

Heterolytic dihydrogen activation by $B(C_6F_5)_3$ and carbonyl compounds

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Experimental details:

All experiments were performed using dual-manifold gas-inlet/vacuum line or in a glove box (MBraun Unilab) under argon atmosphere. H_2 was purchased from AGA Ab and passed through a column of molecular sieves prior to use. All reagents were purchased from Sigma-Aldrich or Strem and purified by conventional methods. Solvents were dried according to published procedures and distilled under argon atmosphere. NMR experiments were performed on a Varian Mercury 300 MHz spectrometer. HRMS (ESI-TOF) mass spectra were recorded on Bruker micrOTOF mass spectrometer.

General procedure:

A solution of $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol) and carbonyl compound (0.1 mmol) in 1 ml of toluene, toluene- d_8 or CD_2Cl_2 was placed in a 25 ml vacuum-dried Schlenk tube equipped with a stirring bar, a teflon stopcock and a glass stopper (sealed with Glindemann sealing rings). The reaction mixture was freeze-thaw degassed and refilled with H_2 or D_2 (2 atm) and then stirred at 110 °C (temperature of oil bath) for 48 h. The solution was transferred to a NMR tube and analyzed. Before analyzing product **3**, it was exposed to moisture and heated at 60 °C in order to release it from its adducts with decomposition products of $B(C_6F_5)_3$. Toluene was evaporated at reduced pressure. The residue was dissolved in $CDCl_3$ and investigated by 1H -NMR. Reported yields determined by NMR-spectroscopy.

The 1H , ^{13}C and ^{19}F NMR spectroscopic data of the products and adducts were identical to values reported in literature.

Benzyl alcohol¹ (**3**): 1H NMR (300MHz, $CDCl_3$) δ 7.35-7.13 (m, 5H), 4.62 (s, 2H).

(4-Methylphenyl)diphenylmethane² (**6a**): 1H NMR (300MHz, $CDCl_3$) δ 7.33-6.95 (m, 14H), 5.50 (s, 1H), 2.31 (s, 3H).

(2-Methylphenyl)diphenylmethane² (**6b**): 1H NMR (300MHz, $CDCl_3$) δ 7.33-6.95 (m, 14H), 5.66 (s, 1H), 2.20 (s, 3H).

Toluene³ (**9**): 1H NMR (300MHz, CD_2Cl_2) δ 7.32-7.05 (m, 5H), 2.34 (s, 3H).

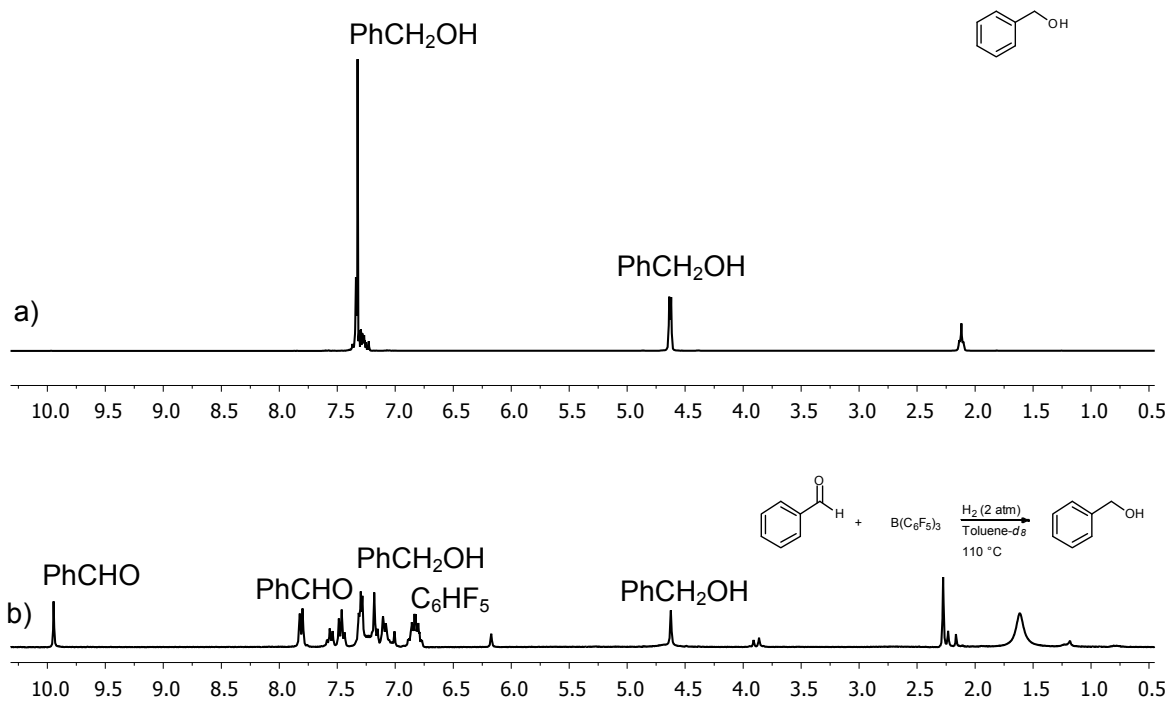
Diphenylmethane⁴ (**10**): 1H NMR (300MHz, $CDCl_3$) δ 7.34-7.13 (m, 10H), 3.97 (s, 2H).

1 A. R. Jagdale, A. S. Paraskar and A. Sudalai, *Synthesis*, 2008, 660.

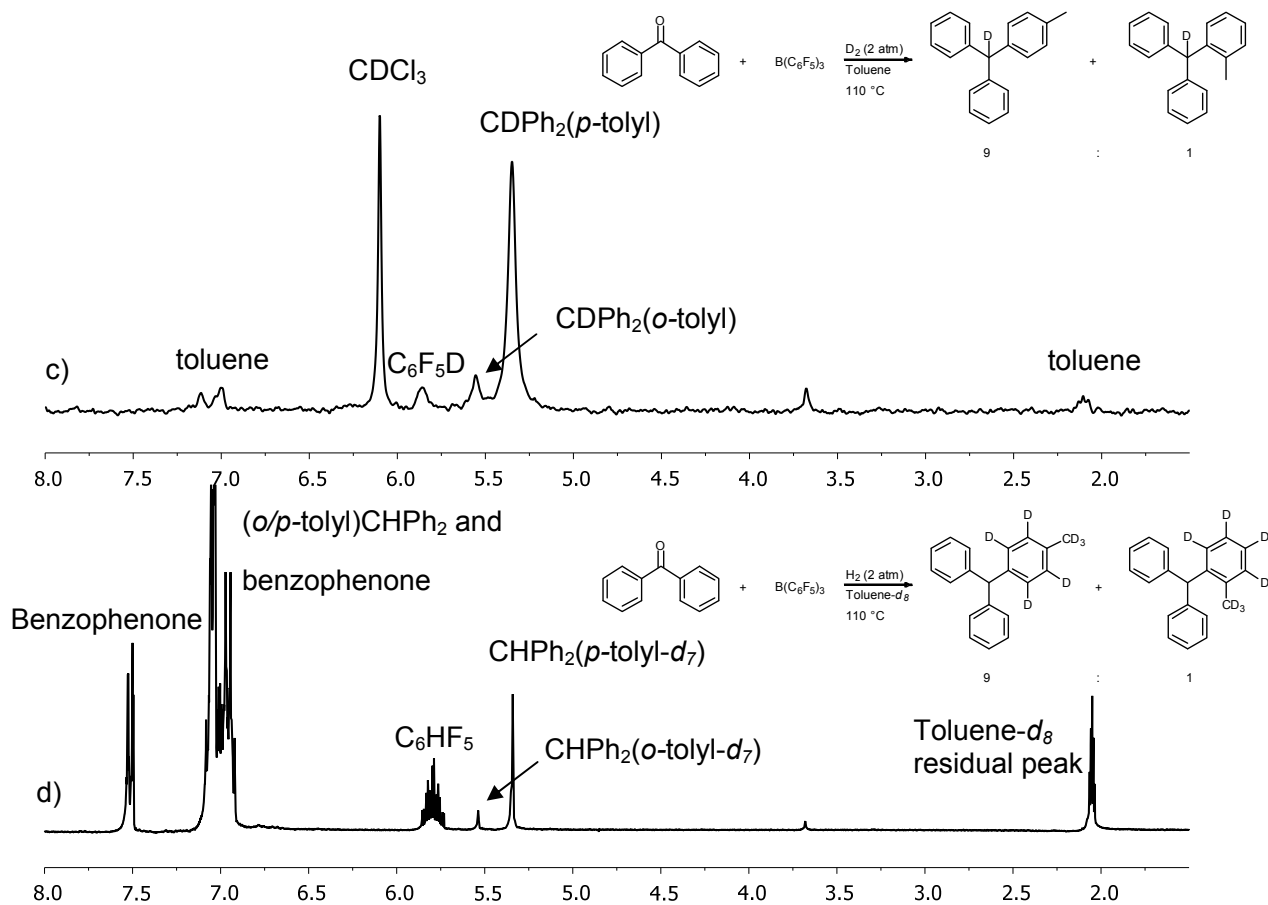
2 J-Y. Yu and R. Kuwano, *Org. Lett.*, 2008, **10**, 973.

3 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics*, 2010, **29**, 2176.

4 E. Alacid and C. Nájera, *Org. Lett.*, 2008, **10**, 5011.

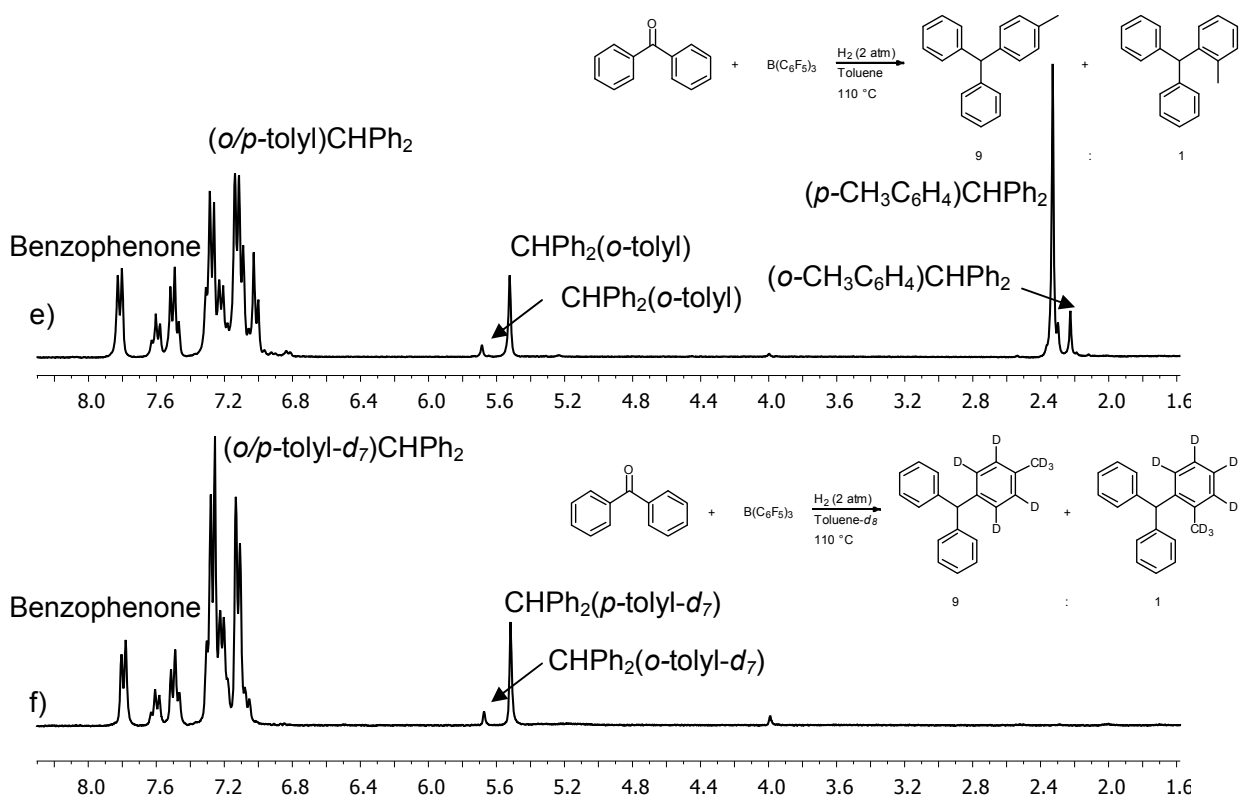


- a) Reference ¹H-NMR spectrum of benzyl alcohol in CDCl₃.
- b) Hydrogenation of benzaldehyde in toluene-*d*₈ (¹H-NMR, CDCl₃, after aqueous work-up).

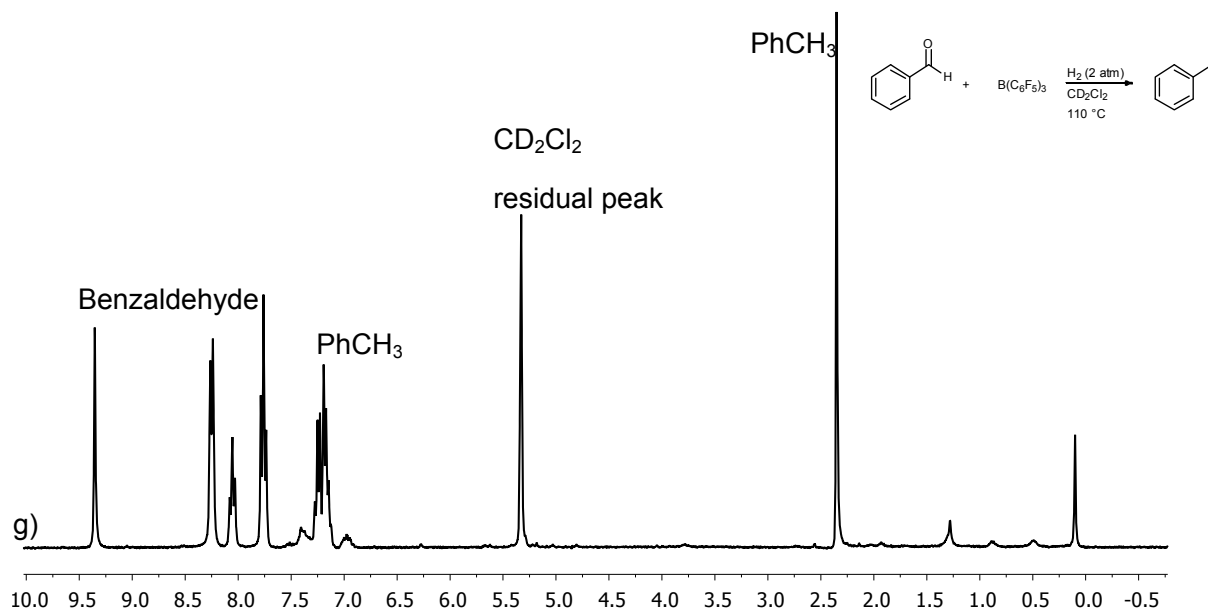


c) Reaction of benzophenone-B(C₆F₅)₃ with deuterium (²H-NMR, Toluene).

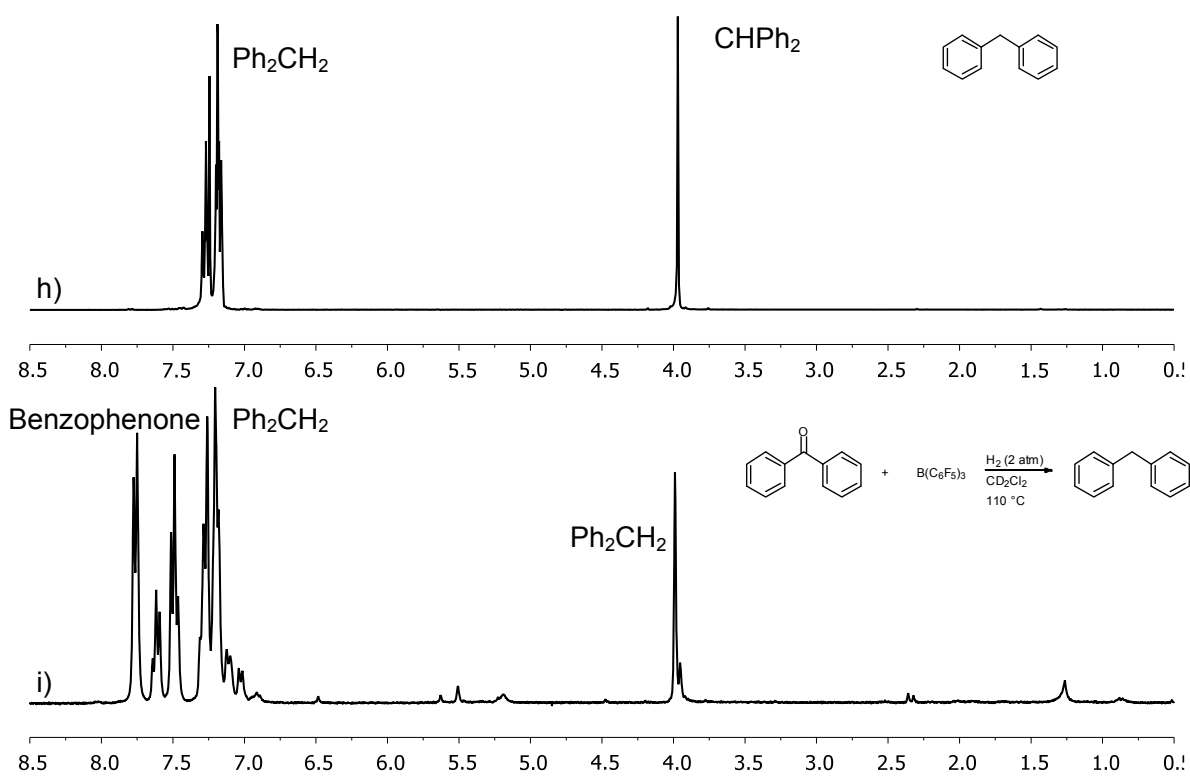
d) Reaction benzophenone-B(C₆F₅)₃ with H₂ (¹H-NMR, Toluene-*d*₈).



- e) Hydrogenation of benzophenone in toluene ($^1\text{H-NMR}$, CDCl_3 , after evaporation of all volatiles).
- f) Hydrogenation of benzophenone in toluene- d_8 ($^1\text{H-NMR}$, CDCl_3 , after evaporation of all volatiles).



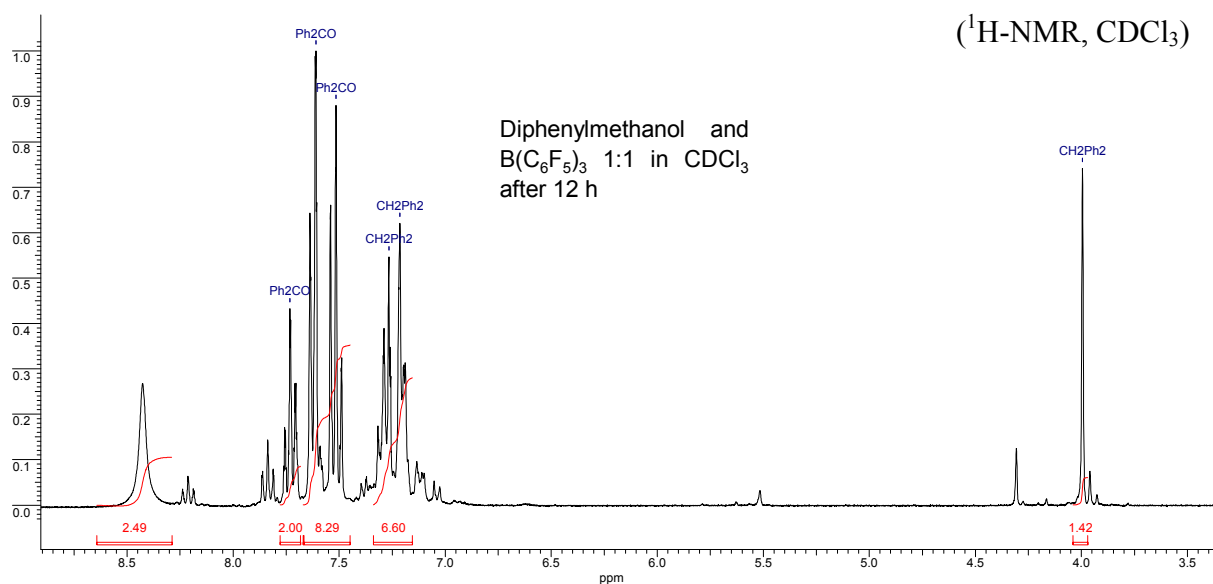
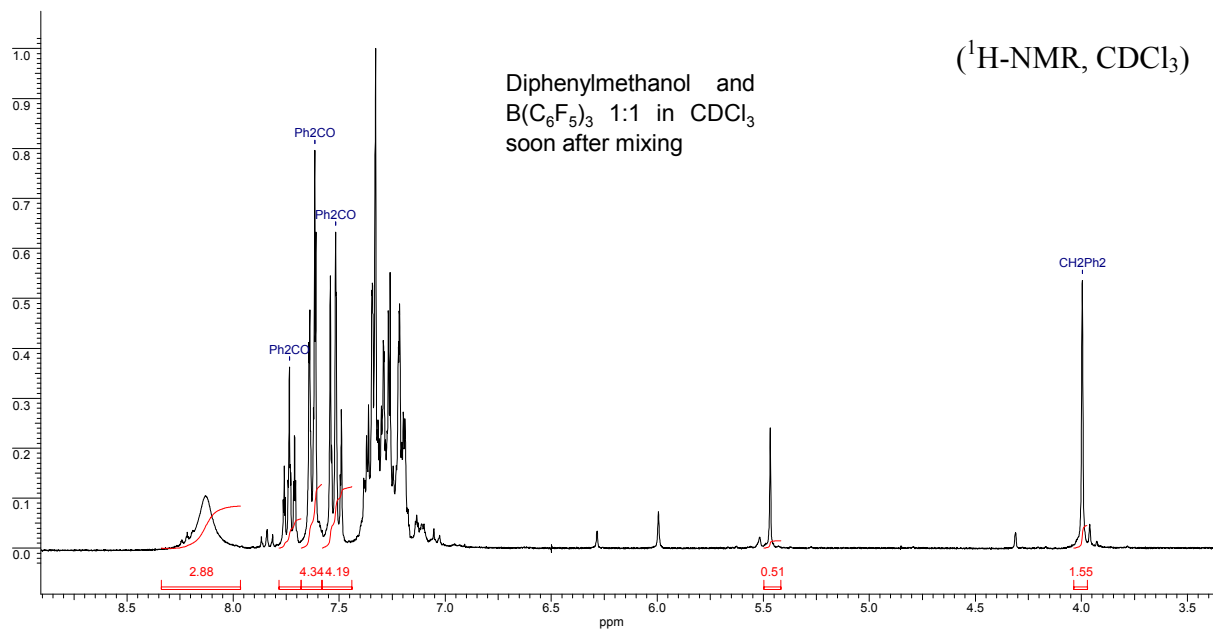
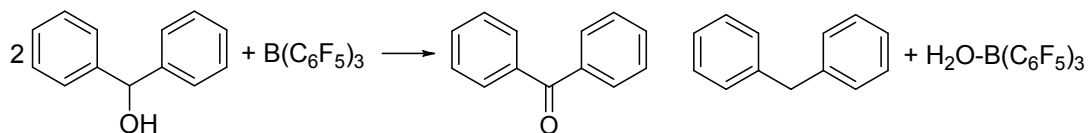
g) Hydrogenation of benzaldehyde in CD_2Cl_2 ($^1\text{H-NMR}$, CD_2Cl_2).

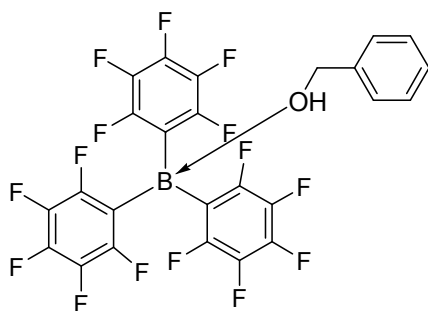


h) Reference $^1\text{H-NMR}$ spectrum of diphenylmethane in CDCl_3 .

i) Hydrogenation of benzophenone in CD_2Cl_2 ($^1\text{H-NMR}$, CDCl_3 , after evaporation of all volatiles)

Diphenylmethanol and tris(pentafluorophenyl)borane give products of dismutation instantly upon mixing in CDCl_3 . Tris(pentafluorophenyl)borane (25 mg, 0.05 mmol) was dissolved in CDCl_3 (0.5 ml) and diphenylmethanol was added (9 mg, 0.1 mmol) and analyzed by NMR-spectroscopy.





**Benzyl alcohol compound with
tris(pentafluorophenyl)borane (1:1)**

Tris(pentafluorophenyl)borane (51 mg, 0.1 mmol) was dissolved in CDCl_3 (0.5 ml) and benzyl alcohol was added (10.5 mg, 0.1 mmol) and analyzed by NMR-spectroscopy. Evaporation of the solution gave white solid. This was recrystallized from hexane (1 ml) to give. Storage in solution or heating during recrystallization promote formation of $\text{B}(\text{C}_6\text{F}_5)_3\text{-H}_2\text{O}$ adduct evidently due to dehydration of benzyl alcohol.

^1H NMR (300 MHz, CHLOROFORM-D) δ , ppm: 4.93 (s, 2 H), 6.32 (m, 1 H) 7.30-7.43 (m, 2 H), 7.43-7.57 (m, 3 H)

^{13}C NMR (75.43 MHz, CHLOROFORM-D) δ , ppm: 73.58 (s), 129.38 (s), 129.83 (s), 130.90 (s), 131.38 (s), 135.38 (dm, $J=230$ Hz), 141.22 (dm, $J=250$ Hz), 147.76 (dm, $J=240$ Hz),

^{19}F NMR (282.21 MHz, CHLOROFORM-D) δ , ppm: -134.1 (d, $J=20$ Hz, 6F), -153.8 (s, 3F), -162.2 (m, 6F).

^{10}B NMR (53.70 MHz, CHLOROFORM-D) δ , ppm: 9.25 (br. s.)

ESI-MS-neg: $[\text{C}_{25}\text{H}_7\text{BF}_{15}\text{O}]^-$, calc.: 619.0360, found.: 619.0369.

