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Frustrated Lewis Pair Behavior of Monomeric (Boryl)iminomethanes Accessed from Isocyanide 1,1-Hydroboration

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Contents

S1. Synthetic Procedures.

S1.1. General considerations. All manipulations were carried out under an atmosphere of purified dinitrogen using standard Schlenk and glovebox techniques. Unless otherwise stated, reagent-grade starting materials were purchased from commercial sources and either used as received or purified by standard procedures.[1] Solvents were dried and deoxygenated according to standard procedures.[2] Benzene-d_6 (Cambridge Isotope Laboratories) was distilled from NaK alloy and stored over 4 Å molecular sieves under N_2 for at least 24 h prior to use. Celite 405 (Fisher Scientific) was dried under vacuum (24 h) at a temperature above 250 ˚C and stored in the glovebox prior to use. The (boryl)iminomethane[3] ^{Cy2}BIM and *m*-terphenyl isocyanide[4] CNAr^{Dipp2} were prepared as previously reported.

Solution ^{1}H, ^{13}C{^{1}H} and ^{11}B NMR spectra were recorded on a Bruker Avance 300, a Varian Mercury 400, a Jeol ECA 500, or a Varian X-SENS 500 spectrometer. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported in ppm relative to $SiMe_4$ (^{1}H and ^{13}C δ = 0.0 ppm) with reference to residual solvent resonances of 7.16 ppm (^{1}H) and 128.06 ppm (^{13}C) for C_6D_6. ^{11}B NMR chemical shifts were referenced externally to a solution of phenylboronic acid in acetone-d_6 (δ = 29 ppm vs. $BF_3{\cdot}Et_2O$ (δ = 0.0 ppm)). FTIR spectra were recorded on a Thermo-Nicolet iS10 FTIR spectrometer. Samples were prepared as C_6D_6 solutions injected into a ThermoFisher solution cell equipped with KBr windows. For solution FTIR spectra, solvent peaks were digitally subtracted from all spectra by comparison with an authentic spectrum obtained immediately prior to that of the sample. The following abbreviations were used for the intensities and characteristics of important IR absorption bands: vs = very strong, s = strong, m = medium, w = weak, vw = very weak; b = broad, vb = very broad, sh = shoulder. High-resolution mass spectrometry (HRMS) was performed using an Agilent 6230 ESI-TOFMS instrument running in positive ion mode. Combustion analyses were performed by Robertson Microlit Laboratories of Madison, NJ (USA).

S1.2. Synthesis of Boralactone 2a. A benzene solution of ^{Cy2}BIM (0.102 g, 0.170 mmol, 3 mL) was placed in an ampoule, degassed, and exposed to CO_2 gas (1 atm). Upon thawing the solution instantly changed in color from yellow to colorless. The ampoule was intermittently shaken over the course of 10 min, whereupon all volatiles were removed *in vacuo*. Dissolution of the resulting residue in 1 mL *n*-pentane and storage at –40 ˚C overnight provided colorless crystals, which were collected and dried *in vacuo*. Yield: 0.070 g, 0.108 mmol, 64%. ^{1}H NMR (499.8 MHz, C_6D_6, 20 ˚C): δ = 7.27 (t, 1H, *J* = 8 Hz, *p*-Ar), 7.25-7.18 (m, 5H), 7.11 (t, 1H, *J* = 8 Hz, *p*-Ar), 7.08 (dd, 1H, *J* = 8, 1 Hz, *m*-Ar), 7.02 (dd, 1H, *J* = 7, 3 Hz, *m*-Ar), 4.01 (septet, 1H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 3.32 (septet, 1H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 3.04 (d, 1H, *J* = 3 Hz, B-C*H*(Cy)-N), 2.59 (septet, 1H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 2.41 (septet, 1H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.69 (bd, 2H, *J* = 14 Hz, Cy), 1.58-1.49 (m, 6H, Cy), 1.55 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.48 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.39-1.32 (m, 2H, Cy), 1.30 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.28 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.18-1.13 (m, 8H, Cy), 1.08 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.07 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.00 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 0.93 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 0.83-0.77 (m, 2H, Cy), 0.50 (qt, 1H, *J* = 13, 2 Hz, Cy), 0.23 (qd, 1H, *J* = 12, 4 Hz, Cy) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 158.3 (*C*(=O)OR), 149.2, 149.1, 147.8, 146.7, 142.6, 141.7, 138.0, 137.7, 136.1, 132.1, 131.8, 129.2, 129.1, 126.7, 124.1, 123.4, 122.9, 122.2, 61.4, 38.0, 31.4, 31.2, 31.0, 30.8, 30.5, 30.4, 29.0, 27.9, 27.8, 27.0, 26.9, 26.9, 26.8, 26.8, 26.7, 26.6, 26.2, 26.2, 26.1 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 54.8 (bs) ppm. FTIR (C_6D_6, KBr

windows, 25 ˚C): 2962 (s), 2923 (vs), 2864 (m), 2853 (m), 1772 (vs), 1575 (w), 1460 (m), 1447 (m), 1420 (m), 1383 (w), 1360 (m), 1319 (w), 1304 (m), 1263 (w), 1245 (m), 1172 (m), 1166 (m), 1103 (m), 1070 (m), 1054 (w), 951 (m), 793 (w), 782 (w), 760 (m) cm^{-1}. Anal. Calc'd. for $C_{44}H_{60}NBO_2$: C, 81.84; H, 9.36; N, 2.17. Found: C, 81.81; H, 9.19; N, 2.18.

S1.3. Synthesis of Exocyclic Enamine 3. To a benzene solution of ^{Cy2}BIM (0.100 g, 0.166 mmol, 3 mL) was added 0.10 mL of a 3.1 M acetonitrile solution in C_6H_6 (0.31 mmol, 1.9 equiv). The solution immediately changed in color from bright yellow to colorless. After stirring for 20 min, all volatiles were removed under reduced pressure. The resulting colorless solid was dissolved in 1 mL *n*-pentane and stored at –40 ˚C for 24 h, affording colorless crystals, which were collected and dried *in vacuo*. Yield: 83 mg, 0.129 mmol, 78%. ^{1}H NMR (500.2 MHz, C_6D_6, 20 ˚C): δ = 7.32 (t, 1H, *J* = 8 Hz, *p*-Ar), 7.26-7.22 (m, 3H), 7.20-7.14 (m, 3H), 7.07 (dd, 1H, *J* = 8, 2 Hz, *m*-Ar), 7.02 (t, 1H, *J* = 8 Hz, *p*-Ar), 5.32 (s, 1H, N-*H*), 3.77 (septet, 1H, *J* = 7 Hz, C*H*$(CH_3)_2$), 3.40 (septet, 1H, *J* = 7 Hz, C*H*$(CH_3)_2$), 3.21 (d, 1H, *J* = 2 Hz, C_{alkene}-*H*), 3.19 (d, 1H, *J* = 2 Hz, C_{alkene}-*H*), 2.87 (d, 1H, *J* = 2 Hz, B-C*H*(Cy)-N), 2.78 (septet, 1H, *J* = 7 Hz, C*H*$(CH_3)_2$), 2.41 (septet, 1H, *J* = 7 Hz, C*H*$(CH_3)_2$), 1.63-1.56 (m, 7H, Cy), 1.48 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.45-1.39 (m, 4H, Cy), 1.37 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.33 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.30 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.23 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.18 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.15-1.10 (m, 4H, Cy), 1.09 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.00-0.90 (m, 3H, Cy), 0.89 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 0.75 (m, 1H, Cy), 0.63-0.49 (m, 2H, Cy), 0.42 (m, 1H, Cy) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 158.1, 149.0, 148.6, 147.6, 146.9, 144.2, 143.4, 142.8, 139.5, 137.6, 133.0, 131.8, 128.7, 128.6, 125.0, 123.4, 123.1, 122.9, 122.2, 64.7, 64.5, 40.9, 31.9, 31.4, 31.2, 31.0, 30.7, 29.9, 29.6, 28.7, 28.3, 27.6, 27.5, 27.3, 27.2, 26.8, 26.6, 26.2, 26.2, 26.0, 24.6, 23.5, 22.7, 22.0 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 48.0 (bs) ppm. FTIR (C_6D_6, KBr windows, 20 ˚C): ν(N-H) = 3440 cm^{-1}, also 2965 (s), 2924 (s), 2856 (m), 2852 (m), 1650 (s), 1602 (w), 1594 (w), 1574 (w), 1468 (m), 1448 (m), 1413 (m), 1382, 1363 (m), 1322 (m), 1302 (m), 1257 (m), 1213 (w), 1189 (w), 1178 (w), 1160 (w), 1128 (w), 1091 (w), 1072 (w), 1056 (w), 1036 (w), 1027 (w), 986 (w), 848 (w), 793 (w), 774 (w), 760 (m), 720 (w), 700 (w), 677 (w), 656 (w) cm^{-1}. HRMS (ESI-TOF): *m/z* calc'd for $C_{43}H_{64}N_2B$ $[M+H]^+$: 642.5193 Found: 642.5193. Anal. Calc'd for $C_{45}H_{63}N_2B$: C, 84.08; H, 9.88; N, 4.36. Found: C, 83.51; H, 9.92; N, 4.19.

S1.4. Synthesis of Heterocycle 4. To an *n*-pentane solution of ^{Cy2}BIM (0.100 g, 0.166 mmol, 2 mL) was added benzonitrile via microsyringe (0.019 mL, 0.184 mmol, 1.1 equiv). The solution was stirred for 30 min, during which time a colorless solid precipitated out of the solution. This solid was isolated via decantation of the solvent and washed with a single portion of *n*-pentane (2 mL) and dried *in vacuo* to afford **4** as an analytically pure colorless solid. Yield: 0.091 g, 0.129 mmol, 78%. Crystals suitable for X-ray diffraction were grown from a 2:1 Et_2O/C_6H_6 solution stored at –40 ˚C. ^{1}H NMR (499.8 MHz, C_6D_6, 20 ˚C): δ = 9.31 (bs, 1H, *Ph*C(NAr)=N), 7.26-7.21 (m, 2H), 7.15-6.99 (m, 8H), 6.82 (bs, 1H, *Ph*C(NAr)=N), 6.18 (bs, 1H, *Ph*C(NAr)=N), 3.37 (d, 1H, *J* = 4 Hz, B-C*H*(Cy)-N), 3.02 (septet, 1H, *J* = 7 Hz, C*H*$(CH_3)_2$), 2.90 (septet, 1H, *J* = 7 Hz, C*H*$(CH_3)_2$), 2.76 (septet, 1H, *J* = 7 Hz, C*H*$(CH_3)_2$), 2.30 (septet, 1H, *J* = 7 Hz, C*H*$(CH_3)_2$), 2.23 (bd, 1H, *J* = 15 Hz, Cy), 2.06-1.90 (m, 2H, Cy), 1.76-1.62 (m, 4H, Cy), 1.53-1.38 (m, 7H, Cy), 1.43 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.31 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 1.22 (d, 2H, *J* = 14 Hz, Cy), 1.13-1.10 (m, 2H, Cy), 1.05 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 0.96 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 0.88 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 0.87 (d, 3H, *J* = 7 Hz, CH(C*H*$_3)_2$), 0.73 (d, 3H, *J*

= 7 Hz, CH(CH_3)$_2$), 0.63 (d, 3H, J = 7 Hz, CH(CH_3)$_2$), 0.63-0.52 (m, 2H, Cy), 0.25-0.13 (m, 2H, Cy). *Note: Two phenyl resonances cannot be conclusively assigned. We believe these resonances are coincident with multiplets between 7.26-7.21 ppm and 7.15-6.99 ppm, which arise from terphenyl unit aryl resonances.* ^{13}C{^{1}H} NMR (125.8 MHz, C_6D_6, 20 ˚C): δ = 182.1 (*C*=N), 149.6, 148.4, 147.3, 147.1, 143.0, 142.0, 141.1, 138.4, 136.0, 134.8, 133.2, 133.1, 130.9, 129.3, 129.2, 126.4, 124.0, 123.3, 123.2, 122.6, 70.6, 38.7, 31.9, 31.5, 31.3, 31.0, 30.6, 29.9, 29.2, 28.6, 27.8, 27.6, 26.8, 26.6, 26.4, 26.1, 25.8, 25.5, 23.1, 22.7, 22.4, 21.7 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 64.4 (bs) ppm. FTIR (C_6D_6, KBr windows, 25 ˚C): 2963 (s), 2924 (vs), 2864 (m), 2850 (m), 1578 (w), 1469 (s), 1445 (m), 1427 (m), 1407 (m), 1383 (w), 1361 (m), 1302 (m), 1251 (m), 1242 (m), 1184 (w), 1077 (w), 1057 (w), 1031 (w), 999 (w), 794 (w), 760 (m), 720 (m), 704 (m) cm^{-1}. HRMS (ESI-TOF, NCMe): *m/z* calc'd for $C_{50}H_{65}N_2B$: 704.5241. Found: 705.5321 [M+H]$^+$. Anal Calc'd for $C_{50}H_{65}N_2B$: C, 85.20; H, 9.29; N, 3.97. Found: C, 85.43; H, 9.11; N, 3.95.

S1.5. Synthesis of (Cy)((CH$_3$)$_3$CC≡C)BCH(Cy)NAr^{Dipp2} (5). To an *n*-pentane solution of ^{Cy2}BIM (0.075 g, 0.125 mmol, 2 mL) was added *t*-BuCCH (0.017 mL, 0.139 mmol, 1.1 equiv) via microsyringe. The solution was stirred for 15 min, whereupon all volatiles were removed *in vacuo*. The resulting residue was dissolved in 0.5 mL of 3:1 hexamethyldisiloxane/*n*-pentane and stored at –40 ˚C overnight, resulting in the formation of colorless crystals, which were collected and dried *in vacuo*. Yield: 0.063 g, 0.092 mmol, 74%. ^{1}H NMR (499.8 MHz, C_6D_6, 20 ˚C): δ = 7.32 (t, 2H, J = 8 Hz, *p*-Ar), 7.23 (d, 2H, J = 8 Hz, *m*-Ar), 7.22 (d, 2H, J = 8 Hz, *m*-Ar), 7.03 (d, 2H, J = 8 Hz, *m*-Ar), 6.78 (t, 1H, J = 8 Hz, *p*-Ar), 3.88 (d, 1H, J = 10 Hz, N-*H*), 3.18 (dd, 1H, J = 10, 8 Hz, B-C*H*(Cy)-N), 3.10 (septet, 4H, J = 7 Hz, C*H*(CH$_3$)$_2$), 1.84-1.81 (m, 2H, Cy), 1.76-1.42 (m, 8H, Cy), 1.43 (d, 6H, J = 7 Hz, CH(CH_3)$_2$), 1.39 (d, 6H, J = 7 Hz, CH(CH_3)$_2$), 1.38-1.05 (m, 8H, Cy), 1.12 (d, 6H, J = 7 Hz, CH(CH_3)$_2$), 1.10 (d, 6H, J = 7 Hz, CH(CH_3)$_2$), 1.04 (s, 9H, *t*-Bu), 1.00-0.82 (m, 4H, Cy) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 148.0, 147.9, 146.4, 138.8, 134.3, 132.4, 128.6, 126.8, 123.6, 123.5, 116.8, 87.8, 56.4, 44.6, 37.2, 31.8, 31.1, 30.9, 30.6, 30.5, 28.9, 28.6, 28.5, 27.9, 27.8, 27.4, 27.3, 27.1, 26.1, 26.0, 23.9, 23.6 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 68.1 (bs) ppm. FTIR (C_6D_6, KBr windows, 25 ˚C): ν(N-H) = 3352 (w), also 2961 (s), 2926 (s), 2866 (m), 2849 (m), 2174 (w, sh), 2155 (w), 1669 (w), 1578 (w), 1491 (w), 1461 (m), 1444 (m), 1412 (m), 1379 (w), 1360 (m), 1258 (m), 1055 (w), 761 (m) cm^{-1}. Anal. Calc'd for $C_{49}H_{70}NB$: C, 86.05; H, 10.31; N, 2.05. Found: C, 85.68; H, 10.74; N, 2.07.

S1.6. Synthesis of $^{9\text{-BBN}}$BIM·THF (1b·THF). CNAr^{Dipp2} (0.250 g, 0.590 mmol) was slurried in 5 mL Et_2O. To this slurry was added a solution of 9-BBN dimer in 4:1 Et_2O/THF (0.072 g, 0.295 mmol, 0.5 equiv, 5 mL) dropwise over the course of 5 min. The solution was stirred for 2 h, whereupon the solvent was removed *in vacuo*. Dissolution of the resulting residue in 7 mL 2:1 Et_2O/C_6H_6 and storage at –40 ˚C for 4 days resulted in the production of colorless crystals, which were collected and dried *in vacuo*. Yield: 0.272 g, 0.441 mmol, 75%. ^{1}H NMR (499.8 MHz, C_6D_6, 20 ˚C): δ = 8.52 (s, 1H, C$_{imine}$-*H*), 7.23 (t, 2H, J = 8 Hz, *p*-Dipp), 7.18 (d, 2H, J = 8 Hz, *m*-Ar), 7.12 (d, 4H, J = 8 Hz, *m*-Dipp), 7.04 (t, 1H, J = 8 Hz, *p*-Ar), 3.51 (m, 4H, THF), 3.03 (septet, 4H, J = 7 Hz, C*H*(CH$_3$)$_2$), 2.12 (m, 2H, 9-BBN), 1.80 (m, 4H, 9-BBN), 1.67 (m, 2H, 9-BBN), 1.48 (m, 4H, 9-BBN), 1.25 (d, 12H, J = 8 Hz, CH(CH_3)$_2$), 1.13 (d, 12H, J = 8 Hz, CH(CH_3)$_2$), 0.80 (bs, 2H, 9-BBN) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 193.5 (*C*$_{imine}$), 153.5, 146.8, 139.0, 131.7, 130.9, 127.9, 122.8, 122.5, 70.2, 31.8, 30.9, 25.5, 25.0, 24.5,

23.6, 22.8 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 7.5 (s) ppm. FTIR (C_6D_6, KBr windows, 25 ˚C): 2961 (s), 2921 (m), 2867 (m), 2852 (m, sh), 2838 (m, sh), 1601 (m), 1577 (m), 1462 (m), 1450 (m, sh), 1415 (m), 1382 (w), 1361 (m), 1353 (w, sh), 1252 (w), 1205 (w), 1188 (w), 1178 (w), 1120 (w), 1071 (w), 1056 (w), 1043 (w), 1017 (w), 914 (w), 868 (m), 846 (w), 759 (m), 679 (w) cm^{-1}. Anal. Calc'd for $C_{43}H_{60}NBO$: C, 83.60; H, 9.79; N, 2.27. Found: C, 82.98; H, 9.70; N, 2.48.

S1.7. Synthesis of (9-BBN)CH_2N(9-BBN)Ar^{Dipp2} (6). Benzene (5 mL) was added to solid $CNAr^{Dipp2}$ (0.068 g, 0.160 mmol) and 9-BBN dimer (0.040 g, 0.164 mmol, 1.0 equiv). The solution was stirred over the course of 3 h and gradually changed in color from colorless to light yellow. All volatile materials were then removed *in vacuo*. The resulting solid was then extracted three times with *n*-pentane (2 mL), leaving behind **6** as an off-white solid, which was dried *in vacuo*. Yield: 0.066 g, 0.099 mmol, 62%. Crystals suitable for X-ray diffraction were grown by storing an *n*-pentane solution at –40 ºC overnight. ^{1}H NMR (499.8 MHz, C_6D_6, 20 ˚C): δ = 7.28 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.23-7.21 (m, 4H), 7.17 (d, 2H, *J* = 8 Hz, *m*-Ar), 7.07 (t, 1H, *J* = 8 Hz, *p*-Ar), 3.45 (s, 2H, B-C*H*$_2$-N), 3.10 (septet, 2H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 3.07 (septet, 2H, *J* = 7 Hz, C*H*(CH$_3$)$_2$), 1.90-1.87 (m, 6H, BBN), 1.85-1.67 (m, 10H, BBN), 1.50-1.45 (m, 4H, BBN), 1.35-1.29 (m, 3H, BBN), 1.34 (d, 6H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.26 (d, 6H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.10 (d, 6H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.06 (d, 6H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 0.98-0.91 (m, 4H, Cy), –1.30 (s, 1H, BBN) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 147.1, 146.9, 146.8, 140.8, 137.8, 134.9, 128.4, 127.8, 127.7, 124.2, 123.6, 123.2, 49.0, 38.2, 34.1, 33.6, 33.1, 31.3, 31.0, 30.5, 30.2, 26.9, 26.1, 23.8, 23.5, 22.9, 22.7 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 63.6 (bs), 46.8 (bs) ppm. FTIR (C_6D_6, KBr windows, 20 ˚C): 2961 (s), 2925 (s), 2899 (m, sh), 2886 (m, sh), 2870 (m, sh), 2844 (m), 2739 (b, m), 1616 (m), 1572 (w), 1551 (w), 1486 (w, sh), 1467 (m), 1450 (s), 1413 (m), 1398 (w, sh), 1383 (m), 1361 (w), 1275 (m), 1249 (m), 1184 (w), 1067 (w), 1053 (w), 1037 (w), 971 (w), 859 (w), 794 (w), 763 (m), 729 (w), 687 (w), 663 (w), 642 (w) cm^{-1}. Anal. Calc'd for $C_{47}H_{67}NB_2$: C, 84.55; H, 10.11; N, 2.10. Found: C, 85.02; H, 10.56; N, 2.00.

S1.8. Synthesis of Boralactone 2b. A benzene solution of $^{9\text{-BBN}}$BIM·THF (0.114 g, 0.185 mmol, 5 mL) was placed in an ampoule, degassed, and exposed to 1 atm CO_2 gas. The ampoule was intermittently shaken over the course of 15 min, whereupon all volatiles were removed *in vacuo*. The resulting residue was washed with 3 mL *n*-pentane and dried *in vacuo*, affording **2b** as a colorless solid. Yield: 0.102 g, 0.173 mmol, 93%. Crystals suitable for X-ray diffraction were grown by storing an *n*-pentane solution at –40 ˚C overnight. ^{1}H NMR (499.8 MHz, C_6D_6, 20 ˚C): δ = 7.27-7.18 (m, 6H), 7.14-7.11 (m, 2H), 7.04 (dd, 1H, *J* = 7, 1 Hz), 3.83 (septet, 1H, *J* = 7 Hz, CH(CH$_3$)$_2$), 3.53 (septet, 1H, *J* = 7 Hz, CH(CH$_3$)$_2$), 3.38 (d, 1H, *J* = 3 Hz, B-C*H*-N), 2.65 (septet, 1H, *J* = 7 Hz, CH(CH$_3$)$_2$), 2.43 (septet, 1H, *J* = 7 Hz, CH(CH$_3$)$_2$), 1.94 (m, 1H, bicycloalkyl), 1.67 (m, 2H, bicycloalkyl), 1.57 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.47 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.36-1.15 (m, 7H, bicycloalkyl), 1.33 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.19 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.08 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.05 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 1.04 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 0.96 (d, 3H, *J* = 7 Hz, CH(C*H*$_3$)$_2$), 0.92 (m, 2H, bicycloalkyl), 0.45 (m, 1H, bicycloalkyl), 0.11 (t, 1H, *J* = 14 Hz, bicycloalkyl) ppm. *Note: Peak assignments of bicycloalkyl backbone protons are tentative*. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 158.2 (B-*C*(O)-OR), 149.4, 149.3, 147.5, 147.0, 142.7, 141.7, 137.6, 136.9, 136.3, 132.3, 132.1, 129.4, 128.9, 126.6, 124.5, 123.7, 122.7, 121.8, 59.7, 31.8, 31.4, 31.4, 30.8, 28.4, 27.4, 27.2, 26.9, 26.4, 26.2, 25.3, 24.0, 23.7, 23.6, 23.3, 22.3, 22.1, 19.9 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ

= 55.7 (s) ppm. FTIR (C_6D_6, KBr windows, 20 ˚C): ν(C=O) = 1772 (vs) cm^{-1}, also 2960 (s), 2925 (s), 2865 (m), 1575 (w), 1466 (m), 1421 (m), 1384 (m), 1360 (m), 1326 (w), 1302 (m), 1293 (w, sh), 1263 (m), 1248 (w), 1239 (w), 1215 (w), 1171 (w), 1148 (w), 1112 (m), 1081 (w), 1067 (w), 1055 (w), 957 (w), 950 (w), 940 (w), 907 (w), 848 (w), 794 (w), 781 (w), 768 (w), 760 (m) cm^{-1}. Anal. Calc'd for $C_{40}H_{52}NBO_2$: C, 81.48; H, 8.89; N, 2.38. Found: C, 81.62; H, 9.40; N, 2.49.

Synthesis of Borninic Acid 7. To a benzene solution of $^{9\text{-BBN}}$BIM·THF (0.082 g, 0.133 mmol, 3 mL) was added deionized H_2O via microsyringe (0.010 mL, 0.556 mmol, 4.2 equiv). The solution was shaken intermittently over the course of 1 h, whereupon all volatiles were removed *in vacuo*. Dissolution of the resulting residue in 2 mL Et_2O and storage at –40 ˚C for 1 week produced colorless crystals, which were collected and dried *in vacuo*. Yield: 0.012 g, 0.021 mmol, 16%. ^{1}H NMR (499.8 MHz, C_6D_6, 20 ˚C): δ = 7.29 (t, 2H, *J* = 8 Hz, *m*-Ar), 7.23 (dd, 2H, *J* = 8, 2 Hz, *m*-Ar), 7.19-7.17 (m, 4H), 6.95 (t, 1H, *J* = 8 Hz, *p*-Ar), 6.11 (bs, 1H, O-*H*), 3.38 (d, 1H, *J* = 11 Hz, N-*H*), 3.01 (septet, 2H, *J* = 7 Hz, C*H*$(CH_3)_2$), 2.99 (septet, 2H, *J* = 7 Hz, C*H*$(CH_3)_2$), 2.60 (dd, 1H, *J* = 11, 3 Hz, R_2B-C*H*R-NHAr), 2.07 (m, 1H, bicycloalkyl), 1.52-1.42 (m, 4H, bicycloalkyl), 1.39-1.30 (m, 6H, bicycloalkyl), 1.34 (d, 6H, *J* = 7 Hz, CH(C$H_3)_2$), 1.31 (d, 6H, *J* = 7 Hz, CH(C$H_3)_2$), 1.26-1.18 (m, 4H, bicycloalkyl), 1.07 (d, 6H, *J* = 7 Hz, CH(C$H_3)_2$), 1.06 (d, 6H, *J* = 7 Hz, CH(C$H_3)_2$) ppm. *Note: Peak assignments of bicycloalkyl backbone protons are tentative.* ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 147.6, 147.4, 146.0, 137.6, 131.8, 129.1, 128.4, 127.6, 124.0, 123.6, 120.0, 38.6, 36.4, 34.0, 31.7, 31.2, 31.1, 30.3, 28.6, 27.0, 26.7, 26.4, 26.2, 25.0, 24.2, 23.4, 22.8, 21.4 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 53.4 (s) ppm. FTIR (C_6D_6, KBr windows, 20 ˚C): ν(O-H) = 3485 (b, w) cm^{-1}, ν(N-H) = 3345 (w), also 2962 (s), 2925 (s), 2866 (m), 1578 (w), 1466 (m), 1417 (m), 1383 (m), 1361 (m), 1250 (w), 1229 (m), 1179 (w), 1117 (m), 1081 (w), 1055 (w), 1043 (w), 989 (w), 944 (w), 934 (w), 867 (w), 795 (w), 778 (w), 759 (m), 698 (w) cm^{-1}. HRMS (ESI-TOF, NCMe): *m/z* calc'd for $C_{39}H_{54}NBO$: 563.4298. Found: 564.4375 $[M+H]^+$. Anal. Calc'd for $C_{39}H_{54}NBO$: C, 83.10; H, 9.66; N, 2.48. Found: C: 81.91; H, 9.99; N, 2.38.

Synthesis of $^{\text{Pin}}$BIM (1c). A toluene (5 mL) solution of $CNAr^{Dipp2}$ (0.102 g, 0.240 mmol) and pinacolborane (0.34 mL, 2.33 mmol, 10.0 equiv) was placed in a sealed ampoule and heated to 100 ºC for 60 h. After cooling to room temperature, all volatiles were removed *in vacuo*. Fractional crystallization from 2:1 hexamethyldisiloxane/*n*-pentane solution provided light yellow crystals of $^{\text{Pin}}$BIM, which were collected and dried *in vacuo*. Yield: 0.037 g, 0.067 mmol, 28%. ^{1}H NMR (499.8 MHz, C_6D_6, 20 ˚C): δ = 7.85 (s, 1H, C_{imine}-*H*), 7.24 (t, 2H, *J* = 8 Hz, *p*-Ar), 7.16 (d, 2H, *J* = 8 Hz, *m*-Ar), 7.15 (d, 4H, *J* = 8 Hz, *m*-Ar), 7.03 (t, 1H, *J* = 8 Hz, *p*-Ar), 3.05 (septet, 4H, *J* = 7 Hz, C*H*$(CH_3)_2$), 1.36 (d, 12H, *J* = 7 Hz, CH(C$H_3)_2$), 1.15 (d, 12H, *J* = 7 Hz, CH(C$H_3)_2$), 0.72 (s, 12H, Pin –CH_3) ppm. ^{13}C{^{1}H} NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 168.2 (C_{imine}), 153.4, 147.1, 136.8, 130.4, 130.0, 128.4, 124.0, 122.9, 83.8, 31.3, 25.3, 24.4, 23.5 ppm. ^{11}B NMR (125.7 MHz, C_6D_6, 20 ˚C): δ = 26.0 (bs) ppm. FTIR (C_6D_6, KBr windows, 20 ˚C): 2961 (s), 2926 (m), 2905 (m, sh), 2867 (m), 1577 (w), 1463 (m), 1420 (m), 1382 (s), 1372 (s), 1362 (s), 1278 (w, sh), 1262 (m), 1143 (m), 1055 (w), 968 (m), 896 (w), 850 (m), 835 (w), 791 (w), 769 (m), 758 (m), 733 (w) cm^{-1}. Anal. Calc'd for $C_{37}H_{50}NBO_2$: C, 80.56; H, 9.14; N, 2.54. Found: C, 80.21; H, 9.02; N, 2.55.

S2. Results of Computational Studies.

S2.1. Computational Details.

Density Functional Theory calculations on the (boryl)iminomethanes ^{Cy2}BIM (**1a**) and $^{9\text{-}BBN}$BIM·THF (**1b**·THF), their adducts with carbon dioxide **2a** and **2b**, and the putative zwitterionic intermediates in CO_2 capture **2a*** and **2b*** were performed with the Amsterdam Density Functional (ADF) program suite,[5,6] version 2013.99.[7] For all atoms, the triple-ζ Slater-type orbital TZ2P ADF basis set was utilized without frozen cores. The local density approximation (LDA) of Vosko, Wilk, and Nusair (VWN)[8] was coupled with the generalized gradient approximation (GCA) corrections described by Becke[9] and Perdew[10,11] for electron exchange and correlation, respectively. Crystallographic atomic coordinates were used as input where appropriate. Optimized geometries and molecular orbitals were visualized with the ADFView graphical routine of the ADF-GUI.[12]

S2.2. Hardware Specifics. DFT calculations were performed on a home-built 72-CPU (1 x 8 master, 8 x 8 slave) Rocks 4.3 Linux cluster featuring Intel Xeon E5335 Quad-Core 2.00 GHz processors. Job control was implemented with the Sun Grid Engine v. 5.3.

S2.3. Input

S2.3.1. Input for geometry optimization of ^{Cy2}BIM (1a)

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 <<< "
TITLE Cy2BIM

MAXMEMORYUSAGE 23000

RELATIVISTIC ZORA

CHARGE 0 0
SCF

DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
ATOMS
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C      -0.52407905      -1.69060415      -3.26787853
H      -0.41847060      -0.97243931      -4.10645783
N       0.88155178       0.00000000       0.88528208
C       0.00000000       0.00000000       0.00000000
H      -1.04854095       0.05622577       0.25650887
C       0.56444189       0.09400638       2.27792745
C       0.75511378      -1.02409897       3.10637211
C       0.52710315      -0.92040129       4.48490082
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C	-0.10225978	1.40178466	4.21653546
H	-0.44118122	2.33150176	4.65622269
C	0.10874295	1.30914923	2.83248243
C	1.15506355	-2.32249853	2.52153558
C	2.53327358	-2.64565412	2.38166279
C	2.88610549	-3.89970013	1.84915900
H	3.92433520	-4.18481876	1.74627704
C	1.90872067	-4.80626085	1.45222364
H	2.19975227	-5.76730381	1.04873064
C	0.56078321	-4.48561035	1.57150012
H	-0.17145814	-5.21843429	1.25861398
C	0.15556621	-3.24310328	2.09347522
C	3.63809415	-1.67773440	2.80144882
H	3.21598878	-0.71192675	3.14940191
C	4.43459535	-2.24464902	3.97808068
H	3.75159600	-2.45770270	4.82585171
H	5.18684686	-1.50301045	4.32000989
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H	5.13422528	-2.21638902	1.28455385
H	5.27444966	-0.53712551	1.92247621
H	3.95464725	-0.94430127	0.77238697
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H	-1.50466883	-1.88627345	2.52774582
C	-2.00015597	-3.82535028	3.24971614
H	-3.06579137	-3.53974089	3.37319939
H	-1.49054594	-3.70094261	4.23090646
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H	-2.08334846	-4.11321059	0.49840286
H	-1.52746924	-2.45198675	0.07368892
H	-3.09167930	-2.68245095	0.92338730
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C	-1.55150211	2.78726054	1.64767806
C	-1.81806609	3.90673722	0.83955178
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H	-1.01167088	5.52632482	-0.30849467
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C	-2.72862195	1.96677026	2.18211990
H	-2.37298558	1.03542257	2.66800320
C	-3.49498208	2.75885405	3.24724917
H	-2.80770598	3.06496654	4.06407832
H	-4.29706138	2.12829223	3.68737414
H	-3.95835984	3.66900600	2.80993689
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H	-4.24475762	2.36500441	0.63455269
H	-4.41357632	0.78118156	1.46840950
H	-3.11788379	1.01265515	0.24831831
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H	2.43610017	2.14541076	2.45318476
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H       3.98050322       3.95369621       2.83718455
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C       0.28809629       1.41671350      -2.24714587
H       0.59888948       2.17758096      -1.49613351
C      -1.17008165       1.72852310      -2.63642910
H      -1.81930137       1.68694754      -1.73517463
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C      -1.28311752       3.13054472      -3.24854469
H      -2.33055865       3.30474180      -3.57711391
H      -1.03549208       3.89491420      -2.48008456
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H      -0.40402043       4.32962705      -4.82928999
H      -0.66005000       2.60357138      -5.26616591
C       1.11051263       2.98021018      -4.05446682
H       1.75742797       3.05069193      -4.95592722
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C       1.22983814       1.57342238      -3.45489980
H       2.28274940       1.41194452      -3.13464149
H       0.98075955       0.83593081      -4.24569259
C       1.96492937      -1.70479532      -2.75039677
H       2.71492629      -1.58721402      -1.93803572
H       2.21731071      -0.98903351      -3.55683849
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C       0.55218677      -1.44267889      -2.19587006
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C       2.06822679      -3.12851950      -3.31574882
H       3.07303430      -3.27327175      -3.76715152
H       1.95442817      -3.86734244      -2.49264840
C       0.99448142      -3.37746348      -4.38351246
H       1.06008651      -4.43098295      -4.73121379
H       1.17767652      -2.71617254      -5.25843852
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GEOMETRY
 Iterations 300
 GO
END

BASIS
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 core none
END

END INPUT
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S2.3.2. Input for geometry optimization of Compound 2a

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TITLE Cy2BIM_CO2

MAXMEMORYUSAGE 23000

RELATIVISTIC ZORA

CHARGE 0 0
SCF

DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
ATOMS
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N       0.33037300       7.41985200       8.99352600
C       1.00891800       4.64816100       9.51955800
C       1.55519700       5.78491100      10.32844200
C       1.41163900       8.10133700      11.11944500
C      -0.17634300       4.02286600       9.96856300
C       1.67831800       4.17915400       8.37337300
C       1.07315000       7.10091300      10.18553100
C       2.50912900       5.53402800      11.32377100
H       2.85237000       4.67530000      11.42215300
C       2.37605100       7.79118900      12.07296900
H       2.64472000       8.44990200      12.67197500
C       0.65777700       9.38355000      11.24800200
C       1.03318000      10.54995000      10.56460100
C       2.94677900       6.53799200      12.15869100
H       3.62235500       6.37238700      12.77599800
C      -0.42640200       9.40230500      12.16487300
C      -1.07103900       7.07381000       8.65358900
H      -1.28413400       6.17246700       8.97384600
C      -0.87745300       4.45827600      11.25816500
H      -0.74655200       5.42518700      11.34940500
C      -2.08509800       8.08967600       9.21129700
H      -1.88492300       8.21522500      10.16239400
C       1.08158100       7.66434800       7.87598000
C       2.99749500       4.76562500       7.91383800
H       3.13816200       5.60412800       8.40122600
C      -1.13239800      10.58607100      12.34455900
H      -1.84576400      10.60951400      12.94077100
C      -0.68458600       2.95984100       9.22940600
H      -1.46655200       2.54056600       9.50806800
C       0.28956100      11.71745100      10.77575400
H       0.52277300      12.49588800      10.32348300
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H	-1.27756500	12.51366100	11.76158300
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H	-0.38145900	7.40604900	12.59678300
C	2.24934500	10.59621400	9.67481400
H	2.55014400	9.67597300	9.52294500
C	1.11250500	3.11162000	7.67509500
H	1.53284900	2.79463100	6.90846900
C	-0.05002700	2.52104600	8.09635300
H	-0.41172600	1.81623800	7.60919200
C	-0.12339600	8.35214900	14.39404600
H	0.81963500	8.49708600	14.28791100
H	-0.26870700	7.55464600	14.90832500
H	-0.51314800	9.10202400	14.84944300
C	-2.26846600	7.94807500	13.18718000
H	-2.66580700	8.68377700	13.65886900
H	-2.40541100	7.13808600	13.68392800
H	-2.67567700	7.86545200	12.32175300
C	-1.95877100	9.44838800	8.53180800
H	-1.07003500	9.80061300	8.69605700
H	-2.05791100	9.33134300	7.57402300
C	-0.24209400	3.79554500	12.48013500
H	-0.35283100	2.84375200	12.42175900
H	-0.66812800	4.11899300	13.27730300
H	0.69372800	4.00766500	12.50884300
C	1.94790900	11.23218900	8.30582900
H	1.23061300	10.75501300	7.88228400
H	2.73163300	11.18847400	7.75315100
H	1.69349500	12.14972700	8.42829200
C	4.15070700	3.81896400	8.26818100
H	4.15248000	3.65694700	9.21442300
H	4.98423700	4.21953300	8.01054400
H	4.03732700	2.98776900	7.80143400
C	-3.50100900	7.57560100	9.10814800
H	-3.58499300	6.76844700	9.63952300
H	-3.68810500	7.34432100	8.18488600
C	3.02098400	5.08454000	6.42129100
H	3.02962800	4.26626300	5.91932200
H	3.80779400	5.59458400	6.21539400
H	2.24031400	5.59332800	6.19045800
C	-2.37637800	4.20040800	11.27555700
H	-2.76787800	4.53392700	10.46494400
H	-2.76935100	4.64795800	12.02847500
H	-2.53792300	3.25659300	11.34423600
C	3.36947800	11.34939000	10.36350600
H	3.09019300	12.25170200	10.53507200
H	4.14522700	11.35657800	9.79801000
H	3.58265400	10.91705400	11.19371200
C	-2.98226300	10.45569000	9.01163400
H	-2.81654200	10.66832300	9.94341800
H	-2.89937700	11.27339300	8.49648200
C	-4.52614500	8.59290200	9.58355700
H	-5.41830500	8.24100000	9.43825400
H	-4.41410100	8.74002800	10.53577100
C	-4.38434700	9.89999300	8.85952100
H	-5.02424900	10.53673400	9.21447500
H	-4.57997800	9.77055600	7.91830800

```
B      -0.96685700       7.08182400       7.08649600
C      -1.95992509       6.79140851       6.02132896
C      -2.79558805       4.51073387       5.36382298
C      -2.02998825       5.30914455       6.43660947
C      -1.22779244       6.91248380       4.67084909
C      -1.99339223       6.11407312       3.59806269
C      -2.06345548       4.63180901       4.01334313
H      -2.95138480       7.18228861       5.92582824
H      -3.78708792       4.90150436       5.26829071
H      -2.84412252       3.48146690       5.65218717
H      -1.03852696       4.91829693       6.53222664
H      -2.53846473       5.22512033       7.37431496
H      -0.23629254       6.52171335       4.76638129
H      -1.17925803       7.94175076       4.38248488
H      -1.48491573       6.19809739       2.66035720
H      -2.98485349       6.50492082       3.50244554
H      -1.07199582       4.24092878       4.10884383
H      -2.59517017       4.07747133       3.26843426
END

GEOMETRY
 Iterations 300
 GO
END

BASIS
 type TZ2P
 core none
END

END INPUT
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S2.3.3. Input for geometry optimization of Compound 2a*

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$ADFBIN/adf -n8 \
 <<< "
TITLE Cy2BIM_CO2

MAXMEMORYUSAGE 23000

RELATIVISTIC ZORA

CHARGE 0 0
SCF

DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
ATOMS
```

O	2.17797669	7.92519584	7.75093539
O	0.17421755	7.50062554	6.74431373
N	0.27864406	7.39559922	9.00940963
C	1.18605839	4.62214987	9.55793258
C	1.55410150	5.81429621	10.40584909
C	1.35309757	8.15967506	11.12393465
C	0.06617366	3.82866817	9.92726094
C	2.01215972	4.22594291	8.47671643
C	1.03406182	7.12107759	10.21261991
C	2.45526943	5.59420035	11.45588996
H	2.86286790	4.59337464	11.58967995
C	2.28833621	7.88913714	12.13527215
H	2.57151059	8.69985233	12.80415981
C	0.72157268	9.52954155	11.14897274
C	1.25734868	10.60191663	10.39561048
C	2.85056810	6.62893259	12.29640789
H	3.58181203	6.45002913	13.08334057
C	-0.34595668	9.76412421	12.05933564
C	-1.11645476	6.97426129	8.70784743
H	-4.26970828	10.65424107	4.11614991
C	-0.75937442	4.12539467	11.18000670
H	-0.69643488	5.20602480	11.37414331
C	-1.31606480	5.17728948	6.16290235
C	-1.16226772	4.48052456	3.70270560
C	1.00626160	7.64411065	7.86550988
C	3.31699780	4.94266738	8.13766620
H	3.28795153	5.93724898	8.59932192
C	-0.91317852	11.04426780	12.11894418
H	-1.73842510	11.23294860	12.80490751
C	-0.24521889	2.69901372	9.15905344
H	-1.10866508	2.08997141	9.42352235
C	0.65289721	11.86418065	10.49154744
H	1.05435890	12.69087409	9.90608544
C	-0.43384483	12.08542345	11.32962980
H	-0.89246671	13.07251667	11.38635841
C	-0.83518923	8.70079979	13.04626835
H	-0.55045219	7.71570141	12.65032904
C	2.53068395	10.45651654	9.57059087
H	2.69766160	9.38957791	9.38626444
C	1.65610206	3.08566123	7.73967976
H	2.27845110	2.78023134	6.89911417
C	0.53304270	2.33400108	8.06418020
H	0.27065521	1.45540243	7.47490284
C	-0.14494815	8.86881084	14.41766742
H	0.94696194	8.80700346	14.34067602
H	-0.48153770	8.08632863	15.11410953
H	-0.39789299	9.84632625	14.85476722
C	-2.35818488	8.69440089	13.25945536
H	-2.69789409	9.59512602	13.78997501
H	-2.64466891	7.83060644	13.87582299
H	-2.90731266	8.63493152	12.31225338
C	-0.84475127	5.57326829	4.73496077
C	-2.81153142	4.78648456	6.15106505
C	-3.12004609	3.69922104	5.11194229
C	-0.17415610	3.40315199	12.41219968
H	-0.19699386	2.31339379	12.26280898
H	-0.76519848	3.63796081	13.31006615

H	0.86445604	3.69928462	12.60318522
C	2.45138065	11.13999754	8.19570000
H	1.57534358	10.80306918	7.62748296
H	3.34434656	10.89123516	7.60656169
H	2.40642713	12.23580078	8.28280982
C	4.51859885	4.17795859	8.73205206
H	4.43707344	4.07119198	9.82209010
H	5.45470747	4.71213987	8.51275535
H	4.59336275	3.16861846	8.29960694
C	-2.65293810	4.10997486	3.70776094
H	-0.73573732	4.27451755	6.44225493
H	-0.56486808	3.58127573	3.93459785
C	3.52420069	5.15440289	6.62819546
H	3.67188883	4.20262916	6.09677174
H	4.42217700	5.76525150	6.46200194
H	2.67629018	5.68161504	6.17488650
C	-2.24668983	3.76001169	11.04232836
H	-2.68877801	4.16366494	10.12235487
H	-2.81141369	4.15672916	11.89725620
H	-2.39589667	2.67107344	11.03515177
C	3.74262165	10.99279514	10.36162893
H	3.63181628	12.06742762	10.57266517
H	4.66653746	10.85297529	9.78130294
H	3.86375053	10.47176030	11.32128139
H	-0.85423279	4.81310741	2.69912783
H	-1.34687327	6.50950685	4.43511074
H	0.23410795	5.78834481	4.73542907
H	-3.41296615	5.68321867	5.93014019
H	-3.12147790	4.45559892	7.15263127
H	-4.19852402	3.47836695	5.10558342
H	-2.61058292	2.76378981	5.40294421
H	-3.24166375	4.98142583	3.37179712
H	-2.84790418	3.30200037	2.98592675
B	-1.07087935	7.02866005	7.10978177
C	-2.25149825	8.26117483	6.47145940
C	-4.35771427	9.53501440	5.94866846
C	-3.79139080	8.21203536	6.49955658
C	-1.77030040	8.46168654	5.02138457
C	-2.33662388	9.78466552	4.47049651
C	-3.87651657	9.73552618	4.49859367
H	-1.90952584	9.07477584	7.07644557
H	-4.01584310	10.34867661	6.55362955
H	-5.42699042	9.50080020	5.96810799
H	-4.13335918	7.39836117	5.89466656
H	-4.12547465	8.07290223	7.50649746
H	-2.11217152	7.64802436	4.41642343
H	-0.70102425	8.49590079	5.00194506
H	-2.00253999	9.92379863	3.46355564
H	-1.99465543	10.59833966	5.07538655
H	-4.21848910	8.92192524	3.89360748
H	-1.89609797	6.71680900	9.40947039

S2.3.4. Input for geometry optimization of $^{9\text{-BBN}}$BIM·THF (1b·THF)

```
$ADFBIN/adf -n8 \
 <<< "
TITLE 9BBNBIM_thf

MAXMEMORYUSAGE 23000

RELATIVISTIC ZORA

CHARGE 0 0
SCF

DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
ATOMS
N       0.00000000       0.00000000       0.00000000
O      -1.55054666       2.42000034      -0.32406448
C       0.66972484       1.09467126       0.00000000
H       1.59738682       1.02543484      -0.00091265
C      -2.39300440      -3.05932567      -0.85964902
H      -1.61971691      -3.31559079      -0.31358339
C      -1.86842956      -2.20681755      -2.01495059
C      -0.52268530      -1.81854203      -2.07726026
C       0.41005046      -2.18564990      -0.95974467
B       0.04010012       2.58326083      -0.00000000
C       0.65443284       3.59267377      -1.11338602
H       0.55764184       3.17790418      -1.99686036
C      -0.11420525       4.93519197      -1.11346196
H       0.31847188       5.53693839      -1.73869247
H      -1.01492940       4.77408015      -1.43914723
C      -0.20630845       5.62866197       0.24299178
H      -0.86863559       6.33491494       0.18813841
H       0.64866141       6.04157217       0.44122466
C       2.51648812       4.17601821       0.62149356
H       2.39523535       5.13508357       0.70495202
H       3.45459518       3.98359848       0.77535522
C       1.68688450       3.47945756       1.71523530
H       1.79248616       3.97598485       2.54170687
H       2.05475940       2.59315748       1.85958775
C       0.17524547       3.33852868       1.42052630
H      -0.22333795       2.76971096       2.11178401
C      -1.95426913       1.93404068      -1.64819967
H      -1.54925327       1.07685517      -1.85118945
H      -1.72660619       2.56942549      -2.34545832
C      -3.46464583       1.81200239      -1.47763164
H      -3.89933504       2.64985177      -1.69909613
H      -3.81658526       1.11517258      -2.05463990
C      -3.69162891       1.47689143      -0.07709020
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H	-3.87569889	0.52842856	0.01395289
H	-4.45151921	1.97038688	0.26625179
C	-2.45516692	1.83765999	0.68045086
H	-2.65589526	2.48136210	1.37776096
H	-2.05772447	1.05082902	1.08640794
C	-2.72231987	-1.81551083	-3.05232514
H	-3.61886982	-2.06239879	-3.02516090
C	-2.25513897	-1.06989881	-4.11727552
H	-2.83980759	-0.80780032	-4.79077329
C	-0.92544723	-0.71121917	-4.18580756
H	-0.61664741	-0.22074635	-4.91400919
C	-0.03740107	-1.07951715	-3.17122963
C	1.43839433	-0.72136299	-3.27461107
H	1.83926980	-0.85778081	-2.39070304
C	1.66843144	0.72600914	-3.66576119
H	2.59572864	0.94643527	-3.54833666
H	1.13128923	1.29718025	-3.11295367
H	1.42409972	0.85191134	-4.58687153
C	2.14447058	-1.65005730	-4.24687777
H	1.76456330	-1.54666930	-5.12140947
H	2.03881132	-2.55914520	-3.95720911
H	3.07907546	-1.43115822	-4.27726940
C	1.01391065	-3.43619031	-0.92042012
H	0.85911169	-4.04382559	-1.60717321
C	1.84346004	-3.78959930	0.13219395
H	2.23902331	-4.63049121	0.15340830
C	2.07820624	-2.88640236	1.14956615
H	2.61752921	-3.13777060	1.86284177
C	1.52238099	-1.59966892	1.13277092
C	1.82913991	-0.67785020	2.27946405
C	3.12173389	-0.14942613	2.42332199
C	4.20898968	-0.36315613	1.37887357
H	3.81439313	-0.87210909	0.63881966
C	5.37439387	-1.18300023	1.93404896
H	5.98823225	-1.38763388	1.22509103
H	5.03911046	-1.99946249	2.31225369
H	5.82617783	-0.67792603	2.61250103
C	4.73154176	0.94932541	0.80669952
H	5.14060414	1.46176439	1.50629380
H	4.00289077	1.44627097	0.43045931
H	5.38039448	0.76572772	0.12438915
C	3.41623874	0.62694853	3.54616578
H	4.26947098	0.98586831	3.64597347
C	2.45850730	0.87020557	4.51230675
H	2.67114936	1.37929401	5.26063601
C	1.17929114	0.35485265	4.36556810
H	0.53932969	0.52608218	5.01883532
C	0.83422971	-0.41619752	3.25206860
C	-0.56038896	-0.99922119	3.10872121
H	-0.76508080	-1.04590217	2.15024791
C	-0.61991481	-2.42526501	3.66462373
H	0.04033073	-2.96861890	3.22585626
H	-1.49228849	-2.79285785	3.50998699
H	-0.44222226	-2.40770133	4.60796730
C	-1.64685693	-0.14935859	3.77365858
H	-1.55767244	-0.20520756	4.72653759
H	-2.51112804	-0.47519001	3.51366084

```
H      -1.55164742       0.76414534       3.49701936
C       2.16061663       3.76211469      -0.81249676
H       2.60642880       2.92220626      -1.00681916
H       2.51965996       4.42759486      -1.42009696
C      -0.58178366       4.68832556       1.40471558
H      -1.53306449       4.50878643       1.36065465
H      -0.40948192       5.14809482       2.24105233
C       0.67971739      -1.24652085       0.06112429
C      -3.04871902      -4.32329985      -1.32361814
H      -3.86125389      -4.11181076      -1.78925166
H      -3.24926842      -4.87648912      -0.56538827
H      -2.45563755      -4.79284315      -1.91499009
C      -3.31635732      -2.29184750       0.02084300
H      -2.90606430      -1.45997680       0.26643109
H      -3.50329057      -2.80244833       0.81064654
H      -4.13552192      -2.11819618      -0.44970880
END

GEOMETRY
 Iterations 300
 GO
END

BASIS
 type TZ2P
 core none
END

END INPUT
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S2.3.5. Input for geometry optimization of Compound 2b

```
$ADFBIN/adf -n8 \
 <<< "
TITLE 9BBNBIM_CO2

MAXMEMORYUSAGE 23000

RELATIVISTIC ZORA

CHARGE 0 0
SCF

DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
ATOMS
O      -1.35928318      -0.18593582       0.15102811
O      -3.19078957       1.12277738       0.36739516
N      -1.10497665       2.05134723       0.00000000
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C	2.58507579	4.17054532	1.97197387
H	2.99393288	4.46515802	2.78905582
H	2.98794589	4.62711864	1.22977852
H	2.71300229	3.22425063	1.87318115
C	1.09103516	4.48077613	2.00993675
H	0.73263503	4.28846182	1.11831819
C	0.31543443	3.62185263	3.00197901
C	-1.02681377	3.24395384	2.75563521
C	-1.73159463	3.84568838	1.56923024
C	-1.60582285	3.38893883	0.24709340
C	-2.09025257	4.16107066	-0.81897327
C	-1.77469659	3.90684241	-2.26682892
C	-0.66070746	4.57531684	-2.83164746
C	0.24763306	5.47683576	-1.99451345
H	0.18299886	5.18222989	-1.06208294
C	1.72545589	5.41479094	-2.40265261
H	2.01226481	4.49898851	-2.42793617
H	2.25441897	5.89825158	-1.76386021
H	1.83427461	5.80830885	-3.27150149
C	1.07024609	-0.18301890	-2.88204442
H	0.80632944	-0.37473776	-3.79553462
H	2.03946170	-0.20625734	-2.85096283
C	0.54084795	-1.30177744	-1.99137269
H	0.88722999	-2.14744622	-2.31661796
H	-0.42545206	-1.33067648	-2.07088794
C	0.91351574	-1.15680444	-0.48255160
H	0.64058778	-1.97623584	-0.01947712
C	2.43211702	-0.98286260	-0.29826749
H	2.71750423	-1.57305453	0.41666769
H	2.86953440	-1.28224314	-1.11062930
C	2.93723121	0.42620899	0.02031836
H	3.90212464	0.37541871	0.10571509
H	2.58891175	0.66824031	0.89266507
C	2.62171172	1.58708871	-0.93815672
H	3.06391223	1.40400804	-1.78188154
H	3.02343920	2.39100072	-0.57314556
C	1.13067141	1.89608781	-1.24038855
H	1.06388088	2.86598378	-1.36382334
C	0.28685942	1.54938873	0.00000000
H	0.75139411	1.81586516	0.82073094
C	-2.00372570	1.04356161	0.19707322
C	0.88195243	5.97257838	2.26856301
H	-0.05555146	6.17564037	2.23049150
H	1.34699070	6.48144252	1.60043965
H	1.22310393	6.19763695	3.13721394
C	0.90169036	3.24700381	4.20806003
H	1.78073761	3.49287727	4.38615656
C	0.19651383	2.51506551	5.14420207
H	0.59618185	2.28733690	5.95246750
C	-1.10107976	2.12107920	4.88145743
H	-1.55973847	1.61102392	5.50946854
C	-1.73448462	2.47432503	3.69255865
C	-3.16783166	2.02949096	3.44883776
H	-3.41483939	2.30072827	2.54010687
C	-4.13329661	2.71062296	4.41762114
H	-3.90999621	2.46414992	5.31817099
H	-5.03126139	2.43242243	4.22301888

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H      -4.06525482       3.66326380       4.32035759
C      -3.29446697       0.50753203       3.53252423
H      -2.65632142       0.10038062       2.94212243
H      -4.18138073       0.24557681       3.27488577
H      -3.12519919       0.22137790       4.43312690
C      -2.49478174       4.98541743       1.81237236
H      -2.60016552       5.28532731       2.68636477
C      -3.09944606       5.68052455       0.77931087
H      -3.65731756       6.40235468       0.96001155
C      -2.86323663       5.28789525      -0.52238754
H      -3.22699571       5.78480384      -1.21928288
C      -0.44099302       4.45116604      -4.20280514
H       0.28376596       4.88681210      -4.58988950
C      -1.28025781       3.69250989      -4.99843004
H      -1.11845469       3.62270910      -5.91158826
C      -2.36067533       3.03754523      -4.43471308
H      -2.91532132       2.52140690      -4.97402712
C      -2.63056502       3.13905178      -3.07277541
C      -3.85784893       2.44522876      -2.50918675
H      -3.85561850       2.56975663      -1.53714945
C      -5.13575959       3.07729836      -3.06253144
H      -5.19498120       3.98923762      -2.76847955
H      -5.89826082       2.58837574      -2.74448952
H      -5.11623305       3.05107433      -4.02196757
C      -3.83053763       0.93879786      -2.79273074
H      -3.86341738       0.79096089      -3.74071039
H      -4.58855770       0.52119173      -2.37725624
H      -3.02255136       0.56096731      -2.43776247
C      -0.23100532       6.93027135      -2.05850507
H      -0.19083442       7.24075495      -2.96602315
H       0.33350876       7.47762936      -1.50775065
H      -1.13572087       6.98347974      -1.74184270
C       0.61551080       1.24700652      -2.54348456
H      -0.35389578       1.24755400      -2.50955854
H       0.87509095       1.82100959      -3.28107486
B       0.00000000       0.00000000       0.00000000
END

GEOMETRY
 Iterations 300
 GO
END

BASIS
 type TZ2P
 core none
END

END INPUT
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S2.3.6. Input for geometry optimization of Compound 2b*

```
$ADFBIN/adf -n8 \
 <<< "
TITLE 9BBNBIM_CO2_nomigration
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```
MAXMEMORYUSAGE 23000

RELATIVISTIC ZORA

CHARGE 0 0
SCF

DIIS
END

XC
 LDA VWN
 GGA Becke Perdew
END

SYMMETRY NOSYM
ATOMS
O       0.25430653      -2.23728304      -0.15102811
O       2.08581292      -0.92856985      -0.36739516
N       0.00000000       0.00000000       0.00000000
C      -3.69005244       2.11919810      -1.97197387
H      -4.09890954       2.41381079      -2.78905582
H      -4.09292255       2.57577141      -1.22977852
H      -3.81797894       1.17290340      -1.87318115
C      -2.19601182       2.42942890      -2.00993675
H      -1.83761169       2.23711460      -1.11831819
C      -1.42041108       1.57050540      -3.00197901
C      -0.07816289       1.19260662      -2.75563521
C       0.62661797       1.79434116      -1.56923024
C       0.50084619       1.33759161      -0.24709340
C       0.98527592       2.10972344       0.81897327
C       0.66971994       1.85549518       2.26682892
C      -0.44426919       2.52396962       2.83164746
C      -1.35260972       3.42548854       1.99451345
H      -1.28797552       3.13088266       1.06208294
C      -2.83043254       3.36344371       2.40265261
H      -3.11724146       2.44764129       2.42793617
H      -3.35939563       3.84690435       1.76386021
H      -2.93925127       3.75696162       3.27150149
C      -1.25143465      -4.93702816      -0.26202810
H      -0.73272793      -5.75019260      -0.36488419
H      -2.18537623      -5.19473947      -0.21487943
C      -1.05665017      -4.08937923      -1.51451742
H      -1.32098096      -4.61256881      -2.28738390
H      -0.11290522      -3.88538599      -1.60739245
C      -1.85960373      -2.75084242      -1.51945038
H      -1.76950954      -2.34281608      -2.40590005
C      -3.35572874      -2.99798020      -1.25318148
H      -3.86475542      -2.48429376      -1.89965094
H      -3.53988164      -3.93541717      -1.42109225
C      -3.87967299      -2.65477601       0.14317569
H      -4.82685093      -2.86351518       0.15634721
H      -3.80061960      -1.69438490       0.25405347
C      -3.24723666      -3.31335490       1.38098298
H      -3.42213869      -4.26622835       1.33227084
H      -3.70942588      -2.97735886       2.16480721
C      -1.72372595      -3.12094149       1.60883803
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H      -1.58639516      -3.08767303       2.57859510
C      -1.39183607      -0.50195849      -0.00000000
B      -1.10497665      -2.05134723      -0.00000000
C       0.89874904      -1.00778561      -0.19707322
C      -1.98692908       3.92123115      -2.26856301
H      -1.04942519       4.12429314      -2.23049150
H      -2.45196735       4.43009529      -1.60043965
H      -2.32808058       4.14628973      -3.13721394
C      -2.00666701       1.19565659      -4.20806003
H      -2.88571426       1.44153004      -4.38615656
C      -1.30149048       0.46371829      -5.14420206
H      -1.70115850       0.23598967      -5.95246750
C      -0.00389690       0.06973197      -4.88145743
H       0.45476181      -0.44032330      -5.50946854
C       0.62950797       0.42297780      -3.69255865
C       2.06285501      -0.02185626      -3.44883776
H       2.30986273       0.24938104      -2.54010686
C       3.02831996       0.65927573      -4.41762114
H       2.80501956       0.41280270      -5.31817099
H       3.92628474       0.38107520      -4.22301888
H       2.96027817       1.61191657      -4.32035759
C       2.18949031      -1.54381519      -3.53252423
H       1.55134477      -1.95096661      -2.94212243
H       3.07640408      -1.80577041      -3.27488577
H       2.02022254      -1.82996933      -4.43312690
C       1.38980509       2.93407021      -1.81237236
H       1.49518886       3.23398009      -2.68636477
C       1.99446940       3.62917733      -0.77931087
H       2.55234091       4.35100745      -0.96001155
C       1.75825997       3.23654803       0.52238754
H       2.12201906       3.73345662       1.21928288
C      -0.66398364       2.39981881       4.20280514
H      -1.38874261       2.83546487       4.58988950
C       0.17528116       1.64116267       4.99843004
H       0.01347803       1.57136188       5.91158826
C       1.25569867       0.98619800       4.43471308
H       1.81034467       0.47005968       4.97402712
C       1.52558836       1.08770456       3.07277541
C       2.75287228       0.39388154       2.50918676
H       2.75064185       0.51840941       1.53714945
C       4.03078294       1.02595113       3.06253145
H       4.09000455       1.93789040       2.76847955
H       4.79328417       0.53702851       2.74448952
H       4.01125640       0.99972711       4.02196757
C       2.72556097      -1.11254937       2.79273074
H       2.75844073      -1.26038634       3.74071039
H       3.48358104      -1.53015550       2.37725624
H       1.91757471      -1.49037992       2.43776247
C      -0.87397133       4.87892412       2.05850507
H      -0.91414223       5.18940772       2.96602315
H      -1.43848541       5.42628214       1.50775065
H       0.03074422       4.93213252       1.74184270
C      -0.86578704      -4.29083621       1.07964681
H       0.04795226      -3.97458776       1.00239539
H      -0.86995634      -4.98783588       1.75423922
H      -2.30810437       0.06975158      -0.00000000
END
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GEOMETRY
 Iterations 300
 GO
END

BASIS
 type TZ2P
 core none
END

END INPUT
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S2.4. Results

S2.4.1. Optimized Coordinates of ^{Cy2}BIM (1a)

H	1.19986532	-3.88509636	-3.81435461
C	0.75129802	-1.96951364	-2.88968103
H	0.33970483	-1.55800104	-3.82836396
N	0.73124256	-0.17222877	0.80637146
C	-0.06232169	0.23260109	-0.12457379
H	-1.04635895	0.65489301	0.16055704
C	0.44233879	-0.00006303	2.16929775
C	0.52895396	-1.14858342	2.99674912
C	0.35862640	-1.01034366	4.37600140
H	0.41143779	-1.90134113	5.00107921
C	0.14866294	0.24245709	4.95232287
H	0.04562059	0.34110731	6.03163617
C	0.07568296	1.36782385	4.13570192
H	-0.08261665	2.35077537	4.57772726
C	0.19418814	1.27766254	2.74059870
C	0.78095663	-2.50982833	2.41498987
C	2.10450906	-3.00046050	2.33081219
C	2.31583720	-4.29577145	1.83928764
H	3.33322561	-4.68328449	1.76934004
C	1.25054912	-5.09759434	1.44067734
H	1.43260117	-6.10417031	1.06496355
C	-0.04981452	-4.60726631	1.52593782
H	-0.88132645	-5.24132796	1.21639318
C	-0.30787785	-3.31642369	2.00607910
C	3.30680953	-2.16195101	2.75199353
H	2.92725565	-1.20249196	3.12762082
C	4.09502764	-2.82437129	3.89692422
H	3.45446719	-3.01147300	4.76966481
H	4.92619108	-2.17765098	4.21476452
H	4.52274578	-3.78789948	3.58305445
C	4.22756092	-1.85320888	1.55711200
H	4.66133760	-2.77453261	1.14096968
H	5.05843377	-1.20425281	1.87113234
H	3.67201586	-1.34457961	0.75882347
C	-1.75199068	-2.83431814	2.11124036
H	-1.72636261	-1.74976941	2.28593151
C	-2.46687808	-3.47451724	3.31778516
H	-3.49593039	-3.09483492	3.40385796

H	-1.94245201	-3.25470477	4.25736960
H	-2.51577106	-4.56814037	3.20714857
C	-2.55711088	-3.07271767	0.82180075
H	-2.70074658	-4.14466199	0.62439962
H	-2.05566901	-2.63353613	-0.05100782
H	-3.55526222	-2.61974194	0.90941666
C	0.08121303	2.54530398	1.93827990
C	-1.19090021	3.13837452	1.74586295
C	-1.27498419	4.35800879	1.05855728
H	-2.25019536	4.82182533	0.90663530
C	-0.13698151	4.98649402	0.56530094
H	-0.22039370	5.93366483	0.03271202
C	1.11136014	4.39998093	0.75942892
H	1.99969322	4.90102040	0.37590139
C	1.24672519	3.18613554	1.44540900
C	-2.47710162	2.50543658	2.27453820
H	-2.22498440	1.50640712	2.65421210
C	-3.05646066	3.31420436	3.45190271
H	-2.33349626	3.40461456	4.27337517
H	-3.96161544	2.82866175	3.84542553
H	-3.32911583	4.33111036	3.13299072
C	-3.54433611	2.32551982	1.17992026
H	-3.89354406	3.29307170	0.79211386
H	-4.41897655	1.79696623	1.58570525
H	-3.15941178	1.74449378	0.33100047
C	2.63881112	2.61543441	1.70006203
H	2.53183860	1.53257907	1.84780401
C	3.24036559	3.20301993	2.99362150
H	3.36781865	4.29218681	2.90101069
H	4.22653262	2.75894661	3.19500408
H	2.59639316	3.00854947	3.86155565
C	3.60991222	2.81527625	0.52565483
H	3.18531547	2.44562907	-0.41724437
H	4.54331899	2.26783715	0.71640148
H	3.87719849	3.87297352	0.38809039
C	-0.38109073	1.31507595	-2.51674074
H	-0.48898978	2.21670251	-1.87669251
C	-1.84097291	0.79054313	-2.72114310
H	-2.28818773	0.49062397	-1.76146057
H	-1.81517376	-0.11549137	-3.35117518
C	-2.73323167	1.84626804	-3.39618560
H	-3.74197190	1.43364152	-3.55673442
H	-2.84536699	2.70502836	-2.71287025
C	-2.13675305	2.32981691	-4.72588408
H	-2.76965576	3.11817503	-5.16207328
H	-2.13670536	1.49345954	-5.44676427
C	-0.69870226	2.83590829	-4.54227010
H	-0.27236019	3.13210555	-5.51327630
H	-0.71172273	3.74375997	-3.91462596
C	0.19360766	1.77948451	-3.87007592
H	1.20638625	2.18495153	-3.73342666
H	0.29297208	0.91245998	-4.54497183
C	2.68957285	-0.33066645	-2.89740455
H	3.21725289	0.45654502	-2.33622755
H	2.35819645	0.12664953	-3.84269292
H	-0.10072010	-2.36753798	-2.31609935
B	0.39448800	0.24061630	-1.64423369

C	1.46453376	-0.83213434	-2.09241115
H	1.85086371	-1.30011063	-1.16873224
C	3.66161411	-1.47885784	-3.21457563
H	4.51748501	-1.10045359	-3.79567884
H	4.07140818	-1.87535003	-2.27018166
C	2.96121533	-2.61356413	-3.97765813
H	3.66079847	-3.44504621	-4.15577206
H	2.65486764	-2.24322659	-4.97209060
C	1.72126142	-3.11560984	-3.22283707
H	2.03543190	-3.59740152	-2.28209692

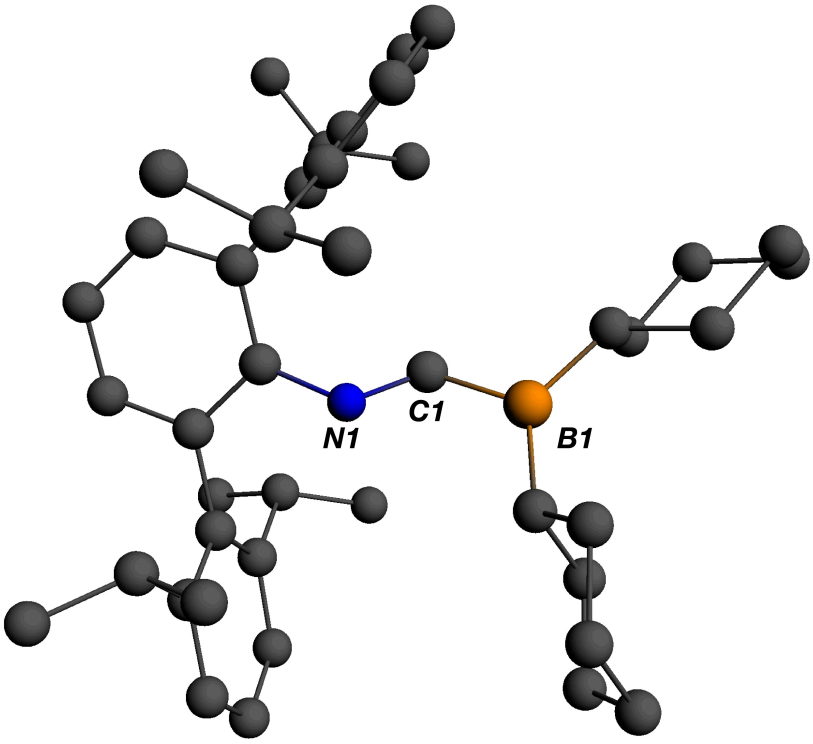


Figure S2.1. Optimized molecular structure of ^{Cy2}BIM (**1a**).

S2.4.2. Optimized Coordinates of Compound 1b

O	2.17797669	7.92519584	7.75093539
O	0.17421755	7.50062554	6.74431373
N	0.27864406	7.39559922	9.00940963
C	1.18605839	4.62214987	9.55793258
C	1.55410150	5.81429621	10.40584909
C	1.35309757	8.15967506	11.12393465
C	0.06617366	3.82866817	9.92726094
C	2.01215972	4.22594291	8.47671643
C	1.03406182	7.12107759	10.21261991
C	2.45526943	5.59420035	11.45588996
H	2.86286790	4.59337464	11.58967995
C	2.28833621	7.88913714	12.13527215

H	2.57151059	8.69985233	12.80415981
C	0.72157268	9.52954155	11.14897274
C	1.25734868	10.60191663	10.39561048
C	2.85056810	6.62893259	12.29640789
H	3.58181203	6.45002913	13.08334057
C	-0.34595668	9.76412421	12.05933564
C	-1.11645476	6.97426129	8.70784743
H	-1.25394278	5.93807021	9.05720446
C	-0.75937442	4.12539467	11.18000670
H	-0.69643488	5.20602480	11.37414331
C	-2.21798016	7.85776345	9.35291441
H	-1.95631150	7.98604839	10.41645268
C	1.00626160	7.64411065	7.86550988
C	3.31699780	4.94266738	8.13766620
H	3.28795153	5.93724898	8.59932192
C	-0.91317852	11.04426780	12.11894418
H	-1.73842510	11.23294860	12.80490751
C	-0.24521889	2.69901372	9.15905344
H	-1.10866508	2.08997141	9.42352235
C	0.65289721	11.86418065	10.49154744
H	1.05435890	12.69087409	9.90608544
C	-0.43384483	12.08542345	11.32962980
H	-0.89246671	13.07251667	11.38635841
C	-0.83518923	8.70079979	13.04626835
H	-0.55045219	7.71570141	12.65032904
C	2.53068395	10.45651654	9.57059087
H	2.69766160	9.38957791	9.38626444
C	1.65610206	3.08566123	7.73967976
H	2.27845110	2.78023134	6.89911417
C	0.53304270	2.33400108	8.06418020
H	0.27065521	1.45540243	7.47490284
C	-0.14494815	8.86881084	14.41766742
H	0.94696194	8.80700346	14.34067602
H	-0.48153770	8.08632863	15.11410953
H	-0.39789299	9.84632625	14.85476722
C	-2.35818488	8.69440089	13.25945536
H	-2.69789409	9.59512602	13.78997501
H	-2.64466891	7.83060644	13.87582299
H	-2.90731266	8.63493152	12.31225338
C	-2.30708688	9.25959065	8.71685918
H	-1.35216397	9.78926709	8.85101134
H	-2.46483140	9.15120849	7.62665165
C	-0.17415610	3.40315199	12.41219968
H	-0.19699386	2.31339379	12.26280898
H	-0.76519848	3.63796081	13.31006615
H	0.86445604	3.69928462	12.60318522
C	2.45138065	11.13999754	8.19570000
H	1.57534358	10.80306918	7.62748296
H	3.34434656	10.89123516	7.60656169
H	2.40642713	12.23580078	8.28280982
C	4.51859885	4.17795859	8.73205206
H	4.43707344	4.07119198	9.82209010
H	5.45470747	4.71213987	8.51275535
H	4.59336275	3.16861846	8.29960694
C	-3.58046801	7.13760872	9.29063551
H	-3.51780939	6.17963481	9.82833268
H	-3.81561538	6.89178137	8.24176229

C	3.52420069	5.15440289	6.62819546
H	3.67188883	4.20262916	6.09677174
H	4.42217700	5.76525150	6.46200194
H	2.67629018	5.68161504	6.17488650
C	-2.24668983	3.76001169	11.04232836
H	-2.68877801	4.16366494	10.12235487
H	-2.81141369	4.15672916	11.89725620
H	-2.39589667	2.67107344	11.03515177
C	3.74262165	10.99279514	10.36162893
H	3.63181628	12.06742762	10.57266517
H	4.66653746	10.85297529	9.78130294
H	3.86375053	10.47176030	11.32128139
C	-3.45958473	10.09773243	9.29186884
H	-3.24630307	10.32623813	10.34916992
H	-3.50916206	11.06551258	8.77021614
C	-4.72747809	7.98496429	9.86236405
H	-5.67999887	7.44512119	9.74694231
H	-4.57749705	8.12064808	10.94649395
C	-4.80370592	9.36318797	9.19029213
H	-5.60641817	9.96432503	9.64470781
H	-5.07151117	9.23356954	8.12691810
B	-1.07087935	7.02866005	7.10978177
C	-2.11276702	6.63721040	5.99598320
C	-3.57124807	4.75918670	5.04332220
C	-2.54670813	5.14914829	6.11975342
C	-1.61544342	6.93936953	4.56397129
C	-2.64292696	6.54001855	3.49537606
C	-3.05511220	5.06668608	3.62964658
H	-3.02592785	7.24234239	6.16851610
H	-4.50702564	5.31910997	5.21685915
H	-3.82187097	3.69080102	5.13500310
H	-1.65669320	4.50358142	6.02128499
H	-2.95983610	4.95437375	7.12054486
H	-0.67570361	6.39067378	4.38936990
H	-1.36316959	8.00537433	4.47081165
H	-2.23646953	6.73216146	2.49048549
H	-3.53927499	7.17671287	3.59758658
H	-2.18090150	4.42636095	3.41837487
H	-3.81992022	4.81145821	2.88010900

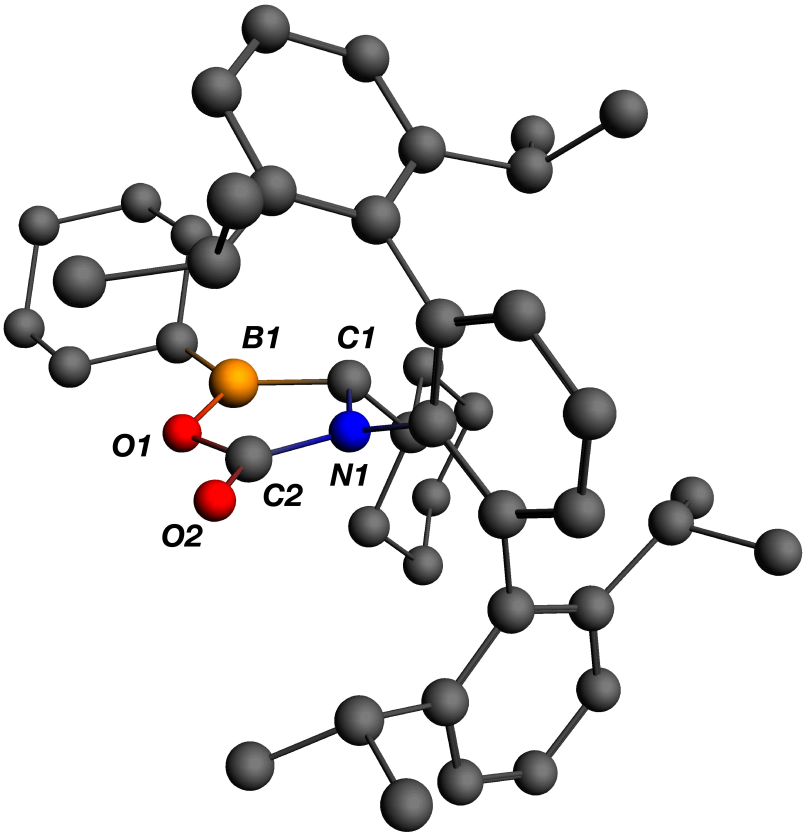


Figure S2.2. Optimized molecular structure of **1b**.

Table S2.1. Comparative metrical parameters between experimental (X-ray crystal structure) and calculated versions of **1b**.

Parameter	Exp. (X-ray)	Calculated	% Difference
C2-O1	1.391(3) Å	1.404 Å	0.9 %
C2-O2	1.198(3) Å	1.210 Å	1.0 %
C2-N1	1.367(3) Å	1.378 Å	0.8 %
O1-B1	1.378(4) Å	1.381 Å	0.2 %

S2.4.3. Optimized Coordinates of 1b*

O	2.40394074	7.47023544	7.50703968
O	0.31976209	7.41350035	6.57665543
N	0.45665370	7.07765607	8.81779151
C	1.63115784	4.47790951	9.52572299
C	1.78205793	5.70953548	10.37412290
C	1.22420861	8.04689425	10.94323377
C	0.47315647	3.67430782	9.68735377
C	2.66475345	4.08159323	8.64237566
C	1.16229425	6.94030733	10.07156349
C	2.50933045	5.62481297	11.56879964
H	2.98393644	4.67791210	11.82000767

C	1.97262345	7.90661176	12.12059673
H	2.03525612	8.75642823	12.79841736
C	0.50121663	9.34314197	10.70438741
C	1.13269091	10.39064715	9.99099181
C	2.61908390	6.71369179	12.42872836
H	3.19542390	6.62712745	13.34850654
C	-0.78023330	9.53296339	11.28054710
C	-0.83193536	7.04422065	8.59963171
H	-4.28341599	11.71287188	5.71172818
C	-0.59275652	3.99178851	10.73488751
H	-0.52503239	5.06370915	10.97015404
C	-1.72299979	5.81041887	6.43426268
C	-1.84152835	4.23997885	4.43110725
C	1.20163214	7.34440774	7.52316122
C	3.97558204	4.85363165	8.51936922
H	3.80740378	5.86239688	8.91683547
C	-1.41667484	10.76995165	11.11129284
H	-2.40283182	10.93081836	11.54629146
C	0.34899950	2.51080965	8.91772496
H	-0.53852769	1.88826024	9.02403928
C	0.45312699	11.60846021	9.84948683
H	0.92595713	12.42182319	9.29972728
C	-0.80992344	11.80032614	10.39991805
H	-1.32126462	12.75471684	10.27793358
C	-1.46146665	8.45963146	12.12924925
H	-0.95730428	7.50296014	11.93039419
C	2.54590918	10.25330064	9.43289961
H	2.78047228	9.18329063	9.36151763
C	2.49245791	2.90559041	7.89819955
H	3.27549472	2.59282827	7.20800203
C	1.34476280	2.13072380	8.02288688
H	1.22854495	1.22463027	7.42870180
C	-1.29157023	8.75615581	13.63348957
H	-0.23272135	8.81941882	13.91598902
H	-1.75981758	7.96566714	14.23830756
H	-1.76768872	9.71275668	13.89437360
C	-2.95292167	8.27476222	11.79886482
H	-3.54317675	9.15798529	12.07986835
H	-3.36047960	7.42061099	12.35762877
H	-3.11999012	8.09660167	10.72824352
C	-1.45013632	5.64611078	4.92006821
C	-3.20605430	5.50268989	6.72998507
C	-3.60845122	4.09710420	6.24858053
C	-0.31191177	3.22700617	12.04563157
H	-0.35328726	2.14139517	11.87290273
H	-1.06216459	3.48090969	12.80930908
H	0.68039398	3.46726936	12.44942221
C	2.69810971	10.83829433	8.01871285
H	1.95723499	10.41988576	7.32607209
H	3.69522171	10.59978690	7.62477475
H	2.59515933	11.93320477	8.01506399
C	5.08242212	4.18269952	9.35953147
H	4.80657937	4.10727331	10.41989857
H	6.01521284	4.76149191	9.29215768
H	5.28715660	3.16524838	8.99387774
C	-3.30747283	3.91071528	4.75353645
H	-1.13202957	5.00699696	6.92091056

H	-1.18744827	3.49677918	4.91915026
C	4.44819129	5.01909815	7.06505123
H	4.73328223	4.05685037	6.61547562
H	5.33482849	5.66782412	7.03685763
H	3.67311246	5.48427250	6.44543332
C	-2.02803065	3.71179134	10.26140296
H	-2.24143455	4.18849780	9.29581641
H	-2.74915429	4.08810903	11.00071349
H	-2.21511406	2.63468284	10.15066898
C	3.57193155	10.89482747	10.38991342
H	3.38381217	11.97368932	10.49778459
H	4.59143427	10.76388867	9.99894608
H	3.53205498	10.44439565	11.39106477
H	-1.66234646	4.15298692	3.34743582
H	-2.02682261	6.39491809	4.35309351
H	-0.38986340	5.83727413	4.70453784
H	-3.84266148	6.24292333	6.21690481
H	-3.42880153	5.60452300	7.80539194
H	-4.67700824	3.91640397	6.44867239
H	-3.04652153	3.34340534	6.82733747
H	-3.96438862	4.57964601	4.16990976
H	-3.54984848	2.88303757	4.43933684
B	-1.15490858	7.24205683	7.06299538
C	-1.92134701	8.68483527	6.79400853
C	-3.83657634	10.29771206	7.30744302
C	-3.28255894	8.87457909	7.49989697
C	-2.05449627	9.04783075	5.29814663
C	-2.59141834	10.47677460	5.10394936
C	-3.93595723	10.67321562	5.82110510
H	-1.24289002	9.44522594	7.23256101
H	-3.16669249	11.01118762	7.81748380
H	-4.82308543	10.39027066	7.79041343
H	-4.01640852	8.15306531	7.10514541
H	-3.19351319	8.66621154	8.57847144
H	-2.74860797	8.34291904	4.80961123
H	-1.08423941	8.93636593	4.79229153
H	-2.69541128	10.70165949	4.03034634
H	-1.85657732	11.19547107	5.50675017
H	-4.69773107	10.03603540	5.33766236
H	-1.47745821	6.86663952	9.46230859

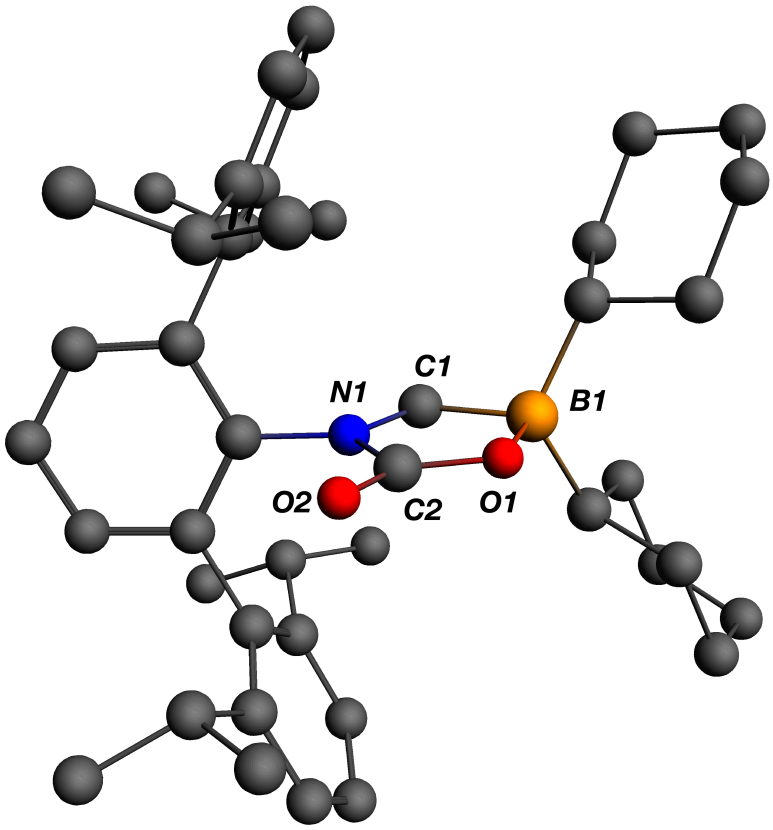


Figure S2.3. Optimized molecular structure of **1b***.

S2.4.4. Optimized Coordinates for $^{9\text{-BBN}}$BIM·THF (1b·THF)

N	-0.02480405	0.04823565	0.05774898
O	-1.46703620	2.54444891	-0.33462914
C	0.69844131	1.11860097	0.05429563
H	1.79915208	0.98580128	0.11187323
C	-2.67419614	-2.70824351	-0.99940831
H	-2.00545103	-2.71430779	-0.12854459
C	-1.92326285	-2.03902268	-2.14713635
C	-0.53510422	-1.77463506	-2.07429016
C	0.23540507	-2.17515528	-0.84876901
B	0.17025899	2.62181049	-0.07817449
C	0.81323274	3.44805007	-1.33601825
H	0.68962971	2.90695233	-2.29234614
C	0.11913813	4.82359935	-1.50564755
H	0.61161523	5.39476143	-2.31342368
H	-0.91423037	4.65323087	-1.85304919
C	0.06605699	5.70157788	-0.23548093
H	-0.66484456	6.51224642	-0.39049575
H	1.03329612	6.20443407	-0.09986201
C	2.76712246	4.16547816	0.25478768
H	2.71805225	5.26136113	0.18949668
H	3.83002017	3.93406282	0.43495093
C	1.93889884	3.68234336	1.46836811
H	2.13353225	4.35767833	2.32058786

H	2.30675797	2.69329410	1.78429688
C	0.40746517	3.56663190	1.23305711
H	-0.00036608	3.10457213	2.15068086
C	-2.00926413	1.98447757	-1.58518080
H	-1.70997346	0.92947622	-1.63721475
H	-1.55864197	2.55136603	-2.40428192
C	-3.51921072	2.17230847	-1.43302415
H	-3.84370555	3.11519148	-1.88987811
H	-4.05777416	1.35390213	-1.92588932
C	-3.76398416	2.20148935	0.10438597
H	-4.40826588	1.37807131	0.43696868
H	-4.24346944	3.14231168	0.40103817
C	-2.36939891	2.07669808	0.72618186
H	-2.19590550	2.72141231	1.59245582
H	-2.09242617	1.03967189	0.95544646
C	-2.61780409	-1.70720786	-3.31967654
H	-3.68654566	-1.91359922	-3.38811397
C	-1.96458360	-1.12441864	-4.40178714
H	-2.51803090	-0.87448464	-5.30677720
C	-0.59682452	-0.87164062	-4.32609413
H	-0.08981757	-0.42266434	-5.17991839
C	0.13804081	-1.19107200	-3.17619474
C	1.64723989	-0.96431510	-3.15747093
H	1.95626537	-0.90888175	-2.10430583
C	2.08332007	0.34407390	-3.83577746
H	3.15806332	0.50844511	-3.67529984
H	1.54433768	1.21049396	-3.43103973
H	1.92021246	0.31585153	-4.92276990
C	2.38920190	-2.15924504	-3.79091587
H	2.11041557	-2.26965055	-4.84974114
H	2.15219016	-3.09960732	-3.27659333
H	3.47757618	-2.00697785	-3.73857173
C	0.67906838	-3.49463148	-0.72934782
H	0.45678475	-4.19614769	-1.53289837
C	1.38268420	-3.91891748	0.39742718
H	1.70546263	-4.95468400	0.48974632
C	1.66729552	-3.00058992	1.40292620
H	2.21547953	-3.31862268	2.28941523
C	1.27458695	-1.65530360	1.31286442
C	1.67045100	-0.74645211	2.44449612
C	3.02123177	-0.33718421	2.56828423
C	4.08840828	-0.70901510	1.53986587
H	3.57942156	-1.17671714	0.68690722
C	5.08142313	-1.74179748	2.10885085
H	5.82221053	-2.02509567	1.34657772
H	4.56962634	-2.65442500	2.44170315
H	5.62527483	-1.32932670	2.97168845
C	4.84958896	0.51775163	1.00571085
H	5.43578989	1.00703778	1.79671079
H	4.16589065	1.26683692	0.58487002
H	5.55131615	0.21368862	0.21555330
C	3.40156436	0.42522157	3.68254294
H	4.43908752	0.74490943	3.78405297
C	2.47928981	0.78407094	4.65850640
H	2.79136405	1.37752120	5.51735298
C	1.15204494	0.38034337	4.53178070
H	0.43583611	0.66350881	5.30226053

C	0.72667346	-0.38726090	3.44049471
C	-0.71924622	-0.87145413	3.37297516
H	-0.97442002	-0.98720815	2.31010958
C	-0.87449643	-2.25258969	4.04269952
H	-0.21935190	-3.00135041	3.57929846
H	-1.91236168	-2.60828664	3.95566334
H	-0.62271044	-2.19196622	5.11236192
C	-1.72656055	0.11729678	3.98160342
H	-1.64069925	0.16575504	5.07660767
H	-2.75260628	-0.20530139	3.75478673
H	-1.58765159	1.13257071	3.58782511
C	2.34548566	3.55521739	-1.10227229
H	2.77601404	2.54443750	-1.18852846
H	2.80655310	4.14356278	-1.91584618
C	-0.29519122	4.93654587	1.05676787
H	-1.38741445	4.77827718	1.07351928
H	-0.07653120	5.58323694	1.92572648
C	0.53071893	-1.23758757	0.17652046
C	-3.01157798	-4.17406087	-1.33631689
H	-3.67601725	-4.23190771	-2.21149651
H	-3.52122453	-4.65800213	-0.49003942
H	-2.10621661	-4.75183601	-1.56444324
C	-3.94799269	-1.94756809	-0.59483253
H	-3.72200600	-0.90279951	-0.34330456
H	-4.40914522	-2.41887136	0.28503208
H	-4.69753439	-1.95026913	-1.39941818

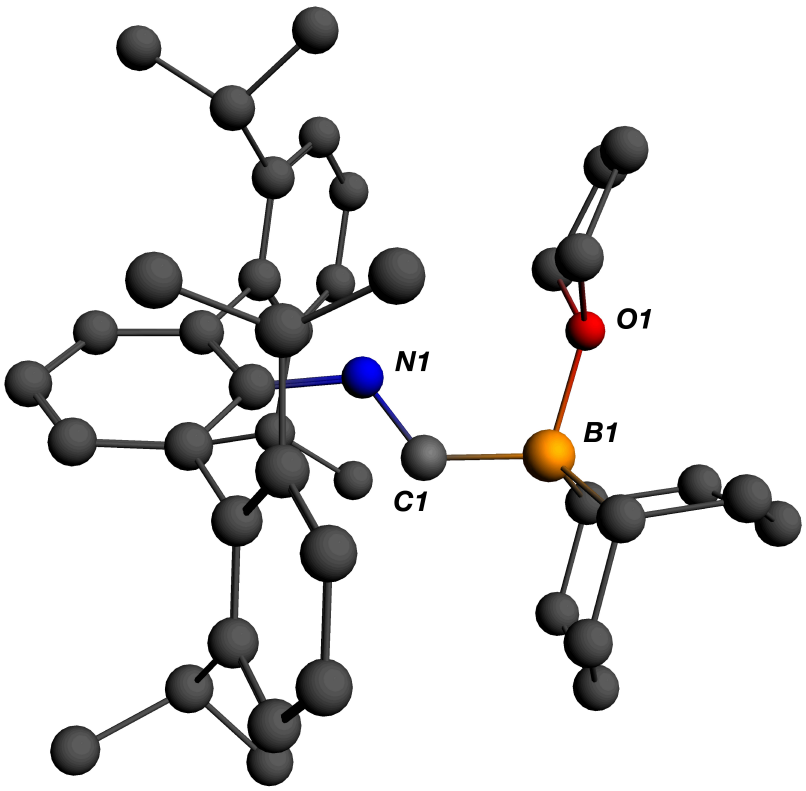


Figure S2.4. Optimized molecular structure of $^{9\text{-BBN}}$BIM·THF (**1b**·THF).

Table S2.2. Comparative metrical parameters between the experimental (X-ray crystal structure) and calculated versions of **2b**.

Parameter	Exp. (X-ray)	Calculated	% Difference
N1-C1	1.280(2) Å	1.292 Å	0.9 %
C1-B1	1.613(2) Å	1.599 Å	0.9 %
B1-O1	1.631(2) Å	1.659 Å	1.7%
N1-C1-B1	125.8(1)º	127.0º	1.0 %
C1-B1-O1	106.7(1)º	107.2º	0.9 %

S2.4.5. Optimized Coordinates of 2b

O	-1.23567943	-0.18567339	0.11118469
O	-3.15177472	1.06115730	0.14671161
N	-1.05454009	2.07590881	-0.06300347
C	2.64372414	4.25539553	2.31226354
H	3.11964307	4.33762859	3.29966013
H	3.14661241	4.97633934	1.65263076
H	2.83834909	3.24586659	1.92938439
C	1.13987450	4.56925739	2.38036446
H	0.76698043	4.64079192	1.34821824
C	0.31758653	3.49787730	3.09845973
C	-1.01000093	3.17652184	2.70573768
C	-1.61088124	3.89025694	1.52098976
C	-1.54392988	3.41377951	0.18530920
C	-2.02961486	4.21044227	-0.88207480
C	-1.89213528	3.87697301	-2.34637844
C	-0.80258100	4.42205312	-3.07817832
C	0.21303179	5.37889966	-2.44945643
H	0.23663631	5.18130183	-1.36777193
C	1.64533379	5.21766512	-2.98940716
H	1.98653348	4.17518388	-2.96492895
H	2.34063894	5.82028956	-2.38824252
H	1.72671847	5.57331308	-4.02622471
C	1.49470966	-0.21718003	-2.68929512
H	1.26695931	-0.49876701	-3.73000141
H	2.59546519	-0.19593486	-2.63135033
C	0.96301684	-1.33395844	-1.77473125
H	1.48530017	-2.27141539	-2.02946546
H	-0.10486192	-1.50734607	-1.98139703
C	1.15423392	-1.08249857	-0.23631966
H	0.82739624	-2.01000509	0.26019200
C	2.64503230	-0.81410456	0.11775054
H	2.89897514	-1.38100098	1.02652346
H	3.28113798	-1.23728472	-0.67814770
C	3.06173368	0.64943072	0.38241964
H	4.14721606	0.65956708	0.57410218
H	2.60233921	0.96663845	1.33207574
C	2.77839334	1.72767769	-0.69143288
H	3.39208790	1.52975479	-1.58429797
H	3.15293882	2.67908459	-0.28373021
C	1.30146966	1.94364303	-1.14107597
H	1.18399948	3.01497718	-1.35499903

C	0.35181268	1.61681201	0.03985656
H	0.78064344	2.01748449	0.97117847
C	-1.94453972	1.02947007	0.07153014
C	0.94316233	5.95128671	3.03917758
H	-0.10932336	6.25916647	3.03733719
H	1.52251952	6.71728459	2.50238153
H	1.28995763	5.92967359	4.08312035
C	0.86411630	2.85974832	4.21965306
H	1.88450964	3.08944533	4.52401309
C	0.12382800	1.94126468	4.95863832
H	0.56800847	1.45021019	5.82430157
C	-1.19081171	1.66978215	4.59789353
H	-1.77570620	0.97193345	5.19608502
C	-1.78550284	2.28251703	3.48401287
C	-3.26507761	2.03102444	3.20651041
H	-3.47283262	2.33136121	2.17214383
C	-4.13945759	2.89928159	4.13595942
H	-3.96671805	2.63936690	5.19144218
H	-5.20473996	2.73697031	3.91554300
H	-3.92747234	3.97009366	4.01387044
C	-3.66855310	0.55247135	3.33549734
H	-3.04620075	-0.09289044	2.70393304
H	-4.71110853	0.42534238	3.01350741
H	-3.59958780	0.19796167	4.37450188
C	-2.24124625	5.11668366	1.76921328
H	-2.31189617	5.46466853	2.79856721
C	-2.78559107	5.87273181	0.73690938
H	-3.29395653	6.81163526	0.95149656
C	-2.66023917	5.42601366	-0.57286472
H	-3.06428289	6.01959797	-1.39107418
C	-0.69981422	4.13873263	-4.44691496
H	0.13878692	4.53900954	-5.01565244
C	-1.65388265	3.36334435	-5.09828481
H	-1.55298092	3.14861105	-6.16197973
C	-2.75117091	2.88853231	-4.38883400
H	-3.51659834	2.31389459	-4.90950303
C	-2.90209517	3.14513598	-3.01826065
C	-4.19159053	2.71747121	-2.32460325
H	-4.00753246	2.70464262	-1.24435177
C	-5.31383225	3.73963153	-2.60482908
H	-5.03901428	4.74921574	-2.27058642
H	-6.23385106	3.44736816	-2.07718939
H	-5.53946307	3.79005924	-3.68100649
C	-4.65904879	1.30543214	-2.71268675
H	-4.98869957	1.25489190	-3.76096931
H	-5.51227212	1.01364827	-2.08535960
H	-3.86619701	0.56325750	-2.55976604
C	-0.22370258	6.84783093	-2.64120320
H	-0.27668338	7.09284368	-3.71245699
H	0.50207136	7.52804065	-2.17079329
H	-1.20777110	7.04491023	-2.19989609
C	0.94551662	1.20834490	-2.46556770
H	-0.15131728	1.21213534	-2.58779764
H	1.32517808	1.82966190	-3.29264252
B	0.12557505	0.05579541	0.08310027

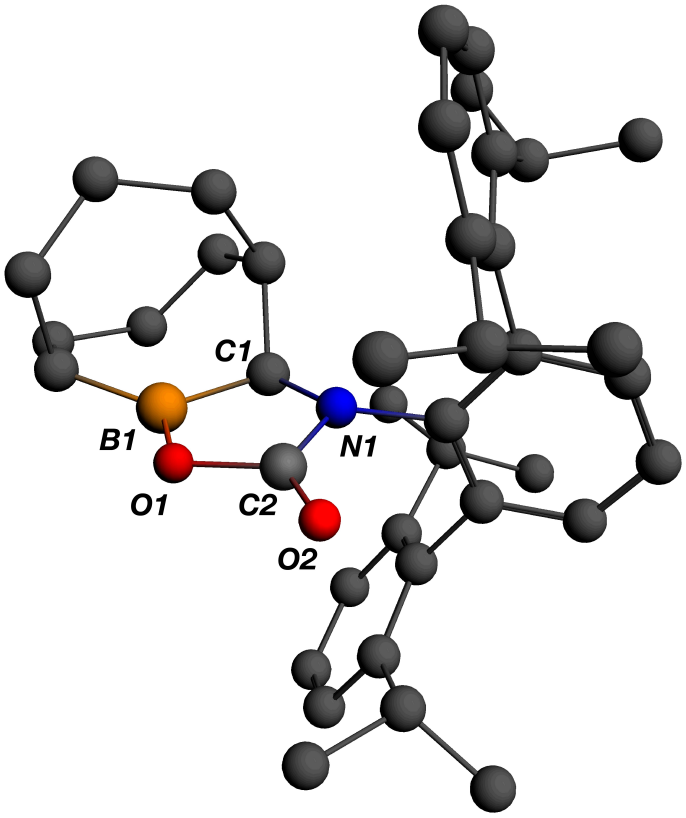


Figure S2.5. Optimized molecular structure of **2b**.

Table S2.3. Comparative metrical parameters between the experimental (X-ray crystal structure) and calculated versions of **2b**.

Parameter	Exp. (X-ray)	Calculated	% Difference
C2-O1	1.389(2)	1.407 Å	1.3 %
C2-O2	1.202(2)	1.210 Å	0.7 %
C2-N1	1.365(2)	1.380 Å	1.1 %
O1-B1	1.381(2)	1.383 Å	0.1 %

S2.4.6. Optimized Coordinates of 2b*

O	0.01645051	-2.19967965	0.07697900
O	2.04029197	-1.15744083	-0.10195510
N	-0.00048037	0.04865527	-0.14810857
C	-3.45451591	1.95915196	-2.48092250
H	-3.96167314	1.88594515	-3.45306129
H	-4.02115050	2.67985970	-1.87470582
H	-3.52129428	0.97485510	-1.99894389
C	-1.99731139	2.42817827	-2.63513518
H	-1.59744914	2.60656838	-1.62645802
C	-1.09813097	1.39955957	-3.31917263

C	0.21615164	1.12346033	-2.86512051
C	0.73861576	1.84295691	-1.65193786
C	0.59711689	1.34892592	-0.33869975
C	1.02387075	2.07733419	0.79044621
C	0.80289865	1.61567023	2.20401440
C	-0.43594919	1.89441283	2.83537020
C	-1.54671934	2.67759749	2.13770674
H	-1.35828765	2.63705476	1.05536238
C	-2.95076322	2.10073497	2.38561406
H	-3.00064476	1.02944906	2.15000582
H	-3.69048556	2.62636985	1.76537055
H	-3.26161914	2.22515422	3.43224559
C	-2.51163269	-4.62804248	0.31807826
H	-2.22278556	-5.68793008	0.39160121
H	-3.61419089	-4.61721193	0.34474035
C	-2.03067817	-4.05142455	-1.02378570
H	-2.53825490	-4.58016666	-1.85050219
H	-0.95371212	-4.24587201	-1.14150850
C	-2.28444347	-2.53208550	-1.16695698
H	-1.85991749	-2.21341740	-2.13122349
C	-3.80332411	-2.18129257	-1.13679442
H	-4.06226141	-1.58098704	-2.02350485
H	-4.38940263	-3.11195076	-1.22773365
C	-4.27581076	-1.41855495	0.11834840
H	-5.37704420	-1.39291699	0.14220112
H	-3.96583002	-0.36427758	0.03482380
C	-3.74145299	-1.99049924	1.44755189
H	-4.31639083	-2.89784901	1.70023919
H	-3.96507017	-1.26809398	2.24881626
C	-2.22018262	-2.33230562	1.45463625
H	-1.74974763	-1.87284807	2.33753313
C	-1.27856967	-0.25041153	-0.07691084
B	-1.47708183	-1.79400975	0.07914495
C	0.83131921	-1.19426796	-0.05071631
C	-1.95688193	3.77822564	-3.38138830
H	-0.93589265	4.17704481	-3.44131507
H	-2.58427712	4.52212925	-2.86837046
H	-2.33452256	3.66259229	-4.40806138
C	-1.56337685	0.74993795	-4.47032692
H	-2.57336959	0.94881666	-4.82844554
C	-0.75630051	-0.14288149	-5.16835618
H	-1.13703753	-0.64266216	-6.05882928
C	0.54027550	-0.38883548	-4.72908528
H	1.17091400	-1.07987596	-5.28716517
C	1.05327130	0.23477540	-3.58274450
C	2.50511552	-0.01227372	-3.18340005
H	2.61851723	0.27405403	-2.12982655
C	3.45417641	0.87109758	-4.01983198
H	3.37660089	0.62347817	-5.08929353
H	4.49681386	0.71149773	-3.70830022
H	3.22566884	1.93937382	-3.90482200
C	2.92213436	-1.48850375	-3.29039271
H	2.24799134	-2.13947448	-2.72091586
H	3.93340467	-1.61696006	-2.88102710
H	2.94372353	-1.83380220	-4.33424094
C	1.35947746	3.08895808	-1.81405622
H	1.47840283	3.48301744	-2.82199448

C	1.81147327	3.81863713	-0.71797804
H	2.29174942	4.78450293	-0.86723087
C	1.63292960	3.32026604	0.56951953
H	1.96026242	3.89840036	1.43203804
C	-0.61668041	1.50022767	4.16744128
H	-1.56446223	1.70556676	4.66451781
C	0.39727856	0.85786389	4.87169659
H	0.23771764	0.55681542	5.90684813
C	1.61700183	0.60985774	4.25157575
H	2.41039260	0.11645697	4.81184082
C	1.84811191	0.98206142	2.91934278
C	3.22598633	0.74176036	2.30900748
H	3.12737210	0.81738026	1.21866009
C	4.22403460	1.82130594	2.77724056
H	3.88722342	2.83333796	2.51458975
H	5.20754785	1.65909140	2.31241265
H	4.35453233	1.78421199	3.86927404
C	3.78332039	-0.65992682	2.60944638
H	4.00094520	-0.79341157	3.67905823
H	4.72491907	-0.80786241	2.06255609
H	3.08542746	-1.44244612	2.28994128
C	-1.50607751	4.16569673	2.54277905
H	-1.67855328	4.27612066	3.62354526
H	-2.28607703	4.73203456	2.01239605
H	-0.53473570	4.62082494	2.30804466
C	-1.96627160	-3.85684004	1.53177476
H	-0.88389785	-4.03397425	1.62231909
H	-2.42883475	-4.25390508	2.45298851
H	-1.98307385	0.57978779	-0.14586616

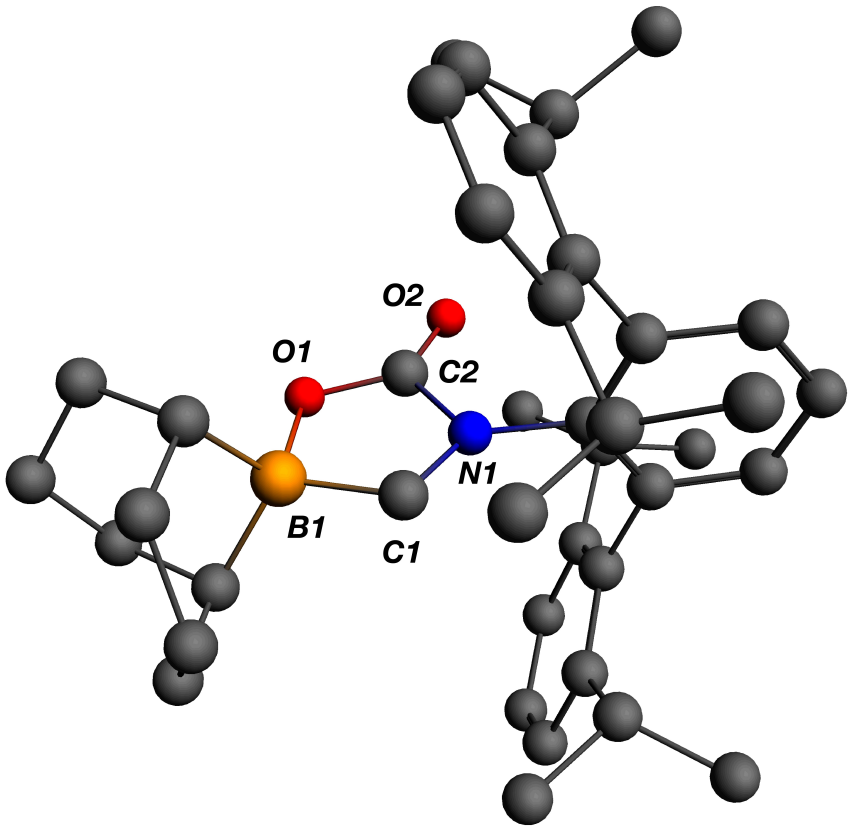
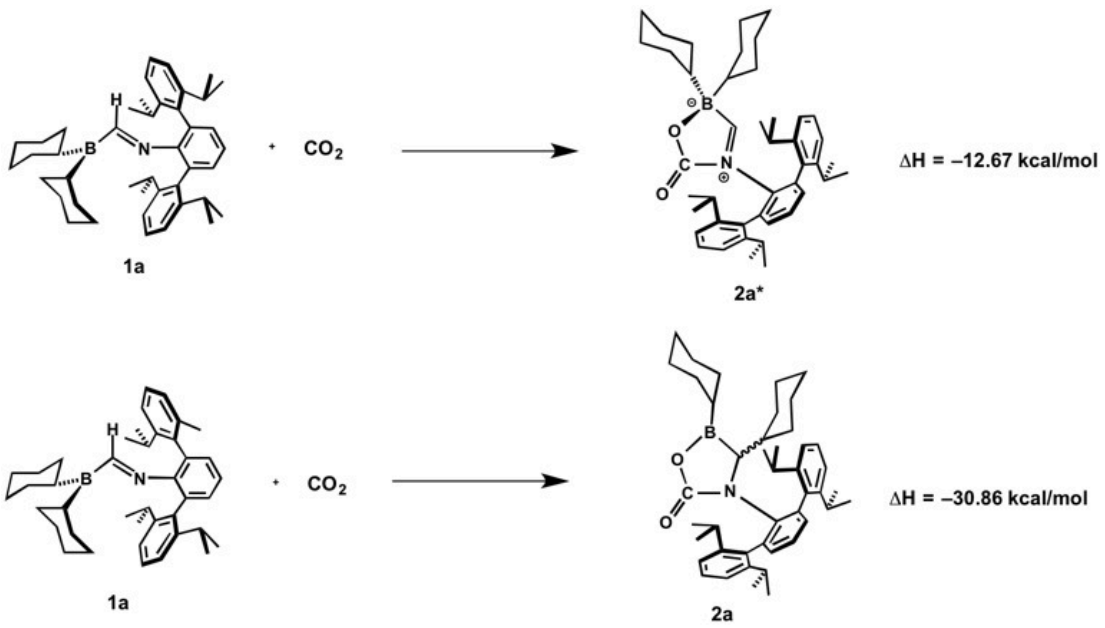


Figure S2.6. Optimized molecular structure of **2b***.

S2.4.7. Energetic Analysis of CO_2 Adduct Formation and Alkyl-group Migration

Table S2.4. Listing of total bonding energies for reactants and products (including putative intermediate **2a***) in the formation of **2a** (BP86/TZ2P)**.**

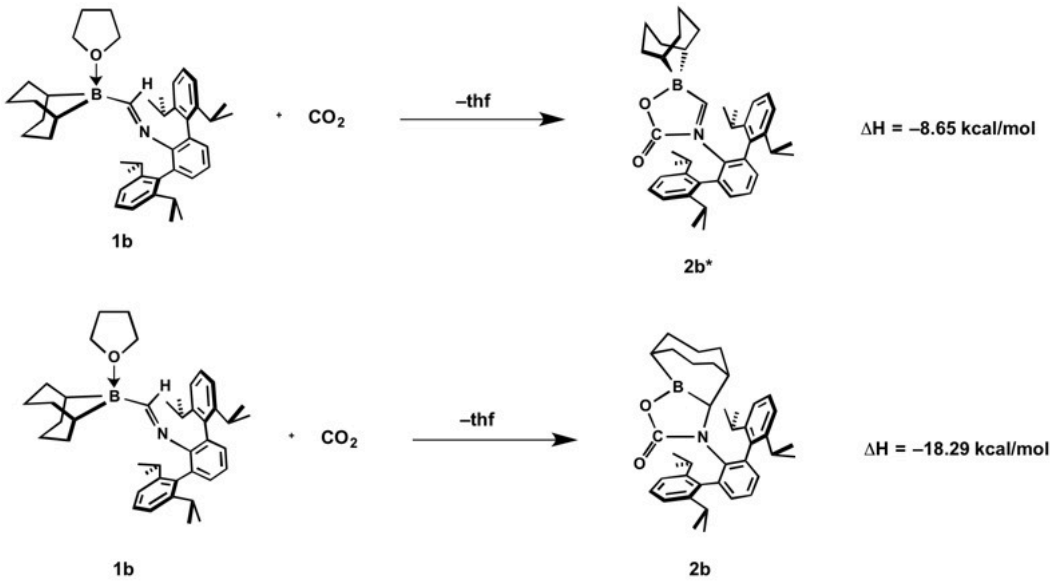
Compound	Total Bonding Energy (kcal/mol)
^{Cy2}BIM (1a)	–14183.97
CO_2	–529.21
2a*	–14725.85
2a	–14744.04



Scheme S2.1. Enthalpies of reaction in the formation of **2a*** and **2a** from ^{Cy2}BIM (**1a**) and CO_2.

Table S2.5. Listing of total bonding energies for reactants and products (including putative intermediate **2b***) in the formation of **2b** (BP86/TZ2P).

Compound	Total Bonding Energy (kcal/mol)
$^{9\text{-BBN}}$BIM·THF (**1b**·THF)	–14323.85
CO_2	–529.21
2b*	–13223.83
2b	–13233.47
THF	–1637.88



Scheme S2.2. Enthalpies of reaction in the formation of **2b*** and **2b** from $^{9\text{-BBN}}$BIM·THF (**1b**·THF) and CO_2.

S3. Crystallographic Structure Determinations

S3.1. General. Single crystal X-ray structure determinations were carried out at low temperature on Bruker Kappa Diffractometers equipped with a Mo or Cu radiation source and a Bruker APEX or APEX-II area detector. All structures were solved via direct methods with SIR 2004[13] and refined by full-matrix least-squares procedures using SHELXL-2013[14]. Crystallographic data collection and refinement information are listed in Table S3.1. The boralactone **2a** contains rotational disorder of the boron-bound cyclohexyl group, which was modeled and refined anisotropically. The exocyclic eneamine **3**•1.5(C_5H_{12}) contains positional disoder of one co-crystallized molecule of *n*-pentane, which was modeled and refined anisotropically. The (boryl)iminomethane $^{9\text{-BBN}}$BIM·THF ((**1b**·THF)·1.5(C_6H_6)) contains positional disoder of the boron-bound THF, as well as positional disorder of one *i*-Pr group. These disordered groups were modeled and refined anisotropically. This structure also contains co-crystallized molecules of benzene (two per unit cell) that were highly disordered and could not be properly modeled. The Platon routine SQUEEZE[15] was utilized to account for these electrons as a diffuse contribution to the overall scattering without specific atom positions. The double-hydroboration product **6** contains positional disorder of a co-crystallized molecule of *n*-pentane, which was modeled and refined anisotropically.

Crystallographic Information Files (CIF) for all structures have been deposited with the Cambridge Crystallographic Data Centre. The Following CCDC structure codes have been assigned:

CCDC 1028214 – Compound **2a**

CCDC 1028222 – Compound **3**
CCDC 1028216 – Compound **4**
CCDC 1028221 – Compound **5**
CCDC 1028217 – Compound **1b**·THF
CCDC 1028215 – Compound **6**
CCDC 1028218 – Compound **2b**
CCDC 1028219 – Compound **7**
CCDC 1028220 – Compound **1c**

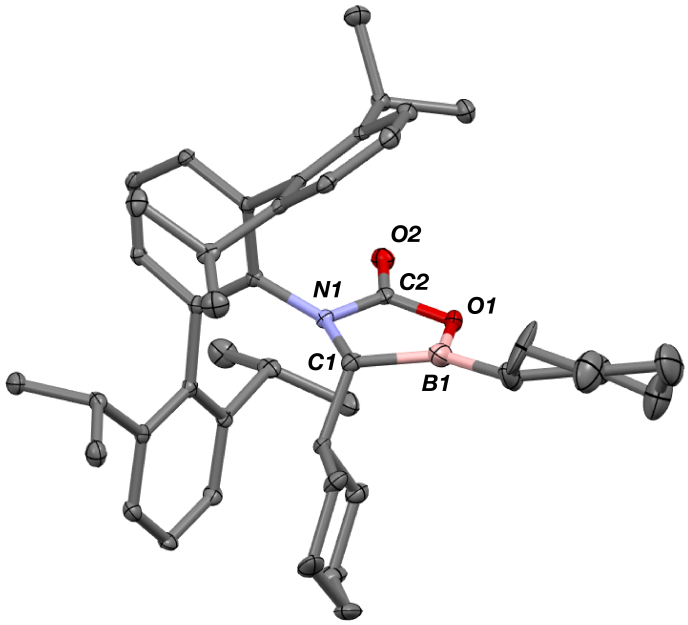


Figure S3.1. Molecular structure of **2a**. Selected bond distances (Å) and angles (º): C2-O1 = 1.391(3); C2-O2 = 1.198(3); C2-N1 = 1.367(3); O1-B1 = 1.378(4); B1-C1 = 1.570(4); C1-N1 = 1.477(3); O1-C2-O2 = 121.4(2); O1-C2-N1 = 112.0(2); N1-C2-O2 = 129.1(2).

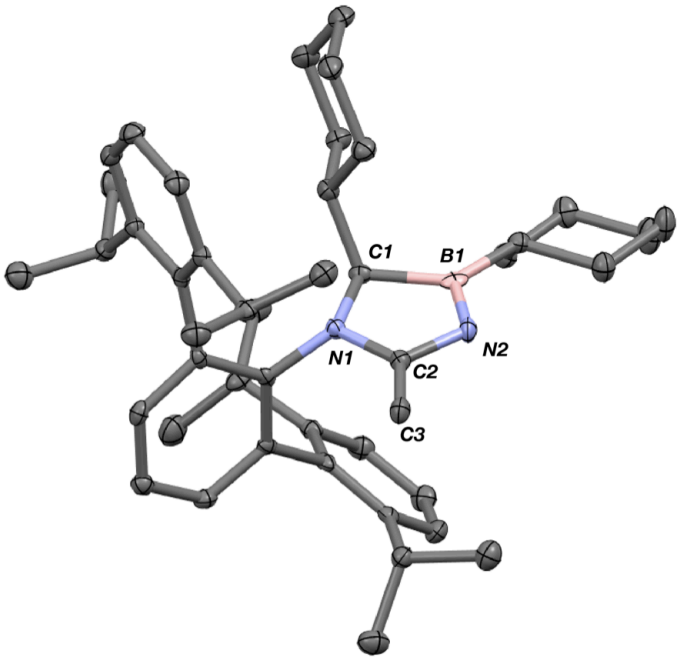


Figure S3.2. Molecular structure of **3**. Selected bond distances (Å) and angles (º): C2-C3 = 1.332(3); C2-N2 = 1.399(3); N2-B1 = 1.396(3); B1-C1 = 1.592(3); C1-N1 = 1.487(3); N1-C2 = 1.402(3). N1-C2-C3 = 128.1(2); N1-C2-N2 = 107.7(2); C3-C2-N2 = 124.3(2).

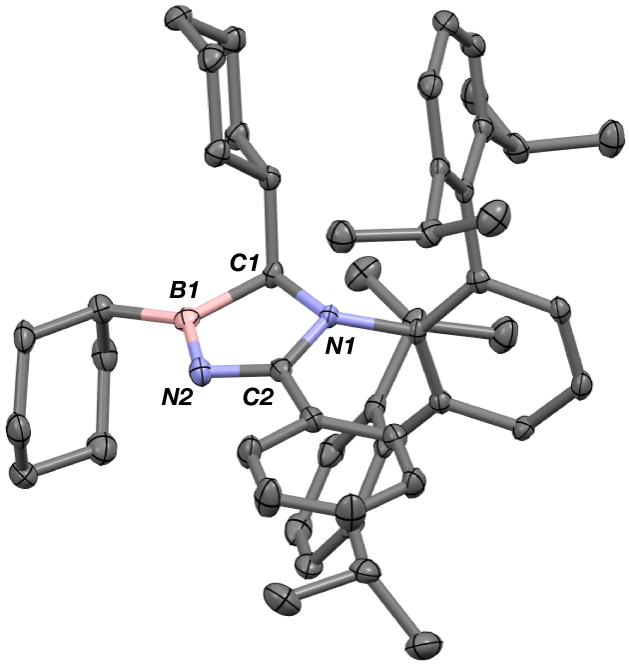


Figure S3.3. Molecular structure of **4**. Selected bond distances (Å) and angles (º): C2-N2 = 1.315(3); C2-N1 = 1.315(3); N2-B1 = 1.434(3); B1-C1 = 1.596(3); C1-N1 = 1.493(3). B1-N2-C2 = 107.6(2); N2-C2-N1 = 116.5(2).

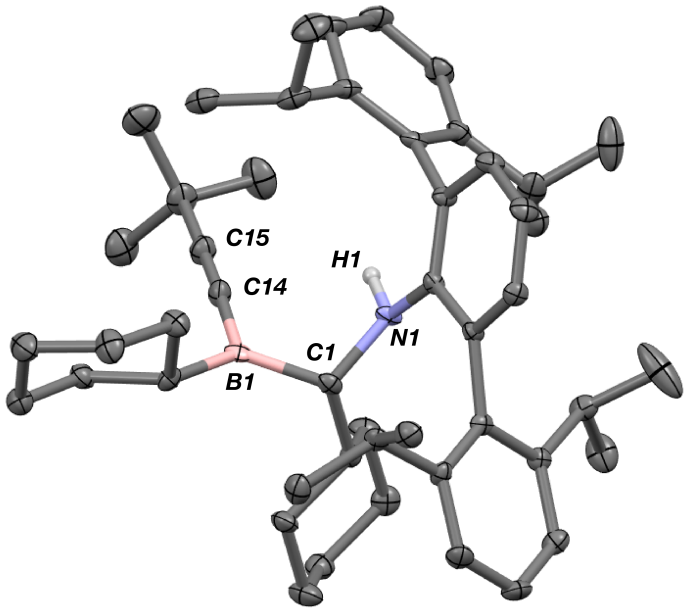


Figure S3.4. Molecular structure of (Cy)((CH$_3$)$_3$CC≡C)BCH(Cy)NHAr^{Dipp2} **(5)**. Selected bond distances (Å) and angles (º): N1-C1 = 1.485(4); C1-B1 = 1.579(5); B1-C14 = 1.522(5); C14-C15 = 1.211(4). B1-C1-N1 = 111.1(2).

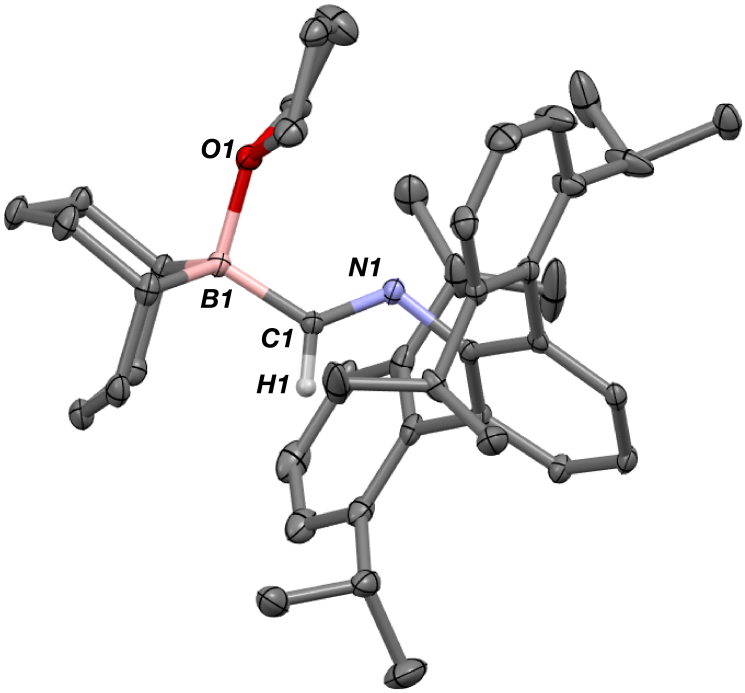


Figure S3.5. Molecular structure of $^{9\text{-BBN}}$BIM·THF (**1b**·THF). Selected bond distances (Å) and angles (º): B1-O1 = 1.631(2); B1-C1 = 1.613(2); C1-N1 = 1.280(2); B1-C1-N1 = 125.8(1); C1-B1-O1 = 106.7(1).

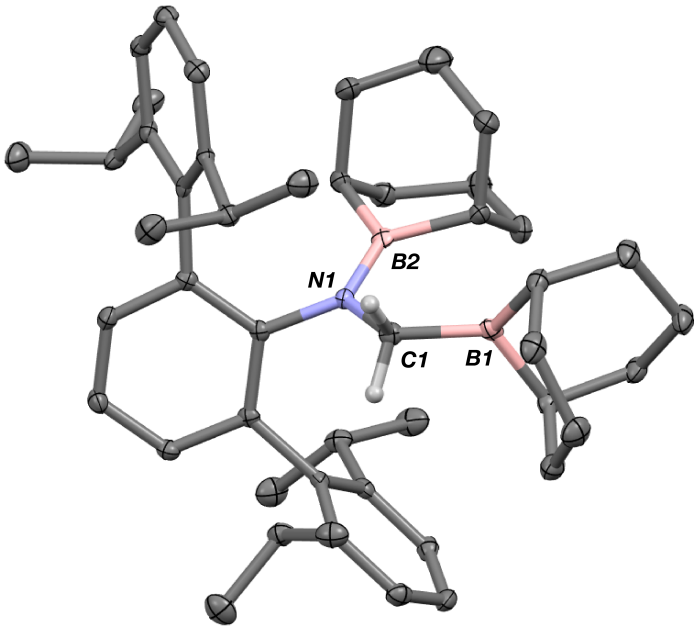


Figure S3.6. Molecular structure of (9-BBN)CH_2N(9-BBN)Ar^{Dipp2} (**6**). Selected bond distances (Å) and angles (º): B1-C1 = 1.600(3); C1-N1 = 1.490(2); N1-B2 = 1.406(3); B1-C1-N1 = 119.2(2); B2-N1-C1 = 120.1(2).

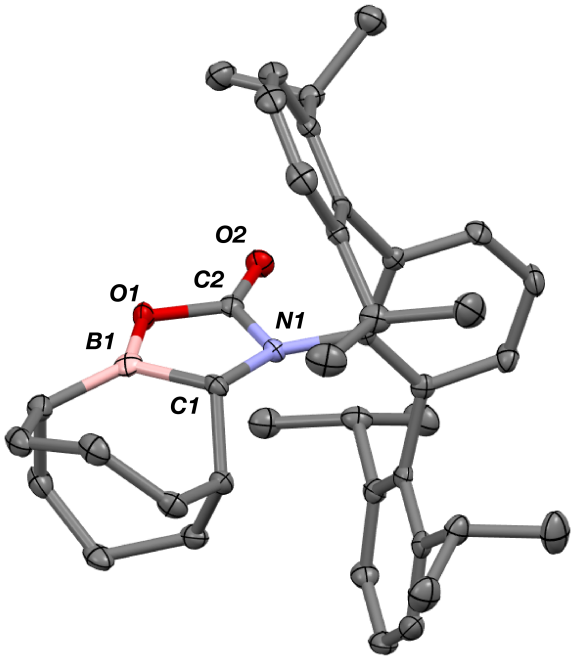


Figure S3.7. Molecular structure of **2b**. Selected bond distances (Å) and angles (º): C2-O1 = 1.389(2); C2-O2 = 1.202(2); C2-N1 = 1.365(2); O1-B1 = 1.381(2); N1-C1 = 1.480(2); C1-B1 = 1.576(2); N1-C2-O2 = 128.5(1); N1-C1-O1 = 110.1(1); O1-C2-O2 = 121.4(1).

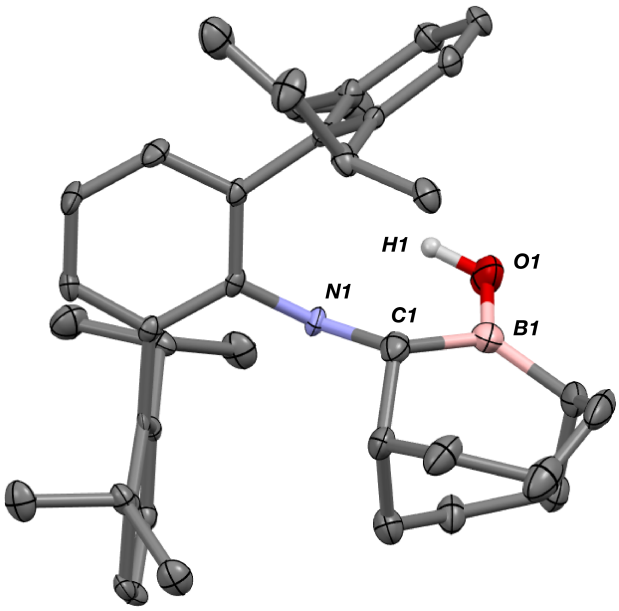


Figure S3.8. Molecular structure of **7**. Selected bond distances (Å) and angles (º): O1-B1 = 1.358(6); B1-C1 = 1.598(6); C1-N1 = 1.477(5). B1-C1-N1 = 109.1(3).

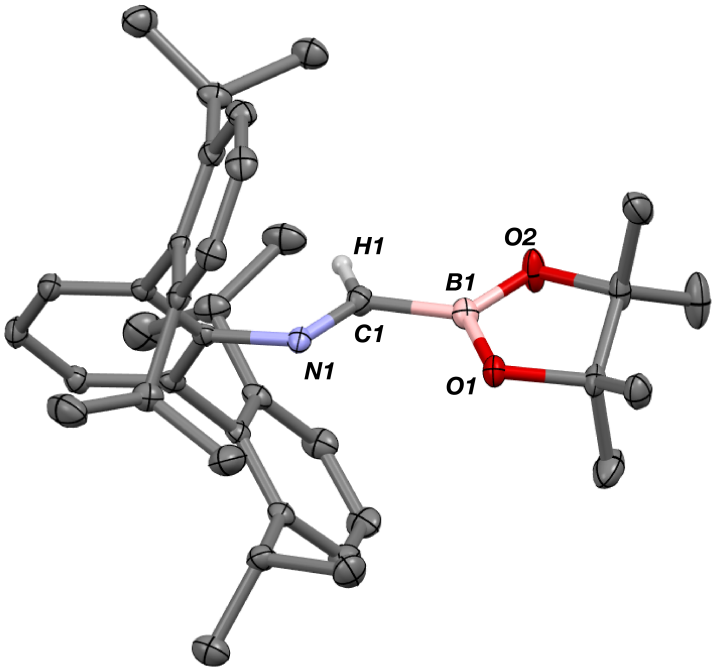


Figure S3.9. Molecular structure of ^{Pin}BIM (**1c**). Selected bond distances (Å) and angles (º): N1-C1 = 1.275(2); C1-B1 = 1.570(2); B1-O1 = 1.356(2); 1.353(2); N1-C1-B1 = 119.2(1).

Table S3.1. Crystallographic data collection and refinement information.

Name	Boralactone **2a**	Enamine **3**•1.5(C_6H_6)	Heterocycle **4**
Formula	$C_{44}H_{60}NBO_2$	$C_{52.5}H_{81}N_2B$	$C_{50}H_{65}N_2B$
Crystal System	Monoclinic	Triclinic	Monoclinic
Space Group	$P2_1/c$	P-1	$P2_1/c$
a, Å	18.442(2)	10.3180(8)	12.3306(9)
b, Å	11.960(1)	12.816(1)	13.054(1)
c, Å	19.592(2)	17.806(1)	25.512(2)
α, deg	90	83.969(4)	90
β, deg	116.965(3)	86.164(4)	90.626(4)
γ, deg	90	85.117(4)	90
V, Å^3	3851.7(7)	2329.1(3)	4106.4(6)
Z	4	2	4
Radiation (λ, Å)	Mo-Kα, 0.71073	Cu-Kα, 1.54178	Mo-Kα, 0.71073
ρ (calcd.), g/cm^3	1.114	1.071	1.140
μ, mm^{-1}	0.066	0.443	0.064
Temp, K	100	100	100
θ max, deg	26.410	44.878	25.371
data/parameters	7152/492	3308/539	7524/486
R_1	0.0626	0.0329	0.0574
wR_2	0.1157	0.0866	0.1163
GOF	1.007	1.046	1.025

Table S3.1. Cont.

Name	(Cy)(*t*-BuC≡C) BCH(Cy)NHAr^{Dipp2} (**5**)	$^{9\text{-BBN}}$BIM·THF ((**1b**·THF)·1.5 (C_6H_6))	(9-BBN)CH_2N(9-BBN) Ar^{Dipp2} (**6**·C_5H_{12})
Formula	$C_{49}H_{70}NB$	$C_{52}H_{69}NBO$	$C_{52}H_{79}NB_2$
Crystal System	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	$P2_1/n$	$P2_1/c$
a, Å	10.9523(6)	10.6296(3)	20.9432(9)
b, Å	12.2836(6)	23.2451(8)	12.5599(6)

c, Å	18.200(1)	18.4090(6)	17.1099(8)
α, deg	77.103(2)	90	90
β, deg	81.075(3)	104.193(1)	91.099(2)
γ, deg	65.736(2)	90	90
V, Å^3	2170.4(2)	4409.8(2)	4499.8(4)
Z	2	4	4
Radiation (λ, Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
ρ (calcd.), g/cm^3	1.046	1.107	1.092
μ, mm^{-1}	0.058	0.063	0.060
Temp, K	100	100	100
θ max, deg	25.371	26.398	25.448
data/parameters	7662/475	9019/496	8280/516
R_1	0.0698	0.0532	0.0557
wR_2	0.1396	0.1316	0.1364
GOF	1.010	1.045	1.033

Table S3.1. Cont.

Name	Boralactone **2b**	Borinic acid **7**	^{Pin}BIM (**1c**)
Formula	$C_{40}H_{52}NBO_2$	$C_{39}H_{54}NBO$	$C_{37}H_{50}NBO_2$
Crystal System	Monoclinic	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a, Å	10.1073(3)	17.347(2)	13.437(1)
b, Å	16.6024(4)	10.634(1)	14.329(1)
c, Å	20.2451(5)	19.7137(2)	18.587(1)
α, deg	90	90	90
β, deg	94.273(1)	112.174(4)	105.742(3)
γ, deg	90	90	90
V, Å^3	3387.8(2)	3367.6(6)	3444.6(5)
Z	4	4	4
Radiation (λ, Å)	Mo-Kα, 0.71073	Mo-Kα, 0.71073	Mo-Kα, 0.71073
ρ (calcd.), g/cm^3	1.156	1.112	1.064
μ, mm^{-1}	0.069	0.064	0.064

Temp, K	100	100	100
θ max, deg	26.399	25.388	25.465
data/parameters	6949/405	6129/395	6102/382
R_1	0.0433	0.0872	0.0382
wR_2	0.0909	0.1893	0.0944
GOF	1.020	1.082	1.019

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