

Supporting Information for

Tetrazenyl-, Imido-, and Azidoaluminate Derivatives of a Sterically Demanding Bis-Silazide Ligand

Han-Ying Liu, Ryan J. Schwamm, Jakub Kenar, Mary F. Mahon and Michael S. Hill *

Department of Chemistry, University of Bath, Claverton Down, Bath BA2 7AY, UK

* Correspondence: msh27@bath.ac.uk

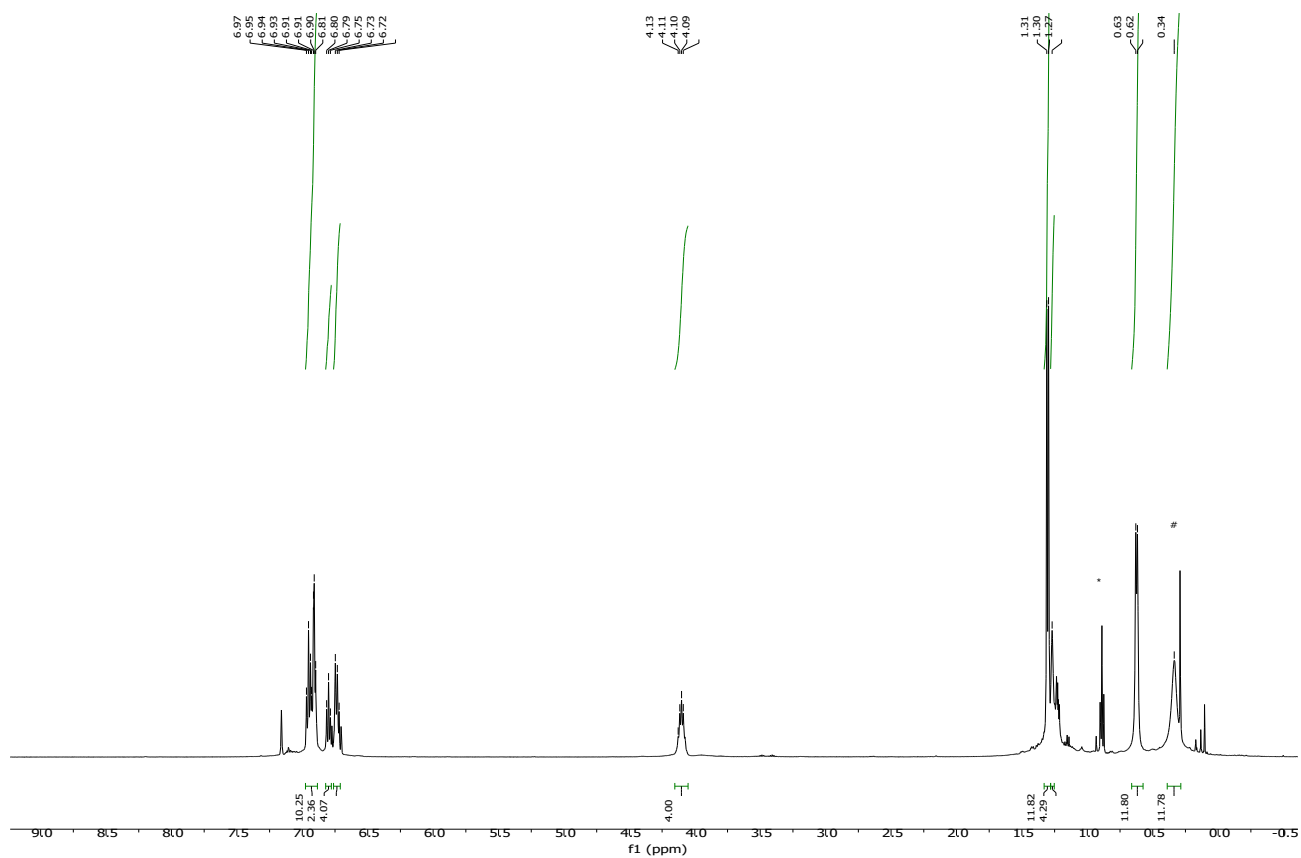


Figure S1. ¹H NMR (500 MHz, 298 K, C₆D₆) spectrum of **1**. *hexanes # grease.

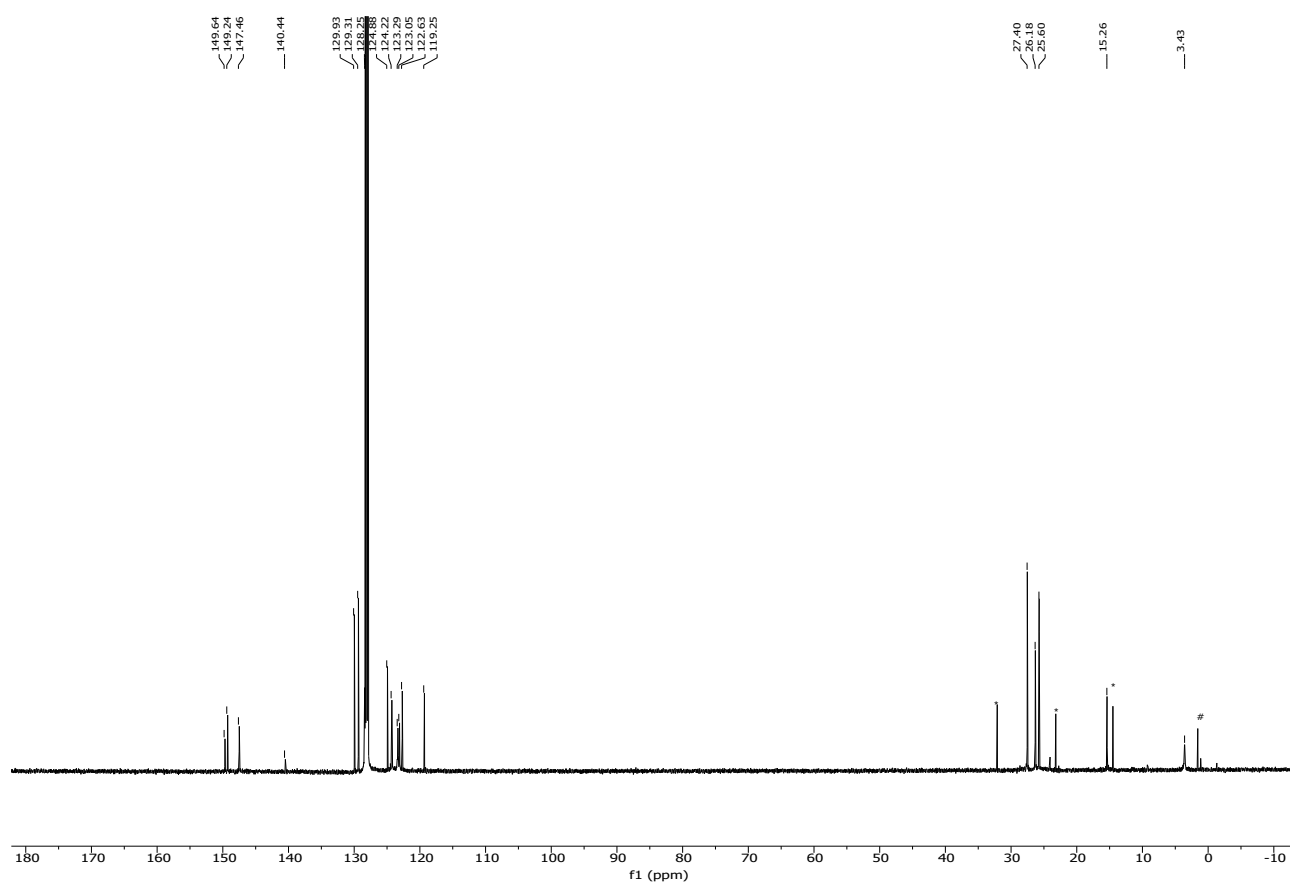


Figure S2. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, C_6D_6) spectrum of **1**. *hexanes # grease.

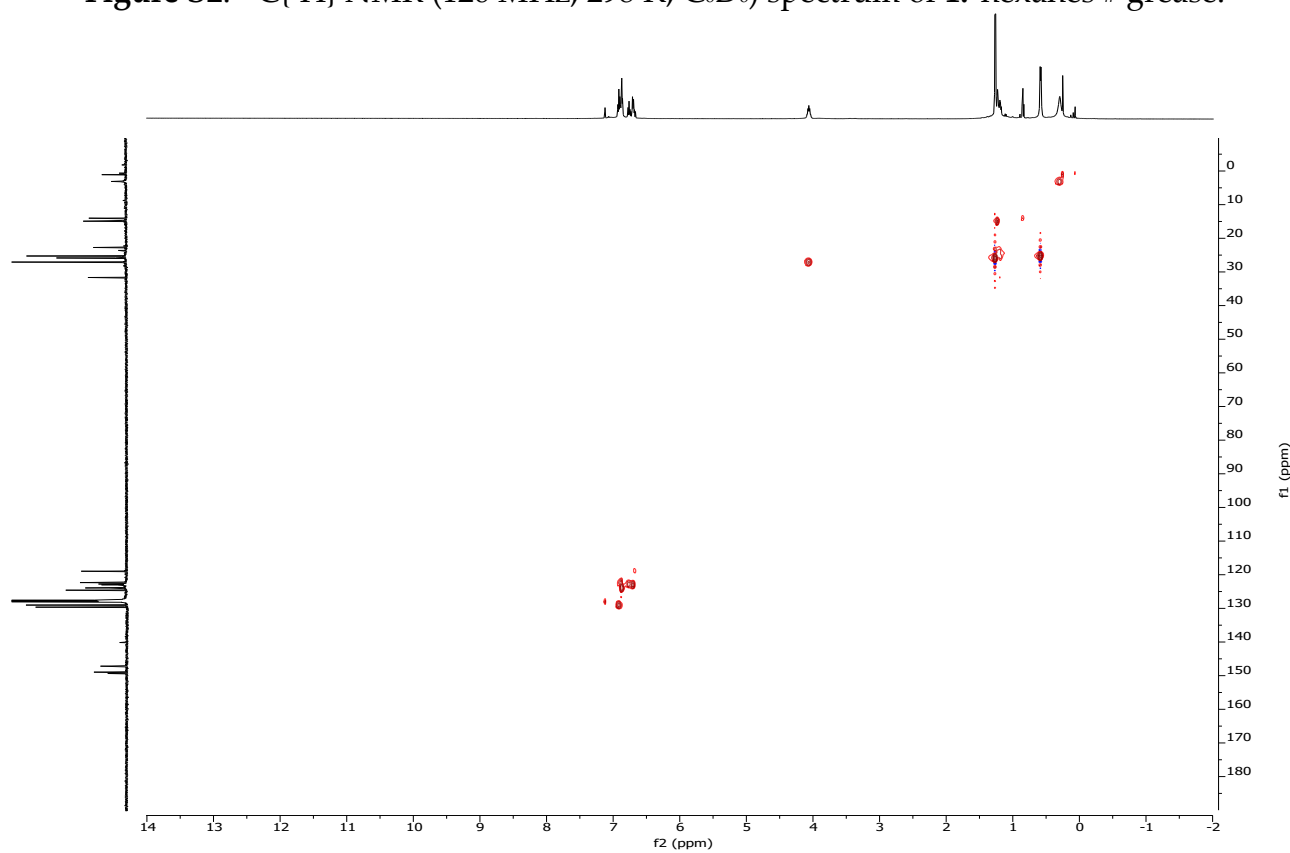


Figure S3. ^1H - ^{13}C HSQC (298 K, C_6D_6) trace of **1**.

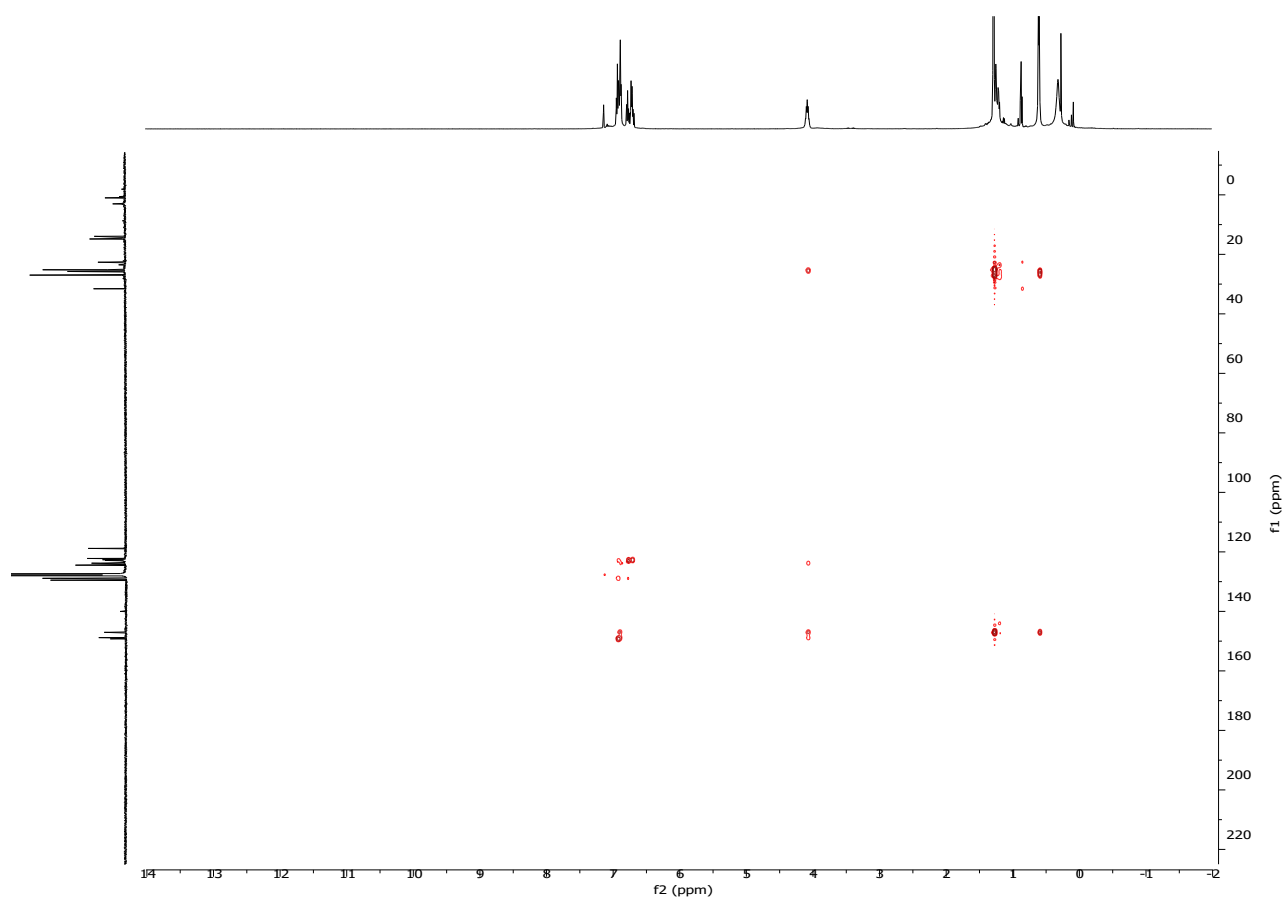


Figure S4. ^1H - ^{13}C HMBC (298 K, C_6D_6) trace of **1**.

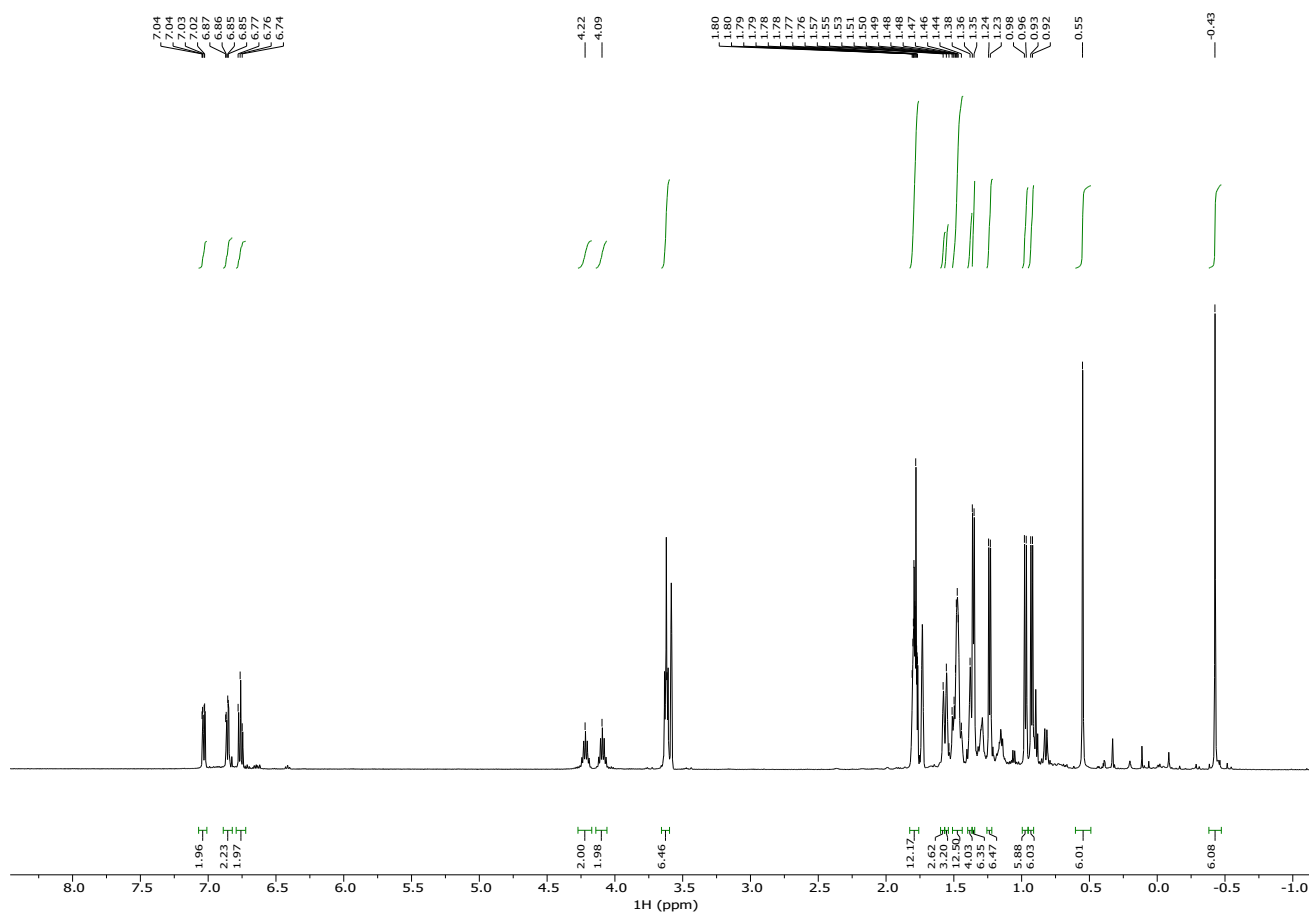


Figure S5. ¹H NMR (500 MHz, 298 K, *d*₈-THF) spectrum of **2**.

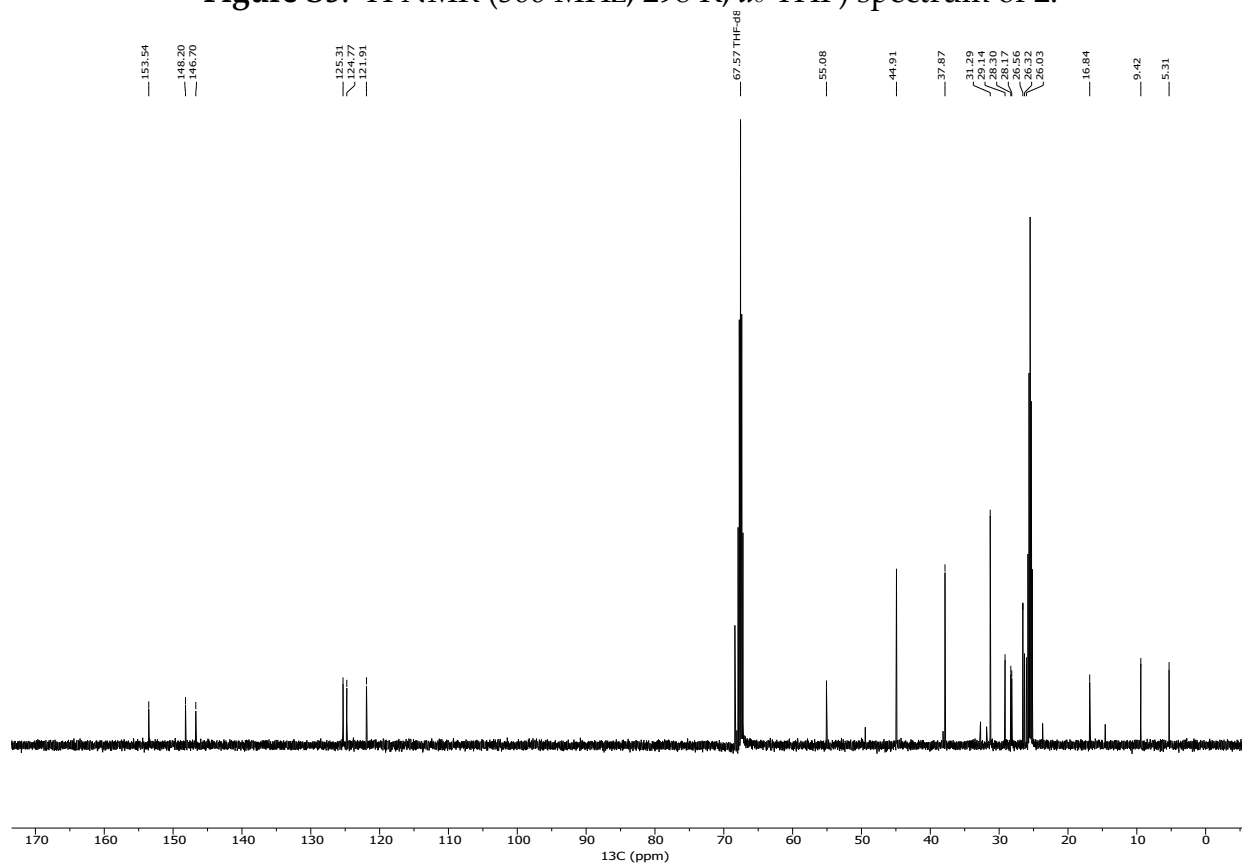


Figure S6. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, d_8 -THF) spectrum of **2**.

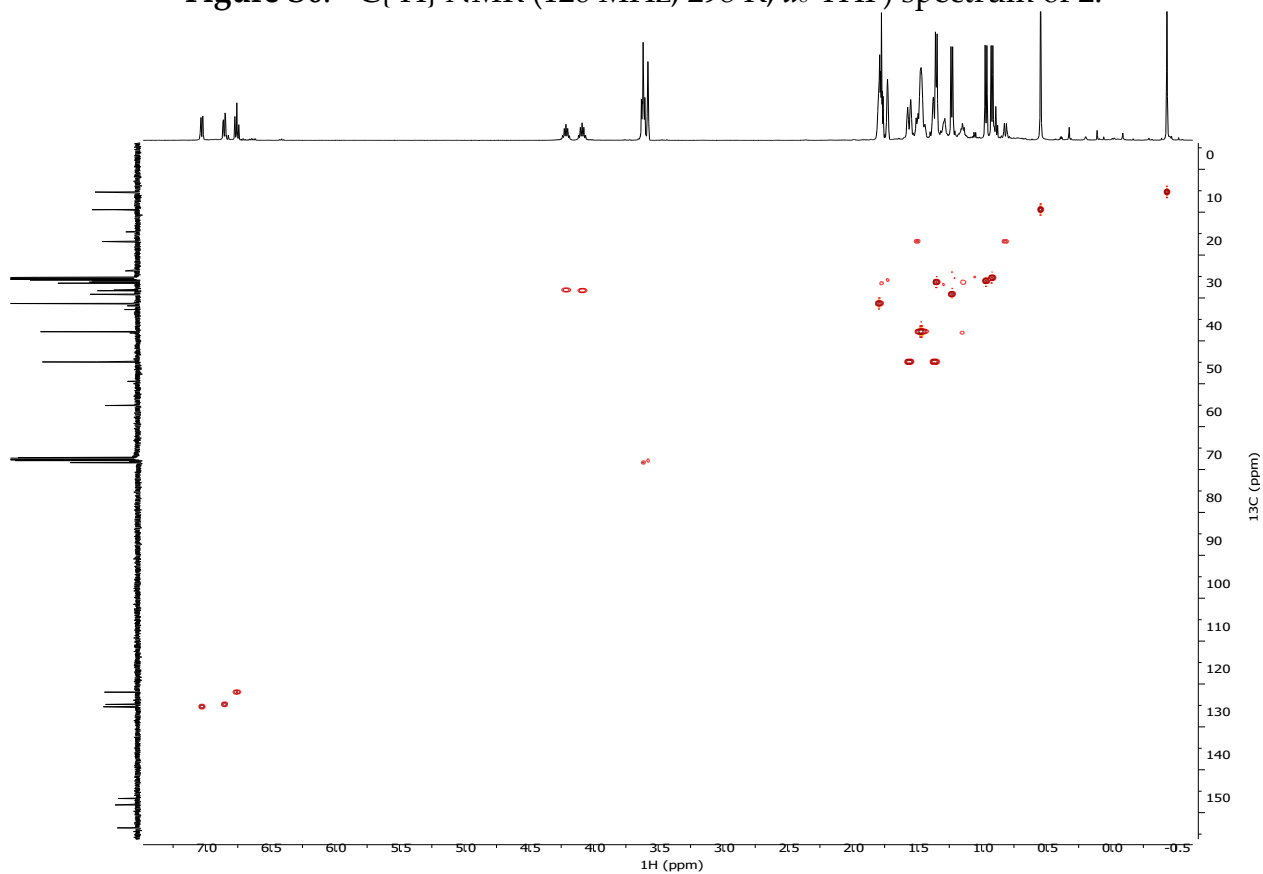


Figure S7. ^1H - ^{13}C HSQC (298 K, d_8 -THF) trace of **2**.

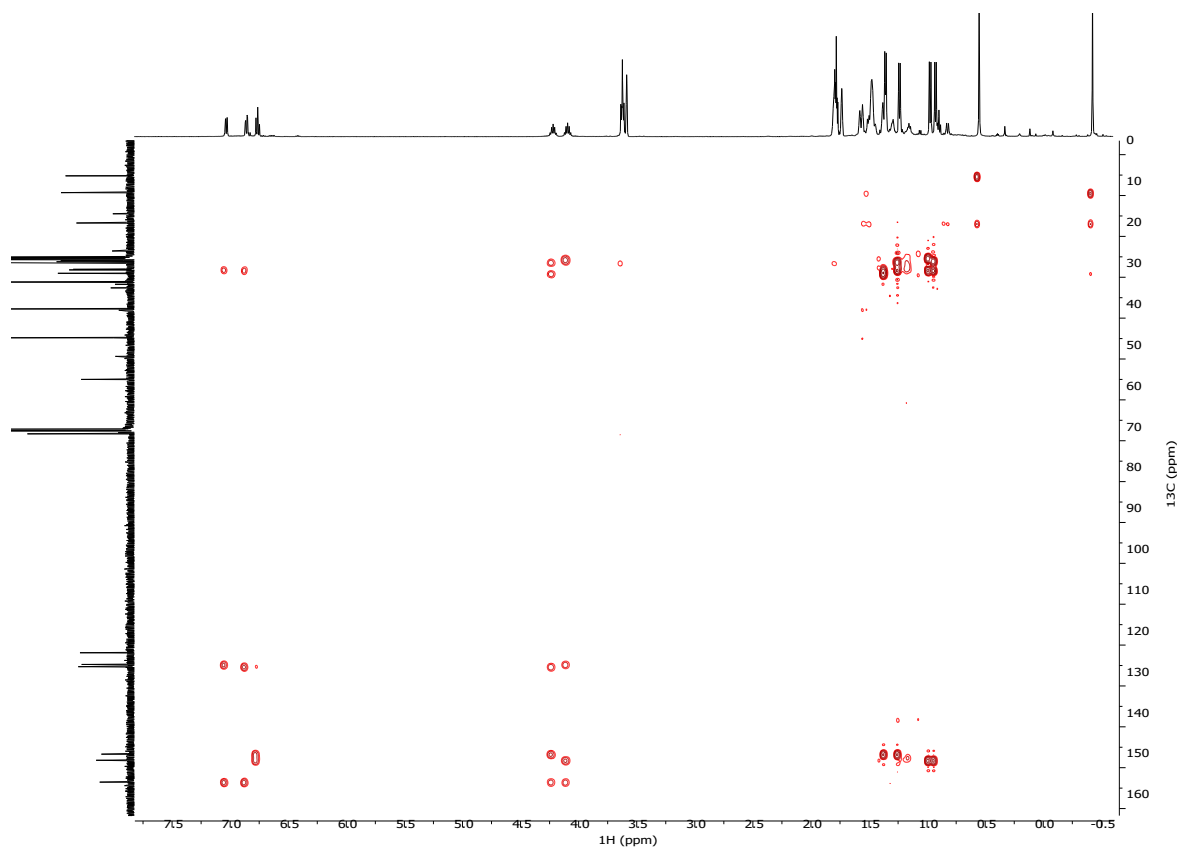


Figure S8. ^1H - ^{13}C HMBC (298 K, d_8 -THF) trace of **2**.

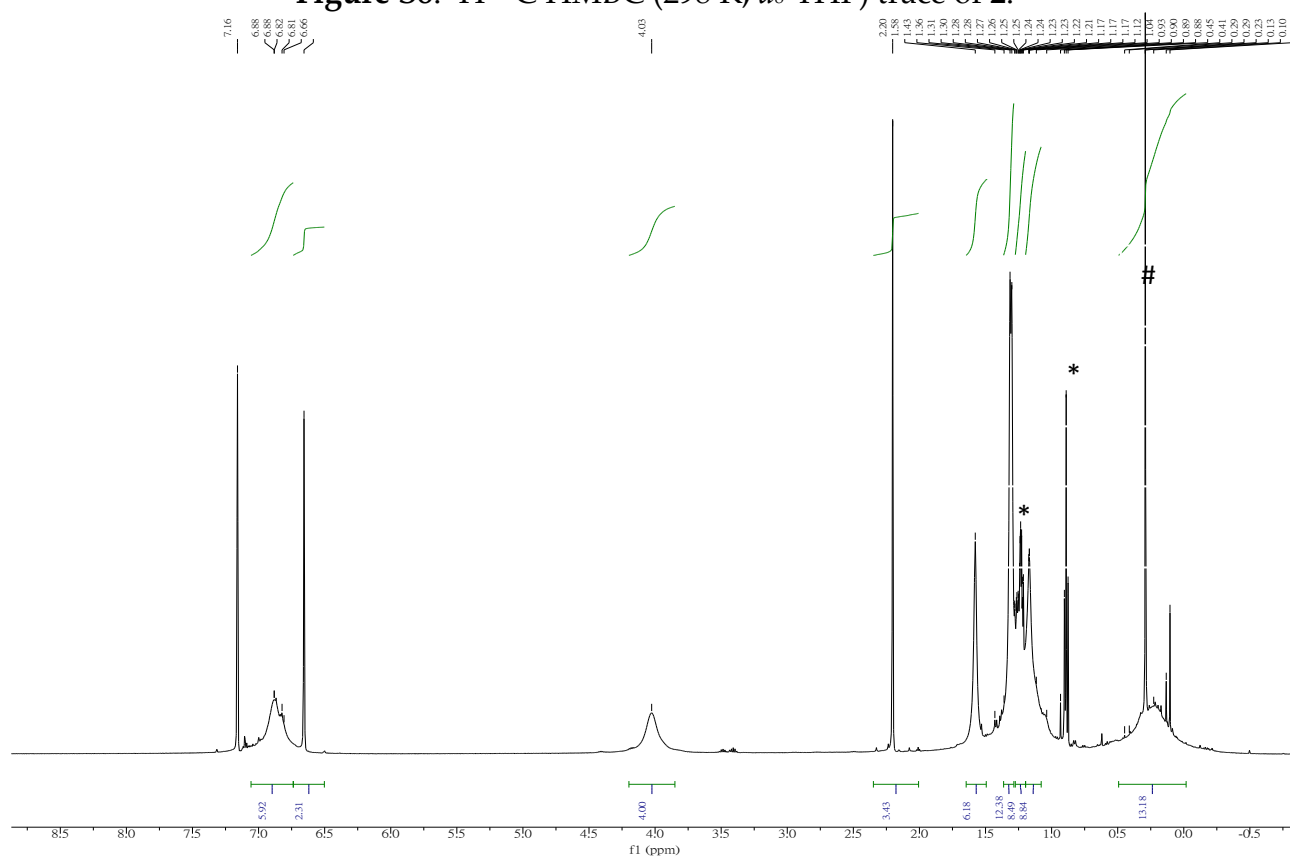


Figure S9. ^1H NMR (500 MHz, 298 K, C_6D_6) spectrum of **3**. *hexanes # grease.

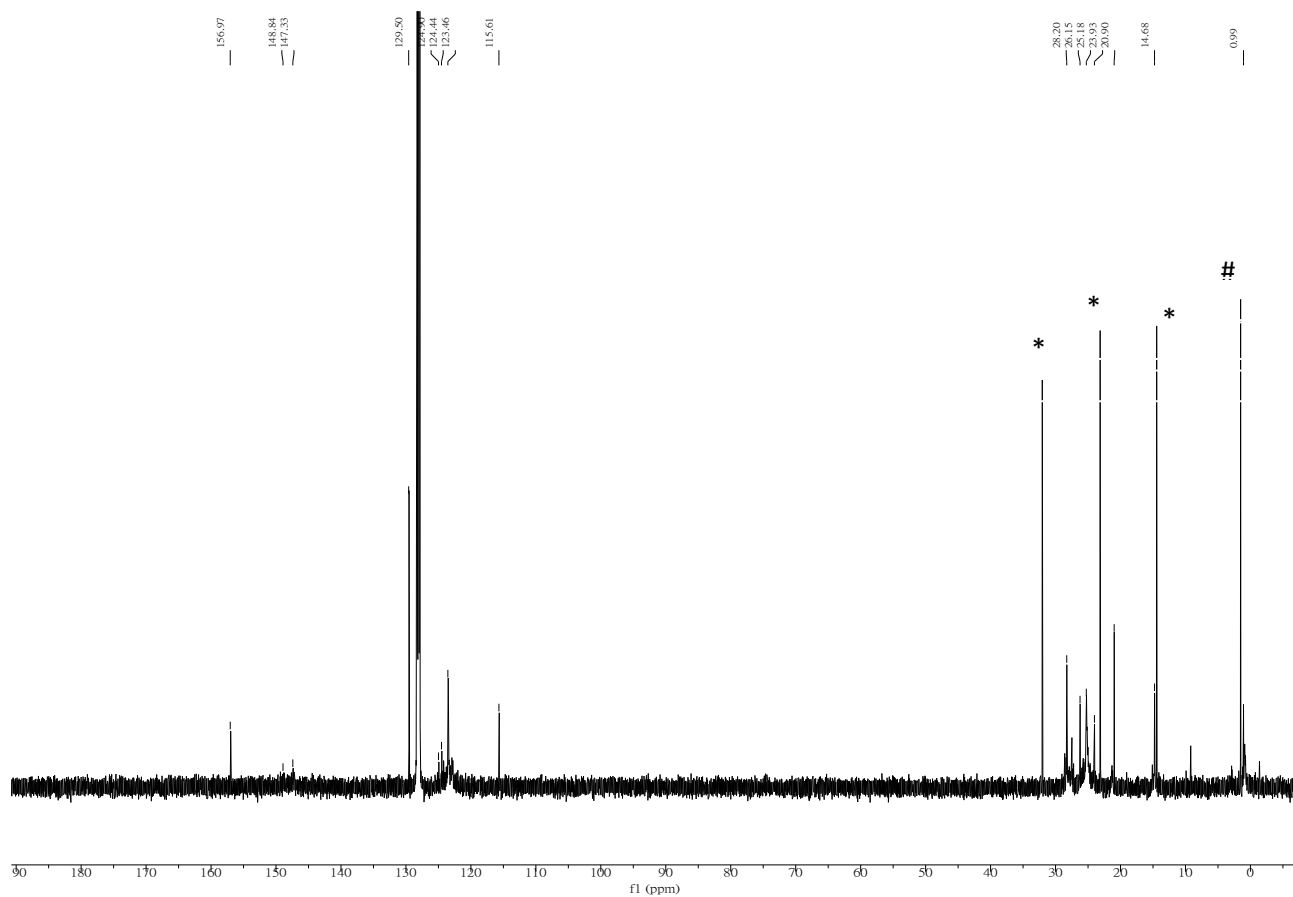


Figure S10. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, C_6D_6) spectrum of **3**. *hexanes # grease.

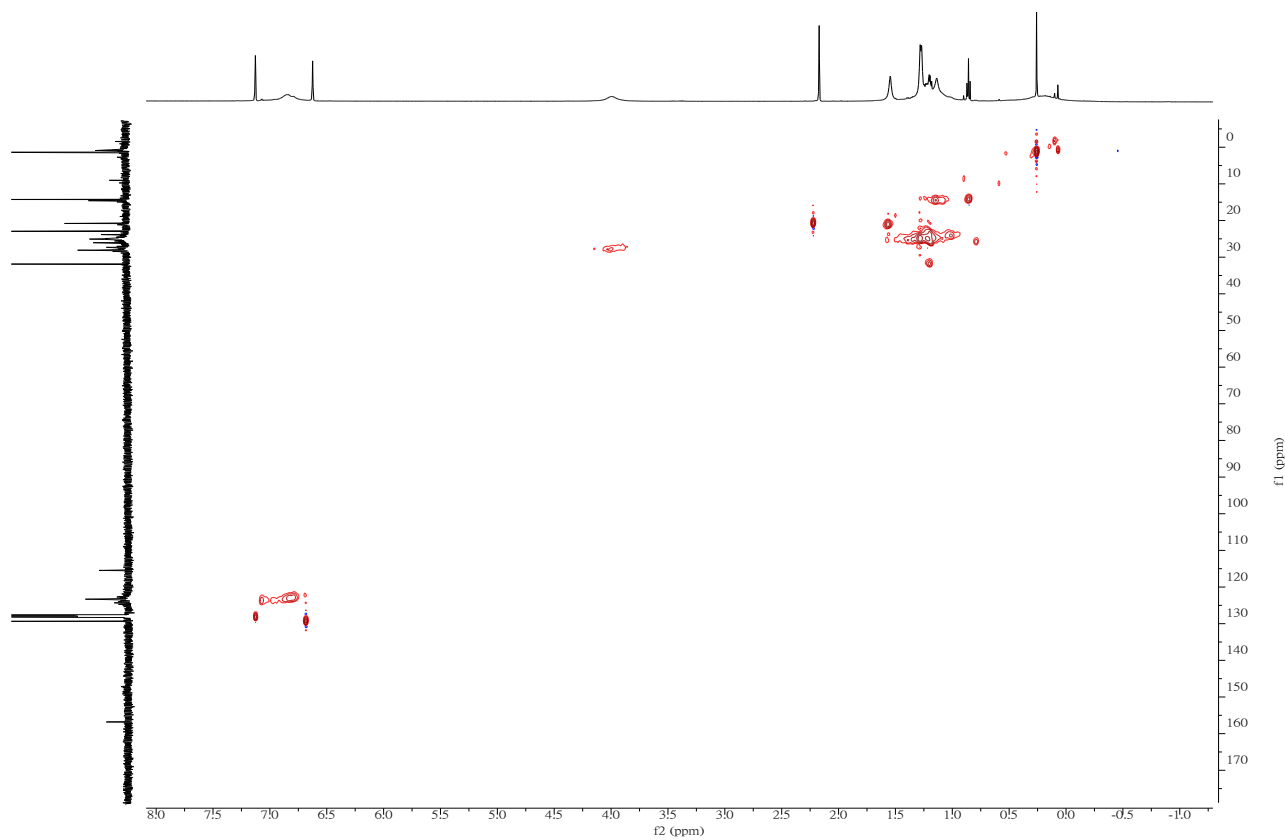


Figure S11. ^1H - ^{13}C HSQC (298 K, C_6D_6) trace of **3**.

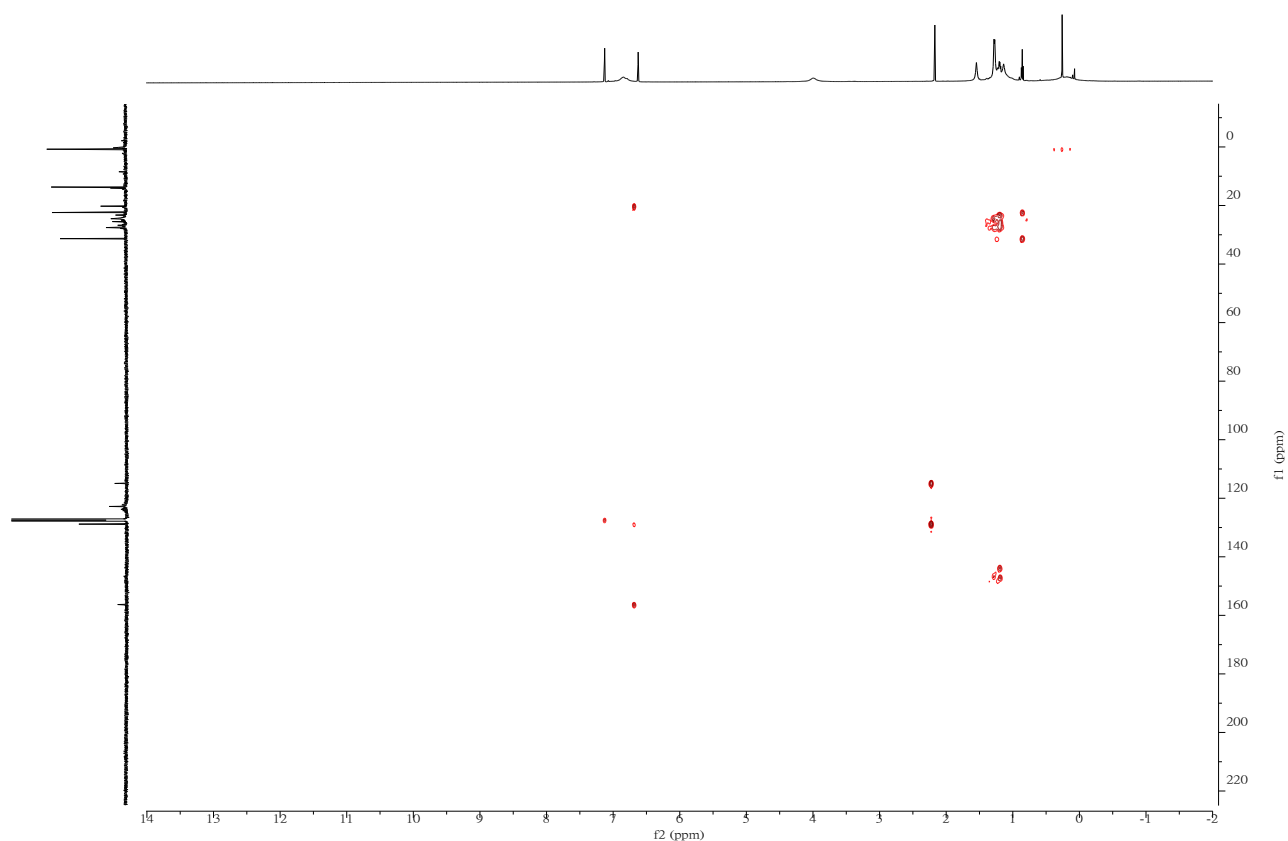


Figure S12. ^1H - ^{13}C HMBC (298 K, C_6D_6) trace of 3.

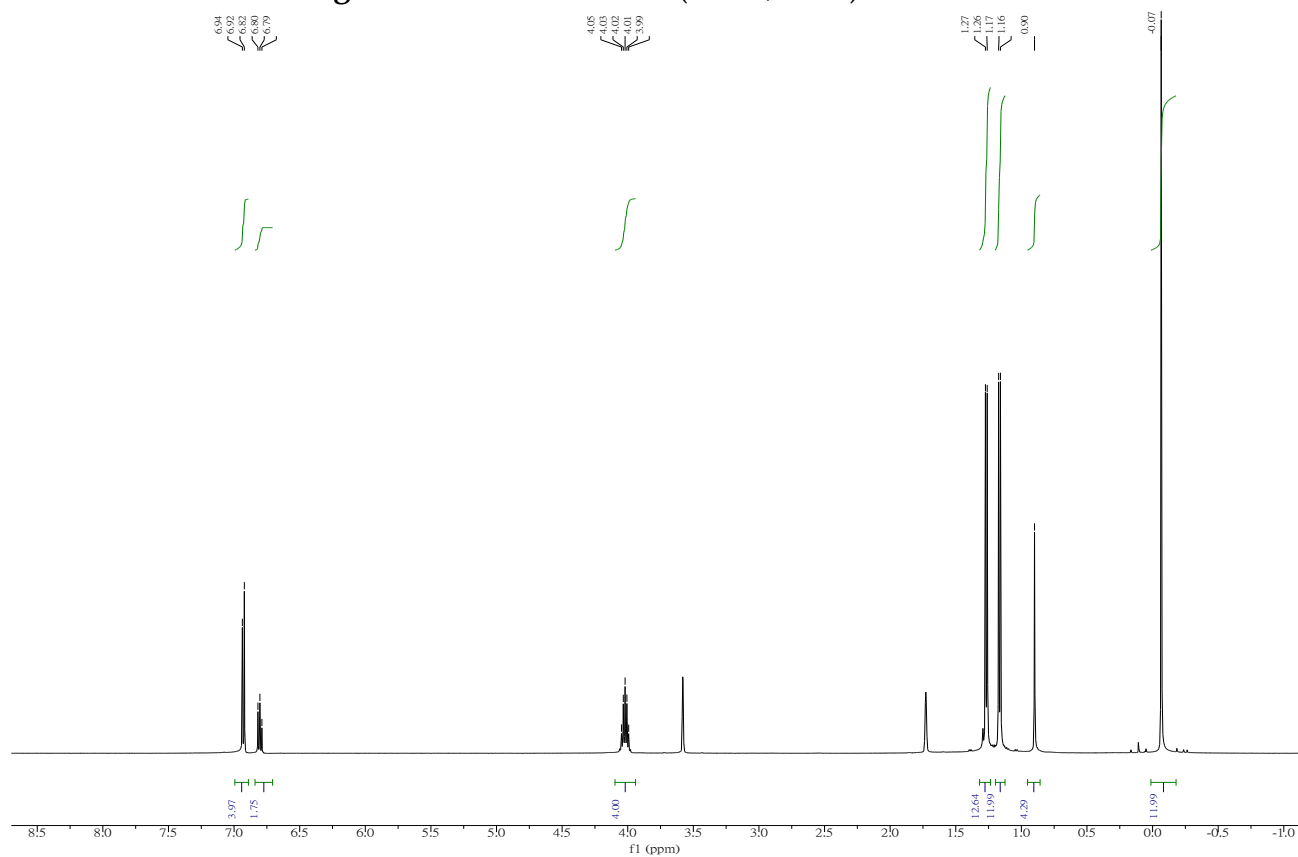


Figure S13. ^1H NMR (500 MHz, 298 K, d_8 -THF) spectrum of 4.

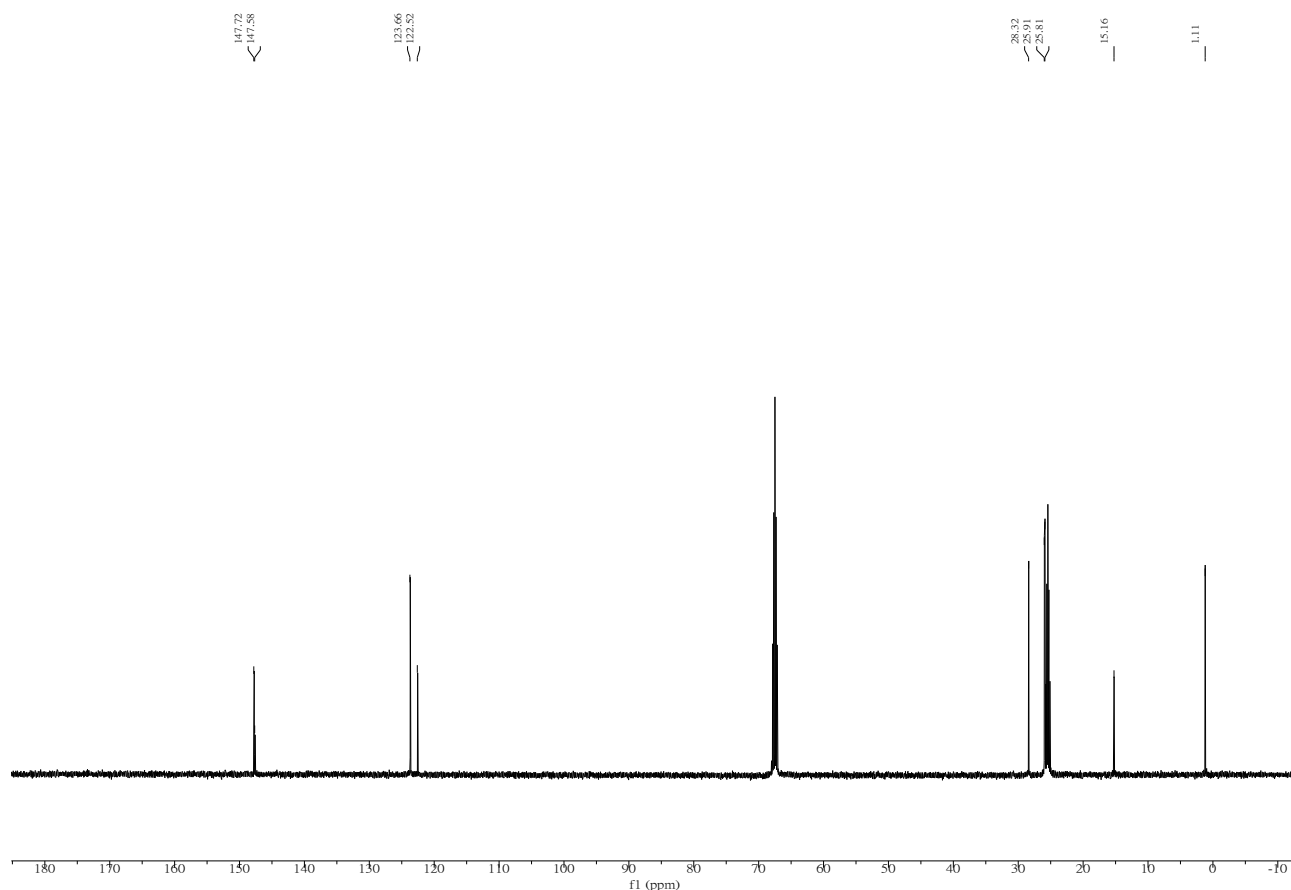


Figure S14. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, d_8 -THF) spectrum of **4**.

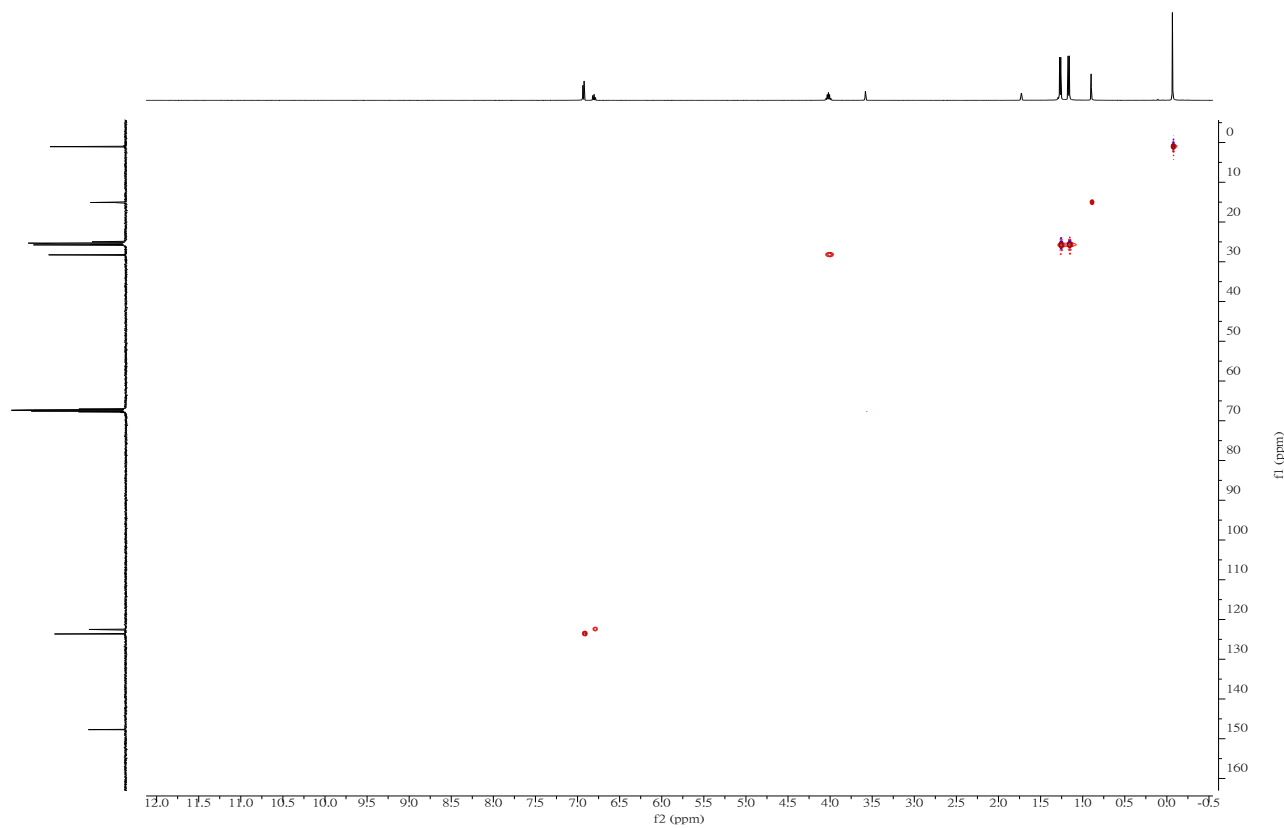


Figure S15. ^1H - ^{13}C HSQC (298 K, d_8 -THF) trace of **4**.

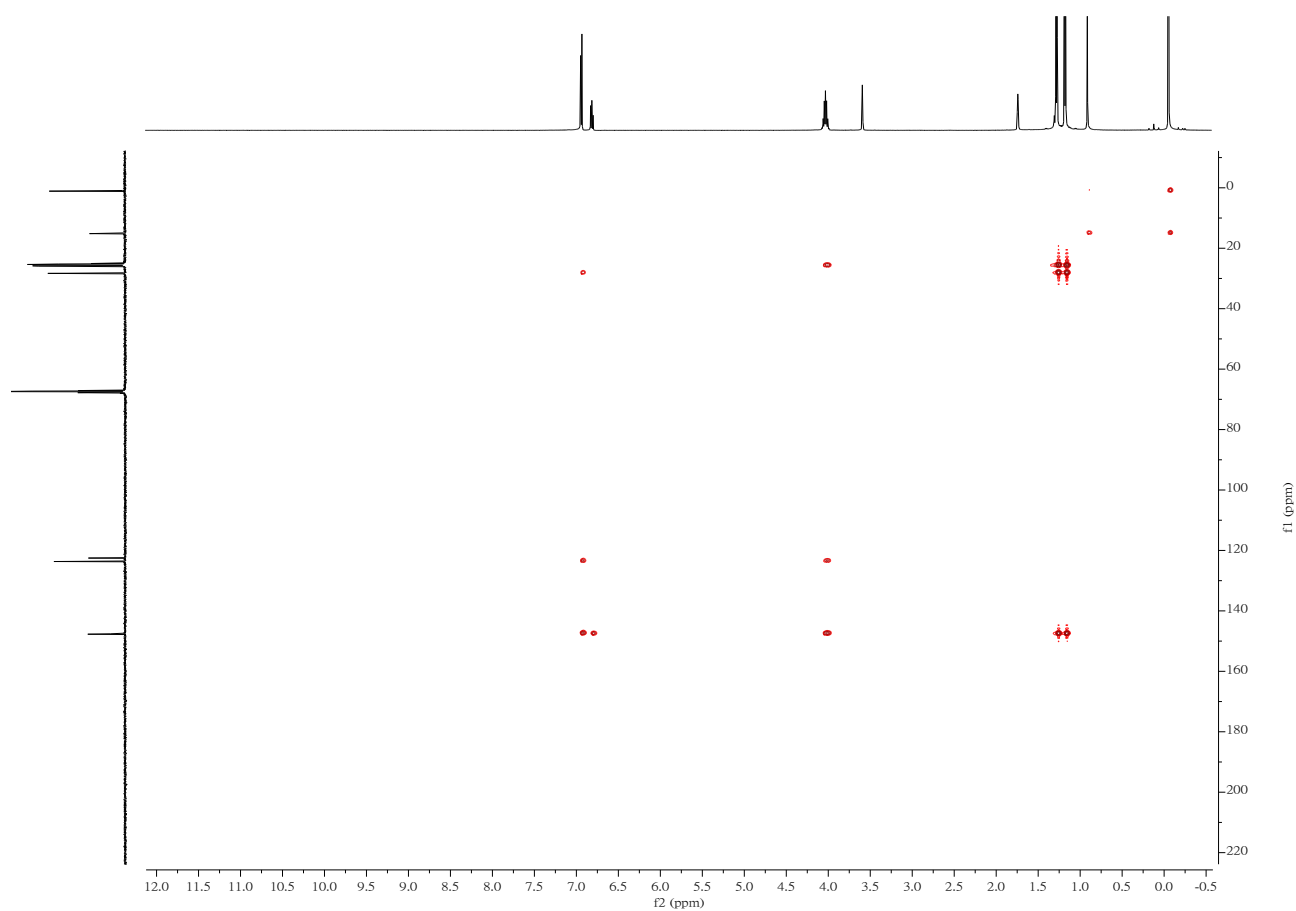


Figure S16. ^1H - ^{13}C HMBC (298 K, d_8 -THF) trace of **4**.

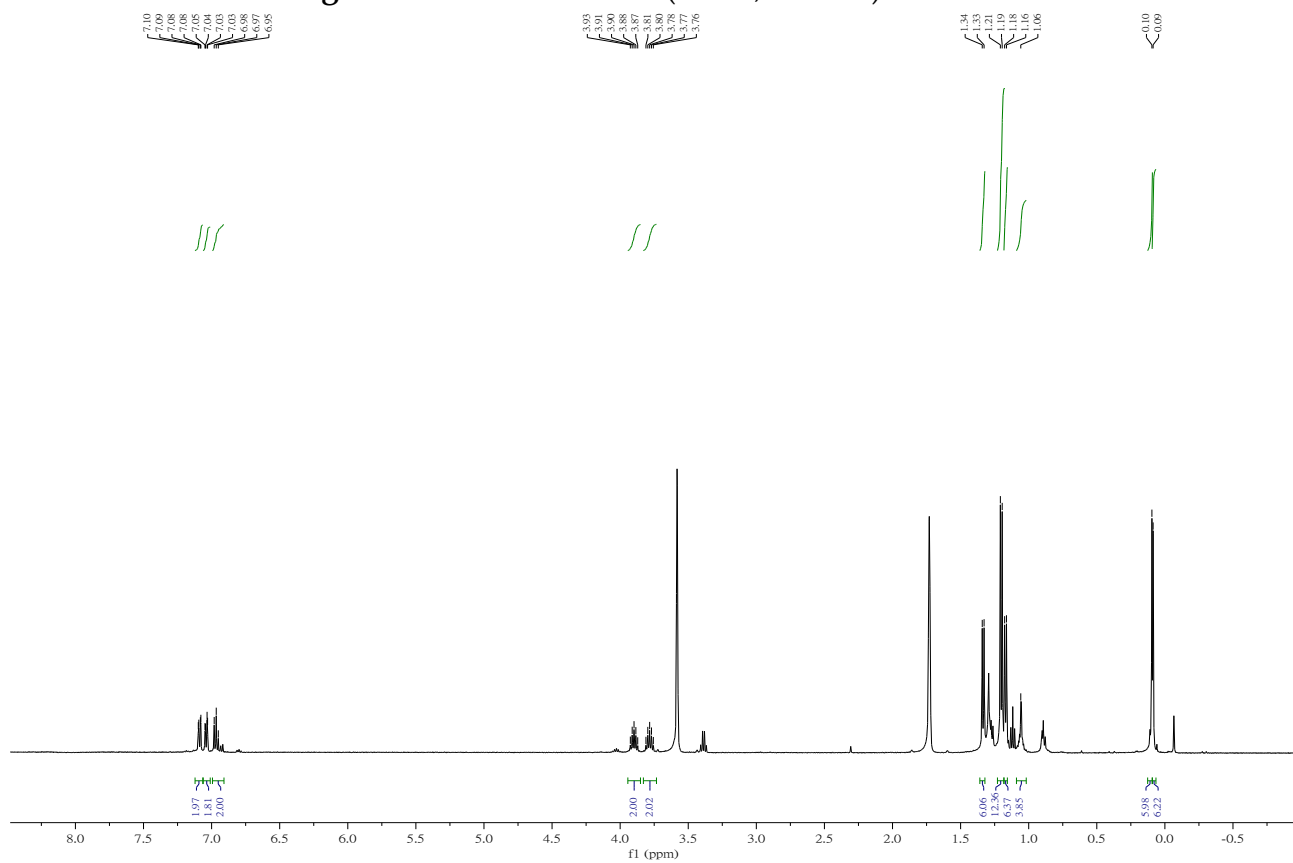


Figure S17. ^1H NMR (500 MHz, 298 K, d_8 -THF) spectrum of **5**.

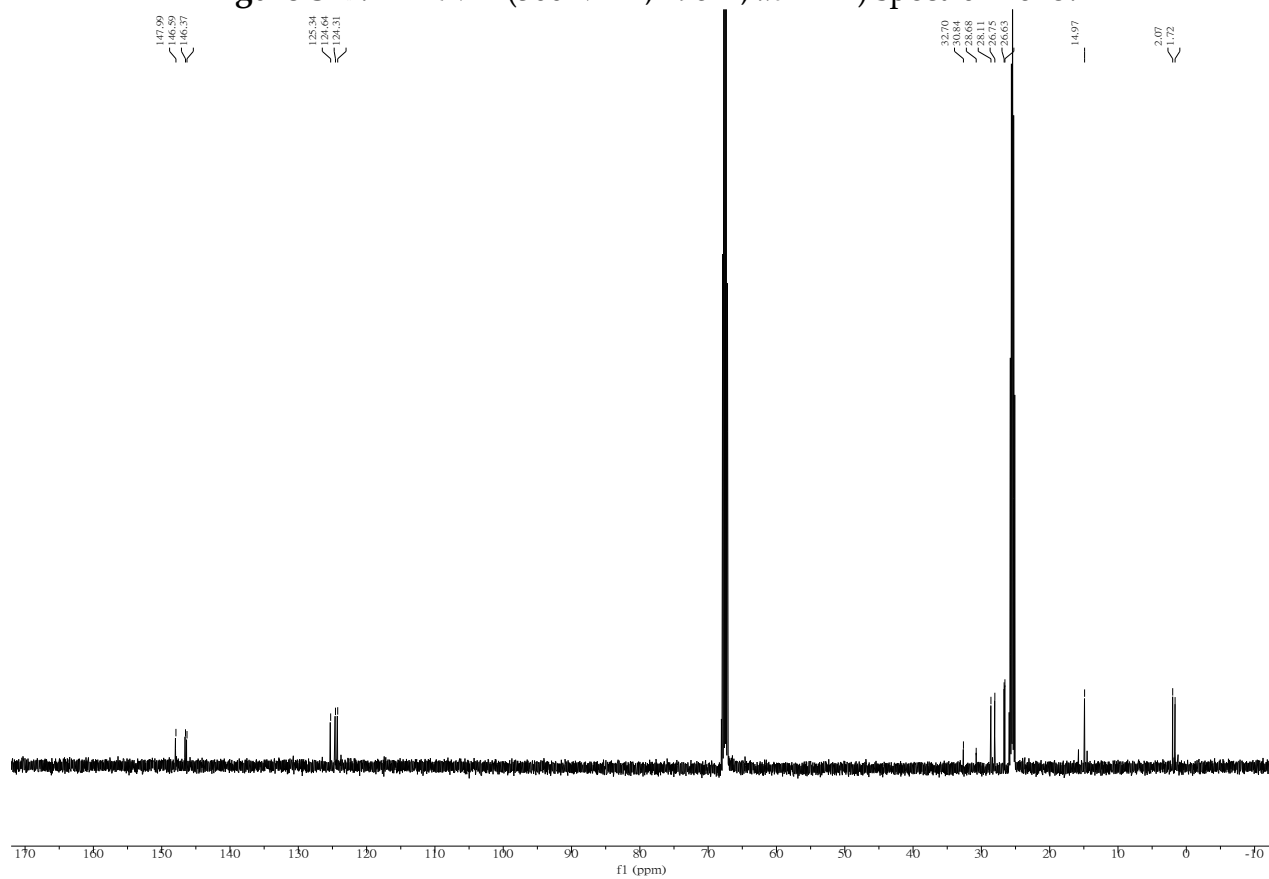


Figure S18. $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, 298 K, d_8 -THF) spectrum of **5**.

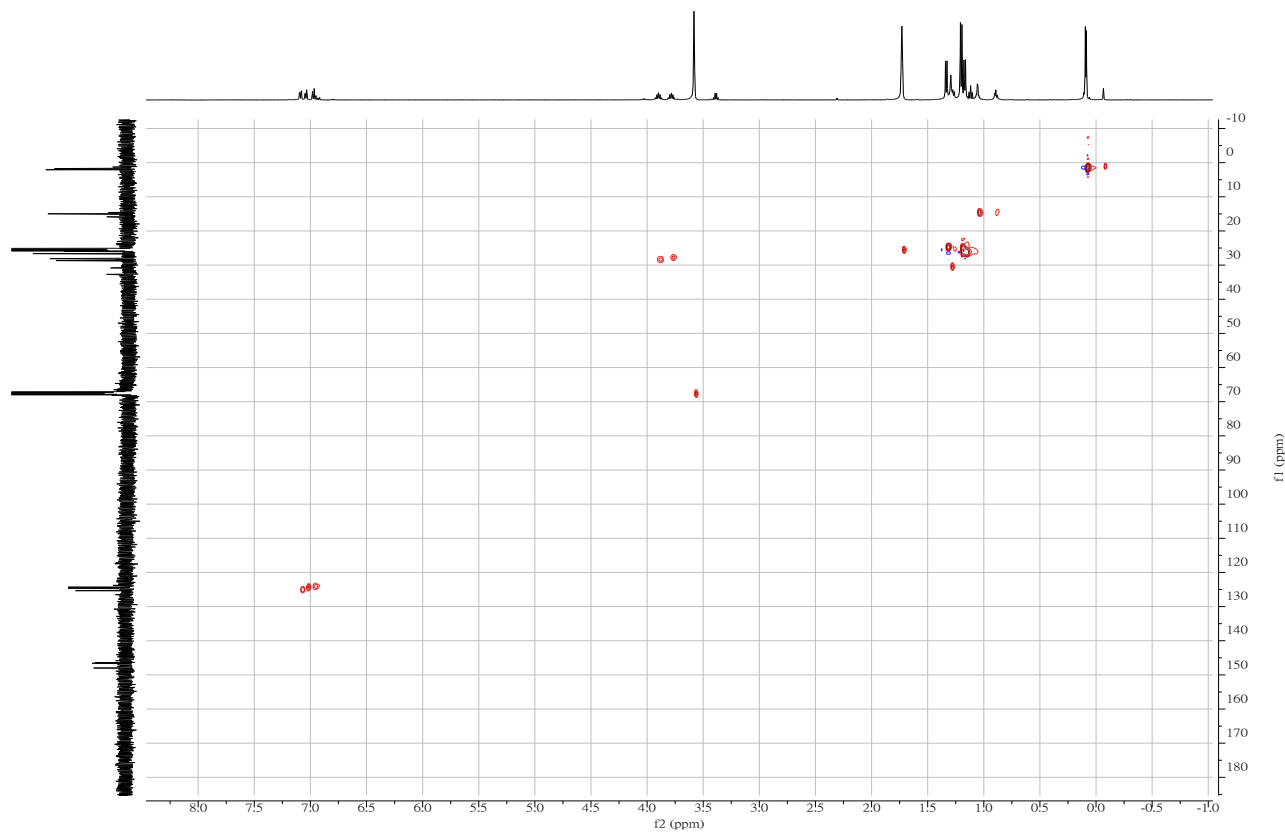


Figure S19. ^1H - ^{13}C HSQC (298 K, d_8 -THF) trace of **5**.

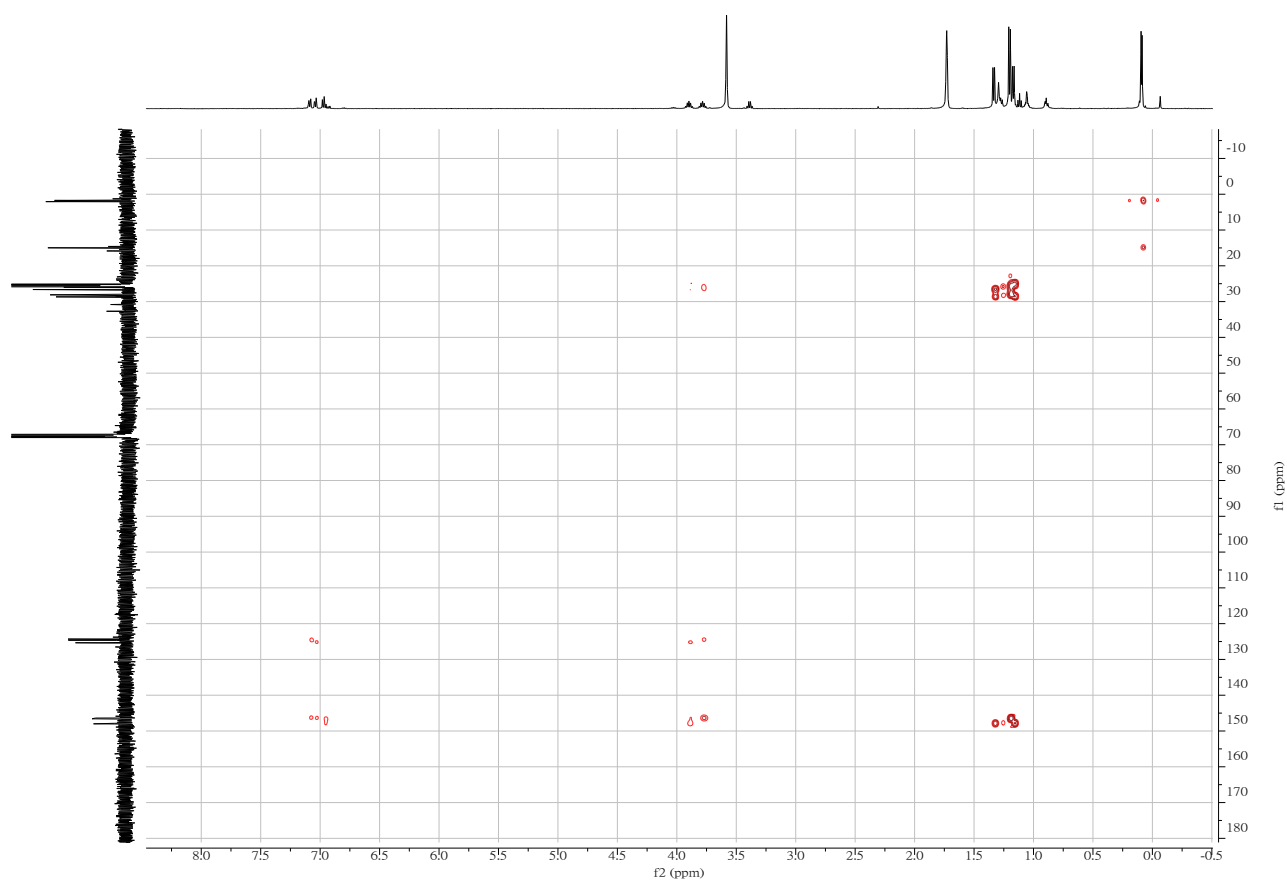


Figure S20. ^1H - ^{13}C HMBC (298 K, d_8 -THF) trace of **5**.

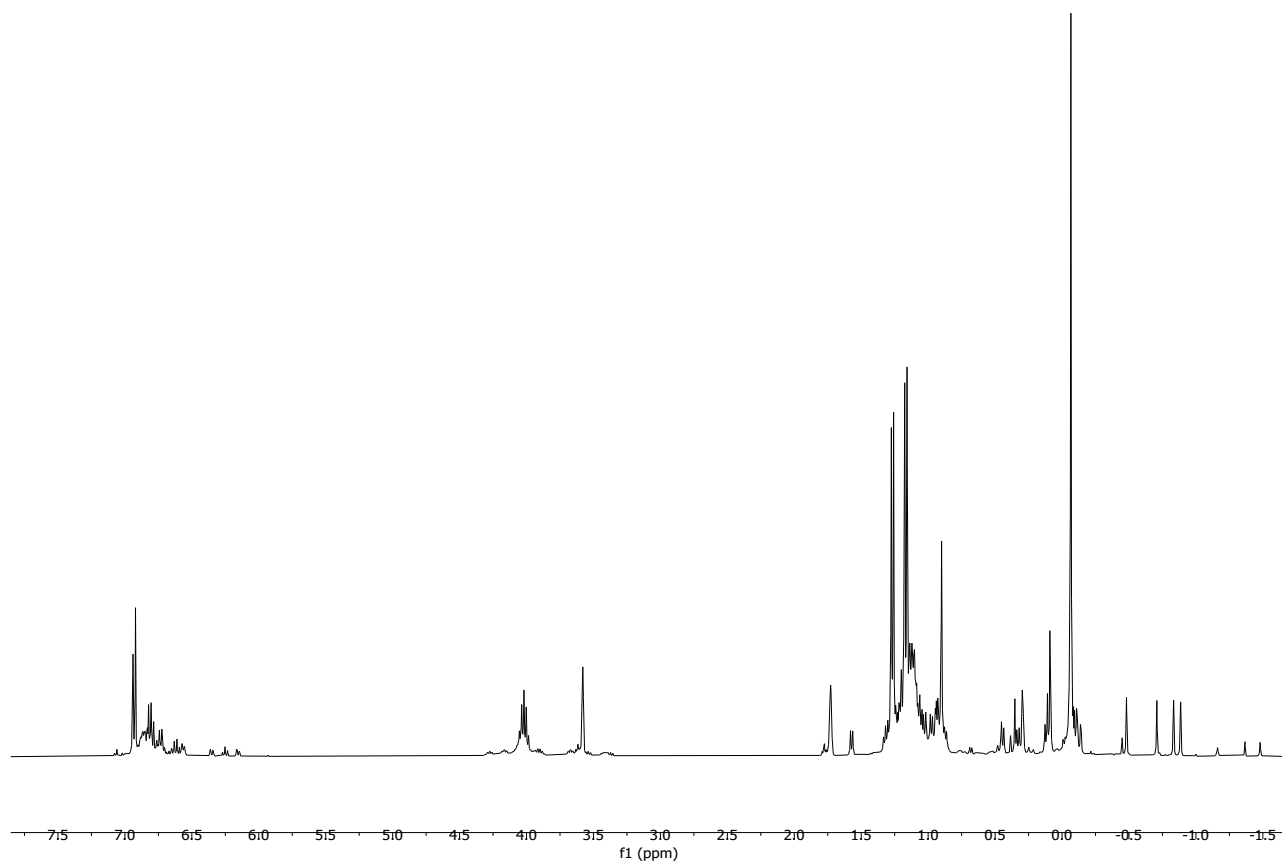


Figure S21. ^1H NMR (500 MHz, 298 K, d_8 -THF) spectrum resulting from the reaction of **4** and **XI**.

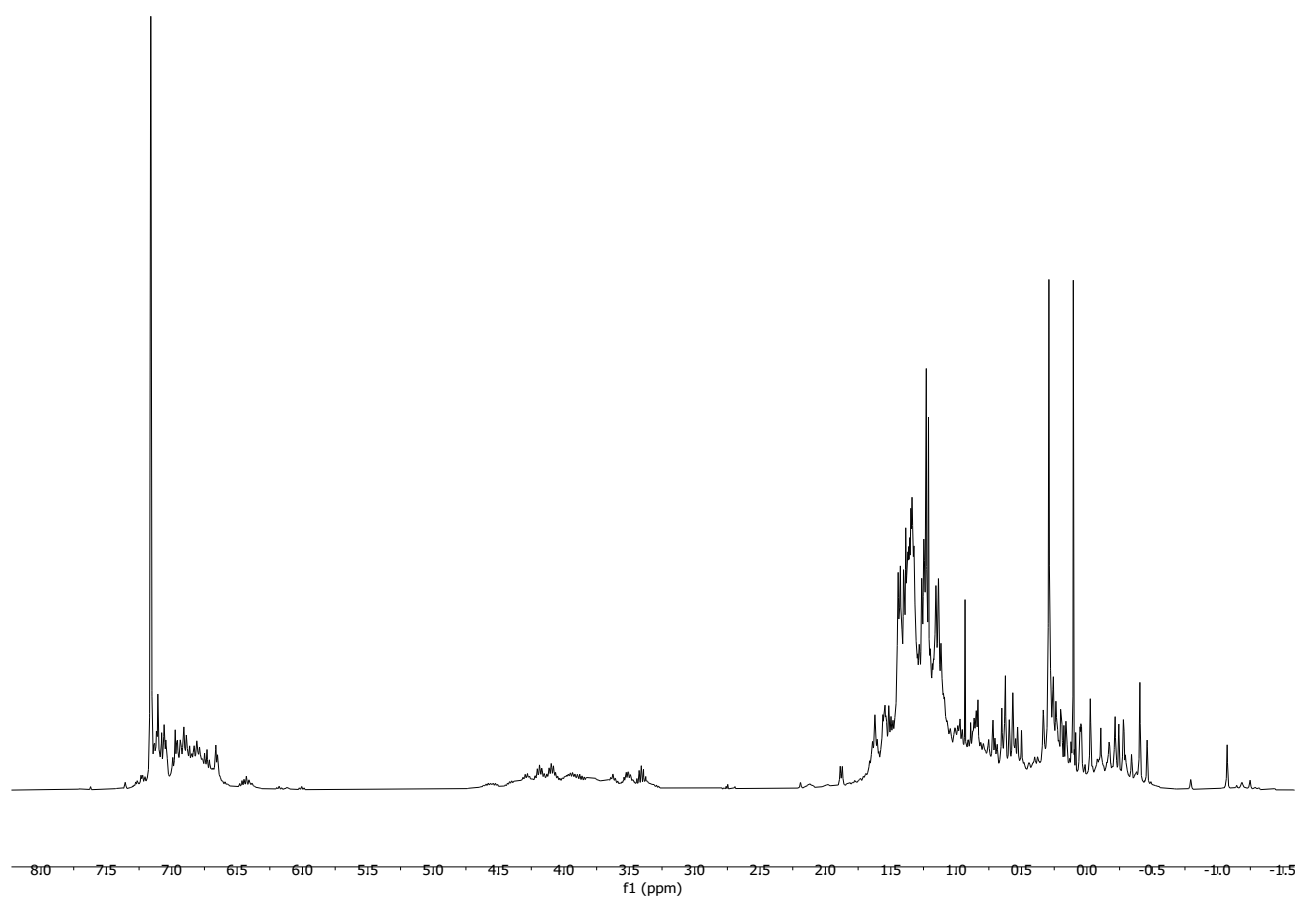


Figure S21. ^1H NMR (500 MHz, 298 K, C_6D_6) spectrum resulting from the reaction of **4** and **XI**.

X-ray crystallography

Data for compounds **1**, **3**, **4** and **5** were collected using an Agilent Supernova diffractometer, while those for **2** were obtained on an Agilent Xcalibur instrument. Diffraction experiments were conducted at 150 K throughout. All structures were solved using SHELXT¹ and refined using SHELXL² *via* the Olex-2³ interface. Where disorder prevailed, appropriate distance and ADP restraints were employed, to assist convergence. Convergences were uneventful and only noteworthy points follow.

A monomer containing one potassium centre constitutes the asymmetric unit in **1** along with some hexane solvent. The gross structure is dominated by 1-D polymers of dimers parallel to the *c* axis, which create structural channels in which the solvent resides. The latter was noted to be both diffuse and disordered (unsurprisingly) and it was treated with the solvent mask algorithm available in Olex-2. Allowance has been made in the formula, as presented, for a total of one molecule of hexane per asymmetric unit (based on the electron density evident prior to masking). The ring based on C31 in the main feature was disordered in a 67:33 ratio and both components were treated as rigid hexagons in the final least squares. The hydrogen atoms attached to C11 were located and refined at a distance of 0.98 Å from the parent atoms, as one of these is implicated in an interaction to K1.

63:37 disorder was modelled for some of the THF ligand carbons in the structure of **2**, where the asymmetric unit comprises half of one molecule in which K1 and Al1 are co-incident with a crystallographic 2-fold rotation axis. The latter serves to generate the remainder of the molecule.

The asymmetric unit in **3** comprises one molecule of the potassium-aluminium complex and half of one molecule of benzene. The remainder of the latter arises by virtue of crystallographic inversion symmetry. The hydrogen atoms attached to C11 and C39 were located and refined subject to being located 0.98 Å from the relevant parent atoms.

The asymmetric unit in **4** comprises a monomer which gives rise to 1-D polymers in the gross structure, parallel to the *a*-axis.

Table S1. Data collection and refinement parameters for **1 – 5**.

Manuscript ID	1	2	3	4	5
Identification code (CIF)	s19msh29	e23msh09	s19msh81	s22msh110	s22msh103
Empirical formula	C ₄₈ H ₇₄ AlKN ₆ Si ₂	C ₆₆ H ₁₁₂ AlKN ₆ O ₄ Si ₂	C ₄₈ H ₇₀ AlKN ₃ Si ₂	C ₃₀ H ₅₀ AlKN ₈ Si ₂	C ₃₄ H ₅₈ AlN ₅ OSi ₂
Formula weight	857.39	1175.87	811.33	645.04	636.01
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic
Space group	C2/c	I2/a	P2 ₁ /c	P2 ₁ /c	Pbca
<i>a</i> / Å	23.7537(4)	20.5341(9)	20.1835(2)	10.4697(2)	19.1282(1)
<i>b</i> / Å	20.6897(2)	15.0828(5)	12.8173(1)	22.0857(3)	16.0198(1)
<i>c</i> / Å	22.8138(3)	23.7906(10)	18.6870(2)	15.8584(2)	24.7293(1)
α / °	90	90	90	90	90
β / °	116.053(2)	114.430(5)	103.109(1)	93.220(1)	90
γ / °	90	90	90	90	90
<i>U</i> / Å ³	10072.7(3)	6708.5(5)	4708.31(8)	3661.16(10)	7577.80(7)
<i>Z</i>	8	4	4	4	8
ρ_{calc} / g cm ⁻³	1.131	1.164	1.145	1.170	1.115
μ / mm ⁻¹	1.824	0.177	1.906	2.368	1.312
<i>F</i> (000)	3712.0	2568.0	1756.0	1384.0	2768.0
Crystal size/ mm ³	0.5 × 0.079 × 0.058	0.526 × 0.416 × 0.315	0.221 × 0.158 × 0.085	0.212 × 0.073 × 0.052	0.315 × 0.251 × 0.153
Radiation	Cu K α (λ = 1.54184)	Mo K α (λ = 0.71073)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)	Cu K α (λ = 1.54184)
2 θ range for data collection/°	6.19 to 146.22	6.05 to 60.78	8.236 to 146.186	8.006 to 146.174	8.038 to 146.078
Index ranges	-27 ≤ <i>h</i> ≤ 29, -25 ≤ <i>k</i> ≤ 23, -28 ≤ <i>l</i> ≤ 24	-26 ≤ <i>h</i> ≤ 26, -21 ≤ <i>k</i> ≤ 19, -33 ≤ <i>l</i> ≤ 31	-24 ≤ <i>h</i> ≤ 24, -10 ≤ <i>k</i> ≤ 15, -22 ≤ <i>l</i> ≤ 22	-12 ≤ <i>h</i> ≤ 12, -27 ≤ <i>k</i> ≤ 27, -16 ≤ <i>l</i> ≤ 19	-23 ≤ <i>h</i> ≤ 23, -19 ≤ <i>k</i> ≤ 19, -30 ≤ <i>l</i> ≤ 23
Reflections collected	28700	32823	30963	47175	105573
Independent reflections, <i>R</i> _{int}	9947, 0.0363	8932, 0.0282	9297, 0.0373	7290, 0.0537	7551, 0.0398
Data/restraints/parameters	9947/160/516	8932/169/413	9297/6/533	7290/0/391	7551/0/400
Goodness-of-fit on <i>F</i> ²	1.042	1.042	1.025	1.020	1.035
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> ≥ 2 σ (<i>I</i>)]	0.0422, 0.1190	0.0389, 0.1019	0.0380, 0.0949	0.0380, 0.0940	0.0322, 0.0886

Final $R1$, $wR2$ [all data]	0.0499, 0.1253	0.0485, 0.1093	0.0460, 0.1000	0.0471, 0.0993	0.0352, 0.0912
Largest diff. peak/hole/ $e \text{ \AA}^{-3}$	0.32/−0.23	0.36/−0.35	0.54/−0.36	0.40/−0.27	0.24/−0.20

References

1. Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H. OLEX2: A Complete Structure Solution, Refinement and Analysis Program. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.
2. Sheldrick, G.M. SHELXT-Integrated Space-Group and Crystal-Structure Determination. *Acta Crystallogr. Sect. A Found. Adv.* **2015**, *A71*, 3–8.
3. Sheldrick, G.M. Crystal Structure Refinement with SHELXL. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *C71*, 3–8.