Supporting Information

Fluorenylidene functionalized lithium phosphonium di- and triylides

*Fabian G. Schröder and Jörg Sundermeyer**

Fachbereich Chemie der Philipps-Universität Marburg, Hans-Meerwein-Str., 35032 Marburg, Germany

Content:

Characterization and Single Crystal X-ray Analysis of [Me_3P^+-FluH]Br^- (1). **1** gives rise to a ^{31}P NMR resonance at 30.8 ppm. The phosphorus bound methyl groups in **1** give rise to a doublet at 2.10 ppm and a $^2J_{HP}$ coupling constant of 13.7 Hz in the proton NMR spectrum and a doublet at 8.0 ppm ($^1J_{CP}$ = 54.4 Hz) in the ^{13}C NMR spectrum, respectively. The carbon atom in 9–position of the fluorene moiety is observed at 43.0 ppm ($^1J_{CP}$ = 46.0 Hz) the proton 9–position is downfield shifted to 6.26 ppm and shows a $^2J_{HP}$ coupling constant of 19.5 Hz.

Single crystals of **1** were obtained by slow evaporation of a supernatant solution in chloroform. **1** crystallizes in the orthorhombic space group *Pbna* with eight identical formula units and chloroform molecules per unit cell. The phosphorus bound substituent form a close to perfect tetrahedron with C-P-C angles of 108.0(1)° to 111.7(1)°. The P-C_{Me} bond lengths are identical within limits of uncertainties (d(P–C14) = 1.780(2) Å) and agree well with values found in [Me_3P^+–$C_5H_2Ph_3$]ClO_4^- (d(P–C_{Me}) = 1.783(2) Å).[1] The P1–C1 bond length amounts to 1.823(2) Å and is slightly shorter than in [$Me_2P^+(FluH)_2$]I^- (d(P–C_{Flu}) = 1.837(2) Å)[2] which is attributed to the smaller sterical demand of one fluorene moiety in **1**. The bromine atom takes part in weak hydrogen bonding to the proton of the chloroform molecule (d(Br1–H17) = 2.54 Å).

Characterization and Single Crystal X-ray Analysis of [Me_3P=Flu] (2). **2** gives rise to a ^{31}P NMR resonance at 1.7 ppm. The protons of the phosphorus bound methyl groups in **2** give rise to one doublet at 1.95 ppm and a $^3J_{HP}$ coupling constant of 13.4 Hz. Their equivalence indicates a fast rotation around the P–C_{Flu} bond. The carbon atom in 9-position of the fluorene moiety shows a doublet at 58.8 Hz in the ^{13}C NMR spectrum. Its $^1J_{CP}$ coupling constant is of 121.1 Hz indicating an increased P–C_{Flu} interaction.

Single crystals of **2** were obtained from toluene at –30 °C. It crystallizes in the monoclinic space group $P2_1/c$ with four identical phosphorus ylides and toluene molecules per unit cell. In **2** the P–C_{Me} bond lengths (d(P1–C14) = 1.792(2) Å) are of the same magnitude and elongated in

comparison to **1**. The P1–C1 distance amounts to 1.729(2) Å and is in the same range as observed in $Me_2P(=Flu)FluH$ ($d(P–C_{Flu})$ = 1.724(2) Å)[2] and in previously reported cyclopentadienylidene phosphoranes (1.717(2)–1.742(3) Å).[3-6] It represents a longer distance as found in non-stabilized phosphorus ylids (e.g. 1.662(8) Å in $Ph_3P=CH_2$)[7] but a significant elongation in comparison to P–C single bonds found in **2** and $Me_2P(=Flu)FluH$ ($d(P–C_{FluH})$ = 1.847(2) Å).[2] This indicates a significant contribution of both the ylid and ylene resonance structure and therefore a aromatization of the five-membered ring. This is documented by a planar configuration of C1 (Σ(<) = 359.4°) and a obvious contraction of the C1–C2 (1.435(2) Å) and C1–C5 (1.441(2) Å) bond length compared to **1** (1.521(3) and 1.515(3) Å).

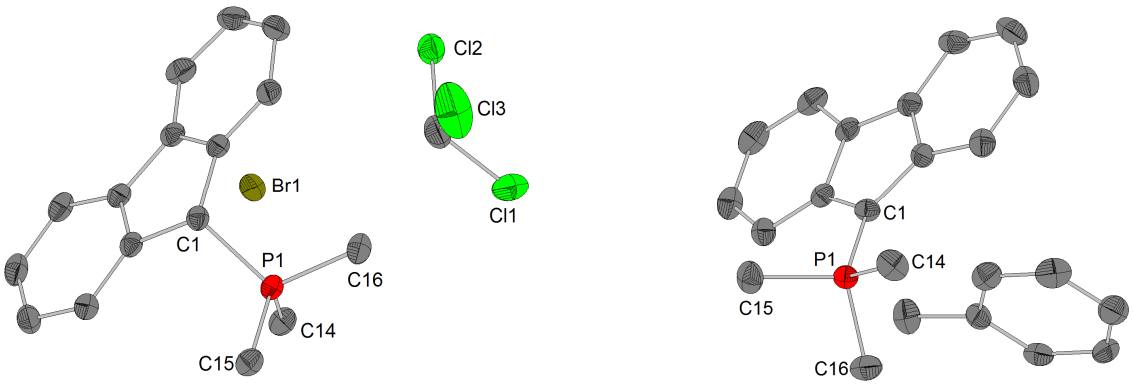


Figure S1. Molecular structures of $[Me_3P^+FluH]Br^-$ (**1**, left) and $Me_3P=Flu$ (**2**, right). Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **1**: P1-C1, 1.823(2); P1-C14, 1.780(2); P1-C15, 1.783(2); P1-C16, 1.785(2); C1-P1-C14, 110.6(1); C1-P1-C15, 108.2(1); C1-P1-C16, 111.7(1); C14-P1-C15, 110.2(1); C14-P1-C16, 108.1(1); C15-P1-C16, 108.0(1). **2**: P1-C1, 1.729(2); P1-C14, 1.792(2); P1-C15, 1.792(2); P1-C16, 1.793(2); C1-P1-C14, 112.7(1); C1-P1-C15, 112.0(1); C1-P1-C16, 113.5(1); C14-P1-C15, 105.9(1); C14-P1-C16, 106.6(1); C15-P1-C16, 105.7(1).

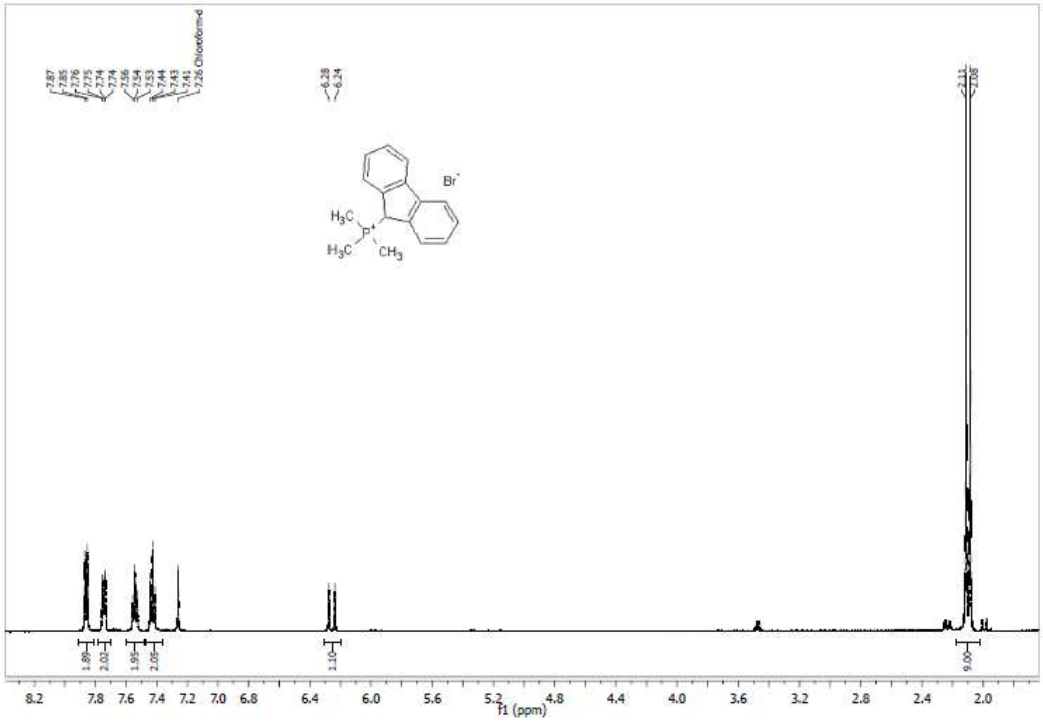
Table S1. Crystallographic data for Compounds **1-4**

Compound	**1**	**2**	**3**[a)]	**4**
Formula	$C_{16}H_{18}P$, $CHCl_3$, Br	$C_{16}H_{17}P$, C_7H_8	$C_{40}H_{52}Li_2O_2P_2$	$C_{40}H_{50}Li_4O_2P_2$
Formula weight	440.55	332.40	640.64	652.50
Crystal system	orthorhombic	monoclinic	triclinic	monoclinic
Space group	*Pbna*	$P2_1/c$	*P*-1	$P2_1/c$
Unit cell dimension				
a (Å)	12.8898(4)	14.5317(8)	8.9171(6)	8.2904(4)
b (Å)	13.7001(4)	15.7241(6)	9.6350(7)	23.4831(15)
c (Å)	21.7692(7)	8.1768(5)	10.9153(8)	9.8369(5)
α (°)	90.00	90.00	95.220(6)	90.00
β (°)	90.00	95.232(5)	103.669(6)	110.339(4)
χ (°)	90.00	90.00	90.252(6)	90.00
V (Å^3)	3844.3(2)	1860.60(17)	907.14(11)	1795.69(17)
Z	8	4	1	2
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069
Calculated density (g cm^{-3})	1.522	1.187	1.173	1.207
Absorption coefficient (mm^{-1})	2.633	0.148	0.152	0.154
Transmission factors (min./max.)	0.6691 and 0.763	0.9376 and 0.9941		0.9683 and 0.9908
Crystal size (mm^3)	0.27 x 0. 90 x 0.06	0.44 x 0.06 x 0.04	0.25 x 0.21 x 0.10	0.21 x 0.12 and 0.06
θ(max) (°)	26.72	26.76	26.99	26.74
Reflections measured	27095	14448	11997	14701
Unique reflections	4045	3918	11997	3806
R_{int}	0.0491	0.0787		0.1009
Number of parameters	202	221	221	236
R_1 [$F^2 > 2\sigma(F^2)$]	0.0329	0.0406	0.0536	0.0372
wR_2	0.0680	0.0659	0.1389	0.0599
GOOF, S	1.095	0. 806	0.985	0.652
Largest difference peak and hole (e Å^3)	0.592 and –0.677	0.231 and –0.287	0.753 and –0.420	0.186 and –0.249

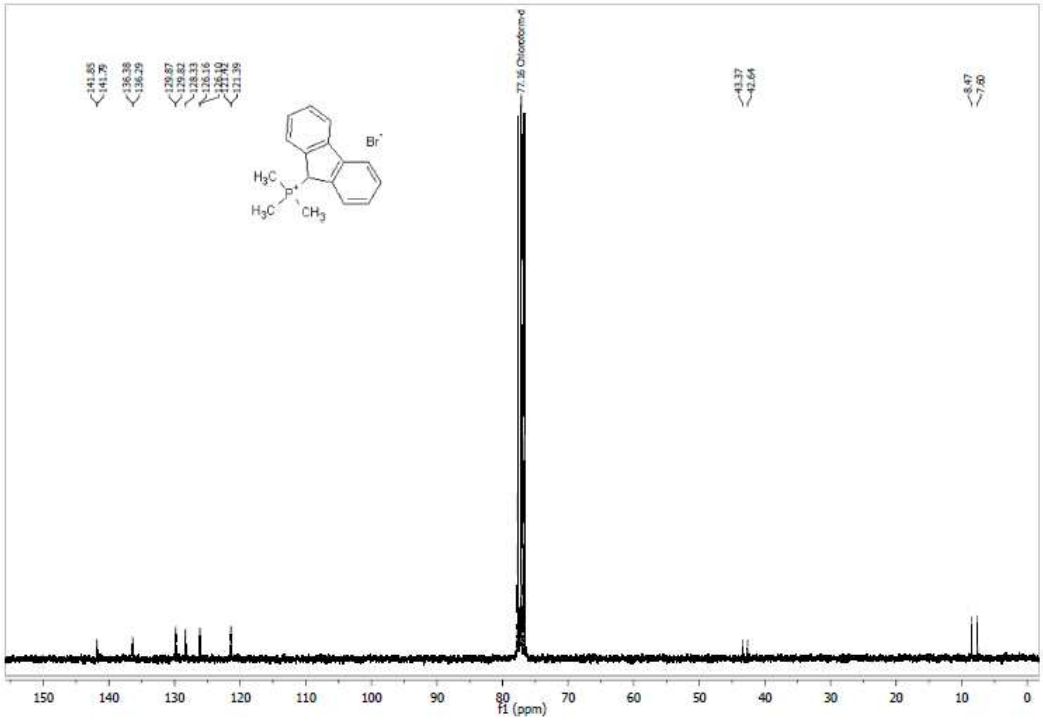
[a)] **3** was obtained as a twin (74/26); therefore, an hklf 5-refinement was undertaken.

NMR Spectra of Compounds 1-4

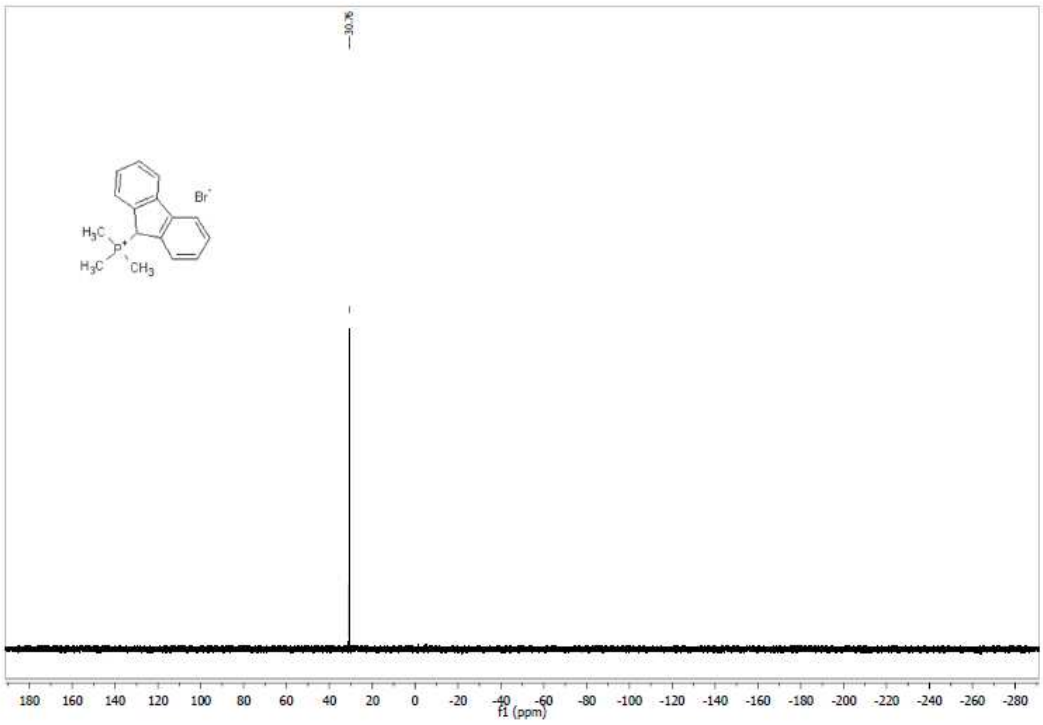
^{1}H NMR of Compound **1** ($CDCl_3$)



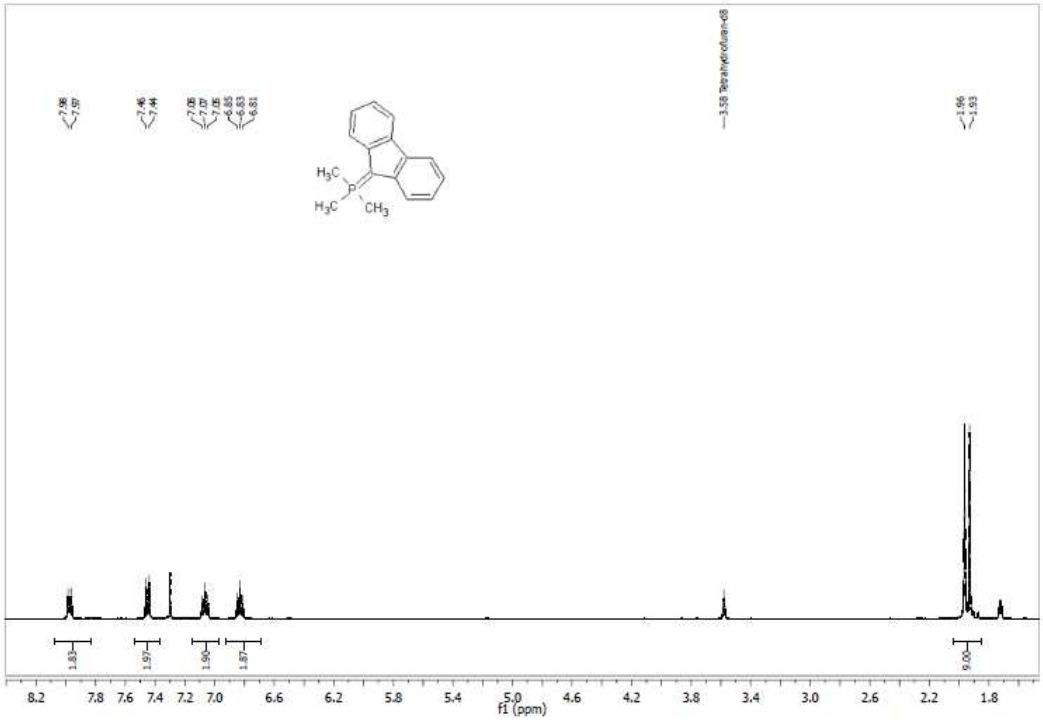
^{13}C NMR of Compound **1** ($CDCl_3$)



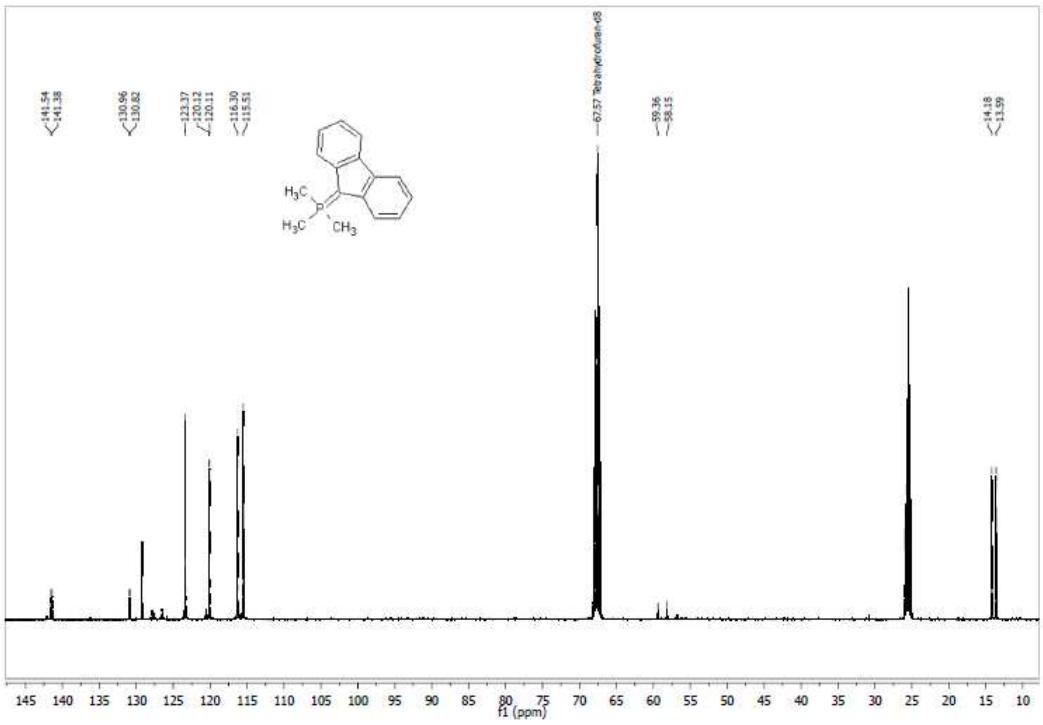
^{31}P NMR of Compound **1** ($CDCl_3$)



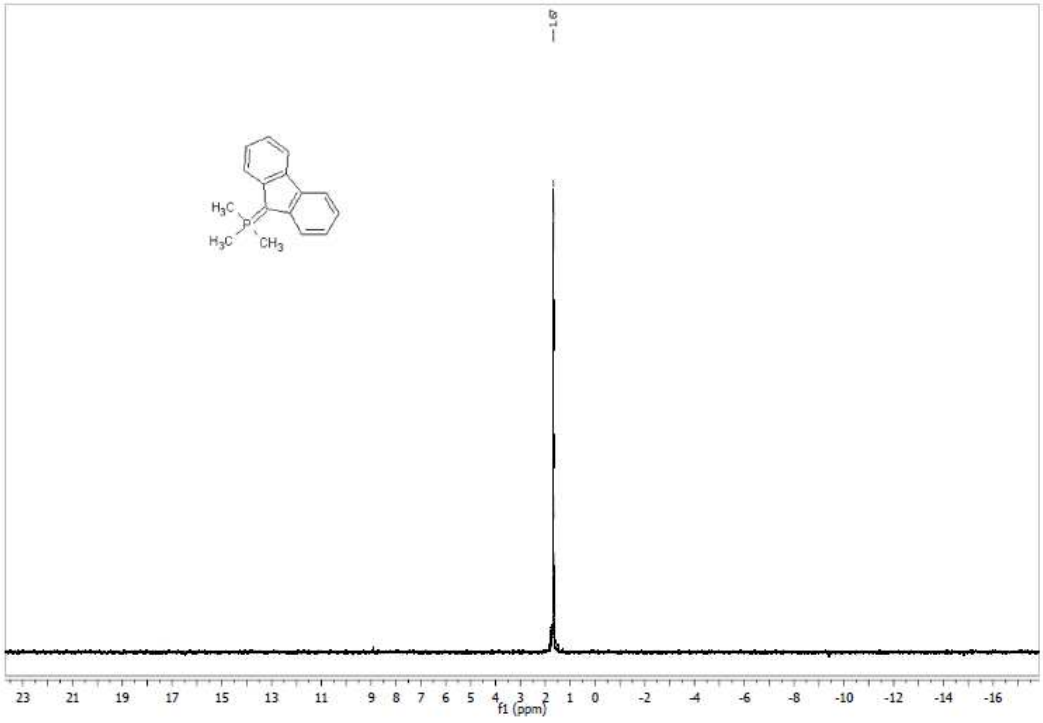
^{1}H NMR of Compound **2** (THF-d_8)



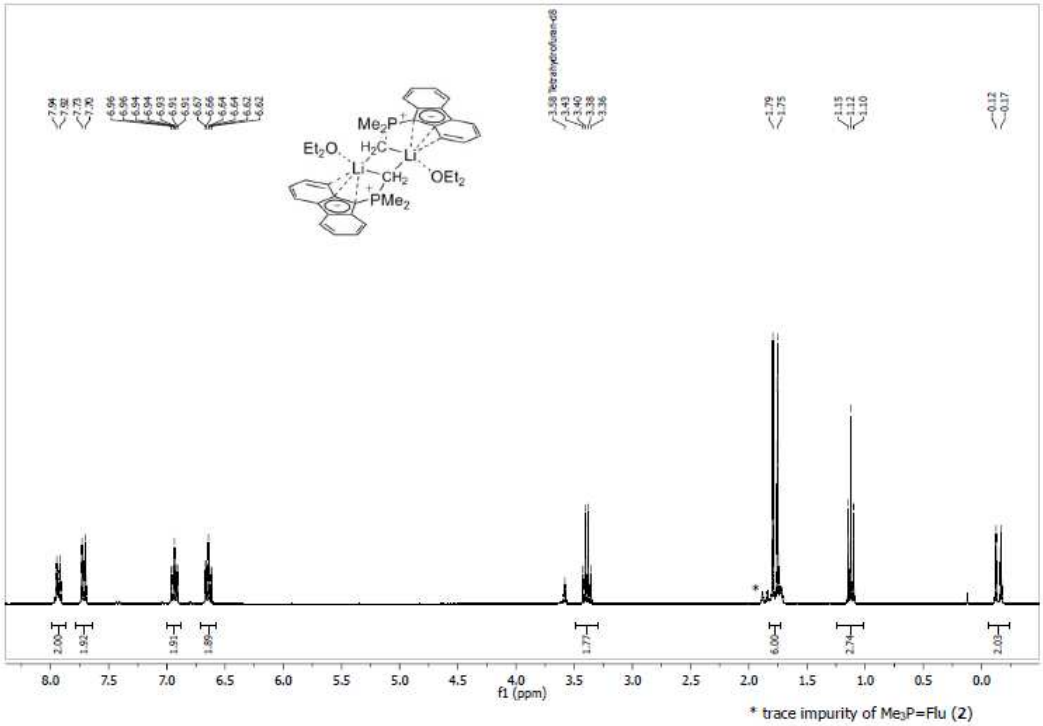
^{13}C NMR of Compound **2** (THF-d_8)



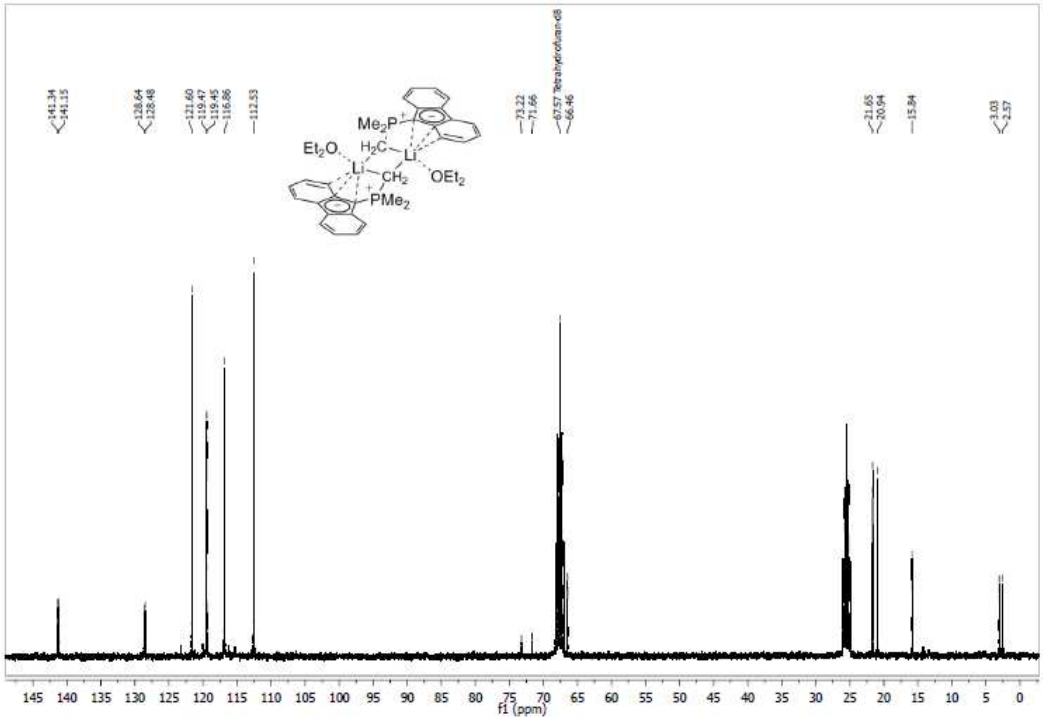
^{31}P NMR of Compound **2** (THF-d_8)



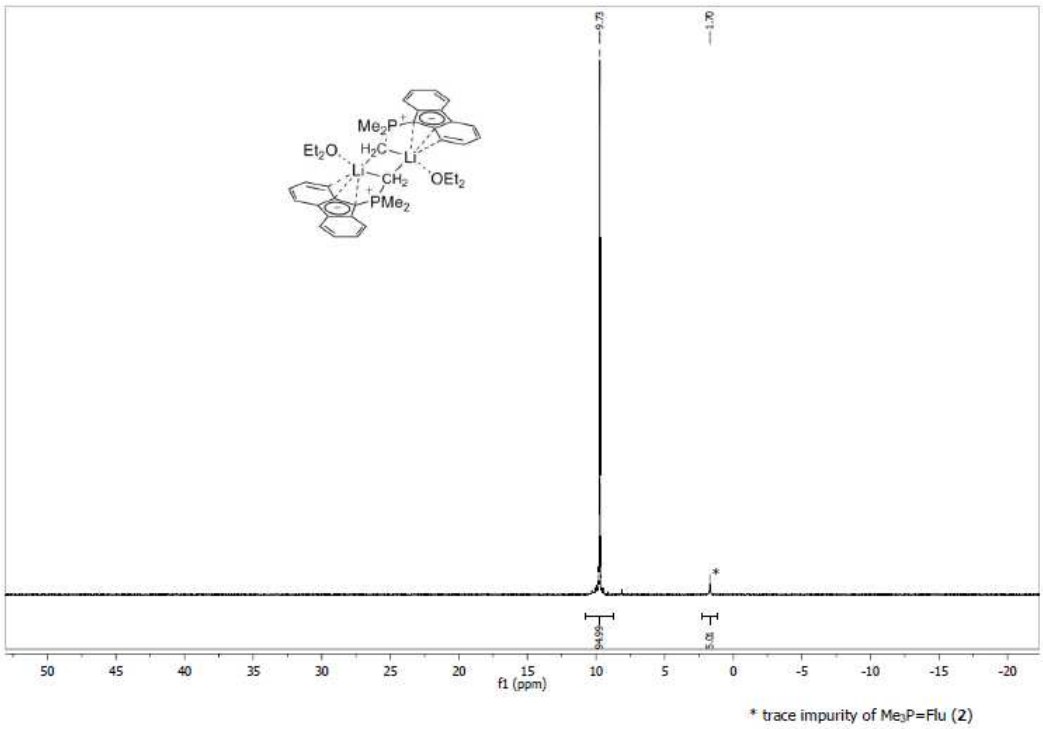
^{1}H NMR of Compound **3** (THF-d_8)



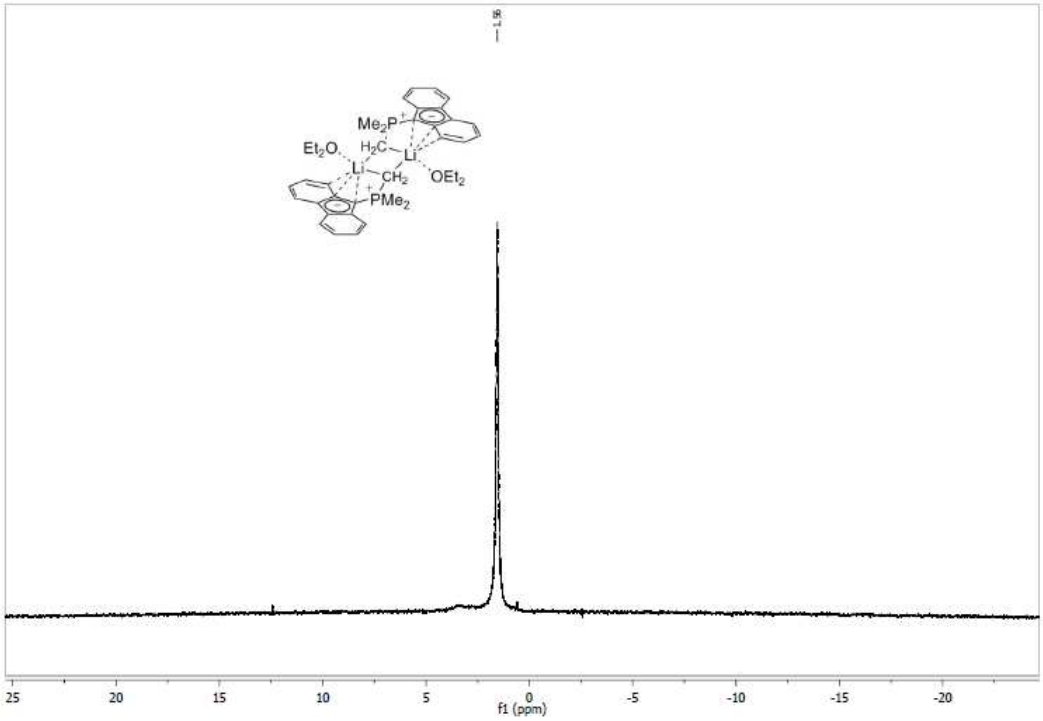
^{13}C NMR of Compound **3** (THF-d_8)



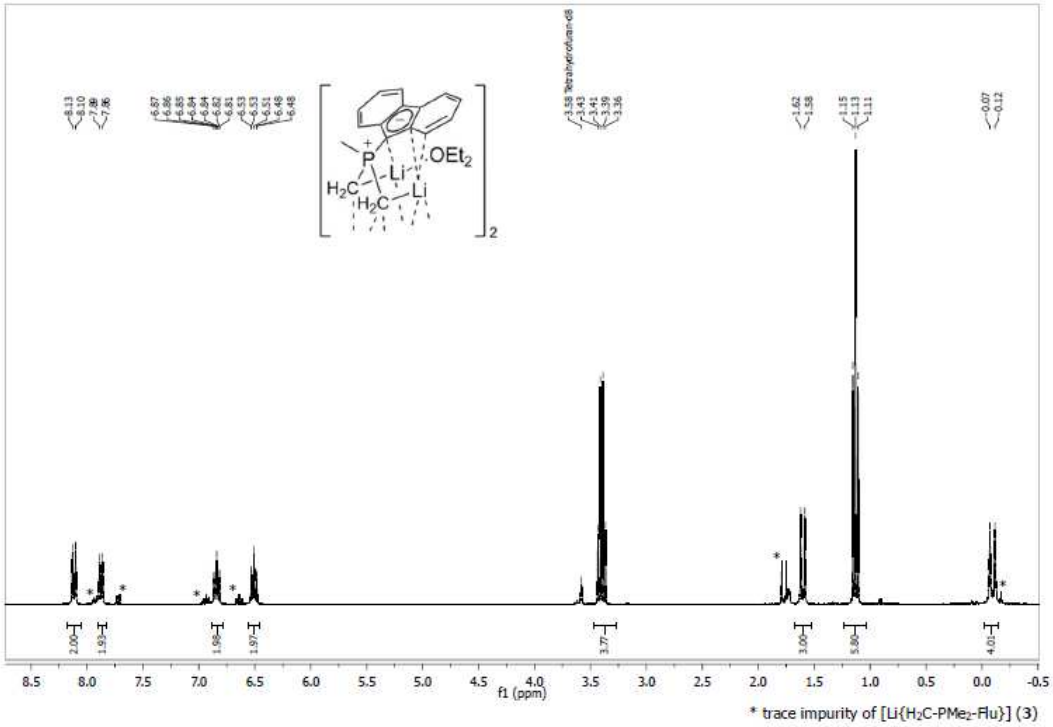
^{31}P NMR of Compound **3** (THF-d_8)



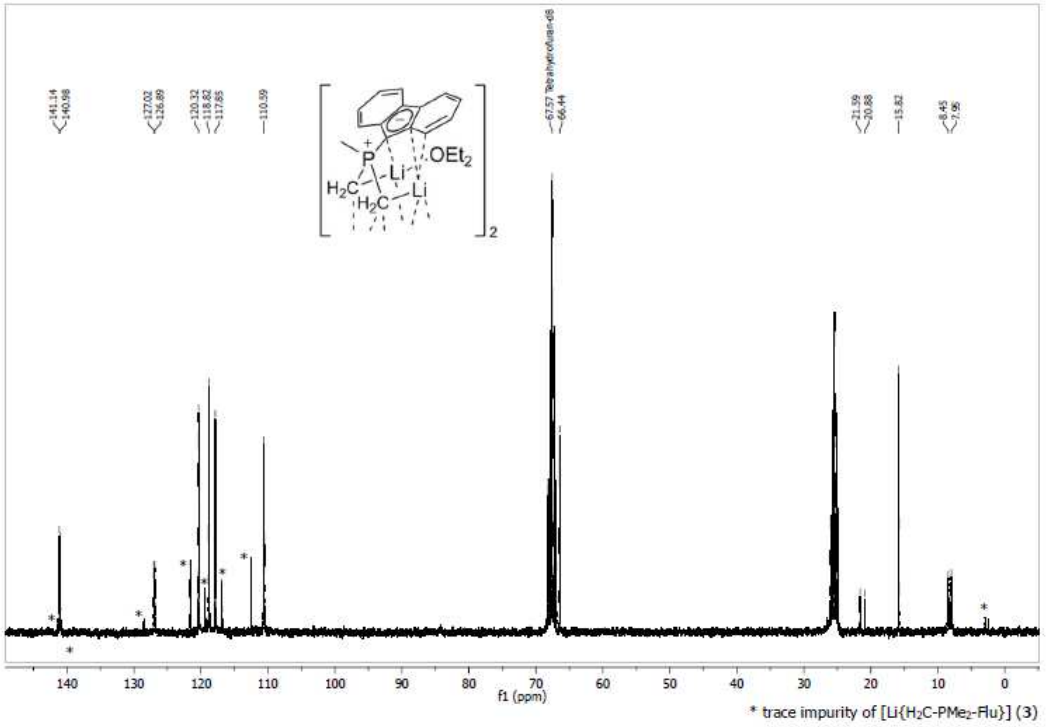
^{7}Li NMR of Compound **3** (THF-d_8)



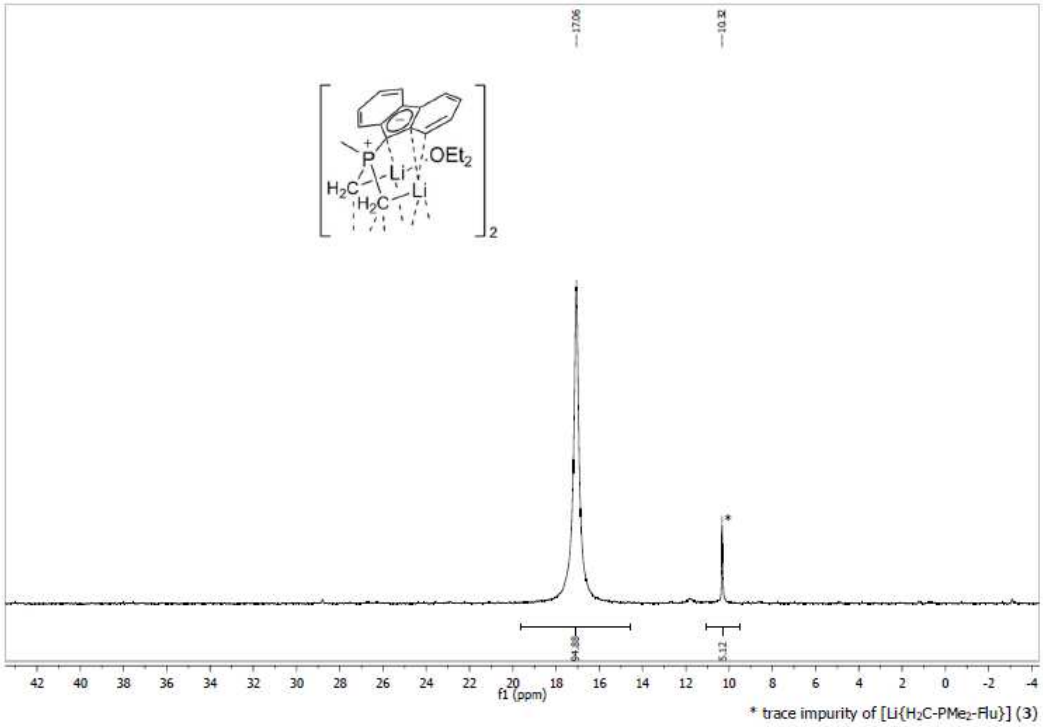
^{1}H NMR of Compound **4** (THF-d_8)



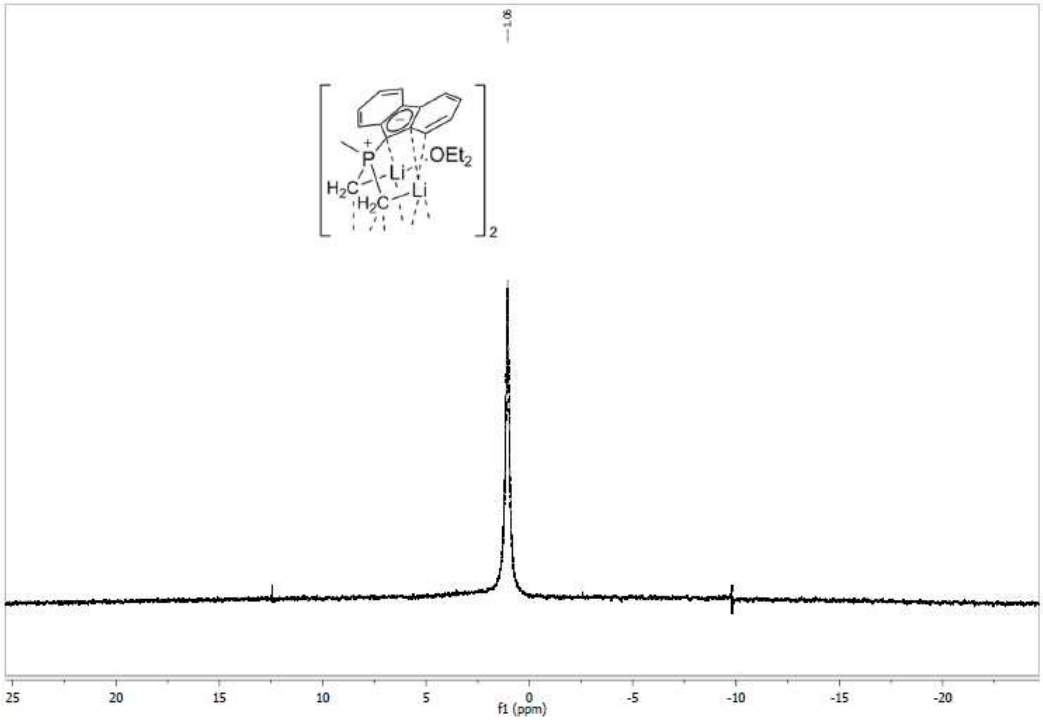
^{13}C NMR of Compound **4** (THF-d_8)



^{31}P NMR of Compound **4** (THF-d_8)



^{7}Li NMR of Compound **4** (THF-d_8)



References

1. T. Xu, W. T. Gong, J.-W. Ye, Y. Lin and G.-L. Ning, *Organometallics*, **2010**, 29, 6744-6748.

2. E. D. Brady, T. P. Hanusa, M. Pink and V. G. Young, *Inorg. Chem.*, **2000**, 39, 6028-6037.

3. C. Lichtenberg, N. S. Hillesheim, M. Elfferding, B. Oelkers and J. Sundermeyer, *Organometallics*, **2012**, 31, 4259-4266.

4. F. G. Schröder, C. Lichtenberg, M. Elfferding and J. Sundermeyer, *Organometallics*, **2013**, 32, 5082-5091.

5. J. H. Brownie, M. C. Baird and H. Schmider, *Organometallics*, **2007**, 26, 1433-1443.

6. H. L. Ammon, G. L. Wheeler and P. H. Watts, *J. Am. Chem. Soc.*, **1973**, 95, 6158-6163.

7. J. C. J. Bart, *Journal of the Chemical Society B: Physical Organic*, **1969**, 350-365.