

RW

NMR Spectroscopic Investigations of Mixed Aggregates
Underlying Highly Enantioselective 1,2-Additions of
Lithium Cyclopropylacetylide to Quinazolinones.

Rodney L. Parsons, Jr.,* Joseph M. Fortunak, Roberta L. Dorow, Gregory D. Harris,
Goss S. Kauffman, and William A. Nugent
Contribution from DuPont Pharmaceuticals
Chemical Process Research and Development
Chambersworks, PRF-112
Deepwater, N. J. 08023

and

Mark D. Winemiller, Timothy F. Briggs, Bosong Xiang, and David B. Collum*
Department of Chemistry and Chemical Biology
Baker Laboratory, Cornell University
Ithaca, New York 14853-1301

Supporting Information

Figure 1. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li}]$ 10b in 80% THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 2. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li}]$ 10b in 80% THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 3. ^{13}C NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li}]$ 10b in 80% THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 4. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]$ 10b in 80% THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 5. ^{15}N NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]$ 10b in 80% THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 6. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 1:1 $[\text{}^6\text{Li},^{13}\text{C}]$ 6/ $[\text{}^6\text{Li}]$ 10b; (B) *J*-resolved spectrum of 1:1 $[\text{}^6\text{Li},^{13}\text{C}]$ 6/ $[\text{}^6\text{Li}]$ 10b in 80% THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 7. (A) $^6\text{Li},^{15}\text{N}$ -HMQC of 1:1 $[\text{}^6\text{Li}]$ 6/ $[\text{}^6\text{Li},^{15}\text{N}]$ 10b; (B) *J*-resolved spectrum of 1:1 $[\text{}^6\text{Li}]$ 6/ $[\text{}^6\text{Li},^{15}\text{N}]$ 10b in 80% THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 8. $^6\text{Li},^6\text{Li}$ -EXSY spectra of 1:1 $[\text{}^6\text{Li}]$ 6/ $[\text{}^6\text{Li},^{15}\text{N}]$ 10b in 80% THF/pentane at $-110\text{ }^\circ\text{C}$. Mixing times are indicated on individual spectra.

Figure 9. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 10. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 11. ^{13}C NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 12. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 13. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 14. ^{15}N NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 15. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 3:1 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$; (B) *J*-resolved spectrum of 3:1 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 16. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 1:1 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$; (B) *J*-resolved spectrum of 1:1 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 17. (A) $^6\text{Li},^{15}\text{N}$ -HMQC of 1:1 $[\text{}^6\text{Li}]\text{6}/[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$; (B) *J*-resolved spectrum of 1:1 $[\text{}^6\text{Li}]\text{6}/[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$.

Figure 18. $^6\text{Li},^6\text{Li}$ -EXSY spectra of 1:1 $[\text{}^6\text{Li}]\text{6}/[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-110\text{ }^\circ\text{C}$. Mixing time was 1.5 sec.

Figure 19. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 20. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 21. ^{13}C NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 22. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (**6**) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 23. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 24. ^{15}N NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 25. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 3:1 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$; (B) *J*-resolved spectrum of 3:1 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 26. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 2:2 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$; (B) *J*-resolved spectrum of 2:2 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 27. (A) $^6\text{Li},^{15}\text{N}$ -HMQC of 2:2 $[\text{}^6\text{Li}]\text{6}/[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$; (B) *J*-resolved spectrum of 2:2 $[\text{}^6\text{Li}]\text{6}/[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 28. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

Figure 29. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

Figure 30. ^{13}C NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

Figure 31. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

Figure 32. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

Figure 33. ^{15}N NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

Figure 34. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 3:1 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

Figure 35. (A) *J*-resolved spectrum of 2:2 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

Figure 36. (A) $^6\text{Li},^{15}\text{N}$ -HMQC of 1:1 $[\text{}^6\text{Li},^{15}\text{N}]\text{6}/[\text{}^6\text{Li}]\text{10b}$; (B) *J*-resolved spectrum of 1:1 $[\text{}^6\text{Li},^{15}\text{N}]\text{6}/[\text{}^6\text{Li}]\text{10b}$ in diethyl ether at $-95\text{ }^\circ\text{C}$.

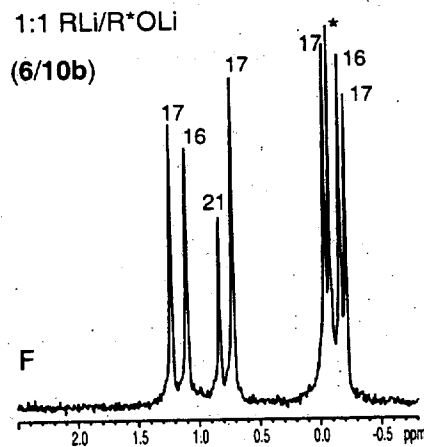
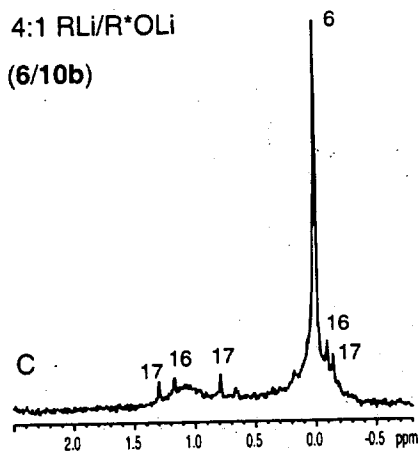
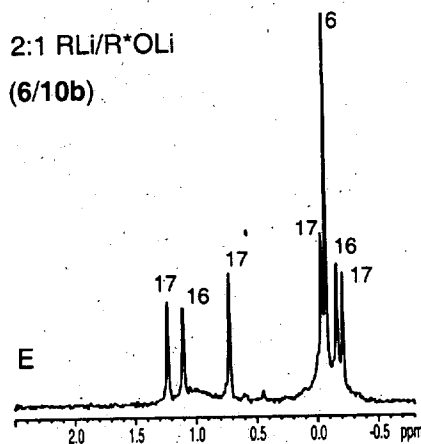
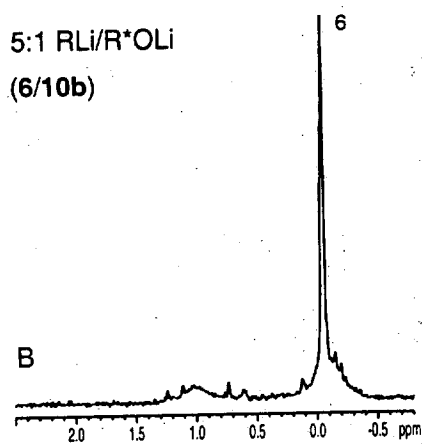
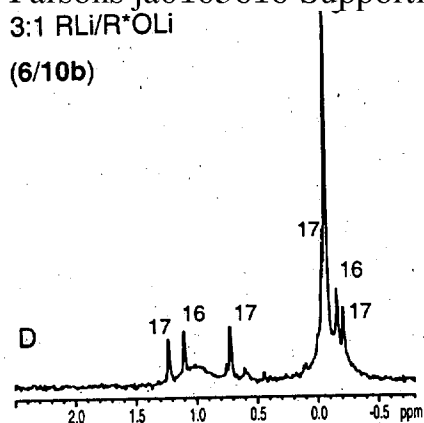
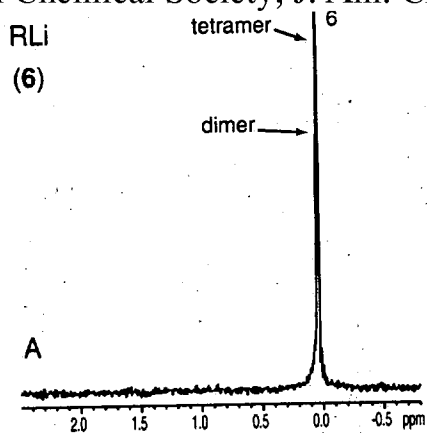
Figure 37. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]\text{LiHMDS}(\ast)$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 38. ^{13}C NMR spectra recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li}]\text{LiHMDS}^*$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 39. ^{15}N NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ (6) and $[\text{}^6\text{Li},^{15}\text{N}]\text{LiHMDS}^*$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 40. (A) *J*-resolved spectrum of 1:2 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{LiHMDS}^*$. (B) $^6\text{Li},^{13}\text{C}$ -HMQC of 1:2 $[\text{}^6\text{Li},^{13}\text{C}]\text{6}/[\text{}^6\text{Li}]\text{LiHMDS}^*$ in DMEA at $-100\text{ }^\circ\text{C}$.

Figure 41. (A) *J*-resolved spectrum of 1:2 $[\text{}^6\text{Li}]\text{6}/[\text{}^6\text{Li},^{15}\text{N}]\text{LiHMDS}^*$. (B) $^6\text{Li},^{15}\text{N}$ -HMQC of 1:2 $[\text{}^6\text{Li}]\text{6}/[\text{}^6\text{Li},^{15}\text{N}]\text{LiHMDS}^*$ in DMEA at $-100\text{ }^\circ\text{C}$.



(Continued)

Next page

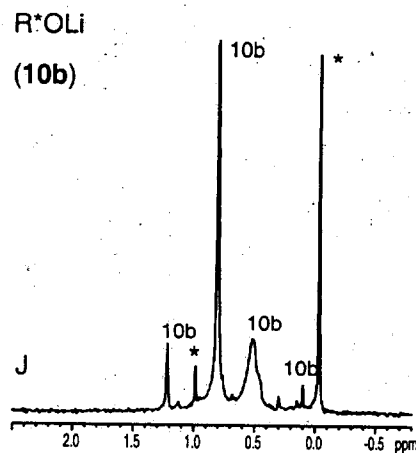
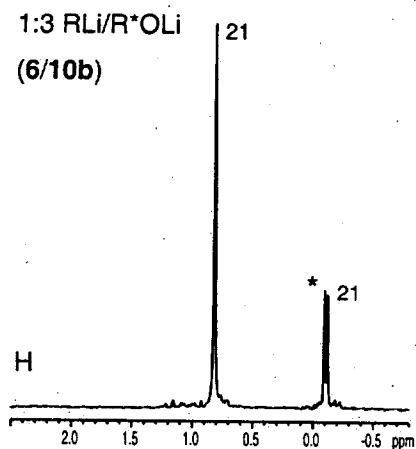
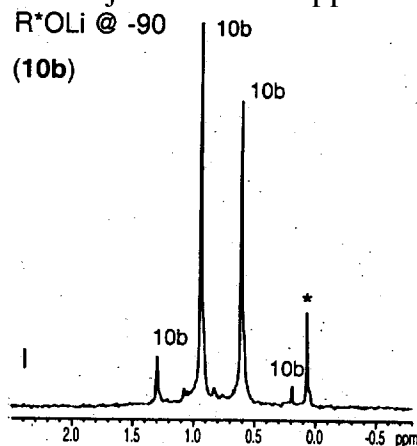
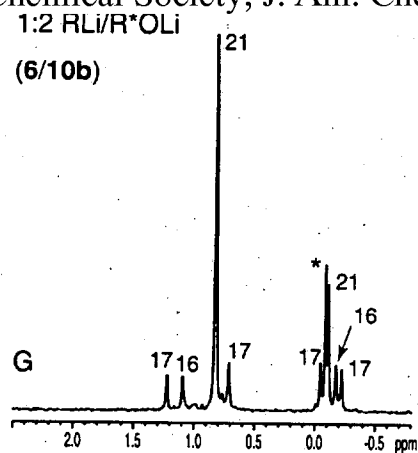


Figure 1. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in 80% THF/pentane at -115°C (except where noted). The total titer of 6 and 10b is 0.1 M in the proportions labeled on each spectrum.

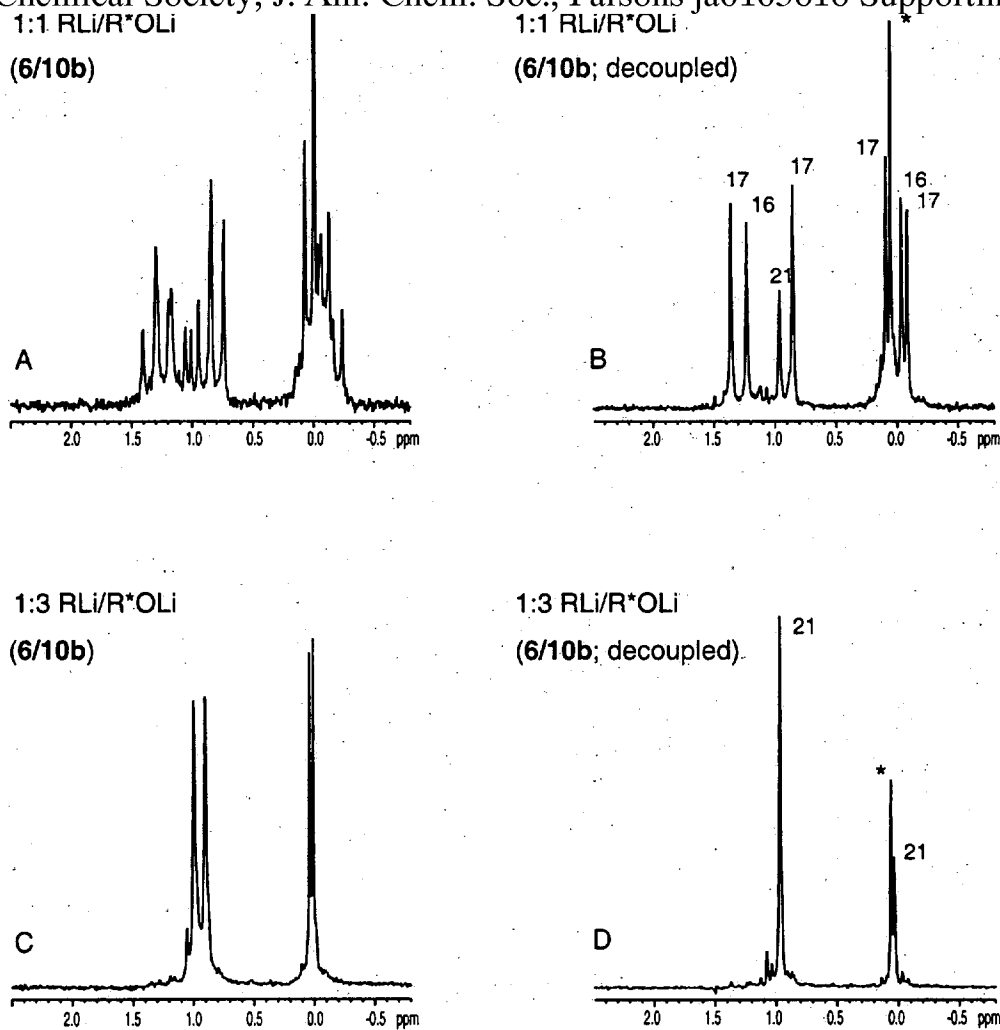


Figure 2. ${}^6\text{Li}$ NMR spectra showing 2:2 RLi/R*OLi (16,17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[{}^6\text{Li}, {}^{13}\text{C}]\text{LiCPA}$ and $[{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[{}^6\text{Li}]\text{LiHMDS}^*$) in 80% THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M in the proportions labeled on each spectrum. Spectra B and D were recorded with ${}^{13}\text{C}$ broad-band decoupling.

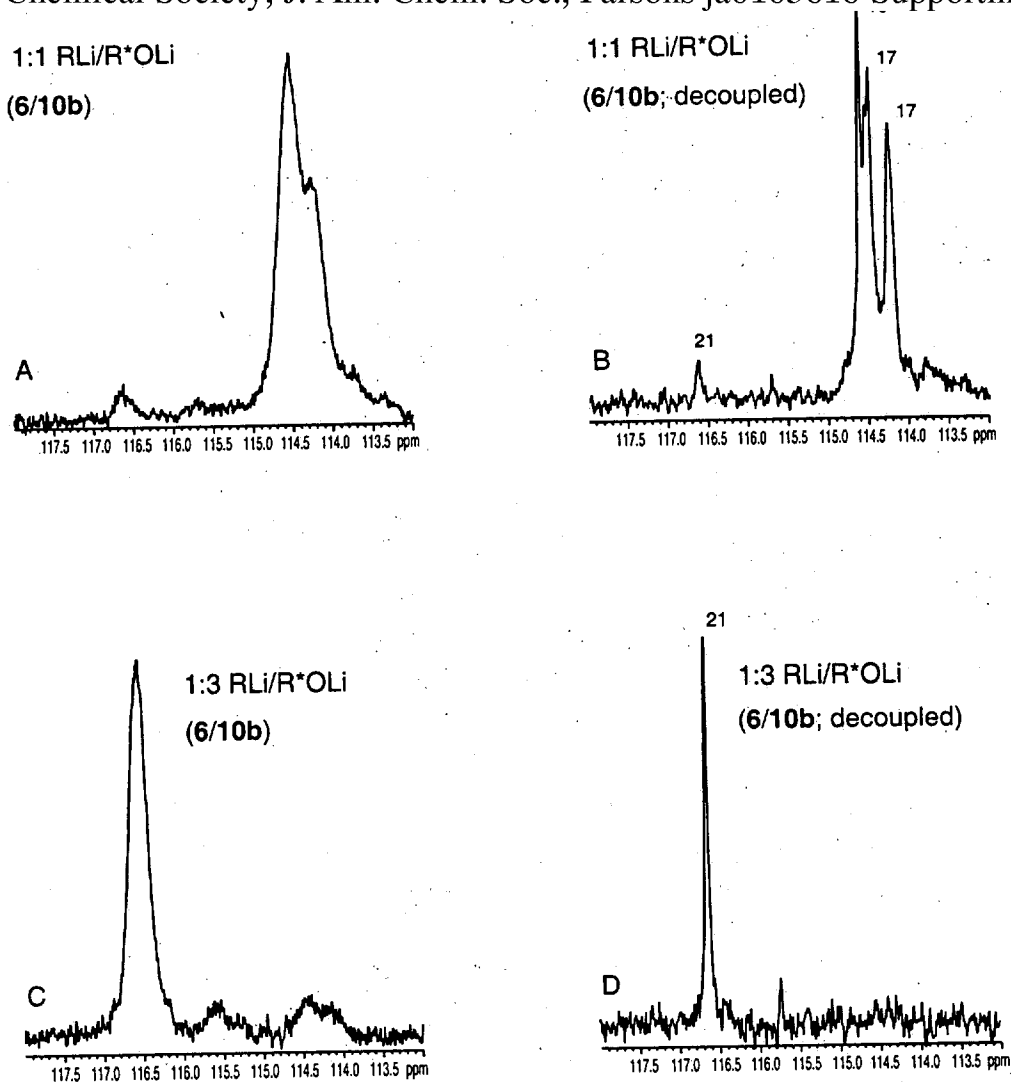


Figure 3. ^{13}C NMR spectra showing 2:2 RLi/R*OLi (16,17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in 80% THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of **6** and **10b** is 0.2 M in the proportions labeled on each spectrum. Spectra B and D were recorded with ^6Li broad-band decoupling.

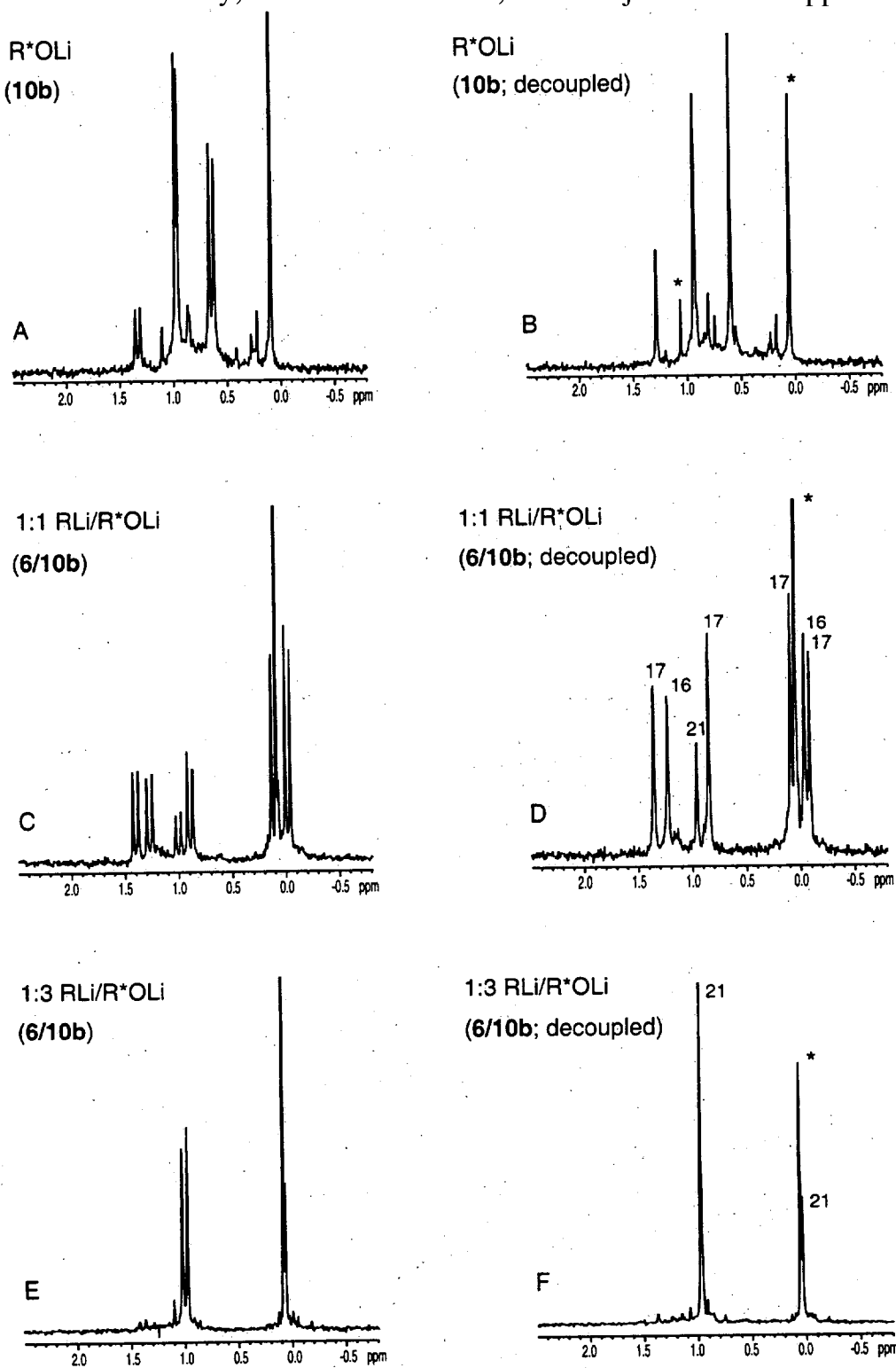


Figure 4. ^6Li NMR spectra showing 2:2 RLi/R*OLi (16,17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in 80% THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{15}N broad-band decoupling.

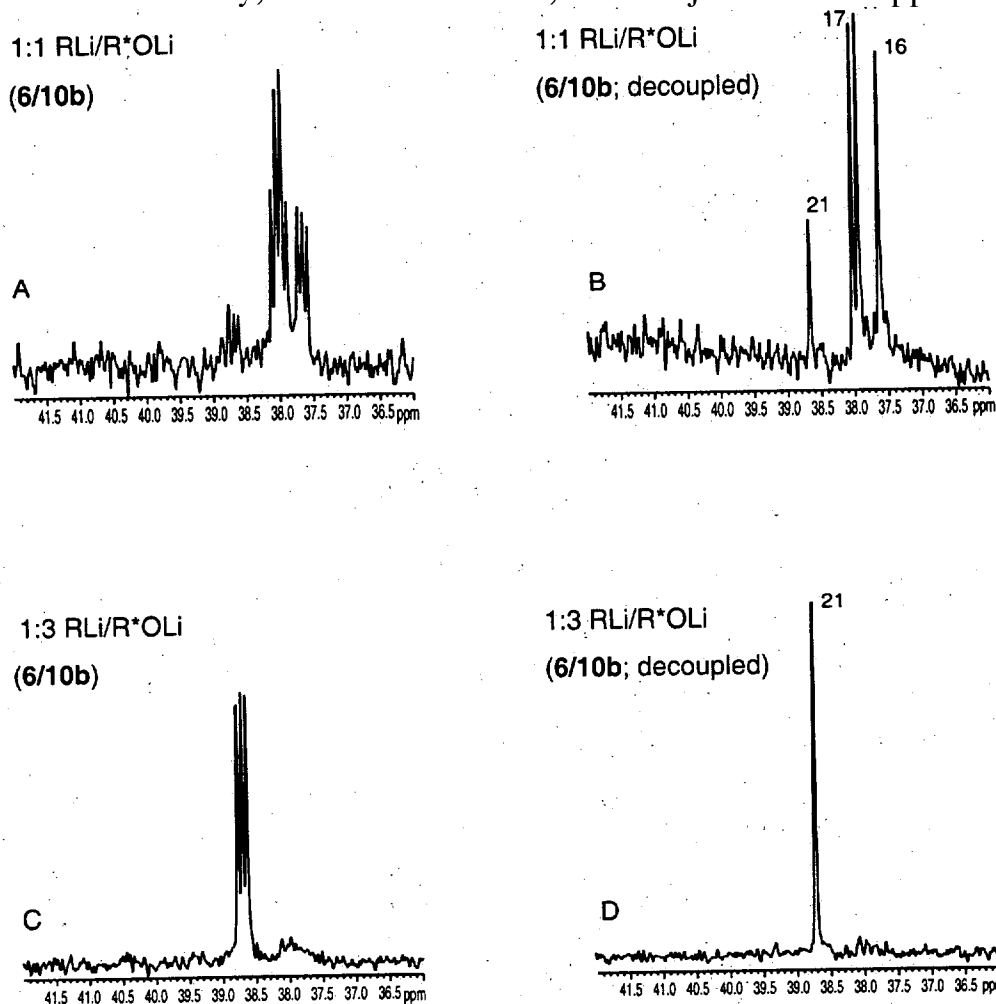


Figure 5. ^{15}N NMR spectra showing 2:2 RLi/R*OLi (16,17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in 80% THF/pentane at -115°C . The total titer of 6 and 10b is 0.2 M in the proportions labeled on each spectrum. Spectra B and D were recorded with ^6Li broad-band decoupling.

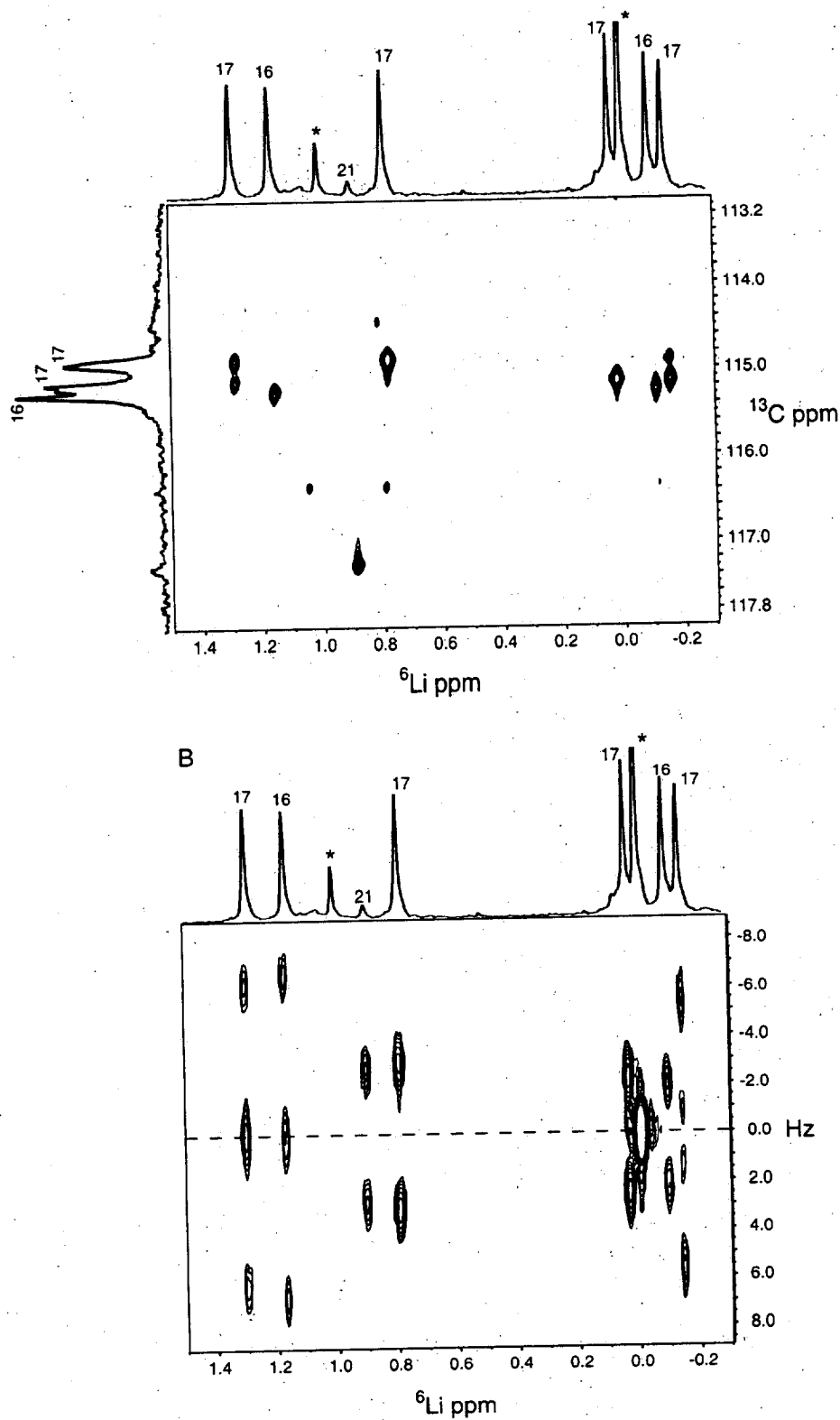


Figure 6. Spectra of 2:2 RLi/R*OLi showing mixed tetramers 16, 17 and 21. Spectra were recorded on mixtures of [$^6\text{Li},^{13}\text{C}$]LiCPA and [^6Li]10b (prepared in situ from the alcohol and 1.3 equiv. of [^6Li]LiHMDS(*)) in 80% THF/pentane at -115°C . The total titer of 6 and 10b is 0.2 M. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 1:1 [$^6\text{Li},^{13}\text{C}$]6/[^6Li]10b; (B) ^6Li J-resolved spectrum of 1:1 [$^6\text{Li},^{13}\text{C}$]6/[^6Li]10b.

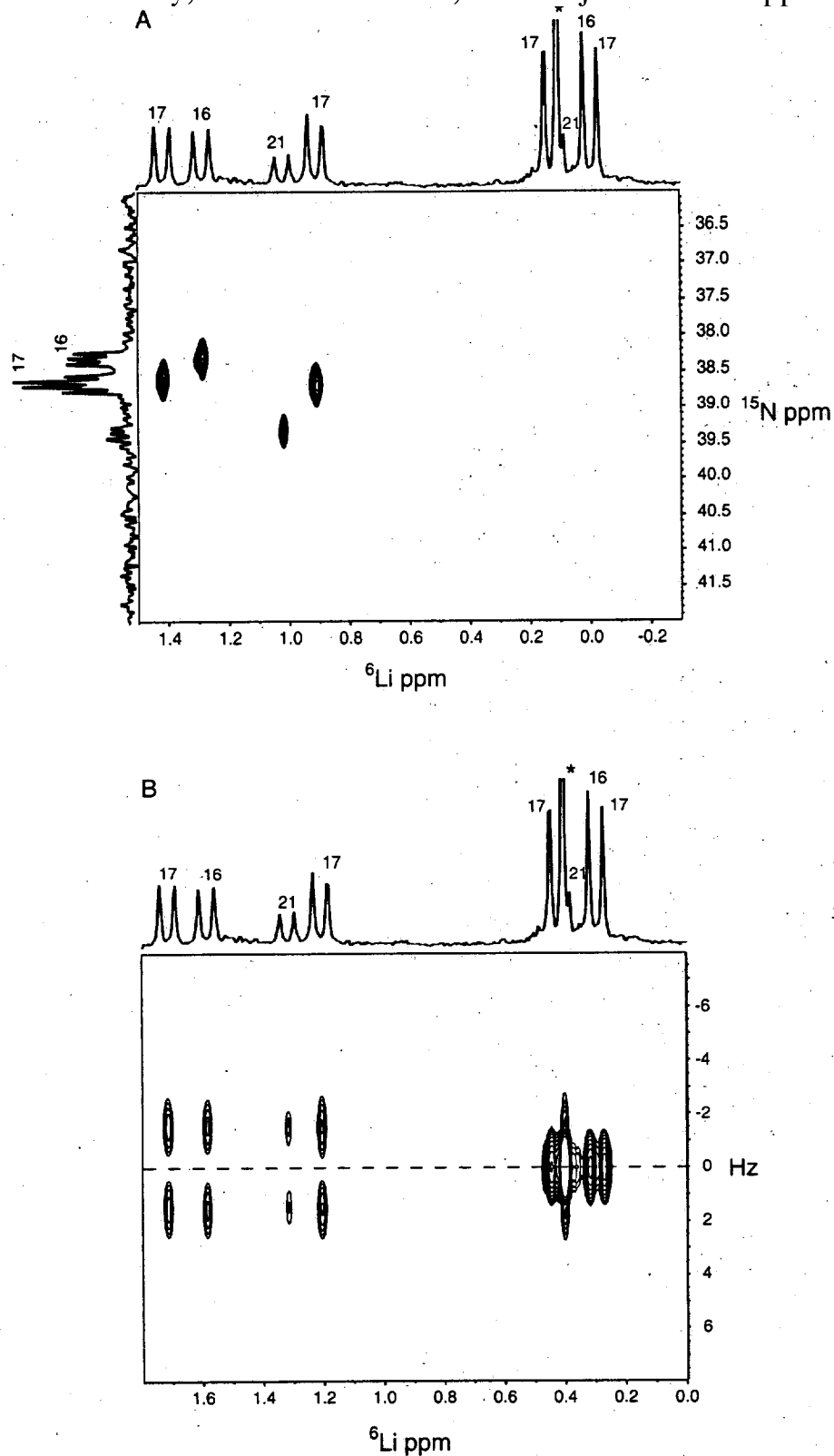
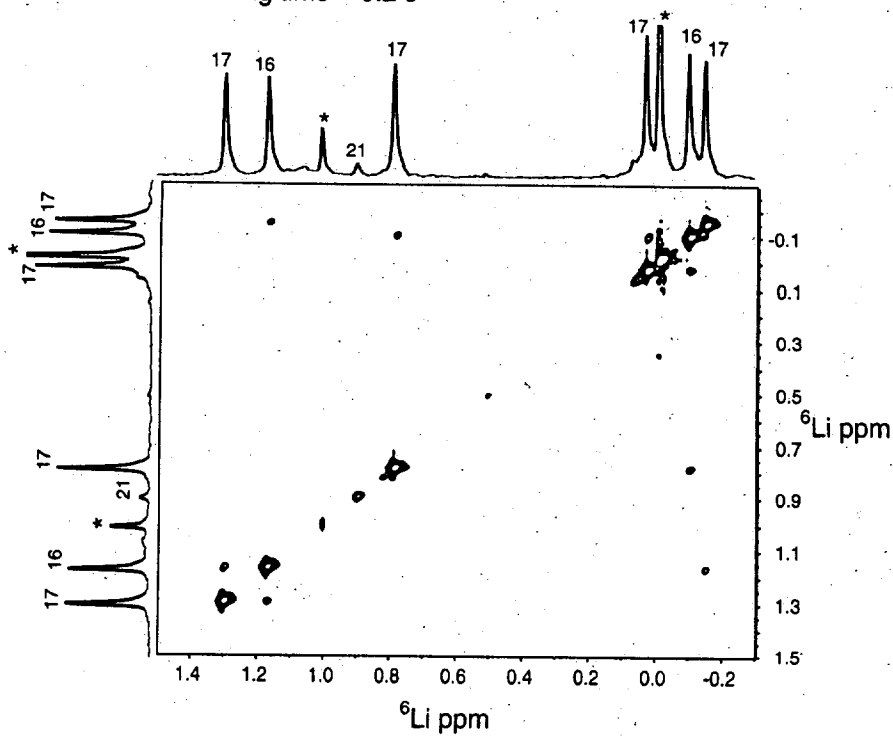
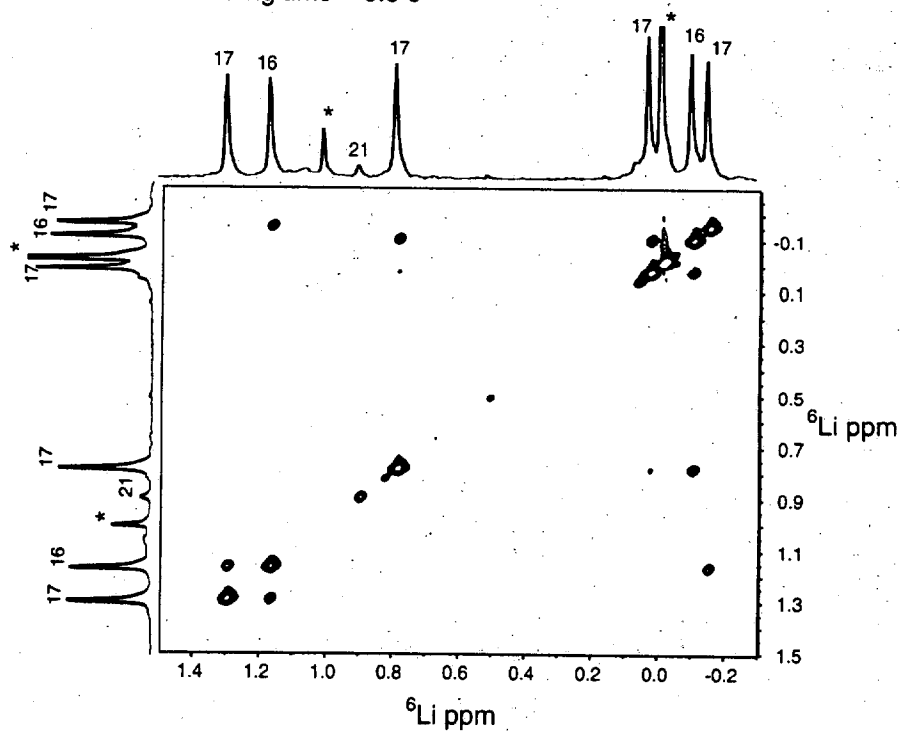


Figure 7. Spectra of 2:2 RLi/R*OLi showing mixed tetramers 16, 17 and 21. Spectra were recorded on mixtures of $[{}^6\text{Li}]\text{LiCPA}$ and $[{}^6\text{Li}, {}^{15}\text{N}]\mathbf{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[{}^6\text{Li}]\text{LiHMDS}^*$) in 80% THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of **6** and **10b** is 0.2 M. (A) ${}^6\text{Li}, {}^{15}\text{N}$ -HMOC of 1:1 $[{}^6\text{Li}]\mathbf{6}/[{}^6\text{Li}, {}^{15}\text{N}]\mathbf{10b}$; (B) ${}^6\text{Li}$ j-resolved spectrum of 1:1 $[{}^6\text{Li}]\mathbf{6}/[{}^6\text{Li}, {}^{15}\text{N}]\mathbf{10b}$.

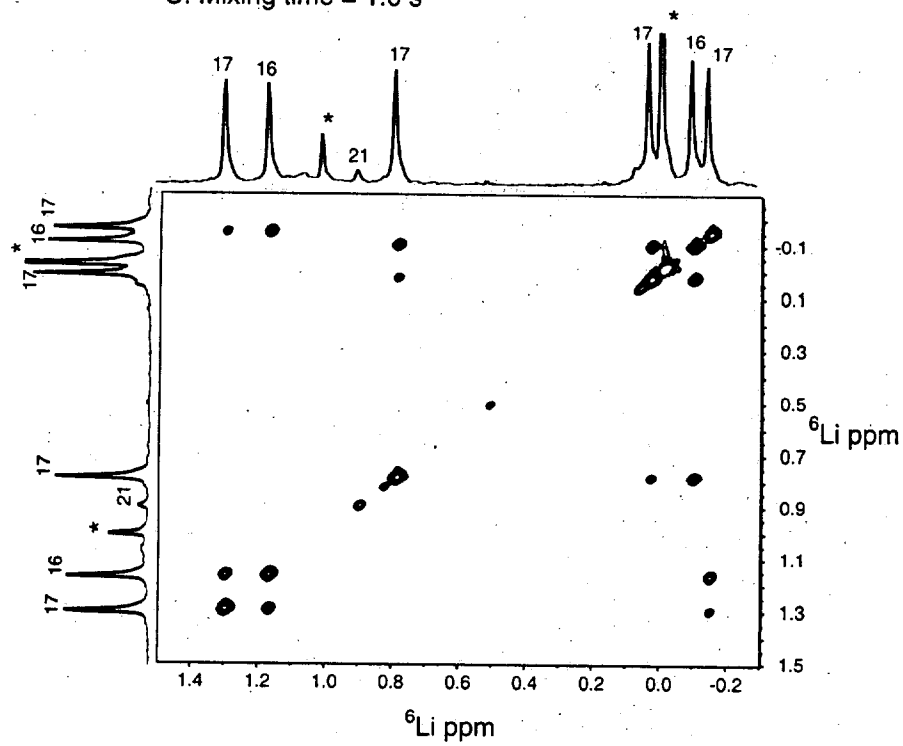


B. Mixing time = 0.5 s

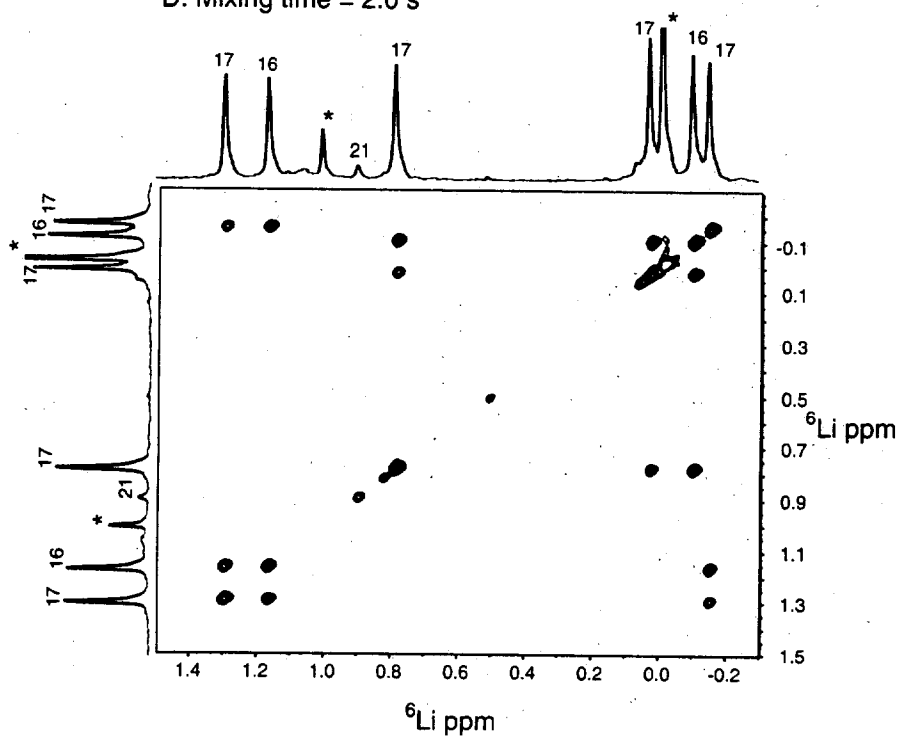


(Continued)

Next page



D. Mixing time = 2.0 s



(Continued)

Next page

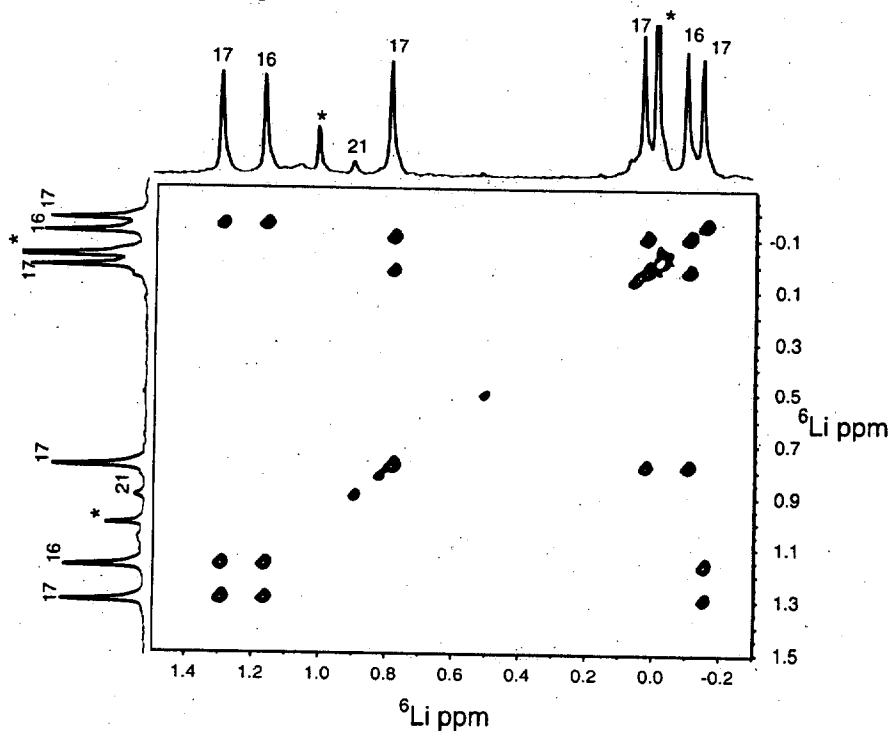
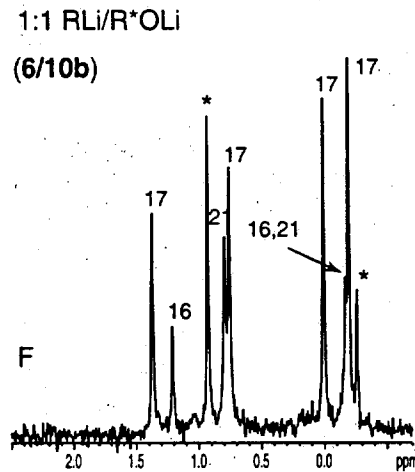
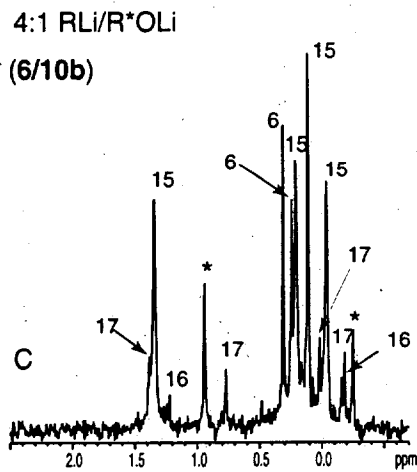
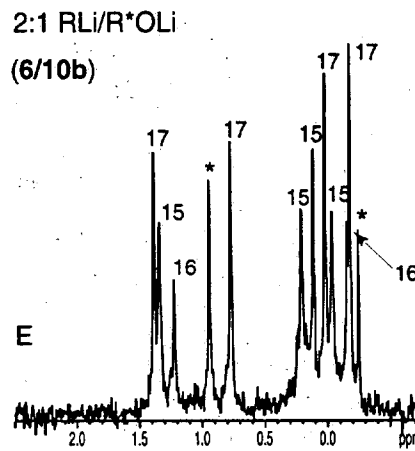
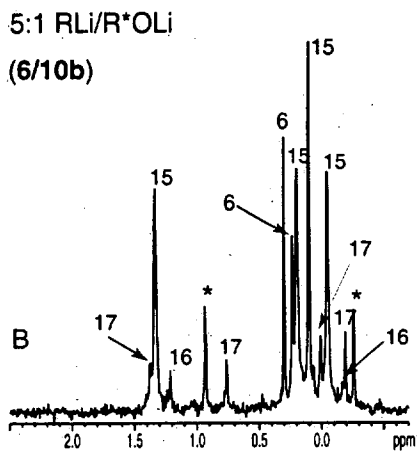
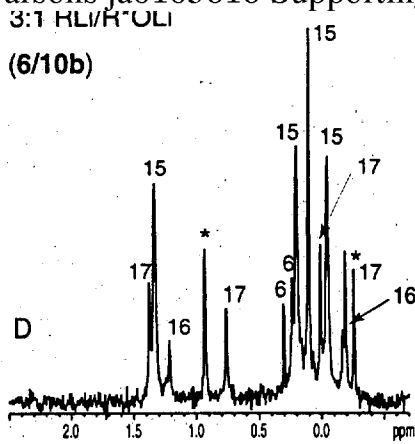
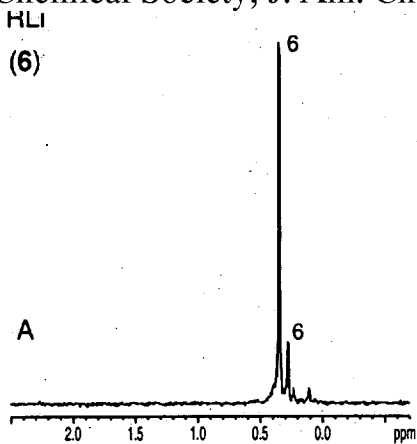


Figure 8. ${}^6\text{Li}$, ${}^6\text{Li}$ -EXSY spectra of 2:2 RLi/R*OLi showing mixed tetramers 16, 17 and 21. Spectra were recorded on mixtures of $[{}^6\text{Li}]\text{LiCPA}$ and $[{}^6\text{Li}]\mathbf{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[{}^6\text{Li}]\text{LiHMDS}^*$) in 80% THF/pentane at $-110\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.5 M. Mixing times are indicated on individual spectra.



(Continued)

Next page

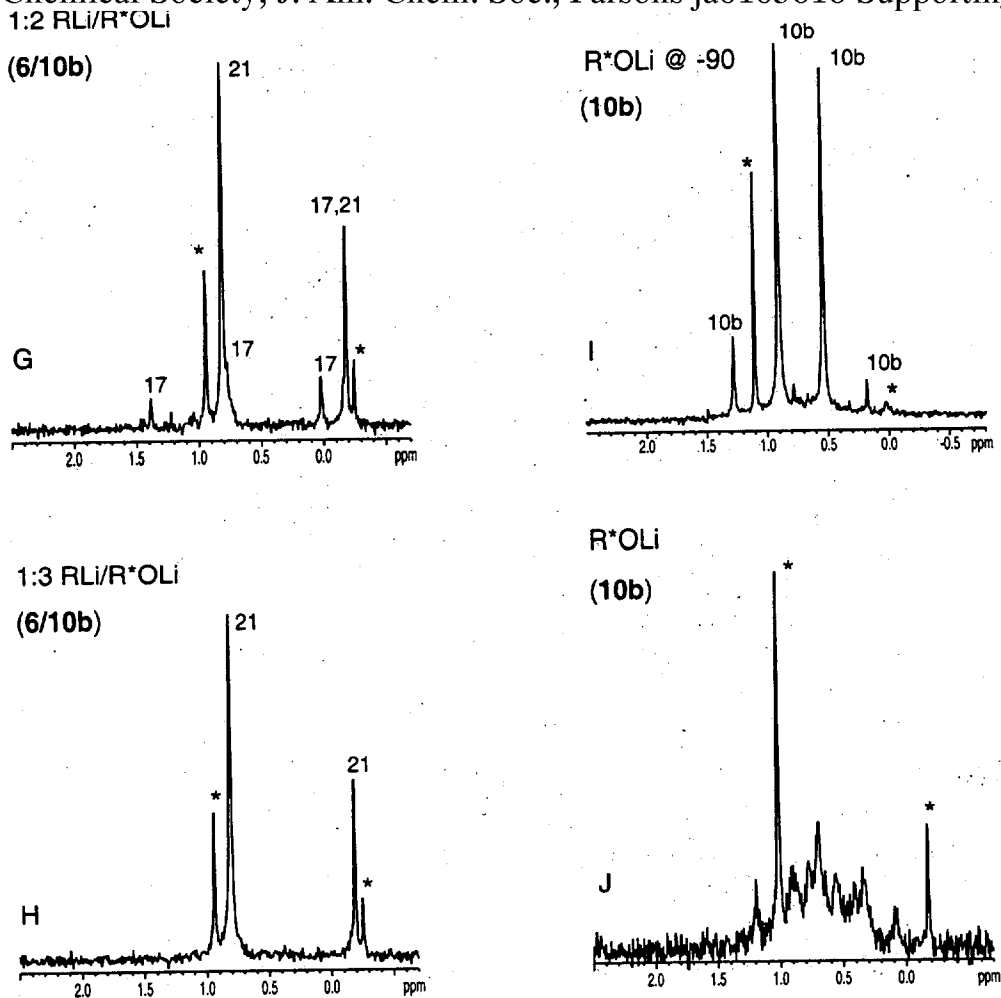


Figure 9. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$ (except where noted). The total titer of 6 and 10b is 0.1 M in the proportions labeled on each spectrum.

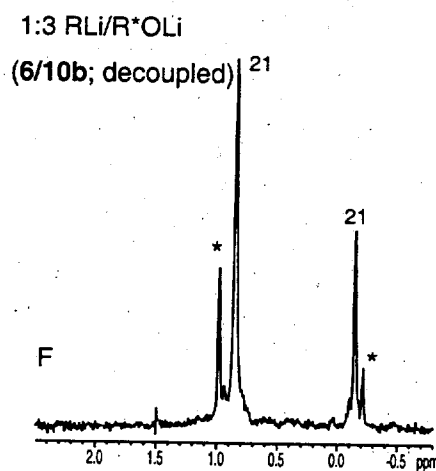
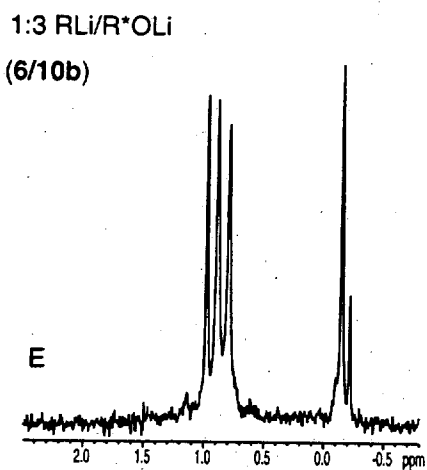
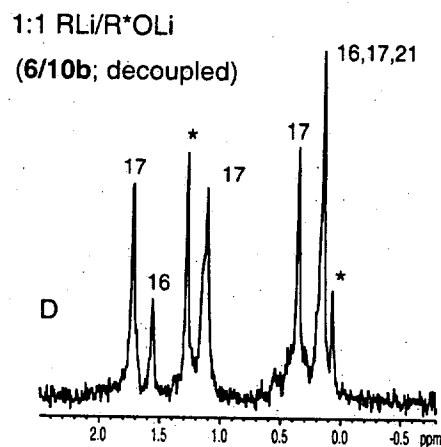
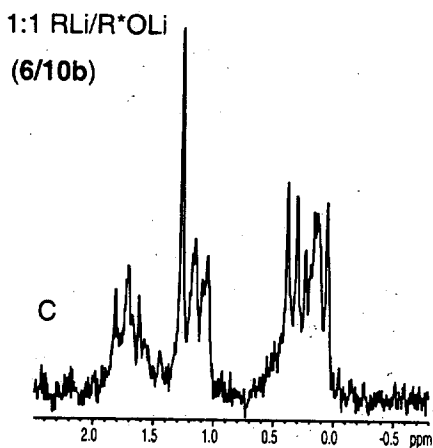
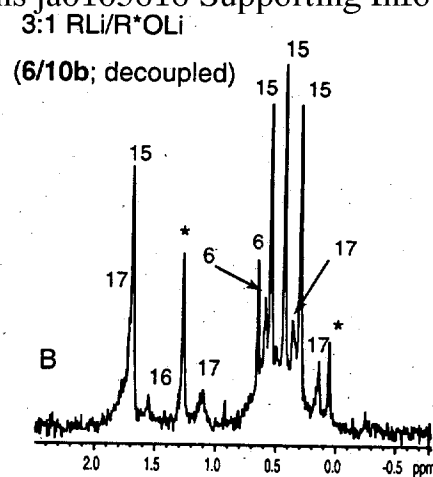
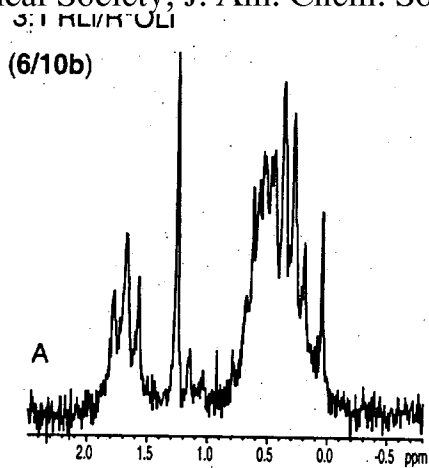
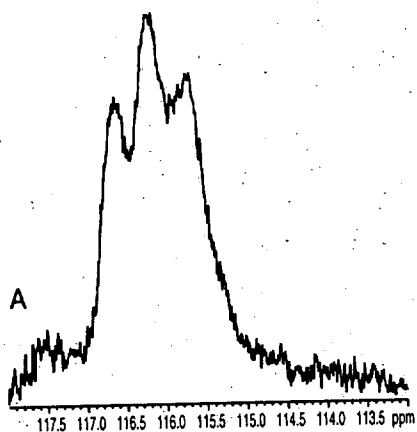


Figure 10. ^6Li NMR spectra showing 3:1 RLi/R*OLi (15), 2:2 RLi/R*OLi (16,17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li}, \text{}^{13}\text{C}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in 3:1:1 toluene/THF/pentane at -115°C . The total titer of 6 and 10b is 0.2 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^{13}C broad-band decoupling.

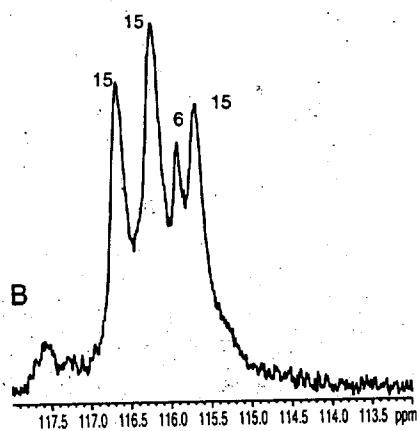
3:1 RLi/R*OLi

(6/10b)



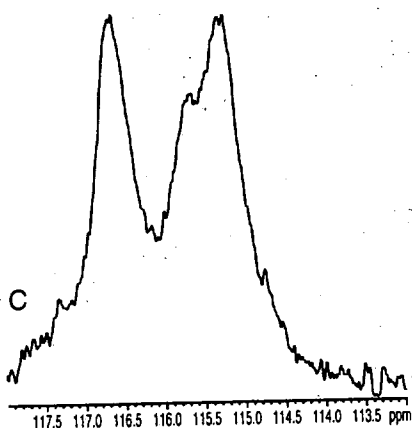
3:1 RLi/R*OLi

(6/10b; decoupled)



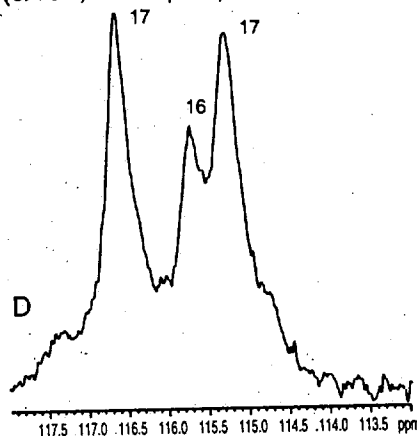
1:1 RLi/R*OLi

(6/10b)



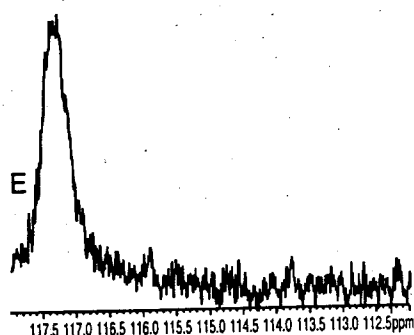
1:1 RLi/R*OLi

(6/10b; decoupled)



1:3 RLi/R*OLi

(6/10b)



1:3 RLi/R*OLi

(6/10b; decoupled)

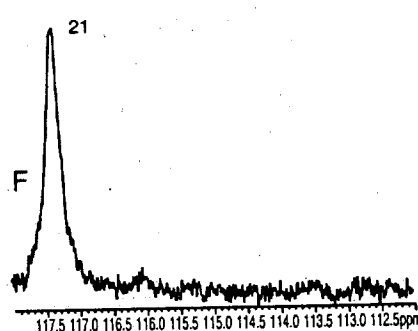


Figure 11. ^{13}C NMR spectra showing 3:1 RLi/R*OLi (15), 2:2 RLi/R*OLi (16,17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$. Spectra B, D, and F were recorded with ^6Li broad-band decoupling.

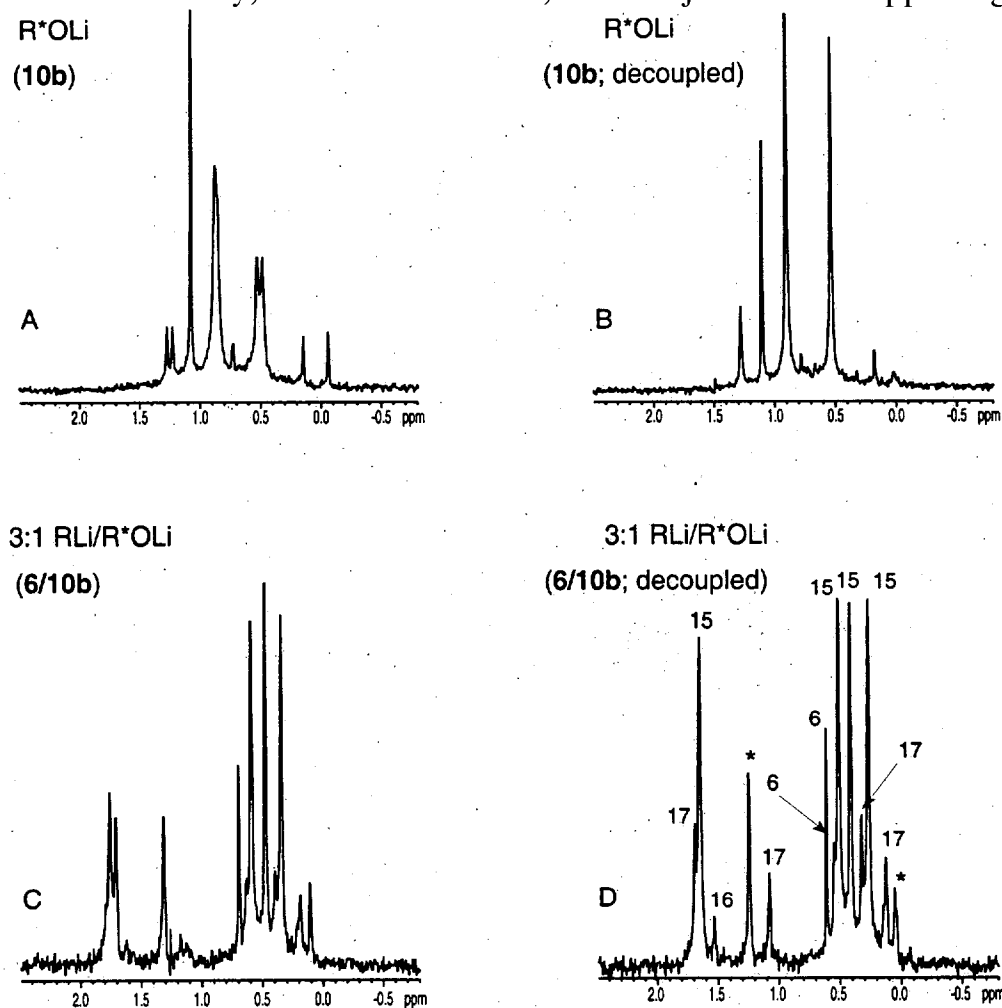


Figure 12. ${}^6\text{Li}$ NMR spectra showing R^*OLi (10b), 3:1 $\text{RLi}/\text{R}^*\text{OLi}$ (15) mixed tetramers. Spectra were recorded on mixtures of $[{}^6\text{Li}]\text{LiCPA}$ and $[{}^6\text{Li}, {}^{15}\text{N}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[{}^6\text{Li}]\text{LiHMDS}^*$) in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M in the proportions labeled on each spectrum. Spectra B and D were recorded with ${}^{15}\text{N}$ broad-band decoupling.

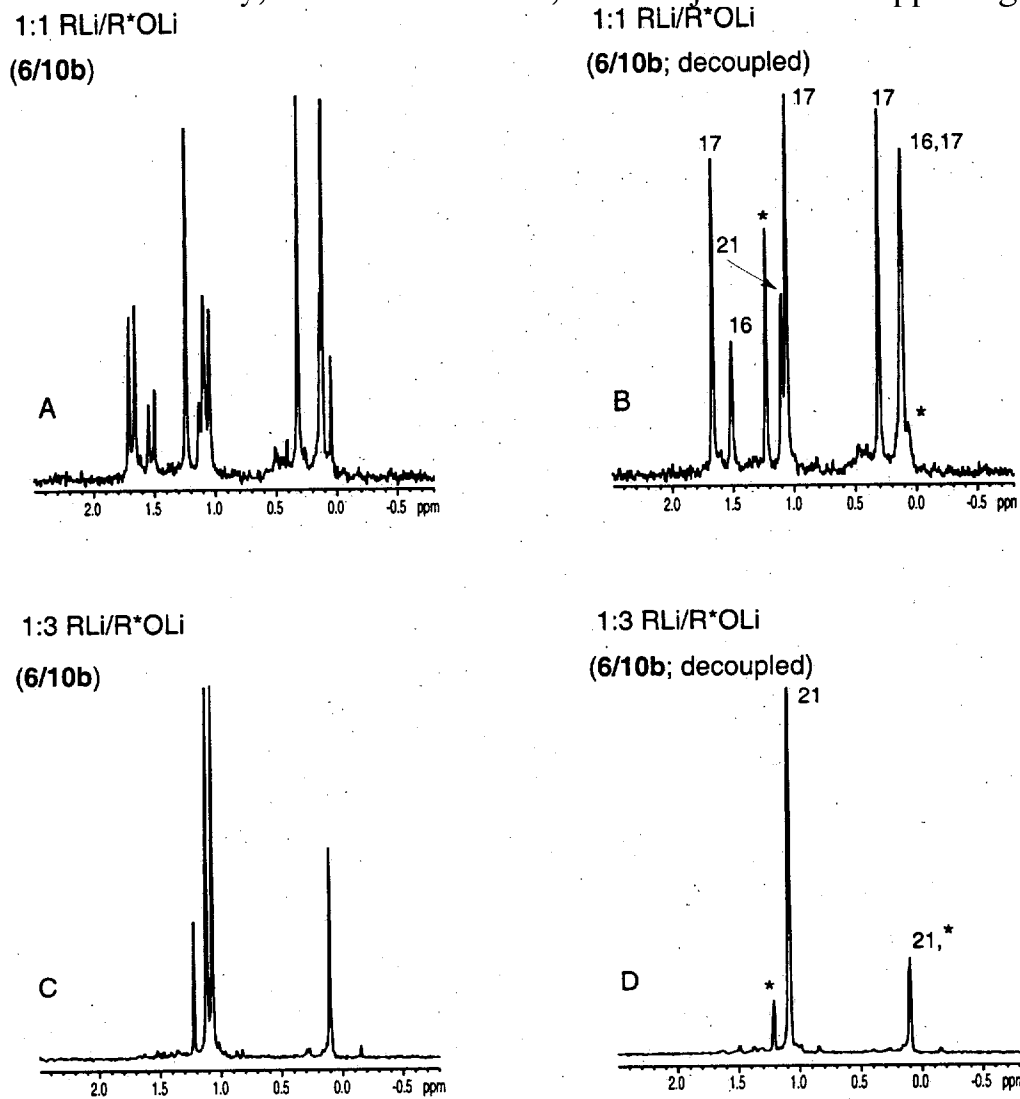


Figure 13. ^6Li NMR spectra showing 2:2 RLi/R*OLi (16,17), 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}(\ast)$) in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M in the proportions labeled on each spectrum. Spectra B and D were recorded with ^{15}N broad-band decoupling.

3:1 RLi/R*OLi

3:1 RLi/R*OLi

(6/10b)

(6/10b; decoupled)

A

B

41.5 41.0 40.5 40.0 39.5 39.0 38.5 38.0 37.5 37.0 36.5 ppm

41.5 41.0 40.5 40.0 39.5 39.0 38.5 38.0 37.5 37.0 36.5 ppm

1:1 RLi/R*OLi

1:1 RLi/R*OLi

(6/10b)

(6/10b; decoupled)

C

D

41.5 41.0 40.5 40.0 39.5 39.0 38.5 38.0 37.5 37.0 36.5 ppm

41.5 41.0 40.5 40.0 39.5 39.0 38.5 38.0 37.5 37.0 36.5 ppm

1:3 RLi/R*OLi

1:3 RLi/R*OLi

(6/10b)

(6/10b; decoupled)

E

F

41.5 41.0 40.5 40.0 39.5 39.0 38.5 38.0 37.5 37.0 36.5 ppm

41.5 41.0 40.5 40.0 39.5 39.0 38.5 38.0 37.5 37.0 36.5 ppm

Figure 14. ^{15}N NMR spectra showing 3:1 RLi/R*OLi (15), 2:2 RLi/R*OLi (16,17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of ^6Li LiCPA and $^6\text{Li},^{15}\text{N}$ 10b (prepared in situ from the alcohol and 1.3 equiv. of ^6Li LiHMDS *) in 3:1:1 toluene/THF/pentane at -115°C . The total titer of 6 and 10b is 0.2 M in the proportions labeled on each spectrum. Spectra B, D, and F were recorded with ^6Li broad-band decoupling.

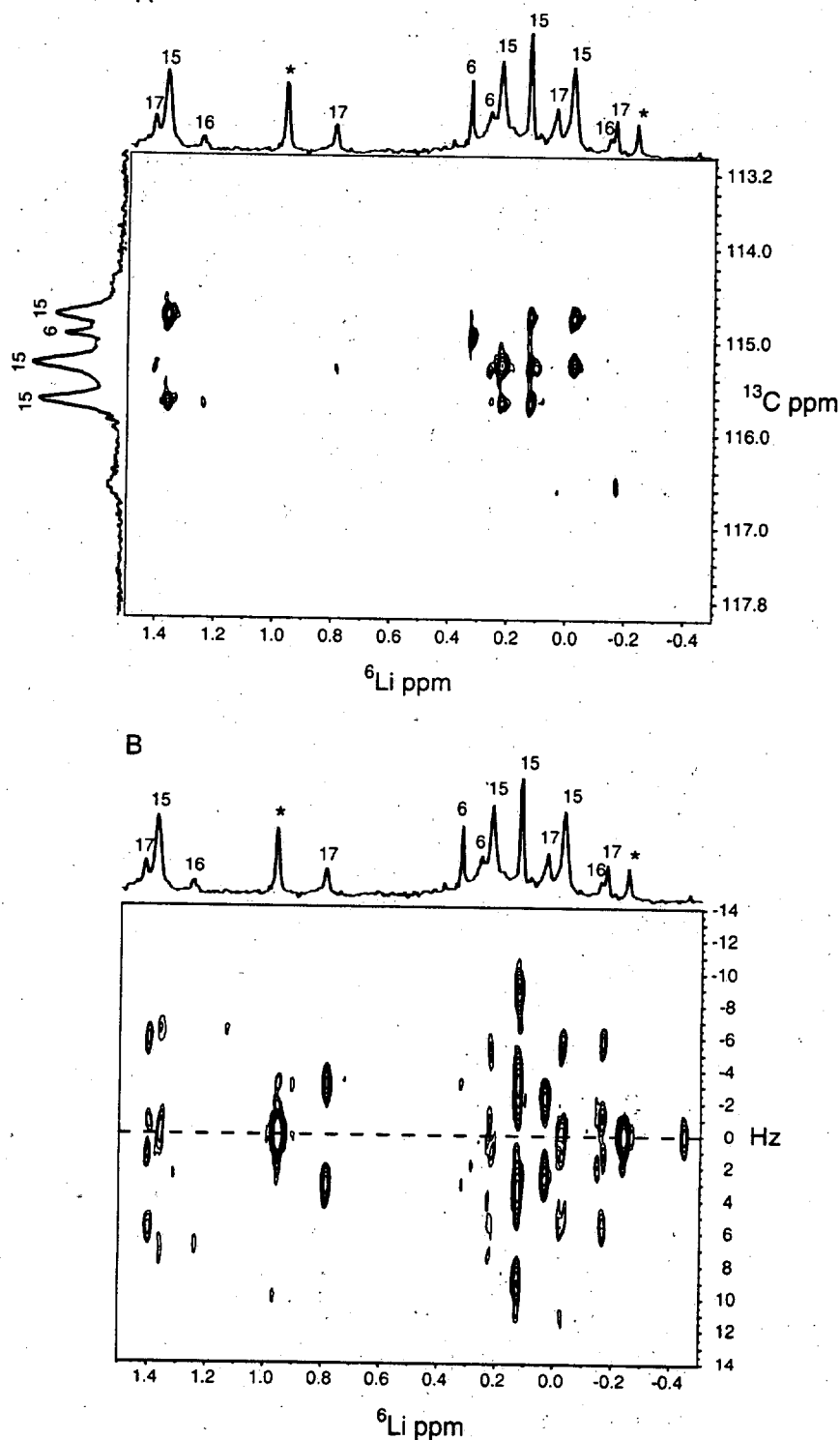


Figure 15. Spectra of 3:1 RLi/R*OLi showing mixed tetramers 15, 16, and 17. Spectra were recorded on mixtures of $[^6\text{Li},^{13}\text{C}]\text{LiCPA}$ and $[^6\text{Li}]\mathbf{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[^6\text{Li}]\text{LiHMDS}^*$) in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 3:1 $[^6\text{Li},^{13}\text{C}]\mathbf{1}/[^6\text{Li}]\mathbf{6}$; (B) ^6Li J -resolved spectrum of 3:1 $[^6\text{Li},^{13}\text{C}]\mathbf{6}/[^6\text{Li}]\mathbf{10b}$.

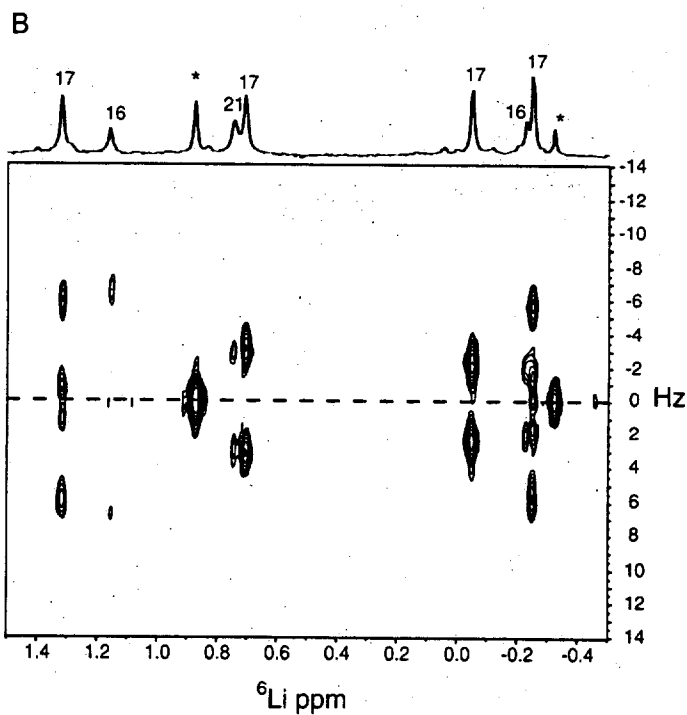
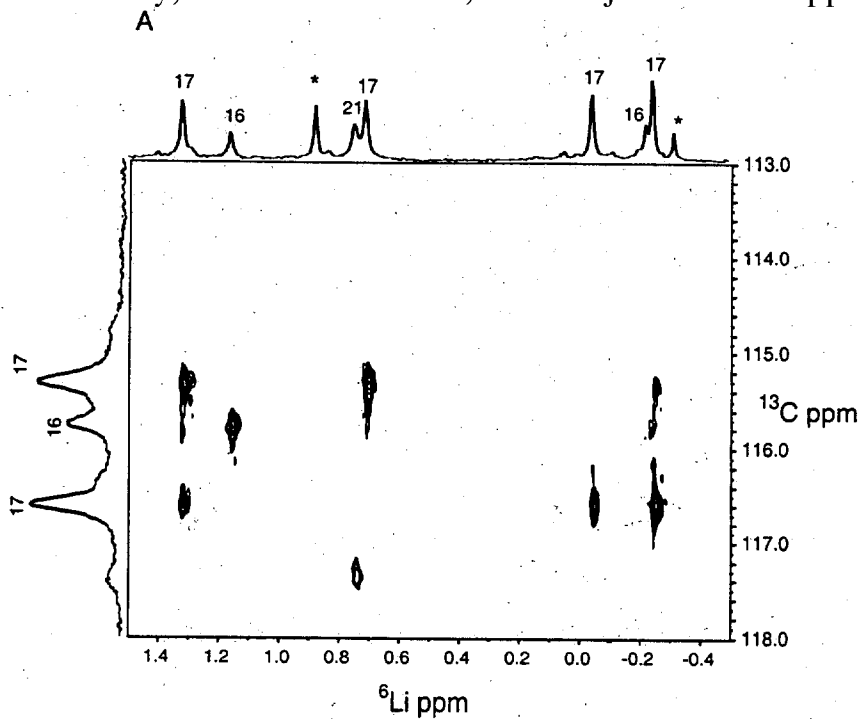


Figure 16. Spectra of 2:2 RLi/R*OLi showing mixed tetramers 16, 17, and 21. Spectra were recorded on mixtures of $[^6\text{Li},^{13}\text{C}]\text{LiCPA}$ and $[^6\text{Li}]\mathbf{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[^6\text{Li}]\text{LiHMDS}^*$) in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 2:2 $[^6\text{Li},^{13}\text{C}]\mathbf{6}/[^6\text{Li}]\mathbf{10b}$; (B) ^6Li J-resolved spectrum of 2:2 $[^6\text{Li},^{13}\text{C}]\mathbf{6}/[^6\text{Li}]\mathbf{10b}$.

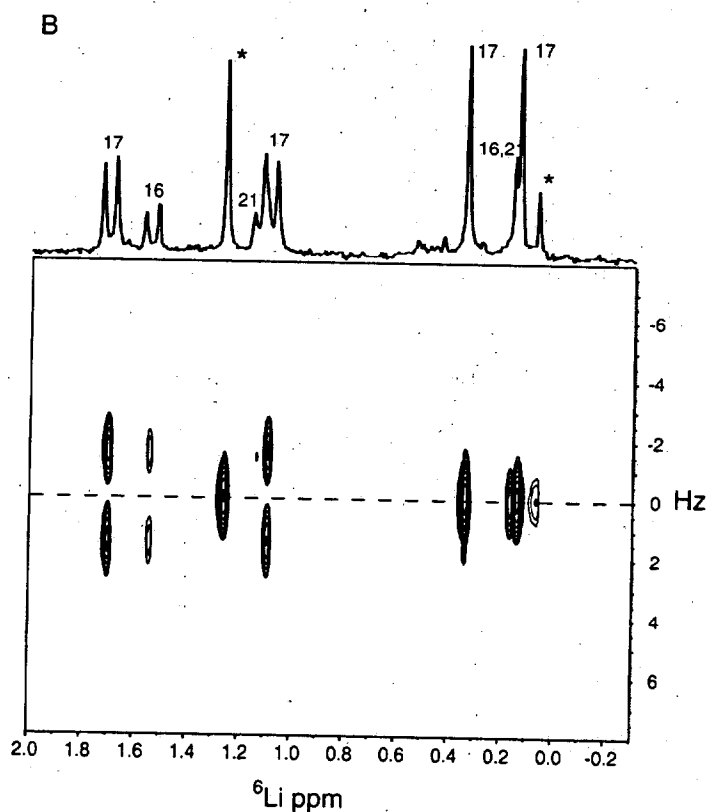
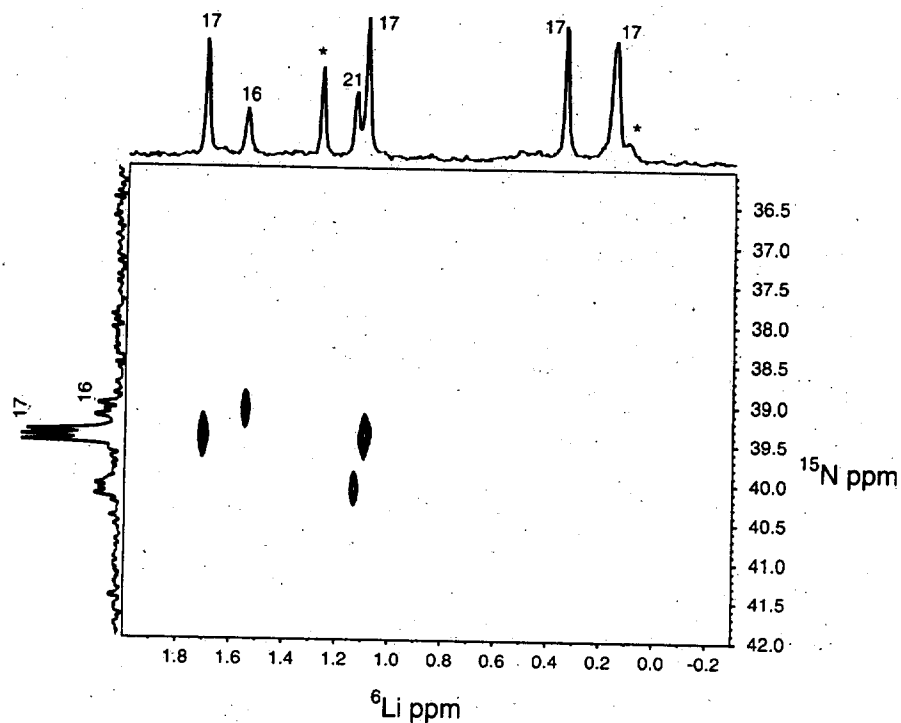


Figure 17. Spectra of 2:2 RLi/R*OLi showing mixed tetramers 16, 17, and 21. Spectra were recorded on mixtures of $[^6\text{Li}]\text{LiCPA}$ and $[^6\text{Li},^{15}\text{N}]\text{10b}$ in 3:1:1 toluene/THF/pentane at $-115\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M. (A) $^6\text{Li},^{15}\text{N}$ -HMQC of 1:1 $[^6\text{Li}]\text{6}/[^6\text{Li},^{15}\text{N}]\text{10b}$; (B) ^6Li J-resolved spectrum of 1:1 $[^6\text{Li}]\text{6}/[^6\text{Li},^{15}\text{N}]\text{10b}$.

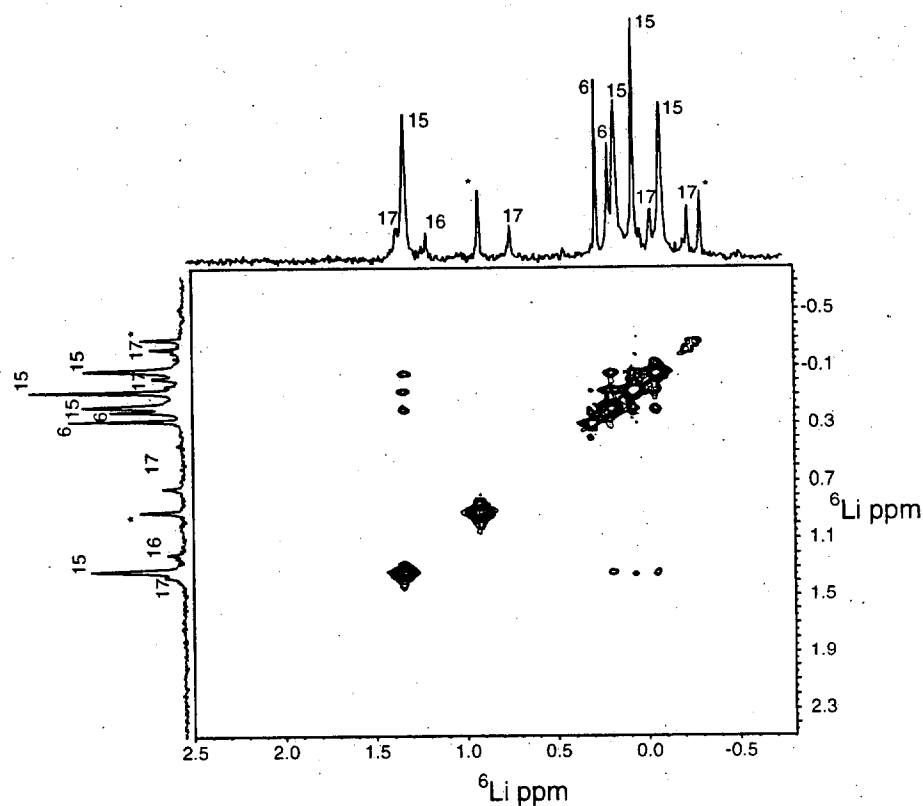
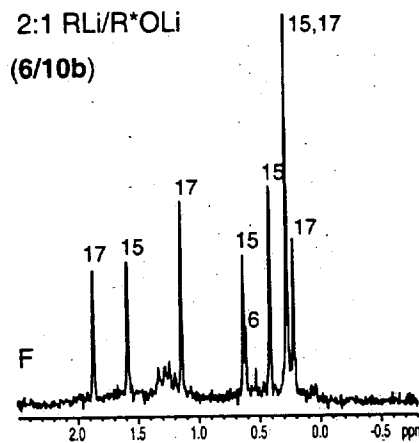
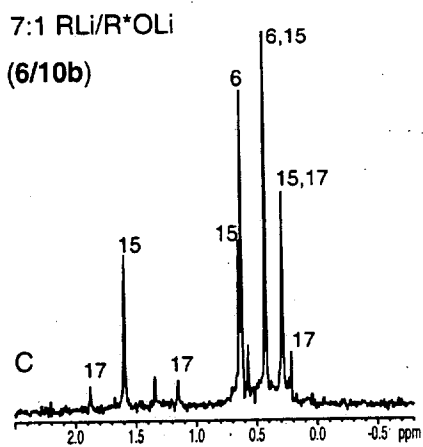
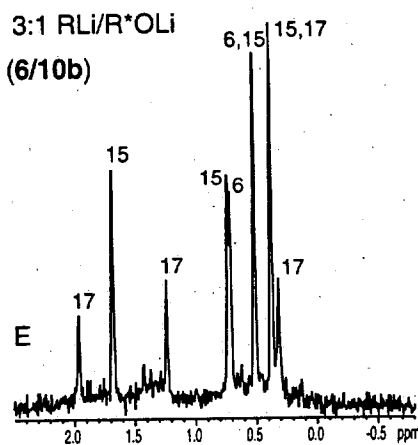
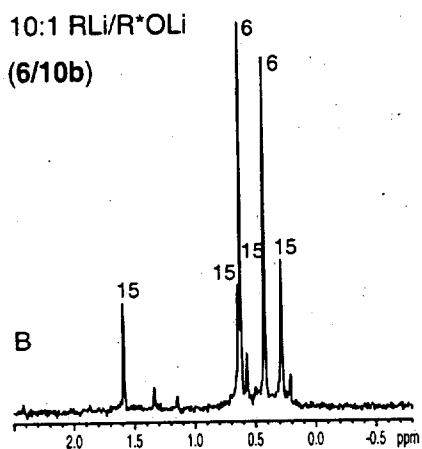
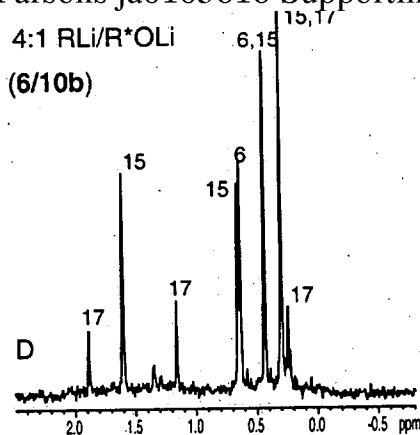
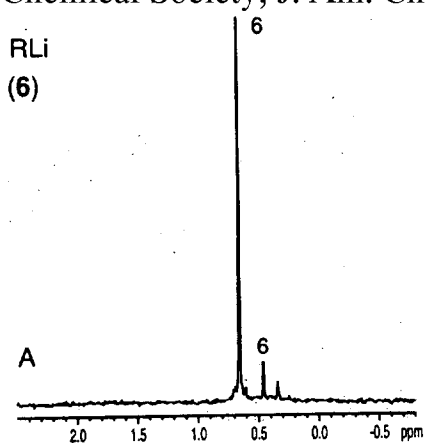


Figure 18. ^6Li , ^6Li -EXSY spectrum of 3:1 RLi/R*OLi showing mixed tetramer **15**. Spectrum was recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in 3:1:1 toluene/THF/pentane at -110°C . The total titer of **6** and **10b** is 0.5 M. Mixing time was 1.5 sec.



(Continued)

Next page

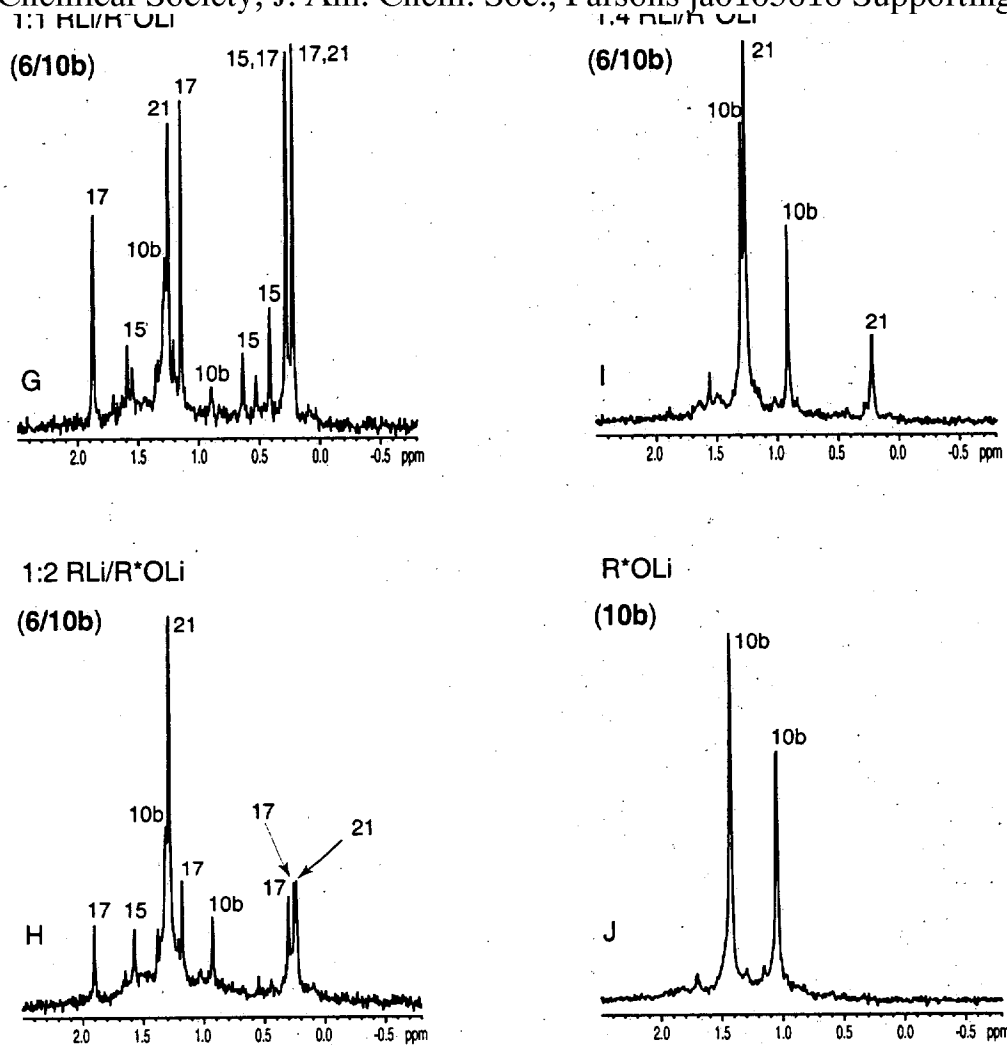


Figure 19. ^6Li NMR spectra recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in DMEA at $-100\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.1 M in the proportions labeled on each spectrum.

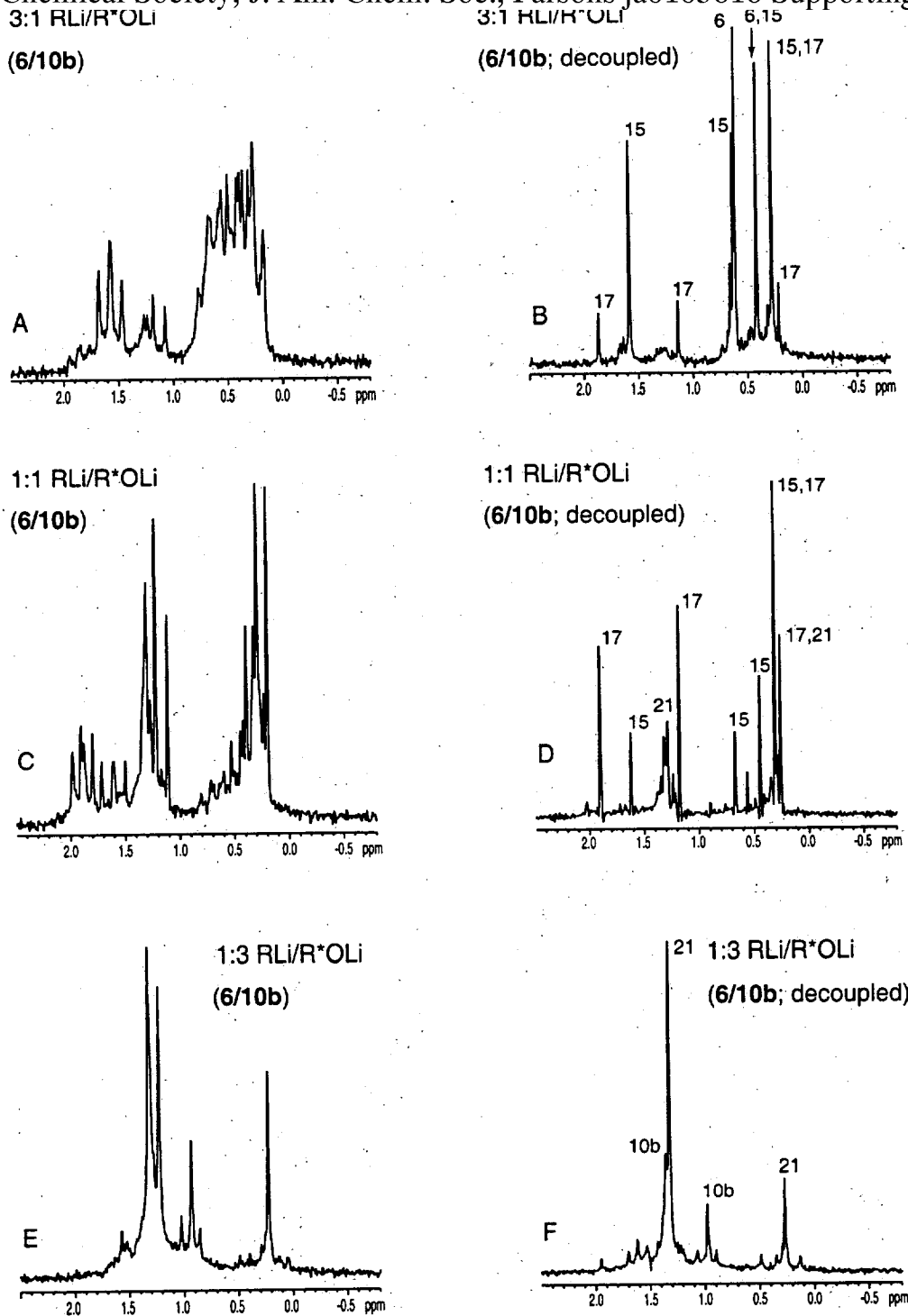


Figure 20. ${}^6\text{Li}$ NMR spectra showing 3:1 RLi/R*OLi (15), 2:2 RLi/R*OLi (17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[{}^6\text{Li}, {}^{13}\text{C}]\text{LiCPA}$ and $[{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[{}^6\text{Li}]\text{LiHMDS}^*$) in DMEA at $-100\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M. Spectra B, D, and F were recorded with ${}^{13}\text{C}$ broad-band decoupling.

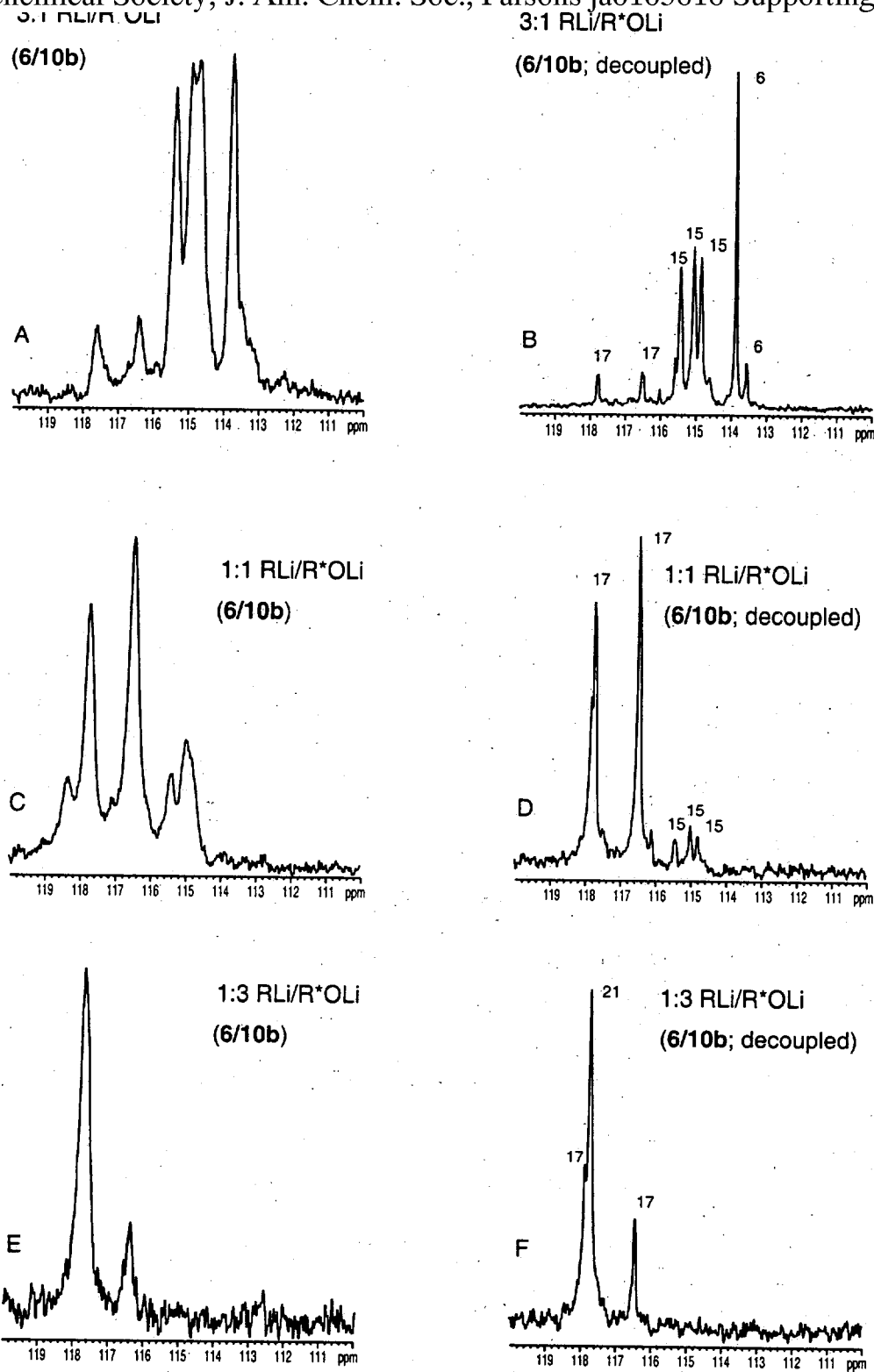


Figure 21. ^{13}C NMR spectra showing 3:1 RLi/R*OLi (15), 2:2 RLi/R*OLi (17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in DMEA at -100°C . The total titer of 6 and 10b is 0.2 M. Spectra B, D, and F were recorded with ^6Li broad-band decoupling.

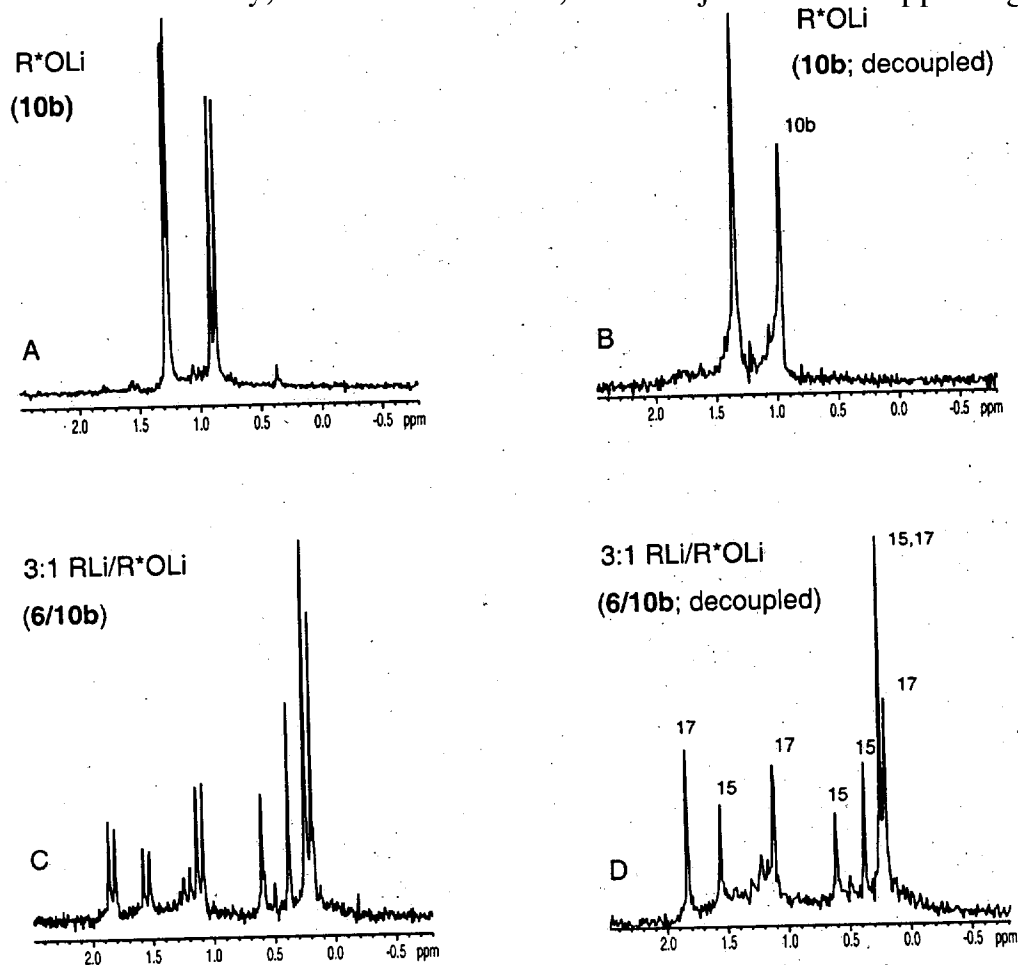


Figure 22. ^6Li NMR spectra showing R^*OLi (10b), 3:1 $\text{RLi}/\text{R}^*\text{OLi}$ (15) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li}, \text{}^{15}\text{N}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in DMEA at -100°C . The total titer of 6 and 10b is 0.2 M. Spectra B and D were recorded with ^{15}N broad-band decoupling.

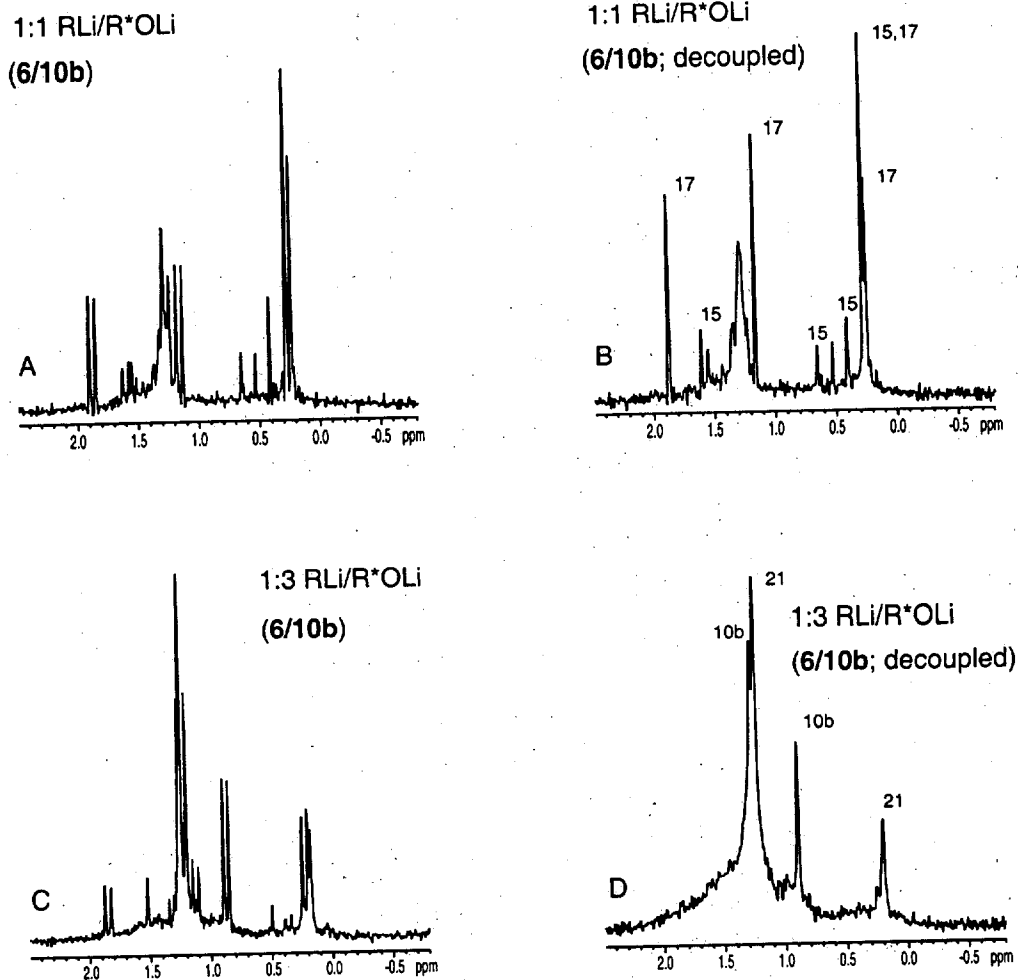


Figure 23. ^6Li NMR spectra showing 2:2 RLi/R*OLi (**17**), 1:3 RLi/R*OLi (**21**) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in DMEA at -100°C . The total titer of **6** and **10b** is 0.2 M. Spectra B and D were recorded with ^{15}N broad-band decoupling.

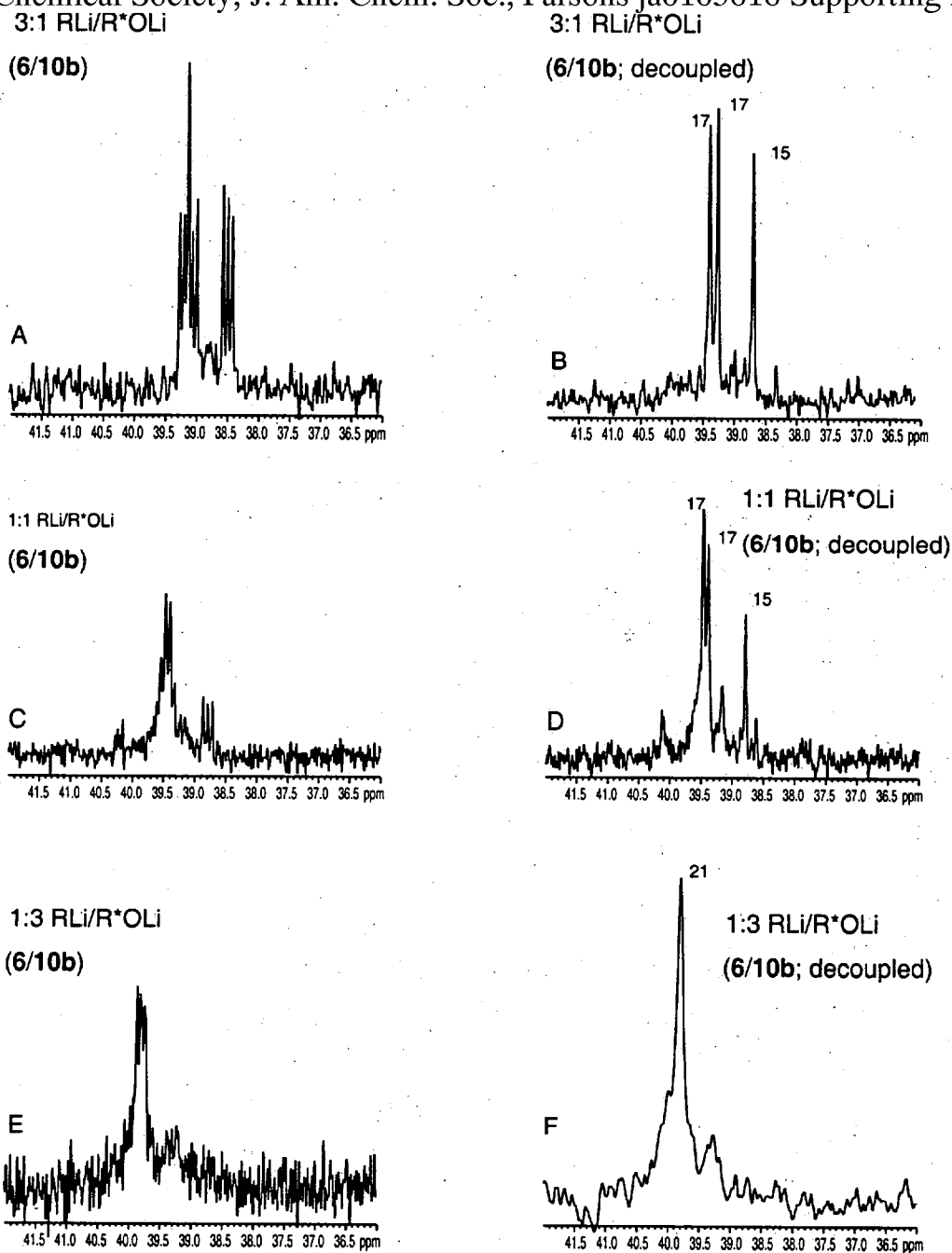


Figure 24. ^{15}N NMR spectra showing 3:1 RLi/R*OLi (15), 2:2 RLi/R*OLi (17) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li}]\text{LiCPA}$ and $[\text{}^6\text{Li},^{15}\text{N}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in DMEA at $-100\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M. Spectra B, D, and F were recorded with ^6Li broad-band decoupling.

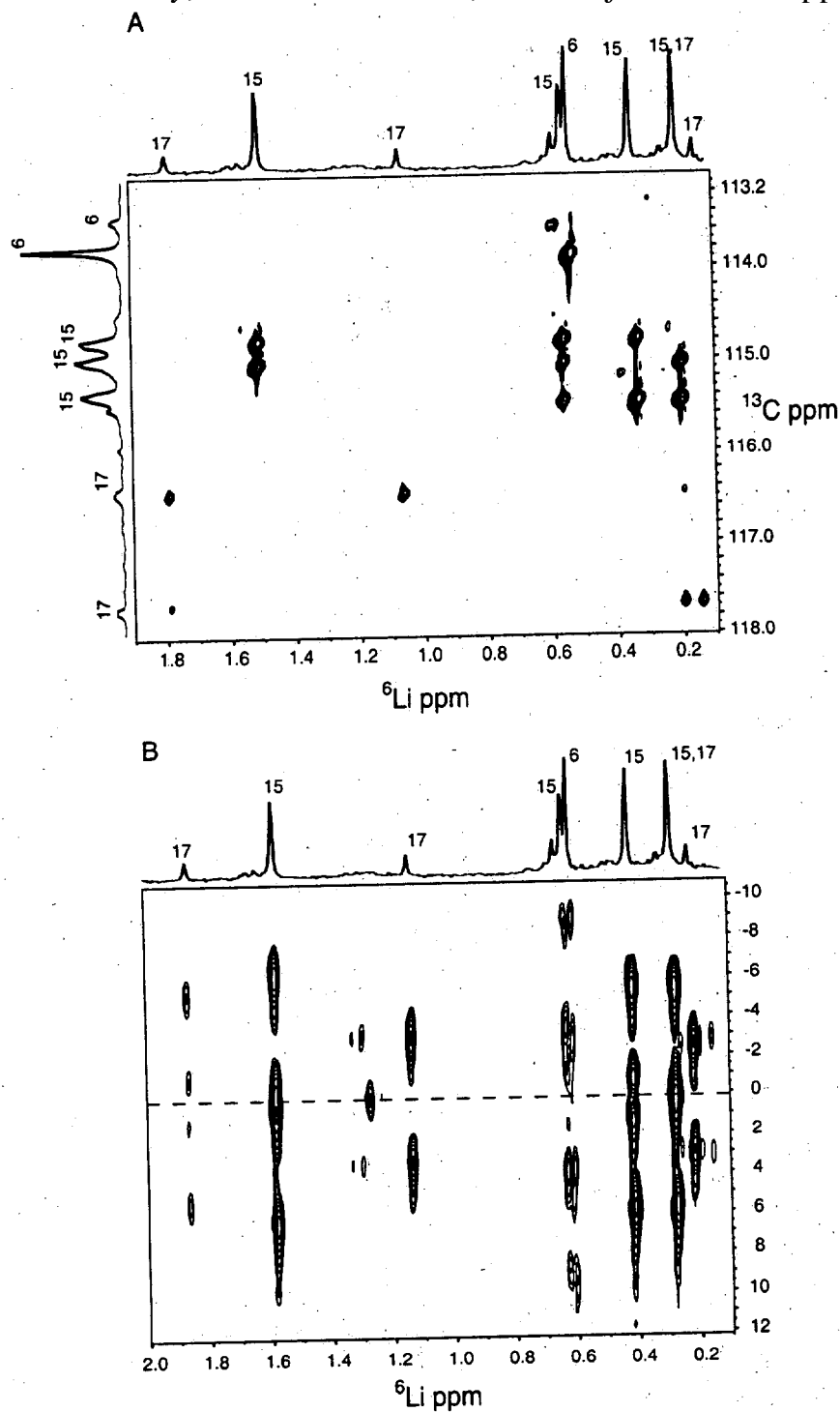


Figure 25. Spectra of 3:1 RLi/R*OLi showing mixed tetramers 15 and 17. Spectra were recorded on mixtures of $[^6\text{Li},^{13}\text{C}]\text{LiCPA}$ and $[^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[^6\text{Li}]\text{LiHMDS}^*$) in DMEA at $-100\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M. (A) $^6\text{Li},^{13}\text{C}$ -HMQC of 3:1 $[^6\text{Li},^{13}\text{C}]\text{6}/[^6\text{Li}]\text{10b}$; (B) ^6Li J-resolved spectrum of 3:1 $[^6\text{Li},^{13}\text{C}]\text{6}/[^6\text{Li}]\text{10b}$.

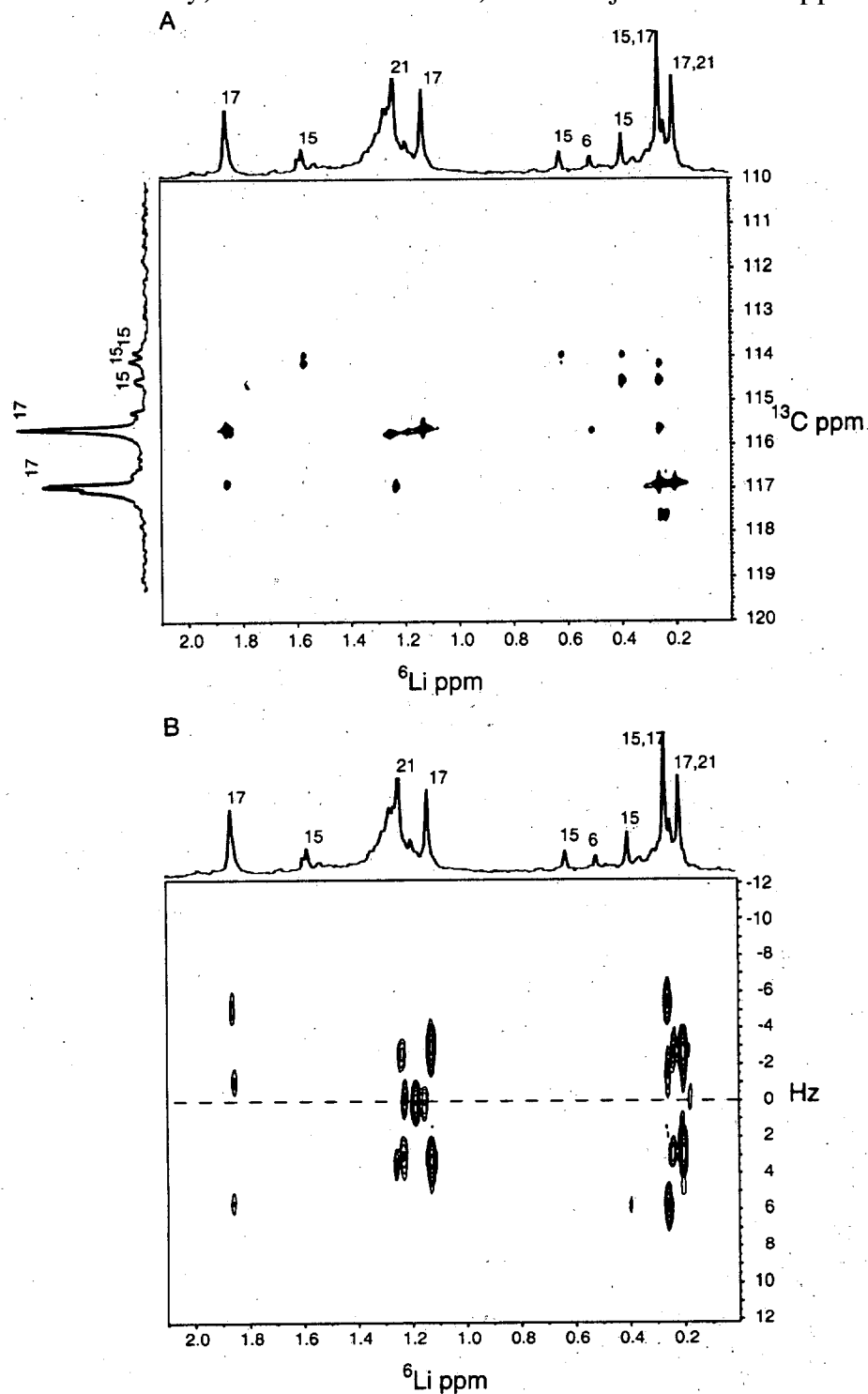


Figure 26. Spectra of 2:2 RLi/R*OLi showing mixed tetramers 15, 17, and 21. Spectra were recorded on mixtures of $[{}^6\text{Li}, {}^{13}\text{C}]\text{LiCPA}$ and $[{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[{}^6\text{Li}]\text{LiHMDS}^*$) in DMEA at $-100\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.2 M. (A) ${}^6\text{Li}, {}^{13}\text{C}$ -HMQC of 2:2 $[{}^6\text{Li}, {}^{13}\text{C}]\text{6}/[{}^6\text{Li}]\text{10b}$; (B) ${}^6\text{Li}$ J-resolved spectrum of 2:2 $[{}^6\text{Li}, {}^{13}\text{C}]\text{6}/[{}^6\text{Li}]\text{10b}$.

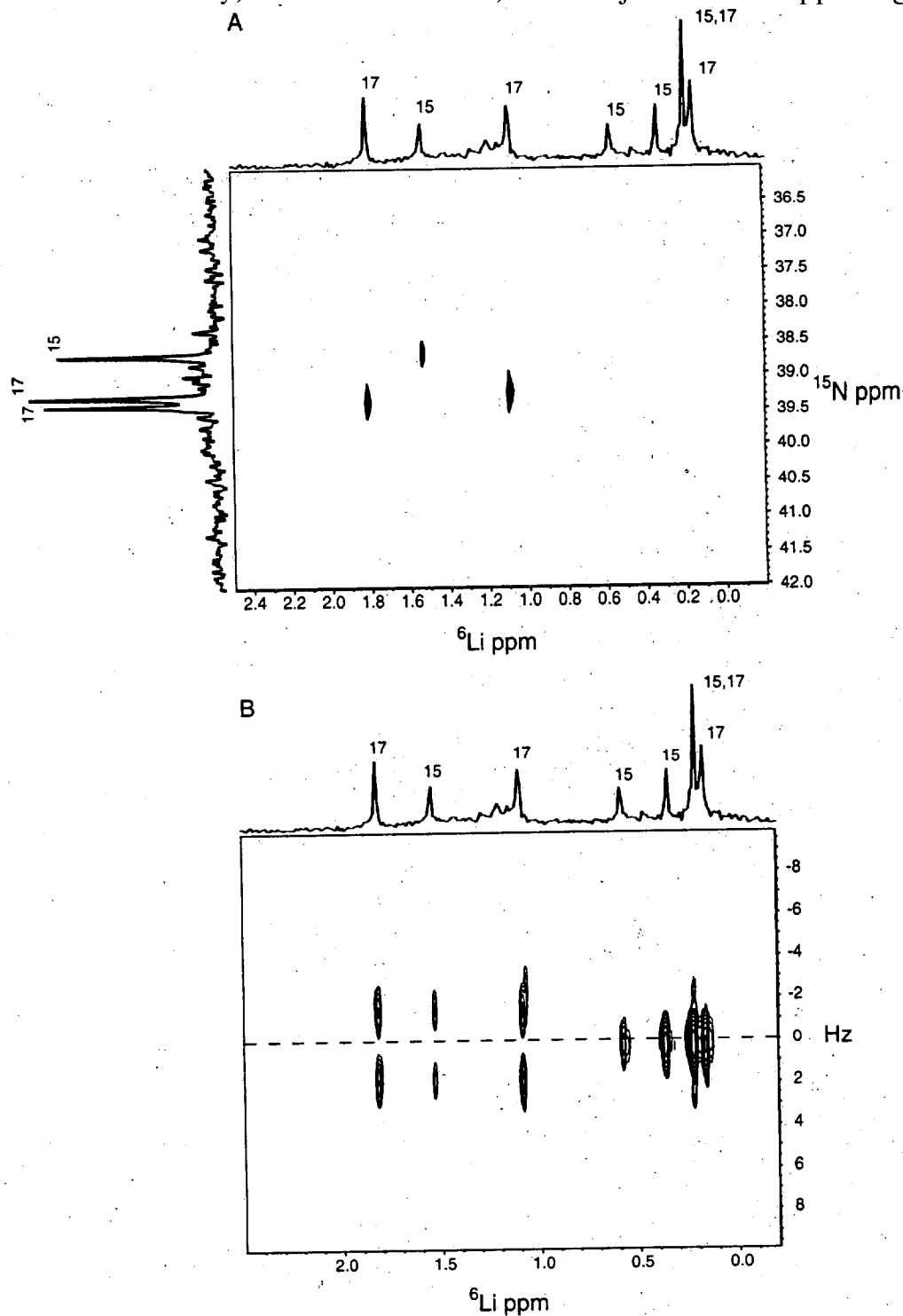
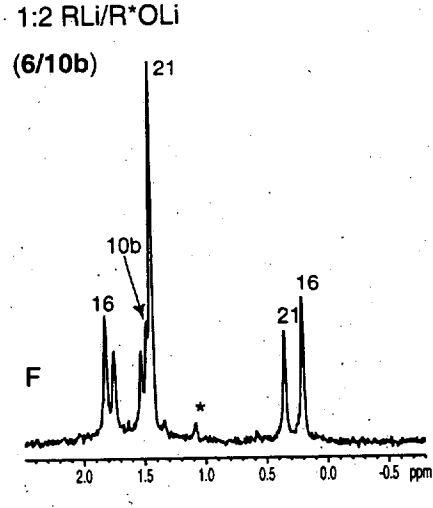
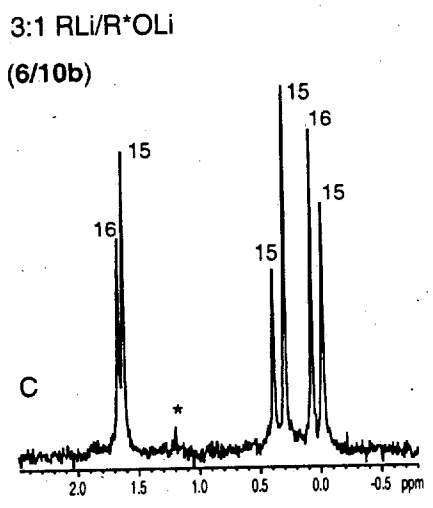
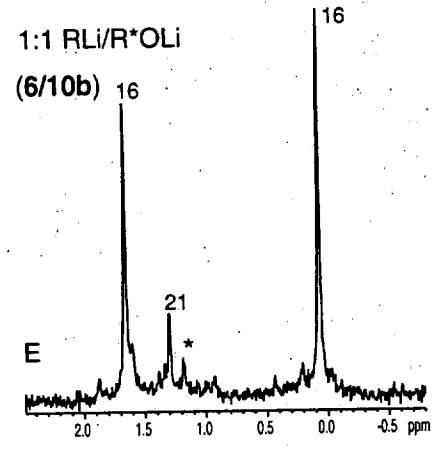
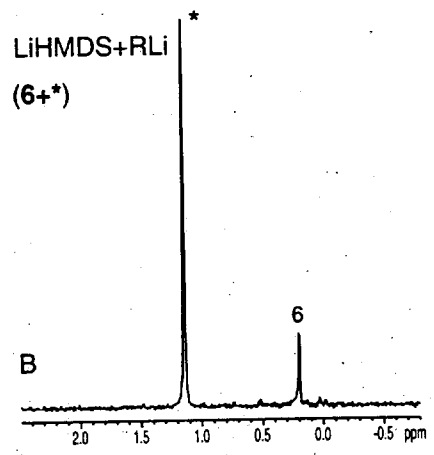
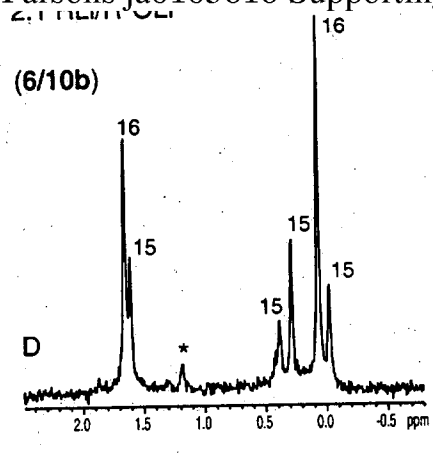
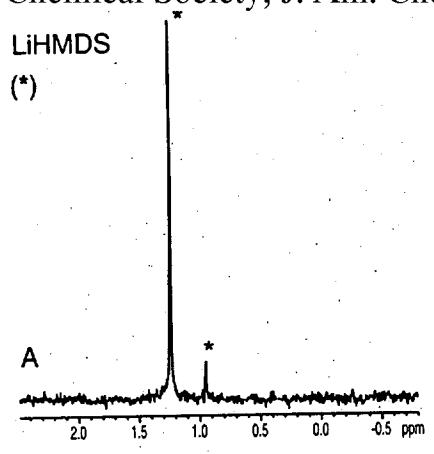


Figure 27. Spectra of 2:2 RLi/R*OLi showing mixed tetramers 15 and 17. Spectra were recorded on mixtures of $[{}^6\text{Li}]\text{LiCPA}$ and $[{}^6\text{Li}, {}^{15}\text{N}]\mathbf{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[{}^6\text{Li}]\text{LiHMDS}^*$) in DMEA at $-100\text{ }^\circ\text{C}$. The total titer of 6 and $\mathbf{10b}$ is 0.2 M. (A) ${}^6\text{Li}, {}^{15}\text{N}$ -HMOC of 1:1 $[{}^6\text{Li}]\mathbf{6}/[{}^6\text{Li}, {}^{15}\text{N}]\mathbf{10b}$; (B) ${}^6\text{Li}$ J-resolved spectrum of 1:1 $[{}^6\text{Li}]\mathbf{6}/[{}^6\text{Li}, {}^{15}\text{N}]\mathbf{10b}$.



(Continued)

Next page

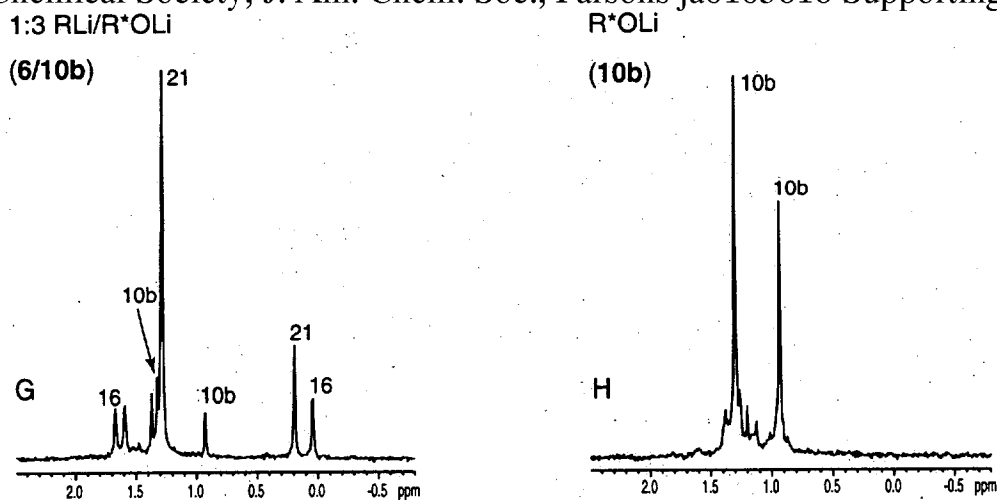


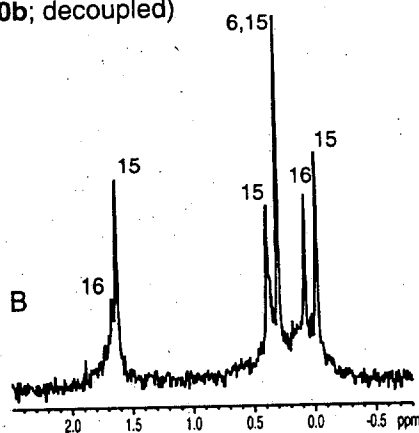
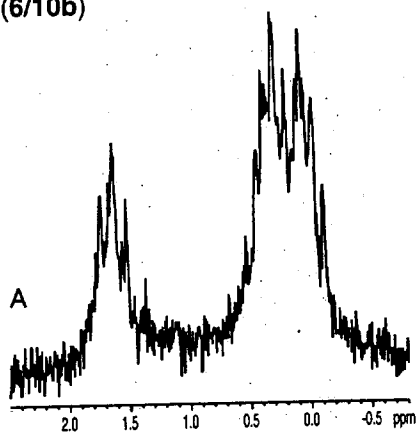
Figure 28. ${}^6\text{Li}$ NMR spectra recorded on mixtures of ${}^6\text{Li}$ and ${}^6\text{Li}$ 10b (prepared in situ from the alcohol and 1.3 equiv. of ${}^6\text{Li}$ LiHMDS(*)) in diethyl ether at $-95\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.1 M in the proportions labeled on each spectrum.

3:1 RLi/R*OLi

3:1 RLi/R*OLi

(6/10b)

(6/10b; decoupled)

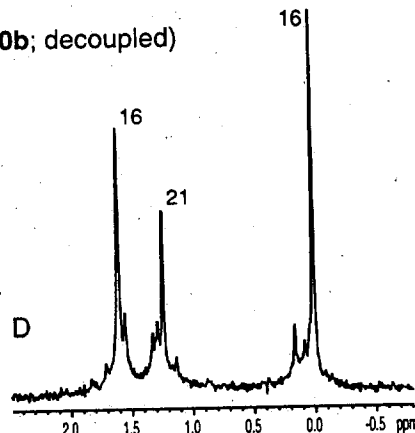
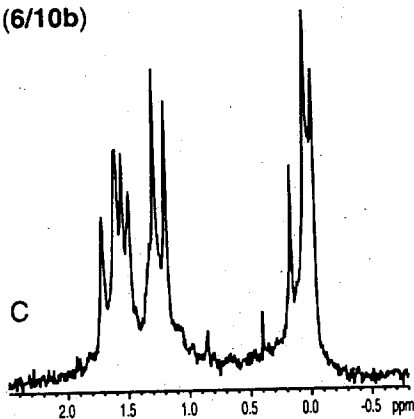


1:1 RLi/R*OLi

1:1 RLi/R*OLi

(6/10b)

(6/10b; decoupled)



1:3 RLi/R*OLi

1:3 RLi/R*OLi

(6/10b)

(6/10b; decoupled)

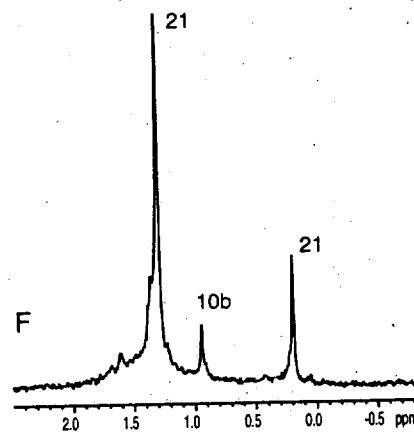
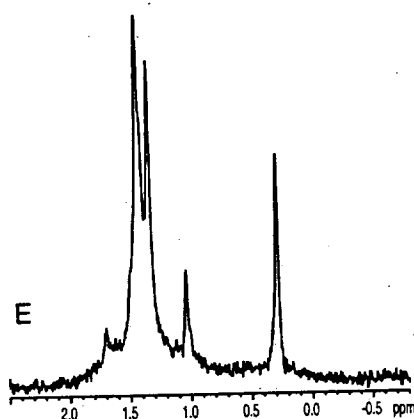
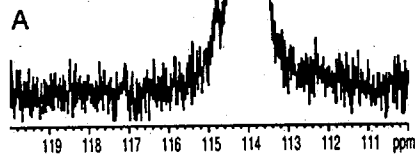


Figure 29. ^6Li NMR spectra showing 3:1 RLi/R*OLi (15), 2:2 RLi/R*OLi (16) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[^6\text{Li},^{13}\text{C}]\text{LiCPA}$ and $[^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[^6\text{Li}]\text{LiHMDS}^*$) in diethyl ether at -95°C . The total titer of 6 and 10b is 0.1 M. Spectra B, D, and F were recorded with ^{13}C broad-band decoupling.

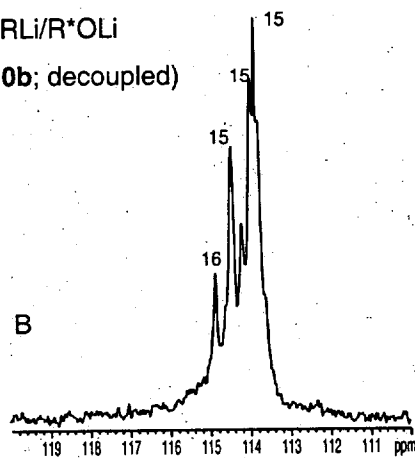
3:1 RLi/R*OLi

(6/10b)



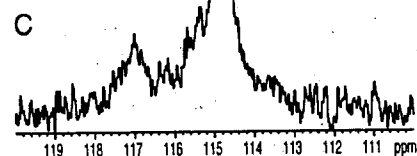
3:1 RLi/R*OLi

(6/10b; decoupled)



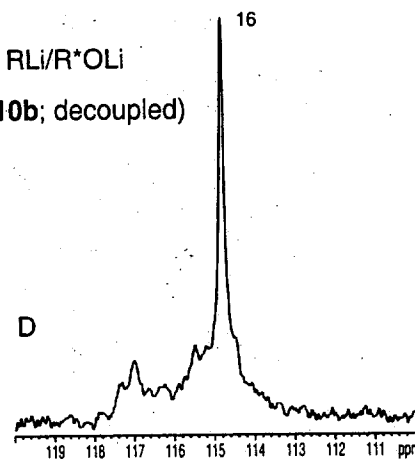
1:1 RLi/R*OLi

(6/10b)



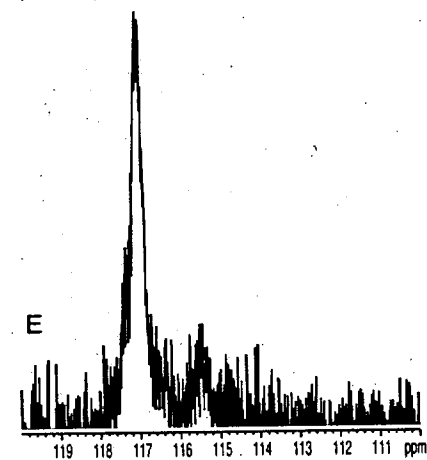
1:1 RLi/R*OLi

(6/10b; decoupled)



1:3 RLi/R*OLi

(6/10b)



1:3 RLi/R*OLi

(6/10b; decoupled)

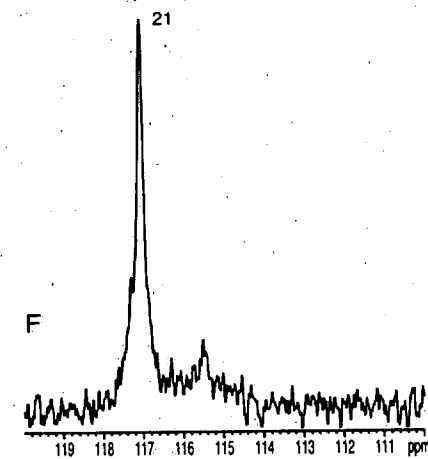


Figure 30. ^{13}C NMR spectra showing 3:1 RLi/R*OLi (15), 2:2 RLi/R*OLi (16) and 1:3 RLi/R*OLi (21) mixed tetramers. Spectra were recorded on mixtures of $[\text{}^6\text{Li},^{13}\text{C}]\text{LiCPA}$ and $[\text{}^6\text{Li}]\text{10b}$ (prepared in situ from the alcohol and 1.3 equiv. of $[\text{}^6\text{Li}]\text{LiHMDS}^*$) in diethyl ether at $-95\text{ }^\circ\text{C}$. The total titer of 6 and 10b is 0.1 M. Spectra B, D, and F were recorded with ^6Li broad-band decoupling.