# Zirconocene Dichlorides as Catalysts in Alkene Carbo- and Cyclometalation by $AlEt_3$: Intermediate Structures and Dynamics

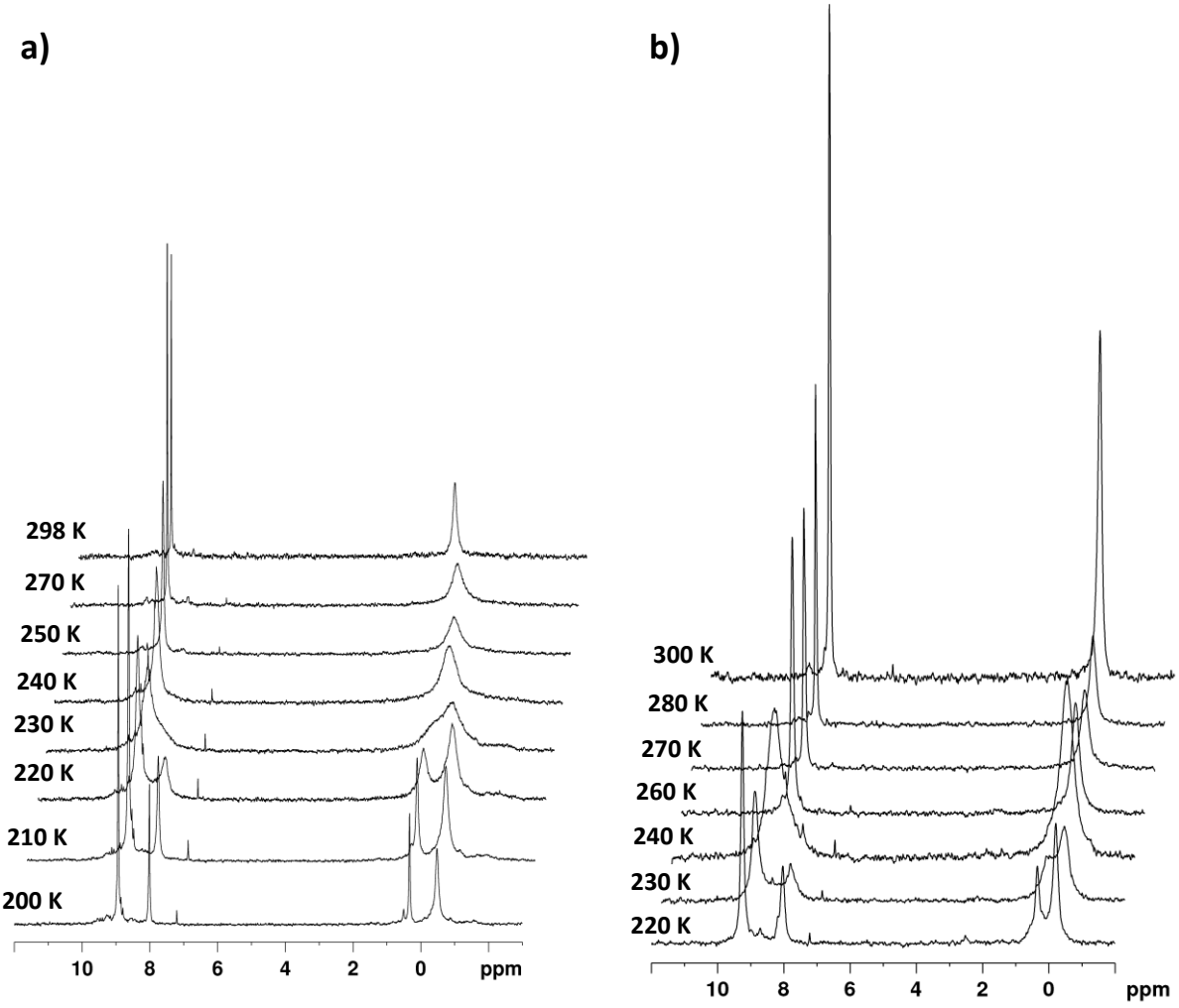
Lyudmila V. Parfenova,*[,a] Pavel V. Kovyazin,[a] Olesia V. Mukhamadeeva,[a] Pavel V. Ivchenko,[b,c] Ilya E. Nifant'ev,[b, c] Leonard M. Khalilov,[a] and Usein M. Dzhemilev[a]

[a]Institute of Petrochemistry and Catalysis of Russian Academy of Sciences, 450075 Ufa, prosp. Oktyabrya, 141, Russian Federation
[b]Department of Chemistry, Lomonosov Moscow State University, 119991 Moscow, 1-3 Leninskiye Gory, Russian Federation
[c]A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninsky prosp. 29, 119991 Moscow, Russian Federation

## *Supporting Information*

**The procedure for the evaluation of the exchange constants using the line- shape analysis.**
The procedure is considered on the example of a solution of triethylaluminum in $CD_2Cl_2$. Thus, the $^{13}C$ NMR spectra in the temperature range 200-300 K were recorded (Fig. S1).

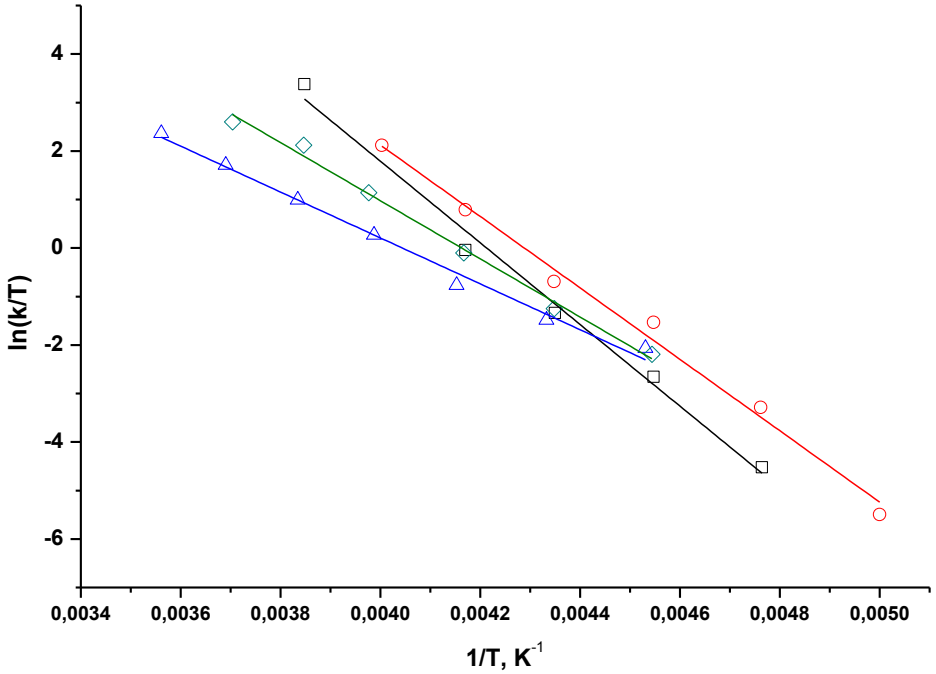
**Figure S1.** VT $^{13}C$ NMR of $(AlEt_3)_2$:
a) 0.5 M/l in $CD_2Cl_2$; b) 0.6 M/l ($AlEt_3$) + 0.1 M/l ($ClAlEt_2$) in $C_7D_8$.




Line-shape analyses were carried out using Dynamic NMR module (version 1.1.2) implemented into the Bruker Topspin 3.2 program, which simulate 1D temperature dependent NMR spectra of coupled half spin nuclei, interactively set up and iteratively refine the model parameters to get the best fit of the measured and simulated 1D NMR spectra and to obtain the reaction speed parameters of exchange processes. The theory of the calculation, special features of the DNMR module (chemical exchange operators, fitting quality, etc.) and detailed procedure are described in the software manual "DNMR Lineshape Analysis" written by Dr. János Rohonczy, 2007.

The details on the constant evaluation via line-shape analysis are presented in the SI of Ref.[37].

**Figure S2.** Plots of ln(k/T) vs 1/T for the ethyl group exchange in $(AlEt_3)_2$ obtained from line-shape analysis:
□ - 4.8 M/l in $CD_2Cl_2$, ○- 0.5 M/l in $CD_2Cl_2$, Δ- 4.0 M/l in $C_7D_8$, ◊- 0.6 M/l ($AlEt_3$) + 0.1 M/l ($ClAlEt_2$) in $C_7D_8$).




**The procedure for the evaluation of the constants of the exchange in $L_2Zr(\mu\text{-}Cl)CH_2CH_2AlEt_2$ (16m,n,p,q) using 2D EXSY.**

2D NMR EXSY (NOESY) spectra were recorded in the phase-sensitive mode using standard Bruker gradient pulse sequences with relaxation delay 1 s, 90º pulse - 8.0 μs, mixing time τ=0.3-1 s. The mixing time was chosen in such a range that diagonal and cross- peaks were observed simultaneously. The areas of the diagonal and cross- peaks for the signals of the $H^5$ and $H^6$ atoms of the $ZrCH_2CH_2Al$ fragment in the -3 - 0 ppm region in the temperature range 290–310 K were determined. Constants of the exchange were calculated by the formula [Ch.L. Perrin, T.J. Dwyer, *Chem. Rev.*, 1990, **90**, 6, 935–967]:

$$k = \frac{1}{\tau}\ln\frac{r+1}{r-1}, \quad \text{where} \quad r = \frac{I_{AA}+I_{BB}}{I_{AB}+I_{BA}}$$

$\tau$ – mixing time, $I_{AA}$, $I_{BB}$- diagonal peak areas, $I_{AB}$, $I_{BA}$- cross-peak areas.

The values of $\Delta H^{\neq}$, $\Delta G^{\neq}$, $\Delta S^{\neq}$ were calculated according to the Eyring equation [J. Sandström, *Dynamic NMR Spectroscopy*. – NY: Academic Press, 1982. – 226p]:

$$\ln(k/T) = -\Delta H^{\neq}/RT + \Delta S^{\neq}/R + \ln(k_b/h),$$

where $k_b$ – the Boltzmann constant, and $h$- the Planck constant.

**Figure S3.** $^{1}$H NMR of $ClAlEt_2$ in $C_7D_8$.

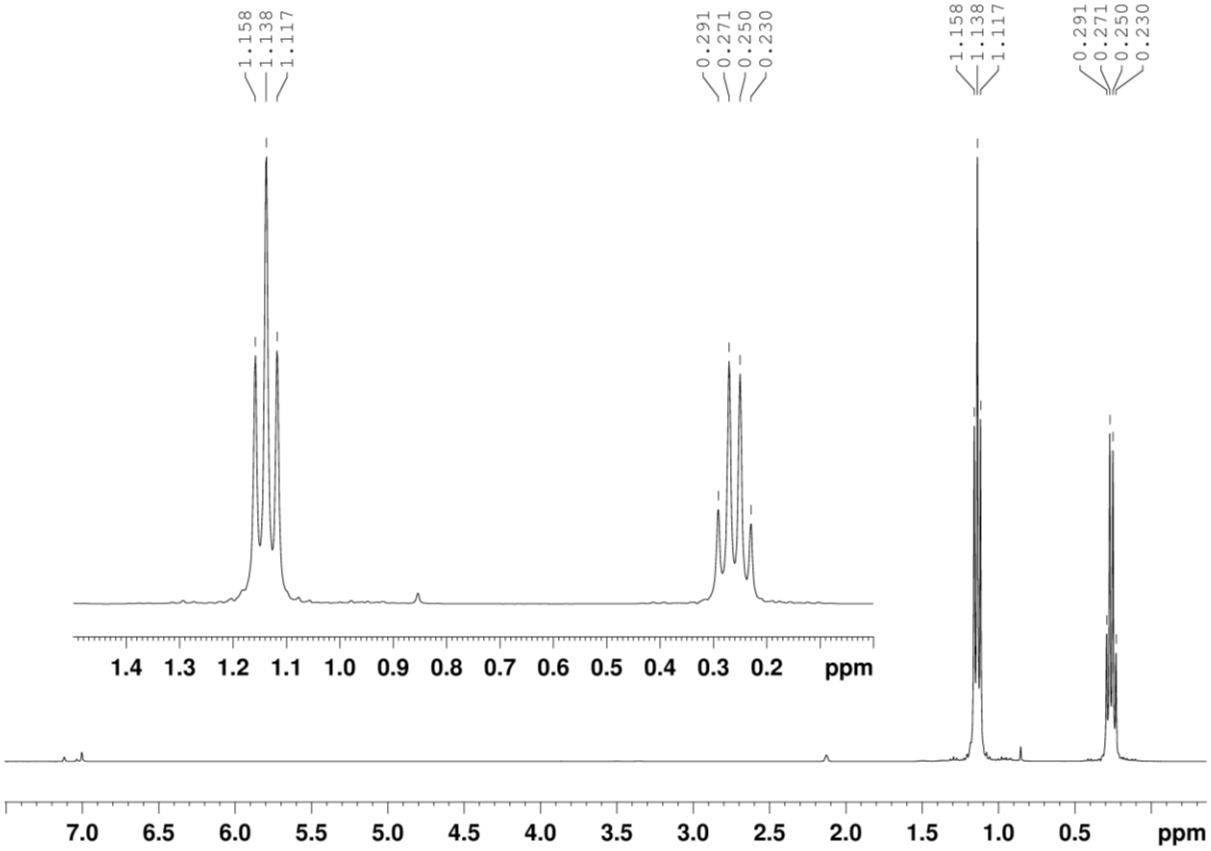



**Figure S4.** $^{13}$C NMR of $ClAlEt_2$ in $C_7D_8$.

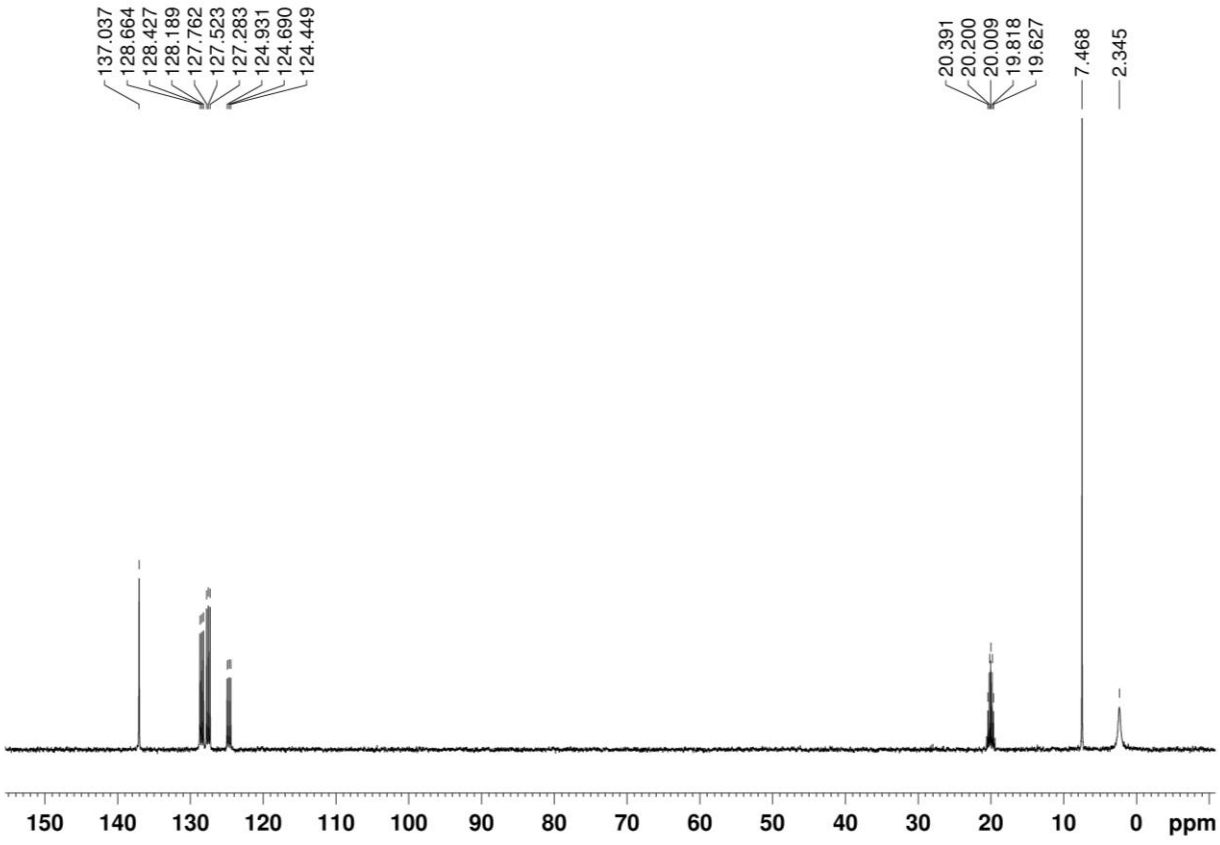


**Figure S5.** $^{1}$H NMR of $Cp_2ZrEtCl$ obtained by the reaction of $Cp_2ZrHCl+C_2H_4$ in $C_7D_8$ (270 K).

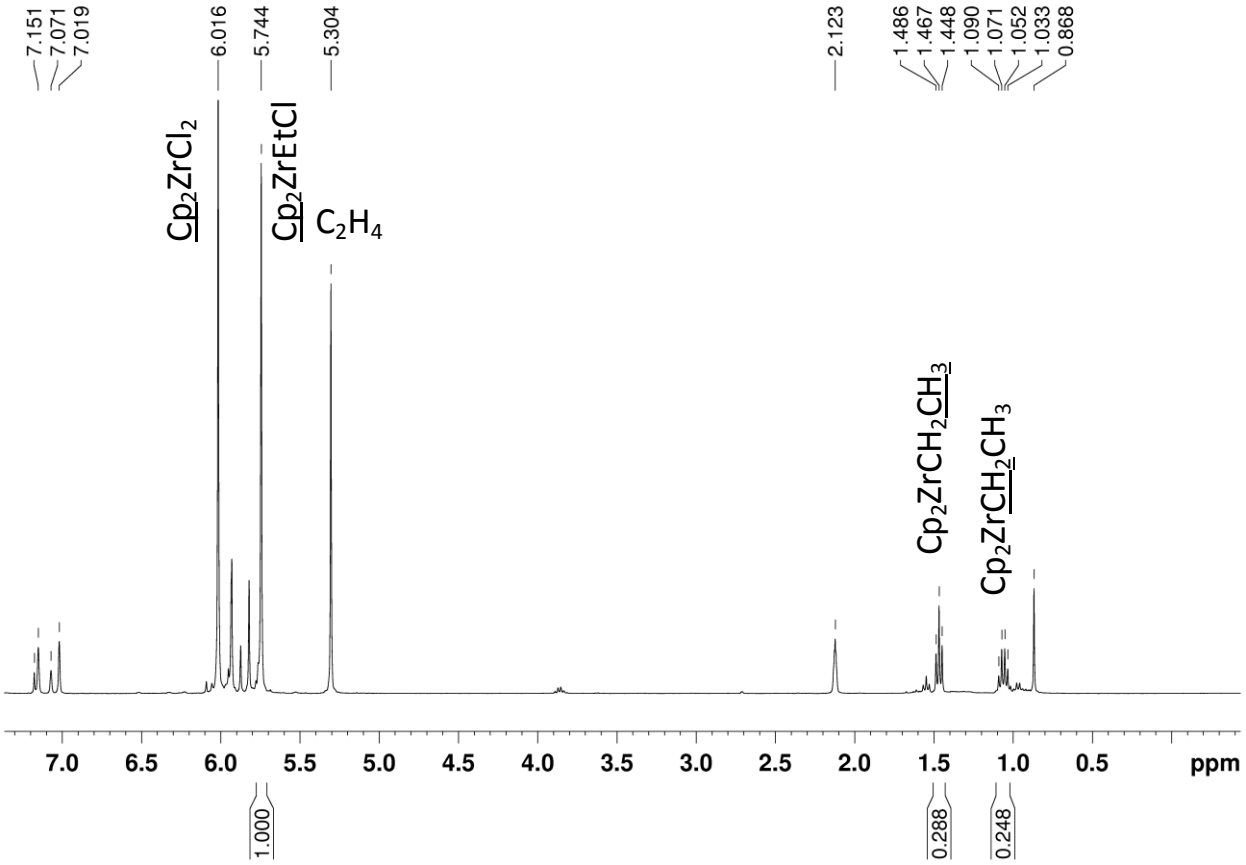



**Figure S6.** HSQC of $Cp_2ZrEtCl$ obtained by the reaction of $Cp_2ZrHCl+C_2H_4$ in $C_7D_8$ (270 K).

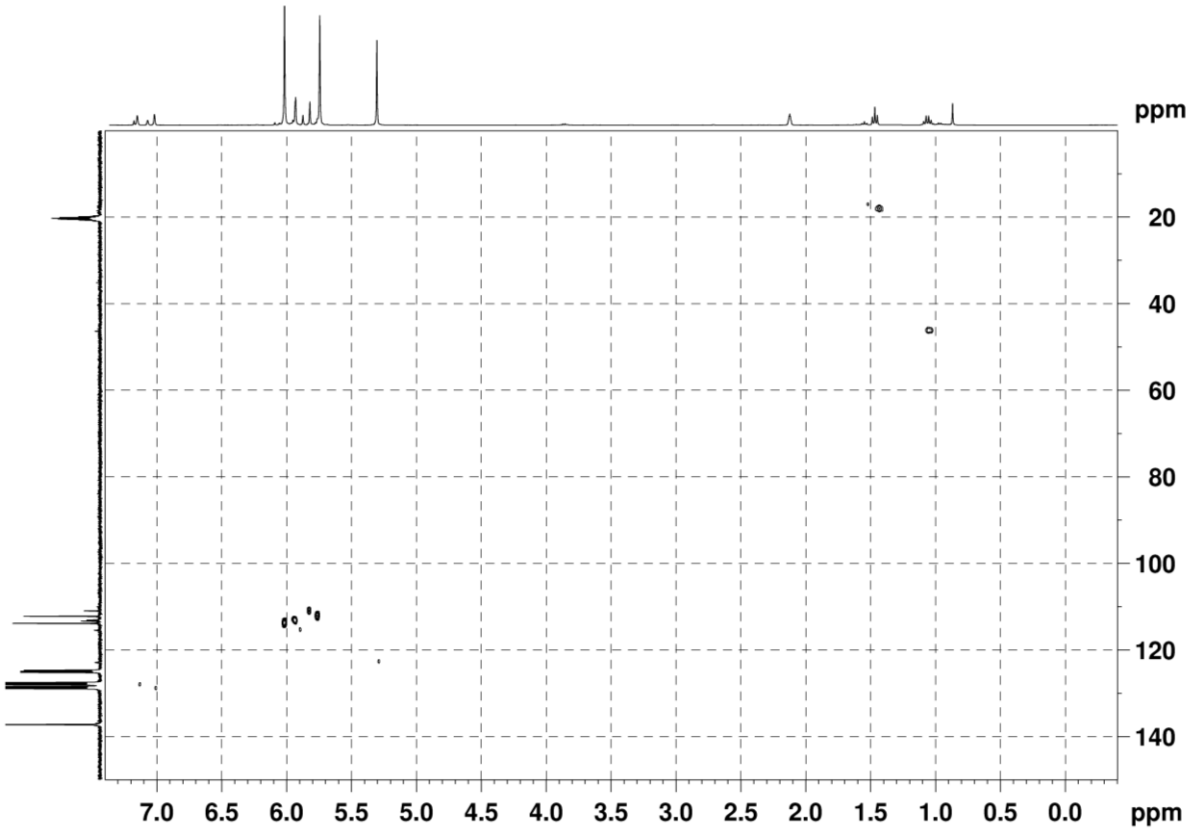


**Figure S7.** $^{1}$H NMR of system $Cp_2ZrCl_2$ (**1a**) - $(AlEt_3)_2$ (1:20) in $C_7D_8$ (5 min).

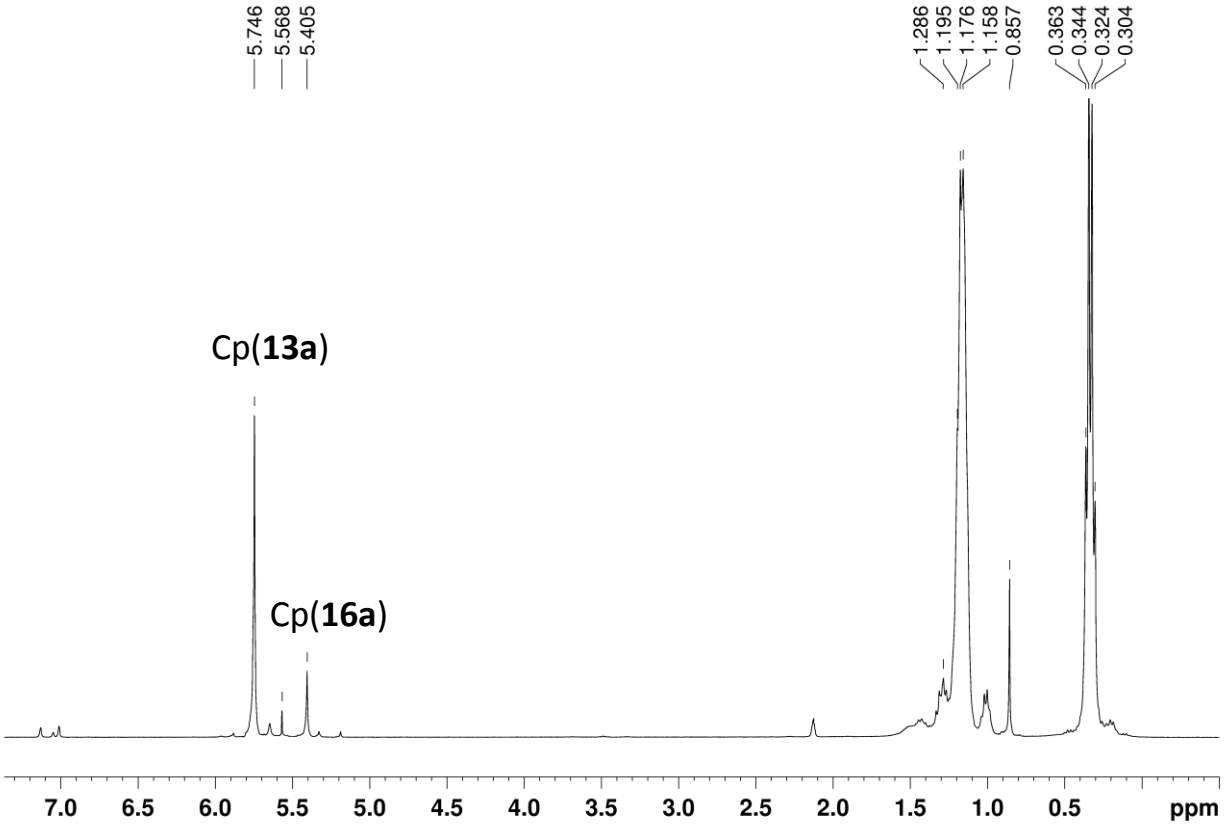



**Figure S8.** $^{1}$H NMR of system $Cp_2ZrCl_2$ (**1a**) - $(AlEt_3)_2$ (1:20) in $C_7D_8$ (20 min).

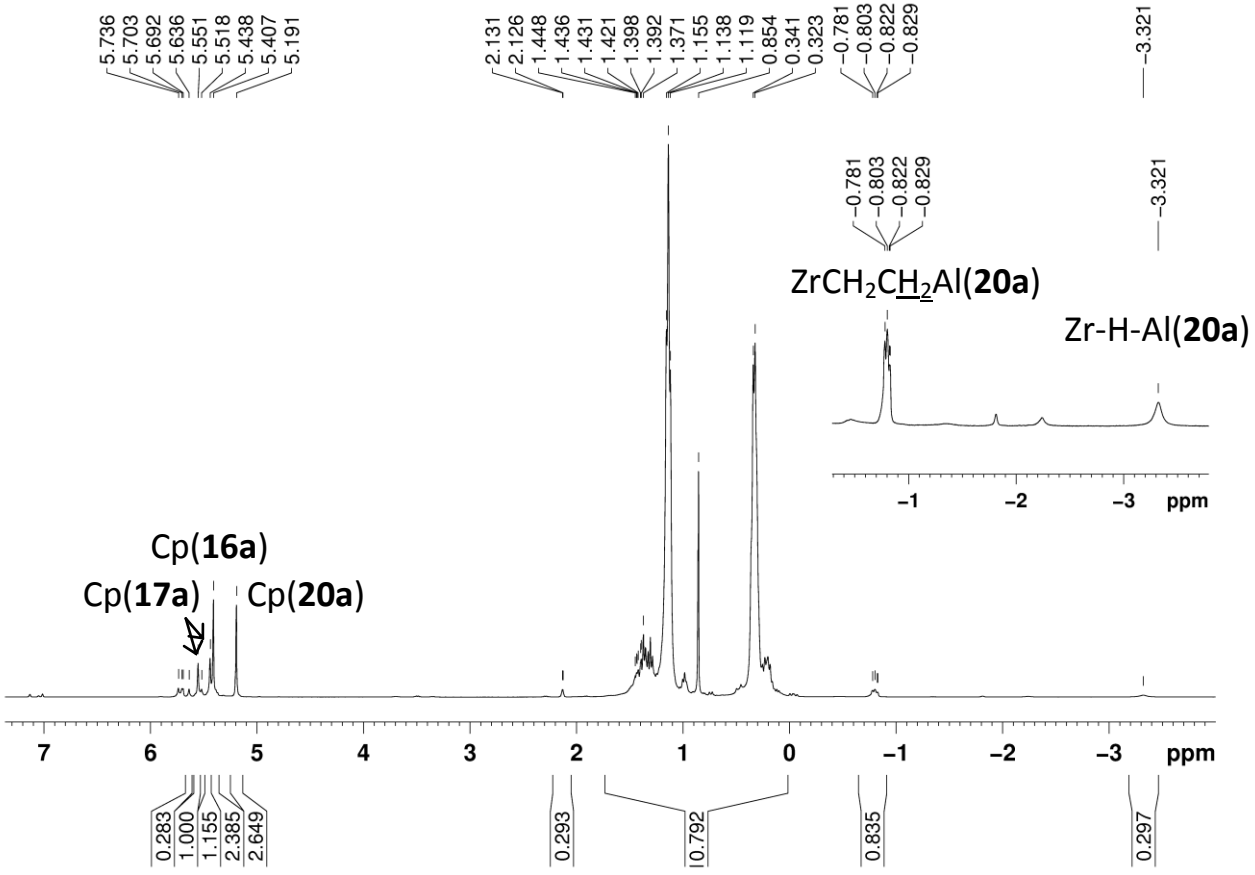


**Figure S9.** $^{13}C$ NMR of system $Cp_2ZrCl_2$ (**1a**) - $(AlEt_3)_2$ (1:20) in $C_7D_8$.

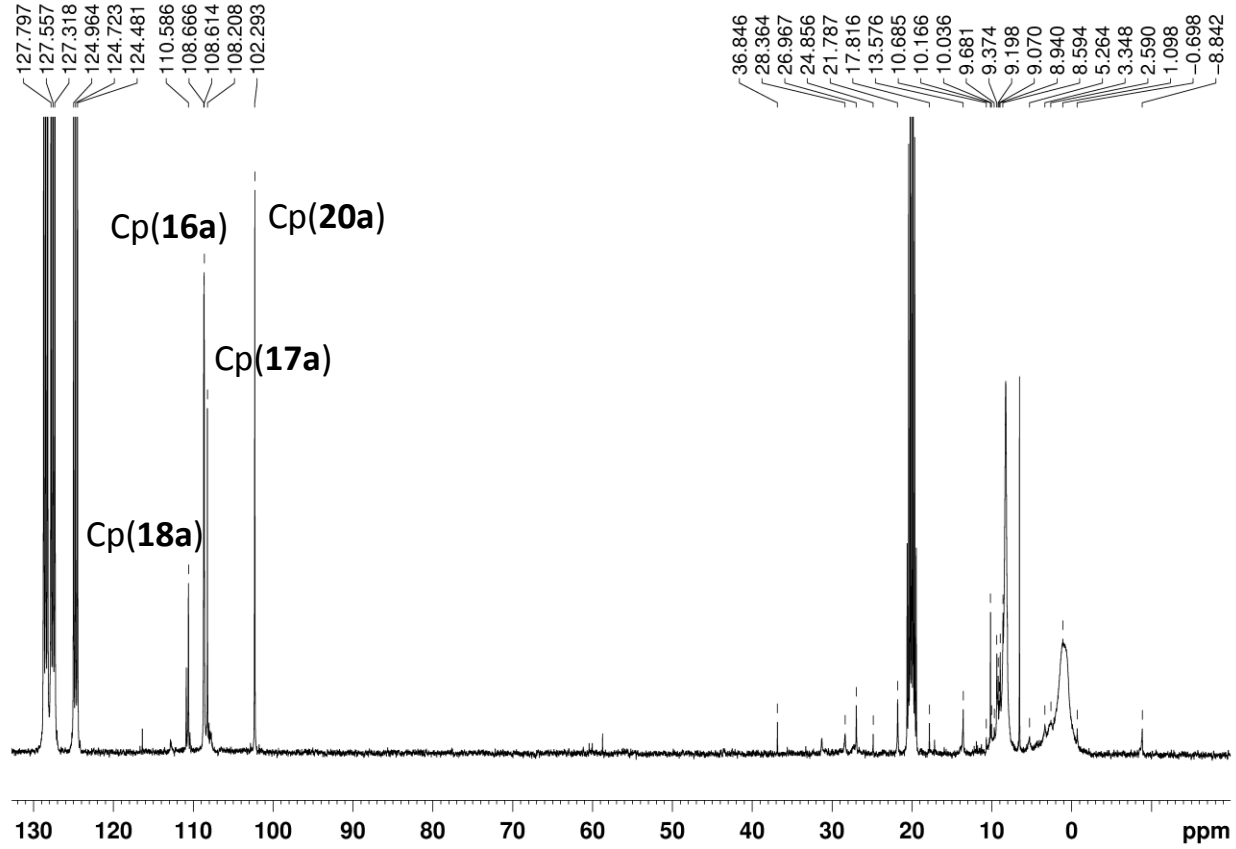



**Figure S10.** HSQC of system $Cp_2ZrCl_2$ (**1a**) - $(AlEt_3)_2$ (1:20) in $C_7D_8$ (20 min).

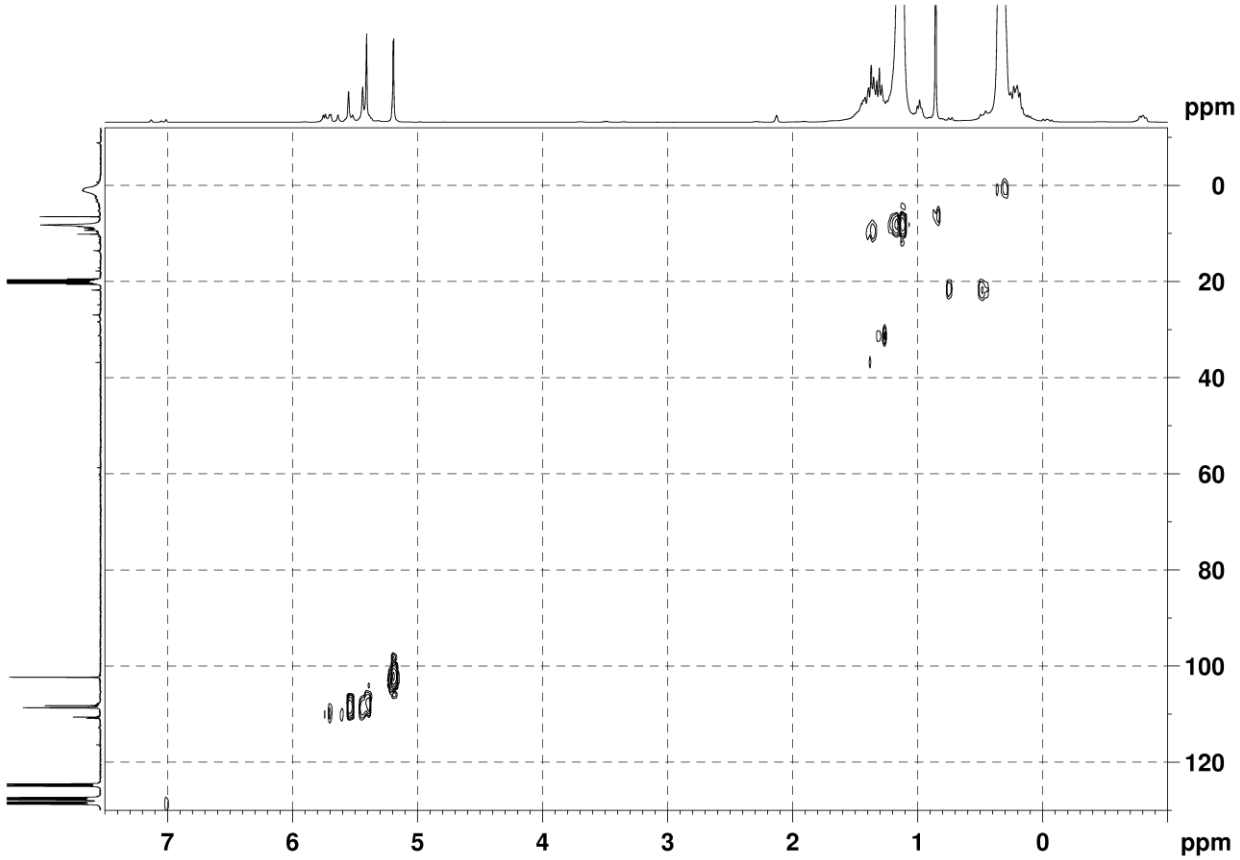


**Figure S11.** HMBC of system $Cp_2ZrCl_2$ (**1a**) - $(AlEt_3)_2$ (1:20) in $C_7D_8$.

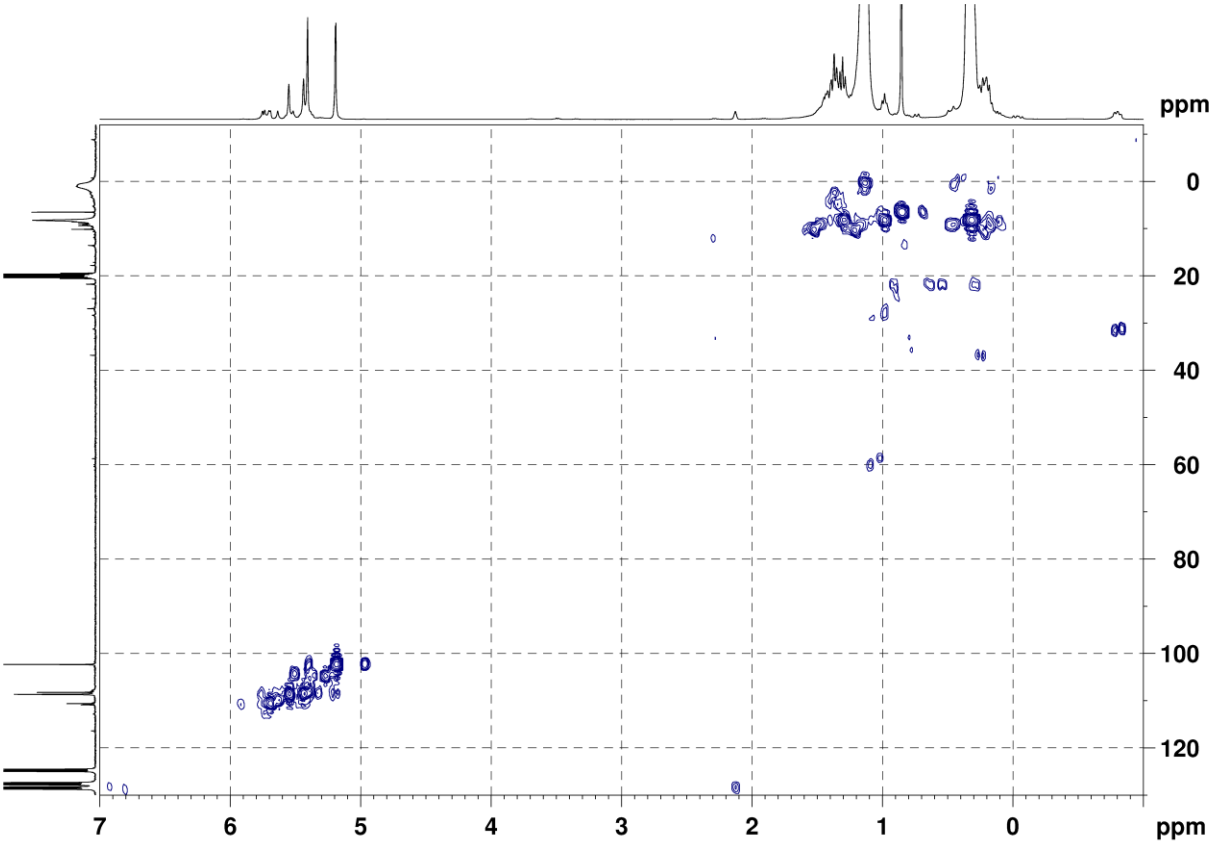



**Figure S12.** EXSY of system $Cp_2ZrCl_2$ (**1a**) - $AlEt_3$ at 290 in $C_7D_8$ ($\tau$= 1 s).

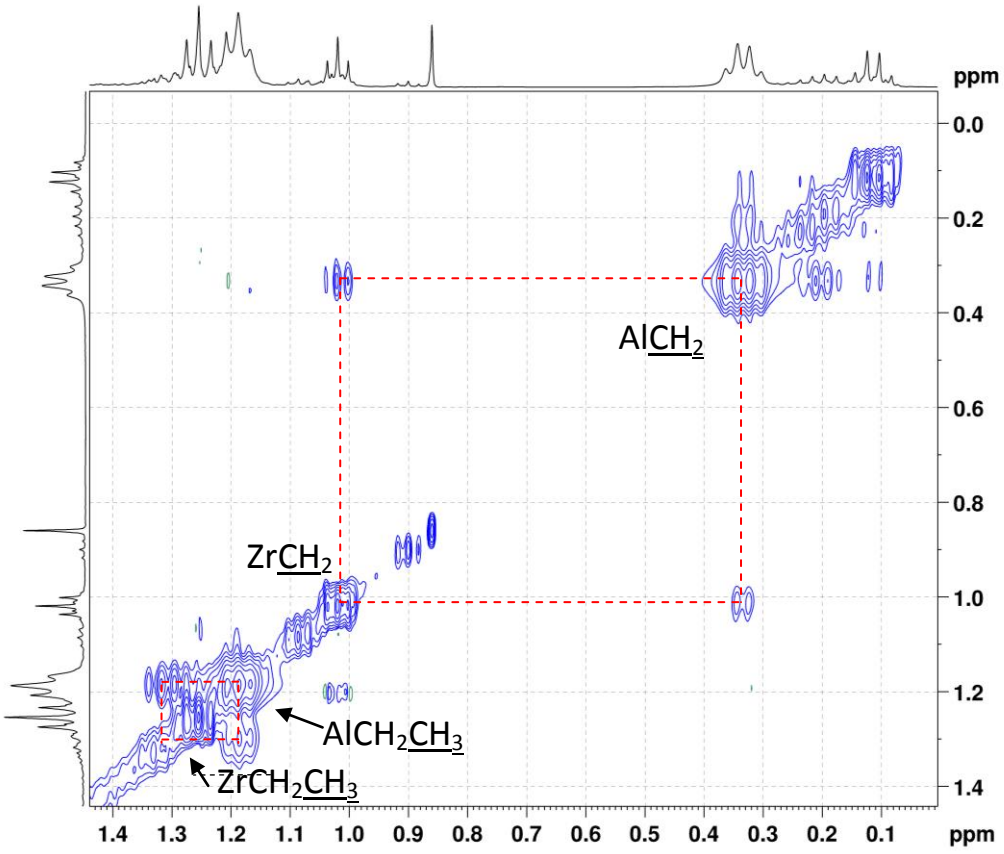


**Figure S13.** $^{1}$H NMR of system $(CpMe)_2ZrCl_2$ (**1b**) -$(AlEt_3)_2$ (1:27) in $C_7D_8$.

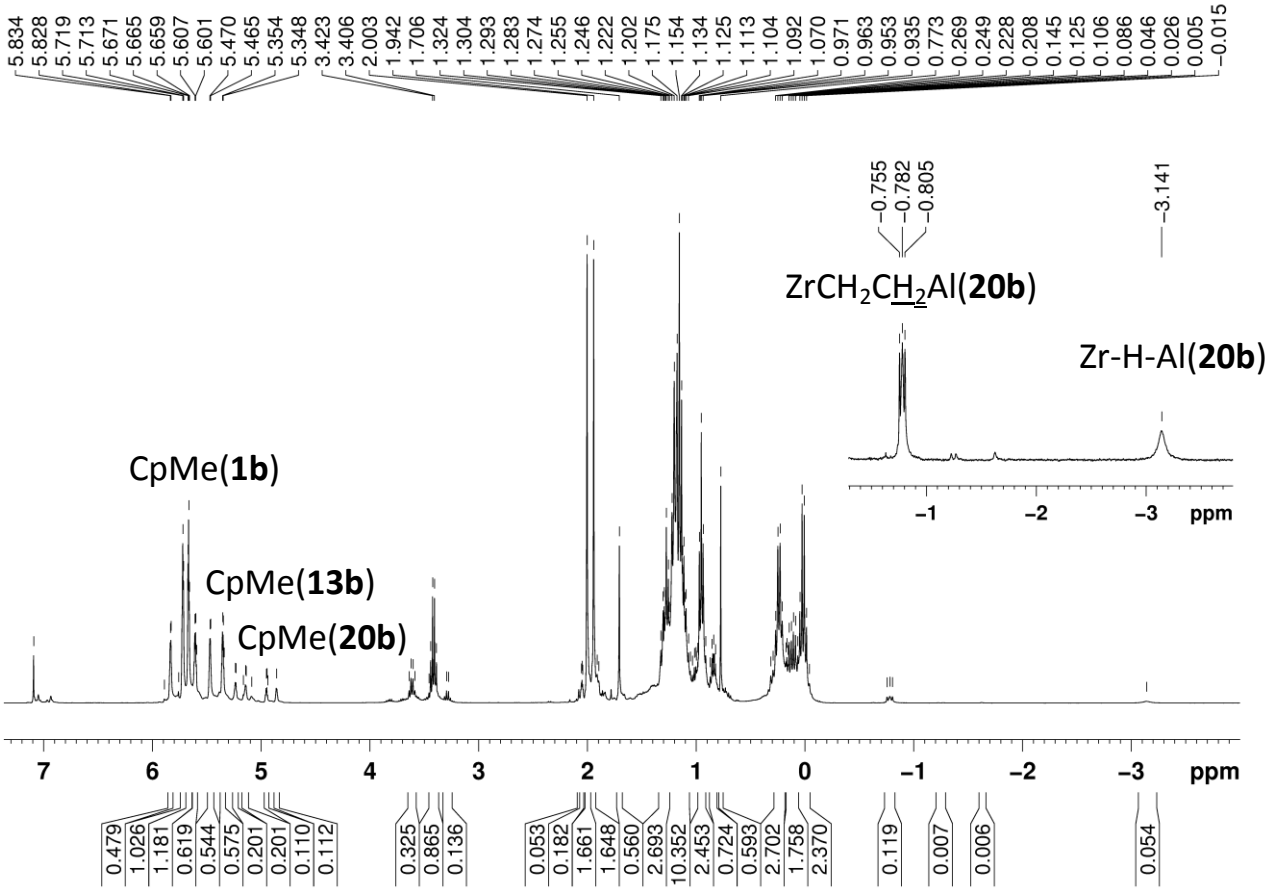



**Figure S14.** $^{13}$C NMR of system $(CpMe)_2ZrCl_2$ (**1b**) - $(AlEt_3)_2$ in $C_7D_8$.

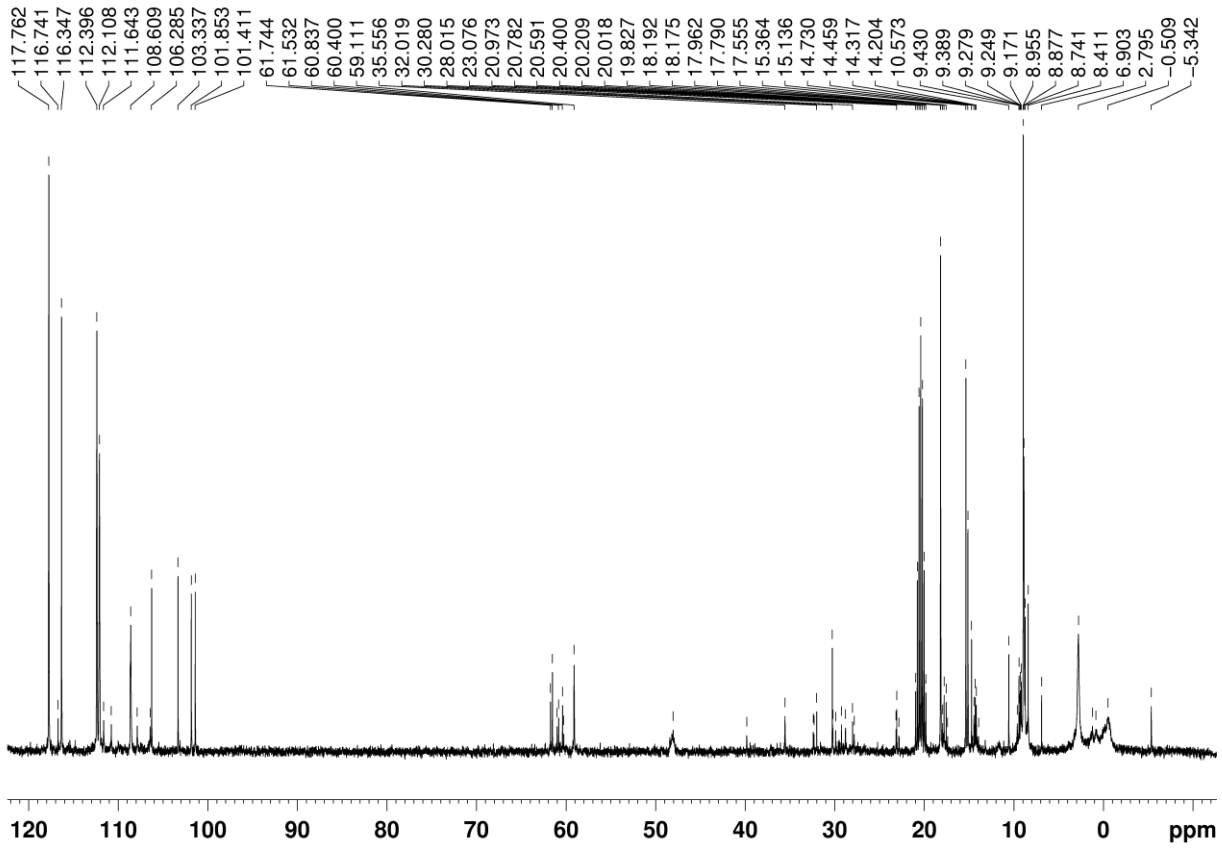


**Figure S15.** COSY HH of system $(CpMe)_2ZrCl_2$ (**1b**) - $(AlEt_3)_2$ in $C_7D_8$.

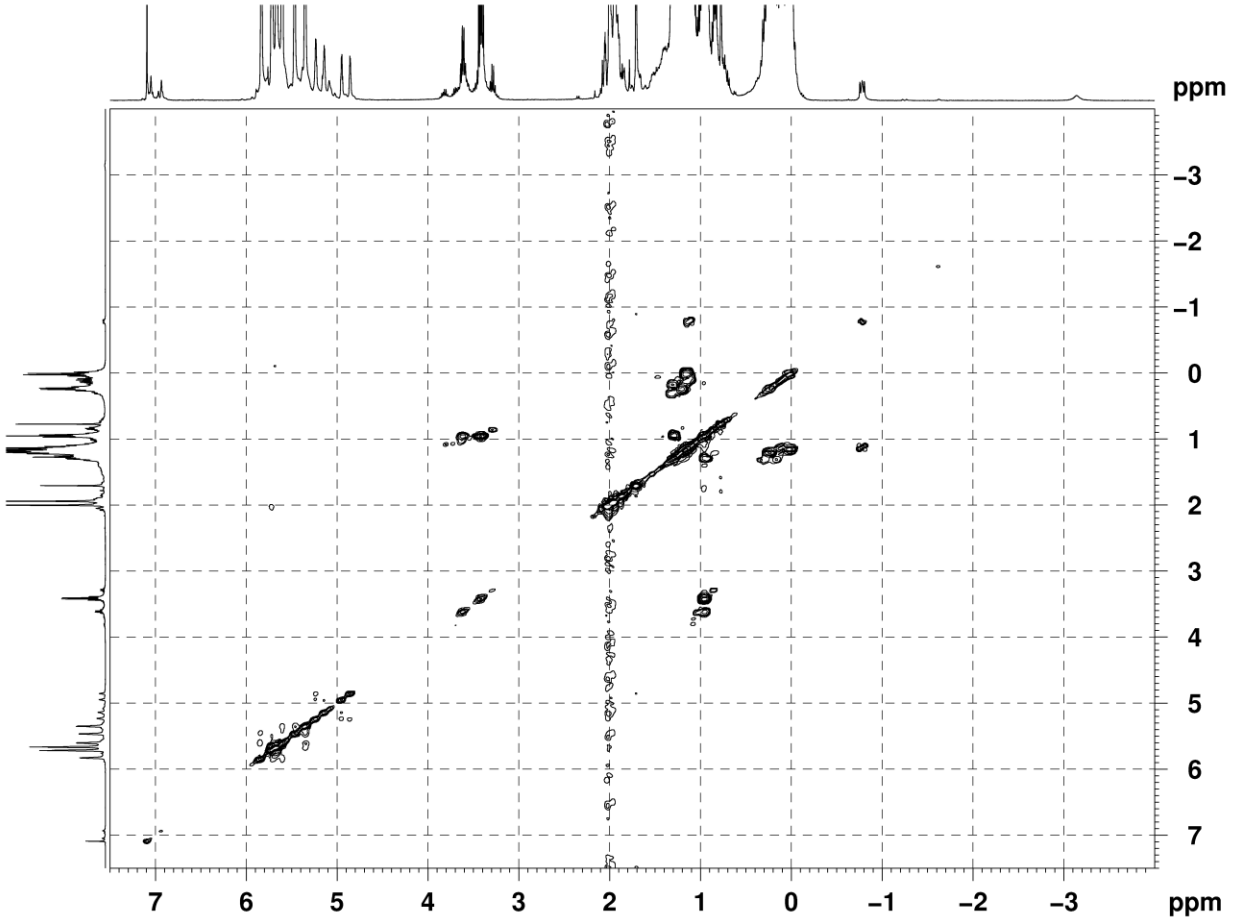



**Figure S16.** HSQC of system $(CpMe)_2ZrCl_2$ (**1b**) - $(AlEt_3)_2$ in $C_7D_8$.

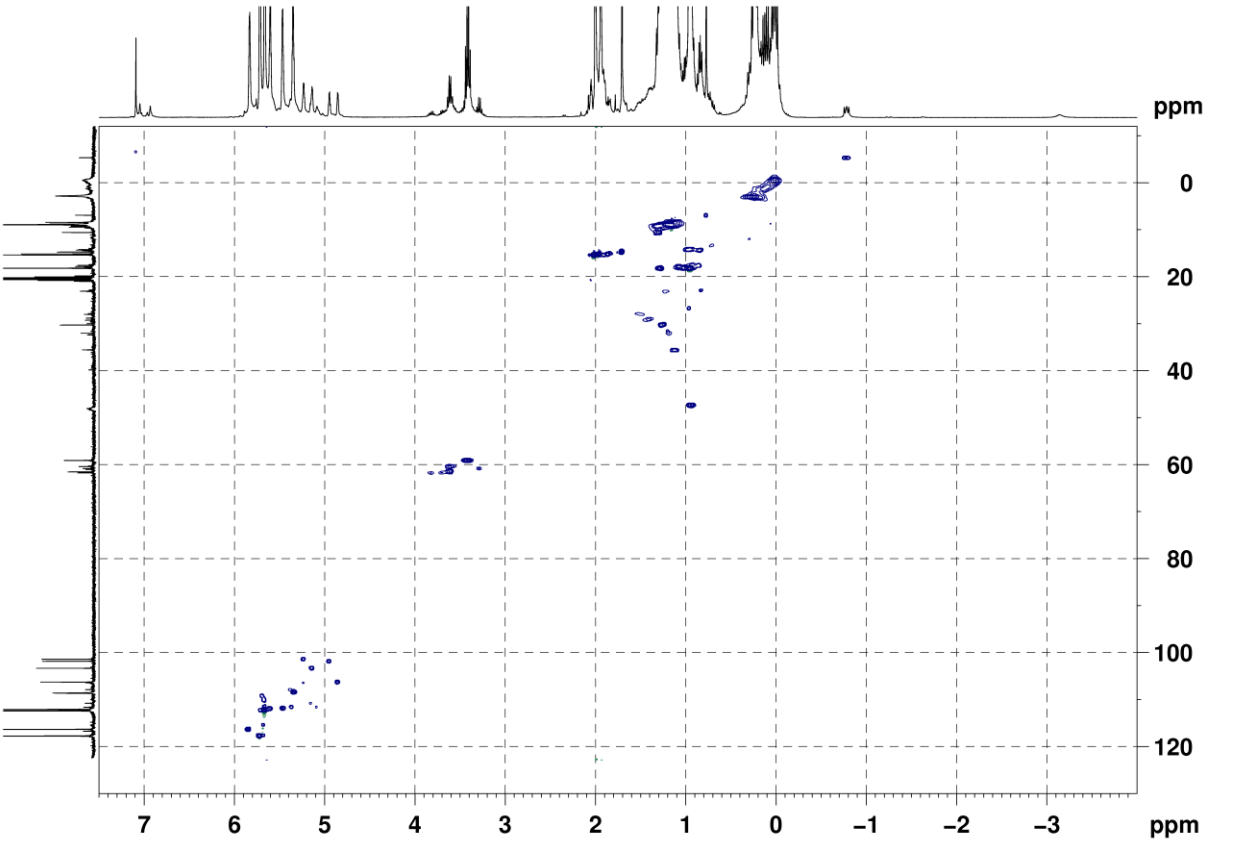


**Figure S17.** $^{1}$H NMR of complex **16a** obtained by the reaction of $Cp_2ZrEtCl$ with $(AlEt_3)_2$ in $C_7D_8$ (300 K).

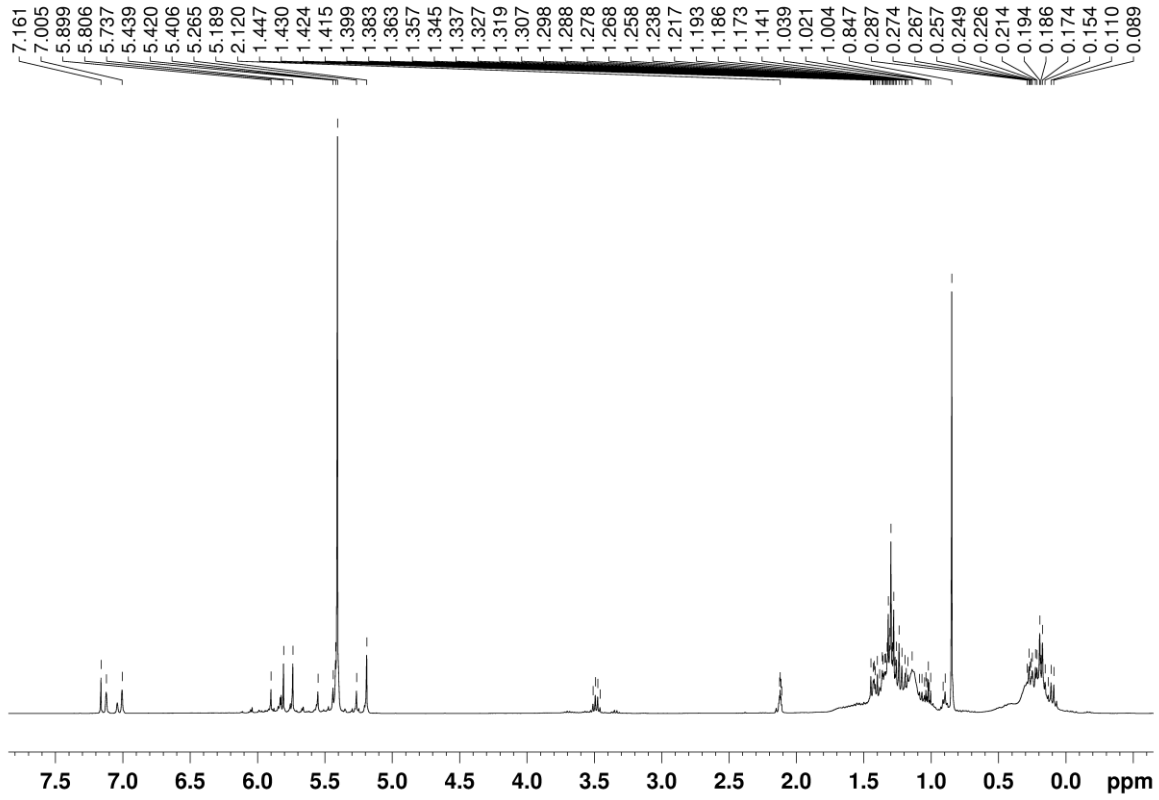



**Figure S18.** $^{13}$C NMR of complex **16a** obtained by the reaction of $Cp_2ZrEtCl$ with $(AlEt_3)_2$ in $C_7D_8$ (300 K).

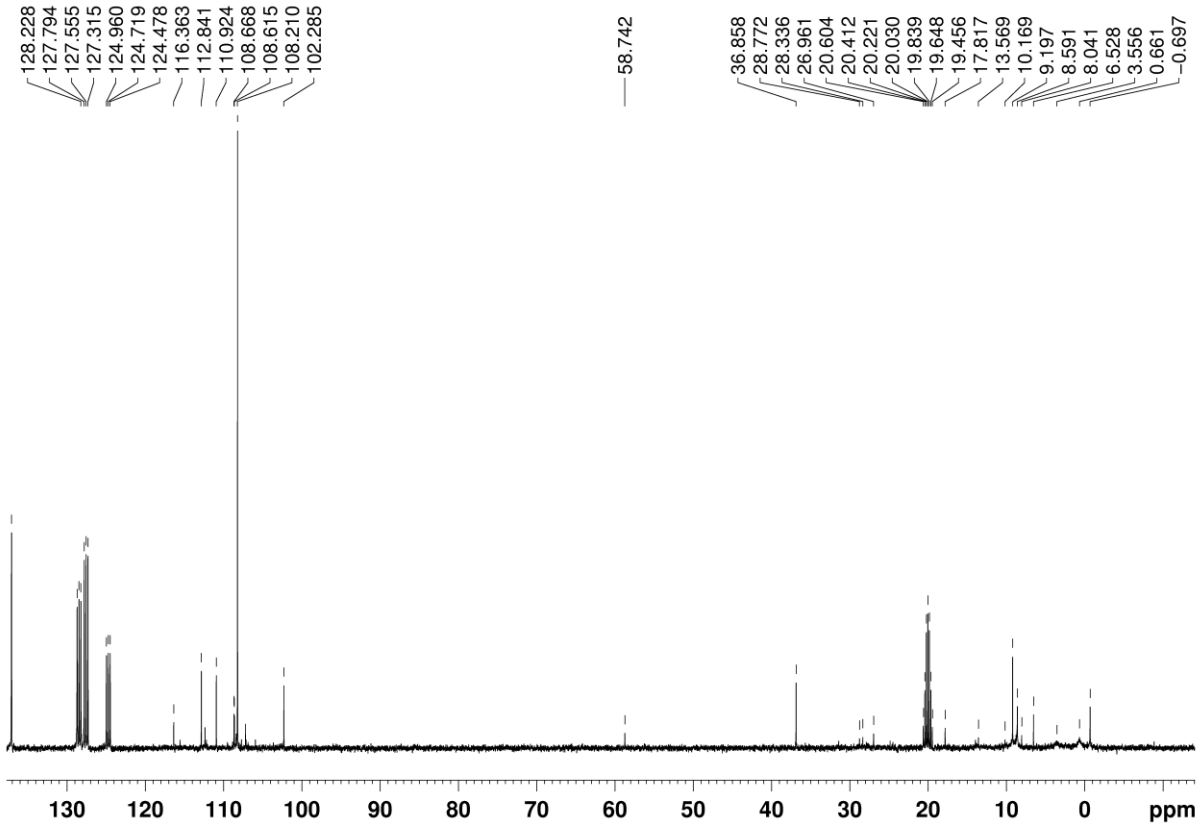


**Figure S19.** HSQC of complex **16a** in $C_7D_8$ (300 K).

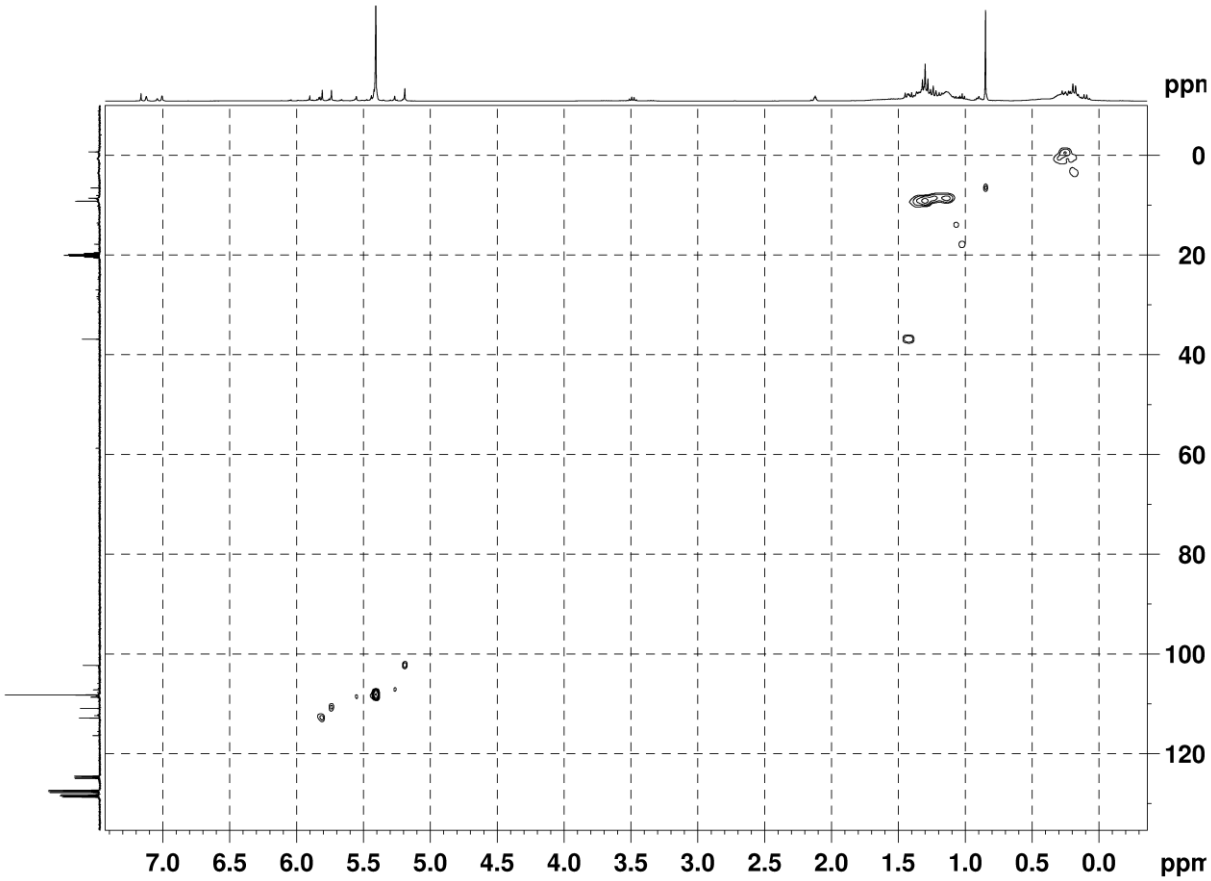



**Figure S20.** $^{13}C$ NMR monitoring of reaction **16a +** 1-hexene in $C_7D_8$.

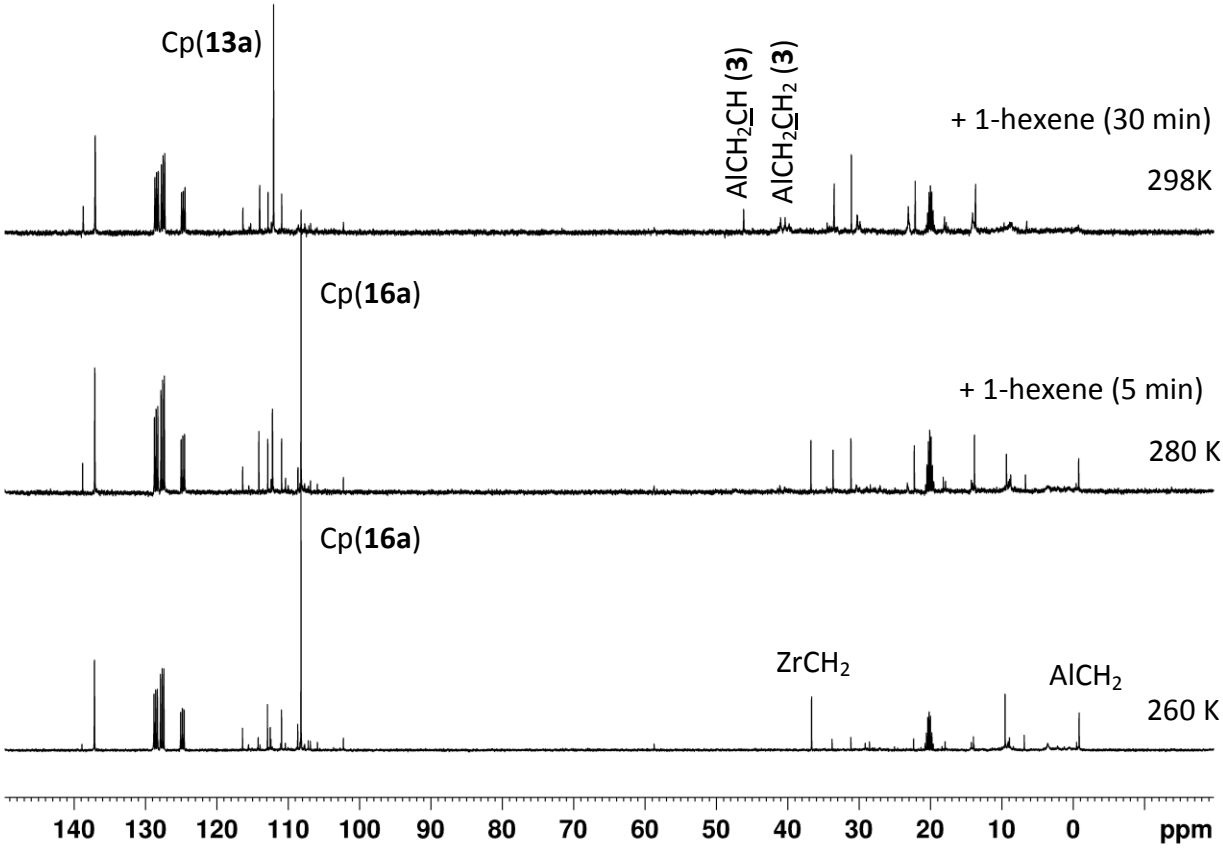


**Figure S21.** $^{1}$H NMR of complex **16h** obtained by the reaction of **1h** with $(AlEt_3)_2$ (1:11) in $C_7D_8$ at 270 K.

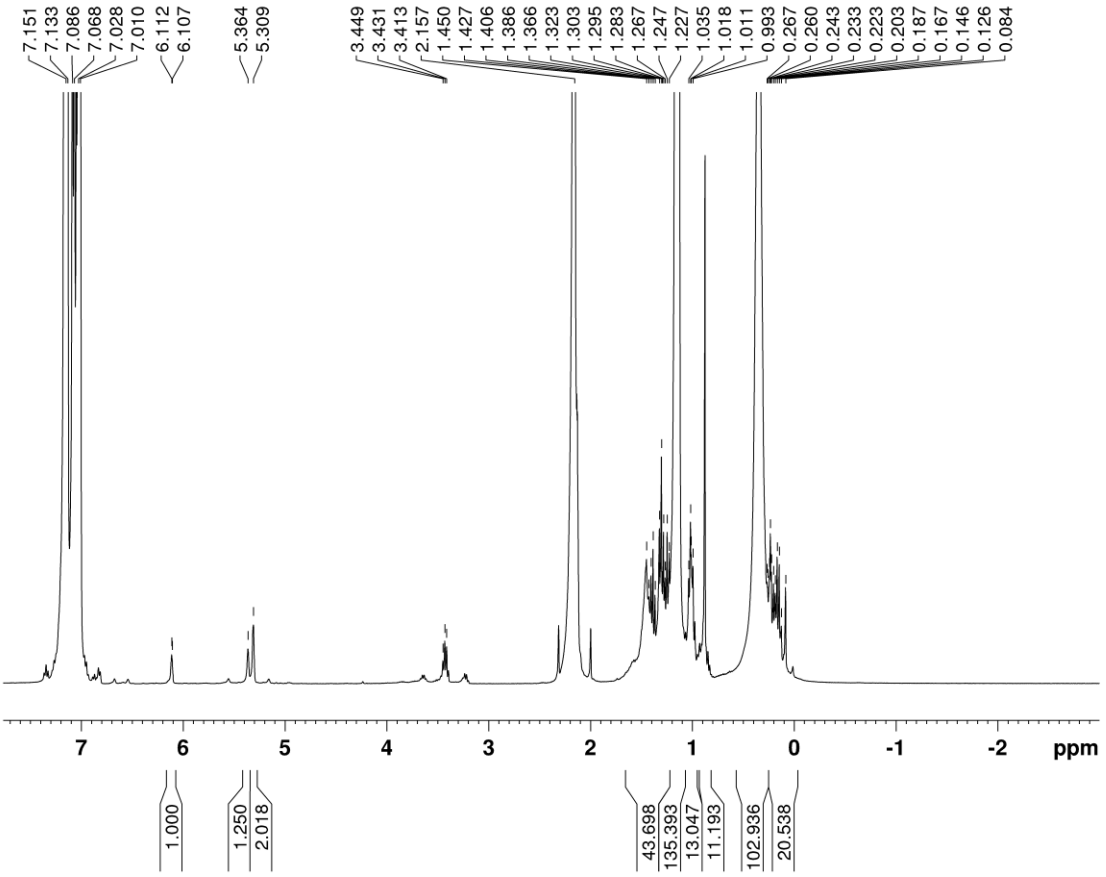



**Figure S22.** COSY HH of complex **16h** in $C_7D_8$ at 270 K.

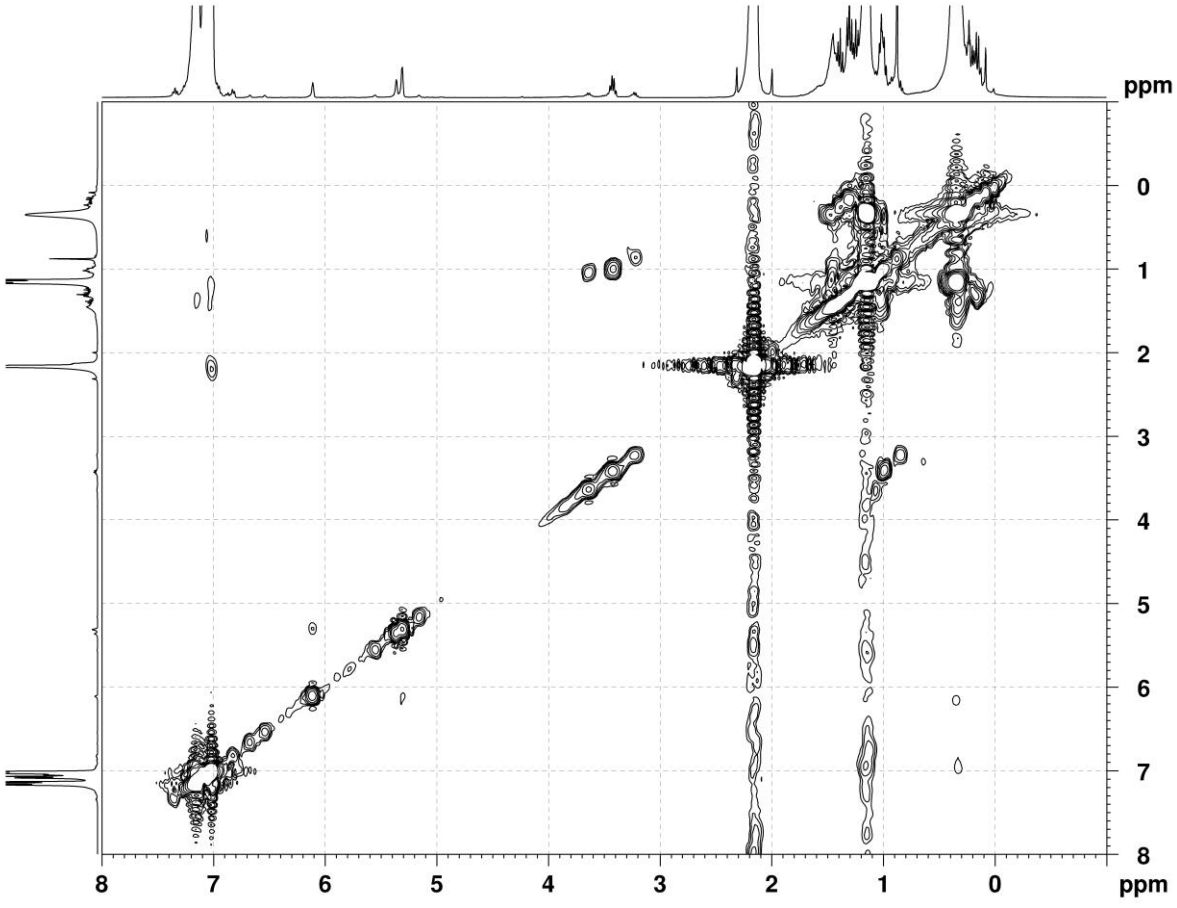


**Figure S23.** EXSY of complex **16h** in $C_7D_8$ at 298 K (τ= 0.3 s).

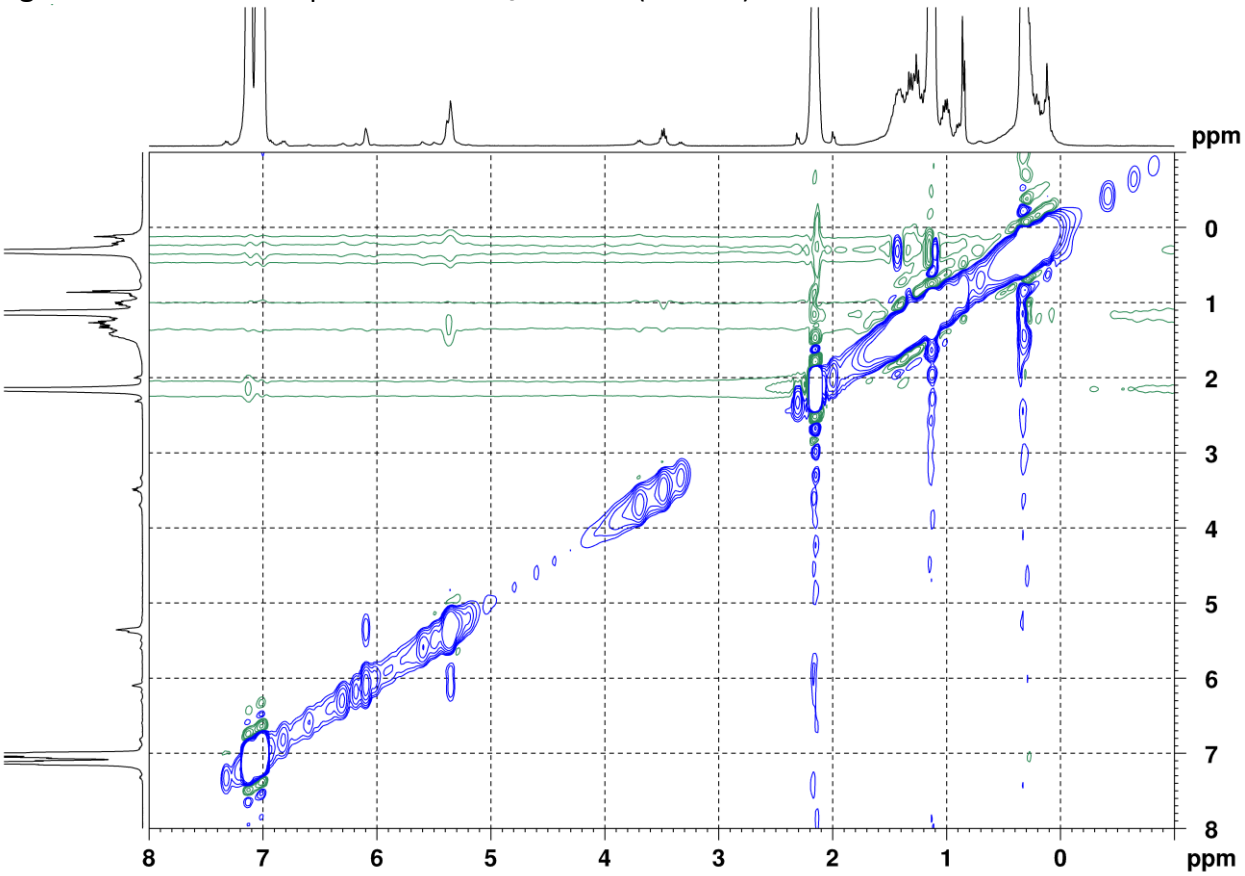



**Figure S24.** HMBC of complex **16h** in $C_7D_8$ at 298 K.

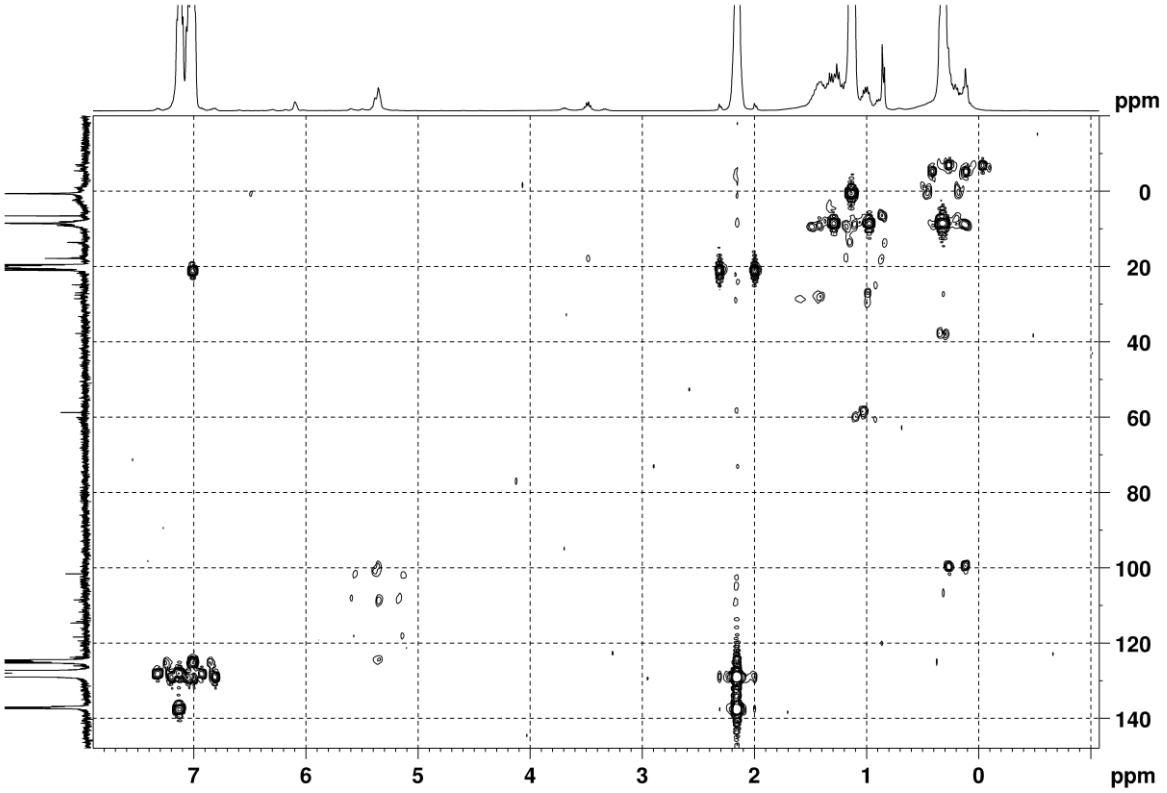


**Figure S25.** $^{1}$H NMR of **16m** obtained by the reaction of **1m** with $(AlEt_3)_2$ (1:13) in $C_7D_8$ at 298 K.

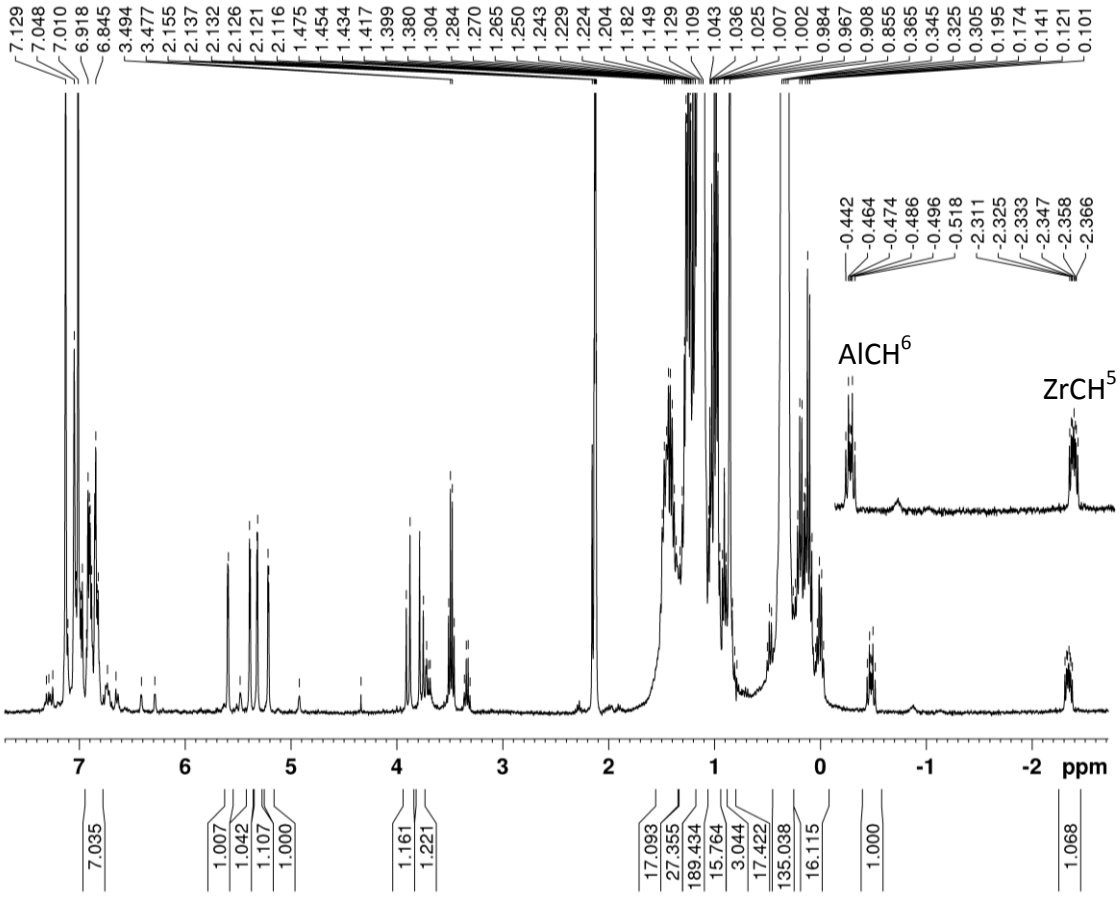



**Figure S26.** COSY HH of **16m** in $C_7D_8$ at 260 K.

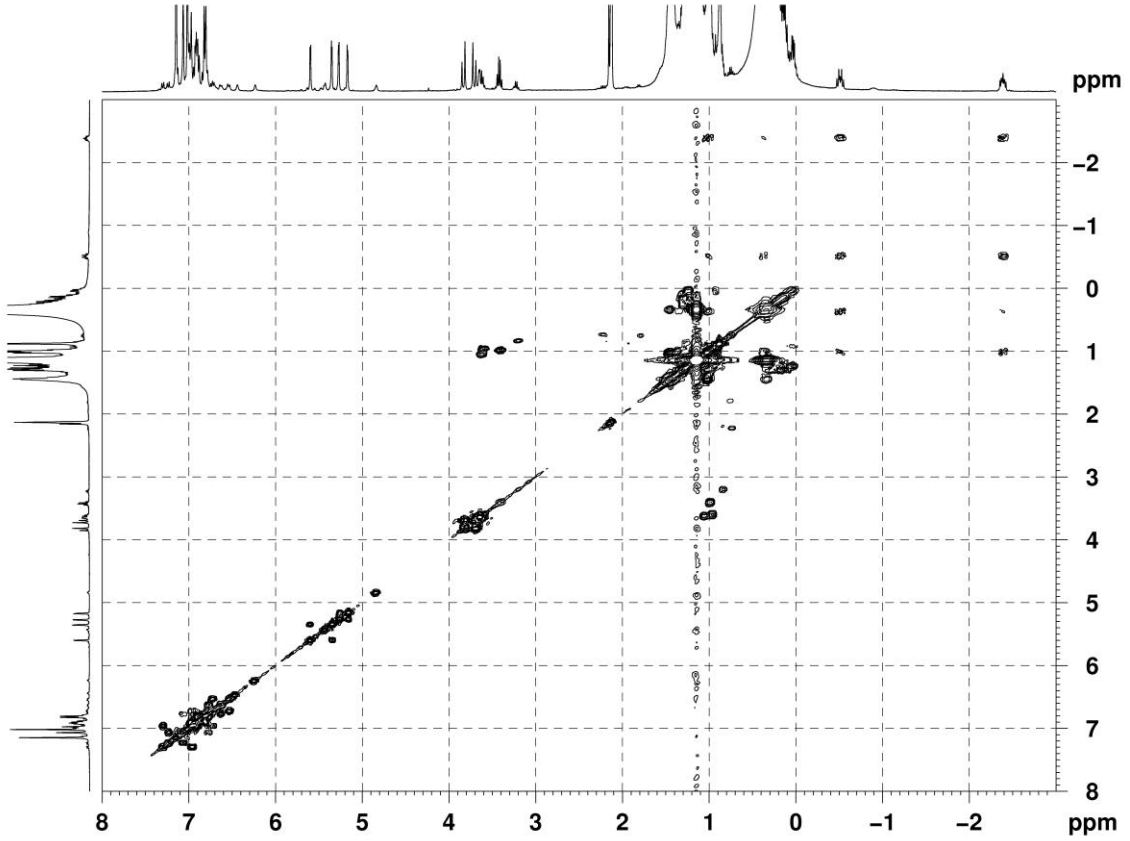


**Figure S27.** $^{13}C$ NMR of **16m** in $C_7D_8$ at 260 K.

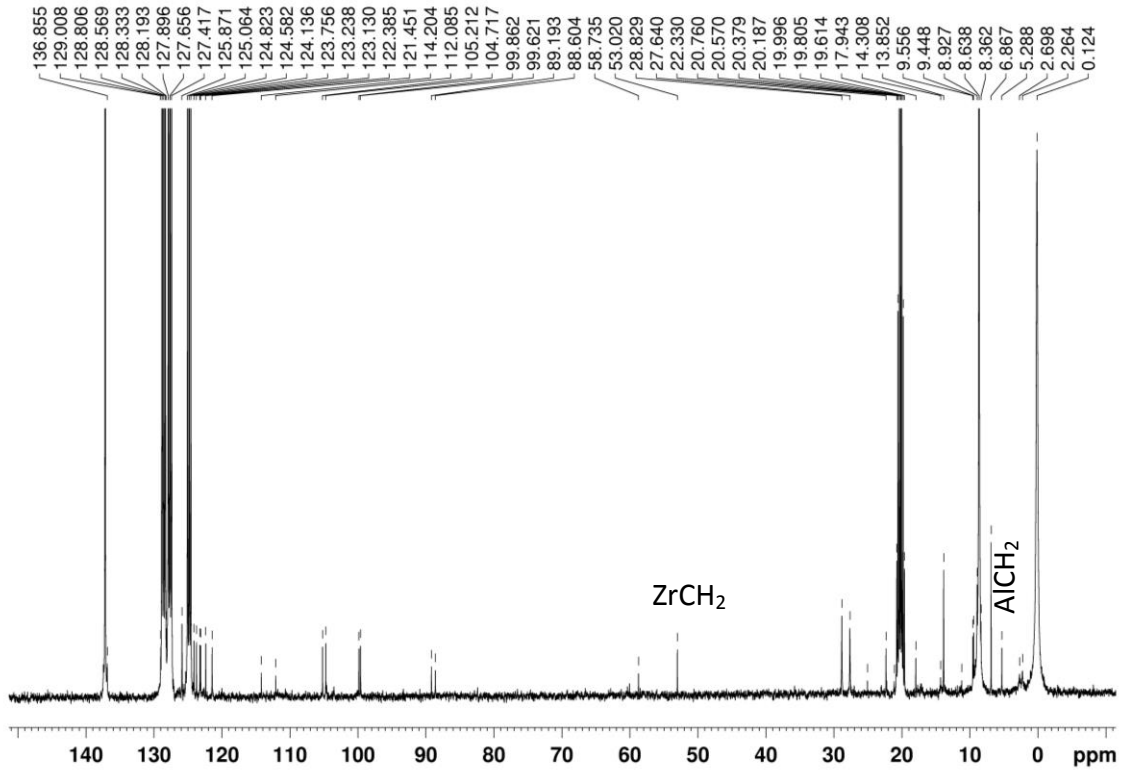



**Figure S28.** HSQC of **16m** in $C_7D_8$ at 260 K.

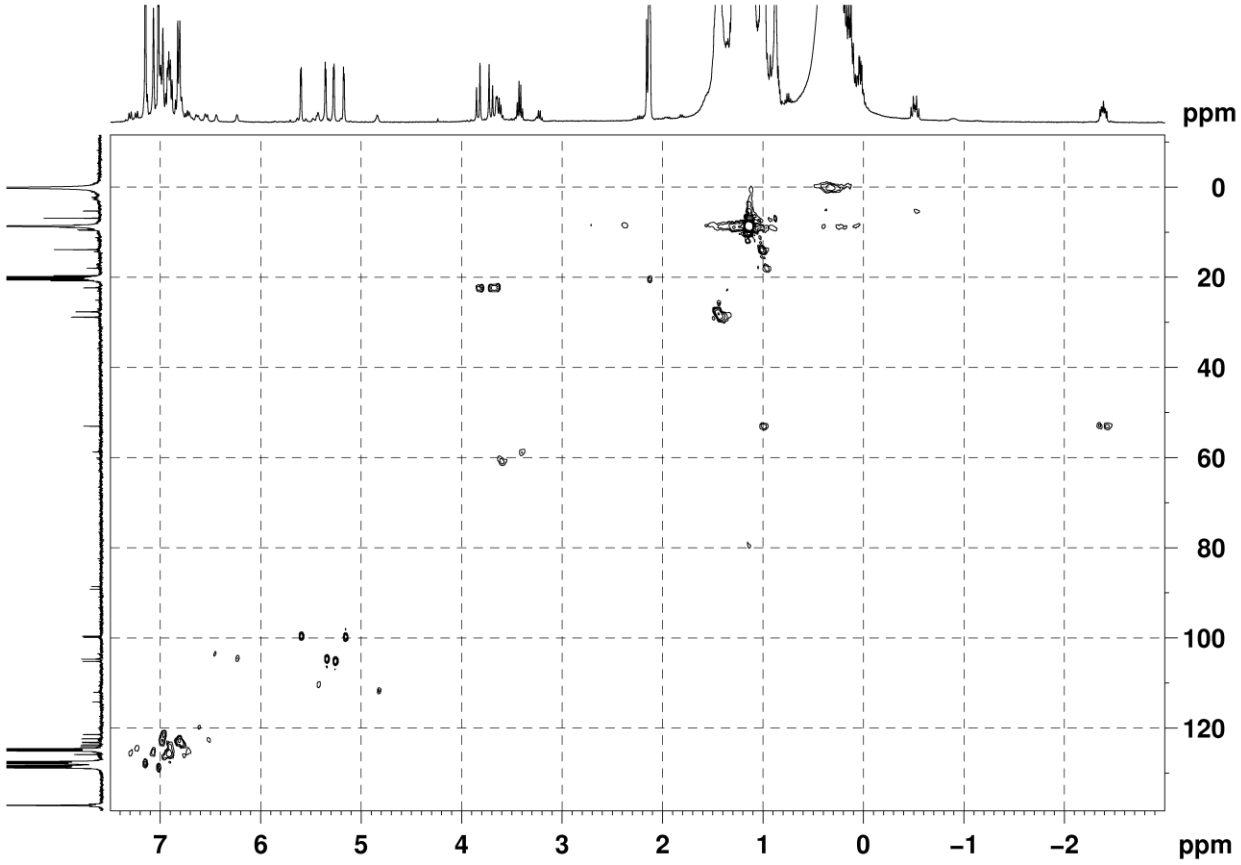


**Figure S29.** EXSY of **16m** in $C_7D_8$ at 298 K (τ= 0.3 s).

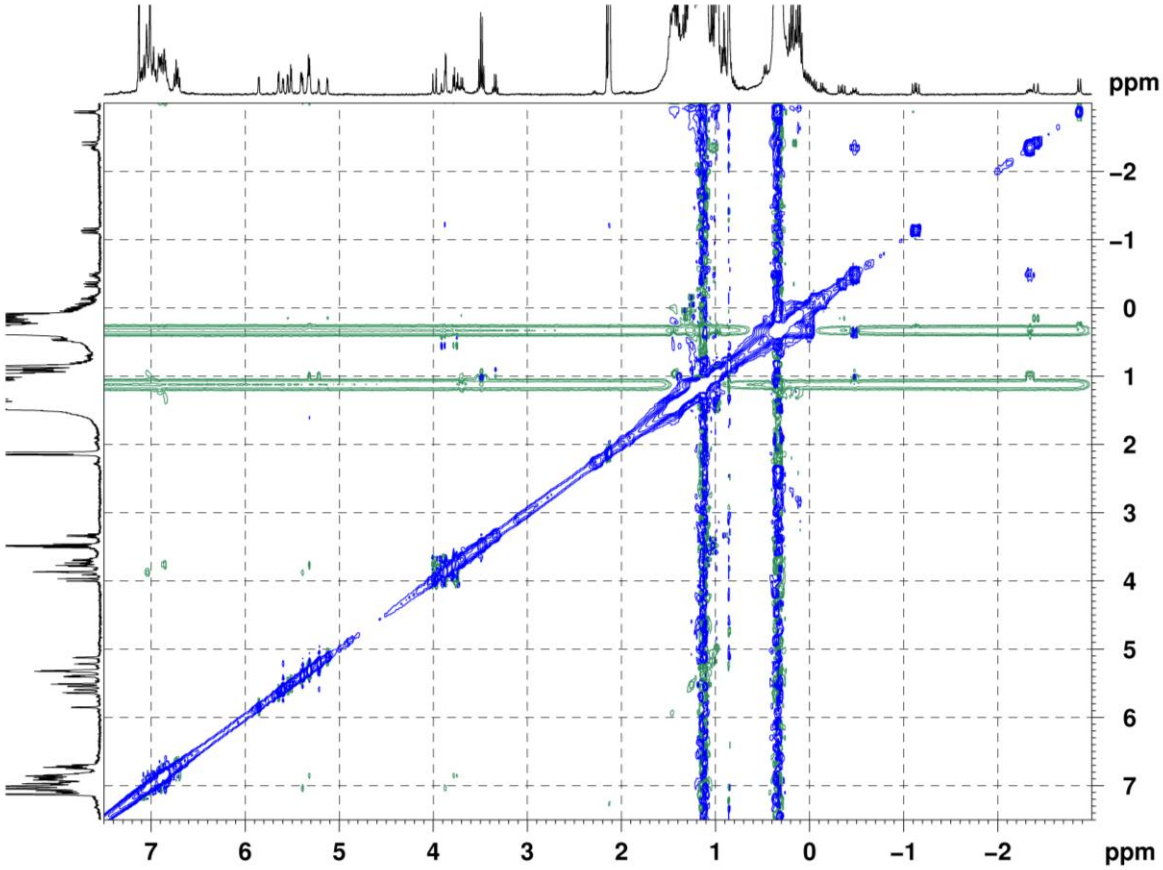



**Figure S30.** $^1$H NMR of **16m** obtained by the reaction of **1m** with $(AlEt_3)_2$ (1:24) in $CD_2Cl_2$ at 270 K.

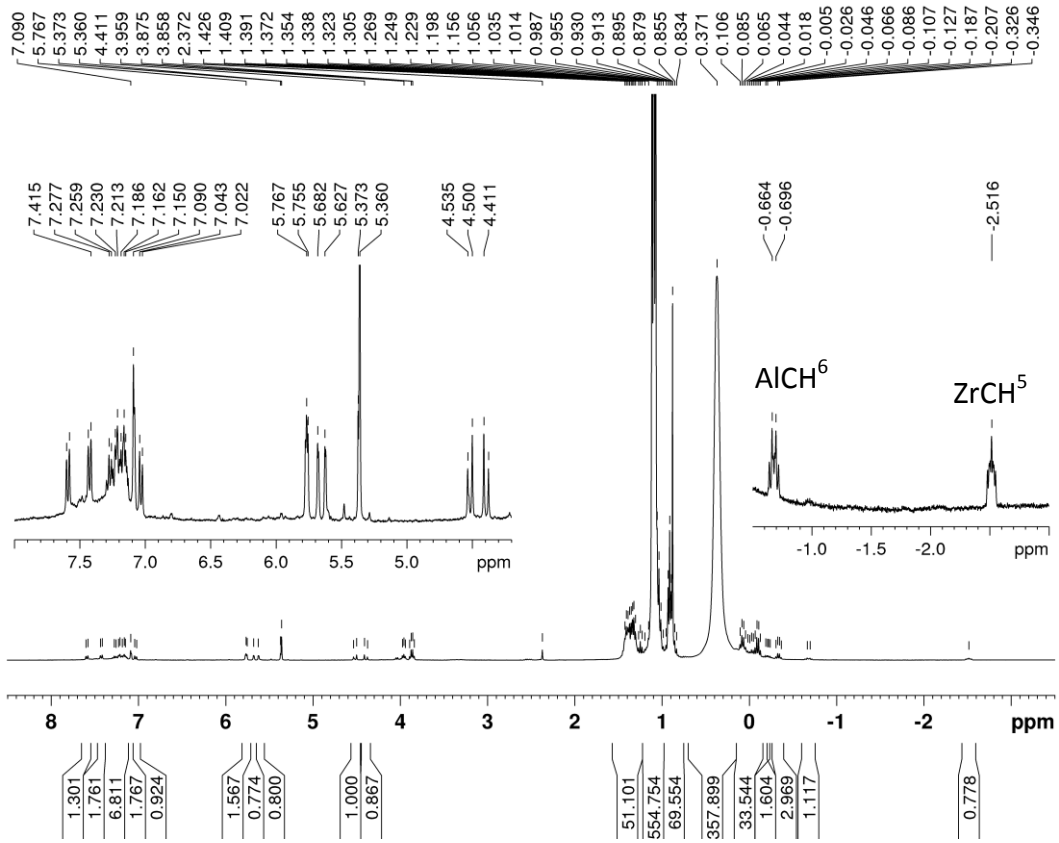


**Figure S31.** $^{1}$H NMR of complex **16n** obtained by the reaction of **1n** with $(AlEt_3)_2$ (1:16) in $C_7D_8$ at 285 K.

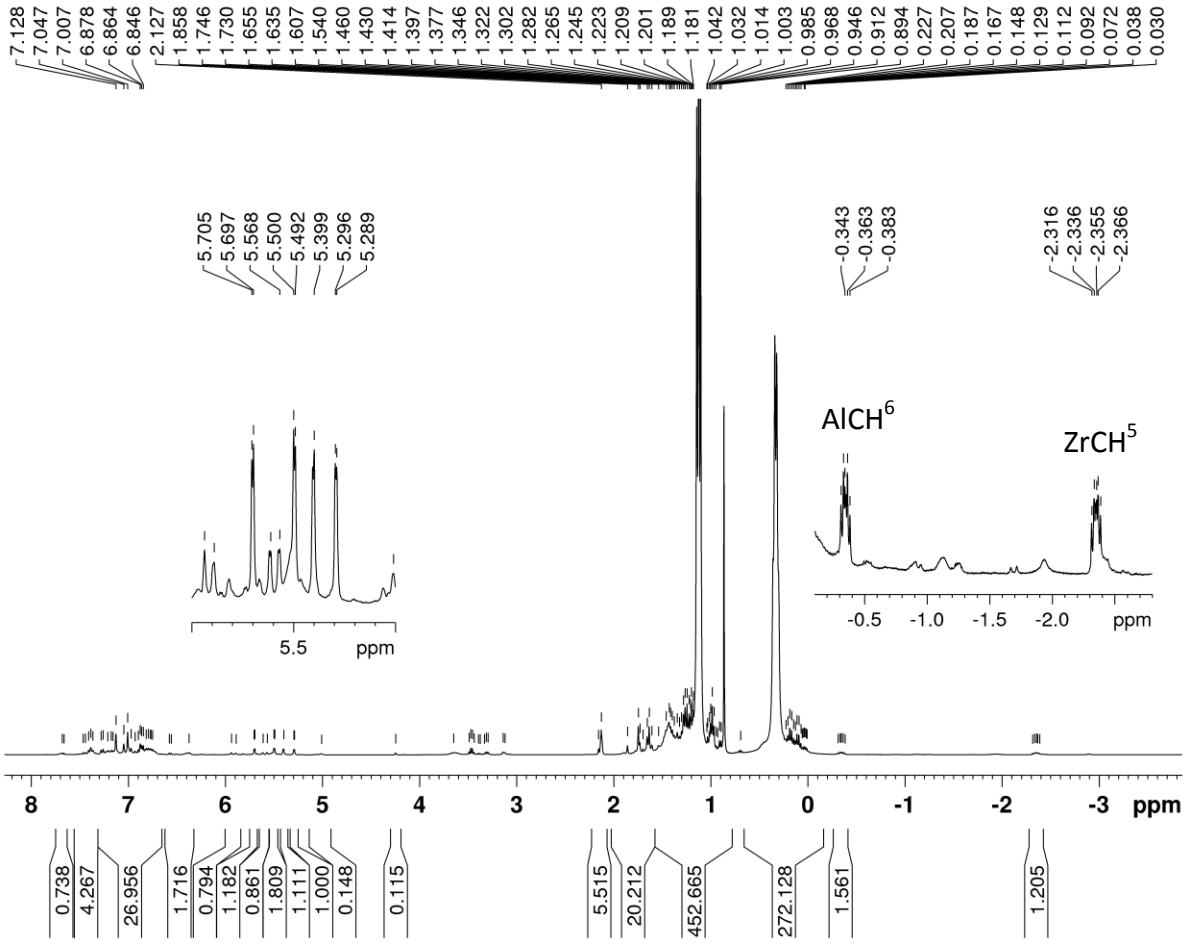



**Figure S32.** COSY HH of **16n** in $C_7D_8$ at 270 K.

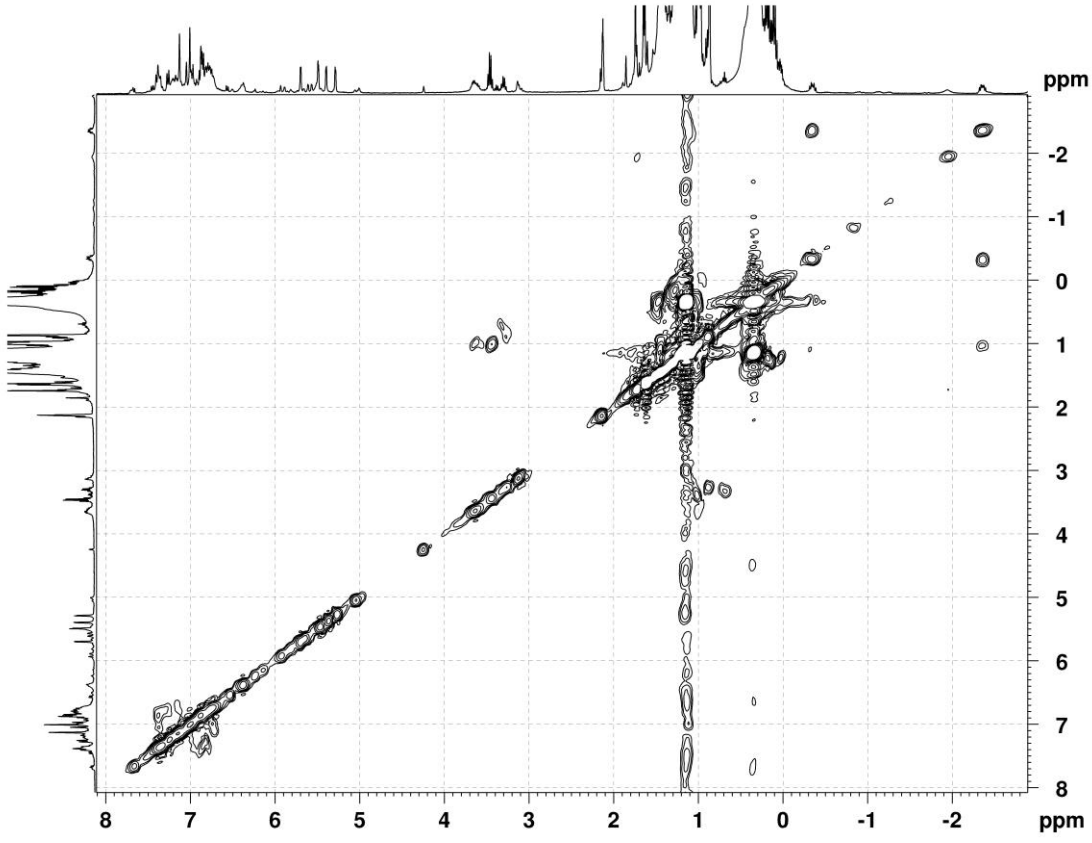


**Figure S33.** $^{13}C$ NMR of **16n** in $C_7D_8$ at 270 K.

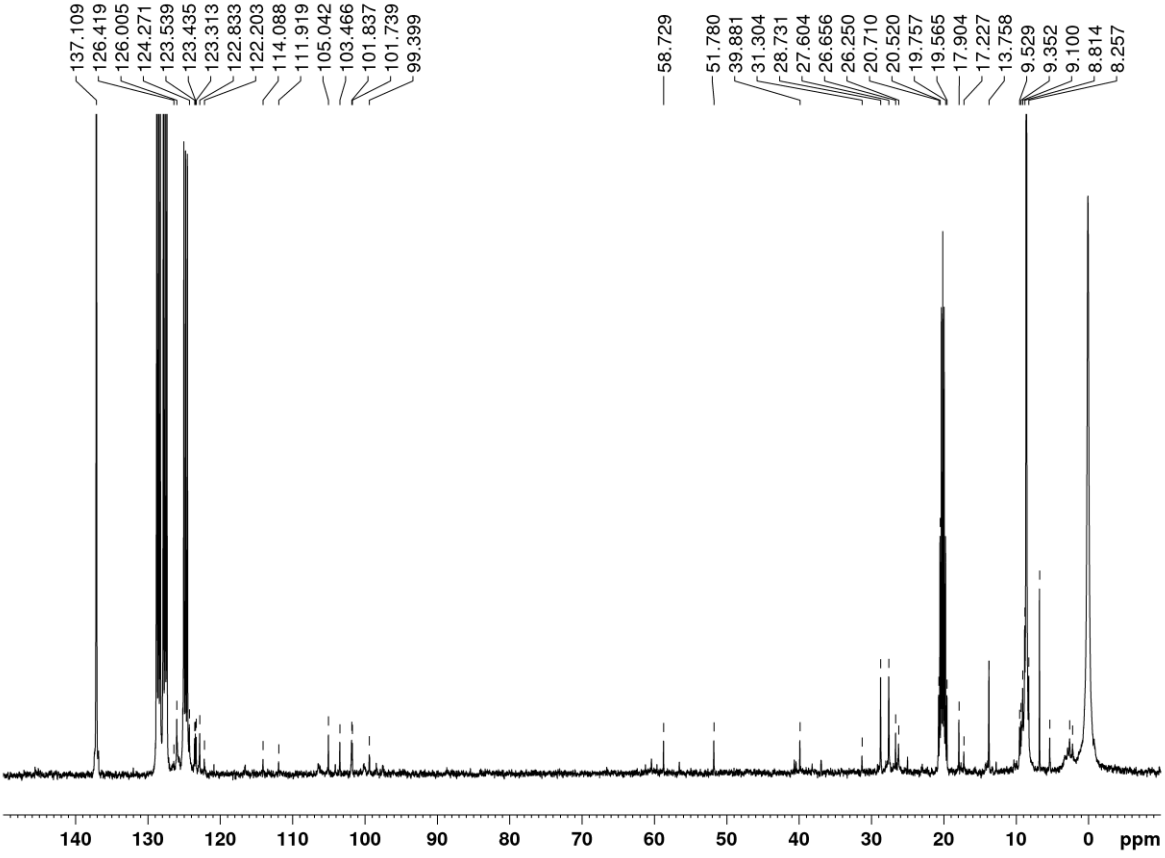



**Figure S34.** HSQC of **16n** in $C_7D_8$ at 270 K.

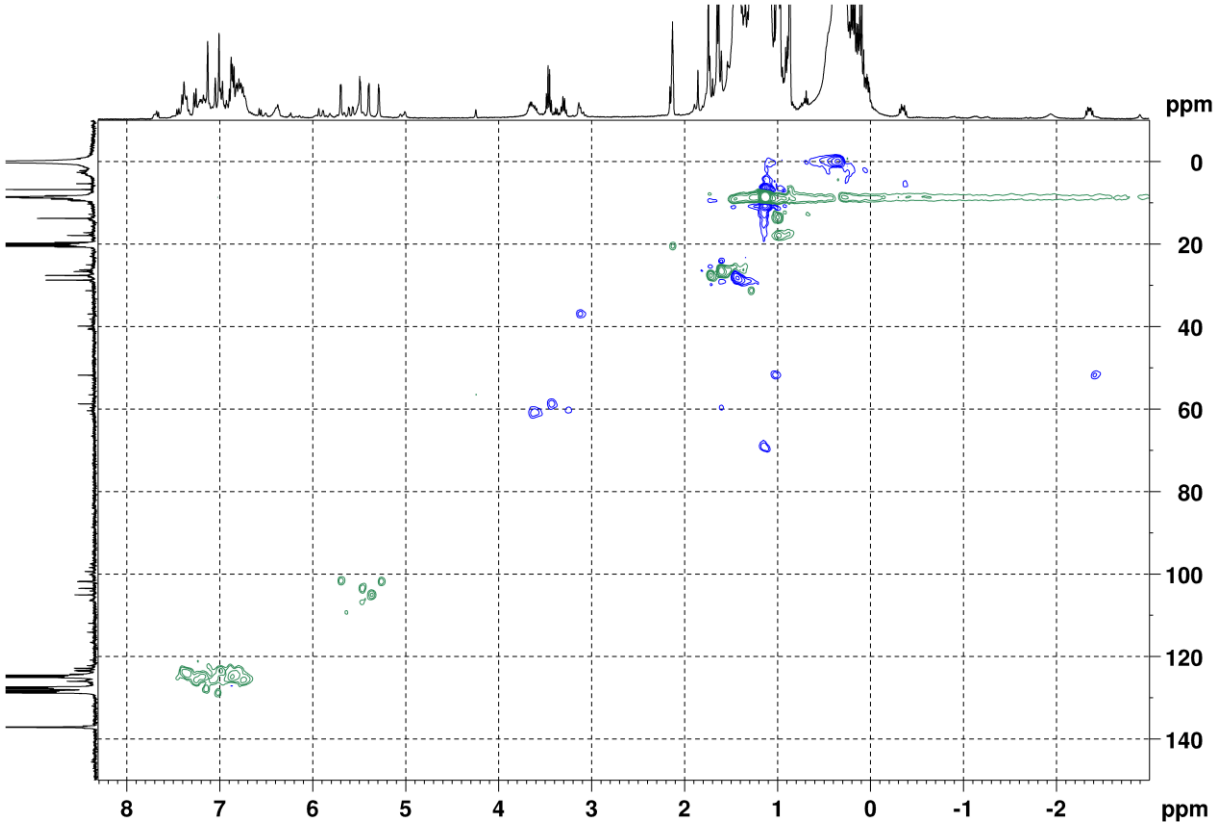


**Figure S35.** HMBC of **16n** in $C_7D_8$ at 270 K.

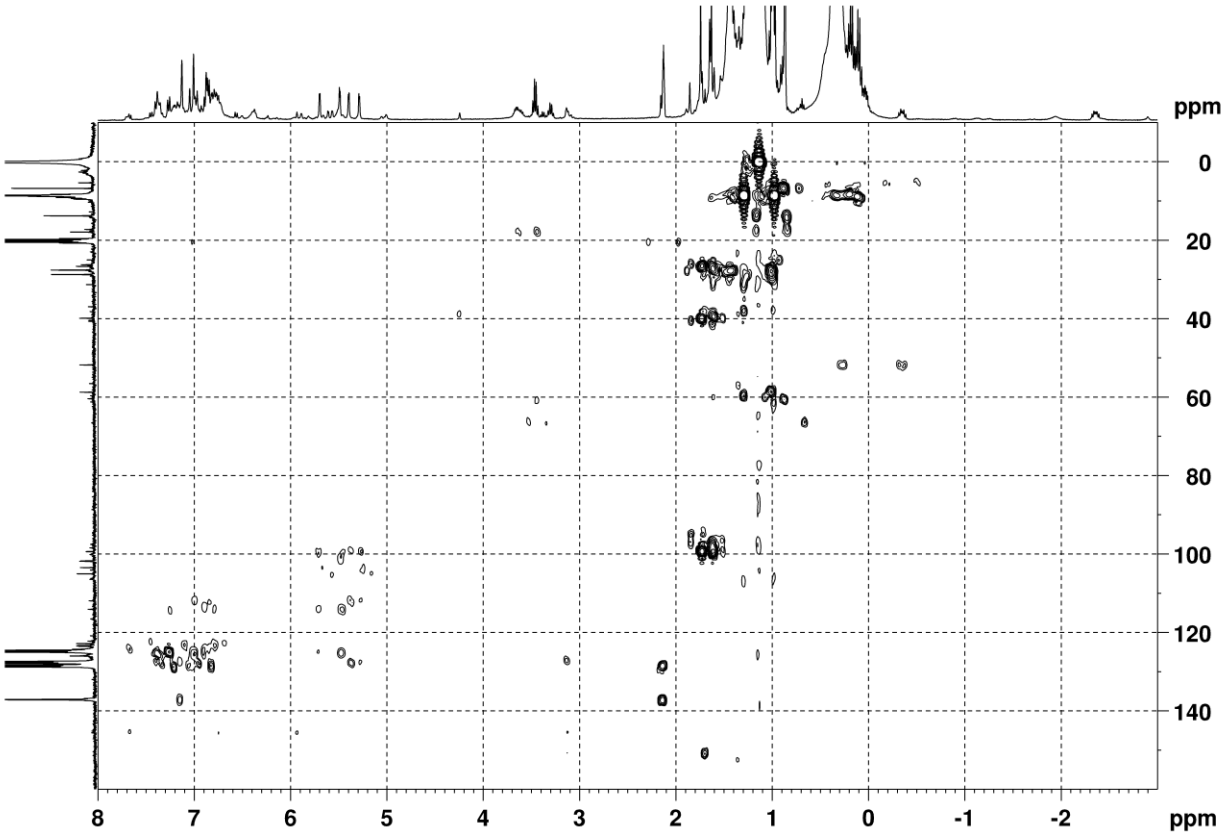



**Figure S36.** EXSY spectrum of **16n** in $C_7D_8$ at 293 K (τ= 0.3 s).

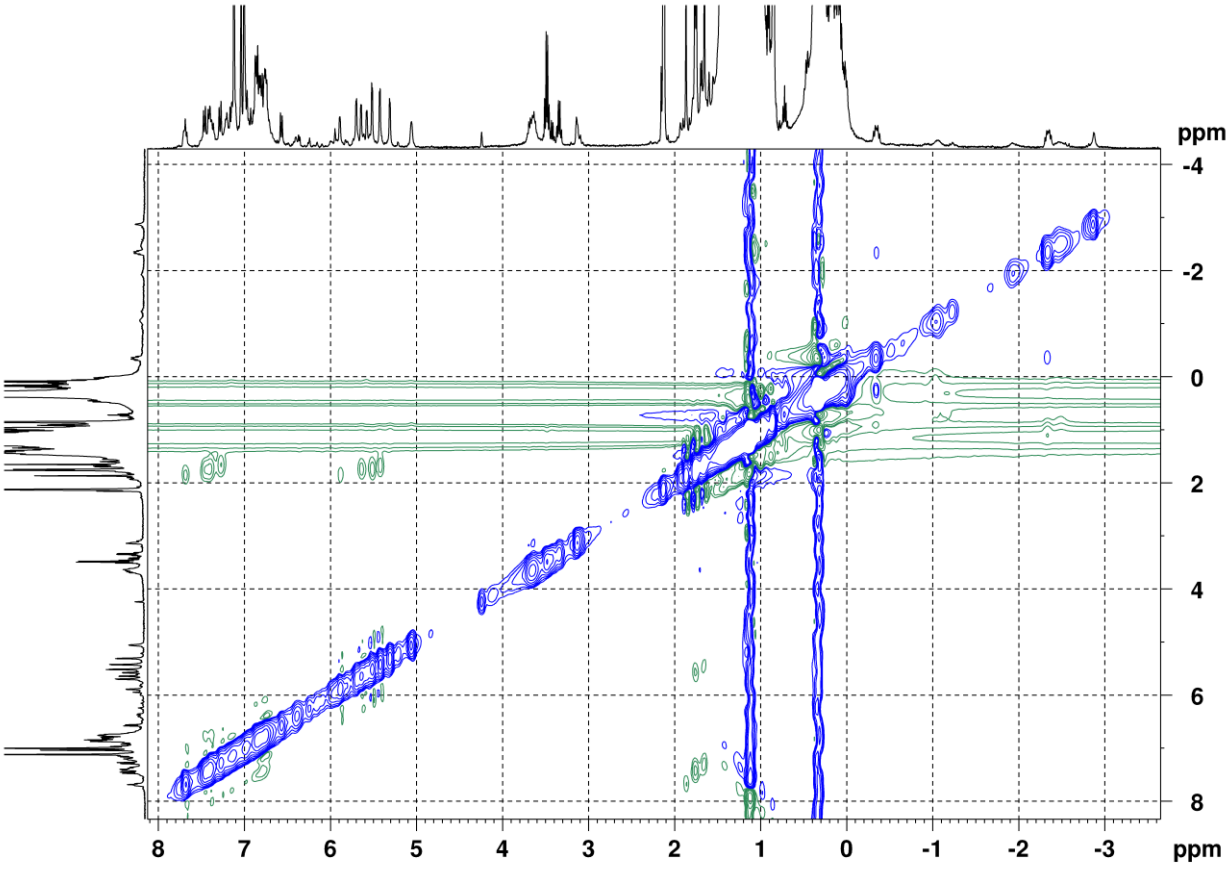


**Figure S37.** $^{1}$H NMR of **16p** obtained by the reaction of **1p** with $(AlEt_3)_2$ (1:13) in $C_7D_8$ at 280 K.

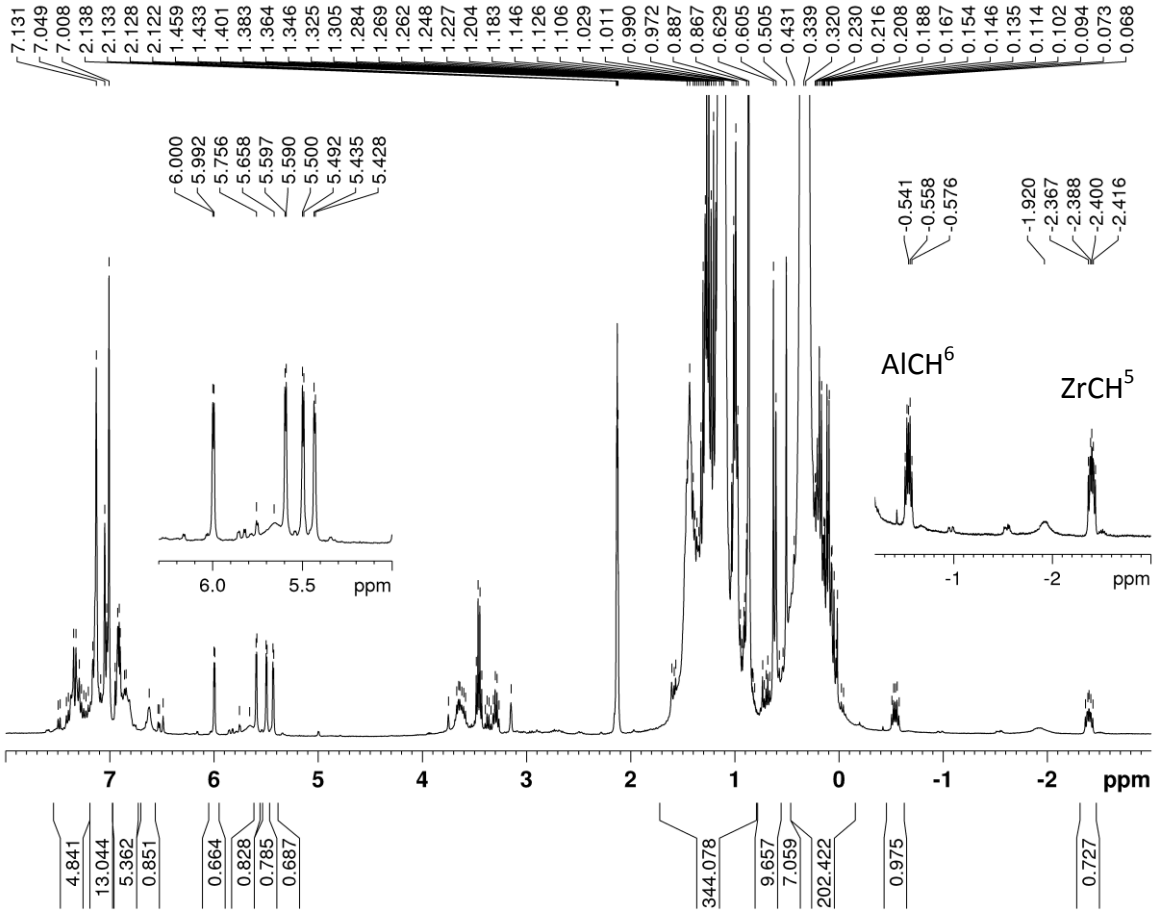



**Figure S38.** COSY HH of **16p** in $C_7D_8$ at 260 K.

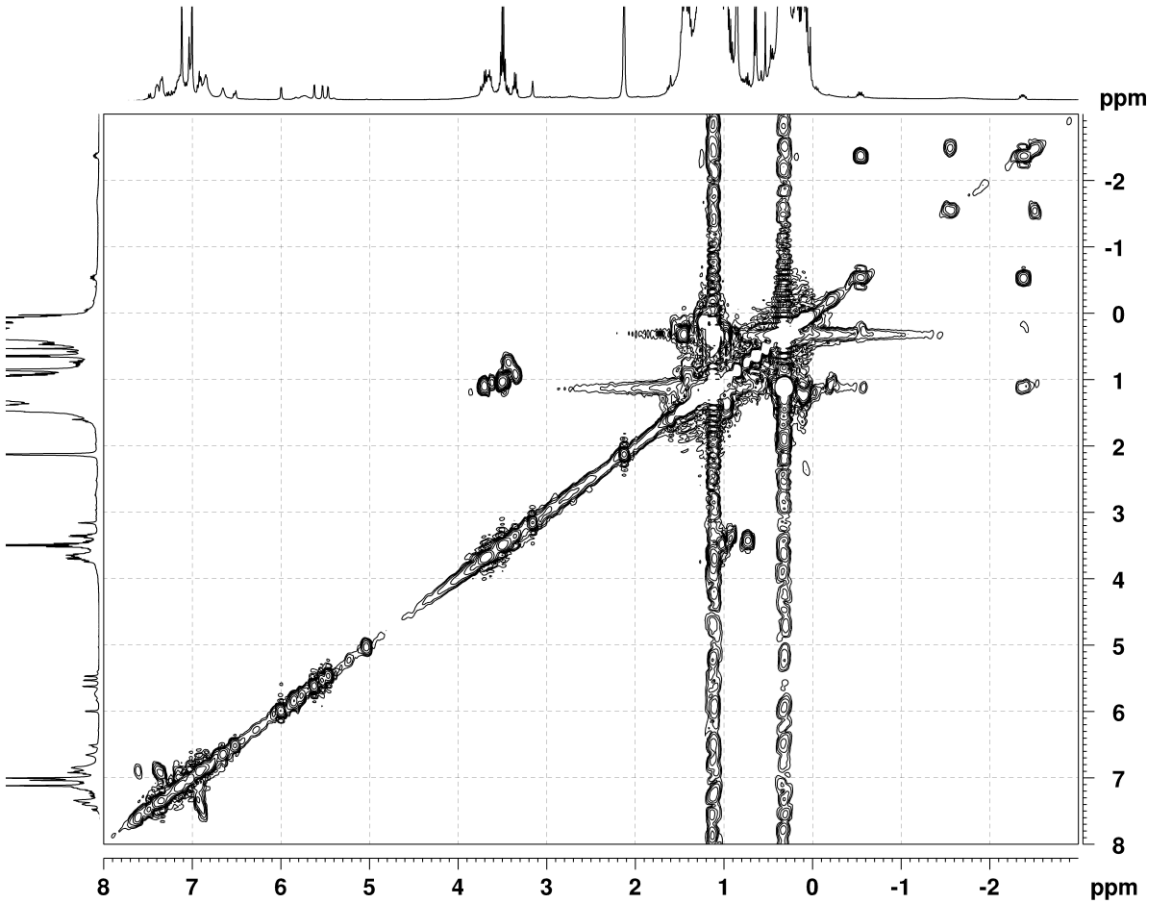


**Figure S39.** HSQC of **16p** in $C_7D_8$ at 270 K.

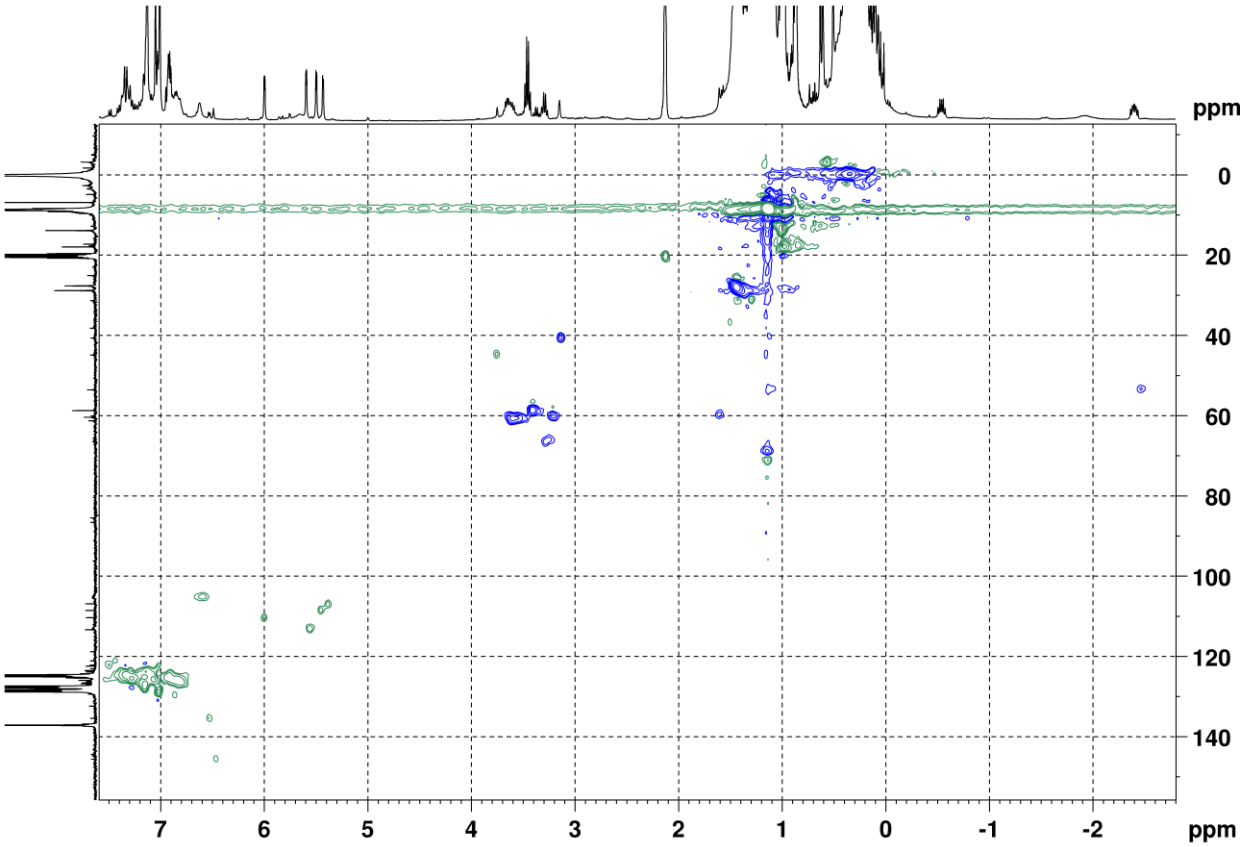



**Figure S40.** HMBC of **16p** in $C_7D_8$ at 270 K.

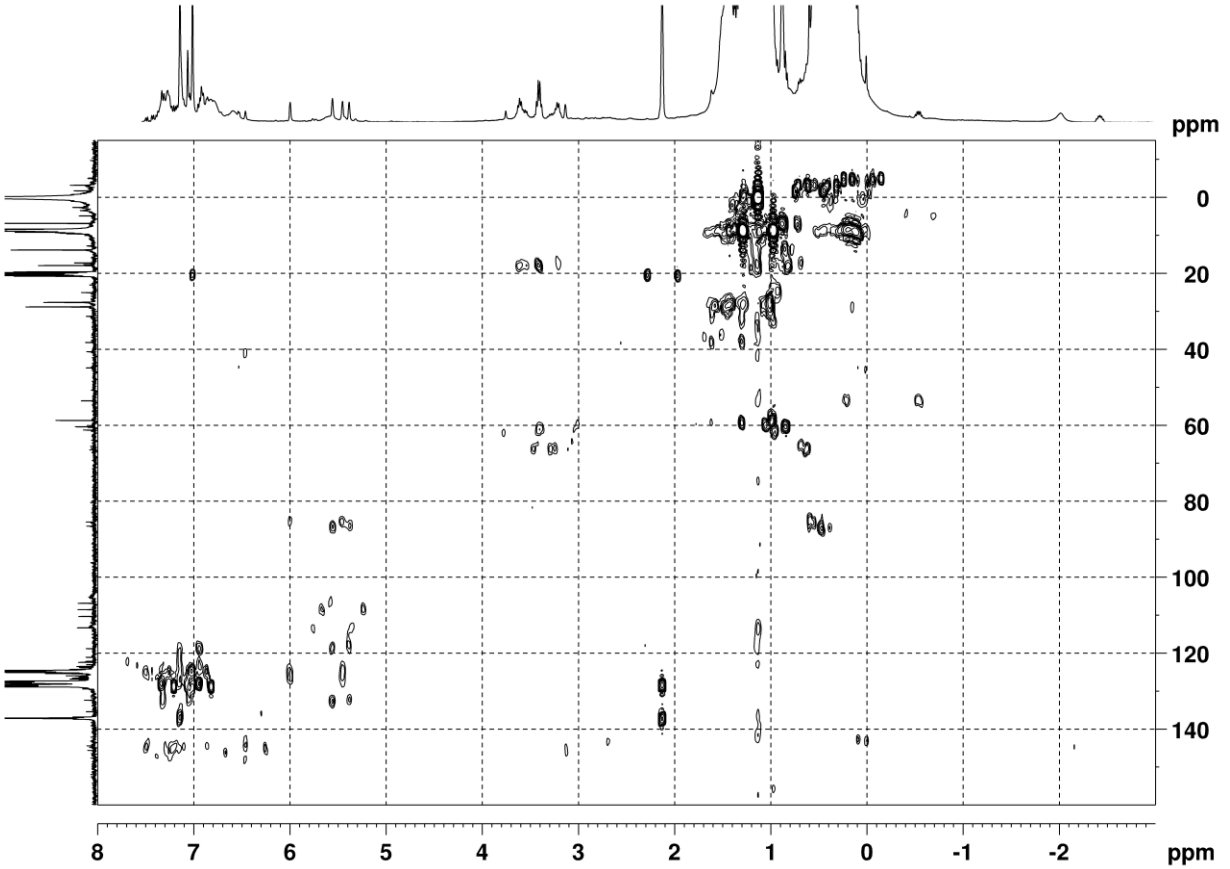


**Figure S41.** EXSY spectrum of **16p** in $C_7D_8$ at 293 K (τ= 0.3 s).

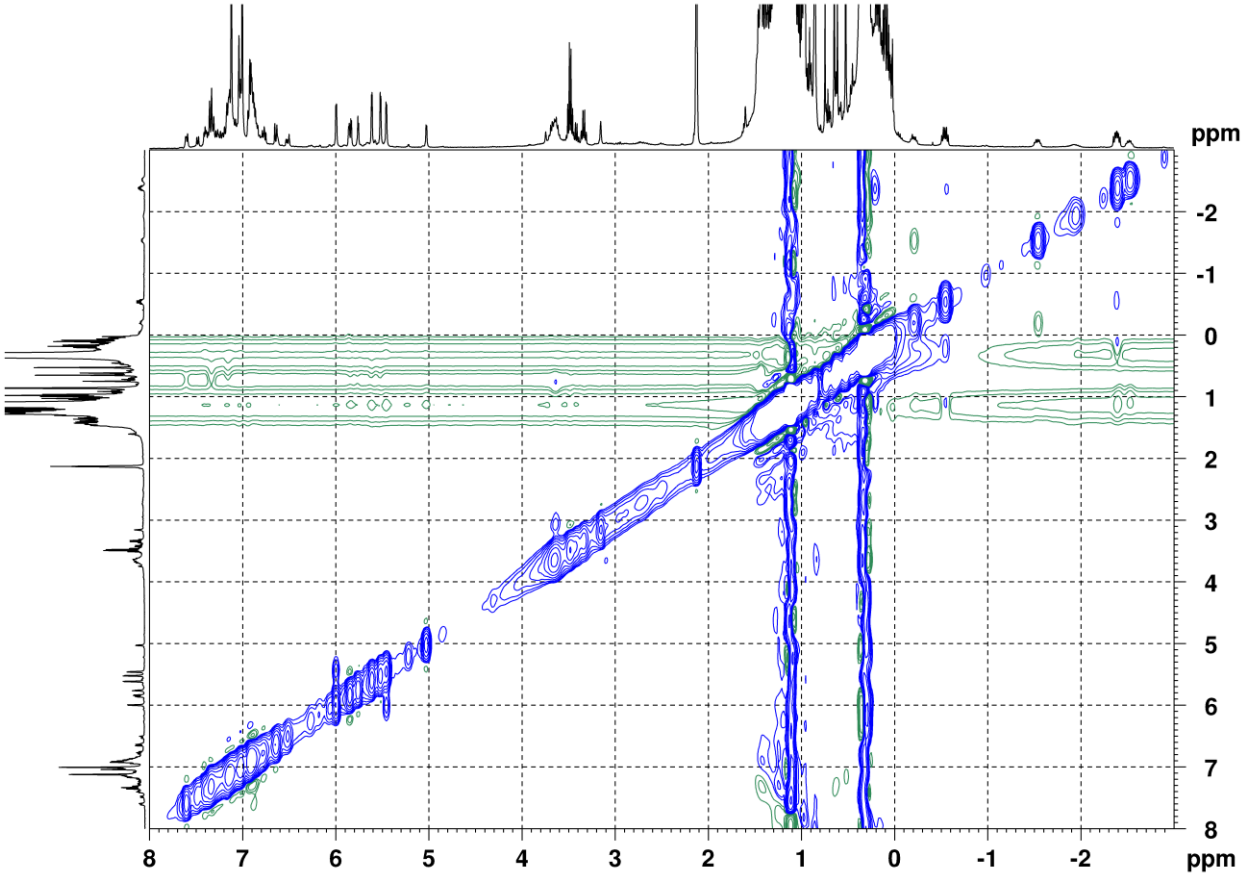



**Figure S42.** $^1$H NMR of **16p** obtained by the reaction of **1p** with $(AlEt_3)_2$ (1:13) in $CD_2Cl_2$ at 280 K.

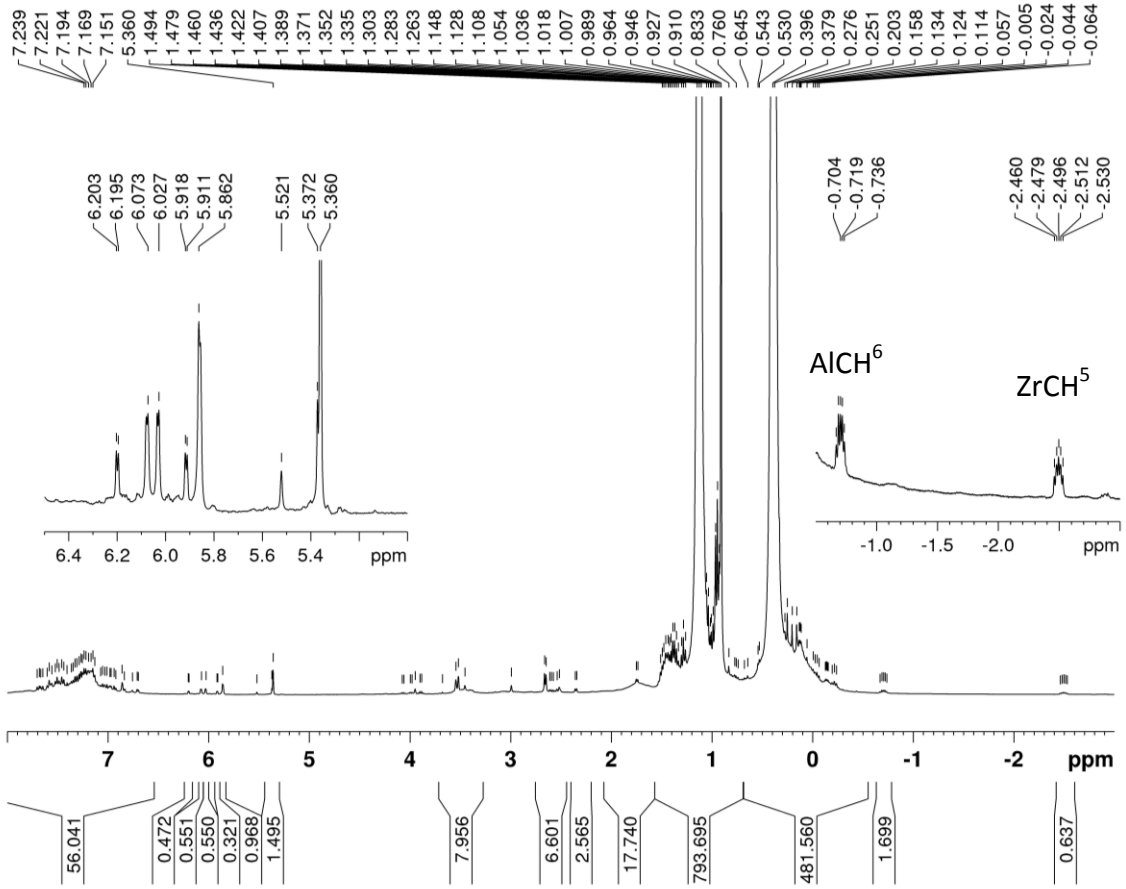


**Figure S43.** $^{1}$H NMR of **16q** obtained by the reaction of **1q** with $(AlEt_3)_2$ (1:2) in $C_7D_8$ at 285 K.

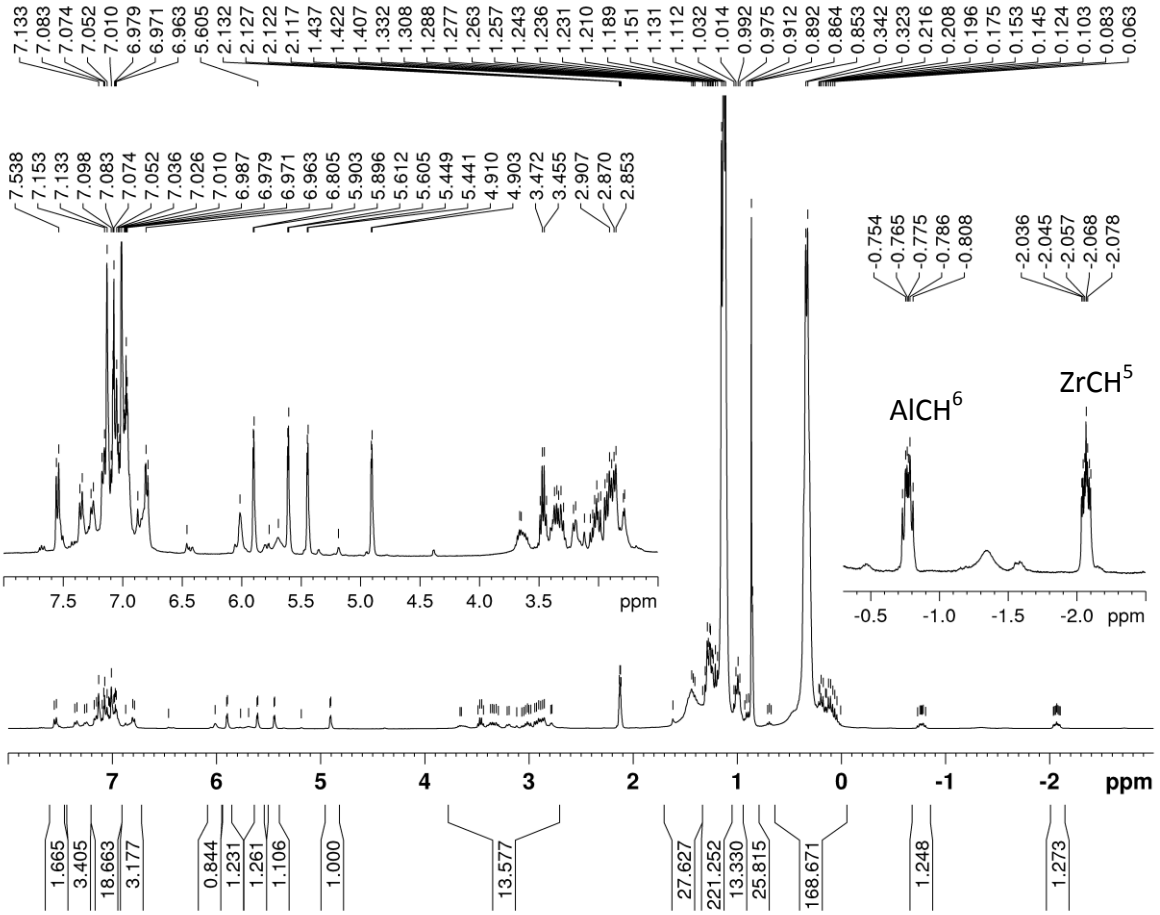



**Figure S44.** COSY HH of **16q** in $C_7D_8$ at 260 K.

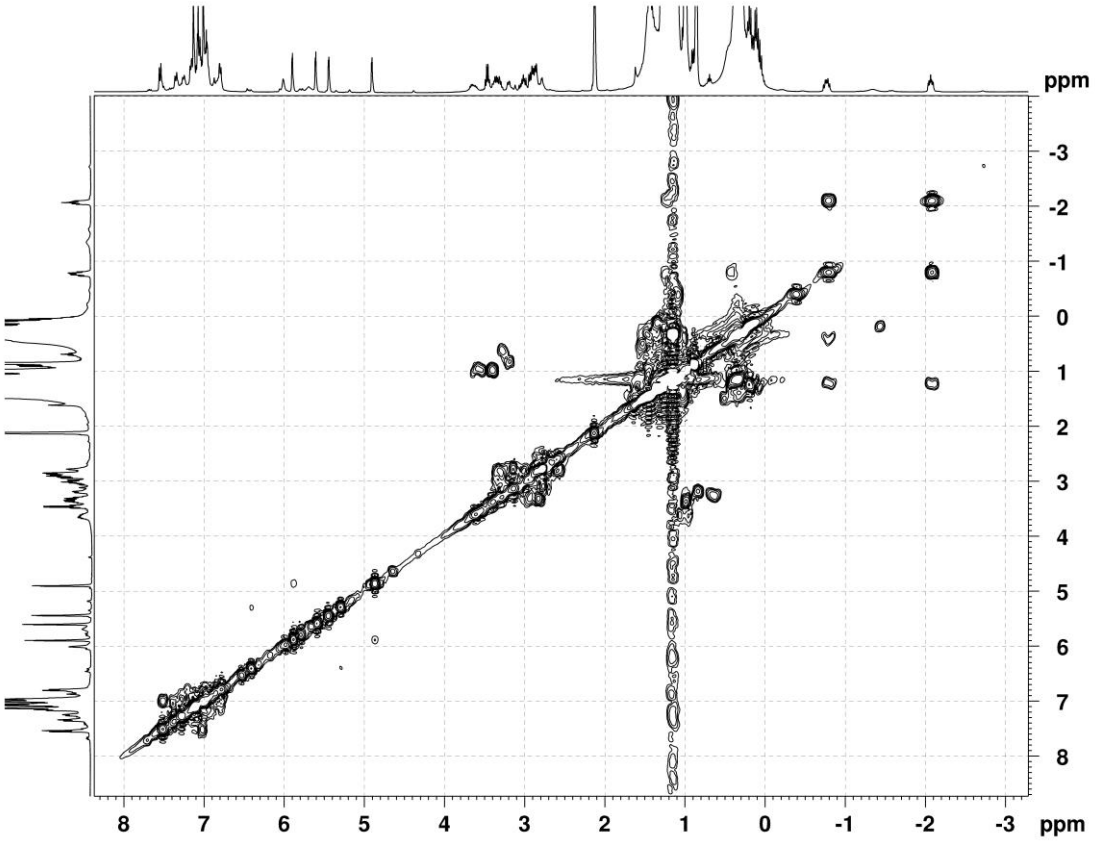


**Figure S45.** $^{13}C$ NMR of **16q** in $C_7D_8$ at 220 K.

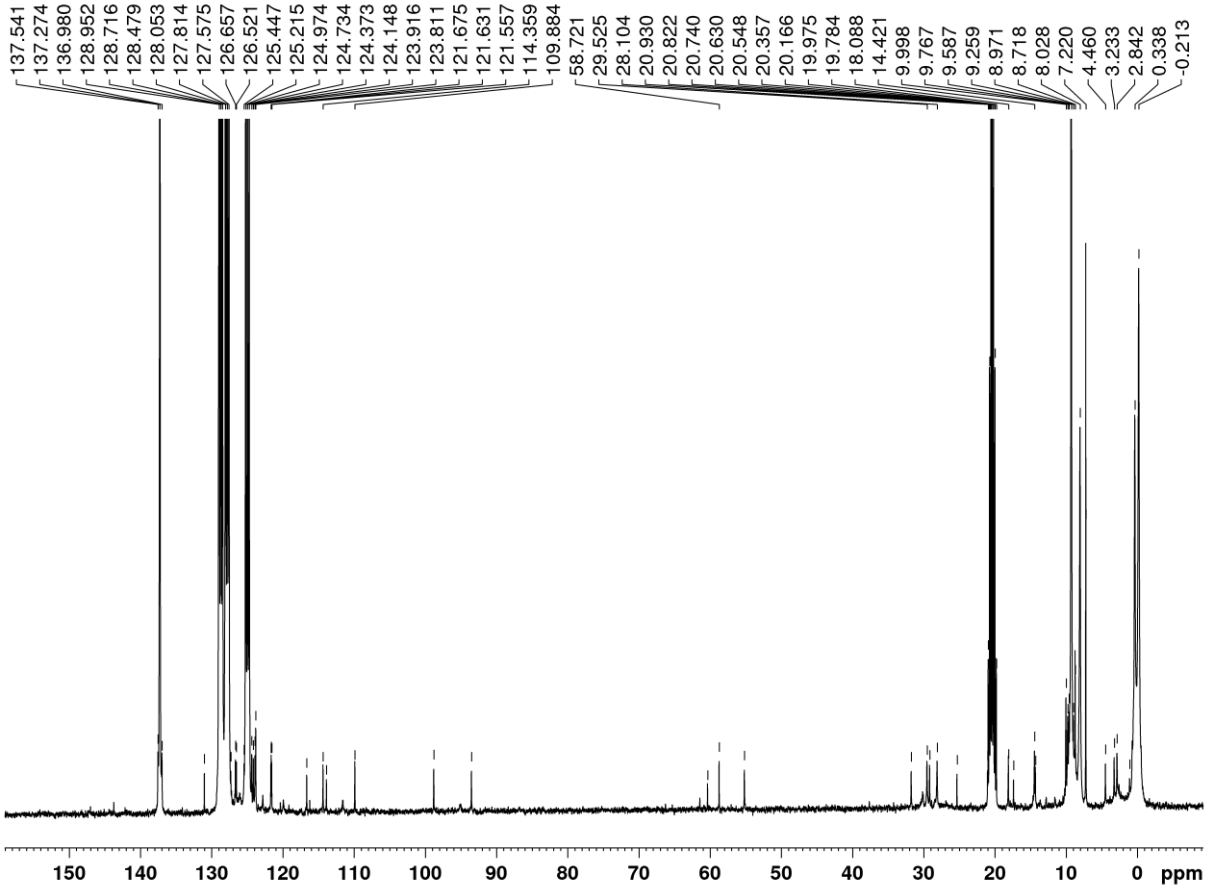



**Figure S46.** HSQC of **16q** in $C_7D_8$ at 220 K.

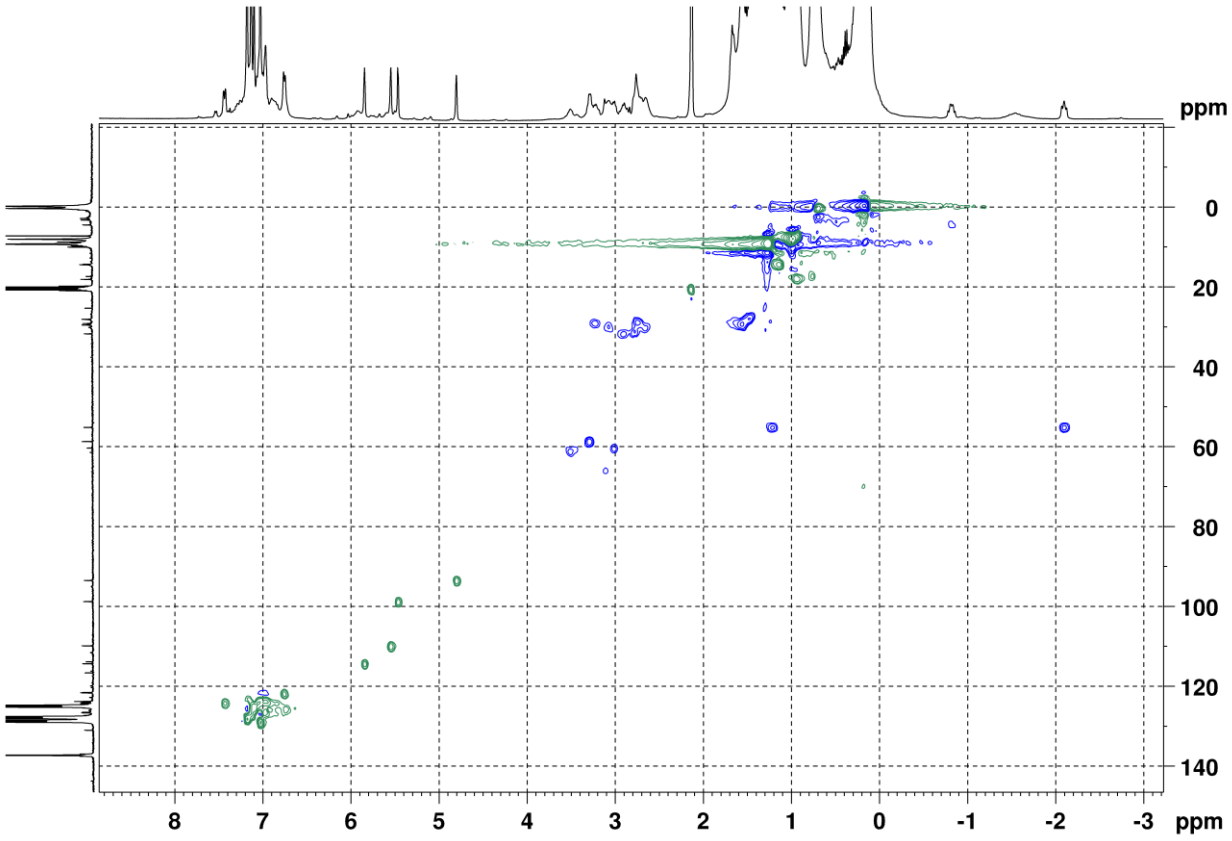


**Figure S47.** HMBC of **16q** in $C_7D_8$ at 220 K.

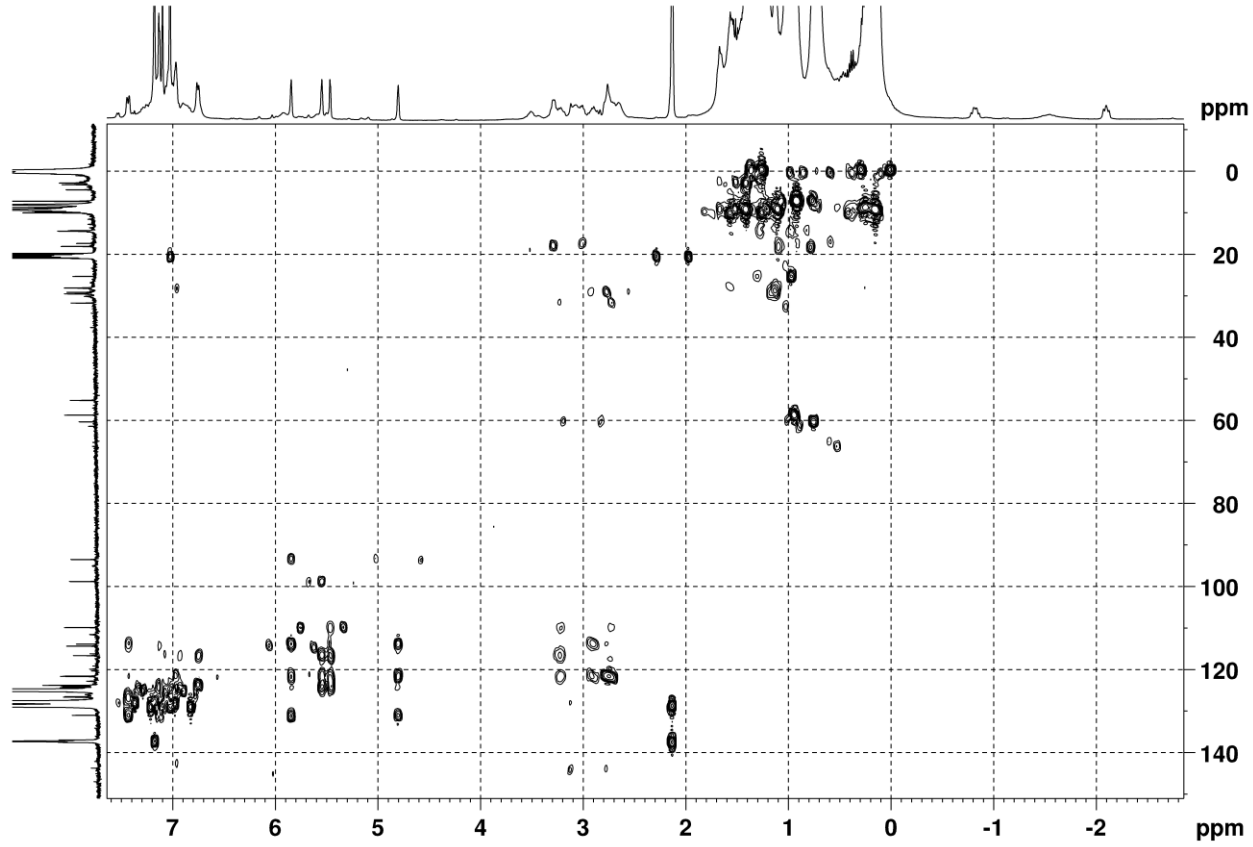



**Figure S48.** EXSY of **16q** in $C_7D_8$ at 290 K (τ= 0.3 s).

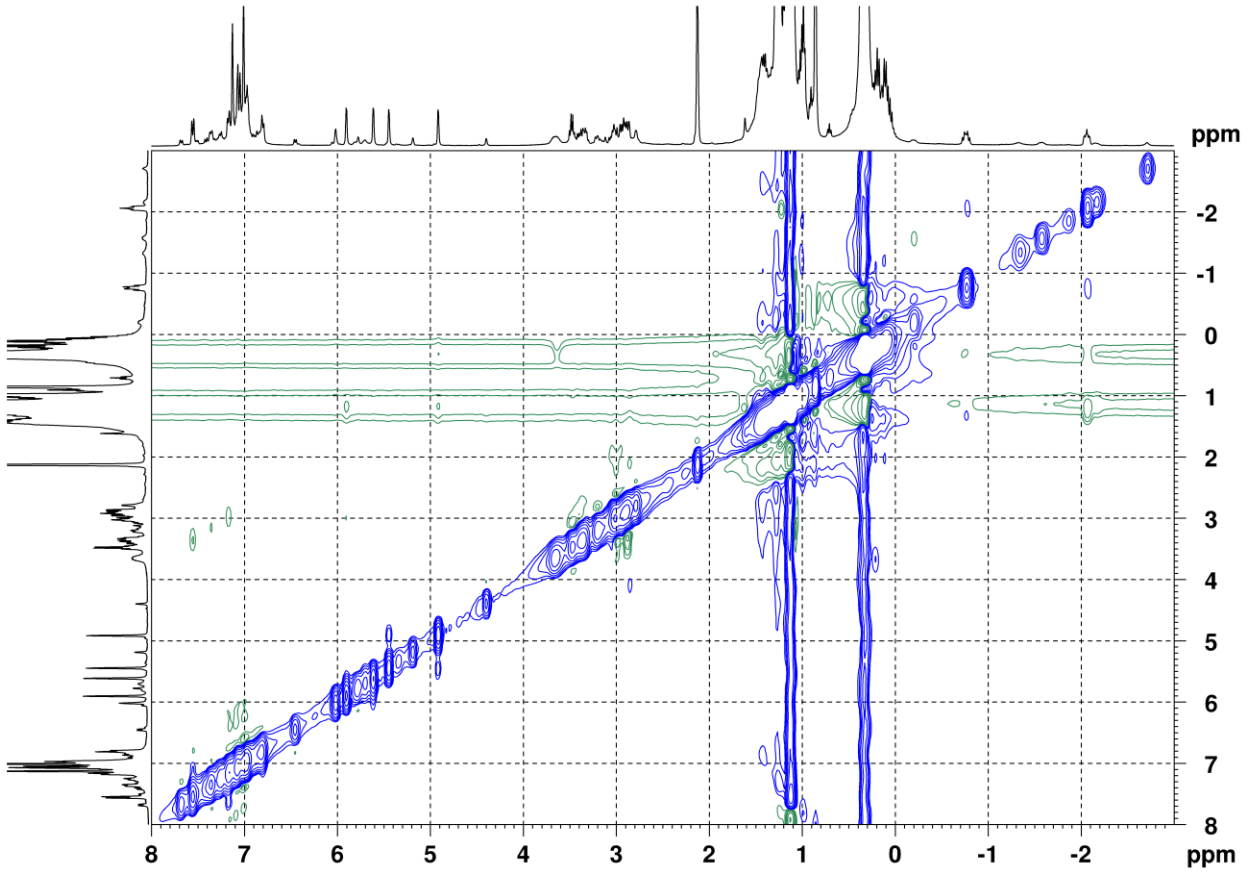


**Figure S49.** $^{1}$H NMR of **16q** obtained by the reaction of **1q** with $(AlEt_3)_2$ (1:13) in $CD_2Cl_2$ at 285 K.

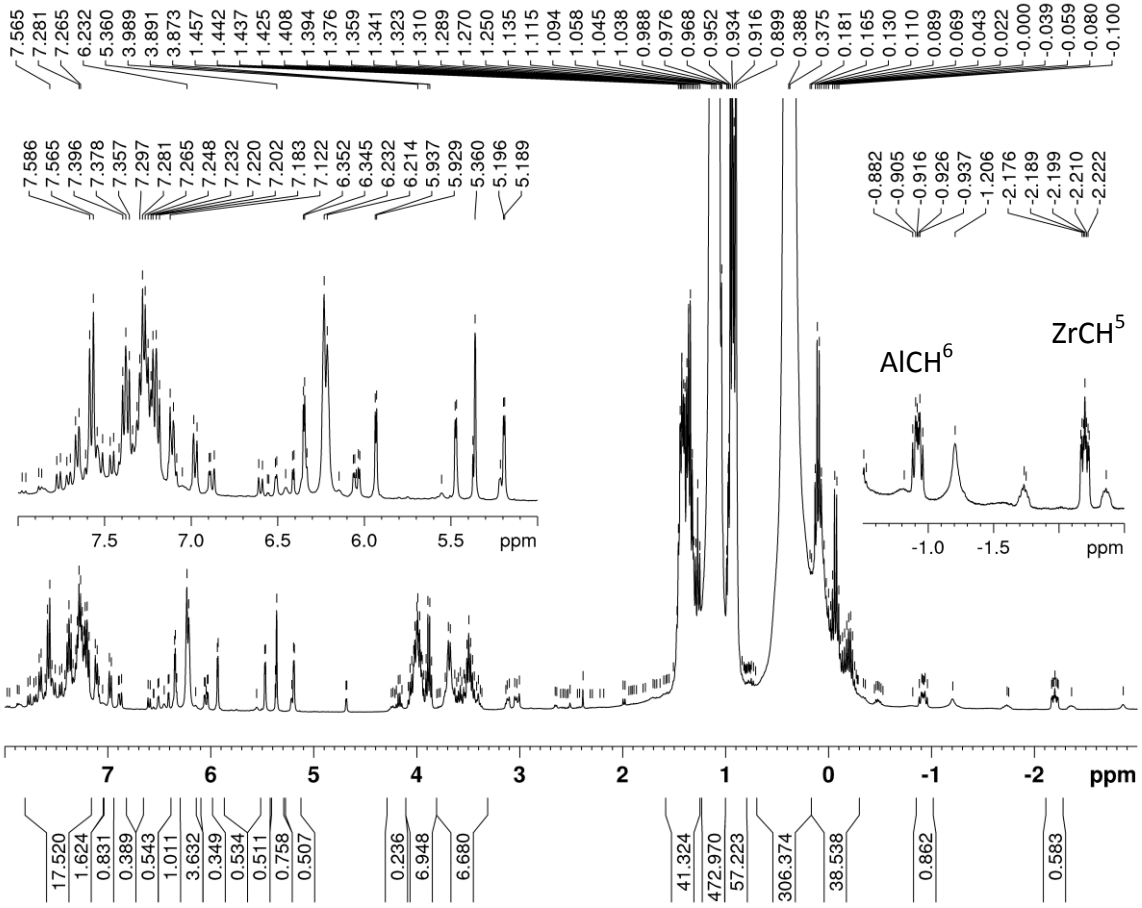



**Figure S50.** $^{1}$H NMR of **17l** obtained by the reaction of **1l** with $(AlEt_3)_2$ (1:24) in $C_7D_8$ at 298 K.

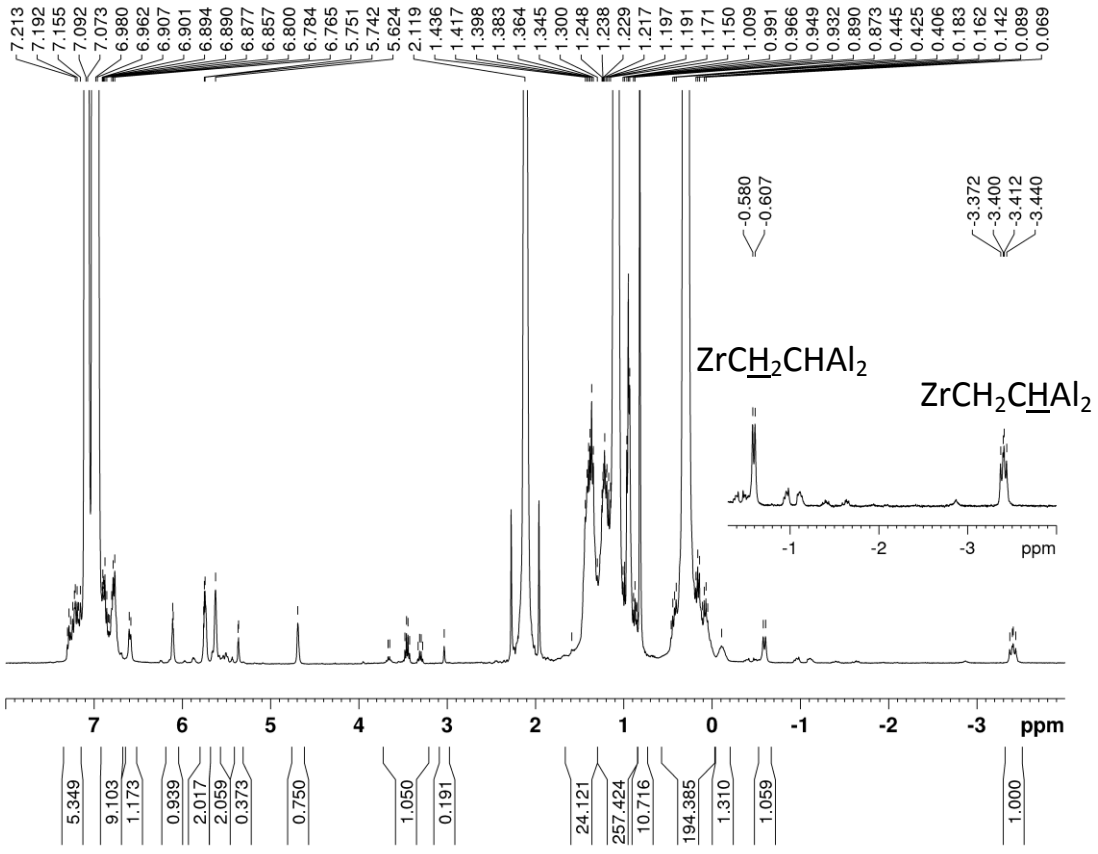


**Figure S51.** COSY HH of **17l** in $C_7D_8$ at 298 K.

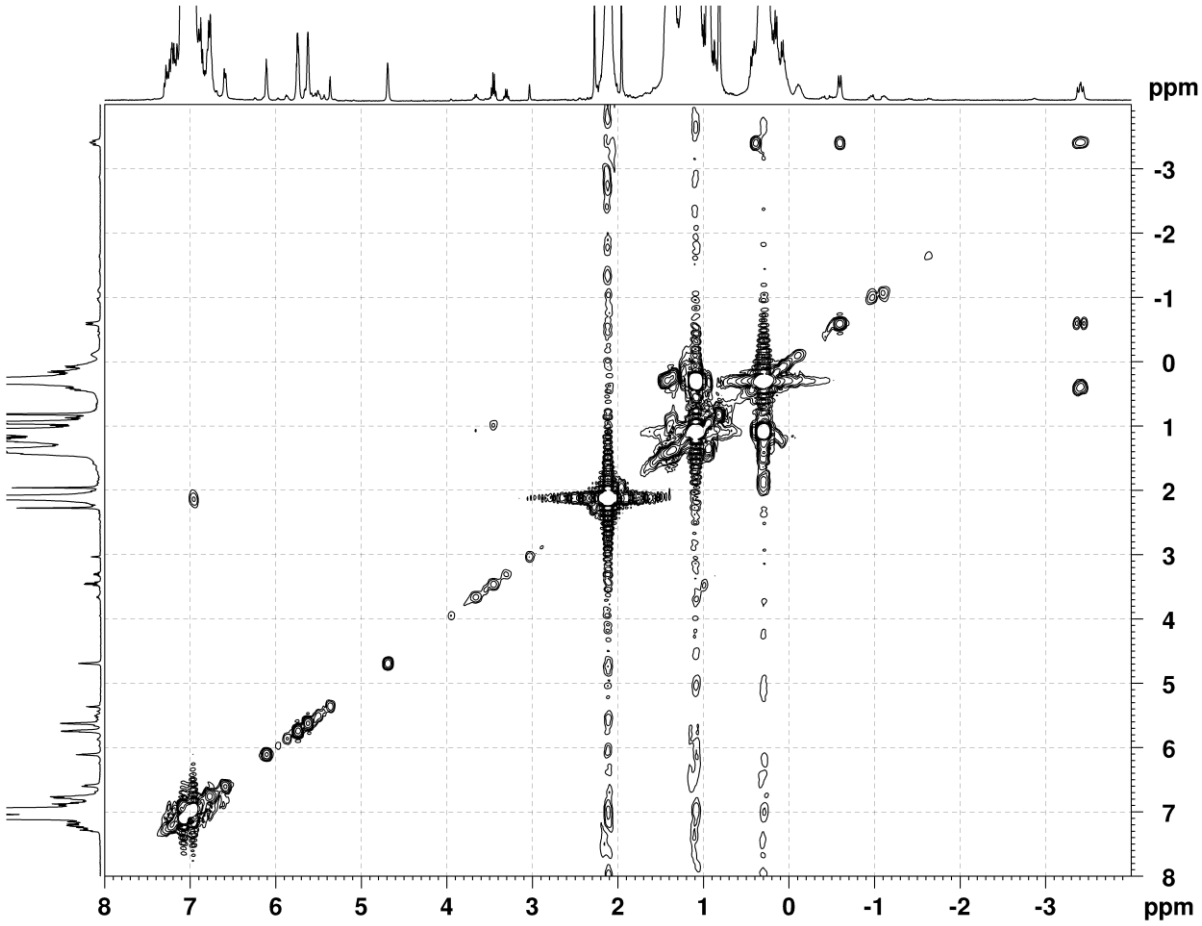



**Figure S52.** $^{13}C$ NMR of **17l** in $C_7D_8$ at 298 K.

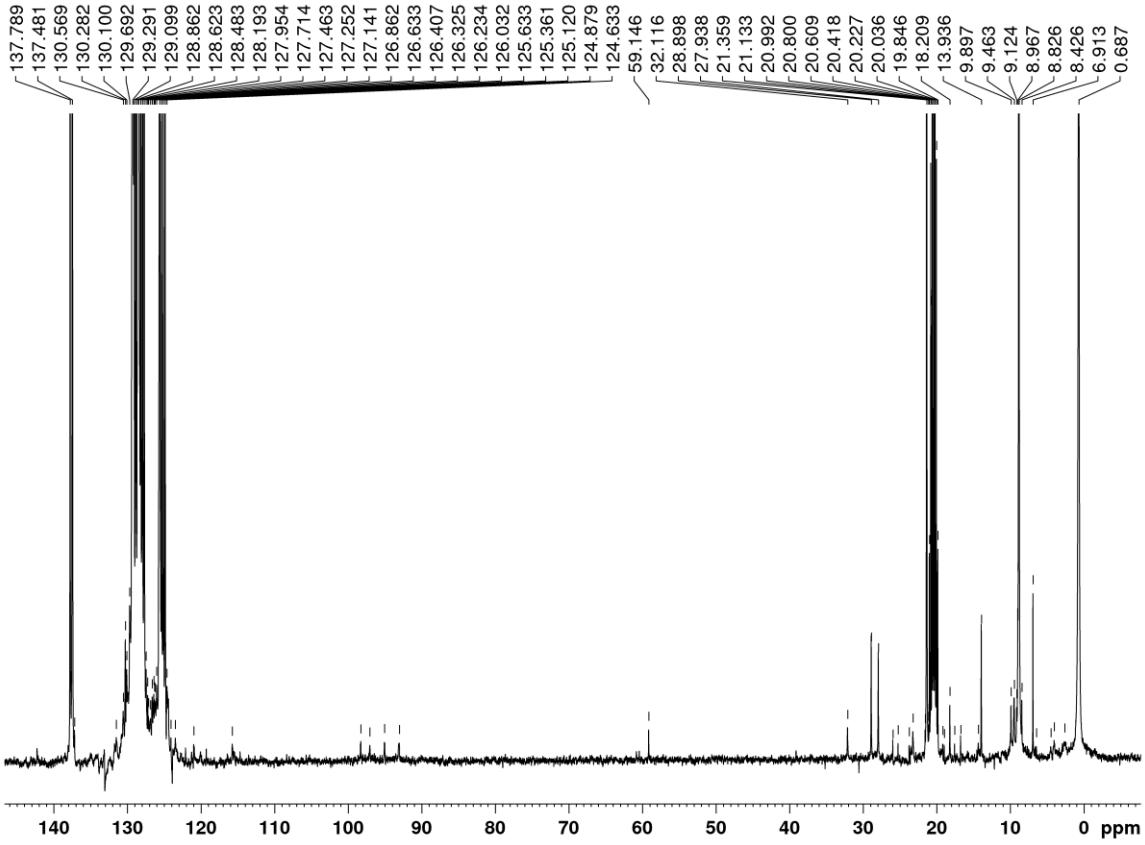


**Figure S53.** HSQC of **17l** in $C_7D_8$ at 298 K.

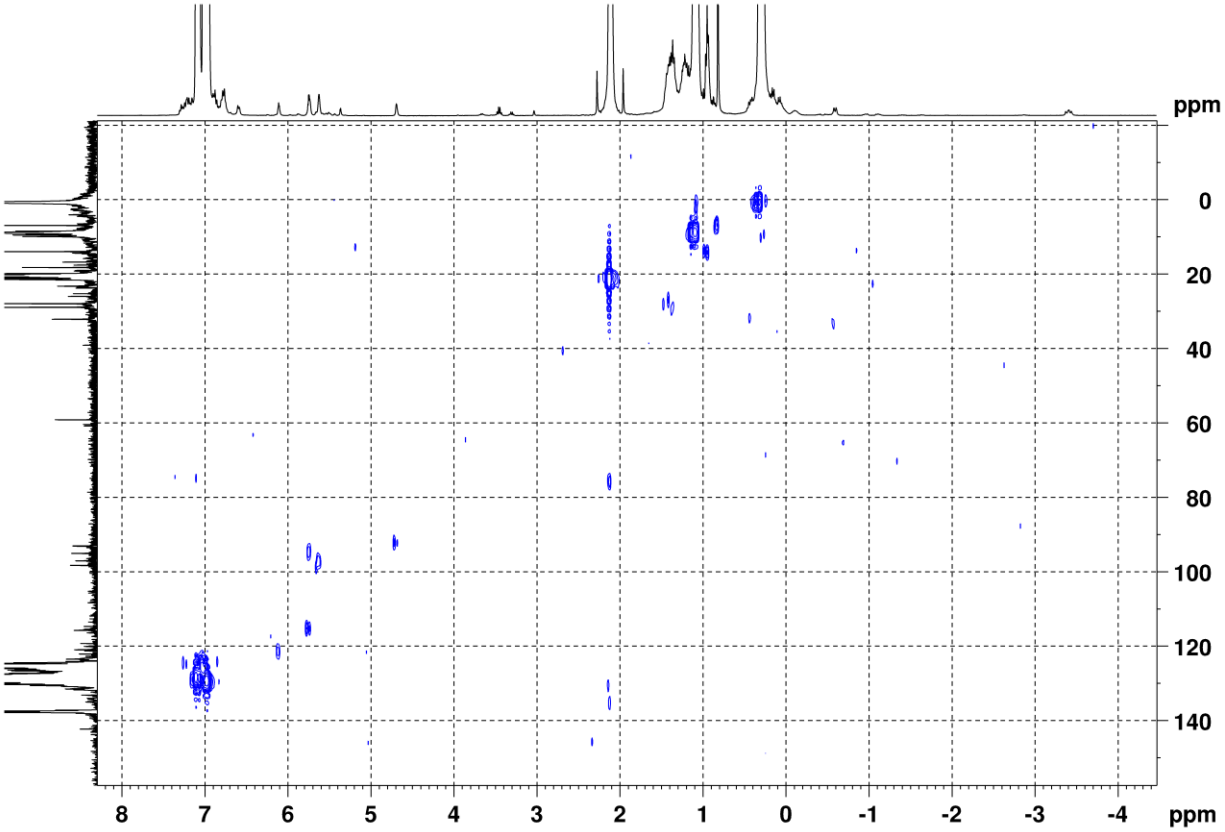



**Figure S54.** HMBC of **17l** in $C_7D_8$ at 298 K.

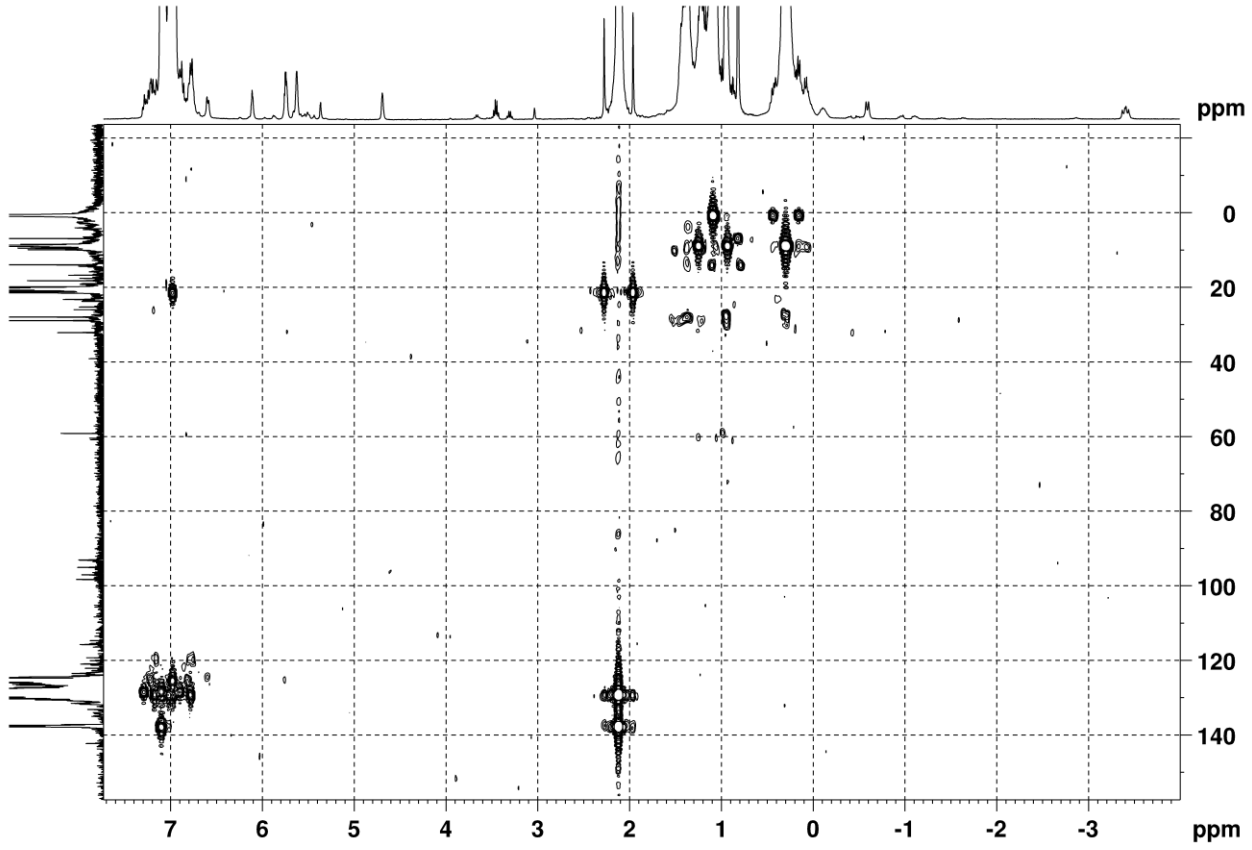


**Figure S55.** NOESY of **17l** in $C_7D_8$ at 298 K.

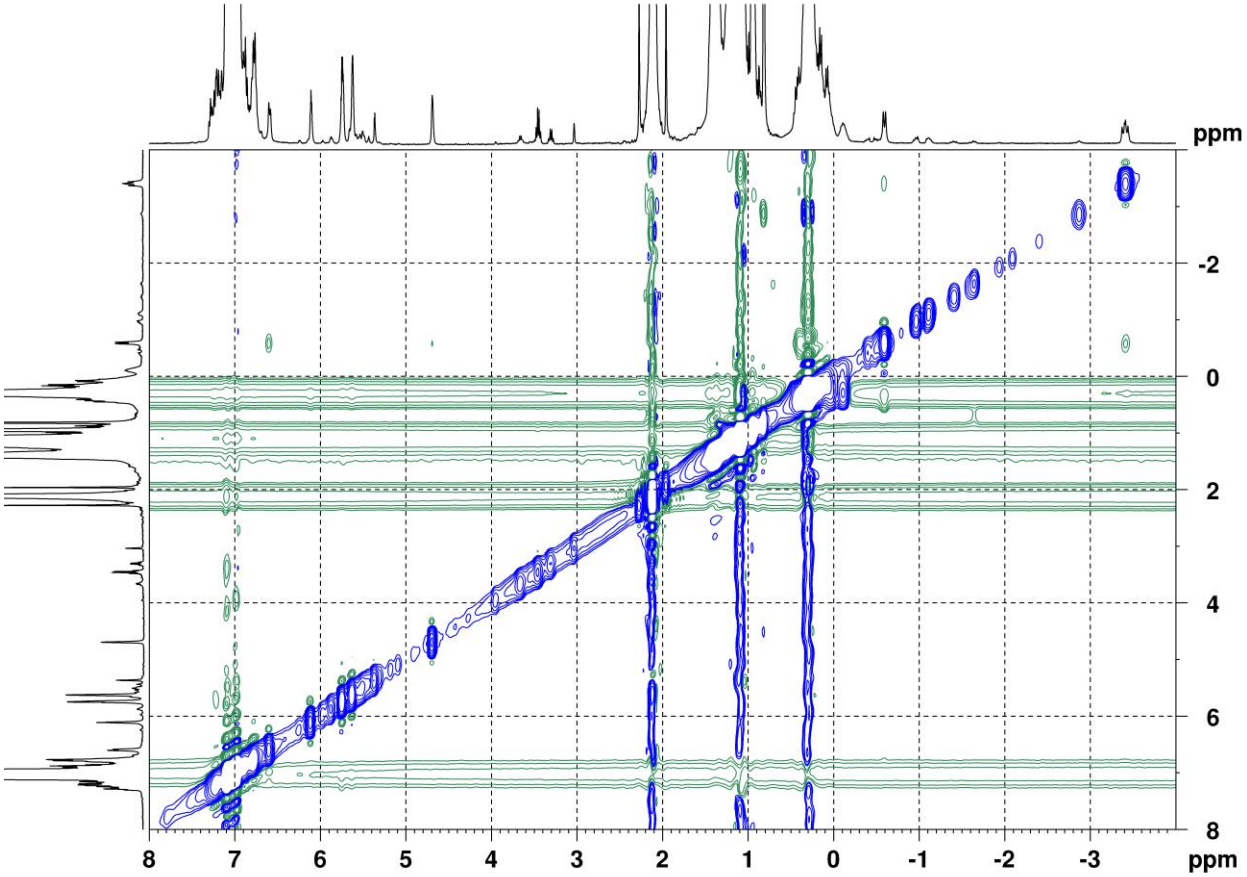



**Figure S56.** $^1$H NMR of **17m** obtained by the reaction of **1m** with $(AlEt_3)_2$ (1:13) in $C_7D_8$ at 299 K.

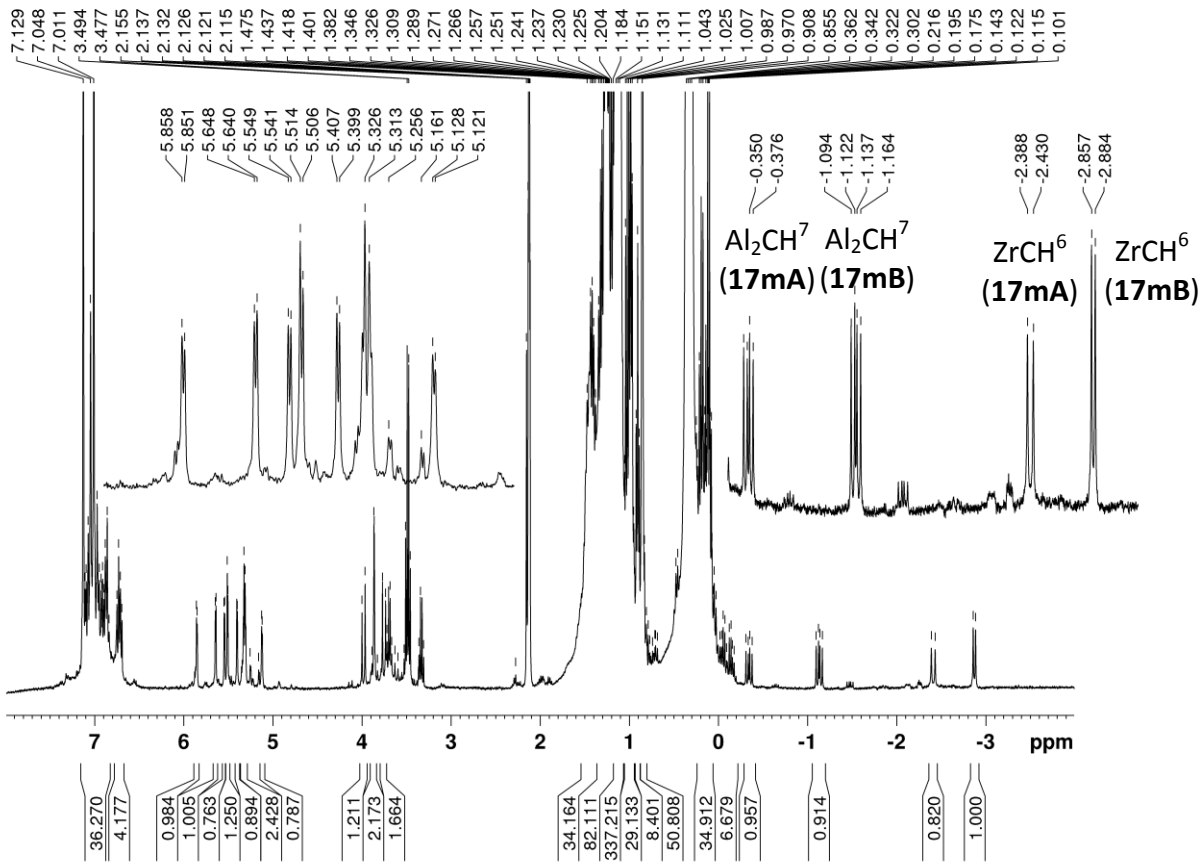


**Figure S57.** COSY HH of **17m** in $C_7D_8$ at 299 K.

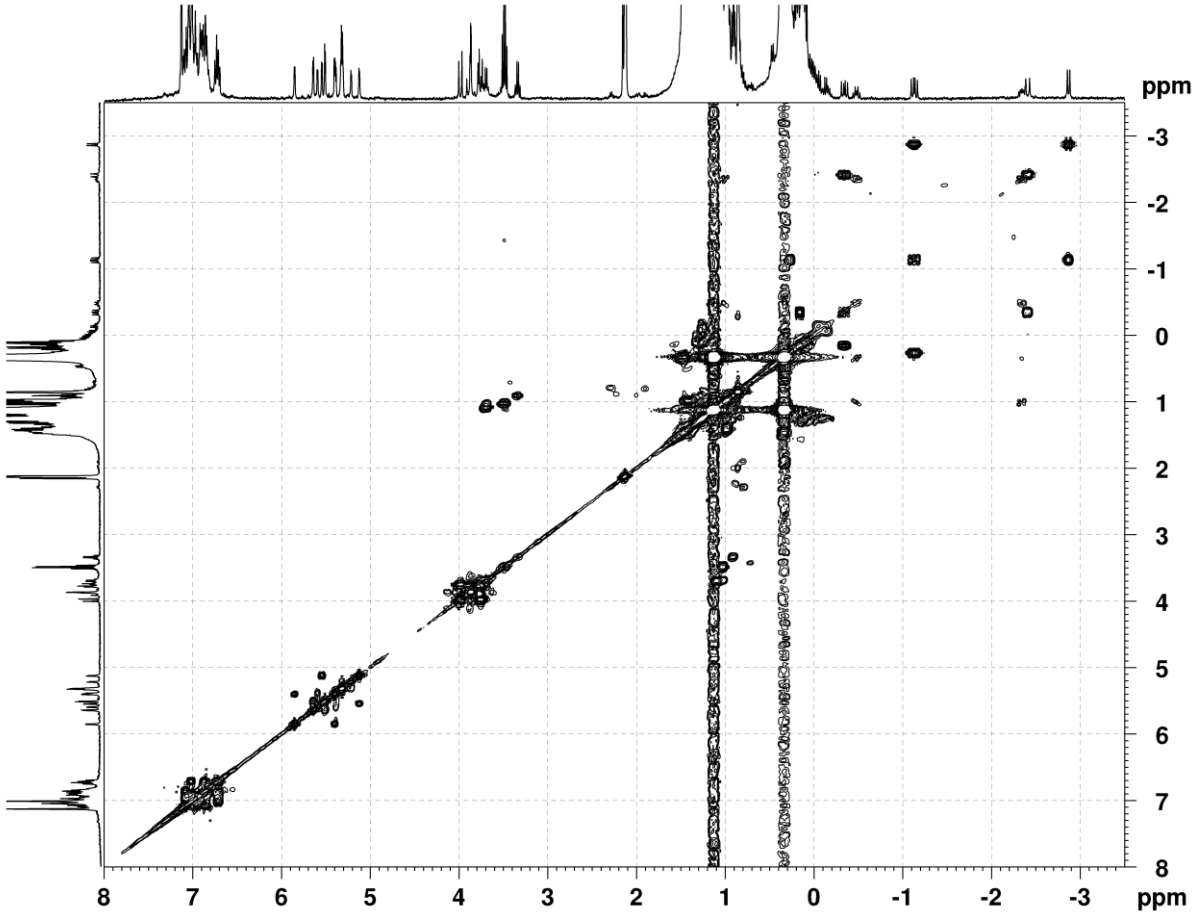



**Figure S58.** $^{13}C$ NMR of **17m** in $C_7D_8$ at 299 K.

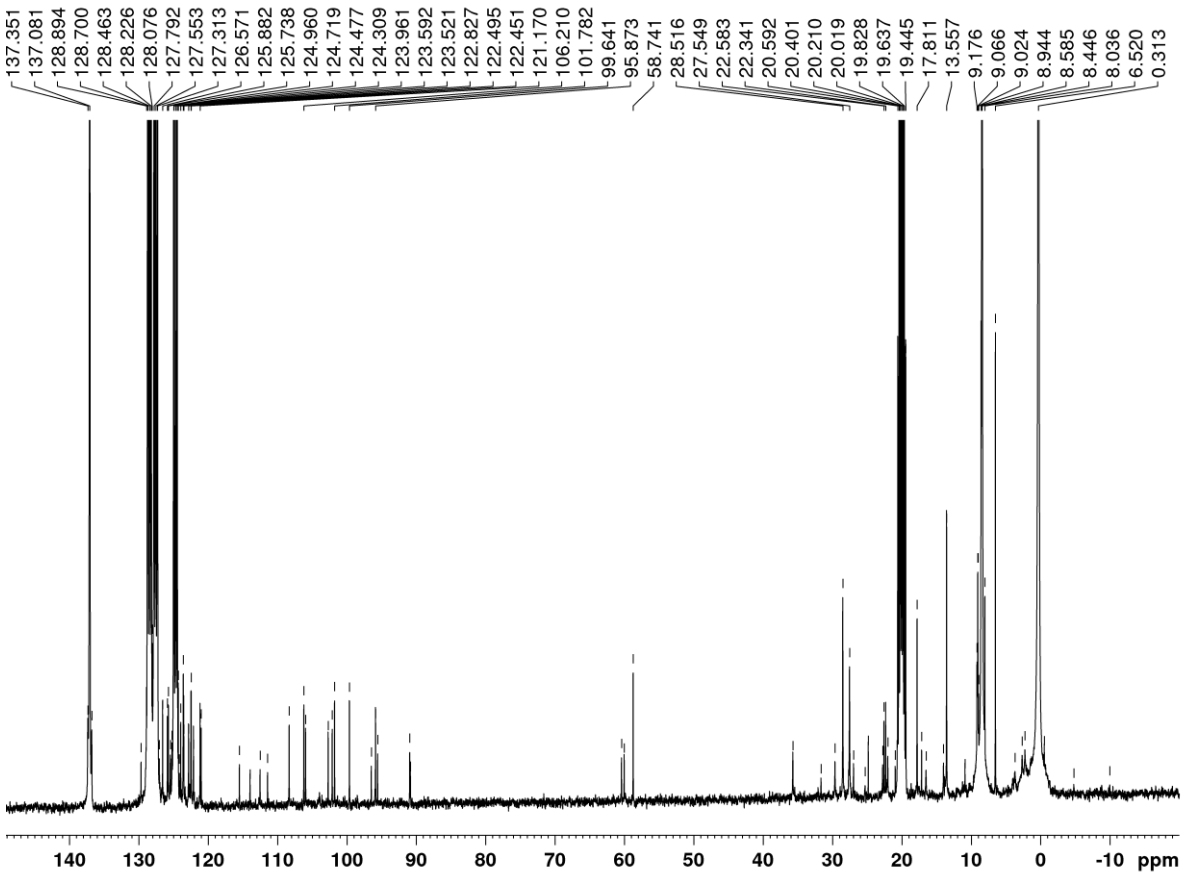


**Figure S59.** HSQC of **17m** in $C_7D_8$ at 299 K.

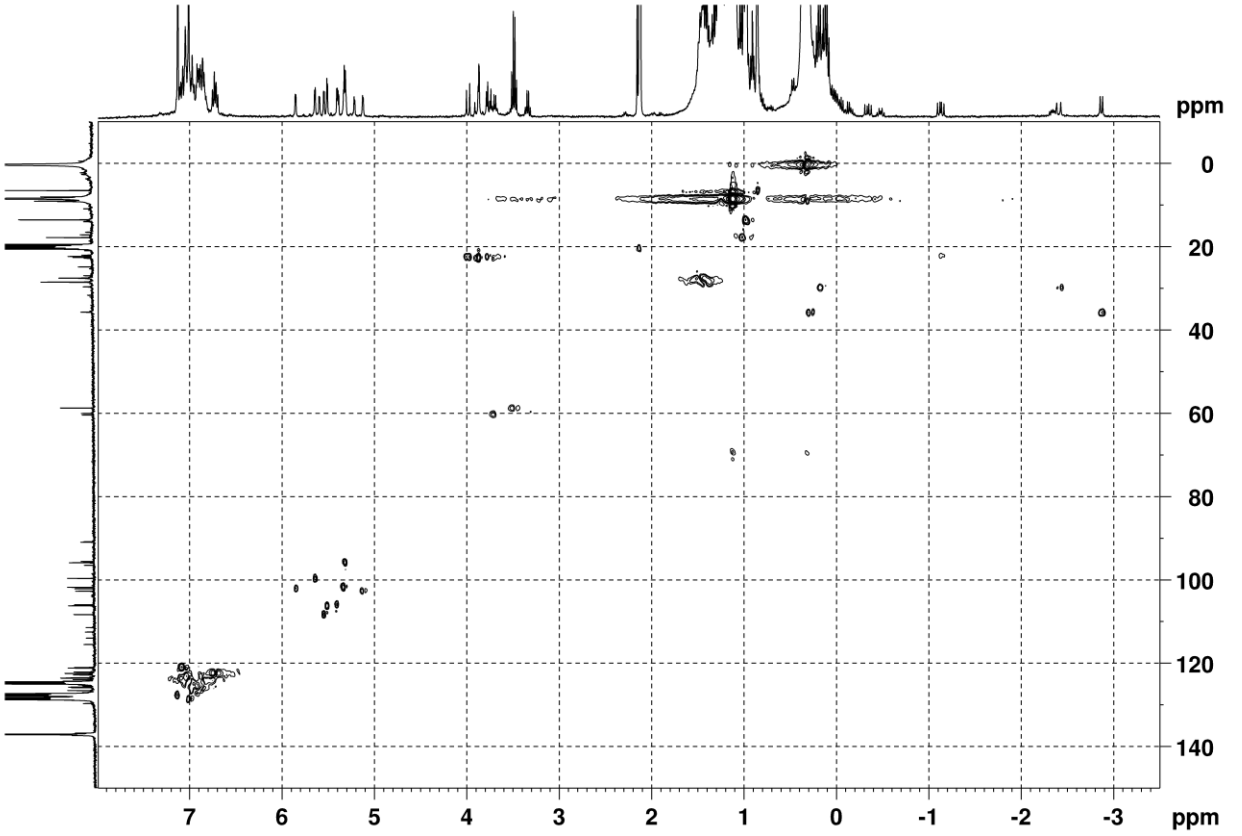



**Figure S60.** HMBC of **17m** in $C_7D_8$ at 299 K.

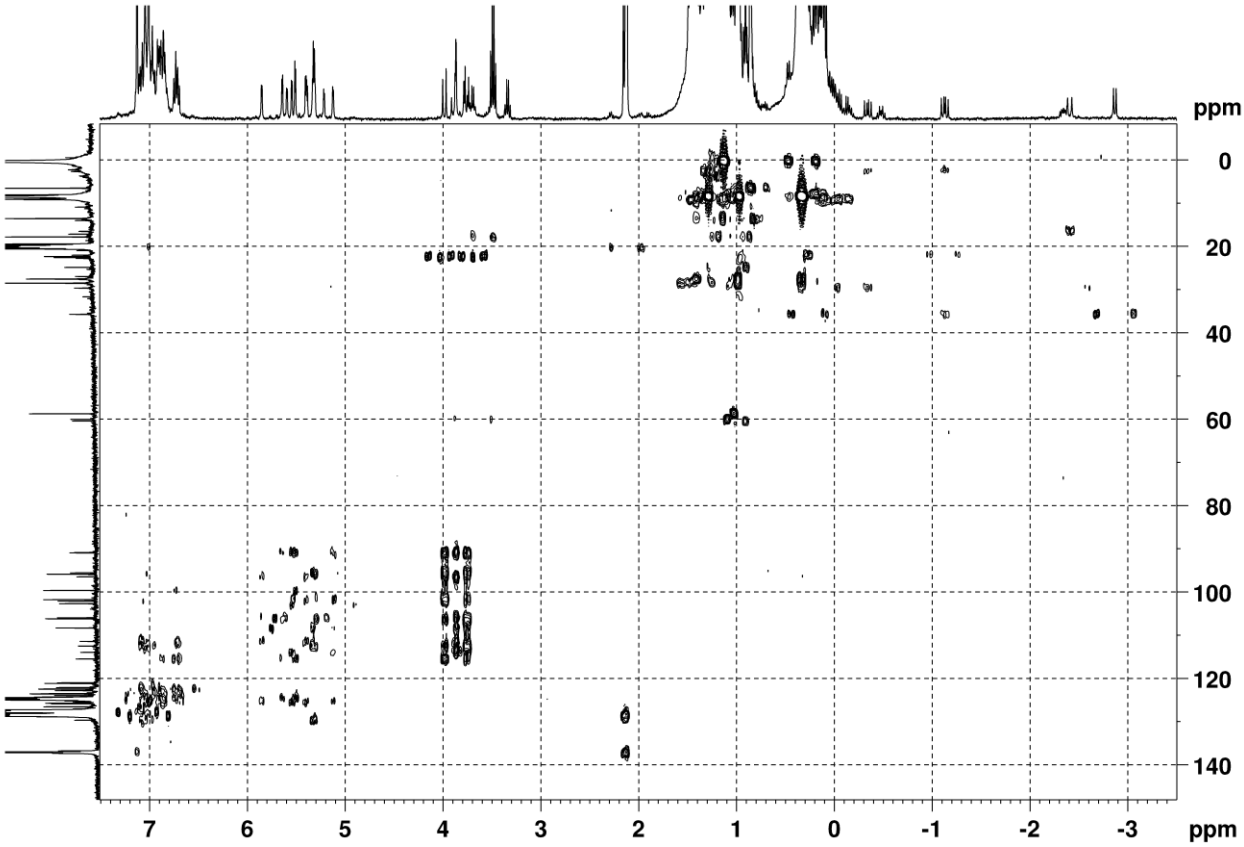


**Figure S61.** NOESY of **17m** in $C_7D_8$ at 299 K.

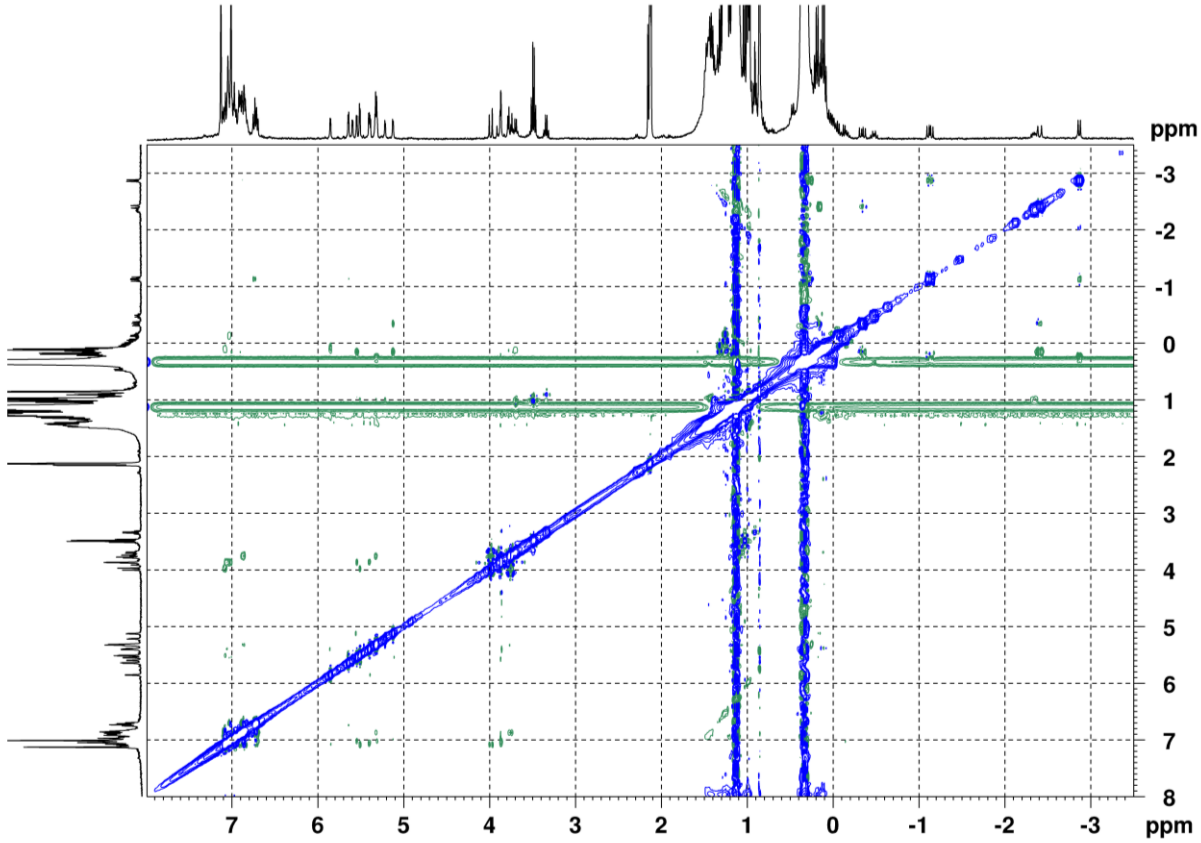



**Figure S62.** $^1$H NMR of system $Cp^*_2ZrCl_2$ (**1c**) - $(AlEt_3)_2$ (1:20) in $C_7D_8$ at 299 K.

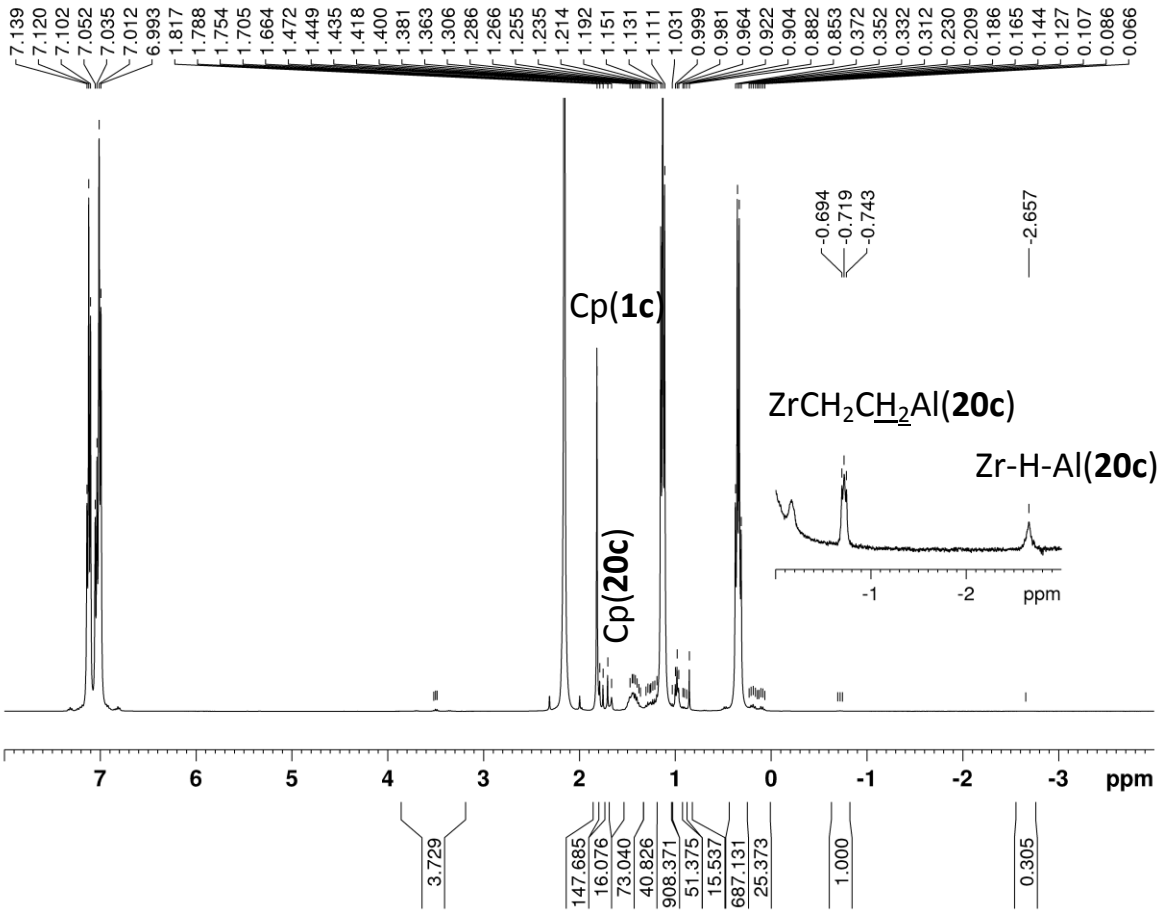


**Figure S63.** COSY HH of system $Cp^*_2ZrCl_2$ (**1c**) - $(AlEt_3)_2$ (1:20) in $C_7D_8$.

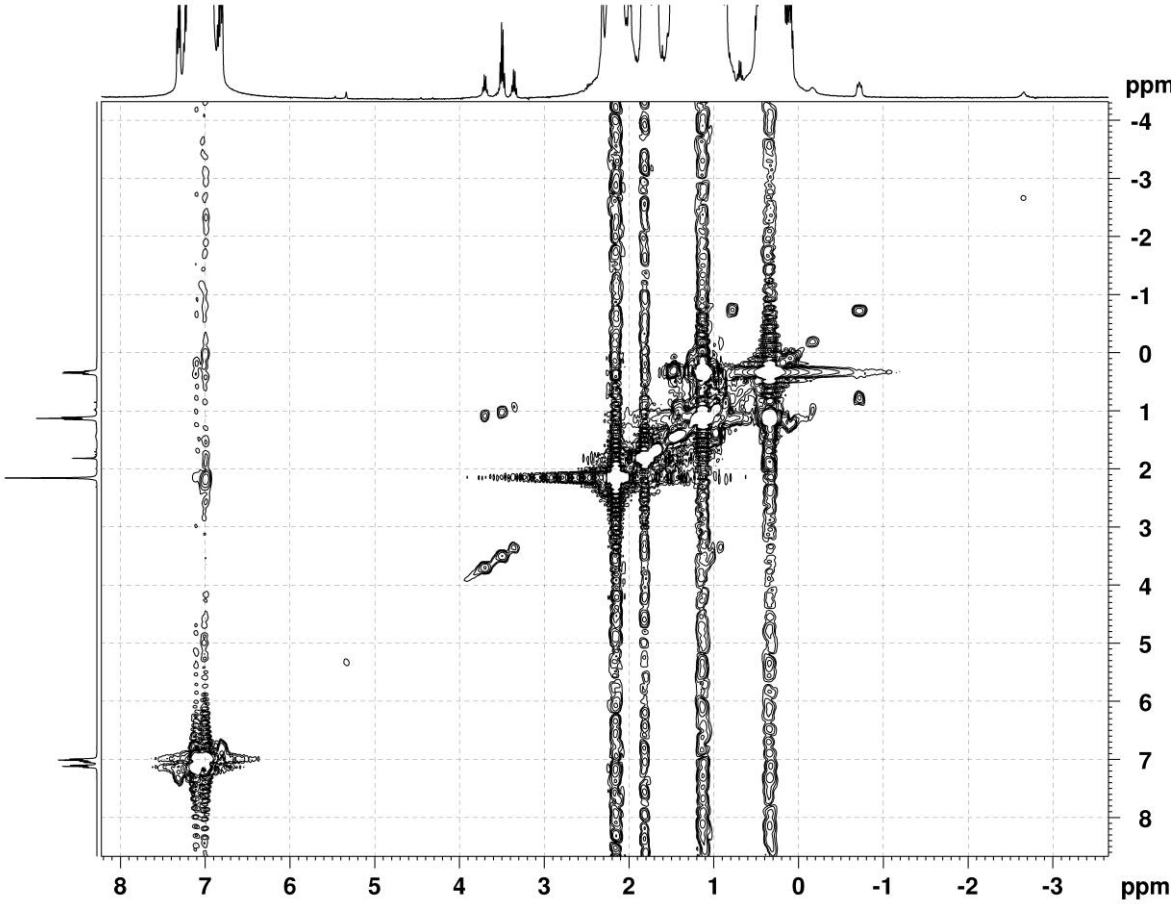



**Figure S64.** $^1H$ NMR of **20h** obtained by the reaction of **1h** with $(AlEt_3)_2$ (1:11) in $C_7D_8$ at 290 K.

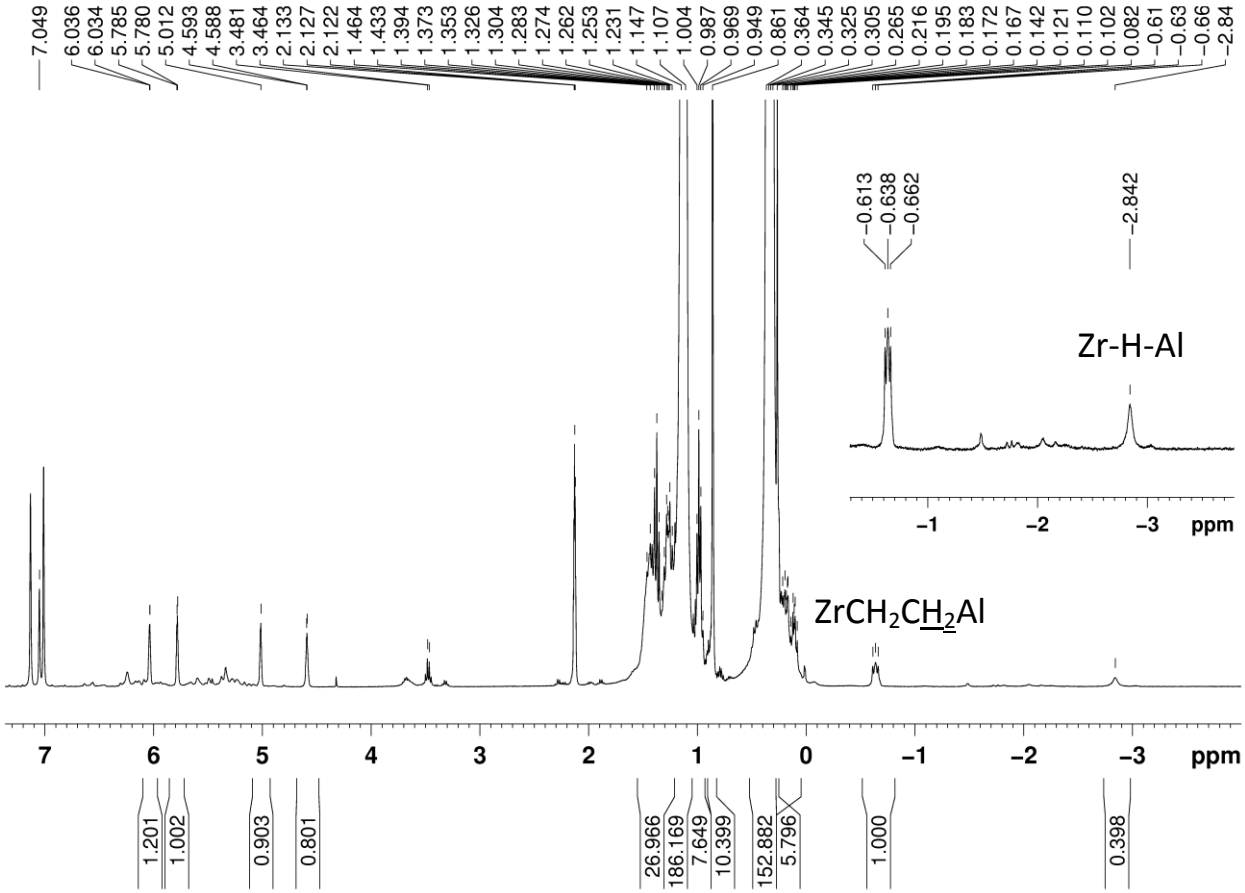


**Figure S65.** COSY HH of **20h** in $C_7D_8$ at 290 K.

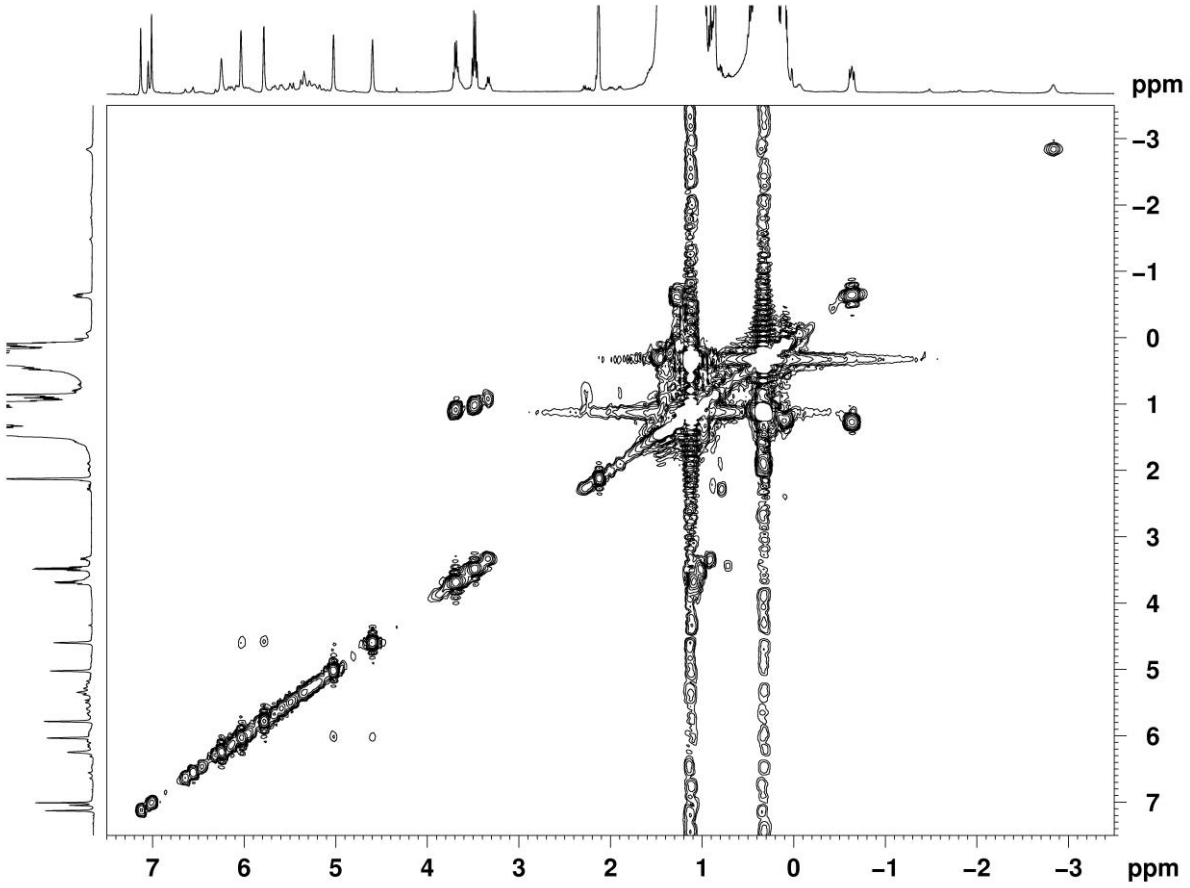



**Figure S66.** $^{13}C$ NMR of **20h** in $C_7D_8$ at 290 K.

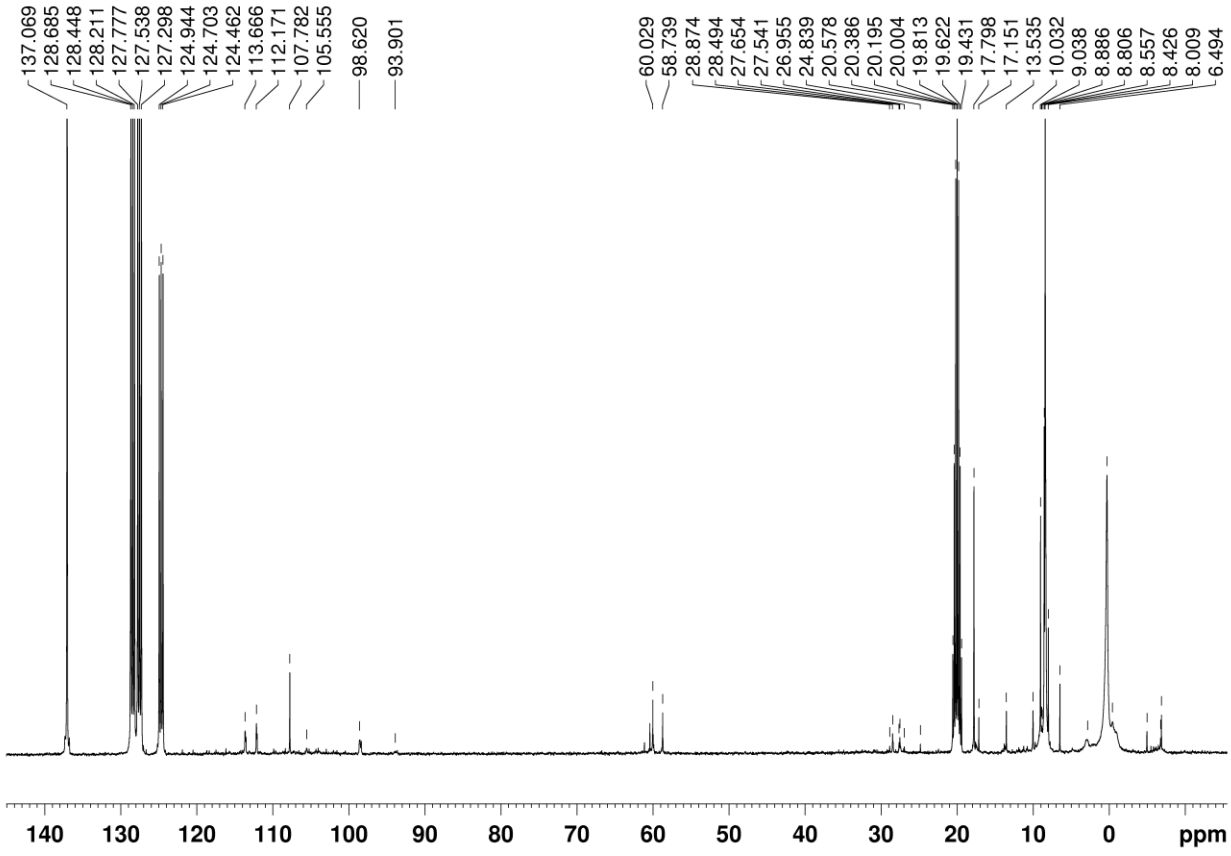


**Figure S67.** HSQC of **20h** in $C_7D_8$ at 290 K.

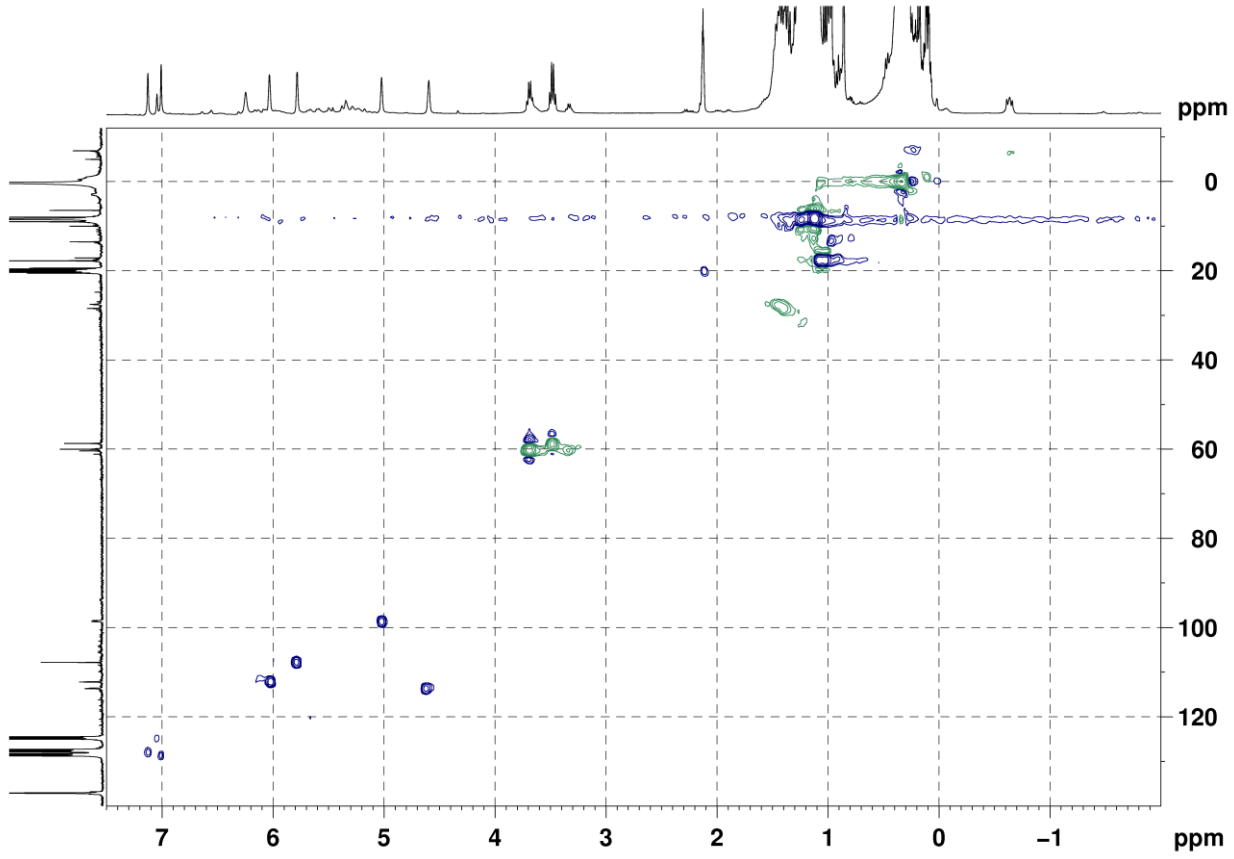



**Figure S68.** HMBC of **20h** in $C_7D_8$ at 290 K.

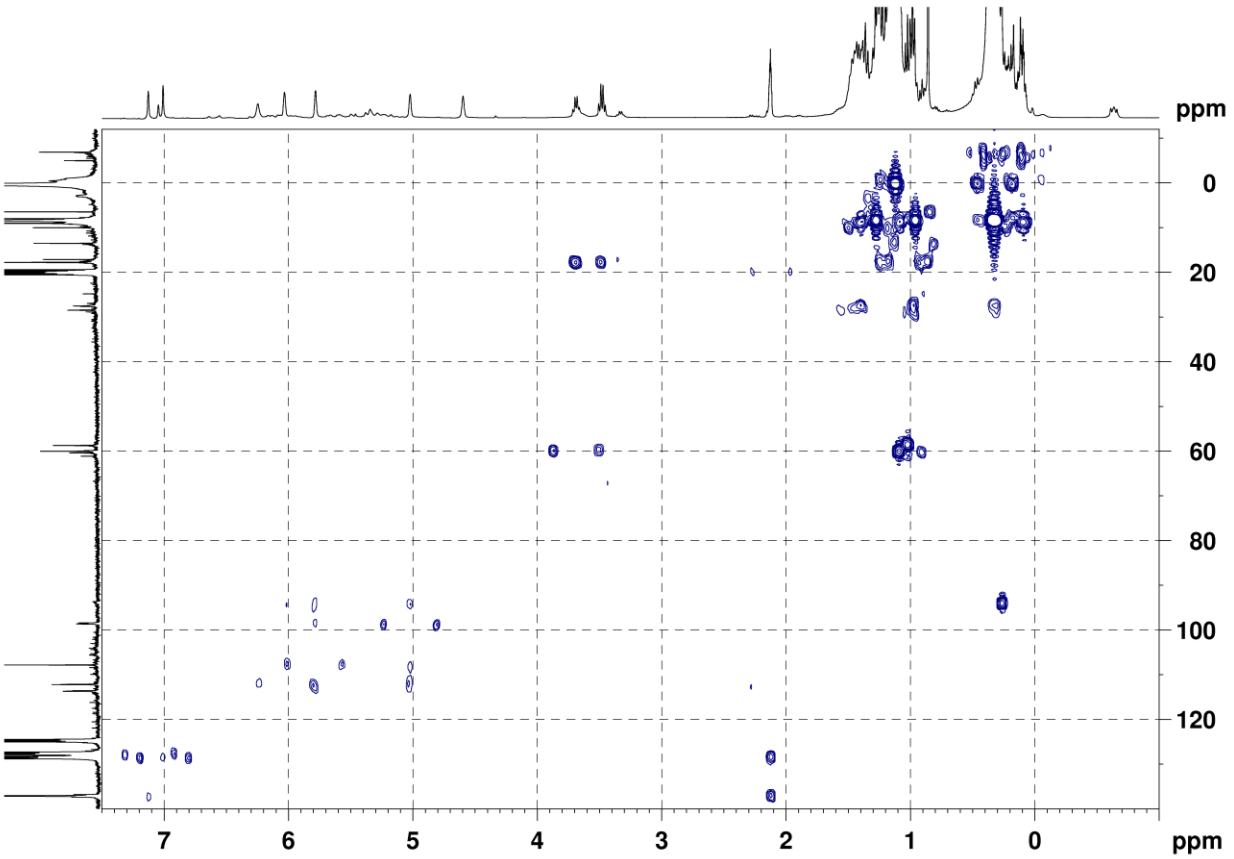


**Figure S69.** $^{1}$H NMR of **20p** obtained by the reaction of **1p** with $(AlEt_3)_2$ (1:13) in $C_7D_8$ at 305 K.

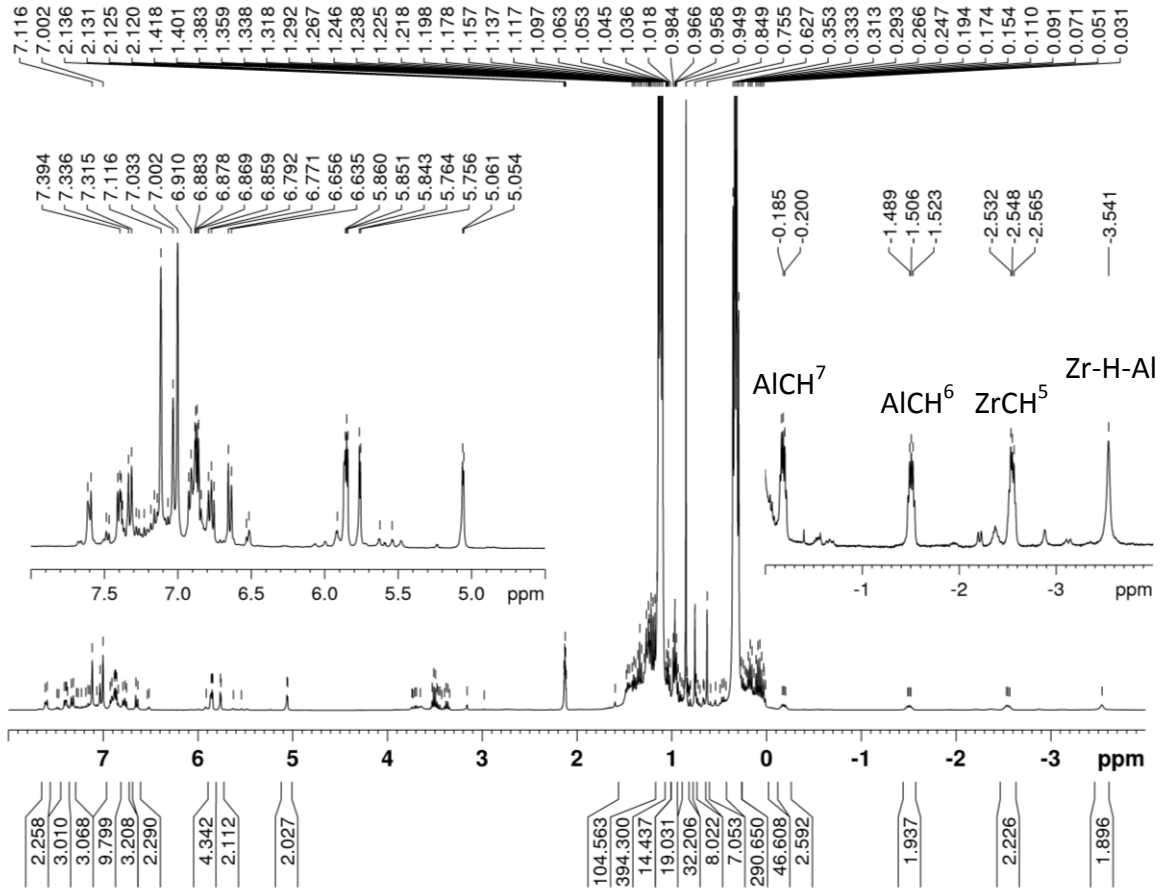



**Figure S70.** COSY HH of **20p** in $C_7D_8$ at 299 K.

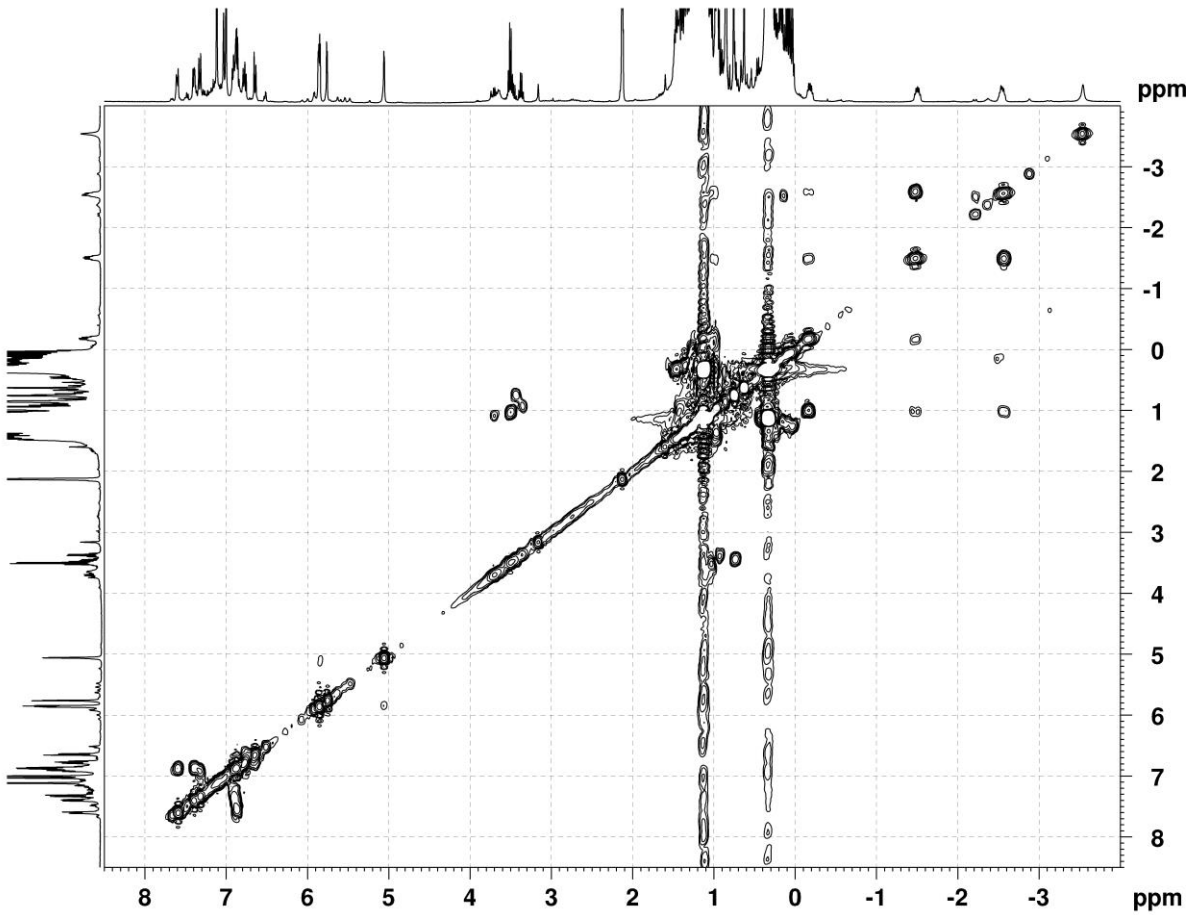


**Figure S71.** $^{13}C$ NMR of **20p** in $C_7D_8$ at 299 K.

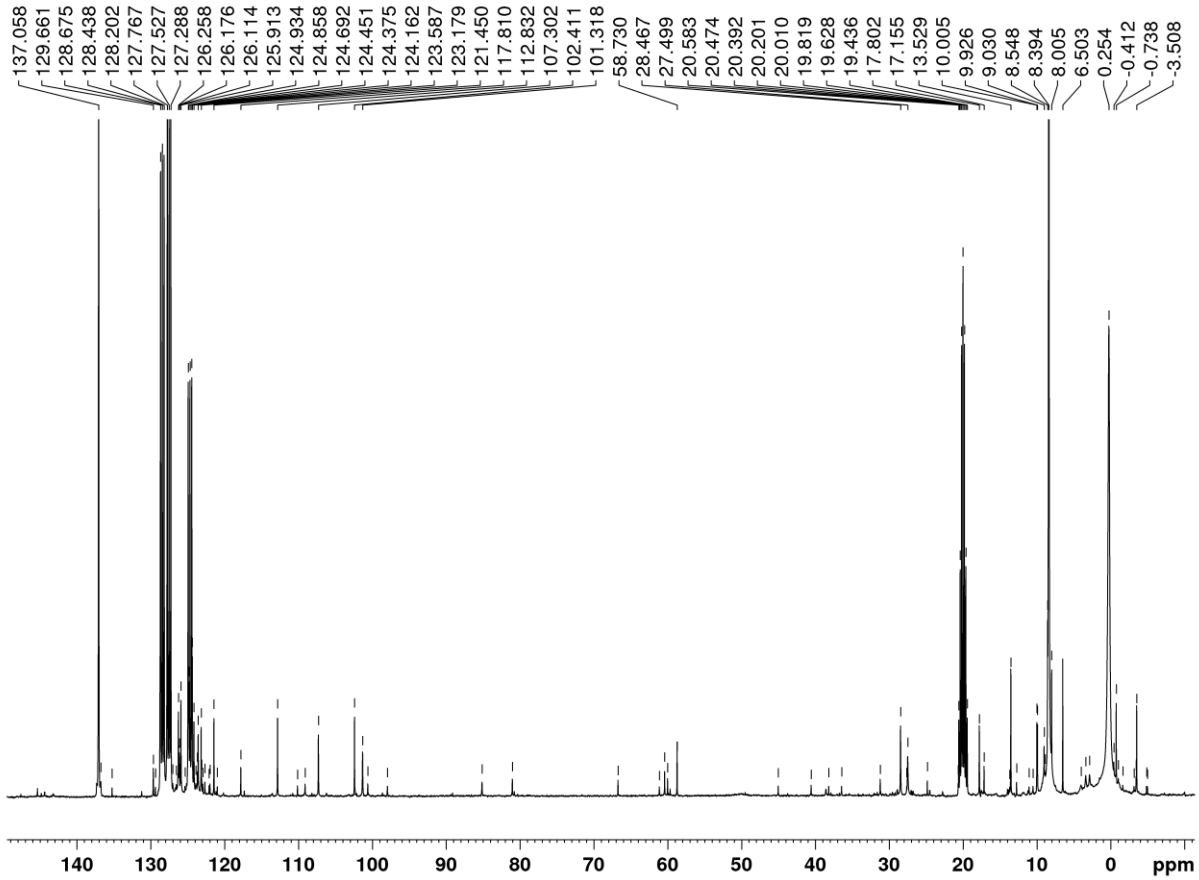



**Figure S72.** HSQC of **20p** in $C_7D_8$ at 299 K.

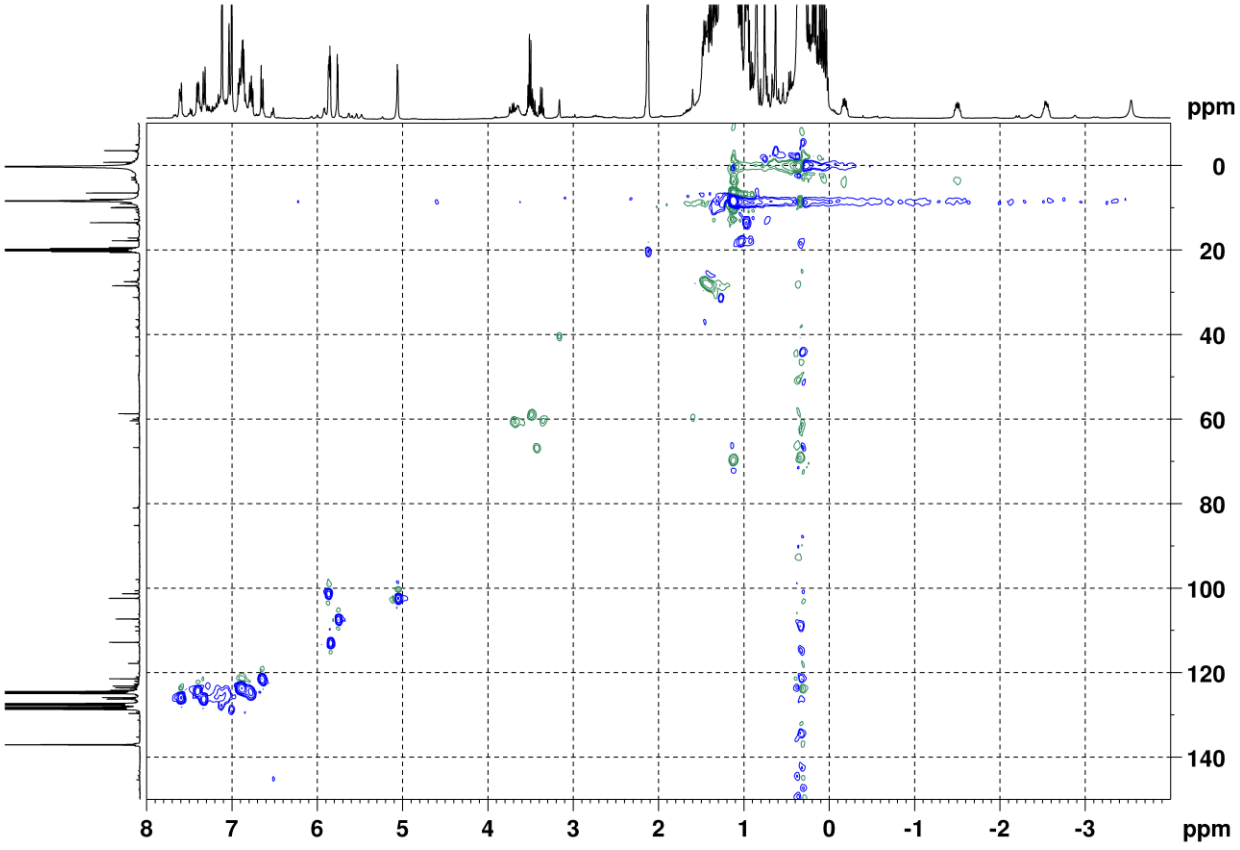


**Figure S73.** HMBC of **20p** in $C_7D_8$ at 299 K.

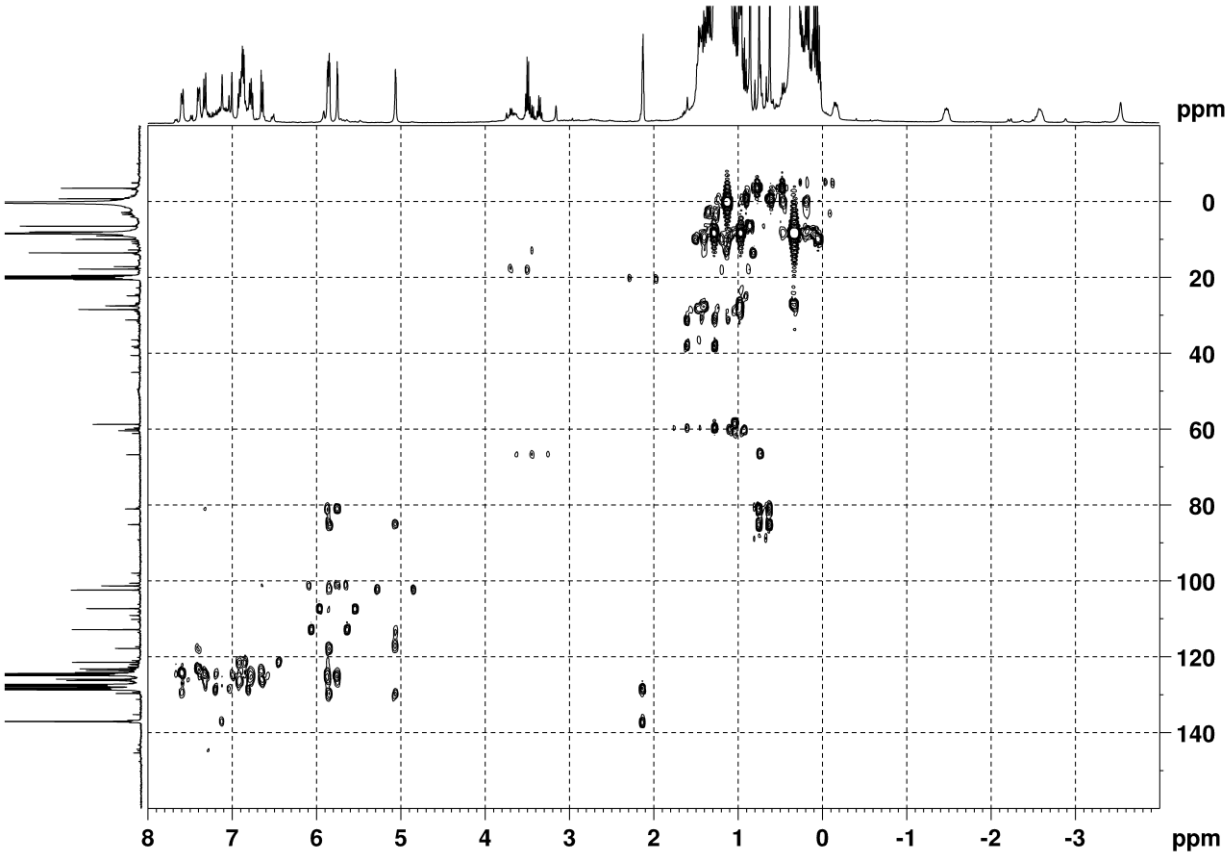


**Figure S74.** $^{1}$H NMR of **20q** obtained by the reaction of **1q** with $(AlEt_3)_2$ (1:13) in $CD_2Cl_2$ at 298 K.

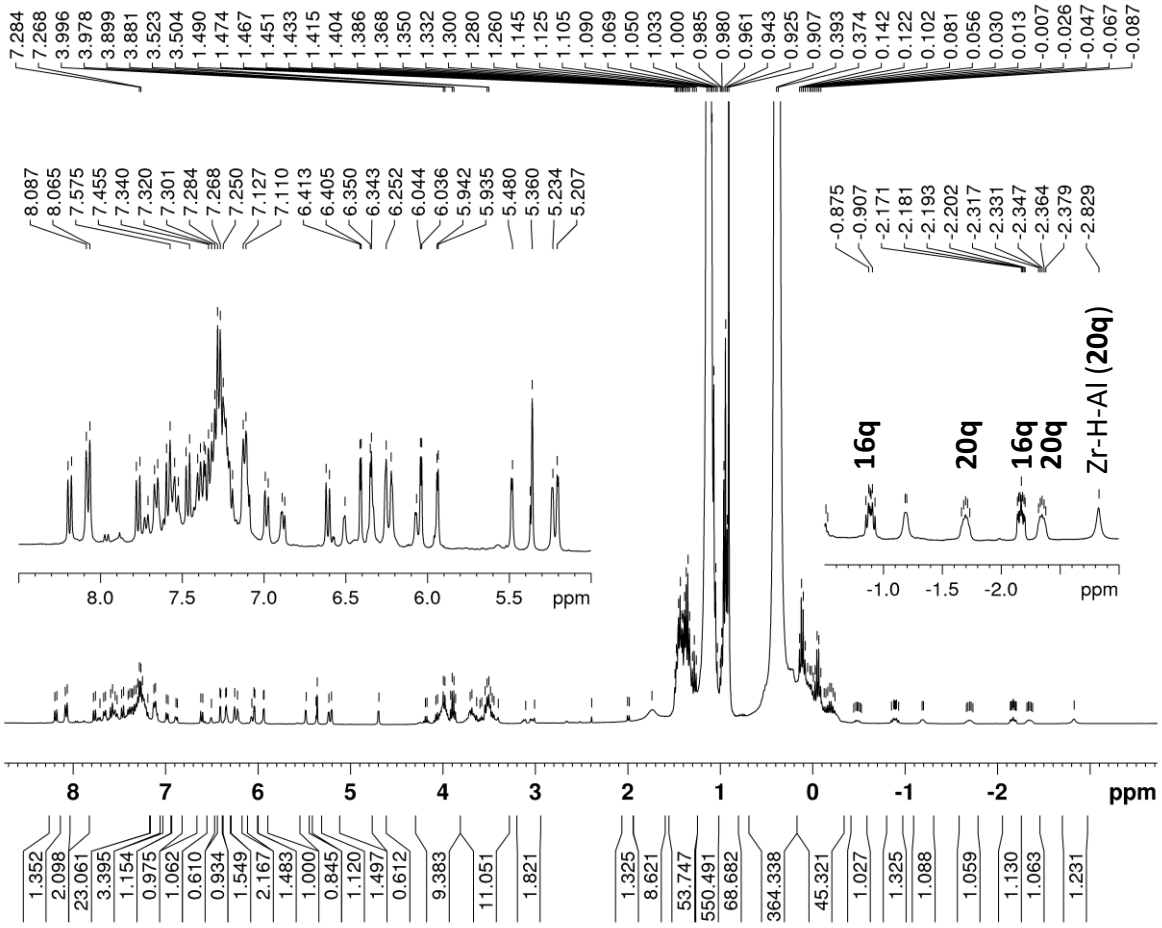



**Figure S75.** COSY HH of **20q** in $CD_2Cl_2$ at 298 K.