Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Exploring the Solid State and Solution Structural Chemistry of the Utility Amide Potassium Hexamethyldisilazide (KHMDS)

Ana I. Ojeda-Amador, Antonio J. Martínez-Martínez,* Gemma M. Robertson, Stuart D. Robertson, Alan R. Kennedy and Charles T. O'Hara*

WestCHEM, Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL (UK).

E-mail: a.j.martinez@strath.ac.uk, charlie.ohara@strath.ac.uk

Table of Contents

CRYSTALLOGRAPHIC AND REFINEMENT DATA

Single-crystal X-ray diffraction intensities were measured at 123(2) K on Oxford Diffraction Xcalibur and Gemini diffractometers with monochromated Mo (λ = 0.71073 Å) or Cu (λ = 1.5418 Å) radiation. The structures were solved by direct methods and refined to convergence on F^2 and against all independent reflections by full-matrix least-squares and SHELXL programs.[1] Structure **10** as treated as a merohedral twin with the two parts related by matrix 1 0 0 0 -1 0 0 0 -1. The BASF parameter refined to 0.40229. Some structures featured disordered groups. These were all modeled over two sites and required restraints on bond lengths and displacement parameters to be applied. Groups treated in this way were the THF ligands of **3**, $SiMe_3$ and TMEDA groups in **4**, toluene solvate molecules in **6** and **9**, and the chelating ligand in one of the independent molecules of **10**. Selected crystallographic data and refinement parameters are summarized in the Tables S1 and S2 and full details are given in the supplementary deposited cif files. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. Deposition numbers CCDC 1537847 to 1537857.

Table S1. Selected crystallographic and refinement data for **1**-**5**.

Compound	**1**	**2**	**3**	**4**	**5**
Formula	$C_{19}H_{44}K_2N_2Si_4$	$C_{26}H_{52}K_2N_2Si_4$	$C_{20}H_{52}K_2N_2O_2Si_4$	$C_{24}H_{68}K_2N_6Si_4$	$C_{32}H_{80}K_2N_6Si_4$
FW	491.12	583.25	543.20	631.40	739.58
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	P-*1*	*C*2/c	$P2_1/n$	$P2_1/c$	$P2_12_12_1$
Wavelength/Å	1.54184	1.54184	0.71073	0.71073	0.71073
a/Å	9.7944(5)	13.1668(11)	11.0570(8)	25.0098(6)	11.8251(2)
b/Å	10.5685(6)	17.0453(11)	12.1726(10)	41.6744(9)	11.9313(3)
c/Å	16.9623(7)	15.7608(12)	12.3879(9)	11.7634(3)	32.6567(8)
α/°	90.218(4)	90	90	90	90
β/°	105.593(4)	95.649(7)	106.209(7)	91.606(2)	90
γ/°	117.417(5)	90	90	90	90
Volume/Å^3	1484.42(14)	3520.1(5)	1601.0(2)	12255.8(5)	4607.50(18)
Z	2	4	4	12	4
Temperature/*K*	123(2)	123(2)	123(2)	123(2)	123(2)
Refls. Collect.	14198	15089	10471	68311	26058
Refls. Unique	5806	3288	4235	26683	9964
Refls. Obs.	5512	2463	3459	16447	9328
No. Parameters	257	205	155	1121	417
$2\theta_{max}$	146.06	139.94	59.97	54.00	54.00
R_{int}	0.0226	0.0497	0.0302	0.0249	0.0295
Goodness of fit	1.075	1.165	1.060	0.950	1.099
$R[F^2>2\sigma]$, *F*	0.0396	0.0416	0.0363	0.0485	0.0368
R_w (all data), F^2	0.1167	0.1353	0.0842	0.1135	0.0771
Abs. Struct.	-	-	-	-	0.009(15)[a]

[a] The refined Flack parameter is essentially zero and indicates that compound **5** is enantiomerically pure.

Table S2. Selected crystallographic and refinement data for **6**-**11**.

Compound	**6**	**7**	**8**	**9**	**10**	**11**
Formula	$C_{35}H_{76}K_2N_2O_8Si_4C_{21}H_{59}K_2N_5Si_4$	$C_{40}H_{112}K_4N_8O_2Si_8C_{59.2}H_{144.8}K_4N_{12}Si_8C_{22}H_{58}KN_5O_2Si_2C_{21}H_{51}KN_2O_6Si_2$				
FW	843.54	572.29	1118.49	1406.19	520.01	522.91
Crystal system	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	*P2₁/c*	*P*2₁/n	*P*2₁/n	*P*-1	*P*2₁/*a*	*P*-1
Wavelength/Å	0.71073	1.54184	1.54184	0.71073	1.54184	0.71073
a/Å	12.4604(4)	12.12710(15)	12.81770(10)	12.2066(4)	22.8421(6)	10.3630(6)
b/Å	12.4931(3)	19.12980(16)	16.92720(10)	12.8113(4)	16.2474(4)	10.6131(6)
c/Å	16.0780(5)	15.53110(14)	15.89150(10)	15.0375(4)	17.8186(6)	15.7120(6)
α/°	90	90	90	79.045(3)	90	88.518(4)
β/°	107.587(3)	99.4140(10)	98.4790(10)	81.833(2)	90.091(2)	84.889(4)
γ/°	90	90	90	79.141(3)	90	61.994(6)
Volume/Å³	2385.86(12)	3554.52(6)	3410.26(4)	2253.60(12)	6612.9(3)	1519.39(16)
Z	2	4	2	1	8	2
Temperature/*K*	123(2)	123(2)	123(2)	123(2)	123(2)	123(2)
Refls. Collect.	17250	44210	36566	22235	52705	54199
Reflns. Unique	5630	7082	6767	10995	12697	8527
Reflns. Obs.	4539	6436	5991	8648	10533	7331
No. Parameters	268	317	296	405	690	298
$2\theta_{max}$	56	146.75	146.22	59.40	146.72	60.49
R_{int}	0.0298	0.0358	0.0302	0.0245	0.0609	0.0360
Goodness of fit	1.221	1.042	1.073	1.064	1.051	1.034
$R[F^2>2\sigma]$, *F*	0.0522	0.0331	0.0306	0.0609	0.0505	0.0295
R_w (all data), F^2	0.1182	0.0901	0.0853	0.1711	0.1457	0.0752

NMR SPECTRA

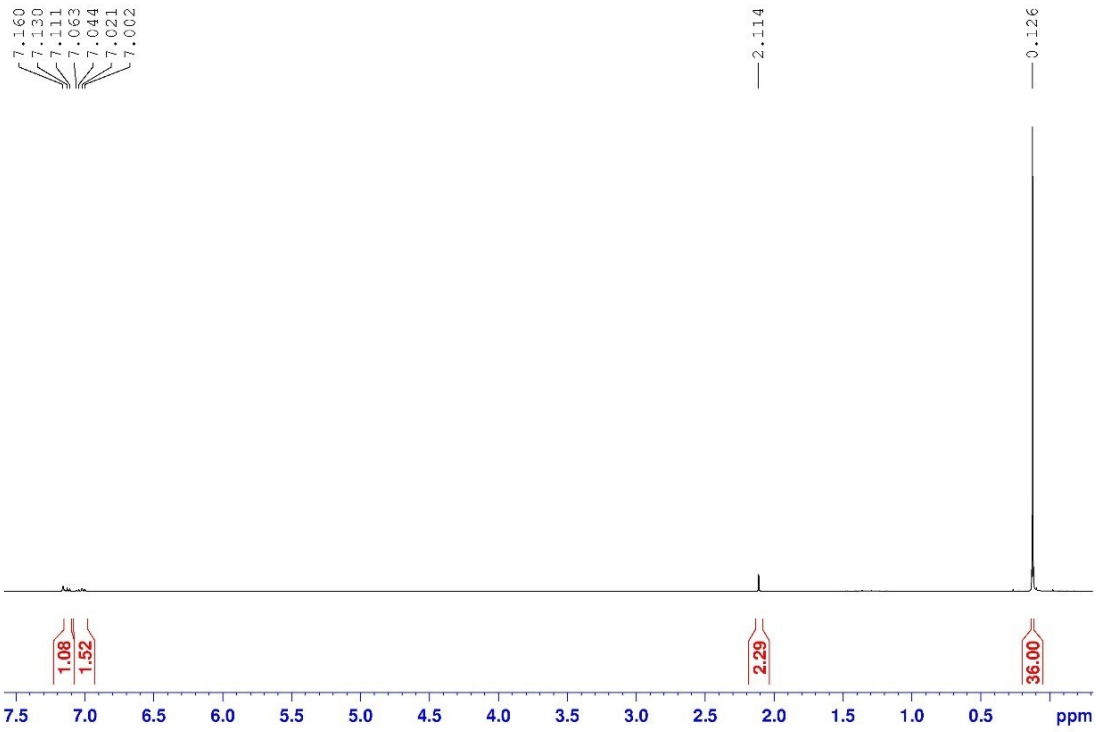

Figure S1. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **1**.

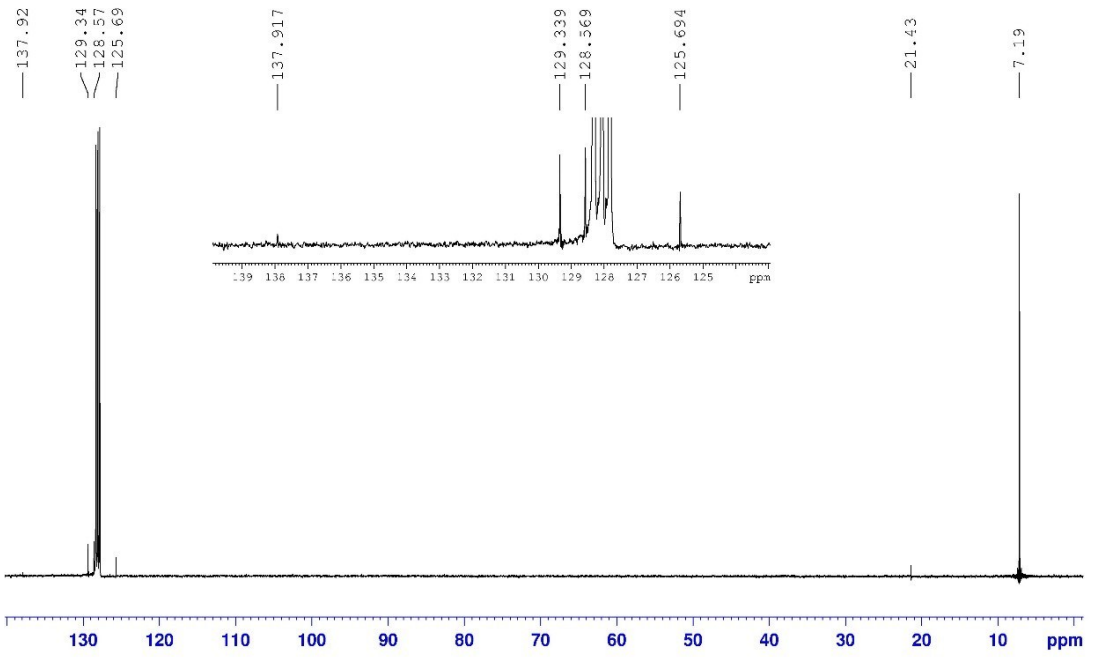

Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **1**.

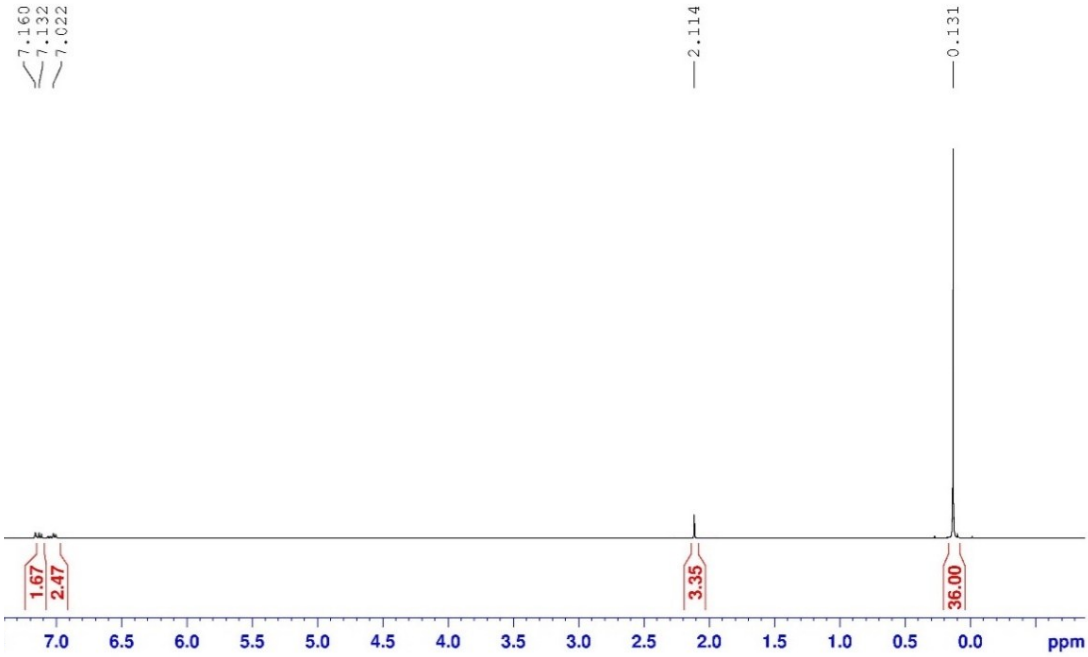

Figure S3. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **2**.

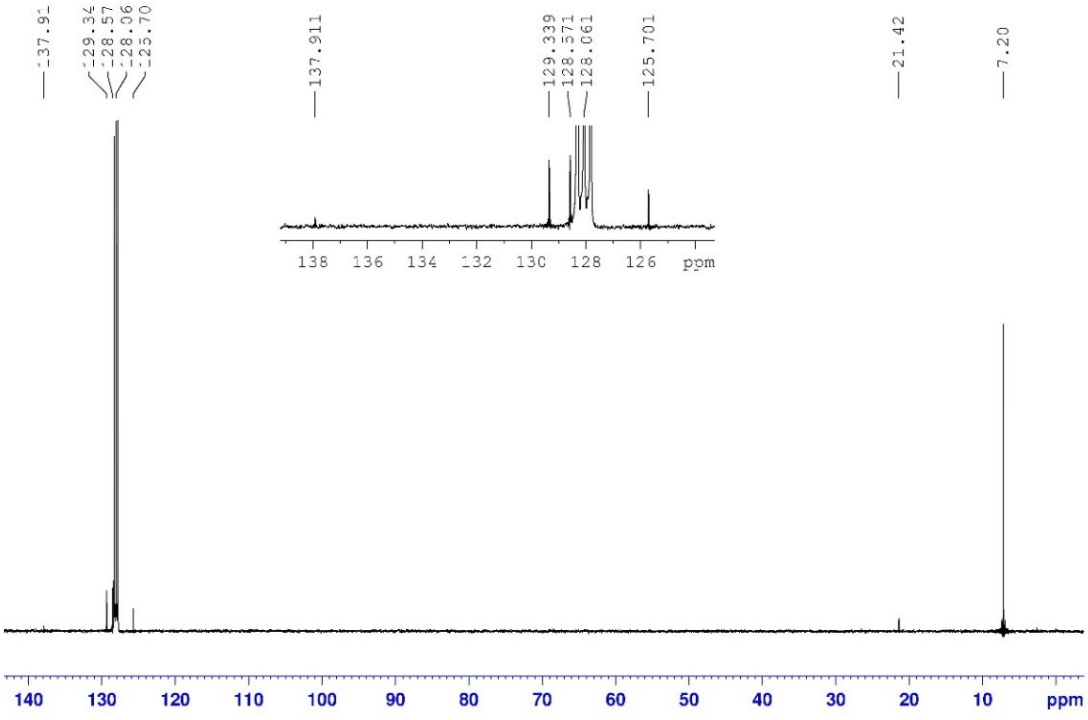

Figure S4. ^{13}C{^{1}H} NMR spectrum (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **2**.

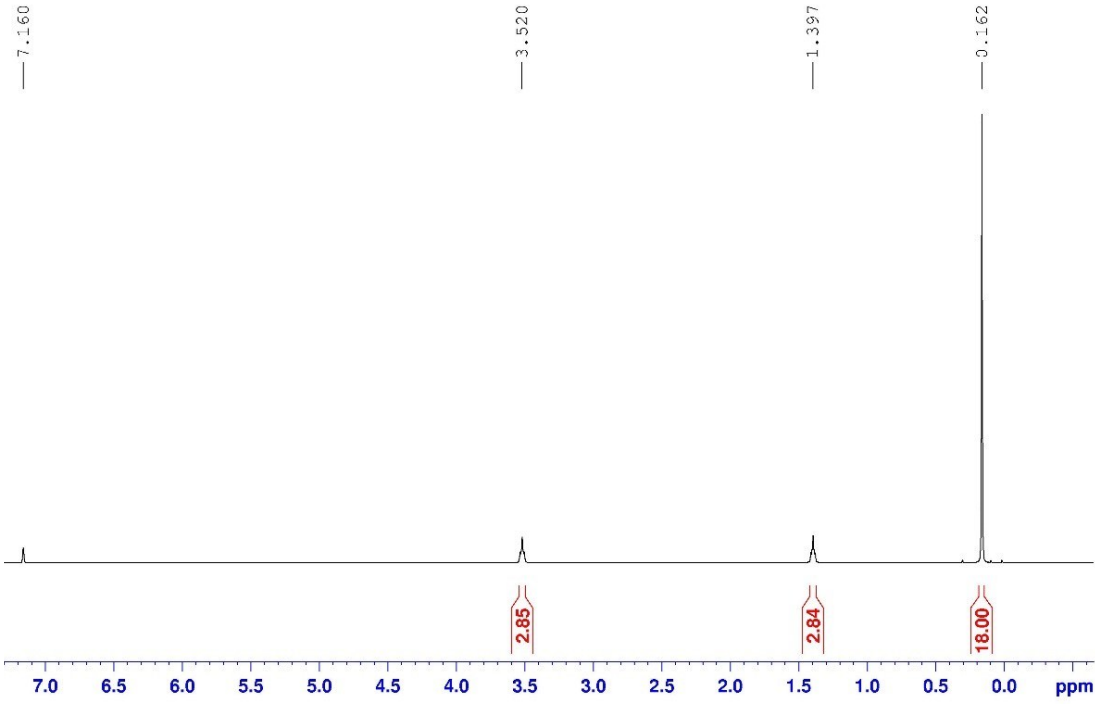

Figure S5. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **3**.

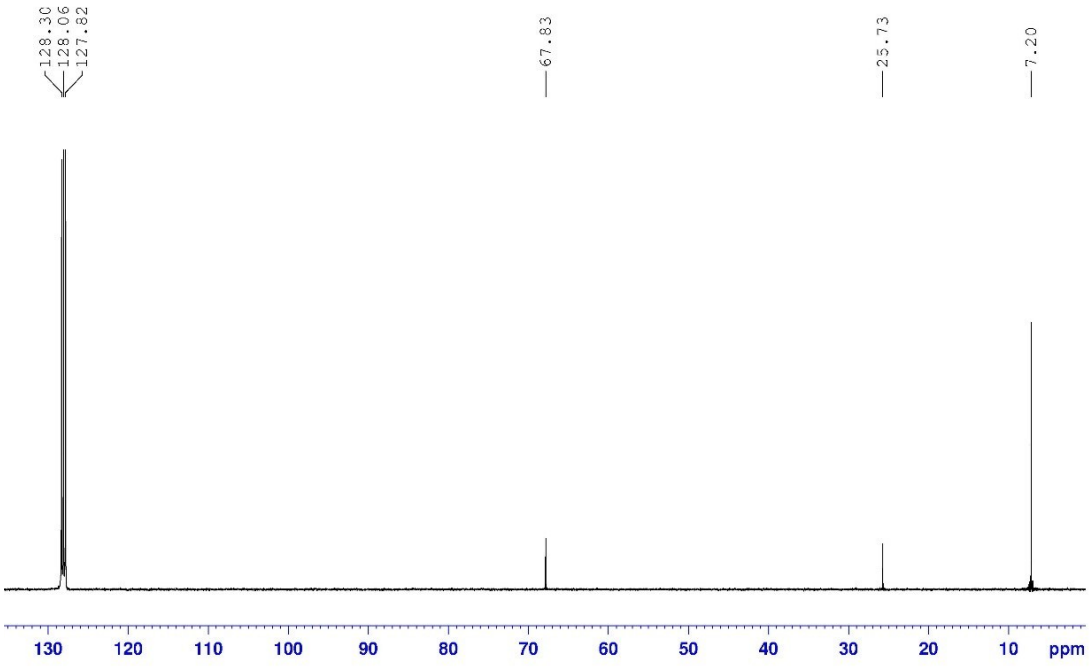

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **3**.

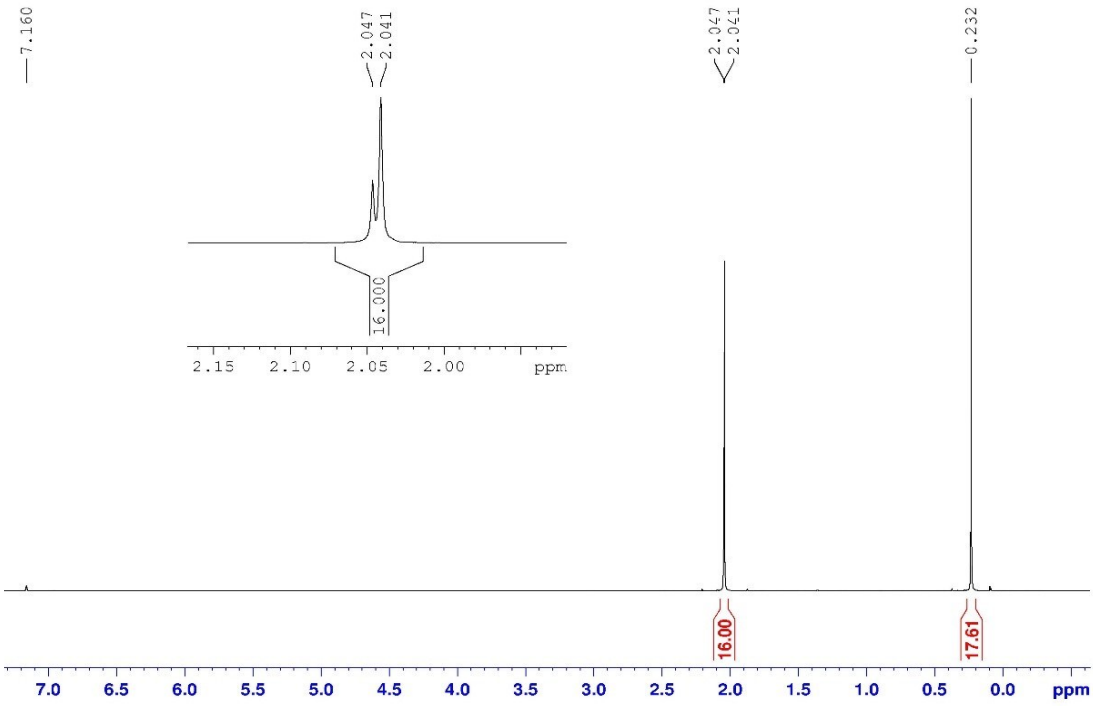

Figure S7. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **4**.

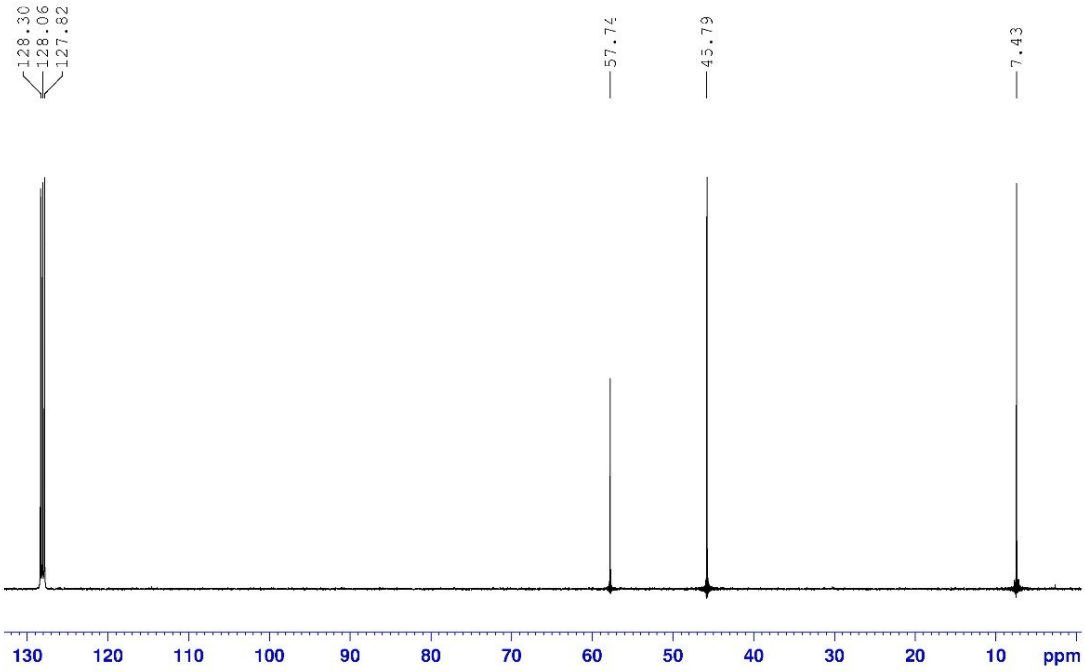

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **4**.

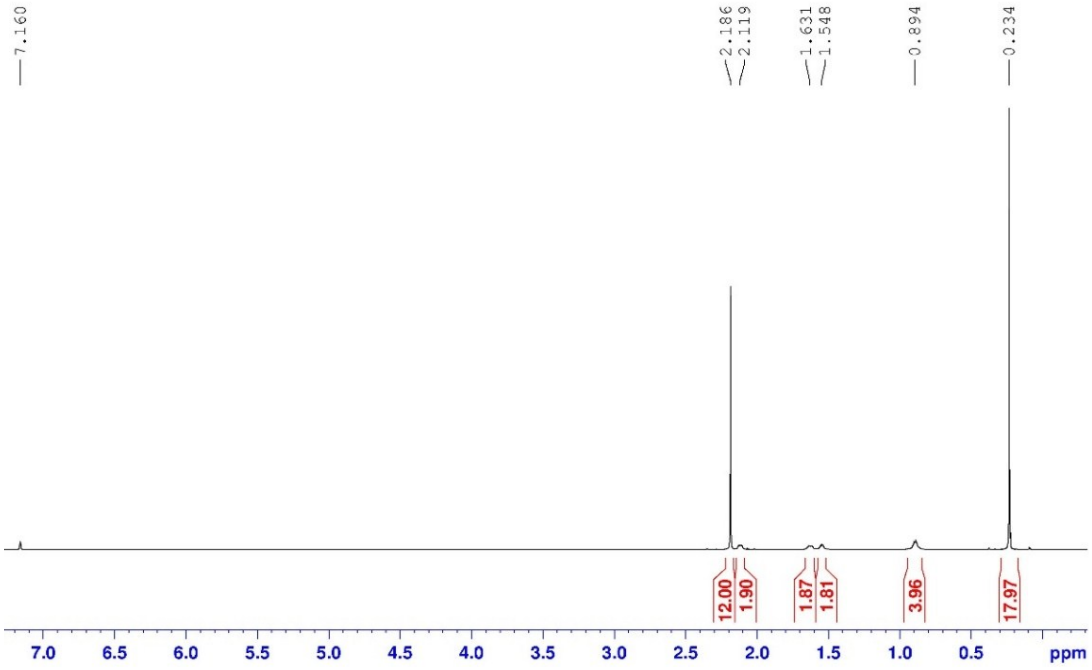

Figure S9. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **5**.

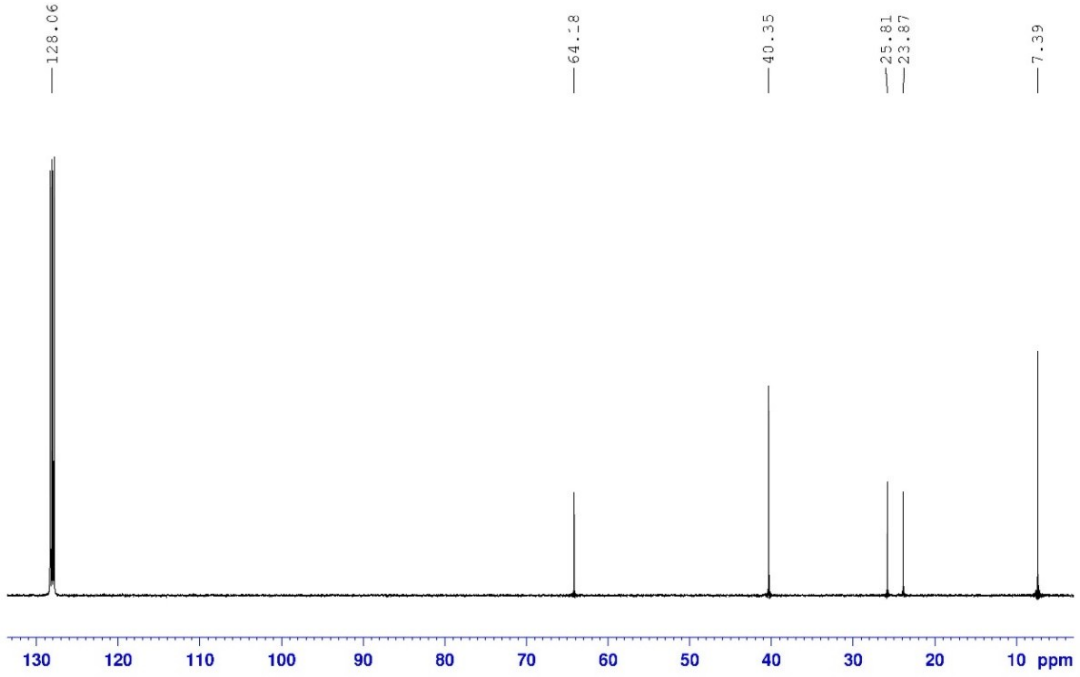

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **5**.

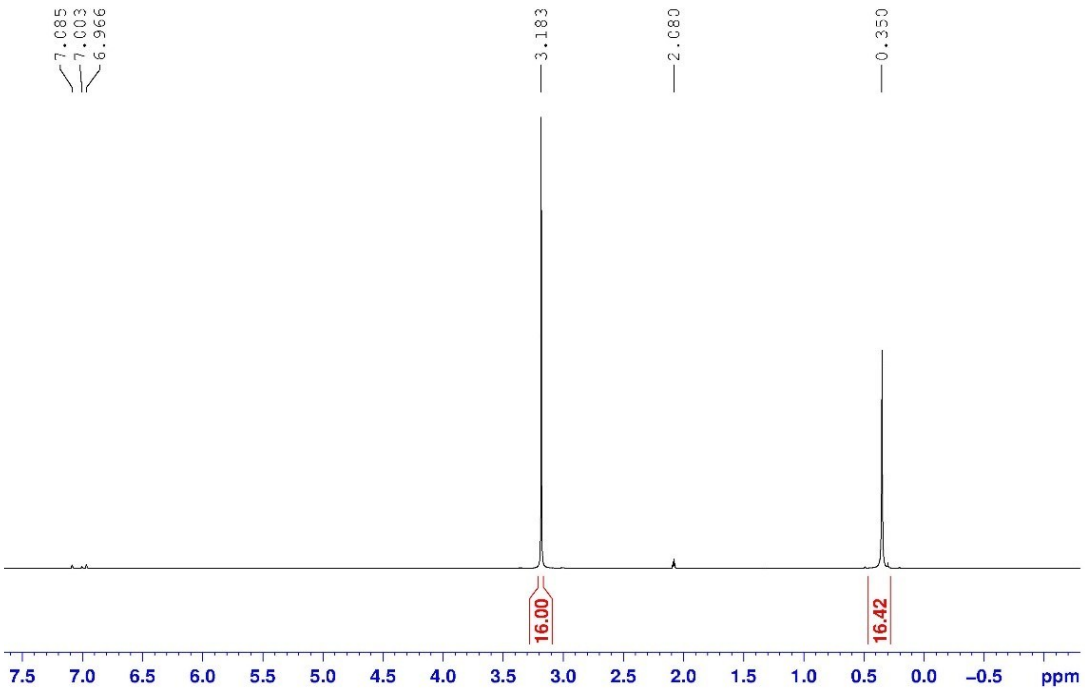

Figure S11. ^{1}H NMR (400.1 MHz, **[D]$_8$**toluene, 300 K) of isolated crystals of **6**.

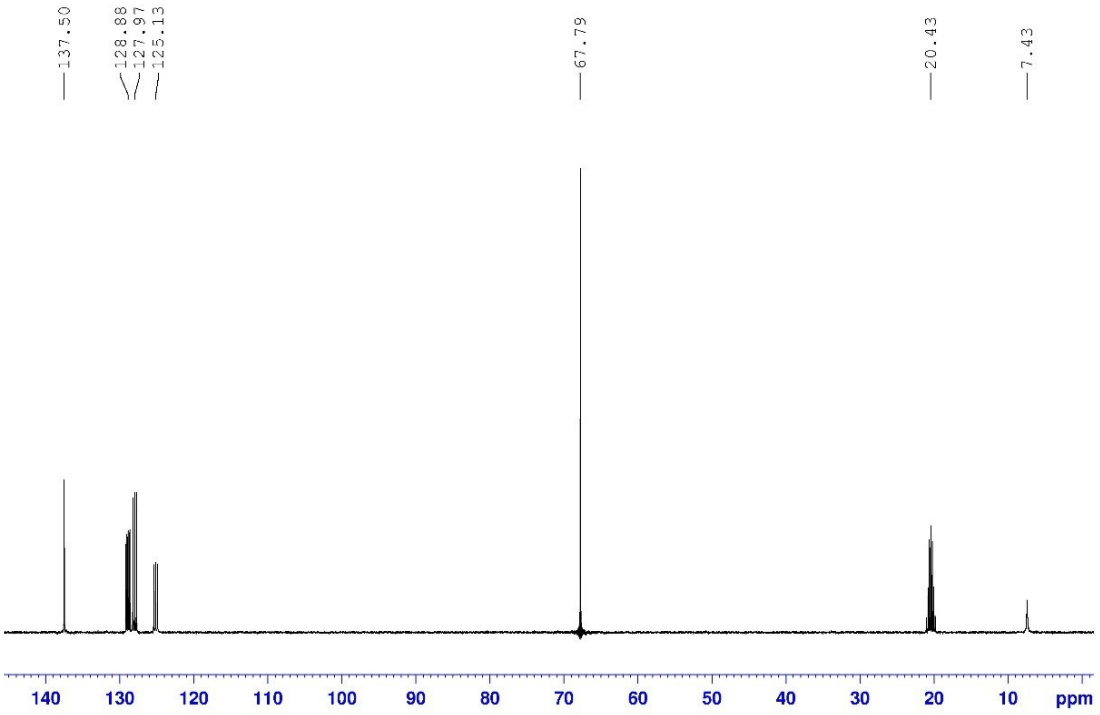

Figure S12. ^{13}C{^{1}H} NMR spectrum (100.6 MHz, **[D]$_8$**toluene, 300 K) of isolated crystals of **6**.

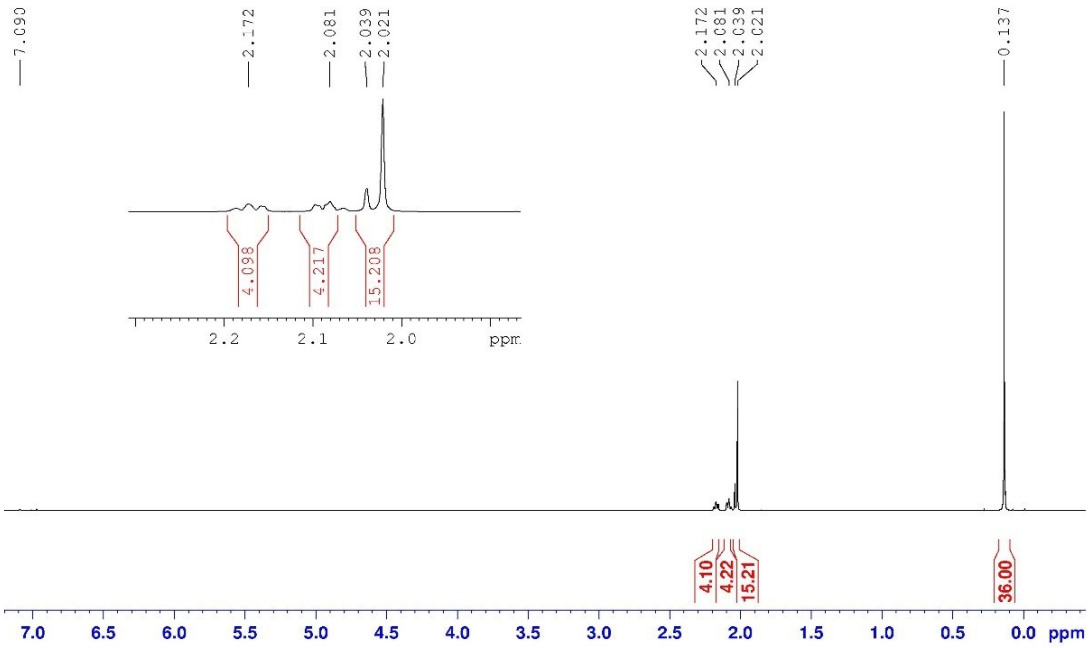

Figure S13. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **7**.

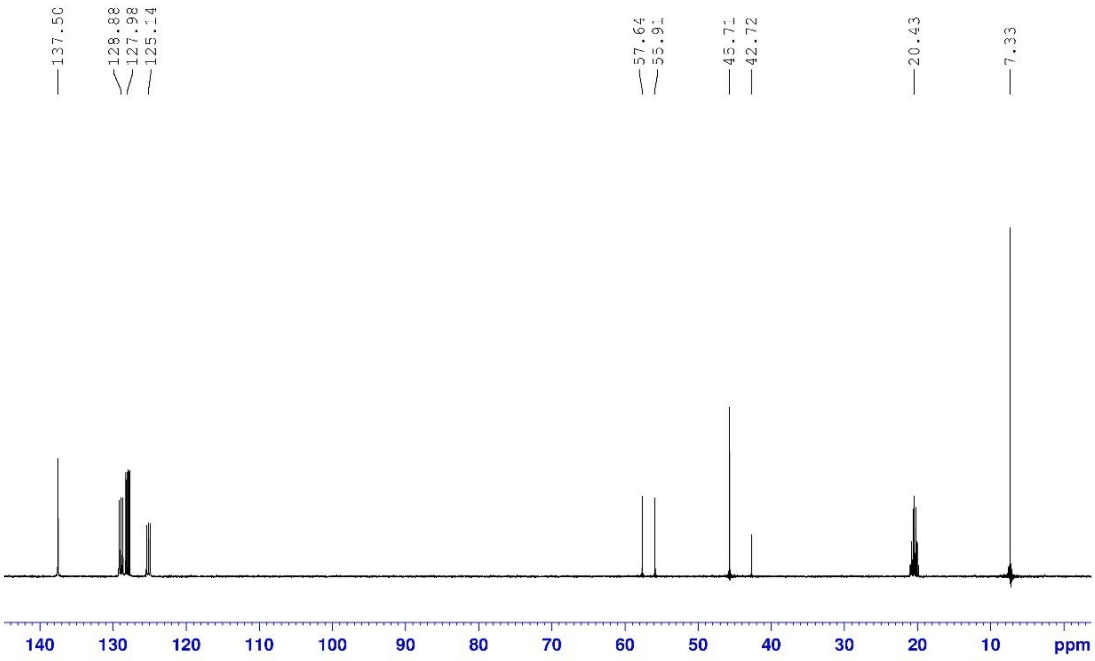

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **7**.

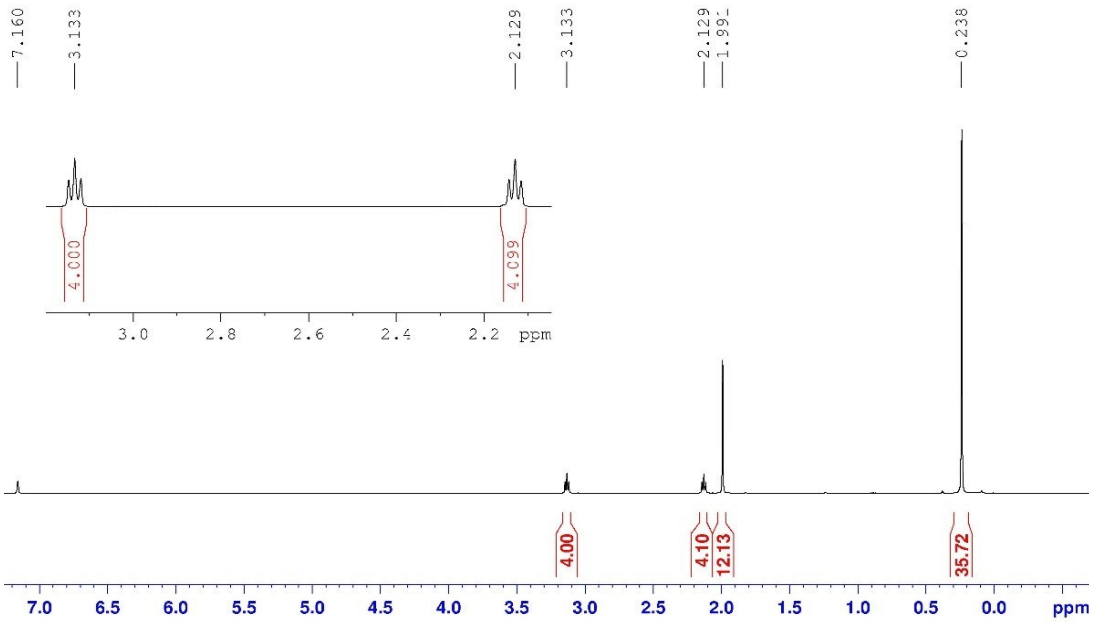

Figure S15. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **8**.

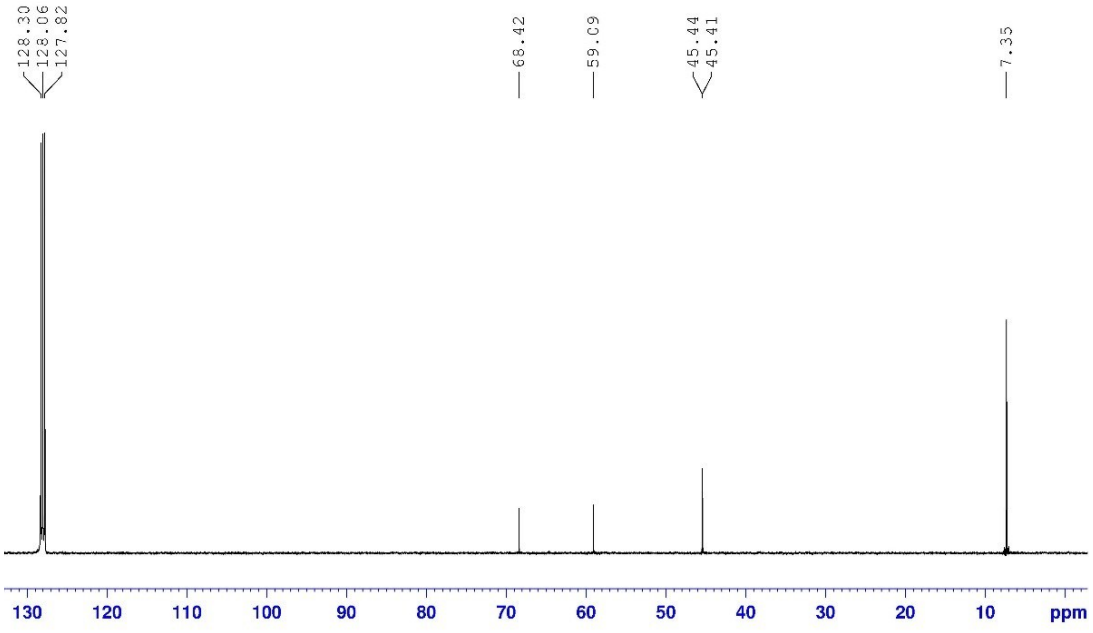

Figure S16. ^{13}C{^{1}H} NMR spectrum (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **8**.

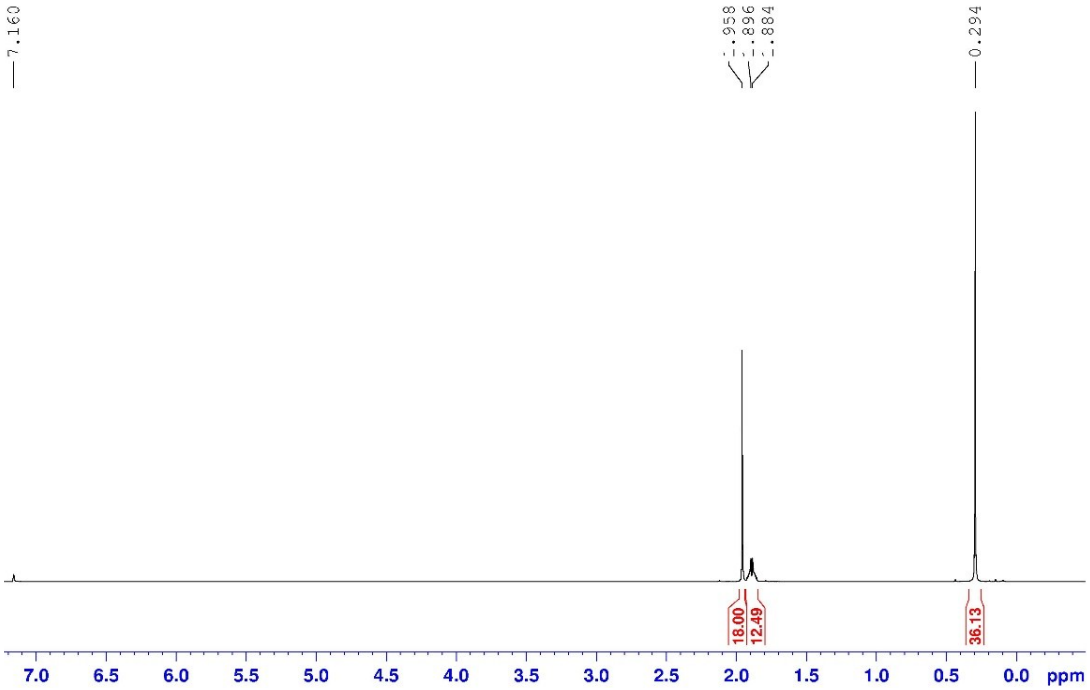

Figure S17. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **9**.

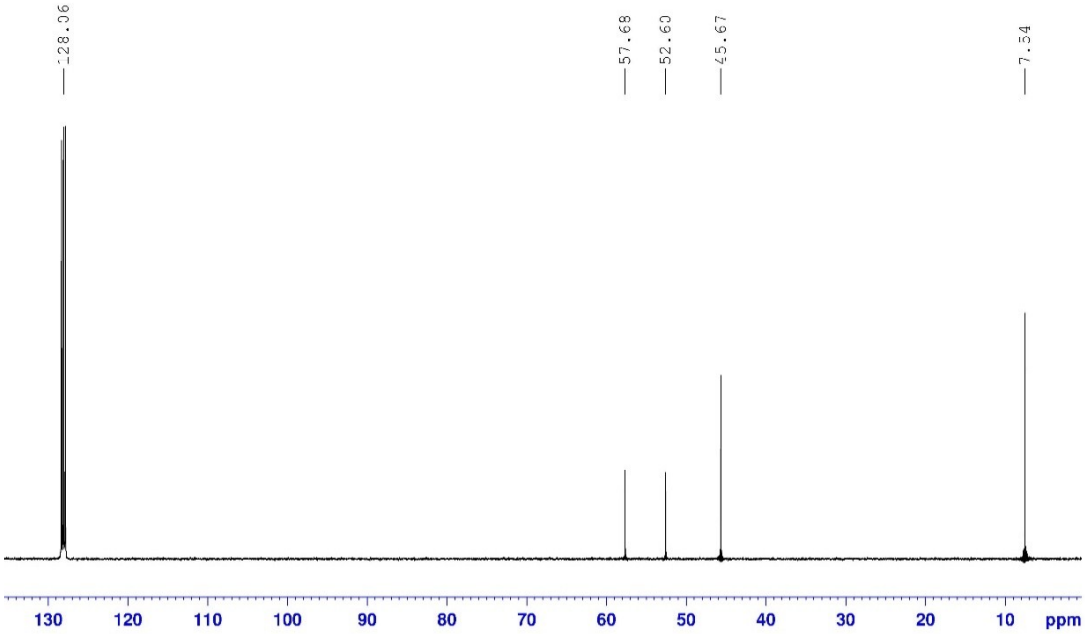

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **9**.

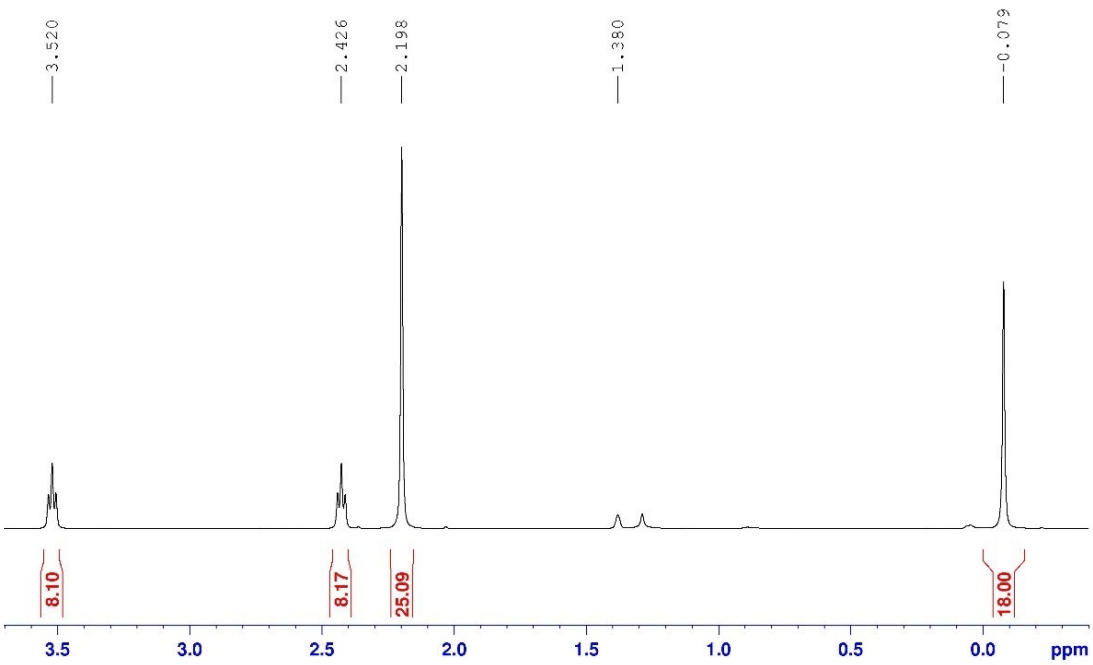

Figure S19. ^{1}H NMR (400.1 MHz, C_6D_{12}, 300 K) of isolated crystals of **10**.

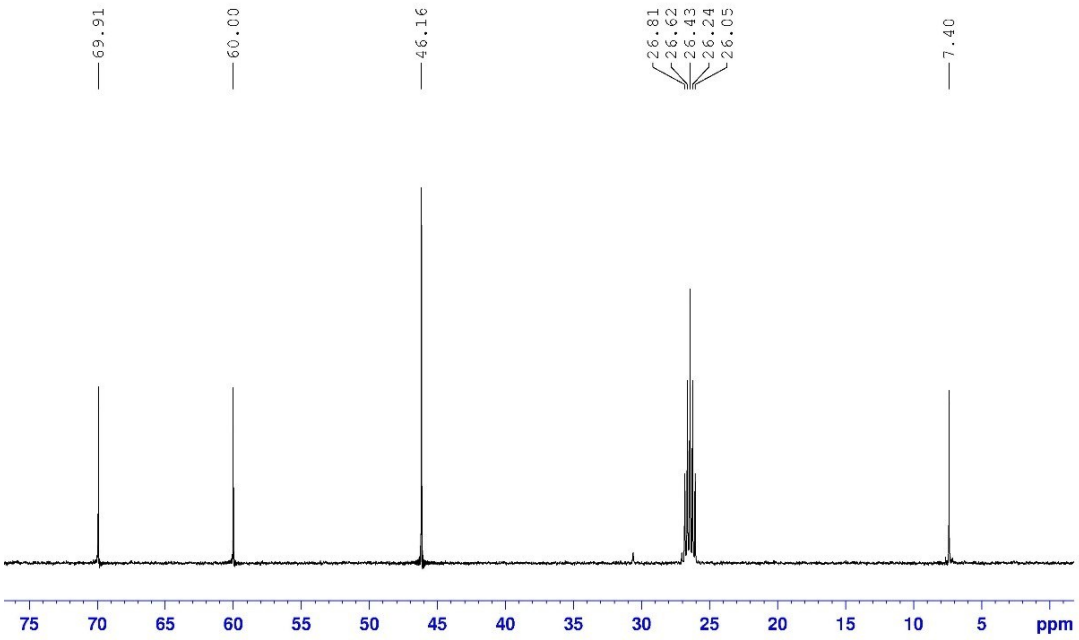

Figure S20. ^{13}C NMR (100.6 MHz, C_6D_{12}, 300 K) of isolated crystals of **10**.

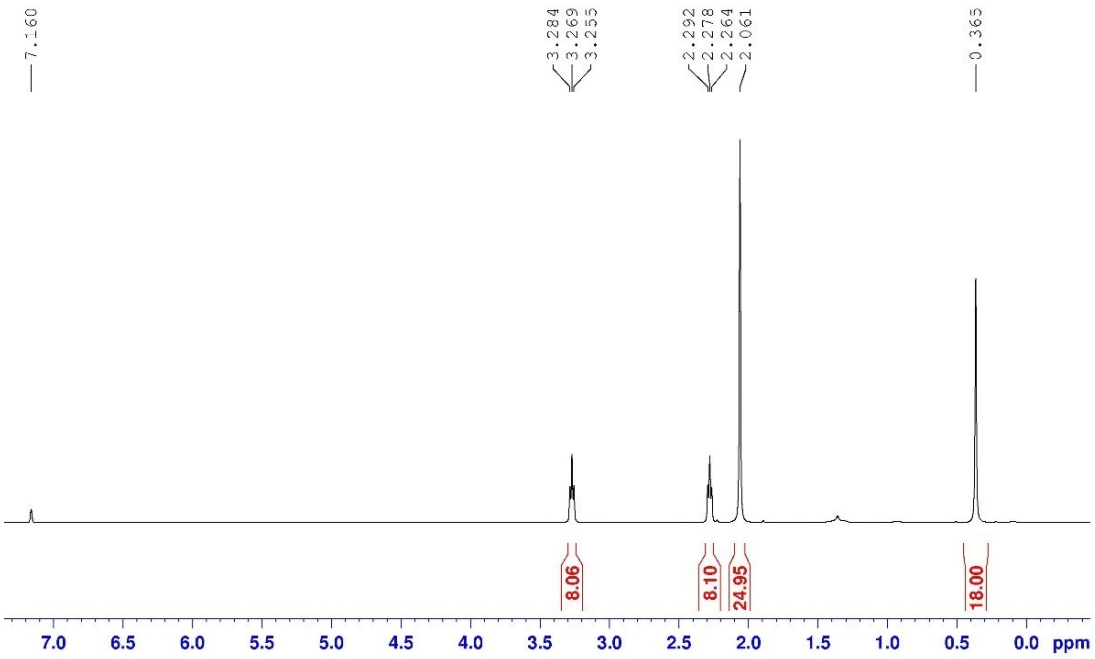

Figure S21. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **10**.

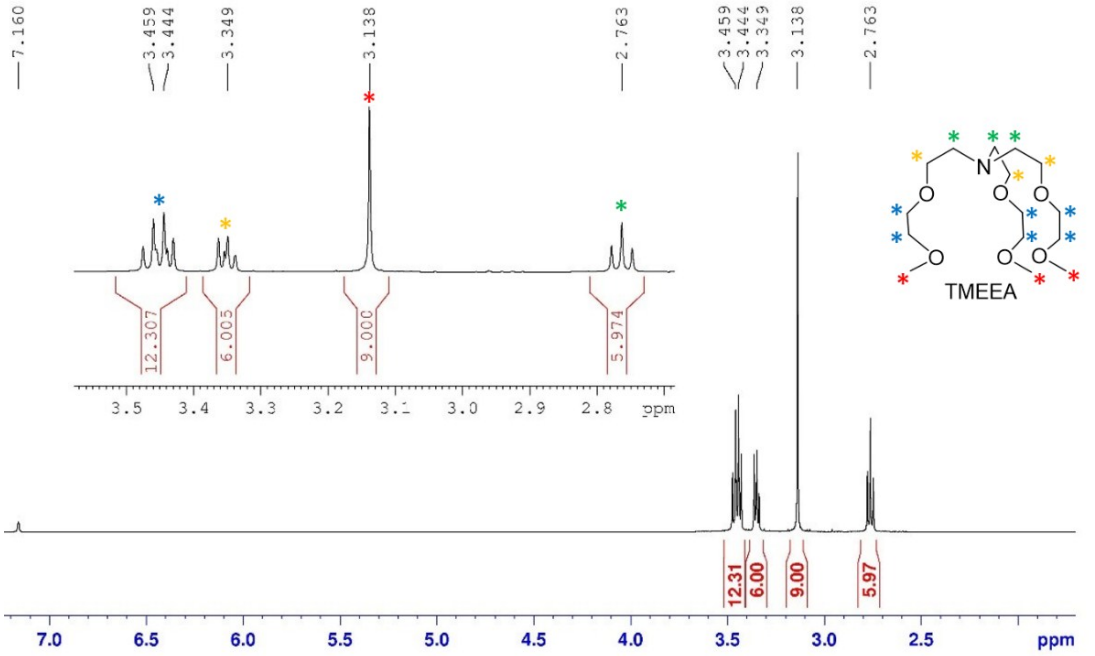

Figure S22. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of **TMEEA**.

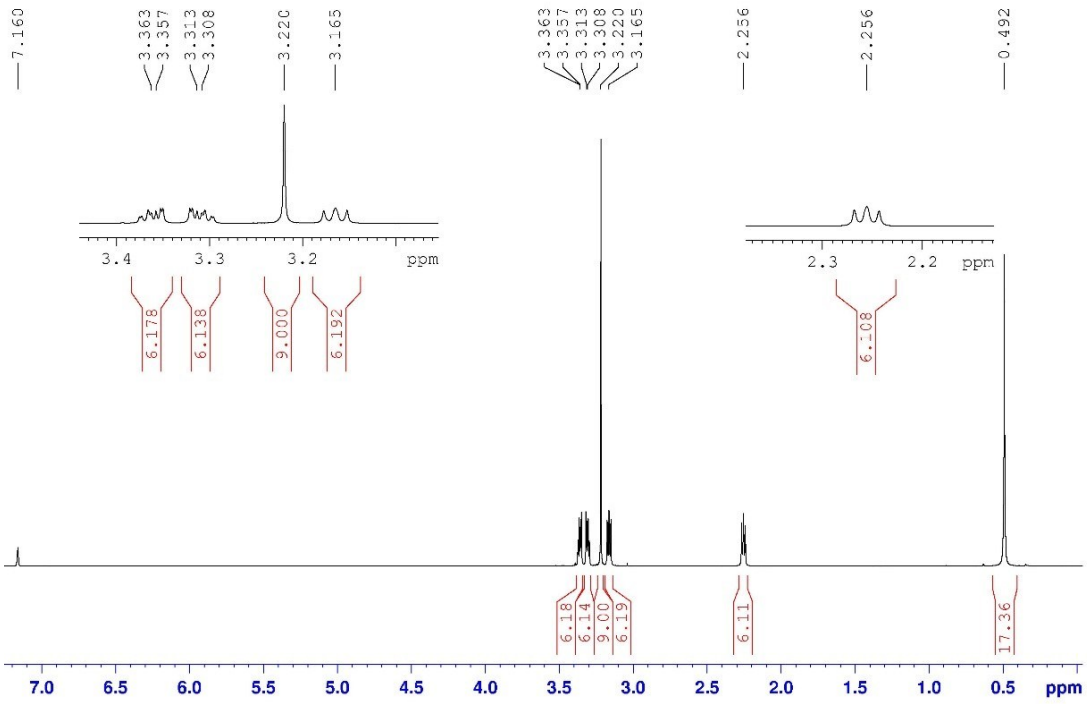

Figure S23. ^{1}H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **11**.

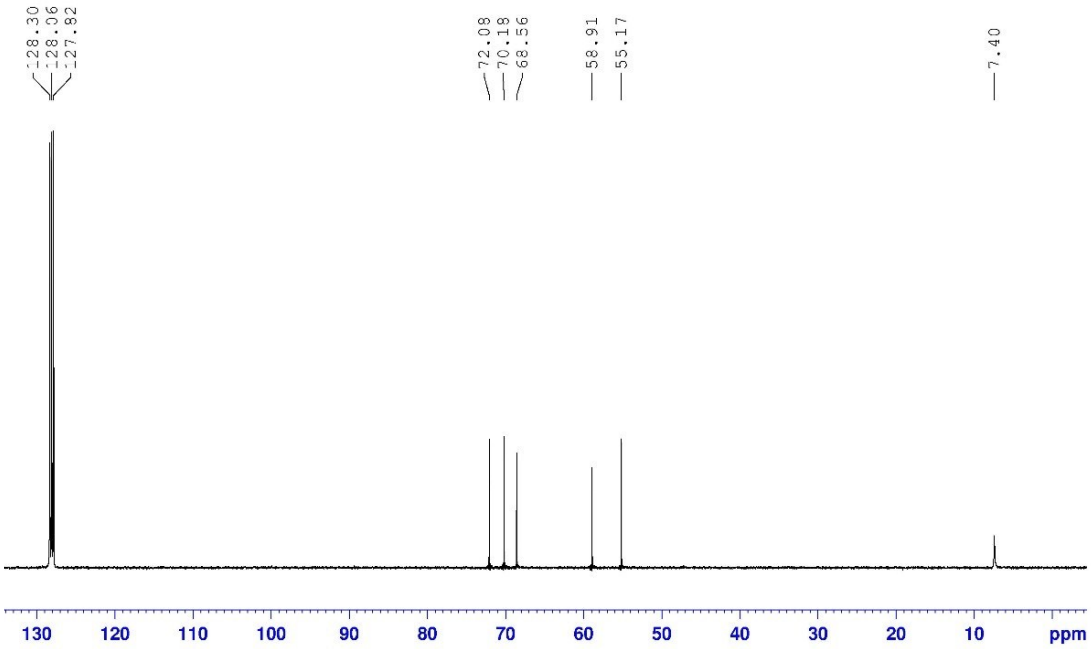

Figure S24. ^{13}C NMR (100.6 MHz, C_6D_6, 300 K) of isolated crystals of **11**.

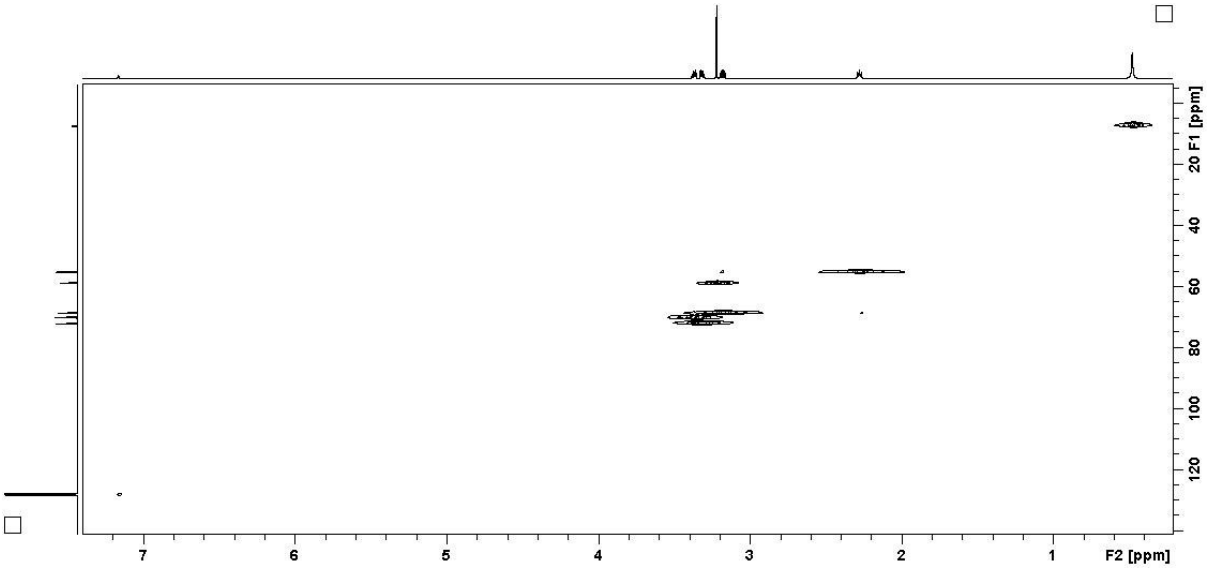

Figure S25. $^{1}H,^{13}C$-HSQC 1H NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **11**.

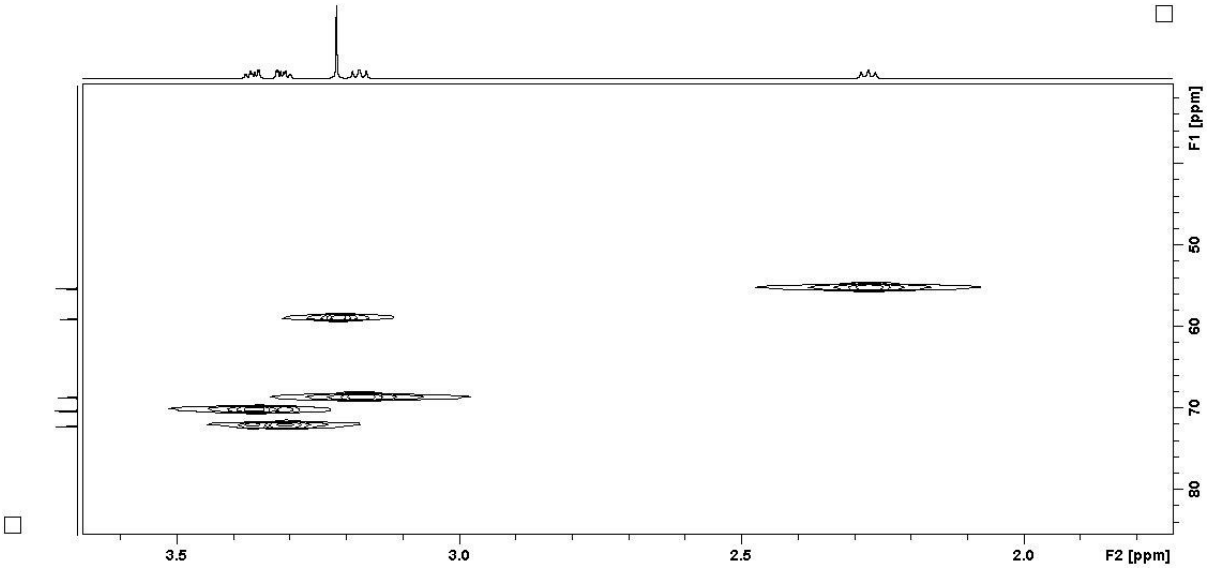

Figure S26. $^{1}H,^{13}C$-HSQC NMR (400.1 MHz, C_6D_6, 300 K) of isolated crystals of **11**.

Solution ^{1}H DOSY NMR Studies

NMR Spectroscopic Analysis Details

The Diffusion-Ordered Spectroscopy (DOSY) NMR experiments were performed on a Bruker AVANCE 400 MHz NMR spectrometer at 300 K operating at 400.1 MHz for ^{1}H under TopSpin (version 2.0, Bruker Biospin, Karlsruhe) and equipped with a BBFO-*z*-atm probe with actively shielded *z*-gradient coil capable of delivering a maximum gradient strength of 54 G cm^{-1}. Diffusion-ordered NMR data were acquired using the Bruker pulse program *dstegp3s* with a double stimulated echo with three spoiling gradients. Sine-shaped gradient pulses were used with a duration of 4 ms together with a diffusion period of 100 ms. Gradient recovery delays of 200 μs followed the application of each gradient pulse. Data were systematically accumulated by linearly varying the diffusion encoding gradients over a range from 2% to 95% of maximum for 64 gradient increment values. The signal decay dimension on the *pseudo*-2D data was generated by Fourier transformation of the time-domain data. DOSY plot were generated by use of the DOSY processing module of TopSpin. Parameters were optimized empirically to find the best quality of data for presentation purposes.

DOSY NMR Samples Preparation

To an NMR tube containing the corresponding compound to be analysed (typically, 20 mg) dissolved in the appropriate deuterated solvent (C_6D_6, D_8-toluene or D_8-THF, 0.5 mL) was added inert internal standards 1,2,3,4- tetraphenylnaphthalene (TPhN, 15 mg), 1-phenylnaphthalene (PhN, 13.2 μL) and tetramethylsilane (TMS, 19.1 μL).

^{1}H DOSY NMR spectroscopic study of **1** in C_6D_6 solution

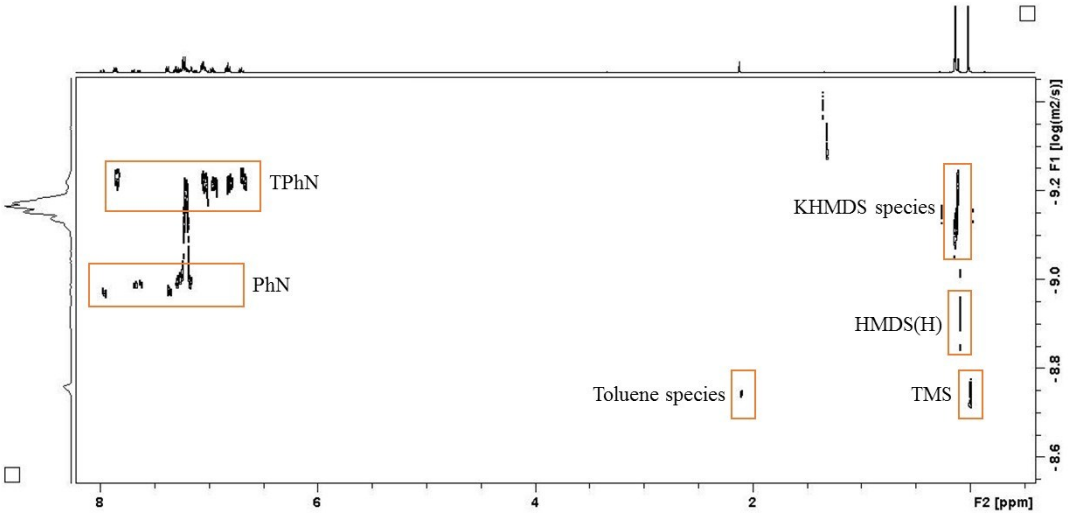

Figure S27. ^{1}H DOSY NMR of **1** in C_6D_6 at 300 K.

Table S3. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **1** in C_6D_6.

Internal standards; R^2 = 0.997			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	Toluene species D / m^2s^{-1}
5.97 x 10^{-10}	1.04 x 10^{-9}	1.74 x 10^{-9}	6.77 x 10^{-10}	1.80 x 10^{-9}

Table S4. MW_{DOSY} for species found in a solution of **1** in C_6D_6.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	6.77 x 10^{-10}	365.99
Toluene species	1.80 x 10^{-9}	85.84

Comments on the ^{1}H DOSY NMR spectrum of 1 in C_6D_6 solution: Two different diffusion coefficients are observed for the two parts conforming the solid state of **1** (HMDS vs toluene ligand, Figure S27). This suggests a different species in C_6D_6 solution to that found in the solid state, as toluene seems to not coordinate to the potassium centre in bulk C_6D_6. The MW_{DOSY} obtained for the HMDS species (MW = 365.99 g/mol, Table S3 and S4) is in agreement with monomerisation of **1** to form the species [(KHMDS)(C_6D_6)$_2$] (MW = 365.77 g/mol) in C_6D_6 solution. The diffusion coefficient obtained for

toluene is close to the theoretical value of free toluene (MW_{DOSY} = 85.84 g/mol, MW_{THEO} = 92.15 g/mol). The conclusion obtained from the ^{1}H DOSY NMR spectroscopic experiment of **1** confirms that the dimeric structure present in solid state does not remain in in C_6D_6 solution.

^{1}H DOSY NMR spectroscopic study of **3** in C_6D_6 solution

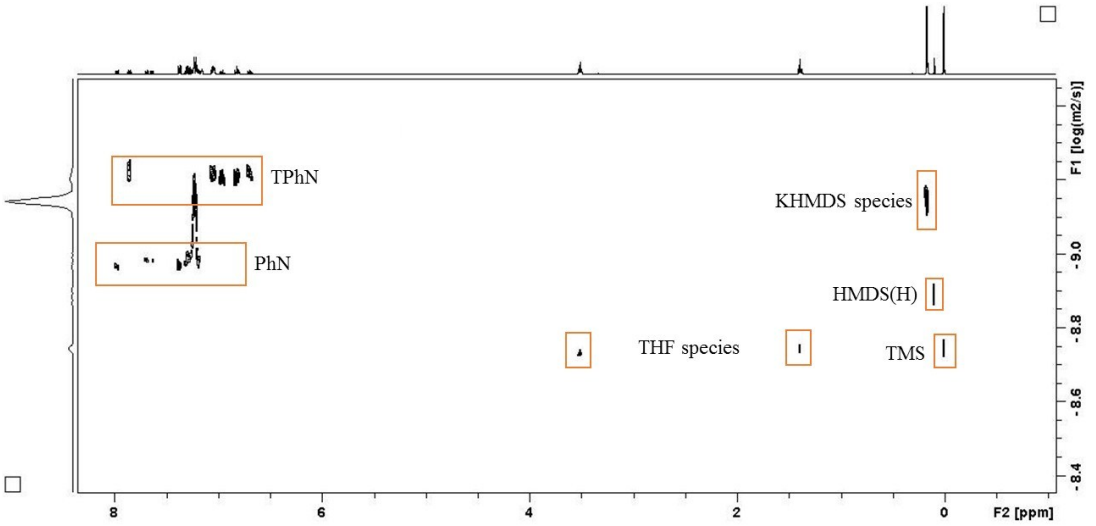

Figure S28. ^{1}H DOSY NMR of **3** in C_6D_6 at 300 K.

Table S5. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **3** in C_6D_6.

Internal standards; R^2 = 0.998			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	THF species D / m^2s^{-1}
6.16 x 10^{-10}	1.07 x 10^{-9}	1.80 x 10^{-9}	7.18 x 10^{-10}	1.85 x 10^{-9}

Table S6. MW_{DOSY} for species found in a solution of **3** in C_6D_6.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	7.18 x 10^{-10}	352.13
THF species	1.85 x 10^{-9}	87.16

Comments on the ^{1}H DOSY NMR spectrum of 3 in C_6D_6 solution: The solid state structure of **3** does not remain intact in C_6D_6 solution, as the THF and the HMDS containing species appear to have different diffusion coefficients, thus indicating that different species are found in solution. The experimental MW_{DOSY} obtained for the HMDS component is 352.13 g/mol, similar to that of **1** in C_6D_6, suggesting that a similar process might be happening for **3** in C_6D_6 solution (see Figure S28, Table S5 and S6). This could be explained by a dynamic exchange and competition between THF and C_6D_6 molecules to coordinate KHMDS. For THF, the observed MW_{DOSY} is 87.16 g/mol which is higher than the theoretical MW_{THEO} of THF (72.11 g/mol), this been in agreement as well with a competition with C_6D_6 molecules for solvation of the potassium centre. The species found in solution could be an equilibria between a monomeric [(KHMDS)$(C_6D_6)_2$] (MW = 365.77 g/mol) and monomeric [(KHMDS)$(THF)_2$] (MW = 357.78 g/mol).

^{1}H DOSY NMR spectroscopic study of **3** in D_8-THF solution

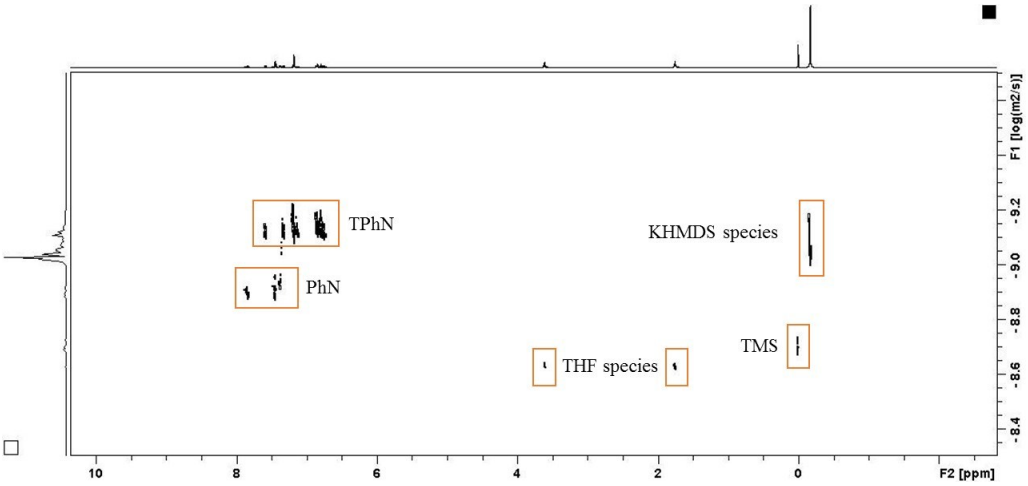

Figure S29. ^{1}H DOSY NMR of **3** in D_8-THF at 300 K.

Table S7. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **3** in D_8-THF.

Internal standards; R^2 = 0.995			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	THF species D / m^2s^{-1}
7.54×10^{-10}	1.27×10^{-9}	2.00×10^{-9}	9.29×10^{-10}	2.32×10^{-9}

Table S8. MW_{DOSY} for species found in a solution of **3** in D_8-THF.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	9.29×10^{-10}	317.65
THF species	2.32×10^{-9}	71.43

Comments on the ^{1}H DOSY NMR spectrum of 3 in C_6D_6 solution: Two diffusion coefficients are obtained for the ligands building **3** (Figure S29). The bulk D_8-THF solvent displace THF for solvation to KHMDS, being the experimental MW_{DOSY} of THF (MW = 71.4 g/mol) the same for the theoretical value (MW_{THEO} of free THF = 72.1 g/mol). Experimental MW_{DOSY} is 317.7 g/mol for the HMDS component, this being in agreement with monomerisation of the alkali metal amide in D_8-THF solution. The theoretical MW_{THEO} of [KHMDS(D_8-THF)$_2$] is 357.8 g/mol, these species being quite close to the obtained MW_{DOSY} (317.7, 8% error) (Table S7 and S8). This result shows that, not only the interactions established between [(KHMDS)$_2$(THF)$_2$] fragments are broken as expected, but the dimeric entity of [KHMDS]$_2$ found in solid state does not remain in solution, but a monomeric species of solvated KHMDS.

^{1}H DOSY NMR spectroscopic study of **4** in C_6D_6 solution

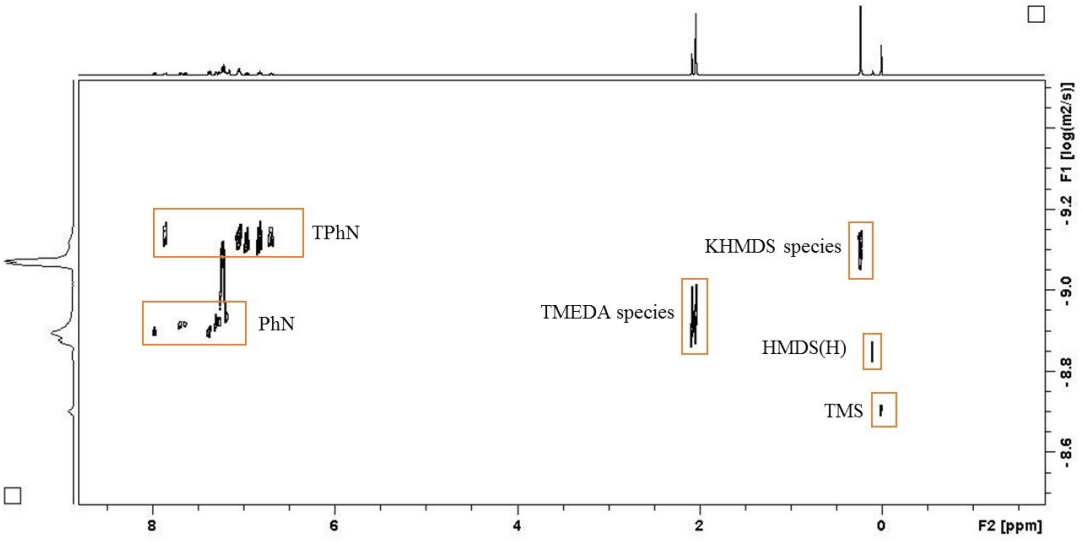

Figure S30. ^{1}H DOSY NMR of **4** in C_6D_6 at 300 K.

Table S9. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **4** in C_6D_6.

Internal standards; R^2 = 0.998			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	TMEDA species D / m^2s^{-1}
7.66 x 10^{-10}	1.25 x 10^{-9}	1.98 x 10^{-9}	8.47 x 10^{-10}	1.29 x 10^{-9}

Table S10. MW_{DOSY} for species found in a solution of **4** in C_6D_6.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	8.47 x 10^{-10}	373.19
TMEDA species	1.29 x 10^{-9}	183.87

Comments on the ^{1}H DOSY NMR spectrum of 4 in C_6D_6 solution: According to the information detailed in Figure S30, Table S9 and S10, the KHMDS species found in C_6D_6 has a lower molecular weight (experimental MW_{DOSY} is 373.0 g/mol for HMDS signal) compared to the theoretical value of **4** [[(TMEDA)$_2$(KHMDS)$_2$] 631.39 g/mol]. Thus, the experimental value obtained for the HMDS ligand is closer to a coordinated monomeric species of the type [(KHMDS)(C_6D_6)$_2$] (MW = 365.77 g/mol) than to a dimeric species of the type [(KHMDS)$_2$(donor)$_2$] (donor = TMEDA or C_6D_6; MW = 631.39 or 565.26 g/mol). This experiment appears to suggest monomeric C_6D_6 solvates of KHMDS in solution as major species over dimeric aggregates. Regarding the experimental MW_{DOSY} for the TMEDA species, it is slightly higher (183.87 g/mol) than the theoretical value of TMEDA (116.21 g/mol). This situation suggests coordination of the bidentate ligand (TMEDA) to the complex, competing with molecules of solvent (C_6D_6) for coordinating to the potassium centre in solution. The ^{1}H NMR of **4** in C_6D_6 (Figure Sx) shows coordination of the ligand to KHMDS as the chemical shift values for the bidentate ligand are different to those found for uncoordinated TMEDA. However, when TMEDA coordinates to an alkali metal normally the signals observed show the Me groups at lower fields than the –CH_2– of the backbone. The inverse disposition of the signals within a solution of **4** in arene solvent, is in concordance with at least a partial de-coordination of the Lewis base ligand from the potassium centre. The same behaviour was observed for **5**, as the solid state structures of **4** and **5** are similar, the only difference being the type of bidentate ligand.

^{1}H DOSY NMR spectroscopic study of **4** in D_8-THF solution

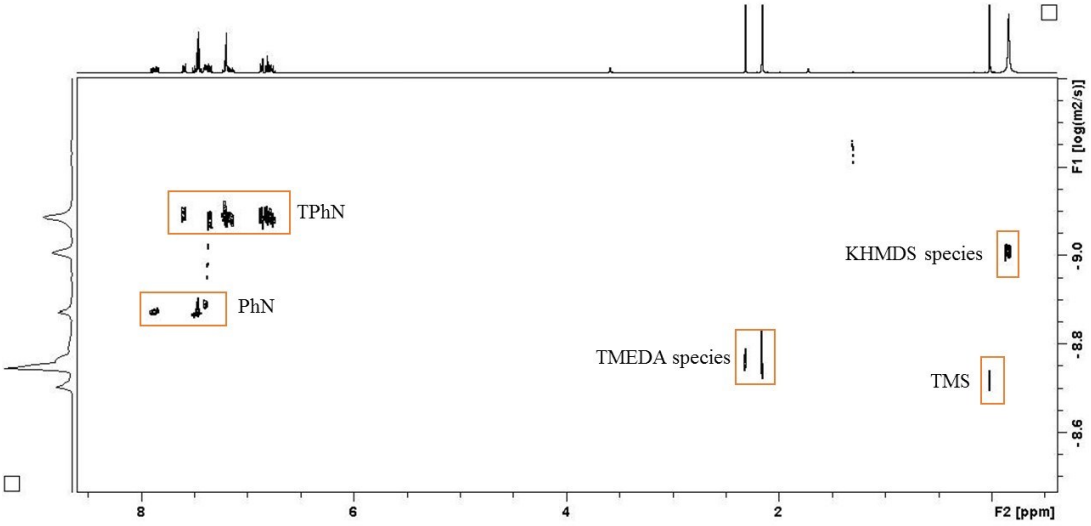

Figure S31. ^{1}H DOSY NMR of **4** in D_8-THF at 300 K.

Table S11. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **4** in D_8-THF.

Internal standards; R^2 = 0.987			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	TMEDA species D / m^2s^{-1}
8.18 x 10^{-10}	1.35 x 10^{-9}	1.97 x 10^{-9}	9.80 x 10^{-10}	1.77 x 10^{-9}

Table S12. MW_{DOSY} for species found in a solution of **4** in D_8-THF.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	7.91 x 10^{-10}	329.25
TMEDA	7.37 x 10^{-9}	112.79

Comments on the ^{1}H DOSY NMR spectrum of 4 in D_8-THF solution: The species found in a solution of **4** in D_8-THF (Figure S31) is in agreement with a monomeric species of the type [KHMDS·$(D_8\text{-THF})_n$] (n = 2 MW 343.47 g/mol; n = 3 MW 415.81 g/mol) and free ligand, MW_{DOSY} of TMEDA is 116.22 g/mol, see Table S11 and Table S12.

^{1}H DOSY NMR spectroscopic study of 6 in D_8-toluene solution

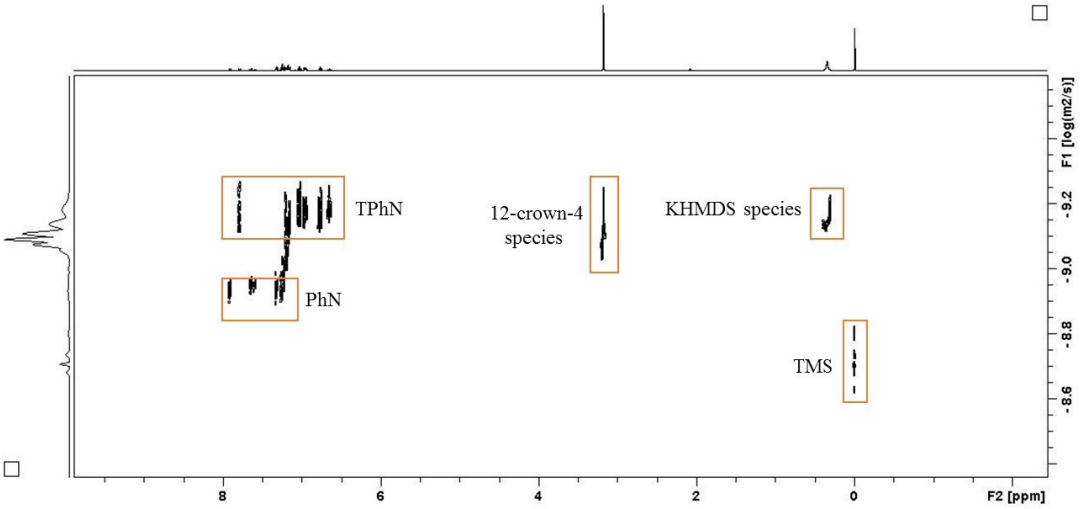

Figure S32. ^{1}H DOSY NMR of **6** in D_8-toluene at 300 K.

Table S13. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **6** in D_8-Toluene.

Internal standards; R^2 = 0.998			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	12-crown-4 species D / m^2s^{-1}
6.72×10^{-10}	1.13×10^{-9}	1.92×10^{-9}	7.91×10^{-9}	7.37×10^{-9}

Table S14. MW_{DOSY} for species found in a solution of **6** in D_8-Toluene**.**

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species 12-crown-4 species	7.91×10^{-9} 7.37×10^{-9}	360.59

Comments on the ^{1}H DOSY NMR spectrum of 6 in D_8-toluene solution: ^{1}H DOSY NMR study (see Figure S32, Table S13 and S14) suggests a monomeric species of **6** in d_8-toluene solution of the type [KHMDS(12-crown-4)]. The dimeric species found in solid state does not remain in coordinating hydrocarbon solution, thus a co-complexation should have taken place between two monomeric [KHMDS(12-crown-4)] species to isolate **6** in the solid state. In contrast with **4**, molecules of solvent do not appear to coordinate the potassium centre as the tetra oxygen ligand appears to be a

stronger competitor to coordinate KHMDS. In this sense, the MW_{DOSY} obtained for the 12-crown-4 species is quite far from the one the free ligand (MW_{DOSY} of 12-crown-4 in **6** is 380.68 g/mol; MW_{THEO} of uncoordinated 12-crown-4 is 176.21 g/mol). Although the affinity of heavy alkali metals to interact with coordinating hydrocarbon solvents through a π-interaction, the four K−O interactions between the potassium centre and the oxygen atoms of the tetradentate ligand seem to be chosen over a π-interaction with molecules of D_8-toluene.

^{1}H DOSY NMR spectroscopic study of **6** in D_8-THF solution

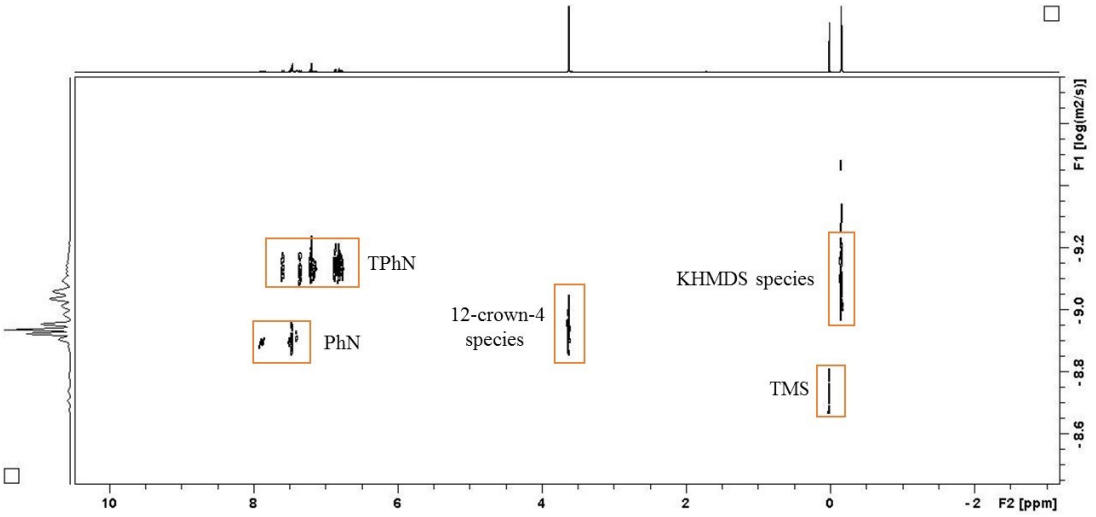

Figure S33. ^{1}H DOSY NMR of **6** in D_8-THF at 300 K.

Table S15. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **6** in D_8-THF.

Internal standards; R^2 = 0.987			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	12-crown-4 species D / m^2s^{-1}
7.26×10^{-10}	1.27×10^{-9}	1.86×10^{-9}	8.79×10^{-10}	1.15×10^{-9}

Table S16. MW_{DOSY} for species found in a solution of **6** in D_8-THF.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	8.79 x 10^{-10}	334.28
12-crown-4 species	1.15 x 10^{-9}	211.06

Comments on the ^{1}H DOSY NMR spectrum of 6 in D_8-THF solution: According to ^{1}H DOSY NMR spectroscopic study (Figure S33 and Table S15 and S16) of **6** in D_8-THF, it suggests the structure found in solid state does not remain in solution, but the monomeric species [KHMDS·(12-crown-4)], it can be envisaged that the more coordinating polar solvent D_8-THF compared with D_8-toluene, will monomerise **6** as well. Looking at the HMDS signal, the observed MW_{DOSY} (334.28 g/mol) suggests monomerisation of KHMDS. This MW_{DOSY} is 11% lower than the theoretical MW_{THEO} for [KHMDS·(12-crown-4)] (MW 375.17 g/mol) due to a competition of the ligand and molecules of solvent to be coordinated and free. MW_{DOSY} for the ligand (12-crown-4 ether) is higher than the theoretical value for the free ligand (MW_{THEO} of 12-crown-4 is 176.21 g/mol), this indicating as well an equilibria between free ligand and coordinated ligand increasing the MW of the donor.

^{1}H DOSY NMR spectroscopic study of **8** in C_6D_6 solution

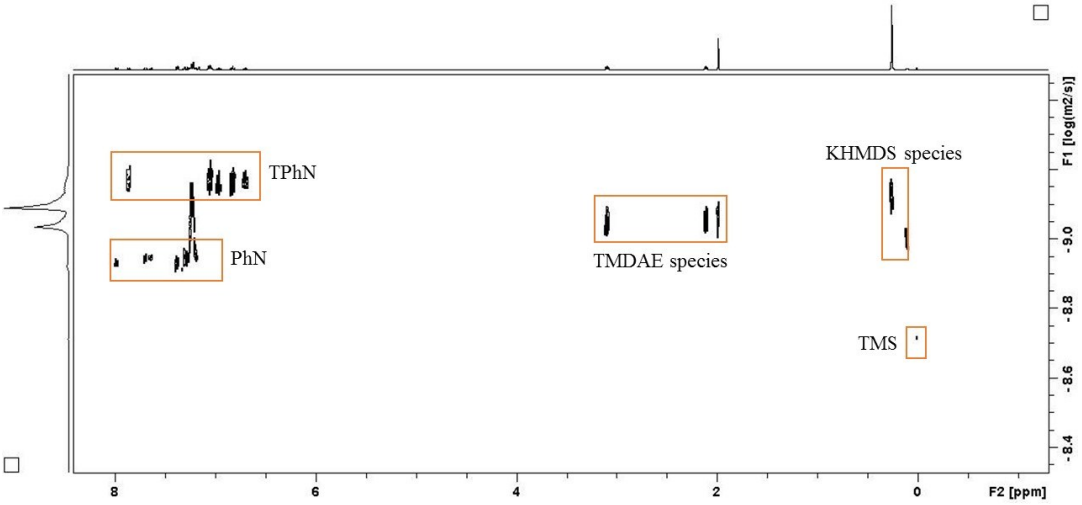

Figure S34. ^{1}H DOSY NMR of **8** in C_6D_6 at 300 K.

Table S17. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **8** in C_6D_6.

Internal standards; R^2 = 0.999			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	TMDAE species D / m^2s^{-1}
7.09×10^{-10}	1.16×10^{-9}	1.94×10^{-9}	8.09×10^{-10}	1.00×10^{-9}

Table S18. MW_{DOSY} for species found in a solution of **8** in C_6D_6.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	8.09×10^{-10}	353.96
TMDAE species	1.00×10^{-9}	252.99

Comments on the ^{1}H DOSY NMR spectrum of 8 in C_6D_6 solution: The solid state aggregation of **8** is not maintained in C_6D_6 solvent as two species with different diffusion coefficients appear in the ^{1}H DOSY spectroscopic study (Figure S34, Table S17-S18). The obtained MW_{DOSY} for the HMDS ligand (353.96 g/mol) suggests monomerisation of the alkali metal amide species to [(KHMDS)$(C_6D_6)_2$] (MW: 365.77 g/mol). According to ^{1}H DOSY, the experimental MW_{DOSY} for the TMDAE species is 252.99 g/mol, whilst the free TMDAE ligand expected would have a MW_{THEO} of 160.26 g/mol. This result suggests at least partial coordination of TMDAE to the potassium centre in solution, competing with molecules of solvent (C_6D_6) to coordinate the metallic centre.

^{1}H DOSY NMR spectroscopic study of **8** in C_6D_6 solution

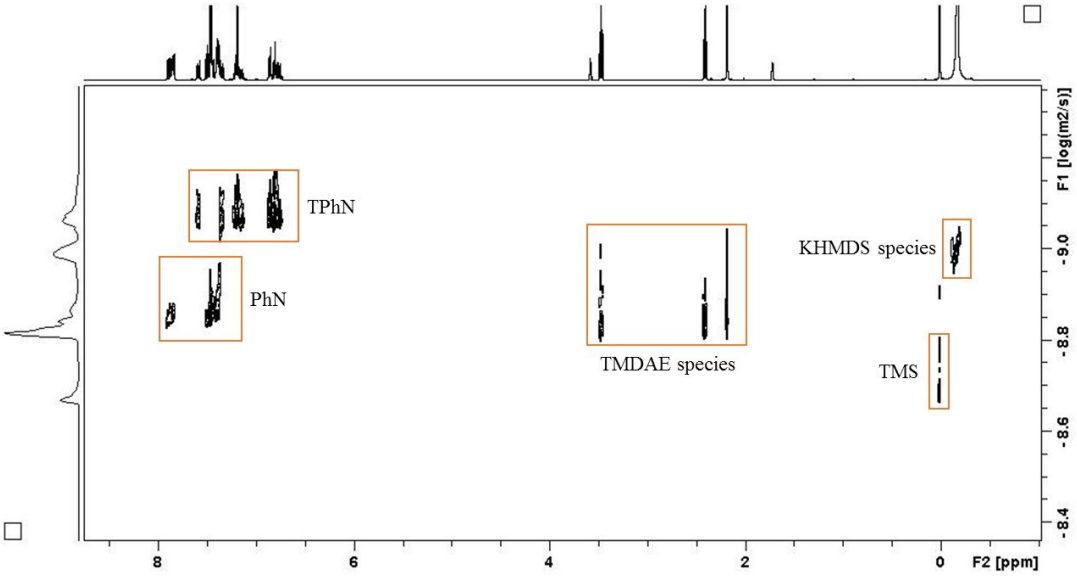

Figure S35. ^{1}H DOSY NMR of **8** in D_8-THF at 300 K.

Table S19. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **8** in D_8-THF.

Internal standards; R^2 = 0.999			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	TMDAE species D / m^2s^{-1}
8.35 x 10^{-10}	1.43 x 10^{-9}	2.12 x 10^{-9}	1.02 x 10^{-9}	1.56 x 10^{-9}

Table S20. MW_{DOSY} for species found in a solution of **8** in D_8-THF.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	1.02 x 10^{-9}	338.82
TMDAE species	1.56 x 10^{-9}	160.28

Comments on the ^{1}H DOSY NMR spectrum of 8 in D_8-THF solution: A ^{1}H NMR DOSY NMR spectroscopic study of **8** in D_8-THF (Figure S35) was carried out. The diffusion coefficients observed in Table S19 and S20 are in agreement with a monomeric species of the type [KHMDS·(d_8-THF)$_n$] (n = 2 MW 343.47 g/mol; n = 3, MW 415.81 g/mol) and free ligand (MW_{THEO} of free TMDAE is 160.26 g/mol).

^{1}H DOSY NMR spectroscopic study of **10** in C_6D_6 solution

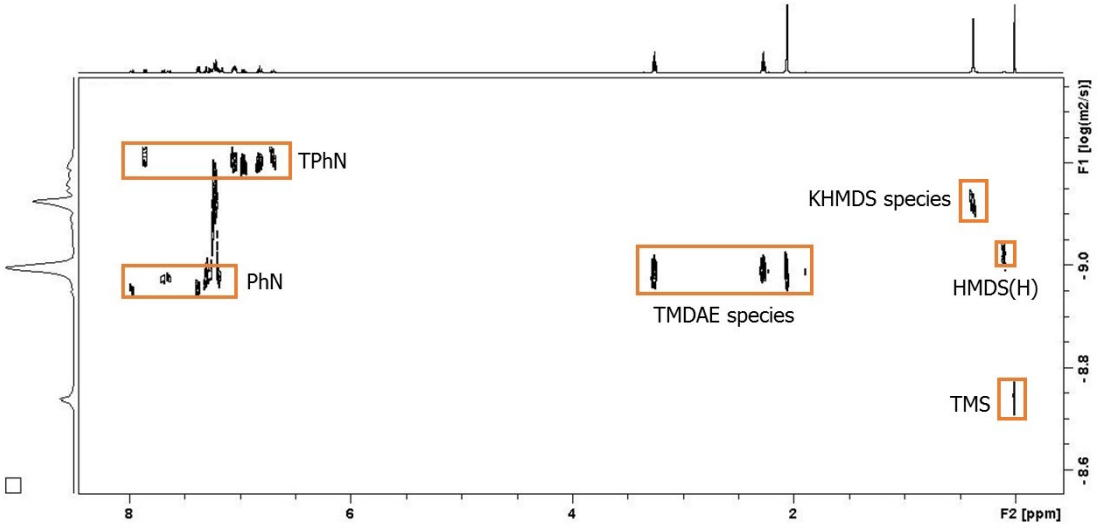

Figure S36. ^{1}H DOSY NMR of **10** in C_6D_6 at 300 K.

Table S21. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **10** in C_6D_6.

Internal standards; R^2 = 0.999			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	TMDAE species D / m^2s^{-1}
6.29 x 10^{-10}	1.09 x 10^{-9}	1.83 x 10^{-9}	7.46 x 10^{-10}	1.00 x 10^{-9}

Table S22. MW_{DOSY} for species found in a solution of **10** in C_6D_6.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	7.46 x 10^{-10}	343.41
TMDAE species	1.00 x 10^{-9}	221.43

Comments on the ^{1}H DOSY NMR spectrum of 10 in C_6D_6 solution: A solution of **10** in C_6D_6 was studied by ^{1}H DOSY NMR spectroscopy showing two different species in solution with diffusion coefficients of 7.46 x 10^{-10} and 1.00 x 10^{-9} (Figure S36). The MW_{DOSY} of the HMDS species is 34% lower than the theoretical MW_{DOSY} value of **10**, this suggesting as well that the identity of **10** is not maintained in C_6D_6 solvent (theoretical MW_{DOSY} of **10** is 520.01 g/mol). The observed MW_{DOSY} for the TMDAE species is 221.43 g/mol, which is higher than the MW_{THEO} of free TMDAE (160.26 g/mol). These results suggest at least partially coordination of the tridentate ligand to the metallic centre, and according to the value of the HMDS ligand, a competition of the tridentate ligand with

molecules of C_6D_6 to coordinate the K metal centre, being an equilibria between free ligand and coordinated ligand increasing finally the MW of the TMDAE species (see Table S21 and S22).

^{1}H DOSY NMR spectroscopic study of **10** in D_8-THF solution

Figure S37. ^{1}H DOSY NMR of **10** in D_8-THF at 300 K.

Table S23. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **10** in D_8-THF.

Internal standards; R^2 = 0.999			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	TMDAE species D / m^2s^{-1}
7.52×10^{-10}	1.3×10^{-9}	1.96×10^{-9}	9.28×10^{-10}	1.41×10^{-9}

Table S24. MW_{DOSY} for species found in a solution of **10** in D_8-THF.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	9.28×10^{-10}	322.25
TMDAE species	1.41×10^{-9}	161.26

Comments on the ^{1}H DOSY NMR spectrum of 10 in D_8-THF solution: The ^{1}H DOSY NMR spectroscopic study of **10** in D_8-THF (Figure S37) suggests a monomeric species in solution as the obtained MW_{DOSY} for the diffusion coefficient of the HMDS ligand is 322.25 g/mol, being in agreement with monomerisation of KHMDS solvated by d_8-THF molecules ([KHMDS(d_8-THF)]n, with n = 2 the MW_{THEO} is 357.78). MW_{DOSY} for the TMDAE species is in agreement with the theoretical MW_{THEO} value of the corresponding free ligand. This suggests that the tridentate ligand is de-coordinated in D_8-THF solution, being molecules of solvent coordinating the alkali metal in solution at ambient temperature. Thus, according to the results obtained by ^{1}H DOSY NMR, the structure found in solid state does not remain in D_8-THF solution (Table S23 and S24).

^{1}H DOSY NMR spectroscopic study of **11** in C_6D_6 solution

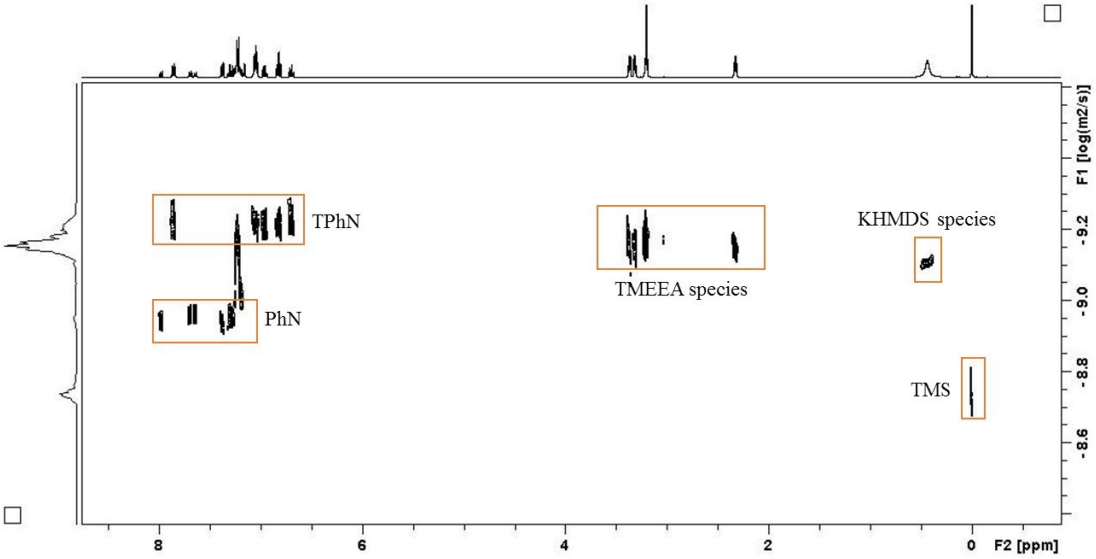

Figure S38. ^{1}H DOSY NMR of **11** in C_6D_6 at 300 K.

Table S25. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **11** in C_6D_6.

Internal standards; R^2 = 0.999			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	TMEEA species D / m^2s^{-1}
6.17×10^{-10}	1.08×10^{-9}	1.82×10^{-9}	7.81×10^{-10}	7.05×10^{-10}

Table S26. MW_{DOSY} for species found in a solution of **30** in C_6D_6.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	7.81 x 10^{-10}	314
TMEEA species	7.05 x 10^{-10}	365.71

Comments on the ^{1}H DOSY NMR spectrum of 11 in C_6D_6 solution: ^{1}H DOSY NMR spectroscopy shows two close but different diffusion coefficients for the HMDS and ligand parts of **11** in C_6D_6 solution (Figure S38). The MW_{DOSY} obtained for the HMDS ligand (314.0 g/mol) suggests a monomeric species in solution coordinated by molecules of C_6D_6 solvent, *i.e.*, the obtained MW_{DOSY} of 314.0 g/mol for the HMDS vs 523 g/mol (expected for [(KHMDS)(NO_6-ligand)]) suggest monomerisation to [KHMDS(arene)$_n$], [(KHMDS)(C_6D_6)$_2$ of 367 g/mol] (see Table S25 and S26). The MW_{DOSY} of the TMEEA ligand (365.71 g/mol) is 36% lower than the theoretical value for **11** (550.97 g/mol) due to competition in the coordination sphere of KHMDS by molecules of C_6D_6 and the ligand, existing an equilibria between **11** and [KHMDS(C_6D_6)$_n$] (n = 2, MW_{THEO} = 365.77 g/mol).

^{1}H DOSY NMR spectroscopic study of **11** in D_8-THF solution

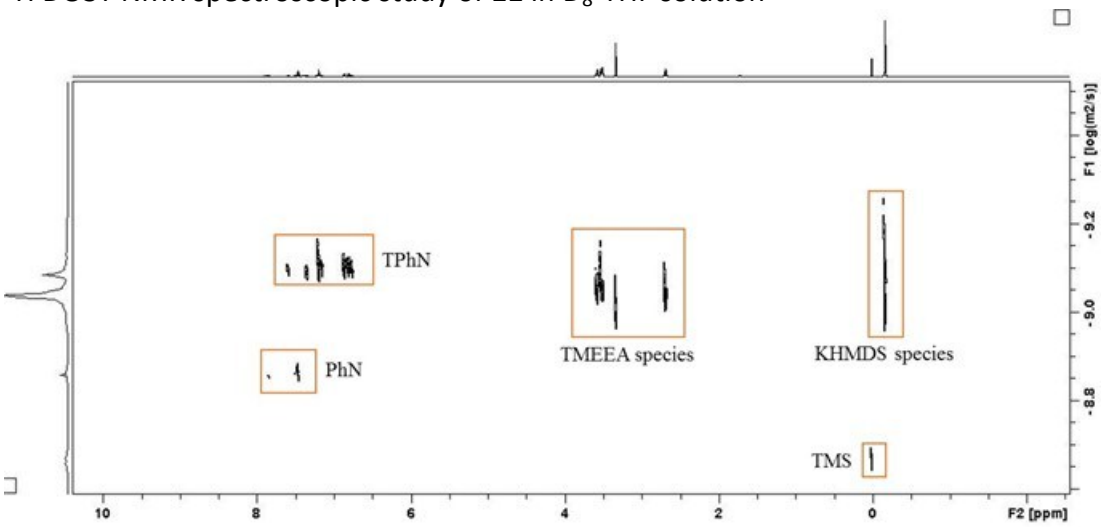

Figure S39. ^{1}H DOSY NMR of **11** in D_8-THF at 300 K.

Table S27. Diffusion coefficients for the internal references (TPhN, PhN and TMS) and for the species present in a solution of **11** in D_8-THF.

Internal standards; R^2 = 0.999			Species in solution	
TPhN D / m^2s^{-1}	PhN D / m^2s^{-1}	TMS D / m^2s^{-1}	KHMDS species D / m^2s^{-1}	TMEEA species D / m^2s^{-1}
8.11×10^{-10}	1.38×10^{-9}	2.14×10^{-9}	9.08×10^{-10}	9.07×10^{-10}

Table S28. MW_{DOSY} for species found in a solution of **11** in D_8-THF.

Species in solution	D (m^2s^{-1})	MW_{DOSY} ($gmol^{-1}$)
KHMDS species	9.08×10^{-10}	375.83
TMEEA species	9.07×10^{-10}	376.67

Comments on the ^{1}H DOSY NMR spectrum of 11 in D_8-THF solution: When **11** is dissolved in D_8-THF, ^{1}H DOSY spectra shows two signals with similar diffusion coefficients (Figure S39). The obtained MW_{DOSY} for these diffusion coefficient values are 375.83 g/mol for the HMDS species and 376.37 g/mol for the TMEEA part (323.43 g/mol expected for free ligand). The MW_{DOSY} obtained for the HMDS species is the highest with respect to the other studied compounds, this suggesting that the heptadentate ligand is a strong competitor to coordinate the metallic centre. Also, regarding the MW_{DOSY} obtained for the TMEEA species, it is higher than that of the free ligand, in contrast to the other studied species, this being in agreement with the strong coordination of the heptadentate ligand to coordinate KHMDS (Table S27 and S28).

REFERENCES

1. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112.