Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

Reactivity of Lewis pairs $R_2PCH_2AlMe_2$ with Carbon Dioxide

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Contents

1. Synthetic procedure

a. General experimental

Unless otherwise specified, manipulations were carried out under an atmosphere of dinitrogen, using standard glovebox and Schlenk techniques. Reactions were carried either in a sealed J-Young NMR tube, in which case NMR conversions are indicated, or in standard flame dried Schlenk glassware. All solvents were distilled from Na/benzophenone, benzene-d_6 and toluene-d_8 were purified by vacuum distillation from Na/K alloy, and dichloromethane-d_2 was degassed using freeze-pump-thaw cycles and stored over molecular sieves. Toluene was stored on Na/K alloy. Bone dry CO_2 was purchased from Praxair and $^{13}CO_2$ (99% isotope label) was purchased from Cambridge Isotope Laboratories. Compound **1-Me**[S1] and $LiCH_2PPh_2$[S2] were synthesized according to literature procedures.

NMR spectra were recorded on a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 100.580 MHz (^{13}C), 161.923 MHz (^{31}P), 104.26 MHz (^{27}Al) or on a Bruker NMR AC-300 at 300MHz (^{1}H), 75.435 MHz (^{13}C), 121.442 MHz (^{31}P). ^{1}H NMR and ^{13}C{^{1}H} NMR chemical shifts are referenced to residual protons in deuterated solvent. The temperatures of the VT NMR experiments were measured using a thermocouple inside the probe, which was calibrated with methanol prior to use. Multiplicities are reported as singlet (s), broad singlet (s, br) doublet (d), triplet (t), multiplet (m), or virtual triplets (vt). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. gHMQC and ^{1}H{^{31}P} NMR experiments were performed in order to assign the spectra. Infrared spectra were recorded on a Thermo-Nicolet Magna 850 FT infrared spectrometer equipped with an MCT detector from a suspension in Nujol® Mull. Frequencies are given in cm^{-1} and intensities are reported as strong (s) or medium (m). None of the samples exhibit stability at room temperature under N_2 over a two or three days period.

Species **2-R** undergo transformation to **3-R** and species **3-R** undergo further unknown transformations (see Figure S5 for a typical result), which prevents obtaining reliable data for elemental analysis.

b. Reactions with 1-Me

$Me_2PCH_2AlMe_2OC(O)$ (2-Me):

First method:

To 40 mg (0.15 mmol) of **1-Me** in 2 ml of toluene was added an excess of CO_2 by filling the headspace of the schlenk flask (10 mL) with an atmosphere of CO_2. A white precipitate formed immediately after the addition of CO_2. The solution was stirred 5 minutes, after which the mixture was cooled to – 60° C. The solvent was removed under vacuum while letting the mixture return to room temperature. Yield 52 mg (> 97%).

Second method:

To a 0.03 M solution of $(Me_2PCH_2AlMe_2)_2$ (8.0 mg, 0.03 mmol) in 1mL of dichloromethane-d_2 was added 1 atm of CO_2 (or $^{13}CO_2$). The sample in a sealed J-Young NMR tube was immediately stored in a -60° C ice-bath after the addition of CO_2. The reaction was then followed by variable-temperature NMR spectroscopy. After 20 minutes at -30°C, the NMR spectra exhibited exclusively signals from the adduct **2-Me (¹³C-2-Me). 2-Me;** ^{1}H NMR (400 MHz, dichloromethane-d_2, -30 °C): δ 1.77 (d, 6H, $^2J_{H-P}$ =13.8 Hz, PMe_2), 0.57 (d, 2H, $^2J_{H-P}$ = 14.6 Hz, PCH_2), -0.85 (s, 6H, $AlMe_2$); $^{31}P\{^1H\}$ (162 MHz, dichloromethane-d_2): δ 16.6 (s). **^{13}C-2-Me;** ^{1}H NMR (400 MHz, dichloromethane-d_2): δ 1.77 (dd, 6H, $^3J_{H-C}$ = 2.5 Hz, $^2J_{H-P}$ =13.8 Hz, PMe_2), 0.57 (dd, 2H, $^3J_{H-C}$= 4.0 Hz, $^2J_{H-P}$ = 14.6 Hz, PCH_2), -0.85 (s, 6H, $AlMe_2$); $^{13}C\{^1H\}$ NMR (101 MHz, dichloromethane-d_2): δ 170.2 (d, $^1J_{C-P}$ = 112 Hz); $^{31}P\{^1H\}$ (162 MHz,

dichloromethane-d_2): δ 16.6 (d, $^1J_{C\text{-}P}$ = 112 Hz). ATR-IR ^{12}C (Nujol mull, cm^{-1}): 1675(s), 1182 (m). ^{13}C: (Nujol mull, cm^{-1}): 1636(s), 1182 (m). The low solubility of **2-Me** at low temperature and the rapid conversion to **3-Me** in solution prevents the acquisition of a ^{13}C NMR spectrum of the ^{12}C sample.

$(Me_2PCH_2COOAlMe_2)_2$ (3-Me): Leaving a 0.03 M solution of **1-Me** in benzene-d_6 or dichloromethane-d_2 to react with one atm of CO_2 (or $^{13}CO_2$) at room temperature overnight leads to a quantitative NMR conversion to **3-Me** (**^{13}C-3-Me**). **3-Me;** ^{1}H NMR (400 MHz, benzene-d_6): δ 1.97 (d, 2H, $^2J_{H\text{-}P}$ = 3.7 Hz, PCH_2), 0.77 (d, 6H, $^2J_{H\text{-}P}$ = 4.6 Hz, PMe_2) -0.32 (s, 6H, AlMe_2); ^{13}C{^{1}H} NMR (101 MHz, benzene-d_6): 179.9 (s, OC(O)), 37.9 (d, $^1J_{C\text{-}P}$ = 29.2 Hz, PCH_2), 12.7 (d, $^1J_{C\text{-}P}$ =17.5 Hz, PMe_2), -10.3 (s, $AlMe_2$); ^{27}Al{^{1}H} NMR (104 MHz, benzene-d_6): 130.9 (s, br); ^{31}P{^{1}H} (122 MHz, benzene-d_6): -44.1 (s). **^{13}C-3-Me;** ^{1}H NMR (400 MHz, dichloromethane-d_2): δ 2.58 (dd, 2H, $^2J_{H\text{-}P}$ = 3.5 Hz, $^2J_{H\text{-}C}$ = 6.0 Hz, PCH_2), 1.13 (d, 6H, $^2J_{H\text{-}P}$ = 4.2 Hz, PMe_2) -0.83 (s, 6H, AlMe_2); ^{13}C{^{1}H} NMR (101 MHz, dichloromethane-d_2): δ 179.5 (s, OC(O)); ^{31}P{^{1}H} (122 MHz, dichloromethane-d_2): -41.8 (s). ATR-IR ^{12}C (Nujol mull, cm^{-1}): 1520(s), 1455 (s), 1395 (s). ^{13}C: (Nujol mull, cm^{-1}): 1500 (m), 1438 (m), 1373 (m). Leaving **3-Me** at the solid state for two days at room temperature gives an oily material. The ^{31}P NMR does not change significantly, but the ^{1}H becomes messy, which probably occurs from rearrangement of the carboxylate moiety, thus preventing the isolation of a clean product for elemental analysis.

C($\kappa_{O,P}$-$PMe_2CH_2AlMe_2O)_2$ (4-Me) : In a sealed J-Young NMR tube, approximately 1.0 equivalent of CO_2 was added to a 0.08 mmol solution of $(Me_2PCH_2AlMe_2)_2$ in 0.8 mL of benzene-d_6 using a known-volume bulb. At the early stage, some solid associated to **2-Me** was present in solution. The reaction was followed by NMR spectroscopy until the desired product became the predominant species, after 18 hours. During the course of that reaction, several other

products are formed (prior and after generation of **4-Me**) and several unidentified products are forming (not all soluble). It is not clear if the degradation of **4-Me** overtime is helped by the degradation of **3-Me** (see General Experimental section). NMR yield 50%. Species **3-Me** is always present in solution at the same time than **4-Me**. ^{1}H NMR (300MHz, benzene-d_6): 0.96 (vt, 6H, J_{H-P} = 6.3 Hz, PMe_2), 0.09 (vt, 2H, J_{H-P} = 9.8 Hz, PCH_2), -0.38 (s, 6H, $AlMe_2$). $^{13}C\{^{1}H\}$ NMR (75 MHz, benzene-d_6): δ 96.1 (t, $^{1}J_{C-P}$ = 99 Hz, OCO), 29.3 (t, J_{C-P} = 23.7 Hz, PMe_2), 1.4 (m, PCH_2), -8.3 (m, $AlMe_2$). $^{31}P\{^{1}H\}$ (122 MHz, benzene-d_6): δ 37.5 (s).

c. Experimental section of the reactions with 1-Ph

$(Ph_2PCH_2AlMe_2)_2$ (1-Ph): A 0.22 M solution of $ClAlMe_2$ (60.9 mg, 0.066 mmol) in toluene was added dropwise to a stirred suspension of $LiCH_2PPh_2$ (135.8 mg, 0.066 mmol) in 15 mL toluene in a glovebox. After 24 hours, the LiCl precipitate was filtered off using a cellulose filter paper. After evaporation of the filtrate under vacuum, 143.0 mg of a white powder was obtained. Yield 85%. Recrystallisation in toluene at – 25 °C gave clear crystals suitable for X-Ray diffraction analyses. The sample showed a slight decolouration to a very pale yellow powder over time. The decolouration did not seem to alter the reactivity in any significant way. ^{1}H NMR (300 MHz, benzene-d_6): δ 7.50 (m, 4H, Ph), 7.00 (m, 6H, Ph), 1.10 (dd, 2H, $^{2}J_{H-P}$ = 12.2 Hz, $^{3}J_{H-P}$ = 6.7 Hz, PCH_2Al), -0.55 (d, 6H, $^{3}J_{H-P}$ = 4.9 Hz, $AlMe_2$). $^{13}C\{^{1}H\}$ NMR (101 MHz, benzene-d_6): δ 134.7 (d, 34.0 Hz, C_{ipso}), 132.1 (d, 11.7 Hz, C_{ortho}), 129.9 (C_{para}), 128.6 (d, 9.2 Hz, C_{meta}), 2.2 (d, 17.9 Hz, PCH_2Al), -8.8 (d, 18.6 Hz, $AlMe_2$). $^{27}Al\{^{1}H\}$ NMR (104 MHz, benzene-d_6): 146.9 (s, br). $^{31}P\{^{1}H\}$ NMR (122 MHz, benzene-d_6): -15.0 (s). IR (Nujol mull, cm^{-1}): 1434(s), 985 (s).

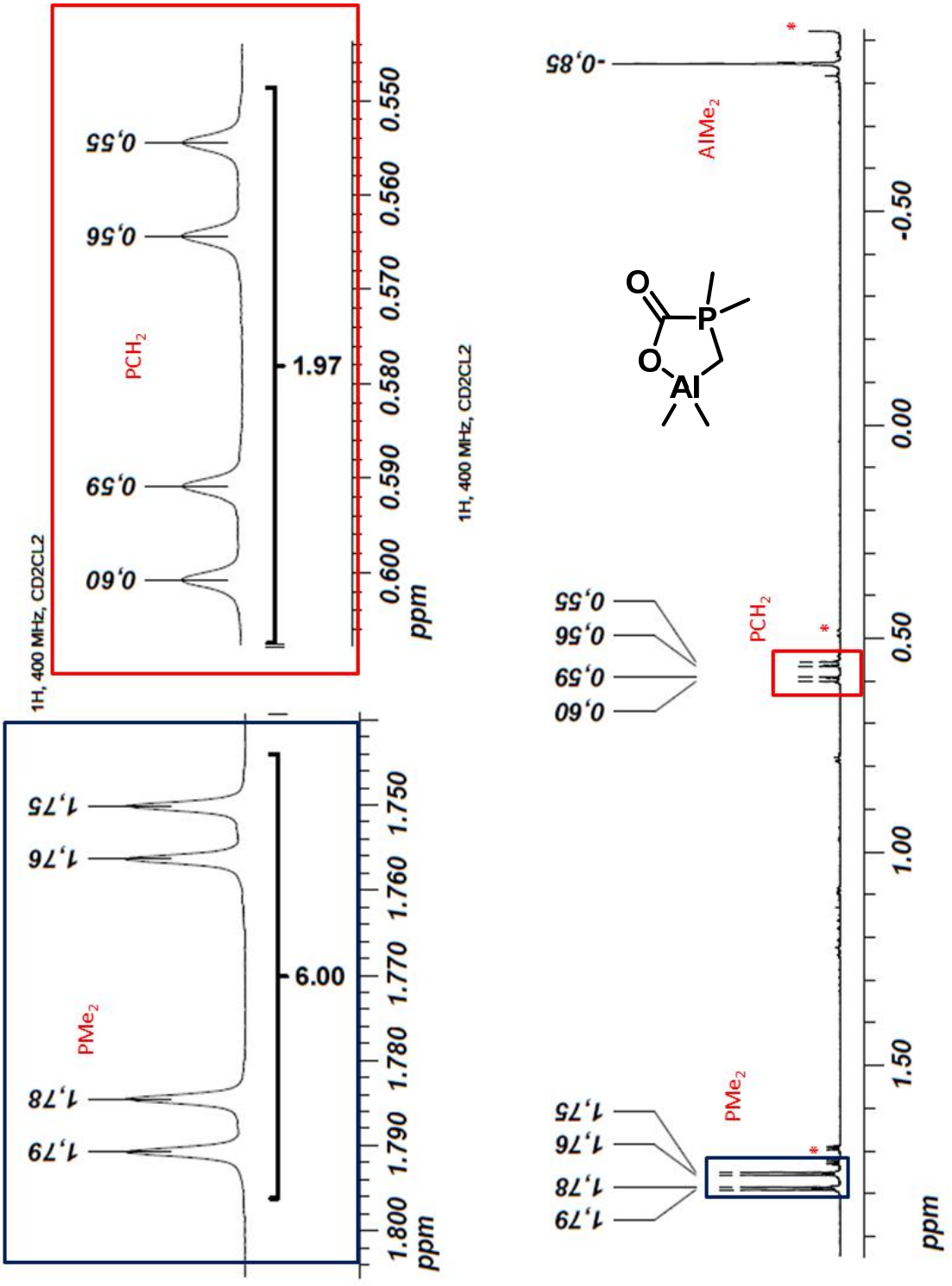
$Ph_2PCH_2AlMe_2OC(O)$ (2-Ph): In a sealed J-Young NMR tube, an excess of CO_2 was added to a 0.09 mmol solution of $(Ph_2PCH_2AlMe_2)_2$ in 0.9 mL of toluene-d_8 at -50° C. The reaction was followed by NMR spectroscopy at -40° C until the desired product became the predominant species. The excess of CO_2 was then removed under reduced pressure and the reaction mixture left to warm to room temperature. NMR analysis revealed quantitative conversion of $(Ph_2PCH_2AlMe_2)_2$ to adduct **2-Ph. 2-Ph:** ^{1}H NMR (400 MHz, toluene-d_8): δ 7.44 (m, 4H, Ph), 6.87 (m, 6H, Ph), 0.76 (dd, 2H, $^2J_{H\text{-}P}$ = 14.8 Hz, PCH_2), -0.36 (s, 6H, AlMe_2); ^{13}C{^{1}H} NMR (101 MHz, toluene-d_8): δ 165.6 (d, $^1J_{C\text{-}P}$ = 110 Hz). ^{31}P {^{1}H} (122 MHz, toluene-d_8): δ 17.9 (d, $^1J_{C\text{-}P}$ =109.5 Hz). **^{13}C-2-Ph:** ^{1}H NMR (400 MHz, toluene-d_8): δ 7.44 (m, 4H, Ph), 6.87 (m, 6H, Ph), 0.76 (dd, 2H, $^2J_{H\text{-}P}$ = 14.8 Hz, $^3J_{H\text{-}C}$ = 3.5 Hz, PCH_2), -0.36 (s, 6H, AlMe_2); ^{13}C{^{1}H} NMR (101 MHz, toluene-d_8): δ 165.6 (d, $^1J_{C\text{-}P}$ = 109.7 Hz). ^{31}P {^{1}H} (122 MHz, toluene-d_8): δ 17.9 (d, $^1J_{C\text{-}P}$ =109.5 Hz). The rapid conversion of **2-Ph** to **3-Ph** in solution prevents the acquisition of a ^{13}C NMR spectrum of the ^{12}C sample.

$(Ph_2PCH_2COOAlMe_2)_2$ (3-Ph): The product **2-Ph** formed **3-Ph** quantitatively (NMR) when left at r.t. overnight. ^{1}H NMR (400 MHz, toluene-d_8): 7.25 (m, 4H, Ph), 7.02 (m, 6H, Ph), 2.75 (dd, 2H, $^2J_{H\text{-}P}$ = 1.1 Hz, PCH_2), -0.48 (s, 6H, AlMe_2). ^{13}C{^{1}H} NMR (101 MHz, toluene-d_8): 180.0 (d, $^2J_{C\text{-}P}$ = 8.2 Hz, C-CO_2-Al), 136.8 (d, $^2J_{C\text{-}P}$ = 15.8 Hz, C_{ortho}), 133.0 (d, $^1J_{C\text{-}P}$ = 20.5 Hz, C_{ipso}), 129.5 (s, C_{para}), 128.9 (d, $^3J_{C\text{-}P}$ = 6.9 Hz, C_{meta}), 38.5 (d, $^1J_{C\text{-}P}$ = 25.7 Hz, PCH_2C), -10.9 (s, br, AlMe_2)). ^{27}Al{^{1}H} (104 MHz, toluene-d_8): 145.9 (s, br). ^{31}P{^{1}H} (122 MHz, toluene-d_8): -12.6 (s). **^{13}C-(3-Ph):** ^{1}H NMR (400 MHz, toluene-d_8): 7.25 (m, 4H, Ph), 7.02 (m, 6H, Ph), 2.75 (dd, 2H, $^2J_{H\text{-}C}$ = 6.5 Hz, $^2J_{H\text{-}P}$ = 1.1 Hz, PCH_2), -0.47 (s, 6H, AlMe_2). ^{13}C{^{1}H} NMR (101 MHz, toluene-d_8): 180.0 (d, $^2J_{C\text{-}P}$ = 8.0 Hz, C-CO_2-Al. ^{31}P{^{1}H} (122 MHz, toluene-

d$_8$): -12.6 (d, $^2J_{C\text{-}P}$ = 8.0 Hz). IR ^{13}C (Nujol mull, cm^{-1}): 1500 (s), 1095 (m); IR ^{12}C (Nujol mull, cm^{-1}): 1548 (s), 1169 (m).

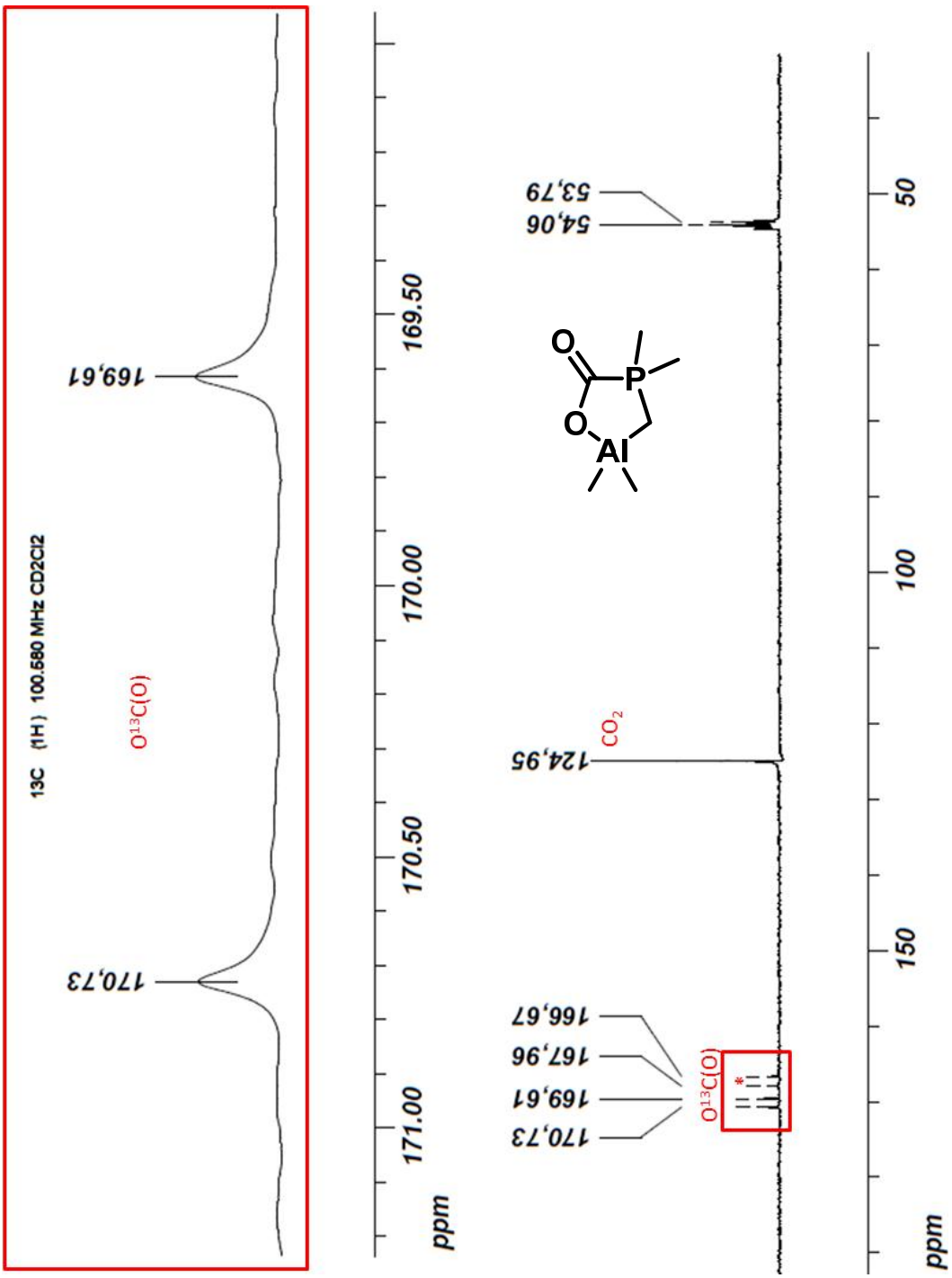
2. NMR Spectra

Fig. S1- ^{1}H NMR spectrum of **^{13}C-2-Me** (400 MHz, dichloromethane-d_2)



* : Denotes the presence of some residual Al-Cl in the starting material.

Fig. S2- $^{13}C\{^{1}H\}$ NMR spectrum of **2-Me** (101 MHz, dichloromethane-d_2)



* : Denotes the presence of some residual Al-Cl in the starting material.

Fig. S3- ^{1}H NMR spectrum of **3-Me** (300 MHz, benzene-d_6)

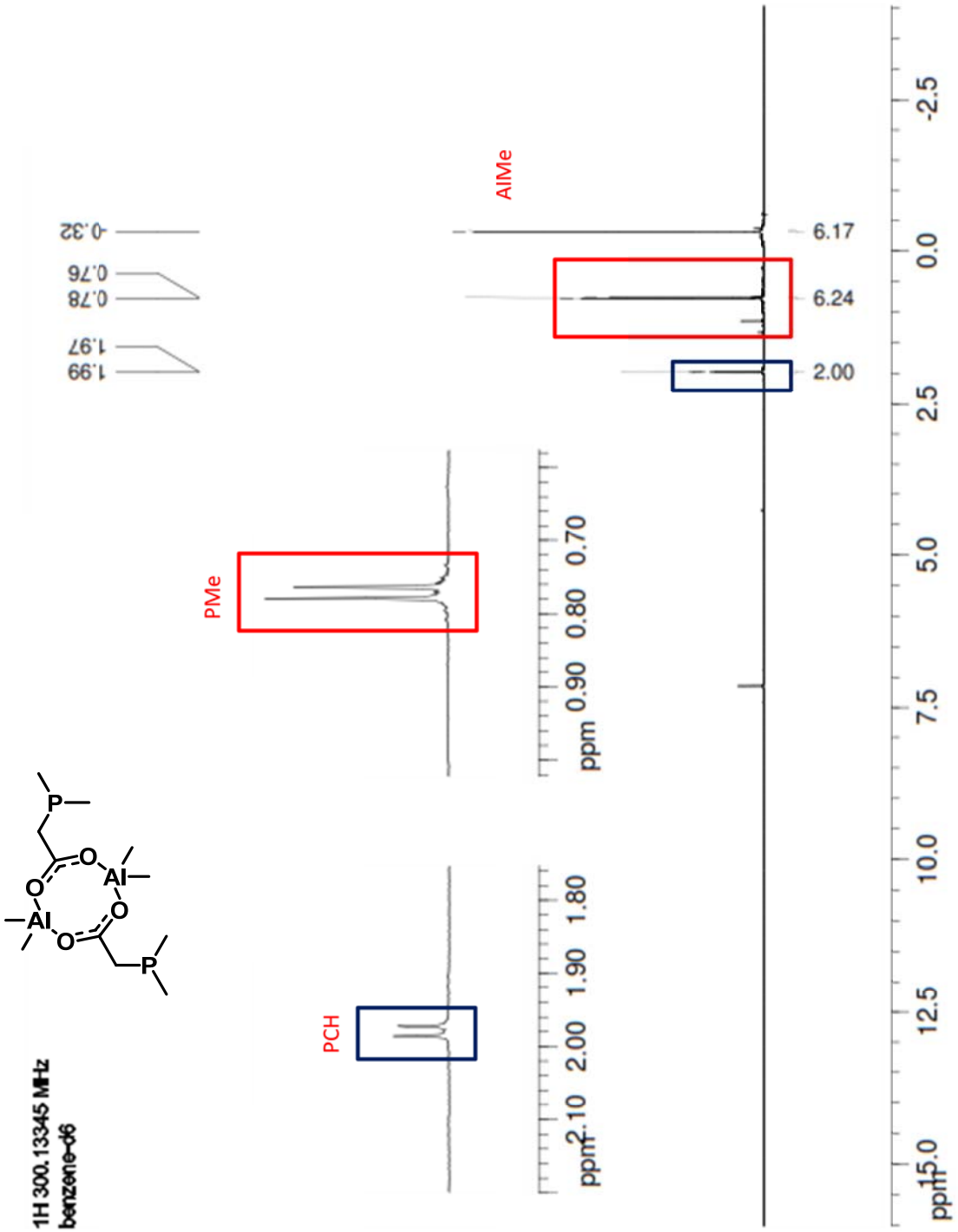


Fig. S4- $^{13}C\{^{1}H\}$ NMR spectrum of **3-Me** (101 MHz, benzene-d_6)

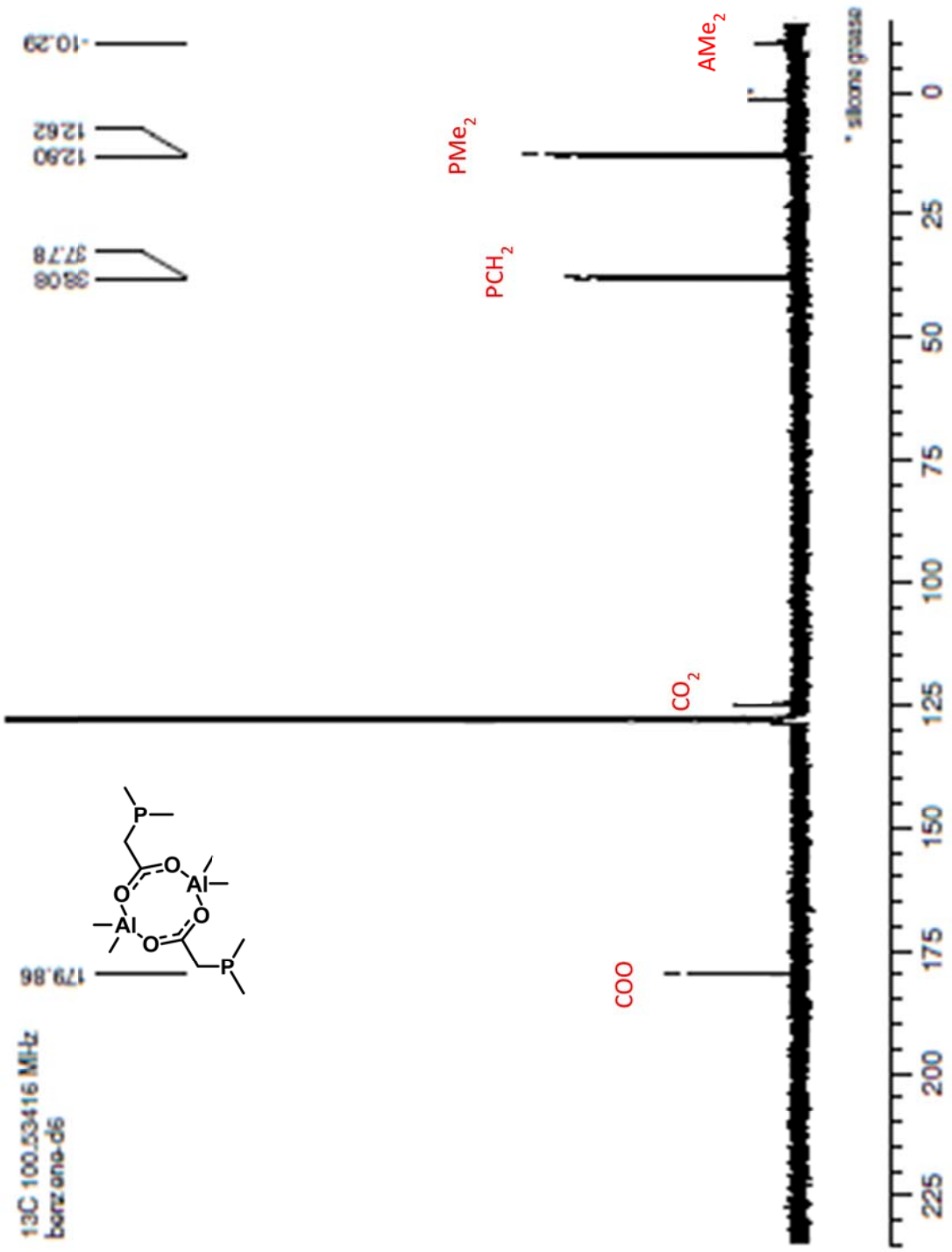


Fig. S5- ^{1}H NMR spectrum of **3-Me** after 4 days under nitrogen. (300 MHz, benzene-d_6) This species is not stable when stored under nitrogen.

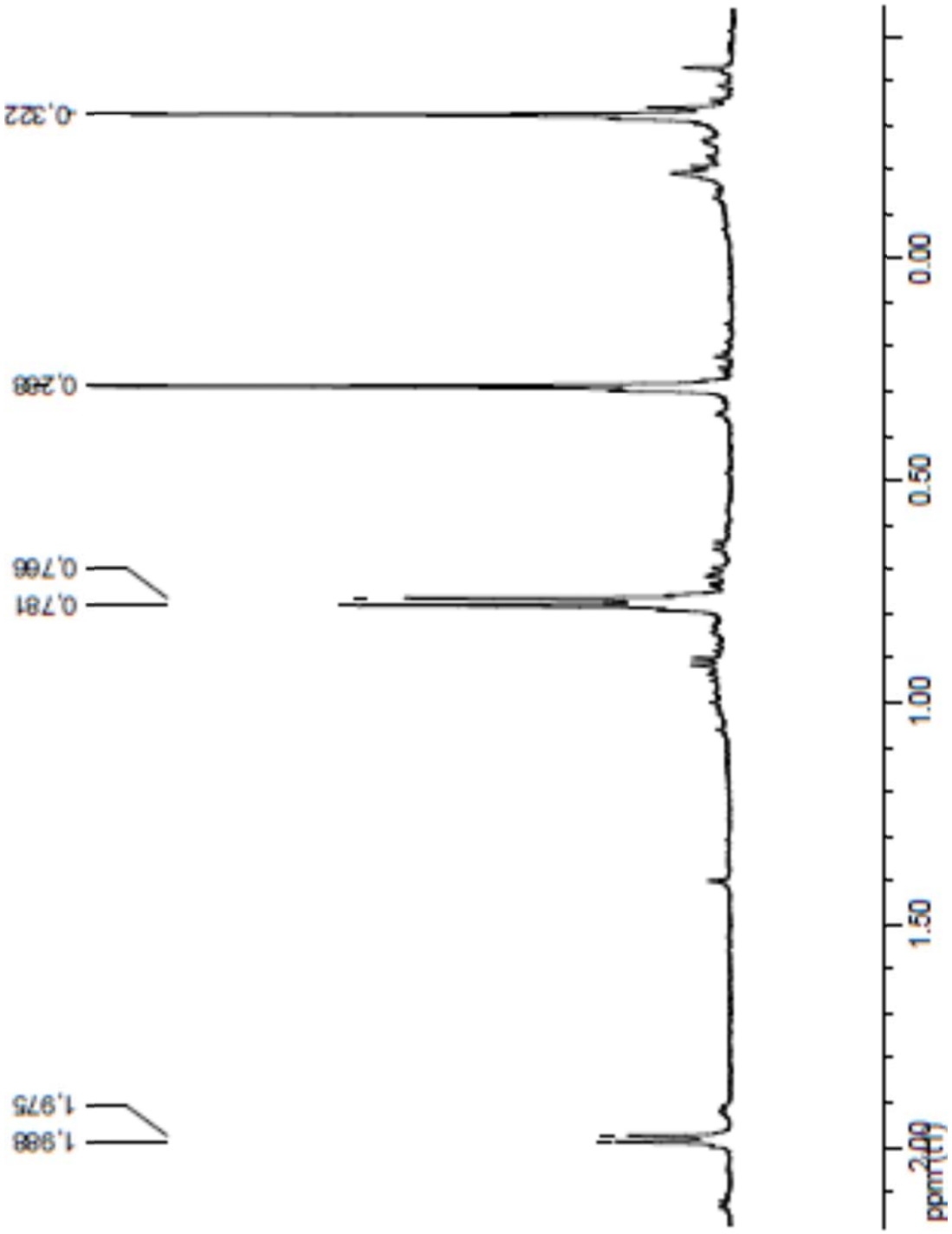


Fig. S6- ^{1}H NMR spectrum of **^{13}C-3-Me** (400 MHz, dichloromethane-d_2)

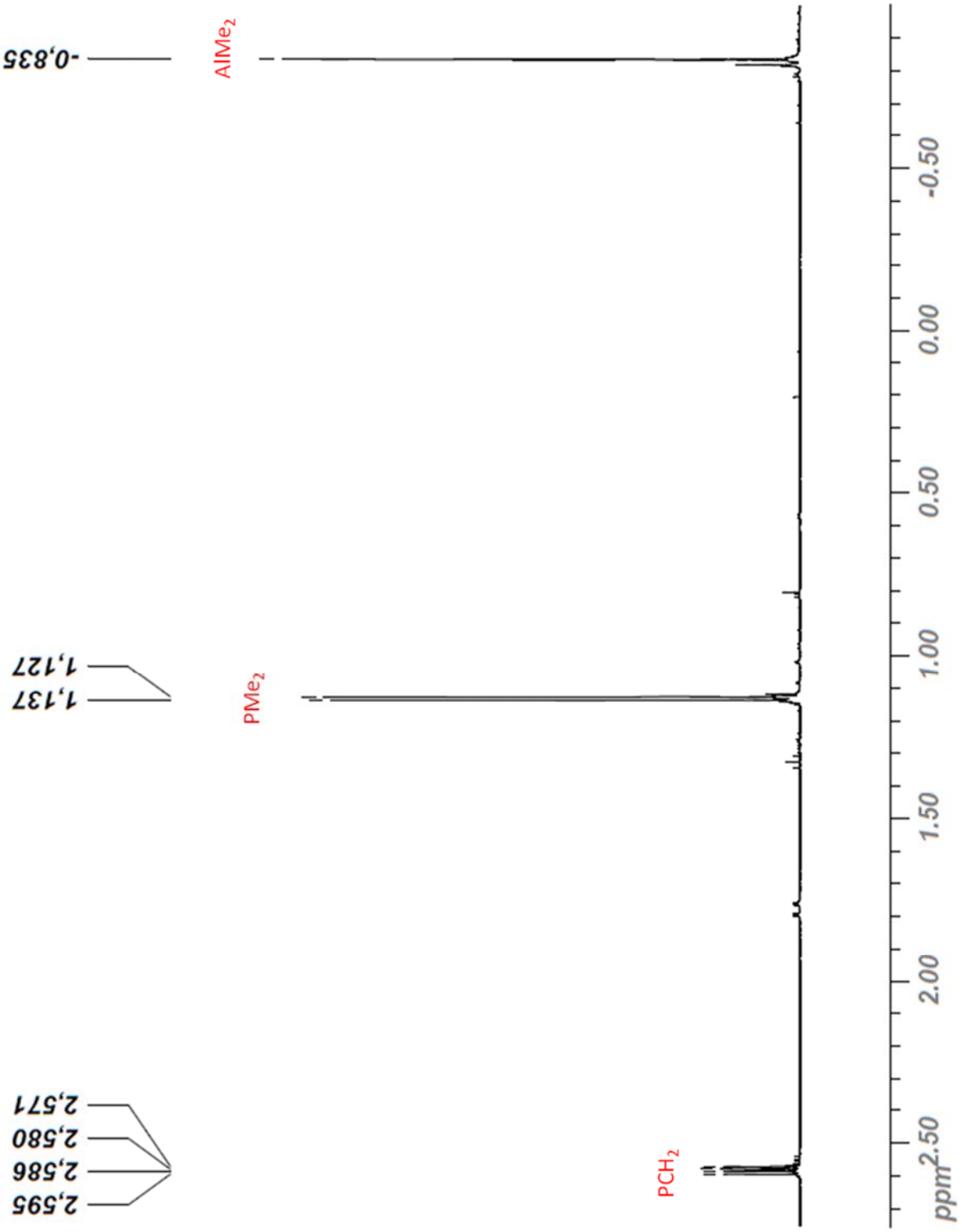


Fig. S7- ^{1}H-^{13}C gHMBC NMR spectrum of **^{13}C-3-Me** (400 MHz, dichloromethane-d_2)

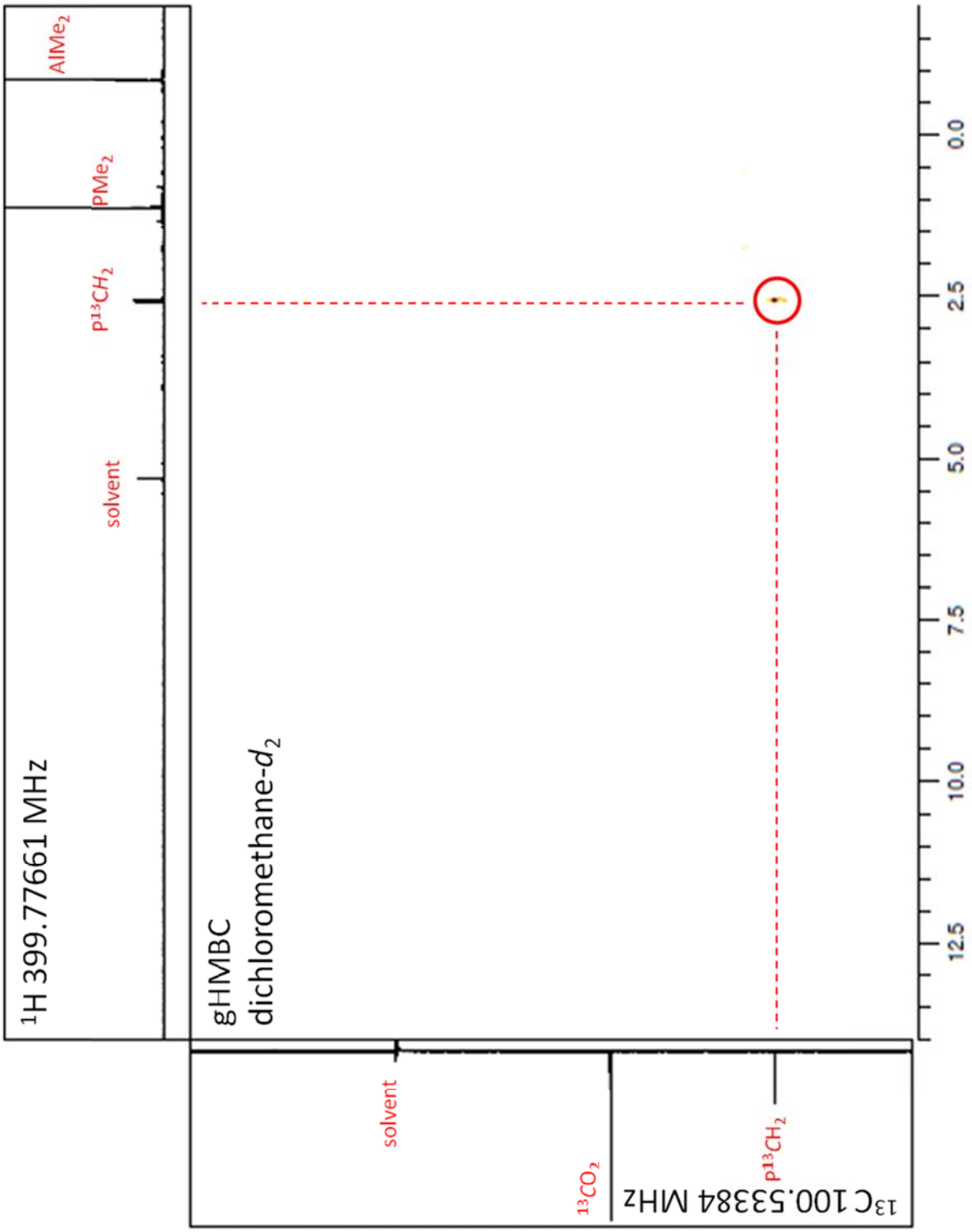


Fig. S8- Selected region of the ^{1}H NMR spectrum of **4-Me** (300 MHz, benzene-d_6).

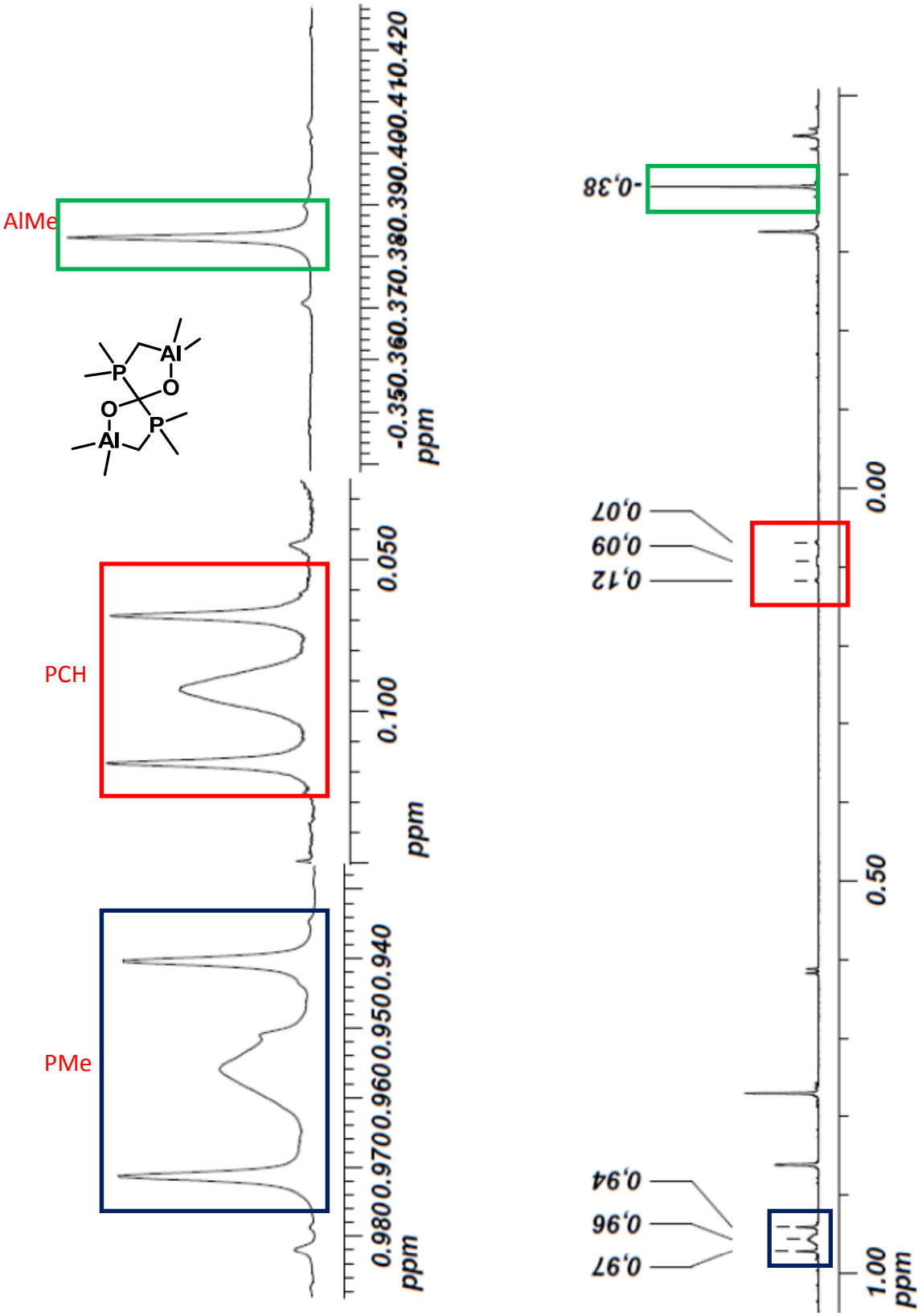

AlMe
PCH
PMe
Al
P
O
O
Al
P
-0.350.360.370.380.390.400.410.420
ppm
0.050
0.100
ppm
0.980.970.960.950.940
ppm
-0,38
0,07
0,09
0,12
0.00
0.50
0,94
0,96
0,97
1.00
ppm

Fig. S9- $^{13}C\{^{1}H\}$ NMR spectrum of **4-Me** (76 MHz, benzene-d_6)

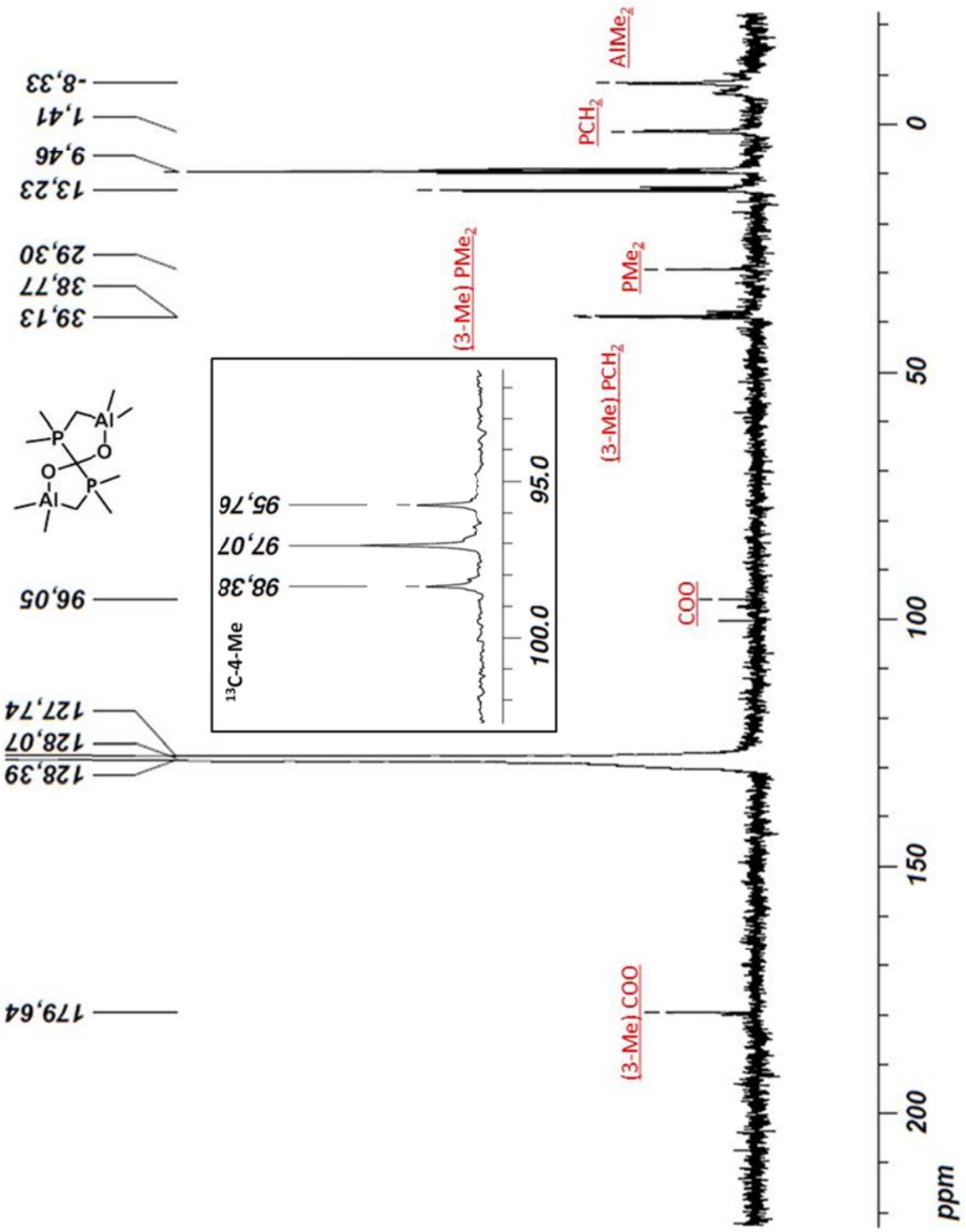


Fig. S10- ^{1}H NMR spectrum of **1-Ph** (300MHz, benzene-d_6)

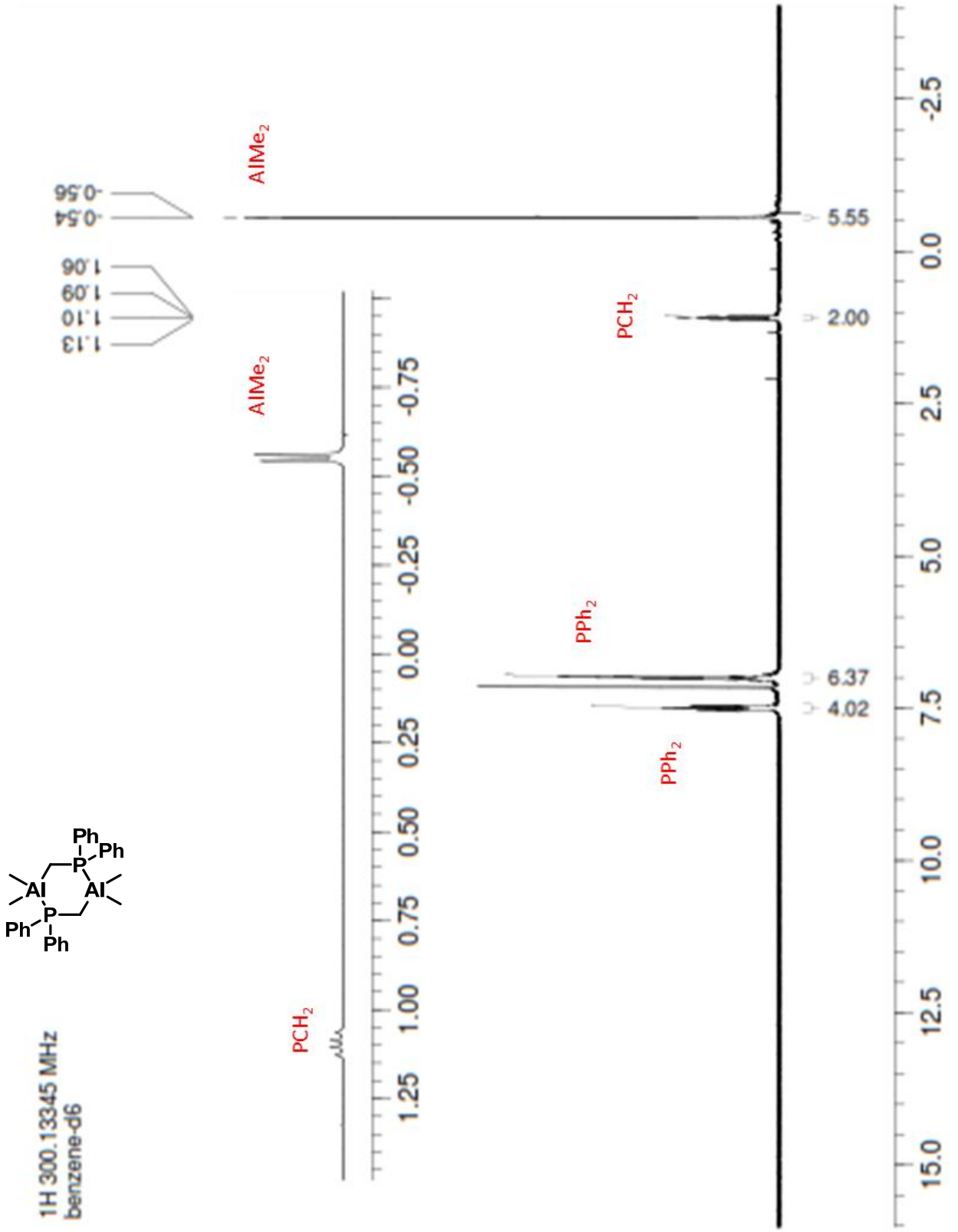


Fig. S11- $^{13}C\{^{1}H\}$ NMR spectrum of **1-Ph** (101 MHz, benzene-d_6)

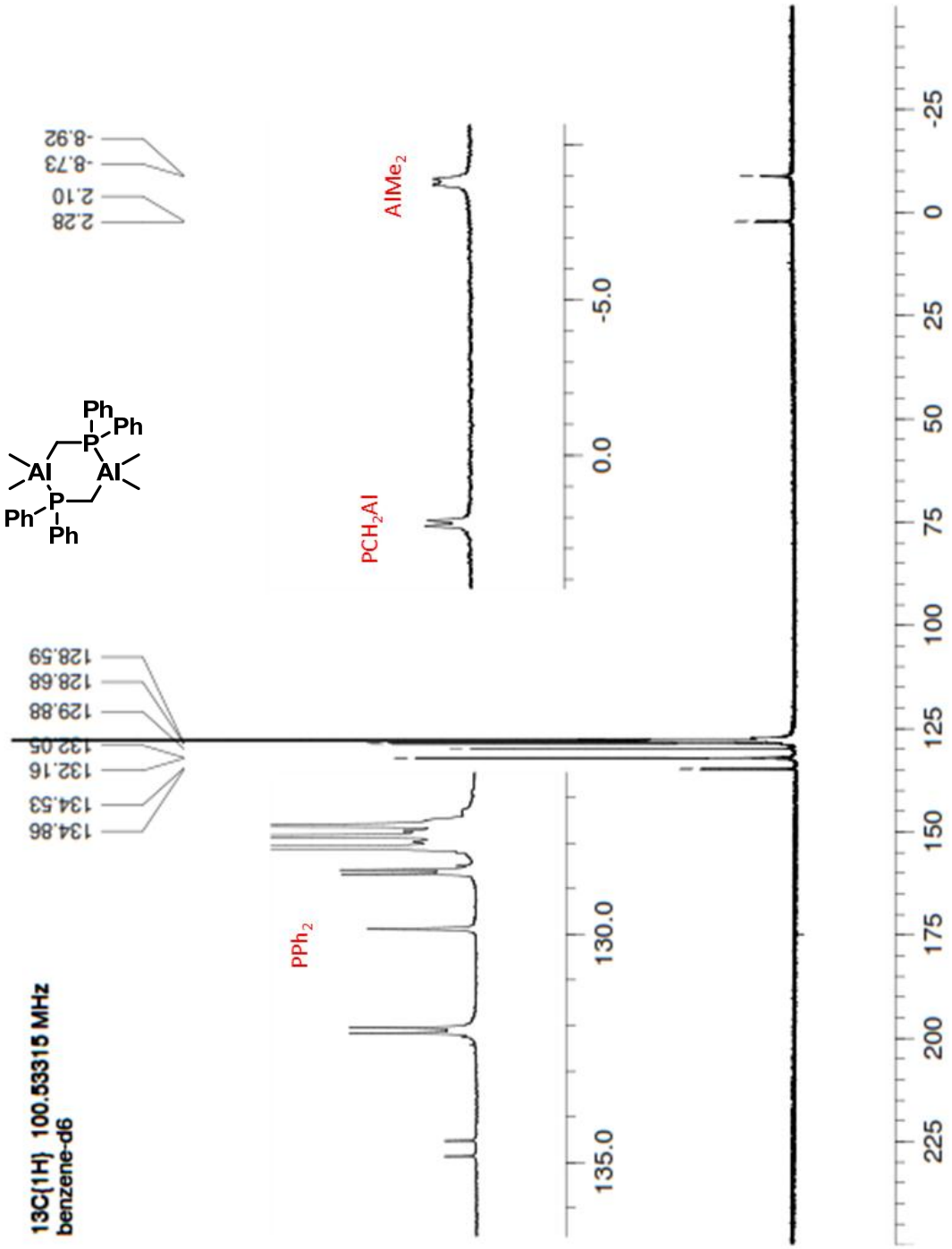


Fig. S12- ^{1}H NMR spectrum of **2-Ph** (400MHz, toluene-d_8)

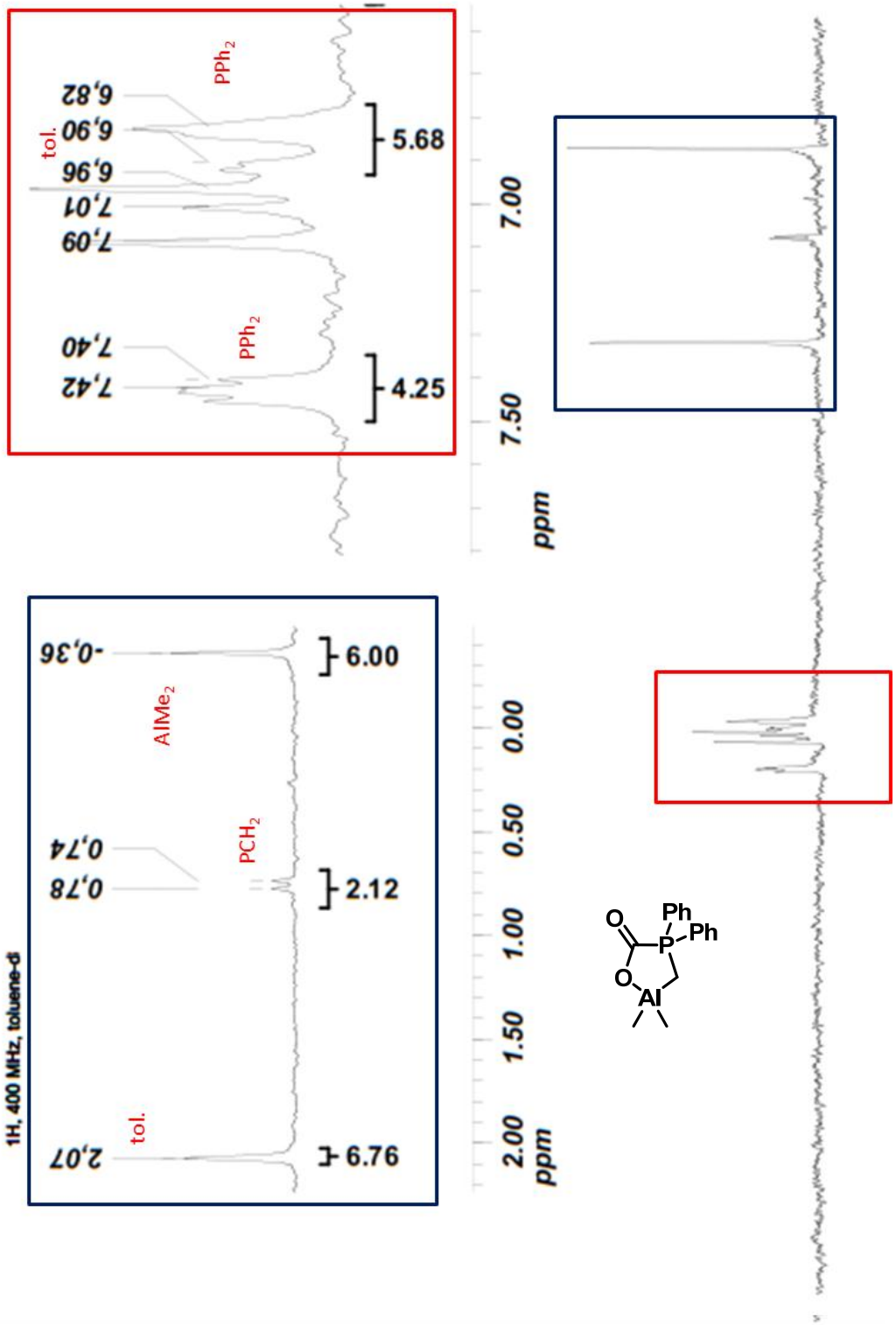


Fig. S13- ^{1}H NMR spectrum of **3-Ph** (400MHz, benzene-d_6)

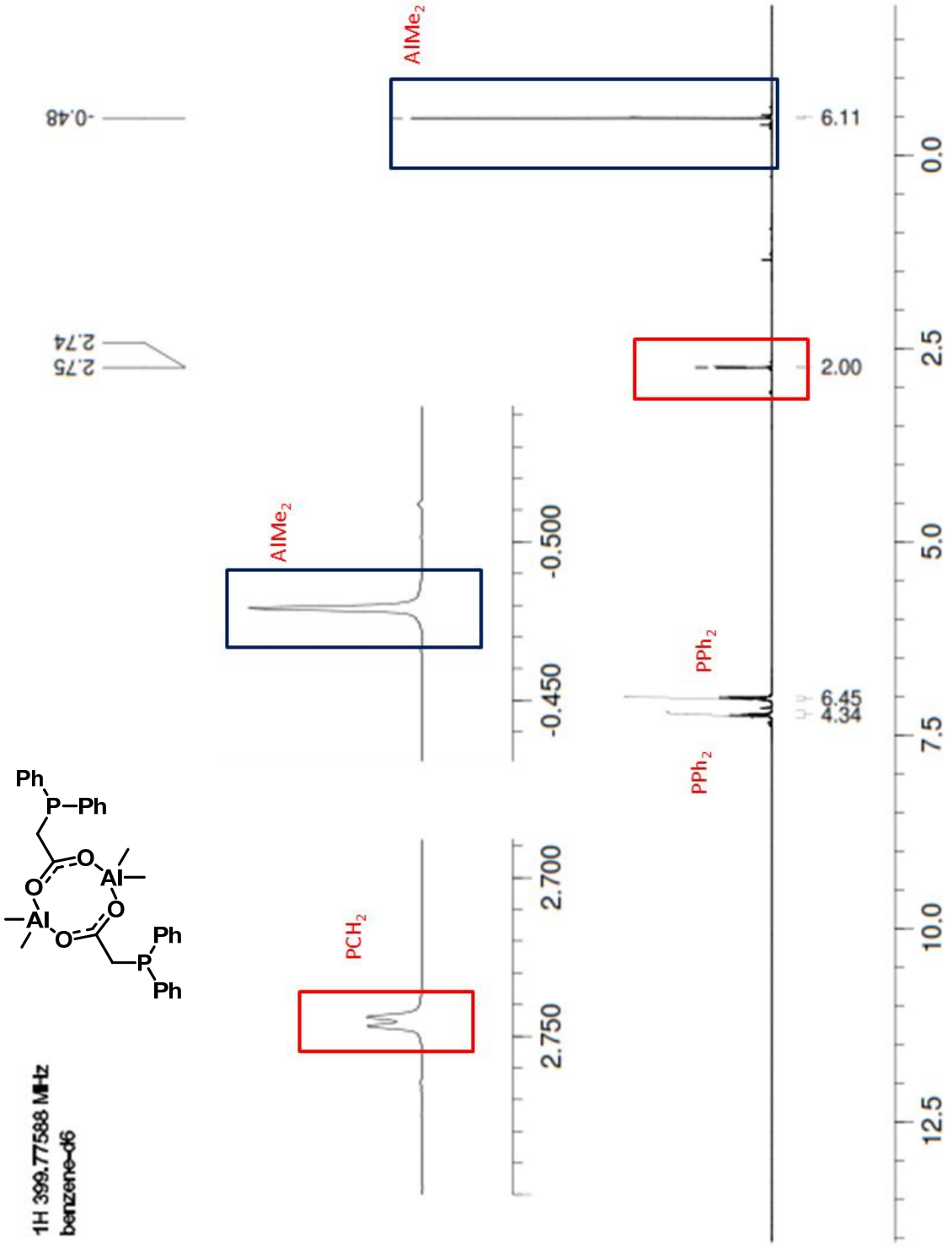
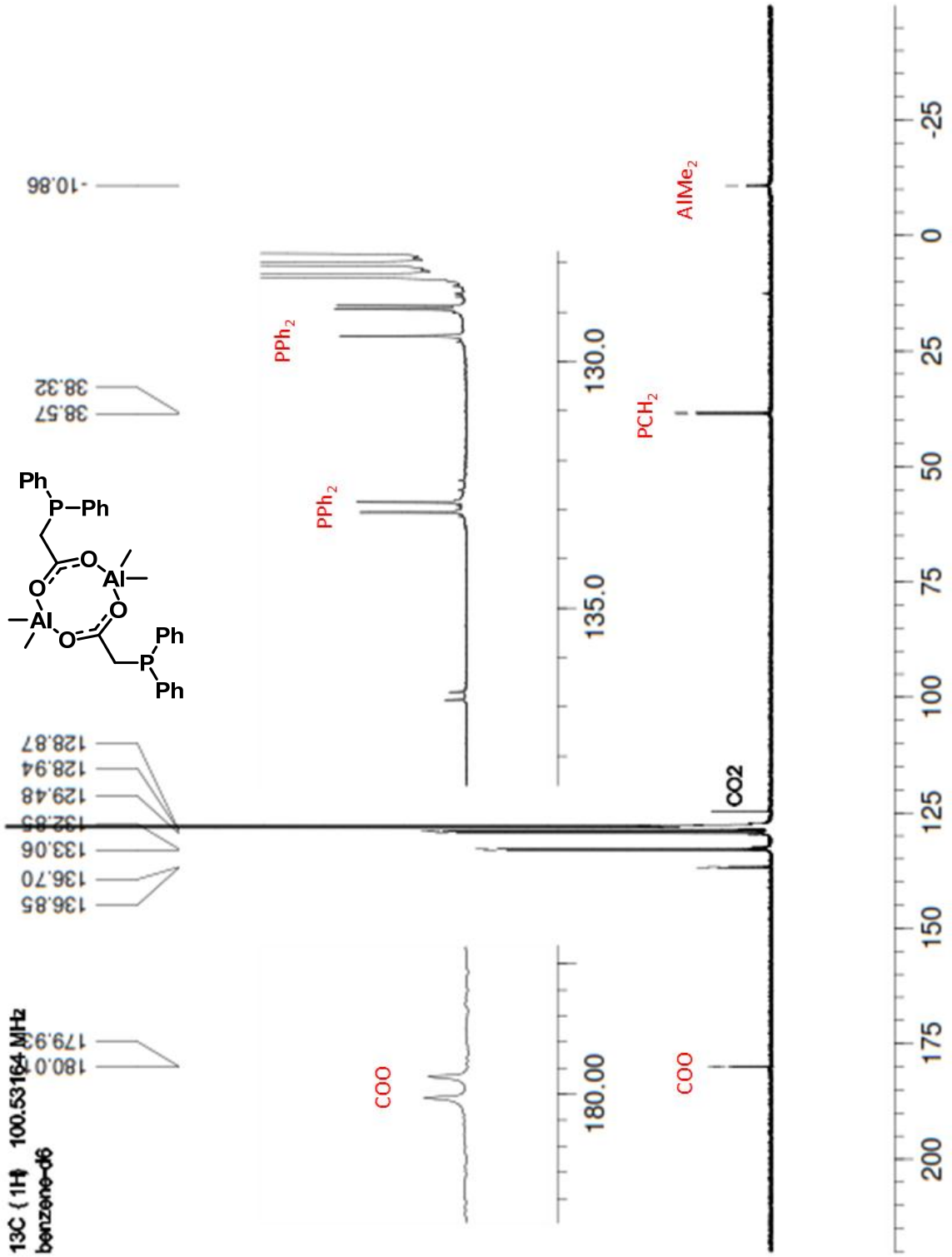
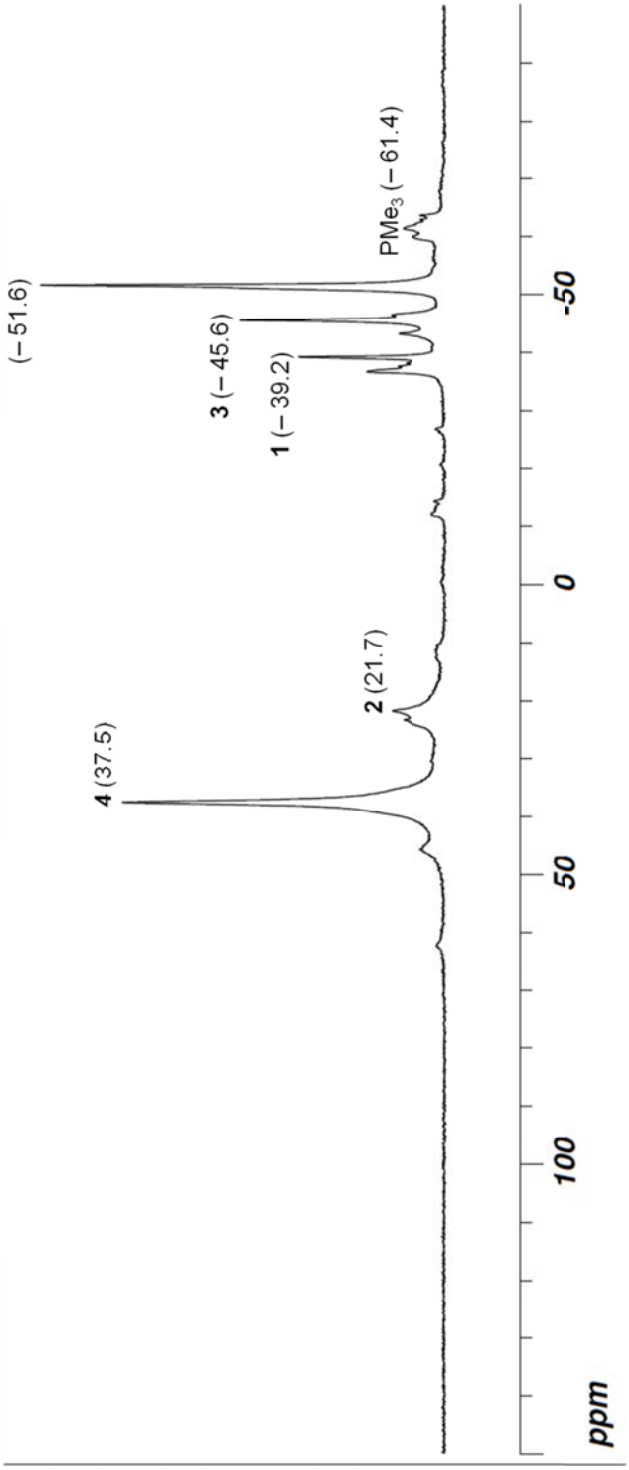


Fig. S14- ^{13}C NMR spectrum of **3-Ph** (101MHz, benzene-d_6)



3. Solid-State NMR Spectrum

Fig. S15- MAS ^{31}P NMR (162 MHz)



4. ATR-IR

Fig. S16- Infrared spectra for reactivity of **1-Me**

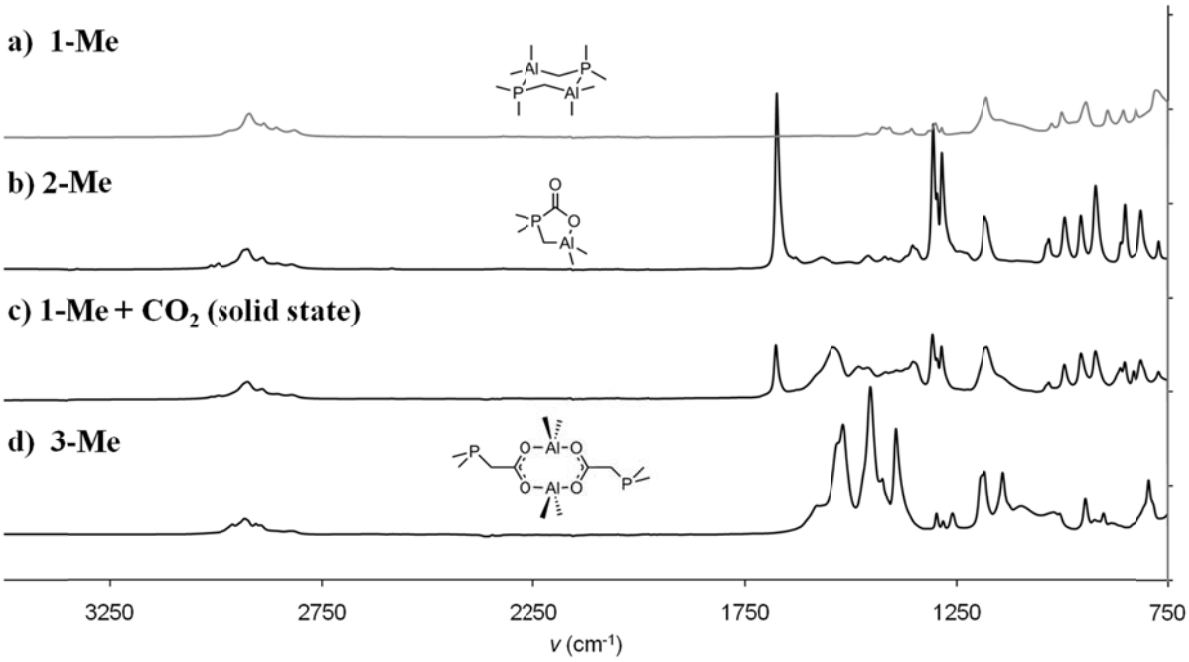


Fig. S17- Infared spectra of **2-Me** and ^{13}**C-2-Me**

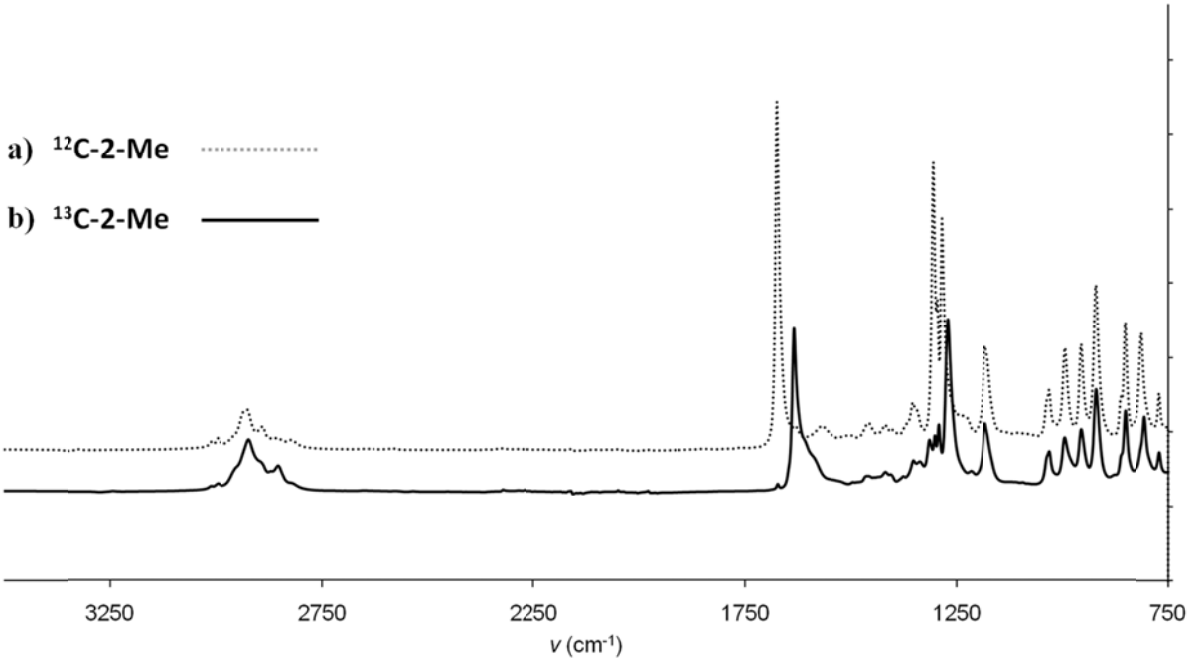
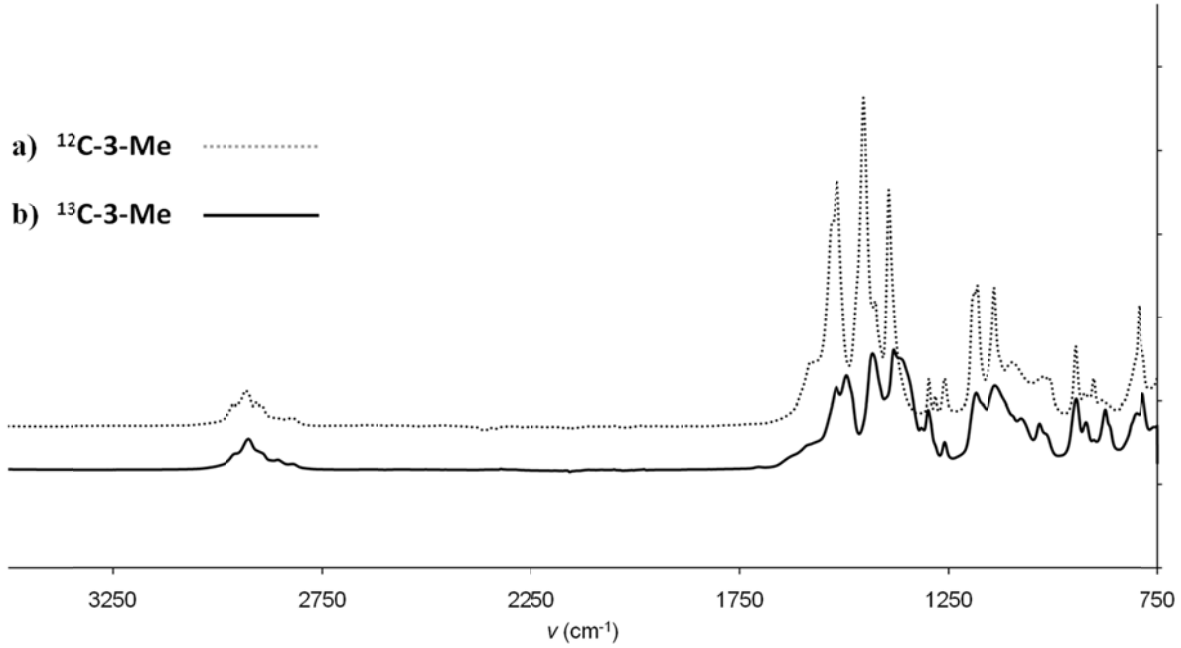


Fig. S18- Infared spectra of **3-Me** and **^{13}C-3-Me**



5. Crystallographic data for 1-Ph

A white bloc crystal having approximate dimensions of 0.20 x 0.20 x 0.10 mm was mounted on a glass fiber using Paratone N hydrocarbon oil. Measurements were made at 200(2) K on a Bruker APEX II area detector diffractometer equipped with graphite monochromated MoKα radiation. Frames corresponding to an arbitrary hemisphere of data were collected using ω scans of 0.5º counted for a total of 60 seconds per frame. An orientation matrix corresponding to cell constants listed in Table S1 was obtained from a least-squares refinement using the measured positions of 4800 centered reflections in the range $2.29º < \theta < 22.14º$. The program used for retrieving cell parameters and data collection was APEX 2.[S3] Data were integrated using the program SAINT.[S4] The data were corrected for Lorentz and polarization effects. The structure was solved and refined using SHELXS-97 and SHELXL-97.[S5] All non-H atoms were refined anisotropically.

The hydrogen atoms were placed at idealized positions. Crystallographic data have been deposited with CCDC (CCDC No. 826175). These data can be obtained upon request from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK, e-mail: deposit@ccdc.cam.ac.uk, or via the Internet at www.ccdc.cam.ac.uk.

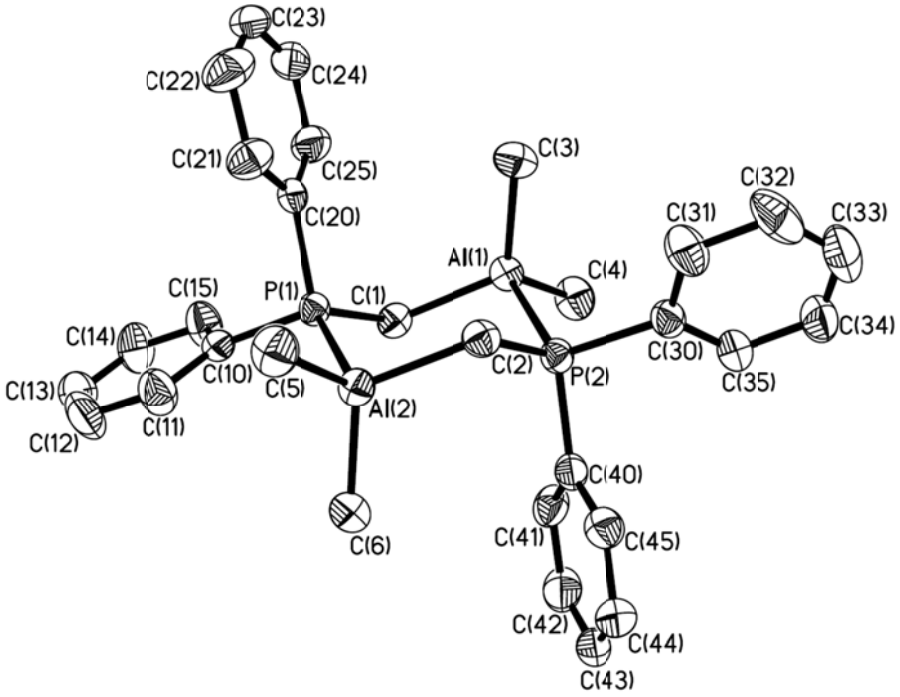


Figure S19- ORTEP drawing of $(Ph_2PCH_2AlMe_2)_2$, **1-Ph**, with anisotropic atomic displacement ellipsoids shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: P1-Al2 2.5183(9), P2-Al1 2.4502(9), P1-C1 1.790(2), Al1-C1 2.021(2), Al2-C2 2.012(2), Al1-C3 1.967(2), Al1-C4 1.976(3), Al2-C5 1.970(3), Al2-C6 1.958(3), P2-Al2 1.792(2), P1-C20 1.822(2), P1-C10 1.830(2), P2-C30 1.825(2), P2-C40 1.817(2), P1-C1-Al1 118.35(12), P2-C2-Al2 117.38(11), C1-P1-Al2 109.76(8), C1-Al1-P2 101.40(7), C2-P2-Al1 108.56(8), C2-Al2-P1 102.29(7), C3-Al1-C4 117.97(11), C5-Al2-C6 114.51(12), C10-P1-C20 100.37(11), C30-P2-C40 102.44(11).

Table S1. Crystal data and structure refinement for compound **1-Ph**.

formula	$C_{30}H_{36}Al_2P_2$
fw	512.49
crystal system	orthorhombic
space group	P2(1)2(1)2(1)
a (Å)	10.7293(7)
b (Å)	15.2840(10)
c (Å)	17.7595(12)
α,*β*,*γ* (deg)	90, 90, 90
V (Å³)	2912.3(3)
Z	4
wavelength (Å)	0.71073
D_{calc} (Mg/m^3)	1.169
F_{000}	1088
θ range for data collection	1.76 to 28.30°.
Index ranges	-14<=h<=14, -20<=k<=20, -23<=l<=23
Reflections collected	36086
Independent reflections	7123 [R(int) = 0.0645]
Observed Reflections	5213 [I>2θ(I)]
Completeness to θ = 28.30°	99.4 %
Absorption correction	Integration
Max. and min. transmission	0.9778 and 0.9562
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7123 / 0 / 311
Goodness-of-fit on F^2	1.020
Final R indices [I>2θ (I)]	R1 = 0.0418, wR2 = 0.0824
R indices (all data)	R1 = 0.0735, wR2 = 0.0941
Absorption coefficient	0.226 mm^{-1}
Largest diff. peak and hole	0.258 and -0.231 e.$Å^{-3}$

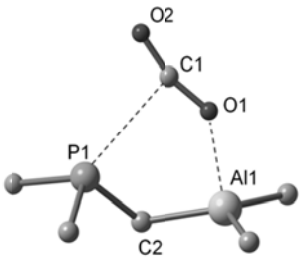
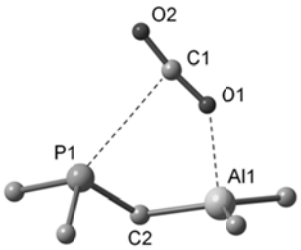
6. Computational details

The density functional theory calculations were carried out with the B3LYP hybrid functional as implemented in the G03 program.[S6] B3LYP is Becke's three parameter functionals (B3)[S7] with the non-local correlation provided by the LYP expression[S8] and VWN functional III for local correlation.[S9] The 6-31g(d,p) basis set was used for all atoms (a single set of first polarization functions were added to each atom).[S10] The geometry optimizations were performed without symmetry constraints.[S11] Vibrational analyses were performed to confirm the optimized stationary points as true minima on the potential energy surface or as transition states, and to obtain the zero-point energy and thermodynamic data. The free Gibbs energies, G, were calculated for T = 298.15 K. For every transition state, the reaction path in both directions was followed using the intrinsic reaction coordinate (IRC).[S12]

Table S2. Energies and δ ^{31}P obtained using DFT.

	E (kcal/mol)	H (kcal/mol)	G (kcal/mol)	δ ^{31}P	
				DFT-GIAO	Experimental (benzene-d_6)
1-Me + CO_2	0	0	0	– 39.8	– 39.0
2-Me	– 4.5	– 3.1	– 1.6	0.6	16.9
3-Me(C)	– 40.0	– 36.5	– 30.2	– 41.0	– 44.0
3-Me(D)	– 25.7	– 23.0	– 22.3	– 24.5	
3-Me(F)	– 16.7	– 14.2	– 12.7	– 40.2	
4-Me	– 0.5	0.9	10.7	31.5	37.5
1-Ph + CO_2	0	0	0		
2-Ph	– 6.7	– 5.0	– 4.5		
3-Ph(C)	– 40.6	– 37.3	– 31.1		
3-Ph(D)	– 26.4	– 23.8	– 24.0		
3-Ph(F)	– 17.6	– 15.1	– 13.6		
4-Ph	0.4	2.1	14.1		

Table S3. Important bond length (Å) and angles (°) in **TS1** and **Int1**.

	TS1	Int1
		
P1-C1	2.896	3.147
Al1-O1	2.178	2.283
C1-O1	1.191	1.180
C1-O2	1.164	1.161
O1-C1-O2	164.40	173.27
P1-C2-Al1	112.62	114.72
ΣP_α	308.17	303.86
ΣAl_α	355.24	356.87

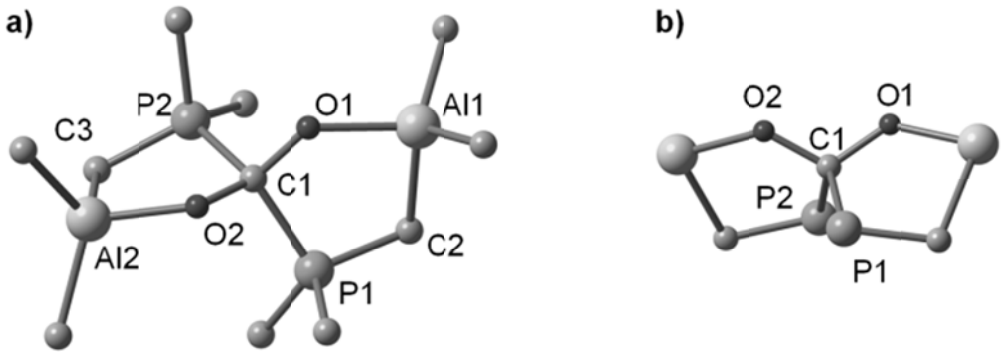
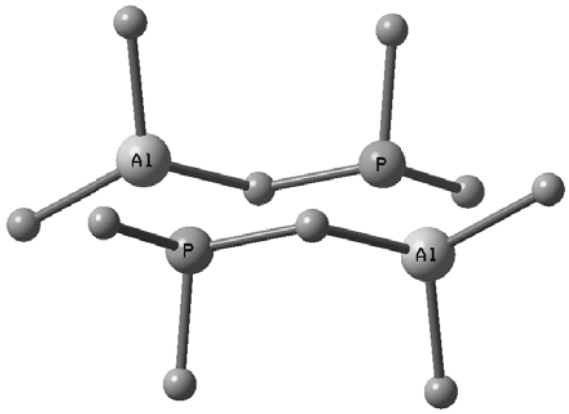


Fig S20. B3LYP/6-31g(d,p) optimized structure of a) **4-Me**; b) sideview of **4-Me**. Hydrogen atoms and methyl groups (b) are omitted for clarity.

1-Me



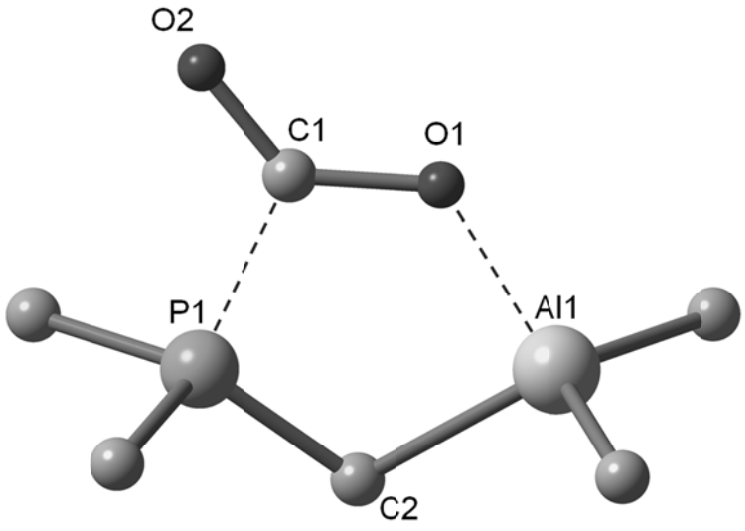
E(RB+HF-LYP) -1565.65878465 # im. Freq. = 0

Sum of electronic and thermal free energies -1565.361671

P	0.86297300	0.68541600	-1.63672600
C	0.36811700	1.92509700	-0.40245700
H	0.94918900	2.84500400	-0.56397700
H	-0.68019400	2.17820900	-0.61242100
Al	0.45487500	1.43549700	1.58001500
P	-0.86589200	-0.68278300	1.65685200
C	-0.37172700	-1.92309700	0.42295000
Al	-0.45644600	-1.43370800	-1.55965900
C	0.75398700	1.47791500	-3.30766500
H	1.33523600	2.40498600	-3.33818400
H	1.12970300	0.79505100	-4.07554800
H	-0.29024300	1.70846600	-3.53397000
C	2.68510100	0.47014200	-1.43486400
H	3.06251300	-0.21156900	-2.20156000
H	3.20036800	1.43155200	-1.52581300
H	2.90557500	0.04990100	-0.45189300

C	0.57464400	-2.74320300	-2.65133000
H	0.06203100	-3.71489600	-2.67331400
H	0.68343200	-2.43227000	-3.69859700
H	1.58507300	-2.93580800	-2.26812300
C	-2.24305800	-0.87759800	-2.25944700
H	-2.22381300	-0.75892600	-3.35081000
H	-3.00602000	-1.63963300	-2.04863300
H	-2.62811200	0.06646800	-1.85177400
C	-0.57485300	2.74525900	2.67263100
H	-0.68445200	2.43362800	3.71960500
H	-0.06103800	3.71629400	2.69561000
H	-1.58489000	2.93943700	2.28918100
C	2.24168900	0.87809600	2.27838400
H	3.00543700	1.63890100	2.06598100
H	2.22334200	0.76070900	3.36990000
H	2.62506800	-0.06693700	1.87138500
H	0.67599600	-2.17780000	0.63389500
H	-0.95438500	-2.84209600	0.58393600
C	-2.68774200	-0.46572600	1.45414200
H	-3.20400200	-1.42665000	1.54463600
H	-3.06481600	0.21619300	2.22081700
H	-2.90735300	-0.04505900	0.47115600
C	-0.75854100	-1.47517800	3.32795400
H	-1.13391100	-0.79177500	4.09552400
H	-1.34078500	-2.40162600	3.35833100
H	0.28532800	-1.70679600	3.55484000

2-Me



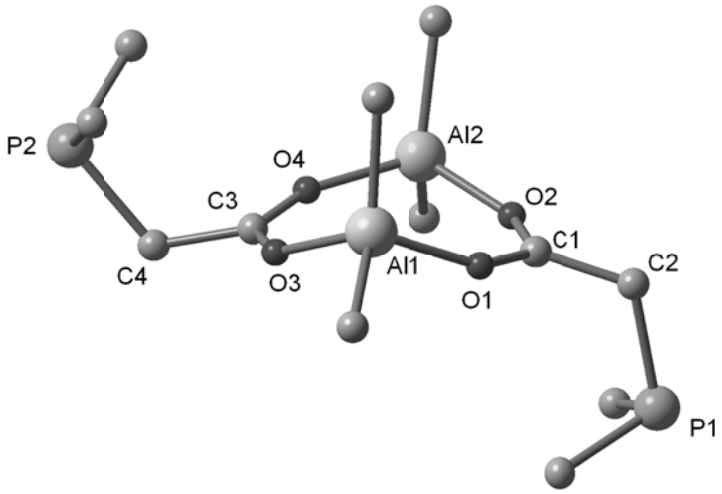
Selected bond lengths [Å] and angles [°]: P1-C1 1.907, C1-O1 1.288, C1-O2 1.216, O1-Al1 1.902, Al1-C2 2.110, P1-C2 1.771, O1-C1-O2 130.76, P1-C1-O2 118.08, C1-P1-C2 105.68, O1-Al1-C2 93.06.

E(RB+HF-LYP) -971.41463773 # im. Freq. = 0

Sum of electronic and thermal free energies -971.267721

Al	1.73071500	0.05071500	0.09462700
C	2.40496200	1.53298100	-1.03496000
C	2.99025400	-1.11510200	1.07385000
C	0.15848600	0.68155800	1.35315500
P	-1.27791700	0.29016300	0.39490100
C	-2.73131400	-0.43880000	1.22874900
C	-1.85951000	1.73298900	-0.56061900
C	-0.70241500	-0.98723300	-0.89844800
O	0.58289600	-1.03234400	-0.96658300
O	-1.55224600	-1.58970600	-1.52540800
H	2.97637700	2.26195400	-0.44455100
H	3.08214600	1.16768400	-1.81724500
H	1.61578700	2.09832100	-1.54970600
H	2.48909800	-1.93125300	1.61000200
H	3.72196200	-1.58212300	0.40294700
H	3.56550900	-0.55109000	1.82031700
H	0.19024200	0.05884400	2.25316100
H	0.18413900	1.73548800	1.64074800
H	-3.37949300	-0.87585300	0.46474400
H	-2.39851200	-1.23209700	1.90268100
H	-3.27405800	0.31594300	1.80296400
H	-1.00685500	2.18628300	-1.07165500
H	-2.58805900	1.40182300	-1.30446200
H	-2.31680700	2.47238800	0.10194000

3-Me(C)



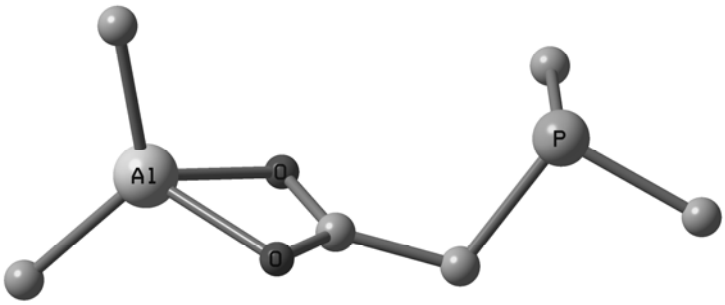
Selected bond lengths [Å] and angles [°]: C1-O1 1.270; C1-O2 1.269; O1-Al1 1.866; O2-Al2 1.866; C3-O3 1.272; C3-O4 1.267; O3-Al1 1.873; O4-Al2 1.859; C1-C2 1.497; C2-P1 1.903; C3-C4 1.497; C4-P2 1.903; O1-C1-O2 124.37; O3-C3-O4 124.13; O1-Al1-O3 105.04; O2-Al2-O4 106.18; C1-O1-Al1 147.67; C1-O2-Al2 148.64; C3-O3-Al1 139.82; C3-O4-Al2 156.46.

E(RB+HF-LYP) -1942.94268966 # im. Freq. = 0

Sum of electronic and thermal free energies -1942.626856

Al	0.46250800	0.39160900	0.76445800
C	-0.11427900	-1.44592000	0.36674200
C	1.83144700	1.33809000	-0.28592800
O	-1.04753000	1.48645700	0.70986600
O	1.07231100	0.43734100	2.52018100
C	-2.01800600	2.02565100	1.32473500
C	1.05957100	0.75649100	3.74666600
O	0.01619100	1.11368900	4.38022200
O	-2.17659400	1.99128100	2.58437400
Al	-1.84762300	1.10182200	4.19092000
C	-2.45829900	-0.76338100	4.00223700
C	-2.50658300	2.30417300	5.59708000
C	2.34278800	0.66671500	4.51166900
C	-3.00772100	2.81051700	0.52124700
P	2.70706400	-1.02422200	5.30488800
P	-2.56930000	4.64200500	0.25016300
C	2.49714500	-2.17661800	3.85747000
C	1.12721400	-1.35398800	6.23471800
C	-2.10330800	5.17803400	1.97240500
C	-0.88396000	4.51018700	-0.53028600
H	-0.46626400	-1.53654400	-0.66869000
H	0.70980900	-2.16161000	0.48002400
H	-0.93086300	-1.79364600	1.01069100
H	2.07659000	2.32733300	0.12094500
H	2.77101700	0.77219000	-0.32304500
H	1.51523100	1.49146200	-1.32524600
H	-1.92680100	-1.33002500	3.22839400
H	-2.34168900	-1.31917400	4.94165100
H	-3.52557700	-0.80720800	3.74967400
H	-2.29037000	1.91755300	6.60090300
H	-2.05501100	3.30223500	5.53840200
H	-3.59364500	2.44226400	5.54045300
H	3.18440700	0.87805300	3.84821500
H	2.33350100	1.38887400	5.33092500
H	-3.10722600	2.37273800	-0.47463200
H	-3.97765300	2.79965900	1.02279600
H	1.53221000	-2.08685600	3.35100700
H	3.29416600	-1.99670900	3.13047500
H	2.60879600	-3.20126700	4.22536700
H	0.23054300	-1.33336600	5.60948000
H	1.20986500	-2.34205900	6.69794800
H	1.01542600	-0.61921400	7.03691700
H	-1.76913800	6.21891500	1.92217900
H	-2.98370300	5.14034800	2.61951500
H	-1.31144900	4.57489300	2.42588700
H	-0.97775900	4.07299300	-1.52830700
H	-0.48568100	5.52283200	-0.64750500
H	-0.17266700	3.91294900	0.04632800

3-Me(D)

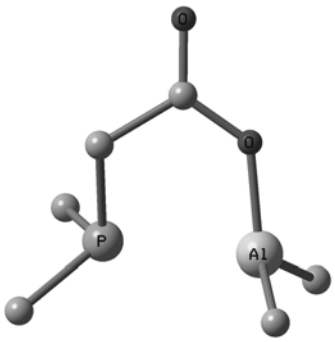


E(RB+HF-LYP) -971.44832982 # im. Freq. = 0

Sum of electronic and thermal free energies -971.30083

Al	2.37647700	0.10711700	-0.04619400
O	0.99935000	-0.85139400	-1.02769600
C	0.20560700	-0.62203700	-0.04881500
O	0.69746500	0.03943900	0.93709600
C	-1.21907100	-1.06268300	-0.06184700
P	-2.38578000	0.40004800	-0.41043800
C	2.73702700	1.88561700	-0.78854600
C	3.73088000	-1.09500100	0.70746400
C	-3.98043700	-0.56679400	-0.42694400
C	-2.47061700	1.13228000	1.29956600
H	-1.35563200	-1.79685700	-0.85829500
H	-1.46929700	-1.50887500	0.90604600
H	1.82983000	2.37979800	-1.15373300
H	3.19052700	2.54897500	-0.04146800
H	3.43905200	1.83504300	-1.63009600
H	4.49755000	-1.35283000	-0.03375400
H	4.25530100	-0.63044200	1.55182900
H	3.30352000	-2.03642800	1.07089600
H	-4.81664800	0.13838300	-0.45456900
H	-4.03243200	-1.17915400	-1.33175200
H	-4.09666500	-1.21284300	0.45000600
H	-2.79472700	0.40723200	2.05415500
H	-1.48249000	1.50866400	1.57457800
H	-3.17024200	1.97344300	1.29278000

3-Me(F)

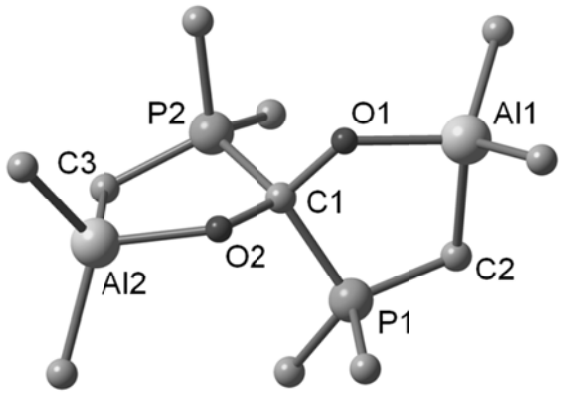


E(RB+HF-LYP) -971.43408824 # im. Freq. = 0

Sum of electronic and thermal free energies -971.285487

P	0.98058900	-0.76141500	0.02311100
C	1.90161400	-1.95198700	-1.04325500
H	2.97049000	-1.72203600	-1.07372900
H	1.76658100	-2.96624200	-0.65761200
H	1.49807600	-1.91653700	-2.05826700
C	1.83721600	-0.84417700	1.65423700
H	1.66116300	-1.81933000	2.11565100
H	2.91415100	-0.68434600	1.54822300
H	1.42635700	-0.07493600	2.31311600
C	1.36727100	0.92788000	-0.62371700
H	2.37070100	1.27981100	-0.37273400
H	1.29132600	0.88620400	-1.71752700
C	0.31776500	1.95651200	-0.12459400
O	0.62381700	3.12102900	0.01008300
O	-0.88609600	1.45764900	0.10145500
Al	-1.49794200	-0.25312000	0.01458800
C	-2.17269600	-0.78191700	-1.76286800
H	-2.29219700	-1.86919000	-1.85090300
H	-3.16206400	-0.34217300	-1.94368900
H	-1.53257800	-0.45565000	-2.59165600
C	-2.33337400	-0.85626800	1.69192900
H	-3.33939800	-0.43127900	1.79984600
H	-2.44780100	-1.94694600	1.72817000
H	-1.76893700	-0.55525400	2.58210700

4-Me



Selected bond lengths [Å] and angles [°]: C1-O1 1.353; C1-O2 1.353; O1-Al1 1.855; O2-Al2 1.854; P1-C1 1.945; P2-C1 1.943; P1-C2 1.772; C2-Al1 2.109; P2-C3 1.773; C3-Al2 2.110; O1-C1-O2 116.63; P1-C1-P2 116.24; P1-C1-O1 103.84; C1-O1-Al1 126.65; O1-Al1-C2 93.295; Al1-C2-P1 101.38; C2-P1-C1 105.80; P2-C1-O2 103.81; C1-O2-Al2 126.45; O2-Al2-C3 93.391; Al2-C3-P2 101.40; C3-P2-C1 105.86.

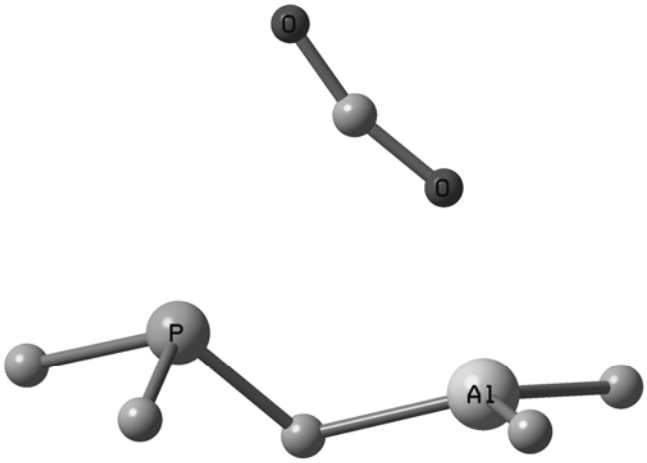
E(RB+HF-LYP) -1754.23763833 # im. Freq. = 0

Sum of electronic and thermal free energies -1753.929095

O	-0.62622300	0.43584900	1.38331800
Al	-2.36806100	0.50013900	2.01622800
C	-1.92113300	1.96980900	3.46261800
P	-0.15132600	1.88382500	3.51406000
C	0.39933500	1.23034000	1.76909100
P	0.68384000	2.57828300	0.39654500
C	2.37721000	3.07699700	0.55373900
Al	3.24654100	1.34270600	1.38177300
O	1.60961400	0.63882200	1.89767700
C	4.36348800	1.80219200	2.96644300
C	4.10687100	0.19146200	0.01327900
C	-0.58994800	3.90218300	0.37146800
C	0.46031200	1.63503700	-1.14551000
C	0.75924400	3.38165400	4.06442300
C	0.36994400	0.54108500	4.62884400
C	-3.61506200	1.21721900	0.63679000
C	-2.88162600	-1.23683500	2.82558500
H	-2.25193300	2.95301500	3.11256000
H	-2.35790600	1.77191500	4.44536600
H	2.79720700	3.37029800	-0.41238500
H	2.47100200	3.91171400	1.25631000
H	3.92814400	2.53368100	3.66160300
H	4.60670400	0.91308000	3.56375400
H	5.32576000	2.22530100	2.64636000
H	3.47142400	-0.03059700	-0.85440300
H	5.02699300	0.64531400	-0.37993500
H	4.39758600	-0.77939900	0.43552000
H	-1.58859000	3.45804000	0.38085700
H	-0.47629000	4.56005200	1.23642400
H	-0.47164100	4.50254400	-0.53489400
H	0.58385400	2.29271600	-2.00970200

H	1.20896100	0.84157500	-1.17927600
H	-0.53263300	1.18301900	-1.14526700
H	0.53896200	3.57691200	5.11764800
H	1.83438900	3.22396900	3.94507700
H	0.45391800	4.25448800	3.48203900
H	-0.15450800	-0.37269300	4.34372600
H	1.44305500	0.38097300	4.51445800
H	0.12673400	0.79618300	5.66343600
H	-3.40152100	2.23088000	0.26996200
H	-3.65269300	0.56883600	-0.24915700
H	-4.64014200	1.24970600	1.03153600
H	-2.18333700	-1.59962800	3.59135000
H	-3.87134900	-1.18936300	3.30029100
H	-2.94092300	-2.02780100	2.06650500

TS1-Me



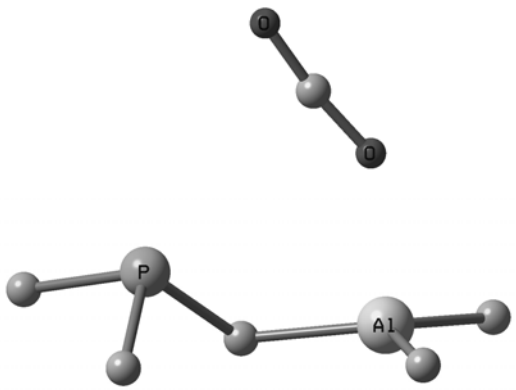
E(RB+HF-LYP) -971.38487824 # im. Freq. = 1

Sum of electronic and thermal free energies -971.242044

Al	1.60317100	-0.60263600	-0.10848800
C	2.04002500	-0.97445400	1.78430300
C	3.06043600	-0.42059200	-1.42819700
C	-0.18884600	-1.15229100	-0.83214600
P	-1.57327400	-0.17940900	-0.10802600
C	-3.06528200	-0.61265400	-1.13420900
C	-1.96051700	-1.11669600	1.44954900
C	0.08083900	2.18162000	0.17025600
O	1.04933000	1.49578700	0.07459500
O	-0.64944300	3.08058500	0.29052100
H	2.18790300	-2.05109800	1.94522900
H	2.97238200	-0.48448700	2.09044300
H	1.26560100	-0.65967300	2.49474900
H	2.73040100	0.02926600	-2.37262800
H	3.89397000	0.18500000	-1.05231900
H	3.48070400	-1.40335000	-1.68241100

H	-0.16635200	-0.92317800	-1.90705000
H	-0.37673400	-2.23137500	-0.74130700
H	-3.96204500	-0.16079500	-0.69879000
H	-2.94179600	-0.21228900	-2.14439600
H	-3.20879500	-1.69681500	-1.20051900
H	-1.11798300	-1.05302900	2.14262700
H	-2.83670700	-0.67985200	1.93743500
H	-2.16167400	-2.17349500	1.24140500

INT1-Me



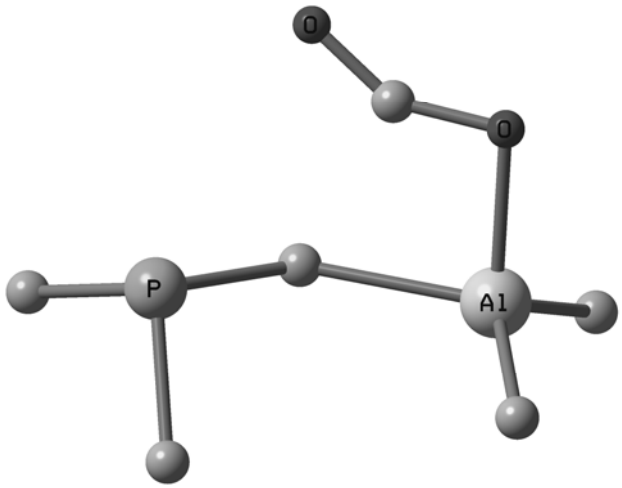
E(RB+HF-LYP) -971.38528462 # im. Freq. = 0

Sum of electronic and thermal free energies -971.244193

Al	1.74918300	-0.76970300	-0.15586400
C	2.10534400	-0.99245200	1.77675300
C	3.24734600	-0.87416600	-1.43695900
C	-0.08894900	-1.05222600	-0.88807500
P	-1.40997000	-0.04171000	-0.07499600
C	-2.92562500	-0.42705300	-1.09280200
C	-1.79390600	-1.07023400	1.42973800
C	0.76513400	2.36249900	0.09408700
O	1.53955400	1.50334800	-0.13989100
O	0.10955300	3.29284000	0.32173200
H	2.06642800	-2.05363700	2.05877400
H	3.10525400	-0.63539000	2.05123700
H	1.38805100	-0.47522500	2.42567500
H	3.01245300	-0.42225200	-2.40815400
H	4.15609700	-0.38957000	-1.06024900
H	3.51418900	-1.92082100	-1.63826700
H	-0.04790000	-0.73321300	-1.93972900
H	-0.36614800	-2.11727400	-0.89935700
H	-3.81220100	0.01274200	-0.62466400
H	-2.81866400	0.01345800	-2.08843800
H	-3.08067900	-1.50655200	-1.20174800
H	-0.94455200	-1.06279800	2.11761700
H	-2.65666000	-0.64818300	1.95395700

H	-2.01883300	-2.10934800	1.16298600

TS2-Me

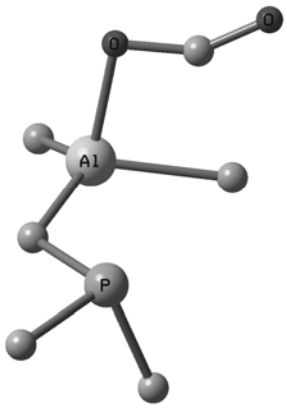


E(RB+HF-LYP) -971.35595152 # im. Freq. = 1

Sum of electronic and thermal free energies -971.212389

Al	-1.60176200	-0.46677700	0.14005500
C	-1.59511300	-1.89167500	-1.20924200
C	-2.72602700	-0.47990800	1.74976100
C	0.35609500	0.23040900	0.65025600
P	1.94167300	0.02929500	-0.33808700
C	3.19287400	0.32292900	1.01759800
C	2.04844700	-1.83232100	-0.42178500
C	-0.75506900	1.68943700	-0.52910600
O	-1.87514500	1.22722900	-0.77573200
O	-0.00438600	2.58595900	-0.62662900
H	-1.24527500	-2.84976100	-0.80656200
H	-2.61640800	-2.06098000	-1.57429700
H	-0.97917200	-1.65838700	-2.08488400
H	-2.57679300	0.39931900	2.38731500
H	-3.79037200	-0.50594000	1.48402900
H	-2.53757600	-1.36387800	2.37196500
H	0.47949200	1.04641600	1.36737900
H	0.24755200	-0.66287300	1.30350600
H	4.19356000	0.09139800	0.63873800
H	3.18094600	1.38017000	1.29841500
H	3.00592200	-0.28368600	1.91088200
H	1.28223000	-2.22331000	-1.09545500
H	3.02396100	-2.10703000	-0.83484800
H	1.93873900	-2.31152000	0.55840400

TS-Al-CH_3

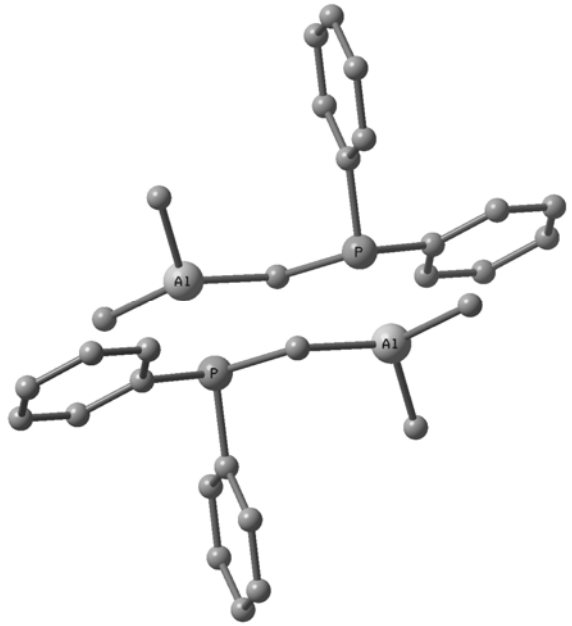


E(RB+HF-LYP) -971.36078479 # im. Freq. = 1

Sum of electronic and thermal free energies -971.216328

Al	-0.97308500	0.87281400	-0.04859800
C	-1.41233700	-0.51095800	1.48389400
C	-2.07508200	2.48371200	0.15503700
C	0.92575700	0.91842000	-0.58376800
P	1.97482800	-0.55907100	-0.15425900
C	3.59681400	-0.09021700	-0.95482800
C	2.41748900	-0.15297100	1.61436600
C	-2.11527100	-1.21052000	-0.43035500
O	-1.85692900	-0.35219700	-1.28054200
O	-2.58883900	-2.25183200	-0.17086700
H	-0.90015400	0.27029100	2.08175100
H	-2.40734700	-0.60127400	1.92128900
H	-0.84824700	-1.42874500	1.64883600
H	-2.08058500	3.07718400	-0.76765800
H	-3.11969000	2.25834600	0.39896700
H	-1.69291500	3.13938000	0.94735500
H	0.88813900	0.95882600	-1.68379600
H	1.41297000	1.85064700	-0.26173400
H	4.37352700	-0.80533800	-0.66491900
H	3.49120500	-0.13644300	-2.04286500
H	3.92274400	0.91873700	-0.67645700
H	1.54713000	-0.28005400	2.26431500
H	3.18973200	-0.84599300	1.96200000
H	2.79310600	0.87134900	1.72377500

1-Ph



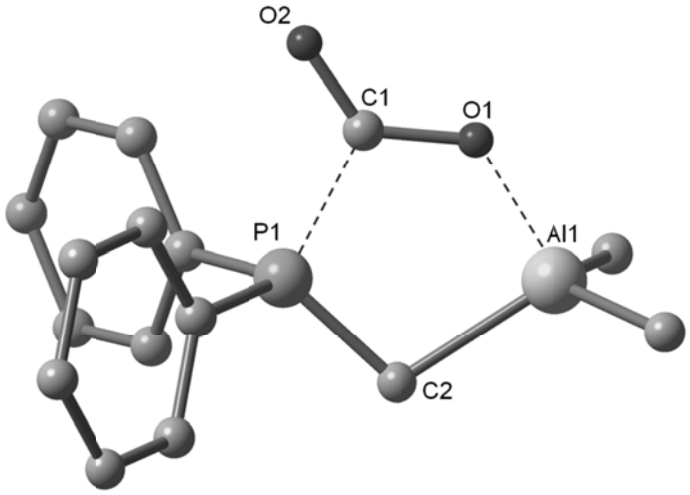
E(RB+HF-LYP) -2332.5969201 # im. Freq. = 0

Sum of electronic and thermal free energies -2332.107243

P	-2.01483200	0.05432400	-0.08570000
P	2.01518700	-0.05499900	0.08601500
Al	-0.63669400	0.94424900	1.83225900
Al	0.63690900	-0.94627600	-1.83103100
C	-1.07576700	0.16130800	-1.63846400
H	-0.77054900	1.20991300	-1.75057000
H	-1.72641400	-0.07229300	-2.49237300
C	1.07673800	-0.16208900	1.63911800
H	1.72744900	0.07258400	2.49269400
H	0.77246800	-1.21089500	1.75189900
C	-0.54391700	2.87600600	1.37377400
H	-1.53229700	3.34871300	1.43122100
H	-0.13707800	3.09383800	0.37990800
H	0.09889200	3.40486600	2.09067000
C	-1.55249400	0.48378300	3.54166300
H	-1.09379900	1.05364400	4.36206900
H	-1.49348000	-0.57262800	3.83205200
H	-2.61524700	0.75730300	3.53929100
C	1.55311300	-0.48769500	-3.54071900
H	2.61613500	-0.76015800	-3.53740900
H	1.49321300	0.56824500	-3.83264900
H	1.09540300	-1.05922900	-4.36050500
C	0.54302900	-2.87747700	-1.37041900
H	-0.10040300	-3.40676200	-2.08643300
H	0.13636300	-3.09379500	-0.37615000
H	1.53105500	-3.35096300	-1.42759700
C	3.57238000	-1.03457200	0.26771300
C	4.60992900	-0.86605600	-0.66431600
H	4.51482300	-0.12650200	-1.45446100

C	3.72182900	-1.99110700	1.28021000
H	2.93147600	-2.13676000	2.00930400
C	2.64278900	1.67288800	-0.03111400
C	3.78962000	3.57406300	0.95342000
H	4.30377200	4.02434100	1.79753400
C	2.47132200	2.40807100	-1.21144000
H	1.96787100	1.95735900	-2.06031600
C	3.31378300	2.26820600	1.04920900
H	3.47017100	1.70914300	1.96713900
C	-3.57110200	1.03534600	-0.26768400
C	-4.61082200	0.86474400	0.66153500
H	-4.51804100	0.12259900	1.44951400
C	-3.71761700	1.99515500	-1.27752500
H	-2.92562800	2.14242600	-2.00451400
C	-4.88096000	2.76321900	-1.36208300
H	-4.98114200	3.50105200	-2.15298000
C	-2.64398700	-1.67305300	0.03044300
C	-3.31414400	-2.26768400	-1.05077900
H	-3.46894200	-1.70838500	-1.96883100
C	-2.47455300	-2.40854800	1.21087100
H	-1.97177300	-1.95837400	2.06042100
C	-3.61123100	-4.30095800	0.22340700
H	-3.98312700	-5.31877200	0.29604700
C	-2.95653000	-3.71643800	1.30623400
H	-2.81788900	-4.27540800	2.22698400
C	-3.79114600	-3.57317400	-0.95575600
H	-4.30462500	-4.02291800	-1.80056600
C	-5.90938200	2.58359400	-0.43788800
H	-6.81382200	3.18109000	-0.50472500
C	-5.77126900	1.63131600	0.57473600
H	-6.56860600	1.48461400	1.29756700
C	3.60769000	4.30152700	-0.22563400
H	3.97869300	5.31962300	-0.29887800
C	2.95213300	3.71633400	-1.30757900
H	2.81193800	4.27506000	-2.22824300
C	5.91221000	-2.58046900	0.43761600
H	6.81724500	-3.17707900	0.50431200
C	4.88595600	-2.75801600	1.36461300
H	4.98843200	-3.49333100	2.15755800
C	5.77116200	-1.63144000	-0.57765600
H	6.56679400	-1.48640200	-1.30269700

2-Ph



Selected bond lengths [Å] and angles [°]: P1-C1 1.919, C1-O1 1.282, C1-O2 1.220, O1-Al1 1.899, Al1-C2 2.105, P1-C2 1.776, O1-C1-O2 129.57, P1-C1-O2 119.33, C1-P1-C2 106.03, O1-Al1-C2 93.40.

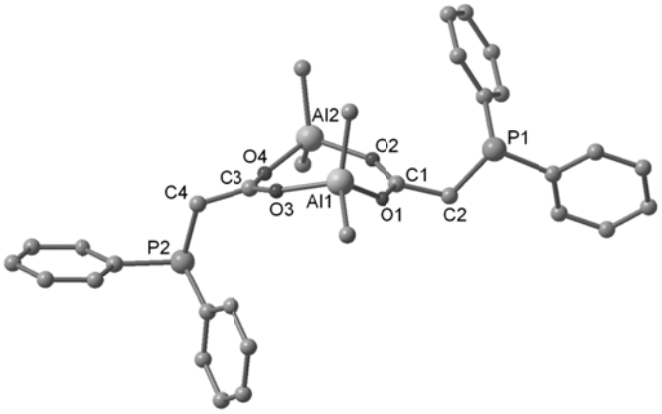
E(RB+HF-LYP) -1354.88716628 # im. Freq. = 0

Sum of electronic and thermal free energies -1354.645137

C	1.25578700	-0.39327900	-1.35404700
H	1.02549100	-1.31388900	-1.89549700
H	1.33233300	0.43984700	-2.05512800
P	0.03861500	-0.08058100	-0.09951200
O	2.18434800	-0.55671100	1.40677200
C	0.93788800	-0.31054200	1.58025500
O	0.30411200	-0.20172500	2.61729400
C	3.75132000	-2.48876400	-0.51374100
H	4.58158100	-2.69809900	0.17235700
H	2.99348800	-3.26296700	-0.33645000
H	4.13772700	-2.65051200	-1.52917900
C	4.24177800	0.91273400	-0.46107700
H	5.08357900	0.86618500	0.24119400
H	4.67843700	0.97668100	-1.46699200
H	3.73063100	1.86673800	-0.27724800
Al	3.04794000	-0.65464700	-0.28200400
C	-0.58168800	1.63665400	-0.13646700
C	-0.77922800	2.27529300	-1.37048100
C	-0.89322000	2.30948100	1.05547900
C	-1.28185600	3.57446800	-1.41146600
H	-0.53889000	1.76445500	-2.29768000
C	-1.39422700	3.61011500	1.00369200
H	-0.73624700	1.81987300	2.01051500
C	-1.58915100	4.24266800	-0.22481000
H	-1.42920700	4.06452700	-2.36895200
H	-1.62776800	4.12995400	1.92770800
H	-1.97701100	5.25636600	-0.25842200
C	-1.37540500	-1.23539700	-0.13834800
C	-1.81628000	-1.74172600	-1.37063300
C	-2.03972800	-1.59781700	1.04442500
C	-2.91108900	-2.60301400	-1.41973500
H	-1.30444500	-1.46992400	-2.28854200
C	-3.13260600	-2.46204700	0.98436800

H	-1.69044700	-1.21587500	1.99752000
C	-3.56956600	-2.96352200	-0.24278700
H	-3.24593400	-2.99428100	-2.37552000
H	-3.63984000	-2.74664600	1.90109500
H	-4.41998100	-3.63765500	-0.28233600

3-Ph(C)



Selected bond lengths [Å] and angles [°]: C1-O1 1.270; C1-O2 1.264; O1-Al1 1.867; O2-Al2 1.870; C3-O3 1.268; C3-O4 1.265; O3-Al1 1.876; O4-Al2 1.870; C1-C2 1.503; C2-P1 1.902; C3-C4 1.506; C4-P2 1.900; O1-C1-O2 124.77; O3-C3-O4 124.86; O1-Al1-O3 104.63; O2-Al2-O4 104.92; C1-O1-Al1 142.09; C1-O2-Al2 148.89; C3-O3-Al1 145.38; C3-O4-Al2 150.15.

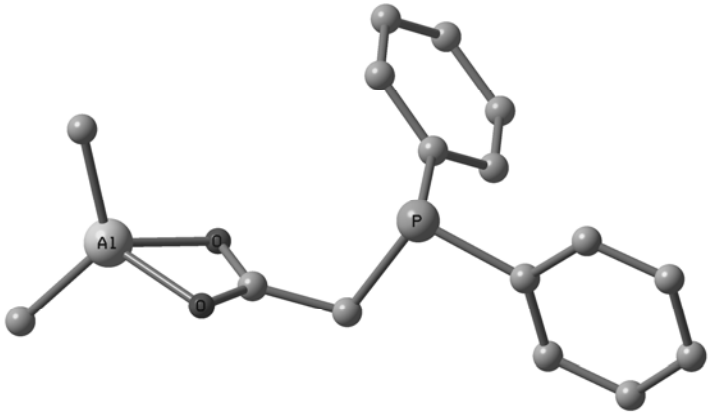
E(RB+HF-LYP) -2709.88233896 # im. Freq. = 0

Sum of electronic and thermal free energies -2709.375005

Al	0.02033600	2.29036000	-0.00611200
C	0.47597100	3.10353400	1.72628500
C	-0.27836000	3.32878700	-1.64675000
O	1.33832800	1.04420100	-0.45845300
O	-1.53362200	1.28166300	0.23263700
C	1.68941000	-0.16417500	-0.57925100
C	-2.13438200	0.29959300	0.75678100
O	-1.56727300	-0.74468500	1.19969300
O	1.08552000	-1.14980500	-0.05357000
Al	0.06946900	-1.62973200	1.43700200
C	0.95385500	-0.92034500	3.04714000
C	-0.36190700	-3.53089900	1.19037100
C	-3.63603700	0.36959300	0.84653100
C	2.92213700	-0.45647900	-1.38729200
P	-4.50012600	0.35974500	-0.84548700
P	4.43000000	-0.66369500	-0.24642300
H	1.48845900	3.52492600	1.71264500
H	-0.20774300	3.92710900	1.96881200
H	0.43463900	2.39692200	2.56360800
H	-0.54552600	2.69341000	-2.50009800
H	-1.09355200	4.05281600	-1.52478500
H	0.61308400	3.89842300	-1.93755500
H	1.89346900	-1.45393600	3.23991600

H	1.19862700	0.14608800	2.97643300
H	0.33211800	-1.04652000	3.94249400
H	-1.04778400	-3.90008200	1.96365000
H	-0.83678400	-3.72198200	0.22022900
H	0.53468600	-4.16129200	1.23652400
H	-4.01344600	-0.41448400	1.50490300
H	-3.90463800	1.34520300	1.26208700
H	2.78990700	-1.41634000	-1.89267700
H	3.08178500	0.34506800	-2.11056100
C	4.78143300	1.10736600	0.17214700
C	4.47984800	1.52727900	1.47621900
C	5.32165200	2.03650700	-0.73085000
C	4.69697500	2.85087600	1.86577800
H	4.07313900	0.81539300	2.18953200
C	5.54266200	3.35626400	-0.34064100
H	5.58002600	1.72544700	-1.73897300
C	5.22819900	3.76638000	0.95765000
H	4.45516300	3.16233500	2.87760300
H	5.96206600	4.06554500	-1.04853800
H	5.40190800	4.79501400	1.25999800
C	5.74543300	-1.04646300	-1.49174600
C	6.98717500	-1.44749500	-0.96764100
C	5.59281100	-1.00784300	-2.88566300
C	8.04807800	-1.77637100	-1.80864400
H	7.12083400	-1.50498500	0.10973600
C	6.65241000	-1.35070800	-3.72925000
H	4.64882000	-0.71163600	-3.33090500
C	7.88259600	-1.73088100	-3.19457700
H	9.00031600	-2.07834300	-1.38236700
H	6.51316300	-1.31696500	-4.80604600
H	8.70518500	-1.99608900	-3.85209600
C	-6.24038400	0.53299400	-0.22179800
C	-6.83809300	1.79765200	-0.33303400
C	-6.97551100	-0.51418200	0.35474000
C	-8.13452600	2.01663100	0.13602000
H	-6.28607300	2.61252600	-0.79444200
C	-8.27323800	-0.29718900	0.81698800
H	-6.53496000	-1.50370400	0.43311000
C	-8.85391700	0.96888500	0.71130600
H	-8.58372900	3.00129700	0.04404700
H	-8.83250300	-1.11685500	1.25920700
H	-9.86533500	1.13532800	1.07059400
C	-4.44124300	-1.42208900	-1.34129700
C	-4.97218900	-1.72601400	-2.60795300
C	-3.87708600	-2.46153300	-0.58675500
C	-4.96325700	-3.03141200	-3.09392300
H	-5.39481800	-0.93167900	-3.21853600
C	-3.85497700	-3.76858300	-1.08197800
H	-3.43361000	-2.26618200	0.38292100
C	-4.40186700	-4.05823100	-2.33110200
H	-5.38481700	-3.24579000	-4.07177900
H	-3.40579700	-4.55676600	-0.48488800
H	-4.38440400	-5.07491400	-2.71262900

3-Ph(D)



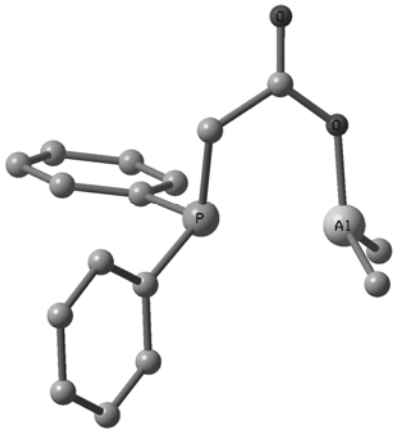
E(RB+HF-LYP) -1354.9185444 # im. Freq. = 0

Sum of electronic and thermal free energies -1354.676192

Al	2.36978000	0.21733400	-0.13376400
O	0.92491600	-0.69991900	-1.05342000
C	0.25580200	-0.63594600	0.03852700
O	0.83996800	-0.07105200	1.03088400
C	-1.13774700	-1.15845200	0.13863900
P	-2.38862800	0.23777600	-0.21225500
C	2.54662800	2.09184300	-0.68459000
C	3.87047400	-0.97350100	0.28797800
H	-1.28459800	-1.91749800	-0.63247500
H	-1.29495600	-1.58013500	1.13392200
H	1.58045500	2.55506000	-0.91455500
H	3.01987100	2.69762500	0.09830700
H	3.17294600	2.19123500	-1.57977200
H	4.54728800	-1.08736300	-0.56795400
H	4.47452300	-0.58058700	1.11532300
H	3.54206600	-1.97841900	0.57654300
C	-2.50926100	1.01801600	1.46447200
C	-1.77700700	2.19815000	1.66704700
C	-3.28050700	0.51228800	2.52198700
C	-1.79737100	2.84660400	2.90242800
H	-1.18877500	2.61198200	0.85264600
C	-3.30804200	1.16587800	3.75369600
H	-3.86992300	-0.38862600	2.38188800
C	-2.56430300	2.33187000	3.94760100
H	-1.22018300	3.75554800	3.04433600
H	-3.91224300	0.76515600	4.56276600
H	-2.58786100	2.83914900	4.90772300
C	-3.95138900	-0.74680600	-0.32814600
C	-5.02417700	-0.12474800	-0.98883700
C	-4.13525500	-2.04887900	0.16318900
C	-6.24883800	-0.77469900	-1.13689500
H	-4.89422400	0.87478800	-1.39558900
C	-5.35736700	-2.70513300	0.00440300
H	-3.32786800	-2.56401100	0.67398100
C	-6.41754400	-2.06874700	-0.64182000
H	-7.06644400	-0.27509500	-1.64820700
H	-5.47998200	-3.71388500	0.38829200

H	-7.36733700	-2.58085100	-0.76438500

3-Ph(F)



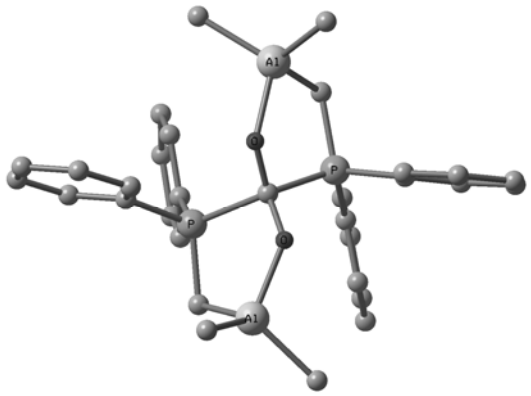
E(RB+HF-LYP) -1354.90450144 # im. Freq. = 0

Sum of electronic and thermal free energies -1354.659634

P	1.02236000	-0.73823200	0.10571600
C	1.24638500	1.00879800	-0.47888000
H	2.20262700	1.45027100	-0.19305300
H	1.18573500	0.99625300	-1.57387100
C	0.09425700	1.91510700	0.03005600
O	0.28735600	3.09824600	0.20340900
O	-1.06428200	1.30224400	0.20756600
Al	-1.50349300	-0.44948300	0.02573700
C	-2.00198100	-0.97888000	-1.80859500
H	-2.05608900	-2.06872500	-1.92286700
H	-2.99742300	-0.58694200	-2.05549200
H	-1.31823100	-0.60640900	-2.58065000
C	-2.44071500	-1.17801900	1.59971100
H	-3.52640500	-1.13872300	1.44269200
H	-2.19256600	-2.22938000	1.79212800
H	-2.23859800	-0.61672000	2.51908400
C	1.91339600	-0.84215500	1.70809500
C	1.17262400	-0.82420100	2.89852200
C	3.31408700	-0.91639600	1.77085800
C	1.82395000	-0.86329300	4.13265700
H	0.08904900	-0.78197700	2.86326400
C	3.95953300	-0.96027000	3.00478300
H	3.90003900	-0.94950000	0.85734100
C	3.21552500	-0.93120000	4.18706800
H	1.24119000	-0.84509900	5.04850100
H	5.04322400	-1.01814400	3.04417500
H	3.72131200	-0.96529900	5.14741400
C	1.94699700	-1.81533500	-1.05325300
C	1.63741000	-3.18526800	-1.06690800

C	2.93612800	-1.33252600	-1.92381000
C	2.30867300	-4.05363000	-1.92571200
H	0.86741400	-3.57405300	-0.40607800
C	3.60240500	-2.20396500	-2.78690600
H	3.19050000	-0.27738700	-1.93540400
C	3.29139700	-3.56390000	-2.78829300
H	2.05874700	-5.11022300	-1.92714300
H	4.36403700	-1.81771900	-3.45761500
H	3.80957900	-4.23952400	-3.46208400

4-Ph



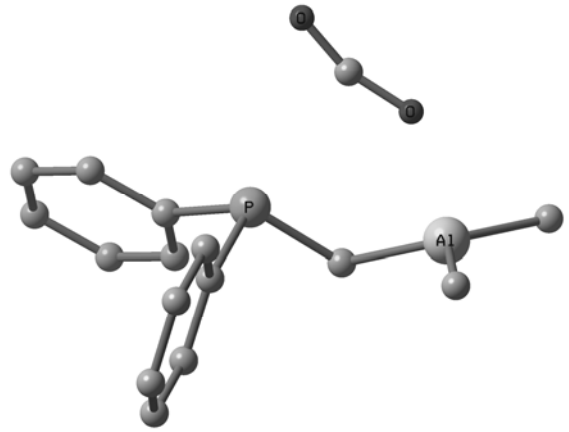
E(RB+HF-LYP) -2521.17433741 # im. Freq. = 0

Sum of electronic and thermal free energies -2520.669166

O	-0.73583600	0.41377200	1.25407600
Al	-2.40695700	0.20574500	2.04611500
C	-1.98755200	1.68760500	3.45634000
P	-0.20959600	1.78274000	3.49658500
C	0.34367300	1.08821100	1.65844800
P	0.77956500	2.51639600	0.36359900
C	2.51576200	2.81330800	0.60571200
Al	3.21174900	0.96296900	1.31468700
O	1.48806800	0.39486700	1.75003500
C	4.33769100	1.17232000	2.95168500
C	3.98917200	-0.19561900	-0.09493100
C	-3.85373400	0.78303400	0.80018600
C	-2.63653200	-1.62371600	2.78061300
H	-2.39809400	2.61172800	3.03593700
H	-2.39106500	1.52201300	4.45828700
H	2.98724500	3.14565300	-0.32241800
H	2.66847000	3.56004600	1.39110900
H	4.73947900	2.18710400	3.08092400
H	3.81437600	0.91253400	3.88132500
H	5.20852100	0.50592600	2.89924500
H	3.41192800	-0.23059300	-1.02616400
H	5.00157400	0.13881100	-0.36173100
H	4.09228300	-1.23213600	0.25390200
H	-4.03137600	1.86610400	0.76290300

H	-3.66454200	0.45737300	-0.23171600
H	-4.80988600	0.32768600	1.09155500
H	-1.88742800	-1.91524100	3.52594300
H	-3.61863200	-1.73319500	3.26149700
H	-2.60054300	-2.37864500	1.98347200
C	-0.30723000	3.98145800	0.44194300
C	-1.69148800	3.83306900	0.24555500
C	0.22241100	5.25518000	0.69205400
C	-2.52849000	4.94578200	0.31143800
H	-2.11290100	2.85606300	0.03434800
C	-0.62021400	6.36576100	0.74892800
H	1.29020900	5.37873400	0.83958200
C	-1.99458400	6.21244500	0.56195200
H	-3.59639700	4.82224200	0.15892000
H	-0.20096500	7.34948800	0.93725200
H	-2.64878400	7.07829700	0.60538300
C	0.51202900	1.78761700	-1.28934000
C	0.31348300	2.64193200	-2.38598200
C	0.56163300	0.39978200	-1.49158000
C	0.17081600	2.11507100	-3.66851600
H	0.26311500	3.71657600	-2.24140800
C	0.41490700	-0.11786200	-2.77865000
H	0.69709600	-0.26669500	-0.64970700
C	0.22086200	0.73434300	-3.86600900
H	0.01716000	2.78341400	-4.51041200
H	0.44902500	-1.19272600	-2.92688500
H	0.10571500	0.32409000	-4.86499000
C	0.45060600	3.41929200	3.99022600
C	-0.41775600	4.49856900	4.21028600
C	1.83474400	3.60746000	4.15313100
C	0.08769400	5.74542700	4.57971000
H	-1.48850100	4.36478600	4.09990800
C	2.33406700	4.85689500	4.51864000
H	2.52166300	2.78068600	4.00803500
C	1.46254600	5.92775500	4.73165500
H	-0.59540000	6.57158100	4.75263400
H	3.40444700	4.98937900	4.64439500
H	1.85426600	6.89831000	5.02166700
C	0.42452900	0.59869300	4.73463600
C	0.61134800	1.01842700	6.06212100
C	0.65644200	-0.74400600	4.39585100
C	1.02183300	0.10892700	7.03526700
H	0.44045500	2.05388400	6.33803100
C	1.06846800	-1.64652800	5.37684400
H	0.54035200	-1.07499300	3.37230000
C	1.25145400	-1.22478600	6.69369800
H	1.16353100	0.44430900	8.05830500
H	1.25101300	-2.68142700	5.10459900
H	1.57491300	-1.93192800	7.45186900

TS1-Ph



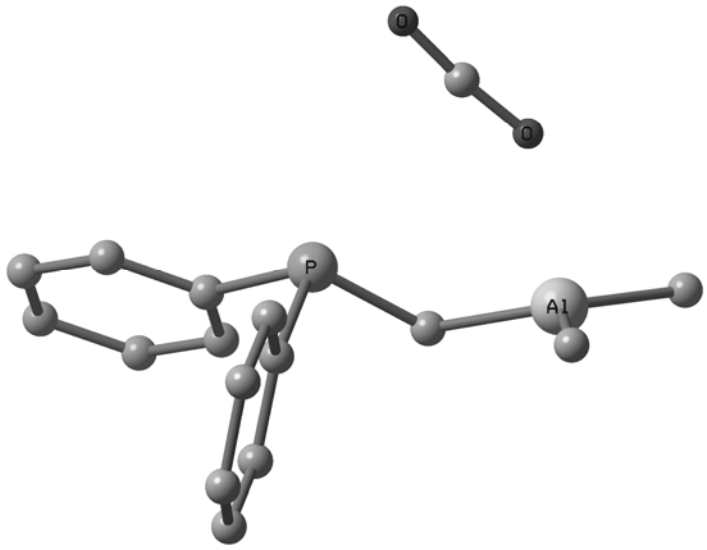
E(RB+HF-LYP) -1354.85785924 # im. Freq. = 1

Sum of electronic and thermal free energies -1354.618926

Al	-2.75415400	-0.91530600	-0.87260800
C	-3.65460200	0.83608400	-0.74687300
C	-3.75682200	-2.50696700	-1.47238600
C	-0.76334700	-0.99167900	-1.17955300
P	0.18038700	-0.37762500	0.26912100
C	-1.80019800	-1.22876300	2.12219400
O	-2.57527800	-1.39523100	1.23107100
O	-1.31436200	-1.17216900	3.18058000
H	-3.82864200	1.24722500	-1.75072200
H	-4.63936700	0.75913300	-0.26971200
H	-3.07879200	1.59073400	-0.19940000
H	-3.25181900	-3.44909100	-1.22588200
H	-4.76387900	-2.55522000	-1.04076700
H	-3.88642100	-2.49973000	-2.56329700
H	-0.52579800	-2.05889600	-1.28795100
H	-0.46327300	-0.49157800	-2.10916200
C	0.23570200	1.45691600	0.03235100
C	-0.31623100	2.28949300	1.01569100
C	0.81654600	2.04640700	-1.10195400
C	-0.30369200	3.67841800	0.86485700
H	-0.75393200	1.85023500	1.90811400
C	0.83145400	3.43163400	-1.25302300
H	1.26825100	1.41862600	-1.86502300
C	0.26854200	4.25058200	-0.27032600
H	-0.73765700	4.30946500	1.63500200
H	1.28402200	3.87405000	-2.13596300
H	0.28077200	5.33009500	-0.38936100
C	1.95003400	-0.85340400	0.01366800
C	2.86922200	-0.56956600	1.03806100
C	2.40586800	-1.51965100	-1.13227600
C	4.21025400	-0.92516100	0.91057200
H	2.53191800	-0.06599100	1.94058300
C	3.74902000	-1.88282800	-1.25649300
H	1.71200400	-1.75571900	-1.93297700
C	4.65407600	-1.58498200	-0.23825600

H	4.90839600	-0.69403800	1.71009000
H	4.08656600	-2.39752500	-2.15178900
H	5.69802300	-1.86840900	-0.33543800

INT1-Ph



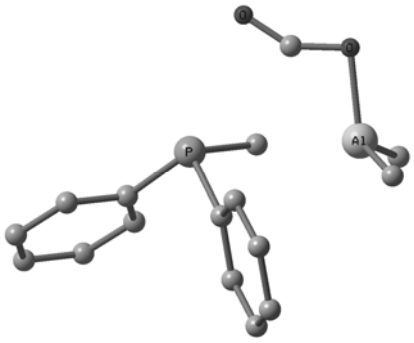
E(RB+HF-LYP) -1354.85862954 # im. Freq. = 0

Sum of electronic and thermal free energies -1354.622566

Al	1.76711800	-0.81388000	-0.13345100
C	2.09586800	-1.05321300	1.79661600
C	3.27896300	-0.86345000	-1.40125000
C	-0.04216200	-1.13288700	-0.93278500
P	-1.41371300	-0.14667500	-0.18709000
C	0.73486300	2.27707100	0.29149700
O	1.50825700	1.47375700	-0.09234600
O	0.06082000	3.14012900	0.67644900
H	2.29159300	-2.11228200	2.01441900
H	2.98200100	-0.50142400	2.13373100
H	1.25391900	-0.76066000	2.43300700
H	3.05755100	-0.36029900	-2.35024500
H	4.18624500	-0.40472500	-0.99039700
H	3.54156300	-1.90005200	-1.65359200
H	0.04438500	-0.81289700	-1.98073600
H	-0.27298200	-2.20761500	-0.94734000
C	-1.79060800	-1.07138400	1.37765500
C	-1.72125800	-0.38631300	2.59880400
C	-2.15121100	-2.42837200	1.38913800
C	-1.99146800	-1.04028100	3.80382500
H	-1.45807600	0.66834500	2.60477200
C	-2.42113100	-3.08335800	2.58946000
H	-2.23371000	-2.97165800	0.45177400
C	-2.33960300	-2.39027800	3.80037900
H	-1.93242500	-0.49424100	4.74105500

H	-2.69950600	-4.13355100	2.58190100
H	-2.55160200	-2.90116300	4.73522100
C	-2.91668700	-0.55304200	-1.19753500
C	-4.14186200	0.02310400	-0.81874400
C	-2.88423700	-1.35089400	-2.34918800
C	-5.30032700	-0.20787500	-1.55684500
H	-4.18817400	0.65474900	0.06510100
C	-4.04407000	-1.57573600	-3.09573900
H	-1.95113100	-1.80405800	-2.66833300
C	-5.25477600	-1.00835300	-2.70140600
H	-6.23866200	0.24116000	-1.24329900
H	-3.99844700	-2.19838700	-3.98512300
H	-6.15597000	-1.18372800	-3.28177000

TS2-Ph



E(RB+HF-LYP) -1354.8285447 # im. Freq. = 1

Sum of electronic and thermal free energies -1354.588427

Al	2.76749300	-0.71103500	0.69179900
C	3.27026300	1.17151200	0.51211700
C	3.20841400	-1.83430400	2.24182900
C	0.74381600	-1.19019200	0.11713500
P	-0.46620300	-0.29497400	-0.99035100
C	2.20431000	-1.95218200	-1.31839100
O	3.33327100	-1.65889700	-0.90975600
O	1.54592000	-2.49061000	-2.12576500
H	2.72117500	1.81178700	1.21165300
H	4.33850000	1.29563200	0.73230700
H	3.09351400	1.57317100	-0.49044900
H	2.81355000	-2.85431500	2.16670900
H	4.29553100	-1.92005700	2.36433800
H	2.82196800	-1.40726600	3.17584400
H	0.42652800	-2.23176000	0.22171500
H	0.64346000	-0.77647500	1.14276700
C	-0.26957800	1.45545800	-0.39533400
C	0.23151800	2.39865000	-1.30405900
C	-0.60545200	1.88327600	0.89934400
C	0.41248100	3.73129300	-0.92648700

H	0.47797000	2.08531300	-2.31516900
C	-0.42587800	3.21303100	1.27871100
H	-1.02878500	1.17745700	1.60926800
C	0.08672900	4.13944800	0.36644700
H	0.80363300	4.44824100	-1.64264900
H	-0.69269700	3.52954300	2.28325700
H	0.22313800	5.17569800	0.66203700
C	-2.10821500	-0.73230500	-0.23759700
C	-3.24815200	-0.32643100	-0.95354700
C	-2.29397700	-1.45784700	0.94796100
C	-4.52940600	-0.61615600	-0.48914300
H	-3.12760300	0.21906100	-1.88637400
C	-3.57802500	-1.75954400	1.40918100
H	-1.43780200	-1.79723800	1.52270600
C	-4.69855400	-1.33684400	0.69534800
H	-5.39601700	-0.28867300	-1.05643600
H	-3.69955400	-2.32482100	2.32909000
H	-5.69616100	-1.57235600	1.05433900

CO_2

E(RB+HF-LYP) -188.57802842 # im. Freq. = 0

Sum of electronic and thermal free energies -188.584397

C	2.10867100	-1.51485100	-0.02978200
O	0.91184200	-1.51485100	-0.02987900
O	3.30541800	-1.51485100	-0.02998700

7. References

S1. Karsch, H. H.; Appelt, A.; Köhler, F.; Müller, G. *Organometallics* **1985**, *4*, 231-238.

S2. Schore, N. E.; LaBelle, B. E. *J. Org. Chem.* **1981**, *46*, 2306-2310.

S3. Bruker (2005). APEX 2 Version 2.0.2. Bruker AXS Inc., Madison, Wisconsin, USA.

S4. Bruker (2003). SAINT Version 7.07a. Bruker AXS Inc., Madison, Wisconsin, USA.

S5. Sheldrick, G.M. (1997). SHELXS-97 and SHELXL-97. Programs for the refinement of crystal structures. University of Gottingen, Germany.

S6. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

S7. Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648-5652.

S8. a) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789; b) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200-206.

S9. Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys*. **1980**, *58*, 1200-1211.

S10. a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257-2261; b) Hariharan, P. C.; Pople, J. A. *Theo. Chim. Acta* **1973**, *28*, 213-221; c) Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; DeFrees, D. J.; Pople, J. A.; Gordon, M. S. *J. Chem. Phys.* **1982**, *77*, 3654-3665.

S11. a) Csaszar, P.; Pulay, P. *J. Mol. Struct.* **1984**, *114*, 31-34; b) Farkas, Ö. PhD (CsC) thesis, Eötvös Loránd University and Hungarian Academy of Sciences, Budapest, **1995**; c) Farkas, Ö.; Schlegel, H. B. *J. Chem Phys*. **1999**, *111*, 10806-10814.

S12. a) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154-2161; b) Gonzalez, C.; Schlegel, H. B. J. Phys. Chem. 1990, 94, 5523-5527.