Supporting Information for

Reversible O-H bond activation by an intramolecular frustrated Lewis pair

by

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1. Experimental Details

General methods

All manipulations were carried out using standard Schlenk line or dry-box techniques under an atmosphere of argon or dinitrogen. Solvents dichloromethane, *n*-hexane, methanol, 2-propanol and deionized water were degassed by sparging with argon and dried by passing through a column of the appropriate drying agent and stored over potassium (*n*-hexane) or 4 Å sieves (DCM, MeOH, 2-propanol). NMR spectra were measured in benzene-d_6 (dried over potassium), dichloromethane-d_2 (dried over CaH_2), or toluene-d_8 (dried over potassium), with the solvent then being distilled under reduced pressure and stored under argon in Teflon valve ampoules. NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. The ^{1}H, ^{13}C, ^{11}B, ^{31}P, and ^{19}F NMR spectra were recorded on Bruker Avance III HD nanobay 400 MHz or Bruker Avance III 500 MHz spectrometer at ambient temperature and referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane (δ = 0 ppm), ^{31}P resonances are referenced externally to H_3PO_4 (85 %), ^{19}F chemical shifts to CF_3COOH, and ^{11}B chemical shifts to $BF_3 \cdot Et_2O$. Chemical shifts are quoted in δ (ppm) and coupling constants in Hz. Elemental analyses were carried out by London Metropolitan University. FLPs **1a** and **1b** were prepared by literature methods,[1] and *p*-$^{t}BuC_6H_4OH$ was sublimed before use. All other reagents were used as received.

Synthesis of 2: FLP **1a** (0.106 g, 0.14 mmol) was dissolved in dichloromethane (2 mL) and H_2O (10 µL, 0.56 mmol) was added at room temperature. The colour of the solution changed from bright yellow to colourless within few hours. The mixture was stirred overnight then filtered, concentrated, and layered with *n*-hexane. Colourless crystals suitable for single-crystal X-ray diffraction studies grew overnight at room temperature to afford **2** in 38% (0.041 g) yield. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.51 (s, 6H, XAN-C(CH_3)$_2$), 6.65 (t, $^{3}J_{HH}$ = 6.0 Hz, 1H, Ar*H*), 6.73 (t, $^{3}J_{HH}$ = 7.5 Hz, 1H, Ar*H*), 7.01 (m, 12H, Ar*H*), 7.20 (dd, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.4 Hz, 1H, Ar*H*), 7.30 (dd, $^{3}J_{HH}$ = 7.5 Hz, $^{4}J_{HH}$ = 1.5 Hz, 1H, Ar*H*), and 8.10 ppm (br s, 2H, H_2O). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 30.1 (XAN-C(CH_3)$_2$), 35.0 (XAN-*C*(CH_3)$_2$), 116.8 (br), 118.5 (br), 120.3 (br), 124.3, 125.4, 128.0, 128.2, 128.4, 128.9 (d, $^{2}J_{PC}$ = 8.3 Hz), 129.6, 130.1, 131.7, 132.1 (br), 132.7 (d, $^{2}J_{PC}$ = 2.9 Hz), 133.0, 133.4 (d, $^{1}J_{PC}$ = 16.7 Hz), 134.4 (m), 137.5 (dm, $^{1}J_{CF}$ = 249 Hz), 140.2 (dm, $^{1}J_{CF}$ = 249 Hz), 148.2 (dm, $^{1}J_{CF}$ = 241 Hz), 154.6 (d, $^{1}J_{PC}$ = 14.5 Hz), and 155.1 ppm (Ar-*C*). $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6, 298 K): δ = 4.5 ppm (br s). $^{31}P\{^{1}H\}$ NMR (162 MHz, C_6D_6, 298 K): δ = -20.5 ppm (s). $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2, 298 K): δ = -133.9 (d, $^{3}J_{FF}$ = 22.9 Hz, 4F, *o*-C*F*), -155.3 (t, $^{3}J_{FF}$ = 17.7 Hz, 2F, *p*-C*F*), and -163.3 ppm (td, $^{3}J_{FF}$ = 22.0 Hz, $^{4}J_{FF}$ = 8.6 Hz, 4F, *m*-C*F*). Elemental anal. calc. for $C_{39}H_{24}BF_{10}O_2P$: C 61.93% and H 3.20%, found C 62.03% and H 3.21%.

Synthesis of 3: FLP **1a** (0.083 g, 0.11 mmol) was dissolved in dichloromethane (3 mL) and MeOH (8 µL, 0.20 mmol) was added at room temperature. The colour of the solution changed from bright yellow to colourless immediately upon addition. The mixture was stirred overnight then filtered, concentrated, and layered with *n*-hexane. Colourless crystals suitable for single-crystal X-ray diffraction studies grew overnight at room temperature to afford **3** in 36% (0.031 g) yield. ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 1.51 (s, 6H, XAN-C(CH_3)$_2$), 2.98 (s, 3H, CH_3OH), 6.62 (t, $^{3}J_{HH}$ = 6.8 Hz, 1H, Ar*H*), 6.71 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 7.02 (m, 10H, Ar*H*), 7.15 (m, 3H, Ar*H*), 7.31 (dd, $^{3}J_{HH}$ = 6.3 Hz, $^{4}J_{HH}$ = 2.7 Hz, 1H, Ar*H*), and 10.80 ppm (d, $^{3}J_{HH}$ = 16.8 Hz, 1H, CH_3OH). $^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 29.4 (XAN-C(CH_3)$_2$), 35.2 (XAN-*C*(CH_3)$_2$), 53.3 (CH_3OH), 118.3 (br), 120.2 (d, $^{2}J_{PC}$ = 9.9 Hz), 125.0, 128.0, 128.2, 128.3, 129.0 (d, $^{2}J_{PC}$ = 8.5 Hz), 129.5, 130.1, 131.8, 131.9 (br), 133.3 (d, $^{1}J_{PC}$ = 17.1 Hz), 134.1, 137.5 (dm, $^{1}J_{CF}$ = 248 Hz), 140.0 (dm, $^{1}J_{CF}$ = 250 Hz), 148.0 (dm, $^{1}J_{CF}$ = 240 Hz), 154.9 (d, $^{1}J_{PC}$ = 15.3 Hz), and 155.4

ppm (Ar-*C*). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 298 K): δ = 5.4 ppm (br s). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ = -19.9 ppm (s). $^{19}F\{^1H\}$ NMR (376 MHz, CD_2Cl_2, 298 K): δ = -133.0 (dd, $^3J_{FF}$ = 24.9 Hz, $^4J_{FF}$ = 6.8 Hz, 4F, *o*-C*F*), -155.9 (t, $^3J_{FF}$ = 21.4 Hz, 2F, *p*-C*F*), and -163.4 ppm (td, $^3J_{FF}$ = 22.7 Hz, $^4J_{FF}$ = 8.8 Hz, 4F, *m*-C*F*). Elemental anal. calc. for $C_{40}H_{26}BF_{10}O_2P$: C 62.36% and H 3.40%, found C 62.13% and H 3.49%.

Synthesis of 4: FLP **1a** (0.074 g, 0.10 mmol) was dissolved in dichloromethane (3 mL) and ^{i}PrOH (12 µL, 0.16 mmol) was added at room temperature. The colour of the solution changed from bright yellow to colourless immediately upon addition. The mixture was stirred overnight then filtered, concentrated, and layered with *n*-hexane. Colourless crystals suitable for single-crystal X-ray diffraction studies grew overnight at room temperature to afford **4** in 37% (0.029 g) yield. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 0.66 (d, 6H, $^3J_{HH}$ = 4.8 Hz, ^{i}Pr CH_3), 1.51 (s, 6H, XAN-C(CH_3)$_2$), 3.39 (br s, 1H, ^{i}Pr C*H*), 6.66 (t, $^3J_{HH}$ = 5.8 Hz, 1H, Ar*H*), 6.72 (t, $^3J_{HH}$ = 7.6 Hz, 1H, Ar*H*), 6.95-7.08 (m, 12H, Ar*H*), 7.19 (d, $^3J_{HH}$ = 7.4 Hz, 1H, Ar*H*), 7.27 (d, $^3J_{HH}$ = 7.9 Hz, 1H, Ar*H*) and 9.17 ppm (br, 1H, ^{i}Pr O*H*). $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 24.5 (*C*H(CH$_3$)$_2$), 30.3 (XAN-C(*C*H$_3$)$_2$), 34.9 (XAN-*C*(CH$_3$)$_2$), 65.1 (CH(*C*H$_3$)$_2$), 116.9, 119.0 (br), 120.6 (d, $^2J_{PC}$ = 7.6 Hz), 124.2, 125.2, 128.0, 128.1, 128.3, 128.9 (d, $^2J_{PC}$ = 7.5 Hz), 129.4, 129.9, 132.0, 132.5, 132.7 (d, $^2J_{PC}$ = 7.8 Hz), 132.9, 133.4 (d, $^1J_{PC}$ = 16.7 Hz), 137.4 (dm, $^1J_{CF}$ = 247 Hz), 140.1 (dm, $^1J_{CF}$ = 249 Hz), 148.3 (dm, $^1J_{CF}$ = 241 Hz), 154.5 (d, $^1J_{PC}$ = 16.0 Hz), and 155.0 ppm (Ar-*C*). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 298 K): δ = 3.7 ppm (br s). $^{31}P\{^1H\}$ NMR (162 MHz, C_6D_6, 298 K): δ = -20.7 ppm (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, 298 K): δ = -133.7 (d, $^3J_{FF}$ = 14.1 Hz, 4F, *o*-C*F*), -155.8 (t, $^3J_{FF}$ = 20.6 Hz, 2F, *p*-C*F*), and -163.5 ppm (m, 4F, *m*-C*F*). Elemental anal. calc. for $C_{42}H_{30}BF_{10}O_2P$: C 63.18% and H 3.79%, found C 63.17% and H 3.46%.

Synthesis of 5a: FLP **1a** (0.079 g, 0.11 mmol) and *p*-^{t}BuC$_6$H$_4$OH (0.056 g, 0.37 mmol) were weighed into a Schlenk flask and dichloromethane (4 mL) was added at room temperature. The colour of the solution changed from bright yellow to colourless immediately. The mixture was stirred for 3h then filtered, concentrated, and layered with *n*-hexane. Colourless crystals suitable for single-crystal X-ray diffraction studies grew overnight at room temperature to afford **5a** in 27% (0.026 g) yield. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 1.11 (s, 9H, tBu-CH_3), 1.39 (s, 6H, XAN-C(CH_3)$_2$), 6.34-6.40 (m, 1H, Ar*H*), 6.51 (td, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, Ar*H*), 6.82-6.84 (m, 2H, Ar*H*), 6.90-6.93 (m, 8H, Ar*H*), 6.98-7.05 (m, 4H, Ar*H*), 7.13 (dd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 1.3 Hz, 1H, Ar*H*), 7.18-7.23 (m, 2H, Ar*H*), 7.60 (d, $^3J_{HH}$ = 6.6 Hz, 1H, Ar*H*), and 9.69 ppm (br s, 1H, O*H*). $^{13}C\{^1H\}$ NMR (101 MHz, C_6D_6, 298 K): δ = 30.5 (XAN-C(*C*H$_3$)$_2$), 31.7 (C(*C*H$_3$)$_3$), 33.9 (*C*(CH$_3$)$_3$), 35.0 (XAN-*C*(CH$_3$)$_2$), 118.7, 123.9 (d, $^2J_{PC}$ = 9.6 Hz), 124.6, 125.3, 126.1, 127.9, 128.2, 129.7 (d, $^1J_{PC}$ = 11.6 Hz), 131.3 (d, $^2J_{PC}$ = 5.1 Hz), 131.3, 133.2, 133.8 (d, $^1J_{PC}$ = 13.3 Hz), 134.2 (d, $^2J_{PC}$ = 4.4 Hz), 135.2, 136.1 (br), 138.8 (br), 141.2, 147.4 (br), 149.8 (br), 155.1, 155.6 (d, $^2J_{P\text{-}C}$ = 6.8 Hz), and 157.6 ppm (Ar-*C*). $^{11}B\{^1H\}$ NMR (128 MHz, C_6D_6, 298 K): δ = 1.3 ppm (s). ^{31}P NMR (162 MHz, C_6D_6, 298 K): δ = -13.0 ppm (s). $^{19}F\{^1H\}$ NMR (376 MHz, C_6D_6, 298 K): δ = -130.1 (d, $^3J_{FF}$ = 25.9 Hz, 4F, *o*-C*F*), -158.0 (br s, 2F, *p*-C*F*), and -164.5 ppm (m, 4F, *m*-C*F*). Elemental anal. calc. for $C_{49}H_{36}BF_{10}O_2P$+CH_2Cl_2: C 61.69% and H 3.93%, found C 61.75% and H 4.13%.

Synthesis of 5b: FLP **1b** (0.174 g, 0.21 mmol) and *p*-^{t}BuC$_6$H$_4$OH (0.089 g, 0.59 mmol) were weighed into a Schlenk flask and dichloromethane (4 mL) was added at room temperature. The colour of the solution changed from bright yellow to colourless immediately. The mixture was stirred for 3h then filtered, concentrated, and layered with *n*-hexane. Colourless crystals suitable for single-crystal X-ray diffraction studies grew overnight at room temperature to afford **5b** in 34% (0.070 g) yield. ^1H NMR (400 MHz, C_6D_6, 298 K): δ = 1.18 (s, 9H, tBu-CH_3), 1.50 (s, 6H, XAN-C(CH_3)$_2$), 1.70 (br, 12H, *o*-CH_3 of Mes), 1.95 (s, 6H, *p*-CH_3 of Mes), 6.47 (d, $^4J_{HH}$ = 4.4 Hz, 4H, *m*-Mes*H*), 6.57-6.62 (m, 1H, Ar*H*), 6.99-7.05 (m, 4H, Ar*H*), 7.25-7.31 (m, 4H, Ar*H*), 7.66 (d, $^3J_{HH}$ = 6.8 Hz, 1H, Ar*H*), and 9.74 ppm (d, $^1J_{PH}$ = 542 Hz, 1H, P*H*).

$^{13}C\{^{1}H\}$ NMR (126 MHz, C_6D_6, 298 K): δ = 21.0 (Mes-*C*H_3), 21.1 (Mes-*C*H_3), 31.8 (C(*C*H_3)$_3$), 33.9 (*C*$(CH_3)_3$), 34.9 (XAN-*C*$(CH_3)_2$), 120.5, 123.4, 123.8 (d, $^{1}J_{PC}$ = 13.3 Hz), 125.0, 126.1, 126.4, 127.5, 128.0, 128.2, 128.4, 131.7 (d, $^{1}J_{PC}$ = 13.2 Hz), 133.3 (br), 135.4 (d, $^{2}J_{PC}$ = 5.7 Hz), 135.8, 137.9 (br), 140.1 (br), 143.8, 145.6, 147.6 (br), 149.4 (br), 155.9, 156.1 (d, $^{2}J_{PC}$ = 1.9 Hz), and 161.4 ppm (Ar-*C*). $^{11}B\{^{1}H\}$ NMR (128 MHz, C_6D_6, 298 K): δ = 0.3 ppm (s). ^{31}P NMR (162 MHz, C_6D_6, 298 K): δ = -27.3 ppm (d, $^{1}J_{PH}$ = 542 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, C_6D_6, 298 K): δ = -129.6 (br s, 4F, *o*-C*F*), -161.3 (br s, 2F, *p*-C*F*), and -165.5 ppm (br s, 4F, *m*-C*F*). Elemental anal. calc. for : C 67.91% and H 4.97%, found C 67.91% and H 5.16%.

2. Variable temperature NMR spectroscopic measurements

A J. Young's NMR tube was charged with **5a** (ca. 20 mg) and 0.5 ml of CD_2Cl_2. The sample was inserted into NMR spectrometer and cooled to 257 K and the changes were followed by ^1H and proton coupled ^{31}P NMR (Figures S1 and S2).

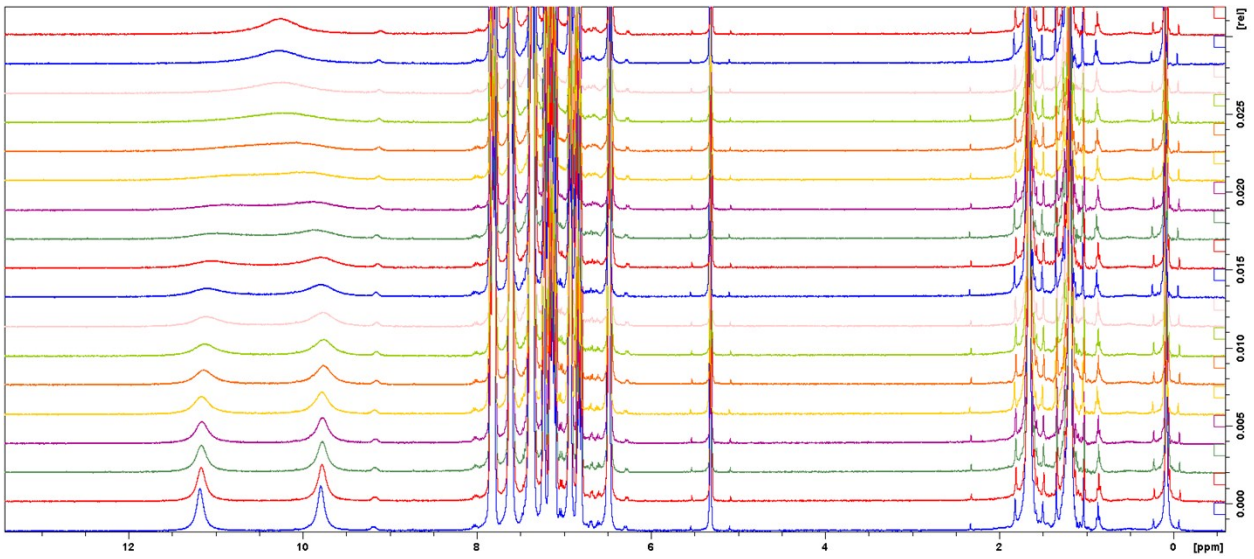

Figure S1. ^1H NMR spectra of **5a** (CD_2Cl_2) in different temperatures (257 K (bottom) to 293 K (top)).

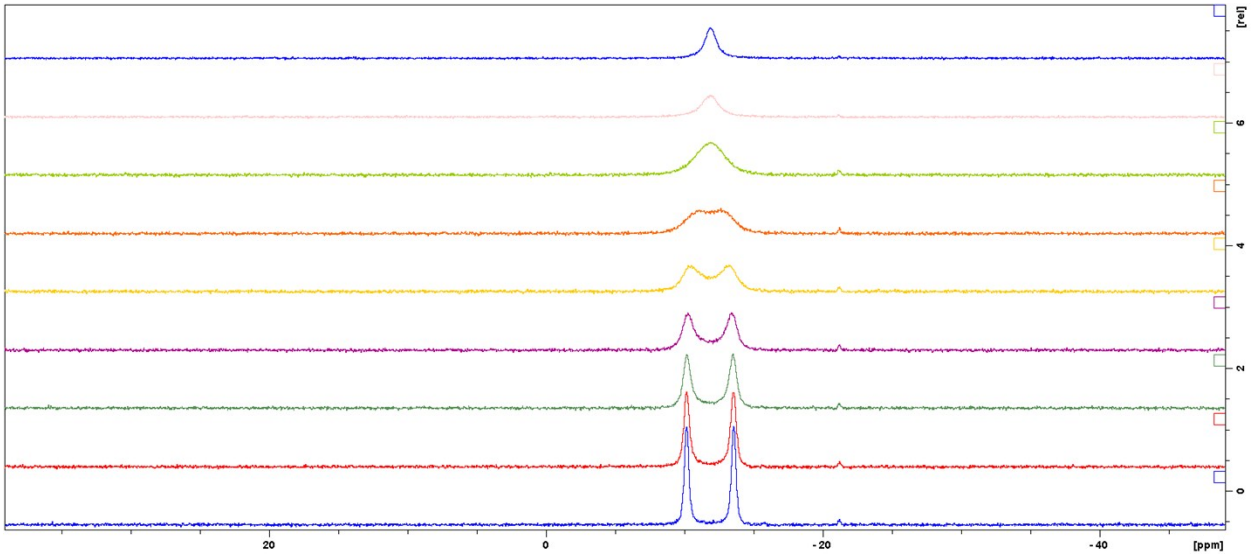

Figure S2. ^{31}P NMR spectra of **5a** (CD_2Cl_2) in different temperatures (257 K (bottom) to 293 K (top)).

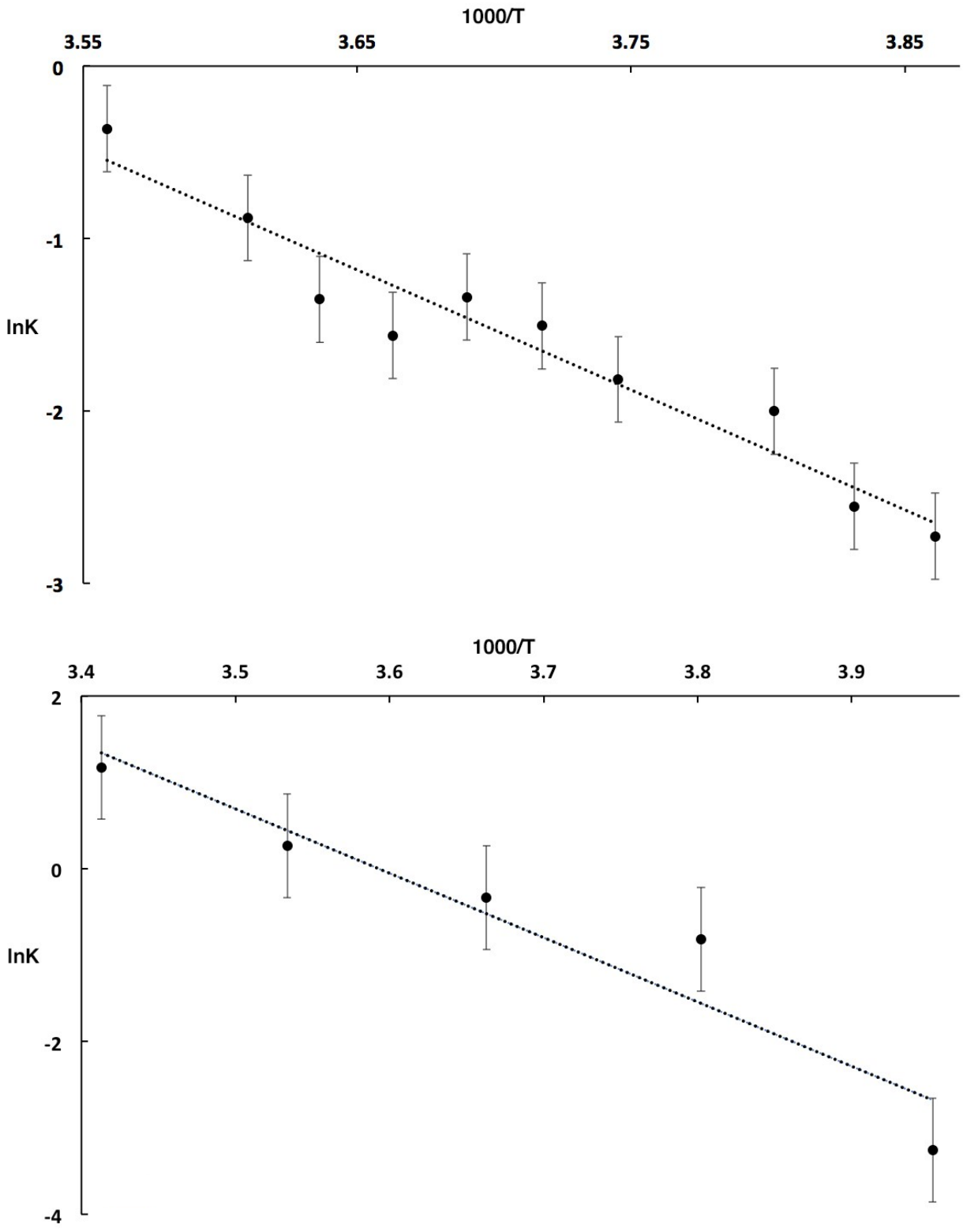

Figure S3. Van't Hoff plots for **5a** in dichloromethane-d_2 (upper) and toluene-d_8 (lower). Least squares linear fits given by $\ln K = -6963/T + 24.23$ ($R^2 = 0.93$) and $\ln K = -7449/T + 26.76$ ($R^2 = 0.91$), respectively.

3. X-ray crystallographic details

Single-crystal X-ray diffraction data for **2**–**5a** were collected at 150 K and **5b** at 100 K on Oxford Diffraction/Agilent SuperNova diffractometers with Cu-Kα (λ = 1.54184 Å) radiation equipped with nitrogen gas Oxford Cryosystems Cryostream unit.[2] Raw frame data were reduced using CrysAlisPro.[3] The structures were solved using SHELXT[4] and refined to convergence on F^2 and against all independent reflections by full-matrix least-squares using SHELXL[5] in combination with the SHELXLE[6] program. Distances and angles were calculated using the full covariance matrix. Selected crystallographic data are summarized in the tables S1 and full details are given in the supplementary deposited CIF files (CCDC 1872780-84). These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Selected crystallographic and refinement data for **2**–**4**, **5a**–**b**.

	2	**3**	**4**	**5a**	**5b**
Formula	$C_{79}H_{50}B_2Cl_2F_{20}O_4P_2$	$C_{40}H_{26}BF_{10}O_2P$	$C_{97}H_{90}B_2Cl_2F_{20}O_4P_2$	$C_{50}H_{38}BCl_2F_{10}O_2P$	$C_{56.20}H_{50.40}BCl_{2.40}F_{10}O_2P$
Fw	1597.65	770.39	1854.14	973.48	1074.62
Cryst. System	Triclinic	Triclinic	Triclinic	Triclinic	Orthorhombic
Space Group	P -1	P -1	P -1	P -1	P b c a
Wavelength/Å	1.54184	1.54184	1.54184	1.54184	1.54184
a/Å	9.0947(3)	11.3306(2)	11.6371(3)	12.3598(4)	20.681(4)
b/Å	13.8820(3)	12.8470(3)	12.5041(3)	13.0701(3)	20.544(4)
c/Å	15.1063(5)	12.9284(3)	17.1917(3)	16.0255(4)	25.330(5)
α/°	65.599(3)	100.460(2)	73.1039(19)	68.699(2)	90
β/°	83.197(2)	109.362(2)	88.8298(17)	86.559(2)	90
γ/°	87.446(2)	96.080(2)	67.407(2)	68.714(3)	90
Volume/Å^3	1724.60(10)	1717.76(7)	2198.10(9)	2239.71(12)	10762(4)
Z	1	2	1	2	8
Temp./K	150(2)	150(2)	150(2)	150(2)	100(2)
Refls. Collect.	23570	39196	44151	27591	180306
$2\theta_{max}$	152.32	152.32	152.23	148.99	156.00
R_{int}	0.0183	0.0373	0.0424	0.0255	0.1260
Goodness of fit	1.033	1.041	1.033	1.026	1.048
$R[F^2>2\sigma]$, F	0.0401	0.0332	0.0648	0.0338	0.0800
R_w (all data), F^2	0.1096	0.0888	0.2010	0.0909	0.2399

4. Computational details and xyz-coordinates of the optimized structures

All computational work reported here utilized the density functional theory (DFT) level with Gaussian09 (Revision D.01) program package.[7] Geometry optimizations were performed with the PBE1PBE exchange-correlation functional using def-TZVP basis sets.[8] Solvent effects were treated with the polarizable continuum model (PCM, dichloromethane).[9] The nature of all stationary points found (minimum or saddle point) was confirmed by full frequency calculations.

xyz-coordinates of the optimized structures:

5a (adduct, dichloromethane)

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C	1.195276	2.385656	-1.671307
C	0.700606	1.944554	-0.455971
C	1.171821	2.459264	0.732706
C	2.158890	3.438643	0.691852
C	2.690601	3.898334	-0.507835
C	2.180216	3.354166	-1.689379
O	-0.217144	0.882989	-0.508549
B	-1.590226	0.591417	0.287790
C	-1.958012	-0.899775	-0.273041
C	-2.295408	-1.994706	0.512480
C	-2.664439	-3.221719	-0.017324
C	-2.734361	-3.385595	-1.387684
C	-2.422713	-2.319723	-2.211287
C	-2.050516	-1.113802	-1.645137
F	-2.298683	-1.918925	1.842910
F	-2.957326	-4.242918	0.782645
F	-3.092401	-4.551990	-1.907611
F	-2.467754	-2.468552	-3.533207
F	-1.769613	-0.122402	-2.501821
C	3.795891	4.945313	-0.574403
C	5.011021	4.344584	-1.291346
C	4.236339	5.408225	0.811159
C	3.291989	6.163745	-1.356168
C	-1.274157	0.748429	1.858802
C	-1.873841	1.716989	2.659741
C	-1.515767	1.891904	3.989268
C	-0.554657	1.076022	4.563893
C	0.065232	0.080581	3.815314
C	-0.298234	-0.026989	2.479163
O	0.350194	-0.945128	1.674911
C	1.640633	-1.243107	1.989450
C	2.072433	-1.227365	3.311687
C	1.035836	-0.942720	4.383012

C	3.406074	-1.534231	3.550872
C	4.265647	-1.866686	2.511278
C	3.807357	-1.882982	1.203820
C	2.483043	-1.559819	0.926775
P	1.792150	-1.415851	-0.762722
C	1.141678	-3.083920	-1.135533
C	0.704358	-3.346848	-2.434497
C	0.166086	-4.582450	-2.753970
C	0.031351	-5.557218	-1.773191
C	0.443597	-5.292721	-0.475937
C	1.002758	-4.062431	-0.156803
C	0.249560	-2.243549	4.641931
C	1.673589	-0.481148	5.685732
C	3.308664	-1.272727	-1.780633
C	3.881645	-0.005676	-1.890334
C	5.052240	0.171386	-2.610689
C	5.653122	-0.911985	-3.238800
C	5.082942	-2.173227	-3.137615
C	3.916137	-2.356865	-2.408040
C	-2.784501	1.582333	-0.206664
C	-4.055802	1.320946	0.297822
C	-5.186368	2.038572	-0.050230
C	-5.072835	3.080619	-0.954670
C	-3.833288	3.374273	-1.490170
C	-2.725558	2.628102	-1.113129
F	-4.229122	0.320655	1.167870
F	-6.371892	1.740175	0.471189
F	-6.140768	3.785792	-1.303944
F	-3.710909	4.368556	-2.364912
F	-1.571811	2.977863	-1.688910
H	4.481266	-2.121697	0.389554
H	5.300501	-2.108351	2.723636
H	3.783841	-1.522894	4.565810
H	-0.294194	1.209244	5.606514
H	-1.992518	2.663709	4.582641
H	-2.626731	2.365677	2.227013
H	0.921633	-3.024024	5.008384
H	-0.234710	-2.599467	3.730933
H	-0.527815	-2.066968	5.389106
H	0.909235	-0.300488	6.442915
H	2.253226	0.434819	5.550955
H	2.331495	-1.254428	6.086132
H	3.408930	0.845084	-1.410978
H	5.490841	1.160193	-2.687418
H	6.564320	-0.772655	-3.809577
H	5.549262	-3.021448	-3.626273
H	3.477260	-3.344609	-2.327032

H	0.785141	-2.582349	-3.201075
H	-0.173099	-4.775708	-3.765076
H	-0.409213	-6.516299	-2.019112
H	0.329541	-6.045942	0.295299
H	1.333252	-3.864632	0.856329
H	0.786426	2.109309	1.679323
H	2.520387	3.830790	1.633255
H	2.558518	3.687832	-2.648859
H	0.797009	1.967699	-2.587375
H	4.633580	4.582256	1.406709
H	3.414659	5.869840	1.364409
H	5.027637	6.154865	0.711305
H	2.421705	6.606905	-0.866286
H	3.002794	5.898820	-2.375230
H	4.075377	6.924360	-1.416869
H	5.817871	5.080335	-1.348861
H	4.766309	4.037583	-2.310609
H	5.384248	3.468936	-0.753596
H	0.331969	0.031260	-0.652728

TS-5a (dichloromethane)

99

scf done: -3401.497378

C	1.437893	2.233655	-1.461237
C	0.750406	1.878540	-0.305426
C	0.933360	2.623526	0.847939
C	1.788366	3.722260	0.830542
C	2.490147	4.096969	-0.311301
C	2.292140	3.321098	-1.456973
O	-0.049570	0.754772	-0.375942
B	-1.410867	0.504952	0.343055
C	-1.944739	-0.904954	-0.333458
C	-2.413794	-2.018760	0.352139
C	-2.938994	-3.138714	-0.275778
C	-3.035771	-3.173330	-1.652808
C	-2.602807	-2.081976	-2.381185
C	-2.076482	-0.988155	-1.716804
F	-2.399583	-2.073136	1.687275
F	-3.358454	-4.182535	0.440054
F	-3.531264	-4.241729	-2.268741
F	-2.685965	-2.098587	-3.711852
F	-1.694802	0.035154	-2.494514
C	3.444896	5.287682	-0.350812
C	4.852841	4.797264	-0.714489
C	3.521703	6.010855	0.992489
C	2.970131	6.289719	-1.411172
C	-1.161393	0.489995	1.955323

C	-1.747870	1.392865	2.842818
C	-1.440141	1.405547	4.196651
C	-0.537872	0.489710	4.716264
C	0.069691	-0.445755	3.884891
C	-0.248356	-0.390613	2.531230
O	0.374922	-1.271721	1.663470
C	1.642862	-1.640714	1.979015
C	2.038869	-1.786342	3.305148
C	0.988377	-1.557230	4.378735
C	3.351360	-2.180561	3.535339
C	4.227800	-2.433706	2.485134
C	3.813918	-2.268330	1.173781
C	2.511139	-1.852754	0.911363
P	1.893695	-1.451093	-0.751942
C	1.203970	-2.978147	-1.473303
C	0.673149	-2.933091	-2.763602
C	0.164819	-4.084949	-3.344046
C	0.161866	-5.279641	-2.634040
C	0.674584	-5.322837	-1.345162
C	1.199995	-4.176137	-0.764316
C	0.152693	-2.846897	4.516002
C	1.616808	-1.232974	5.729203
C	3.402742	-1.068192	-1.714232
C	4.101163	0.101184	-1.410389
C	5.268470	0.409305	-2.090801
C	5.744190	-0.441440	-3.081693
C	5.052553	-1.605153	-3.385096
C	3.885537	-1.922658	-2.701842
C	-2.584937	1.598508	-0.069381
C	-3.859198	1.400076	0.460137
C	-4.957082	2.192036	0.173744
C	-4.818702	3.249409	-0.705858
C	-3.584757	3.477559	-1.279969
C	-2.510729	2.655789	-0.965750
F	-4.086712	0.374054	1.292542
F	-6.142887	1.941453	0.728161
F	-5.857240	4.025176	-0.999665
F	-3.435771	4.480840	-2.145422
F	-1.375061	2.944799	-1.609101
H	4.505519	-2.434097	0.356067
H	5.243071	-2.748873	2.695059
H	3.704243	-2.301794	4.552262
H	-0.316453	0.501046	5.776437
H	-1.908393	2.131802	4.852074
H	-2.449404	2.128208	2.464512
H	0.788820	-3.676291	4.836323
H	-0.319104	-3.117594	3.569468

H	-0.634603	-2.702819	5.260090
H	0.844628	-1.100487	6.488352
H	2.223077	-0.325242	5.688661
H	2.246609	-2.057317	6.068234
H	3.733452	0.775116	-0.644862
H	5.805188	1.319782	-1.849022
H	6.655085	-0.196043	-3.616075
H	5.421243	-2.274400	-4.154117
H	3.357916	-2.838212	-2.939750
H	0.665777	-2.003171	-3.323352
H	-0.240249	-4.046172	-4.348660
H	-0.242777	-6.177563	-3.087145
H	0.670659	-6.252574	-0.787778
H	1.609006	-4.217057	0.238596
H	0.415284	2.358942	1.758733
H	1.902606	4.285575	1.748469
H	2.809801	3.569917	-2.377105
H	1.279322	1.662082	-2.368672
H	3.884867	5.354178	1.787510
H	2.550502	6.411984	1.293980
H	4.216740	6.850465	0.913187
H	1.969863	6.662230	-1.175235
H	2.936418	5.840635	-2.406282
H	3.651445	7.144578	-1.453329
H	5.548039	5.641128	-0.750188
H	4.870563	4.308619	-1.691429
H	5.221023	4.083897	0.027912
H	0.747085	-0.249879	-0.589711

5a (OH-activated product, dichloromethane)

99

scf done: -3401.505932

P	2.584118	-0.830739	-0.704866
H	1.325509	-0.186308	-0.838350
F	-3.968816	-1.149394	1.287429
F	-6.498003	-0.633639	0.688398
F	-7.119113	1.292805	-1.131625
F	-5.120302	2.683191	-2.335208
F	-2.600648	2.196591	-1.770422
F	-1.393580	-2.596708	1.785178
F	-1.412009	-5.001706	0.715744
F	-1.589841	-5.330583	-1.975140
F	-1.726800	-3.144551	-3.584502
F	-1.704741	-0.708573	-2.550093
O	0.851724	-0.705045	1.641108
O	-0.522840	0.779482	-0.562051
C	2.145448	-0.613356	2.016571

C	3.108748	-0.658901	1.004070
C	4.462928	-0.575639	1.323491
H	5.209508	-0.602567	0.538360
C	4.842036	-0.432978	2.644589
H	5.890946	-0.355250	2.902959
C	3.873680	-0.391369	3.641196
H	4.192852	-0.288343	4.670881
C	2.518175	-0.494681	3.354830
C	1.427151	-0.590027	4.403659
C	0.161632	0.022950	3.821129
C	-0.804100	0.644709	4.606045
H	-0.631231	0.793117	5.664414
C	-1.999754	1.059220	4.044830
H	-2.748891	1.543144	4.662217
C	-2.240884	0.845056	2.696036
H	-3.185791	1.181247	2.283291
C	-1.309587	0.243364	1.848051
C	-0.111787	-0.124008	2.462556
C	1.154688	-2.086868	4.663981
H	2.054584	-2.574662	5.048256
H	0.844983	-2.598667	3.750494
H	0.355388	-2.195024	5.401124
C	1.843006	0.067460	5.715680
H	1.057552	-0.040528	6.464268
H	2.056735	1.130815	5.586693
H	2.727918	-0.419415	6.128840
C	3.815590	-0.043393	-1.772736
C	3.996717	1.337260	-1.677878
H	3.389929	1.929884	-1.002378
C	4.955663	1.954904	-2.463505
H	5.095355	3.027440	-2.394479
C	5.733234	1.202290	-3.336150
H	6.482190	1.690106	-3.949516
C	5.554553	-0.170871	-3.424478
H	6.162149	-0.758059	-4.102934
C	4.595721	-0.800515	-2.642904
H	4.460398	-1.873155	-2.713671
C	2.403693	-2.568445	-1.166053
C	1.851792	-2.888315	-2.407387
H	1.506150	-2.109907	-3.079364
C	1.751405	-4.217282	-2.786315
H	1.322660	-4.469545	-3.749075
C	2.187384	-5.221272	-1.929723
H	2.101319	-6.259631	-2.228636
C	2.728398	-4.900127	-0.692722
H	3.063869	-5.683576	-0.023540
C	2.841836	-3.572159	-0.306485

H	3.266033	-3.322079	0.659152
C	-3.127503	0.524806	-0.160488
C	-4.197080	-0.167916	0.400476
C	-5.527304	0.068734	0.101374
C	-5.848722	1.043765	-0.824288
C	-4.827381	1.748704	-1.428482
C	-3.506214	1.474914	-1.099759
C	-1.501347	-1.497821	-0.321867
C	-1.452795	-2.651768	0.448890
C	-1.476279	-3.933715	-0.082398
C	-1.571388	-4.108792	-1.448321
C	-1.638521	-2.993129	-2.260775
C	-1.603509	-1.731915	-1.690379
C	-0.164151	2.070412	-0.493598
C	-0.574992	2.980825	0.479643
H	-1.249319	2.667877	1.263783
C	-0.126679	4.297731	0.451809
H	-0.476748	4.961768	1.233470
C	0.735278	4.774541	-0.531238
C	1.126728	3.855585	-1.509481
H	1.783658	4.169382	-2.314826
C	0.690888	2.542989	-1.497257
H	0.985997	1.862919	-2.289804
C	1.238357	6.215479	-0.581620
C	0.704943	7.052149	0.579805
H	1.014970	6.647530	1.546980
H	-0.386455	7.113309	0.567424
H	1.094920	8.070722	0.505515
C	0.787335	6.872451	-1.892966
H	-0.303400	6.888362	-1.964885
H	1.174048	6.338863	-2.764320
H	1.148296	7.904304	-1.944680
C	2.771627	6.228858	-0.517316
H	3.143851	7.257050	-0.558222
H	3.214183	5.680370	-1.352390
H	3.126686	5.774004	0.411453
B	-1.570184	0.067969	0.236269

5b (adduct, dichloromethane)

117

scf done: -3637.161628

C	-0.218286	2.795211	-1.665271
C	-0.567485	2.248365	-0.443022
C	-0.712614	3.037553	0.676327
C	-0.514817	4.410983	0.557657
C	-0.163604	5.001778	-0.652272
C	-0.019030	4.160124	-1.760382

O	-0.729067	0.841390	-0.389472
B	-1.941462	-0.025018	0.285932
C	-1.635982	-1.543009	-0.250897
C	-1.644563	-2.691298	0.532563
C	-1.550195	-3.970774	0.007578
C	-1.455057	-4.148952	-1.358436
C	-1.454274	-3.040091	-2.182979
C	-1.544418	-1.779887	-1.620239
F	-1.771894	-2.627859	1.860595
F	-1.550219	-5.033728	0.811742
F	-1.363321	-5.369832	-1.872168
F	-1.381433	-3.194832	-3.503105
F	-1.572875	-0.754199	-2.481390
C	0.064124	6.503578	-0.804551
C	1.499908	6.751367	-1.285915
C	-0.138502	7.255685	0.509141
C	-0.921528	7.062720	-1.839137
C	-1.876653	0.255855	1.876202
C	-2.912909	0.895848	2.556195
C	-2.860917	1.142717	3.919936
C	-1.771066	0.709040	4.656298
C	-0.708007	0.059360	4.036047
C	-0.767759	-0.090496	2.652911
O	0.305877	-0.634208	1.974534
C	1.542625	-0.559019	2.554116
C	1.681301	-0.500850	3.939079
C	0.434621	-0.590404	4.800017
C	2.970218	-0.434614	4.457660
C	4.079927	-0.442186	3.626320
C	3.914038	-0.501057	2.252656
C	2.641352	-0.559844	1.690091
P	2.357100	-0.348887	-0.118494
C	2.199247	-1.954649	-1.025797
C	2.068689	-1.811529	-2.422681
C	1.949623	-2.945635	-3.221384
C	1.935197	-4.225168	-2.687503
C	2.015313	-4.342856	-1.304989
C	2.141498	-3.243700	-0.460473
C	0.089195	-2.082294	4.990142
C	0.641558	0.039600	6.174204
C	3.992730	0.367696	-0.635910
C	4.102618	1.771581	-0.552769
C	5.260465	2.399633	-0.997412
C	6.333885	1.685576	-1.514776
C	6.237951	0.301786	-1.522142
C	5.102985	-0.377877	-1.079330
C	-3.414199	0.340615	-0.350592

C	-4.492765	-0.398204	0.138204
C	-5.795311	-0.266212	-0.307990
C	-6.079170	0.635980	-1.316474
C	-5.046080	1.375563	-1.854265
C	-3.752738	1.209385	-1.377809
F	-4.296971	-1.316578	1.092680
F	-6.772042	-1.002921	0.217177
F	-7.320944	0.781086	-1.763419
F	-5.293598	2.238441	-2.838304
F	-2.826788	1.949576	-1.992653
H	4.781876	-0.477114	1.604862
H	5.076282	-0.394146	4.050491
H	3.115170	-0.383430	5.529448
H	-1.757067	0.866318	5.727522
H	-3.679849	1.654513	4.413004
H	-3.786171	1.220407	2.001850
H	0.905704	-2.594521	5.505929
H	-0.078305	-2.576242	4.031088
H	-0.820127	-2.182026	5.588410
H	-0.256812	-0.067720	6.783537
H	0.889132	1.101108	6.102215
H	1.441439	-0.468203	6.714966
H	5.325535	3.481535	-0.925518
H	7.086450	-0.283717	-1.864839
H	1.857321	-2.815288	-4.295763
H	1.978724	-5.332466	-0.858289
H	-0.974923	2.600925	1.629869
H	-0.634199	5.017285	1.446290
H	0.251238	4.573390	-2.725423
H	-0.125162	2.156469	-2.534859
H	0.559436	6.921522	1.281332
H	-1.156573	7.142407	0.890884
H	0.035620	8.321965	0.345917
H	-1.954788	6.901110	-1.521205
H	-0.791754	6.594688	-2.817383
H	-0.766027	8.138493	-1.959576
H	1.674654	7.824398	-1.404635
H	1.693809	6.273173	-2.248538
H	2.225178	6.366372	-0.564138
H	0.172373	0.418707	-0.256951
C	5.183305	-1.878409	-1.064660
H	4.760274	-2.301172	-0.152726
H	4.650370	-2.330626	-1.903884
H	6.228028	-2.187553	-1.125782
C	7.552611	2.384404	-2.036665
H	7.411513	2.677257	-3.082031
H	7.763506	3.294168	-1.470796

H	8.431268	1.738287	-1.993608
C	3.027462	2.625330	0.050981
H	3.353930	3.665007	0.101348
H	2.103740	2.590638	-0.528021
H	2.783206	2.303056	1.067094
C	2.223638	-3.521310	1.012395
H	3.151678	-3.150026	1.451421
H	1.402053	-3.055505	1.559822
H	2.174250	-4.596255	1.190801
C	1.841079	-5.437244	-3.564460
H	2.828992	-5.882817	-3.718911
H	1.205523	-6.203478	-3.115742
H	1.436062	-5.185783	-4.546206
C	2.092323	-0.476732	-3.111310
H	1.674321	-0.560582	-4.115380
H	1.519169	0.276687	-2.564675
H	3.111670	-0.090882	-3.201727

5b (OH-activated product, dichloromethane)

117

scf done: -3637.173194

P	2.611099	-0.550228	-0.072281
H	1.493860	0.275041	-0.309702
F	-4.297015	-1.274789	1.119117
F	-6.810669	-0.941487	0.366575
F	-7.458876	0.935944	-1.495139
F	-5.493877	2.469355	-2.578665
F	-2.988473	2.164637	-1.861431
F	-1.721634	-2.591573	1.736582
F	-1.545012	-4.968993	0.633135
F	-1.534165	-5.259162	-2.068312
F	-1.691381	-3.052714	-3.649772
F	-1.857841	-0.641181	-2.582338
O	0.396982	-0.647833	1.916157
O	-0.874401	0.881544	-0.519049
C	1.602815	-0.652577	2.530785
C	2.745199	-0.657665	1.721944
C	4.012777	-0.644870	2.301031
H	4.893724	-0.618877	1.669818
C	4.142054	-0.634419	3.675093
H	5.124657	-0.616984	4.130308
C	3.002535	-0.641807	4.468600
H	3.117867	-0.639998	5.545073
C	1.725894	-0.662015	3.921845
C	0.462231	-0.785492	4.745897
C	-0.649658	-0.064373	4.000878
C	-1.704062	0.556708	4.661469

H	-1.691983	0.643297	5.740334
C	-2.784005	1.044558	3.947993
H	-3.602238	1.534095	4.465066
C	-2.828629	0.873526	2.573814
H	-3.699138	1.237686	2.040180
C	-1.800226	0.271501	1.844162
C	-0.697794	-0.123820	2.607341
C	0.091569	-2.282259	4.821829
H	0.887120	-2.843249	5.319769
H	-0.063000	-2.704762	3.827399
H	-0.833144	-2.405933	5.390800
C	0.652335	-0.261860	6.166068
H	-0.260847	-0.395536	6.746763
H	0.921495	0.796698	6.178339
H	1.428953	-0.826021	6.684824
C	4.080612	0.343539	-0.672200
C	4.106592	1.731623	-0.412792
C	5.180146	2.474301	-0.886146
H	5.199635	3.540686	-0.684634
C	6.226243	1.894038	-1.592776
C	6.196296	0.519638	-1.790433
H	7.024046	0.042226	-2.305267
C	5.150830	-0.281683	-1.341885
C	2.269281	-2.080467	-0.986311
C	1.868908	-1.893829	-2.325319
C	1.691068	-3.012744	-3.128342
H	1.390172	-2.867260	-4.160780
C	1.874747	-4.301776	-2.644962
C	2.228470	-4.454560	-1.309242
H	2.354559	-5.455374	-0.908451
C	2.438718	-3.374692	-0.459532
C	-3.484423	0.454243	-0.283080
C	-4.535757	-0.313194	0.213691
C	-5.859099	-0.171175	-0.164720
C	-6.194413	0.778734	-1.111257
C	-5.191405	1.555526	-1.653712
C	-3.876231	1.375751	-1.244828
C	-1.734881	-1.453779	-0.355075
C	-1.685543	-2.619514	0.397898
C	-1.612017	-3.891153	-0.152650
C	-1.611181	-4.047027	-1.523611
C	-1.683674	-2.921381	-2.321165
C	-1.748012	-1.670818	-1.730662
C	-0.650750	2.204917	-0.491030
C	-0.992206	3.064115	0.552946
H	-1.498973	2.678101	1.425764
C	-0.682435	4.419957	0.487325

H	-0.970312	5.040080	1.328264
C	-0.032461	4.987043	-0.604123
C	0.296468	4.116941	-1.648368
H	0.795207	4.498873	-2.533754
C	-0.001264	2.767691	-1.598627
H	0.246454	2.126006	-2.436542
C	0.312991	6.471523	-0.699011
C	-0.122690	7.245827	0.543738
H	0.367340	6.872329	1.446960
H	-1.204243	7.195708	0.694510
H	0.148077	8.298990	0.430723
C	-0.389640	7.085124	-1.917380
H	-1.475086	6.989271	-1.829088
H	-0.083696	6.598063	-2.846114
H	-0.146146	8.148785	-2.000946
C	1.829918	6.637792	-0.859524
H	2.089641	7.697565	-0.943252
H	2.197408	6.131019	-1.754915
H	2.359473	6.224995	0.003632
B	-1.918906	0.102646	0.210918
C	3.040783	2.440569	0.367789
H	3.339044	3.472402	0.551869
H	2.088091	2.472517	-0.168900
H	2.862284	1.970803	1.338063
C	5.265286	-1.758780	-1.592370
H	5.059756	-2.353194	-0.701390
H	4.580287	-2.096988	-2.372678
H	6.279566	-1.993320	-1.915773
C	7.350125	2.726274	-2.126666
H	7.103789	3.100438	-3.125389
H	7.539322	3.593012	-1.491221
H	8.270341	2.146197	-2.211651
C	2.839027	-3.675926	0.955427
H	3.801649	-3.234624	1.221449
H	2.105288	-3.307374	1.674489
H	2.923091	-4.754148	1.089736
C	1.712171	-5.491871	-3.538024
H	2.675052	-5.772553	-3.976493
H	1.340290	-6.355242	-2.984156
H	1.025205	-5.281898	-4.359060
C	1.611141	-0.538509	-2.913490
H	1.388393	-0.624919	-3.976657
H	0.750128	-0.065678	-2.431396
H	2.466782	0.134667	-2.810456

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