Mechanism of NHC-Catalyzed Conjugate Additions of Diboron and Borosilane Reagents to α,β-Unsaturated Carbonyl Compounds

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SUPPORTING INFORMATION

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General. Infrared (IR) spectra were recorded on a Bruker FT-IR Alpha (ATR mode) spectrophotometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz), 500 (500 MHz) or 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm). ^{11}B NMR were recorded on a Varian Unity INOVA 500 (128 MHz) with BF_3•$(OEt)_2$ resonance as the external reference (thf-d_8: δ 0.0 ppm). ^{19}F NMR were recorded on a Varian Unity INOVA 400 (376 MHz) with CF_3COOH resonance as the external reference (thf-d_8: δ –76.55 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br s = broad singlet), and coupling constants (Hz). High-resolution mass spectrometry was performed on a JEOL AccuTOF-DART (positive mode) or ESI-MS (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomeric ratios were determined by HPLC analysis (high-performance liquid chromatography) with a Shimadzu chromatograph (Chiral Technologies Chiralpak AD-H (4.6 x 250 mm)) in comparison with authentic racemic materials. Specific rotations were measured on a Rudolph Research Analytical Autopol IV Polarimeter. X-ray structures for compound **15**, **34** and **43** were obtained, as described in the cif files, with a Microfocus sealed Cu tube from Incote. It is well established that the aforementioned detector allows for the determination of absolute configuration of molecules that do not have a heavy atom. The absolute configuration was verified by the flack parameter of 0.0 with a standard deviation of 2 and corroborated by Bijvoet parameter test. The melting point of compound **16** was determined using a Thomas Hoover Uni-melt capillary melting point apparatus.

Unless otherwise noted, reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 ºC) or flame-dried glassware with standard dry box or vacuum-line techniques. Solvents were purified under a positive pressure of dry Ar by a modified Innovative Technologies purification system: toluene was purified through a copper oxide and alumina column; CH_2Cl_2 and Et_2O were purged with Ar and purified by passage through two alumina columns. Tetrahydrofuran (Aldrich) was purified by distillation from sodium benzophenone ketyl prior to use. Methanol and *i*-propanol were distilled over sodium. $CDCl_3$ and d_8-thf were purchased from Cambridge Isotope Laboratories and used as received. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher Scientific) under air.

■ **Reagents:**

1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride was purchased from Aldrich and used as received.

Bis(pinacolato)diboron $[B_2(pin)_2]$ was purchased from Frontier Scientific. It was purified by

recrystallization from hot anhydrous pentane and subsequently dried under high vacuum at 50 ºC for 18 h.

Chlorodimethylphenylsilane ($PhMe_2SiCl$) was purchased from Aldrich and used as received.

Copper (I) cyanide was purchased from Aldrich and used as received.

2-Cyclohexen-1-one was purchased from Aldrich and distilled *in vacuo* prior to use.

3-Cyclopropyl-2-cyclohexen-1-one (**9**) was prepared following a procedure disclosed previously.[1]

1,8-Diazabicyclo[5.4.0]undec-7-ene (dbu) was purchased from Aldrich and distilled *in vacuo* prior to use.

1,3-Dicyclohexylimidazolium tetrafluoroborate was purchased from Aldrich or TCI America and purified by silica gel chromatography followed by trituration from CH_2Cl_2/hexanes prior to use.

Dimethylphenylsilylpinacolatoborane [$PhMe_2Si–B(pin)$)] was purchased from Aldrich and distilled *in vacuo* prior to use.

Lithium bromide was purchased from Strem and used as received.

Potassium bis(trimethylsilyl)amide (KHMDS) was purchased from Aldrich and used as received.

Sodium *tert*-butoxide (NaO*t*-Bu) was purchased from Strem and used as received.

Trimethyl borate was purchased from Aldrich and used as received.

Zinc chloride (anhydrous) was purchased from Strem and used as received.

Unless otherwise noted, all the other α,β-unsaturated carbonyls, imidazolinium salts and the corresponding β-boryl (or silyl) carbonyls were reported previously.[2]

■ Preparations and Analytical Data for Compounds (10–17 in Scheme 5)

I. Preparations and analytical data for α,β-unsaturated carbonyls

2-Cyclopropyl-2-cyclohexen-1-one (**substrate for 12**) was prepared based on modification of a reported procedure.[3] Under dry N_2 atmosphere in a flame-dried round-bottom flask, anhydrous $ZnCl_2$ (1.2 g, 8.8 mmol, 1.1 equiv) and 16 mL of 0.58 mol/L cyclopropyl magnesium bromide solution in thf (9.3 mmol, 1.2 equiv) were mixed. The resulting milky-white mixture was allowed to stir at 22 ºC for 30 min, at which time a solution of 2-iodo-2-cyclohexen-1-one (1.7 g, 7.8 mmol, 1.0 equiv) and $Pd(PPh_3)_2Cl_2$ (242 mg, 0.34 mmol, 0.044 equiv) in dmf (20 mL) was added drop-wise. The mixture was allowed to stir at 22 ºC for 12 h, at which time aqueous 10% (wt.) citric acid was added drop-wise to quench the excess organometallic reagent. The mixture was diluted with Et_2O, layers were separated, and the aqueous layer was washed with Et_2O twice. Combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to give brown oil. Purification by silica gel chromatography (5:1 hexanes:Et_2O), followed by distillation (200 ºC, high vacuum) gave 2-cyclopropyl-2-cyclohexen-1-one as a colorless oil (661 mg, 4.8 mmol, 62% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.42 (1H, dd, J = 4.3, 4.3 Hz), 2.45–

2.42 (2H, m), 2.33–2.29 (2H, m), 1.98–1.91 (2H, m), 1.78–1.71 (1H, m), 0.75–0.70 (2H, m), 0.38–0.34 (2H, m). The spectroscopic data match those reported previously.[4]

3-(2,2-Diphenylcyclopropyl)-2-cyclohexen-1-one (**substrate for 13**) was prepared following a modified procedure.[5] Under a dry N_2 atmosphere at –20 ºC, a solution of 2,2-diphenylcyclopropyl magnesium bromide (0.19 mol/L in thf, 25 mL, 4.8 mmol, 0.98 equiv) was added drop-wise to the solution of CuCN (536 mg, 6.0 mmol, 1.2 equiv) and LiBr (1.0 g, 12 mmol, 2.4 equiv) in thf (5 mL). The resulting creamy yellow mixture was allowed to stir at 0 ºC for 5 min. Then it was allowed to cool to –78 ºC with vigorous stirring, to which a solution of 3-iodo-2-cyclohexen-1-one (1.1 g, 4.9 mmol, 1.0 equiv) in thf (5 mL) was added drop-wise. The mixture was allowed to stir at –50 ºC for 12 h, before excess organometallic reagent was quenched by addition of water. The mixture was diluted with water (50 mL) and saturated aqueous NH_4Cl until pH = 7, followed by addition of Et_2O. The layers were then separated, and the aqueous layer was washed with Et_2O twice. The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give light yellow oil. Purification by silica gel chromatography (2:1 hexanes:Et_2O) gave 3-(2,2-diphenylcyclopropyl)-2-cyclohexen-1-one as a viscous colorless oil (1.0 g, 3.6 mmol, 74% yield). IR (neat): 3056 (w), 3023 (w), 2945 (w), 2867 (w), 1660 (s), 1621 (m), 1600 (m), 1494 (m), 1446 (m), 1426 (w), 1396 (w), 1378 (w), 1346 (m), 1324 (m), 1295 (w), 1191 (w), 1179 (w), 1127 (w), 1078 (w), 1038 (w), 1021 (w), 1001 (w), 968 (w), 930 (w), 882 (m), 850 (w), 812 (w), 749 (s), 696 (s), 632 (w), 616 (w), 575 (w), 550 (m), 512 (w), 452 (w), 435 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.30–7.15 (10H, m), 5.78 (1H, s), 2.46 (1H, dd, J = 8.0, 6.3 Hz), 2.18 (2H, dddd, J = 39.6, 16.4, 6.4, 6.4 Hz), 2.07 (1H, ddd, J = 17.6, 5.6, 5.6 Hz), 1.99 (1H, dd, J = 6.4, 6.4 Hz), 1.81 (1H, ddd, J = 18.0, 5.6, 5.6 Hz), 1.70–1.66 (2H, m), 1.63 (1H, dd, J = 8.4 , 5.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 199.2, 163.4, 145.9, 140.0, 130.0, 128.6, 128.5, 127.8, 127.1, 126.9, 126.6, 40.3, 37.4, 33.8, 29.8, 22.5, 19.4; HRMS (DART): Calcd for $C_{21}H_{21}O_1$ $[M+H]^+$: 289.15924, Found: 289.15900.

2-(2,2-Diphenylcyclopropyl)-2-cyclohexen-1-one (**16**) was prepared according to the procedure described for 2-cyclopropyl-2-cyclohexen-1-one. 2-Iodo-2-cyclohexen-1-one (1.5 g, 6.9 mmol, 1.0 equiv), 0.26 mol/L solution of 2,2-diphenylcyclopropyl magnesium bromide in thf (31 mL, 8.1 mmol, 1.2 equiv), anhydrous $ZnCl_2$ (1.4 g, 10 mmol, 1.5 equiv), $Pd(PPh_3)_2Cl_2$ (267 mg, 0.38 mmol, 0.055 equiv), and dmf (30 mL) gave 2-(2,2-diphenylcyclopropyl)-2-cyclohexen-1-one as a colorless crystalline solid (871 mg, 3.0 mmol, 44% yield) after purification by silica gel chromatography (10:1 to 5:1 hexanes:Et_2O) and subsequent recrystallization at –15 ºC from minimal amount of CH_2Cl_2 and Et_2O, and excess pentane. m.p. = 120–121 ºC. IR (neat): 3057 (m), 3022 (m), 2926 (m), 2865 (s), 2828 (m), 1670 (s), 1600 (m), 1495 (s), 1447 (s), 1430 (m), 1393 (m), 1335 (m), 1178 (m), 1147 (m), 1129 (m), 1073 (m), 1043 (m), 1024 (m), 908 (m), 770 (s), 753 (m), 704 (s), 599 (m), 552 (m), 537 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.60–7.58 (2H, m), 7.28 (2H, dd, J = 7.6, 7.6 Hz), 7.18–7.05 (6H, m), 6.17 (1H, dd, J = 4.0, 4.0 Hz), 2.76 (1H, app t. J = 7.6 Hz), 2.37 (1H, BB' of AA'BB' as app ddd, J = 16.4, 9.6, 4.4 Hz), 2.23 (1H, AA' of AA'BB' as app ddd, J = 16.4, 8.0, 4.4 Hz), 2.21–2.14 (1H, m), 1.96–1.87 (1H, m), 1.86–1.78 (1H, m), 1.71 (1H, dd, J = 6.4, 5.6 Hz), 1.58–1.47 (1H, m), 1.35 (1H, dd, J = 8.4, 5.2 Hz);

^{13}C NMR ($CDCl_3$, 100 MHz): δ 200.2, 146.6, 144.2, 141.2, 136.7, 130.1, 129.2, 128.4, 127.9, 126.3, 126.2, 38.7, 38.3, 25.9, 25.0, 22.8, 15.8; HRMS (DART): Calcd for $C_{21}H_{21}O_1$ $[M+H]^+$: 289.15924, Found: 289.15903.

II. Preparations and analytical data for NHC-catalyzed BCA and SCA products

3-Cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanone (**10**): Under dry N_2 atmosphere, in a flame-dried vial (8 x 1 cm) equipped with a stir bar, 1,3-dicyclohexylimidazolium tetrafluoroborate (11 mg, 0.033 mmol, 0.096 equiv), NaO*t*-Bu (3.8 mg, 0.040 mmol, 0.12 equiv) and thf (2.0 mL) were subsequently added. The resulting mixture was allowed to stir at 22 ºC for 2 h, at which time $B_2(pin)_2$ (93 mg, 0.37 mmol, 1.1 equiv) and 3-cyclopropyl-2-cyclohexen-1-one (47 mg, 0.34 mmol, 1.0 equiv) were introduced. The reaction mixture was allowed to stir at 22 ºC for 6 h, at which time water (2 mL) was added with vigorous stirring for 15 min. The mixture was then diluted with EtOAc (~4 mL). The layers were separated, and the aqueous layer was washed with EtOAc three times. Combined organic layers were dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo* to give a white solid. Purification by silica gel chromatography gave 3-cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanone as a colorless oil (77 mg, 0.29 mmol, 85% yield). IR (neat): 3080 (w), 2978 (m), 2934 (w), 2872 (w), 1710 (s), 1447 (w), 1390 (m), 1372 (s), 1310 (s), 1281 (m), 1262 (m), 1229 (w), 1212 (m), 1167 (m), 1141 (s), 1125 (s), 1111 (m), 1088 (w), 1071 (w), 1035 (w), 1018 (w), 968 (w), 916 (m), 853 (s), 824 (w), 775 (w), 730 (s), 693 (w), 669 (m), 647 (m), 579 (w), 539 (w), 520 (w), 478 (w), 461 (w), 426 (w), 412 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.43 (1H, B of AB, J_{AB} = 14.0 Hz), 2.22–2.16 (2H, m), 2.05–1.90 (2H, m), 1.98 (1H, A of AB, J_{AB} = 14.0 Hz), 1.73–1.62 (1H, m), 1.46 (1H, app ddd, J = 12.8, 12.8, 2.4 Hz), 1.16 (12H, s), 0.72–0.65 (1H, m), 0.36–0.21 (4H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 212.0, 83.6, 48.4, 41.4, 32.6, 24.9, 24.7, 24.4, 18.9, 1.5, 1.0; HRMS (ESI^+): Calcd for $C_{15}H_{26}BO_3$ $[M+H]^+$: 265.19750, Found: 265.19750. No products due to ring-opening of the cyclopropane ring were observed.

2-Cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanone (**12**): 2-cyclopropyl-2-cyclohexen-1-one was subjected to the same reaction conditions as above (see compound **10**). 2-Cyclopropyl-2-cyclohexen-1-one (30 mg, 0.22 mmol, 1.0 equiv), 1,3-dicyclohexylimidazolium tetrafluoroborate (14 mg, 0.044 mmol, 0.20 equiv), NaO*t*-Bu (4.6 mg, 0.048 mmol, 0.22 equiv.), $B_2(pin)_2$ (63 mg, 0.25 mmol, 1.1 equiv) and thf (1.5 mL) furnished 2-cyclopropyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanone as a colorless oil (39 mg, 0.15 mmol, 67% yield) after purification by silica gel chromatography (10:1 hexanes:Et_2O). IR (neat): 3079 (w), 2978 (m), 2931 (m), 2853 (w), 1707 (s), 1449 (w), 1406 (w), 1372 (s), 1323 (s), 1257 (m), 1213 (m), 1167 (m), 1142 (s), 1047 (w), 1019 (m), 983 (m), 971 (m), 925 (w), 905 (w), 871 (w), 852 (s), 813 (w), 735 (m), 716 (w), 688 (m), 668 (m), 578 (w), 527 (w), 441 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.55–2.47 (1H, m), 2.24–2.18 (1H, m), 2.03–1.88 (2H, m), 1.80-1.66 (3H, m), 1.62–1.58 (1H, m), 1.23 (6H, s), 1.22 (6H, s), 1.13–1.04 (1H, m), 0.54–0.42 (2H, m), 0.22–0.18 (1H, m), 0.14–0.09 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.3, 83.6,

83.4, 57.1, 40.4, 27.9, 25.1, 24.9, 24.5, 10.8, 5.4, 4.1; HRMS (DART): Calcd for $C_{15}H_{26}BO_3$ $[M+H]^+$: 265.19750, Found: 265.19700.

2-(2,2-Diphenylcyclopropyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanone (14): Following the procedure described above for compound **12**, 2-(2,2-diphenylcyclopropyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohexanone was prepared in 45% yield. IR (neat): 3023 (w), 2975 (w), 2929 (w), 2860 (w), 1703 (s), 1599 (w), 1494 (m), 1446 (m), 1409 (m), 1371 (m), 1261 (s), 1228 (s), 1215 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.26 (m, 8H), 7.18–7.11 (m, 2H), 2.54–2.44 (m, 1H), 2.29 (d, J = 13.9 Hz, 1H), 2.19–2.04 (m, 2H), 2.02–1.87 (m, 2H), 1.79 (d, J = 2.4 Hz, 1H), 1.74 (d, J = 10.6 Hz, 1H), 1.70–1.56 (m, 1H), 1.50 (t, J = 5.6 Hz, 1H), 1.18 (dd, J = 8.8, 5.2 Hz, 1H), 1.08 (s, 6H), 1.05 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 213.4, 146.9, 140.5, 130.3, 128.8, 128.5, 128.3, 126.4, 126.2, 83.5, 50.3, 40.0, 37.2, 28.1, 26.2, 24.8, 24.5, 22.4, 17.9; HRMS (DART): Calcd for $C_{27}H_{34}B_1O_3$ $[M+H]^+$: 417.26010, Found: 417.26075. Compound **14** is air-sensitive and was found to undergo oxidation on silica gel to afford **15**, of which the X-ray crystal structure was obtained.

3-(Dimethyl(phenyl)silyl)-2-(2,2-diphenylcyclopropyl)cyclohexanone (17): Under a dry N_2 atmosphere enone **16** (20 mg, 0.071 mmol, 1.0 equiv), ICy·HBF_4 (**3a**) (2.3 mg, 0.0071 mmol, 0.10 equiv), $PhMe_2Si$–B(pin) (20 mg, 0.078 mmol, 1.1 equiv), dbu (2.2 mg, 0.014 mmol, 0.20 equiv) and thf (0.11 mL) were mixed in a flamed-dried vial (8 x 1 cm) equipped with a stir bar. The resulting mixture was allowed to stir at 22 ºC while H_2O (0.11 mL) was added. After the reaction mixture was allowed to stir at 22 ºC for 12 h, it was diluted with Et_2O. The layers were separated, and the aqueous layer was washed with Et_2O three times. Combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give a colorless solid. Purification by silica gel chromatography (50:1 hexanes:Et_2O) afforded 3-(dimethyl(phenyl)silyl)-2-(2,2-diphenylcyclopropyl)cyclohexenone **17** as a colorless oil (7.2 mg, 0.017 mmol, 24 % yield). No products due to cyclopropane ring opening were observed. IR (neat): 3056 (w), 3023 (w), 2927 (m), 2857 (w), 2836 (w), 1663 (m), 1600 (w), 1494 (m), 1446 (w), 1428 (w), 1369 (w), 1352 (w), 1253 (m), 1193 (m), 1171 (m), 1137 (m), 1118 (m), 1077 (w), 1023 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.60–7.55 (m, 2H), 7.42–7.27 (m, 5H), 7.25–7.06 (m, 8H), 2.66–2.58 (m, 1H), 2.02 (t, J = 5.8 Hz, 2H), 1.65 (dd, J = 6.9, 5.1 Hz, 1H), 1.52–1.44 (m, 1H), 1.41–1.36 (m, 2H), 1.36–1.26 (m, 1H), 1.26–1.15 (m, 1H), 1.07–0.95 (m, 1H), 0.77 (dd, J = 16.0, 5.4 Hz, 1H), 0.47 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 147.7, 147.4, 142.1, 138.4, 133.5, 130.6, 129.7, 128.2, 128.0, 127.9, 127.9, 126.1, 125.5, 112.6, 35.1, 30.9, 30.5, 28.4, 26.4, 23.3, 22.6, 18.7, 0.16, 0.01; HRMS (DART): Calcd for $C_{29}H_{33}Si_1O_1$ $[M+H]^+$: 425.23007, Found: 425.22897.

■ Analytical Data for ^{13}C-Labeled Imidazolinium Salt 7c

^{13}C-Labeled Imidazolinium Salt 7c was prepared according to the reported procedure.[6] IR (neat): 3061 (m), 3035 (m), 2923 (w), 1618 (m), 1574 (s), 1487 (m), 1457 (m), 1444 (m), 1275 (s), 1216 (s), 1054 (s), 827 (s), 770 (s), 755 (s), 736 (s), 699 (s), 595 (m), 522 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.95 (d, $J_{C\text{-}H}$ = 208.8 Hz, 1H), 7.56–7.44 (m, 6H), 7.35–7.30 (m, 6H),

7.25–7.16 (m, 6H), 7.10–7.04 (m, 4H), 6.71–6.69 (m, 4H), 4.68 (s, 2H), 2.28 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 157.2 (^{13}C labeled carbon), 139.8, 138.1, 134.6, 133.7, 131.4, 131.3, 131.0, 130.7, 129.9, 129.4, 129.3, 129.2, 128.4, 128.3, 128.1, 99.1, 75.0, 20.8; ^{11}B NMR (d_8-thf, 160 MHz): δ –1.7 (s); ^{19}F NMR (d_8-thf, 376 MHz): δ –152 (s, 4F); HRMS (ESI$^+$): Calcd for $^{12}C_{40}{}^{13}C_1H_{35}N_2$ [M–BF_4]$^+$: 556.2828, Found: 556.2837; Specific Rotation: $[\alpha]_D^{22}$ –489.8 (*c* 1.1, $CHCl_3$).

■ Analytical Data for Compound 43

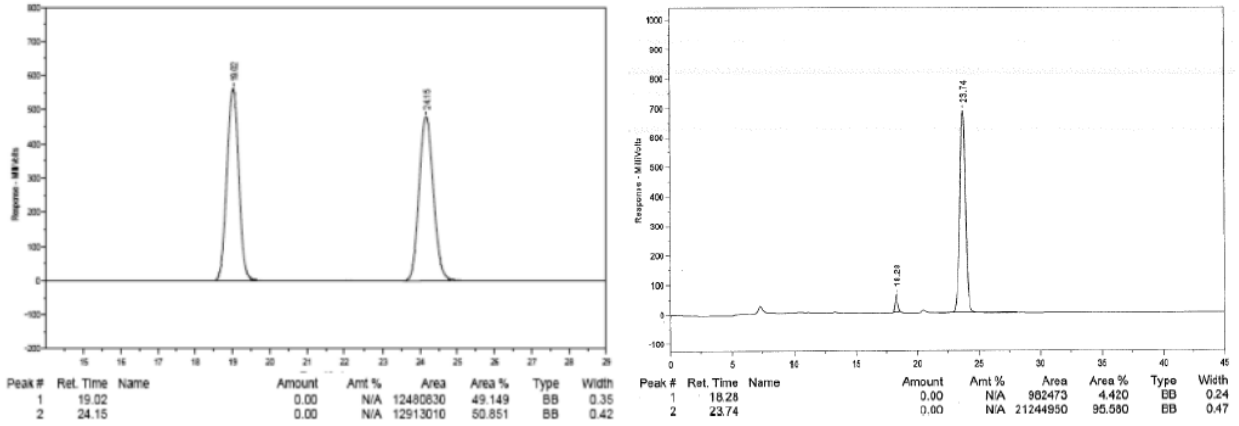
Formamide **43:** In a N_2 filled glove box, imidazolinium tetrafluoroborate salt **7c** (19.2 mg, 0.030 mmol, 1.0 equiv), KHMDS (6.0 mg, 0.030 mmol, 1.0 equiv) and thf (0.50 mL, 0.06 M solution of **7c**) were charged into an oven-dried vial (8 x 1 cm) equipped with a stir bar. The mixture was moved out of the glove box and allowed to stir at 22 ºC under N_2 atm for 30 min. Then 1.5 mL H_2O was added into the reaction mixture, resulting in a colorless homogeneous solution. This solution was allowed to stir at 22 ºC under N_2 atm for 1.75 h, before addition of Et_2O (2 mL). The layers were separated and the aqueous layer was washed with Et_2O twice. Combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo* to give a colorless oil, which was purified by silica gel chromatography (6:1 hexanes:Et_2O) to yield 16 mg (0.028 mmol, 93% yield) of formamide **43** as a viscous oil with ~15% unknown impurities. Various chromatography conditions (different eluting solvents or Al_2O_3 chromatography) as well as recrystallizations were not effective to obtain a pure sample of **43**. The ^{1}H NMR signals of those impurities are at 7.57 (m), 5.03 (m), 4.88 (m), 3.84 (m), 3.63 (m), 1.38 (d, J = 5.6 Hz), 0.977 (d, J = 5.6 Hz) ppm. Nevertheless, the X-ray crystal structure of **43** was still obtained. IR (neat): 3406 (w), 3060 (w), 3029 (w), 2923 (m), 2854 (m), 1674 (s), 1615 (m), 1578 (m), 1570 (m), 1521 (m), 1490 (m), 1454 (m), 1442 (m), 1424 (m), 1303 (m), 1287 (m), 1263 (m), 1199 (w), 1177 (w), 1136 (w), 1073 (w), 1009 (m), 804 (m), 763 (m), 745 (m), 699 (s), 636 (w), 548 (m) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (s, 1H), 7.51–7.37 (5H, m), 7.21–7.18 (1H, m), 7.08–6.87 (14H, m), 6.58–6.33 (6H, m), 5.66 (1H, br s), 5.34 (1H, app d, J = 6.8 Hz), 4.92 (1H, br s), 2.32 (3H, s), 2.26 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.6, 144.0, 140.8, 139.3, 138.7, 138.3, 138.2, 131.5, 130.2, 130.2, 129.8, 129.1, 128.8, 128.1, 128.1, 128.0, 127.9, 127.8, 127.4, 127.0, 126.7, 126.3, 118.0, 112.0, 62.5, 61.2, 21.9, 21.2; HRMS (ESI$^+$): Calcd for $C_{41}H_{37}N_2O_1$ [M+H]$^+$: 573.29059, Found: 573.28998; Optical rotation: $[\alpha]_D^{21}$ –147.7 (c 0.70, $CHCl_3$).

■ Analytical Data for *β*-Silyl Carbonyl 33c

(*R*)-4-(Dimethyl(phenyl)silyl)-4-(4-(trifluoromethyl)phenyl)butan-2-one (33c): In dry N_2 atomsphere, imidazolinium tetrafluoroborate salt **7c** (14 mg, 0.023 mmol, 7.5 mol %) was charged into an oven-dried vial (8 x 1 cm) equipped with a stir bar. Dbu was added into the vial by syringe (10 μL, 10 mg, 0.068 mmol, 22.5 mol %), followed by addition of $PhMe_2Si$–B(pin) (90 μL, 87 mg, 0.33 mmol, 1.1 equiv). The mixture was allowed to stir for ~ 5 seconds before it was added a solution of (*E*)-4-(4-(trifluoromethyl)phenyl)but-3-en-2-one (64 mg, 0.30 mmol, 1.0 equiv) in 1.0 mL thf by syringe. This was immediately followed by addition of water (18 μL, 18 mg, 3.3 equiv). The mixture was allowed to stir for 1 h at 22 ºC. Pentane (5 mL) was added to

the solution (to facilitate imidazolinium salt precipitation), and the resulting solution was dried over anhydrous $MgSO_4$, filtered, and concentrated *in vacuo*. The resulting clear oil was purified by silica gel chromatography (5:1 hexanes:Et_2O) to give 90 mg (0.26 mmol, 86% yield) of (*R*)-4-(Dimethyl(phenyl)silyl)-4-(4-(trifluoromethyl)phenyl)butan-2-one (**33c**). The spectroscopic data match those reported previously.[7] The absolute configuration was assigned by analogy to *β*-silyl ketones previously reported.[2c] IR (neat): 3070 (w), 2960 (w), 1718 (m), 1615 (w), 1580 (w), 1515 (w), 1419 (w), 1357 (w), 1323 (s), 1251(w), 1188 (w), 1161 (s), 1108 (s), 1067 (s), 1015 (w), 998 (w), 952 (w), 910 (w), 850 (w), 831 (w), 807 (s), 773 (s), 734 (s), 670 (m), 646 (s), 611 (s), 599 (w), 569 (w), 537 (w), 513 (w), 467 (w), 420 (w) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.43 (overlapping d, J = 8 Hz, 2H), 7.42–7.33 (m, 5H), 7.02 (overlapping d, J = 8 Hz, 2H), 2.99 (dd, J = 11.0, 3.5 Hz, 1H), 2.93 (dd, J = 16.5, 11.0 Hz, 1H), 2.69 (dd, J = 16.5, 3.5 Hz, 1H), 1.97 (s, 3H), 0.25 (s, 3H), 0.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 146.9, 146.9, 154.0, 134.2, 129.7, 128.0, 127.8, 125.2 (q, $J_{C\text{-}F}$ = 29.6, 14.8 Hz), 43.8, 31.7, 30.1, –4.1, –5.2; ^{19}F NMR (376 MHz, d_8-thf): –60 ppm (s, 3F). Optical rotation: $[\alpha]_D^{22}$ +5.6 (*c* 1.8, $CHCl_3$) for a sample with 87:13 er.

Enantiomeric purity was determined by HPLC analysis in comparison with authentic racemic material (96:4 er shown, Chiralpak AD-H column, 99/1 hexanes/*i*-propanol, 0.3 mL/min, 220 nm).



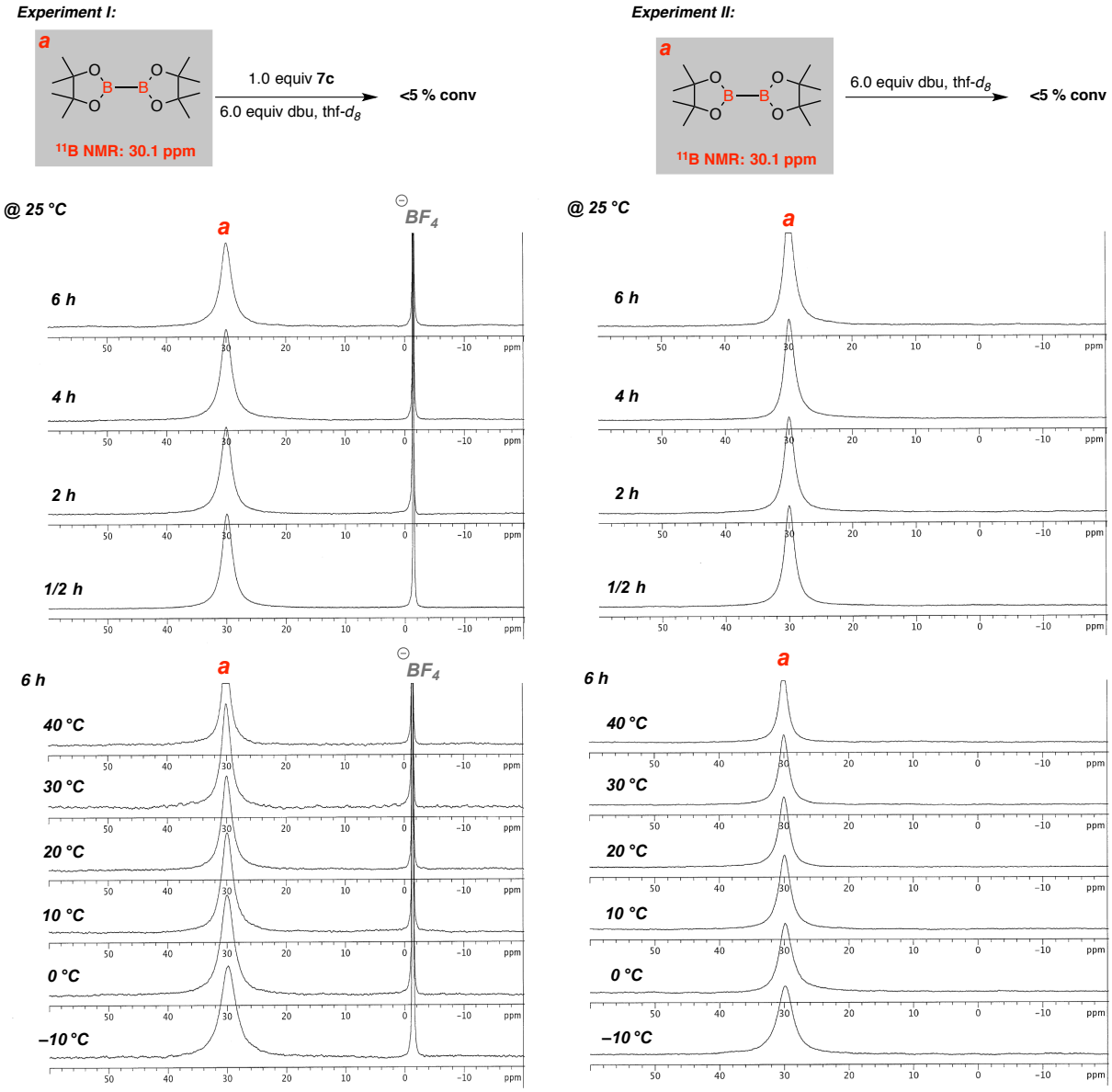
Peak #	Time (min)	Area (%)	Peak #	Time (min)	Area (%)
1	19.02	49.149	1	18.28	4.420
2	24.15	50.851	2	23.74	95.580

■ NMR Studies on Probing the Formation of Chiral NHC•diboron Complex

General procedure: In a N_2 filled glove box, an oven-dried vial (8 x 1 cm) equipped with a stir bar was charged with **7c** (39 mg, 0.060 mmol, 1.0 equiv), dbu (55 mg, 0.36 mmol, 6.0 equiv) and thf-d_8 (0.60 mL, 0.10 M solution of **7c**). The mixture was allowed to stir for 30 min at 22 °C. $B_2(pin)_2$(15 mg, 0.060 mmol, 1.0 equiv) was added to the vial, followed by the addition of MeOH (73 μL, 58 mg, 1.8 mmol, 30 equiv). The mixture was transferred into a Wilmad LabGlass 600 MHz Quartz NMR tube, which was sealed with a NMR cap before removal from the glove box. The ^{11}B NMR spectra were recorded subsequently.

Figure S1 shows the spectra of a series of control experiments where NHC was not present.

Figure S1. ^{11}B NMR spectra of control experiments



■ NMR Studies on Probing the Formation of Chiral NHC•borosilane Complex

General procedure: In a N_2 filled glove box, an oven-dried vial (8 x 1 cm) equipped with a stir bar was charged with **7c** (39 mg, 0.060 mmol, 1.0 equiv), dbu (55 mg, 0.36 mmol, 6.0 equiv) and thf-d_8 (0.60 mL, 0.10 M solution of **7c**). The mixture was allowed to stir for 30 min at 22 °C. $PhMe_2Si$–B(pin)(16 mg, 0.060 mmol, 1.0 equiv) was added to the vial, followed by the addition of H_2O (6.5 μL, 6.5 mg, 0.36 mmol, 6.0 equiv). The mixture was transferred into a Wilmad LabGlass 600 MHz Quartz NMR tube, which was sealed with a NMR cap before removal from

the glovebox. The ^{11}B NMR spectra were recorded subsequently.

Figures S2–S6 show the ^{11}B NMR spectra where either H_2O (6.0 equiv) or MeOH (30 or 2.0 equiv) was present. Unfortunately, we could not detect the formation of the chiral NHC•borosilane complex. This is probably due to significant decompositions of $PhMe_2Si$–B(pin) under these homogeneous solutions. Indeed, H–$SiMe_2Ph$ was generated during the NMR experiments and detected by ^{1}H NMR spectrum by means of the signal that appears at 4.4 ppm.

Figure S2. ^{11}B NMR spectra for reaction of (pin)B–$SiMe_2Ph$ with H_2O and dbu (thf-d_8, 25 °C)

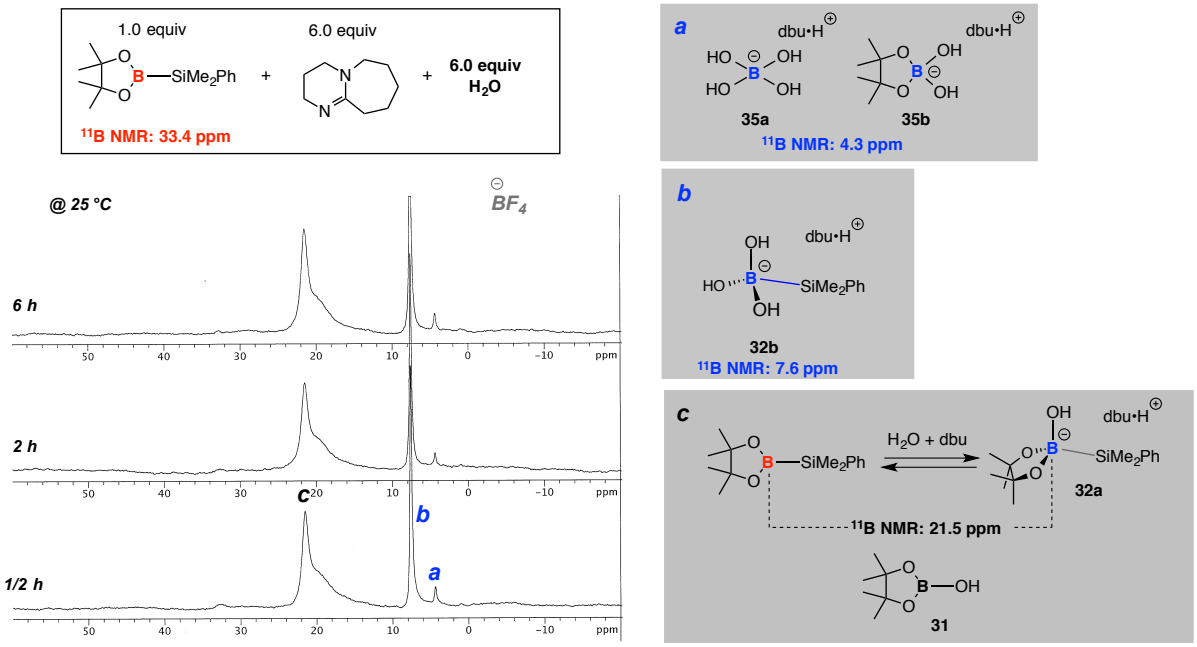


Figure S3. ^{11}B NMR spectra for reaction of (pin)B–$SiMe_2Ph$ with a chiral NHC in the presence of 30 equiv MeOH and dbu (thf-d_8, 25 °C)

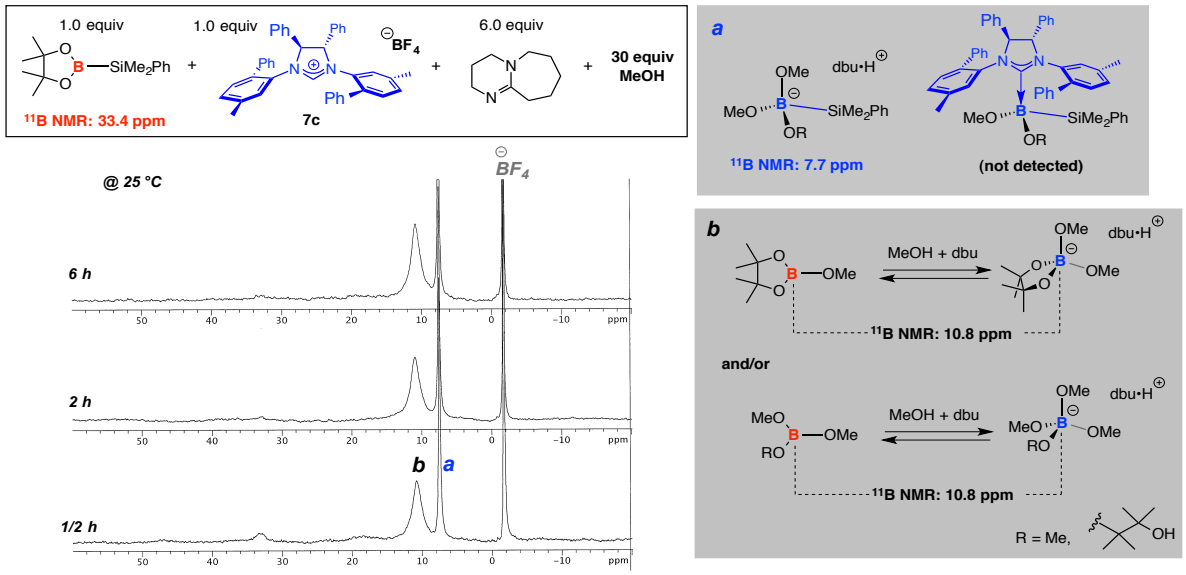


Figure S4. ^{11}B NMR spectra for reaction of (pin)B–SiMe$_2$Ph with 30 equiv MeOH and dbu (thf-d_8, 25 °C)

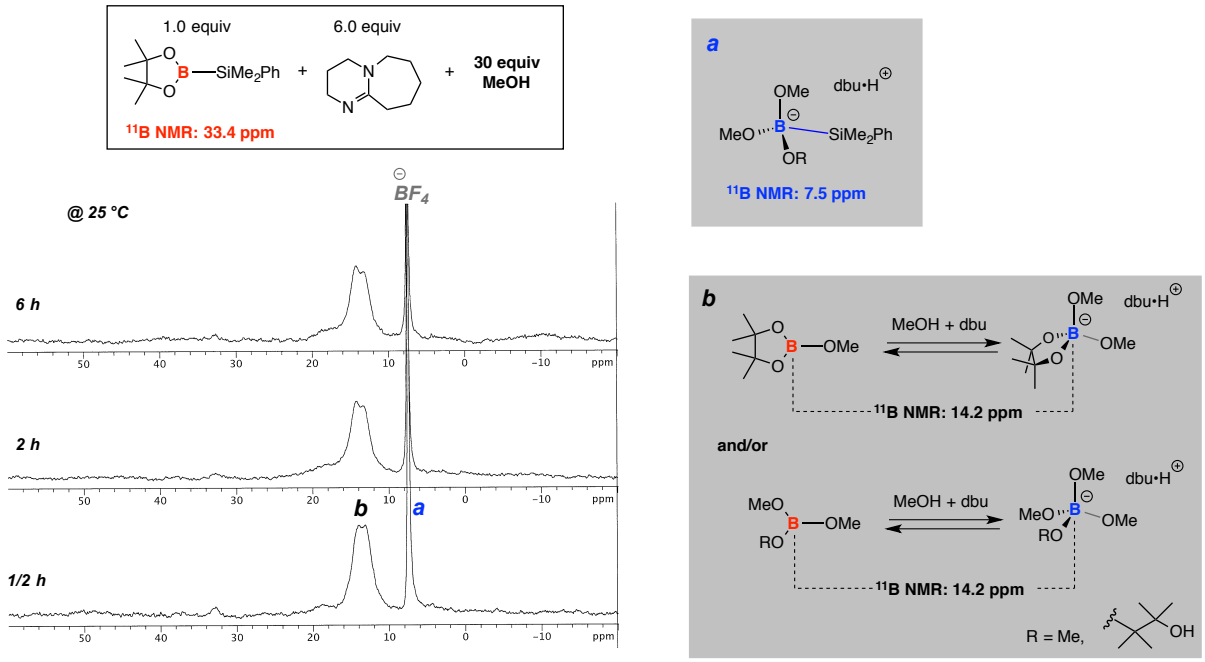


Figure S5. ^{11}B NMR spectra for reaction of (pin)B–SiMe$_2$Ph with a chiral NHC in the presence of 2.0 equiv MeOH and dbu (thf-d_8, 25 °C)

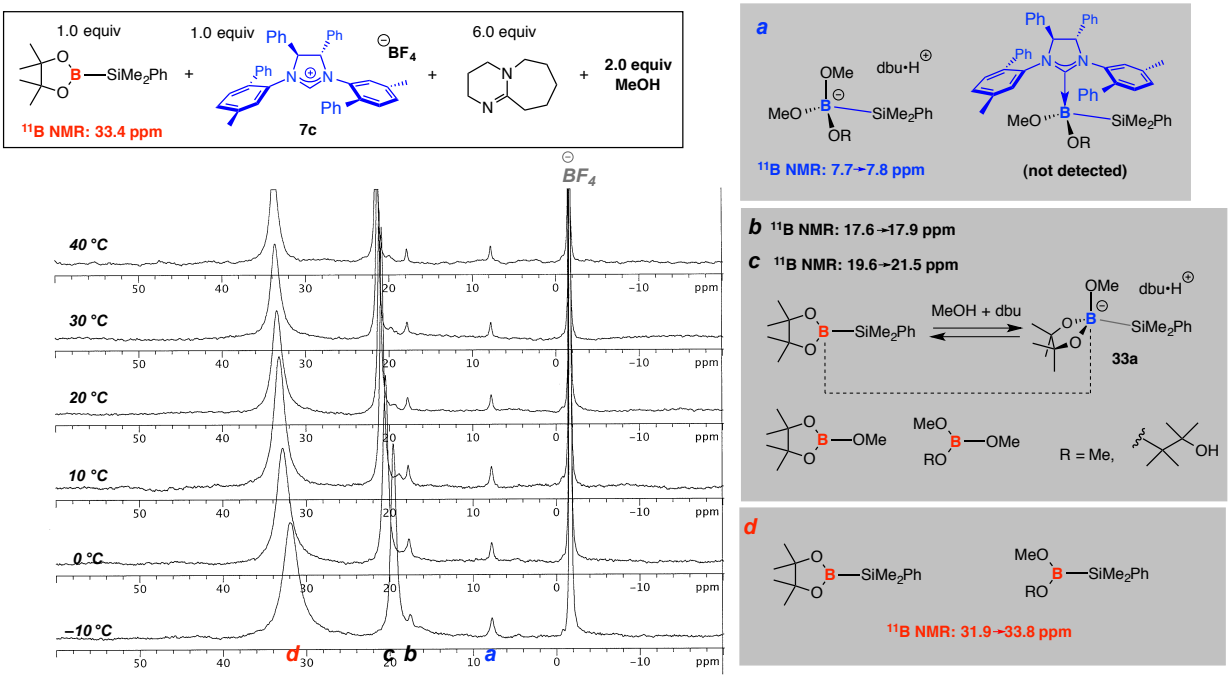
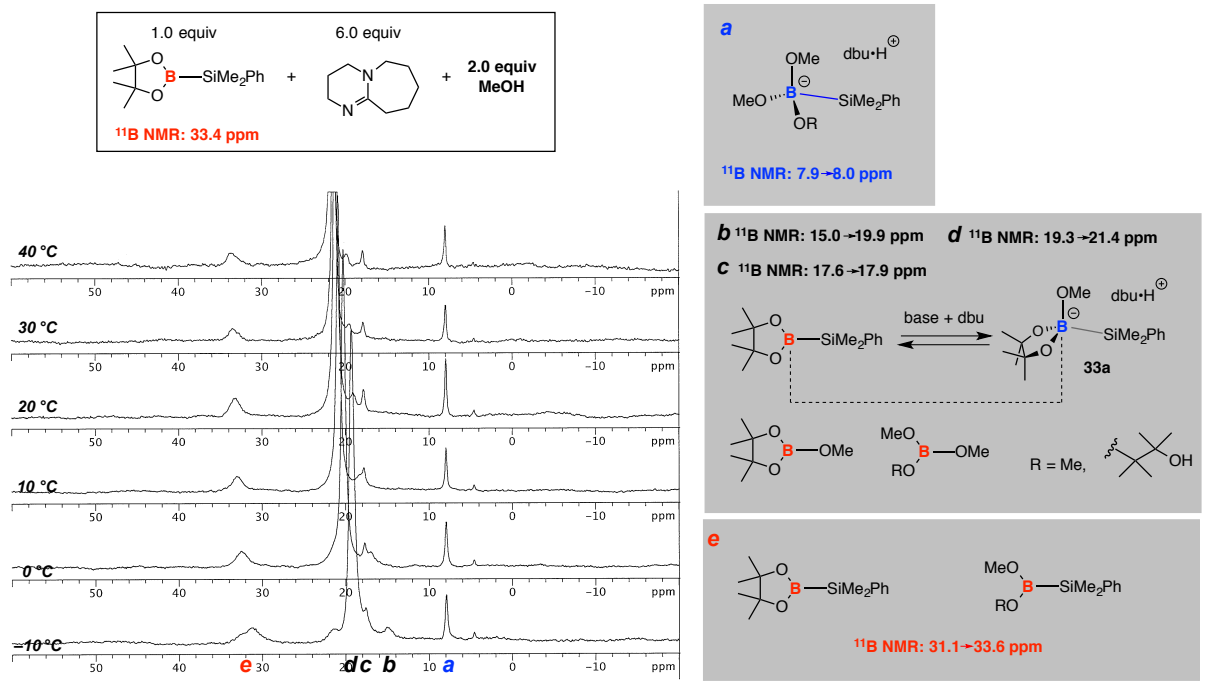
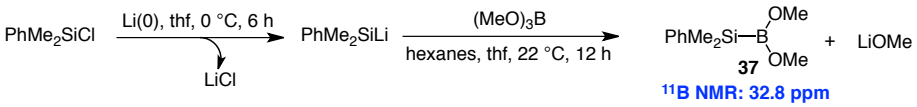


Figure S6. ^{11}B NMR spectra for reaction of (pin)B–SiMe$_2$Ph with 2.0 equiv MeOH and dbu (thf-d_8, 25 °C)



Dimethyl(dimethyl(phenyl)silyl)boronate (37) was obtained as a mixture, through the use of a modified procedure reported for the synthesis of PhMe$_2$Si–B(pin).[8] A 100 mL flame–dried Schlenk flask equipped with a stir bar was charged with Li (0.12 g, 18 mmol, 6.0 equiv) and mineral oil (5 mL) under argon. The mixture was allowed to heat to 180 °C and stirred vigorously for 10 min. The suspension was then allowed to cool to 22 °C. The Li particles were washed with thf (3 x 5 mL). Then 3 mL of thf was added into the flask. To the suspension, chlorodimethylphenylsilane (0.5 mL, 3.0 mmol, 1.0 equiv) was added drop-wise at 0 °C. The resulting suspension was allowed to stir at 0 °C for 6 h to generate dimethylphenylsilyllithium completely. To a stirred solution of trimethylborate (0.49 mL, 3.6 mmol, 1.2 equiv) in hexanes (3.0 mL) in another flame–dried Schlenk flask was added the previously prepared dimethylphenylsilyllithium solution drop-wise at 0 °C. The resulting solution was allowed to stir at 22 °C for 12 h. The mixture was filtered through a plug of celite twice, diluted with hexanes and the filtrate was concentrated *in vacuo*. Purification of the resulting light yellow oil by silica gel chromatography or distillation *in vacuo* resulted in complete decomposition of the desired product. The desired product also decomposed in a day at 22 °C under N_2. Thus the material was used immediately after syntesis. The presence of dimethyl(dimethyl(phenyl)silyl)boronate **(37)** was confirmed by HRMS (DART): Calcd for $C_{10}H_{18}Si_1O_2B_1$ $[M+H]^+$: 209.11691, Found: 209.11632. Due to the instability of the compound and lack of an effective purification method, other characterization data were not available.

Scheme S1. Synthesis of $PhMe_2Si–B(OMe)_2$ (**37**)



^{11}B NMR: 32.8 ppm

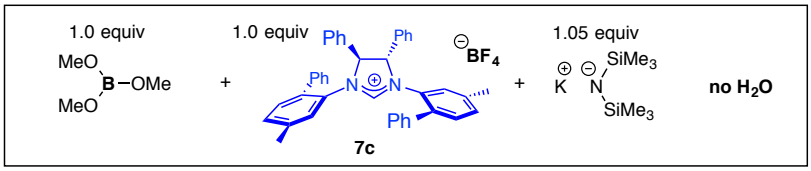
a mixture of products

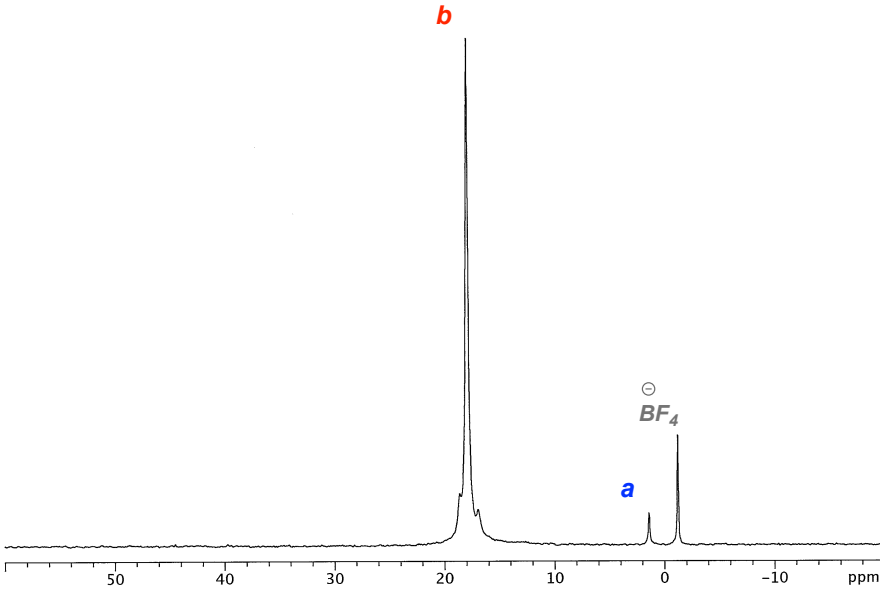
compound 37 was confirmed by HRMS

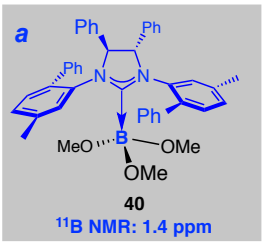
Preparation of NHC•borosilane Complex (39): In a N_2 filled glove box, an oven-dried vial (8 x 1 cm) equipped with a stir bar was charged with imidazolinium salt **7c** (19 mg, 0.030 mmol, 1.0 equiv), KHMDS (6.0 mg, 0.030 mmol, 1.0 equiv) and thf-d_8 (0.60 mL, 0.05 M solution of **7c**). The resulting mixture was allowed to stir for 30 min at 22 °C. Dimethyl(dimethyl(phenyl)silyl)boronate **(37)** (6.2 mg as a mixture, 0.030 mmol, 1.0 equiv) was then added to the vial. The mixture was transferred into a Wilmad LabGlass 600 MHz Quartz NMR tube, which was sealed with a NMR cap before removal from the glovebox. The ^{11}B NMR spectra were recorded subsequently.

As mentioned in the manuscript, we detected a new signal (–0.4 ppm, signal **a**), which may correspond to the chiral NHC•borosilane complex **39**. Control experiment including the same chiral NHC and $B(OMe)_3$ indicated a different signal at 1.4 ppm (complex **40**, signal **a**, Figure S7). When an achiral imidazolium salt (**3b**) was used instead of **7c**, we also detected the NHC•borosilane complex **41** (0.1 ppm, signal **a**, Figure S8). The ^{11}B NMR spectrum of $PhMe_2Si–B(OMe)_2$(**37**) in a mixture is shown in Figure S9.

Figure S7. ^{11}B NMR spectrum for reaction of $B(OMe)_3$ with a chiral NHC (thf-d_8, 25 °C)







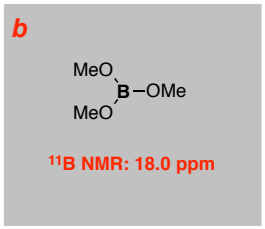


Figure S8. ^{11}B NMR spectrum for reaction of $(MeO)_2B–SiMe_2Ph$ with an achiral NHC (thf-d_8, 25 °C)

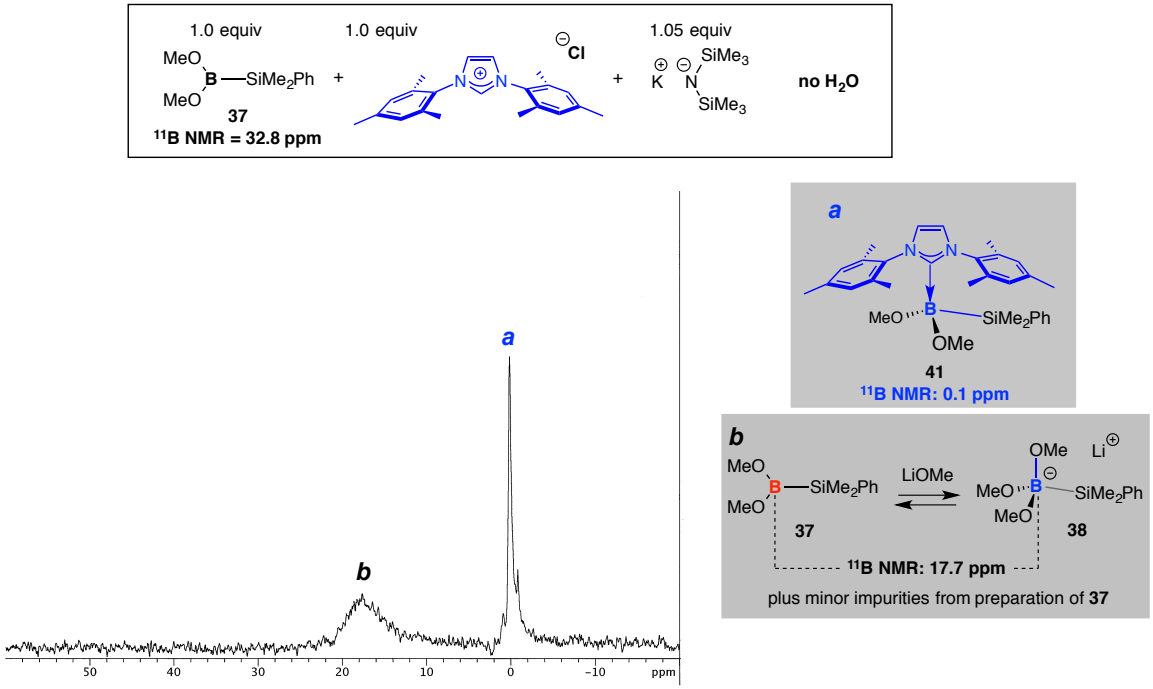
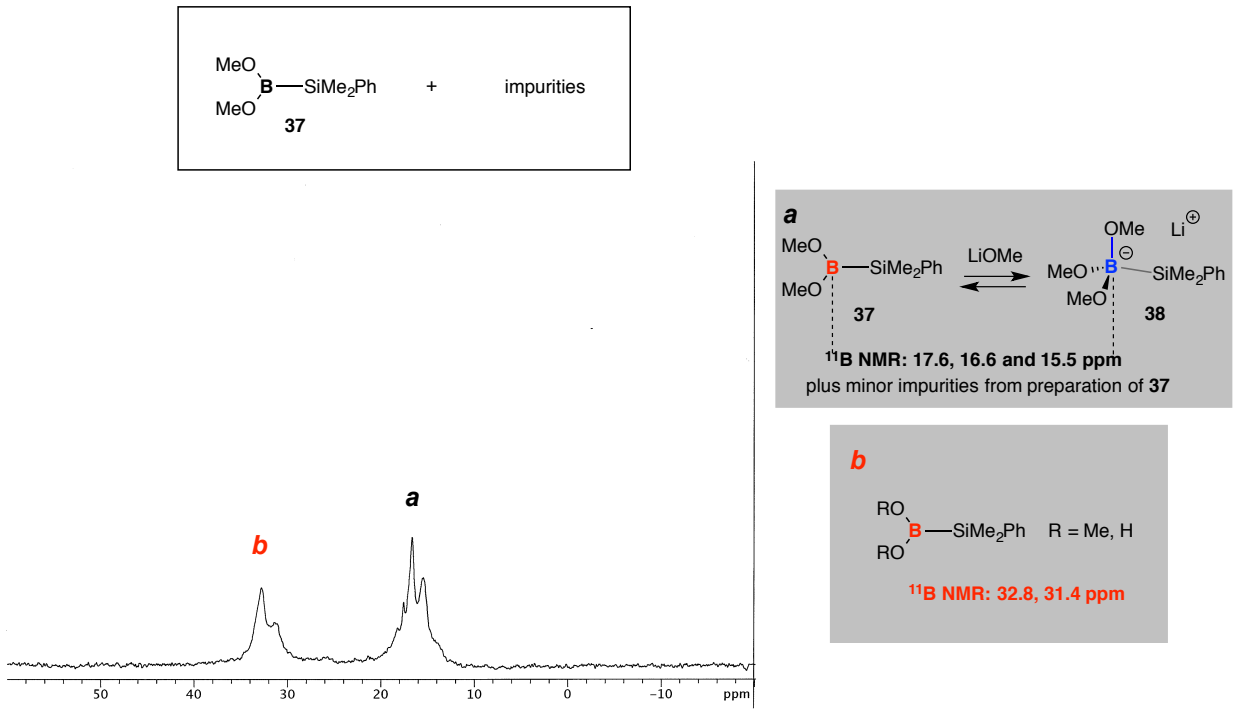


Figure S9. ^{11}B NMR spectrum of $(MeO)_2B–SiMe_2Ph$ as a mixture



Preparation of ^{13}C-labeled NHC•borosilane Complex (39): According to the procedure previously mentioned, ^{13}C-labeled NHC•borosilane complex (**39**) was prepared through deprotonation and coordination with $PhMe_2Si–B(OMe)_2$ (**37**) (Scheme S2). As mentioned in the

manuscript, complex NHC•BF_3 (**42**) was formed during the deprotonation, which was characterized by ^{13}C NMR (Figure S10), ^{11}B NMR and ^{19}F NMR (Figure S12). The broad signals in the ^{11}B NMR and ^{19}F NMR of complex **42** are probably due to a fast equilibrium between complex **42** and NHC + KBF_4 in the solution (Figure S12). Treatment of complex **42** with $PhMe_2Si–B(OMe)_2$ (**37**) resulted in the ^{13}C-labeled NHC•borosilane complex (**39**), of which a new signal in the ^{13}C NMR spectrum has been detected (181.2 ppm, Figure S11). However, we did not detect any $^{11}B–^{13}C$(carbene) coupling. This is likely because the NHC•borosilane complex formation and dissociation are reversible and occur rapidly in solution.

Scheme S2. Probing the Formation of a Chiral NHC•Borosilane Complex by Spectroscopic Analysis of a ^{13}C-Labeled Chiral NHC

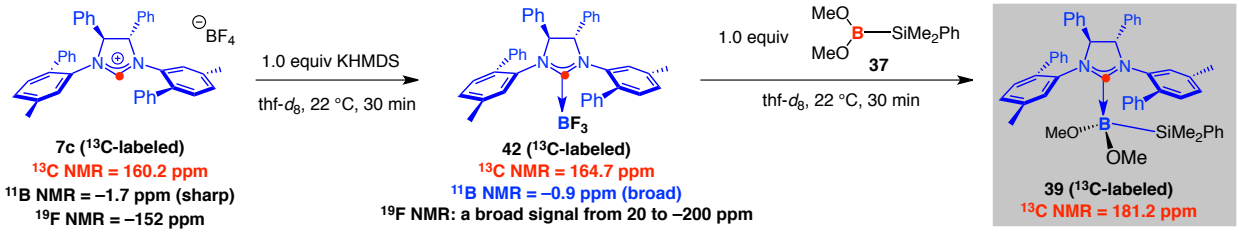
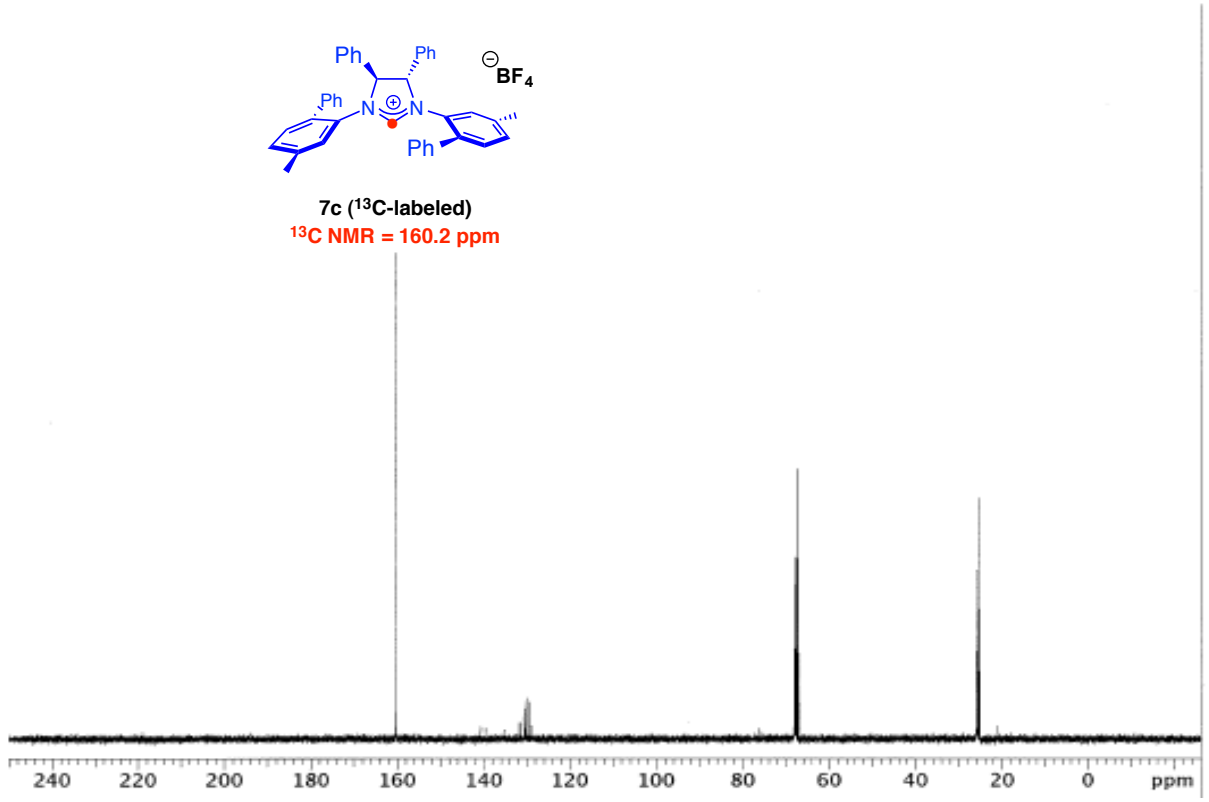


Figure S10. ^{13}C NMR spectra for a chiral NHC and its complex with BF_3



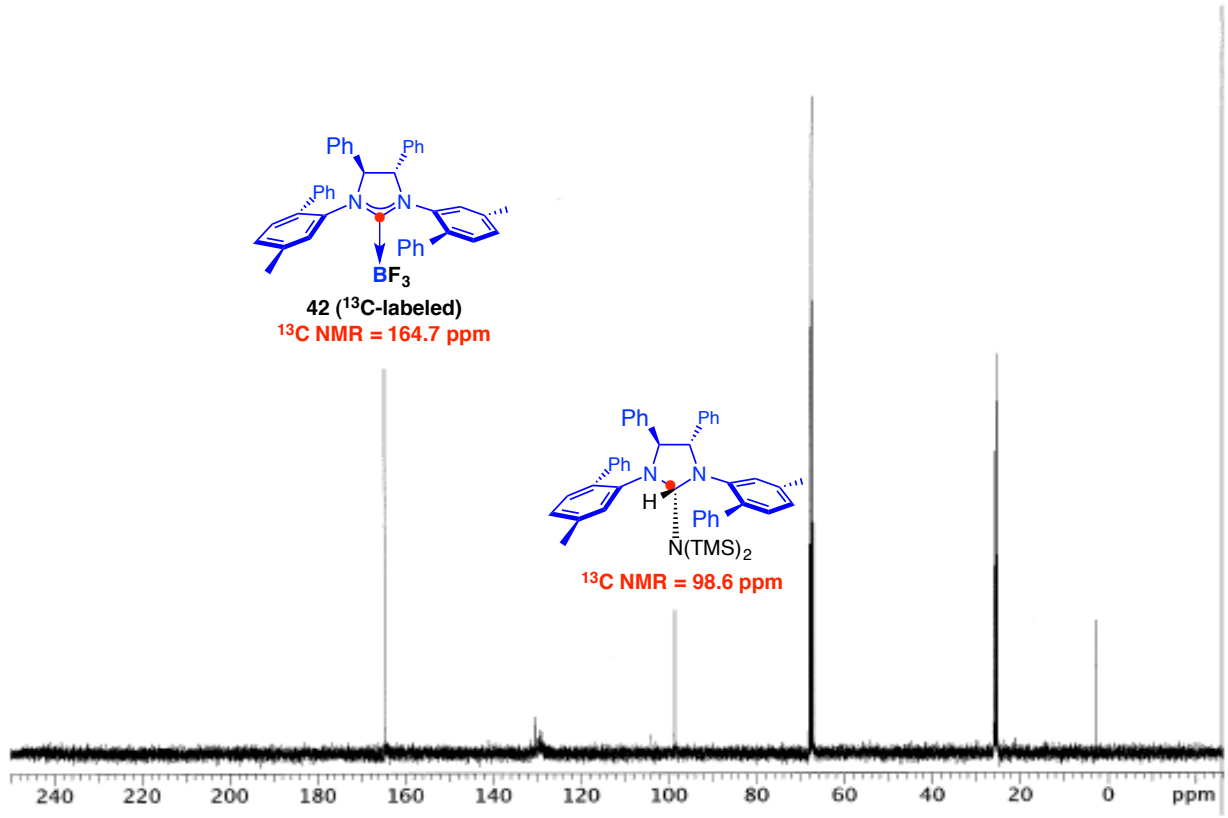


Figure S11. ^{13}C NMR spectrum for a chiral NHC•Borosilane Complex

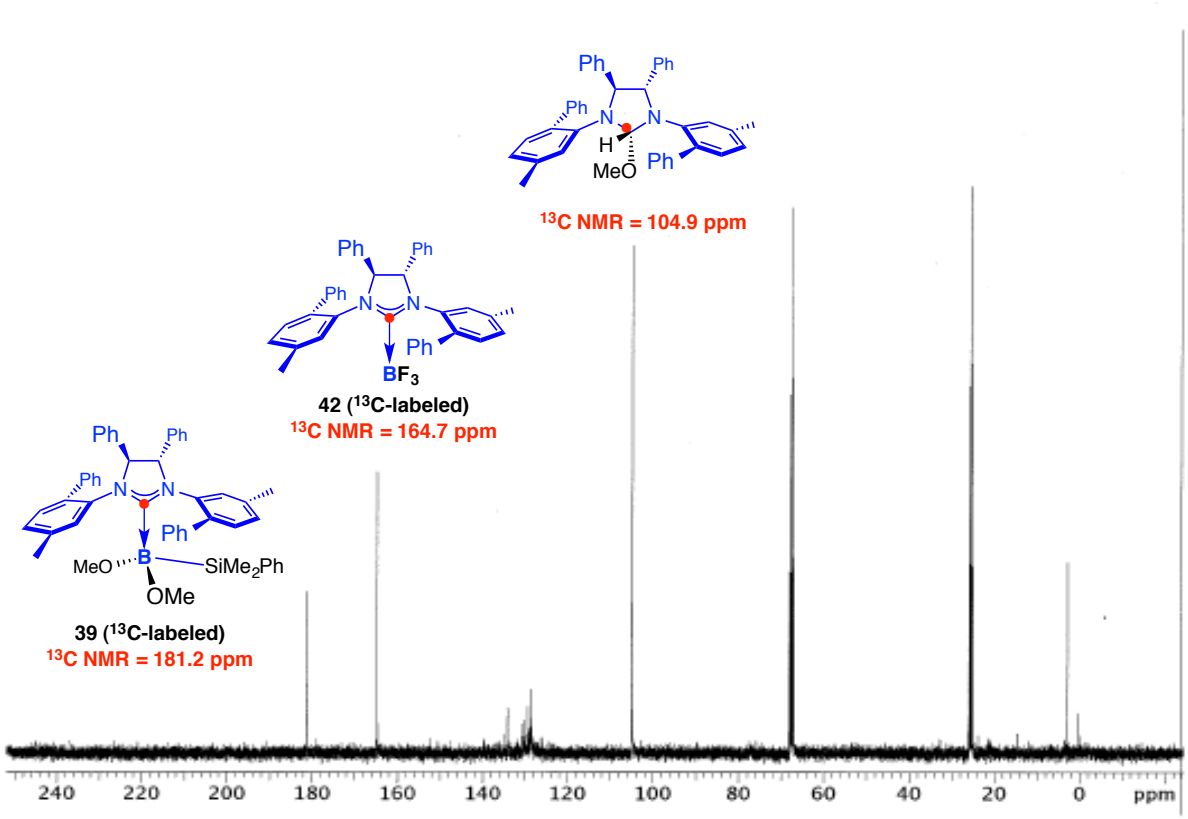
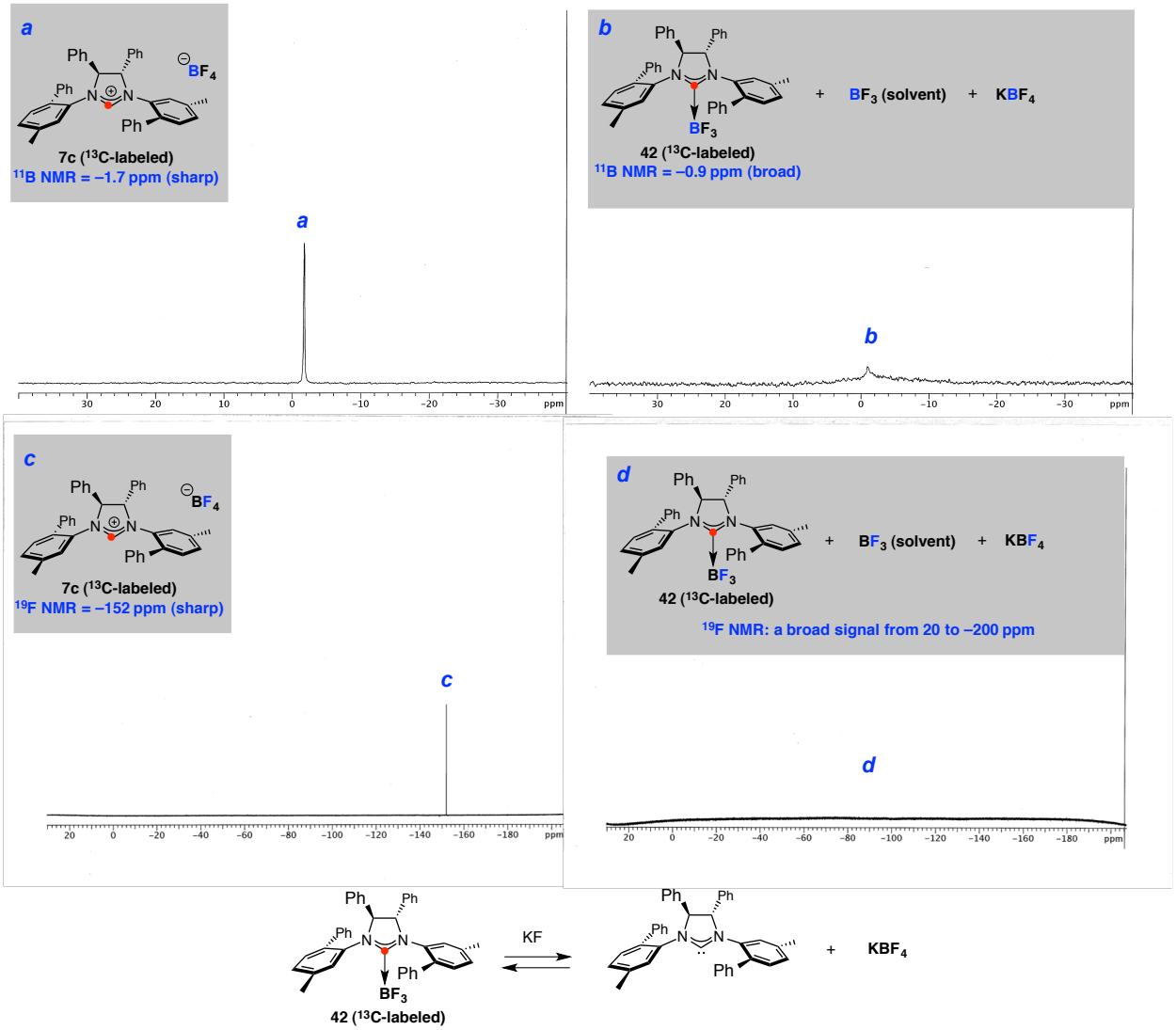


Figure S12. ^{11}B NMR and ^{19}F NMR spectra for a chiral NHC and its complex with BF_3

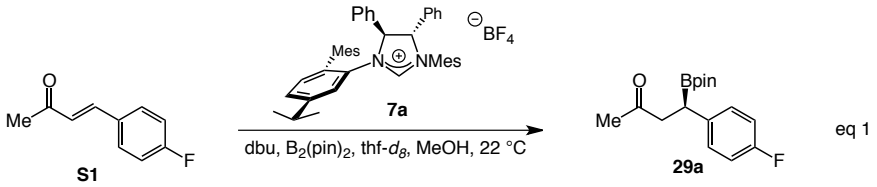


The fast equilibrium between complex 42 and NHC + KBF_4 results in the broadness of signal *b* and *d*

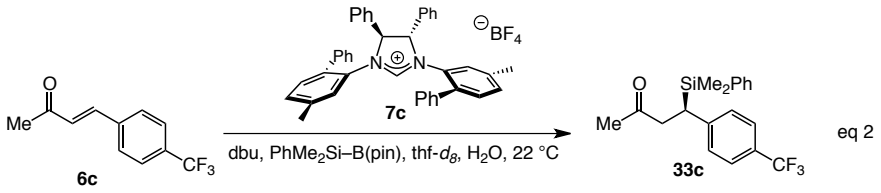
■ Kinetic Studies of Chiral NHC Catalyzed BCA and SCA Reactions

^{19}F NMR pre-acquisition delay technique was used to study how the concentration of each component among the starting materials influences the rates of those reactions. For the BCA reactions, *p*-fluorophenyl substituted enone (**S1**) was chosen as the substrate, while *p*-trifluoromethylphenyl substituted enone (**6c**) as the substrate for the SCA reactions, because a significant amount of the proto-deboration product was detected in BCA reactions with **6c**. In either type of reaction, the rate of the reaction was found to be first order to [enone], [B_2(pin)$_2$] (or [$PhMe_2Si$–B(pin)]) and [imidazolinium salt], while zero order to [dbu] (Scheme S3). The k_{obs} value was calculated for each transformation as well.

Scheme S3. The results of kinetic studies on NHC catalyzed BCA reactions (eq 1) and SCA reactions (eq 2)



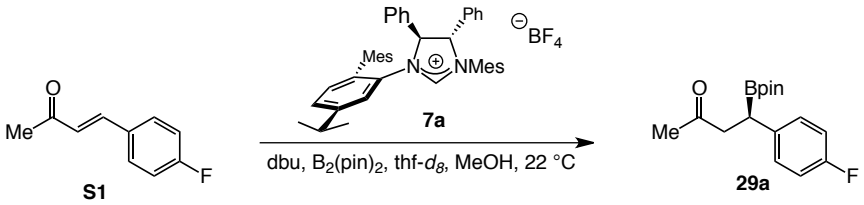
***rate* = k_{obs}[enone][7a][B_2(pin)$_2$], k_{obs} = 0.014 $L^2mol^{-2}s^{-1}$**
C–B bond formation is likely the turnover limiting step.



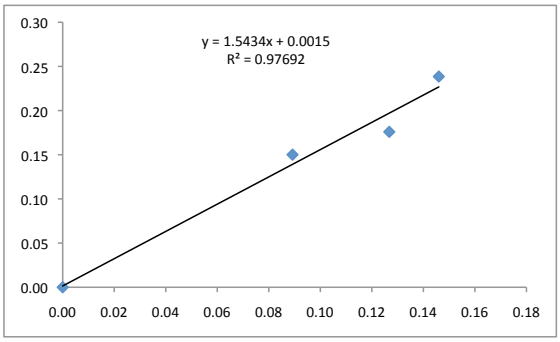
***rate* = k_{obs}[enone][7c][$PhMe_2Si$–B(pin)], k_{obs} = 0.63 $L^2mol^{-2}s^{-1}$**
C–Si bond formation is likely the turnover limiting step.

General procedure: In a N_2 filled glove box, an oven-dried vial (8 x 1 cm) equipped with a stir bar was charged with **7a** or **7c**, dbu and thf-d_8 (0.60 mL). The mixture was allowed to stir for 30 min at 22 °C. B_2(pin)$_2$ or $PhMe_2Si$–B(pin) was added to the vial, followed by the addition of enone **S1** or **6c**. The mixture was transferred into an oven-dried NMR tube, sealed with a cap with Teflon tape and brought out of the glove box. MeOH (0.16 mL, 4.0 mmol) or H_2O (8.6 mL, 0.048 mmol) was added to the NMR tube by syringe and the tube was inverted twice for mixing. The sample was immediately inserted into the NMR spectrometer probe and ^{19}F NMR spectra were collected every 30 seconds until the reaction reached approximately 15% conversion (initial kinetics). Substrate and product concentrations were determined by ^{19}F NMR analysis with the BF_4^- signal serving as the internal reference (–151 ppm). After each experiment, the conversion values ([enone] vs reaction time) were plotted and the curve was fitted with a second-order polynomial function through the use of Microsoft Excel. The initial rate of each reaction was determined as the coefficient of the term αx^1 (x = reaction time) of the function. By varying the concentration of one component in the reaction at a time, a series of the initial rates were obtained. Scheme S4 and S5 show the relationships between the initial rate of the reaction and the concentration of each component. Based on those results, we drew the conclusions shown in Scheme S3.

Scheme S4. The results of kinetic study on NHC catalyzed BCA reactions



initial rate (mM/min)

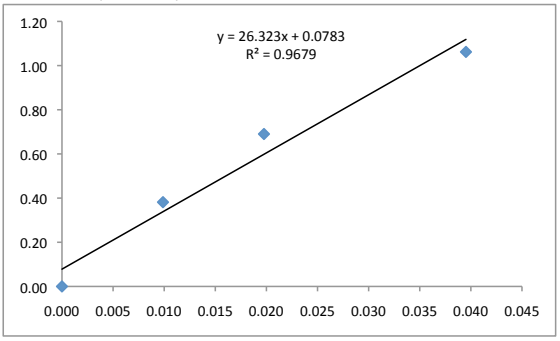


[enone] (M)

[enone] (M)	initial rate (mM/min)
0	0
0.0892	0.150
0.127	0.176
0.146	0.239

[**7a**] = 0.0117 M
$[B_2(pin)_2]$ = 0.146 M
[dbu] = 0.293 M

initial rate (mM/min)

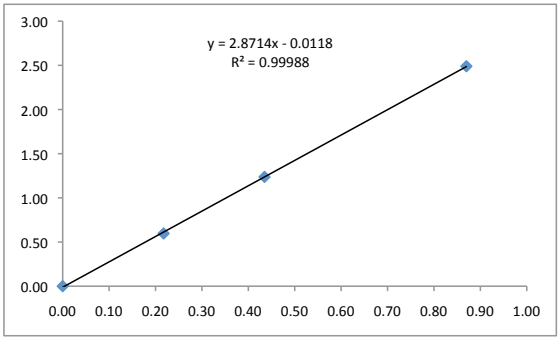


[**7a**] (M)

[**7a**] (M)	initial rate (mM/min)
0	0
0.0099	0.382
0.0198	0.690
0.0395	1.06

[enone] = 0.258 M
$[B_2(pin)_2]$ = 0.162 M
[dbu] = 0.646 M

initial rate (mM/min)

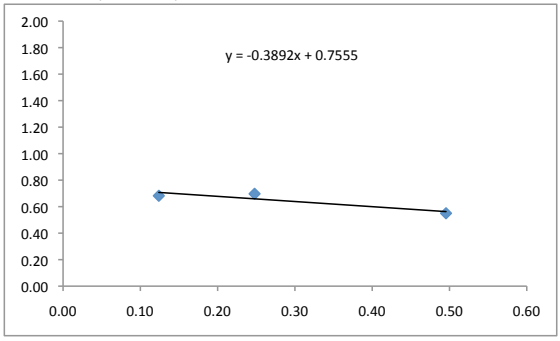


$[B_2(pin)_2]$ (M)

$[B_2(pin)_2]$ (M)	initial rate (mM/min)
0	0
0.218	0.597
0.435	1.24
0.870	2.49

[**7a**] = 0.0129 M
[enone] = 0.258 M
[dbu] = 0.646 M

initial rate (mM/min)

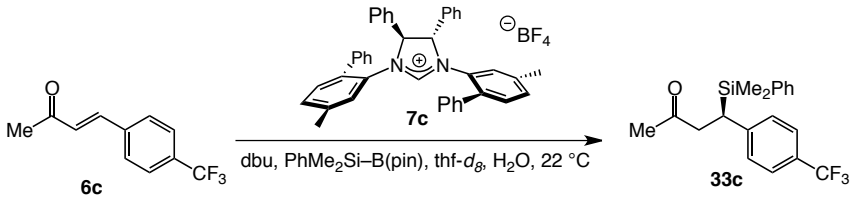


[dbu] (M)

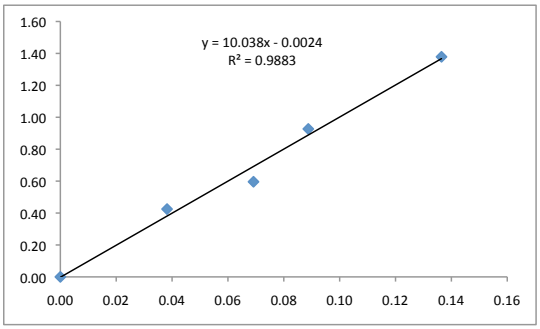
[dbu] (M)	initial rate (mM/min)
0.124	0.682
0.248	0.697
0.496	0.550

[enone] = 0.129 M
$[B_2(pin)_2]$ = 0.646 M
[**7a**] = 0.0129 M

Scheme S5. The results of kinetic study on NHC catalyzed SCA reactions



initial rate (mM/min)

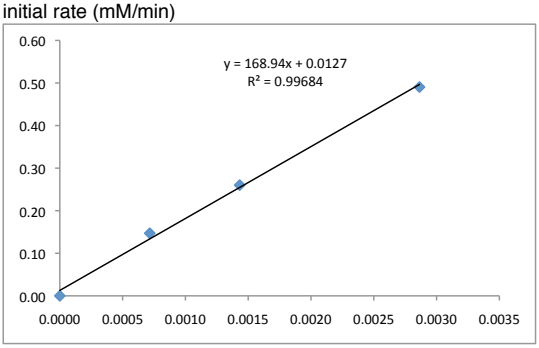


[enone] (M)

[enone] (M)	initial rate (mM/min)
0	0
0.0382	0.425
0.0692	0.596
0.0888	0.927
0.136	1.38

[**7c**] = 0.00286 M
[$PhMe_2Si–B(pin)$] = 0.0956 M
[dbu] = 0.191 M

initial rate (mM/min)

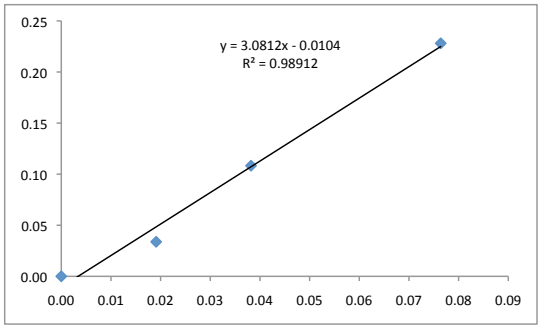


[**7c**] (M)

[**7c**] (M)	initial rate (mM/min)
0	0
0.000716	0.147
0.00143	0.260
0.00286	0.491

[enone] = 0.0191 M
[$PhMe_2Si–B(pin)$] = 0.191 M
[dbu] = 0.191 M

initial rate (mM/min)

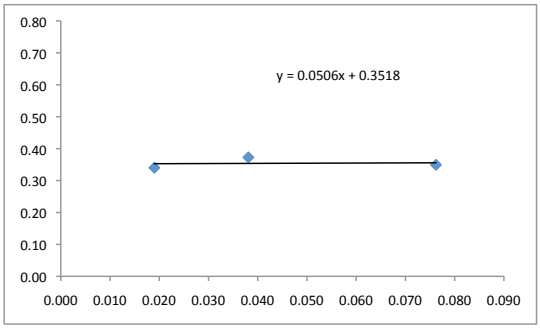


[$PhMe_2Si–B(pin)$] (M)

[$PhMe_2Si–B(pin)$] (M)	initial rate (mM/min)
0	0
0.0191	0.0338
0.0382	0.108
0.0764	0.228

[**7c**] = 0.00286 M
[enone] = 0.0382 M
[dbu] = 0.382 M

initial rate (mM/min)



[dbu] (M)

[dbu] (M)	initial rate (mM/min)
0.0190	0.340
0.0381	0.373
0.0762	0.349

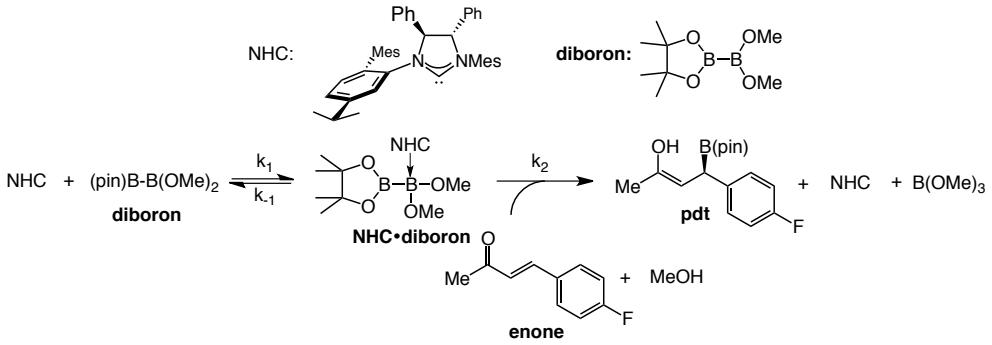
[enone] = 0.0191 M
[$PhMe_2Si–B(pin)$] = 0.191 M
[**7c**] = 0.00286 M

In addition to the aforementioned kinetic studies, the rate law derivation was also performed according to our proposed mechanism in a simplified model.[9] Here we used NHC-catalyzed boron conjugate additions as an example, and the similar rate law derivation can be performed for the corresponding SCA reactions. Based on the steady state assumption, the concentration of NHC•dibron complex does not change in the reaction mixture. Thus, the rate law can be derived as equation 6. Although further simplifications of the rate law can be performed based on additional assumptions (equations 7–10), we think the rate law of the NHC catalyzed BCA

reactions is probably close to equation 11. This is because the fast equilibrium between NHC + diboron and NHC•dibron complex (supported by previously mentioned ^{11}B NMR studies) probably results in $k_{-1}>>k_2$[enone] and k_1[diboron]. Thus, k_1[diboron]+k_{-1}+k_2[enone] ≈ k_{-1}, leading to the simplified rate law as equation 11, which is consistent with the previously mentioned ^{19}F NMR kinetic study.

Scheme S6. The rate law derivation of chiral NHC catalyed BCA reactions

In a simplified model:



eq 1 $[NHC] = [NHC]_0 - [NHC•diboron]$ $[NHC]_0$: Initial concentration of NHC

according to the steady state assumption:

eq 2 $d[NHC•diboron]/dt = k_1[NHC][diboron] - k_{-1}[NHC•diboron] - k_2[NHC•diboron][enone] = 0$

eq 3 $k_1([NHC]_0 - [NHC•diboron])[diboron] - k_{-1}[NHC•diboron] - k_2[NHC•diboron][enone] = 0$

eq 4 $$[NHC•diboron] = \frac{k_1[NHC]_0[diboron]}{k_1[diboron] + k_{-1} + k_2[enone]}$$

eq 5 $d[pdt]/dt = k_2[NHC•diboron][enone]$

eq 6 $$d[pdt]/dt = \frac{k_1k_2[NHC]_0[diboron][enone]}{k_1[diboron] + k_{-1} + k_2[enone]}$$

When [enone] is low, the rate law can be simplified to:

eq 7 $$d[pdt]/dt = \frac{k_1k_2[NHC]_0[diboron][enone]}{k_1[diboron] + k_{-1}}$$ The reaction is first order to enone.

When [enone] is high, the rate law can be simplified to:

eq 8 $$d[pdt]/dt = \frac{k_1k_2[NHC]_0[diboron][enone]}{k_2[enone]} = k_1[NHC]_0[diboron]$$

The reaction is zero order to enone (saturation kinetics)

When [diboron] is low:

eq 9 $$d[pdt]/dt = \frac{k_1k_2[NHC]_0[diboron][enone]}{k_{-1} + k_2[enone]}$$ The reaction is first order to diboron.

When [diboron] is high:

eq 10 $$d[pdt]/dt = \frac{k_1k_2[NHC]_0[diboron][enone]}{k_1[diboron]} = k_2[NHC]_0[enone]$$

The reaction is zero order to diboron (saturation kinetics)

In our case, it is probably k_1[diboron] + k_{-1} + k_2[enone] ≈ k_{-1}, because of fast and reversible coordination of NHC to diboron. Thus, the rate law can be simplified to:

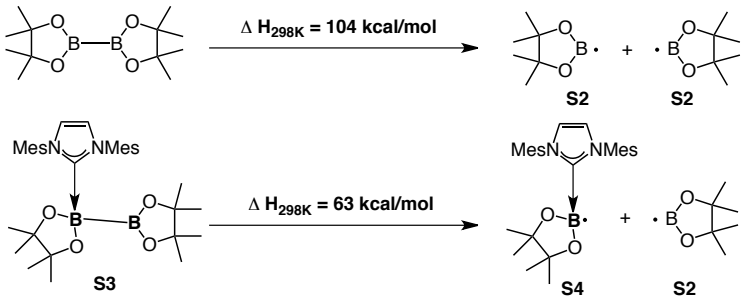
eq 11 $$d[pdt]/dt = \frac{k_1 k_2 [NHC]_0 [diboron][enone]}{k_{-1}}$$

The reaction is first order to NHC, diboron and enone.

■ Calculations on BDE for B–B Bonds in $B_2(pin)_2$ and NHC•$B_2(pin)_2$

Density Functional Theory (DFT) calculations were carried out in an effort to estimate the homolytic bond dissociation energy (BDE) for B–B bonds in $B_2(pin)_2$ and NHC•$B_2(pin)_2$. The B97-D functional and 6-31G* basis set were employed for geometry optimizations and frequency calculations. As shown in Scheme S7, the enthalpy change to break the B–B bond homolytically in $B_2(pin)_2$ is 104 kcal/mol, while the one required to break the B–B bond in NHC•diboron is 63 kcal/mol. These calculations suggest that a significant weakening of the B–B bond in $B_2(pin)_2$ occurs upon NHC coordination.

Scheme S7. Calculated BDE for B–B Bonds in $B_2(pin)_2$ and NHC•$B_2(pin)_2$



1. $B_2(pin)_2$

```
----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
42

H      2.854     -1.219     -0.824
H      1.357     -1.022     -1.777
H      2.853     -1.596     -2.573
C      2.259     -1.637     -1.648
H     -2.396     -0.296      3.377
H     -3.075     -0.372      1.176
H      0.698     -2.077     -3.722
H     -4.557     -0.553      2.161
C     -3.946     -1.014      1.371
C     -2.489     -1.258      3.896
H     -1.678     -1.338      4.634
H     -4.545     -1.084      0.453
H     -3.452     -1.284      4.430
H      3.827     -3.427     -0.414
C      1.885     -3.088     -1.299
O     -1.154     -2.319      2.152
O      1.164     -3.039     -0.021
C      0.845     -3.164     -3.703
H      1.813     -3.402     -4.171
B     -0.192     -3.045     -0.309
```

```
C     3.150    -3.931    -1.118
B    -1.413    -2.771     0.867
H     3.669    -4.044    -2.082
C    -2.403    -2.430     2.916
C    -3.497    -2.428     1.778
C     0.808    -3.706    -2.272
O    -0.456    -3.298    -1.645
H     0.046    -3.636    -4.293
O    -2.763    -2.980     0.633
H     2.913    -4.926    -0.723
H    -1.430    -3.759     4.312
H    -5.244    -2.952     2.953
C    -2.331    -3.762     3.684
C    -4.717    -3.310     2.055
H    -5.407    -3.258     1.202
C     0.813    -5.245    -2.288
H    -3.214    -3.892     4.326
H     1.709    -5.629    -2.797
H    -2.272    -4.609     2.986
H     0.787    -5.643    -1.264
H    -0.079    -5.594    -2.825
H    -4.427    -4.357     2.207
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --    21.6143                37.2646                56.3220
 Red. masses --     3.4904                 3.6209                 4.2094
 Zero-point correction=                           0.353458 (Hartree/Particle)
 Thermal correction to Energy=                    0.373612
 Thermal correction to Enthalpy=                  0.374556
 Thermal correction to Gibbs Free Energy=         0.306373
 Sum of electronic and zero-point Energies=          -821.692390
 Sum of electronic and thermal Energies=             -821.672236
 Sum of electronic and thermal Enthalpies=           -821.671291
 Sum of electronic and thermal Free Energies=        -821.739475

         Item               Value     Threshold  Converged?
 Maximum Force            0.000095     0.000450     YES
 RMS     Force            0.000013     0.000300     YES
```

---

2. (pin)B• radical (S2)

```
 Cartesian coordinates (Angstroms):
---------------------------------------
21

H     7.883     0.033     4.666
H     7.162    -0.990     6.604
H     8.715    -0.204     7.014
C     8.172    -1.160     7.001
H     8.719    -0.339     3.136
C     8.773    -0.435     4.229
H     8.087    -1.534     8.031
H     9.668     0.100     4.583
O     7.599    -2.584     4.200
B     7.355    -3.524     5.162
```

```
C     8.871    -1.913     4.606
C     8.923    -2.200     6.159
O     8.151    -3.476     6.273
H     9.777    -2.515     2.745
C     9.996    -2.598     3.818
C    10.324    -2.439     6.721
H    10.939    -1.535     6.585
H    10.255    -2.654     7.796
H    10.963    -2.116     4.021
H    10.067    -3.662     4.082
H    10.818    -3.283     6.225
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --    99.0141               218.6294               231.3430
 Red. masses --     3.5799                 1.2073                 1.1507
 Zero-point correction=                           0.174434 (Hartree/Particle)
 Thermal correction to Energy=                    0.184103
 Thermal correction to Enthalpy=                  0.185047
 Thermal correction to Gibbs Free Energy=         0.140664
 Sum of electronic and zero-point Energies=           -410.763313
 Sum of electronic and thermal Energies=              -410.753643
 Sum of electronic and thermal Enthalpies=            -410.752699
 Sum of electronic and thermal Free Energies=         -410.797082

          Item               Value     Threshold  Converged?
 Maximum Force            0.000042     0.000450     YES
 RMS     Force            0.000012     0.000300     YES
```

---

3. NHC•$B_2(pin)_2$ (S3)

```
 Cartesian coordinates (Angstroms):
---------------------------------------
57

N     3.932    -3.875     3.718
B     6.204    -4.877     4.942
C     3.526    -3.479     2.449
C     5.184    -4.414     3.682
C     4.555    -3.780     1.599
N     5.554    -4.354     2.372
H     8.008    -1.489     7.984
H     7.104    -0.996     6.526
H    10.233    -2.518     7.812
C     8.109    -1.127     6.952
H     8.621    -0.153     6.964
O     8.196    -3.436     6.261
C     8.908    -2.165     6.142
C    10.311    -2.326     6.733
H    10.896    -1.405     6.583
H    10.843    -3.166     6.268
H     7.868     0.040     4.597
H     9.653     0.124     4.558
C     8.868    -1.900     4.591
C     8.774    -0.426     4.189
H    10.984    -2.093     4.049
H     8.747    -0.343     3.093
```

```
C    10.022    -2.583     3.834
H    10.092    -3.643     4.116
H     9.827    -2.515     2.754
B     7.371    -3.582     5.148
O     7.637    -2.586     4.192
H     2.553    -3.039     2.268
H     4.660    -3.652     0.529
H     4.252    -6.646     8.151
C     4.518    -7.186     7.229
H     6.542    -5.744     8.428
H     3.652    -7.171     6.553
O     5.376    -5.205     6.137
H     4.744    -8.232     7.494
C     5.740    -6.523     6.579
C     6.880    -6.400     7.613
H     7.149    -7.381     8.033
H     7.764    -5.945     7.147
H     4.293    -6.874     4.265
C     6.222    -7.211     5.247
C     5.036    -7.677     4.370
O     6.916    -6.142     4.584
H     4.538    -8.560     4.800
C     7.196    -8.379     5.452
H     6.730    -9.163     6.070
H     5.419    -7.939     3.373
H     8.115    -8.035     5.942
H     7.462    -8.817     4.477
C     3.113    -3.695     4.926
C     6.879    -4.738     1.863
H     7.227    -5.603     2.436
H     7.571    -3.899     2.007
H     6.782    -4.986     0.798
H     3.008    -2.620     5.136
H     3.620    -4.206     5.752
H     2.121    -4.134     4.753

                     1                      2                      3
                     A                      A                      A
 Frequencies --    13.1324                28.0149                41.4303
 Red. masses --     3.6689                 4.1722                 3.6310
 Zero-point correction=                           0.478619 (Hartree/Particle)
 Thermal correction to Energy=                    0.506874
 Thermal correction to Enthalpy=                  0.507818
 Thermal correction to Gibbs Free Energy=         0.421531
 Sum of electronic and zero-point Energies=         -1126.198115
 Sum of electronic and thermal Energies=            -1126.169860
 Sum of electronic and thermal Enthalpies=          -1126.168916
 Sum of electronic and thermal Free Energies=       -1126.255203

         Item               Value     Threshold  Converged?
 Maximum Force            0.000014     0.000450     YES
 RMS     Force            0.000002     0.000300     YES

----------------------------------------
```

4. NHC•B(pin) radical (S4)

```
----------------------------------------
 Cartesian coordinates (Angstroms):
```

```
---------------------------------------
36

N     3.956    -3.438     3.720
B     5.314    -5.547     4.503
C     3.952    -2.595     2.612
C     4.944    -4.436     3.547
C     4.871    -3.061     1.717
N     5.510    -4.161     2.280
H     3.294    -1.735     2.561
H     5.127    -2.708     0.724
H     3.963    -7.175     7.987
C     4.510    -7.738     7.217
H     5.622    -5.354     8.038
H     3.780    -8.222     6.555
O     4.594    -5.857     5.679
H     5.112    -8.514     7.714
C     5.420    -6.788     6.434
C     6.284    -5.959     7.403
H     6.897    -6.608     8.046
H     6.948    -5.285     6.842
H     4.512    -8.291     4.298
C     6.272    -7.479     5.299
C     5.513    -8.626     4.605
O     6.424    -6.404     4.329
H     5.410    -9.494     5.272
C     7.660    -7.950     5.738
H     7.571    -8.708     6.532
H     6.075    -8.930     3.711
H     8.264    -7.113     6.110
H     8.181    -8.404     4.882
C     3.402    -3.073     5.014
C     6.282    -5.127     1.514
H     5.637    -5.944     1.138
H     7.059    -5.565     2.151
H     6.746    -4.610     0.663
H     2.543    -2.407     4.853
H     4.156    -2.554     5.636
H     3.078    -3.976     5.543

                     1                      2                      3
                     A                      A                      A
 Frequencies --    39.9707                49.5078                68.2978
 Red. masses --     3.1681                 3.5434                 2.7894
 Zero-point correction=                           0.300481 (Hartree/Particle)
 Thermal correction to Energy=                    0.318372
 Thermal correction to Enthalpy=                  0.319316
 Thermal correction to Gibbs Free Energy=         0.255351
 Sum of electronic and zero-point Energies=          -715.334087
 Sum of electronic and thermal Energies=             -715.316196
 Sum of electronic and thermal Enthalpies=           -715.315252
 Sum of electronic and thermal Free Energies=        -715.379218

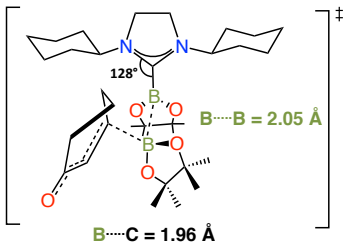
         Item               Value     Threshold  Converged?
 Maximum Force            0.000024     0.000450     YES
 RMS     Force            0.000005     0.000300     YES
---------------------------------------
```

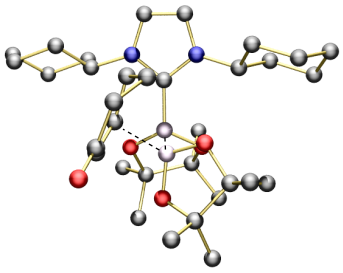
■ Calculations on Stereochemical Models for BCA and SCA Reactions

Density Functional Theory (DFT) calculations were carried out in an effort to gain more insight into the mechanism of the aforementioned NHC-catalyzed conjugate addition reactions of a B(pin) or $SiPhMe_2$ unit to acyclic and cyclic α,β-unsaturated carbonyl compounds. We have previously demonstrated that the B–B bond (or B–Si bond) upon coordination of a Lewis basic NHC becomes polarized (activated), whereupon the resulting nucleophilic B(pin) (or $SiPhMe_2$) unit of the complex readily attacks the electrophilic enone. The forming of the C–B (or C–Si) bond is, according to our kinetic studies, likely to be the turnover limiting step. Since it involves the enantioselective transfer of the B(pin) or $SiPhMe_2$ unit to the *α,β*-unsaturated carbonyl, we believe this is also the stereochemical determining step. Consequently, we decided to focus our DFT studies on this step with the intention to further understand how these catalytic reactions operate and the origin of enantioselectivity. All ground state and transition state geometries were optimized using DFT methodology. The B97-D functional and 6-31G* basis set were employed. Tetrahydrofuran solvation (or tetrahydrofuran/MeOH in boryl conjugate additions catalyzed by a chiral NHC) was modeled using the PCM model. Frequency calculations were carried out on all optimized geometries at the same level of theory to determine the whether these are minima or first-order saddle-points on the potential energy surface.

Our computational investigations began with a non-enantioselective reaction, where the boron conjugate addition to cyclohexenone is catalyzed by a small achiral NHC derived from 1,3-dicyclohexylimidazolium salt (**3a**). The transition state of the B(pin) transfer step is depicted as **A** (Scheme S8). The calculations show that the B(pin) transfer occurs in a concerted manner, that is, as the B–B bond breaks the C–B bond forms simultaneously. At the transition state, the distance between the two boron atoms is 2.05 Å, and the distance between the β carbon of cyclohexenone and the boron is 1.96 Å. The intrinsic free energy of activation $\Delta G^{\ddagger}$ is 18.0 kcal/mol.

Scheme S8. The transition state of the C–B bond formation in an achiral NHC catalyzed BCA reaction





A

$\Delta G^{\ddagger}$ = 18.0 kcal/mol

Ground State of A

```
----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
98

H     -4.036      0.114     -3.129
```

C	-3.888	0.792	-2.285
H	-2.484	-0.457	-1.317
O	-5.353	2.371	-3.285
C	-3.041	0.481	-1.272
C	-4.616	2.077	-2.337
C	-2.819	1.377	-0.080
H	-1.893	1.960	-0.240
C	-4.361	3.055	-1.182
H	-3.512	3.696	-1.487
C	-4.005	2.336	0.135
H	-5.239	3.710	-1.079
H	-4.877	1.754	0.478
H	-3.768	3.070	0.920
H	-2.628	0.765	0.814
N	0.446	1.293	-1.163
B	0.030	-1.320	-0.336
C	0.926	2.482	-0.624
C	0.509	0.288	-0.237
C	1.276	2.217	0.669
N	1.005	0.875	0.889
H	-4.932	-2.170	0.010
H	-4.269	-0.748	0.859
H	-4.305	-4.452	0.662
C	-4.553	-1.803	0.975
H	-5.358	-1.871	1.723
O	-2.365	-2.585	0.307
C	-3.344	-2.656	1.393
C	-3.772	-4.117	1.565
H	-4.451	-4.217	2.426
H	-2.903	-4.771	1.721
H	-3.881	-0.394	3.089
H	-4.148	-1.868	4.063
C	-2.546	-2.054	2.610
C	-3.382	-1.232	3.593
H	-2.363	-3.803	3.919
H	-2.731	-0.830	4.384
C	-1.715	-3.107	3.364
H	-1.095	-3.679	2.659
H	-1.053	-2.594	4.077
B	-1.387	-1.649	0.644
O	-1.586	-1.169	1.947
H	0.971	3.399	-1.196
H	1.688	2.855	1.440
H	0.474	-2.994	-4.097
C	1.295	-2.959	-3.363
H	-1.080	-4.009	-2.443
H	1.913	-2.077	-3.577
O	-0.033	-1.704	-1.773
H	1.914	-3.862	-3.496
C	0.716	-2.915	-1.942
C	-0.233	-4.118	-1.748
H	0.275	-5.074	-1.955
H	-0.628	-4.129	-0.724
H	2.632	-0.933	-1.494
C	1.798	-2.828	-0.798
C	2.990	-1.922	-1.177
O	1.076	-2.216	0.277
H	3.597	-2.357	-1.987

```
C     2.328    -4.188    -0.322
H     2.814    -4.728    -1.152
H     3.631    -1.791    -0.291
H     1.512    -4.809     0.076
H     3.072    -4.038     0.476
C     0.659     0.635    -4.938
C    -0.186     1.823    -5.441
C     1.173     0.879    -3.505
H     1.510     0.452    -5.614
H     0.040    -0.279    -4.937
C    -0.015     1.153    -2.566
H     1.855     1.747    -3.487
H     1.717     0.001    -3.137
C    -0.807     2.385    -3.041
C    -1.341     2.130    -4.465
H    -0.148     3.269    -3.063
H    -1.634     2.596    -2.349
H     0.459     2.716    -5.526
H    -0.585     1.610    -6.446
H    -1.917     3.005    -4.806
H    -2.037     1.274    -4.435
C     0.779     0.147     4.646
C     2.286    -0.022     4.930
C     0.541     0.915     3.330
H     0.284     0.671     5.480
H     0.311    -0.849     4.560
C     1.254     0.190     2.177
H     0.936     1.941     3.430
H    -0.532     0.975     3.101
C     2.765     0.044     2.430
H     0.825    -0.808     2.078
C     2.995    -0.719     3.750
H     3.228     1.045     2.491
H     3.216    -0.493     1.583
H     2.737     0.975     5.084
H     2.436    -0.597     5.858
H     4.075    -0.811     3.947
H     2.594    -1.743     3.640
H    -0.666     0.275    -2.576
```

```
                     1                     2                     3
                     A                     A                     A
 Frequencies --    13.1939               20.1958               27.1962
 Red. masses --     5.4714                6.9319                4.3492
 Zero-point correction=                           0.849032 (Hartree/Particle)
 Thermal correction to Energy=                    0.893423
 Thermal correction to Enthalpy=                  0.894367
 Thermal correction to Gibbs Free Energy=         0.773357
 Sum of electronic and zero-point Energies=          -1824.698238
 Sum of electronic and thermal Energies=             -1824.653847
 Sum of electronic and thermal Enthalpies=           -1824.652903
 Sum of electronic and thermal Free Energies=        -1824.773914

         Item               Value     Threshold  Converged?
 Maximum Force            0.000019     0.000450     YES
 RMS     Force            0.000003     0.000300     YES

---------------------------------------
```

Transition State of A

```
---------------------------------------
 Cartesian coordinates (Angstroms):
---------------------------------------
98

N     0.832     1.315    -1.396
B    -0.064    -1.069    -0.525
C     1.472     2.434    -0.885
C     0.622     0.399    -0.406
C     1.652     2.214     0.451
N     1.118     0.966     0.730
C    -2.512     0.470    -0.728
H    -5.004    -3.079     0.342
H    -4.854    -1.494     1.131
H    -3.333    -4.797     0.533
C    -4.615    -2.558     1.230
H    -5.122    -2.958     2.121
O    -2.497    -2.284     0.099
C    -3.098    -2.796     1.317
C    -2.828    -4.306     1.379
H    -3.225    -4.732     2.315
H    -1.753    -4.523     1.319
H    -4.134    -0.867     3.188
H    -3.730    -2.336     4.125
C    -2.385    -1.953     2.456
C    -3.309    -1.475     3.581
H    -1.461    -3.575     3.594
H    -2.730    -0.866     4.293
C    -1.158    -2.666     3.051
H    -0.448    -2.929     2.258
H    -0.657    -1.992     3.760
B    -1.906    -1.036     0.362
O    -1.899    -0.774     1.744
C    -4.602     2.022     0.741
O    -6.154     0.414    -0.183
C    -4.952     0.773    -0.087
C    -3.893     0.126    -0.810
C    -2.194     1.799    -0.026
H    -4.186    -0.724    -1.428
C    -3.125     2.079     1.166
H    -2.888     3.065     1.599
H    -2.936     1.321     1.939
H    -5.277     2.060     1.612
H    -4.845     2.903     0.116
H    -1.942     0.306    -1.648
H    -1.154     1.839     0.314
H    -2.310     2.604    -0.775
H     1.742     3.275    -1.509
H     2.103     2.831     1.217
H     0.551    -2.828    -4.127
C     1.221    -2.947    -3.262
H    -1.386    -3.630    -2.910
H     1.985    -2.158    -3.303
O    -0.167    -1.536    -1.880
H     1.719    -3.927    -3.341
C     0.396    -2.869    -1.968
C    -0.754    -3.885    -2.045
```

H	-0.364	-4.906	-2.185
H	-1.370	-3.842	-1.141
H	2.690	-1.450	-1.244
C	1.255	-2.983	-0.641
C	2.696	-2.464	-0.816
O	0.591	-2.077	0.274
H	3.285	-3.121	-1.474
C	1.278	-4.381	-0.017
H	1.744	-5.102	-0.707
H	3.181	-2.424	0.171
H	0.262	-4.723	0.219
H	1.868	-4.358	0.913
C	1.422	0.717	-5.136
C	0.581	1.887	-5.688
C	1.786	0.947	-3.655
H	2.340	0.586	-5.730
H	0.842	-0.219	-5.218
C	0.502	1.159	-2.832
H	2.433	1.836	-3.563
H	2.337	0.085	-3.248
C	-0.319	2.352	-3.352
C	-0.682	2.115	-4.833
H	0.271	3.281	-3.266
H	-1.225	2.470	-2.739
H	1.193	2.807	-5.679
H	0.300	1.692	-6.736
H	-1.258	2.974	-5.215
H	-1.335	1.227	-4.902
C	0.318	0.811	4.483
C	1.710	0.363	4.972
C	0.382	1.393	3.057
H	-0.106	1.565	5.166
H	-0.369	-0.050	4.488
C	1.048	0.390	2.094
H	0.965	2.329	3.081
H	-0.627	1.625	2.686
C	2.445	-0.039	2.569
H	0.407	-0.489	2.017
C	2.351	-0.637	3.988
H	3.116	0.837	2.579
H	2.853	-0.773	1.858
H	2.364	1.249	5.060
H	1.633	-0.087	5.976
H	3.355	-0.930	4.335
H	1.739	-1.555	3.948
H	-0.100	0.250	-2.900

	1	2	3
	A	A	A
Frequencies --	-342.3384	16.5905	25.4934
Red. masses --	9.7213	4.9027	4.2430

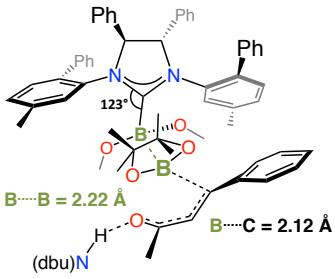
Zero-point correction=	0.848393 (Hartree/Particle)
Thermal correction to Energy=	0.891892
Thermal correction to Enthalpy=	0.892836
Thermal correction to Gibbs Free Energy=	0.775068
Sum of electronic and zero-point Energies=	-1824.671940
Sum of electronic and thermal Energies=	-1824.628442
Sum of electronic and thermal Enthalpies=	-1824.627497

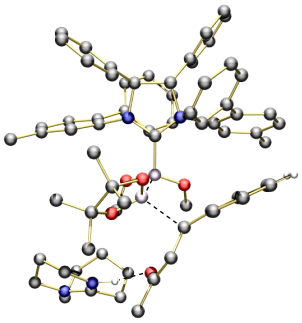
```
 Sum of electronic and thermal Free Energies=        -1824.745265

         Item               Value     Threshold  Converged?
 Maximum Force            0.000009     0.000450     YES
 RMS     Force            0.000001     0.000300     YES
----------------------------------------
```

Next, we investigated the enantioselective boryl conjugate addition to acyclic enones. Additional noteworthy points merit mention: 1) Boryl conjugate additions catalyzed by chiral NHCs only proceed in the presence of MeOH. Experiments indicate that MeOH may play a dual role in the reaction by acting as a proton source and promoting hydrolysis of one of the pinacolato groups in $B_2(pin)_2$. Our computational studies suggest that this hydrolysis eases the coordination of the bulky, chiral NHC to the boron center. 2) Excess dbu was used instead of catalytic NaO*t*-Bu. Besides deprotonation of the imidazolinium salt to generate the NHC, we speculate that the protonated form of dbu ($dbuH^+$) may serve as a Lewis acid to activate the carbonyl group of the enone. Two transition states (**I** and **II**) for the addition of B(pin) unit to the acyclic enone that results in the two observed enantiomeric products were optimized (Scheme S9). In the favored transition state **I**, the distance between the two borons is 2.22 Å and the one between the β carbon of the enone and the boron is 2.12 Å. The activation energy of **I** ($\Delta G^{\ddagger}$ = 25.8 kcal/mol) is higher than the transition state **A** that involves an achiral NHC ($\Delta G^{\ddagger}$ = 18.0 kcal/mol). One of the many reasons could be that the more sterically hindered chiral NHC hampers formation of the C–B bond, compared to the small achiral NHC. The unfavored transition state **II** is 1.4 kcal/mol higher in energy than **I**, probably because of the steric repulsion between the phenyl substituent of the enone and the N-aryl motif of the NHC (highlighted in **II**). Such interactions may also lead to the variation of the N–C–B angle from 123° to 133° in TS **I** and **II**, respectively.

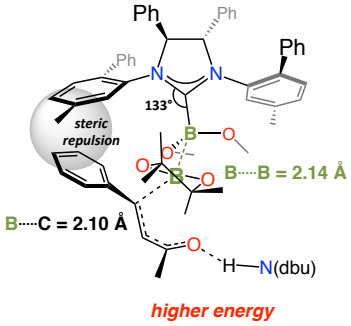
Scheme S9. The transition state of the C–B bond formation in an achiral NHC catalyzed BCA reaction

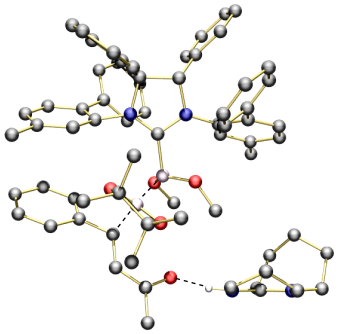




I

$\Delta G^{\ddagger}$ = 25.8 kcal/mol





II

$\Delta G^{\ddagger}$ = 27.2 kcal/mol

Ground State of I and II

```
----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
158

H      7.209      5.333     -5.950
H      8.733      6.239     -7.090
C      7.509      5.588     -4.924
H      6.713      7.538     -5.479
H      6.840      5.032     -4.258
C      9.643      6.515     -6.542
C      7.356      7.132     -4.685
H     10.476      6.473     -7.255
H      9.031      8.567     -6.684
C      8.912      5.059     -4.721
N      9.902      5.482     -5.516
H      8.308      3.877     -3.184
C      9.502      7.923     -5.924
H      6.825      7.277     -3.733
N      9.128      4.186     -3.742
H     11.556      4.264     -5.985
C      8.673      7.934     -4.622
H     10.577      2.677     -3.990
C     11.311      5.077     -5.284
C     10.449      3.621     -3.438
H      8.438      8.976     -4.357
H     10.501      8.338     -5.716
```

H	11.941	5.944	-5.525
H	9.292	7.537	-3.800
C	11.525	4.639	-3.831
H	10.473	3.397	-2.364
H	12.523	4.195	-3.728
H	11.460	5.514	-3.167
C	4.979	2.299	-0.420
B	6.664	-0.247	-3.945
O	7.395	0.010	-5.107
B	7.338	-0.993	-2.491
C	7.375	-2.664	-2.813
N	8.238	-3.309	-3.637
N	6.413	-3.535	-2.438
H	10.056	0.935	-1.953
O	8.734	-0.604	-2.219
H	8.173	-7.583	1.739
H	8.967	-5.276	1.187
C	7.498	-6.869	1.264
C	7.944	-5.574	0.950
H	5.820	-8.243	1.193
C	6.177	-7.238	0.959
C	7.083	-4.658	0.330
H	7.437	-3.657	0.091
H	6.216	-1.851	0.309
H	12.676	-0.732	-2.076
H	3.198	-4.541	0.701
H	13.819	-1.987	-2.611
H	12.586	-2.357	-1.369
C	5.313	-6.320	0.344
C	12.777	-1.807	-2.304
C	5.753	-5.018	0.017
H	7.880	-1.231	0.015
C	6.804	-0.987	-0.057
H	4.292	-6.614	0.094
H	6.599	-0.133	0.614
C	3.497	-3.941	-0.160
H	10.910	-6.645	-0.886
C	4.821	-4.064	-0.640
H	10.157	-2.547	-2.027
H	1.572	-2.984	-0.343
O	6.421	-0.650	-1.378
C	11.804	-2.220	-3.388
C	2.585	-3.058	-0.744
H	9.084	-5.057	-1.481
C	10.480	-2.549	-3.065
C	10.513	-6.627	-1.903
H	13.222	-2.053	-5.019
C	9.487	-5.734	-2.234
C	12.193	-2.288	-4.740
C	5.178	-3.276	-1.759
H	6.728	-5.618	-2.235
H	8.420	1.243	-1.276
H	11.830	-8.195	-2.623
H	4.847	-6.945	-2.538
C	2.967	-2.244	-1.830
C	11.028	-7.499	-2.879
C	8.974	0.782	-2.116
C	9.541	-2.879	-4.053

C	4.263	-2.390	-2.341
C	6.568	-4.899	-3.049
H	1.609	-0.569	-1.666
C	8.964	-5.705	-3.540
C	11.275	-2.670	-5.724
C	2.007	-1.245	-2.441
C	4.546	-6.373	-3.418
H	8.676	1.319	-3.038
H	2.513	-0.634	-3.203
C	7.856	-4.740	-3.899
C	9.931	-2.972	-5.413
C	10.512	-7.471	-4.185
H	2.768	-7.551	-3.793
C	5.336	-5.289	-3.835
H	4.574	-1.804	-3.200
H	11.590	-2.727	-6.767
C	9.483	-6.573	-4.515
C	3.377	-6.706	-4.121
H	1.146	-1.749	-2.911
O	5.347	0.195	-4.072
H	10.910	-8.144	-4.947
H	7.619	-4.842	-4.964
C	4.942	-4.533	-4.954
H	9.085	-6.536	-5.530
H	6.820	2.579	-4.669
C	9.026	-3.419	-6.505
H	7.408	-2.089	-5.993
C	2.989	-5.950	-5.239
H	10.451	-4.853	-7.279
H	8.093	2.400	-5.910
H	5.550	-3.686	-5.272
C	6.577	0.862	-5.982
H	5.179	-1.523	-6.109
C	5.120	0.560	-5.473
C	7.014	2.310	-5.715
C	7.733	-2.880	-6.665
C	9.458	-4.420	-7.404
C	3.775	-4.860	-5.655
H	2.078	-6.206	-5.784
H	3.565	-0.940	-5.620
H	4.533	2.586	-4.917
C	4.489	-0.668	-6.151
H	7.900	0.705	-7.684
H	6.647	-0.562	-7.646
C	6.846	0.497	-7.443
C	4.157	1.748	-5.520
H	3.176	1.444	-5.126
H	6.476	3.009	-6.372
H	3.478	-4.265	-6.521
C	6.892	-3.337	-7.690
H	4.246	-0.460	-7.204
C	8.615	-4.878	-8.427
H	6.212	1.110	-8.102
H	4.024	2.089	-6.559
H	5.894	-2.907	-7.802
H	8.963	-5.660	-9.105
C	7.325	-4.341	-8.572
H	6.665	-4.700	-9.363

```
H     1.411     0.039     2.906
H     2.574    -1.322     1.157
C     2.128     0.510     2.231
C     2.779    -0.256     1.249
H     1.896     2.485     3.104
C     2.402     1.887     2.344
C     3.700     0.346     0.383
H     4.207    -0.243    -0.383
C     3.325     2.491     1.486
C     3.994     1.729     0.492
H     3.531     3.557     1.587
C     5.406     3.595    -0.443
C     6.423     4.068    -1.384
O     6.880     3.346    -2.297
H     6.095     6.188    -1.551
C     6.893     5.505    -1.211
H     7.077     5.732    -0.149
H     7.801     5.696    -1.797
H     5.022     4.332     0.265
H     5.429     1.597    -1.130
```

```
                     1                     2                     3
                     A                     A                     A
 Frequencies --    11.1958               14.2595               17.3692
 Red. masses --     5.4444                5.4240                4.8245
 Zero-point correction=                           1.315344 (Hartree/Particle)
 Thermal correction to Energy=                    1.392892
 Thermal correction to Enthalpy=                  1.393836
 Thermal correction to Gibbs Free Energy=         1.195678
 Sum of electronic and zero-point Energies=         -3280.109200
 Sum of electronic and thermal Energies=            -3280.031652
 Sum of electronic and thermal Enthalpies=          -3280.030707
 Sum of electronic and thermal Free Energies=       -3280.228866

         Item               Value     Threshold  Converged?
 Maximum Force            0.000022     0.000450     YES
 RMS     Force            0.000002     0.000300     YES
```

Transition State of I

```
 Cartesian coordinates (Angstroms):
---------------------------------------
158

H     3.890     3.060     7.855
H     5.444     4.300     5.701
H     4.514     1.743     8.868
C     4.396     2.082     7.827
H     2.588     0.912     7.606
H     4.018     3.393     3.937
H     6.263     3.204     7.549
H     5.264     4.387     3.143
H     3.201     1.578     6.095
C     3.511     1.096     7.036
C     5.875     3.540     5.037
C     5.093     3.467     3.719
```

C	5.816	2.253	7.235
H	6.931	3.794	4.857
N	5.819	2.244	5.756
H	6.481	1.454	7.587
C	4.159	-0.265	6.702
H	4.382	-0.812	7.630
C	5.545	2.248	2.906
C	5.634	1.095	5.089
H	3.422	-0.860	6.143
H	4.852	2.032	2.084
H	6.552	2.410	2.490
N	5.559	1.057	3.765
C	5.475	-0.201	5.851
H	6.353	-0.323	6.500
H	5.361	0.127	3.320
H	5.494	-1.024	5.126
H	-4.552	-1.051	5.292
H	-2.140	-1.604	4.917
C	-3.897	-0.338	4.786
C	-2.545	-0.651	4.569
H	-5.452	1.148	4.506
C	-4.401	0.897	4.348
C	-1.703	0.260	3.914
H	-0.651	0.033	3.770
H	2.638	1.862	3.258
H	-2.823	-4.136	3.942
H	-1.580	3.933	4.423
H	-1.245	-4.934	3.804
H	-2.718	-5.801	3.301
C	-3.558	1.812	3.698
C	-2.226	-4.817	3.313
C	-2.199	1.504	3.470
H	0.281	-5.712	-0.560
H	2.133	0.530	4.345
C	2.343	0.803	3.296
H	1.192	-3.967	0.963
H	-3.950	2.772	3.356
H	3.163	0.180	2.917
C	-1.122	3.763	3.447
H	-5.874	-1.479	2.671
C	0.989	-4.979	-0.944
C	-1.320	2.518	2.819
C	1.507	-4.004	-0.080
H	-1.613	-2.257	2.579
H	-0.216	5.725	3.370
O	1.173	0.656	2.508
C	-2.069	-4.264	1.913
C	-0.355	4.774	2.851
H	-3.632	-0.578	2.096
O	4.803	-1.273	2.574
H	6.914	-0.036	1.254
C	-1.718	-2.918	1.724
C	-5.573	-1.406	1.624
H	0.943	-5.747	-2.972
C	1.359	-4.997	-2.297
H	-2.609	-6.095	0.889
H	0.875	-1.419	4.329
C	5.280	-1.444	1.400

C	-4.309	-0.896	1.304
C	2.443	-3.055	-0.543
C	3.105	-2.155	0.439
C	-2.304	-5.053	0.771
C	-0.709	2.324	1.558
H	-3.088	1.489	0.829
B	0.848	-0.473	1.722
C	4.497	-1.914	0.314
C	6.753	-1.124	1.171
H	2.427	-1.951	3.604
H	-7.430	-2.218	0.850
H	-3.565	3.627	0.090
C	0.217	4.587	1.580
C	-6.445	-1.819	0.601
C	1.332	-2.071	3.564
N	-1.020	1.152	0.784
C	-0.566	-0.115	0.928
H	7.366	-1.605	1.950
C	-1.536	-2.388	0.441
O	0.825	-1.781	2.263
C	2.263	-4.033	-2.779
C	0.001	3.355	0.939
H	7.105	-1.446	0.179
C	2.803	-3.080	-1.910
C	-2.334	1.215	0.075
H	0.794	6.661	1.313
N	-1.413	-0.964	0.309
C	-3.904	-0.801	-0.040
C	-2.151	-4.515	-0.512
C	1.038	5.667	0.909
C	-3.015	3.463	-0.840
B	2.365	-0.196	0.127
H	1.072	-3.117	3.788
H	2.117	5.496	1.066
C	-2.541	-0.246	-0.385
H	2.547	-4.027	-3.834
C	-1.743	-3.181	-0.713
C	-6.046	-1.719	-0.742
H	-3.517	5.398	-1.672
C	-2.333	2.249	-1.030
H	0.356	3.198	-0.075
H	3.504	-2.340	-2.290
H	-2.312	-5.146	-1.387
C	-4.775	-1.213	-1.061
C	-2.983	4.459	-1.828
O	2.013	-0.099	-1.217
H	0.865	5.677	-0.179
O	3.231	0.837	0.493
H	-6.720	-2.037	-1.540
H	-2.374	-0.339	-1.464
C	-1.612	2.039	-2.220
H	-4.451	-1.146	-2.101
H	4.316	-0.412	-2.628
C	-1.554	-2.659	-2.087
H	0.320	-1.664	-1.646
C	-2.264	4.244	-3.015
H	-3.378	-3.538	-2.857
H	2.902	-0.197	-3.693

```
H    -1.065     1.108    -2.372
C     2.781     0.962    -1.870
H     2.409     3.285    -0.205
C     3.675     1.568    -0.689
C     3.590     0.318    -3.007
C    -0.434    -1.862    -2.401
C    -2.500    -2.934    -3.097
C    -1.579     3.032    -3.209
H    -2.237     5.017    -3.786
H     4.064     3.375     0.435
H     5.402     0.240    -0.882
C     3.456     3.064    -0.428
H     1.194     1.431    -3.260
H     1.078     2.324    -1.733
C     1.779     1.946    -2.484
C     5.182     1.314    -0.856
H     5.721     1.755    -0.005
H     4.135     1.089    -3.572
H    -1.014     2.860    -4.127
C    -0.277    -1.336    -3.689
H     3.768     3.660    -1.300
C    -2.339    -2.409    -4.389
H     2.298     2.797    -2.948
H     5.555     1.780    -1.780
H     0.602    -0.727    -3.911
H    -3.086    -2.622    -5.156
C    -1.229    -1.601    -4.688
H    -1.107    -1.185    -5.690
H     2.752    -2.290     1.456
H     4.990    -2.048    -0.650
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --  -412.8472               14.9871                19.2513
 Red. masses --    10.7239                5.3091                 4.8421
 Zero-point correction=                           1.316385 (Hartree/Particle)
 Thermal correction to Energy=                    1.392395
 Thermal correction to Enthalpy=                  1.393339
 Thermal correction to Gibbs Free Energy=         1.202838
 Sum of electronic and zero-point Energies=          -3280.074135
 Sum of electronic and thermal Energies=             -3279.998125
 Sum of electronic and thermal Enthalpies=           -3279.997181
 Sum of electronic and thermal Free Energies=        -3280.187682

         Item               Value     Threshold  Converged?
 Maximum Force            0.000055     0.000450     YES
 RMS     Force            0.000006     0.000300     YES
```

Transition State of II

```
 Cartesian coordinates (Angstroms):
---------------------------------------
158

H     5.653    19.226     5.250
C     5.926    18.178     5.066
```

H	4.046	17.855	4.034
H	5.730	18.004	7.204
C	5.104	17.577	3.920
H	5.458	17.968	2.957
N	5.651	17.452	6.314
H	7.004	18.123	4.844
H	2.759	16.347	8.468
H	2.451	16.385	6.026
H	5.070	16.390	8.491
C	5.112	16.241	6.371
C	2.342	15.432	6.564
C	3.149	15.505	7.878
H	1.273	15.344	6.814
C	4.699	15.701	7.721
C	5.230	16.048	3.928
N	4.910	15.505	5.269
H	4.527	15.597	3.216
H	6.250	15.736	3.656
H	2.981	14.592	8.469
C	2.733	14.284	5.611
H	2.212	14.431	4.652
H	5.216	14.743	7.875
C	4.257	14.181	5.365
H	2.402	13.315	6.018
H	4.741	13.615	6.171
H	4.470	13.652	4.428
H	-3.177	21.413	12.061
H	-0.964	20.499	11.331
C	-2.438	22.068	11.597
C	-1.196	21.555	11.183
H	-3.688	23.837	11.712
C	-2.723	23.430	11.404
C	-0.247	22.394	10.579
H	0.712	21.987	10.260
H	2.261	19.592	10.789
H	-1.599	16.366	8.913
H	0.346	26.078	11.431
H	-1.248	17.827	9.885
H	0.082	16.819	9.276
C	-1.771	24.273	10.811
C	-0.916	17.222	9.027
C	-0.521	23.765	10.390
H	2.916	24.598	12.206
H	1.601	18.852	9.296
C	2.356	19.549	9.694
H	3.099	22.508	10.856
H	-1.994	25.330	10.658
H	3.361	19.189	9.425
C	0.815	25.877	10.466
H	-4.547	21.269	9.443
C	3.680	24.516	11.432
C	0.489	24.681	9.797
C	3.777	23.342	10.674
H	-0.397	19.914	8.772
H	1.964	27.705	10.480
O	2.129	20.873	9.201
C	-0.858	18.049	7.761
C	1.731	26.790	9.931

H	-2.270	22.066	8.862
H	4.282	21.122	9.396
O	5.658	19.160	8.437
H	8.263	18.851	8.216
C	-0.548	19.417	7.815
C	-4.281	21.425	8.396
H	4.467	26.509	11.767
C	4.547	25.591	11.183
H	-1.369	16.418	6.429
H	2.312	18.242	7.244
C	6.501	20.112	8.288
C	-2.996	21.879	8.072
C	4.755	23.210	9.665
C	4.914	21.898	8.981
C	-1.103	17.475	6.497
C	1.118	24.446	8.546
H	-1.450	24.053	7.948
B	2.185	21.206	7.817
C	6.208	21.465	8.589
C	7.884	19.769	7.740
H	3.867	19.138	7.189
H	-6.218	20.819	7.629
H	-1.494	26.362	7.759
C	2.359	26.543	8.700
C	-5.217	21.173	7.377
C	2.877	19.034	6.727
N	0.550	23.453	7.672
C	0.844	22.164	7.455
H	8.605	20.587	7.888
C	-0.417	20.176	6.644
H	7.003	22.195	8.434
O	2.161	20.249	6.774
C	5.504	25.485	10.158
C	2.014	25.371	8.007
H	7.817	19.574	6.656
C	5.600	24.311	9.402
C	-0.789	23.840	7.096
H	3.299	28.495	8.578
N	-0.175	21.582	6.780
C	-2.636	22.084	6.728
C	-1.009	18.244	5.331
C	3.367	27.501	8.110
C	-1.065	26.319	6.756
B	3.986	22.124	7.115
H	2.986	18.756	5.668
H	4.390	27.119	8.270
C	-1.241	22.550	6.371
H	6.173	26.322	9.946
C	-0.648	19.607	5.374
C	-4.860	21.378	6.034
H	-1.207	28.453	6.426
C	-0.669	25.076	6.231
H	2.425	25.176	7.024
H	6.335	24.247	8.599
H	-1.187	17.783	4.358
C	-3.571	21.830	5.711
C	-0.896	27.494	6.008
O	4.547	21.371	6.070

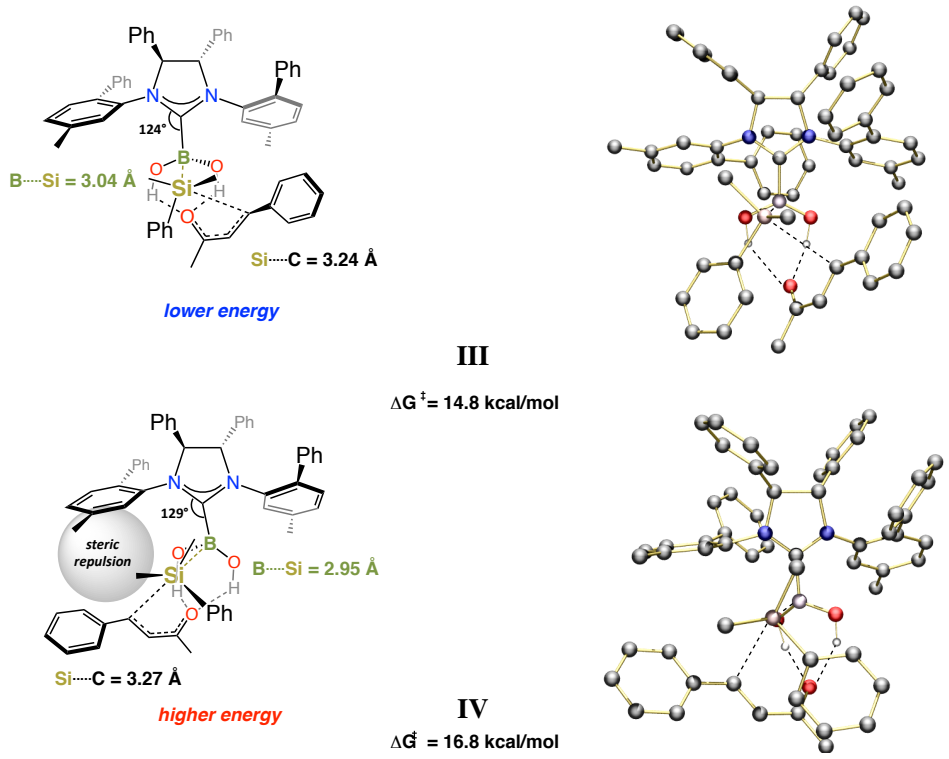
```
H     3.220    27.613     7.023
O     3.984    23.476     6.783
H    -5.583    21.184     5.239
H    -1.174    22.667     5.282
C    -0.093    25.021     4.948
H    -3.282    21.979     4.669
H     6.896    22.655     6.273
C    -0.498    20.386     4.119
H     1.458    21.138     4.633
C    -0.322    27.433     4.728
H    -2.419    19.786     3.324
H     7.031    21.269     5.164
H     0.238    24.067     4.535
C     5.114    22.266     5.073
H     2.443    23.083     4.677
C     4.418    23.649     5.401
C     6.638    22.290     5.272
C     0.665    21.152     3.885
C    -1.515    20.370     3.142
C     0.078    26.193     4.199
H    -0.187    28.345     4.144
H     2.668    24.831     4.910
H     6.189    24.770     6.022
C     3.155    23.909     4.566
H     5.314    20.746     3.540
H     3.707    21.517     3.576
C     4.784    21.700     3.686
C     5.336    24.875     5.339
H     4.766    25.771     5.628
H     7.120    22.934     4.521
H     0.527    26.138     3.206
C     0.796    21.898     2.705
H     3.402    24.027     3.501
C    -1.382    21.119     1.962
H     5.109    22.397     2.897
H     5.715    25.018     4.315
H     1.700    22.485     2.535
H    -2.183    21.106     1.220
C    -0.229    21.889     1.743
H    -0.127    22.477     0.828
```

```
                     1                     2                     3
                     A                     A                     A
 Frequencies --  -404.1519              14.9932              17.9827
 Red. masses --    10.7915               4.6450               4.8961
 Zero-point correction=                           1.316048 (Hartree/Particle)
 Thermal correction to Energy=                    1.391914
 Thermal correction to Enthalpy=                  1.392859
 Thermal correction to Gibbs Free Energy=         1.203083
 Sum of electronic and zero-point Energies=          -3280.072629
 Sum of electronic and thermal Energies=             -3279.996763
 Sum of electronic and thermal Enthalpies=           -3279.995818
 Sum of electronic and thermal Free Energies=        -3280.185594

         Item               Value     Threshold  Converged?
 Maximum Force            0.000004     0.000450     YES
 RMS     Force            0.000000     0.000300     YES
```

Next, computations were carried out on the NHC catalyzed enantioselective silyl conjugate addition to an acyclic enone (Scheme S10). There are several differences compared to the boron conjugate addition variants: 1) The calculated B–Si bond length of $PhMe_2Si$–B(pin) is 2.05 Å, which is significantly longer than the bond length of B–B in $B_2(pin)_2$ (1.70 Å). 2) The reaction proceeds more efficiently when H_2O is used as a co-solvent with thf instead MeOH. As mentioned in the manuscript, H_2O is probably responsible for the hydrolysis of the B(pin) unit, generating $(HO)_2B$–$SiPhMe_2$, which may facilitate effective coordination of NHC to the boron center. The computational study suggests an interesting feature of the transformation: Instead of Lewis acid activation of the carbonyl group by $dbuH^+$, an intramolecular chelation by the two hydroxyl groups of the $(HO)_2B$–$SiPhMe_2$ to the carbonyl group of the enone takes place in the favored transition state **III**. The activation barrier of **III** is 14.8 kcal/mol. The unfavored pathway via transition state **IV**, which also involves such a chelation, is 2.0 kcal/mol higher in energy than **III**. This is probably due to the steric repulsion between the $SiMe_2Ph$ unit and the N-Ar motif of the NHC. Such interactions may also lead to the variation of the N–C–B angle from 124° to 129° in TS **III** and **IV**, respectively.

Scheme S10. The transition state of the C–Si bond formation in an achiral NHC catalyzed SCA reaction



Ground State of III and IV

```
----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
123

C      0.381     -0.958      3.147
```

H	2.208	1.536	1.258
H	3.612	0.479	1.138
C	2.688	0.655	1.711
H	2.976	0.916	2.745
H	-0.520	-0.336	3.020
Si	1.567	-0.903	1.625
H	4.595	-1.313	1.923
H	0.883	-0.640	4.078
C	4.126	-2.295	2.002
C	2.719	-2.407	1.906
H	6.029	-3.297	2.279
H	0.036	-1.995	3.293
C	4.945	-3.419	2.202
C	2.169	-3.710	2.012
C	4.374	-4.699	2.300
H	1.087	-3.842	1.933
C	2.980	-4.842	2.201
H	5.008	-5.576	2.450
H	2.525	-5.833	2.274
H	6.934	4.421	-0.696
H	8.395	2.395	-0.703
C	6.490	3.430	-0.809
C	7.314	2.288	-0.812
C	5.099	3.292	-0.950
H	4.452	4.170	-0.946
H	7.400	0.136	-0.954
C	6.754	1.014	-0.953
H	5.842	-4.233	-0.327
H	6.020	-4.238	-2.095
C	5.282	-4.205	-1.275
H	6.339	-1.787	-1.092
C	4.536	2.018	-1.093
H	4.614	-5.073	-1.337
C	5.352	0.859	-1.096
H	1.037	-3.150	-0.265
C	4.480	-2.914	-1.359
C	5.261	-1.668	-1.222
H	3.456	1.907	-1.194
O	0.203	-2.648	-0.266
C	4.689	-0.433	-1.237
H	3.604	-0.373	-1.341
B	0.576	-1.214	-0.221
C	-0.809	-0.319	-0.095
H	-3.997	-4.485	-1.635
C	-3.575	-4.027	-0.738
H	-4.106	-5.685	0.544
C	1.311	2.661	-2.660
C	-3.632	-4.703	0.489
C	-2.964	-2.763	-0.850
O	1.383	-0.811	-1.384
H	0.131	0.852	-2.540
C	0.454	1.751	-2.023
H	2.309	4.572	-2.451
C	1.656	3.839	-1.973
C	-2.421	-2.200	0.327
C	-3.087	-4.134	1.655
N	-1.986	-0.833	0.320
C	-2.492	-2.864	1.554

C	0.002	1.961	-0.712
H	2.026	-1.539	-1.521
N	-0.939	1.032	-0.168
H	-2.090	-2.368	2.438
C	1.173	4.076	-0.682
C	0.342	3.149	-0.013
H	1.455	4.990	-0.157
C	-3.078	0.183	0.408
C	-2.318	1.513	0.179
O	3.252	-2.950	-1.551
H	-2.263	2.091	1.108
H	-3.760	-0.014	-0.434
C	-3.155	-4.838	2.994
C	1.859	2.357	-4.036
H	-4.104	5.546	-1.429
H	-3.140	4.103	0.374
C	-3.813	4.517	-1.650
C	-3.279	3.708	-0.634
H	-4.379	4.634	-3.739
C	-3.967	4.004	-2.948
C	-2.905	2.383	-0.911
C	-3.587	2.679	-3.228
C	-3.058	1.872	-2.213
H	-3.700	2.272	-4.234
H	-2.755	0.849	-2.431
H	-6.779	-1.275	2.876
H	-5.517	-0.925	0.750
C	-5.808	-0.776	2.895
C	-5.104	-0.574	1.698
H	-5.806	-0.497	5.045
C	-5.261	-0.340	4.112
C	-3.852	0.066	1.705
C	-4.010	0.301	4.126
C	-3.310	0.500	2.929
H	-3.579	0.645	5.068
H	-2.339	0.995	2.949
H	-3.617	-5.832	2.898
H	-3.747	-4.251	3.716
H	-2.149	-4.964	3.427
H	1.129	1.798	-4.642
H	2.766	1.731	-3.956
H	2.135	3.278	-4.573
H	-0.744	-0.775	-4.468
H	-0.767	-1.965	-2.286
C	-1.705	-1.698	-2.770
C	-1.699	-1.038	-4.008
C	-2.929	-2.052	-2.159
C	-2.906	-0.723	-4.655
H	-2.896	-0.206	-5.617
C	-4.137	-1.737	-2.819
C	-4.127	-1.076	-4.057
H	-5.086	-2.005	-2.348
H	-5.070	-0.832	-4.549
H	-1.505	6.140	3.061
H	-0.688	5.511	0.796
C	-0.647	4.786	1.610
C	-1.113	5.136	2.886
C	-0.148	3.490	1.350

```
C    -1.087     4.196     3.930
H    -1.451     4.466     4.923
C    -0.128     2.557     2.408
C    -0.588     2.906     3.685
H     0.250     1.557     2.228
H    -0.554     2.166     4.487

                     1                     2                     3
                     A                     A                     A
 Frequencies --    11.3593               17.9751               19.4696
 Red. masses --     5.6808                5.2571                5.4842
 Zero-point correction=                           0.987387 (Hartree/Particle)
 Thermal correction to Energy=                    1.050836
 Thermal correction to Enthalpy=                  1.051780
 Thermal correction to Gibbs Free Energy=         0.884080
 Sum of electronic and zero-point Energies=          -2929.352738
 Sum of electronic and thermal Energies=             -2929.289288
 Sum of electronic and thermal Enthalpies=           -2929.288344
 Sum of electronic and thermal Free Energies=        -2929.456045

         Item               Value     Threshold  Converged?
 Maximum Force            0.000015     0.000450     YES
 RMS     Force            0.000002     0.000300     YES
----------------------------------------
```

Transition State of III

```
----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
123

C     0.889    -1.344     2.902
H     3.290     1.241     2.679
H     4.613     0.084     2.721
C     3.535     0.194     2.909
H     3.355     0.028     3.988
H     0.178    -0.511     2.809
Si    2.491    -1.057     1.857
H     5.388    -1.873     2.281
H     1.132    -1.471     3.974
C     4.813    -2.797     2.206
C     3.408    -2.728     2.011
H     6.569    -4.031     2.496
H     0.373    -2.248     2.552
C     5.488    -4.021     2.334
C     2.721    -3.967     1.920
C     4.780    -5.231     2.243
H     1.641    -3.967     1.760
C     3.389    -5.196     2.029
H     5.302    -6.186     2.337
H     2.825    -6.130     1.958
H     6.104     4.314     1.606
H     7.617     2.332     1.786
C     5.810     3.360     1.164
C     6.660     2.243     1.267
C     4.581     3.237     0.492
H     3.906     4.092     0.412
H     6.952     0.155     0.813
```

C	6.286	1.013	0.713
H	5.257	-4.678	-0.318
H	6.694	-3.786	-0.875
C	5.647	-4.024	-1.115
H	6.269	-1.631	-0.153
C	4.209	2.009	-0.062
H	5.596	-4.576	-2.066
C	5.044	0.870	0.043
H	1.778	-3.210	-0.578
C	4.772	-2.782	-1.195
C	5.279	-1.563	-0.604
H	3.252	1.909	-0.573
O	0.945	-2.770	-0.326
C	4.570	-0.383	-0.535
H	3.599	-0.320	-1.021
B	0.986	-1.441	-0.761
C	-0.248	-0.508	-0.304
H	-2.604	-4.939	-1.559
C	-2.433	-4.366	-0.646
H	-3.016	-5.990	0.660
C	0.993	2.042	-3.743
C	-2.672	-4.955	0.606
C	-2.004	-3.032	-0.759
O	1.754	-1.017	-1.822
H	-0.083	0.304	-3.037
C	0.384	1.247	-2.762
H	1.995	3.929	-4.100
C	1.528	3.284	-3.353
C	-1.771	-2.317	0.442
C	-2.487	-4.224	1.792
N	-1.314	-0.960	0.412
C	-2.028	-2.899	1.690
C	0.354	1.644	-1.417
H	2.505	-1.672	-1.938
N	-0.382	0.830	-0.504
H	-1.849	-2.311	2.588
C	1.469	3.699	-2.018
C	0.894	2.891	-1.013
H	1.901	4.658	-1.728
C	-2.333	0.119	0.613
C	-1.529	1.392	0.277
O	3.645	-2.900	-1.760
H	-1.126	1.836	1.194
H	-3.108	-0.035	-0.154
C	-2.752	-4.829	3.155
C	1.061	1.561	-5.177
H	-3.687	5.541	0.023
H	-2.295	3.825	1.192
C	-3.435	4.606	-0.482
C	-2.659	3.642	0.180
H	-4.473	5.125	-2.313
C	-3.877	4.372	-1.795
C	-2.332	2.437	-0.462
C	-3.545	3.168	-2.441
C	-2.780	2.202	-1.775
H	-3.881	2.984	-3.464
H	-2.513	1.271	-2.274
H	-5.890	-1.037	3.415

```
H    -4.778    -0.835     1.192
C    -4.896    -0.592     3.342
C    -4.274    -0.474     2.091
H    -4.714    -0.234     5.473
C    -4.236    -0.142     4.496
C    -2.991     0.093     1.976
C    -2.958     0.434     4.389
C    -2.340     0.552     3.136
H    -2.441     0.791     5.282
H    -1.346     0.996     3.075
H    -3.161    -5.847     3.067
H    -3.467    -4.214     3.725
H    -1.824    -4.882     3.750
H     0.120     1.074    -5.475
H     1.864     0.813    -5.297
H     1.266     2.392    -5.869
H     0.131    -2.651    -4.910
H    -0.097    -3.600    -2.613
C    -0.810    -2.859    -2.975
C    -0.678    -2.313    -4.260
C    -1.834    -2.423    -2.111
C    -1.576    -1.329    -4.705
H    -1.476    -0.907    -5.707
C    -2.736    -1.440    -2.570
C    -2.608    -0.895    -3.857
H    -3.560    -1.126    -1.928
H    -3.320    -0.140    -4.198
H     0.190     6.181     2.227
H     0.235     5.365    -0.126
C     0.519     4.697     0.689
C     0.480     5.150     2.016
C     0.879     3.365     0.392
C     0.794     4.275     3.070
H     0.754     4.623     4.103
C     1.219     2.503     1.457
C     1.165     2.950     2.784
H     1.524     1.479     1.236
H     1.429     2.264     3.590

                     1                     2                     3
                     A                     A                     A
 Frequencies --   -64.2757              14.2858              19.1044
 Red. masses --     6.5243               5.1471               5.2584
 Zero-point correction=                           0.987137 (Hartree/Particle)
 Thermal correction to Energy=                    1.049482
 Thermal correction to Enthalpy=                  1.050426
 Thermal correction to Gibbs Free Energy=         0.886814
 Sum of electronic and zero-point Energies=          -2929.332124
 Sum of electronic and thermal Energies=             -2929.269780
 Sum of electronic and thermal Enthalpies=           -2929.268836
 Sum of electronic and thermal Free Energies=        -2929.432448

         Item               Value     Threshold  Converged?
 Maximum Force            0.000004     0.000450     YES
 RMS     Force            0.000001     0.000300     YES

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```

Transition State of IV

```
---------------------------------------
 Cartesian coordinates (Angstroms):
---------------------------------------
123

H     7.578     3.886    -0.549
H     5.332     4.129    -1.632
C     6.720     3.326    -0.170
C     5.458     3.459    -0.777
C     6.864     2.465     0.932
H     7.839     2.352     1.413
C     4.357     2.742    -0.284
C     5.759     1.743     1.410
C     4.470     1.866     0.828
H     5.894     1.083     2.269
C     3.334     0.728     3.400
H     3.400     1.733     3.856
H     3.388     2.865    -0.769
H     0.866     2.075     0.597
C     1.511     2.164     1.480
H     0.870     2.027     2.367
H     1.898     3.198     1.511
Si     2.980     0.876     1.498
H     4.269     0.191     3.620
H     2.524     0.183     3.908
C    -2.049    -4.479    -2.520
C    -0.751    -3.941    -2.520
C     0.973    -1.671    -5.874
C    -2.776    -4.533    -1.319
C    -0.184    -3.448    -1.334
C    -2.207    -4.054    -0.130
C     0.573    -0.440    -5.088
C    -0.907    -3.500    -0.124
C     0.379    -0.523    -3.700
C     0.348     0.799    -5.715
C    -0.245    -3.855     2.273
C    -4.704     1.062    -3.381
C    -0.344    -2.993     1.160
C    -3.698     1.347    -2.442
C    -4.779    -0.213    -3.964
C     0.010     0.603    -2.953
C    -0.026     1.924    -4.968
C     0.139    -3.378     3.532
C     0.441    -0.297    -0.697
C    -0.010    -1.634     1.367
N    -0.304     0.420    -1.567
C    -0.183     1.860    -3.570
C    -2.772     0.357    -2.079
N    -0.316    -0.682     0.341
C    -3.852    -1.206    -3.600
C    -1.750    -0.287     0.175
C    -1.699     0.657    -1.059
C     0.437    -2.017     3.736
C     0.355    -1.153     2.631
C    -2.854    -0.923    -2.659
C    -0.512     3.072    -2.783
C    -3.177    -0.478     2.236
```

C	0.805	-1.495	5.107
C	-2.320	0.307	1.444
C	-1.588	3.908	-3.147
C	0.257	3.400	-1.646
C	-3.659	0.008	3.461
C	-1.948	1.589	1.891
C	-1.906	5.034	-2.372
C	-0.065	4.521	-0.869
C	-3.283	1.286	3.903
C	-1.151	5.338	-1.226
C	-2.427	2.075	3.115
O	2.490	-1.808	-0.978
B	2.032	-0.501	-0.933
O	4.963	-1.067	-1.694
O	2.609	0.553	-1.641
C	5.926	-0.843	-0.899
C	7.131	-0.093	-1.443
C	4.860	-1.777	1.148
C	5.940	-1.224	0.493
C	3.690	-2.912	3.002
C	4.833	-2.214	2.538
C	3.615	-3.379	4.318
C	5.896	-1.989	3.451
C	4.675	-3.144	5.213
C	5.813	-2.444	4.772
H	3.551	0.341	-1.814
H	3.452	-1.757	-1.254
H	-2.489	-4.854	-3.446
H	-0.175	-3.906	-3.447
H	1.099	-1.438	-6.942
H	0.209	-2.462	-5.784
H	1.920	-2.090	-5.496
H	-3.787	-4.947	-1.308
H	0.830	-3.049	-1.333
H	-2.771	-4.094	0.804
H	0.489	-1.477	-3.186
H	0.474	0.885	-6.797
H	-0.499	-4.908	2.142
H	-5.423	1.835	-3.657
H	-3.623	2.339	-1.995
H	-5.557	-0.434	-4.697
H	-0.169	2.886	-5.465
H	0.181	-4.068	4.378
H	-3.904	-2.201	-4.047
H	-2.304	-1.205	-0.074
H	-1.763	1.710	-0.753
H	0.519	-0.086	2.753
H	-2.135	-1.693	-2.379
H	-3.456	-1.476	1.892
H	0.478	-0.451	5.232
H	1.897	-1.525	5.256
H	0.343	-2.106	5.898
H	-2.191	3.652	-4.020
H	1.109	2.771	-1.392
H	-4.323	-0.610	4.068
H	-1.268	2.199	1.298
H	-2.748	5.667	-2.657
H	0.536	4.753	0.013

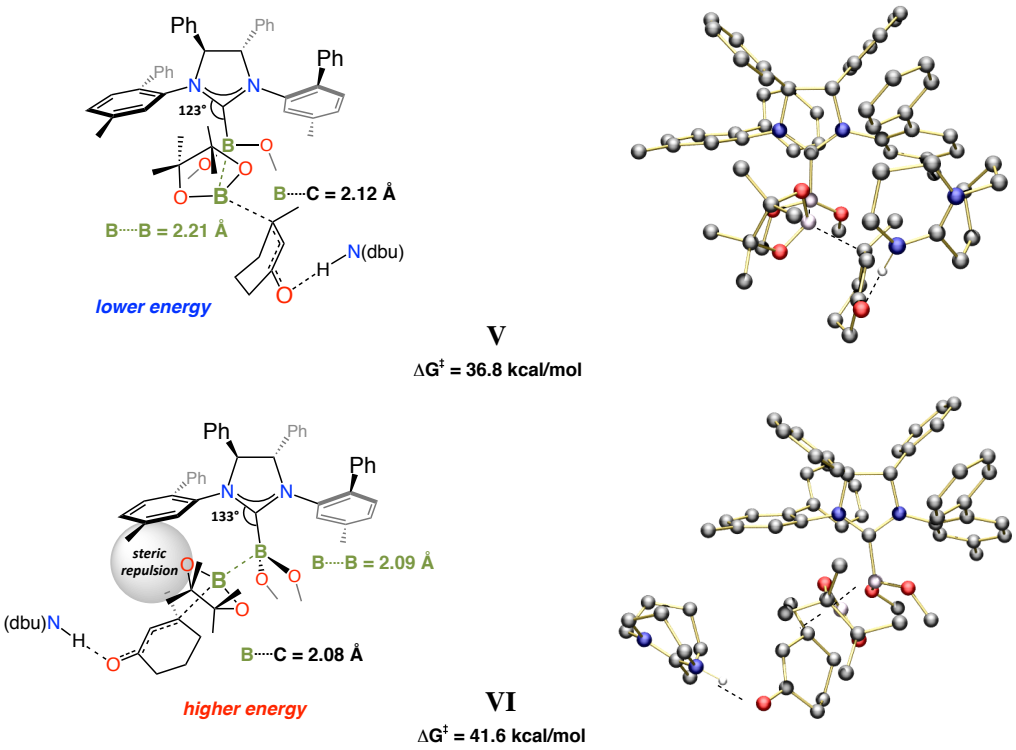
```
H    -3.653     1.666     4.857
H    -1.405     6.210    -0.619
H    -2.130     3.069     3.455
H     7.307    -0.377    -2.491
H     8.036    -0.272    -0.844
H     6.918     0.990    -1.408
H     3.964    -2.014     0.583
H     6.858    -1.000     1.038
H     2.853    -3.067     2.319
H     2.724    -3.915     4.648
H     6.784    -1.446     3.126
H     4.614    -3.499     6.243
H     6.638    -2.253     5.462
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --  -104.6940               16.3073                19.7720
 Red. masses --     7.1023                5.4909                 5.1635
 Zero-point correction=                           0.987198 (Hartree/Particle)
 Thermal correction to Energy=                    1.049456
 Thermal correction to Enthalpy=                  1.050400
 Thermal correction to Gibbs Free Energy=         0.887837
 Sum of electronic and zero-point Energies=          -2929.329938
 Sum of electronic and thermal Energies=             -2929.267680
 Sum of electronic and thermal Enthalpies=           -2929.266736
 Sum of electronic and thermal Free Energies=        -2929.429299

         Item               Value     Threshold  Converged?
 Maximum Force            0.000273     0.000450     YES
 RMS     Force            0.000045     0.000300     YES
```

When we moved to investigate the enantioselective boron conjugate addition to a cyclic enone catalyzed by the same chiral NHC, experimental results obtained from reactions with this and several other chiral NHCs showed poor enantioselectivity when cyclohexenone is used as substrate (for instance, 55:45 er with NHC derived from **7c**). However, the boron conjugate addition to a sterically more hindered β-methyl substituted cyclohexenone resulted in good enantioselectivity (er = 84:16, NHC derived from **7c**). Two transition states (**V** and **VI**) for the addition of B(pin) unit to the enone that result in the two observed enantiomeric products were optimized (Scheme S11). In the favored transition state **V**, the substrate approaches the NHC•diboron complex from the right side. The distance between the two boron centers is 2.21 Å and the forming C····B bond length is 2.12 Å. The activation barrier $\Delta G^{\ddagger}$ = 36.8 kcal/mol. The longer bond lengths and the higher activation energy compared to TS **I** (Scheme S9) may be due to the sterically more demanding substrate (a trisubstituted olefin). The transition state **VI**, which is higher in energy than **V** by 4.8 kcal/mol, leads to the minor product. The breaking B····B bond length is 2.09 Å and the forming C····B bond length is 2.08 Å. Unfavorable steric interactions (highlighted in **VI**), which might be responsible for the variation in the N–C–B bond angle (from 123° to 133°), may explain why the reaction mainly follows the pathway involving transition state **V**.

Scheme S11. The transition state of the C–B bond formation in a chiral NHC catalyzed BCA reaction to a cyclic enone



Ground State of V and VI

```
----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
155

H     -9.870     16.269     -5.607
H    -10.681     24.295     -6.232
H    -11.169     15.183     -5.097
H     -9.337     17.856     -6.975
C    -10.917     16.236     -5.279
H    -12.892     15.083     -7.150
H    -10.466     23.363     -8.812
H    -11.039     22.688     -3.976
H    -11.510     24.339      0.610
C    -11.737     23.989     -6.363
H    -11.997     25.275     -0.826
N    -11.770     16.697     -6.395
H    -11.073     22.118     -0.379
C    -10.168     18.544     -6.755
C    -13.071     16.008     -6.579
H    -10.286     16.859     -3.327
C    -12.350     24.554     -0.068
C    -11.562     23.209     -8.773
C    -11.444     17.798     -7.084
H    -11.931     25.256     -8.127
C    -11.919     22.257     -4.486
C    -11.856     22.540     -5.952
```

C	-11.119	17.090	-4.011
H	-13.189	16.816	-9.271
H	-12.335	24.590	-5.662
C	-12.195	24.235	-7.813
H	-13.435	15.735	-5.579
H	-10.077	19.376	-7.465
H	-9.069	18.777	-4.883
H	-11.970	21.184	-4.267
C	-11.916	21.539	-6.879
C	-12.074	22.127	-0.815
C	-11.784	21.773	-8.311
N	-12.205	18.247	-8.080
C	-10.050	19.075	-5.281
H	-12.885	25.317	-3.212
H	-11.938	23.310	-9.802
C	-13.437	17.568	-8.506
H	-13.149	25.051	0.504
H	-11.981	19.174	-8.495
H	-12.053	16.804	-3.507
C	-12.860	23.293	-0.731
C	-14.085	16.914	-7.282
O	-11.801	20.837	-9.142
H	-12.805	22.764	-4.066
H	-12.046	20.507	-6.553
C	-11.155	18.602	-4.314
H	-14.960	16.321	-7.579
H	-11.948	20.082	-1.488
C	-12.569	20.977	-1.438
C	-13.942	25.454	-3.500
H	-14.019	26.343	-4.155
H	-13.291	24.143	-7.851
H	-10.064	20.172	-5.319
H	-14.090	18.324	-8.955
H	-11.059	19.160	-3.371
H	-14.524	25.672	-2.586
C	-14.148	23.253	-1.282
H	-12.145	18.864	-4.724
H	-14.413	17.698	-6.587
O	-14.368	24.279	-4.165
C	-13.847	20.943	-2.038
H	-14.818	24.105	-1.172
C	-14.625	22.124	-1.959
H	-15.597	26.275	-5.890
H	-14.388	22.417	-9.132
H	-14.392	21.086	-7.243
H	-13.550	18.433	-1.091
H	-16.147	26.224	0.064
C	-14.331	19.691	-2.672
B	-15.819	24.063	-4.356
H	-15.236	23.852	-9.770
C	-14.097	18.451	-2.035
C	-15.373	22.835	-9.373
O	-15.631	23.671	-7.091
C	-16.610	26.143	-5.465
O	-16.603	25.315	-4.320
B	-16.016	23.144	-5.859
C	-15.308	20.572	-7.559
C	-15.060	19.699	-3.883

H	-17.001	27.134	-5.174
C	-17.172	25.863	-0.052
N	-15.981	22.146	-2.406
H	-15.253	20.638	-4.399
H	-15.188	20.239	-8.600
H	-17.024	25.666	-2.215
C	-14.588	17.255	-2.577
C	-16.284	22.887	-8.144
C	-16.547	23.095	-3.184
H	-15.834	22.215	-10.157
H	-15.455	19.691	-6.923
H	-17.255	25.729	-6.264
C	-17.652	25.542	-1.331
C	-16.376	21.040	2.527
H	-17.620	25.962	2.070
C	-16.784	22.247	1.930
H	-14.402	16.311	-2.062
H	-16.210	20.991	3.605
H	-16.937	23.140	2.539
C	-17.999	25.719	1.075
C	-16.180	19.898	1.732
C	-16.995	22.309	0.547
C	-16.518	21.505	-7.434
C	-15.576	18.505	-4.405
O	-16.626	21.896	-6.020
C	-15.341	17.278	-3.763
C	-16.390	19.964	0.345
C	-16.801	21.167	-0.252
H	-15.862	18.959	2.190
H	-17.301	23.248	0.086
C	-16.989	21.242	-1.750
H	-17.356	24.642	-8.811
H	-16.227	19.084	-0.281
C	-17.593	23.618	-8.487
H	-16.181	18.533	-5.312
N	-17.882	22.955	-3.125
H	-16.876	20.240	-2.182
H	-15.750	16.354	-4.175
C	-18.978	25.082	-1.499
C	-19.317	25.259	0.915
C	-17.799	20.773	-7.836
H	-18.245	23.673	-7.605
C	-18.335	21.871	-2.209
H	-18.133	23.106	-9.298
C	-18.894	23.799	-3.686
H	-17.774	20.532	-8.911
C	-19.504	24.768	-2.857
H	-17.882	20.455	-4.495
C	-19.805	24.948	-0.364
H	-17.879	19.832	-7.273
H	-18.854	22.345	-1.362
C	-19.388	23.513	-4.963
H	-18.898	22.733	-5.543
H	-19.965	25.139	1.786
H	-18.692	21.379	-7.632
C	-18.859	20.233	-4.068
C	-20.635	25.435	-3.366
C	-19.268	20.894	-2.894

```
C   -20.501    24.204    -5.475
H   -21.124    26.188    -2.744
H   -20.470    24.515    -7.622
C   -21.124    25.161    -4.651
H   -20.827    24.586    -0.489
C   -21.012    23.916    -6.871
C   -19.722    19.330    -4.702
H   -19.402    18.825    -5.615
C   -20.546    20.650    -2.367
H   -20.870    22.856    -7.135
H   -22.002    25.696    -5.020
H   -20.862    21.173    -1.461
H   -22.082    24.159    -6.961
C   -20.999    19.080    -4.168
C   -21.411    19.741    -3.000
H   -21.671    18.376    -4.663
H   -22.403    19.555    -2.583
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --    13.8700                20.4338                24.1635
 Red. masses --     5.1341                 5.5709                 4.6885
 Zero-point correction=                           1.299632 (Hartree/Particle)
 Thermal correction to Energy=                    1.374340
 Thermal correction to Enthalpy=                  1.375284
 Thermal correction to Gibbs Free Energy=         1.186880
 Sum of electronic and zero-point Energies=          -3165.919920
 Sum of electronic and thermal Energies=             -3165.845212
 Sum of electronic and thermal Enthalpies=           -3165.844268
 Sum of electronic and thermal Free Energies=        -3166.032672

          Item               Value     Threshold  Converged?
 Maximum Force            0.000038     0.000450     YES
 RMS     Force            0.000002     0.000300     YES
```

Transition State of V

```
 Cartesian coordinates (Angstroms):
---------------------------------------
155

B     0.296    -0.717    -0.421
B     0.158    -0.286     1.743
H     2.124    -3.348    -4.301
H     3.935    -3.968    -3.322
H     3.886    -4.179    -1.058
N     1.727    -4.322    -4.381
H    -0.032    -3.560    -5.188
C     3.660    -4.994    -3.048
C     3.729    -5.174    -1.492
H     4.611    -5.785    -1.247
C     0.459    -4.534    -5.089
C     2.317    -5.286    -3.680
H     4.388    -5.659    -3.539
H     0.669    -4.925    -6.098
C     2.478    -5.795    -0.842
```

H	1.592	-5.207	-1.124
H	2.561	-5.708	0.250
H	-0.675	-5.073	-3.332
C	-0.397	-5.526	-4.293
N	1.769	-6.504	-3.554
H	-1.315	-5.772	-4.842
C	2.239	-7.272	-1.218
C	0.399	-6.808	-4.034
H	3.500	-7.551	-2.982
C	2.432	-7.535	-2.727
H	2.947	-7.924	-0.681
H	0.482	-7.420	-4.945
H	1.223	-7.561	-0.911
H	-0.091	-7.408	-3.255
H	2.011	-8.505	-3.023
C	0.373	2.141	1.232
O	-0.397	1.008	1.629
N	-0.955	-2.623	2.586
C	-2.286	-3.267	2.864
C	-1.064	-1.321	2.236
C	2.009	0.438	3.306
O	1.376	-0.486	2.434
C	-3.253	-2.063	2.780
N	-2.366	-0.962	2.295
H	-3.603	-1.776	3.783
H	-2.488	-3.974	2.051
C	-2.505	-5.390	4.217
C	-2.088	-3.979	6.609
C	-2.501	-6.075	5.443
C	-2.308	-4.000	4.186
C	-2.098	-3.297	5.386
C	-2.291	-5.371	6.640
H	-1.933	-2.221	5.362
H	-1.922	-3.423	7.534
H	-2.283	-5.903	7.593
H	-2.656	-7.155	5.462
H	-2.648	-5.932	3.280
C	-4.244	-2.685	0.536
C	-6.843	-2.200	1.482
C	-4.440	-2.276	1.868
C	-5.342	-2.853	-0.318
C	-6.645	-2.612	0.155
C	-5.741	-2.030	2.336
H	-3.231	-2.849	0.166
H	-5.183	-3.165	-1.351
H	-7.500	-2.743	-0.511
H	-7.852	-2.009	1.853
H	-5.886	-1.700	3.367
C	-4.451	1.949	1.233
C	-4.557	2.643	2.452
C	-3.673	0.780	1.210
C	-3.908	2.173	3.602
C	-2.979	0.339	2.339
C	-3.108	1.013	3.576
C	1.599	-5.327	2.925
C	2.404	-4.792	3.936
C	0.488	-4.631	2.403
H	3.261	-5.360	4.303

C	2.112	-3.534	4.495
C	0.221	-3.352	2.953
C	0.994	-2.843	4.005
H	0.701	-1.894	4.448
H	-4.016	2.709	4.546
C	-5.147	2.427	-0.023
C	2.249	-1.533	-0.417
H	-1.061	-2.930	-3.069
H	0.348	-1.874	-3.352
H	-3.103	-2.145	-2.112
C	-0.740	-1.898	-3.269
H	-1.169	-1.583	-4.233
O	-0.769	-1.522	-0.863
C	-1.270	-0.996	-2.142
C	-2.797	-1.091	-2.167
H	-3.179	-0.671	-3.110
H	-3.263	-0.552	-1.339
H	0.744	0.216	-3.801
H	-0.836	0.887	-4.305
C	-0.695	0.482	-2.170
C	-0.071	0.891	-3.512
H	-2.563	1.608	-2.402
H	0.332	1.912	-3.425
C	-1.702	1.552	-1.718
H	-2.056	1.340	-0.703
H	-1.200	2.531	-1.712
O	0.363	0.455	-1.172
H	-3.624	0.174	0.312
H	-5.166	3.548	2.506
C	2.964	-2.935	5.593
H	1.842	-6.305	2.506
H	-0.099	2.595	0.350
H	1.407	1.869	0.972
H	0.386	2.871	2.059
H	2.148	-0.043	4.290
H	1.429	1.362	3.445
H	3.002	0.706	2.906
H	-0.857	-0.705	8.180
C	-1.310	-0.363	7.248
H	0.584	-0.125	6.220
H	-3.341	-0.484	7.998
C	-0.501	-0.047	6.144
C	-2.706	-0.236	7.147
C	-3.289	0.206	5.949
C	-1.085	0.386	4.944
H	-4.373	0.301	5.867
H	-0.471	0.663	4.093
C	-2.484	0.518	4.833
H	-2.409	-6.965	-1.529
C	-1.821	-6.493	-0.740
H	-1.946	-4.501	-1.593
H	-1.533	-8.327	0.383
C	-1.559	-5.113	-0.777
C	-1.329	-7.256	0.333
C	-0.589	-6.643	1.354
C	-0.805	-4.503	0.233
H	-0.236	-7.237	2.199
H	-0.605	-3.437	0.167

```
C    -0.314    -5.257     1.320
H     2.346    -2.373     6.312
H     3.703    -2.230     5.176
H     3.516    -3.714     6.139
H    -4.454     3.006    -0.658
H    -6.003     3.075     0.217
H    -5.505     1.576    -0.624
C     3.699    -0.107    -2.602
O     2.796    -1.797    -4.057
C     2.833    -1.340    -2.862
C     2.217    -1.992    -1.764
C     3.196    -0.369    -0.117
H     1.700    -2.931    -1.966
C     3.385     0.620    -1.281
H     4.203     1.318    -1.039
H     2.467     1.207    -1.401
H     3.610     0.572    -3.466
H     4.747    -0.464    -2.596
C     2.302    -2.646     0.613
H     2.862     0.153     0.786
H     4.173    -0.830     0.130
H     2.091    -2.285     1.618
H     3.326    -3.061     0.613
H     1.617    -3.458     0.351
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --  -436.7168               13.9287                19.4402
 Red. masses --     9.1130                4.7660                 3.7134
 Zero-point correction=                           1.300794 (Hartree/Particle)
 Thermal correction to Energy=                    1.374062
 Thermal correction to Enthalpy=                  1.375006
 Thermal correction to Gibbs Free Energy=         1.192412
 Sum of electronic and zero-point Energies=          -3165.865602
 Sum of electronic and thermal Energies=             -3165.792334
 Sum of electronic and thermal Enthalpies=           -3165.791390
 Sum of electronic and thermal Free Energies=        -3165.973984

          Item               Value     Threshold  Converged?
 Maximum Force            0.000060     0.000450     YES
 RMS     Force            0.000009     0.000300     YES
```

Transition State of VI

```
 Cartesian coordinates (Angstroms):
---------------------------------------
155

H     4.586    -9.825    -2.482
C     4.297    -9.236    -1.597
H     5.216    -8.977    -1.055
H     4.354    -7.302    -2.571
H     2.698    -8.406    -3.967
C     3.619    -7.927    -2.045
C     2.382    -8.128    -2.948
C     3.437   -10.145    -0.652
```

H	1.861	-10.231	-2.668
H	1.827	-7.179	-3.027
C	1.439	-9.242	-2.444
H	3.327	-7.358	-1.149
H	0.460	-9.188	-2.935
C	2.165	-9.513	-0.127
N	1.202	-9.150	-0.988
N	2.028	-9.358	1.184
C	-0.045	-8.496	-0.526
H	-0.330	-7.759	-1.289
H	0.795	-6.931	0.709
C	0.826	-8.790	1.808
H	-0.837	-9.259	-0.473
C	0.157	-7.815	0.833
H	1.142	-8.284	2.729
H	-0.816	-7.491	1.225
H	0.138	-9.607	2.077
H	2.868	-9.571	1.790
H	4.034	-10.457	0.213
H	3.137	-11.063	-1.180
H	3.402	-4.800	-2.880
H	5.715	-4.023	-3.334
H	1.926	-5.048	0.597
C	4.029	-4.458	-2.054
C	5.333	-4.020	-2.312
H	6.634	-1.569	-3.029
H	8.817	-0.576	-3.704
C	2.067	-4.793	-0.464
C	7.562	-1.941	-2.591
C	3.509	-4.435	-0.746
C	8.792	-1.383	-2.969
H	1.402	-3.942	-0.691
H	1.734	-5.641	-1.081
C	6.174	-3.555	-1.280
C	7.502	-2.976	-1.631
H	6.775	-7.424	-0.876
H	1.882	-0.010	-0.164
C	9.986	-1.859	-2.401
H	5.534	-6.282	-0.303
H	4.306	-0.424	-0.609
H	10.944	-1.428	-2.696
C	6.527	-6.691	-0.085
C	4.345	-3.998	0.292
C	8.705	-3.441	-1.059
C	5.662	-3.595	0.039
C	2.525	-0.389	0.633
C	9.935	-2.889	-1.447
H	4.423	-7.796	1.117
C	3.888	-0.614	0.382
H	7.271	-5.894	-0.130
C	5.365	-8.165	1.527
H	7.478	-10.146	0.890
H	8.684	-4.237	-0.316
O	4.241	-9.943	2.647
C	6.553	-7.426	1.246
H	3.978	-3.952	1.311
H	6.435	-1.053	0.099
H	10.858	-3.266	-1.002

C	1.992	-0.657	1.904
C	5.318	-9.317	2.357
H	8.605	-7.936	0.754
N	6.379	-2.917	1.080
C	4.724	-1.101	1.400
C	7.747	-9.630	1.828
H	8.714	-0.966	-0.119
C	6.171	-1.428	1.097
H	2.541	-5.940	2.821
C	7.899	-8.119	1.576
H	10.363	0.732	-0.859
H	3.445	-7.463	3.066
C	6.640	-9.869	2.872
C	8.881	-0.076	0.486
C	3.119	-6.535	3.546
H	6.507	-10.936	3.109
C	9.815	0.883	0.073
O	8.843	-5.333	1.433
C	2.826	-1.147	2.925
H	8.707	-10.046	2.174
H	10.745	-5.588	0.735
O	5.103	-5.331	2.859
B	6.271	-6.096	2.816
C	7.332	-3.323	1.931
C	4.186	-1.369	2.672
B	7.901	-4.864	2.391
C	10.190	-5.716	1.678
H	2.461	-6.791	4.391
H	8.340	-7.678	2.475
C	7.189	-0.950	2.163
C	8.169	0.101	1.686
C	4.316	-5.700	4.032
C	10.041	2.029	0.856
H	10.126	-2.957	1.513
H	3.131	-3.892	3.957
H	6.896	-9.334	3.802
H	2.418	-1.359	3.915
H	10.769	2.776	0.534
N	7.860	-2.238	2.544
H	10.254	-6.774	1.982
H	4.426	-8.495	4.739
O	6.419	-6.847	3.997
H	4.827	-1.766	3.459
C	3.799	-4.405	4.664
H	13.667	-2.412	2.660
H	6.670	-0.578	3.055
H	10.659	-5.092	2.451
C	8.398	1.245	2.468
C	10.255	-2.571	2.523
C	9.330	2.209	2.053
C	5.351	-6.513	4.926
C	4.789	-7.814	5.517
O	8.227	-4.683	3.765
C	9.113	-2.181	3.232
H	12.638	-2.739	1.233
C	12.755	-2.921	2.312
H	4.631	-3.732	4.903
H	3.238	-4.618	5.587

```
H     3.961    -7.588     6.209
C    11.539    -2.449     3.079
H     9.173    -6.532     4.080
H     7.851     1.373     3.404
H     9.502     3.097     2.665
C     9.072    -5.534     4.528
H     5.583    -8.322     6.086
H     6.823    -2.863     4.885
C     5.968    -5.678     6.062
H    12.906    -4.006     2.446
H    10.069    -5.070     4.615
H     6.471    -4.789     5.666
C     9.212    -1.596     4.515
C     6.855    -1.892     5.377
C     8.032    -1.119     5.279
H     4.850    -2.025     6.181
C     5.752    -1.416     6.101
C    11.648    -1.876     4.361
H     5.200    -5.369     6.787
H     8.636    -5.644     5.530
H     6.713    -6.294     6.588
C    10.508    -1.453     5.055
C     8.077     0.137     5.925
C     5.803    -0.162     6.732
H    12.634    -1.756     4.815
C     6.971     0.613     6.644
H     8.978     0.746     5.839
H     4.939     0.207     7.289
H    10.612    -1.014     6.049
H     7.019     1.591     7.127
H     0.931    -0.486     2.099
```

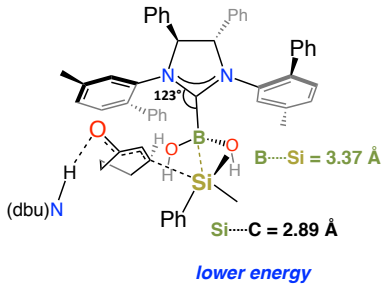
```
                     1                      2                      3
                     A                      A                      A
 Frequencies --  -428.1144               18.9897                20.5813
 Red. masses --     9.7758                4.8919                 5.0981
 Zero-point correction=                           1.301737 (Hartree/Particle)
 Thermal correction to Energy=                    1.374277
 Thermal correction to Enthalpy=                  1.375221
 Thermal correction to Gibbs Free Energy=         1.195115
 Sum of electronic and zero-point Energies=          -3165.859718
 Sum of electronic and thermal Energies=             -3165.787178
 Sum of electronic and thermal Enthalpies=           -3165.786233
 Sum of electronic and thermal Free Energies=        -3165.966340

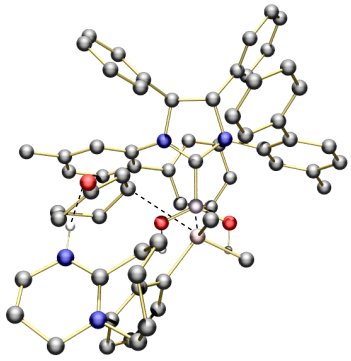
         Item               Value     Threshold  Converged?
 Maximum Force            0.000021     0.000450     YES
 RMS     Force            0.000002     0.000300     YES
```

Finally, computations were carried out on the NHC catalyzed enantioselective silyl conjugate addition to a cyclic enone. The geometry optimized transition state geometries (**VII** (favored) and **VIII** (unfavored)) are depicted in Scheme S12. In **VII** the cyclohexenone molecule approaches the NHC•borosilane complex from beneath the *left* N-aryl group of the NHC. This is in contrast to the substrate approaching from beneath the *right* N-aryl group of the NHC in **V**

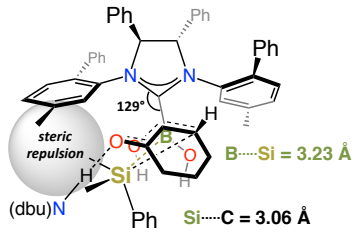
(Scheme S11). The reasons for this difference have been discussed in the manuscript. The activation energy of forming transition state **VII** is 19.0 kcal/mol. However, forming TS **VIII** requires a higher activation barrier ($\Delta G^{\ddagger}$ = 20.6 kcal/mol), which may be due to the steric repulsion between the $SiMe_2Ph$ unit and the N-aryl motif of the NHC. The larger N–C–N angle (129° vs 123° in **VII**) may also be the result of this steric interaction.

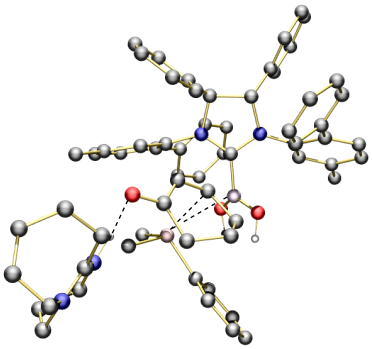
Scheme S12. The transition state of the C–Si bond formation in a chiral NHC catalyzed SCA reaction to a cyclic enone





VII
$\Delta G^{\ddagger}$ = 19.0 kcal/mol





VIII
$\Delta G^{\ddagger}$ = 20.6 kcal/mol

Ground State of VII and VIII

```
----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
145

H     -5.151     -0.058      1.771
O     -3.637      0.697      2.665
H     -4.726      3.018      2.291
C     -3.160      1.592      1.931
C     -4.012      2.778      1.489
H     -4.599      2.430      0.619
C     -1.818      1.481      1.370
C     -3.164      3.996      1.070
H     -2.646      4.393      1.959
H     -3.814      4.793      0.680
C     -1.371      2.348      0.422
C     -2.113      3.587      0.020
H     -2.593      3.393     -0.956
H     -1.383      4.395     -0.155
H     -1.232      0.610      1.656
H     -0.440      2.150     -0.114
```

C	-1.244	-1.922	-2.127
H	-1.345	-1.987	-1.036
H	-2.240	-2.088	-2.576
H	-0.589	-2.750	-2.434
Si	-0.553	-0.246	-2.764
C	-2.090	0.920	-2.733
C	-3.201	0.673	-1.892
H	-3.177	-0.182	-1.217
C	-4.339	1.493	-1.906
H	-5.187	1.258	-1.260
C	-4.391	2.615	-2.752
H	-5.274	3.257	-2.762
C	-3.295	2.901	-3.582
H	-3.322	3.770	-4.244
C	-2.169	2.058	-3.574
C	-0.212	-0.544	-4.630
H	-1.056	-1.054	-5.125
H	-0.023	0.404	-5.161
H	-1.343	2.280	-4.256
H	0.691	-1.165	-4.748
H	-0.076	2.478	-2.357
O	0.753	2.277	-1.897
B	1.108	0.847	-2.024
C	1.772	0.400	-0.519
H	3.862	5.391	-1.053
C	3.193	4.817	-0.410
H	2.356	6.579	0.521
C	2.093	-3.453	-2.774
C	2.344	5.488	0.479
C	3.233	3.409	-0.490
O	2.187	0.616	-3.014
H	2.678	-1.374	-2.547
C	2.205	-2.238	-2.079
H	1.418	-5.507	-2.626
C	1.495	-4.544	-2.117
C	2.352	2.688	0.353
C	1.487	4.767	1.327
N	2.316	1.248	0.383
C	1.510	3.365	1.246
C	1.683	-2.087	-0.787
H	2.846	1.323	-2.896
N	1.941	-0.868	-0.075
H	0.846	2.786	1.883
C	0.987	-4.399	-0.822
C	1.047	-3.171	-0.131
H	0.496	-5.243	-0.335
C	2.983	0.542	1.537
C	2.713	-0.952	1.206
H	2.072	-1.399	1.973
H	4.058	0.756	1.474
C	0.551	5.453	2.300
C	2.606	-3.568	-4.193
H	5.722	-4.206	2.735
H	3.620	-2.865	2.909
C	5.473	-3.480	1.959
C	4.293	-2.725	2.060
H	7.239	-3.898	0.773
C	6.326	-3.307	0.856

C	3.968	-1.787	1.067
C	5.994	-2.377	-0.146
C	4.821	-1.620	-0.040
H	6.646	-2.249	-1.012
H	4.551	-0.910	-0.821
H	3.391	3.175	5.387
H	4.245	2.225	3.243
C	2.781	2.467	4.825
C	3.266	1.927	3.624
H	1.128	2.525	6.226
C	1.509	2.102	5.295
C	2.489	1.016	2.888
C	0.731	1.185	4.567
C	1.222	0.646	3.371
H	-0.258	0.893	4.925
H	0.612	-0.053	2.805
H	0.616	4.991	3.298
H	-0.498	5.366	1.968
H	0.788	6.524	2.393
H	2.841	-4.612	-4.450
H	3.508	-2.954	-4.339
H	1.848	-3.209	-4.910
H	4.976	3.085	-4.802
H	3.460	4.067	-3.085
C	4.152	3.269	-2.811
C	4.997	2.705	-3.779
C	4.142	2.782	-1.483
C	5.852	1.645	-3.436
H	6.504	1.199	-4.189
C	5.020	1.730	-1.151
C	5.863	1.164	-2.117
H	5.067	1.367	-0.127
H	6.535	0.352	-1.833
H	0.218	-4.803	4.169
H	1.329	-4.894	1.941
C	0.640	-4.081	2.176
C	0.018	-4.024	3.431
C	0.409	-3.079	1.207
C	-0.853	-2.966	3.741
H	-1.336	-2.920	4.719
C	-0.467	-2.021	1.533
C	-1.095	-1.966	2.787
H	-0.649	-1.240	0.796
H	-1.771	-1.140	3.018
H	-5.051	-5.278	1.453
H	-6.016	-3.805	1.350
H	-3.869	-3.377	2.468
H	-8.127	-1.802	0.824
C	-5.109	-4.296	0.960
H	-7.476	0.403	1.698
C	-3.880	-3.461	1.372
C	-7.907	-1.015	0.087
C	-7.050	0.074	0.742
N	-5.712	-0.473	1.017
H	-8.856	-0.587	-0.260
H	-6.255	-4.996	-0.736
C	-5.281	-4.515	-0.558
H	-3.398	-1.319	1.500

```
C    -3.825    -2.015     0.773
H    -2.953    -3.974     1.080
C    -5.168    -1.485     0.338
H    -4.504    -5.199    -0.936
C    -7.156    -1.625    -1.103
H    -7.679    -2.515    -1.475
N    -5.794    -2.050    -0.699
H    -6.959     0.952     0.083
C    -5.187    -3.212    -1.391
H    -3.163    -2.008    -0.101
H    -7.065    -0.905    -1.931
H    -4.143    -2.971    -1.623
H    -5.711    -3.316    -2.349
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --    14.8637                21.8550                24.4984
 Red. masses --     5.4974                 4.9285                 4.2487
 Zero-point correction=                           1.202599 (Hartree/Particle)
 Thermal correction to Energy=                    1.273168
 Thermal correction to Enthalpy=                  1.274112
 Thermal correction to Gibbs Free Energy=         1.094801
 Sum of electronic and zero-point Energies=          -3237.884351
 Sum of electronic and thermal Energies=             -3237.813782
 Sum of electronic and thermal Enthalpies=           -3237.812838
 Sum of electronic and thermal Free Energies=        -3237.992150

         Item               Value     Threshold  Converged?
 Maximum Force            0.000000     0.000450     YES
 RMS     Force            0.000000     0.000300     YES
```

Transition State of VII

```
 Cartesian coordinates (Angstroms):
---------------------------------------
145

H    -5.626     0.232     1.755
O    -4.060     0.103     2.382
H    -4.421     2.605     1.868
C    -3.271     0.808     1.669
C    -3.757     2.151     1.114
H    -4.367     1.956     0.216
C    -1.929     0.409     1.392
C    -2.592     3.089     0.747
H    -2.081     3.408     1.671
H    -2.973     3.995     0.248
C    -1.117     1.070     0.475
C    -1.581     2.363    -0.166
H    -2.068     2.160    -1.133
H    -0.714     3.000    -0.378
H    -1.574    -0.493     1.893
H    -0.058     0.847     0.450
C    -2.192    -2.290    -0.615
H    -2.584    -1.924     0.347
H    -3.043    -2.697    -1.192
```

H	-1.499	-3.119	-0.405
Si	-1.329	-0.894	-1.640
C	-2.790	0.104	-2.357
C	-4.048	0.122	-1.704
H	-4.192	-0.493	-0.816
C	-5.109	0.921	-2.158
H	-6.067	0.901	-1.634
C	-4.943	1.744	-3.285
H	-5.765	2.368	-3.640
C	-3.705	1.750	-3.953
H	-3.564	2.381	-4.834
C	-2.653	0.944	-3.491
C	-0.629	-1.840	-3.195
H	-1.339	-2.634	-3.491
H	-0.513	-1.172	-4.067
H	-1.703	0.962	-4.037
H	0.349	-2.304	-2.997
H	0.257	1.936	-2.856
O	0.852	1.906	-2.088
B	1.595	0.745	-2.021
C	2.375	0.486	-0.634
H	3.294	5.511	-1.464
C	2.731	4.923	-0.738
H	1.682	6.636	0.059
C	4.739	-2.466	-2.990
C	1.827	5.556	0.125
C	2.966	3.537	-0.669
O	1.879	-0.099	-3.066
H	4.472	-0.410	-2.370
C	4.218	-1.451	-2.176
H	4.840	-4.613	-3.267
C	4.432	-3.801	-2.661
C	2.212	2.795	0.272
C	1.108	4.817	1.084
N	2.379	1.376	0.390
C	1.309	3.428	1.137
C	3.377	-1.747	-1.093
H	1.300	0.040	-3.834
N	2.979	-0.661	-0.252
H	0.734	2.823	1.834
C	3.616	-4.098	-1.565
C	3.058	-3.085	-0.756
H	3.381	-5.137	-1.329
C	3.119	0.843	1.580
C	3.316	-0.650	1.208
H	2.564	-1.253	1.728
H	4.089	1.362	1.617
C	0.106	5.479	2.006
C	5.605	-2.123	-4.184
H	6.196	-3.338	3.731
H	3.939	-2.454	3.121
C	6.093	-2.623	2.913
C	4.825	-2.123	2.578
H	8.209	-2.605	2.443
C	7.224	-2.211	2.189
C	4.685	-1.201	1.527
C	7.084	-1.295	1.132
C	5.819	-0.789	0.805

H	7.958	-0.979	0.560
H	5.703	-0.091	-0.022
H	2.534	2.966	5.717
H	3.829	2.468	3.639
C	2.139	2.260	4.985
C	2.872	1.975	3.822
H	0.319	1.872	6.097
C	0.895	1.644	5.199
C	2.370	1.069	2.874
C	0.391	0.733	4.253
C	1.130	0.443	3.099
H	-0.578	0.257	4.407
H	0.727	-0.251	2.361
H	0.015	4.926	2.953
H	-0.894	5.506	1.540
H	0.397	6.517	2.229
H	6.331	-2.924	-4.394
H	6.152	-1.183	-4.019
H	4.986	-1.990	-5.088
H	4.603	2.407	-4.903
H	2.893	3.396	-3.374
C	3.800	2.947	-2.968
C	4.759	2.383	-3.823
C	3.976	2.913	-1.570
C	5.916	1.790	-3.292
H	6.666	1.358	-3.956
C	5.143	2.318	-1.046
C	6.107	1.763	-1.900
H	5.306	2.315	0.033
H	7.010	1.316	-1.480
H	2.188	-5.592	3.084
H	3.568	-4.980	1.103
C	2.620	-4.473	1.285
C	1.846	-4.807	2.406
C	2.206	-3.450	0.403
C	0.647	-4.123	2.665
H	0.047	-4.378	3.541
C	0.992	-2.781	0.664
C	0.221	-3.112	1.787
H	0.659	-1.988	-0.009
H	-0.720	-2.591	1.965
H	-8.448	-4.233	1.694
H	-8.459	-2.470	1.747
H	-6.247	-3.379	2.315
H	-9.194	0.476	1.578
C	-8.075	-3.334	1.180
H	-7.259	1.943	2.037
C	-6.534	-3.326	1.254
C	-8.759	1.026	0.730
C	-7.319	1.427	1.070
N	-6.494	0.217	1.160
H	-9.370	1.919	0.544
H	-9.754	-3.126	-0.171
C	-8.668	-3.295	-0.245
H	-4.976	-1.770	1.243
C	-5.827	-2.076	0.623
H	-6.131	-4.225	0.763
C	-6.735	-0.880	0.450

```
H    -8.522    -4.263    -0.750
C    -8.764     0.137    -0.520
H    -9.748    -0.333    -0.656
N    -7.768    -0.954    -0.404
H    -6.904     2.095     0.297
C    -8.034    -2.207    -1.143
H    -5.420    -2.332    -0.365
H    -8.535     0.722    -1.425
H    -7.091    -2.559    -1.578
H    -8.696    -1.949    -1.979
```

```
                     1                     2                     3
                     A                     A                     A
 Frequencies --   -87.1398              12.7987              16.3093
 Red. masses --     6.0834               5.2748               5.2315
 Zero-point correction=                           1.200175 (Hartree/Particle)
 Thermal correction to Energy=                    1.270579
 Thermal correction to Enthalpy=                  1.271524
 Thermal correction to Gibbs Free Energy=         1.090060
 Sum of electronic and zero-point Energies=          -3237.851811
 Sum of electronic and thermal Energies=             -3237.781407
 Sum of electronic and thermal Enthalpies=           -3237.780463
 Sum of electronic and thermal Free Energies=        -3237.961926

         Item               Value     Threshold  Converged?
 Maximum Force            0.000003     0.000450     YES
 RMS     Force            0.000000     0.000300     YES
```

Transition State of VIII

```
---------------------------------------
 Cartesian coordinates (Angstroms):
---------------------------------------
145

H     9.613     3.082     6.257
H     9.203     1.864     5.050
H     9.265    -0.495     3.174
C     9.518     2.914     5.174
H    11.564     2.284     4.848
H     7.489     3.635     5.206
C    10.902     3.101     4.518
C     9.402    -0.269     2.106
H     9.766    -1.175     1.603
C     8.404     3.832     4.628
H     7.254    -0.530     1.725
H    11.359     4.047     4.851
H    11.337     0.636     2.539
C     8.064     0.177     1.504
C    10.438     0.852     1.945
N     7.690     1.474     2.080
H     8.675     4.886     4.797
C     8.576     2.365     2.505
N     9.897     2.149     2.419
C     8.062     3.654     3.107
C    10.849     3.136     2.973
H     6.974     3.681     2.960
H     8.142     0.273     0.408
```

H	11.831	2.912	2.537
H	10.739	0.963	0.892
H	10.560	4.134	2.618
H	8.486	4.485	2.523
H	4.315	-0.658	-6.281
H	2.753	-2.479	-5.555
C	4.113	-0.821	-5.220
C	3.226	-1.833	-4.812
C	4.755	-0.040	-4.244
H	5.472	0.728	-4.544
C	2.968	-2.034	-3.445
H	2.350	-2.888	-3.153
H	4.587	3.289	-1.815
H	5.523	1.501	-0.326
C	4.481	-0.244	-2.882
C	3.562	-1.230	-2.430
H	3.099	1.394	-1.871
H	1.256	0.035	-3.034
C	4.089	3.056	-0.860
C	5.085	2.412	0.123
H	5.920	3.093	0.347
H	0.498	-2.205	-2.843
C	2.862	2.153	-1.114
H	5.006	0.371	-2.146
O	0.549	0.338	-2.433
H	2.062	2.760	-1.564
H	3.748	4.012	-0.428
H	1.548	-3.485	-0.873
O	-0.053	-2.021	-2.061
B	0.039	-0.705	-1.685
C	4.402	2.010	1.430
H	6.670	1.698	2.230
Si	3.004	-1.390	-0.600
C	2.542	-3.268	-0.457
C	2.348	1.500	0.153
H	3.287	-3.894	-0.983
O	5.055	2.001	2.524
C	3.034	1.606	1.355
H	5.411	-0.686	-0.089
H	1.306	1.196	0.170
H	2.525	-3.570	0.600
C	4.613	-1.206	0.468
H	4.999	-2.201	0.754
H	2.576	1.273	2.287
H	4.432	-0.629	1.389
C	-0.878	-0.231	-0.439
H	-0.298	-5.101	1.807
C	0.059	-4.077	1.926
H	1.576	-4.627	3.361
C	-3.505	0.567	-3.875
C	1.117	-3.808	2.802
C	-0.588	-3.056	1.197
H	-2.758	-0.839	-2.404
C	-2.844	0.211	-2.690
H	-4.207	2.243	-5.055
C	-3.671	1.939	-4.154
C	-0.112	-1.735	1.399
C	1.612	-2.501	2.956

N	-0.796	-0.604	0.845
C	0.979	-1.474	2.239
C	-2.323	1.194	-1.833
N	-1.769	0.766	-0.586
H	1.325	-0.450	2.341
C	-3.153	2.916	-3.296
C	-2.445	2.570	-2.127
H	-3.265	3.974	-3.542
C	-1.721	0.202	1.720
C	-2.291	1.258	0.727
H	-1.832	2.235	0.918
H	-2.517	-0.472	2.065
C	2.805	-2.189	3.832
C	-4.039	-0.497	-4.810
H	-6.144	3.576	2.004
H	-3.667	3.307	1.813
C	-5.728	2.697	1.509
C	-4.336	2.545	1.408
H	-7.664	1.844	1.034
C	-6.581	1.724	0.964
C	-3.792	1.415	0.776
C	-6.039	0.597	0.320
C	-4.650	0.441	0.231
H	-6.698	-0.156	-0.116
H	-4.228	-0.421	-0.283
H	-0.663	0.153	6.277
H	-1.906	-0.663	4.273
C	-0.505	0.629	5.309
C	-1.210	0.173	4.184
H	0.957	2.046	6.054
C	0.403	1.693	5.183
C	-1.015	0.777	2.929
C	0.598	2.301	3.931
C	-0.107	1.846	2.809
H	1.309	3.122	3.822
H	0.075	2.310	1.840
H	3.001	-3.005	4.545
H	2.648	-1.256	4.396
H	3.709	-2.051	3.214
H	-3.377	-0.616	-5.685
H	-5.037	-0.228	-5.190
H	-4.105	-1.473	-4.304
H	-2.200	-5.648	-2.317
H	-0.467	-4.976	-0.662
C	-1.434	-4.473	-0.674
C	-2.407	-4.839	-1.613
C	-1.666	-3.420	0.239
C	-3.637	-4.163	-1.657
H	-4.396	-4.445	-2.390
C	-2.913	-2.765	0.199
C	-3.890	-3.130	-0.740
H	-3.145	-1.991	0.927
H	-4.854	-2.618	-0.742
H	-2.517	6.517	0.398
H	-3.593	4.841	-1.105
C	-2.548	4.725	-0.813
C	-1.942	5.660	0.042
C	-1.823	3.605	-1.266

```
C    -0.609     5.488     0.452
H    -0.147     6.212     1.126
C    -0.478     3.452    -0.864
C     0.126     4.381    -0.008
H     0.072     2.584    -1.222
H     1.163     4.235     0.300
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --   -81.1664                8.0797                11.4952
 Red. masses --     5.8588                4.5796                 5.3125
 Zero-point correction=                          1.199457 (Hartree/Particle)
 Thermal correction to Energy=                   1.270430
 Thermal correction to Enthalpy=                 1.271374
 Thermal correction to Gibbs Free Energy=        1.085323
 Sum of electronic and zero-point Energies=         -3237.845123
 Sum of electronic and thermal Energies=            -3237.774149
 Sum of electronic and thermal Enthalpies=          -3237.773205
 Sum of electronic and thermal Free Energies=       -3237.959257

         Item               Value     Threshold  Converged?
 Maximum Force            0.000003     0.000450     YES
 RMS     Force            0.000001     0.000300     YES
```

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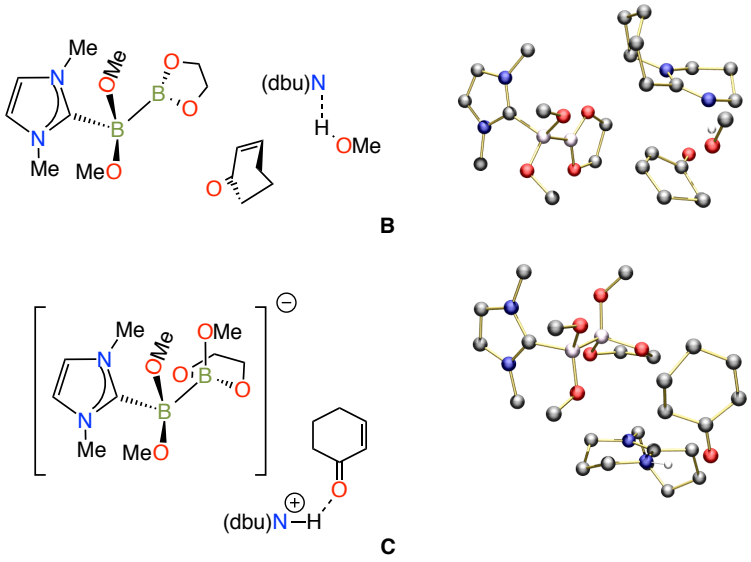
■ Computational Analysis of a Doubly Coordinated Diboron Complex

Density Functional Theory (DFT) calculations were carried out to study the probability of a methoxide coordination to the NHC•diboron complex. Two ground states (**B** and **C**, Scheme S13) were optimized using the B97-D functional and 6-31G* basis set, with tetrahydrofuran solvation modeled using the PCM model. Ethylene glycol was employed instead of pinacol to simplify the calculations. Ground state **C**, which includes the methoxide coordination to the NHC•diboron complex, is 20.2 kcal/mol higher in energy than ground state **B** (involving a mono-coordinated diboron complex). In addition, we cannot find any low-energy transition state about the reaction between the bis-coordinated diboron and enones. Thus, we consider bis-coordinated diboron **C** not an active species in the NHC-catalyzed boryl conjugate additions.

Scheme S13. Ground states of mono-coordinated diboron (**B**) and bis-coordinated diboron (**C**)



B

C

ΔΔG(C – B) = 20.2 kcal/mol

Ground State of B

```
----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
83

O      1.476      0.918     -1.379
B      0.422      1.786     -1.084
H      3.107      1.411     -2.585
C      2.020      1.266     -2.680
H      1.816      0.443     -3.381
O      0.283      2.778     -2.055
C      1.271      2.562     -3.095
H      1.934      3.440     -3.143
H      0.753      2.447     -4.059
H     -1.676     -4.809     -4.512
C     -1.133     -3.994     -4.005
H     -3.504     -3.612     -2.542
N     -1.785     -3.737     -2.720
H      0.446     -5.301     -3.300
C      0.355     -4.349     -3.848
H     -1.949     -4.690      0.837
H     -1.223     -3.100     -4.649
H      0.843     -4.465     -4.828
H      0.189     -5.077     -0.266
C     -1.259     -3.835      0.747
C     -1.063     -3.222     -1.759
H     -2.818     -3.042     -0.582
C     -1.738     -2.927     -0.430
C      0.170     -4.403      0.606
H      0.398     -5.023      1.488
C      1.046     -3.234     -3.054
N      0.274     -2.919     -1.842
H     -1.339     -3.260      1.686
```

H	2.055	-3.545	-2.743
H	1.139	-2.326	-3.675
H	-1.559	-1.874	-0.176
C	1.285	-3.352	0.429
C	0.993	-2.330	-0.703
H	2.229	-3.882	0.220
H	0.416	-1.481	-0.318
H	1.431	-2.791	1.367
H	1.928	-1.906	-1.092
H	-4.306	-0.993	-2.546
C	-3.629	-0.383	-3.164
H	-2.284	-0.142	-1.389
H	-4.081	0.627	-3.228
O	-0.939	0.299	0.644
H	-4.439	-0.901	-5.126
H	-3.305	-2.084	-4.443
C	-2.297	-0.272	-2.473
C	-3.496	-1.008	-4.568
C	-1.725	0.096	1.810
B	-0.510	1.710	0.408
C	-1.108	-0.331	-3.121
C	-2.334	-0.369	-5.357
H	-0.176	-0.313	-2.562
C	-4.812	-4.795	-1.716
O	-4.496	-3.567	-2.354
H	-2.555	0.701	-5.534
C	-1.012	-0.427	-4.583
H	-2.189	-0.839	-6.341
O	0.081	-0.501	-5.169
C	0.620	2.218	1.530
C	0.387	4.682	1.069
C	1.578	0.016	2.294
N	0.999	3.516	1.724
N	1.522	1.482	2.238
C	2.440	2.303	2.881
C	2.110	3.587	2.554
H	0.298	4.479	-0.004
H	1.041	5.546	1.244
H	-0.611	4.863	1.480
H	2.557	4.535	2.828
H	3.232	1.900	3.501
H	1.274	-0.330	3.293
H	2.609	-0.306	2.091
H	0.895	-0.372	1.535
C	-2.641	2.542	-0.443
O	-1.620	2.679	0.524
H	-4.263	-4.932	-0.760
H	-4.590	-5.676	-2.356
H	-5.891	-4.801	-1.491
H	-3.314	3.416	-0.373
H	-3.249	1.629	-0.277
H	-2.235	2.489	-1.471
H	-1.993	-0.972	1.867
H	-2.649	0.700	1.789
H	-1.168	0.369	2.730

```
                     A                      A                      A
 Frequencies --    16.5166                22.8540                26.6261
 Red. masses --     4.4560                 4.4344                 4.4417
 Zero-point correction=                          0.705267(Hartree/Particle)
 Thermal correction to Energy=                   0.748325
 Thermal correction to Enthalpy=                 0.749269
 Thermal correction to Gibbs Free Energy=        0.625196
 Sum of electronic and zero-point Energies=          -1698.710368
 Sum of electronic and thermal Energies=             -1698.667310
 Sum of electronic and thermal Enthalpies=           -1698.666366
 Sum of electronic and thermal Free Energies=        -1698.790439

          Item               Value     Threshold  Converged?
 Maximum Force            0.000041     0.000450     YES
 RMS     Force            0.000005     0.000300     YES

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```

Ground State of C

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----------------------------------------
 Cartesian coordinates (Angstroms):
----------------------------------------
83

H     0.510     1.558     1.940
C     1.480     1.150     1.591
H     1.600     0.150     2.062
O     1.565     1.096     0.189
H     2.289     1.805     1.977
H    -3.464    -2.559    -2.969
C    -2.378    -2.428    -2.866
H    -2.390    -3.963    -1.342
N    -1.862    -3.612    -2.162
H    -2.014    -3.155    -4.884
C    -1.693    -2.328    -4.232
H    -1.061    -7.234    -2.345
H    -2.180    -1.528    -2.258
H    -1.966    -1.381    -4.716
H    -0.852    -5.866    -4.368
C    -0.141    -6.647    -2.480
C    -0.654    -4.127    -2.369
H    -0.969    -5.511    -0.783
C    -0.245    -5.359    -1.593
C     0.041    -6.393    -3.992
H     0.072    -7.363    -4.512
C    -0.174    -2.385    -4.032
N     0.188    -3.607    -3.273
H     0.693    -7.256    -2.099
H     0.348    -2.435    -4.997
H     0.183    -1.512    -3.463
H     0.722    -5.147    -1.116
C     1.293    -5.580    -4.383
C     1.471    -4.277    -3.564
H     1.230    -5.333    -5.454
H     1.983    -4.482    -2.614
H     2.203    -6.185    -4.239
H     2.091    -3.554    -4.107
H    -2.150    -0.455     3.632
```

C	-1.929	-1.129	2.788
H	-1.518	-2.746	4.279
H	-0.919	-0.867	2.417
O	-1.464	1.936	0.449
H	-2.789	0.049	1.178
H	-3.960	-1.023	2.024
C	-1.886	-2.555	3.266
C	-2.931	-0.941	1.631
C	-2.522	2.862	0.427
B	-1.024	1.254	-0.807
C	-2.241	-3.610	2.487
C	-2.686	-2.009	0.549
H	-2.181	-4.639	2.850
C	-3.310	0.889	-1.840
O	-2.076	0.361	-1.412
H	-1.689	-1.781	0.114
C	-2.640	-3.421	1.085
H	-3.424	-1.952	-0.264
O	-2.860	-4.414	0.351
C	-0.548	2.390	-1.919
C	-0.924	1.110	-4.058
C	0.364	4.109	-0.316
N	-0.426	2.241	-3.279
N	0.136	3.549	-1.651
C	0.665	4.102	-2.811
C	0.312	3.277	-3.838
H	-0.129	0.766	-4.735
H	-1.805	1.410	-4.647
H	-1.192	0.324	-3.350
B	0.484	0.304	-0.524
O	0.219	-0.989	0.243
O	1.112	-0.204	-1.803
H	0.519	3.323	-4.901
H	1.246	5.016	-2.791
C	1.916	-1.294	-1.391
C	1.132	-1.963	-0.220
H	-0.536	4.628	0.042
H	1.196	4.822	-0.388
H	0.618	3.286	0.355
H	1.825	-2.299	0.581
H	0.576	-2.859	-0.566
H	2.088	-1.987	-2.236
H	2.905	-0.947	-1.025
H	-4.045	0.962	-1.014
H	-3.740	0.223	-2.615
H	-3.203	1.902	-2.283
H	-2.380	3.605	1.238
H	-3.511	2.382	0.587
H	-2.579	3.417	-0.534

	1	2	3
	A	A	A
Frequencies --	20.5065	34.8427	39.7655
Red. masses --	4.4531	4.6439	3.8072

Zero-point correction= 0.706972(Hartree/Particle)
Thermal correction to Energy= 0.747521
Thermal correction to Enthalpy= 0.748465
Thermal correction to Gibbs Free Energy= 0.635128

```
 Sum of electronic and zero-point Energies=     -1698.686408
 Sum of electronic and thermal Energies=        -1698.645859
 Sum of electronic and thermal Enthalpies=      -1698.644915
 Sum of electronic and thermal Free Energies=   -1698.758252

         Item               Value     Threshold  Converged?
 Maximum Force            0.000223     0.000450     YES
 RMS     Force            0.000019     0.000300     YES

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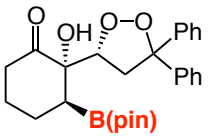
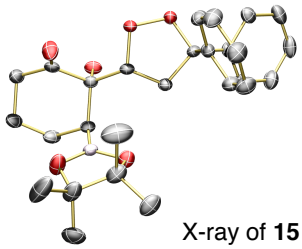
```

Besides the aforementioned pathways that were proposed for the NHC catalyzed boryl or silyl conjugate additions, multiple mechanisms were also explored using model systems on which DFT calculations were carried out. One of them includes a step where the chiral NHC inserts into the B–B or B–Si bond of the corresponding diboron and borosilane reagents. For example, the activation energy of the insertion process of the NHC (derived from **7c**) into $PhMe_2Si$–$B(OH)_2$ is 22.2 kcal/mol. This transformation is also endergonic by 6.0 kcal/mol. However, we cannot find any low-energy transition state about the following reaction between those insertion products and enones. We also investigated a Lewis base activation of the insertion product, generating the corresponding B(pin) or $SiMe_2Ph$ bound N-heterocyclic carbanion. However, MeOH or water (being present) would rapidly protonate the formed carbanions, quenching the reaction. We also considered a similar pathway to the one previously reported by Fernández and co-workers.[10] However, no low-energy transition state can be found for the C–B or C–Si bond formation step.

■ **X-ray Structures for Compounds 15, 34 and 43:**



15



X-ray of **15**

Table 1. Crystal data and structure refinement for compound **15**

Identification code	C27H33BO6	
Empirical formula	C27 H33 B O6	
Formula weight	464.34	
Temperature	143(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P b c a	
Unit cell dimensions	a = 18.8781(9) Å	a= 90°.
	b = 12.1056(5) Å	b= 90°.

	c = 21.2885(9) Å g = 90°.
Volume	4865.1(4) $Å^3$
Z	8
Density (calculated)	1.268 Mg/m^3
Absorption coefficient	0.088 mm^{-1}
F(000)	1984
Crystal size	0.17 x 0.02 x 0.02 mm^3
Theta range for data collection	1.91 to 26.00°.
Index ranges	-23<=h<=23, -14<=k<=14, -26<=l<=26
Reflections collected	64871
Independent reflections	4780 [R(int) = 0.0899]
Completeness to theta = 26.00∞	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9983 and 0.9853
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4780 / 0 / 310
Goodness-of-fit on F^2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0450, wR2 = 0.0943
R indices (all data)	R1 = 0.0840, wR2 = 0.1110
Extinction coefficient	na
Largest diff. peak and hole	0.408 and -0.214 e. $Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **15**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	1503(1)	522(2)	2566(1)	23(1)
O(1)	1491(1)	-2315(1)	2112(1)	39(1)
O(2)	920(1)	296(1)	2912(1)	45(1)
O(3)	1377(1)	1282(1)	2103(1)	31(1)

O(4)	3147(1)	-1286(1)	2353(1)	29(1)
O(5)	3074(1)	-1134(1)	708(1)	27(1)
O(6)	2561(1)	-1597(1)	1175(1)	28(1)
C(1)	1953(1)	-1955(2)	2449(1)	25(1)
C(2)	2078(1)	-2348(2)	3109(1)	32(1)
C(3)	1940(1)	-1379(2)	3560(1)	36(1)
C(4)	2374(1)	-368(2)	3379(1)	33(1)
C(5)	2256(1)	-8(2)	2690(1)	24(1)
C(6)	2424(1)	-988(1)	2247(1)	21(1)
C(7)	365(1)	1074(2)	2719(1)	43(1)
C(8)	599(1)	1370(2)	2052(1)	36(1)
C(9)	-346(1)	505(2)	2775(2)	65(1)
C(10)	409(1)	2068(2)	3166(1)	53(1)
C(11)	372(1)	502(2)	1562(1)	61(1)
C(12)	410(1)	2515(2)	1826(1)	42(1)
C(13)	2316(1)	-680(1)	1559(1)	22(1)
C(14)	2745(1)	312(1)	1343(1)	24(1)
C(15)	2888(1)	21(2)	659(1)	23(1)
C(16)	2231(1)	197(2)	251(1)	24(1)
C(17)	1970(1)	1269(2)	182(1)	30(1)
C(18)	1373(1)	1473(2)	-176(1)	37(1)
C(19)	1026(1)	609(2)	-470(1)	39(1)
C(20)	1281(1)	-451(2)	-405(1)	38(1)
C(21)	1882(1)	-657(2)	-48(1)	30(1)
C(22)	3531(1)	577(2)	369(1)	25(1)
C(23)	3791(1)	1568(2)	608(1)	32(1)
C(24)	4360(1)	2090(2)	320(1)	38(1)
C(25)	4675(1)	1627(2)	-200(1)	39(1)
C(26)	4420(1)	643(2)	-440(1)	39(1)
C(27)	3850(1)	125(2)	-162(1)	31(1)

Table 3. Bond lengths [Å] and angles [°] for compound **15**

B(1)-O(2)	1.352(3)
B(1)-O(3)	1.369(3)
B(1)-C(5)	1.582(3)
O(1)-C(1)	1.211(2)
O(2)-C(7)	1.468(2)
O(3)-C(8)	1.475(2)
O(4)-C(6)	1.429(2)
O(4)-H(4O)	0.85(2)
O(5)-C(15)	1.445(2)
O(5)-O(6)	1.4959(17)
O(6)-C(13)	1.454(2)
C(1)-C(2)	1.502(3)
C(1)-C(6)	1.532(3)
C(2)-C(3)	1.539(3)
C(2)-H(2A)	0.9900
C(2)-H(2B)	0.9900
C(3)-C(4)	1.523(3)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-C(5)	1.546(3)
C(4)-H(4A)	0.9900
C(4)-H(4B)	0.9900
C(5)-C(6)	1.548(2)
C(5)-H(5)	1.0000
C(6)-C(13)	1.527(3)
C(7)-C(9)	1.513(3)
C(7)-C(8)	1.530(3)
C(7)-C(10)	1.536(3)
C(8)-C(12)	1.510(3)
C(8)-C(11)	1.540(3)
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800

C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-C(14)	1.519(2)
C(13)-H(13)	1.0000
C(14)-C(15)	1.522(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-C(22)	1.520(3)
C(15)-C(16)	1.530(3)
C(16)-C(21)	1.380(3)
C(16)-C(17)	1.396(3)
C(17)-C(18)	1.383(3)
C(17)-H(17)	0.9500
C(18)-C(19)	1.383(3)
C(18)-H(18)	0.9500
C(19)-C(20)	1.377(3)
C(19)-H(19)	0.9500
C(20)-C(21)	1.388(3)
C(20)-H(20)	0.9500
C(21)-H(21)	0.9500
C(22)-C(23)	1.391(3)
C(22)-C(27)	1.392(3)
C(23)-C(24)	1.388(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.375(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.383(3)
C(25)-H(25)	0.9500

C(26)-C(27)	1.380(3)
C(26)-H(26)	0.9500
C(27)-H(27)	0.9500

O(2)-B(1)-O(3)	112.73(17)
O(2)-B(1)-C(5)	123.92(18)
O(3)-B(1)-C(5)	123.33(17)
B(1)-O(2)-C(7)	107.35(16)
B(1)-O(3)-C(8)	105.99(15)
C(6)-O(4)-H(4O)	106.5(15)
C(15)-O(5)-O(6)	104.73(12)
C(13)-O(6)-O(5)	107.00(11)
O(1)-C(1)-C(2)	123.62(18)
O(1)-C(1)-C(6)	121.84(17)
C(2)-C(1)-C(6)	114.39(16)
C(1)-C(2)-C(3)	108.37(16)
C(1)-C(2)-H(2A)	110.0
C(3)-C(2)-H(2A)	110.0
C(1)-C(2)-H(2B)	110.0
C(3)-C(2)-H(2B)	110.0
H(2A)-C(2)-H(2B)	108.4
C(4)-C(3)-C(2)	111.34(17)
C(4)-C(3)-H(3A)	109.4
C(2)-C(3)-H(3A)	109.4
C(4)-C(3)-H(3B)	109.4
C(2)-C(3)-H(3B)	109.4
H(3A)-C(3)-H(3B)	108.0
C(3)-C(4)-C(5)	112.84(17)
C(3)-C(4)-H(4A)	109.0
C(5)-C(4)-H(4A)	109.0
C(3)-C(4)-H(4B)	109.0
C(5)-C(4)-H(4B)	109.0
H(4A)-C(4)-H(4B)	107.8
C(4)-C(5)-C(6)	109.46(15)

C(4)-C(5)-B(1)	113.70(16)
C(6)-C(5)-B(1)	113.19(15)
C(4)-C(5)-H(5)	106.7
C(6)-C(5)-H(5)	106.7
B(1)-C(5)-H(5)	106.7
O(4)-C(6)-C(13)	109.90(15)
O(4)-C(6)-C(1)	108.52(14)
C(13)-C(6)-C(1)	112.19(15)
O(4)-C(6)-C(5)	107.07(14)
C(13)-C(6)-C(5)	111.78(14)
C(1)-C(6)-C(5)	107.17(14)
O(2)-C(7)-C(9)	108.58(17)
O(2)-C(7)-C(8)	101.78(16)
C(9)-C(7)-C(8)	115.8(2)
O(2)-C(7)-C(10)	106.8(2)
C(9)-C(7)-C(10)	110.9(2)
C(8)-C(7)-C(10)	112.13(19)
O(3)-C(8)-C(12)	108.95(16)
O(3)-C(8)-C(7)	101.63(16)
C(12)-C(8)-C(7)	116.19(19)
O(3)-C(8)-C(11)	106.17(17)
C(12)-C(8)-C(11)	110.2(2)
C(7)-C(8)-C(11)	112.9(2)
C(7)-C(9)-H(9A)	109.5
C(7)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(7)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(7)-C(10)-H(10A)	109.5
C(7)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(7)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5

H(10B)-C(10)-H(10C)	109.5
C(8)-C(11)-H(11A)	109.5
C(8)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(8)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(8)-C(12)-H(12A)	109.5
C(8)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(8)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(6)-C(13)-C(14)	105.29(14)
O(6)-C(13)-C(6)	108.09(14)
C(14)-C(13)-C(6)	114.33(15)
O(6)-C(13)-H(13)	109.7
C(14)-C(13)-H(13)	109.7
C(6)-C(13)-H(13)	109.7
C(13)-C(14)-C(15)	101.61(14)
C(13)-C(14)-H(14A)	111.4
C(15)-C(14)-H(14A)	111.4
C(13)-C(14)-H(14B)	111.4
C(15)-C(14)-H(14B)	111.4
H(14A)-C(14)-H(14B)	109.3
O(5)-C(15)-C(22)	105.32(14)
O(5)-C(15)-C(14)	101.35(14)
C(22)-C(15)-C(14)	115.28(16)
O(5)-C(15)-C(16)	111.91(15)
C(22)-C(15)-C(16)	110.88(15)
C(14)-C(15)-C(16)	111.57(15)
C(21)-C(16)-C(17)	118.66(18)
C(21)-C(16)-C(15)	122.96(17)
C(17)-C(16)-C(15)	118.37(16)

C(18)-C(17)-C(16)	120.72(18)
C(18)-C(17)-H(17)	119.6
C(16)-C(17)-H(17)	119.6
C(19)-C(18)-C(17)	120.04(19)
C(19)-C(18)-H(18)	120.0
C(17)-C(18)-H(18)	120.0
C(20)-C(19)-C(18)	119.6(2)
C(20)-C(19)-H(19)	120.2
C(18)-C(19)-H(19)	120.2
C(19)-C(20)-C(21)	120.53(19)
C(19)-C(20)-H(20)	119.7
C(21)-C(20)-H(20)	119.7
C(16)-C(21)-C(20)	120.48(18)
C(16)-C(21)-H(21)	119.8
C(20)-C(21)-H(21)	119.8
C(23)-C(22)-C(27)	118.86(18)
C(23)-C(22)-C(15)	121.05(17)
C(27)-C(22)-C(15)	120.01(17)
C(24)-C(23)-C(22)	120.3(2)
C(24)-C(23)-H(23)	119.9
C(22)-C(23)-H(23)	119.9
C(25)-C(24)-C(23)	120.2(2)
C(25)-C(24)-H(24)	119.9
C(23)-C(24)-H(24)	119.9
C(24)-C(25)-C(26)	119.9(2)
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-H(25)	120.0
C(27)-C(26)-C(25)	120.2(2)
C(27)-C(26)-H(26)	119.9
C(25)-C(26)-H(26)	119.9
C(26)-C(27)-C(22)	120.5(2)
C(26)-C(27)-H(27)	119.8
C(22)-C(27)-H(27)	119.8

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **15**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	26(1)	17(1)	26(1)	-4(1)	1(1)	2(1)
O(1)	44(1)	41(1)	32(1)	0(1)	-2(1)	-18(1)
O(2)	32(1)	39(1)	64(1)	22(1)	15(1)	15(1)
O(3)	23(1)	32(1)	37(1)	6(1)	-3(1)	3(1)
O(4)	22(1)	30(1)	34(1)	-7(1)	-2(1)	7(1)
O(5)	33(1)	22(1)	26(1)	1(1)	7(1)	4(1)
O(6)	40(1)	20(1)	25(1)	-4(1)	9(1)	-2(1)
C(1)	28(1)	22(1)	26(1)	-6(1)	5(1)	7(1)
C(2)	42(1)	26(1)	28(1)	1(1)	3(1)	6(1)
C(3)	53(1)	33(1)	22(1)	1(1)	2(1)	13(1)
C(4)	44(1)	30(1)	25(1)	-7(1)	-6(1)	8(1)
C(5)	26(1)	21(1)	24(1)	-5(1)	-2(1)	1(1)
C(6)	19(1)	20(1)	24(1)	-3(1)	0(1)	3(1)
C(7)	29(1)	33(1)	66(2)	12(1)	8(1)	10(1)
C(8)	24(1)	31(1)	54(2)	2(1)	-8(1)	2(1)
C(9)	29(1)	36(1)	129(3)	24(2)	16(2)	5(1)
C(10)	48(2)	53(2)	56(2)	-8(1)	11(1)	22(1)
C(11)	50(2)	55(2)	77(2)	-24(2)	-30(1)	10(1)
C(12)	32(1)	35(1)	60(2)	9(1)	-14(1)	5(1)
C(13)	25(1)	18(1)	24(1)	-5(1)	1(1)	2(1)
C(14)	26(1)	21(1)	24(1)	-4(1)	1(1)	0(1)
C(15)	28(1)	17(1)	25(1)	-2(1)	1(1)	3(1)
C(16)	25(1)	24(1)	23(1)	-1(1)	3(1)	-2(1)
C(17)	31(1)	25(1)	35(1)	-4(1)	-2(1)	-1(1)
C(18)	35(1)	30(1)	46(1)	-1(1)	-6(1)	6(1)

C(19)	33(1)	41(1)	42(1)	2(1)	-10(1)	1(1)
C(20)	43(1)	32(1)	38(1)	-2(1)	-12(1)	-8(1)
C(21)	39(1)	22(1)	30(1)	0(1)	-3(1)	-1(1)
C(22)	24(1)	27(1)	23(1)	5(1)	-3(1)	3(1)
C(23)	33(1)	32(1)	32(1)	1(1)	4(1)	-1(1)
C(24)	36(1)	38(1)	39(1)	8(1)	-4(1)	-8(1)
C(25)	25(1)	58(2)	36(1)	19(1)	-1(1)	-6(1)
C(26)	32(1)	60(2)	25(1)	7(1)	4(1)	6(1)
C(27)	32(1)	37(1)	26(1)	2(1)	-1(1)	4(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for compound **15**

	x	y	z	U(eq)
H(4O)	3243(12)	-1800(20)	2093(11)	43
H(2A)	2572	-2610	3155	38
H(2B)	1755	-2969	3208	38
H(3A)	1430	-1188	3552	43
H(3B)	2062	-1604	3994	43
H(4A)	2883	-533	3443	40
H(4B)	2247	253	3661	40
H(5)	2614	578	2599	28
H(9A)	-363	-123	2485	98
H(9B)	-724	1028	2670	98
H(9C)	-410	240	3206	98
H(10A)	255	1843	3587	79
H(10B)	102	2661	3012	79
H(10C)	899	2333	3185	79
H(11A)	495	-237	1714	91
H(11B)	617	644	1165	91

H(11C)	-141	549	1496	91
H(12A)	553	3058	2143	63
H(12B)	-102	2562	1759	63
H(12C)	658	2667	1431	63
H(13)	1802	-545	1477	27
H(14A)	3191	383	1584	29
H(14B)	2470	1005	1380	29
H(17)	2204	1865	384	36
H(18)	1202	2206	-221	44
H(19)	614	746	-714	46
H(20)	1044	-1045	-606	45
H(21)	2055	-1391	-9	36
H(23)	3578	1888	969	39
H(24)	4532	2769	483	45
H(25)	5067	1982	-393	47
H(26)	4638	323	-799	47
H(27)	3673	-545	-333	38

Table 6. Torsion angles [°] for compound **15**

O(3)-B(1)-O(2)-C(7)	-7.6(2)
C(5)-B(1)-O(2)-C(7)	171.04(19)
O(2)-B(1)-O(3)-C(8)	-13.9(2)
C(5)-B(1)-O(3)-C(8)	167.44(17)
C(15)-O(5)-O(6)-C(13)	-23.31(16)
O(1)-C(1)-C(2)-C(3)	-116.1(2)
C(6)-C(1)-C(2)-C(3)	59.4(2)
C(1)-C(2)-C(3)-C(4)	-53.9(2)
C(2)-C(3)-C(4)-C(5)	54.8(2)
C(3)-C(4)-C(5)-C(6)	-56.5(2)
C(3)-C(4)-C(5)-B(1)	71.2(2)
O(2)-B(1)-C(5)-C(4)	-26.4(3)
O(3)-B(1)-C(5)-C(4)	152.16(18)

O(2)-B(1)-C(5)-C(6)	99.4(2)
O(3)-B(1)-C(5)-C(6)	-82.1(2)
O(1)-C(1)-C(6)-O(4)	-130.42(18)
C(2)-C(1)-C(6)-O(4)	53.93(19)
O(1)-C(1)-C(6)-C(13)	-8.8(2)
C(2)-C(1)-C(6)-C(13)	175.56(15)
O(1)-C(1)-C(6)-C(5)	114.27(19)
C(2)-C(1)-C(6)-C(5)	-61.38(19)
C(4)-C(5)-C(6)-O(4)	-59.63(19)
B(1)-C(5)-C(6)-O(4)	172.41(15)
C(4)-C(5)-C(6)-C(13)	179.96(15)
B(1)-C(5)-C(6)-C(13)	52.0(2)
C(4)-C(5)-C(6)-C(1)	56.65(19)
B(1)-C(5)-C(6)-C(1)	-71.32(19)
B(1)-O(2)-C(7)-C(9)	147.3(2)
B(1)-O(2)-C(7)-C(8)	24.7(2)
B(1)-O(2)-C(7)-C(10)	-93.1(2)
B(1)-O(3)-C(8)-C(12)	151.26(19)
B(1)-O(3)-C(8)-C(7)	28.09(19)
B(1)-O(3)-C(8)-C(11)	-90.1(2)
O(2)-C(7)-C(8)-O(3)	-31.4(2)
C(9)-C(7)-C(8)-O(3)	-148.96(17)
C(10)-C(7)-C(8)-O(3)	82.4(2)
O(2)-C(7)-C(8)-C(12)	-149.49(18)
C(9)-C(7)-C(8)-C(12)	93.0(2)
C(10)-C(7)-C(8)-C(12)	-35.7(3)
O(2)-C(7)-C(8)-C(11)	81.9(2)
C(9)-C(7)-C(8)-C(11)	-35.7(3)
C(10)-C(7)-C(8)-C(11)	-164.29(19)
O(5)-O(6)-C(13)-C(14)	-4.81(17)
O(5)-O(6)-C(13)-C(6)	-127.39(14)
O(4)-C(6)-C(13)-O(6)	54.87(18)
C(1)-C(6)-C(13)-O(6)	-65.96(18)
C(5)-C(6)-C(13)-O(6)	173.62(14)

O(4)-C(6)-C(13)-C(14)	-62.01(19)
C(1)-C(6)-C(13)-C(14)	177.16(15)
C(5)-C(6)-C(13)-C(14)	56.7(2)
O(6)-C(13)-C(14)-C(15)	29.40(18)
C(6)-C(13)-C(14)-C(15)	147.88(15)
O(6)-O(5)-C(15)-C(22)	161.67(13)
O(6)-O(5)-C(15)-C(14)	41.23(16)
O(6)-O(5)-C(15)-C(16)	-77.77(16)
C(13)-C(14)-C(15)-O(5)	-43.53(17)
C(13)-C(14)-C(15)-C(22)	-156.66(15)
C(13)-C(14)-C(15)-C(16)	75.72(18)
O(5)-C(15)-C(16)-C(21)	-2.2(3)
C(22)-C(15)-C(16)-C(21)	115.1(2)
C(14)-C(15)-C(16)-C(21)	-115.0(2)
O(5)-C(15)-C(16)-C(17)	177.28(16)
C(22)-C(15)-C(16)-C(17)	-65.4(2)
C(14)-C(15)-C(16)-C(17)	64.5(2)
C(21)-C(16)-C(17)-C(18)	0.1(3)
C(15)-C(16)-C(17)-C(18)	-179.38(18)
C(16)-C(17)-C(18)-C(19)	0.3(3)
C(17)-C(18)-C(19)-C(20)	-0.4(3)
C(18)-C(19)-C(20)-C(21)	0.1(4)
C(17)-C(16)-C(21)-C(20)	-0.5(3)
C(15)-C(16)-C(21)-C(20)	179.01(19)
C(19)-C(20)-C(21)-C(16)	0.4(3)
O(5)-C(15)-C(22)-C(23)	-135.11(18)
C(14)-C(15)-C(22)-C(23)	-24.3(3)
C(16)-C(15)-C(22)-C(23)	103.7(2)
O(5)-C(15)-C(22)-C(27)	48.1(2)
C(14)-C(15)-C(22)-C(27)	158.87(17)
C(16)-C(15)-C(22)-C(27)	-73.2(2)
C(27)-C(22)-C(23)-C(24)	-0.2(3)
C(15)-C(22)-C(23)-C(24)	-177.10(18)
C(22)-C(23)-C(24)-C(25)	-0.6(3)

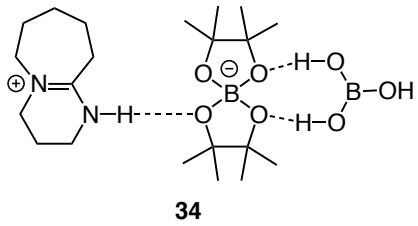
C(23)-C(24)-C(25)-C(26)	0.7(3)
C(24)-C(25)-C(26)-C(27)	0.1(3)
C(25)-C(26)-C(27)-C(22)	-0.9(3)
C(23)-C(22)-C(27)-C(26)	0.9(3)
C(15)-C(22)-C(27)-C(26)	177.84(18)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for compound **15** [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(4)-H(4O)...O(3)#1	0.85(2)	2.43(2)	3.1246(19)	139(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1/2,y-1/2,z



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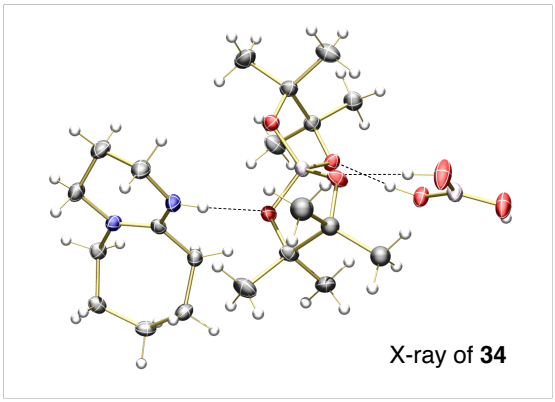


Table 1. Crystal data and structure refinement for compound **34**

Identification code	C21H44B2N2O7	
Empirical formula	C21 H44 B2 N2 O7	
Formula weight	458.20	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P c	
Unit cell dimensions	a = 8.1777(3) Å	a= 90°

	b = 17.5288(6) Å	b= 101.375(2)°
	c = 18.6171(6) Å	g = 90°
Volume	2616.25(16) $Å^3$	
Z	4	
Density (calculated)	1.163 Mg/m^3	
Absorption coefficient	0.684 mm^{-1}	
F(000)	1000	
Crystal size	0.15 x 0.10 x 0.06 mm^3	
Theta range for data collection	5.52 to 67.81°	
Index ranges	-9<=h<=8, -20<=k<=20, -21<=l<=22	
Reflections collected	17780	
Independent reflections	6250 [R(int) = 0.0324]	
Completeness to theta = 66.50∞	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9601 and 0.9044	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6250 / 2 / 615	
Goodness-of-fit on F^2	1.013	
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0815	
R indices (all data)	R1 = 0.0315, wR2 = 0.0823	
Extinction coefficient	na	
Largest diff. peak and hole	0.199 and -0.170 e. $Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **34**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
B(1)	949(2)	9786(1)	2556(1)	18(1)
O(1)	-236(2)	10323(1)	2772(1)	20(1)
O(2)	2585(2)	10090(1)	2895(1)	19(1)

O(3)	548(2)	9012(1)	2784(1)	19(1)
O(4)	858(2)	9707(1)	1756(1)	20(1)
C(1)	601(2)	11009(1)	3038(1)	20(1)
C(2)	2400(2)	10713(1)	3367(1)	20(1)
C(3)	617(2)	8485(1)	2202(1)	21(1)
C(4)	94(2)	8992(1)	1510(1)	21(1)
C(5)	562(3)	11553(1)	2397(1)	26(1)
C(6)	-311(3)	11372(1)	3594(1)	28(1)
C(7)	3780(3)	11289(1)	3343(1)	29(1)
C(8)	2538(3)	10408(1)	4146(1)	28(1)
C(9)	2405(3)	8193(1)	2283(1)	28(1)
C(10)	-557(3)	7823(1)	2254(1)	32(1)
C(11)	755(3)	8726(1)	843(1)	26(1)
C(12)	-1790(2)	9115(1)	1301(1)	26(1)
C(13)	4602(2)	9684(1)	6225(1)	26(1)
C(14)	5601(2)	8980(1)	6117(1)	26(1)
C(15)	5066(2)	8690(1)	5338(1)	27(1)
N(1)	3242(2)	8652(1)	5117(1)	22(1)
C(17)	2585(2)	8206(1)	4447(1)	27(1)
C(18)	1793(3)	7452(1)	4605(1)	29(1)
C(19)	47(3)	7534(1)	4768(1)	30(1)
C(20)	-105(2)	8066(1)	5400(1)	24(1)
C(21)	397(2)	8898(1)	5295(1)	22(1)
C(22)	2248(2)	9026(1)	5476(1)	18(1)
N(2)	2828(2)	9502(1)	6009(1)	20(1)
B(2)	6646(3)	9348(1)	3329(1)	20(1)
O(5)	6673(2)	9961(1)	2880(1)	25(1)
O(6)	8017(2)	8899(1)	3576(1)	27(1)
O(7)	5215(2)	9162(1)	3555(1)	27(1)
B(3)	5635(2)	4644(1)	2708(1)	19(1)
O(8)	7050(2)	4204(1)	2561(1)	22(1)
O(9)	4166(2)	4243(1)	2303(1)	22(1)
O(10)	5790(2)	5445(1)	2476(1)	23(1)
O(11)	5476(2)	4715(1)	3479(1)	24(1)

C(24)	6456(2)	3502(1)	2202(1)	24(1)
C(25)	4657(2)	3709(1)	1809(1)	22(1)
C(26)	5372(3)	5951(1)	3014(1)	24(1)
C(28)	6468(3)	2886(1)	2789(1)	33(1)
C(29)	7626(3)	3273(1)	1697(1)	39(1)
C(30)	3430(3)	3045(1)	1704(1)	28(1)
C(31)	4608(3)	4105(1)	1078(1)	32(1)
C(32)	3505(3)	6096(1)	2831(1)	34(1)
C(33)	6295(3)	6702(1)	2994(1)	35(1)
C(27)	6021(8)	5479(2)	3711(2)	26(1)
C(34)	5223(8)	5689(2)	4353(2)	49(2)
C(35)	7915(5)	5498(2)	3952(2)	44(1)
C(27X)	5538(17)	5470(8)	3784(9)	24(4)
C(34X)	4259(16)	5626(6)	4250(5)	28(3)
C(35X)	7264(16)	5526(6)	4212(7)	36(3)
C(36)	9483(3)	5566(1)	1725(1)	31(1)
C(37)	10214(3)	5437(1)	1047(1)	33(1)
C(38)	9792(2)	6109(1)	526(1)	28(1)
N(3)	7993(2)	6269(1)	386(1)	22(1)
C(40)	7281(2)	6675(1)	-300(1)	24(1)
C(41)	6694(3)	7484(1)	-177(1)	25(1)
C(42)	4995(3)	7528(1)	39(1)	27(1)
C(43)	4875(2)	7118(1)	748(1)	26(1)
C(44)	5245(2)	6257(1)	731(1)	24(1)
C(45)	7079(2)	6086(1)	874(1)	21(1)
N(4)	7725(2)	5767(1)	1502(1)	24(1)
B(4)	1333(3)	4044(1)	3426(1)	26(1)
O(12)	2791(2)	4027(1)	3934(1)	42(1)
O(13)	1261(2)	4167(1)	2701(1)	26(1)
O(14)	-112(2)	3935(1)	3670(1)	37(1)

Table 3. Bond lengths [Å] and angles [°] for compound **34**

B(1)-O(2)	1.462(2)
B(1)-O(1)	1.463(2)
B(1)-O(3)	1.478(2)
B(1)-O(4)	1.483(2)
O(1)-C(1)	1.425(2)
O(2)-C(2)	1.429(2)
O(3)-C(3)	1.432(2)
O(4)-C(4)	1.435(2)
C(1)-C(5)	1.523(2)
C(1)-C(6)	1.528(2)
C(1)-C(2)	1.566(2)
C(2)-C(7)	1.521(3)
C(2)-C(8)	1.528(2)
C(3)-C(10)	1.521(3)
C(3)-C(9)	1.529(3)
C(3)-C(4)	1.554(2)
C(4)-C(11)	1.522(2)
C(4)-C(12)	1.528(3)
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800
C(6)-H(6A)	0.9800
C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800
C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800
C(7)-H(7C)	0.9800
C(8)-H(8A)	0.9800
C(8)-H(8B)	0.9800
C(8)-H(8C)	0.9800
C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800
C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800

C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800
C(11)-H(11A)	0.9800
C(11)-H(11B)	0.9800
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-N(2)	1.463(2)
C(13)-C(14)	1.515(3)
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.519(3)
C(14)-H(14A)	0.9900
C(14)-H(14B)	0.9900
C(15)-N(1)	1.469(2)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
N(1)-C(22)	1.323(2)
N(1)-C(17)	1.480(2)
C(17)-C(18)	1.526(3)
C(17)-H(17A)	0.9900
C(17)-H(17B)	0.9900
C(18)-C(19)	1.524(3)
C(18)-H(18A)	0.9900
C(18)-H(18B)	0.9900
C(19)-C(20)	1.526(3)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-C(21)	1.537(3)
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.501(2)
C(21)-H(21A)	0.9900

C(21)-H(21B)	0.9900
C(22)-N(2)	1.312(2)
N(2)-H(2N)	0.90(3)
B(2)-O(7)	1.358(2)
B(2)-O(5)	1.364(2)
B(2)-O(6)	1.373(3)
O(5)-H(5O)	0.81(3)
O(6)-H(6O)	0.83(3)
O(7)-H(7O)	0.80(3)
B(3)-O(8)	1.461(2)
B(3)-O(9)	1.466(2)
B(3)-O(11)	1.471(2)
B(3)-O(10)	1.482(2)
O(8)-C(24)	1.437(2)
O(9)-C(25)	1.425(2)
O(10)-C(26)	1.429(2)
O(11)-C(27)	1.449(4)
C(24)-C(29)	1.522(3)
C(24)-C(28)	1.534(3)
C(24)-C(25)	1.551(3)
C(25)-C(31)	1.523(2)
C(25)-C(30)	1.523(3)
C(26)-C(32)	1.519(3)
C(26)-C(33)	1.521(3)
C(26)-C(27)	1.543(4)
C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800
C(28)-H(28C)	0.9800
C(29)-H(29A)	0.9800
C(29)-H(29B)	0.9800
C(29)-H(29C)	0.9800
C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800
C(30)-H(30C)	0.9800

C(31)-H(31A)	0.9800
C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800
C(32)-H(32A)	0.9800
C(32)-H(32B)	0.9800
C(32)-H(32C)	0.9800
C(33)-H(33A)	0.9800
C(33)-H(33B)	0.9800
C(33)-H(33C)	0.9800
C(27)-C(34)	1.514(5)
C(27)-C(35)	1.526(7)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-N(4)	1.459(3)
C(36)-C(37)	1.518(3)
C(36)-H(36A)	0.9900
C(36)-H(36B)	0.9900
C(37)-C(38)	1.521(3)
C(37)-H(37A)	0.9900
C(37)-H(37B)	0.9900
C(38)-N(3)	1.470(2)
C(38)-H(38A)	0.9900
C(38)-H(38B)	0.9900
N(3)-C(45)	1.325(2)
N(3)-C(40)	1.478(2)
C(40)-C(41)	1.528(3)
C(40)-H(40A)	0.9900
C(40)-H(40B)	0.9900
C(41)-C(42)	1.522(3)
C(41)-H(41A)	0.9900

C(41)-H(41B)	0.9900
C(42)-C(43)	1.524(3)
C(42)-H(42A)	0.9900
C(42)-H(42B)	0.9900
C(43)-C(44)	1.541(3)
C(43)-H(43A)	0.9900
C(43)-H(43B)	0.9900
C(44)-C(45)	1.501(3)
C(44)-H(44A)	0.9900
C(44)-H(44B)	0.9900
C(45)-N(4)	1.309(3)
N(4)-H(4N)	0.84(3)
B(4)-O(13)	1.358(3)
B(4)-O(14)	1.360(3)
B(4)-O(12)	1.368(3)
O(12)-H(12O)	0.91(4)
O(13)-H(13O)	0.91(3)
O(14)-H(14O)	0.82(4)

O(2)-B(1)-O(1)	104.25(14)
O(2)-B(1)-O(3)	116.52(14)
O(1)-B(1)-O(3)	108.37(13)
O(2)-B(1)-O(4)	109.15(13)
O(1)-B(1)-O(4)	115.50(14)
O(3)-B(1)-O(4)	103.50(14)
C(1)-O(1)-B(1)	109.89(13)
C(2)-O(2)-B(1)	110.20(13)
C(3)-O(3)-B(1)	109.30(12)
C(4)-O(4)-B(1)	109.49(13)
O(1)-C(1)-C(5)	108.68(14)
O(1)-C(1)-C(6)	108.79(15)
C(5)-C(1)-C(6)	109.42(15)
O(1)-C(1)-C(2)	101.89(13)
C(5)-C(1)-C(2)	112.79(15)

C(6)-C(1)-C(2)	114.83(15)
O(2)-C(2)-C(7)	108.68(14)
O(2)-C(2)-C(8)	108.60(14)
C(7)-C(2)-C(8)	110.09(15)
O(2)-C(2)-C(1)	102.62(13)
C(7)-C(2)-C(1)	114.40(15)
C(8)-C(2)-C(1)	112.03(14)
O(3)-C(3)-C(10)	108.92(14)
O(3)-C(3)-C(9)	108.72(14)
C(10)-C(3)-C(9)	109.96(16)
O(3)-C(3)-C(4)	102.29(13)
C(10)-C(3)-C(4)	114.55(16)
C(9)-C(3)-C(4)	111.98(14)
O(4)-C(4)-C(11)	109.01(14)
O(4)-C(4)-C(12)	108.16(14)
C(11)-C(4)-C(12)	109.76(15)
O(4)-C(4)-C(3)	101.78(13)
C(11)-C(4)-C(3)	114.67(15)
C(12)-C(4)-C(3)	112.95(15)
C(1)-C(5)-H(5A)	109.5
C(1)-C(5)-H(5B)	109.5
H(5A)-C(5)-H(5B)	109.5
C(1)-C(5)-H(5C)	109.5
H(5A)-C(5)-H(5C)	109.5
H(5B)-C(5)-H(5C)	109.5
C(1)-C(6)-H(6A)	109.5
C(1)-C(6)-H(6B)	109.5
H(6A)-C(6)-H(6B)	109.5
C(1)-C(6)-H(6C)	109.5
H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5
C(2)-C(7)-H(7A)	109.5
C(2)-C(7)-H(7B)	109.5
H(7A)-C(7)-H(7B)	109.5

C(2)-C(7)-H(7C)	109.5
H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5
C(2)-C(8)-H(8A)	109.5
C(2)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(2)-C(8)-H(8C)	109.5
H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(3)-C(9)-H(9A)	109.5
C(3)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(3)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(3)-C(10)-H(10A)	109.5
C(3)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10B)	109.5
C(3)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(4)-C(11)-H(11A)	109.5
C(4)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11B)	109.5
C(4)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(4)-C(12)-H(12A)	109.5
C(4)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(4)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(2)-C(13)-C(14)	108.51(15)

N(2)-C(13)-H(13A)	110.0
C(14)-C(13)-H(13A)	110.0
N(2)-C(13)-H(13B)	110.0
C(14)-C(13)-H(13B)	110.0
H(13A)-C(13)-H(13B)	108.4
C(13)-C(14)-C(15)	109.80(16)
C(13)-C(14)-H(14A)	109.7
C(15)-C(14)-H(14A)	109.7
C(13)-C(14)-H(14B)	109.7
C(15)-C(14)-H(14B)	109.7
H(14A)-C(14)-H(14B)	108.2
N(1)-C(15)-C(14)	111.58(14)
N(1)-C(15)-H(15A)	109.3
C(14)-C(15)-H(15A)	109.3
N(1)-C(15)-H(15B)	109.3
C(14)-C(15)-H(15B)	109.3
H(15A)-C(15)-H(15B)	108.0
C(22)-N(1)-C(15)	121.84(15)
C(22)-N(1)-C(17)	121.99(16)
C(15)-N(1)-C(17)	116.08(14)
N(1)-C(17)-C(18)	113.11(14)
N(1)-C(17)-H(17A)	109.0
C(18)-C(17)-H(17A)	109.0
N(1)-C(17)-H(17B)	109.0
C(18)-C(17)-H(17B)	109.0
H(17A)-C(17)-H(17B)	107.8
C(19)-C(18)-C(17)	114.02(16)
C(19)-C(18)-H(18A)	108.7
C(17)-C(18)-H(18A)	108.7
C(19)-C(18)-H(18B)	108.7
C(17)-C(18)-H(18B)	108.7
H(18A)-C(18)-H(18B)	107.6
C(18)-C(19)-C(20)	115.69(17)
C(18)-C(19)-H(19A)	108.4

C(20)-C(19)-H(19A)	108.4
C(18)-C(19)-H(19B)	108.4
C(20)-C(19)-H(19B)	108.4
H(19A)-C(19)-H(19B)	107.4
C(19)-C(20)-C(21)	114.66(15)
C(19)-C(20)-H(20A)	108.6
C(21)-C(20)-H(20A)	108.6
C(19)-C(20)-H(20B)	108.6
C(21)-C(20)-H(20B)	108.6
H(20A)-C(20)-H(20B)	107.6
C(22)-C(21)-C(20)	113.34(15)
C(22)-C(21)-H(21A)	108.9
C(20)-C(21)-H(21A)	108.9
C(22)-C(21)-H(21B)	108.9
C(20)-C(21)-H(21B)	108.9
H(21A)-C(21)-H(21B)	107.7
N(2)-C(22)-N(1)	122.05(17)
N(2)-C(22)-C(21)	117.58(15)
N(1)-C(22)-C(21)	120.35(15)
C(22)-N(2)-C(13)	122.58(15)
C(22)-N(2)-H(2N)	120.3(15)
C(13)-N(2)-H(2N)	117.1(15)
O(7)-B(2)-O(5)	119.81(17)
O(7)-B(2)-O(6)	117.15(17)
O(5)-B(2)-O(6)	123.04(17)
B(2)-O(5)-H(5O)	114(2)
B(2)-O(6)-H(6O)	111.5(19)
B(2)-O(7)-H(7O)	112(2)
O(8)-B(3)-O(9)	104.40(14)
O(8)-B(3)-O(11)	116.95(15)
O(9)-B(3)-O(11)	108.75(14)
O(8)-B(3)-O(10)	109.19(14)
O(9)-B(3)-O(10)	114.41(15)
O(11)-B(3)-O(10)	103.53(14)

C(24)-O(8)-B(3)	109.36(14)
C(25)-O(9)-B(3)	109.91(13)
C(26)-O(10)-B(3)	109.65(13)
C(27)-O(11)-B(3)	106.7(2)
O(8)-C(24)-C(29)	108.47(16)
O(8)-C(24)-C(28)	108.52(15)
C(29)-C(24)-C(28)	109.72(17)
O(8)-C(24)-C(25)	102.82(14)
C(29)-C(24)-C(25)	115.02(17)
C(28)-C(24)-C(25)	111.87(16)
O(9)-C(25)-C(31)	108.43(15)
O(9)-C(25)-C(30)	108.81(15)
C(31)-C(25)-C(30)	109.42(15)
O(9)-C(25)-C(24)	102.16(13)
C(31)-C(25)-C(24)	112.61(16)
C(30)-C(25)-C(24)	114.96(16)
O(10)-C(26)-C(32)	108.39(15)
O(10)-C(26)-C(33)	109.33(16)
C(32)-C(26)-C(33)	109.33(16)
O(10)-C(26)-C(27)	99.63(19)
C(32)-C(26)-C(27)	116.2(3)
C(33)-C(26)-C(27)	113.3(2)
C(24)-C(28)-H(28A)	109.5
C(24)-C(28)-H(28B)	109.5
H(28A)-C(28)-H(28B)	109.5
C(24)-C(28)-H(28C)	109.5
H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5
C(24)-C(29)-H(29A)	109.5
C(24)-C(29)-H(29B)	109.5
H(29A)-C(29)-H(29B)	109.5
C(24)-C(29)-H(29C)	109.5
H(29A)-C(29)-H(29C)	109.5
H(29B)-C(29)-H(29C)	109.5

C(25)-C(30)-H(30A)	109.5
C(25)-C(30)-H(30B)	109.5
H(30A)-C(30)-H(30B)	109.5
C(25)-C(30)-H(30C)	109.5
H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5
C(25)-C(31)-H(31A)	109.5
C(25)-C(31)-H(31B)	109.5
H(31A)-C(31)-H(31B)	109.5
C(25)-C(31)-H(31C)	109.5
H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5
C(26)-C(32)-H(32A)	109.5
C(26)-C(32)-H(32B)	109.5
H(32A)-C(32)-H(32B)	109.5
C(26)-C(32)-H(32C)	109.5
H(32A)-C(32)-H(32C)	109.5
H(32B)-C(32)-H(32C)	109.5
C(26)-C(33)-H(33A)	109.5
C(26)-C(33)-H(33B)	109.5
H(33A)-C(33)-H(33B)	109.5
C(26)-C(33)-H(33C)	109.5
H(33A)-C(33)-H(33C)	109.5
H(33B)-C(33)-H(33C)	109.5
O(11)-C(27)-C(34)	107.8(3)
O(11)-C(27)-C(35)	110.1(3)
C(34)-C(27)-C(35)	109.4(3)
O(11)-C(27)-C(26)	102.1(2)
C(34)-C(27)-C(26)	113.7(3)
C(35)-C(27)-C(26)	113.3(3)
C(27)-C(34)-H(34A)	109.5
C(27)-C(34)-H(34B)	109.5
H(34A)-C(34)-H(34B)	109.5
C(27)-C(34)-H(34C)	109.5

H(34A)-C(34)-H(34C)	109.5
H(34B)-C(34)-H(34C)	109.5
C(27)-C(35)-H(35A)	109.5
C(27)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(27)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
N(4)-C(36)-C(37)	109.03(16)
N(4)-C(36)-H(36A)	109.9
C(37)-C(36)-H(36A)	109.9
N(4)-C(36)-H(36B)	109.9
C(37)-C(36)-H(36B)	109.9
H(36A)-C(36)-H(36B)	108.3
C(36)-C(37)-C(38)	109.76(16)
C(36)-C(37)-H(37A)	109.7
C(38)-C(37)-H(37A)	109.7
C(36)-C(37)-H(37B)	109.7
C(38)-C(37)-H(37B)	109.7
H(37A)-C(37)-H(37B)	108.2
N(3)-C(38)-C(37)	110.77(16)
N(3)-C(38)-H(38A)	109.5
C(37)-C(38)-H(38A)	109.5
N(3)-C(38)-H(38B)	109.5
C(37)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	108.1
C(45)-N(3)-C(38)	120.82(16)
C(45)-N(3)-C(40)	122.01(16)
C(38)-N(3)-C(40)	117.10(14)
N(3)-C(40)-C(41)	113.46(14)
N(3)-C(40)-H(40A)	108.9
C(41)-C(40)-H(40A)	108.9
N(3)-C(40)-H(40B)	108.9
C(41)-C(40)-H(40B)	108.9

H(40A)-C(40)-H(40B)	107.7
C(42)-C(41)-C(40)	114.63(16)
C(42)-C(41)-H(41A)	108.6
C(40)-C(41)-H(41A)	108.6
C(42)-C(41)-H(41B)	108.6
C(40)-C(41)-H(41B)	108.6
H(41A)-C(41)-H(41B)	107.6
C(41)-C(42)-C(43)	114.98(16)
C(41)-C(42)-H(42A)	108.5
C(43)-C(42)-H(42A)	108.5
C(41)-C(42)-H(42B)	108.5
C(43)-C(42)-H(42B)	108.5
H(42A)-C(42)-H(42B)	107.5
C(42)-C(43)-C(44)	113.42(15)
C(42)-C(43)-H(43A)	108.9
C(44)-C(43)-H(43A)	108.9
C(42)-C(43)-H(43B)	108.9
C(44)-C(43)-H(43B)	108.9
H(43A)-C(43)-H(43B)	107.7
C(45)-C(44)-C(43)	112.63(15)
C(45)-C(44)-H(44A)	109.1
C(43)-C(44)-H(44A)	109.1
C(45)-C(44)-H(44B)	109.1
C(43)-C(44)-H(44B)	109.1
H(44A)-C(44)-H(44B)	107.8
N(4)-C(45)-N(3)	122.20(18)
N(4)-C(45)-C(44)	117.19(16)
N(3)-C(45)-C(44)	120.60(16)
C(45)-N(4)-C(36)	124.02(16)
C(45)-N(4)-H(4N)	117.3(17)
C(36)-N(4)-H(4N)	118.7(17)
O(13)-B(4)-O(14)	118.94(19)
O(13)-B(4)-O(12)	123.55(19)
O(14)-B(4)-O(12)	117.51(18)

B(4)-O(12)-H(12O)	109(2)
B(4)-O(13)-H(13O)	113.6(17)
B(4)-O(14)-H(14O)	112(2)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **34**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
B(1)	17(1)	19(1)	19(1)	2(1)	5(1)	1(1)
O(1)	17(1)	19(1)	25(1)	-3(1)	5(1)	-1(1)
O(2)	18(1)	19(1)	20(1)	-2(1)	5(1)	-2(1)
O(3)	23(1)	17(1)	18(1)	0(1)	8(1)	-2(1)
O(4)	23(1)	18(1)	18(1)	0(1)	5(1)	-4(1)
C(1)	24(1)	17(1)	20(1)	-2(1)	7(1)	-1(1)
C(2)	22(1)	19(1)	19(1)	-1(1)	4(1)	0(1)
C(3)	27(1)	16(1)	22(1)	-2(1)	10(1)	0(1)
C(4)	23(1)	20(1)	20(1)	-4(1)	5(1)	-2(1)
C(5)	32(1)	20(1)	26(1)	3(1)	5(1)	1(1)
C(6)	33(1)	24(1)	28(1)	-3(1)	10(1)	6(1)
C(7)	27(1)	27(1)	32(1)	-6(1)	4(1)	-7(1)
C(8)	32(1)	32(1)	19(1)	0(1)	6(1)	4(1)
C(9)	33(1)	24(1)	26(1)	-1(1)	7(1)	8(1)
C(10)	43(1)	21(1)	32(1)	-3(1)	12(1)	-7(1)
C(11)	29(1)	26(1)	23(1)	-5(1)	8(1)	-3(1)
C(12)	25(1)	27(1)	26(1)	-5(1)	3(1)	-1(1)
C(13)	24(1)	27(1)	28(1)	-3(1)	4(1)	-6(1)
C(14)	20(1)	29(1)	27(1)	4(1)	2(1)	1(1)
C(15)	21(1)	32(1)	28(1)	3(1)	9(1)	5(1)
N(1)	24(1)	24(1)	17(1)	0(1)	5(1)	4(1)

C(17)	34(1)	29(1)	17(1)	-2(1)	6(1)	7(1)
C(18)	44(1)	22(1)	20(1)	-4(1)	2(1)	7(1)
C(19)	38(1)	22(1)	27(1)	-1(1)	-1(1)	-3(1)
C(20)	23(1)	25(1)	25(1)	1(1)	4(1)	-2(1)
C(21)	20(1)	22(1)	22(1)	-2(1)	2(1)	1(1)
C(22)	21(1)	18(1)	16(1)	3(1)	4(1)	2(1)
N(2)	21(1)	22(1)	19(1)	-3(1)	6(1)	0(1)
B(2)	19(1)	28(1)	15(1)	-1(1)	4(1)	0(1)
O(5)	17(1)	31(1)	28(1)	8(1)	6(1)	2(1)
O(6)	21(1)	34(1)	26(1)	10(1)	8(1)	4(1)
O(7)	20(1)	34(1)	27(1)	8(1)	8(1)	3(1)
B(3)	20(1)	17(1)	19(1)	1(1)	6(1)	-2(1)
O(8)	20(1)	19(1)	29(1)	-3(1)	6(1)	-1(1)
O(9)	21(1)	23(1)	23(1)	-6(1)	7(1)	-1(1)
O(10)	29(1)	18(1)	25(1)	1(1)	13(1)	0(1)
O(11)	38(1)	17(1)	18(1)	-1(1)	5(1)	0(1)
C(24)	25(1)	20(1)	29(1)	-3(1)	7(1)	0(1)
C(25)	28(1)	20(1)	19(1)	-3(1)	7(1)	0(1)
C(26)	33(1)	17(1)	21(1)	-3(1)	6(1)	0(1)
C(28)	39(1)	23(1)	33(1)	0(1)	-3(1)	-1(1)
C(29)	35(1)	30(1)	55(1)	-12(1)	19(1)	1(1)
C(30)	32(1)	26(1)	27(1)	-6(1)	6(1)	-5(1)
C(31)	51(1)	26(1)	20(1)	-1(1)	7(1)	-3(1)
C(32)	36(1)	22(1)	50(1)	0(1)	18(1)	6(1)
C(33)	41(1)	21(1)	42(1)	-2(1)	5(1)	-6(1)
C(27)	46(3)	17(2)	16(2)	-3(1)	7(2)	-3(1)
C(34)	101(5)	24(2)	26(2)	-4(1)	26(2)	1(2)
C(35)	51(2)	27(2)	43(2)	-2(1)	-22(2)	-6(1)
C(36)	26(1)	33(1)	34(1)	10(1)	7(1)	7(1)
C(37)	25(1)	36(1)	39(1)	4(1)	9(1)	9(1)
C(38)	24(1)	33(1)	28(1)	0(1)	11(1)	2(1)
N(3)	24(1)	23(1)	21(1)	1(1)	8(1)	3(1)
C(40)	29(1)	26(1)	17(1)	-1(1)	6(1)	-1(1)
C(41)	34(1)	22(1)	19(1)	0(1)	5(1)	-2(1)

C(42)	34(1)	23(1)	24(1)	2(1)	2(1)	7(1)
C(43)	24(1)	30(1)	26(1)	1(1)	7(1)	7(1)
C(44)	23(1)	25(1)	24(1)	1(1)	7(1)	-1(1)
C(45)	26(1)	16(1)	24(1)	-2(1)	8(1)	-2(1)
N(4)	23(1)	26(1)	25(1)	7(1)	8(1)	2(1)
B(4)	23(1)	30(1)	27(1)	10(1)	7(1)	2(1)
O(12)	23(1)	75(1)	27(1)	19(1)	5(1)	1(1)
O(13)	19(1)	37(1)	24(1)	5(1)	6(1)	1(1)
O(14)	24(1)	58(1)	30(1)	18(1)	10(1)	3(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for compound **34**

	x	y	z	U(eq)
H(5A)	-588	11719	2211	39
H(5B)	988	11291	2006	39
H(5C)	1260	11998	2561	39
H(6A)	-1420	11541	3343	41
H(6B)	327	11811	3824	41
H(6C)	-427	10996	3970	41
H(7A)	4860	11063	3561	43
H(7B)	3593	11745	3620	43
H(7C)	3774	11429	2833	43
H(8A)	3679	10230	4331	42
H(8B)	1758	9983	4142	42
H(8C)	2265	10815	4463	42
H(9A)	2681	7871	2721	41
H(9B)	3174	8627	2331	41
H(9C)	2507	7893	1850	41

H(10A)	-139	7531	2702	47
H(10B)	-617	7490	1827	47
H(10C)	-1672	8020	2268	47
H(11A)	383	9078	435	38
H(11B)	332	8212	704	38
H(11C)	1977	8715	961	38
H(12A)	-2047	9442	867	39
H(12B)	-2184	9359	1709	39
H(12C)	-2348	8621	1194	39
H(13A)	4863	9843	6746	32
H(13B)	4890	10109	5923	32
H(14A)	5419	8578	6467	31
H(14B)	6805	9106	6214	31
H(15A)	5511	9033	5000	32
H(15B)	5542	8176	5299	32
H(17A)	3507	8101	4188	32
H(17B)	1742	8517	4118	32
H(18A)	1737	7111	4176	35
H(18B)	2521	7205	5029	35
H(19A)	-350	7021	4879	36
H(19B)	-707	7720	4320	36
H(20A)	602	7866	5855	29
H(20B)	-1275	8058	5469	29
H(21A)	-28	9048	4780	26
H(21B)	-139	9232	5610	26
H(2N)	2130(30)	9742(14)	6248(12)	25
H(5O)	7590(40)	10065(16)	2806(15)	37
H(6O)	8800(40)	9004(16)	3365(15)	40
H(7O)	4460(40)	9437(17)	3378(15)	40
H(28A)	7622	2772	3025	50
H(28B)	5934	2423	2559	50
H(28C)	5855	3071	3157	50
H(29A)	8727	3153	1991	58
H(29B)	7726	3695	1364	58

H(29C)	7177	2824	1412	58
H(30A)	2333	3226	1451	42
H(30B)	3343	2835	2182	42
H(30C)	3826	2648	1409	42
H(31A)	3449	4223	851	48
H(31B)	5088	3769	753	48
H(31C)	5254	4579	1157	48
H(32A)	3231	6400	2381	52
H(32B)	3168	6374	3235	52
H(32C)	2912	5608	2759	52
H(33A)	5864	6964	2531	53
H(33B)	7489	6601	3035	53
H(33C)	6126	7024	3404	53
H(34A)	4006	5677	4198	73
H(34B)	5578	6203	4523	73
H(34C)	5569	5323	4752	73
H(35A)	8432	5363	3538	67
H(35B)	8262	5132	4351	67
H(35C)	8268	6012	4123	67
H(34D)	3137	5585	3948	42
H(34E)	4425	6142	4456	42
H(34F)	4387	5253	4649	42
H(35D)	8056	5422	3892	55
H(35E)	7421	5153	4612	55
H(35F)	7456	6041	4417	55
H(36A)	9597	5097	2027	37
H(36B)	10091	5983	2024	37
H(37A)	9755	4962	799	39
H(37B)	11440	5382	1189	39
H(38A)	10414	6566	742	33
H(38B)	10139	5993	58	33
H(40A)	6324	6378	-570	28
H(40B)	8133	6701	-611	28
H(41A)	7529	7728	213	30

H(41B)	6651	7782	-632	30
H(42A)	4151	7309	-363	33
H(42B)	4709	8072	88	33
H(43A)	3739	7190	847	32
H(43B)	5673	7354	1157	32
H(44A)	4737	5996	1104	28
H(44B)	4721	6050	245	28
H(4N)	7080(30)	5677(14)	1790(14)	29
H(12O)	3630(50)	4220(20)	3731(19)	62
H(13O)	2280(40)	4218(16)	2580(14)	39
H(14O)	-930(50)	3999(19)	3346(18)	55

Table 6. Torsion angles [°] for compound **34**

O(2)-B(1)-O(1)-C(1)	15.59(17)
O(3)-B(1)-O(1)-C(1)	140.32(14)
O(4)-B(1)-O(1)-C(1)	-104.16(16)
O(1)-B(1)-O(2)-C(2)	7.35(17)
O(3)-B(1)-O(2)-C(2)	-112.00(16)
O(4)-B(1)-O(2)-C(2)	131.29(14)
O(2)-B(1)-O(3)-C(3)	-106.85(16)
O(1)-B(1)-O(3)-C(3)	136.05(14)
O(4)-B(1)-O(3)-C(3)	12.95(18)
O(2)-B(1)-O(4)-C(4)	136.89(14)
O(1)-B(1)-O(4)-C(4)	-106.09(16)
O(3)-B(1)-O(4)-C(4)	12.18(18)
B(1)-O(1)-C(1)-C(5)	89.43(16)
B(1)-O(1)-C(1)-C(6)	-151.50(14)
B(1)-O(1)-C(1)-C(2)	-29.84(16)
B(1)-O(2)-C(2)-C(7)	-146.22(15)
B(1)-O(2)-C(2)-C(8)	94.02(16)
B(1)-O(2)-C(2)-C(1)	-24.72(16)
O(1)-C(1)-C(2)-O(2)	32.72(15)

C(5)-C(1)-C(2)-O(2)	-83.60(16)
C(6)-C(1)-C(2)-O(2)	150.12(14)
O(1)-C(1)-C(2)-C(7)	150.23(14)
C(5)-C(1)-C(2)-C(7)	33.9(2)
C(6)-C(1)-C(2)-C(7)	-92.37(18)
O(1)-C(1)-C(2)-C(8)	-83.58(16)
C(5)-C(1)-C(2)-C(8)	160.09(15)
C(6)-C(1)-C(2)-C(8)	33.8(2)
B(1)-O(3)-C(3)-C(10)	-152.29(16)
B(1)-O(3)-C(3)-C(9)	87.90(16)
B(1)-O(3)-C(3)-C(4)	-30.67(17)
B(1)-O(4)-C(4)-C(11)	-151.54(15)
B(1)-O(4)-C(4)-C(12)	89.16(16)
B(1)-O(4)-C(4)-C(3)	-30.02(17)
O(3)-C(3)-C(4)-O(4)	36.58(16)
C(10)-C(3)-C(4)-O(4)	154.25(15)
C(9)-C(3)-C(4)-O(4)	-79.66(17)
O(3)-C(3)-C(4)-C(11)	154.09(15)
C(10)-C(3)-C(4)-C(11)	-88.24(19)
C(9)-C(3)-C(4)-C(11)	37.8(2)
O(3)-C(3)-C(4)-C(12)	-79.15(17)
C(10)-C(3)-C(4)-C(12)	38.5(2)
C(9)-C(3)-C(4)-C(12)	164.61(15)
N(2)-C(13)-C(14)-C(15)	53.78(19)
C(13)-C(14)-C(15)-N(1)	-47.1(2)
C(14)-C(15)-N(1)-C(22)	17.7(2)
C(14)-C(15)-N(1)-C(17)	-165.58(15)
C(22)-N(1)-C(17)-C(18)	-75.0(2)
C(15)-N(1)-C(17)-C(18)	108.30(19)
N(1)-C(17)-C(18)-C(19)	77.7(2)
C(17)-C(18)-C(19)-C(20)	-56.4(2)
C(18)-C(19)-C(20)-C(21)	60.6(2)
C(19)-C(20)-C(21)-C(22)	-80.8(2)
C(15)-N(1)-C(22)-N(2)	5.9(3)

C(17)-N(1)-C(22)-N(2)	-170.61(16)
C(15)-N(1)-C(22)-C(21)	-172.35(16)
C(17)-N(1)-C(22)-C(21)	11.1(2)
C(20)-C(21)-C(22)-N(2)	-118.59(17)
C(20)-C(21)-C(22)-N(1)	59.8(2)
N(1)-C(22)-N(2)-C(13)	2.9(3)
C(21)-C(22)-N(2)-C(13)	-178.77(15)
C(14)-C(13)-N(2)-C(22)	-33.6(2)
O(9)-B(3)-O(8)-C(24)	-10.14(17)
O(11)-B(3)-O(8)-C(24)	110.04(17)
O(10)-B(3)-O(8)-C(24)	-132.90(15)
O(8)-B(3)-O(9)-C(25)	-12.88(17)
O(11)-B(3)-O(9)-C(25)	-138.42(14)
O(10)-B(3)-O(9)-C(25)	106.41(16)
O(8)-B(3)-O(10)-C(26)	-137.58(15)
O(9)-B(3)-O(10)-C(26)	105.86(16)
O(11)-B(3)-O(10)-C(26)	-12.32(19)
O(8)-B(3)-O(11)-C(27)	103.9(3)
O(9)-B(3)-O(11)-C(27)	-138.2(3)
O(10)-B(3)-O(11)-C(27)	-16.2(3)
B(3)-O(8)-C(24)-C(29)	149.11(16)
B(3)-O(8)-C(24)-C(28)	-91.73(17)
B(3)-O(8)-C(24)-C(25)	26.89(17)
B(3)-O(9)-C(25)-C(31)	-90.52(17)
B(3)-O(9)-C(25)-C(30)	150.55(15)
B(3)-O(9)-C(25)-C(24)	28.58(17)
O(8)-C(24)-C(25)-O(9)	-33.35(17)
C(29)-C(24)-C(25)-O(9)	-151.05(16)
C(28)-C(24)-C(25)-O(9)	82.90(17)
O(8)-C(24)-C(25)-C(31)	82.76(17)
C(29)-C(24)-C(25)-C(31)	-34.9(2)
C(28)-C(24)-C(25)-C(31)	-160.99(16)
O(8)-C(24)-C(25)-C(30)	-151.01(14)
C(29)-C(24)-C(25)-C(30)	91.3(2)

C(28)-C(24)-C(25)-C(30)	-34.8(2)
B(3)-O(10)-C(26)-C(32)	-88.56(18)
B(3)-O(10)-C(26)-C(33)	152.34(16)
B(3)-O(10)-C(26)-C(27)	33.4(3)
B(3)-O(11)-C(27)-C(34)	156.4(3)
B(3)-O(11)-C(27)-C(35)	-84.3(3)
B(3)-O(11)-C(27)-C(26)	36.4(4)
O(10)-C(26)-C(27)-O(11)	-42.1(4)
C(32)-C(26)-C(27)-O(11)	74.0(4)
C(33)-C(26)-C(27)-O(11)	-158.1(3)
O(10)-C(26)-C(27)-C(34)	-157.9(3)
C(32)-C(26)-C(27)-C(34)	-41.8(4)
C(33)-C(26)-C(27)-C(34)	86.1(4)
O(10)-C(26)-C(27)-C(35)	76.2(3)
C(32)-C(26)-C(27)-C(35)	-167.7(2)
C(33)-C(26)-C(27)-C(35)	-39.8(3)
N(4)-C(36)-C(37)-C(38)	50.5(2)
C(36)-C(37)-C(38)-N(3)	-51.7(2)
C(37)-C(38)-N(3)-C(45)	26.5(2)
C(37)-C(38)-N(3)-C(40)	-156.50(16)
C(45)-N(3)-C(40)-C(41)	65.2(2)
C(38)-N(3)-C(40)-C(41)	-111.72(18)
N(3)-C(40)-C(41)-C(42)	-80.0(2)
C(40)-C(41)-C(42)-C(43)	60.4(2)
C(41)-C(42)-C(43)-C(44)	-60.0(2)
C(42)-C(43)-C(44)-C(45)	80.6(2)
C(38)-N(3)-C(45)-N(4)	0.9(3)
C(40)-N(3)-C(45)-N(4)	-175.93(16)
C(38)-N(3)-C(45)-C(44)	179.53(16)
C(40)-N(3)-C(45)-C(44)	2.7(3)
C(43)-C(44)-C(45)-N(4)	109.26(18)
C(43)-C(44)-C(45)-N(3)	-69.5(2)
N(3)-C(45)-N(4)-C(36)	-1.2(3)
C(44)-C(45)-N(4)-C(36)	-179.88(17)

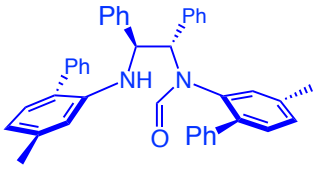
C(37)-C(36)-N(4)-C(45)	-25.7(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for compound **34** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...O(4)#1	0.90(3)	1.81(3)	2.7076(19)	175(2)
O(5)-H(5O)...O(1)#2	0.81(3)	1.85(3)	2.6523(18)	172(3)
O(6)-H(6O)...O(3)#2	0.83(3)	1.96(3)	2.7743(18)	167(3)
O(7)-H(7O)...O(2)	0.80(3)	1.98(3)	2.7811(19)	177(3)
N(4)-H(4N)...O(10)	0.84(3)	1.85(3)	2.6909(19)	176(3)
O(12)-H(12O)...O(11)	0.91(4)	1.89(4)	2.780(2)	169(3)
O(13)-H(13O)...O(9)	0.91(3)	1.72(3)	2.6272(17)	175(3)
O(14)-H(14O)...O(8)#3	0.82(4)	2.01(4)	2.825(2)	177(3)

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+2,z+1/2 #2 x+1,y,z #3 x-1,y,z



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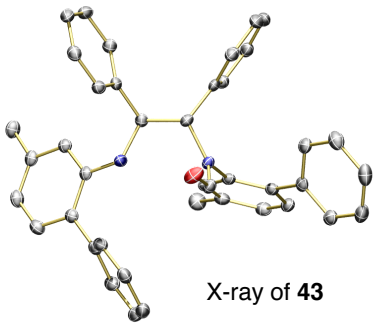


X-ray of **43**

Table 1. Crystal data and structure refinement for compound **43**

Identification code	C41H36N2O
Empirical formula	C41 H36 N2 O
Formula weight	572.72
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	Trigonal

Space group	P 3(2)	
Unit cell dimensions	a = 9.7301(5) Å	a= 90°.
	b = 9.7301(5) Å	b= 90°.
	c = 28.7268(16) Å	g = 120°.
Volume	2355.3(2) $Å^3$	
Z	3	
Density (calculated)	1.211 Mg/m^3	
Absorption coefficient	0.555 mm^{-1}	
F(000)	912	
Crystal size	0.20 x 0.15 x 0.10 mm^3	
Theta range for data collection	5.25 to 68.04°.	
Index ranges	-11<=h<=11, -11<=k<=11, -33<=l<=34	
Reflections collected	21349	
Independent reflections	5490 [R(int) = 0.0216]	
Completeness to theta = 67.00∞	98.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9466 and 0.8971	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5490 / 4 / 408	
Goodness-of-fit on F^2	1.047	
Final R indices [I>2sigma(I)]	R1 = 0.0268, wR2 = 0.0681	
R indices (all data)	R1 = 0.0269, wR2 = 0.0682	
Absolute structure parameter	0.05(17)	
Extinction coefficient	na	
Largest diff. peak and hole	0.140 and -0.174 e. $Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for compound **43**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
O(1)	220(1)	9992(1)	3214(1)	30(1)
N(1)	2603(1)	10281(1)	2986(1)	17(1)

N(2)	880(1)	7601(1)	2441(1)	19(1)
C(1)	2320(1)	10524(1)	2493(1)	17(1)
C(2)	1805(1)	9041(1)	2176(1)	18(1)
C(3)	3683(1)	12007(1)	2278(1)	18(1)
C(4)	3479(2)	13305(2)	2192(1)	24(1)
C(5)	4679(2)	14675(2)	1989(1)	29(1)
C(6)	6106(2)	14774(2)	1872(1)	30(1)
C(7)	6334(2)	13506(2)	1960(1)	26(1)
C(8)	5131(1)	12127(2)	2160(1)	21(1)
C(9)	4047(1)	10369(1)	3143(1)	18(1)
C(10)	4470(1)	9306(1)	2959(1)	20(1)
C(11)	5865(2)	9344(1)	3086(1)	23(1)
C(12)	6808(2)	10434(2)	3425(1)	25(1)
C(13)	6371(1)	11458(2)	3620(1)	23(1)
C(14)	5002(1)	11481(1)	3481(1)	20(1)
C(15)	4658(1)	12664(1)	3701(1)	20(1)
C(16)	4289(1)	13646(2)	3438(1)	23(1)
C(17)	4063(2)	14794(2)	3651(1)	28(1)
C(18)	4187(2)	14988(2)	4130(1)	30(1)
C(19)	4553(2)	14023(2)	4395(1)	28(1)
C(20)	4790(1)	12879(2)	4183(1)	24(1)
C(21)	6356(2)	8262(2)	2858(1)	32(1)
C(22)	1465(1)	10033(1)	3303(1)	21(1)
C(23)	572(1)	6121(1)	2287(1)	18(1)
C(24)	939(1)	5881(1)	1836(1)	20(1)
C(25)	641(1)	4394(2)	1682(1)	22(1)
C(26)	-74(2)	3116(2)	1985(1)	25(1)
C(27)	-423(2)	3342(2)	2440(1)	24(1)
C(28)	-110(1)	4814(1)	2601(1)	20(1)
C(29)	-420(1)	5040(1)	3094(1)	20(1)
C(30)	-1430(1)	5617(1)	3213(1)	21(1)
C(31)	-1667(2)	5856(1)	3675(1)	24(1)
C(32)	-898(2)	5528(2)	4028(1)	27(1)
C(33)	82(2)	4925(2)	3915(1)	28(1)
C(34)	315(2)	4670(2)	3454(1)	25(1)
C(35)	1158(2)	4212(2)	1202(1)	28(1)

C(36)	852(1)	9161(1)	1773(1)	18(1)
C(37)	1492(1)	9629(1)	1329(1)	21(1)
C(38)	575(2)	9699(2)	967(1)	24(1)
C(39)	-974(2)	9331(1)	1047(1)	24(1)
C(40)	-1612(1)	8896(1)	1491(1)	23(1)
C(41)	-705(1)	8808(1)	1850(1)	20(1)

Table 3. Bond lengths [Å] and angles [°] for compound **43**

O(1)-C(22)	1.2184(15)
N(1)-C(22)	1.3595(15)
N(1)-C(9)	1.4366(15)
N(1)-C(1)	1.4829(14)
N(2)-C(23)	1.3875(15)
N(2)-C(2)	1.4463(15)
N(2)-H(2N)	0.875(13)
C(1)-C(3)	1.5192(16)
C(1)-C(2)	1.5626(15)
C(1)-H(1)	0.986(12)
C(2)-C(36)	1.5239(16)
C(2)-H(2)	0.994(12)
C(3)-C(4)	1.3951(17)
C(3)-C(8)	1.3972(17)
C(4)-C(5)	1.3868(19)
C(4)-H(4)	0.9500
C(5)-C(6)	1.384(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.382(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.3885(18)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-C(10)	1.3937(17)
C(9)-C(14)	1.4049(17)
C(10)-C(11)	1.3889(18)

C(10)-H(10)	0.9500
C(11)-C(12)	1.3942(19)
C(11)-C(21)	1.5071(18)
C(12)-C(13)	1.3820(19)
C(12)-H(12)	0.9500
C(13)-C(14)	1.4008(17)
C(13)-H(13)	0.9500
C(14)-C(15)	1.4910(17)
C(15)-C(20)	1.3955(17)
C(15)-C(16)	1.3981(18)
C(16)-C(17)	1.3856(19)
C(16)-H(16)	0.9500
C(17)-C(18)	1.384(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.387(2)
C(18)-H(18)	0.9500
C(19)-C(20)	1.3857(19)
C(19)-H(19)	0.9500
C(20)-H(20A)	0.9500
C(21)-H(21A)	0.9800
C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800
C(22)-H(22)	0.9500
C(23)-C(24)	1.3966(17)
C(23)-C(28)	1.4226(16)
C(24)-C(25)	1.3972(17)
C(24)-H(24)	0.9500
C(25)-C(26)	1.3871(18)
C(25)-C(35)	1.5095(18)
C(26)-C(27)	1.3958(19)
C(26)-H(26)	0.9500
C(27)-C(28)	1.3854(18)
C(27)-H(27)	0.9500
C(28)-C(29)	1.4885(17)
C(29)-C(30)	1.3962(18)
C(29)-C(34)	1.4009(18)

C(30)-C(31)	1.3878(18)
C(30)-H(30)	0.9500
C(31)-C(32)	1.3879(19)
C(31)-H(31)	0.9500
C(32)-C(33)	1.385(2)
C(32)-H(32)	0.9500
C(33)-C(34)	1.3873(19)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-C(37)	1.3927(17)
C(36)-C(41)	1.3931(16)
C(37)-C(38)	1.3922(17)
C(37)-H(37)	0.9500
C(38)-C(39)	1.3822(19)
C(38)-H(38)	0.9500
C(39)-C(40)	1.3880(18)
C(39)-H(39)	0.9500
C(40)-C(41)	1.3879(17)
C(40)-H(40)	0.9500
C(41)-H(41)	0.9500

C(22)-N(1)-C(9)	119.07(9)
C(22)-N(1)-C(1)	117.86(9)
C(9)-N(1)-C(1)	123.00(9)
C(23)-N(2)-C(2)	123.06(10)
C(23)-N(2)-H(2N)	117.0(10)
C(2)-N(2)-H(2N)	117.3(10)
N(1)-C(1)-C(3)	113.32(9)
N(1)-C(1)-C(2)	114.12(9)
C(3)-C(1)-C(2)	111.35(9)
N(1)-C(1)-H(1)	102.9(8)
C(3)-C(1)-H(1)	108.3(8)
C(2)-C(1)-H(1)	106.0(8)

N(2)-C(2)-C(36)	111.48(9)
N(2)-C(2)-C(1)	110.15(9)
C(36)-C(2)-C(1)	107.43(9)
N(2)-C(2)-H(2)	111.7(9)
C(36)-C(2)-H(2)	107.7(8)
C(1)-C(2)-H(2)	108.1(9)
C(4)-C(3)-C(8)	118.39(11)
C(4)-C(3)-C(1)	118.69(11)
C(8)-C(3)-C(1)	122.93(11)
C(5)-C(4)-C(3)	120.78(12)
C(5)-C(4)-H(4)	119.6
C(3)-C(4)-H(4)	119.6
C(6)-C(5)-C(4)	120.20(12)
C(6)-C(5)-H(5)	119.9
C(4)-C(5)-H(5)	119.9
C(7)-C(6)-C(5)	119.74(12)
C(7)-C(6)-H(6)	120.1
C(5)-C(6)-H(6)	120.1
C(6)-C(7)-C(8)	120.28(12)
C(6)-C(7)-H(7)	119.9
C(8)-C(7)-H(7)	119.9
C(7)-C(8)-C(3)	120.60(12)
C(7)-C(8)-H(8)	119.7
C(3)-C(8)-H(8)	119.7
C(10)-C(9)-C(14)	120.43(11)
C(10)-C(9)-N(1)	118.60(10)
C(14)-C(9)-N(1)	120.96(10)
C(11)-C(10)-C(9)	121.87(11)
C(11)-C(10)-H(10)	119.1
C(9)-C(10)-H(10)	119.1
C(10)-C(11)-C(12)	117.81(11)
C(10)-C(11)-C(21)	120.96(12)
C(12)-C(11)-C(21)	121.22(11)
C(13)-C(12)-C(11)	120.60(11)
C(13)-C(12)-H(12)	119.7
C(11)-C(12)-H(12)	119.7

C(12)-C(13)-C(14)	122.24(11)
C(12)-C(13)-H(13)	118.9
C(14)-C(13)-H(13)	118.9
C(13)-C(14)-C(9)	116.95(11)
C(13)-C(14)-C(15)	118.32(10)
C(9)-C(14)-C(15)	124.73(11)
C(20)-C(15)-C(16)	118.01(11)
C(20)-C(15)-C(14)	119.73(11)
C(16)-C(15)-C(14)	122.15(11)
C(17)-C(16)-C(15)	120.63(12)
C(17)-C(16)-H(16)	119.7
C(15)-C(16)-H(16)	119.7
C(18)-C(17)-C(16)	120.76(12)
C(18)-C(17)-H(17)	119.6
C(16)-C(17)-H(17)	119.6
C(17)-C(18)-C(19)	119.21(12)
C(17)-C(18)-H(18)	120.4
C(19)-C(18)-H(18)	120.4
C(20)-C(19)-C(18)	120.23(12)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(19)-C(20)-C(15)	121.15(12)
C(19)-C(20)-H(20A)	119.4
C(15)-C(20)-H(20A)	119.4
C(11)-C(21)-H(21A)	109.5
C(11)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(11)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(1)-C(22)-N(1)	125.05(11)
O(1)-C(22)-H(22)	117.5
N(1)-C(22)-H(22)	117.5
N(2)-C(23)-C(24)	121.86(11)
N(2)-C(23)-C(28)	119.31(10)
C(24)-C(23)-C(28)	118.82(11)

C(23)-C(24)-C(25)	121.90(11)
C(23)-C(24)-H(24)	119.1
C(25)-C(24)-H(24)	119.1
C(26)-C(25)-C(24)	118.81(11)
C(26)-C(25)-C(35)	121.04(11)
C(24)-C(25)-C(35)	120.10(11)
C(25)-C(26)-C(27)	119.96(11)
C(25)-C(26)-H(26)	120.0
C(27)-C(26)-H(26)	120.0
C(28)-C(27)-C(26)	121.92(12)
C(28)-C(27)-H(27)	119.0
C(26)-C(27)-H(27)	119.0
C(27)-C(28)-C(23)	118.54(11)
C(27)-C(28)-C(29)	120.85(11)
C(23)-C(28)-C(29)	120.56(11)
C(30)-C(29)-C(34)	118.40(11)
C(30)-C(29)-C(28)	121.81(11)
C(34)-C(29)-C(28)	119.79(11)
C(31)-C(30)-C(29)	120.68(11)
C(31)-C(30)-H(30)	119.7
C(29)-C(30)-H(30)	119.7
C(30)-C(31)-C(32)	120.39(12)
C(30)-C(31)-H(31)	119.8
C(32)-C(31)-H(31)	119.8
C(33)-C(32)-C(31)	119.44(12)
C(33)-C(32)-H(32)	120.3
C(31)-C(32)-H(32)	120.3
C(32)-C(33)-C(34)	120.51(12)
C(32)-C(33)-H(33)	119.7
C(34)-C(33)-H(33)	119.7
C(33)-C(34)-C(29)	120.54(12)
C(33)-C(34)-H(34)	119.7
C(29)-C(34)-H(34)	119.7
C(25)-C(35)-H(35A)	109.5
C(25)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5

C(25)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(37)-C(36)-C(41)	118.68(11)
C(37)-C(36)-C(2)	122.11(10)
C(41)-C(36)-C(2)	119.21(10)
C(38)-C(37)-C(36)	120.40(11)
C(38)-C(37)-H(37)	119.8
C(36)-C(37)-H(37)	119.8
C(39)-C(38)-C(37)	120.37(11)
C(39)-C(38)-H(38)	119.8
C(37)-C(38)-H(38)	119.8
C(38)-C(39)-C(40)	119.69(11)
C(38)-C(39)-H(39)	120.2
C(40)-C(39)-H(39)	120.2
C(41)-C(40)-C(39)	119.97(11)
C(41)-C(40)-H(40)	120.0
C(39)-C(40)-H(40)	120.0
C(40)-C(41)-C(36)	120.86(11)
C(40)-C(41)-H(41)	119.6
C(36)-C(41)-H(41)	119.6

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for compound **43**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	22(1)	48(1)	21(1)	1(1)	2(1)	18(1)
N(1)	17(1)	20(1)	14(1)	-2(1)	0(1)	8(1)
N(2)	22(1)	19(1)	14(1)	0(1)	2(1)	9(1)
C(1)	17(1)	21(1)	13(1)	0(1)	-1(1)	10(1)
C(2)	16(1)	19(1)	18(1)	0(1)	2(1)	8(1)

C(3)	22(1)	20(1)	12(1)	-3(1)	-3(1)	10(1)
C(4)	29(1)	24(1)	20(1)	-2(1)	-4(1)	15(1)
C(5)	42(1)	19(1)	25(1)	0(1)	-6(1)	14(1)
C(6)	30(1)	21(1)	22(1)	3(1)	-3(1)	1(1)
C(7)	22(1)	27(1)	20(1)	0(1)	-1(1)	6(1)
C(8)	21(1)	22(1)	18(1)	0(1)	-1(1)	9(1)
C(9)	17(1)	20(1)	15(1)	3(1)	2(1)	7(1)
C(10)	20(1)	22(1)	17(1)	2(1)	0(1)	9(1)
C(11)	23(1)	24(1)	22(1)	6(1)	4(1)	12(1)
C(12)	20(1)	28(1)	27(1)	5(1)	-1(1)	12(1)
C(13)	20(1)	25(1)	21(1)	1(1)	-3(1)	8(1)
C(14)	18(1)	19(1)	18(1)	3(1)	1(1)	7(1)
C(15)	14(1)	19(1)	22(1)	-2(1)	-1(1)	4(1)
C(16)	20(1)	24(1)	23(1)	-2(1)	-5(1)	8(1)
C(17)	21(1)	24(1)	39(1)	-2(1)	-4(1)	11(1)
C(18)	20(1)	27(1)	39(1)	-13(1)	-2(1)	10(1)
C(19)	23(1)	31(1)	23(1)	-8(1)	-1(1)	8(1)
C(20)	19(1)	24(1)	23(1)	-1(1)	-2(1)	6(1)
C(21)	30(1)	34(1)	38(1)	-1(1)	2(1)	21(1)
C(22)	19(1)	24(1)	16(1)	-2(1)	-1(1)	8(1)
C(23)	14(1)	20(1)	21(1)	-2(1)	-3(1)	9(1)
C(24)	17(1)	22(1)	21(1)	0(1)	-1(1)	9(1)
C(25)	16(1)	26(1)	25(1)	-5(1)	-4(1)	12(1)
C(26)	23(1)	22(1)	33(1)	-6(1)	-3(1)	12(1)
C(27)	22(1)	21(1)	31(1)	3(1)	1(1)	11(1)
C(28)	15(1)	21(1)	22(1)	0(1)	-1(1)	8(1)
C(29)	17(1)	16(1)	23(1)	3(1)	1(1)	5(1)
C(30)	20(1)	19(1)	22(1)	3(1)	0(1)	8(1)
C(31)	21(1)	19(1)	27(1)	1(1)	4(1)	6(1)
C(32)	26(1)	24(1)	21(1)	-1(1)	1(1)	6(1)
C(33)	24(1)	30(1)	25(1)	3(1)	-6(1)	9(1)
C(34)	21(1)	25(1)	28(1)	3(1)	-2(1)	10(1)
C(35)	27(1)	31(1)	28(1)	-8(1)	-1(1)	16(1)
C(36)	20(1)	14(1)	18(1)	-2(1)	-2(1)	7(1)
C(37)	20(1)	22(1)	20(1)	0(1)	2(1)	10(1)
C(38)	29(1)	24(1)	16(1)	2(1)	1(1)	12(1)

C(39)	27(1)	20(1)	23(1)	0(1)	-7(1)	10(1)
C(40)	20(1)	19(1)	27(1)	0(1)	-2(1)	9(1)
C(41)	21(1)	19(1)	18(1)	1(1)	1(1)	9(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^{-3}) for compound **43**

	x	y	z	U(eq)
H(2N)	763(18)	7701(18)	2738(5)	23
H(1)	1390(16)	10672(16)	2514(5)	20
H(2)	2779(16)	9102(17)	2044(5)	21
H(4)	2506	13250	2273	28
H(5)	4522	15547	1931	35
H(6)	6926	15711	1732	36
H(7)	7318	13578	1884	31
H(8)	5295	11257	2216	25
H(10)	3783	8534	2741	24
H(12)	7760	10474	3523	30
H(13)	7020	12169	3857	28
H(16)	4193	13524	3109	28
H(17)	3820	15456	3467	34
H(18)	4023	15772	4274	35
H(19)	4643	14147	4724	34
H(20A)	5046	12230	4368	29
H(21A)	5409	7254	2778	48
H(21B)	7020	8063	3073	48
H(21C)	6959	8764	2574	48
H(22)	1654	9880	3618	25
H(24)	1404	6754	1627	24
H(26)	-327	2087	1883	30
H(27)	-889	2460	2647	29
H(30)	-1961	5847	2974	25

H(31)	-2360	6246	3751	29
H(32)	-1042	5716	4344	32
H(33)	598	4683	4155	34
H(34)	977	4242	3381	30
H(35A)	2309	4644	1199	42
H(35B)	879	4788	976	42
H(35C)	622	3085	1118	42
H(37)	2561	9902	1272	25
H(38)	1016	10003	664	28
H(39)	-1598	9374	800	29
H(40)	-2669	8660	1549	27
H(41)	-1151	8502	2152	24

Table 6. Torsion angles [°] for compound **43**

C(22)-N(1)-C(1)-C(3)	128.26(11)
C(9)-N(1)-C(1)-C(3)	-48.74(14)
C(22)-N(1)-C(1)-C(2)	-102.88(12)
C(9)-N(1)-C(1)-C(2)	80.12(13)
C(23)-N(2)-C(2)-C(36)	76.20(13)
C(23)-N(2)-C(2)-C(1)	-164.64(10)
N(1)-C(1)-C(2)-N(2)	32.55(13)
C(3)-C(1)-C(2)-N(2)	162.40(9)
N(1)-C(1)-C(2)-C(36)	154.15(9)
C(3)-C(1)-C(2)-C(36)	-76.00(11)
N(1)-C(1)-C(3)-C(4)	-107.76(12)
C(2)-C(1)-C(3)-C(4)	121.97(11)
N(1)-C(1)-C(3)-C(8)	72.63(13)
C(2)-C(1)-C(3)-C(8)	-57.64(14)
C(8)-C(3)-C(4)-C(5)	0.67(17)
C(1)-C(3)-C(4)-C(5)	-178.95(11)
C(3)-C(4)-C(5)-C(6)	-0.43(19)
C(4)-C(5)-C(6)-C(7)	-0.35(19)
C(5)-C(6)-C(7)-C(8)	0.87(19)
C(6)-C(7)-C(8)-C(3)	-0.61(18)

C(4)-C(3)-C(8)-C(7)	-0.15(17)
C(1)-C(3)-C(8)-C(7)	179.46(11)
C(22)-N(1)-C(9)-C(10)	121.97(12)
C(1)-N(1)-C(9)-C(10)	-61.06(15)
C(22)-N(1)-C(9)-C(14)	-56.78(15)
C(1)-N(1)-C(9)-C(14)	120.18(12)
C(14)-C(9)-C(10)-C(11)	-2.74(17)
N(1)-C(9)-C(10)-C(11)	178.50(10)
C(9)-C(10)-C(11)-C(12)	3.31(17)
C(9)-C(10)-C(11)-C(21)	-175.59(11)
C(10)-C(11)-C(12)-C(13)	-1.13(18)
C(21)-C(11)-C(12)-C(13)	177.76(12)
C(11)-C(12)-C(13)-C(14)	-1.65(19)
C(12)-C(13)-C(14)-C(9)	2.22(17)
C(12)-C(13)-C(14)-C(15)	-177.98(11)
C(10)-C(9)-C(14)-C(13)	-0.06(17)
N(1)-C(9)-C(14)-C(13)	178.67(10)
C(10)-C(9)-C(14)-C(15)	-179.84(11)
N(1)-C(9)-C(14)-C(15)	-1.10(18)
C(13)-C(14)-C(15)-C(20)	-45.85(16)
C(9)-C(14)-C(15)-C(20)	133.92(12)
C(13)-C(14)-C(15)-C(16)	130.40(12)
C(9)-C(14)-C(15)-C(16)	-49.82(17)
C(20)-C(15)-C(16)-C(17)	-0.02(18)
C(14)-C(15)-C(16)-C(17)	-176.34(11)
C(15)-C(16)-C(17)-C(18)	-0.42(19)
C(16)-C(17)-C(18)-C(19)	0.46(19)
C(17)-C(18)-C(19)-C(20)	-0.07(19)
C(18)-C(19)-C(20)-C(15)	-0.37(19)
C(16)-C(15)-C(20)-C(19)	0.42(18)
C(14)-C(15)-C(20)-C(19)	176.82(11)
C(9)-N(1)-C(22)-O(1)	177.25(12)
C(1)-N(1)-C(22)-O(1)	0.13(18)
C(2)-N(2)-C(23)-C(24)	-9.43(17)
C(2)-N(2)-C(23)-C(28)	169.31(10)
N(2)-C(23)-C(24)-C(25)	179.43(10)

C(28)-C(23)-C(24)-C(25)	0.68(17)
C(23)-C(24)-C(25)-C(26)	1.56(17)
C(23)-C(24)-C(25)-C(35)	-175.85(11)
C(24)-C(25)-C(26)-C(27)	-2.66(17)
C(35)-C(25)-C(26)-C(27)	174.73(12)
C(25)-C(26)-C(27)-C(28)	1.56(19)
C(26)-C(27)-C(28)-C(23)	0.71(18)
C(26)-C(27)-C(28)-C(29)	-176.98(11)
N(2)-C(23)-C(28)-C(27)	179.42(11)
C(24)-C(23)-C(28)-C(27)	-1.80(16)
N(2)-C(23)-C(28)-C(29)	-2.88(16)
C(24)-C(23)-C(28)-C(29)	175.90(11)
C(27)-C(28)-C(29)-C(30)	-122.39(13)
C(23)-C(28)-C(29)-C(30)	59.97(15)
C(27)-C(28)-C(29)-C(34)	57.64(16)
C(23)-C(28)-C(29)-C(34)	-120.00(13)
C(34)-C(29)-C(30)-C(31)	1.67(17)
C(28)-C(29)-C(30)-C(31)	-178.30(11)
C(29)-C(30)-C(31)-C(32)	0.15(18)
C(30)-C(31)-C(32)-C(33)	-1.48(19)
C(31)-C(32)-C(33)-C(34)	1.0(2)
C(32)-C(33)-C(34)-C(29)	0.9(2)
C(30)-C(29)-C(34)-C(33)	-2.19(18)
C(28)-C(29)-C(34)-C(33)	177.78(11)
N(2)-C(2)-C(36)-C(37)	-135.71(11)
C(1)-C(2)-C(36)-C(37)	103.52(12)
N(2)-C(2)-C(36)-C(41)	44.98(14)
C(1)-C(2)-C(36)-C(41)	-75.79(12)
C(41)-C(36)-C(37)-C(38)	-1.70(17)
C(2)-C(36)-C(37)-C(38)	178.98(11)
C(36)-C(37)-C(38)-C(39)	1.08(18)
C(37)-C(38)-C(39)-C(40)	0.35(18)
C(38)-C(39)-C(40)-C(41)	-1.11(18)
C(39)-C(40)-C(41)-C(36)	0.47(17)
C(37)-C(36)-C(41)-C(40)	0.94(17)
C(2)-C(36)-C(41)-C(40)	-179.73(11)

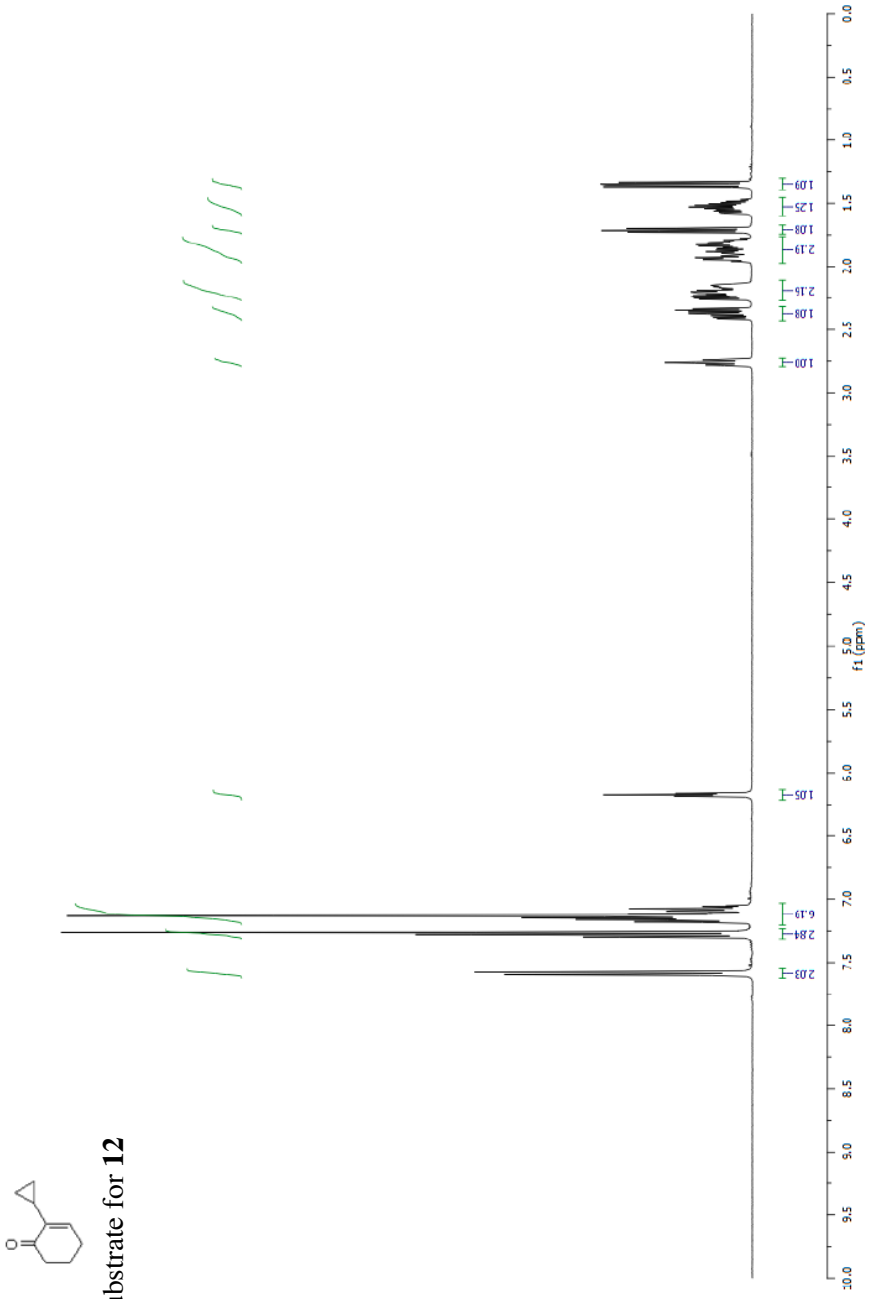
Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for compound **43** [Å and °]

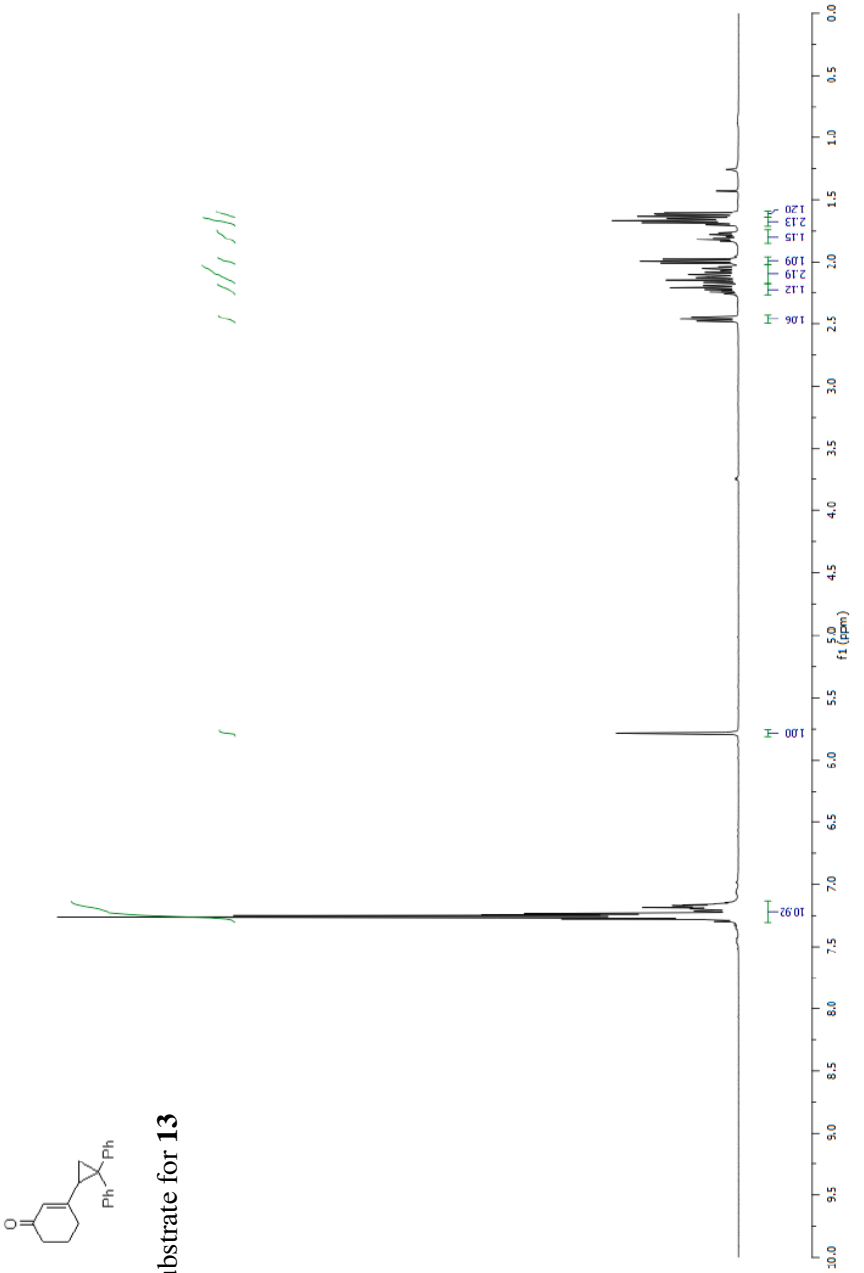
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(2)-H(2N)...N(1)	0.875(13)	2.349(15)	2.7729(14)	110.0(12)

Symmetry transformations used to generate equivalent atoms:

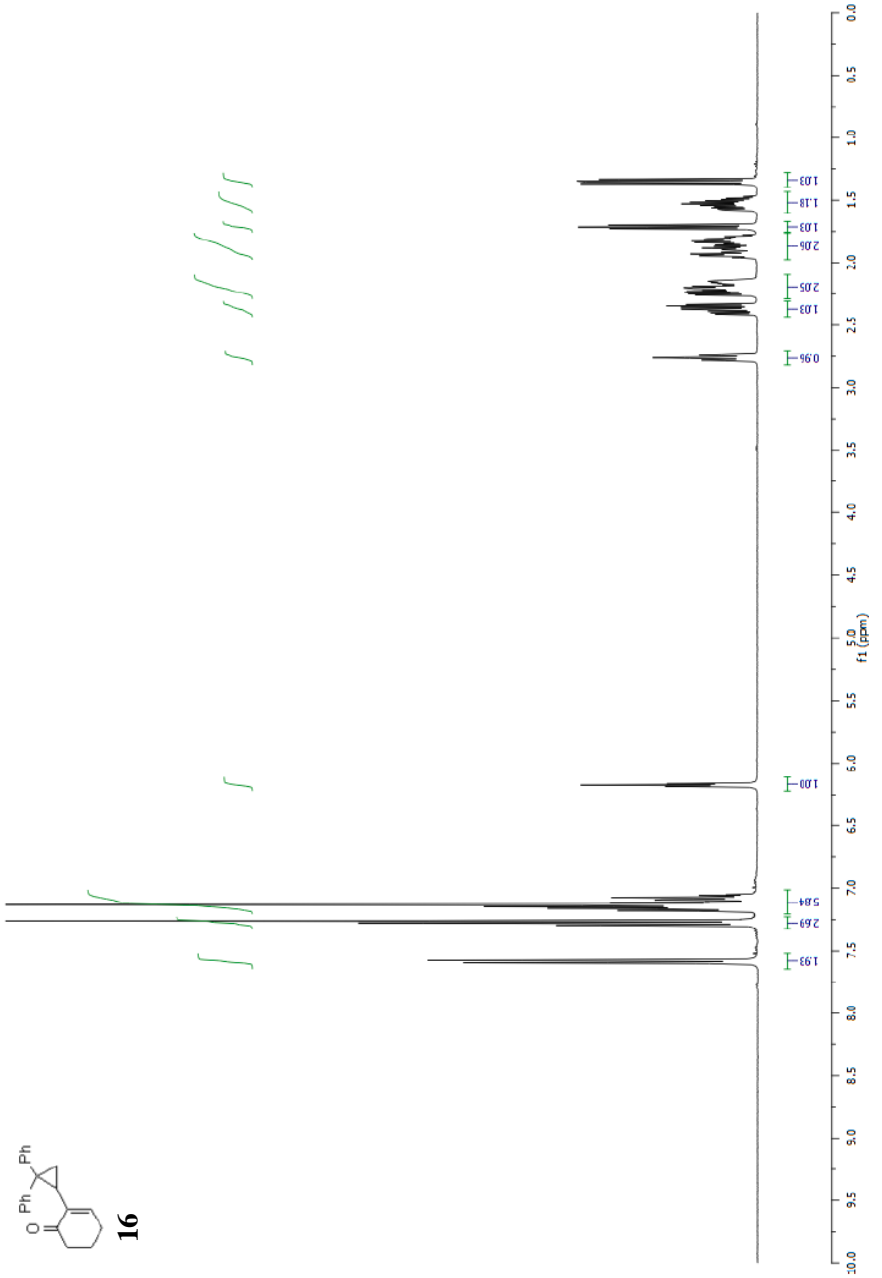
■ ^{1}H NMR Spectra

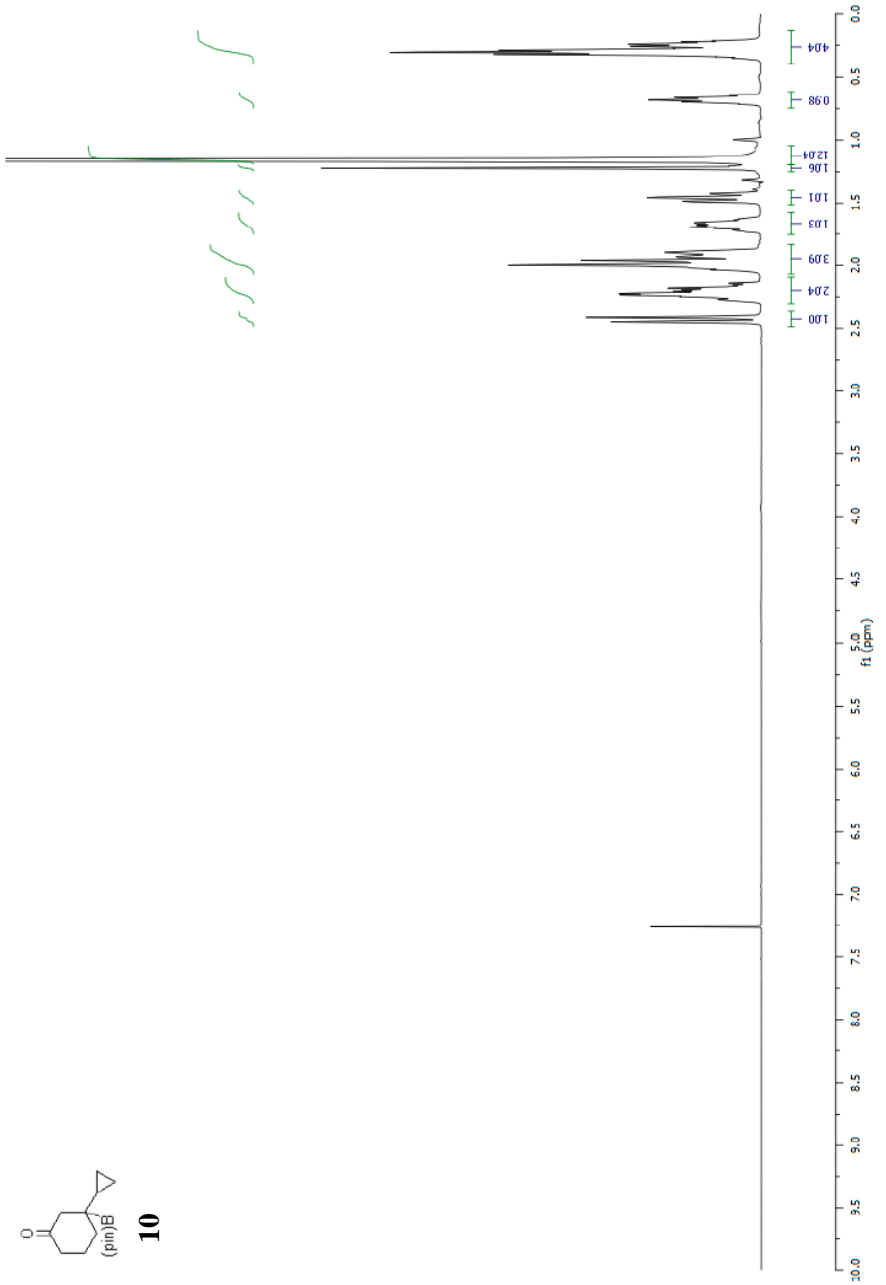


substrate for **12**

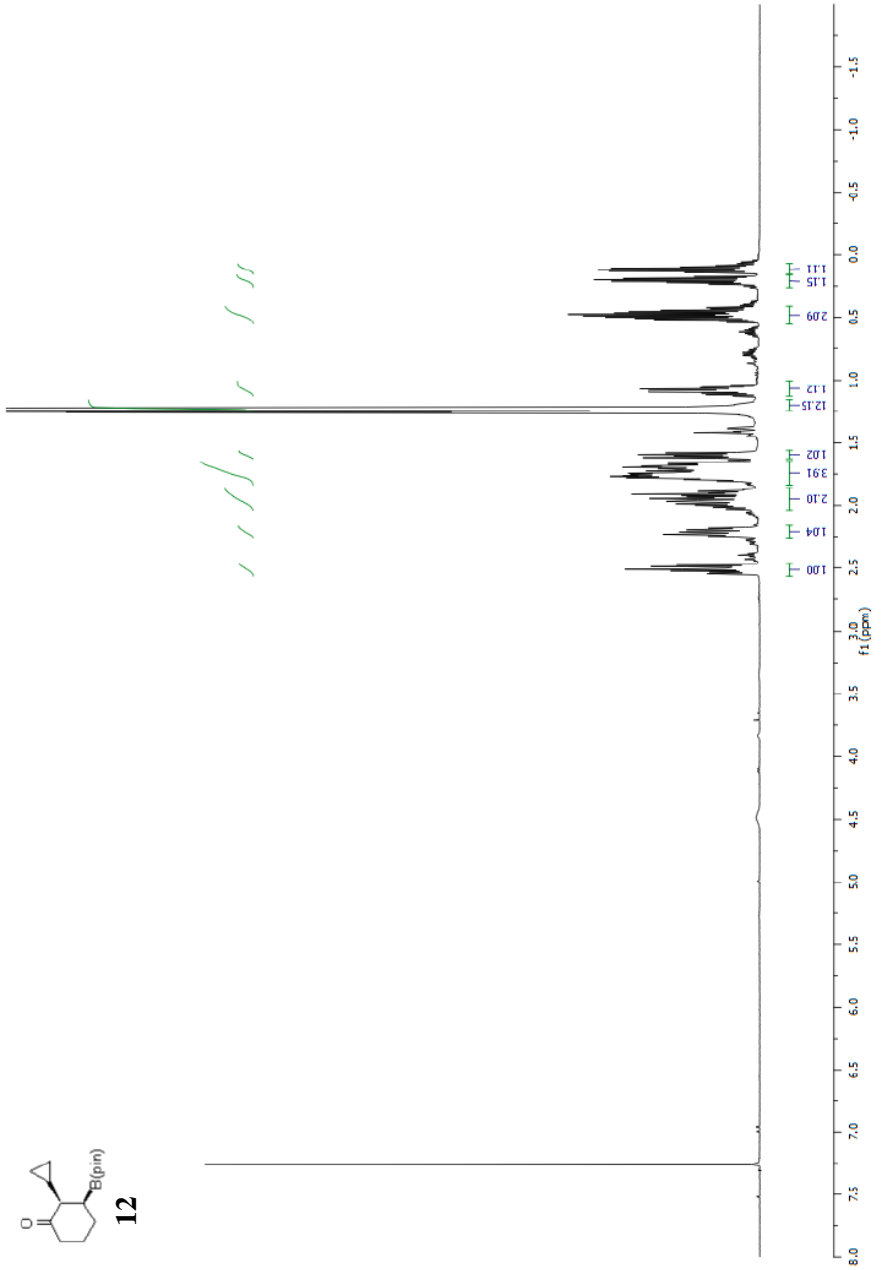


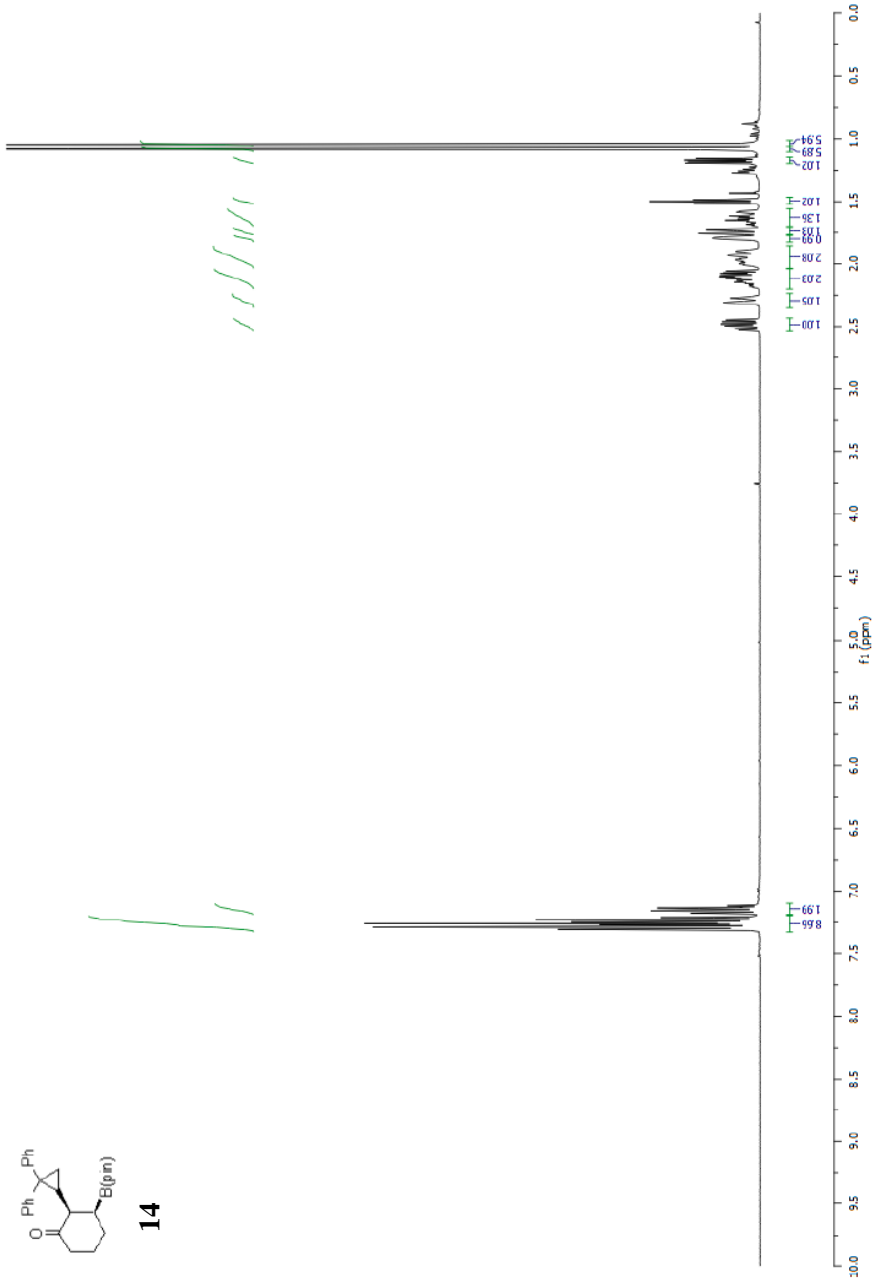
substrate for **13**

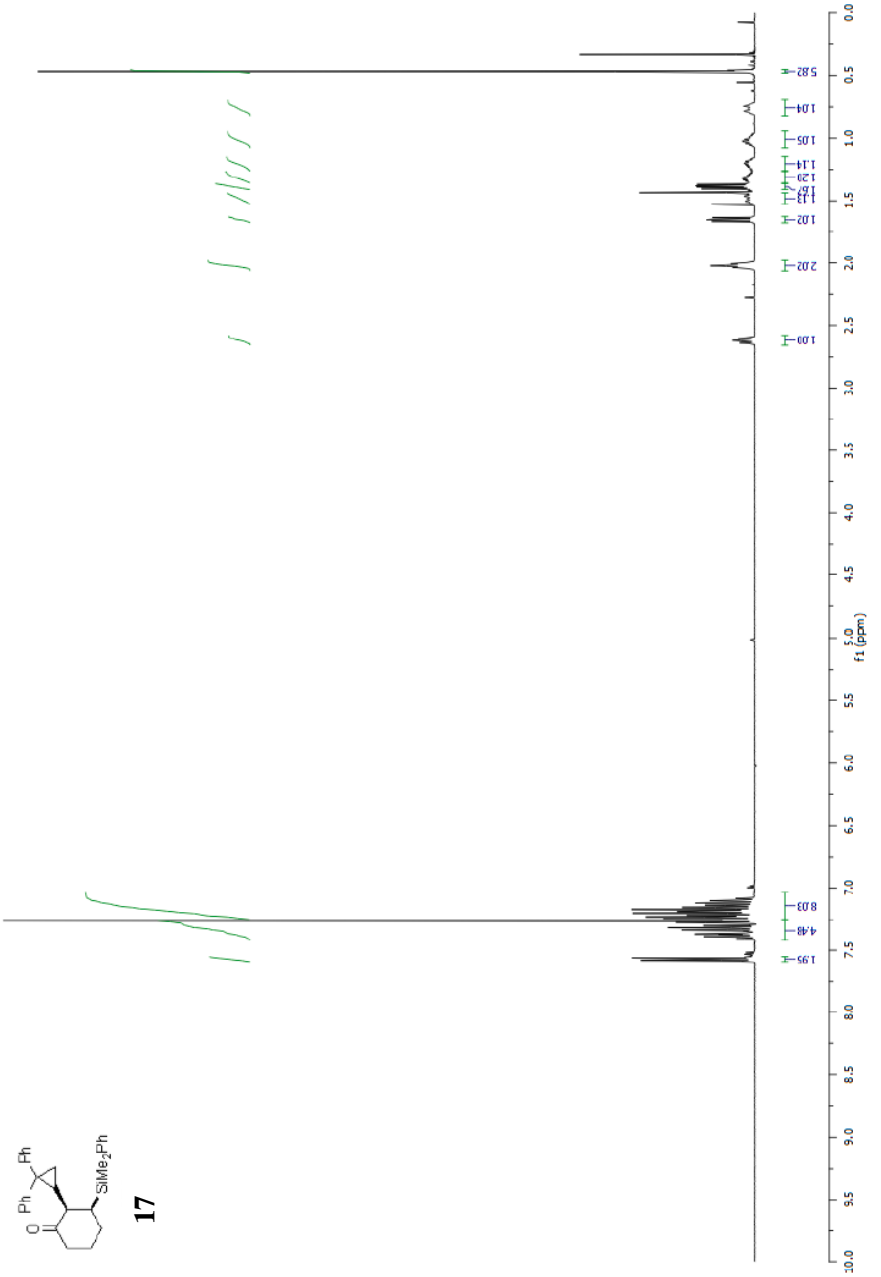

Ph
Ph
O
16
1.03
1.18
1.03
2.06
2.05
1.03
0.96
1.00
5.04
2.69
1.93
f1 (ppm)

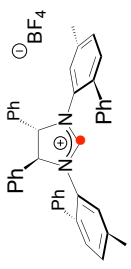


10

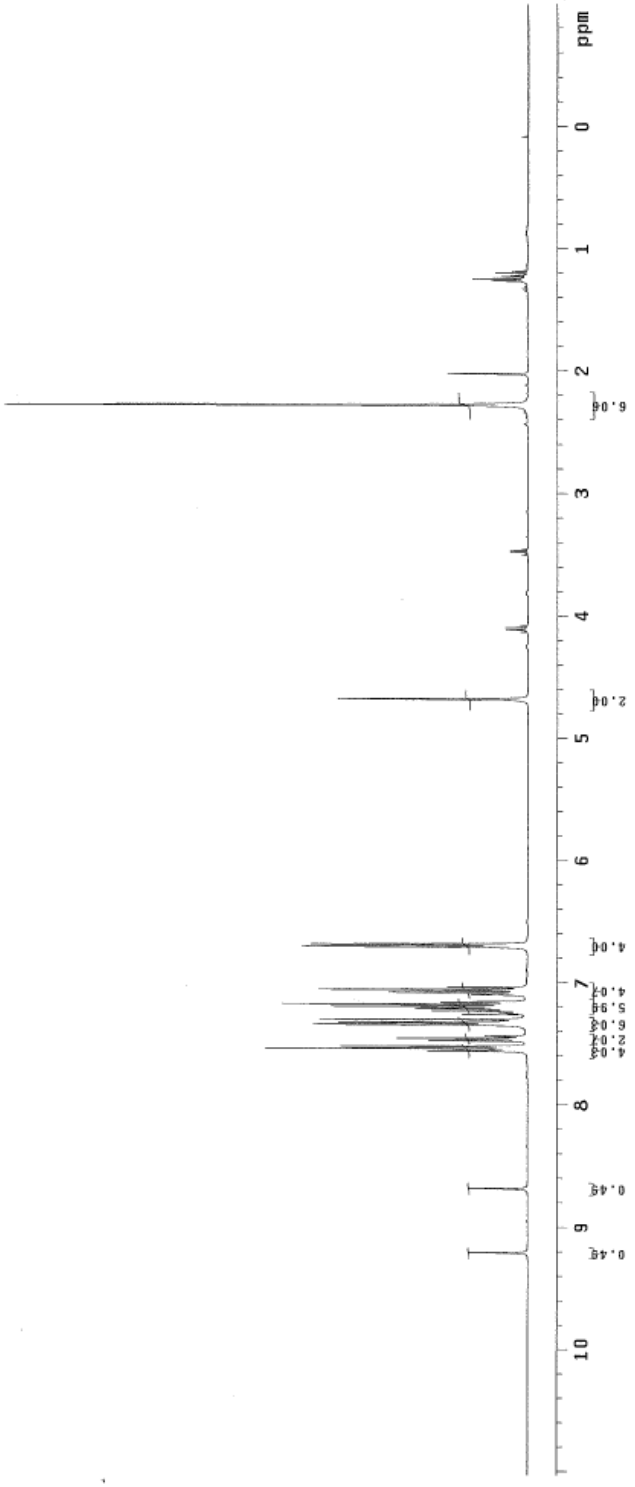

B(pin)
O
12
1.00
1.04
2.10
3.91
1.02
12.15
1.12
2.09
1.15
1.11
f1 (ppm)

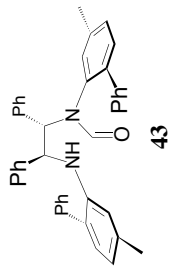

Ph
Ph
O
B(pin)
14
f1 (ppm)


Ph
Ph
O
SiMe2Ph
17
5.82
1.04
1.05
1.14
1.29
1.24
1.13
1.02
2.02
1.00
8.03
4.48
1.95
f1 (ppm)

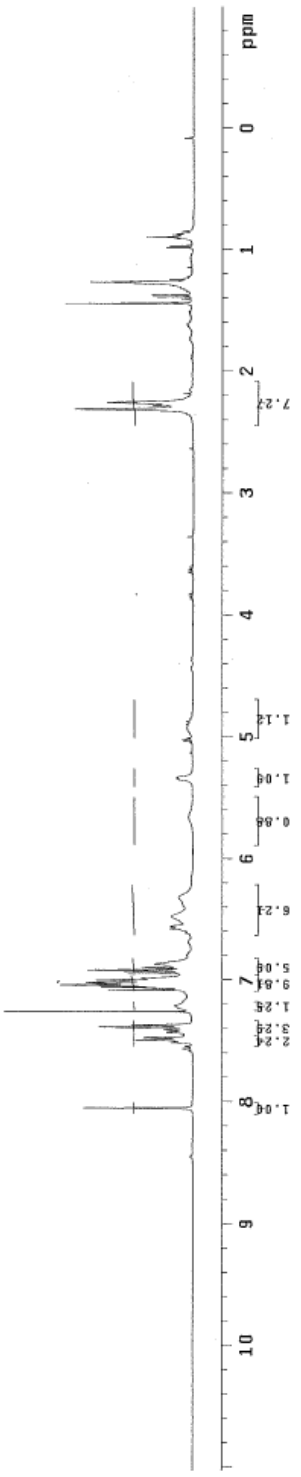


7c (^{13}C-labeled)

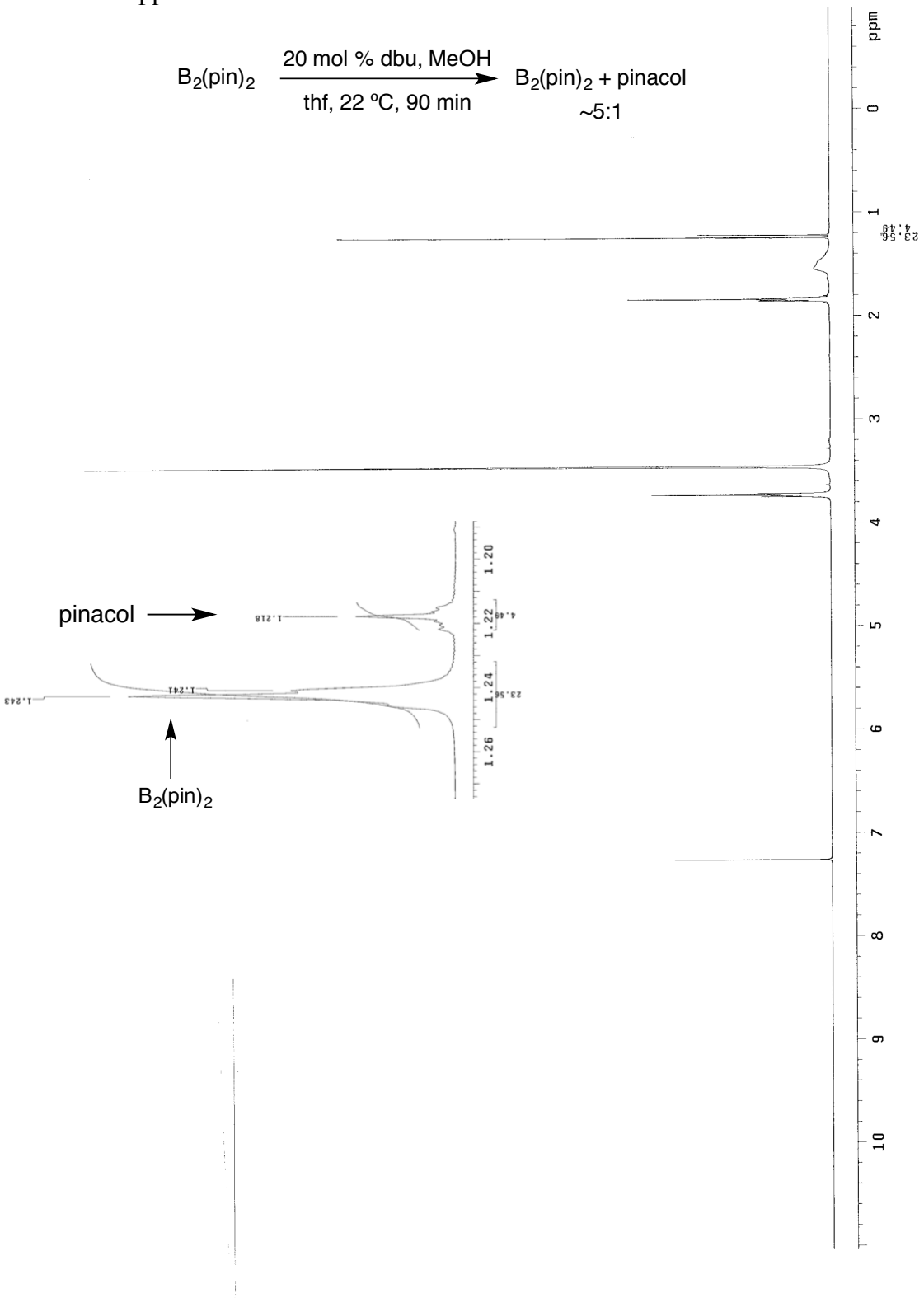



Ph
N
Ph
O
NH
Ph
Ph

43


ppm
0
1
2
3
4
5
6
7
8
9
10
7.22
1.12
1.06
6.86
6.24
5.06
9.81
1.25
3.24
2.24
1.06

Reaction of $B_2(pin)_2$ with dbu and MeOH in thf after 90 min is shown below. Free pinacol was observed at δ 1.22 ppm.



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