

Supporting Information

A Window into the Workings of Anti-B₁₈H₂₂ Luminescence. Blue-Fluorescent Isomeric Pair 3,3'-Cl₂-B₁₈H₂₀ and 3,4'-Cl₂-B₁₈H₂₀ (and Others)

Marcel Ehn,^a Dmytro Bavol,^a Jonathan Bould,^a Vojtěch Strnad,^{a,b} Miroslava Litecká,^a Kamil Lang,^a Kaplan Kirakci,^a William Clegg,^c Paul G. Waddell,^c and Michael G. S. Londesborough.^{a,*}

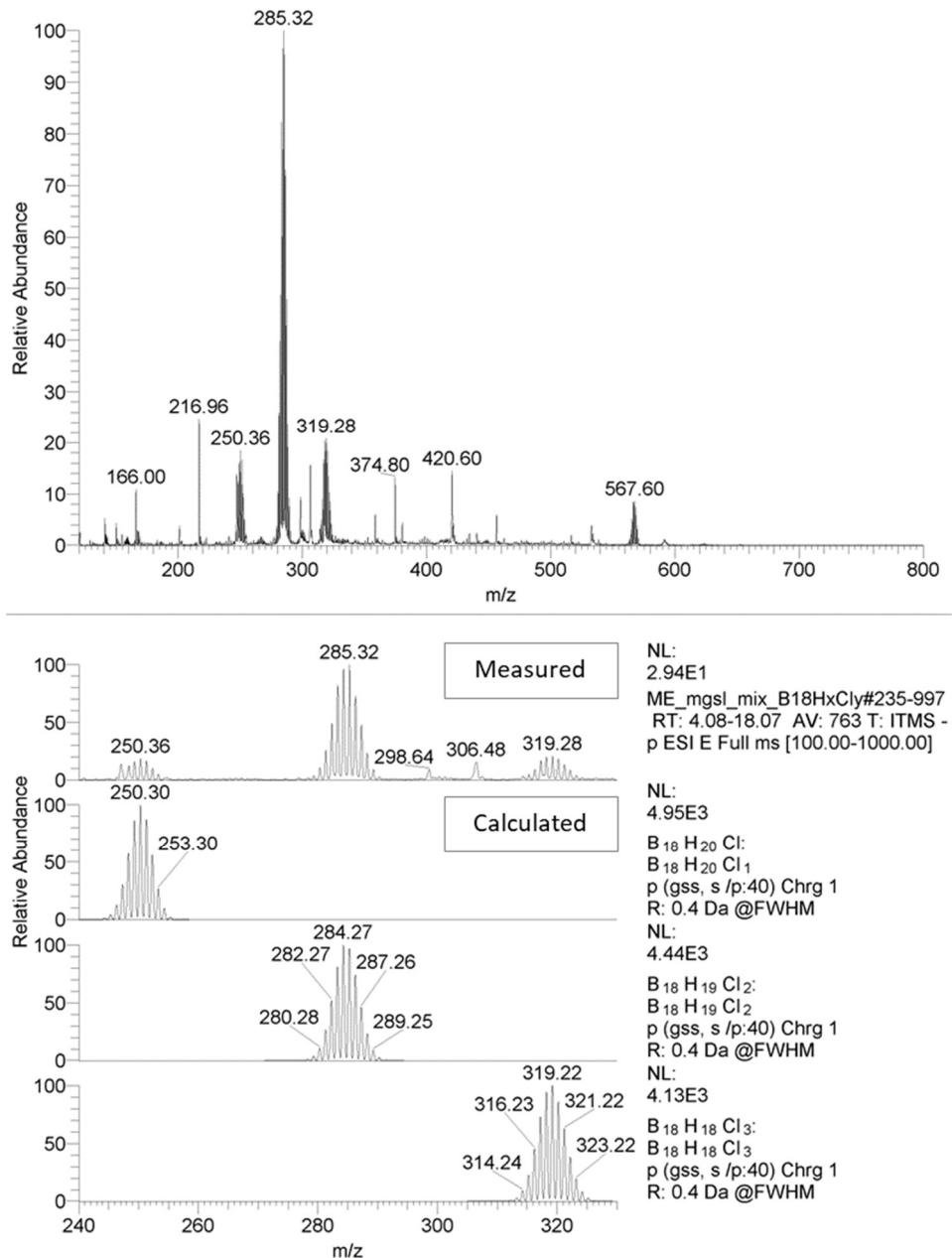


Figure S1. Mass spectrum for the reaction mixture after 5 days stirring at room temperature.

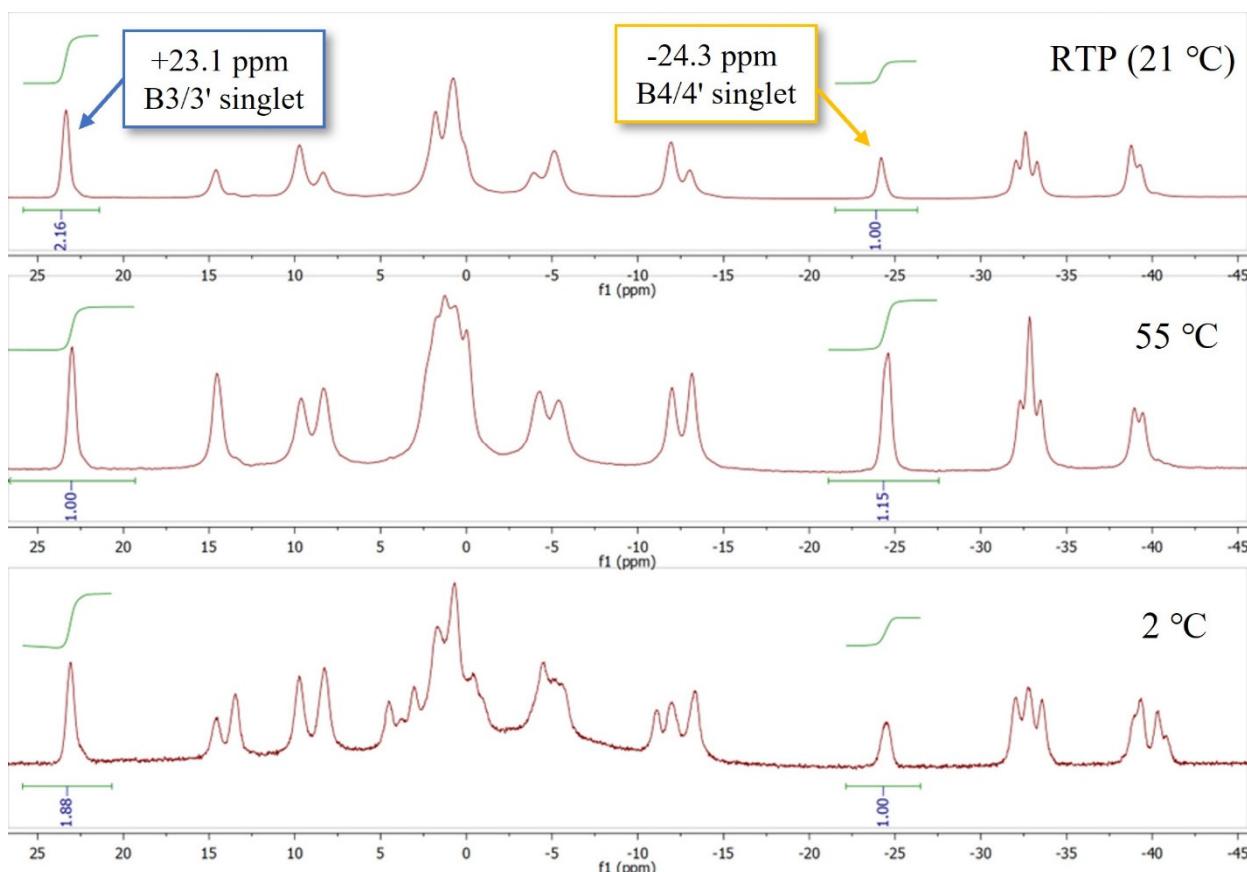


Figure S2. $^{11}\text{B}-\{\text{H}\}$ NMR spectra for the reaction mixture after (i) 5 days stirring at room temperature (21°C), (ii) 90 mins at 55°C , and (iii) 30 days at 2°C . The spectra show the effect of temperature on the relative propensity for chlorination of **1** at the B3/3' and/or B4/4' positions, and also how low-temperature reaction results in significant amounts of 3-Cl- $\text{B}_{18}\text{H}_{21}$ (compound **7**) whilst RTP and higher temperature reactions form primarily 3,3'-Cl₂- $\text{B}_{18}\text{H}_{20}$ (compound **2**) and 3,4'-Cl₂- $\text{B}_{18}\text{H}_{20}$ (compound **3**).

Table S1. Interatomic distances (Å) for 3,3'-Cl₂- $\text{B}_{18}\text{H}_{20}$ (compound **2**).

B1–H1	1.038(16)	B1–B2	1.8030(18)
B1–B3	1.7742(18)	B1–B4	1.8246(19)
B1–B5	1.7520(18)	B1–B10	1.7737(19)
B2–H2	1.072(15)	B2–B3	1.7888(18)
B2–B5	1.8133(18)	B2–B5a	1.7364(18)
B2–B7	1.7798(18)	B3–Cl3	1.7918(13)
B3–B4	1.8009(19)	B3–B7	1.7435(18)
B3–B8	1.7599(19)	B4–H4	1.125(16)
B4–B8	1.7776(19)	B4–B9	1.7082(19)
B4–B10	1.7785(19)	B5–B5a	1.784(3)
B5–B7a	1.8195(18)	B5–B10	2.0279(19)

B5–H57'	1.308(17)	B7–H7	1.047(16)
B7–B8	2.0017(19)	B8–H8	1.073(16)
B8–B9	1.803(2)	B8–H89	1.256(16)
B9–H9	1.089(17)	B9–B10	1.779(2)
B9–H89	1.251(16)	B9–H910	1.273(17)
B10–H10	1.053(16)	B10–H910	1.256(17)
B11–H11	1.047(15)	B11–B12	1.7877(18)
B11–B13	1.8142(18)	B11–B14	1.8135(19)
B11–B15	1.7554(18)	B11–B20	1.7538(19)
B12–H12	1.060(15)	B12–B13	1.7815(18)
B12–B15	1.8317(19)	B12–B15b	1.7422(18)
B12–B17	1.7814(18)	B13–Cl13	1.8211(13)
B13–B14	1.7846(19)	B13–B17	1.7367(18)
B13–B18	1.7418(19)	B14–H14	1.058(17)
B14–B18	1.7867(19)	B14–B19	1.706(2)
B14–B20	1.813(2)	B15–B15b	1.800(3)
B15–B17b	1.8439(19)	B15–B20	1.9785(19)
B15–H157	1.302(17)	B17–H17	1.051(16)
B17–B18	1.969(2)	B18–H18	1.073(17)
B18–B19	1.824(2)	B18–H189	1.260(19)
B19–H19	1.043(17)	B19–B20	1.783(2)
B19–H189	1.269(18)	B19–H192	1.284(18)
B20–H20	1.068(16)	B20–H192	1.227(18)

Symmetry operations for equivalent atoms

a $-x, -y+1, -z$ b $-x+1, -y+1, -z+1$

Table S2. Interatomic distances (\AA) for 3,4'-Cl₂-B₁₈H₂₀ (compound 3).

B1–H1	1.03(4)	B1–B2	1.803(5)
B1–B3	1.788(5)	B1–B4	1.804(5)
B1–B5	1.746(5)	B1–B10	1.749(5)
B2–H2	1.01(4)	B2–B3	1.768(5)
B2–B5	1.797(4)	B2–B6	1.754(5)
B2–B7	1.804(5)	B3–Cl13	1.805(4)
B3–B4	1.785(5)	B3–B7	1.760(6)
B3–B8	1.767(5)	B4–H4	1.182(12)
B4–B8	1.797(6)	B4–B9	1.724(7)
B4–B10	1.770(6)	B5–B6	1.805(5)
B5–B10	1.978(4)	B5–B2'	1.774(5)
B5–B7'	1.810(5)	B5–H57'	1.29(3)
B6–B7	1.817(5)	B6–H67	1.43(4)

B6–B1'	1.756(5)	B6–B2'	1.803(4)
B6–B10'	1.987(4)	B7–H7	1.13(4)
B7–B8	1.964(5)	B7–H67	1.27(4)
B8–H8	1.14(5)	B8–B9	1.783(6)
B8–H89	1.16(5)	B9–H9	1.07(4)
B9–B10	1.776(6)	B9–H89	1.22(4)
B9–H910	1.16(4)	B10–H10	1.18(4)
B10–H910	1.24(5)	B1'–H1'	1.08(4)
B1'–B2'	1.775(5)	B1'–B3'	1.790(5)
B1'–B4'	1.797(5)	B1'–B10'	1.755(5)
B2'–H2'	1.13(4)	B2'–B3'	1.747(4)
B2'–B7'	1.800(5)	B3'–H3'	1.18(4)
B3'–B4'	1.774(5)	B3'–B7'	1.752(5)
B3'–B8'	1.752(4)	B4'–Cl4'	1.804(4)
B4'–B8'	1.795(5)	B4'–B9'	1.715(5)
B4'–B10'	1.786(5)	B7'–H7'	1.17(4)
B7'–B8'	1.945(5)	B7'–H57'	1.22(4)
B8'–H8'	1.08(4)	B8'–B9'	1.787(5)
B8'–H89'	1.17(4)	B9'–H9'	1.02(4)
B9'–B10'	1.786(6)	B9'–H89'	1.21(4)
B9'–H91'	1.29(3)	B10'–H10'	1.06(5)
B10'–H91'	1.24(4)		

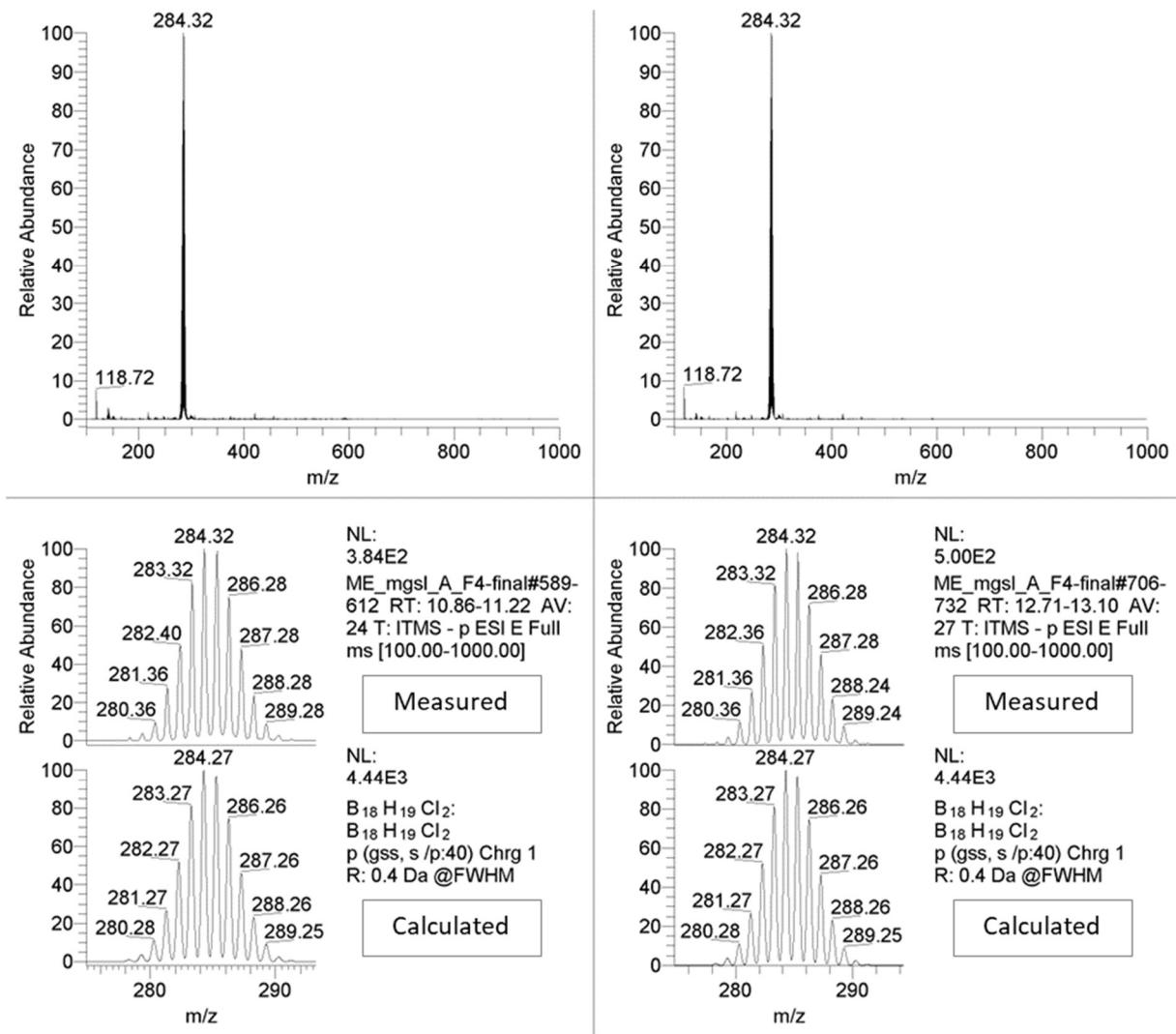


Figure S3. Mass spectra of 3,3'-Cl₂-B₁₈H₂₀ - left (compound 2) and 3,4'-Cl₂-B₁₈H₂₀ - right (compound 3).

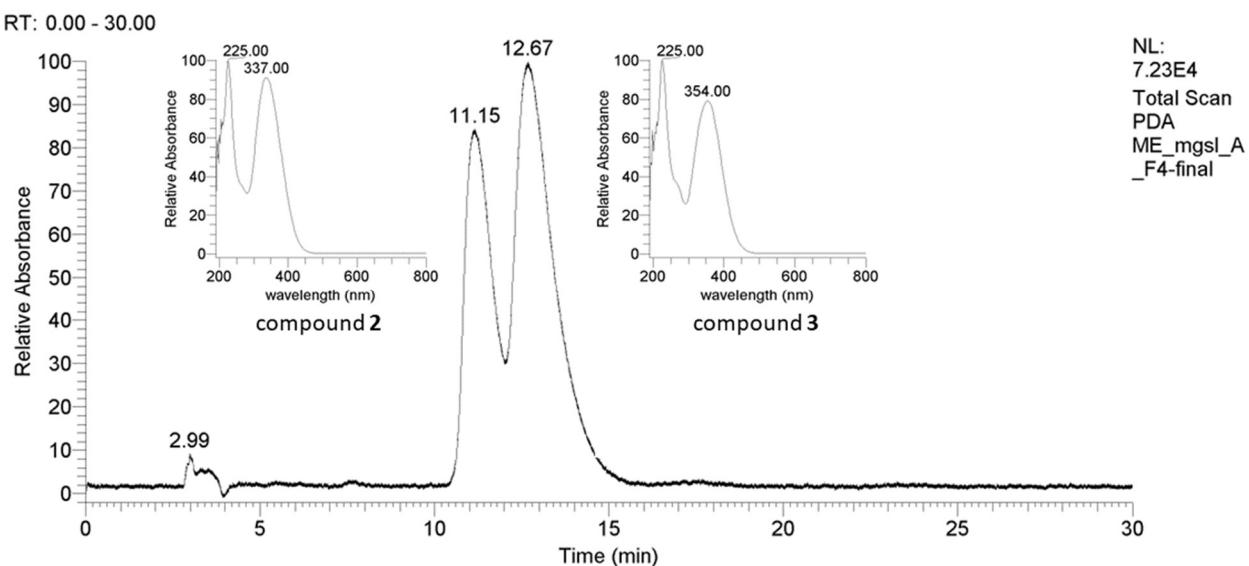


Figure S4. HPLC chromatogram of separation of 3,3'-Cl₂-B₁₈H₂₀; $t_R = 11.15$ min (compound **2**) and

$3,4'$ -Cl₂-B₁₈H₂₀; $t_R = 12.67$ min (compound 3); and their absorption spectra.

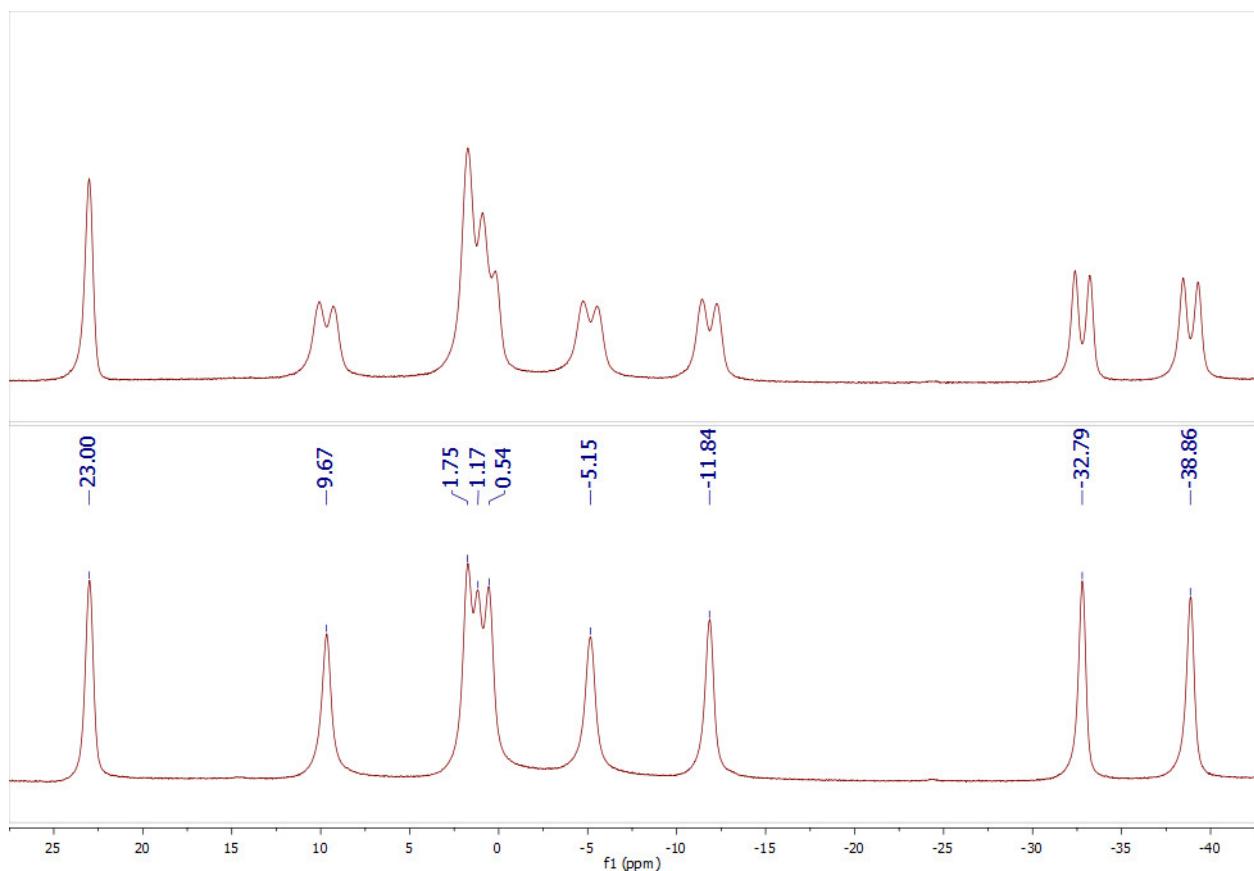


Figure S5. ^{11}B and $^{11}\text{B}-\{\text{H}\}$ NMR spectra for $3,3'$ -Cl₂-B₁₈H₂₀ (compound 2).

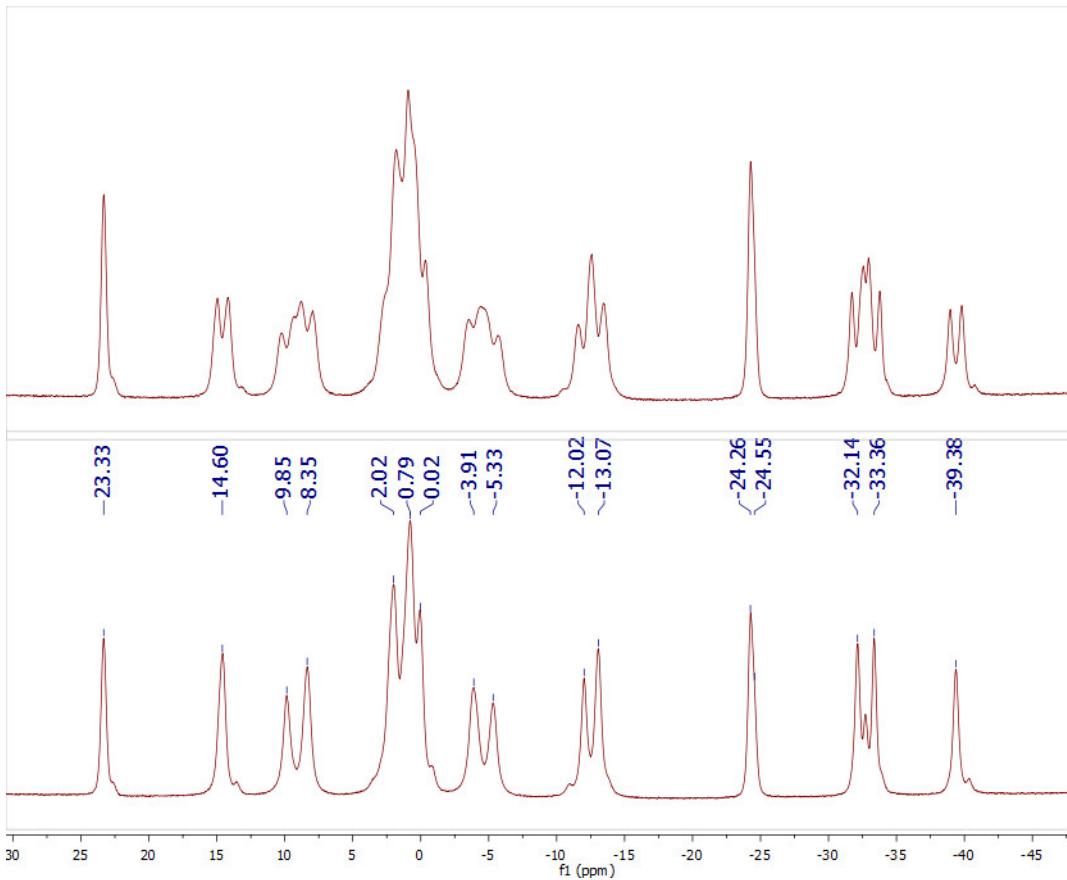


Figure S6. ^{11}B and $^{11}\text{B}-\{\text{H}\}$ NMR spectra for 3,4'-Cl₂-B₁₈H₂₀ (compound **3**). These spectra contain 3,3'-Cl₂-B₁₈H₂₀ (compound **2**) impurities.

Table S3. Interatomic distances (\AA) for 4,4'-Cl₂-B₁₈H₂₀ (compound **4**).

B1–H1	1.100(10)	B1–B2	1.783(18)
B1–B3	1.823(17)	B1–B4	1.789(16)
B1–B5	1.761(16)	B1–B10	1.748(17)
B2–H2	1.100(10)	B2–B3	1.736(16)
B2–B5	1.833(19)	B2–B5a	1.786(17)
B2–B7	1.806(17)	B3–H3	1.099(10)
B3–B4	1.795(18)	B3–B7	1.755(17)
B3–B8	1.777(16)	B4–Cl4	1.808(11)
B4–B8	1.801(17)	B4–B9	1.719(17)
B4–B10	1.778(17)	B5–B5a	1.85(3)
B5–B7a	1.806(17)	B5–B10	1.979(17)
B5–H57	1.32(4)	B7–H7	1.100(10)
B7–B8	1.989(18)	B8–H8	1.099(10)
B8–B9	1.789(19)	B8–H89	1.32(4)
B9–H9	1.100(10)	B9–B10	1.771(16)
B9–H89	1.32(4)	B9–H91	1.32(4)

B10–H10	1.100(10)	B10–H91	1.32(4)
B11–H11	1.100(10)	B11–B12	1.806(18)
B11–B13	1.782(19)	B11–B14	1.785(17)
B11–B15	1.792(16)	B11–B20	1.766(18)
B12–H12	1.099(10)	B12–B13	1.768(16)
B12–B15	1.813(18)	B12–B15b	1.748(16)
B12–B17	1.784(17)	B13–H13	1.099(10)
B13–B14	1.776(18)	B13–B17	1.755(17)
B13–B18	1.755(17)	B14–Cl14	1.800(12)
B14–B18	1.821(19)	B14–B19	1.722(17)
B14–B20	1.774(18)	B15–B15b	1.83(2)
B15–B17b	1.798(16)	B15–B20	1.991(17)
B15–H157	1.32(4)	B17–H17	1.099(10)
B17–B18	1.974(17)	B18–H18	1.100(10)
B18–B19	1.802(19)	B18–H189	1.32(4)
B19–H19	1.100(10)	B19–B20	1.783(18)
B19–H189	1.32(4)	B19–H191	1.32(4)
B20–H20	1.100(10)	B20–H191	1.32(4)
B21–H21	1.100(10)	B21–B22	1.805(19)
B21–B23	1.826(18)	B21–B24	1.782(17)
B21–B25	1.737(17)	B21–B30	1.737(18)
B22–H22	1.101(10)	B22–B23	1.762(18)
B22–B25	1.803(19)	B22–B25c	1.789(17)
B22–B27	1.819(17)	B23–H23	1.100(10)
B23–B24	1.77(2)	B23–B27	1.783(18)
B23–B28	1.748(17)	B24–Cl24	1.820(13)
B24–B28	1.803(18)	B24–B29	1.738(18)
B24–B30	1.783(19)	B25–B25c	1.80(3)
B25–B27c	1.830(18)	B25–B30	1.992(19)
B25–H257	1.32(4)	B27–H27	1.100(10)
B27–B28	1.961(19)	B28–H28	1.100(10)
B28–B29	1.80(2)	B28–H289	1.32(4)
B29–H29	1.100(10)	B29–B30	1.806(17)
B29–H289	1.32(4)	B29–H291	1.32(4)
B30–H30	1.100(10)	B30–H291	1.32(4)
B31–H31	1.099(10)	B31–B32	1.797(18)
B31–B33	1.790(18)	B31–B34	1.800(17)
B31–B35	1.776(16)	B31–B40	1.763(18)
B32–H32	1.099(10)	B32–B33	1.769(16)
B32–B35	1.808(18)	B32–B35d	1.766(16)
B32–B37	1.805(17)	B33–H33	1.099(10)
B33–B34	1.78(2)	B33–B37	1.765(17)
B33–B38	1.734(17)	B34–Cl34	1.788(12)

B34–B38	1.78(2)	B34–B39	1.699(17)
B34–B40	1.783(19)	B35–B35d	1.79(2)
B35–B37d	1.819(17)	B35–B40	1.994(17)
B35–H357	1.32(4)	B37–H37	1.100(11)
B37–B38	1.966(19)	B38–H38	1.100(10)
B38–B39	1.78(2)	B38–H389	1.32(4)
B39–H39	1.100(10)	B39–B40	1.772(18)
B39–H389	1.32(4)	B39–H391	1.32(4)
B40–H40	1.101(10)	B40–H391	1.32(4)

Symmetry operations for equivalent atoms

a $-x+2, -y+2, -z+1$ b $-x+1, -y, -z$ c $-x+1, -y+1, -z+1$ d $-x+2, -y+1, -z+2$

Table S4. Interatomic distances (\AA) for 3,1'-Cl₂-B₁₈H₂₀ (compound 5).

B1–H1	1.120	B1–Cl1	1.619(6)
B1–B2	1.805(8)	B1–B3	1.775(9)
B1–B4	1.787(10)	B1–B5	1.759(7)
B1–B10	1.744(10)	B2–H2	1.098(15)
B2–B3	1.772(8)	B2–B5	1.793(8)
B2–B6	1.745(7)	B2–B7	1.787(8)
B3–H3	1.120	B3–Cl3	1.795(6)
B3–B4	1.786(10)	B3–B7	1.747(8)
B3–B8	1.746(10)	B4–H4	1.098(14)
B4–B8	1.818(10)	B4–B9	1.724(12)
B4–B10	1.759(10)	B5–B6	1.804(6)
B5–B10	1.982(10)	B5–B2'	1.776(7)
B5–B7'	1.813(9)	B5–H57'	1.236(17)
B6–B7	1.810(8)	B6–B1'	1.760(7)
B6–B2'	1.802(8)	B6–B10'	2.021(9)
B6–H67	1.234(18)	B7–H7	1.095(14)
B7–B8	1.944(10)	B7–H67	1.233(18)
B8–H8	1.100(15)	B8–B9	1.802(12)
B8–H89	1.231(17)	B9–H9	1.095(14)
B9–B10	1.792(11)	B9–H89	1.233(18)
B9–H910	1.232(18)	B10–H10	1.098(15)
B10–H910	1.237(18)	B1'–H1'	1.120
B1'–Cl1'	1.682(6)	B1'–B2'	1.772(9)
B1'–B3'	1.779(9)	B1'–B4'	1.782(9)
B1'–B10'	1.767(10)	B2'–H2'	1.097(14)
B2'–B3'	1.752(9)	B2'–B7'	1.783(9)
B3'–H3'	1.120	B3'–Cl3'	1.778(7)
B3'–B4'	1.742(12)	B3'–B7'	1.770(9)

B3'-B8'	1.748(11)	B4'-H4'	1.095(14)
B4'-B8'	1.754(12)	B4'-B9'	1.723(11)
B4'-B10'	1.790(10)	B7'-H7'	1.096(14)
B7'-B8'	2.012(10)	B7'-H57'	1.234(17)
B8'-H8'	1.096(14)	B8'-B9'	1.766(12)
B8'-H89'	1.234(18)	B9'-H9'	1.096(14)
B9'-B10'	1.749(11)	B9'-H89'	1.234(18)
B9'-H91'	1.231(18)	B10'-H10'	1.108(14)
B10'-H91'	1.231(18)	Cl4-H4	0.98(6)
Cl4'-H4'	0.87(5)		

Table S5. Interatomic distances (\AA) for 7,3'-Cl₂-B₁₈H₂₀ (compound **6**).

B1-H1	1.04(2)	B1-B2	1.790(2)
B1-B3	1.789(2)	B1-B4	1.799(2)
B1-B5	1.760(2)	B1-B10	1.751(2)
B2-H2	1.069(18)	B2-B3	1.771(2)
B2-B5	1.818(2)	B2-B6	1.762(2)
B2-B7	1.803(2)	B3-H3	1.143(18)
B3-B4	1.780(2)	B3-B7	1.760(2)
B3-B8	1.761(2)	B4-H4	1.23(2)
B4-B8	1.796(2)	B4-B9	1.725(2)
B4-B10	1.791(2)	B5-B6	1.805(2)
B5-B10	1.967(2)	B5-B2'	1.771(2)
B5-B7'	1.822(2)	B5-H57'	1.28(2)
B6-B7	1.821(2)	B6-B1'	1.759(2)
B6-B2'	1.795(2)	B6-B10'	1.996(2)
B6-H67	1.31(2)	B7-Cl7	1.7952(16)
B7-B8	1.968(2)	B7-H67	1.24(2)
B8-H8	1.09(2)	B8-B9	1.792(2)
B8-H89	1.230(19)	B9-H9	1.05(2)
B9-B10	1.781(2)	B9-H89	1.25(2)
B9-H91	1.24(2)	B10-H10	1.06(2)
B10-H91	1.26(2)	B1'-H1'	1.09(2)
B1'-B2'	1.802(2)	B1'-B3'	1.780(2)
B1'-B4'	1.802(2)	B1'-B10'	1.757(2)
B2'-H2'	1.06(2)	B2'-B3'	1.762(2)
B2'-B7'	1.793(2)	B3'-Cl3'	1.8050(17)
B3'-B4'	1.776(2)	B3'-B7'	1.771(2)
B3'-B8'	1.763(2)	B4'-H4'	1.26(2)
B4'-B8'	1.804(3)	B4'-B9'	1.722(3)
B4'-B10'	1.779(2)	B7'-H7'	1.08(2)

B7'-B8'	1.958(2)	B7'-H57'	1.26(2)
B8'-H8'	1.120(19)	B8'-B9'	1.798(2)
B8'-H89'	1.23(2)	B9'-H9'	1.09(2)
B9'-B10'	1.784(3)	B9'-H89'	1.26(2)
B9'-H91'	1.23(2)	B10'-H10'	1.05(2)
B10'-H91'	1.25(2)		

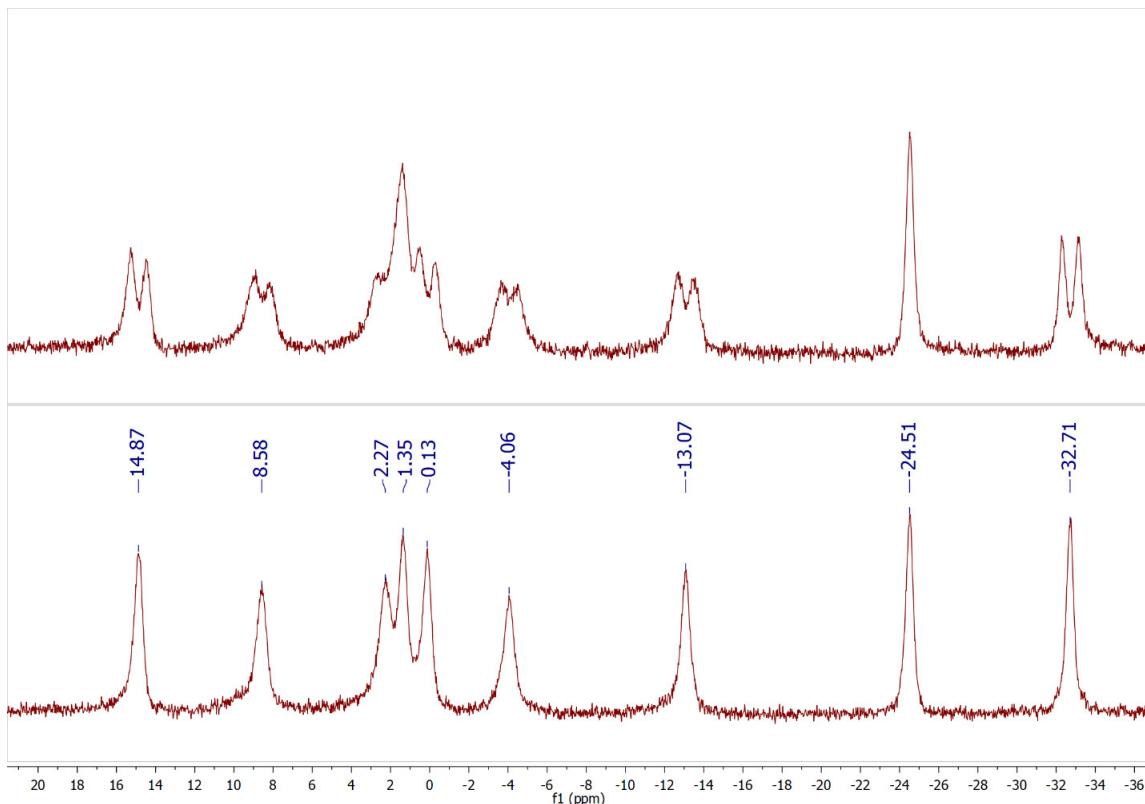


Figure S7. ^{11}B and $^{11}\text{B}-\{\text{H}\}$ NMR spectra for $4,4'\text{-Cl}_2\text{-B}_{18}\text{H}_{20}$ (compound 4).

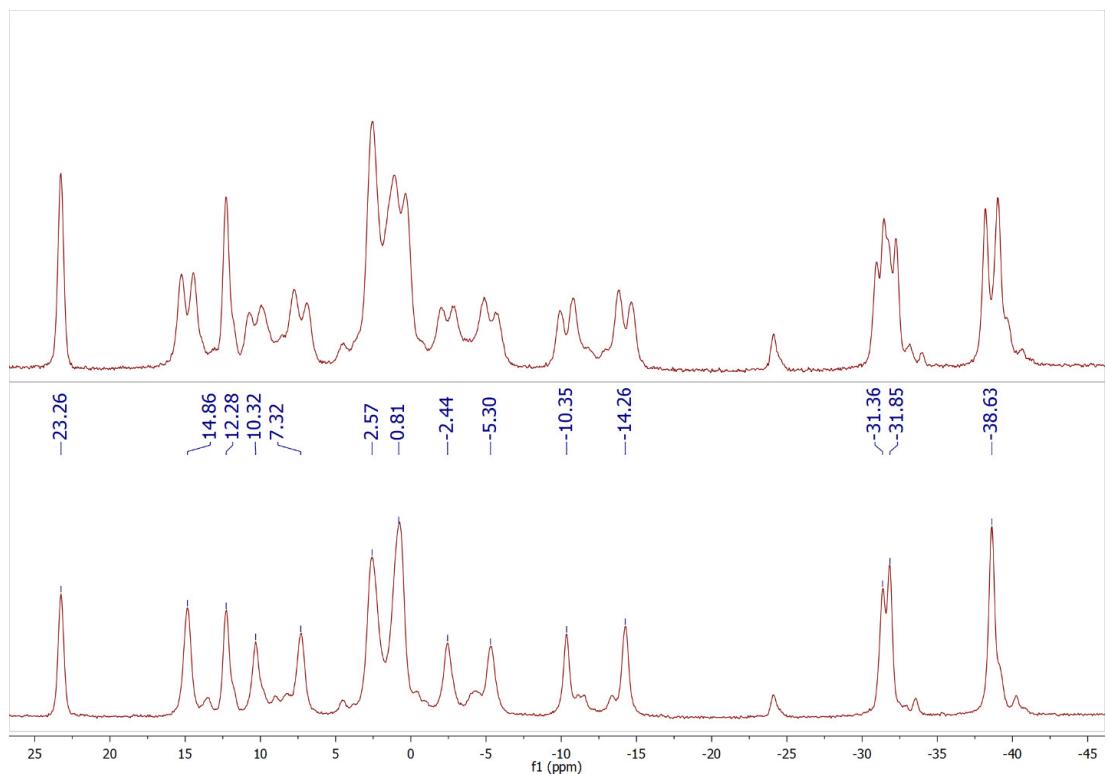


Figure S8. ^{11}B and $^{11}\text{B}-\{\text{H}\}$ NMR spectra for $3,1'\text{-Cl}_2\text{-B}_{18}\text{H}_{20}$ (compound 5). These spectra contain $3\text{-Cl-B}_{18}\text{H}_{21}$ (compound 7) impurities.

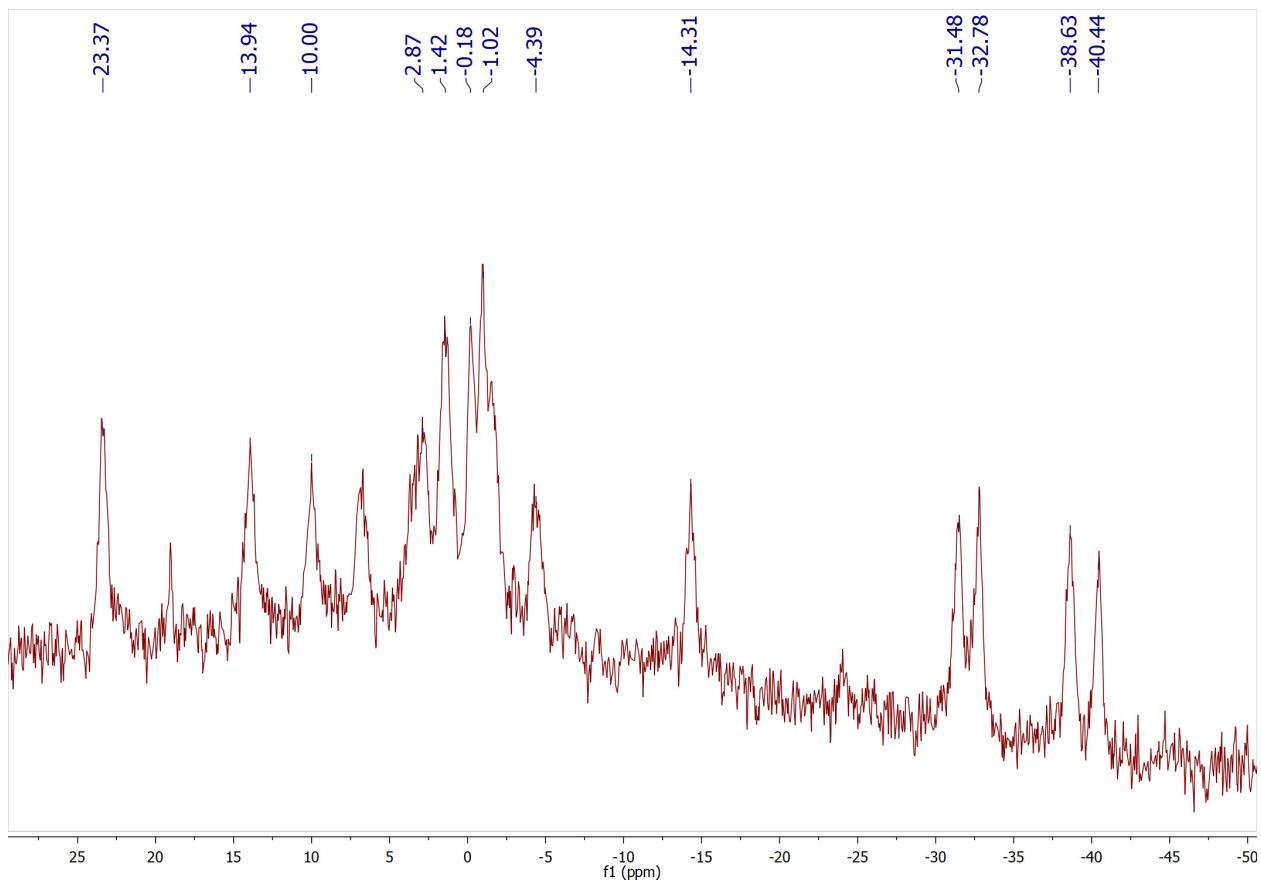


Figure S9. ^{11}B -{ ^1H } NMR spectrum for 7,3'-Cl₂-B₁₈H₂₀ (compound **6**).

Table S6. Interatomic distances (\AA) for 3-Cl-B₁₈H₂₁ and 4-Cl-B₁₈H₂₁ (compounds **7** and **8**).

B1–H1	1.08(2)	B1–B2	1.781(3)
B1–B3	1.786(3)	B1–B4	1.794(3)
B1–B5a	1.754(4)	B1–B10	1.755(4)
B2–H2	1.15(2)	B2–B3	1.756(4)
B2–B5	1.764(4)	B2–B5a	1.811(3)
B2–B7	1.789(3)	B3–H3	1.120
B3–Cl3	1.730(4)	B3–B4	1.779(3)
B3–B7	1.746(4)	B3–B8	1.749(3)
B4–H4	1.120	B4–Cl4	1.681(3)
B4–B8	1.799(4)	B4–B9	1.713(4)
B4–B10	1.774(4)	B5–B5a	1.802(4)
B5–B7	1.820(3)	B5–B10a	1.972(3)
B5–H57	1.29(2)	B7–H7	1.12(2)
B7–B8	1.966(4)	B7–H57	1.24(2)
B8–H8	1.04(2)	B8–B9	1.797(3)
B8–H89	1.31(2)	B9–H9	1.11(2)
B9–B10	1.782(3)	B9–H89	1.29(2)
B9–H910	1.27(2)	B10–H10	1.09(2)
B10–H910	1.32(2)		

Symmetry operations for equivalent atoms

a $-x+1, -y+1, -z+1$

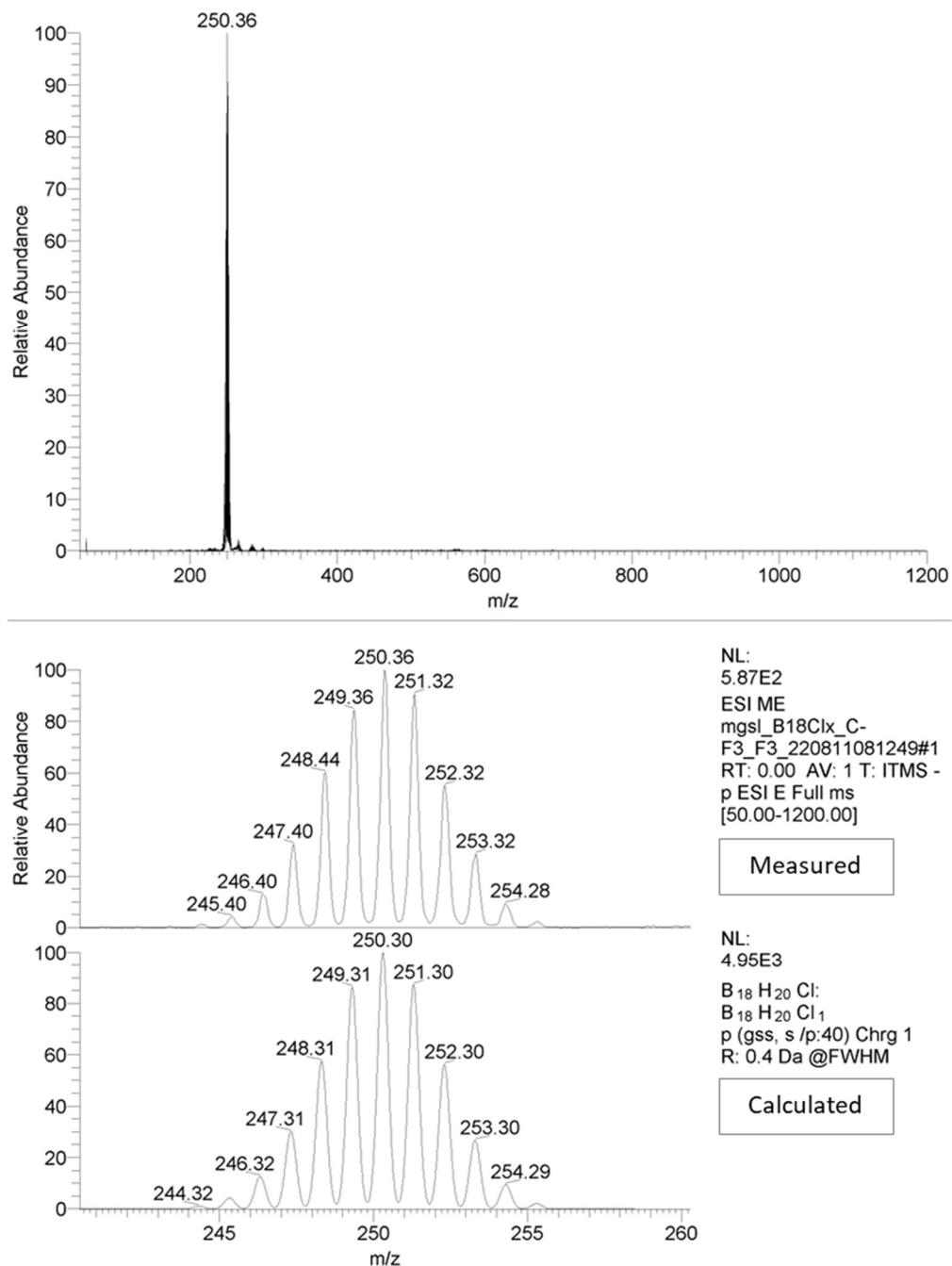


Figure S10. Mass spectrum of 3-Cl-B₁₈H₂₁ (compound 7 and 8).

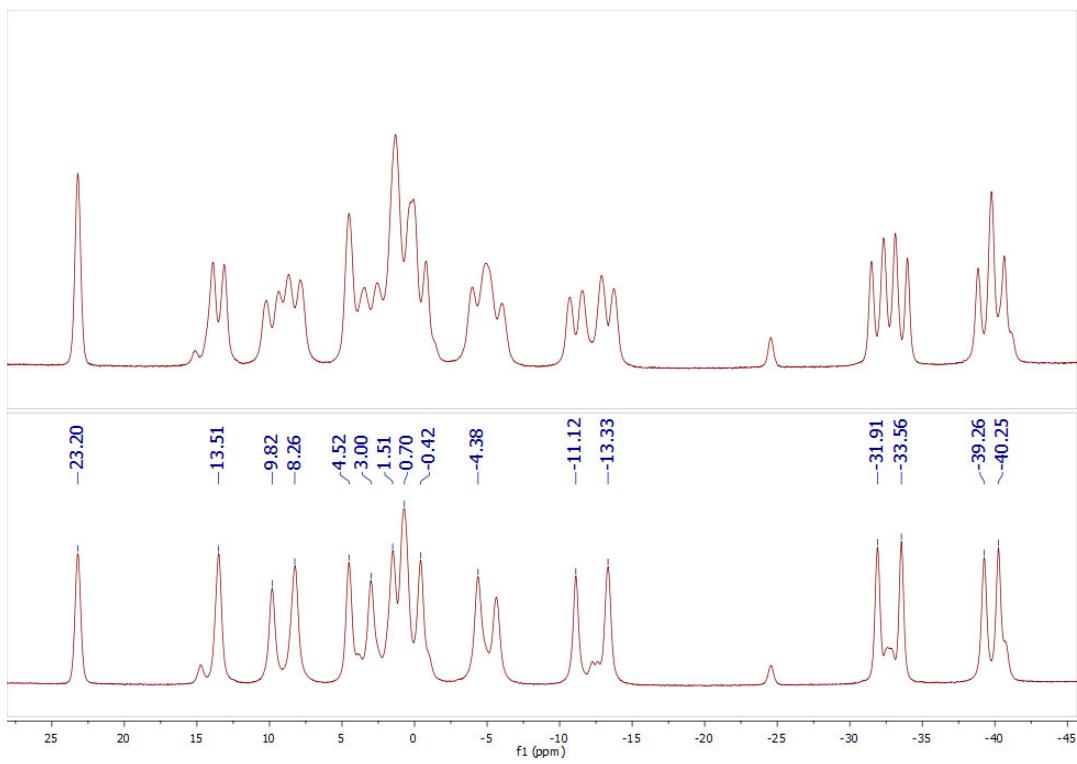


Figure S11. ^{11}B and $^{11}\text{B}-\{\text{H}\}$ NMR spectra for $3\text{-Cl-B}_{18}\text{H}_{21}$ (compound 7). These spectra contain $4\text{-Cl-B}_{18}\text{H}_{21}$ (compound 8) impurities.

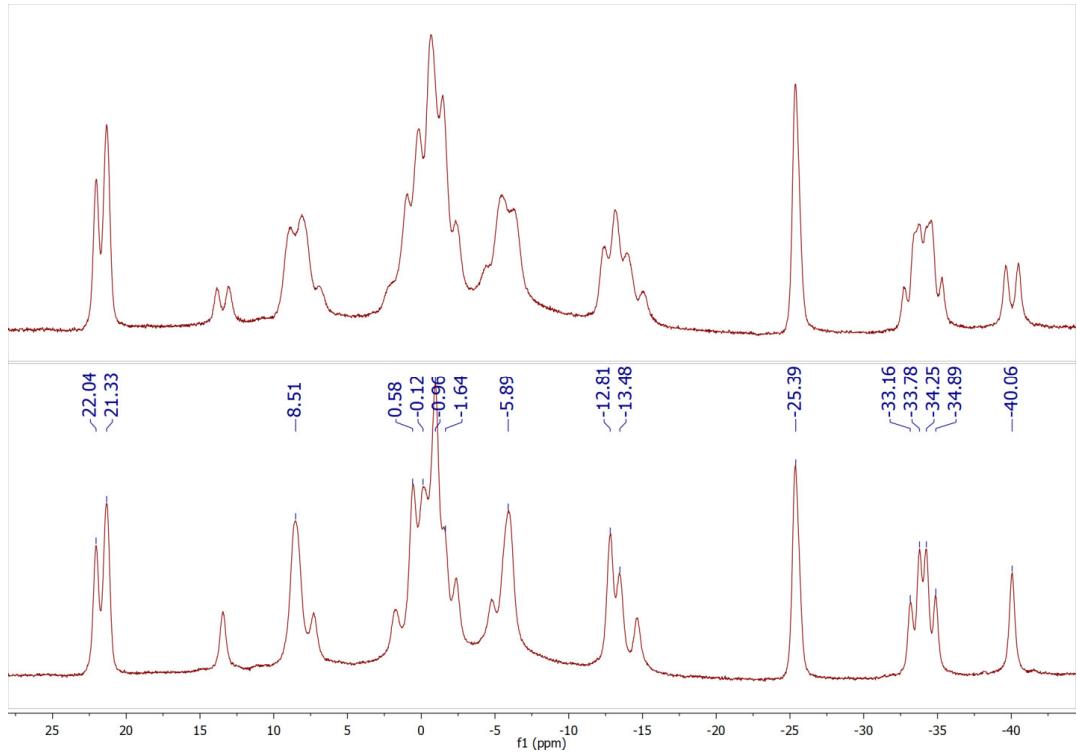


Figure S12. ^{11}B and $^{11}\text{B}-\{\text{H}\}$ NMR spectra for $3,4,3'\text{-Cl}_3\text{-B}_{18}\text{H}_{19}$ (compound 9). These spectra contain $3,4,4'\text{-Cl}_3\text{-B}_{18}\text{H}_{19}$ (compound 10) impurities.

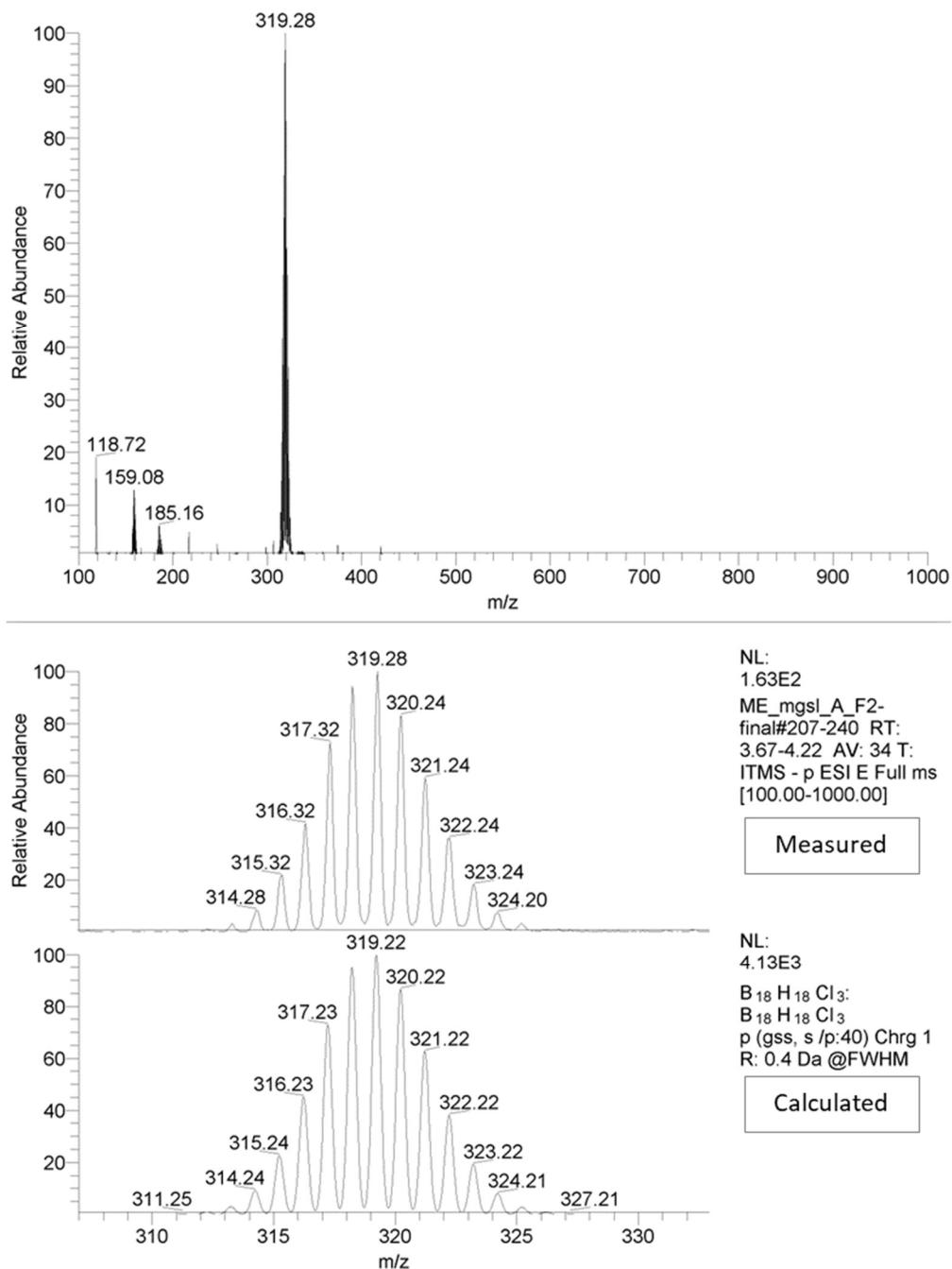


Figure S13. Mass spectrum of trichlorinated species.

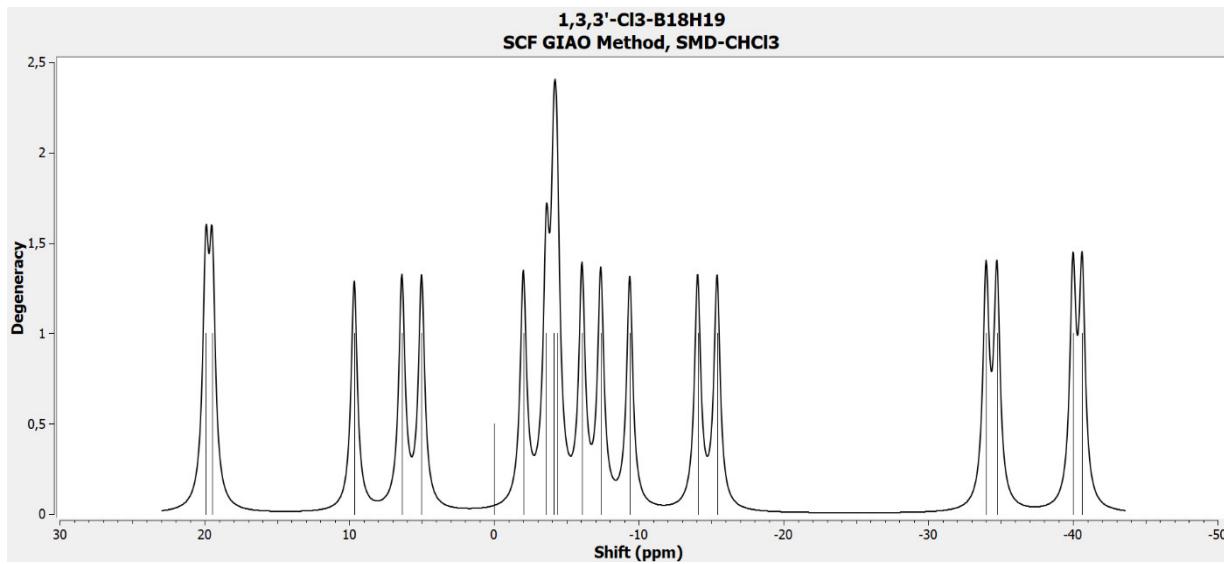


Figure S14. Calculated $^{11}\text{B}-\{^1\text{H}\}$ spectrum for 1,3,3'-Cl₃-B₁₈H₁₉.

Table S7. Calculated proton and boron-11 NMR data for 1,3,3'-Cl₃-B₁₈H₁₉ in CDCl₃ solution.

1,3,3'-Cl ₃ -B ₁₈ H ₁₉		
Assignment	$\delta(^{11}\text{B})/\text{pp}$	$\delta(^1\text{H})/\text{pp}$
m	m	m
B3'	+19.9	—a
B3	+19.5	—a
B1	+9.7	—a
B10	+6.4	+4.77
B10'	+5.0	+4.97
B6	-2.0	—b
B9	-3.6	+3.98
B5	-4.1	—b
B1'	-4.3	+4.06
B9'	-6.1	+3.90
B8'	-7.4	+3.90
B8	-9.4	+3.90
B7'	-14.1	+3.90
B7	-15.4	+3.90
B2'	-34.0	+0.58
B2	-34.7	+0.65
B4'	-40.0	+1.15
B4	-40.6	+1.05
$\mu\text{H8,9}$		-1.82
$\mu\text{H8',9'}$		-1.73
$\mu\text{H9,10}$		-0.10
$\mu\text{H9',10'}$		+0.40
$\mu\text{H6,7}$		+0.24
$\mu\text{H5,7'}$		+0.24

a) Chlorine substituent, b) Site of conjunction

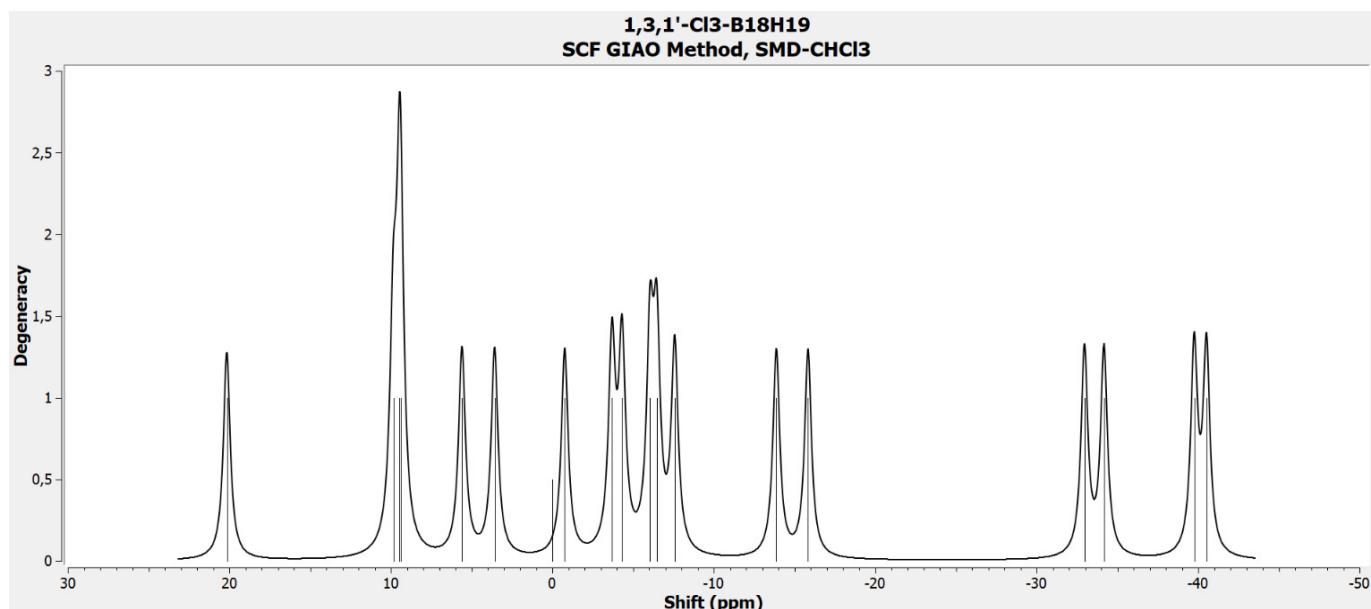


Figure S15. Calculated $^{11}\text{B}-\{\text{H}\}$ spectrum for $1,3,1'\text{-Cl}_3\text{-B}_{18}\text{H}_{19}$.

Table S8. Calculated proton and boron-11 NMR data for $1,3,1'\text{-Cl}_3\text{-B}_{18}\text{H}_{19}$ in CDCl_3 solution.

Assign- ment	1,3,1'-Cl ₃ -B ₁₈ H ₁₉	
	$\delta(^{11}\text{B})/\text{ppm}$	$\delta(^1\text{H})/\text{ppm}$
B3	+20.2	—a
B1	+9.8	—a
B1'	+9.5	—a
B3'	+9.4	+4.99
B10	+5.6	+4.99
B10'	+3.6	+4.99
B5	-0.8	—b
B9'	-3.7	+3.94
B6	-4.3	—b
B9	-6.1	+3.94
B8'	-6.5	+3.79
B8	-7.6	+3.94
B7'	-13.9	+3.79
B7	-15.8	+3.94
B2	-33.0	+0.81
B2'	-34.2	+0.67
B4	-39.8	+1.20
B4'	-40.5	+1.14

$\mu\text{H8,9}$	-1.68
$\mu\text{H8',9'}$	-2.18
$\mu\text{H9,10}$	+0.52
$\mu\text{H9',10'}$	+0.37
$\mu\text{H6,7}$	+0.57
$\mu\text{H5,7'}$	-0.06

a) Chlorine substituent, b) Site of conjunction

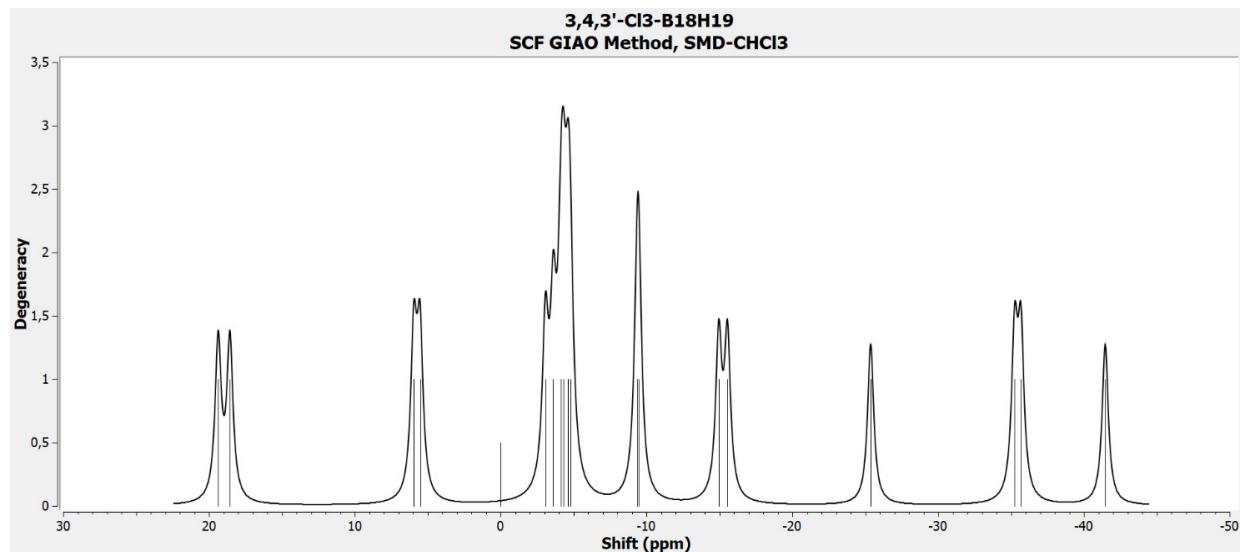


Figure S16. Calculated $^{11}\text{B}-\{^1\text{H}\}$ spectrum for 3,4,3'-Cl₃-B₁₈H₁₉ (compound 9).

Table S9. Calculated proton and boron-11 NMR data for 3,4,3'-Cl₃-B₁₈H₁₉ in CDCl₃ solution.

3,4,3'-Cl ₃ -B ₁₈ H ₁₉		
Assignment	$\delta(^{11}\text{B})/\text{ppm}$	$\delta(^1\text{H})/\text{ppm}$
B3'	+19.4	— ^a
B3	+18.6	— ^a
B10'	+5.9	+4.74
B10	+5.5	+5.00
B1	-3.1	+4.16
B9'	-3.6	+4.00
B5	-4.1	— ^b
B9	-4.3	+4.22
B1'	-4.6	+4.00
B6	-4.8	— ^b
B8	-9.4	+4.00
B8'	-9.5	+3.85
B7'	-15.0	+3.85
B7	-15.6	+3.85
B4	-25.4	— ^a
B2	-35.3	+0.58
B2'	-35.7	+0.36
B4'	-41.5	+0.99
$\mu\text{H}8,9$		-1.35
$\mu\text{H}8',9'$		-1.86
$\mu\text{H}9,10$		+0.42
$\mu\text{H}9',10'$		-0.13
$\mu\text{H}6,7$		-0.03
$\mu\text{H}5,7'$		-0.13

a) Chlorine substituent, b) Site of conjunction

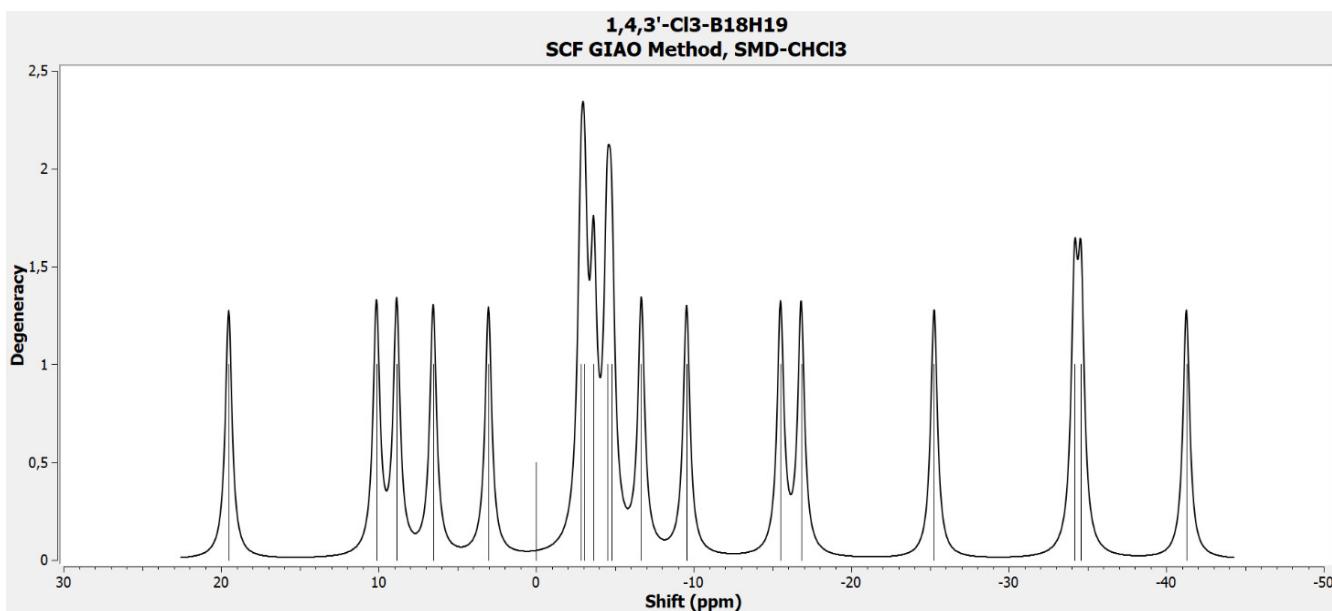


Figure S17. Calculated $^{11}\text{B}-\{^1\text{H}\}$ spectrum for $1,4,3'\text{-Cl}_3\text{-B}_{18}\text{H}_{19}$.

Table S10. Calculated proton and boron-11 NMR data for 1,4,3'-Cl₃-B₁₈H₁₉ in CDCl₃ solution.

Assignment	1,4,3'-Cl ₃ -B ₁₈ H ₁₉	
	$\delta(^{11}\text{B})/\text{ppm}$	$\delta(^1\text{H})/\text{ppm}$
B3'	+19.5	— ^a
B3	+10.3	+4.94
B1	+8.8	— ^a
B10'	+6.5	+4.78
B10	+3.0	+5.08
B5	-2.8	— ^b
B6	-3.1	— ^b
B9'	-3.7	+4.00
B9	-4.5	+4.22
B1'	-4.8	+4.00
B8	-6.7	+4.00
B8'	-9.6	+3.91
B7	-15.5	+3.63
B7'	-16.8	+3.85
B4	-25.2	—
B2'	-34.2	+0.54
B2	-34.6	+0.63
B4'	-41.3	+1.02
$\mu\text{H}8,9$		-1.60
$\mu\text{H}8',9'$		-1.77
$\mu\text{H}9,10$		+0.76
$\mu\text{H}9',10'$		+0.02
$\mu\text{H}6,7$		-0.40
$\mu\text{H}5,7'$		+0.43

a) Chlorine substituent, b) Site of conjunction

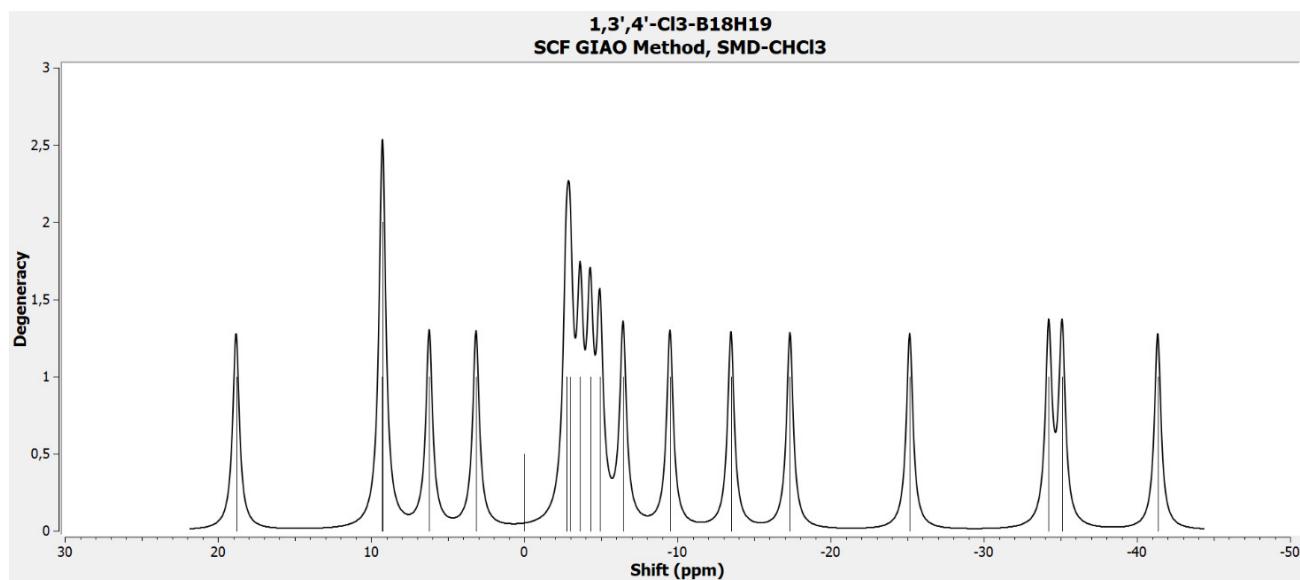


Figure S18. Calculated $^{11}\text{B}-\{\text{H}\}$ spectrum for 1,3',4'-Cl₃-B₁₈H₁₉.

Table S11. Calculated proton and boron-11 NMR data for 1,3',4'-Cl₃-B₁₈H₁₉ in CDCl₃ solution.

Assign- ment	1,3',4'-Cl ₃ -B ₁₈ H ₁₉	
	$\delta(^{11}\text{B})/\text{ppm}$	$\delta(^1\text{H})/\text{ppm}$
B3'	+18.8	— ^a
B3	+9.3	+4.95
B1	+9.3	— ^a
B10'	+6.2	+5.05
B10	+3.2	+4.95
B6	-2.7	— ^b
B1'	-3.0	+4.15
B9	-3.6	+3.99
B9'	-4.3	+4.23
B5	-4.9	— ^b
B8	-6.4	+3.72
B8'	-9.5	+4.04
B7	-13.5	+3.72
B7'	-17.3	+3.91
B4'	-25.2	— ^a
B2'	-34.2	+0.86
B2	-35.1	+0.40
B4	-41.4	+1.07
$\mu\text{H}8,9$		-2.18
$\mu\text{H}8',9'$		-1.28
$\mu\text{H}9,10$		+0.40
$\mu\text{H}9',10'$		+0.54
$\mu\text{H}6,7$		+0.41
$\mu\text{H}5,7'$		+0.30

a) Chlorine substituent, b) Site of conjunction

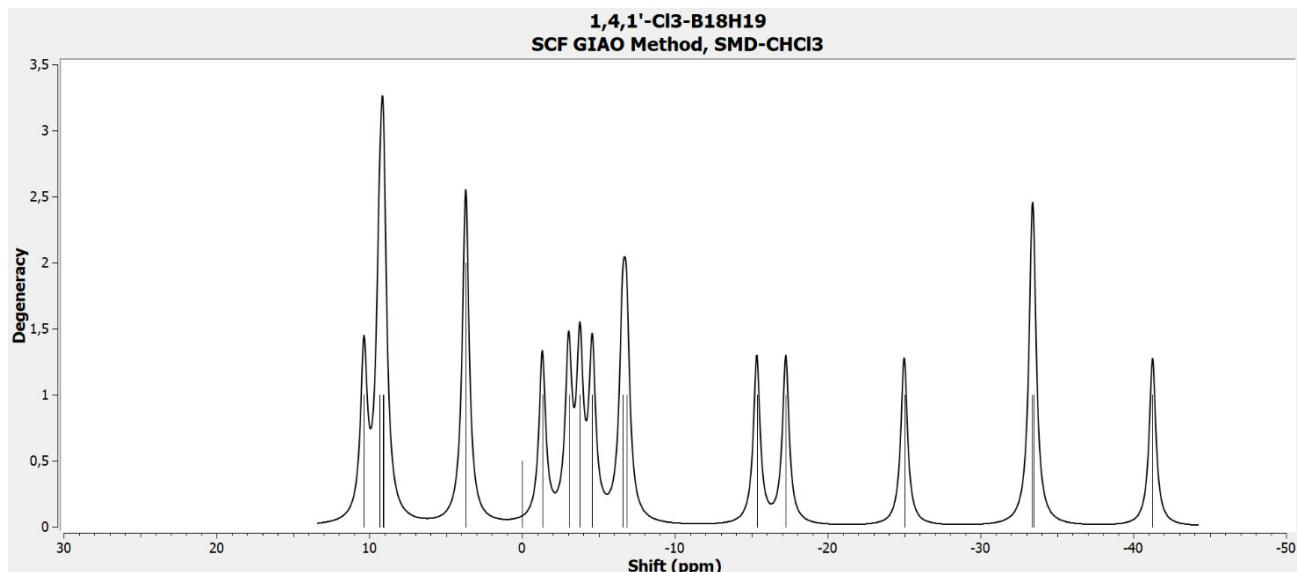


Figure S19. Calculated ¹¹B-<{¹H} spectrum for 1,4,1'-Cl₃-B₁₈H₁₉.

Table S12. Calculated proton and boron-11 NMR data for 1,4,1'-Cl₃-B₁₈H₁₉ in CDCl₃ solution.

Assignment	1,4,1'-Cl ₃ -B ₁₈ H ₁₉	$\delta(^{11}\text{B})/\text{ppm}$	$\delta(^1\text{H})/\text{ppm}$
B3		+10.4	+4.98
B3'		+9.3	+4.98
B1'		+9.1	—a
B1		+9.1	—a
B10'		+3.7	+4.98
B10		+3.7	+5.12
B5		-1.3	—b
B6		-3.0	—b
B9'		-3.8	+4.02
B9		-4.6	+4.23
B8'		-6.6	+3.75
B8		-6.8	+4.02
B7'		-15.4	+3.75
B7		-17.3	+3.67
B4		-25.0	—a
B2		-33.4	+0.87
B2'		-33.5	+0.58
B4'		-41.3	+1.10
$\mu\text{H8},9$			-1.52
$\mu\text{H8}',9'$			-2.09
$\mu\text{H9},10$			+0.87
$\mu\text{H9}',10'$			+0.49
$\mu\text{H6},7$			-0.09
$\mu\text{H5},7'$			+0.15

a) Chlorine substituent, b) Site of conjunction

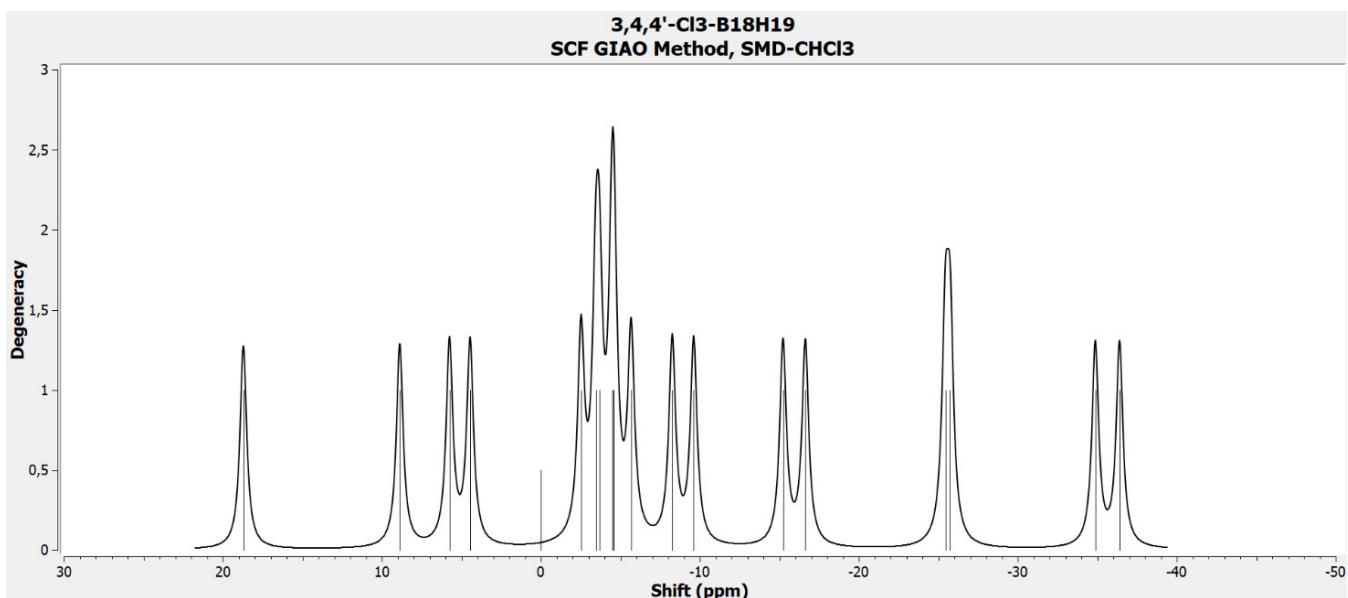


Figure S20. Calculated ¹¹B-^{1}H} spectrum for 3,4,4'-Cl₃-B₁₈H₁₉ (compound **10**).

Table S13. Calculated proton and boron-11 NMR data for 3,4,4'-Cl₃-B₁₈H₁₉ in CDCl₃ solution.

Assignment	3,4,4'-Cl ₃ -B ₁₈ H ₁₉	$\delta(^{11}\text{B})/\text{ppm}$	$\delta(^1\text{H})/\text{ppm}$
B3		+18.7	—a
B3'		+8.9	+4.70
B10		+5.7	+5.02
B10'		+4.5	+5.02
B9'		-2.5	+4.32
B1		-3.5	+4.02
B5		-3.7	—b
B9		-4.5	+4.23
B1'		-4.6	+3.88
B6		-5.7	—b
B8'		-8.3	+4.02
B8		-9.6	+4.02
B7'		-15.2	+3.66
B7		-16.6	+3.82
B4'		-25.4	—a
B4		-25.7	—a
B2		-34.9	+0.51
B2'		-36.4	+0.38
$\mu\text{H8,9}$			-1.30
$\mu\text{H8',9'}$			-1.69
$\mu\text{H9,10}$			+0.51
$\mu\text{H9',10'}$			+0.38
$\mu\text{H6,7}$			+0.03
$\mu\text{H5,7'}$			-0.67

a) Chlorine substituent, b) Site of conjunction

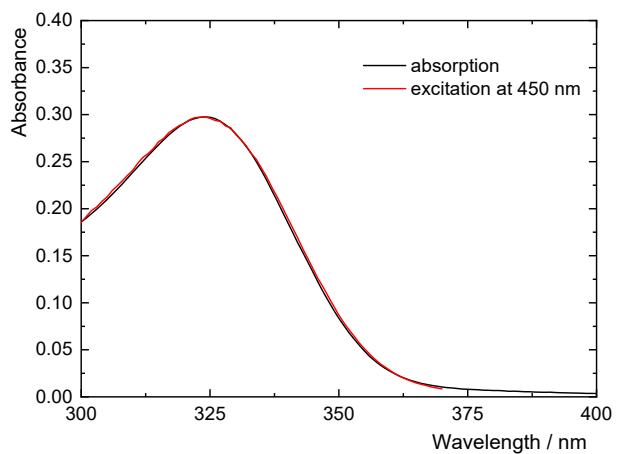


Figure S21. Absorption and excitation spectra for 3,3'-Cl₂-B₁₈H₂₀ (compound 2).

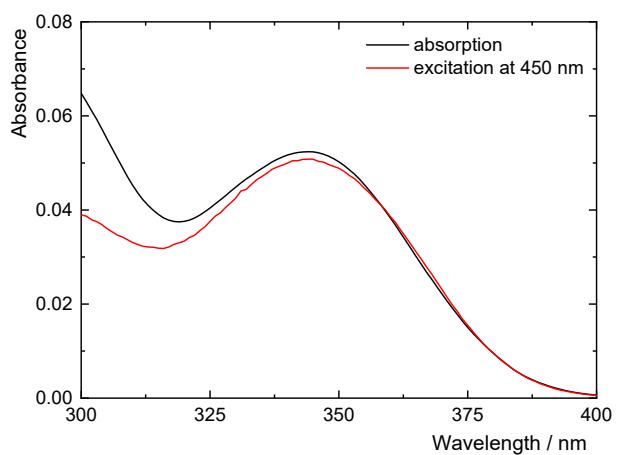


Figure S22. Absorption and excitation spectra for 4,4'-Cl₂-B₁₈H₂₀ (compound 4).

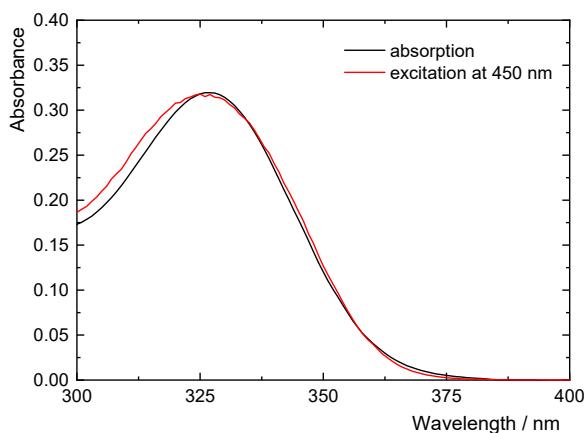


Figure S23. Absorption and excitation spectra for 3-Cl-B₁₈H₂₁ (compound 7).

Table S14. Crystal and refinement data for other forms of compound 2.

	2a	2b	2c
Chemical formula	B ₁₈ H ₂₀ Cl ₂	B ₁₈ H ₂₀ Cl ₂	B ₁₈ H ₂₀ Cl ₂
<i>M</i> _r	285.6	285.6	285.6
Crystal system	triclinic	monoclinic	monoclinic
Space group	<i>P</i> 1	<i>P</i> 2 ₁ /c	<i>P</i> 2 ₁ /n
<i>a</i> ()	11.5180(2)	11.2999(3)	7.1315(5)
<i>b</i> ()	15.8456(2)	12.8306(3)	11.2652(4)
<i>c</i> ()	20.4360(2)	11.0325(3)	10.4227(6)
()	69.7276(8)		
()	74.6731(14)	95.209(2)	106.413(6)
()	69.0113(14)		
<i>V</i> ( ³)	3224.46(9)	1592.94(7)	803.21(8)
<i>Z</i>	8	4	2
Crystal size (mm ³)	0.21×0.11×0.07	0.15×0.10×0.01	0.09×0.07×0.05
<i>T</i> (K)	100	150	150
Radiation, ()	CuK, 1.54184	CuK, 1.54184	CuK, 1.54184
Reflections measured	100755	11501	5794
Unique reflections	15567	2820	1428
<i>R</i> _{int}	0.1818	0.0432	0.0410
Parameters, restraints	1043, 0	267, 11	137, 9
<i>R</i> (<i>F</i> , <i>F</i> ² >2)	0.0472	0.0358	0.0374
<i>R</i> _w (<i>F</i> ² , all data)	0.1665	0.0901	0.1020
Goodness of fit (<i>F</i> ²)	1.067	1.026	1.037
Flack parameter			
Max, min  (e  ⁻³)	0.64, -0.53	0.41, -0.33	0.29, -0.14
CCDC deposition number	2256516	2178829	2178830

Table S15. B-B and B-Cl bond lengths in ordered molecules of B₁₈H₂₂ and B₁₈H₂₀Cl₂. Differences from corresponding values in B₁₈H₂₂ are on the next page; red for Cl-substituted sites.

	B18H22	2: 3,3'	2: 3,3'	3: 3,4'	4: 4,4'	4: 4,4'	4: 4,4'	4: 4,4'	6: 7,3'
site 1	0	3	3	3	4	4	4	4	7
site 2	0	3'	3'	4'	4'	4'	4'	4'	3'
1-2	1.791	1.803	1.788	1.803	1.783	1.806	1.805	1.797	1.790
1-3	1.795	1.774	1.814	1.788	1.823	1.782	1.826	1.790	1.789
1-4	1.792	1.825	1.814	1.804	1.789	1.785	1.782	1.800	1.799
1-5	1.755	1.752	1.755	1.746	1.761	1.792	1.737	1.776	1.760
1-10	1.755	1.774	1.754	1.749	1.748	1.766	1.737	1.763	1.751
2-3	1.761	1.789	1.782	1.768	1.736	1.768	1.762	1.769	1.771
2-5	1.810	1.813	1.832	1.797	1.833	1.813	1.803	1.808	1.818
2-6	1.770	1.736	1.742	1.754	1.786	1.748	1.789	1.766	1.762
2-7	1.794	1.780	1.781	1.804	1.806	1.784	1.819	1.805	1.803
3-4	1.783	1.801	1.785	1.785	1.795	1.776	1.770	1.780	1.780
3-7	1.762	1.744	1.737	1.760	1.755	1.755	1.783	1.765	1.760
3-8	1.753	1.760	1.742	1.767	1.777	1.755	1.748	1.734	1.761
4-8	1.806	1.778	1.787	1.797	1.801	1.821	1.803	1.780	1.796
4-9	1.720	1.708	1.706	1.724	1.719	1.722	1.738	1.699	1.725
4-10	1.779	1.779	1.813	1.770	1.778	1.774	1.783	1.783	1.791
5-6	1.805	1.784	1.800	1.805	1.850	1.830	1.800	1.790	1.805
5-10	1.984	2.028	1.979	1.978	1.979	1.991	1.992	1.994	1.967
5-2'	1.770	1.736	1.742	1.774	1.786	1.748	1.789	1.766	1.771
5-7'	1.820	1.820	1.844	1.810	1.806	1.798	1.830	1.819	1.822
6-7	1.820	1.820	1.844	1.817	1.806	1.798	1.830	1.819	1.821
6-1'	1.755	1.752	1.755	1.756	1.761	1.792	1.737	1.776	1.759
6-2'	1.810	1.813	1.832	1.803	1.833	1.813	1.803	1.766	1.795
6-10'	1.984	2.028	1.979	1.987	1.979	1.991	1.992	1.994	1.996
7-8	1.970	2.002	1.969	1.964	1.989	1.974	1.961	1.966	1.968
8-9	1.802	1.803	1.824	1.783	1.789	1.802	1.800	1.780	1.792
9-10	1.783	1.779	1.783	1.776	1.771	1.783	1.806	1.772	1.781
1'-2'	1.791	1.803	1.788	1.775	1.783	1.806	1.805	1.797	1.802
1'-3'	1.795	1.774	1.814	1.790	1.823	1.782	1.826	1.790	1.780
1'-4'	1.792	1.825	1.814	1.797	1.789	1.785	1.782	1.800	1.802
1'-10'	1.755	1.774	1.754	1.755	1.748	1.766	1.737	1.763	1.757
2'-3'	1.761	1.789	1.782	1.747	1.736	1.768	1.762	1.769	1.762
2'-7'	1.794	1.780	1.781	1.800	1.806	1.784	1.819	1.805	1.793
3'-4'	1.783	1.801	1.785	1.774	1.795	1.776	1.770	1.780	1.776
3'-7'	1.762	1.744	1.737	1.752	1.755	1.755	1.783	1.765	1.771
3'-8'	1.753	1.760	1.742	1.752	1.777	1.755	1.748	1.734	1.763
4'-8'	1.806	1.778	1.787	1.795	1.801	1.821	1.803	1.780	1.804
4'-9'	1.720	1.708	1.706	1.715	1.719	1.722	1.738	1.699	1.722
4'-10'	1.779	1.779	1.813	1.786	1.778	1.774	1.783	1.783	1.779
7'-8'	1.970	2.002	1.969	1.945	1.989	1.974	1.961	1.966	1.958
8'-9'	1.802	1.803	1.824	1.787	1.789	1.802	1.800	1.780	1.798
9'-10'	1.783	1.779	1.783	1.786	1.771	1.783	1.806	1.772	1.784
B-Cl		1.792	1.821	1.805	1.808	1.800	1.820	1.788	1.795
B-Cl'		1.792	1.821	1.804	1.808	1.800	1.820	1.788	1.805

	2: 3,3'	2: 3,3'	3: 3,4'	4: 4,4'	4: 4,4'	4: 4,4'	4: 4,4'	6: 7,3'
site 1	3	3	3	4	4	4	4	7
site 2	3'	3'	4'	4'	4'	4'	4'	3'
1-2	-0.012	0.003	-0.012	0.008	-0.015	-0.014	-0.006	0.001
1-3	0.021	-0.019	0.007	-0.028	0.013	-0.031	0.005	0.006
1-4	-0.033	-0.022	-0.012	0.003	0.007	0.010	-0.008	-0.007
1-5	0.003	0.000	0.009	-0.006	-0.037	0.018	-0.021	-0.005
1-10	-0.019	0.001	0.006	0.007	-0.011	0.018	-0.008	0.004
2-3	-0.028	-0.021	-0.007	0.025	-0.007	-0.001	-0.008	-0.010
2-5	-0.003	-0.022	0.013	-0.023	-0.003	0.007	0.002	-0.008
2-6	0.034	0.028	0.016	-0.016	0.022	-0.019	0.004	0.008
2-7	0.014	0.013	-0.010	-0.012	0.010	-0.025	-0.011	-0.009
3-4	-0.018	-0.002	-0.002	-0.012	0.007	0.013	0.003	0.003
3-7	0.018	0.025	0.002	0.007	0.007	-0.021	-0.003	0.002
3-8	-0.007	0.011	-0.014	-0.024	-0.002	0.005	0.019	-0.008
4-8	0.028	0.019	0.009	0.005	-0.015	0.003	0.026	0.010
4-9	0.012	0.014	-0.004	0.001	-0.002	-0.018	0.021	-0.005
4-10	0.000	-0.034	0.009	0.001	0.005	-0.004	-0.004	-0.012
5-6	0.021	0.005	0.000	-0.045	-0.025	0.005	0.015	0.000
5-10	-0.044	0.005	0.006	0.005	-0.007	-0.008	-0.010	0.017
5-2'	0.034	0.028	-0.004	-0.016	0.022	-0.019	0.004	-0.001
5-7'	0.000	-0.024	0.010	0.014	0.022	-0.010	0.001	-0.002
6-7	0.000	-0.024	0.003	0.014	0.022	-0.010	0.001	-0.001
6-1'	0.003	0.000	-0.001	-0.006	-0.037	0.018	-0.021	-0.004
6-2'	-0.003	-0.022	0.007	-0.023	-0.003	0.007	0.044	0.015
6-10'	-0.044	0.005	-0.003	0.005	-0.007	-0.008	-0.010	-0.012
7-8	-0.032	0.001	0.006	-0.019	-0.004	0.009	0.004	0.002
8-9	-0.001	-0.022	0.019	0.013	0.000	0.002	0.022	0.010
9-10	0.004	0.000	0.007	0.012	0.000	-0.023	0.011	0.002
1'-2'	-0.012	0.003	0.016	0.008	-0.015	-0.014	-0.006	-0.011
1'-3'	0.021	-0.019	0.005	-0.028	0.013	-0.031	0.005	0.015
1'-4'	-0.033	-0.022	-0.005	0.003	0.007	0.010	-0.008	-0.010
1'-10'	-0.019	0.001	0.000	0.007	-0.011	0.018	-0.008	-0.002
2'-3'	-0.028	-0.021	0.014	0.025	-0.007	-0.001	-0.008	-0.001
2'-7'	0.014	0.013	-0.006	-0.012	0.010	-0.025	-0.011	0.001
3'-4'	-0.018	-0.002	0.009	-0.012	0.007	0.013	0.003	0.007
3'-7'	0.018	0.025	0.010	0.007	0.007	-0.021	-0.003	-0.009
3'-8'	-0.007	0.011	0.001	-0.024	-0.002	0.005	0.019	-0.010
4'-8'	0.028	0.019	0.011	0.005	-0.015	0.003	0.026	0.002
4'-9'	0.012	0.014	0.005	0.001	-0.002	-0.018	0.021	-0.002
4'-10'	0.000	-0.034	-0.007	0.001	0.005	-0.004	-0.004	0.000
7'-8'	-0.032	0.001	0.025	-0.019	-0.004	0.009	0.004	0.012
8'-9'	-0.001	-0.022	0.015	0.013	0.000	0.002	0.022	0.004
9'-10'	0.004	0.000	-0.003	0.012	0.000	-0.023	0.011	-0.001