Solution Structures of the Mixed Aggregates Derived from Lithium Acetylides and a Camphor-Derived Amino Alkoxide.

by

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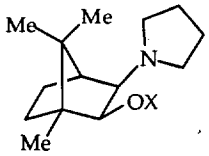
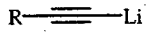
Supporting Information



13; X = H
14; X = Li



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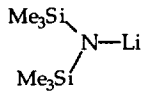
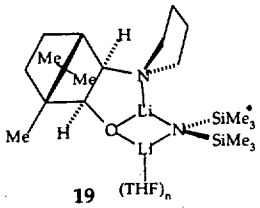
15; R = Ph



LiHMDS



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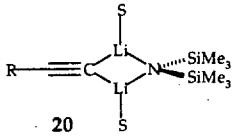

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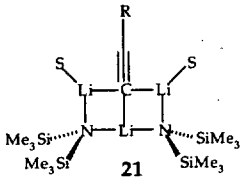

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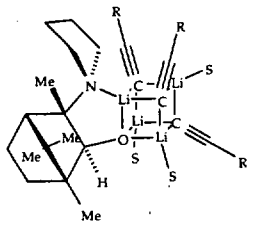

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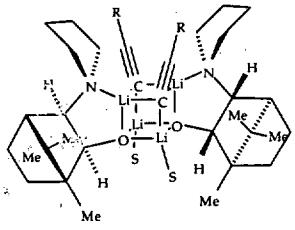

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Figure 1. ^{6}Li NMR spectra of [^{6}Li]LiCPA/[^{6}Li]**14** mixtures in 50% THF/pentane at -115 °C.

Figure 2. ^{6}Li NMR spectra of [^{6}Li,^{13}C]LiCPA/[^{6}Li]**14** mixtures in 50% THF/pentane at -115 °C.

Figure 3. ^{13}C NMR spectra of [^{6}Li,^{13}C]LiCPA/[^{6}Li]**14** mixtures in 50% THF/pentane at -115 °C.

Figure 4. ^{6}Li NMR spectra of [^{6}Li]LiCPA/[^{6}Li,^{15}N]**14** mixtures in 50% THF/pentane at -115 °C.

Figure 5. ^{15}N NMR spectra of [^{6}Li]LiCPA/[^{6}Li,^{15}N]**14** mixtures in 50% THF/pentane at -115 °C.

Figure 6. ^{6}Li, ^{13}C-HMQC and ^{1}J(^{6}Li,^{13}C)-resolved spectra of a 3:1 [^{6}Li,^{13}C]LiCPA/[^{6}Li]**14** mixture in 50% THF/pentane at -115 °C.

Figure 7. ^{6}Li,^{6}Li-EXSY spectra of 3:1 a [^{6}Li]LiCPA/[^{6}Li]**14** mixture in 50% THF/pentane at –110 °C.

Figure 8. ^{6}Li NMR spectra of [^{6}Li]PhCCLi/[^{6}Li]**14** mixtures in 3:1:1 toluene/THF/pentane at -115 °C.

Figure 9. ^{6}Li NMR spectra of [^{6}Li,^{13}C]PhCCLi/[^{6}Li]**14** mixtures in 3:1:1 toluene/THF/pentane at -115 °C.

Figure 10. ^{13}C NMR spectra of [^{6}Li]PhCCLi/[^{6}Li]**14** mixtures in 3:1:1 toluene/THF/pentane at -115 °C.

Figure 11. ^{6}Li NMR spectra of [^{6}Li]PhCCLi/[^{6}Li,^{15}N]**14** mixtures in 3:1:1 toluene/THF/pentane at -115 °C.

Figure 12. ^{15}N NMR spectra of [^{6}Li]PhCCLi/[^{6}Li,^{15}N]**14** mixtures in 3:1:1 toluene/THF/pentane at -115 °C.

Figure 13. ^{6}Li, ^{13}C-HMQC and ^{1}J(^{6}Li,^{13}C)-resolved spectra of a 3:1 [^{6}Li,^{13}C]PhCCLi /^{6}Li]**14** mixture in 3:1:1 THF/pentane at -115 °C.

Figure 14. ^{6}Li NMR spectra of [^{6}Li]LiCPA/[^{6}Li]**14** mixtures in 3:1:1 toluene/THF/pentane at -115 °C.

Figure 15. ^{6}Li NMR spectra of [^{6}Li]PhCCLi/[^{6}Li]**14** mixtures in 50% THF/pentane at -115 °C.

Figure 16. ^{6}Li NMR spectra of [^{6}Li]*t*-BuCCLi/[^{6}Li]**14** mixtures in 50% THF/pentane at -115 °C.

Figure 17. ^{6}Li NMR spectra of [^{6}Li]LiCPA/[^{6}Li]**14** mixtures in neat Me_2NEt at -100 °C.

Figure 18. ^{6}Li NMR spectra of [^{6}Li]PhCCLi/[^{6}Li]**14** mixtures in neat Me_2NEt at -100 °C.

Figure 19. ^{6}Li and ^{15}N NMR spectra of [^{6}Li]**14**/[^{6}Li,^{15}N]LiHMDS in neat Me_2NEt at -100 °C.

Figure 20. ^{6}Li and ^{15}N NMR spectra of [^{6}Li,^{15}N]**14**/[^{6}Li,^{15}N]LiHMDS in neat Me_2NEt at -100 °C.

Figure 21. ^{6}Li NMR spectra of [^{6}Li]LiCPA/[^{6}Li,^{15}N]LiHMDS mixtures and [^{6}Li,^{13}C]LiCPA/[^{6}Li]LiHMDS in Me_2NEt at –100 °C.

Figure 22. ^{13}C NMR spectra of [^{6}Li,^{13}C]LiCPA/[^{6}Li]LiHMDS mixtures in Me_2NEt at –100 °C.

Figure 23. ^{15}N NMR spectra of a [^{6}Li]LiCPA/[^{6}Li,^{15}N]LiHMDS mixture in Me_2NEt at –100 °.

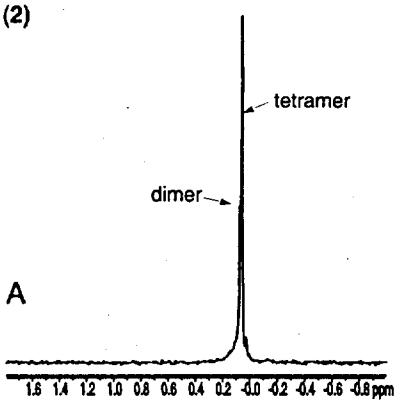
Figure 24. (A) ^{1}J(^{6}Li,^{13}C)-resolved spectrum of 1:1 [^{6}Li,^{13}C]LiCPA/[^{6}Li]LiHMDS. (B) ^{6}Li,^{13}C-HMQC of 1:1 [^{6}Li,^{13}C]LiCPA/[^{6}Li]LiHMDS in Me_2NEt at –100 °C.

Figure 25. (A) ^{1}J(^{6}Li,^{13}C)-resolved spectrum of 1:1 [^{6}Li]LiCPA/[^{6}Li,^{15}N]LiHMDS. (B) ^{6}Li,^{15}N-HMQC of 1:1 [^{6}Li]LiCPA/[^{6}Li,^{15}N]LiHMDS in Me_2NEt at –100 °C.

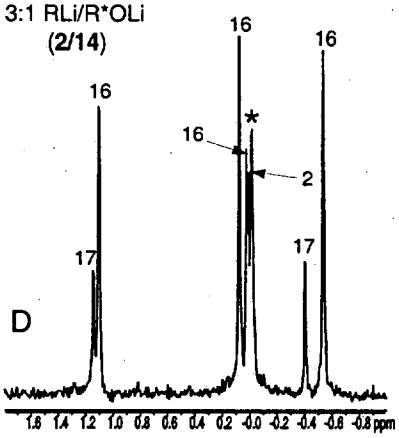
Figure 26. ^{6}Li and ^{13}C NMR spectra of [^{6}Li,^{13}C]PhCCLi]/[^{6}Li]LiHMDS in neat Me_2NEt at -100 °C.

Figure 27. ^{6}Li and ^{15}N NMR spectra of [^{6}Li]PhCCLi]/[^{6}Li,^{15}N]LiHMDS in neat Me_2NEt at -100 °C.

RLi
(2)



3:1 RLi/R*OLi
(2/14)



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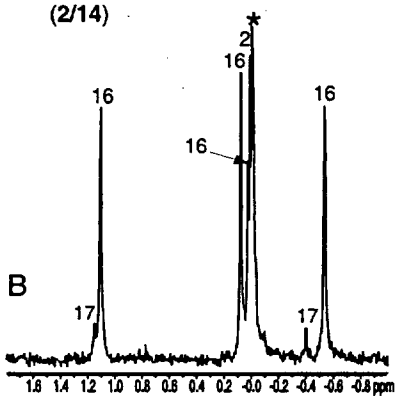
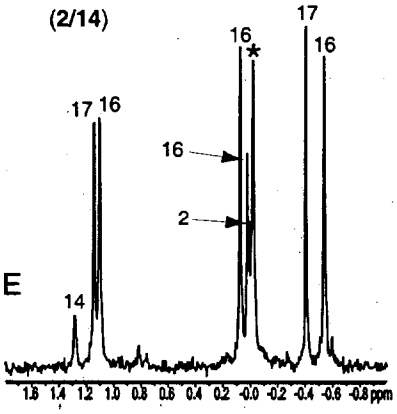
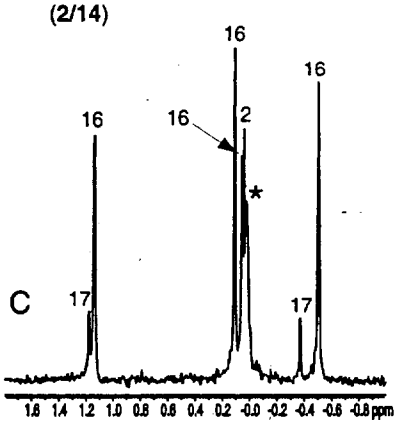
(2/14)



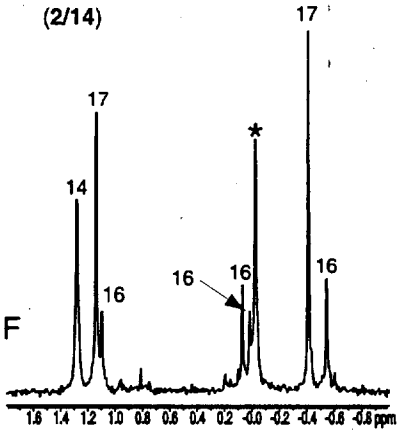
2:1 RLi/R*OLi
(2/14)



4:1 RLi/R*OLi
(2/14)



1:1 RLi/R*OLi
(2/14)



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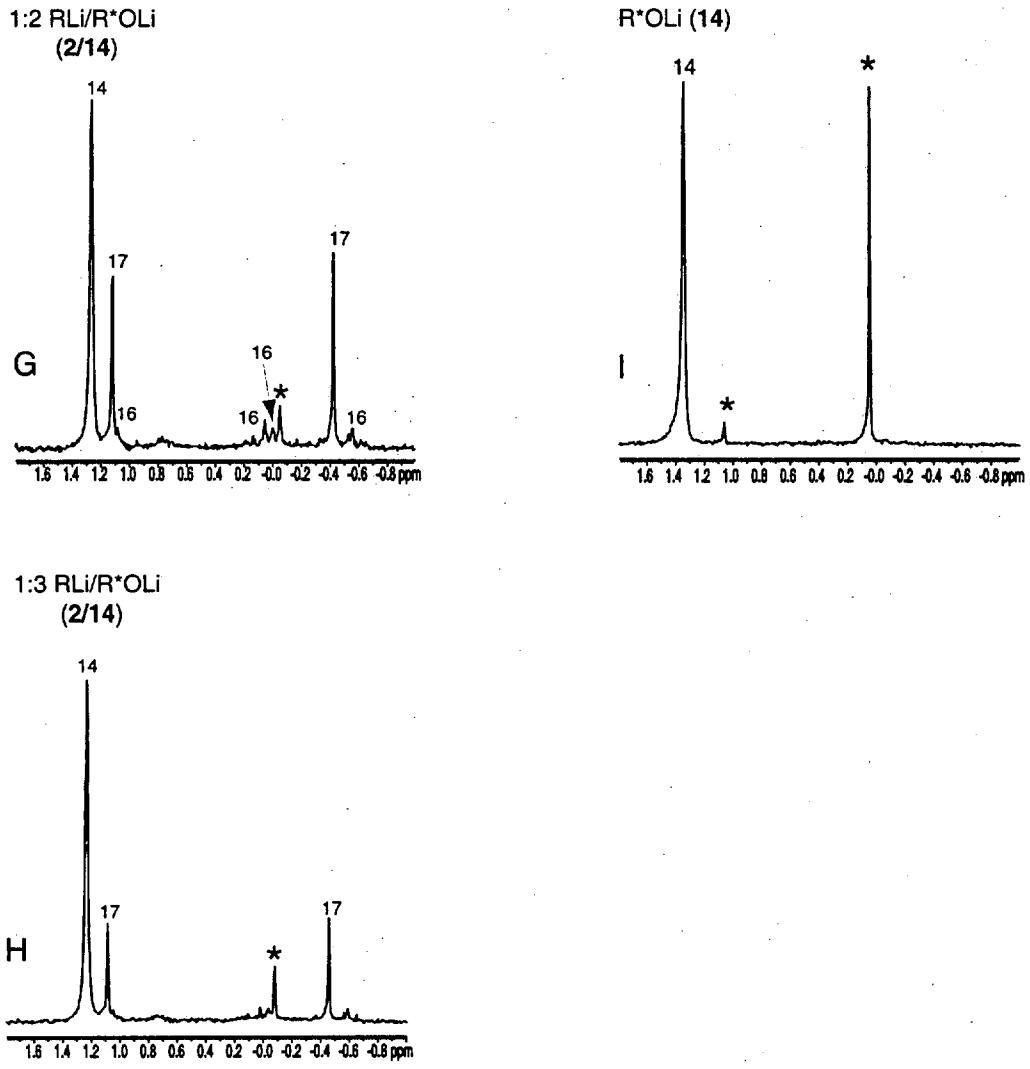


Figure 1. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]LiCPA (**2**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and ≥ 1.0 equiv of [^{6}Li]LiHMDS) in 50% THF/pentane at -115 °C. The total titer of LiCPA and **14** is 0.10 M in the proportions labeled on each spectrum. (LiHMDS is denoted by *.)

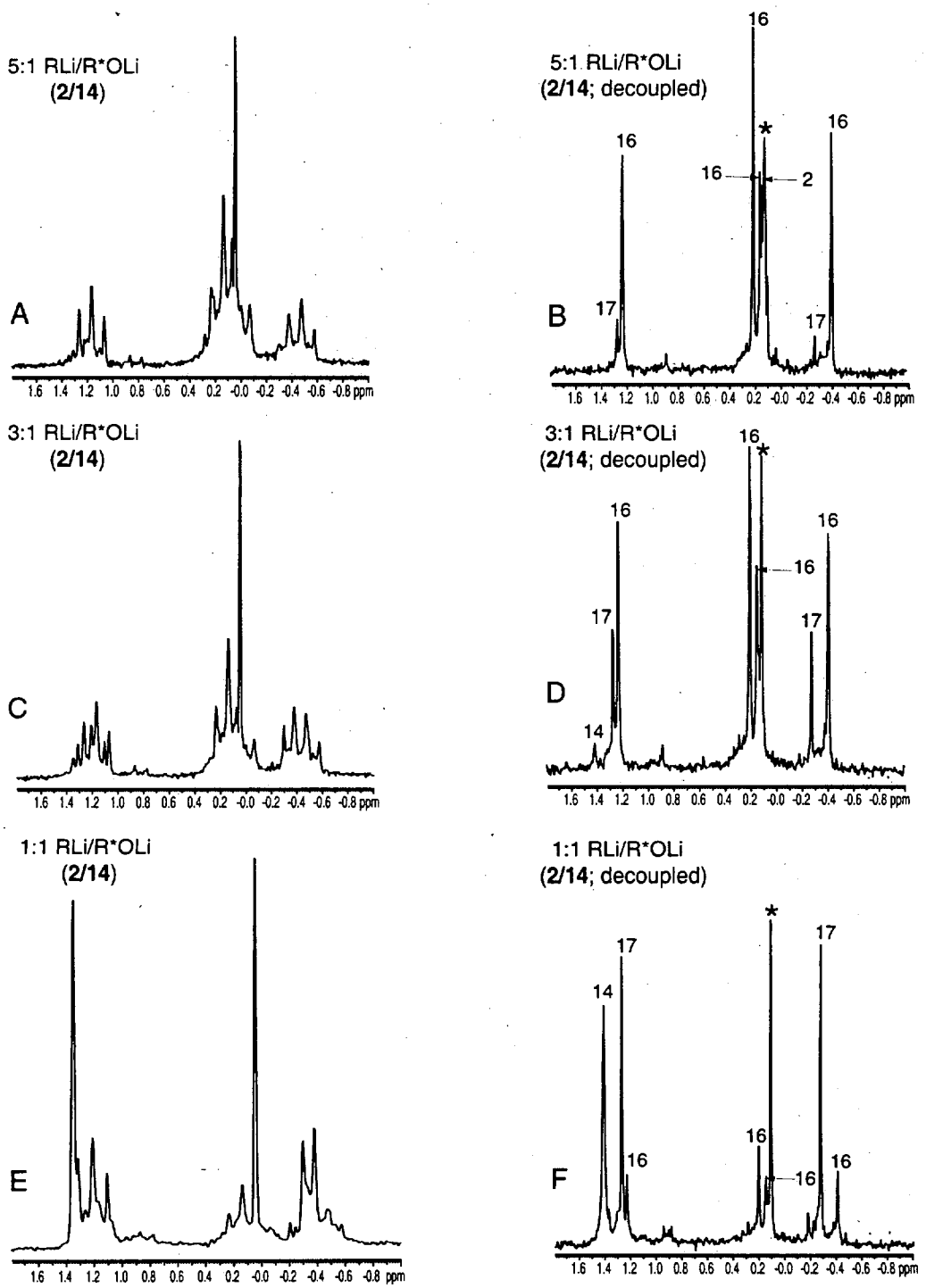


Figure 2. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li,^{13}C]LiCPA (**2**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and ≥ 1.0 of [^{6}Li]LiHMDS) in 50% THF/pentane at -115 °C. The total titer of LiCPA and **14** is 0.2 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{13}C broad-band decoupling. (LiHMDS is denoted by *.)

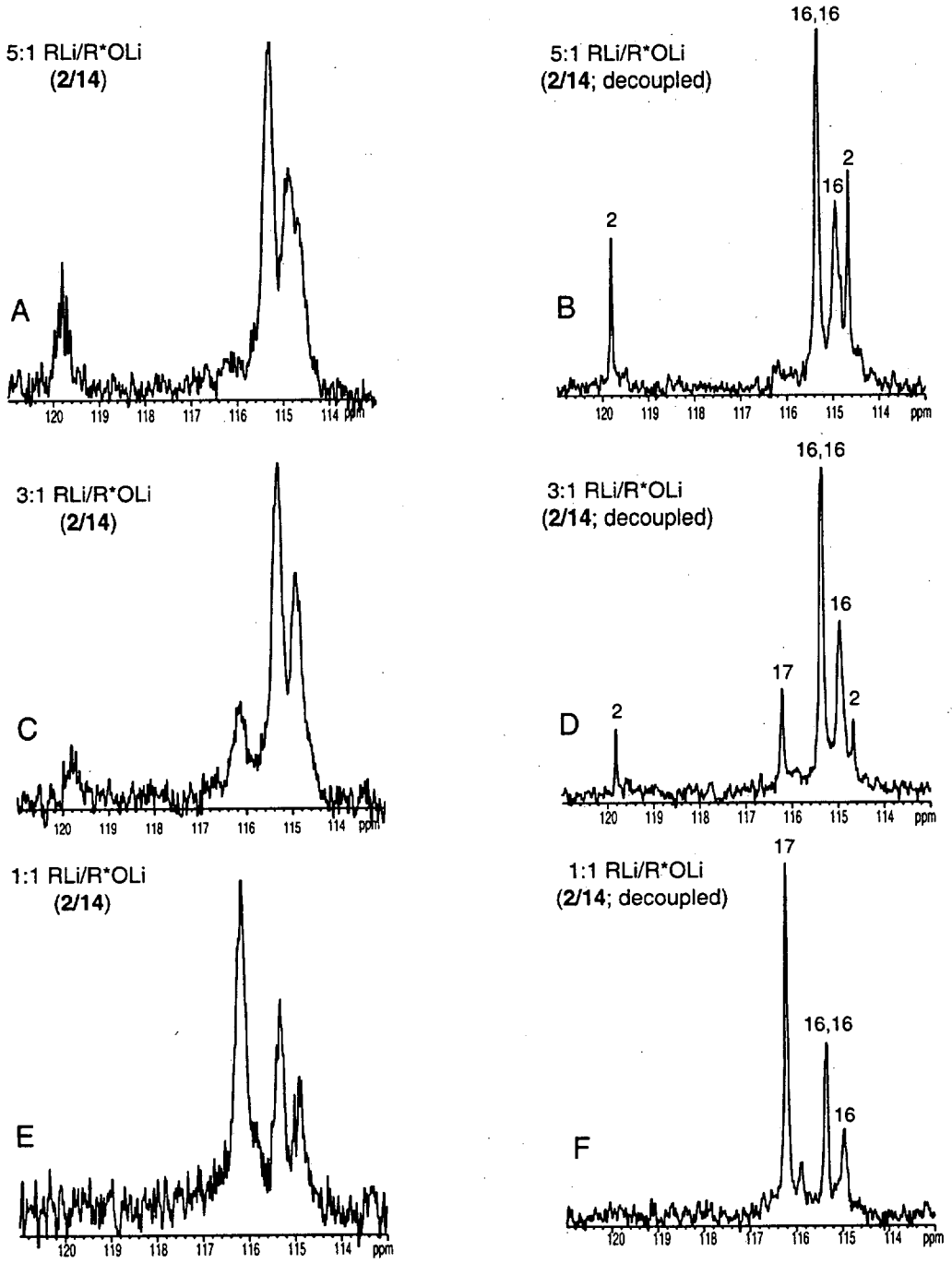


Figure 3. ^{13}C NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li,^{13}C]LiCPA (**2**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and ≥ 1.0 equiv of [^{6}Li]LiHMDS) in 1:1 THF/pentane at -115 °C. The total titer of LiCPA and **14** is 0.2 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{6}Li broad-band decoupling.

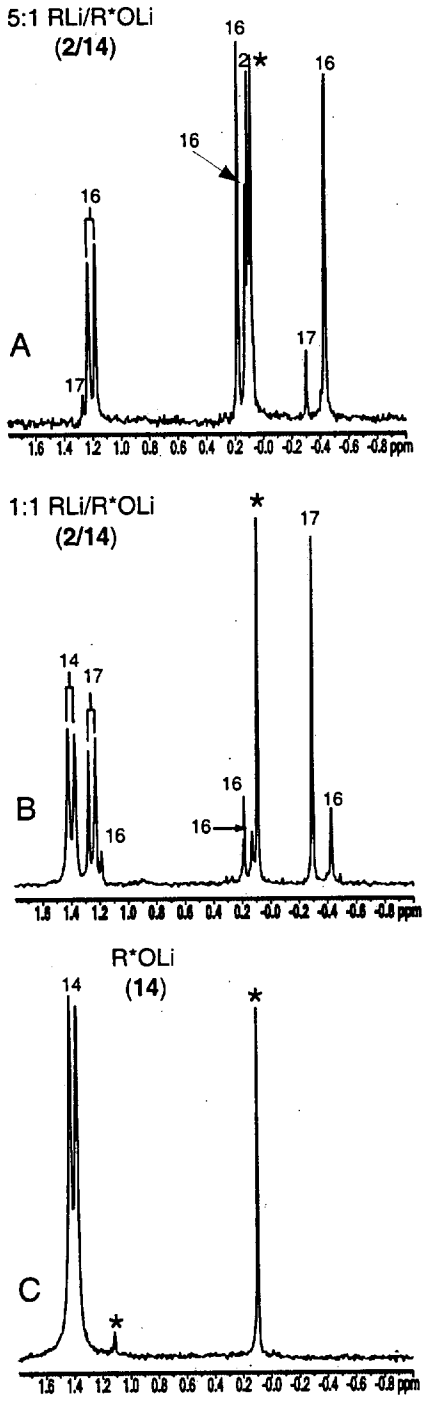


Figure 4. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]LiCPA (**2**) and [^{6}Li,^{15}N]**14** (prepared *in situ* from the alcohol **13** and $\geq$ 1.0 equiv of [^{6}Li]LiHMDS) in 50% THF/pentane at -115 °C. The total titer of LiCPA and **14** is 0.1 M in the proportions labeled on each spectrum. (LiHMDS is denoted by *.)

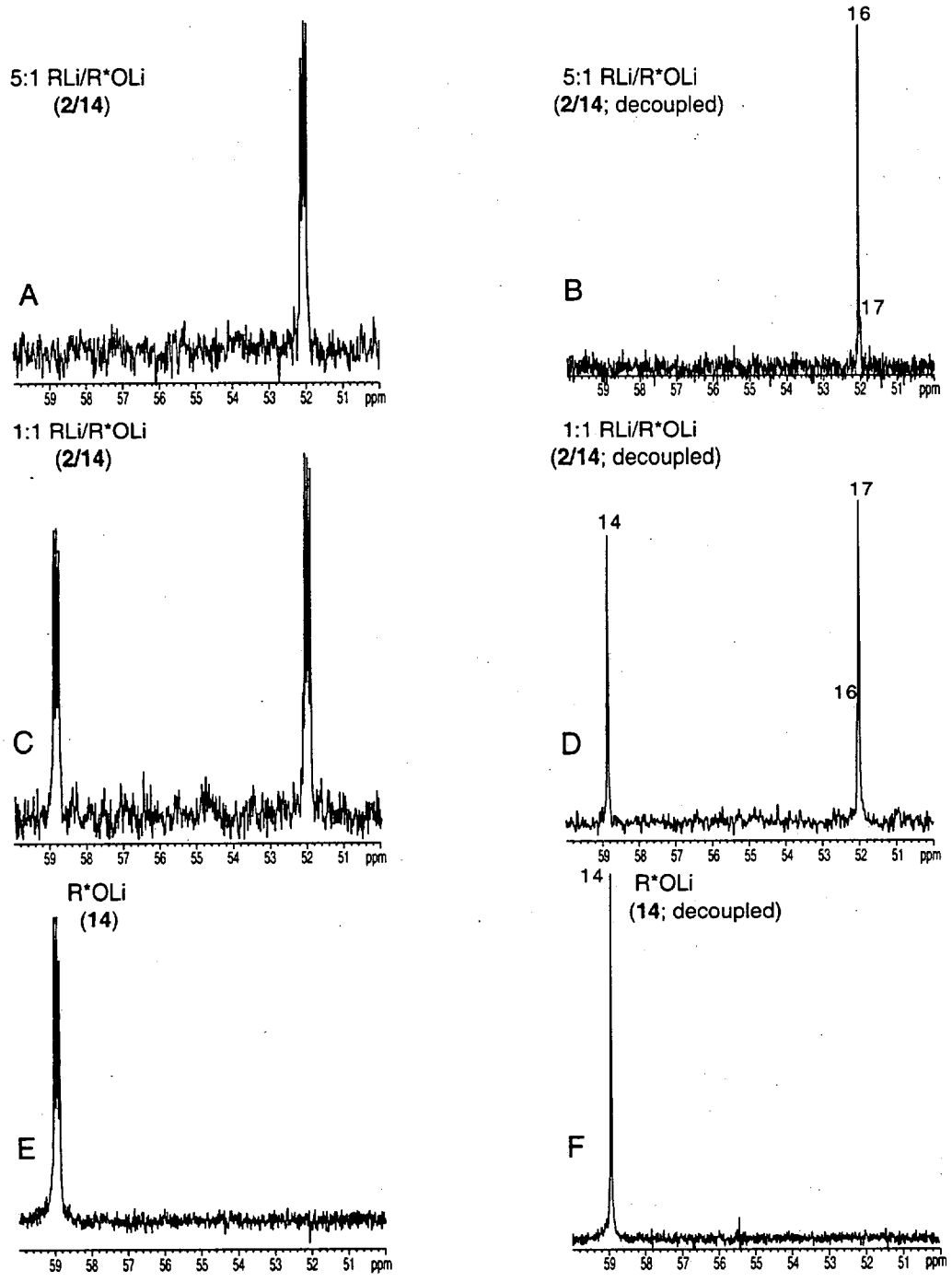


Figure 5. ^{15}N NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]LiCPA (**2**) and [^{6}Li,^{15}N]**14** (prepared *in situ* from the alcohol [^{15}N]**13** and ≥ 1.0 equiv of [^{6}Li]LiHMDS) in 50% THF/pentane at -115 °C. The total titer of LiCPA and **14** is 0.1 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{6}Li broad-band decoupling.

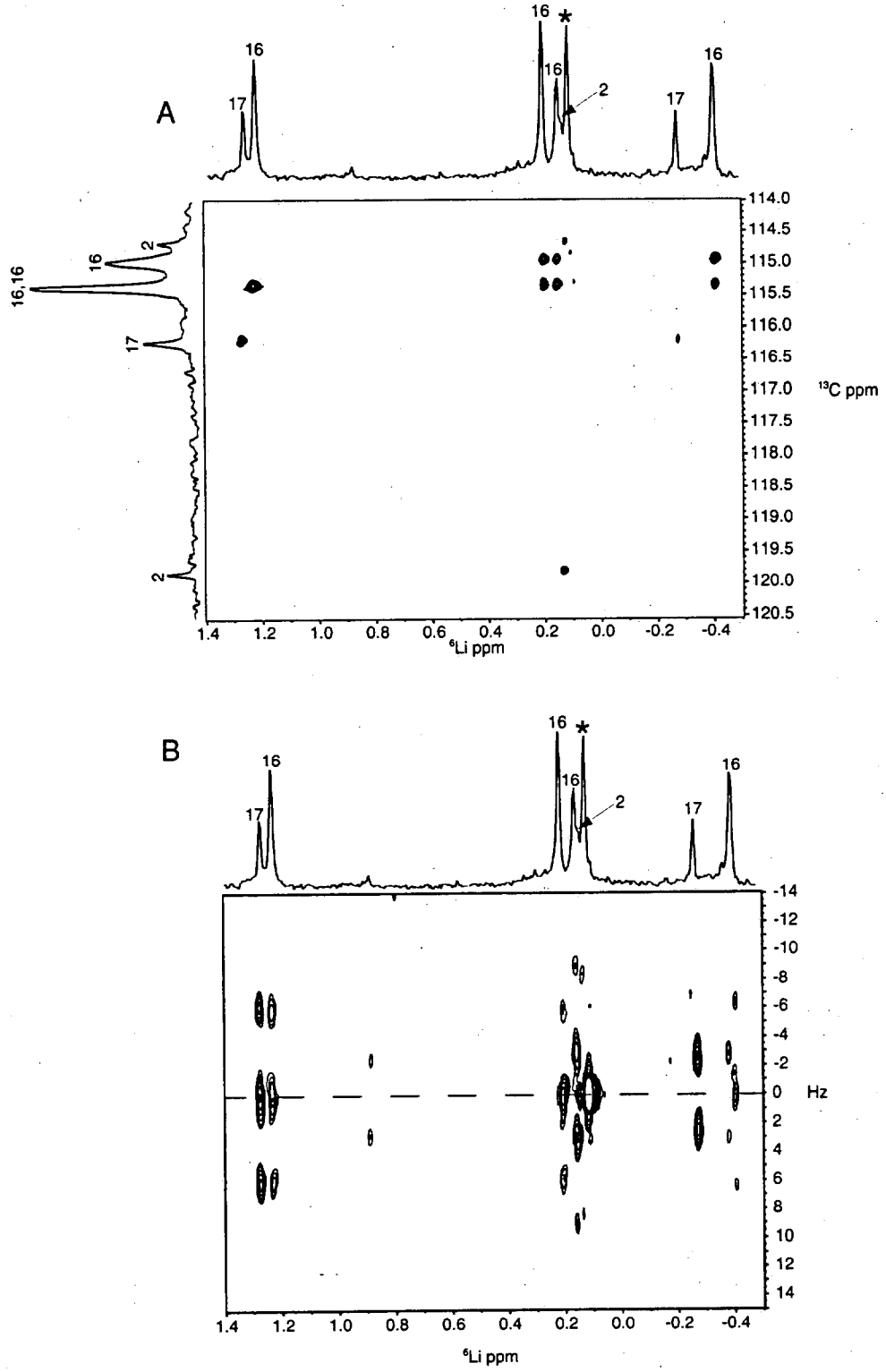
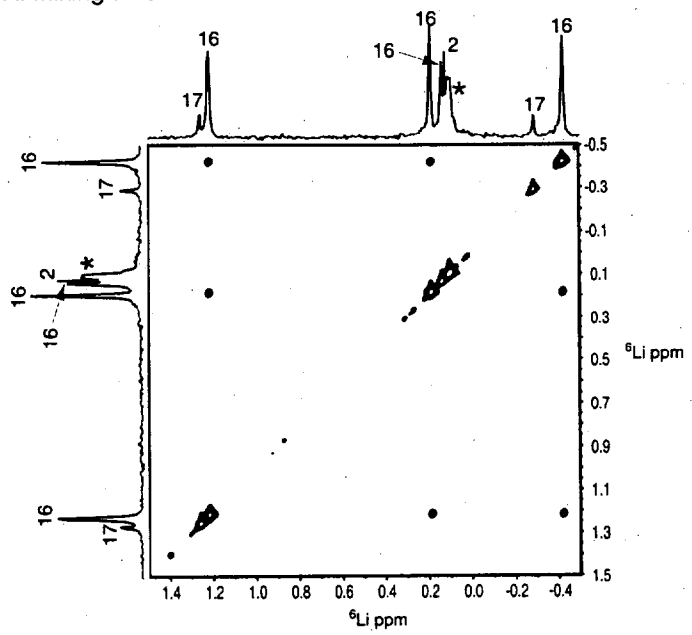
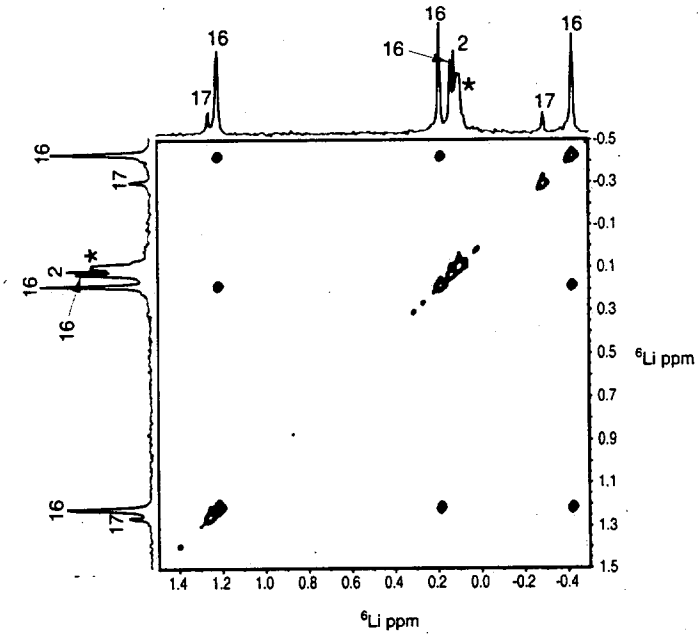


Figure 6. Spectra of 3:1 RLi/R*OLi showing mixed tetramers **16** and **17**. Spectra were recorded on mixtures of [^{6}Li,^{13}C]LiCPA (**2**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and ≥ 1.0 equiv of [^{6}Li]LiHMDS) in 50% THF/pentane at -115 °C. The total titer of LiCPA and **14** is 0.2 M. (A) ^{6}Li,^{13}C-HMQC spectrum; (B) ^{1}J(^{6}Li,^{13}C)-resolved spectrum. (LiHMDS is denoted by *.)

A. Mixing time = 0.2 s



B. Mixing time = 0.5 s



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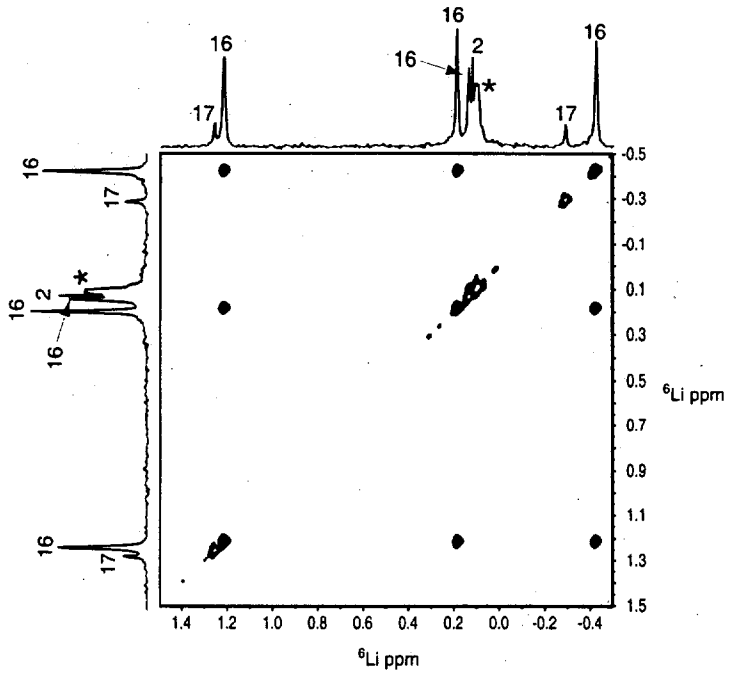
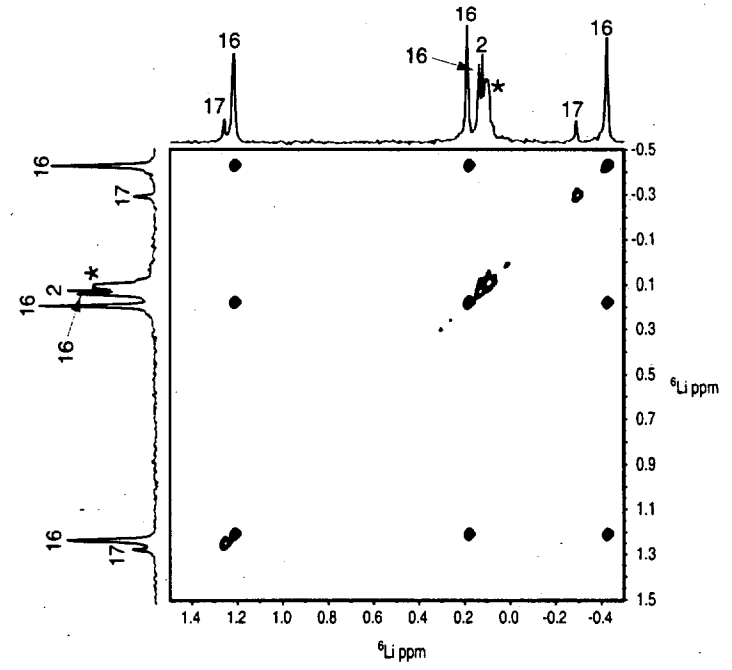
C. Mixing time = 1.0 s



D. Mixing time = 2.0 s



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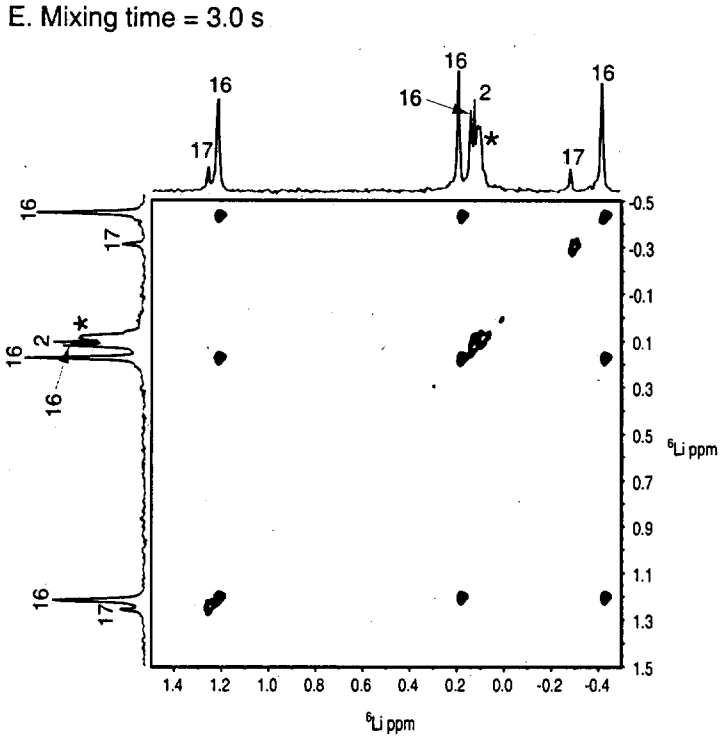
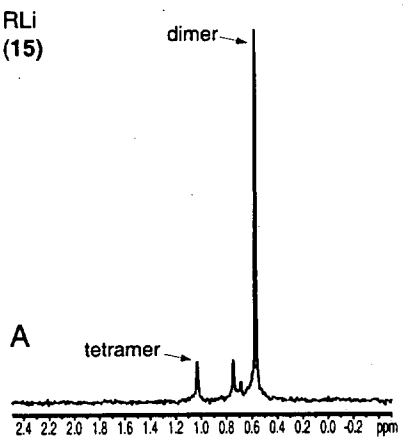
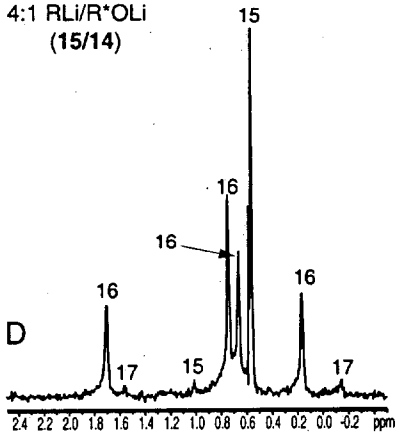
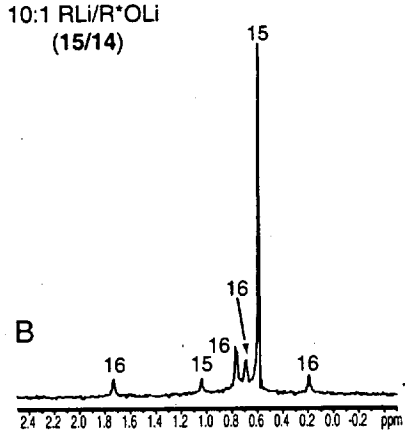
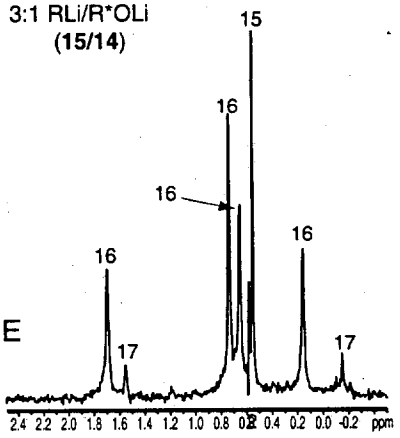


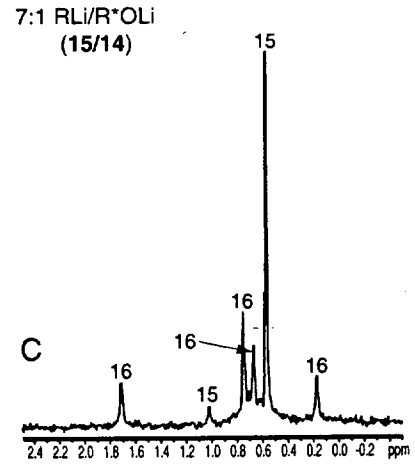
Figure 7. ^{6}Li,^{6}Li-EXSY spectra of 3:1 RLi/R*OLi showing mixed tetramers **16** and **17**. Spectra were recorded on mixtures of [^{6}Li]LiCPA (**2**) and [^{6}Li]**14** (prepared in situ from the alcohol **13** and $\geq$ 1.0 equiv. of [^{6}Li]LiHMDS) in 50% THF/pentane at –110 °C. The total titer of LiCPA and **14** is 0.5 M. Mixing times are indicated on individual spectra. (LiHMDS is denoted by *.)

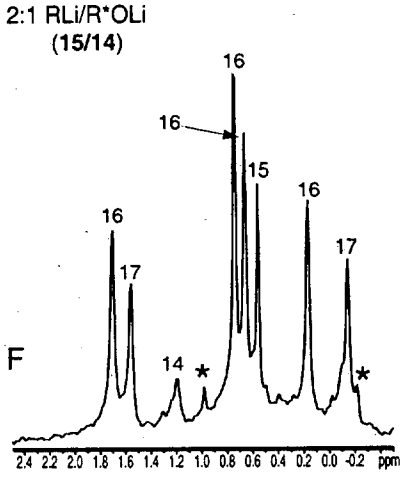












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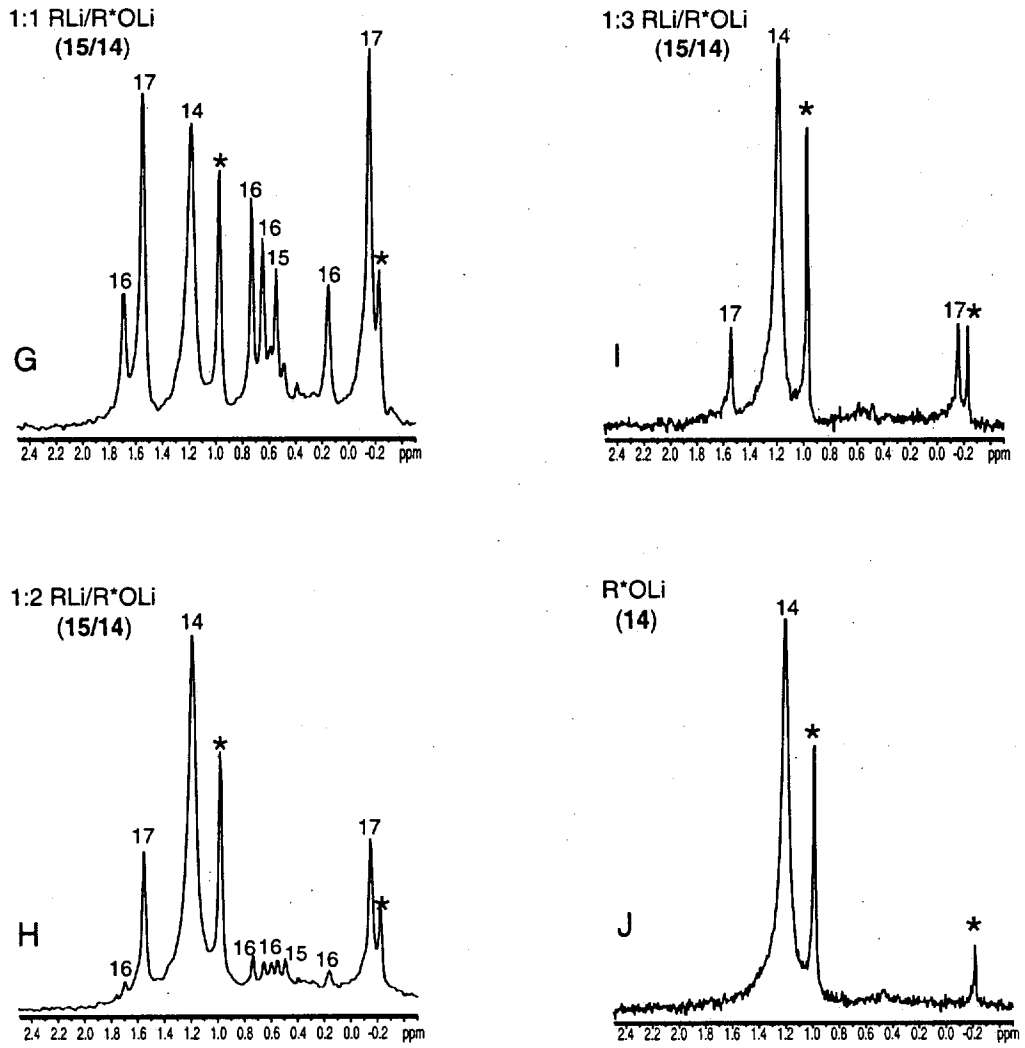


Figure 8. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]PhCCLi (**15**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and $\geq$ 1.0 equiv of [^{6}Li]LiHMDS) in 3:1:1 toluene/THF/pentane at -115 °C. The total titer of PhCCLi and **14** is 0.10 M in the proportions labeled on each spectrum. (LiHMDS is denoted by *.)

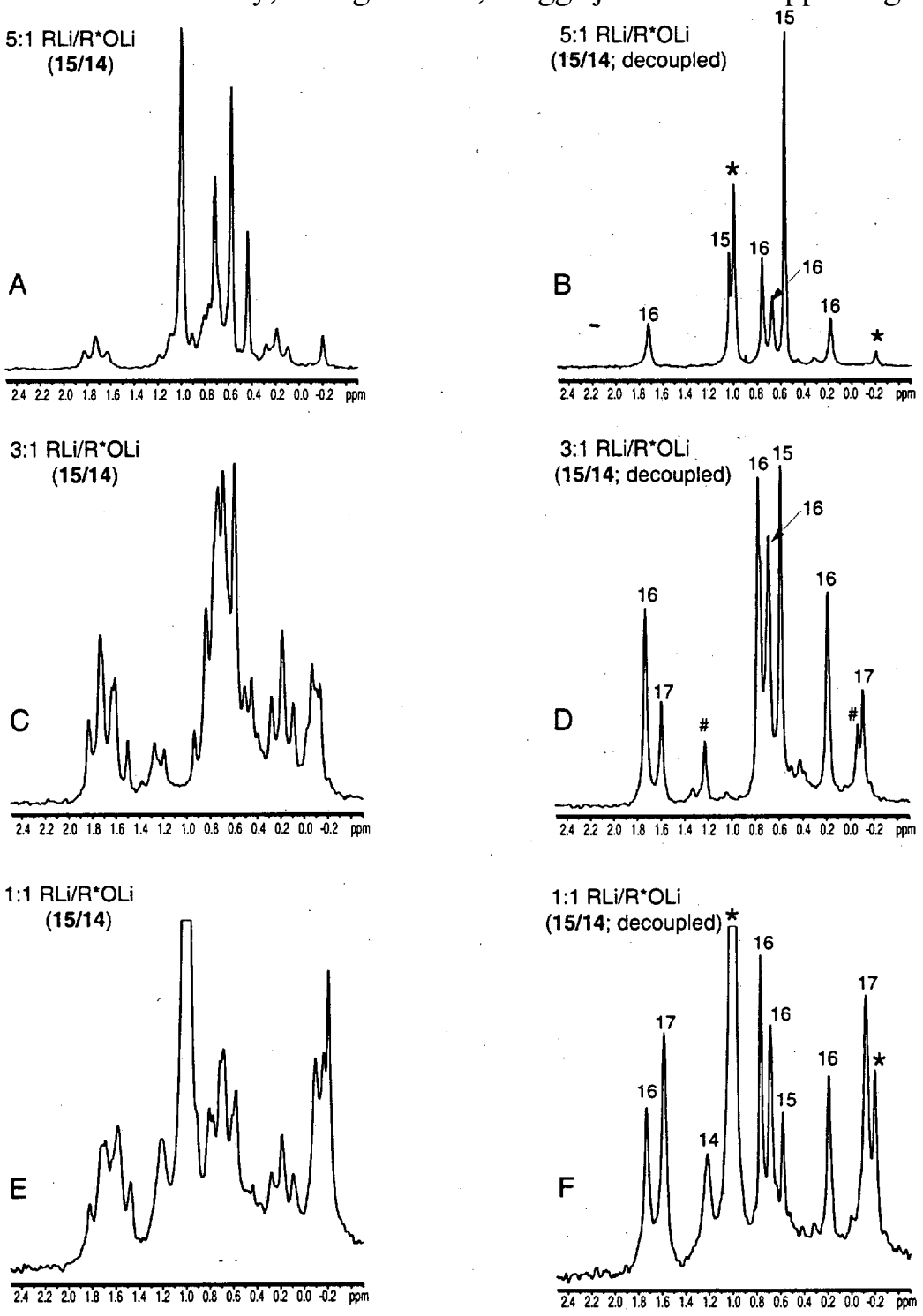


Figure 9. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li,^{13}C]PhCCLi (**15**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and $\geq$ 1.0 equiv of [^{6}Li]LiHMDS) in 3:1:1 toluene/THF/pentane at -115 °C. The total titer of PhCCLi and **14** is 0.2 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{13}C broad-band decoupling. (LiHMDS is denoted by *. Uncharacterized species are denoted by #.)

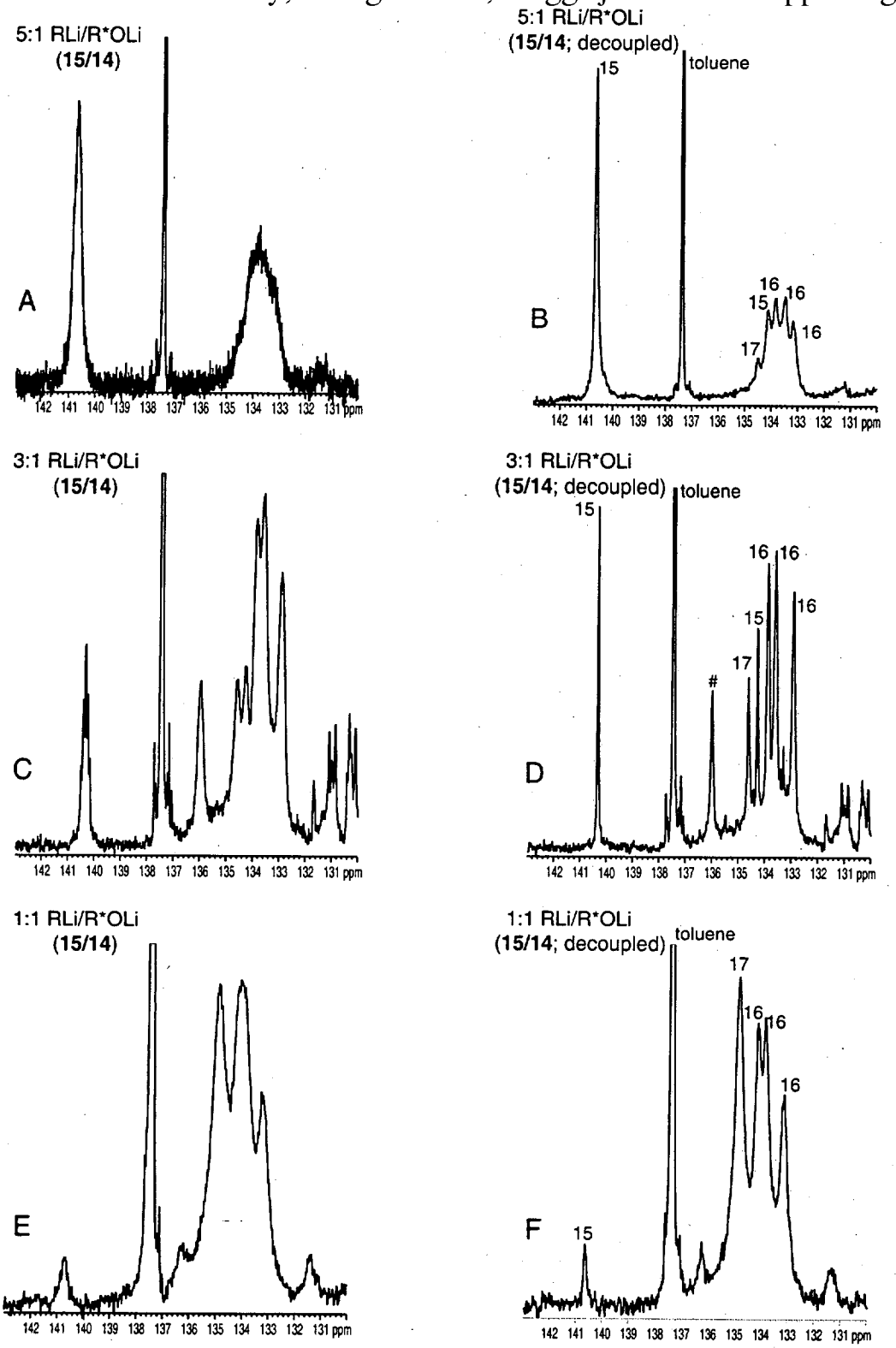


Figure 10. ^{13}C NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li,^{13}C]PhCCLi (**15**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and ≥ 1.0 equiv of [^{6}Li]LiHMDS) in 3:1:1 toluene/THF/pentane at -115 °C. The total titer of PhCCLi and **14** is 0.2 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{6}Li broad-band decoupling. (LiHMDS is denoted by *. Uncharacterized species are denoted by #.)

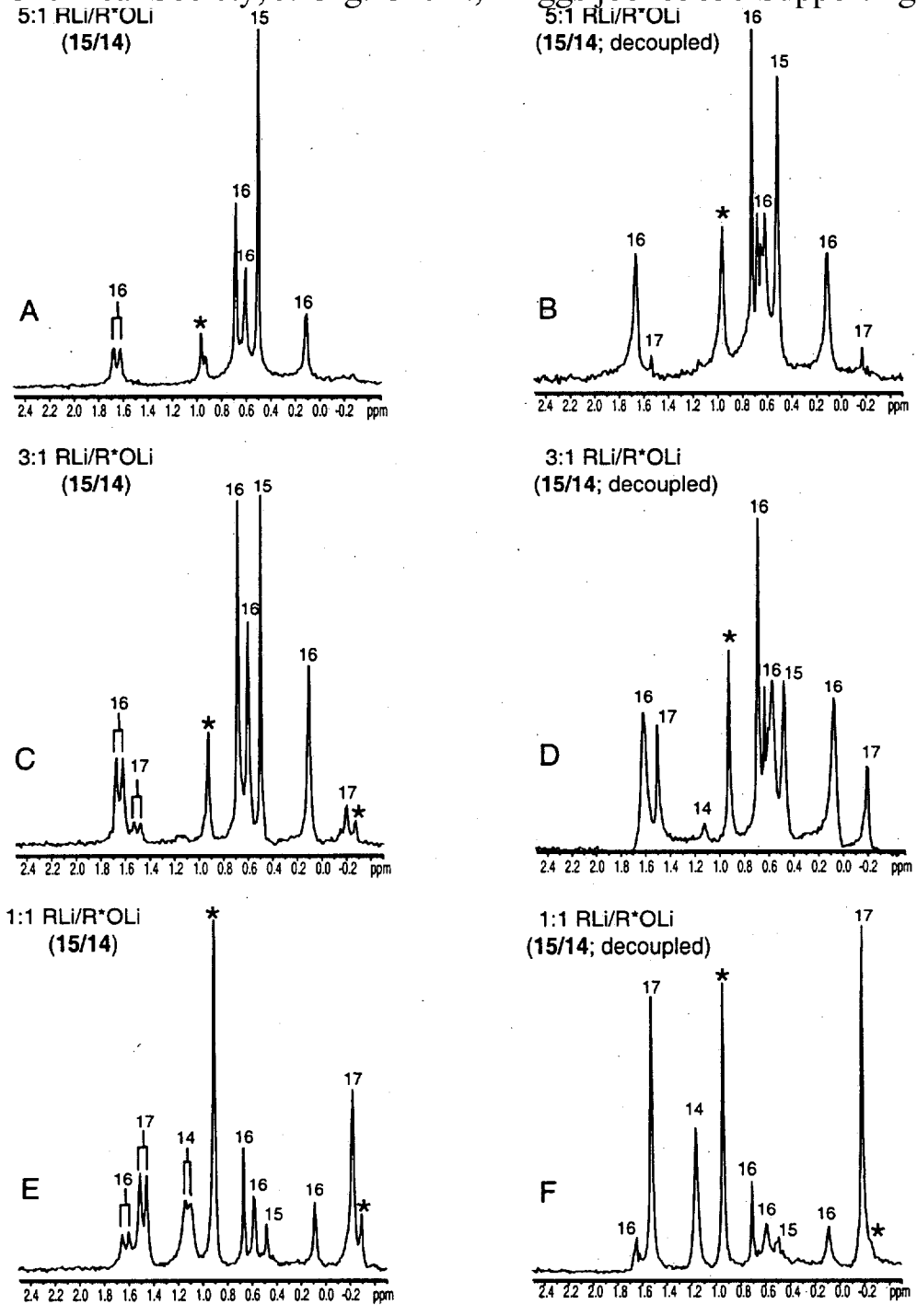


Figure 11. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]PhCCLi (**15**) and [^{6}Li,^{15}N]**14** (prepared *in situ* from the alcohol [^{15}N]**13** and ≥ 1.0 equiv of [^{6}Li]LiHMDS) in 3:1:1 toluene/THF/pentane at -115 °C. The total titer of PhCCLi and **14** is 0.1 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{15}N broad-band decoupling. (LiHMDS is denoted by *.)

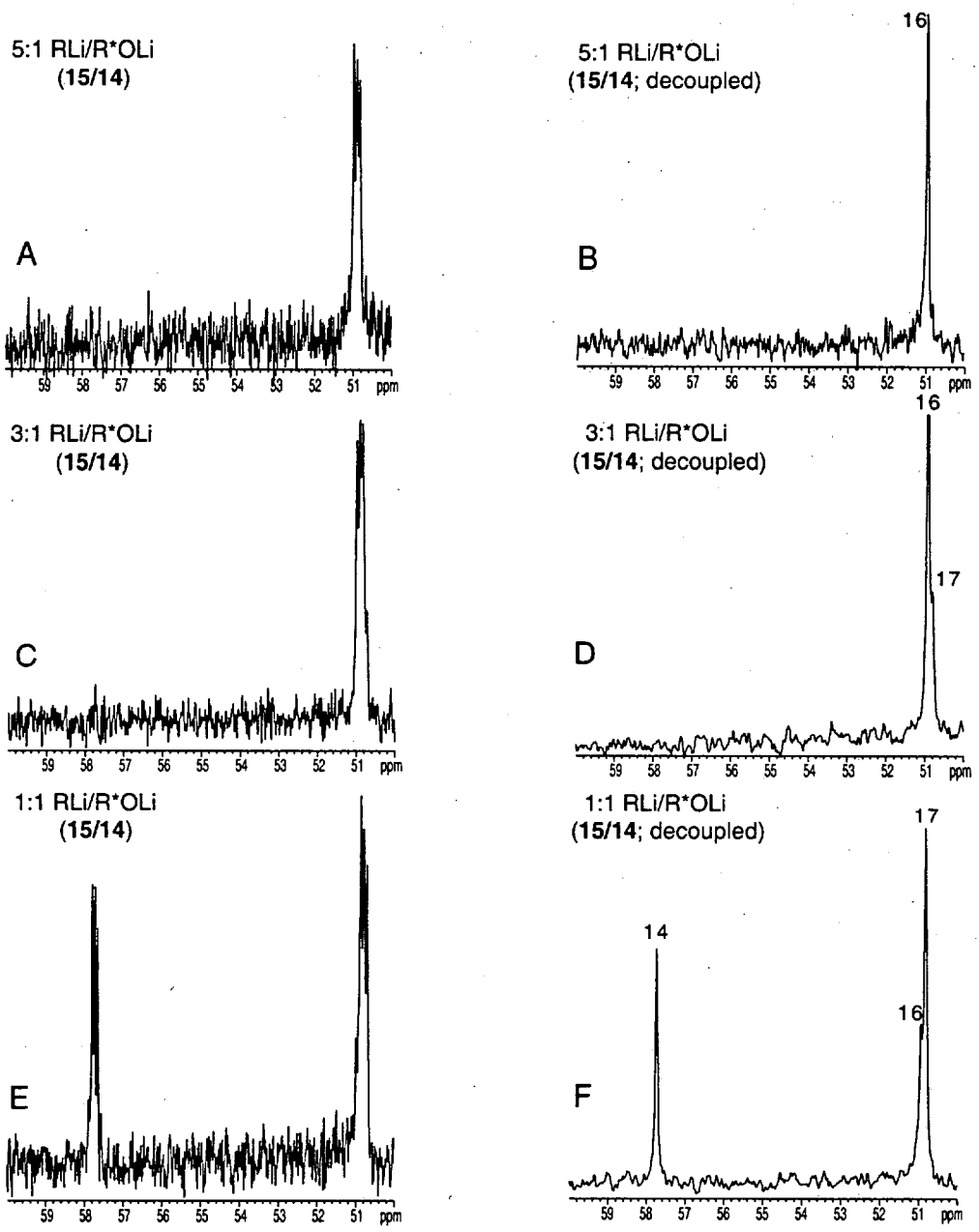


Figure 12. ^{15}N NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]PhCCLi (**15**) and [^{6}Li,^{15}N]**14** (prepared *in situ* from the alcohol [^{15}N]**13** and ≥ 1.0 equiv of [^{6}Li]LiHMDS) in 3:1:1 toluene/THF/pentane at -115 °C. The total titer of PhCCLi and **14** is 0.1 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{6}Li broad-band decoupling.

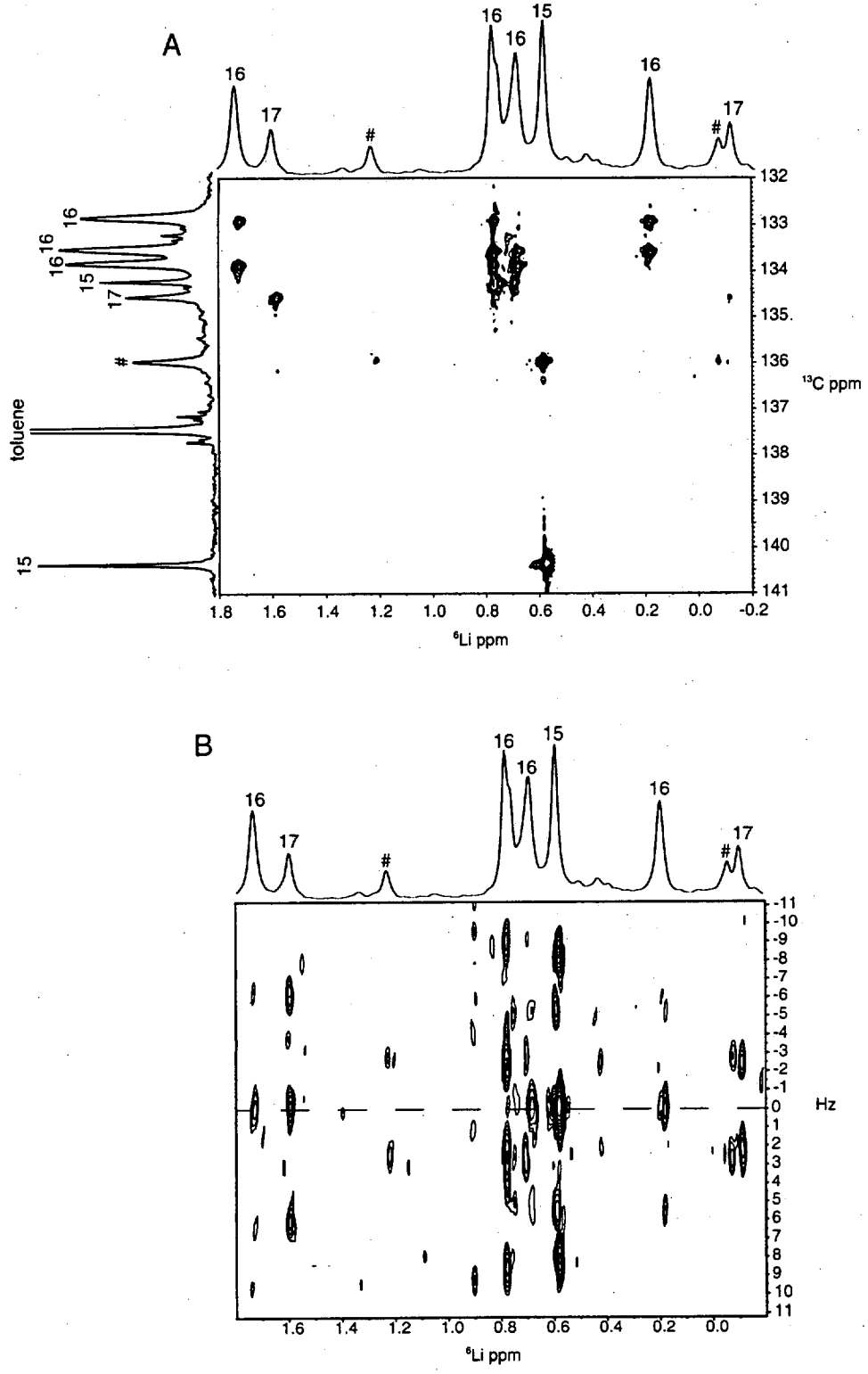
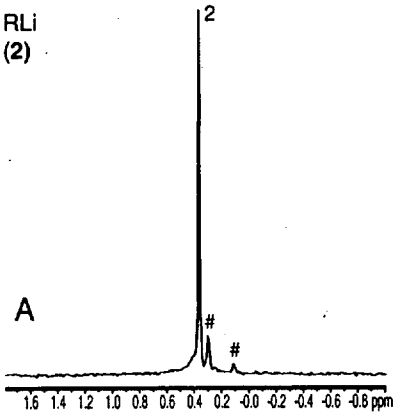
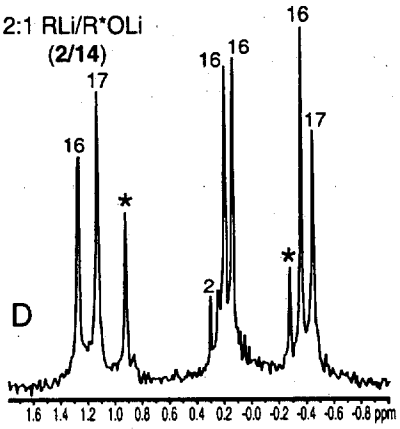


Figure 13. Spectra of 3:1 RLi/R*OLi showing mixed tetramers **16** and **17**. Spectra were recorded on mixtures of [^{6}Li,^{13}C]PhCCLi (**15**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and $\geq$ 1.0 equiv of [^{6}Li]LiHMDS) in 3:1:1 toluene/THF/pentane at -115 °C. The total titer of PhCCLi and **14** is 0.2 M. (A) ^{6}Li,^{13}C-HMQC spectrum; (B) ^{1}J(^{6}Li,^{13}C)-resolved spectrum. (Uncharacterized species are denoted by #.)

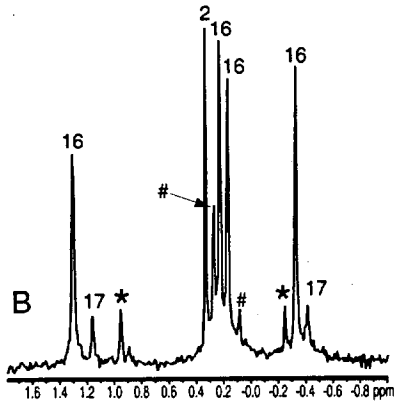
RLi
(2)



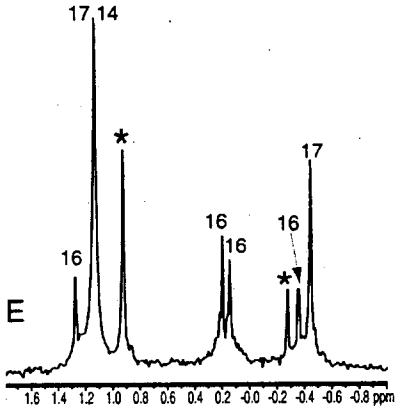
2:1 RLi/R*OLi
(2/14)



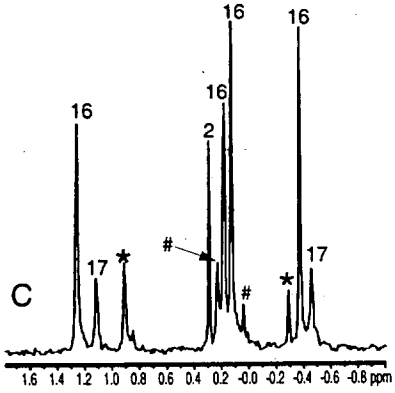
4:1 RLi/R*OLi
(2/14)



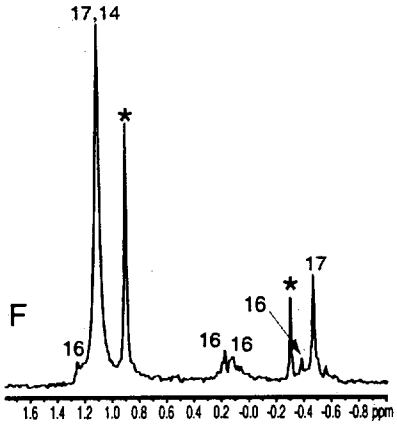
1:1 RLi/R*OLi
(2/14)



3:1 RLi/R*OLi
(2/14)



1:2 RLi/R*OLi
(2/14)



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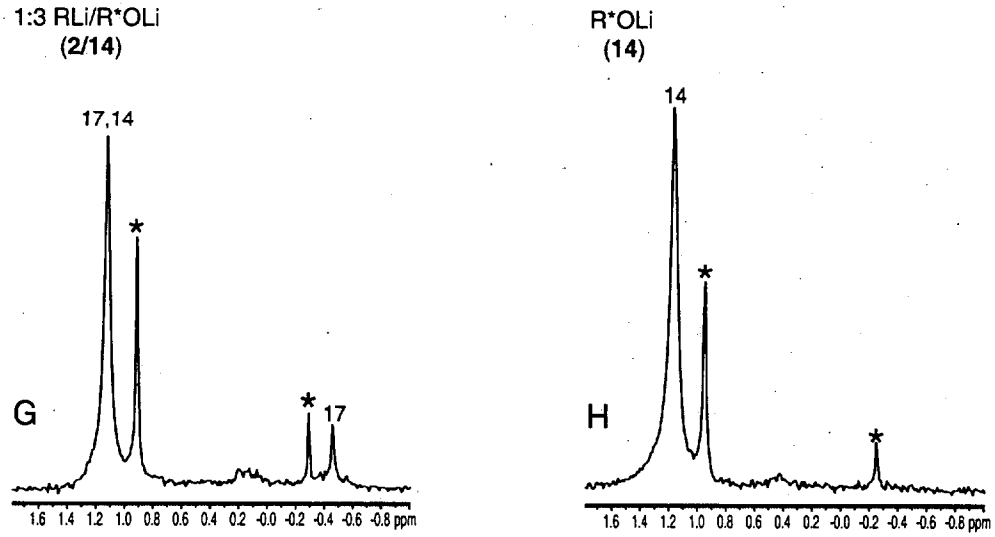
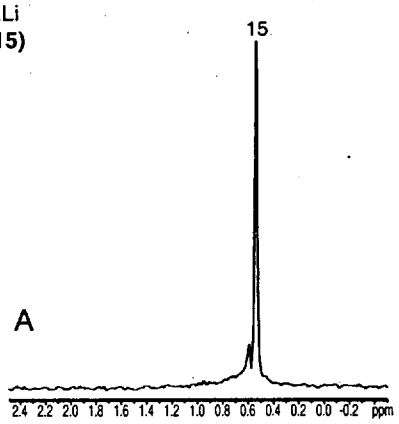
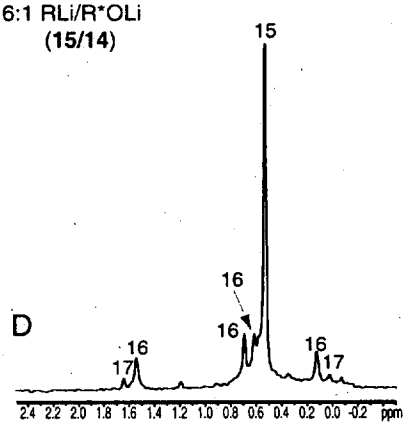


Figure 14. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]LiCPA (**2**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and $\geq$ 1.0 equiv of [^{6}Li]LiHMDS) in 3:1:1 toluene/THF/pentane at -115 °C. The total titer of LiCPA and **14** is 0.10 M in the proportions labeled on each spectrum. (LiHMDS is denoted by *.)

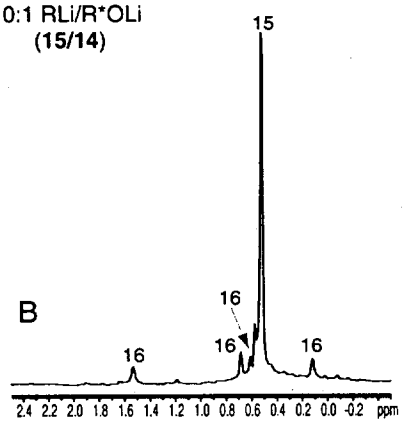
RLi
(15)



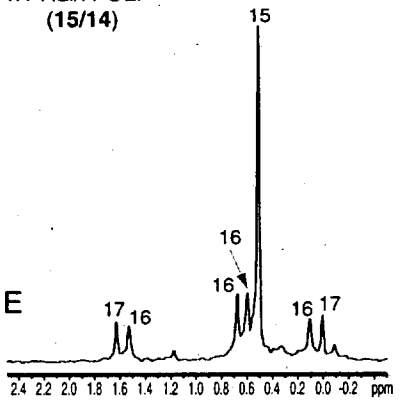
6:1 RLi/R*OLi
(15/14)



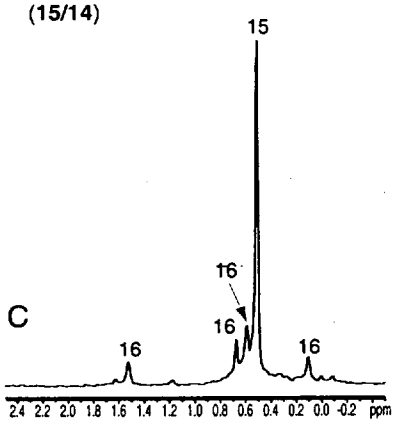
10:1 RLi/R*OLi
(15/14)



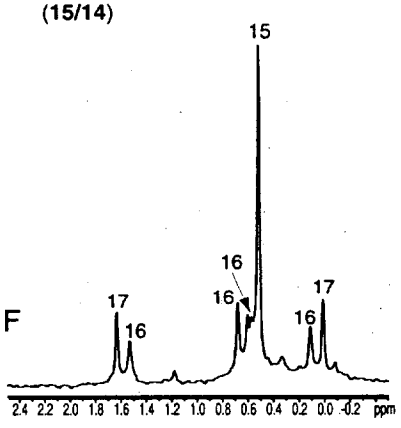
4:1 RLi/R*OLi
(15/14)



8:1 RLi/R*OLi
(15/14)



3:1 RLi/R*OLi
(15/14)



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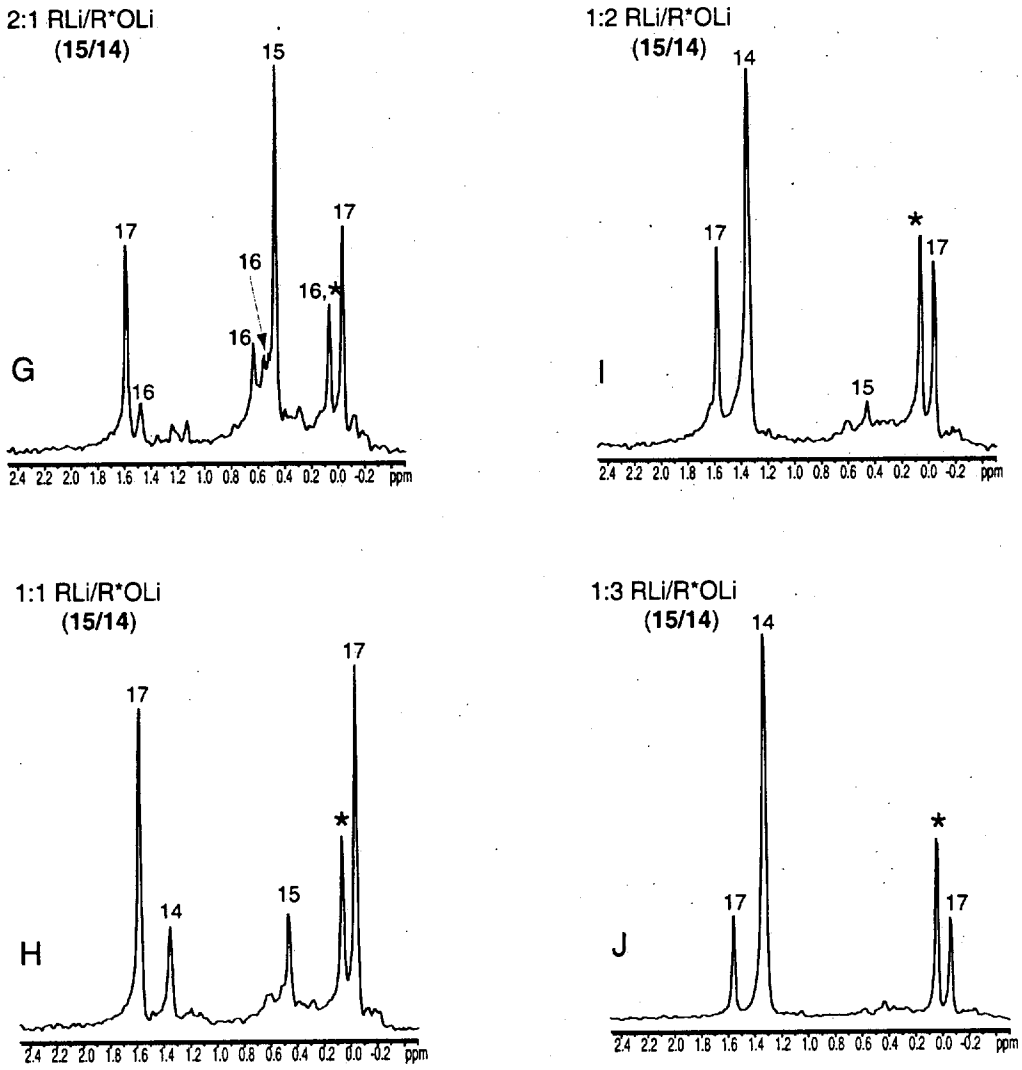
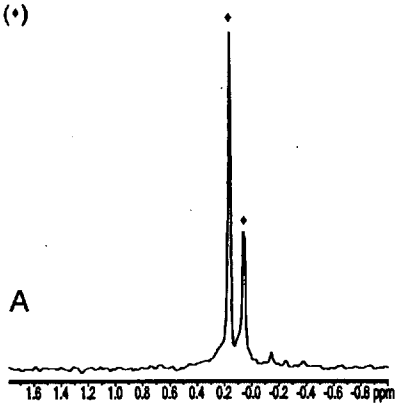
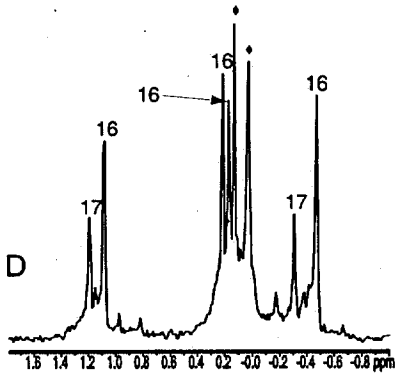


Figure 15. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]PhCCLi (**15**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and $\geq$ 1.0 equiv of [^{6}Li]LiHMDS) in 50% THF/pentane at -115 °C. The total titer of PhCCLi and **14** is 0.10 M in the proportions labeled on each spectrum. (LiHMDS is denoted by *.)

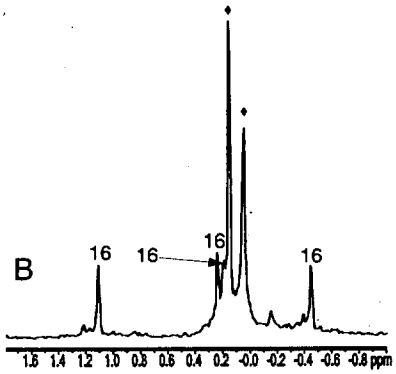
RLi
(•)



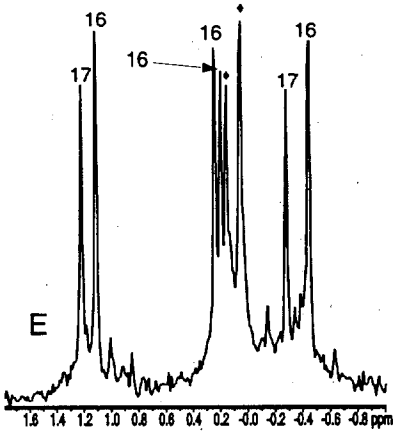
4:1 RLi/R*OLi
(•/14)



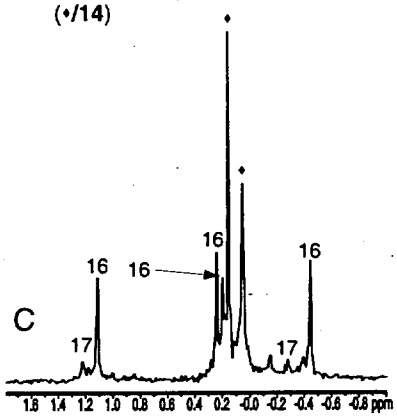
10:1 RLi/R*OLi
(•/14)



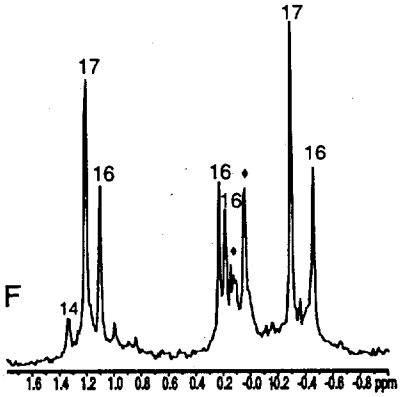
3:1 RLi/R*OLi
(•/14)



7:1 RLi/R*OLi
(•/14)



2:1 RLi/R*OLi
(•/14)



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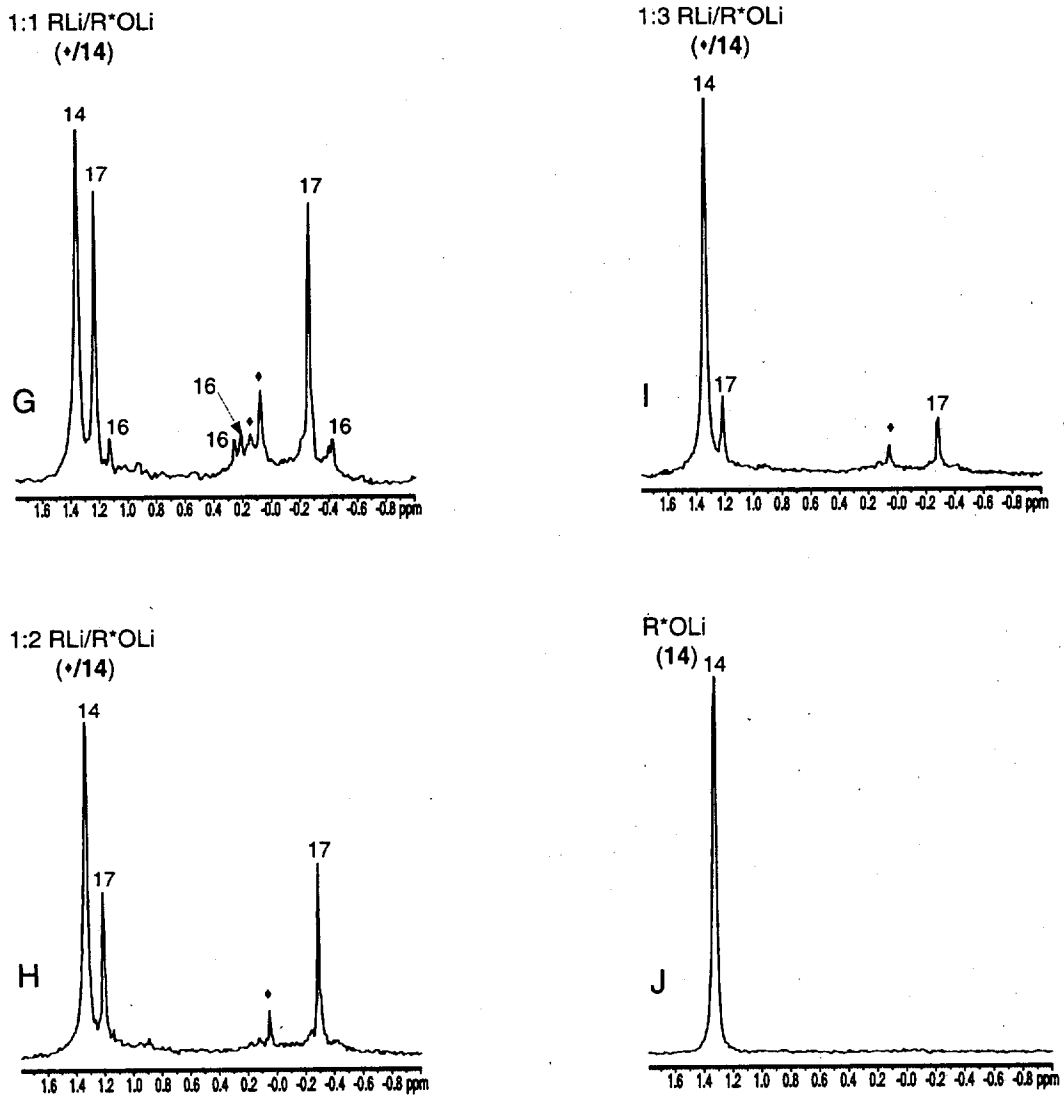

Figure 16. ^{6}Li NMR spectra showing 3:1 RLi/R*OLi (**16**) and 2:2 RLi/R*OLi (**17**) mixed tetramers. Spectra were recorded on mixtures of [^{6}Li]*t*-BuCCLi(•) and [^{6}Li]**14** (prepared *in situ* from the alcohol and $\geq$ 1.0 equiv of [^{6}Li]LiHMDS) in 50% THF/pentane at -115 °C. The total titer of *t*-BuCCLi and **14** is 0.10 M in the proportions labeled on each spectrum.

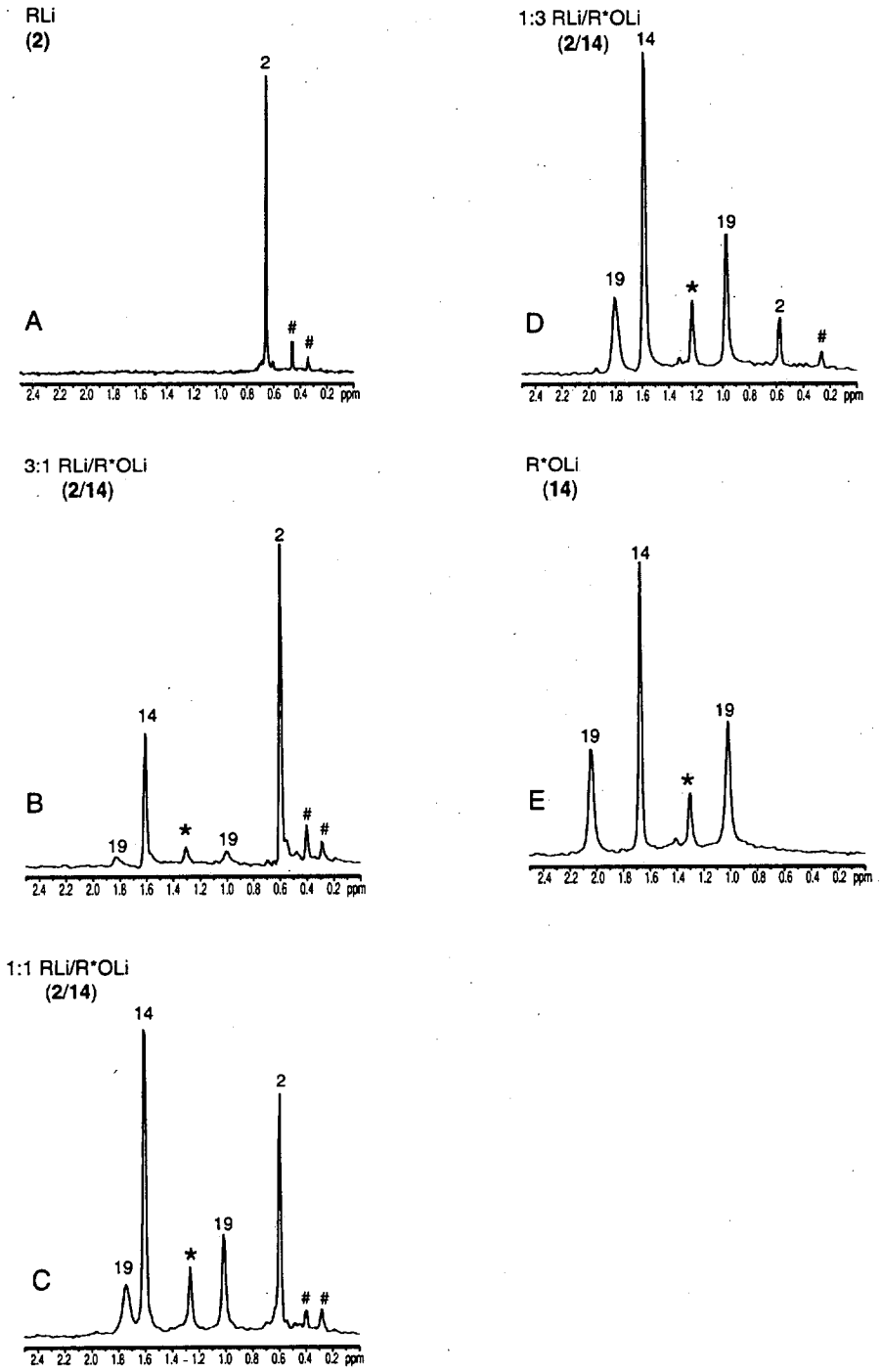

Figure 17. ^{6}Li NMR spectra showing no mixed aggregation. Spectra were recorded on mixtures of [^{6}Li]LiCPA (**2**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and ≥ 1.0 equiv of [^{6}Li]LiHMDS) in neat Me_2NEt at -100 °C. The total titer of LiCPA and **14** is 0.10 M in the proportions labeled on each spectrum. (LiHMDS is denoted by *. Impurity derived from the acetylide denoted as #.)

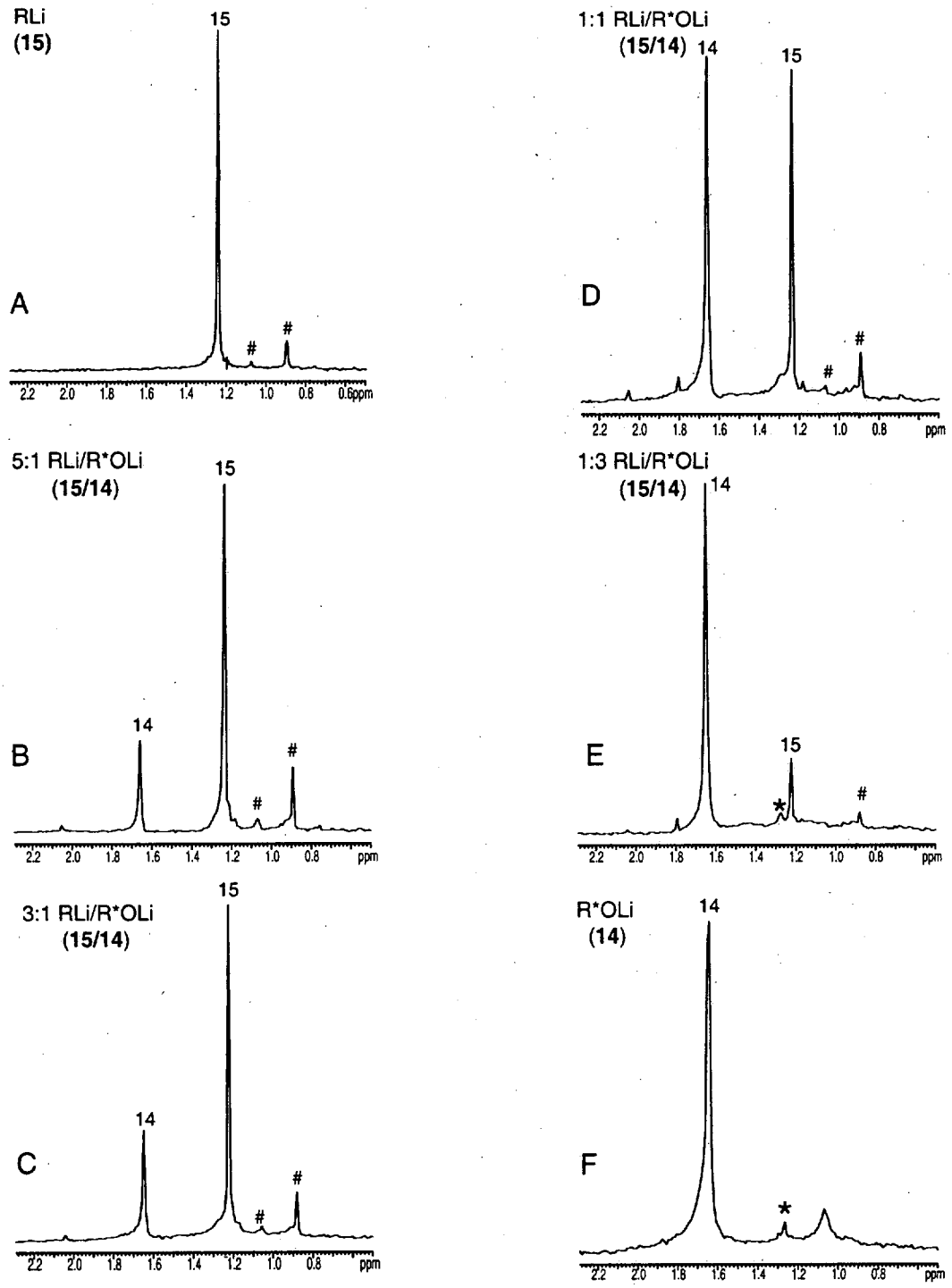

Figure 18. ^{6}Li NMR spectra showing no mixed aggregation. Spectra were recorded on mixtures of [^{6}Li]PhCCLi (**15**) and [^{6}Li]**14** (prepared *in situ* from the alcohol **13** and $\geq$ 1.0 equiv of [^{6}Li]LiHMDS) in neat Me_2NEt at -100 °C. The total titer of PhCCLi and **14** is 0.10 M in the proportions labeled on each spectrum. (LiHMDS is denoted by *. Impurity derived from the acetylide denoted by #.)

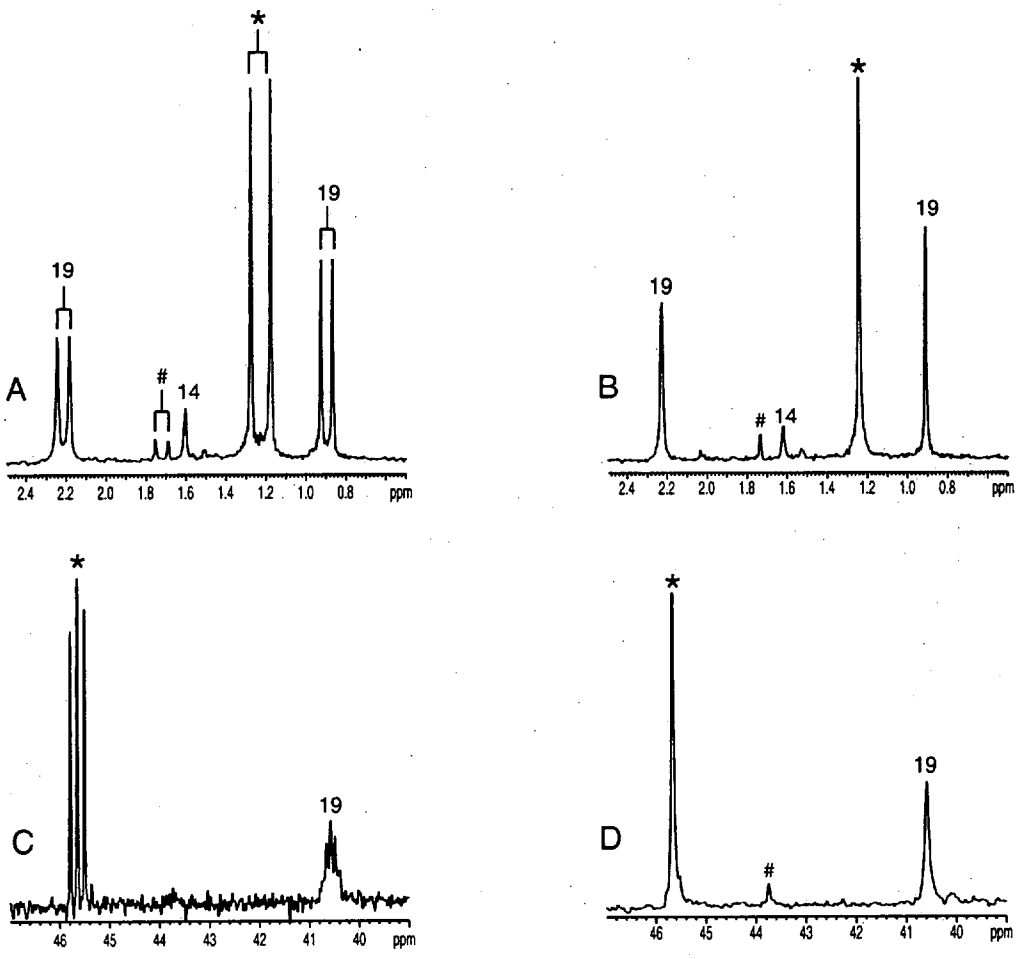

Figure 19. ^{6}Li and ^{15}N NMR spectra of a 1:3 [^{6}Li]**14**/[^{6}Li,^{15}N]LiHMDS mixture in Me_2NEt at –100 °C. (A) ^{6}Li spectrum; (B) ^{6}Li spectrum (^{15}N broad-band decoupled); (C) ^{15}N spectrum; (D) ^{15}N spectrum (^{6}Li broad-band decoupled). (LiHMDS is denoted by *. Uncharacterized species are denoted by #.)

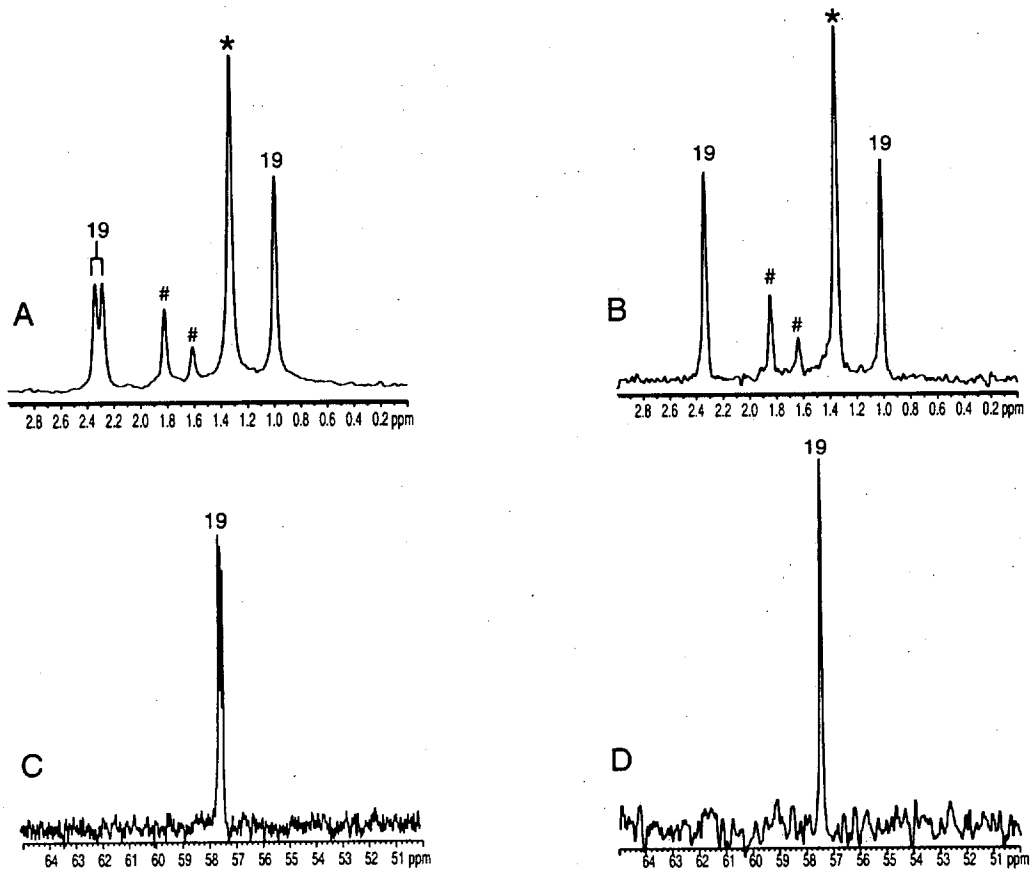

Figure 20. ^{6}Li and ^{15}N NMR spectra of a 1:3 [^{6}Li,^{15}N]**14**/[^{6}Li]LiHMDS mixture in Me_2NEt at –100 °C. (A) ^{6}Li spectrum; (B) ^{6}Li spectrum (^{15}N decoupled); (C) ^{15}N spectrum; (D) ^{15}N spectrum (^{6}Li decoupled). (LiHMDS is denoted by *. Uncharacterized species are denoted by #.)

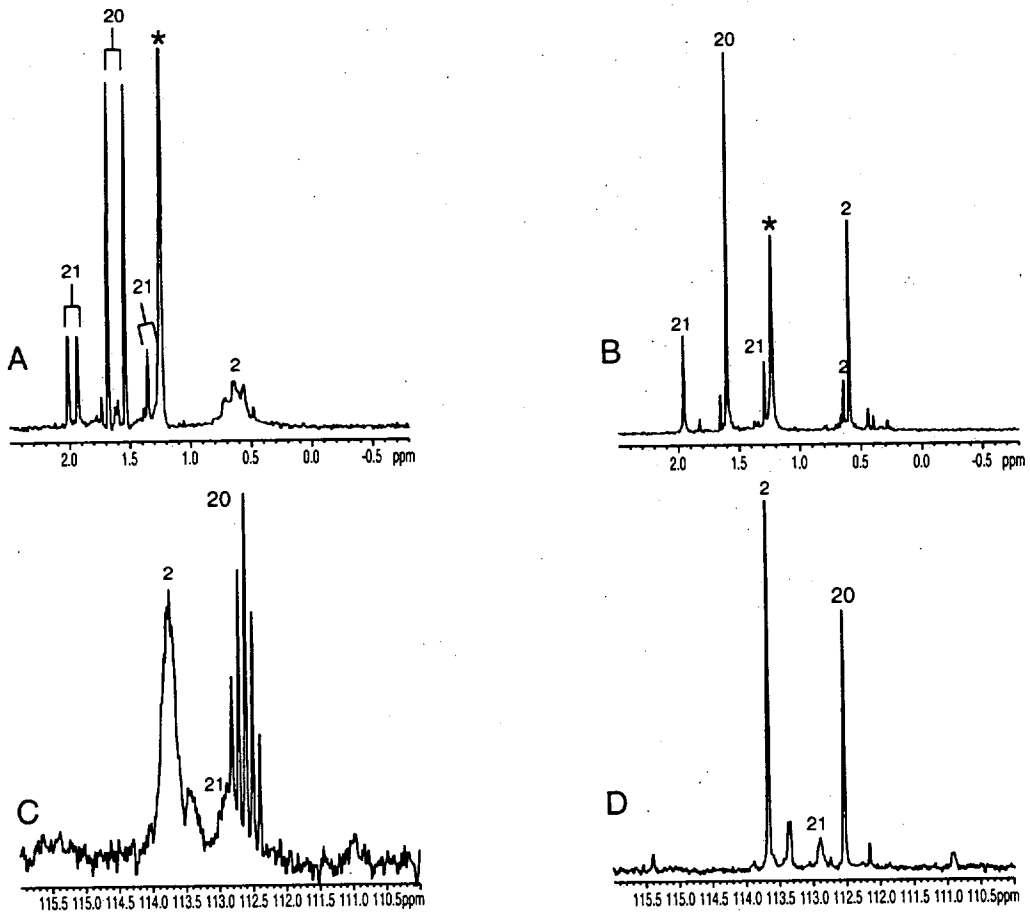

Figure 21. ^{6}Li and ^{13}C NMR spectra of a 1:1 [^{6}Li, ^{13}C]LiCPA/[^{6}Li]LiHMDS mixture in Me_2NEt at –100 °C. (A) ^{6}Li spectrum; (B) ^{6}Li spectrum (^{13}C decoupled); (C) ^{13}C spectrum; (D) ^{13}C spectrum (^{6}Li decoupled). (LiHMDS is denoted by *.)

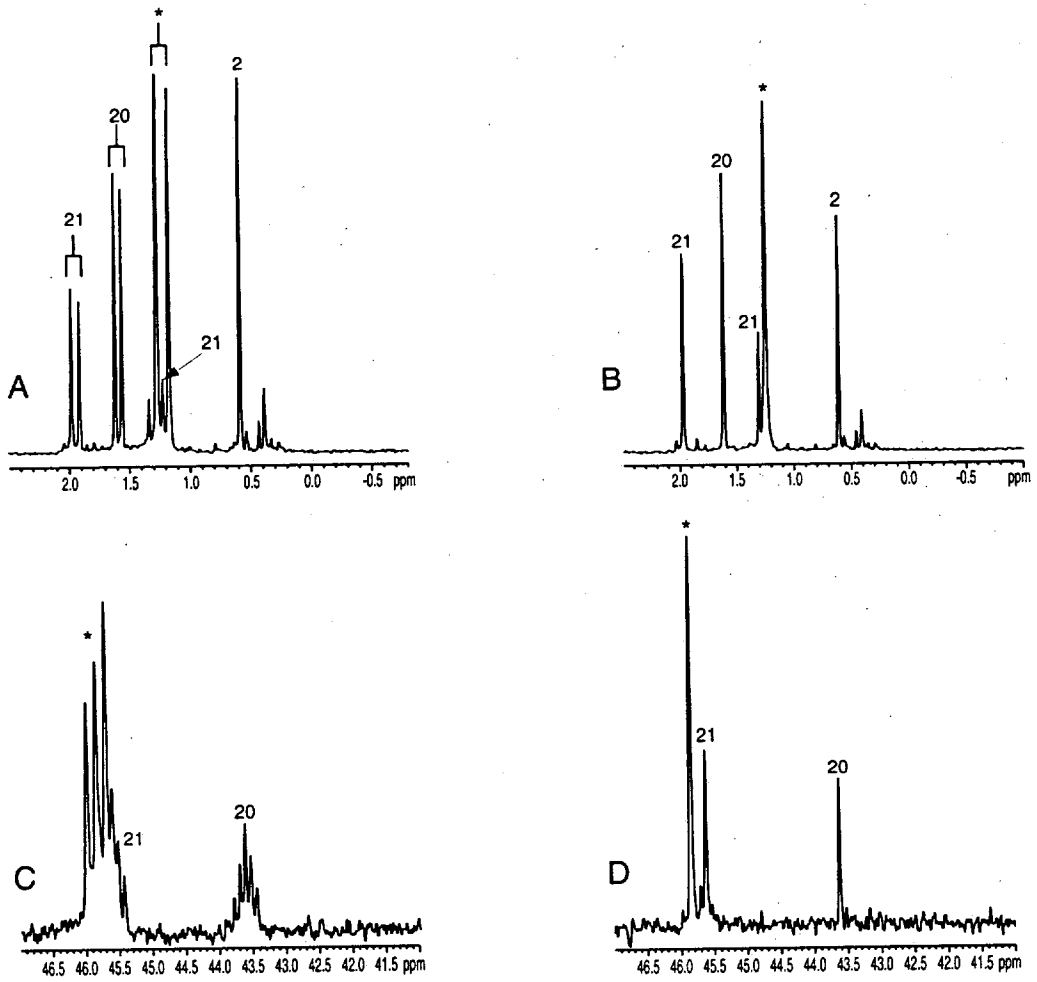

Figure 22. ^{6}Li NMR and ^{15}N spectra of a 1:1.5 [^{6}Li]LiCPA/[^{6}Li,^{15}N]LiHMDS mixture in Me_2NEt at –100 °C. (A) ^{6}Li spectrum; (B) ^{6}Li spectrum (^{15}N broad-band decoupled); (C) ^{15}N spectrum; (D) ^{15}N spectrum (^{6}Li broad-band decoupled). (LiHMDS is denoted by *.)

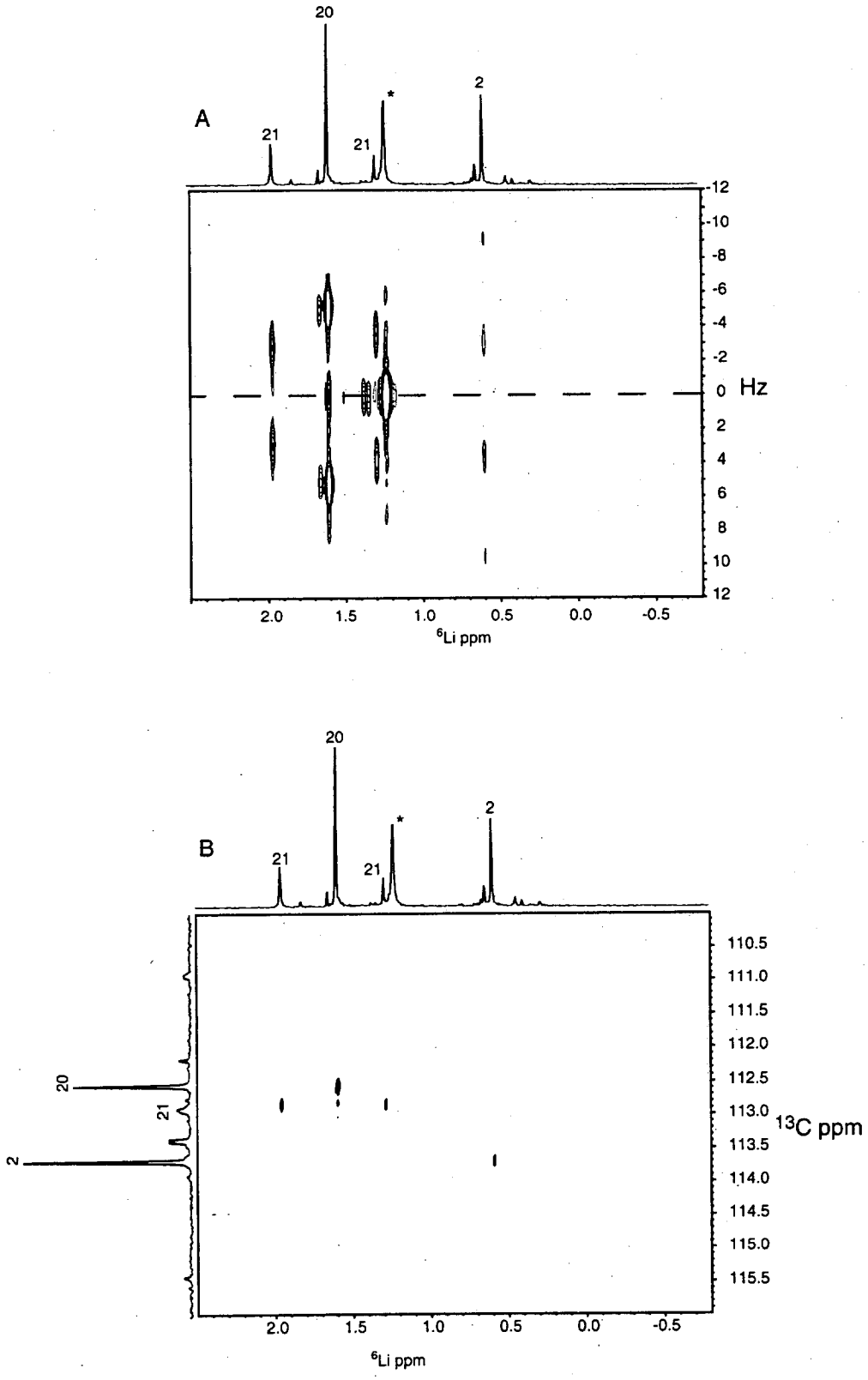

Figure 23. Spectra of a 1:1 [^{6}Li,^{13}C]LiCPA/[^{6}Li]LiHMDS mixture in Me_2NEt at –100 °C: (A) $^{1}J(^{6}Li,^{13}C)$-resolved spectrum; (B) ^{6}Li,^{13}C-HMQC spectrum. (LiHMDS is denoted by *.)

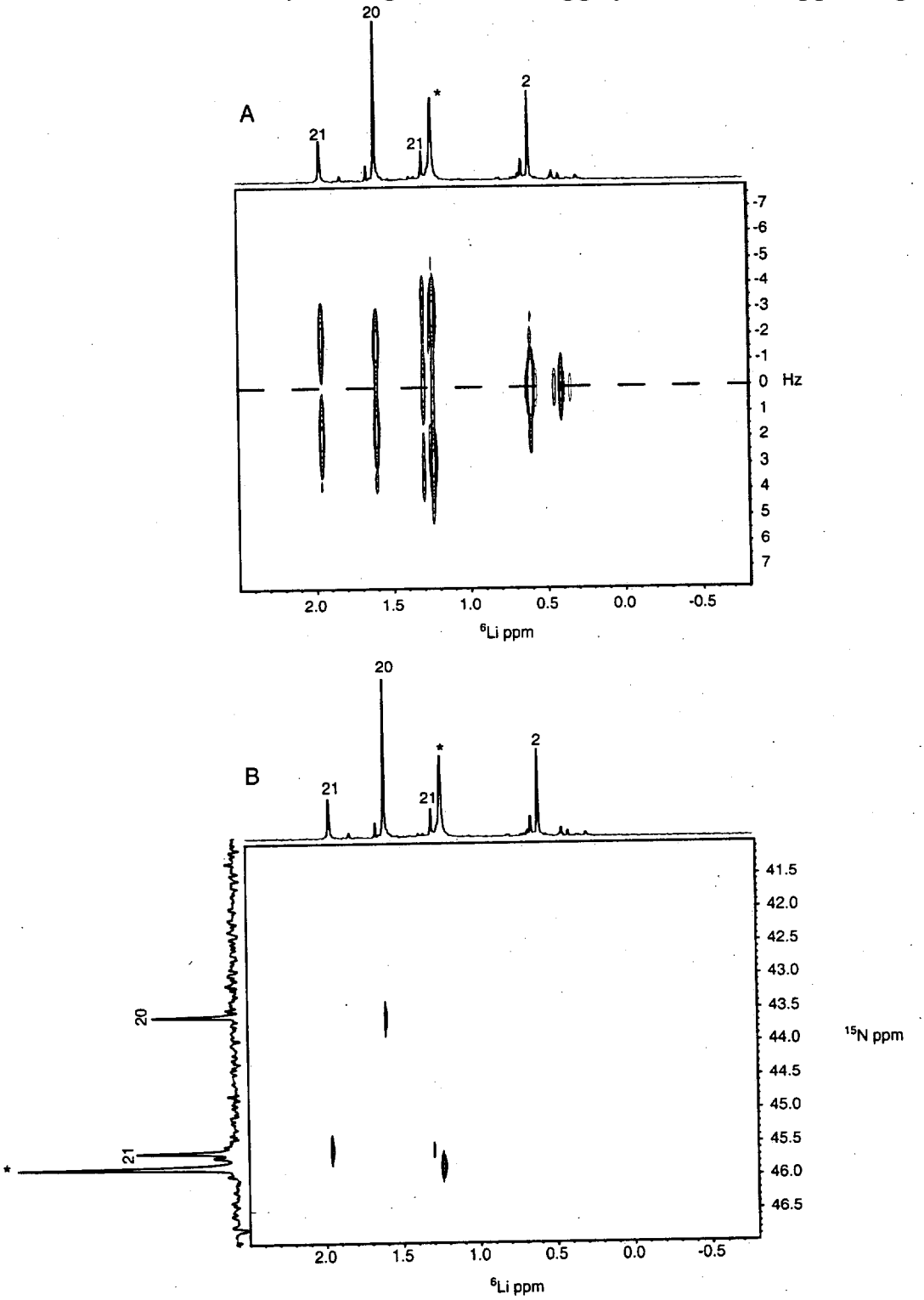

Figure 24. Spectra of a 1:1.5 [^{6}Li]LiCPA/[^{6}Li,^{15}N]LiHMDS in Me_2NEt at –100 °C. (A) ^1J(^{6}Li,^{15}N)-resolved spectrum; (B) ^{6}Li,^{15}N-HMQC spectrum. (LiHMDS is denoted by *.)

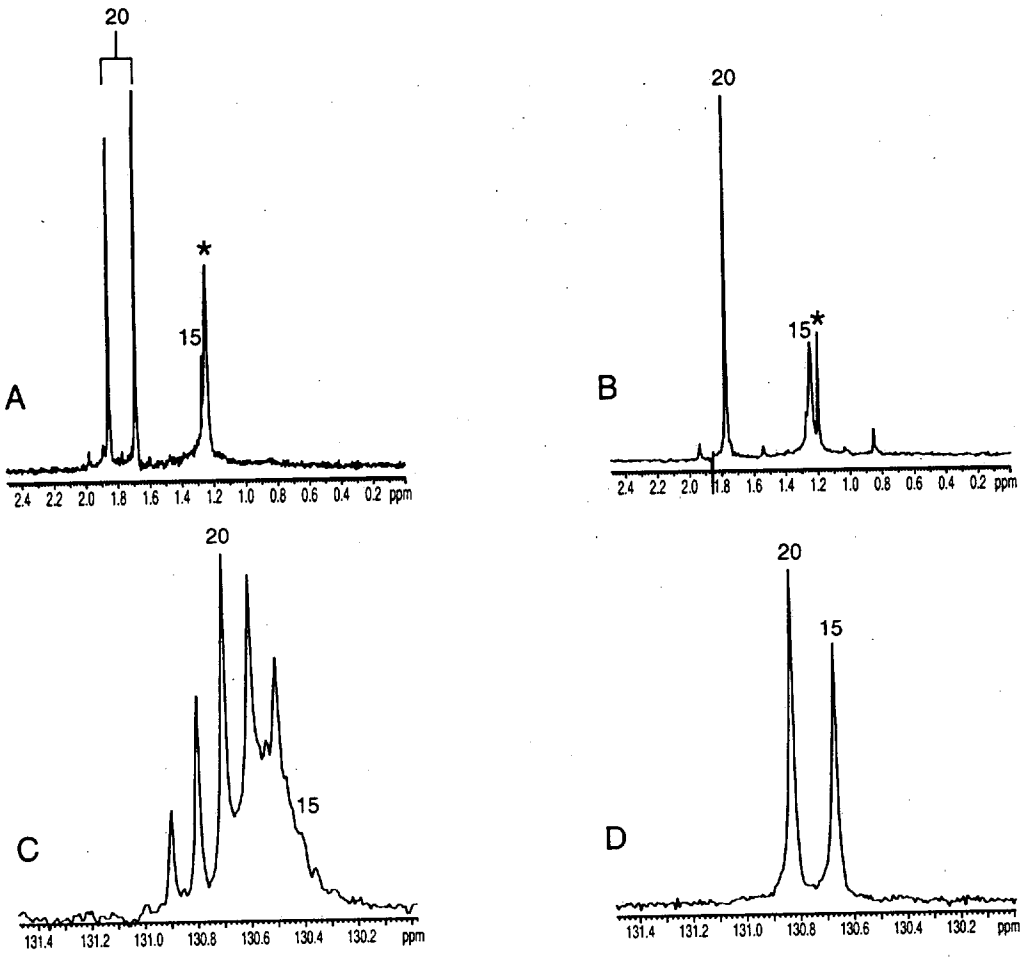

Figure 25. ^{6}Li and ^{13}C NMR spectra of a 1:1.5 [^{6}Li, ^{13}C]PhCCLi/[^{6}Li]LiHMDS mixture in Me_2NEt at –100 °C. (A) ^{6}Li spectrum; (B) ^{6}Li spectrum (^{13}C broad-band decoupled); (C) ^{13}C spectrum; (D) ^{13}C spectrum (^{6}Li broad-band decoupled). (LiHMDS is denoted by *.)

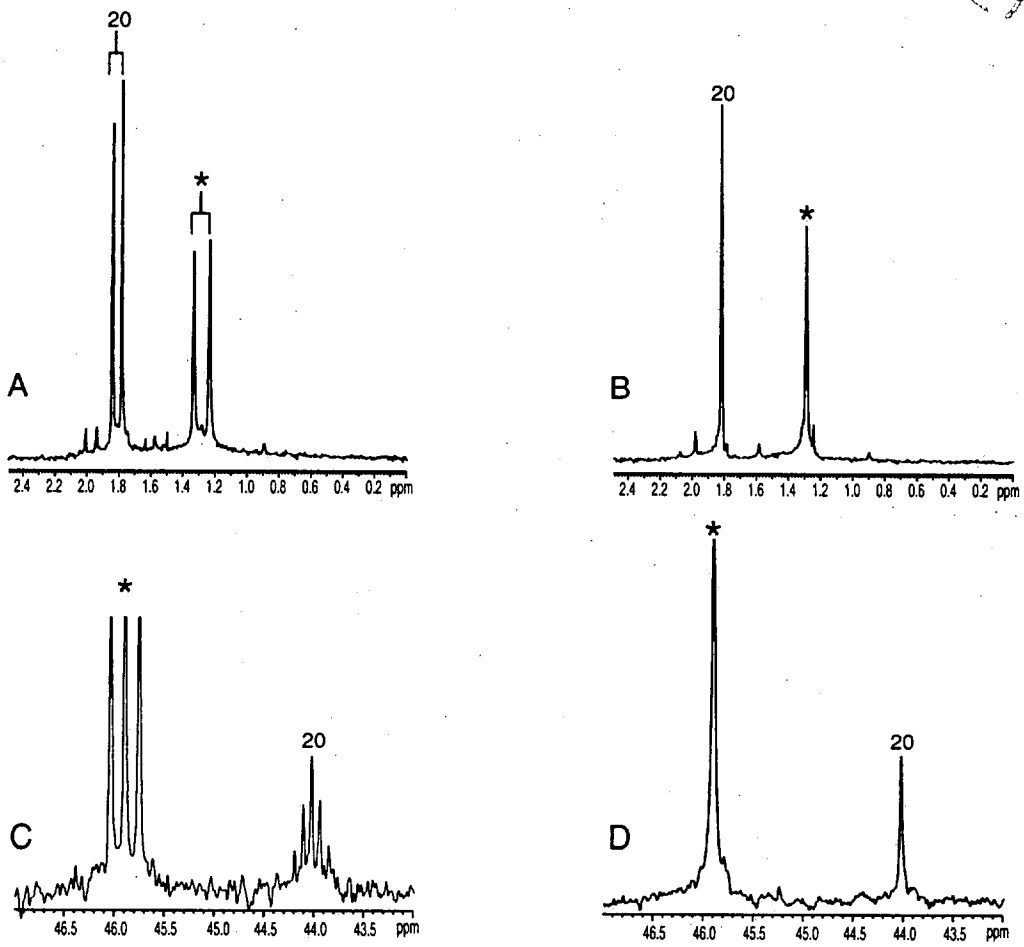

Figure 26. ^{6}Li and ^{15}N NMR spectra of a 1:3 [^{6}Li]PhCCLi/[^{6}Li,^{15}N]LiHMDS mixture in Me_2NEt at –100 °C. (A) ^{6}Li spectrum; (B) ^{6}Li spectrum (^{15}N broad-band decoupled); (C) ^{15}N spectrum; (D) ^{15}N spectrum (^{6}Li broad-band decoupled). (LiHMDS is denoted by *.)