Supplementary Information (SI) for ChemComm.

Fluorenyl-Tethered N-Heterocyclic Carbene Complexes of the Heavy Alkali Metals

Stuart Burnett[1], Alan R. Kennedy[1], Stephen M. Mansell[2] and Catherine E. Weetman[1]**

[1]Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, U.K.

[2]Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh EH14 4AS, U.K.

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1. General Experimental

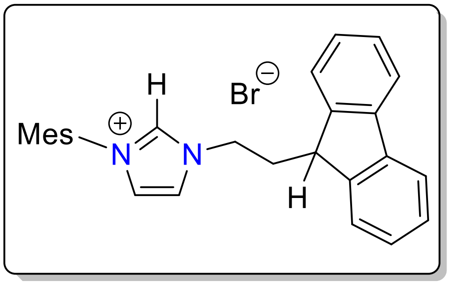
All manipulations were carried out using standard Schlenk and glove box techniques under a dry argon or dinitrogen atmosphere. Toluene, benzene and THF were taken from an Innovative Technology Solvent Purification system and stored over activated 4Å molecular sieves. Pentane was dried by distillation over sodium benzophenone and stored over activated 4Å molecular sieves prior to use. Benzene-d_6 and THF-d_8 was purchased from Sigma-Aldrich and stored over activated 4Å molecular sieves. All other reagents were purchased from Sigma-Aldrich, Fluorochem or Alfa Aeser and used as received.

NMR spectra were recorded on a Bruker AV3-400 spectrometer operating at 400.4 MHz (^{1}H), 100.7 MHz (^{13}C{^{1}H}), 155.5 MHz (^{7}Li) and 65.6 MHz (^{133}Cs) and were measured at 298K. All chemical shifts are expressed in parts per million (δ, ppm) and where appropriate were referenced to the residual ^{1}H or ^{13}C{^{1}H} resonances of the solvent used.

1-bromo-2-(9-fluorenyl)ethane[1], 1-mesityl-1H-imidazole[2], rubidium hexamethyldisilazane ($RbN(SiMe_3)_2$)[3] and caesium hexamethyldisilazane ($CsN(SiMe_3)_2$)[4] were synthesised according to literature procedure. Synthesis of **1** was carried out using a modified procedure and is detailed below.

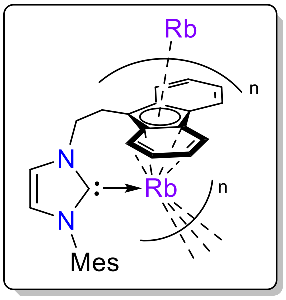
2. Synthetic Procedures

2.1 [9-($C_{13}H_9$)C_2H_4N(CH)C_2H_2N(Mes)][Br] (FluEthMesImi Br) 1



1-bromo-2-(9-fluorenyl)ethane (2.30 g, 8.42 mmol) and 1-mesityl-1H-imidazole (1.57 g, 8.42 mmol) were added to a J. Young's Schlenk flask and stirred at 100 ºC for 24 hours. After cooling to ambient temperature, the resulting solid was dissolved in a minimum amount of dry DCM (3 mL) and subsequently added to stirring diethyl ether (20 mL). The resulting precipitate was isolated by filtration, washed with diethyl ether (10 mL), dried *in vacuo* and stored in the glovebox. Yield = 3.3 g (85 %). ^{1}H NMR spectroscopic data is consistent with previous literature reports.[5]

2.2 Synthesis of (FluEth)IMesRb 2

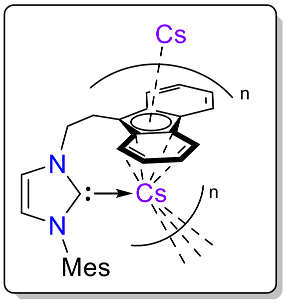


1 (200 mg, 0.435 mmol) was added to a J. Young's Schlenk flask, suspended in toluene (5 mL) and cooled to -80 ºC before addition of *n*BuLi (1.6 M, 0.27 mL, 0.435 mmol). The reaction mixture was then warmed to ambient temperature and stirred overnight. The solution was then filtered on to a -80 ºC toluene solution of RbN($SiMe_3$)$_2$ (107 mg, 0.435 mmol), warmed to ambient temperature and stirred overnight. The resulting precipitate was isolated by filtration, washed with toluene (5 mL) and dried *in vacuo* to yield **2** as a red powder. Crystals suitable for single crystal X-ray diffraction analysis were grown by layering pentane on to a THF solution of **2**. Yield = 100 mg (25 %).

^{1}H NMR (THF-*d*$_8$): δ = 1.64 (s, 6H, Ar-*o*-C*H*$_3$), 2.18 (s, 3H, Ar-*p*-C*H*$_3$), 3.54-3.56 (m, 2H, NCH$_2$C*H*$_2$Fl), 4.37-4.39 (m, 2H, NC*H*$_2$CH$_2$Fl), 6.42-6.46 (m, 2H, Fluorenyl-*H*), 6.74 (s, 2H, Mes-Ar-*m*-*H*), 6.80-6.84 (m, 2H and 1H, Fluorenyl-*H* and (Mes)NC*H*CHNEt), 7.15 (d of t, $^{2}J_{HH}$ = 1.0 Hz, $^{3}J_{HH}$ = 8.2 Hz, 2H, Fluorenyl-*H*), 7.40 (d, J_{HH} = 1.6 Hz, 1H, (Mes)NCHC*H*NEt), 7.89 (d of t, $^{2}J_{HH}$ = 0.8 Hz, $^{3}J_{HH}$ = 7.7 Hz, 2H, Fluorenyl-*H*).

^{13}C{^{1}H} NMR (THF-*d*$_8$): δ = 18.2 (Ar-*o*-*C*H$_3$), 21.1 (Ar-*p*-*C*H$_3$), 29.7 (NCH$_2$*C*H$_2$Fl), 54.2 (*NCH$_2$CH$_2$Fl*), 91.8 (NCH$_2$CH$_2$*C*), 109.3 (Fluorenyl-*C*), 114.4 (Fluorenyl-*C*), 119.6 (Fluorenyl-*C*), 120.3 ((Mes)NCH*C*HNEt and Fluorenyl-*C*), 121.4 (Fluorenyl-*C*), 121.7 ((Mes)N*C*HCHNEt), 129.3 (Mes-Ar-*m*-*C*), 135.7 (Fluorenyl-*C*), 136.3 (Mes-Ar-*C*), 137.6 (Mes-Ar-*C*), 139.6 (Mes-Ar-*C*), 211.4 (NHC$_{carbene}$).

2.3 Synthesis of (FluEth)IMesCs 3

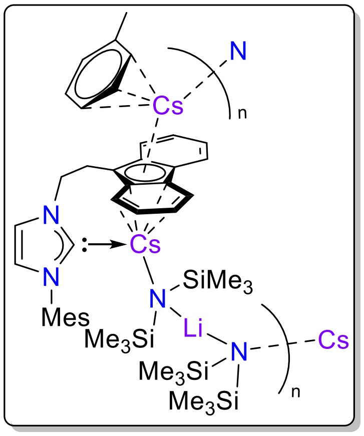


1 (200 mg, 0.435 mmol) was added to a J. Young's Schlenk flask, suspended in toluene (5 mL) and cooled to -80 ºC before addition of *n*BuLi (1.6 M, 0.27 mL, 0.435 mmol). The reaction mixture was then warmed to ambient temperature and stirred overnight. The solution was then filtered on to a -80 ºC toluene solution of CsN(SiMe$_3$)$_2$ (128 mg, 0.435 mmol), warmed to ambient temperature and stirred overnight. The resulting precipitate was isolated by filtration, washed with toluene (5 mL) and dried *in vacuo* to yield **3** as a red powder. Crystals suitable for single crystal X-ray diffraction analysis were grown by layering benzene on to a THF solution of **3**. Yield = 153 mg (34%).

^{1}H NMR (THF-d_8): δ = 1.68 (s, 6H, Ar-*o*-CH_3), 2.19 (s, 3H, Ar-*p*-CH_3), 3.55-3.58 (m, 2H, NCH_2CH_2Fl), 4.38-4.40 (m, 2H, NCH_2CH_2Fl), 6.43-6.46 (m, 2H, Fluorenyl-*H*), 6.76 (br s, 2H Ar-*m*-*H*), 6.80-6.84 (m, 2H, Fluorenyl-*H*), 6.85 (d, J_{HH} = 1.6 Hz, 1H, (Mes)NC*H*CHNEt), 7.15 (d of t, $^2J_{HH}$ = 0.8 Hz, $^3J_{HH}$ = 8.1 Hz, 2H, Fluorenyl-*H*), 7.43 (d, J_{HH} = 1.6 Hz, 1H, (Mes)NCHC*H*NEt), 7.87 (d of t, $^2J_{HH}$ = 0.7 Hz, $^3J_{HH}$ = 7.7 Hz, 2H, Fluorenyl-*H*).

^{13}C{^{1}H} NMR (THF-d_8): δ = 18.2 (Ar-*o*-CH_3), 20.9 (Ar-*p*-CH_3), 29.6 (NCH_2CH_2Fl), 54.2 (NCH_2CH_2Fl), 92.3 (NCH_2CH_2C), 109.3 (Fluorenyl-*C*), 114.5 (Fluorenyl-*C*), 119.5 (Fluorenyl-*C*), 120.1 ((Mes)NCHCHNEt), 120.3 (Fluorenyl-*C*), 121.6 ((Mes)NCHCHNEt), 121.8 (Fluorenyl-*C*), 129.2 (Mes-Ar-*m*-*C*), 136.0 (Mes-Ar-*C*), 136.1 (Mes-Ar-*C*), 137.5 (Mes-Ar-*C*). No resonance attributable to the carbenic carbon centre in **3** was observed, though could be seen in the corresponding ^{1}H-^{13}C HMBC NMR spectrum at 212.7 ppm (Figure S10).

2.4 Synthesis of (FluEth)IMesCs/CsLiN(SiMe$_3$)$_2$ 4



Method 1: **1** (200 mg, 0.435 mmol) was added to a J. Young's Schlenk flask, suspended in toluene (5 mL) and cooled to -80 ºC before addition of *n*BuLi (1.6 M, 0.27 mL, 0.435 mmol). The reaction mixture was then warmed to ambient temperature and stirred overnight. The solution was then filtered on to a -80 ºC toluene solution of $CsN(SiMe_3)_2$ (128 mg, 0.435 mmol) and $LiN(SiMe_3)_2$ (73 mg, 0.435 mmol), warmed to ambient temperature and stirred overnight. The resulting red solution was concentrated to *ca.* 2 mL then placed at -30 ºC overnight, affording red

crystals of **4**. Concentration of the filtrate and storage at -30 ºC afforded a second crop of **4**. Yield = 133 mg (29%).

Method 2: To a benzene-*d*$_6$ suspension of **3** (10 mg, 19.6 µmol) was added $CsLi(N(SiMe_3)_2)_2$ (5.9 mg, 19.6 µmol) at ambient temperature. Immediate formation of **4** was indicated by the dissolution of insoluble starting materials, which was confirmed by ^{1}H NMR spectroscopy after only 10 minutes at ambient temperature. The reaction was followed over the course of 3 days, after which no further formation of **4** was observed.

^{1}H NMR (benzene-*d*$_6$): δ = 0.33 (s, 36H, NSi(C*H*$_3$)$_3$), 1.57 (s, 6H, Ar-*o*-C*H*$_3$), 2.09 (s, 3H, Ar-*p*-C*H*$_3$), 2.11 (s, 3H, Tol-C*H*$_3$), 3.43-3.46 (m, 2H, NCH$_2$C*H*$_2$Fl), 4.14-4.17 (m, 2H, NC*H*$_2$CH$_2$Fl), 6.24 (d, J_{HH} = 1.6 Hz, 1H, (Mes)NCHC*H*NEt), 6.64 (s, 2H, Ar-*m-H*), 6.81 (d, J_{HH} = 1.5 Hz, 1H, (Mes)NC*H*CHNEt), 6.88-6.92 (m, 2H, Fluorenyl-*H*), 7.00-7.06 (m, 3H, Tol-Ar-*H*), 7.11-7.13 (m, 2H, Tol-Ar-*H*), 7.18-7.22 (m, 2H, Fluorenyl-*H*), 7.24-7.27 (m, 2H, Fluorenyl-*H*), 8.03 (d of t, $^2J_{HH}$ = 1.0 Hz, $^3J_{HH}$ = 7.8 Hz, 2H, Fluorenyl-*H*).

^{13}C{^{1}H} NMR (benzene-*d*$_6$): δ = 6.9 (NSi(*C*H$_3$)$_3$), 17.7 (Ar-*o*-*C*H$_3$), 20.9 (Ar-*p*-*C*H$_3$), 28.4 (NCH$_2$*C*H$_2$Fl), 52.9 (N*C*H$_2$CH$_2$Fl), 92.7 (NCH$_2$CH$_2$*C*), 111.0 (Fluorenyl-*C*), 115.1 (Fluorenyl-*C*), 119.2 ((Mes)N*C*HCHNEt), 119.8 (Fluorenyl-*C*), 120.0 (Fluorenyl-*C*), 121.1 ((Mes)NCH*C*HNEt), 121.7 (Fluorenyl-*C*), 125.7 (Tol-Ar-*C*), 129.0 (Mes-Ar-*m*-*C*), 129.3 (Tol-Ar-*C*), 134.6 (Mes-Ar-*C*), 135.2 (Mes-Ar-*C*), 137.7 (Tol-Ar-*C*). No resonance attributable to the carbenic carbon centre in **4** was observed, though could be seen in the corresponding ^{1}H-^{13}C HMBC NMR spectrum at 210.9 ppm (Figure S15).

^{7}Li NMR (benzene-*d*$_6$): δ = 2.1.

^{133}Cs NMR (benzene-*d*$_6$): δ = -18.6.

3. NMR Spectroscopy

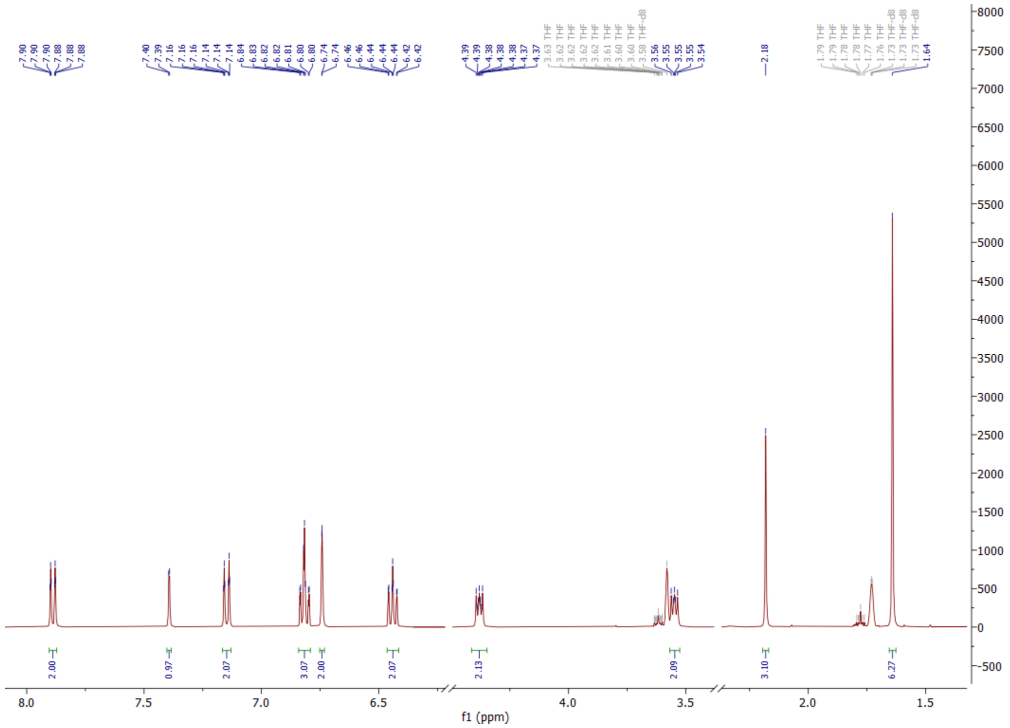


*Figure S1 - ^{1}H NMR spectrum of (FluEth)IMesRb **2**.*

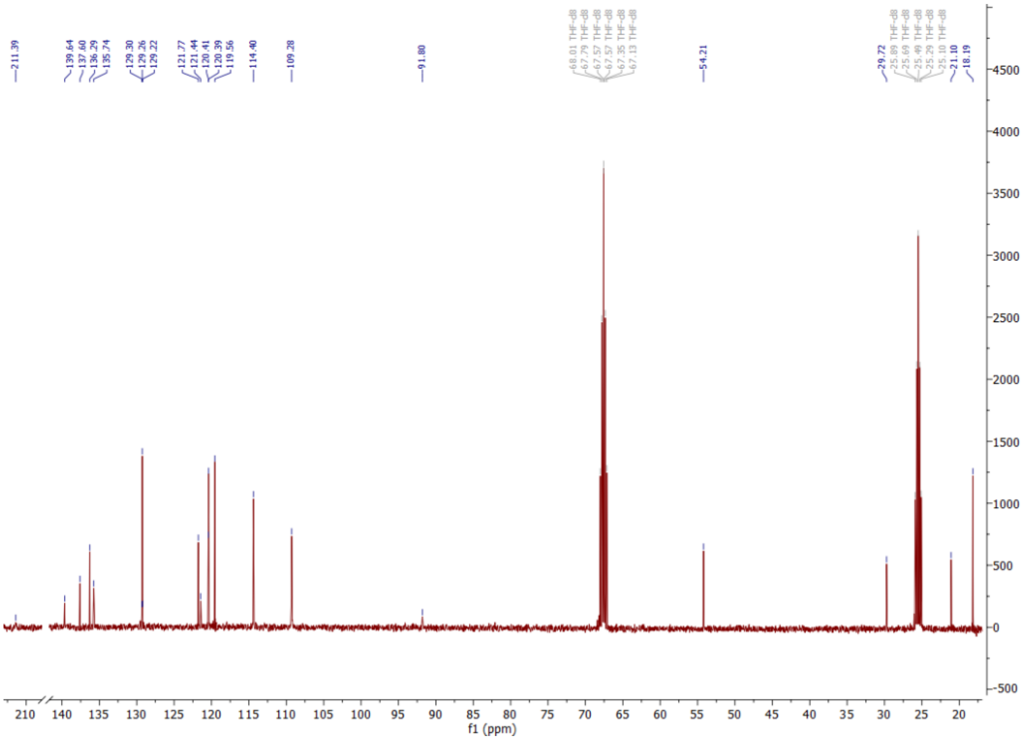


*Figure S2 - $^{13}C\{^{1}H\}$ NMR spectrum of **2**.*

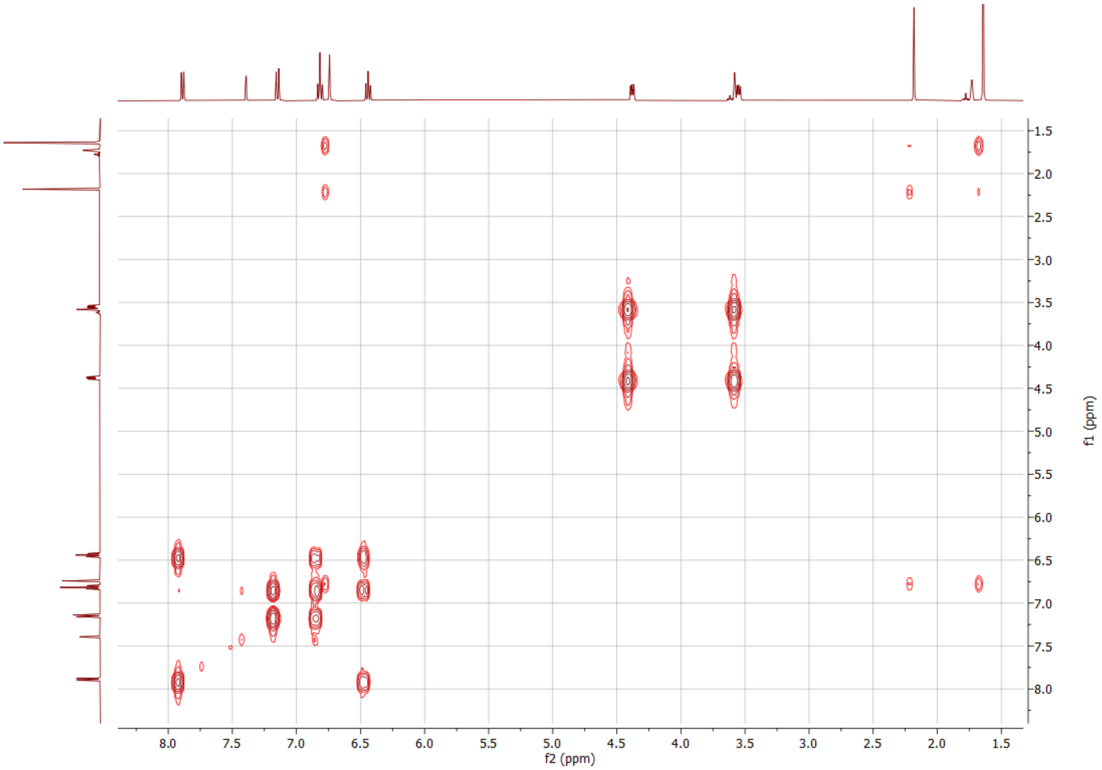


*Figure S3 - ${}^{1}H$-${}^{1}H$ COSY NMR spectrum of **2**.*

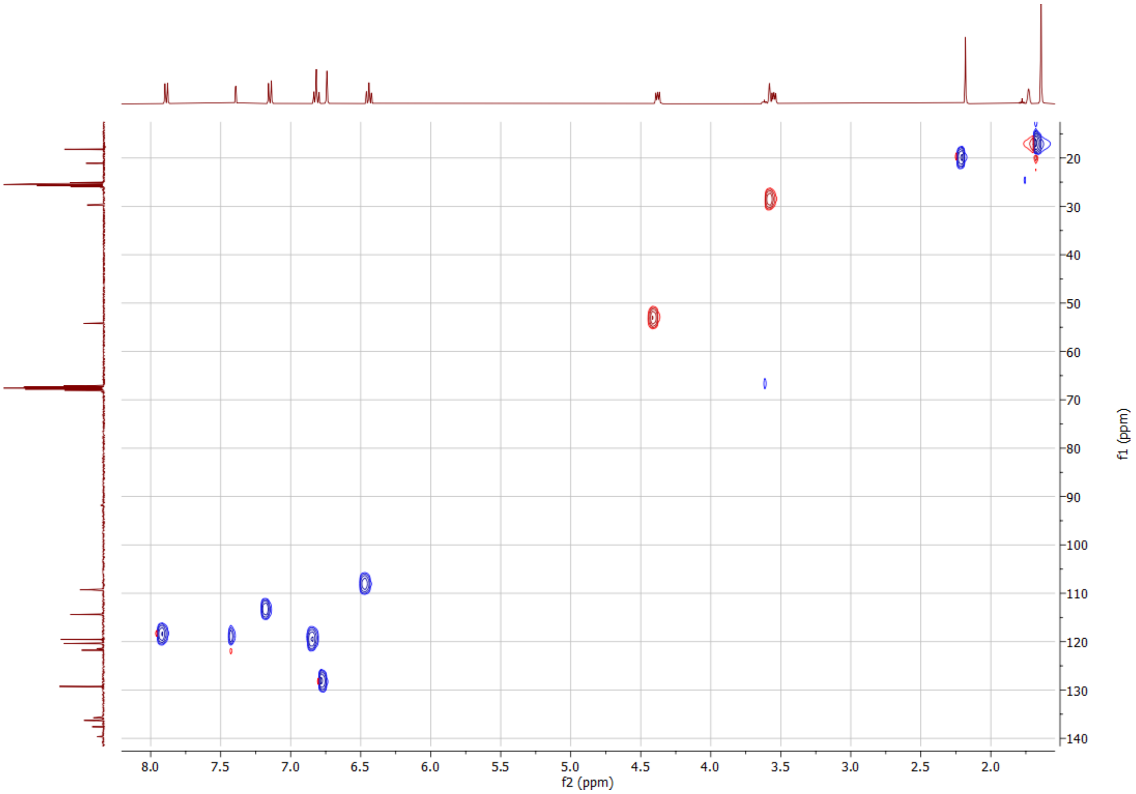


*Figure S4 - ${}^{1}H$-${}^{13}C$ HSQC NMR spectrum of **2**.*

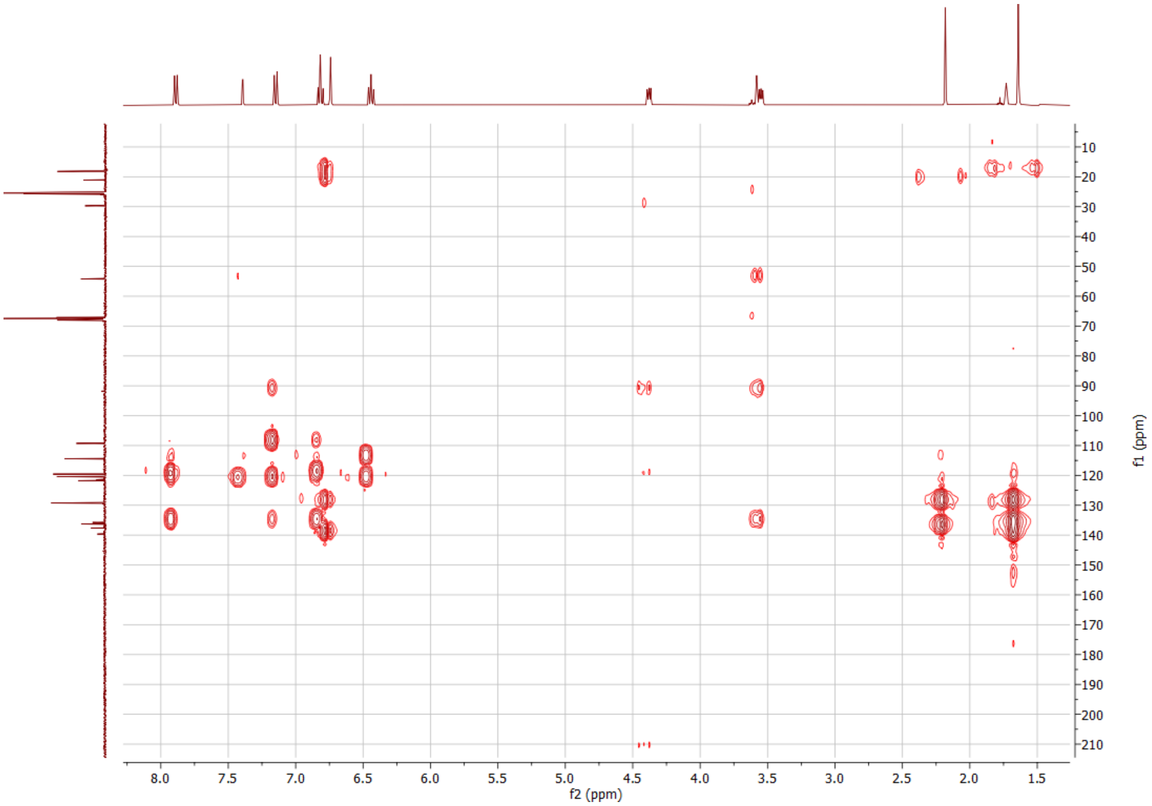


*Figure S5 - ^{1}H-^{13}C HMBC NMR spectrum of **2**.*

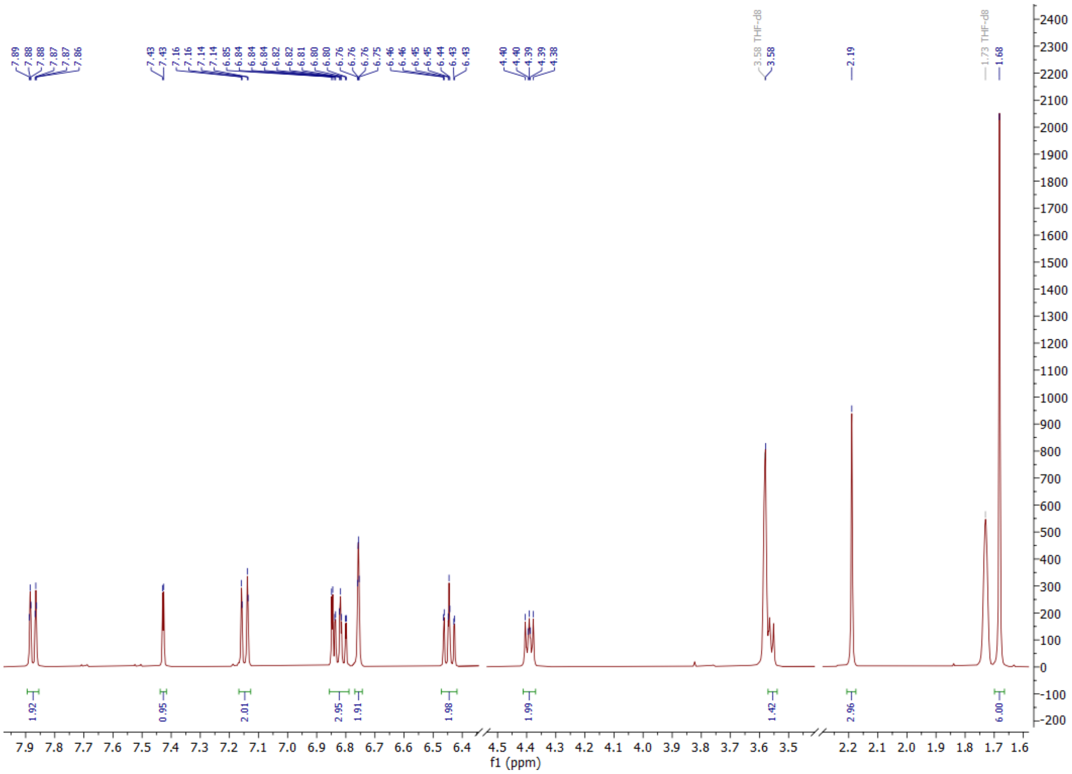


*Figure S6 - ^{1}H NMR spectrum of (FluEth)IMesCs **3**.*

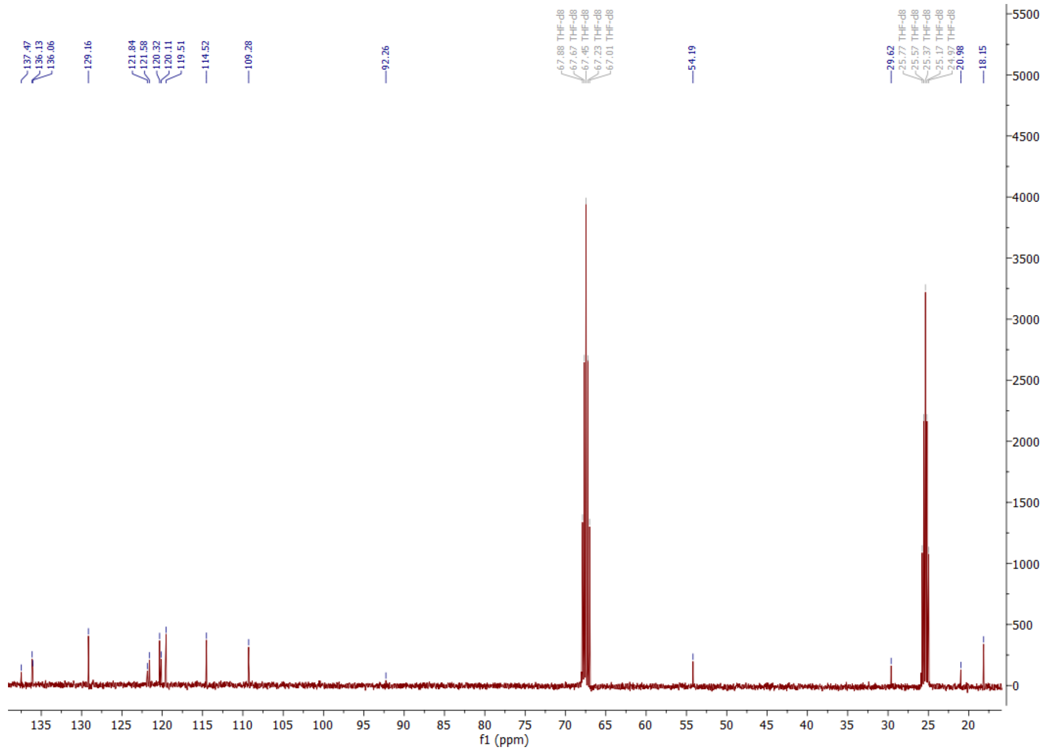


*Figure S7 - $^{13}C\{^1H\}$ NMR spectrum of **3**.*

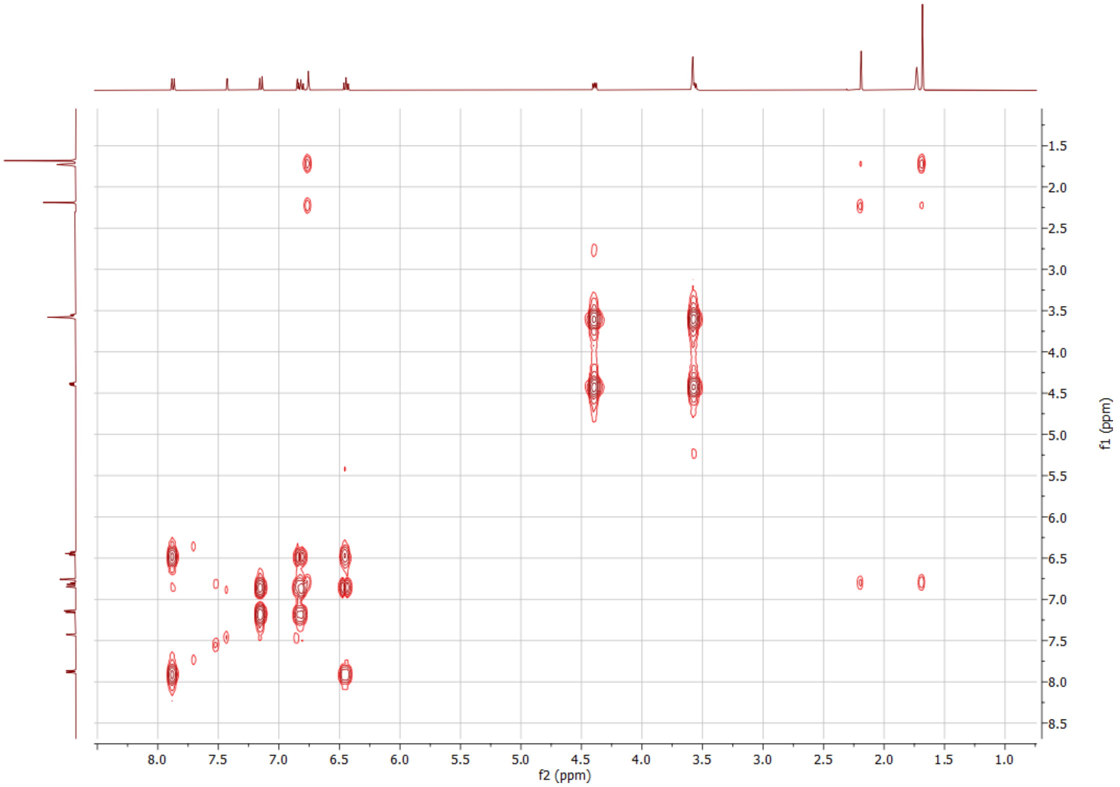


*Figure S8 - ^1H-^1H COSY NMR spectrum of **3**.*

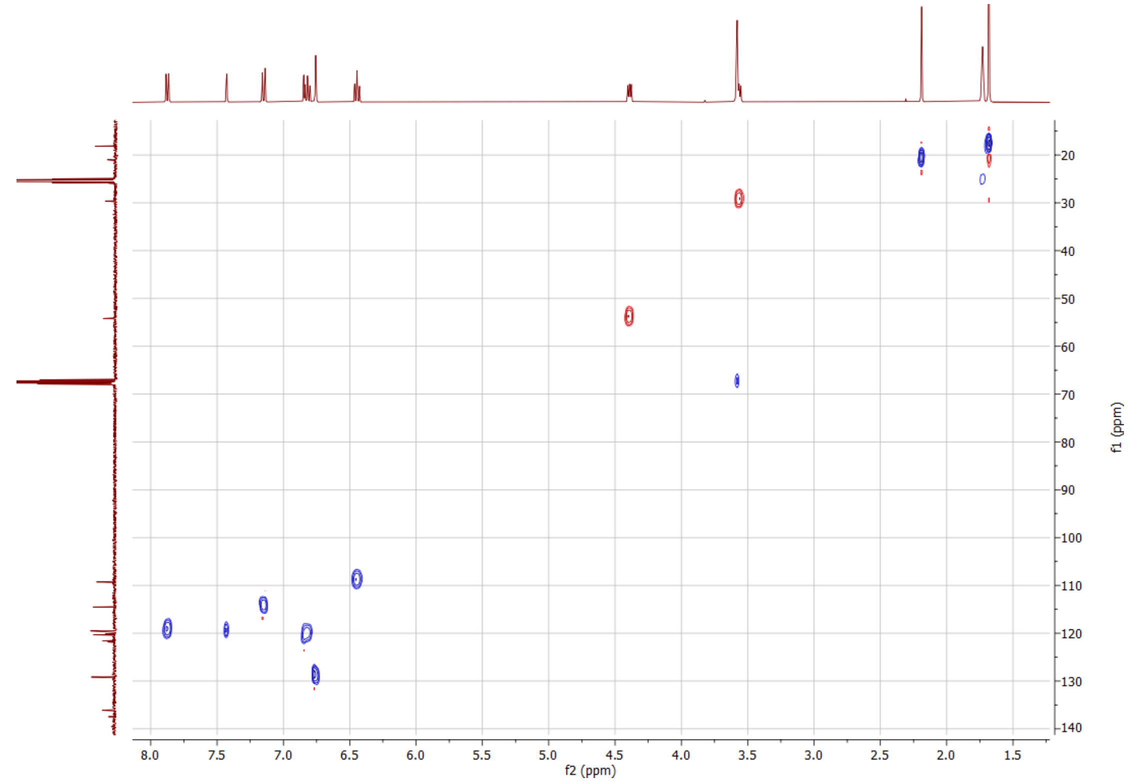


*Figure S9 - ^{1}H-^{13}C HSQC NMR spectrum of **3**.*

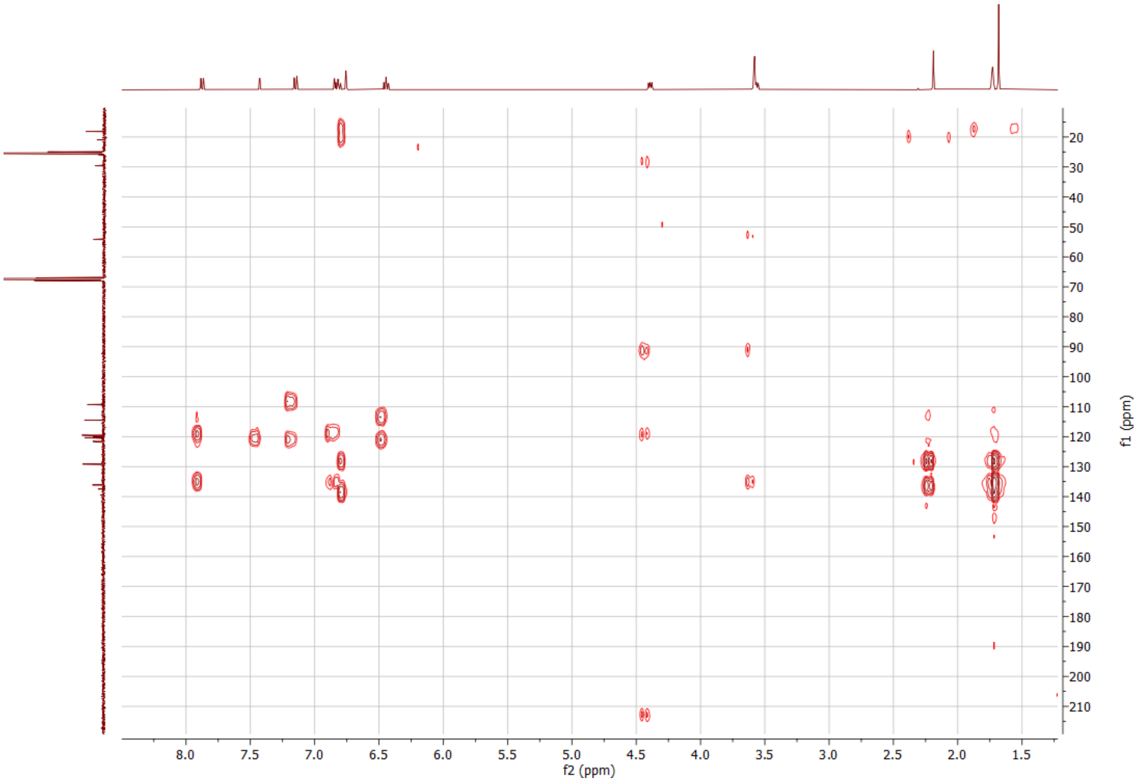


*Figure S10 - ^{1}H-^{13}C HMBC NMR spectrum of **3**.*

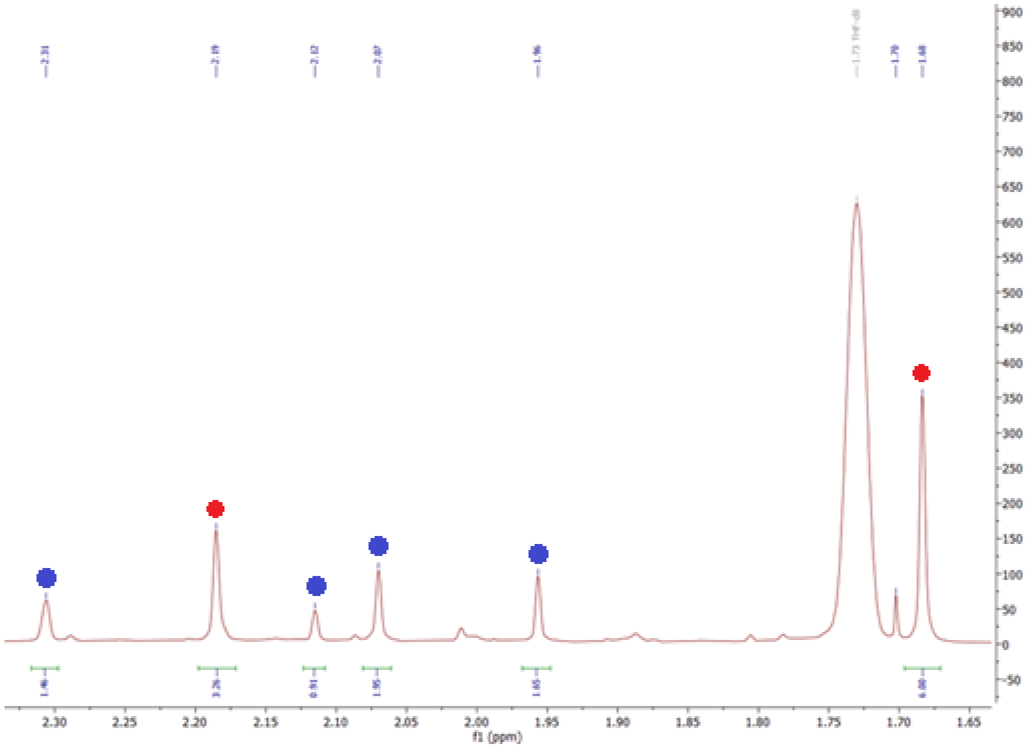


*Figure S11 - ^{1}H NMR spectrum of **3** after 3 days at 80°C (only aliphatic region shown for clarity). Mesityl CH_3 resonances attributable to complex **3** denoted by red circle, while those attributable to unknown decomposition products denoted by blue circle.*

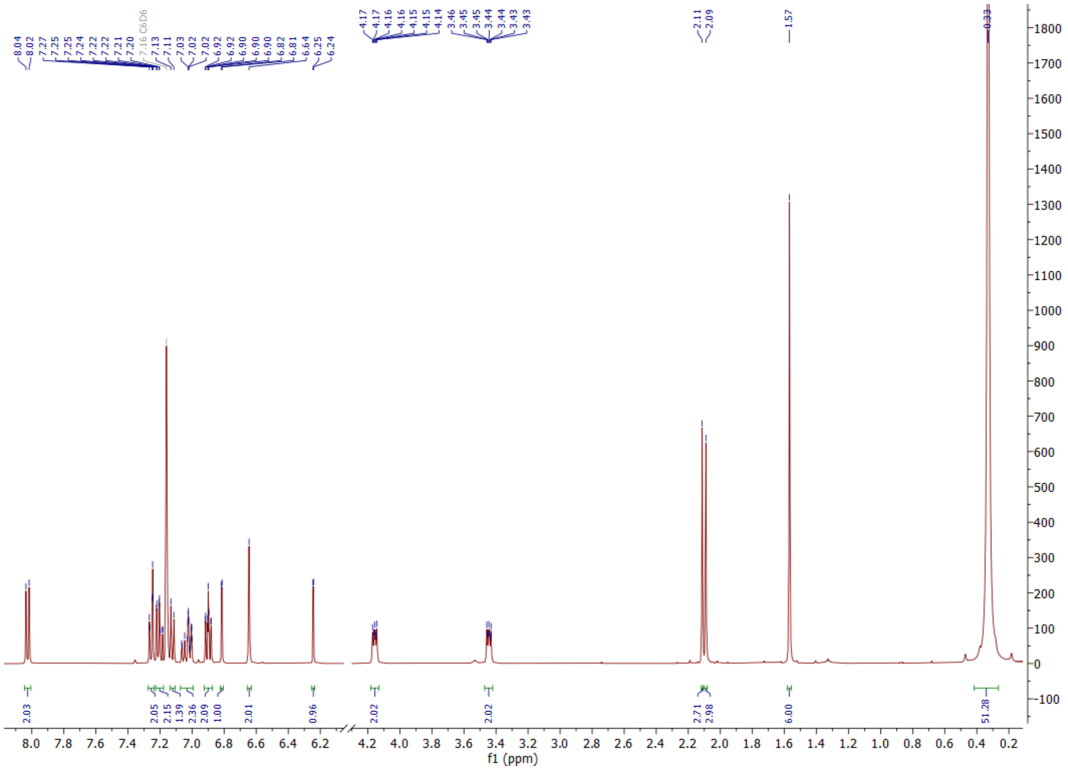


*Figure S12 - ^{1}H NMR spectrum of (FluEth)IMesCs/CsLiN($SiMe_3$)$_2$ **4**.*

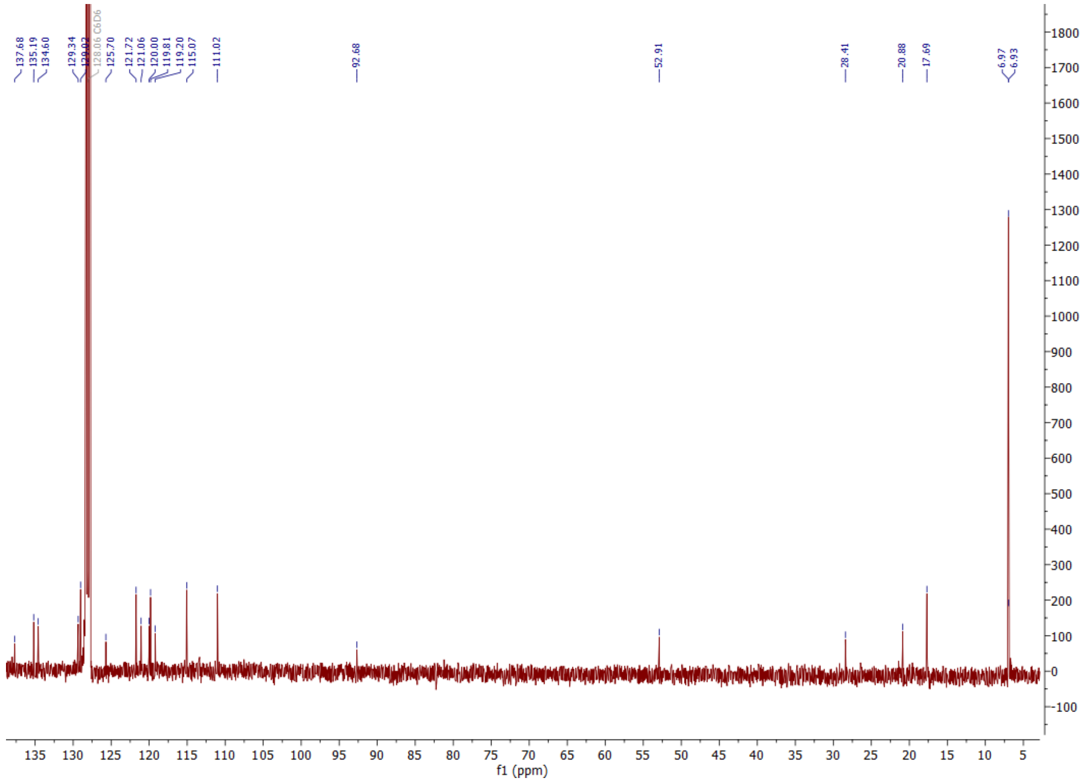


*Figure S13 - $^{13}C\{^{1}H\}$ NMR spectrum of **4**.*

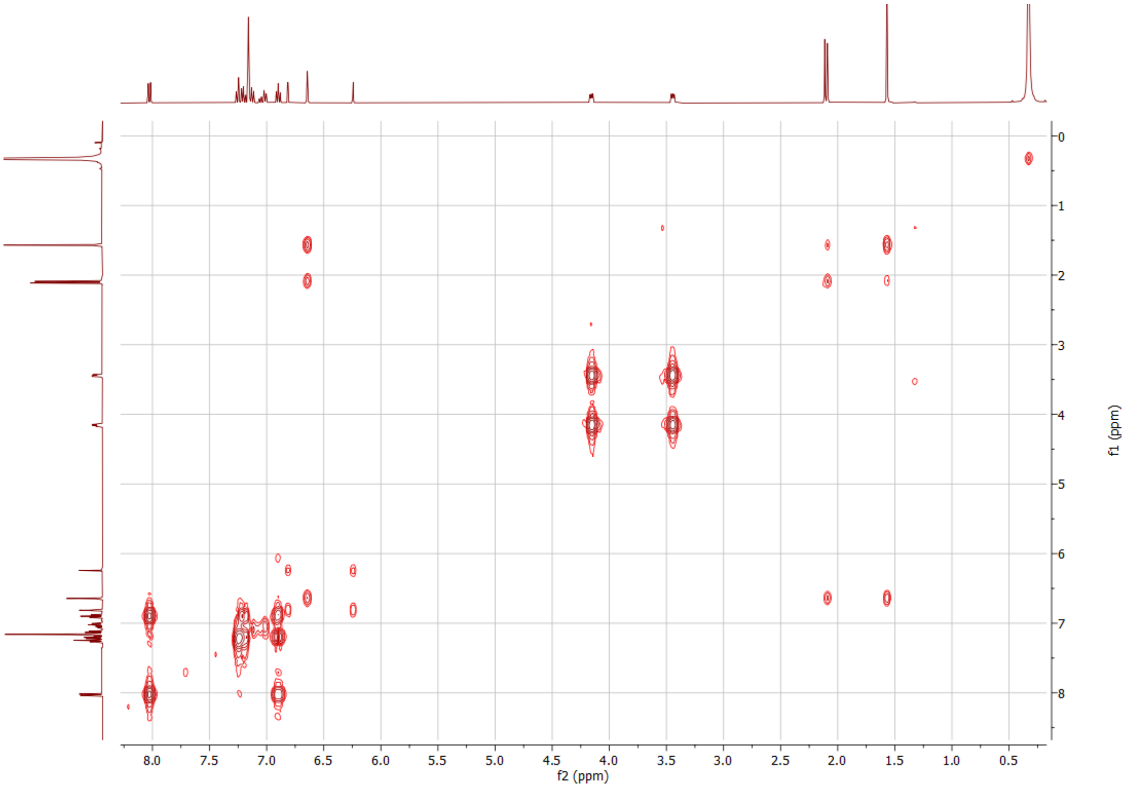


*Figure S14 - ^{1}H-^{1}H COSY NMR spectrum of **4**.*

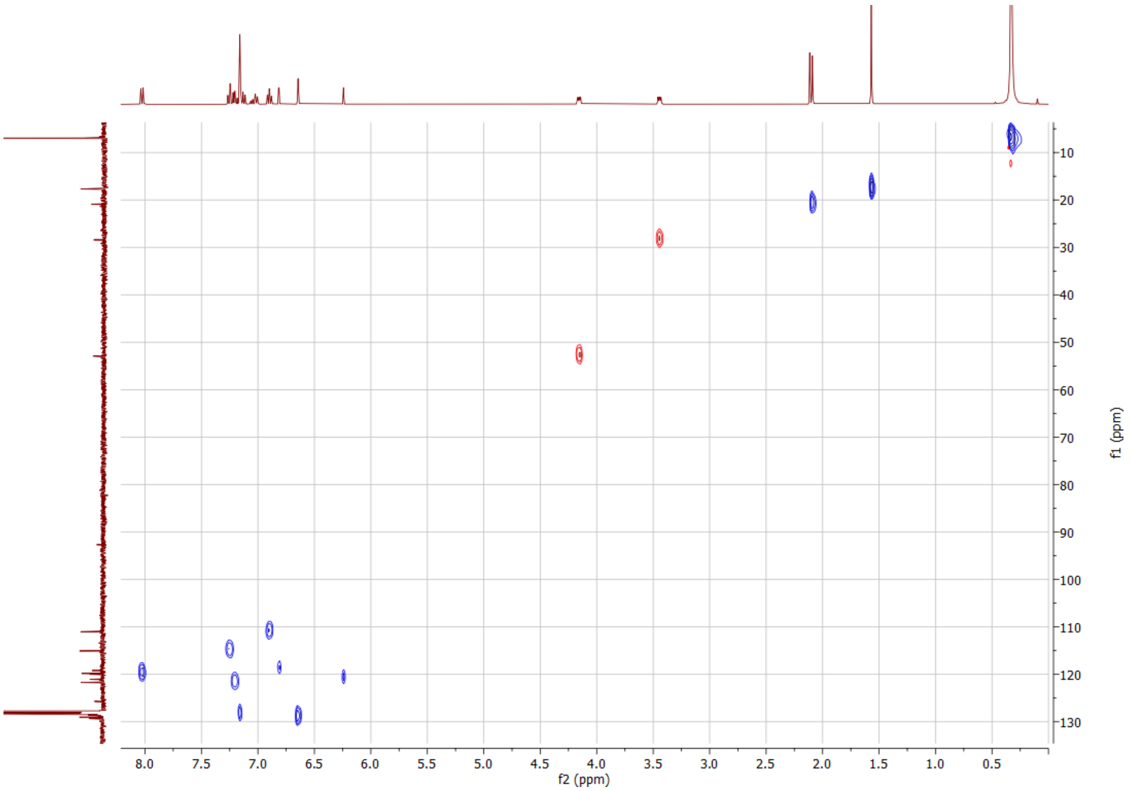


*Figure S15 - ^{1}H-^{13}C HSQC NMR spectrum of **4**.*

*Figure S16 - ^{1}H-^{13}C HMBC NMR spectrum of **4**.*

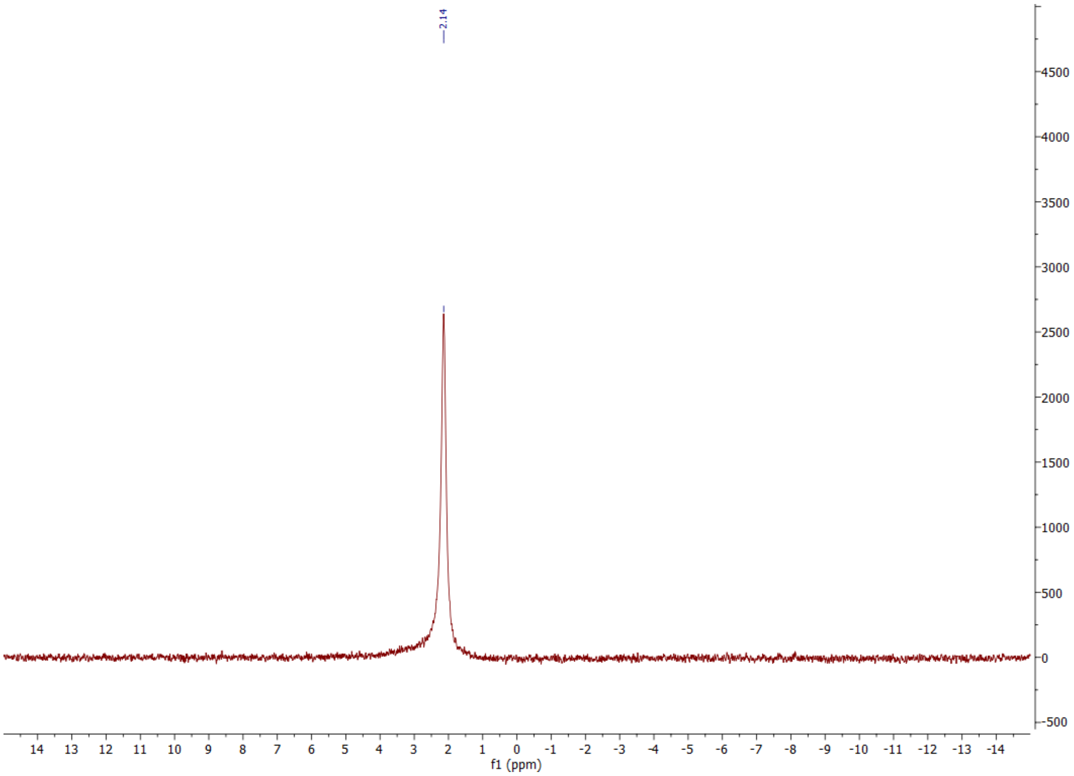


Figure S17 - ^{7}Li NMR spectrum of ***4****.*

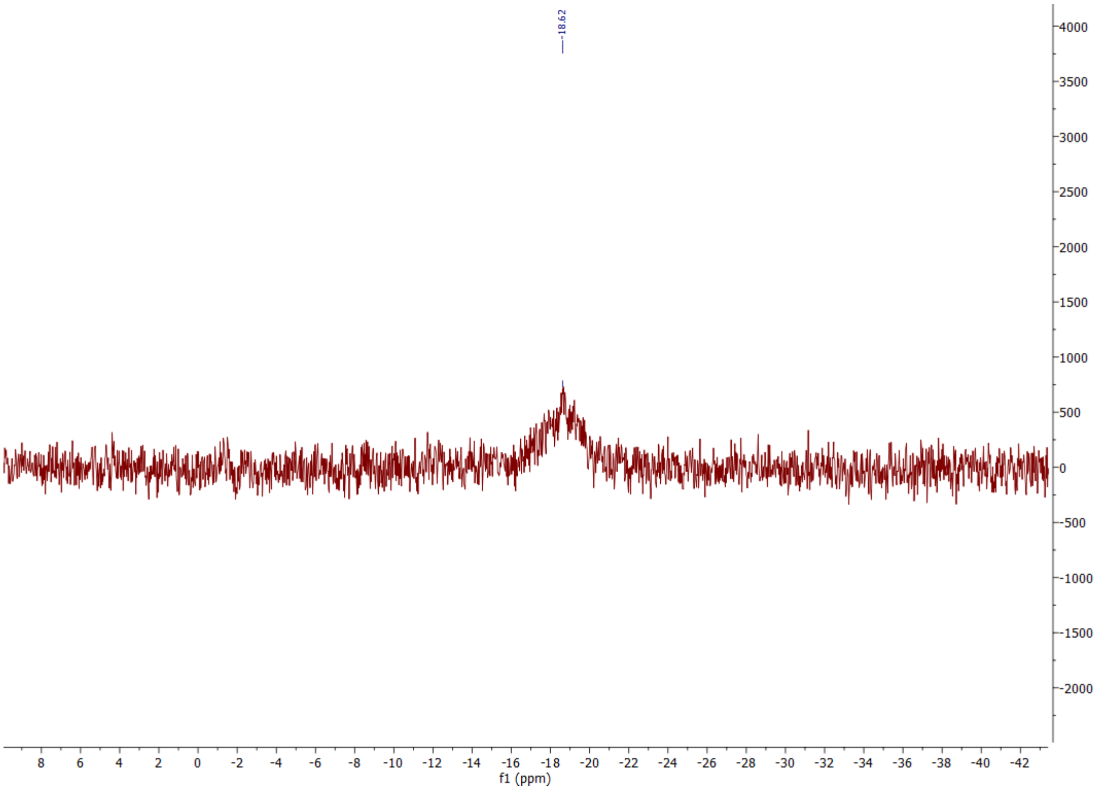


Figure S18 - ^{133}Cs NMR spectrum of ***4****.*

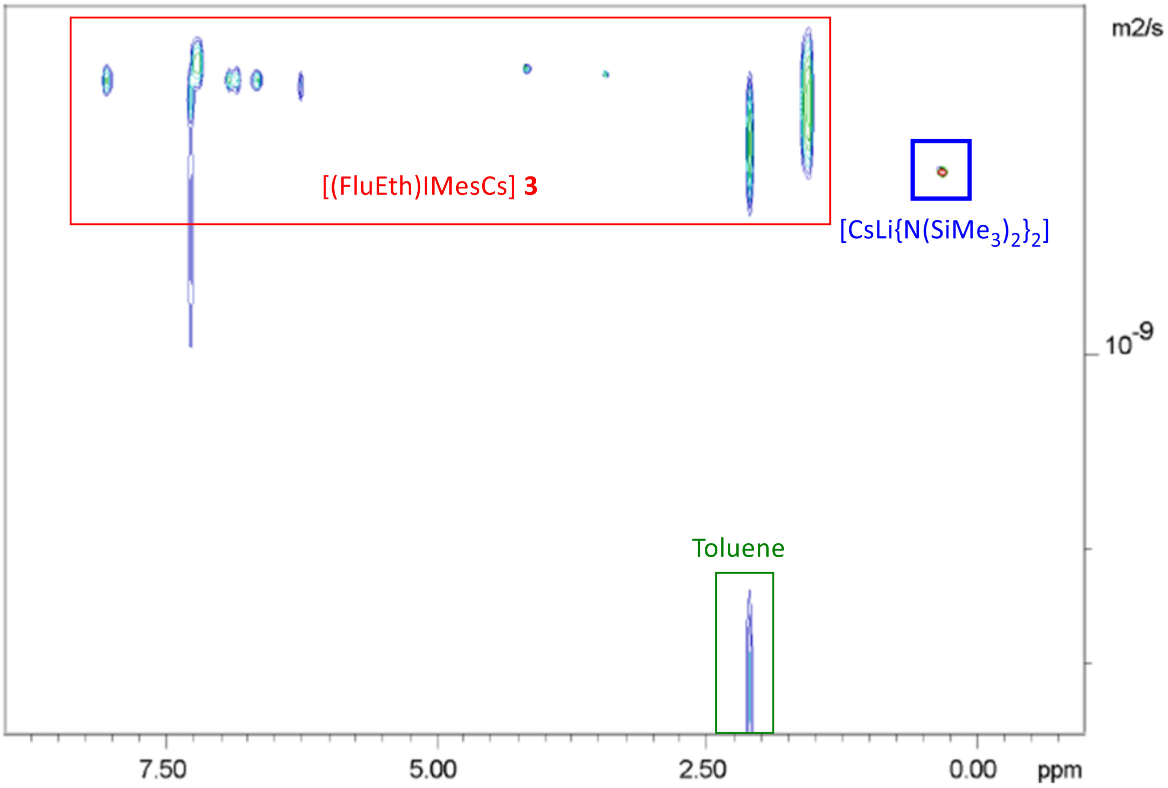


*Figure S19 - ^{1}H DOSY NMR spectrum of **4**.*

4. X-Ray Crystallography Data

Crystallographic data was measured with a Rigaku Synergy-i instrument with monochromated Cu−Kα (λ 1.54184 Å) radiation. The measured data were processed with the CrysAlisPro software package.[6] The structures were solved with the ShelXT structure solution program and refined with ShelXL-2018 to convergence against F^2.[7] Final refinement was within OLEX or WinGX.[8,9] All ordered non-hydrogen atoms were refined using anisotropic thermal parameters. The toluene ligands of **4** was modelled as disordered over two positions. Appropriate constraints and restraints were added to the disordered groups to force approximation to expected geometries and displacement behaviours. Selected crystallographic and refinement data is given in Table S1.

Full details of single crystal diffraction data for are reported in crystallographic information files (CIF) accompanying this document and deposited with the CCDC as deposition numbers 2501678 to 2501680. Full details on data collection, reduction and refinement can be found in the individual CIFs.

Table S1 – Selected crystallographic and refinement parameters.

Compound	**2**	**3**	**4**
CCDC no.	2501678	2501679	2501680
Empirical formula	$C_{27}H_{25}N_2Rb_1$	$C_{27}H_{25}N_2Cs_1$	$C_{46}H_{69}N_4Cs_2Li_1Si_4$
Formula weight	462.96	510.40	1063.17
Temperature/K	100(2)	200(2)	200(2)
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	$P2_1/c$	$P2_1/c$	$Pca2_1$
a/Å	14.3566(1)	14.4348(1)	25.3737(3)
b/Å	11.8396(1)	12.0323(1)	12.0154(1)
c/Å	26.4983(3)	26.6844(1)	17.5574(2)
α/°	90	90	90
β/°	101.790(1)	100.598(1)	90
γ/°	90	90	90
Volume/Å^3	4409.06(7)	4555.59(5)	5352.81(10)
Z	8	8	4
ρ_{calc}g/cm^3	1.395	1.488	1.319
μ/mm^{-1}	3.192	12.782	11.714
Reflections collected	67895	71963	29964
Independent reflections	8826	8640	9458
R merge	0.0686	0.0525	0.0426
Restraints/parameters	0/547	0/547	147/528
Reflections obs	7577	8286	7783
Goodness-of-fit on F^2	1.027	1.042	1.024
Final R indexes [I>=2σ (I)]	0.0561, 0.1452	0.0299, 0.0829	0.0789, 0.1982
Final R indexes [all data]	0.0638, 0.1512	0.0308, 0.0835	0.0912, 0.2063
Largest diff. peak/hole/e Å^{-3}	2.476/-0.663	1.240/-1.062	3.374, -1.847

5. References

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