Supporting Information - I. Fernández and F. Breher et al.

⁷Li,¹⁵N Heteronuclear Multiple Quantum Shift Correlation – A Fast and Reliable 2D NMR method on natural abundant nucleii

Ignacio Fernández,^{a,*} Pascual Oña Burgos,^a Felix Armbruster,^b Ivo Krummenacher,^b Frank

Breher^{b,*}

 ^a Área de Química Orgánica, Universidad de Almería, Crta. Sacramento s/n, 04230, Almeria, Spain. Fax: +34 950 015648; Tel: +34 950 015481; E-mail: <u>ifernan@ual.es</u>
^b Institut für Anorganische Chemie, Universität Karlsruhe (TH),Engesserstraße 15, 76131 Karlsruhe, Germany. Fax: +49 721 608 7021; Tel:+49 721 608 4855; E-mail: breher@aoc1.uni-karlsruhe.de

Contents

- NMR methods in general
- Figure S1. ¹H, ¹⁵N gHMQC NMR spectrum of **1** at 283 K.
- Figure S2. ¹H, ¹⁵N gHMQC NMR spectrum of **2** at 283 K.
- Figure S3. ¹H, ¹⁵N gHMQC NMR spectrum of **3** at 213 K.
- Figure S4. ¹H, ¹⁵N gHMQC NMR spectrum of **4** at 213 K.
- Figure S5. ¹H, ¹¹⁹Sn gHMQC NMR spectrum of **4** at 213 K.
- Figure S6. ⁷Li,¹H HOESY NMR spectrum of **1** at 283 K.
- Figure S7. ⁷Li, ¹H HOESY NMR spectrum of **3** at 283 K.
- Figure S8. ⁷Li,¹⁵N HMQC NMR spectrum of **1** at 283 K. D1 1s.
- Figure S9. ⁷Li, ¹⁵N HMQC NMR spectrum of 2 at 283 K, D1 = 5s.
- Figure S10. ⁷Li, ¹⁵N HMQC NMR spectrum of $\mathbf{2}$ at 283 K, D1 = 1s.
- Figure S11. ⁷Li, ¹⁵N HMQC NMR spectrum of **3** at 283 K and D1 = 5s.
- Figure S12. ⁷Li, ¹⁵N HMQC NMR spectrum of **3** at 283 K and D1 = 1s.
- Figure S13. ⁷Li, ¹⁵N HMQC NMR spectrum of 4 at 213 K and D1 = 1s.
- Figure S14. ⁷Li, ¹⁵N HMQC NMR spectrum of 4 at 213 K and D1 = 300ms.
- Figure S15. ⁷Li, ¹⁵N HMQC NMR spectrum of **5** at 273 K and D1 = 1s.
- Figure S16-18. ⁷Li T1 inversion-recovery experiments of **1-3** at 283 K.
- Figure S19. ⁷Li T1 inversion-recovery experiments of **4** at 213 K.
- Figure S20. ¹H and ⁷Li NMR spectra of **4** as a function of temperature.

Supporting Information – I. Fernández and F. Breher et al.

NMR methods in general. Spectra were measured on a Bruker Avance 500 spectrometer equipped with a third radiofrequency channel. A 5-mm indirect triple probe head was used. The outer coil was doubly tuned for ¹H and ⁷Li, and the inner coil was tuned for ¹⁵N, ²⁹Si and ¹¹⁹Sn. The 90° pulse widths and operating frequencies were: 11.4 μ s (¹H, 500 MHz), 26.7 μ s (⁷Li, 194.4 MHz), 31 μ s (¹⁵N, 50.7 MHz), 11 μ s (²⁹Si, 99.4 MHz) and 16 μ s (¹¹⁹Sn, 186.4 MHz). The attenuation levels used were 0 dB for proton and lithium, –3 dB for nitrogen and –2 dB for silicon and tin. The spectral references used were TMS for ¹H and ²⁹Si, 1M LiBr in D₂O for ⁷Li, NH₃ for ¹⁵N, and SnMe₄ for ¹¹⁹Sn. For the ⁷Li, ¹⁵N HMQC NMR experiments the 90° pulse widths and attenuation levels were 22.7 μ s / 0 dB for lithium, and 95 μ s / –3 dB for nitrogen. NMR samples of **1-5** were prepared in oven-dried 5-mm NMR tubes and sealed under nitrogen. The final concentration in all five samples were 0.1 M. Unless otherwise stated, standard Bruker software routines (TOPSPIN and XWINNMR) were used for the 1D and 2D NMR measurements.

Supplementating defiain (Esil) for - Cleiniaal abolton unitations eher et al.



Figure S1. ¹H, ¹⁵N gHMQC NMR spectrum of 1, δ 233.3 and 285.9. Experimental time = 2h 43min (500 MHz, 283 K in THF- d_8 solution).

Supplomentation and the field for Clientian and the senter et al. This journal is (c) The Royal Society of Chemistry 2009



Figure S2. ¹H,¹⁵N gHMQC NMR spectrum of **2**, δ 234.7 and 289.3 ppm. Experimental time = 2h 43min (500 MHz, 283 K in THF- d_8 solution). Resonances marked with an asterisk are due to toluene, which was used as solvent in the synthesis of **2**.



Figure S3. ¹H,¹⁵N gHMQC NMR spectrum of **3**, δ 244.4 and 289.5 ppm. Experimental time = 3h 27min (500 MHz, 283 K in THF- d_8 solution). Resonances marked with an asterisk are due to minor amounts of decomposition products.

Current Data Parameters NAME n5tin 1 EXPNO 31
 PROCNO
 1

 F2 - Acquisition Parameters Date_____20081204
 20081204

 Time
 21.45

 INSTRUM
 spect

 INSTRUM
 spect

 PROBHD
 5 mm TBI 1H-31

 PULPROG
 inv4gplmdaf

 TD
 1024

 SOLVENT
 THF

 NS
 32

 FIDRES
 4.882813 Hz

 AQ
 0.1025500 sec

 RG
 23170.5

 DW
 100.0000 usec

 DE
 4.50 usec

 TE
 193.0 K

 d0
 0.0000000 sec

 D1
 1.00000000 sec

 D16
 0.00001400 sec

 D16
 0.00001400 sec

 D16
 0.00001400 sec

 N0
 0.0000400 sec

 D16
 0.00001400 sec

 N0
 0.0000400 sec

 Emergence
 CHANNEL f1

 NUC1
 1H

 P1
 10.50 usec

 p2
 21.00 usec

 PL1
 0.00 dB

 SFO1
 500.1318260 MHz
 ppm - 180 ======= CHANNEL f2 ======== 15N 22.80 usec -3.00 dB 50.6914160 MHz NUC2 P3 PL2 SFO2 -200
 =====
 GRADIENT CHANNEL =====

 GPNAM1
 SINE.100

 GPNAM2
 SINE.100

 GPNAM3
 SINE.100

 GPPAM3
 SINE.100

 GPPAM3
 SINE.100

 GP2
 30.00 %

 GPZ3
 50.10 %

 GPC
 50.10 %
 GPNAM1 GPNAM2 GPNAM3 GPZ1 GPZ2 GPZ3 P16 -220 1000.00 usec -240 F1 - Acquisition parameters ND0 2 TD 256 SF01 50.69142 MHz FIDRES 39.617142 Hz 2 256 50.69142 MHz 39.617142 Hz 200.073 ppm QF 260 SW FnMODE
 F2 - Processing parameters

 SI
 1024

 SF
 500.1300000 MHz

 WDW
 QSINE

 SB
 0

 LB
 0.00 Hz

 GB
 0

 PC
 1.40
 -280 - 300 F1 - Processing parameters SI 2048 MC2 QF SF 50.6777330 MHz WDW QSINE SSB 0 LB 0.00 Hz GB 0 320 340 - 360 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 6.0 1.5 1.0 ppm

Figure S4. ¹H,¹⁵N gHMQC NMR spectrum of **4**, δ 254.7 and 291.4 ppm. Experimental time = 2h 43min (500 MHz, 213 K in THF- d_8 solution).



Figure S5. ¹H, ¹¹⁹Sn gHMQC NMR spectrum of 4, δ -311.2 ppm. Experimental time = 1h 25min (500 MHz, 213 K in THF- d_8 solution).



Figure S6. ⁷Li, ¹H HOESY NMR spectrum of **1**. Experimental time = 3h 29min (194.4 MHz, 283 K in THF- d_8 solution).

Supplymentaring diefial (ESil) for -Cliefficial above nunications et al.



Figure S6. ⁷Li, ¹H HOESY NMR spectrum of **2**. Experimental time = 6h 59min (194.4 MHz, 283 K in THF- d_8 solution).



Figure S7. ⁷Li, ¹H HOESY NMR spectrum of **3**. Experimental time = 3h 29min (194.4 MHz, 283 K in THF- d_8 solution). Resonances marked with an asterisk are due to minor amounts of decomposition products or impurities.

Supply mentaring a terrar and for -Cherrical a determinications where et al.



Figure S8. ⁷Li,¹⁵N HMQC NMR spectrum of **1**, δ 286.1 ppm. D1 = 10s, experimental time = 7h 33min (194.4 MHz, 283 K in THF- d_8 solution). Qsine processing in both dimensions prior Fourier transformation.



Figure S8. ⁷Li, ¹⁵N HMQC NMR spectrum of 1, δ 286.1 ppm. D1 = 1s, experimental time = 40 min (194.4 MHz, 283 K in THF-*d*₈ solution). Qsine processing in both dimensions prior Fourier transformation.

Supplomentation and the field for Clientian and the senter et al. This journal is (c) The Royal Society of Chemistry 2009



Figure S9. ⁷Li,¹⁵N HMQC NMR spectrum of **2**, δ 289.3 ppm. D1 = 5s, experimental time = 4h 20 min (194.4 MHz, 283 K in THF- d_8 solution). Exponential processing in both dimensions prior Fourier transformation.

Supplymentaring/alterial: (ESil) for-Cherrical and manications et al.



Figure S10. ⁷Li,¹⁵N HMQC NMR spectrum of **2**, δ 289.5 ppm. D1 = 1s, experimental time = 1h 55min (194.4 MHz, 283 K in THF- d_8 solution). Exponential processing in both dimensions prior Fourier transformation.



Figure S11. ⁷Li,¹⁵N HMQC NMR spectrum of **3**, δ 289.5 ppm. D1 = 5s, experimental time = 3h 34min (194.4 MHz, 283 K in THF- d_8 solution). Exponential processing in both dimensions prior Fourier transformation.



Figure S12. ⁷Li,¹⁵N HMQC NMR spectrum of **3**, δ 289.5 ppm. D1 = 1s, experimental time = 57 min (194.4 MHz, 283 K in THF- d_8 solution). Exponential processing in both dimensions prior Fourier transformation.



Figure S13. ⁷Li,¹⁵N HMQC NMR spectrum of **4**, δ 291.4 ppm. D1 = 1s, experimental time = 49 min (194.4 MHz, 213 K in THF- d_8 solution). Exponential processing in both dimensions prior Fourier transformation.



Figure S14. ⁷Li,¹⁵N HMQC NMR spectrum of **4**, δ 291.4 ppm. D1 = 300 ms, experimental time = 22 min (194.4 MHz, 213 K in THF- d_8 solution). Exponential processing in both dimensions prior Fourier transformation.

Supplymentaring/alterial: (ESil) for-Cherrical and manications et al. This journal is (c) The Royal Society of Chemistry 2009



Figure S15. ⁷Li, ¹⁵N HMQC NMR spectrum of 5, δ 78.66 ppm. D1 = 1s, experimental time = 49 min (194.4 MHz, 213 K in THF solution). Gaussian processing in both dimensions prior Fourier transformation.



Figure S16. ⁷Li T1 inversion-recovery experiment of **1** at 283 K (194.4 MHz, in THF- d_8 solution). T1 = 3.04 s.

7Li T1, e20 sil2, THF-d8, 283 K



Figure S17. ⁷Li T1 inversion-recovery experiment of **2** at 283 K (194.4 MHz, in THF- d_8 solution). T1 = 418 ms.



Figure S18. ⁷Li T1 inversion-recovery experiment of **3** at 283 K (194.4 MHz, in THF- d_8 solution). T1 = 418 ms.



Figure S19. ⁷Li T1 inversion-recovery experiment of **4** at 213 K (194.4 MHz, in THF- d_8 solution). T1 = 216 ms.

Supplementation of the Royal Society of Chemistry 2009



Figure S20. ¹H (left) and ⁷Li (right) NMR spectra of **4** as a function of temperature (500 and 194.4 MHz, in THF-*d*₈ solution).