Unsymmetrical 1,1-diborated multisubstituted sp^3-carbons formed via a metal-free concerted-asynchronous mechanism

Ana B. Cuenca, Jessica Cid, Diego García, Jorge J. Carbó* and Elena Fernández*

Department Química Física i Inorgànica. University Rovira i Virgili. C/Marcel·lí Domingo, s/n 43007 Tarragona, Spain

e-mails: j.carbo@urv.cat, mariaelena.fernandez@urv.cat

Table of contents

1. General information

Solvents and reagents: Solvents and reagents were obtained from commercial suppliers and dried and/or purified (if needed) by standard procedures, as specified in "*Purification of Laboratory Chemicals*".[1] Methanol was purchased from Fisher Scientific, Inc. and was dried by calcium hydride distillation. Toluene employed for insertion reactions was dried and purified with a solvent purification system Pure SOLV system-4, by passing the solvent through two activated alumina columns after being purged with argon. Toluene used for base-assisted proto-deborylation reactions was dried by distillation from sodium wire. Potassium *tert*-butoxide was purchased from Sigma-Aldrich Inc., used as received and stored under nitrogen in a glove box. All reactions were conducted in oven and flame-dried glassware under an inert atmosphere of argon, using Schlenk-type techniques. *Flash chromatography* was performed on standard silica gel (Merck Kieselgel 60 F_{254} 400-630 mesh). *Thin layer chromatography* was performed on Merck Kieselgel 60 F_{254} which was developed using standard visualizing agents: UV fluorescence (254 and 366 nm) or potassium permanganate/Δ. *NMR spectra* were recorded at a Varian Goku 400 or a Varian Mercury 400 spectrometer. ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts (δ) are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: 7.26 ppm (^{1}H)) and (CDCl3: 77.16 ppm (^{13}C). ^{11}B{^{1}H} NMR chemical shifts (δ) are reported in ppm relative to $(CH_3)_2O\cdots BF_3$. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. *High resolution mass spectra (HRMS)* were recorded using a 6210 Time of Flight (TOF) mass spectrometer from Agilent Technologies (Waldbronn, Germany) with an ESI interface and it was performed at the Servei de Recursos Científics i Tècnics (Universitat Rovira I Virgili, Tarragona). *GC-MS analyses* were performed on a HP6890 gas chromatograph and an Agilent Technologies 5973 Mass selective detector (Waldbronn, Germany) equipped with an achiral capillary column HP-5 (30m, 0.25mm i. d., 0.25µm thickness) using He as the carrier gas. Sodium hydride 60 % dispersion in mineral oil and all the carbonylic compounds were purchased from Sigma-Aldrich, Inc. *p*-Toluenesulfonyl hydrazide, 98% was purchased from Alfa-Aesar, Inc. and used as received.

1 Perrin D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, Pergamon Press, **1988**, 3rd Ed.

2. Experimental Procedures

I. Synthesis of Bpin-Bdan

To prepare the mixed diboron reagent Bpin-Bdan a slightly modified version of the previously described protocol[2] was used. Thus Tetrakis(dimethylamino)diboron ($B_2(NMe_2)_4$) was synthesize from B_2Cat_2 instead of BCl_3SMe_2. Once prepared the $B_2(NMe_2)_4$ was sought to react with 1,8-diaminonaphthalene and pinacol in a 1:1:1 ratio in dichloromethane. The slurry was stirred at room temperature for 36 h. After evaporation of volatile materials under vacuum, the solid residue was washed with hot toluene (×3) to collect washings containing the desired product. After evaporation of toluene from the solution under vacuum, the resultant solid was washed with hexane (×3). The solid material was dried under vacuum. Following this procedure a global isolated yield of (83 %) was attained in a 26.6 mmol scale reaction.

II. Stepwise protocol for the insertion reactions of tosylhydrazones into the Bpin-Bdan molecule

Step A: Preparation of aldehyde and ketone tosylhydrazones[3,4]

An oven-dried round-bottomed flask was charged with *p*-toluenesulfonyl hydrazide (6 mmol) and methanol (6 mL). The formed suspension was rapidly stirred and the corresponding aldehyde or ketone (6 mmol) was added dropwise as a methanol solution (6 mL). A mildly exothermic reaction ensued and the hydrazide dissolved. The mixture was stirred at room temperature. In most of the cases (but not in every one) within 5-30 min the tosylhydrazone began to precipitate. TLC analysis was performed until the spot of carbonyl compound disappeared. In the cases were the precipitate appeared, after approximately 120-180 min the mixture was cooled to 0^{o}C and the product removed by filtration, washed with a small quantity of methanol and dried under vacuum. In the rest of

2 Iwadate, N.; Suginome, M. *J. Am. Chem. Soc.*, **2010**, *132*, 2548.

3 Li, H.; Wang, L.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed*. **2012**, *51*, 2943.

4 Aggarwal, V. K.; Alonso, E.; Bae, I.; Hynd, G.; Lydon, K. M.; Palmer, M. J.; Patel, M.; Porcelloni, M.; Richardson, J.; Stenson, R. A.; Studley, J. R.; Vasse, J. L.; Winn, C. L. *J. Am. Chem. Soc.*, **2003**, *125*, 10926.

the cases, exceeding methanol was removed to dryness and tosylhydrazones were as well dried under vacuum. Purity of obtained tosylhydrazones was evaluated by ^{1}H NMR and, if needed, they were recrystallized from methanol.

Step B: General procedure for the insertion reactions of tosylhydrazones into the Bpin-Bdan molecule

Into an oven-dried resealable Teflon screw-cap Schlenk reaction tube equipped with a magnetic stir bar in Argon was charged with the corresponding *N*-tosylhydrazone (0.25 mmol), 60% NaH (1.2 mmol, 12 mg) and 2 mL of dry Toluene. The mixture was stirred at room temperature for 1 h. Then Bpin-Bdan (1.2 mmol, 88.2 mg) was added along with additional 1.5 mL of dry Toluene. Then the Schlenk tube was sealed and heated at 110 ^{o}C for 16 h. After the reaction was cooled down to room temperature, the obtained suspension was filtered over a Celite® pad and solvent was gently concentrated on a rotary evaporator. This crude residue was purified by silica gel flash chromatography to afforded the 1,1-diborylation compounds.

III. **One-pot general protocol for the insertion reactions of tosylhydrazones into the Bpin-Bdan molecule**

Into an oven-dried resealable Teflon screw-cap Schlenk reaction tube equipped with a magnetic stir bar in Argon was charged with *p*-toluenesulfonyl hydrazide (0.25 mmol) and the corresponding aldehyde or ketone (0.25 mmol) was added dropwise. The flask was rinse with 0.5 mL of methanol and the mixture was stirred at room temperature for a period of time approximately 120-180 min. In most of the cases (but not in every one) within 5-30 min the tosylhydrazone began to precipitate. TLC analysis was performed until the spot of carbonyl compound disappeared. At this point methanol was removed and the obtained *N*-tosylhydrazones were dried under vacuum for an additional period of time of 3-4 h. Next (1.2 mmol, 12 mg) of 60% NaH was added in 2 mL of dry

Toluene. The mixture was stirred at room temperature for 1 h. Then Bpin-Bdan (1.2 mmol, 88.2 mg)[5] was added along with additional 1.5 mL of dry Toluene. Then the Schlenk tube was sealed and heated at 110 ^{o}C for 16 h. After the reaction was cooled down to room temperature, the obtained suspension was filtered over a Celite® pad and solvent was gently concentrated on a rotary evaporator. This crude residue was purified by silica gel flash chromatography to afforded the 1,1-diborylation compounds.

3. Spectral Data of 1,1-diboration compounds:

Compound (**3**): *2-(3-phenyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2,3 dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine*: Flash column chromatography (petroleum ether/EtOAc = 15:1) yielded **3** (75 % yield) as an off-white sticky solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32 (m, 2H), 7.24 (m, 3H), 7.13 (dd, *J* = 8.2, 7.4 Hz, 2H), 7.03 (dd, *J* = 8.2, 0.8 Hz, 2H), 6.31 (dd, *J* = 7.4, 0.8 Hz, 2H), 5.83 (br s, 2H), 2.77 (m, 1H), 2.65 (ddd, *J* = 13.4, 9.7, 6.4 Hz, 1H), 2.02 (m, 1H), 1.87 (m, 1H), 1.30 (s, 6H), 1.29 (s, 6H), 0.88 (dd, *J* = 9.8, 5.6 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 142.6, 141.3, 136.3, 128.6, 128.4, 127.6, 125.9, 119.6, 117.3, 105.5, 83.3, 38.5, 28.6, 25.2, 24.6; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.3; HRMS-(ESI+) for $C_{25}H_{31}B_2N_2O_2$ $[M+H]^+$: calculated: 413.2572, found: 413.2572.

Compound (**5**): *2-(cyclohexyl(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine* (**5**): Flash column chromatography (petroleum ether/EtOAc = 30:1) yielded **5** (49 % yield) as an off-white sticky solid.

[5] Reaction with substrate **2** was also run in the presence of only 1equiv. of Bpin-Bdan, however, it turned out to be a less efficient transformation and **3** was isolated in only 49 % yield.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.08 (dd, *J* = 8.2, 7.3 Hz, 2H), 6.98 (dd, *J* = 8.2, 0.9 Hz, 2H), 6.28 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.79 (br s, 2H), 1.80 (m, 2H), 1.58 (m, 6H), 1.23 (m, 12H), 1.16-0.83 (m, 4H), 0.55 (d, *J* = 10.7 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.4, 136.4, 127.6, 119.6, 117.3, 105.5, 83.2, 37.4, 36.5, 36.1, 27.0, 26.9, 26.3, 24.9, 24.8; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.9; HRMS-(ESI+) for $C_{23}H_{33}B_2N_2O_2$ $[M+H]^+$: calculated: 391.2728, found: 391.2721.

Compound (**7**): *2-(2-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine* Flash column chromatography (petroleum ether/EtOAc = 40:1) yielded **7** (71 % yield) as an off-white sticky solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.10 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.00 (dd, *J* = 8.4, 0.9 Hz, 2H), 6.29 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.80 (br s, 2H), 2.02 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 1.03 (d, *J* = 6.5 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.53 (d, *J* = 10.5 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.8, 136.4, 127.6, 119.6, 117.3, 105.5, 83.2, 27.9, 25.8, 25.5, 24.9, 24.8; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.0; HRMS-(ESI+) for $C_{20}H_{29}B_2N_2O_2$ $[M+H]^+$: calculated: 351.2415, found: 351.2405.

Compound (**9**): *2-(3-methyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine.* Flash column chromatography (hexane/EtOAc = 50:1) yielded **9** (73 % yield) as an off-white sticky solid.

^{1}H NMR (CD_2Cl_2, 400 MHz) δ 7.09 (dd, *J* = 8.2, 7.3 Hz, 2H), 7.00 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.29 (dd, *J* = 7.3, 1.1 Hz, 2H), 5.78 (br s, 2H), 1.58 (m, 2H), 1.39 (m, 1H), 1.25 (s, 6H), 1.24 (s, 6H), 0.93 (d, *J* = 6.3 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.86 (dd, *J* = 9.3, 6.1 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, CD_2Cl_2) δ 141.4, 136.3, 127.6, 119.6, 117.3, 105.5, 83.2, 35.5, 30.1, 25.1, 24.6, 23.0, 22.4;

^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.0; HRMS-(ESI+) for $C_{21}H_{31}B_2N_2O_2$ $[M+H]^+$: calculated: 365.2572, found: 365.2578.

Compound (**11**): *2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)heptyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine.* Flash column chromatography (petroleum ether/EtOAc = 60:1) yielded **11** (77 % yield) as an off-white sticky solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.09 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.99 (dd, *J* = 8.3, 0.9 Hz, 2H), 6.29 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.80 (br s, 2H), 1.57 (m, 4H), 1.35 (m, 6H), 1.26 (s, 6H), 1.24 (s, 6H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.75 (dd, *J* = 9.4, 6.1 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.4, 136.4, 127.6, 119.6, 117.3, 105.5, 83.2, 32.4, 31.9, 29.5, 26.5, 25.1, 24.6, 22.7, 14.2; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.9; HRMS-(ESI+) for $C_{23}H_{35}B_2N_2O_2$ $[M+H]^+$: calculated: 393.2885, found: 393.2894.

Compound (**13**): *2-(4-phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-yl)-2,3-dihydro-1H-naphtho[1,8 de][1,3,2]diazaborinine.* Flash column chromatography (petroleum ether/EtOAc = 25:1) yielded **13** (43 % yield) as an off-white sticky solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.18 (m, 2H), 7.13 (m, *J* = 7.1 Hz, 3H), 7.09 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.90 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.30 (dd, *J* = 7.3,1.0 Hz, 2H), 5.90 (br s, 2H), 2.69 (td, *J* = 12.6, 5.1 Hz, 1H), 2.56 (td, *J* = 12.7, 4.7 Hz, 1H), 1.89 (td, *J* = 12.8, 4,7 Hz, 1H), 1.79 (td, *J* = 12.7, 5.2 Hz, 1H), 1.26 (s, 12H), 1.22 (s, 3H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 143.4, 141.4, 136.4, 128.5, 128.4, 127.7, 125.8, 119.6, 117.3, 105.6, 83.4, 38.2, 34.4, 29.8, 24.9, 16.6; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 35.6; HRMS-(ESI+) for $C_{26}H_{33}B_2N_2O_2$ $[M+H]^+$: calculated: 427.2728, found: 427.2723.

Compound (**15**): *2-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexan-2-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine.* Flash column chromatography (hexane/EtOAc = 57:1) yielded **15** (27 % yield) as an off-white sticky solid.

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.10 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.99 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.30 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.89 (br s, 2H), 1.55 (m, 2H), 1.30 (m, 4H), 1.25 (m, 6H), 1.24 (s, 6H), 1.11 (s, 3H), 0.90 (apparent t, *J* = 6.9 Hz, 4H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.6, 136.4, 127.7, 119.6, 117.2, 105.5, 83.3, 35.5, 30.0, 24.9, 24.8, 23.6, 16.6, 14.3; ^{11}B NMR (128.3 MHz, CDCl3) δ 34.7; HRMS-(ESI+) for $C_{22}H_{33}B_2N_2O_2$ $[M+H]^+$: calculated: 379.2728, found: 379.2720.

Compound (**16a**): *2-(1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4(trifluoromethyl)cyclohexyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine.* Flash column chromatography (petroleum ether/EtOAc = 35:1) yielded **16a** (20 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer* **16a**) ($CDCl_3$, 400 MHz) δ 7.09 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.00 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.29 (dd, *J* = 7.2, 1.0 Hz, 2H), 5.74 (br s, 2H), 2.17 (apparent d, *J* = 10.0 Hz, 2H), 1.95 (apparent d, *J* = 9.8 Hz, 2H), 1.37 (m, 5H), 1.25 (s, 12H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.1, 136.3, 127.9 (q, J^{1}_{CF} = 278.5 Hz) 127.7, 119.6, 117.6, 105.7, 83.8, 41.9 (q, J^{2}_{CF} = 26.2 Hz), 28.7, 24.9 (q, q, J^{3}_{CF} = 2.3 Hz), 24.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -74.3; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.9; HRMS-(ESI+) for $C_{23}H_{30}B_2F_3N_2O_2$ $[M+H]^+$: calculated: 445.2445 found: 445.2438.

Compound (**17a**): Flash column chromatography (hexane/EtOAc = 65:1) yielded **17a** (25 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer* **17a**) ($CDCl_3$, 400 MHz) δ 7.08 (ddd, *J* = 8.2, 7.3, 0.7 Hz, 2H), 6.98 (dd, *J* = 8.3, 0.9 Hz, 2H), 6.28 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.78 (br s, 2H), 2.04 (m, 2H), 1.72 (dd, *J* = 13.3, 3.4 Hz, 2H), 1.34 (m, 3H), 1.25 (s, 12H), 0.98 (qd, *J* = 12.8, 3.3 Hz, 2H), 0.87 (d, *J* = 6.4 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.5, 136.4, 127.7, 119.6, 117.3, 105.5, 83.4, 35.6, 32.8, 30.3, 24.8, 23.3; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.3; HRMS-(ESI+) for $C_{23}H_{33}B_2N_2O_2$ $[M+H]^+$: calculated: 391.2728, found: 391.2744.

Compounds (**17a** and **17b**):

^{1}H NMR (mixture 35:65 two diastereoisomers *(ds)* **17a** *and* **17b**) ($CDCl_3$, 400 MHz) δ 7.09 (apparent m, 0.35 x 2H **17a** + 0.65 x 2H **17b**), 6.98 (apparent m, 0.35 x 2H **17a** + 0.65 x 2H **17b**), 6.31 (dd, *J* = 7.3, 1.0 Hz, 2H **17b**), 6.27 (dd, *J* = 7.3, 1.0 Hz, 2H **17a**), 5.77 (br s, 0.35 x 2H **17a** + 0.65 x 2H **17b**), 2.04 (apparent m, 2H **17a**), 1.90 (apparent m, 2H **17b**), 1.73-1.29 (m, 0.35 x 5H **17a** + 0.65 x 5H **17b**), 1.25 (s, 12H **17a**), 1.19 (s, 12H **17b**), 1.15-0.90 (m, 0.35 x 2H **17a** + 0.65 x 2H **17b**), 0.86 (apparent m, 0.35 x 3H **17a** + 0.65 x 3H **17b**); ^{13}C {^{1}H} NMR (75.4 MHz, CDCl3) δ 141.6, 141.5, 136.4, 136.3, 127.7, 119.6, 119.4, 117.3, 117.2, 105.5, 83.4, 83.2, 35.6, 33.9, 32.8, 30.3, 28.5, 24.8, 24.7, 23.3, 22.8; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.3. $[M+H]^+$: calculated: 391.2728, found: 391.2698.

Compound (**18a**): Flash column chromatography (hexane/EtOAc = 55:1) yielded **18a** (22 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer* **18a**) ($CDCl_3$, 400 MHz) δ 7.08 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.98 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.28 (dd, *J* = 7.3, 1.0 Hz, 2H),

5.78 (br s, 2H), 2.09 (apparent d, *J* = 13.5 Hz, 2H), 1.71 (apparent d, *J* = 10.6 Hz, 2H), 1.41 (m, 1H), 1.31 (m, 2H), 1.25 (s, 12H), 1.06 (m, 3H), 0.86 (d, *J* = 6.8 Hz, 6H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.5, 136.4, 127.7, 119.6, 117.3, 105.5, 83.4, 44.0, 33.2, 30.6, 29.8, 24.9, 19.7; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.2; HRMS-(ESI+) for $C_{25}H_{37}B_2N_2O_2$ $[M+H]^+$: calculated: 419.3041, found: 419.3040.

Compounds (**18a** and **18b**):

^{1}H NMR (mixture 80:20 two diastereoisomers *(ds)* **18a** *and* **18b**) ($CDCl_3$, 400 MHz) δ 7.09 (apparent m, 0.8 x 2H **18a** + 0.2 x 2H **18b**), 6.98 (apparent m, 0.8 x 2H **18a** + 0.2 x 2H **18b**), 6.31 (dd, *J* = 7.3, 1.0 Hz, 2H **18b**), 6.28 (dd, *J* = 7.3, 1.0 Hz, 2H **18a**), 5.77 (br s, 0.8 x 2H **18a** + 0.2 x 2H **18b**), 2.09 (apparent d, *J* = 13.5 Hz, 2H **18a**), 1.97 (apparent d, *J* = 13.5 Hz, 2H **18b**), 1.71 (apparent d, *J* = 10.6 Hz, 2H **18a**), 1.64 (m, 2H **18b**), 1.41 (m, 0.8 x 1H **18a** + 0.2 x 1H **18b**), 1.31 (m, 0.8 x 2H **18a** + 0.2 x 2H **18b**), 1.25 (s, 12H **18a**), 1.19 (s, 12H **18b**), 1.06 (m, 0.8 x 3H **18a** + 0.2 x 3H **18b**), 0.86 (d, *J* = 6.8 Hz, 6H **18a**), 0.81 (d, *J* = 6.8 Hz, 6H **18b**); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.6, 141.5, 136.4, 136.3, 127.7, 119.6, 119.4, 117.3, 117.2, 105.5, 83.4, 83.2, 44.1, 44.0, 33.2, 30.6, 29.8, 24.8, 24.7, 20.2, 19.7; ^{11}B NMR (128.3 MHz, CDCl3) δ 32.5; $[M+H]^+$: calculated: 419.3041, found: 419.3062.

Compound (**19a**): *2-(4-tert-butyl-1-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexyl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine*. Flash column chromatography (petroleum ether/EtOAc = 30:1) yielded **16a** (40 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer*) ($CDCl_3$, 400 MHz) δ 7.08 (dd, *J* = 8.1, 7.5 Hz, 2H), 6.98 (dd, *J* = 8.3, 0.8 Hz, 2H), 6.28 (dd, *J* = 7.3, 0.9 Hz, 2H), 5.78 (br s, 2H), 2.11 (apparent d, *J* = 13.0 Hz, 2H), 1.80 (apparent dd, *J* = 12.2, 1.9 Hz, 2H), 1.28 (apparent td, *J* = 12.7, 2.5 Hz, 2H), 1.25 (s, 12H), 1.04 (dd, *J* = 12.0, 3.1 Hz, 2H), 0.97 (m, 1H), 0.84 (s, 9H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.3, 136.3, 127.5, 119.6, 117.1, 105.4, 83.2, 47.9, 32.5, 30.7, 27.4, 27.3,

24.7; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.6; HRMS-(ESI+) for $C_{26}H_{39}B_2N_2O_2$ $[M+H]^+$: calculated: 433.3198, found: 433.3186.

Compounds (**19a** and **19b**):

^{1}H NMR (mixture 70:30 two diastereoisomers *(ds)* **19a** *and* **19b**) ($CDCl_3$, 400 MHz) δ 7.09 (apparent m, 0.7 x 2H **19a** + 0.3 x 2H **19b**), 6.98 (apparent td, *J* = 8.4, 1.0 Hz, 0.7 x 2H **19a** + 0.3 x 2H **19b**), 6.32 (dd, *J* = 7.3, 1.0 Hz, 2H **19b**), 6.28 (dd, *J* = 7.3, 0.9 Hz, 2H **19a**), 5.78 (br s, 0.7 x 2H **19a** + 0.3 x 2H **19b**), 2.09 (m, 0.7 x 2H **19a** + 0.3 x 2H **19b**), 1.80 (apparent d, *J* = 12.4, 2H **19a**), 1.72 (apparent d, *J* = 11.3, 2H **19b**), 1.24 (m, 0.7 x 14H **19a** + 0.3 x 2H **19b**), 1.17 (s, 12H **19b**), 1.00 (m, 0.7 x 3H **19a** + 0.3 x 3H **19b**), 0.84 (s, 9H **19a**), 0.78 (s, 9H **19b**); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.5, 136.4, 127.7, 119.6, 117.3, 117.2, 105.6, 105. 5, 83.4, 83.1, 48.9, 48.1, 32.7, 30.9, 30.4, 27.7, 27.6, 27.5, 26.8, 24.9, 24.7; ^{11}B NMR (128.3 MHz, CDCl3) δ 31.4.

Compound (**20a**): Flash column chromatography (petroleum ether/EtOAc = 40:1) yielded **20a** (32 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer* **20a**) ($CDCl_3$, 400 MHz) δ 7.30 (m, 2H), 7.19 (m, 3H), 7.10 (dd, *J* = 8.3, 7.3 Hz, 2H), 7.00 (dd, *J* = 8.3, 1.1 Hz, 2H), 6.30 (dd, *J* = 7.2, 1.1 Hz, 2H), 5.82 (br s, 2H), 2.47 (m, 1H), 2.21 (m, 2H), 1.94 (m, 2H), 1.54 (m, 4H), 1.30 (s, 12H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 147.8, 141.2, 136.4, 128.3, 127.5, 126.7, 125.8, 119.7, 117.2, 105.5, 83.4, 44.4, 34.2, 30.4, 29.7, 24.8; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.4; HRMS-(ESI+) for $C_{28}H_{35}B_2N_2O_2$ $[M+H]^+$: calculated: 453.2885 found: 453.2875.

Compounds (**20a** and **20b**):

^{1}H NMR (mixture 54:46 two diastereoisomers *(ds)* **20a** *and* **20b**) ($CDCl_3$, 400 MHz) δ 7.33-6.99 (m, 0.54 x 9H **20a** + 0.46 x 9H **20b**), 6.34 (apparent d, *J* = 7.3, 2H **20b**), 6.30 (apparent d, *J* = 7.3 Hz, 2H **20a**), 5.83 (br s, 2H **20b**), 5.82 (br s, 2H **20a**), 2.49 (m, 0.54 x 1H **20a** + 0.46 x 1H **20b**), 2.22-1.34 (m, 0.54 x 8H **20a** + 0.46 x 8H **20b**), 1,26 (s, 12H **20b**), 1.22 (s, 12H **20a**); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 148.1, 147.4, 141.5, 141.4, 136.4, 136.3, 128.5, 128.3, 127.7, 127.0, 126.8, 126.0, 125.8, 117.4, 105.7, 105.6, 83.5, 83.4, 44.6, 44.4, 34.4, 33.7, 30.6, 29.8, 24.9, 24.7; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.7.

Compound (**21a**): Flash column chromatography (hexane/EtOAc = 50:1) yielded **21a** (25 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer* **21a**) ($CDCl_3$, 400 MHz) δ 7.33 (m, 2H), 7.25 (m, 2H), 7.21 (m, 1H), 7.08 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.99 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.27 (dd, *J* = 7.3, 1.1 Hz, 2H), 5.78 (br s, 2H), 2.61 (tt, *J* = 11.9, 3.1 Hz, 1H), 2.23 (m, 1H), 2.11 (m, 1H), 1.93 (m, 2H), 1.46 (m, 4H), 1.31 (s, 6H), 1.30 (s, 6H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 148.1, 141.4, 136.4, 128.4, 127.7, 127.0, 126.1, 119.6, 117.4, 105.6, 83.5, 44.5, 39.0, 33.3, 29.8, 27.1, 25.1, 24.8; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.5; HRMS-(ESI+) for $C_{28}H_{35}B_2N_2O_2$ $[M+H]^+$: calculated: 453.2885, found: 453.2882.

Compounds (**21a** and **21b**):

^{1}H NMR (mixture 83:17 two diastereoisomers *(ds)* **21a** *and* **21b**) ($CDCl_3$, 400 MHz) δ 7.34-7.16 (m, 0.83 x 5H **21b** + 0.17 x 5H **21a**), 7.12 (dd, *J* = 8.1, 7.3 Hz, 2H **21b**), 7.08 (dd, *J* = 8.3, 7.3 Hz, 2H **21a**), 7.02 (dd, *J* = 8.3, 0.8 Hz, 2H **21b**), 6.99 (dd, *J* = 8.3, 1.0 Hz, 2H **21a**), 6.35 (dd, *J* = 7.3, 0.9 Hz, 2H *minor ds*), 6.27 (dd, *J* = 7.3, 1.1 Hz, 2H **21a**), 5.83 (br s, 2H **21b**), 5.78 (br s, 2H **21a**), 2.60

(m, *J* = 10.9, 2.6 Hz, 0.83 x 1H **21b** + 0.17 x 1H **21a**), 2.13 (m, 0.83 x 2H **21b** + 0.17 x 2H **21a**), 1.86 (m, 0.83 x 2H **21b** + 0.17 x 2H **21a**), 1.63-1.15 (m, 0.83 x 16H **21b** + 0.17 x 16H **21a**); ^{13}C {^{1}H} NMR (only the signals of the *minor ds* are reported) (100 MHz, CDCl3) δ 147.9, 141.5, 136.6, 128.4, 127.7, 127.0, 126.1, 119.4, 117.4, 105.7, 83.2, 43.4, 38.1, 34.2, 29.1, 26.0, 24.8, 24.6; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.5; $[M+H]^+$: calculated: 453.2885, found: 453.2880.

Compound (**22a**): Flash column chromatography (petroleum ether/EtOAc = 60:1) yielded **22a** (32 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer* **22a**) ($CDCl_3$, 400 MHz) δ 7.09 (apparent t, *J* = 8.0, 2H), 6.98 (dd, *J* = 8.2, 1.6 Hz, 2H), 6.28 (dd, *J* = 7.4, 1.6 Hz, 2H), 5.99 (br s, 2H), 1.96 (m, 1H), 1.68 (m, 2H), 1.60 (m, 2H), 1.37 (m, 4H), 1.28 (s, 6H), 1.26 (s, 6H), 1.13 (d, *J* = 7.1 Hz, 3H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.7, 136.4, 127.7, 119.6, 117.1, 105.5, 82.9, 35.2, 33.8, 31.5, 26.2, 25.8, 25.1, 24.9, 20.3; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 34.5; $[M+H]^+$: calculated: 391.2728, found: 391.2723.

Compound (**23a**): Flash column chromatography (petroleum ether/EtOAc = 30:1) yielded **23a** (40 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer* **23a**) ($CDCl_3$, 400 MHz) δ 7.08 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.97 (dd, *J* = 8.3, 1.0 Hz, 2H), 6.27 (dd, *J* = 7.3, 1.0 Hz, 2H), 6.04 (br s, 2H), 1.99 (m, 1H), 1.68 (m, 8H), 1.43 (m, 1H), 1.35-1.13 (m, 15H), 0.97 (m, 3H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.7, 136.4, 127.7, 119.6, 117.1, 105.5, 82.8, 47.6, 40.6, 35.7, 35.3, 34.2, 31.1, 27.8, 26.8, 26.5, 25.2, 25.1; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 33.9; HRMS-(ESI+) for $C_{26}H_{37}B_2N_2O_2$ $[M+H]^+$: calculated: 431.3041, found: 431.3054.

Compound (**24a**): *2-((3R,5S,10S,13R,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine* (**24a**): Flash column chromatography (petroleum ether/EtOAc = 50:1) yielded **24a** (24 % yield) as an off-white sticky solid.

^{1}H NMR (*major diastereoisomer* **24a**) ($CDCl_3$, 400 MHz) δ 7.08 (dd, *J* = 8.3, 7.3 Hz, 2H), 6.97 (dd, *J* = 8.4, 0.9 Hz, 2H), 6.28 (dd, *J* = 7.3, 1.0 Hz, 2H), 5.76 (br s, 2H), 1.97 (dt, *J* = 12.3, 3.2 Hz, 1H), 1.87-1.48 (m, 10H), 1.34 (m, 6H), 1.24 (m, 13H), 1.19-0.95 (m, 12H), 0.90 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.77 (s, 3H), 0.65 (s, 3H), 0.58 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.5, 136.4, 127.7, 119.6, 117.2, 105.5, 83.4, 56.7, 56.4, 55.3, 47.4, 42.7, 40.2, 39.6, 39.0, 36.3, 36.0, 35.9, 35.6, 32.4, 32.3, 29.2, 28.4, 28.2, 25.5, 24.9, 24.7, 24.3, 23.9, 22.9, 22.7, 20.9, 18.8, 12.3, 12.2; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.3; HRMS-(ESI+) for $C_{43}H_{67}B_2N_2O_2$ $[M+H]^+$: calculated: 665.5389, found: 665.5396.

Compound (**24b**): *2-((3S,5S,10S,13R,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hexadecahydro-1H-cyclopenta[a]phenanthren-3-yl)-2,3-dihydro-1H-naphtho[1,8-de][1,3,2]diazaborinine* (**24a**): Flash column chromatography (petroleum ether/EtOAc = 50:1) yielded **24a** (10 % yield) as an off-white sticky solid.

^{1}H NMR (*minor diastereoisomer* **24b**) ($CDCl_3$, 400 MHz) δ 7.11 (dd, *J* = 8.1, 7.2 Hz, 2H), 7.00 (dd, *J* = 8.3, 0.8 Hz, 2H), 6.32 (dd, *J* = 7.4, 0.8 Hz, 2H), 5.78 (br s, 2H), 1.91 (m, 1H), 1.82-1.41 (m, 10H), 1.32-1.23 (m, 8H), 1.18 (s, 12H), 1.12-0.99 (m, 8H), 0.85 (m, 12H), 0.78 (s, 3H), 0.62 (s, 3H), 0.59 (m, 1H); ^{13}C {^{1}H} NMR (100 MHz, $CDCl_3$) δ 141.6, 136.3, 127.7, 119.4, 117.2, 105.6, 83.2, 56.5, 56.3, 53.6, 46.0, 42.7, 40.0, 39.6, 37.8, 36.2, 35.9, 35.6, 32.4, 31.9,

29.3, 28.4, 28.1, 24.8, 24.7, 24.3, 24.0, 22.9, 22.7, 20.8, 18.8, 12.2, 12.0; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 28.2; HRMS-(ESI+) for $C_{43}H_{67}B_2N_2O_2$ $[M+H]^+$: calculated: 665.5389, found: 665.5387.

Procedures for the proto-deborylation reaction of 1,1-diboron compounds

Protocol A:

Into an oven-dried resealable Teflon screw-cap Schlenk reaction tube equipped with a magnetic stir bar in Argon was charged with 0.05 mmol of **22a**, 0.25 mmol (5 equiv) of Potassium *tert*-butoxide (KO*t*Bu) then 0.5 mL of dry Toluene were added. The thus obtained suspension was stirred for 12h at room temperature. After this period of time the mixture was filtered over a Celite® pad and solvent was gently concentrated on a rotary evaporator. This crude residue was purified by silica gel flash chromatography to afford the corresponding proto-deborylation compounds.

Compound (*trans*-**25(H)**: Prepared following protocol A (89% conversion) and purified by a short flash column chromatography (hexane/EtOAc = 60:1) yielded (*trans*-**25(H)**).

^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.10 (dd, *J* = 8.0, 7.1, 2H), 7.00 (dd, *J* = 8.1, 2.4 Hz, 2H), 6.30 (dd, *J* = 7.4, 1.0 Hz, 2H), 5.60 (br s, 2H), 1.75 (m, 2H), 1.24 (m, 4H), 1.01-0.84 (m, 6H), 0.55 (t, *J* = 10.4 Hz, 1H); ^{13}C {^{1}H} NMR (100 MHz, CDCl3) δ 141.5, 136.5, 132.0, 127.7, 119.8, 117.4, 105.6, 36.6, 34.5, 29.9, 27.2, 26.9, 23.1, 22.8; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 32.4; HRMS-(ESI+) for $C_{17}H_{22}BN_2$ $[M+H]^+$: calculated: 265.1856, found: 265.1859.

Protocol B:

Into an oven-dried resealable Teflon screw-cap Schlenk reaction tube equipped with a magnetic stir bar in Argon was charged with 0.07 mmol of a mixture of (**17a** and **17b** (65:35)), 0.21 mmol (3 equiv) of Potassium *tert*-butoxide (KO*t*Bu) then 0.5 mL of dry Toluene were added. The thus obtained suspension was stirred for 1h at 0 ºC. After this period of time the mixture was filtered over a Celite® pad and solvent was gently concentrated on a rotary evaporator. This crude residue (96% conversion) was purified by silica gel flash chromatography (hexane/EtOAc = 60:1) to afford the corresponding proto-deborylation compounds *trans*-**26(H)** and *cis*-**26(H)**.

Compounds (*trans*-**26(H)** and *cis*-**26(H)**: Short flash column chromatography (hexane/EtOAc = 60:1) yielded a mixture *trans*/*cis* (76:24) of (**26(H)**).

^{1}H NMR (mixture of the two diastereoisomers (*ds*)) ($CDCl_3$, 400 MHz) δ 7.09 (apparent m, 0.76 x 2H *trans*-**26(H)** + 0.24 x 2H *cis*-**26(H)**), 6.99 (apparent m, 0.76 x 2H *trans*-**26(H)** + 0.24 x 2H *cis*-**26(H)**), 6.31 (dd, *J* = 7.3, 1.0 Hz, 2H *trans*-**26(H)**), 6.29 (dd, *J* = 7.3, 1.0 Hz, 2H *cis*-**26(H)**), 5.66 (s, 2H *trans*-**26(H)**), 5.59 (s, 2H *cis*-**26(H)**), 1.78 (m, 0.76 x 2H *trans*-**26(H)** + 0.24 x 2H *cis*-**26(H)**), 1.60 (m, 0.76 x 2H *trans*-**26(H)** + 0.24 x 2H *cis*-**26(H)**), 1.24 (m, 0.76 x 2H *trans*-**26(H)** + 0.24 x 2H *cis*-**26(H)**), 1.13 (m, 0.76 x 2H *trans*-**26(H)** + 0.24 x 2H *cis*-**26(H)**), 0.89 (m, 0.76 x 5H *trans*-**26(H)** + 0.24 x 5H *cis*-**26(H)**); ^{13}C {^{1}H} NMR (mixture of the two diastereoisomers (*ds*), only *major ds* (*trans*-**26(H)**) signals are given) (100 MHz, $CDCl_3$) δ 141.4, 136.4, 127.7, 119.5, 117.4, 105.5, 36.6, 33.7, 28.9, 26.3, 23.2; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 31.9; HRMS-(ESI+) for $C_{17}H_{22}BN_2$ $[M+H]^+$: calculated: 265.1856, found: 265.1861.

Compounds (*cis*-**27(H)**: Prepared following protocol A (full conversion (99%)) and purified by a short flash column chromatography (hexane/EtOAc = 60:1) yielded the *cis*-(**27(H)**).

^{1}H NMR ($CDCl_3$, 400 MHz) 7.32 (m, 2H), 7.22 (m, 3H), 7.12 (ddd, *J* = 8.3, 7.3, 0.7, 2H), 7.02 (dd, *J* = 8.4, 1.0 Hz, 2H), 6.33 (dd, *J* = 7.3, 0.9 Hz, 2H), 5.72 (br s, 2H), 2.62 (ddt, *J* = 11.2, 7.7, 3.5 Hz, 1H), 1.93-1.79 (m, 4H), 1.68-1.45 (m, 4H), 0.87 (m, 1H); ^{13}C {^{1}H} NMR (75.4 MHz, $CDCl_3$) δ 147.6, 141.2, 136.4, 128.5, 127.7, 127.0, 126.1, 119.5, 117.6, 105.7, 42.4, 35.2, 34.8, 29.8, 27.4, 25.4; ^{11}B NMR (128.3 MHz, $CDCl_3$) δ 31.7; HRMS-(ESI+) for $C_{22}H_{23}BN_2Na$ $[M+Na]^+$: calculated: 349.1851, found: 349.1859.

4. X-ray experimental details

Crystal structure determination for **16a**, **23a** and **24a** were carried out using a Apex DUO Kappa 4-axis goniometer equipped with an APPEX 2 4K CCD area detector, a Microfocus Source E025 IuS using Mo Kα radiation (λ = 0.71073 Å), Quazar MX multilayer Optics as monochromator and an Oxford Cryosystems low temperature device Cryostream 700 plus (T = -173 °C). Full-sphere data collection was used with ω and φ scans. APEX-2[6] software was used for the data collection, data reduction was performed using Bruker Saint[7] V/.60A and the absorption correction using SADABS.[8] Crystal structure solution was achieved using direct methods as implemented in SHELXTL[9] and visualized using the program XP. Missing atoms were subsequently located from difference Fourier synthesis and added to the atom list. Least-squares refinement on F^2 using all measured intensities was carried out using the program SHELXTL. All non-hydrogen atoms were refined including anisotropic displacement parameters.

Crystal structure data of **16a**:

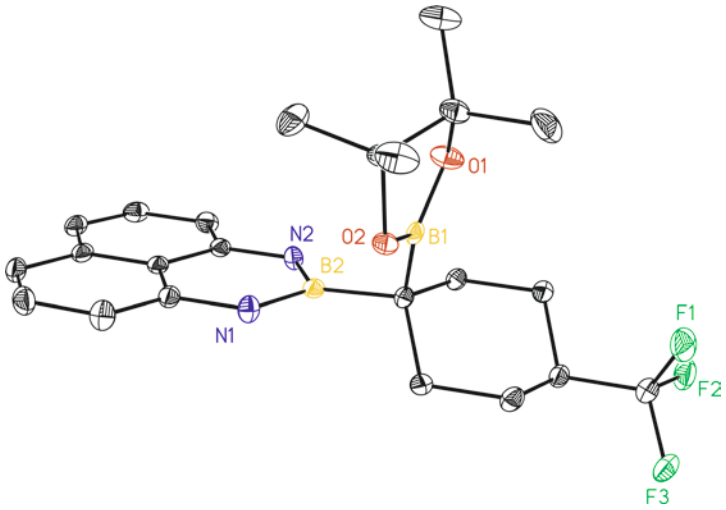


Table 1. Crystal data and structure refinement for mo_AC_CF3_0m.

Identification code	mo_AC_CF3_0m
Empirical formula	$C_{23}\ H_{29}\ B_2\ F_3\ N_2\ O_2$
Formula weight	444.10
Temperature	100(2) K

6 APEX II versions v1.0-22, v2009.1-0 and v2009.1-02. Bruker, Bruker AXS Inc., Madison, WI, 2007.

7 Bruker SAINT versions V.2.10(2003), V/.60A and V7.60A. Bruker (2007). Bruker AXS Inc., Madison, WI.

8 SADABS version 2.03, Bruker AXS Inc.: Madison, WI, 2001.

9 Sheldrick, G.M. Acta Cryst. 2008 A64, 112-122. SHELXTL versions V6.12 and 6.14.

Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 13.3258(3)Å	α= 90°.
	b = 12.8123(3)Å	β = 116.6129(8)°.
	c = 14.6052(4)Å	γ = 90°.
Volume	2229.42(10) $Å^3$	
Z	4	
Density (calculated)	1.323 mg/m^3	
Absorption coefficient	0.099 mm^{-1}	
F(000)	936	
Crystal size	0.20 x 0.10 x 0.05 mm^3	
Theta range for data collection	2.227 to 27.514°.	
Index ranges	-13<=h<=16,-15<=k<=16,-18<=l<=18	
Reflections collected	17498	
Independent reflections	5055[R(int) = 0.0264]	
Completeness to theta =27.514°	98.4%	
Absorption correction	Empirical	
Max. and min. transmission	0.995 and 0.957	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5055/ 231/ 360	
Goodness-of-fit on F^2	1.042	
Final R indices [I>2sigma(I)]	R1 = 0.0398, wR^2 = 0.1030	
R indices (all data)	R1 = 0.0507, wR^2 = 0.1098	
Largest diff. peak and hole	0.354 and -0.253 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for mo_AC_CF3_0m.

Bond lengths----------	
B1-O1	1.3631(17)
B1-O2'	1.368(9)
B1-O2	1.3792(18)
B1-C5	1.5729(19)
B2-N2	1.4155(18)
B2-N1	1.4219(17)
B2-C5	1.5935(17)
F1-C1	1.3511(16)
F2-C1	1.3461(16)
F3-C1	1.3467(16)
N1-C22	1.3963(16)
N2-C14	1.3979(15)
O1-C8	1.4639(17)
O1-C8'	1.598(12)
C1-C2	1.5049(17)
C2-C7	1.5319(17)
C2-C3	1.5322(18)
C3-C4	1.5306(16)
C4-C5	1.5457(16)
C5-C6	1.5525(17)
C6-C7	1.5310(17)
O2-C9	1.4697(18)
C8-C11	1.518(2)
C8-C10	1.522(2)
C8-C9	1.557(2)
C9-C12	1.519(2)
C9-C13	1.528(2)
O2'-C9'	1.473(9)
C8'-C10'	1.518(5)
C8'-C11'	1.518(5)
C8'-C9'	1.551(5)
C9'-C12'	1.520(5)
C9'-C13'	1.526(5)
C14-C15	1.3793(18)
C14-C23	1.4236(17)
C15-C16	1.4079(18)
C16-C17	1.3674(19)
C17-C18	1.4213(19)
C18-C19	1.4183(19)
C18-C23	1.4280(17)
C19-C20	1.370(2)
C20-C21	1.4038(18)
C21-C22	1.3789(18)
C22-C23	1.4229(18)

Angles----------

O1-B1-O2'	108.0(5)
O1-B1-O2	113.17(12)
O1-B1-C5	123.40(11)
O2'-B1-C5	127.0(5)
O2-B1-C5	123.17(12)
N2-B2-N1	115.75(11)
N2-B2-C5	122.42(11)
N1-B2-C5	121.77(11)
C22-N1-B2	123.34(11)
C14-N2-B2	124.05(11)
B1-O1-C8	107.06(10)
B1-O1-C8'	103.1(4)
F2-C1-F3	106.38(10)
F2-C1-F1	106.10(11)
F3-C1-F1	106.02(11)
F2-C1-C2	112.39(11)
F3-C1-C2	112.57(11)
F1-C1-C2	112.85(11)
C1-C2-C7	110.86(10)
C1-C2-C3	110.80(10)
C7-C2-C3	111.12(10)
C4-C3-C2	110.18(10)
C3-C4-C5	112.94(10)
C4-C5-C6	109.37(10)
C4-C5-B1	111.96(10)
C6-C5-B1	110.93(10)
C4-C5-B2	111.08(10)
C6-C5-B2	110.24(10)
B1-C5-B2	103.15(10)
C7-C6-C5	112.13(10)
C6-C7-C2	111.29(10)
B1-O2-C9	105.71(12)
O1-C8-C11	108.04(16)
O1-C8-C10	107.98(13)
C11-C8-C10	110.74(14)
O1-C8-C9	101.33(11)
C11-C8-C9	115.07(15)
C10-C8-C9	112.93(13)
O2-C9-C12	109.36(18)
O2-C9-C13	106.37(12)
C12-C9-C13	110.76(14)
O2-C9-C8	101.80(11)
C12-C9-C8	115.22(16)
C13-C9-C8	112.55(13)
B1-O2'-C9'	107.8(9)
C10'-C8'-C11'	111.9(7)
C10'-C8'-C9'	114.1(7)
C11'-C8'-C9'	115.7(7)
C10'-C8'-O1	101.6(13)

C11'-C8'-O1	120.1(9)
C9'-C8'-O1	91.4(7)
O2'-C9'-C12'	106.3(10)
O2'-C9'-C13'	106.9(16)
C12'-C9'-C13'	110.7(7)
O2'-C9'-C8'	102.7(8)
C12'-C9'-C8'	115.9(6)
C13'-C9'-C8'	113.4(7)
C15-C14-N2	122.24(11)
C15-C14-C23	120.28(11)
N2-C14-C23	117.47(11)
C14-C15-C16	120.00(12)
C17-C16-C15	121.16(12)
C16-C17-C18	120.64(12)
C19-C18-C17	122.76(12)
C19-C18-C23	118.72(12)
C17-C18-C23	118.53(12)
C20-C19-C18	120.34(12)
C19-C20-C21	121.31(12)
C22-C21-C20	120.13(12)
C21-C22-N1	121.80(12)
C21-C22-C23	120.09(11)
N1-C22-C23	118.10(11)
C22-C23-C14	121.22(11)
C22-C23-C18	119.39(11)
C14-C23-C18	119.38(11)

Table 3. Torsion angles [°] for mo_AC_CF3_0m.

N2-B2-N1-C22	-1.91(18)
C5-B2-N1-C22	175.45(11)
N1-B2-N2-C14	-0.12(18)
C5-B2-N2-C14	-177.46(11)
O2'-B1-O1-C8	-9.4(6)
O2-B1-O1-C8	9.65(14)
C5-B1-O1-C8	-176.00(11)
O2'-B1-O1-C8'	-39.0(7)
O2-B1-O1-C8'	-20.0(4)
C5-B1-O1-C8'	154.4(3)
F2-C1-C2-C7	177.75(11)
F3-C1-C2-C7	57.64(14)
F1-C1-C2-C7	-62.32(15)
F2-C1-C2-C3	-58.39(14)
F3-C1-C2-C3	-178.50(11)
F1-C1-C2-C3	61.55(15)
C1-C2-C3-C4	179.80(10)
C7-C2-C3-C4	-56.49(13)
C2-C3-C4-C5	56.58(14)
C3-C4-C5-C6	-54.60(13)
C3-C4-C5-B1	68.77(13)
C3-C4-C5-B2	-176.50(10)
O1-B1-C5-C4	20.53(16)
O2'-B1-C5-C4	-143.5(7)
O2-B1-C5-C4	-165.68(11)
O1-B1-C5-C6	143.01(11)
O2'-B1-C5-C6	-21.0(7)
O2-B1-C5-C6	-43.19(16)
O1-B1-C5-B2	-98.97(13)
O2'-B1-C5-B2	97.0(7)
O2-B1-C5-B2	74.82(14)
N2-B2-C5-C4	-8.41(17)
N1-B2-C5-C4	174.41(11)
N2-B2-C5-C6	-129.80(13)
N1-B2-C5-C6	53.02(15)
N2-B2-C5-B1	111.70(13)
N1-B2-C5-B1	-65.48(15)
C4-C5-C6-C7	53.59(13)
B1-C5-C6-C7	-70.38(13)
B2-C5-C6-C7	176.00(10)
C5-C6-C7-C2	-55.57(14)
C1-C2-C7-C6	-179.73(10)
C3-C2-C7-C6	56.59(14)
O1-B1-O2-C9	12.58(14)
O2'-B1-O2-C9	90.0(17)
C5-B1-O2-C9	-161.79(12)
B1-O1-C8-C11	-147.29(13)
C8'-O1-C8-C11	-61.2(8)

B1-O1-C8-C10	92.89(13)
C8'-O1-C8-C10	179.0(8)
B1-O1-C8-C9	-25.97(13)
C8'-O1-C8-C9	60.2(8)
B1-O2-C9-C12	-149.92(14)
B1-O2-C9-C13	90.43(13)
B1-O2-C9-C8	-27.59(13)
O1-C8-C9-O2	32.24(13)
C11-C8-C9-O2	148.50(15)
C10-C8-C9-O2	-83.01(14)
O1-C8-C9-C12	150.45(17)
C11-C8-C9-C12	-93.3(2)
C10-C8-C9-C12	35.2(2)
O1-C8-C9-C13	-81.26(14)
C11-C8-C9-C13	35.0(2)
C10-C8-C9-C13	163.49(14)
O1-B1-O2'-C9'	9.5(10)
O2-B1-O2'-C9'	-100(2)
C5-B1-O2'-C9'	175.5(5)
B1-O1-C8'-C10'	164.5(7)
C8-O1-C8'-C10'	62.8(8)
B1-O1-C8'-C11'	-71.5(7)
C8-O1-C8'-C11'	-173.2(12)
B1-O1-C8'-C9'	49.5(5)
C8-O1-C8'-C9'	-52.2(6)
B1-O2'-C9'-C12'	-97.3(10)
B1-O2'-C9'-C13'	144.5(9)
B1-O2'-C9'-C8'	24.9(11)
C10'-C8'-C9'-O2'	-145.7(14)
C11'-C8'-C9'-O2'	82.4(12)
O1-C8'-C9'-O2'	-42.3(8)
C10'-C8'-C9'-C12'	-30.3(15)
C11'-C8'-C9'-C12'	-162.2(11)
O1-C8'-C9'-C12'	73.1(10)
C10'-C8'-C9'-C13'	99.4(19)
C11'-C8'-C9'-C13'	-32.5(16)
O1-C8'-C9'-C13'	-157.2(14)
B2-N2-C14-C15	-178.25(12)
B2-N2-C14-C23	2.22(18)
N2-C14-C15-C16	-178.56(12)
C23-C14-C15-C16	0.96(19)
C14-C15-C16-C17	-0.1(2)
C15-C16-C17-C18	-0.4(2)
C16-C17-C18-C19	-179.74(12)
C16-C17-C18-C23	0.06(19)
C17-C18-C19-C20	179.08(13)
C23-C18-C19-C20	-0.72(19)
C18-C19-C20-C21	-0.2(2)
C19-C20-C21-C22	0.7(2)
C20-C21-C22-N1	179.12(12)

C20-C21-C22-C23	-0.1(2)
B2-N1-C22-C21	-177.55(12)
B2-N1-C22-C23	1.68(18)
C21-C22-C23-C14	179.83(12)
N1-C22-C23-C14	0.58(18)
C21-C22-C23-C18	-0.86(18)
N1-C22-C23-C18	179.89(11)
C15-C14-C23-C22	178.02(12)
N2-C14-C23-C22	-2.43(17)
C15-C14-C23-C18	-1.28(18)
N2-C14-C23-C18	178.26(11)
C19-C18-C23-C22	1.26(18)
C17-C18-C23-C22	-178.55(12)
C19-C18-C23-C14	-179.42(11)
C17-C18-C23-C14	0.77(18)

Crystal structure data of **23a**:

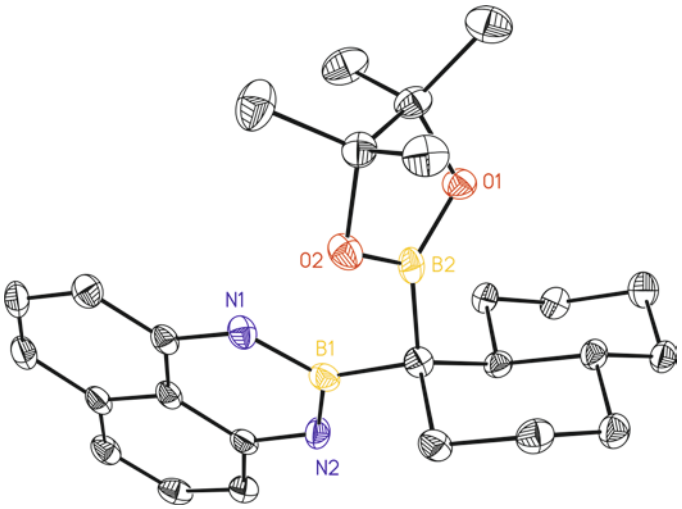


Table 1. Crystal data and structure refinement for mo_121Dias.

Identification code	mo_121Dias	
Empirical formula	$C_{26}\ H_{36}\ B_2\ N_2\ O_2$	
Formula weight	430.19	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 16.4632(13)Å	α= 90°.
	b = 10.9630(9)Å	β = 99.031(3)°.
	c = 13.1045(9)Å	γ = 90°.
Volume	2335.9(3) $Å^3$	
Z	4	
Density (calculated)	1.223 mg/m^3	
Absorption coefficient	0.075 mm^{-1}	
F(000)	928	
Crystal size	0.20 x 0.10 x 0.10 mm^3	
Theta range for data collection	1.252 to 26.415°.	
Index ranges	-20<=h<=20,-9<=k<=13,-15<=l<=16	
Reflections collected	19893	
Independent reflections	4782[R(int) = 0.0555]	
Completeness to theta =26.415°	99.4%	
Absorption correction	Empirical	
Max. and min. transmission	0.993 and 0.764	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4782/ 0/ 293	
Goodness-of-fit on F^2	1.051	
Final R indices [I>2sigma(I)]	R1 = 0.0476, wR^2 = 0.1135	
R indices (all data)	R1 = 0.0975, wR^2 = 0.1480	
Largest diff. peak and hole	0.248 and -0.249 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for mo_121Dias.

Bond lengths----------	
B1-N1	1.419(3)
B1-N2	1.428(3)
B1-C1	1.596(3)
B2-O1	1.376(3)
B2-O2	1.379(3)
B2-C1	1.579(3)
N1-C12	1.389(3)
N2-C20	1.397(3)
O1-C21	1.455(2)
O2-C22	1.467(2)
C1-C2	1.559(3)
C1-C10	1.565(3)
C2-C3	1.533(3)
C2-C7	1.534(3)
C3-C4	1.524(3)
C4-C5	1.510(3)
C5-C6	1.526(3)
C6-C7	1.522(3)
C7-C8	1.532(3)
C8-C9	1.528(3)
C9-C10	1.526(3)
C11-C16	1.420(3)
C11-C12	1.425(3)
C11-C20	1.427(3)
C12-C13	1.377(3)
C13-C14	1.401(3)
C14-C15	1.367(3)
C15-C16	1.421(3)
C16-C17	1.415(3)
C17-C18	1.369(3)
C18-C19	1.399(3)
C19-C20	1.382(3)
C21-C23	1.508(3)
C21-C24	1.531(3)
C21-C22	1.556(3)
C22-C26	1.512(3)
C22-C25	1.519(3)

Angles----------

N1-B1-N2	114.37(19)
N1-B1-C1	122.77(19)
N2-B1-C1	122.85(19)
O1-B2-O2	111.63(19)
O1-B2-C1	127.54(18)
O2-B2-C1	120.77(19)
C12-N1-B1	124.78(18)
C20-N2-B1	124.33(18)
B2-O1-C21	108.05(15)
B2-O2-C22	108.03(16)
C2-C1-C10	107.73(16)
C2-C1-B2	113.41(17)
C10-C1-B2	107.98(16)
C2-C1-B1	111.54(16)
C10-C1-B1	108.84(16)
B2-C1-B1	107.23(17)
C3-C2-C7	110.90(16)
C3-C2-C1	112.88(16)
C7-C2-C1	112.34(16)
C4-C3-C2	112.57(16)
C5-C4-C3	110.82(16)
C4-C5-C6	110.24(17)
C7-C6-C5	112.70(16)
C6-C7-C8	111.69(16)
C6-C7-C2	110.81(16)
C8-C7-C2	110.76(17)
C9-C8-C7	112.59(17)
C10-C9-C8	111.56(17)
C9-C10-C1	111.02(16)
C16-C11-C12	119.71(18)
C16-C11-C20	119.58(18)
C12-C11-C20	120.70(18)
C13-C12-N1	122.27(18)
C13-C12-C11	119.76(19)
N1-C12-C11	117.95(18)
C12-C13-C14	120.4(2)
C15-C14-C13	121.2(2)
C14-C15-C16	120.5(2)
C17-C16-C11	118.98(19)
C17-C16-C15	122.50(19)
C11-C16-C15	118.52(19)
C18-C17-C16	120.2(2)
C17-C18-C19	121.3(2)
C20-C19-C18	120.4(2)
C19-C20-N2	122.70(18)
C19-C20-C11	119.50(19)
N2-C20-C11	117.77(18)
O1-C21-C23	109.47(17)
O1-C21-C24	106.01(15)

C23-C21-C24	110.4(2)
O1-C21-C22	102.45(15)
C23-C21-C22	114.82(17)
C24-C21-C22	113.03(18)
O2-C22-C26	107.96(17)
O2-C22-C25	106.83(17)
C26-C22-C25	110.41(17)
O2-C22-C21	102.19(15)
C26-C22-C21	115.00(18)
C25-C22-C21	113.65(17)

Table 3. Torsion angles [°] for mo_121Dias.

N2-B1-N1-C12	-3.3(3)
C1-B1-N1-C12	175.65(18)
N1-B1-N2-C20	2.6(3)
C1-B1-N2-C20	-176.37(18)
O2-B2-O1-C21	-11.9(2)
C1-B2-O1-C21	165.3(2)
O1-B2-O2-C22	-6.9(2)
C1-B2-O2-C22	175.70(17)
O1-B2-C1-C2	10.5(3)
O2-B2-C1-C2	-172.46(17)
O1-B2-C1-C10	129.8(2)
O2-B2-C1-C10	-53.2(2)
O1-B2-C1-B1	-113.0(2)
O2-B2-C1-B1	64.0(2)
N1-B1-C1-C2	-143.90(19)
N2-B1-C1-C2	34.9(3)
N1-B1-C1-C10	97.4(2)
N2-B1-C1-C10	-83.8(2)
N1-B1-C1-B2	-19.2(3)
N2-B1-C1-B2	159.66(19)
C10-C1-C2-C3	175.95(16)
B2-C1-C2-C3	-64.6(2)
B1-C1-C2-C3	56.6(2)
C10-C1-C2-C7	-57.7(2)
B2-C1-C2-C7	61.7(2)
B1-C1-C2-C7	-177.12(16)
C7-C2-C3-C4	53.8(2)
C1-C2-C3-C4	-179.11(16)
C2-C3-C4-C5	-56.0(2)
C3-C4-C5-C6	56.2(2)
C4-C5-C6-C7	-56.9(2)
C5-C6-C7-C8	179.05(17)
C5-C6-C7-C2	55.0(2)
C3-C2-C7-C6	-52.5(2)
C1-C2-C7-C6	-179.87(16)
C3-C2-C7-C8	-177.03(16)
C1-C2-C7-C8	55.6(2)
C6-C7-C8-C9	-176.78(17)
C2-C7-C8-C9	-52.8(2)
C7-C8-C9-C10	54.3(2)
C8-C9-C10-C1	-57.4(2)
C2-C1-C10-C9	58.1(2)
B2-C1-C10-C9	-64.8(2)
B1-C1-C10-C9	179.16(16)
B1-N1-C12-C13	-176.77(19)
B1-N1-C12-C11	1.4(3)
C16-C11-C12-C13	0.0(3)
C20-C11-C12-C13	179.63(18)

C16-C11-C12-N1	-178.28(17)
C20-C11-C12-N1	1.4(3)
N1-C12-C13-C14	177.97(19)
C11-C12-C13-C14	-0.2(3)
C12-C13-C14-C15	0.4(3)
C13-C14-C15-C16	-0.3(3)
C12-C11-C16-C17	179.69(18)
C20-C11-C16-C17	0.0(3)
C12-C11-C16-C15	0.1(3)
C20-C11-C16-C15	-179.55(18)
C14-C15-C16-C17	-179.5(2)
C14-C15-C16-C11	0.0(3)
C11-C16-C17-C18	0.1(3)
C15-C16-C17-C18	179.63(19)
C16-C17-C18-C19	0.2(3)
C17-C18-C19-C20	-0.7(3)
C18-C19-C20-N2	-177.23(18)
C18-C19-C20-C11	0.8(3)
B1-N2-C20-C19	178.0(2)
B1-N2-C20-C11	-0.1(3)
C16-C11-C20-C19	-0.4(3)
C12-C11-C20-C19	179.90(19)
C16-C11-C20-N2	177.64(17)
C12-C11-C20-N2	-2.0(3)
B2-O1-C21-C23	146.39(18)
B2-O1-C21-C24	-94.6(2)
B2-O1-C21-C22	24.11(19)
B2-O2-C22-C26	142.69(18)
B2-O2-C22-C25	-98.56(18)
B2-O2-C22-C21	21.1(2)
O1-C21-C22-O2	-26.90(18)
C23-C21-C22-O2	-145.46(18)
C24-C21-C22-O2	86.73(19)
O1-C21-C22-C26	-143.56(17)
C23-C21-C22-C26	97.9(2)
C24-C21-C22-C26	-29.9(3)
O1-C21-C22-C25	87.81(19)
C23-C21-C22-C25	-30.8(3)
C24-C21-C22-C25	-158.56(18)

Crystal structure data of **24a**:

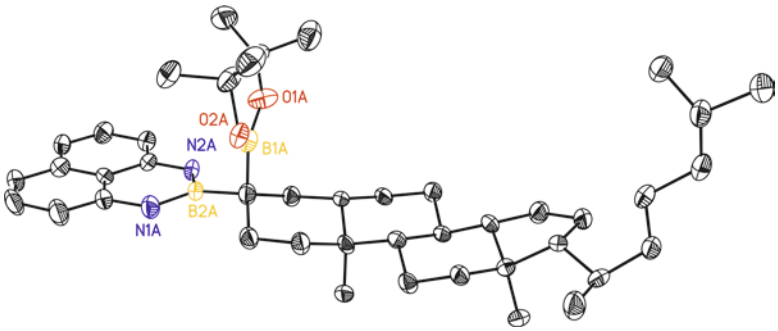


Table 1. Crystal data and structure refinement for mo_Cholestone_DiasI_15.

Identification code	mo_Cholestone_DiasI_15	
Empirical formula	$C_{43}\ H_{66}\ B_2\ N_2\ O_2$	
Formula weight	664.59	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2	
Unit cell dimensions	a = 7.2020(9)Å	α= 90°.
	b = 39.014(4)Å	β = 90.614(4)°.
	c = 13.9823(17)Å	γ = 90°.
Volume	3928.5(8) $Å^3$	
Z	4	
Density (calculated)	1.124 Mg/m^3	
Absorption coefficient	0.066 mm^{-1}	
F(000)	1456	
Crystal size	0.40 x 0.10 x 0.04 mm^3	
Theta range for data collection	1.547 to 28.372°.	
Index ranges	-9<=h<=9,0<=k<=52,0<=l<=18	
Reflections collected	39294	
Independent reflections	9504[R(int) = 0.0843]	
Completeness to theta =28.372°	97.3%	
Absorption correction	Empirical	
Max. and min. transmission	0.997 and 0.534	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	9504/ 517/ 1154	
Goodness-of-fit on F^2	1.032	
Final R indices [I>2sigma(I)]	R1 = 0.0639, wR^2 = 0.1648	
R indices (all data)	R1 = 0.0855, wR^2 = 0.1817	
Flack parameter	x =1(2)	
Largest diff. peak and hole	0.293 and -0.332 e.$Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for mo_Cholestone_DiasI_15.

Bond lengths----------	
B2A-N2A	1.394(8)
B2A-N1A	1.420(8)
B2A-C17A	1.610(7)
N1A-C7A	1.418(7)
N2A-C15A	1.406(6)
B1A-O1A	1.333(9)
B1A-O2A	1.347(10)
B1A-C17A	1.600(9)
O1A-C1A	1.464(9)
O2A-C2A	1.472(9)
C1A-C4A	1.509(9)
C1A-C3A	1.511(11)
C1A-C2A	1.563(12)
C2A-C5A	1.529(11)
C2A-C6A	1.547(11)
O1A'-C1A'	1.469(9)
O2A'-C2A'	1.474(10)
C1A'-C4A'	1.508(10)
C1A'-C3A'	1.510(11)
C1A'-C2A'	1.564(12)
C2A'-C5A'	1.529(12)
C2A'-C6A'	1.545(11)
C7A-C8A	1.394(9)
C7A-C16A	1.411(9)
C8A-C9A	1.410(9)
C9A-C10A	1.366(10)
C10A-C11A	1.408(9)
C11A-C12A	1.407(9)
C11A-C16A	1.441(8)
C12A-C13A	1.355(9)
C13A-C14A	1.420(8)
C14A-C15A	1.373(9)
C15A-C16A	1.422(8)
C17A-C18A	1.522(7)
C17A-C33A	1.539(8)
C18A-C19A	1.528(7)
C19A-C20A	1.533(7)
C20A-C34A	1.543(8)
C20A-C21A	1.544(7)
C20A-C32A	1.544(7)
C21A-C22A	1.537(7)
C21A-C29A	1.539(7)
C22A-C23A	1.532(7)
C23A-C24A	1.517(7)
C24A-C35A	1.543(7)
C24A-C28A	1.551(7)

C24A-C25A	1.562(7)
C25A-C36A	1.533(7)
C25A-C26A	1.564(8)
C26A-C27A	1.543(8)
C27A-C28A	1.521(7)
C28A-C29A	1.522(7)
C29A-C30A	1.544(7)
C30A-C31A	1.519(7)
C31A-C32A	1.526(7)
C32A-C33A	1.538(7)
C36A-C38A	1.509(7)
C36A-C37A	1.540(9)
C38A-C39'	1.495(10)
C38A-C39A	1.532(6)
C39A-C40A	1.514(6)
C40A-C41A	1.504(7)
C41A-C42A	1.519(6)
C41A-C43A	1.528(7)
C39'-C40'	1.535(10)
C40'-C41'	1.507(10)
C41'-C43'	1.522(10)
C41'-C42'	1.529(10)
B1B-O2B"	1.345(9)
B1B-O1B"	1.352(9)
B1B-O1B	1.361(7)
B1B-O2B	1.387(7)
B1B-C17B	1.575(8)
B2B-N2B	1.417(7)
B2B-N1B	1.434(7)
B2B-C17B	1.583(8)
N1B-C7B	1.397(6)
N2B-C15B	1.385(7)
O1B-C1B	1.434(8)
O2B-C2B	1.448(8)
C1B-C4B	1.513(9)
C1B-C3B	1.550(10)
C1B-C2B	1.573(9)
C2B-C5B	1.505(10)
C2B-C6B	1.520(9)
O1B"-C1B"	1.431(9)
O2B"-C2B"	1.446(9)
C1B"-C4B"	1.515(10)
C1B"-C3B"	1.552(10)
C1B"-C2B"	1.571(9)
C2B"-C5B"	1.507(10)
C2B"-C6B"	1.522(9)
C7B-C8B	1.359(8)
C7B-C16B	1.438(7)
C8B-C9B	1.417(8)
C9B-C10B	1.368(8)

C10B-C11B	1.406(8)
C11B-C16B	1.416(7)
C11B-C12B	1.429(7)
C12B-C13B	1.346(9)
C13B-C14B	1.431(8)
C14B-C15B	1.377(7)
C15B-C16B	1.413(8)
C17B-C33B	1.536(7)
C17B-C18B	1.560(7)
C18B-C19B	1.538(7)
C19B-C20B	1.531(6)
C20B-C34B	1.530(8)
C20B-C21B	1.549(7)
C20B-C32B	1.551(7)
C21B-C22B	1.533(6)
C21B-C29B	1.534(7)
C22B-C23B	1.537(7)
C23B-C24B	1.521(7)
C24B-C35B	1.529(8)
C24B-C25B	1.543(8)
C24B-C28B	1.548(6)
C25B-C36B	1.541(7)
C25B-C26B	1.553(8)
C26B-C27B	1.550(8)
C27B-C28B	1.530(7)
C28B-C29B	1.518(8)
C29B-C30B	1.523(6)
C30B-C31B	1.527(7)
C31B-C32B	1.528(6)
C32B-C33B	1.534(7)
C36B-C38B	1.510(7)
C36B-C37B	1.524(8)
C36B-C38"	1.533(10)
C38B-C39B	1.510(7)
C39B-C40B	1.521(7)
C40B-C41B	1.494(7)
C41B-C42B	1.524(8)
C41B-C43B	1.537(7)
C38"-C39"	1.507(10)
C39"-C40"	1.523(10)
C40"-C41"	1.513(10)
C41"-C42"	1.519(10)
C41"-C43"	1.524(10)

Angles----------

N2A-B2A-N1A	116.7(5)
N2A-B2A-C17A	123.2(5)
N1A-B2A-C17A	119.9(5)
C7A-N1A-B2A	122.5(5)
B2A-N2A-C15A	124.1(5)
O1A-B1A-O2A	114.1(6)
O1A-B1A-C17A	123.7(7)
O2A-B1A-C17A	121.7(6)
B1A-O1A-C1A	108.4(6)
B1A-O2A-C2A	106.6(6)
O1A-C1A-C4A	106.8(7)
O1A-C1A-C3A	104.8(7)
C4A-C1A-C3A	111.7(7)
O1A-C1A-C2A	103.4(5)
C4A-C1A-C2A	115.0(7)
C3A-C1A-C2A	113.9(7)
O2A-C2A-C5A	109.7(6)
O2A-C2A-C6A	104.6(7)
C5A-C2A-C6A	110.1(8)
O2A-C2A-C1A	102.3(6)
C5A-C2A-C1A	115.9(7)
C6A-C2A-C1A	113.3(7)
O1A'-C1A'-C4A'	106.8(8)
O1A'-C1A'-C3A'	105.9(9)
C4A'-C1A'-C3A'	111.7(9)
O1A'-C1A'-C2A'	102.4(6)
C4A'-C1A'-C2A'	115.4(8)
C3A'-C1A'-C2A'	113.5(8)
O2A'-C2A'-C5A'	109.0(8)
O2A'-C2A'-C6A'	105.1(9)
C5A'-C2A'-C6A'	110.2(10)
O2A'-C2A'-C1A'	102.2(6)
C5A'-C2A'-C1A'	116.2(9)
C6A'-C2A'-C1A'	113.1(8)
C8A-C7A-C16A	121.5(5)
C8A-C7A-N1A	120.6(6)
C16A-C7A-N1A	117.8(5)
C7A-C8A-C9A	118.0(7)
C10A-C9A-C8A	122.0(6)
C9A-C10A-C11A	121.2(5)
C12A-C11A-C10A	123.2(5)
C12A-C11A-C16A	118.7(6)
C10A-C11A-C16A	118.0(6)
C13A-C12A-C11A	120.9(5)
C12A-C13A-C14A	121.0(6)
C15A-C14A-C13A	120.2(6)
C14A-C15A-N2A	122.8(5)
C14A-C15A-C16A	120.0(5)
N2A-C15A-C16A	117.2(5)

C7A-C16A-C15A	121.7(5)
C7A-C16A-C11A	119.2(5)
C15A-C16A-C11A	119.1(6)
C18A-C17A-C33A	110.1(4)
C18A-C17A-B1A	111.3(5)
C33A-C17A-B1A	108.4(5)
C18A-C17A-B2A	112.2(4)
C33A-C17A-B2A	113.1(5)
B1A-C17A-B2A	101.4(4)
C17A-C18A-C19A	113.3(4)
C18A-C19A-C20A	115.1(5)
C19A-C20A-C34A	108.5(4)
C19A-C20A-C21A	109.9(4)
C34A-C20A-C21A	110.8(4)
C19A-C20A-C32A	107.8(4)
C34A-C20A-C32A	111.6(5)
C21A-C20A-C32A	108.2(4)
C22A-C21A-C29A	109.8(4)
C22A-C21A-C20A	115.1(4)
C29A-C21A-C20A	113.5(4)
C23A-C22A-C21A	113.7(4)
C24A-C23A-C22A	112.3(5)
C23A-C24A-C35A	111.3(4)
C23A-C24A-C28A	107.1(4)
C35A-C24A-C28A	112.0(5)
C23A-C24A-C25A	116.5(5)
C35A-C24A-C25A	109.5(4)
C28A-C24A-C25A	99.9(4)
C36A-C25A-C24A	120.7(4)
C36A-C25A-C26A	112.5(4)
C24A-C25A-C26A	102.6(4)
C27A-C26A-C25A	107.1(4)
C28A-C27A-C26A	104.1(5)
C27A-C28A-C29A	119.3(5)
C27A-C28A-C24A	103.8(4)
C29A-C28A-C24A	115.1(4)
C28A-C29A-C21A	107.7(4)
C28A-C29A-C30A	111.3(4)
C21A-C29A-C30A	111.2(4)
C31A-C30A-C29A	112.8(4)
C30A-C31A-C32A	110.9(5)
C31A-C32A-C33A	112.6(5)
C31A-C32A-C20A	111.4(4)
C33A-C32A-C20A	113.4(4)
C32A-C33A-C17A	111.6(5)
C38A-C36A-C25A	112.4(4)
C38A-C36A-C37A	110.9(5)
C25A-C36A-C37A	113.3(4)
C39'-C38A-C36A	117.0(7)
C36A-C38A-C39A	115.0(4)

C40A-C39A-C38A	111.8(5)
C41A-C40A-C39A	116.0(5)
C40A-C41A-C42A	112.0(5)
C40A-C41A-C43A	112.8(5)
C42A-C41A-C43A	109.4(5)
C38A-C39'-C40'	109.7(10)
C41'-C40'-C39'	112.5(10)
C40'-C41'-C43'	111.3(10)
C40'-C41'-C42'	110.9(10)
C43'-C41'-C42'	110.0(10)
O2B"-B1B-O1B"	112.6(9)
O1B-B1B-O2B	110.2(6)
O2B"-B1B-C17B	122.0(6)
O1B"-B1B-C17B	124.8(7)
O1B-B1B-C17B	124.7(5)
O2B-B1B-C17B	125.0(5)
N2B-B2B-N1B	115.2(5)
N2B-B2B-C17B	122.5(5)
N1B-B2B-C17B	121.9(5)
C7B-N1B-B2B	123.7(5)
C15B-N2B-B2B	124.1(5)
B1B-O1B-C1B	110.4(5)
B1B-O2B-C2B	108.9(5)
O1B-C1B-C4B	110.9(6)
O1B-C1B-C3B	103.4(6)
C4B-C1B-C3B	109.1(6)
O1B-C1B-C2B	102.4(5)
C4B-C1B-C2B	116.4(6)
C3B-C1B-C2B	113.7(6)
O2B-C2B-C5B	109.0(6)
O2B-C2B-C6B	107.1(6)
C5B-C2B-C6B	110.5(6)
O2B-C2B-C1B	101.7(5)
C5B-C2B-C1B	114.7(6)
C6B-C2B-C1B	113.1(6)
B1B-O1B"-C1B"	110.0(7)
B1B-O2B"-C2B"	109.9(7)
O1B"-C1B"-C4B"	110.8(8)
O1B"-C1B"-C3B"	103.5(8)
C4B"-C1B"-C3B"	108.5(8)
O1B"-C1B"-C2B"	103.8(6)
C4B"-C1B"-C2B"	116.1(8)
C3B"-C1B"-C2B"	113.3(8)
O2B"-C2B"-C5B"	108.7(8)
O2B"-C2B"-C6B"	107.2(8)
C5B"-C2B"-C6B"	110.2(8)
O2B"-C2B"-C1B"	103.2(6)
C5B"-C2B"-C1B"	114.0(8)
C6B"-C2B"-C1B"	113.0(7)
C8B-C7B-N1B	122.1(5)

C8B-C7B-C16B	120.5(5)
N1B-C7B-C16B	117.3(5)
C7B-C8B-C9B	119.9(5)
C10B-C9B-C8B	121.2(5)
C9B-C10B-C11B	120.0(5)
C10B-C11B-C16B	119.9(5)
C10B-C11B-C12B	121.6(5)
C16B-C11B-C12B	118.5(5)
C13B-C12B-C11B	120.6(5)
C12B-C13B-C14B	120.9(5)
C15B-C14B-C13B	119.9(5)
C14B-C15B-N2B	122.0(5)
C14B-C15B-C16B	119.7(5)
N2B-C15B-C16B	118.3(5)
C15B-C16B-C11B	120.3(5)
C15B-C16B-C7B	121.2(5)
C11B-C16B-C7B	118.5(5)
C33B-C17B-C18B	109.0(4)
C33B-C17B-B1B	110.2(4)
C18B-C17B-B1B	110.3(4)
C33B-C17B-B2B	113.8(4)
C18B-C17B-B2B	109.9(4)
B1B-C17B-B2B	103.5(4)
C19B-C18B-C17B	111.8(4)
C20B-C19B-C18B	114.4(4)
C34B-C20B-C19B	109.4(4)
C34B-C20B-C21B	110.2(4)
C19B-C20B-C21B	109.8(4)
C34B-C20B-C32B	112.3(4)
C19B-C20B-C32B	107.9(4)
C21B-C20B-C32B	107.2(4)
C22B-C21B-C29B	110.3(4)
C22B-C21B-C20B	114.3(4)
C29B-C21B-C20B	114.9(4)
C21B-C22B-C23B	112.9(4)
C24B-C23B-C22B	112.8(4)
C23B-C24B-C35B	110.6(5)
C23B-C24B-C25B	116.9(5)
C35B-C24B-C25B	110.7(4)
C23B-C24B-C28B	106.6(4)
C35B-C24B-C28B	111.7(5)
C25B-C24B-C28B	99.9(4)
C36B-C25B-C24B	120.3(4)
C36B-C25B-C26B	112.1(4)
C24B-C25B-C26B	103.4(5)
C27B-C26B-C25B	107.2(4)
C28B-C27B-C26B	103.0(4)
C29B-C28B-C27B	119.3(5)
C29B-C28B-C24B	116.2(4)
C27B-C28B-C24B	103.9(4)

C28B-C29B-C30B	111.6(4)
C28B-C29B-C21B	108.3(4)
C30B-C29B-C21B	111.9(4)
C29B-C30B-C31B	112.7(4)
C30B-C31B-C32B	111.1(4)
C31B-C32B-C33B	113.5(4)
C31B-C32B-C20B	112.0(4)
C33B-C32B-C20B	113.2(4)
C32B-C33B-C17B	112.2(4)
C38B-C36B-C37B	114.1(5)
C37B-C36B-C38"	98(3)
C38B-C36B-C25B	112.3(5)
C37B-C36B-C25B	113.5(4)
C38"-C36B-C25B	119(2)
C39B-C38B-C36B	115.5(5)
C38B-C39B-C40B	111.0(5)
C41B-C40B-C39B	116.3(5)
C40B-C41B-C42B	112.6(6)
C40B-C41B-C43B	111.8(6)
C42B-C41B-C43B	108.5(6)
C39"-C38"-C36B	112.6(11)
C38"-C39"-C40"	112.2(11)
C41"-C40"-C39"	111.9(11)
C40"-C41"-C42"	111.7(10)
C40"-C41"-C43"	110.7(11)
C42"-C41"-C43"	110.5(10)

Table 3. Torsion angles [°] for mo_Cholestone_DiasI_15.

N2A-B2A-N1A-C7A	-3.1(8)
C17A-B2A-N1A-C7A	171.4(5)
N1A-B2A-N2A-C15A	2.4(8)
C17A-B2A-N2A-C15A	-171.9(5)
O2A-B1A-O1A-C1A	-10.9(9)
C17A-B1A-O1A-C1A	176.5(6)
O1A-B1A-O2A-C2A	22.1(8)
C17A-B1A-O2A-C2A	-165.1(6)
B1A-O1A-C1A-C4A	-126.0(8)
B1A-O1A-C1A-C3A	115.3(8)
B1A-O1A-C1A-C2A	-4.3(8)
B1A-O2A-C2A-C5A	-145.9(7)
B1A-O2A-C2A-C6A	96.0(8)
B1A-O2A-C2A-C1A	-22.4(7)
O1A-C1A-C2A-O2A	15.9(7)
C4A-C1A-C2A-O2A	131.9(7)
C3A-C1A-C2A-O2A	-97.2(7)
O1A-C1A-C2A-C5A	135.1(7)
C4A-C1A-C2A-C5A	-108.8(9)
C3A-C1A-C2A-C5A	22.0(10)
O1A-C1A-C2A-C6A	-96.1(8)
C4A-C1A-C2A-C6A	19.9(10)
C3A-C1A-C2A-C6A	150.7(8)
O1A'-C1A'-C2A'-O2A'	2.6(10)
C4A'-C1A'-C2A'-O2A'	118.3(11)
C3A'-C1A'-C2A'-O2A'	-111.0(11)
O1A'-C1A'-C2A'-C5A'	121.1(11)
C4A'-C1A'-C2A'-C5A'	-123.2(13)
C3A'-C1A'-C2A'-C5A'	7.5(14)
O1A'-C1A'-C2A'-C6A'	-109.8(11)
C4A'-C1A'-C2A'-C6A'	5.8(14)
C3A'-C1A'-C2A'-C6A'	136.5(12)
B2A-N1A-C7A-C8A	-175.1(6)
B2A-N1A-C7A-C16A	1.5(8)
C16A-C7A-C8A-C9A	1.6(10)
N1A-C7A-C8A-C9A	178.1(6)
C7A-C8A-C9A-C10A	-0.4(11)
C8A-C9A-C10A-C11A	-0.4(11)
C9A-C10A-C11A-C12A	-177.1(6)
C9A-C10A-C11A-C16A	0.0(10)
C10A-C11A-C12A-C13A	178.7(6)
C16A-C11A-C12A-C13A	1.5(9)
C11A-C12A-C13A-C14A	-0.8(10)
C12A-C13A-C14A-C15A	-0.4(9)
C13A-C14A-C15A-N2A	-176.9(5)
C13A-C14A-C15A-C16A	0.7(9)
B2A-N2A-C15A-C14A	177.6(6)
B2A-N2A-C15A-C16A	-0.1(8)

C8A-C7A-C16A-C15A	177.6(6)
N1A-C7A-C16A-C15A	1.0(8)
C8A-C7A-C16A-C11A	-1.9(9)
N1A-C7A-C16A-C11A	-178.5(5)
C14A-C15A-C16A-C7A	-179.5(5)
N2A-C15A-C16A-C7A	-1.7(8)
C14A-C15A-C16A-C11A	0.1(8)
N2A-C15A-C16A-C11A	177.8(5)
C12A-C11A-C16A-C7A	178.4(5)
C10A-C11A-C16A-C7A	1.1(9)
C12A-C11A-C16A-C15A	-1.2(8)
C10A-C11A-C16A-C15A	-178.5(5)
O1A-B1A-C17A-C18A	157.7(6)
O2A-B1A-C17A-C18A	-14.4(7)
O1A-B1A-C17A-C33A	36.5(8)
O2A-B1A-C17A-C33A	-135.6(6)
O1A-B1A-C17A-B2A	-82.7(7)
O2A-B1A-C17A-B2A	105.2(6)
N2A-B2A-C17A-C18A	-154.9(6)
N1A-B2A-C17A-C18A	31.0(7)
N2A-B2A-C17A-C33A	-29.5(7)
N1A-B2A-C17A-C33A	156.3(5)
N2A-B2A-C17A-B1A	86.3(7)
N1A-B2A-C17A-B1A	-87.9(6)
C33A-C17A-C18A-C19A	51.4(7)
B1A-C17A-C18A-C19A	-68.7(6)
B2A-C17A-C18A-C19A	178.4(5)
C17A-C18A-C19A-C20A	-52.7(7)
C18A-C19A-C20A-C34A	-69.3(6)
C18A-C19A-C20A-C21A	169.4(4)
C18A-C19A-C20A-C32A	51.7(6)
C19A-C20A-C21A-C22A	59.2(6)
C34A-C20A-C21A-C22A	-60.8(6)
C32A-C20A-C21A-C22A	176.6(5)
C19A-C20A-C21A-C29A	-173.0(4)
C34A-C20A-C21A-C29A	67.0(5)
C32A-C20A-C21A-C29A	-55.6(6)
C29A-C21A-C22A-C23A	55.1(6)
C20A-C21A-C22A-C23A	-175.3(5)
C21A-C22A-C23A-C24A	-54.6(6)
C22A-C23A-C24A-C35A	-70.2(6)
C22A-C23A-C24A-C28A	52.6(6)
C22A-C23A-C24A-C25A	163.3(4)
C23A-C24A-C25A-C36A	78.4(6)
C35A-C24A-C25A-C36A	-49.0(7)
C28A-C24A-C25A-C36A	-166.7(5)
C23A-C24A-C25A-C26A	-155.5(4)
C35A-C24A-C25A-C26A	77.1(5)
C28A-C24A-C25A-C26A	-40.6(5)
C36A-C25A-C26A-C27A	151.6(4)

C24A-C25A-C26A-C27A	20.3(5)
C25A-C26A-C27A-C28A	8.7(6)
C26A-C27A-C28A-C29A	-164.8(5)
C26A-C27A-C28A-C24A	-35.0(6)
C23A-C24A-C28A-C27A	169.4(5)
C35A-C24A-C28A-C27A	-68.3(6)
C25A-C24A-C28A-C27A	47.5(5)
C23A-C24A-C28A-C29A	-58.4(6)
C35A-C24A-C28A-C29A	64.0(6)
C25A-C24A-C28A-C29A	179.7(4)
C27A-C28A-C29A-C21A	-175.1(4)
C24A-C28A-C29A-C21A	60.4(6)
C27A-C28A-C29A-C30A	-53.0(6)
C24A-C28A-C29A-C30A	-177.4(4)
C22A-C21A-C29A-C28A	-55.5(5)
C20A-C21A-C29A-C28A	173.9(4)
C22A-C21A-C29A-C30A	-177.8(4)
C20A-C21A-C29A-C30A	51.7(6)
C28A-C29A-C30A-C31A	-170.3(5)
C21A-C29A-C30A-C31A	-50.2(6)
C29A-C30A-C31A-C32A	54.3(6)
C30A-C31A-C32A-C33A	172.1(4)
C30A-C31A-C32A-C20A	-59.2(5)
C19A-C20A-C32A-C31A	177.6(4)
C34A-C20A-C32A-C31A	-63.4(5)
C21A-C20A-C32A-C31A	58.7(6)
C19A-C20A-C32A-C33A	-54.2(6)
C34A-C20A-C32A-C33A	64.9(6)
C21A-C20A-C32A-C33A	-173.0(4)
C31A-C32A-C33A-C17A	-174.9(4)
C20A-C32A-C33A-C17A	57.5(6)
C18A-C17A-C33A-C32A	-53.9(6)
B1A-C17A-C33A-C32A	68.1(5)
B2A-C17A-C33A-C32A	179.7(4)
C24A-C25A-C36A-C38A	175.0(5)
C26A-C25A-C36A-C38A	53.6(6)
C24A-C25A-C36A-C37A	-58.3(7)
C26A-C25A-C36A-C37A	-179.7(5)
C25A-C36A-C38A-C39'	39(3)
C37A-C36A-C38A-C39'	-89(3)
C25A-C36A-C38A-C39A	61.9(7)
C37A-C36A-C38A-C39A	-66.0(7)
C39'-C38A-C39A-C40A	-80(2)
C36A-C38A-C39A-C40A	179.4(6)
C38A-C39A-C40A-C41A	-178.9(6)
C39A-C40A-C41A-C42A	176.3(6)
C39A-C40A-C41A-C43A	-59.7(8)
C36A-C38A-C39'-C40'	-178(2)
C39A-C38A-C39'-C40'	93(4)
C38A-C39'-C40'-C41'	171(3)

C39'-C40'-C41'-C43'	73(3)
C39'-C40'-C41'-C42'	-164(3)
N2B-B2B-N1B-C7B	-0.4(9)
C17B-B2B-N1B-C7B	-174.0(5)
N1B-B2B-N2B-C15B	-2.5(9)
C17B-B2B-N2B-C15B	171.1(6)
O2B"-B1B-O1B-C1B	-21.5(14)
O1B"-B1B-O1B-C1B	81(8)
O2B-B1B-O1B-C1B	-5.3(9)
C17B-B1B-O1B-C1B	173.3(5)
O2B"-B1B-O2B-C2B	86(3)
O1B"-B1B-O2B-C2B	-18.2(15)
O1B-B1B-O2B-C2B	-12.1(8)
C17B-B1B-O2B-C2B	169.3(5)
B1B-O1B-C1B-C4B	143.4(8)
B1B-O1B-C1B-C3B	-99.8(8)
B1B-O1B-C1B-C2B	18.5(8)
B1B-O2B-C2B-C5B	143.8(7)
B1B-O2B-C2B-C6B	-96.7(7)
B1B-O2B-C2B-C1B	22.3(7)
O1B-C1B-C2B-O2B	-24.1(7)
C4B-C1B-C2B-O2B	-145.2(7)
C3B-C1B-C2B-O2B	86.7(8)
O1B-C1B-C2B-C5B	-141.6(7)
C4B-C1B-C2B-C5B	97.3(8)
C3B-C1B-C2B-C5B	-30.8(9)
O1B-C1B-C2B-C6B	90.5(8)
C4B-C1B-C2B-C6B	-30.7(10)
C3B-C1B-C2B-C6B	-158.8(8)
O2B"-B1B-O1B"-C1B"	-7(2)
O1B-B1B-O1B"-C1B"	-87(8)
O2B-B1B-O1B"-C1B"	9(2)
C17B-B1B-O1B"-C1B"	-178.3(9)
O1B"-B1B-O2B"-C2B"	7(2)
O1B-B1B-O2B"-C2B"	13.0(17)
O2B-B1B-O2B"-C2B"	-75(2)
C17B-B1B-O2B"-C2B"	178.6(8)
B1B-O1B"-C1B"-C4B"	129.1(18)
B1B-O1B"-C1B"-C3B"	-114.7(18)
B1B-O1B"-C1B"-C2B"	3.8(18)
B1B-O2B"-C2B"-C5B"	117.4(15)
B1B-O2B"-C2B"-C6B"	-123.5(15)
B1B-O2B"-C2B"-C1B"	-3.9(15)
O1B"-C1B"-C2B"-O2B"	0.0(14)
C4B"-C1B"-C2B"-O2B"	-121.8(15)
C3B"-C1B"-C2B"-O2B"	111.6(15)
O1B"-C1B"-C2B"-C5B"	-117.6(14)
C4B"-C1B"-C2B"-C5B"	120.6(16)
C3B"-C1B"-C2B"-C5B"	-6.1(16)
O1B"-C1B"-C2B"-C6B"	115.4(15)

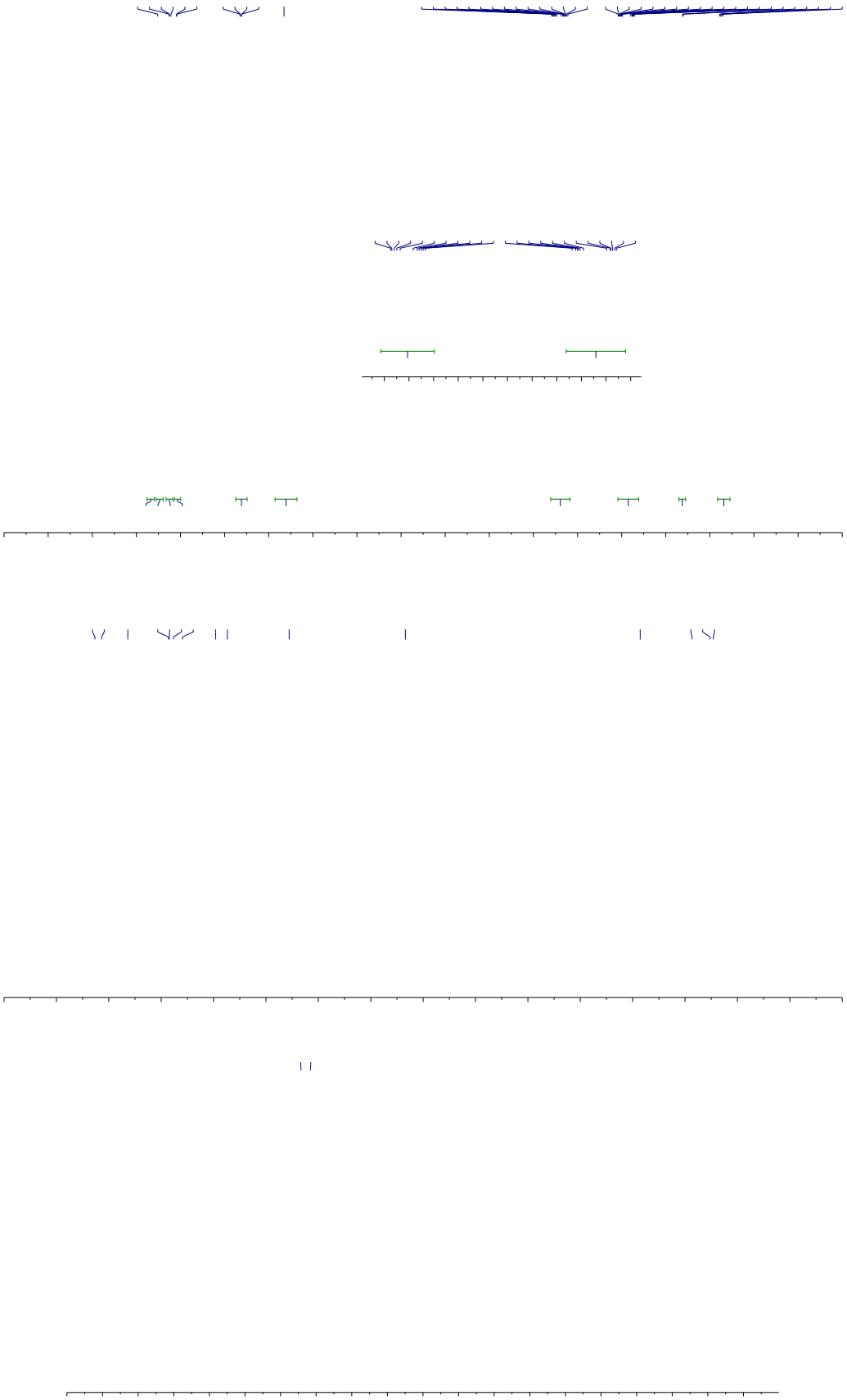
C4B"-C1B"-C2B"-C6B"	-6.4(17)
C3B"-C1B"-C2B"-C6B"	-133.0(15)
B2B-N1B-C7B-C8B	178.4(6)
B2B-N1B-C7B-C16B	2.4(8)
N1B-C7B-C8B-C9B	-177.4(6)
C16B-C7B-C8B-C9B	-1.5(9)
C7B-C8B-C9B-C10B	1.6(10)
C8B-C9B-C10B-C11B	-1.0(10)
C9B-C10B-C11B-C16B	0.3(10)
C9B-C10B-C11B-C12B	179.7(6)
C10B-C11B-C12B-C13B	-177.1(6)
C16B-C11B-C12B-C13B	2.3(9)
C11B-C12B-C13B-C14B	-2.7(10)
C12B-C13B-C14B-C15B	1.7(10)
C13B-C14B-C15B-N2B	179.1(6)
C13B-C14B-C15B-C16B	-0.3(10)
B2B-N2B-C15B-C14B	-176.3(6)
B2B-N2B-C15B-C16B	3.1(9)
C14B-C15B-C16B-C11B	0.1(9)
N2B-C15B-C16B-C11B	-179.4(5)
C14B-C15B-C16B-C7B	178.6(6)
N2B-C15B-C16B-C7B	-0.9(9)
C10B-C11B-C16B-C15B	178.4(6)
C12B-C11B-C16B-C15B	-1.0(9)
C10B-C11B-C16B-C7B	-0.1(9)
C12B-C11B-C16B-C7B	-179.6(5)
C8B-C7B-C16B-C15B	-177.8(6)
N1B-C7B-C16B-C15B	-1.7(8)
C8B-C7B-C16B-C11B	0.8(9)
N1B-C7B-C16B-C11B	176.8(5)
O2B"-B1B-C17B-C33B	33.0(12)
O1B"-B1B-C17B-C33B	-156.3(16)
O1B-B1B-C17B-C33B	-163.3(7)
O2B-B1B-C17B-C33B	15.1(7)
O2B"-B1B-C17B-C18B	153.4(12)
O1B"-B1B-C17B-C18B	-35.9(17)
O1B-B1B-C17B-C18B	-42.9(8)
O2B-B1B-C17B-C18B	135.5(6)
O2B"-B1B-C17B-B2B	-89.1(12)
O1B"-B1B-C17B-B2B	81.7(16)
O1B-B1B-C17B-B2B	74.6(8)
O2B-B1B-C17B-B2B	-106.9(6)
N2B-B2B-C17B-C33B	154.5(5)
N1B-B2B-C17B-C33B	-32.4(8)
N2B-B2B-C17B-C18B	32.0(8)
N1B-B2B-C17B-C18B	-154.9(5)
N2B-B2B-C17B-B1B	-85.9(6)
N1B-B2B-C17B-B1B	87.2(6)
C33B-C17B-C18B-C19B	53.4(6)
B1B-C17B-C18B-C19B	-67.7(5)

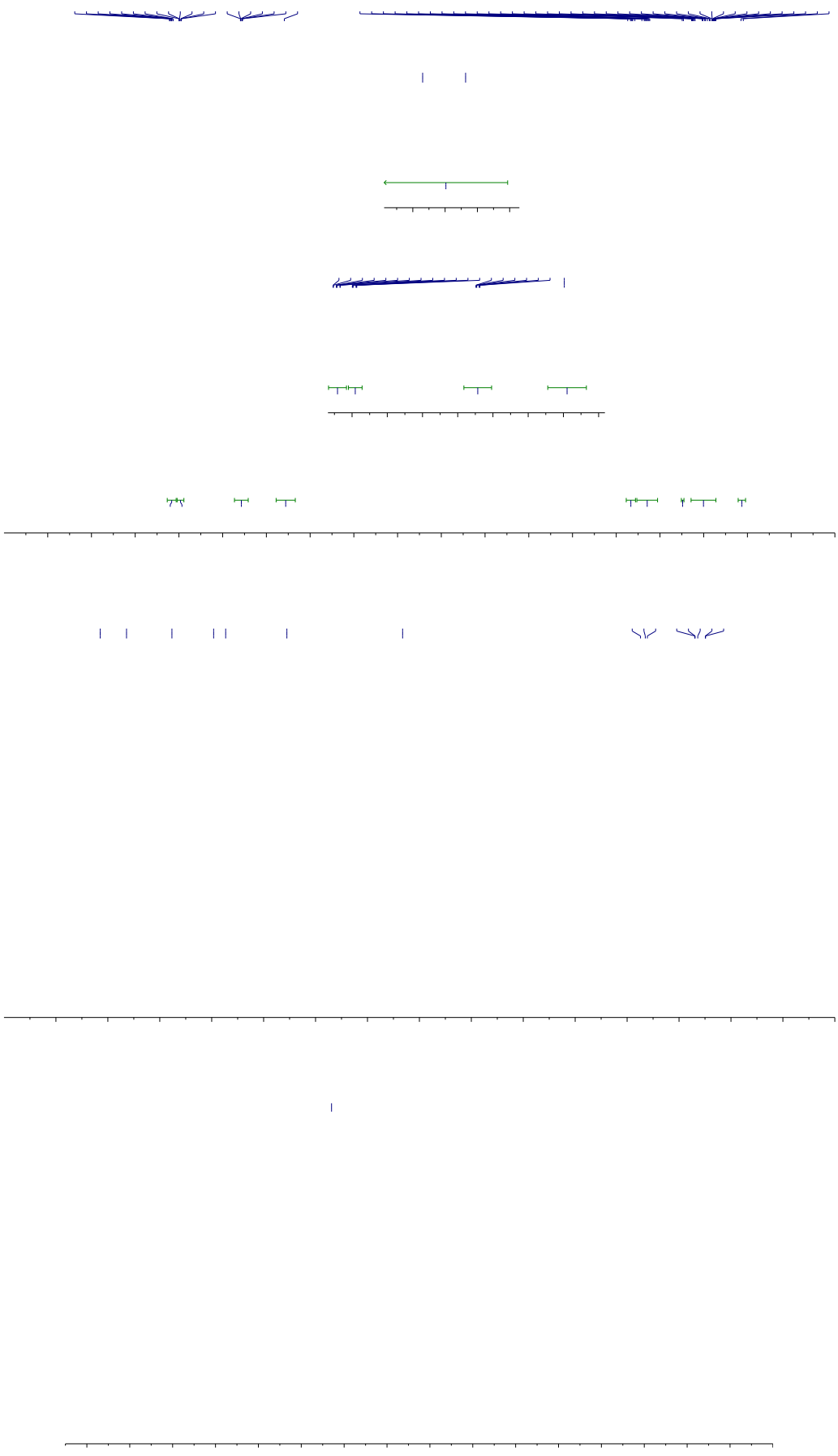
B2B-C17B-C18B-C19B	178.7(5)
C17B-C18B-C19B-C20B	-55.4(6)
C18B-C19B-C20B-C34B	-68.7(6)
C18B-C19B-C20B-C21B	170.2(5)
C18B-C19B-C20B-C32B	53.8(6)
C34B-C20B-C21B-C22B	-60.4(6)
C19B-C20B-C21B-C22B	60.2(6)
C32B-C20B-C21B-C22B	177.1(4)
C34B-C20B-C21B-C29B	68.5(6)
C19B-C20B-C21B-C29B	-170.9(4)
C32B-C20B-C21B-C29B	-54.0(6)
C29B-C21B-C22B-C23B	55.2(6)
C20B-C21B-C22B-C23B	-173.6(4)
C21B-C22B-C23B-C24B	-55.7(6)
C22B-C23B-C24B-C35B	-68.8(6)
C22B-C23B-C24B-C25B	163.3(4)
C22B-C23B-C24B-C28B	52.8(6)
C23B-C24B-C25B-C36B	79.0(6)
C35B-C24B-C25B-C36B	-48.8(7)
C28B-C24B-C25B-C36B	-166.6(5)
C23B-C24B-C25B-C26B	-155.0(4)
C35B-C24B-C25B-C26B	77.1(5)
C28B-C24B-C25B-C26B	-40.7(5)
C36B-C25B-C26B-C27B	151.0(5)
C24B-C25B-C26B-C27B	20.0(6)
C25B-C26B-C27B-C28B	9.3(6)
C26B-C27B-C28B-C29B	-166.6(5)
C26B-C27B-C28B-C24B	-35.3(6)
C23B-C24B-C28B-C29B	-57.0(6)
C35B-C24B-C28B-C29B	63.8(6)
C25B-C24B-C28B-C29B	-179.1(4)
C23B-C24B-C28B-C27B	169.9(5)
C35B-C24B-C28B-C27B	-69.3(6)
C25B-C24B-C28B-C27B	47.8(5)
C27B-C28B-C29B-C30B	-52.0(6)
C24B-C28B-C29B-C30B	-177.7(4)
C27B-C28B-C29B-C21B	-175.6(4)
C24B-C28B-C29B-C21B	58.7(6)
C22B-C21B-C29B-C28B	-54.6(6)
C20B-C21B-C29B-C28B	174.5(4)
C22B-C21B-C29B-C30B	-178.0(5)
C20B-C21B-C29B-C30B	51.1(6)
C28B-C29B-C30B-C31B	-170.9(4)
C21B-C29B-C30B-C31B	-49.4(6)
C29B-C30B-C31B-C32B	53.8(6)
C30B-C31B-C32B-C33B	171.3(5)
C30B-C31B-C32B-C20B	-59.0(6)
C34B-C20B-C32B-C31B	-63.8(6)
C19B-C20B-C32B-C31B	175.6(5)
C21B-C20B-C32B-C31B	57.4(6)

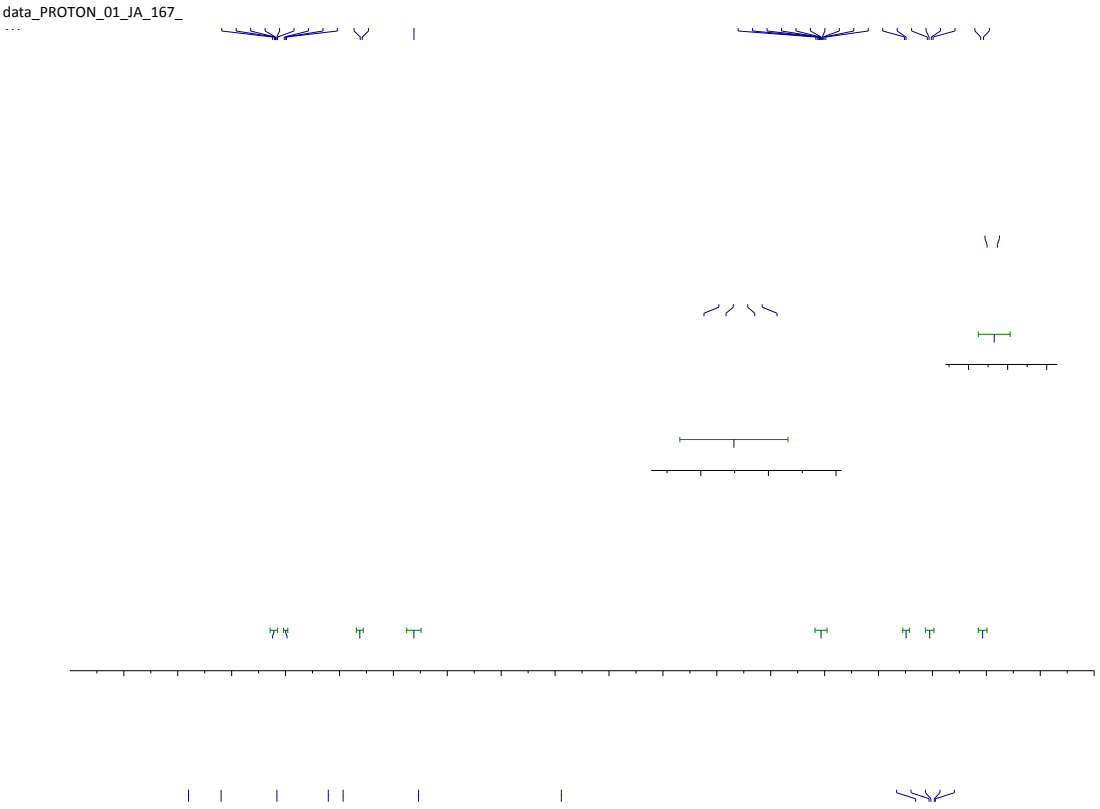
C34B-C20B-C32B-C33B	66.2(5)
C19B-C20B-C32B-C33B	-54.4(6)
C21B-C20B-C32B-C33B	-172.7(4)
C31B-C32B-C33B-C17B	-173.1(5)
C20B-C32B-C33B-C17B	57.8(6)
C18B-C17B-C33B-C32B	-55.0(6)
B1B-C17B-C33B-C32B	66.2(5)
B2B-C17B-C33B-C32B	-178.0(5)
C24B-C25B-C36B-C38B	173.8(5)
C26B-C25B-C36B-C38B	52.0(7)
C24B-C25B-C36B-C37B	-54.9(7)
C26B-C25B-C36B-C37B	-176.7(6)
C24B-C25B-C36B-C38"	-170(2)
C26B-C25B-C36B-C38"	68(2)
C37B-C36B-C38B-C39B	-62.1(8)
C38"-C36B-C38B-C39B	-49(6)
C25B-C36B-C38B-C39B	69.0(7)
C36B-C38B-C39B-C40B	175.8(6)
C38B-C39B-C40B-C41B	-179.5(7)
C39B-C40B-C41B-C42B	-65.8(9)
C39B-C40B-C41B-C43B	171.8(8)
C38B-C36B-C38"-C39"	114(9)
C37B-C36B-C38"-C39"	-78(5)
C25B-C36B-C38"-C39"	45(5)
C36B-C38"-C39"-C40"	166(4)
C38"-C39"-C40"-C41"	86(4)
C39"-C40"-C41"-C42"	61(3)
C39"-C40"-C41"-C43"	-175(3)

---

5. ^{1}H, ^{11}B and ^{13}C spectra:

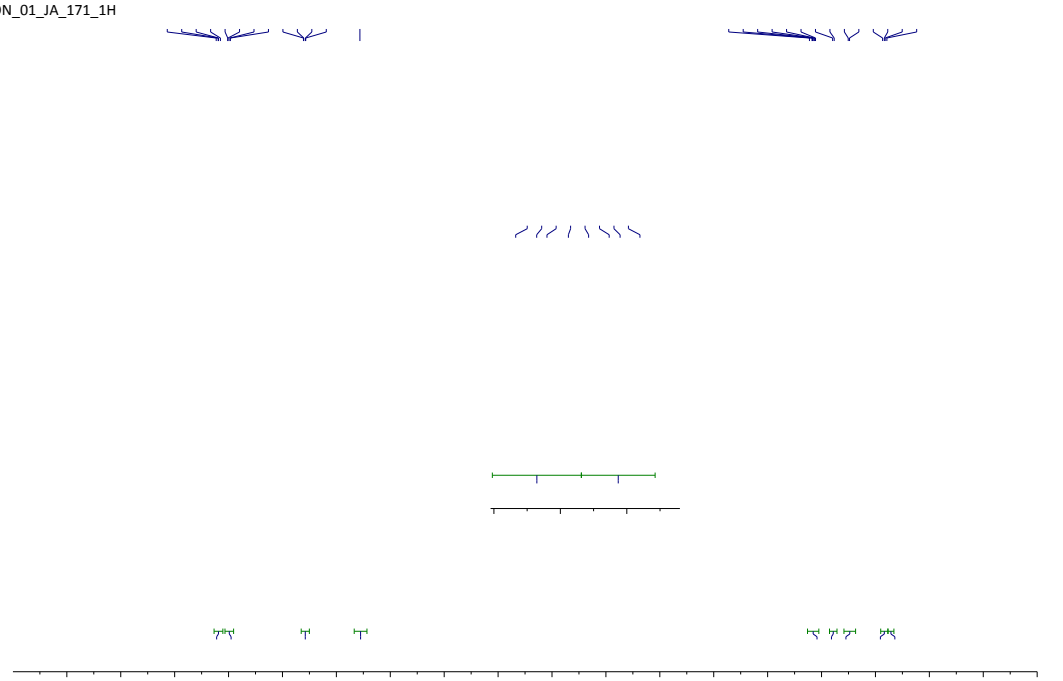




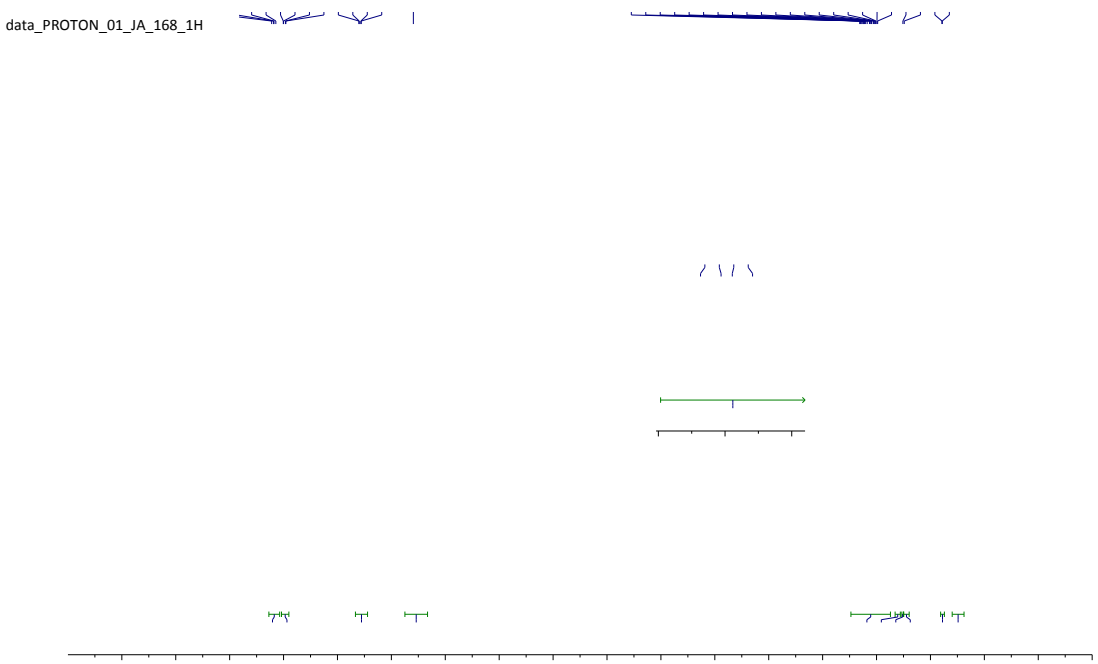

data_PROTON_01_JA_167_

data_CARBON_01_JA_167_13

data_PROTON_01_JA_171_1H

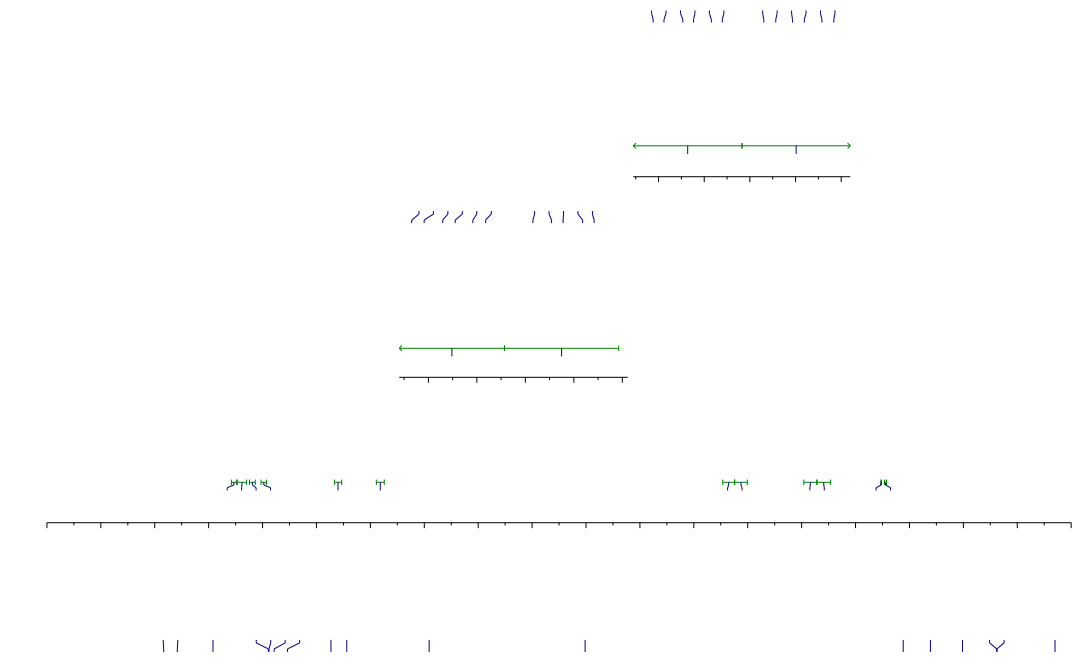


data_CARBON_01_JA_171_13C


data_PROTON_01_JA_168_1H

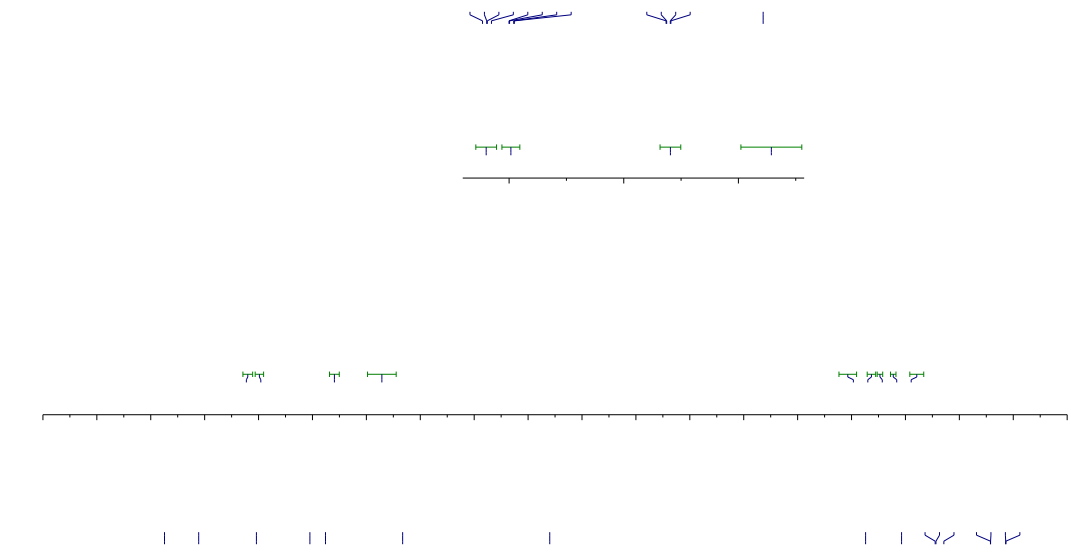

data_CARBON_01_JA_168_13C

data_PROTON_01_JA_34_1H

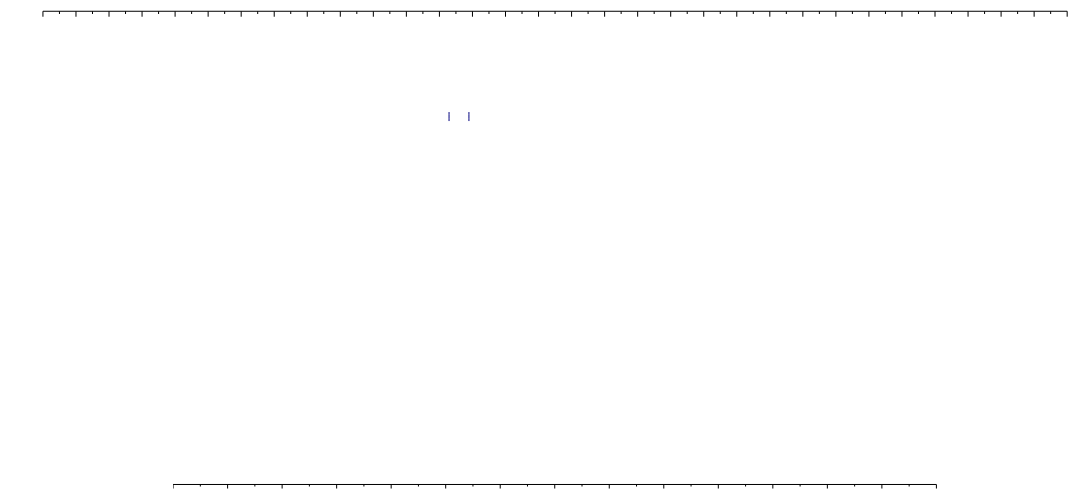


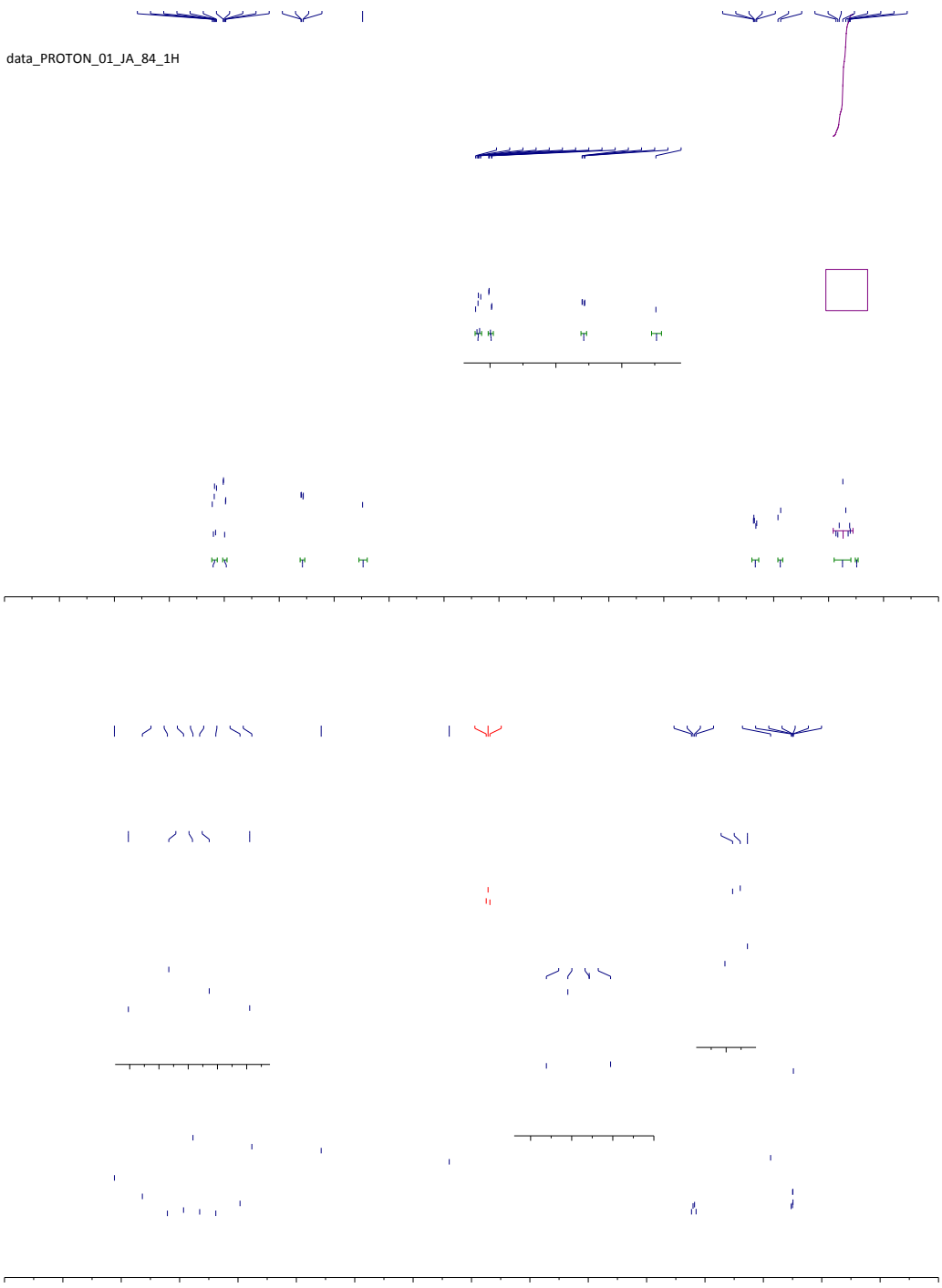
data_PROTON_01_JA_34_13C

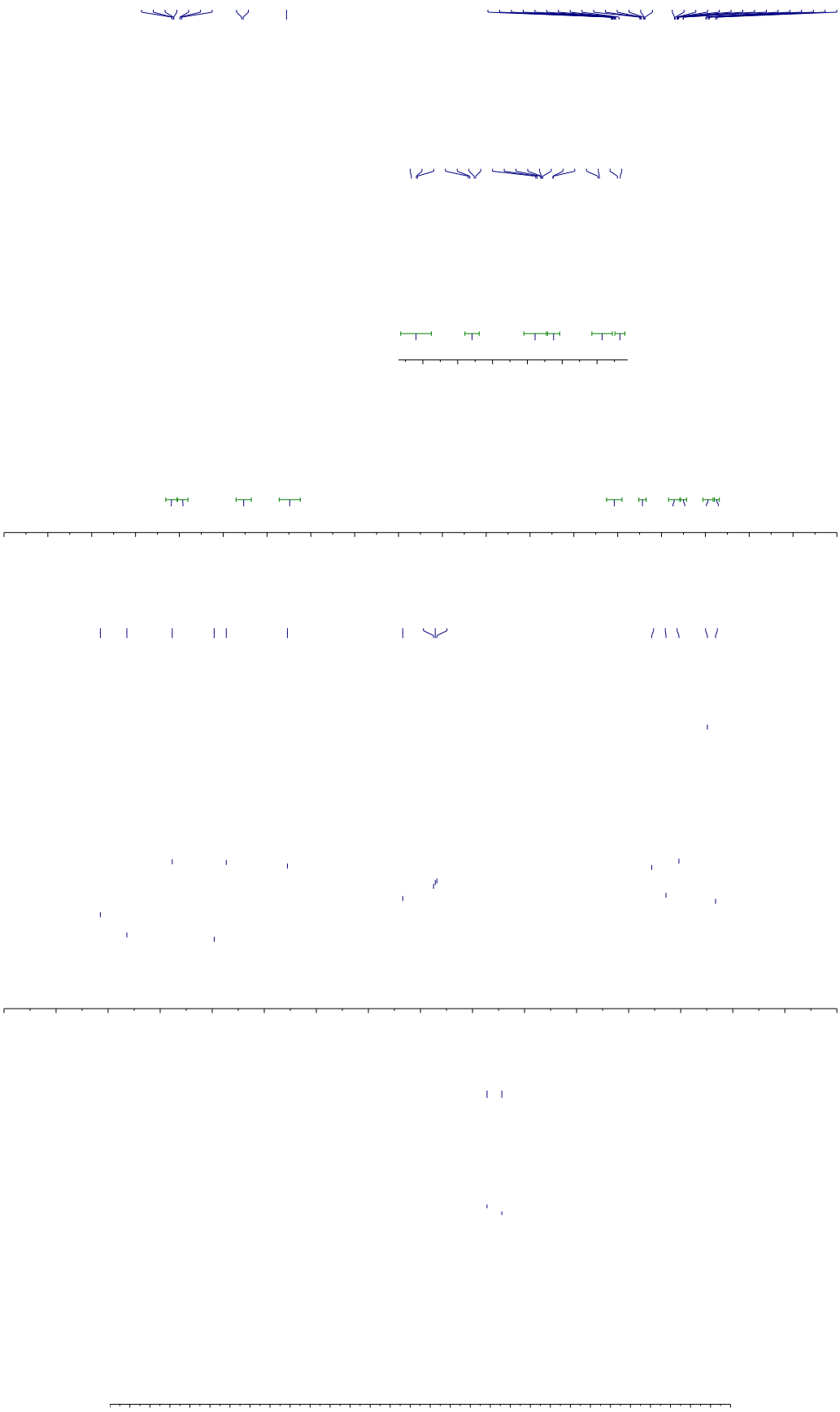
data_PROTON_01_JA_169_1H

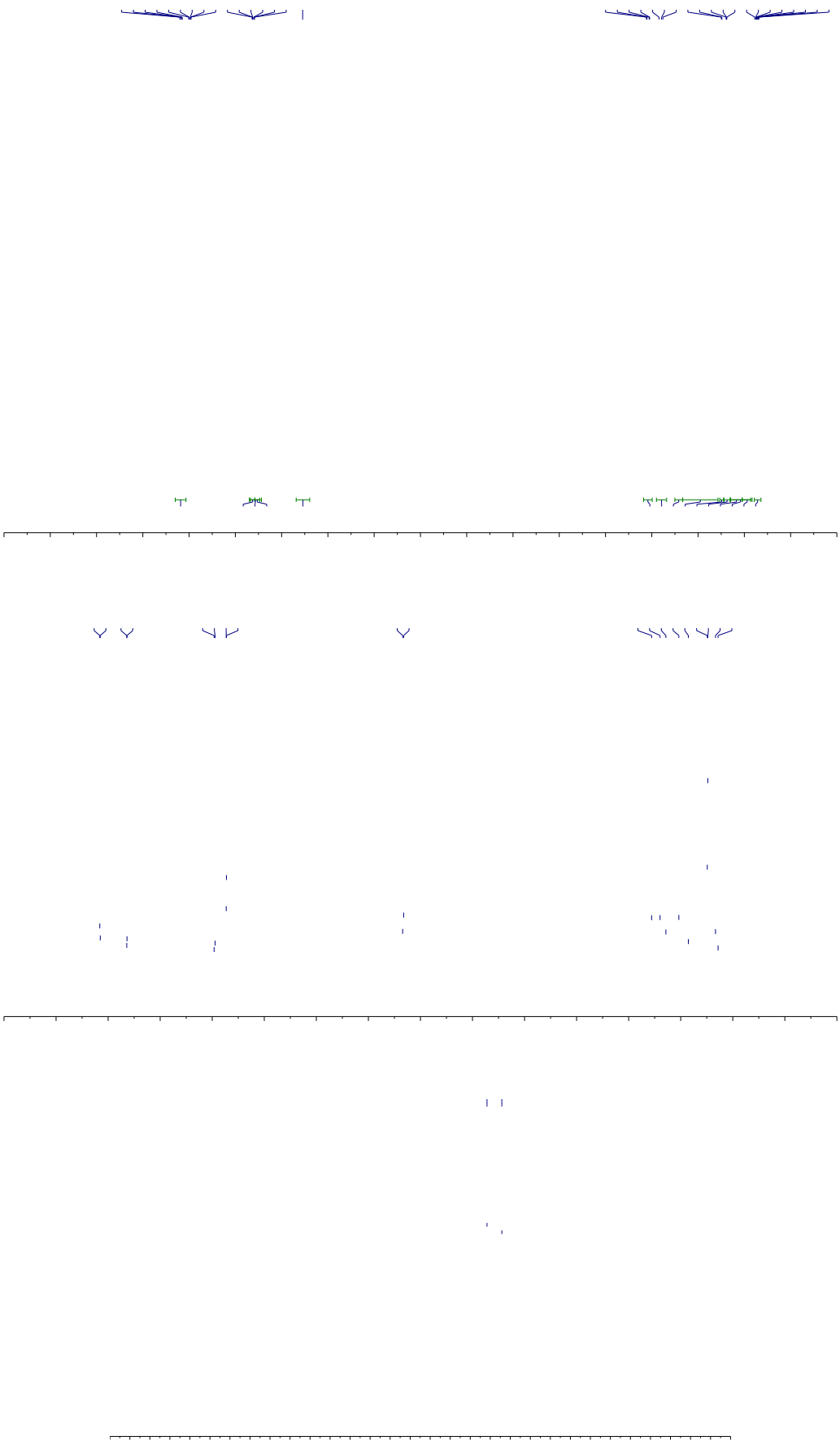


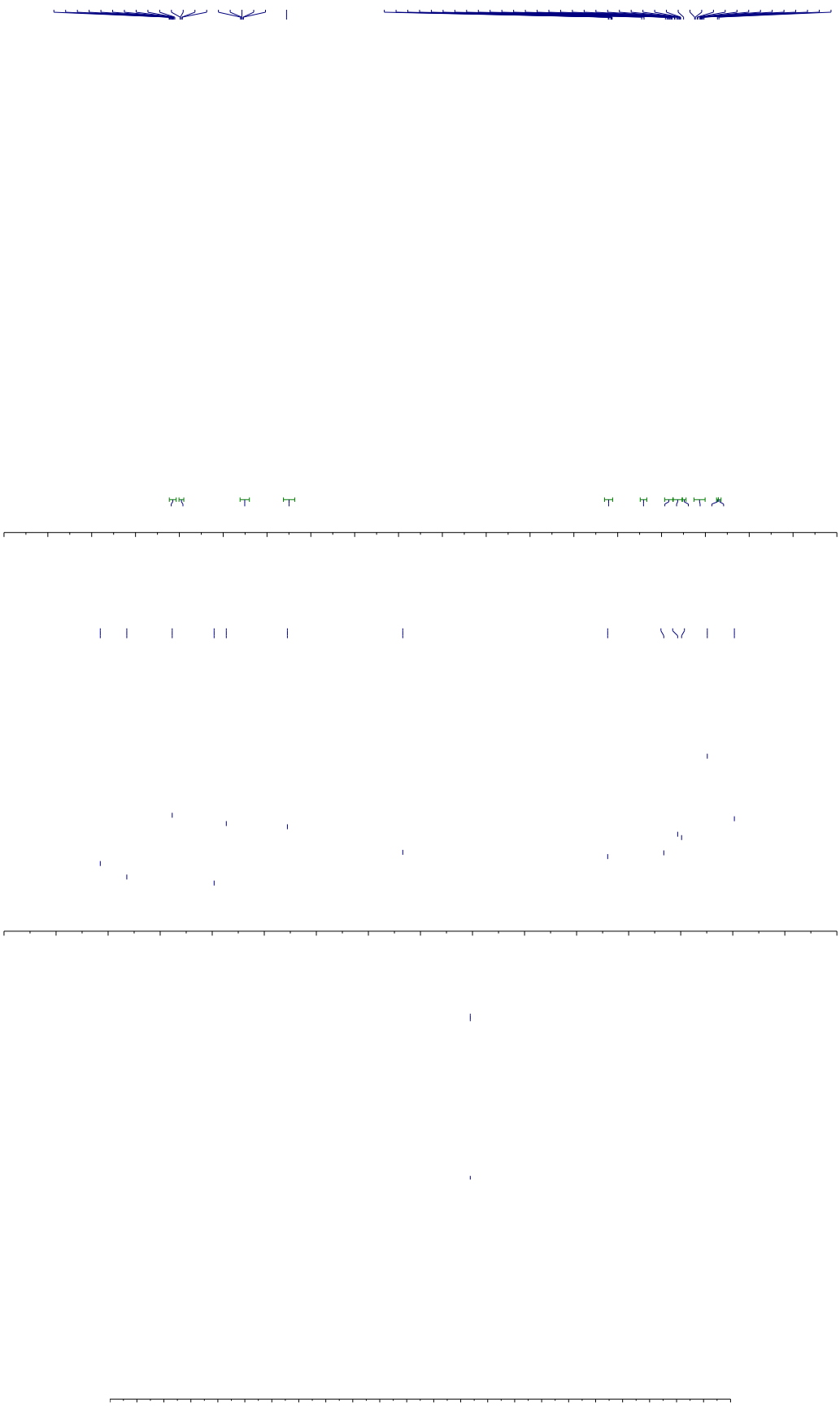
data_CARBON_01_JA_169_13C

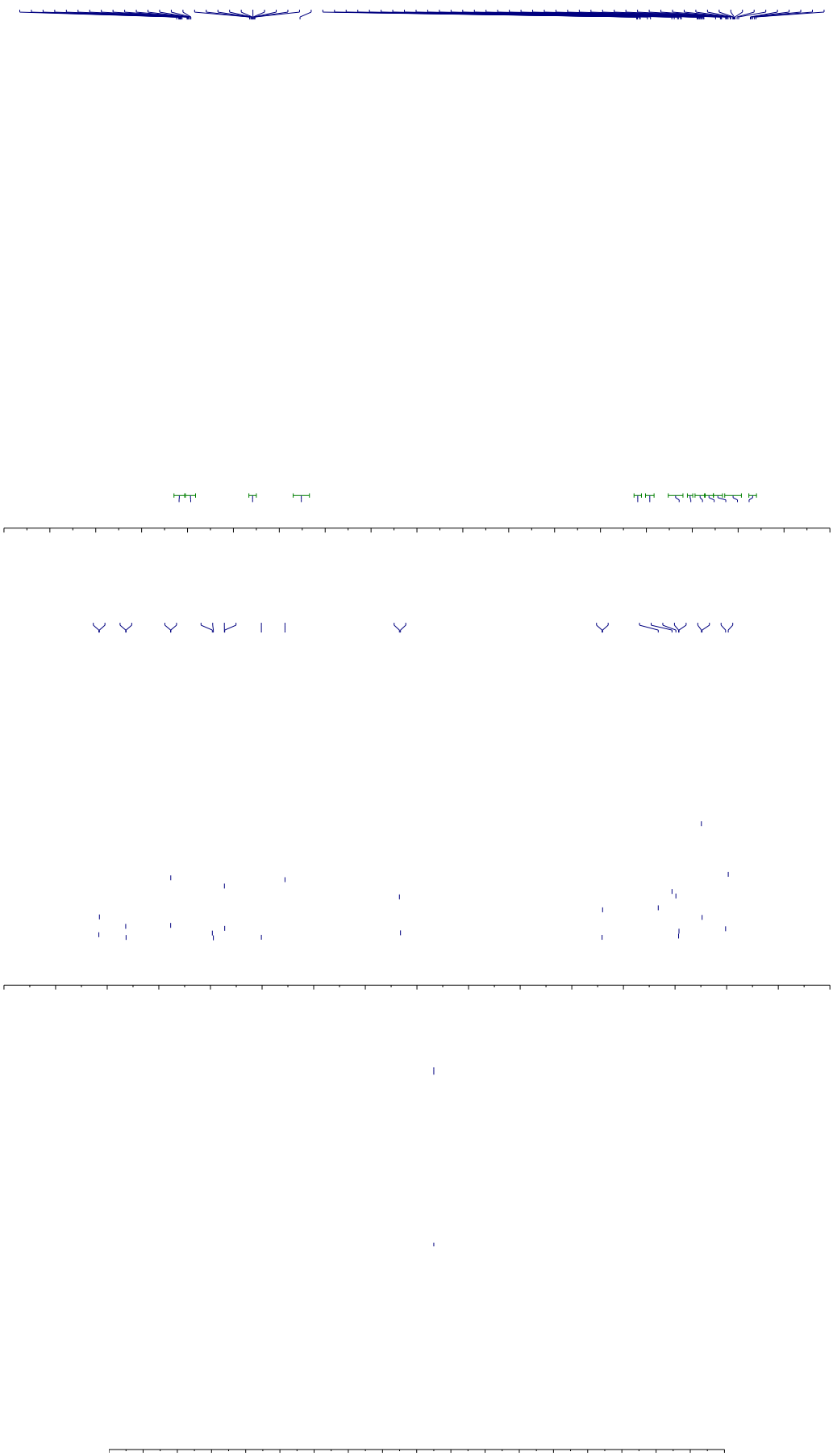


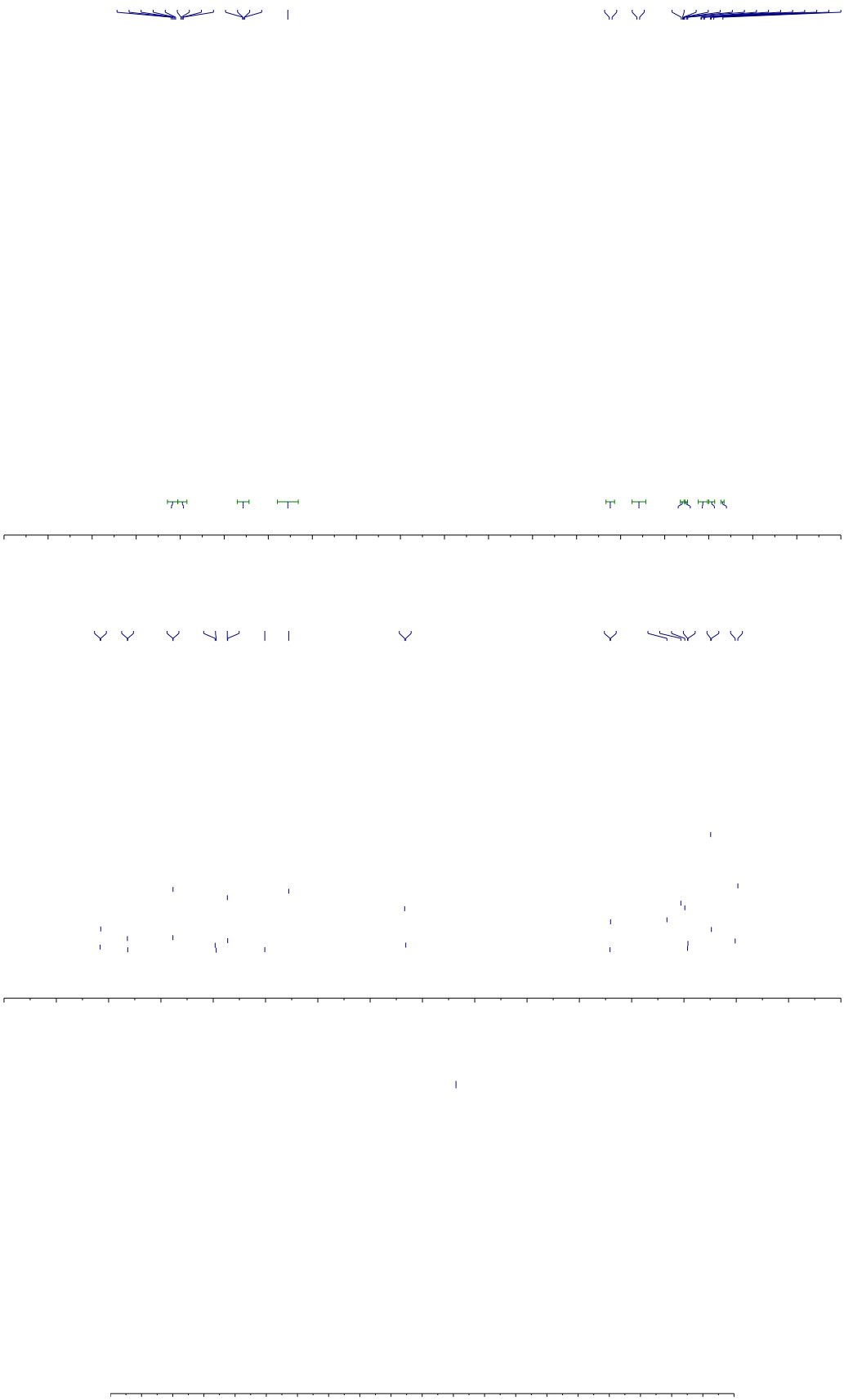

data_PROTON_01_JA_84_1H

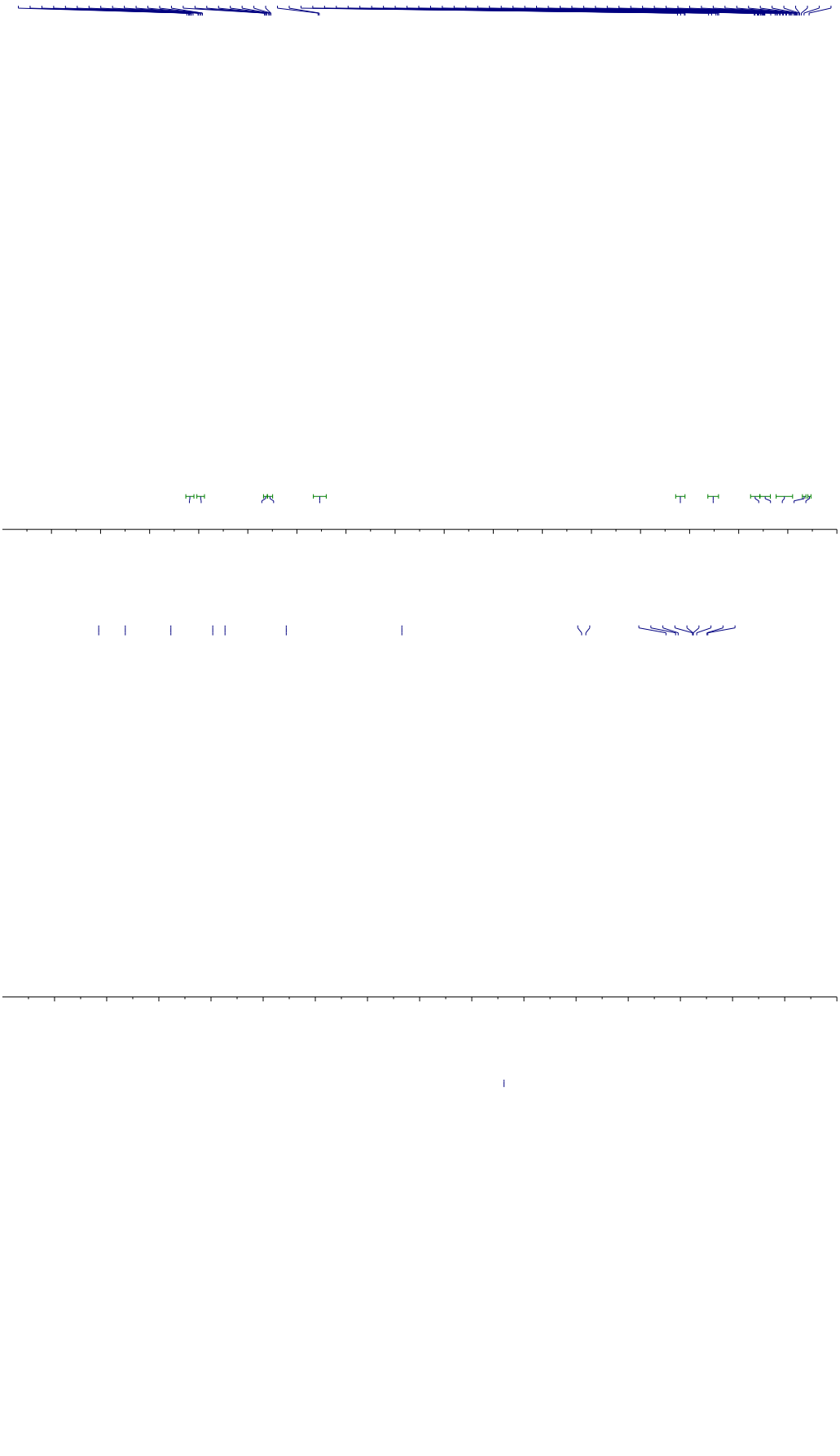


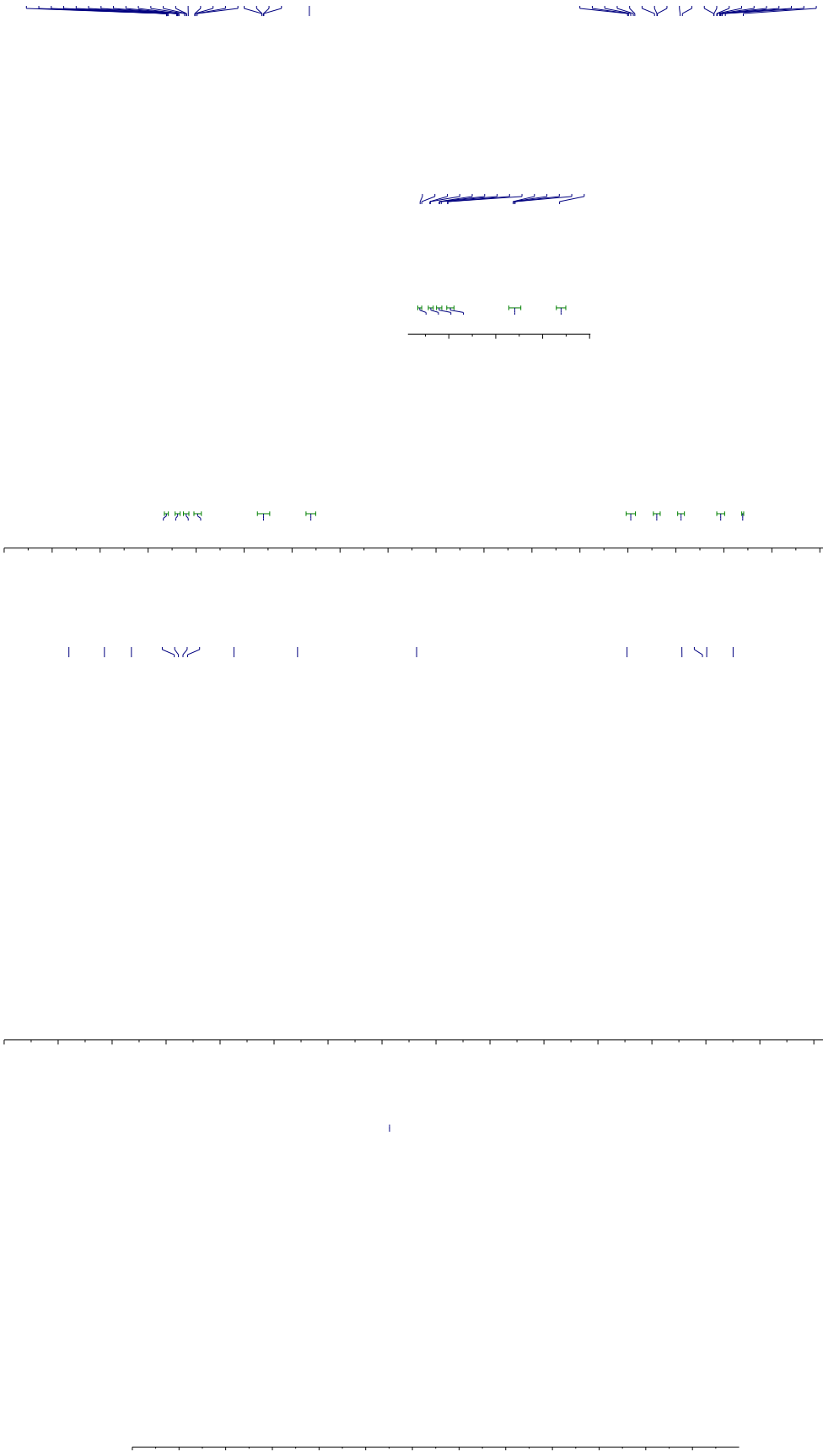


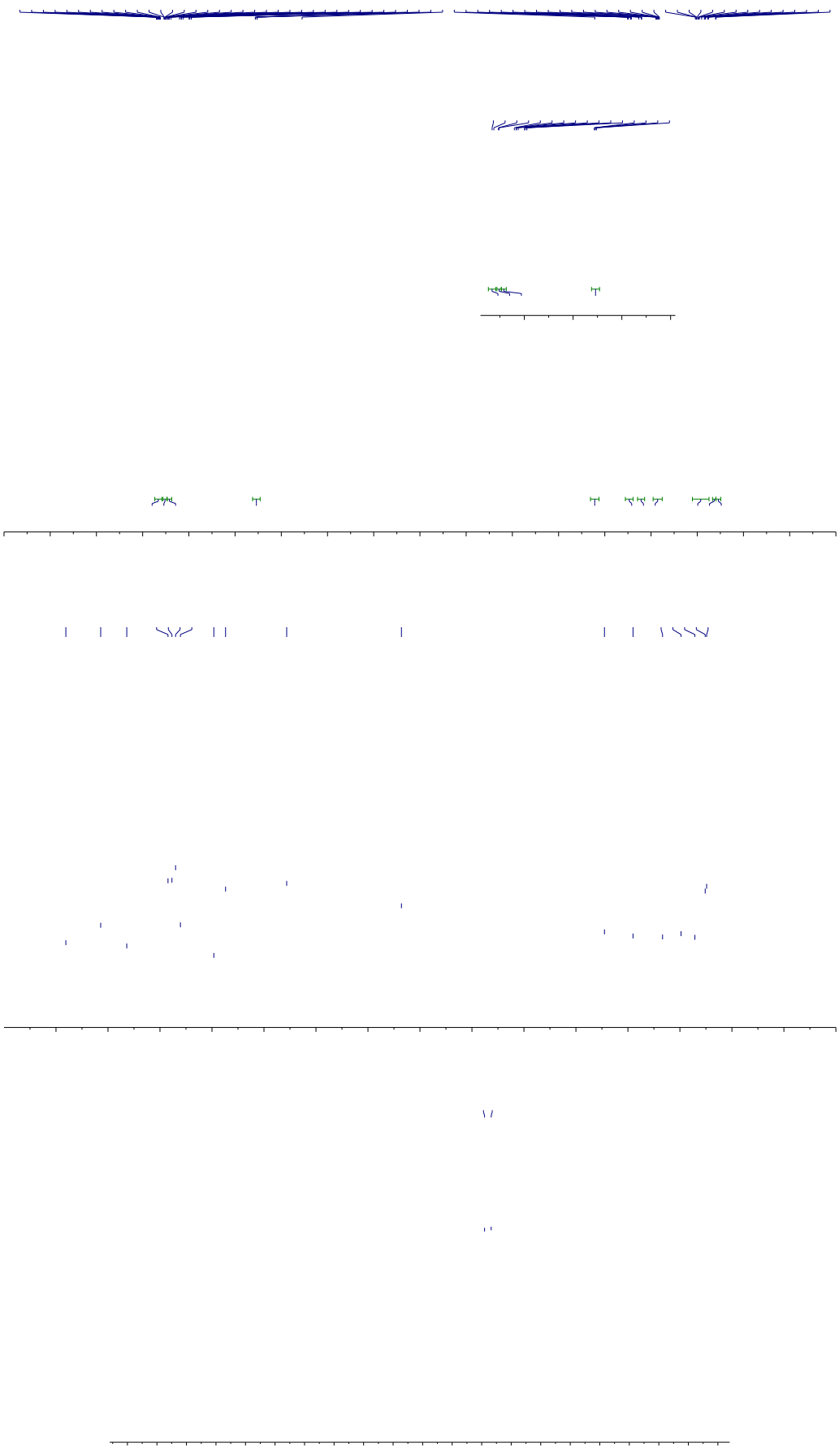


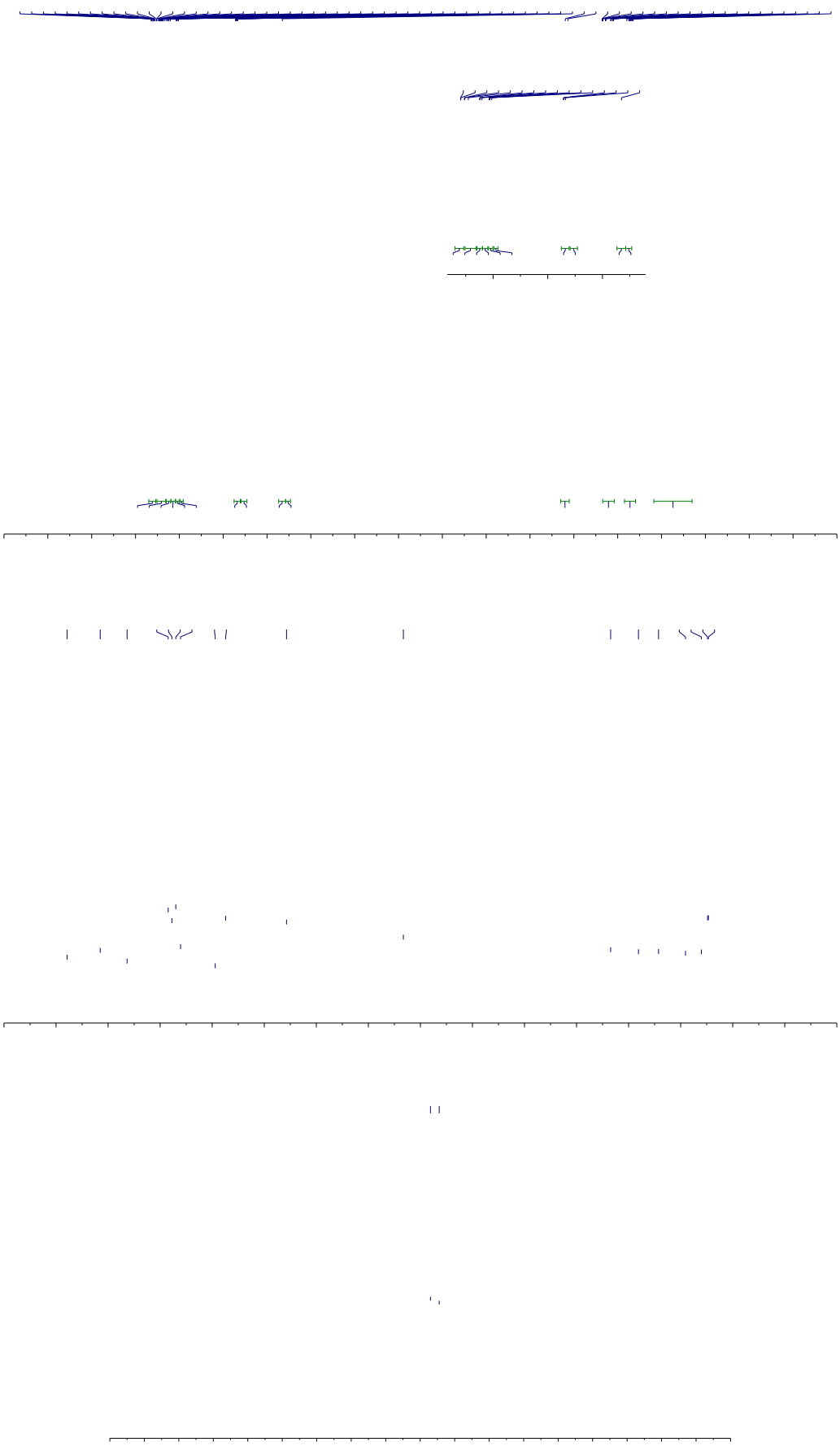


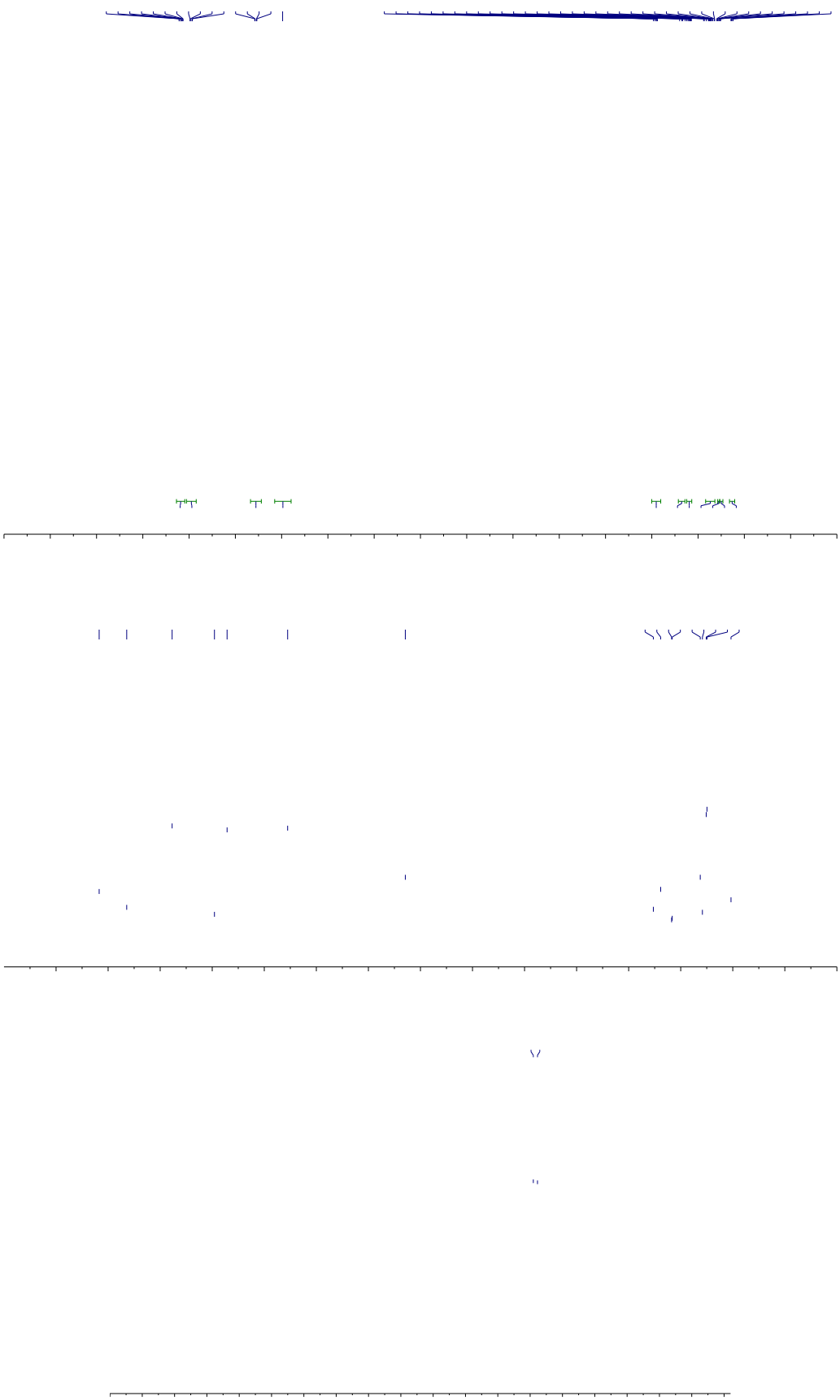


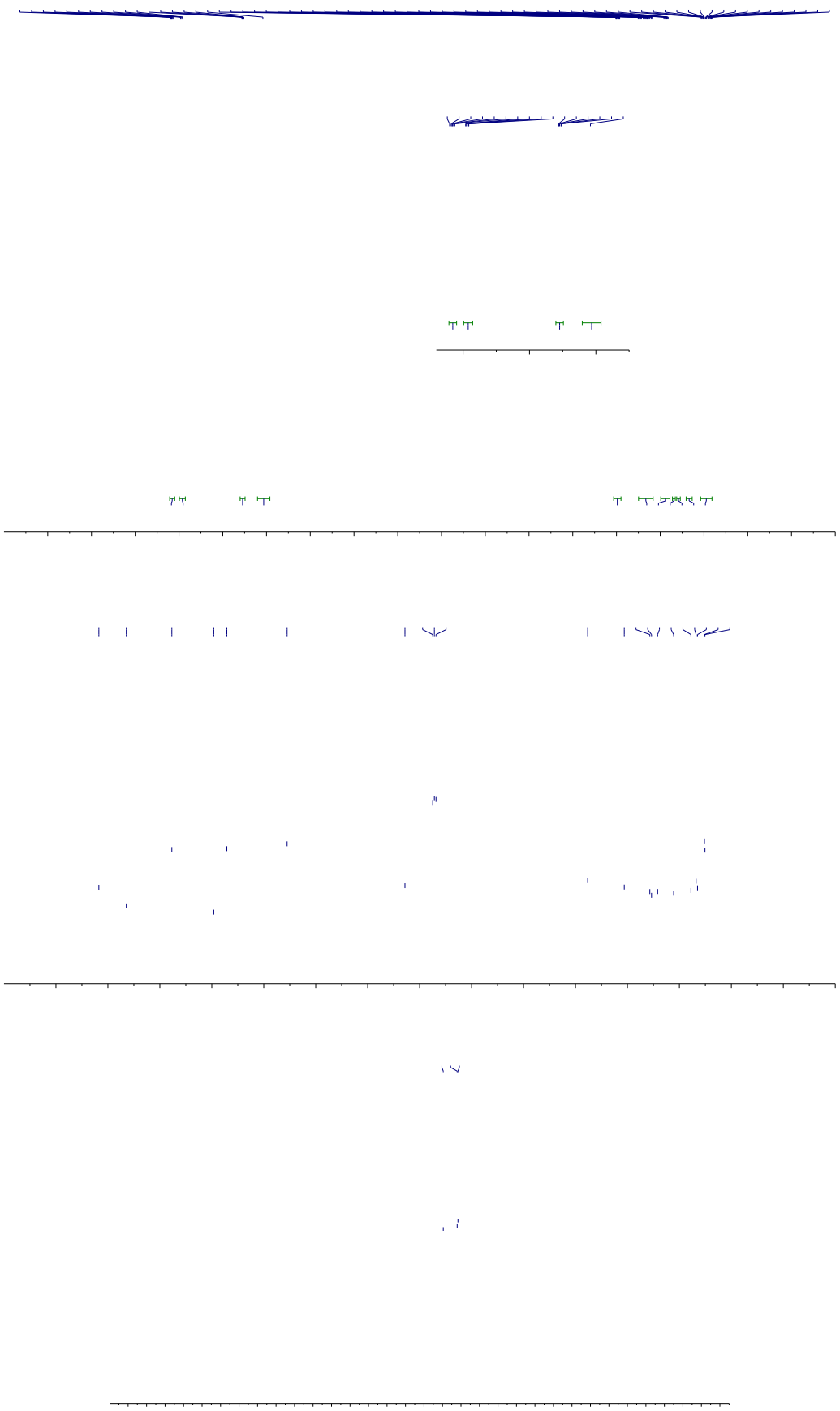


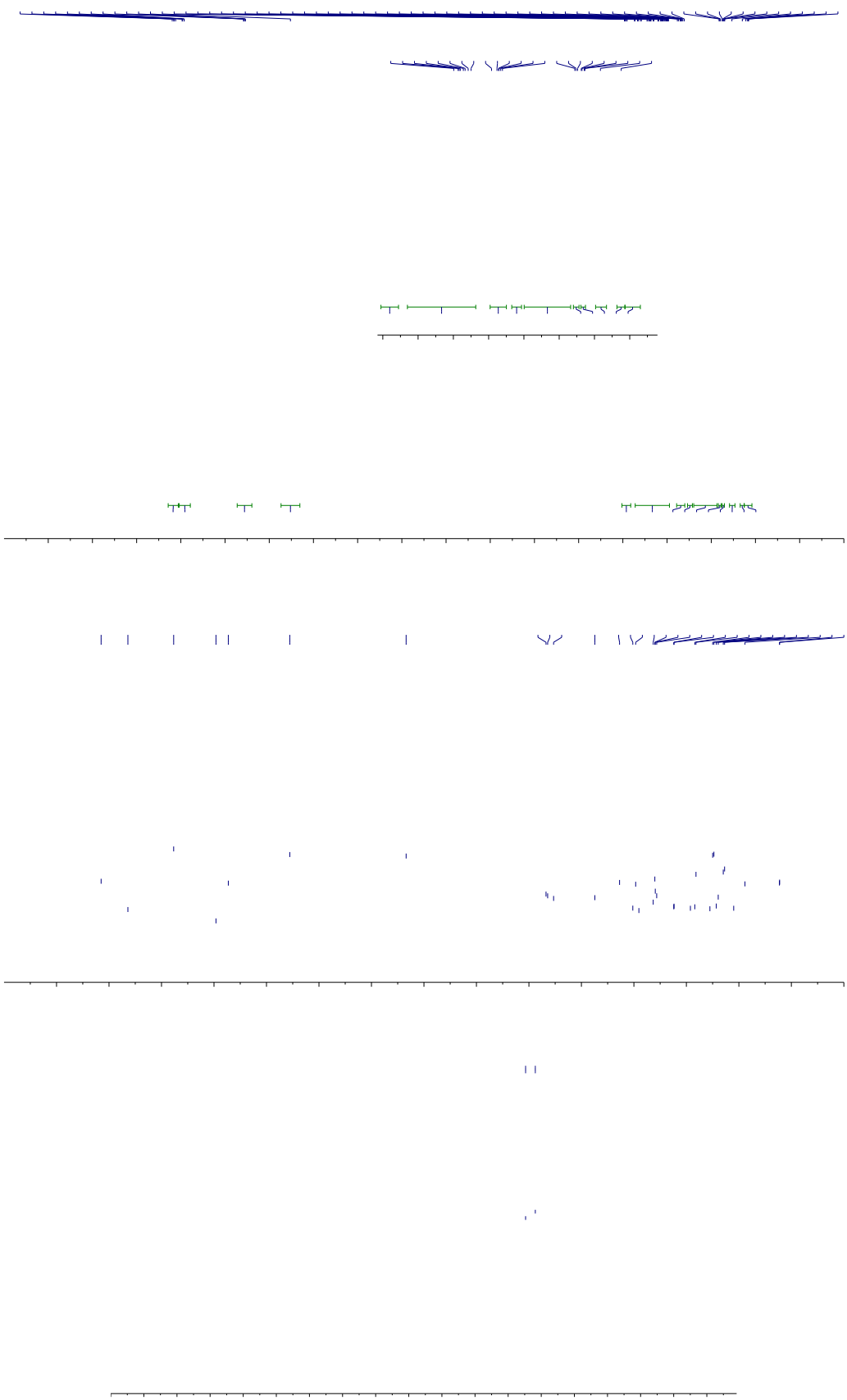


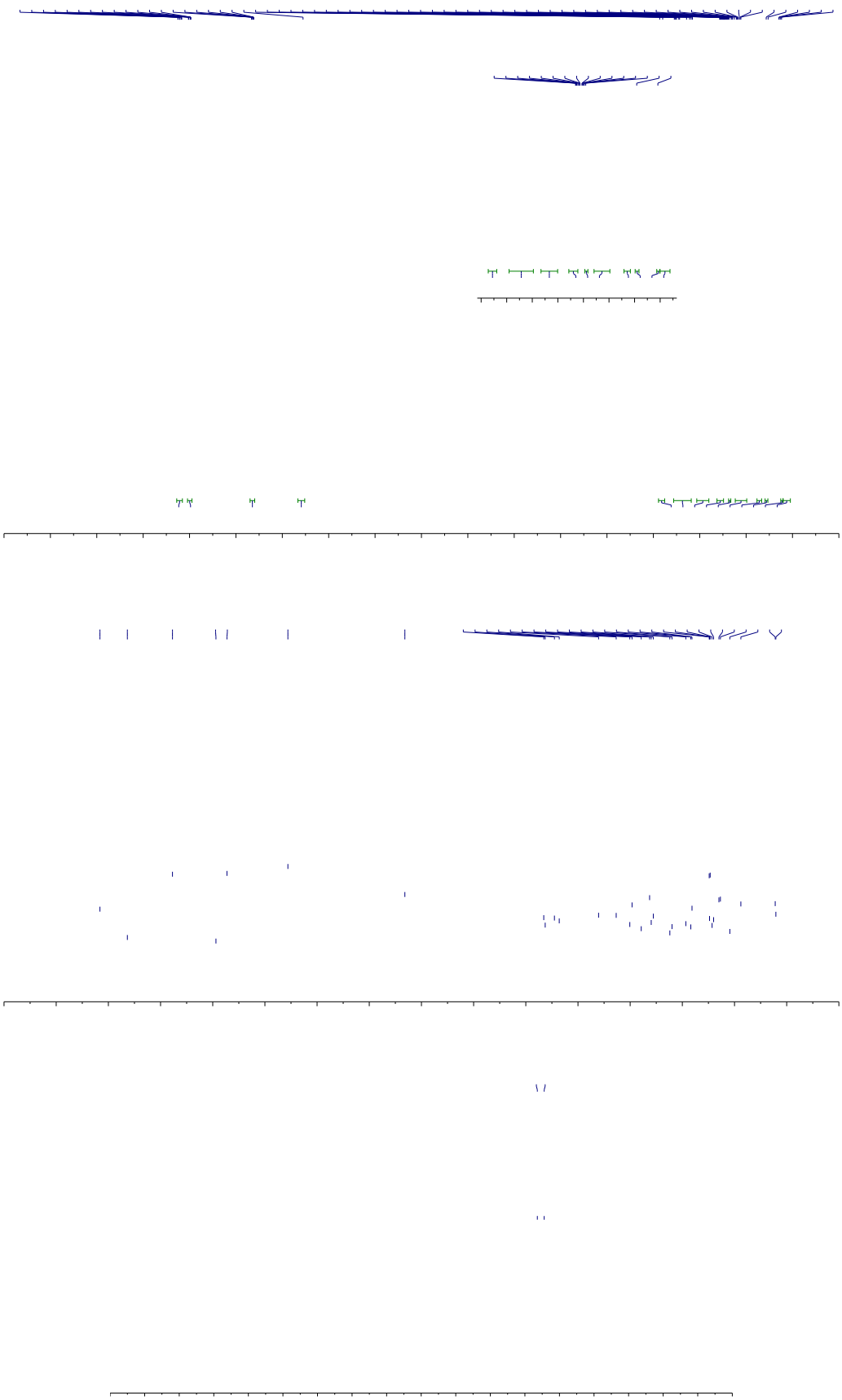


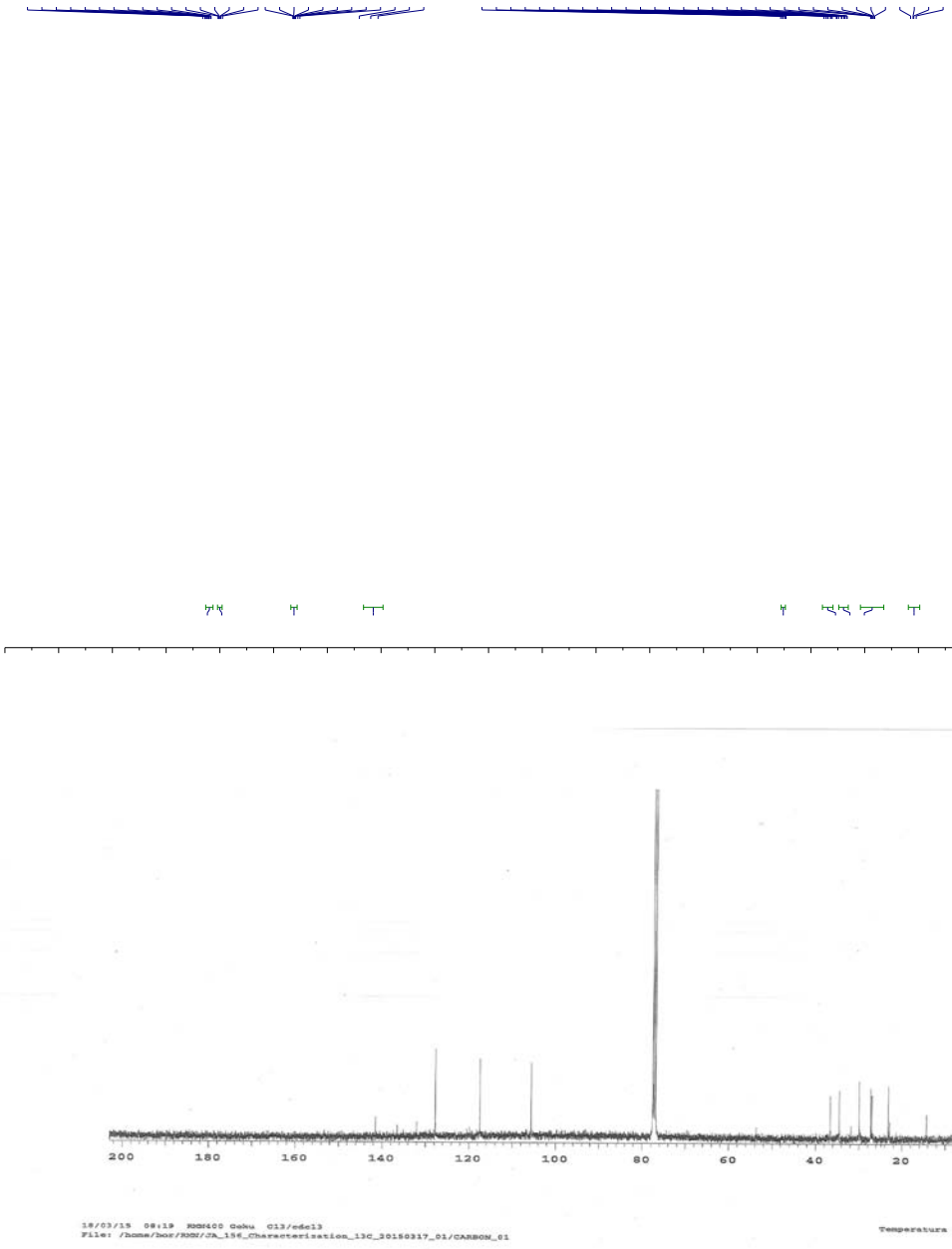


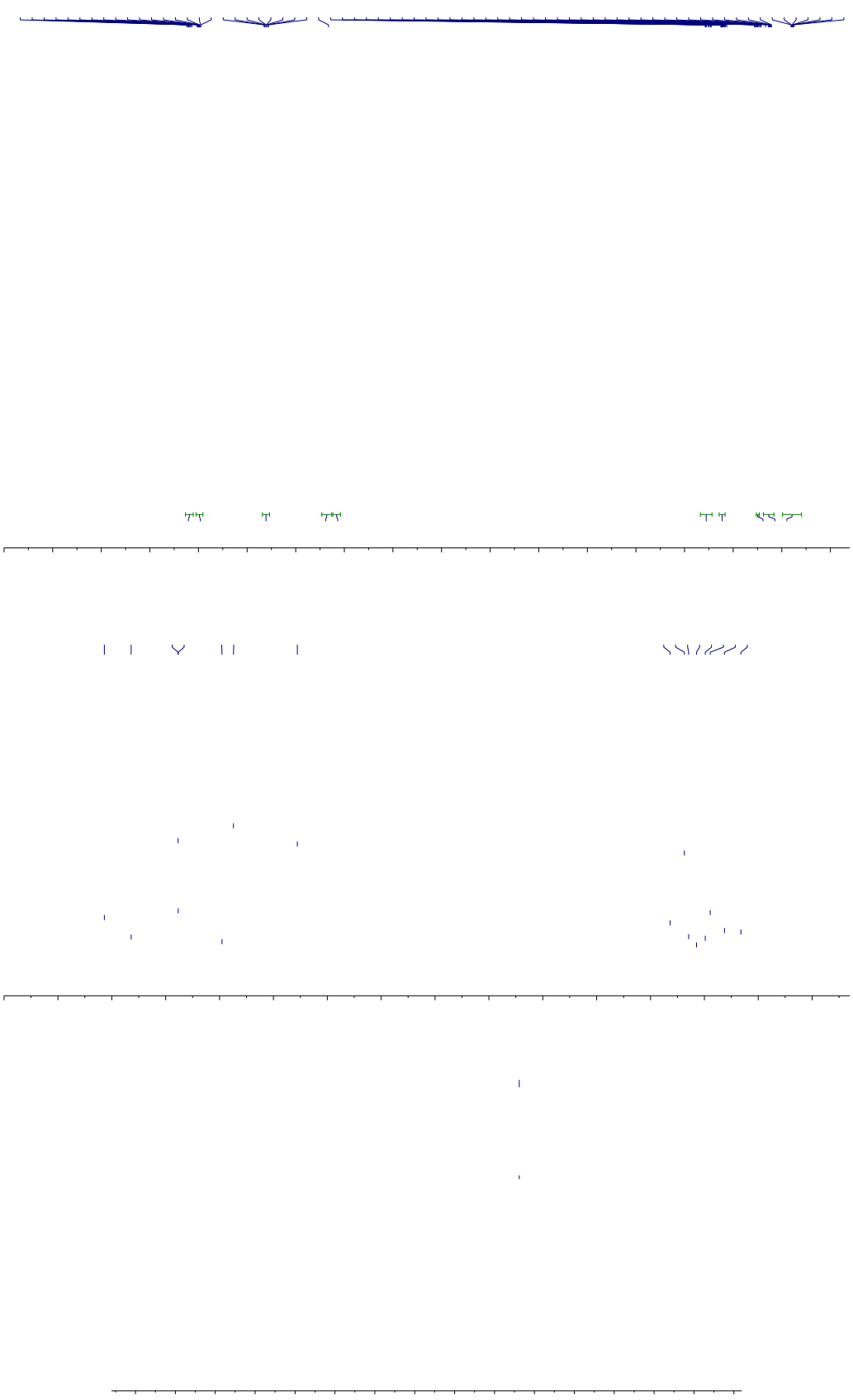


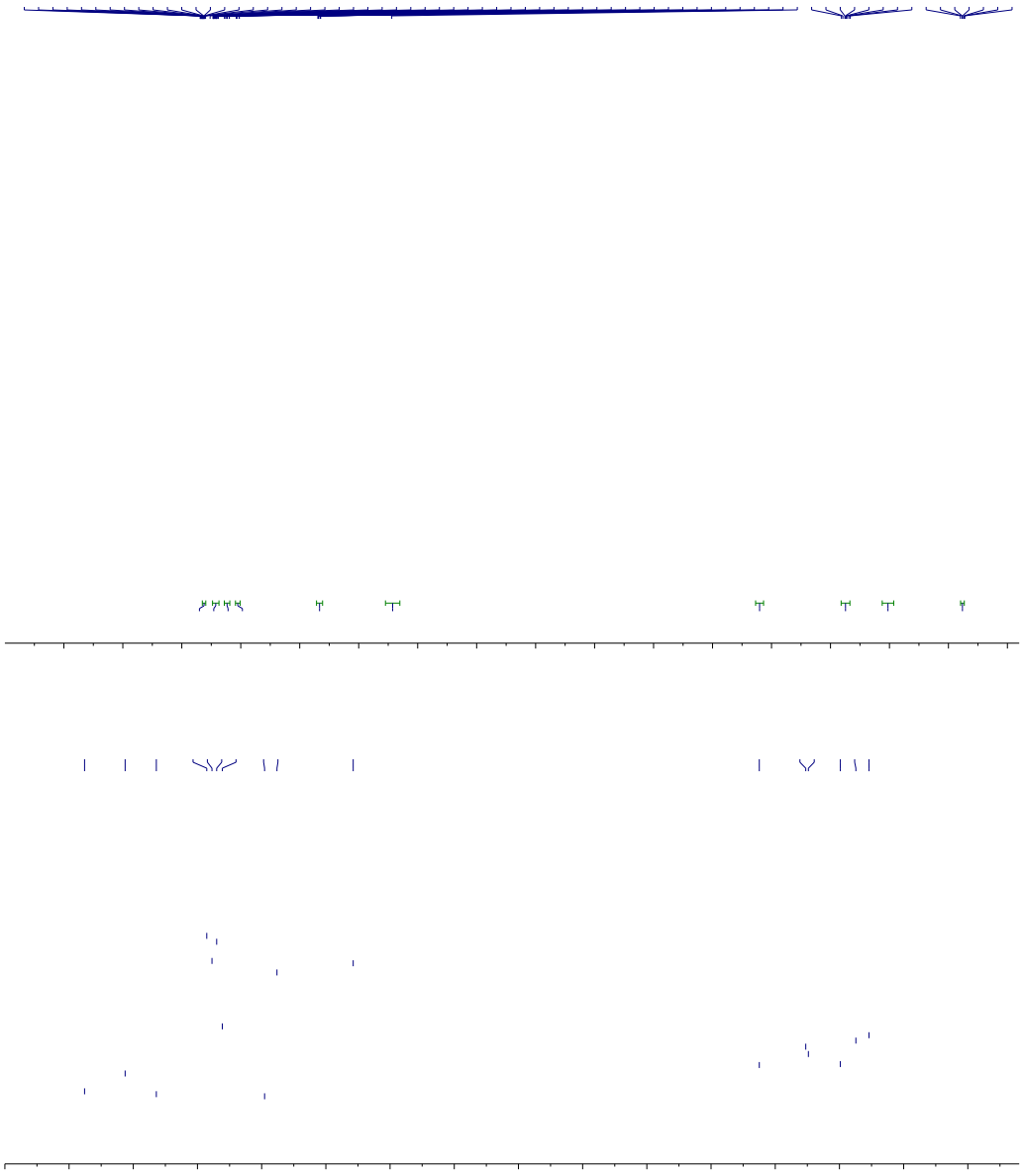







200
180
160
140
120
100
80
60
40
20
ppm
Temperatura ambient





6. Computational details

All calculations were performed by using the Gaussian09 series of programs.[10] Full quantum mechanical calculations on model systems were performed within the framework of density functional theory (DFT)[11] by using the B3LYP functional.[12] All the atoms were represented by means of the 6-31G(d,p) basis set[13] and geometry-optimizations were full, with no restrictions. Both minima and transition state structures were characterized with a frequency calculation, finding a unique negative frequency mode in the transition states geometries. The fragment charges of Bpin and Bdan carbenoids were analysed by using the NBO method.[14]

[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A., Jr., Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.02; Gaussian, Inc.: Wallingford, CT, 2009.

[11] a) R. G. Parr, W. Yang, in Density Functional Theory of Atoms and Molecules, Oxford University Press, Oxford, UK, 1989; b) T. Ziegler, *Chem. Rev.* **1991**, *91*, 651.

[12] a) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785; b) A. D. Becke, *J. Chem. Phys*. **1993**, *98*, 5648; c) P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *98*, 11623.

[13] a) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. Defrees, J. A. Pople, J. Chem. Phys. **1982**, *77*, 3654; b) W. J. Hehre, R. Ditchfield, J. A. Pople, J. Chem. Phys. **1972**, *56*, 2257; c) P. C. Hariharan, J. A. Pople, Theor. Chim. Acta **1973**, *28*, 213.

[14] A. E. Reed, L. A. Curtiss, F. Weinhold, Chem. Rev. **1985**, *88*, 899.

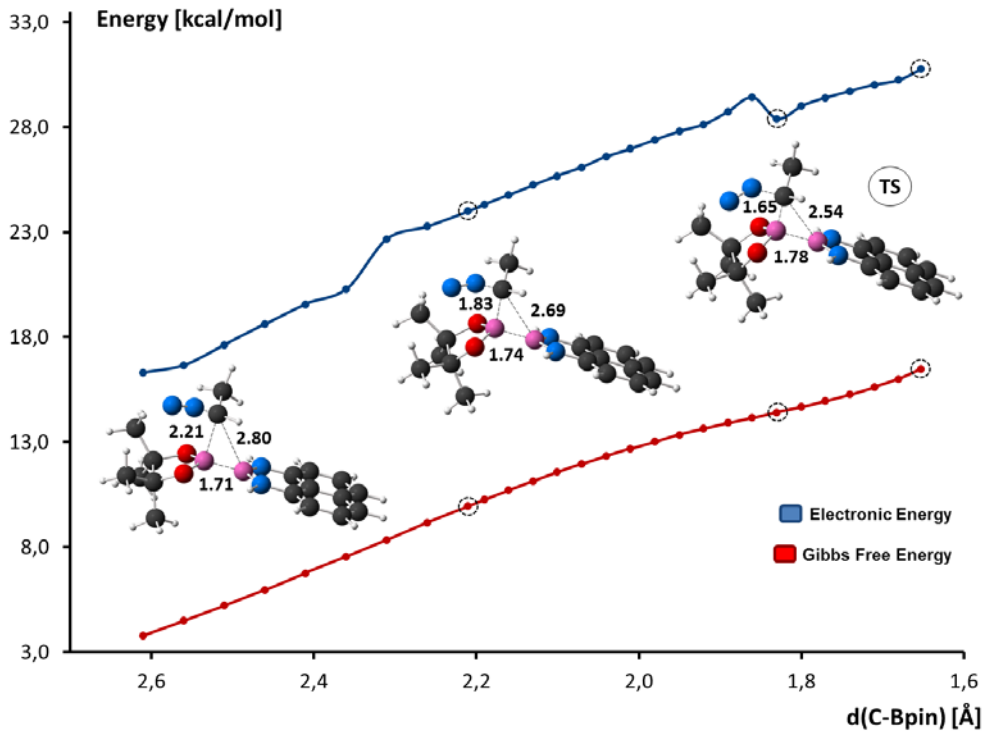
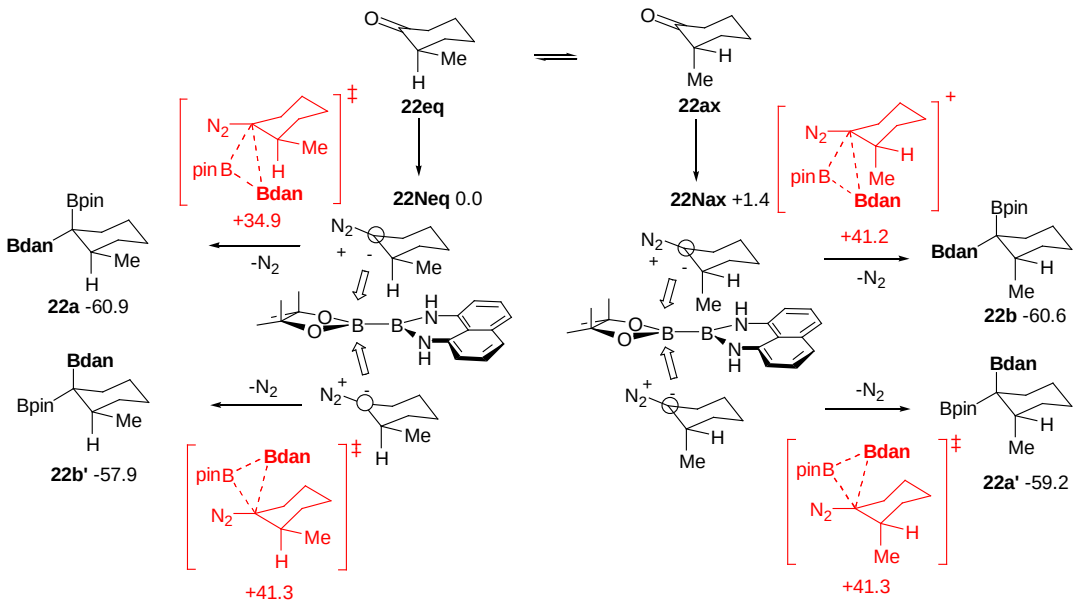
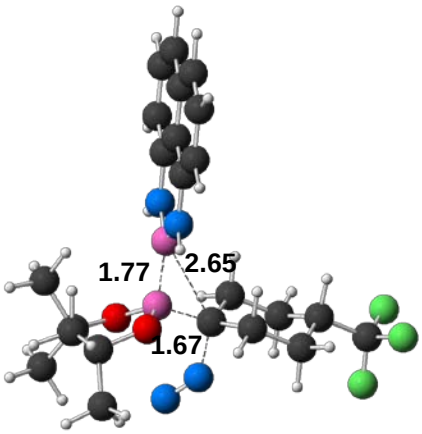


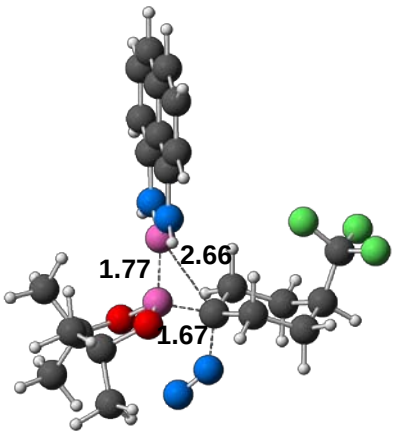
Figure S1. Relaxed potential energy scan along different values of the $C_{carbenoid}$-B_{Bpin} bond. Energies in kcal.mol^{-1} and distance in Å.



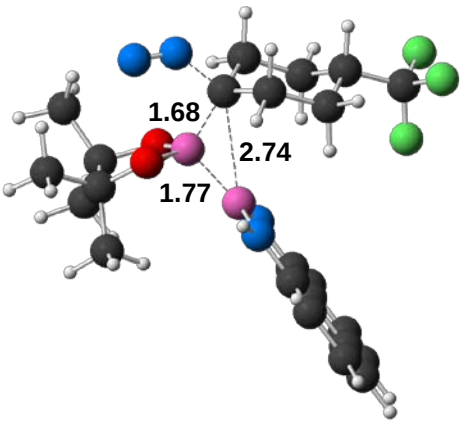
Scheme S1. Proposed diastereroisomeric pathways for the 1,1-diboration of 2-Me-cyclohexanone with Bpin-Bdan. Relative Gibbs free energies in kcal.mol^{-1}.



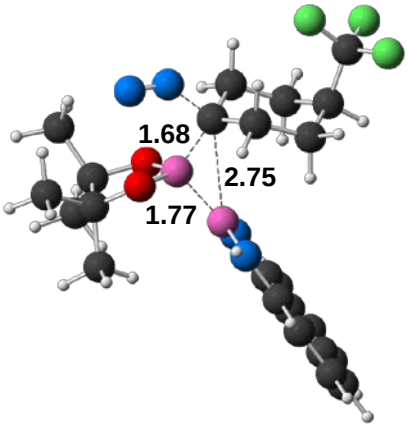
16a



16b

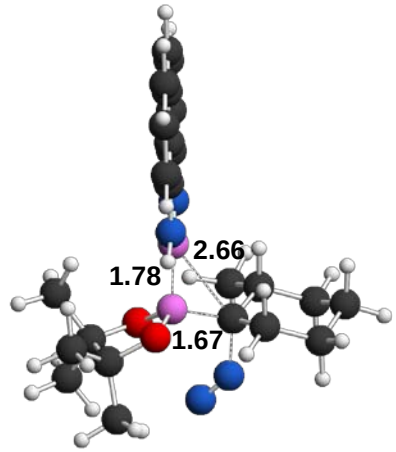


16b'

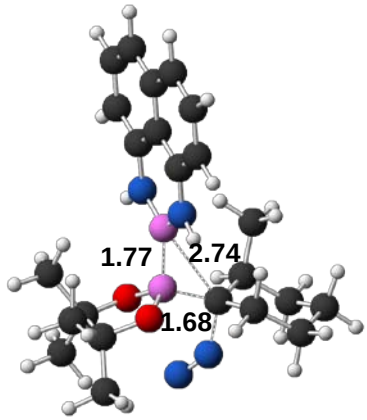


16a'

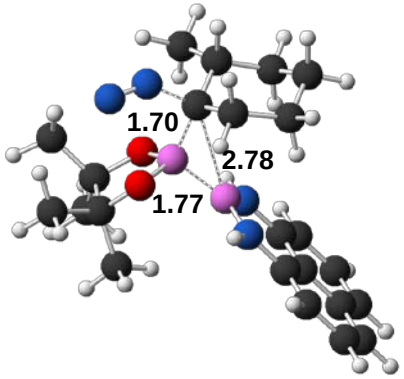
Figure S2. Molecular structure and main geometric parameters (in Å) of the transition states for the possible paths of 1,1-diboration of 4-CF_3-cyclohexanone.



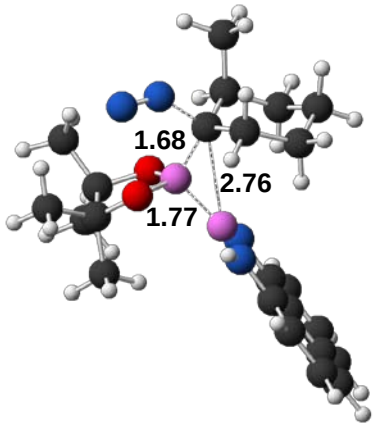
22a



22b



22b’



22a’

Figure S3. Molecular structure and main geometric parameters (in Å) of the transition states for the possible paths in 1,1-diboration of 2-Me-cyclohexanone.

Scheme S2. Proposed mechanism for methoxy-assisted deborylation and generation of α-boron-stabilized carbanion. Relative Gibbs free energies in kcal.mol^{-1}.

7. Geometries

Cartesian coordinates (in Å) and electronic energies for the reported stationary points:

Structure **TS16a**. Energy (a.u.): -1612.767651

C	4.303861	-2.735192	-2.345246
C	4.899064	-3.036780	-1.139848
C	4.420302	-2.454635	0.065523
C	3.307592	-1.556980	0.002408
C	2.708232	-1.265692	-1.263707
C	3.208591	-1.850265	-2.417965
H	5.853762	-3.406579	1.381238
H	4.679297	-3.182844	-3.261504
H	5.742784	-3.719211	-1.094221
C	5.009551	-2.725097	1.330627
C	2.818832	-0.954042	1.204815
H	2.751548	-1.622879	-3.377737
C	3.424807	-1.240356	2.419478
C	4.519030	-2.127876	2.471476
H	3.050568	-0.777269	3.328696
H	4.978816	-2.339186	3.433169
N	1.619394	-0.386240	-1.287254
N	1.730376	-0.084698	1.100002
B	1.089055	0.249691	-0.126092
C	0.194297	3.609094	0.823561
C	0.473689	3.594264	-0.744594
B	-0.208235	1.460737	-0.095035
O	-0.190579	2.395871	-1.194576
O	-0.094683	2.235398	1.133857
C	1.966291	3.462246	-1.098688
H	2.056524	3.286124	-2.174476
H	2.523911	4.371118	-0.852998
H	2.436110	2.621518	-0.582449
C	-0.109815	4.782713	-1.513163
H	0.340132	5.724014	-1.180339
H	0.103207	4.666527	-2.580154
H	-1.191662	4.849452	-1.392938
C	1.394459	4.050432	1.673485
H	1.687205	5.082241	1.450696
H	1.124334	4.000814	2.732937
H	2.259386	3.403058	1.518213
C	-1.021974	4.457122	1.233528
H	-1.247341	4.255902	2.285265
H	-0.825929	5.529131	1.127195
H	-1.910626	4.213985	0.648904
H	1.270508	-0.152120	-2.206034
H	1.449525	0.399673	1.942724
N	-2.733076	1.572591	-0.452322
N	-2.821286	2.579249	-0.949260
C	-1.554913	0.475909	-0.113501
C	-1.730363	-0.529919	-1.260906
C	-1.911567	-0.116932	1.248531
C	-3.047879	-1.318916	-1.220916
H	-0.890883	-1.227889	-1.175859
H	-1.612470	-0.018551	-2.222304
C	-3.215628	-0.926717	1.278463
H	-1.067434	-0.765040	1.513698

H	-1.923989	0.683919	1.993096
C	-3.264394	-1.974894	0.153542
H	-3.040521	-2.083309	-2.003746
H	-3.893799	-0.655058	-1.434841
H	-3.321640	-1.417162	2.250879
H	-4.072847	-0.251540	1.169576
H	-2.473977	-2.718678	0.322013
C	-4.566964	-2.754257	0.186438
F	-4.598534	-3.710058	-0.769591
F	-5.639609	-1.952157	-0.015613
F	-4.747964	-3.370910	1.375703

Structure **16a**. Energy (a.u.): -1503.387706

B	1.057959	-0.661753	-0.008205
B	-0.924911	0.865811	0.206877
C	-4.668001	-2.141464	-0.446868
C	-3.153419	-2.106872	-0.371543
H	-2.829261	-3.145050	-0.527260
C	-2.678048	-1.640969	1.016302
H	-3.103825	-0.653700	1.228305
H	-3.059304	-2.322276	1.784179
C	-1.145677	-1.558472	1.088624
H	-0.741706	-2.578281	0.987959
H	-0.858821	-1.198545	2.083014
C	-0.540412	-0.649171	-0.010501
C	-1.035007	-1.149088	-1.405238
H	-0.669281	-0.492806	-2.200858
H	-0.612681	-2.144758	-1.605354
C	-2.566013	-1.231899	-1.493079
H	-2.991690	-0.223435	-1.418266
H	-2.868301	-1.629902	-2.467557
C	-1.690284	2.791031	1.186990
C	-1.028900	3.121826	-0.210336
C	-3.224224	2.776563	1.151444
H	-3.634982	3.783498	1.033030
H	-3.595655	2.363587	2.093281
H	-3.602253	2.150039	0.338619
C	-1.201664	3.645345	2.355274
H	-0.122887	3.559274	2.495639
H	-1.688651	3.315345	3.277184
H	-1.451978	4.699977	2.199850
C	-1.877874	3.982419	-1.143799
H	-2.842592	3.518477	-1.355638
H	-1.353988	4.118991	-2.094190
H	-2.053296	4.972493	-0.710249
C	0.384388	3.707486	-0.094060
H	0.366864	4.723735	0.310218
H	0.836579	3.747999	-1.089292
H	1.024924	3.091155	0.542388
C	3.236405	-1.558090	0.802444
C	3.957719	-2.414965	1.620383
H	3.431954	-3.083026	2.297883
C	5.366927	-2.420127	1.571451
H	5.912321	-3.100066	2.220285
C	6.054743	-1.583416	0.720038
H	7.140344	-1.595179	0.689117
C	5.352601	-0.689001	-0.133068
C	6.016903	0.194985	-1.026140
H	7.102393	0.187868	-1.061464
C	5.292718	1.045733	-1.832713
H	5.809646	1.717194	-2.513017

C	3.883427	1.065066	-1.796506
H	3.328645	1.740910	-2.442147
C	3.197650	0.217681	-0.938176
C	3.922558	-0.677307	-0.090316
F	-5.212505	-0.910259	-0.277950
F	-5.201961	-2.942968	0.504163
F	-5.101602	-2.603435	-1.643107
N	1.803518	0.204630	-0.863264
H	1.321549	0.876825	-1.445586
N	1.838290	-1.522822	0.815346
H	1.399437	-2.163154	1.460931
O	-0.889749	1.798443	-0.809878
O	-1.265986	1.416067	1.417314

Structure **TS16b**. Energy (a.u.): -1612.765640

C	-4.666486	-0.968833	-2.408931
C	-5.319950	-1.106635	-1.203832
C	-4.587201	-1.130653	0.014101
C	-3.162674	-1.003505	-0.036451
C	-2.512642	-0.857577	-1.302502
C	-3.263396	-0.844018	-2.469016
H	-6.296662	-1.376394	1.321575
H	-5.235374	-0.954243	-3.334734
H	-6.401368	-1.201298	-1.167667
C	-5.215401	-1.281985	1.280272
C	-2.408127	-1.036938	1.178833
H	-2.764185	-0.734532	-3.428495
C	-3.058682	-1.190675	2.394504
C	-4.462704	-1.311286	2.434172
H	-2.479668	-1.215828	3.313923
H	-4.952872	-1.429378	3.396877
N	-1.118910	-0.730339	-1.313795
N	-1.020196	-0.911825	1.085899
B	-0.310928	-0.760604	-0.139168
C	2.649800	-2.530438	0.889449
C	2.465440	-2.750640	-0.678256
B	1.462172	-0.728343	-0.091722
O	2.114619	-1.439581	-1.165040
O	1.913035	-1.326435	1.157397
C	1.308580	-3.703570	-1.031378
H	1.150385	-3.677281	-2.113432
H	1.529261	-4.735794	-0.743026
H	0.373724	-3.404462	-0.551558
C	3.724923	-3.215405	-1.414631
H	4.047454	-4.199574	-1.058265
H	3.510774	-3.298665	-2.484450
H	4.549211	-2.511828	-1.291803
C	2.061694	-3.653485	1.756136
H	2.555849	-4.612029	1.563744
H	2.207322	-3.407823	2.812678
H	0.990359	-3.773641	1.585705
C	4.108731	-2.303125	1.321648
H	4.115526	-1.983265	2.368109
H	4.704523	-3.218378	1.242137
H	4.596828	-1.525976	0.731210
H	-0.694071	-0.695822	-2.229699
H	-0.495902	-1.017666	1.944518
N	3.352574	0.934230	-0.456558
N	4.130044	0.257742	-0.912475
C	1.747592	0.918883	-0.152771
C	1.193345	1.725336	-1.336152

C	1.559794	1.628172	1.186512
C	1.595368	3.211197	-1.335530
H	0.106153	1.641357	-1.270441
H	1.490629	1.250921	-2.277624
C	1.945287	3.116925	1.184801
H	0.498840	1.517610	1.428800
H	2.111723	1.083336	1.957613
C	1.345665	3.918937	0.011848
H	1.065610	3.736538	-2.135963
H	2.664716	3.299159	-1.560613
H	1.657118	3.576026	2.135378
H	3.036224	3.202641	1.115719
C	-0.123110	4.256338	0.227821
F	-0.600951	5.022942	-0.778484
F	-0.921197	3.160247	0.299891
F	-0.301488	4.946582	1.376345
H	1.833498	4.900436	-0.019786

Structure **16b**. Energy (a.u.): -1503.384781

B	0.738113	-0.460146	0.045271
B	-1.128443	1.214824	0.170643
C	-3.612775	-1.589175	-0.273353
C	-3.057824	-1.138462	1.094750
H	-3.413899	-0.117733	1.275000
H	-3.484806	-1.761431	1.887694
C	-1.521323	-1.142808	1.175372
H	-1.173109	-2.183135	1.142788
H	-1.226281	-0.734264	2.148545
C	-0.856421	-0.332410	0.032474
C	-1.372459	-0.868950	-1.342726
H	-0.971716	-0.263590	-2.161973
H	-1.004133	-1.889437	-1.498711
C	-2.907697	-0.861770	-1.437976
H	-3.255839	0.178957	-1.433074
H	-3.232408	-1.291718	-2.391420
C	-1.745231	3.242696	1.047879
C	-1.011314	3.452567	-0.335613
C	-3.271649	3.369974	0.955563
H	-3.581944	4.406843	0.795711
H	-3.713542	3.020741	1.892801
H	-3.675358	2.759506	0.142817
C	-1.219084	4.097195	2.199623
H	-0.158701	3.917996	2.384792
H	-1.766319	3.853884	3.114745
H	-1.363643	5.162634	1.992527
C	-1.738498	4.357331	-1.328203
H	-2.737369	3.984148	-1.560465
H	-1.171963	4.406346	-2.262518
H	-1.827970	5.375275	-0.934835
C	0.448425	3.900536	-0.187011
H	0.517757	4.927817	0.182199
H	0.936901	3.859532	-1.164903
H	1.001340	3.247800	0.493568
C	2.842915	-1.483223	0.898519
C	3.497933	-2.360765	1.749816
H	2.922952	-2.963830	2.447870
C	4.902953	-2.471017	1.707239
H	5.395707	-3.165623	2.382141
C	5.652292	-1.717975	0.829819
H	6.734166	-1.810488	0.804346
C	5.019607	-0.806169	-0.058225

C	5.748721	-0.006223	-0.979810
H	6.830884	-0.093887	-1.009766
C	5.090430	0.864850	-1.820368
H	5.656586	1.471179	-2.522355
C	3.686313	0.988063	-1.791729
H	3.183490	1.677924	-2.464574
C	2.938689	0.224880	-0.906237
C	3.594148	-0.688339	-0.022538
N	1.547708	0.316384	-0.837728
H	1.117120	0.996683	-1.449942
N	1.451458	-1.343596	0.904942
H	0.963408	-1.930590	1.565840
O	-0.986875	2.099475	-0.881346
O	-1.458813	1.846174	1.345542
C	-3.598603	-3.101240	-0.438965
H	-4.681578	-1.343656	-0.310041
F	-4.166410	-3.473370	-1.610607
F	-4.297892	-3.710831	0.547898
F	-2.352811	-3.640621	-0.421983

Structure **TS16b'**. Energy (a.u.): -1612.760760

C	-3.526617	-2.935006	-2.399907
C	-4.189046	-3.108001	-1.204385
C	-3.627772	-2.620282	0.007302
C	-2.368707	-1.941960	-0.040598
C	-1.706020	-1.775104	-1.297621
C	-2.284239	-2.270540	-2.456973
H	-5.223122	-3.300174	1.305289
H	-3.962535	-3.314016	-3.320336
H	-5.145627	-3.621257	-1.170214
C	-4.266129	-2.788000	1.266170
C	-1.782899	-1.456247	1.170983
H	-1.775135	-2.142690	-3.408886
C	-2.434865	-1.645388	2.380424
C	-3.677015	-2.311230	2.416920
H	-1.984598	-1.274716	3.297525
H	-4.172482	-2.446512	3.374542
N	-0.476379	-1.106812	-1.306109
N	-0.550620	-0.800947	1.082076
B	0.160551	-0.599619	-0.135338
C	3.487864	-1.061648	1.132533
C	3.381481	-1.658503	-0.337476
B	1.805232	0.059669	-0.111856
O	2.650178	-0.643122	-1.058929
O	2.389008	-0.139782	1.208618
C	2.570947	-2.965154	-0.412159
H	2.390908	-3.207743	-1.463374
H	3.112217	-3.800109	0.042797
H	1.600260	-2.876724	0.080515
C	4.722450	-1.878600	-1.043686
H	5.321902	-2.627186	-0.514842
H	4.543296	-2.247140	-2.058202
H	5.300886	-0.957395	-1.119753
C	3.318570	-2.101828	2.248396
H	4.103626	-2.864691	2.209127
H	3.383476	-1.603424	3.220476
H	2.347751	-2.597253	2.190814
C	4.788143	-0.280320	1.392376
H	4.692047	0.245863	2.346924
H	5.657125	-0.943448	1.456030
H	4.984935	0.464451	0.618949

H	0.004196	-1.089769	-2.194513
H	-0.111742	-0.547360	1.957148
N	3.120128	2.008509	-1.057931
N	3.993774	1.437341	-1.486978
C	1.632144	1.683793	-0.500004
C	1.439740	2.620044	0.707840
C	0.755178	2.106312	-1.701249
C	-0.040494	2.826217	1.065041
H	1.868607	3.600503	0.468027
H	1.987270	2.211491	1.560274
C	-0.712646	2.376785	-1.323578
H	1.166820	3.029106	-2.127916
H	0.807490	1.342387	-2.483073
C	-0.826492	3.355230	-0.144611
H	-0.110344	3.531242	1.898891
H	-0.491365	1.886043	1.396212
H	-1.229190	2.780341	-2.200090
H	-1.217341	1.444186	-1.059901
H	-0.418975	4.332260	-0.438914
C	-2.279847	3.615621	0.208843
F	-2.389779	4.503725	1.224321
F	-2.919441	2.488408	0.591304
F	-2.960051	4.127082	-0.843396

Structure **16b'**. Energy (a.u.): -1503.384952

B	-0.004685	0.363722	0.030531
B	-0.629460	-2.026773	0.085529
C	4.938146	-0.060941	-0.245394
C	3.642528	-0.845130	-0.161022
H	3.942351	-1.902105	-0.179688
C	2.739103	-0.567550	-1.375350
H	2.511788	0.505394	-1.411813
H	3.275985	-0.811400	-2.298131
C	1.437477	-1.375292	-1.287123
H	1.683736	-2.445538	-1.343909
H	0.821270	-1.174906	-2.169490
C	0.645578	-1.099198	0.025778
C	1.586023	-1.357526	1.234780
H	1.072623	-1.144208	2.179835
H	1.829425	-2.428687	1.281284
C	2.901359	-0.564043	1.157645
H	2.699316	0.512034	1.217565
H	3.546667	-0.816471	2.005750
C	-2.570060	-3.028261	-0.601641
C	-2.259340	-3.412129	0.899188
C	-3.634885	-1.932944	-0.743890
H	-4.631956	-2.303403	-0.488425
H	-3.654486	-1.589439	-1.781881
H	-3.410376	-1.071376	-0.109345
C	-2.898072	-4.203452	-1.520172
H	-2.087259	-4.933292	-1.547939
H	-3.058242	-3.838615	-2.538757
H	-3.813339	-4.708999	-1.195138
C	-3.420902	-3.224692	1.872829
H	-3.776540	-2.193085	1.883249
H	-3.094271	-3.479025	2.885164
H	-4.257890	-3.881346	1.613170
C	-1.656622	-4.814068	1.057382
H	-2.398601	-5.596566	0.873083
H	-1.284130	-4.926833	2.079145

H	-0.816918	-4.964992	0.373008
C	-1.339048	2.109347	-1.155035
C	-1.994469	2.561073	-2.290994
H	-2.011418	1.942460	-3.184562
C	-2.633020	3.818212	-2.285810
H	-3.139665	4.153518	-3.186717
C	-2.622850	4.620044	-1.165369
H	-3.117555	5.586908	-1.171357
C	-1.963030	4.193176	0.019146
C	-1.927885	4.981276	1.201526
H	-2.420539	5.949220	1.202467
C	-1.278737	4.522284	2.326812
H	-1.257667	5.131653	3.226207
C	-0.634138	3.268311	2.338414
H	-0.125944	2.923166	3.235182
C	-0.644183	2.470718	1.203839
C	-1.311133	2.919643	0.022227
F	4.727091	1.276753	-0.227214
F	5.617979	-0.340053	-1.382622
F	5.764369	-0.346157	0.789210
N	-0.014478	1.222439	1.169136
H	0.436190	0.948805	2.030050
N	-0.695441	0.870048	-1.112156
H	-0.791001	0.305183	-1.944315
O	-1.207964	-2.465857	1.251113
O	-1.307960	-2.442674	-1.037840

Structure **TS16a'**. Energy (a.u.): -1612.760356

C	4.766908	-0.941827	-2.385668
C	5.406981	-1.088876	-1.174469
C	4.723590	-0.807137	0.039802
C	3.360151	-0.376896	-0.021422
C	2.721213	-0.234931	-1.293959
C	3.424869	-0.515095	-2.456300
H	6.379561	-1.258057	1.361237
H	5.298842	-1.156940	-3.308510
H	6.441221	-1.417709	-1.130846
C	5.345246	-0.930299	1.312314
C	2.660021	-0.079395	1.190422
H	2.935945	-0.404634	-3.420878
C	3.304025	-0.206746	2.412601
C	4.646846	-0.633300	2.462509
H	2.766839	0.022487	3.329194
H	5.132545	-0.727503	3.430045
N	1.386114	0.185628	-1.315462
N	1.328996	0.332638	1.086971
B	0.628720	0.489339	-0.144499
C	-1.290529	3.311718	0.925954
C	-0.930466	3.480782	-0.615022
B	-0.996685	1.193188	-0.110453
O	-1.182017	2.170345	-1.165918
O	-1.165873	1.899426	1.155709
C	0.550770	3.820021	-0.865414
H	0.751501	3.745725	-1.938071
H	0.790449	4.837553	-0.542238
H	1.223856	3.130148	-0.351484
C	-1.794927	4.494111	-1.370822
H	-1.654676	5.503345	-0.969250
H	-1.501675	4.507834	-2.424864
H	-2.854543	4.242170	-1.321553

C	-0.332281	4.040884	1.878552
H	-0.351485	5.124115	1.716630
H	-0.636579	3.851599	2.912612
H	0.695103	3.691085	1.762731
C	-2.729525	3.726674	1.280420
H	-2.940675	3.404715	2.304572
H	-2.866687	4.811757	1.230166
H	-3.467221	3.259566	0.625821
H	0.996997	0.345874	-2.233835
H	0.877359	0.634135	1.940672
N	-3.385389	0.667975	-0.752896
N	-3.654248	1.632817	-1.270344
C	-2.049249	-0.108773	-0.260736
C	-2.436782	-0.788400	1.064516
C	-1.856673	-1.128676	-1.405820
C	-1.493700	-1.949492	1.429063
H	-3.452700	-1.181784	0.977537
H	-2.429579	-0.037980	1.858617
C	-0.964763	-2.327779	-1.022225
H	-2.836575	-1.515466	-1.698745
H	-1.435269	-0.620256	-2.279112
C	-1.345891	-2.999235	0.311163
H	-1.853001	-2.426050	2.346080
H	-0.494949	-1.558519	1.643247
H	-0.998092	-3.061216	-1.834191
H	0.073537	-1.999703	-0.941494
C	-2.559080	-3.907968	0.183136
H	-0.537581	-3.685646	0.589322
F	-3.686472	-3.254014	-0.208546
F	-2.849446	-4.513649	1.356102
F	-2.343897	-4.883563	-0.728271

Structure **16a'**. Energy (a.u.): -1503.382511

B	0.540412	-0.462645	0.013097
B	-1.067572	1.415572	0.107345
C	-2.451359	-2.845680	-0.210244
C	-1.781099	-2.158047	-1.418927
H	-0.760919	-2.554585	-1.495569
H	-2.297865	-2.449001	-2.339559
C	-1.715748	-0.627270	-1.300631
H	-2.730944	-0.217931	-1.348540
H	-1.197717	-0.224000	-2.177100
C	-1.030108	-0.159292	0.019657
C	-1.778556	-0.801056	1.220703
H	-1.301329	-0.521210	2.167772
H	-2.791302	-0.387437	1.280395
C	-1.868361	-2.335298	1.125626
H	-0.863900	-2.765550	1.215502
H	-2.454680	-2.735631	1.959607
C	-0.767290	3.594151	-0.526626
C	-1.309987	3.526772	0.954884
C	0.743516	3.846989	-0.610754
H	0.998306	4.870553	-0.320810
H	1.073289	3.691507	-1.641673
H	1.299903	3.155353	0.027578
C	-1.514358	4.553041	-1.450937
H	-2.574309	4.303130	-1.521892
H	-1.087565	4.500181	-2.456642
H	-1.421061	5.585719	-1.098904
C	-0.533461	4.360996	1.971594
H	0.517084	4.068775	2.015948

H	-0.964944	4.219796	2.966648
H	-0.590555	5.426920	1.727002
C	-2.811718	3.819604	1.066912
H	-3.030988	4.876958	0.891372
H	-3.149675	3.560588	2.073974
H	-3.387734	3.223003	0.353952
C	2.732451	-0.360362	-1.179245
C	3.475178	-0.066445	-2.313581
H	2.975826	0.319258	-3.198681
C	4.870348	-0.269679	-2.317449
H	5.432782	-0.033635	-3.216765
C	5.524179	-0.759603	-1.207859
H	6.599314	-0.912872	-1.220920
C	4.799828	-1.071464	-0.025258
C	5.428223	-1.574047	1.146521
H	6.503002	-1.730402	1.140132
C	4.683626	-1.856271	2.270944
H	5.173165	-2.239160	3.162279
C	3.287731	-1.658068	2.292264
H	2.716700	-1.886541	3.188569
C	2.637064	-1.171464	1.168076
C	3.383553	-0.868872	-0.012643
N	1.254446	-0.964234	1.142352
H	0.774748	-1.176198	2.005080
N	1.349106	-0.174912	-1.128822
H	0.939699	0.243007	-1.952517
O	-1.133945	2.118507	1.285669
O	-0.990354	2.232580	-0.998359
C	-3.969321	-2.759131	-0.256129
H	-2.260837	-3.923944	-0.278226
F	-4.448436	-1.491344	-0.172756
F	-4.457446	-3.283027	-1.405493
F	-4.531690	-3.452628	0.762160

Structure **TS22a**. Energy (a.u.): -1315.046958

C	4.802417	0.843415	2.196283
C	5.472343	0.378549	1.085568
C	4.751193	-0.110140	-0.037868
C	3.320889	-0.104526	0.006502
C	2.652940	0.387574	1.171939
C	3.393660	0.851710	2.249714
H	6.482163	-0.614068	-1.238923
H	5.362687	1.212244	3.051320
H	6.558059	0.376152	1.054101
C	5.396635	-0.609221	-1.201967
C	2.577671	-0.600809	-1.111127
H	2.881979	1.222023	3.134522
C	3.245771	-1.083081	-2.227890
C	4.654958	-1.082115	-2.262974
H	2.675937	-1.460380	-3.072887
H	5.158588	-1.463736	-3.147180
N	1.253346	0.384071	1.179536
N	1.185392	-0.577887	-1.025272

B	0.454771	-0.102727	0.101102
C	-2.260919	-2.369989	-0.552856
C	-2.131633	-2.218858	1.026421
B	-1.317597	-0.267226	0.029778
O	-1.952197	-0.803272	1.213532
O	-1.628535	-1.185652	-1.064242
C	-0.898165	-2.930835	1.612450
H	-0.791413	-2.638595	2.661203
H	-0.997253	-4.019801	1.569698
H	0.021023	-2.648917	1.093117
C	-3.369446	-2.652105	1.817320
H	-3.568912	-3.720481	1.681986
H	-3.199902	-2.473973	2.883571
H	-4.255788	-2.089686	1.520730
C	-1.531840	-3.591984	-1.130257
H	-1.944331	-4.528706	-0.739536
H	-1.650261	-3.602982	-2.218368
H	-0.463121	-3.565225	-0.909623
C	-3.713265	-2.392009	-1.059540
H	-3.702890	-2.308792	-2.150619
H	-4.224103	-3.323417	-0.793938
H	-4.296986	-1.558647	-0.665624
H	0.829312	0.693997	2.042219
H	0.667618	-0.997457	-1.787017
N	-3.408676	1.226548	-0.060232
N	-4.144245	0.601064	0.515154
C	-1.757013	1.310309	-0.308861
C	-1.339645	2.460941	0.634954
C	-1.595312	1.655459	-1.791436
C	-1.854950	3.842046	0.177685
H	-0.247366	2.472793	0.524309
C	-2.103483	3.044520	-2.201747
H	-0.517737	1.590336	-1.986791
H	-2.054606	0.859906	-2.385106
C	-1.540539	4.141780	-1.292290
H	-1.416310	4.609064	0.827104
H	-2.941510	3.890566	0.336805
H	-1.835105	3.232578	-3.247613
H	-3.200827	3.058884	-2.154548
H	-0.452045	4.207644	-1.428001
H	-1.949719	5.119086	-1.573052
C	-1.658780	2.214245	2.118232
H	-1.117475	2.934049	2.740892
H	-2.726547	2.351038	2.321180
H	-1.404814	1.199827	2.433508

Structure **22a**. Energy (a.u.): -1205.663198

C	5.408801	1.431586	0.853147
C	5.722504	0.147728	0.463200
C	4.705762	-0.733415	0.004452
C	3.356106	-0.260628	-0.042908
C	3.061062	1.076385	0.366680
C	4.081901	1.905847	0.808582
H	6.000798	-2.427730	-0.376537
H	6.192963	2.098012	1.202343
H	6.748174	-0.207718	0.500699
C	4.977408	-2.065444	-0.410410
C	2.316782	-1.129582	-0.500032
H	3.853636	2.922325	1.119084
C	2.624008	-2.423544	-0.897612
C	3.956584	-2.880805	-0.849167

H	1.831932	-3.080131	-1.248088
H	4.174767	-3.897281	-1.165869
N	1.732438	1.504933	0.304030
N	1.012313	-0.635775	-0.526543
B	0.649249	0.691241	-0.146452
C	-2.958356	-1.939944	-0.332425
C	-3.164825	-1.438441	1.146948
B	-1.828511	0.041943	0.005923
O	-2.688989	-0.063261	1.073900
O	-1.863530	-1.093858	-0.789848
C	-2.269148	-2.157177	2.164751
H	-2.320599	-1.626242	3.119071
H	-2.590579	-3.190003	2.328572
H	-1.224563	-2.164706	1.840959
C	-4.611116	-1.422562	1.636509
H	-5.027023	-2.435394	1.657656
H	-4.648175	-1.021779	2.653366
H	-5.245617	-0.797787	1.005628
C	-2.535740	-3.401072	-0.473205
H	-3.312941	-4.069101	-0.087640
H	-2.382787	-3.638869	-1.529937
H	-1.605651	-3.609809	0.058839
C	-4.152999	-1.648435	-1.249751
H	-3.856262	-1.828395	-2.286607
H	-5.005833	-2.293603	-1.018968
H	-4.474181	-0.606512	-1.166766
H	1.577352	2.458437	0.597474
H	0.300181	-1.268923	-0.869020
C	-0.850558	1.240635	-0.315939
C	-1.119164	2.538068	0.515726
C	-0.970527	1.596447	-1.844781
C	-2.475329	3.175338	0.147364
H	-0.352588	3.272555	0.210989
C	-2.316228	2.243545	-2.204214
H	-0.163867	2.294914	-2.112180
H	-0.816133	0.697736	-2.450265
C	-2.587891	3.488228	-1.350549
H	-2.616027	4.093645	0.732270
H	-3.280944	2.490948	0.445591
H	-2.330337	2.501689	-3.270619
H	-3.123913	1.512741	-2.053497
H	-1.857672	4.267618	-1.612287
H	-3.577649	3.901737	-1.580429
C	-1.004338	2.358231	2.039211
H	-1.076961	3.328708	2.543797
H	-1.804277	1.719113	2.419549
H	-0.050217	1.904800	2.327184

Structure **TS22b**. Energy (a.u.): -1315.037040

C	-4.821776	-0.605825	-2.246851
C	-5.486629	-0.219444	-1.103287
C	-4.761340	0.120191	0.071176
C	-3.331954	0.059930	0.038975
C	-2.669541	-0.343383	-1.163361
C	-3.414227	-0.671890	-2.287342
H	-6.487134	0.557667	1.305462
H	-5.385655	-0.866387	-3.138602
H	-6.571599	-0.172962	-1.082093
C	-5.402329	0.510345	1.278594
C	-2.584670	0.387481	1.214382
H	-2.906115	-0.979096	-3.197785

C	-3.248859	0.758530	2.374963
C	-4.657217	0.817134	2.396421
H	-2.676894	1.003628	3.266259
H	-5.156806	1.110483	3.315891
N	-1.272833	-0.389338	-1.154730
N	-1.190765	0.318045	1.143957
B	-0.464886	-0.067373	-0.021891
C	2.038201	-2.314147	1.044486
C	1.882422	-2.527149	-0.535304
B	1.288482	-0.313401	-0.001239
O	1.755390	-1.188863	-1.057122
O	1.656021	-0.949268	1.260700
C	0.621193	-3.316692	-0.933610
H	0.536499	-3.313420	-2.025006
H	0.676608	-4.358831	-0.604506
H	-0.289999	-2.874911	-0.527425
C	3.085182	-3.192376	-1.215830
H	3.213463	-4.222864	-0.867766
H	2.914751	-3.221703	-2.296405
H	4.011913	-2.646563	-1.039669
C	1.116751	-3.205176	1.893777
H	1.342999	-4.268839	1.762072
H	1.259256	-2.959764	2.950591
H	0.064313	-3.040321	1.655264
C	3.476554	-2.484369	1.563584
H	3.504793	-2.187690	2.616478
H	3.815069	-3.523327	1.494224
H	4.186037	-1.855699	1.022980
H	-0.833589	-0.722401	-2.001989
H	-0.701373	0.448709	2.018427
N	3.527447	0.797671	-0.285559
N	4.133429	-0.050346	-0.706643
C	1.946692	1.232371	-0.097614
C	1.757161	2.153105	-1.335248
C	1.906804	1.999226	1.225832
C	2.717763	3.368458	-1.273546
H	2.000441	1.557051	-2.223680
C	2.800526	3.251403	1.259938
H	0.859453	2.287647	1.372443
H	2.158112	1.310171	2.037288
C	2.591707	4.158190	0.038640
H	2.514921	4.020585	-2.131003
H	3.753511	3.023900	-1.387010
H	2.612774	3.807250	2.185779
H	3.850461	2.931691	1.298853
H	3.321761	4.975774	0.049998
H	1.603328	4.631046	0.095977
C	0.304192	2.644418	-1.500101
H	-0.381276	1.826724	-1.715787
H	-0.067238	3.168303	-0.615511
H	0.267369	3.348873	-2.337960

Structure **22b**. Energy (a.u.): -1205.662112

C	-4.102080	-2.112717	-1.737528
C	-5.000262	-1.580395	-0.838169
C	-4.593069	-0.565509	0.070038
C	-3.237358	-0.109899	0.029772
C	-2.327626	-0.681168	-0.914087
C	-2.764296	-1.670488	-1.783955
H	-6.510709	-0.329518	1.049868
H	-4.423141	-2.887752	-2.428353

H	-6.028979	-1.927788	-0.810734
C	-5.480519	0.013088	1.017730
C	-2.806854	0.907880	0.937155
H	-2.070342	-2.099615	-2.502081
C	-3.703679	1.446234	1.848536
C	-5.038105	0.992274	1.880348
H	-3.372632	2.219871	2.536672
H	-5.723953	1.428445	2.601645
N	-1.011827	-0.215611	-0.918882
N	-1.476328	1.329535	0.868260
B	-0.520163	0.807504	-0.050422
C	3.002145	-1.712113	1.141028
C	2.507211	-2.202897	-0.278376
B	1.794443	-0.053711	0.113508
O	2.049147	-0.963334	-0.894494
O	2.228289	-0.496481	1.340447
C	1.294741	-3.140823	-0.210032
H	0.911279	-3.302467	-1.221709
H	1.562574	-4.114733	0.210027
H	0.488756	-2.712286	0.391332
C	3.588566	-2.810378	-1.169959
H	4.002784	-3.718288	-0.719020
H	3.156041	-3.081888	-2.137198
H	4.403854	-2.108221	-1.351903
C	2.704200	-2.664741	2.297738
H	3.228299	-3.617109	2.165609
H	3.046905	-2.218021	3.235331
H	1.635412	-2.864109	2.391670
C	4.481109	-1.303392	1.166200
H	4.693695	-0.802416	2.114597
H	5.141783	-2.171232	1.080127
H	4.717347	-0.606886	0.356839
H	-0.383340	-0.676904	-1.562994
H	-1.218552	2.050201	1.526889
C	1.001797	1.291818	-0.114641
C	1.321258	1.882111	-1.541164
C	1.333152	2.331429	0.991949
C	2.774655	2.405561	-1.591694
H	1.255098	1.059941	-2.264299
C	2.776455	2.853259	0.903824
H	0.649918	3.190806	0.918297
H	1.170475	1.885017	1.980038
C	3.089314	3.424749	-0.486023
H	2.972579	2.844857	-2.578032
H	3.457858	1.550701	-1.492247
H	2.948820	3.613856	1.675608
H	3.465624	2.026710	1.122989
H	4.142832	3.725026	-0.544746
H	2.502394	4.339287	-0.644856
C	0.317515	2.957802	-1.995615
H	-0.696690	2.551575	-2.065445
H	0.281813	3.814332	-1.314924
H	0.588756	3.340573	-2.986129

Structure **TS22b'**. Energy (a.u.): -1315.037064

C	-4.689449	-0.582260	-2.304814
C	-5.337658	-0.572815	-1.088862
C	-4.601059	-0.428866	0.118495
C	-3.179112	-0.285907	0.044899
C	-2.534058	-0.298337	-1.232172
C	-3.288688	-0.446414	-2.387376

H	-6.301741	-0.535054	1.456218
H	-5.261135	-0.695713	-3.222056
H	-6.417333	-0.678682	-1.035689
C	-5.222433	-0.428445	1.397037
C	-2.419339	-0.150424	1.249820
H	-2.793666	-0.456183	-3.355112
C	-3.063522	-0.160661	2.478873
C	-4.464985	-0.299888	2.541122
H	-2.481695	-0.058416	3.391167
H	-4.949636	-0.304188	3.513819
N	-1.143708	-0.157537	-1.264215
N	-1.034013	-0.010339	1.134895
B	-0.327195	-0.000209	-0.103513
C	2.497872	-1.913588	0.880546
C	2.184377	-2.196272	-0.655288
B	1.444431	-0.028311	-0.121205
O	1.930684	-0.883136	-1.195039
O	1.908741	-0.627811	1.123604
C	0.925794	-3.055607	-0.877916
H	0.692192	-3.066827	-1.946679
H	1.082188	-4.088765	-0.552943
H	0.055245	-2.658959	-0.352071
C	3.338740	-2.824172	-1.443148
H	3.577125	-3.821679	-1.058802
H	3.046404	-2.929561	-2.492355
H	4.239120	-2.210727	-1.406473
C	1.862688	-2.922651	1.848505
H	2.245211	-3.935605	1.682127
H	2.105156	-2.637791	2.877011
H	0.775402	-2.941539	1.754650
C	3.999642	-1.819211	1.202074
H	4.114952	-1.455805	2.227630
H	4.494790	-2.793197	1.129368
H	4.518338	-1.122873	0.540921
H	-0.715918	-0.246676	-2.175069
H	-0.510127	-0.013608	1.999596
N	3.470727	1.301909	-0.839613
N	4.078231	0.484537	-1.322608
C	1.947157	1.571554	-0.379165
C	2.052293	2.591850	0.783470
C	1.379461	2.263904	-1.647742
C	0.680262	3.247543	1.047756
H	2.690730	3.402513	0.401899
C	0.066734	3.032738	-1.392860
H	2.122557	2.983772	-2.012546
H	1.244832	1.516013	-2.435851
C	0.166919	3.983604	-0.195303
H	0.794573	3.948335	1.883255
H	-0.046780	2.492238	1.366994
H	-0.182510	3.588082	-2.304949
H	-0.749006	2.325274	-1.227583
H	0.850980	4.811404	-0.430913
H	-0.812151	4.433671	0.003998
C	2.704647	2.066312	2.067696
H	2.114974	1.275548	2.532318
H	3.698190	1.650620	1.872562
H	2.820796	2.892633	2.777535

Structure **22b'**. Energy (a.u.): -1205.658413

C	-4.945602	0.429664	-1.814068
C	-5.263194	-0.598054	-0.952746

C	-4.307163	-1.069828	-0.012580
C	-3.015936	-0.454578	0.021472
C	-2.715136	0.609660	-0.882904
C	-3.674976	1.039927	-1.787919
H	-5.560987	-2.599559	0.871104
H	-5.682878	0.782887	-2.530013
H	-6.245333	-1.061035	-0.980883
C	-4.581542	-2.130612	0.892795
C	-2.036245	-0.915987	0.953987
H	-3.443130	1.849875	-2.474817
C	-2.342548	-1.955994	1.820658
C	-3.617832	-2.555597	1.781679
H	-1.595667	-2.302279	2.530288
H	-3.837434	-3.367425	2.469942
N	-1.444720	1.187895	-0.819308
N	-0.785655	-0.295974	0.951639
B	-0.420307	0.788663	0.092346
C	3.209395	-1.775811	0.234679
C	2.887479	-1.637075	-1.302553
B	1.942970	0.104910	-0.147123
O	2.396226	-0.269804	-1.390986
O	2.288665	-0.813123	0.827101
C	1.742500	-2.545218	-1.770588
H	1.448469	-2.250716	-2.781621
H	2.042806	-3.597049	-1.792625
H	0.865740	-2.446280	-1.124594
C	4.088673	-1.780706	-2.234823
H	4.525851	-2.781696	-2.156445
H	3.767551	-1.632879	-3.269752
H	4.862757	-1.043574	-2.014647
C	2.926871	-3.149367	0.839540
H	3.561443	-3.914784	0.380673
H	3.144250	-3.130904	1.911507
H	1.883172	-3.440867	0.710415
C	4.624638	-1.314669	0.605787
H	4.701489	-1.242748	1.694190
H	5.384083	-2.018671	0.253029
H	4.843097	-0.329085	0.185478
H	-1.279656	1.923460	-1.489679
H	-0.101700	-0.693336	1.580530
C	1.066623	1.400747	0.094132
C	1.467415	2.152890	1.426644
C	1.315973	2.367996	-1.110177
C	0.777660	3.529433	1.527797
H	2.548864	2.351997	1.347216
C	0.668351	3.756531	-0.977262
H	2.399120	2.520546	-1.219062
H	1.002596	1.887361	-2.043826
C	1.078618	4.437643	0.331763
H	1.094264	4.018091	2.458272
H	-0.309446	3.381792	1.611722
H	0.950749	4.375075	-1.838472
H	-0.427301	3.684090	-0.996014
H	2.155693	4.657571	0.306002
H	0.565847	5.401000	0.441698
C	1.254181	1.385338	2.741399
H	0.189610	1.233253	2.948517
H	1.751853	0.413503	2.735402
H	1.665185	1.966482	3.574841

Structure **TS22a'**. Energy (a.u.): -1315.037474

C	-4.751532	-0.213566	-2.346637
C	-5.397111	-0.274889	-1.130829
C	-4.652832	-0.269637	0.080305
C	-3.225495	-0.192202	0.011447
C	-2.583162	-0.127338	-1.265600
C	-3.345909	-0.139749	-2.424868
H	-6.355422	-0.401896	1.413172
H	-5.329183	-0.221295	-3.267129
H	-6.480637	-0.331696	-1.080945
C	-5.272161	-0.344938	1.357651
C	-2.459170	-0.197398	1.219797
H	-2.853265	-0.091559	-3.392688
C	-3.101694	-0.277394	2.447163
C	-4.508315	-0.350228	2.504715
H	-2.514164	-0.281688	3.361508
H	-4.991818	-0.411183	3.476105
N	-1.187210	-0.051852	-1.294646
N	-1.069184	-0.119286	1.108595
B	-0.364372	-0.040388	-0.128107
C	2.416506	-2.035936	0.900455
C	2.055919	-2.347439	-0.617142
B	1.404258	-0.146765	-0.130036
O	1.851907	-1.038365	-1.188649
O	1.838167	-0.743503	1.131963
C	0.750950	-3.147979	-0.784475
H	0.481488	-3.162809	-1.844446
H	0.867498	-4.182301	-0.446535
H	-0.080304	-2.700256	-0.235806
C	3.160524	-3.051978	-1.410622
H	3.363823	-4.045499	-0.996949
H	2.838298	-3.179506	-2.448512
H	4.088233	-2.479202	-1.416153
C	1.808583	-3.023169	1.906787
H	2.181490	-4.040889	1.747366
H	2.084038	-2.720714	2.921914
H	0.718828	-3.039092	1.846490
C	3.928719	-1.940776	1.171134
H	4.077400	-1.549632	2.182201
H	4.418056	-2.918451	1.109677
H	4.429865	-1.265495	0.475460
H	-0.769686	-0.083295	-2.213906
H	-0.539091	-0.212726	1.965037
N	3.477482	1.093283	-0.939630
N	3.976295	0.250556	-1.495166
C	1.968670	1.423990	-0.326485
C	2.194295	2.198996	0.994150
C	1.396229	2.305297	-1.458219
C	0.893061	2.948623	1.377908
H	2.393903	1.448475	1.764783
C	0.163272	3.128118	-1.027353
H	2.168894	3.009279	-1.787636
H	1.154420	1.675200	-2.320924
C	0.405849	3.897978	0.275614
H	1.078496	3.499237	2.307845
H	0.104046	2.220971	1.594498
H	-0.088921	3.816120	-1.842916
H	-0.696490	2.464495	-0.903743
H	1.139222	4.697883	0.110848
H	-0.520547	4.390292	0.592394
C	3.392326	3.168907	0.963325
H	3.436092	3.727298	1.904429
H	4.337218	2.629030	0.854958
H	3.331370	3.898957	0.150413

Structure **22a'**. Energy (a.u.): -1205.659449

C	-4.054905	-1.943558	-1.955704
C	-4.844058	-1.644271	-0.866394
C	-4.354438	-0.798951	0.166259
C	-3.031349	-0.267212	0.049686
C	-2.235739	-0.595014	-1.091660
C	-2.749871	-1.424371	-2.078294
H	-6.132515	-0.863055	1.402308
H	-4.438304	-2.590561	-2.740124
H	-5.848365	-2.049081	-0.781740
C	-5.126914	-0.462905	1.311078
C	-2.516810	0.581107	1.078347
H	-2.142177	-1.669405	-2.945581
C	-3.302132	0.884433	2.181211
C	-4.605516	0.357735	2.287587
H	-2.907824	1.529969	2.961834
H	-5.203559	0.608812	3.159477
N	-0.947970	-0.060975	-1.167078
N	-1.221000	1.082600	0.930657
B	-0.371616	0.798576	-0.180230
C	2.971456	-1.769648	1.055878
C	2.614889	-2.206599	-0.420034
B	1.902482	-0.061029	-0.037870
O	2.256079	-0.937991	-1.040752
O	2.195863	-0.547753	1.215169
C	1.376300	-3.108090	-0.507854
H	1.088391	-3.214447	-1.557585
H	1.574831	-4.106443	-0.107082
H	0.527505	-2.678821	0.030877
C	3.766284	-2.821661	-1.213487
H	4.105523	-3.754037	-0.750032
H	3.428969	-3.053227	-2.227881
H	4.615580	-2.140592	-1.289909
C	2.547803	-2.751570	2.146807
H	3.066719	-3.709361	2.034554
H	2.805087	-2.341200	3.127455
H	1.471926	-2.932825	2.130675
C	4.446046	-1.385970	1.238118
H	4.571391	-0.915653	2.217367
H	5.100226	-2.261767	1.192246
H	4.769519	-0.671530	0.475973
H	-0.401929	-0.360722	-1.962618
H	-0.901912	1.668841	1.687996
C	1.147229	1.298901	-0.308966
C	1.508979	2.415020	0.730217
C	1.439873	1.804846	-1.756785
C	0.793542	3.742618	0.381300
H	1.154185	2.088724	1.718199
C	0.719619	3.122929	-2.076340
H	2.520690	1.949897	-1.886831
H	1.169254	1.041279	-2.493880
C	1.069302	4.214701	-1.055163
H	1.091868	4.519662	1.096973
H	-0.290207	3.612334	0.497191
H	0.978215	3.455243	-3.089579
H	-0.366791	2.954900	-2.072036
H	2.127632	4.487075	-1.163862
H	0.496571	5.127000	-1.261691
C	3.026206	2.631559	0.891194
H	3.225027	3.427538	1.617951
H	3.512948	1.722563	1.254312
H	3.509668	2.921567	-0.046841

Cartesian coordinates in Å and the electronic energies for structures Scheme S2:

Structure **[CH_3(H)C(MeO$^-$→Bpin)(Bdan)]**. Energy (a.u.): -1125.478835

C	3.475905	2.500829	-1.152560
C	4.495006	1.840488	-0.494180
C	4.271647	0.548913	0.054458
C	2.978578	-0.048518	-0.094563
C	1.938490	0.654672	-0.790008
C	2.203521	1.924468	-1.307649
H	6.265266	0.279612	0.863578
H	3.656007	3.491538	-1.565282
H	5.474476	2.298515	-0.382276
C	5.282199	-0.170527	0.750983
C	2.724733	-1.343723	0.463651
H	1.416039	2.456558	-1.833696
C	3.743772	-2.010887	1.142472
C	5.012310	-1.416832	1.277424
H	3.548474	-2.993402	1.565832
H	5.791468	-1.957703	1.810873
N	0.710935	0.043894	-0.918767
N	1.463333	-1.891549	0.298781
B	0.374317	-1.252447	-0.400910
C	-2.477118	0.895818	1.316215
C	-2.710977	1.453003	-0.160939
B	-2.272591	-0.854736	-0.295307
O	-2.109064	0.462853	-0.982526
O	-2.298488	-0.496520	1.149238
C	-2.034633	2.803254	-0.444299
H	-2.200102	3.077480	-1.492457
H	-2.451442	3.601912	0.181781
H	-0.956085	2.764391	-0.272690
C	-4.203835	1.575948	-0.540224
H	-4.721832	2.351367	0.038258
H	-4.267137	1.840836	-1.601598
H	-4.703850	0.615198	-0.412860
C	-1.198158	1.452369	1.977950
H	-1.270928	2.519965	2.221047
H	-1.025243	0.900596	2.908218
H	-0.327172	1.296941	1.337372
C	-3.658865	1.142000	2.272241
H	-3.428156	0.702673	3.249421
H	-3.855532	2.212092	2.421206
H	-4.569597	0.667964	1.900526
H	-0.077322	0.578308	-1.282970
H	1.327640	-2.806782	0.704255
C	-1.026555	-1.888835	-0.661178
H	-1.138656	-2.777944	-0.016862
C	-1.139260	-2.359854	-2.136019
H	-1.001136	-1.518253	-2.825763
H	-0.398069	-3.126761	-2.409944
H	-2.138897	-2.761661	-2.333122
O	-3.580625	-1.435639	-0.716498

C	-4.043553	-2.536820	-0.000351
H	-5.081408	-2.759436	-0.297927
H	-3.454987	-3.457614	-0.185890
H	-4.034150	-2.367021	1.089716

Structure **TS[CH_3(H)C(MeO→Bpin)(Bdan)]$^-$**. Energy (a.u.): -1125.439603

C	4.196155	-2.048376	1.326265
C	4.811603	-1.465828	0.235217
C	4.212791	-0.345140	-0.405394
C	2.973073	0.159893	0.098959
C	2.345355	-0.466067	1.231678
C	2.977378	-1.564665	1.829720
H	5.750528	-0.095216	-1.916988
H	4.660639	-2.904952	1.812777
H	5.754269	-1.850915	-0.145900
C	4.809159	0.288299	-1.531283
C	2.348121	1.298018	-0.524019
H	2.509420	-2.042309	2.688091
C	2.975944	1.884916	-1.632657
C	4.190315	1.375168	-2.119152
H	2.509746	2.743724	-2.111201
H	4.650849	1.854832	-2.981785
N	1.154348	0.033899	1.687877
N	1.171870	1.767127	-0.012276
B	0.431879	1.208696	1.143092
C	-2.189965	-0.926916	-1.346882
C	-2.951686	-1.604684	-0.125750
B	-2.943532	0.667740	0.126924
O	-3.107232	-0.532044	0.815252
O	-2.508118	0.468275	-1.184266
C	-2.185568	-2.740795	0.556831
H	-2.767200	-3.108156	1.408674
H	-2.018928	-3.579341	-0.129180
H	-1.220493	-2.395635	0.930181
C	-4.370126	-2.084884	-0.484368
H	-4.360463	-2.943006	-1.165724
H	-4.882198	-2.379551	0.436707
H	-4.950800	-1.280144	-0.944235
C	-0.667037	-1.089633	-1.287685
H	-0.364428	-2.122786	-1.491974
H	-0.212839	-0.443770	-2.044230
H	-0.272074	-0.786398	-0.318603
C	-2.689712	-1.357927	-2.730953
H	-2.133326	-0.811673	-3.499075
H	-2.527061	-2.429320	-2.895701
H	-3.751344	-1.139378	-2.866711
H	0.780348	-0.424369	2.506642
H	0.767410	2.550218	-0.505530
C	-0.848201	1.724829	1.643704
H	-1.148369	2.722939	1.308439
C	-1.484061	1.317539	2.958308
H	-1.295834	0.259001	3.197000
H	-1.131082	1.891919	3.839551
H	-2.578661	1.420199	2.949339
O	-3.672841	1.777881	0.488552
C	-3.553815	2.944844	-0.293487
H	-4.293973	3.670753	0.062839
H	-2.553811	3.385751	-0.195699
H	-3.738398	2.743787	-1.357621

Structure **[CH_3(H)C(Bdan)]$^-$**. Energy (a.u.): -598.970169

C	3.485829	2.434917	-1.218506
C	4.453072	1.915007	-0.378501
C	4.275201	0.623875	0.194291
C	3.090360	-0.115151	-0.113184
C	2.092971	0.443671	-0.991206
C	2.317928	1.722170	-1.529772
H	6.144889	0.608360	1.299372
H	3.627029	3.423671	-1.654229
H	5.353831	2.477867	-0.145275
C	5.243288	0.047476	1.064668
C	2.883274	-1.425303	0.452571
H	1.571563	2.154046	-2.194054
C	3.870468	-1.947763	1.306073
C	5.027708	-1.209901	1.597901
H	3.725175	-2.935746	1.739215
H	5.772048	-1.646161	2.263610
N	0.973069	-0.280216	-1.268315
N	1.746574	-2.106450	0.142360
B	0.642474	-1.639799	-0.748990
H	0.316239	0.170844	-1.888710
H	1.660362	-3.017219	0.570604
C	-0.553582	-2.408196	-1.046670
H	-0.675470	-3.401178	-0.597220
C	-1.700048	-1.996987	-1.933324
H	-1.547909	-0.995984	-2.369368
H	-1.877118	-2.663961	-2.803623
H	-2.685003	-1.939769	-1.423161

Structure **[CH_3(H)C(Bpin)(MeO^-→Bdan)]**. Energy (a.u.): -1125.469695

C	3.768494	-0.797765	2.330553
C	4.054158	-1.570044	1.219754
C	3.318866	-1.379564	0.017258
C	2.305545	-0.368010	-0.027167
C	2.009069	0.414859	1.145725
C	2.762891	0.179214	2.309796
H	4.320535	-2.944893	-1.104941
H	4.333694	-0.948246	3.250033
H	4.829646	-2.331869	1.251036
C	3.549524	-2.178553	-1.137933
C	1.542752	-0.160954	-1.231087
H	2.552277	0.768404	3.200344
C	1.790975	-0.998390	-2.333755
C	2.786264	-1.985982	-2.273845
H	1.215354	-0.852521	-3.245854
H	2.959970	-2.608851	-3.150963
N	0.991931	1.320240	1.108724
N	0.588821	0.811572	-1.253542
B	0.365018	1.887145	-0.171653
C	-3.118295	-1.071954	-0.587889
C	-2.624861	-1.217335	0.904239
B	-2.016607	0.838615	0.087538
O	-2.309731	0.145457	1.256850
O	-2.429058	0.112636	-1.030959
C	-1.328910	-2.031868	1.035644
H	-0.942829	-1.917533	2.052232
H	-1.495965	-3.097806	0.844854
H	-0.559014	-1.667085	0.351933

C	-3.672600	-1.742889	1.887850
H	-3.984425	-2.761033	1.627557
H	-3.243600	-1.768239	2.894312
H	-4.557218	-1.102835	1.917036
C	-2.737299	-2.229679	-1.513176
H	-3.183406	-3.172448	-1.175329
H	-3.104064	-2.025708	-2.524605
H	-1.654232	-2.351719	-1.567596
C	-4.624021	-0.781952	-0.704811
H	-4.845819	-0.488877	-1.735523
H	-5.235303	-1.656235	-0.454926
H	-4.913705	0.045592	-0.050897
H	0.914495	1.880432	1.946645
H	0.005268	0.804934	-2.078229
C	-1.282980	2.195016	0.007690
H	-1.598438	2.696459	-0.921616
C	-1.538044	3.144340	1.194341
H	-1.349226	2.637965	2.149463
H	-0.873975	4.015936	1.145670
H	-2.572708	3.514870	1.239944
O	1.084838	3.162478	-0.455134
C	0.866286	3.810844	-1.664481
H	1.557358	4.664073	-1.751718
H	1.042504	3.158969	-2.540497
H	-0.159761	4.216214	-1.772366

Structure **TS[CH_3(H)C(Bpin)(MeO→Bdan)]**$^-$. Energy (a.u.): -1125.434865

B	0.919488	1.822497	-0.803450
C	-3.408821	-0.403467	-0.420907
C	-3.027147	-1.195292	0.891711
B	-1.889497	0.845945	0.829918
O	-2.381623	-0.204215	1.676051
O	-2.351947	0.548469	-0.521183
C	-2.029421	-2.339191	0.633596
H	-1.667080	-2.706036	1.598965
H	-2.480538	-3.180354	0.092481
H	-1.161701	-1.984706	0.073111
C	-4.224177	-1.741298	1.681906
H	-4.804540	-2.463364	1.093698
H	-3.862869	-2.251185	2.581309
H	-4.887752	-0.935293	2.002579
C	-3.448079	-1.244633	-1.700019
H	-4.220173	-2.021637	-1.645485
H	-3.675823	-0.602576	-2.558251
H	-2.486205	-1.727872	-1.887355
C	-4.731231	0.375491	-0.276941
H	-4.835966	1.049631	-1.133445
H	-5.608326	-0.281425	-0.244348
H	-4.712758	0.986090	0.630043
C	-1.065968	1.984918	1.217944
H	-1.033031	2.870218	0.586287
C	-0.514284	2.186042	2.611794
H	-0.638015	1.279809	3.219150
H	0.567628	2.421604	2.634159
H	-0.998080	3.004351	3.183368
O	0.405361	2.975347	-1.368179
C	-0.721530	2.909811	-2.220697
H	-0.971121	3.932281	-2.526376
H	-0.501601	2.324139	-3.126761
H	-1.585017	2.460129	-1.718741
C	1.467086	-0.590541	-1.017985

C	2.981469	0.916483	0.262768
N	0.656126	0.489135	-1.308593
N	2.146325	1.964721	-0.051080
C	2.657213	-0.387569	-0.240916
C	1.172506	-1.875639	-1.479658
C	3.521665	-1.492982	0.046065
C	4.137529	1.088136	1.025137
C	4.979794	-0.004984	1.295019
C	2.025962	-2.953863	-1.187625
C	3.177955	-2.780591	-0.447508
C	4.692635	-1.268765	0.821487
H	2.388014	2.865004	0.336138
H	-0.304802	0.261557	-1.544619
H	0.279195	-2.030054	-2.078890
H	1.766949	-3.943121	-1.559945
H	3.831552	-3.620950	-0.227578
H	5.349318	-2.107772	1.037203
H	5.875020	0.157360	1.892341
H	4.377357	2.075759	1.411796

Structure **[CH_3(H)C(Bpin)]$^-$**. Energy (a.u.): -489.881019

C	-2.913381	-0.957245	-0.376277
C	-2.962202	0.249487	0.637702
B	-1.357975	0.660959	-1.000308
O	-2.314376	1.275629	-0.085221
O	-1.669421	-0.763650	-1.017122
C	-2.147674	-0.038247	1.917815
H	-2.025539	0.900330	2.468835
H	-2.629003	-0.769238	2.580553
H	-1.152096	-0.402539	1.649959
C	-4.368836	0.723097	1.026582
H	-4.939379	-0.064928	1.535314
H	-4.292652	1.578546	1.707679
H	-4.929193	1.049853	0.147515
C	-2.934285	-2.351587	0.263829
H	-3.857459	-2.526599	0.831562
H	-2.869080	-3.115906	-0.519192
H	-2.080567	-2.489291	0.931664
C	-4.031606	-0.864557	-1.437449
H	-3.815425	-1.585004	-2.233527
H	-5.028742	-1.082782	-1.033311
H	-4.038646	0.134874	-1.880981
C	-0.308633	1.328148	-1.738713
H	0.303920	0.755883	-2.442934
C	0.034865	2.790999	-1.629575
H	-0.609504	3.287391	-0.889989
H	1.079261	3.005181	-1.308740
H	-0.083556	3.375899	-2.569607

8. Computational study on diazoalkane insertion into symmetrical diboron Bpin-Bpin.

Scheme S3 Proposed mechanism for diazo compound type insertion of $CH_3(H)CN_2$ into Bpin-Bpin. Calculated free energies (and electronic energies in brackets) in $kcal.mol^{-1}$

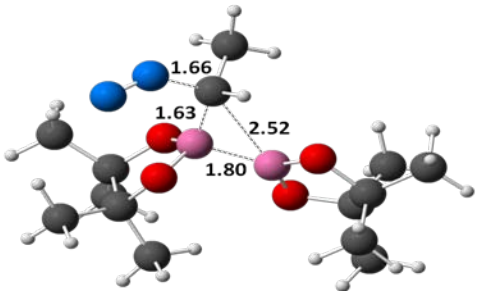


Figure S4 Molecular structure and main geometric parameters of the transition state for diazo compound type insertion into the Bpin-Bpin molecule. Distances in angstroms.