Electronic Supplementary Material (ESI) for ChemComm.

Interaction of Formaldehyde with a Water-Tolerant Frustrated Lewis Pair

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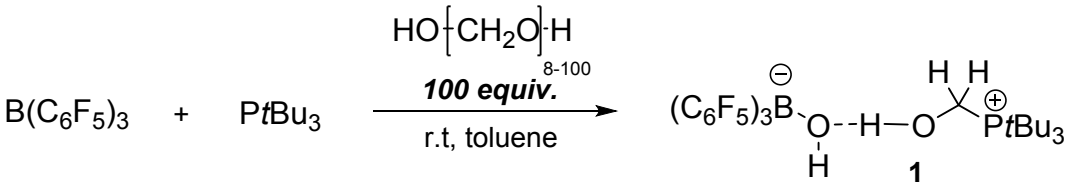
General Procedures. All reactions involving air or moisture-sensitive compounds were carried out under argon using standard Schlenk techniques. Solvents used in reaction were dried and distilled prior to use. Unless otherwise noted, all materials were obtained from commercial suppliers and were used without further purification. NMR experiments were performed on Bruker AV-300, or AV-400 spectrometer. ^{1}H, $^{13}C\{^{1}H\}$-NMR spectra are referenced to $SiMe_4$ or the residual solvent peak. ^{31}P, ^{11}B, ^{19}F NMR spectra were referenced externally to 85 % H_3PO_4 at 0 ppm, $BF_3{\cdot}Et_2O$ at 0 ppm and CF_3CO_2H at 78.5 ppm relative to $CFCl_3$ at 0 ppm, respectively. Chemical shifts are given in ppm and spin-spin coupling constants, *J*, are given in Hz. Compounds **1**, **2** and **4** have been studied by single X-ray diffraction.

Materials. $B(C_6F_5)_3$ was purchased from abcr (97 % purity), *t*-Bu_3P, Trimethylaluminum solution (2.0 M in toluene) and paraformaldehyde were purchased from Sigma Aldrich. $Al(C_6F_5)_3$ and **3** was prepared according to the literature procedure; J. Chen, E. Y. Chen, *Dalton Trans.* **2016**, *45*, 6105-6110 and M. Klahn, A. Spannenberg, U. Rosenthal, *Acta Crystallogr Sect E Struct Rep Online* **2012**, *68*, o1549 respectively.

Synthesis of 1 starting from $B(C_6F_5)_3$/P*t*Bu$_3$



In a Schlenk flask (50 mL), $B(C_6F_5)_3$ (102.0 mg, 0.2 mmol) and *t*-Bu_3P (41.0 mg, 0.2 mmol) were dissolved in toluene (20 mL) and stirred for 10 minutes. Then paraformaldehyde (600 mg, 20 mmol) was added to the reaction mixture. The reaction mixture was stirred overnight (20 hours) at room temperature. The slurry was filtered to remove solvent and subsequently, precipitates were washed with dichloromethane (3 x 5 mL) to extract the desired product from excess paraformaldehyde. All volatiles were collected into a second Schlenk flask (50 mL) and then volatiles were removed in *vacuo* to yield **1** (102 mg, 67.0 %) as a white solid. Crystals suitable for X-ray diffraction analysis were obtained from a mixture of dichloromethane and n-hexane at -30 °C. Elemental analysis Calcd (%) for $C_{31}H_{31}BF_{15}O_2P$: C, 48.84; H, 4.10; B, 1.42; F, 37.38; P, 4.06; found C, 49.87; H, 4.67; B, 0.92; F, 35.92; P, 3.96

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.44 (d, *J* = 13.71 Hz, 27H), 2.16 (br, OH, 1H), 4.17 (m, 2H), 7.82 (br, OH, 1H), ppm.

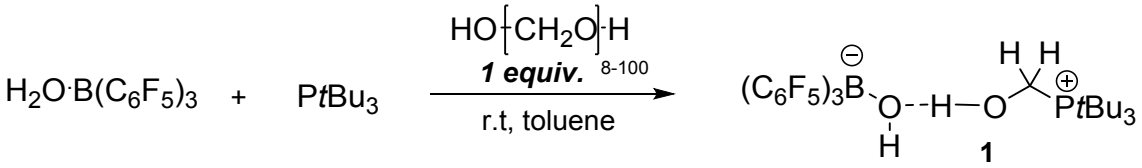
^{11}B-NMR (96 MHz, CD_2Cl_2): δ = - 4.0 ppm.

^{13}C{^{1}H}-NMR (75 MHz, CD_2Cl_2): δ = 29.6, 38.8 (d, *J* = 27.1 Hz), perfluorinated phenyl ring were not observed.

^{19}F{^{1}H}-NMR (282 MHz, CD_2Cl_2): δ = -135.9, -162.4 and -166.4 ppm.

^{31}P-NMR (121 MHz, CD_2Cl_2): δ = 42.3 ppm

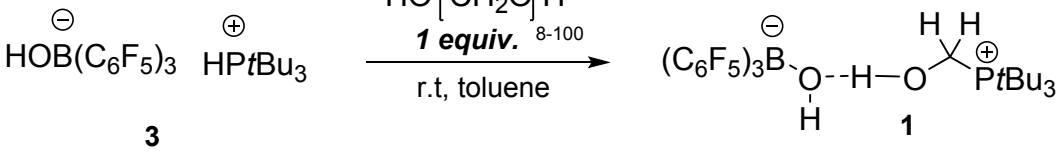
Synthesis of 1 starting from $H_2O{\cdot}B(C_6F_5)_3$/P*t*Bu$_3$



In a Schlenk flask (10 mL), $H_2O{\cdot}B(C_6F_5)_3$ (53.0 mg, 0.1 mmol) and *t*-Bu_3P (20.2 mg, 0.1 mmol) were dissolved in toluene (5 mL) and stirred for 10 minutes. Then paraformaldehyde (3.3 mg, 0.11 mmol) was added to the reaction mixture. The reaction mixture was stirred overnight (20 hours) at room temperature, whereupon a light precipitate formed. Removing the supernatant by syringe and the

residue was washed with a mixture of anhydrous toluene:pentane (1:1) (2 x 2 mL). All volatiles were removed in *vacuo* to yield **1** (43 mg, 56.4 %) as a colourless solid

Synthesis of 1 starting from 3



In a Schlenk flask (10 mL), **3** (102.0 mg, 0.14 mmol) was dissolved in toluene (5 mL) and stirred for 5 minutes. Then paraformaldehyde (4.2 mg, 0.14 mmol) was added to the reaction mixture. The reaction mixture was stirred overnight (20 hours) at room temperature, whereupon a light precipitate formed. Removing the supernatant by syringe and the residue was washed with a mixture of anhydrous toluene:pentane (1:1) (2 x 2 mL). All volatiles were removed in *vacuo* to yield **1** (55.0 mg, 51.6 %) as a colorless solid.

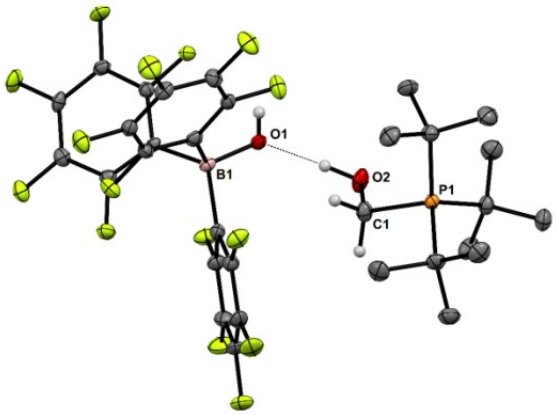
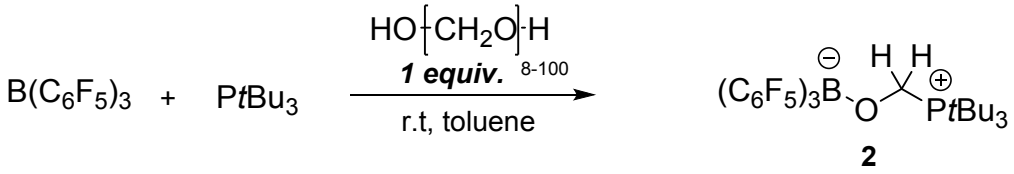


Table 2. X-ray crystal structure analysis for 1

	a15_a66_a
Crystal data	
Chemical formula	$C_{31}H_{31}BF_{15}O_2P$
M_r	779.77
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, *b*, *c* (Å)	9.2422 (14), 11.3099 (17), 18.117 (3)
α, β, γ (°)	104.882 (2), 104.203 (2), 96.931 (2)
V (Å^3)	1739.8 (5)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.26
Crystal size (mm)	0.17 × 0.31× 0.42
Data collection	
Diffractometer	Bruker APEX CCD
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	26777, 10030, 6722
R_{int}	0.052
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.718
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.065, 0.208, 1.17
No. of reflections	10030
No. of parameters	486
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.20, -1.57

Synthesis of 2 starting from $B(C_6F_5)_3$/P*t*Bu$_3$



2

In a Schlenk flask (10 mL), $B(C_6F_5)_3$ (51.2 mg, 0.1 mmol) and *t*-Bu_3P (20.2 mg, 0.1 mmol) were dissolved in toluene (5 mL) and stirred for 10 minutes. Then paraformaldehyde (3.3 mg, 0.11 mmol) was added to the reaction mixture. The pale yellow solution became colourless after stirring the mixture at room temperature for one hour. The reaction mixture was stirred overnight (20 hours) at room temperature, whereupon a light precipitate formed. Removing the supernatant by syringe and the residue was washed with anhydrous toluene (2 x 2 mL) and one time with anhydrous *n*-pentane (3 mL). All volatiles were removed in *vacuo* to yield **2** (55.0 mg, 74 %) as a colorless solid. (Note: The desired product **2** is slightly soluble in toluene). In order to improve the yield, *n*-pentane (1 mL) is added to the toluene solution, more product as white precipitate is obtained). Crystals suitable for X-ray diffraction analysis were obtained from a mixture of dichloromethane and *n*-hexane at -30 °C. Elemental analysis Calcd (%) for $C_{31}H_{29}BF_{15}OP$: C, 50.02; H, 3.93; B, 1.45; F, 38.29; P, 4.16; found C, 49.81; H, 4.65; B, 0.86; F, 36.69; P, 4.40

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.44 (d, *J* = 13.71 Hz, 27H), 4.18 (m, 2H), ppm.

^{11}B-NMR (96 MHz, CD_2Cl_2): δ = - 2.2 ppm.

^{13}C{^{1}H}-NMR (75 MHz, CD_2Cl_2): δ = 29.6, 38.8 (d, *J* = 27.2 Hz), perfluorinated phenyl ring were not observed.

^{19}F{^{1}H}-NMR (282 MHz, CD_2Cl_2): δ = -132.3, -161.2 and -165.9 ppm.

^{31}P-NMR (121 MHz, CD_2Cl_2): δ = 43.7 ppm

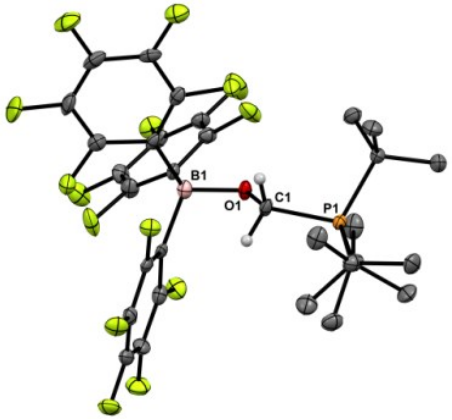
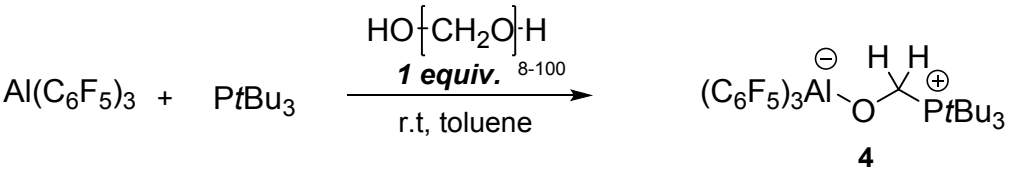


Table 1. X-ray crystal structure analysis for 2

	a15_a69m_a
Crystal data	
Chemical formula	$C_{31}H_{29}BF_{15}OP$
M_r	744.32
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	120
a, b, c (Å)	12.866 (3), 15.691 (4), 15.444 (4)
β (°)	96.980 (4)
V (Å^3)	3094.8 (12)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.21
Crystal size (mm)	0.15× 0.16× 0.31
Data collection	
Diffractometer	Bruker APEX CCD
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22145, 5090, 4128
R_{int}	0.135
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.583
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.134, 0.287, 1.61
No. of reflections	5090
No. of parameters	442
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	1.11, -0.48

Synthesis of 4 starting from $Al(C_6F_5)_3$/P*t*Bu$_3$



4

In a Schlenk flask (30 mL), $Al(C_6F_5)_3$ (105.5 mg, 0.20 mmol), *t*Bu$_3$P (40.46 mg, 0.20 mmol) were dissolved in toluene (7.5 mL) and stirred for 30 minutes at room temperature. Then paraformaldehyde (6.6 mg, 0.22 mmol) was added and the reaction mixture was stirred overnight (20 hours) at room temperature. After stirring, a colorless precipitate was obtained. The color of the solution changed from colorless to amber. Removing the supernatant by syringe and the residue was washed with anhydrous toluene (2 x 2 mL) and one time with anhydrous *n*-pentane (3 mL). All volatiles were removed in *vacuo* to yield **4** (65.2, 42.9 %) as a colourles solid. Crystals suitable for X-ray diffraction analysis were obtained from a mixture of dichloromethane and n-hexane at -30 °C.

^{1}H-NMR (400 MHz, CD_2Cl_2): δ = 1.48 (d, *J* = 13.4 Hz, 27H), 4.82 (s, 2H), ppm.

^{13}C{^{1}H}-NMR (75 MHz, CD_2Cl_2): δ = 29.7, 38.7 (d, *J* = 26.3 Hz), perfluorinated phenyl ring were not observed.

^{19}F{^{1}H}-NMR (282 MHz, CD_2Cl_2): δ = -123.1 (d, 6F), -157.0 (t, 3F), -163.7 (m, 6F) ppm.

^{31}P-NMR (162 MHz, CD_2Cl_2): δ = 40.6 ppm.

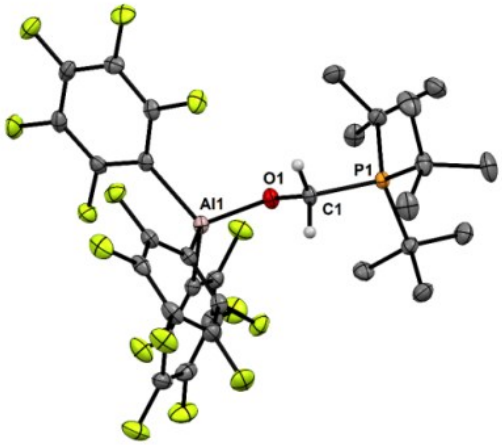
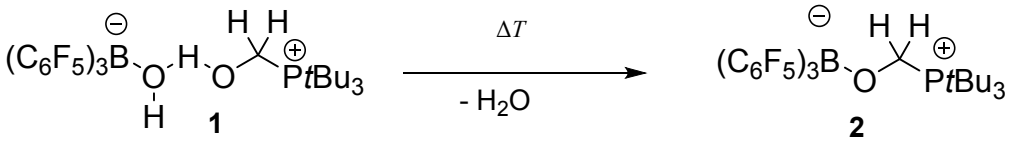


Table 3. X-ray crystal structure analysis for 4

	n16_a43_a
Crystal data	
Chemical formula	$C_{31}H_{29}AlF_{15}OP$
M_r	1288.65
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	9.5107 (18), 11.529 (2), 15.630 (3)
α, β, γ (°)	105.489 (3), 92.093 (3), 104.513 (3)
V (Å^3)	1589.0 (5)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.19
Crystal size (mm)	0.18 × 0.18 × 0.08
Data collection	
Diffractometer	Bruker APEX CCD
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22799, 8091, 5530
R_{int}	0.066
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.673
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.051, 0.163, 0.92
No. of reflections	8091
No. of parameters	442
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e Å^{-3})	0.39, -0.35

Synthesis of 2 starting from 1



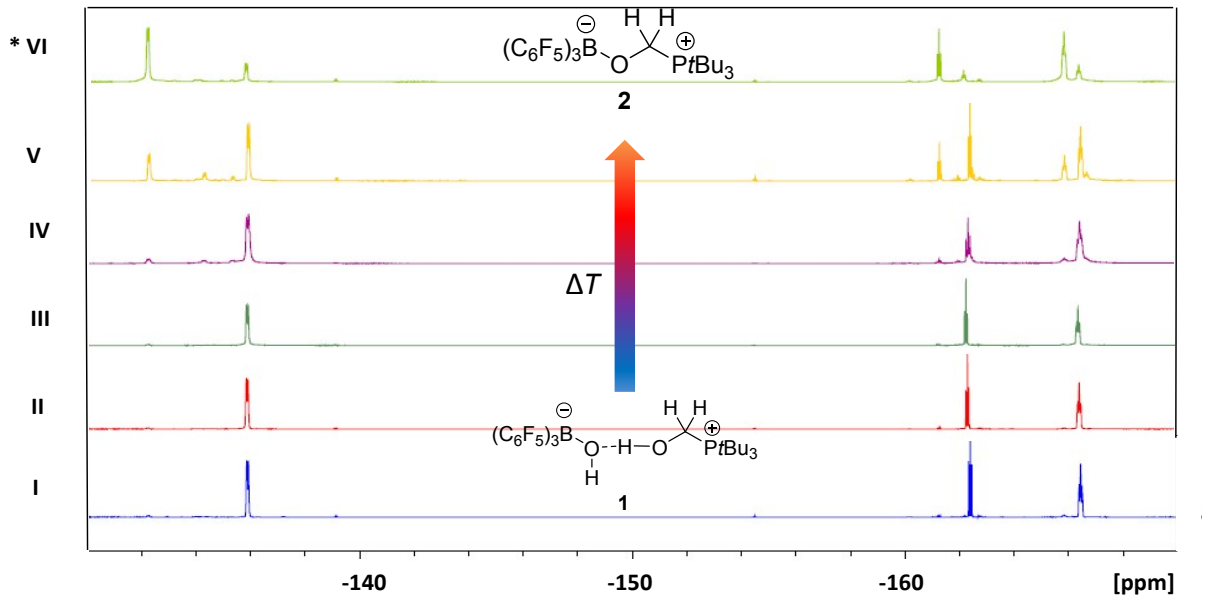


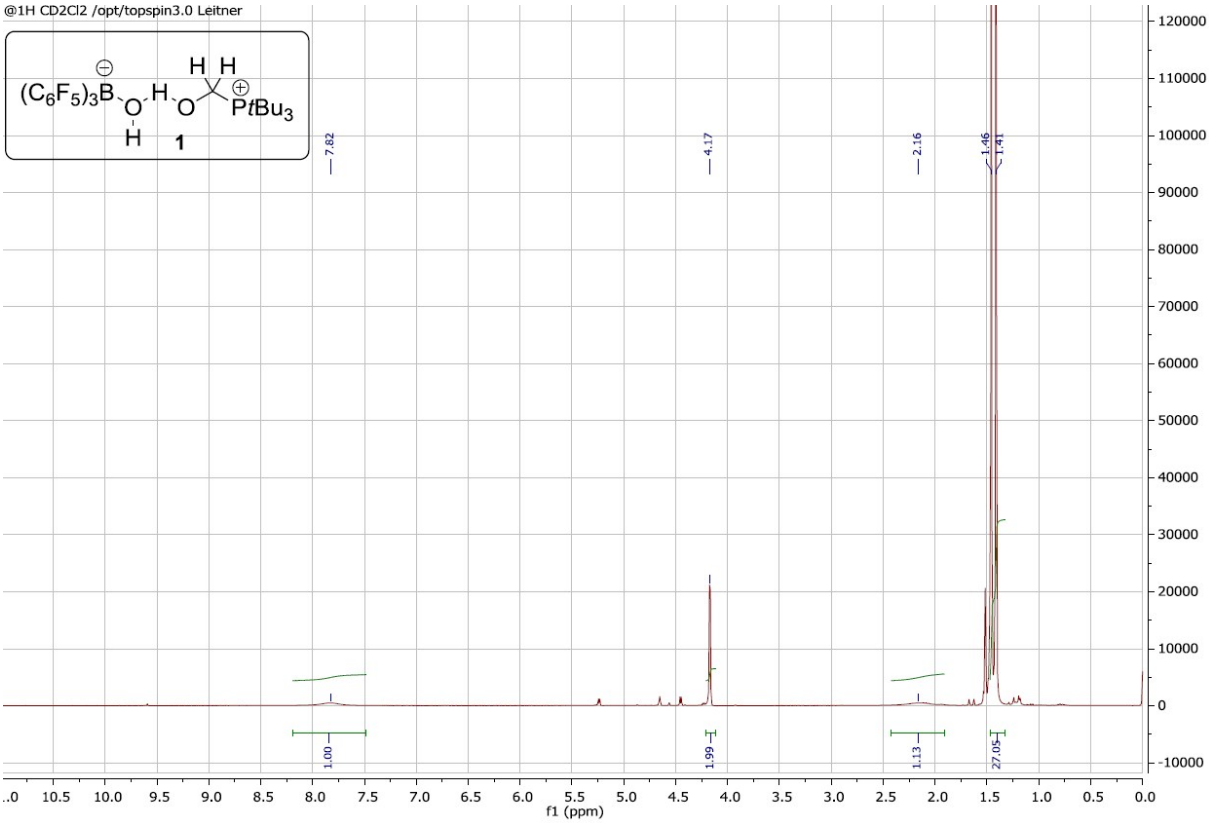
Figure 1S. ^{19}F-NMR spectra of compound **1** treated at different temperature for one hour; I) 25 °C, II) 65 °C, III) 80 °C, IV) 90 °C, V) 100 °C, *VI) 100 °C (extended heating for four hours)

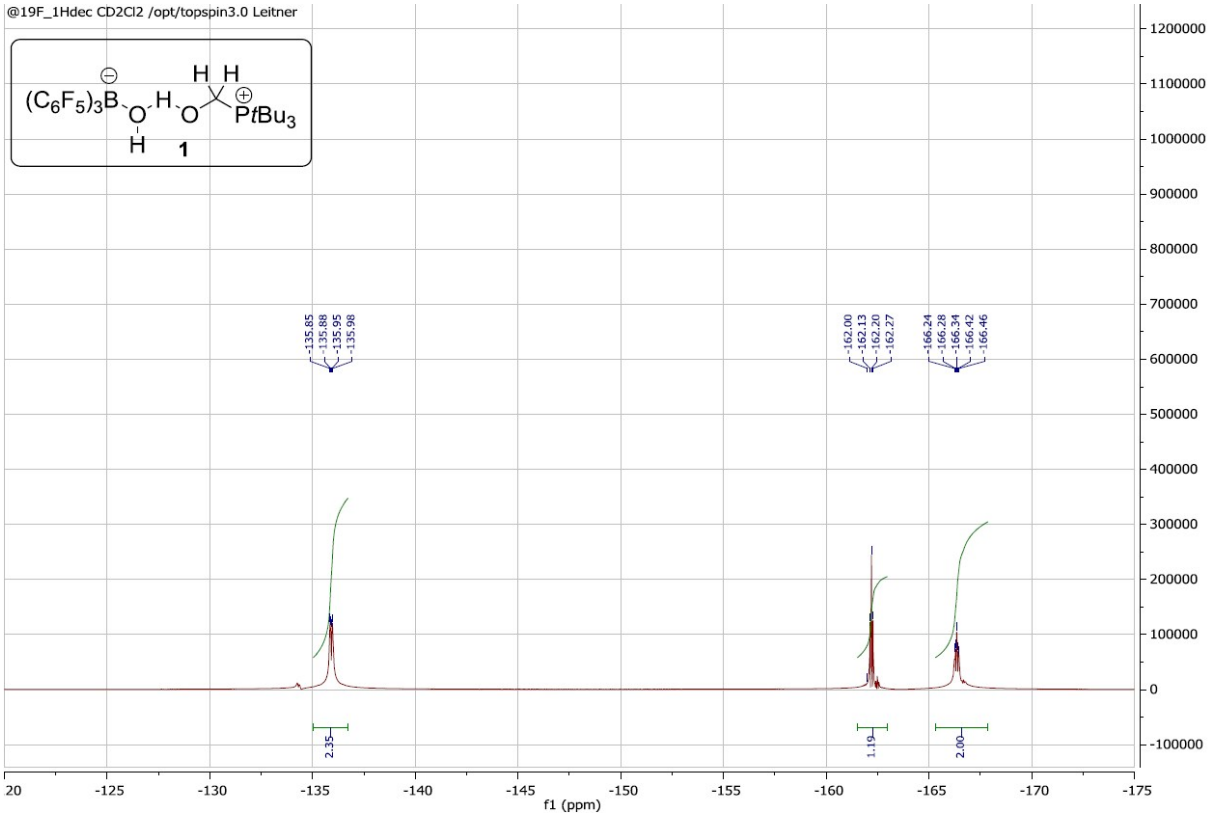
The synthesis of **2** starting from **1** was done via heating the solution of **1** in CD_2Cl_2. In a Young type NMR tube (tolerating high pressure), compound **1** (20 mg) was dissolved completely in CD_2Cl_2 (0.5 mL) and heated to different temperatures. (Note: ^{19}F NMR experiments were performed at room temperature after each heating step). No changes in ^{19}F NMR spectrum were observed at 65 and 80 °C showing that compound **1** is stable at these temperatures (Figure 1S). At 90 °C and after one hour a set of peaks (3 peaks) appeared at -132.3, -161.2 and -165.9 ppm which correspond to compound **2**. Increasing the temperature to 100 °C for longer time (4 hours) showed the transformation of **1** to **2**.

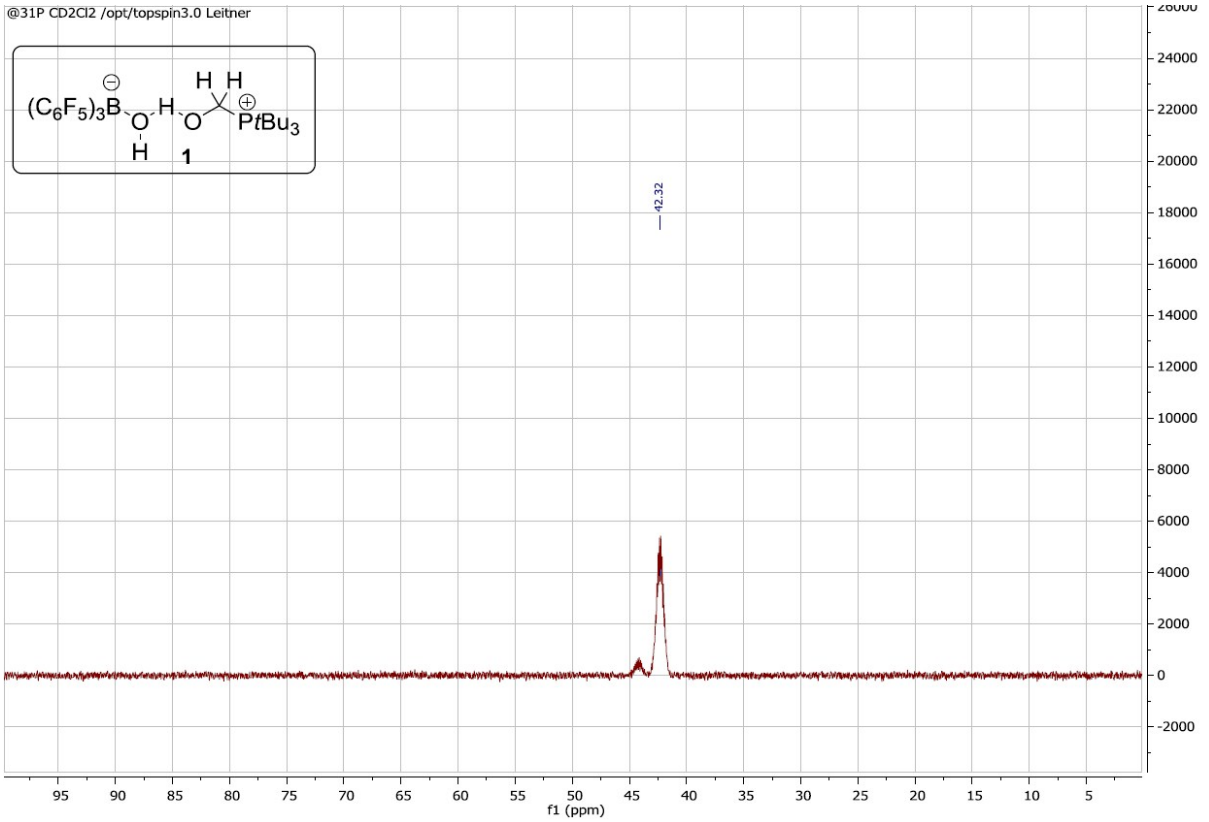
Table 1S. Comparison between selected bond length of **1**, **2** and **4** (Å).

Structure data	**1**	**2**	**4**
B1-O1	1.485 (4)	1.491 (7)	-
Al1-O1	-	-	1.718 (18)
C1-O1	-	1.404 (7)	-
C1-O2	1.412 (3)	-	-
C1-P1	1.843 (3)	1.847 (5)	1.849 (2)

Selected NMR spectra:



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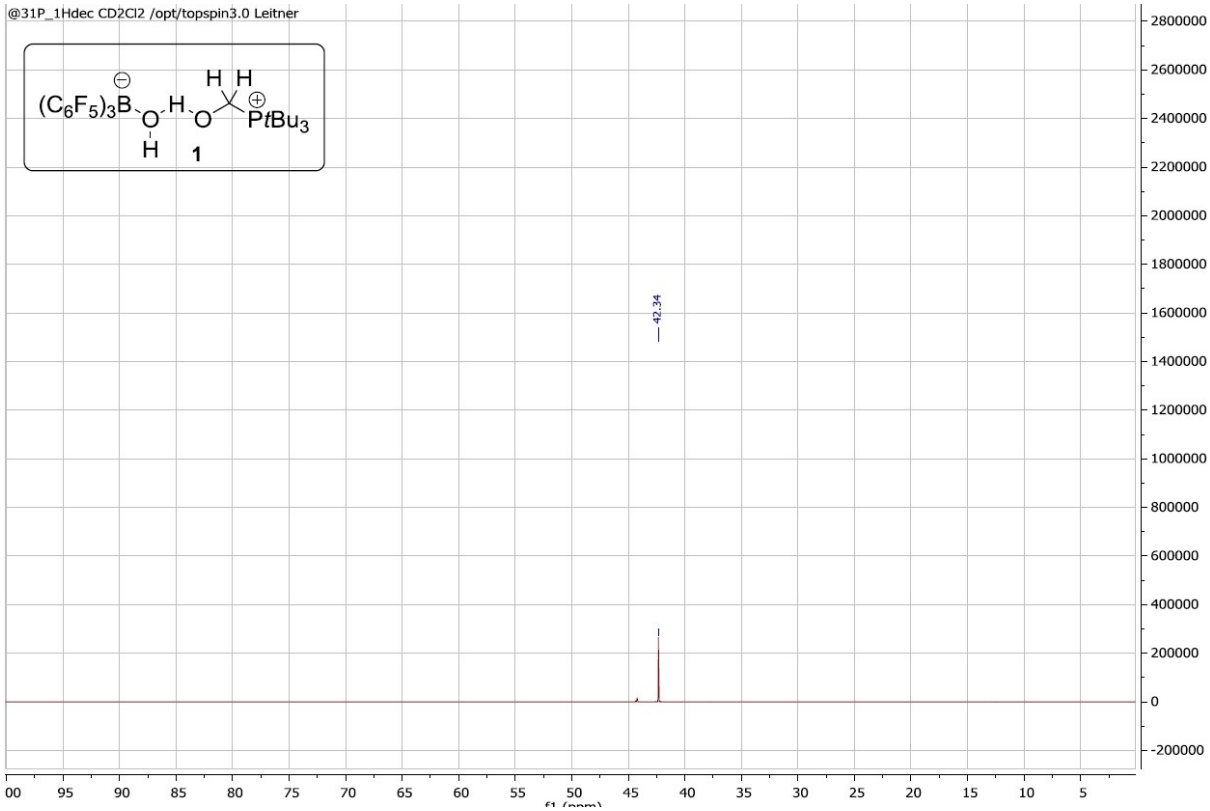
(C6F5)3B
O
H
H H
O
PtBu3
1
42.32
f1 (ppm)


@31P_1Hdec CD2Cl2 /opt/topspin3.0 Leitner
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H
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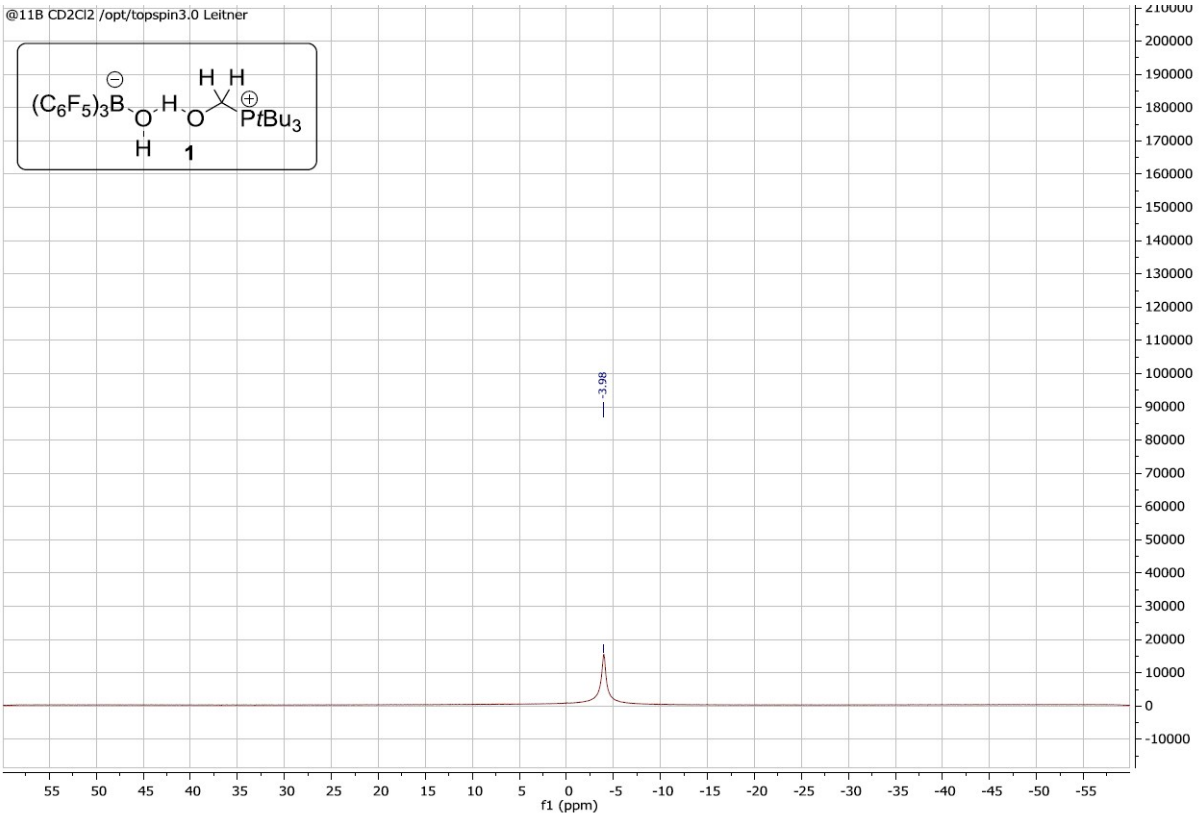
O
PtBu3
1
42.34
f1 (ppm)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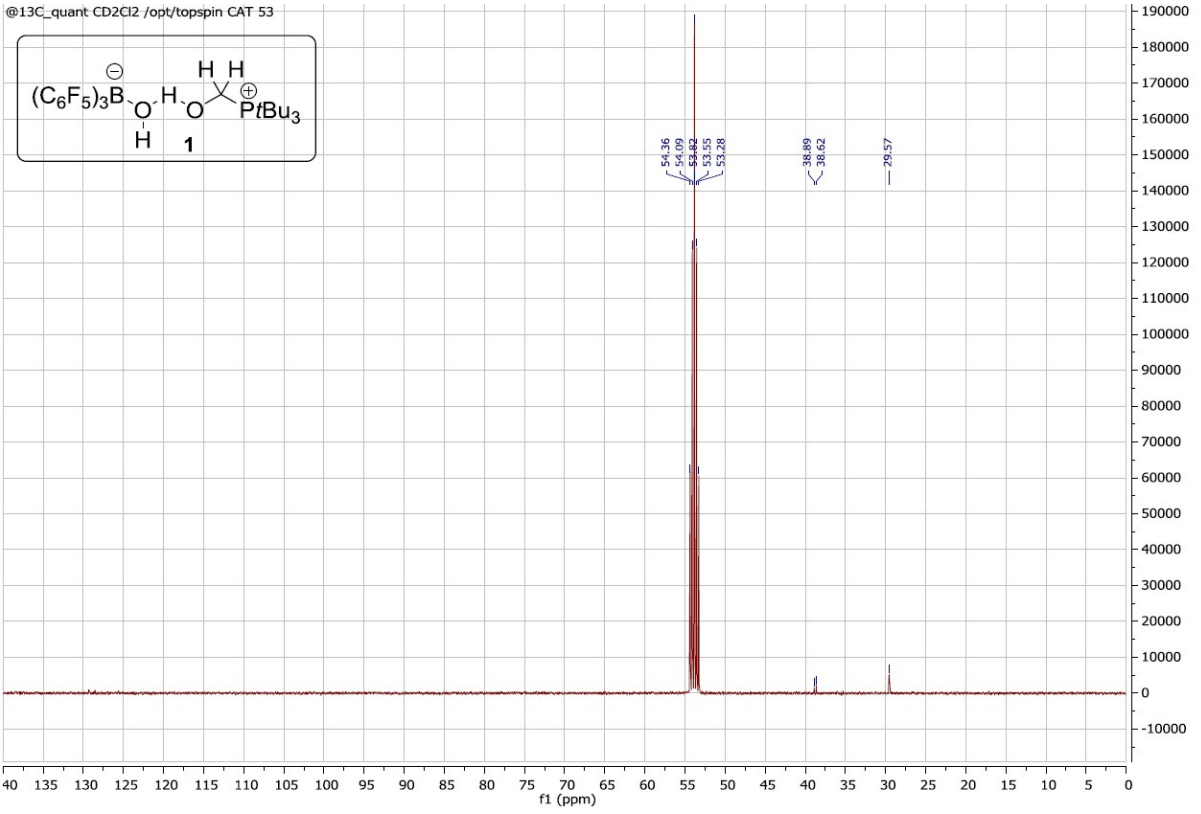
H H
PtBu3
1
-3.98
f1 (ppm)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(C6F5)3B
H H
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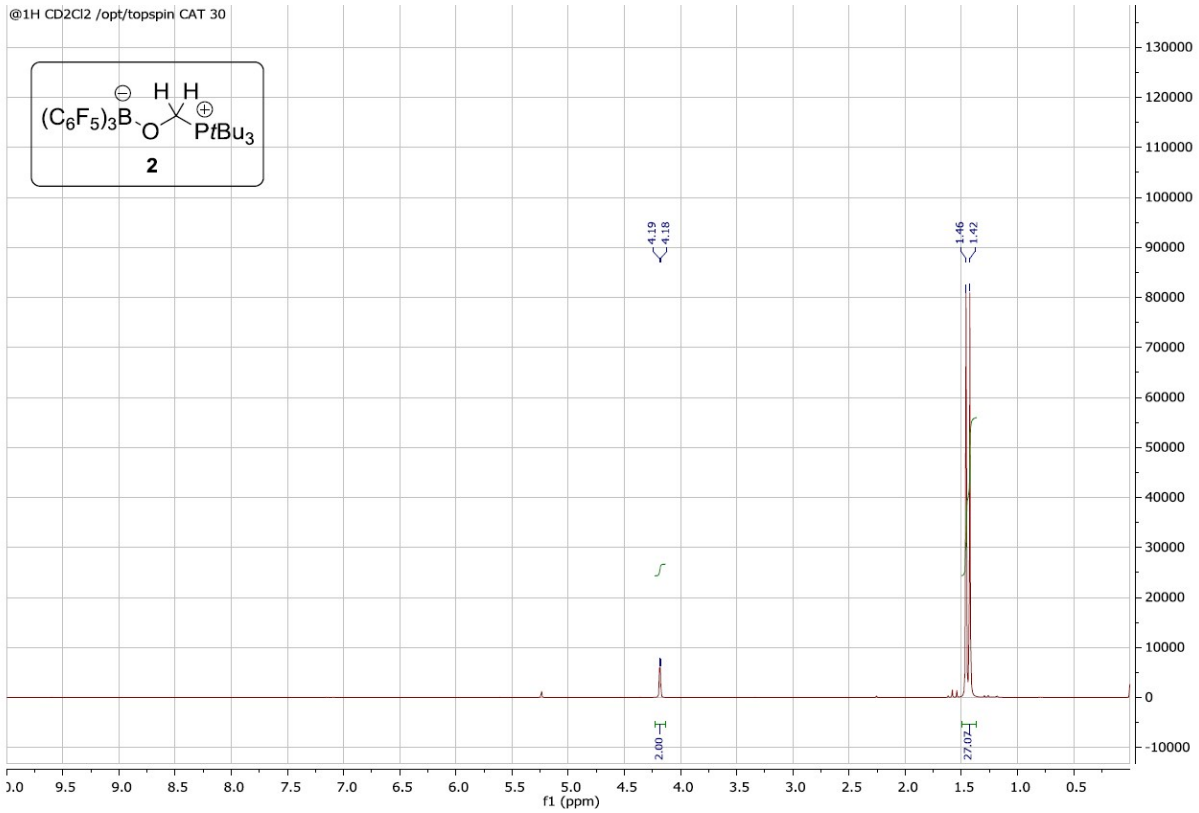
54.09
53.82
53.55
53.28
38.89
38.62
29.57
f1 (ppm)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$(C_6F_5)_3B$ O H H $PtBu_3$
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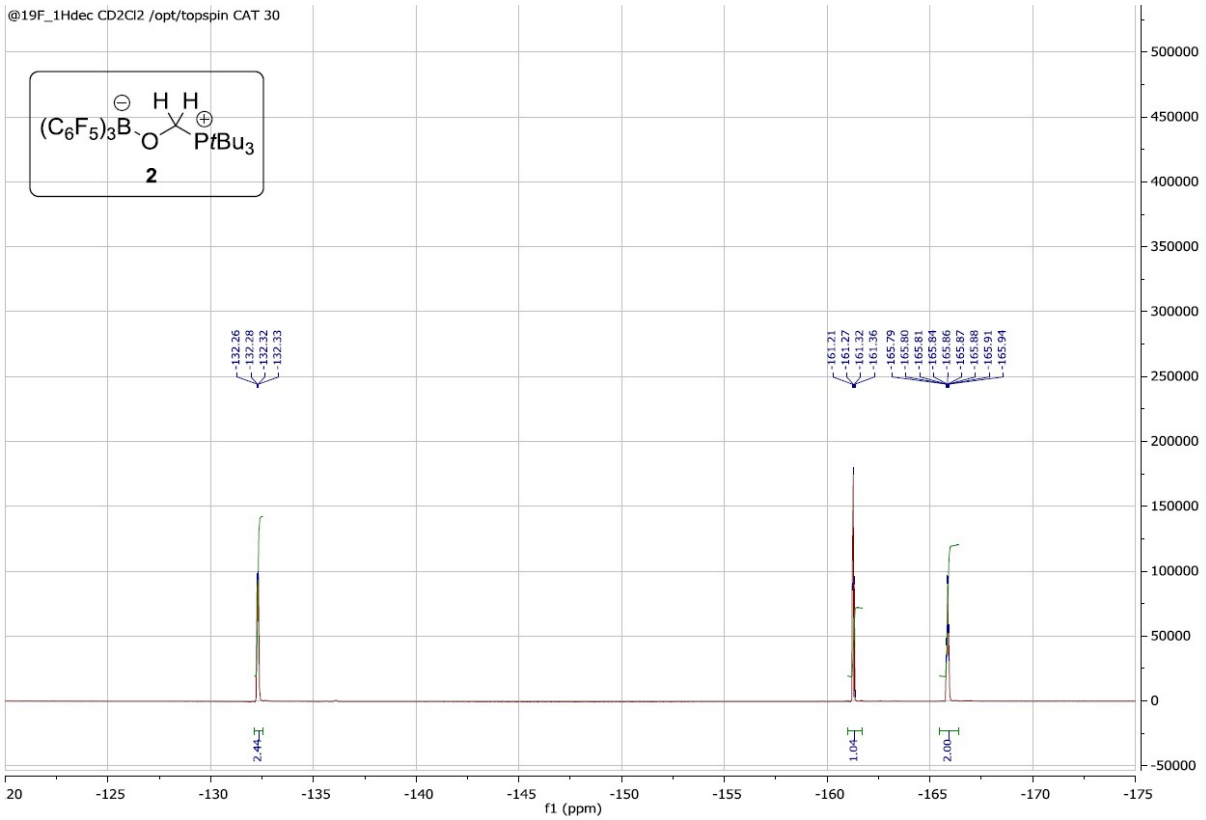
4.18
1.46
1.42
2.00
27.07
f1 (ppm)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$(C_6F_5)_3B$ O H H $PtBu_3$
2
-132.26
-132.28
-132.32
-132.33
-161.21
-161.27
-161.32
-161.36
-165.79
-165.80
-165.81
-165.84
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-165.87
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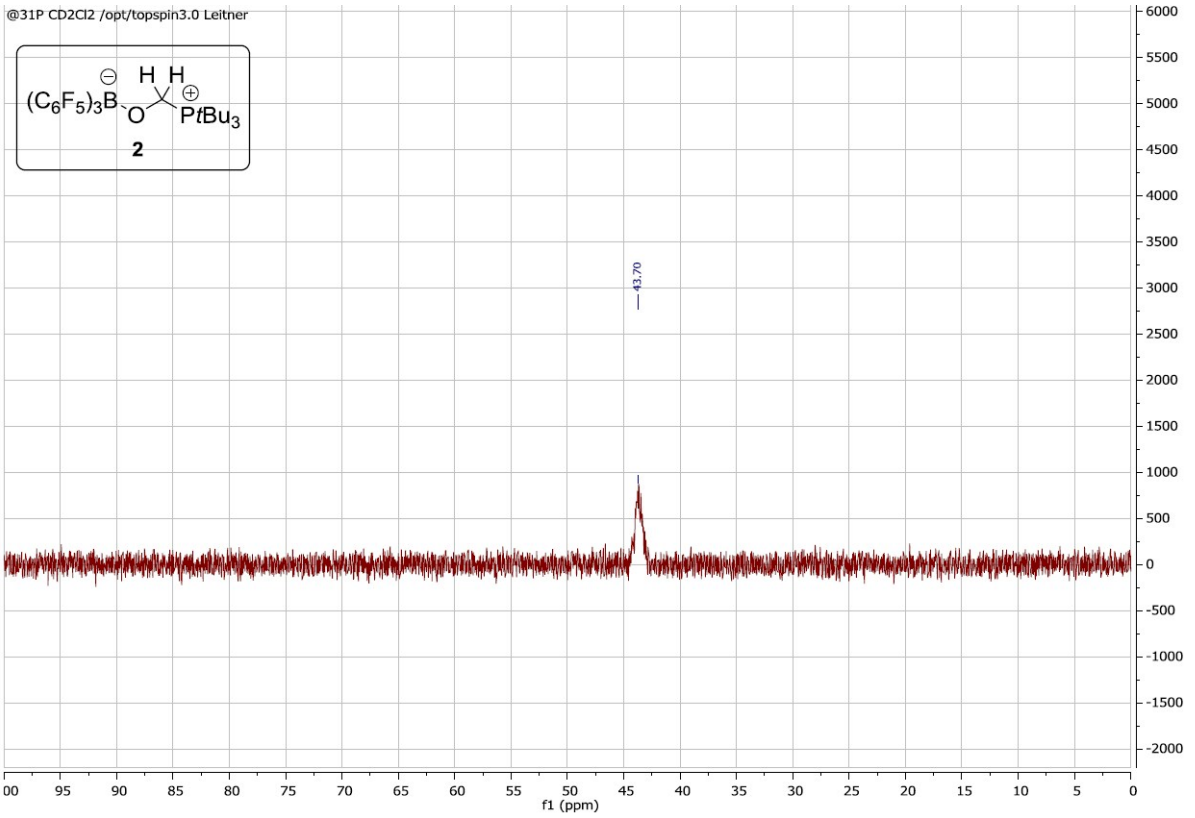
-165.94
2.44
1.04
2.00
f1 (ppm)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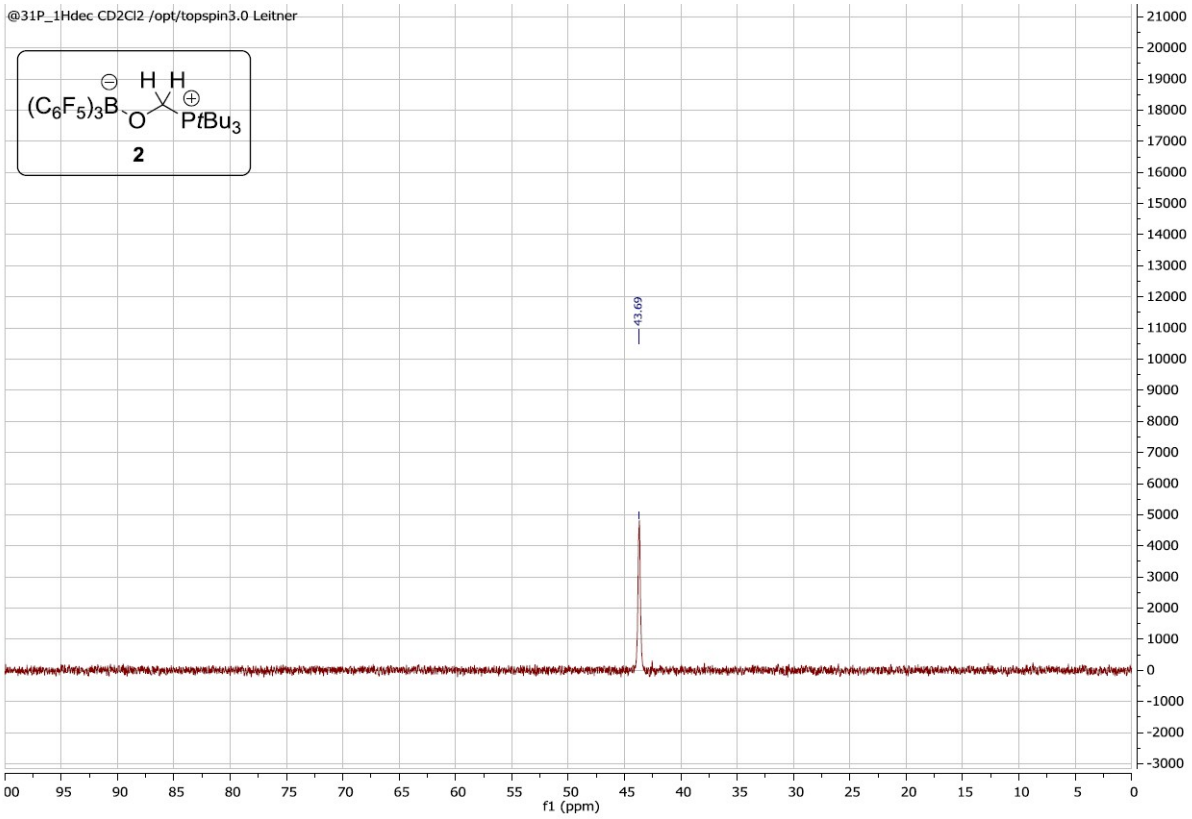
O
H H
PtBu3
2
43.70
f1 (ppm)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PtBu3
2
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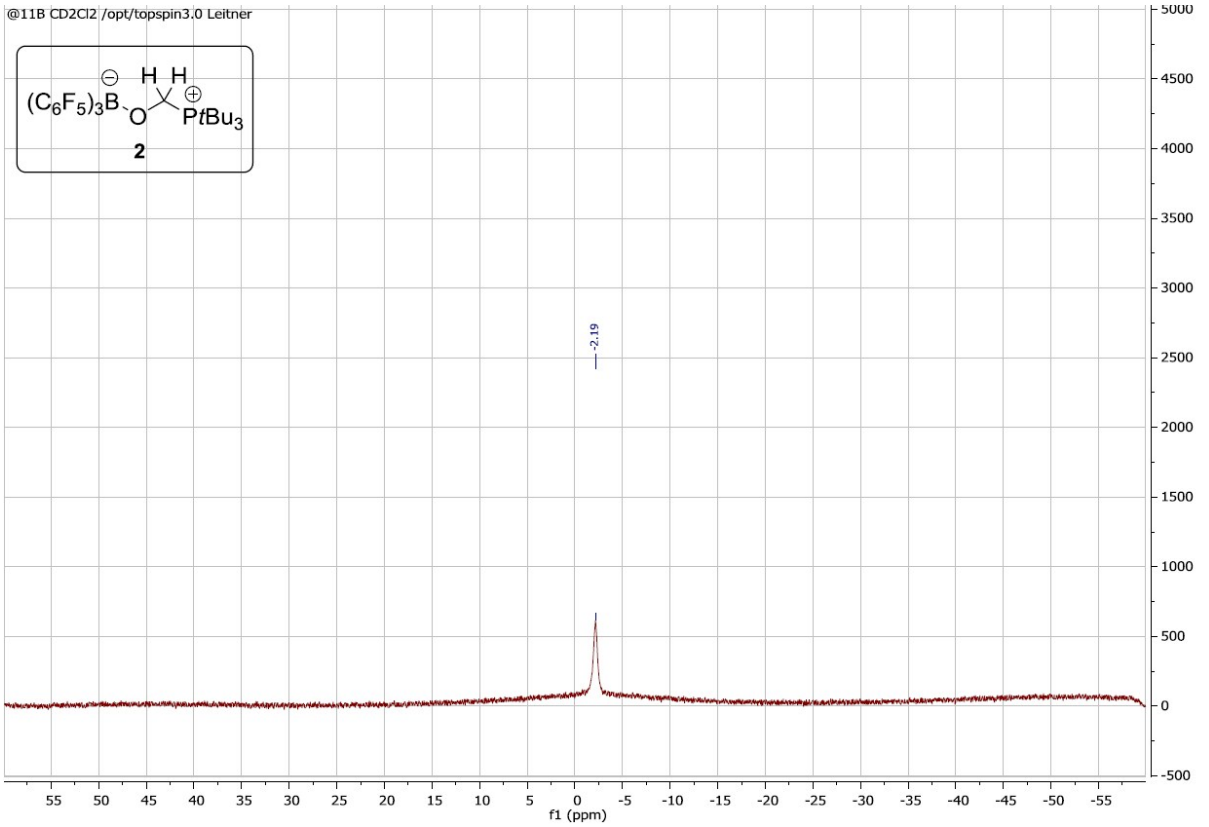
f1 (ppm)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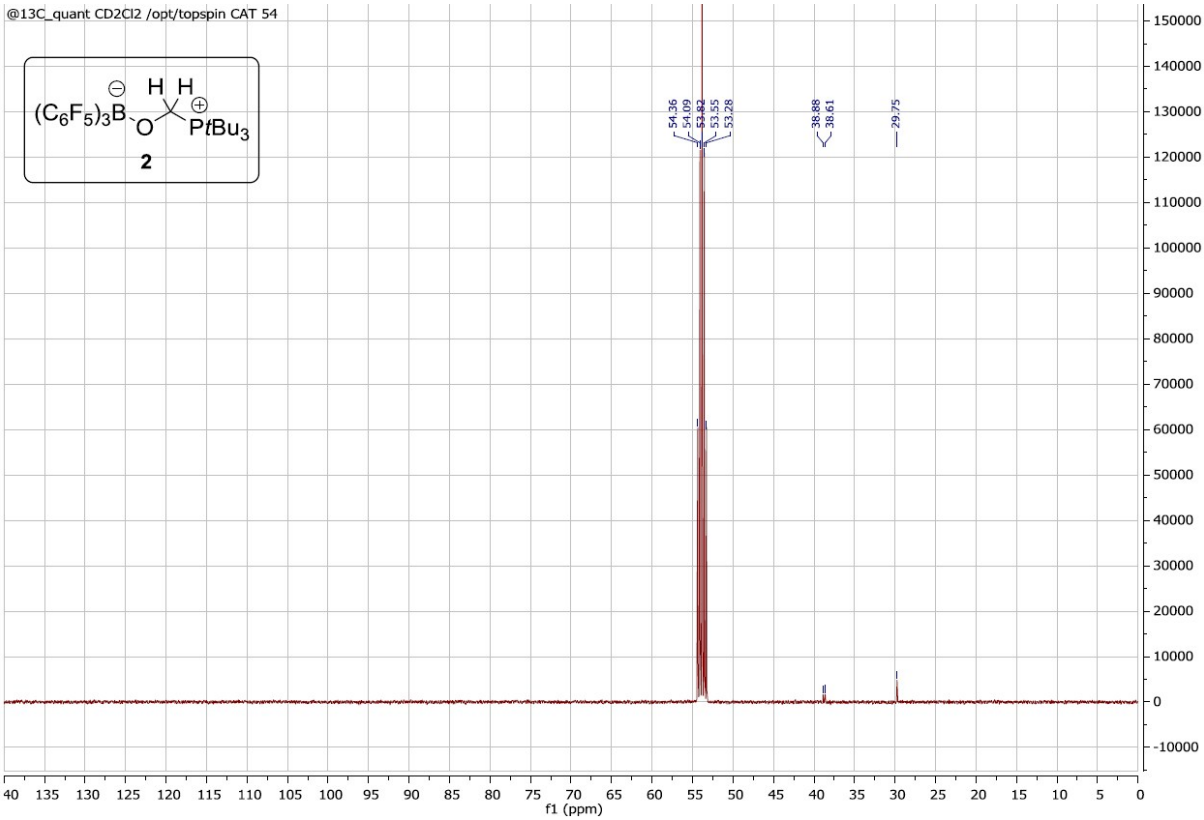
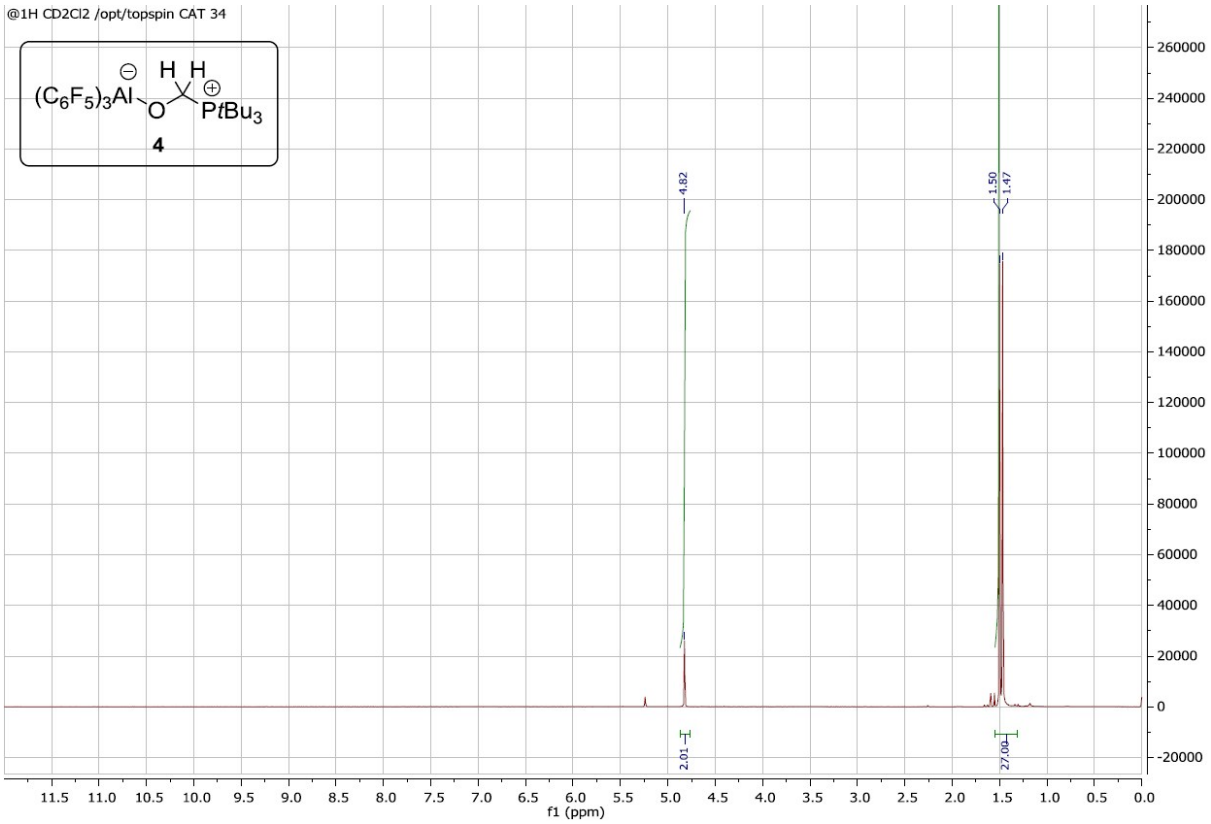
PtBu3
2
2.19
f1 (ppm)


@13C_quant CD2Cl2 /opt/topspin CAT 54
(C6F5)3B
O
H H
PtBu3
2
54.36
54.09
53.82
53.55
53.28
38.88
38.61
29.75
f1 (ppm)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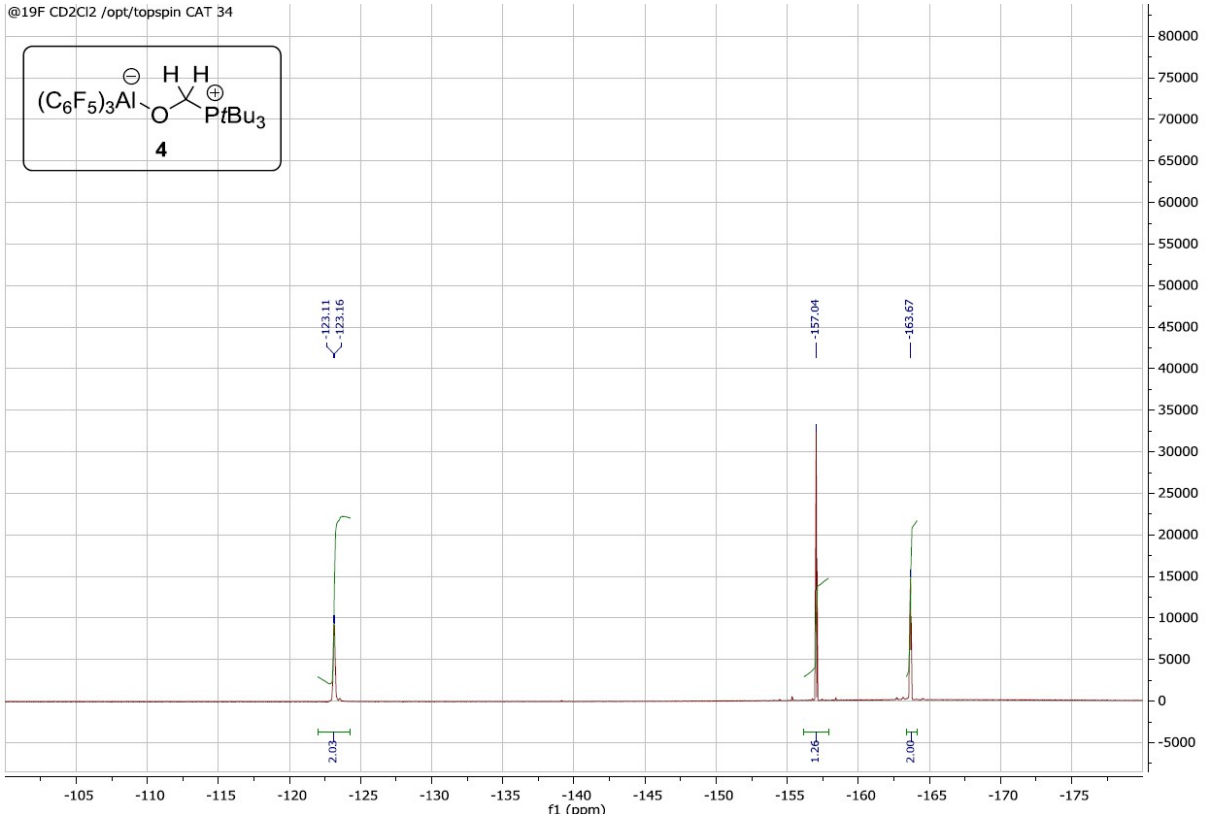
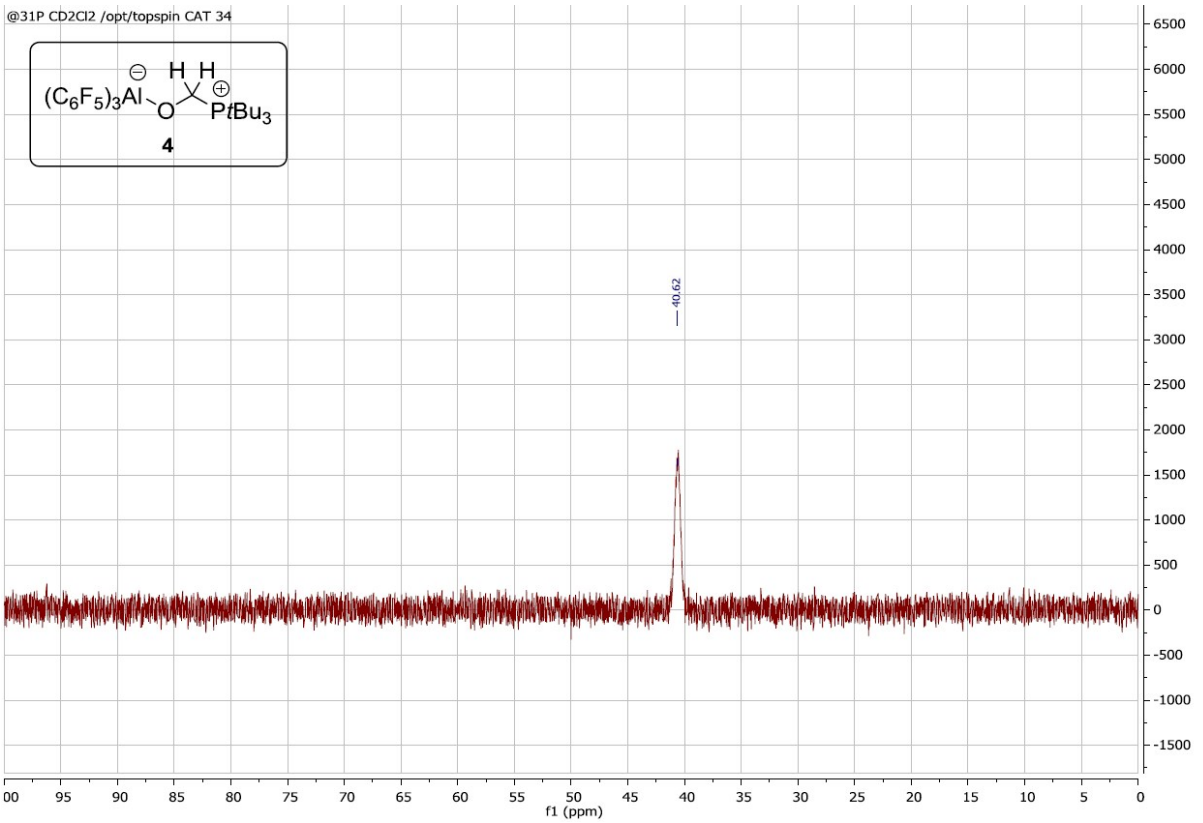
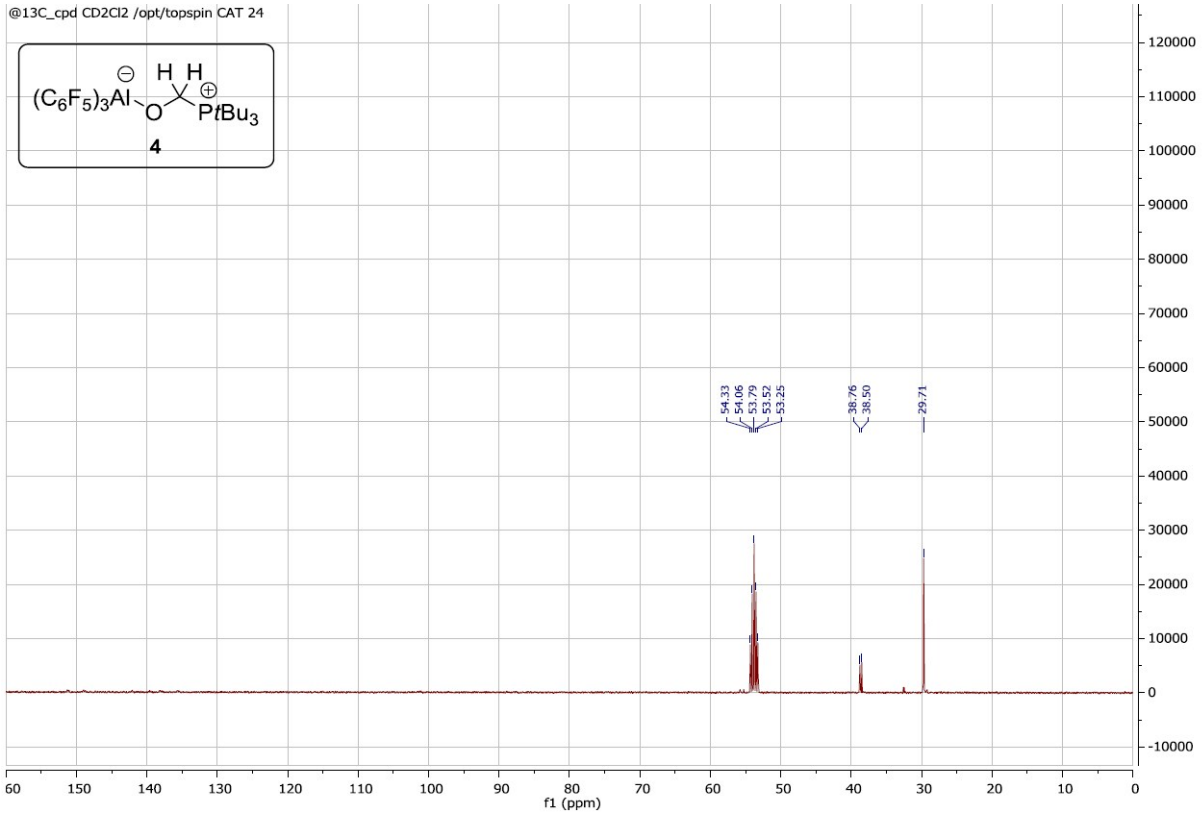
O
H H
PtBu3
4
4.82
1.50
1.47
2.01
27.00
f1 (ppm)


@19F CD2Cl2 /opt/topspin CAT 34
(C6F5)3Al
O
H H
PtBu3
4
-123.11
-123.16
-157.04
-163.67
2.03
1.26
2.00
f1 (ppm)


@31P CD2Cl2 /opt/topspin CAT 34
(C6F5)3Al
O
H H
PtBu3
4
40.62
f1 (ppm)


@13C_cpd CD2Cl2 /opt/topspin CAT 24
(C6F5)3Al
O
H H
PtBu3
4
54.33
54.06
53.79
53.52
53.25
38.76
38.50
29.71
f1 (ppm)