Supporting Information for:

A Highly Active Phosphine-Borane Organocatalyst for the Reduction of CO_2 to Methanol using Hydroboranes.

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Contents

1. Synthetic procedure

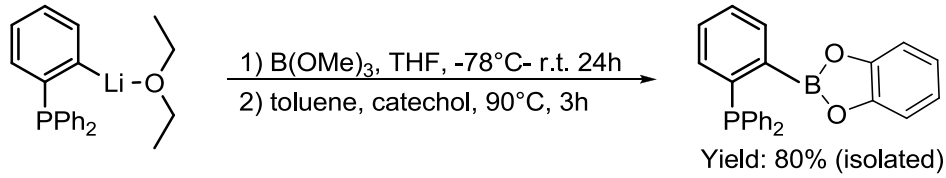
a. General experimental

Unless otherwise specified, manipulations were carried out under an atmosphere of dinitrogen, using standard glovebox and Schlenk techniques. Reactions were carried either in a sealed J-Young NMR tube, in which case NMR conversions are indicated, or in standard flame dried Schlenk glassware. Catalytic reactions over 1 atm of pressure were carried out in a sealed Fischer-Porter bottle. All solvents were distilled from Na/benzophenone, benzene-d_6 was purified by vacuum distillation from Na/K alloy. 1,2 dibromobenzene was purchased from Sigma-Aldrich and used as received. $B(OMe)_3$ was dried on Na^0 and distilled prior to use. Bone dry CO_2 was purchased from Praxair and used as received. $^{13}CO_2$ (99% isotope label) was purchased from Cambridge Isotope Laboratories and also used as received. Lithiated o-bromophenyldiphenylphosphine, CH_3OBcat and catBOBcat were synthesized in good yields by following literature procedures. [S1,S2,S3]

NMR spectra were recorded on a Agilent Technologies NMR spectrometer at 500 MHz (^1H), 125.758 MHz (^{13}C), 202.456 MHz (^{31}P), 160.46 MHz (^{11}B), on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^1H), 100.580 MHz (^{13}C), 161.923 MHz (^{31}P). ^1H NMR and $^{13}C\{^1H\}$ NMR chemical shifts are referenced to residual protons or carbons in deuterated solvent. $^{11}B\{^1H\}$ was calibrated using an external reference of $B(OMe)_3$. Multiplicities are reported as singlet (s), broad singlet (s, br) doublet (d), triplet (t), multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. gHMQC, gHSQC, NOESY 2D, gDQCOSY and $^1H\{^{31}P\}$ NMR experiments were performed in order to properly assign spectra. GC spectra were recorded on a Hewlett Packard GC-FID 6890 Series with an HP-5 (Crosslinked 5% PHME siloxane) column, using an isotherm at 50°C. Injection volumes were 1 μL.

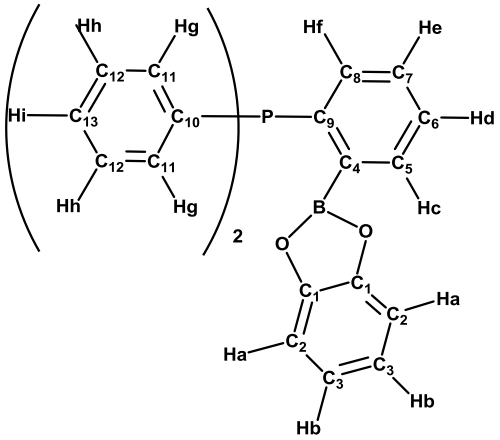
b. Synthesis of 1

Figure S1: Synthesis of 1[S4]



Yield: 80% (isolated)

503 mg (1.47 mmol) of 2-(diphenylphosphino)phenyllithium was placed in a Schlenk vessel and dissolved in *ca.* 10 mL of THF. The solution was cooled to -78°C and 1.0 mL (8.97 mmol) of $B(OMe)_3$ was added at once. The solution was slowly warmed to r.t. and left to react for 24 hours. The solution was filtered from the precipitated lithium salts and evaporated to dryness in order to remove excess $B(OMe)_3$. The resulting oily residue was then dissolved in *ca.* 10 mL of toluene and added to a solution of 162 mg (1.47 mmol) of catechol in *ca.* 10 mL of toluene. The mixture was heated at 90°C for a period of 3 hours. After cooling the solution to room temperature, the solution was concentrated to half its original volume by evaporation causing the unreacted catechol to precipitate. The solution was then filtered and evaporated to dryness, yielding 450 mg (80%) of pure **1** as a white powder. Colorless needles suitable for X-ray diffraction were grown from a saturated solution of toluene at -40°C.



^{1}H NMR (500 MHz, benzene-d$_6$): δ 8.08 (d, 1H, $^{3}J_{H-H}$=7.0 Hz; Hc), 7.46 (t, 4H, $^{3}J_{H-H}$=7.3 Hz; Hh); 7.09-6.99 (m, 9H; Hd,e,f,g,i); 6.97 (dd, 2H, $^{3}J_{H-H}$=5.8 Hz, $^{4}J_{H-H}$=3.4 Hz; Ha), 6.71 (dd, 2H, $^{3}J_{H-H}$=5.8 Hz, $^{4}J_{H-H}$=3.4 Hz; Hb). ^{31}P{^{1}H} (203 MHz, benzene-d$_6$): δ -4.57 (s). ^{11}B{^{1}H} (160.46 MHz, benzene-*d*$_6$): δ 33.1 (s) ^{13}C{^{1}H} (101 MHz, benzene-d$_6$)**:** δ 148.9 (s; C1), 145.8 (d, $^{1}J_{P-C}$= 20.5 Hz ; C9), 138.6 (d, $^{2}J_{P-C}$= 13 Hz; C11), 136.7 (d, $^{2}J_{P-C}$= 10.0 Hz; C5), 134.4 (d, $^{1}J_{P-C}$= 20.0 Hz; C10), 133.9 (s; C6 or C7 or C8), 131.7 (s; C6 or C7 or C8), 128.78 (s; C13), 128.83 (d, $^{3}J_{P-C}$= 2.9 Hz; C12), 128.4 (s; C6 or C7 or C8), 122.9 (s; C3), 112.8 (s; C2). M/Z (M+H^{+}) = 380.1227 calc= 380.11.

Figure S2: ^{1}H NMR spectrum of **1** (500 MHz, benzene-d_6),

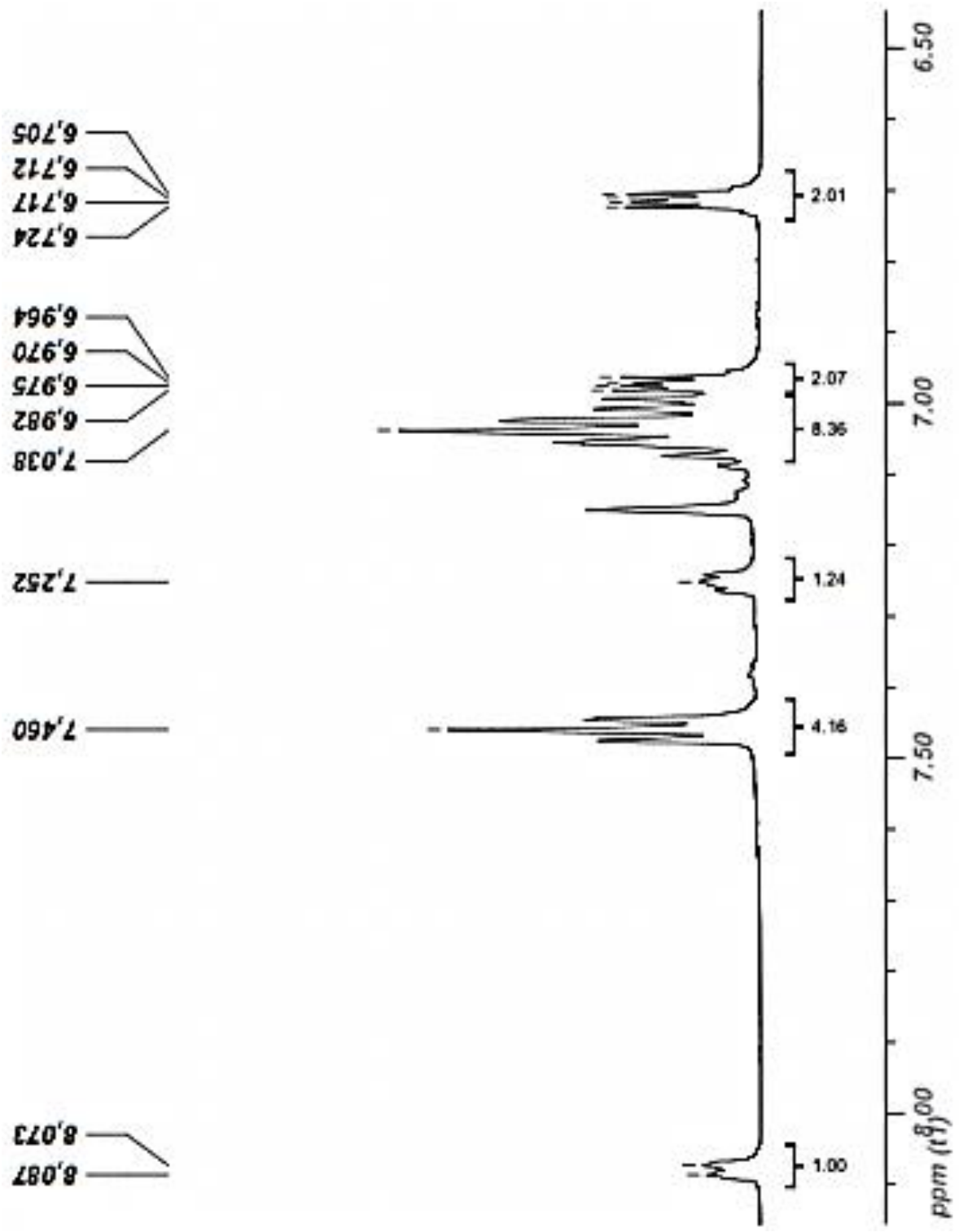


Figure S3: $^{13}C\{^{1}H\}$ spectrum of **1** (101 MHz, benzene-d_6)**:**

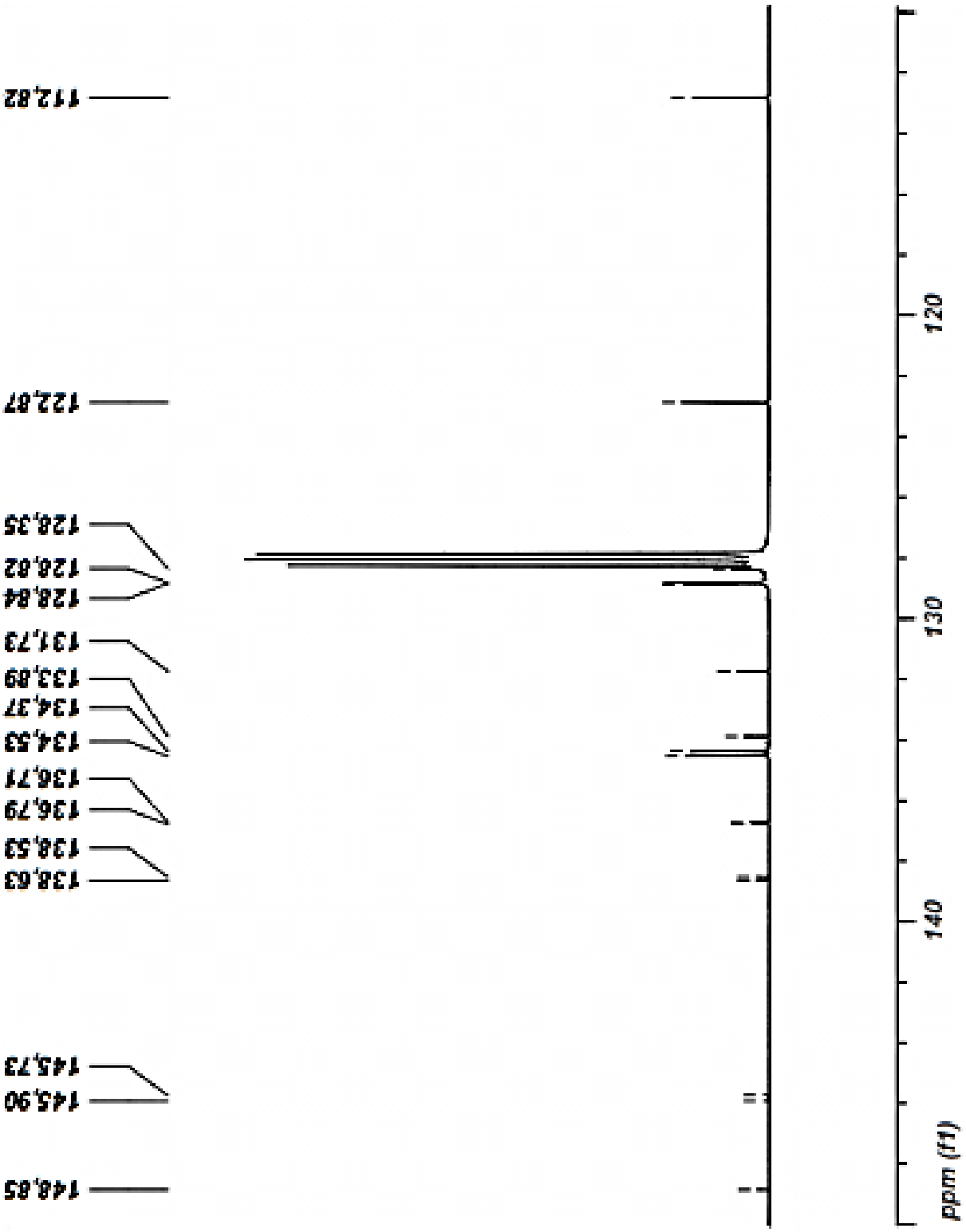


Figure S4: $^{31}P\{^{1}H\}$ NMR spectrum of **1** (202.456 MHz, benzene-d_6),

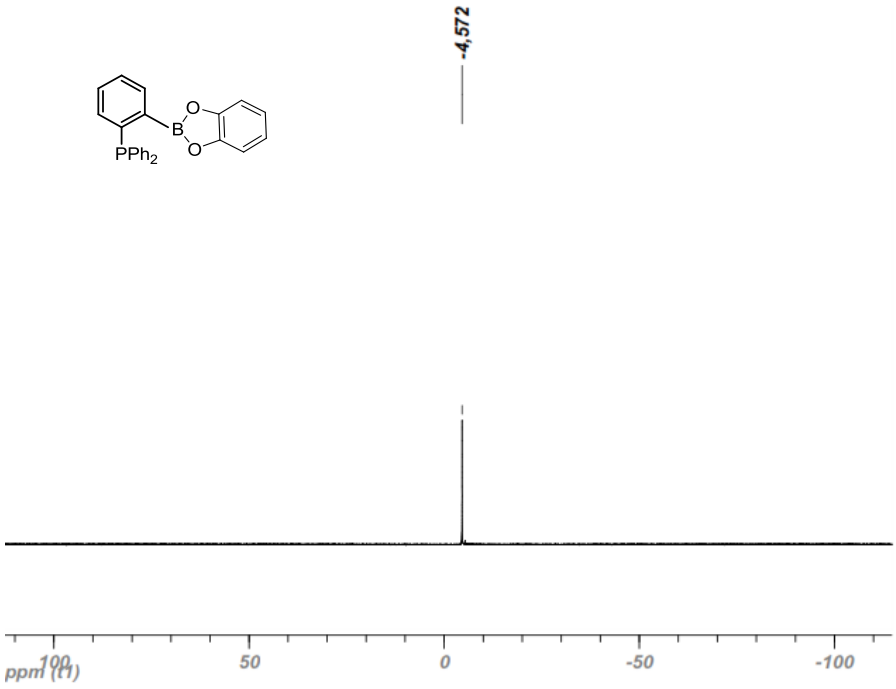
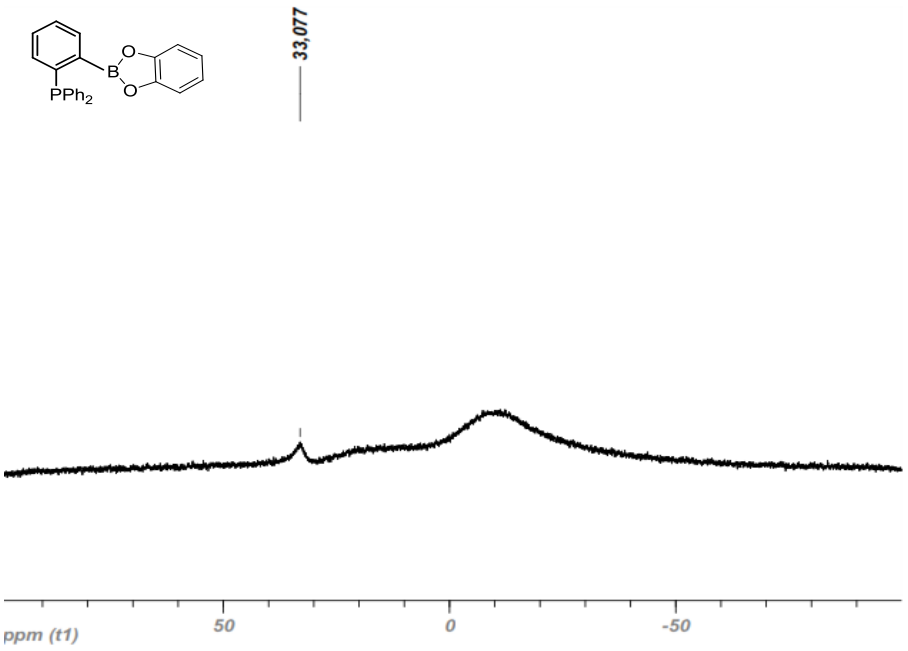


Figure S5: $^{11}B\{^{1}H\}$ NMR spectrum of **1** (160.46 MHz MHz, benzene-d_6),



2. Reactivity

a. General procedure for catalytic reduction of carbon dioxide

2.0 mg (5.3 mmol) of **1** was dissolved in *ca.* 0.6 mL of C_6D_6 containing an internal standard of hexamethylbenzene**.** The reducing agent (HBcat, HBpin, 9-BBN or $BH_3.SMe_2$) was added to the solution and the mixture was introduced in a J-Young NMR tube. The J-young NMR tube was frozen in a liquid nitrogen bath after which *ca.* 1atm. of CO_2 was introduced. The reaction was then followed by NMR spectroscopy. Subsequent loadings of reductants and CO_2 were introduced in the J-young NMR tube using the exact same procedure. Yields are reported by ^1H NMR according to the integration of hexamethylbenzene which was used as an internal standard. The full characterization of the products obtained with HBcat and $BH_3.SMe_2$ is described below, but the characterization of the reduction of CO_2 with 9-BBN and HBpin is solely based on ^1H NMR spectroscopy and on the similarity with other reagents.

b. Reactivity with HBcat

Figure S6. Typical catalytic reduction of CO_2 by 1 in the presence of catecholborane (See general procedure)

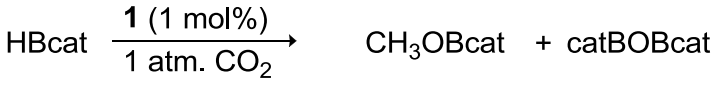


Figure S7: ^{1}H NMR spectrum of the solution depicted in fig.S6, **before addition of CO_2** (500 MHz, benzene-d_6). *=Internal standard (hexamethylbenzene)

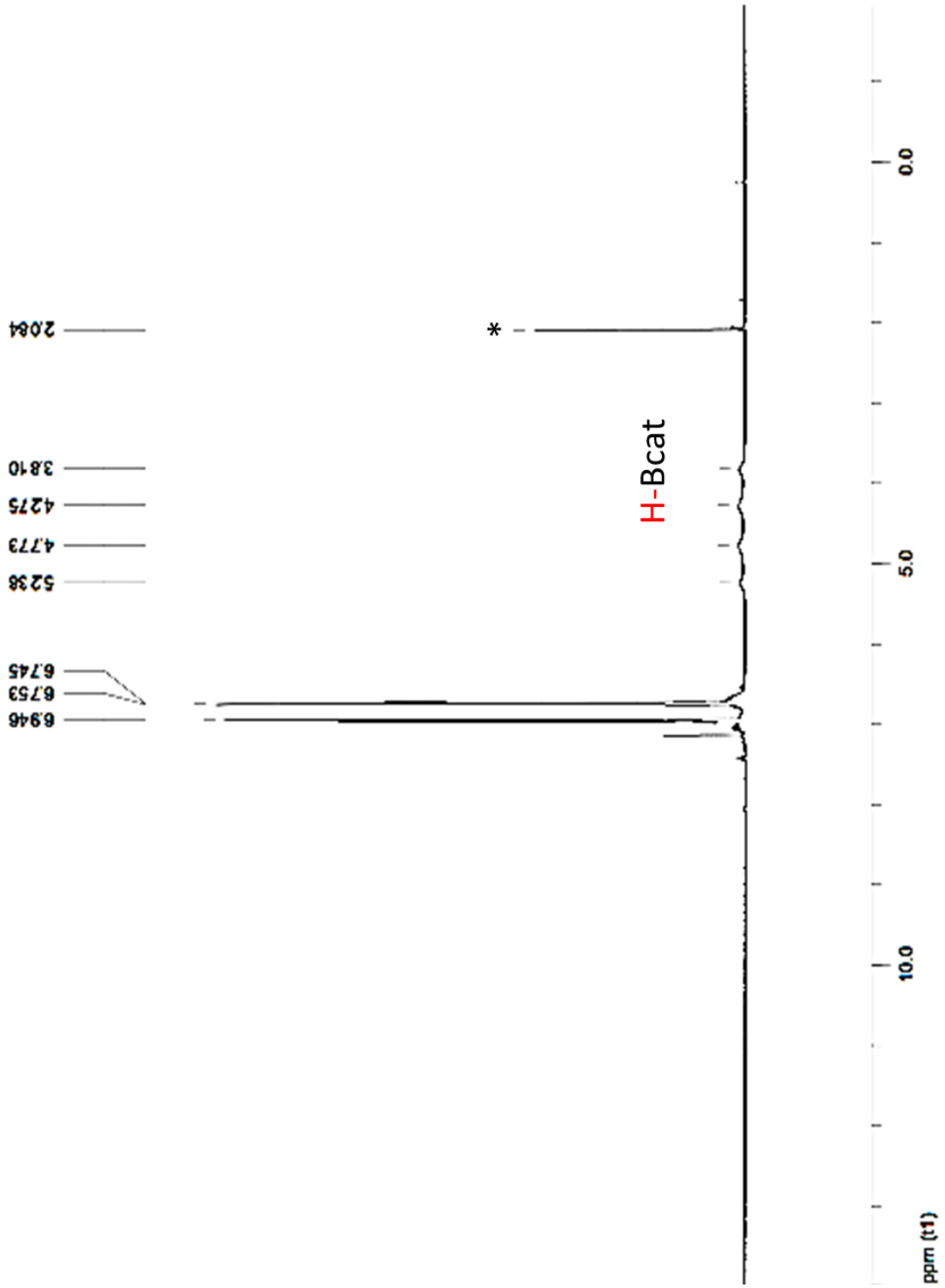
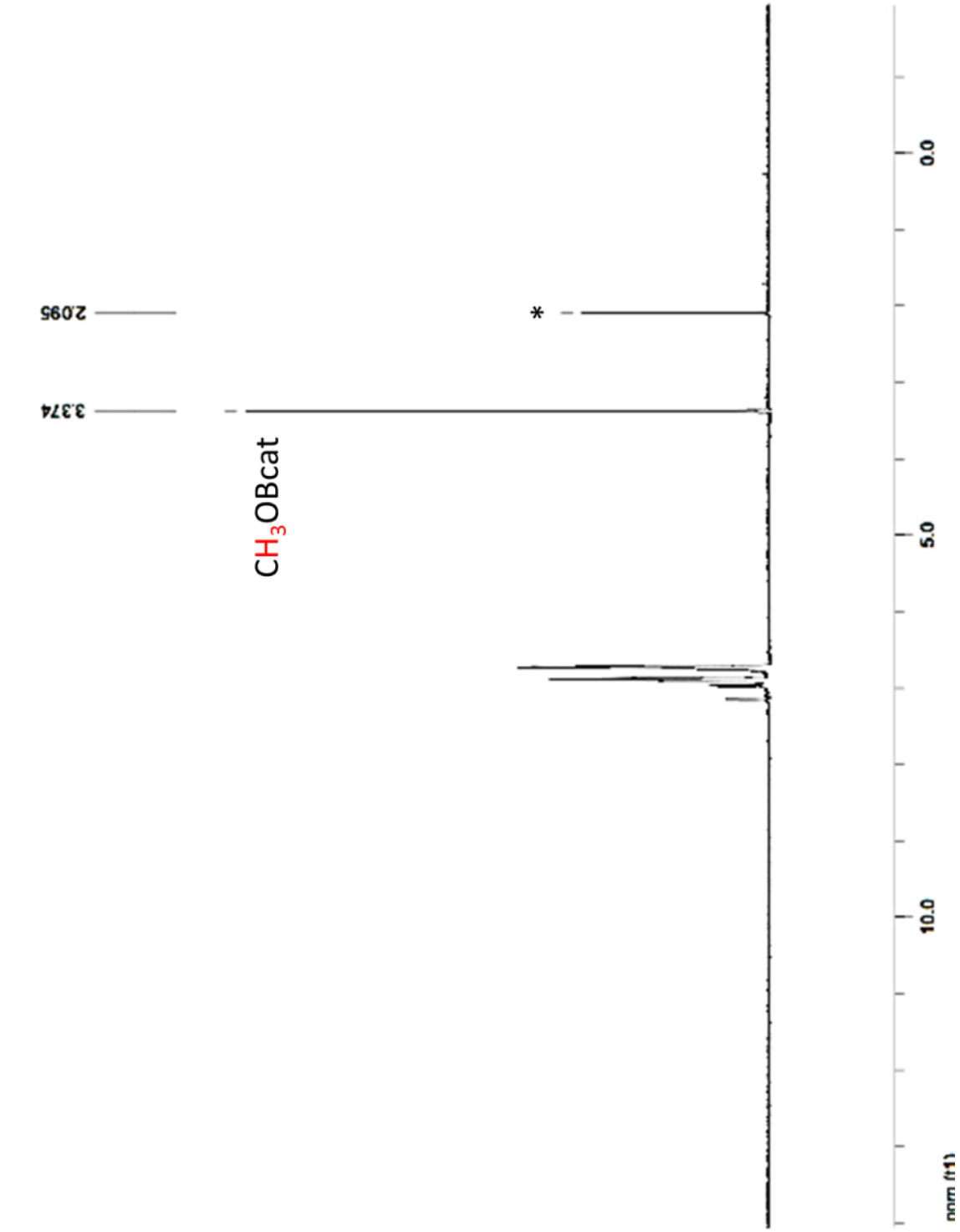


Figure S8: ^{1}H NMR spectrum of the solution depicted in fig. S6, **after 1.75 h at 70° under 1 atm. of CO_2** (500 MHz, benzene-d_6) *=Internal standard (hexamethylbenzene)



The ^{11}B, ^{1}H and ^{13}C chemical shifts for generated CH_3OBcat are consistent with those of independently synthesized product. ^{1}H NMR (500 MHz, benzene-d_6): 6.9 (m, 2H), 6.7 (m, 2H), 3.37, (s, 3H). δ $^{11}B\{^{1}H\}$ (160.46 MHz, benzene-d_6): δ 23.4 (s). $^{13}C\{^{1}H\}$ (101 MHz, benzene-d_6)**:** δ 148.5 (s), 122.5 (s), 112.2 (s), 53.1 (s) ppm

Figure S9. Catalytic reduction of $^{13}CO_2$ by **1** in the presence of catecholborane (See general procedure)

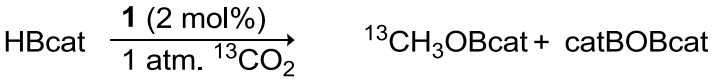


Figure S10: ^{1}H NMR spectrum of the solution depicted in figure S9, **after 3h at 25°C under 1 atm. of $^{13}CO_2$** (500 MHz, benzene-d_6),

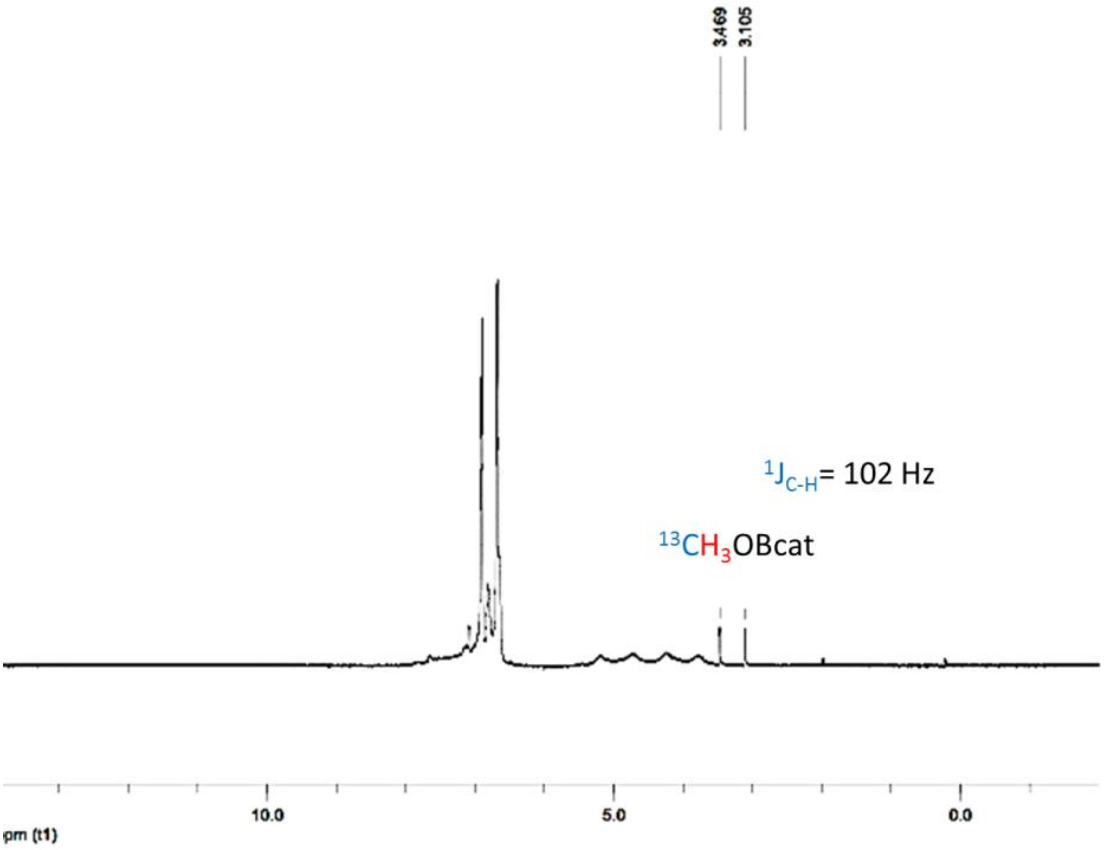
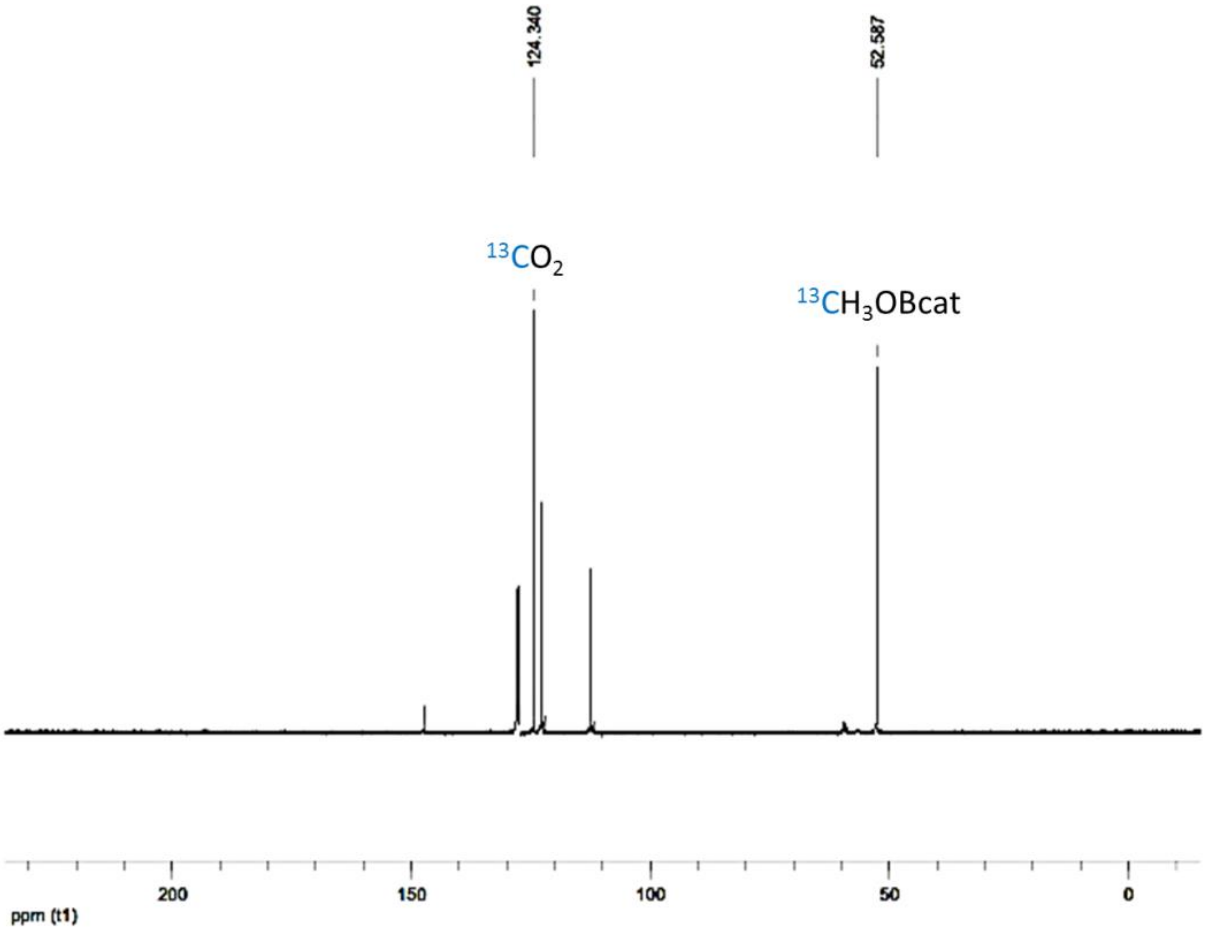


Figure S11: $^{13}C\{^{1}H\}$ NMR spectrum of the solution depicted in figure S9, **after 3h at 25°C. under 1 atm. of $^{13}CO_2$** (101MHz, benzene-d_6)



c. Reactivity with $BH_3.SMe_2$

Figure S12. Typical catalytic reduction of CO_2 by **1** in the presence of $BH_3.SMe_2$ (See general procedure)

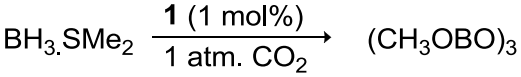


Figure S13: ^{1}H NMR spectrum of the solution depicted in figure S12, **before addition of CO_2** (500 MHz, benzene-d_6). *=Internal standard (hexamethylbenzene)

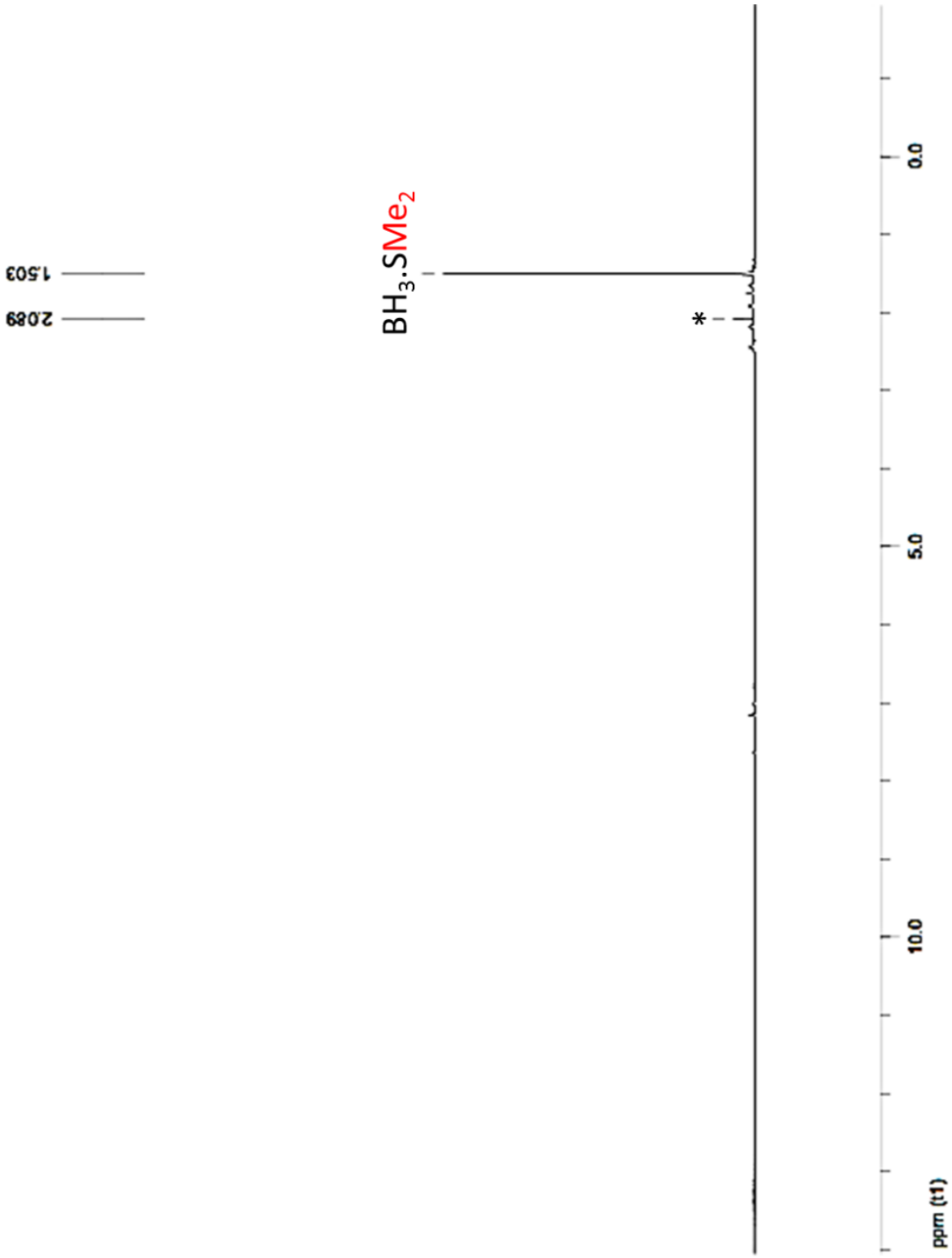
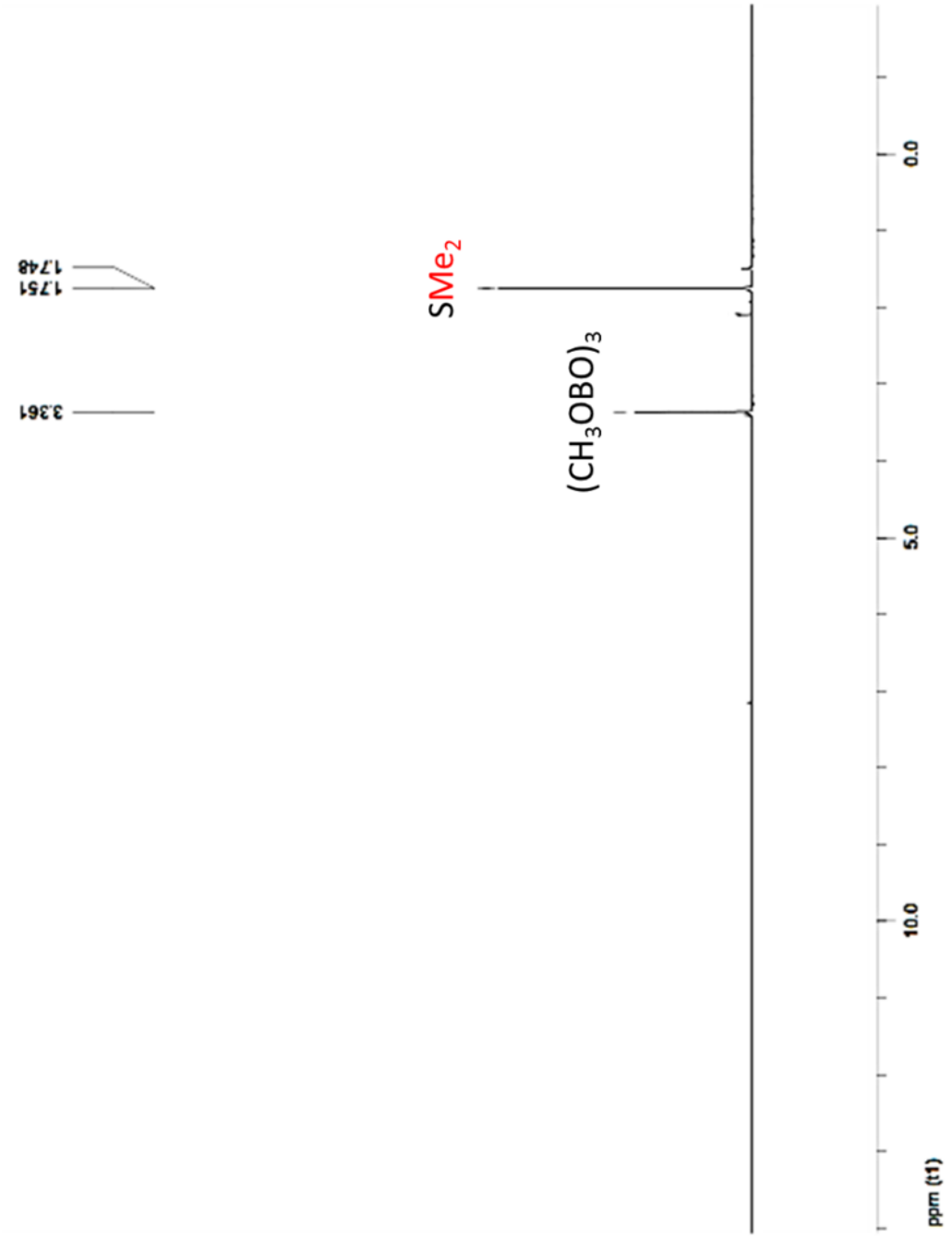


Figure S14: ^{1}H NMR spectrum of the solution depicted in figure S12, **after 1h at 70°C** (500 MHz, benzene-d_6). *=Internal standard (hexamethylbenzene)



The ^{11}B, ^{1}H and ^{13}C chemical shifts for generated $(CH_3OBO)_3$ are consistent with reported literature values.[S5] ^{1}H NMR (500 MHz, benzene-d_6): 3.37, (s, 3H) δ $^{11}B\{^{1}H\}$ (160.46 MHz, benzene-d_6). δ 19.1 (s, br). $^{13}C\{^{1}H\}$ (101 MHz, benzene-d_6)**:** δ 51.3 (s) ppm.

Important Notice: A 1:1 mixture of PPh_3 and reducing agents ($BH_3.SMe_2$, HBcat) did not show any activity after 24 h at 70°C.

d. General procedure for big scale (> 100 équ. reducing agent) catalytic reduction of carbon dioxide

2.0 mg (5.3 mmol) of **1** was dissolved in *ca.* 1 mL of C_6H_6 per 100 equivalents of reducing agent ($BH_3.SMe_2$ or HBcat)**.** The reducing agent was added to the solution and the mixture was introduced in a Fischer-Porter bottle. The Fischer-Porter bottle was frozen in a liquid nitrogen bath and put under vacuum for 15 min after which *ca.* 2 atm of CO_2 was introduced (in order to ensure sufficient amount of CO_2 for complete reduction). The mixture was left to react at 70°C for the specified amount of time (see figure S15) after which the contents of the Fischer-Porter bottle were quenched using *ca.* 2 mL of H_2O per 100 equivalents of reducing agent. This was left to stir at r.t. for 1 hour to ensure complete quenching of the mixture. Yields have been determined using GC-FID with isopropanol as internal standard. Methanol yields have been determined using GC-FID with isopropanol as the internal standard. A calibration plot was obtained using three aqueous solutions of isopropanol (1% v/v) containing methanol (0.5, 1 and 2 % v/v) to ensure linearity of the iPrOH/MeOH signal.

e. Reactivity with methylformate

2.0 mg (5.3 mmol) of **1** was dissolved in *ca.* 0.6 mL of C_6D_6**.** 4 µL (65 mmol) of methylformate was added to the solution and the mixture was introduced in a J-Young NMR tube for NMR characterization. 26.8 mg (224 mmol) of HBcat was then added to the solution and left to react at 23° C for 20 hours. Yield is reported by NMR integration using toluene as internal standard. Yield: approx. 90% conversion.

Figure S15: Catalytic reduction of methylformate by b and HBcat

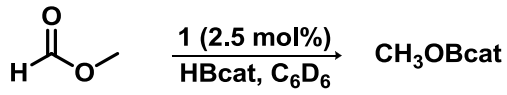


Figure S16: ^{1}H NMR spectrum (selected region) of the solution of the reaction described in figure S15., **before the addition of HBcat** (500 MHz, benzene-d_6),

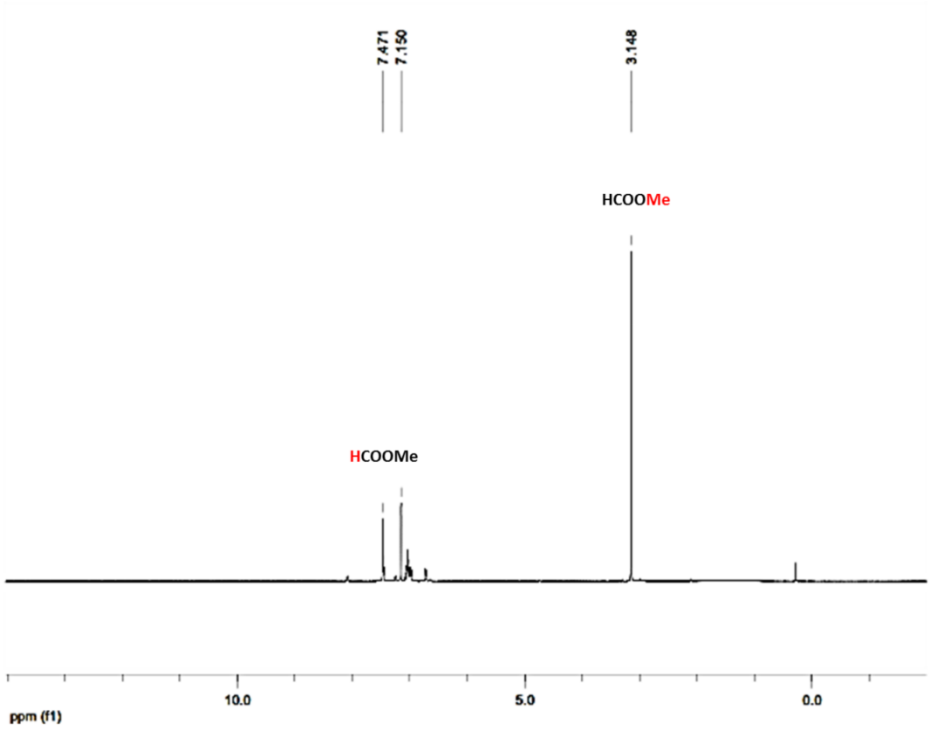
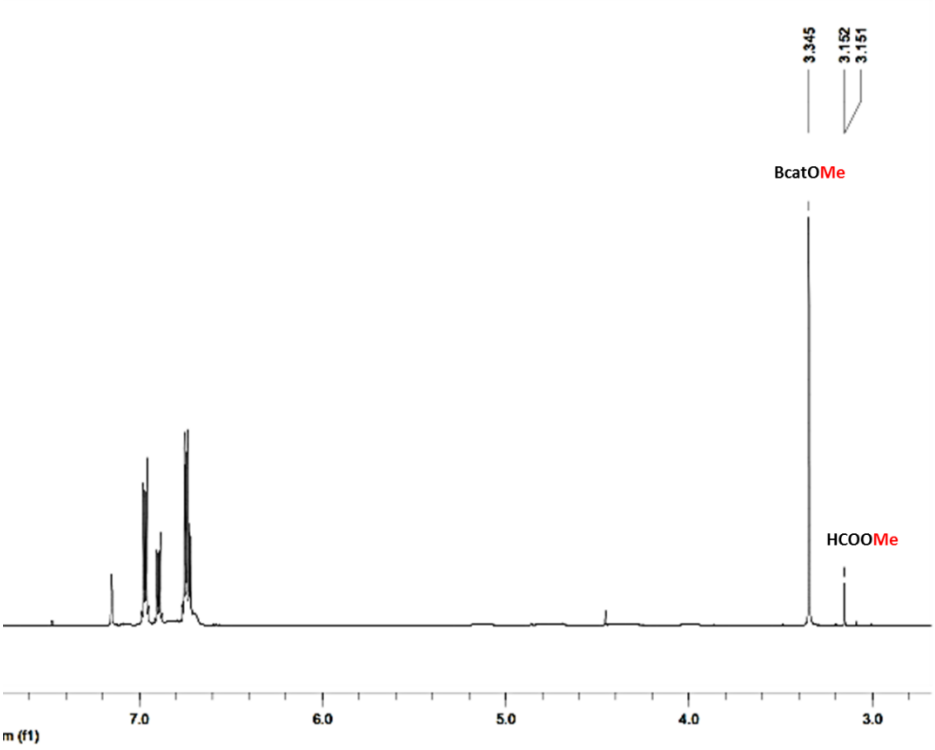


Figure S17: ^{1}H NMR spectrum (selected region) of the solution depicted in figure S15, **after 20h at 23°C with HBcat** (500 MHz, benzene-d_6),



Note that HCOOMe does not react with HBcat in the absence of **1**

f.In-Situ preparation of IM2

8.7 mg (22.9 mmol) of **2** was dissolved in *ca.* 0.6 mL of benzene-d_6 along with excess (2.3 mg) of paraformaldehyde. The mixture was heated for 15 min at 70°C in a J-Young NMR tube before NMR characterization. Crude Yield (approx 74% by NMR integration). Not isolated

Figure S18: Preparation of IM2

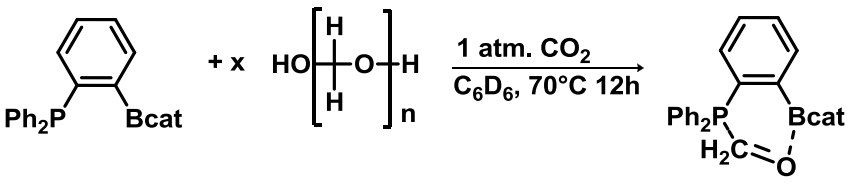


Figure S19: ^{1}H NMR spectrum (selected region) of the solution depicted in figure S18, **after 15 min at 70°C** (400 MHz, benzene-d_6),

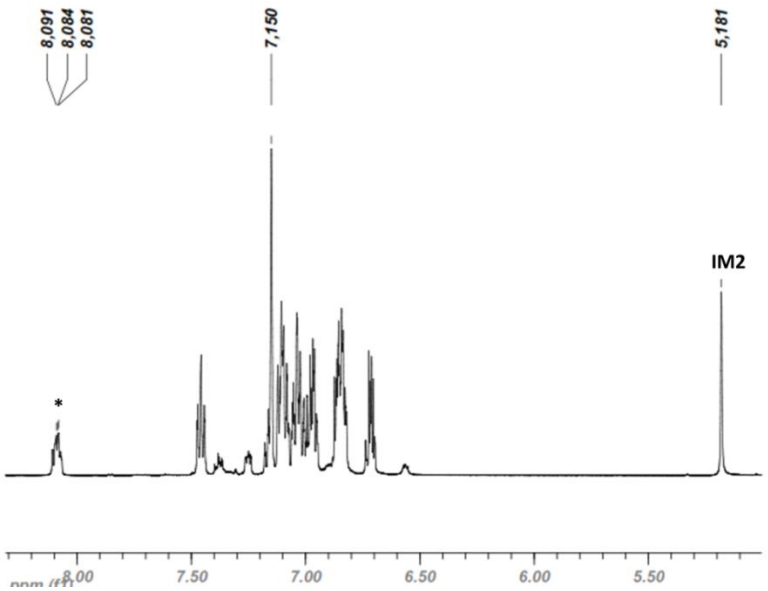


Figure S20: $^{31}P\{^{1}H\}$ NMR spectrum of the solution depicted in figure S15, **after 15 min at 70°C** (202.456 MHz, benzene-d_6)

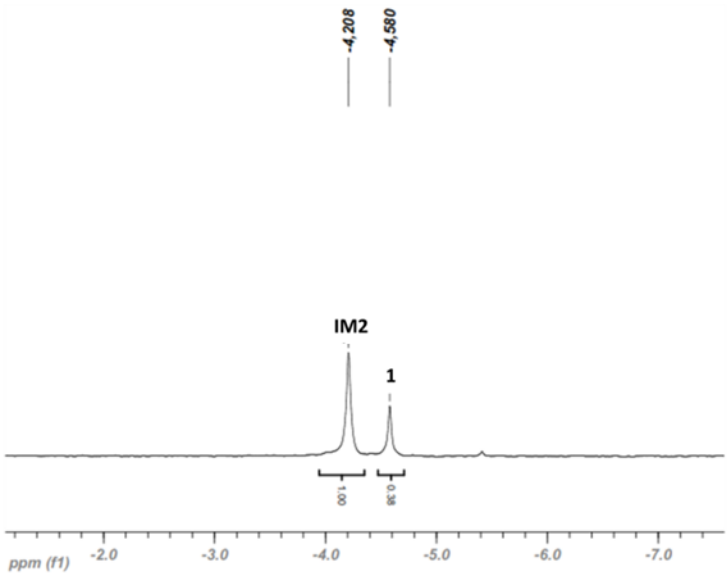


Figure S21. Typical GC-FID spectra (after 1 hour at 70°C with 300 equiv. of $BH_3.SMe_2$)

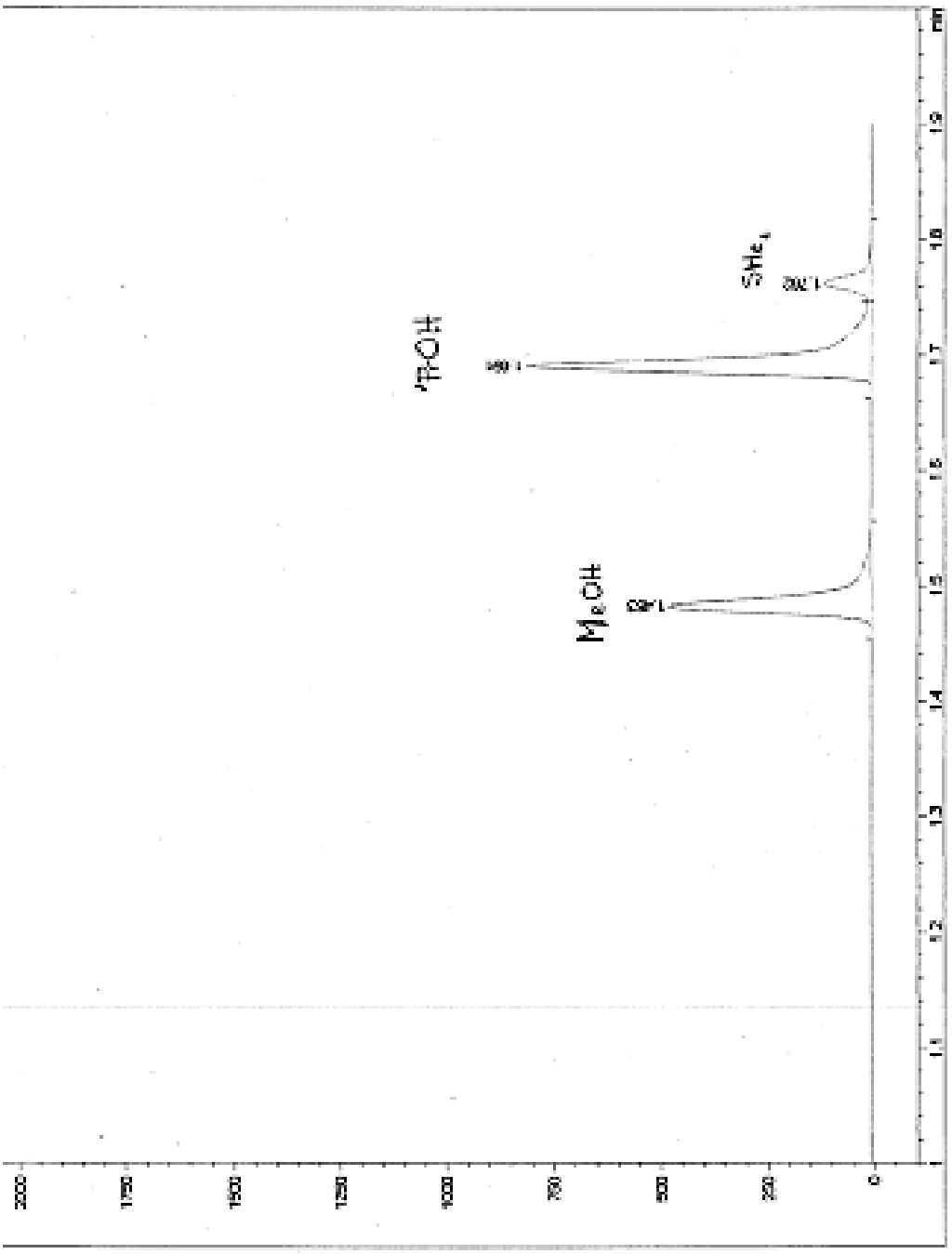


Figure S22: Additionnal computational studies (not selected for manuscript)

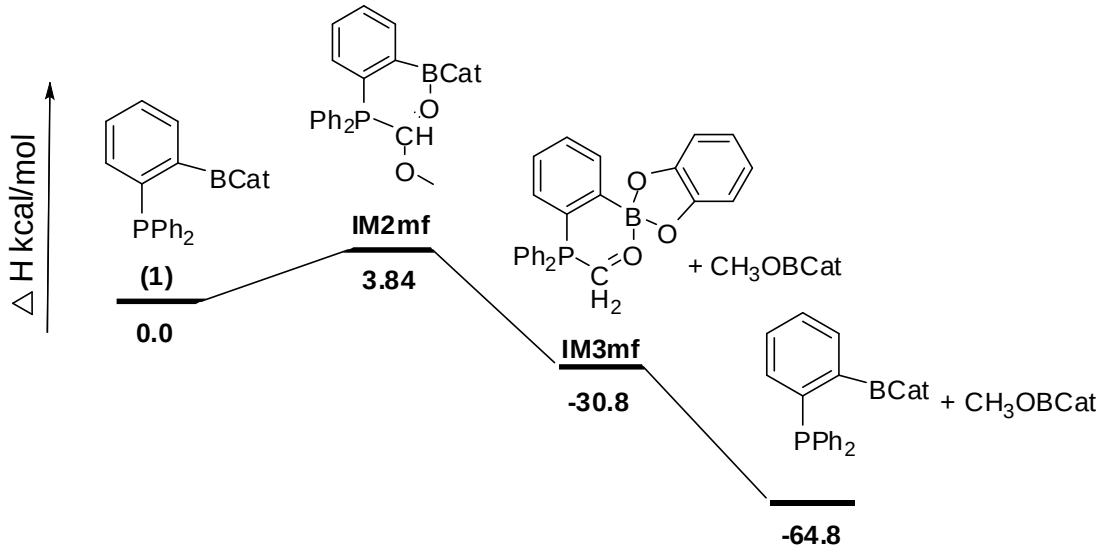
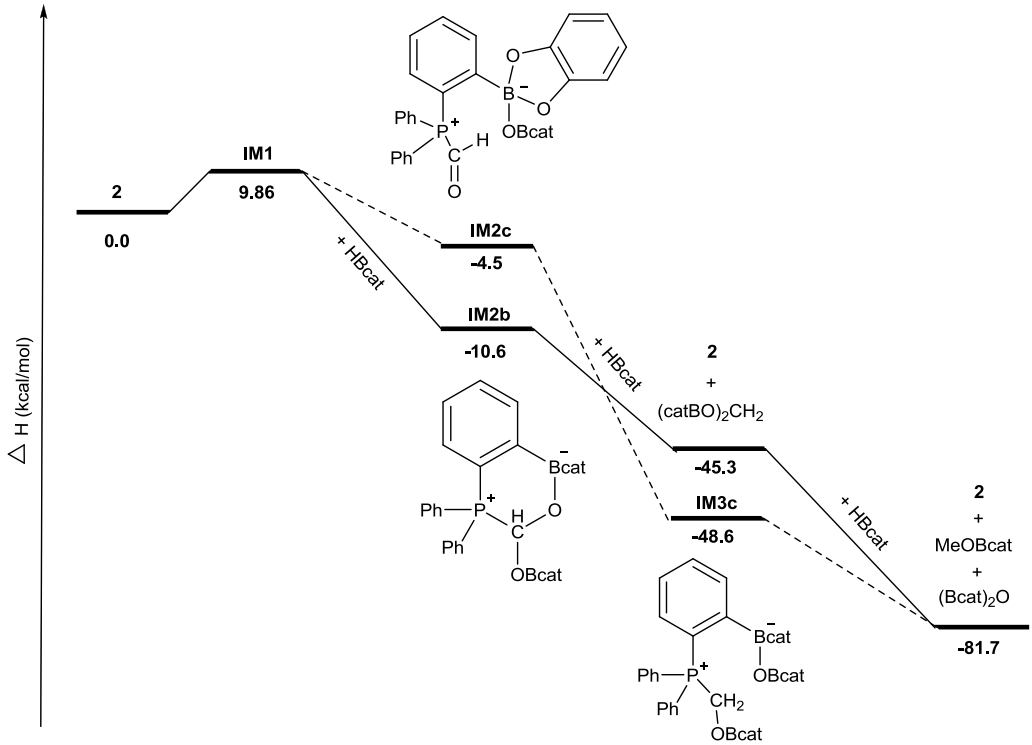


Figure S23



2. Crystallographic information:

A colorless block crystal of PB1 with approximate dimensions of 0.44 x 0.38 x 0.32 mm was mounted on CryoLoops with Paratone-N and optically aligned on a Bruker SMART APEX-II X-ray diffractometer with 1K CCD detector using a digital camera. Initial intensity measurements were performed using a fine-focused sealed tube, graphite-monochromated, X-ray source (Mo $K\alpha$, λ = 0.71073 Å) at 50 kV and 30 mA. Standard APEX-II[S6] software package was used for determining the unit cells, generating the data collection strategy, and controlling data collection. SAINT[S7] was used for data integration including Lorentz and polarization corrections. Semi-empirical absorption corrections were applied using SCALE (SADABS[S8,S9]). The structures of all compounds were solved by direct methods and refined by full-matrix least-squares methods with SHELX-97[S10] in the SHELXTL6.14 package.. All of the H atoms (on C atoms) were generated geometrically and refined in riding mode. Crystallographic information for all obtained phases is summarized in Table 1. Atomic coordinates and additional structural information are provided in the .cif files of the Supporting Information. Crystallographic data have been deposited with CCDC (CCDC No. 936490). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.

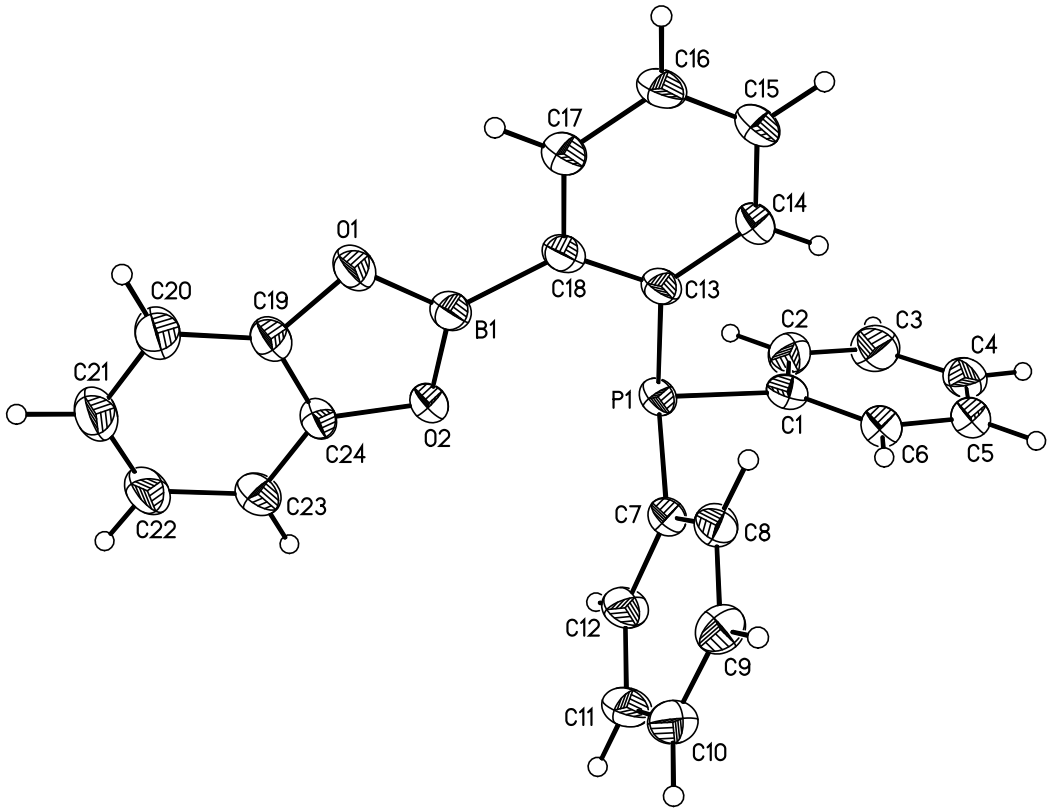


Figure S24 - ORTEP drawing of **1** in the asymmetric unit cell, with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P(1)-C(13) 1.8429(19), C(18)-B(1) 1.553(3), C(13)-C(18) 1.412(3), C(17)-C(18)-B(1) 114.71(17), C(13)-C(18)-B(1) 127.07(16), C(18)-C(13)-P(1) 119.67(13), C(14)-C(13)-P(1) 120.86(15).

Table S1. Crystal data and structure refinement for 1

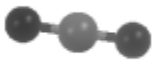
Empirical formula	C24 H18 B O2 P	
Formula weight	380.16	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P -1	
Unit cell dimensions	a = 10.492(2) Å b = 10.674(2) Å c = 11.004(2) Å	α= 93.029(9)° β = 114.593(9)° γ = 116.839(8)°
Volume	954.8(3) A^3	
Z	2	
Calculated density	1.322 Mg/m^3	
Absorption coefficient	0.161 mm^{-1}	
F(000)	396	
Reflections collected / unique	19023 / 4709 [R(int) = 0.0539]	
Completeness to theta = 28.35	98.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9503 and 0.9384	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4709 / 0 / 253	
Goodness-of-fit on F^2	1.078	
Final R indices [I>2sigma(I)]	R1 = 0.0537, wR2 = 0.1504	
R indices (all data)	R1 = 0.0687, wR2 = 0.1705	

3. Computational Details:

Calculations were performed with the GAUSSIAN 03 suite of programs.[11] The B3PW91[12,13] functional was used in combination with the 6-31+G** basis set for B,C,H, and O atoms,[14,15] and the SDD basis set with an additional polarization function (one d function with a 0.34 exponent and a 1.0 contraction coefficient) for P atoms,[16] . The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency). All geometry optimization were carried out without any symmetry constraints.

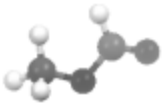
Cartesian coordinates of all optimized structures

CO2: Sum of electronic and thermal enthalpies= -188.488909



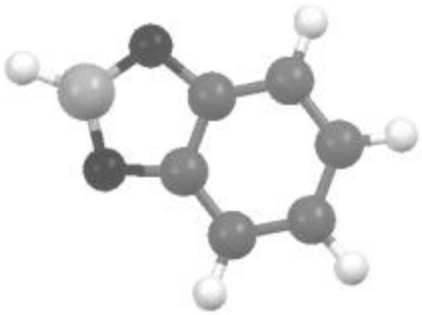
C	0.000000	0.000000	0.060008	O	0.000000	0.000000	-1.107884
O	0.000000	0.000000	1.227876	XX	1.000000	0.000000	0.060008

Methyl formate: Sum of electronic and thermal enthalpies= -228.900228



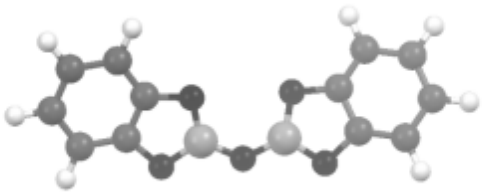
C	0.189339	-0.264905	0.201921	C	1.253751	0.072079	-1.892069
O	-0.009235	-0.049835	1.363818	H	2.283273	-0.252325	-2.063137
O	1.103087	0.410433	-0.518347	H	0.569458	-0.732633	-2.187515
H	-0.349781	-1.030393	-0.393068	H	1.046413	0.958413	-2.496938

HBCat : Sum of electronic and thermal enthalpies = -406.766102



C	0.314324	0.000061	-0.240307	H	0.974598	-0.000074	3.048825
C	0.037022	0.000011	1.114724	H	3.280580	-0.000054	2.185282
C	1.140718	-0.000037	1.975779	H	3.730172	0.000036	-0.278840
C	2.450197	-0.000024	1.485597	O	1.584363	0.000094	-2.103979
C	2.718291	0.000029	0.111509	O	-0.561215	0.000175	-1.300605
C	1.619920	0.000057	-0.728302	B	0.240330	-0.000135	-2.427337
H	-0.983388	0.000022	1.482318	H	-0.173780	-0.000161	-3.535716

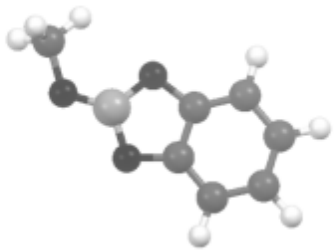
catBOBcat: Sum of electronic and thermal enthalpies = -887.649582



C	-0.021519	0.033173	1.546569	O	-0.400902	0.195857	5.630938
C	1.017028	0.496689	2.364867	O	1.367801	0.963382	7.127617
C	0.772534	0.505768	3.724651	H	-2.413585	-0.713213	3.892677
C	-0.442226	0.076407	4.260184	H	-2.019536	-0.748660	1.417228
C	-1.473770	-0.382515	3.464105	H	0.125238	0.008057	0.471014
C	-1.237684	-0.396081	2.083086	H	1.965356	0.832457	1.959565
O	1.604121	0.904635	4.745027	B	0.777346	1.117409	8.337015
B	0.861354	0.705556	5.897981	O	1.499764	1.045626	9.517529

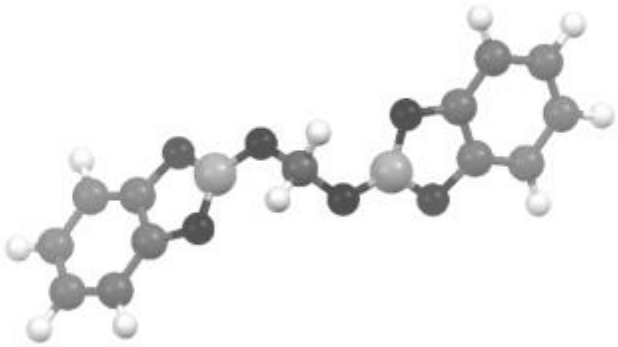
O	-0.564964	1.390684	8.555759	C	-0.375017	1.587199	12.651829
C	-0.678705	1.490040	9.923979	H	-2.772170	1.910900	10.216200
C	0.572286	1.281146	10.505540	H	-2.484218	1.997566	12.704881
C	-1.805034	1.750825	10.680213	H	-0.275843	1.629836	13.732264
C	0.759888	1.323546	11.873721	H	1.737176	1.160203	12.314809
C	-1.627307	1.795882	12.069266				

CH_3OBCat: Sum of electronic and thermal enthalpies = -521.267837



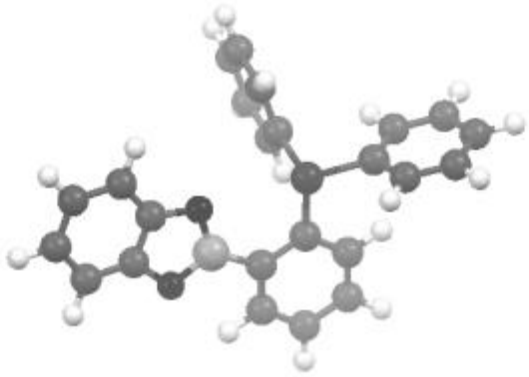
C	0.346943	0.066353	0.012225	C	3.598436	-2.770126	5.288578
O	0.486794	0.261553	1.412118	C	3.946117	-3.538824	4.176296
B	1.260162	-0.546442	2.154632	H	-0.719114	0.064237	-0.231165
O	1.415898	-0.370179	3.526958	H	0.826507	0.896460	-0.515735
O	1.989583	-1.640681	1.683403	H	0.794989	-0.875449	-0.317427
C	2.608685	-2.150770	2.800962	H	2.464340	-1.062572	6.033660
C	2.260439	-1.381123	3.912904	H	3.999444	-3.030299	6.263610
C	2.741241	-1.666844	5.176495	H	4.612817	-4.386952	4.300019
C	3.452483	-3.239990	2.898676	H	3.715528	-3.829932	2.027190

CatBOCH2OBCat:- Sum of electronic and thermal enthalpies = 1002.093229



C	-0.849787	0.507365	0.162578
C	-0.596935	-0.635913	0.922124
C	0.619701	-0.852743	1.538929
C	1.595550	0.137747	1.362659
C	1.343663	1.281535	0.602325
C	0.104506	1.489974	-0.018071
O	-1.719768	-1.433489	0.928903
B	-2.644260	-0.736230	0.157722
O	-2.134160	0.459338	-0.326056
H	0.803110	-1.744536	2.128408
H	2.567550	0.010276	1.829518
H	2.123542	2.028349	0.487842
H	-0.102784	2.374701	-0.610239
O	-3.897690	-1.154803	-0.137737
C	-4.418515	-2.316071	0.459911
H	-5.157044	-2.723775	-0.235397
H	-3.626986	-3.042682	0.661856
O	-5.008595	-2.005665	1.698001
B	-6.302245	-1.610191	1.758921
O	-6.891534	-1.196855	2.944501
O	-7.193764	-1.595761	0.690904
C	-8.377927	-1.155080	1.238879
C	-8.192991	-0.915270	2.601310
C	-9.594300	-0.953753	0.616424
C	-10.642387	-0.494904	1.425881
C	-10.458737	-0.255697	2.789296
C	-9.218891	-0.463114	3.408766
H	-9.064484	-0.279695	4.466534
H	-11.293627	0.099900	3.385590
H	-11.617255	-0.322068	0.980081
H	-9.724218	-1.141991	-0.443810

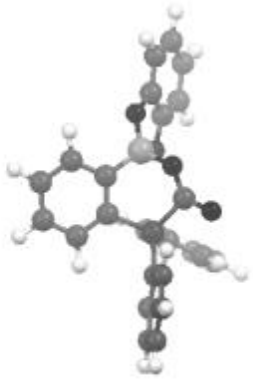
1: Sum of electronic and thermal enthalpies = -1106.563866



P	0.491948	-0.486128	-0.537748
C	0.592806	-0.332768	1.329149
C	1.777758	0.157646	1.939279
B	3.035793	0.669710	1.194817
C	-0.455926	-0.773889	2.144328
C	-0.360611	-0.731695	3.535212
C	0.793572	-0.245191	4.141740
C	1.845412	0.193029	3.344029
O	4.200922	1.033455	1.872749
O	3.193427	0.844820	-0.173809
C	4.469828	1.317460	-0.345016
C	5.122616	1.648811	-1.517785
C	6.438837	2.109020	-1.389726
C	7.053968	2.224689	-0.139816
C	6.381794	1.885835	1.040901
C	5.082439	1.432610	0.902128
H	4.633994	1.554700	-2.481346
H	6.992661	2.381501	-2.283164
H	8.076632	2.585093	-0.080836
H	6.849711	1.970924	2.015780
C	0.053653	1.254999	-1.033375
C	-1.143746	-1.353745	-0.761601
C	-2.381776	-0.710579	-0.886245
C	-3.545947	-1.450669	-1.091373
C	-3.490510	-2.841715	-1.170003
C	-2.262947	-3.492520	-1.050862
C	-1.098383	-2.752131	-0.857770
H	-2.434844	0.372640	-0.827739

H	-4.499206	-0.937675	-1.189752	H	0.634159	0.852066	-3.070059
H	-4.399162	-3.415701	-1.330521	H	0.084455	3.121540	-3.887738
H	-2.210090	-4.575862	-1.119088	H	-0.775004	4.839260	-2.309760
H	-0.140253	-3.262244	-0.785941	H	-1.098386	4.261086	0.084763
C	0.241182	1.595092	-2.379920	H	-0.575714	1.985498	0.895910
C	-0.063646	2.874319	-2.839810	H	-1.363147	-1.157103	1.689041
C	-0.545615	3.838249	-1.954539	H	-1.194223	-1.078969	4.140426
C	-0.725634	3.513699	-0.610942	H	0.875990	-0.209946	5.224477
C	-0.431198	2.229410	-0.152664	H	2.750914	0.569682	3.811944

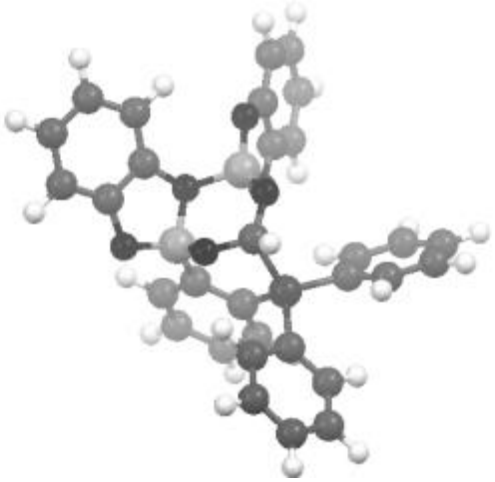
IM1: Sum of electronic and thermal enthalpies = -1295.037049



C	7.834580	8.008903	0.874066	O	8.601670	5.536038	2.700784
C	6.572192	7.487686	1.183592	O	7.983978	1.695593	0.104849
C	5.479228	8.345313	1.360244	C	7.629922	0.667194	0.922839
C	5.649756	9.720715	1.217849	C	6.599639	1.061848	1.789553
C	6.905598	10.239504	0.906297	H	6.781639	2.199266	-2.090899
C	7.994961	9.384951	0.737469	H	4.679473	5.720389	-3.407586
P	6.331808	5.681586	1.270192	H	5.604910	3.462810	-3.873485
C	4.994577	5.352396	2.463872	H	4.964463	6.727032	-1.157172
C	5.113506	5.871444	3.760406	H	4.504108	7.942629	1.617998
C	4.113538	5.613637	4.692913	H	4.801992	10.385308	1.356024
C	3.005876	4.843461	4.335398	H	7.037633	11.312600	0.801132
C	2.898350	4.321474	3.047343	H	8.975678	9.789593	0.506105
C	3.894799	4.568289	2.105539	H	8.689306	7.350389	0.763714
C	6.007241	4.994713	-0.371701	H	3.828249	4.142699	1.109909
C	5.341999	5.729031	-1.362636	H	2.041636	3.712695	2.774255
C	5.190955	5.167102	-2.625193	H	2.227711	4.643973	5.066699
C	5.712369	3.896330	-2.882412	H	4.202287	6.009885	5.700070
C	6.372958	3.184231	-1.884104	H	5.982278	6.461257	4.038632
C	6.538943	3.711849	-0.596256	C	6.049834	0.182395	2.704499
B	7.234894	2.842589	0.569353	C	6.564380	-1.124354	2.736972
O	6.262196	2.359765	1.557717	C	7.588082	-1.515843	1.877511

C	8.140232	-0.617645	0.949257	H	8.938928	-0.911524	0.275508
H	5.253480	0.499171	3.370779	C	7.982508	4.877610	1.895164
H	6.155868	-1.837822	3.447392	O	8.264311	3.751251	1.363639
H	7.969951	-2.531975	1.923525				

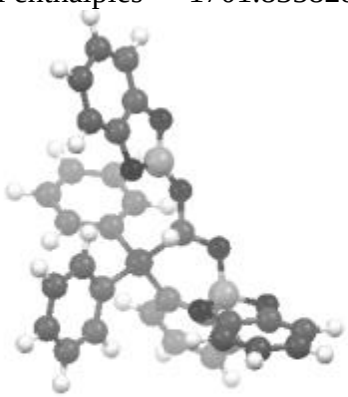
IM2: Sum of electronic and thermal enthalpies = -1701.841805



C	-1.135658	0.029002	-0.847426	B	-1.027051	-3.679967	2.395503
C	-0.648712	-0.199274	0.448336	O	0.235036	-2.950408	2.495061
C	0.713883	-0.444723	0.652581	C	1.209566	-3.870369	2.267965
C	1.584706	-0.438191	-0.434489	C	0.637513	-5.114282	1.966785
C	1.103284	-0.198667	-1.720248	C	1.416871	-6.218856	1.679805
C	-0.257079	0.030913	-1.926608	C	2.811278	-6.050421	1.707453
P	-1.828442	-0.319144	1.830625	C	3.381339	-4.817287	2.013577
C	-1.021868	-0.148884	3.453502	C	2.581577	-3.698707	2.301400
C	-1.354720	-1.080479	4.454816	O	-0.721463	-5.029351	2.003268
C	-0.749783	-0.896486	5.705582	C	-3.071569	1.017620	1.646997
C	0.135545	0.150718	5.947279	C	-2.759165	2.215800	0.991780
C	0.442566	1.061472	4.935456	C	-3.708145	3.232625	0.915974
C	-0.142235	0.916440	3.682150	C	-4.966764	3.059786	1.490537
B	-2.404377	-2.284419	4.245185	C	-5.276260	1.869993	2.148013
O	-1.645768	-3.633270	3.860535	C	-4.333673	0.847834	2.234224
C	-2.334707	-4.634736	4.547296	H	-1.565860	-6.452107	3.699780
C	-3.176686	-4.022415	5.480158	H	-2.943526	-7.862816	5.243574
C	-3.940694	-4.790579	6.344573	H	-4.434639	-6.806571	6.908559
C	-3.841871	-6.183986	6.244279	H	-4.592114	-4.311765	7.068242
C	-3.001405	-6.780387	5.307509	H	-1.782854	2.354370	0.537390
C	-2.220320	-6.005617	4.436478	H	-3.462075	4.160283	0.407300
O	-3.115345	-2.669565	5.440225	H	-5.705314	3.853979	1.428055
C	-2.794164	-2.024858	1.884966	H	-6.254189	1.734395	2.600536
O	-3.345577	-2.058096	3.138988	H	-4.568505	-0.070954	2.764265
O	-2.007050	-3.069054	1.521473	H	-2.194010	0.206933	-1.015382

H	-0.636676	0.207696	-2.928650	H	-0.997179	-1.590125	6.504020
H	1.786829	-0.199050	-2.564489	H	3.019465	-2.737544	2.553151
H	2.640523	-0.634047	-0.274362	H	4.462811	-4.715532	2.035564
H	1.079900	-0.667709	1.647837	H	3.452172	-6.899946	1.489195
H	0.088546	1.625211	2.890954	H	0.962055	-7.175212	1.441633
H	1.129174	1.882299	5.122113	H	-3.589026	-1.897687	1.138596
H	0.584387	0.264156	6.930599				

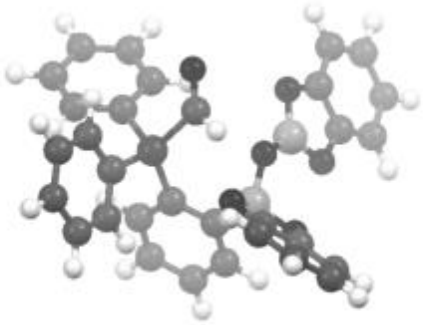
IM2b: Sum of electronic and thermal enthalpies = -1701.835828



C	8.239301	-0.331468	1.463866	C	6.639462	7.742618	0.989673
C	7.765581	0.962181	1.337314	C	7.729560	8.129803	0.195552
C	6.812615	1.478844	2.231422	C	7.974717	9.481392	-0.026488
C	6.309655	0.714080	3.268808	C	7.141472	10.447220	0.539511
C	6.788035	-0.600961	3.401435	C	6.059863	10.062591	1.329905
C	7.733418	-1.112666	2.516827	C	5.805649	8.711528	1.559242
O	8.092559	1.882780	0.396041	H	6.805649	2.174969	-1.801757
B	7.403057	3.109813	0.773041	H	4.796185	5.618364	-3.432584
O	8.426107	4.129515	1.262761	H	5.640833	3.295222	-3.684395
C	7.985659	5.080596	2.070350	H	5.128410	6.821056	-1.286083
O	8.976481	6.067081	2.213609	H	4.961914	8.412949	2.173399
O	6.496158	2.756957	1.897697	H	5.409603	10.813595	1.769017
C	6.615221	3.822360	-0.450160	H	7.337150	11.501301	0.364305
C	6.124649	5.138018	-0.346186	H	8.820001	9.779939	-0.639309
C	5.477334	5.798143	-1.401228	H	8.381865	7.379027	-0.240006
C	5.297428	5.125585	-2.604292	H	3.695776	4.846959	0.807215
C	5.773464	3.818308	-2.740428	H	1.756396	4.517571	2.313116
C	6.422378	3.184676	-1.683521	H	1.908322	5.180939	4.700497
P	6.373727	5.954647	1.250159	H	4.007120	6.169964	5.583415
C	4.931459	5.722271	2.343206	H	5.948205	6.501949	4.091504
C	5.026485	6.085442	3.693895	H	5.571231	1.123243	3.951819
C	3.933921	5.892357	4.535929	H	6.411662	-1.224117	4.208263
C	2.756144	5.334685	4.038921	H	8.089176	-2.132134	2.639181
C	2.668639	4.963657	2.698007	H	8.977076	-0.720269	0.768768
C	3.754586	5.152748	1.846800	B	9.179898	6.743091	3.364820

O	10.235951	7.627449	3.523571	C	10.908627	8.998021	5.481551
O	8.386932	6.658949	4.509904	H	11.775029	9.444587	5.006002
C	8.992368	7.511056	5.410900	H	11.148174	10.000169	7.368068
C	10.107107	8.095413	4.809086	H	9.180961	8.963249	8.428492
C	8.624222	7.795475	6.711014	H	7.759871	7.328213	7.170517
C	9.429967	8.710245	7.402446	H	7.603626	4.740386	3.043759
C	10.545089	9.297452	6.801143				

IM2c: Sum of electronic and thermal enthalpies = -1701.825010



C	-1.080683	1.770361	-0.995580	C	6.030924	-3.446784	2.716188
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C	-2.030116	2.635606	-1.511196	H	-3.387424	2.951543	-3.154649
O	0.210278	-0.093769	-0.971678	H	-2.288435	3.548674	-0.984014
B	0.537513	0.753242	0.221680	H	3.180892	-4.710205	1.363186
O	1.975795	1.142245	0.095178	H	5.213349	-5.436391	2.572819
C	2.929581	-0.969782	-0.987631	H	6.925038	-3.767803	3.243055
P	2.236699	-2.007908	0.531143	H	6.595523	-1.365699	2.706707
C	1.125154	-1.297386	1.800734	H	4.571642	-0.624707	1.508723
C	0.393375	-0.117565	1.579468	H	3.207525	-4.034059	-1.340958
C	-0.457354	0.289238	2.616884	H	2.072246	-5.843560	-2.583999
C	-0.572156	-0.431311	3.802902	H	-0.362801	-6.225490	-2.281046
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C	1.026371	-2.036881	2.990926	H	-0.536750	-2.963671	0.512118
O	-0.383023	1.891807	0.158264	H	1.616713	-2.936588	3.141664
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C	0.134503	-5.432617	-1.729666	H	2.127562	-0.532455	-1.596921
C	1.503046	-5.220416	-1.900569	B	2.675646	2.064076	0.752393
C	2.143172	-4.202280	-1.199764	O	2.182438	3.100080	1.555391
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C	5.071580	-4.385120	2.339679	C	4.441404	3.144541	1.518869

C	3.353837	4.864091	2.844825	H	4.727672	6.209093	3.809845
C	5.706998	3.608418	1.824090	H	6.758911	5.126762	2.927817
C	5.783442	4.728635	2.664020	H	6.594044	3.126909	1.425738
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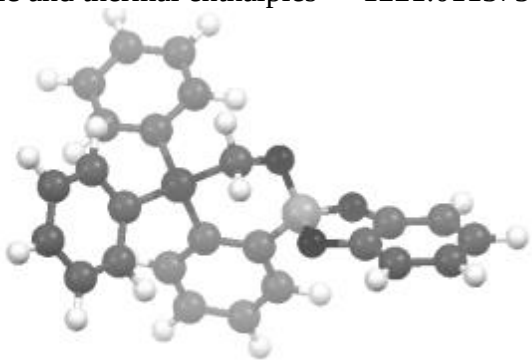
IM3 : Sum of electronic and thermal enthalpies = -1221.011375



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C	-0.807320	1.724707	-2.201640	O	4.075397	-0.731990	2.339381
C	-1.348149	2.846398	-2.823966	H	6.096428	3.071703	1.330842
C	-1.483612	4.041543	-2.117262	H	8.294436	2.301050	2.254868
C	-1.074819	4.117264	-0.786702	H	8.519482	0.044799	3.235440
P	0.447476	0.378653	-0.090792	H	6.552706	-1.506831	3.319046
C	-0.373215	-1.173855	-0.598384	H	-2.337666	-0.318073	-0.900362
C	-1.737242	-1.223089	-0.909477	H	-3.382485	-2.480816	-1.485154
C	-2.324729	-2.442073	-1.241358	H	-2.018916	-4.554735	-1.518857
C	-1.557296	-3.606151	-1.259589	H	0.396590	-4.463292	-0.949690
C	-0.200185	-3.556008	-0.941571	H	1.451259	-2.299811	-0.335611
C	0.398834	-2.344582	-0.605263	H	-0.705198	0.796247	-2.756369
C	0.490383	0.517078	1.717134	H	-1.662024	2.786755	-3.861962
C	1.735001	0.350497	2.352787	H	-1.905818	4.915002	-2.605794
C	1.712537	0.406470	3.756328	H	-1.175289	5.048075	-0.236466
C	0.537320	0.611196	4.471738	H	-0.210829	3.060451	0.880196
C	-0.682154	0.767484	3.805614	H	-1.653818	0.821784	1.888729
C	-0.710377	0.712886	2.418880	H	-1.600991	0.922836	4.363855
B	3.157679	0.119803	1.580532	H	0.563793	0.642354	5.558222
O	3.860690	1.421823	1.392982	H	2.650813	0.267676	4.286062
C	5.131006	1.211494	1.815796	C	2.252054	0.308892	-0.628246
C	6.206242	2.081444	1.763032	O	2.918949	-0.514946	0.236663
C	7.433833	1.637979	2.285325	H	2.262408	-0.073996	-1.657301
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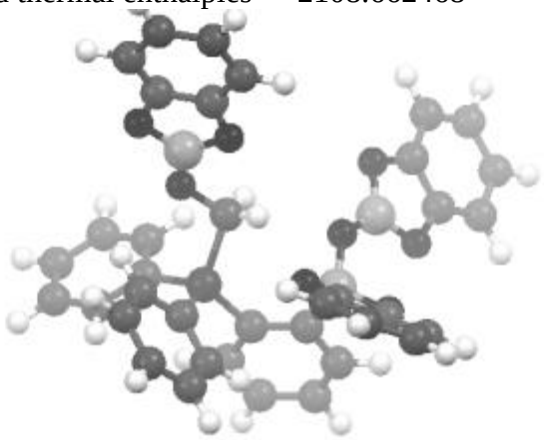
IM3c: Sum of electronic and thermal enthalpies = -2108.662468



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C	0.268651	0.439997	-0.999842	H	-4.194548	-1.638229	0.410081
C	-0.421825	0.215364	-2.199622	H	-3.992155	-3.970922	1.237300
C	-0.754100	1.296571	-3.012037	H	-1.746112	-4.989847	1.533745
C	-0.404943	2.592202	-2.630772	H	0.281420	-3.694211	1.013564
C	0.279791	2.811082	-1.436432	H	-0.701183	-0.791006	-2.494100
P	0.726333	-0.973336	0.060053	H	-1.285664	1.124293	-3.943318
C	-0.807235	-1.925884	0.397341	H	-0.665156	3.432660	-3.267973
C	-2.071629	-1.350862	0.234248	H	0.561169	3.817733	-1.143219
C	-3.214822	-2.088769	0.539053	H	1.172631	1.903462	0.301584
C	-3.100023	-3.396839	1.004071	H	-0.578772	-0.612824	2.544032
C	-1.839312	-3.970532	1.171202	H	0.124432	0.172946	4.767957
C	-0.694296	-3.239002	0.872334	H	2.510773	0.775392	5.166079
C	1.406617	-0.447332	1.675604	H	4.154668	0.595739	3.320929
C	2.764209	-0.114157	1.865706	O	4.313533	-1.647526	0.585540
C	3.116390	0.326390	3.151548	B	5.065843	-2.416107	1.361521
C	2.191383	0.430717	4.185691	O	5.272520	-3.783241	1.087482
C	0.855146	0.095058	3.968135	O	5.723122	-2.051220	2.549144
C	0.459688	-0.346259	2.712002	C	6.335373	-3.191450	2.990140
B	3.931682	-0.230338	0.735200	C	6.063106	-4.239605	2.105531
O	3.419773	0.250841	-0.589046	C	6.561320	-5.512852	2.309565
C	4.245436	1.256600	-0.979707	C	7.354644	-5.707842	3.449436
C	4.194996	2.002103	-2.143800	C	7.626408	-4.661582	4.332175
C	5.165957	3.003696	-2.320288	C	7.116992	-3.373096	4.115641
C	6.142591	3.230628	-1.354798	H	6.346540	-6.317970	1.614544
C	6.189221	2.468063	-0.175610	H	7.324225	-2.551366	4.793073
C	5.229823	1.484452	-0.003063	H	8.246388	-4.845516	5.204885
O	5.078839	0.645287	1.044144	H	7.766496	-6.693650	3.645378
H	3.432648	1.811686	-2.893106	C	1.795622	-2.160321	-0.918740
H	5.151616	3.604291	-3.225822	O	0.973987	-2.707930	-1.931309
H	6.884616	4.008835	-1.512346	B	1.456311	-2.861976	-3.190245
H	6.948991	2.635249	0.581571	O	0.654998	-3.333989	-4.219517

O	2.747132	-2.576730	-3.603733	H	4.767942	-2.422123	-5.547427
C	2.751044	-2.882502	-4.947225	H	4.297302	-3.106017	-7.914117
C	1.486772	-3.342076	-5.318063	H	2.066777	-3.919407	-8.571399
C	1.199528	-3.725568	-6.613823	H	0.213965	-4.083130	-6.891816
C	2.246097	-3.628434	-7.540769	H	2.154659	-2.935617	-0.237259
C	3.510752	-3.167566	-7.168200	H	2.650811	-1.598568	-1.298743
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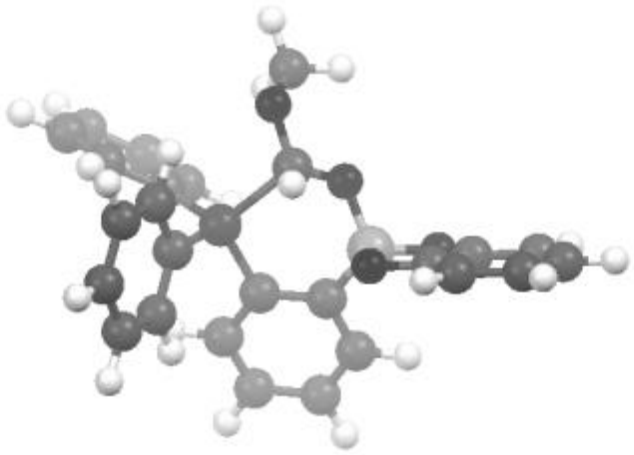
IM2mf: Sum of electronic and thermal enthalpies = **-1335.4579**



C	4.780956	-0.865883	-0.056592	C	-4.519536	-1.675612	-1.127031
C	4.526052	0.438460	-0.511340	C	-3.515226	-2.251364	-0.348097
C	5.549408	1.262260	-0.945380	C	-2.293120	-1.603791	-0.190426
C	6.856694	0.746711	-0.920443	C	-0.593204	2.196172	-1.020003
C	7.109228	-0.547004	-0.472394	C	-0.614779	3.162810	-0.009007
C	6.065757	-1.378263	-0.030321	C	-0.712536	4.511518	-0.344050
O	3.199326	0.716658	-0.432154	C	-0.784021	4.899659	-1.681443
B	2.552428	-0.549185	-0.007938	C	-0.749198	3.938945	-2.691454
O	1.792464	-1.136227	-1.202107	C	-0.647361	2.588034	-2.366051
C	1.076389	-0.271289	-1.900476	H	5.340870	2.270123	-1.291521
O	0.527171	-0.738956	-3.065444	H	7.680051	1.370776	-1.257386
O	3.631268	-1.469459	0.338416	H	8.128259	-0.924348	-0.462805
C	1.499581	-0.312564	1.208413	H	6.251710	-2.388465	0.321412
C	0.172054	0.131244	1.043950	H	-2.921023	1.170816	-2.071434
C	-0.699646	0.326861	2.129177	H	-5.082652	0.009182	-2.347231
C	-0.244786	0.095656	3.421210	H	-5.472638	-2.182848	-1.246483
C	1.067136	-0.344453	3.616638	H	-3.683536	-3.206084	0.141811
C	1.912519	-0.547062	2.530225	H	-1.516775	-2.050696	0.423805
P	-0.417082	0.412477	-0.652471	H	-0.597806	1.842135	-3.155749
C	-2.070122	-0.368066	-0.816402	H	-0.789178	4.239938	-3.734268
C	-3.080137	0.208690	-1.594779	H	-0.855828	5.952914	-1.937421
C	-4.300695	-0.446368	-1.746469	H	-0.725099	5.260445	0.442462

H	-0.539413	2.863632	1.031836	H	1.564660	0.688965	-2.112537
H	-1.726774	0.642537	1.962164	C	0.205866	-2.128420	-3.089545
H	-0.908720	0.247280	4.267729	H	-0.184159	-2.321956	-4.089691
H	1.425656	-0.537999	4.624685	H	1.094011	-2.736277	-2.904665
H	2.924198	-0.909512	2.688925	H	-0.560898	-2.373989	-2.346589

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