Supporting Information

Method of Continuous Variation: Characterization of Alkali Metal Enolates Using ^{1}H and ^{19}F NMR Spectroscopies

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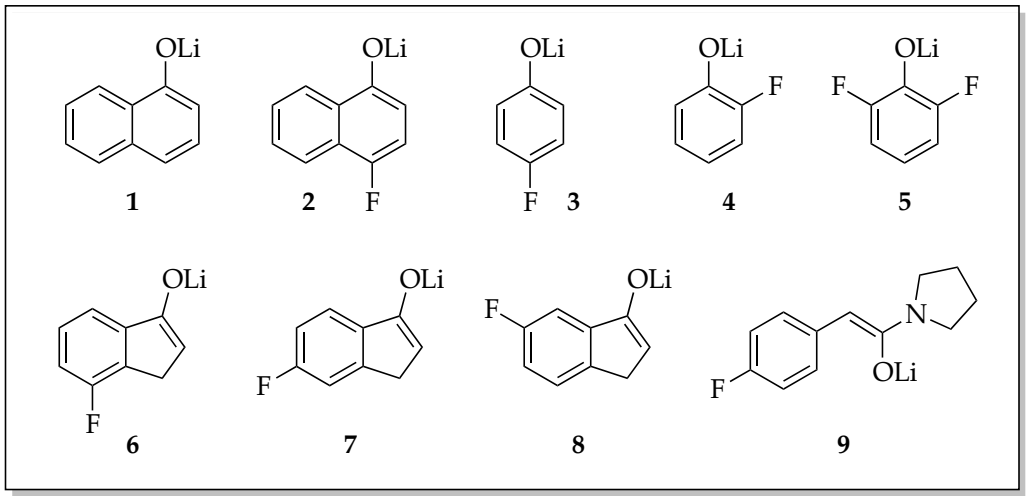
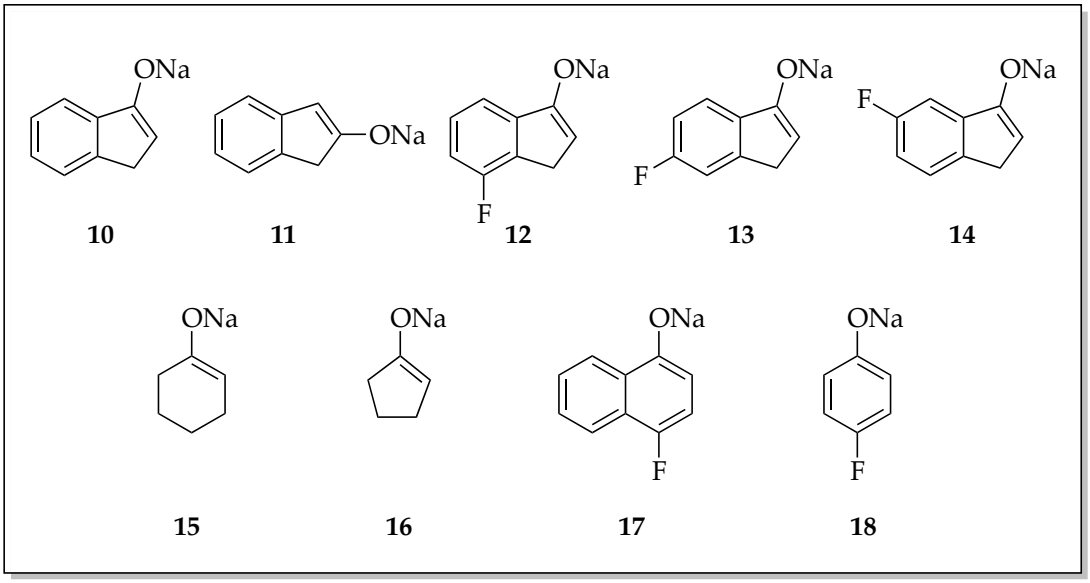




X_A = the mole fraction of enolate/phenolate subunits **A**

X_B = the mole fraction of enolate/phenolate subunits **B**

I. Lithium Phenolates: Job Plots using ^{19}F NMR.

For a full list of Job plots and their corresponding page numbers, refer to pages S3.

II. Lithium Salts of 1-Naphthol and 4-Fluorophenol: Job Plots using ^{19}F NMR.

For a full list of Job plots and their corresponding page numbers, refer to pages S3.

III. Lithium Enolates: Job Plots using ^{19}F and ^{1}H NMR.

For a full list of solvent swaps and their corresponding page numbers, refer to page S4.

IV. Sodium Enolates and Phenolates: Job Plots using ^{19}F and ^{1}H NMR.

For a full list of solvent swaps and their corresponding page numbers, refer to page S5-S6.

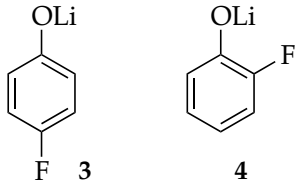
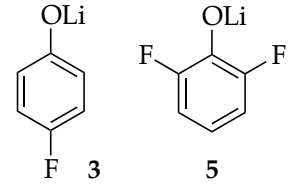
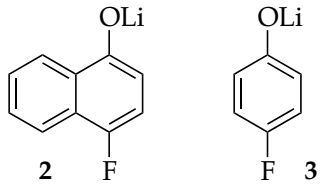
V. NaICA Characterization.

Refer to pages S36-S40.

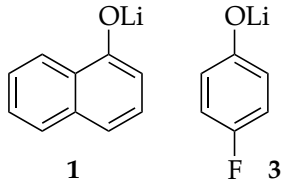
VI. Matlab files for a singly-tagged ensembles.

Refer to pages S41-S47.

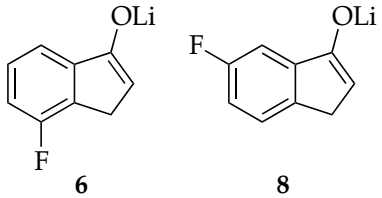
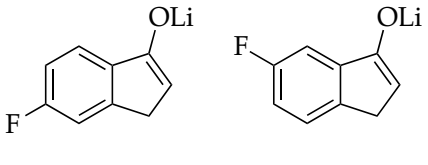
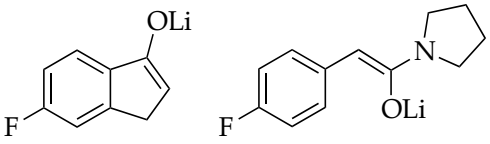
I. Lithium Phenolates: Job Plots using ^{19}F NMR.

Substrates	Solvent	Structure	NMR	Page
	TMEDA	dimer	^{19}F	S7
	TMEDA	dimer	^{19}F	S8
	TMEDA	dimer	^{19}F	S9
	THF	tetramer	^{19}F	S10

II. Lithium Salts of 1-Naphthol and 4-Fluorophenol: Job Plots using ^{19}F NMR

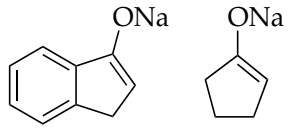
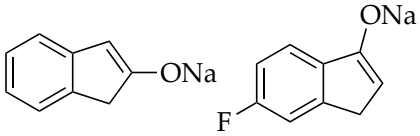
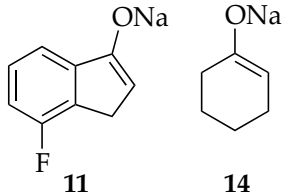
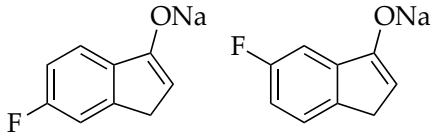
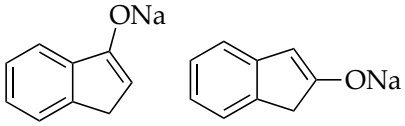
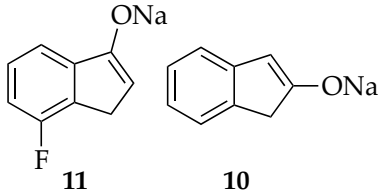
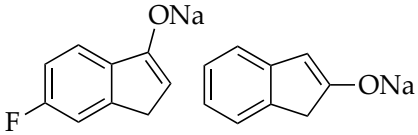
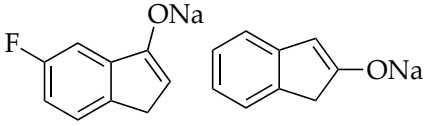
Substrates	Solvent	Structure	NMR	Page
	NMP	tetramer	^{19}F	S11
	DMF	tetramer	^{19}F	S12
	DMSO	tetramer	^{19}F	S13
	DMPU	tetramer	^{19}F	S14
	n-$PrNH_2$	tetramer	^{19}F	S15
	Et_2NH	tetramer	^{19}F	S16
	n-Pr_2NH	tetramer	^{19}F	S17
	piperidine	tetramer	^{19}F	S18
	t-butanol	tetramer	^{19}F	S19

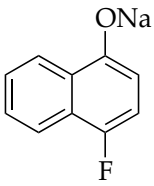
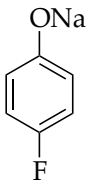
III. Lithium Enolates and Phenolates: Job Plots using ^{19}F and ^{1}H NMR.

Substrates	Solvent	Structure	NMR	Page
 **6** **8**	THF	tetramer	^{1}H	S20
	TMEDA	dimer	^{1}H	S21
	TMEDA	dimer	^{19}F	S22
 **7** **8**	THF	tetramer	^{1}H	S23
	TMEDA	dimer	^{1}H	S24
	TMEDA	dimer	^{19}F	S25
 **7** **9***	TMEDA	dimer	^{1}H	S26

* The carboxamide was ^{15}N labeled; ensemble/envelope resolution could not be obtained using ^{15}N NMR spectroscopy.

IV. Sodium Enolates and Phenolates: Job Plots using ^{19}F and ^{1}H NMR.

Substrates	Solvent	Structure	NMR	Page
 **9** **15**	TMEDA	tetramer	^{1}H	S27
 **10** **12**	TMEDA	tetramer	^{1}H	S28
 **11** **14**	TMEDA	tetramer	^{1}H	S29
 **12** **13**	TMEDA	tetramer	^{1}H	S30
 **9** **10**	THF	tetramer*	^{1}H	S31
 **11** **10**	THF	tetramer*	^{1}H	S32
 **12** **10**	THF	tetramer*	^{1}H	S33
 **13** **10**	THF	tetramer	^{1}H	S34

Substrates	Solvent	Structure	NMR	Page
 **16**  **17**	THF	tetramer*	^{19}F	S35

*overlap and/or exchange rates prevented creation of Job plots.

Dimer Job Plots in TMEDA

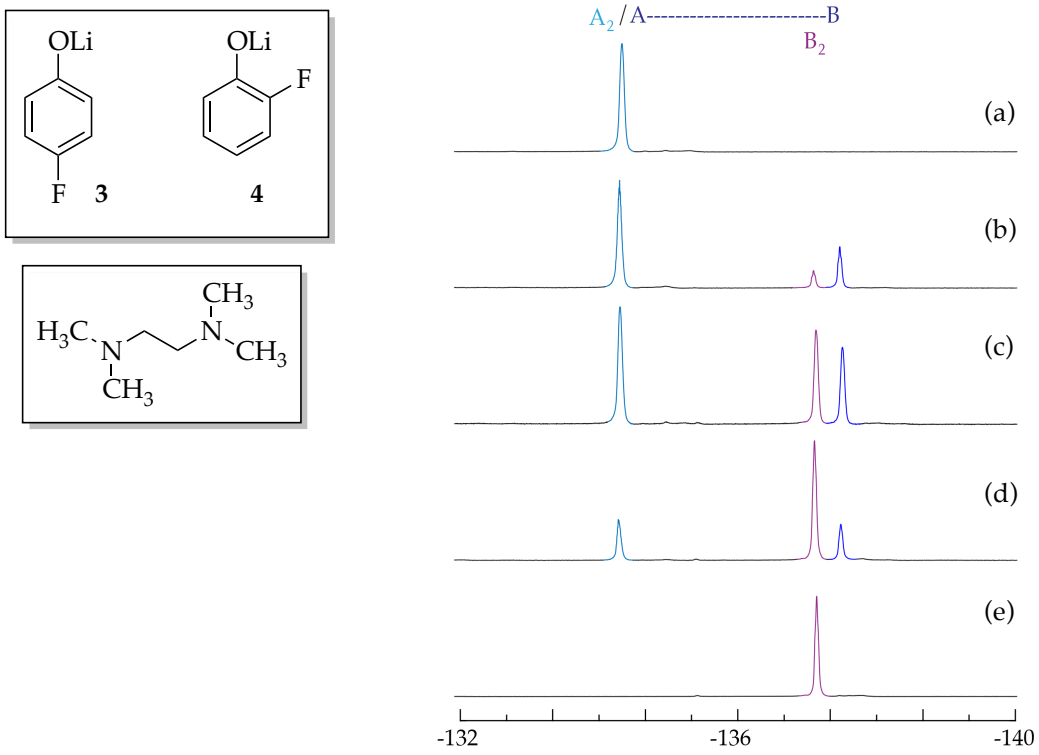


Figure 1. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**A**) and [^{6}Li]**4** (**B**) in 0.50 M TMEDA/toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.62, 0.42, 0.19, and 0.00, respectively.

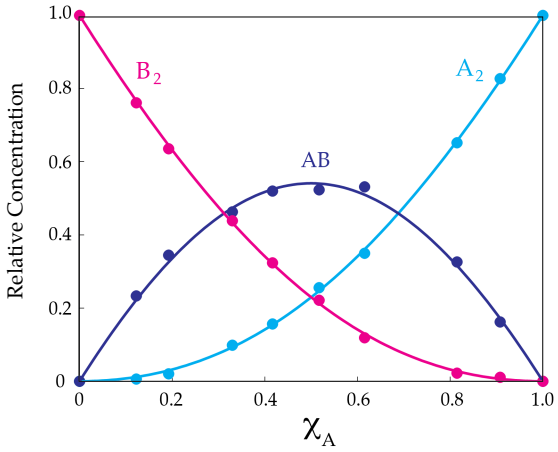


Figure 2. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**3** (**A**) and [^{6}Li]**4** (**B**) in 0.50 M TMEDA/toluene at -80 °C.

Dimer Job Plots in TMEDA

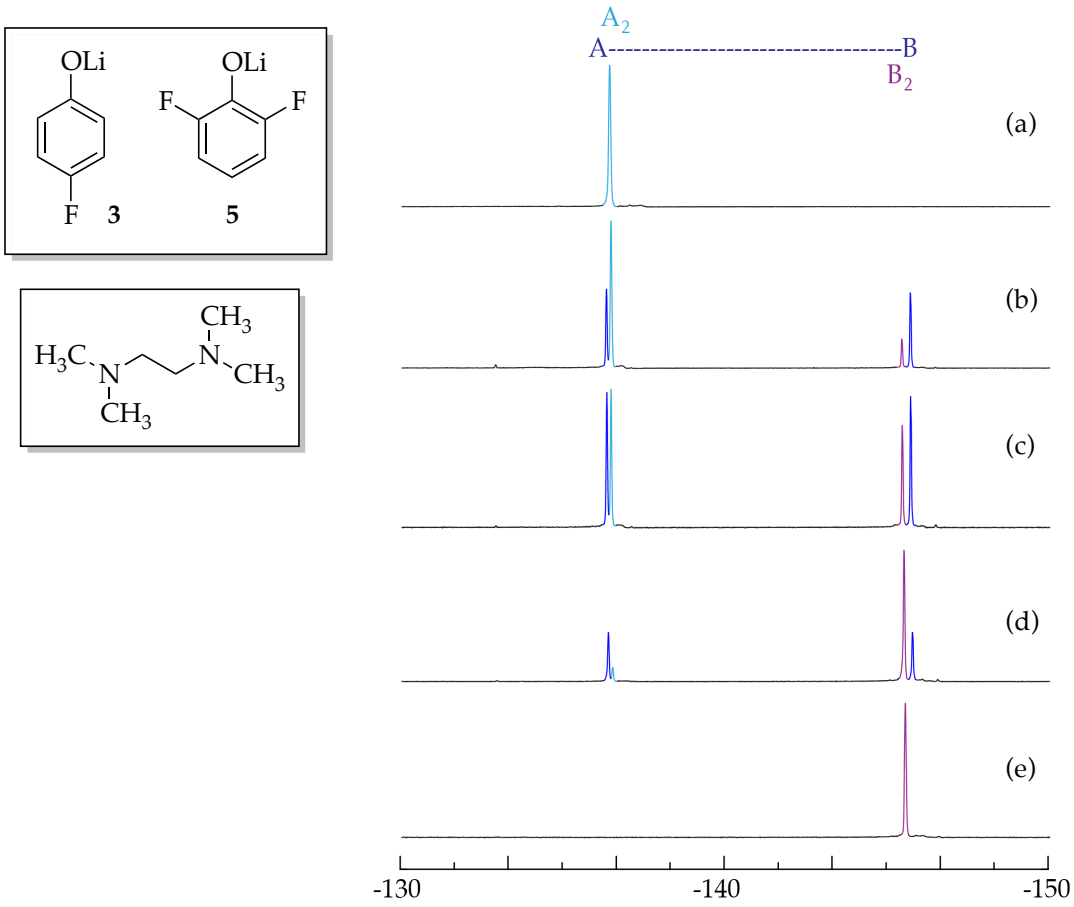


Figure 3. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**A**) and [^{6}Li]**5** (**B**) in 0.50 M TMEDA/toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.75, 0.57, 0.40, and 0.00, respectively.

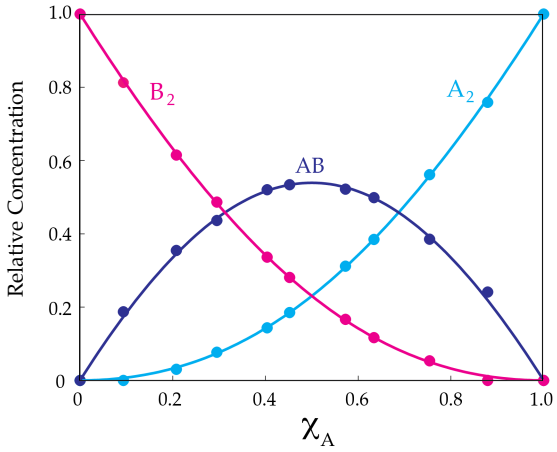


Figure 4. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**3** (**A**) and [^{6}Li]**5** (**B**) in 0.50 M TMEDA/toluene at -80 °C.

Dimer Job Plots in TMEDA

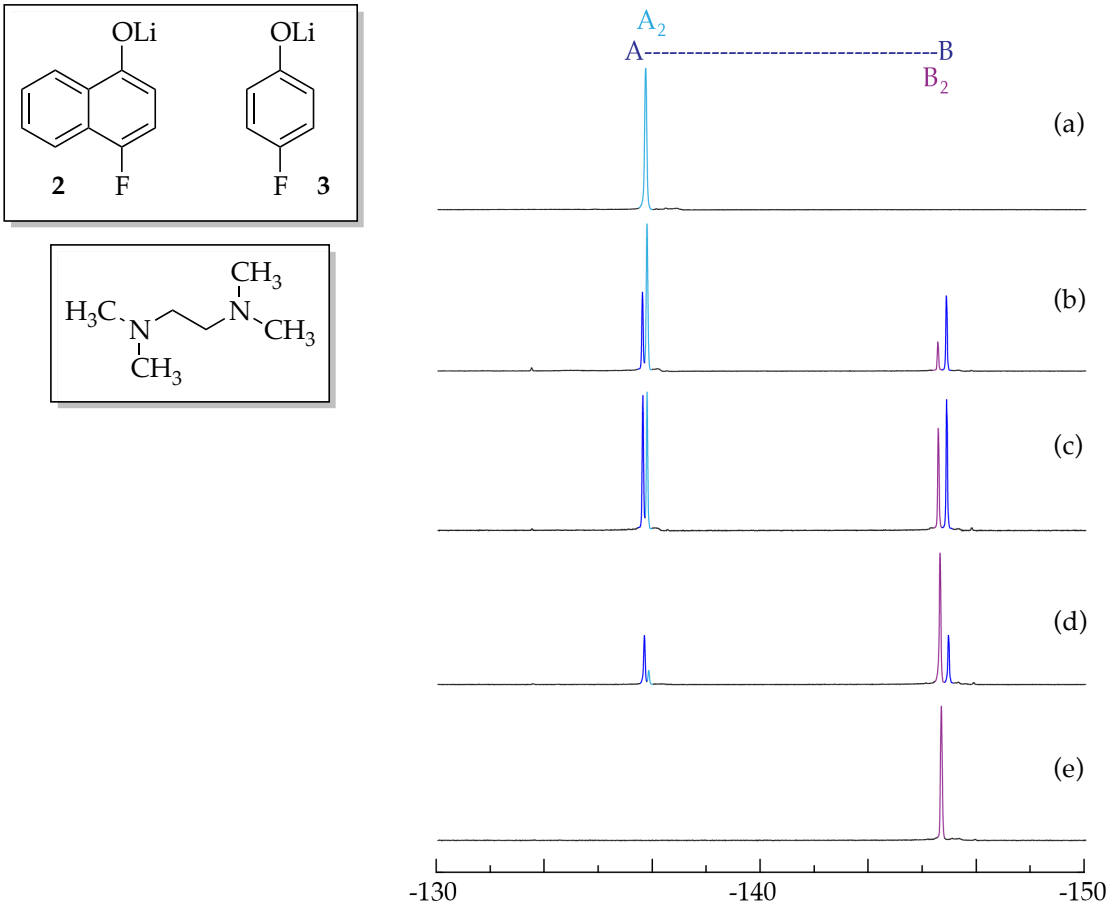


Figure 5. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**2** (**A**) and [^{6}Li]**3** (**B**) in 0.50 M TMEDA/toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.70, 0.41, 0.24, and 0.00, respectively.

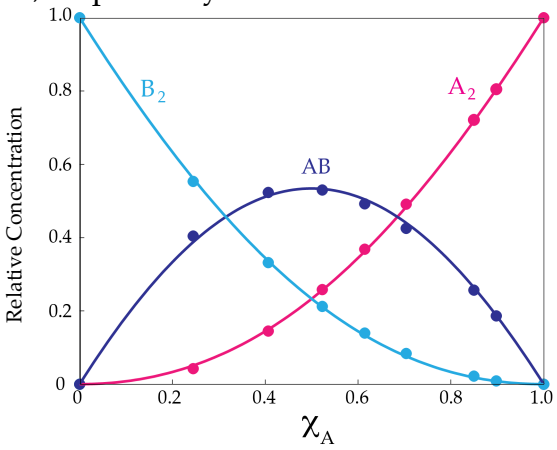


Figure 6. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**2** (**A**) and [^{6}Li]**3** (**B**) in 0.50 M TMEDA/toluene at -80 °C.

Tetramer Job Plots in THF

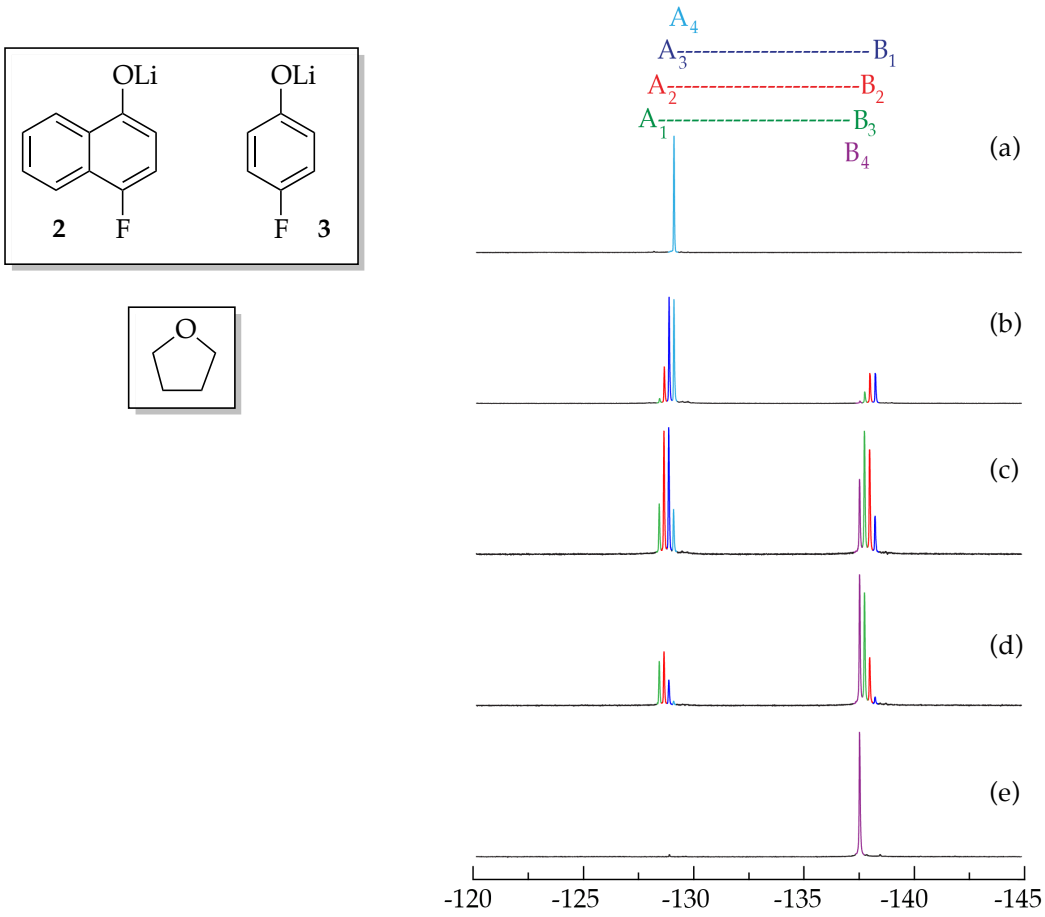


Figure 7. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**2** (**A**) and [^{6}Li]**3** (**B**) in 0.50 M TMEDA/toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.75, 0.47, 0.27, and 0.00, respectively.

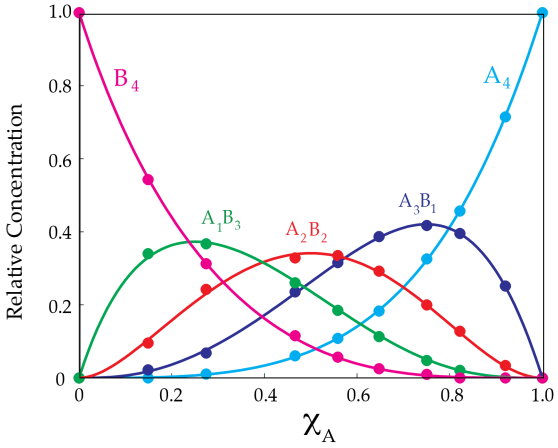


Figure 8. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**2** (**A**) and [^{6}Li]**3** (**B**) in 0.50 M TMEDA/toluene at -80 °C.

Tetramer Job Plots in *N*-methylpyrrolidone

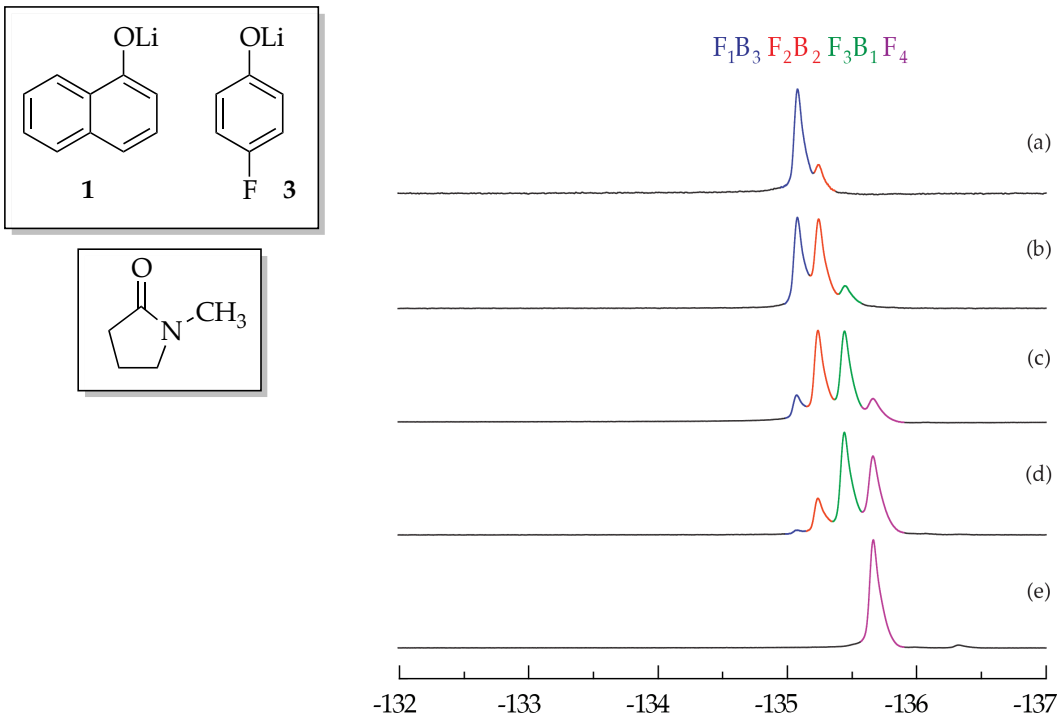


Figure 9. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M NMP/toluene at -80 °C. The measured mole fractions of **F** in (a)-(e) are 0.28, 0.37, 0.42, 0.78, and 1.00, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR.

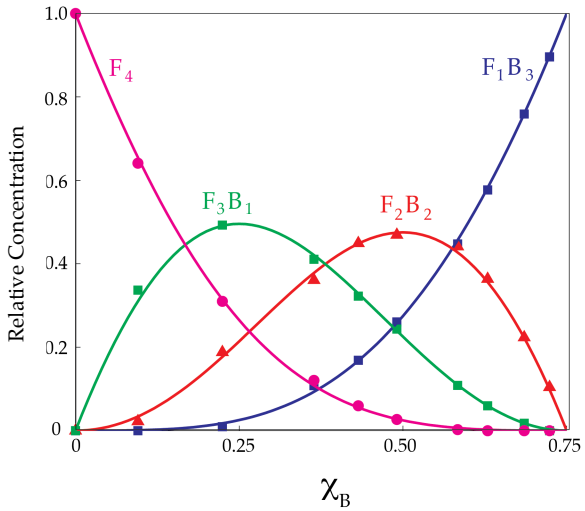


Figure 10. Job plot showing the relative integrations versus the measured mole fractions of **B** for 0.10 M mixtures of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M NMP/toluene at -80 °C.

Tetramer Job Plots in Dimethylformamide

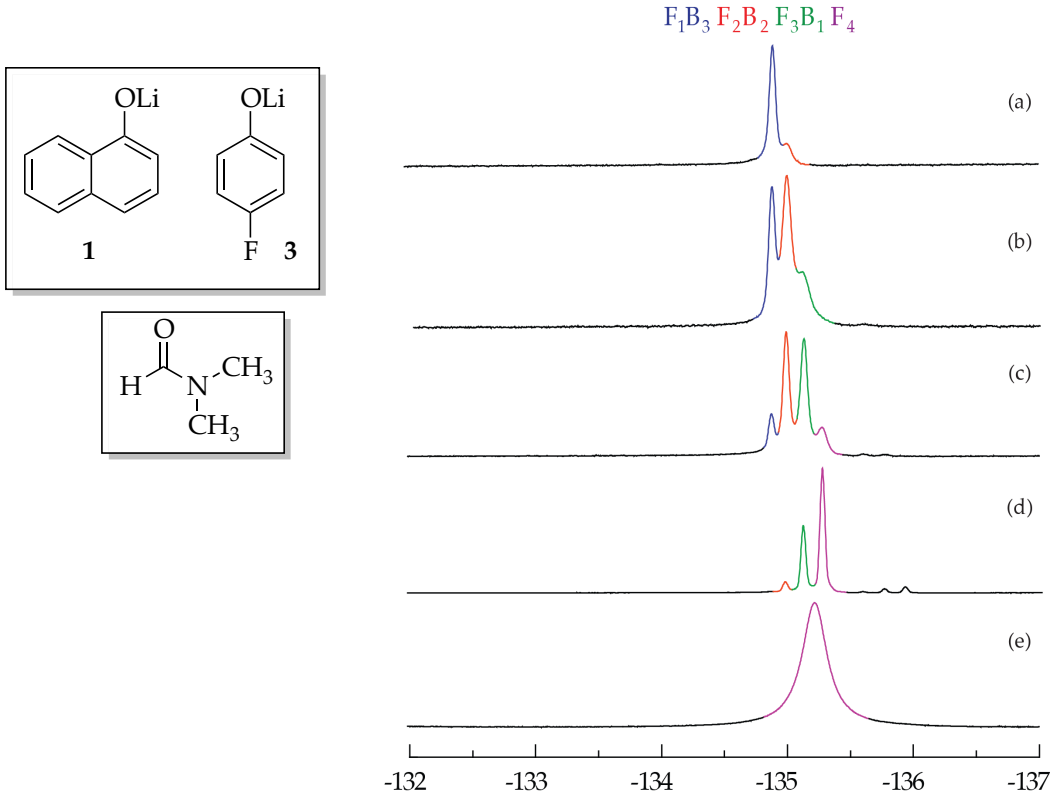


Figure 11. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M DMF/toluene at -80 °C. The measured mole fractions of **F** in (a)-(e) are 0.27, 0.41, 0.55, 0.87, and 1.00, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR.

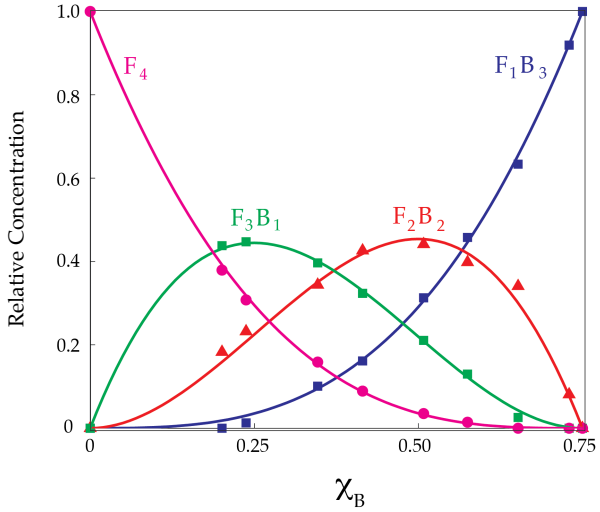


Figure 12. Job plot showing the relative integrations versus the measured mole fractions of **B** for 0.10 M mixtures of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M DMF/toluene at -80 °C.

Tetramer Job Plots in Dimethylsulfoxide

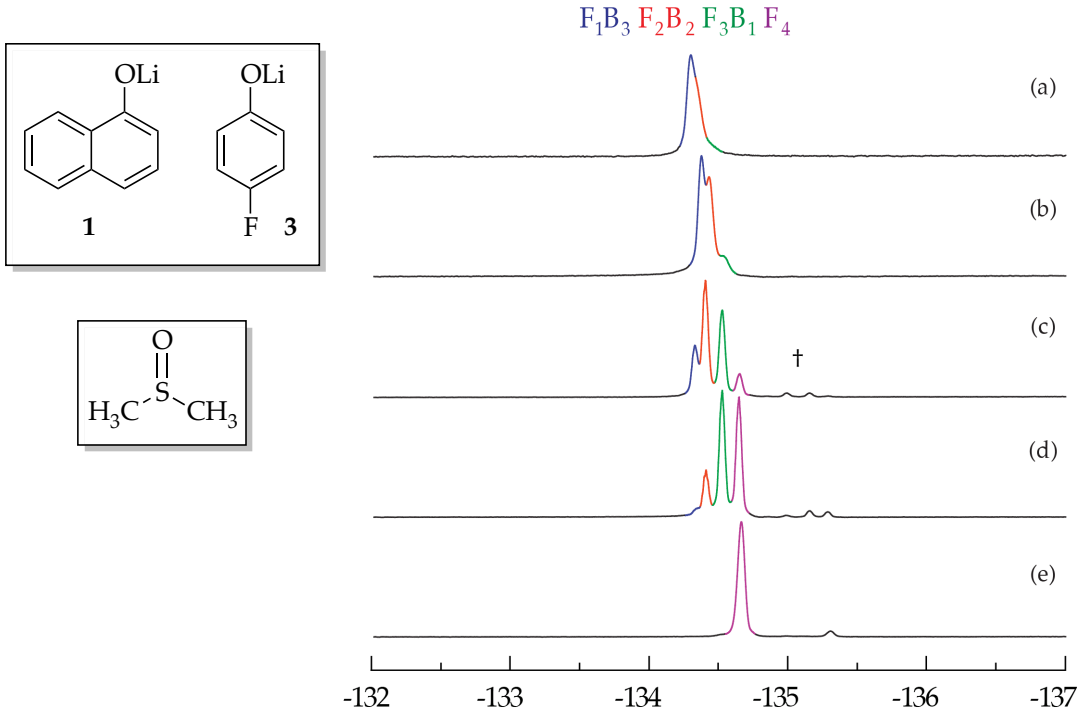


Figure 13. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M DMSO/toluene at -80 °C. The measured mole fractions of **F** in (a)-(e) are 0.27, 0.34, 0.49, 0.65, and 1.00, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR. † denotes unknown fluorinated material, possibly minor aggregation states.

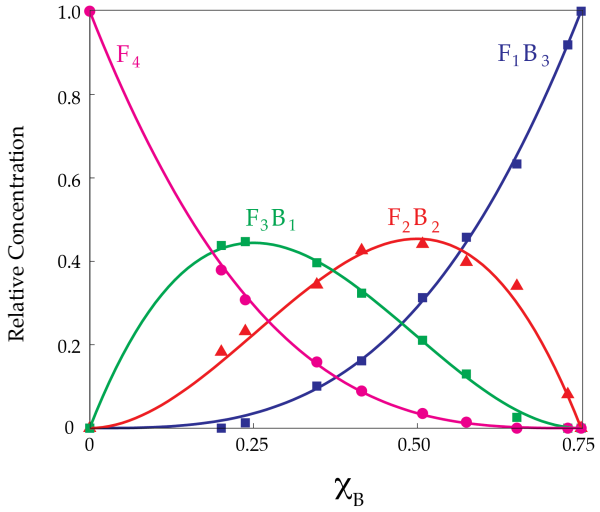


Figure 14. Job plot showing the relative integrations versus the measured mole fractions of **B** for 0.10 M mixtures of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M DMSO/toluene at -80 °C.

Tetramer Job Plots in Dimethylpropyleneurea

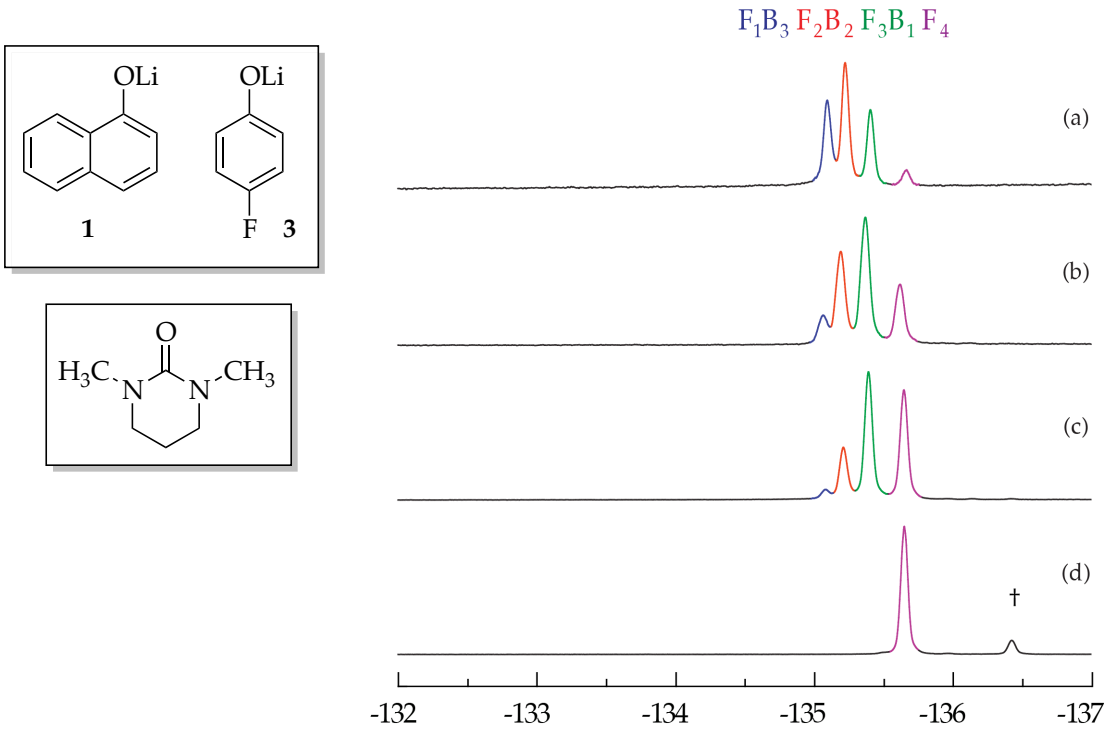


Figure 15. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M DMPU/toluene at -80 °C. The measured mole fractions of **F** in (a)-(e) are 0.43, 0.64, 0.72, and 1.00, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR. † denotes unknown fluorinated material, possibly minor aggregation states.

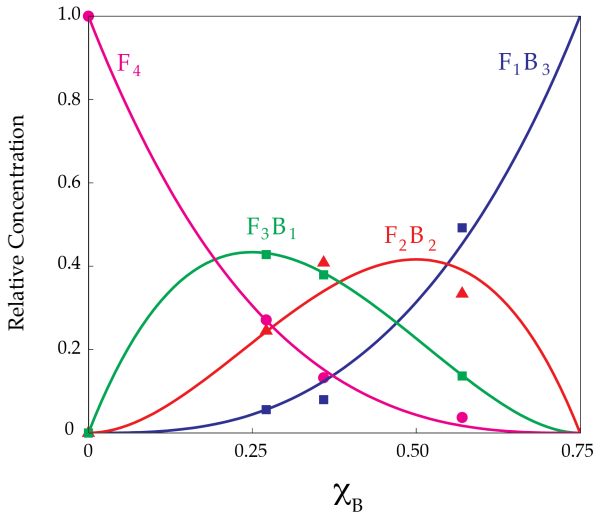


Figure 16. Job plot showing the relative integrations versus the measured mole fractions of **B** for 0.10 M mixtures of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M DMPU/toluene at -80 °C.

Tetramer Job Plots in *n*-Propylamine

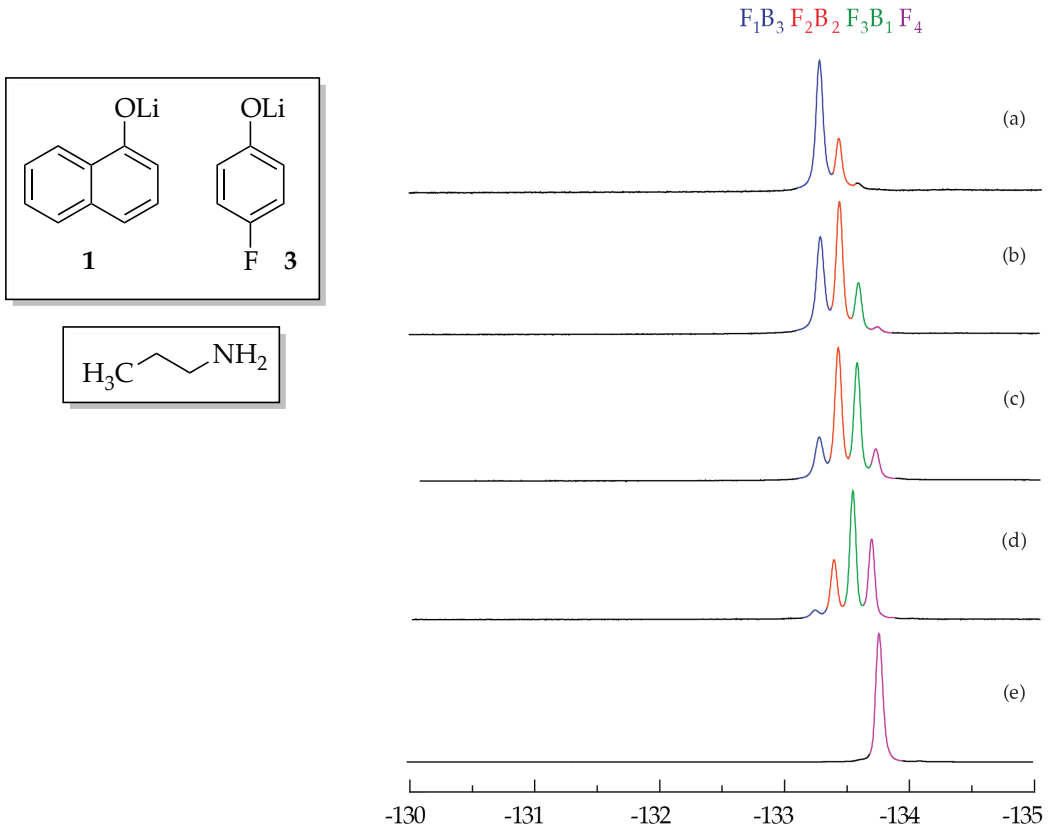


Figure 17. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M *n*-PrNH$_2$/toluene at -80 °C. The measured mole fractions of **F** in (a)-(e) are 0.30, 0.38, 0.51, 0.69, and 1.00, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR.

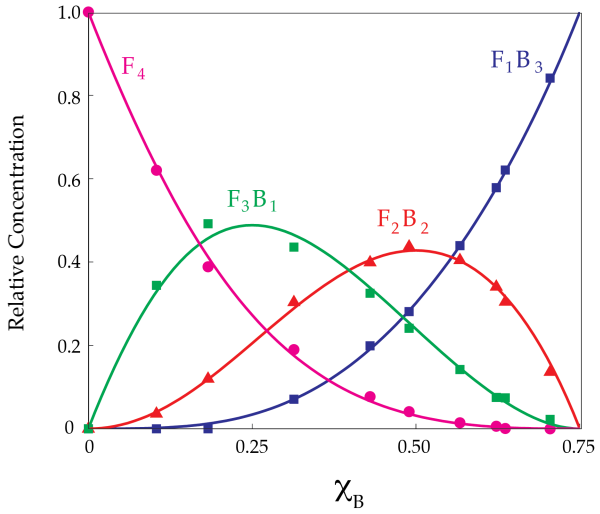


Figure 18. Job plot showing the relative integrations versus the measured mole fractions of **B** for 0.10 M mixtures of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M *n*-PrNH$_2$/ toluene at -80 °C.

Tetramer Job Plots in Diethylamine

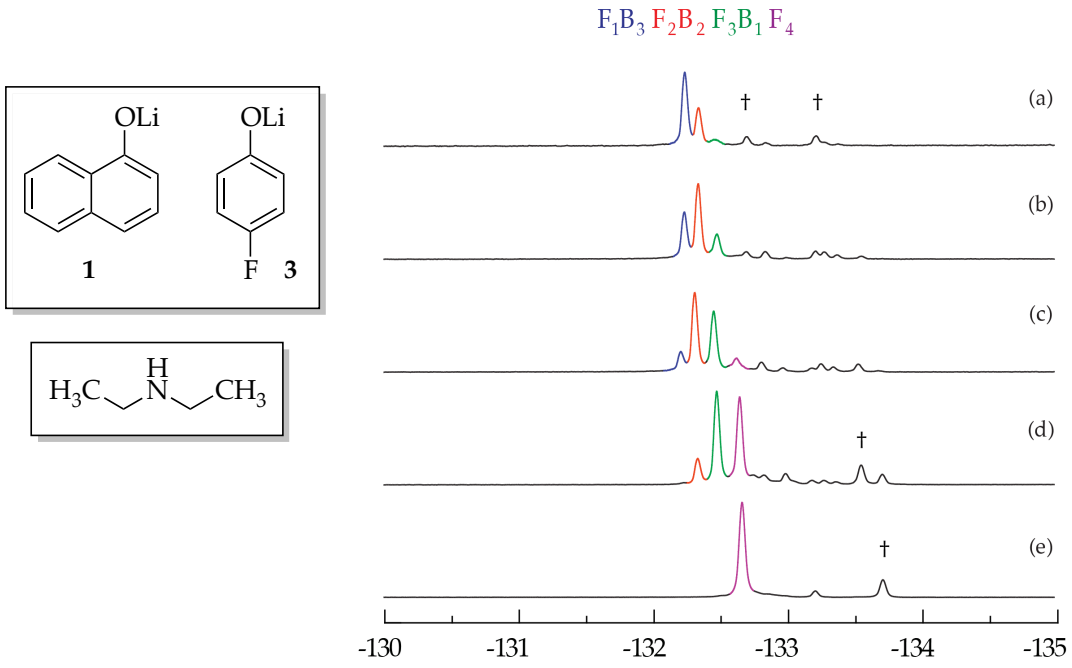


Figure 19. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M Et_2NH/toluene at -80 °C. The measured mole fractions of **F** in (a)-(e) are 0.31, 0.40, 0.55, 0.63, and 1.00, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR. † denotes unknown fluorinated material, possibly minor aggregation states.

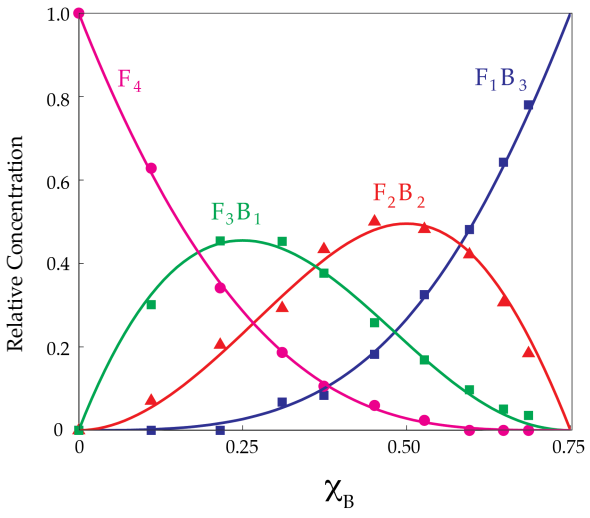


Figure 20. Job plot showing the relative integrations versus the measured mole fractions of **B** for 0.10 M mixtures of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M Et_2NH/toluene at -80 °C. F_1B_3 is the last ^{19}F NMR visible aggregate, reaching a maximum of 0.75 along the x-axis; B_4 is not visible.

Tetramer Job Plots in Dipropylamine

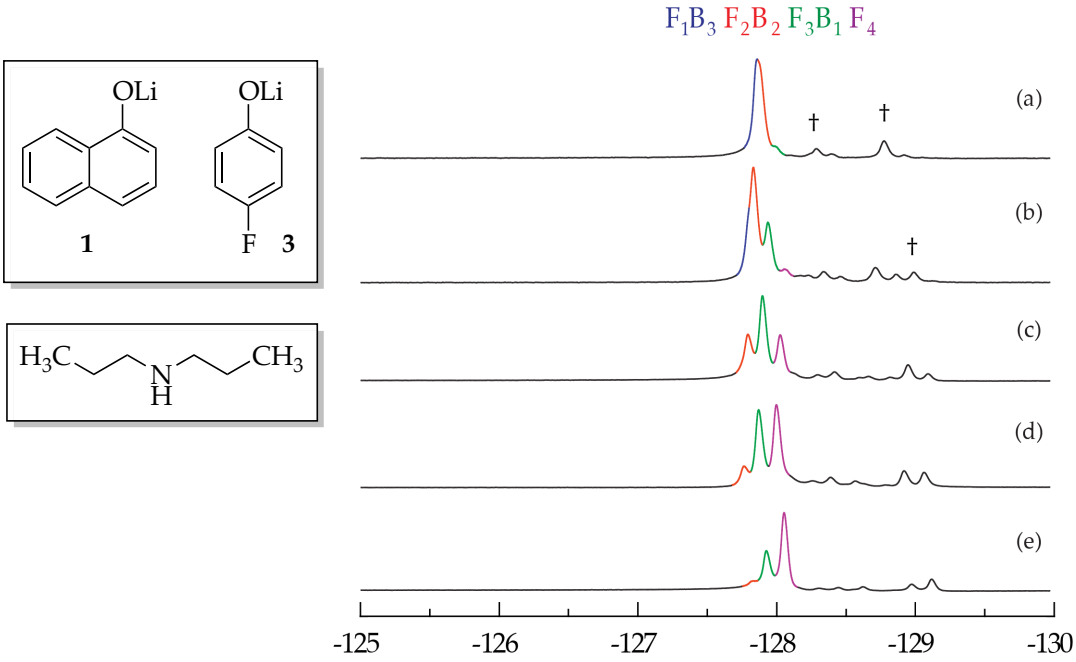


Figure 21. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M *n*-Pr_2NH/toluene at -90 °C. The measured mole fractions of **F** in (a)-(e) are 0.50, 0.53, 0.69, 0.83, and 0.88, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR. † denotes unknown fluorinated material, possibly minor aggregation states.

Tetramer Job Plots in Piperidine

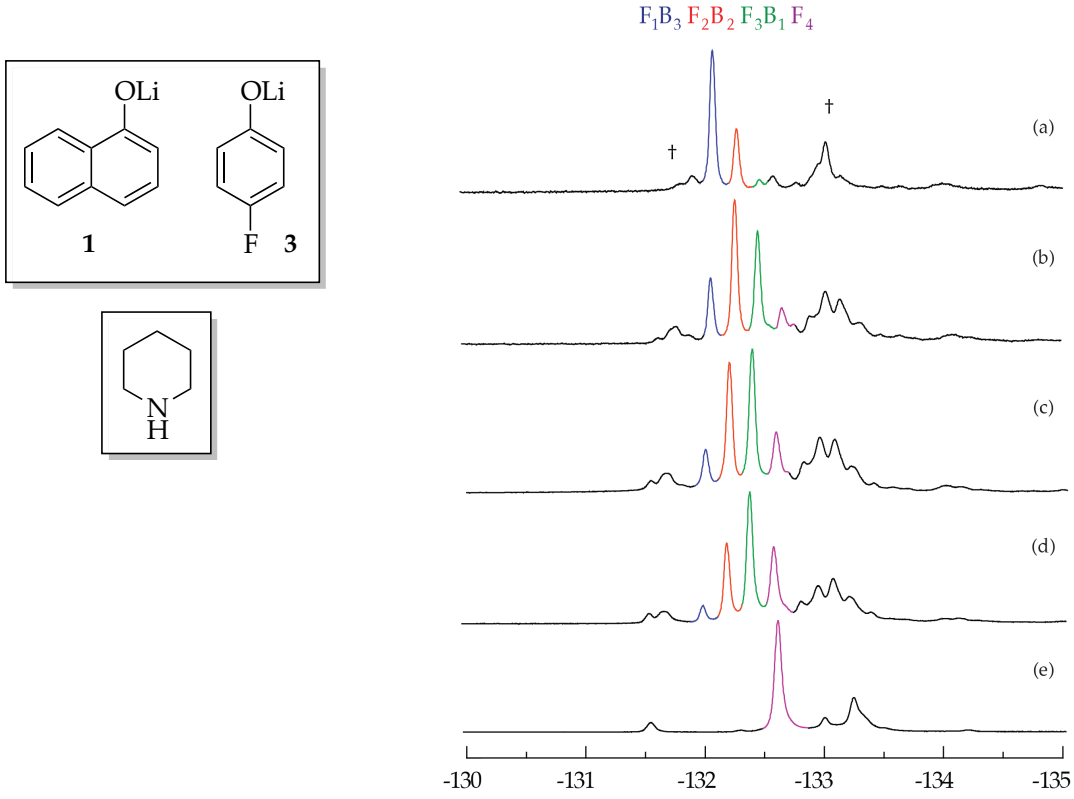


Figure 22. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M piperidine/toluene at -80 °C. The measured mole fractions of **F** in (a)-(e) are 0.31, 0.51, 0.57, 0.67, and 1.00, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR. † denotes unknown fluorinated material, possibly minor aggregation states.

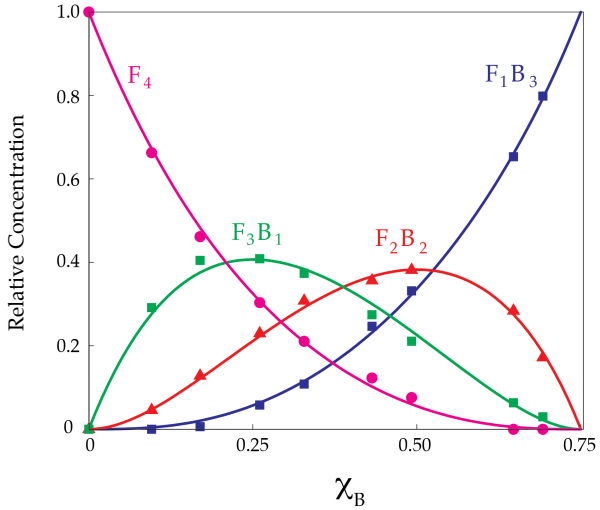


Figure 23. Job plot showing the relative integrations versus the measured mole fractions of **B** for 0.10 M mixtures of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M piperidine/toluene at -80 °C.

Tetramer Job Plots in *t*-Butanol

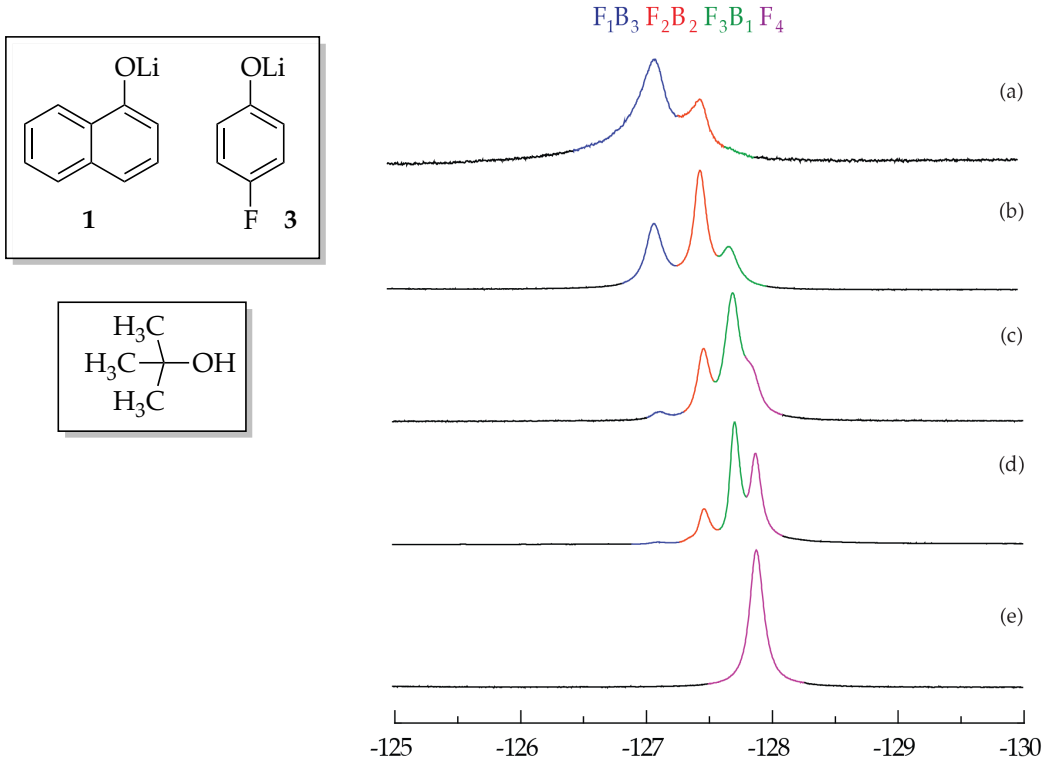


Figure 24. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M *t*-BuOH/toluene at -90 °C. The measured mole fractions of **F** in (a)-(e) are 0.27, 0.41, 0.66, 0.77, and 1.00, respectively. The 1-naphtholate homoaggregate is invisible by fluorine NMR.

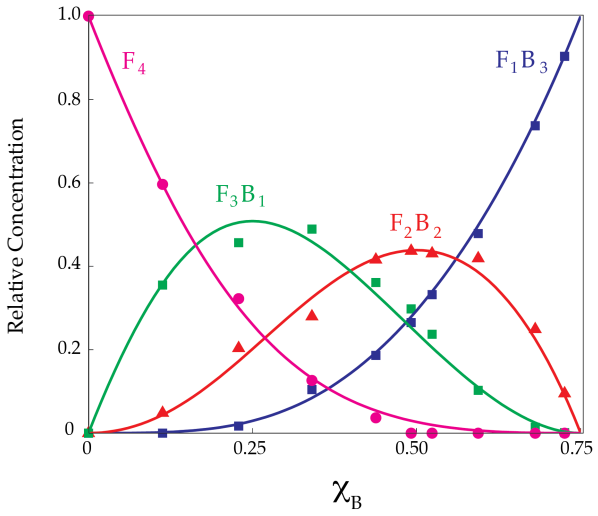


Figure 25. Job plot showing the relative integrations versus the measured mole fractions of **B** for 0.10 M mixtures of [^{6}Li]**3** (**F**) and [^{6}Li]**1** (**B**) in 0.50 M *t*-BuOH /toluene at -90 °C.

Tetramer Job Plots in Tetrahydrofuran

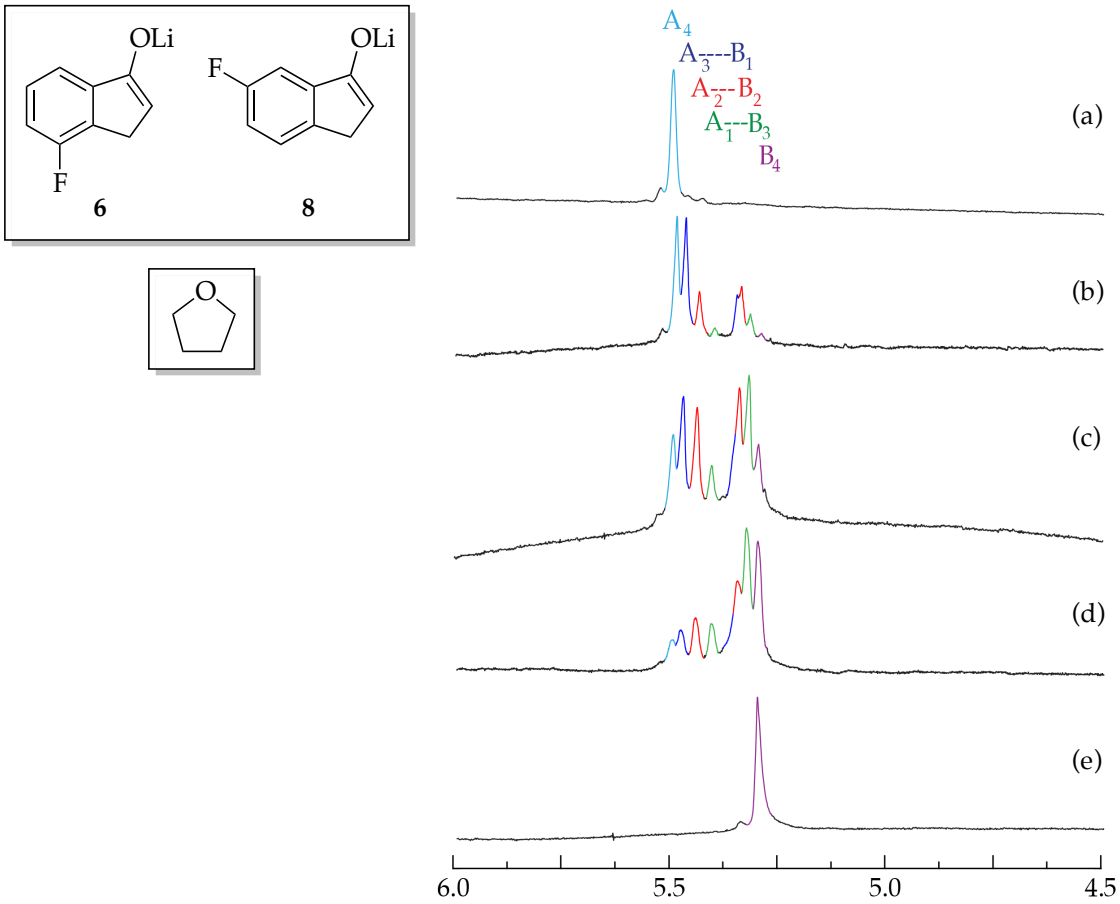


Figure 26. ^{1}H NMR spectra of 0.10 M solutions of [^{6}Li]**8** (**A**) and [^{6}Li]**6** (**B**) in 0.50 M THF/toluene at -80 °C. The expected mole fractions of **A** in (a)-(e) are 1.0, 0.8, 0.5, 0.3, and 0.0, respectively.

Dimer Job Plots in TMEDA

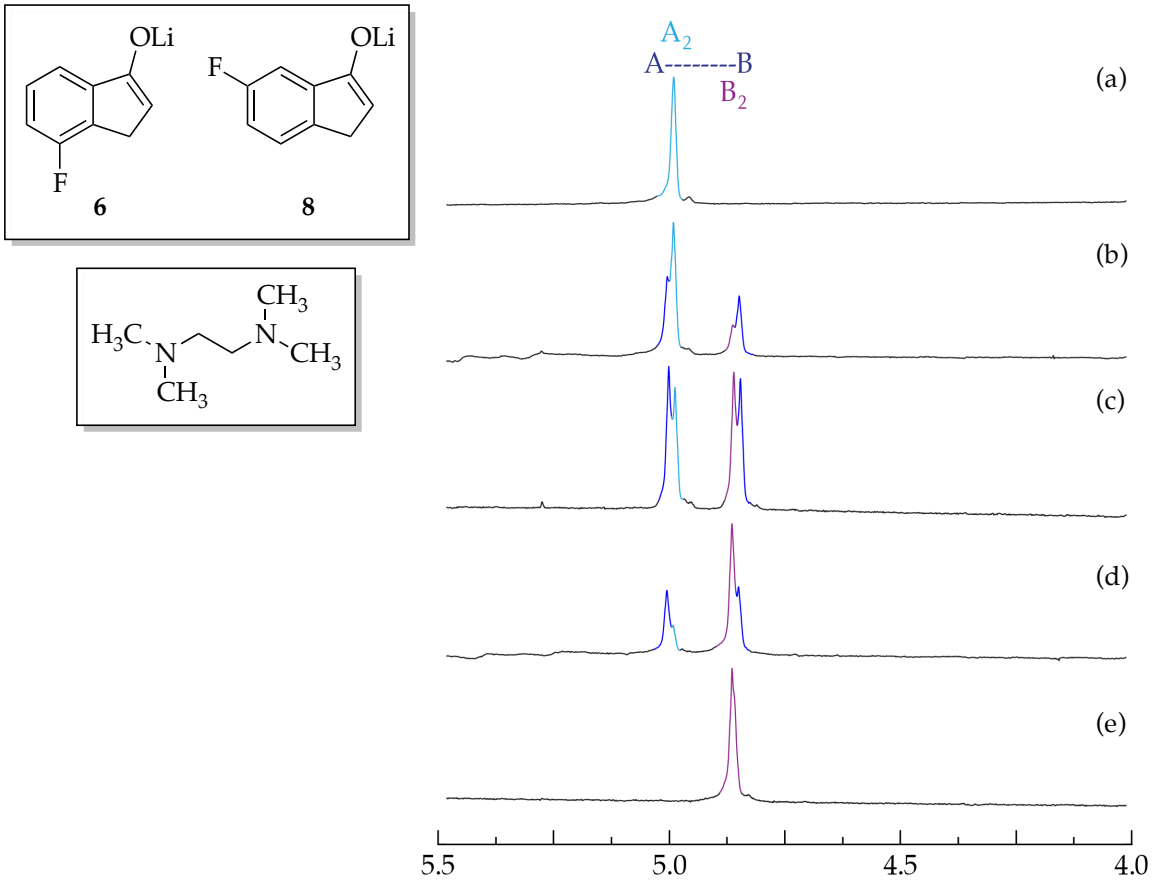


Figure 27. ^{1}H NMR spectra of 0.10 M solutions of [^{6}Li]**8** (**A**) and [^{6}Li]**6** (**B**) in 0.50 M TMEDA / toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.65, 0.47, 0.27, and 0.00, respectively.

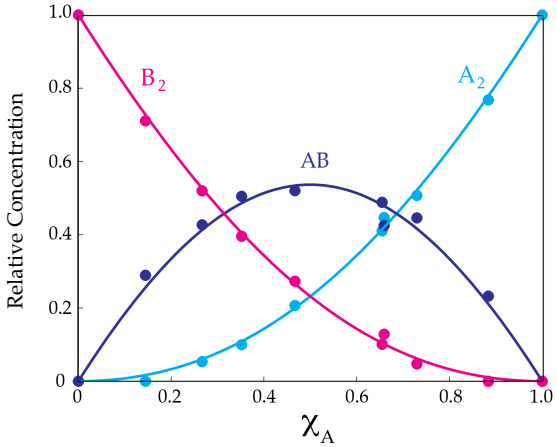


Figure 28. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**8** (**A**) and [^{6}Li]**6** (**B**) in 0.50 M TMEDA / toluene at -80 °C.

Dimer Job Plots in TMEDA

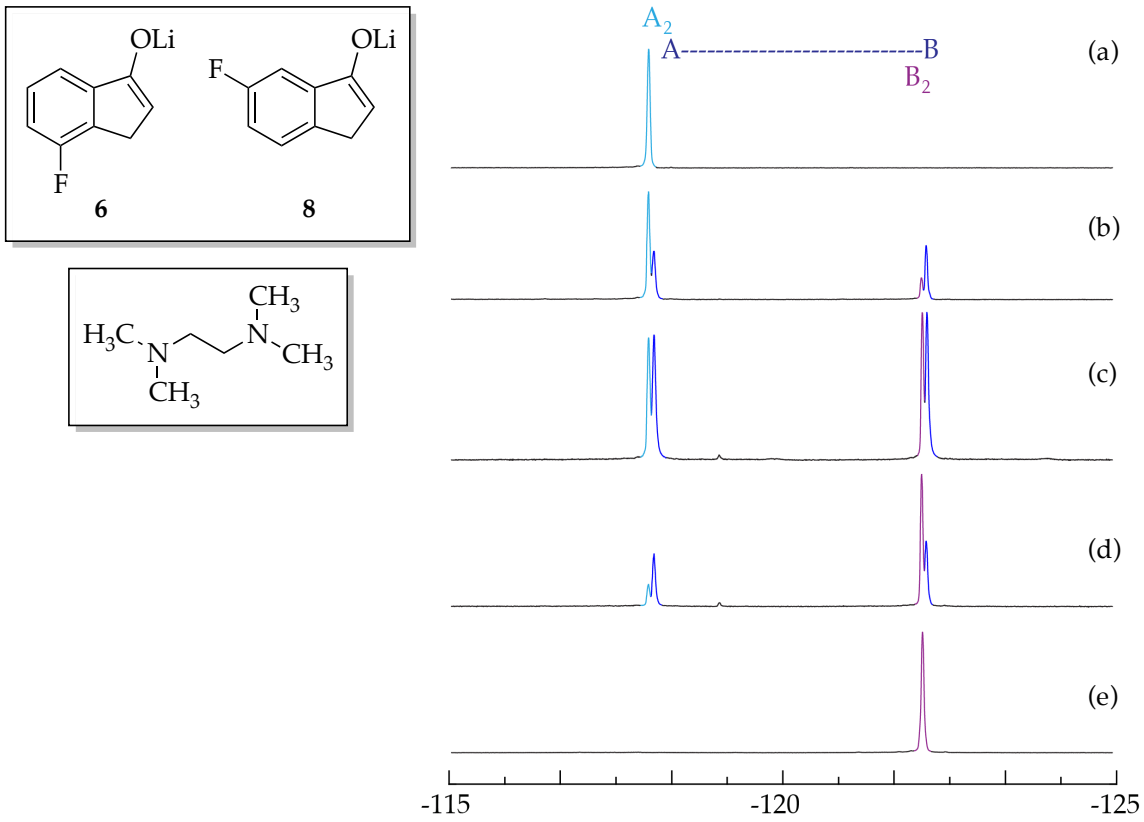


Figure 29. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**8** (**A**) and [^{6}Li]**6** (**B**) in 0.50 M TMEDA/toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.72, 0.50, 0.29, and 0.00, respectively. † denotes unknown aggregation states.

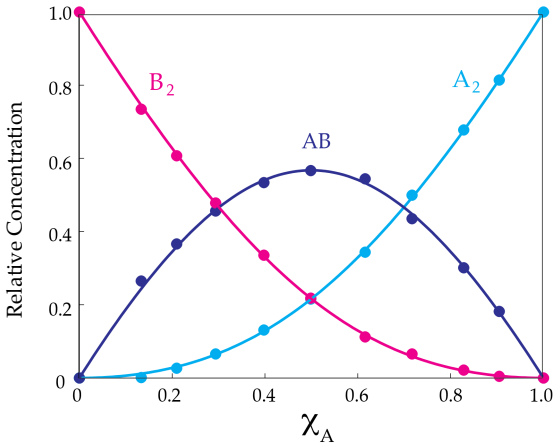


Figure 30. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**8** (**A**) and [^{6}Li]**6** (**B**) in 0.50 M TMEDA/toluene at -80 °C.

Tetramer Job Plots in Tetrahydrofuran

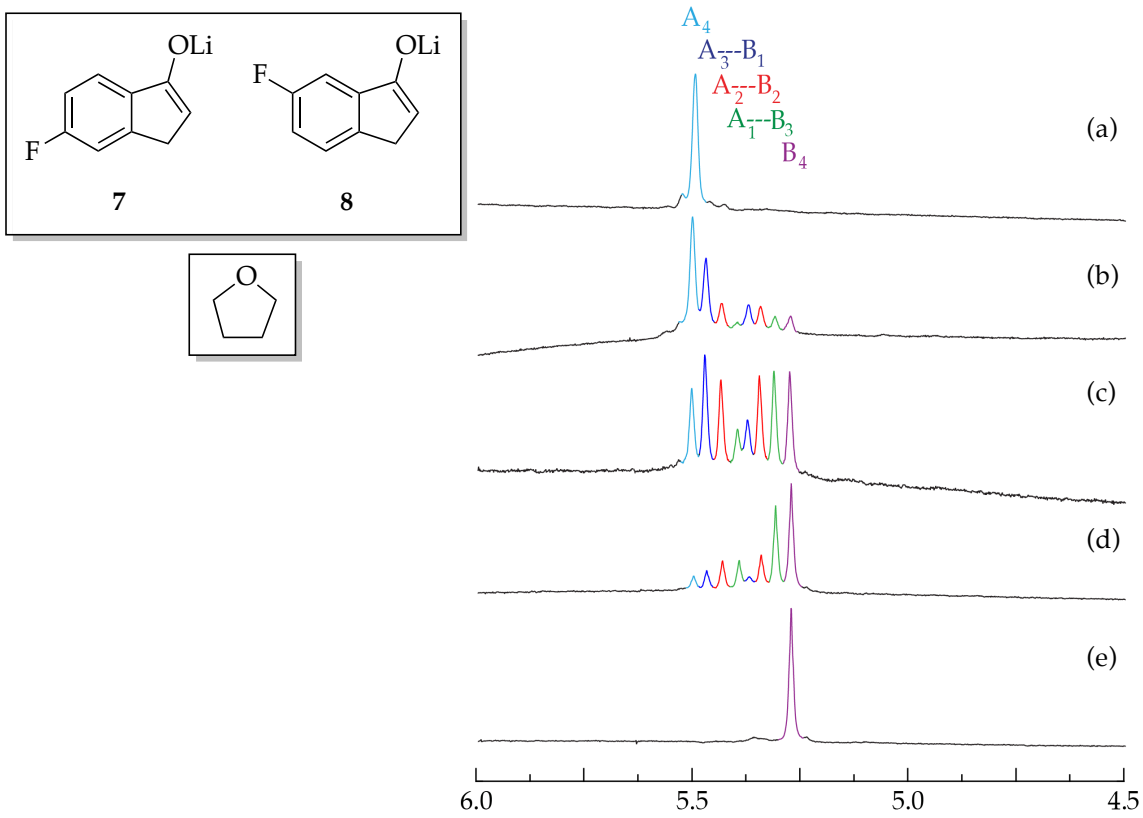


Figure 31. ^{1}H NMR spectra of 0.10 M solutions of [^{6}Li]**8** (**A**) and [^{6}Li]**7** (**B**) in 0.50 M THF/toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.69, 0.50, 0.40, and 0.00, respectively. † denotes unknown aggregation states.

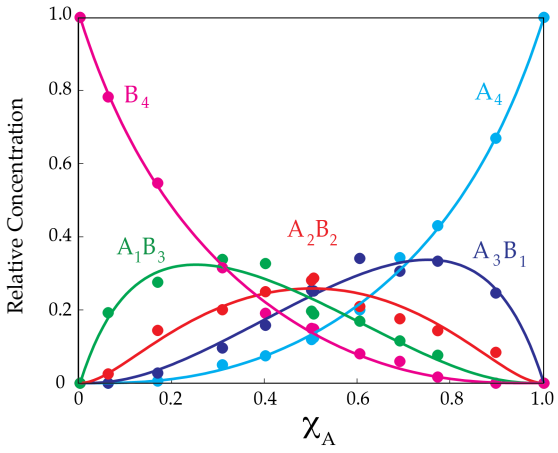


Figure 32. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**8** (**A**) and [^{6}Li]**7** (**B**) in 0.50 M THF/toluene at -80 °C.

Dimer Job Plots in TMEDA

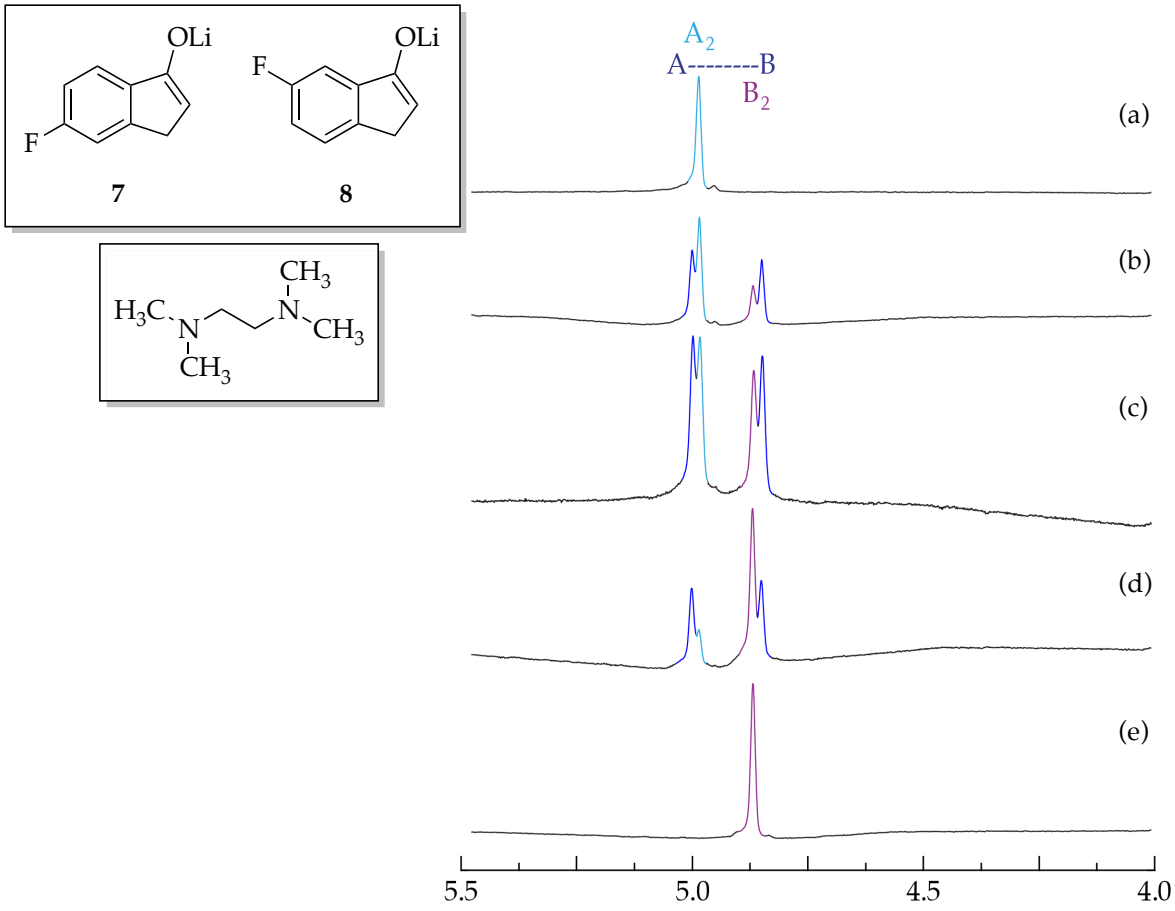


Figure 33. ^{1}H NMR spectra of 0.10 M solutions of [^{6}Li]**8** (**A**) and [^{6}Li]**7** (**B**) in 0.50 M TMEDA / toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.58, 0.50, 0.30, and 0.00, respectively.

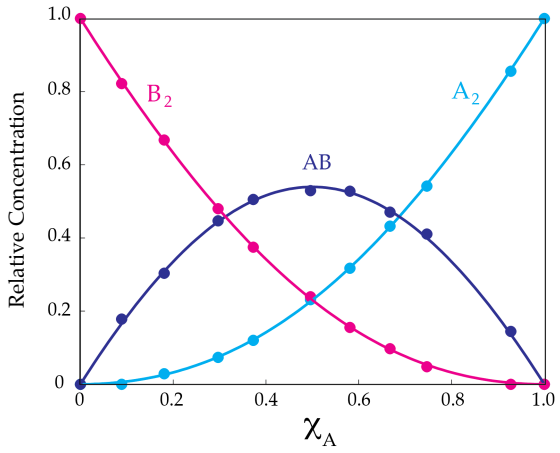


Figure 34. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**8** (**A**) and [^{6}Li]**7** (**B**) in 0.50 M THF / toluene at -80 °C.

Dimer Job Plots in TMEDA

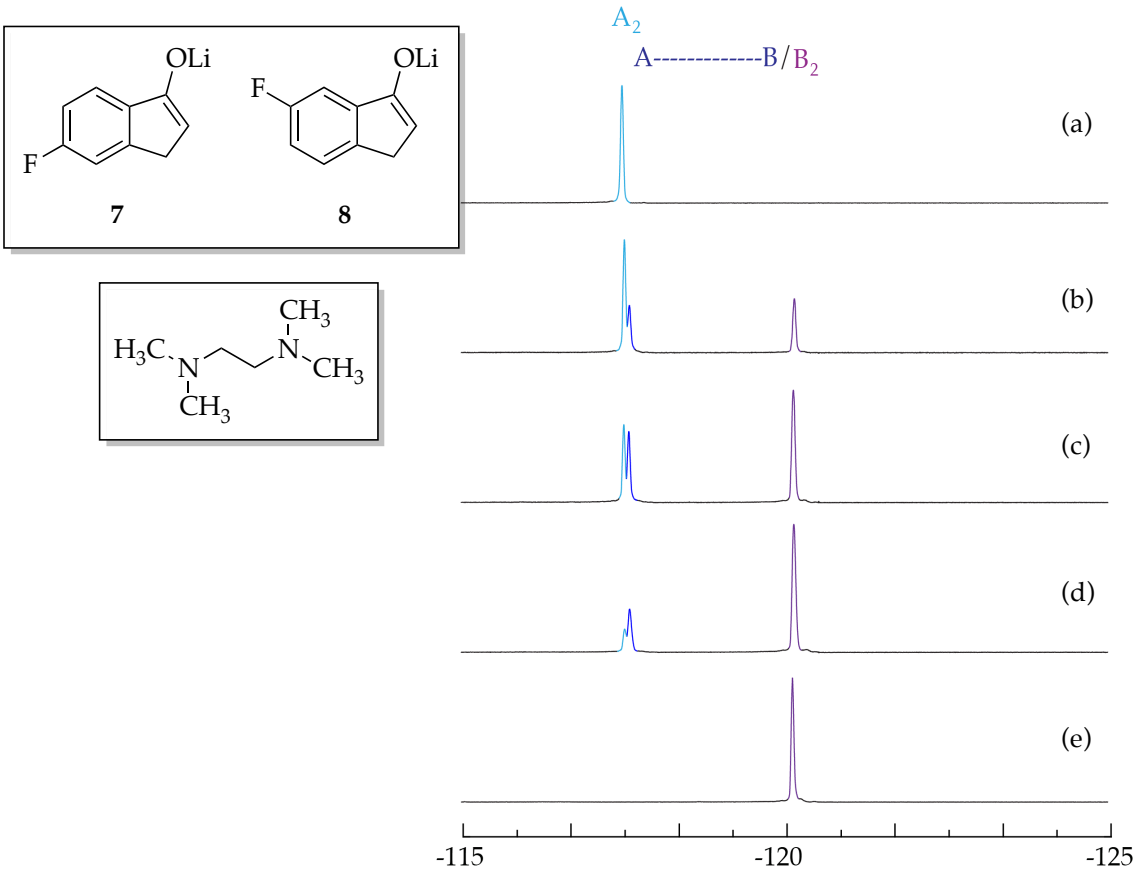


Figure 35. ^{19}F NMR spectra of 0.10 M solutions of [^{6}Li]**8** (**A**) and [^{6}Li]**7** (**B**) in 0.50 M TMEDA/toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.71, 0.50, 0.31, and 0.00, respectively.

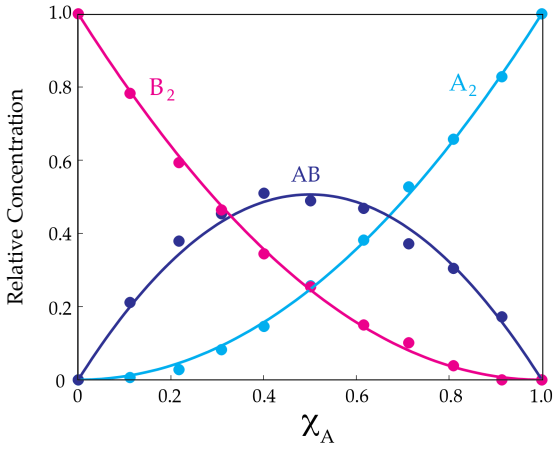


Figure 36. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**8** (**A**) and [^{6}Li]**7** (**B**) in 0.50 M TMEDA/toluene at -80 °C.

Dimer Job Plots in TMEDA

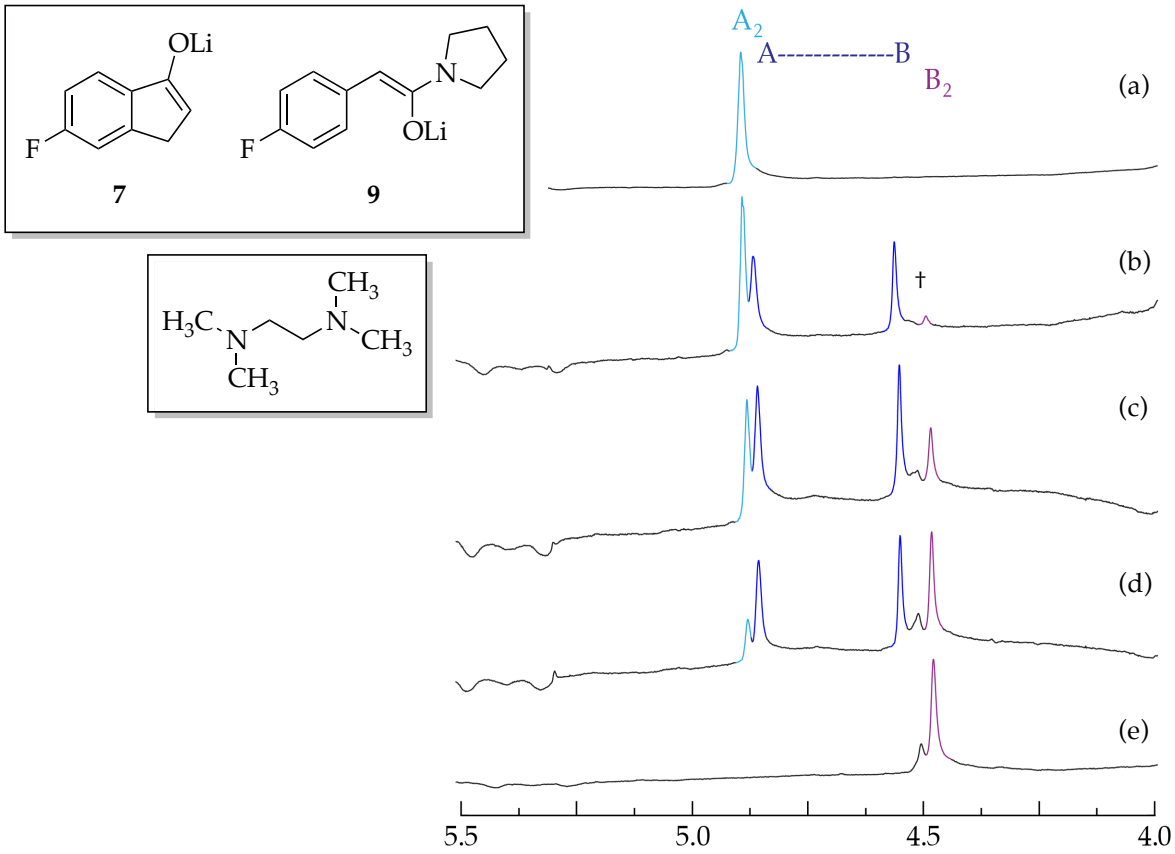


Figure 37. ^{1}H NMR spectra of 0.10 M solutions of [^{6}Li]**7** (**A**) and [^{6}Li]**9** (**B**) in 0.50 M TMEDA/toluene at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.59, 0.47, 0.30, and 0.00, respectively. † denotes unknown aggregation states.

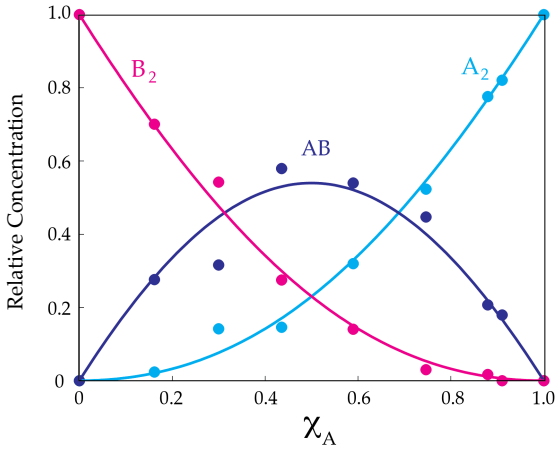


Figure 38. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [^{6}Li]**7** (**A**) and [^{6}Li]**9** (**B**) in 0.50 M TMEDA/toluene at -80 °C.

Tetramer Job Plots in TMEDA

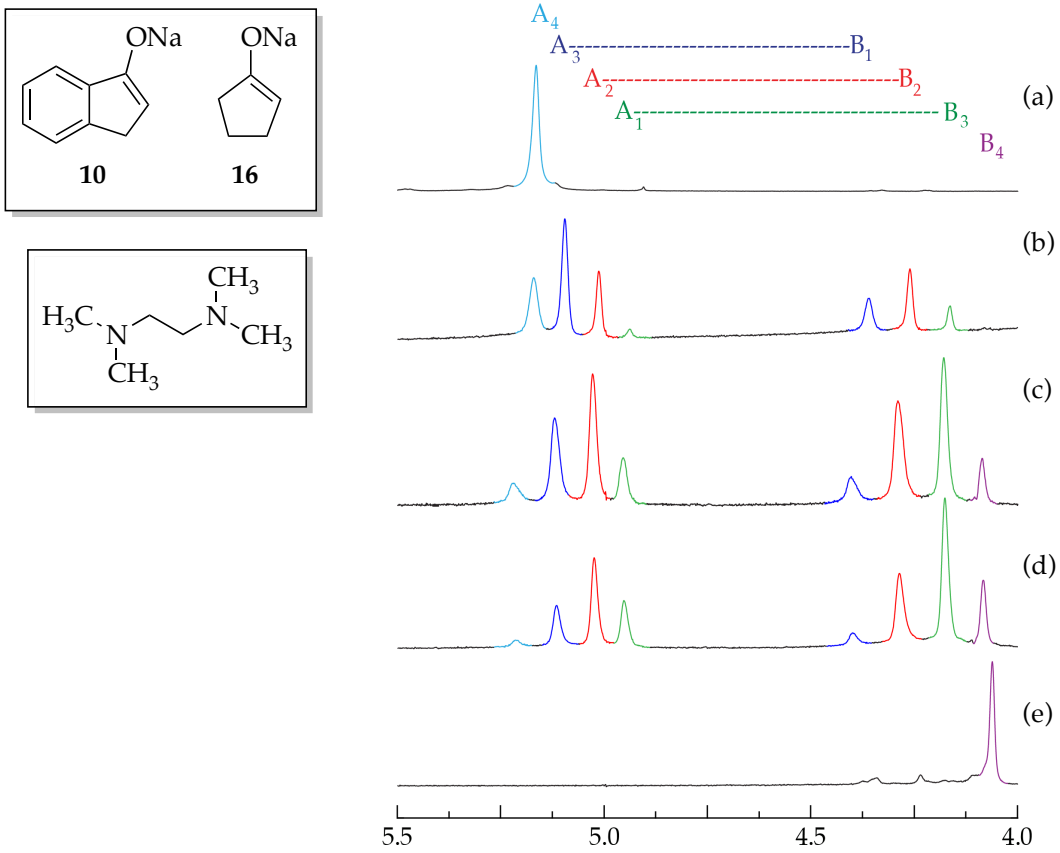


Figure 39. ^{1}H NMR spectra of 0.10 M solutions of [Na]**10** (**A**) and [Na]**16** (**B**) in 0.50 M TMEDA / toluene-d_8 at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.69, 0.48, 0.39, and 0.00, respectively.

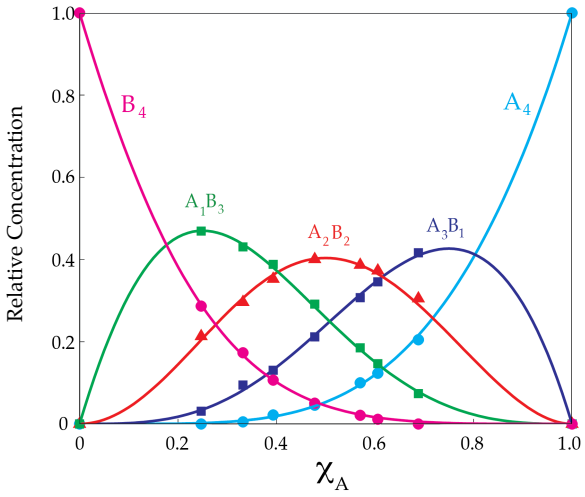


Figure 40. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [Na]**10** (**A**) and [Na]**16** (**B**) in 0.50 M TMEDA / toluene-d_8 at -80 °C.

Tetramer Job Plots in TMEDA

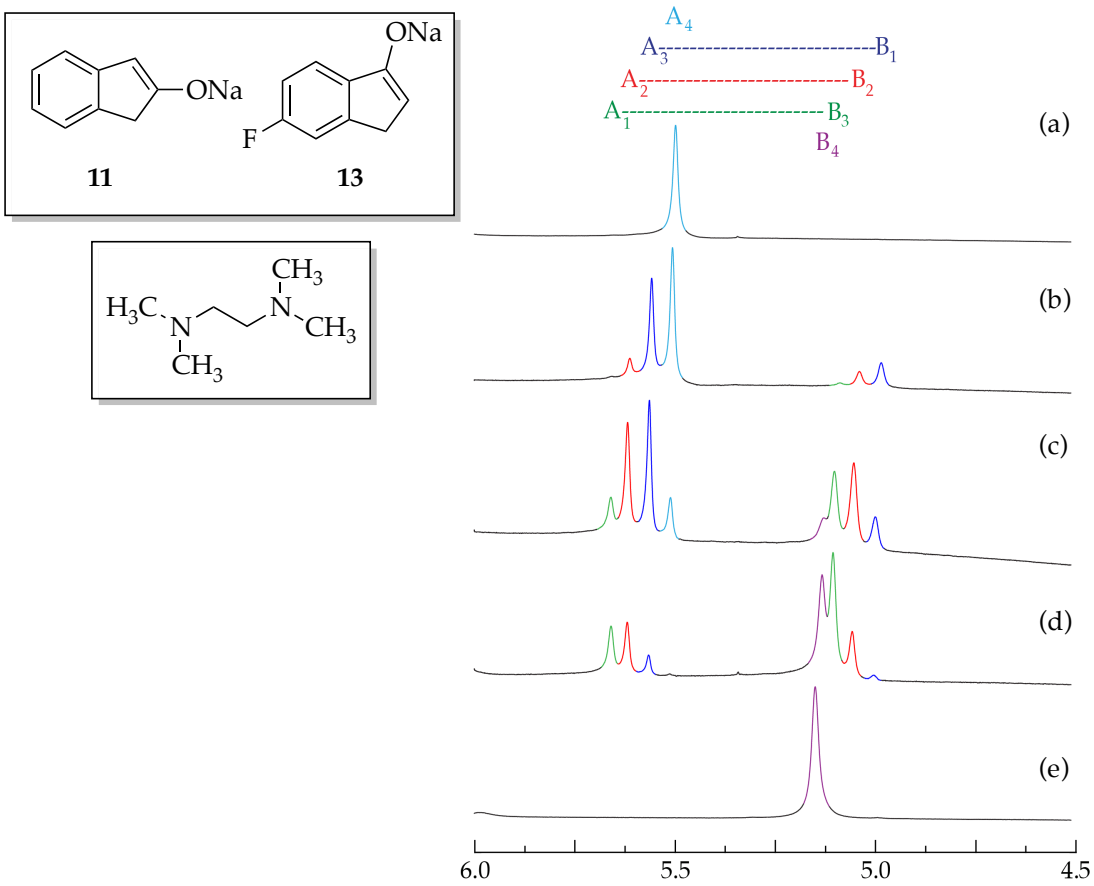


Figure 41. ^{1}H NMR spectra of 0.10 M solutions of [Na]**11** (**A**) and [Na]**13** (**B**) in 0.50 M TMEDA / toluene-d_8 at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.77, 0.50, 0.23, and 0.00, respectively.

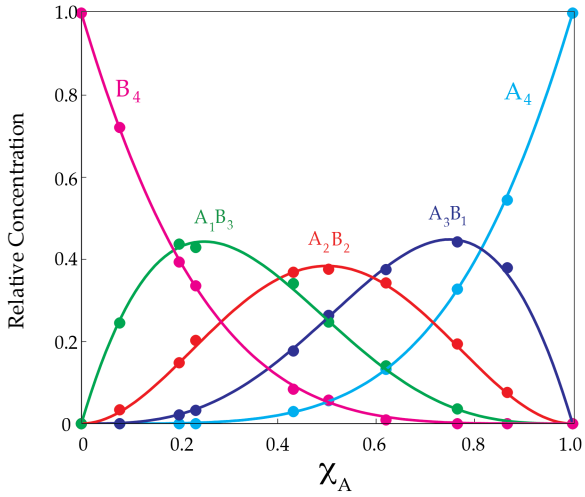


Figure 42. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [Na]**11** (**A**) and [Na]**13** (**B**) in 0.50 M TMEDA / toluene-d_8 at -80 °C.

Tetramer Job Plots in TMEDA

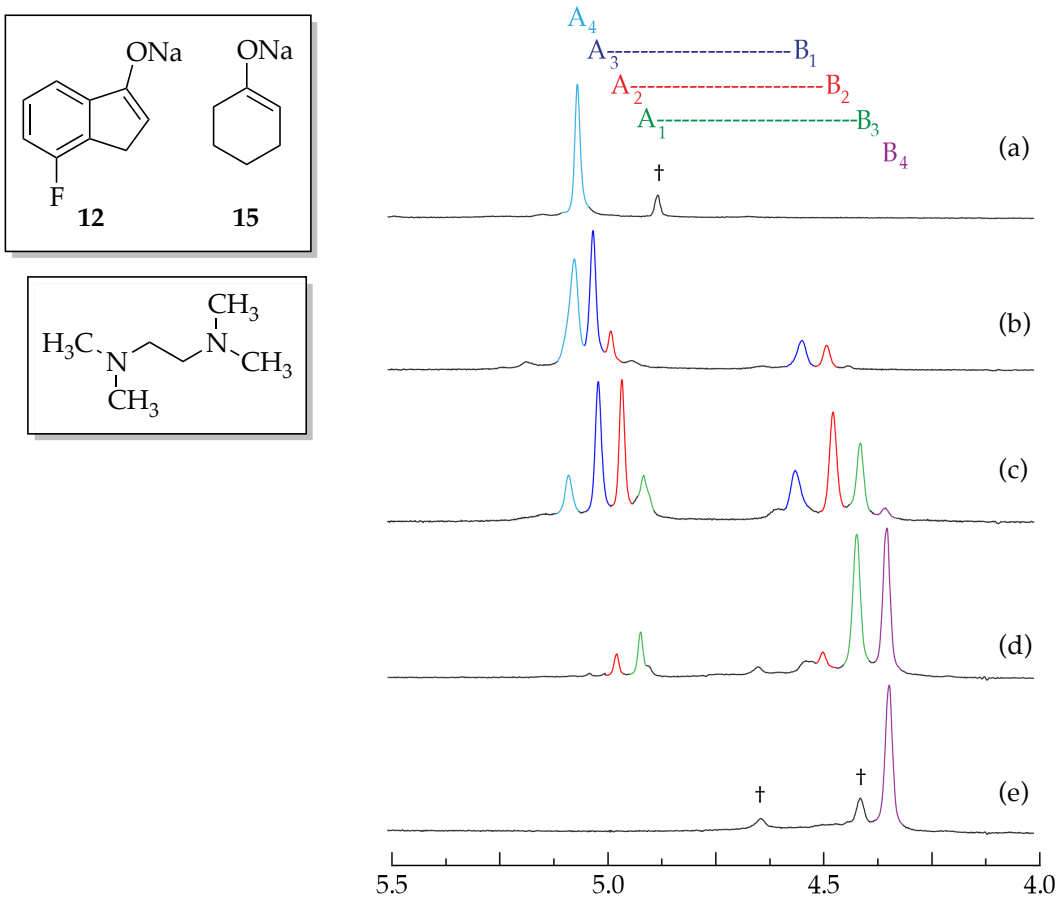


Figure 43. ^{1}H NMR spectra of 0.10 M solutions of [Na]**12** (**A**) and [Na]**15** (**B**) in 0.50 M TMEDA / toluene-d_8 at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.79, 0.56, 0.21, and 0.00, respectively. † denotes unknown aggregation states.

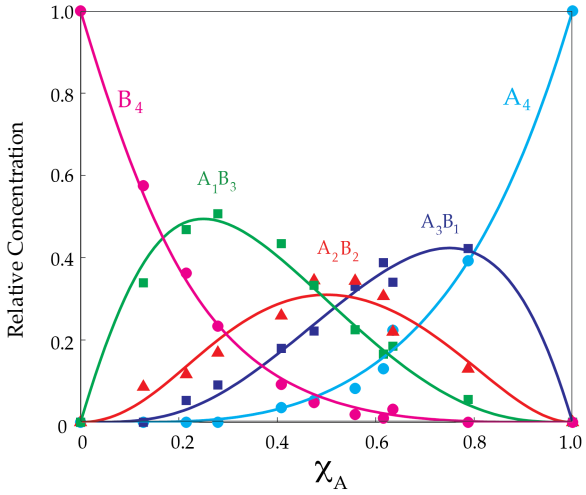


Figure 44. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [Na]**12** (**A**) and [Na]**15** (**B**) in 0.50 M TMEDA / toluene-d_8 at -80 °C.

Tetramer Job Plots in TMEDA

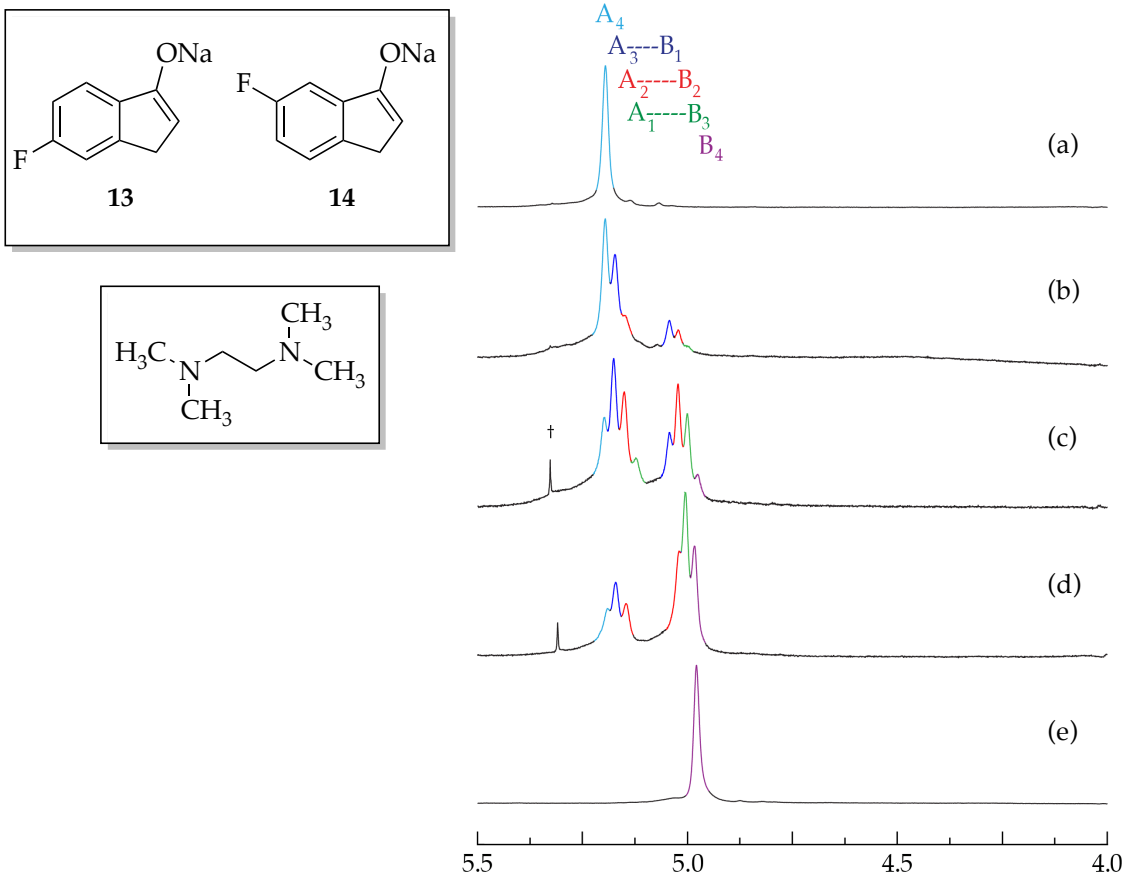


Figure 45. ^{1}H NMR spectra of 0.10 M solutions of [Na]**14** (**A**) and [Na]**13** (**B**) in 0.50 M TMEDA / toluene-d_8 at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.80, 0.60, 0.34, and 0.00, respectively. † denotes unknown aggregation states.

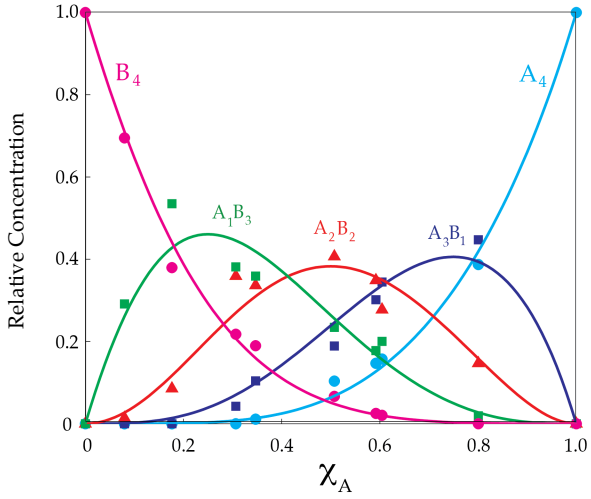


Figure 46. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [Na]**14** (**A**) and [Na]**13** (**B**) in 0.50 M TMEDA / toluene-d_8 at -80 °C.

Tetramer Stack Plots in THF

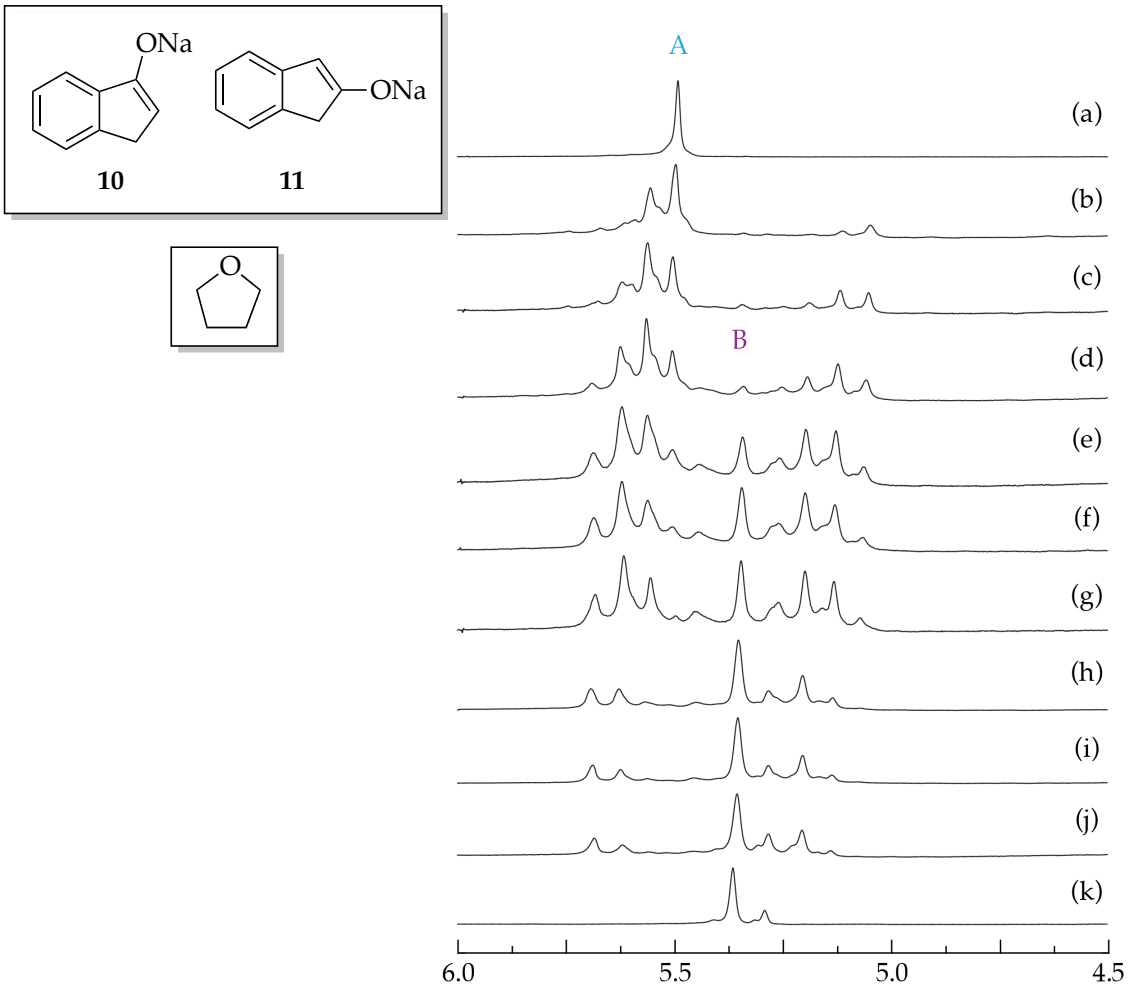


Figure 47. ^{1}H NMR spectra of 0.10 M solutions of [Na]**11** (**A**) and [Na]**10** (**B**) in 0.50 M THF/toluene-d_8 at -80 °C. Spectra (b)-(j) show a superposition of ensembles, though the dominant one appears to be tetramer. The expected mole fractions are in 0.01 increments.

Tetramer Stack Plots in THF

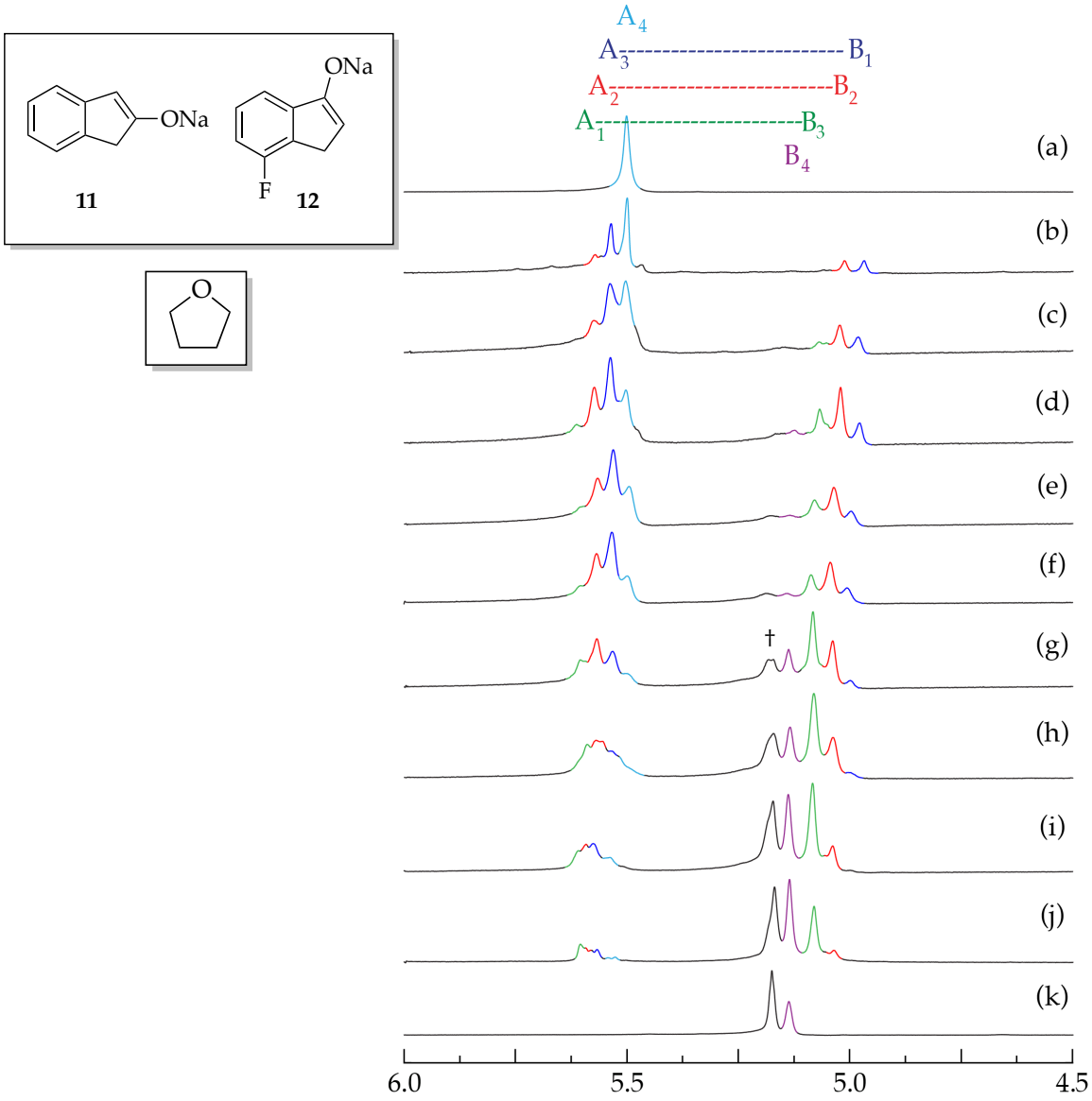


Figure 48. ^{1}H NMR spectra of 0.10 M solutions of [Na]**11** (**A**) and [Na]**12** (**B**) in 0.50 M THF / toluene-d_8 at -80 °C. At low mole fraction of **11**, the ensemble has poor resolution on the **A** side. The expected mole fractions are in 0.01 increments. † denotes unknown aggregation states.

Tetramer Stack Plots in THF

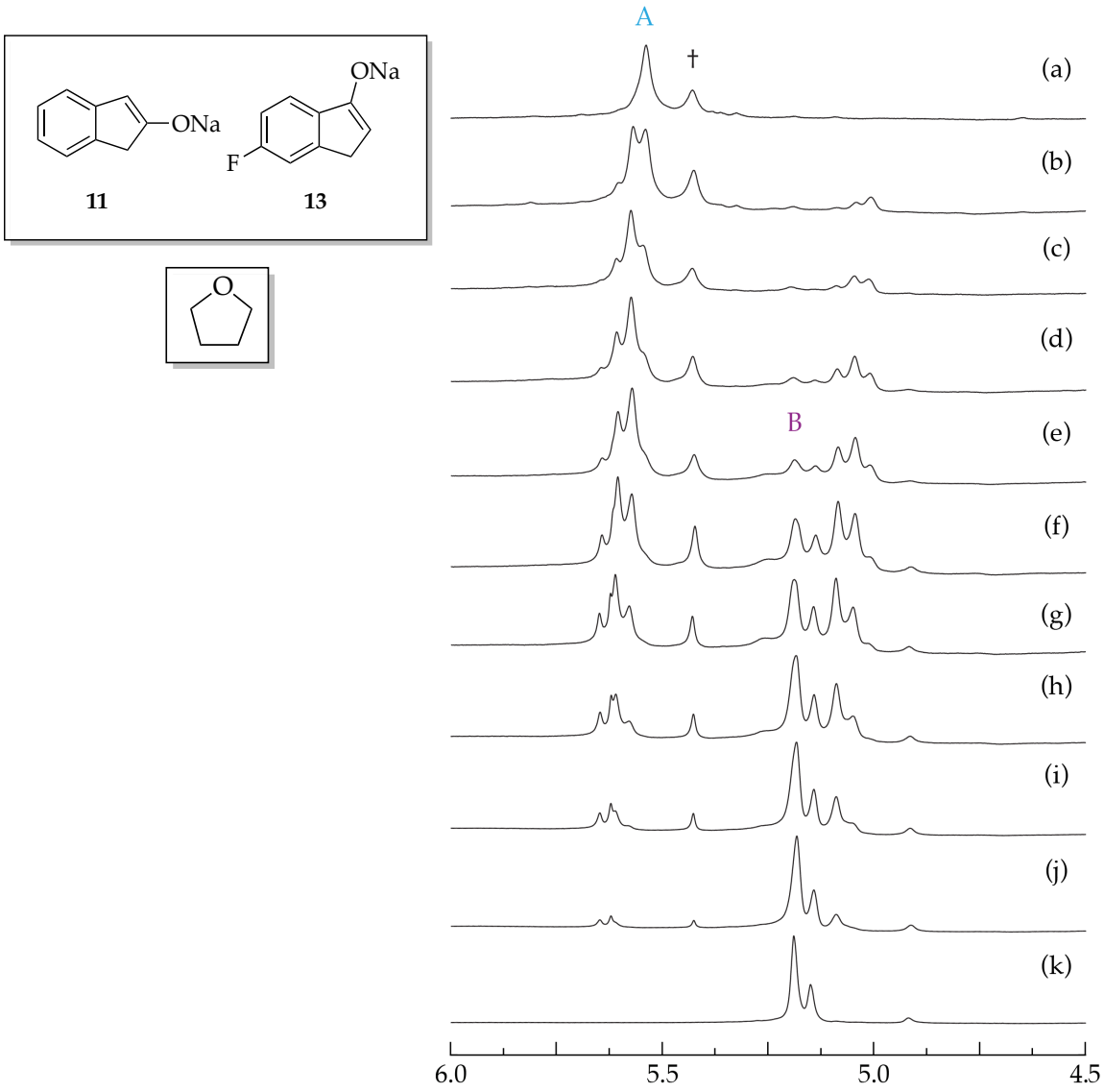


Figure 49. ^{1}H NMR spectra of 0.10 M solutions of [Na]**11** (**A**) and [Na]**13** (**B**) in 0.50 M THF / toluene-d_8 at -80 °C. The expected mole fractions are in 0.01 increments. † denotes suspected mixed aggregate with NaHMDS.

Tetramer Job Plots in THF

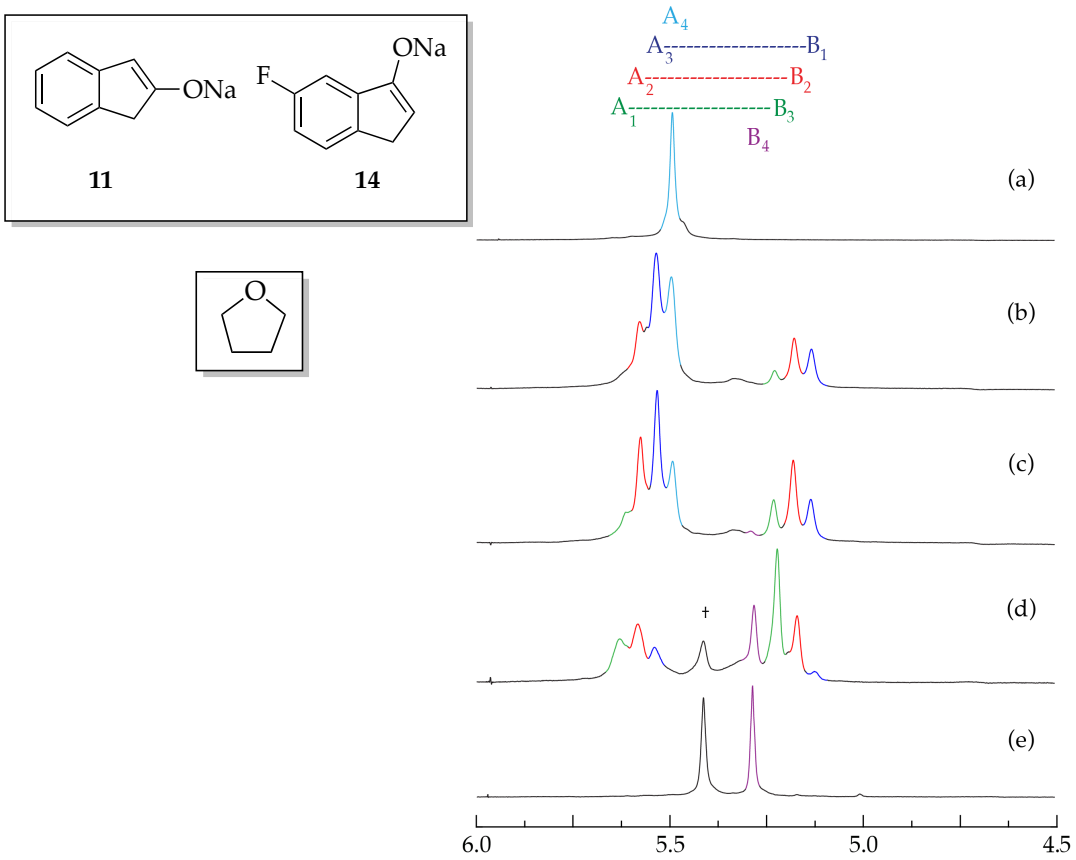


Figure 50. ^{1}H NMR spectra of 0.10 M solutions of [Na]**11** (**A**) and [Na]**14** (**B**) in 0.50 M THF / toluene-d_8 at -80 °C. The measured mole fractions of **A** in (a)-(e) are 1.00, 0.81, 0.63, 0.34, and 0.00, respectively. † denotes unknown aggregation states.

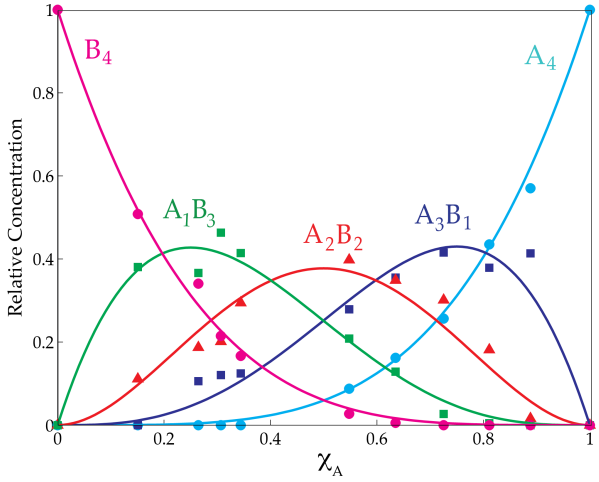


Figure 51. Job plot showing the relative integrations versus the measured mole fractions of **A** for 0.10 M mixtures of [Na]**11** (**A**) and [Na]**14** (**B**) in 0.50 M THF / toluene-d_8 at -80 °C.

Tetramer Stack Plots in THF

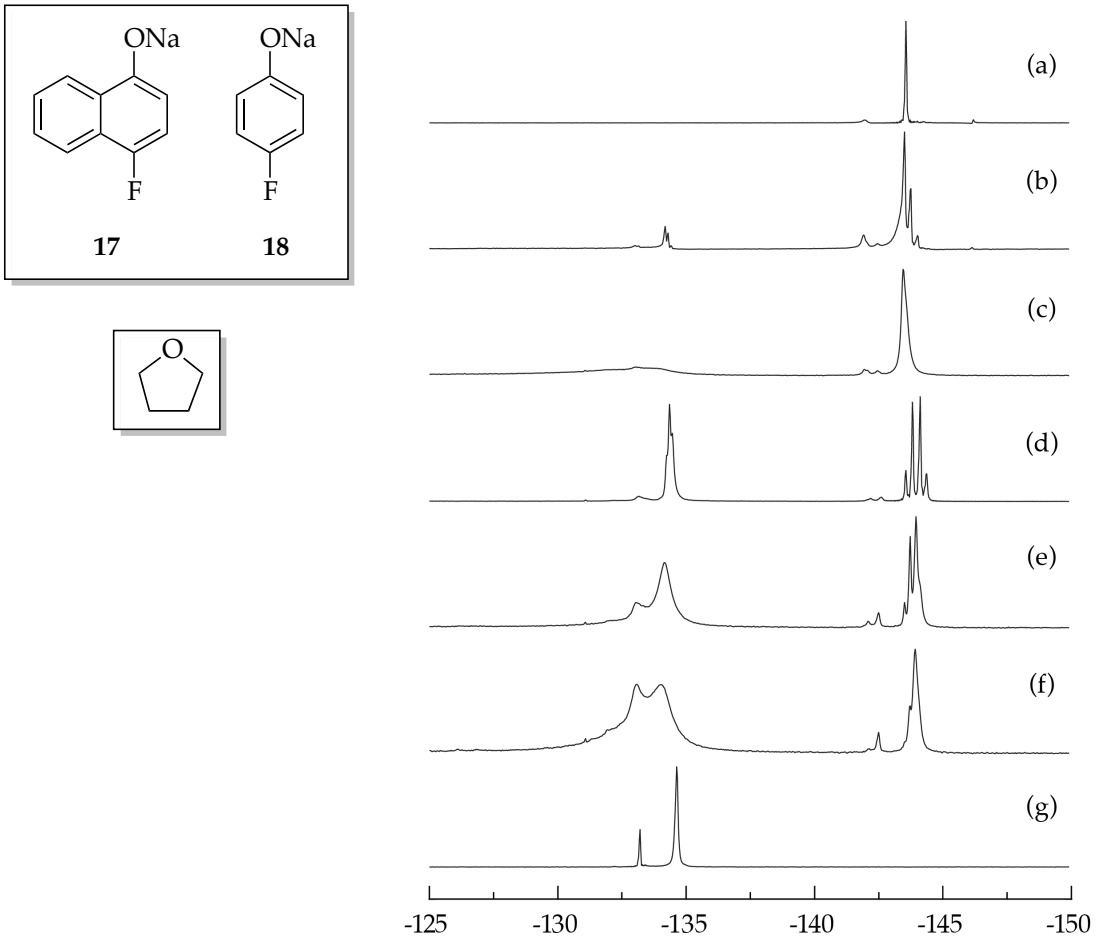


Figure 52. ^{1}H NMR spectra of 0.10 M solutions of [Na]**17** and [Na]**18** in 0.50 M THF / toluene-d_8 at -80 °C. The expected mole fractions of **17** in (a)-(g) are 1.0, 0.8, 0.6, 0.5, 0.4, 0.2 and 0.0, respectively.

V. NaICA Characterization.

Sodium isopropylcyclohexylamide NMR characterization.

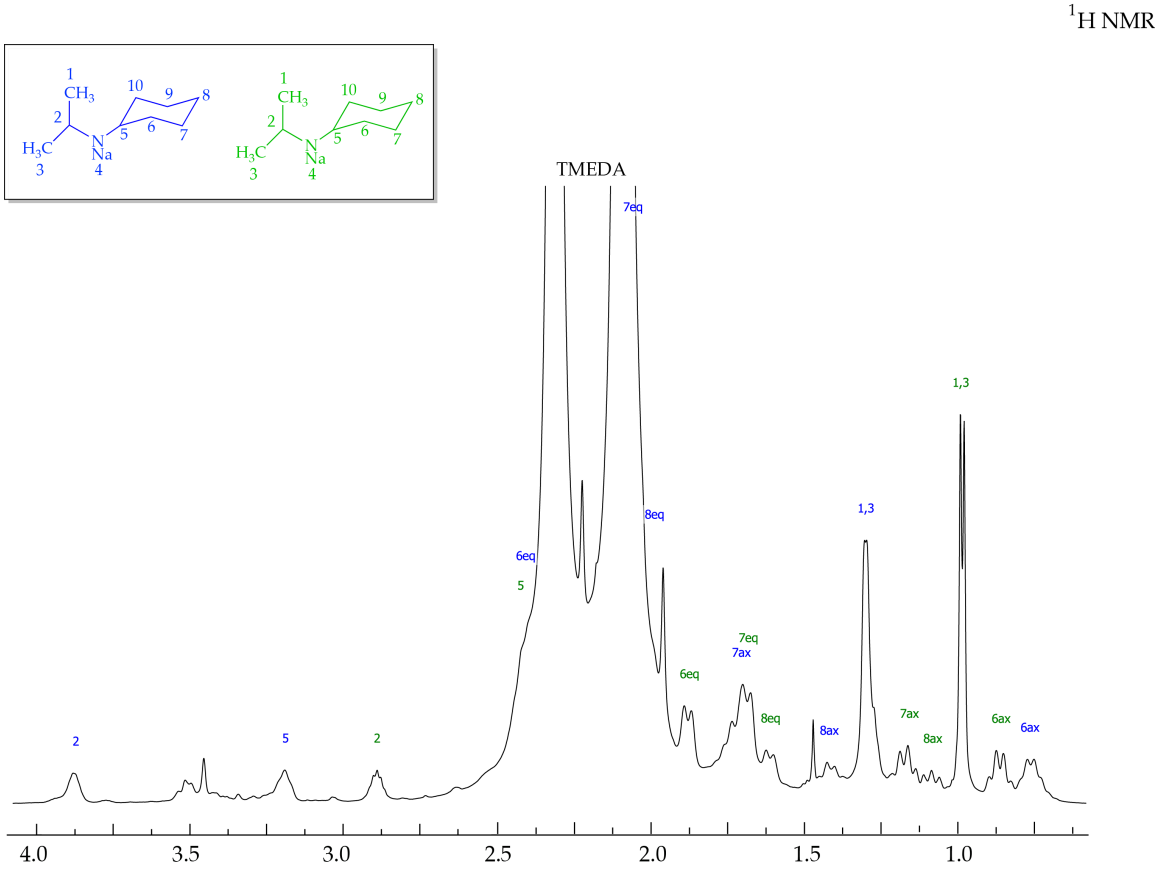


Figure 53. ^{1}H NMR of 0.1 M NaICA in 0.5 M TMEDA with a toluene-d_8 cosolvent at -80 °C.

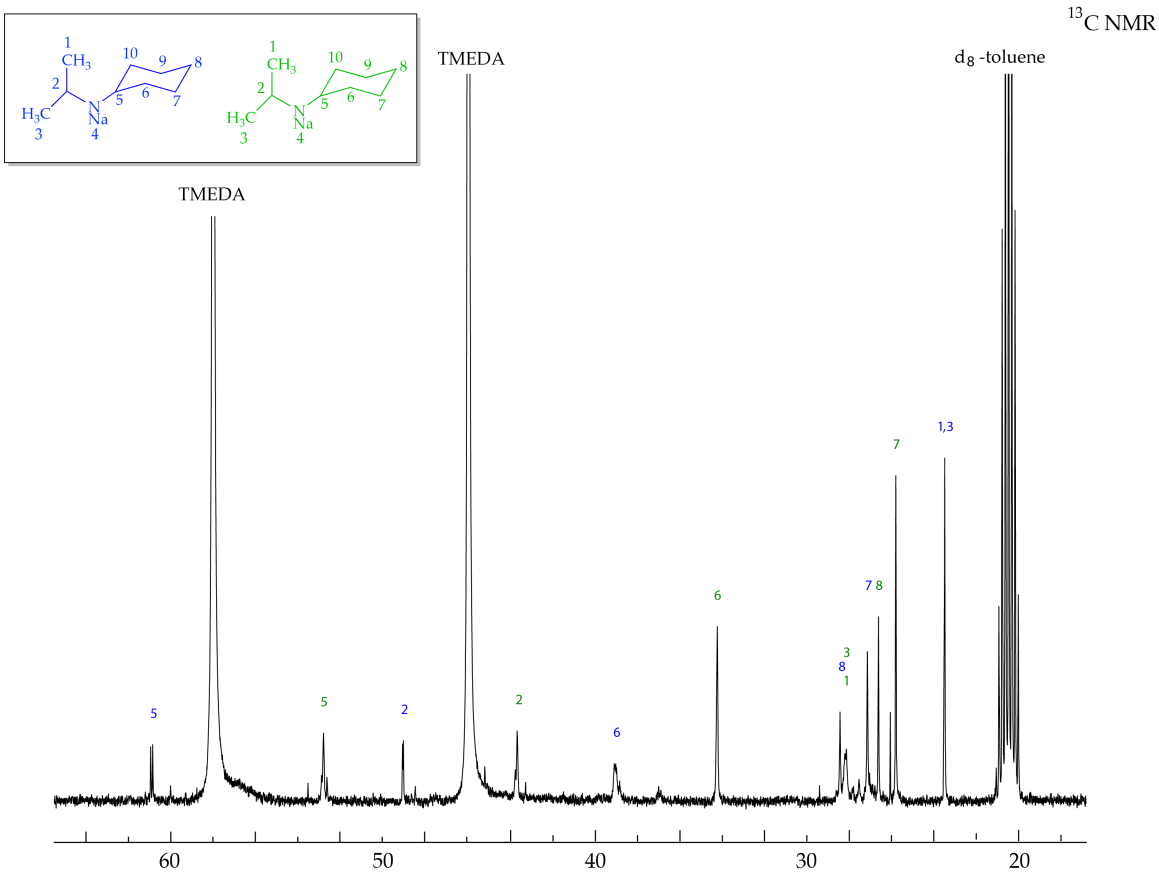


Figure 54. ^{13}C NMR of 0.1 M NaICA in 0.5 M TMEDA with a toluene-d_8 cosolvent at -80 °C.

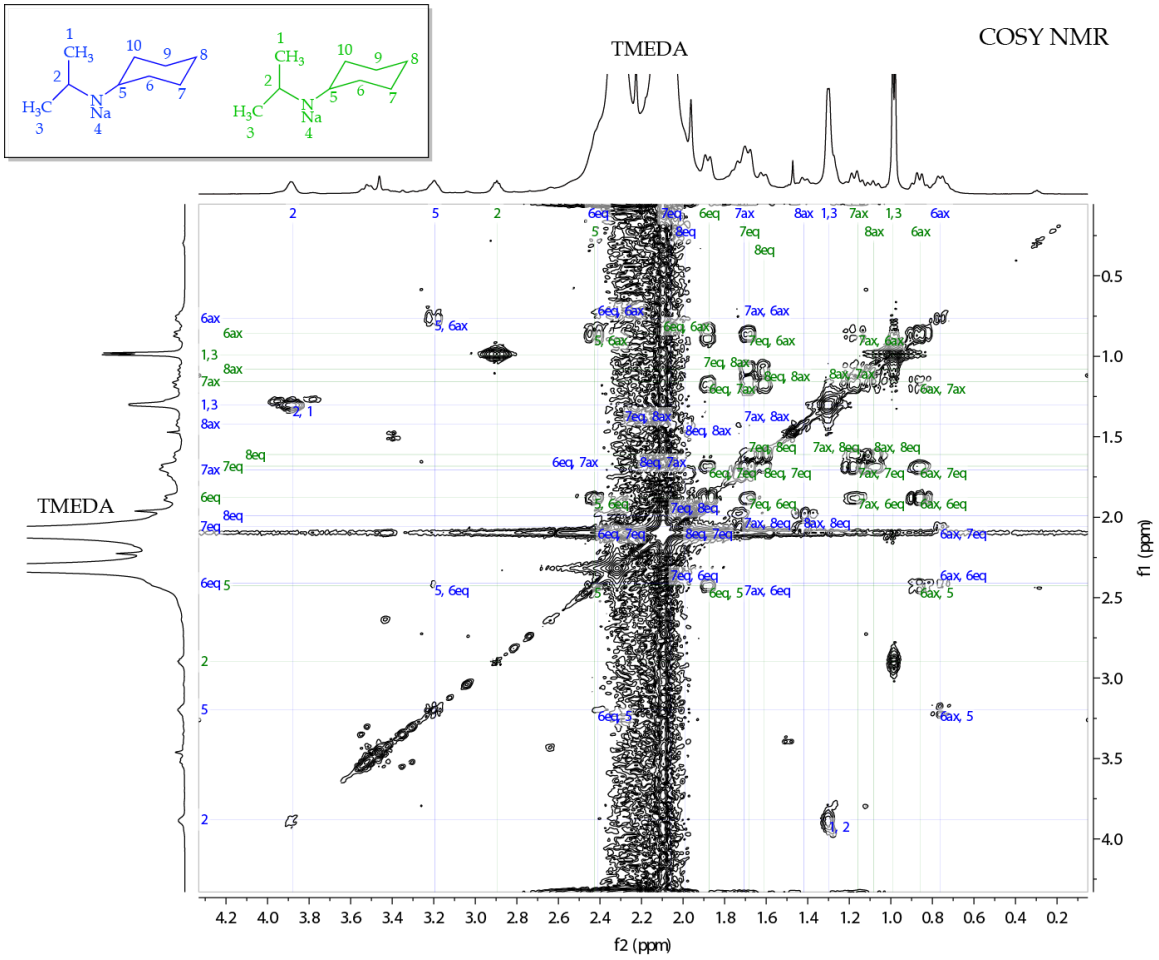


Figure 55. COSY NMR of 0.1 M NaICA in 0.5 M TMEDA with a toluene-d_8 cosolvent at -80 °C.

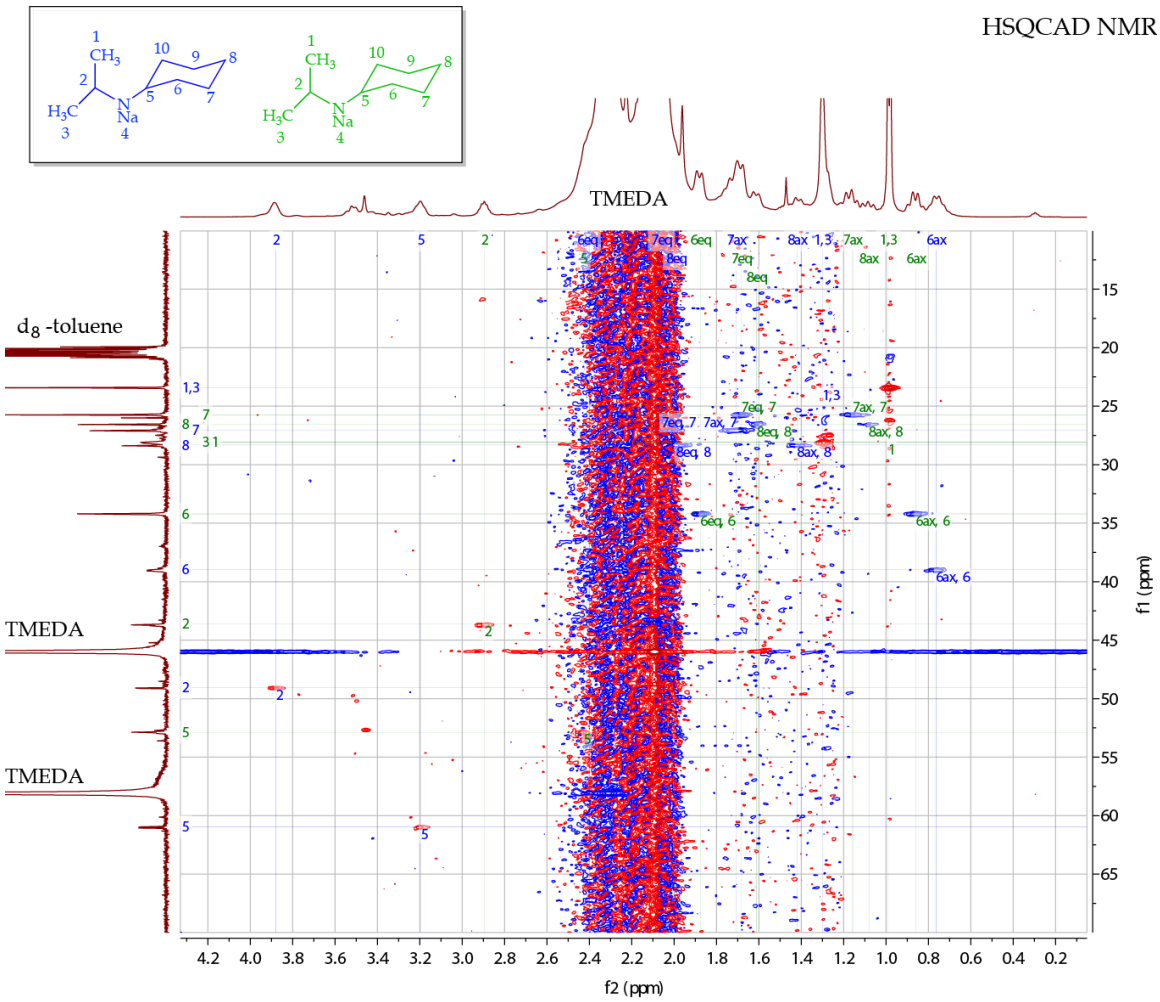


Figure 56. HSQCAD NMR of 0.1 M NaICA in 0.5 M TMEDA with a toluene-d_8 cosolvent at -80 °C.

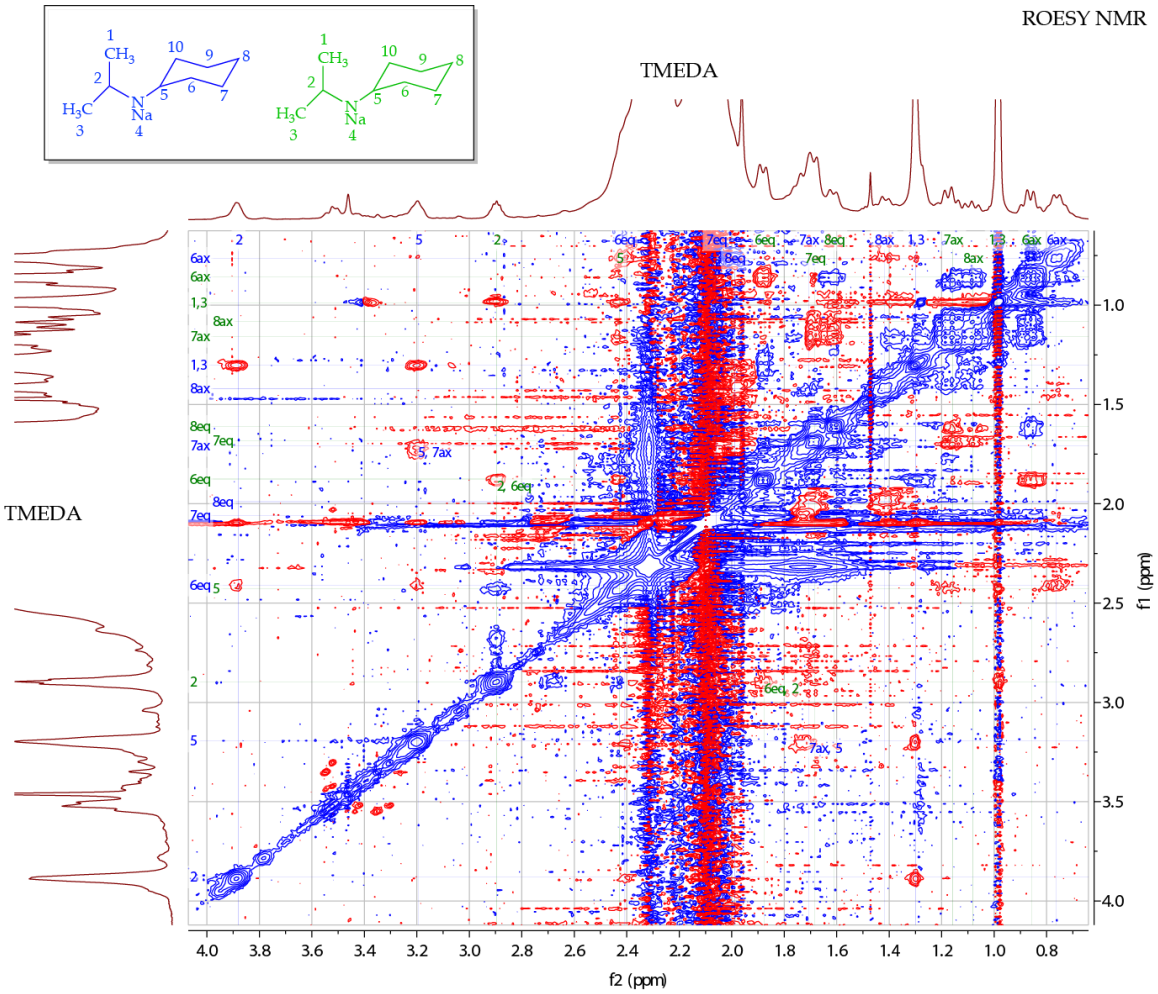


Figure 57. ROESY NMR of 0.1 M NaICA in 0.5 M TMEDA with a toluene-d_8 cosolvent at -80 °C.

VI. Matlab files for a singly-tagged ensembles.

The Matlab folders described below in the bold titles are labeled for ^{19}F, though obviously the nuclei does not matter for the parametric fit. To start the process, open **Data1_19F.m** and insert the measured mole fractions and normalized NMR integrals into their appropriate matrix and save the file without changing the file name. Using the Matlab command window, type the following:

Data1_19F *% variables will appear in the workspace*

try_fit_19F(XA_19F, phi, peak_assignment, Expt_Populations)
% only done to check whether the data is entered correctly; generates a plot

[phi_new, error] = refine_fit_19F(XA_19F,phi, peak_assignment, Expt_Populations)
% does the curve fitting through an iterative process; gives phi values and errors

phi = phi_new *% replaces the old phi values with the new phi values from the fit*

try_fit_19F(XA_19F, phi, peak_assignment, Expt_Populations)
% Generates a Job plot with the parametric fit, which can be exported to Adobe Illustrator

Tetramer:

A tetramer will appear like a trimer, and the x-axis will scale to 0.75, corresponding to the stoichiometry of the last visible aggregate, A_3B_1.

Data1_19F.m:

```
% This script sets up variables for an ensemble of
% aggregates of the same aggregation number.
%
%       XA(j): the measured mole fractions.
%       Expt_Populations(j,k): the normalized NMR integrals
%       peak_assignment: sets the order of NMR peaks.
%       phi: sets the relative energies of each n-mer.


% First, list the mole fractions of A such that it
% correlates with the rows in the Expt_Populations.

%DISCLAIMER: this part is only relevant if your B_n is the
%fluorinated part, but will help align the axis and numbers
%correctly. We are using a tetramer A4 and B4 purely for
%illustrative purposes.

%If using the same format as with lithium, the
```

```
%homoaggregrate on the right (B4) will be the curve on the
%left of the Job plot. Usually Mole Fraction is calculated
%with respect to A4. Since B is the fluorinated part, we
%have to calculate it with respect to B4. 1-[MF] is
%necessary if we want the plot to run from 0 to 0.75
%instead of 0.25 to 1.0.

%Lithium format: L to R
% A4 A3B1 A2B2 A1B3 B4

%calc MF w.r.t A = A4 + 0.75*A3B1 + 0.5*A2B2 + 0.25*A1B3

%19F format if B4 is fluorinated: L to R
%A3B1 A2B2 A1B3 B4

%calc MF w.r.t. B (Fluorine) = 0.25*A3B1 + 0.5*A2B2 +
%0.75*A1B3 + B4

% pure F (B4) should be at point 0, not 1.
% If following this setup, it will be at MF =1 with
% experimental populations of 0 0 0 1. Hence, 1 -[Xa_19F]

XA_19F = 1-[0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1];

% Next, list the experimental populations of the
% aggregates. The number of rows must match XA_19F.

Expt_Populations =
[0.9     0.09    0.01    0
 0.x     0.x     0.x    0.x
 0.x     0.x     0.x    0.x
 0.x     0.x     0.x    0.x
 0.x     0.x     0.x    0.x
 0.x     0.x     0.x    0.x
 0.x     0.x     0.x    0.x
 0.x     0.x     0.x    0.x
 0.x     0.x     0.x    0.x
  0       0       0      1;];
```

```
% following the described format will put it as [4 3 2 1]
% corresponding to A3B1, A2B2, A3B1, B4.
% if peaks overlap, assign them twice. e.g. [3 2 1 1]

peak_assignment = [4 3 2 1];

% Assign the "energy" of each n-mer using the computer's
expected ordering.
phi = [ 1 1 1 1 ];
```

Error_of_Model_19F.m:

```
% The description of this file has been previously
% reported; Please refer to the supporting information in
% J. Am. Chem. Soc. 2008, 130, 4859.

function [mean_error, pop_error] =
Error_of_Model_19F(XA_19F,phi, peak_assignment,
Expt_Populations, Expt_weights)

    if (nargin<5) % If no info on data given assume all
points equally precise.
                Expt_weights=ones(size(Expt_Populations));
    end

    % Compute values from the model.
    Concentrations = multimers_19F(XA_19F,phi);
    PP = Populations(Concentrations, peak_assignment);

    % Compute the mean error.
    diff = PP - Expt_Populations;
    mean_error = sqrt(sum(sum(diff.*diff.*Expt_weights)) /
sum(sum(Expt_weights)));

    % Compute the error for each population independently.
    pop_error = sum(diff.*Expt_weights,1) ./
sum(Expt_weights,1);
    pop_error(2,:) = sqrt(sum(diff.*diff.*Expt_weights,1)
./ sum(Expt_weights,1));
```

Refine_fit_19F.m:

```
% The description of this file has been previously
% reported; Please refer to the supporting information in
% J. Am. Chem. Soc. 2008, 130, 4859.

function [phi_new, error] = refine_fit_19F(XA_19F,phi,
```

```
peak_assignment, Expt_Populations)

if (nargin<5)
     Expt_weight = ones(size(Expt_Populations));
 end

N = length(phi)-1;
param = [ 2:(N+1)];
% We need to select an initial step size of each for trial
improvements 10% is a good starting figure.
step_size = 0.1*phi(param),

% Initialize Search
N_no_progress = 0; % Number of steps since error last
improved.
N_max_trials = 30; % Give up if after 30 steps things have
got no better.
[error_best, temp] = Error_of_Model_19F(XA_19F,phi,
peak_assignment, Expt_Populations) ; % Initial Quality of
Fit
fprintf(1,'\n Initial Error of Fit = %f percent.\n',
error_best * 100);

% Iteratively try to improve fit.
while (N_no_progress < N_max_trials)

    flag = 0;

    for k=1:length(param) % Try tweaking each parameter in
turn.

        % Step to the right
            phi_testr = phi;
            phi_testr(param(k))=abs(phi(param(k)) +
step_size(k));
            [error_testr, temp] =
Error_of_Model_19F(XA_19F,phi_testr, peak_assignment,
Expt_Populations, Expt_weight);

        % Step to the left
            phi_testl = phi;
            phi_testl(param(k))=abs(phi(param(k)) -
step_size(k));
            [error_testl, temp] =
Error_of_Model_19F(XA_19F,phi_testl,
peak_assignment,Expt_Populations, Expt_weight);

        % Decide if you want to step.
```

```
        if (error_testr<error_best)
                % Positive step better so keep going that
way.
                error_best=error_testr; phi=phi_testr;
step_size(k) = step_size(k) * 1.5;
                N_no_progress=0;
        elseif      (error_testl <error_best) % Negative
step better so keep going that way
                error_best=error_testl; phi=phi_testl;
step_size(k) = step_size(k) * 1.5;
                N_no_progress=0;
        else
            flag = flag + 1; % Failure.  Add it to the
list.
        end
    end

    if (flag>2) % Failed to improve by stepping in any
direction
        step_size = step_size * (0.75 + 0.25*rand);  %
Reduce step size
        N_no_progress=N_no_progress+1;
    end

    % After adjust each element of rel_weight, report new
fit.
    fprintf(1,'\nError - %f , Last Good Step - %d , Mean
Step Size - %f \n ',error_best, N_no_progress,
100*mean(step_size./phi(param)));
    fprintf(1,' Phi - %f',phi);

    end

    error=error_best;
    phi_new = phi;
```

try_fit_19F.m:

```
% The description of this file has been previously
% reported; Please refer to the supporting information in
% J. Am. Chem. Soc. 2008, 130, 4859.

function try_fit_19F(XA_19F, phi, peak_assignment,
Expt_Populations)


    % If no experimental errors given, weight all points
```

```
equally.
    if (nargin<5)
                Expt_weights=ones(size(Expt_Populations));
    else
                Expt_weights = 1./( Expt_Errors +
mean(mean(Expt_Errors)));
    end

    % Plot the measured values of NMR populations
     % hold on ; cscheme='brgmkcybgrmkcy'; axis([0 0.75 0
1]); xlabel('X_A'); ylabel('Mole Fractions');

     % set(gca,'XTick',[0 0.25 0.50 0.75])

          hold on ; cscheme='brgmbrcbcybgrmkcy'; axis([0.0
0.75 0.0 1.0]);
            set(gca,'XTick',[0.0 0.25 0.50
0.75],'FontSize',14,'FontName','Palatino')
            set(gca,'YTick',[0.0 0.2 0.4 0.6 0.8 1.0])

xlabel('X_B','FontSize',16,'FontName','Palatino');
          %xlabel('X_n_o_
_f_l_u_o_r_i_n_e','FontSize',16,'FontName','Palatino');
           ylabel('Relative
Integration','FontSize',16,'FontName','Palatino');


      for j=1:size(Expt_Populations,2)
            if (nargin<5)
                plot(XA_19F,
Expt_Populations(:,j),sprintf('%so',cscheme(j)),'MarkerSize
',25,'Marker','.');
            else
                errorbar(XA_19F, Expt_Populations(:,j),
Expt_Errors(:,j),sprintf('%so',cscheme(j)));
            end
      end

    % Plot the model on
      XAc = [0:0.01:0.75];
TP=Populations(multimers_19F(XAc,phi), peak_assignment);
      for j=1:size(TP,2)
          plot(XAc,TP(:,j), sprintf('%c',cscheme(j)),
'LineWidth',2);
      end

    % Compute how good the model is and AepoAt to the useA.
    [mean_error, pop_error] =
```

```
Error_of_Model_19F(XA_19F,phi, peak_assignment,
Expt_Populations, Expt_weights);
    N = length(phi)-1;
            fprintf(1,'\nThe Mean mismatch is %f
peAcent.\n', mean_error*100);
            for j=1:size(pop_error,2)
            fprintf(1,'Predicted value of species A%dB%d
+A%dB%d exceeds measurement by %f percent and mean square
error of %f percent.\n ',j-1,N-j+1,N-j+1,j-
1,pop_error(1,j)*100,pop_error(2,j)*100);
            end
```

multimers.m and **populations.m:**

The description and contents of these files have been previously reported; Please refer to the supporting information in *J. Am. Chem. Soc.* **2008**, 130, 4859.