Heterolytic dihydrogen activation with the 1,8-bis(diphenylphosphino)-naphthalene/B(C_6F_5)$_3$ pair and its application for metal-free catalytic hydrogenation of silyl enol ethers

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Supplementary Information

Experimental section:

All manipulations were carried out under argon using Schlenk-type glassware or in a glovebox unless otherwise noted. Solvents, including deuterated solvents used for NMR spectroscopy, were dried and distilled prior to use according to standard procedures. Elemental analyses were performed with a Foss-Heraeus CHN-O-Rapid instrument. NMR spectra were measured using a Bruker AC200 P, a Varian 500 MHz INOVA, or a Varian Unity Plus 600 NMR spectrometer. Most assignments were based on a series of NOE, TOCSY, and 2D NMR experiments. 1,8-Bis(diphenylphosphino)naphthalene was synthesized according literature procedures (R. D. Jackson, S. James, A. G. Orpen, P. G. Pringle, *J. Organomet. Chem.*, 1993, **458**, C3-C4.)
Data set was collected with a Nonius KappaCCD diffractometer, equipped with a rotating anode generator. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction SORTAV (R.H. Blessing, *Acta Cryst.* **1995**, *A51*, 33-37; R.H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421-426), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, Universität Göttingen, 1997), graphics SCHAKAL (E. Keller, Universität Freiburg, 1997).
CCDC 630677 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

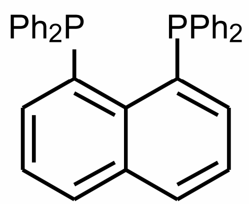
1,8-Bis(diphenylphosphino)naphthalene (5) + B(C_6F_5)$_3$: 5 (20.0mg, 0,040 mmol) and B(C_6F_5)$_3$ (20.6 mg, 0.040 mmol) was mixed in d_8-toluene (1 mL). ^{1}H NMR (500 MHz, d_8-toluene, 298K): δ 6.95 (14 H, m, *o*, *p*-Ph and 3,6-Naph), 7.23 (8 H, br. s, *m*-Ph), 7.45 (2 H, dm, J = 7.8 Hz, 2,7-Naph), 7.49 (2 H, br. d, J = 7.7 Hz, 4,5-Naph). ^{31}P{^{1}H} NMR (202 MHz, d_8-toluene, 298K): δ 13.8. ^{11}B{^{1}H} NMR (160 MHz, d_8-toluene, 298K): δ 59.0. ^{19}F NMR (470 MHz, d_8-toluene, 298K): δ –129.0 (br. s, *o*-C_6F_5), -142.2 (br. s, *p*-C_6F_5), -160.4 (br. s, *m*-C_6F_5).

6: A mixture of 1,8-bis(diphenylphosphino)naphthalene (150 mg, 0.30 mmol) and B(C_6F_5)$_3$ (155 mg, 0.30 mmol) in toluene (15 ml) was stirred under a H_2 atmosphere (2 bar) at room temperature for 3 h. Afterwards the reaction flask was closed and stirred for another 14 h. The colorless reaction mixture was condensed to ~3 ml, and pentane (30 ml) was added, resulting in the formation of a white precipitate. This precipitate was collected by filtration and rinsed with pentane (15 ml), affording complex **6** as a white solid (245mg, 80%). Single crystals of complex **6** were obtained through vapor diffusion of pentane into a solution of dichloromethane. ^{1}H NMR (500 MHz, CD_2Cl_2, 298K): δ 3.60 (1 H, br. q (1:1:1:1), J_{BH} ≈ 92 Hz , B*H*), 7.16 (8 H, br. s, *o*-Ph), 7.41 (8 H, br. m, *m*-Ph), 7.55 (4 H, br. m, *p*-Ph), 7.67 (4 H, br. m, 2,3,6,7-Naph), 8.34 (2 H, br. d, J = 7.9 Hz, 4,5-Naph), 10.1 (1 H, br. t, J_{PH} = 280 Hz, P*H*). ^{13}C{^{1}H} NMR (125 MHz, CD_2Cl_2, 298K): δ 127.1, 141.8 (2,7 / 3,6-Naph), 130.1 (*m*-Ph), 132.6 (*p*-Ph), 133.5 (*o*-Ph), 136.6 (4,5-Naph), 136.7 (dm, J_{CF} = 252 Hz, m-C_6F_5), 138.2 (dm, J_{CF} = 246 Hz, *p*-C_6F_5), 148.5 (dm, J_{CF} = 238 Hz, *o*-C_6F_5).[1,8,9,10-Naph and C(*i*-Ph) were not observed]. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 298K): δ 1.5 (m, minor isomer), -3.5 (br s, $\nu_{1/2}$ ≈ 150 Hz, major isomer), -20.0 (m, minor isomer). ^{31}P NMR (202 MHz, CD_2Cl_2, 298K): δ 1.5 (dm, J_{PH} ≈ 415 Hz, minor isomer), -3.5 (br d, J_{PH} ≈ 280 Hz, $\nu_{1/2}$ = 150 Hz; major isomer), -20.0 (m, minor isomer). [ratio: 1 : 13 : 1]. ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2, 193K): δ 10.0 (d, J_{PP} ≈ 110 Hz, $\nu_{1/2}$ = 20 Hz; major isomer), 1.9 (d, J_{PP} ≈ 46 Hz, minor isomer), -18.8 (d, J_{PP} ≈ 110 Hz, $\nu_{1/2}$ ≈ 10 Hz; major isomer), -21.2 (d, J_{PP} ≈ 46 Hz, minor isomer); ^{31}P NMR (202 MHz, CD_2Cl_2, 193K): δ 10.0 (dd, J_{PH} ≈ 557 Hz, J_{PP} ≈ 110 Hz, $\nu_{1/2}$ = 50 Hz; major isomer), 1.9 (dm, J_{PH} ≈ 410 Hz, minor isomer), -18.8 (d, J_{PP} ≈ 110 Hz, $\nu_{1/2}$ = 30 Hz; major isomer), -21.2 (m, minor isomer), [ratio: 13 : 1 : 13 : 1]. ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298K): δ -25.8 (s, $\nu_{1/2}$ ≈ 50 Hz); ^{11}B NMR (160 MHz, CD_2Cl_2, 298K): δ -25.8 (d, J_{BH} ≈ 92 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298K): δ -134.3 (m, *o*-C_6F_5), -165.1 (m, *p*-C_6F_5), -168.0 (m, *m*-C_6F_5).

^{1}H NMR (500 MHz, C_6D_6, 298K): δ 4.49 (1 H, br, B*H*), 6.67-7.07 (22 H, m, Ph and 3,6-Naph), 7.31 (2 H, br. s, 2,7-Naph), 7.57 (2 H, br. d, *J* = 7.1 Hz, 4,5-Naph), 9.68 (1 H, br. t, J_{PH} = 280 Hz, P*H*). $^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6,, 298K): δ 2.3 (m, minor isomer), -4.3 (br s, $\nu_{1/2} \approx$ 150 Hz, major isomer), -20.6 (m, minor isomer). $^{11}B\{^{1}H\}$ NMR (96 MHz, C_6D_6, 298K): δ -22.8 (s, $\nu_{1/2} \approx$ 50 Hz); ^{11}B NMR (96 MHz, C_6D_6, 298K): δ -22.8 (d, $J_{BH} \approx$ 84 Hz). ^{19}F NMR (282 MHz, C_6D_6, 298K): δ 132.0 (m, *o*-C_6F_5), -163.7 (m, *p*-C_6F_5), -166.4 (m, *m*-C_6F_5).
Elemental analysis: Found C, 62.11; H, 2.45. Calc. for $C_{52}H_{28}BF_{15}P_2$: C, 61.81, H, 2.79%. Crystal data for $C_{34}H_{27}P_2 \cdot HB(C_6F_5)_3$, *M* = 1010.49, triclinic, space group *P*1bar (No. 2), *a* = 9.7493(5), *b* = 13.3554(6), *c* = 19.3935(9) Å, α = 100.853(2), β = 99.692(2), γ = 94.678(4)°, *V* = 2427.8(2) Å^3, D_c = 1.382 g cm^{-3}, μ = 1.645 mm^{-1}, *Z* = 2, λ = 1.54178 Å, *T* = 223(2) K, 29126 reflections collected (±*h*, ±*k*, ±*l*), $[(sin\theta)/\lambda]$ = 0.60 Å^{-1}, 8515 independent (R_{int} = 0.062) and 6735 observed reflections $[I \geq 2\sigma(I)]$, 639 refined parameters, R = 0.060, wR^2 = 0.172.

6-D_2: Following the procedure of the synthesis of **6**, **6**-D_2 was prepared from 1,8-bis(diphenylphosphino)naphthalene (150 mg, 0.30 mmol) and $B(C_6F_5)_3$ (155 mg, 0.30 mmol) under D_2 atmosphere (1.7 bar). **6**-D_2 was isolated as a white solid (217mg, 71%). ^{2}H NMR (77 MHz, toluene, 298K): δ 4.34 (1 D, $\nu_{1/2}$ = 20 Hz, B*D*), 9.73((1 D, br. t, $J_{PD} \approx$ 40 Hz, P*D*).

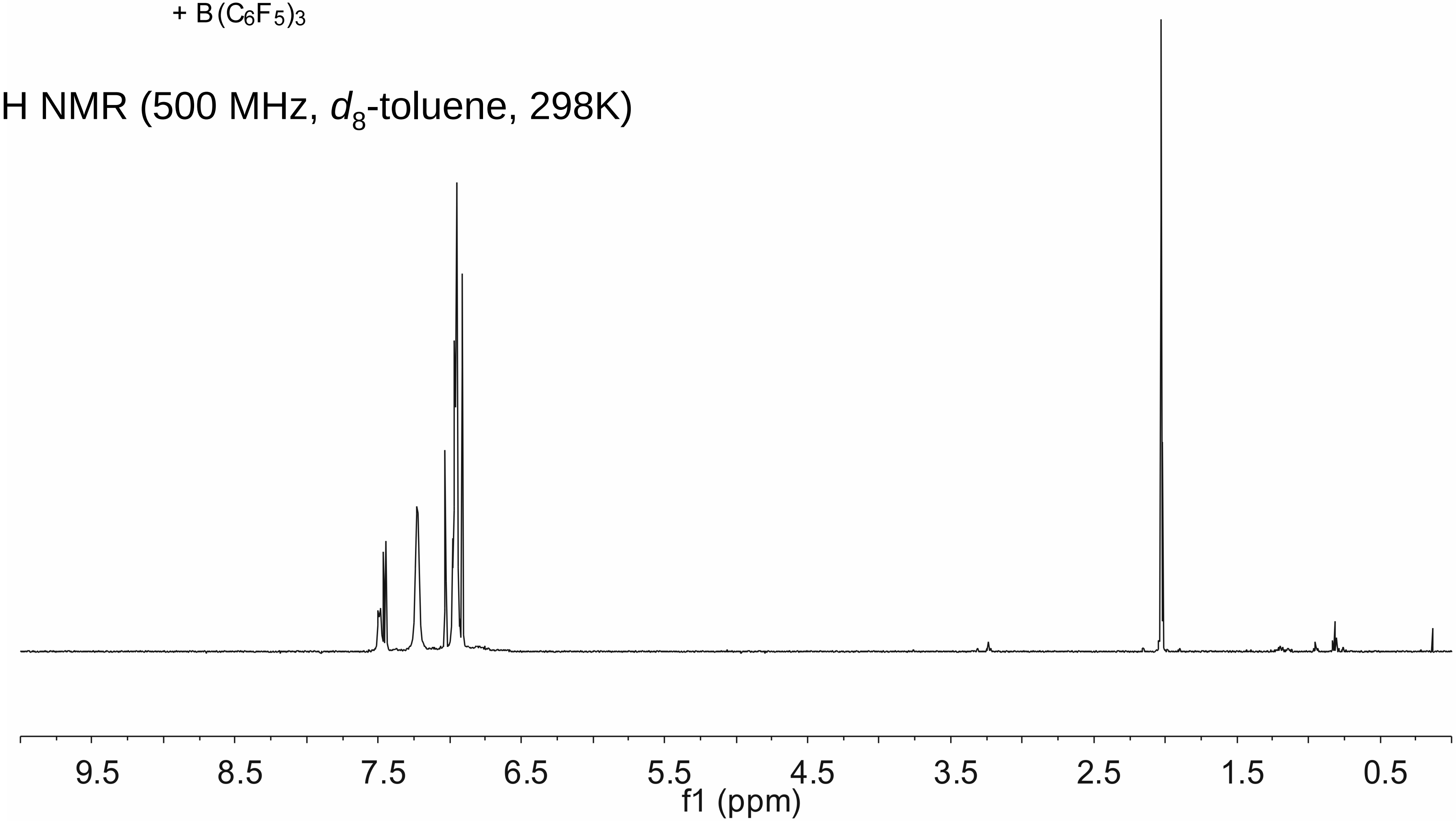
General procedures for the hydrogenation of silyl enol ethers:
A mixture of 1,8-bis(diphenylphosphino)naphthalene (20 mol%), $B(C_6F_5)_3$ (20 mol%) and silyl enol ether (200 mg) in benzene (3ml) was stirred under H_2 atmosphere (2 bar) at room temperature for 20 h. Afterwards pentane (30 ml) was added to the reaction mixture, and resulting white slurry was passed through Celite. Solvent was removed under vacuum, yielding the respective silyl ether as colorless oil.
Trimethyl(1-phenylethoxy)silane: 192 mg, yield 95%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.06 (9 H, *s*, Si(CH_3)$_3$), 1.39 (3 H, *d*, *J* = 6.3 Hz, CCH_3), 4.74 (1 H, *q*, *J* = 6.4 Hz, C*H*), 7.04-7.34 (5 H, *m*, C_6H_5). ^{13}C NMR (75.5 MHz, C_6D_6) : δ 0.0, 27.2, 70.9, 125.7, 127.2, 128.3, 146.8.
(3,3-Dimethyl-2-butoxy)trimethylsilane: 181 mg, yield 89%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.11 (9 H, *s*, Si(CH_3)$_3$), 0.89 (9 H, *s*, C(CH_3)$_3$),), 1.02 (3 H, *d*, *J* = 6.0 Hz, CCH_3), 3.36 (1 H, *q*, *J* = 6.1 Hz, C*H*). ^{13}C NMR (75.5 MHz, C_6D_6): δ 0.0, 18.2, 25.5, 34.8, 75.7.
(Cyclohexyloxy)trimethylsilane: 174 mg, yield 86%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.12 (9 H, *s*, Si(CH_3)$_3$), 1.00-1.85 (10 H, *m*, CH_2), 3.58 (1H, *m*, C*H*). ^{13}C NMR (75.5 MHz, C_6D_6): δ 0.0, 23.9, 25.4, 35.9, 70.3.
(Cyclopentyloxy)trimethylsilane: 172 mg, yield 85%. ^{1}H NMR (300 MHz, C_6D_6): δ 0.12 (9 H, *s*, Si(CH_3)$_3$), 1.30-1.80 (8 H, *m*, CH_2), 4.12 (1H, *m*, C*H*). ^{13}C NMR (75.5 MHz, C_6D_6): δ 0.0, 23.2, 35.7, 74.1.
Isopropoxytrimethylsilane: ^{1}H NMR (300 MHz, C_6D_6): 0.10 (9 H, *s*, Si(CH_3)$_3$), 1.09 (6 H, *d*, *J* = 6.1 Hz, CCH_3), 3.83 (1 H, *m*, C*H*).

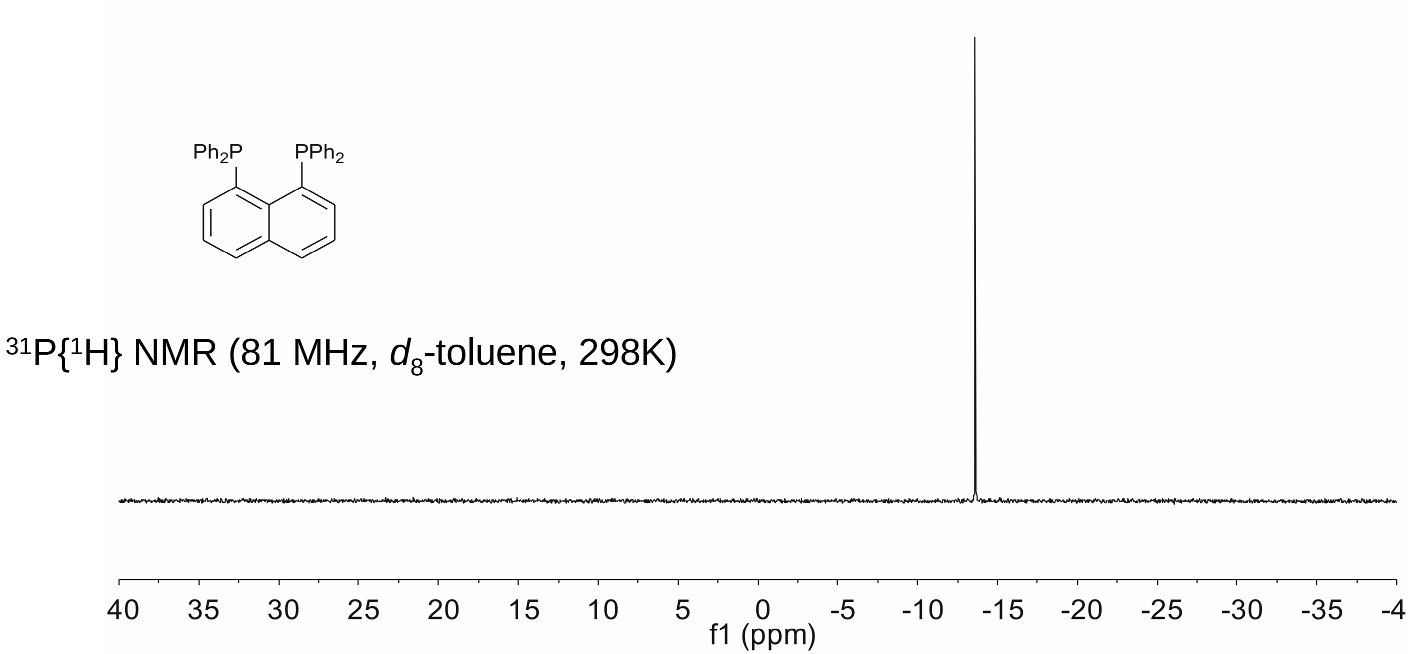


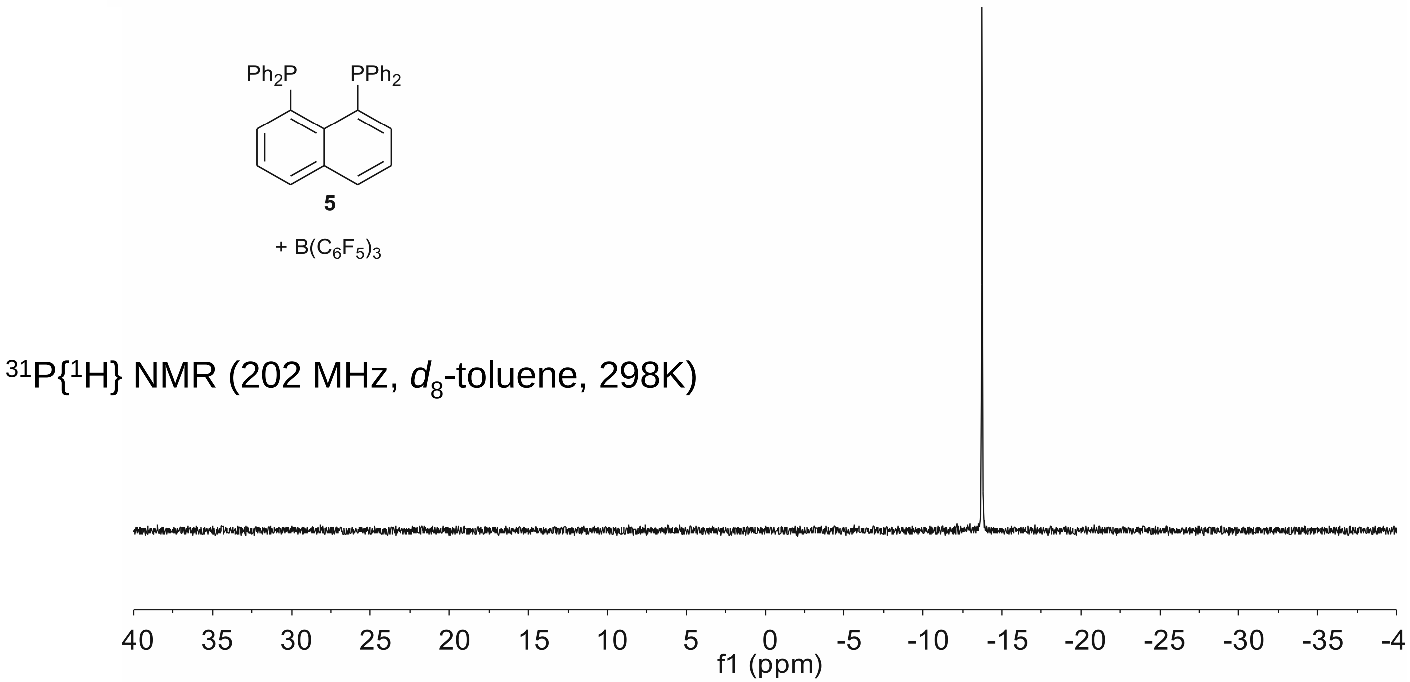
5

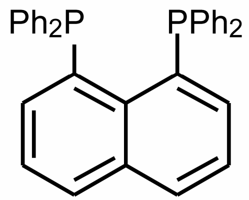
+ $B(C_6F_5)_3$

^{1}H NMR (500 MHz, d_8-toluene, 298K)




Ph2P
PPh2
31P{1H} NMR (81 MHz, d8-toluene, 298K)
40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -4
f1 (ppm)

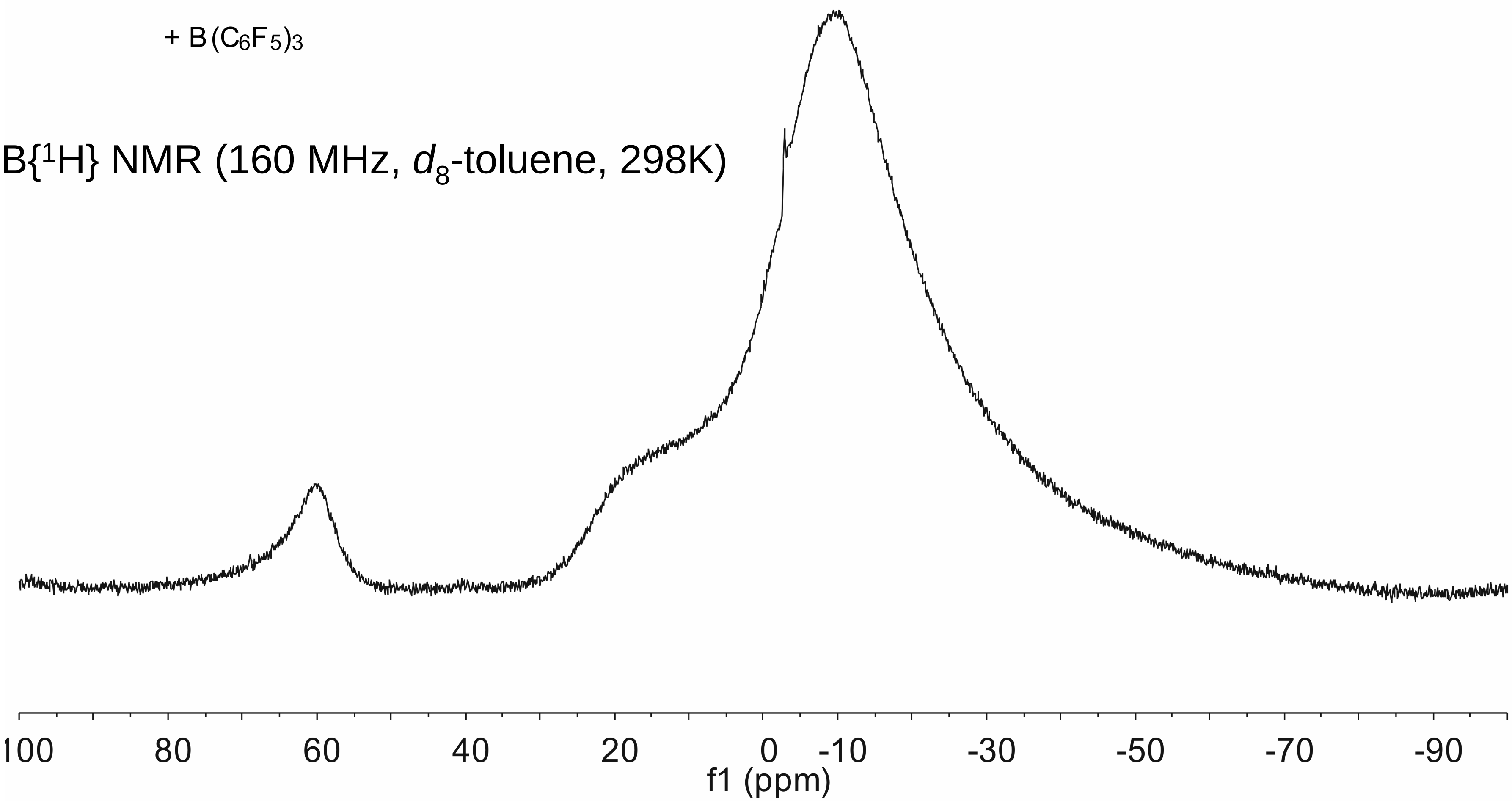

Ph2P
PPh2
5
+ B(C6F5)3
31P{1H} NMR (202 MHz, d8-toluene, 298K)
40 35 30 25 20 15 10 5 0 -5 -10 -15 -20 -25 -30 -35 -4
f1 (ppm)

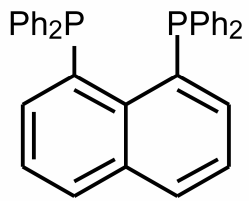


5

+ B(C_6F_5)$_3$

^{11}B{^{1}H} NMR (160 MHz, d_8-toluene, 298K)

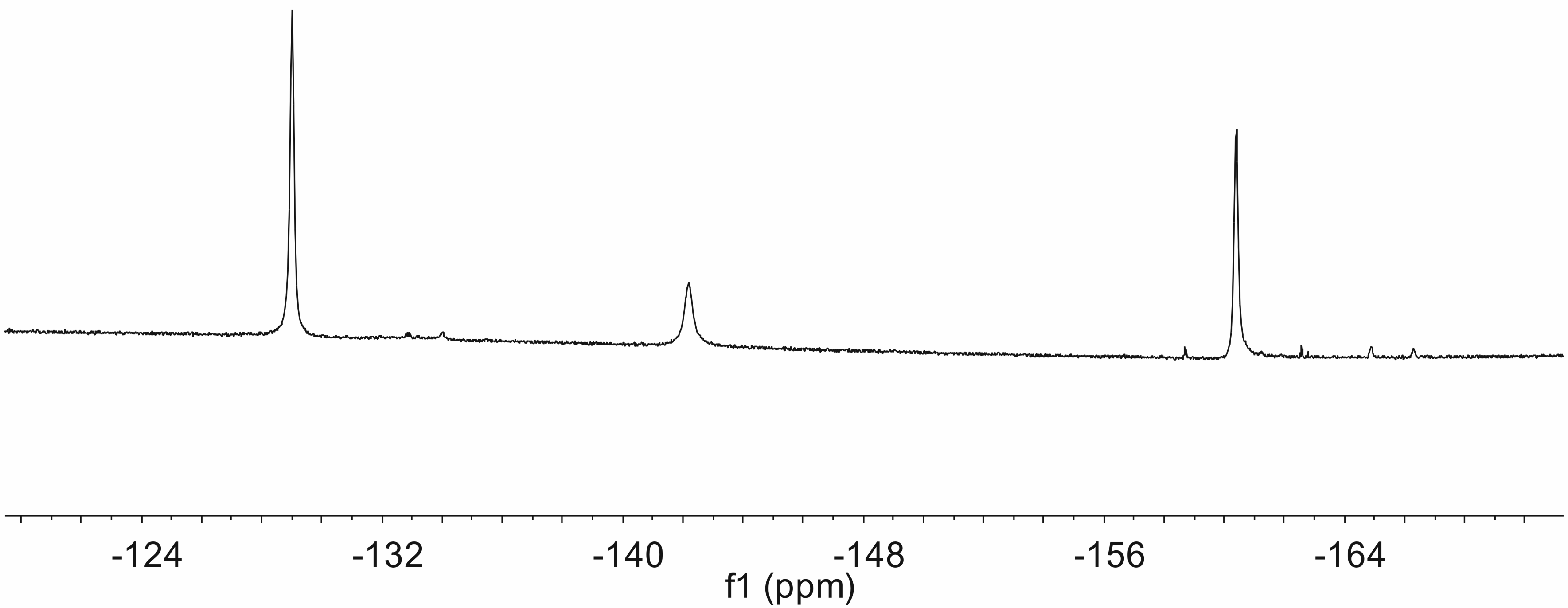


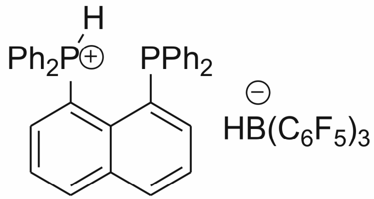


5

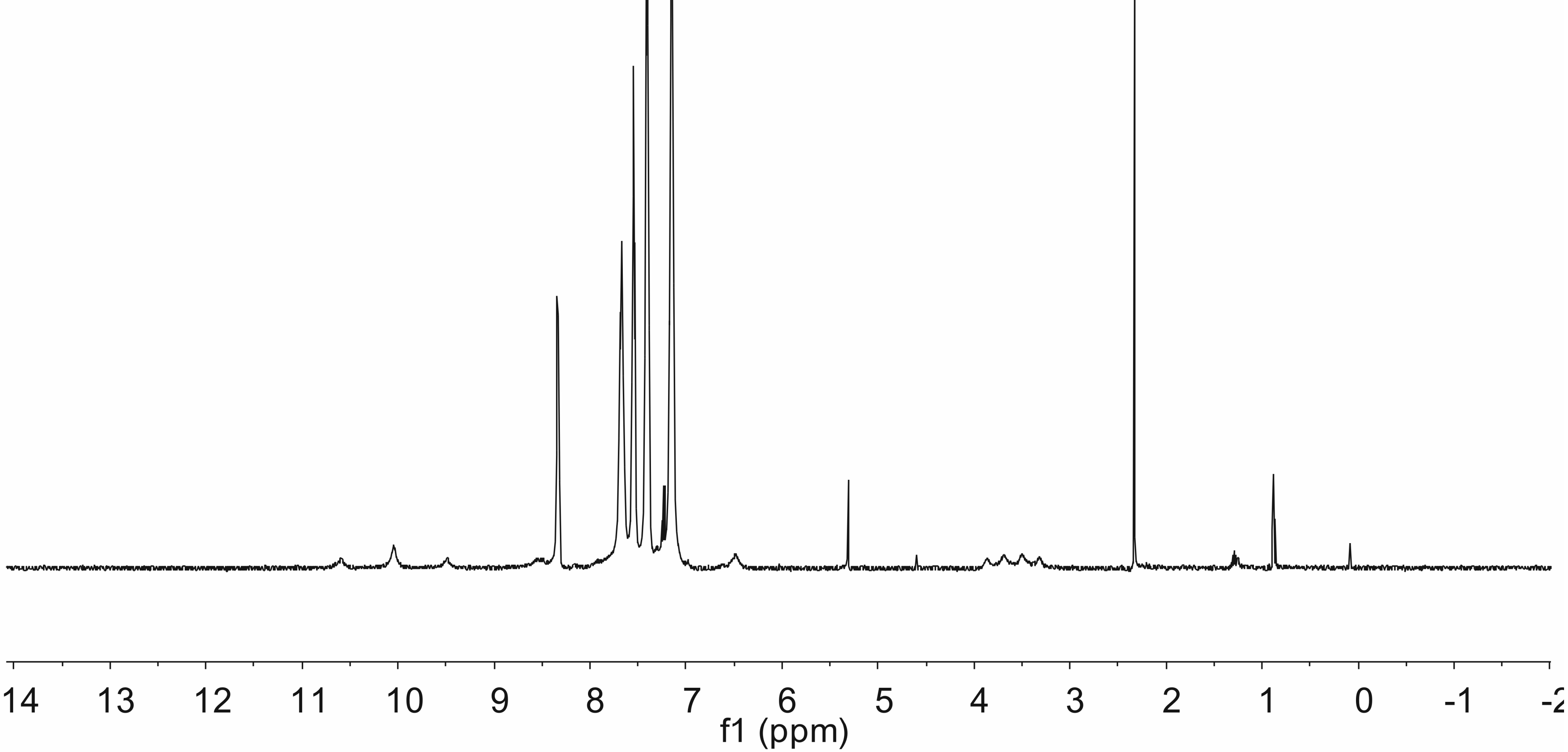
+ $B(C_6F_5)_3$

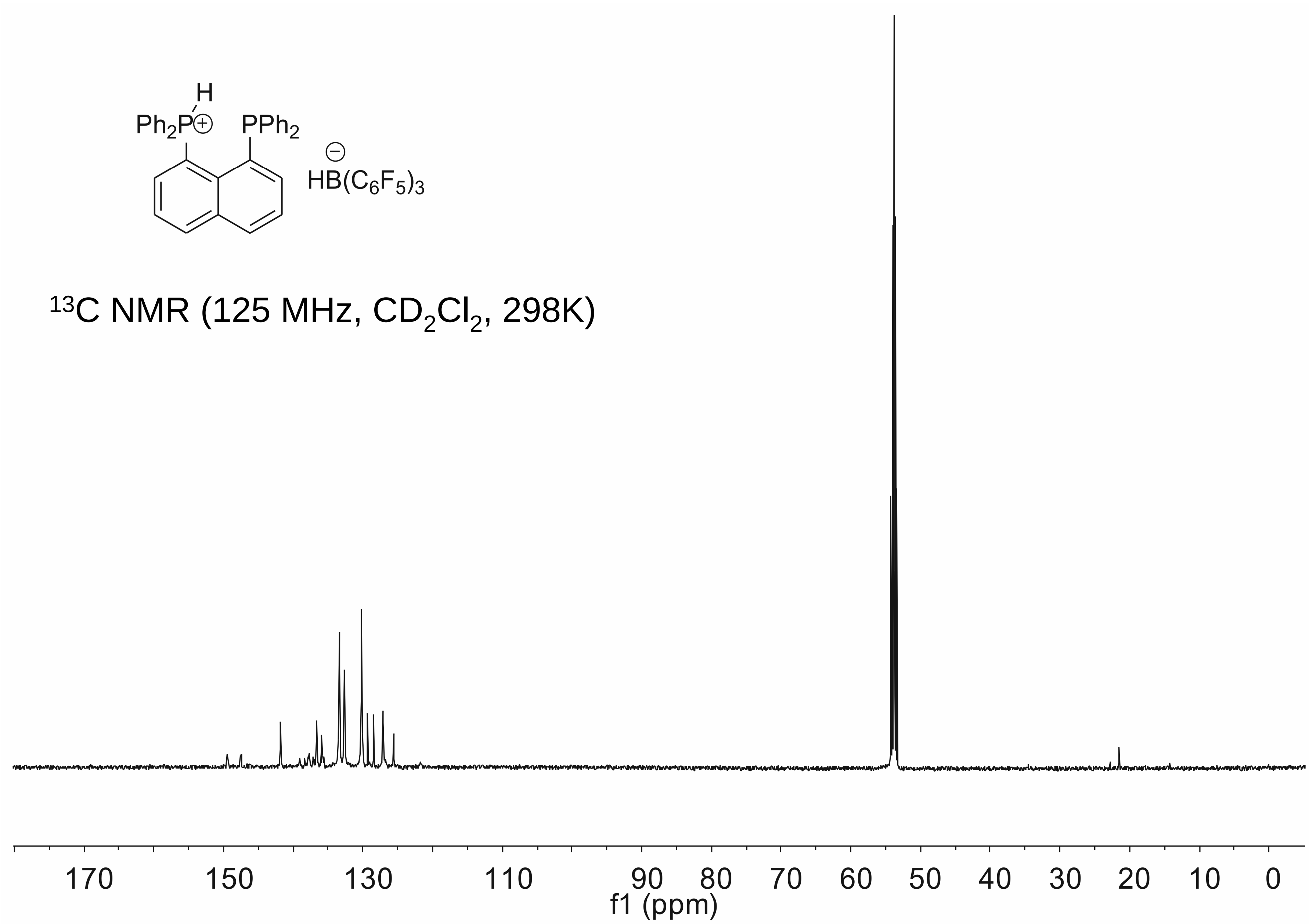
^{19}F NMR (470 MHz, d_8-toluene, 298K)

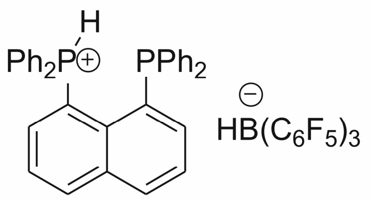




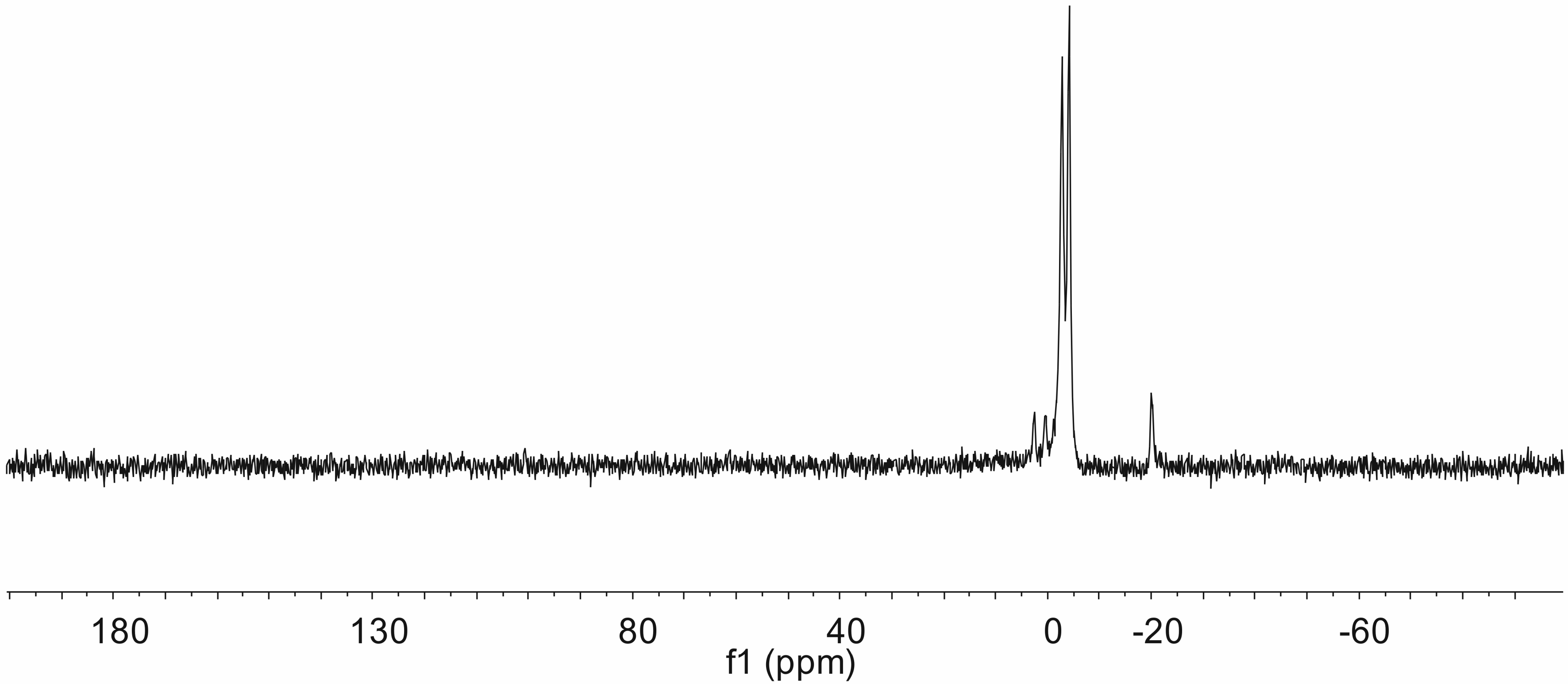
^{1}H NMR (500 MHz, CD_2Cl_2, 298K)

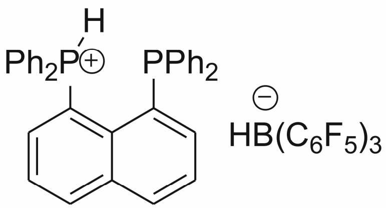


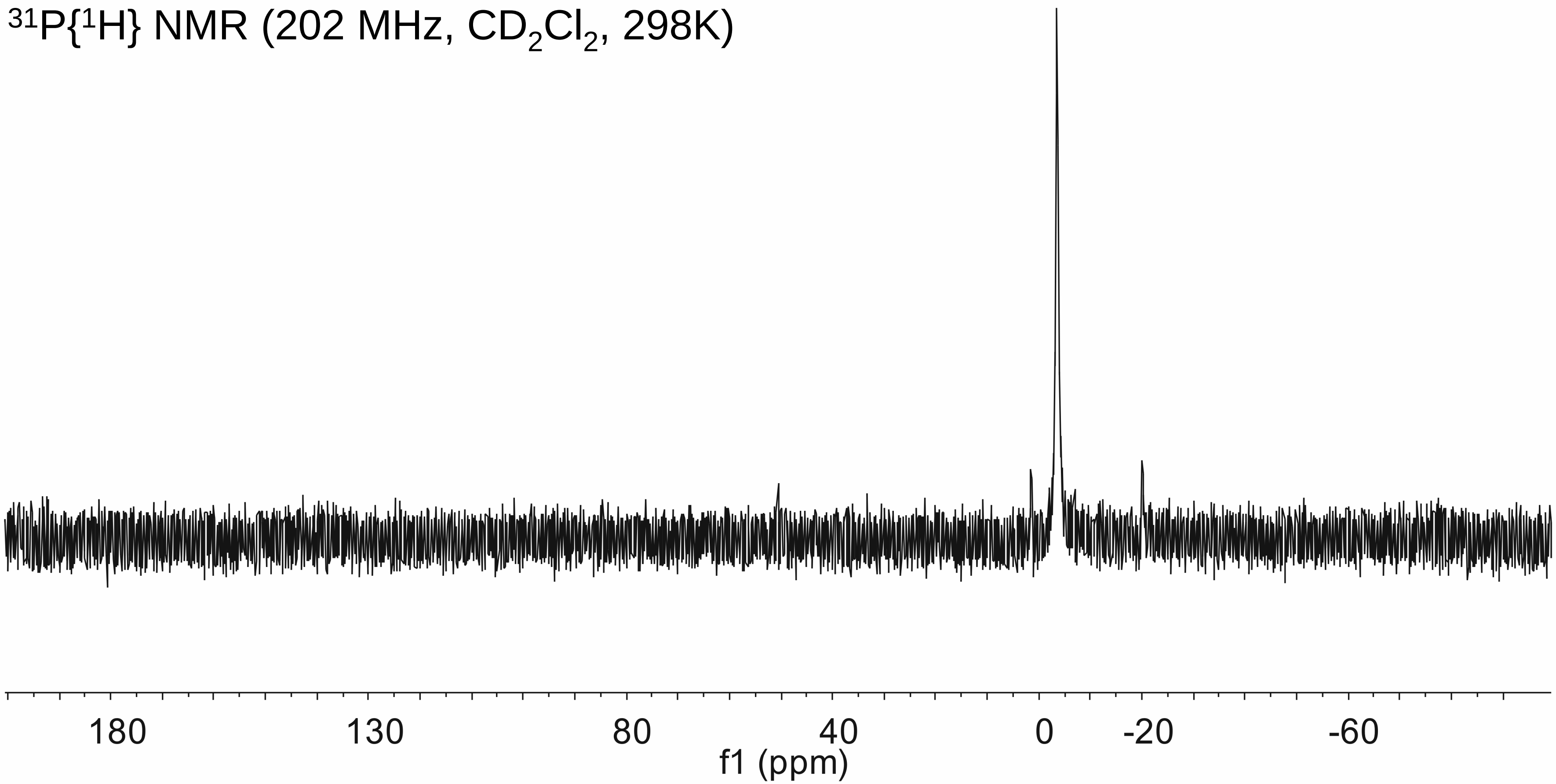

H
$Ph_2P^{\oplus}$
PPh_2
$\ominus$
$HB(C_6F_5)_3$
^{13}C NMR (125 MHz, CD_2Cl_2, 298K)
170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

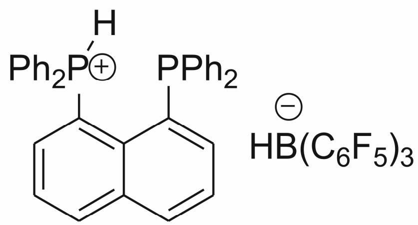


^{31}P NMR (202 MHz, CD_2Cl_2, 298K)

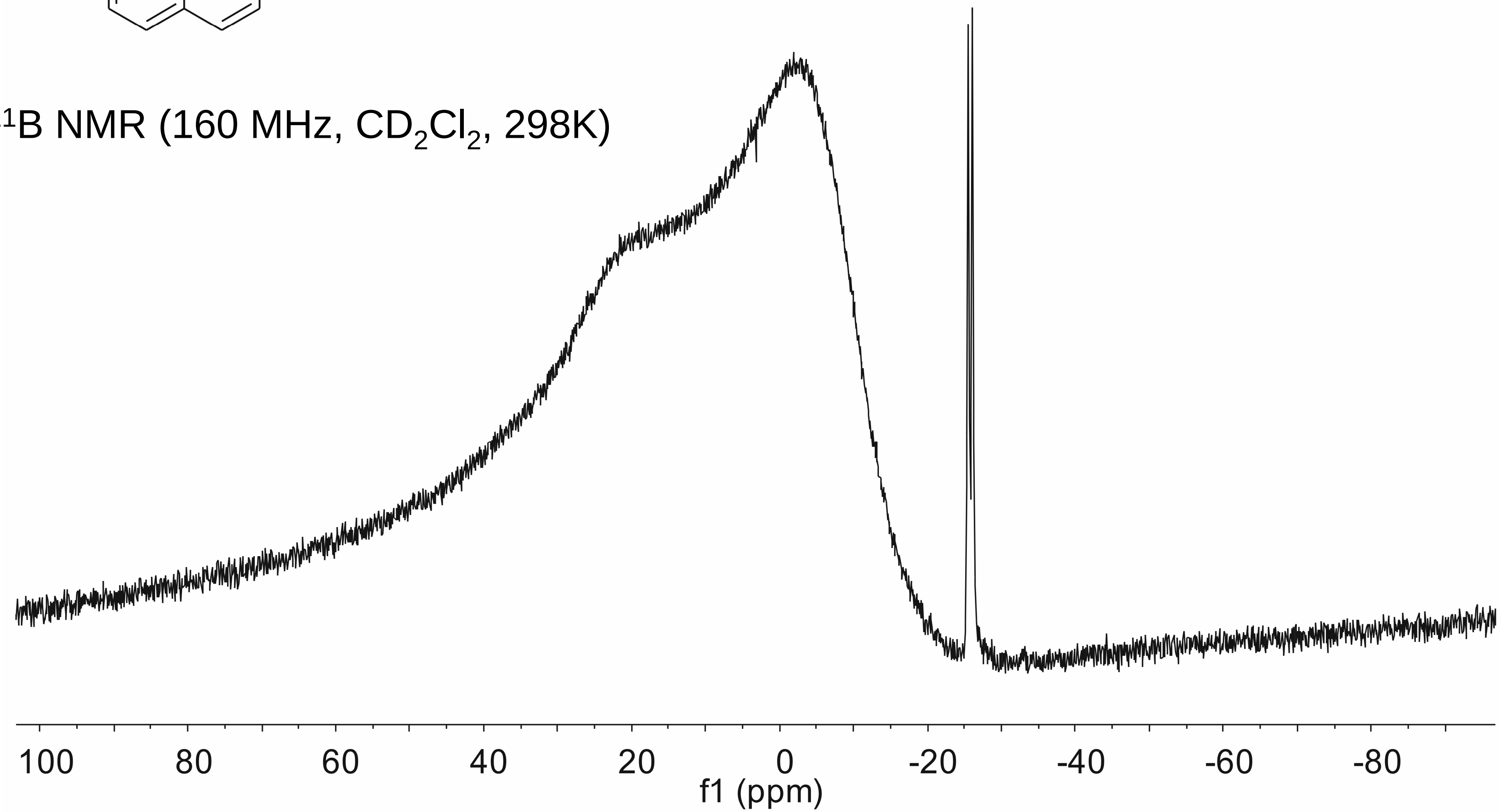


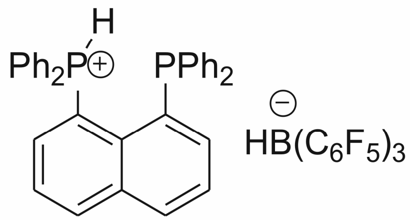

H
Ph2P⊕ PPh2
⊖
HB(C6F5)3


31P{1H} NMR (202 MHz, CD2Cl2, 298K)
180
130
80
40
0
-20
-60
f1 (ppm)

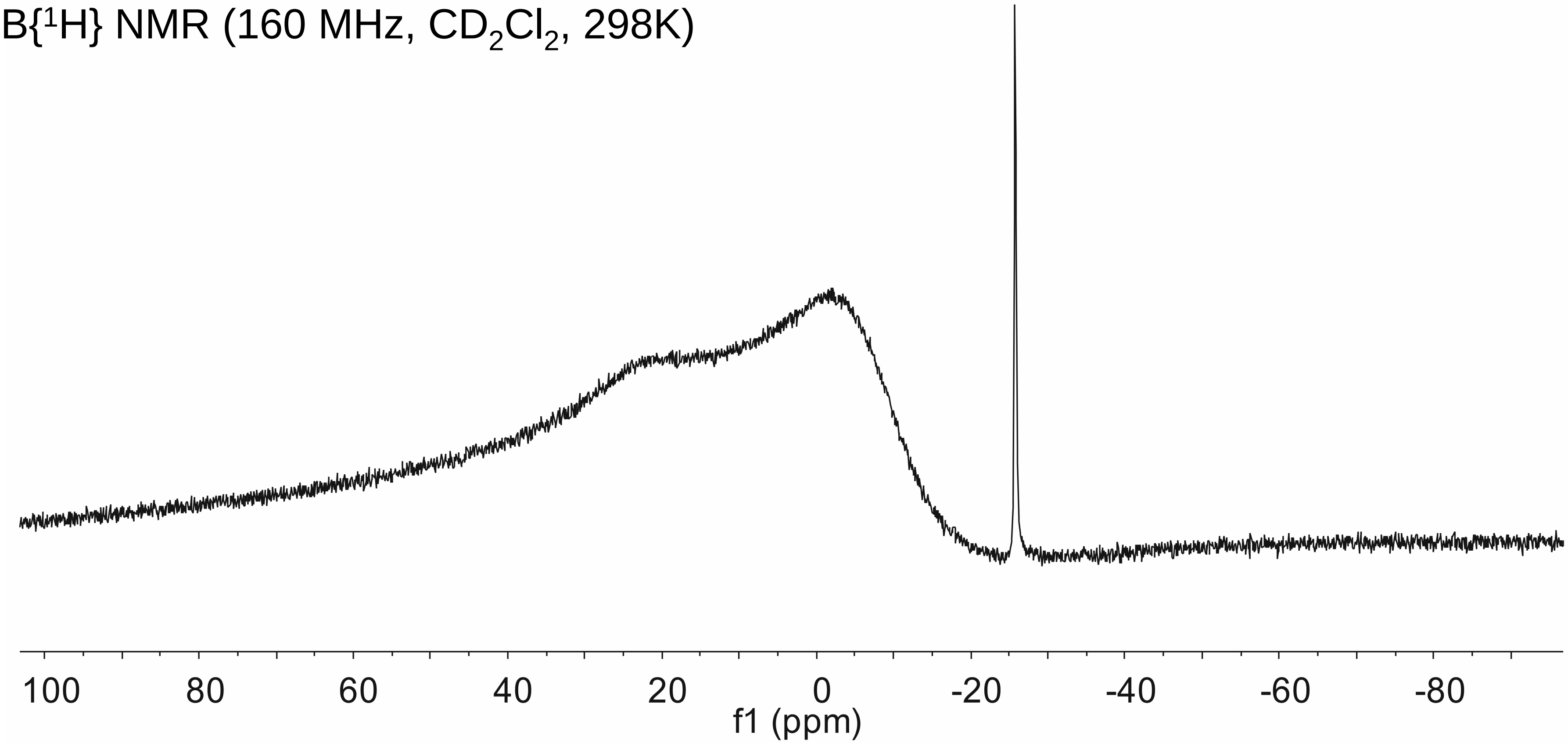


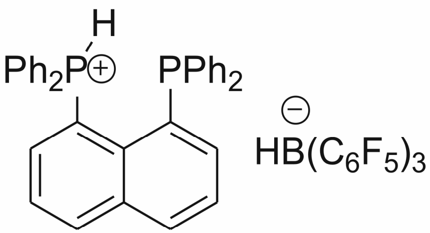
^{11}B NMR (160 MHz, CD_2Cl_2, 298K)



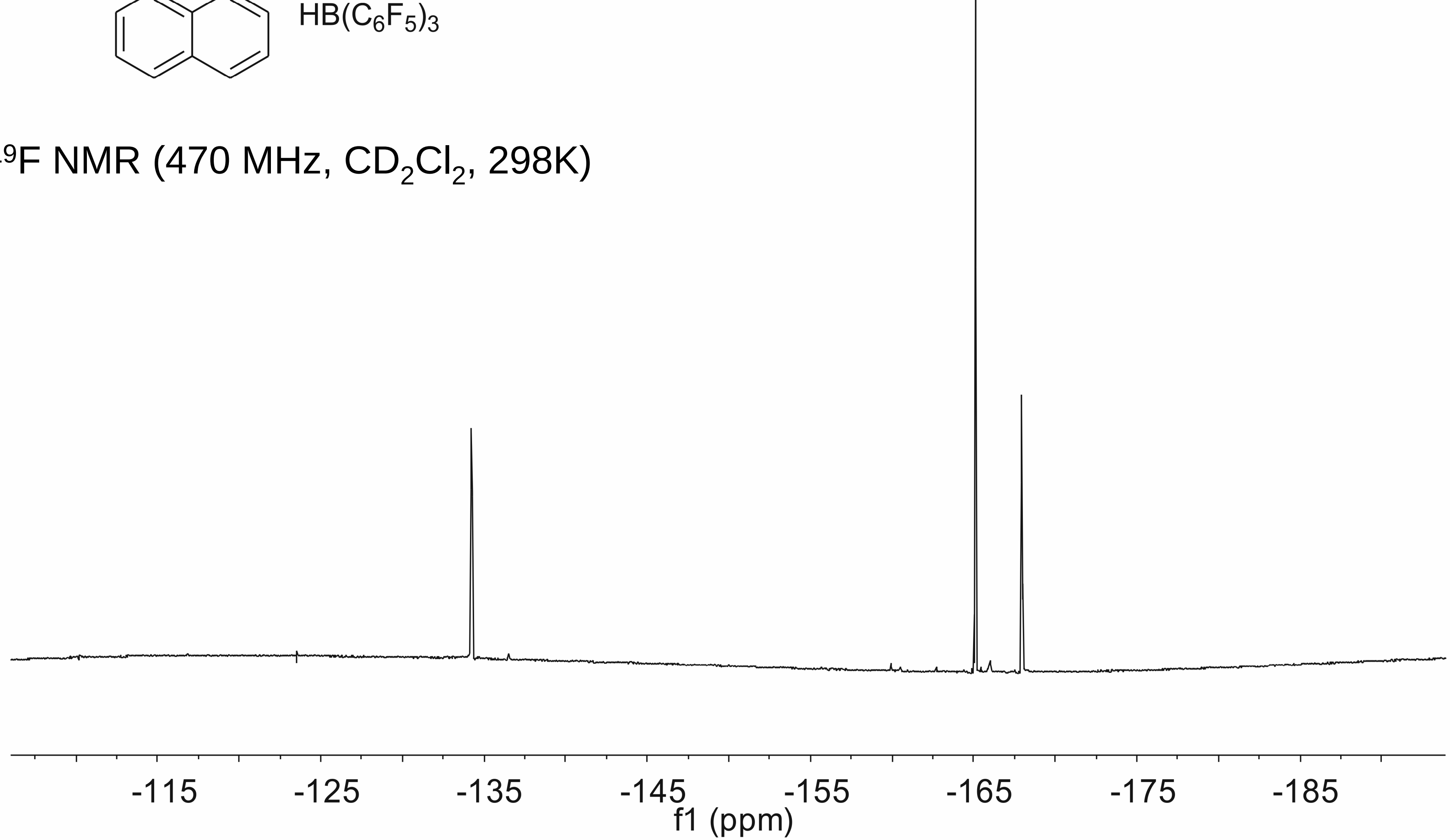


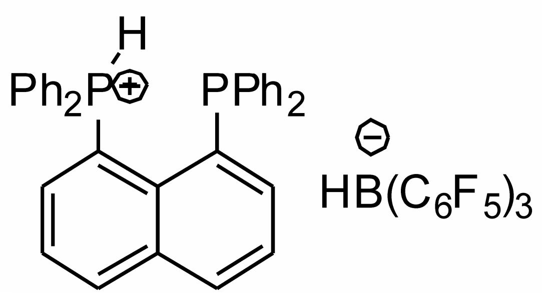
$^{11}B\{^1H\}$ NMR (160 MHz, CD_2Cl_2, 298K)

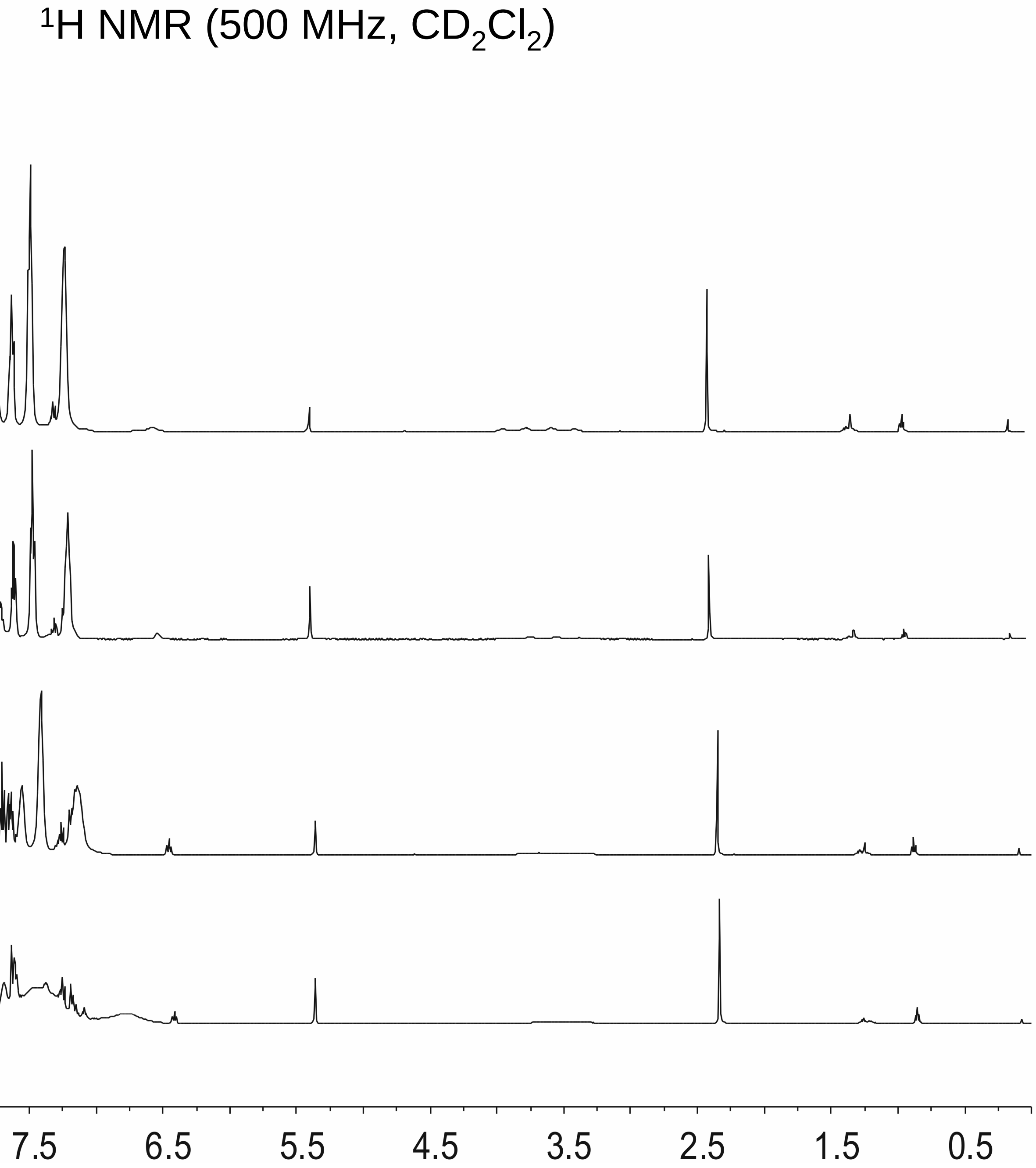


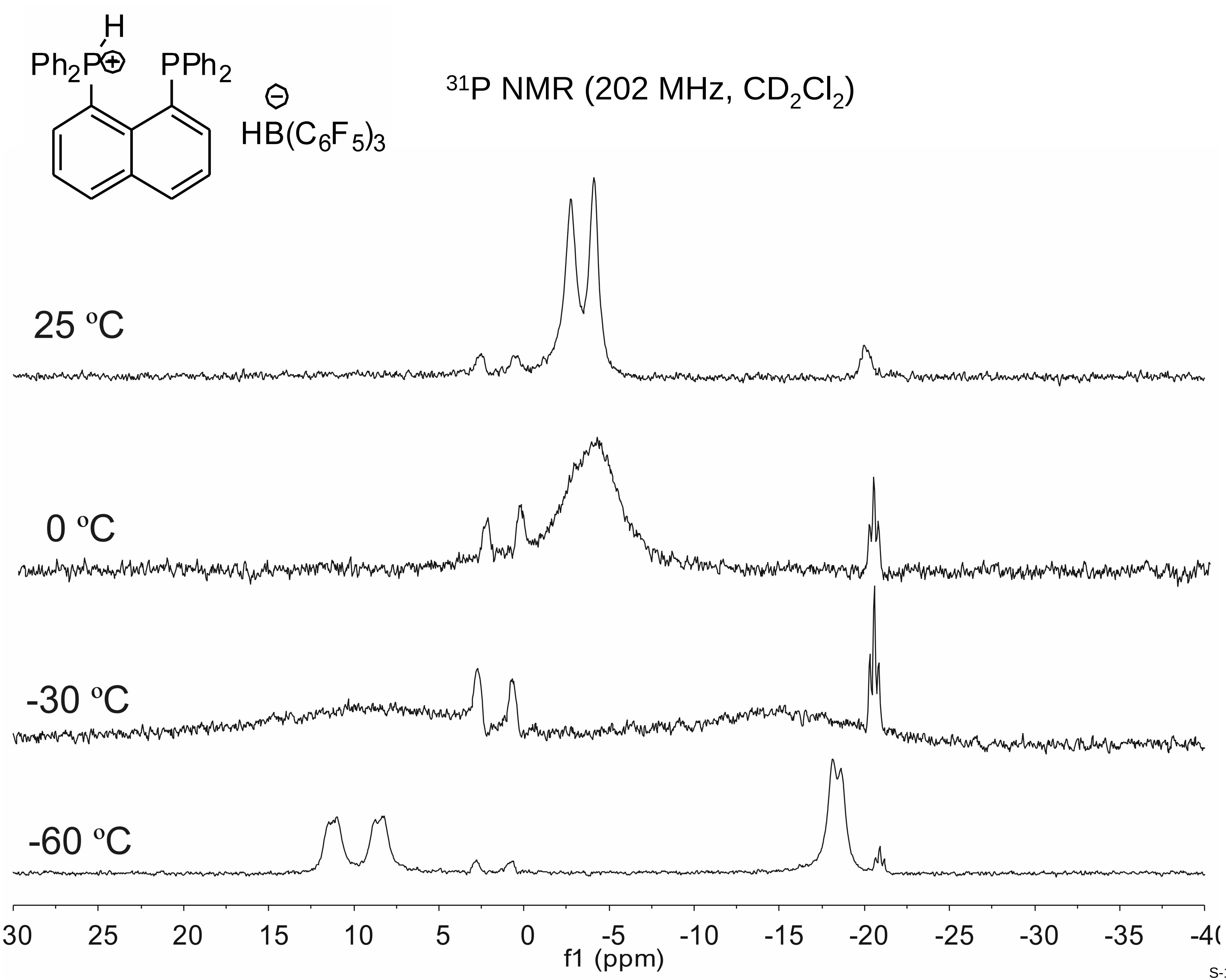


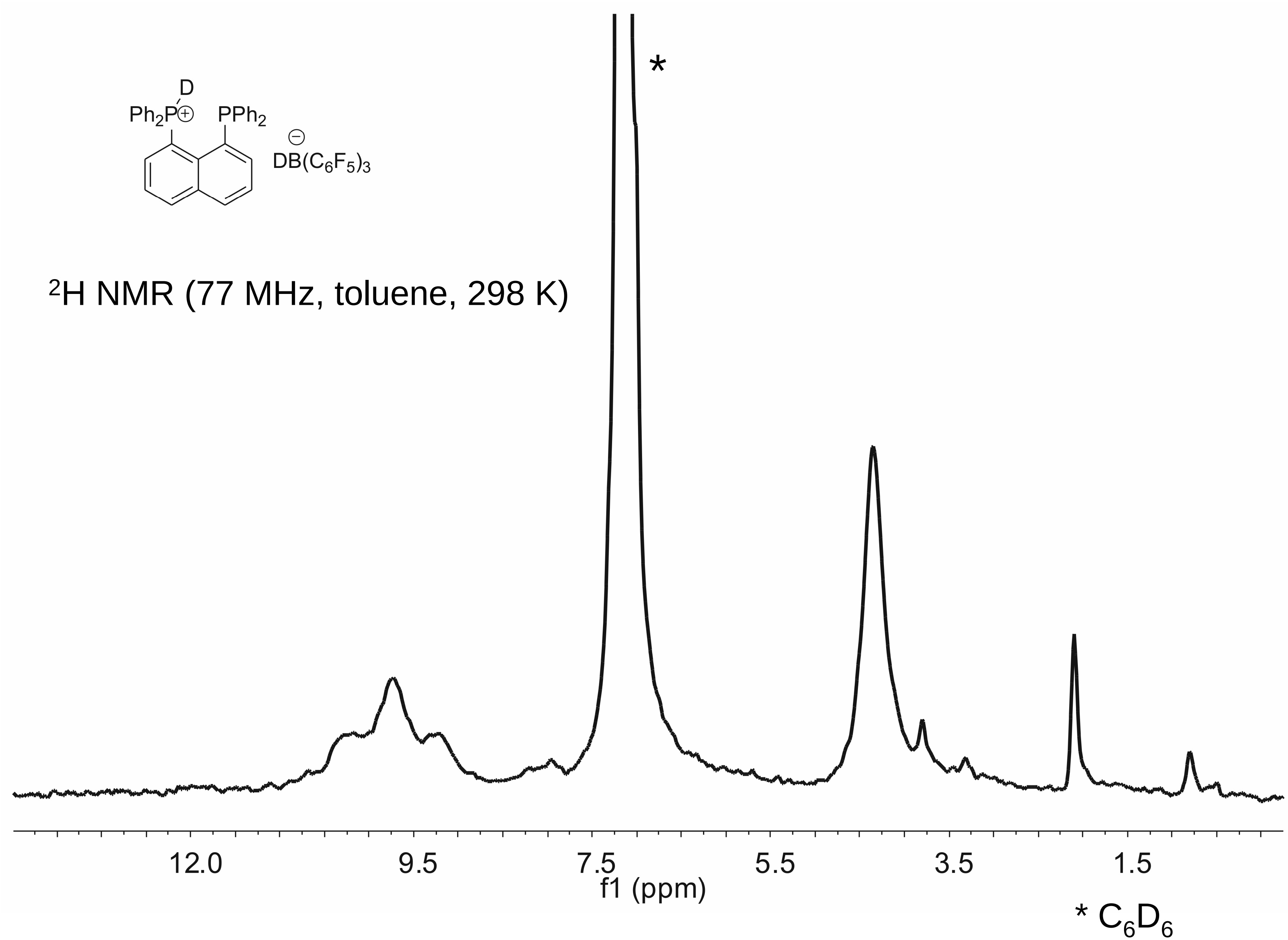
^{19}F NMR (470 MHz, CD_2Cl_2, 298K)




H
Ph2P
PPh2
HB(C6F5)3

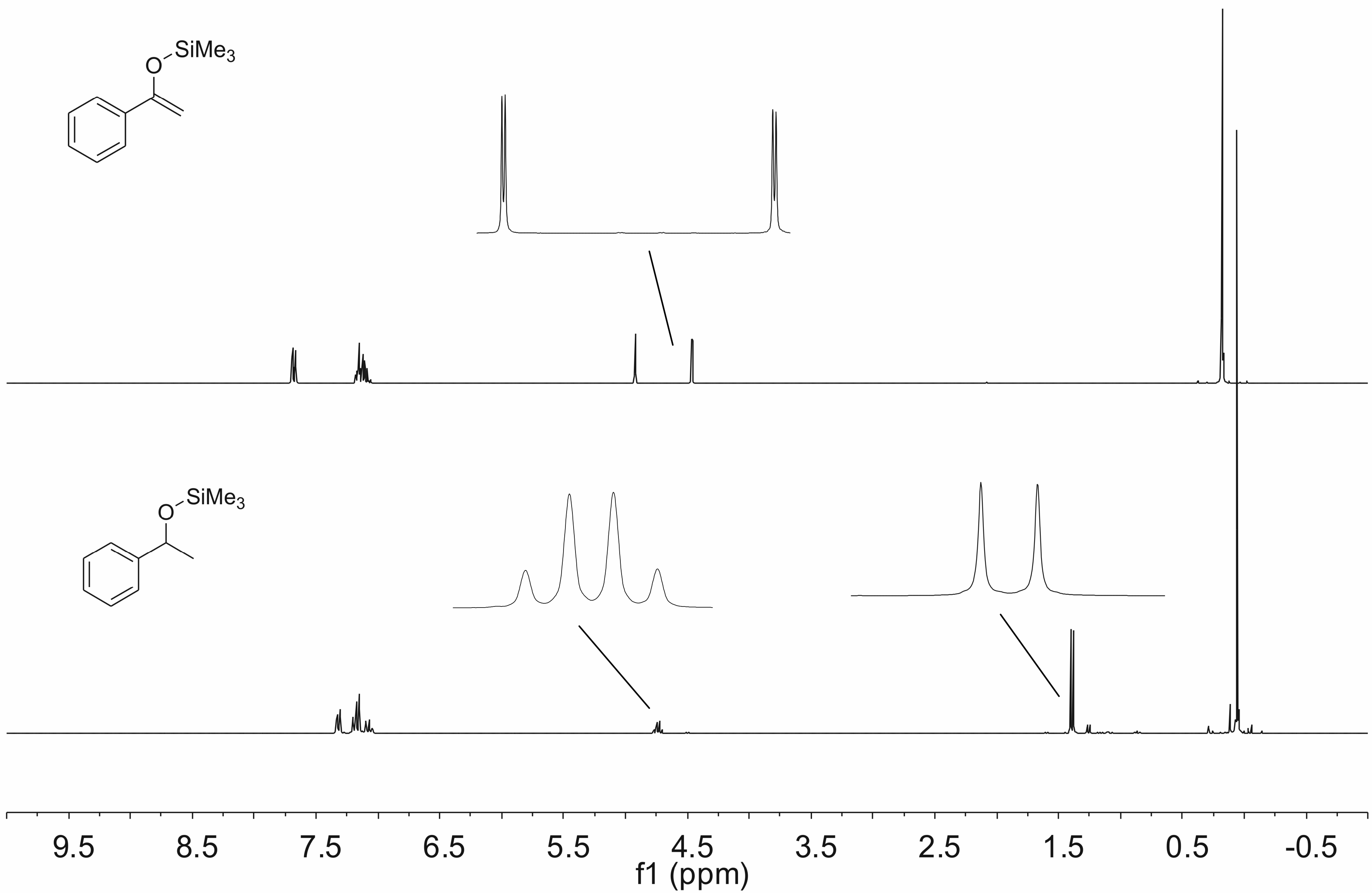

1H NMR (500 MHz, CD2Cl2)
25 °C
0 °C
-30 °C
-60 °C
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5


H
Ph2P
PPh2
HB(C6F5)3
31P NMR (202 MHz, CD2Cl2)
25 oC
0 oC
-30 oC
-60 oC
30
25
20
15
10
5
0
-5
-10
-15
-20
-25
-30
-35
f1 (ppm)

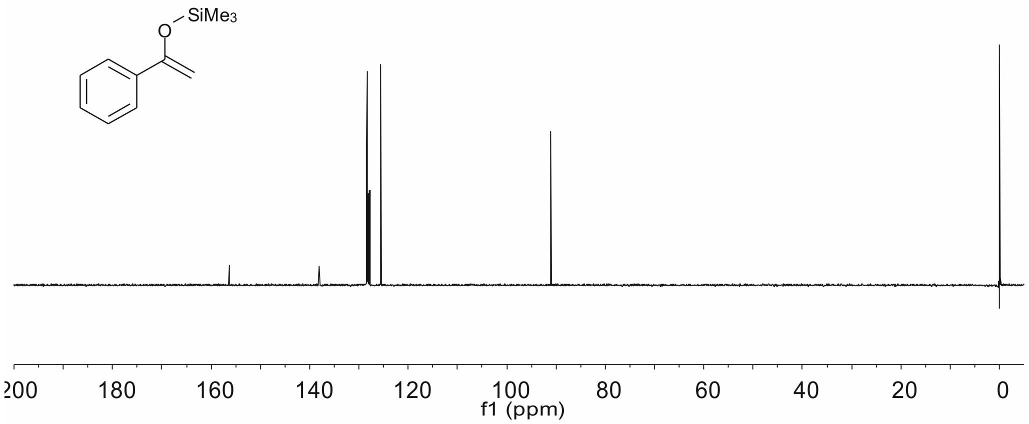


D
$Ph_2P^{\oplus}$ PPh2
$\ominus$
$DB(C_6F_5)_3$
^2H NMR (77 MHz, toluene, 298 K)
*
12.0
9.5
7.5
5.5
3.5
1.5
f1 (ppm)
* C_6D_6

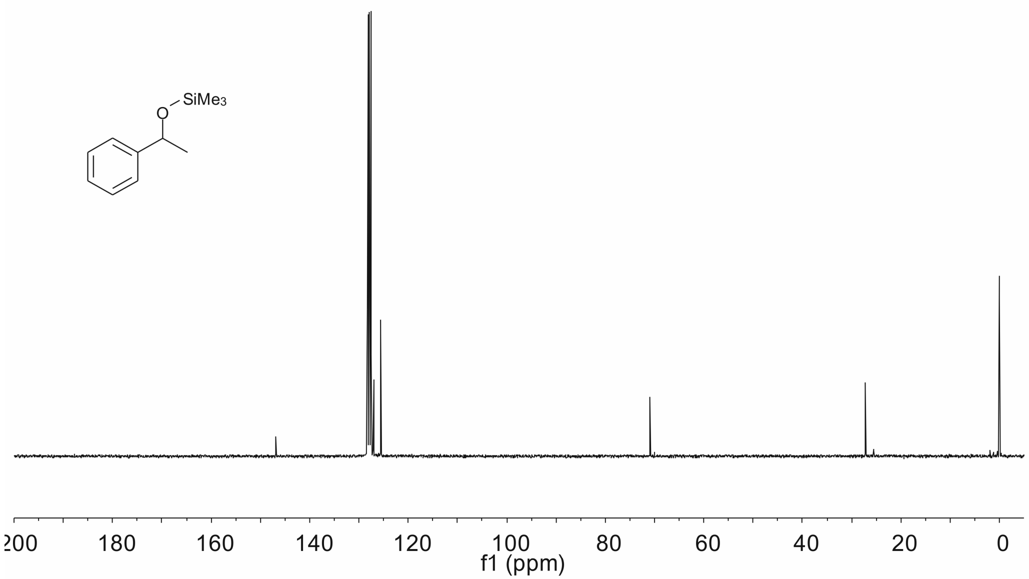
^{1}H NMR (300 MHz, C_6D_6)

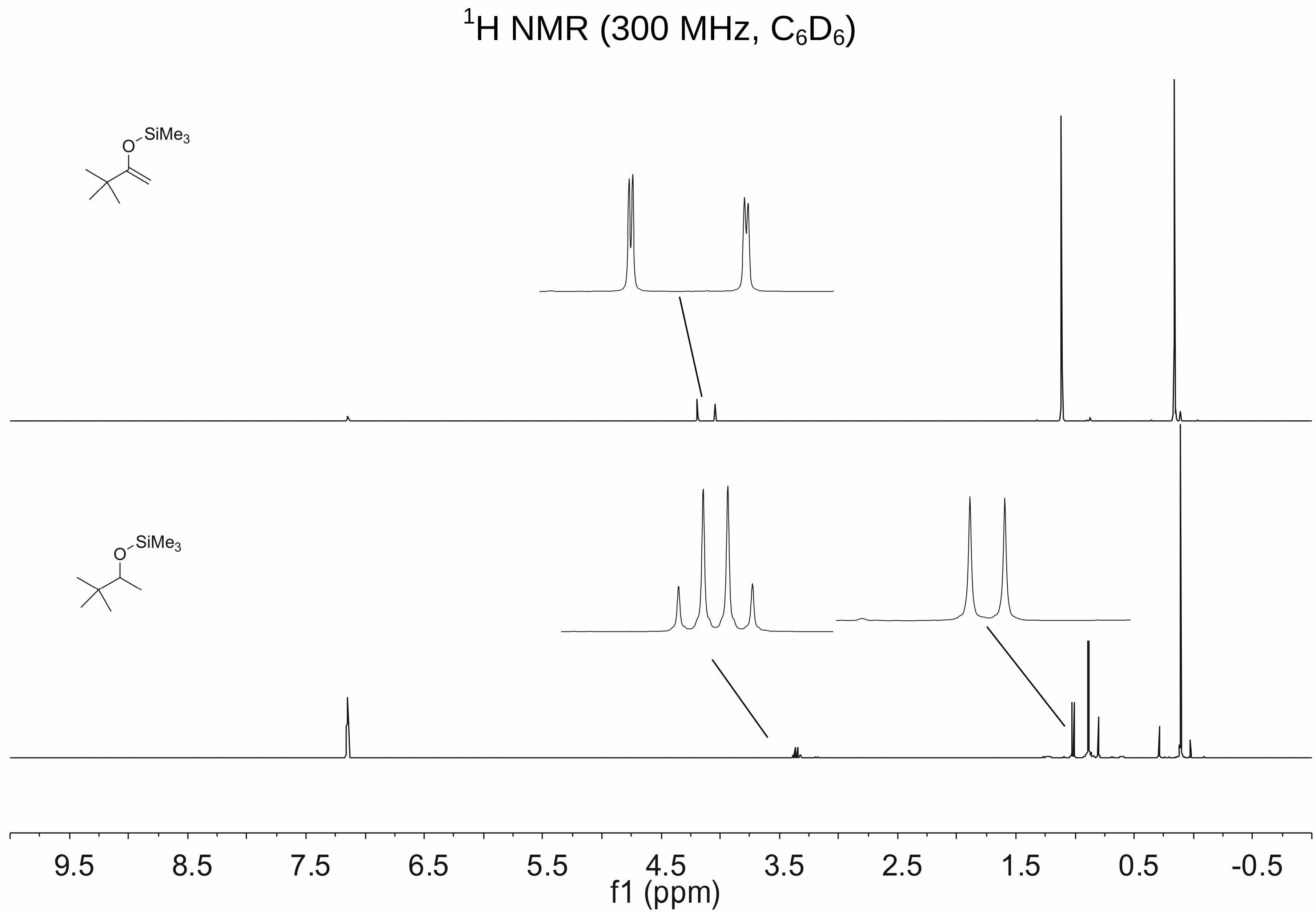


^{13}C NMR (125.7 MHz, C_6D_6)



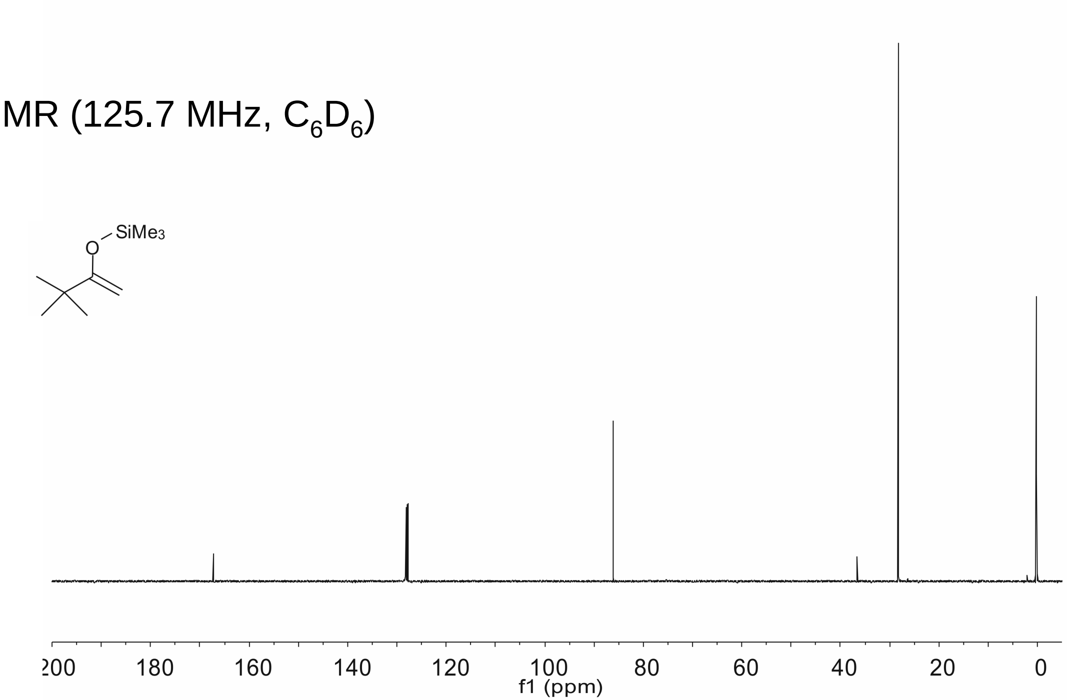
^{13}C NMR (75.5 MHz, C_6D_6)



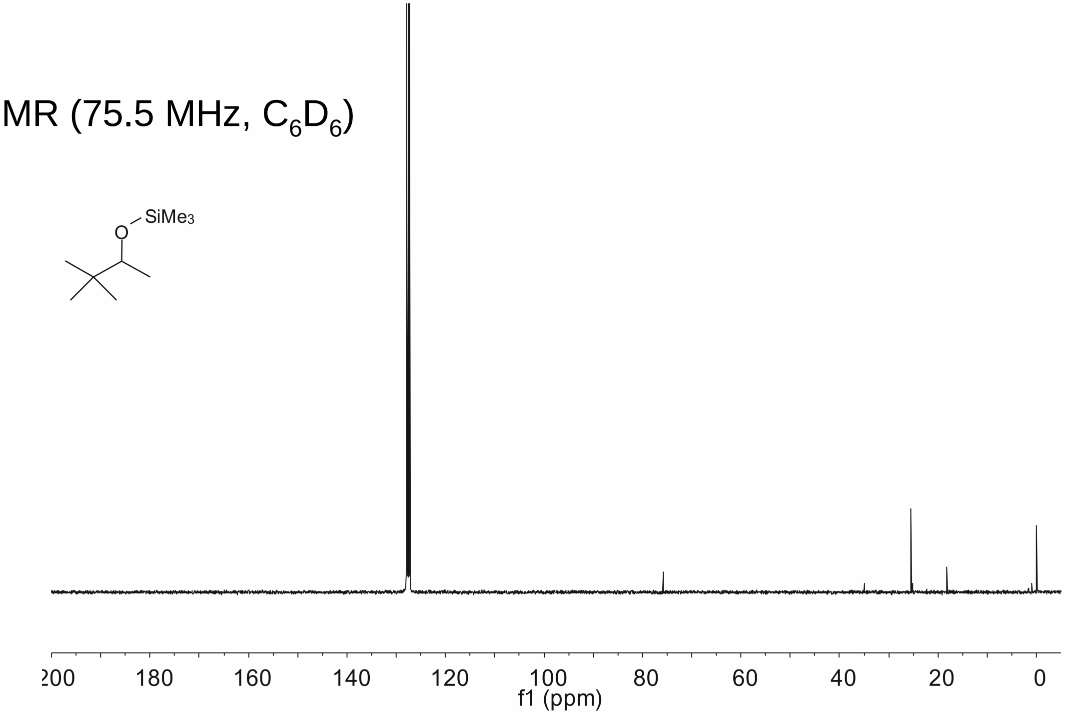


1H NMR (300 MHz, C6D6)
SiMe3
O
SiMe3
O
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

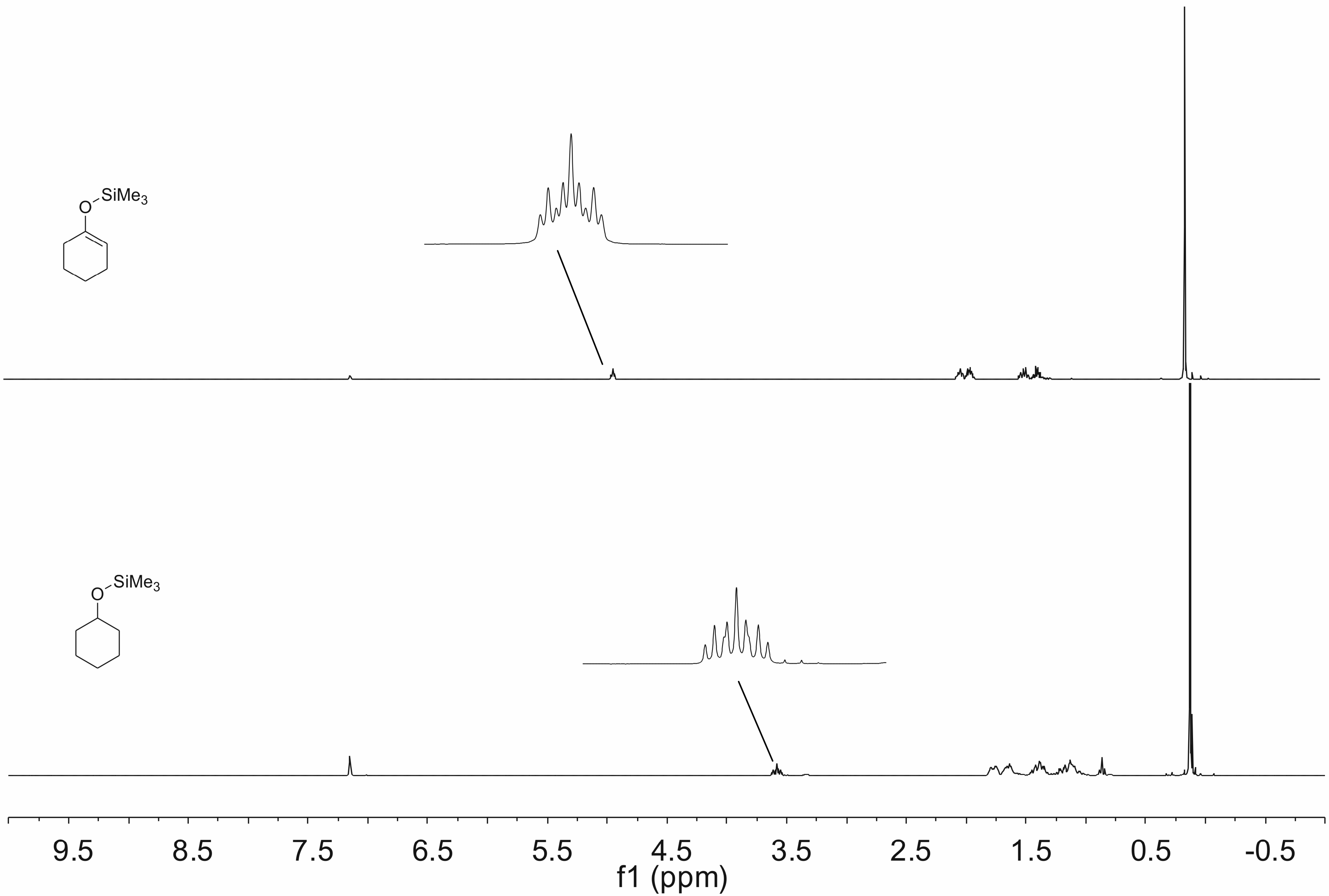
^{13}C NMR (125.7 MHz, C_6D_6)



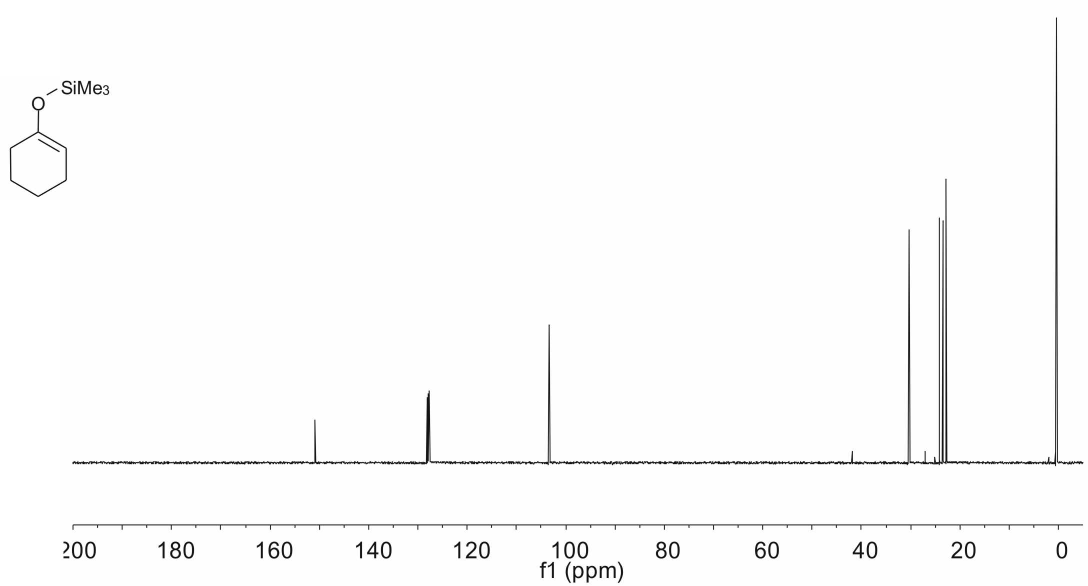
^{13}C NMR (75.5 MHz, C_6D_6)



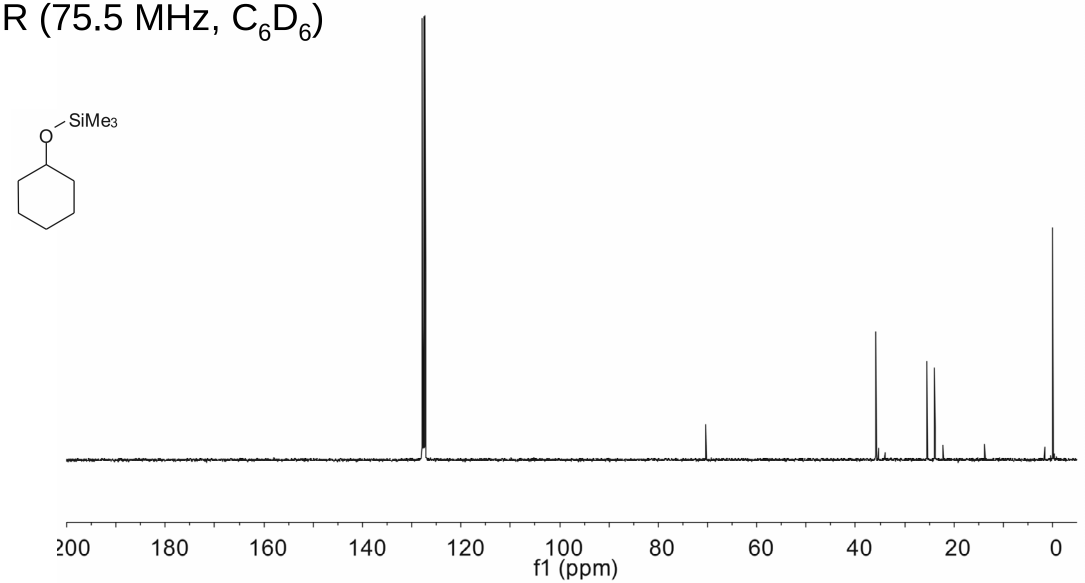
^1H NMR (300 MHz, C_6D_6)

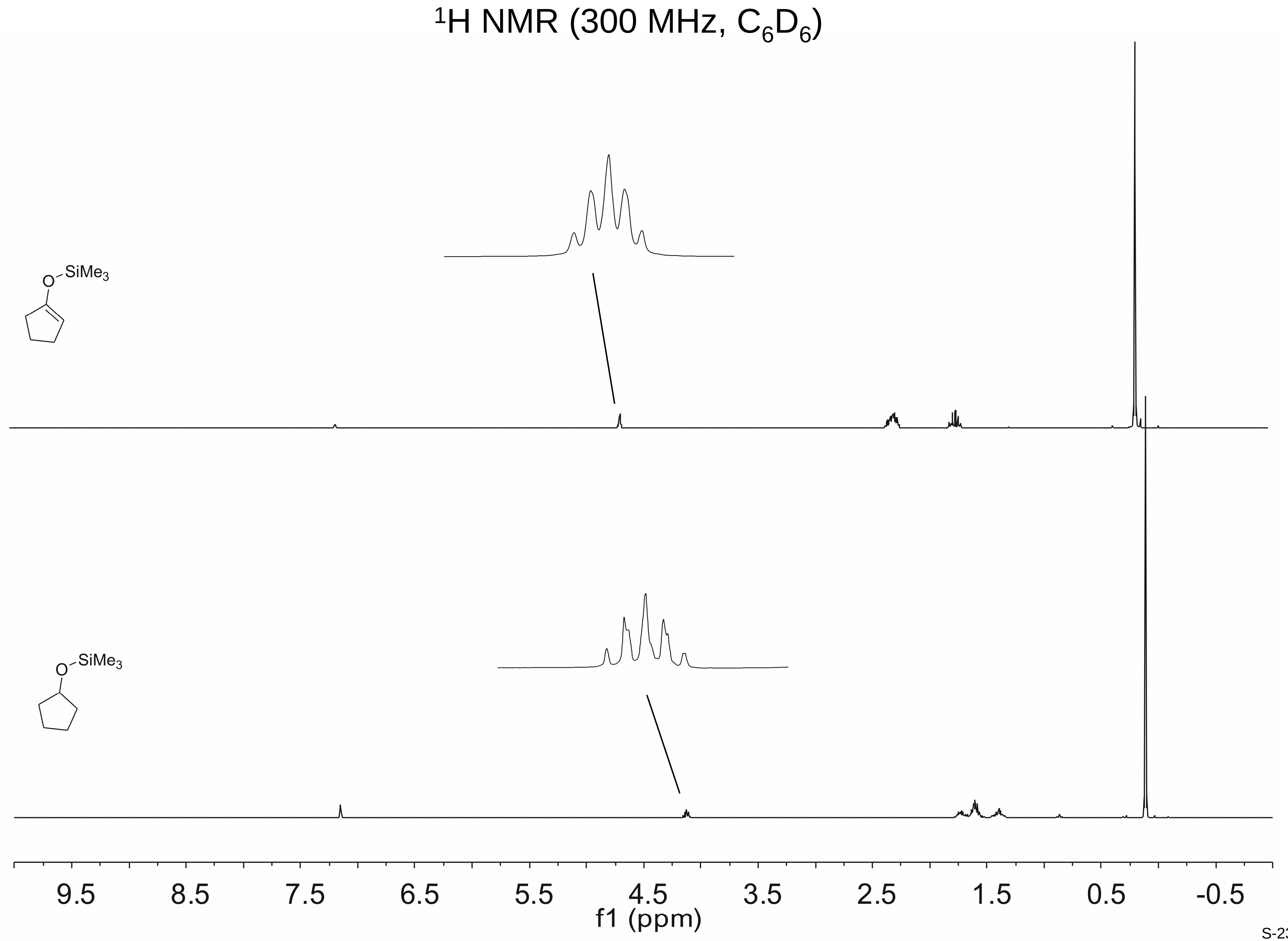


^{13}C NMR (125.7 MHz, C_6D_6)



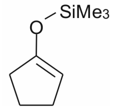
^{13}C NMR (75.5 MHz, C_6D_6)

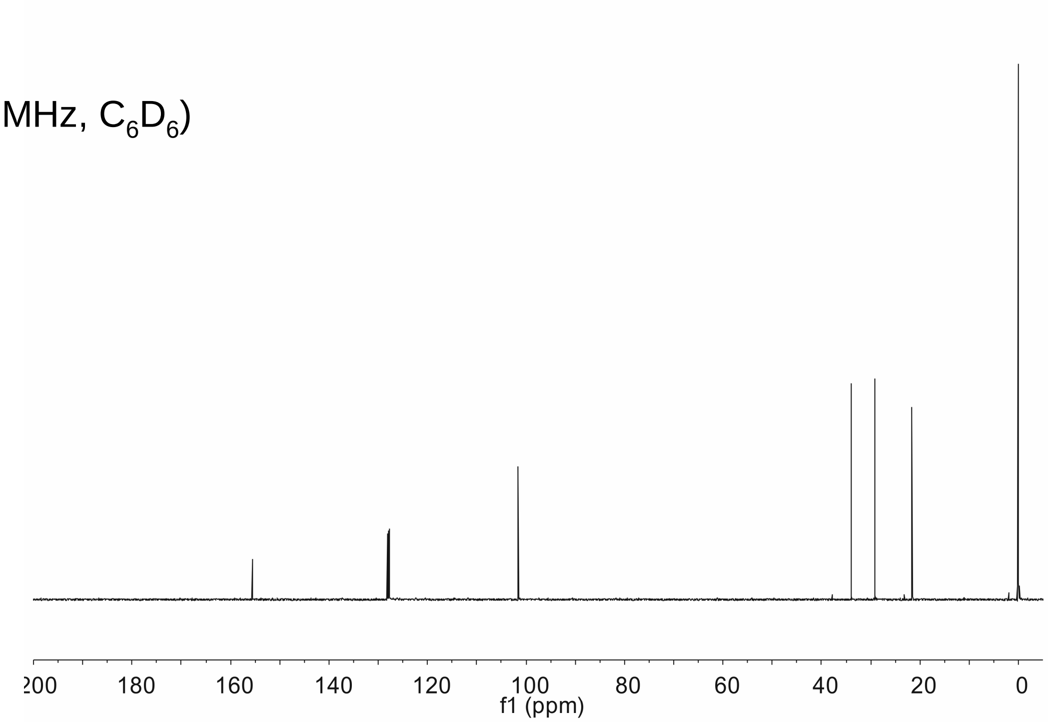




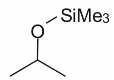
^1H NMR (300 MHz, C_6D_6)
SiMe3
O
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

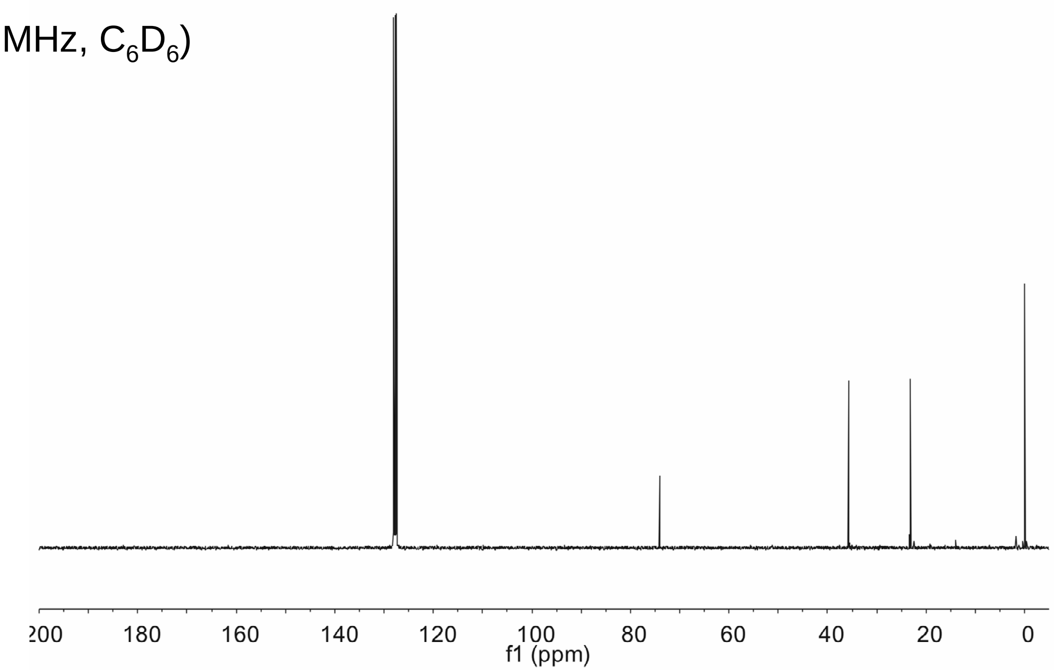
^{13}C NMR (125.7 MHz, C_6D_6)

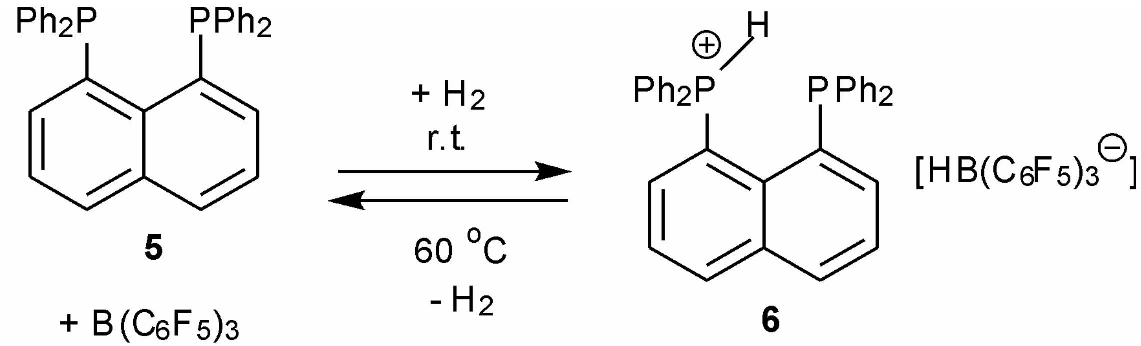


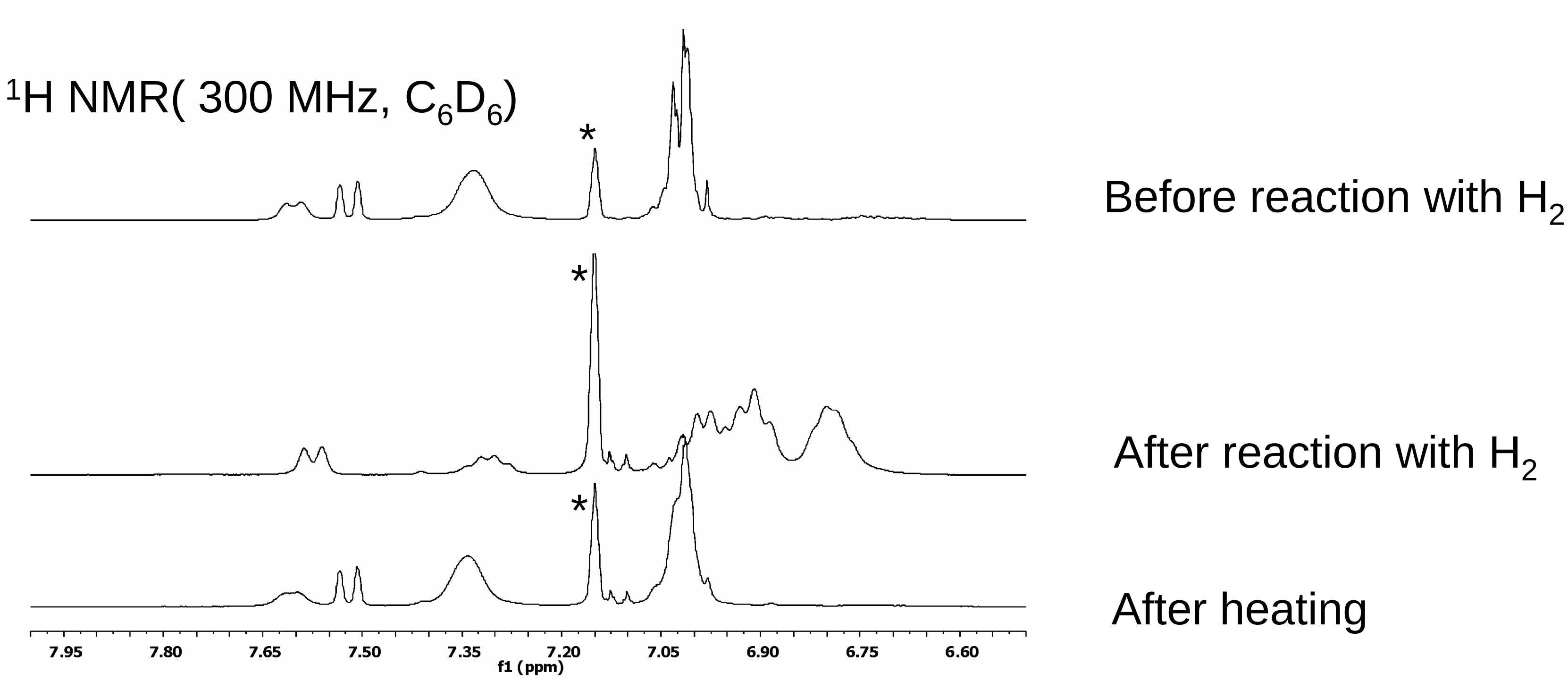


^{13}C NMR (75.5 MHz, C_6D_6)

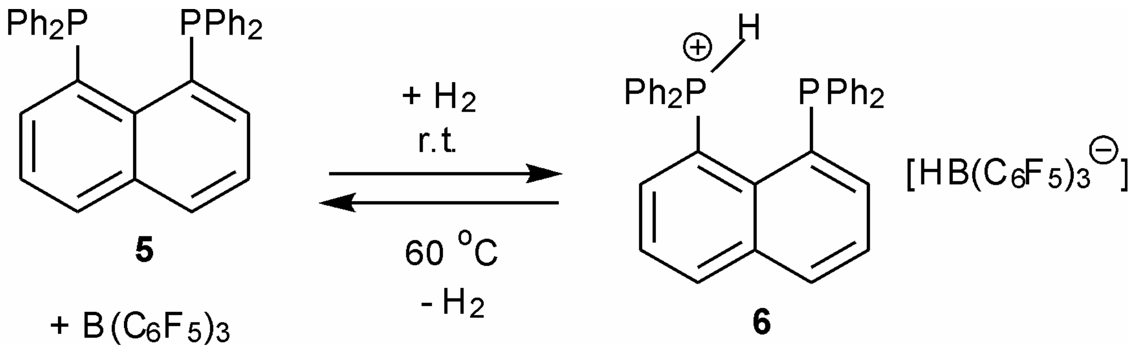




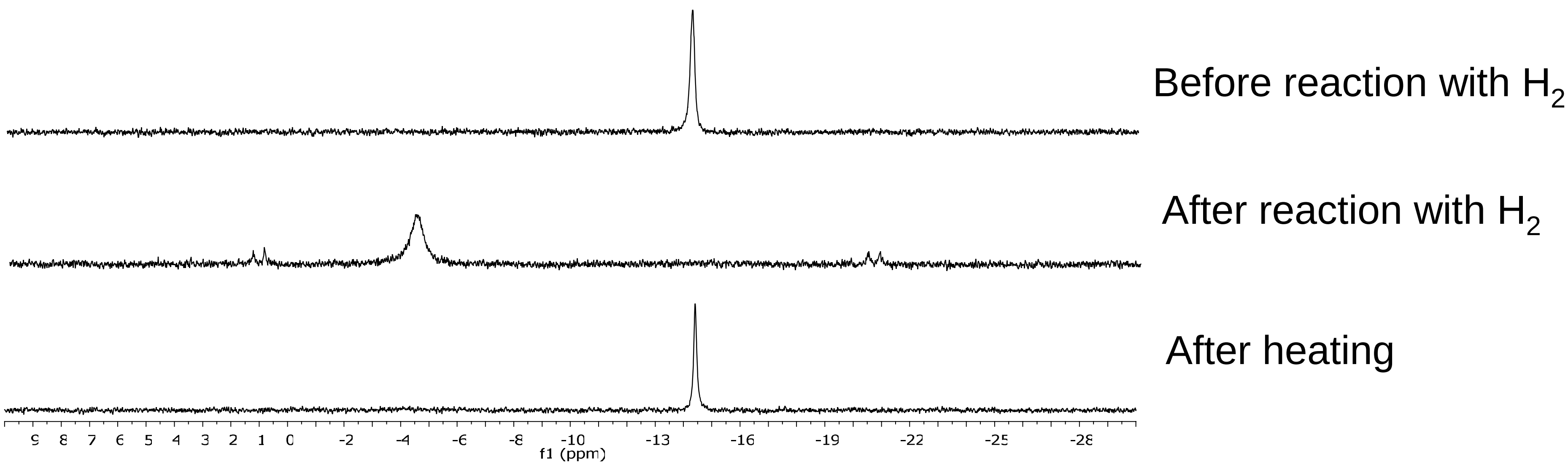

Ph2P
PPh2
5
+ B(C6F5)3
+ H2
r.t.
60 °C
- H2
H
Ph2P
PPh2
[HB(C6F5)3]
6

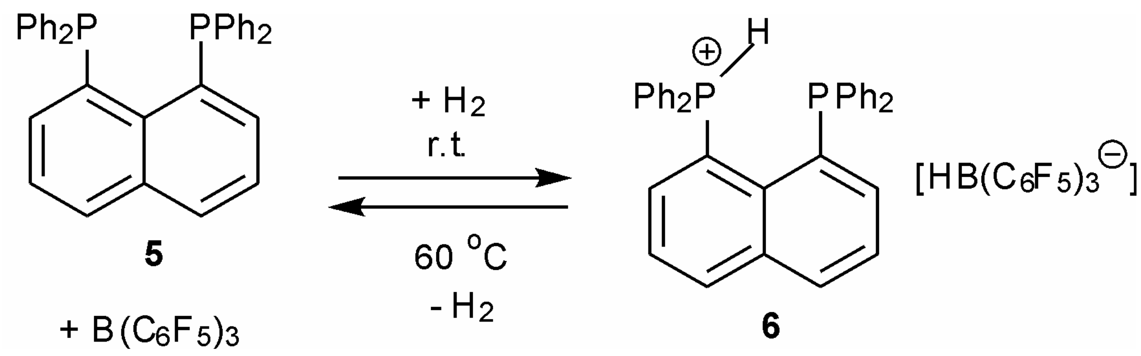

1H NMR(300 MHz, C6D6)
Before reaction with H2
After reaction with H2
After heating
7.95
7.80
7.65
7.50
7.35
7.20
7.05
6.90
6.75
6.60
f1 (ppm)

* solvent

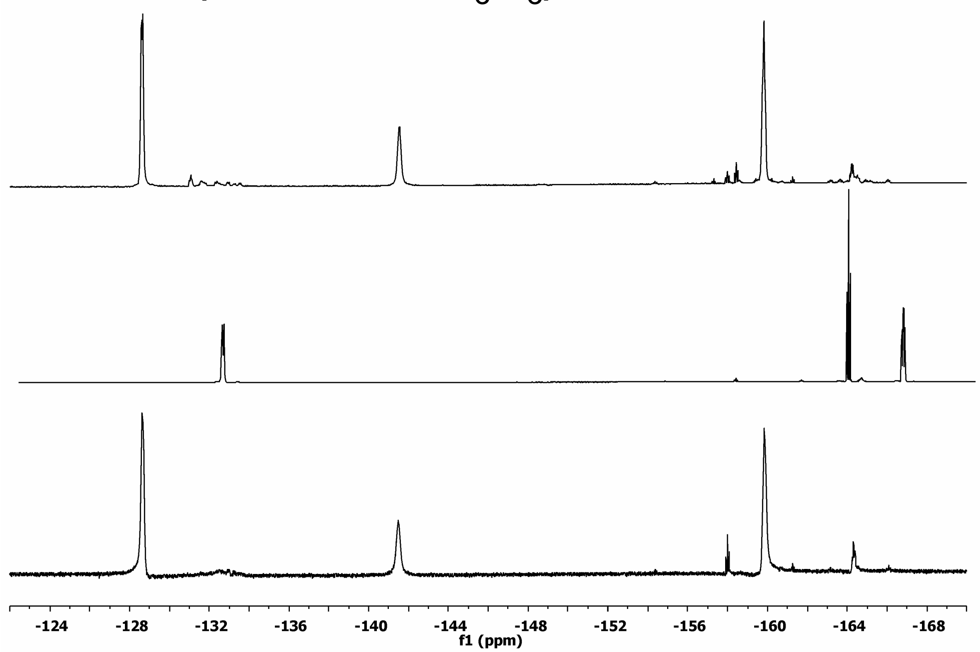


$^{31}P\{^{1}H\}$ NMR (121 MHz, C_6D_6)





^{19}F NMR (282 MHz, C_6D_6)



Before reaction with H_2

After reaction with H_2

After heating

checkCIF/PLATON report

No syntax errors found. **CIF dictionary** **Interpreting this report**

Datablock: erk4541b

Bond precision: C-C = 0.0048 A Wavelength=1.54178

Cell:	**a=9.7493(5)**	**b=13.3554(6)**	**c=19.3935(9)**
	alpha=100.853(2)	**beta=99.692(2)**	**gamma=94.678(4)**
Temperature:	**223 K**		

	Calculated	Reported
Volume	2427.8(2)	2427.8(2)
Space group	P -1	P-1
Hall group	-P 1	?
Moiety formula	C34 H27 P2, C18 H B F15	?
Sum formula	C52 H28 B F15 P2	C52 H28 B F15 P2
Mr	1010.49	1010.49
Dx,g cm-3	1.382	1.382
Z	2	2
Mu (mm-1)	1.645	1.645
F000	1020.0	1020.0
F000’	1025.16	
h,k,lmax	11,16,23	11,15,23
Nref	8852	8515
Tmin,Tmax	0.744,0.952	0.559,0.952
Tmin’	0.518	

Correction method= AbsCorr=MULTI-SCAN

Data completeness= Ratio = 0.962 Theta(max)= 68.050

R(reflections)= 0.0603(6735) wR2(reflections)= 0.1716(8515)

S = 1.074 Npar= 639

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level A

PLAT601_ALERT_2_A Structure Contains Solvent Accessible VOIDS of . 282.00 A**3

Alert level B

PLAT415_ALERT_2_B Short Inter D-H..H-X H1 .. H1A .. 2.08 Ang.

Alert level C

```
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full Low .......       0.96
PLAT230_ALERT_2_C Hirshfeld Test Diff for    F66    --  C66     ..       5.25 su
PLAT230_ALERT_2_C Hirshfeld Test Diff for    C64    --  C65     ..       6.74 su
PLAT242_ALERT_2_C Check Low       Ueq as Compared to Neighbors for        C64
PLAT340_ALERT_3_C Low Bond Precision on C-C Bonds (x 1000) Ang ...          5
```

1 **ALERT level A** = In general: serious problem
1 **ALERT level B** = Potentially serious problem
5 **ALERT level C** = Check and explain
0 **ALERT level G** = General alerts; check

0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
5 ALERT type 2 Indicator that the structure model may be wrong or deficient
2 ALERT type 3 Indicator that the structure quality may be low
0 ALERT type 4 Improvement, methodology, query or suggestion
0 ALERT type 5 Informative message, check

Publication of your CIF in IUCr journals

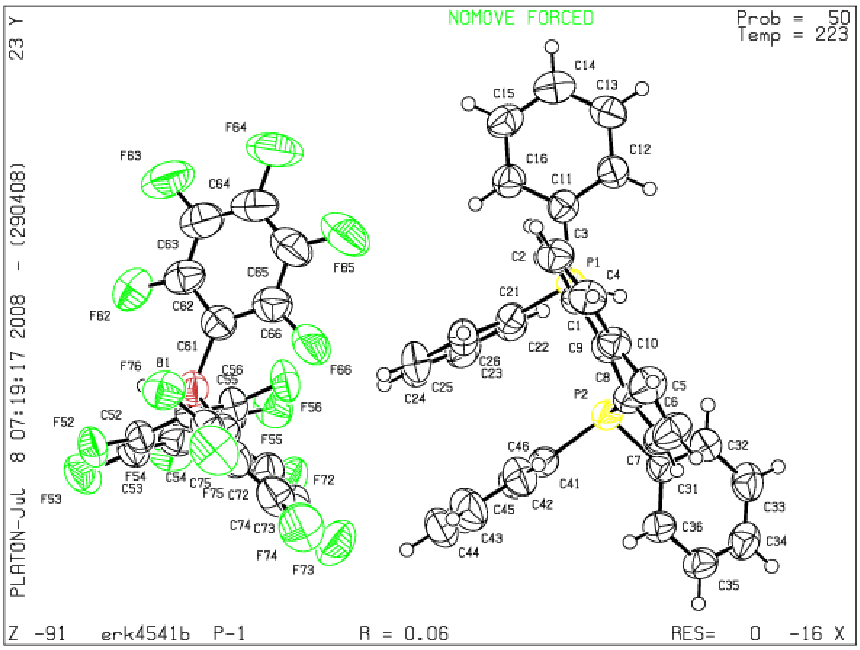
A basic structural check has been run on your CIF. These basic checks will be run on all CIFs submitted for publication in IUCr journals (*Acta Crystallographica*, *Journal of Applied Crystallography*, *Journal of Synchrotron Radiation*); however, if you intend to submit to *Acta Crystallographica Section C* or *E*, you should make sure that full publication checks are run on the final version of your CIF prior to submission.

Publication of your CIF in other journals

Please refer to the *Notes for Authors* of the relevant journal for any special instructions relating to CIF submission.

PLATON version of 29/04/2008; check.def file version of 22/04/2008 /tmp/checkcif/_@@dvn25862/_@dvn25938/test.cif

Datablock erk4541b - ellipsoid plot



Comment on CHECKCIF

Comments on CHECKCIF:

PLAT601: The compound was crystallized from a "cocktail" of different solvent. These are disordered and mixed in a void. All attempts do refine the solvent molecules lead to no chemically meaningful results. Therefore the SQUEEZE program in the PLATON program suite was applied.

PLAT415: Hydrogen atoms at phosphorus and boron are localized from difference Fourier maps and refined free with isotropic thermal parameters.

PLAT029: Data collection was done with a Cu-CCD detector. The geometrical limitations lead to a completeness less than 100%.