Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Rational Electronic Tuning of CBS Catalyst for Highly Enantioselective Borane Reduction of Trifluoroacetophenone

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Contents

General Experimental Methods.

All reactions were carried out under an argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. Solvents, which were purchased as dehydrated solvents grade commercial products from Kanto Chemical Co., Inc., were stored in Schlenk tubes under an argon atmosphere. The reagents were purchased at the highest commercial quality and used without further purification, unless otherwise noted. Preparative column chromatography was carried out by using silica gel (Fuji Silysia BW-127 ZH, 100-270 mesh). ^{1}H NMR and ^{13}C NMR spectra were measured at 300 MHz and 75 MHz, respectively, and chemical shifts are given relative to tetramethylsilane (TMS). ^{19}F NMR spectra were measured at 282 MHz, and chemical shifts are given relative to CCl_3F using C_6F_6 as a secondary reference (–162.9 ppm).

(*S*)-Tetrahydro-1-methyl-3,3-diphenyl-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1a)[1]

(*S*)-(-)-α,α-Diphenyl-2-pyrrolidinemethanol (25.3g, 0.100 mmol) was suspended in toluene (2 mL) and heated to 70 °C to afford a colorless solution. After addition of trimethylboroxine (10 μL, 0.072 mmol), the reaction mixture was stirred for 1.5 h at ambient temperature. The toluene and excess trimethylboroxine and water were distilled off until only 1 mL remained. The reaction was chased with toluene (3 x 1 mL) each time distilling until 1 mL remained. After the third time the remaining toluene was distilled off at atmospheric pressure and then under high vacuum to yield an off-white solid. The product was carried on to the borane reduction without purification.

^{1}H NMR (300 MHz, $CDC1_3$) δ 7.55-7.12 (m, 10H), 4.36 (dd, *J* = 5.7, 9.9 Hz, 1H), 3.40-3.32 (m, 1H), 3.10-3.01 (m, 1H), 1.93-1.57 (m, 3H), 0.90-0.76 (m, 1H), 0.39 (s, 3H); ^{13}C NMR (75.5 MHz, $CDC1_3$) δ 147.6, 143.9, 128.1, 127.7, 127.1, 126.5, 126.3, 126.1, 87.7, 72.6, 42.9, 30.2, 26.3, -5.5.

(*S*)-Tetrahydro-1-(4-methylphenyl)-3,3-diphenyl-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1b) [1]

(*S*)-(-)-α,α-Diphenyl-2-pyrrolidinemethanol (25.3 mg, 0.100 mmol) and 4-methylphenylboronic acid (13.6 mg, 0.100 mmol) were taken up in 4 mL of toluene. The reaction mixture was heated at reflux temperature for 4 h under argon using a Dean-Stark trap filled with 4A molecular sieves to remove water. The reaction mixture was then cooled and concentrated in vacuo to afford the title compound as a colorless oil. The product was carried on to the borane reduction without purification.

^{1}H NMR (300 MHz, $CDC1_3$) δ 7.90 (d, *J* = 7.8 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.46-7.18 (m, 10H), 4.64 (dd, *J* = 5.7, 9.6 Hz, 1H), 3.67-3.58 (m, 1H), 3.43-3.35 (m, 1H), 2.45 (s, 3H), 2.02-1.68 (m, 3H), 1.03-0.90 (m, 1H); ^{13}C NMR (75.5 MHz, $CDC1_3$) δ147.4,143.8, 140.3, 134.7, 128.6, 128.1, 127.7, 127.1, 126.7, 126.4, 126.3, 87.6, 74.3, 43.8, 29.9, 27.5, 21.7.

(*S*)-Tetrahydro-1,3,3-triphenyl-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1c)[1]

Following the procedure for compound **1b**, **1c** was prepared from (*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (25.3 mg, 0.100 mmol) and phenylboronic acid (12.2 mg, 0.100 mmol) as a colorless oil. The product was carried on to the borane reduction without purification.

^{1}H NMR (300 MHz, $CDC1_3$) δ 7.98-7.95 (m, 2H), 7.63-7.61 (m, 2H), 7.46-7.16 (m, 11H), 4.62 (dd, *J* = 5.7, 9.9 Hz, 1H), 3.63-3.55 (m, 1H), 3.39-3.33 (m, 1H), 1.92-1.69 (m, 3H), 1.00-0.86 (m, 1H); ^{13}C NMR (75.5 MHz, $CDC1_3$) δ 147.3, 143.8, 134.6, 130.3, 128.1, 127.8, 127.7, 127.1, 126.7, 126.4, 126.3, 87.7, 74.3, 43.7, 29.9, 27.6.

(*S*)-1-(4-Fluorophenyl)tetrahydro-3,3-diphenyl-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1d) [1]

Following the procedure for compound **1b**, **1d** was prepared from (*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (25.3 mg, 0.100 mmol) and 4-fluorophenylboronic acid (14.0 mg, 0.100 mmol) as a colorless oil. The product was carried on to the borane reduction without purification.

^{1}H NMR (300 MHz, $CDC1_3$) δ 8.01-7.96 (m, 2H), 7.67-7.64 (m, 2H), 7.46-7.15 (m, 10H), 4.65 (dd, *J* = 9.9, 5.7 Hz, 1H), 3.64-3.56 (m, 1H), 3.44-3.36 (m, 1H), 2.02-1.74 (m, 3H), 1.05-0.91 (m, 1H); ^{13}C NMR (75.5 MHz, $CDC1_3$) δ 164.4 (d, J_{CF} = 249 Hz), 147.2, 143.7, 136.7 (d, J_{CF} = 8.0 Hz), 128.2, 127.8, 127.2, 126.7, 126.3, 126.3, 114.9, 87.7, 74.4, 43.7, 29.9, 27.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -110.9 (m, 1F).

(*S*)-Tetrahydro-3,3-diphenyl-1-[4-(trifluoromethyl)phenyl]-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1e)[1]

Following the procedure for compound **1b**, **1e** was prepared from (*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (25.3 mg, 0.100 mmol) and 4-(trifluoromethyl)phenylboronic acid (19.0 mg, 0.100 mmol) as a colorless oil. The product was carried on to the borane reduction without purification.

^{1}H NMR (300 MHz, $CDC1_3$) δ 8.08 (d, *J* = 7.5 Hz 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 7.2 Hz, 2H), 7.51-7.18 (m, 8H), 4.70 (dd, *J* = 9.9, 5.7 Hz, 1H), 3.64-3.55 (m, 1H), 3.45-3.37 (m, 1H), 2.06-1.76 (m, 3H), 1.06-0.92 (m, 1H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 147.0, 143.5, 134.8, 132.0, 128.2, 127.8, 127.3, 126.8, 126.3, 126.2, 124.4 (q, J_{CF} = 3.8 Hz), 124.3 (q, J_{CF} = 272 Hz), 88.0, 74.4, 43.5, 29.9, 27.6; ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.0 (s, 3F)

(*S*)-1-(3,5-Difluorophenyl)tetrahydro-3,3-diphenyl-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1f)

Following the procedure for compound **1b**, **1f** was prepared from

(*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (25.3 mg, 0.100 mmol) and 3,5-difluorophenylboronic acid (15.8 mg, 0.100 mmol) as a colorless oil. The product was carried on to the borane reduction without purification.

^{1}H NMR (300 MHz, $CDC1_3$) δ 7.71 (d, J = 6.9 Hz, 2H), 7.56-7.26 (m, 10H), 7.01 (m 1H), 4.76 (dd, J = 9.9, 5.7 Hz, 1H), 3.68-3.59 (m, 1H), 3.48-3.40 (m, 1H), 2.12-1.82 (m, 3H), 1.12-0.99 (m, 1H); ^{13}C NMR (75.5 MHz, $CDC1_3$) δ 162.9 (dd, J_{CF} = 250, 11 Hz), 146.9, 143.3, 128.2, 127.8, 127.3, 126.8, 126.3, 126.2, 114.9, 105.6 (t, J_{CF} = 25 Hz), 88.0, 74.5, 43.3, 29.8, 27.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -111.6 (m, 2F).

(*S*)-Tetrahydro-3,3-diphenyl-1-(3,4,5-trifluorophenyl)-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1g)

Following the procedure for compound **1b**, **1g** was prepared from (*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (25.3 mg, 0.100 mmol) and 3,4,5-trifluorophenylboronic acid (17.6 mg, 0.100 mmol) as a colorless oil. The product was carried on to the borane reduction without purification.

^{1}H NMR (300 MHz, $CDC1_3$) δ 7.67-7.57 (m, 4H), 7.22-7.49 (m, 8H), 4.72 (dd, J = 9.9, 5.7 Hz, 1H), 3.62-3.53 (m, 1H), 3.45-3.37 (m, 1H), 2.10-1.81 (m, 3H), 1.08-0.95 (m, 1H); ^{13}C NMR (75.5 MHz, $CDC1_3$) δ 151.1 (ddd, J_{CF} = 251, 9.7, 2.8 Hz), 146.8, 143.2, 141.2 (dt, J_{CF} = 254, 15Hz), 128.2, 127.8, 127.4, 126.9, 126.3, 126.1, 118.0 (dd, J_{CF} = 13, 5.7 Hz), 88.1, 74.5, 43.3, 29.8, 27.6; ^{19}F NMR (282 MHz, $CDCl_3$), -136.5 (m, 2F), -159.06 (m, 1F).

(*S*)-Tetrahydro-3,3-diphenyl-1-(2,4,6-trifluorophenyl)-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1h)

Following the procedure for compound **1b**, **1h** was prepared from (*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (25.3 mg, 0.100 mmol) and 2,4,6-trifluorophenylboronic acid (17.6 mg, 0.100 mmol) as a colorless oil. The product was carried on to the borane reduction without purification.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 (d, J = 7.2 Hz, 2H), 7.48 (d, J = 7.2 Hz, 2H) 7.39-7.18 (m, 7H), 6.73-6.65 (m 1H), 4.63 (dd, J = 9.9, 5.7 Hz, 1H), 3.39-3.30 (m, 1H), 3.26-3.17 (m, 1H), 1.93-1.70 (m, 3H), 1.03-0.90 (m, 1H); ^{13}C NMR (151 MHz, $CDC1_3$) δ 166.6 (ddd, J_{CF} = 246, 17, 15 Hz), 164.7 (dt, J_{CF} = 251, 16 Hz), 147.1, 143.3, 128.2, 127.8, 127.3, 126.7, 126.4, 126.2, 100.1 (m), 88.7, 73.5, 43.1, 30.5, 26.5; ^{19}F NMR (282 MHz, $CDCl_3$) δ -98.0 (m, 2F), -106.6 (m, 1F).

(*S*)-1-(Pentafluorophenyl)tetrahydro-3,3-diphenyl-1*H*,3*H*-pyrrolo[1,2-c][1,3,2]oxazaborole (1i) [2]

A 20 mL of dry Schlenk tube was charged with Mg (26.7 mg, 1.10 mmol), THF (0.3 mL), bromopentafluorobenzene (30 μL, 0.24 mmol) and trace amount of I_2 under an argon atmosphere. Then, THF (1.0 mL) was added, followed by addition of bromopentafluorobenzene (95 μL, 0.76 mmol) dropwise over 15 min. After the mixture was added to 1.0 mL of THF solution of trimethyl borate (330 μL, 3.0 mmol) at -78 °C, the resulting mixture was stirred for 1 h. The solvent was removed under reduced pressure to give white solid of crude dimethyl pentafluorophenylboronate. After addition of (*S*)-(-)-α,α-diphenyl-2-pyrrolidinemethanol (253 mg, 1.00 mmol) and benzene (40 mL) to the crude dimethyl pentafluorophenylboronate, the mixture was stirred for 3 h under conditions of azeotrope with Dean-Stark trap containing molecular sieves 3A. The solvent was removed under the pressure of <1 mmHg at 30 °C for 1 h to give pale yellow solid. After addition of Et_2O to the solid, the white suspension was filtered through glass wool under argon atmosphere. The solvent was removed under the pressure of <1 mmHg at 40 °C for 1h to give **1i**.

^{1}H NMR (300 MHz, $CDCl_3$) δ 0.93–1.03 (m, 1H), 1.72–1.80 (m, 1H), 1.81–1.95 (m, 2H), 3.18–3.38 (m, 2H), 4.65 (dd, *J* = 5.9, 10.0 Hz, 1H), 7.03–7.43 (m, 8H), 7.42–7.57 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$ (except for C6F5)) δ 26.3, 30.0, 43.0, 72.8, 87.6, 126.0, 126.3, 126.4, 127.0, 127.6, 128.0, 144.1, 147.8; ^{19}F NMR (282 MHz, $CDCl_3$) δ -163.1 – -162.9 (m, 2F), -152.3 (t, *J* = 21 Hz, 1F), -130.5 – -130.4 (m, 2F).

Typical Procedure for CBS-catalyzed asymmetric borane reduction of α,α,α-trifluoroacetophenone (2).

To a solution of the freshly prepared CBS catalyst (0.100 mmol) in THF (1.0 mL) was added borane-dimethyl sulfide complex (95 μL, 1.0 mmol) under a argon atmosphere at room temperature. The resulting solution was stirred for 30 min. A solution of α,α,α-trifluoroacetophenone (140 μL, 1.0 mmol) in 1 mL of THF was then added dropwise over 1 h at 40 °C by using syringe pump. After the addition, the resulting solution was stirred for 1 h and quenched with 2 mL of methanol in an ice bath. At the time, the starting material **2** was not detected by ^{19}F NMR, which was measured with C_6D_6-containing capillary. After concentration under reduced pressure, the residue was purified on a silica gel column with a mixture of hexane and ethyl acetate (4:1, v/v) as an eluent to give (*S*)-1-phenyl-2,2,2-trifluoroethanol ((*S*)-**3**) in >99% yield with 90% ee.

GC (column, CP, CP-CYCLODEX B 236M; column temp, 110 °C); t_R of (*S*), 30.4 min (95.2%); t_R of (*R*), 32.7 min (4.8%). $[\alpha]_D^{25}$ = +23.0 (*c* 1.56, $CHCl_3$) {lit.[3] >99% ee of *S*-enantiomer, $[\alpha]_D^{21}$ +23.5 (*c* 0.5, CH_3Cl)}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (m, 5H), 5.03 (q, *J* = 6.6 Hz, 1H), 2.56 (bs, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -79.5 (d, *J* = 7.1 Hz, 3F).

CBS-catalyzed asymmetric borane reduction of 4-methyl-α,α,α-trifluoroacetophenone (6a).

Following the procedure for reduction of **2**, (*S*)-4-methyl-α-(trifluoromethyl)-benzenemethanol was obtained in 86% ee. At the end of the reduction, the starting material **6a** was not detected by ^{19}F NMR.

GC (column, CP, CP-CYCLODEX B 236M; column temp, 120 °C); t_R of (*S*), 24.3 min (93.1%); t_R of (*R*), 26.5 min (6.9%). $[\alpha]_D^{25}$ = +28.0 (*c* 1.6, EtOH) {lit.[4] 100% ee of *R*-enantiomer, $[\alpha]_D^{25}$ −31.2 (*c* 0.814, EtOH)}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (d, *J*=7.8 Hz, 2H), 7.14 (d, *J*=7.8 Hz, 2H), 4.92-4.88 (m, 1H), 2.50 (bs, 1H), 2.30 (s, 3H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.5 (d, *J* = 6.9 Hz, 3F).

CBS-catalyzed asymmetric borane reduction of 4-fluoro-α,α,α-trifluoroacetophenone (6b).

Following the procedure for reduction of **2**, (*S*)-4-fluoro-α-(trifluoromethyl)-benzenemethanol was obtained in 90% ee. At the end of the reduction, the starting material **6b** was not detected by ^{19}F NMR.

GC (column, CP, CP-CYCLODEX B 236M; column temp, 120 °C); t_R of (*S*), 20.9 min (95.0%); t_R of (*R*), 22.7 min (5.0%). $[\alpha]_D^{25}$ = +19.9 {lit.[5] 72.5% ee of *R*-enantiomer, $[\alpha]_D^{24.6}$ −16.3 (*c* 0.246, CH_2Cl_2)}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.39 (m, 2H), 7.11- 7.02 (m, 2H), 5.04-5.01 (m, 1H), 2.60 (bs, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.9 (d, *J* = 7.0 Hz, 3F).

CBS-catalyzed asymmetric borane reduction of *m*-(trifluoromethyl)-α,α,α-trifluoroacetophenone (6c).

Following the procedure for reduction of **2**, (*S*)-α,3-bis(trifluoromethyl)-benzenemethanol was obtained in 54% ee. At the end of the reduction, the starting material **6c** was not detected by ^{19}F NMR.

GC (column, CP, CP-CYCLODEX B 236M; column temp, 115 °C); t_R of (*S*), 33.9 min (77.2%); t_R of (*R*), 37.4 min (22.8%). $[\alpha]_D^{25}$ = +10.1 {lit.[6] 85.9% ee of *R*-enantiomer, $[\alpha]_D^{20}$ −17.1 (*c* 1.51, EtOH)}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.77 (m, 1H), 7.70 (m, 1H), 7.68 (m, 1H), 7.58-7.53 (m, 1H), 5.12 (q, J_{HF} = 6.6 Hz, 1H), 2.73 (bs, 1H); ^{19}F NMR (282 MHz, $CDCl_3$) δ -64.3 (s, 3F), -80.0 (d, *J* = 7.3 Hz, 3F).

Cartesian coordinates

Acetophenone

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
n^{O} orbital energy (HOMO):-0.25513 a.u.
$\pi^{*C=O}$ orbital energy (LUMO):-0.06223 a.u.

C	0.006294	0.000000	0.004503
C	0.006192	0.000000	1.394576
C	1.209723	0.000000	2.089556
C	2.425359	0.000000	1.399940
C	2.412801	0.000000	0.001350
C	1.212983	0.000000	-0.691615
H	-0.932539	0.000000	-0.536822
H	-0.931217	0.000000	1.937807
H	1.195153	0.000000	3.171961
H	3.363300	0.000000	-0.516106
H	1.213606	0.000000	-1.775127
C	3.752685	0.000000	2.096604
O	4.785604	0.000000	1.457979
C	3.788569	0.000000	3.612919
H	4.827801	0.000000	3.933591
H	3.282724	0.880815	4.016595
H	3.282724	-0.880815	4.016595

α,α,α-Trifluoroacetophenone (2)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
n^{O} orbital energy (HOMO-2): -0.28857 a.u.
$\pi^{*C=O}$ orbital energy (LUMO): -0.09031 a.u.

C	1.663313	2.935444	0.000000
C	2.191288	1.649084	0.000000
C	1.346728	0.547315	0.000000
C	-0.040963	0.731144	0.000000
C	-0.563831	2.030676	0.000000
C	0.283044	3.125389	0.000000
H	2.327226	3.791881	0.000000
H	3.264372	1.502812	0.000000
H	1.771871	-0.445967	0.000000
H	-1.639160	2.152039	0.000000
H	-0.127908	4.127529	0.000000
C	-1.017204	-0.386539	0.000000
O	-2.213346	-0.233374	0.000000
C	-0.479393	-1.848066	0.000000
F	-1.475812	-2.724852	0.000000
F	0.283044	-2.080240	1.088982
F	0.283044	-2.080240	-1.088982

4-Methyl-α,α,α-trifluoroacetophenone (6a)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
n^{O} orbital energy (HOMO-2): -0.28455 a.u.
$\pi^{*C=O}$ orbital energy (LUMO): -0.09031 a.u.

C	2.964276	−0.182432	−0.003081
C	2.012976	−1.202333	−0.003721
C	0.654445	−0.919699	−0.001980
C	0.213389	0.406975	−0.000294
C	1.164813	1.436580	−0.000766
C	2.514258	1.144159	−0.002546
H	2.339962	−2.235816	−0.006446
H	−0.052911	−1.736304	−0.003229
H	0.814622	2.460667	−0.001023
H	3.237227	1.952562	−0.004449
C	−1.213680	0.799085	0.000361
O	−1.599678	1.942504	0.000832
C	−2.293905	−0.323578	0.000682
F	−3.518120	0.189956	0.002192
F	−2.170217	−1.113069	1.088808
F	−2.172287	−1.111526	−1.088841
C	4.437914	−0.489189	0.004655
H	4.898554	−0.164962	0.942245
H	4.625504	−1.557085	−0.109169
H	4.953167	0.035249	−0.803872

4-Fluoro-α,α,α-trifluoroacetophenone (6b)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
n^{O} orbital energy (HOMO-1): -0.29238 a.u.
$\pi^{*C=O}$ orbital energy (LUMO) ($\pi^{*C=O}$): -0.09206 a.u.

C	2.714408	1.164227	0.000000
C	2.375472	−0.179046	0.000000
C	1.033542	−0.526148	0.000000
C	0.044657	0.465884	0.000000
C	0.426235	1.814729	0.000000
C	1.761052	2.173037	0.000000
H	3.156659	−0.927407	0.000000
H	0.765615	−1.572706	0.000000
H	−0.349647	2.568921	0.000000
H	2.076358	3.208071	0.000000
C	−1.408074	0.178740	0.000000
O	−2.261499	1.031307	0.000000
C	−1.872813	−1.307206	0.000000
F	−3.196528	−1.395125	0.000000
F	−1.408074	−1.955775	1.088741
F	−1.408074	−1.955775	−1.088741
F	4.012248	1.503049	0.000000

m-(Trifluoromethyl)-α,α,α-trifluoroacetophenone (6c)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
n^{O} orbital energy (HOMO-1): -0.30034 a.u.
$\pi^{*C=O}$ orbital energy (LUMO): -0.10359 a.u.

C	−1.739288	1.990444	0.000000
C	−0.392844	1.647646	0.000000
C	−0.004582	0.312293	0.000000
C	−0.974257	−0.691384	0.000000
C	−2.330675	−0.340476	0.000000
C	−2.708215	0.989944	0.000000
H	−2.027990	3.032670	0.000000
H	1.047956	0.068816	0.000000
H	−3.066735	−1.133626	0.000000
H	−3.757516	1.256481	0.000000
C	−0.651696	−2.143202	0.000000
O	−1.488879	−3.009384	0.000000
C	0.843394	−2.576142	0.000000
F	0.957886	−3.897216	0.000000
F	1.478300	−2.096349	1.088857
F	1.478300	−2.096349	−1.088857
C	0.680942	2.704920	0.000000
F	0.170987	3.949907	0.000000
F	1.478300	2.597030	1.081763
F	1.478300	2.597030	−1.081763

CBS 1a-BH_3 adduct (4a)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO+4): 0.00877 a.u.

C	0.077426	−0.027328	0.135134
C	−1.089023	−0.010094	−0.916831
N	−2.310388	−0.526439	−0.174675
B	−1.917846	−0.493068	1.267972
O	−0.608486	−0.183635	1.402842
C	0.876384	1.281934	0.180849
C	0.766887	2.156872	1.260427
C	1.488201	3.347527	1.284890
C	2.325011	3.684090	0.229973
C	2.442991	2.814891	−0.849837
C	1.730364	1.623934	−0.870523
C	−1.528753	1.333358	−1.504769
C	−3.009980	1.096534	−1.807795
C	−3.488328	0.331389	−0.576667
H	−0.887853	−0.714805	−1.717949
H	0.125339	1.899293	2.091151
H	1.393480	4.010613	2.136958
H	2.886552	4.610439	0.249973
H	3.099558	3.060143	−1.676340
H	1.855510	0.950491	−1.709038
H	−0.943230	1.607200	−2.382194
H	−1.414699	2.136788	−0.772982
H	−3.126379	0.479186	−2.701107
H	−3.569623	2.020375	−1.959204
H	−3.733436	1.022123	0.233604
H	−4.343941	−0.312682	−0.758826
C	−2.855136	−0.743086	2.486310
H	−3.879140	−0.405327	2.315357
H	−2.914062	−1.820995	2.666517
H	−2.471345	−0.274677	3.394394
B	−2.605325	−2.139093	−0.501810
H	−3.616722	−2.417106	0.094544
H	−2.728688	−2.193772	−1.704050
H	−1.638318	−2.742895	−0.101758
C	1.044365	−1.207886	−0.026856
C	1.626743	−1.768023	1.111563
C	1.424089	−1.697252	−1.276047
C	2.552228	−2.797100	1.002404
H	1.342929	−1.399907	2.087933
C	2.355875	−2.723993	−1.386634
H	0.993099	−1.292903	−2.183415
C	2.922515	−3.279724	−0.247821
H	2.984719	−3.224276	1.899554
H	2.628764	−3.094015	−2.367787
H	3.642796	−4.084585	−0.332772

CBS 1b-BH_3 adduct (4b)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO): -0.04419 a.u.

C	1.215968	0.024848	0.075239
C	0.911805	−0.145398	1.603358
N	−0.556859	0.222504	1.771921
B	−1.103052	0.186783	0.375309
O	−0.098043	0.064495	−0.527379
C	1.982775	−1.162966	−0.523624
C	1.940878	1.331174	−0.276788
C	1.344420	−2.090531	−1.345697
C	2.043164	−3.174379	−1.870073
C	3.388319	−3.351446	−1.576674
C	4.033472	−2.430329	−0.758024
C	3.338891	−1.344568	−0.242082
C	1.677760	1.942485	−1.503914
C	2.353761	3.094154	−1.883241
C	3.315178	3.652060	−1.048113
C	3.591466	3.046808	0.170103
C	2.909107	1.896515	0.551909
C	1.037750	−1.538126	2.224019
C	0.040237	−1.475813	3.381620
C	−1.154897	−0.751254	2.765018
H	1.481944	0.569334	2.188474
H	0.298288	−1.959565	−1.583251
H	1.528910	−3.880133	−2.512057
H	3.932308	−4.194383	−1.985835
H	5.085350	−2.551035	−0.526979
H	3.866572	−0.625783	0.371817
H	0.928814	1.517902	−2.158184
H	2.125527	3.558579	−2.835426
H	3.840315	4.552774	−1.342750
H	4.332438	3.473709	0.835538
H	3.139143	1.457403	1.514464
H	2.058376	−1.751911	2.540717
H	0.748076	−2.312980	1.509937
H	0.448778	−0.890397	4.208104
H	−0.232827	−2.459227	3.766234
H	−1.807090	−1.451488	2.240291
H	−1.746572	−0.194020	3.486031
C	−2.581495	0.163056	−0.084841
C	−3.675071	0.381824	0.766216
C	−2.863038	−0.110963	−1.433125
C	−4.977743	0.322434	0.294056
H	−3.504395	0.632239	1.804744
C	−4.165978	−0.171638	−1.903413
H	−2.041824	−0.271810	−2.121537
C	−5.247924	0.039527	−1.046487
H	−5.801443	0.507772	0.975367
H	−4.349292	−0.381437	−2.951958
B	−0.712738	1.801974	2.309030
H	−0.067410	1.836843	3.332904
H	−0.251761	2.501254	1.440807
H	−1.889433	1.986935	2.489589
C	−6.666083	−0.053169	−1.546727
H	−7.069058	−1.059343	−1.392318
H	−7.320627	0.642681	−1.018534
H	−6.728114	0.162988	−2.614586

CBS 1c-BH_3 adduct (4c)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO): -0.04752 a.u.

C	0.918874	0.026447	0.097851
C	0.467493	−0.162275	1.587176
N	−1.013758	0.192349	1.614134
B	−1.418864	0.172670	0.170968
O	−0.330800	0.069355	−0.630340
C	1.745036	−1.151998	−0.437573
C	1.666949	1.340048	−0.166514
C	1.189407	−2.079885	−1.317517
C	1.940237	−3.156253	−1.781693
C	3.254918	−3.325736	−1.369638
C	3.817781	−2.404261	−0.492917
C	3.071849	−1.325762	−0.036755
C	1.507106	1.972778	−1.400476
C	2.209574	3.131883	−1.700586
C	3.094772	3.676123	−0.776839
C	3.267477	3.050460	0.450086
C	2.558472	1.892508	0.752233
C	0.545519	−1.559294	2.205365
C	−0.562805	−1.517399	3.258703
C	−1.697846	−0.797364	2.533451
H	0.970605	0.552133	2.231128
H	0.167826	−1.955895	−1.647695
H	1.490808	−3.862430	−2.470175
H	3.839158	−4.163107	−1.732051
H	4.845593	−2.518818	−0.169164
H	3.537326	−0.606016	0.624365
H	0.817791	1.558737	−2.123430
H	2.061981	3.612957	−2.660377
H	3.640640	4.582550	−1.009827
H	3.947312	3.466976	1.183842
H	2.706309	1.437390	1.723605
H	1.532214	−1.766700	2.618995
H	0.334764	−2.330098	1.460135
H	−0.244685	−0.937571	4.127778
H	−0.863177	−2.507272	3.604355
H	−2.287604	−1.497909	1.939722
H	−2.363342	−0.253227	3.197912
C	−2.846875	0.149891	−0.434989
C	−4.016502	0.361411	0.310421
C	−2.986013	−0.116987	−1.807658
C	−5.268750	0.303706	−0.287395
H	−3.945302	0.601459	1.362861
C	−4.235682	−0.177194	−2.408170
H	−2.097335	−0.274157	−2.407226
C	−5.381115	0.032028	−1.646746
H	−6.158443	0.477797	0.306298
H	−4.318589	−0.383907	−3.468827
H	−6.358773	−0.012020	−2.112930
B	−1.233605	1.765321	2.149446
H	−0.675807	1.798543	3.223123
H	−0.710290	2.476720	1.327568
H	−2.423182	1.935379	2.232791

CBS 1d-BH_3 adduct (4d)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO): -0.04767 a.u.

C	1.198713	0.021681	0.082091
C	0.881609	−0.174494	1.603649
N	−0.590301	0.185386	1.765062
B	−1.122661	0.158052	0.364053
O	−0.111635	0.047535	−0.532165
C	1.991286	−1.144801	−0.524466
C	1.903601	1.345167	−0.245562
C	1.378632	−2.071250	−1.367032
C	2.102127	−3.135075	−1.898776
C	3.446639	−3.293133	−1.592160
C	4.066239	−2.373176	−0.752739
C	3.347019	−1.307181	−0.229471
C	1.632317	1.974174	−1.461966
C	2.291632	3.142073	−1.820320
C	3.244392	3.698860	−0.974600
C	3.528704	3.076281	0.232958
C	2.862925	1.909700	0.593945
C	1.004416	−1.578328	2.198882
C	0.002421	−1.537221	3.353315
C	−1.190140	−0.798775	2.747681
H	1.444734	0.530617	2.206973
H	0.333138	−1.955778	−1.615144
H	1.607745	−3.840122	−2.556900
H	4.009819	−4.120442	−2.007113
H	5.117283	−2.479147	−0.511092
H	3.855152	−0.588380	0.400631
H	0.890571	1.550389	−2.124911
H	2.057443	3.619782	−2.764411
H	3.756702	4.612051	−1.252840
H	4.263031	3.502048	0.906391
H	3.098907	1.457380	1.548907
H	2.023598	−1.798647	2.515459
H	0.717218	−2.339405	1.469106
H	0.408761	−0.969189	4.192933
H	−0.273365	−2.527549	3.717493
H	−1.847288	−1.488882	2.215724
H	−1.776951	−0.247812	3.477454
C	−2.597348	0.136828	−0.110887
C	−3.696458	0.360945	0.732782
C	−2.859944	−0.138731	−1.463854
C	−4.998826	0.308026	0.257112
H	−3.532157	0.608872	1.772507
C	−4.153730	−0.198471	−1.958956
H	−2.029883	−0.305857	−2.139197
C	−5.202727	0.025440	−1.082830
H	−5.849741	0.488272	0.901289
H	−4.361229	−0.410176	−2.999984
B	−0.764871	1.761931	2.305386
H	−0.098798	1.811643	3.314549
H	−0.339515	2.470134	1.426315
H	−1.941207	1.922243	2.511626
F	−6.463568	−0.030131	−1.551539

CBS 1e-BH_3 adduct (4e)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO): -0.06674 a.u.

C	2.006074	0.023352	0.051549
C	1.879030	−0.322095	1.575792
N	0.427126	−0.039885	1.942485
B	−0.264630	0.077952	0.621544
O	0.628403	0.086075	−0.394570
C	2.725919	−1.062909	−0.758462
C	2.656340	1.383940	−0.233336
C	2.030761	−1.892535	−1.636820
C	2.697260	−2.881706	−2.355083
C	4.065306	−3.059942	−2.202678
C	4.767157	−2.234253	−1.330470
C	4.104506	−1.242244	−0.620773
C	2.249573	2.104673	−1.357859
C	2.852883	3.311267	−1.684574
C	3.883555	3.816357	−0.899611
C	4.303116	3.102349	0.214134
C	3.694084	1.896034	0.543904
C	2.120648	−1.765196	2.022232
C	1.250621	−1.875108	3.275465
C	−0.029016	−1.148983	2.866537
H	2.485192	0.352884	2.171150
H	0.966104	−1.760472	−1.767761
H	2.139522	−3.512540	−3.037368
H	4.583096	−3.829734	−2.762198
H	5.836969	−2.355920	−1.208250
H	4.672993	−0.591762	0.032028
H	1.447261	1.720499	−1.972782
H	2.514380	3.859479	−2.555870
H	4.352429	4.759626	−1.152813
H	5.101160	3.485717	0.838686
H	4.039190	1.369699	1.424816
H	3.176138	−1.962613	2.207529
H	1.784398	−2.472672	1.260393
H	1.721655	−1.361796	4.116472
H	1.056554	−2.905797	3.574291
H	−0.699617	−1.820772	2.327356
H	−0.567394	−0.708729	3.701403
C	−1.791755	0.086835	0.321064
C	−2.783293	0.129086	1.311257
C	−2.208290	0.028115	−1.018243
C	−4.130389	0.109118	0.981398
H	−2.502042	0.203418	2.352471
C	−3.552421	0.008262	−1.358091
H	−1.463367	−0.000793	−1.803600
C	−4.514942	0.046305	−0.354166
B	0.279411	1.461978	2.673597
H	1.057049	1.425899	3.599424
H	0.585283	2.273649	1.834541
H	−0.868699	1.557202	3.024927
C	−5.976935	0.070200	−0.709862
H	−3.856504	−0.042018	−2.395303
H	−4.883694	0.140250	1.757580
F	−6.731068	−0.557858	0.214086
F	−6.220950	−0.522253	−1.895583
F	−6.444404	1.333745	−0.801115

CBS 1f-BH_3 adduct (4f)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO): -0.06160 a.u.

C	1.350549	0.055969	0.120122
C	1.016271	0.135949	1.649663
N	-0.465369	0.483998	1.728855
B	-0.972908	0.207675	0.349801
O	0.045579	-0.046382	-0.502624
C	2.162073	-1.191176	-0.255658
C	2.042683	1.306519	-0.438002
C	1.572508	-2.262509	-0.924870
C	2.315539	-3.396230	-1.242414
C	3.655780	-3.478936	-0.890982
C	4.252435	-2.413701	-0.224478
C	3.514088	-1.279378	0.084307
C	1.782415	1.692589	-1.754065
C	2.432171	2.782955	-2.315938
C	3.364286	3.502617	-1.576735
C	3.637475	3.121345	-0.270358
C	2.981300	2.032395	0.293933
C	1.163716	-1.129040	2.496295
C	0.138672	-0.904683	3.609747
C	-1.060681	-0.328127	2.859962
H	1.554648	0.955380	2.115550
H	0.530976	-2.208040	-1.208119
H	1.839693	-4.215235	-1.769007
H	4.233649	-4.361190	-1.138913
H	5.300041	-2.460838	0.048561
H	4.003136	-0.450717	0.580459
H	1.056864	1.140996	-2.335967
H	2.207087	3.071851	-3.335808
H	3.869544	4.355315	-2.014163
H	4.355881	3.676509	0.320935
H	3.209137	1.769100	1.319233
H	2.182082	-1.257684	2.862084
H	0.909554	-2.019874	1.916766
H	0.512890	-0.179090	4.335089
H	-0.117656	-1.818303	4.147158
H	-1.680671	-1.126480	2.448064
H	-1.683374	0.323162	3.467025
C	-2.446378	0.085124	-0.138175
C	-3.552485	0.431965	0.648473
C	-2.667937	-0.418459	-1.429397
C	-4.827004	0.267864	0.138260
H	-3.436116	0.859855	1.633688
C	-3.960875	-0.563278	-1.893900
H	-1.841802	-0.690383	-2.072287
C	-5.067470	-0.229457	-1.131425
B	-0.681433	2.128126	1.977246
H	-0.037649	2.371282	2.971904
H	-0.249997	2.675587	0.992368
H	-1.864333	2.295090	2.128955
F	-5.883895	0.605735	0.901209
F	-4.161755	-1.047592	-3.135052
H	-6.072885	-0.347425	-1.511387

CBS 1g-BH_3 adduct (4g)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO): -0.06148 a.u.

C	−1.597665	−0.060948	0.094121	H	−1.210428	−0.913335	−2.440161
C	−1.339746	−0.291611	1.623060	H	−2.344398	−2.717483	−3.669101
N	0.132434	−0.671008	1.740019	H	−4.084241	−4.087411	−2.549742
B	0.709719	−0.278178	0.418026	H	−4.664647	−3.624101	−0.183732
O	−0.262062	0.071713	−0.454905	H	−3.534866	−1.843812	1.041538
C	−2.368211	1.233674	−0.198500	H	−2.546956	0.999165	2.906709
C	−2.282650	−1.239095	−0.610915	H	−1.219009	1.826086	2.102144
C	−1.723628	2.357488	−0.713273	H	−0.965282	−0.246938	4.346003
C	−2.429421	3.533169	−0.953130	H	−0.308603	1.392668	4.351223
C	−3.787722	3.605725	−0.676548	H	1.327425	0.846485	2.666932
C	−4.439237	2.488680	−0.164338	H	1.266319	−0.693606	3.541638
C	−3.737485	1.313173	0.066231	C	2.204668	−0.136829	0.016102
C	−1.969354	−1.503714	−1.945421	C	3.267223	−0.581341	0.813917
C	−2.610370	−2.522560	−2.636874	C	2.500191	0.490141	−1.204456
C	−3.585880	−3.290462	−2.011017	C	4.571261	−0.396826	0.399748
C	−3.911544	−3.029772	−0.687234	H	3.096744	−1.105268	1.743775
C	−3.264306	−2.012740	0.006801	C	3.810080	0.666154	−1.600353
C	−1.513175	0.888615	2.580316	H	1.711897	0.841621	−1.856918
C	−0.548154	0.540339	3.714505	C	4.862431	0.228380	−0.806064
C	0.680368	0.021537	2.970807	B	0.316936	−2.334234	1.842611
H	−1.910118	−1.142594	1.981498	H	−0.383295	−2.660875	2.772693
H	−0.667120	2.312209	−0.936284	H	−0.062945	−2.780364	0.787787
H	−1.910408	4.393104	−1.360074	H	1.488152	−2.532588	2.042804
H	−4.336799	4.520666	−0.863927	F	6.124942	0.402699	−1.194391
H	−5.501114	2.527988	0.048013	F	5.592429	−0.822630	1.156325
H	−4.268329	0.447136	0.440594	F	4.097982	1.266553	−2.764424

CBS 1h-BH_3 adduct (4h)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO): -0.05822 a.u.

C	−1.403474	−0.064831	−0.116985	H	−0.865945	2.499218	0.572246
C	−1.118484	−1.171904	−1.185282	H	−1.908949	4.577302	−0.238371
N	0.387033	−1.120684	−1.443660	H	−3.669260	4.491259	−1.984556
B	0.919817	−0.272344	−0.330152	H	−4.365837	2.296702	−2.906178
O	−0.091491	0.263301	0.385803	H	−3.330544	0.235267	−2.107925
C	−2.255496	−0.543238	1.068021	H	−2.444759	−2.899181	−1.010683
C	−2.021932	1.214606	−0.697197	H	−1.199360	−2.820325	0.229656
C	−1.722944	−0.604596	2.354703	H	−0.754654	−3.389816	−2.749602
C	−2.502490	−1.036504	3.424511	H	−0.258544	−4.417408	−1.400823
C	−3.822310	−1.416080	3.225160	H	1.416199	−2.843008	−0.688166
C	−4.363693	−1.350967	1.945162	H	1.519945	−2.622559	−2.437994
C	−3.589522	−0.912850	0.879747	C	2.396209	0.042831	0.087221
C	−1.639605	2.453757	−0.181756	C	3.551569	−0.552775	−0.437553
C	−2.227079	3.624097	−0.644108	C	2.673075	1.028192	1.052712
C	−3.213406	3.577497	−1.622508	C	4.846861	−0.226518	−0.080595
C	−3.604377	2.348460	−2.137021	C	3.940389	1.407163	1.455830
C	−3.012636	1.177059	−1.677730	C	5.012986	0.762701	0.869424
C	−1.405038	−2.629883	−0.826760	F	1.659564	1.676997	1.648091
C	−0.414055	−3.383618	−1.711889	F	3.432328	−1.532254	−1.347791
C	0.859662	−2.554525	−1.580488	F	6.254727	1.104728	1.238558
H	−1.598438	−0.922917	−2.126991	H	5.689240	−0.729817	−0.532262
H	−0.700381	−0.297728	2.522644	H	4.077592	2.179094	2.199053
H	−2.070607	−1.071478	4.417923	B	0.711475	−0.226749	−2.829547
H	−4.427970	−1.752539	4.058115	H	0.296832	0.884946	−2.603497
H	−5.395597	−1.635152	1.775607	H	1.901837	−0.265902	−2.990611
H	−4.038589	−0.847712	−0.103225	H	0.089194	−0.788091	−3.702103

CBS 1i-BH_3 adduct (4i)

B3LYP/6-311g(2d,p)// B3LYP/6-311g(2d,p)
π^{*B} orbital energy (LUMO): -0.07002 a.u.

C	1.760807	0.113606	−0.094410	H	1.176127	−2.526757	−0.271483
C	1.531916	1.520141	−0.743632	H	2.191481	−4.248701	−1.707629
N	0.029864	1.616685	−1.011260	H	3.967170	−3.634732	−3.327872
B	−0.547164	0.459217	−0.263340	H	4.706244	−1.272986	−3.489801
O	0.425413	−0.321389	0.246985	H	3.697738	0.438261	−2.071129
C	2.590396	0.148803	1.196472	H	2.918048	3.043845	−0.019812
C	2.362148	−0.920626	−1.055632	H	1.656842	2.616242	1.129773
C	2.017479	−0.163243	2.428184	H	1.267511	4.139269	−1.502704
C	2.779121	−0.126720	3.593280	H	0.793239	4.690142	0.107323
C	4.120824	0.224493	3.545597	H	−0.942902	3.032916	0.272403
C	4.702008	0.530436	2.319082	H	−1.038934	3.402176	−1.453725
C	3.945398	0.486550	1.156407	C	−2.046671	0.062286	−0.007179
C	1.955998	−2.252973	−0.968628	C	−3.157619	0.861377	−0.297049
C	2.528222	−3.221472	−1.782887	C	−2.353069	−1.198510	0.529388
C	3.523198	−2.878862	−2.691241	C	−4.466251	0.454144	−0.088710
C	3.937903	−1.556865	−2.780530	C	−3.650834	−1.636761	0.744760
C	3.360944	−0.586079	−1.969236	C	−4.715628	−0.805306	0.433487
C	1.866889	2.770597	0.068430	F	−1.389789	−2.064298	0.861478
C	0.914885	3.808748	−0.523361	F	−3.009155	2.096899	−0.786600
C	−0.390037	3.032031	−0.667770	F	−5.964035	−1.209582	0.641009
H	2.017306	1.569675	−1.713563	B	−0.307099	1.232256	−2.613395
H	0.977845	−0.454778	2.474495	H	0.042679	0.083254	−2.746776
H	2.316226	−0.379102	4.540109	H	−1.489999	1.388383	−2.757470
H	4.712556	0.252472	4.452699	H	0.365093	2.002528	−3.258293
H	5.751031	0.796683	2.265256	F	−5.483600	1.265754	−0.380205
H	4.423618	0.704400	0.209820	F	−3.882101	−2.848885	1.251657

Transition state $5h_{fav}$

ONIOM (MP2/6-31G(d,p):B3LYP/6-31G(d))//ONIOM (MP2/6-31G(d,p):B3LYP/6-31G(d))
Energy with ZPE correction: -2049.519910 Hartree
Gibbs Free Energy: -2049.587509 Hartree

C	1.977435	0.052139	0.027234
C	1.308073	0.425809	1.410625
N	0.168375	-0.542123	1.587627
B	-0.147203	-0.979512	0.127986
O	0.970256	-0.728382	-0.627957
C	3.257877	-0.808960	0.111615
C	3.218242	-2.178090	-0.183695
C	4.370111	-2.963569	-0.100848
C	5.586475	-2.395292	0.275040
C	5.643406	-1.028223	0.550726
C	4.494194	-0.243402	0.459810
C	2.135305	0.324611	2.693278
C	1.970231	-1.136926	3.160668
C	0.770654	-1.701950	2.373812
B	-1.014988	0.113294	2.501089
C	2.255327	1.297181	-0.824810
C	2.068047	1.234410	-2.212435
C	2.726531	2.490108	-0.261826
C	2.349129	2.339764	-3.015171
C	3.015678	3.594552	-1.067236
C	2.828833	3.523050	-2.447573
C	-1.075099	-2.151286	-0.383414
C	-1.744509	-3.118414	0.375393
C	-1.282217	-2.289518	-1.768350
C	-2.530805	-4.140387	-0.146145
C	-2.055457	-3.278341	-2.363883
C	-2.670642	-4.197125	-1.524526
H	0.864897	1.416084	1.297424
H	2.284417	-2.626583	-0.500977
H	4.312522	-4.022454	-0.339265
H	6.482745	-3.006212	0.339665
H	6.587323	-0.564915	0.825592
H	4.572550	0.824026	0.639050
H	1.717715	1.011625	3.432497
H	3.181732	0.593637	2.536851
H	1.790821	-1.184937	4.237829
H	2.867393	-1.723302	2.945465
H	1.093425	-2.481312	1.679125
H	-0.006801	-2.113491	3.010219
H	-1.386486	1.108170	1.884036
H	-1.877404	-0.704828	2.591329
H	-0.533331	0.453219	3.546337
H	1.675806	0.323321	-2.650042
H	2.863963	2.573678	0.813140
H	2.191173	2.276049	-4.088583
H	3.381140	4.510573	-0.610509
H	3.052881	4.380991	-3.075951
H	-3.016593	-4.855387	0.505999
H	-2.174885	-3.319996	-3.439372
O	-1.288310	0.613031	-0.465592
C	-2.073425	1.327678	0.189785
C	-3.439182	0.710557	0.592975
C	-1.968656	2.809633	0.148688
C	-2.837421	3.667291	0.847108
C	-0.955433	3.360424	-0.654612
C	-2.689099	5.047260	0.738338
C	-0.813829	4.740770	-0.758689
C	-1.679516	5.587318	-0.062189
H	-3.618587	3.264118	1.478469
H	-0.296570	2.693952	-1.198935
H	-3.362976	5.702861	1.282430
H	-0.027025	5.151551	-1.384278
H	-1.569730	6.665546	-0.143369
F	-4.356720	1.133062	-0.314600
F	-3.411587	-0.624287	0.542122
F	-3.884302	1.080902	1.809871
F	-3.424814	-5.170812	-2.064749
F	-0.714054	-1.399776	-2.604634
F	-1.634622	-3.097275	1.720576

Transition state $5h_{disfav}$

ONIOM (MP2/6-31G(d,p):B3LYP/6-31G(d))
Energy with ZPE correction: -2049.513747 Hartree
Gibbs Free Energy: -2049.581534 Hartree

C	2.183146	0.036335	0.028213	H	1.904258	1.064433	-4.226671
C	1.608350	-0.502600	-1.349576	H	2.878152	1.797977	-2.948205
N	0.334683	0.283237	-1.595585	H	1.010112	2.318058	-1.694883
B	-0.070002	0.695657	-0.150189	H	-0.009243	1.809031	-3.045133
O	1.081897	0.753323	0.601917	H	-1.021965	-1.555376	-1.950396
C	3.370444	1.018664	-0.079330	H	-1.692438	0.169126	-2.668284
C	3.184255	2.389399	0.142935	H	-0.166582	-0.809563	-3.561400
C	4.252195	3.284298	0.045366	H	1.827403	-0.100398	2.711053
C	5.529945	2.826376	-0.272984	H	3.356440	-2.422594	-0.565912
C	5.732649	1.460355	-0.476323	H	2.507777	-1.887381	4.286393
C	4.666904	0.567075	-0.370568	H	4.028946	-4.197529	0.993615
C	2.438537	-0.323259	-2.621752	H	3.615374	-3.948066	3.435927
C	2.076009	1.082395	-3.147251	H	-3.484088	4.092246	-0.723969
C	0.799410	1.501608	-2.389456	H	-2.603138	2.735121	3.278100
B	-0.716659	-0.509499	-2.537807	O	-0.719023	-1.037614	0.366068
C	2.560832	-1.118431	0.967754	C	-1.546129	-1.749182	-0.248180
C	2.328144	-0.988585	2.342702	C	-2.995592	-1.429153	-0.319874
C	3.175794	-2.285401	0.497342	C	-3.546619	-0.767989	0.789182
C	2.704032	-2.001780	3.223397	C	-3.828042	-1.816467	-1.381337
C	3.557139	-3.297998	1.380303	C	-4.912620	-0.497144	0.835441
C	3.323752	-3.159187	2.747754	H	-2.899193	-0.497640	1.615175
C	-1.218352	1.700232	0.287749	C	-5.188992	-1.529734	-1.334758
C	-1.983055	2.557136	-0.512777	H	-3.404749	-2.307097	-2.249267
C	-1.505049	1.826025	1.658792	C	-5.734543	-0.873621	-0.227387
C	-2.932901	3.458716	-0.040305	H	-5.331933	0.008590	1.700442
C	-2.435154	2.698643	2.208797	H	-5.825922	-1.814711	-2.167195
C	-3.137995	3.512088	1.329402	H	-6.798788	-0.656369	-0.195389
H	1.318541	-1.538654	-1.200307	C	-1.154003	-3.236719	-0.362252
H	2.200675	2.752213	0.416820	F	0.172108	-3.395838	-0.490978
H	4.080935	4.342238	0.227326	F	-1.752945	-3.872188	-1.387778
H	6.361120	3.522238	-0.348866	F	-1.538384	-3.846222	0.781430
H	6.725916	1.083422	-0.705712	F	-0.872174	1.010961	2.528685
H	4.857099	-0.494479	-0.491949	F	-4.047216	4.371898	1.822003
H	2.141238	-1.088279	-3.342920	F	-1.809422	2.549901	-1.851133
H	3.508932	-0.434874	-2.439383				

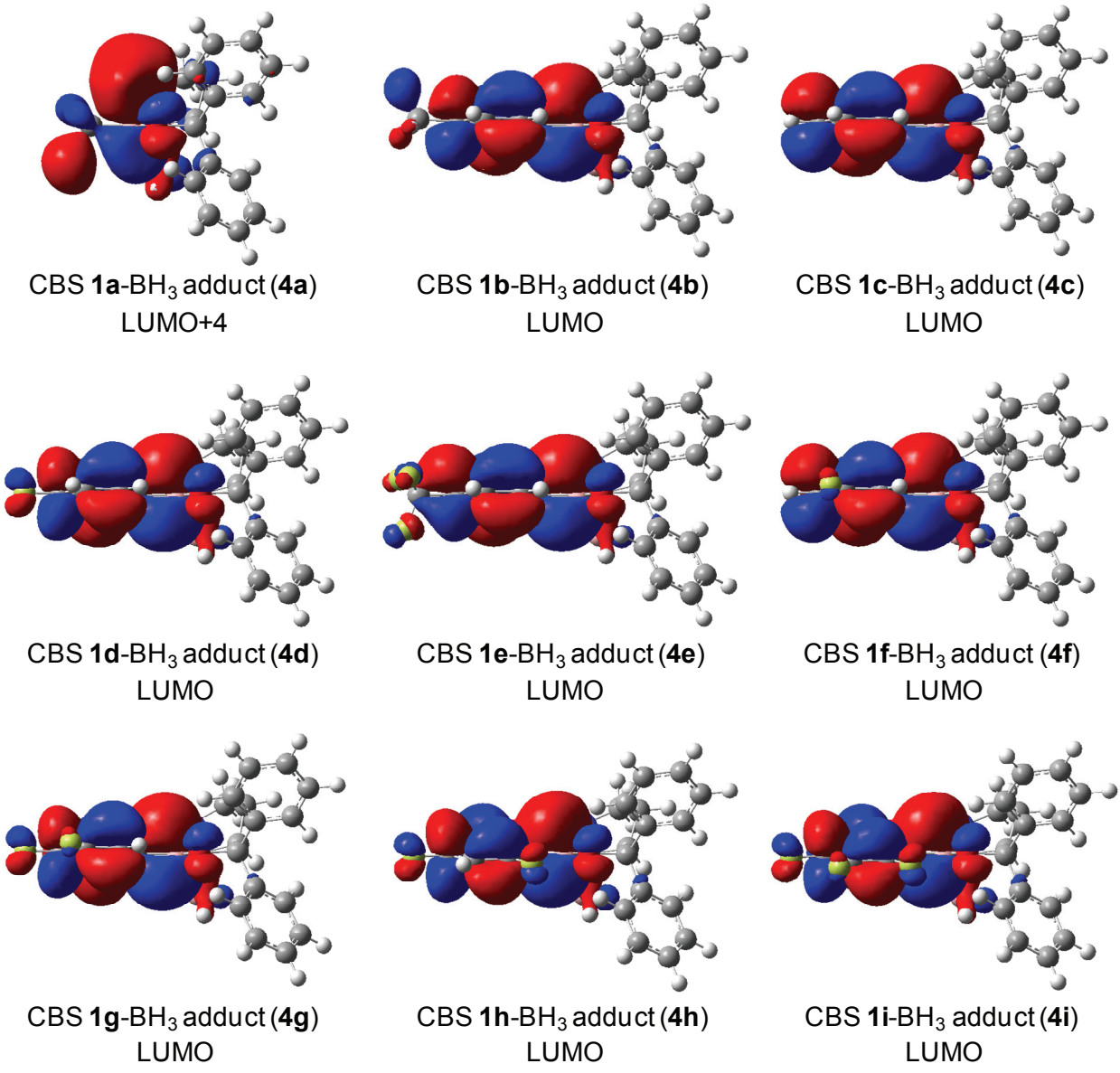

Fig. S1 Schematic presentation of π^{*B} orbital (LUMO+4 of **4a** or LUMO of **4b**-**4i**).

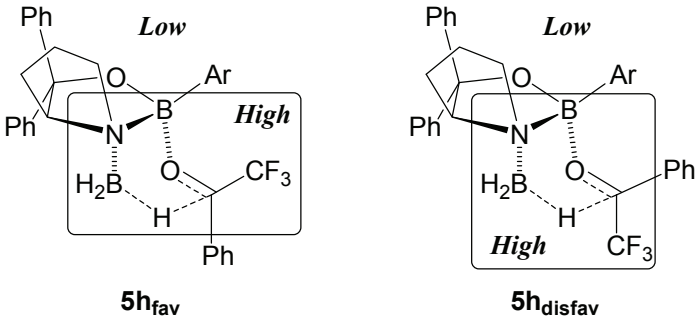

Fig. S2 Partitioning TS model into high (MP2/6-31G(d,p)) and low (B3LYP/6-31G(d)) levels for the ONIOM calculations.

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