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SUPPORTING INFORMATION FOR

Metal-Free Dehydrogenation of Formic Acid to H_2 and CO_2 Using Boron-Based Catalysts

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1. Experimental details

1.1. General considerations

All reactions and manipulations were performed at 20 ºC in a recirculating mBraun LabMaster DP inert atmosphere (Ar) drybox and vacuum Schlenk lines. Glassware was dried overnight at 120ºC or flame-dried before use. ^{1}H, ^{13}C and ^{11}B NMR spectra were obtained using a Bruker DPX 200 MHz spectrometer. Chemical shifts for ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were referenced to solvent impurities. ^{11}B NMR spectra were externally referenced using BF_3•Et_2O. Unless otherwise noted, reagents were purchased from commercial suppliers and dried over 4 Å molecular sieves prior to use. 4 Å molecular sieves (Aldrich) were dried under dynamic vacuum at 250 °C for 48 h prior to use. Tetrahydrofuran (THF), d_8-tetrahydrofuran (d_8-THF), toluene, pentane and d_6-benzene were dried over a sodium(0)/benzophenone mixture and vacuum-distilled before use. CD_3CN and CD_2Cl_2 were dried over CaH_2 and vacuum-distilled before use. Boranes (*B*-I-9-BBN, *B*-Cl-9-BBN, *B*-OMe-9-BBN, *B*-OTf-9-BBN, 9-BBN dimer, BCy_2I and BCy_2Cl, PinBOMe, CatBCl, CatBBr, BCl_3, BH_3•SMe_2, $PhBCl_2$, $BMes_2F$) and $H^{13}CO_2H$ were obtained from Aldrich and used as received. HCO_2H (99 %) was obtained from Acros and degassed prior to use. Triethylamine was purchased from Carlo Erba and degassed prior to use. Cyclohexene was purchased from Aldrich, passed through a column of alumina, dried over CaH_2 and vacuum-distilled before use.

1.2. Crystallography

The data were collected at 150(2) K on a Nonius Kappa-CCD area detector diffractometer[1] using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The crystals were introduced into glass capillaries with a protective coating of Paratone-N oil (Hampton Research). The unit cell parameters were determined from ten frames, then refined on all data. The data (combinations of φ- and ω-scans with a minimum redundancy of 4 for 90% of the reflections) were processed with HKL2000.[2] Absorption effects in [$\mathbf{2}^+$, I^-] were corrected empirically with the program SCALEPACK.[2] The structures were solved by direct methods with SHELXS-97[3] or by intrinsic phasing with SHELXT,[4] expanded by subsequent difference Fourier synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. One carbon atom of the $TBDH^+$ cation in [$TBDH^+$, $\mathbf{5}^-$] is disordered over two positions which were refined with occupancies constrained to sum to unity. The hydrogen atoms bound to nitrogen atoms in [$TBDH^+$, $\mathbf{5}^-$] were found on a difference Fourier map and the carbon-bound hydrogen atoms were introduced at calculated positions in both compounds; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom (1.5 for CH_3, with optimized geometry).

Crystal data for [$\mathbf{2}^+$, I^-]: $C_{16}H_{29}BIN_3$, M = 401.13, monoclinic, space group $C2/c$, a = 17.3182(7), b = 19.7092(5), c = 12.0924(5) Å, β = 120.773(2)°, V = 3546.3(2) Å^3, Z = 8. Refinement of 191 parameters on 5407 independent reflections out of 60769 measured reflections (R_{int} = 0.027) led to R_1 = 0.024, wR_2 = 0.060, S = 1.049, $\Delta\rho_{min}$ = –0.61, $\Delta\rho_{max}$ = 0.60 e Å^{-3}.

Crystal data for [$TBDH^+$, $\mathbf{5}^-$]: $C_{17}H_{30}BN_3O_4$, M = 351.25, orthorhombic, space group $P2_12_12_1$, a = 7.1546(4), b = 12.8526(7), c = 20.4294(6) Å, V = 1878.59(16) Å^3, Z = 4. Refinement of 237 parameters on 3552 independent reflections out of 42486 measured reflections (R_{int} = 0.021) led to R_1 = 0.038, wR_2 = 0.088, S = 1.068, $\Delta\rho_{min}$ = –0.13, $\Delta\rho_{max}$ = 0.16 e Å^{-3}.

The molecular plots were drawn with ORTEP-3.[5] CCDC-1035083 and -1035084 contain the supplementary crystallographic data for compounds [$\mathbf{2}^+$, I^-] and [$TBDH^+$, $\mathbf{5}^-$], respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Outcome of the catalytic experiments

Definitions: In ^{1}H NMR experiments, conversion of formic acid was determined by integration of the formic acid/formate proton (H-COOH) and the protons of the bis(formyloxy)borate species ($R_2B(OC\underline{H}O)_2^-$) versus the internal standard (C_{Ar}-H, δ = 6.79 ppm in CD_3CN). Qualitatively, H_2 (δ = 4.57 ppm in CD_3CN, δ = 4.55 ppm in d_8-THF) and $^{13}CO_2$ (δ = 125.8 ppm in CD_3CN, δ = 125.69 ppm in d_8-THF) are detected by ^{1}H and ^{13}C NMR spectroscopy.

In all experiments, the chemical shift of the formate proton slightly depends on the pH of the solution *i.e.* on the amount of free base and actual formate concentration. On the contrary the bis(formyloxy)borate protons do not exhibit pH-dependency (Δδ < 0.1 ppm).

Turnover number at time *t* (TON) is: $TON = \frac{n^{i}_{HCOOH} - n^{t}_{HCOOH}}{n_{cat.}} = \frac{\rho}{x}$

- n^{i}_{HCOOH} is the initial number of moles of formic acid
- n^{t}_{HCOOH} is the number of moles of formate (including bis(formyloxy)borate) at time *t*
- $n_{cat.}$ is the initial number of moles of catalyst at time *t*
- ρ is the actual measured conversion (%)
- x is the molar percentage (mol%) of catalyst introduced for the reaction.

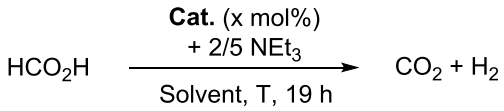
Turnover frequency number (TOF) after *t* hours is: $TOF(h^{-1}) = \frac{TON}{t}$

Observation: For the reactions with R_2B-X (R_2B = Cy_2B or BBN, X = I, Cl, OTf, OMe) in CD_3CN, FA and the base must be either pre-mixed or added sequentially prior to the borane to ensure that the catalysis takes place. Indeed, when the borane and the base are added prior to formic acid, temporary deactivation of the catalyst was observed that resulted in a lengthy activation period of the catalytic system.

Control experiments.

a) The heating of the 5 HCOOH / 2 NEt_3 mixture in either CD_3CN or THF showed no detectable conversion after 48h at 130°C (Entries 1 and 2, Table S1).
b) The heating of pure HCOOH with BBN–I (5 mol%), but without external base (NEt_3 or MTBD) led to no reaction after 30 h at 130°C in acetonitrile (Entry 11, Table S1).

Table S1. Organocatalytic dehydrogenation of formic acid with triethylamine



Entry	Catalyst [mol%]	Temp [°C]	Solvent	Conversion [%]	TON (time, h)
1	–	130	CD_3CN	< 5	–
2	–	130	TDF	< 5	–
3	**BBN-I** (5.0)	130	TDF	48	9.6 (19)
4	**BBN-I** (5.0)	130	C_6D_6	< 5	–
5	**BBN-I** (5.0)	130	Tol-d_8	< 5	–
6	**BBN-I** (5.0)	130	CD_3OD	< 5	–
7	**BBN-I** (5.0)	130	CD_3CN	84	16.8 (19)
8	**BBN-I** (5.0)	100	CD_3CN	< 5	–
9	**BBN-I** (5.0)	110	CD_3CN	< 5	–
10	**BBN-I** (5.0)	120	CD_3CN	18	3.6 (19)
11	**BBN-I** (5.0)	130	CD_3CN	< 5[a]	–
12	**BBN-OTf** (5.0)	130	CD_3CN	59	11.8 (19)
13	**BBN-OMe** (5.0)	130	CD_3CN	88	17.5 (19)
14	**[TBDH$^+$, 5$^-$]** (5.0)	130	CD_3CN	67	13.4 (19)
15	**[TBDH$^+$, 5$^-$]** (2.0)	130	CD_3CN	59	23.6 (19)
16	**BBN-H** (5.0)	130	CD_3CN	52	10.4 (19)
17	**Cy_2B-I** (10.0)	130	CD_3CN	> 99	10 (4.5)
18	**Cy_2B-I** (5.0)	130	CD_3CN	> 99	20 (19)
19	**Cy_2B-I** (1.0)	130	CD_3CN	79	79 (19), 100 (40)
20	**Cy_2B-Cl** (5.0)	130	CD_3CN	> 99	20 (19)
21	**Cy_2B-OTf** (5.0)	130	CD_3CN	> 99	20 (19)
22	**[Et_3NH^+, 6$^-$]** (5.0)	130	CD_3CN	> 99	20 (8)
23	**[Et_3NH^+, 6$^-$]** (2.5)	130	CD_3CN	> 99	20 (9)
24	**[Et_3NH^+, 6$^-$]** (1.0)	130	CD_3CN	78	78 (19), 100 (26)
25	**catB-Cl** (5.0)	130	CD_3CN	< 5	–
26	**catB-Br** (5.0)	130	CD_3CN	< 5	–
27	**pinB-OMe**(5.0)	130	CD_3CN	< 5	–
28	**$B(C_6F_5)_3$** (5.0)	130	CD_3CN	< 5	–
29	**$PhBCl_2$** (5.0)	130	CD_3CN	< 5	–
30	**Mes_2B-F** (5.0)	130	CD_3CN	< 5	–
31	**BCl_3** (5.0)	130	CD_3CN	44	8.8 (19)

[a] No base added.

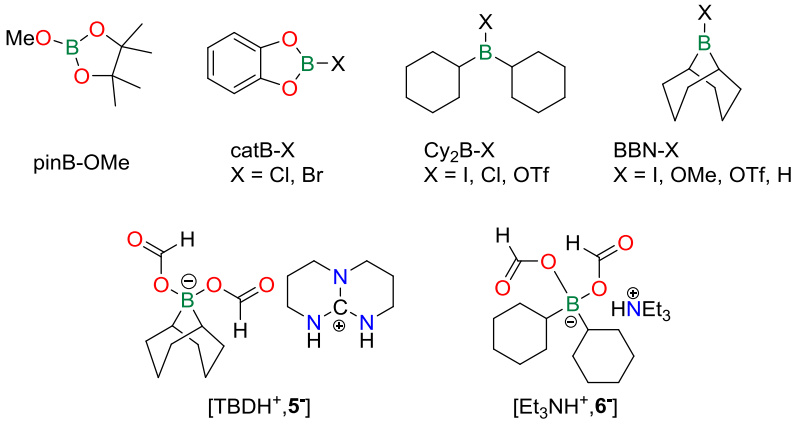
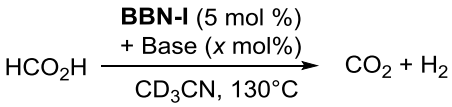


Table S2. Influence of the initial pH (*i.e.* the amount of base added) on the reaction conversion.



Entry	Base [mol%]	Conversion [%] (16h)	Conversion [%] (19h)
1	**0 (NEt_3)**	< 5	< 5
2	**0 (MTBD)**	< 5	< 5
3	**5 (MTBD)**	< 5	< 5
4	**10 (MTBD)**	–	49
2	**10 (NEt_3)**	< 5	< 5
3	**30 (NEt_3)**	52	86
4	**40 (NEt_3)**	57	85
5	**50 (NEt_3)**	62	86
6	**80 (NEt_3)**	70	86
7	**100 (NEt_3)**	68	81

3. Procedures for the catalytic dehydrogenation of formic acid.

Caution: *Full decomposition of formic acid generates high pressure in a sealed tube!*

Reaction in Wilmad medium-wall NMR tubes:

General procedure for the catalytic dehydrogenation of formic acid / triethylamine azeotropic mixture (molar ratio 5:2) with borane catalysts.

In a glovebox, an oven-dried Wilmad NMR tube was charged with preformed and degassed HCO_2H / Et_3N (5:2, molar ratio) (18.0 µL, 0.2 mmol FA), mesitylene as an internal standard and solvent (0.20 mL). To this homogeneous solution was added the borane (*x* mol%) via syringe and the tube was capped and shaked vigorously to ensure complete dissolution of the borane catalyst. When solid catalysts were used (*e.g.* [$TBDH^+$, **5**$^-$] or [Et_3NH^+, **6**$^-$]), the addition order was reversed.

A first ^{1}H NMR spectrum was then acquired to set the initial formic acid (formate) / mesitylene ratio (the singlet 6.79 ppm in CD_3CN was used) and the tube was immersed in a pre-heated silicon-oil bath at the indicated temperature (oil-bath temperature). The reactions were periodically cooled down to room temperature and monitored by NMR spectroscopy.

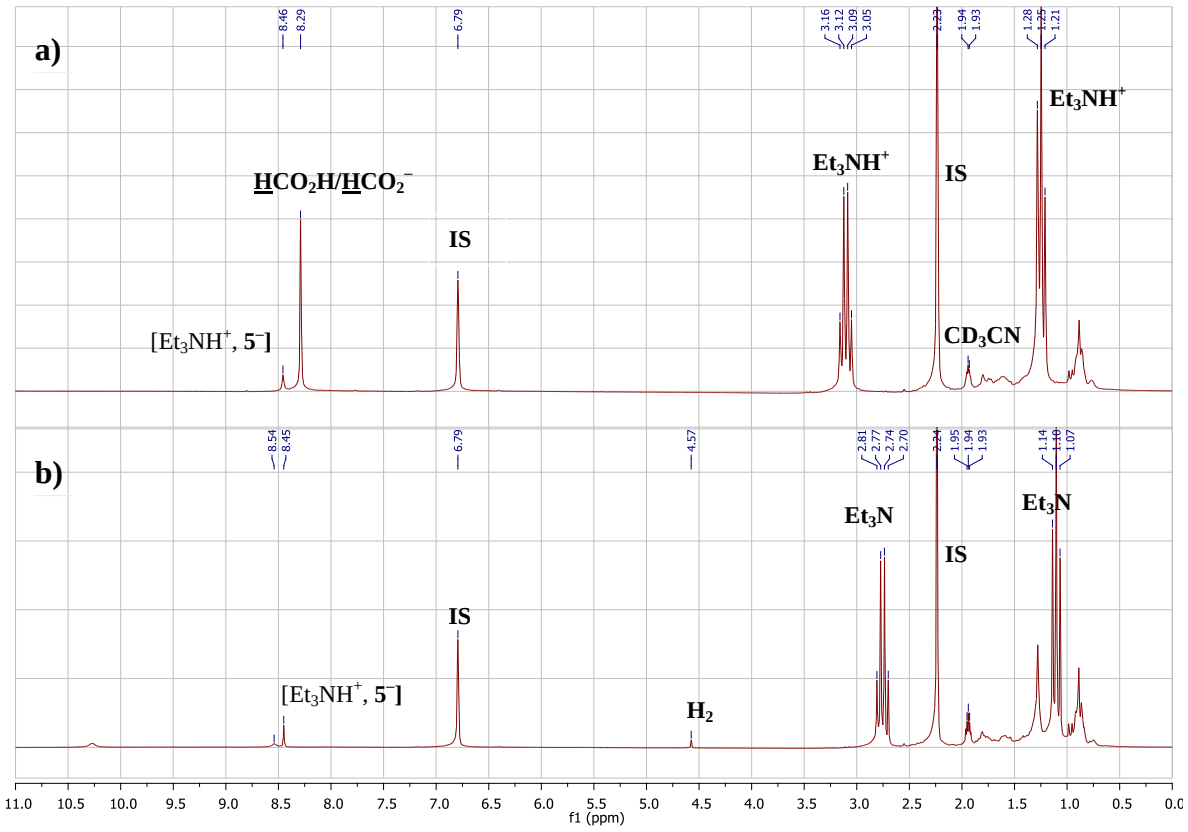


Figure S1. Typical ^{1}H NMR spectra obtained in CD_3CN for the catalytic dehydrogenation of 5 FA/2 TEA with 5 mol% BBN–I. a) crude reaction mixture before heating; t = 0. b) crude reaction mixture after 19 h at 130°C, 87 % conversion , H_2 gas visible at δ = 4.57 ppm.

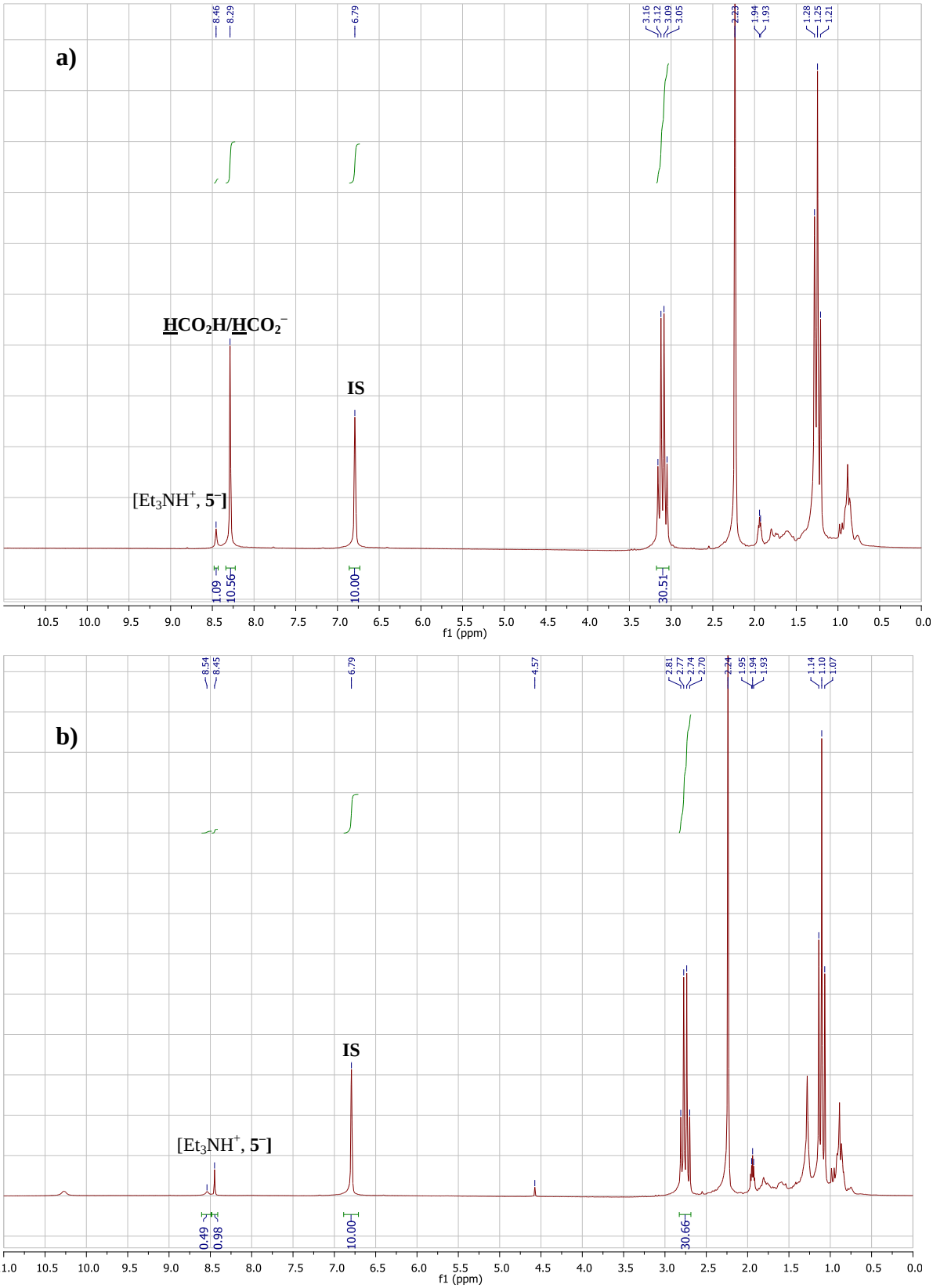


Figure S2. Typical ^{1}H NMR spectra obtained in CD_3CN for the catalytic dehydrogenation of 5 FA/2 TEA with 5 mol% BBN–I; a) before heating. b) after 19 h at 130°C. Integrations show that the amount of [**5**$^-$, Et_3NH^+] is constant and that the conversion reaches 87 % after 19h.

Reaction with $H^{13}CO_2H$: The same procedure given page S9 was used and $H^{12}CO_2H$ was replaced with $H^{13}CO_2H$. $^{13}CO_2$ was the sole ^{13}C enriched product detected along with formates ions and trace of carbonate. Typical spectra are given in Figure S6.

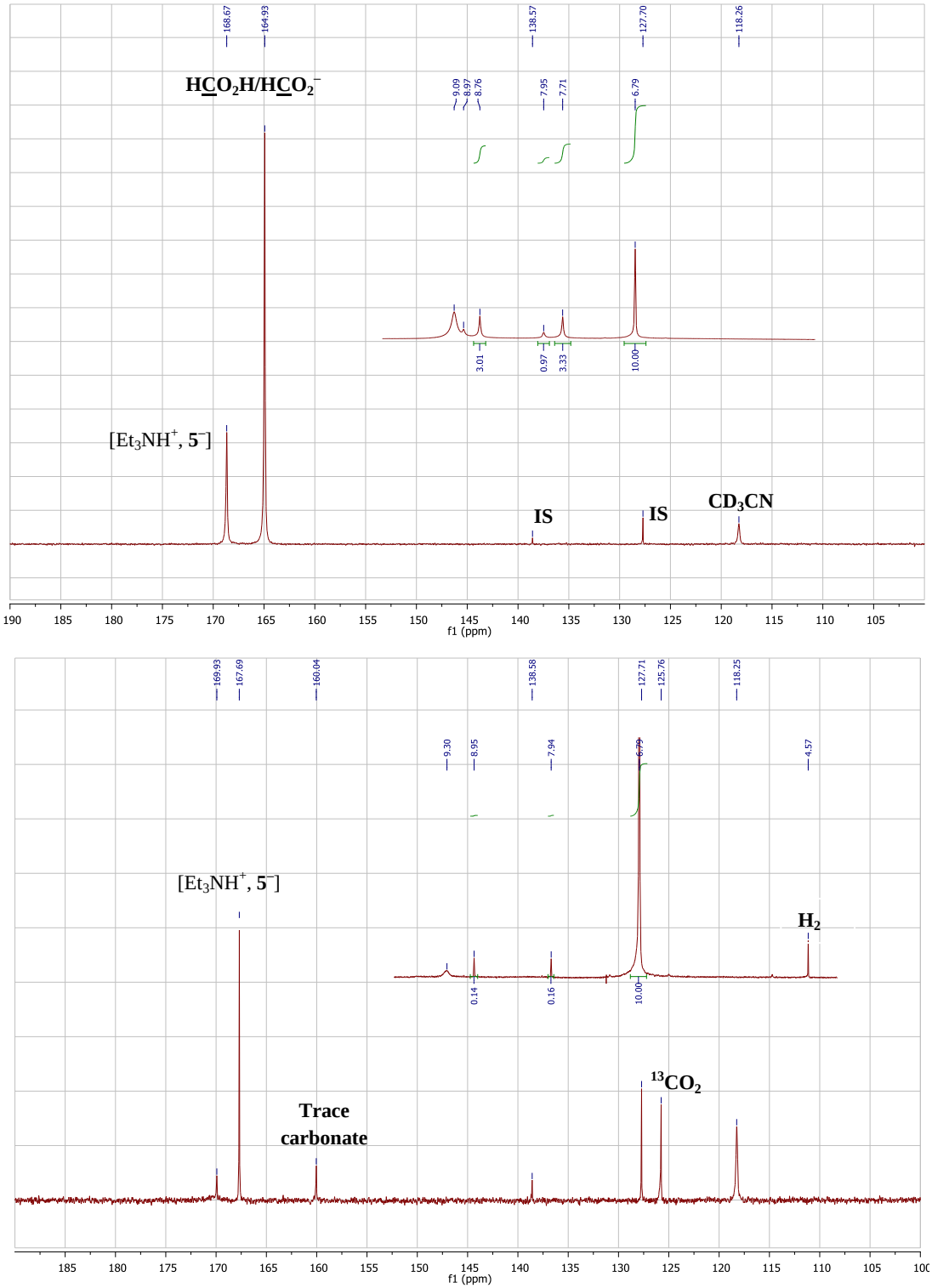


Figure S3. ^{1}H and ^{13}C NMR spectra obtained in CD_3CN for the catalytic dehydrogenation of 5 FA/2 TEA with 10 mol% BBN–I; a) before heating. b) after 19 h at 130°C.

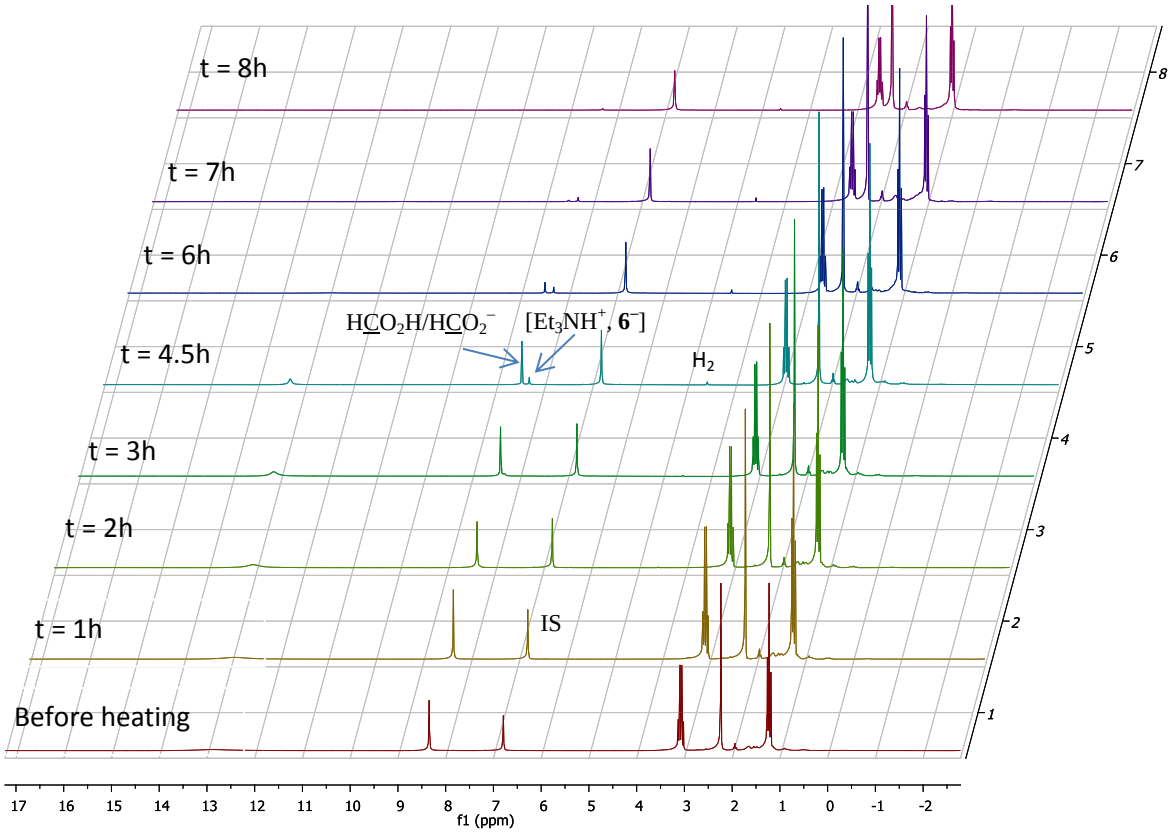


Figure S4. ^{1}H NMR spectra obtained in CD_3CN for the catalytic dehydrogenation of 5 FA/2 TEA with 5 mol% [Et_3NH^+, **6**$^-$] over 8 hours. There is overlap between signals of **6**$^-$ and $\underline{H}CO_2^-$ until 4.5h (65 % conversion).

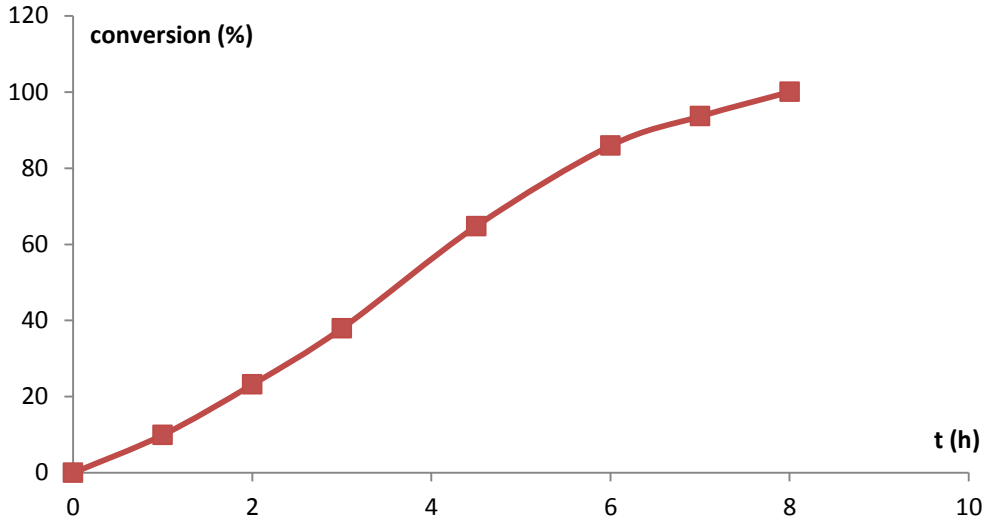
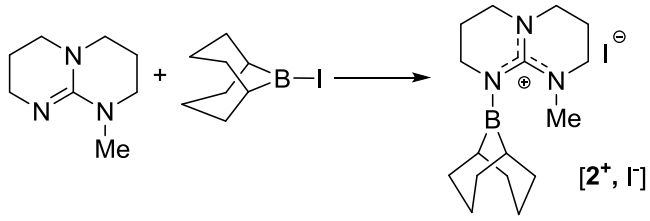


Figure S5. Plot of FA conversion versus time using 5 mol% [Et_3NH^+, **6**$^-$] in CD_3CN.

4. Synthetic procedures.

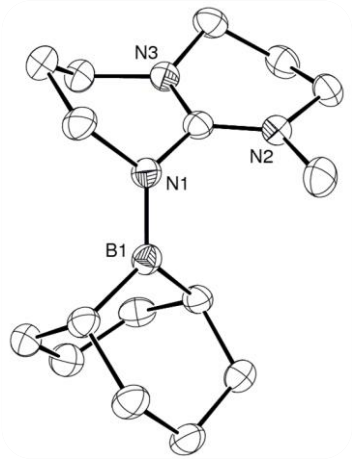
a) Synthesis of [2^+, I^-].



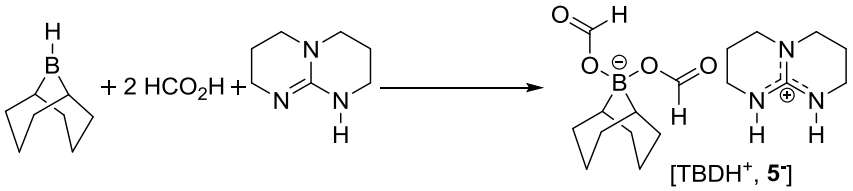
A 25-mL, flame dried round-bottomed flask equipped with a stirring bar and a J-Young valve was charged with MTBD (53.1 mg, 0,347 mmol, 1 equiv) and 3.5 mL of THF. A solution of BBN-I (1 M in hexane, 350 µL, 0.350 mmol, 1.01 equiv.) was then added dropwise at RT over 5 min affording a white solid instantaneously. The resulting suspension was stirred for 2 hours at RT in the glovebox. The white precipitate was then filtered, washed with diethyl ether (3 x 5 mL) and dried under high-vacuum to afford 112 mg of [$\mathbf{2}^+$, I^-] **(**0.28 mmol, 81 %). Crystals suitable for X-Ray diffraction were obtained from the slow cooling of a saturated THF solution of [$\mathbf{2}^+$, I^-].

^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.13 (m, 1H), 3.95 (m, 1H), 3.75 (m, 2H), 3.48 (m, 4H), 3.10 (s, 3H), 2,49-1,18 (m, 18H) ppm.
^{13}C NMR (50 MHz, CD_2Cl_2): δ 158.7, 48.7, 48.4, 43.4, 41.2, 36.1, 35.5, 31.5, 30.9, 25.9, 24.9, 20.9, 20.4 ppm.
^{11}B NMR (64 MHz, CD_2Cl_2): δ 57,2 ppm.
Elemental Analysis: cald for $C_{16}H_{29}BIN_3$ (M 401,14 g.mol^{-1}) : C : 47.91, H : 7.29, N : 10.48. Found : C : 48.26, H 6.96; N 11.63.

Figure S6. ORTEP view of compound $\mathbf{2}^+$ in [$\mathbf{2}^+$, I^-]. Displacement ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted.



b) Synthesis of [TBDH$^+$, 5$^-$].



A 25-mL, flame dried round-bottomed flask equipped with a stirring bar and a J-Young valve was charged with 9-BBN dimer (342 mg, 1.4 mmol, 0.5 equiv.) and 5 mL of toluene. The resulting suspension was stirred vigorously at RT to ensure complete dissolution of the hydroborane reagent. The flask was then sequentially charged with formic acid (258 mg, 211 µL, 5.6 mmol, 2 equiv), added *via* syringe, and TBD (390 mg, 2.8 mmol, 1 equiv), poured in one portion. While H_2 release is quite slow when only formic acid is added, the addition of the base considerably increases the rate of H_2 evolution. The reaction mixture was stirred at RT for 2 h to ensure full conversion of the starting borane (until evolution of H_2 ends). Pentane (*c.a*. 5 mL) was added then added to the reaction mixture and the resulting white solid was isolated by filtration and washed with pentane (*c.a*. 3 x 2 mL). [TBDH$^+$, **5**$^-$] was obtained in almost quantitative yield (930 mg, 2.6 mmol, 93 %), after removal of the volatiles under reduced pressure. Crystals suitable for X-Ray diffraction analysis were obtained from the slow cooling of a saturated toluene solution of [TBDH$^+$, **5**$^-$]. [TBDH$^+$, **5**$^-$] was purified by recrystallization from warm toluene.

^{1}H NMR (200 MHz, CD_3CN) δ 8.40 (s, 2H), 6.94 (bs, 2H), 3.23 (dd, *J* = 11.3, 5.3 Hz, 8H), 2.06 – 1.21 (m, 16H), 0.72 (bs, 2H).
^{13}C NMR (50 MHz, CD_3CN) δ 167.23, 152.07, 47.43, 38.74, 32.07, 25.62, 21.16.
^{11}B NMR (64 MHz, CD_3CN) δ 8.87.
Elemental Analysis : calcd (%) for $C_{17}H_{30}BN_3O_4$ (351.25 g.mol^{-1}): C 58.13, H 8.61, N 11.96; found: C 58.12, H 8.58 N 12.16.

Figure S7. ORTEP view of compound [TBDH$^+$, **5**$^-$]. Displacement ellipsoids are drawn at the 50% probability level and carbon-bound hydrogen atoms are omitted. Only one position of the disordered atom is represented.

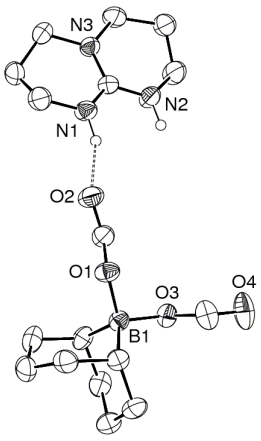
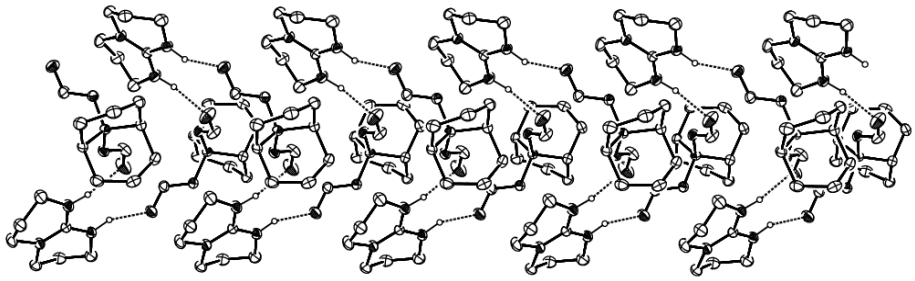
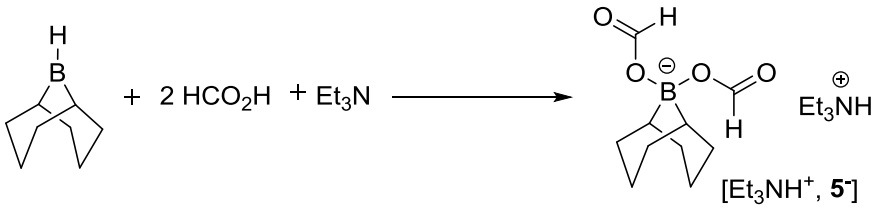


Figure S8. View of the hydrogen bonded one-dimensional polymer in compound [$TBDH^+$, $\mathbf{5}^-$]. Displacement ellipsoids are drawn at the 30% probability level. Carbon-bound hydrogen atoms are omitted and hydrogen bonds are shown as dashed lines.

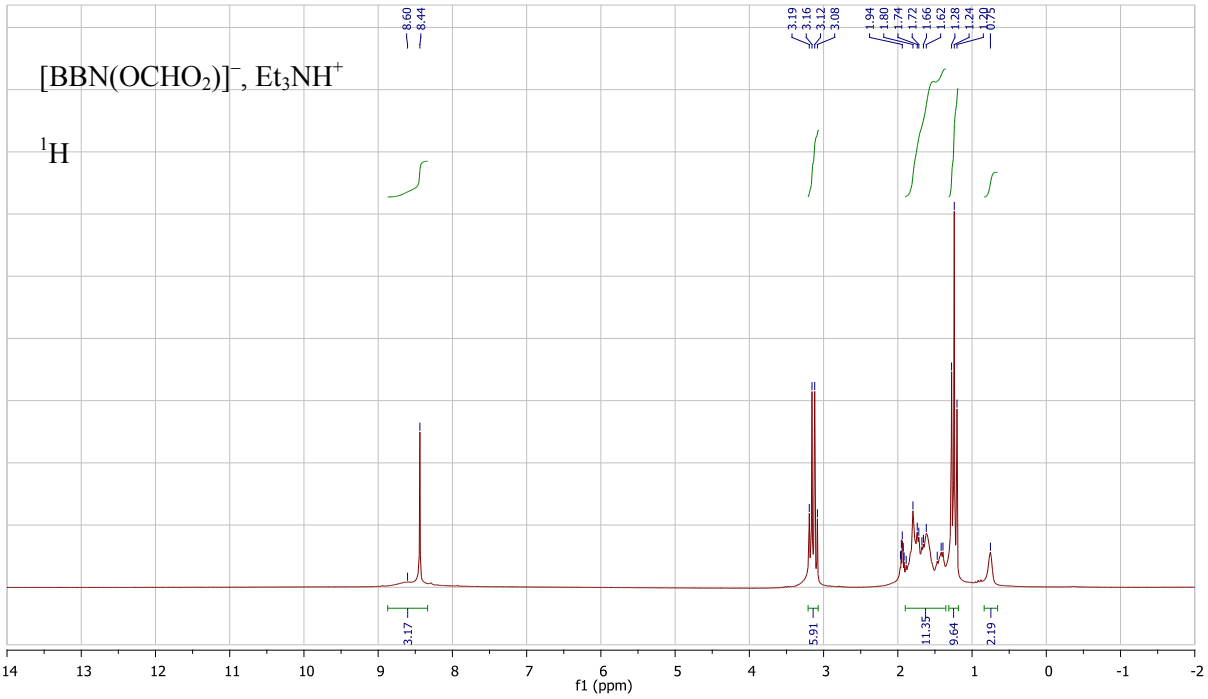


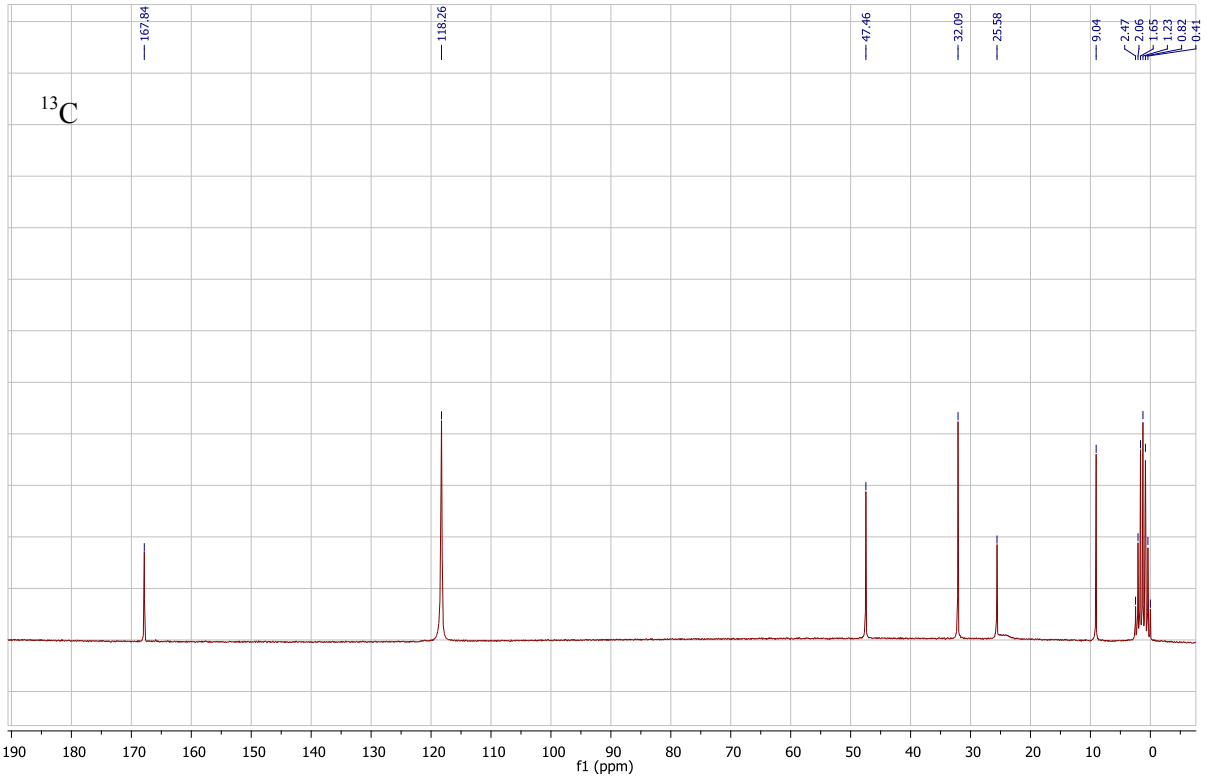
c) Synthesis of [Et_3NH^+, $\mathbf{5}^-$].

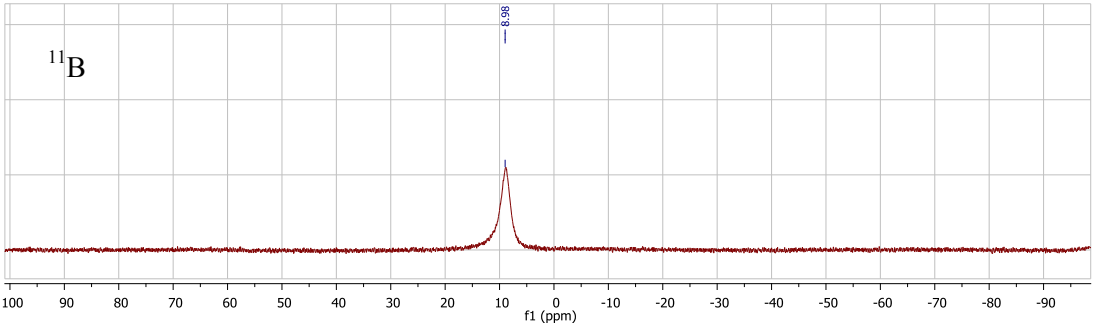


The procedure detailed for the synthesis of [$TBDH^+$, $\mathbf{5}^-$] was employed for the synthesis of [Et_3NH^+, $\mathbf{5}^-$], by replacing TBD with NEt_3. A colorless oil was obtained, which gradually crystallized at – 35°C in the glovebox freezer. The resulting waxy white solid was washed with pentane (3 x 2 mL) and dried under high vacuum to give [Et_3NH^+, $\mathbf{5}^-$] in quantitative yield. Attempts to crystallize [Et_3NH^+, $\mathbf{5}^-$] in several solvents (Et_2O, THF, toluene, benzene, MeCN and pentane) failed due to the formation of an oil, whose solubility increases with solvent polarity. [Et_3NH^+, $\mathbf{5}^-$] may be best described as ionic liquid.

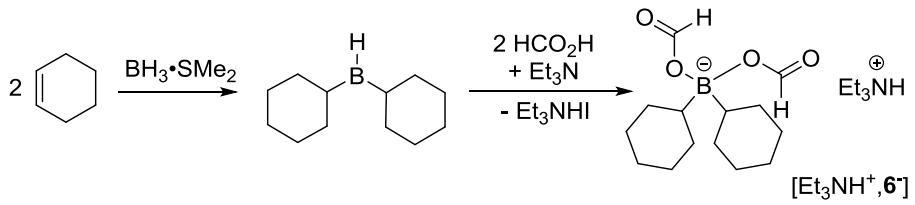
^{1}H NMR (200 MHz, CD_3CN) δ 8.60 (bs, 1H), 8.44 (s, 2H), 3.14 (q, J = 7.3 Hz, 6H), 1.88 – 1.36 (m, 12H), 1.24 (t, J = 7.3 Hz, 9H), 0.75 (bs, 2H) ppm.
^{13}C NMR (50 MHz, CD_3CN) δ 167.84, 47.46, 32.09, 25.58, 9.04 ppm.
^{11}B NMR (64 MHz, CD_3CN) δ 8.98 ppm.
Elemental Analysis: calcd (%) for $C_{16}H_{32}BNO_4$ (313.25 g.mol^{-1}): C 61.35, H 10.30, N 4.47; found: C 58.29, H 10.13, N 4.28.


[BBN(OCHO2)]−, Et3NH+
1H
8.60
8.44
3.19
3.16
3.12
3.08
1.94
1.80
1.74
1.72
1.66
1.62
1.28
1.24
0.79
3.17
5.91
11.35
9.64
2.19
f1 (ppm)


13C
167.84
118.26
47.46
32.09
25.58
9.04
2.47
2.06
1.65
1.23
0.82
0.41
f1 (ppm)


11B
8.98
f1 (ppm)

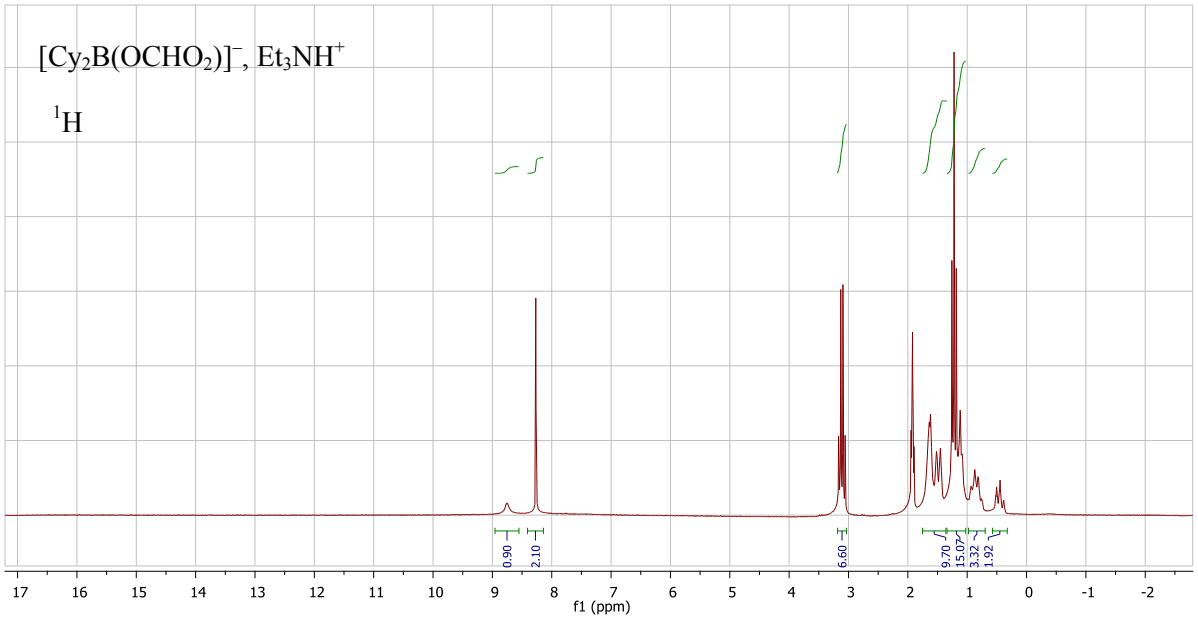
d) Synthesis of [Et_3NH^+, **6**$^-$]**.**

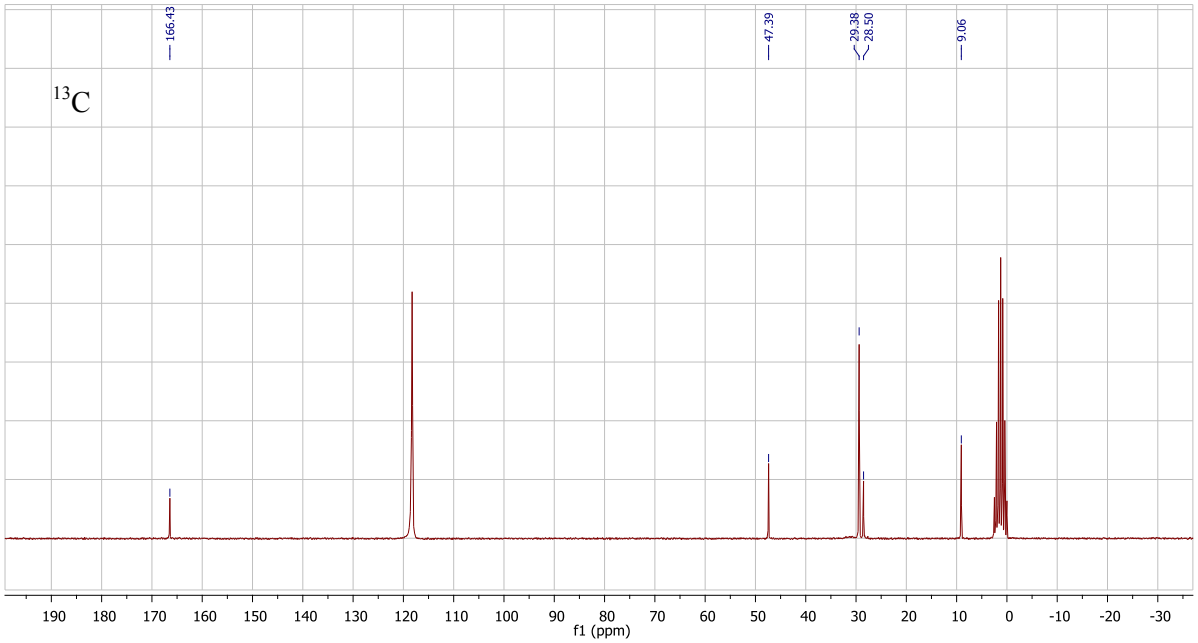


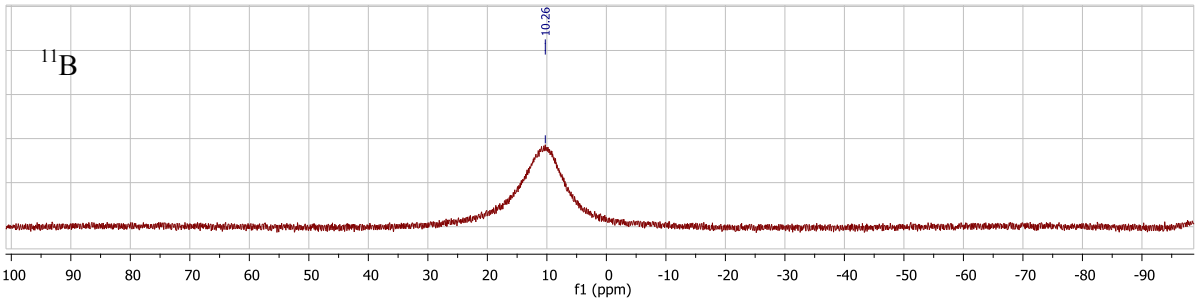
Following a reported procedure[6], a 50 mL, flame-dried, round-bottomed flask equipped with a stirring bar and a J-Young valve was charged with cyclohexene (1.1 mL, 11.2 mmol) and dry diethyl ether (5 mL). In a glovebox, the resulting mixture was cooled down in the freezer at –35°C and borane-dimethyl sulfide complex (2.8 mL, 5.6 mmol, 2M in toluene) was added dropwise over 5 min. The reaction flask was then quickly removed from the glovebox and immersed in an ice-bath and the resulting reaction mixture was stirred for 3h at 0°C. The white solid formed was allowed to settle without stirring and the supernatant was removed carefully by syringe. The remaining solid was then dried under high-vacuum to give dicyclohexylborane (918 mg, 92 %) as a free-flowing powder that was used without further purification.

The procedure detailed for the synthesis of [TBDH$^+$, **5**$^-$] was employed for the synthesis of [Et_3NH^+, **6**$^-$], by replacing TBD with NEt_3 and 9-BBN dimer by Cy_2BH. A colorless oil was obtained, which crystallized by addition of cold pentane to afford a waxy white solid, that was washed with pentane (3 x 2 mL) and dried under high-vacuum to give [Et_3NH^+, **6**$^-$] (901 mg, 90 %).

^{1}H NMR (200 MHz, CD_3CN) δ 8.77 (s, 1H, NH), 8.29 (s, 2H, HC(O)O), 3.13 (t, *J*= 7.2 Hz, 6H), 1.65 (d, *J* = 4.3 Hz, 4H), 1.50 (d, *J* = 12.8 Hz, 4H), 1.24 (t, *J* = 7.3 Hz, 9H), 1.12 (d, *J* = 7.6 Hz, 4H), 1.01 – 0.73 (m, 4H), 0.48 (tt, *J* = 12.0 Hz, 2H, CH-B) ppm.
^{13}C NMR (50 MHz, CD_3CN) δ 166.43, 47.39, 29.38, 28.50, 9.06. ppm.
^{11}B NMR (64 MHz, CD_3CN) δ 11.17 ppm.
Elemental Analysis: calcd (%) for $C_{20}H_{40}BNO_4$ (369.30 g.mol^{-1}): C 65.04, H 10.92, N 3.79; found: C 63.05, H 11.03, N 3.41.


[Cy2B(OCHO2)]−, Et3NH+
1H
0.90
2.10
6.60
9.70
15.07
3.32
1.92
f1 (ppm)


13C
166.43
47.39
29.38
28.50
9.06
f1 (ppm)


11B
10.26
f1 (ppm)

5. Gases Analysis

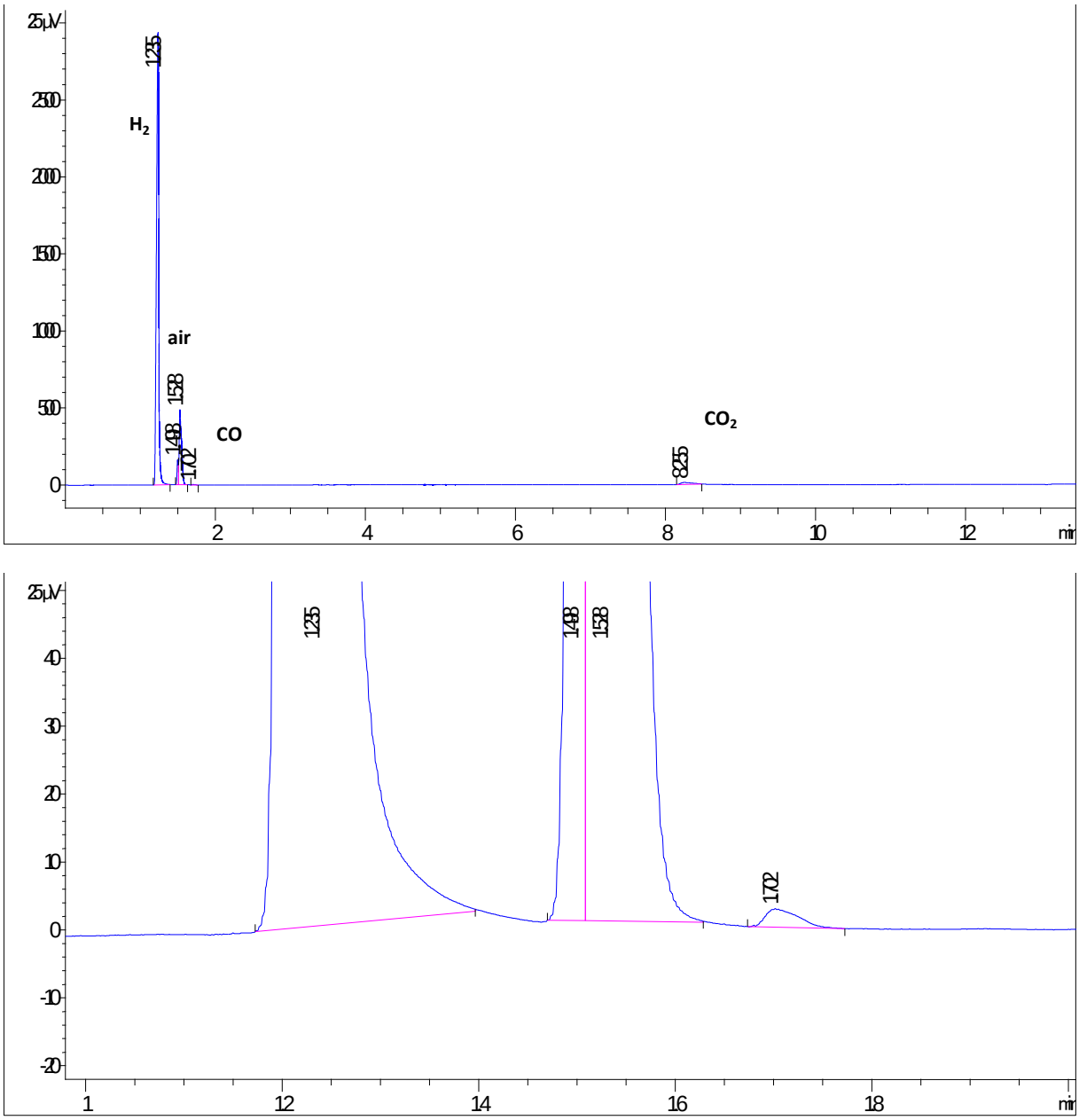


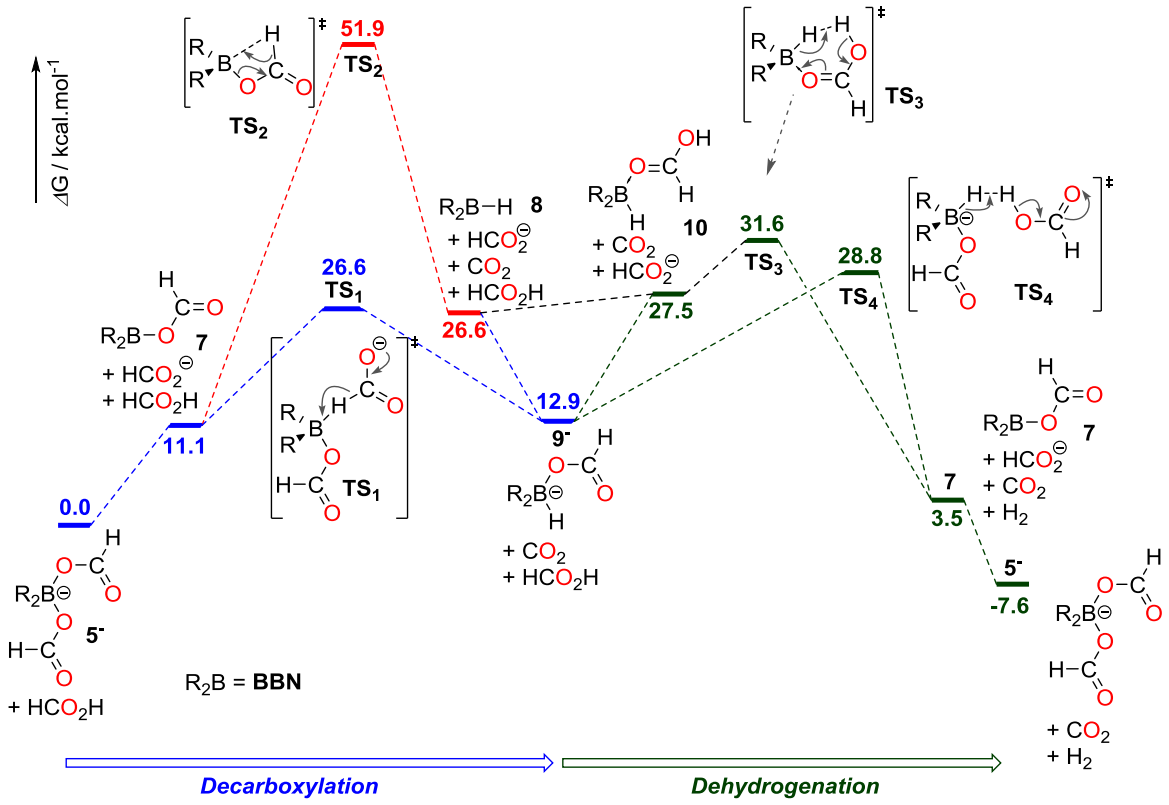
Figure S9. GC-TCD spectra of reaction gases.

CO_2 was detected but due to its high solubility in acetonitrile only small amounts were present in the gas phase (confirmed by ^{13}C NMR spectra).
CO was also detected in very low amount (maximum 172 ppm), that is a selectivity greater than 99.8 % for CO_2 and H_2 at 130°C.

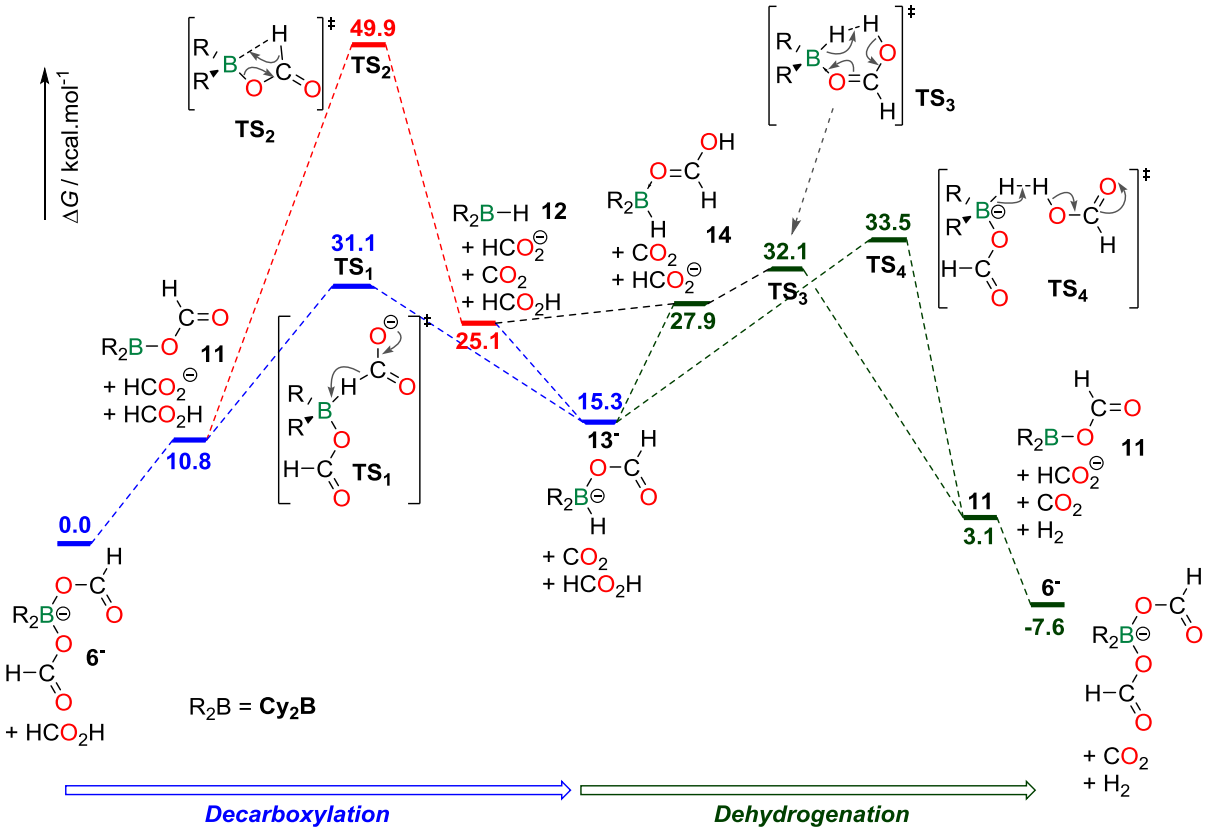
6. Computational details and structures

Density functional theory[7a] was applied to determine the structural and energetic features of the intermediates and transition states described herein. Calculations were performed using Gaussian09 code.[7b] The 6-311+G(d,p) basis set[7c,d] was used for atoms C, H, B and O. The hybrid exchange correlation functional M06 was used.[7e] All structures were calculated without geometrical constraint; stationary points were characterized by frequency calculations (one negative frequency for a transition state, no negative frequency for minima). Solvent effects (acetonitrile) were included in structure-optimization and frequency calculations using the PCM model implemented in the Gaussian code.[7f,g]

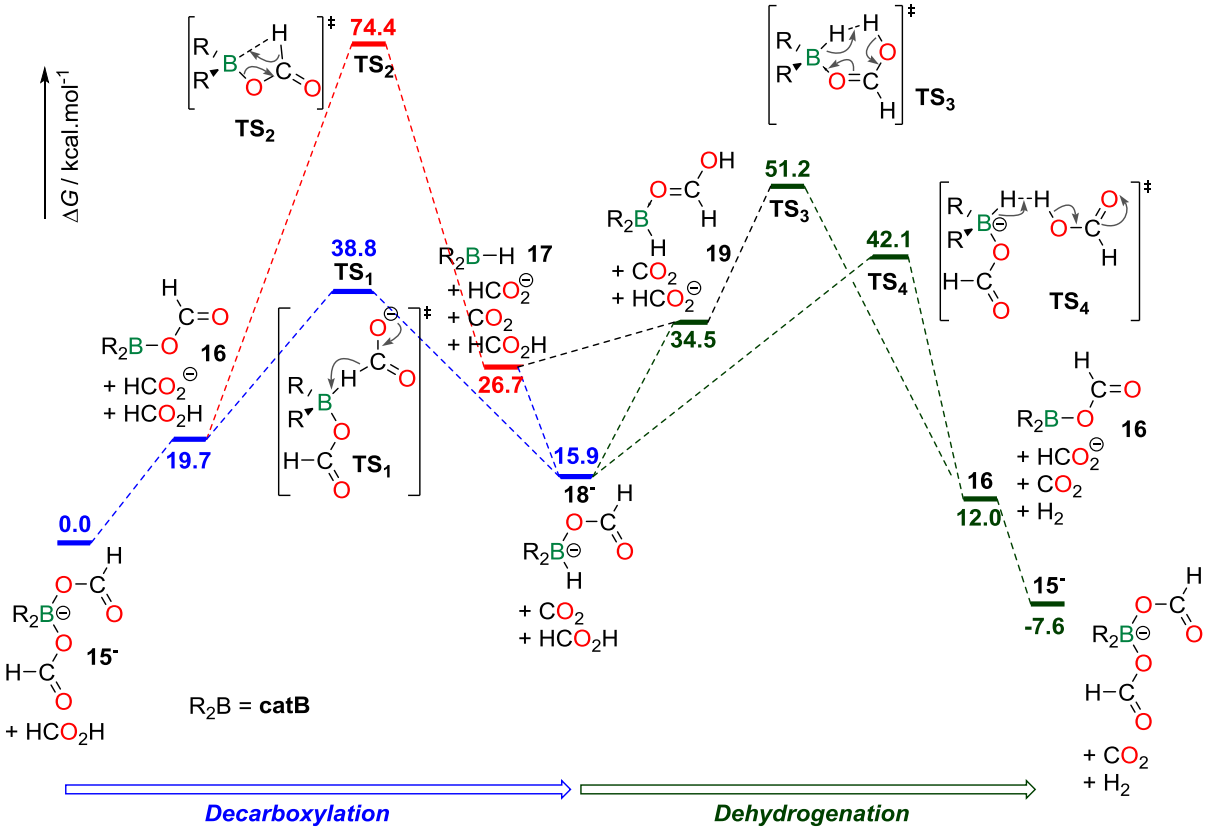
6.1. Computed pathways for the dehydrogenation of formic acid



Scheme S1. Computed pathways for the dehydrogenation of formic acid catalyzed by BBN–H derivatives in acetonitrile (at the M06-2X/6-311+G(d,p) level of theory).



Scheme S2. Computed pathways for the dehydrogenation of formic acid catalyzed by Cy_2B–H derivatives in acetonitrile (at the M06-2X/6-311+G(d,p) level of theory).



Scheme S3. Computed pathways for the dehydrogenation of formic acid catalyzed by catB–H derivatives in acetonitrile (at the M06-2X/6-311+G(d,p) level of theory).

6.2. HCOOH, $HCOO^-$, H_2 and CO_2

HCOOH

6	0.124864000	0.367270000	0.000000000
1	0.040591000	1.462147000	0.000000000
8	1.166726000	-0.220876000	-0.000005000
8	-1.042992000	-0.280322000	0.000005000
1	-1.779648000	0.343820000	0.000008000

Sum of electronic and zero-point Energies= -189.720079
Sum of electronic and thermal Energies= -189.716856
Sum of electronic and thermal Enthalpies= -189.715911
Sum of electronic and thermal Free Energies= -189.744145
Lowest vibration frequency (/ cm^{-1}): 524.69

$HCOO^-$

6	0.000000000	0.331203000	0.000000000
1	-0.000045000	1.448738000	0.000000000
8	1.124378000	-0.214724000	0.000000000
8	-1.124372000	-0.214770000	0.000000000

Sum of electronic and zero-point Energies= -189.274822
Sum of electronic and thermal Energies= -189.271854
Sum of electronic and thermal Enthalpies= -189.270910
Sum of electronic and thermal Free Energies= -189.298621
Lowest vibration frequency (/ cm^{-1}): 758.00

CO_2

6	0.000000000	0.000000000	0.000000000
8	0.000000000	0.000000000	1.154894000
8	0.000000000	0.000000000	-1.154894000

Sum of electronic and zero-point Energies= -188.565905
Sum of electronic and thermal Energies= -188.563298
Sum of electronic and thermal Enthalpies= -188.562354
Sum of electronic and thermal Free Energies= -188.586584
Lowest vibration frequency (/ cm–1): 682.44

H_2

1	0.000000000	0.000000000	0.370300000
1	0.000000000	0.000000000	-0.370300000

Sum of electronic and zero-point Energies= -1.158287
Sum of electronic and thermal Energies= -1.155926
Sum of electronic and thermal Enthalpies= -1.154982
Sum of electronic and thermal Free Energies= -1.169768
Vibration frequency (/ cm^{-1}): 4464.39

6.3. 9-BBN derivatives

5^-

6	1.059045000	-1.139198000	1.515482000
6	0.174642000	0.055474000	1.105951000
6	1.068444000	-0.118507000	-1.321592000
6	1.996971000	-1.275876000	-0.900950000
1	1.410080000	-1.017764000	2.549505000
1	2.955693000	-1.216923000	-1.435095000
1	1.522384000	-2.208502000	-1.225389000
6	0.885935000	1.418141000	1.249224000
1	0.124696000	2.194977000	1.122624000
1	1.277632000	1.535655000	2.269528000
6	1.702902000	1.277074000	-1.193147000
1	2.616898000	1.349203000	-1.798328000
1	-0.689213000	0.072497000	1.777426000
1	0.821563000	-0.270600000	-2.382898000
6	2.282052000	-1.386970000	0.611546000
1	3.081539000	-0.698470000	0.888942000
1	2.679292000	-2.387245000	0.819012000
6	2.026701000	1.693956000	0.250917000
1	2.941955000	1.198069000	0.576748000
1	2.256005000	2.765752000	0.268079000
1	0.995910000	2.003732000	-1.612724000
1	0.433508000	-2.040163000	1.510333000
5	-0.273153000	-0.163888000	-0.428656000
8	-1.272175000	0.828497000	-1.029808000
6	-2.138860000	1.598098000	-0.442522000
1	-2.812126000	2.060476000	-1.184686000
8	-2.253928000	1.854341000	0.737559000
8	-0.910360000	-1.543643000	-0.672393000
6	-2.052650000	-1.908547000	-0.180323000
1	-2.300570000	-2.946311000	-0.458968000
8	-2.811108000	-1.246297000	0.501098000

Sum of electronic and zero-point Energies= -716.350287
Sum of electronic and thermal Energies= -716.336381
Sum of electronic and thermal Enthalpies= -716.335437
Sum of electronic and thermal Free Energies= -716.390012
Lowest vibration frequency (/ cm–1): 68.63

7

6	0.934049000	-0.875172000	1.631865000	1	2.270972000	1.610224000	0.208812000
6	-0.185722000	0.056132000	1.101698000	1	1.265760000	2.923514000	-0.326116000
6	0.668253000	-0.394398000	-1.327164000	1	0.144911000	1.606295000	-1.963969000
6	1.830405000	-1.243984000	-0.762754000	1	0.499955000	-1.871595000	1.779766000
1	1.252963000	-0.530287000	2.621789000	5	-0.540808000	-0.421763000	-0.342950000
1	2.731003000	-1.084898000	-1.367135000	8	-1.798414000	-0.815752000	-0.803216000
1	1.558250000	-2.298155000	-0.889610000	6	-2.964475000	-0.513816000	-0.207724000
6	0.234557000	1.545550000	0.965345000	1	-3.724338000	-1.272819000	-0.422642000
1	-0.674224000	2.121718000	0.756807000	8	-3.164326000	0.476201000	0.432861000
1	0.615912000	1.904291000	1.928059000				
6	0.994213000	1.120433000	-1.467214000				
1	1.853032000	1.245630000	-2.135872000				
1	-1.023445000	0.011379000	1.801331000				
1	0.410154000	-0.773744000	-2.320501000				
6	2.165209000	-1.006192000	0.721643000				
1	2.797520000	-0.125618000	0.829076000				
1	2.771846000	-1.844988000	1.076462000				
6	1.266125000	1.845493000	-0.138806000				

Sum of electronic and zero-point Energies= -527.035464
Sum of electronic and thermal Energies= -527.024174
Sum of electronic and thermal Enthalpies= -527.023230
Sum of electronic and thermal Free Energies= -527.073633
Lowest vibration frequency (/ cm–1): 26.71

TS_1

6	-0.525586000	-1.939767000	-1.169966000	1	-1.976263000	1.404605000	1.416025000
6	-0.446656000	-0.404204000	-1.306208000	1	0.488778000	-2.331325000	-1.316835000
6	-0.540341000	-0.188385000	1.290078000	6	2.946496000	-0.402036000	0.016026000
6	-0.495549000	-1.726900000	1.415865000	1	1.396372000	-0.534331000	0.084529000
1	-1.140485000	-2.368864000	-1.973465000	8	3.263374000	-0.239421000	1.144267000
1	-1.058976000	-2.054400000	2.300096000	8	3.193688000	-0.545427000	-1.131533000
1	0.544961000	-2.033941000	1.578036000	5	0.324116000	0.170849000	-0.022426000
6	-1.819776000	0.287828000	-1.409844000	8	0.924092000	1.560543000	-0.195117000
1	-1.649140000	1.353554000	-1.593695000	6	0.376507000	2.727564000	-0.060307000
1	-2.377404000	-0.092741000	-2.277453000	1	1.117384000	3.528188000	-0.218015000
6	-1.993803000	0.337015000	1.197676000	8	-0.780949000	2.989021000	0.197614000
1	-2.604945000	-0.137693000	1.979382000				
1	0.103517000	-0.186776000	-2.231913000				
1	-0.097238000	0.228935000	2.204660000				
6	-1.047183000	-2.466065000	0.183829000				
1	-2.137535000	-2.423128000	0.204203000				
1	-0.796500000	-3.529927000	0.264898000				
6	-2.707374000	0.138814000	-0.159796000				
1	-3.188403000	-0.840881000	-0.187550000				
1	-3.526758000	0.863575000	-0.226743000				

Sum of electronic and zero-point Energies= -716.287104
Sum of electronic and thermal Energies= -716.272726
Sum of electronic and thermal Enthalpies= -716.271782
Sum of electronic and thermal Free Energies= -716.329525
Lowest vibration frequencies (/ cm–1): – 337.60, 36.29

TS_2

6	-0.853836000	1.299810000	1.295054000	6	-2.011571000	-1.431451000	-0.000233000
6	-0.196465000	-0.098690000	1.312008000	1	-2.838803000	-0.722381000	0.000170000
6	-0.196811000	-0.097844000	-1.312204000	1	-2.478312000	-2.421501000	-0.000501000
6	-0.853929000	1.300748000	-1.294195000	1	-0.617440000	-2.201118000	-1.450342000
1	-1.535286000	1.401759000	2.147620000	1	-0.059844000	2.040650000	1.447192000
1	-1.535333000	1.403541000	-2.146694000	5	0.665964000	-0.228501000	-0.000247000
1	-0.059777000	2.041553000	-1.445688000	8	3.673406000	-0.649244000	-0.000092000
6	-1.192824000	-1.281055000	1.295609000	6	2.660393000	-0.087451000	-0.000143000
1	-0.616836000	-2.202109000	1.448787000	8	1.946381000	0.893667000	0.000027000
1	-1.880137000	-1.203326000	2.145816000	1	1.492587000	-1.204754000	-0.000723000
6	-1.193291000	-1.280126000	-1.296265000				
1	-1.880904000	-1.201718000	-2.146167000				
1	0.397685000	-0.177904000	2.229259000				
1	0.397089000	-0.176606000	-2.229652000				
6	-1.608126000	1.657861000	0.000578000				
1	-2.590266000	1.185546000	0.000445000				
1	-1.803781000	2.734681000	0.000978000				

Sum of electronic and zero-point Energies= -526.972605
Sum of electronic and thermal Energies= -526.962048
Sum of electronic and thermal Enthalpies= -526.961104

Sum of electronic and thermal Free Energies= -527.008696

Lowest vibration frequencies (/ cm–1): – 507.52, 76.12

8

6	1.283244000	1.287056000	-0.187030000
6	0.005518000	1.300786000	0.710872000
6	0.002650000	-1.300667000	0.710958000
6	1.279484000	-1.290265000	-0.188114000
1	1.253094000	2.150409000	-0.861332000
1	1.245939000	-2.152808000	-0.863310000
1	2.151236000	-1.443787000	0.460067000
6	-1.321311000	1.290341000	-0.077894000
1	-2.133451000	1.447267000	0.642012000
1	-1.352059000	2.146251000	-0.762465000
6	-1.324889000	-1.287158000	-0.076594000
1	-1.358801000	-2.143745000	-0.760163000
1	0.044904000	2.219806000	1.302600000
1	0.040293000	-2.219633000	1.302891000
6	1.498359000	-0.001542000	-0.999494000
1	0.859121000	-0.000170000	-1.881343000
1	2.523870000	-0.002889000	-1.381655000
6	-1.612290000	0.001566000	-0.863618000
1	-1.051221000	0.000242000	-1.797358000
1	-2.666792000	0.002897000	-1.157034000
1	-2.136940000	-1.440718000	0.644145000
1	2.154980000	1.437033000	0.462032000
5	0.189001000	-0.000076000	1.559979000
1	0.616230000	-0.000478000	2.676498000

Sum of electronic and zero-point Energies= -338.429544

Sum of electronic and thermal Energies= -338.421224

Sum of electronic and thermal Enthalpies= -338.420280

Sum of electronic and thermal Free Energies= -338.462437

Lowest vibration frequency (/ cm–1): 41.87

9

6	1.159199000	-1.756657000	0.481039000
6	-0.097124000	-0.892396000	0.703186000
6	0.692150000	0.712991000	-1.175172000
6	1.936843000	-0.164471000	-1.405190000
1	1.516003000	-2.183077000	1.430108000
1	2.803972000	0.445871000	-1.696414000
1	1.724455000	-0.822300000	-2.258080000
6	0.092954000	0.228156000	1.741853000
1	-0.890595000	0.680534000	1.924678000
1	0.424417000	-0.180907000	2.707582000
6	0.895515000	1.827253000	-0.129407000
1	1.755169000	2.461412000	-0.391755000
1	-0.877436000	-1.559010000	1.092508000
1	0.474589000	1.212999000	-2.131079000
6	2.339349000	-1.046657000	-0.208943000
1	2.885642000	-0.446636000	0.520365000
1	3.054507000	-1.803401000	-0.552635000
6	1.065457000	1.348296000	1.325289000
1	2.093435000	1.019644000	1.487971000
1	0.927499000	2.204474000	1.996356000
1	0.011936000	2.475191000	-0.170522000
1	0.865103000	-2.609796000	-0.144253000
5	-0.532557000	-0.251992000	-0.725255000
8	-1.788619000	0.662105000	-0.581078000
6	-2.949391000	0.206450000	-0.255365000
1	-3.703919000	1.010140000	-0.194228000
8	-3.264045000	-0.951185000	-0.030119000
1	-0.790388000	-1.110323000	-1.568488000

Sum of electronic and zero-point Energies= -527.746017

Sum of electronic and thermal Energies= -527.734893

Sum of electronic and thermal Enthalpies= -527.733949

Sum of electronic and thermal Free Energies= -527.782793

Lowest vibration frequency (/ cm–1): 48.37

10

6	1.136280000	-1.600970000	0.907713000
6	-0.009565000	-0.573971000	1.026261000
6	0.594044000	0.356459000	-1.329044000
6	1.743161000	-0.668719000	-1.433840000
1	1.589316000	-1.783246000	1.890677000
1	2.592776000	-0.237582000	-1.978950000
1	1.382818000	-1.508521000	-2.040982000
6	0.406879000	0.769611000	1.657277000
1	-0.505797000	1.351324000	1.836398000
1	0.859646000	0.603998000	2.643529000
6	0.997406000	1.697354000	-0.684300000
1	1.833790000	2.150813000	-1.232235000
1	-0.765143000	-1.018580000	1.689880000
1	0.264049000	0.574012000	-2.353257000
6	2.249659000	-1.229234000	-0.090197000
1	2.935257000	-0.517411000	0.370744000
1	2.851537000	-2.122288000	-0.290076000
6	1.365454000	1.624724000	0.808757000
1	2.385575000	1.255552000	0.920083000
6	1.380222000	2.641600000	1.215693000
1	0.151405000	2.386156000	-0.795512000
1	0.695292000	-2.554191000	0.590128000
5	-0.558856000	-0.340151000	-0.467623000
8	-1.807255000	0.704328000	-0.375319000
6	-2.952125000	0.310317000	-0.146888000
1	-3.769592000	1.019700000	-0.035969000
8	-3.287093000	-0.931969000	-0.022069000
1	-1.024030000	-1.348387000	-0.994871000
1	-2.495218000	-1.484499000	-0.212488000

Sum of electronic and zero-point Energies= -528.169564

Sum of electronic and thermal Energies= -528.158367

Sum of electronic and thermal Enthalpies= -528.157423

Sum of electronic and thermal Free Energies= -528.206318

Lowest vibration frequency (/ cm–1): 53.91

TS_3

6	-1.471020000	-1.005297000	-1.391628000	1	-1.742709000	2.714698000	0.660572000
6	-0.445763000	0.145928000	-1.353951000	1	0.182075000	1.767148000	1.673428000
6	-0.045690000	-0.313428000	1.187116000	1	-0.963491000	-1.889700000	-1.797480000
6	-1.073726000	-1.461948000	1.129609000	5	0.641933000	-0.185384000	-0.244075000
1	-2.281027000	-0.769597000	-2.092223000	8	1.819737000	0.779014000	-0.259762000
1	-1.623715000	-1.525297000	2.076268000	6	2.985839000	0.289206000	-0.080019000
1	-0.515622000	-2.402355000	1.037281000	1	3.814130000	0.996696000	-0.034920000
6	-1.048228000	1.523943000	-0.995222000	8	3.179125000	-0.934535000	0.023126000
1	-0.264207000	2.276136000	-1.141490000	1	1.978640000	-1.324797000	-0.276644000
1	-1.852023000	1.775647000	-1.697771000	1	1.094819000	-1.412137000	-0.596763000
6	-0.649769000	1.069098000	1.522045000	Sum of electronic and zero-point Energies= -			
1	-1.190779000	1.023450000	2.474889000	528.162127			
1	-0.002772000	0.232379000	-2.353345000	Sum of electronic and thermal Energies= -			
1	0.678029000	-0.552961000	1.977001000	528.151386			
6	-2.084354000	-1.382748000	-0.029703000	Sum of electronic and thermal Enthalpies= -			
1	-2.881320000	-0.683103000	0.221923000	528.150442			
1	-2.575009000	-2.356514000	-0.128677000	Sum of electronic and thermal Free Energies= -			
6	-1.582114000	1.653602000	0.444152000	528.198471			
1	-2.566628000	1.191251000	0.517018000	Lowest vibration frequencies (/ cm–1): – 1270.19, 52.72			

TS_4

6	-1.958806000	-1.230501000	-1.421229000	1	-1.287947000	-1.720756000	-2.138455000
6	-1.511594000	0.235650000	-1.285270000	5	-0.133725000	0.343051000	-0.497421000
6	-0.265603000	-0.332877000	0.936180000	8	2.045711000	3.111106000	-0.061425000
6	-0.699122000	-1.803674000	0.763642000	6	1.443980000	2.086195000	0.147355000
1	-2.961611000	-1.282105000	-1.862021000	1	1.593830000	1.487822000	1.052067000
1	-0.868898000	-2.255577000	1.748661000	8	0.537444000	1.618771000	-0.692480000
1	0.152388000	-2.337078000	0.324817000	1	0.580740000	-0.636662000	-1.412365000
6	-2.490421000	1.130284000	-0.484573000	1	1.262051000	-0.529118000	-0.994499000
1	-2.142552000	2.165892000	-0.576747000	8	2.814175000	-0.248443000	-0.397701000
1	-3.486094000	1.096061000	-0.942831000	6	3.319527000	-1.295646000	0.093904000
6	-1.269765000	0.544329000	1.722164000	1	4.337335000	-1.171233000	0.526083000
1	-1.458567000	0.104122000	2.708428000	8	2.812176000	-2.426192000	0.145227000
1	-1.434351000	0.662606000	-2.292381000	Sum of electronic and zero-point Energies= -			
1	0.674039000	-0.351040000	1.499032000	717.456902			
6	-1.942864000	-2.040761000	-0.112070000	Sum of electronic and thermal Energies= -			
1	-2.846351000	-1.833425000	0.461887000	717.441000			
1	-1.994324000	-3.106044000	-0.359664000	Sum of electronic and thermal Enthalpies= -			
6	-2.614962000	0.789507000	1.011850000	717.440055			
1	-3.262261000	-0.077839000	1.139812000	Sum of electronic and thermal Free Energies= -			
1	-3.129685000	1.614519000	1.514790000	717.501756			
1	-0.797394000	1.517637000	1.909798000	Lowest vibration frequencies (/ cm–1): –239.09, 49.43			

6.4. Cy_2B derivatives

6^-

5	0.000014000	0.000035000	-0.658033000	6	-3.855598000	-0.771616000	0.105305000
8	0.239404000	-1.132572000	-1.685783000	1	-2.753679000	0.386571000	-1.336565000
8	-0.239417000	1.132676000	-1.685739000	1	-2.390111000	-1.333837000	-1.381428000
6	-0.084131000	2.407031000	-1.533079000	6	-4.143391000	0.369578000	1.083162000
1	-0.315191000	2.947354000	-2.466862000	1	-3.148872000	1.466945000	2.664445000
6	0.083728000	-2.406907000	-1.533388000	1	-2.771803000	-0.253250000	2.621114000
1	0.314508000	-2.947101000	-2.467317000	1	-4.712401000	-0.924309000	-0.559692000
8	-0.264989000	-3.016336000	-0.538817000	1	-3.722656000	-1.702626000	0.671779000
8	0.264534000	3.016353000	-0.538426000	1	-5.033409000	0.147369000	1.680440000
6	-1.361328000	-0.241796000	0.190539000	1	-4.363243000	1.281063000	0.512096000
6	-1.674978000	0.901185000	1.168076000	6	1.361387000	0.241788000	0.190517000
6	-2.584917000	-0.495705000	-0.703638000	6	1.675261000	-0.901542000	1.167579000
1	-1.213150000	-1.148326000	0.792880000	6	2.584854000	0.496209000	-0.703676000
6	-2.939135000	0.629684000	1.990335000	1	1.213140000	1.148065000	0.793222000
1	-1.810453000	1.835547000	0.607663000	6	2.939489000	-0.630263000	1.989799000
1	-0.824275000	1.066598000	1.838143000	1	1.810746000	-1.835675000	0.606784000

1	0.824654000	-1.067292000	1.837684000	1	4.363477000	-1.280904000	0.511119000
6	3.855597000	0.771900000	0.105243000	Sum of electronic and zero-point Energies=			-873.463224
1	2.753636000	-0.385771000	-1.337009000				
1	2.389872000	1.334620000	-1.381072000	Sum of electronic and thermal Energies=			-873.443977
6	4.143612000	-0.369675000	1.082588000				
1	3.149386000	-1.467782000	2.663540000	Sum of electronic and thermal Enthalpies=			-873.443033
1	2.772158000	0.252398000	2.620961000				
1	4.712311000	0.924954000	-0.559786000	Sum of electronic and thermal Free Energies=			-873.510453
1	3.722633000	1.702660000	0.672124000				
1	5.033683000	-0.147630000	1.679847000	Lowest vibration frequency (/ cm–1): 48.64			

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6	-0.466192000	3.004293000	-0.292650000	6	2.180134000	0.187672000	1.182748000
1	-1.517782000	2.761383000	-0.099038000	1	0.796146000	-1.316915000	0.512697000
8	-0.078756000	4.112465000	-0.518819000	6	3.110587000	-1.612917000	-0.959775000
8	0.378553000	1.964552000	-0.224082000	1	2.308257000	0.282559000	-1.602386000
5	-0.001593000	0.614351000	-0.158139000	1	1.243917000	-1.084802000	-1.923123000
6	-1.498262000	0.159102000	-0.315610000	6	3.351579000	-0.770559000	1.406246000
6	-1.681462000	-1.199981000	-1.015342000	1	2.565283000	1.152803000	0.834167000
6	-2.062649000	0.084760000	1.128731000	1	1.662488000	0.377807000	2.128814000
1	-2.100760000	0.889245000	-0.870488000	6	4.076763000	-1.062879000	0.091176000
6	-3.147841000	-1.641133000	-1.003081000	1	3.634803000	-1.788030000	-1.903632000
1	-1.077397000	-1.960679000	-0.506562000	1	2.724028000	-2.582064000	-0.621650000
1	-1.317950000	-1.143291000	-2.045643000	1	4.048000000	-0.352026000	2.138523000
6	-3.525288000	-0.365201000	1.138327000	1	2.973412000	-1.711255000	1.825519000
1	-1.462535000	-0.629793000	1.707796000	1	4.896180000	-1.768024000	0.255882000
1	-1.969141000	1.052391000	1.633581000	1	4.524321000	-0.134462000	-0.284928000
6	-3.695137000	-1.706110000	0.423746000	Sum of electronic and zero-point Energies=			-684.149111
1	-3.249679000	-2.613342000	-1.493312000				
1	-3.742355000	-0.926118000	-1.585034000	Sum of electronic and thermal Energies=			-684.132885
1	-3.886357000	-0.433647000	2.168208000				
1	-4.133661000	0.394468000	0.633132000	Sum of electronic and thermal Enthalpies=			-684.131941
1	-4.748665000	-1.998801000	0.413527000				
1	-3.153727000	-2.481089000	0.980404000	Sum of electronic and thermal Free Energies=			-684.194617
6	1.190399000	-0.361885000	0.140494000				
6	1.932833000	-0.660864000	-1.185433000	Lowest vibration frequency (/ cm–1): 19.39			

TS_1

6	-0.218659000	1.991367000	-1.949431000	6	-1.311852000	-0.504680000	0.316963000
1	0.058742000	0.722293000	-1.129411000	6	-2.513248000	0.284725000	0.861906000
8	0.861389000	2.371140000	-2.260576000	6	-1.739252000	-1.200983000	-0.989374000
8	-1.398776000	2.094188000	-1.986307000	1	-1.091540000	-1.302755000	1.048573000
5	0.044106000	0.371743000	0.133083000	6	-3.749910000	-0.598014000	1.057615000
8	-0.010802000	1.737983000	0.814186000	1	-2.750361000	1.091019000	0.155340000
6	0.074524000	1.887952000	2.099210000	1	-2.255641000	0.762611000	1.811351000
1	0.065265000	2.951786000	2.383436000	6	-2.961321000	-2.103776000	-0.802490000
8	0.152453000	1.011355000	2.938968000	1	-1.983030000	-0.424263000	-1.725655000
6	1.465790000	-0.355859000	0.386087000	1	-0.909651000	-1.776191000	-1.410222000
6	1.632201000	-1.664194000	-0.400983000	6	-4.141472000	-1.310812000	-0.238330000
6	2.667626000	0.562655000	0.115796000	1	-4.590896000	-0.002911000	1.429059000
1	1.491341000	-0.622847000	1.455301000	1	-3.531081000	-1.351938000	1.825375000
6	2.973158000	-2.351413000	-0.123917000	1	-3.240874000	-2.573999000	-1.751077000
1	1.558805000	-1.449396000	-1.477673000	1	-2.708565000	-2.914677000	-0.106872000
1	0.814800000	-2.352988000	-0.163495000	1	-5.001390000	-1.966638000	-0.069672000
6	4.008564000	-0.118163000	0.402166000	1	-4.452538000	-0.561162000	-0.977456000
1	2.641904000	0.875636000	-0.936828000	Sum of electronic and zero-point Energies=			-873.412471
1	2.582427000	1.479309000	0.709640000				
6	4.148305000	-1.412696000	-0.401498000	Sum of electronic and thermal Energies=			-873.393153
1	3.065938000	-3.263657000	-0.722426000				
1	3.003648000	-2.657488000	0.929830000	Sum of electronic and thermal Enthalpies=			-873.392209
1	4.840125000	0.558075000	0.178271000				
1	4.069084000	-0.355637000	1.472243000	Sum of electronic and thermal Free Energies=			-873.460790
1	5.097074000	-1.908314000	-0.173840000				
1	4.165063000	-1.168577000	-1.471690000	Lowest vibration frequencies (/ cm–1): –430.19, 37.57			

TS_2

6	-0.074304000	2.515782000	0.083913000	6	2.576552000	0.784343000	0.323624000
1	0.181928000	1.403123000	-1.067916000	1	1.256564000	-0.664957000	1.193332000
8	0.013647000	3.557433000	-0.418618000	6	3.023102000	-2.019968000	-0.458606000
8	-0.253006000	1.755568000	1.009238000	1	1.809057000	-0.852485000	-1.804408000
5	0.016292000	0.507948000	-0.161511000	1	0.895317000	-2.018559000	-0.855332000
6	-1.356221000	-0.255987000	-0.369788000	6	3.879178000	0.061972000	0.674568000
6	-1.652539000	-1.200994000	0.809324000	1	2.704983000	1.302079000	-0.637635000
6	-2.556357000	0.669851000	-0.623501000	1	2.370985000	1.554047000	1.075437000
1	-1.226387000	-0.880087000	-1.268524000	6	4.189026000	-1.035500000	-0.344921000
6	-2.956643000	-1.977218000	0.607395000	1	3.241590000	-2.783979000	-1.210416000
1	-1.726293000	-0.607609000	1.731224000	1	2.897809000	-2.539431000	0.499572000
1	-0.822068000	-1.899752000	0.951584000	1	4.705911000	0.775973000	0.728706000
6	-3.854776000	-0.112426000	-0.832640000	1	3.779268000	-0.389588000	1.669309000
1	-2.689655000	1.333400000	0.241738000	1	5.106788000	-1.563271000	-0.070992000
1	-2.358660000	1.311625000	-1.489753000	1	4.365120000	-0.574510000	-1.324925000
6	-4.133671000	-1.033189000	0.356968000	Sum of electronic and zero-point Energies= -			
1	-3.157551000	-2.611377000	1.475883000	684.088834			
1	-2.842876000	-2.644155000	-0.256384000	Sum of electronic and thermal Energies= -			
1	-4.690650000	0.576459000	-0.984698000	684.073260			
1	-3.767428000	-0.716804000	-1.743971000	Sum of electronic and thermal Enthalpies= -			
1	-5.050701000	-1.604701000	0.188088000	684.072316			
1	-4.299935000	-0.420677000	1.252271000	Sum of electronic and thermal Free Energies= -			
6	1.390243000	-0.186354000	0.209458000	684.132303			
6	1.718125000	-1.298397000	-0.804060000	Lowest vibration frequencies (/ cm–1): –503.77, 37.67			

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5	-0.001168000	-0.025472000	0.810238000	6	-3.728346000	-1.142987000	0.028147000
1	0.001581000	-0.040041000	2.012625000	1	-2.539380000	-0.732761000	1.779263000
6	1.347723000	0.210904000	0.053534000	1	-1.999949000	-2.138962000	0.872619000
6	2.364322000	1.107004000	0.774806000	6	-3.266000000	1.169503000	-0.868545000
6	1.945845000	-1.209635000	-0.140859000	1	-2.070678000	1.657392000	0.855083000
1	1.161416000	0.614686000	-0.952957000	1	-1.210818000	1.824390000	-0.674261000
6	3.706159000	1.161932000	0.041723000	6	-4.277630000	0.273792000	-0.151285000
1	2.523006000	0.712421000	1.787189000	1	-4.448616000	-1.762855000	0.569914000
1	1.958042000	2.116576000	0.892909000	1	-3.589880000	-1.602016000	-0.958709000
6	3.288480000	-1.150594000	-0.876251000	1	-3.659017000	2.185913000	-0.963932000
1	2.099995000	-1.677046000	0.841176000	1	-3.104117000	0.789517000	-1.884466000
1	1.246078000	-1.846723000	-0.691318000	1	-5.220576000	0.251270000	-0.704753000
6	4.282241000	-0.242519000	-0.149284000	1	-4.496656000	0.701058000	0.835437000
1	4.413426000	1.790559000	0.590500000	Sum of electronic and zero-point Energies= -			
1	3.560421000	1.627094000	-0.941187000	495.544392			
1	3.700930000	-2.158391000	-0.980808000	Sum of electronic and thermal Energies= -			
1	3.120857000	-0.764180000	-1.888827000	495.531172			
1	5.225640000	-0.197812000	-0.700652000	Sum of electronic and thermal Enthalpies= -			
1	4.507320000	-0.674216000	0.834162000	495.530228			
6	-1.352650000	-0.237923000	0.051791000	Sum of electronic and thermal Free Energies= -			
6	-2.386771000	-1.120872000	0.763450000	495.585304			
6	-1.923666000	1.195864000	-0.130902000	Lowest vibration frequency (/ cm–1): 17.07			
1	-1.171424000	-0.635327000	-0.958138000				

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6	0.060033000	2.644263000	-0.430923000	1	-2.627932000	0.109263000	1.765013000
1	0.145707000	2.005470000	-1.327668000	1	-2.568921000	1.610748000	0.855154000
8	0.034253000	3.861920000	-0.544041000	6	-4.101878000	-1.360368000	-0.081844000
8	-0.001198000	2.011791000	0.688622000	1	-2.995339000	-2.998203000	-0.970786000
5	-0.020785000	0.434007000	0.690296000	1	-2.943026000	-1.496485000	-1.889029000
1	-0.027859000	0.161848000	1.890252000	1	-4.820901000	0.534796000	0.685337000
6	-1.425868000	-0.014107000	-0.016590000	1	-4.045954000	0.633461000	-0.892795000
6	-1.580888000	-1.527599000	-0.219453000	1	-5.043927000	-1.618567000	-0.575651000
6	-2.646481000	0.523532000	0.746527000	1	-4.121705000	-1.832891000	0.908995000
1	-1.459611000	0.432950000	-1.028116000	6	1.340055000	-0.164699000	-0.007477000
6	-2.913805000	-1.910329000	-0.872492000	6	2.573192000	0.750491000	0.093429000
1	-1.507030000	-2.030043000	0.756795000	6	1.719036000	-1.524333000	0.610284000
1	-0.755766000	-1.910467000	-0.829153000	1	1.160224000	-0.342044000	-1.084439000
6	-3.981554000	0.154670000	0.093098000	6	3.823808000	0.140265000	-0.549816000

1	2.776495000	0.952401000	1.155630000	1	4.429521000	-1.104905000	1.099799000
1	2.384073000	1.725229000	-0.367087000	Sum of electronic and zero-point Energies=			-684.855721
6	2.946769000	-2.163577000	-0.044076000				
1	1.934138000	-1.362760000	1.676047000	Sum of electronic and thermal Energies=			-684.839664
1	0.874045000	-2.216796000	0.574847000				
6	4.154750000	-1.229903000	0.044394000	Sum of electronic and thermal Enthalpies=			-684.838720
1	4.679078000	0.815891000	-0.442053000				
1	3.644781000	0.025134000	-1.626903000	Sum of electronic and thermal Free Energies=			-684.899408
1	3.177311000	-3.125359000	0.426583000				
1	2.727141000	-2.370144000	-1.099691000	Lowest vibration frequency (/ cm–1): 36.44			
1	5.021927000	-1.668092000	-0.459575000				

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5	-0.062897000	0.533989000	0.144441000	6	-1.733645000	-1.483681000	0.120041000
8	0.033188000	1.968586000	-0.650297000	6	-2.664922000	0.845738000	0.185250000
6	0.450973000	3.004257000	-0.130637000	1	-1.523347000	-0.012954000	-1.413082000
1	0.529775000	3.919970000	-0.713614000	6	-3.099141000	-2.014408000	-0.327434000
8	0.819255000	3.109247000	1.103608000	1	-1.667475000	-1.550592000	1.215918000
1	-0.053602000	0.828588000	1.345310000	1	-0.942927000	-2.126288000	-0.280503000
1	0.659025000	2.236292000	1.536817000	6	-4.031819000	0.323834000	-0.266407000
6	1.256757000	-0.316365000	-0.260226000	1	-2.640436000	0.869596000	1.283994000
6	2.501101000	0.520060000	-0.606448000	1	-2.532274000	1.879442000	-0.152818000
6	1.627366000	-1.291677000	0.873935000	6	-4.236726000	-1.125599000	0.177844000
1	1.023159000	-0.922627000	-1.151432000	1	-3.239748000	-3.043157000	0.018838000
6	3.707313000	-0.352568000	-0.966538000	1	-3.127536000	-2.039887000	-1.424235000
1	2.768112000	1.149080000	0.256910000	1	-4.833247000	0.958330000	0.124989000
1	2.289344000	1.198625000	-1.438415000	1	-4.091407000	0.374090000	-1.361133000
6	2.817147000	-2.185362000	0.515668000	1	-5.201522000	-1.502218000	-0.174959000
1	1.885418000	-0.700183000	1.763673000	1	-4.261191000	-1.163721000	1.274470000
1	0.766934000	-1.905811000	1.154423000	Sum of electronic and zero-point Energies=			-685.280570
6	4.039708000	-1.340661000	0.152819000				
1	4.576921000	0.272749000	-1.191550000	Sum of electronic and thermal Energies=			-685.264301
1	3.473721000	-0.913625000	-1.880230000				
1	3.054533000	-2.856891000	1.346757000	Sum of electronic and thermal Enthalpies=			-685.263357
1	2.547848000	-2.817921000	-0.339683000				
1	4.877797000	-1.980227000	-0.139470000	Sum of electronic and thermal Free Energies=			-685.324953
1	4.360446000	-0.780596000	1.040537000				
6	-1.501343000	-0.027349000	-0.309566000	Lowest vibration frequency (/ cm–1): 29.59			

TS_3

6	-0.789264000	2.930396000	-0.619270000				
1	-1.029506000	3.562880000	-1.474096000	6	-1.162462000	-1.324428000	-0.729134000
8	-0.943504000	3.345348000	0.543189000	1	-0.950199000	-0.858025000	1.350354000
8	-0.343354000	1.764053000	-0.878525000	6	-3.653666000	-0.731369000	0.739080000
5	-0.009431000	0.806629000	0.269016000	1	-2.785579000	0.919117000	-0.322540000
1	-0.127023000	1.488526000	1.446327000	1	-2.572214000	1.010356000	1.424080000
1	-0.500092000	2.313455000	1.165283000	6	-2.269818000	-2.371451000	-0.574617000
6	1.558173000	0.465424000	0.250595000	1	-1.298022000	-0.792450000	-1.680974000
6	1.923038000	-0.608382000	1.286609000	1	-0.194494000	-1.829587000	-0.787018000
6	2.091933000	0.063688000	-1.137310000	6	-3.644608000	-1.718621000	-0.428850000
1	2.101064000	1.383598000	0.528964000	1	-4.632729000	-0.250456000	0.824548000
6	3.427512000	-0.887500000	1.321231000	1	-3.483473000	-1.279239000	1.674278000
1	1.396204000	-1.539259000	1.036153000	1	-2.262297000	-3.055604000	-1.428538000
1	1.570861000	-0.310333000	2.280954000	1	-2.063817000	-2.974201000	0.318967000
6	3.598638000	-0.209079000	-1.102299000	1	-4.416501000	-2.481436000	-0.291853000
1	1.579497000	-0.840331000	-1.486317000	1	-3.887479000	-1.180792000	-1.354056000
1	1.869714000	0.850478000	-1.864098000	Sum of electronic and zero-point Energies=			-685.274358
6	3.942556000	-1.280477000	-0.065118000				
1	3.652692000	-1.674718000	2.047095000	Sum of electronic and thermal Energies=			-685.258504
1	3.952401000	0.016129000	1.655717000				
1	3.953187000	-0.512391000	-2.092021000	Sum of electronic and thermal Enthalpies=			-685.257560
1	4.123913000	0.719415000	-0.844898000				
1	5.022538000	-1.451650000	-0.036712000	Sum of electronic and thermal Free Energies=			-685.318248
1	3.476862000	-2.228637000	-0.363242000				
6	-1.157775000	-0.302322000	0.422744000	Lowest vibration frequencies (/ cm–1): –1242.96, 36.06			
6	-2.556507000	0.321921000	0.571548000				

TS_4

5	-0.275915000	0.434302000	-0.293857000	1	4.242921000	-0.888443000	-0.259522000
8	-0.845879000	3.845056000	-1.189427000	6	-1.764556000	-0.161493000	-0.387442000
6	-0.941289000	2.642010000	-1.146133000	6	-1.845371000	-1.679172000	-0.161298000
1	-1.680133000	2.098543000	-1.752755000	6	-2.796093000	0.547623000	0.508344000
8	-0.166603000	1.891680000	-0.398972000	1	-2.068049000	0.004531000	-1.436666000
1	-0.260977000	0.207832000	1.238863000	6	-3.262464000	-2.218593000	-0.374923000
1	0.435287000	0.581359000	1.365068000	1	-1.530244000	-1.906452000	0.866803000
8	1.829604000	1.381854000	1.967370000	1	-1.149373000	-2.198721000	-0.826169000
6	2.341199000	0.790384000	2.954225000	6	-4.215197000	0.014204000	0.292981000
1	3.298017000	1.223119000	3.325540000	1	-2.516471000	0.388570000	1.559096000
8	1.904907000	-0.210307000	3.549546000	1	-2.783699000	1.630626000	0.350593000
6	0.966735000	-0.375082000	-0.902283000	6	-4.273229000	-1.497268000	0.517145000
6	2.111740000	0.531185000	-1.384749000	1	-3.288159000	-3.295510000	-0.184548000
6	1.536972000	-1.462785000	0.027875000	1	-3.543084000	-2.072731000	-1.425660000
1	0.567373000	-0.893822000	-1.791884000	1	-4.915579000	0.525056000	0.960167000
6	3.230942000	-0.268643000	-2.056912000	1	-4.529297000	0.239072000	-0.734052000
1	2.510889000	1.071672000	-0.518248000	1	-5.283494000	-1.872559000	0.330807000
1	1.729965000	1.286582000	-2.078587000	1	-4.041303000	-1.711864000	1.567913000
6	2.643637000	-2.273913000	-0.650180000	Sum of electronic and zero-point Energies= -874.563638			
1	1.949545000	-0.974339000	0.918671000				
1	0.746579000	-2.131570000	0.379109000	Sum of electronic and thermal Energies= -874.543032			
6	3.771500000	-1.359749000	-1.131355000				
1	4.040732000	0.398613000	-2.368278000	Sum of electronic and thermal Enthalpies= -874.542088			
1	2.837635000	-0.737659000	-2.968355000				
1	3.035366000	-3.028287000	0.039237000	Sum of electronic and thermal Free Energies= -874.614597			
1	2.223942000	-2.812807000	-1.509545000				
1	4.547795000	-1.940836000	-1.638210000	Lowest vibration frequencies (/ cm–1): –231.08, 27.89			

3.1. CatB derivatives

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6	1.004715000	-0.474494000	-0.542965000	1	-2.076927000	3.079078000	-0.555189000
6	2.055422000	-0.846515000	-1.355496000	8	-0.154162000	2.470706000	-0.690782000
6	3.355383000	-0.738333000	-0.832095000	8	-1.928175000	-0.985375000	0.971796000
6	3.570377000	-0.270916000	0.457967000	6	-2.925985000	-1.512940000	0.305046000
6	2.494849000	0.108704000	1.279462000	1	-3.486961000	-2.224498000	0.927407000
6	1.221868000	-0.000916000	0.759741000	8	-3.229097000	-1.284852000	-0.842498000
1	1.877782000	-1.210196000	-2.360530000	Sum of electronic and zero-point Energies= -784.802517			
1	4.199888000	-1.025407000	-1.447452000				
1	4.581054000	-0.196052000	0.841394000	Sum of electronic and thermal Energies= -784.790175			
1	2.652862000	0.476386000	2.286321000				
8	-0.318166000	-0.497399000	-0.822604000	Sum of electronic and thermal Enthalpies= -784.789231			
5	-1.010908000	0.013125000	0.369719000				
8	0.045130000	0.296056000	1.354411000	Sum of electronic and thermal Free Energies= -784.842332			
8	-1.846719000	1.208105000	0.091031000				
6	-1.317236000	2.298265000	-0.410223000	Lowest vibration frequency (/ cm–1): 35.33			

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6	-1.009543000	-0.778139000	0.014765000	5	1.155335000	-0.499611000	-0.040195000
6	-2.296906000	-1.266953000	0.058578000	8	0.628982000	0.771297000	-0.071658000
6	-3.321709000	-0.315060000	0.046350000	8	2.477561000	-0.861821000	-0.082472000
6	-3.048307000	1.051390000	-0.006961000	6	3.522559000	-0.002458000	-0.020954000
6	-1.735857000	1.533273000	-0.050346000	1	4.458319000	-0.549128000	-0.169308000
6	-0.737887000	0.584306000	-0.038027000	8	3.433668000	1.168720000	0.174861000
1	-2.497493000	-2.329519000	0.100078000	Sum of electronic and zero-point Energies= -595.476471			
1	-4.350824000	-0.650403000	0.079198000				
1	-3.869030000	1.757562000	-0.015062000	Sum of electronic and thermal Energies= -595.467291			
1	-1.510803000	2.590960000	-0.091661000				
8	0.179672000	-1.473142000	0.013932000				

Sum of electronic and thermal Enthalpies= -595.466347

Sum of electronic and thermal Free Energies= -595.512336

Lowest vibration frequency (/ cm–1): 29.73

TS_1

6	-1.296698000	-0.110666000	0.616292000	8	1.768609000	-1.192881000	-0.573805000
6	-2.310678000	0.100515000	1.525783000	6	2.578741000	-1.404778000	0.453053000
6	-3.626289000	0.078447000	1.038012000	1	2.250658000	-0.951375000	1.395837000
6	-3.890627000	-0.148542000	-0.307932000	8	3.580431000	-2.065605000	0.355721000
6	-2.851513000	-0.363710000	-1.226183000	1	1.194146000	0.903823000	-0.804388000
6	-1.562150000	-0.340892000	-0.738263000	8	2.890418000	1.412905000	0.347607000
1	-2.093468000	0.276234000	2.572102000				
1	-4.446792000	0.243618000	1.725623000				
1	-4.915480000	-0.158091000	-0.658677000				
1	-3.047046000	-0.543031000	-2.276156000				
8	0.046696000	-0.146237000	0.842290000				
5	0.654098000	-0.290895000	-0.464917000				
8	-0.398518000	-0.531736000	-1.419836000				
6	1.941366000	1.922395000	-0.171213000				
8	1.349186000	2.934388000	-0.397859000				

Sum of electronic and zero-point Energies= -784.738912

Sum of electronic and thermal Energies= -784.726178

Sum of electronic and thermal Enthalpies= -784.725234

Sum of electronic and thermal Free Energies= -784.780520

Lowest vibration frequencies (/ cm–1): –578.88, 27.21

TS_2

6	-0.878395000	0.697112000	-0.074766000	8	2.350209000	-0.000301000	0.959503000
6	-2.046171000	1.424535000	-0.018088000	6	3.165755000	0.000001000	0.035048000
6	-3.242220000	0.695820000	0.039682000	1	2.115994000	-0.000043000	-1.115543000
6	-3.242282000	-0.695627000	0.039636000	8	4.233140000	0.000284000	-0.396667000
6	-2.046301000	-1.424452000	-0.018196000				
6	-0.878454000	-0.697139000	-0.074835000				
1	-2.033710000	2.506842000	-0.017922000				
1	-4.182898000	1.230459000	0.085438000				
1	-4.183008000	-1.230184000	0.085375000				
1	-2.033945000	-2.506761000	-0.018092000				
8	0.412657000	1.162351000	-0.139593000				
5	1.211493000	-0.000124000	-0.171707000				
8	0.412559000	-1.162484000	-0.139693000				

Sum of electronic and zero-point Energies= -595.390423

Sum of electronic and thermal Energies= -595.381691

Sum of electronic and thermal Enthalpies= -595.380747

Sum of electronic and thermal Free Energies= -595.425125

Lowest vibration frequencies (/ cm–1): –656.46, 68.64

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6	0.270077000	0.694644000	-0.000007000	8	1.571692000	-1.139573000	-0.000038000
6	-0.897543000	1.428468000	0.000002000	1	3.527600000	0.000012000	0.000142000
6	-2.089122000	0.697746000	0.000013000				
6	-2.089131000	-0.697737000	0.000013000				
6	-0.897560000	-1.428457000	0.000000000				
6	0.270072000	-0.694644000	-0.000010000				
1	-0.884769000	2.510512000	-0.000005000				
1	-3.032659000	1.228990000	0.000018000				
1	-3.032679000	-1.228962000	0.000019000				
1	-0.884776000	-2.510503000	-0.000006000				
8	1.571721000	1.139550000	-0.000042000				
5	2.351843000	0.000000000	0.000081000				

Sum of electronic and zero-point Energies= -406.884377

Sum of electronic and thermal Energies= -406.878396

Sum of electronic and thermal Enthalpies= -406.877452

Sum of electronic and thermal Free Energies= -406.914560

Lowest vibration frequency (/ cm–1): 221.67

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6	-0.959178000	-0.776723000	-0.196601000	6	3.166578000	0.055136000	0.763265000
6	-2.203129000	-1.246747000	0.175800000	1	3.649700000	-0.169553000	1.726666000
6	-3.211699000	-0.303398000	0.439009000	8	3.656309000	0.841311000	-0.021485000
6	-2.962463000	1.058069000	0.326711000	1	1.948865000	-0.714321000	-1.629248000
6	-1.694173000	1.531910000	-0.051667000				
6	-0.706246000	0.602006000	-0.309224000				
1	-2.389472000	-2.311029000	0.259384000				
1	-4.195736000	-0.647905000	0.734306000				
1	-3.753633000	1.769258000	0.533266000				
1	-1.491575000	2.592601000	-0.142683000				
8	0.142029000	-1.487441000	-0.515698000				
5	1.251078000	-0.505711000	-0.670841000				
8	0.566399000	0.820559000	-0.700166000				
8	2.060053000	-0.613430000	0.610944000				

Sum of electronic and zero-point Energies= -596.194457

Sum of electronic and thermal Energies= -596.185031

Sum of electronic and thermal Enthalpies= -596.184087

Sum of electronic and thermal Free Energies= -596.230420

Lowest vibration frequency (/ cm–1): 37.43

19 (H-bond found between proton of FA and one O from catechol backbone)

6	0.895877000	-0.874406000	0.093466000	6	-2.762406000	0.279193000	-0.887394000
6	2.119443000	-1.140482000	-0.485952000	1	-3.456672000	0.267858000	-1.726214000
6	3.008686000	-0.066665000	-0.631004000	8	-2.617200000	1.428016000	-0.321260000
6	2.670996000	1.214461000	-0.207102000	1	-1.979584000	-1.400491000	1.604928000
6	1.426371000	1.476740000	0.383431000	1	-1.913973000	1.357018000	0.377996000
6	0.563160000	0.412233000	0.519732000	Sum of electronic and zero-point Energies= -			
1	2.375238000	-2.140703000	-0.812448000	596.610833			
1	3.977262000	-0.241178000	-1.083811000	Sum of electronic and thermal Energies= -			
1	3.378471000	2.024616000	-0.333152000	596.601282			
1	1.151437000	2.468154000	0.721284000	Sum of electronic and thermal Enthalpies= -			
8	-0.118992000	-1.743395000	0.358694000	596.600337			
5	-1.223750000	-0.945519000	0.808441000	Sum of electronic and thermal Free Energies= -			
8	-0.694595000	0.400461000	1.076501000	596.646371			
8	-2.187487000	-0.761847000	-0.551666000	Lowest vibration frequency (/ cm–1): 52.70			

TS_3

6	-0.948540000	0.698396000	0.004903000	6	3.517347000	-0.000010000	-0.379061000
6	-2.120141000	1.422916000	0.018653000	1	4.308933000	-0.000035000	-1.128520000
6	-3.319184000	0.695361000	0.034063000	8	3.767106000	0.000028000	0.828906000
6	-3.319183000	-0.695360000	0.034085000	1	1.618997000	-0.000017000	1.379154000
6	-2.120139000	-1.422914000	0.018694000	1	2.548449000	0.000025000	1.270380000
6	-0.948539000	-0.698392000	0.004906000	Sum of electronic and zero-point Energies= -			
1	-2.108392000	2.505449000	0.016912000	596.584071			
1	-4.260465000	1.230882000	0.047711000	Sum of electronic and thermal Energies= -			
1	-4.260463000	-1.230883000	0.047764000	596.574967			
1	-2.108387000	-2.505447000	0.016984000	Sum of electronic and thermal Enthalpies= -			
8	0.337559000	1.164784000	-0.021619000	596.574023			
5	1.157779000	0.000005000	0.073914000	Sum of electronic and thermal Free Energies= -			
8	0.337554000	-1.164781000	-0.021646000	596.619671			
8	2.310619000	-0.000029000	-0.840317000	Lowest vibration frequencies (/ cm–1): –1374.46, 38.68			

TS_4

6	1.531546000	0.488744000	0.502015000	8	-2.257804000	-2.403957000	-0.609761000
6	2.534017000	1.416598000	0.686759000	1	-0.958876000	0.016473000	-0.956001000
6	3.773805000	1.136585000	0.096971000	1	-1.723511000	0.284760000	-0.753037000
6	3.978371000	-0.027434000	-0.638348000	6	-3.307734000	1.947410000	-0.403367000
6	2.951971000	-0.964722000	-0.819414000	1	-4.352376000	2.282855000	-0.230816000
6	1.736136000	-0.678459000	-0.236554000	8	-2.425764000	2.809826000	-0.482333000
1	2.363172000	2.318517000	1.260740000	8	-3.164700000	0.691075000	-0.498986000
1	4.585741000	1.843354000	0.216444000	Sum of electronic and zero-point Energies= -			
1	4.948121000	-0.214112000	-1.083354000	785.889702			
1	3.101081000	-1.873819000	-1.388126000	Sum of electronic and thermal Energies= -			
8	0.249610000	0.514479000	0.977070000	785.875898			
5	-0.381421000	-0.601164000	0.380461000	Sum of electronic and thermal Enthalpies= -			
8	0.587040000	-1.422512000	-0.250530000	785.874954			
8	-1.480858000	-1.138174000	1.078430000	Sum of electronic and thermal Free Energies= -			
6	-2.354398000	-1.962881000	0.501358000	785.932827			
1	-3.178729000	-2.193142000	1.184209000	Lowest vibration frequencies (/ cm–1): –597.86, 21.39			

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