

Supporting Information

Diamidocarbene Induced B–H Activation: A New Class of Initiator-Free Olefin Hydroboration Reagents

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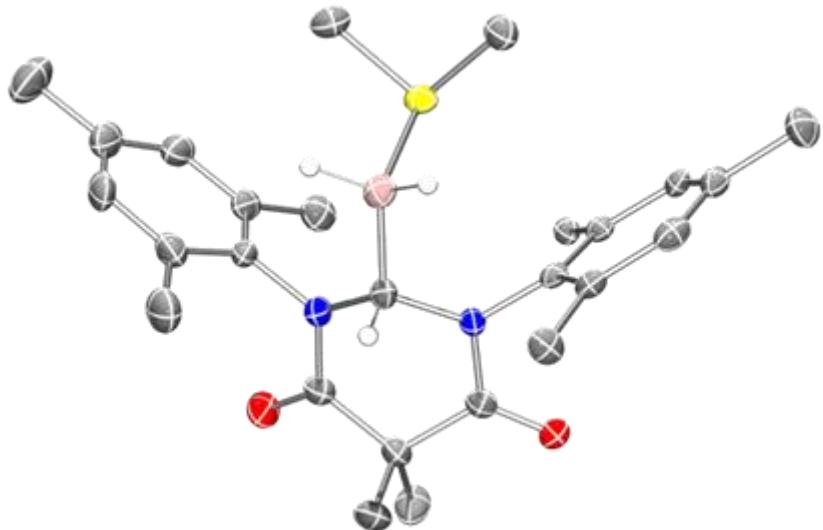


Figure S1. POV-Ray representation of **1·SMe₂** with thermal ellipsoids set to 50% probability. Most of the H atoms have been omitted for clarity.

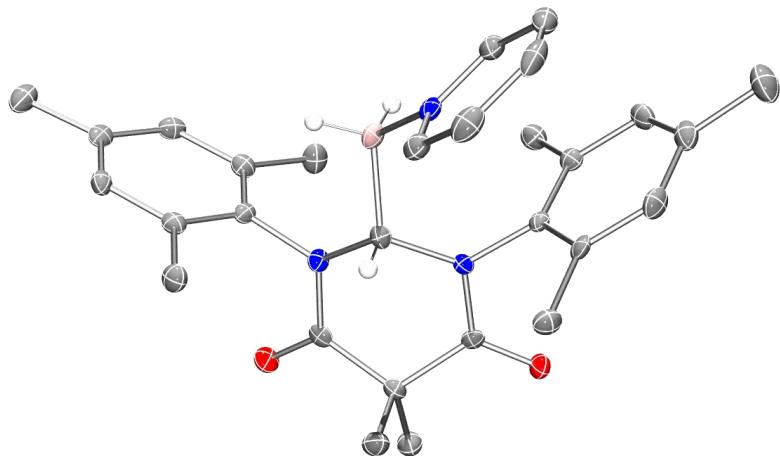


Figure S2. POV-Ray representation of **1·py** with thermal ellipsoids set to 50% probability. Most of the H atoms have been omitted for clarity.

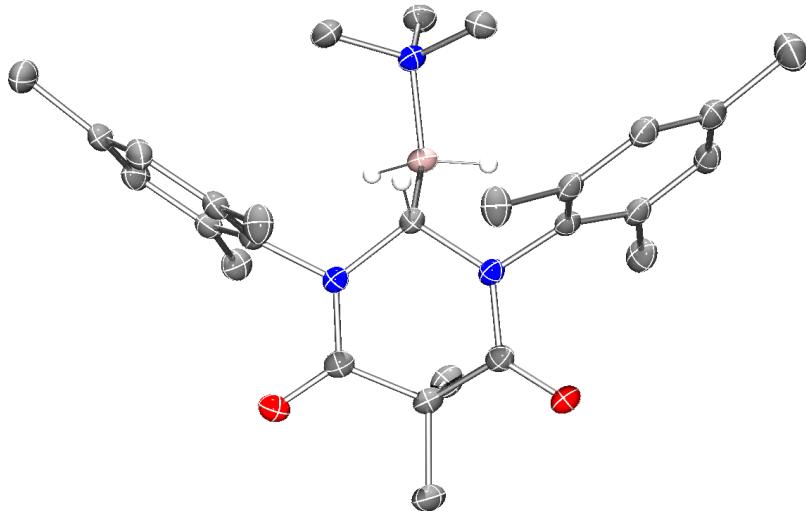


Figure S3. POV-Ray representation of **1·NMe₃** with thermal ellipsoids set to 50% probability. Most of the H atoms have been omitted for clarity.

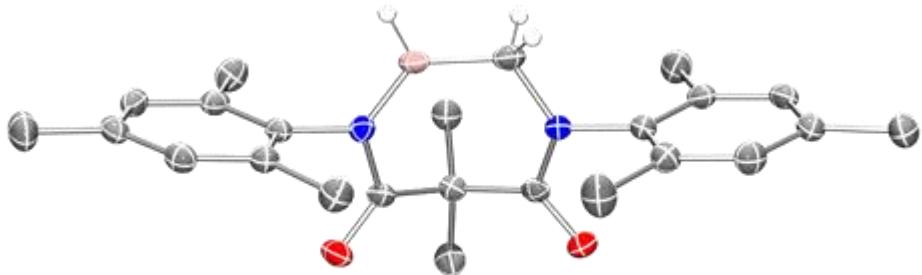


Figure S4. POV-Ray representation of **2** with thermal ellipsoids set to 50% probability. Most of the H atoms have been omitted for clarity.

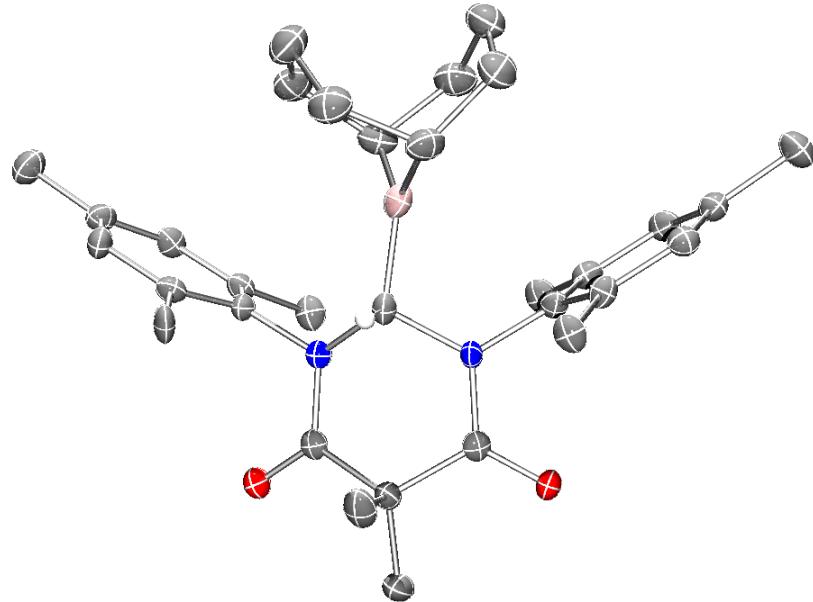


Figure S5. POV-Ray representation of **3** with thermal ellipsoids set to 50% probability. Most of the H atoms have been omitted for clarity.

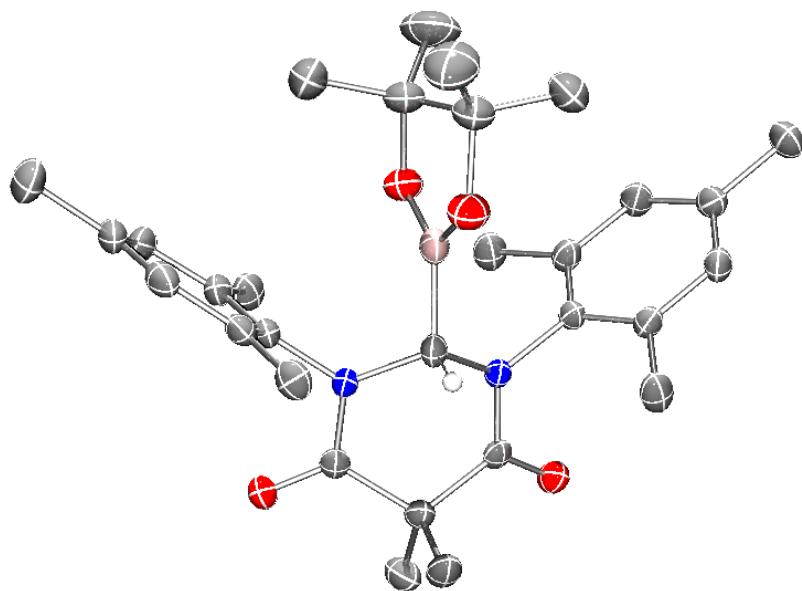


Figure S6. POV-Ray representation of **4** with thermal ellipsoids set to 50% probability. Most of the H atoms have been omitted for clarity.

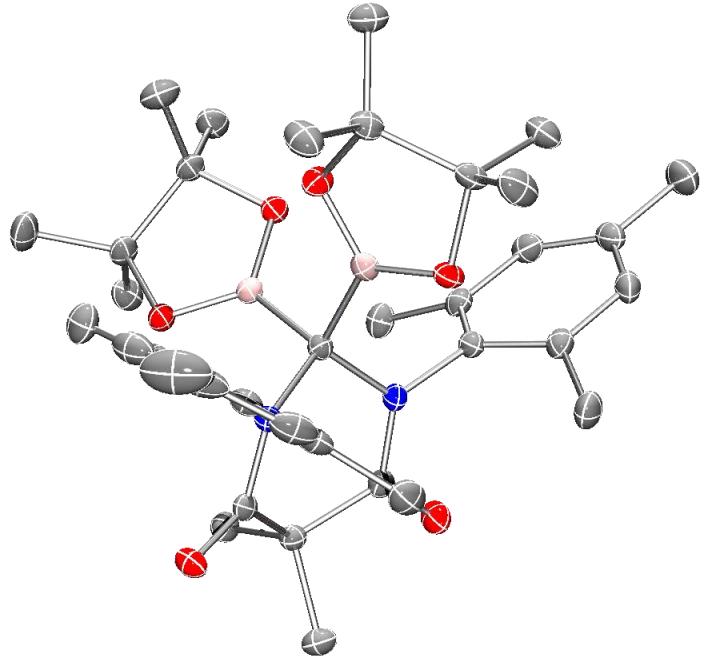


Figure S7. POV-Ray representation of **5** with thermal ellipsoids set to 50% probability. The H atoms have been omitted for clarity.

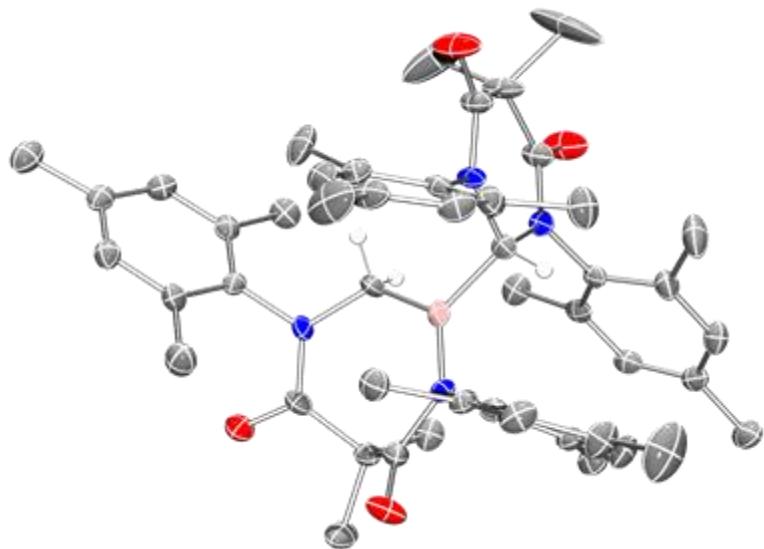


Figure S8. POV-Ray representation of **2DAB-BH₃** with thermal ellipsoids set to 50% probability. Most of the H atoms have been omitted for clarity.

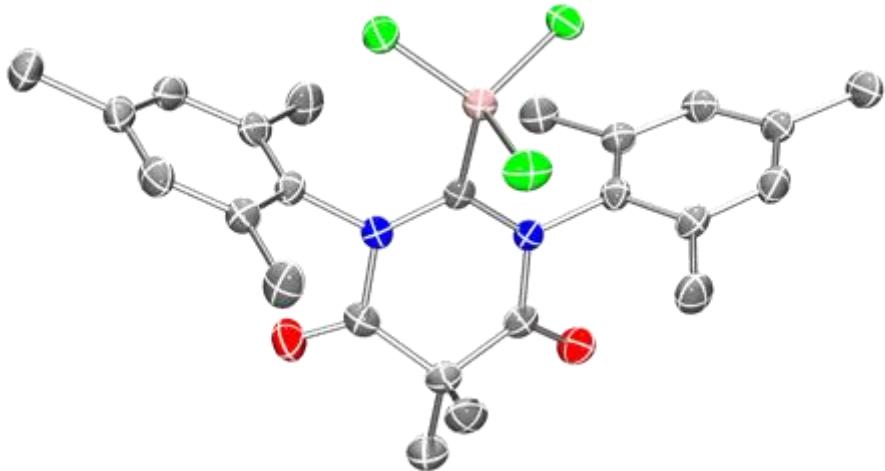


Figure S9. POV-Ray representation of **DAC-BCl₃** with thermal ellipsoids set to 50% probability. The H atoms have been omitted for clarity.

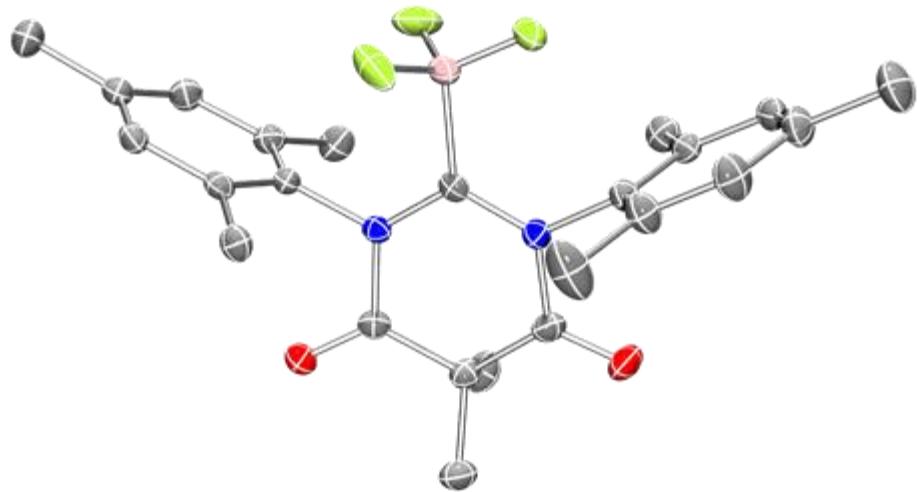


Figure S10. POV-Ray representation of **DAC-BF₃** with thermal ellipsoids set to 50% probability. The H atoms have been omitted for clarity.

Table S1. Summary of crystal data, data collection, and structure refinement details for **1·SMe₂**, **1·py**, **1·NMe₃**, **2**, and **2DAB-BH₃**.

	1·SMe₂	1·py	1·NMe₃	2	2DAB-BH₃
CCDC	1022989	1022990	1422628,1422632	1022992	1422631
Formula	C ₂₆ H ₃₇ N ₂ O ₂ BS	C ₂₉ H ₃₆ N ₃ O ₂ B	C ₂₇ H ₄₀ N ₃ O ₂ B	C ₂₄ H ₃₁ N ₂ O ₂ B	C ₄₈ H ₅₉ N ₄ O ₄ B
M _r	452.46	469.44	449.4	390.33	766.80
crystal size (mm ³)	0.20 × 0.20 × 0.20	0.20 × 0.20 × 0.20	0.25 × 0.15 × 0.09	0.20 × 0.20 × 0.20	0.10 × 0.10 × 0.10
crystal system	monoclinic	orthorhombic	monoclinic	triclinic	monoclinic
space group	P I 2 ₁ /n I	P c a 21	P I 2 ₁ I	P -I	P I 2/c I
a (Å)	16.852(12)	22.5736(33)	8.8352(12)	11.658(28)	16.8362(3)
b (Å)	13.4987(97)	8.3284(12)	12.6874(17)	12.6990(30)	12.0920(3)
c (Å)	12.8256(90)	13.9430(21)	12.1513(17)	15.4975(36)	23.6248(4)
α (°)	90	90	90.000(0)	85.322(5)	90.000(0)
β (°)	90.981(11)	90	109.329(3)	72.721(5)	91.107(2)
γ (°)	90	90	90.000(0)	88.791(5)	90.000(0)
V (Å ³)	2917.07(36)	2621.31(7)	1285.33(15)	2183.60(38)	4808.72(3)
Z	4	4	2	4	4
ρ _{calc} (g cm ⁻³)	1.22	1.23	1.16	1.19	1.06
μ (mm ⁻¹)	0.320	0.079	0.072	0.074	0.524
F(000)	1144.0	1048.0	488.0	840.0	1648.0
T (K)	120(2)	150(2)	150(3)	120(2)	130(2)
scan mode	ω	ω	ω	ω	ω
hkl range	-20 → +20 -16 → +16 -15 → +15	-26 → +26 -9 → +9 -16 → +16	-10 → +10 -15 → +15 -14 → +14	-13 → +13 -15 → +15 -18 → +18	-19 → +20 -14 → +13 -28 → +18
measd reflns	41353	36680	18790	29315	16102
unique reflns [R _{int}]	5129 [0.152]	4610 [0.094]	4504	7676 [0.057]	9019 [0.025]
refinement reflns	5129	4610	4504	7676	9019
refined parameters	324	341	317	547	530
GOOD on F ²	1.006	1.006	1.006	1.006	1.006
R1 ^a (all data)	0.093 (0.122)	0.040 (0.044)	0.032(0.034)	0.054 (0.070)	0.043 (0.056)
wR2 ^b (all data)	0.171 (0.187)	0.101 (0.103)	0.079(0.080)	0.129 (0.142)	0.110 (0.123)
ρ _{fin} (max/min)	0.620	0.180	0.156	0.259	0.279
(e Å ⁻³)	-0.502	-0.220	-0.157	-0.250	-0.191

^a R1 = $\sum ||Fo| - |Fc|| / \sum |Fo|$. ^b wR2 = $\{[\sum w(Fo^2 - Fc^2)^2] / [\sum w(Fo^2)]\}^{1/2}$.

Table S2. Summary of crystal data, data collection, and structure refinement details for **3**, **4**, **5**, **DAC-BCl₃**, and **DAC-BF₃**.

	DAC-9BBN (3)	DAC-Bpin (4)	DAC-bispin (5)	DAC-BCl ₃	DAC-BF ₃
CCDC	1429210	1422629,1422634	1422630,1422633	1022986	1022987
Formula	C ₃₈ H ₄₉ N ₂ O ₄ B	C ₃₀ H ₄₁ N ₂ O ₄ B	C ₃₆ H ₅₂ N ₂ O ₆ B ₂	C ₂₄ H ₂₈ N ₂ O ₂ BCl ₃	C ₂₄ H ₂₈ N ₂ O ₂ BF ₃
M _r	576.60	504.46	630.41	493.66	444.30
crystal size (mm ³)	0.24 × 0.22 × 0.13	0.23 × 0.12 × 0.06	0.39 × 0.33 × 0.15	0.20 × 0.20 × 0.20	0.39 × 0.11 × 0.10
crystal system	Monoclinic	triclinic	orthorhombic	triclinic	M onoclinic
space group	P 1 2 ₁ I	P-I	P c c n	P -I	P 1 2 ₁ c I
a (Å)	8.1720(70)	8.1190(20)	20.2950(30)	9.5178(39)	15.5890(17)
b (Å)	16.7830(80)	11.8750(30)	18.1860(20)	10.8696(43)	16.4336(17)
c (Å)	12.1300(70)	14.9580(50)	19.2810(30)	14.2715(48)	9.1255(10)
α (°)	90.000(0)	82.730(20)	90.000(0)	102.578(10)	90
β (°)	100.440(20)	86.700(30)	90.000(0)	108.454(22)	90.038(3)
γ (°)	90.000(0)	82.128(18)	90.000(0)	97.337(9)	90
V (Å ³)	1636.10(63)	1415.88(52)	7116.33(17)	1335.73(134)	2337.80(4)
Z	2	2	8	2	4
ρ _{calc} (g cm ⁻³)	1.17	1.18	1.18	1.32	1.26
μ (mm ⁻¹)	0.543	0.611	0.621	0.371	0.096
F(000)	576.6	544.0	2720.0	558.0	936.0
T (K)	123(2)	123(2)	93(2)	100(2)	120(2)
scan mode	ω	ω	ω	ω	ω
hkl range	-9 → +9 -11 → +20 -14 → +10	-6 → +9 -14 → +14 -18 → +17	-24 → +12 -21 → +20 -23 → +23	-11 → +11 -12 → +12 -16 → +16	-18 → +18 -18 → +18 -10 → +10
measd reflns	15042	25486	53226	18988	4056
unique reflns [R _{int}]	4509 [0.047]	5148 [0.039]	6502 [0.021]	4680 [0.080]	4056 [0.000]
refinement reflns	4509	5148	6502	4680	4056
refined parameters	396	346	431	324	298
GOOF on F ²	1.006	1.006	1.006	1.006	1.006
R1 ^a (all data)	0.053 (0.064)	0.046 (0.060)	0.035 (0.038)	0.053 (0.075)	0.031 (0.033)
wR2 ^b (all data)	0.146 (0.153)	0.125 (0.133)	0.091 (0.093)	0.111 (0.122)	0.089 (0.090)
ρ _{fin} (max/min) (e Å ⁻³)	0.302 -0.208	0.584 -0.221	0.298 -0.246	0.289 -0.315	0.223 -0.161

^a R1 = Σ||Fo| - |Fc||/Σ|Fo|. ^b wR2 = {[Σw(Fo² - Fc²)²]/Σw(Fo²)²}^{1/2}.

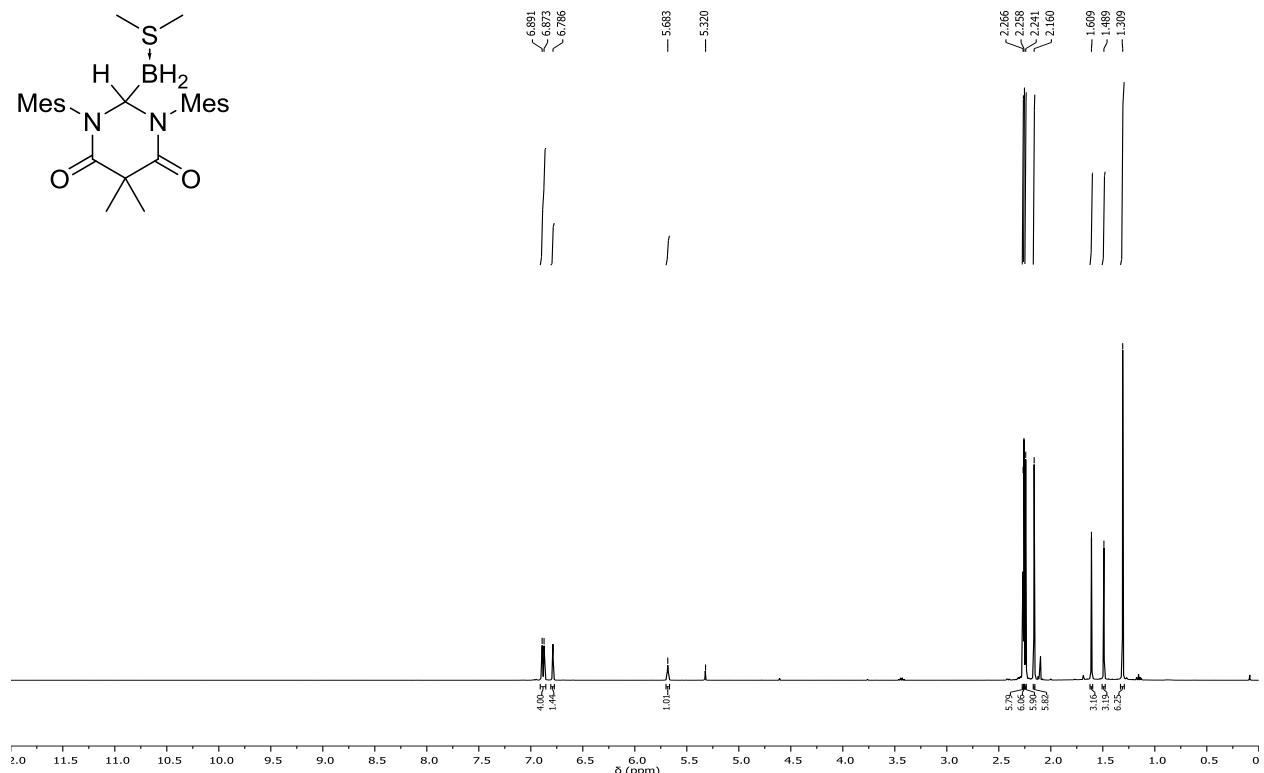


Figure S11. ¹H NMR spectrum of **1SMe₂**.

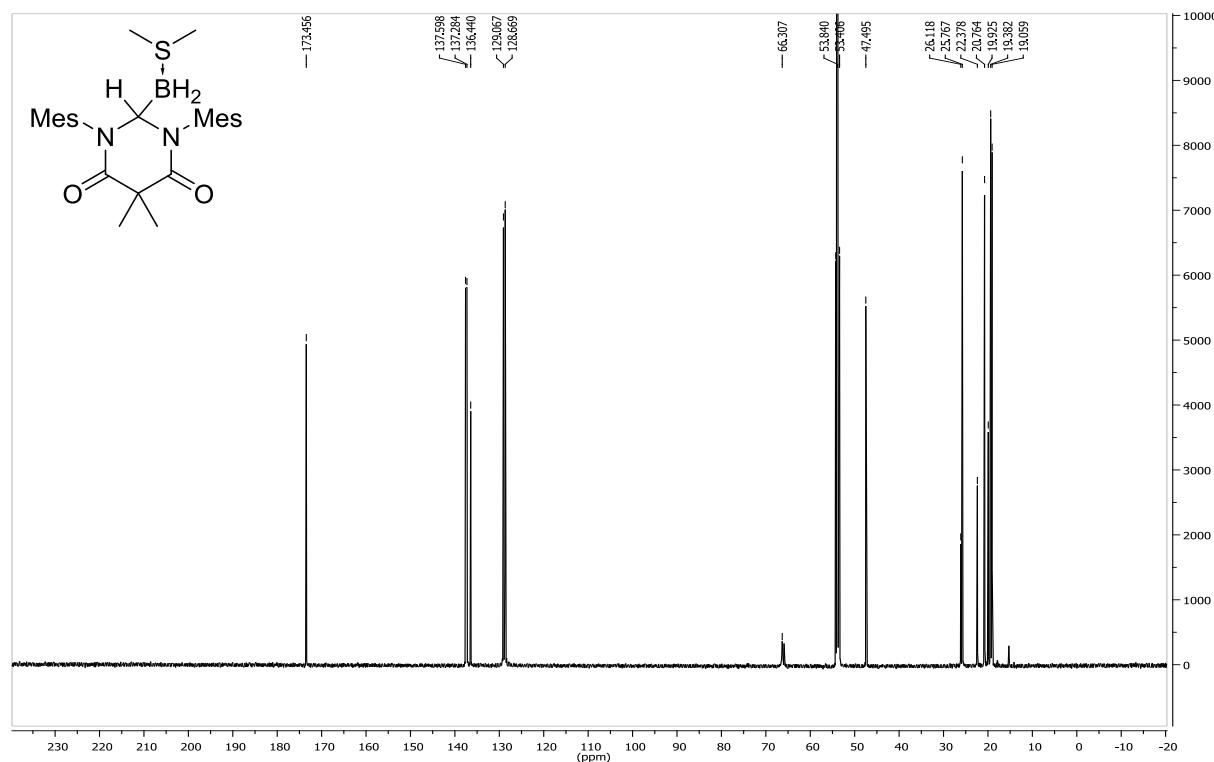


Figure S12. ¹³C NMR spectrum of **1SMe₂**.

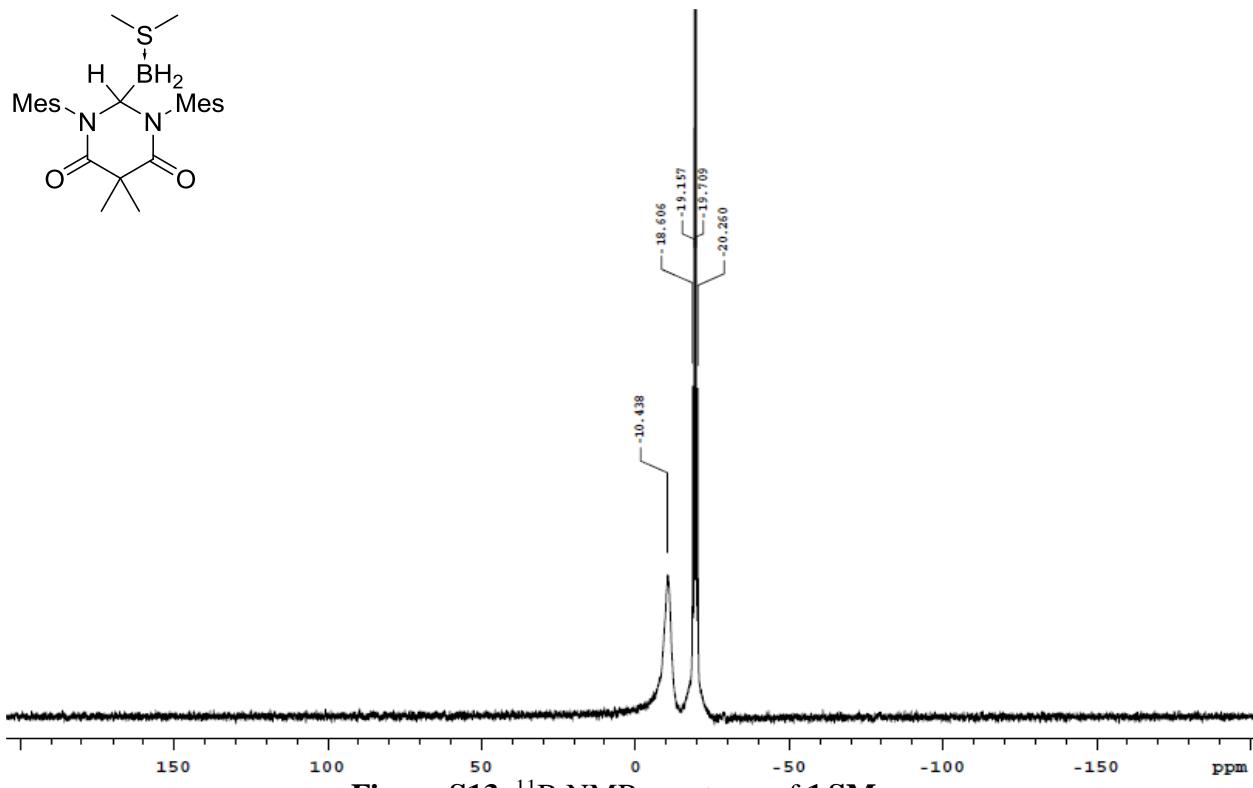


Figure S13. ¹¹B NMR spectrum of **1SMe₂**.

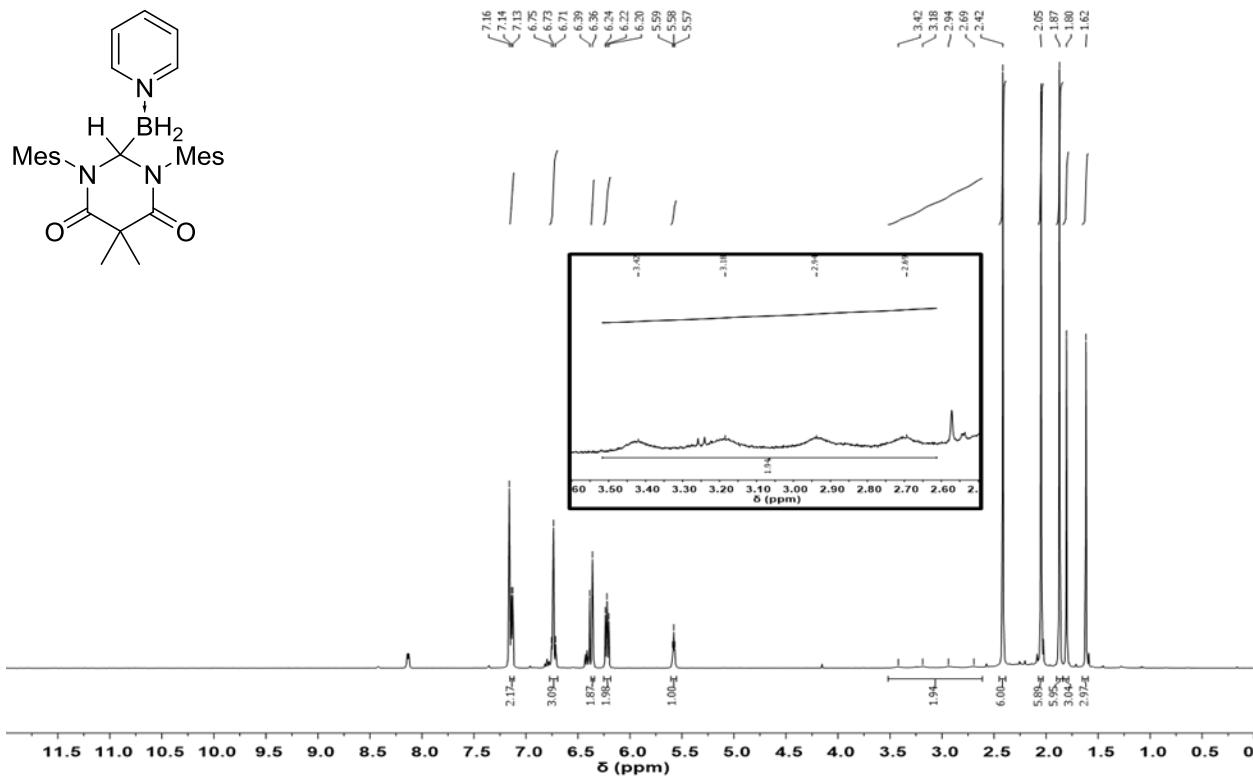


Figure S14. ¹H NMR spectrum of **1py**.

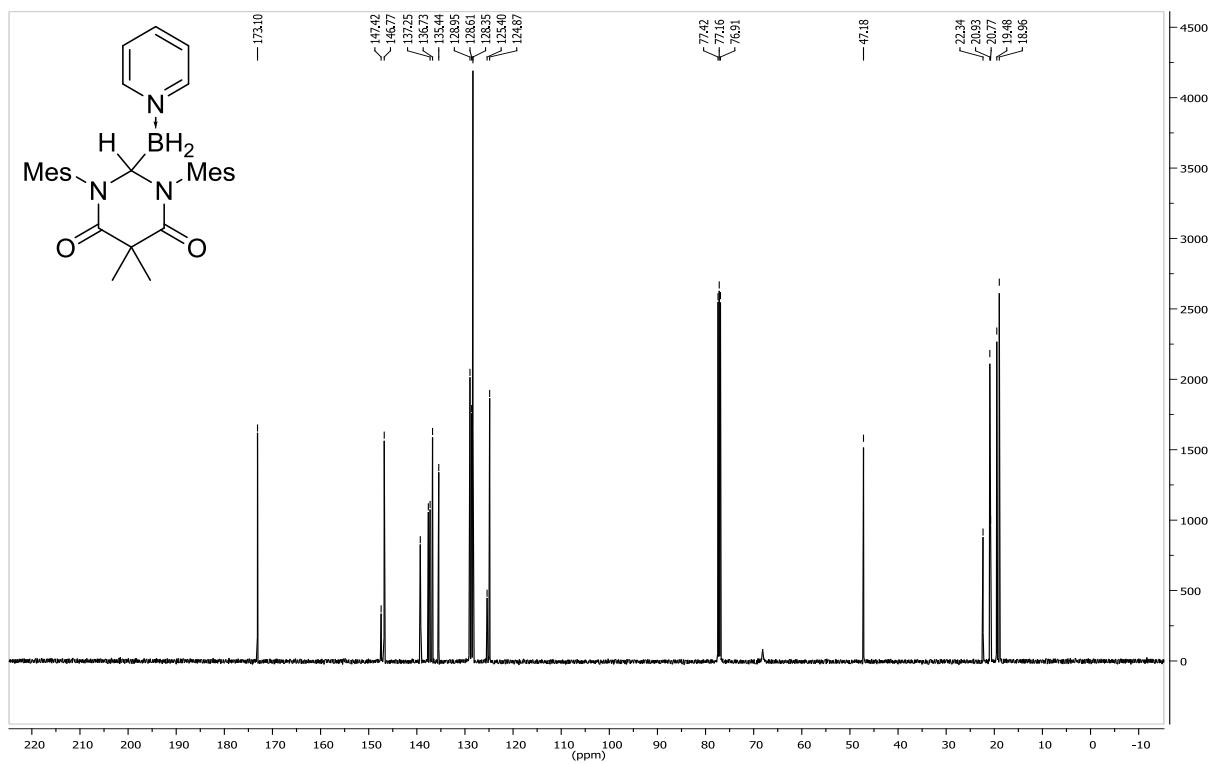


Figure S15. ^{13}C NMR spectrum of **1**py.

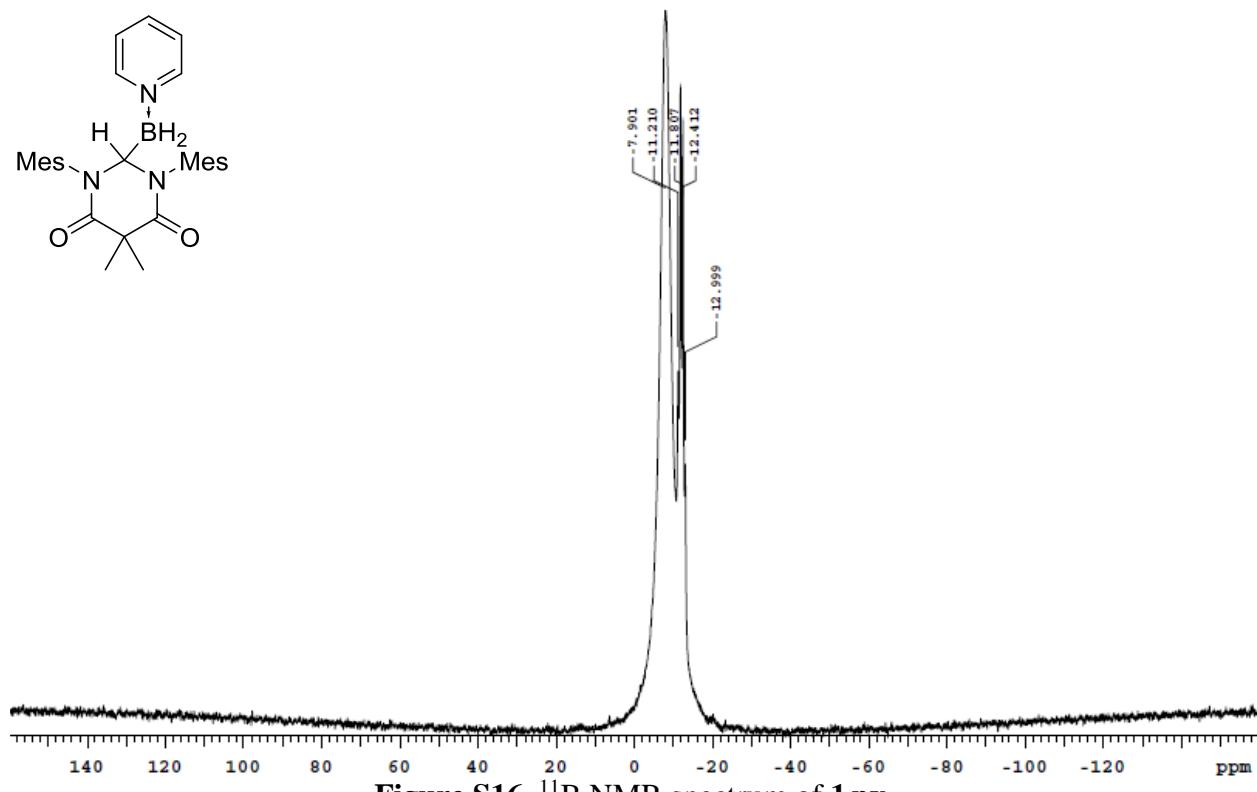


Figure S16. ^{11}B NMR spectrum of **1**py.

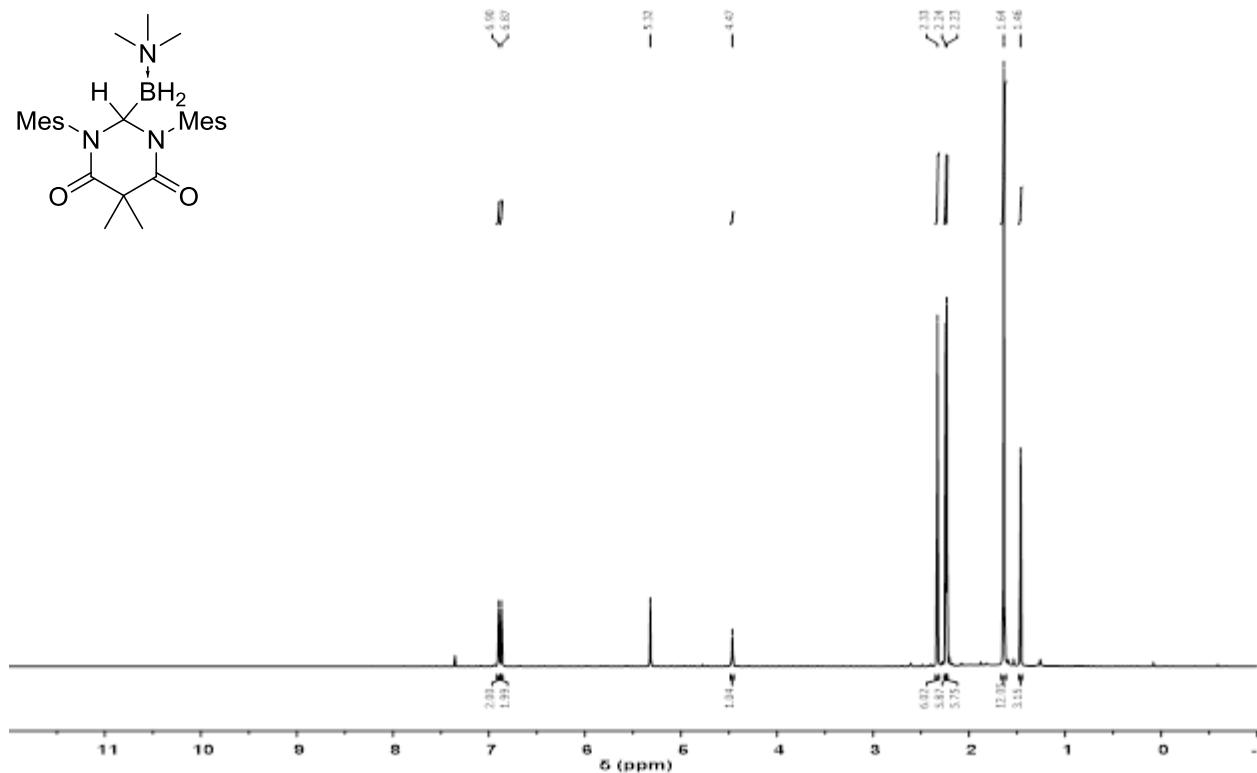
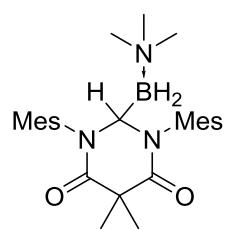


Figure S17. ^1H NMR spectrum of **1**· NMe_3 .

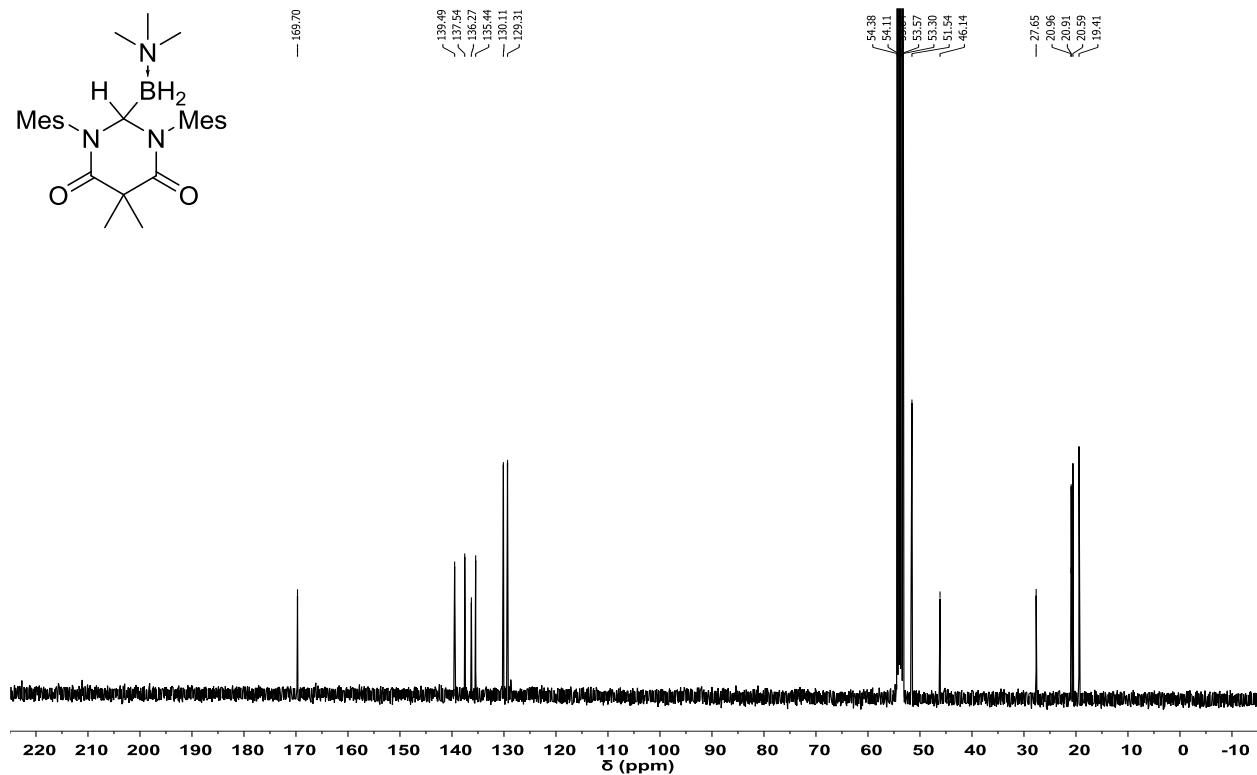
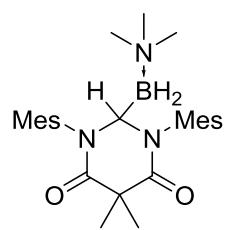


Figure S18. ^{13}C NMR spectrum of **1**· NMe_3 .

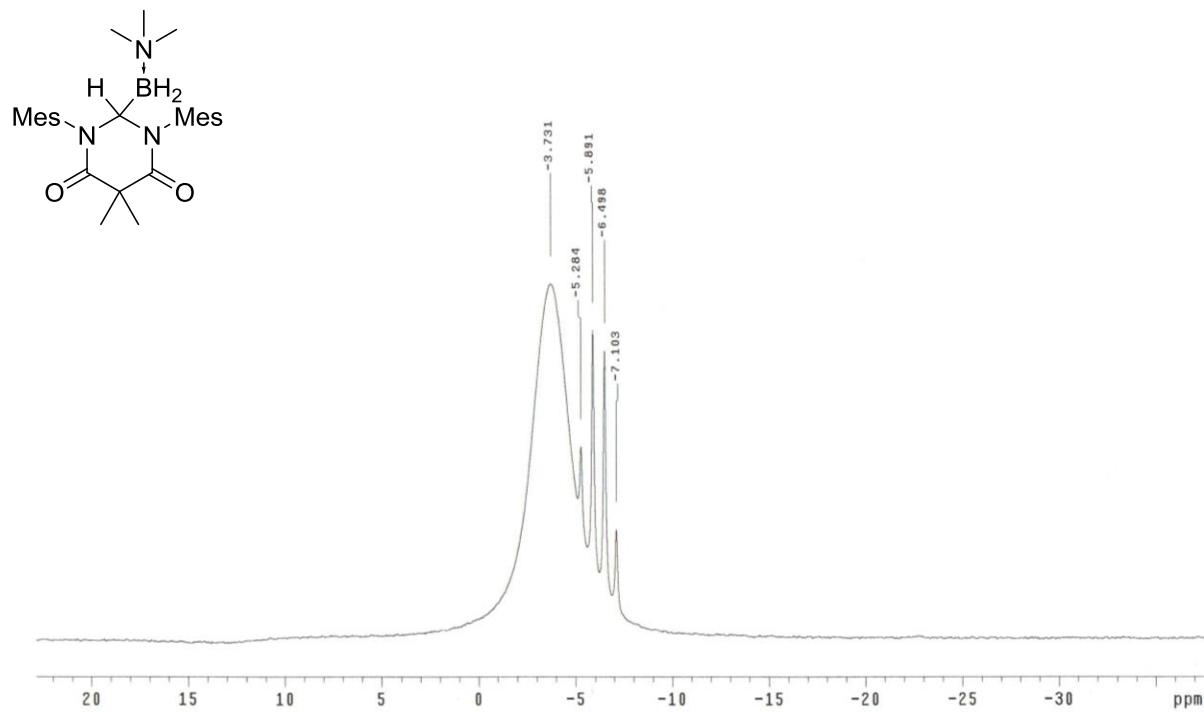


Figure S19. ¹¹B NMR spectrum of **1·NMe₃**.

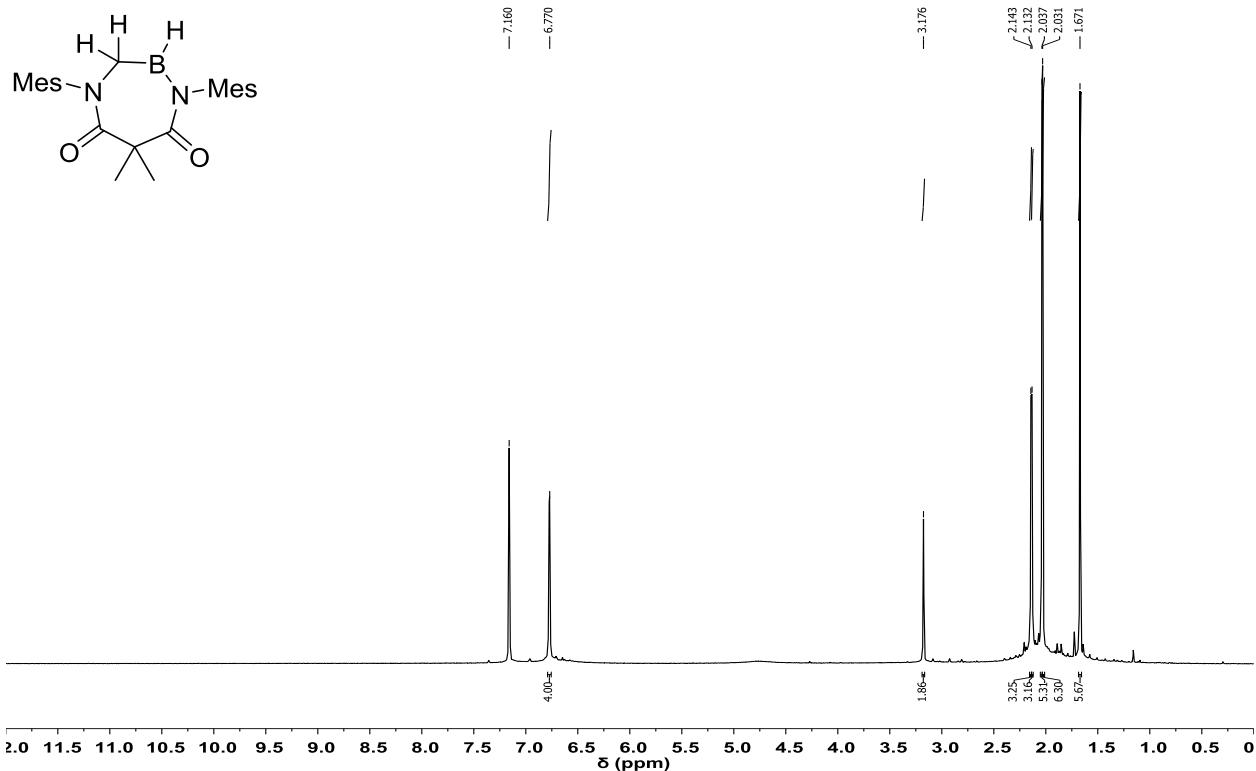


Figure S20. ¹H NMR spectrum of **2**.

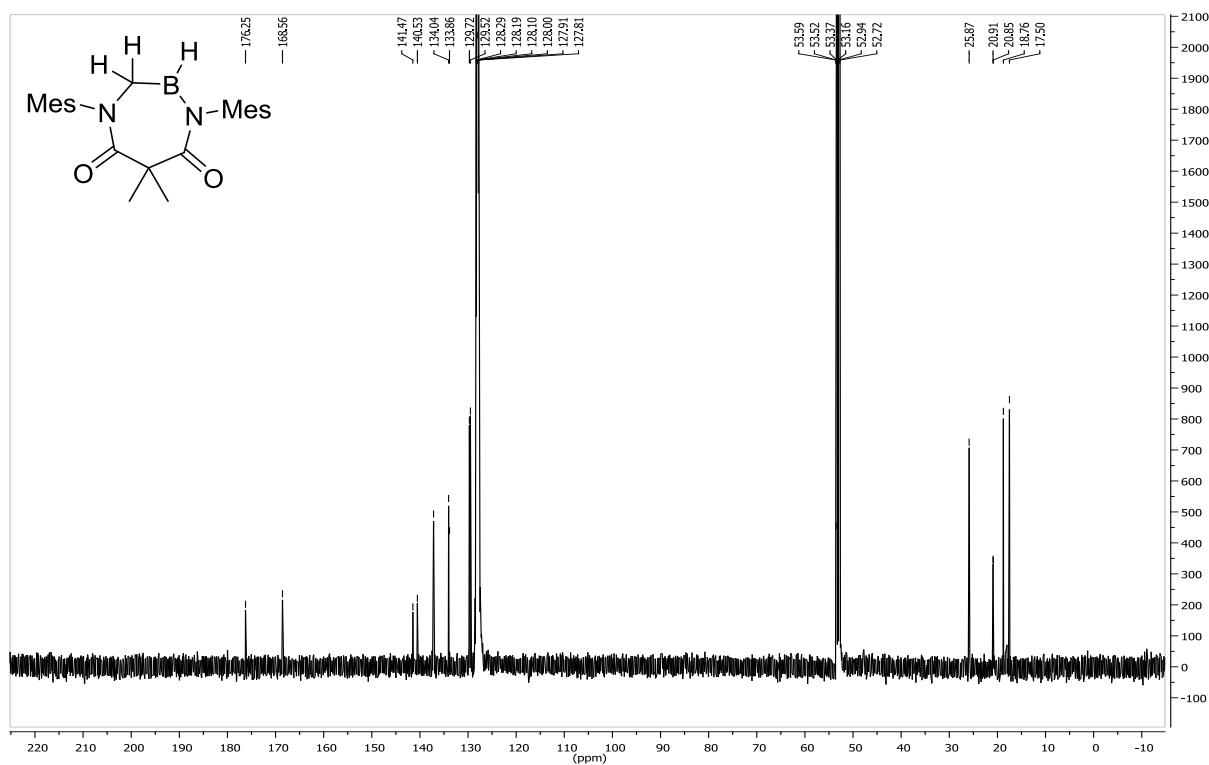


Figure S21. ¹³C NMR spectrum of **2**.

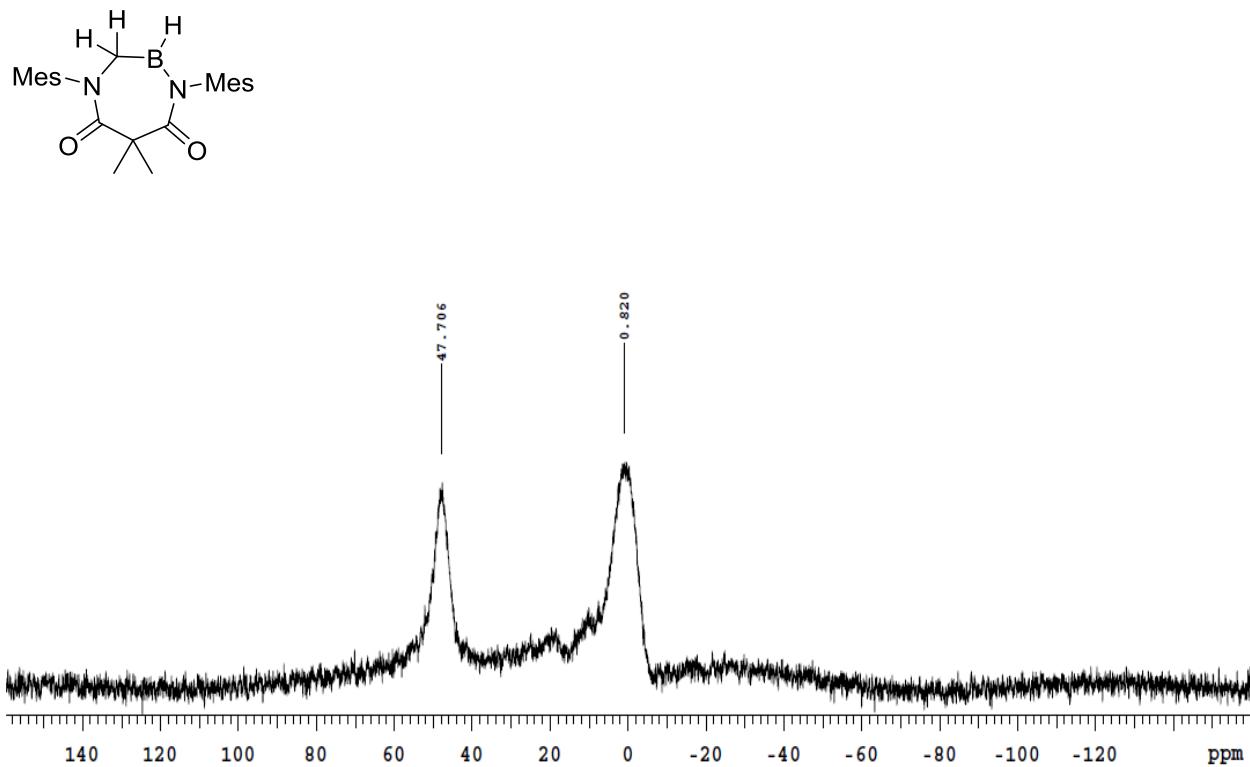


Figure S22. ¹¹B NMR spectrum of **2**.

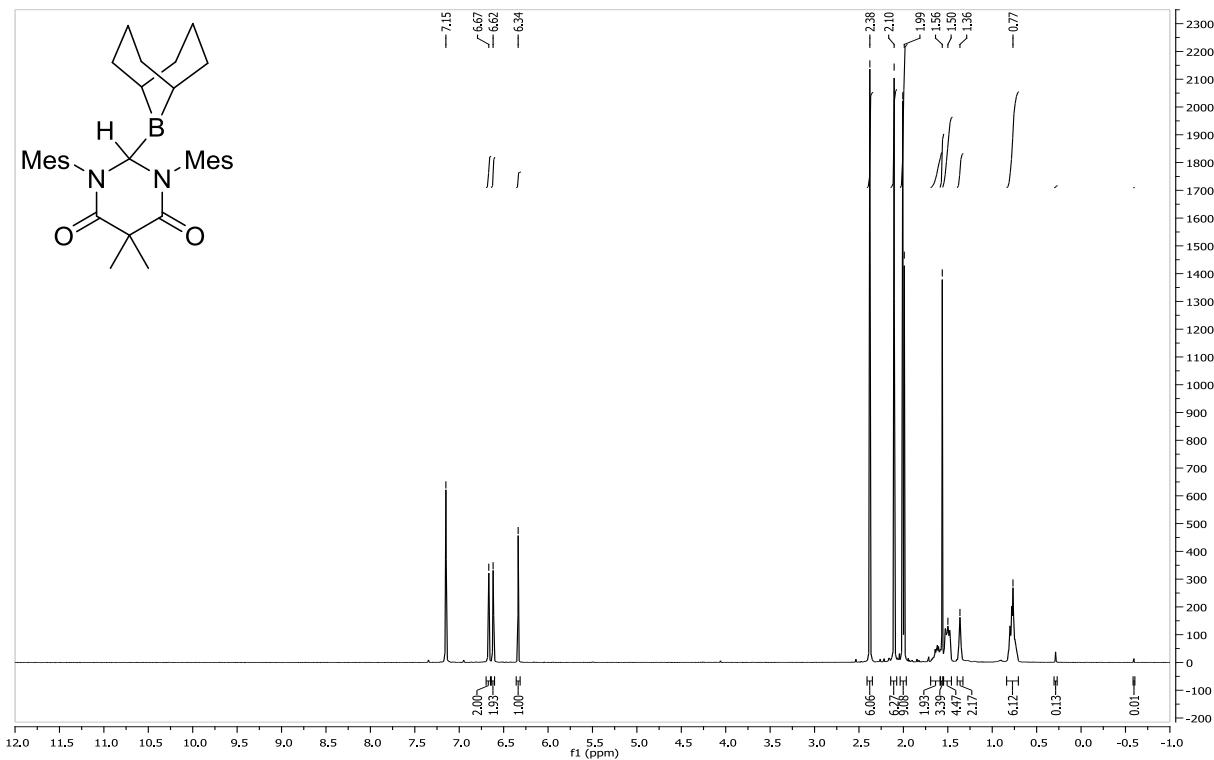


Figure S23. ^1H NMR spectrum of 3.

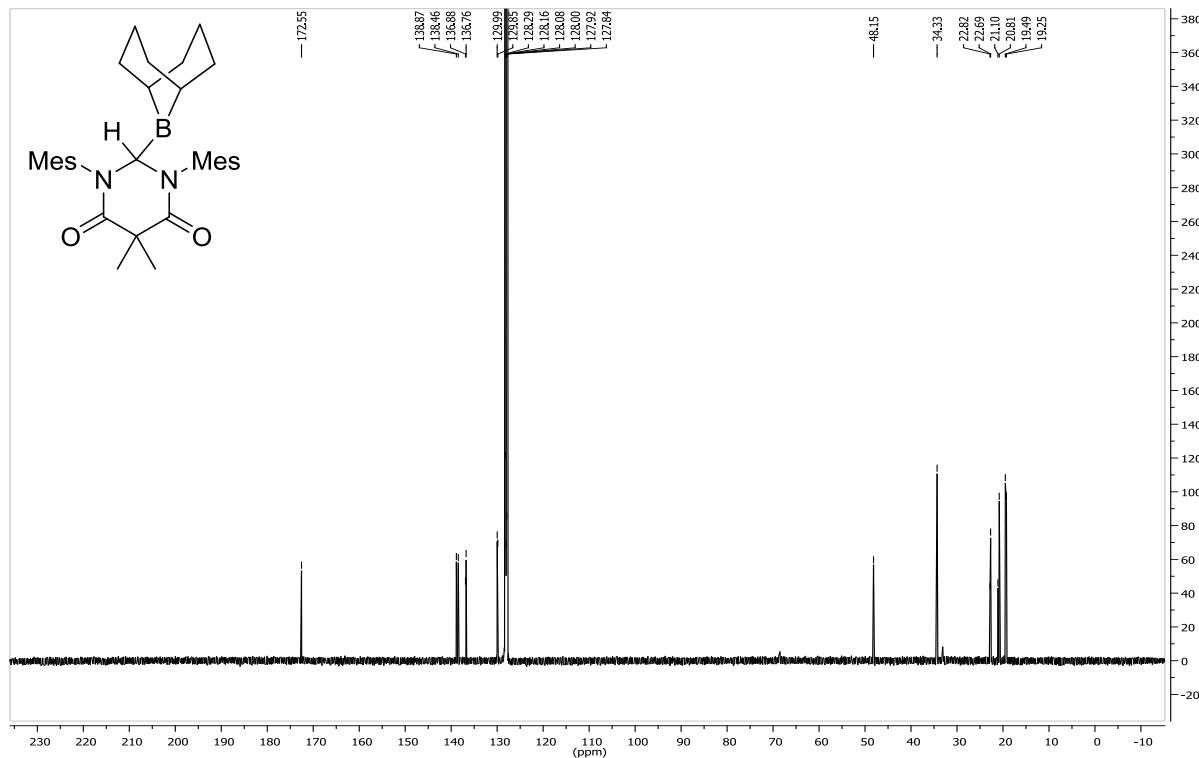


Figure S24. ^{13}C NMR spectrum of 3.

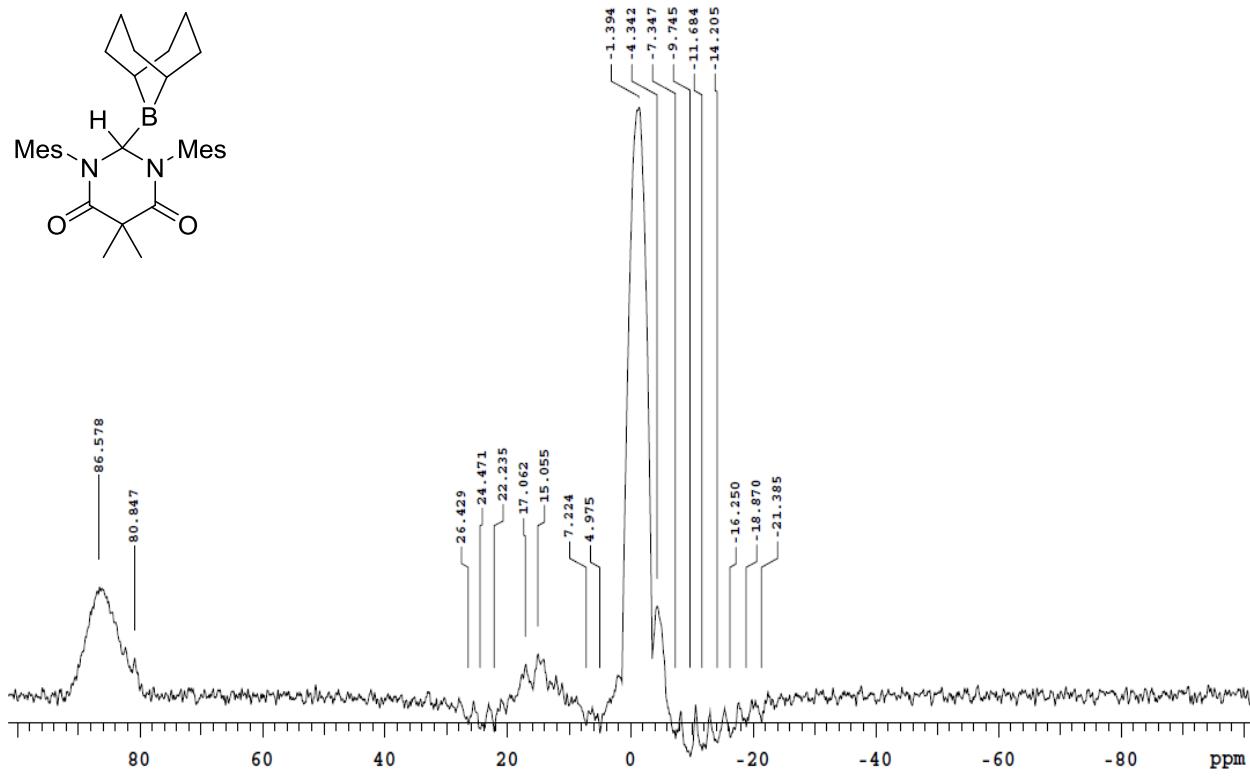


Figure S25. ¹¹B NMR spectrum of 3.

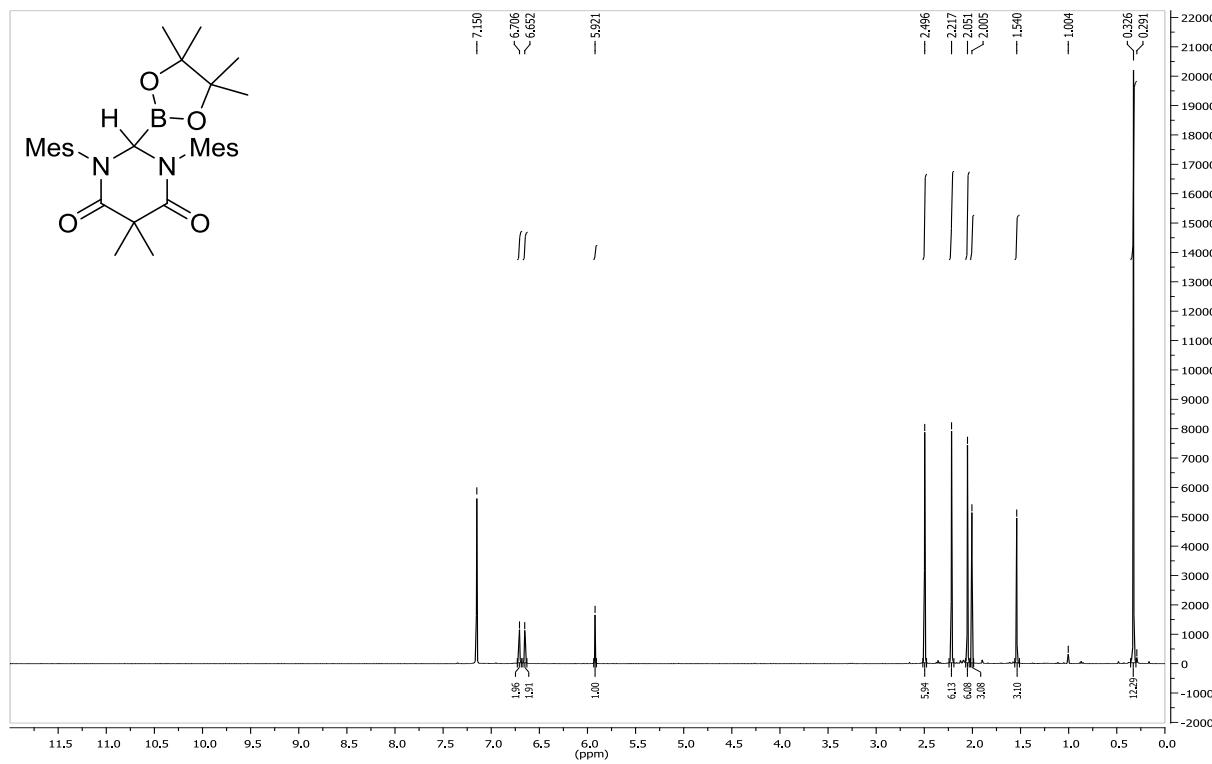


Figure S26. ¹H NMR spectrum of 4.

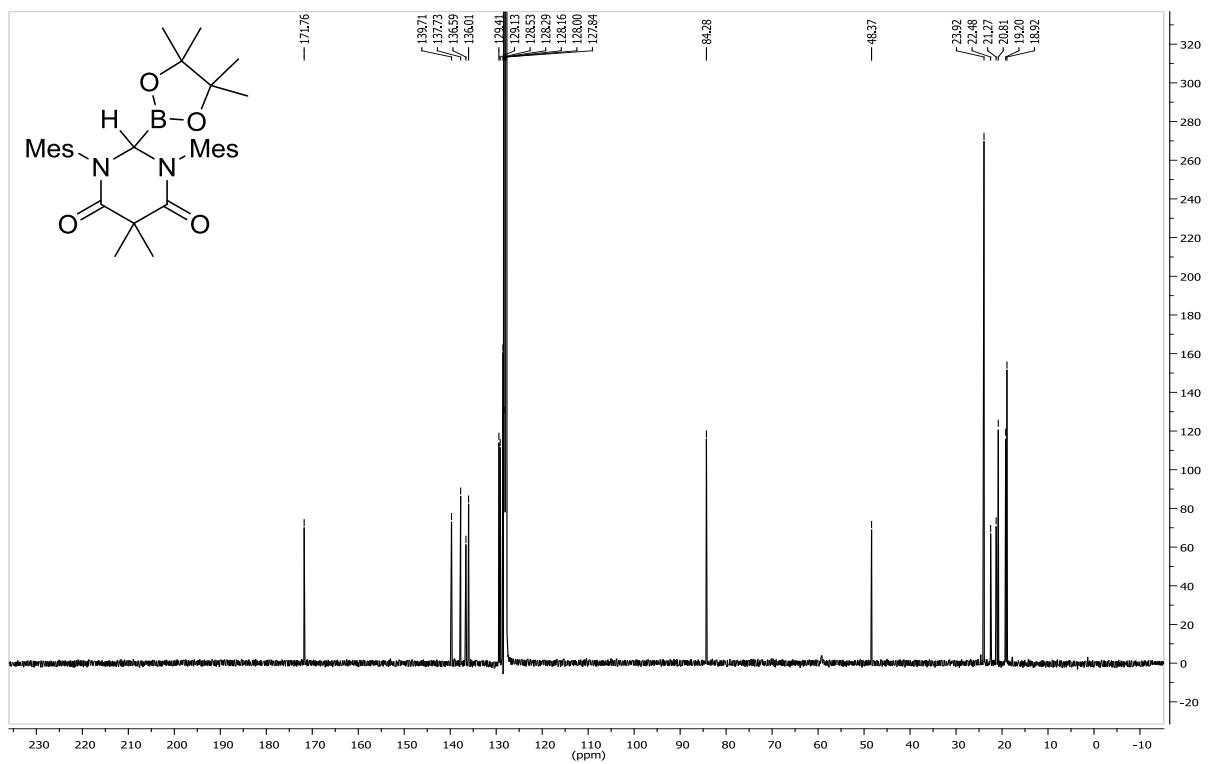


Figure S27. ^{13}C NMR spectrum of 4.

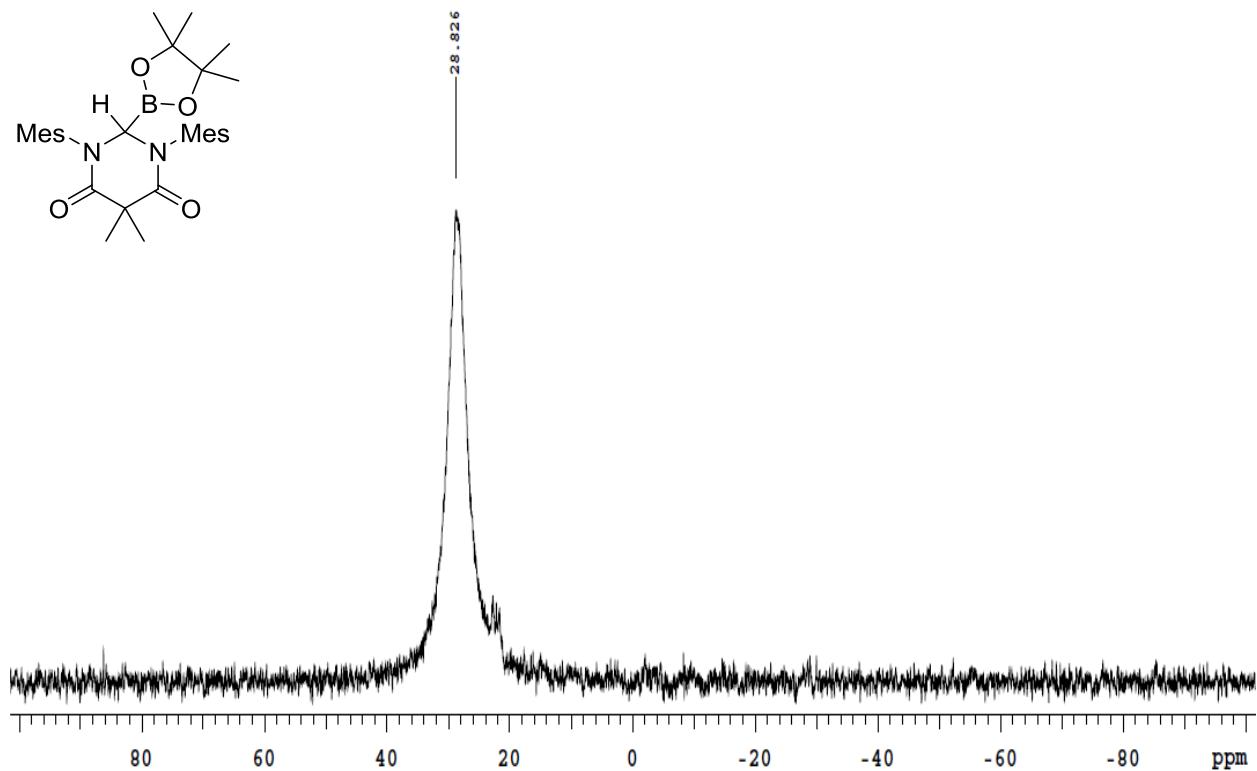


Figure S28. ^{11}B NMR spectrum of 4.

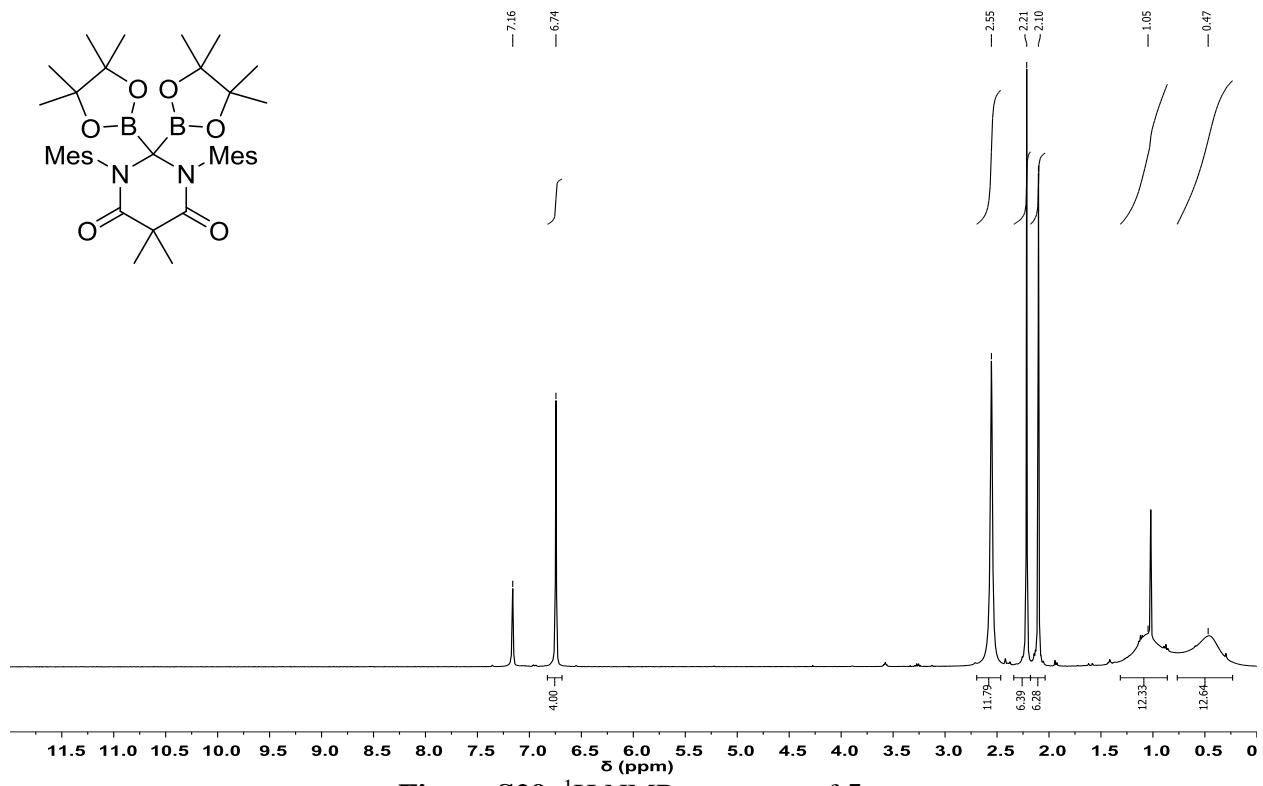


Figure S29. ^1H NMR spectrum of **5**.

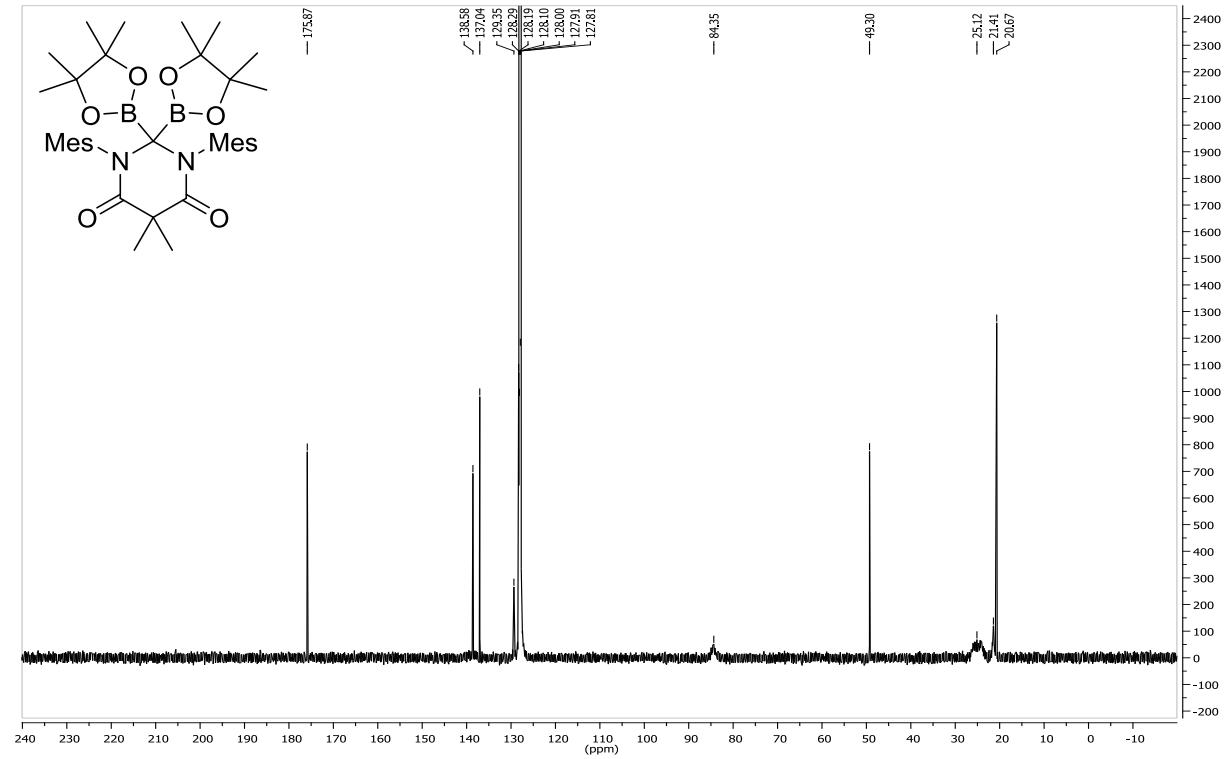


Figure S30. ^{13}C NMR spectrum of **5**.

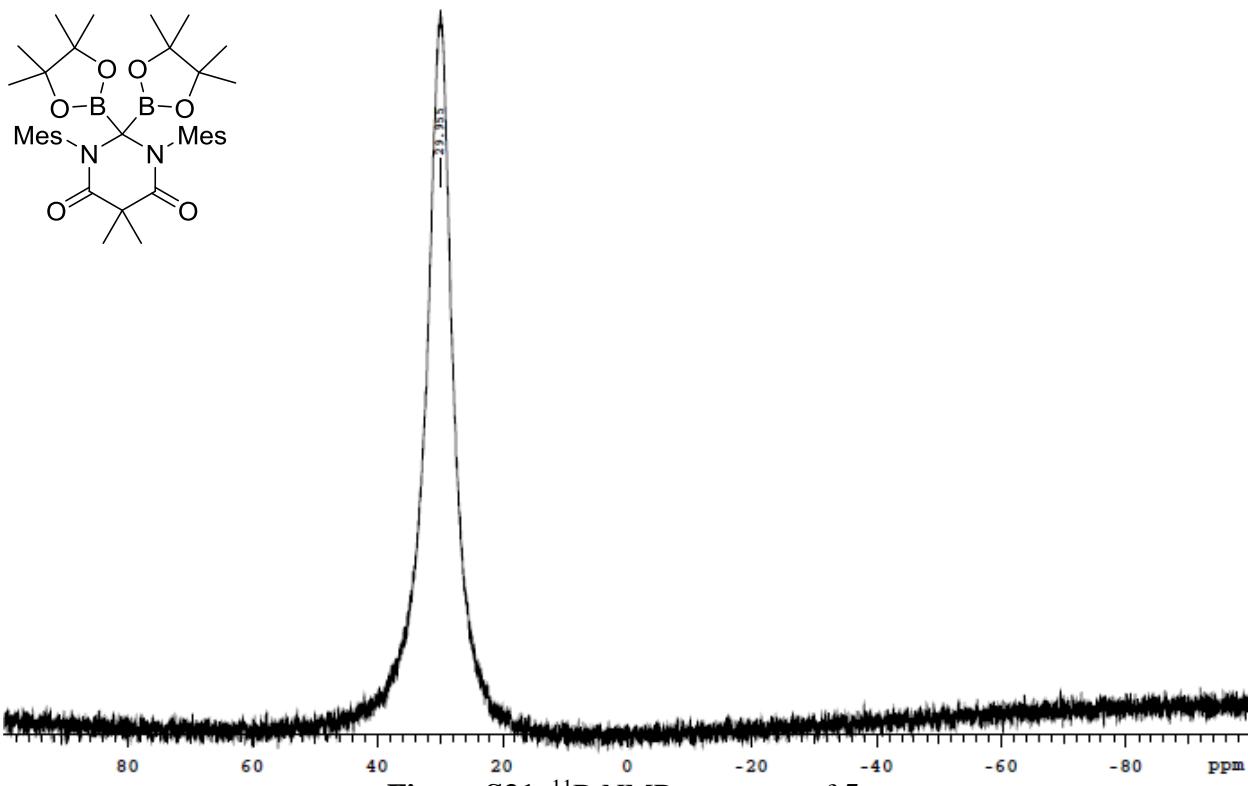


Figure S31. ^{11}B NMR spectrum of **5**.

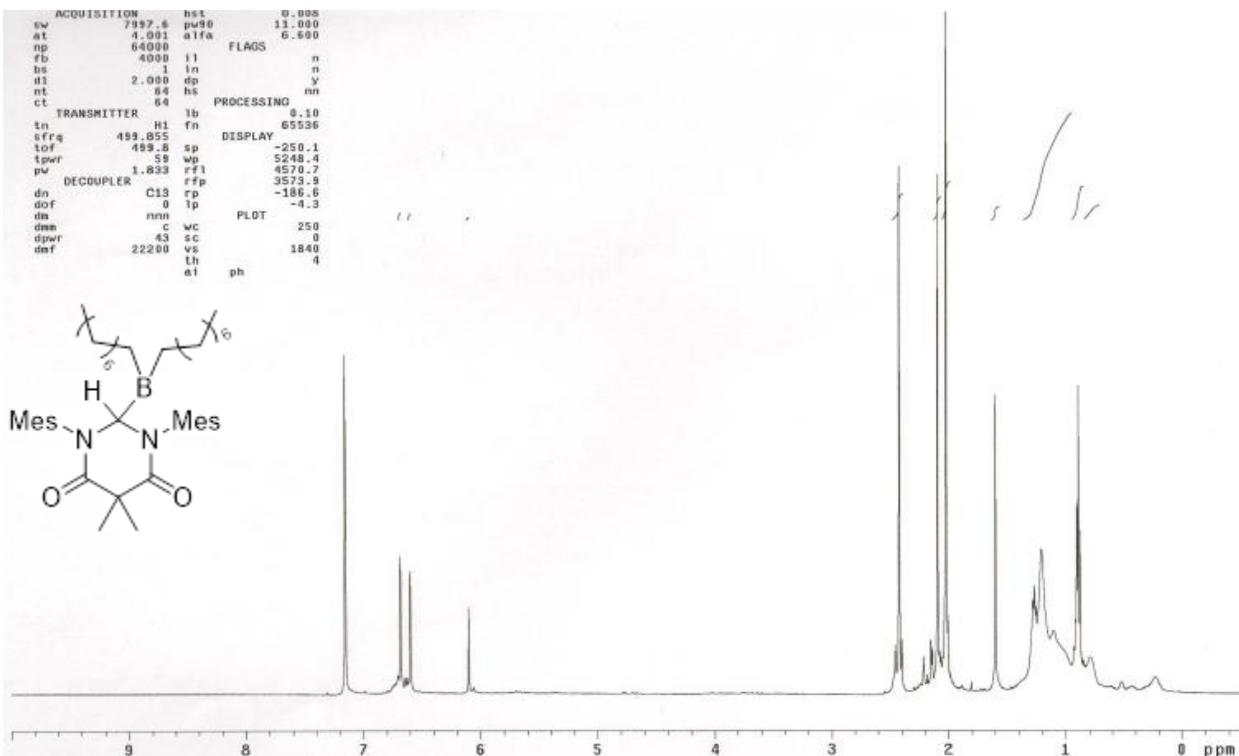


Figure S32. ^1H NMR spectrum of **6**; the integrals recorded in the aliphatic region (0.80–1.28 ppm) were larger than expected.

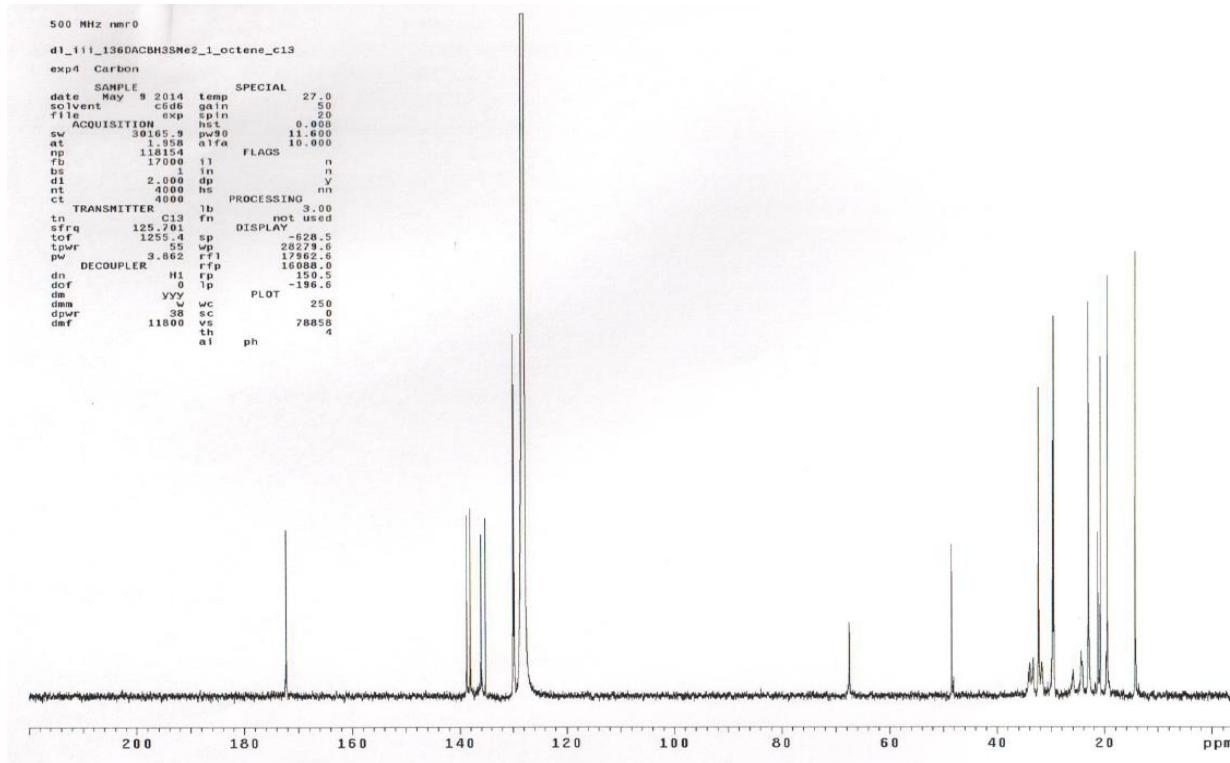


Figure S33. ^{13}C NMR spectrum of **6**.

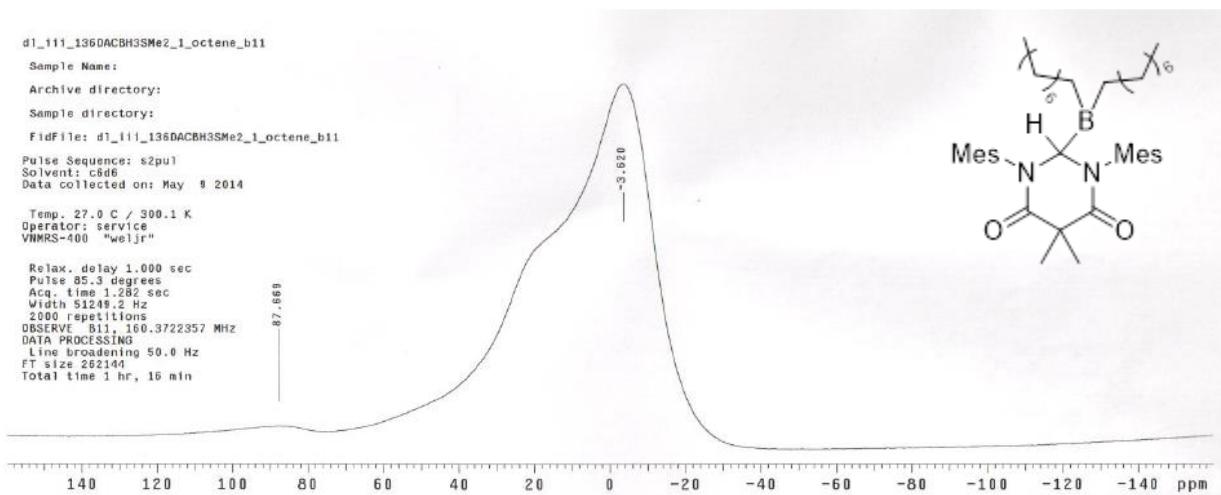


Figure S34. ^{11}B NMR spectrum of **6**.

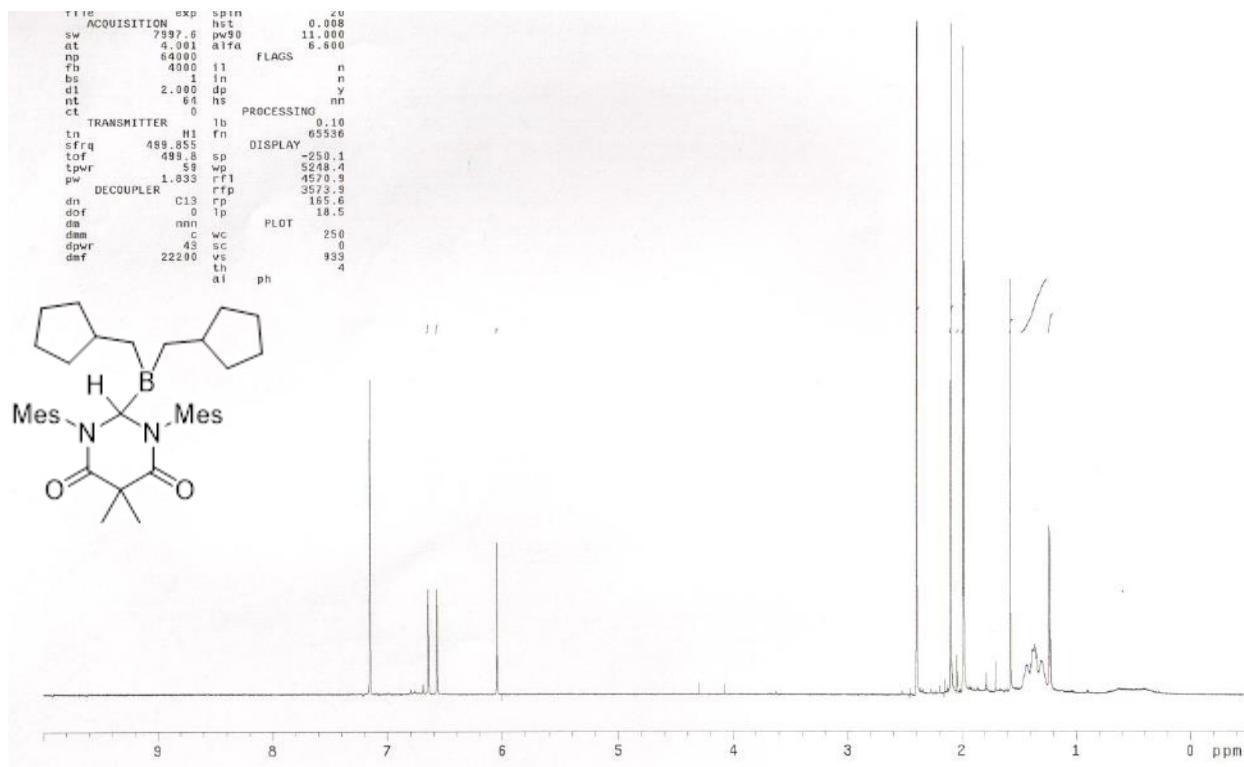


Figure S35. ^1H NMR spectrum of 7.

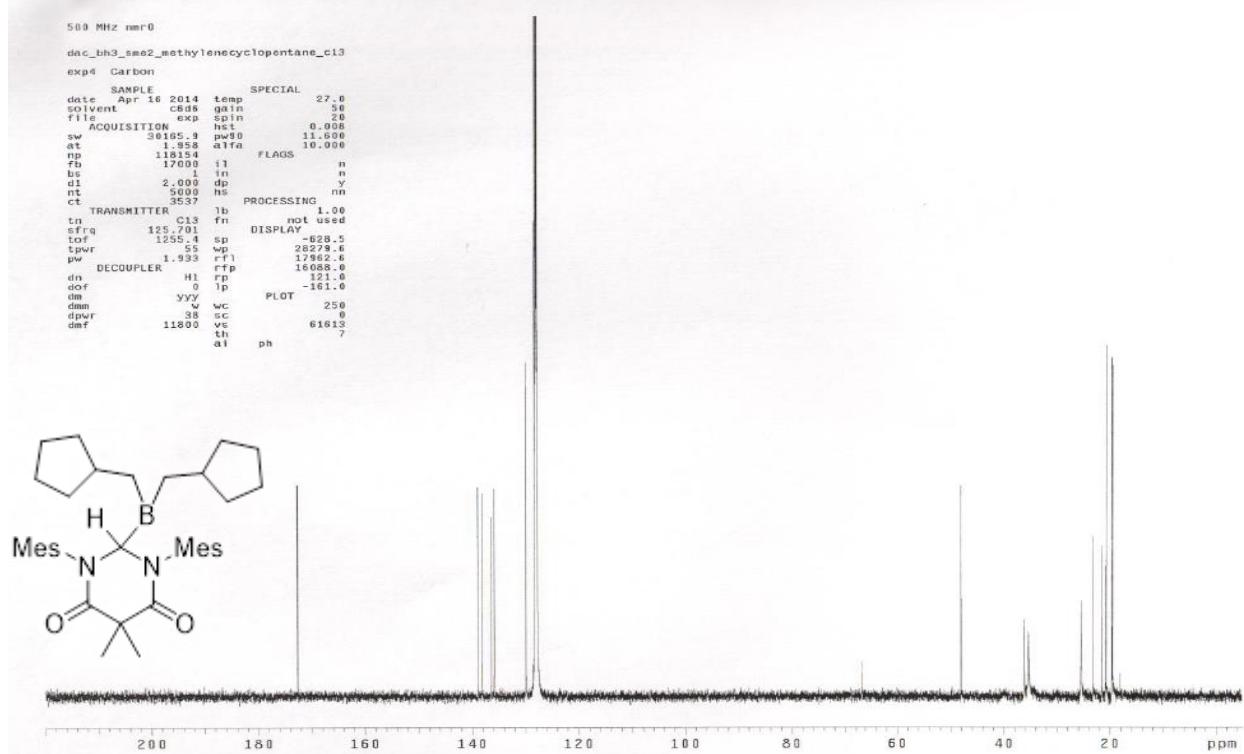


Figure S36. ^{13}C NMR spectrum of 7.

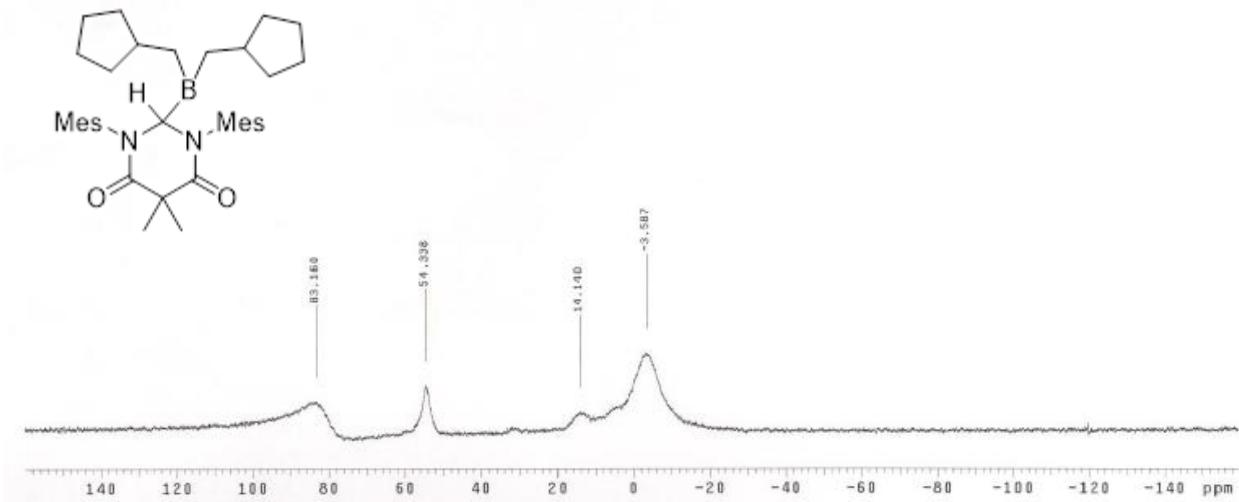


Figure S37. ^{11}B NMR spectrum of 7.

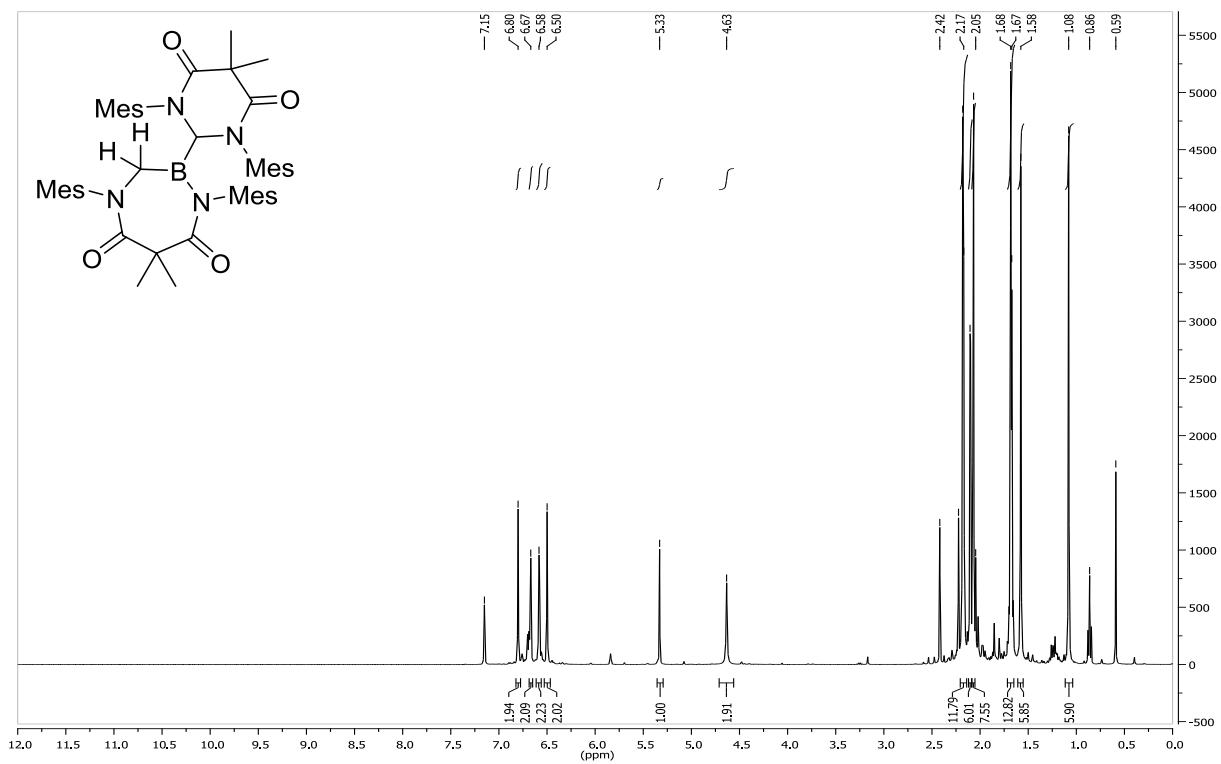


Figure S38. ^1H NMR spectrum of 2DAB-BH₃.

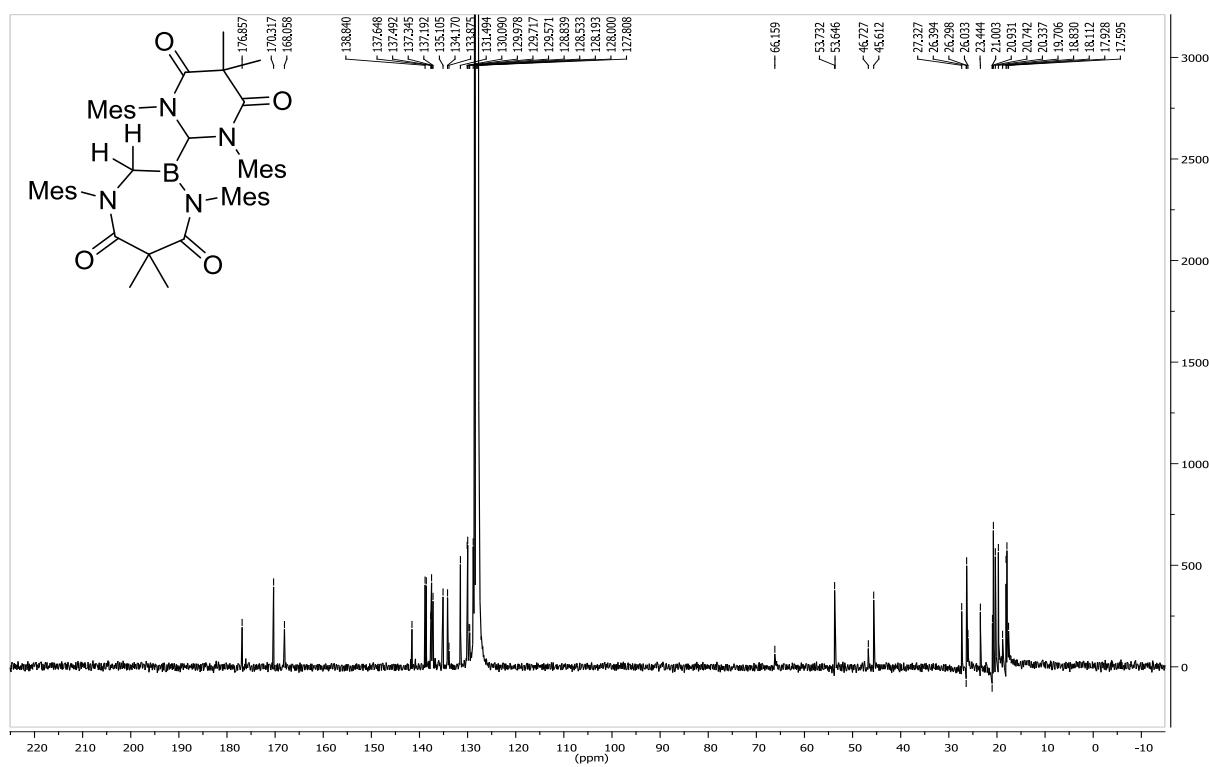


Figure S39. ¹³C NMR spectrum of **2DAC-BH₃**.

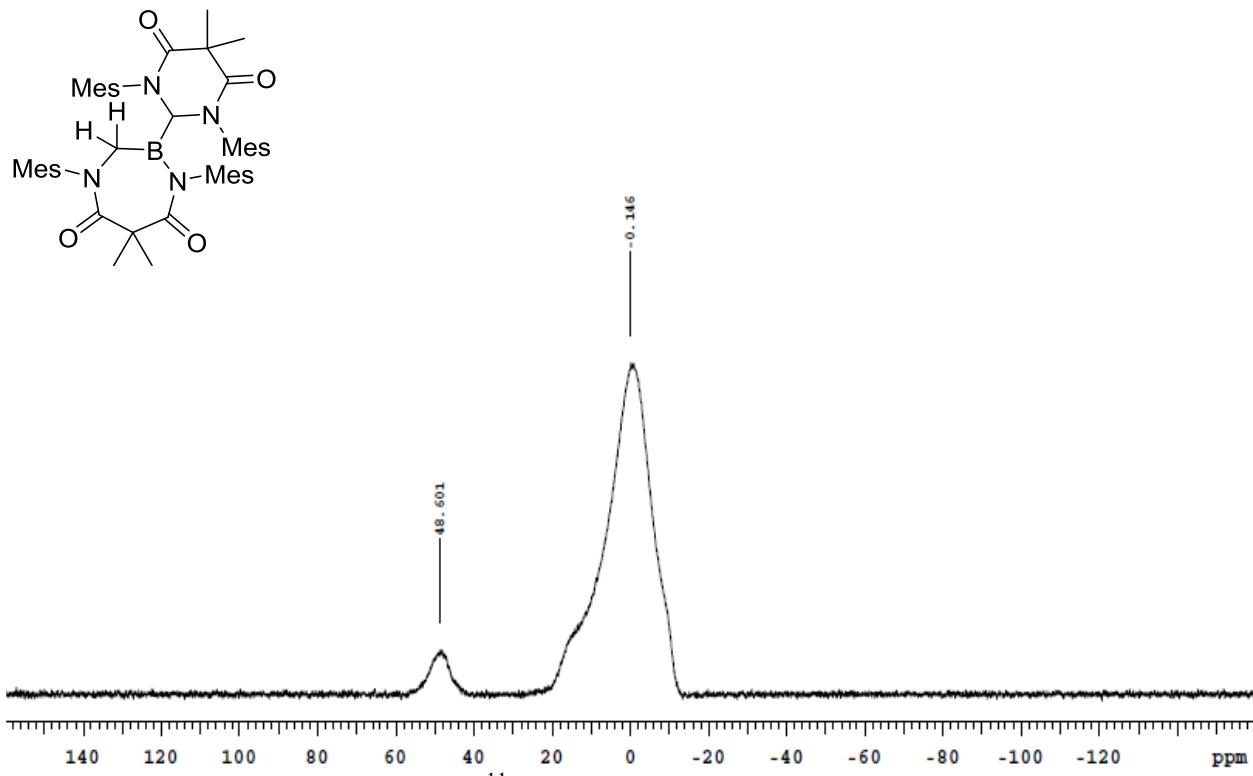


Figure S40. ¹¹B NMR spectrum of **2DAC-BH₃**.

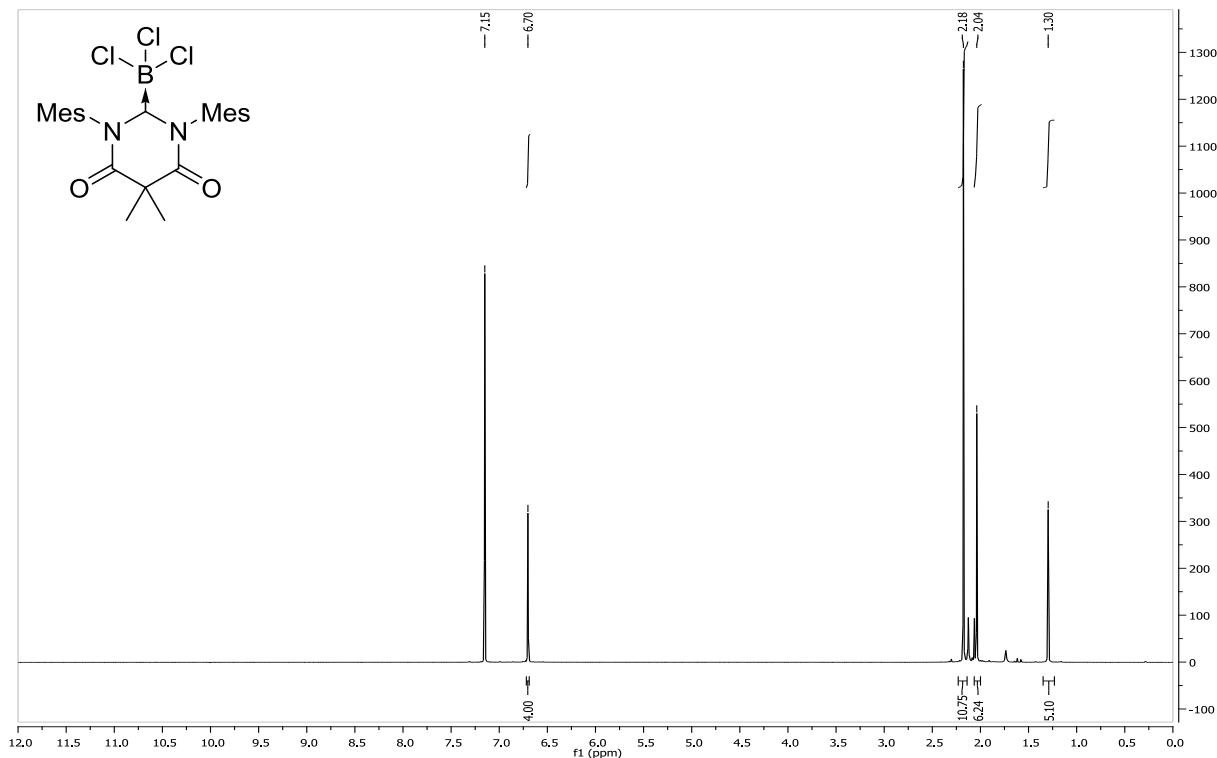


Figure S41. ¹H NMR spectrum of **DAC-BCl₃**.

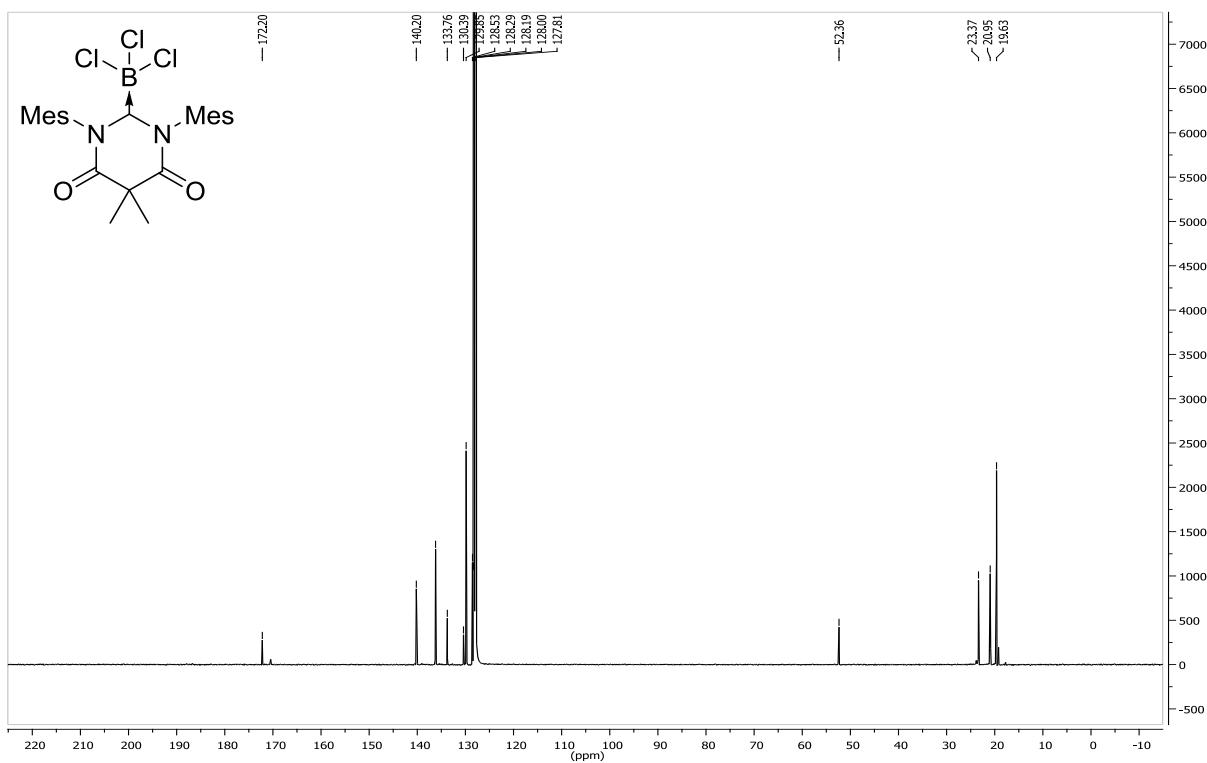


Figure S42. ¹³C NMR spectrum of **DAC-BCl₃**.

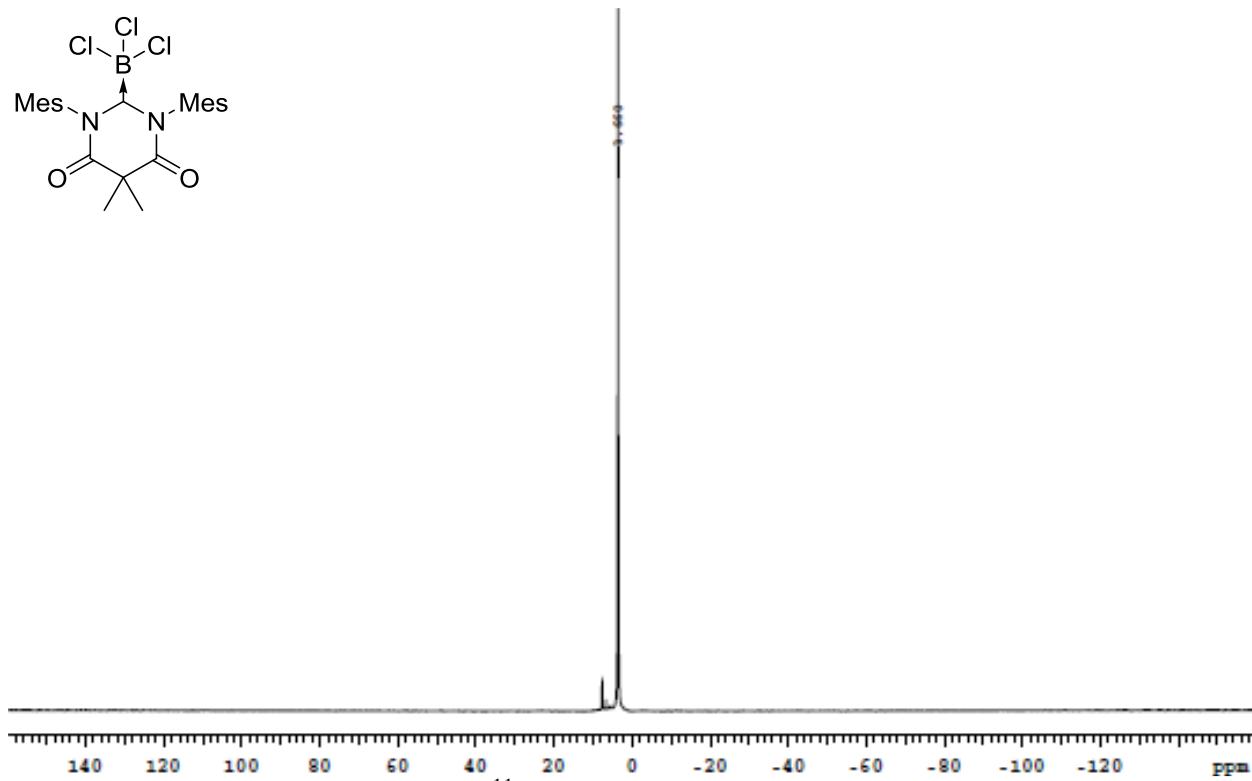


Figure S43. ¹¹B NMR spectrum of **DAC-BCl₃**.

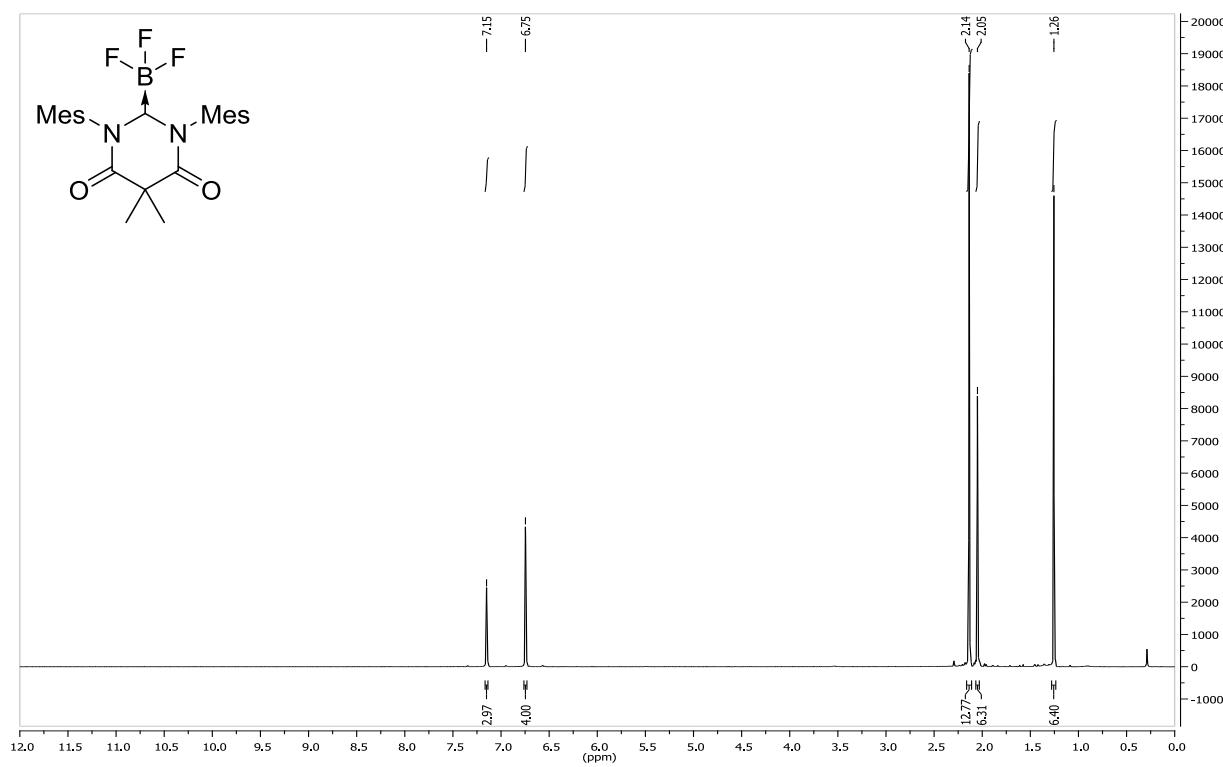


Figure S44. ¹H NMR spectrum of **DAC-BF₃**.

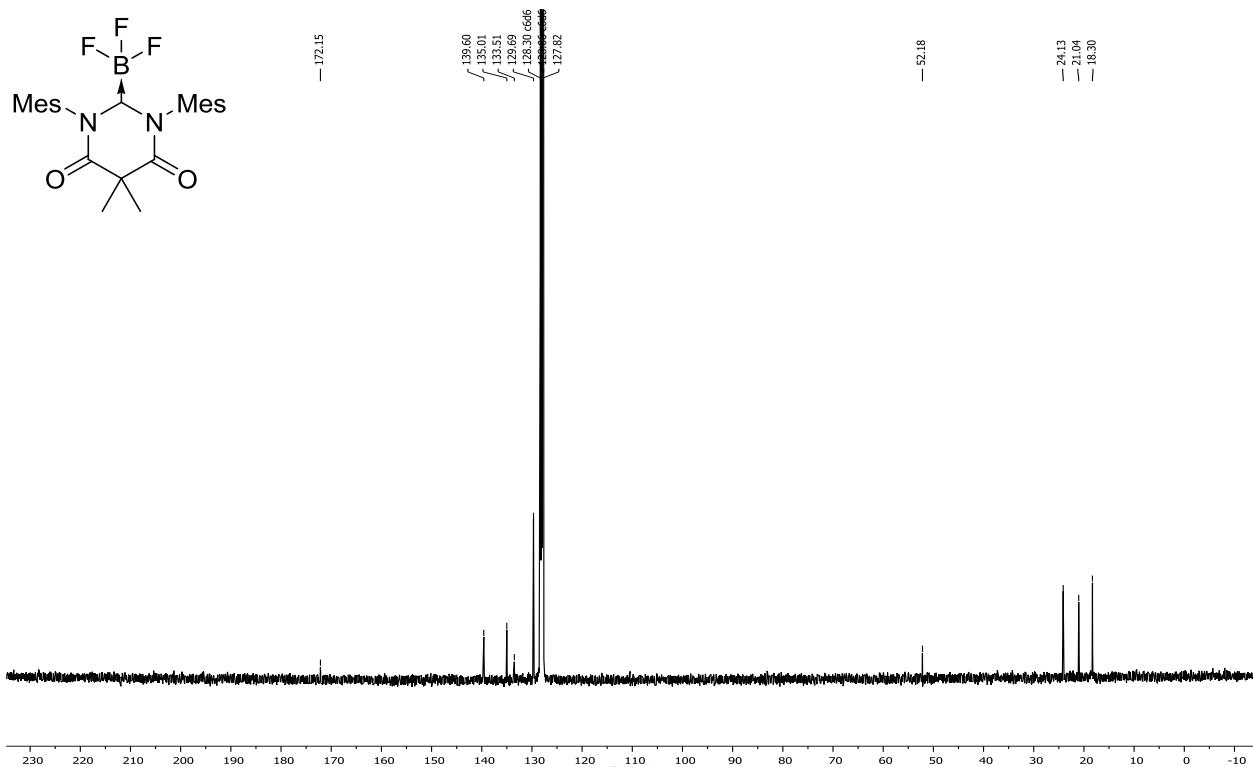


Figure S45. ¹³C NMR spectrum of **DAC-BF₃**.

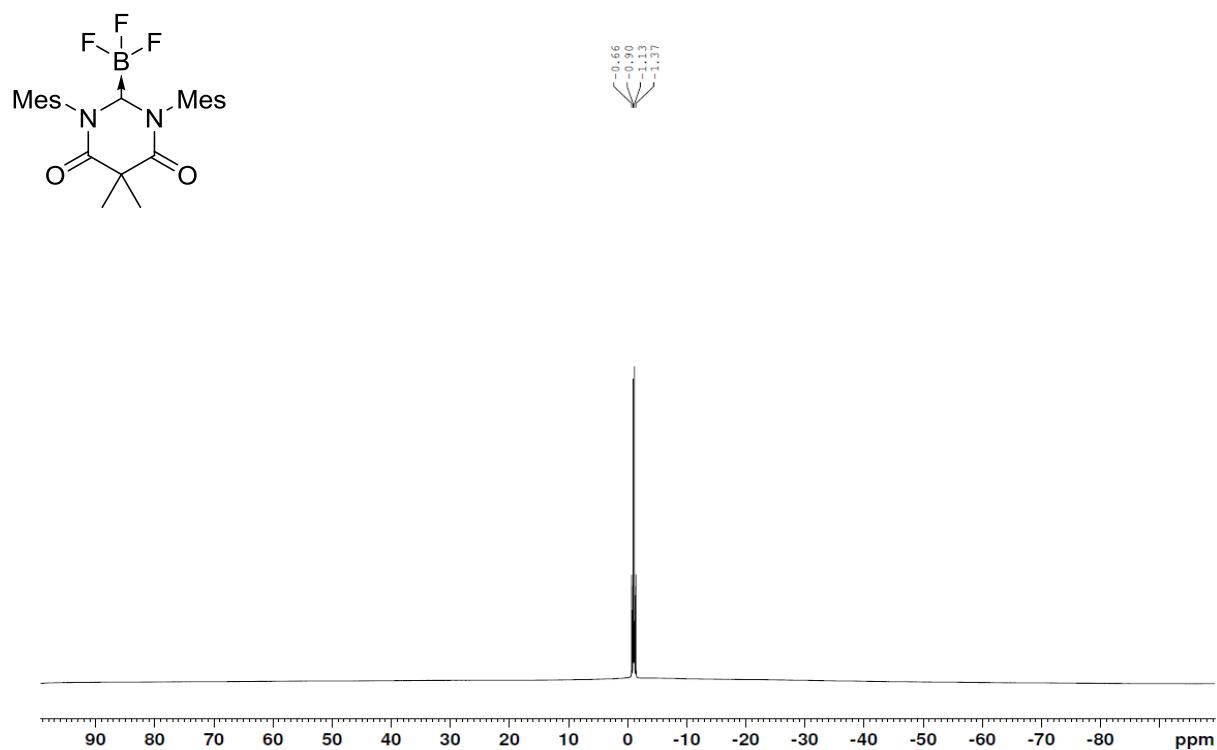


Figure S46. ¹¹B NMR spectrum of **DAC-BF₃**.

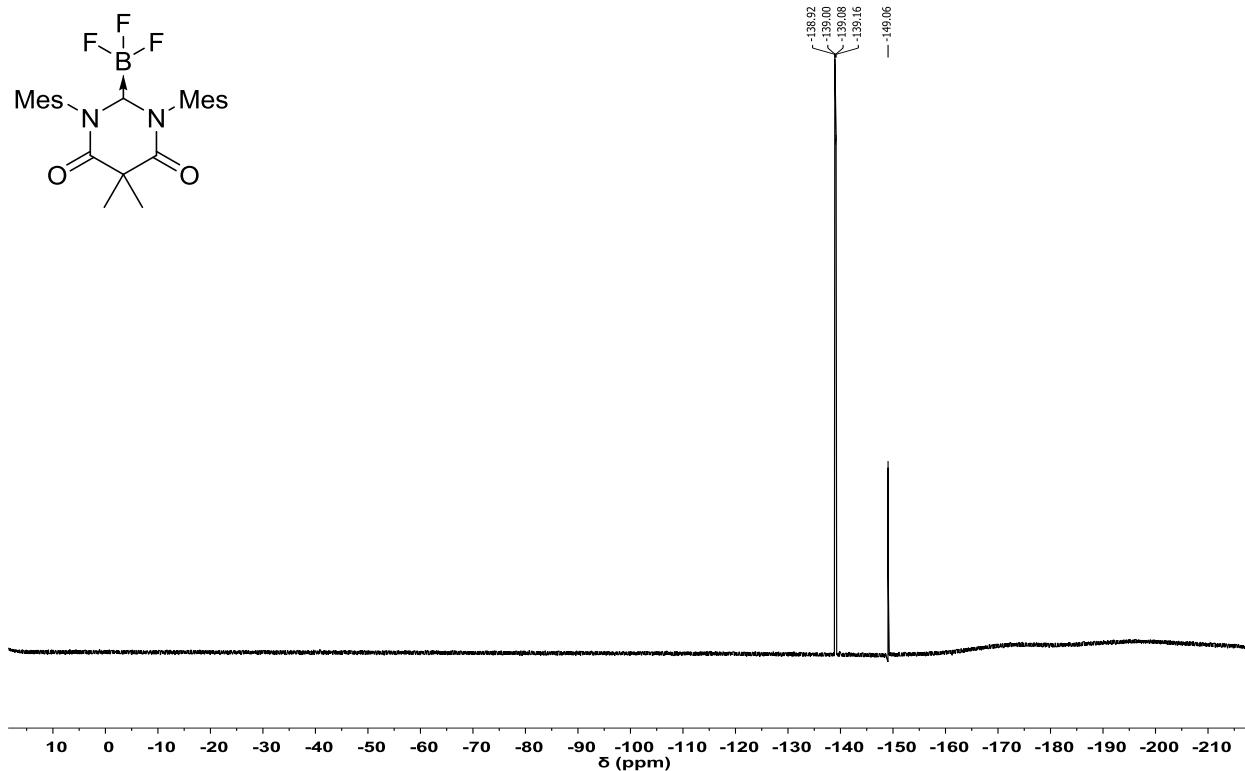


Figure S47. ¹⁹F NMR spectrum of DAC-BF₃.

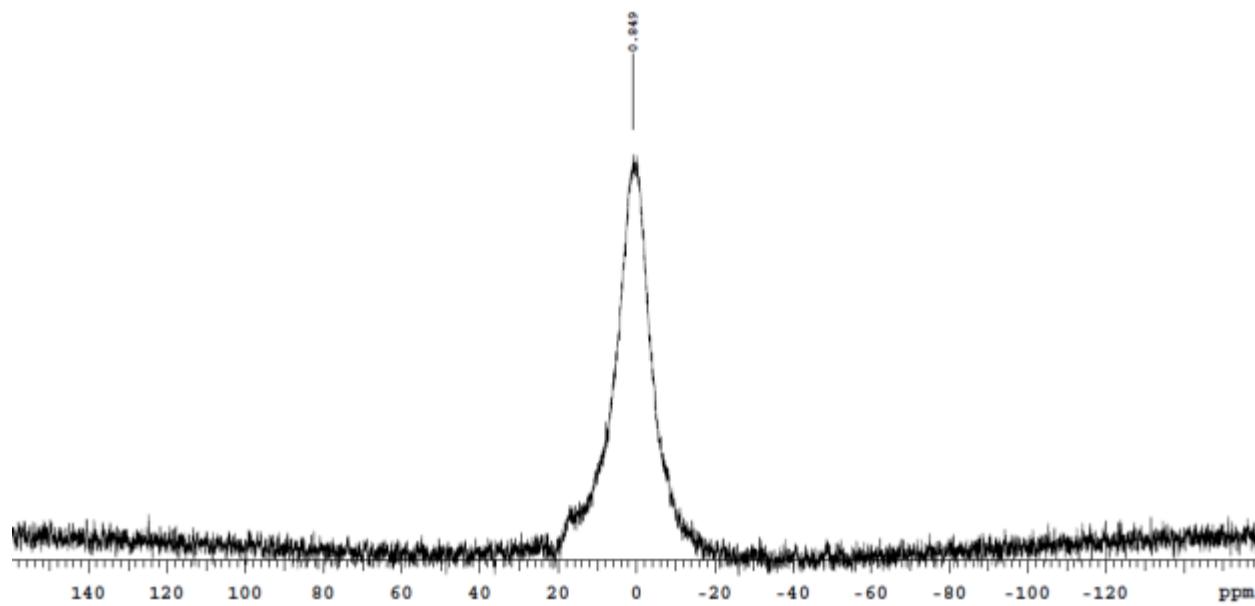


Figure S48. ¹¹B NMR spectrum of C₆D₆ as a reference.