

Unusual alkyl group activation and cationic complex formation from a novel lutetium dialkyl complex supported by a tridentate monoanionic ligand

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## General Methods

All reactions were conducted under a dry argon atmosphere using standard Schlenk techniques and all compounds were handled in a helium or argon-filled dry box. All solvents were distilled under argon from sodium or sodium benzophenone ketyl or passed over activated alumina, stored over molecular sieves, and degassed prior to use. All NMR spectra were obtained on a Bruker Avance 300 with  $C_6D_6$ ,  $C_7D_8$ ,  $CD_2Cl_2$ , or  $d_8$ -THF as solvents and referenced to residual solvent peaks unless otherwise noted. The  $^1H$  and  $^{13}C$  NMR resonances for **3** were assigned by standard COSY, NOESY, HETCOR, HMQC,<sup>1</sup> and HMBC.<sup>1,2</sup> The HMBC and HMQC experiments were acquired on a Bruker DRX-500 with triple axis gradients. The 2D spectra are included at the end of the ESI.

**[2-{(2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)N=CMe}-6-{(2,6-Pr<sup>i</sup><sub>2</sub>C<sub>6</sub>H<sub>3</sub>)NCMe<sub>2</sub>}C<sub>5</sub>H<sub>3</sub>N]Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>2</sub> (**2**):** To a stirring, toluene solution of Lu(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>3</sub>(THF)<sub>2</sub> (1.20 g, 2.07 mmol, 15 ml toluene) was added a toluene solution of **1** (1.03 g, 2.07 mmol, 20 ml toluene). The resulting mixture turned red immediately, was stirred for 3 h and then concentrated to approximately 20 ml. Placing the red solution at -30 °C overnight induced the crystallization of **2** as red microcrystals that were isolated by filtration, washed with hexanes, and dried under vacuum (35 % isolated yield).  $^1H$  NMR ( $CD_2Cl_2$ , -50 °C):  $\delta$  -1.81 (d,  $^2J_{H-H} = 11.5$  Hz, 1H,  $CH_2Lu$ ), -1.66 (d,  $^2J_{H-H} = 11.5$  Hz, 1H,  $CH_2Lu$ ), -1.24 (d,  $^2J_{H-H} = 11.5$  Hz, 1H,  $CH_2Lu$ ), -0.75 (ov, 1H,  $CH_2Lu$ , overlap confirmed by COSY), -0.75 (s, 9H, Si( $CH_3$ )<sub>3</sub>), -0.45 (s, 9H, Si( $CH_3$ )<sub>3</sub>), 0.90 (d,  $^3J_{H-H} = 6.5$  Hz, 3H, isopropyl  $CH_3$ ), 0.95 (d,  $^3J_{H-H} = 6.5$  Hz, 3H, isopropyl  $CH_3$ ), 1.02 (d,  $^3J_{H-H} = 6.5$  Hz, 3H, isopropyl  $CH_3$ ), 1.10 (s, 3H,  $NCCCH_3$ ), 1.19 (ov, m, 12H, isopropyl  $CH_3$ ), 1.31 (d,  $^3J_{H-H} = 6.5$  Hz, 3H,

isopropyl  $CH_3$ ), 1.67 (s, 3H,  $NCCCH_3$ ), 2.30 (s, 3H,  $N=CCH_3$ ), 2.64 (m, 1H, isopropyl methine), 2.86 (m, 1H, isopropyl methine), 3.12 (m, 1H, isopropyl methine), 4.22 (m, 1H, isopropyl methine), 7.0-7.3 (ov, m, 6H, diisopropyl aryl protons), 7.84 (d,  $^3J_{H-H} = 8.0$  Hz,  $C_5H_3N$ -*m*-proton), 7.89 (d,  $^3J_{H-H} = 7.5$  Hz,  $C_5H_3N$ -*m*-proton), 8.13 (t,  $^3J_{H-H} = 8.0$  Hz,  $C_5H_3N$ -*p*-proton).  $^{13}C$  NMR (reported  $^1J_{C-H}$  are from the gated  $^{13}C$  spectrum,  $CD_2Cl_2$ ,  $-50$  °C): 3.1 ( $Si(CH_3)_3$ ,  $^1J_{C-H} = 117$  Hz), 3.3 ( $Si(CH_3)_3$ ,  $^1J_{C-H} = 117$  Hz), 20.2, 22.6, 23.2, 24.4, 24.7, 25.0, 25.2, 26.1, 26.9, 27.6, 27.8, 28.0, 28.1, 29.6, 37.3, 39.8 ( $LuCH_2$ ,  $^1J_{C-H} = 99$  Hz), 43.6 ( $LuCH_2$ ,  $^1J_{C-H} = 99$  Hz), 67.9, 122.5, 122.7, 122.8, 123.2, 124.2, 125.0, 126.2, 127.2, 138.9, 139.1, 140.3, 141.8, 147.2, 148.5, 148.8, 149.1, 176.8, 177.4.  $^{13}C$  NMR  $\{^1H\}$  ( $CD_2Cl_2$ ,  $25$  °C):  $\delta$  4.0, 20.5, 24.5, 25.2, 27.5, 28.2, 29.3, 43.5 (br), 68.2, 122.9, 123.3, 123.6, 125.2, 126.1, 127.9, 139.7, 140.7, 143.1, 147.8, 149.4, 150.3, 177.5, 178.6.

**[2- $\{(2,6-Pr^i_2C_6H_3)N=CMe\}$ -6- $\{(2,6-Pr^i_2C_6H_3)NCMe_2\}$  $C_5H_3NLu(CH_2SiMe_2CH_2SiMe_3)(THF)[MeB(C_6F_5)_3]$  (**3**):** To a  $CH_2Cl_2$  solution of **2** ( $0.070$ g,  $8.28 \times 10^{-5}$  mol,  $5.0$  ml  $CH_2Cl_2$ ) was added  $2.0$  eq of THF ( $13.50$   $\mu$ l,  $1.66 \times 10^{-4}$  mol) followed by  $1.0$  eq of  $B(C_6F_5)_3$  ( $0.042$ ,  $8.28 \times 10^{-5}$  mol,  $0.5$  ml  $CH_2Cl_2$ ). After  $2$ h of stirring the solvent was removed under vacuum giving **3** as a red solid in  $88$  % yield by NMR techniques.  $^1H$  NMR ( $CD_2Cl_2$ ,  $25$  °C):  $\delta$   $-0.83$  (d,  $^2J_{H-H} = 11.0$  Hz,  $1H$ ,  $CH_2Lu$ ),  $-0.63$  (d,  $^2J_{H-H} = 13.5$  Hz,  $1H$ ,  $SiCH_2Si$ ),  $-0.46$  (d,  $^2J_{H-H} = 13.5$  Hz,  $1H$ ,  $SiCH_2Si$ ),  $-0.45$  (d,  $^2J_{H-H} = 11.0$  Hz,  $1H$ ,  $CH_2Lu$ ),  $-0.25$  (s,  $3H$ ,  $LuCH_2Si(CH_3)$ ),  $-0.21$  (s,  $3H$ ,  $LuCH_2Si(CH_3)$ ),  $-0.09$  (s,  $9H$ ,  $Si(CH_3)_3$ ),  $0.45$  (br,  $3H$ ,  $CH_3B$ ),  $0.90$  (d,  $^3J_{H-H} = 7.0$  Hz, isopropyl  $CH_3$ ),  $0.99$  (d,  $^3J_{H-H} = 6.5$  Hz, isopropyl  $CH_3$ ),  $1.10$  (d,  $^3J_{H-H} = 6.5$  Hz, isopropyl  $CH_3$ ),  $1.12$  (d,  $^3J_{H-H} = 7.0$  Hz, isopropyl  $CH_3$ ),  $1.19$  (d,  $^3J_{H-H} = 7.0$  Hz, isopropyl  $CH_3$ ),  $1.25$  (d,  $^3J_{H-H} = 7.0$  Hz, isopropyl  $CH_3$ ),  $1.28$  (d,  $^3J_{H-H} = 7.0$  Hz, isopropyl  $CH_3$ ),  $1.31$  (s,  $3H$ ,  $NCCCH_3$ ),  $1.35$  (d,  $^3J_{H-H} = 6.5$

Hz, isopropyl  $CH_3$ ), 1.58 (ov, m, 2H,  $\beta$ -THF protons), 1.67 (ov, m, 2H,  $\beta$ -THF protons), 1.90 (s, 3H,  $NCCCH_3$ ), 2.34 (m, 1H, isopropyl methine), 2.50 (s, 3H,  $N=CCH_3$ ), 2.62 (m, 2H,  $\alpha$ -THF protons), 2.90 (ov, m, 1H, isopropyl methine), 2.93 (ov, m, 1H, isopropyl methine), 3.23 (m, 2H,  $\alpha$ -THF protons), 4.12 (m, 1H, isopropyl methine), 7.14 (ov, m, 1H, diisopropyl aryl-*m*-proton), 7.14 (ov, m, 1H, diisopropyl aryl-*p*-proton), 7.25 (m, 1H, diisopropyl aryl-*m*-proton), 7.30 (m, 1H, diisopropyl aryl-*m*-proton), 7.42 (ov, m, 1H, diisopropyl aryl-*m*-proton), 7.42 (ov, m, 1H, diisopropyl aryl-*p*-proton), 8.02 (d,  $^3J_{H-H} = 8$  Hz,  $C_5H_3N$ -*m*-proton), 8.06 (d,  $^3J_{H-H} = 8$  Hz,  $C_5H_3N$ -*m*-proton), 8.32 (t,  $^3J_{H-H} = 8$  Hz,  $C_5H_3N$ -*p*-proton).  $^{13}C$  NMR ( $CD_2Cl_2$ , 25 °C, reported  $^1J_{C-H}$  are from the gated  $^{13}C$  spectrum,  $C_6F_5$  resonances not reported,  $H_3CB$  resonance not observed):  $\delta$  1.7 ( $Si(CH_3)_3$ ,  $^1J_{C-H} = 118$  Hz), 4.3 ( $SiCH_3$ ,  $^1J_{C-H} = 117$  Hz), 4.5 ( $SiCH_3$ ,  $^1J_{C-H} = 117$  Hz), 8.4 ( $Si(CH_3)_2CH_2Si(CH_3)_3$ ,  $^1J_{C-H} = 108$  Hz), 20.7, 23.0, 24.0, 24.9, 25.2, 25.6, 25.7 (THF  $\beta$ -carbon), 26.2, 27.2, 27.5, 27.7, 28.7, 28.9, 29.1, 30.8, 39.4, 47.4 (t,  $^1J_{C-H} = 96$  Hz,  $CH_2Lu$ ), 69.8, 73.0 (THF  $\alpha$ -carbon), 124.7, 124.8, 125.5, 125.6, 126.1, 126.9, 127.6, 129.8, 139.5, 139.8, 140.2, 141.9, 142.9, 149.5, 149.6, 150.1, 179.1, 181.1.  $^{19}F$  NMR ( $CD_2Cl_2$ , 25 °C):  $\delta$  -134.34 (d,  $^3J_{F-F} = 20.5$  Hz, *o*-fluorine), -166.5 (t,  $^3J_{F-F} = 20.5$  Hz, *p*-fluorine), -169.07 (m, *m*-fluorine).  $^{11}B$  NMR ( $CD_2Cl_2$ , 25 °C):  $\delta$  -12.0. See Figure 1 for the full assignments for **3**. Note that the positions of the diisopropyl aryl rings were assigned by NOESY spectroscopy. For example an nOe between protons at 4.12 ppm and 1.90 ppm put those fragments on the same side of the molecule and nOes between protons at 2.50 ppm and 0.99 ppm put those fragments on the same side of the molecule.

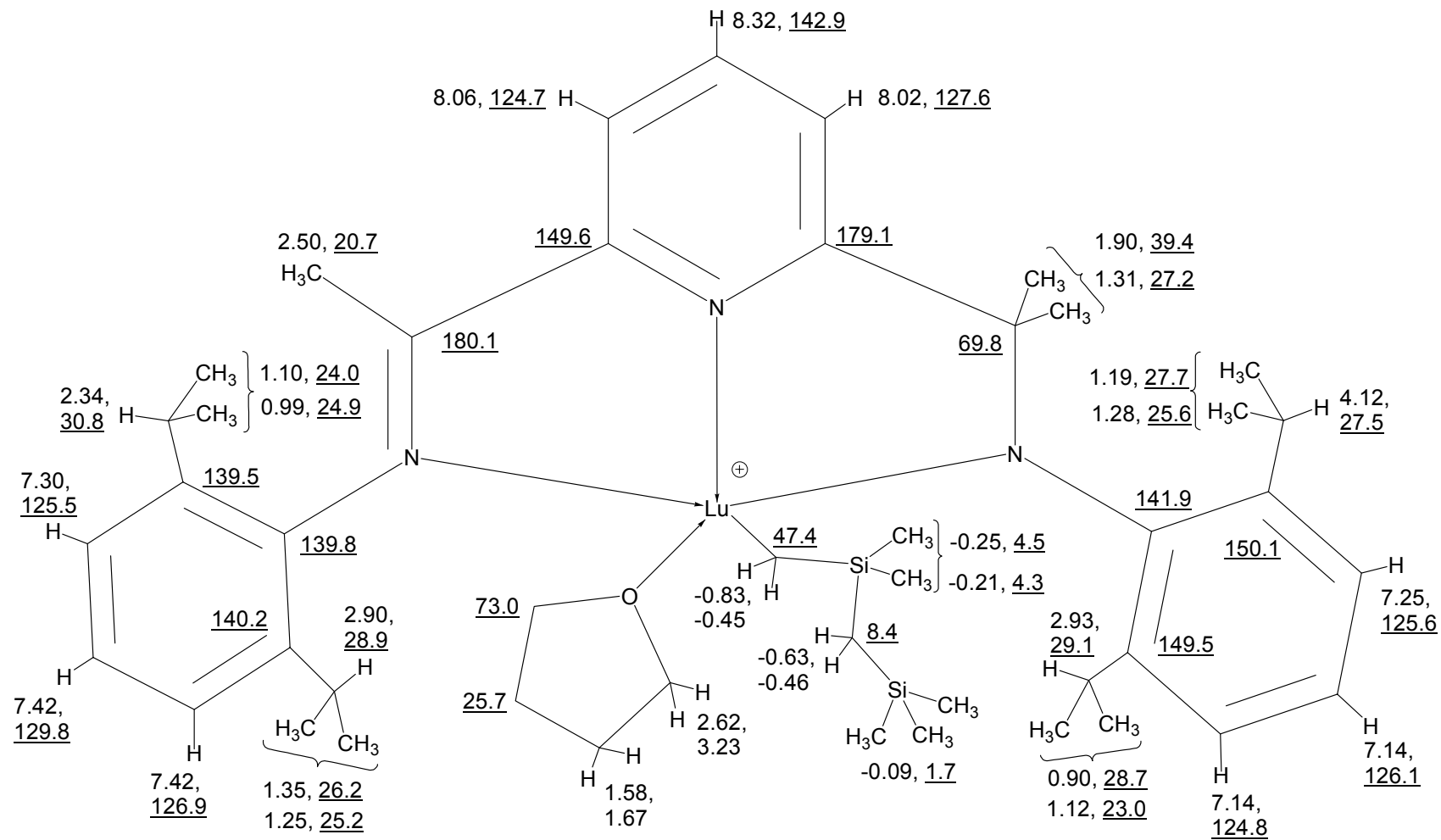
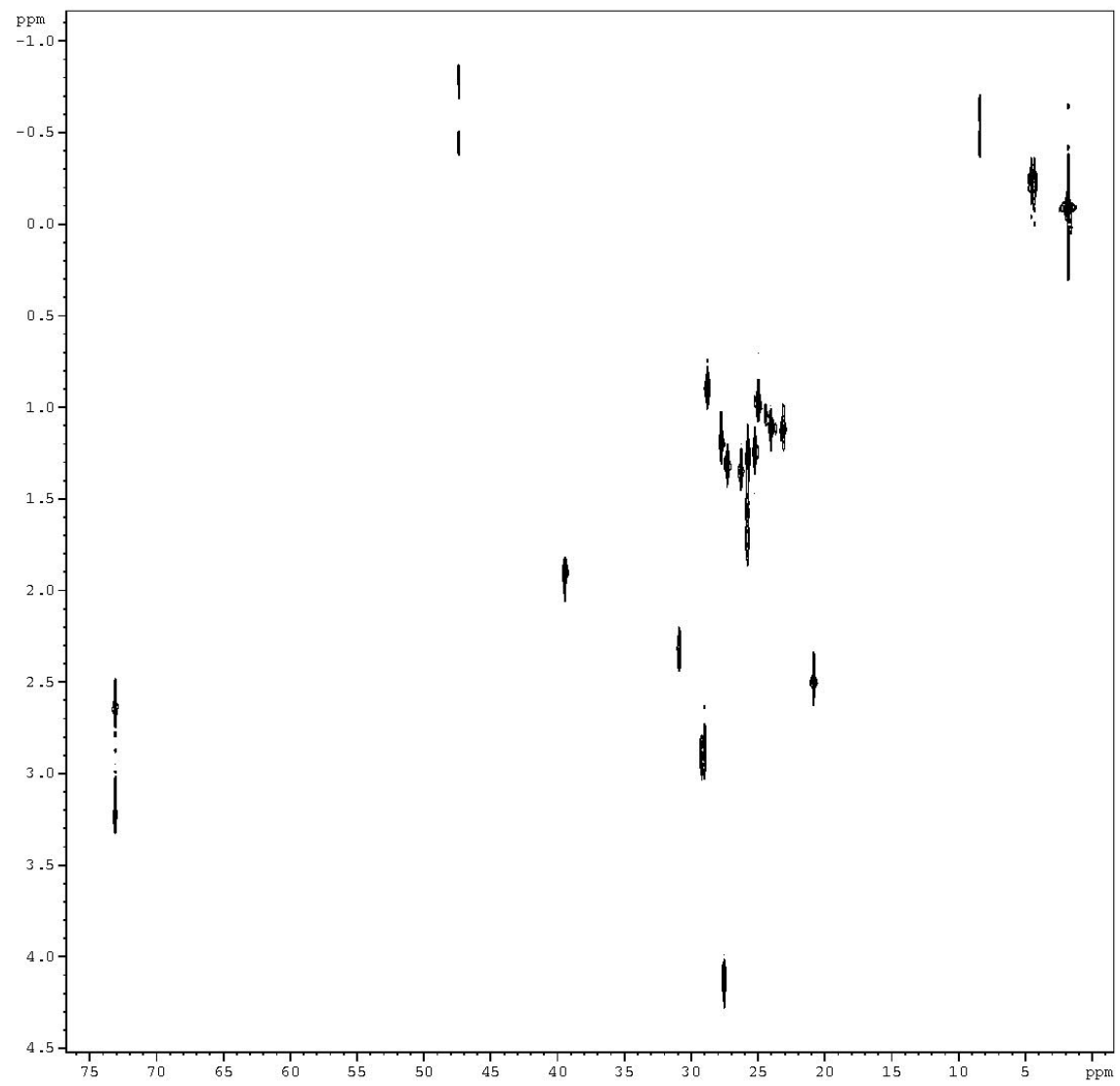


Figure 1. Chemical shift assignment for **3**.  $^{13}\text{C}$  resonances are underlined. The anion has been omitted.

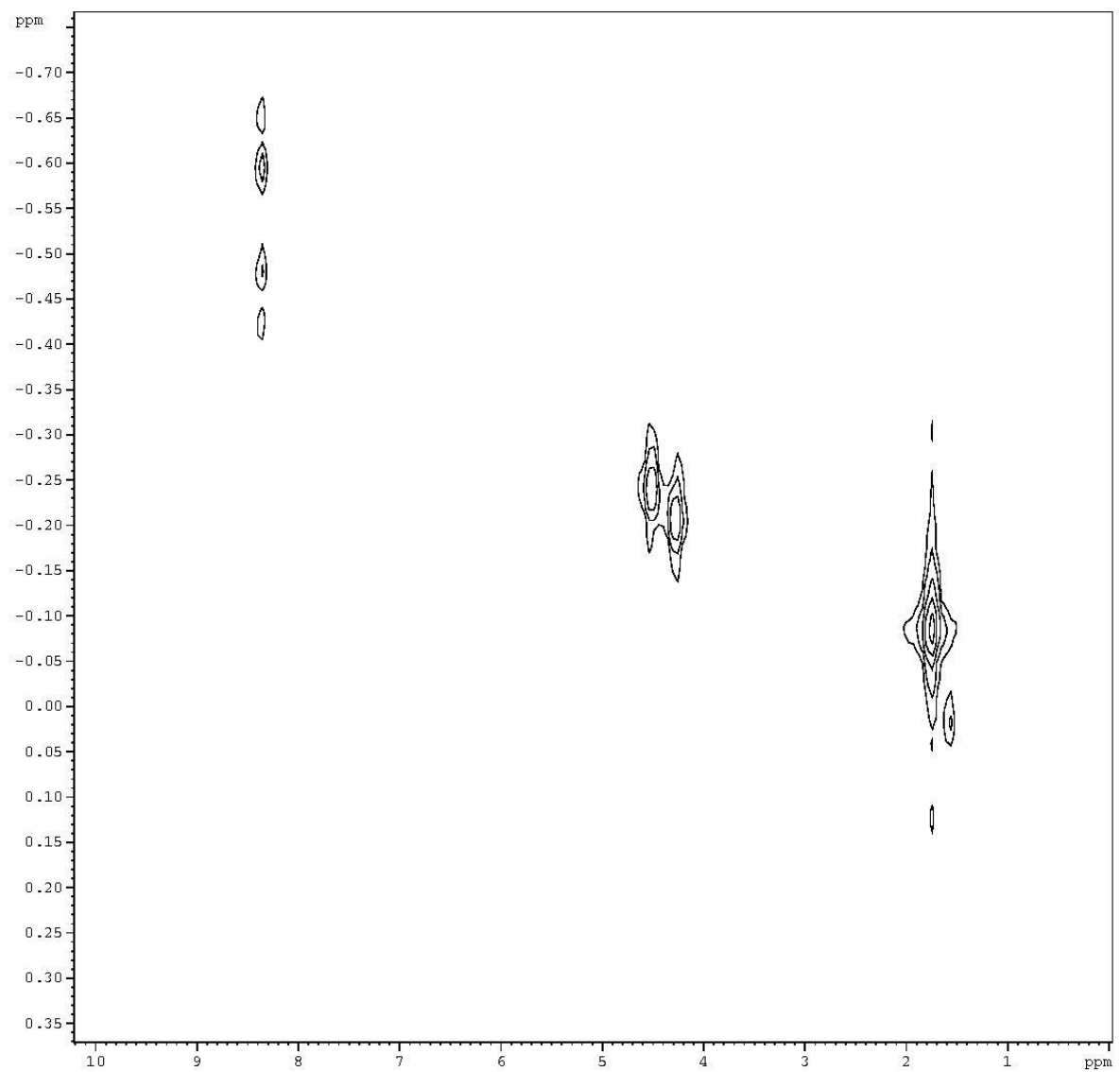
**Hydrolysis of 3:** an excess of H<sub>2</sub>O was added to an NMR sample of **3**. Formation of (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub> was confirmed by comparison with the <sup>1</sup>H NMR spectrum of an authentic sample of (CH<sub>3</sub>)<sub>3</sub>SiCH<sub>2</sub>Si(CH<sub>3</sub>)<sub>3</sub>.



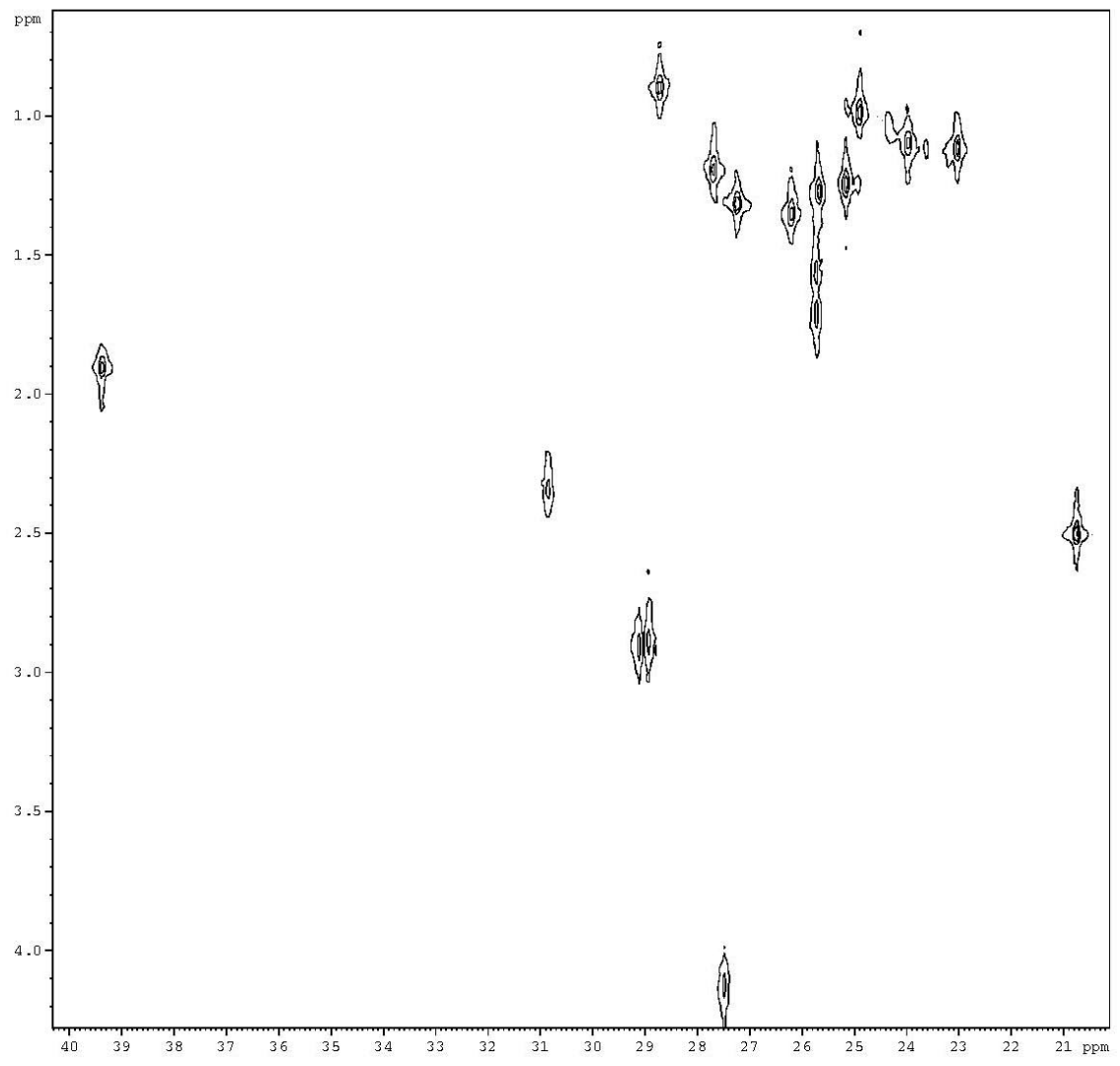


HETCOR of 3

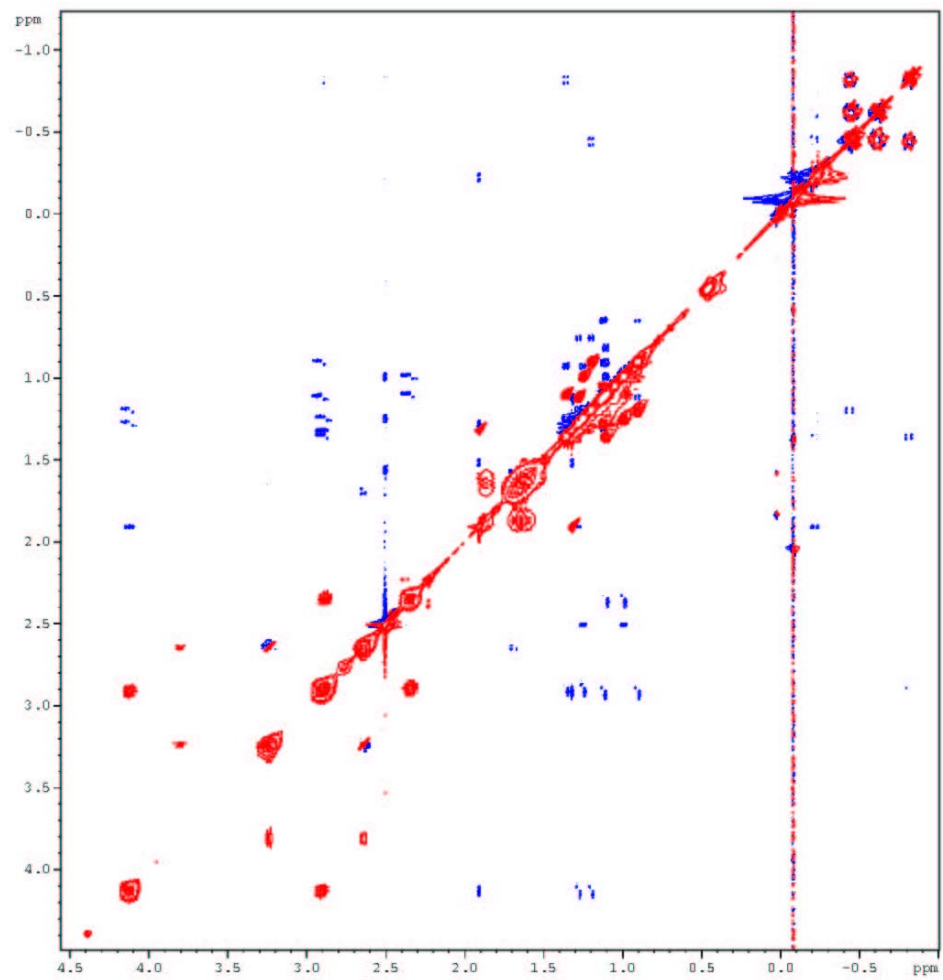




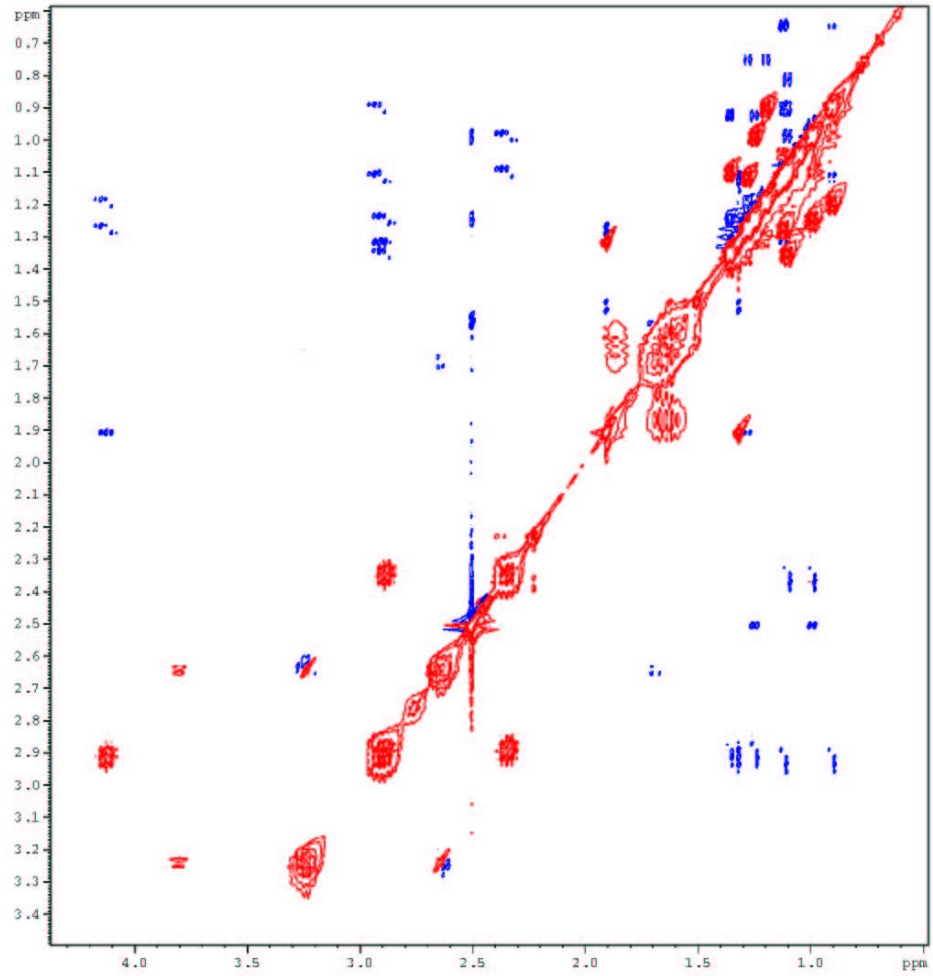
10



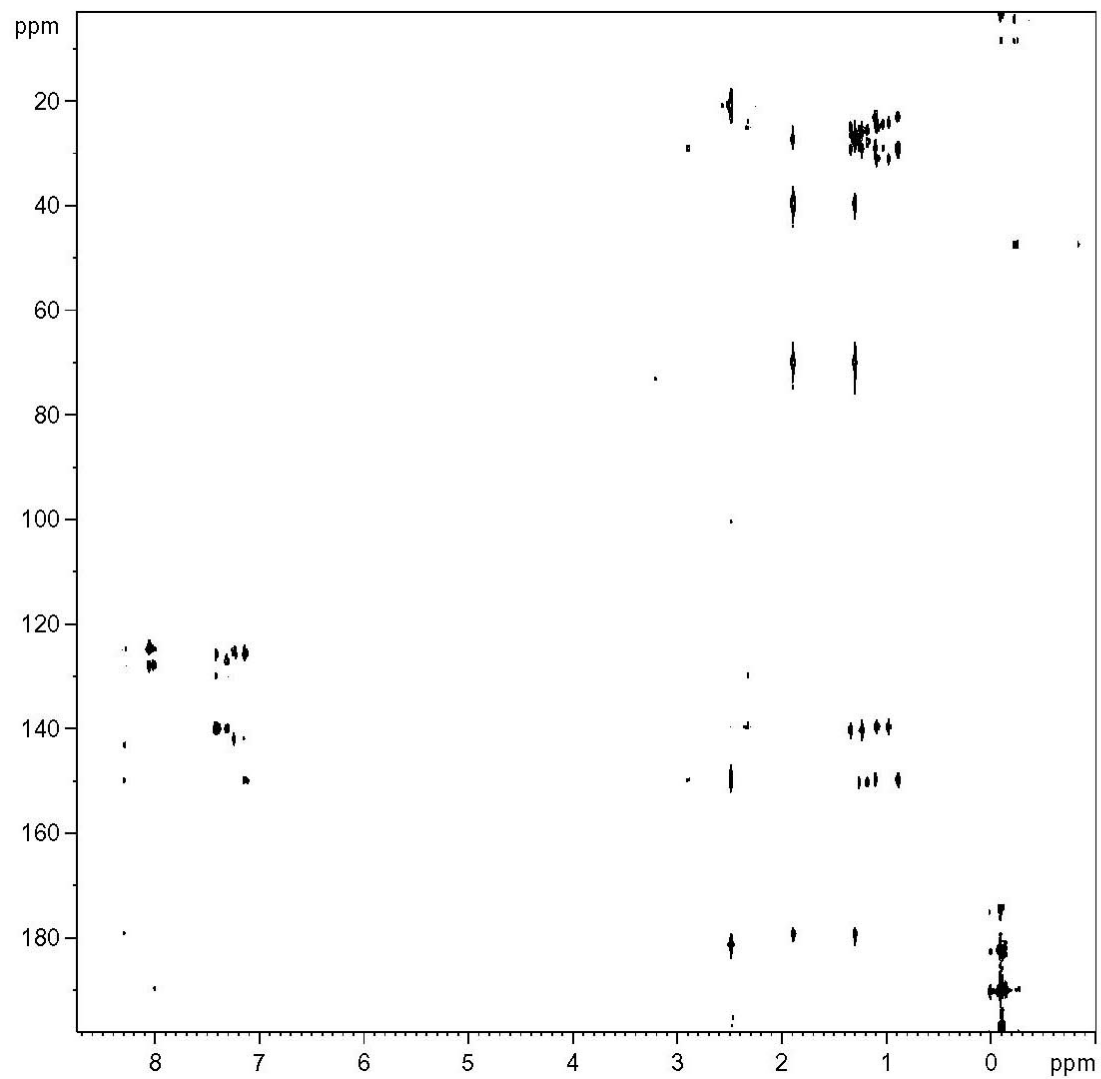
HETCOR of 3



NOESY of 3

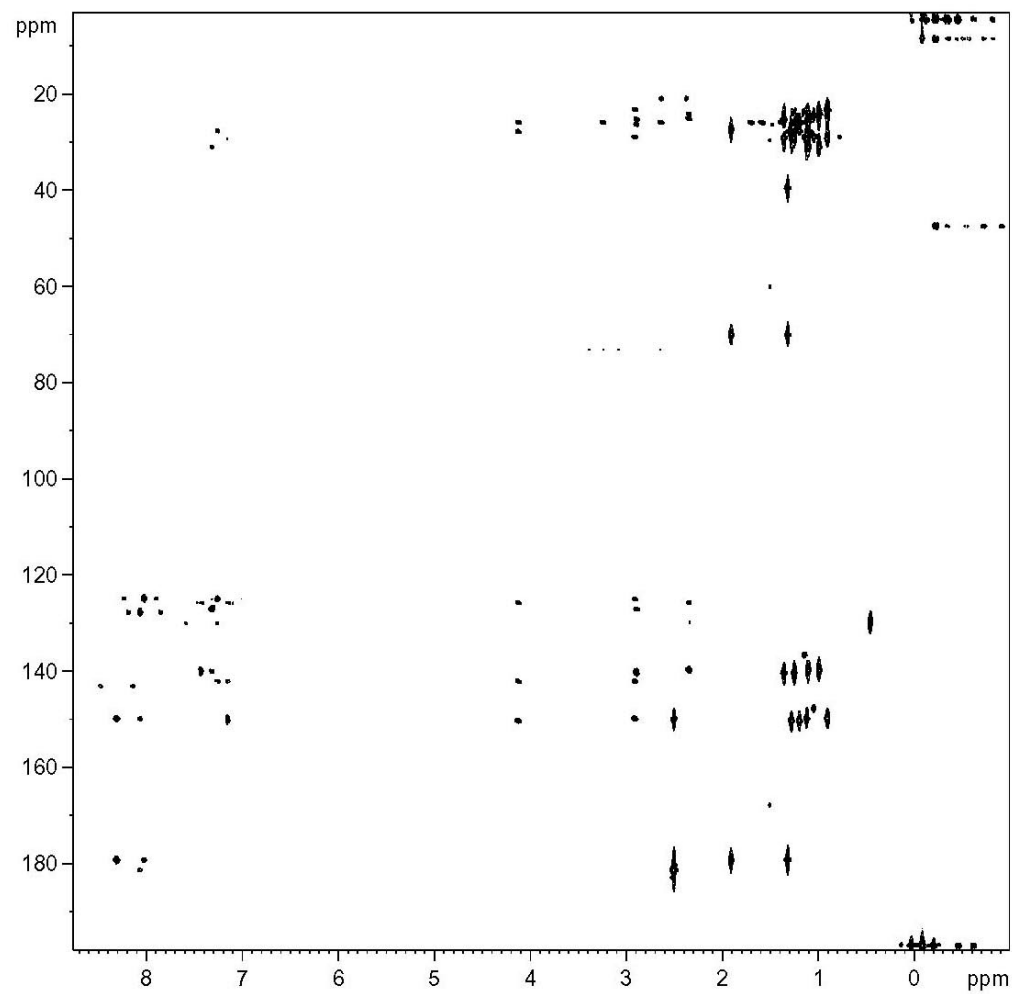


NOESY of 3



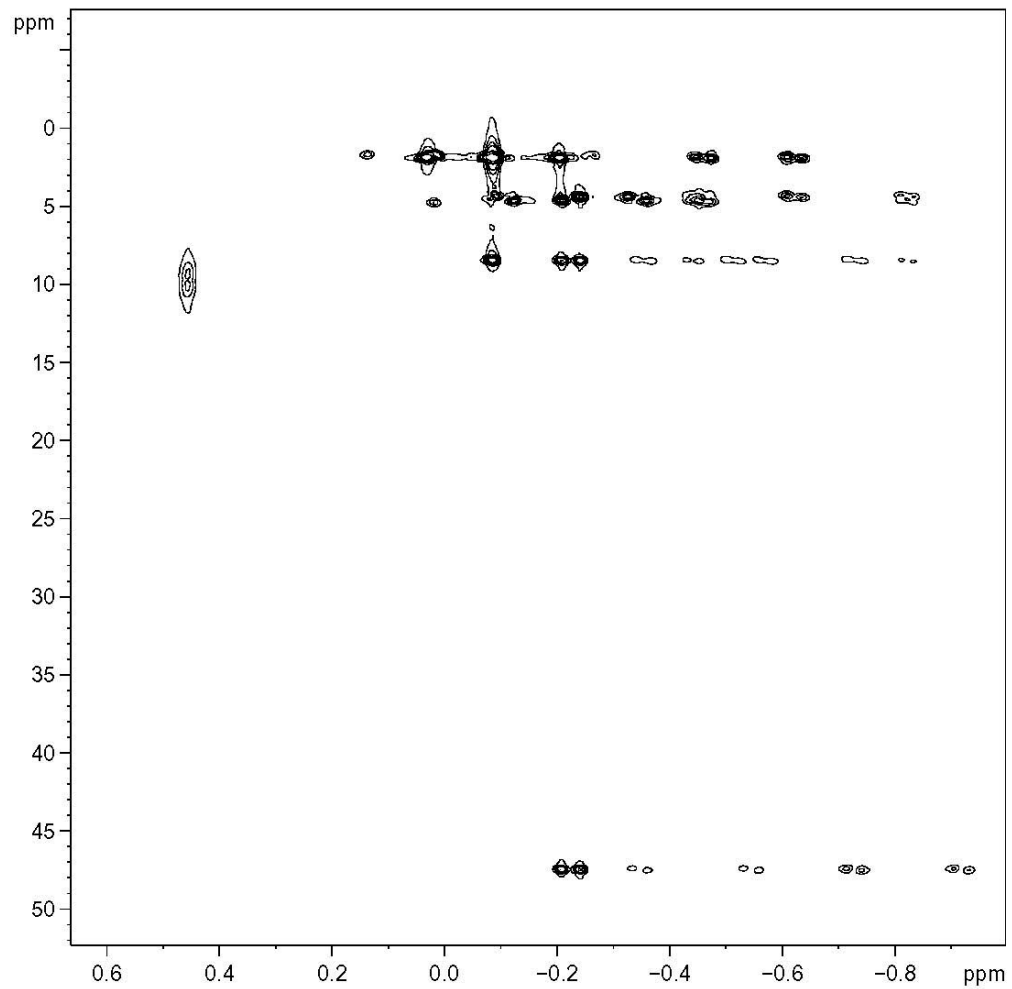
$^1\text{H}$ - $^{13}\text{C}$  HMQC spectrum

The  $^{13}\text{C}$  resonance at 1.7 ppm is folded in this spectrum.



<sup>1</sup>H-<sup>13</sup>C HMBC spectrum

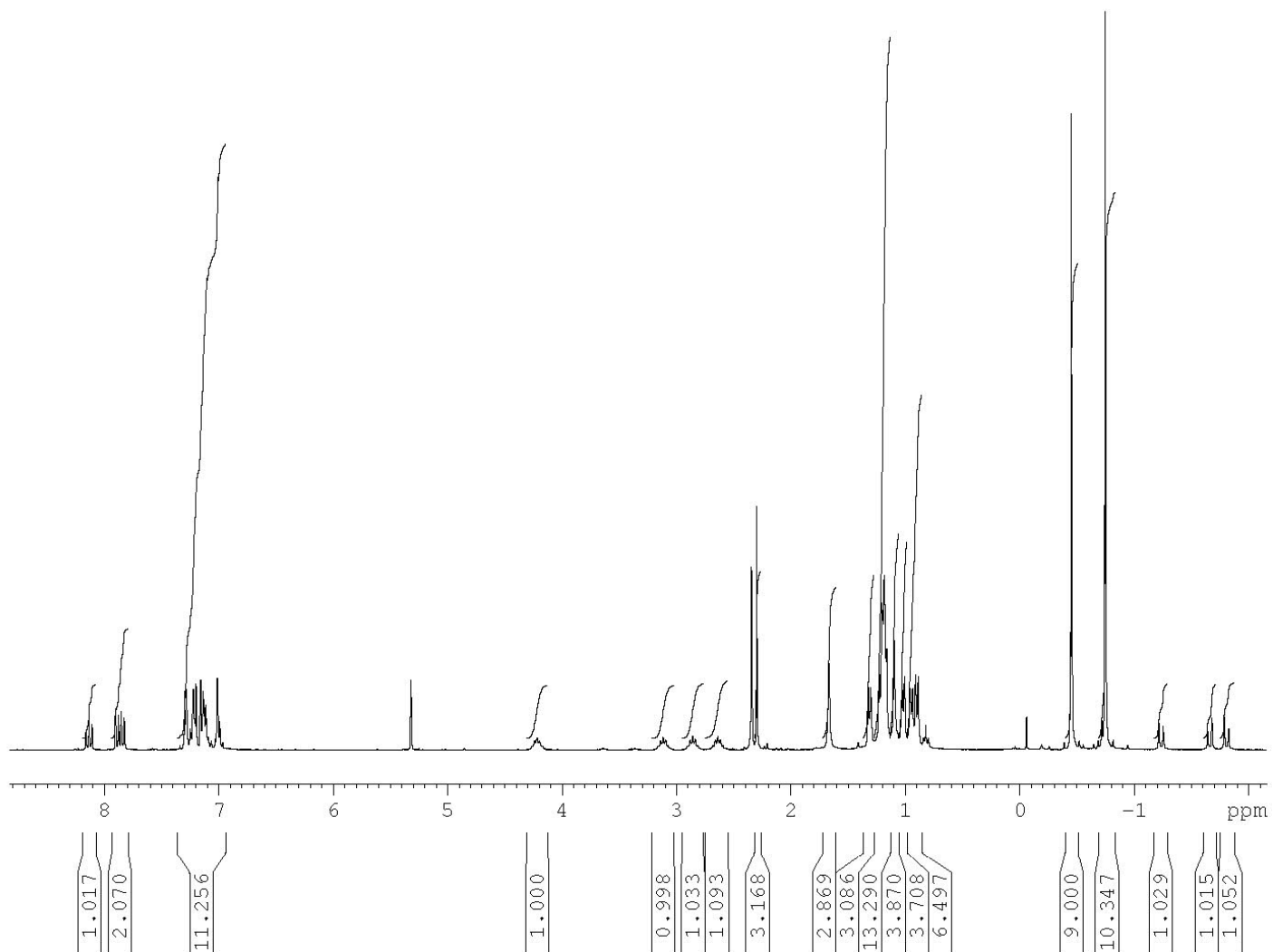
The <sup>13</sup>C resonance at 1.7 ppm is folded in this spectrum.



<sup>1</sup>H-<sup>13</sup>C HMBC spectrur

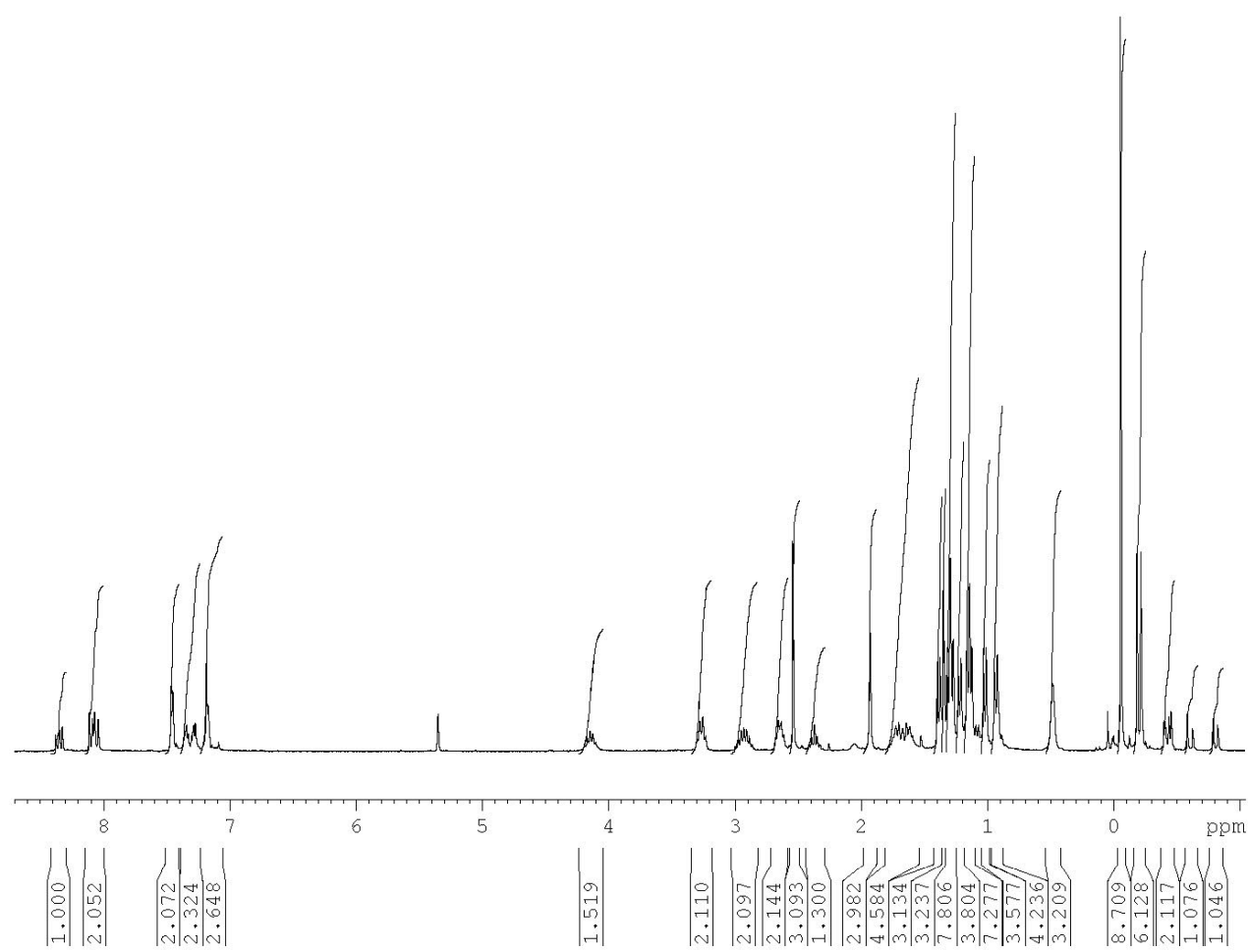
The sw in F1 has been increased to eliminate the folding of the resonance at 1.7 ppm in this spectrum.

$^1\text{H}$  NMR spectrum of **2** ( $\text{CD}_2\text{Cl}_2$ ,  
-50°C, contains residual toluene).





<sup>1</sup>H NMR spectrum of **3** (CD<sub>2</sub>Cl<sub>2</sub>, 25°C).



## References

- 1 R. E. Hurd and B. K. John, *J. Mag. Reson.*, 1991, **91**, 648.
- 2 A. Bax and M. F. Summers, *J. Am. Chem. Soc.*, 1986, **108**, 2093.