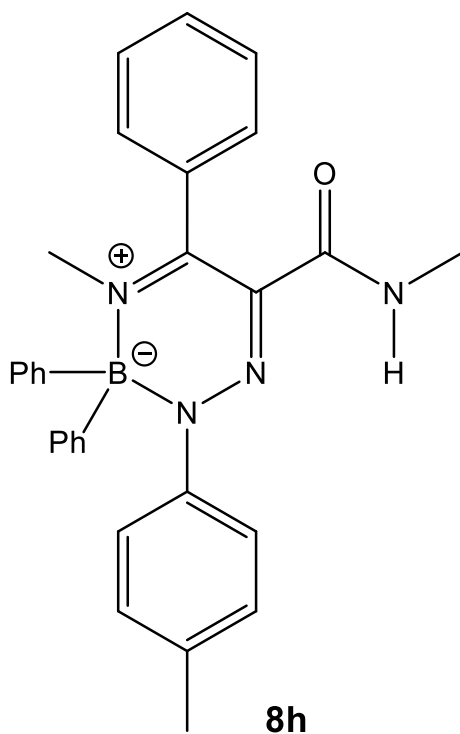


Figure S97. 500 MHz ^1H NMR of compound **8h** in CDCl_3

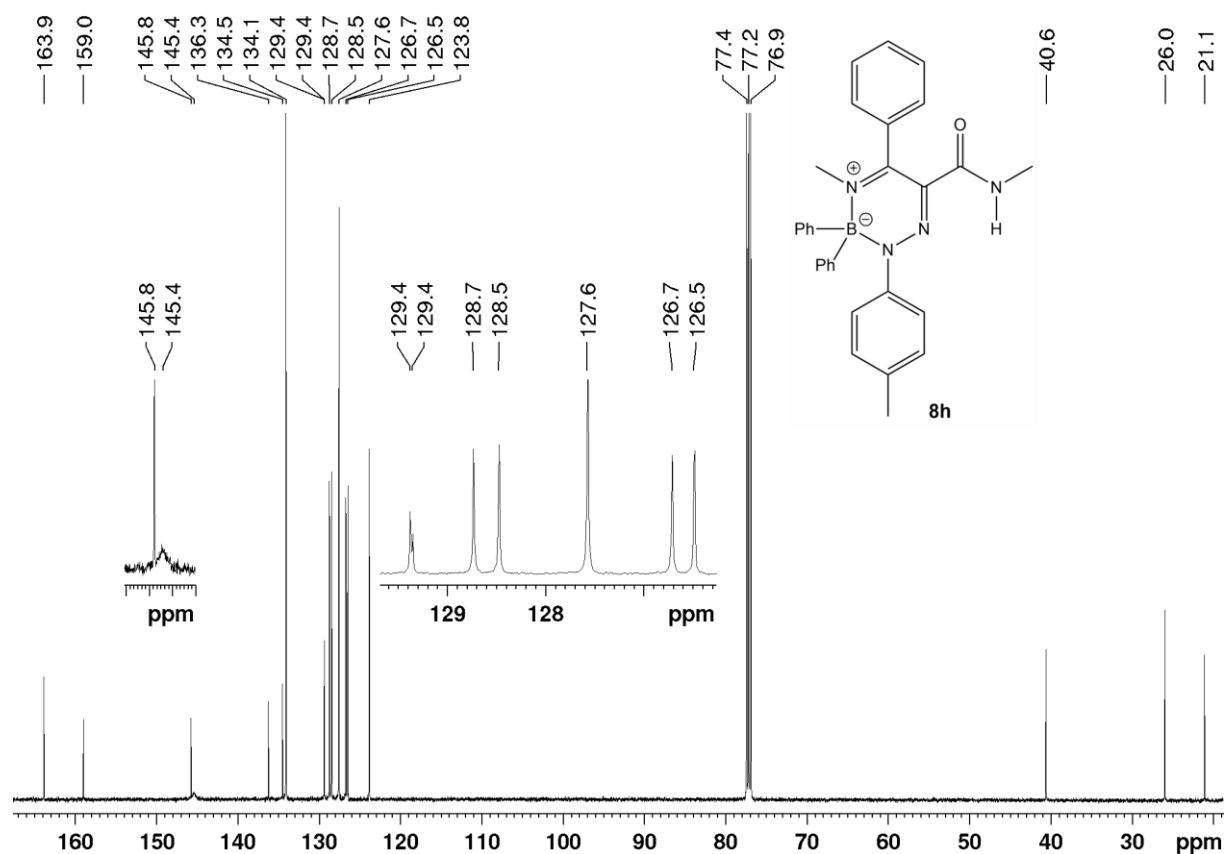


Figure S98. 125 MHz ^{13}C NMR of compound **8h** in CDCl_3

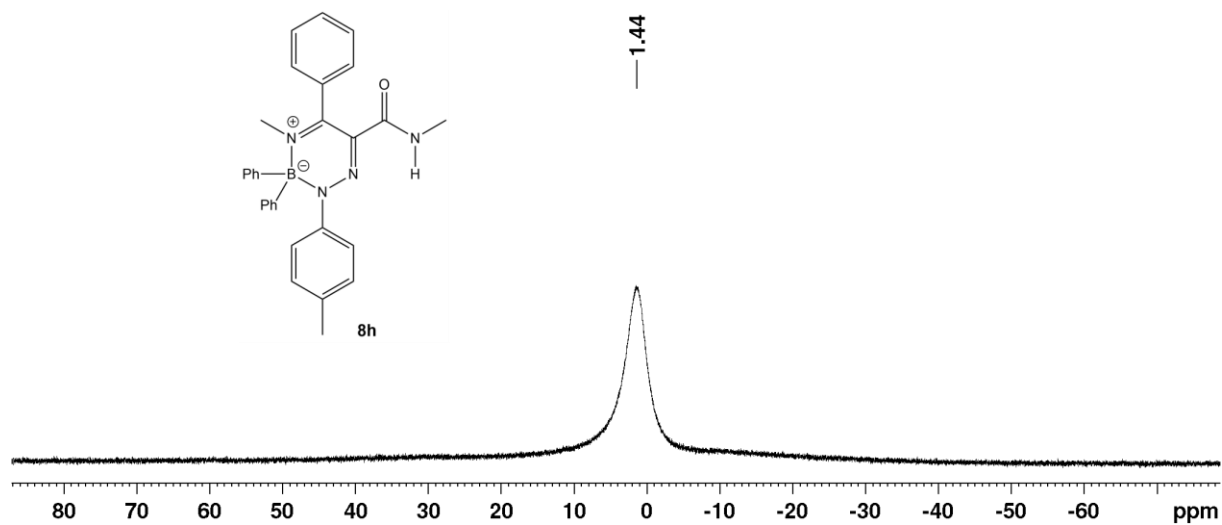


Figure S99. 160 MHz ^{11}B NMR of compound **8h** in CDCl_3

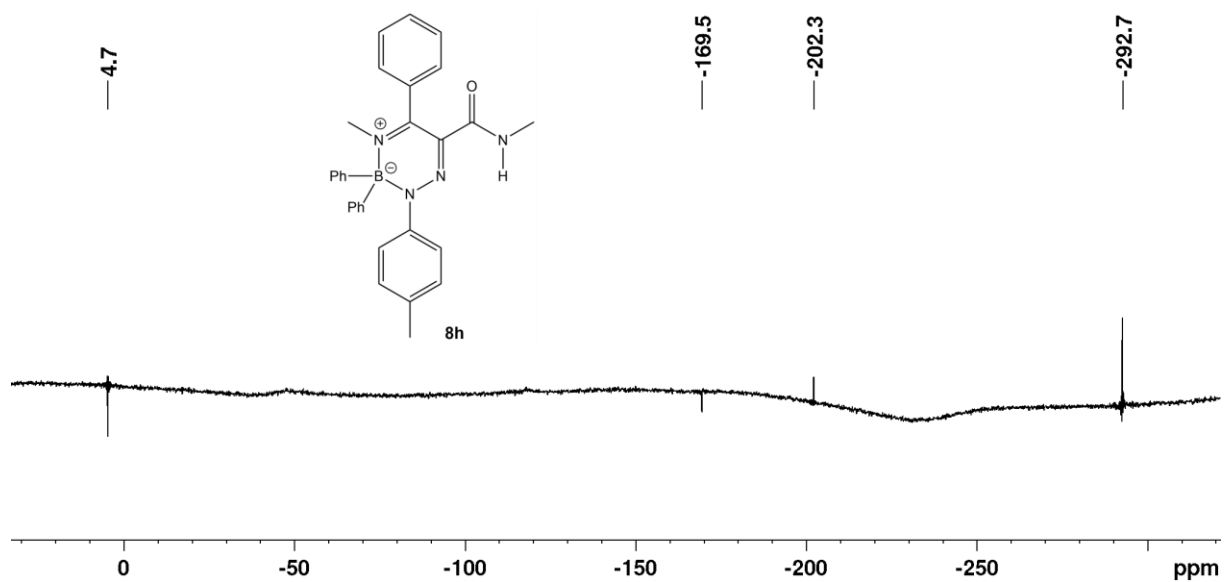


Figure S100. 50 MHz ^{15}N NMR of compound **8h** in CDCl_3

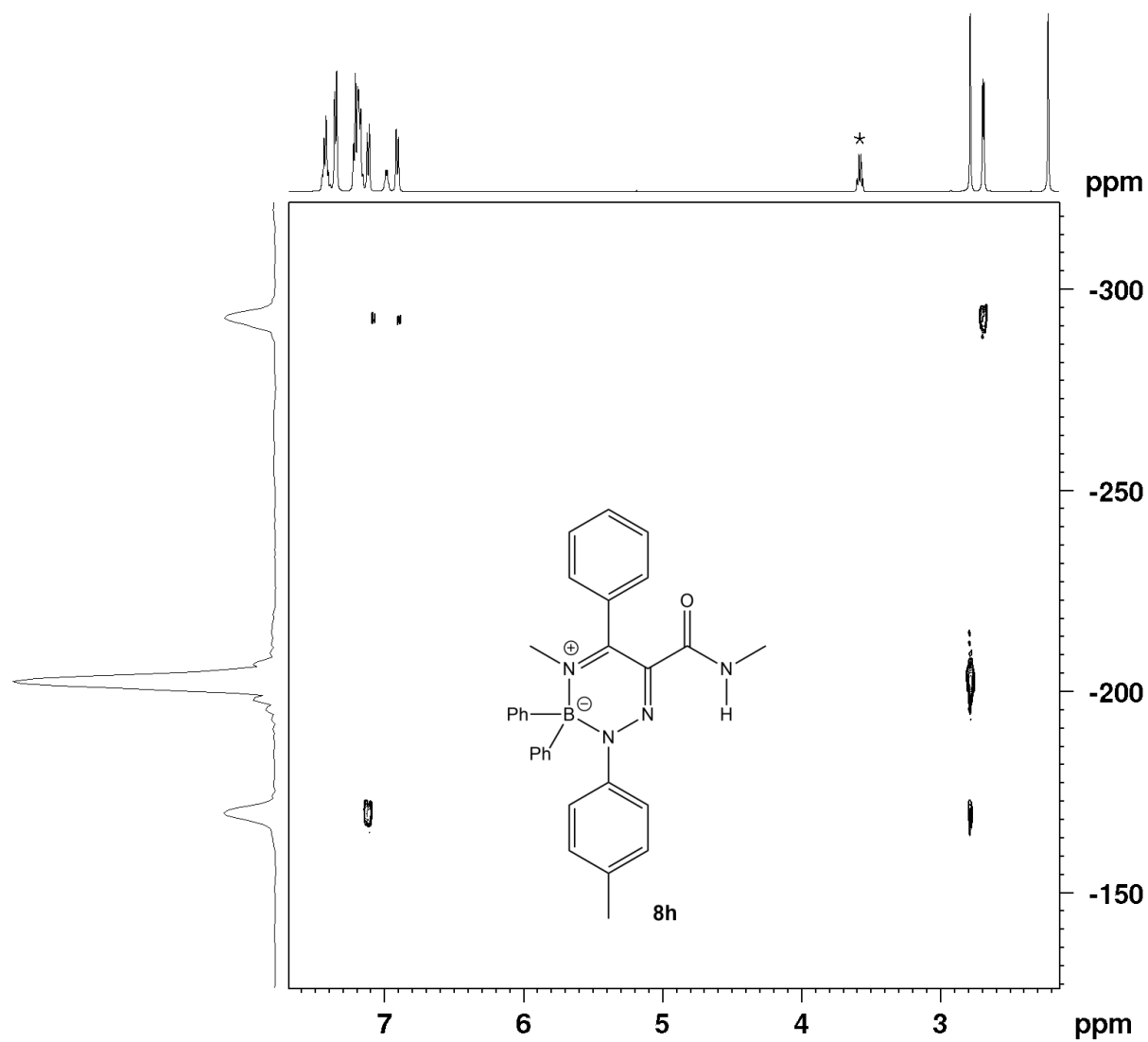


Figure S101. 500 MHz ^1H - ^{15}N HMBC NMR of compound **8h** in CDCl_3 (* CH_2 from ethanol)

2.23 Oxazaborine–Triazaborine 9g

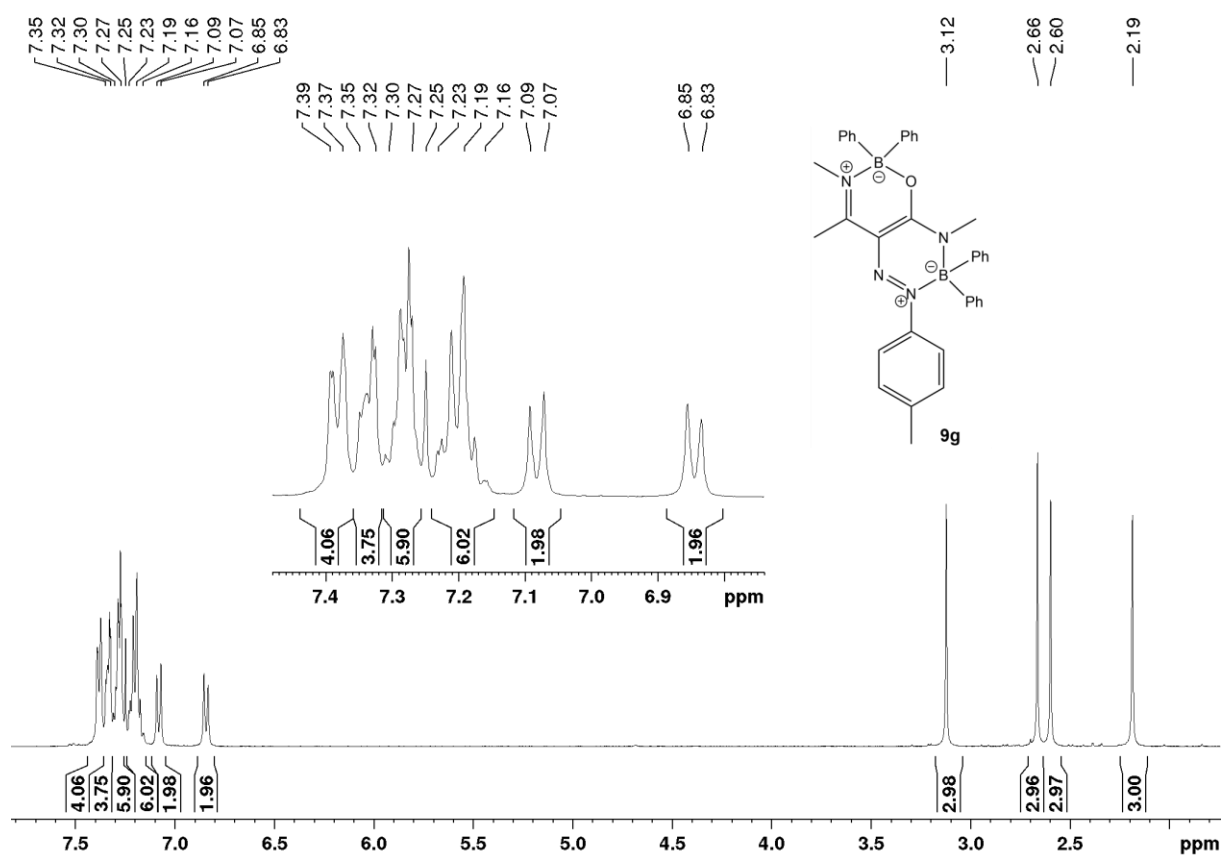
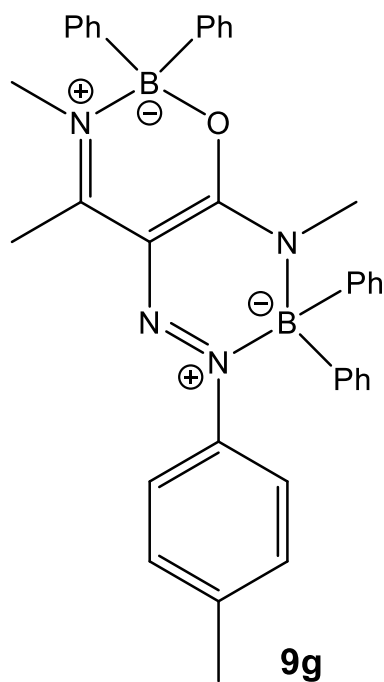


Figure S102. 400 MHz ^1H NMR of compound **9g** in CDCl_3

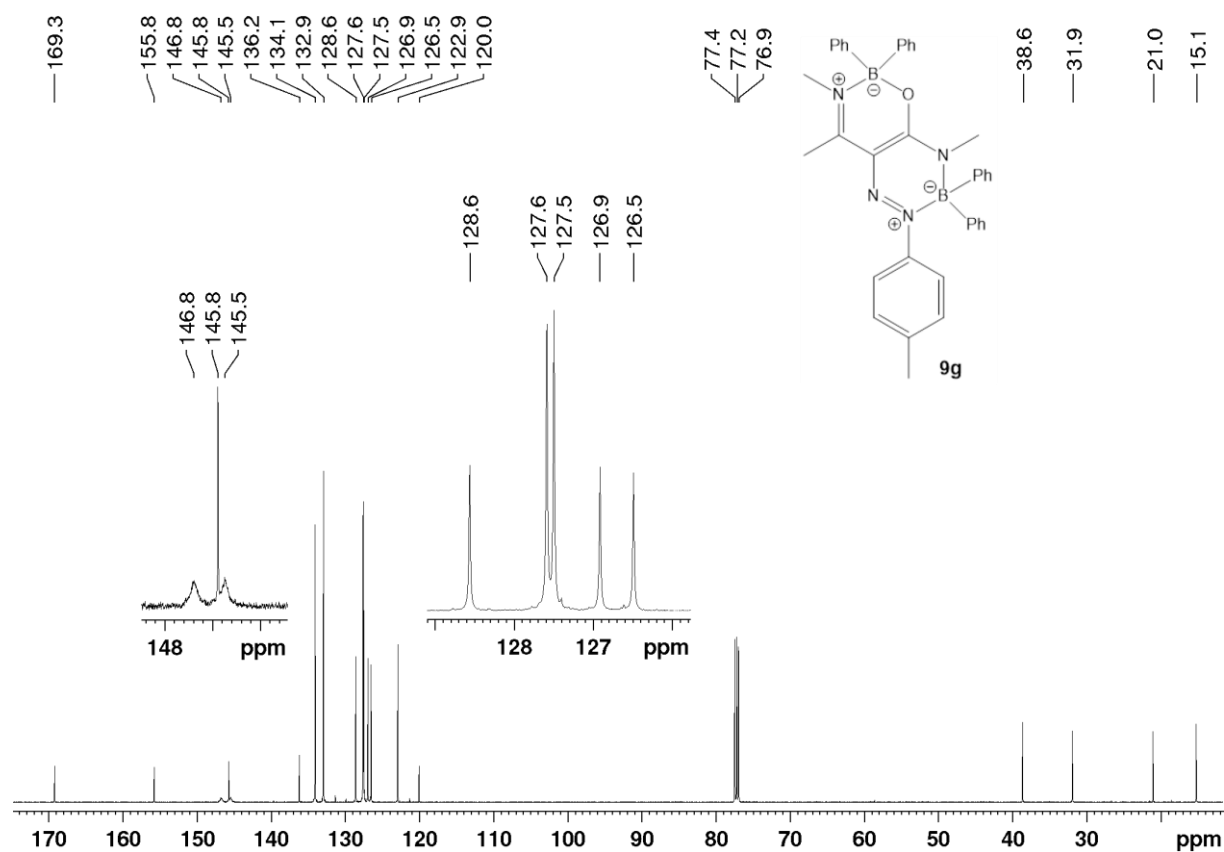


Figure S103. 125 MHz ^{13}C NMR of compound **9g** in CDCl_3

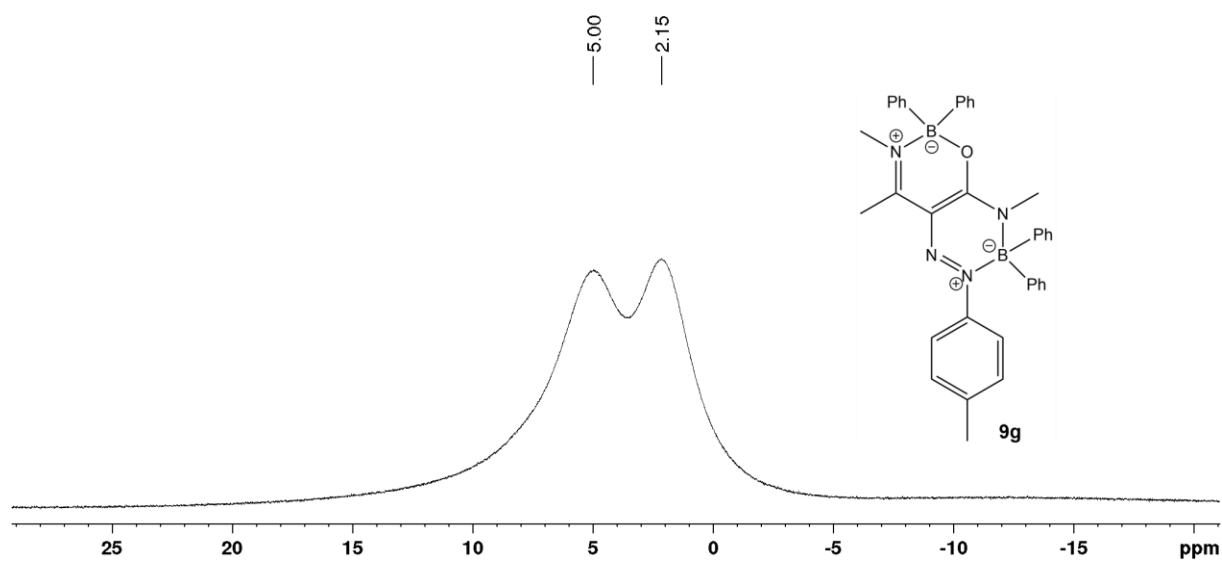


Figure S104. 160 MHz ^{11}B NMR of compound **9g** in CDCl_3

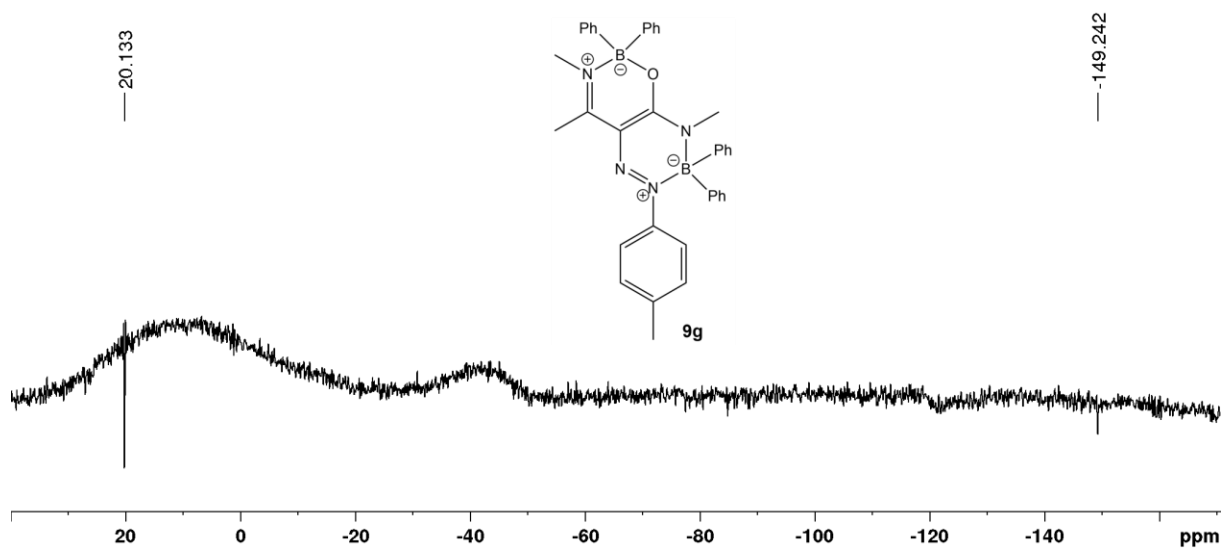


Figure S105. 50 MHz ^{15}N NMR of compound **9g** in CDCl_3

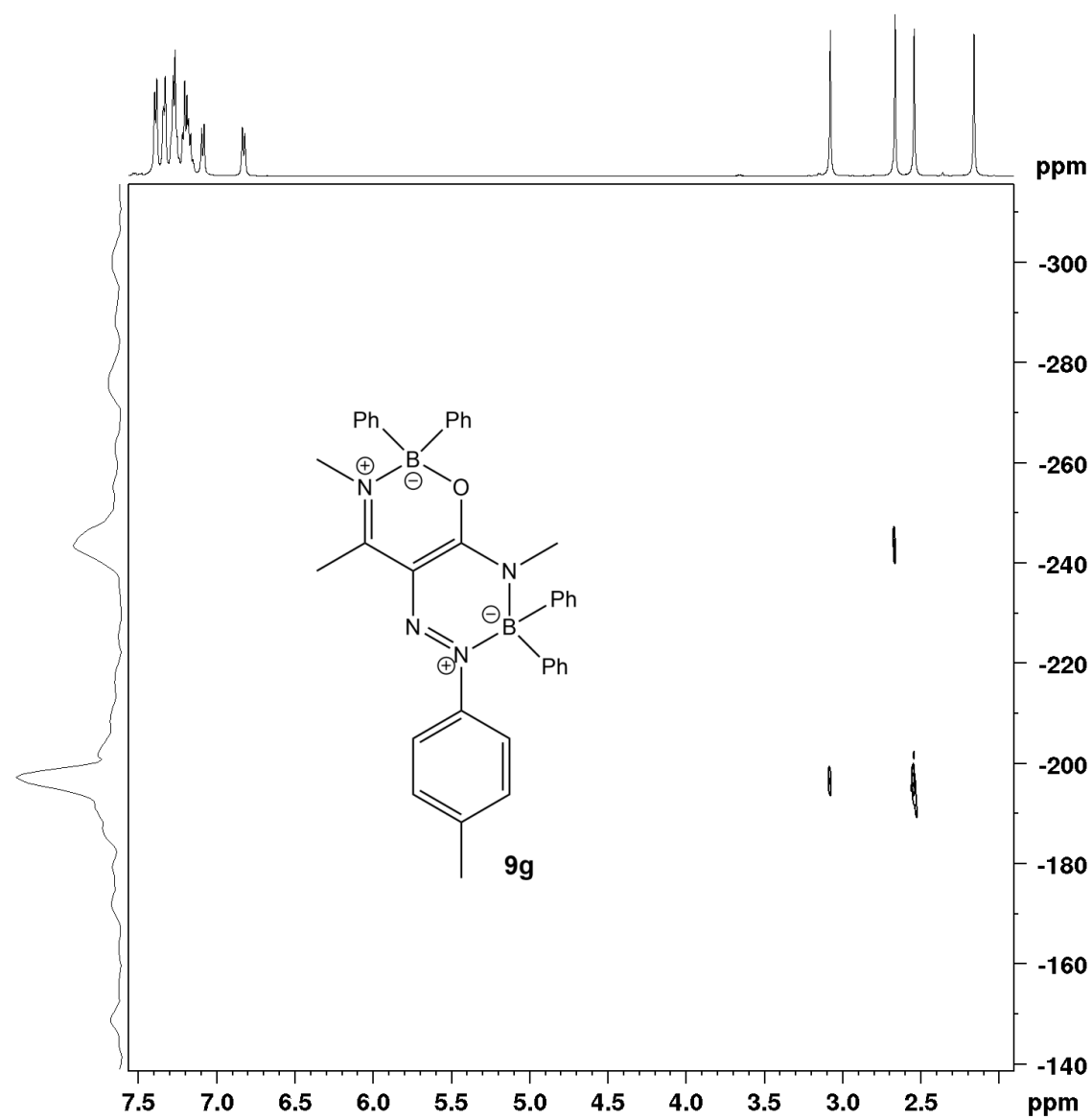


Figure S106. 500 MHz ^1H - ^{15}N HMBC NMR of compound **9g** in CDCl_3

2.24 Oxazaborine–Triazaborine 9h

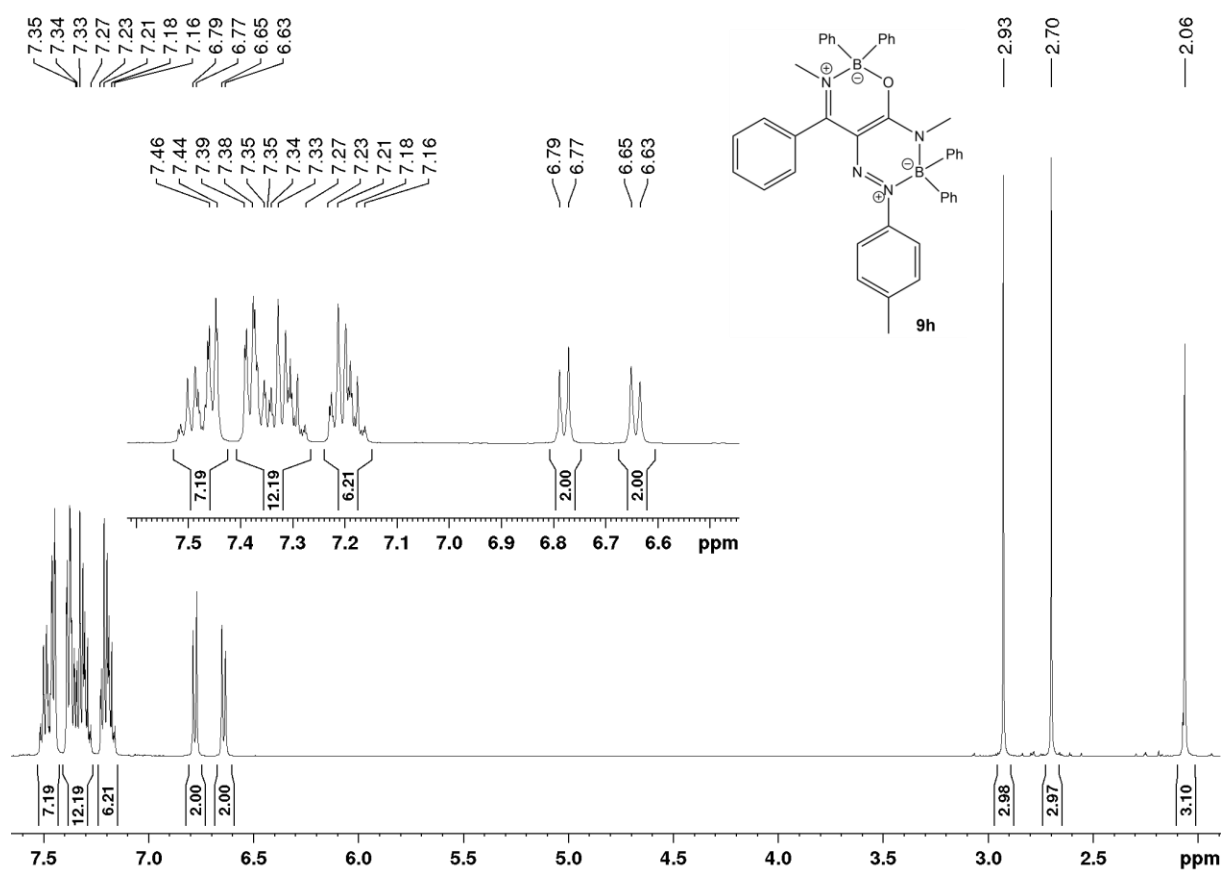
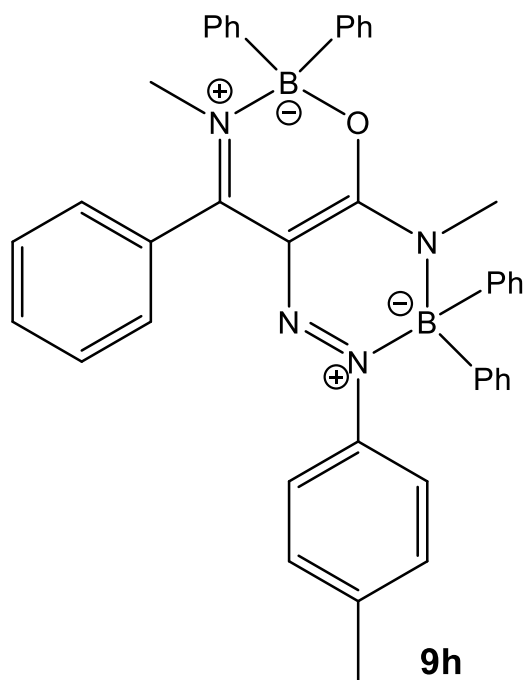


Figure S107. 500 MHz ^1H NMR of compound **9h** in CDCl_3

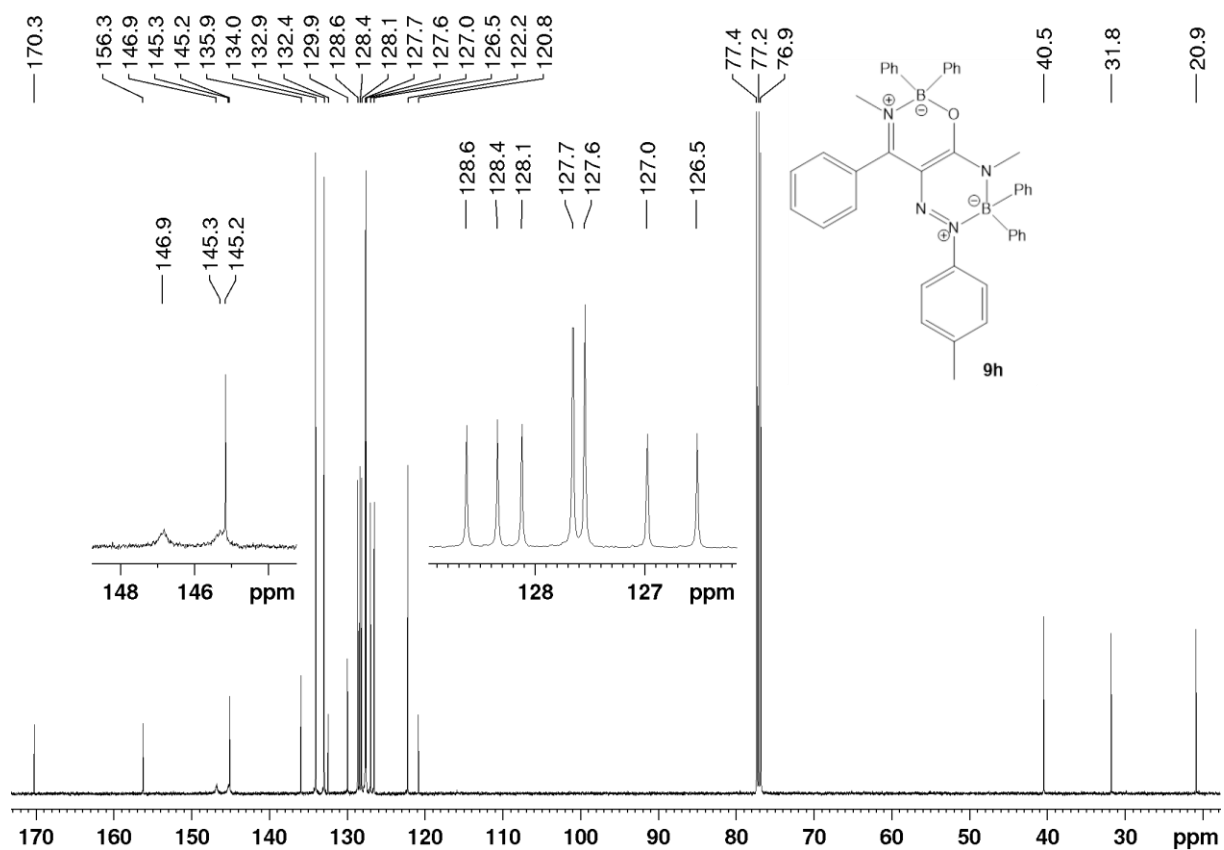


Figure S108. 125 MHz ^{13}C NMR of compound **9h** in CDCl_3

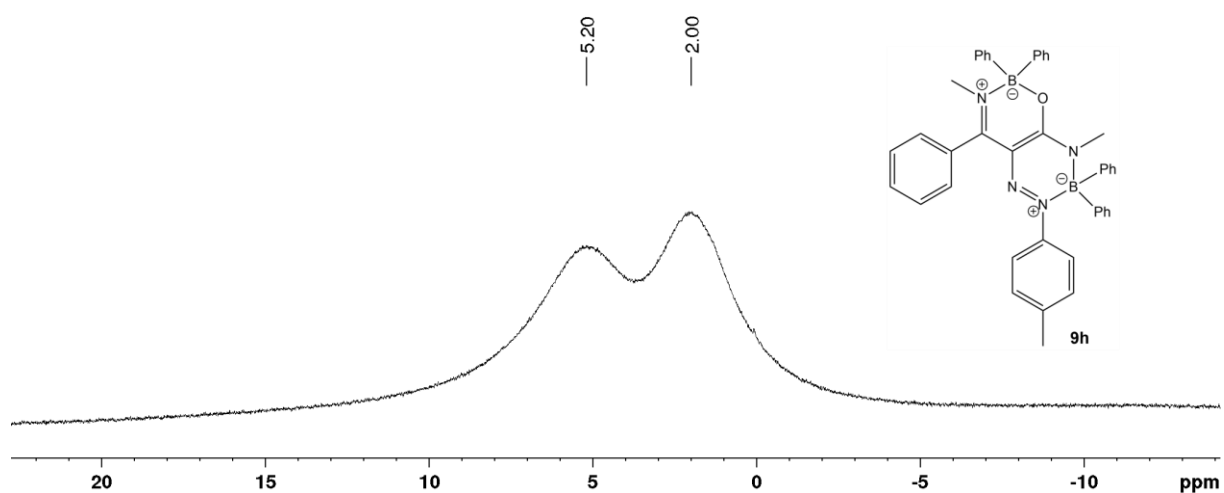


Figure S109. 160 MHz ^{11}B NMR of compound **9h** in CDCl_3

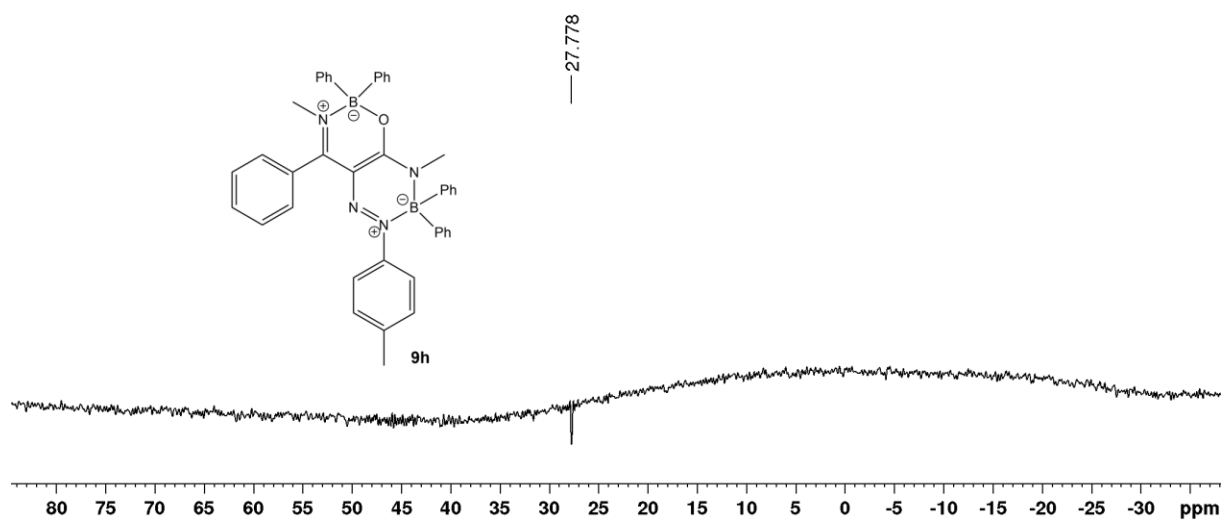


Figure S110. 50 MHz ¹⁵N NMR of compound **9h** in CDCl₃

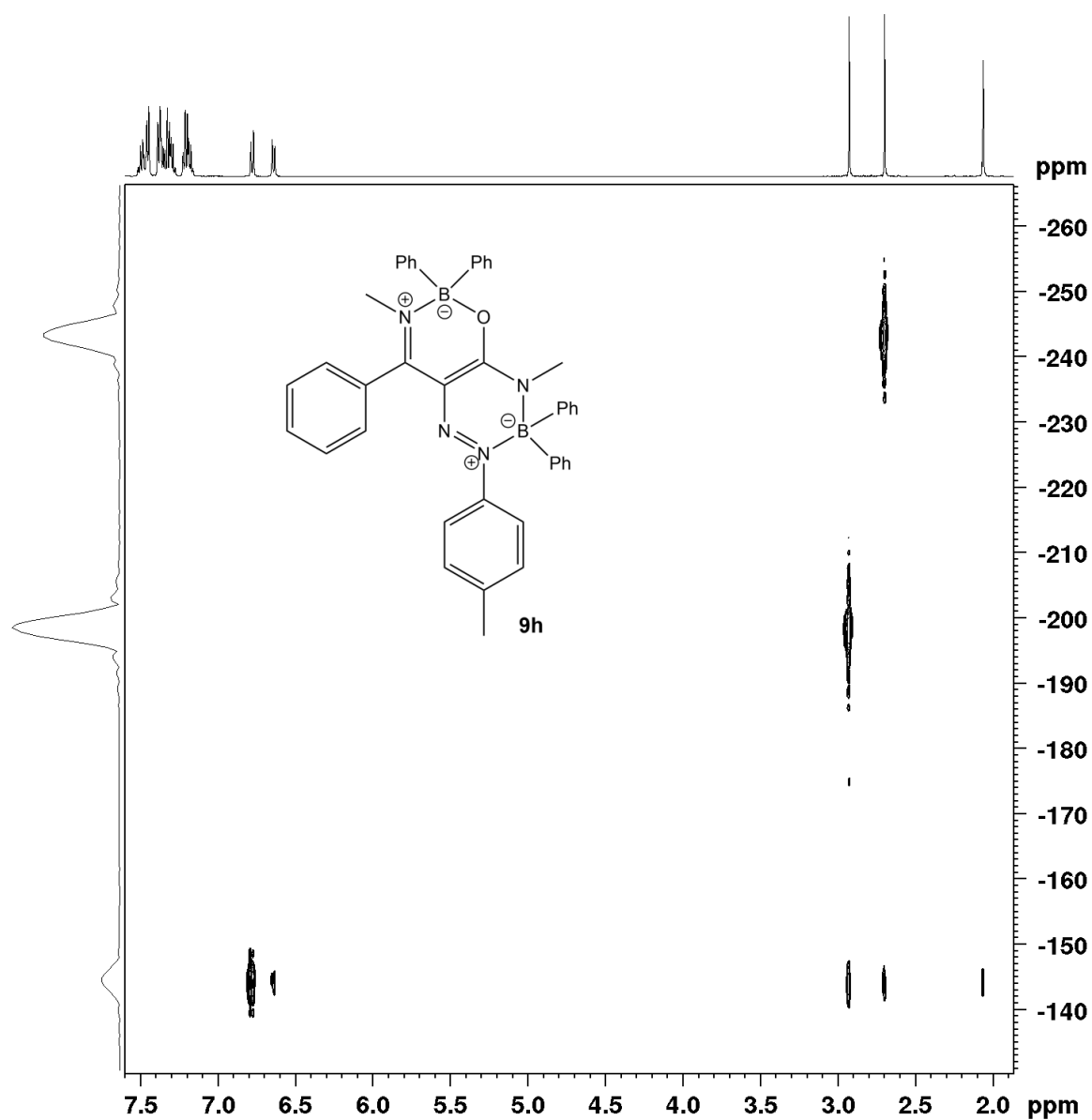


Figure S111. 500 MHz ¹H-¹⁵N HMBC NMR of compound **9h** in CDCl₃

3. UV-Vis spectra

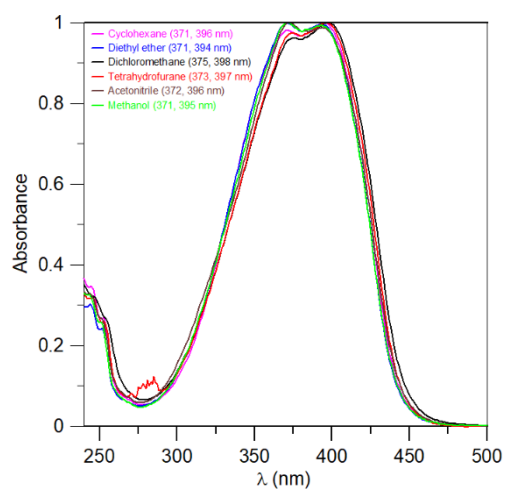


Figure S112. Normalized UV-VIS spectrum of oxazaborine **6g**.

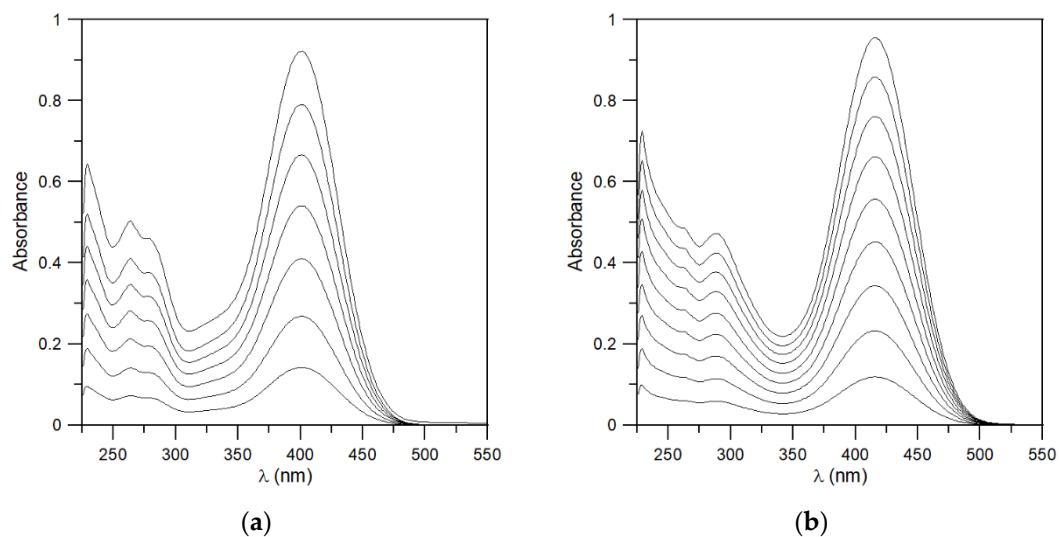


Figure S113. UV-Vis spectrum in CH_2Cl_2 . (a) triazaborinone **5a** and (b) triazaborinone **5b**.

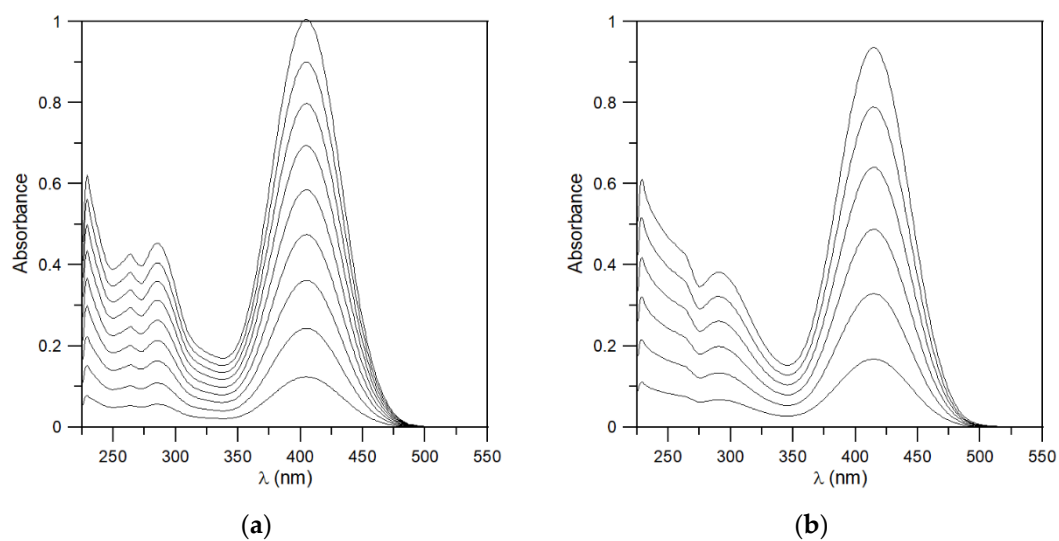


Figure S114. UV-Vis spectrum in CH_2Cl_2 . (a) triazaborinone **5c** and (b) triazaborinone **5d**.

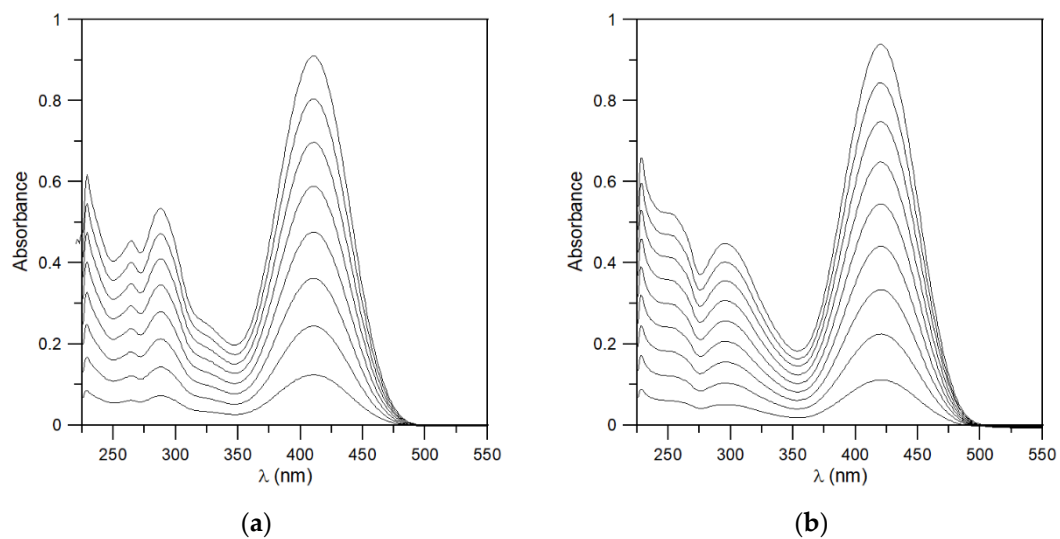


Figure S115. UV-Vis spectrum in CH_2Cl_2 . (a) triazaborinone **5g** and (b) triazaborinone **5h**.

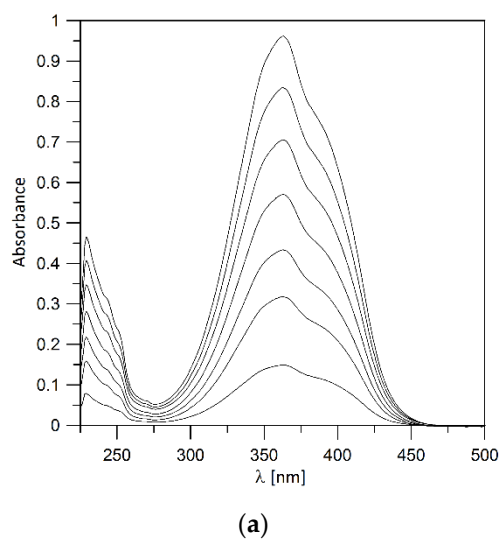


Figure S116. UV-Vis spectrum in CH_2Cl_2 oxazaborine **6a**.

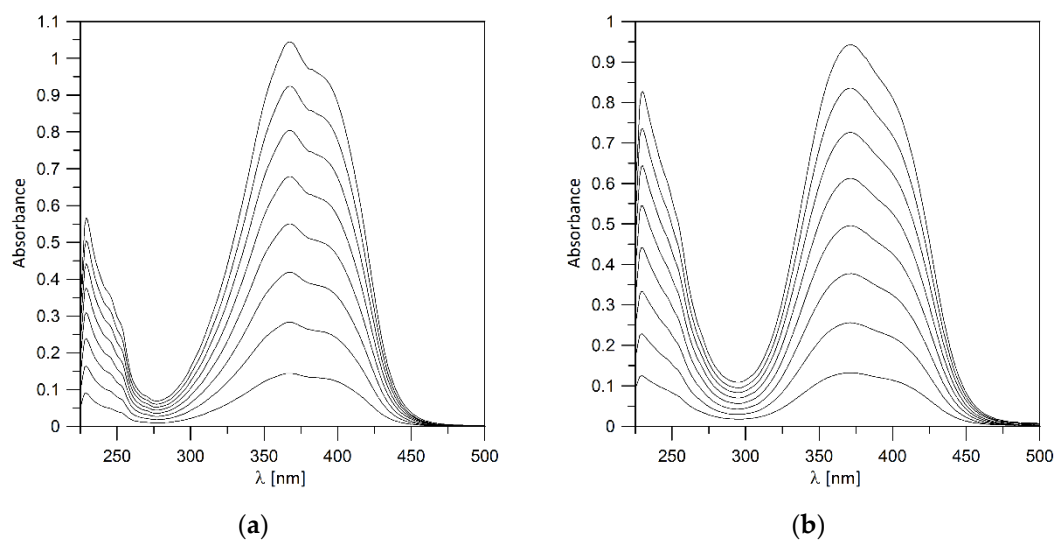


Figure S117. UV-Vis spectrum in CH_2Cl_2 . (a) oxazaborine **6e** and (b) oxazaborine **6f**.

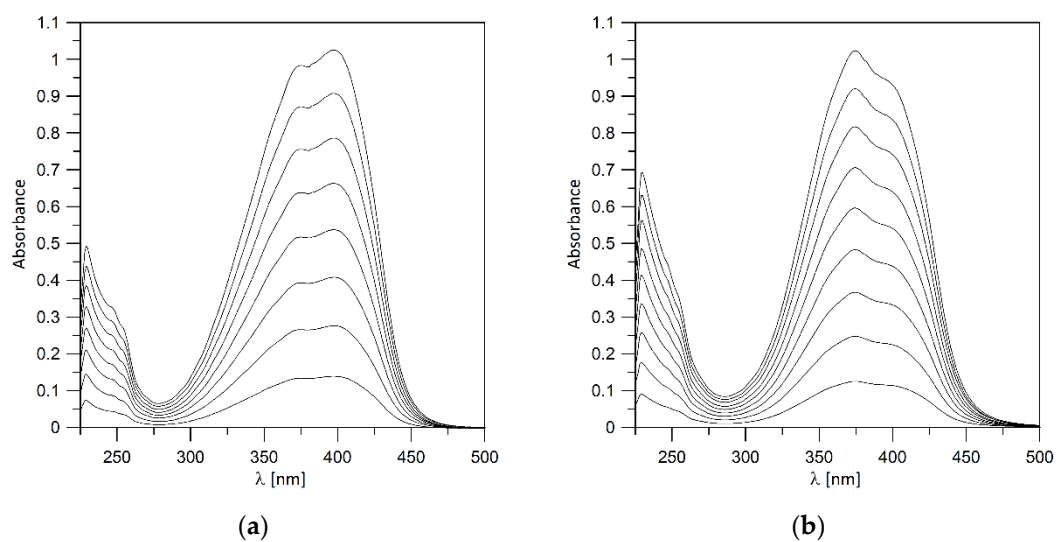


Figure S118. UV-Vis spectrum in CH_2Cl_2 . (a) oxazaborine **6g** and (b) oxazaborine **6h**.

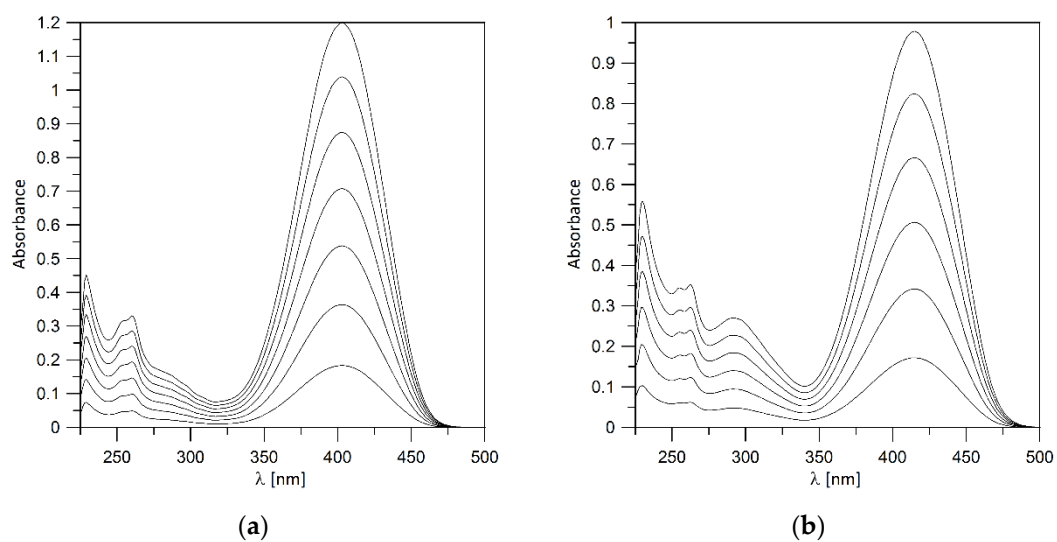


Figure S119. UV-Vis spectrum in CH_2Cl_2 . (a) diazaborine **7a** and (b) diazaborinone **7b**.

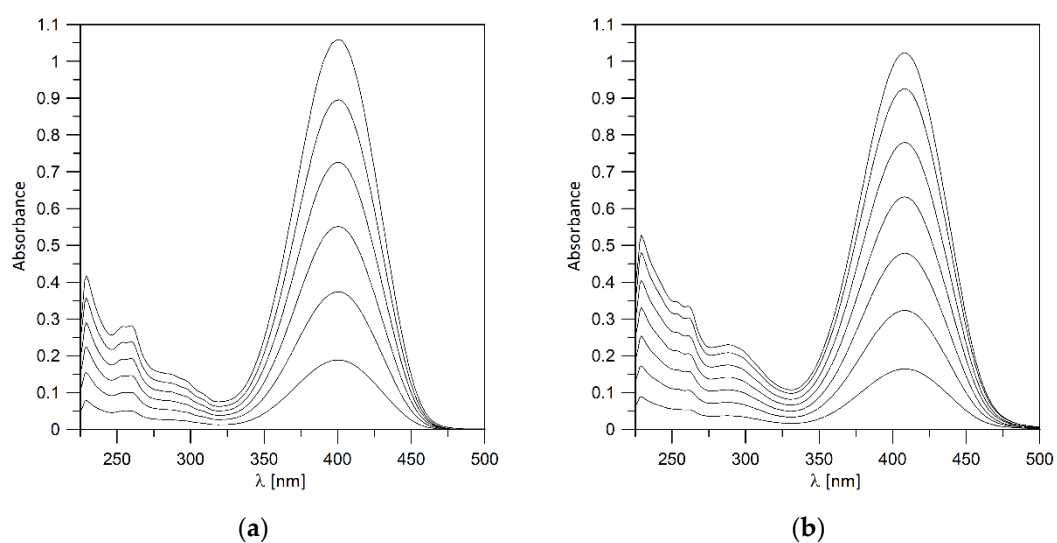


Figure S120. UV-Vis spectrum in CH_2Cl_2 . (a) diazaborine **7c** and (b) diazaborinone **7d**.

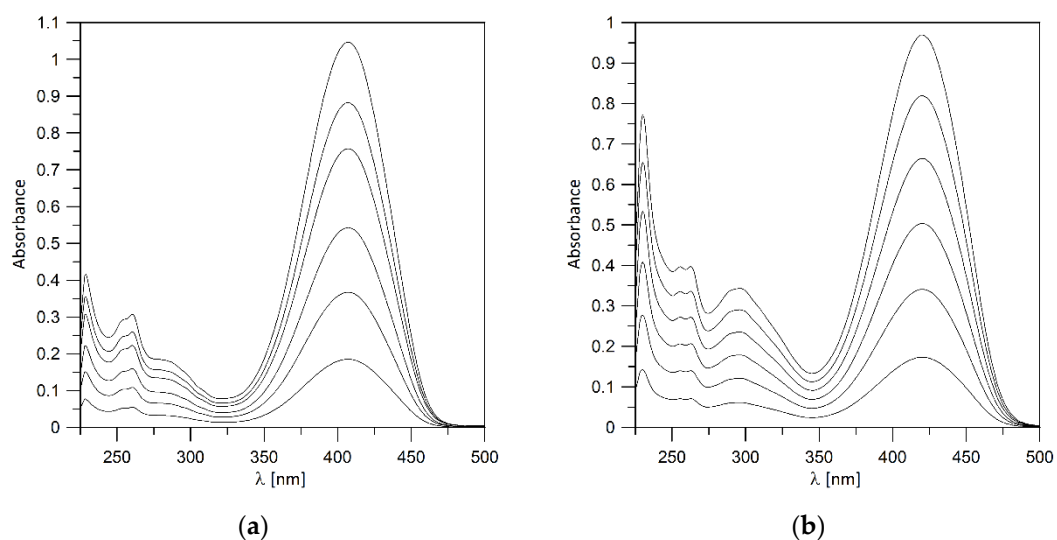


Figure S121. UV-Vis spectrum in CH_2Cl_2 . (a) diazaborine **7e** and (b) diazaborinone **7f**.

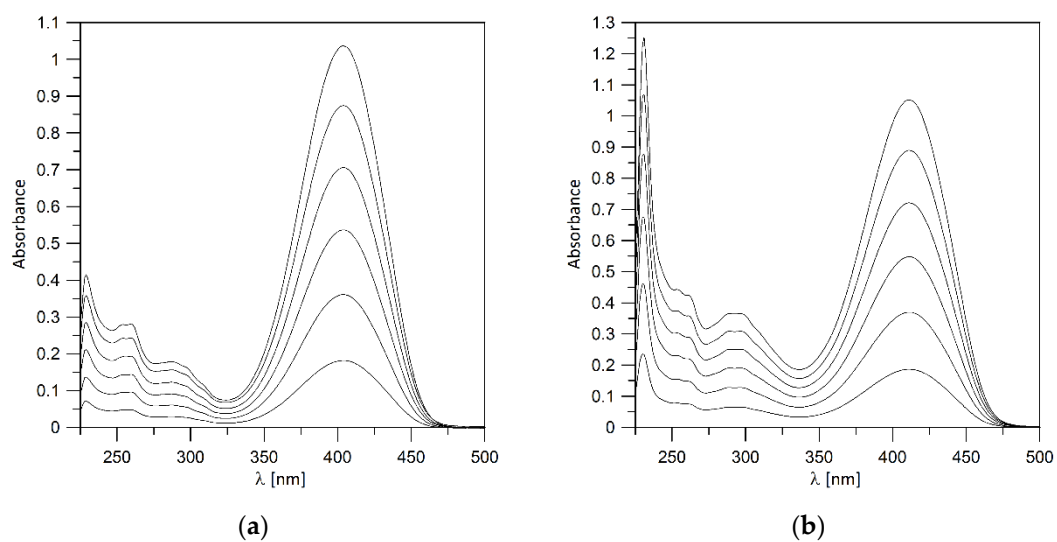


Figure S122. UV-Vis spectrum in CH_2Cl_2 . (a) diazaborine **7g** and (b) diazaborinone **7h**.

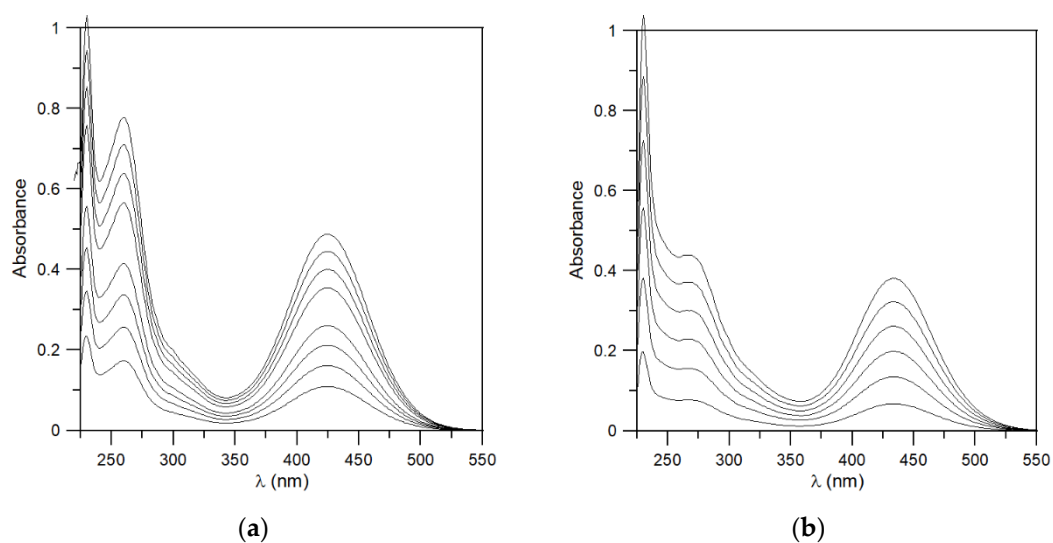


Figure S123. UV-Vis spectrum in CH_2Cl_2 . (a) triazaborine **8e** and (b) triazaborine **8h**.

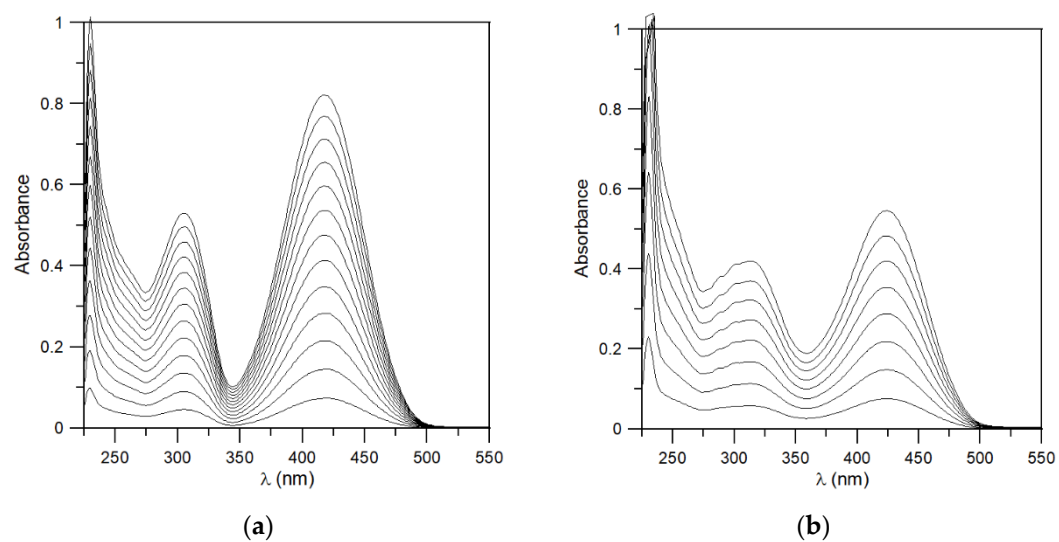


Figure S124. UV-Vis spectrum in CH_2Cl_2 . (a) oxazaborine-triazaborine **9g** and (b) oxazaborine-triazaborine **9h**.

Table S1. UV–Vis parameters of prepared heterocyclic compounds in CH₂Cl₂.

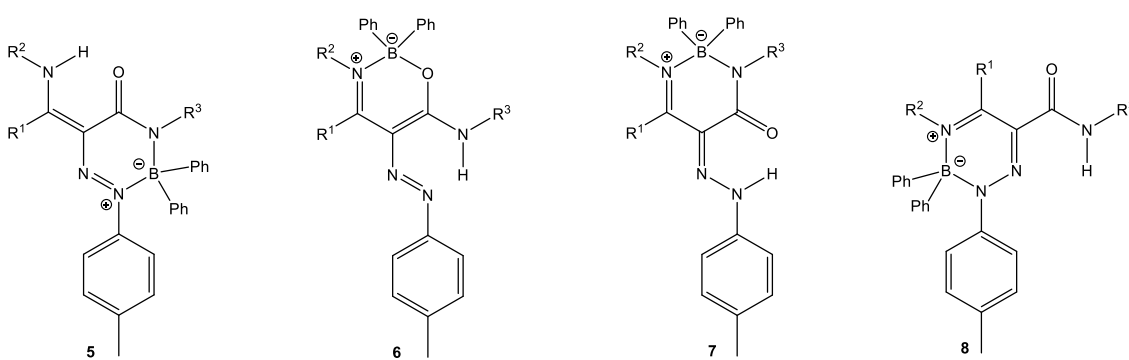
					
Compound	R ¹	R ²	R ³	λ_{max} (nm)	ϵ (l·cm ⁻¹ ·mol ⁻¹)
Triazaborinone 5a	Me	H	H	401	21 908
Triazaborinone 5b	Ph	H	H	416	25 105
Triazaborinone 5c	Me	Me	H	405	26 250
Triazaborinone 5d	Ph	Me	H	415	35 561
Triazaborinone 5g	Me	Me	Me	411	26 641
Triazaborinone 5h	Ph	Me	Me	421	24 867
Oxazaborine 6a	Me	H	H	363	31 114
Oxazaborine 6e	Me	H	Me	368	30 400
Oxazaborine 6f	Ph	H	Me	371	27 476
Oxazaborine 6g	Me	Me	Me	398	29 882
Oxazaborine 6h	Ph	Me	Me	374	26 909
Diazaborinone 7a	Me	H	H	403	39 358
Diazaborinone 7b	Ph	H	H	415	37 224
Diazaborinone 7c	Me	Me	H	400	40 031
Diazaborinone 7d	Ph	Me	H	408	35 159
Diazaborinone 7e	Me	H	Me	407	40 023
Diazaborinone 7f	Ph	H	Me	420	36 707
Diazaborinone 7g	Me	Me	Me	404	39 328
Diazaborinone 7h	Ph	Me	Me	410	39 778
Triazaborine 8e	Me	H	Me	424	11 714
Triazaborine 8g	Me	Me	Me		
Triazaborine 8h	Ph	Me	Me	434	14 541
Oxazaborine–triazaborine 9g	Me	Me	Me	418	25 284
Oxazaborine–triazaborine 9h	Ph	Me	Me	425	25 697

Table S2. UV–Vis parameters of triazaborine **5g**. λ_{max} (nm), ϵ (l·cm⁻¹·mol⁻¹)

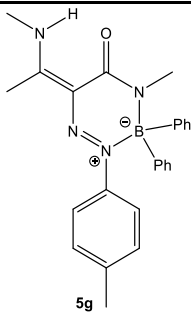
 5g											
Cyclohexane		Et ₂ O		CH ₂ Cl ₂		THF		MeOH		Formamide	
λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
412	21 450	409	22 509	411	26 641	409	22 676	405	22 371	408	6 292

Table S3. UV–Vis parameters of oxazaborine **6g**. λ_{max} (nm), ϵ (l·cm⁻¹·mol⁻¹)

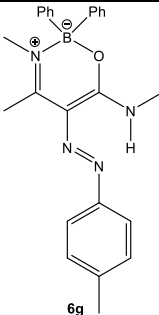
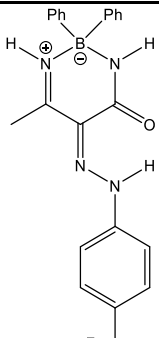
 6g											
Cyclohexane		Et ₂ O		CH ₂ Cl ₂		THF		Acetonitril		Methanol	
λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
395	28 600	394	27 789	398	29 882	396	29 174	394	26 841	393	27 196

Table S4. UV–Vis parameters of diazaborinone **7a**. λ_{max} (nm), ϵ (l·cm⁻¹·mol⁻¹)

 7a							
CH ₂ Cl ₂		THF		Acetonitril		Methanol	
λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
403	39 358	398	38 398	395	38 592	392	19 064

4. Crystallographic data

Table S5. Crystal data.

Compound	5c	5d	5g	6a	6e	7f
Formula	C ₂₄ H ₂₅ BN ₄ O	C ₂₉ H ₂₇ BN ₄ O · 0.5 C ₇ H ₈	C ₂₅ H ₂₇ BN ₄ O	C ₂₃ H ₂₃ BN ₄ O	C ₂₄ H ₂₅ BN ₄ O	C ₂₉ H ₂₇ BN ₄ O
M	396.29	504.42	410.31	382.26	396.29	458.36
System	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic	Triclinic
Space Group	<i>P</i> −1	<i>P</i> −1	<i>P</i> −1	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> −1
<i>a</i> /Å	9.7716(2)	9.5356(6)	9.1045(2)	10.0193(5)	14.3675(3)	6.3703(1)
<i>b</i> /Å	10.5152(2)	9.6497(4)	10.2052(3)	17.7580(12)	9.4464(2)	10.4288(2)
<i>c</i> /Å	12.2365(4)	16.2161(10)	12.4674(5)	24.0839(17)	16.5228(4)	19.0078(5)
α /°	82.6401(9)	96.902(3)	86.2535(9)	90	90	82.4168(10)
β /°	71.5304(10)	105.457(3)	75.3584(9)	92.7624(17)	105.1227(9)	89.1976(9)
γ /°	63.6440(11)	99.699(3)	88.8020(19)	90	90	80.3378(16)
U/Å ³	1068.47(5)	1396.05(14)	1118.36(6)	4280.1(5)	2164.84(8)	1233.93(5)
Z	2	2	2	8	4	2
D _c /g cm ^{−3}	1.232	1.200	1.218	1.186	1.216	1.234
T/K	295	295	295	295	295	295
μ /cm ^{−1}	0.77	0.73	0.75	0.74	0.76	0.76
θ_{\min} – θ_{\max} /°	3.9–27.8	2.9–28.0	3.7–27.0	2.0–24.0	3.4–27.0	1.1–27.8
Unique Refl.ns	4998	6708	4853	6451	4678	5793
R _{int}	0.017	0.049	0.022	0.084	0.021	0.021
Observed Refl.ns	3772	4215	3284	2577	3687	3827
[I>2 σ (I)]						
R (Obs. Refl.ns)	0.0504	0.0677	0.0505	0.0746	0.0621	0.0474
wR (All Refl.ns)	0.1333	0.1653	0.1429	0.1934	0.1751	0.1310
S	1.042	1.026	1.024	1.045	1.031	1.025
$\Delta\rho_{\max}$; $\Delta\rho_{\min}$ /e Å ^{−3}	0.241; −0.195	0.362; −0.250	0.198; −0.207	0.158; −0.185	0.422; −0.220	0.185; −0.176
CCDC deposition number	2127610	2127611	2127612	2127613	2127614	2127615

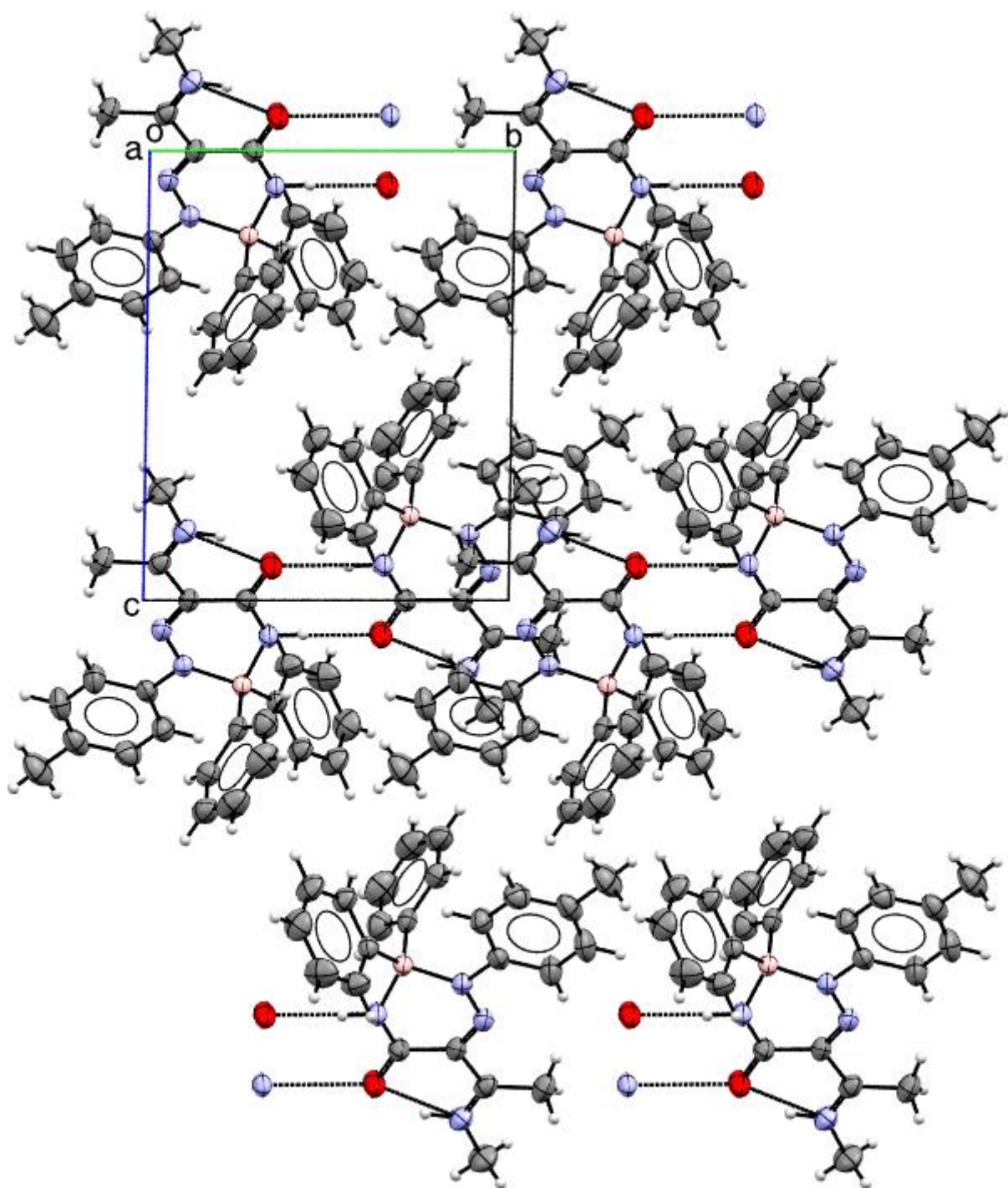


Figure S125. ORTEP view of the crystal structure of **5c** in the direction of the crystallographic axis *a*.

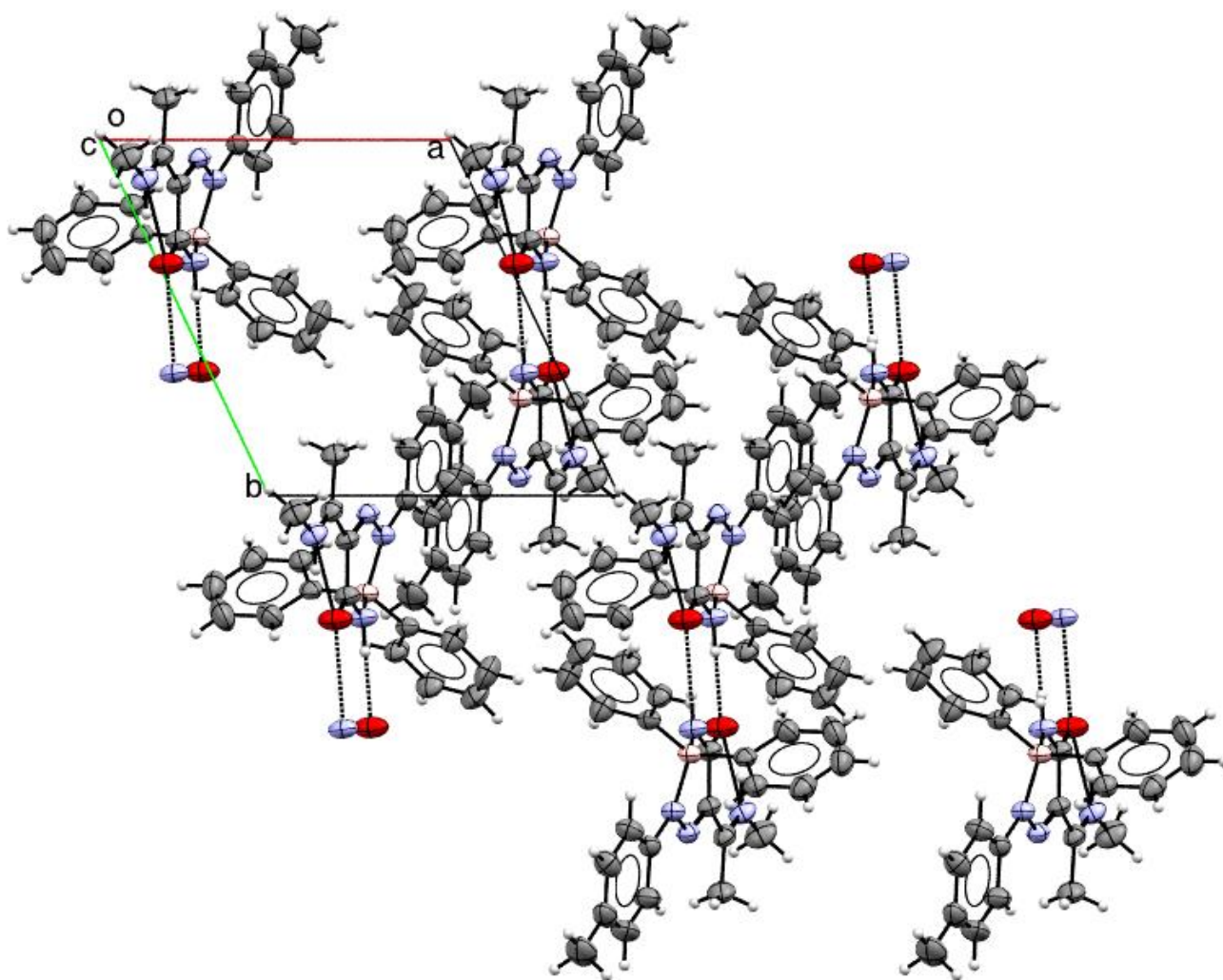


Figure S126. ORTEP view of the crystal structure of **5c** in the direction of the crystallographic axis *c*.

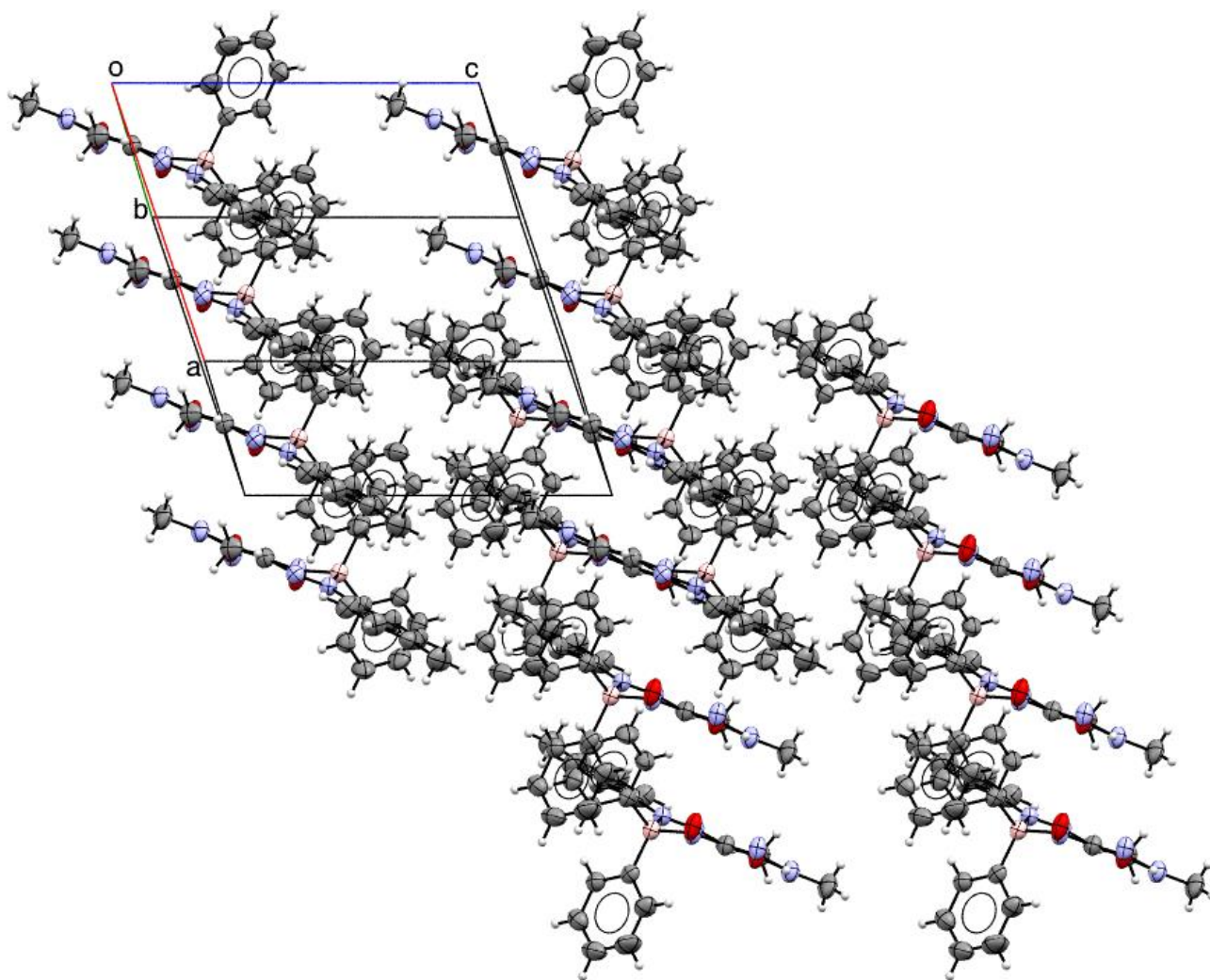


Figure S127. ORTEP view of the crystal structure of **5c** in the direction of the reciprocal cell axis b^* .

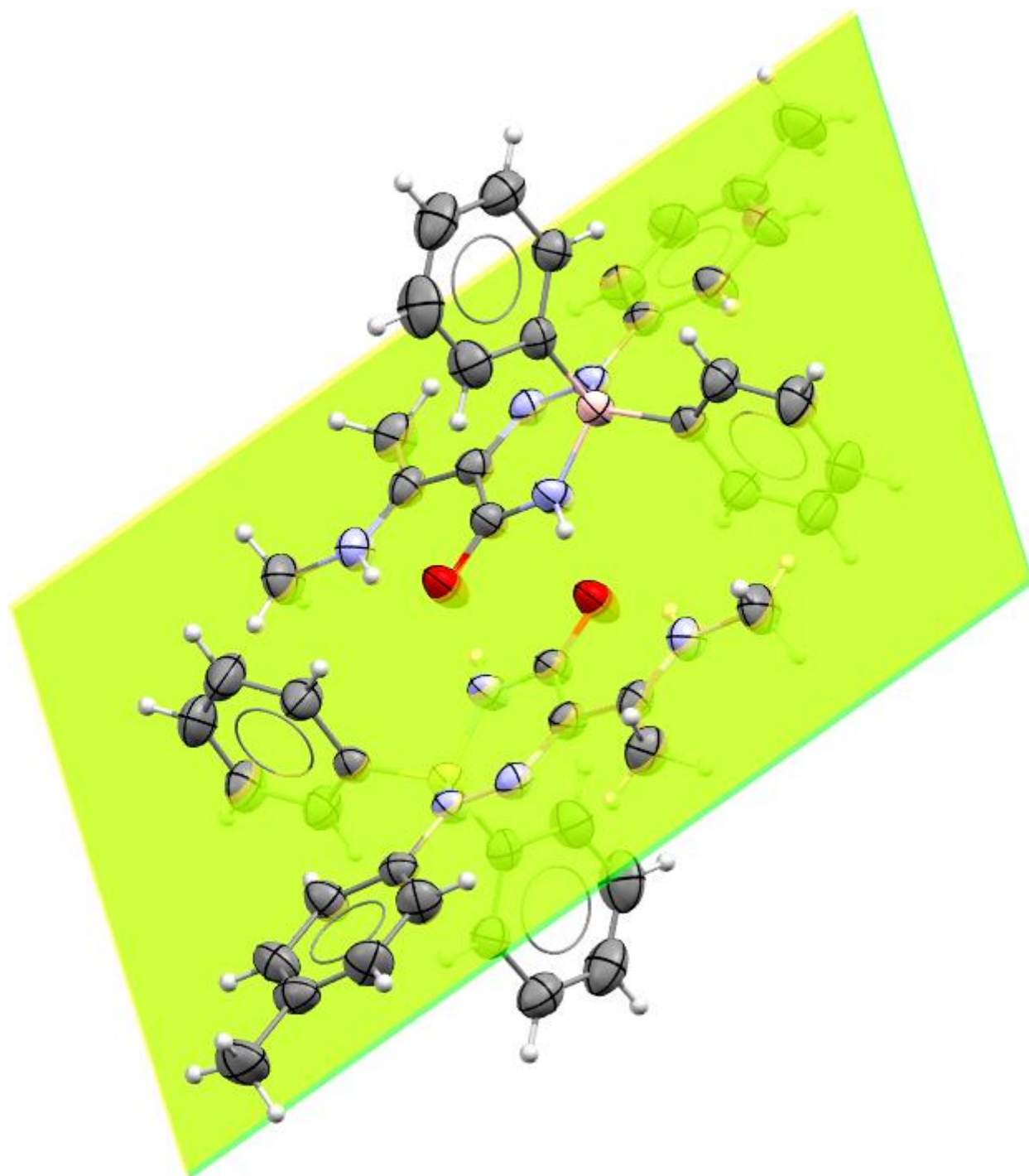


Figure S128. Triazaborine **5c**. The planes on which the double bonds C=N, C=N, and C=O lie.

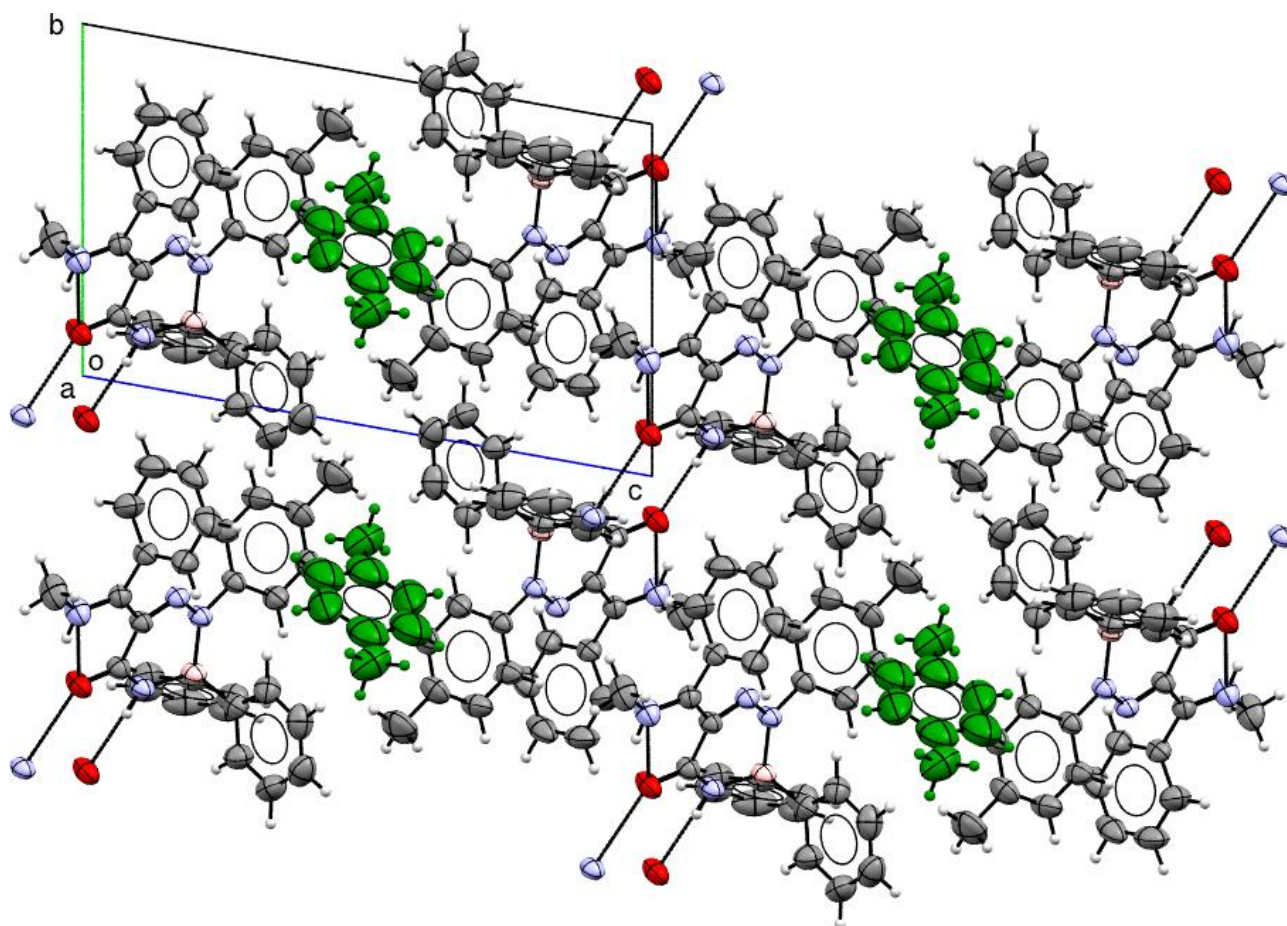


Figure S129. ORTEP view of the crystal packing of triazaborinone **5d** in the direction of the crystallographic axis *a*.

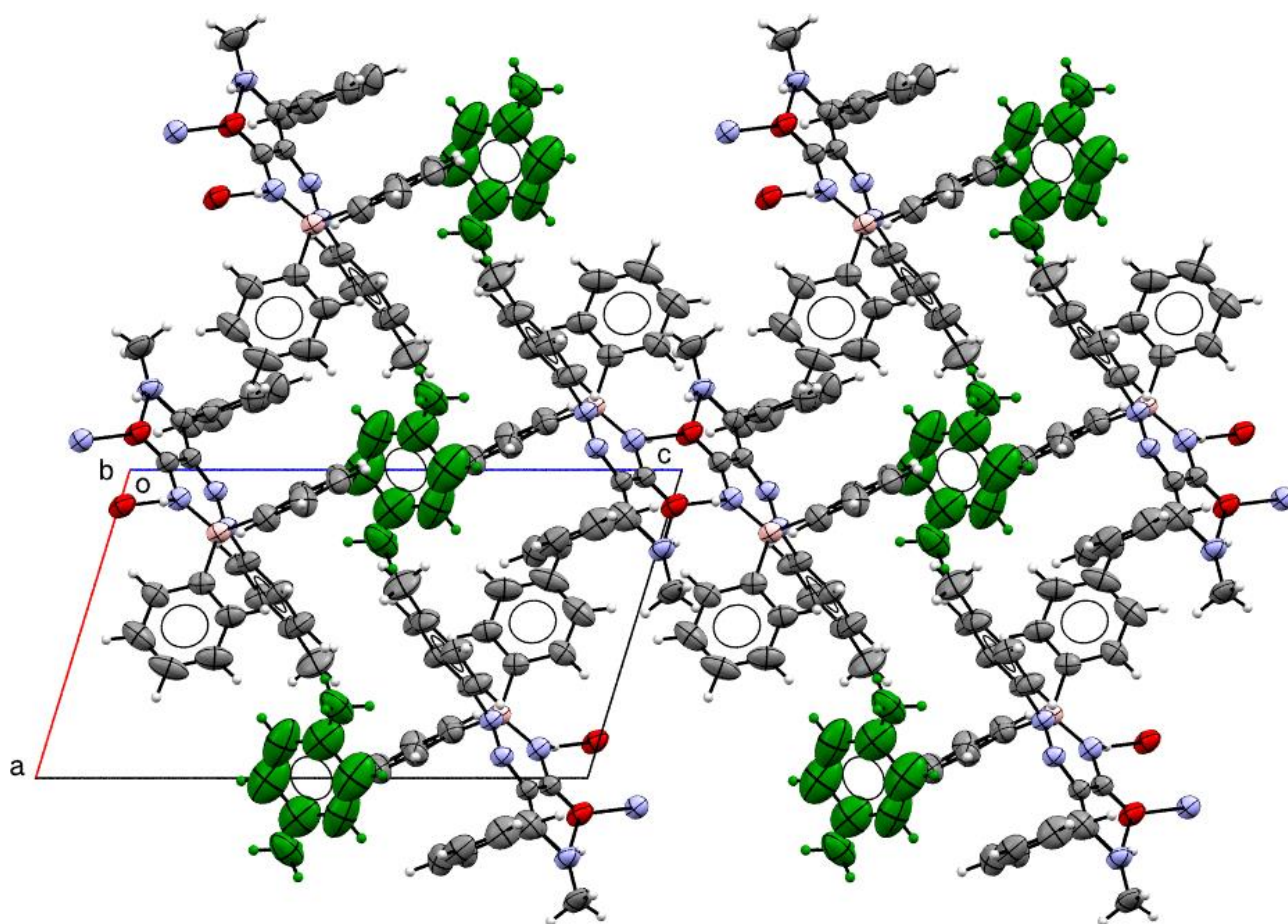


Figure S130. ORTEP view of the crystal packing of triazaborinone **5d** in the direction of the crystallographic axis *b*.

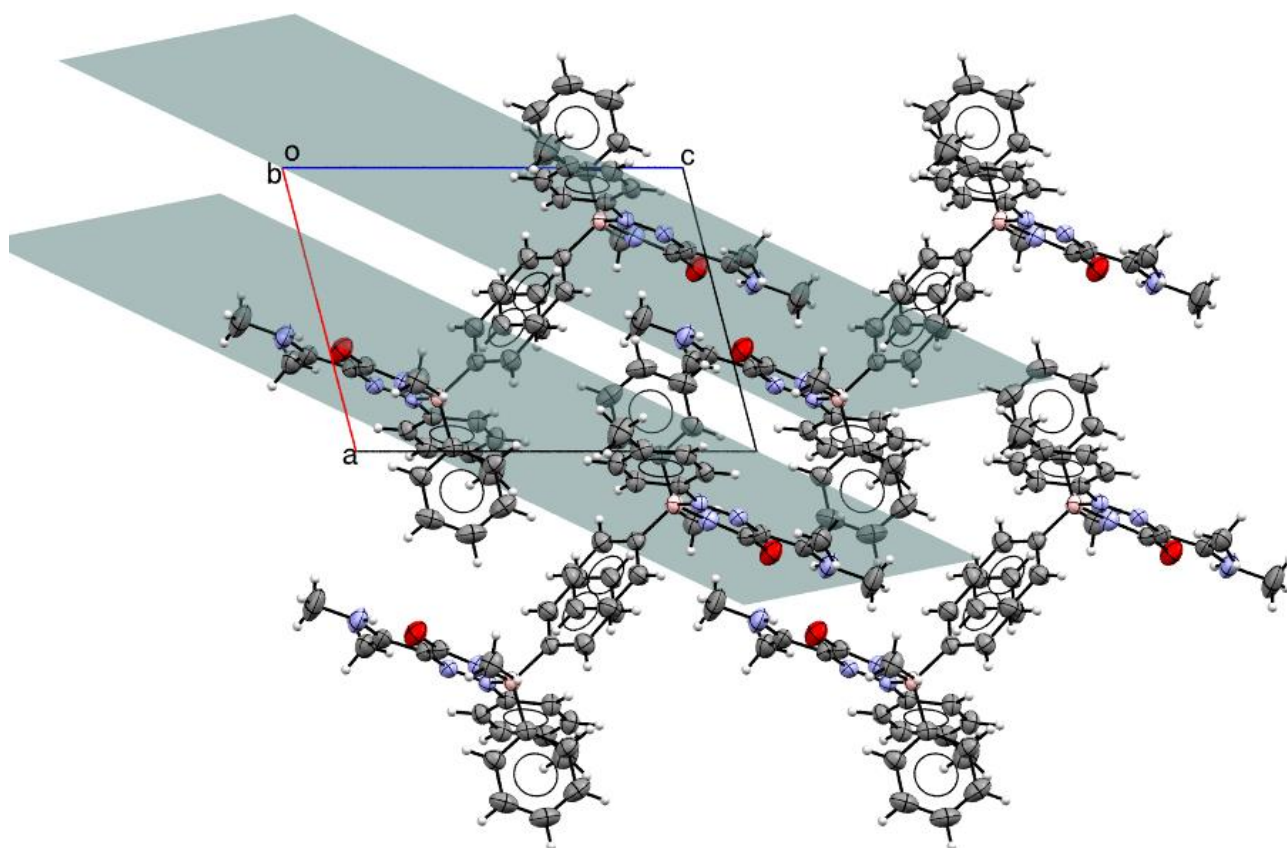


Figure S131. ORTEP view of the crystal structure of **5g** in the direction of the crystallographic axis *b*.

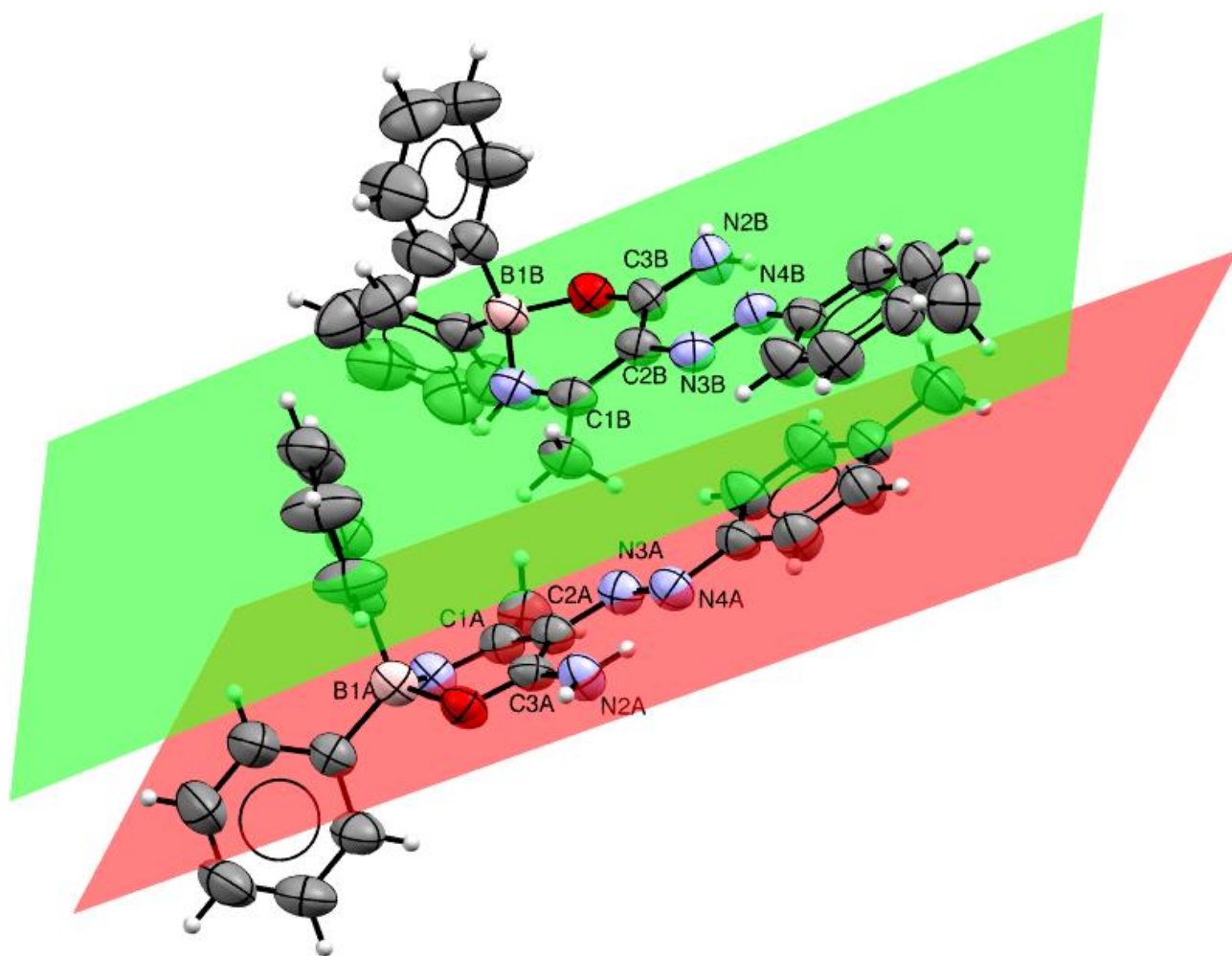


Figure S132. ORTEP diagram of the oxazaborine **6a** asymmetric unit.

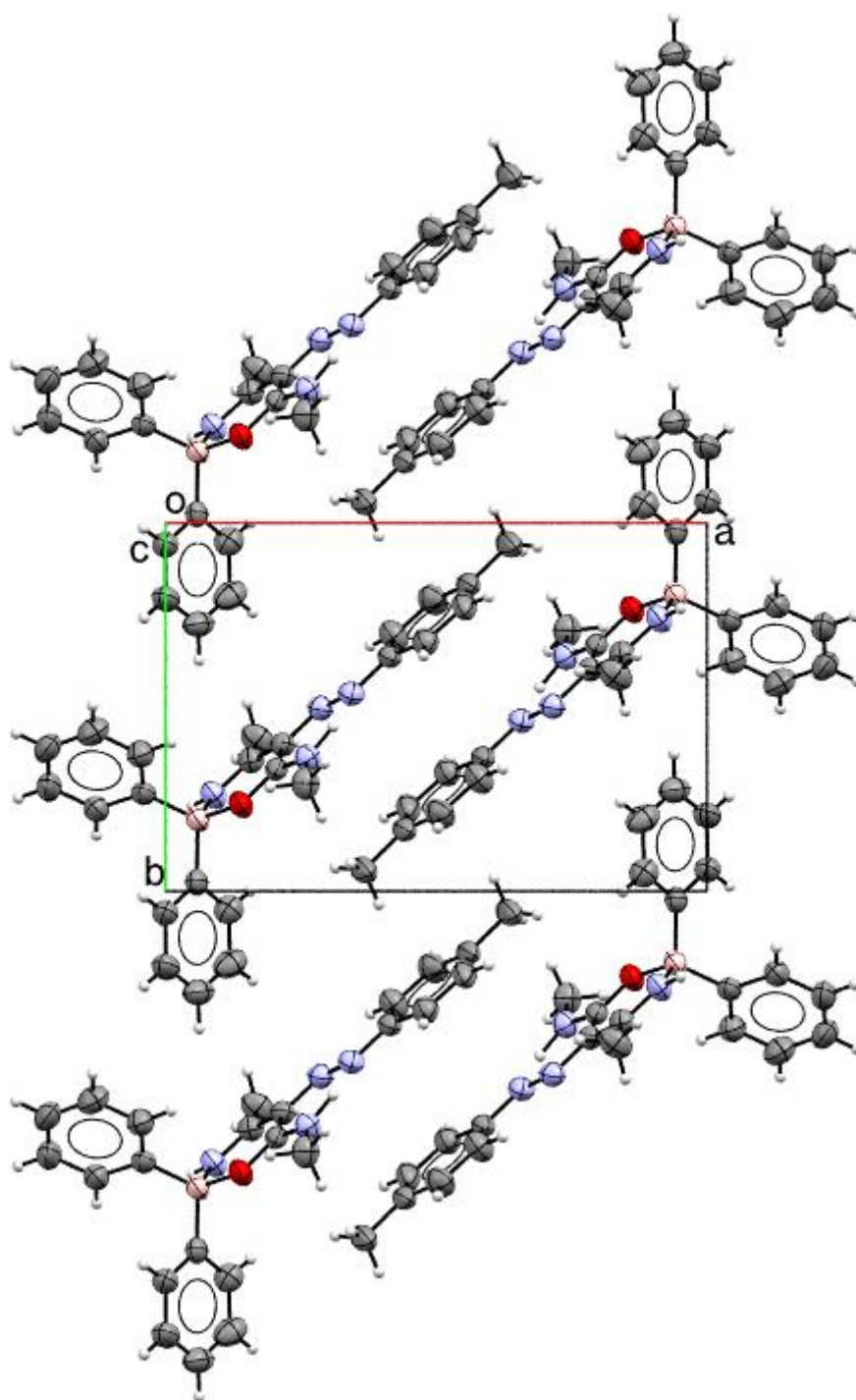


Figure S133. ORTEP view of the π - π stacking chain of **6e** in the direction of the crystallographic axis *c*.

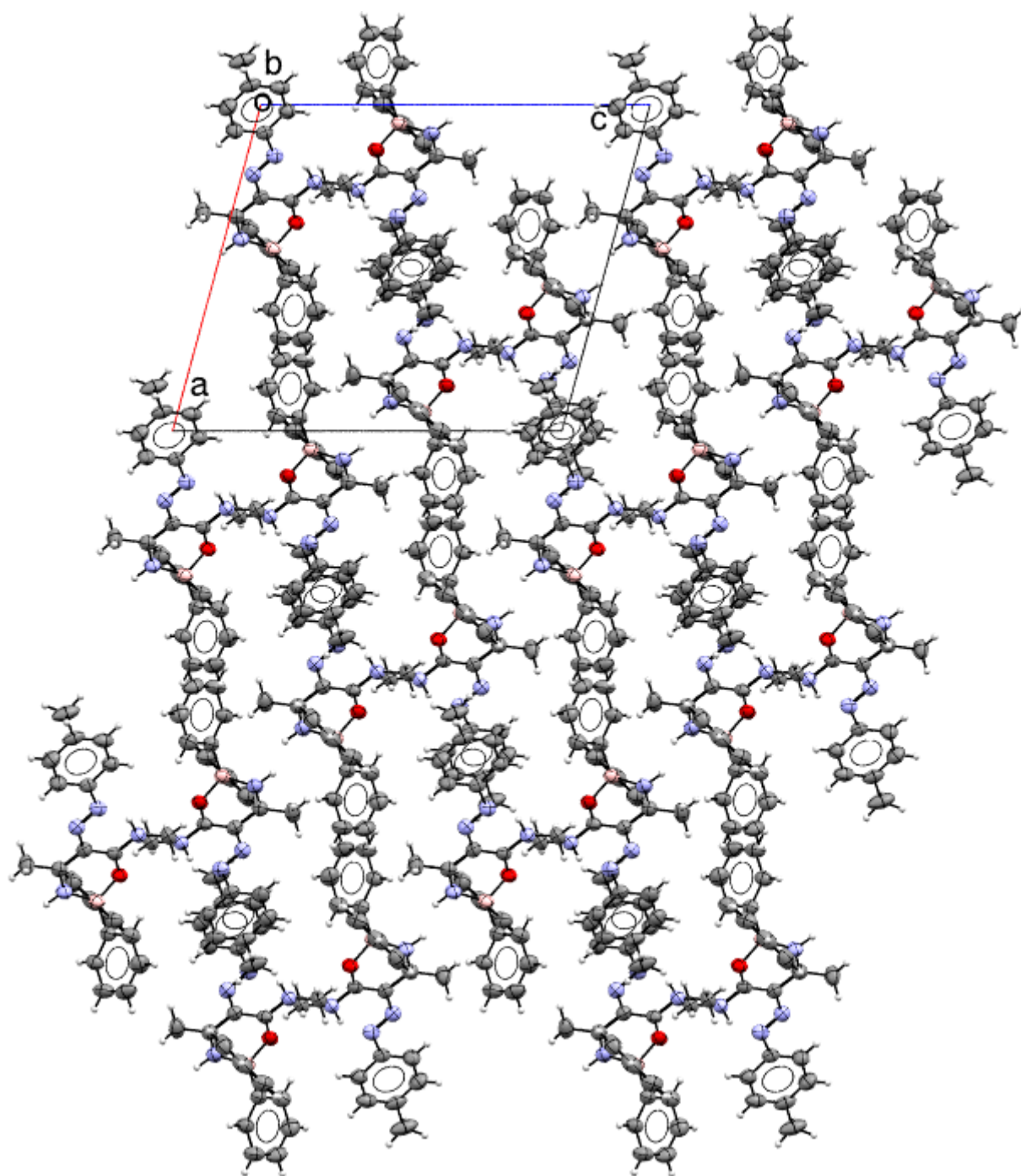


Figure S134. ORTEP view of the crystal structure of **6e** in the direction of the crystallographic axis *b*.

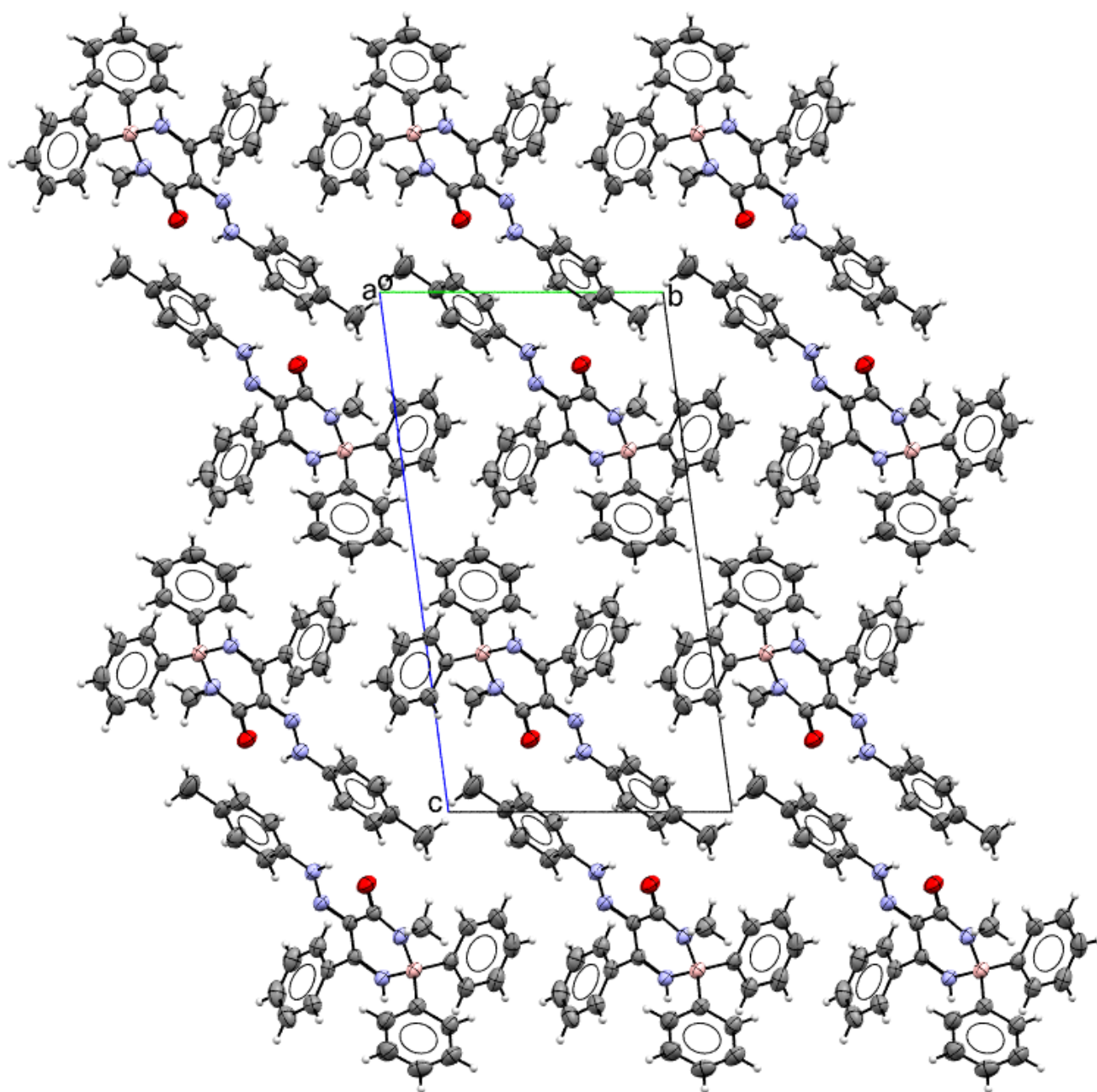


Figure S135. ORTEP view of the crystal packing of diazaborinone **7f** in the direction of the crystallographic axis *a*.

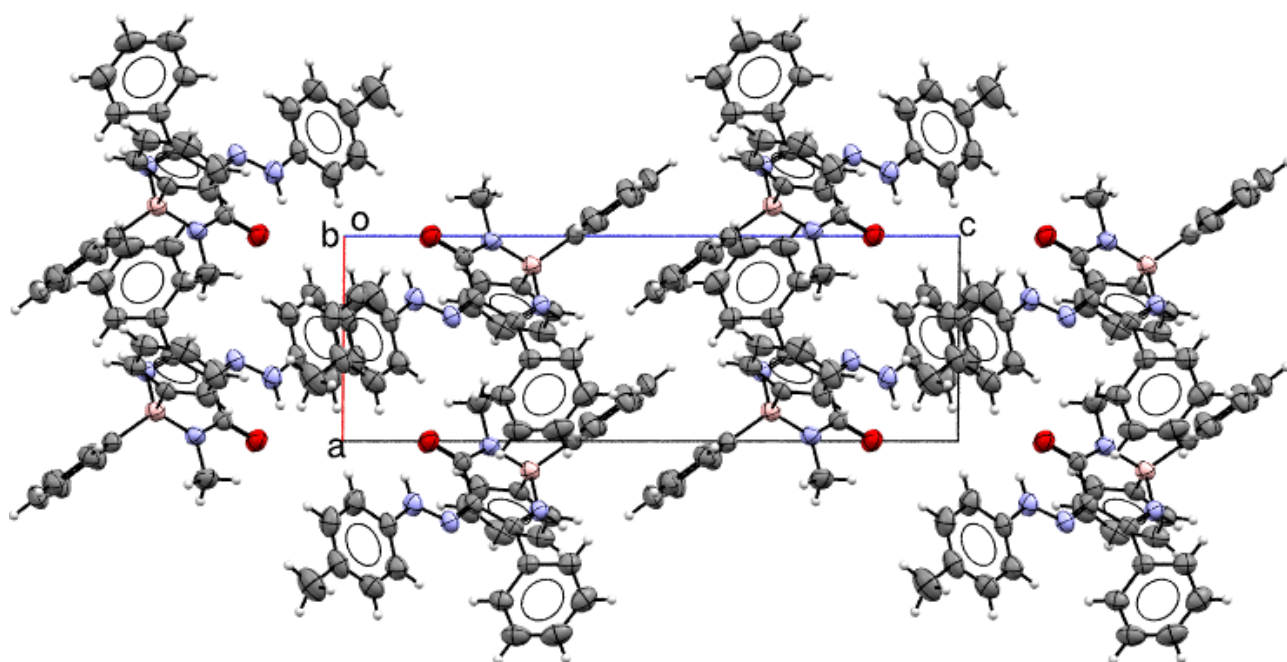


Figure S136. ORTEP view of the crystal packing of diazaborinone **7f** in the direction of the crystallographic axis *b*.

5. Fluorescence

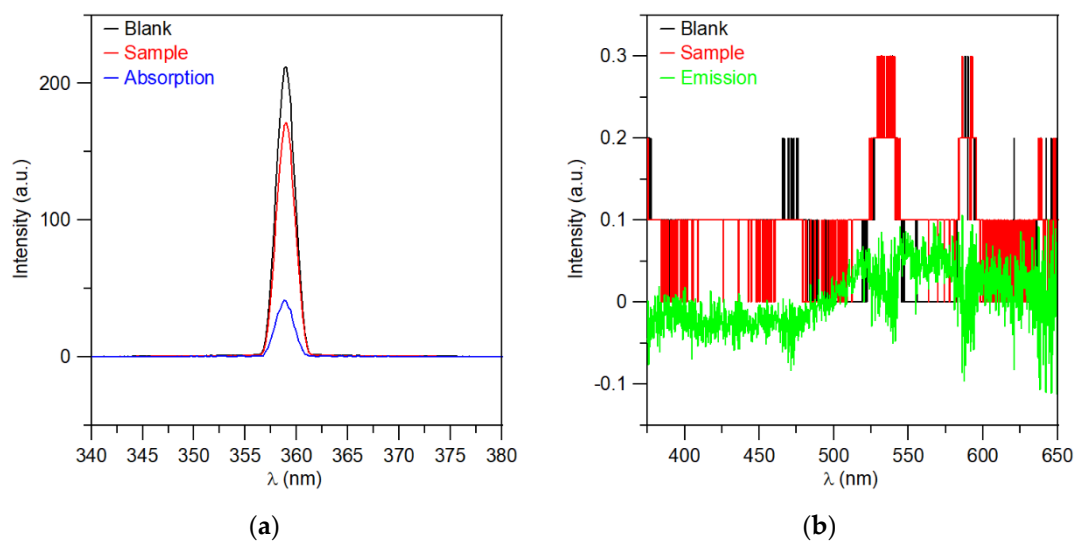


Figure S137. Triazaborinone 5g. (a) Absorption spectrum and (b) Emission spectrum.

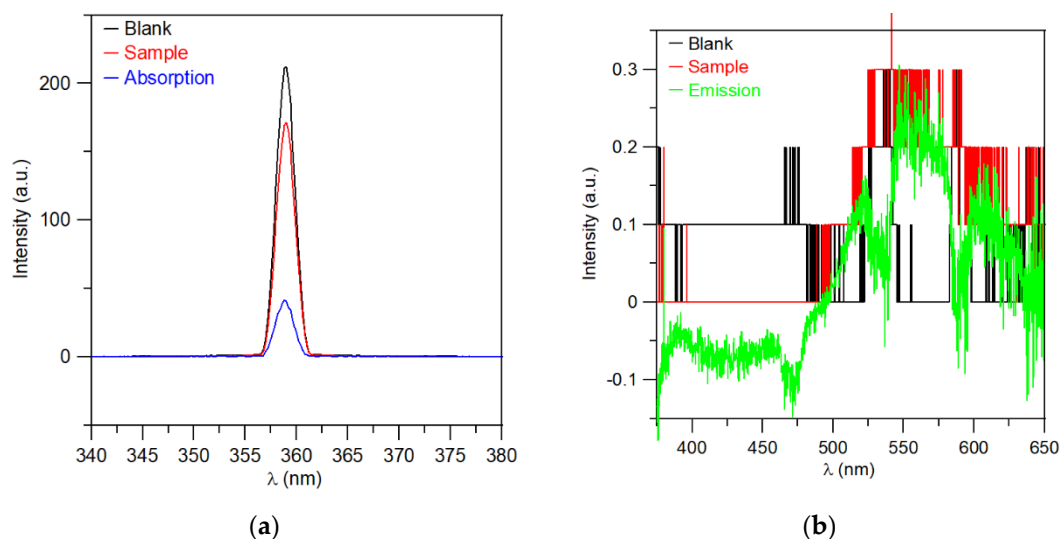


Figure S138. Triazaborinone 5h. (a) Absorption spectrum and (b) Emission spectrum.

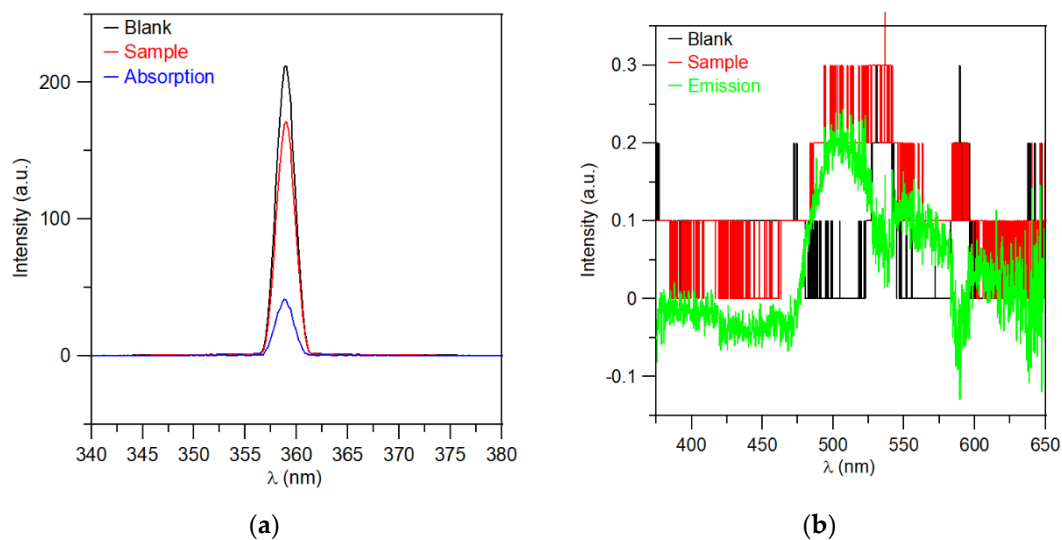


Figure S139. Diazaborinone 7a. (a) Absorption spectrum and (b) Emission spectrum.