Supporting Information for

Heterometallic aluminates: alkali metals trapped by an aluminium aryloxide claw.

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Diffusion-Ordered NMR Spectroscopy (DOSY) experiments

In Diffusion-Ordered NMR Spectroscopy (DOSY) experiments, a series of pulsed field gradient (PFG) stimulated echo experiments is performed and the results allow to generate a two dimensional spectrum where signals are dispersed depending on their diffusion coefficients.[1]

The diffusion coefficient (D) of a molecule is inversely proportional to its hydrodynamic radius as given in the Stokes-Einstein equation: $D = kT/(6\pi\eta r_H)$, from where the relation between the diffusion coefficient of a molecule, D, and its volume, V, can be easily linearized by taking the logarithm of both sides: $\log D = A\cdot\log V + B$. In previous studies,[2] we have observed that, for these kind of heterometallic aryloxide derivatives, the results were equivalents when plotting D *vs* V and D *vs* FW. Hence, considering the approximation that the FW is proportional to the volume for this kind of derivatives, we used the equation $\log D = A'\cdot\log FW + B'$ to calculate the FW of **3b** and **3c** in solution.

The DOSY experiments are very sensitive to experimental conditions and temperature fluctuation, convention and viscosity change produce variations on the diffusion coefficient value from one experiment to another for the same particle.[3,4] This problem can be overcome by using internal standards of known size. As such, by measuring their diffusion coefficients in the same experiment as the compound we are interested in, it will be possible to generate a calibration curve giving information on the size of the compound in solution.[4,5] It has been generally accepted that when the r^2 value for the calibration curve is higher than 0.97, the typical error between the experimental FW and the theoretical one would be from -10% to +10%.[6]

^{1}H DOSY of 3b and 3c in the presence of internal standards:

All NMR experiments were carried out on a Bruker AV400 spectrometer equipped with a probe PABBO BB-1H/D Z-GRD. 2D DOSY experiments were recorded under routine conditions at 298K with the bipolar-gradient LED (BPLED)[7] pulse sequence using a diffusion time of 100 ms and a LED delay of 5 ms. For each experiment, sine-shaped PFGs, with a duration of 1.5 ms followed by a recovery delay of 100 μs were incremented from 2% to 95% of the maximum strength in 16 equally spaced steps.

Diffusion coefficients were calculated by fitting intensity data to the Stejskal-Tanner expression with estimates of errors taken from the variability in the calculated diffusion coefficients by consideration of different NMR responses for the same molecules of interest.

In our case, the internal standards chosen were the compounds: 1,2,3,4-tetraphenylnaphthlene-TPhN (432.55 g mol^{-1}); 1-phenylnaphthalene-PhN (204.27 g mol^{-1}) and tetramethylsilane-TMS (82.22 g mol^{-1}).

Figures S1 and S2 show the DOSY experiment of the mixture of compounds **3b** and **3c**, respectively, with the internal standards that allow the determination of the translational self-diffusion coefficients (D) for all species in solution. Figures S3 and S4 show the correlation diagrams between log D and log FW for the internal standard, and as we can observe, r^2 values are higher than 0.98, so we can apply these calibration curves in order to obtain the average size of each compound.

Figure S1. 2D DOSY NMR experiment of the mixture of TMS, PhN, TPhN and **3b** in C_6D_6. The x- and y-axis represent the regular ^{1}H chemical shift and the relative diffusion rate, respectively.

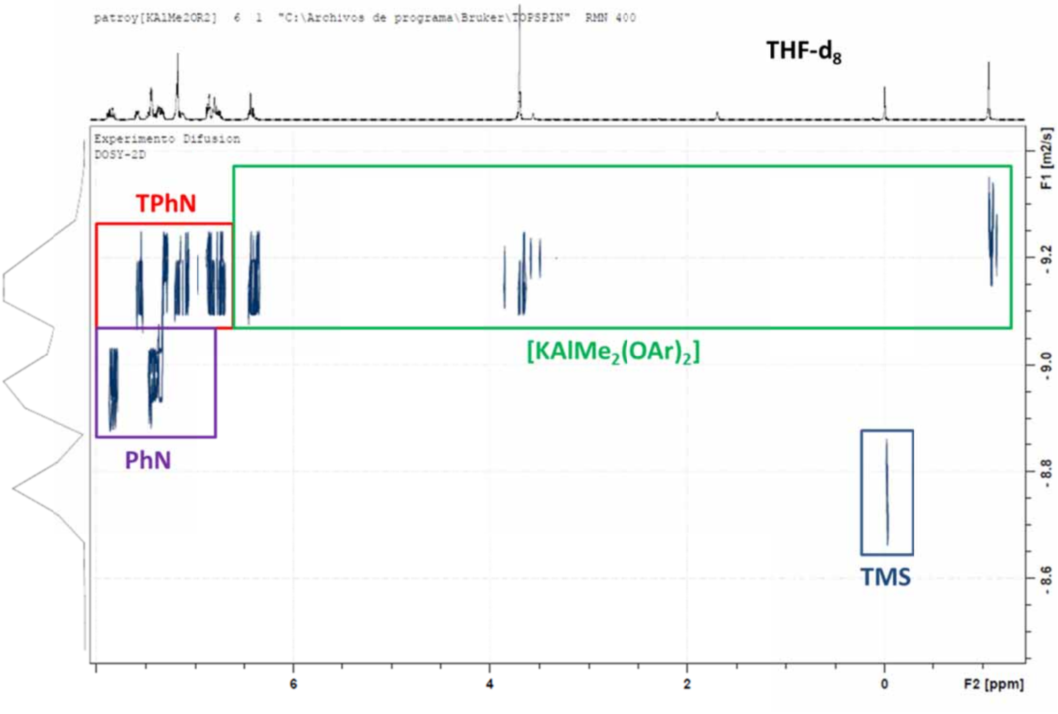
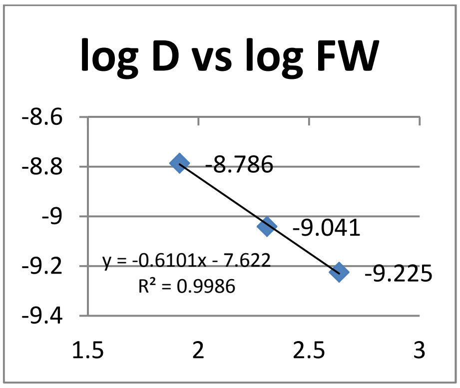
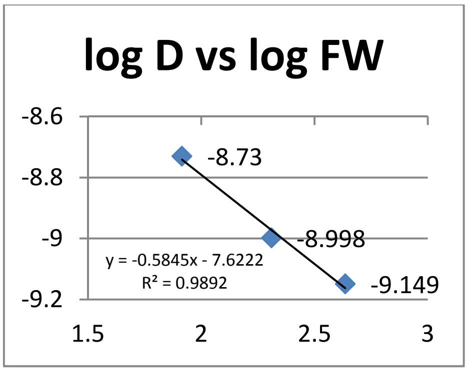


Figure S2. 2D DOSY NMR experiment of the mixture of TMS, PhN, TPhN and **3c** in THF-d_8. The x- and y-axis represent the regular ^{1}H chemical shift and the relative diffusion rate, respectively.



	TMS	PhN	TPhN	**3b**
log D	-8.786	-9.041	-9.225	-9.252
log FW	1.915	2.310	2.636	

Figure S3. Log *D* – log FW representation from the ^{1}H-DOSY data obtained for the mixture of **3b,** TPhN, PhN and TMS in C_6D_6 (data for **3b** is not included)



	TMS	PhN	TPhN	**3c**
log D	-8,73	-8,998	-9,149	-9,143
log FW	1,915	2,310	2,636	

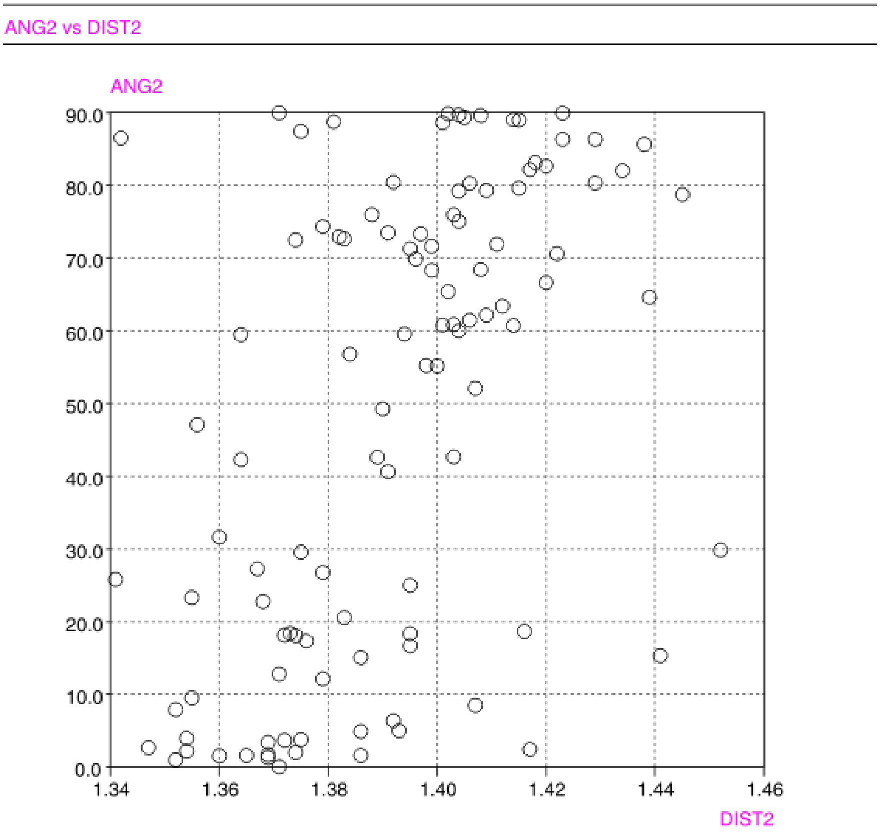
Figure S4. Log *D* – log FW representation from the ^{1}H-DOSY data obtained for the mixture of **3c,** TPhN, PhN and TMS in C_6D_6 (data for **3c** is not included)

Table S1. D-FW analysis of ^{1}H DOSY data for **3b** and **3c**.

Compound	FW (g mol^{-1})	log D	Predicted FW (g mol^{-1})	% error
$3b\cdot C_7H_8$	470	- 9.103	478.29	1.7%
3c	400	- 9.143	402.40	0.6%

As shown in table S1, the ^{1}H DOSY data indicates that compounds **3b** and **3c** are heterobimetallic in solution [$AlMMe_2(OR)_2$] (M = Na, K; R = 2,6-$(MeO)_2C_6H_3O$), being **3b** solvated by a toluene molecule. Previous studies for the lithium-aluminium counterpart gave a tetrametallic structure [$AlLiMe_2(OR)_2$]$_2$ in solution.[2]

Figure S5. Vista scatterogram plot of Al-O distance (DIST2) *vs* dihedral angle between the Al_2O_2 plane and a phenyl ring (ANG2). CSD search performed for $(AlOAr)_2$ derivatives, 106 observations.



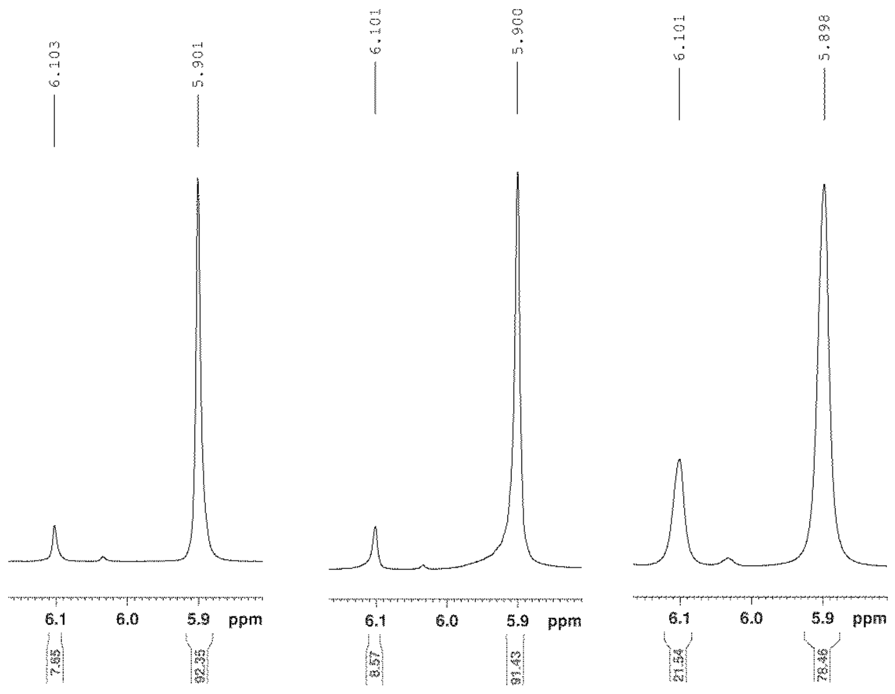
Study of the reactivity of $[AlMMe_2\{2,6\text{-}(MeO)_2C_6H_3O\}_2]_2$ (M = Li, Na (3b), K (3c)) compounds towards $[ZrCp_2Cl_2]$.

In a typical procedure $[ZrCp_2Cl_2]$ (0.02 g, 68.42 µmol) and an equimolecular amount of the heterometallic derivative (0.025 g, 68.42 µmol for $[AlLiMe_2\{2,6\text{-}(MeO)_2C_6H_3O\}_2]_2$; 0.026 g, 68.42 µmol for **3b;**0.028 g, 68.42 µmol for **3c**) were dissolved in 0.5 mL of deuterated benzene in a Teflon valvulated NMR tube. The reaction progress was followed at various times (figures S7-S9). In figure S6 an expansion of the area for the hydrogen atoms from the Cp rings for $[ZrCp_2Cl_2]$ and $[ZrCp_2Cl(OAr)]$, that include the integral values, is shown for the comparison of the reaction progress for the three heterometallic compounds.

Spectroscopic data

Table S2. ^{1}H NMR data for **2, 3**, [$ZrCp_2Cl(OAr)$] and [$ZrCp_2Cl_2$] in C_6D_6. δ (ppm), J (Hz).

	2	**[$LiAlMe_2\{OAr\}_2]_2$**	**3b**	**3c**	**[$ZrCp_2Cl(OAr)$]**	**[$ZrCp_2Cl_2$]**
Cp					6.19 (s, 10H)	5.90 (s, 10H)
AlCH_3	-0.27 (s, 6H)	-0.50 (s, 3H)	-0.49 (s, 3H)	-0.50 (s, 3H)		
OCH_3	3.38 (s, 6H)	3.36 (s, 6H)	3.40 (s, 6H)	3.35 (s, 6H)	3.45 (s, 6H)	
m-OAr,	6.24 (d, 2H, J = 8)	6.31 (d, 2H, J = 8)	6.29 (d, 2H, J = 8)	6.30 (d, 2H)	6.40 (d, 2H, J = 8)	
p-OAr,	6.65 (t, 1H, J = 8)	6.64 (t, 1H, J = 8)	6.56 (t, 1H, J = 8)	6.48 (t, 1H)	6.72 (t, 1H, J = 8)	



a) b) c).

Figure S6. Expansion of the area for the hydrogen atoms from the Cp rings for [$ZrCp_2Cl_2$] and [$ZrCp_2Cl(OAr)$]. Integral values are included for the comparison of the reaction progress. a) [$AlLiMe_2\{2,6\text{-}(MeO)_2C_6H_3O\}_2]_2$; b) **3b**; c) **3c**.

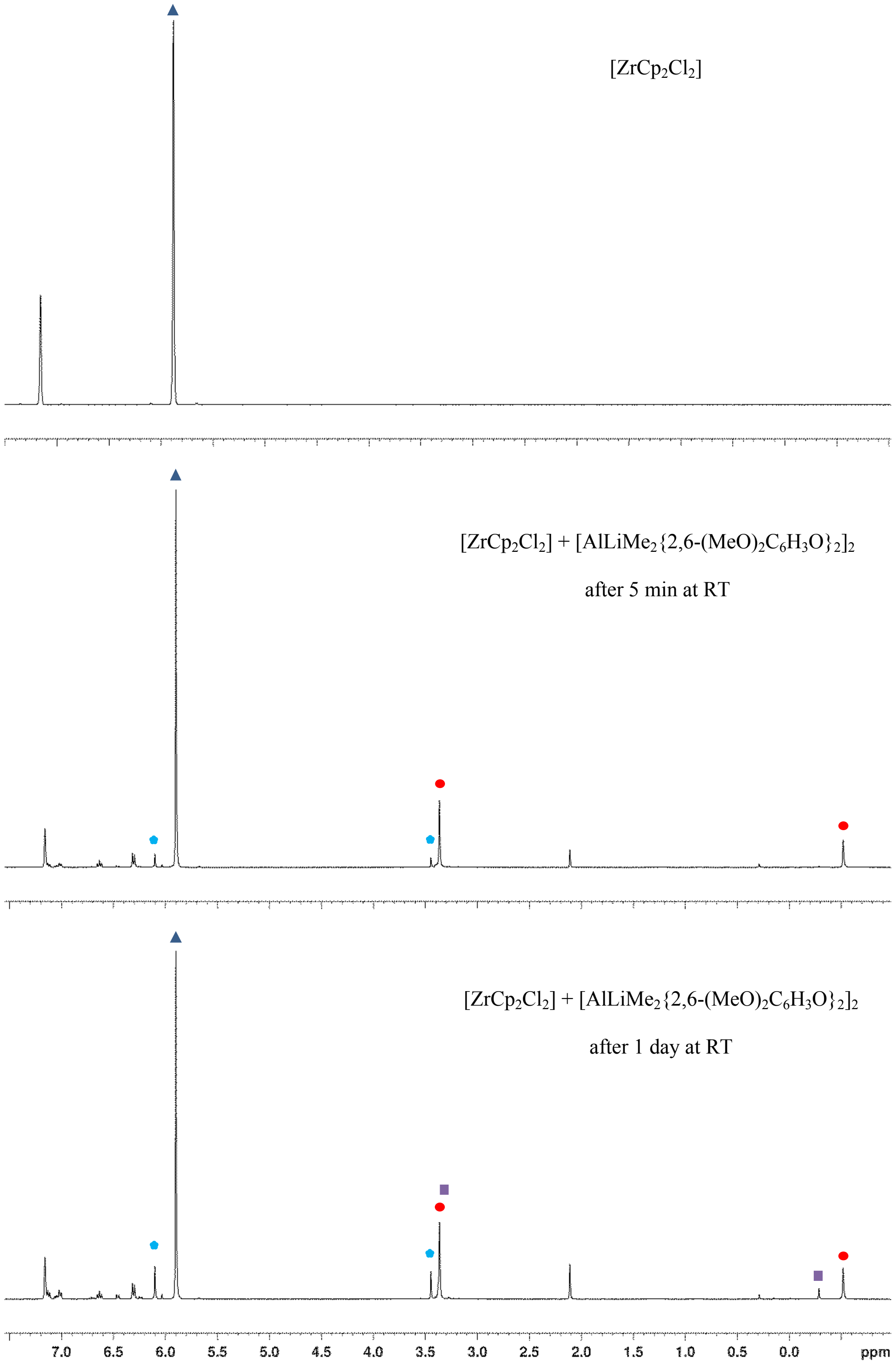


Figure S7. ^{1}H NMR spectra of the evolution of the reaction of [AlLiMe$_2${2,6-(MeO)$_2$C$_6$H$_3$O}$_2$]$_2$ with [ZrCp$_2$Cl$_2$]. The resonances for the OMe, Cp and Al-Me groups have been marked with the following code: Blue triangle: [ZrCp$_2$Cl$_2$], Blue star: [ZrCp$_2$Cl(OAr)], red dot: [AlLiMe$_2${2,6-(MeO)$_2$C$_6$H$_3$O}$_2$]$_2$; Violet square: **2**.

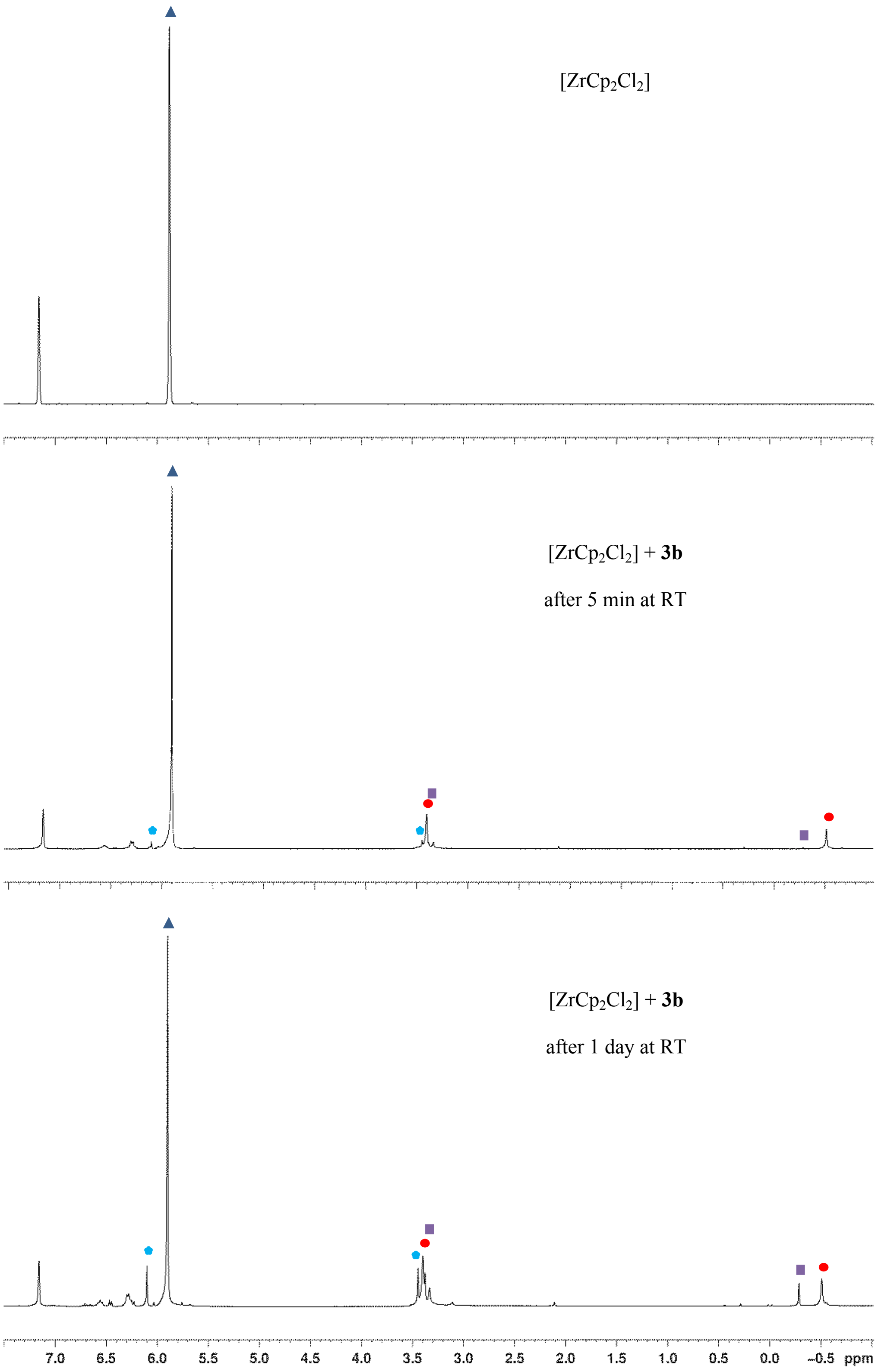


Figure S8. ^{1}H NMR spectra of the evolution of the reaction of $[AlNaMe_2\{2,6\text{-}(MeO)_2C_6H_3O\}_2]_2$ (**3b**) with $[ZrCp_2Cl_2]$. The resonances for the OMe, Cp and Al-Me groups have been marked with the following code: Blue triangle: $[ZrCp_2Cl_2]$, Blue star: $[ZrCp_2Cl(OAr)]$, red dot: **3b**; Violet square: **2**.

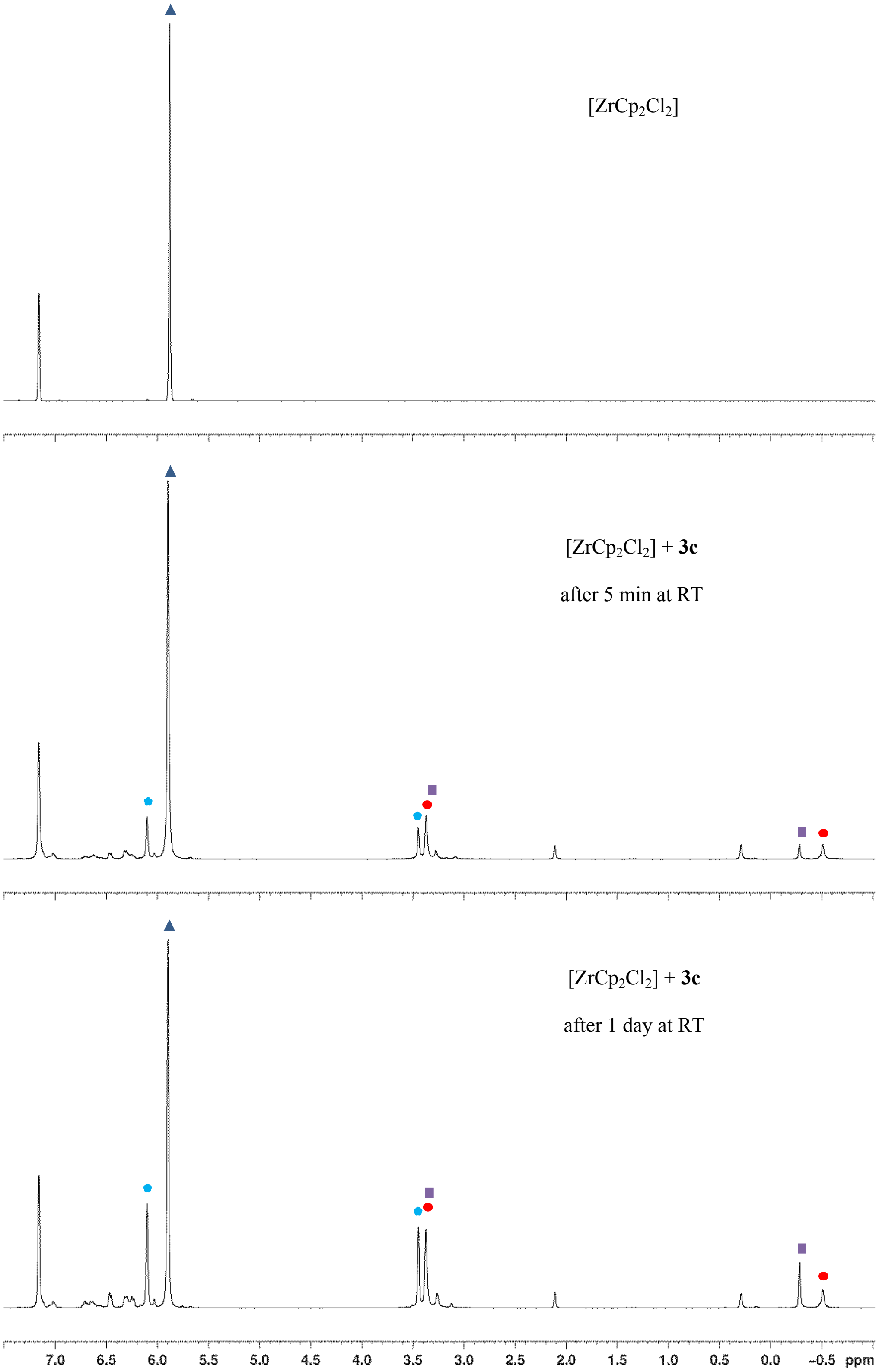


Figure S9. ^{1}H NMR spectra of the evolution of the reaction of [$AlKMe_2\{2,6\text{-}(MeO)_2C_6H_3O\}_2]_2$ (**3c**) with [$ZrCp_2Cl_2$]. The resonances for the OMe, Cp and Al-Me groups have been marked with the following code: Blue triangle: [$ZrCp_2Cl_2$], Blue star: [$ZrCp_2Cl(OAr)$], red dot: **3c**; Violet square: **2**.

References.

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