Supplementary Data for:

Frustrated Lewis pair (FLP)-catalyzed hydrodehalogenation of benzyl-halides

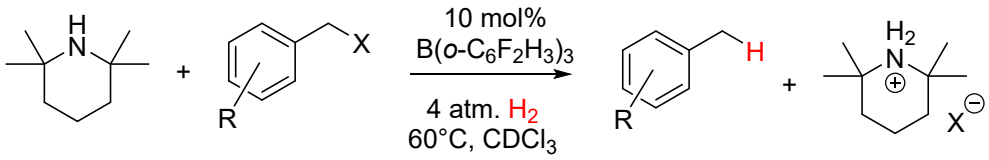
Tongtong Wang[a,b], Maotong Xu[a], Andrew R. Jupp[a], Shi-Ming Chen[a], Zheng-Wang Qu*[c], Stefan Grimme[c], and Douglas W. Stephan*[a]

General Considerations

Unless otherwise specified, all manipulations were performed under an inert atmosphere of dry, oxygen-free N_2 using Schlenk techniques or a Vacuum Atmospheres glovebox. Solvents were dried by a Grubbs type Innovative Technologies solvent purification system, degassed on Schlenk line and stored over activated 4 Å molecular sieves prior to use. Benzene-d_6 and $CDCl_3$ was purchased from Sigma-Aldrich. Benzene-d_6 was degassed on Schlenk line and stored over activated 4 Å molecular sieves prior to use. $CDCl_3$ was dried with CaH_2 and distilled prior to use. All glassware was dried in a 180 °C oven overnight prior to use. All reagents were used as received without further purifications, unless otherwise specified. B(*o*-$C_6F_2H_3)_3$ was prepared according to reported methods.[1] NMR spectra were obtained on Bruker Advance III 400 MHz, and Agilent NMR spectrometers. The ^1H and ^{13}C NMR spectra were referenced to residual solvent resonances of benzene-d_6 (^1H = 7.16 ppm; ^{13}C = 128.06 ppm) and chloroform-*d* (^1H = 7.26 ppm; ^{13}C = 77.16 ppm). Chemical shifts (δ) are reported in ppm and coupling constants are listed in hertz. Multiplicity is reported as follows: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. NMR spectra were recorded at room temperature. Abbreviation used in the SI: 2,2,6,6-tetramethylpiperidine (TMP).

Hydrodehalogenation experiments: Substrate scopes

These experiments were performed in a similar manner with varying substrates, therefore only one procedure is listed:



A solution of B(*o*-$C_6F_2H_3)_3$ (1.8 mg, 0.0051 mmol, 1 equivalent), 4-chloro-benzyl bromide (10.6 mg, 0.051 mmol, 10 equivalents), TMP (7.1 mg, 0.053 mmol, 10 equivalents) and 0.01 mL toluene (internal standard) in 0.4 mL C_6D_6 or $CDCl_3$ was transferred to a J-young tube. The J-young tube was charged with H_2 at -196°C (liquid N_2 bath). After warming up back to room temperature, the reaction was heated at 60°C. The experiments were monitored by NMR studies. The -CH_3 from toluene is found at 2.11 ppm[2] in C_6D_6 or 2.36 ppm[2] in $CDCl_3$, the integration of the -CH_3 from toluene is set to 1. The yields of the hydrodehalogenation

experiments were determined from comparing the -CH_3 integration of the produced alkane with the -CH_3 integration of the 0.01 mL toluene internal standard.

4-Chloro-benzyl bromide (C_6D_6)

Yield = 86.0%; ^{1}H NMR spectrum of 4-chloro toluene, 400 Hz: 7.05 ppm (overlapped with toluene), 6.65 ppm (d, J = 8 Hz), 1.89 ppm (s, -CH_3)

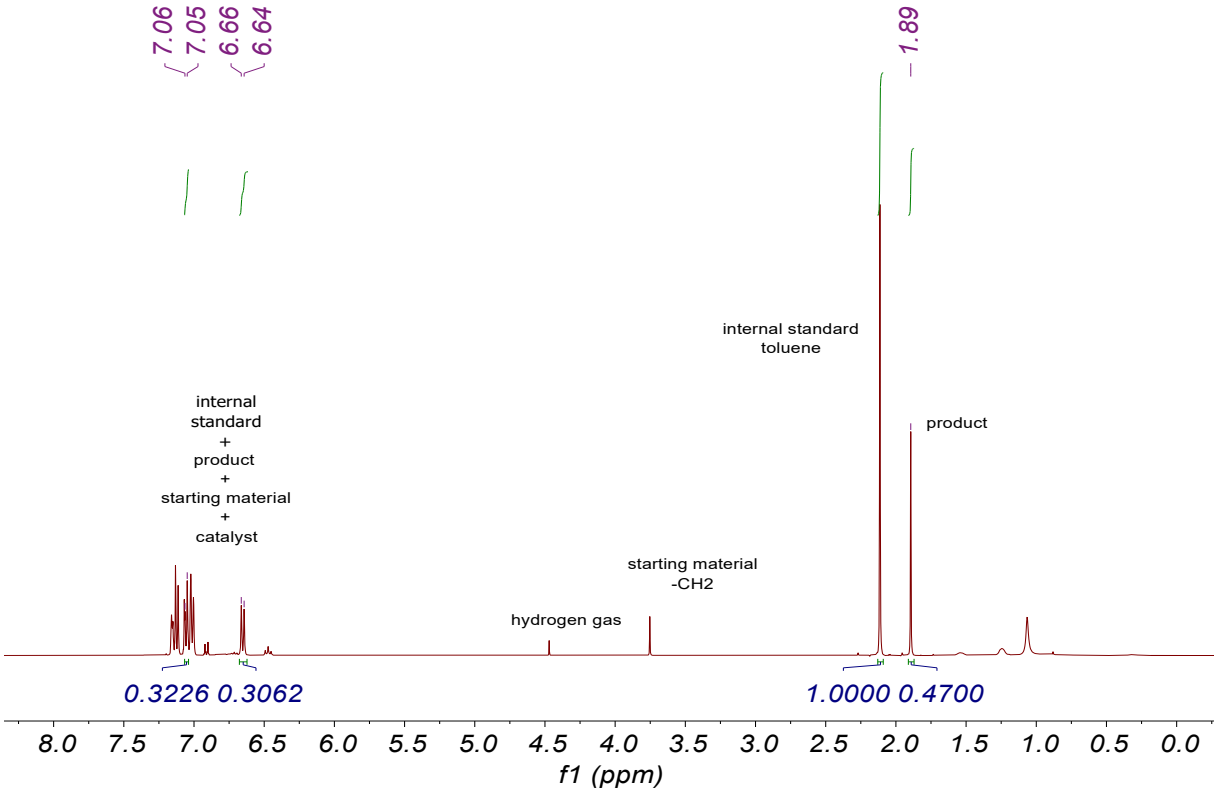


Figure S 1. ^{1}H NMR spectrum containing 4-chloro toluene

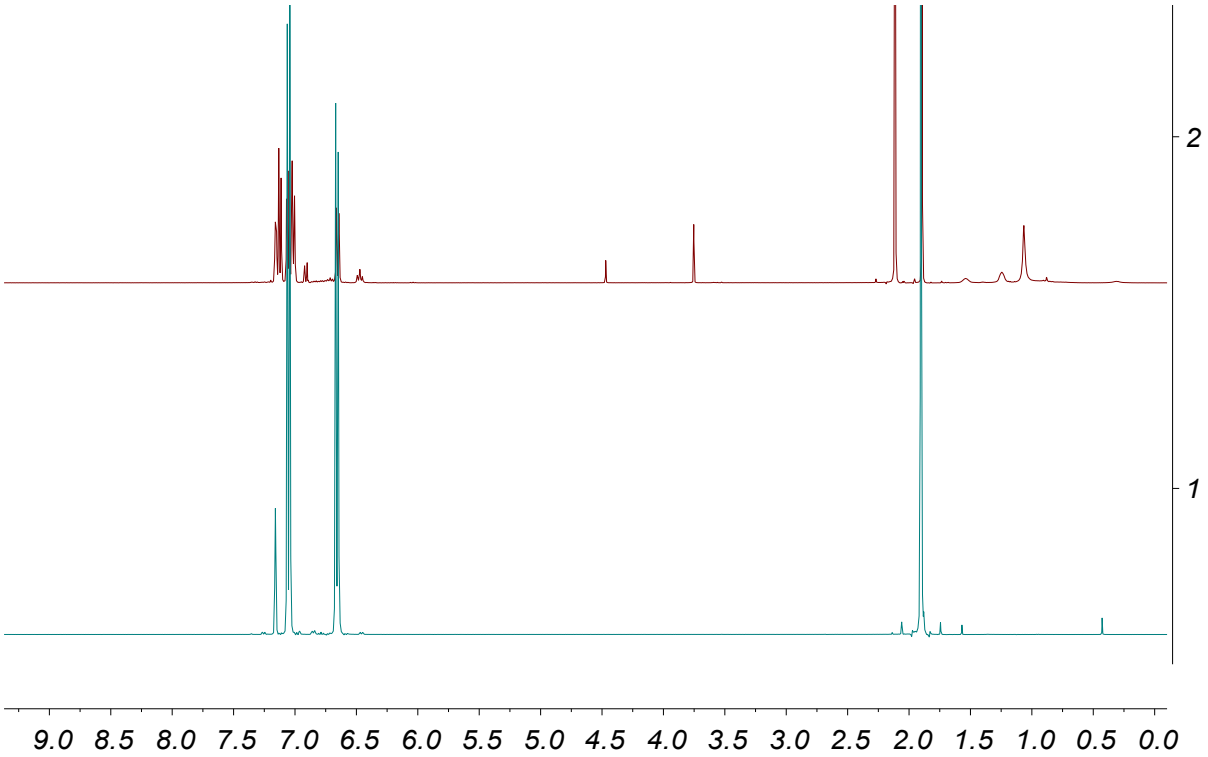


Figure S 2. [1]H NMR spectra (top: reaction mixture; bottom: authentic sample of 4-chloro-toluene in C_6D_6)

4-Chloro-benzyl bromide ($CDCl_3$)

Yield = 90.3%; [1]H NMR spectrum of 4-chloro toluene[3], 400 Hz: 7.11 ppm (d, J = 8 Hz), 2.33 ppm (s, -CH_3), the rest of aromatic signals were overlapped with toluene

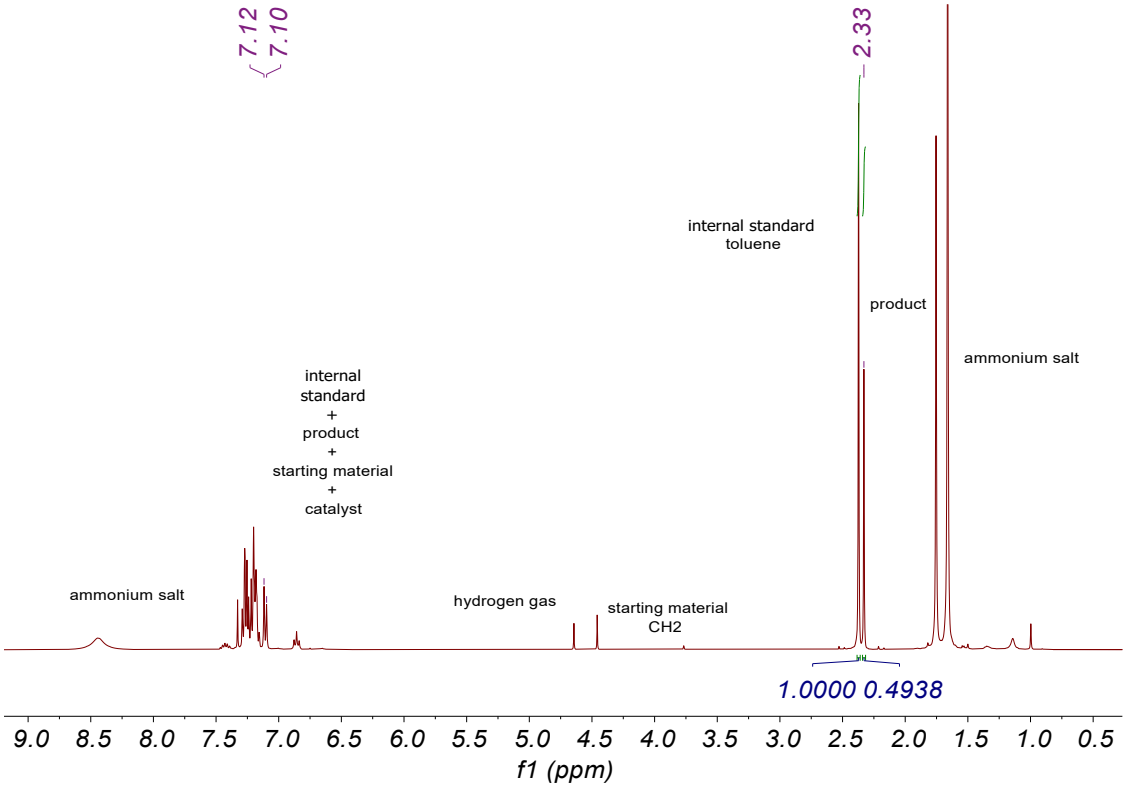


Figure S 3. [1]H NMR spectrum containing 4-chloro toluene

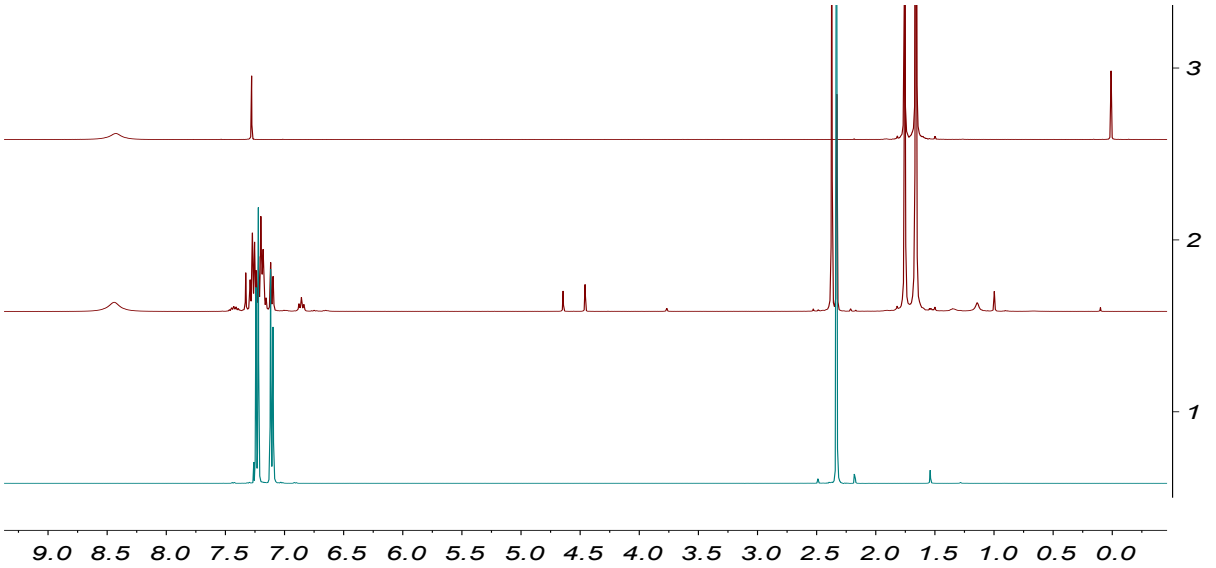


Figure S 4. ^{1}H NMR spectra (top: authentic sample of TMP•HBr in $CDCl_3$; middle: reaction mixture in $CDCl_3$; bottom: authentic sample of 4-chloro-toluene in $CDCl_3$)

4-Bromo-benzyl bromide

Yield = 99%; ^{1}H NMR spectrum of 4-bromo toluene[4], 400 Hz: 2.29 ppm (-CH_3)

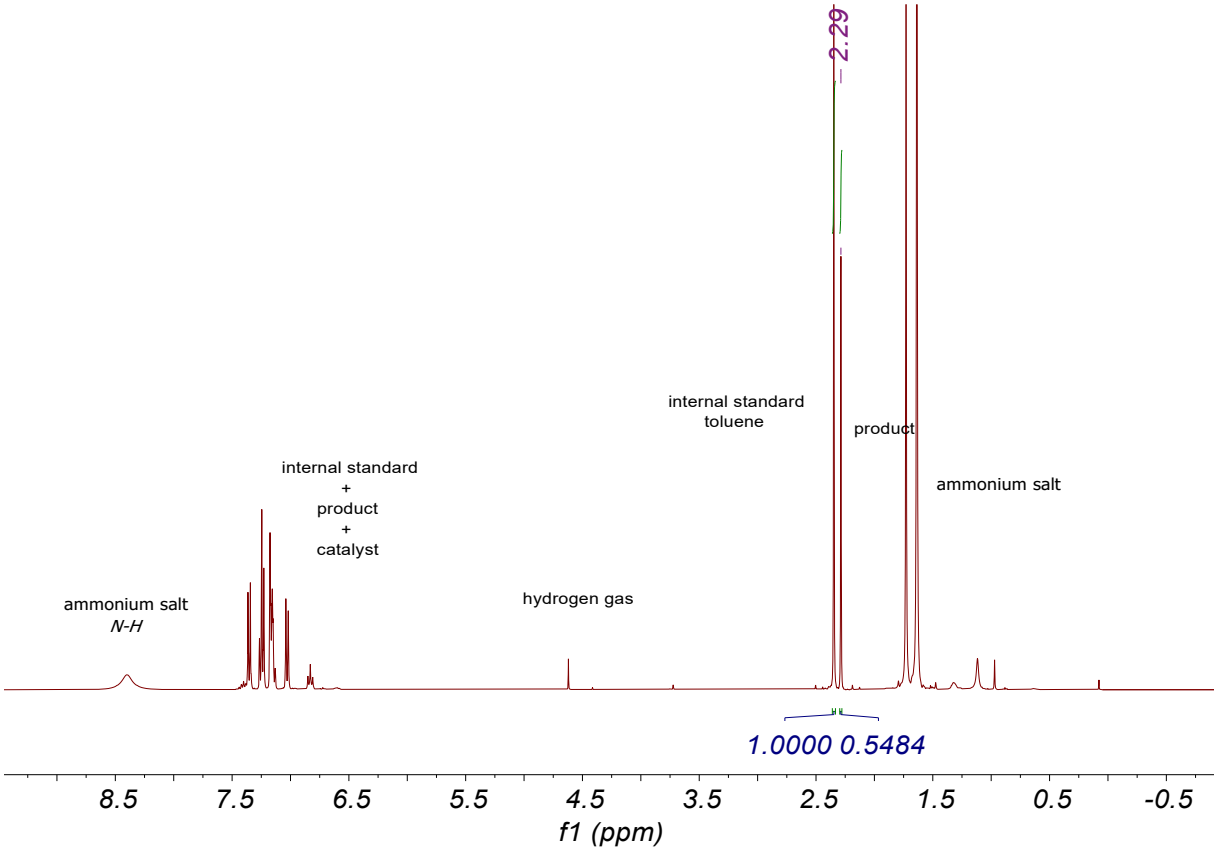


Figure S 5. ^{1}H NMR spectrum containing 4-bromo toluene

2-Bromo-benzyl bromide

Yield = 81 %; ^{1}H NMR spectrum of 2-bromo toluene[5], 400 Hz: 2.39 ppm (-CH_3)

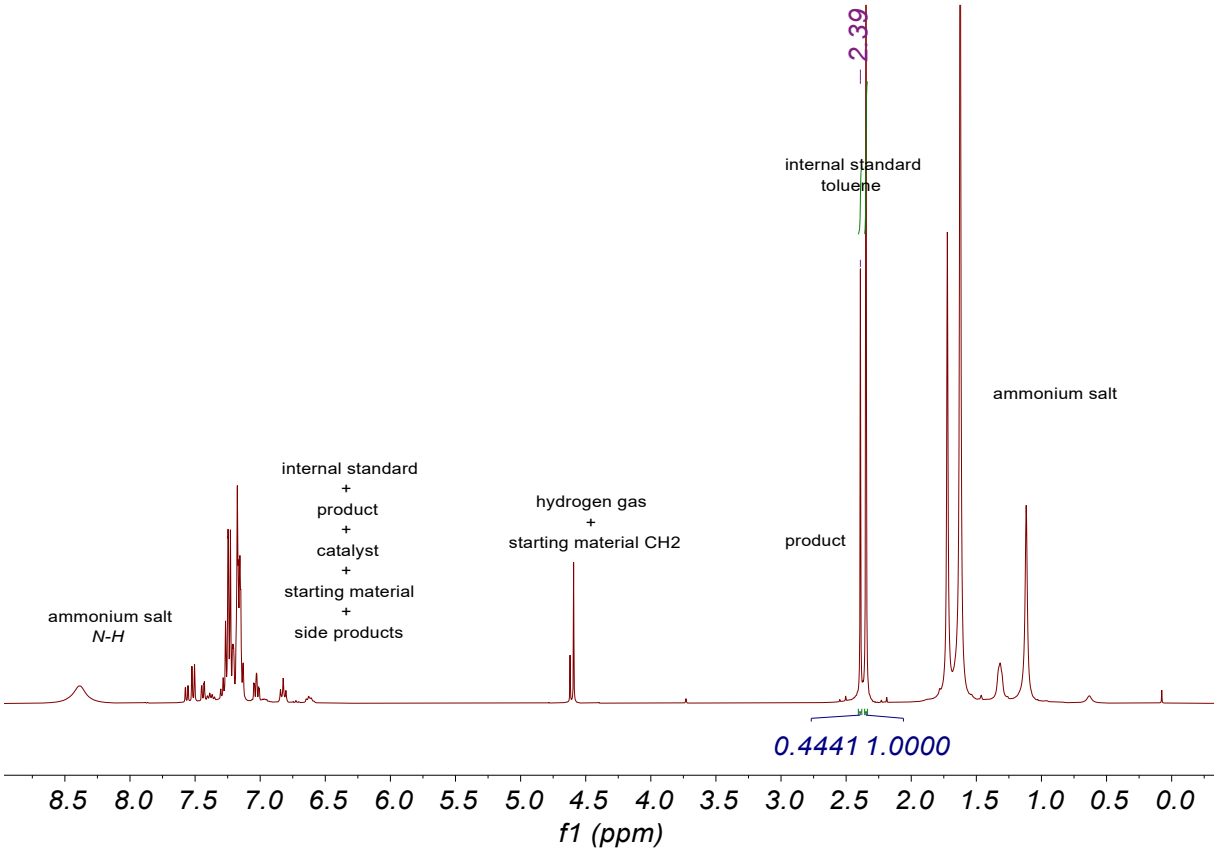


Figure S 6. ^{1}H NMR spectrum containing 2-bromo toluene

2-Iodo-benzyl bromide

Yield = 96%; ^{1}H NMR spectrum of 2-iodo toluene[6], 400 Hz: 2.42 ppm (-CH_3)

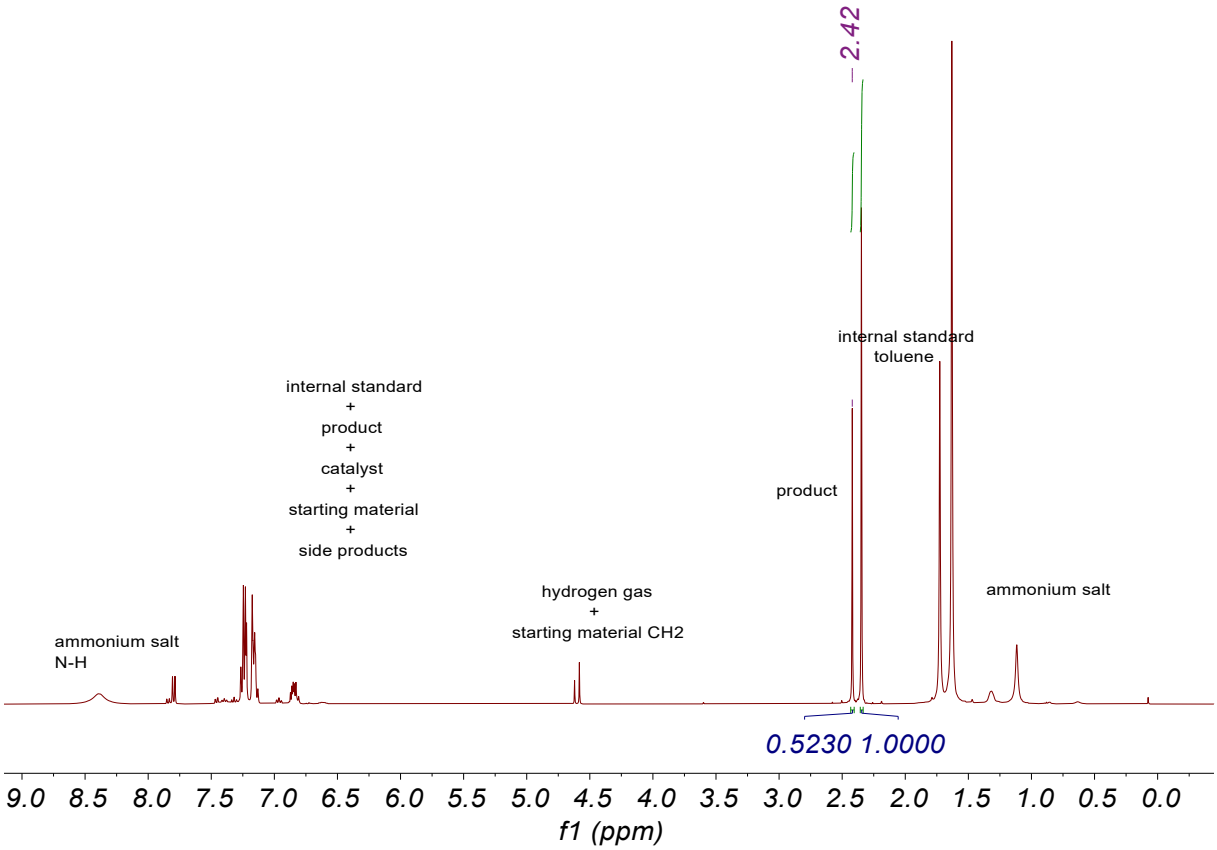


Figure S 7. ^{1}H NMR spectrum containing 2-iodo toluene

3, 4-Difluoro-benzyl bromide

Note: Yield was determined from ratio of product and starting material in the $^{19}F\{^{1}H\}$ NMR spectrum.

Yield =99 %; ^{1}H NMR spectrum of 3,4-difluoro toluene[7], 400 Hz: 2.30 ppm (-CH_3); $^{19}F\{^{1}H\}$f NMR spectrum, 376 Hz: -138.99 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz), -143.28 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz)

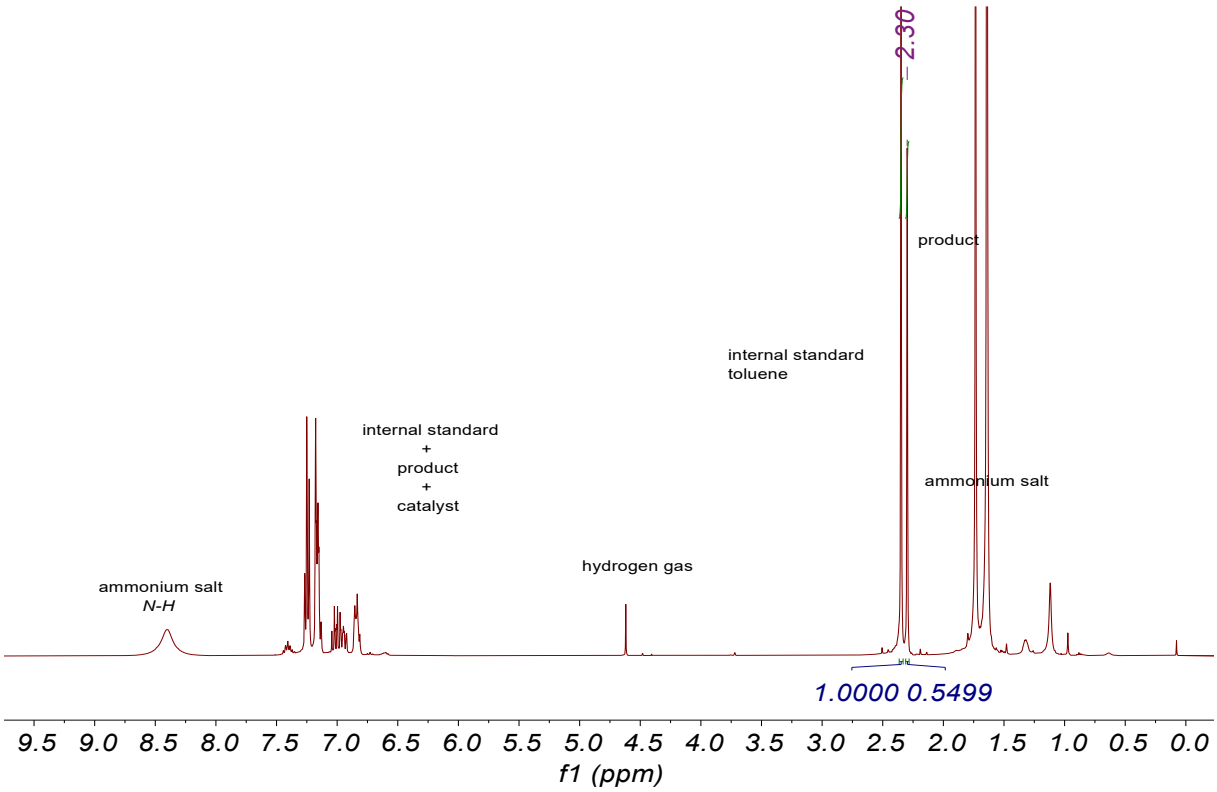


Figure S 8. ^{1}H NMR spectrum containing 3,4-difluoro toluene

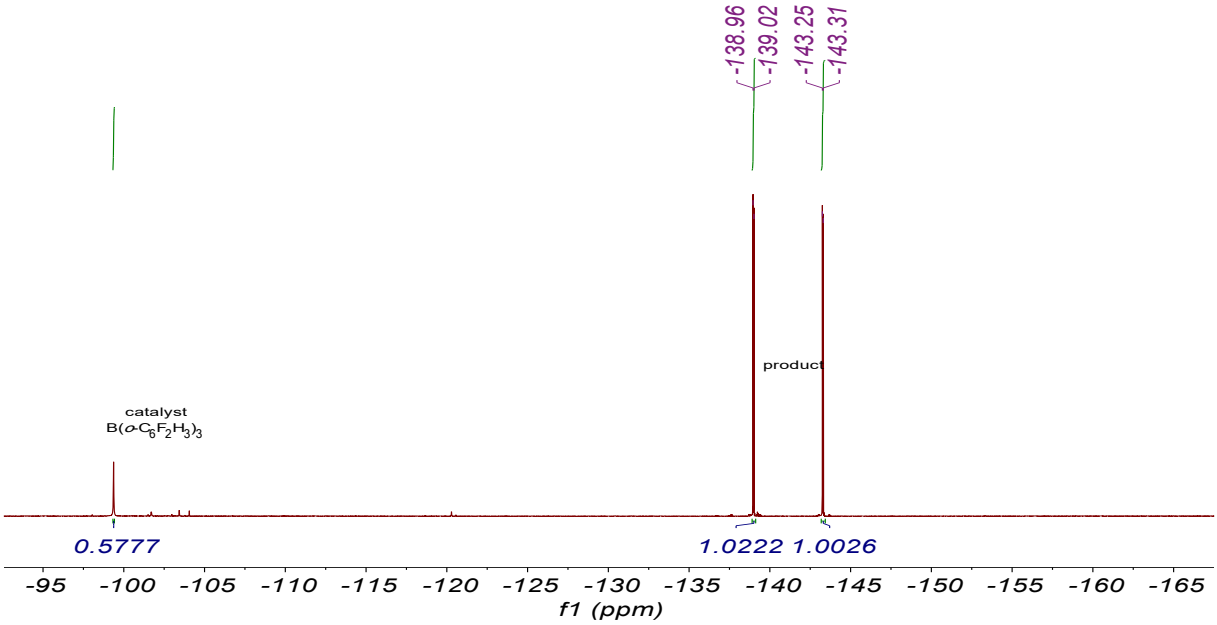


Figure S 9. $^{19}F\{^{1}H\}$ NMR spectrum containing 3,4-difluoro toluene

3-Fluoro-benzyl bromide

Note: Yield was determined from ratio of product and starting material in the $^{19}F\{^{1}H\}$ NMR spectrum.

Yield = 83 %; ^{1}H NMR spectrum of 3-fluoro toluene[8], 400 Hz: 2.34 ppm (-CH_3) ; $^{19}F\{^{1}H\}$ NMR spectrum, 376 Hz: -112.45 ppm (s, unreacted 3-fluoro-benzyl bromide), -114.28 ppm (s, 3-fluoro-toluene)

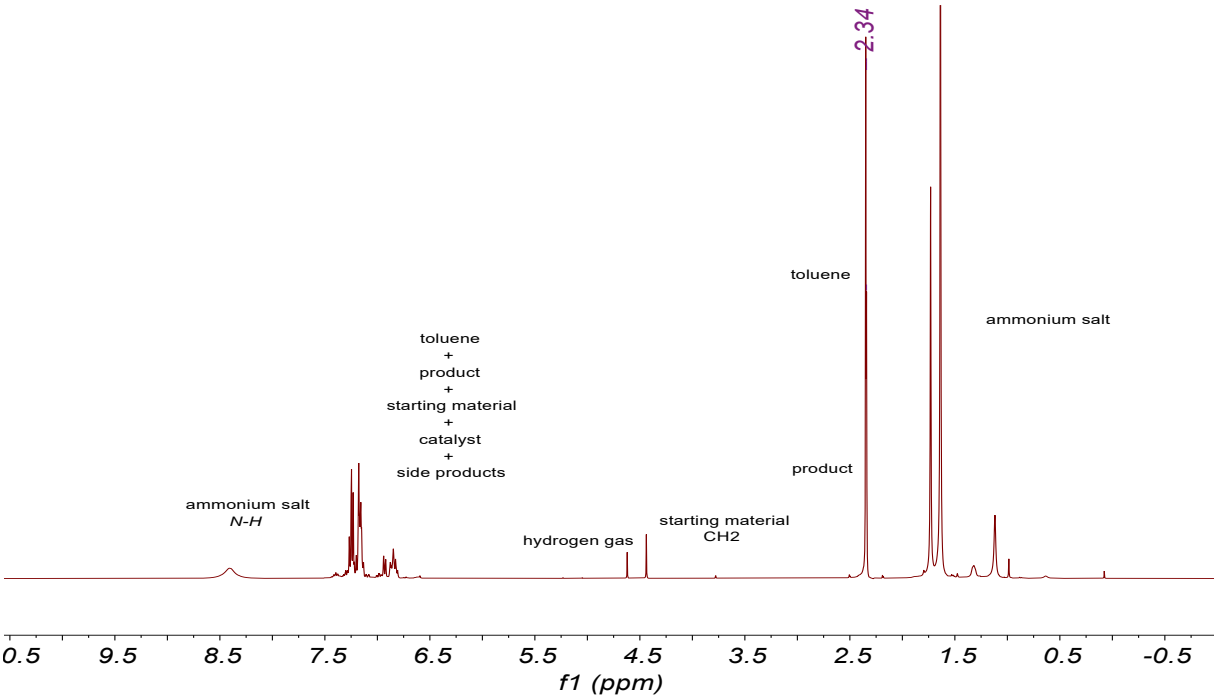


Figure S 10. ^{1}H NMR spectrum containing 3-fluoro toluene

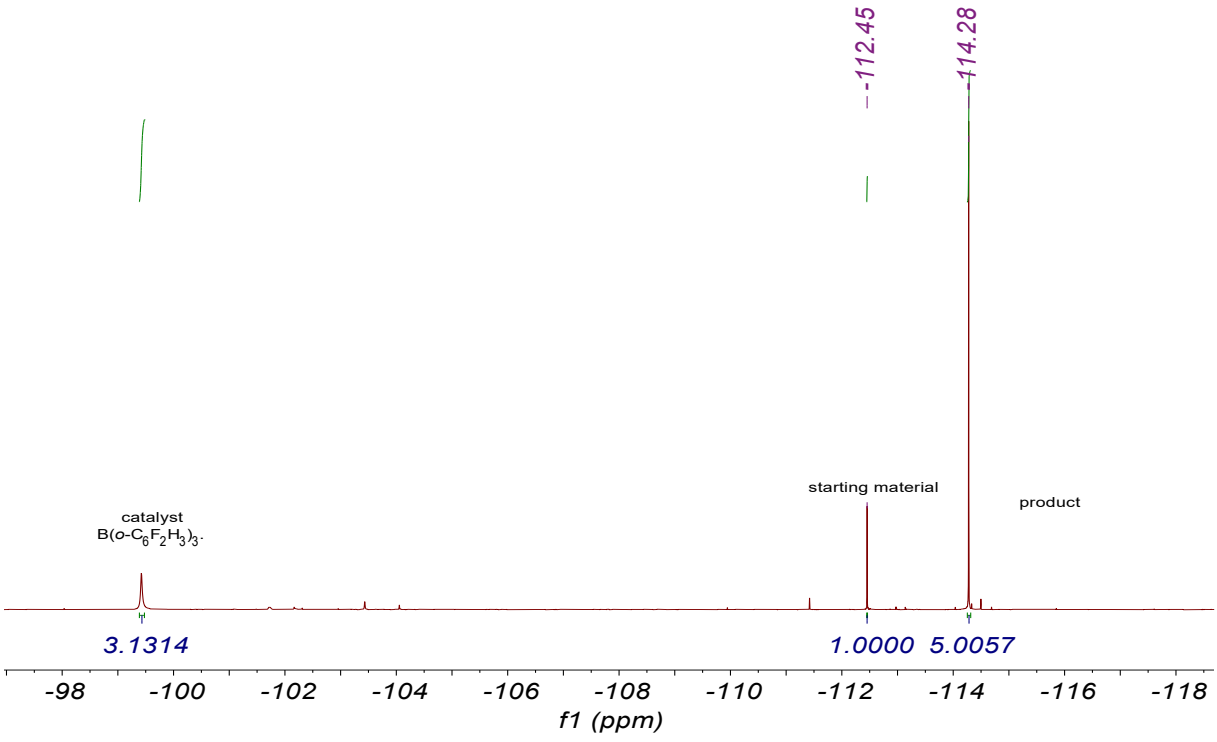


Figure S 11. $^{19}F\{^{1}H\}$ NMR spectrum containing 3-fluoro toluene

3-Cyano-benzyl bromide

Yield = 53 %; ^{1}H NMR spectrum of 3-cyano toluene[9], 400 Hz: 2.39 ppm (-CH_3).

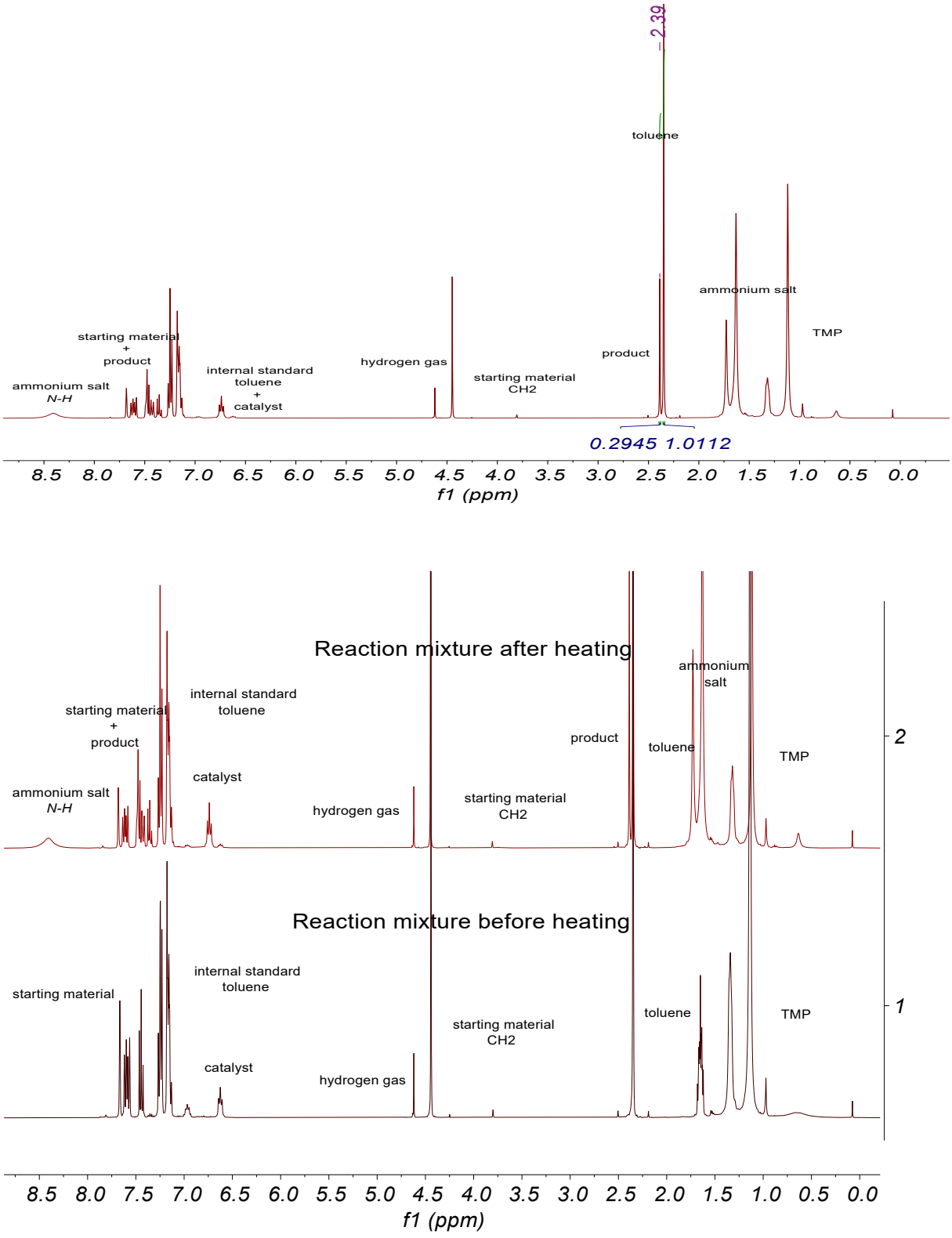


Figure S 12. ^{1}H NMR spectrum containing 3-cyano toluene, after heating in $CDCl_3$ (top spectrum); ^{1}H NMR spectrum before heating in $CDCl_3$ (bottom spectrum)

2,2'-Bis(bromomethyl)-1,1'-biphenyl

Note: 5 equivalents of 2,2'-Bis(bromomethyl)-1,1'-biphenyl was added, as each molecule contains 2 C-Br bonds

Yield = 96 %; ^{1}H NMR spectrum of 2,2'-dimethylbiphenyl[10], 400 Hz: 2.05 ppm (-CH_3)

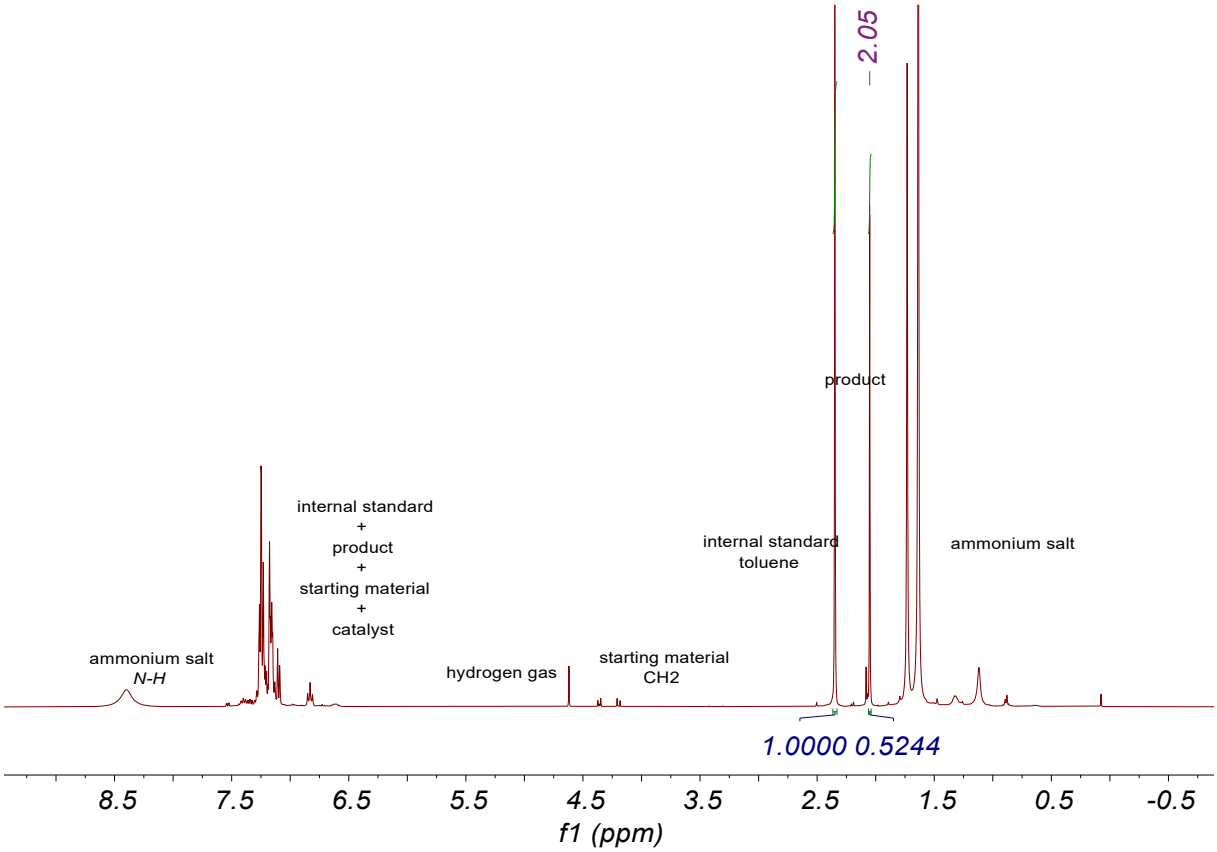


Figure S 13. ^{1}H NMR spectrum containing 2,2'-dimethylbiphenyl

Benzyl iodide

Note: 0.01 mL 4-tert-butylbenzene was used as internal standard

Yield = 83 %; ^{1}H NMR spectrum of toluene, 400 Hz: 2.35 ppm (-CH_3).

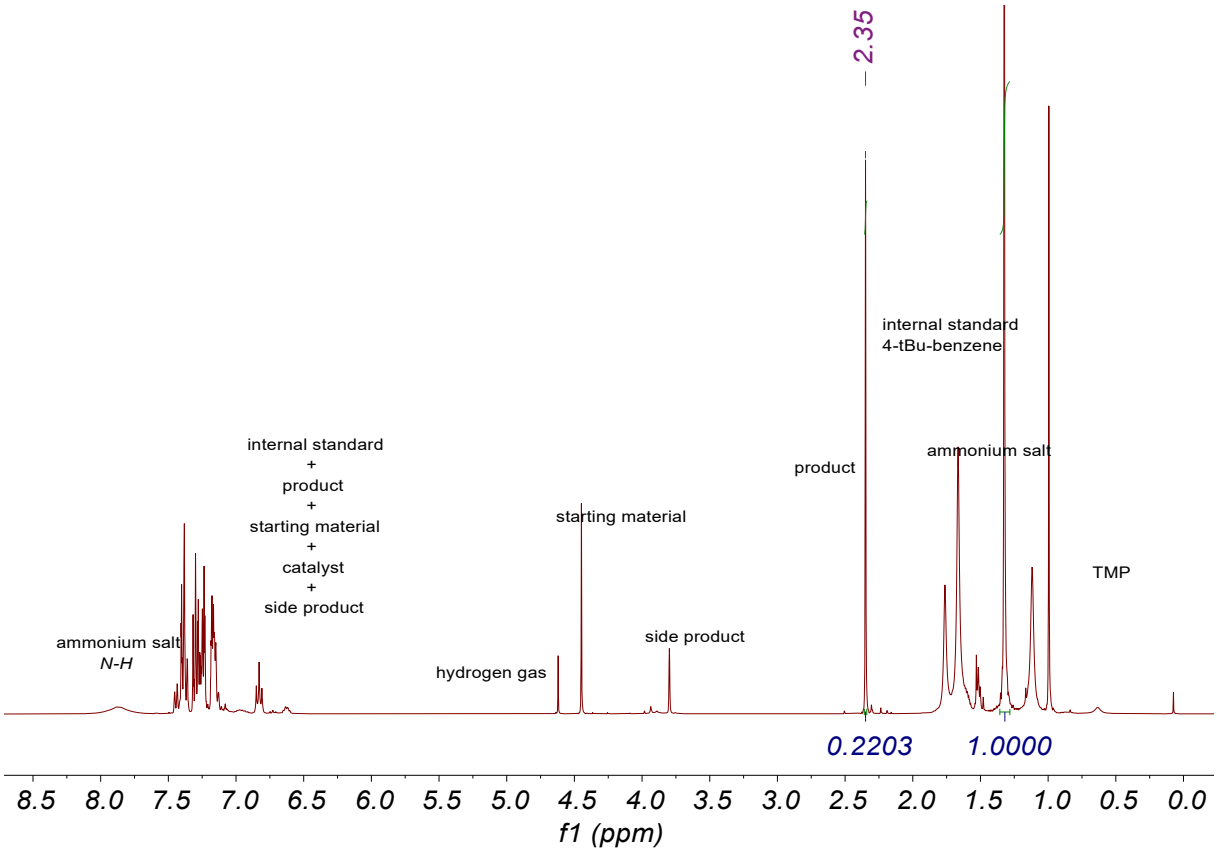


Figure S 14. ^{1}H NMR spectrum containing toluene and tert-butylbenzene

2-Bromo-benzyl iodide

Yield = 94 %; ^{1}H NMR spectrum of 2-bromo toluene[5], 400 Hz: 2.39 ppm (-CH_3).

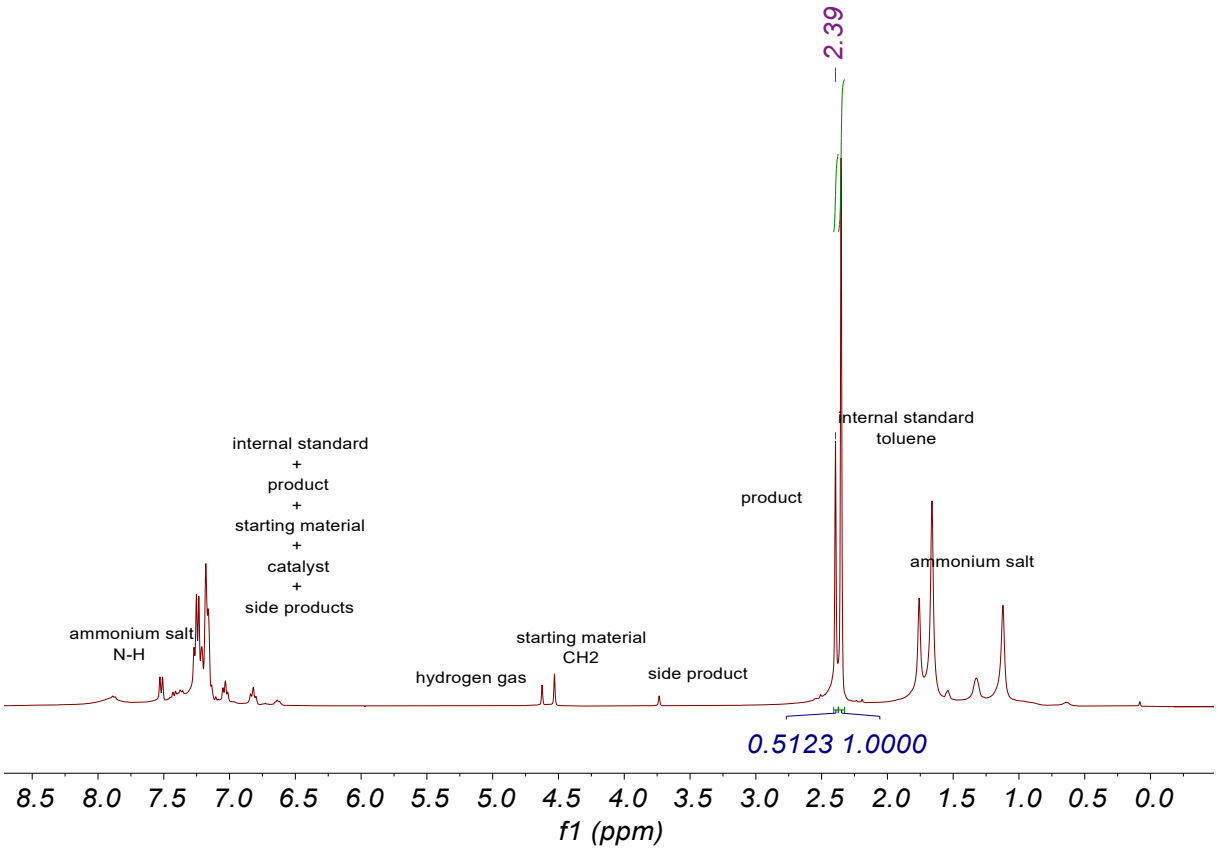


Figure S 15. ^{1}H NMR spectrum containing 2-bromo toluene

2-Iodo-benzyl iodide

Yield = 85 %; ^{1}H NMR spectrum of 2-iodo toluene[6], 400 Hz: 2.43 ppm (-CH_3).

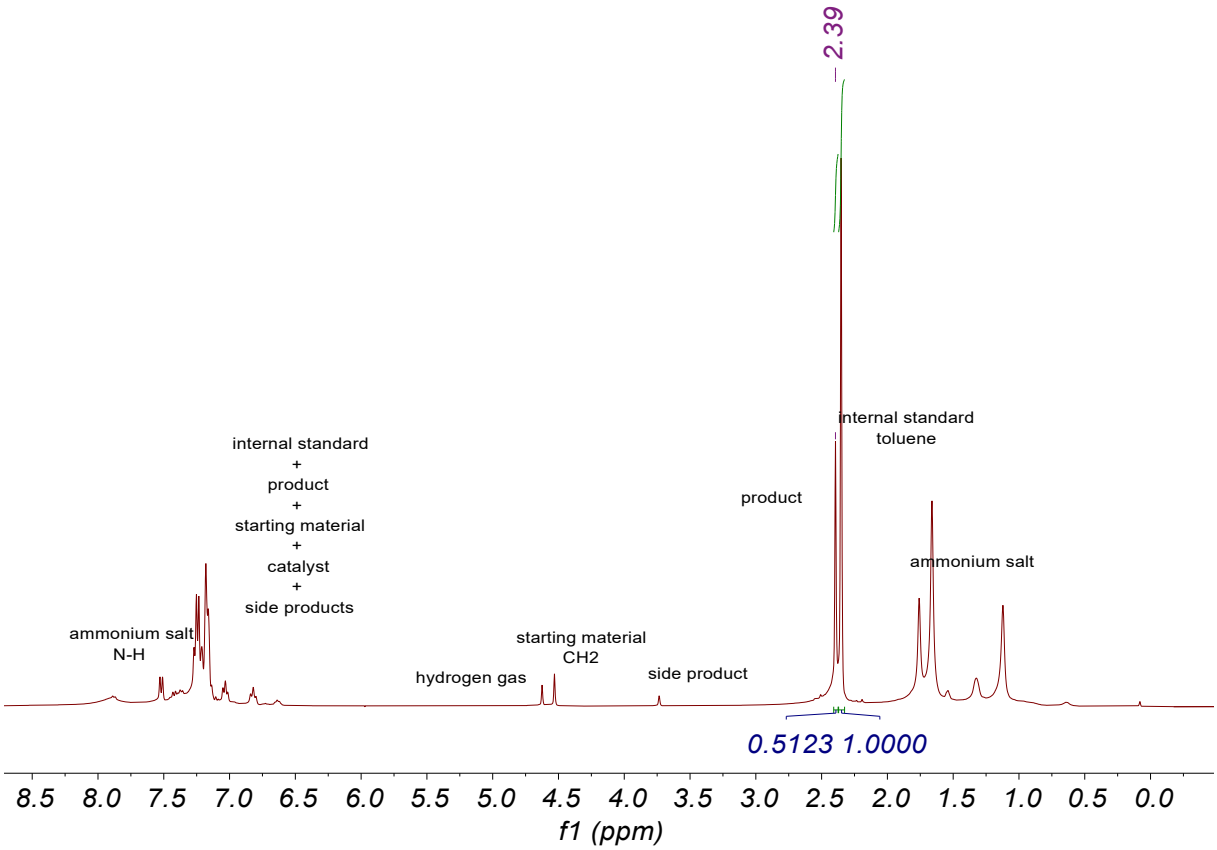


Figure S 16. ^{1}H NMR spectrum containing 2-iodo toluene

4-Chloro-benzyl iodide

Yield = 95 %; ^{1}H NMR spectrum of 4-chloro toluene[3], 400 Hz: 2.32 ppm (-CH_3).

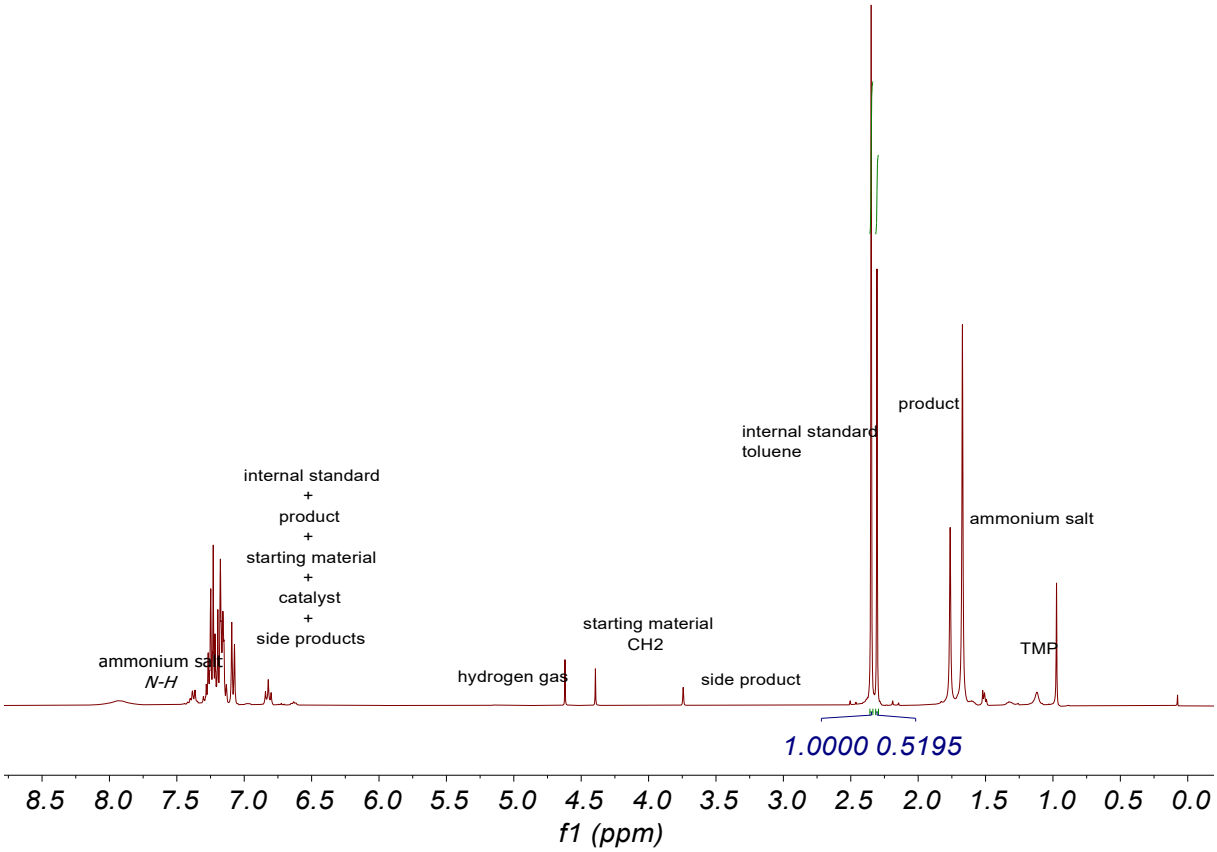


Figure S 17. ^{1}H NMR spectrum containing 4-chloro toluene

Benzyl chloride

Note: 0.01 mL 4-tert-butylbenzene was used as internal standard

Yield = 87 %; ^{1}H NMR spectrum of toluene, 400 Hz: 2.35 ppm (-CH_3).

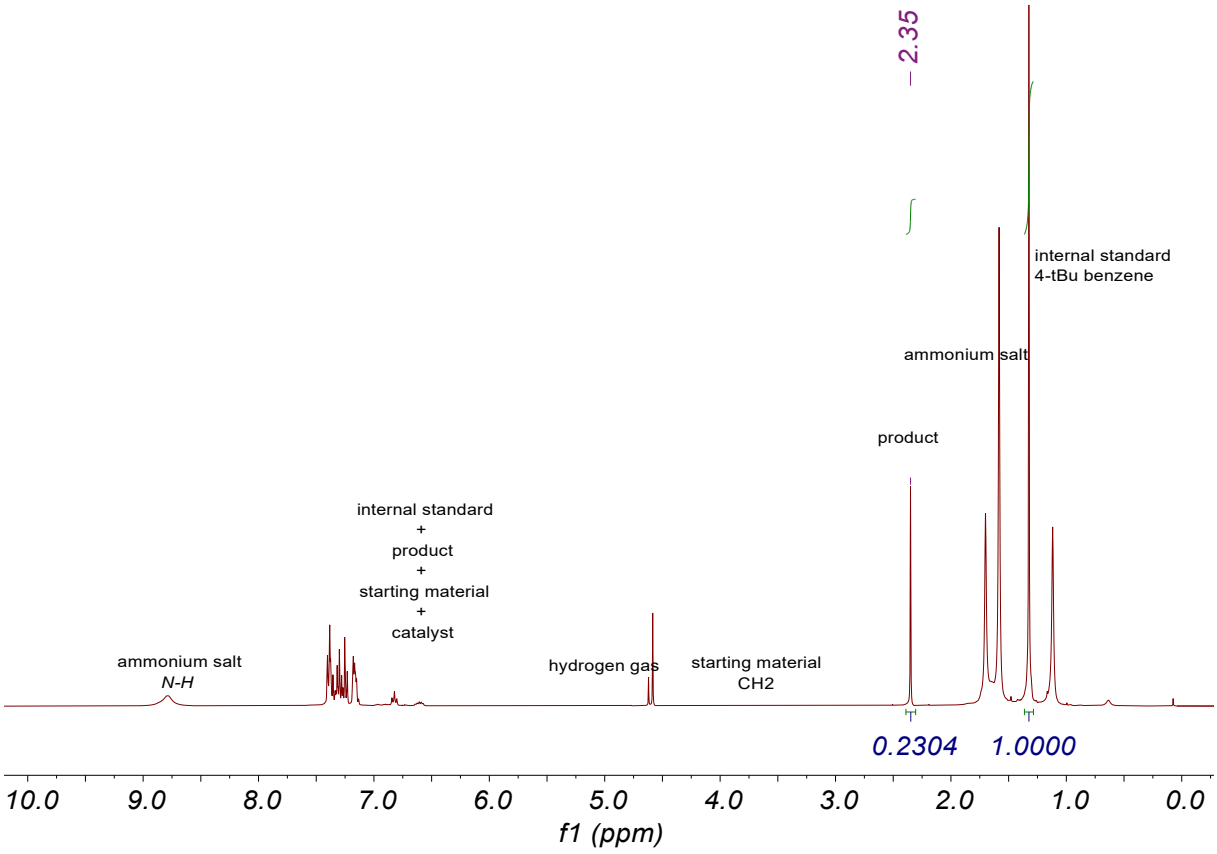


Figure S 18. ^{1}H NMR spectrum containing toluene and tert-butylbenzene

4-Tert-butyl-benzyl chloride

Yield = 86 %; ^{1}H NMR spectrum of 4-*tert*-butyl toluene,[11] 400 Hz: 2.31 ppm (-CH_3), 1.31 ppm (-*tBu*)

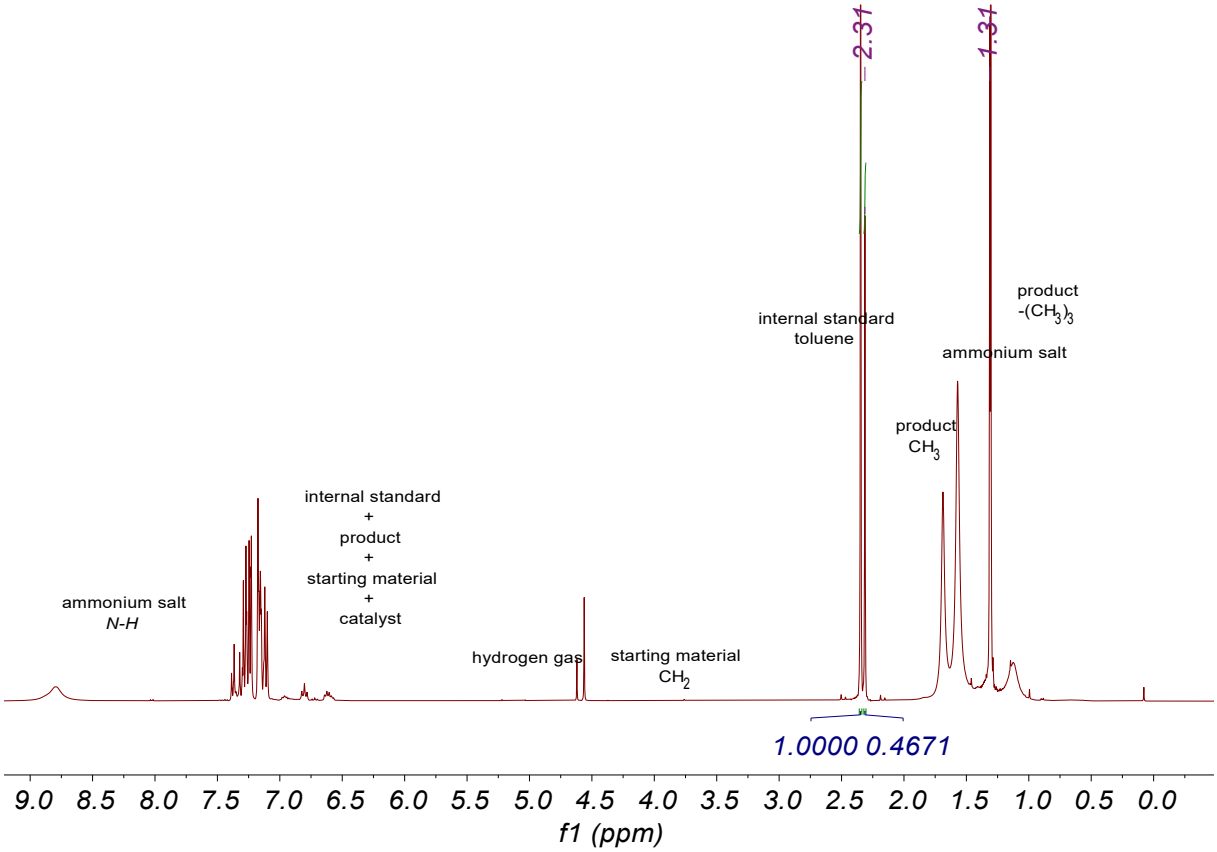


Figure S 19. ^{1}H NMR spectrum containing 4-tert-butyl toluene

2,4,6-Trimethyl-benzyl chloride

Yield = 95 %; ^{1}H NMR spectrum of 1,2,3,5-tetramethylbenzene[12], 400 Hz: 6.83 ppm (s, 2H), 2.25 ppm (bs, 9H), 2.14 ppm (s, 3H)

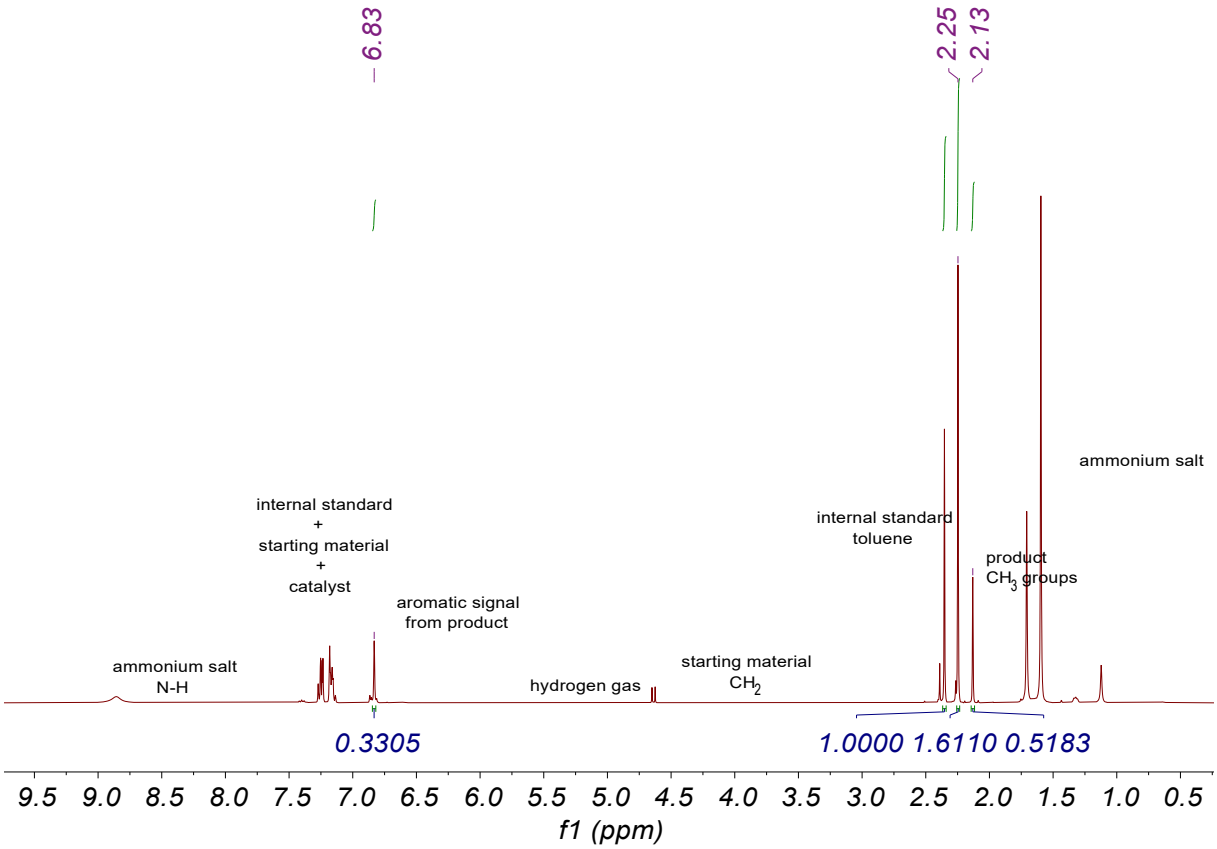


Figure S 20. ^{1}H NMR spectrum containing 1,2,3,5-tetramethylbenzene

4-Bromo-benzyl chloride

Yield = 87 %; ^{1}H NMR spectrum of 4-bromo toluene[4], 400 Hz: 2.29 ppm (-CH_3)

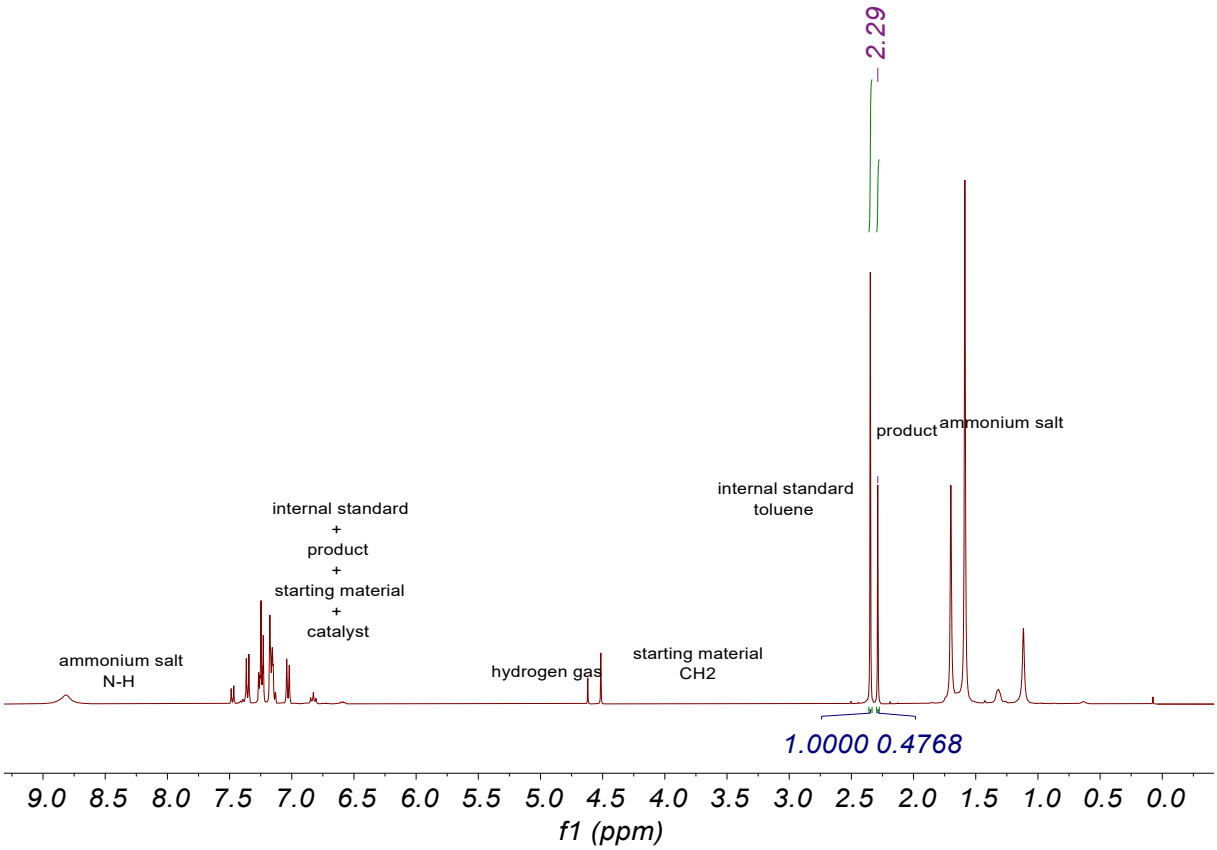


Figure S 21. ^{1}H NMR spectrum containing 4-bromo toluene

3, 4-Difluoro-benzyl chloride

Note: Yield was determined from ratio of product and starting material in the $^{19}F\{^{1}H\}$ NMR spectrum.

Yield = 60 %; ^{1}H NMR spectrum of 3,4-difluoro toluene[7], 400 Hz: 2.30 ppm (-CH_3) ; $^{19}F\{^{1}H\}$ NMR spectrum, 376 Hz: -136.8 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz, unreacted 3,4-difluoro-benzyl chloride), -137.8 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz, unreacted 3,4-difluoro-benzyl chloride) , -139.0 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz, 3,4-difluoro-toluene), -143.27 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz, 3,4-difluoro-toluene)

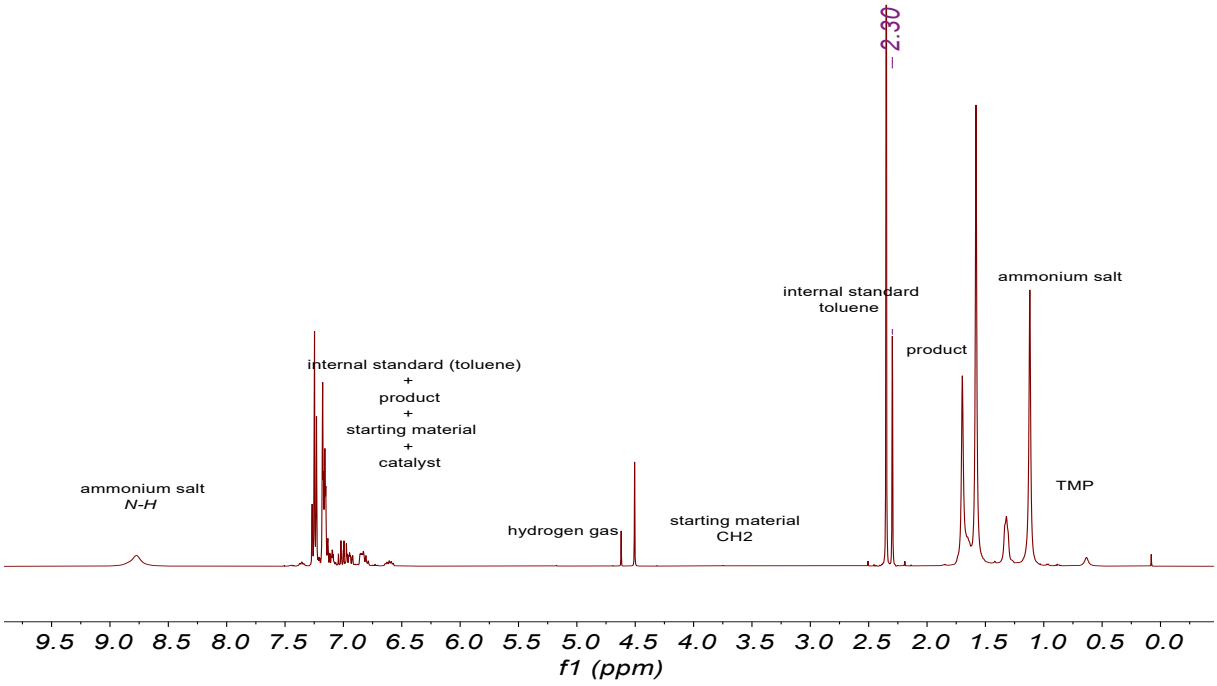


Figure S 22. ^{1}H NMR spectrum containing 3,4-difluoro toluene

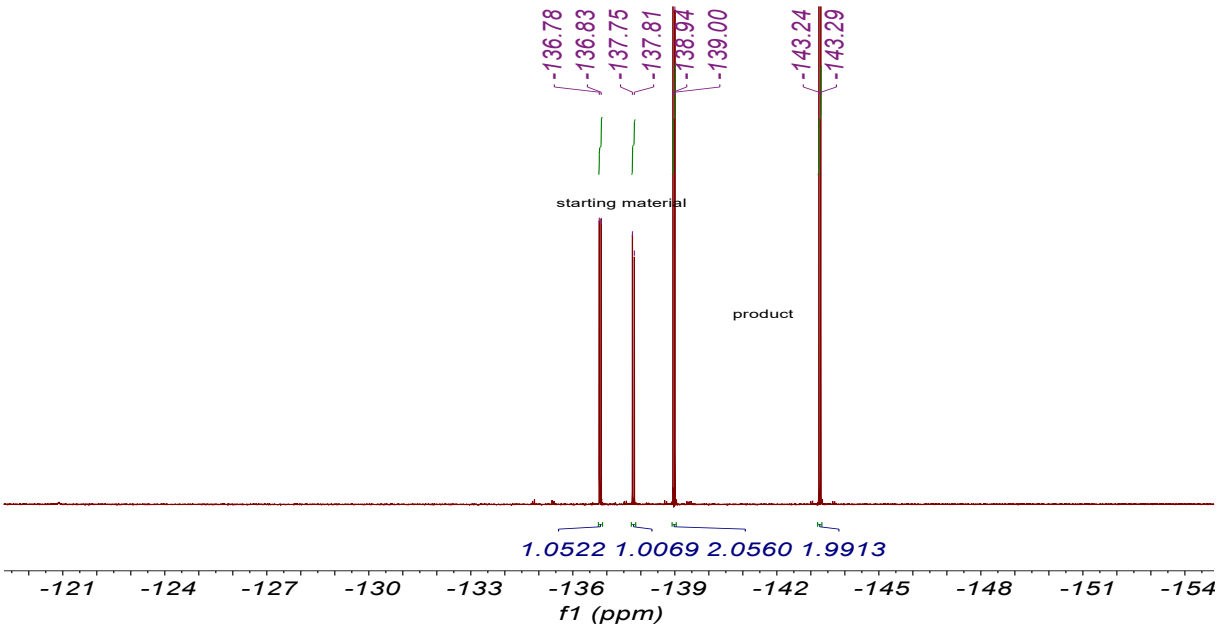


Figure S 23. $^{19}F\{^{1}H\}$ NMR spectrum containing 3,4-difluoro toluene

4-Nitro-benzyl chloride

Yield = 58 %; ^{1}H NMR spectrum of 4-nitro toluene[13], 400 Hz: 8.12 ppm (d, J = 9 Hz, 2H), 7.32 ppm (d, J = 9 Hz, 2H), 2.47 ppm (s, -CH_3, 3H)

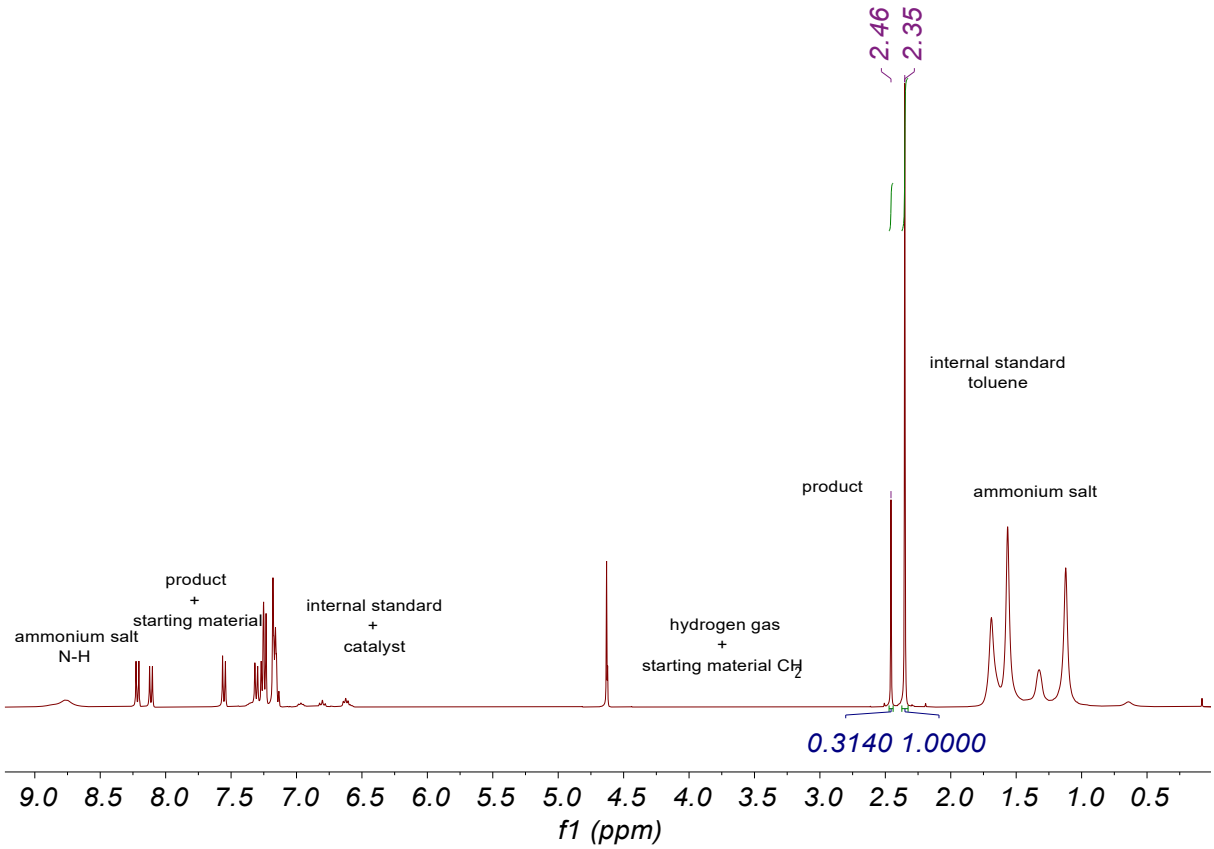


Figure S 24. ^{1}H NMR spectrum containing 4-nitro toluene

1-Bromoheptane

Note: the reaction was performed in C_6D_6

Yield = 36%; ^{1}H NMR spectrum of heptane, 400 Hz: 0.90 ppm (-CH_3)

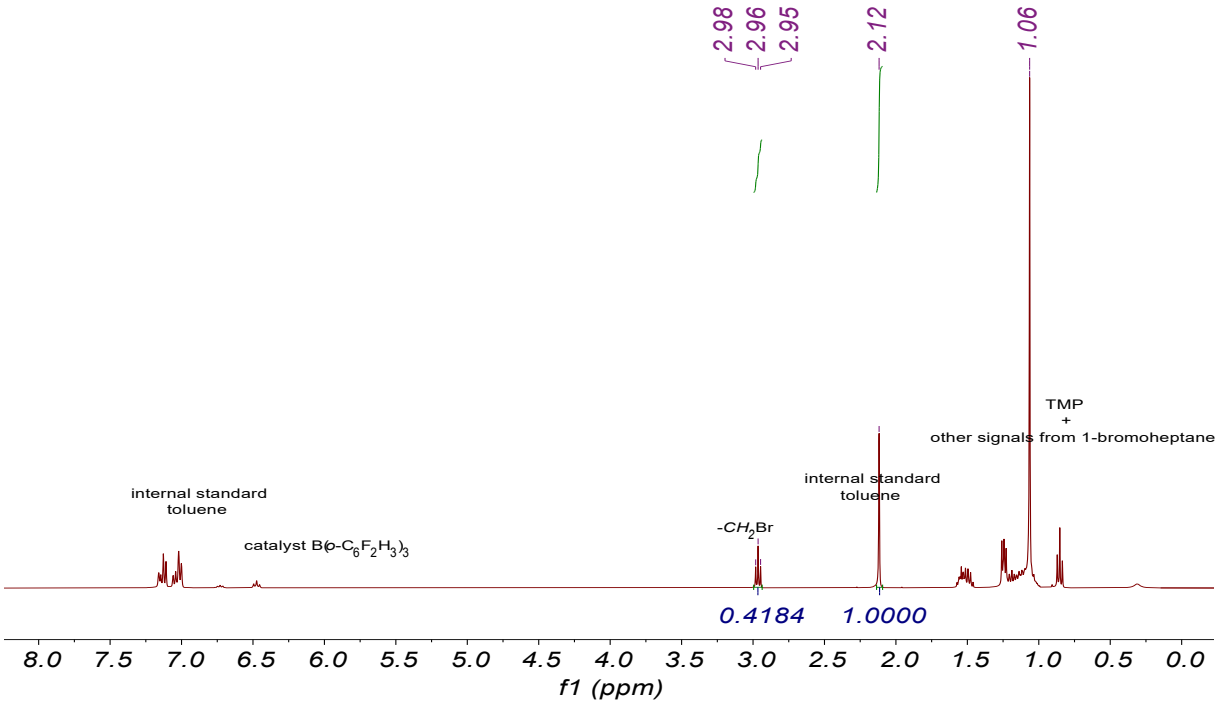


Figure S 25. ^{1}H NMR spectrum of 1-bromoheptane, measured before H_2 addition

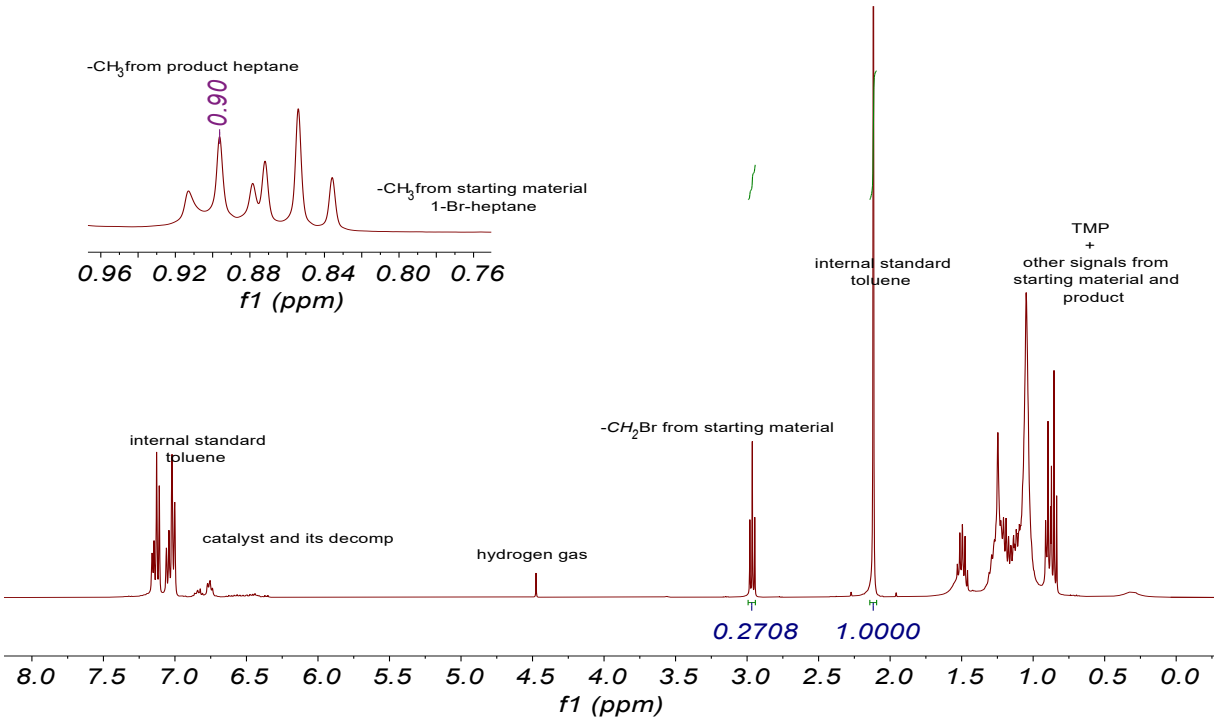


Figure S 26. ^{1}H NMR spectrum containing heptane and unreacted 1-bromoheptane, measured after 60 hours at 120°C

Benzyl bromide

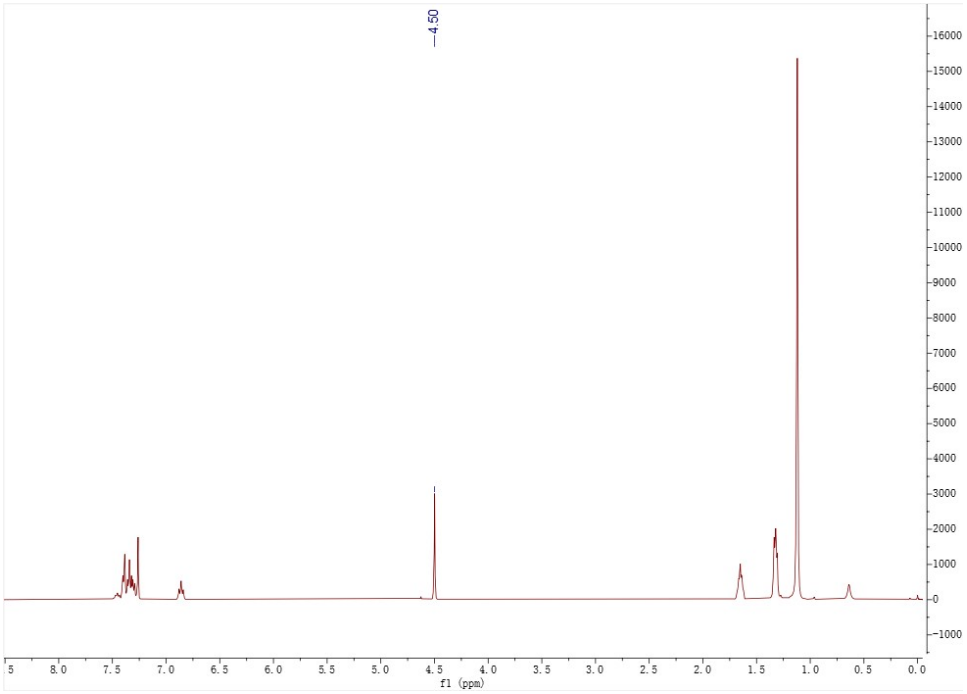


Figure S 27 ^{1}H NMR spectrum of crude reaction mixture for benzyl bromide at t = 0 h

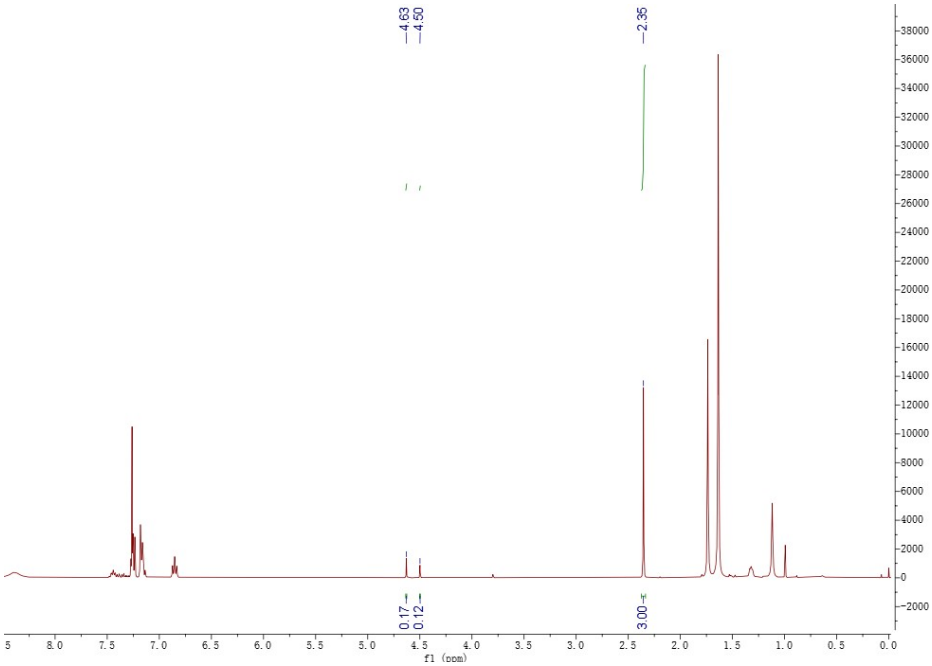


Figure S28 ^{1}H NMR spectrum of reaction mixture for benzyl bromide after heating for 33 h

Large Scale Synthesis.

The reaction of 4-$BrC_6H_4CH_2Br$ was performed as described above but on a 5 g scale (20 mmol). The ^{1}H NMR of the crude reaction mixture after 36 h showed a 98% conversion rate. After work-up, we isolated 2.3737 g (70% isolated yield) of the pure product 4-$BrC_6H_4CH_3$ as white to colorless crystals at room temperature (m.p. 28.5°C).

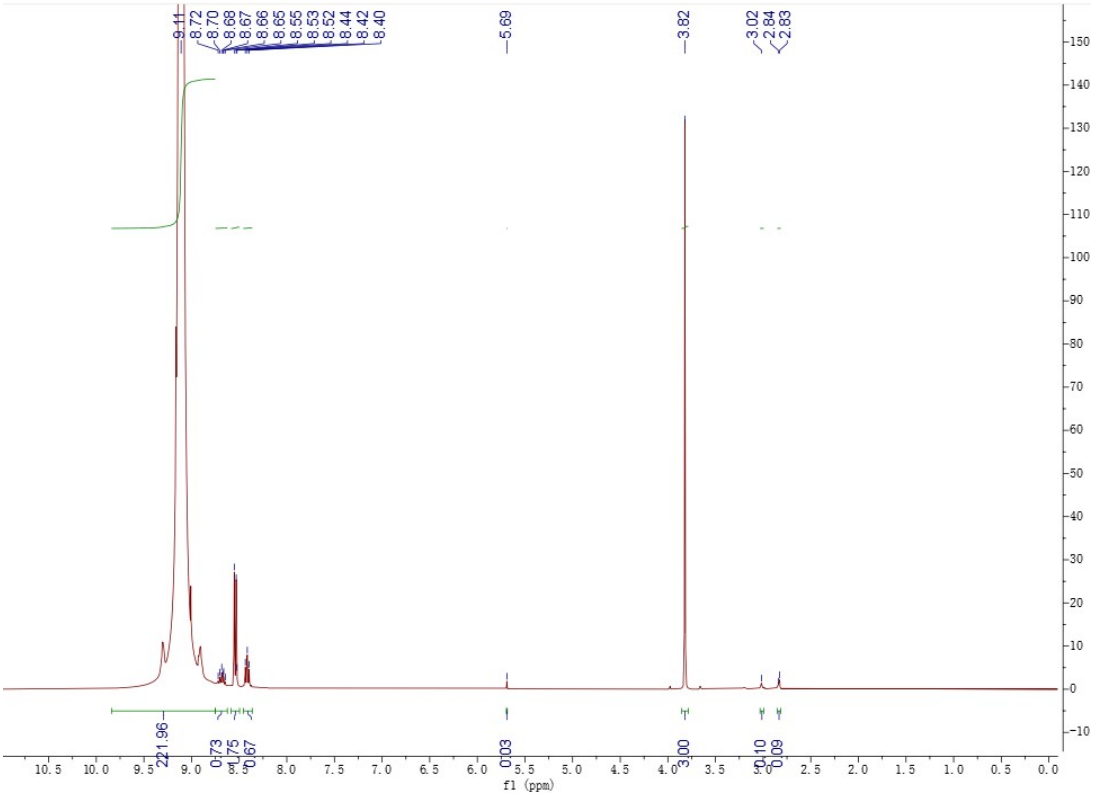


Figure S29 ^{1}H NMR of the crude reaction mixture after 36 h

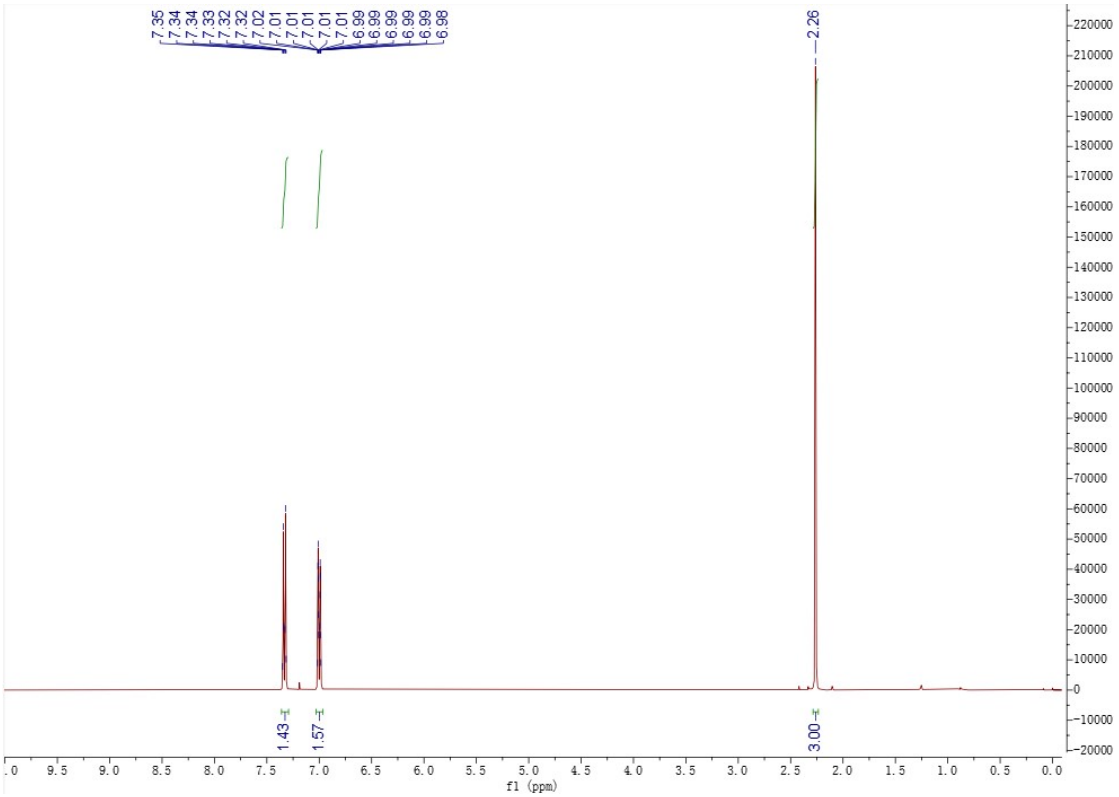


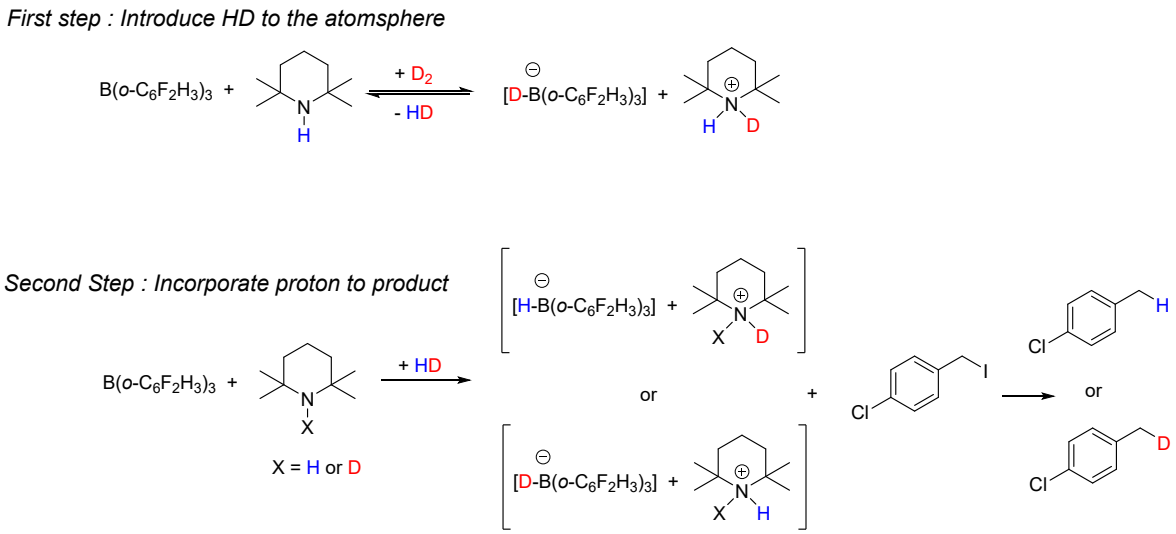
Figure S 30 ^{1}H NMR of the product 4-Br$C_6H_4CH_3$

Deuterodehalogenation experiments: Substrate scopes

These experiments were performed in a similar manner with varying substrates, therefore only one procedure is listed:

A solution of B(*o*-$C_6F_2H_3$)$_3$ (1.8 mg, 0.0051 mmol, 1 equivalent), 4-chloro-benzyl iodide (13.0 mg, 0.051 mmol, 10 equivalents), TMP (7.1 mg, 0.053 mmol, 10 equivalents) and 0.01 mL toluene (internal standard) in 0.4 ml $CDCl_3$ was transferred to a J-young tube. The J-young tube was charged with D_2 at -78°C (dry ice acetone bath). The reaction was heated at 60°C and the experiment was monitored by NMR studies.

Note: Due to the reversibility of FLP hydrogenation, hydrogen atom from TMP was released to the atmosphere as HD gas, and eventually incorporate into the products affording R-CH_3 byproducts



Scheme S 1. Reversible molecular hydrogen activation by a TMP and B(o-$C_6F_2H_3$)$_3$ FLP and the related H/D scrambling

4-Chloro-benzyl iodide

Overall Yield = 85 % [82% deuteration degree]; ^{1}H NMR spectrum, 400 Hz: 2.31 ppm (s, -CH_3), 2.29 ppm (t, -CH_2D, $^2J_{H\text{-}D}$ = 2.4 Hz)

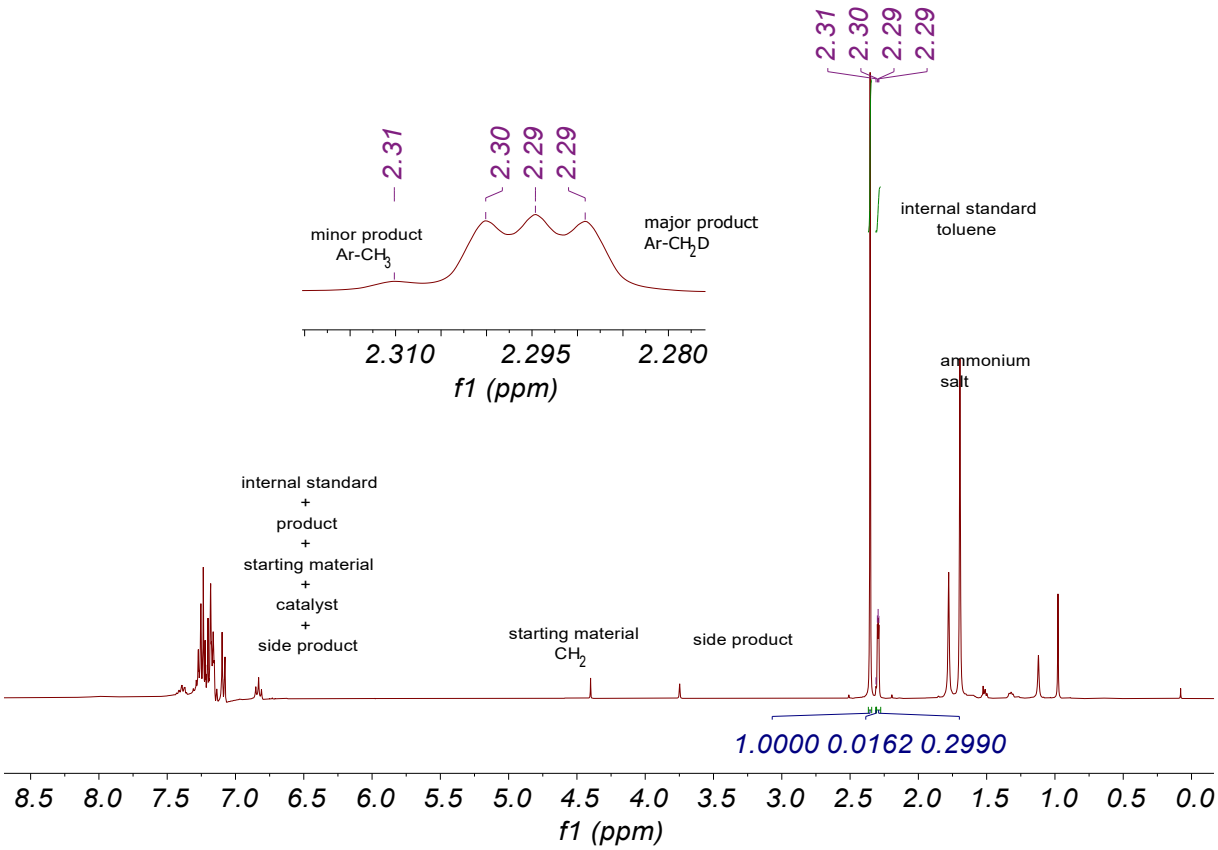


Figure 31. ^{1}H NMR spectrum from deuterodehalogenation experiment of 4-chloro-benzyl iodide

3,4-Difluoro-benzyl bromide

Note: Yield was determined from ^{1}H NMR integration.

Overall Yield = 92% [89% deuteration degree]; ^{1}H NMR spectrum, 400 Hz: 2.29 ppm (bm, -*CH_2D*); $^{19}F\{^{1}H\}$ NMR spectrum, 376 Hz: -136.7 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz, unreacted 3,4-difluoro-benzyl bromide), -137.5 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz, unreacted 3,4-difluoro-benzyl bromide), -139.0 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz, 3,4-difluoro-toluene), -143.3 ppm (d, $^{3}J_{F\text{-}F}$ = 21 Hz, 3,4-difluoro-toluene)

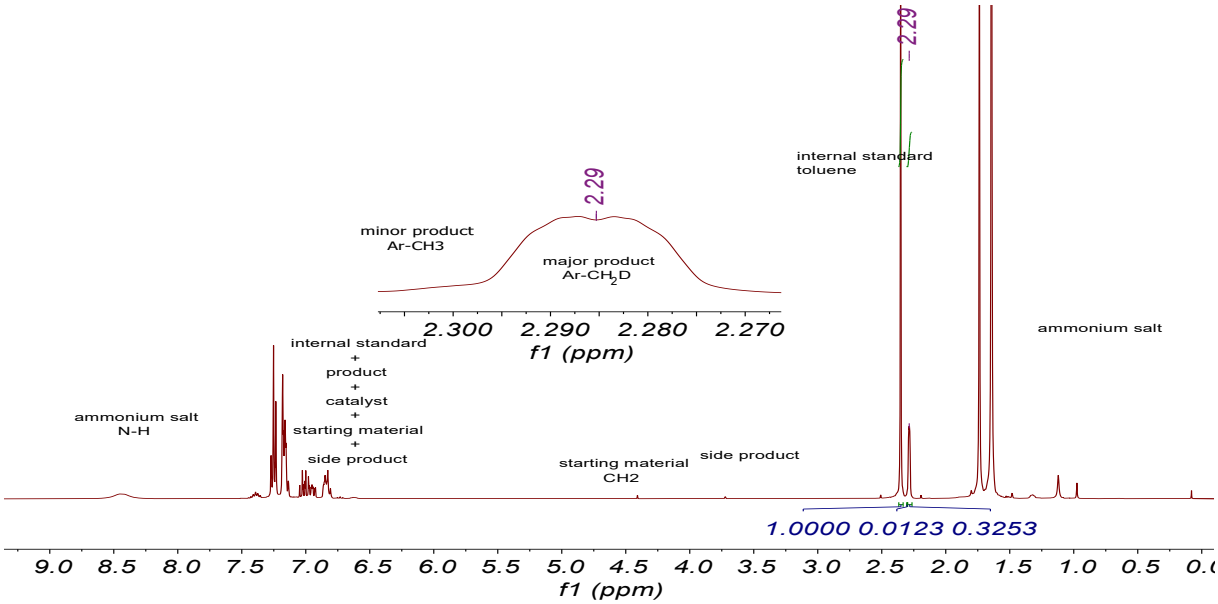


Figure S 32. ^{1}H NMR spectrum from deuterodehalogenation experiment of 3,4-difluoro-benzyl bromide

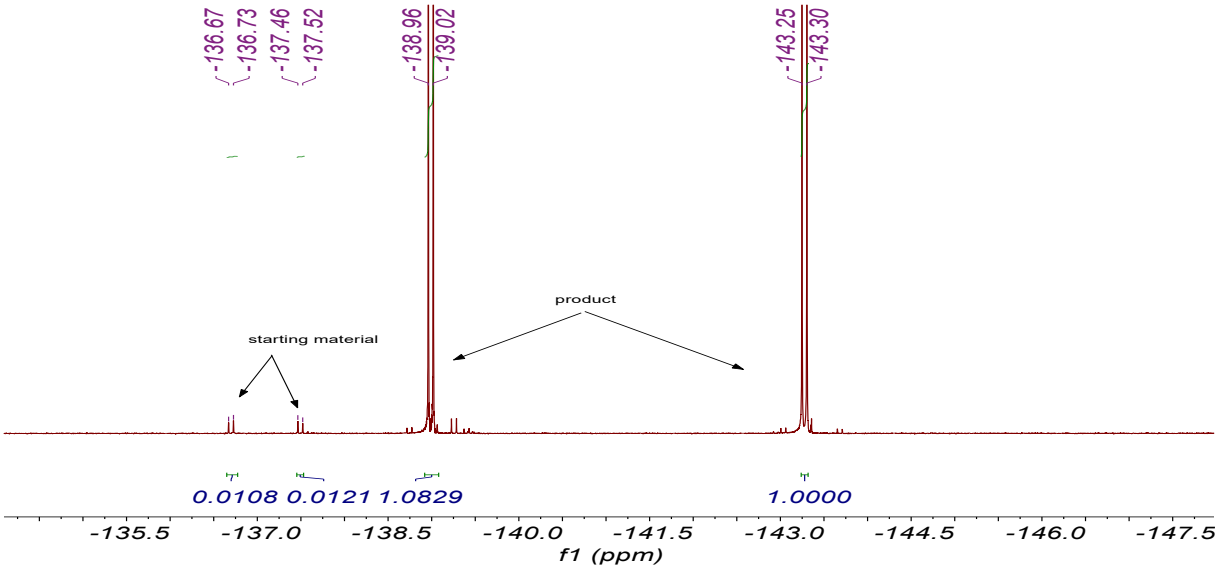


Figure S 33. $^{19}F\{^{1}H\}$ NMR spectrum from deuterodehalogenation experiment of 3,4-difluoro-benzyl bromide

4-Bromo-benzyl chloride

Overall Yield = 87 % [80% deuteration degree]; ^{1}H NMR spectrum, 400 Hz: 2.29 ppm (s, -CH_3), 2.28 ppm (t, -CH_2D, $^{2}J_{H\text{-}D}$ = 2.1 Hz)

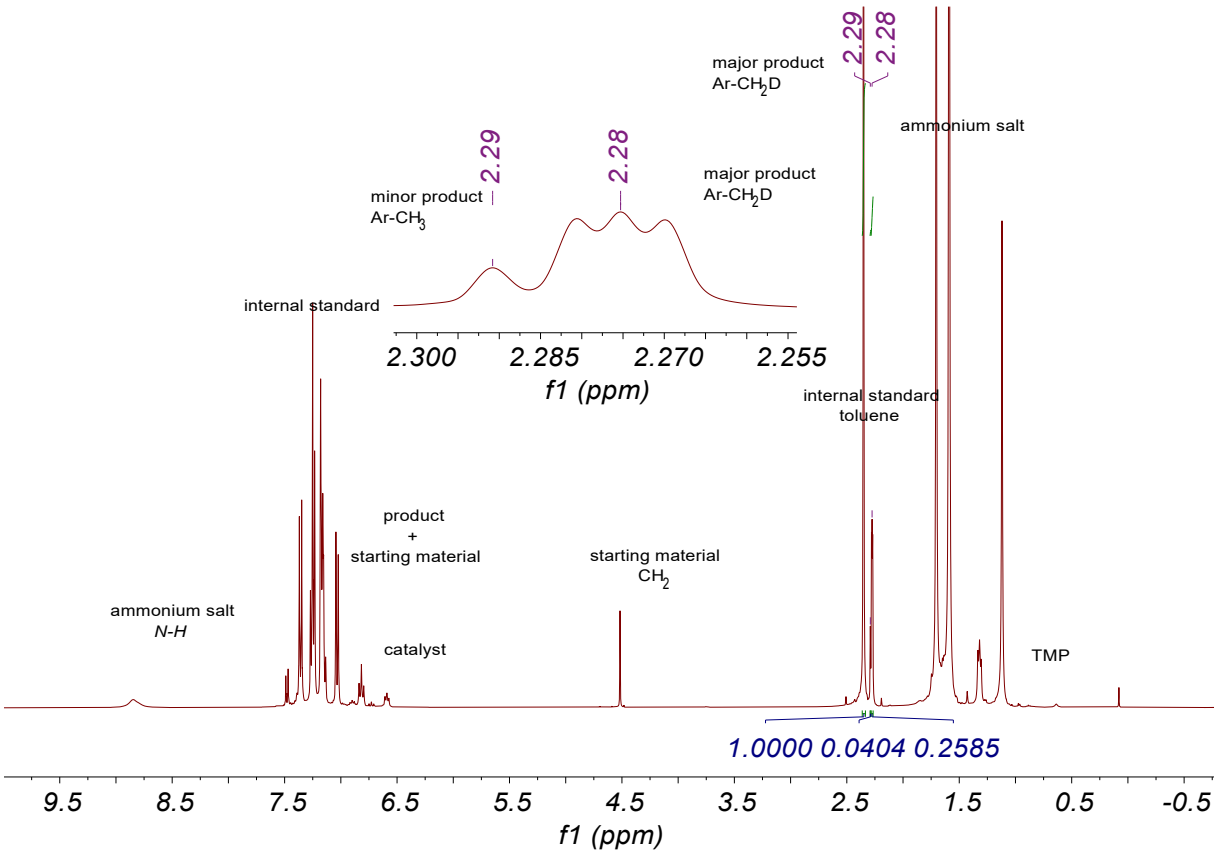


Figure S 34. ^{1}H NMR spectrum from deuterodehalogenation experiment of 4-Bromo-benzyl chloride

Computational Details:

The quantum chemical DFT calculations have been performed with the TURBOMOLE 7.4 suite of programs[14] The structures are fully optimized at the TPSS-D3/def2-TZVP + COSMO level of theory, which combines the TPSS meta-GGA density functional[15] with the BJ-damped DFT-D3 dispersion correction[16] and the def2-TZVP basis set,[17] using the Conductor-like Screening Model (COSMO) continuum solvation model[18] for $CHCl_3$ solvent (dielectric constant $\varepsilon = 4.8$ and solvent diameter $R_{solv} = 3.17$ Å). The density-fitting RI-J approach[17a, 19] is used to accelerate the geometry optimization and numerical harmonic frequency calculations[20] in solution. The optimized structures are characterized by frequency analysis to identify the nature of located stationary points (no imaginary frequency for true minima and only one imaginary frequency for transition state) and to provide thermal corrections (at 298.15 K and 1 atm) according to the modified ideal gas–rigid rotor–harmonic oscillator model.[21] This choice of dispersion-corrected meta-GGA functional makes the efficient exploration of all potential reaction paths possible.

The final solvation free energies in $CHCl_3$ are computed with the COSMO-RS solvation model[22] (parameter file: BP_TZVP_C30_1601.ctd) using the COSMOtherm program package[[23] on the above TPSS-D3 optimized structures, and corrected by +1.89 kcal·mol^{-1} to account for higher reference solute concentration of 1 mol·L^{-1} usually used in solution. To check the effects of the chosen DFT functional on the reaction energies and barriers, single-point calculations at the meta-GGA TPSS-D3[15] and hybrid-meta-GGA PW6B95-D3[24] levels are performed using a larger def2-QZVP basis set.[17b, 25] The final reaction Gibbs free energies (ΔG) are determined from the electronic single-point energies plus TPSS-D3 thermal corrections and COSMO-RS solvation free energies. The computed relative free energies from both DFT functionals are mostly in very good mutual agreement for reaction energies of about 0.5 ± 1.4 kcal/mol (average ± standard deviations), though about 5.2 ± 1.3 kcal/mol higher reaction barriers are found at the PW6B95-D3 level as expected. In our discussion, higher-level PW6B95-D3 Gibbs free energies (in kcal/mol, at 298.15 K and 1 mol/L concentration) will be used in our discussion unless specified otherwise. The applied DFT methods in combination with the large AO basis set provide usually accurate electronic energies leading to errors for chemical energies (including barriers) on the order of typically 1-2 kcal/mol. This has been tested thoroughly for the huge data base data base GMTKN55[26] which is the common standard in the field of DFT benchmarking.

Table S1. TPSS-D3/def2-TZVP + COSMO computed imaginary frequency (ImF), zero-point energies (ZPE), gas-phase enthalpic (Hc) and Gibbs free-energy (Gc) corrections; the COSMO-RS computed solvation enthalpic (Hsol) and Gibbs free-energy (Gsol) corrections in THF solution; TPSS-D3/def2-QZVP and PW6B95-D3/def2-QZVP single-point energies (TPSS-D3 and PW6B95-D3); the total PW6B95-D3 free energies G_P; the relative electronic energies (ΔE_T and ΔE_P) and Gibbs free-energies (ΔG_T and ΔG_P) at the TPSS-D3 and PW6B95-D3 levels.

Reactions in $CHCl_3$ solution	Im cm^{-1}	ZPE kcal /mol	Hc kcal /mol	Gc kcal /mol	Hsol kcal /mol	Gsol kcal /mol	TPSS-D3 E_h	PW6B95-D3 E_h	G_P E_h	ΔE_T kcal /mol	ΔE_P kcal /mol	ΔG_P kcal /mol	ΔG_T kcal /mol
both bases 2,2,6,6-tetramethylpiperidine (TMP) and 2,4,6-collidine (Col) are unbound to borane $B(o\text{-}C_6H_3F_2)_3$ (Bo_3)													
Bo_3 + TMP	0	307.35	328.16	257.81	-30.73	-21.23	-1725.50576	-1727.32069	-1726.93765	0.00	0.00	0.00	0.00
TMP.Bo_3	0	310.57	330.89	276.26	-25.42	-19.16	-1725.48989	-1727.30212	-1726.88940	9.96	11.65	30.28	28.59
Bo_3 + Col	0	247.31	266.56	198.93	-32.88	-22.17	-1682.55144	-1684.32659	-1684.03888	0.00	0.00	0.00	0.00
Col.Bo_3	0	248.73	267.77	214.80	-27.21	-20.48	-1682.57192	-1684.34826	-1684.03558	-12.85	-13.60	2.07	2.82
Stable ion pairs ammonium $TMPH^+$ and halide anions in $CHCl_3$ solution													
$TMPH^+ + Cl^-$	0	177.55	186.25	146.89	-159.13	-126.10	-870.14345	-870.90930	-870.87014	0.00	0.00	0.00	0.00
$TMPH^+Cl^-$	0	176.70	185.32	153.49	-39.32	-23.51	-870.32084	-871.08497	-870.87482	-111.32	-110.24	-2.94	-4.02
$TMPH^+ + Br^-$	0	177.55	186.25	146.17	-152.88	-121.66	-2984.02661	-2985.68026	-2985.63518	0.00	0.00	0.00	0.00
$TMPH^+Br^-$	0	176.86	185.53	153.12	-40.07	-24.68	-2984.19434	-2985.84641	-2985.63872	-105.25	-104.26	-2.22	-3.21
$TMPH^+ + I^-$	0	177.55	186.25	145.76	-144.50	-116.34	-707.51907	-708.24612	-708.19323	0.00	0.00	0.00	0.00
$TMPH^+I^-$	0	176.92	185.67	152.74	-39.94	-25.87	-707.67579	-708.40122	-708.19603	-98.34	-97.32	-1.76	-2.78
Facile H_2 activation with TMP/Bo_3 FLP leads to stable ion pair $TMPH^+HBo_3^-$ in $CHCl_3$ solution													
Bo_3 + TMP + H_2	0	313.69	336.57	256.94	-31.39	-20.16	-1726.68636	-1728.49663	-1728.11026	0.00	0.00	0.00	0.00
TS1	70i	315.40	337.44	278.73	-26.17	-19.75	-1726.69280	-1728.50099	-1728.08527	-4.04	-2.74	15.68	14.37
$TMPH^+HBo_3^-$ (**A**)	0	322.63	344.04	286.67	-34.40	-26.64	-1726.72020	-1728.53092	-1728.11353	-21.24	-21.52	-2.05	-1.77
$TMPH^+ + HBo_3^-$	0	322.08	343.00	272.05	-113.96	-100.15	-1726.57837	-1728.38814	-1728.10818	67.76	68.08	1.31	0.99
Neutral transition state for C-Cl activation of p-$BrC_6H_4CH_2Cl$ (p-BrBzCl) is preferred over a barrier of 19.4 kcal/mol.													
A + *p*-BrBzCl	0	390.93	418.09	333.26	-48.11	-35.85	-5031.63172	-5035.29342	-5034.81343	0.00	0.00	0.00	0.00
$TMPH^+$.*p*-BrBzCl.HBo_3^-	0	391.23	419.30	348.09	-55.10	-43.34	-5031.62233	-5035.28350	-5034.79484	5.89	6.22	11.67	11.33
TS2	289i	388.23	416.71	344.23	-52.36	-41.26	-5031.61659	-5035.26842	-5034.78259	9.49	15.69	19.36	13.16
p-BrBzH + Bo_3 + $TMPH^+Cl^-$	0	390.34	417.52	318.57	-68.33	-44.30	-5031.65308	-5035.31675	-5034.87065	-13.40	-14.64	-35.90	-34.66

...while anionic borate C-Cl activation is kinetically 1.8 kcal/mol less favorable													
A - $TMPH^+$ + *p*-BrBzCl	0	213.38	233.32	176.94	3.72	11.62	-4621.79887	-4625.03075	-4624.72725	0.00	0.00	0.00	0.00
p-BrBzCl.HBo_3^-	0	212.84	233.24	175.84	-64.23	-53.76	-4621.68038	-4624.91155	-4624.71400	74.36	74.80	8.32	7.88
TS2$^-$	355i	211.37	231.42	175.01	-79.93	-61.06	-4621.65706	-4624.87816	-4624.69355	88.99	95.76	21.15	14.38
p-BrBzH + Bo_3 + Cl^-	0	213.64	233.69	155.64	-136.31	-99.42	-4621.64284	-4624.87841	-4624.77978	97.91	95.59	-32.96	-30.64
Neutral transition state for C-Br activation of p-$BrC_6H_4CH_2Br$ (p-BrBzBr): 0.7 kcal/mol lower barrier than C-Cl activation													
A + *p*-BrBzBr	0	390.38	417.68	332.11	-48.98	-36.47	-7145.50322	-7150.05194	-7149.57478	0.00	0.00	0.00	0.00
TS2Br	236i	388.40	416.78	344.69	-53.08	-42.00	-7145.49052	-7150.03037	-7149.54500	7.97	13.53	18.69	13.12
p-BrBzH + Bo_3 + $TMPH^+Br^-$	0	390.50	417.73	318.19	-69.08	-45.47	-7145.52657	-7150.07819	-7149.63455	-14.65	-16.47	-37.51	-35.68
Neutral C-I activation of p-$BrC_6H_4CH_2I$ (p-BrBzI): 1.3 kcal/mol lower barrier than C-Cl activation													
A + *p*-BrBzI	0	390.13	417.50	331.46	-51.09	-37.87	-4868.98627	-4872.60775	-4872.13386	0.00	0.00	0.00	0.00
TS2I	186i	388.00	416.55	343.79	-55.58	-44.00	-4868.97290	-4872.58585	-4872.10508	8.39	13.74	18.06	12.70
p-BrBzH + Bo_3 + $TMPH^+I^-$	0	390.56	417.87	317.81	-68.95	-46.66	-4869.00802	-4872.63300	-4872.19185	-13.65	-15.84	-36.39	-34.20
Proton affinities of 2,4,6-collidine (Col) and 2,6-lutidine (Lut) are 1.5 and 3.4 kcal/mol smaller that TMP base, respectively													
$TMPH^+$ + Col	0	284.80	297.77	243.44	-66.56	-56.06	-776.31664	-777.13985	-776.83522	0.00	0.00	0.00	0.00
TMP + $ColH^+$	0	283.95	296.96	242.58	-63.57	-54.27	-776.31383	-777.13886	-776.83275	1.76	0.62	1.55	2.69
$TMPH^+$ + Lut	0	267.31	279.47	227.24	-65.18	-55.15	-736.97170	-737.75323	-737.47295	0.00	0.00	0.00	0.00
TMP + $LutH^+$	0	266.49	278.67	226.44	-64.41	-55.33	-736.96304	-737.74623	-737.46753	5.43	4.39	3.40	4.44
Except for F^-, other halide anions are not bound to Bo_3 as a weak Lewis acid in solution													
Bo_3 + F^-	0	140.05	155.03	102.94	-139.43	-104.60	-1415.96044	-1417.44050	-1417.43713	0.00	0.00	0.00	0.00
FBo_3^-	0	140.19	154.54	110.73	-68.39	-55.55	-1416.09367	-1417.57501	-1417.48407	-83.61	-84.40	-29.46	-28.66
Bo_3 + Cl^-	0	140.05	155.03	102.38	-125.45	-92.21	-1776.37825	-1778.09603	-1778.07380	0.00	0.00	0.00	0.00
$ClBo_3^-$	0	139.70	154.21	110.20	-68.43	-55.95	-1776.43747	-1778.15594	-1778.06647	-37.16	-37.59	4.60	5.03
Bo_3 + Br^-	0	140.05	155.03	101.66	-119.20	-87.78	-3890.26141	-3892.86699	-3892.83885	0.00	0.00	0.00	0.00
$BrBo_3^-$	0	139.50	154.18	109.55	-69.38	-56.58	-3890.30677	-3892.91280	-3892.82537	-28.46	-28.74	8.46	8.74
Bo_3 + I^-	0	239.04	271.76	176.10	-62.24	-53.37	-3526.40376	-3530.03722	-3529.83562	0.00	0.00	0.00	0.00
IBo_3^-	0	239.07	271.48	176.82	-76.86	-64.15	-3526.36787	-3529.99951	-3529.81394	22.52	23.67	13.61	12.47
Reversible binding of 3-$(CN)C_6H_4CH_2Br$ (3-NCBzBr) to borane Bo_3 via the CN group													
3-NCBzBr + Bo_3	0	213.07	232.69	162.82	-35.78	-24.96	-4253.63125	-4256.63046	-4256.40475	0.00	0.00	0.00	0.00
3-NCBzBr.Bo_3	0	213.86	233.72	177.52	-33.48	-25.35	-4253.65229	-4256.64984	-4256.40432	-13.20	-12.16	0.27	-0.77
...leading to still facile C-Br bond reduction													

3-NCBzBr + **A**	0	395.65	423.18	337.67	-52.03	-38.02	-4664.28380	-4667.71198	-4667.22844	0.00	0.00	0.00	0.00
$TMPH^+$.3-NCBzBr.HBo_3^-	0	394.43	423.48	350.15	-59.31	-46.62	-4664.26983	-4667.69404	-4667.20733	8.76	11.25	13.24	10.76
3TS2Br	231i	393.70	422.39	349.89	-55.23	-42.92	-4664.27219	-4667.69183	-4667.19964	7.28	12.64	18.07	12.71
3-NCBzH + Bo_3 + $TMPH^+Br^-$	0	395.86	423.32	323.89	-72.53	-47.17	-4664.30861	-4667.73949	-4667.28947	-15.57	-17.27	-38.30	-36.61
Alkyl halide reduction: direct reduction with HBo_3^- anion is preferred, especially upon heating													
Butyl chloride (BuCl) as model substrate: reduction with HBo_3^- encounters a sizeable barrier of 26.3 kcal/mol													
HBo_3^- + BuCl	0	221.51	239.72	173.87	-69.61	-57.08	-1934.95735	-1936.83545	-1936.64331	0.00	0.00	3.36	0.00
bTS2$^-$	427i	220.33	239.14	185.62	-74.63	-57.93	-1934.94412	-1936.81336	-1936.60687	8.30	13.86	26.23	17.30
BuH + Bo_3 + Cl^-	0	221.94	241.03	167.35	-129.61	-94.30	-1934.94073	-1936.82258	-1936.69713	10.43	8.07	-30.41	-31.42
*...reduction with ion-pair complex **A** is also possible, but disfavored upon heating due to enhanced ionization of **A**.*													
A + BuCl	0	399.61	425.53	344.82	-41.88	-31.04	-2344.93201	-2347.24089	-2346.73484	0.00	0.00	0.00	0.00
bTS2	382i	397.17	424.34	354.59	-49.94	-39.36	-2344.89839	-2347.19833	-2346.69298	21.10	26.71	26.27	20.66
BuH + Bo_3 + $TMPH^+Cl^-$	0	398.64	424.86	330.28	-61.63	-39.18	-2344.95096	-2347.26092	-2346.78800	-11.89	-12.57	-33.36	-32.68
Butyl bromide (BuBr): direct reduction with HBo_3^- anion encpunters 2.8 kcal/mol lower barrier than C-Cl bond reduction													
HBo_3^- + BuBr	0	221.07	239.38	172.74	-70.47	-57.69	-4048.82778	-4051.59299	-4051.40362	0.00	0.00	3.36	2.76
bTS2Br$^-$	405i	220.04	239.02	184.71	-70.41	-56.24	-4048.82231	-4051.57946	-4051.37171	3.44	8.50	23.38	17.72
BuH + Bo_3 + Br^-	0	221.94	241.03	166.63	-123.37	-89.86	-4048.82388	-4051.59355	-4051.46218	2.45	-0.35	-33.39	-31.19
*... reduction with ion-pair complex **A** is less favorable and disfavored upon heating.*													
A + BuBr	0	399.16	425.19	343.69	-42.74	-31.65	-4458.80245	-4461.99844	-4461.49515	0.00	0.00	0.00	0.00
bTS2Br	327i	396.26	423.97	351.83	-51.14	-40.59	-4458.76867	-4461.95592	-4461.45692	21.20	26.68	23.99	18.51
BuH + Bo_3 + $TMPH^+Br^-$	0	398.80	425.07	329.90	-62.38	-40.34	-4458.82446	-4462.02237	-4461.55190	-13.81	-15.01	-35.61	-34.41
Butyl iodide (BuI):: direct reduction with HBo_3^- anion encpunters 3.8 kcal/mol lower barrier than C-Cl bond													
HBo_3^- + BuI	0	220.74	239.12	171.95	-72.48	-59.01	-1772.30957	-1774.14759	-1773.96159	0.00	0.00	3.36	2.76
bTS2I$^-$	406i	219.81	238.84	184.20	-68.17	-55.83	-1772.30832	-1774.13872	-1773.93115	0.78	5.57	22.46	17.08
BuH + Bo_3 + I^-	0	221.94	241.03	166.21	-114.98	-84.54	-1772.31634	-1774.15941	-1774.02022	-4.25	-7.42	-33.43	-30.86
*... reduction with ion-pair complex **A** is less favorable and disfavored upon heating.*													
A + BuI	0	398.84	424.93	342.90	-44.74	-32.97	-2182.28423	-2184.55303	-2184.05312	0.00	0.00	0.00	0.00
bTS2I	300i	396.64	424.10	353.31	-52.55	-41.60	-2182.25484	-2184.51500	-2184.01524	18.45	23.87	23.77	18.35
BuH + Bo_3 + $TMPH^+I^-$	0	398.86	425.22	329.52	-62.25	-41.54	-2182.30591	-2184.57717	-2184.10920	-13.60	-15.15	-35.19	-33.65

Table S2. TPSS-D3/def2-TZVP + COSMO optimized Cartesian coordinates (in Å) in $CHCl_3$ solution. Each structure is labeled by the specific name (See Table S1), followed by the number of atoms, the total energy (in hartrees), and the detailed atomic coordinates (in double-column text list).

3-NCBzBr.Bo_3 : loose complex of 3-NCBzBr
50
Energy = -4253.526647796
C -4.4770112 -0.9435286 -0.6742570
C -4.7631682 -2.1701560 -0.0558591
C -3.1642594 -0.4741506 -0.6777320
C -5.5581065 -0.1499042 -1.3264170
C -3.7590078 -2.9221571 0.5526085
H -5.7860298 -2.5361434 -0.0522178
C -2.1562683 -1.2351893 -0.0631500
H -2.9161292 0.4703050 -1.1513563
H -6.3518896 -0.7698982 -1.7370132
H -5.1837978 0.5481075 -2.0715811
Br -6.4845502 1.0082875 0.0174594
C -2.4461954 -2.4640533 0.5569994
H -3.9990580 -3.8697843 1.0229494
C -0.8227529 -0.7612976 -0.0670657
H -1.6519043 -3.0357391 1.0241653
N 0.2667377 -0.3865624 -0.0591454
B 1.7734087 0.0972996 -0.0095737
C 1.6952400 1.7004129 -0.3087543
C 2.5099082 -0.7657887 -1.1847084
C 2.2508181 -0.2890787 1.5052559
C 0.7547326 2.5264052 0.3161992
C 2.5353642 2.4035827 -1.1766360
C 3.7341110 -1.4282416 -1.0613643
C 1.9531903 -0.8954333 -2.4611244
C 2.0007806 -1.5503834 2.0562433
C 2.9440995 0.5516027 2.3804681
C 0.6080342 3.8902876 0.1090274
F -0.0920724 1.9556445 1.2342753
C 2.4557453 3.7672494 -1.4364474
F 3.5408661 1.7314541 -1.8136608
C 4.3474205 -2.1670661 -2.0669659
F 4.4187922 -1.3387859 0.1185450
C 2.4983237 -1.6146988 -3.5147043
F 0.7718395 -0.2417491 -2.7151738
C 2.3522465 -1.9635748 3.3325815
F 1.3648764 -2.4808724 1.2681924
C 3.3339990 0.2134420 3.6718636
F 3.3040842 1.7992217 1.9548561
C 1.4746256 4.5138113 -0.7880165
H -0.1569773 4.4399500 0.6468226
H 3.1571010 4.2211218 -2.1284593
C 3.7149353 -2.2631134 -3.3045216
H 5.3015782 -2.6452543 -1.8728098
H 1.9832720 -1.6521478 -4.4686257
C 3.0272123 -1.0580089 4.1507454
H 2.1105637 -2.9681107 3.6628796
H 3.8701868 0.9384409 4.2749054
H 1.3910691 5.5800646 -0.9733485
H 4.1727443 -2.8338170 -4.1063629
H 3.3203663 -1.3463369 5.1552744

3-NCBzBr : 3-(CN)$C_6H_4CH_2$Br
16
Energy = -2937.499472916
C -0.7344925 -0.4990792 0.2640899
C -0.8069584 -1.5469545 1.1926506
C -0.9422571 0.8121873 0.6965949
C -0.4303705 -0.7760365 -1.1685875
C -1.0835792 -1.2921817 2.5350955
H -0.6446889 -2.5679286 0.8581355
C -1.2197496 1.0677493 2.0477615
H -0.8902664 1.6366063 -0.0075741
H 0.1473748 -1.6862374 -1.3127196
H 0.0329849 0.0655171 -1.6784893
Br -2.1163442 -1.1037931 -2.2038430
C -1.2927612 0.0121725 2.9729328
H -1.1337349 -2.1122487 3.2441215
C -1.4244532 2.4123253 2.4856426
H -1.5072355 0.2221099 4.0150977
N -1.5902474 3.5062143 2.8433930

3-NCBzH : 3-(CN)$C_6H_4CH_3$
16
Energy = -364.0332370445
C -0.8035948 -0.5108839 0.2223276
C -0.8552274 -1.5501340 1.1628432
C -0.9906948 0.7983224 0.6707372
C -0.5747324 -0.7980632 -1.2402421
C -1.0934319 -1.2953321 2.5142461
H -0.7038187 -2.5741937 0.8305489
C -1.2304595 1.0585856 2.0304065
H -0.9495566 1.6267113 -0.0303227
H 0.0555685 -1.6821289 -1.3739072
H -0.1000375 0.0503750 -1.7412507
H -1.5283256 -0.9919537 -1.7472919
C -1.2839974 0.0081151 2.9615339
H -1.1269272 -2.1172969 3.2228511
C -1.4165309 2.4056413 2.4680819
H -1.4665377 0.2201309 4.0094279
N -1.5684756 3.5025269 2.8243123

3TS2Br : 3-NCBzBr reduction with ion-pair **A**
81

Energy = -4664.133336526

B	2.4876251	0.0691731	-0.2490680
C	3.2988518	1.3188944	-0.9110378
C	2.1250231	0.2106277	1.3238939
C	3.2263159	-1.3045979	-0.7215088
C	4.2065406	2.1658572	-0.2677100
C	3.1797138	1.6080451	-2.2737474
C	2.1412395	-0.8058468	2.2845435
C	1.6176158	1.4081432	1.8470246
C	4.4985743	-1.6552443	-0.2586757
C	2.7454963	-2.2036056	-1.6721013
C	4.9214774	3.1926330	-0.8756631
F	4.4269898	1.9954882	1.0724491
C	3.8510051	2.6137413	-2.9578709
F	2.3224331	0.8348533	-3.0205620
C	1.7696256	-0.6669991	3.6178919
F	2.5399495	-2.0628249	1.9118208
C	1.2377256	1.6365207	3.1618538
F	1.4483852	2.4618318	0.9804792
C	5.2323282	-2.7649331	-0.6543637
F	5.0757493	-0.8370045	0.6753156
C	3.4105495	-3.3379058	-2.1274358
F	1.5026180	-1.9838582	-2.2272012
C	4.7373941	3.4162883	-2.2394513
H	5.6034311	3.7951294	-0.2843038
H	3.6809435	2.7537155	-4.0204125
C	1.3233820	0.5756536	4.0622334
H	1.8297269	-1.5233491	4.2815507
H	0.8664118	2.6120683	3.4572249
C	4.6723340	-3.6180024	-1.6066921
H	6.2118637	-2.9483460	-0.2250525
H	2.9442272	-3.9748395	-2.8720249
H	5.2822015	4.2108399	-2.7401820
H	1.0222227	0.7115037	5.0957994
H	5.2179310	-4.4949232	-1.9416629
H	1.3663642	0.0721424	-0.7904219
H	-4.4947709	0.3767879	-1.4185264
N	-5.4662187	0.1506512	-1.1056676
C	-5.4547888	-1.3425367	-0.7108202
H	-6.0607855	0.2627841	-1.9337057
C	-5.8554902	1.2348071	-0.0756220
C	-4.6562367	-1.4466963	0.5937212
C	-6.8828909	-1.8766875	-0.5875139
C	-4.7329728	-2.0599704	-1.8558854
C	-5.0280821	0.9635118	1.1873118
C	-7.3637868	1.2139030	0.1798613
C	-5.4631365	2.5673232	-0.7206564
C	-5.1413076	-0.4819081	1.6778610
H	-4.7109682	-2.4849735	0.9351936
H	-3.6022330	-1.2380849	0.3721092
H	-7.4870296	-1.6004887	-1.4582351
H	-6.8292390	-2.9681936	-0.5518713
H	-7.3908728	-1.5386087	0.3154961
H	-4.6522374	-3.1215841	-1.6078004
H	-5.2908832	-1.9710663	-2.7946353
H	-3.7263935	-1.6572863	-2.0026328
H	-5.3536166	1.6689920	1.9577823
H	-3.9760781	1.1880938	0.9681135
H	-7.6840386	0.3723165	0.7936688
H	-7.9253017	1.2005102	-0.7603631
H	-7.6250178	2.1330740	0.7111663
H	-6.0426321	2.7518157	-1.6321212
H	-5.6751513	3.3740941	-0.0141383
H	-4.3972539	2.5909605	-0.9664232
H	-6.1720308	-0.7116638	1.9709317
H	-4.5308891	-0.6077092	2.5759779
C	-0.8369351	-0.3591223	-0.0535699
C	-0.8075303	-1.7623132	-0.0289361
C	-1.1170410	-2.4580827	1.1364548
C	-1.4857042	-1.7717591	2.2898955
C	-1.5438223	-0.3680724	2.2661997
C	-1.2076658	0.3360539	1.1027121
H	-0.5024955	-2.3001339	-0.9196804
H	-1.0647677	-3.5417474	1.1501053
H	-1.2366443	1.4199640	1.0997573
C	-0.4265358	0.3793555	-1.2494852
H	-0.0346193	-0.1594370	-2.0973708
H	-0.1202765	1.4092580	-1.1403235
Br	-2.4016491	0.9579751	-2.3095676
H	-1.7292225	-2.3053620	3.2019400
C	-1.9746117	0.3465239	3.4245325
N	-2.3735462	0.9221697	4.3527732

Bo_3 : borane B(*o*-$C_6H_3F_2$)$_3$ as weak Lewis acid 34

Energy = -1316.007829334

B	-0.0002691	-0.0006596	-0.0088208
C	-0.7613403	1.3629446	-0.0814149
C	1.5628748	-0.0251225	-0.0197746
C	-0.8022077	-1.3398799	0.0753303
C	-1.9244705	1.5546556	-0.8434331
C	-0.3472740	2.5130162	0.6085401
C	2.3243285	-0.8930415	0.7787434
C	2.3400263	0.8182548	-0.8294177
C	-0.4326698	-2.5029531	-0.6182033
C	-1.9607551	-1.4949330	0.8526185
C	-2.6176958	2.7507810	-0.9407686
F	-2.3930683	0.5039271	-1.5736524
C	-1.0026094	3.7337350	0.5754971
F	0.7576221	2.4223940	1.4009849
C	3.7093954	-0.9331730	0.8044433
F	1.6632598	-1.7367076	1.6203517
C	3.7253124	0.8179378	-0.8710140
F	1.6942740	1.6776726	-1.6669085
C	-1.1247835	-3.7028366	-0.5749864
F	0.6649465	-2.4475613	-1.4240766
C	-2.6890751	-2.6690580	0.9607304
F	-2.3869608	-0.4298942	1.5881061
C	-2.1464983	3.8453124	-0.2153081
H	-3.4994151	2.8156363	-1.5683869
H	-0.6222654	4.5678440	1.1543714
C	4.4085568	-0.0674844	-0.0370460

H 4.2184789 -1.6249987 1.4660478
H 4.2466944 1.4936488 -1.5396561
C -2.2614456 -3.7782147 0.2304894
H -0.7783897 -4.5487862 -1.1579659
H -3.5644855 -2.7060832 1.5993657
H -2.6744628 4.7921215 -0.2667857
H 5.4937358 -0.0820851 -0.0420102
H -2.8177163 -4.7081841 0.2900351

$BrBo_3^-$: unstable anion $BrB(o\text{-}C_6H_3F_2)_3^-$
35
Energy = -3890.238717873
B -0.0014367 0.0031267 0.5174967
C 0.9351803 -1.2752407 0.1538140
C -1.5745007 -0.1721320 0.1453559
C 0.6372006 1.4506451 0.1422086
Br -0.0028076 0.0146667 2.7348247
C 2.0475893 -1.2569833 -0.6941337
C 0.6971279 -2.5583994 0.6710122
C -2.5705550 0.6770534 0.6525786
C -2.1091676 -1.1506802 -0.6994563
C 0.0623136 2.4016046 -0.7076948
C 1.8691252 1.8883432 0.6535735
C 2.8866413 -2.3356345 -0.9602149
F 2.3592189 -0.1018332 -1.3654510
C 1.4858753 -3.6807089 0.4597010
F -0.4208530 -2.7541927 1.4295983
C -3.9354092 0.5537475 0.4328349
F -2.1863535 1.7459333 1.4098298
C -3.4612114 -1.3407414 -0.9720627
F -1.2603687 -2.0020044 -1.3603944
C 0.5764583 3.6662715 -0.9809158
F -1.0954845 2.0915025 -1.3748769
C 2.4468850 3.1309937 0.4339976
F 2.6001615 1.0212274 1.4137049
C 2.6062679 -3.5608908 -0.3624936
H 3.7307935 -2.2016753 -1.6288454
H 1.2092101 -4.6232072 0.9209632
C -4.3862233 -0.4817795 -0.3857935
H -4.6164150 1.2677204 0.8845694
H -3.7628438 -2.1438645 -1.6366012
C 1.7810790 4.0375176 -0.3909333
H 0.0347747 4.3286182 -1.6483253
H 3.4025041 3.3647185 0.8919653
H 3.2454627 -4.4193385 -0.5461173
H -5.4480209 -0.6075158 -0.5756501
H 2.2065964 5.0178440 -0.5836303

Br^- : bromide anion
1
Energy = -2574.218173369
Br 0.0000000 0.0000000 0.0000000

bTS2Br$^-$: TS for BuBr reduction with HBo_3^-
49
Energy = -4048.738026589
B 0.8000973 -0.0075306 0.0004059
C 1.1110824 1.4227128 0.7111825
C 1.0093457 -1.3260099 0.9136953
C 1.4851484 -0.0126979 -1.4738182
H -0.4642209 -0.0021740 -0.1719895
C 1.9612458 1.6631793 1.7936841
C 0.5422204 2.5984662 0.2107364
C 1.6417620 -2.5186005 0.5447835
C 0.4429382 -1.4095159 2.1939339
C 2.8624738 0.1641325 -1.6361105
C 0.8159009 -0.1129939 -2.6926612
C 2.2189150 2.9098541 2.3543661
F 2.6153537 0.6037668 2.3643387
C 0.7419722 3.8789101 0.7116593
F -0.2877566 2.4922114 -0.8764178
C 1.7427954 -3.6588858 1.3363819
F 2.2196486 -2.6081879 -0.6940624
C 0.4990595 -2.5025225 3.0462375
F -0.2493858 -0.3186079 2.6532823
C 3.5359142 0.2431821 -2.8474309
F 3.6268636 0.2528374 -0.5014051
C 1.4091143 -0.0433972 -3.9496513
F -0.5438047 -0.3035896 -2.6834053
C 1.5952894 4.0292715 1.8047156
H 2.8957967 2.9890974 3.1990034
H 0.2419318 4.7246402 0.2512403
C 1.1654251 -3.6454049 2.6041697
H 2.2628376 -4.5308923 0.9534133
H 0.0241826 -2.4531360 4.0204658
C 2.7888359 0.1390882 -4.0218566
H 4.6125519 0.3784729 -2.8615649
H 0.7951643 -0.1306970 -4.8401958
H 1.7758667 5.0145672 2.2238419
H 1.2278571 -4.5220276 3.2417407
H 3.2809466 0.1975373 -4.9880591
C -2.1186788 0.0920076 0.0075755
H -2.0699511 0.4831471 -0.9957160
H -1.9254807 0.7719177 0.8228006
Br -4.4754758 0.9320298 0.0534588
C -2.3707088 -1.3635208 0.2728333
C -2.9262406 -2.1384048 -0.9245877
H -3.0442972 -1.4504927 1.1324616
H -1.4223321 -1.8216032 0.5871896
C -3.1356709 -3.6188424 -0.5942264
H -3.8738529 -1.6803211 -1.2306771
H -2.2309445 -2.0395704 -1.7665321
H -3.5359800 -4.1652168 -1.4553441
H -2.1907156 -4.0932531 -0.3020190
H -3.8401876 -3.7382363 0.2378720

bTS2Br : TS for BuBr reduction with $TMPH^+HBo_3^-$
79
Energy = -4458.636657743
B 2.6671506 0.0770924 -0.0359549
C 2.9524326 1.6662854 0.1766481
C 2.9620733 -0.8705689 1.2454442

C	3.2890278	-0.3993672	-1.4614552
H	1.4218857	-0.0003235	-0.1485078
C	3.8365274	2.2546324	1.0843738
C	2.3004220	2.6136302	-0.6181645
C	3.6754427	-2.0741634	1.2671714
C	2.4015844	-0.5733816	2.4955147
C	4.6171397	-0.1532396	-1.8218672
C	2.5759156	-1.0351770	-2.4763850
C	4.0555682	3.6207126	1.2272379
F	4.5688284	1.4404566	1.9070673
C	2.4582548	3.9919579	-0.5422324
F	1.4187426	2.1532899	-1.5681106
C	3.8426889	-2.8946139	2.3787916
F	4.2738544	-2.5097233	0.1147797
C	2.5203642	-1.3320825	3.6511999
F	1.6516630	0.5734412	2.5974155
C	5.2024268	-0.4742177	-3.0398352
F	5.4303942	0.4355889	-0.8890000
C	3.0795176	-1.3934172	-3.7224373
F	1.2544671	-1.3500980	-2.2523245
C	3.3524590	4.4974856	0.4018241
H	4.7664662	3.9768549	1.9659942
H	1.8974071	4.6401992	-1.2076569
C	3.2573256	-2.5143211	3.5848421
H	4.4226765	-3.8071740	2.2877707
H	2.0448640	-1.0007281	4.5683289
C	4.4136204	-1.1031565	-4.0035617
H	6.2472261	-0.2410806	-3.2171583
H	2.4361559	-1.8846891	-4.4448469
H	3.5037132	5.5690526	0.4906043
H	3.3727969	-3.1359606	4.4673753
H	4.8381599	-1.3689886	-4.9670664
C	-0.3784189	0.1007875	0.0848803
H	-0.2707490	0.0836950	-0.9886119
H	-0.0991919	1.0129197	0.5915433
Br	-2.6196050	0.8433622	-0.0759121
C	-0.5154804	-1.1689429	0.8659635
C	-1.0354925	-2.3655344	0.0678757
H	-1.1404635	-0.9814242	1.7463710
H	0.4830101	-1.4121036	1.2573549
C	-1.1373617	-3.6233106	0.9353027
H	-2.0174377	-2.1239017	-0.3561063
H	-0.3609994	-2.5480928	-0.7754062
H	-1.5069644	-4.4758769	0.3557343
H	-0.1581320	-3.8937841	1.3472405
H	-1.8212841	-3.4651725	1.7781253
H	-4.6319169	-1.6806781	0.2948376
C	-5.7193174	-1.7497524	0.1715606
C	-6.1154972	-0.9324863	-1.0659621
C	-6.4084332	-1.2813321	1.4569423
H	-5.9558355	-2.7978619	-0.0384172
N	-5.9265595	0.5550834	-0.6999053
C	-7.5520854	-1.1937571	-1.5225554
C	-5.1465674	-1.1855116	-2.2258422
C	-6.0882920	0.1904567	1.7363317
H	-7.4917706	-1.4356257	1.3915295
H	-6.0584865	-1.8916679	2.2951207
H	-4.8962024	0.7008335	-0.6292779
H	-6.2458538	1.1283971	-1.4877636
C	-6.5267782	1.1269530	0.6022764
H	-7.8851345	-0.4385572	-2.2424270
H	-7.5719156	-2.1644971	-2.0254217
H	-8.2625686	-1.2311154	-0.6965309
H	-5.1645002	-2.2503902	-2.4726777
H	-5.4414953	-0.6232836	-3.1188757
H	-4.1240188	-0.9087388	-1.9492262
H	-6.5784701	0.5303541	2.6542996
H	-5.0064233	0.3050966	1.8809646
C	-8.0466123	1.2570200	0.4813511
C	-5.9022214	2.5170156	0.7574214
H	-8.5664924	0.3027710	0.5656882
H	-8.3312153	1.7333327	-0.4630143
H	-8.3927562	1.8994184	1.2957106
H	-6.2287020	3.1895405	-0.0437863
H	-6.2246901	2.9419198	1.7118466
H	-4.8086708	2.4612722	0.7568906

bTS2I⁻ : TS for BuI reduction with HBo_3^-

49

Energy = -1772.274389080

B	1.1911518	0.0340555	-0.0086429
C	1.3239955	1.4785031	0.7269524
C	1.5659813	-1.2642215	0.8788486
C	1.8572570	0.1415010	-1.4876096
H	-0.0645455	-0.1162836	-0.1819599
C	2.1607807	1.8066920	1.7968172
C	0.5888912	2.5774630	0.2706545
C	2.3109207	-2.3768780	0.4703547
C	1.0436848	-1.4302917	2.1694302
C	3.2022125	0.4815538	-1.6595784
C	1.1870362	-0.0053540	-2.7018867
C	2.2597709	3.0626081	2.3866234
F	2.9648276	0.8320538	2.3249708
C	0.6242889	3.8602122	0.8030731
F	-0.2454882	2.3861594	-0.8014275
C	2.5512950	-3.5146555	1.2351774
F	2.8634034	-2.3807528	-0.7836421
C	1.2360816	-2.5271526	2.9966665
F	0.2477770	-0.4302067	2.6653136
C	3.8454196	0.6683285	-2.8755335
F	3.9654956	0.6325150	-0.5307726
C	1.7513914	0.1627717	-3.9627729
F	-0.1416584	-0.3506713	-2.6825475
C	1.4755903	4.0988543	1.8818534
H	2.9390058	3.2128902	3.2196207
H	0.0018501	4.6408292	0.3779841
C	2.0076216	-3.5850974	2.5154348
H	3.1496647	-4.3200911	0.8221768
H	0.7819110	-2.5475609	3.9818675
C	3.0999031	0.5058836	-4.0439685
H	4.8986318	0.9294325	-2.8972644
H	1.1400710	0.0260174	-4.8487733

H 1.5295276 5.0886215 2.3251234
H 2.1772110 -4.4620013 3.1324904
H 3.5688390 0.6460538 -5.0134639
C -1.7232848 -0.2466510 0.0573568
H -1.7566223 0.1825926 -0.9312910
H -1.5889604 0.4247479 0.8911222
I -4.3456025 0.3700842 0.2006928
C -1.7783707 -1.7298694 0.2797310
C -2.2337919 -2.5419217 -0.9353087
H -2.4184938 -1.9363201 1.1440736
H -0.7712995 -2.0614886 0.5720649
C -2.2300636 -4.0453730 -0.6431986
H -3.2396169 -2.2143934 -1.2251694
H -1.5675273 -2.3246976 -1.7784361
H -2.5333125 -4.6226971 -1.5230037
H -1.2299475 -4.3831095 -0.3449425
H -2.9216994 -4.2875025 0.1735017

bTS2I : TS for BuI reduction with $TMPH^{+}HBo_3^{-}$
79
Energy = -2182.173215212
B 2.6291573 0.1213427 -0.0209039
C 3.0540144 1.6744832 0.2188690
C 3.2061931 -0.9473842 1.0522804
C 2.7968438 -0.2567480 -1.5936138
H 1.4030578 0.1034041 0.2236611
C 4.1759511 2.1526470 0.8997025
C 2.2722801 2.7078358 -0.3060692
C 3.8347566 -2.1687662 0.7859137
C 3.0077454 -0.7512008 2.4261977
C 3.9818535 -0.0279542 -2.2991386
C 1.7910995 -0.7804108 -2.4049817
C 4.5007366 3.4932803 1.0782402
F 5.0526292 1.2458376 1.4338733
C 2.5222799 4.0683285 -0.1768630
F 1.1512071 2.3599677 -1.0231800
C 4.2441592 -3.0931472 1.7423436
F 4.0899821 -2.5116492 -0.5161522
C 3.3848486 -1.6165517 3.4430269
F 2.3713695 0.4025313 2.8155575
C 4.1823908 -0.2684754 -3.6522442
F 5.0561644 0.4531328 -1.5973489
C 1.9034583 -1.0524769 -3.7644641
F 0.5712779 -1.0696090 -1.8362007
C 3.6571956 4.4607039 0.5332641
H 5.4052408 3.7589147 1.6158889
H 1.8523780 4.7888339 -0.6345245
C 4.0161613 -2.8086267 3.0873750
H 4.7342171 -4.0087264 1.4270748
H 3.1869519 -1.3569402 4.4777435
C 3.1199524 -0.7888700 -4.3924145
H 5.1477375 -0.0611832 -4.1025660
H 1.0568519 -1.4626568 -4.3054843
H 3.8961555 5.5142075 0.6409691
H 4.3294533 -3.5106991 3.8540766
H 3.2414701 -0.9918833 -5.4521463
C -0.2719391 0.2593171 0.9168038
H -0.4207371 0.3705438 -0.1460975
H 0.2056437 1.0828554 1.4271149
I -2.5718231 1.2287152 1.4018610
C -0.2888023 -1.0854415 1.5814075
C -1.1758641 -2.1412778 0.9213975
H -0.5558963 -0.9621025 2.6371456
H 0.7505008 -1.4466979 1.5791368
C -1.0448796 -3.5046728 1.6053288
H -2.2184487 -1.8038114 0.9638616
H -0.9062941 -2.2262173 -0.1371402
H -1.6847271 -4.2521602 1.1240079
H -0.0111469 -3.8662566 1.5610289
H -1.3327150 -3.4428092 2.6614211
H -4.4389382 -1.4429262 0.8898875
C -5.3298281 -1.6992698 0.3020949
C -5.2193529 -1.0097607 -1.0642572
C -6.5801841 -1.2869743 1.0853655
H -5.3098327 -2.7801936 0.1309337
N -5.3733754 0.5051012 -0.8049867
C -6.2609507 -1.4976567 -2.0714174
C -3.8139014 -1.1613967 -1.6529391
C -6.5820845 0.2253517 1.3311751
H -7.4892799 -1.5960182 0.5566194
H -6.5888200 -1.8067638 2.0480866
H -4.5022454 0.7915933 -0.3050123
H -5.3629762 0.9939347 -1.7066787
C -6.5489132 1.0472180 0.0355955
H -6.2991393 -0.8465805 -2.9511070
H -5.9579456 -2.4935298 -2.4065741
H -7.2621579 -1.5787885 -1.6483713
H -3.5865805 -2.2240055 -1.7686822
H -3.7439123 -0.6864326 -2.6376680
H -3.0681199 -0.7176839 -0.9864048
H -7.4696749 0.5312002 1.8940398
H -5.7049161 0.4923772 1.9347359
C -7.8546161 0.9710319 -0.7577847
C -6.2001631 2.5124045 0.3138720
H -8.2487942 -0.0419983 -0.8369581
H -7.7327005 1.3836651 -1.7649467
H -8.5985074 1.5794782 -0.2362330
H -6.1690904 3.0956354 -0.6132123
H -6.9692282 2.9415363 0.9614253
H -5.2340143 2.5998896 0.8221188

bTS2^{-} : TS for BuCl reduction with HBo_3^{-}
49
Energy = -1934.900701441
B 0.3616955 -0.0576826 0.0196454
C 1.2221682 1.2349640 0.5044801
C -0.0236166 -1.1411636 1.1561696
C 1.0249750 -0.6258569 -1.3507066
H -0.7877488 0.4253109 -0.2850839
C 2.0715832 1.3173227 1.6111768
C 1.2133429 2.4142527 -0.2478659
C 0.0363365 -2.5350392 1.0462071

C	-0.5847945	-0.7370453	2.3762065
C	2.3414259	-1.0962812	-1.3695457
C	0.4370954	-0.6411951	-2.6144669
C	2.8188151	2.4338162	1.9717109
F	2.2066575	0.2208949	2.4199781
C	1.9241950	3.5720960	0.0423298
F	0.4405560	2.4414803	-1.3808023
C	-0.3693513	-3.4415003	2.0213558
F	0.5263297	-3.0900378	-0.1060726
C	-1.0113622	-1.5714215	3.3989055
F	-0.7511021	0.6077489	2.5835082
C	3.0318328	-1.5390558	-2.4892145
F	3.0125393	-1.1399224	-0.1749732
C	1.0540362	-1.0661943	-3.7875313
F	-0.8607658	-0.2141248	-2.7423121
C	2.7373553	3.5754712	1.1755590
H	3.4477221	2.3960279	2.8553794
H	1.8378957	4.4372878	-0.6066705
C	-0.8956623	-2.9490868	3.2133699
H	-0.2723922	-4.5060668	1.8346949
H	-1.4291372	-1.1453805	4.3049906
C	2.3701134	-1.5189505	-3.7181505
H	4.0543371	-1.8894634	-2.3927663
H	0.5067544	-1.0368530	-4.7240997
H	3.3078109	4.4623312	1.4346218
H	-1.2219133	-3.6339817	3.9901039
H	2.8782644	-1.8565085	-4.6164685
C	-2.2140085	1.1880841	-0.2845977
H	-1.9880745	1.3600638	-1.3237405
H	-1.8042087	1.8735455	0.4407517
Cl	-3.9575776	2.7953795	-0.5818927
C	-3.0680189	0.0346060	0.1571596
C	-3.8276813	-0.6533933	-0.9795498
H	-3.7670663	0.3990601	0.9175501
H	-2.4271108	-0.7013519	0.6618293
C	-4.6709626	-1.8260989	-0.4713903
H	-4.4658792	0.0892008	-1.4718245
H	-3.1075858	-1.0093253	-1.7259058
H	-5.2071074	-2.3157308	-1.2919634
H	-4.0410196	-2.5794815	0.0177798
H	-5.4133773	-1.4860023	0.2608276

bTS2 : TS for BuCl reduction with $TMPH^{+}HBo_3^{-}$

79

Energy = -2344.804434501

B	2.2902504	0.0520469	-0.0574966
C	2.6973194	1.6182468	0.1298587
C	2.2978866	-0.8531091	1.2867297
C	3.0862859	-0.5366000	-1.3484641
H	1.0738714	0.0687042	-0.3631082
C	3.5111959	2.1680025	1.1238567
C	2.2639236	2.5770372	-0.7908669
C	2.8093277	-2.1480786	1.4304408
C	1.6511794	-0.4161314	2.4515924
C	4.4824195	-0.5323628	-1.4199884
C	2.4976911	-1.0217576	-2.5150233
C	3.8549158	3.5115238	1.2326368
F	4.0304910	1.3369696	2.0801323
C	2.5565661	3.9347407	-0.7560041
F	1.4771641	2.1506366	-1.8343870
C	2.7365446	-2.9233083	2.5838981
F	3.4397487	-2.7331984	0.3648466
C	1.5354281	-1.1213577	3.6411706
F	1.0556802	0.8212026	2.4210716
C	5.2428668	-0.9492500	-2.5040435
F	5.1697979	-0.0941845	-0.3183698
C	3.1794587	-1.4591935	-3.6461088
F	1.1240951	-1.0917819	-2.5814919
C	3.3659696	4.4035366	0.2789842
H	4.4940344	3.8383570	2.0465515
H	2.1626581	4.5948140	-1.5218803
C	2.0943463	-2.3977347	3.7032211
H	3.1774009	-3.9148351	2.5904594
H	1.0168202	-0.6782826	4.4849187
C	4.5726826	-1.4183295	-3.6348909
H	6.3261265	-0.9081529	-2.4548564
H	2.6241489	-1.8188935	-4.5062681
H	3.6179282	5.4579808	0.3391592
H	2.0247393	-2.9808239	4.6164009
H	5.1344911	-1.7520657	-4.5020333
C	-0.6984649	0.3712337	-0.3844672
H	-0.4617242	0.3057566	-1.4348190
H	-0.4203860	1.2794148	0.1295948
Cl	-2.7135925	1.2383798	-0.8744391
C	-1.0445737	-0.8520314	0.4069180
C	-1.4155272	-2.0710185	-0.4390362
H	-1.8414796	-0.6014374	1.1174382
H	-0.1704137	-1.1002968	1.0240882
C	-1.6940353	-3.3023553	0.4268514
H	-2.2905184	-1.8338484	-1.0562261
H	-0.5913889	-2.2816015	-1.1292333
H	-1.9586652	-4.1687358	-0.1882270
H	-0.8109309	-3.5650760	1.0206015
H	-2.5199910	-3.1193448	1.1249455
H	-4.1192854	-1.2648613	0.3351259
C	-5.1902875	-1.4760042	0.4371049
C	-5.9011623	-0.9469448	-0.8155786
C	-5.7044125	-0.8446709	1.7348454
H	-5.3091216	-2.5638871	0.4545437
N	-5.8152730	0.5899554	-0.7456289
C	-7.3535401	-1.4138994	-0.9260790
C	-5.1396679	-1.3292073	-2.0893523
C	-5.5248713	0.6768321	1.7016062
H	-6.7552884	-1.1072135	1.9030366
H	-5.1442306	-1.2549369	2.5808731
H	-4.7987505	0.8163568	-0.8759826
H	-6.3112730	0.9851047	-1.5510502
C	-6.2530770	1.3438620	0.5260934
H	-7.8966608	-0.8462113	-1.6889143
H	-7.3441294	-2.4628663	-1.2350136
H	-7.8982675	-1.3490779	0.0157463
H	-5.0704009	-2.4187253	-2.1466552

H -5.6634115 -0.9732161 -2.9834748
H -4.1278908 -0.9127455 -2.0795235
H -5.8941152 1.1350221 2.6246125
H -4.4563358 0.9141456 1.6221674
C -7.7759794 1.3237206 0.6730271
C -5.7750035 2.7856706 0.3254272
H -8.1617140 0.3612981 1.0088730
H -8.2697205 1.5943043 -0.2663359
H -8.0497497 2.0728142 1.4210290
H -6.2901413 3.2579939 -0.5186329
H -6.0035381 3.3600532 1.2272361
H -4.6949829 2.8219751 0.1537728

BuBr : butyl bromide
14
Energy = -2732.019888806
C 0.2045790 1.1874797 0.2326837
H 0.2001321 1.3588563 1.3091876
H 0.6710972 2.0255383 -0.2824623
Br 1.5020028 -0.3078605 -0.0174629
C -1.1678735 0.8484627 -0.3173748
H -1.0905292 0.6201014 -1.3873029
H -1.7628569 1.7713184 -0.2343329
C -1.8882057 -0.2860882 0.4167227
H -1.2831008 -1.1981263 0.3492893
H -1.9613842 -0.0339332 1.4831455
C -3.2861808 -0.5489934 -0.1515750
H -3.7836497 -1.3633715 0.3855429
H -3.9182514 0.3435544 -0.0725658
H -3.2310465 -0.8277703 -1.2104967

BuCl : butyl chloride
14
Energy = -618.1892039884
C 0.2220921 1.1638476 0.2296404
H 0.2106294 1.3426678 1.3059746
H 0.6820457 2.0098733 -0.2807434
Cl 1.3888861 -0.2263427 -0.0123219
C -1.1579460 0.8426309 -0.3175917
H -1.0807322 0.6134564 -1.3875988
H -1.7457480 1.7690920 -0.2343417
C -1.8820243 -0.2899591 0.4162768
H -1.2791792 -1.2033404 0.3499517
H -1.9547108 -0.0373355 1.4827465
C -3.2804470 -0.5494006 -0.1514515
H -3.7804182 -1.3623812 0.3855396
H -3.9105597 0.3445863 -0.0726072
H -3.2271553 -0.8282271 -1.2104748

BuH :
14
Energy = -158.5503410499
C 0.2953551 1.0606817 0.2169789
H 0.2678684 1.3206170 1.2820235
H 0.7973365 1.8761393 -0.3153720
H 0.9113354 0.1596537 0.1102138
C -1.1179499 0.8242932 -0.3249151
H -1.0672375 0.5939017 -1.3981261
H -1.7063376 1.7479623 -0.2348019
C -1.8531209 -0.3109851 0.3974629
H -1.2642631 -1.2344404 0.3082760
H -1.9049540 -0.0800180 1.4704886
C -3.2658146 -0.5483571 -0.1455831
H -3.7683382 -1.3630223 0.3874706
H -3.8820370 0.3527587 -0.0409465
H -3.2371102 -0.8100169 -1.2101714

BuI : butyl iodide
14
Energy = -455.5534125942
C 0.1872737 1.2104379 0.2364692
H 0.1827719 1.3814401 1.3130272
H 0.6537786 2.0483475 -0.2787964
I 1.6484684 -0.4085960 -0.0230161
C -1.1809813 0.8579821 -0.3174166
H -1.1030620 0.6296090 -1.3872663
H -1.7856910 1.7753808 -0.2354774
C -1.8963568 -0.2799054 0.4155814
H -1.2865716 -1.1894673 0.3460759
H -1.9690703 -0.0299479 1.4824864
C -3.2933751 -0.5499839 -0.1517764
H -3.7849935 -1.3684230 0.3844775
H -3.9304008 0.3387187 -0.0701419
H -3.2370580 -0.8264249 -1.2112282

$ClBo_3^-$: unstable anion $ClB(o\text{-}C_6H_3F_2)_3^-$
35
Energy = -1776.408880598
B -0.0012213 0.0032839 0.5743124
C 0.9339420 -1.2753482 0.1741511
C -1.5735741 -0.1701384 0.1649037
C 0.6380644 1.4496991 0.1632746
Cl -0.0042176 0.0112882 2.5659831
C 2.0279006 -1.2576504 -0.6957881
C 0.7111197 -2.5554569 0.7023693
C -2.5747991 0.6636853 0.6840867
C -2.0991631 -1.1308653 -0.7039408
C 0.0735254 2.3832272 -0.7107139
C 1.8592646 1.9000615 0.6860528
C 2.8606436 -2.3368754 -0.9803606
F 2.3294101 -0.1006825 -1.3699312
C 1.4929250 -3.6797917 0.4733194
F -0.3884398 -2.7493952 1.4905523
C -3.9380563 0.5454425 0.4488666
F -2.1984508 1.7173467 1.4689941
C -3.4485297 -1.3162093 -0.9940224
F -1.2433331 -1.9712814 -1.3711844
C 0.5909695 3.6424650 -1.0036079
F -1.0805690 2.0621884 -1.3805552
C 2.4415224 3.1378204 0.4481650
F 2.5789918 1.0497916 1.4780595
C 2.5924868 -3.5621385 -0.3767425

H 3.6911828 -2.2033547 -1.6660347
H 1.2275648 -4.6213453 0.9433201
C -4.3800242 -0.4703964 -0.3986309
H -4.6243114 1.2469686 0.9122532
H -3.7434638 -2.1060323 -1.6773797
C 1.7877647 4.0262926 -0.4054503
H 0.0579905 4.2911839 -1.6912502
H 3.3907272 3.3814929 0.9144475
H 3.2248150 -4.4220145 -0.5770707
H -5.4397094 -0.5911299 -0.6032785
H 2.2158665 5.0025807 -0.6127313

Cl^- : chloride anion
1
Energy = -460.3767818432
Cl 0.0000000 0.0000000 0.0000000

$Col.Bo_3$: unstable adduct of collidine
54
Energy = -1682.493942293
B -0.1311368 -0.1015628 0.4151915
C 0.4897235 1.3969328 0.1227790
C 1.0528403 -1.0228053 -0.2867595
C -1.6524845 -0.3387717 -0.1740713
C -0.0443617 2.3816591 -0.7161836
C 1.7912392 1.7160222 0.5367558
C 2.0261063 -1.8273272 0.3141344
C 1.2799146 -0.8771440 -1.6641787
C -2.7301063 0.3950133 0.3386118
C -2.0788840 -1.2606415 -1.1389398
C 0.6007467 3.5574209 -1.0894936
F -1.2940909 2.2144747 -1.2403041
C 2.5018177 2.8594685 0.2109697
F 2.4229525 0.8332261 1.3779926
C 3.0739245 -2.4635459 -0.3422095
F 1.9795556 -2.0306222 1.6712360
C 2.2965305 -1.4752117 -2.3928504
F 0.4356751 -0.0625828 -2.3677748
C -4.0603797 0.2871078 -0.0362116
F -2.4607205 1.3303763 1.3054740
C -3.3878532 -1.4281575 -1.5797179
F -1.1737957 -2.1212310 -1.6995731
C 1.8877146 3.7978725 -0.6187374
H 0.0909204 4.2556807 -1.7448448
H 3.5029828 3.0029736 0.6029908
C 3.2057177 -2.2875487 -1.7165918
H 3.7672691 -3.0721657 0.2286518
H 2.3666846 -1.2965274 -3.4605187
C -4.3905307 -0.6411798 -1.0218518
H -4.8044627 0.9231775 0.4310723
H -3.5992266 -2.1758212 -2.3367811
H 2.4111880 4.7069133 -0.8975321
H 4.0139643 -2.7717720 -2.2554655
H -5.4200346 -0.7534769 -1.3468140
N -0.3040681 -0.4565661 2.0403990
C -0.6051273 -1.7586665 2.3658741
C -0.1954042 0.4477107 3.0729580
C -0.6844535 -2.1786492 3.6888184
C -0.9132837 -2.7962894 1.3260340
C -0.2719820 0.0264985 4.3976214
C -0.0339160 1.9343428 2.8901392
C -0.4931061 -1.3011466 4.7478969
H -0.9008157 -3.2258251 3.8741476
H -0.3473048 -2.6847850 0.4053607
H -0.7131502 -3.7828463 1.7493921
H -1.9775348 -2.7465984 1.0700617
H -0.1652859 0.7831626 5.1685331
H -0.4278162 2.4162130 3.7883421
H 1.0190431 2.2130820 2.8033876
H -0.5635949 2.3175781 2.0248197
C -0.5643861 -1.7432150 6.1814612
H 0.3066882 -1.3852816 6.7401080
H -1.4548474 -1.3229249 6.6638362
H -0.6122247 -2.8319106 6.2587091

$ColH^+Br^-$: ion pair of $ColH^+$ and bromide anion
22
Energy = -2941.179551137
C 0.6370046 -1.1965796 0.0018663
C 2.0244650 -1.2018400 0.0149042
C 2.7430331 -0.0005674 0.0200024
C 2.0249361 1.2010940 0.0173635
C 0.6375561 1.1964127 0.0040869
N 0.0027591 0.0000259 -0.0040199
H 2.5442973 -2.1543859 0.0246379
H 2.5451562 2.1534198 0.0285288
C -0.2071705 -2.4343632 -0.0039664
H 0.0164072 -3.0333800 -0.8926158
H 0.0207913 -3.0450445 0.8754047
H -1.2702422 -2.1811722 -0.0004146
C -0.2062230 2.4344721 -0.0014241
H -1.2689287 2.1819701 0.0327152
H 0.0449458 3.0610802 0.8600082
H -0.0061532 3.0168178 -0.9068213
H -1.0619606 0.0003152 -0.0091454
Br -3.1859106 0.0011843 -0.0140906
C 4.2454546 -0.0006889 0.0049154
H 4.6027718 0.0089180 -1.0325062
H 4.6455032 0.8866170 0.5020625
H 4.6454821 -0.8967202 0.4860350

$ColH^+HBo_3^-$: ion pair of $ColH^+$ and $HB(o\text{-}C_6H_3F_2)_3^-$
56
Energy = -1683.689057524
B -0.2541909 -0.2148593 0.1807666
C -1.6428922 -0.7862474 -0.4554900
C -0.3959309 0.0330803 1.7838254
C 0.4119481 1.0080103 -0.6718140
C -2.5451520 -0.0930434 -1.2650847
C -2.0466546 -2.1030179 -0.2188754
C 0.5413020 -0.4206968 2.7110862
C -1.4826101 0.6627741 2.3965032

C	0.8502699	0.7931892	-1.9830728
C	0.6910940	2.3065671	-0.2357628
C	-3.7118840	-0.6194556	-1.8096001
F	-2.2858405	1.2213949	-1.5552048
C	-3.1922181	-2.7087292	-0.7205613
F	-1.2502880	-2.8833536	0.5875851
C	0.4507513	-0.2998419	4.0927742
F	1.6819520	-1.0453260	2.2374026
C	-1.6586098	0.8265742	3.7648422
F	-2.4577929	1.1835377	1.5883155
C	1.5093230	1.7074972	-2.7933786
F	0.6225047	-0.4495140	-2.5328780
C	1.3429692	3.2867544	-0.9793195
F	0.3131781	2.6746425	1.0270150
C	-4.0341340	-1.9473975	-1.5318240
C	-0.6739624	0.3327379	4.6215489
C	1.7594466	2.9782743	-2.2733827
H	0.5177651	-1.1590962	0.0775562
C	2.8384124	-2.6984161	-1.3241456
C	4.0210487	-3.1382230	-1.8964966
C	5.1868242	-2.3655487	-1.8134012
C	5.1220371	-1.1396041	-1.1413453
C	3.9346093	-0.7023189	-0.5722281
N	2.8454496	-1.5008722	-0.6853821
H	4.0276683	-4.0937374	-2.4099003
H	6.0017956	-0.5107978	-1.0565874
C	1.5488753	-3.4543100	-1.3668857
H	1.7059283	-4.4328789	-1.8222720
H	1.1385688	-3.5810628	-0.3607970
H	0.8055829	-2.8990156	-1.9478591
C	3.7813393	0.6041106	0.1359646
H	3.1766728	0.4889836	1.0384469
H	4.7620111	1.0034800	0.3989659
H	3.2715404	1.3235196	-0.5158666
H	1.9332619	-1.1887215	-0.2760796
C	6.4765563	-2.8532490	-2.4074997
H	6.9874244	-3.5061191	-1.6884072
H	6.2963167	-3.4378905	-3.3134604
H	7.1461053	-2.0214218	-2.6389208
H	-4.3478391	0.0060181	-2.4278108
H	-4.9392133	-2.3857342	-1.9412534
H	-3.4128185	-3.7424059	-0.4744338
H	-2.5414037	1.3338494	4.1402983
H	-0.7811125	0.4438003	5.6962874
H	1.2399090	-0.6908042	4.7267143
H	1.5141381	4.2651896	-0.5424284
H	2.2720762	3.7230210	-2.8741654
H	1.8084073	1.4278871	-3.7981628

ColH$^+$I$^-$: ion pair of ColH$^+$ and iodide anion
22
Energy = -664.7125508351

C	0.6476751	-1.1982120	0.0039474
C	2.0346189	-1.2018987	0.0156432
C	2.7532492	-0.0004066	0.0180327
C	2.0350226	1.2013406	0.0153569
C	0.6480817	1.1981151	0.0040731
N	0.0145030	0.0000532	-0.0027237
H	2.5543598	-2.1544426	0.0263274
H	2.5550983	2.1537182	0.0249780
C	-0.1947039	-2.4364545	-0.0003289
H	0.0315697	-3.0375762	-0.8867958
H	0.0319289	-3.0438695	0.8816275
H	-1.2590056	-2.1874200	0.0002585
C	-0.1938916	2.4366399	0.0005929
H	-1.2582616	2.1879757	0.0070671
H	0.0375039	3.0465975	0.8795207
H	0.0279937	3.0350224	-0.8888667
H	-1.0406693	0.0002323	-0.0093624
I	-3.4290341	0.0007146	-0.0252768
C	4.2552095	-0.0006290	0.0010080
H	4.6115692	0.0006742	-1.0368150
H	4.6556960	0.8905867	0.4907601
H	4.6554613	-0.8931760	0.4885022

ColH$^+$: *N*-protonated 2,6-collidine
21
Energy = -366.9096052395

N	0.0000261	-0.8542024	0.0055878
H	0.0000611	-1.8721910	0.0131510
C	1.2044519	-0.2251694	-0.0017745
C	1.2036099	1.1594377	-0.0145891
C	2.4384823	-1.0700841	0.0018177
C	-0.0000779	1.8773546	-0.0183620
H	2.1548465	1.6805174	-0.0248055
C	-1.2044420	-0.2252442	-0.0014636
H	3.0443167	-0.8516342	-0.8828701
H	3.0445568	-0.8437837	0.8844123
H	2.1959706	-2.1353561	0.0066732
C	-1.2037080	1.1593375	-0.0147779
C	-0.0001625	3.3767489	-0.0033631
C	-2.4383957	-1.0702549	0.0030755
H	-2.1549824	1.6803302	-0.0249430
H	-0.8923344	3.7776518	-0.4901012
H	-0.0012937	3.7290314	1.0362135
H	0.8929337	3.7777639	-0.4882965
H	-2.1958146	-2.1354214	0.0175358
H	-3.0487214	-0.8369432	0.8808349
H	-3.0399868	-0.8590265	-0.8863076

Col : 2,6-collidine
20
Energy = -366.4654118029

N	0.0000534	-0.9367324	0.0075364
C	1.1582162	-0.2474601	0.0003620
C	1.1928562	1.1496777	-0.0119146
C	2.4302367	-1.0573894	0.0024117
C	-0.0000744	1.8770029	-0.0152018
H	2.1493715	1.6674158	-0.0229072
C	-1.1581944	-0.2475680	0.0008348
H	3.0392996	-0.8336760	-0.8811625
H	3.0401618	-0.8277778	0.8839240

H	2.1894134	-2.1222843	0.0062207
C	-1.1929502	1.1495567	-0.0119452
C	-0.0001564	3.3834798	-0.0000071
C	-2.4301578	-1.0576012	0.0037498
H	-2.1495270	1.6671939	-0.0227800
H	-0.8893883	3.7848219	-0.4949797
H	-0.0019345	3.7530862	1.0332785
H	0.8906739	3.7848881	-0.4920222
H	-2.1893182	-2.1224163	0.0171865
H	-3.0442546	-0.8207576	0.8803945
H	-3.0350605	-0.8412248	-0.8845498

cTS1 : TS for H_2 cleavage with Col/Bo_3 FLP
56
Energy = -1683.688531535

B	0.0279485	0.8369227	0.0894856
C	-0.3644576	1.2474929	1.6173622
C	0.8032493	2.0642862	-0.6478537
C	-1.1778823	0.1401268	-0.7659150
C	-1.6347278	1.5618068	2.1057282
C	0.6187253	1.3317433	2.6068886
C	2.0173820	1.9118481	-1.3175206
C	0.3655912	3.3905933	-0.6373323
C	-1.8545349	-0.9813127	-0.2729111
C	-1.5957912	0.4666844	-2.0604023
C	-1.9337116	1.9006720	3.4209321
F	-2.6910404	1.5453507	1.2332610
C	0.4098588	1.6605158	3.9408351
F	1.9197521	1.0678493	2.2429904
C	2.7552313	2.9315158	-1.9077252
F	2.5493683	0.6426804	-1.4295820
C	1.0360583	4.4703612	-1.1982477
F	-0.8386356	3.6602831	-0.0412567
C	-2.8154439	-1.7281303	-0.9395426
F	-1.5342484	-1.4109071	0.9970400
C	-2.5523629	-0.2227840	-2.8015211
F	-1.0288780	1.5424310	-2.6889491
C	-0.8932169	1.9469216	4.3483008
H	-2.9581065	2.1263011	3.6992959
H	1.2475892	1.6945524	4.6297819
C	2.2516177	4.2302594	-1.8399564
H	3.6930817	2.7061768	-2.4049617
H	0.6087053	5.4658452	-1.1353460
C	-3.1662944	-1.3365023	-2.2320787
H	-3.2718457	-2.5838923	-0.4532704
H	-2.7992890	0.1164404	-3.8022537
H	-1.0956657	2.2106217	5.3819173
H	2.8016098	5.0513525	-2.2896377
H	-3.9137571	-1.8932332	-2.7884703
H	0.8978406	-0.0240336	0.2116140
H	0.9604243	-1.4150360	-0.0140514
N	1.0639954	-2.4606648	-0.0611007
C	0.9686940	-3.0672185	-1.2684636
C	1.2463169	-3.1145563	1.1131777
C	1.0766554	-4.4495606	-1.3110975
C	0.7266937	-2.2071986	-2.4669356
C	1.3506303	-4.4958673	1.0776379
C	1.3208809	-2.2912126	2.3588618
C	1.2700599	-5.1882311	-0.1378878
H	1.0061160	-4.9485900	-2.2717121
H	1.2018463	-1.2303468	-2.3529580
H	1.1059439	-2.6991152	-3.3645774
H	-0.3509020	-2.0423261	-2.5901028
H	1.4970999	-5.0324755	2.0088151
H	0.3690785	-1.7784997	2.5306800
H	1.5485517	-2.9273278	3.2149153
H	2.0904067	-1.5189950	2.2654015
C	1.4164264	-6.6818642	-0.1848118
H	0.8070304	-7.1130202	-0.9836867
H	2.4628636	-6.9411685	-0.3902013
H	1.1397329	-7.1371240	0.7691399

cTS2Br : TS for *p*-BrBzBr reduction with **cA**
71
Energy = -7102.353251272

B	2.5494293	-0.0200263	0.1807182
C	3.8908433	0.6662959	-0.4422781
C	1.7410307	0.8633751	1.2738613
C	2.9308440	-1.5484519	0.6037526
H	1.7472914	-0.0961397	-0.7704169
C	4.7485377	1.5680942	0.1947827
C	4.3354507	0.3277828	-1.7240864
C	1.1039134	0.3930244	2.4274265
C	1.5040373	2.2299436	1.0733897
C	3.7930481	-1.8215235	1.6710384
C	2.5454122	-2.7072236	-0.0686736
C	5.9146575	2.0947593	-0.3510118
F	4.4370792	1.9892918	1.4597280
C	5.4818228	0.8084671	-2.3447300
F	3.5799752	-0.5612816	-2.4506584
C	0.3688339	1.1657429	3.3202723
F	1.1781541	-0.9419010	2.7278939
C	0.7991876	3.0756390	1.9189841
F	1.9874220	2.7996258	-0.0792453
C	4.2334209	-3.0778789	2.0635746
F	4.2417299	-0.7566870	2.4056088
C	2.9361427	-4.0032758	0.2540340
F	1.6984575	-2.5995195	-1.1513395
C	6.2819843	1.7070909	-1.6389211
H	6.5120627	2.7909585	0.2288710
H	5.7330371	0.4810954	-3.3483522
C	0.2264376	2.5281658	3.0660227
H	-0.0824749	0.6960210	4.1878441
H	0.6940836	4.1260615	1.6678919
C	3.7936754	-4.1854898	1.3370640
H	4.9008241	-3.1770138	2.9134747
H	2.5755448	-4.8383295	-0.3377995
H	7.1869646	2.1023793	-2.0902128
H	-0.3397847	3.1549826	3.7480769
H	4.1188435	-5.1838541	1.6134978
C	0.3042303	0.1001714	-1.9641814
C	-0.6296563	0.0746173	-0.8454588

H	0.7622190	-0.8141063	-2.3057543
H	0.8044292	1.0257912	-2.2087845
C	-1.0152454	-1.1406506	-0.2586752
C	-1.1231023	1.2746923	-0.3101720
C	-1.8844702	-1.1635973	0.8256817
H	-0.6024234	-2.0692396	-0.6372981
C	-1.9993351	1.2691230	0.7689498
H	-0.8130379	2.2201932	-0.7434324
C	-2.3717683	0.0456397	1.3210629
H	-2.1664849	-2.1015596	1.2903777
H	-2.3680754	2.1976037	1.1878335
Br	-3.5571753	0.0270755	2.8173928
Br	-1.1140594	0.2507092	-3.8491850
H	-3.0579093	-0.0127380	-2.6484729
N	-3.8605685	-0.1285131	-1.9967315
C	-4.4636978	0.9936605	-1.5277123
C	-4.1998853	-1.3872405	-1.6284633
C	-5.4892946	0.8447740	-0.6104238
C	-3.9976885	2.3076994	-2.0679300
C	-5.2275093	-1.5422774	-0.7105846
C	-3.4629811	-2.5223300	-2.2645868
C	-5.8905616	-0.4287747	-0.1840615
H	-5.9761271	1.7336723	-0.2240708
H	-2.9359078	2.2731798	-2.3232302
H	-4.5548583	2.5501703	-2.9807209
H	-4.1760194	3.1004023	-1.3394024
H	-5.5066598	-2.5447584	-0.4049975
H	-4.0385447	-2.9026357	-3.1166958
H	-2.4854510	-2.2022788	-2.6327075
H	-3.3390818	-3.3393658	-1.5509353
C	-6.9877628	-0.5868299	0.8269241
H	-6.5993606	-0.3500259	1.8248116
H	-7.8096203	0.1051996	0.6218165
H	-7.3701797	-1.6095122	0.8431068

FBo_3^- : anion $FB(o\text{-}C_6H_3F_2)_3^-$
35
Energy = -1416.073184679

B	-0.0036598	0.0042331	0.6744481
C	0.9328819	-1.2737563	0.2104251
C	-1.5754380	-0.1700491	0.2006704
C	0.6365276	1.4501808	0.2000355
F	-0.0072911	0.0099414	2.1253804
C	1.9334506	-1.2819375	-0.7620513
C	0.7931286	-2.5215551	0.8274784
C	-2.5899850	0.5773446	0.8084674
C	-2.0771735	-1.0382252	-0.7696564
C	0.1426793	2.3172147	-0.7752191
C	1.7909843	1.9524083	0.8102698
C	2.7470487	-2.3643544	-1.0855122
F	2.1503408	-0.1448366	-1.5025188
C	1.5602759	-3.6516015	0.5682505
F	-0.2036778	-2.6792039	1.7562117
C	-3.9507340	0.4758686	0.5426233
F	-2.2337420	1.5238177	1.7347080
C	-3.4196536	-1.2042914	-1.0990528
F	-1.1968732	-1.7987346	-1.5010910
C	0.6769976	3.5590940	-1.1077423
F	-0.9549964	1.9368377	-1.5089736
C	2.3901996	3.1776163	0.5413807
F	2.4253118	1.1714007	1.7421932
C	2.5579952	-3.5638574	-0.4023636
H	3.5016097	-2.2569039	-1.8582977
H	1.3659141	-4.5714790	1.1106418
C	-4.3679641	-0.4376962	-0.4251280
H	-4.6533531	1.1065780	1.0780492
H	-3.6993934	-1.9161993	-1.8691013
C	1.8149191	3.9943207	-0.4319104
H	0.2057618	4.1564741	-1.8817702
H	3.2872776	3.4687568	1.0786008
H	3.1771938	-4.4265663	-0.6301452
H	-5.4234794	-0.5447282	-0.6574976
H	2.2557308	4.9586006	-0.6673646

H_2 : dihydrogen
2
Energy = -1.180052220925

H	0.0279549	0.0000000	0.0000000
H	0.7720451	0.0000000	0.0000000

HBo_3^- : anion $HB(o\text{-}C_6H_3F_2)_3^-$
35
Energy = -1316.726774603

B	-0.1181709	-0.0793067	0.6656742
C	0.8719635	-1.3006432	0.2135957
C	-1.6607752	-0.2021896	0.1389891
C	0.5873308	1.3511398	0.2825204
H	-0.1892245	-0.1009459	1.8779413
C	1.5131531	-1.3846853	-1.0250935
C	1.2212544	-2.3579311	1.0555585
C	-2.6301689	0.6835243	0.6248636
C	-2.2147632	-1.1456128	-0.7287404
C	0.2349159	2.2345829	-0.7402299
C	1.6829899	1.8154944	1.0169865
C	2.4131089	-2.3690507	-1.4159716
F	1.2251630	-0.4254449	-1.9636913
C	2.1093769	-3.3858294	0.7488413
F	0.6464652	-2.4225955	2.3019495
C	-3.9842386	0.6756580	0.3162291
F	-2.2143800	1.6687036	1.4884507
C	-3.5571100	-1.2297185	-1.0931264
F	-1.3935179	-2.0898404	-1.2975606
C	0.8539430	3.4505855	-1.0156518
F	-0.8054247	1.8989366	-1.5707795
C	2.3631449	3.0109121	0.8106656
F	2.1506378	1.0272802	2.0410753
C	2.7143193	-3.3845258	-0.5072020
H	2.8543114	-2.3374454	-2.4073325
H	2.3118836	-4.1613660	1.4809425
C	-4.4523283	-0.3036858	-0.5615793
H	-4.6442688	1.4179295	0.7541053
H	-3.8780328	-2.0065797	-1.7801710

C 1.9336367 3.8416380 -0.2248269
H 0.4938085 4.0637185 -1.8359940
H 3.2030801 3.2732163 1.4463697
H 3.4120544 -4.1715057 -0.7786375
H -5.5045406 -0.3434384 -0.8276777
H 2.4392178 4.7837332 -0.4160543

HepBr : heptyl bromide
23
Energy = -2850.030810198
C 5.5874678 -0.9368069 -0.1789576
C 4.5220209 0.0214916 0.3637222
H 5.3182579 -1.9791761 0.0295369
H 5.6920054 -0.8305044 -1.2654117
H 6.5664954 -0.7448249 0.2738986
C 3.1375859 -0.2182190 -0.2494878
H 4.4549391 -0.0830033 1.4552759
H 4.8271617 1.0589397 0.1695000
C 2.0652891 0.7363002 0.2864676
H 3.2025352 -0.1145241 -1.3422118
H 2.8294243 -1.2554745 -0.0546963
H 1.9981638 0.6300925 1.3785318
H 2.3736362 1.7738678 0.0935759
C 0.6834358 0.4923438 -0.3290052
C -0.3814143 1.4473395 0.2163247
H 0.3741733 -0.5423620 -0.1339611
H 0.7428670 0.6029072 -1.4208769
C -1.7558646 1.2819998 -0.4042034
H -0.4559305 1.3516959 1.3061943
H -0.0799670 2.4860461 0.0106511
H -2.4793759 2.0030672 -0.0273026
H -1.7346925 1.3004595 -1.4938932
Br -2.5680273 -0.4852621 0.0384834

I^- : iodide anion
1
Energy = -297.7563068331
I 0.0000000 0.0000000 0.0000000

p-BrBzBr : 4-$BrC_6H_4CH_2Br$ benzyl bromide
15
Energy = -5418.666311868
C -0.7204262 -0.5107281 0.2685371
C -0.7953075 -1.5591539 1.1949087
C -1.0768532 -1.3106413 2.5363147
C -1.2852404 0.0057733 2.9447020
C -1.2155183 1.0703510 2.0475085
C -0.9339506 0.8017239 0.7100078
H -0.6306449 -2.5820550 0.8669616
H -1.1309135 -2.1250455 3.2501024
H -1.3747335 2.0882356 2.3854799
H -0.8793898 1.6248529 0.0025875
Br -1.6708472 0.3607518 4.7830985
C -0.4086158 -0.7858204 -1.1596106
H 0.1615140 -1.7001590 -1.3074642
H 0.0598404 0.0540705 -1.6676044
Br -2.0902608 -1.1016204 -2.2226744

p-BrBzCl.HBO_3^- : loose complex of *p*-BrBzCl
50
Energy = -4621.575086898
B 2.8076919 -0.1116996 -0.5110654
C 3.8447958 0.9690816 -1.1735472
C 2.2066040 0.3543069 0.9323967
C 3.4839753 -1.5991211 -0.5515520
H 1.8537912 -0.1374515 -1.2569791
C 4.6004827 1.9430708 -0.5177070
C 4.0506687 0.9902143 -2.5566140
C 2.2834237 -0.3013563 2.1619289
C 1.4191568 1.5095402 1.0106586
C 4.7834046 -1.8902012 -0.1277488
C 2.8453328 -2.7192867 -1.0856178
C -0.9015312 0.1627316 -1.9434428
C 5.4535077 2.8586697 -1.1279083
F 4.5202843 2.0264357 0.8499123
C 4.8835665 1.8633096 -3.2482159
F 3.3780380 0.0675093 -3.3207814
C 1.6699987 0.1079081 3.3433836
F 3.0131036 -1.4644859 2.2511304
C 0.7763115 1.9924432 2.1414838
F 1.2511997 2.2426152 -0.1398256
C 5.4152811 -3.1248184 -0.2175500
F 5.5105200 -0.8790351 0.4476339
C 3.3971162 -3.9908225 -1.2145934
F 1.5474396 -2.5906057 -1.5292367
C -1.3643342 0.0929195 -0.5273675
H 0.0611658 -0.3237328 -2.0883645
H -0.8799798 1.1801918 -2.3296997
Cl -2.0773958 -0.7299468 -3.0682209
C 5.5924403 2.8157887 -2.5148367
H 5.9940381 3.5784086 -0.5207874
H 4.9681181 1.7909585 -4.3281740
C 0.9079253 1.2737718 3.3296428
H 1.7883454 -0.4871205 4.2436560
H 0.1765547 2.8946034 2.0799020
C 4.7047395 -4.1900366 -0.7735060
H 6.4315850 -3.2415843 0.1458521
H 2.8108054 -4.7937733 -1.6504718
C -0.8598584 -0.8924415 0.3286059
C -2.2800798 1.0261471 -0.0282438
H 6.2498276 3.5172127 -3.0206083
H 0.4075174 1.6111798 4.2319659
H 5.1660646 -5.1698341 -0.8577216
C -1.2608514 -0.9531174 1.6618087
H -0.1308828 -1.6041928 -0.0453300
C -2.6921645 0.9834784 1.3017531
H -2.6714592 1.8014985 -0.6819965
C -2.1726660 -0.0112284 2.1270491
H -0.8519783 -1.7033518 2.3283383
H -3.3925520 1.7145582 1.6905043
Br -2.7098477 -0.0639947 3.9666780

p-BrBzCl : 4-Br$C_6H_4CH_2Cl$
15
Energy = -3304.834593415

C	-0.7318572	-0.5128793	0.2618005
C	-0.8032837	-1.5607024	1.1876343
C	-1.0786576	-1.3117349	2.5307508
C	-1.2841915	0.0047902	2.9395294
C	-1.2182525	1.0688416	2.0417328
C	-0.9417927	0.7992195	0.7028779
H	-0.6416738	-2.5839415	0.8590785
H	-1.1294625	-2.1257261	3.2452778
H	-1.3762438	2.0868388	2.3799839
H	-0.8887702	1.6221246	-0.0049744
Br	-1.6602466	0.3608442	4.7800324
C	-0.4366276	-0.7908588	-1.1757175
H	0.1456034	-1.7003305	-1.3152266
H	0.0455956	0.0486301	-1.6740182
Cl	-1.9914865	-1.0745801	-2.1259066

p-BrBzH : 4-Br$C_6H_4CH_3$
15
Energy = -2845.198601622

C	-0.7288033	-0.5147668	0.2513507
C	-0.8015715	-1.5553159	1.1864915
C	-1.0813579	-1.3087502	2.5309996
C	-1.2893394	0.0051216	2.9426283
C	-1.2199872	1.0660010	2.0433823
C	-0.9390093	0.7942357	0.7039948
H	-0.6349060	-2.5803623	0.8643010
H	-1.1319288	-2.1249888	3.2434913
H	-1.3774109	2.0853156	2.3790365
H	-0.8809370	1.6219423	0.0012704
Br	-1.6706588	0.3614334	4.7861890
C	-0.4573905	-0.7979287	-1.2050590
H	0.1563739	-1.6954881	-1.3263716
H	0.0548786	0.0423172	-1.6831646
H	-1.3959312	-0.9644614	-1.7491639

p-BrBzI : 4-Br$C_6H_4CH_2I$
15
Energy = -3142.201146561

C	-0.7045198	-0.5080853	0.2772410
C	-0.7851648	-1.5567981	1.2045880
C	-1.0737124	-1.3088187	2.5443381
C	-1.2859208	0.0072279	2.9519377
C	-1.2129373	1.0721026	2.0553605
C	-0.9231828	0.8044440	0.7196856
H	-0.6211767	-2.5799478	0.8769165
H	-1.1300681	-2.1237930	3.2573216
H	-1.3765573	2.0897622	2.3919512
H	-0.8670881	1.6280014	0.0128115
Br	-1.6826187	0.3614236	4.7894865
C	-0.3793849	-0.7808687	-1.1436395
H	0.1836370	-1.6982256	-1.2973350
H	0.0818777	0.0587808	-1.6578260
I	-2.2145303	-1.1346699	-2.3499824

TMP.Bo_3 : unstable N..B adduct of TMP and Bo_3
63
Energy = -1725.402884447

B	0.2823631	0.0252145	-0.0019820
C	0.6670398	1.6167348	-0.2088058
C	1.0884664	-0.6900166	1.2545204
C	0.7412458	-0.9604589	-1.2317179
C	1.2028521	2.2327060	-1.3502574
C	0.4477301	2.5556232	0.8100098
C	1.0113465	-2.0801133	1.4588475
C	2.1231143	-0.1307744	2.0226243
C	2.1024643	-0.9763203	-1.5796255
C	0.0353911	-1.9674072	-1.8900519
C	1.5145548	3.5829411	-1.4709871
F	1.4167424	1.4952972	-2.4787880
C	0.7151532	3.9132415	0.7711608
F	-0.1077760	2.0938003	1.9901009
C	1.7773735	-2.8369261	2.3293754
F	0.0639250	-2.7836466	0.7592877
C	2.9336113	-0.8204556	2.9207399
F	2.4305721	1.1936791	1.9019299
C	2.6964816	-1.8106990	-2.5137882
F	2.9399471	-0.1056058	-0.9358561
C	0.5490080	-2.8411442	-2.8410115
F	-1.2850229	-2.1465773	-1.5765032
C	1.2698333	4.4325824	-0.3967935
H	1.9282450	3.9461086	-2.4056321
H	0.5010677	4.5308866	1.6363559
C	2.7557186	-2.1889912	3.0812011
H	1.6016616	-3.9045273	2.4052647
H	3.6971889	-0.2731730	3.4632304
C	1.9001716	-2.7530784	-3.1628929
H	3.7588951	-1.7190762	-2.7125501
H	-0.1047133	-3.5780790	-3.2952403
H	1.5015718	5.4901797	-0.4704037
H	3.3764337	-2.7472075	3.7747243
H	2.3327750	-3.4213634	-3.9006104
N	-1.5462967	0.3044275	0.3017042
C	-2.4319823	0.7688206	-0.9363215
H	-1.3520055	1.2011813	0.7435892
C	-2.4169096	-0.3429368	1.4481364
C	-3.5210659	-0.2579984	-1.3150454
C	-3.0721807	2.1418980	-0.6254957
C	-1.5949199	1.0010772	-2.2014267
C	-3.3108090	-1.4423359	0.8737297
C	-3.2557678	0.7649413	2.1245723
C	-1.5639887	-0.9263065	2.5769582
C	-4.2877760	-0.9066247	-0.1667664
H	-4.2127184	0.2814405	-1.9737402
H	-3.0621111	-1.0408133	-1.9192073
H	-2.3623019	2.8091014	-0.1231845
H	-3.3369779	2.6073782	-1.5799061
H	-3.9825306	2.0842447	-0.0309594
H	-2.3023017	1.0774572	-3.0343353
H	-1.0448534	1.9397168	-2.1521782

H	-0.9023892	0.1933121	-2.4213229
H	-3.8500206	-1.8952205	1.7142147
H	-2.6752529	-2.2189912	0.4366181
H	-3.7181225	0.3348118	3.0175750
H	-2.6162194	1.5929024	2.4479530
H	-4.0564298	1.1627636	1.5081558
H	-0.7985247	-0.2297798	2.9222888
H	-2.2413496	-1.1269823	3.4130523
H	-1.1069559	-1.8691348	2.2986850
H	-4.9809498	-0.1944279	0.2955314
H	-4.9023233	-1.7222466	-0.5637081

$TMPH^{+}$.3-NCBzBr.HBo_3^{-} : loose complex
81
Energy = -4664.135103832

B	2.4613807	0.0943287	-0.4084011
C	3.3440283	1.2640318	-1.1380599
C	2.1153056	0.3757799	1.1573327
C	3.1788796	-1.3313130	-0.7562670
C	4.2746110	2.1222166	-0.5456515
C	3.2484081	1.4651672	-2.5185689
C	2.1457896	-0.5364729	2.2153805
C	1.6095310	1.6169059	1.5648832
C	4.4468152	-1.6795496	-0.2807399
C	2.6631827	-2.2935193	-1.6238402
C	5.0326122	3.0799897	-1.2126987
F	4.4737366	2.0427488	0.8078037
C	3.9636678	2.3962514	-3.2624506
F	2.3699466	0.6760545	-3.2244290
C	1.7867805	-0.2670129	3.5333793
F	2.5459674	-1.8259310	1.9678428
C	1.2391568	1.9754469	2.8532952
F	1.4352604	2.5822485	0.5989920
C	5.1464592	-2.8380856	-0.5907387
F	5.0602469	-0.8051448	0.5768246
C	3.2905383	-3.4809946	-1.9899501
F	1.4205931	-2.0863766	-2.1880042
C	4.8721637	3.2150348	-2.5909953
H	5.7285078	3.6984020	-0.6546478
H	3.8092938	2.4681885	-4.3343629
C	1.3383964	1.0114863	3.8564247
H	1.8575145	-1.0530058	4.2784055
H	0.8671863	2.9750202	3.0528095
C	4.5517703	-3.7519741	-1.4623441
H	6.1268436	-3.0120191	-0.1588776
H	2.7977982	-4.1642444	-2.6743031
H	5.4509890	3.9527001	-3.1386997
H	1.0465278	1.2496168	4.8742541
H	5.0693341	-4.6686260	-1.7289458
H	1.3755679	0.0966362	-0.9593730
H	-4.5476533	0.2169638	-1.3200229
N	-5.5067305	-0.0070107	-0.9849560
C	-5.4568076	-1.4603437	-0.4578629
H	-6.1038401	0.0123946	-1.8188541
C	-5.9328240	1.1536142	-0.0553658
C	-4.6722195	-1.4277695	0.8581999
C	-6.8731262	-2.0204981	-0.3025288
C	-4.7006426	-2.2517091	-1.5294048
C	-5.1124349	1.0161315	1.2330294
C	-7.4420084	1.1097123	0.1851267
C	-5.5687230	2.4353328	-0.8097033
C	-5.1894856	-0.3826526	1.8491274
H	-4.7096578	-2.4326282	1.2900613
H	-3.6200241	-1.2185176	0.6307480
H	-7.5046168	-1.7567928	-1.1573469
H	-6.8008511	-3.1107586	-0.2671474
H	-7.3636404	-1.6899048	0.6134222
H	-4.5854951	-3.2828736	-1.1858513
H	-5.2513512	-2.2672902	-2.4764014
H	-3.7053893	-1.8324985	-1.7047579
H	-5.4654187	1.7770245	1.9354092
H	-4.0647515	1.2516319	1.0056068
H	-7.7539987	0.2713729	0.8070991
H	-7.9915031	1.0732794	-0.7615688
H	-7.7243256	2.0318978	0.7001720
H	-6.1408892	2.5257060	-1.7395482
H	-5.8098723	3.2939809	-0.1776597
H	-4.5005507	2.4704197	-1.0442649
H	-6.2153179	-0.6123560	2.1588641
H	-4.5795069	-0.4112513	2.7561728
C	-0.9838730	-0.2323219	-0.1670662
C	-0.8617493	-1.6196217	-0.0092668
C	-1.0475541	-2.2118501	1.2381352
C	-1.3886679	-1.4361070	2.3414843
C	-1.5421613	-0.0486871	2.1847963
C	-1.3228764	0.5526493	0.9375670
H	-0.5735191	-2.2259727	-0.8607555
H	-0.9172565	-3.2827840	1.3535734
H	-1.4083427	1.6295691	0.8369542
C	-0.6986227	0.4065168	-1.4729778
H	-0.1935787	-0.2214186	-2.1962407
H	-0.2720701	1.4010699	-1.4115063
Br	-2.4990802	0.8221407	-2.4688544
H	-1.5358945	-1.8868901	3.3165415
C	-1.9516513	0.7529506	3.2925258
N	-2.3403754	1.3962631	4.1799152

$TMPH^{+}Br^{-}$: ion pair of $TMPH^{+}$ and bromide anion
31
Energy = -2984.132618144

H	-4.1573809	-0.8799956	-1.3306247
N	-5.2011129	-0.9495033	-1.1131886
C	-5.3305335	-2.0420915	-0.0394474
H	-5.6569502	-1.2741393	-1.9717266
C	-5.6618832	0.4875568	-0.8200111
C	-4.6707558	-1.4851064	1.2302808
C	-6.7931333	-2.4421629	0.1719165
C	-4.5482429	-3.2418741	-0.5854267
C	-4.9832994	0.9026792	0.4933394
C	-7.1889168	0.5797390	-0.7606288
C	-5.1464882	1.3261874	-1.9950752
C	-5.2052320	-0.1045130	1.6270426

H	-4.8267464	-2.2128502	2.0337174
H	-3.5907410	-1.4148536	1.0497824
H	-7.2980875	-2.6189443	-0.7838319
H	-6.8064882	-3.3800994	0.7344322
H	-7.3630139	-1.7058382	0.7387717
H	-4.5443637	-4.0322788	0.1705501
H	-5.0210810	-3.6388761	-1.4912747
H	-3.5156150	-2.9604874	-0.8139714
H	-5.3638166	1.8924845	0.7667429
H	-3.9068737	1.0003230	0.3040628
H	-7.6091586	0.1728509	0.1591538
H	-7.6504519	0.0714432	-1.6140415
H	-7.4635509	1.6371325	-0.8142575
H	-5.6323842	1.0290807	-2.9318311
H	-5.3839302	2.3771876	-1.8073462
H	-4.0628458	1.2181184	-2.1034006
H	-6.2678825	-0.1616727	1.8925949
H	-4.6798011	0.2408239	2.5231325
Br	-2.0082138	-0.6724468	-1.5718430

$TMPH^+Cl^-$: ion pair of $TMPH^+$ and chloride anion

31

Energy = -870.2975199493

H	-4.1396506	-0.8783609	-1.3319643
N	-5.1949214	-0.9490485	-1.1141529
C	-5.3250501	-2.0395301	-0.0424300
H	-5.6529095	-1.2733090	-1.9714051
C	-5.6555150	0.4852693	-0.8215949
C	-4.6668740	-1.4843998	1.2292343
C	-6.7866454	-2.4441288	0.1699298
C	-4.5396473	-3.2389194	-0.5866398
C	-4.9794892	0.9027370	0.4927121
C	-7.1826996	0.5818104	-0.7635841
C	-5.1372386	1.3254137	-1.9949987
C	-5.2026097	-0.1044145	1.6263063
H	-4.8234075	-2.2123466	2.0324768
H	-3.5872912	-1.4125771	1.0483456
H	-7.2905565	-2.6249087	-0.7857197
H	-6.7978368	-3.3806469	0.7351584
H	-7.3596108	-1.7080019	0.7341582
H	-4.5352123	-4.0298863	0.1689024
H	-5.0111847	-3.6366009	-1.4930569
H	-3.5085099	-2.9531363	-0.8147566
H	-5.3610042	1.8923676	0.7655552
H	-3.9030077	0.9990516	0.3046019
H	-7.6050764	0.1728122	0.1544055
H	-7.6444915	0.0768660	-1.6189537
H	-7.4553313	1.6400288	-0.8142041
H	-5.6219271	1.0289330	-2.9327886
H	-5.3743090	2.3767185	-1.8078578
H	-4.0540613	1.2136267	-2.1004483
H	-6.2659529	-0.1626936	1.8893709
H	-4.6793031	0.2413597	2.5235850
Cl	-2.1976508	-0.6862119	-1.5325940

$TMPH^+HBo_3^-$ (**A**): ion pair of $TMPH^+$ and HBo_3^-

65

Energy = -1726.639265607

B	-0.9911784	-0.0264045	-0.1481487
C	-0.8347054	-1.0221275	1.1385965
C	-1.6699754	1.4239501	0.1718269
C	-1.7321388	-0.6581303	-1.4539203
C	-1.2050595	-2.3687665	1.2215165
C	-0.1624941	-0.6075603	2.2922035
C	-1.4782569	2.4965452	-0.7043640
C	-2.5028346	1.7602304	1.2415226
C	-3.1136771	-0.8544756	-1.5243433
C	-1.0884531	-0.9834943	-2.6464696
C	-0.9555963	-3.2142954	2.2996612
F	-1.8515710	-2.9464191	0.1626504
C	0.1303563	-1.3752475	3.4096550
F	0.2944699	0.6991593	2.3273043
C	-2.0090071	3.7725818	-0.5661574
F	-0.6881255	2.2831563	-1.8116700
C	-3.0759897	3.0092044	1.4574981
F	-2.8017743	0.7959826	2.1680023
C	-3.8135340	-1.3134114	-2.6319391
F	-3.8478810	-0.5870913	-0.3983924
C	-1.7063730	-1.4494432	-3.8022801
F	0.2826912	-0.8471328	-2.7128799
C	-0.2792241	-2.7094987	3.4071329
H	-1.2879795	-4.2462682	2.2553944
H	0.6551899	-0.9351260	4.2512756
C	-2.8212447	4.0267326	0.5391542
H	-1.7919492	4.5346578	-1.3074919
H	-3.7099597	3.1668582	2.3240635
C	-3.0908327	-1.6127094	-3.7881573
H	-4.8907210	-1.4345914	-2.5822503
H	-1.1125773	-1.6740585	-4.6823425
H	-0.0727192	-3.3471110	4.2608176
H	-3.2572591	5.0109038	0.6808280
H	-3.6051652	-1.9740891	-4.6734425
H	0.1554588	0.2273507	-0.5199780
H	1.5338813	0.1233459	-0.0026690
N	2.5087837	0.1222926	0.4004041
C	3.1961069	-1.1806405	-0.0559390
H	2.3633915	0.0798556	1.4151871
C	3.1251701	1.4941521	0.0569546
C	3.5475156	-1.0268134	-1.5426343
C	4.4189107	-1.4664911	0.8190753
C	2.1564271	-2.2884871	0.1350904
C	3.4353767	1.4792465	-1.4451731
C	4.3608521	1.7585387	0.9200366
C	2.0465298	2.5311768	0.3821893
C	4.2820471	0.2759737	-1.8678651
H	4.1479908	-1.8973348	-1.8264329
H	2.6200208	-1.0709554	-2.1242693
H	4.1753939	-1.3734655	1.8831497
H	4.7284466	-2.4994839	0.6384137
H	5.2673266	-0.8194750	0.5953983
H	2.5886277	-3.2325949	-0.2080125
H	1.8749427	-2.4011776	1.1873577

H	1.2564334	-2.0851511	-0.4499430
H	3.9394760	2.4204413	-1.6872034
H	2.4863762	1.4691933	-1.9971725
H	4.6259090	2.8138457	0.8112129
H	4.1480722	1.5764315	1.9788275
H	5.2271293	1.1648518	0.6286799
H	1.8212422	2.5499366	1.4521255
H	2.4176458	3.5178007	0.0910581
H	1.1249251	2.3286519	-0.1666061
H	5.2624483	0.3029930	-1.3780542
H	4.4702331	0.3240751	-2.9448989

$TMPH^+I^-$: ion pair of $TMPH^+$ and I^-
31
Energy = -707.6660012153

H	-4.1719922	-0.8834463	-1.3359094
N	-5.2086365	-0.9507184	-1.1126140
C	-5.3376036	-2.0439317	-0.0366215
H	-5.6676525	-1.2754343	-1.9695032
C	-5.6698591	0.4880279	-0.8178253
C	-4.6699589	-1.4854400	1.2279705
C	-6.8004143	-2.4375479	0.1791768
C	-4.5629815	-3.2469914	-0.5852787
C	-4.9922037	0.9020853	0.4959019
C	-7.1962117	0.5785353	-0.7615987
C	-5.1549641	1.3267626	-1.9925530
C	-5.2096149	-0.1077747	1.6281734
H	-4.8158715	-2.2137420	2.0320739
H	-3.5917951	-1.4097557	1.0396303
H	-7.3100115	-2.6109468	-0.7741846
H	-6.8129772	-3.3766621	0.7388779
H	-7.3651229	-1.7019085	0.7510106
H	-4.5616397	-4.0376898	0.1696140
H	-5.0383406	-3.6403268	-1.4907839
H	-3.5284612	-2.9735576	-0.8140845
H	-5.3756145	1.8895004	0.7717656
H	-3.9164393	1.0047754	0.3064962
H	-7.6186488	0.1760234	0.1584297
H	-7.6561095	0.0685787	-1.6142939
H	-7.4689525	1.6357359	-0.8196099
H	-5.6366057	1.0271497	-2.9300995
H	-5.3955578	2.3767586	-1.8064454
H	-4.0706763	1.2249265	-2.0987362
H	-6.2711585	-0.1693379	1.8946558
H	-4.6839421	0.2376144	2.5234598
I	-1.7789580	-0.6533891	-1.6095017

$TMPH^+$: *N*-protonated TMP base
30
Energy = -409.8608774370

N	0.0000468	-0.8733783	-0.4076635
H	0.0003230	-1.8342685	-0.0478344
H	-0.0002504	-0.9595636	-1.4302983
C	1.3504371	-0.2140321	-0.0276428
C	1.2571788	1.2673310	-0.4149589
C	1.6329908	-0.4295824	1.4594626
C	2.3958613	-0.9463691	-0.8729448
C	0.0000853	1.9561777	0.1233414
H	2.1629950	1.7583916	-0.0461143
H	1.2730375	1.3488662	-1.5099532
C	-1.3502428	-0.2139525	-0.0275484
H	1.5056118	-1.4803330	1.7404267
H	2.6755865	-0.1590136	1.6453967
H	1.0082309	0.1870570	2.1054351
H	3.3767386	-0.5021923	-0.6856229
H	2.4478969	-2.0088351	-0.6116414
H	2.1791517	-0.8507236	-1.9427487
C	-1.2568695	1.2672923	-0.4151214
H	-0.0002169	1.9612489	1.2189777
H	0.0003832	3.0033502	-0.1923874
C	-1.6332912	-0.4295201	1.4595231
H	-2.1626352	1.7587564	-0.0466526
H	-1.2727475	1.3483867	-1.5101756
H	-2.6760568	-0.1592074	1.6448809
H	-1.5058663	-1.4802814	1.7404111
H	-1.0091273	0.1870575	2.1061729
C	-2.3957747	-0.9464882	-0.8727064
H	-2.4478645	-2.0088280	-0.6109254
H	-3.3766156	-0.5021613	-0.6856003
H	-2.1790023	-0.8513868	-1.9425537

TMP : 2,2,6,6-tetramethylpiperidine base
29
Energy = -409.4106549065

N	0.0000615	-0.8389435	-0.4426625
H	-0.0000470	-1.8287692	-0.1932031
C	1.2879114	-0.2343657	-0.0314387
C	1.2525138	1.2580455	-0.4061358
C	1.6422941	-0.4128196	1.4639836
C	2.3684351	-0.9441014	-0.8609180
C	0.0006575	1.9618708	0.1242024
H	2.1630267	1.7413544	-0.0316824
H	1.2645981	1.3367518	-1.5015539
C	-1.2878967	-0.2344041	-0.0316102
H	1.5366285	-1.4642091	1.7553539
H	2.6819195	-0.1135470	1.6429902
H	1.0059405	0.1864779	2.1186705
H	3.3571409	-0.5182841	-0.6562113
H	2.4027476	-2.0132436	-0.6161300
H	2.1479127	-0.8410027	-1.9275302
C	-1.2523712	1.2585693	-0.4041507
H	0.0016920	1.9654589	1.2217038
H	0.0003582	3.0123478	-0.1899520
C	-1.6426202	-0.4148636	1.4635508
H	-2.1621630	1.7415816	-0.0276237
H	-1.2663440	1.3386967	-1.4994144
H	-2.6823007	-0.1159966	1.6428803
H	-1.5367771	-1.4665904	1.7536555
H	-1.0063799	0.1837295	2.1189966
C	-2.3684862	-0.9424446	-0.8624448
H	-2.4029029	-2.0120407	-0.6195562
H	-3.3571071	-0.5169342	-0.6566799

H -2.1484490 -0.8375109 -1.9291307

TS1 : TS for H_2 cleavage with TMP/Bo_3 FLP
65
Energy = -1726.603722349
B -1.3587196 -0.0879436 -0.0181756
C -1.0785646 -1.6326671 0.1302955
C -1.5793492 0.8110813 1.2636673
C -1.7849984 0.5224374 -1.4155816
C -1.5859103 -2.6151950 -0.7330890
C -0.2724069 -2.1644371 1.1498107
C -1.1901139 2.1562026 1.3238579
C -2.2153431 0.3695808 2.4309228
C -2.9042659 1.3521024 -1.5724368
C -1.0971509 0.2981021 -2.6153820
C -1.3290045 -3.9757749 -0.6304273
F -2.4208951 -2.2325209 -1.7407034
C 0.0324008 -3.5063405 1.3106101
F 0.2801709 -1.3011832 2.0484988
C -1.3629704 2.9894863 2.4183446
F -0.5695681 2.6934291 0.2317641
C -2.4383572 1.1472822 3.5579225
F -2.6840546 -0.9123325 2.4669927
C -3.3082606 1.9266013 -2.7696406
F -3.6884780 1.5987656 -0.4820936
C -1.4273126 0.8516598 -3.8424587
F -0.0058333 -0.5194023 -2.5827514
C -0.5059293 -4.4183456 0.4029638
H -1.7718615 -4.6613838 -1.3444380
H 0.6742052 -3.8202593 2.1264162
C -1.9976610 2.4702691 3.5462966
H -1.0115431 4.0145494 2.3780113
H -2.9474461 0.7205456 4.4151998
C -2.5503770 1.6762556 -3.9123637
H -4.1960658 2.5489042 -2.7953047
H -0.8230557 0.6300831 -4.7152927
H -0.2861967 -5.4764261 0.5041712
H -2.1541067 3.0997543 4.4165510
H -2.8392038 2.1180243 -4.8607585
H 0.3862146 0.4544123 -0.2357729
H 1.0923308 0.1648465 -0.0256372
N 2.9252078 -0.2621321 0.4839997
C 3.5416162 -0.8704746 -0.7216409
H 2.8537185 -0.9513373 1.2329951
C 3.4161527 1.0307025 1.0246823
C 3.5086833 0.1943373 -1.8327138
C 4.9754067 -1.4072826 -0.5093641
C 2.6486338 -2.0602284 -1.1015136
C 3.3843882 2.0460496 -0.1315042
C 4.8195736 0.9649366 1.6679053
C 2.4206659 1.4441189 2.1181792
C 4.1092419 1.5295956 -1.3792813
H 4.0382541 -0.1921003 -2.7116468
H 2.4625569 0.3523523 -2.1220382
H 5.0214580 -2.0288010 0.3920279
H 5.2612560 -2.0288498 -1.3655432
H 5.7159508 -0.6110442 -0.4145487
H 3.0128476 -2.5274028 -2.0226983
H 2.6615746 -2.8190710 -0.3097193
H 1.6164421 -1.7382479 -1.2521679
H 3.8233257 2.9904962 0.2112394
H 2.3344309 2.2435290 -0.3829733
H 5.0137008 1.8957413 2.2129741
H 4.8732655 0.1354685 2.3817781
H 5.6162430 0.8368481 0.9330960
H 2.4194856 0.7123181 2.9351122
H 2.6996975 2.4178794 2.5341858
H 1.4076407 1.5086108 1.7176518
H 5.1814537 1.4147492 -1.1748455
H 4.0253064 2.2659355 -2.1871028

TS2Br : TS for p-BrBzBr reduction with ion pair **A**
80
Energy = -7145.299979305
B 2.6480082 0.0518486 -0.4015785
C 3.6764038 1.0301764 -1.2051921
C 2.0841529 0.6165669 1.0096692
C 3.2963713 -1.4438907 -0.3948073
C 4.5784626 1.9417722 -0.6481509
C 3.7732314 0.9742038 -2.5990417
C 1.8390924 -0.1249617 2.1707482
C 1.6572089 1.9444003 1.1451813
C 4.4388873 -1.7476662 0.3527824
C 2.8719529 -2.5233631 -1.1683020
C 5.4787658 2.7249711 -1.3632667
F 4.5958379 2.1013747 0.7113910
C 4.6382466 1.7215836 -3.3888575
F 2.9426865 0.1050763 -3.2650482
C 1.2983365 0.3723095 3.3516810
F 2.1332863 -1.4631214 2.1760161
C 1.1245673 2.5251014 2.2879322
F 1.7434344 2.7596244 0.0421071
C 5.1030192 -2.9663867 0.3685778
F 4.9512854 -0.7588044 1.1493818
C 3.4747766 -3.7768130 -1.2147778
F 1.7557903 -2.3755315 -1.9635039
C 5.5050517 2.6102321 -2.7525534
H 6.1383214 3.4044222 -0.8329922
H 4.6279522 1.6017604 -4.4673331
C 0.9481418 1.7194617 3.4118273
H 1.1521205 -0.2944425 4.1949438
H 0.8428811 3.5729893 2.2805381
C 4.6072076 -3.9958493 -0.4329176
H 5.9814631 -3.0968700 0.9922035
H 3.0605460 -4.5512032 -1.8522462
H 6.1973835 3.2093069 -3.3363305
H 0.5254660 2.1338975 4.3219329
H 5.1016158 -4.9624163 -0.4477095
H 1.6242360 0.0009221 -1.1099083
H -4.0682924 0.1357436 -2.6780194
N -5.0756150 -0.0415229 -2.4521959
C -5.0991514 -1.3107889 -1.5738321

H	-5.5326044	-0.2538488	-3.3452949
C	-5.6391367	1.2922212	-1.9172123
C	-4.4994687	-0.9167209	-0.2196127
C	-6.5189853	-1.8696487	-1.4671522
C	-4.2001172	-2.3191155	-2.2971228
C	-4.9943638	1.5218465	-0.5437262
C	-7.1677158	1.2486507	-1.8631473
C	-5.1938870	2.3572416	-2.9241315
C	-5.1485900	0.3239012	0.3970336
H	-4.5848161	-1.7797006	0.4477707
H	-3.4296150	-0.7248661	-0.3606437
H	-6.9961321	-1.9356560	-2.4507428
H	-6.4487891	-2.8829141	-1.0620883
H	-7.1590984	-1.2894651	-0.8026476
H	-4.1144672	-3.2173245	-1.6799324
H	-4.6260107	-2.6084868	-3.2643071
H	-3.1983268	-1.9095693	-2.4577340
H	-5.4418618	2.4233880	-0.1134803
H	-3.9257515	1.7272141	-0.6911840
H	-7.5518196	0.6461770	-1.0402928
H	-7.5872585	0.8734068	-2.8025690
H	-7.5262590	2.2722121	-1.7235459
H	-5.6543370	2.1917283	-3.9045927
H	-5.5128655	3.3376169	-2.5600772
H	-4.1056209	2.3656784	-3.0375657
H	-6.2052967	0.1417068	0.6243637
H	-4.6591078	0.5461169	1.3496524
C	-0.7016902	-0.1434875	-0.5779674
C	-0.7840957	-1.4848192	-0.1714200
C	-1.3020598	-1.8201422	1.0741461
C	-1.7538203	-0.7995154	1.9097966
C	-1.6921474	0.5406324	1.5336279
C	-1.1613386	0.8602544	0.2894011
H	-0.4055475	-2.2647061	-0.8231745
H	-1.3466829	-2.8547066	1.3943733
H	-2.0308366	1.3184676	2.2072820
H	-1.0927922	1.9006020	-0.0124751
Br	-2.4865215	-1.2486060	3.6144224
C	-0.0801191	0.2078961	-1.8473498
H	0.3422171	-0.5664222	-2.4674781
H	0.2876902	1.2122062	-1.9929301
Br	-1.8793241	0.5934521	-3.3252564

TS2Cl^{-} : TS for *p*-BrBzCl reduction with HBo_3^-
50
Energy = -4621.557149725

B	1.4597666	0.0671256	0.0996253
C	2.8126304	0.8873609	-0.2779462
C	0.2831728	0.8914194	0.8362021
C	1.9058977	-1.3494126	0.7661772
H	0.9160137	-0.2041510	-1.0332984
C	3.3574602	1.9697223	0.4202797
C	3.6144808	0.4907749	-1.3532596
C	-0.5926293	0.3905287	1.8066030
C	-0.0517253	2.1986481	0.4579207
C	2.4954754	-1.3846921	2.0343859
C	1.8513300	-2.6112319	0.1750391
C	0.0063437	-0.2792673	-2.3996775
C	4.5478320	2.6151706	0.1022692
F	2.6877503	2.4552064	1.5103512
C	4.8100144	1.0828735	-1.7414984
F	3.1958682	-0.5795857	-2.1013866
C	-1.6435597	1.0915029	2.3867955
F	-0.4369125	-0.9004207	2.2353704
C	-1.0676097	2.9733232	0.9990663
F	0.6622090	2.7732762	-0.5634185
C	2.9762477	-2.5154424	2.6795060
F	2.6033134	-0.1989053	2.7120916
C	2.3082976	-3.7944211	0.7482869
F	1.3010758	-2.7355819	-1.0772260
C	-1.2780588	-0.3560827	-1.7188481
H	0.5708482	-1.1665240	-2.6273442
H	0.4104029	0.6775860	-2.6899959
Cl	-0.7987824	-0.4044677	-4.6877133
C	5.2788942	2.1642007	-0.9960301
H	4.8827489	3.4506205	0.7085781
H	5.3495934	0.6990920	-2.6011193
C	-1.8741220	2.4045162	1.9831985
H	-2.2668800	0.6028325	3.1280381
H	-1.2303318	3.9814918	0.6327486
C	2.8782121	-3.7406260	2.0182656
H	3.4113236	-2.4298582	3.6698796
H	2.2151189	-4.7266903	0.2008088
C	-1.7436543	-1.5738427	-1.1987511
C	-2.0380344	0.8050474	-1.5100206
H	6.2099757	2.6518350	-1.2688429
H	-2.6900204	2.9736183	2.4178798
H	3.2441603	-4.6471325	2.4908466
C	-2.9275979	-1.6333208	-0.4721576
H	-1.1585657	-2.4754918	-1.3448178
C	-3.2264537	0.7639292	-0.7898781
H	-1.6918958	1.7489417	-1.9182502
C	-3.6491964	-0.4575382	-0.2723098
H	-3.2759736	-2.5721443	-0.0564453
H	-3.8011422	1.6662276	-0.6176005
Br	-5.2566800	-0.5175003	0.7684275

TS2I : TS for *p*-BrBzI reduction with ion pair **A**
80
Energy = -4868.834918491

B	2.8126034	-0.0089654	-0.2654658
C	3.7706424	0.8255440	-1.2895841
C	2.3662459	0.7671213	1.0859230
C	3.4665593	-1.4916572	-0.0823387
C	4.7087443	1.8085171	-0.9597844
C	3.7530503	0.5504589	-2.6607652
C	2.2186618	0.2087027	2.3604135
C	1.9540033	2.1060535	1.0580924
C	4.6831661	-1.6850866	0.5800777
C	2.9667997	-2.6770125	-0.6196782
C	5.5405883	2.4651403	-1.8612585
F	4.8373176	2.1803890	0.3517889

C	4.5440535	1.1596254	-3.6272776
F	2.8776531	-0.4088300	-3.1120676
C	1.7787588	0.8816108	3.4951111
F	2.5121501	-1.1178338	2.5396683
C	1.5208815	2.8563463	2.1425031
F	1.9483187	2.7481898	-0.1565593
C	5.3526106	-2.8932191	0.7217331
F	5.2704803	-0.5869698	1.1503664
C	3.5689609	-3.9286560	-0.5280926
F	1.7708177	-2.6457077	-1.3044724
C	5.4532267	2.1331458	-3.2127533
H	6.2362950	3.2163112	-1.5008538
H	4.4461443	0.8710898	-4.6689418
C	1.4372862	2.2277388	3.3838576
H	1.7027647	0.3486476	4.4368906
H	1.2414880	3.8955624	2.0034427
C	4.7801293	-4.0324481	0.1535737
H	6.2930386	-2.9321239	1.2620202
H	3.0936431	-4.7907753	-0.9848471
H	6.0900072	2.6295898	-3.9388909
H	1.0928128	2.7776048	4.2541868
H	5.2761194	-4.9946337	0.2415700
H	1.7399015	-0.1557447	-0.8740499
H	-4.3243102	-0.1663533	-1.8827675
N	-5.2749580	-0.2745078	-1.4615799
C	-5.1426932	-1.3691614	-0.3791684
H	-5.8759400	-0.6298479	-2.2126772
C	-5.7472218	1.1479711	-1.0870374
C	-4.3389704	-0.7561569	0.7723705
C	-6.5232396	-1.8700352	0.0483046
C	-4.3636595	-2.5071316	-1.0460022
C	-4.8893838	1.5972790	0.1031208
C	-7.2466977	1.1522644	-0.7825845
C	-5.4748621	2.0072610	-2.3250636
C	-4.8898149	0.5875113	1.2533450
H	-4.3158468	-1.4865026	1.5868991
H	-3.3027140	-0.6165956	0.4411764
H	-7.1478161	-2.1061774	-0.8197563
H	-6.3812025	-2.7924870	0.6178054
H	-7.0566672	-1.1648727	0.6856469
H	-4.1931189	-3.2941787	-0.3068183
H	-4.9259987	-2.9389060	-1.8813454
H	-3.3934406	-2.1586912	-1.4135496
H	-5.2626030	2.5725001	0.4311669
H	-3.8582712	1.7444337	-0.2457829
H	-7.4909913	0.7071250	0.1815840
H	-7.8117720	0.6347282	-1.5649727
H	-7.5803297	2.1934216	-0.7639289
H	-6.0720945	1.6712648	-3.1801883
H	-5.7519948	3.0410438	-2.1020260
H	-4.4153620	1.9837661	-2.5986604
H	-5.8973004	0.4725286	1.6692935
H	-4.2587792	0.9599935	2.0650792
C	-0.5794088	-0.1633630	-0.1802056
C	-0.6557576	-1.4183745	0.4466198
C	-1.0607227	-1.5290815	1.7714041
C	-1.4088771	-0.3713469	2.4664294
C	-1.3551923	0.8870067	1.8710589
C	-0.9359092	0.9827024	0.5494594
H	-0.3571796	-2.3069217	-0.0990753
H	-1.0977558	-2.4964412	2.2593462
H	-1.6124732	1.7756095	2.4348031
H	-0.8717882	1.9581510	0.0774873
Br	-1.9918189	-0.5132228	4.2785413
C	-0.0540595	-0.0429388	-1.5325462
H	0.3363575	-0.9165483	-2.0308326
H	0.3151587	0.9157454	-1.8661819
I	-2.0572465	0.1181333	-3.0700883

TS2 : TS for *p*-BrBzCl reduction with ion pair **A**

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Energy = -5031.465453133

B	2.6043120	0.0592025	-0.4066396
C	3.5977200	1.0485577	-1.2391107
C	2.0566174	0.6228702	1.0111018
C	3.2808730	-1.4241097	-0.3984651
C	4.4869964	1.9901133	-0.7122486
C	3.6757930	0.9685254	-2.6329840
C	1.8539745	-0.1148846	2.1827145
C	1.6048187	1.9423748	1.1464077
C	4.4602755	-1.6886827	0.3059374
C	2.8432894	-2.5299748	-1.1256752
C	5.3593628	2.7790332	-1.4552079
F	4.5210074	2.1752871	0.6436445
C	4.5124450	1.7193904	-3.4493909
F	2.8555235	0.0680185	-3.2700279
C	1.3274965	0.3795822	3.3712313
F	2.1789422	-1.4458150	2.1915164
C	1.0853663	2.5204622	2.2965416
F	1.6494993	2.7505414	0.0356462
C	5.1461796	-2.8952523	0.3240641
F	4.9872174	-0.6709542	1.0556012
C	3.4644439	-3.7746434	-1.1642626
F	1.6956005	-2.4190040	-1.8806479
C	5.3682545	2.6387443	-2.8423608
H	6.0114588	3.4825124	-0.9474906
H	4.4895913	1.5786811	-4.5251238
C	0.9501922	1.7195518	3.4293953
H	1.2151235	-0.2832600	4.2224765
H	0.7818820	3.5622677	2.2882683
C	4.6329879	-3.9544397	-0.4266139
H	6.0534182	-2.9943301	0.9106906
H	3.0363844	-4.5727521	-1.7621559
H	6.0388762	3.2415630	-3.4472400
H	0.5391497	2.1319605	4.3455556
H	5.1424228	-4.9132528	-0.4370730
H	1.5679025	-0.0205297	-1.0951859
H	-3.9467927	0.1104885	-2.6290235
N	-4.9714141	-0.0281934	-2.4461764
C	-5.0870318	-1.3074576	-1.5916743
H	-5.3985919	-0.2089822	-3.3605945
C	-5.5052570	1.3184237	-1.9160259

C	-4.5413464	-0.9598324	-0.2021442
C	-6.5310493	-1.8117610	-1.5635143
C	-4.1936620	-2.3403884	-2.2870348
C	-4.9242929	1.5006345	-0.5076571
C	-7.0351577	1.3390763	-1.9396801
C	-4.9649227	2.3804868	-2.8789164
C	-5.1718743	0.2956896	0.4034133
H	-4.6945683	-1.8295212	0.4441521
H	-3.4593685	-0.8088839	-0.2857709
H	-6.9611537	-1.8439870	-2.5702810
H	-6.5208351	-2.8328862	-1.1725422
H	-7.1805271	-1.2164462	-0.9216954
H	-4.1833269	-3.2545166	-1.6875376
H	-4.5772654	-2.5897352	-3.2826569
H	-3.1683061	-1.9727243	-2.3833359
H	-5.3580728	2.4123391	-0.0849031
H	-3.8426364	1.6655119	-0.5968716
H	-7.4850967	0.7369109	-1.1507280
H	-7.4212838	1.0003677	-2.9068745
H	-7.3583827	2.3737073	-1.7958745
H	-5.3713681	2.2429246	-3.8872512
H	-5.2730727	3.3664489	-2.5207458
H	-3.8727365	2.3509391	-2.9285526
H	-6.2449754	0.1520974	0.5749125
H	-4.7224355	0.4839670	1.3828624
C	-0.7434031	-0.2077357	-0.5283024
C	-0.8300960	-1.5495231	-0.1243578
C	-1.3350027	-1.8841194	1.1266247
C	-1.7694058	-0.8620951	1.9703070
C	-1.7036086	0.4782956	1.5968079
C	-1.1845625	0.7970049	0.3471781
H	-0.4673881	-2.3307653	-0.7834158
H	-1.3851292	-2.9191263	1.4444249
H	-2.0295908	1.2566932	2.2760746
H	-1.1123406	1.8370940	0.0464711
Br	-2.4812653	-1.3102193	3.6838227
C	-0.1500858	0.1463667	-1.8096719
H	0.2725548	-0.6204536	-2.4393217
H	0.1772437	1.1615305	-1.9762989
Cl	-1.9027521	0.4420096	-3.1671456

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