Supporting Information for:

Ambiphilic molecules for trapping reactive intermediates: interrupted Nazarov of allenyl vinyl ketones with $Me_2PCH_2AlMe_2$

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Contents

1. Synthetic procedure

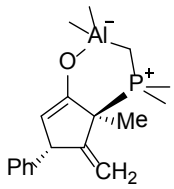
a. General experimental

Unless otherwise specified, manipulations were carried out under an atmosphere of dinitrogen, using standard glovebox and Schlenk techniques. Reactions were carried out 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. Compounds $(PMe_2CH_2AlMe_2)_2$ (**1**)[S1], (E)-4-methyl-1-phenylhexa-1,4,5-trien-3-one (**2**) and (E)- 1-(4-methoxyphenyl)- 4-methylhexa-1,4,5-trien-3-one (**2-OMe**)[S2] were prepared according to previously published procedures.

NMR spectra were recorded on a Agilent Technologies NMR spectrometer at 500 MHz (^{1}H), 125.758 MHz (^{13}C), 202.456 MHz (^{31}P), a Varian Inova NMR AS400 spectrometer, at 400.0 MHz (^{1}H), 100.580 MHz (^{13}C), 161.923 MHz (^{31}P), or 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 yields were determined using cyclohexane as an internal standard. 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), or multiplet (m). Chemical shifts are reported in ppm. Coupling constants are reported in Hz. gHMQC, gHSQC, NOESY 2D, gDQCOSY and ^{1}H{^{31}P} NMR experiments were performed in order to properly assign the spectra. High-resolution mass spectral analyses were performed with

an Agilent 6210 time of flight LC/MS using electrospray ionisation with acetonitrile containing 0.1 % trifluoroacetic acid as elution solvent.

b. Reactions with 2



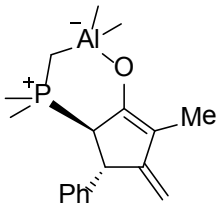
3

A 0.058 M solution of **2** (10.6 mg, 0.058 mmol) in 1 mL of dichloromethane-d_2 was chilled to – 35 °C and rapidly added to 7.6 mg (0.029 mmol) of $(PMe_2CH_2AlMe_2)_2$ (**1**). The bright yellow solution was immediately characterized by NMR spectroscopy at – 50 °C, which reveals complete conversion to **3**. **^{1}H NMR** (– 50°C, dichloromethane-d_2, **fig. S1**)**:** δ 7.42 (m, 2H, Ph), 7.32 (m, 3H, Ph), 6.86 (dd, 1H, $^3J_{H\text{-}H}$ = 15.6 Hz, $^4J_{H\text{-}P}$ = 5.4 Hz, HC=CO) 6.31 (dd, 1H, $^3J_{H\text{-}H}$ = 15.6 Hz, $^4J_{H\text{-}P}$ = 3.0 Hz, HCPh), 4.91 (m, 2H, =CH_2), 1.67 (ddd, 3H, $^5J_{H\text{-}H}$ = 3.0 Hz, $^5J_{H\text{-}H}$ = 3.0 Hz, $^3J_{H\text{-}P}$ = 1.0 Hz, C-Me), 1.64 (d, $^2J_{H\text{-}P}$ = 12.8 Hz, P-Me), 1.48 (d, $^2J_{H\text{-}P}$ = 12.7 Hz, P-Me), 0.27 (dd, $^2J_{H\text{-}H}$ =12.9 Hz, $^2J_{H\text{-}P}$ =12.4 Hz, P-C*H*-Al), 0.15 (dd, $^2J_{H\text{-}H}$ = 12.9 Hz, $^2J_{H\text{-}P}$ =13.2 Hz, P-C*H*-Al), – 0.86 (s, 3H, Al-Me), – 0.98 (s, 3H, Al-Me); **^{13}C{^{1}H} NMR** (– 50°C, dichloromethane-d_2, **fig. S3**)**:** δ 204.4 (d, $^2J_{C\text{-}P}$ = 6.1 Hz), 136.4 (d, $^4J_{C\text{-}P}$ = 3.7 Hz), 132.0 (d, $^3J_{C\text{-}P}$ = 9.5 Hz), 129.1 (d, $^3J_{C\text{-}P}$ = 4.0 Hz), 128.9 (s), 127.0 (d, $^5J_{C\text{-}P}$ = 1.7 Hz), 101.6 (d, $^2J_{C\text{-}P}$ = 4.3 Hz), 78.9 (d, $^1J_{C\text{-}P}$ = 65.9 Hz), 78.4 (d, $^3J_{C\text{-}P}$ = 2.0 Hz), 15.2 (d, $^2J_{C\text{-}P}$ = 3.6 Hz), 11.0 (d, $^1J_{C\text{-}P}$ = 46.9 Hz), 10.3 (d, $^1J_{C\text{-}P}$ = 41.4 Hz), – 1.3 (d, $^1J_{C\text{-}P}$ = 28.2 Hz), – 7.3 (s, br), – 7.6 (s, br); **^{31}P{^{1}H} NMR** (– 50 °C, dichloromethane-d_2)**:** δ 41.8.

Notes:

The evidence that best shows that the phosphorus atom is bonded to the **C**-CH_3 carbon is the doublet $^{13}C\{^1H\}$ resonance at δ 78.9 that exhibits large $^1J_{C\text{-}P}$ coupling (65.9 Hz) and does not correlate with any proton in the gHMQC spectrum (**fig. S4**). Coupling with ^{31}P was confirmed by selective decoupling of the ^{31}P resonance (**fig. S2**) and H-H coupling by gDQCOSY (**fig. S5**). A correlation between the C**H**(Ph) and P-C**H**$_3$ resonances in the 2D NOESY spectrum (**fig. S6**) confirms the relative stereochemistry of **3**.

Alternately, a solution containing 5.5 mg (0.030 mmol) of **2** and 1.6 µL of cyclohexane (0.015 mmol) (as internal standard) in 1 mL of benzene-d_6 was added to 4.0 mg (0.015 mmol) of **1**. This immediately gave a homogeneous yellow solution of **3** that gradually converts to **4**. **NMR yield:** 80 % (5 minutes after the addition) (20 % **4**). **^{1}H NMR** (benzene-d_6, **fig. S7**)**:** δ 7.34 (dd, 1H, $^3J_{H\text{-}H}$ = 15.5 Hz, $^4J_{H\text{-}P}$ = 5.5 Hz, HRC=CO), 7.31 (m, 2H, Ph), 7.05 (m, 3H, Ph), 6.11 (dd, 1H, $^3J_{H\text{-}H}$ = 15.5 Hz, $^4J_{H\text{-}P}$ = 3.2 Hz, CHPh), 4.45 (m, 2H, =CH_2), 1.87 (ddd, 3H, $^5J_{H\text{-}H}$ = 3.2 Hz, $^5J_{H\text{-}H}$ = 3.2 Hz, $^3J_{H\text{-}P}$ = 1.2 Hz, C-Me), 0.86 (d, $^2J_{H\text{-}P}$ = 12.8 Hz, P-Me), 0.72 (d, $^2J_{H\text{-}P}$ = 12.6 Hz, P-Me), 0.10 (dd, $^2J_{H\text{-}H}$ = $^2J_{H\text{-}P}$ =12.6 Hz, P-C*H*-Al), 0.00 (dd, $^2J_{H\text{-}H}$ = $^2J_{H\text{-}P}$ =12.6 Hz, P-C*H*-Al), – 0.05 (s, 3H, Al-Me), – 0.17 (s, 3H, Al-Me); **^{31}P{^{1}H} NMR** (benzene-d_6)**:** δ 39.0.

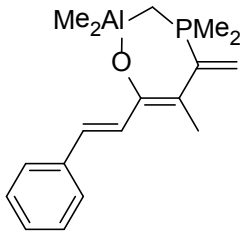


4

After leaving the previously described benzene-d_6 solution of **3** for 20 h at 23 °C, NMR spectroscopy reveals a complete conversion to compound **4**. **^{1}H NMR** (benzene-d_6, **fig. S8):** δ 6.95 (m, 3H, Ph), 6.73 (m, 2H, Ph), 4.95 (m, 2H, =CH2), 4.71 (m, overlap, 2H, (P)HC-CH(Ph)), 2.04 (t, 3H, $^5J_{H-H}$ = 3.0 Hz, C-CH3), 0.45 (d, 3H, $^2J_{H-P}$ = 12.2 Hz, PCH3), 0.43 (d, 3H, $^2J_{H-P}$ = 12.3 Hz, PCH3), 0.27 (dd, 1H, $^2J_{H-P}$ = 17.3 Hz, $^2J_{H-H}$ = 12.7 Hz, P-CH-Al), -0.09 (s br, 3H, Al-CH3), -0.14 (s br, 3H, Al-CH3), - 0.14 (overlap) (dd, 1H, $^2J_{H-P}$ = 14.0 Hz, $^2J_{H-H}$ = 12.7 Hz, P-CH-Al); **^{13}C{^{1}H} NMR** (benzene-d_6, **fig. S10**): δ 210.7 (d, $^2J_{C-P}$ =3.4 Hz), 159.7 (d, $^3J_{C-P}$ =9.1 Hz), 136.1 (d, $^3J_{C-P}$ =5.0 Hz), 129.0 (d, $^4J_{C-P}$ =3.4 Hz), 128.2 to 127.6 (m), 102.0 (d, $^3J_{C-P}$ =4.6 Hz), 90.3 (d, $^2J_{C-P}$ =8.8 Hz), 76.5 (d, $^4J_{C-P}$ =1.7 Hz), 43.0 (d, $^1J_{C-P}$ =55.4 Hz), 16.3 (s), 9.9 (d, $^1J_{C-P}$ =49.0 Hz), 9.1 (d, $^1J_{C-P}$ =47.8 Hz), 2.5 (d br, $^1J_{C-P}$ =27.6 Hz), -6.3 (s br), -7.0 (s br); **^{31}P{^{1}H} NMR** (benzene-d_6)**:** δ 29.0.

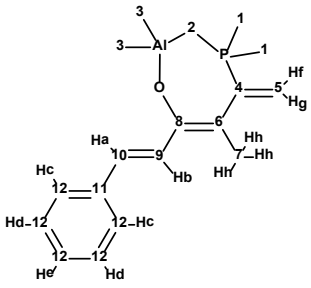
Notes:

Coupling with phosphorous of the aliphatic carbons are clearly demonstrated by selective decoupling of the ^{31}P resonance (**fig. S9**) confirming the location of the phosphorous atom. This is confirmed by the large coupling constant of the aliphatic carbon bonded to the phosphorus as shown on the ^{13}C NMR spectrum $^1J_{C-P}$ =55.4 Hz (**fig. S10**). Direct ^{1}H -^{13}C correlations seen on the gHMQC spectrum (**fig. S11**) all confirm the rearrangement to **4-Me**. Correlation between the terminal methyl group protons and the terminal vinyl group protons as shown by the gDQCOSY spectrum (**fig. S12**) is also consistent with the proposed structure. The 2DNOESY spectrum confirms the relative configuration. First, we can discriminate protons **d** and **e**. In fact, proton d correlates strongly with the aromatic protons (select region A4) at the ortho position which suggests it is the aromatic proton. That proton correlating with the methyl groups of the phosphorus atoms suggest it is cis to the phosphorous atom (select region A2) **(fig. S13)**.



5

To a solution of 6.1 mg (0.033 mmol) of **2a** in 1 mL of benzene-d_6 was added 8.8 mg of **1** (0.033mmol). This caused the color of the solution to change from very pale to bright yellow. The solution was tranferred to a J-Young NMR tube and left to react at 23 °C for an additionnal two hours before characterization. The appearance of the sample remained the same during this additionnal two hours after which product **5** was fully characterized.



5

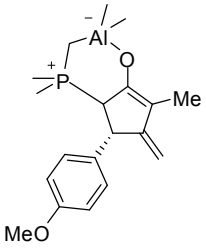
^{1}H NMR (benzene-d_6, **fig. S14):** δ 7.72 (d, 1H, $^2J_{\text{H-H}trans}$ = 15.4 Hz, Ha) 7.43 (d, 2H, $^3J_{\text{H-H}}$ = 8 Hz, Hc), 7.38 (d, 1H, $^2J_{\text{H-H}trans}$ = 15.4 Hz, Hb) 7.09 (t, 2H,$^3J_{\text{H-H}}$ = 7.5 Hz,Hd), 7.02 (m, 1H, He), 5.32 (d, $^3J_{\text{H-P}}$ = 44 Hz, Hg), 4.78 (d, $^3J_{\text{H-P}}$ = 22.0 Hz, Hf), 1.89 (s, 3H, Hh), 0.87 (d, 6H, $^2J_{\text{H-P}}$ = 12.5 Hz, PMe_2), 0.24 (d, 2H, $^2J_{\text{H-P}}$ = 15.7 Hz, PCH_2Al), –0.18 (s, 6H, AlMe); **^{13}C{^{1}H} NMR**

(benzene-d_6, **fig. S15):** δ 155.5 (d, $^{5}J_{C\text{-}P}$ = 1.9 Hz, C8), 140.4 (d, $^{1}J_{C\text{-}P}$ = 76 Hz, C4), 138.14 (s, C11), 133.24 (s, C10), 128.9 (s) and 128.4-127.8 (s) (C12), 124.99 (d, $^{4}J_{C\text{-}P}$ = 1.5 Hz, C9), 121.2 (d, $^{2}J_{C\text{-}P}$ = 9.0 Hz, C5), 108.1 (d, $^{2}J_{C\text{-}P}$ = 6.7 Hz, C6), 14.6 (d, $^{1}J_{C\text{-}P}$ = 56.3 Hz,C7), 13.9 (d, $^{1}J_{C\text{-}P}$ = 21.4 Hz,C1), 7.6 (d, $^{1}J_{C\text{-}P}$ = 31 Hz,C2), **RMN ^{31}P{^{1}H}:** δ ^{31}P NMR (benzene-d_6): 28.4.

Notes:

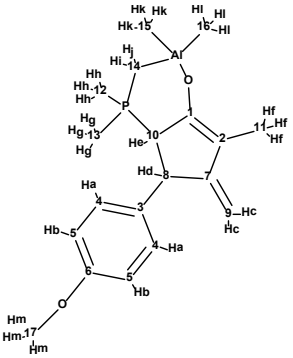
The gHSQC (**fig. S16**) NMR spectrum helped assign the spectra and the 2D NOESY NMR (**fig. S17**) spectrum allowed identification of conformation *Z* for the central C=C bond of **5**.

c. Reactions with 2-OMe



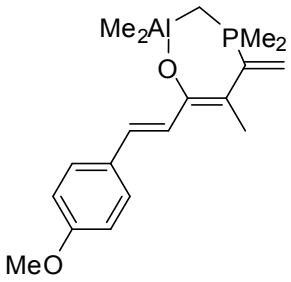
4-OMe

To a solution of 6.7 mg (0.031mmol) of **9** in 1 mL of benzene-d_6 was added 4.1 mg of **1** (0.016 mmol). This caused the color of the solution to change from very pale to bright yellow. The solution was tranferred to a J-Young NMR tube and left to react at 23 °C for an additionnal 48h before characterization. The appearance of the sample remained the same during this additionnal 48 hours (except for the appearance of a very subtle orange precipitate) after which product **4-OMe** was fully characterized as a 30:70 mixture of **4-OMe** and **5-OMe**.



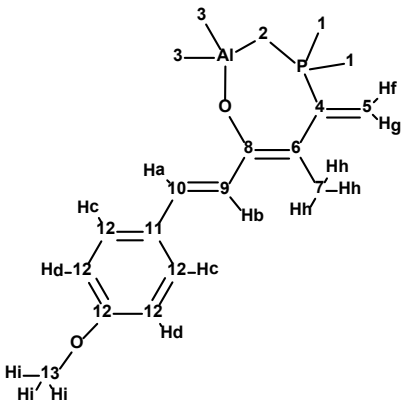
^{1}H NMR (benzene-d_6, **fig. S20**)**:** δ 6.68-6.66 (m, 2H, **Hb**), 6.61-6.58 (m, 2H, **Ha**), 4.97 (m, 2H, **Hc**), 4.74-4.73 (m, **Hd**), 4.69-4.63 (m, **He**), 3.26 (s, 3H, **Hm**) 2.07 (td, 3H, $^5J_{H\text{-}H}$ = 3.0 Hz, $^5J_{H\text{-}P}$ = 3.0 Hz, **Hf**), 0.52-0.44 (m, 6H, **Hh,Hg**), 0.33-0.25 (m, 2H, **Hi,Hl**), -0.07 (s br, 3H, **Hj or Hk**), -0.12 (s br, 3H, **Hj or Hk**), **^{13}C{^{1}H} NMR** (benzene-d_6, **fig. S21**): δ 221.2 (s, **C6**); 210.7 (s, **C1**); 159.8-159.5 (m, **C2**); 130.9 (s, **C4** or **C5**); 129.0 (s, **C4** or **C5**); 90.8 (d, $^2J_{C\text{-}P}$ =8.2 Hz, **C7**), 76.5 (s, **C8**), 54.8 (s, **C17**) 42.2 (d, $^1J_{C\text{-}P}$ =56.4 Hz, **C10**), 16.4 (s**, C11**), 10.21-8.97 (m, **C12-C13**), 2.7-2.4 (m, **C14**) -7.4 (s br,**C15**, **C16**). **^{31}P{^{1}H} NMR** (benzene-d_6)**:** δ 29.4.

***Note:** gHMQC, gDQCOSY and 2DNOESY spectra were performed to help assign spectra. All were very similar to spectra recorded for species **4** and the same correlation are observed. The spectra were omitted.



5-OMe

To a solution of 4.8 mg (0.022 mmol) of **9** in 1 mL of benzene-d_6 was added 5.9 mg of **1** (0.022 mmol). This caused the color of the solution to change from very pale to bright yellow. The solution was tranferred to a J-Young NMR tube and left to react at 23 °C for an additionnal 48h before characterization. The appearance of the sample remained the same during this additionnal 48 hours after which product **5-OMe** was fully characterized.



^{1}H NMR (benzene-d_6, **fig. S22):** δ 7.73 (d, 1H, $^{2}J_{\text{H-H}trans}$ = 15.3 Hz, **Ha**) 7.41-7.38 (m, 2H, Hc), 7.30 (d, 1H, $^{2}J_{\text{H-H}trans}$ = 15.1 Hz, Hb) 6.75-6.69 (m, 2H, Hd), 5.33 (d, $^{3}J_{\text{H-P}}$ = 43 Hz, Hg), 4.78 (d, $^{3}J_{\text{H-P}}$ = 22.0 Hz, Hf), 3.25 (s, 3H, Hi) 1.94 (s, 3H, Hh), 0.88 (d, 6H, $^{2}J_{\text{H-P}}$ = 12.7 Hz, PMe_2), 0.26 (d, 2H, $^{2}J_{\text{H-P}}$ = 15.7 Hz, PCH_2Al), –0.18 (s, 6H, AlMe); **^{13}C{^{1}H} NMR** (benzene-d_6, **fig. S23):** δ 160.0 (s, **C14**) 156.0 (d, $^{5}J_{\text{C-P}}$ = 1.9 Hz, **C8**), 140.4 (d, $^{1}J_{\text{C-P}}$ = 76.7 Hz, **C4**), 133.0 (s, **C11**), 130.9 (s, **C10**), 128.9 (s, **C12**), 122.9 (d, $^{4}J_{\text{C-P}}$ = 1.2 Hz, **C9**), 120.5 (d, $^{2}J_{\text{C-P}}$ = 9.6 Hz, **C5**),114.5 (s, **C13**) 107.3 (d, $^{2}J_{\text{C-P}}$ = 5.4 Hz, **C6**), 14.7 (d, $^{1}J_{\text{C-P}}$ = 56.0 Hz, **C7**), 13.1 (d, $^{1}J_{\text{C-P}}$ = 20.0 Hz, **C1**), 7.7 (d, $^{1}J_{\text{C-P}}$ = 27.6 Hz, **C2**) **NMR ^{31}P{^{1}H}:** δ ^{31}P NMR (benzene-d_6): 29.4.

***Note:** gHMQC, gDQCOSY and 2DNOESY spectra were performed to help assign spectra. All were very similar for spectra recorded for species **5** and all the same correlation are observed. They were omitted to ligthen the text.

2. NMR Spectra

Fig. S1- ^{1}H NMR spectrum of **3 (**400 MHz – 50°C, dichloromethane-d_2)

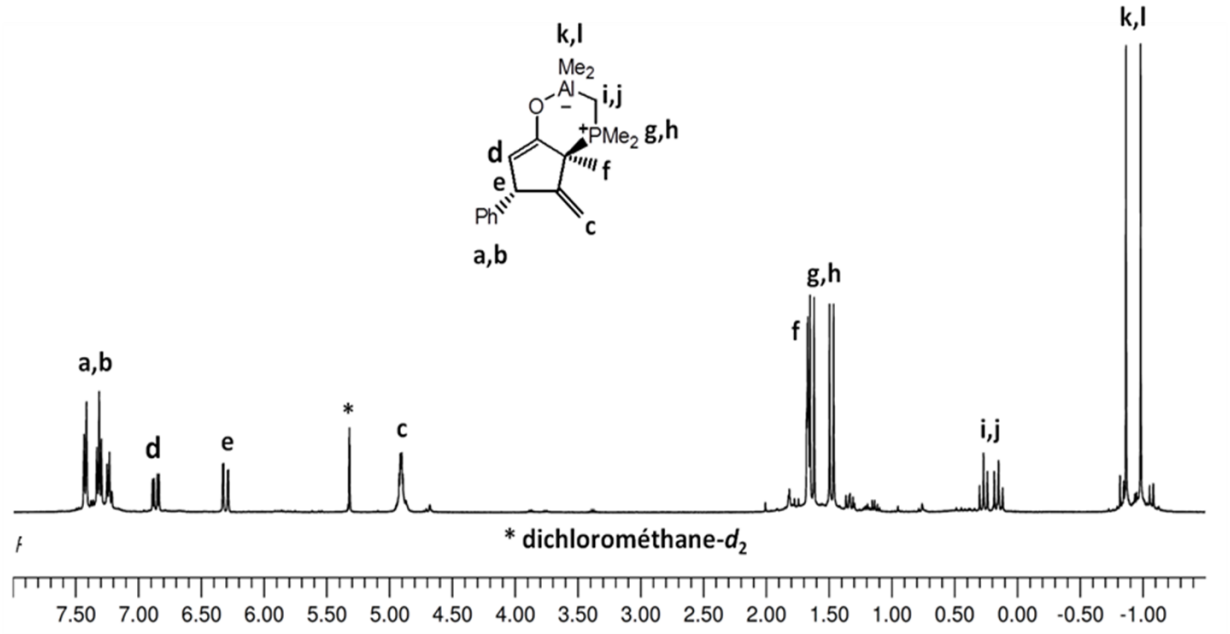


Fig. S2- ^{1}H{sel^{31}P@41.8} NMR spectrum of **3 (**400 MHz – 50°C, dichloromethane-d_2), selected regions:

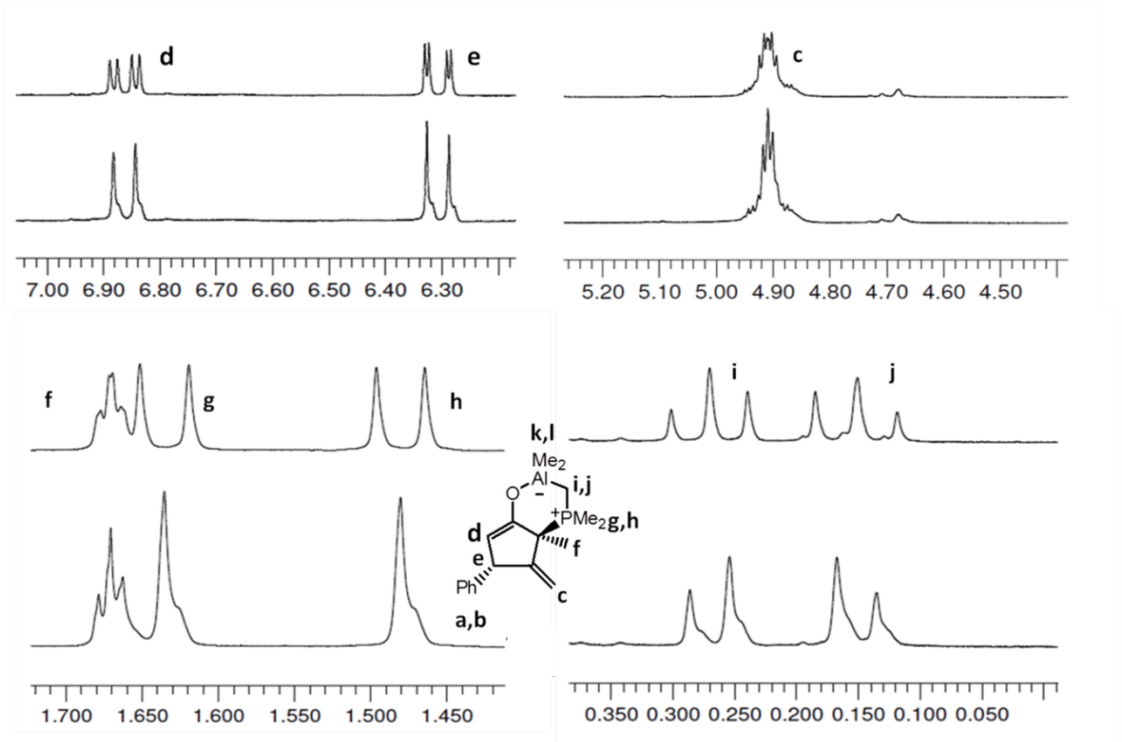


Fig. S3- ^{13}**C** NMR spectrum of **3** (100.613 MHz, dichloromethane-d_2, -50°C)

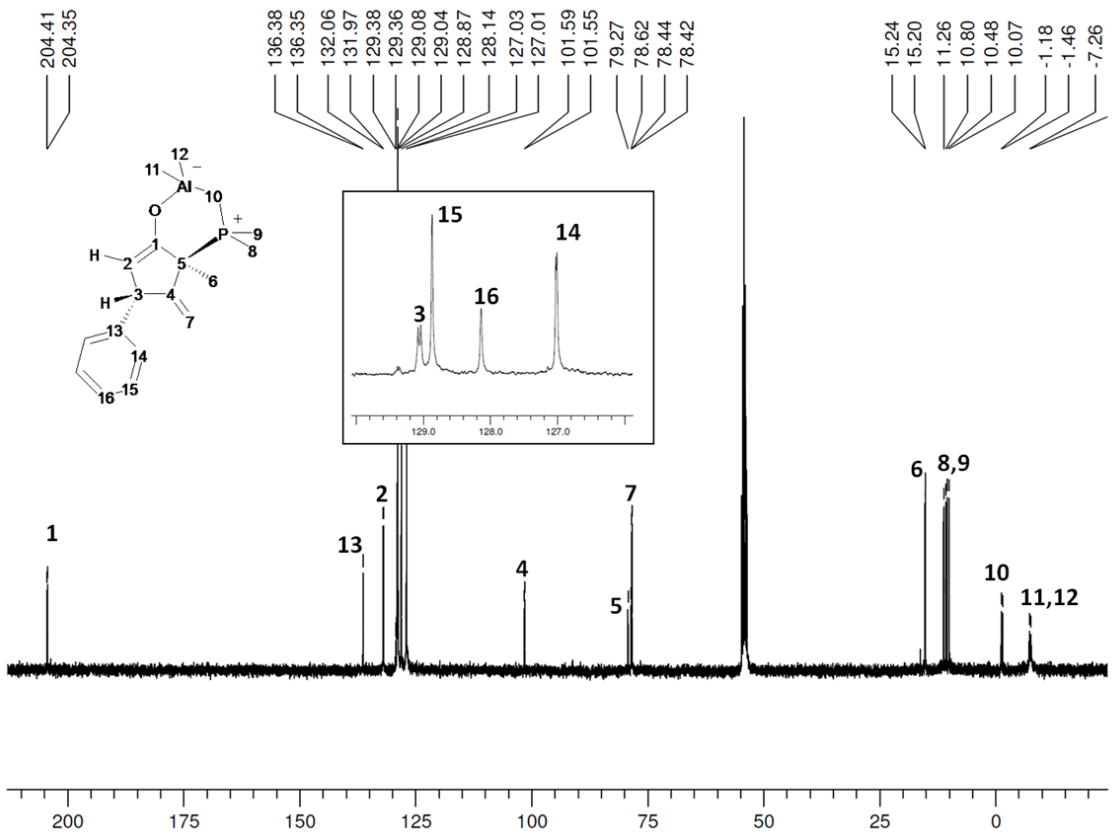


Fig. S4- gHMQC NMR spectrum of **3** (400/100.613 MHz, dichloromethane-d_2, -50°C)

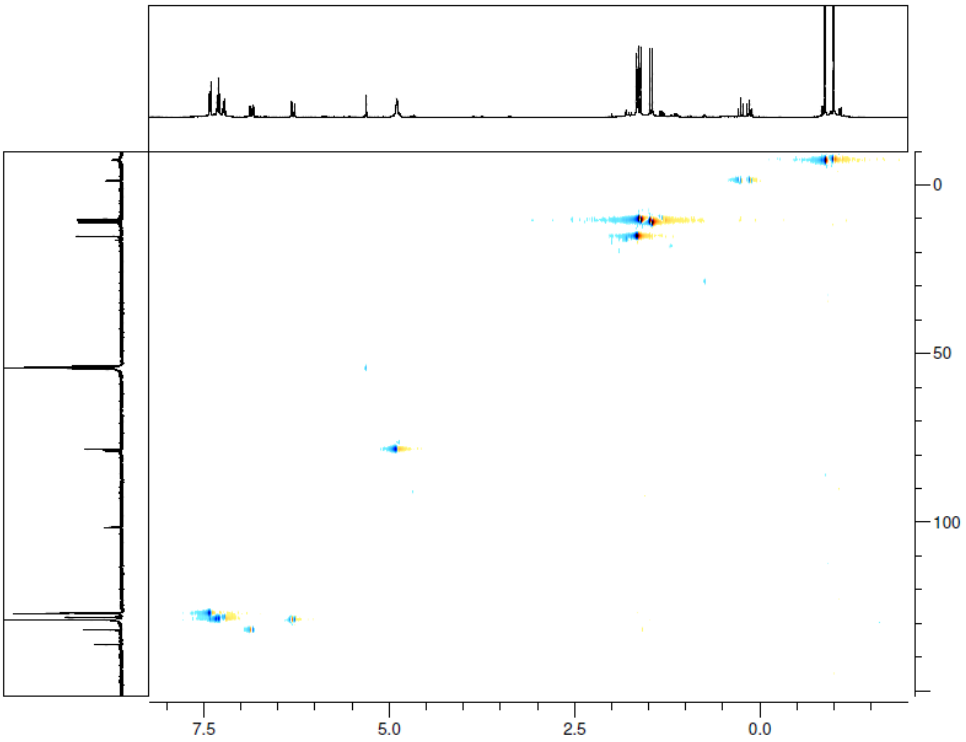


Fig. S5- gDQCOSY NMR spectrum of **3** (400MHz, dichloromethane-d_2, -50°C)

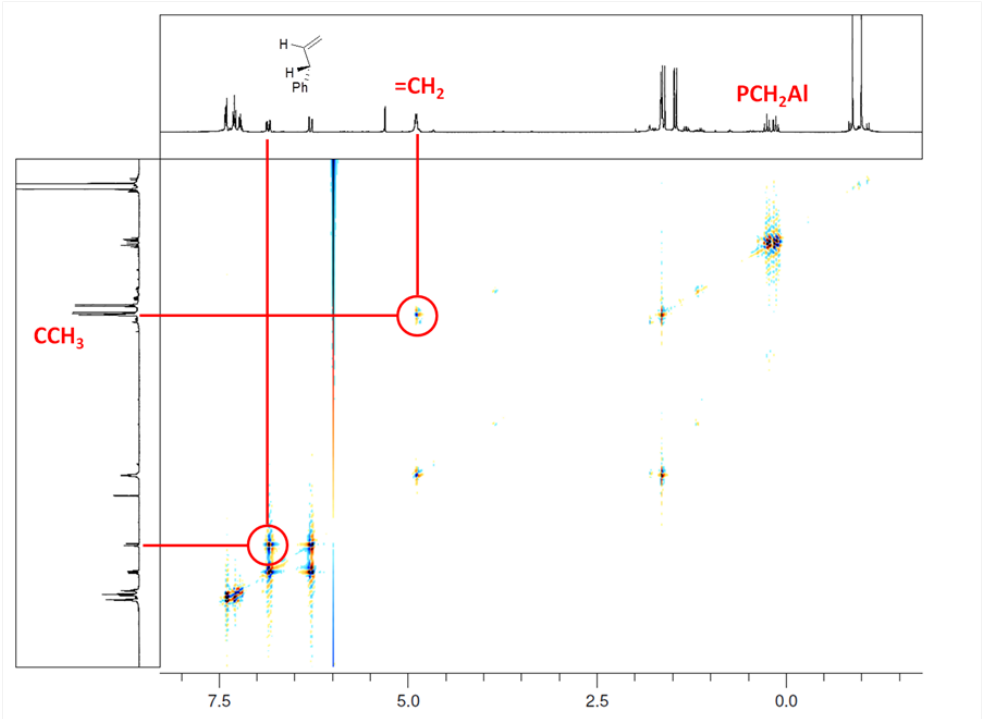


Fig. S6- 2DNOESY NMR spectrum of **3** (400MHz, dichloromethane-d_2, -50°C)

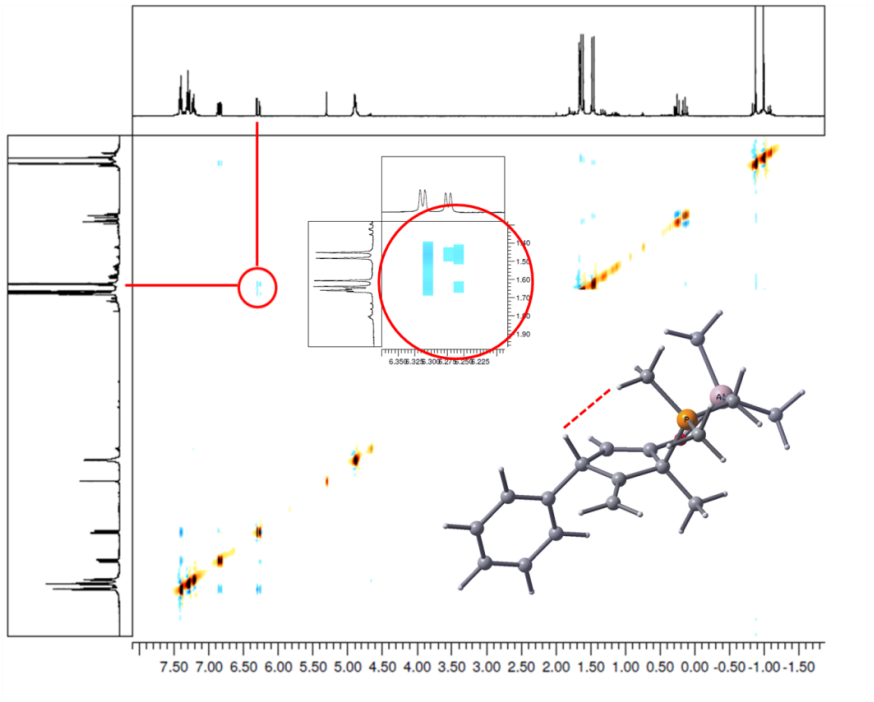


Fig. S7 NMR spectrum of **3** (20 % **4**) (400 MHz, benzene-d_6)

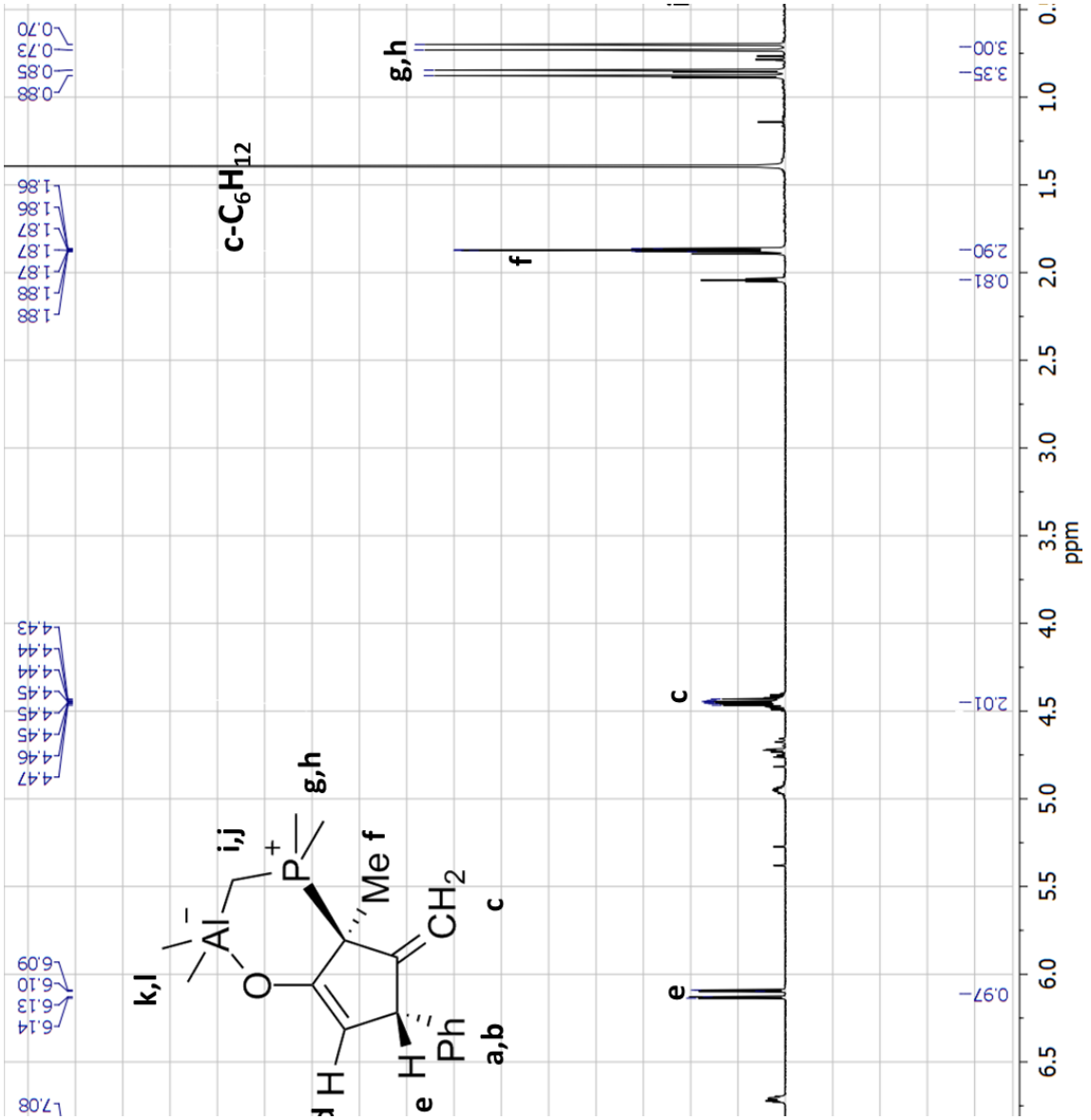


Fig. S8- ^{1}H NMR spectrum of **4** (400 MHz 23°C, benzene-d_6)

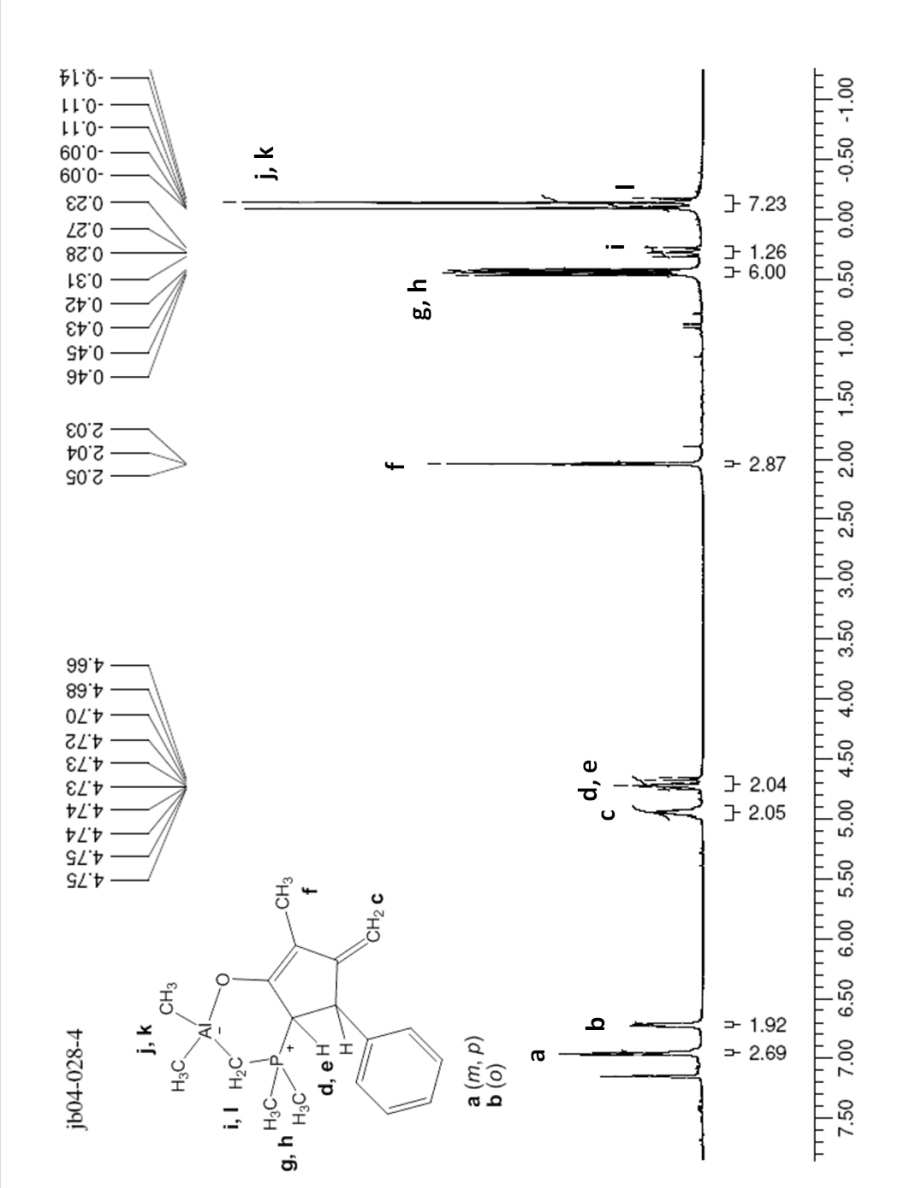


Fig. S9- ^{1}H {sel^{31}P@29.0} NMR spectrum of **4 (**400 MHz 23°C, benzene-d_6), selected regions

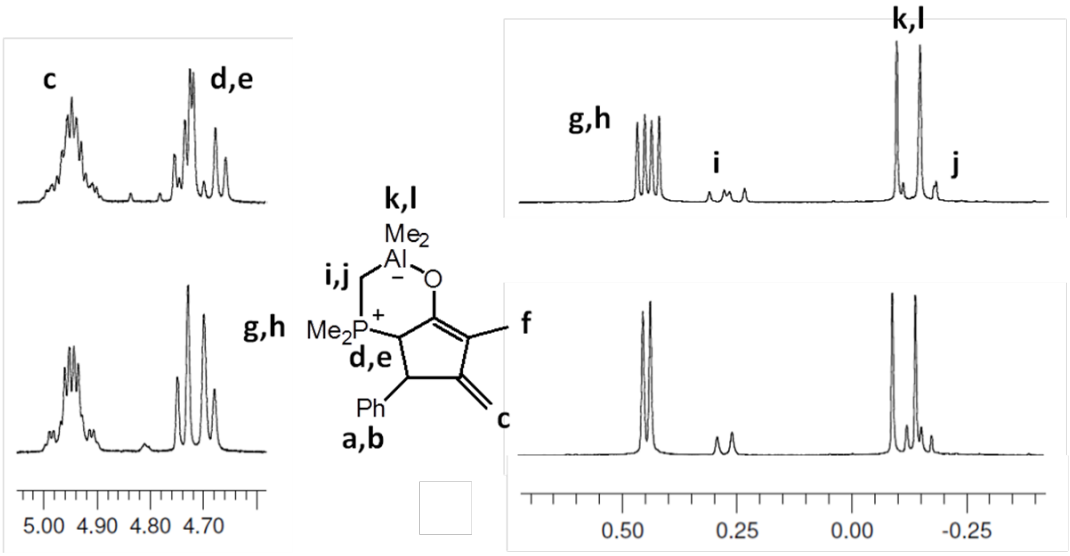


Fig. S10- $^{13}C\{^{1}H\}$ NMR spectrum of **4** (100. 613 Mhz 23°C, benzene-d_6)

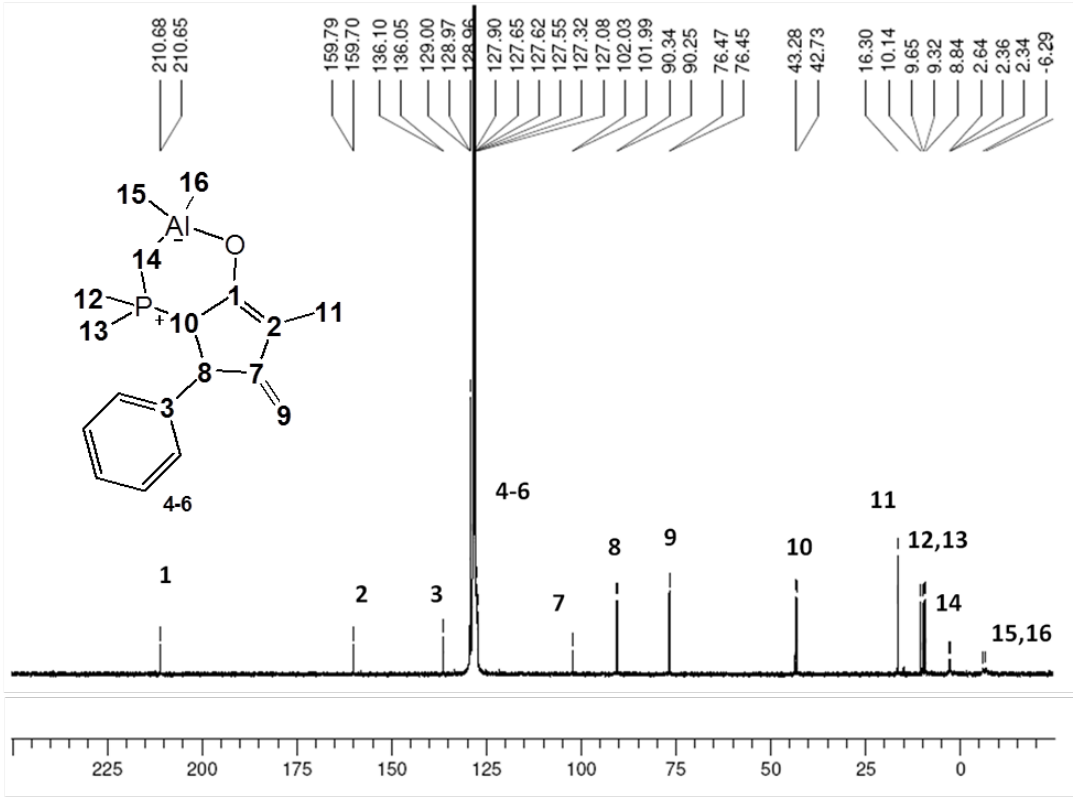


Fig. S11- gHMQC NMR spectrum of **4** (400/100.613 MHz, benzene-d_6, 23°C)

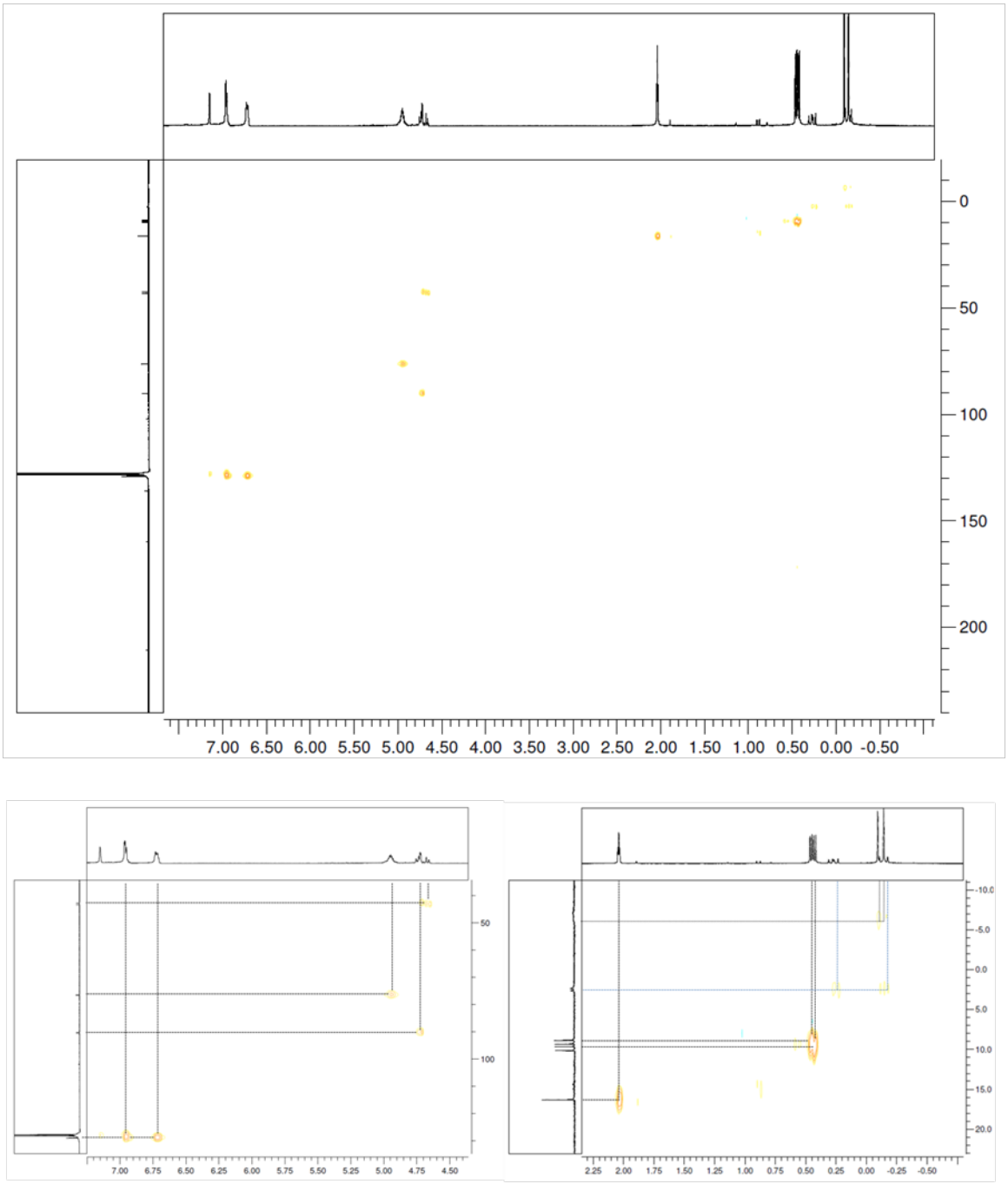


Fig. S12- gDQCOSY NMR spectrum of **4** (400 MHz, benzene-d_6, 23°C)

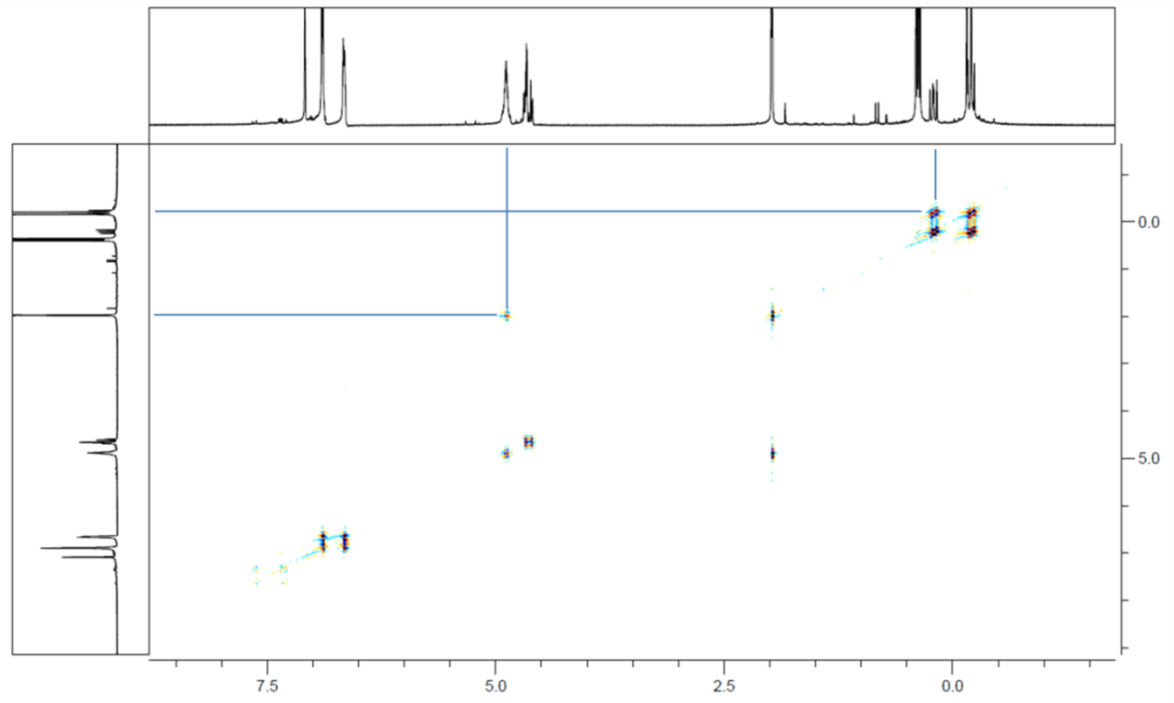


Fig. S13- 2DNOESY NMR spectrum of **4** (400 MHz, benzene-d_6, 23°C)

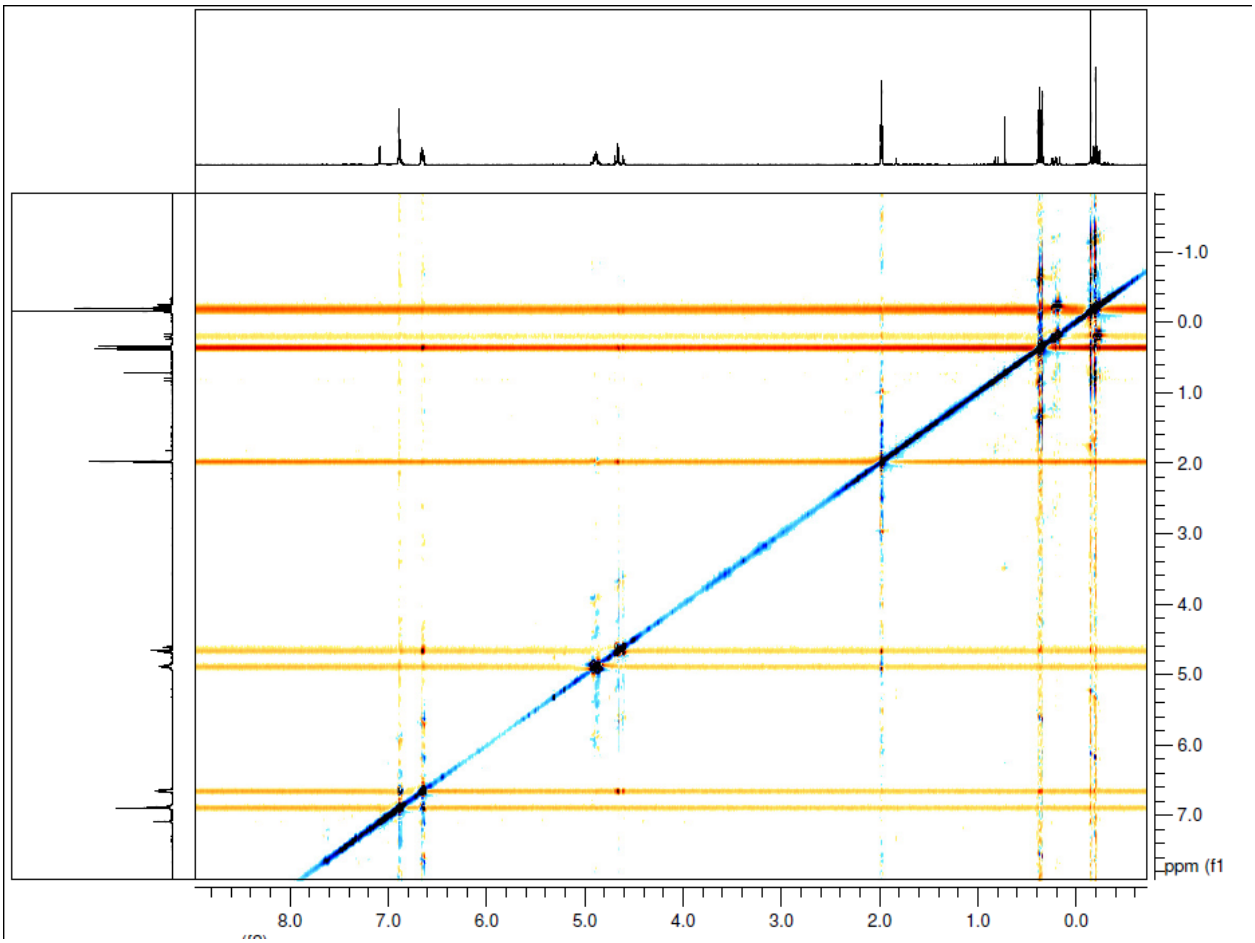


Fig. S13-b- 2DNOESY NMR spectrum of **4** (400 MHz, benzene-d_6, 23°C) , select regions

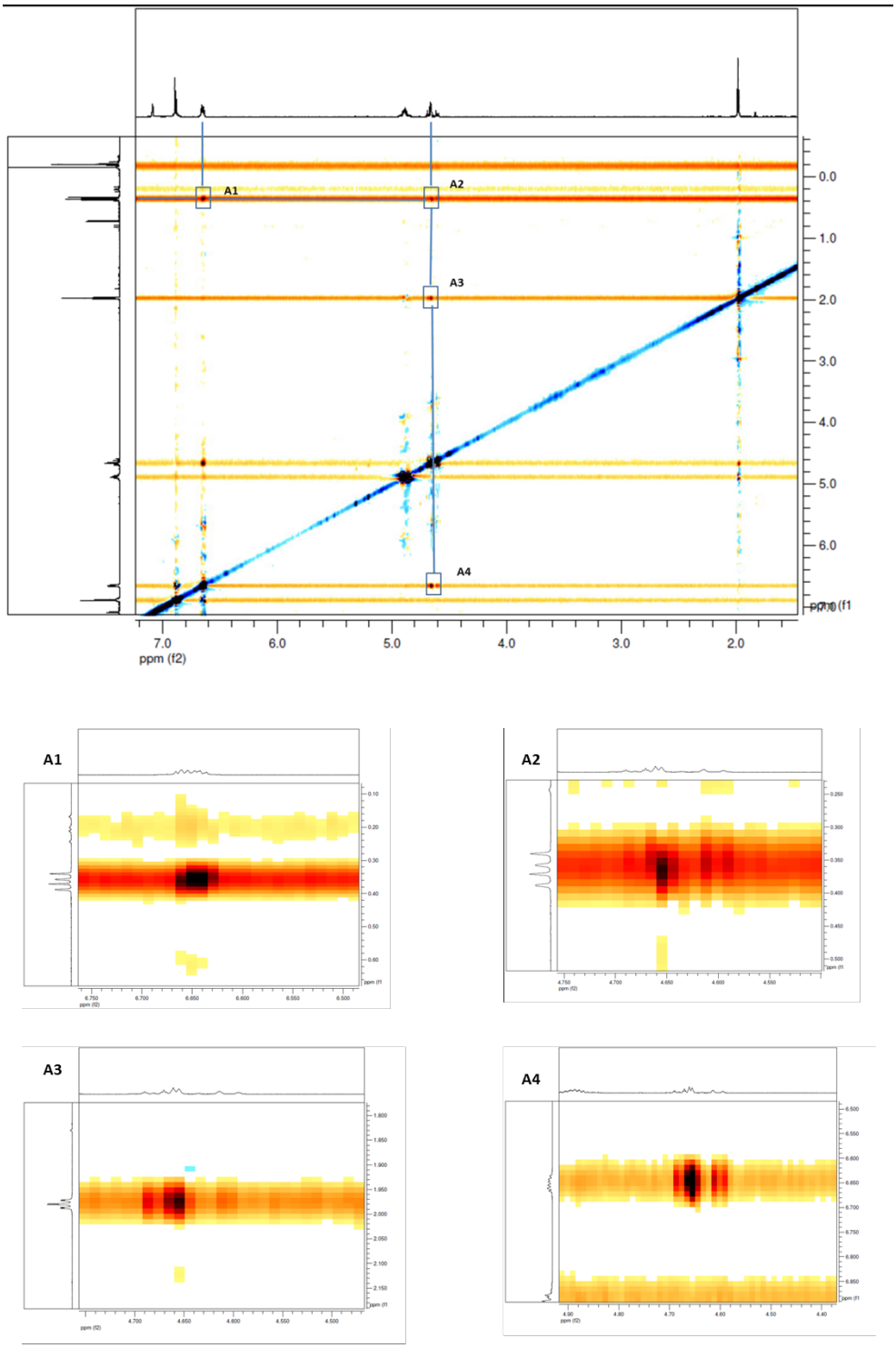


Fig. S14- ^{1}H NMR spectrum of **5** (500 MHz, benzene-d_6)

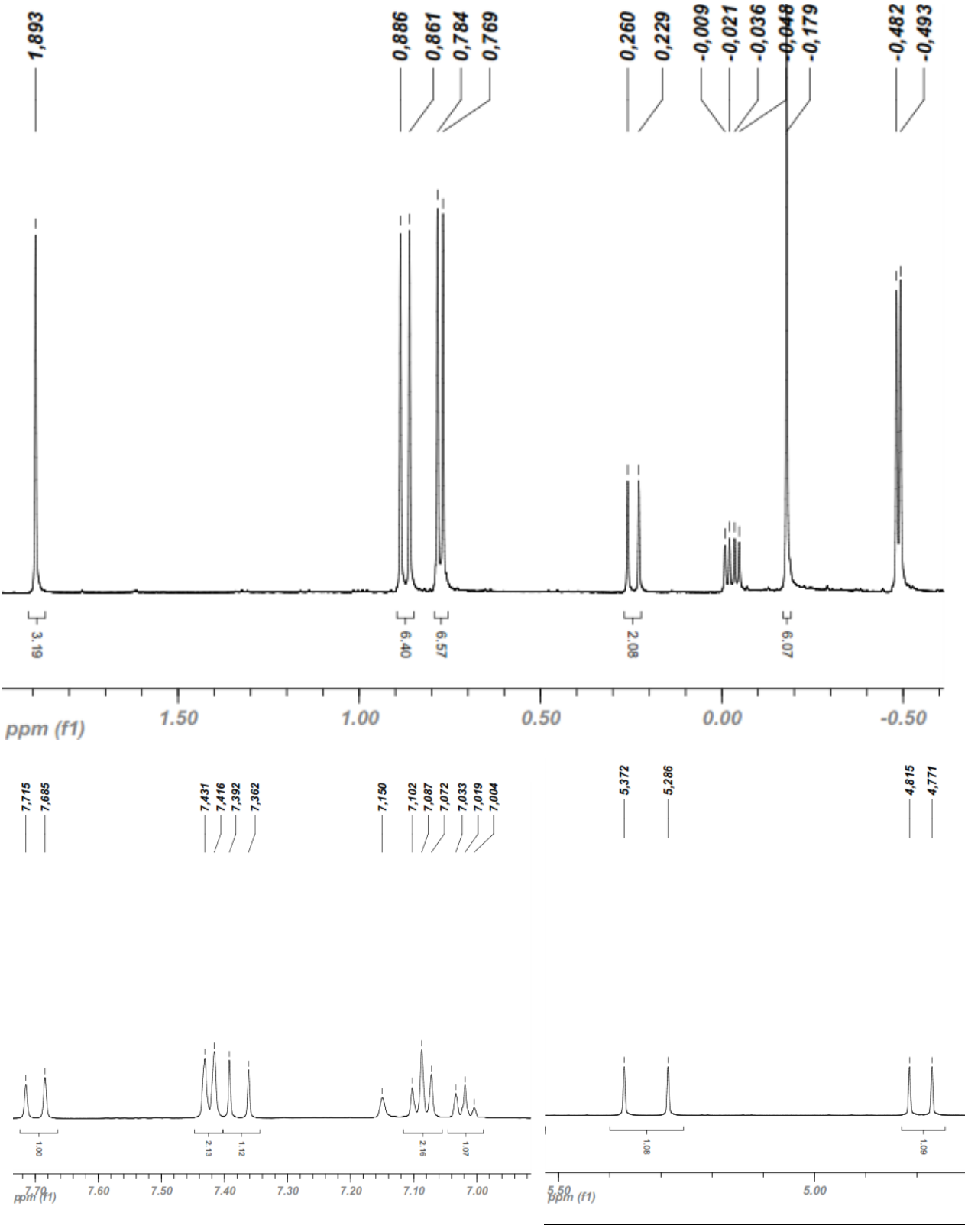


Figure S15: $^{13}C\{^{1}H\}$ NMR spectrum of **5** (125.758 MHz, benzene-d_6), selected regions

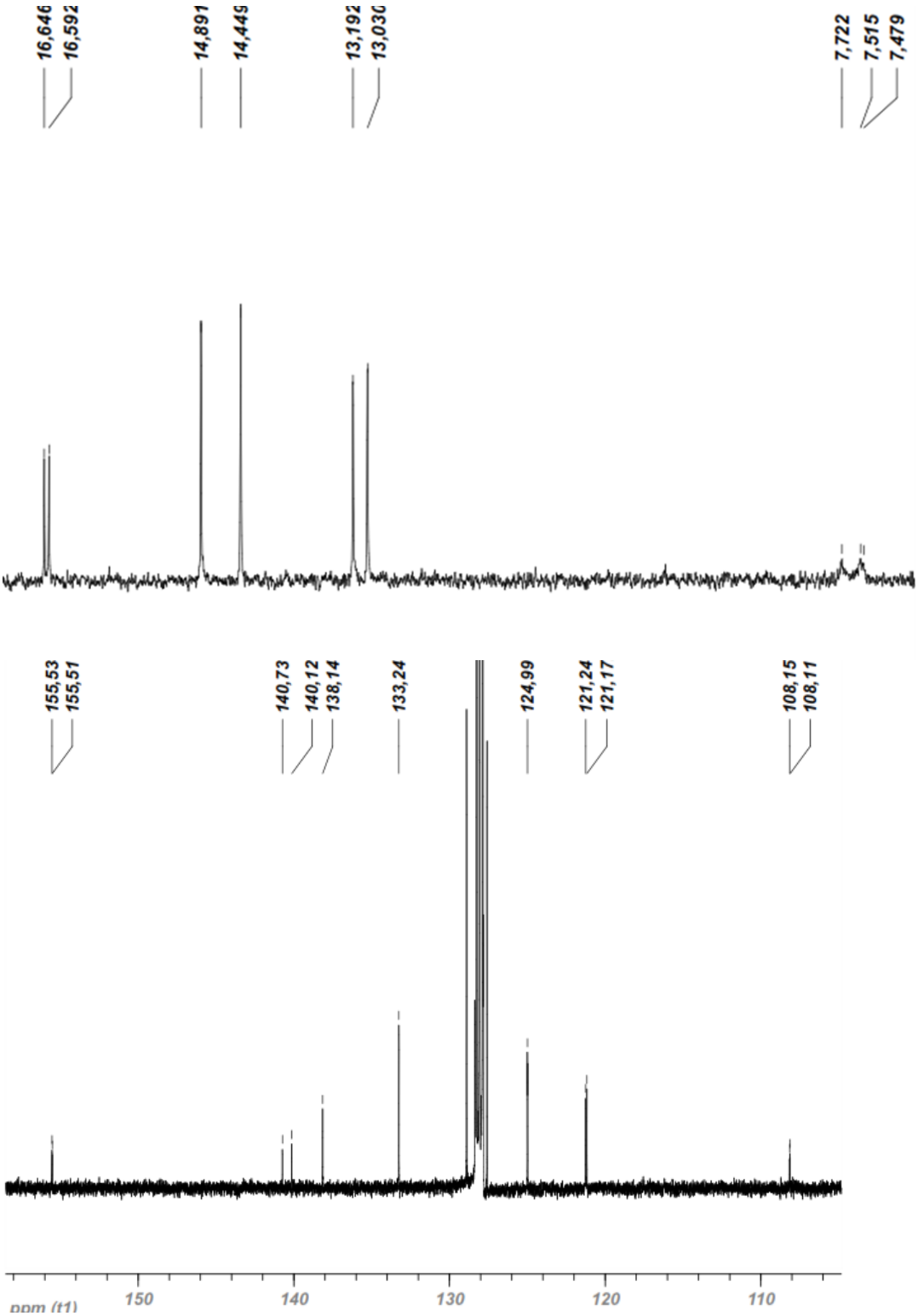

16,646
16,592
14,891
14,449
13,192
13,030
7,722
7,515
7,479
155,53
155,51
140,73
140,12
138,14
133,24
124,99
121,24
121,17
108,15
108,11
ppm (t1)
150
140
130
120
110

Figure S16: gHSQC NMR spectrum of **5** (500 /125.758 MHz ,benzene-d_6)

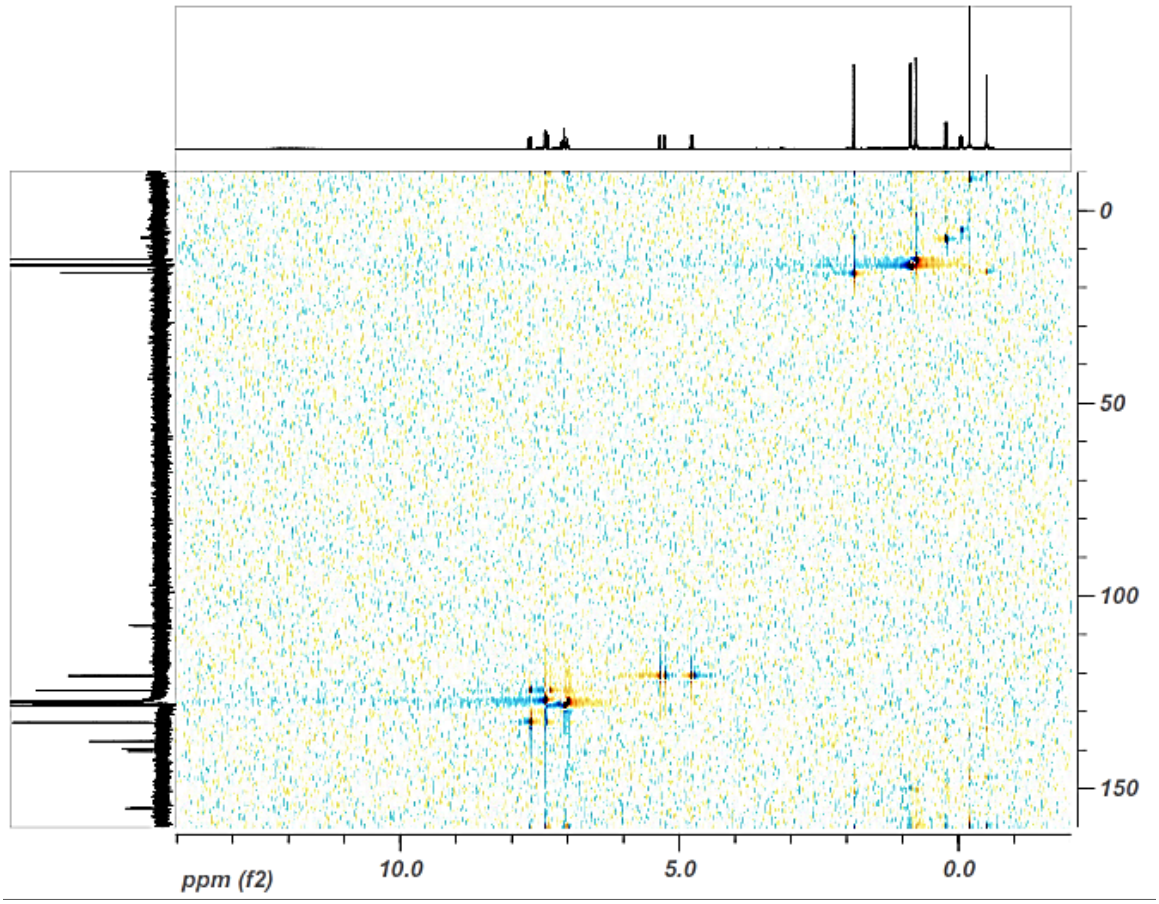


Figure S17: NOESY-2D NMR spectrum of **5** (500 MHz, benzene-d_6), select regions

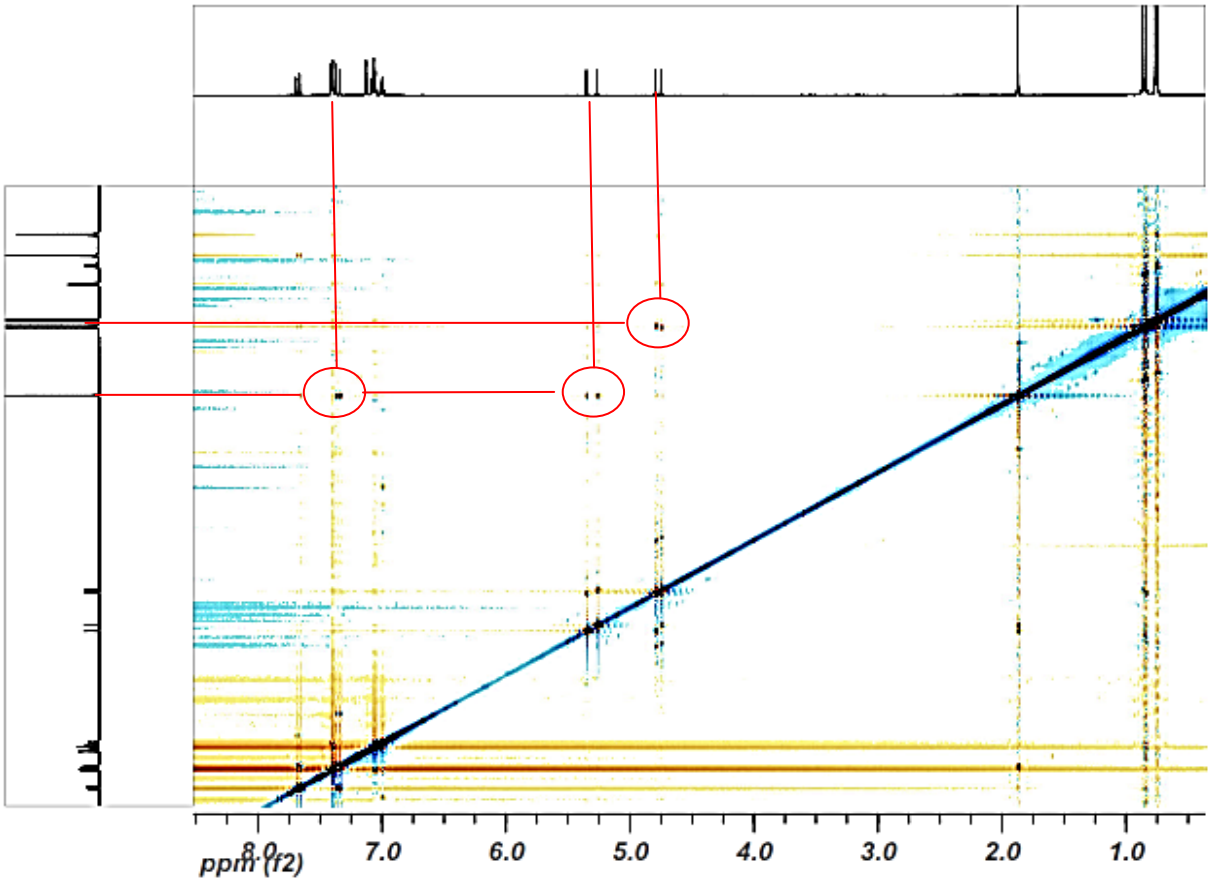

8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f2)

Fig. S18- ^{1}H NMR spectrum of **4-OMe** (400 MHz 23°C, benzene-d_6), selected regions
(** Denotes the presence of product **5-OMe**)

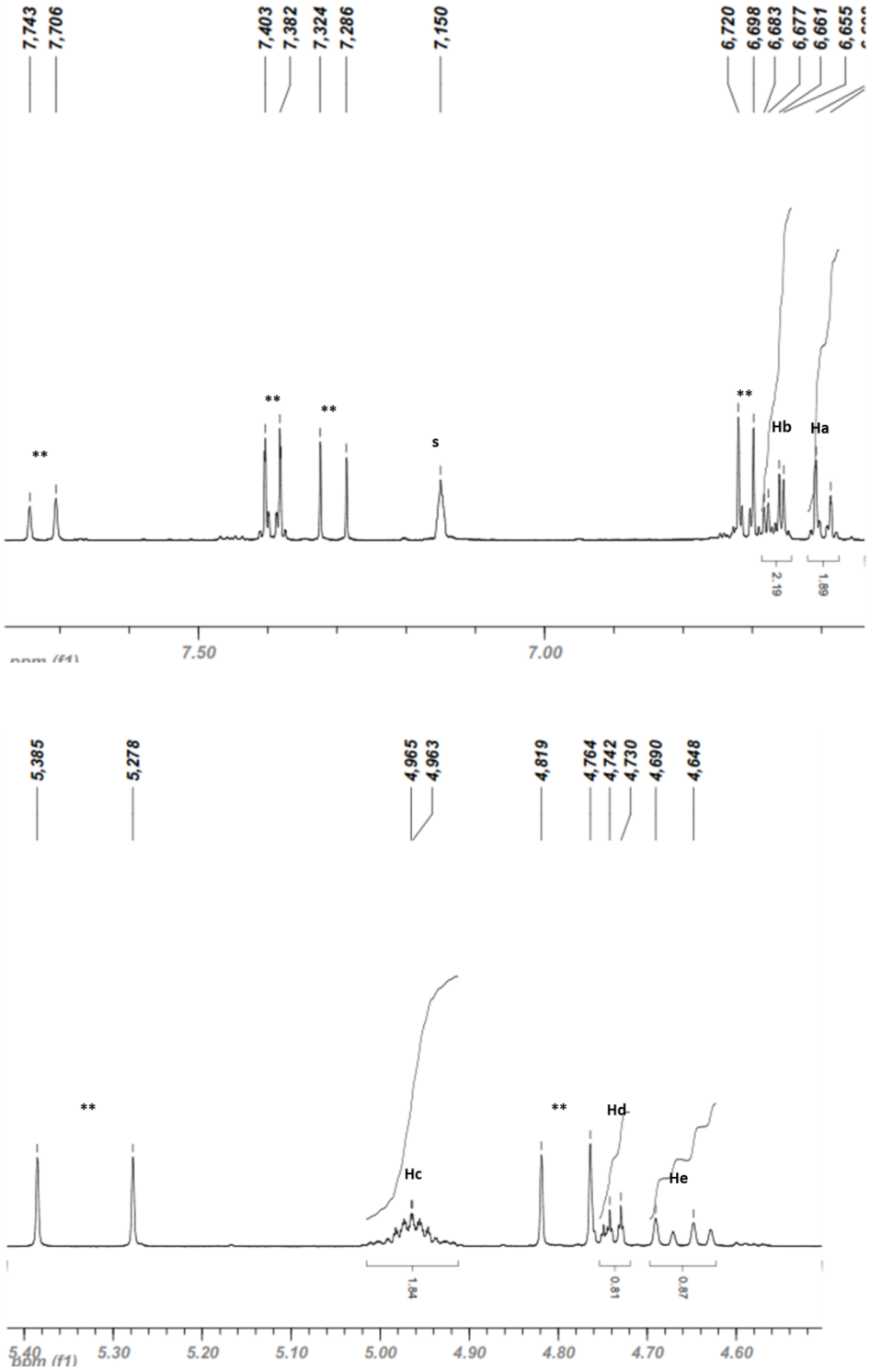


Fig. S18- ^{1}H NMR spectrum of **4-OMe** (400 MHz 23°C, benzene-d_6), selected regions (continued)
(** Denotes the presence of product **5-OMe**)

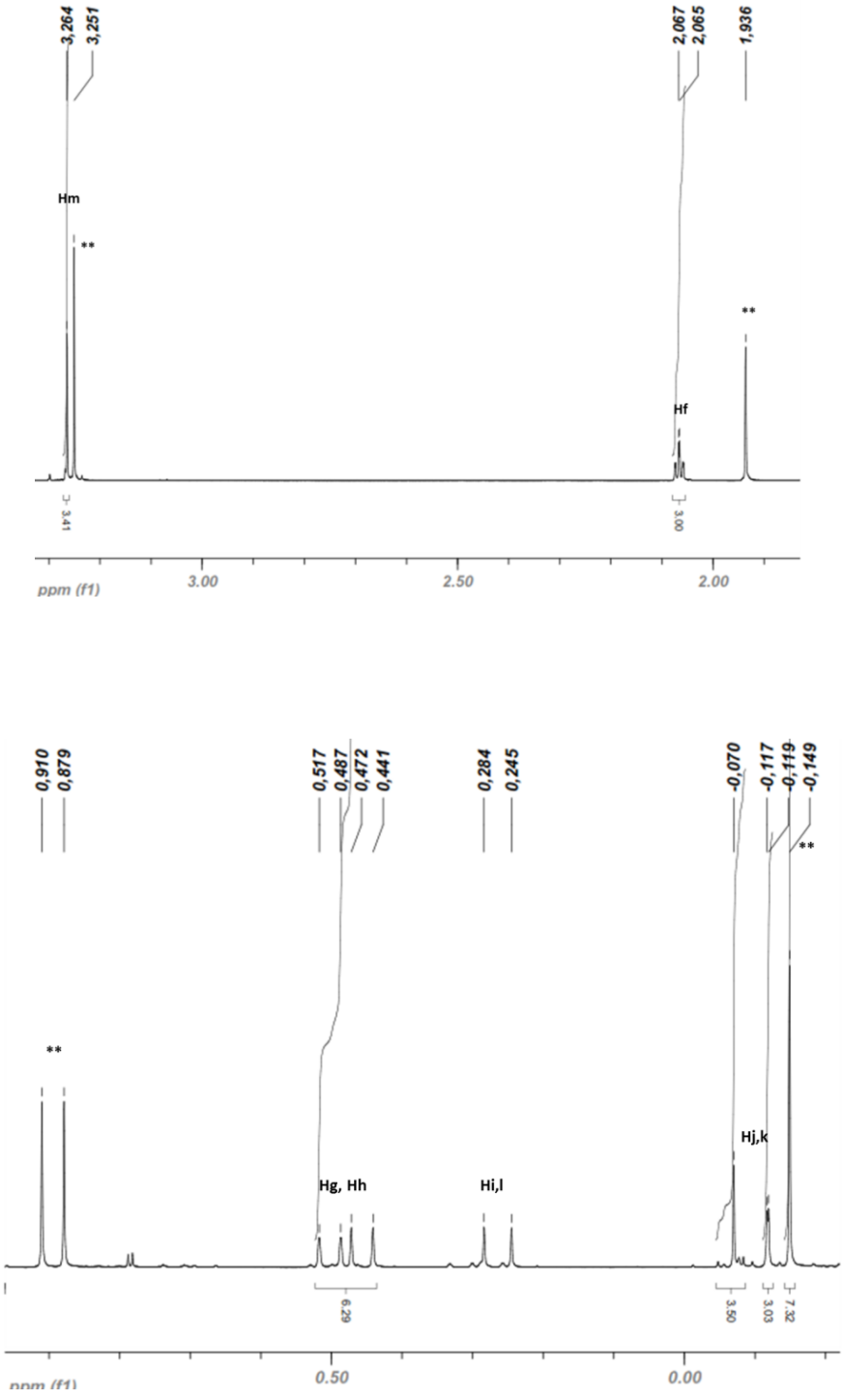


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of **4-OMe** (100.613 MHz, benzene-d_6) , selected regions
(* Denotes the presence of residual starting material $(Me_2PCH_2AlMe_2)_2$)

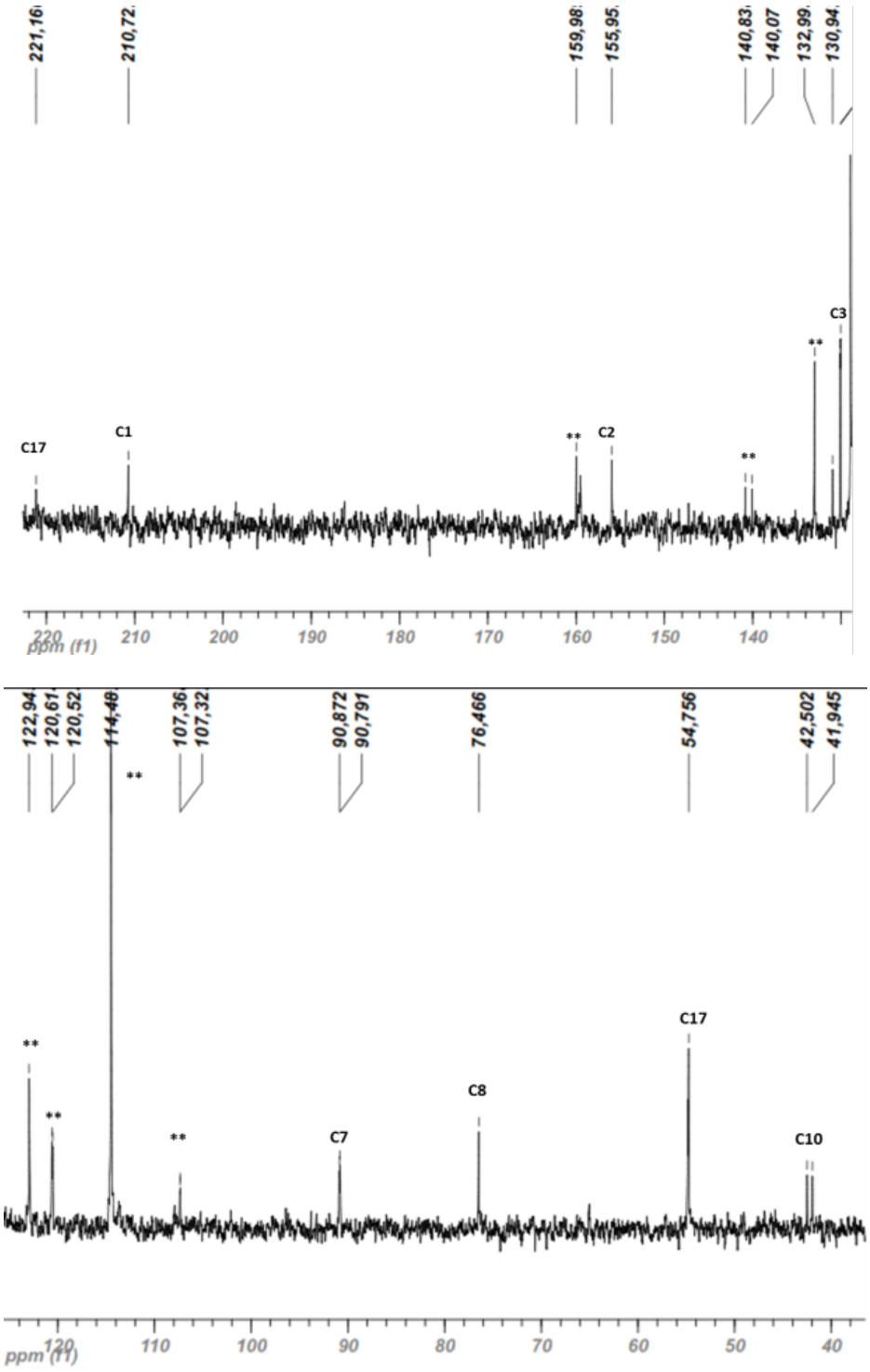


Figure S19: $^{13}C\{^{1}H\}$ NMR spectrum of **4-OMe** (100.613 MHz, benzene-d_6) , selected regions (continued) (* Denotes the presence of residual starting material $(Me_2PCH_2AlMe_2)_2$)

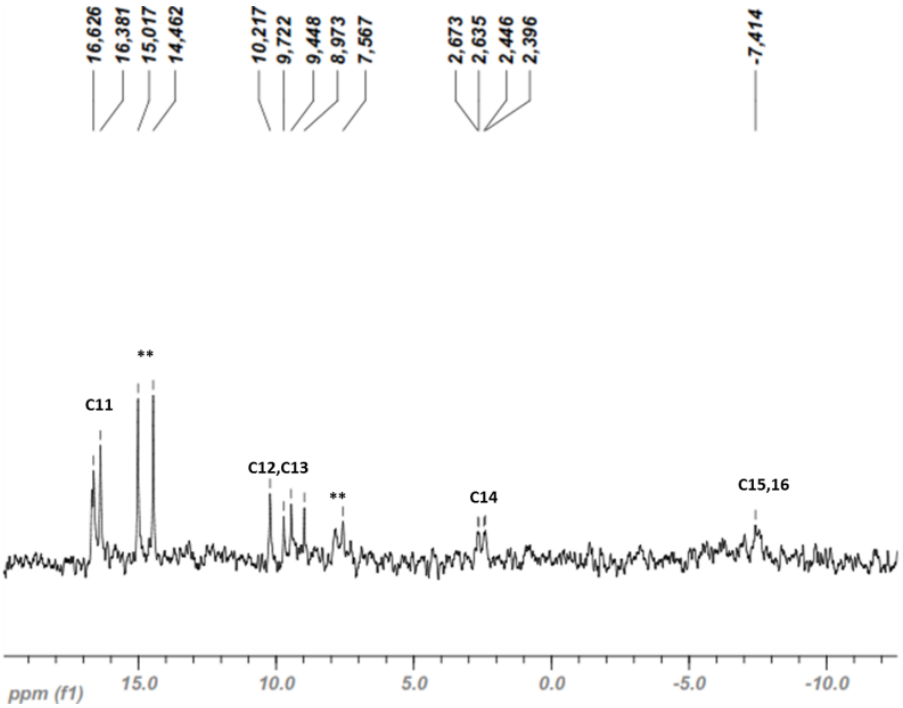


Fig. S20- ^{1}H NMR spectrum of **MeO-5 (**400 MHz 23°C, benzene-d_6)

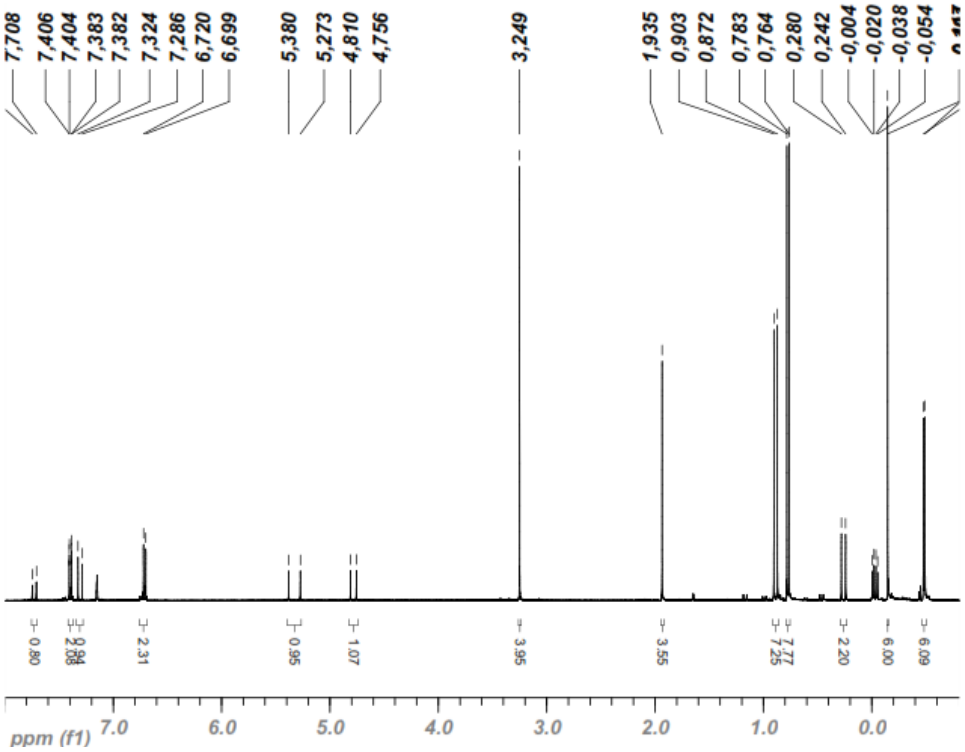


Fig. S20-b- ^{1}H NMR spectrum of **5-OMe** (400 MHz 23°C, benzene-d_6), selected regions
(* Denotes the presence of residual starting material $(Me_2PCH_2AlMe_2)_2$)

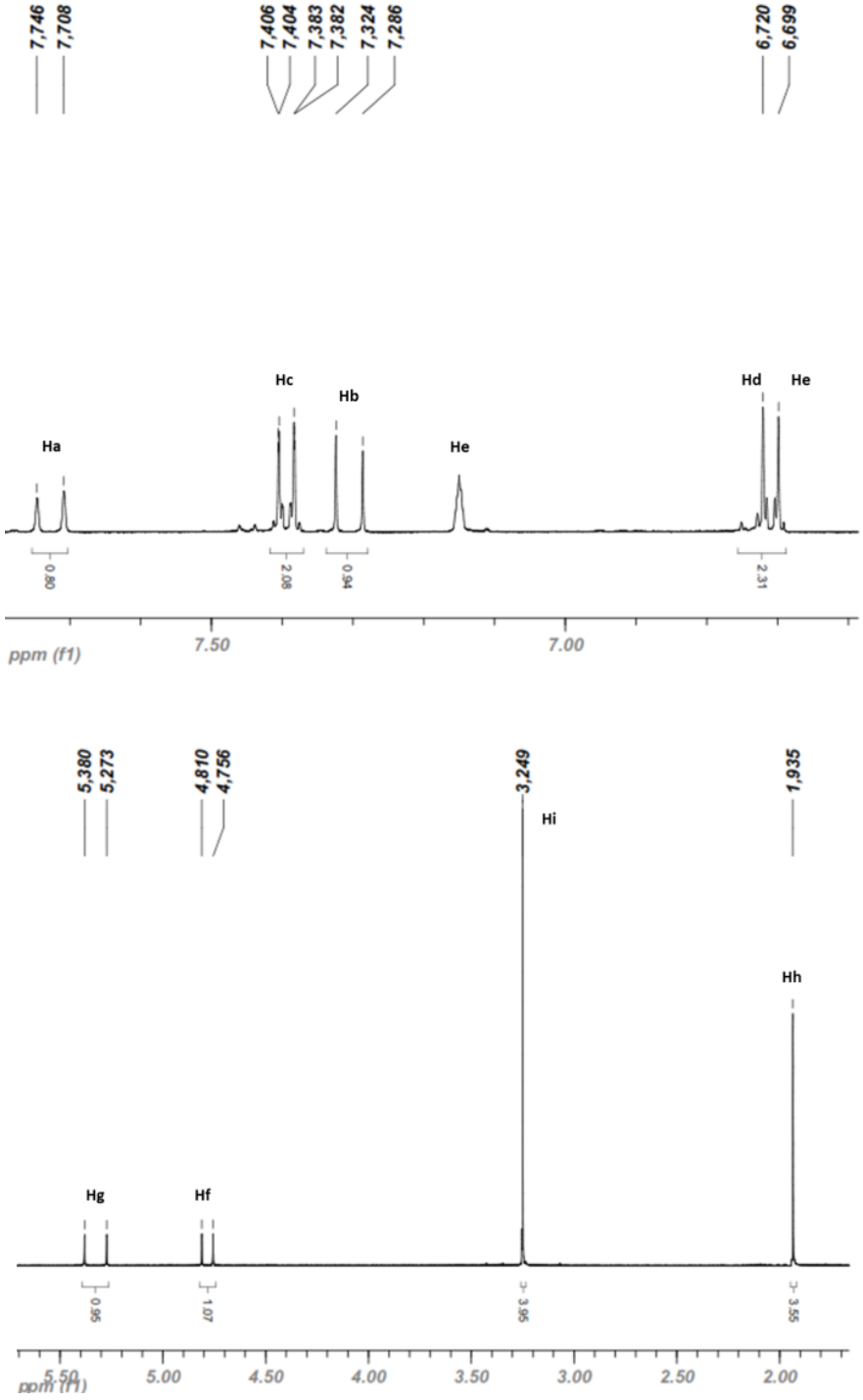


Fig. S20-b- ^{1}H NMR spectrum of **5-OMe (**400 MHz 23°C, benzene-d_6), selected regions (continued)
(* Denotes the presence of residual starting material $(Me_2PCH_2AlMe_2)_2$)

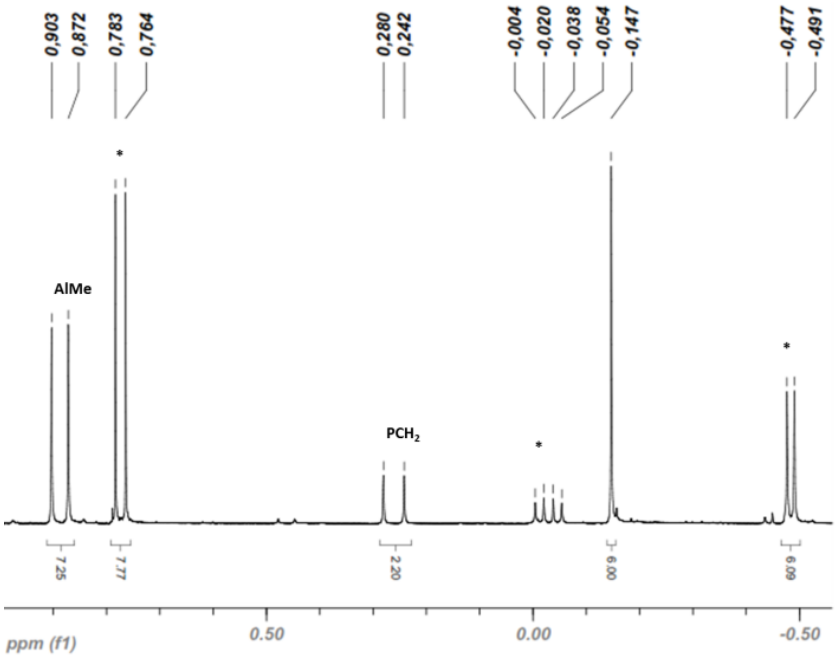


Figure S21: $^{13}C\{^{1}H\}$ NMR spectrum of **MeO-5** (100.613 MHz, benzene-d_6) ,

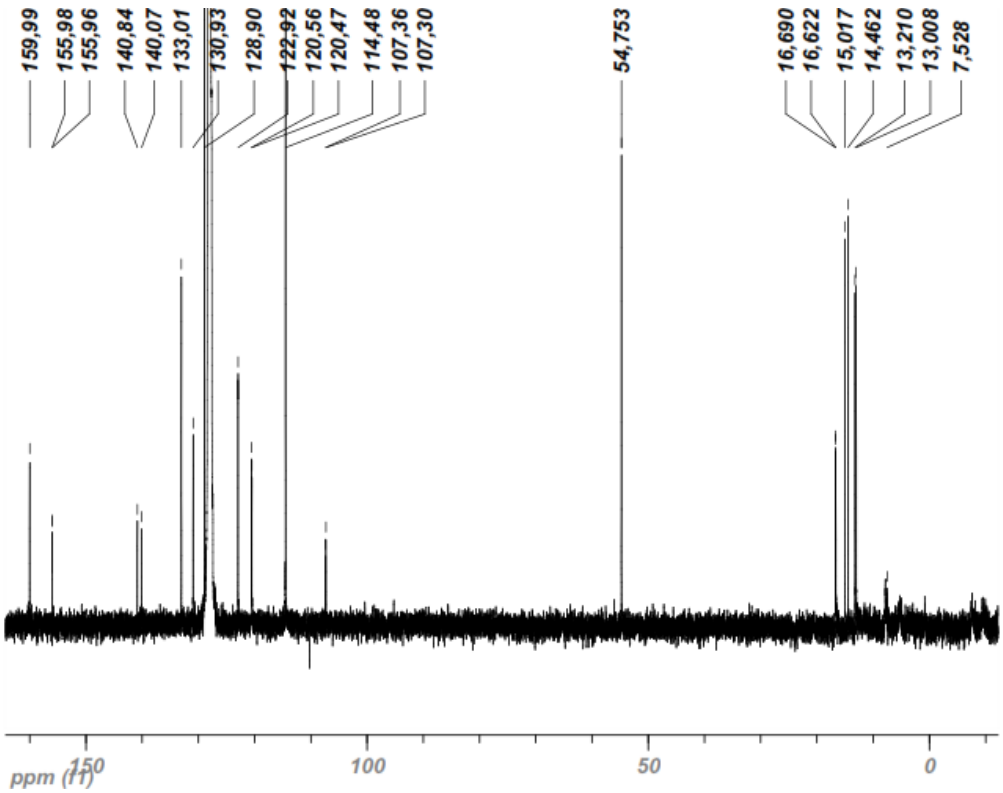


Figure S21-b: $^{13}C\{^{1}H\}$ NMR spectrum of **5-OMe**. (100.613 MHz, benzene-d_6) , select regions
(* Denotes the presence of residual starting material $(Me_2PCH_2AlMe_2)_2$)

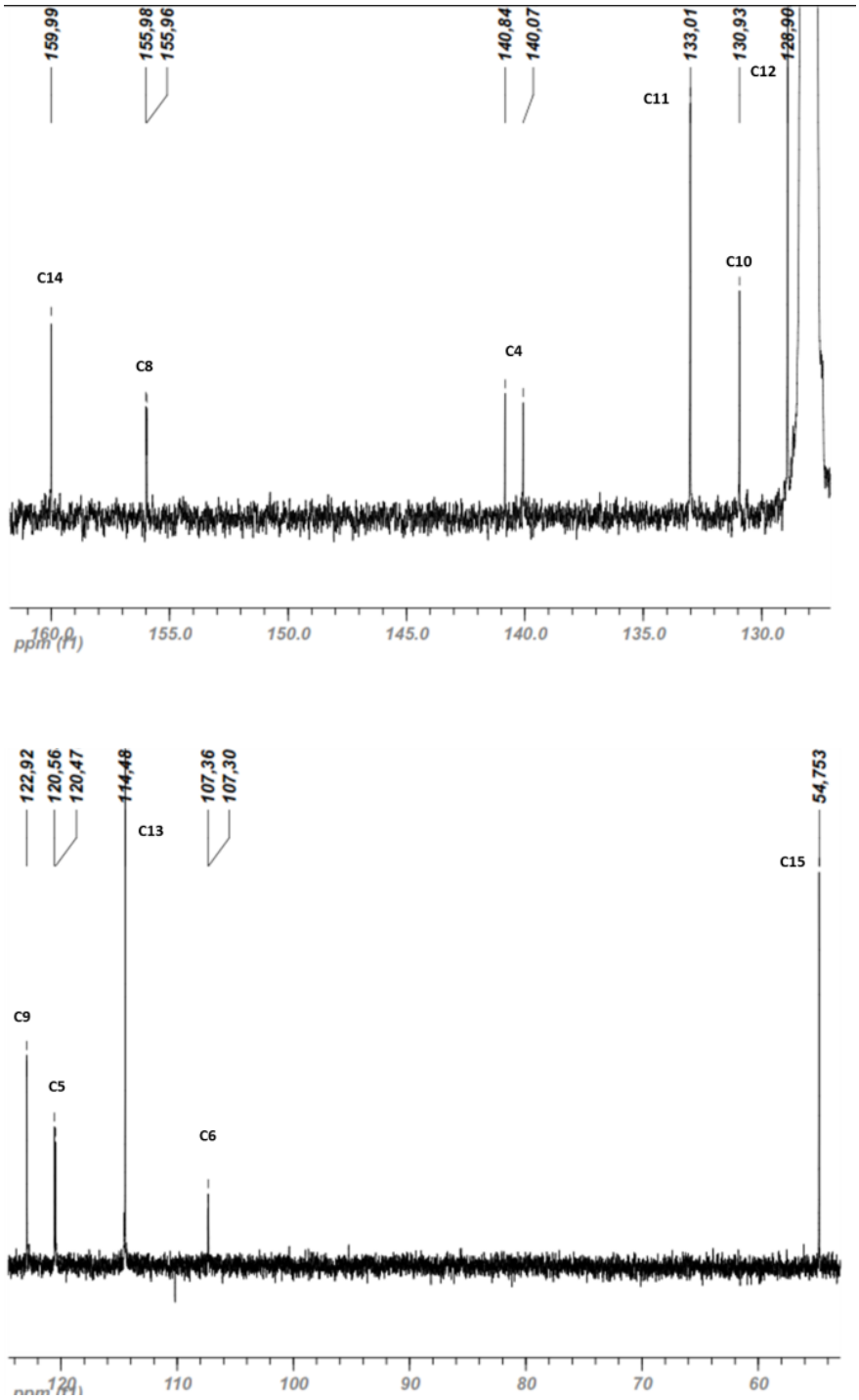


Figure S21-b: $^{13}C\{^{1}H\}$ NMR spectrum of **5-OMe**. (100.613 MHz, benzene-d_6) , select regions (continued) (* Denotes the presence of residual starting material $(Me_2PCH_2AlMe_2)_2$)

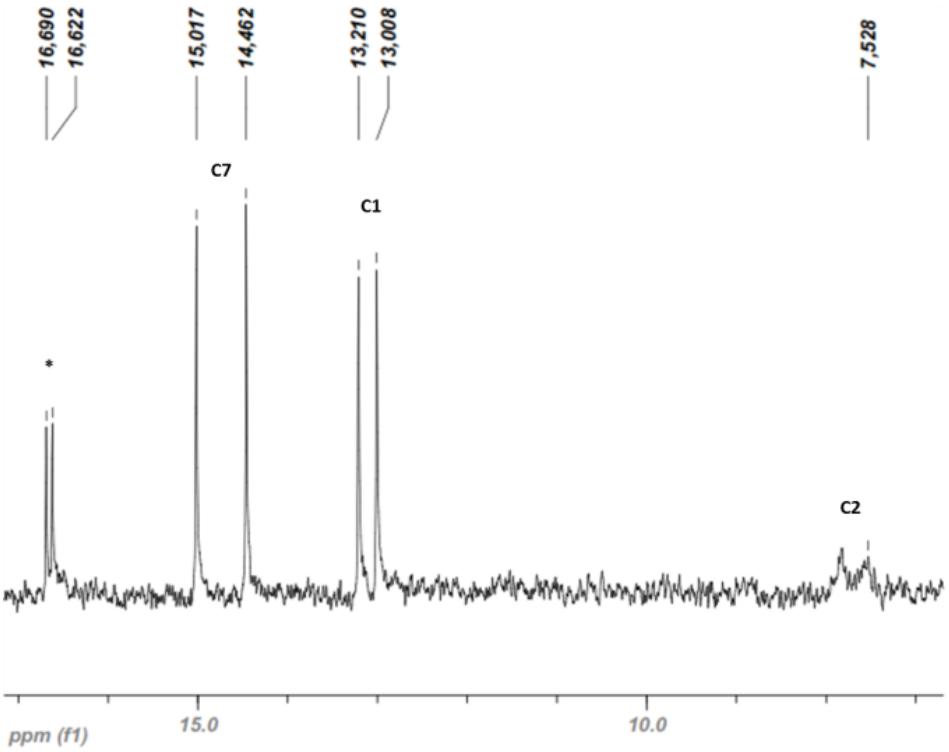
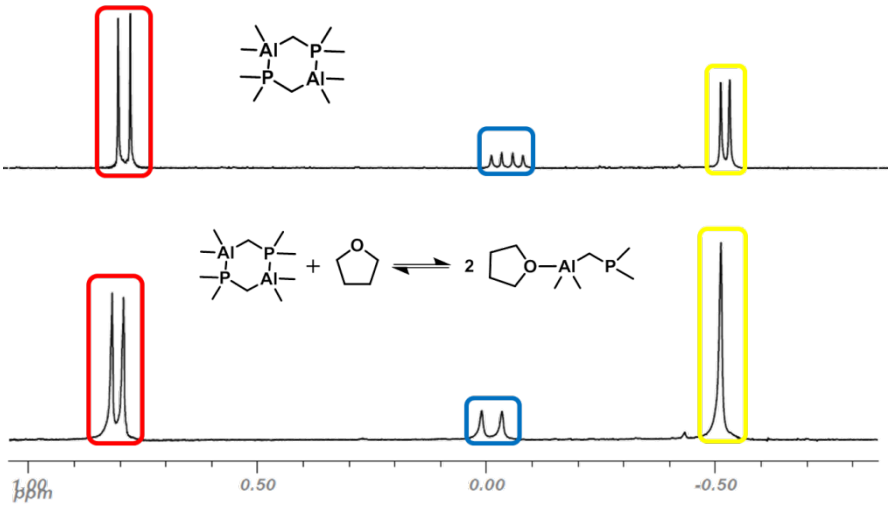


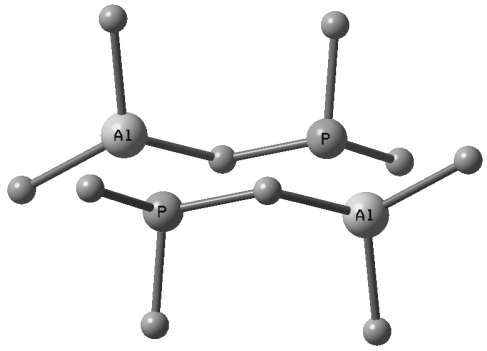
Fig. S22- ^{1}H NMR spectrum of **1 (**breaking of dimer with THF) **(**400 MHz, benzene-d_6)



3. Computational details

The density functional theory calculations were carried out with the B3LYP hybrid functional as implemented in the G03 program.[S3] B3LYP is Becke's three parameter functionals (B3[S4] with the non-local correlation provided by the LYP expression[S5] and VWN functional III for local correlation.[S6] The 6-31g(d,p) basis set was used for all atoms (a single set of first polarization functions were added to each atom).[S7] The geometry optimizations were performed without symmetry constraints. [S8] 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).[S9]

1



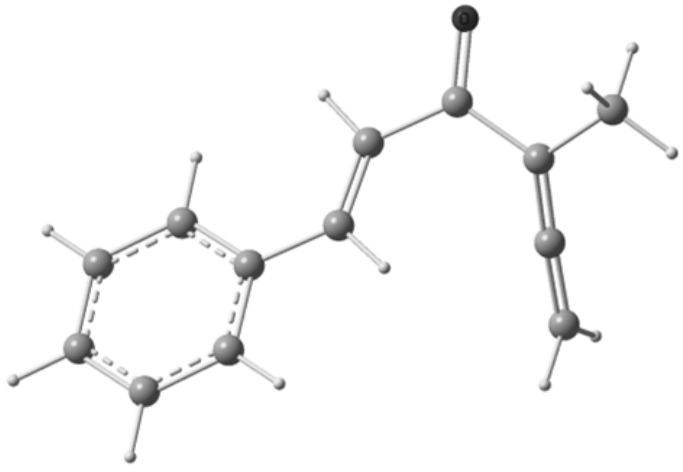
E(RB+HF-LYP) -1565.65878465 # im. Freq. = 0

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

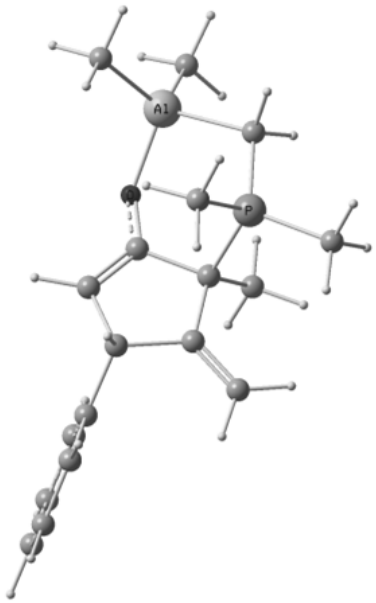


E(RB+HF-LYP) -577.78136393 # im. Freq. = 0

Sum of electronic and thermal free energies -577.614259

C	-2.18390700	-0.25234400	0.58382300
O	-1.55745500	0.63599700	1.15572600
C	-1.42543200	-1.44537900	0.06070200
C	-1.84580900	-2.15737200	-0.96435700
C	-2.21086000	-2.85806700	-2.00414900
H	-2.78968700	-3.77361800	-1.90360800
H	-1.95530300	-2.54608300	-3.01449500
C	-3.64866500	-0.11977500	0.43092200
H	-3.98903700	0.90253900	0.57334800
C	-4.52284000	-1.13300500	0.27448100
H	-4.12887800	-2.14359000	0.20968300
C	-5.98352800	-1.03729400	0.20385200
C	-6.73324400	-2.22553200	0.13487000
C	-6.67869300	0.18757800	0.19620600
C	-8.12437100	-2.19745300	0.06612500
H	-6.21209900	-3.17941500	0.13819800
C	-8.06713000	0.21606300	0.12693700
H	-6.12886600	1.12210700	0.24041700
C	-8.79687700	-0.97525200	0.06245000
H	-8.68207000	-3.12785800	0.01520600
H	-8.58524200	1.17050600	0.12153900
H	-9.88107700	-0.94795600	0.00835300
C	-0.06808900	-1.67782100	0.69274800
H	0.52816900	-0.76422300	0.62283000
H	-0.17551900	-1.90789700	1.75828100
H	0.45900300	-2.49899400	0.20418800

3

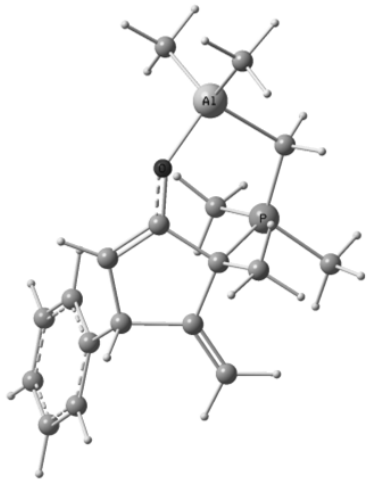


E(RB+HF-LYP) -1360.66636219 # im. Freq. = 0

Sum of electronic and thermal free energies -1360.330331

C	0.45200900	-0.85298800	-0.04782400
C	0.46007000	0.56974100	-0.65463400
C	-0.70478500	1.20533100	-0.40581600
C	-1.68685100	0.38016100	0.38860800
H	-0.92092600	2.21401500	-0.73711900
H	-1.80314400	0.78788600	1.40721000
C	-0.97441100	-0.98476000	0.48018600
C	-1.55318300	-2.11957200	0.87847900
H	-2.59786700	-2.13944100	1.17340000
H	-1.02932800	-3.07071000	0.88418600
O	1.51760800	0.99496500	-1.31420000
Al	3.22627400	1.20123900	-0.67953600
C	3.30339600	-0.41975800	0.67094000
H	3.69448700	-1.27591100	0.11020500
H	3.98667400	-0.20841500	1.50131800
P	1.71574000	-0.84378500	1.33030600
C	1.21641200	0.40438000	2.56266600
H	1.97743100	0.46057800	3.34509700
H	1.13076600	1.37760300	2.07658700
H	0.25766600	0.13153600	3.00870600
C	1.67019400	-2.44724700	2.22561700
H	0.66535700	-2.65738500	2.59833700
H	1.98841500	-3.25415900	1.56149400
H	2.36814600	-2.39559200	3.06588800
C	0.84336200	-1.92454100	-1.08597700
H	0.86127100	-2.93224000	-0.65948900
H	0.10344400	-1.91600300	-1.89047900
H	1.81889000	-1.70608900	-1.52606300
C	-3.09229600	0.28833100	-0.19631900
C	-4.21464100	0.37335000	0.63542200
C	-3.29097500	0.10619700	-1.57173000
C	-5.50589600	0.26990000	0.11250000
H	-4.07668600	0.53008100	1.70308800
C	-4.57738600	0.00396400	-2.09766800
H	-2.42668400	0.05701500	-2.22803700
C	-5.69077000	0.08349800	-1.25684500
H	-6.36429700	0.34193000	0.77460500
H	-4.71303500	-0.13333500	-3.16687200
H	-6.69312200	0.00751900	-1.66824200
C	4.51807800	0.84068000	-2.14083600
H	4.45256200	1.59436300	-2.93629600
H	5.55823000	0.85240000	-1.78734500
H	4.35868900	-0.13385100	-2.62173900
C	3.40911000	2.91055500	0.32505500
H	4.37072800	2.97273900	0.85382800
H	3.37599200	3.77123100	-0.35589100
H	2.62764000	3.08777000	1.07714400

3'



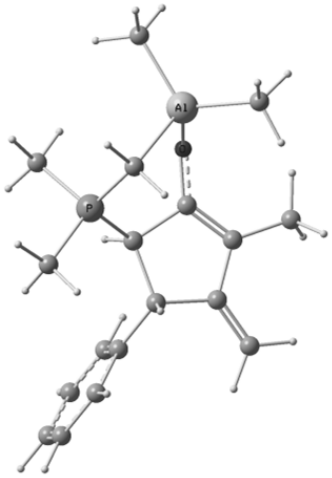
E(RB+HF-LYP) -1360.66479 # im. Freq. = 0

Sum of electronic and thermal free energies -1360.24897

C	-0.55321400	1.19135000	0.33046100
C	-0.59520100	-0.02202200	1.29029300
C	0.64319800	-0.33212100	1.73077700
C	1.72178600	0.57434700	1.20417300
H	0.83777300	-1.11906000	2.44981600
H	2.13491900	1.19711100	2.01452000
C	0.93822100	1.52171500	0.26639200
C	1.48352600	2.53638500	-0.40697900
H	2.55310900	2.71961400	-0.37558000
H	0.89493200	3.23322900	-0.99489600
O	-1.74310100	-0.56790500	1.62478300
Al	-3.19456800	-1.08902000	0.63711300
C	-2.95469500	0.13604200	-1.05767800
H	-3.30416300	-0.37909400	-1.95994600
H	-3.57062700	1.03001700	-0.91104000
P	-1.27132500	0.62953800	-1.30453400
C	-1.06503300	1.92787000	-2.58871600
H	-1.54889000	1.57507200	-3.50396500
H	-1.55610300	2.85167900	-2.27397600
H	-0.01021300	2.12447400	-2.78908900
C	-0.30474500	-0.78921700	-1.91286100
H	0.75684000	-0.53632400	-1.95062800
H	-0.45205400	-1.64045300	-1.24640500
H	-0.65456300	-1.05747600	-2.91334100
C	2.92160600	-0.10919800	0.54962400
C	4.17363800	0.52173400	0.54563700
C	2.81187200	-1.36697500	-0.05699400
C	5.27561900	-0.06902600	-0.07352800
H	4.28944000	1.48072900	1.04560900
C	3.91254000	-1.96387900	-0.67419700
H	1.85993400	-1.88725900	-0.02012900
C	5.14741700	-1.31404600	-0.69137500
H	6.23656800	0.43781200	-0.06320800

H	3.80682700	-2.94297600	-1.13347800
H	6.00507500	-1.77948100	-1.16823700
C	-3.01972800	-3.00002000	0.10582900
H	-3.10217900	-3.65994700	0.97945400
H	-3.81686100	-3.30444700	-0.58705500
H	-2.06913700	-3.25831000	-0.38160600
C	-4.86134000	-0.54164100	1.56384900
H	-5.75653200	-0.74678900	0.96071900
H	-4.99553800	-1.08027800	2.51089100
H	-4.88494800	0.52885200	1.80901600
C	-1.40181000	2.36314100	0.87683100
H	-0.98847200	2.67024900	1.84117900
H	-1.38113400	3.23260800	0.21212800
H	-2.43893400	2.06149100	1.04033000

4



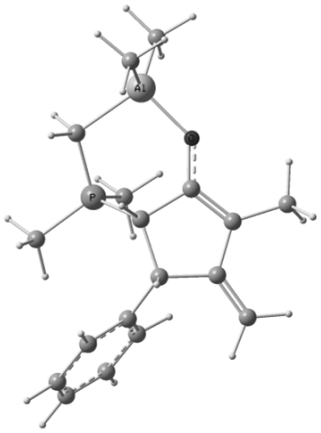
E(RB+HF-LYP) -1360.68504307 # im. Freq. = 0

Sum of electronic and thermal free energies -1360.351535

C	1.04278100	0.28853000	-0.99648400
C	0.18131900	-1.96461900	-1.29006300
C	-0.61408800	-1.38802900	-0.34348800
C	-0.09566000	0.00479200	0.02896900
H	0.67527200	0.98195600	-1.76529500
H	0.29250100	-0.00210200	1.05827600
C	2.29007900	0.90470700	-0.38909600
C	2.79227300	2.12210200	-0.86259900
C	2.97525800	0.26174700	0.65343100
C	3.93946000	2.69389500	-0.30599100
H	2.28613600	2.62613200	-1.68320100
C	4.11653100	0.83028600	1.21416700
H	2.62052900	-0.69976900	1.01517500
C	4.60233400	2.05130800	0.73789100

H	4.31264700	3.63871100	-0.69076100
H	4.63296400	0.31679100	2.02003800
H	5.49344800	2.49247000	1.17440400
C	1.25730600	-1.07336800	-1.68612500
C	2.26682100	-1.32462500	-2.53620100
H	2.36593700	-2.28834500	-3.02427400
H	3.02589800	-0.58087600	-2.75445200
C	-0.00456100	-3.34627900	-1.83484300
H	-0.13725700	-3.33310700	-2.92432700
H	0.87002400	-3.97697600	-1.62968300
H	-0.88084000	-3.81836400	-1.38525600
O	-1.68603200	-1.89293300	0.21886900
Al	-2.89853400	-1.30702100	1.47274800
C	-2.52771700	0.77065100	1.44410200
H	-3.46346700	1.33740400	1.39061500
H	-2.01329500	1.02720400	2.37746700
P	-1.48222300	1.21202700	0.08974300
C	-2.40659600	1.10745000	-1.47860200
H	-3.22937700	1.82669700	-1.46791600
H	-1.75156900	1.32314200	-2.32586900
H	-2.81147300	0.09907900	-1.58394700
C	-0.78371200	2.90617400	0.16996000
H	-0.15961200	3.12351600	-0.69986900
H	-1.60231700	3.62940200	0.22133800
H	-0.17197100	3.00120900	1.07053100
C	-2.42011500	-1.98123200	3.27778300
H	-3.07268400	-1.56587000	4.05824800
H	-2.51261200	-3.07295800	3.34372100
H	-1.38876000	-1.73844200	3.56859400
C	-4.72228500	-1.65957500	0.77176500
H	-4.91448000	-2.73492900	0.66447000
H	-5.50109000	-1.27106600	1.44245000
H	-4.90815300	-1.21295900	-0.21489400

4’



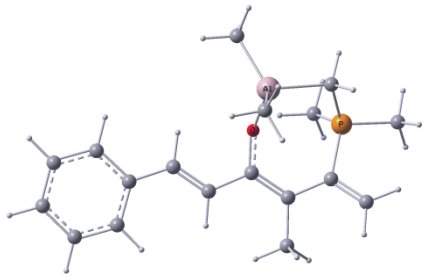
E(RB+HF-LYP) -1360.68000 # im. Freq. = 0

Sum of electronic and thermal free energies -1360.34334

C	0.86535000	1.92321100	-1.20068900

C	1.32695400	0.75057800	-0.67704200
C	0.23168200	-0.32659700	-0.66758600
C	-0.96222400	0.34965000	-1.43814900
H	-0.94841900	-0.11349700	-2.43198400
C	-0.51723100	1.80826600	-1.61963400
C	-1.29372800	2.77344100	-2.14413300
H	-2.32253500	2.58670200	-2.43250900
H	-0.91204300	3.77619400	-2.30428400
O	2.51959300	0.52379600	-0.18459100
Al	3.30653200	-0.91485900	0.65288300
C	1.59161500	-1.92668500	1.31715500
H	1.50542800	-2.85536000	0.73959900
H	1.67115100	-2.18873900	2.37850300
P	0.10409800	-0.99237800	1.06695300
C	0.03541100	0.38999200	2.25283700
H	0.09598800	-0.00653100	3.26966300
H	0.88413300	1.05246300	2.07392900
H	-0.89692300	0.94441800	2.13434300
C	-1.39770600	-2.00488600	1.35825200
H	-2.30704600	-1.40426100	1.37965500
H	-1.48617900	-2.76214900	0.57596200
H	-1.26395600	-2.51221100	2.31866000
C	1.68278400	3.16928400	-1.34073300
H	1.75153500	3.48617200	-2.38915100
H	1.23742500	4.00558400	-0.78592400
H	2.69404200	3.00516300	-0.96267700
C	-2.36648000	0.14731300	-0.89445900
C	-2.91611800	0.99223000	0.08198900
C	-3.14995000	-0.91510700	-1.36660600
C	-4.19258300	0.75686300	0.59588400
H	-2.35190700	1.85939600	0.41031500
C	-4.42834200	-1.15170400	-0.85935600
H	-2.75224500	-1.56395800	-2.14364900
C	-4.95130800	-0.32048800	0.13251600
H	-4.60079000	1.42513000	1.34888500
H	-5.01716500	-1.97974000	-1.24344100
H	-5.94699100	-0.49886500	0.52754300
C	4.23649200	-2.07289100	-0.66711600
H	5.09948700	-1.56680600	-1.11876900
H	4.62240800	-2.99290000	-0.20620700
H	3.59031000	-2.38659400	-1.49878100
C	4.34056800	-0.23134100	2.20360800
H	4.77202300	-1.04787500	2.79911300
H	5.18286300	0.39607000	1.88418600
H	3.74430700	0.37955800	2.89526600
H	0.57535800	-1.21594000	-1.21544600

5



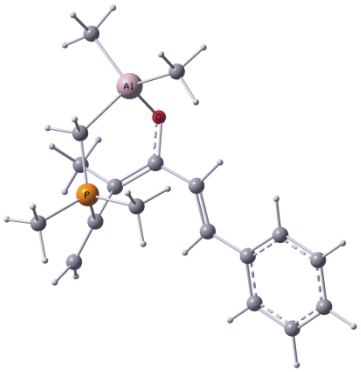
E(RB+HF-LYP) -1360.6622324 # im. Freq. = 0

Sum of electronic and thermal free energies -1360.33159

C	-2.13064400	-1.43440600	-0.34038300
C	-1.30017100	-0.42679600	0.12008700
C	-1.77935400	0.68089400	0.95220600
H	-2.82131900	0.68388900	1.24533100
C	-0.96688400	1.67750100	1.36536100
H	0.07303600	1.62902700	1.05263300
C	-3.59290000	-1.52041300	0.04350500
H	-3.77723400	-2.30108800	0.79458400
H	-3.97839800	-0.58784200	0.45137000
H	-4.20929300	-1.76813700	-0.82890000
C	-1.65142700	-2.54434200	-1.17551000
C	-2.36244300	-3.68940200	-1.33855500
H	-3.28669400	-3.85755700	-0.79938800
H	-2.04772400	-4.49867700	-1.98289000
C	-1.32813700	2.82887800	2.19338200
C	-0.31721000	3.73807100	2.55893600
C	-2.63725100	3.08391000	2.64937500
C	-0.59611100	4.85141900	3.34829700
H	0.69869000	3.55838200	2.21727800
C	-2.91636000	4.19547000	3.43702500
H	-3.44400500	2.40794400	2.38338000
C	-1.89800000	5.08576500	3.79187900
H	0.20338100	5.53567500	3.61747000
H	-3.93312900	4.37117300	3.77691600
H	-2.11985700	5.95262700	4.40727800
O	-0.01181500	-0.38435900	-0.20109700
P	-0.09574500	-2.46734500	-2.15401600
C	-0.01984300	-0.91211700	-3.10949600
H	0.02460100	-0.06876200	-2.42292300
H	0.87659700	-0.92833400	-3.73603000
H	-0.90221900	-0.83773800	-3.75011600
C	-0.22930000	-3.73062900	-3.48855400
H	-1.14414500	-3.61310900	-4.07400400
H	0.63565100	-3.59472600	-4.14407600
H	-0.18456100	-4.74116800	-3.07843900
C	1.37697800	-2.74344100	-1.19542000
Al	1.46839100	-1.34516500	0.33825600

C	1.16698900	-2.21615900	2.09864500
H	1.99025900	-2.89707800	2.35589400
H	1.10246100	-1.48630300	2.91605100
H	0.24471000	-2.81090700	2.13574600
C	3.05685800	-0.17396300	0.10634700
H	3.09752500	0.30561100	-0.88131400
H	3.08444300	0.63636300	0.84709500
H	3.99783100	-0.72913600	0.22339800
H	2.23738600	-2.68016500	-1.87281900
H	1.32223700	-3.76333100	-0.79704500

5'



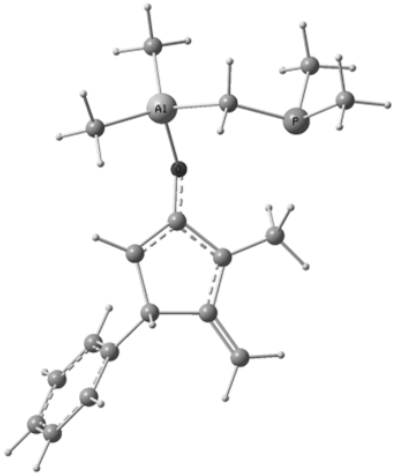
E(RB+HF-LYP) -1360.62109954 # im. Freq. = 0

Sum of electronic and thermal free energies -1360.331590

C	-2.18390700	-0.25234400	0.58382300
O	-1.55745500	0.63599700	1.15572600
C	-1.42543200	-1.44537900	0.06070200
C	-1.84580900	-2.15737200	-0.96435700
C	-3.01216691	-2.69583236	-1.19903294
H	-3.56142553	-3.23178097	-0.42802264
H	-3.48338789	-2.62082832	-2.17666662
C	-3.64866500	-0.11977500	0.43092200
H	-3.98903700	0.90253900	0.57334800
C	-4.52284000	-1.13300500	0.27448100
H	-4.12887800	-2.14359000	0.20968300
C	-5.98352800	-1.03729400	0.20385200
C	-6.73324400	-2.22553200	0.13487000
C	-6.67869300	0.18757800	0.19620600
C	-8.12437100	-2.19745300	0.06612500
H	-6.21209900	-3.17941500	0.13819800
C	-8.06713000	0.21606300	0.12693700
H	-6.12886600	1.12210700	0.24041700
C	-8.79687700	-0.97525200	0.06245000
H	-8.68207000	-3.12785800	0.01520600
H	-8.58524200	1.17050600	0.12153900
H	-9.88107700	-0.94795600	0.00835300
C	-0.06808900	-1.67782100	0.69274800
H	0.52816900	-0.76422300	0.62283000
H	-0.17551900	-1.90789700	1.75828100
H	0.45900300	-2.49899400	0.20418800

P	-0.14829374	-1.98296613	-1.72916060
C	0.56231401	-0.30881104	-1.29425675
H	1.13355692	-0.38704232	-0.39289034
H	1.19460481	0.02769483	-2.08916061
Al	-0.69216770	1.44164810	-0.38239109
C	-0.06114482	3.33981680	-0.10102705
H	0.44633839	3.68082974	-0.97913353
H	-0.90349198	3.97081832	0.09181577
H	0.60797371	3.37326751	0.73327592
C	-2.04341300	1.66431989	-1.86729966
H	-2.87988036	2.22598988	-1.50709255
H	-1.59110176	2.18364255	-2.68621266
H	-2.37501520	0.70127702	-2.19515392
C	0.97325961	-3.32643012	-1.07028081
H	1.33776761	-3.91773493	-1.88415583
H	1.79868213	-2.88117892	-0.55517981
H	0.42507322	-3.94909625	-0.39450083
C	-0.28294031	-2.13925137	-3.58774749
H	0.67509183	-1.96373241	-4.03076839
H	-0.61733733	-3.12396515	-3.83957560
H	-0.98361919	-1.41948170	-3.95636753

INT



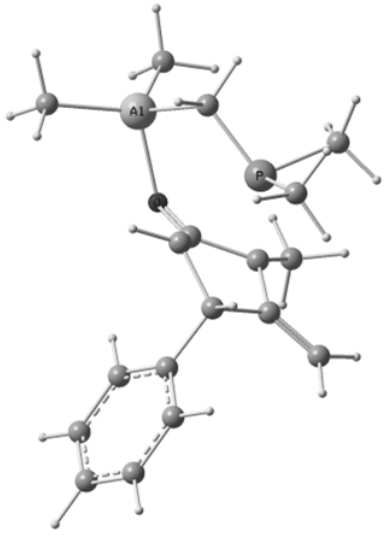
E(RB+HF-LYP) -1360.61534551 # im. Freq. = 0

Sum of electronic and thermal free energies -1360.286827

C	2.14921500	-0.42747500	-0.74437100
C	0.35121200	-1.26453600	0.61474300
C	0.09576900	0.13790300	0.38355000
C	1.14233200	0.62211700	-0.40589600
H	2.11979100	-0.62720800	-1.82747000
H	1.21096100	1.64530700	-0.75648600
C	3.58887700	-0.06860200	-0.38782400
C	4.60439300	-0.18980400	-1.34167300

C	3.91615600	0.38171200	0.89873000
C	5.92584200	0.12523100	-1.01767700
H	4.36109700	-0.52761700	-2.34607700
C	5.23394700	0.69692000	1.22292800
H	3.13491700	0.48661700	1.64659200
C	6.24340600	0.56882600	0.26543300
H	6.70305100	0.02708100	-1.76975800
H	5.47332400	1.04600000	2.22299900
H	7.26960700	0.81728300	0.51867700
C	1.58167100	-1.65059400	-0.01861300
C	2.14500700	-2.87463600	0.00481700
H	1.69134200	-3.70237400	0.53979000
H	3.08583700	-3.06829700	-0.50050300
C	-0.62486000	-2.09710500	1.31089600
H	-1.57385100	-2.07823700	0.70889800
H	-0.30731300	-3.12636000	1.48164800
H	-0.92257300	-1.61801300	2.25074300
O	-0.94092500	0.74468500	0.85212500
Al	-2.23325100	1.85414000	0.01943300
C	-3.42880100	0.52742400	-0.97429200
H	-4.39539700	1.01685400	-1.17548500
H	-2.96130600	0.34914500	-1.95364800
P	-3.73360700	-1.12289800	-0.23493300
C	-4.74627400	-0.72040500	1.27225000
H	-5.59163300	-0.06802400	1.02583600
H	-5.13040200	-1.64049300	1.72370800
H	-4.12144500	-0.20797600	2.00773300
C	-5.05805900	-1.89091700	-1.30558700
H	-5.39622600	-2.83877700	-0.87370700
H	-5.92165300	-1.22512800	-1.41927300
H	-4.64763900	-2.09836100	-2.29837600
C	-1.26845200	3.01142900	-1.30155300
H	-1.97723700	3.68833400	-1.79971700
H	-0.51273400	3.65934600	-0.83450700
H	-0.76528200	2.46206200	-2.11065400
C	-3.09931200	2.81595700	1.53067300
H	-2.40536400	3.51545400	2.01644700
H	-3.95681500	3.41585900	1.19527100
H	-3.47608000	2.15293700	2.32053400

TS_{3-4}



E(RB+HF-LYP) -1360.57826 # im. Freq. = 1

Sum of electronic and thermal free energies -1360.24382

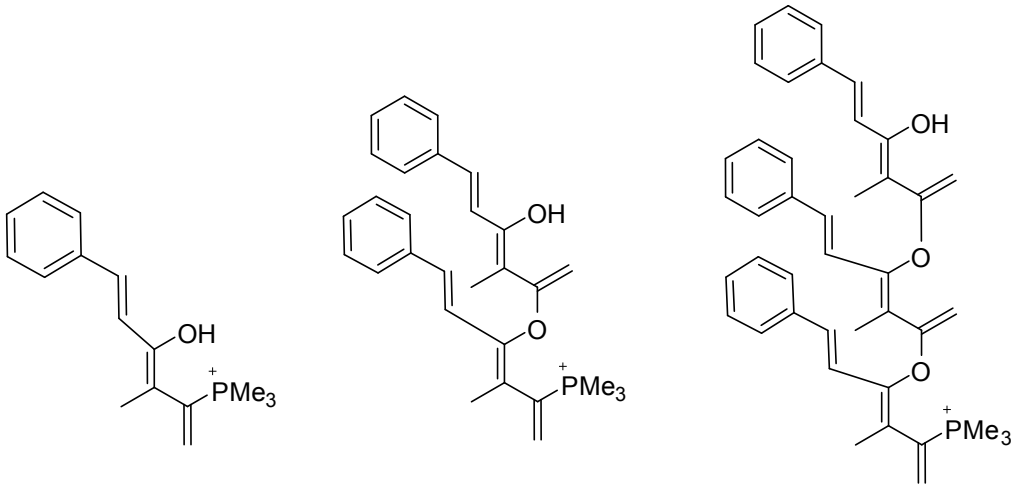
C	-0.25195900	-0.98810700	1.15652700
C	-0.43839700	0.33521600	0.54816900
C	0.15097500	0.19665000	-0.78639400
C	1.42252400	-0.63717200	-0.57831900
H	0.16175600	1.04608600	-1.46340900
H	1.63496200	-1.26994400	-1.44486100
C	1.02135700	-1.52216600	0.62969100
C	1.71019400	-2.57417000	1.09567800
H	2.64842400	-2.87871000	0.64302200
H	1.37780800	-3.13673800	1.96217100
O	-1.24999700	1.21314800	0.96164600
Al	-2.80801500	1.65163300	-0.10122500
C	-2.66056400	-0.05544200	-1.28741900
H	-3.63696600	-0.54456200	-1.35907300
H	-2.35217300	0.31013400	-2.27307300
P	-1.42924100	-1.24260500	-0.73838200
C	-0.68730700	-2.34776300	-2.02309700
H	-1.49706300	-2.95805400	-2.43158700
H	-0.22479300	-1.76109300	-2.81708800
H	0.05343600	-3.01009600	-1.56763800
C	-2.53924900	-2.54092200	0.07274500
H	-1.93929800	-3.35558500	0.48744600
H	-3.11969700	-2.08415600	0.87803800
H	-3.23426500	-2.95263300	-0.66696100
C	-0.78978600	-1.34369500	2.51065700
H	-1.02179000	-2.41012100	2.58705900
H	-0.04765200	-1.11825300	3.28766600
H	-1.69539600	-0.77472200	2.73496700
C	2.68591400	0.17929300	-0.31289200

C	3.90506900	-0.24372600	-0.85783400
C	2.67737400	1.33462600	0.48036300
C	5.08591200	0.45819800	-0.61201300
H	3.92906300	-1.13028600	-1.48713800
C	3.85564100	2.03763700	0.72978700
H	1.74483700	1.69932100	0.90139800
C	5.06527500	1.60214100	0.18541800
H	6.01893500	0.11381300	-1.04912900
H	3.82667000	2.93127900	1.34659100
H	5.98116800	2.15361600	0.37615200
C	-4.33008500	1.60930400	1.16468800
H	-4.23654800	2.38349700	1.93711000
H	-5.28461700	1.79456800	0.65383200
H	-4.43521100	0.65088000	1.68953100
C	-2.46570300	3.30179700	-1.14136300
H	-3.29480000	3.52260400	-1.82755200
H	-2.36070900	4.17971600	-0.49113100
H	-1.55640600	3.25192700	-1.75421600

c. HRMS and hydrolysis study

10^+, 11^+ and 12^+ (+ RMN)

Attemps to obtain HRMS data for products **3**, **4** and **5** afforded product $\mathbf{10}^+$ due to hydrolysis of the aluminum moeity. In fact, addition of water to **4** led to the obtention of b-Me (see $\mathbf{10}^+$). The presence of $\mathbf{10}^+$ in solution afforded polymerization to products $\mathbf{11}^+$ and $\mathbf{12}^+$ preventing the acquisition of suitable elemental analysis data.



10+ **11+** **12+**

$\mathbf{10}^+$: To a solution of 4a-Me (0.03 mmol) in 1 mL of C_6D_6 was added 0.5 µL of water (0.03 mmol). A precipitate immediatly formed (most probably a mixture of insoluble aluminum oxides/hydroxides) while product 6-Me remained in solution, allowing it's caracterisation:

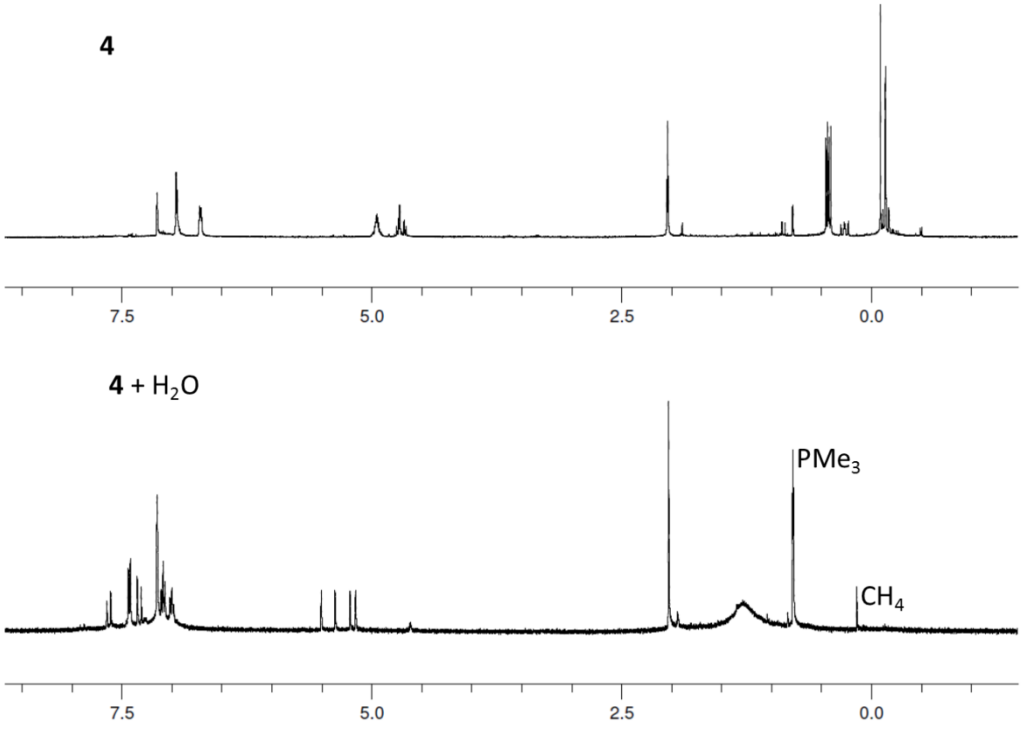
^{1}H NMR (400 MHz, **fig. S23**): δ 7.63 (d, $^3J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.33 (d, $^3J_{H\text{-}H}$ = 15.4 Hz, 1H), 7.12 – 6.96 (m, 3H), 5.44 (d, $^3J_{H\text{-}P}$ = 55.2 Hz, 1H), 5.19 (d, $^3J_{H\text{-}P}$ = 22.5 Hz, 1H), 2.03 (s, 2H), 1.16 (very broad, OH)

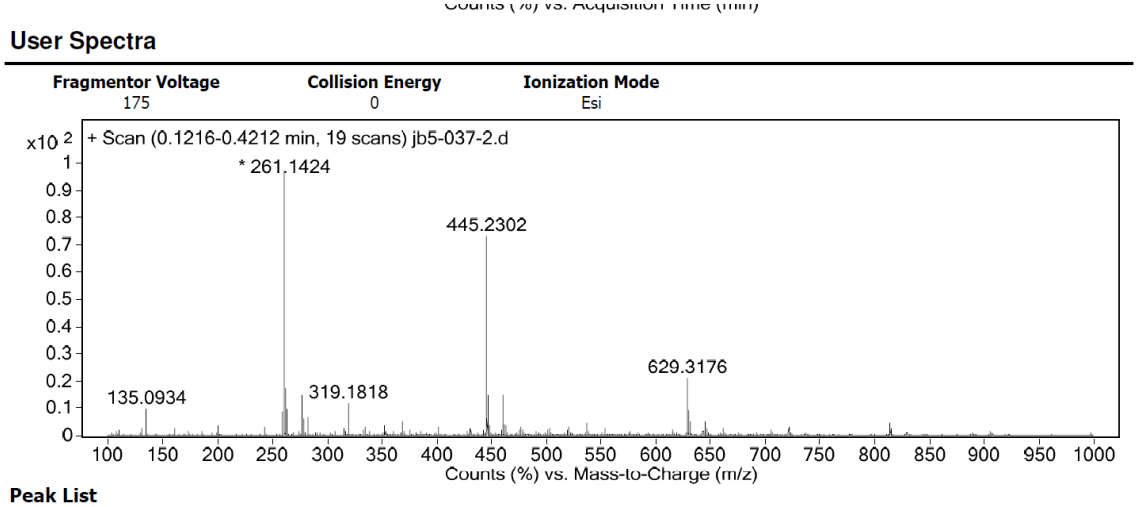
jb05-037 HRMS (**fig. S24**)

10^+: calcd: 261.1403 obtained: 261.1424 (error 8 ppm) (saturated peak)

11^+: calcd: 445.2291 obtained: (error 2.5 ppm)

12^+: calcd: 629.3179 obtained: 629.3176 (error0.5 ppm)





Peak List

m/z	z	Abund
261.1424	1	1327227
261.3412		145796
262.1439	1	242919
277.1355		199711
319.1818		154288
445.2302	4	969125
446.2326	1	295584
447.2372	1	196900
461.2251		206823
629.3176	1	290594

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