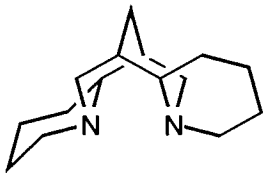
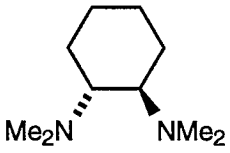
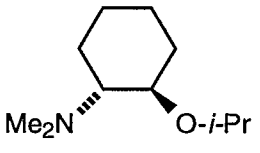


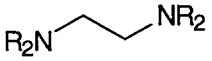
A (sparteine)



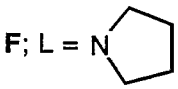
B (*trans*-TMCDA)



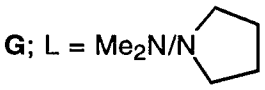
C



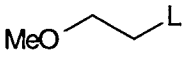
D; L = NMe_2
E; L = NEt_2



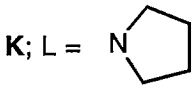
F; L =



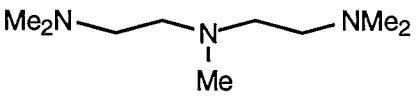
G; L = Me_2N/



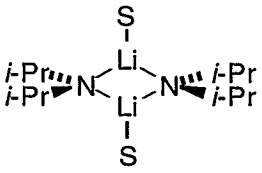
H; L = OMe (DME)
I; L = NMe_2
J; L = NEt_2



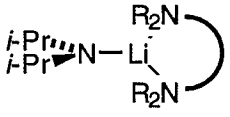
K; L =



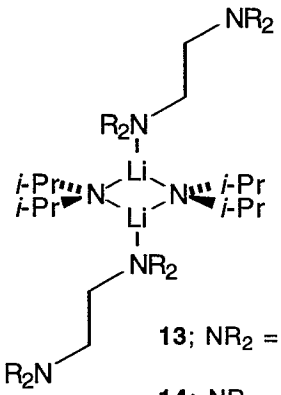
L (PMDTA)



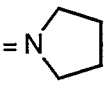
1; S = THF
2; S = Et_2O
3; S = *n*-BuOMe
4; S = *t*-BuOMe
5; S = THP
6; S = 2-MeTHF
7; S = 2,2-Me_2THF



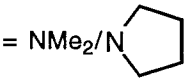
8; diamine = **A**
9; diamine = **F**
10; diamine = **G**
11; diamine = **B**
12; diamine = **E**



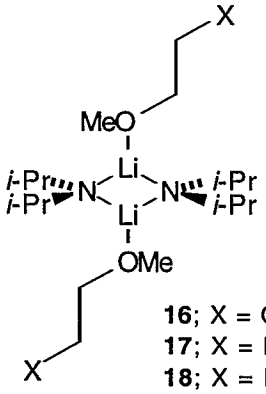
13; NR_2 = NMe_2



14; NR_2 =

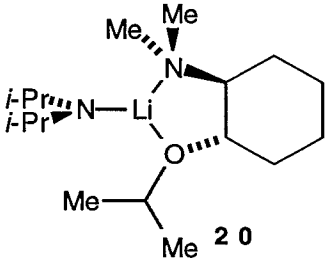


15; NR_2 = NMe_2/



16; X = OMe
17; X = NMe_2
18; X = NEt_2

19; X =



20

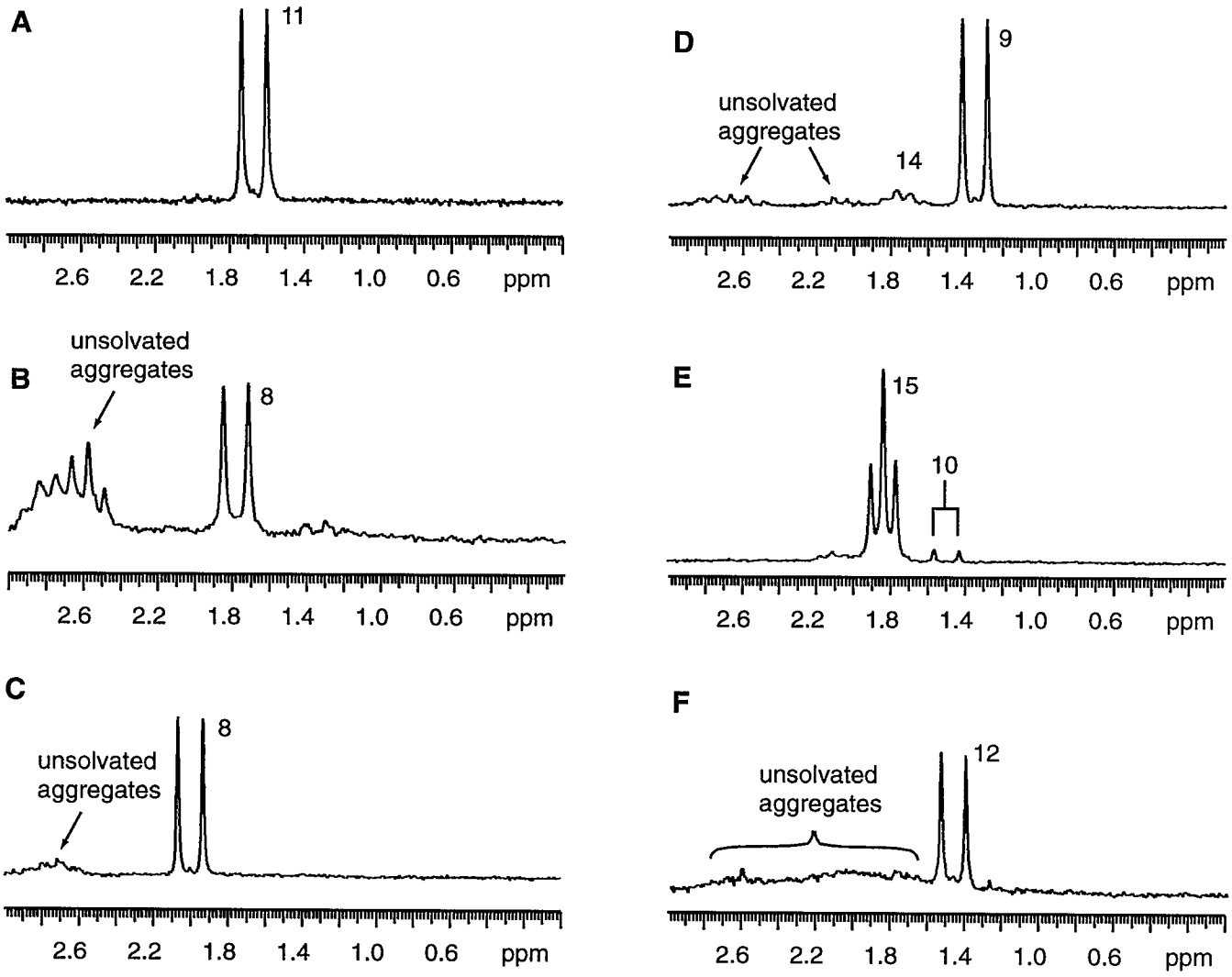


Figure I. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C. The samples also contain: (A) 2.0 equiv of TMCDA; (B) 1.5 equiv of sparteine; (C) 5.0 equiv of sparteine; (D) 2.0 equiv of dipyrrolidinoethane; (E) 2.0 equiv of **G**; (F) 5.0 equiv of **E** (TEEDA).

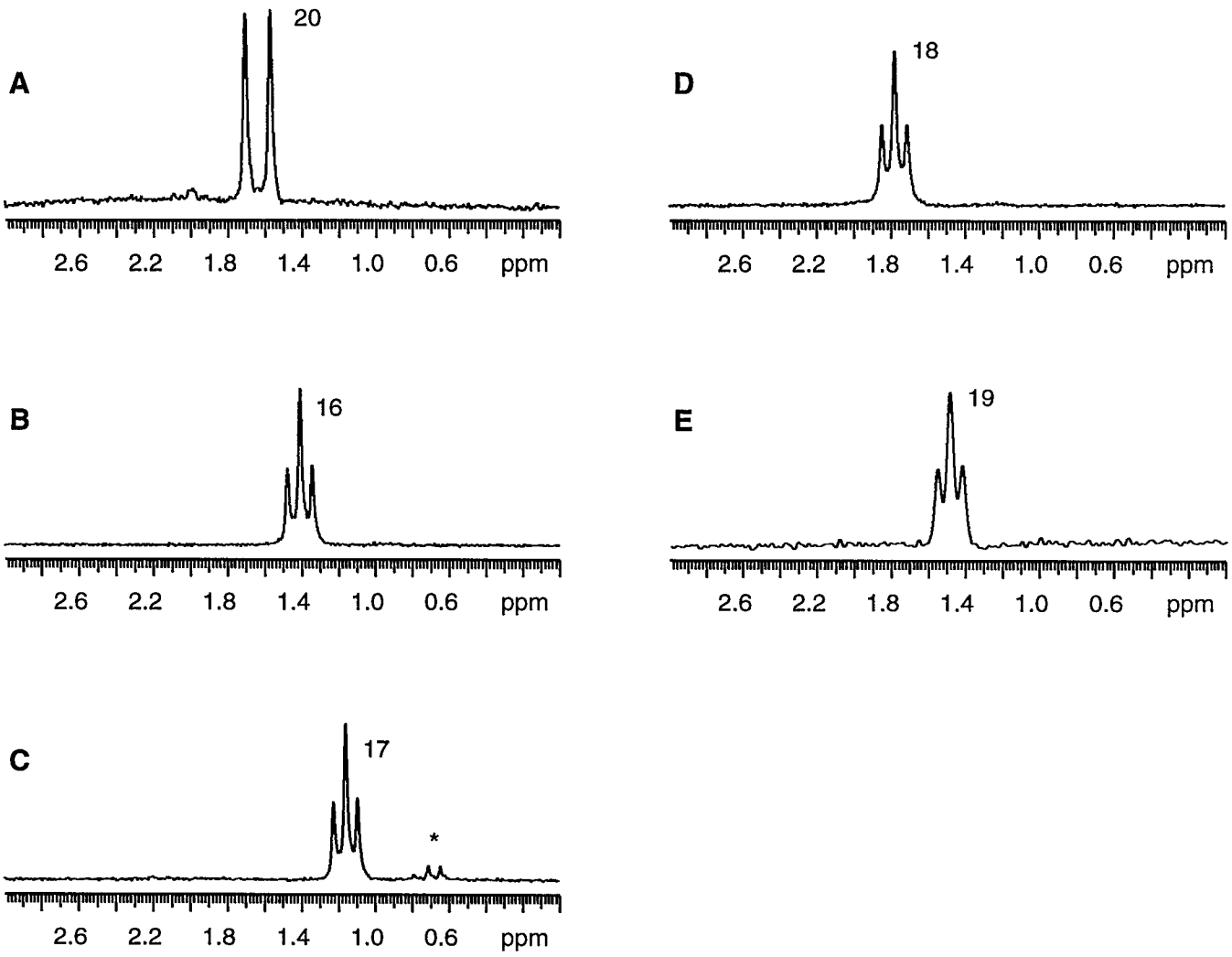


Figure II. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C. The samples also contain: (A) 2 equiv of **C**; (B) 2 equiv of DME; (C) 2 equiv of $MeO(CH_2)_2NMe_2$ (*denotes possible decomposition derived LDA-LiX mixed dimer); (D) 2 equiv of $MeOCH_2CH_2NEt_2$; (E) 2 equiv of $MeOCH_2CH_2N(CH_2)_4$.

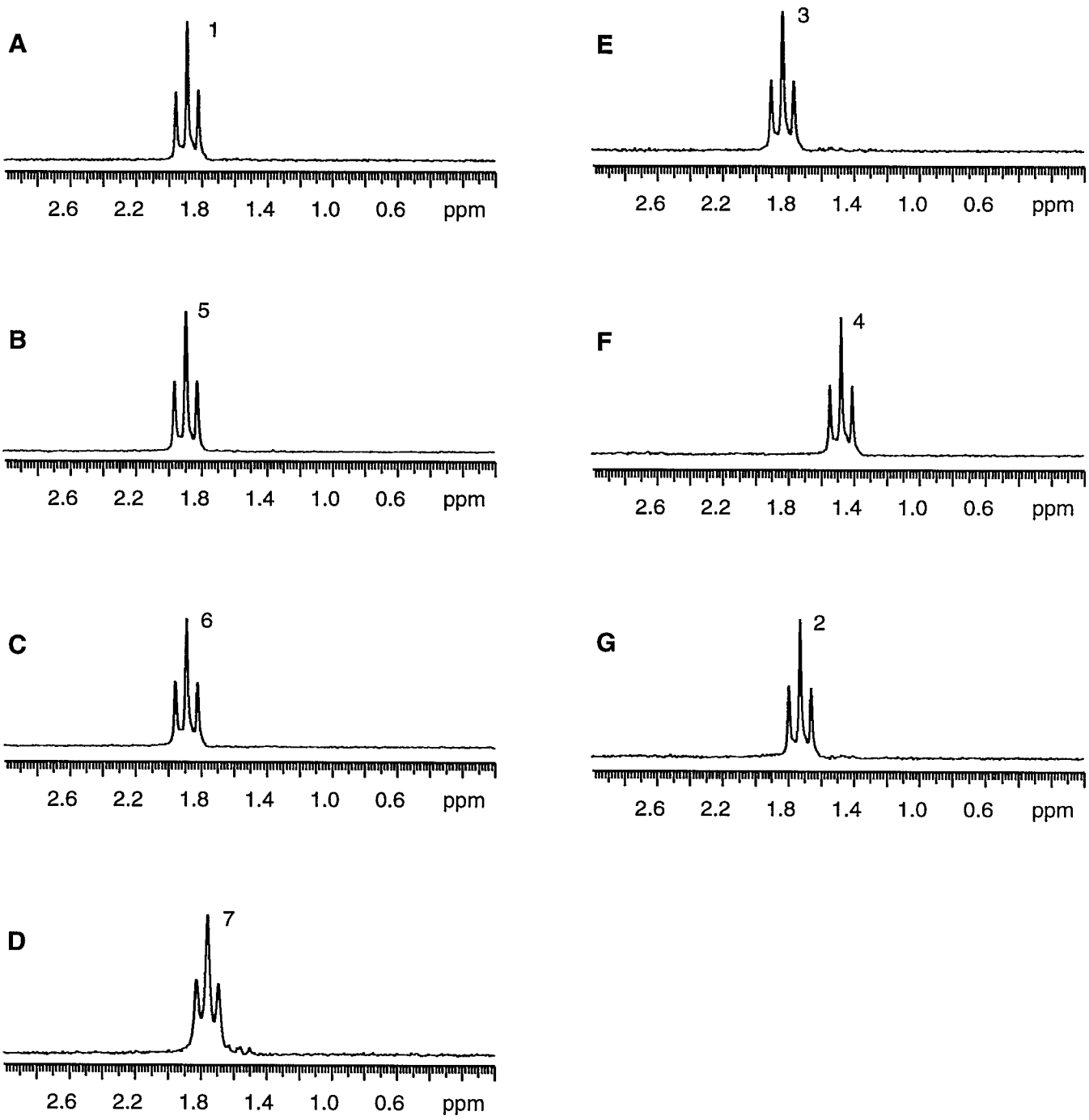


Figure III. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C. The samples also contain: (A) 4 equiv of THF; (B) 4 equiv of THP; (C) 2 equiv of 2-MeTHF; (D) 4 equiv of 2,2-Me_2THF; (E) 2 equiv of *n*-BuOMe; (F) 5 equiv of *t*-BuOMe; (G) 4 equiv of Et_2O.

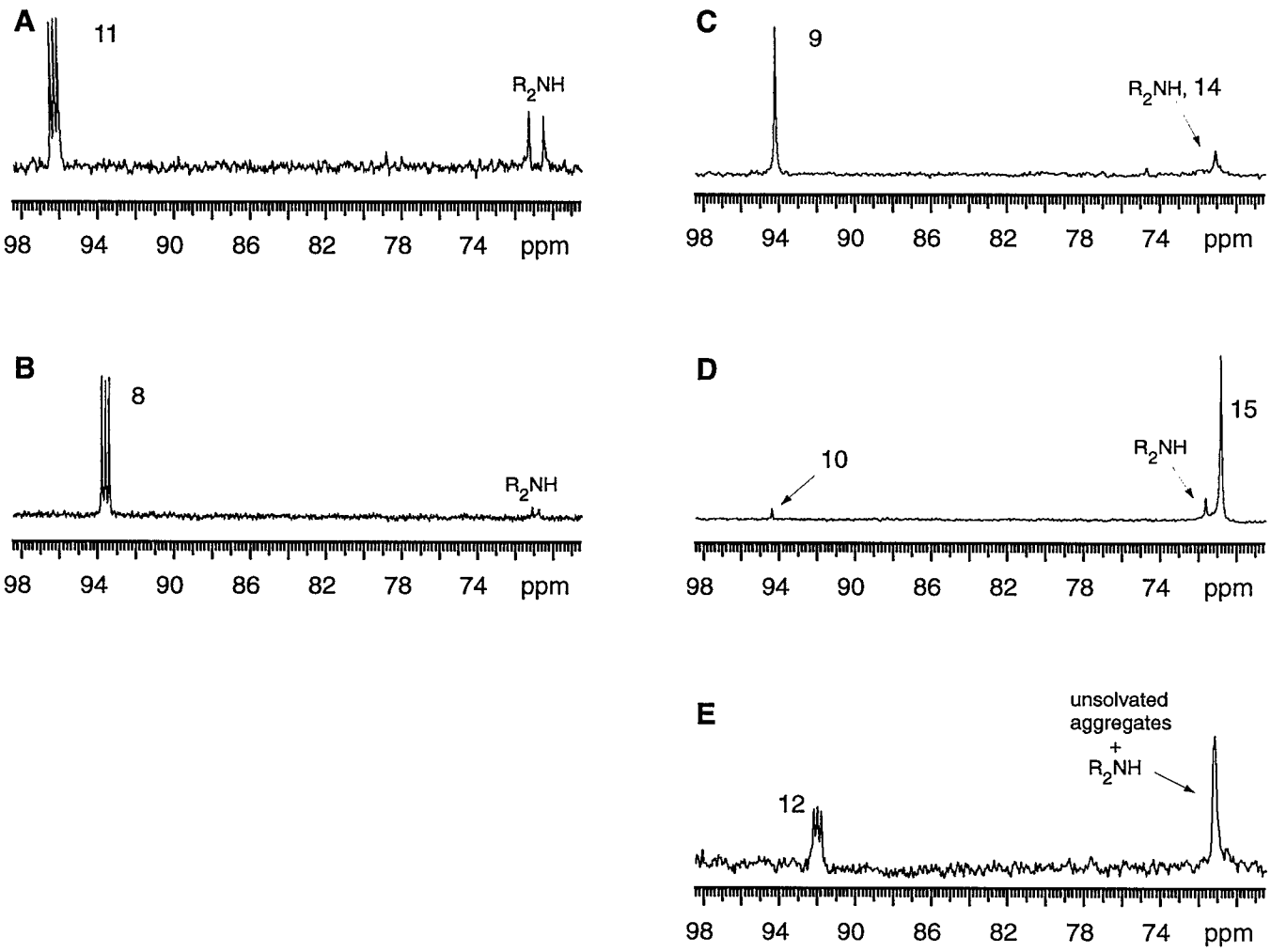


Figure IV. ^{15}N NMR spectra recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C. The samples also contain: (A) 2.0 equiv of TMCDA; (B) 5.0 equiv of sparteine; (C) 2.0 equiv of dipyrrolidinoethane (^{6}Li decoupled); (D) 2.0 equiv of **G**; (E) 5.0 equiv of **E.**

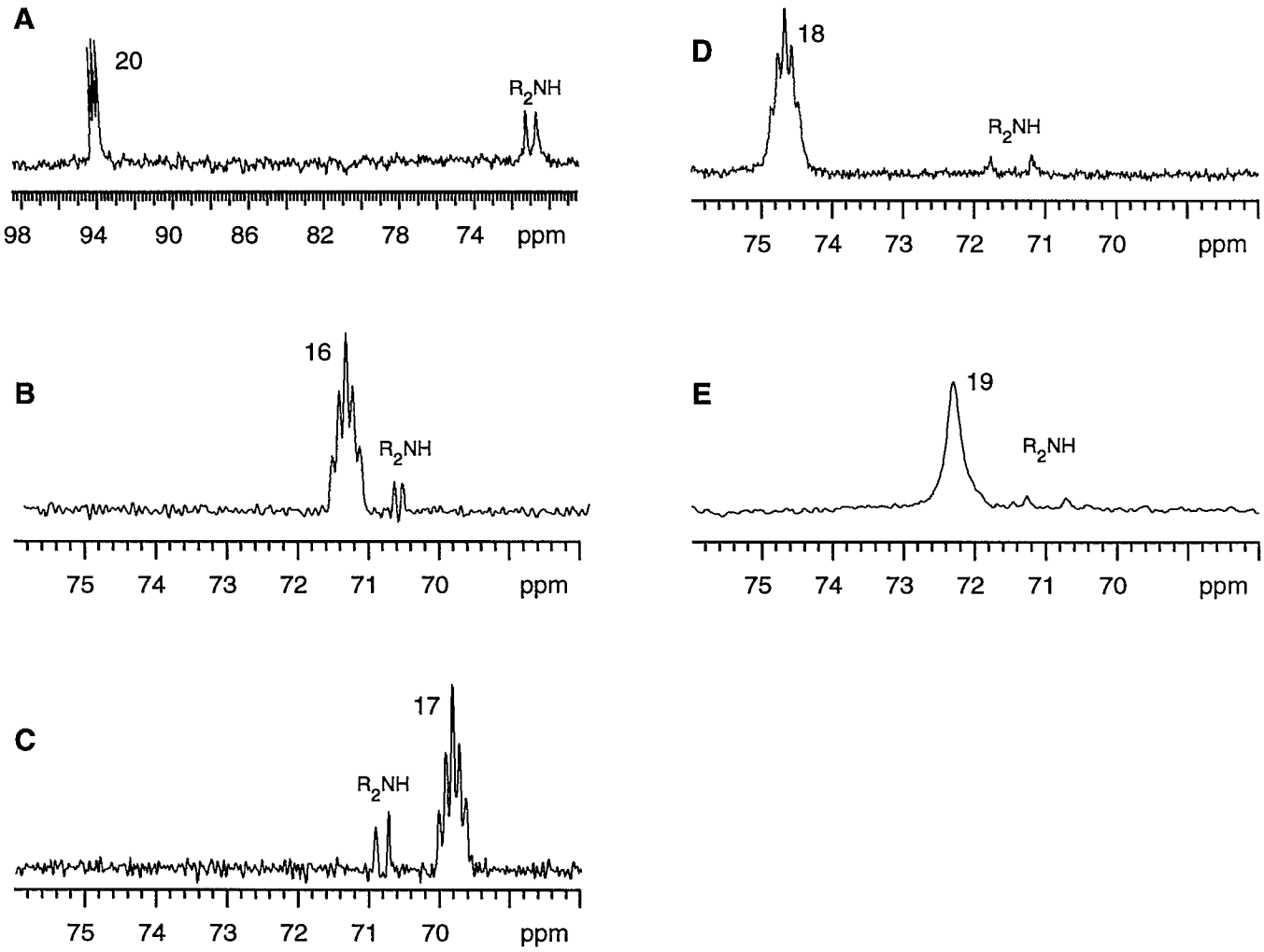


Figure V. ^{15}N NMR spectra recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C. The samples also contain: (A) 2 equiv of **C** ; (B) 2 equiv of DME; (C) 2 equiv of $MeO(CH_2)_2NMe_2$; (D) 2 equiv of $MeOCH_2CH_2NEt_2$; (E) 2 equiv of $MeOCH_2CH_2N(CH_2)_4$.

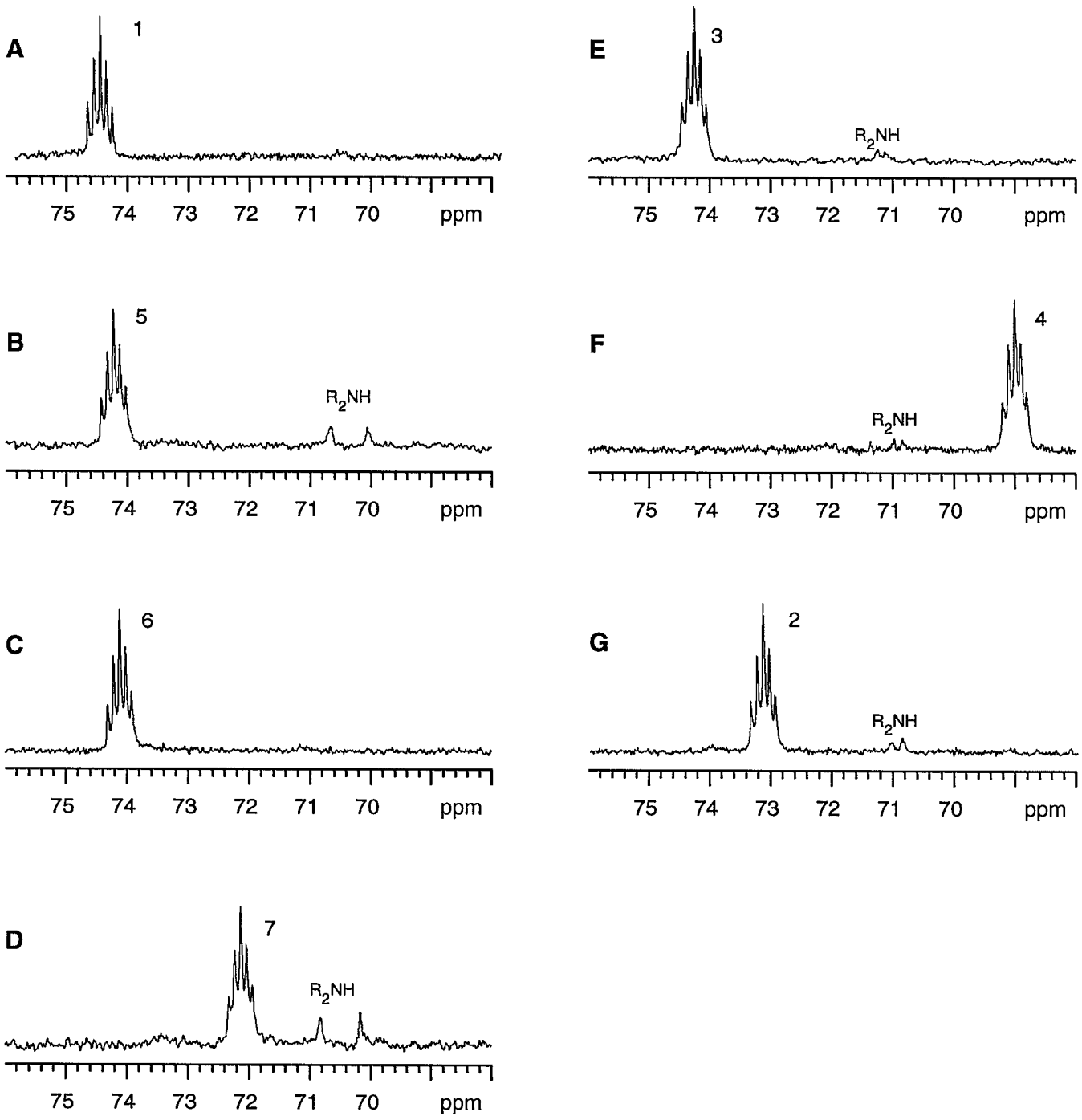


Figure VI. ^{15}N NMR spectra recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C. The samples also contain: (A) 4 equiv of THF; (B) 4 equiv of 2,2-Me_2THF; (C) 4 equiv of THP; (D) 2 equiv of 2-MeTHF; (E) 2 equiv of *n*-BuOMe; (F) 5 equiv of *t*-BuOMe; (G) 4 equiv of Et_2O.

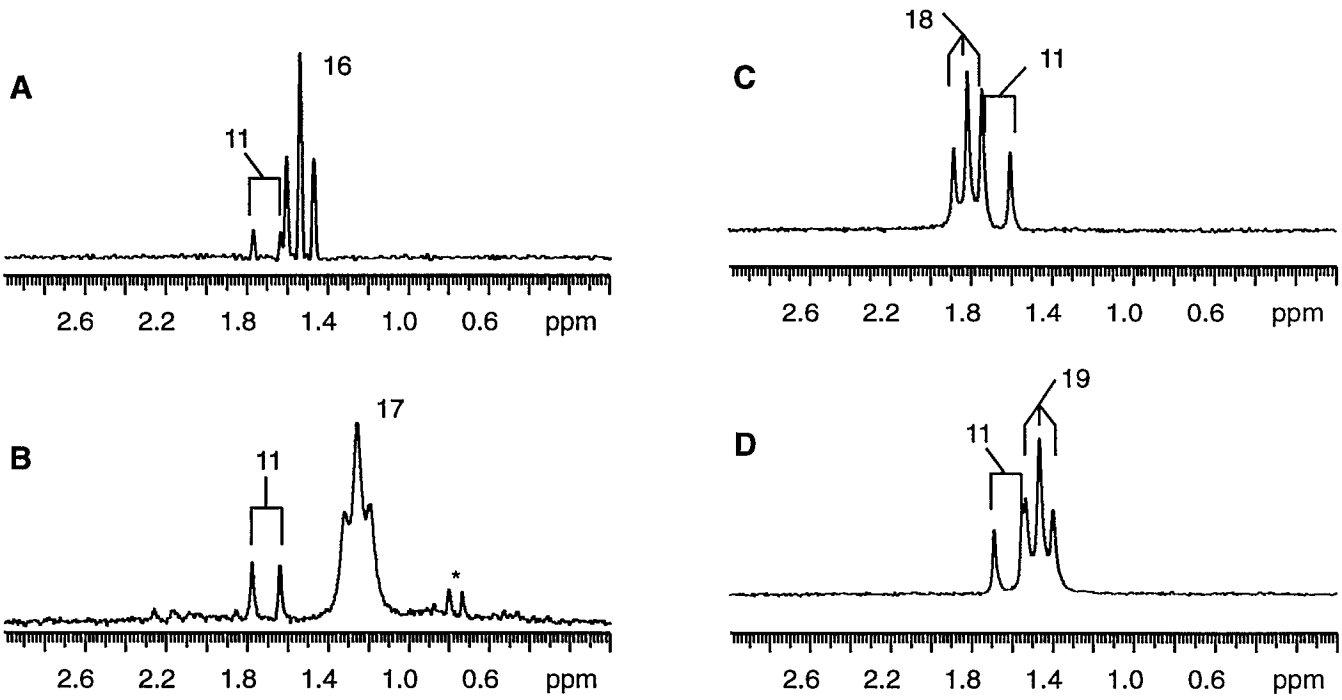


Figure VII. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C. The samples also contain: (A) 2 equiv of TMCDA and 2 equiv of DME; (B) 2 equiv of TMCDA and 2 equiv of $MeO(CH_2)_2NMe_2$; (C) 2 equiv of TMCDA and 2 equiv of $MeOCH_2CH_2NEt_2$; (D) 2 equiv of TMCDA and 2 equiv of $MeOCH_2CH_2N(CH_2)_4$.

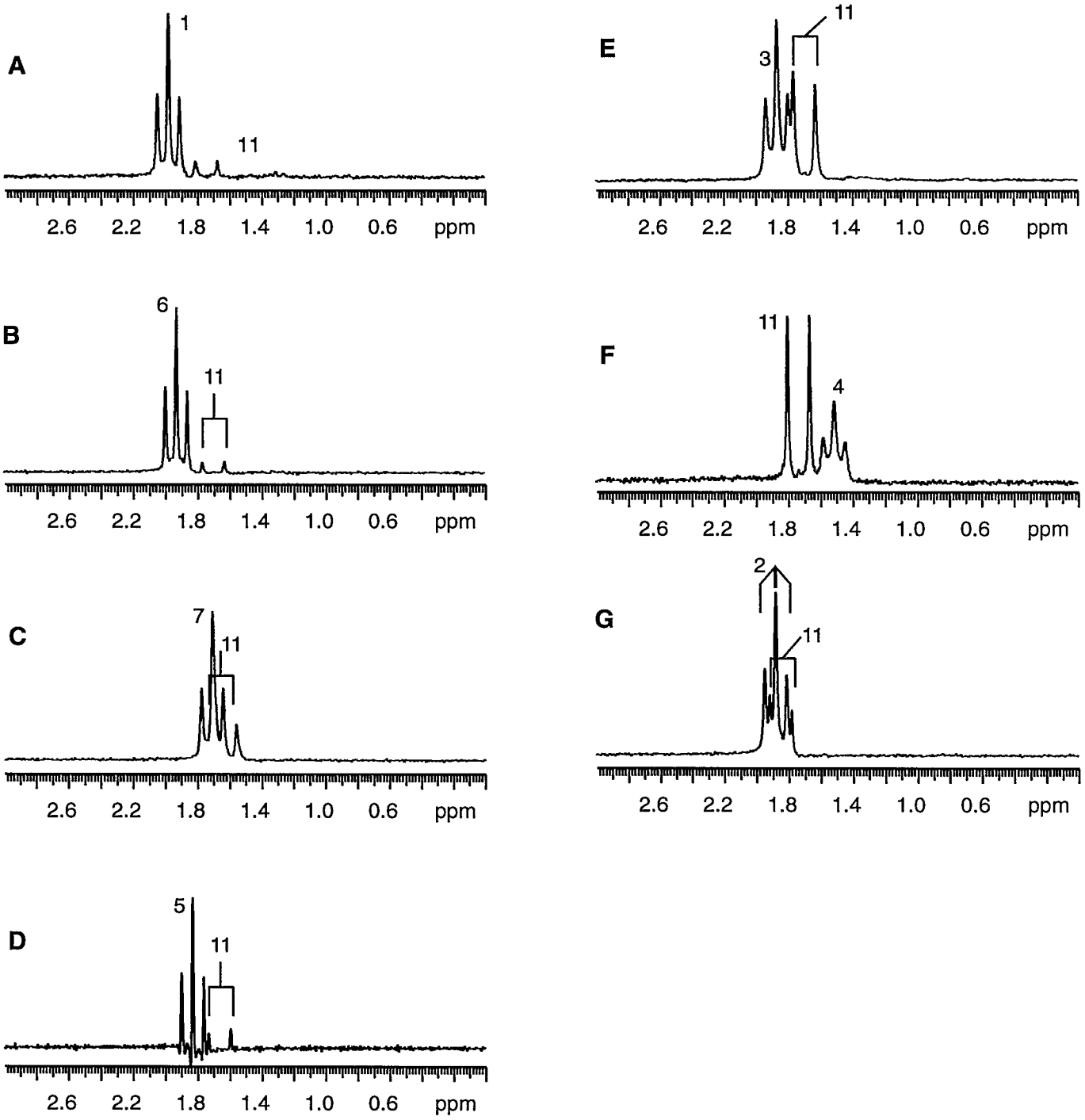


Figure VIII. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li,^{15}N]LDA in 2:1 toluene:pentane at -90 °C. The samples also contain: (A) 10 equiv of TMCDA and 2 equiv of THF; (B) 10 equiv of TMCDA and 2 equiv of THP; (C) 2 equiv of TMCDA and 2 equiv of 2-MeTHF; (D) 2 equiv of TMCDA and 4 equiv of 2,2-Me_2THF; (E) 2 equiv of TMCDA and 2 equiv of *n*-BuOMe; (F) 2 equiv of TMCDA and 5 equiv of *t*-BuOMe; (G) 2 equiv of TMCDA and 20 equiv of Et_2O.

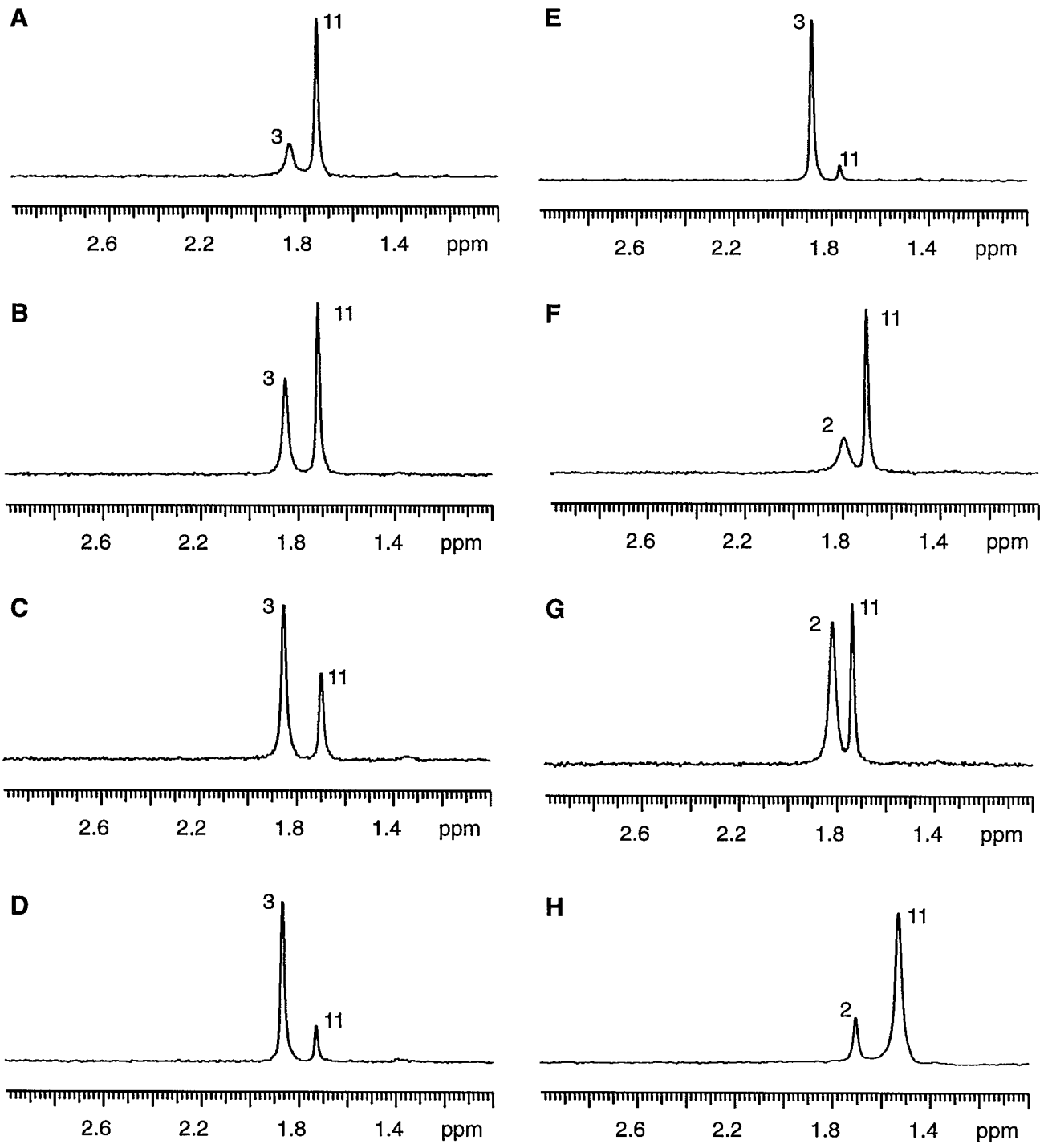


Figure IX. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li]LDA in 2:1 toluene:pentane at -80 °C. The samples also contain: (A) 10.0 equiv of TMCDA and 2.0 equiv *n*-BuOMe; (B) 5.0 equiv of TMCDA and 2.0 equiv *n*-BuOMe; (C) 2.0 equiv of TMCDA and 2.0 equiv *n*-BuOMe; (D) 2.0 equiv of TMCDA and 5.0 equiv *n*-BuOMe; (E) 2.0 equiv of TMCDA and 10.0 equiv *n*-BuOMe; (F) 2.0 equiv of TMCDA and 5.0 equiv Et_2O; (G) 2.0 equiv of TMCDA and 10.0 equiv Et_2O; (H) 2.0 equiv of TMCDA and 20.0 equiv Et_2O.

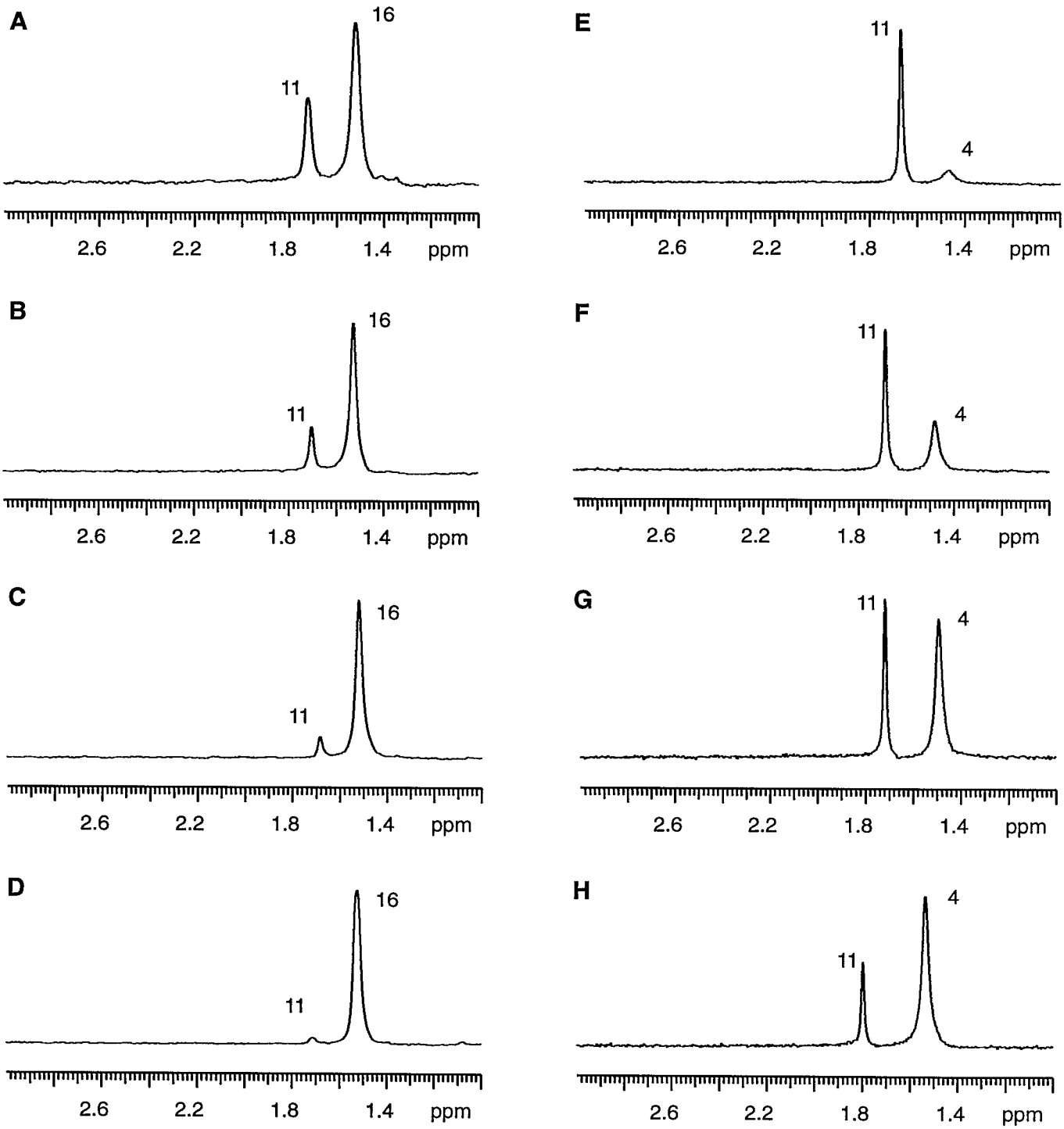


Figure X. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li]LDA in 2:1 toluene:pentane at -80 °C. The samples also contain: (A) 10.0 equiv of TMCDA and 2.0 equiv DME; (B) 5.0 equiv of TMCDA and 2.0 equiv DME; (C) 2.0 equiv of TMCDA and 2.0 equiv DME; (D) 2.0 equiv of TMCDA and 5.0 equiv DME; (E) 5.0 equiv of TMCDA and 2.0 equiv *t*-BuOMe; (F) 2.0 equiv of TMCDA and 2.0 equiv *t*-BuOMe; (G) 2.0 equiv of TMCDA and 5.0 equiv *t*-BuOMe; (H) 2.0 equiv of TMCDA and 10.0 equiv *t*-BuOMe.

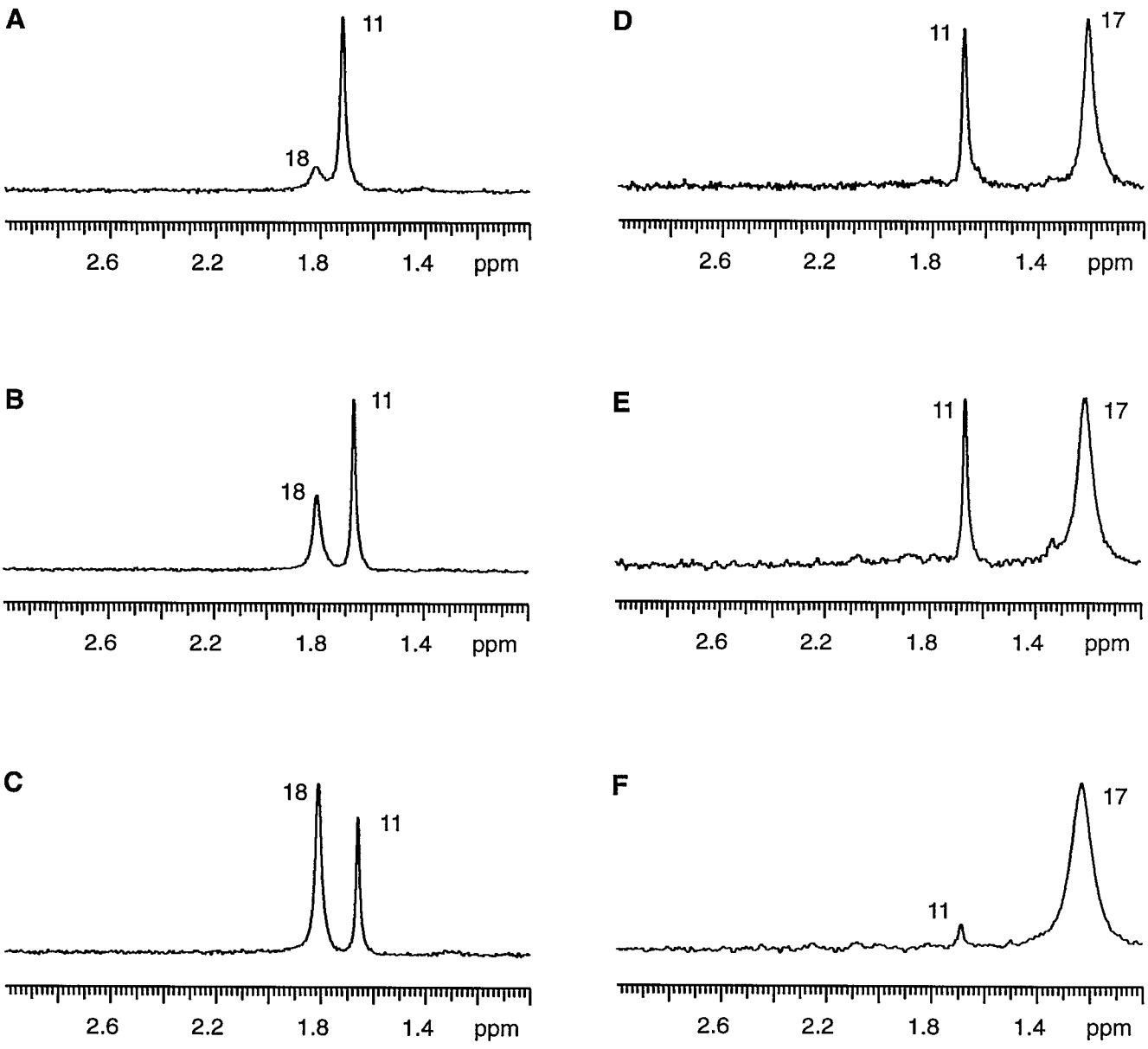


Figure XI. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li]LDA in 2:1 toluene:pentane at -80 °C. The samples also contain: (A) 15.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2NEt_2$; (B) 5.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2NEt_2$; (C) 2.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2NEt_2$; (D) 10.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2NMe_2$; (E) 5.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2NMe_2$; (F) 2.0 equiv of TMCDA and 5.0 equiv $MeO(CH_2)_2NMe_2$.

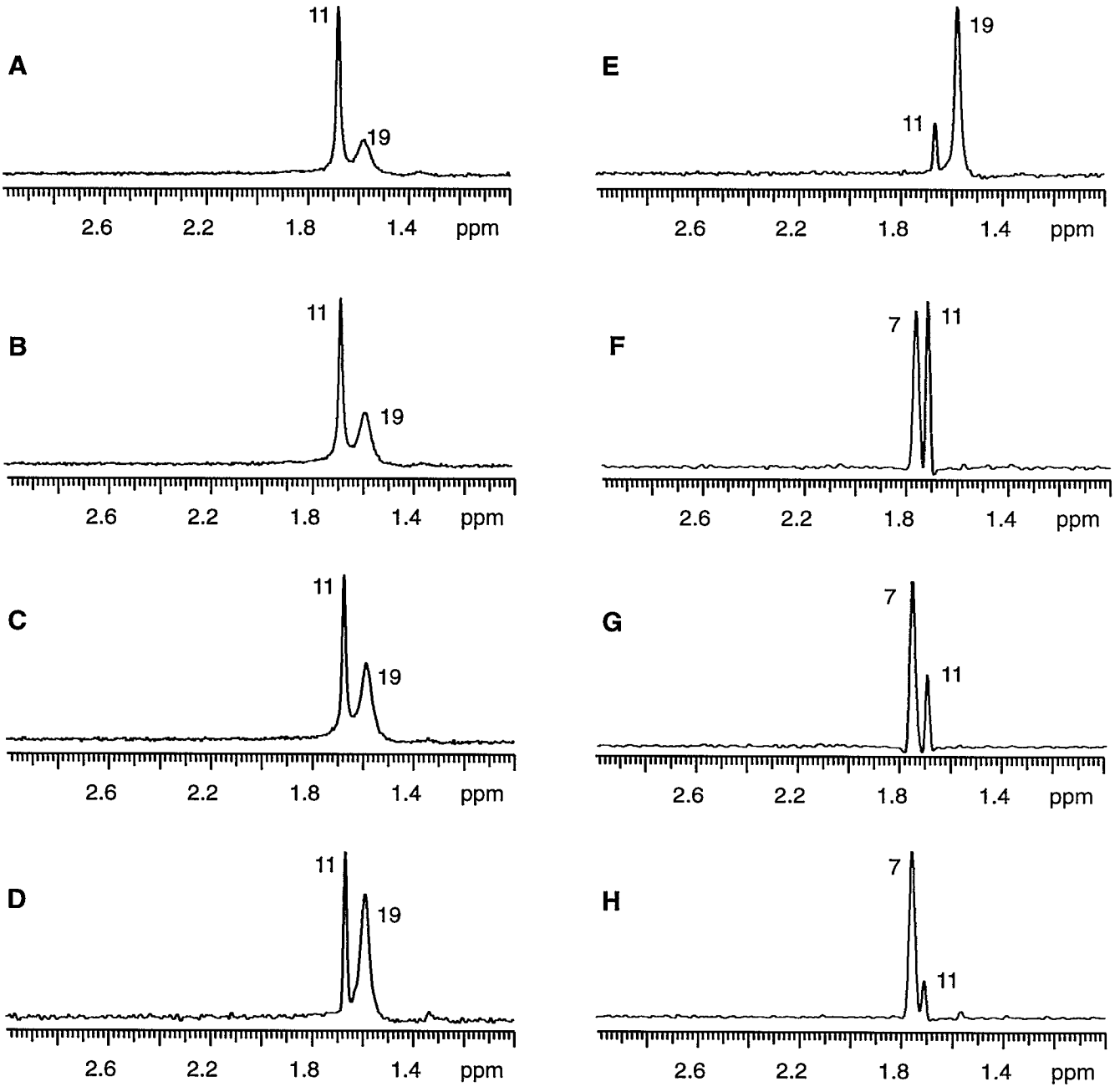


Figure XII. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li]LDA in 2:1 toluene:pentane at -80 °C. The samples also contain: (A) 8.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2N(CH_2)_4$; (B) 6.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2N(CH_2)_4$; (C) 4.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2N(CH_2)_4$; (D) 2.0 equiv of TMCDA and 2.0 equiv $MeO(CH_2)_2N(CH_2)_4$; (E) 2.0 equiv of TMCDA and 4.0 equiv $MeO(CH_2)_2N(CH_2)_4$; (F) 4.0 equiv of TMCDA and 2.0 equiv 2,2-Me_2THF; (G) 2.0 equiv of TMCDA and 2.0 equiv 2,2-Me_2THF; (H) 2.0 equiv of TMCDA and 4.0 equiv 2,2-Me_2THF.

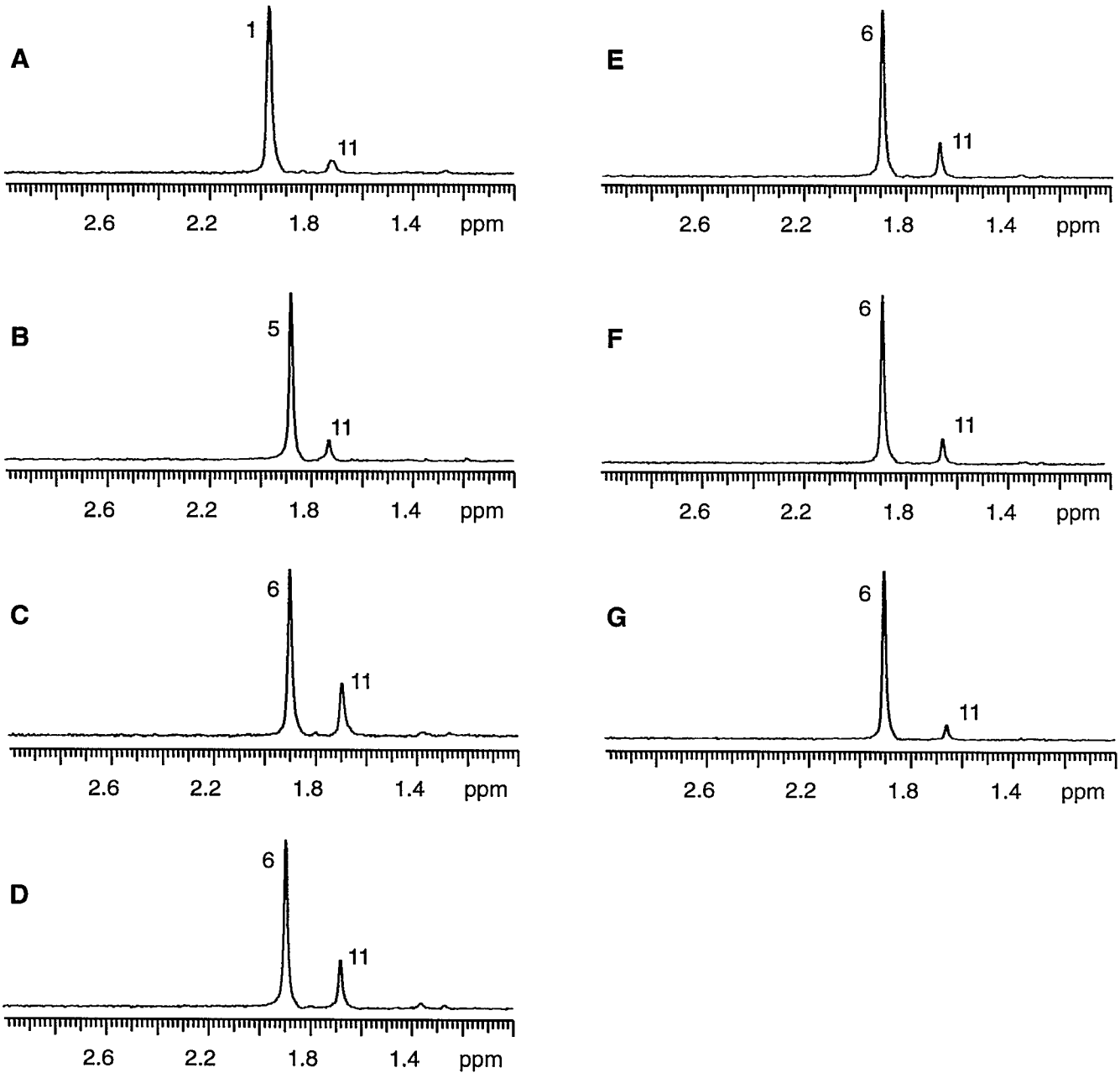


Figure XIII. ^{6}Li NMR spectra recorded on samples containing 0.10 M [^{6}Li]LDA in 2:1 toluene:pentane at -80 °C. The samples also contain: (A) 10.0 equiv of TMCDA and 2.0 equiv THF; (B) 10.0 equiv of TMCDA and 2.0 equiv THP; (C) 10.0 equiv of TMCDA and 2.0 equiv 2-MeTHF; (D) 8.0 equiv of TMCDA and 2.0 equiv 2-MeTHF; (E) 6.0 equiv of TMCDA and 2.0 equiv 2-MeTHF; (F) 4.0 equiv of TMCDA and 2.0 equiv 2-MeTHF; (G) 2.0 equiv of TMCDA and 2.0 equiv 2-MeTHF.

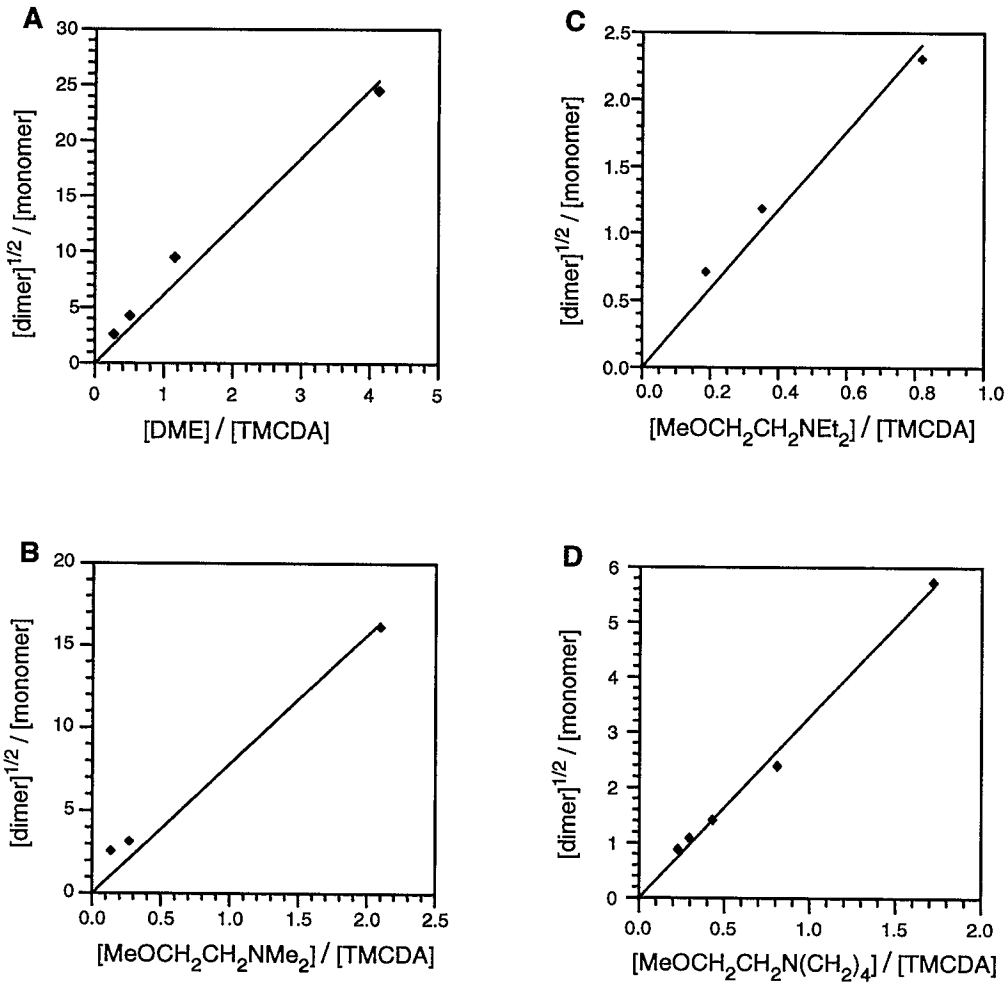


Figure XIV. Determination of the relative binding contants, K_{eq}, of ethereal ligands to LDA dimer. The functions represent linear least-squares fits to eq (2) in the manuscript. The plots show data for the following ethereal ligands: (A) DME; (B) $MeOCH_2CH_2NMe_2$; (C) $MeOCH_2CH_2NEt_2$; (D) $MeOCH_2CH_2N(CH_2)_4$.

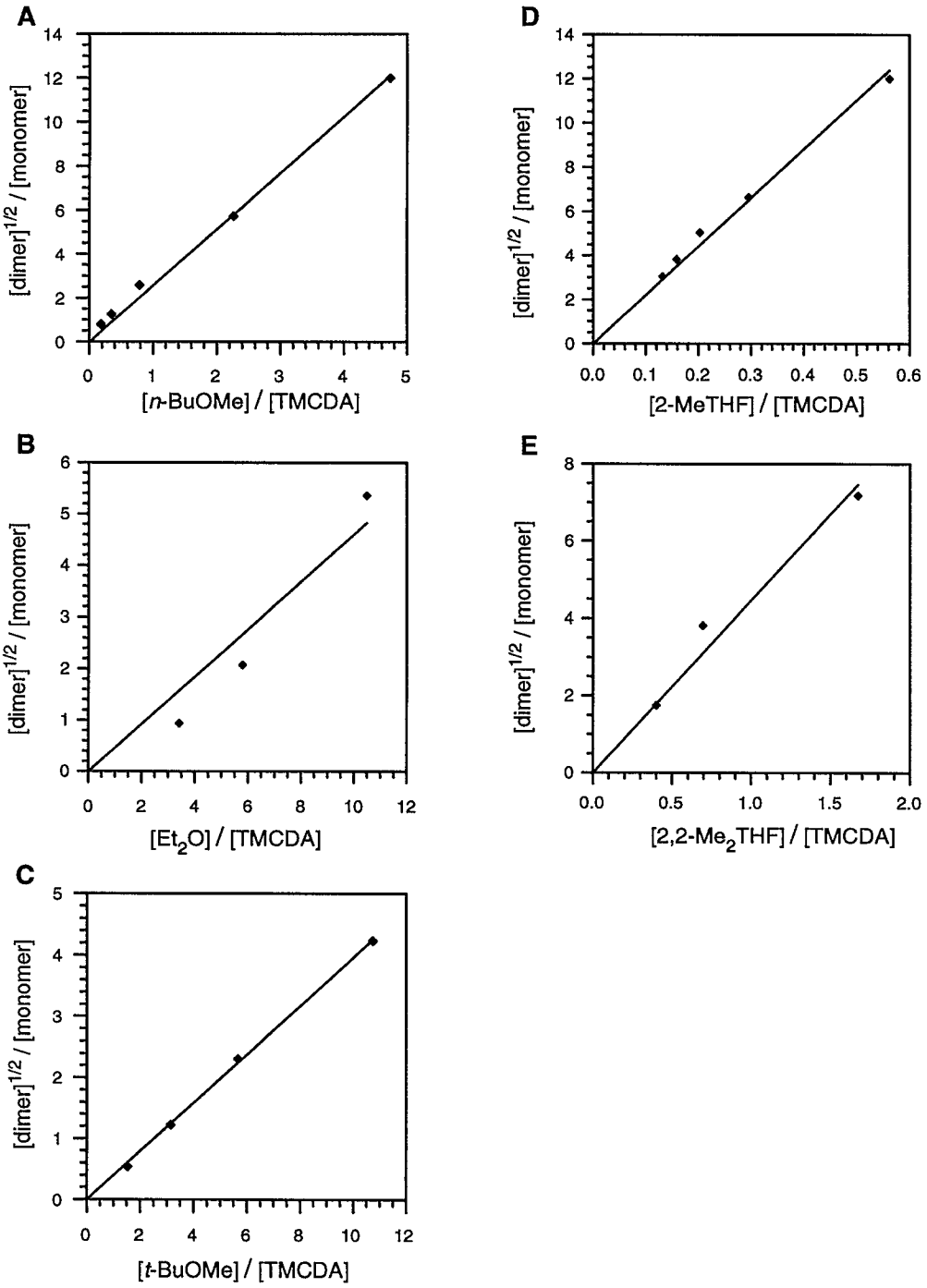


Figure XV. Determination of the relative binding contants, K_{eq}, of ethereal ligands to LDA dimer. The functions represent linear least-squares fits to eq (2) in the manuscript. The plots show data for the following ethereal ligands: (A) *n*-BuOMe; (B) Et_2O; (C) *t*-BuOMe; (D) 2-MeTHF; (E) 2,2-Me_2THF.

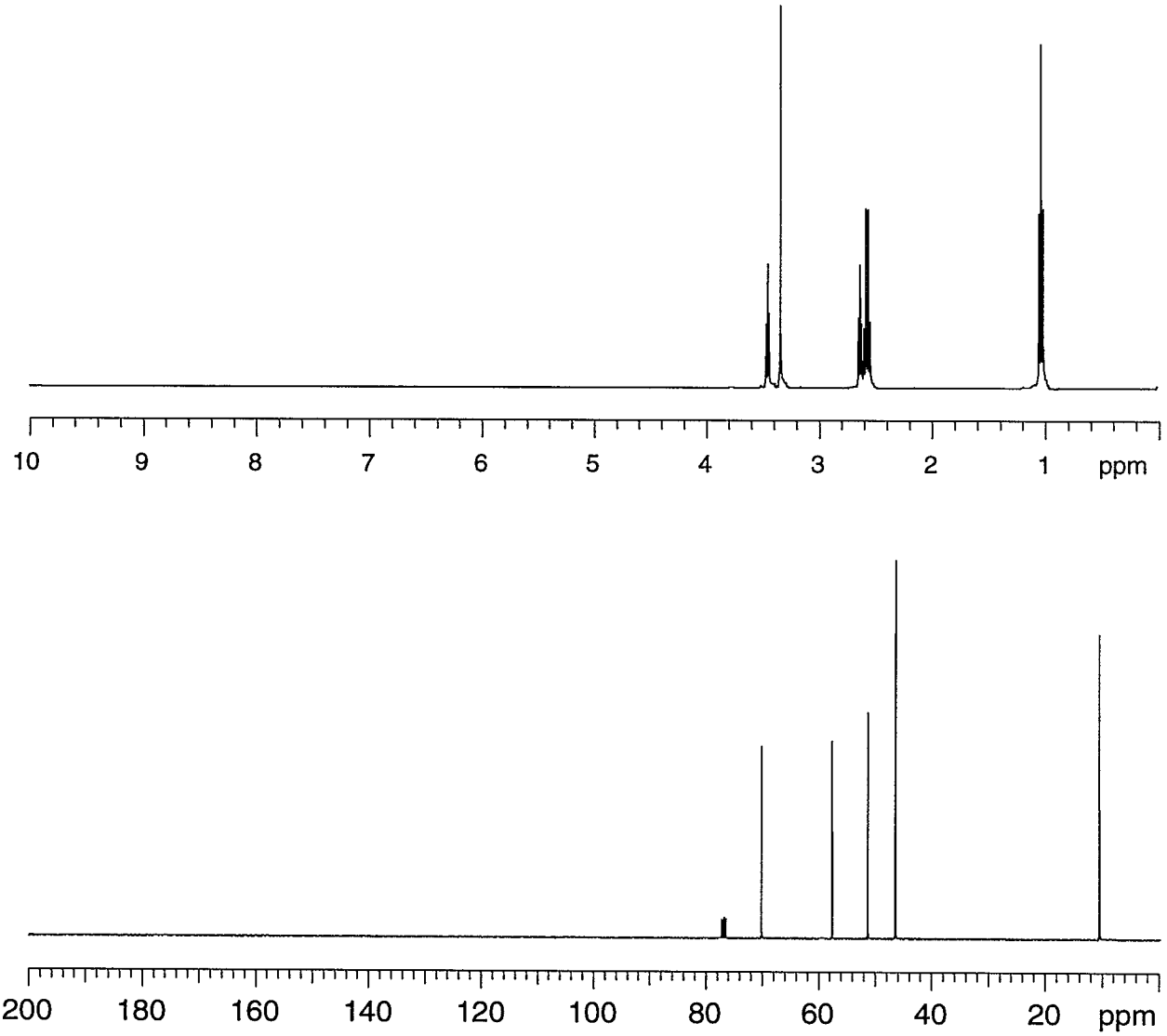


Figure XVIA. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for $MeOCH_2CH_2NEt_2$ (**J**) in $CDCl_3$. ^{1}H NMR ($CDCl_3$) δ1.03 (t, J=7.4 Hz, 6H), 2.56 (quartet, J=7.4 Hz, 4H), 2.63 (t, J=6.2 Hz, 2H), 3.33 (s, 3H), 3.45 (t, J=6.2 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ10.8, 46.7, 51.5, 57.8, 70.4.

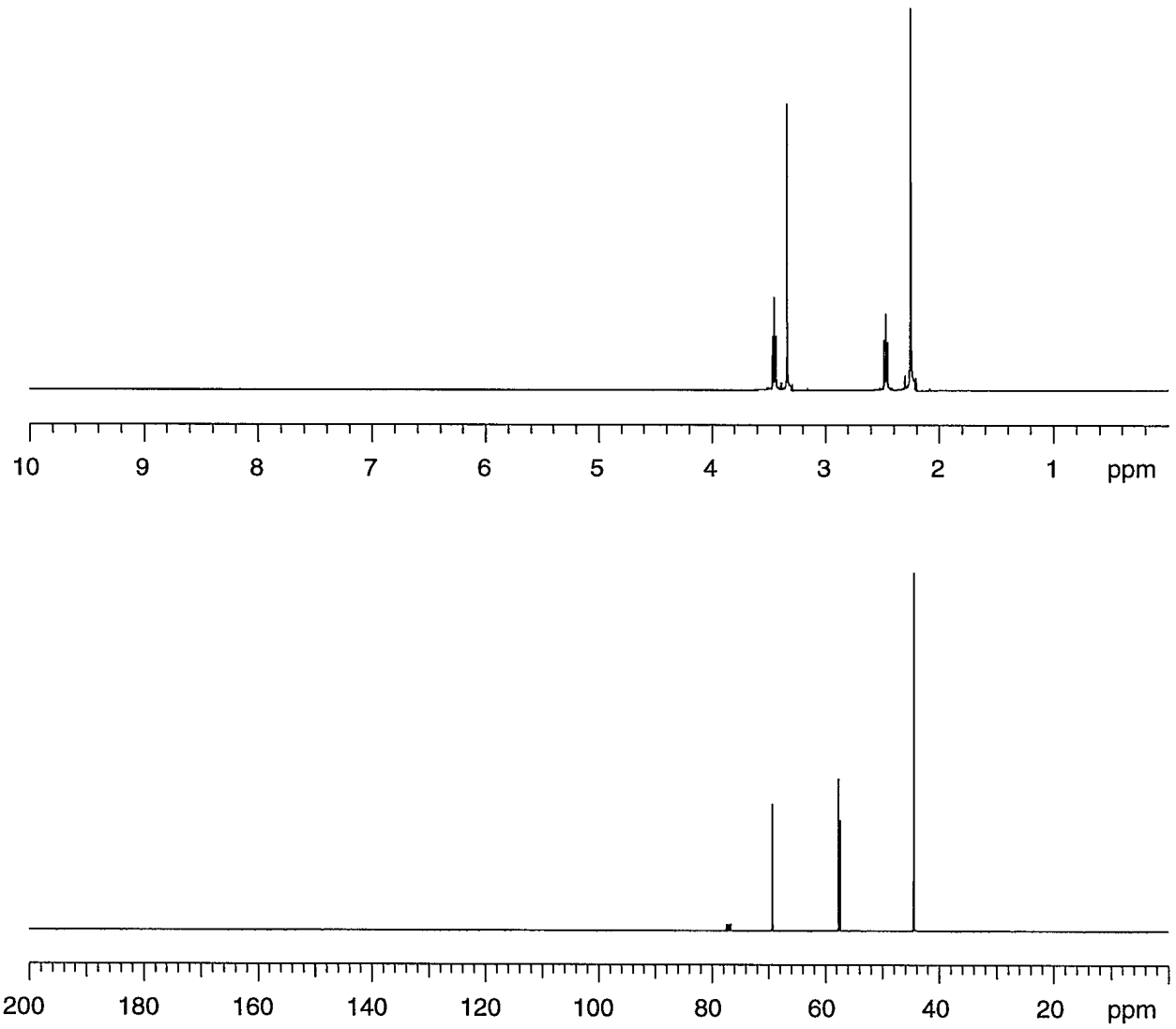


Figure XVIB. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for $MeOCH_2CH_2NMe_2$ (**I**) in $CDCl_3$. ^{1}H NMR ($CDCl_3$) δ2.25 (s, 6H), 2.47 (t, J=5.6 Hz, 2H), 3.34 (s, 3H), 3.45 (t, J=5.7Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ44.5, 57.4, 57.6, 69.3.

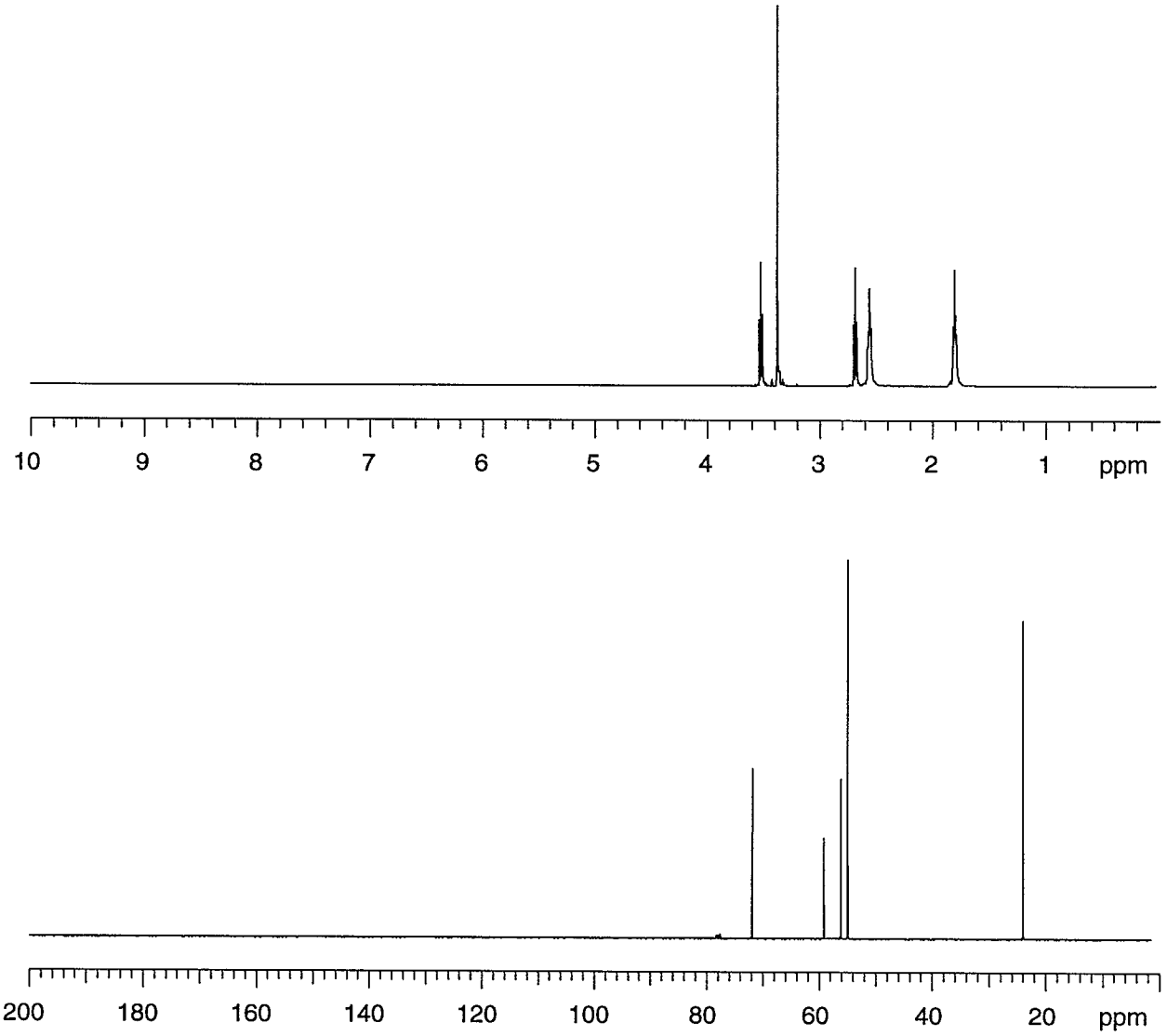


Figure XVIC. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for $MeOCH_2CH_2N(CH_2)_4$ (**K**) in $CDCl_3$. ^{1}H NMR ($CDCl_3$) δ1.78 (br m,4H), 2.54 (br m, 4H), 2.66 (t, J=5.8 Hz, 2H), 3.36 (s, 3H), 3.50 (t, J=5.8 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ22.8, 53.9, 55.1, 58.2, 71.0.

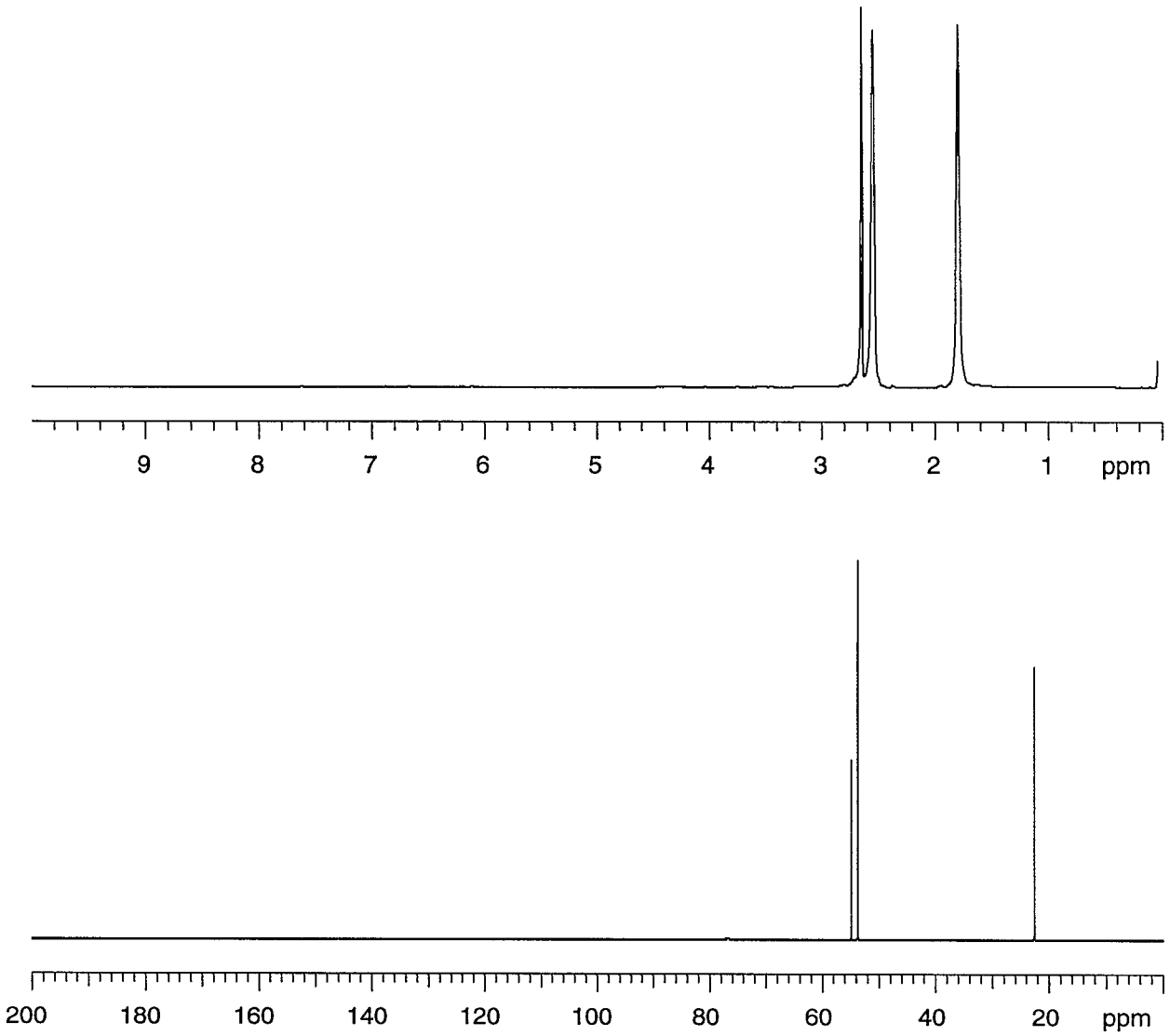


Figure XVID. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for dipyrrolidinoethane (**F**) in $CDCl_3$. ^{1}H NMR ($CDCl_3$) δ1.77 (br m, 8H),2.52 (br m, 8H), 2.62 (s, 4H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ22.7, 53.8, 54.9.

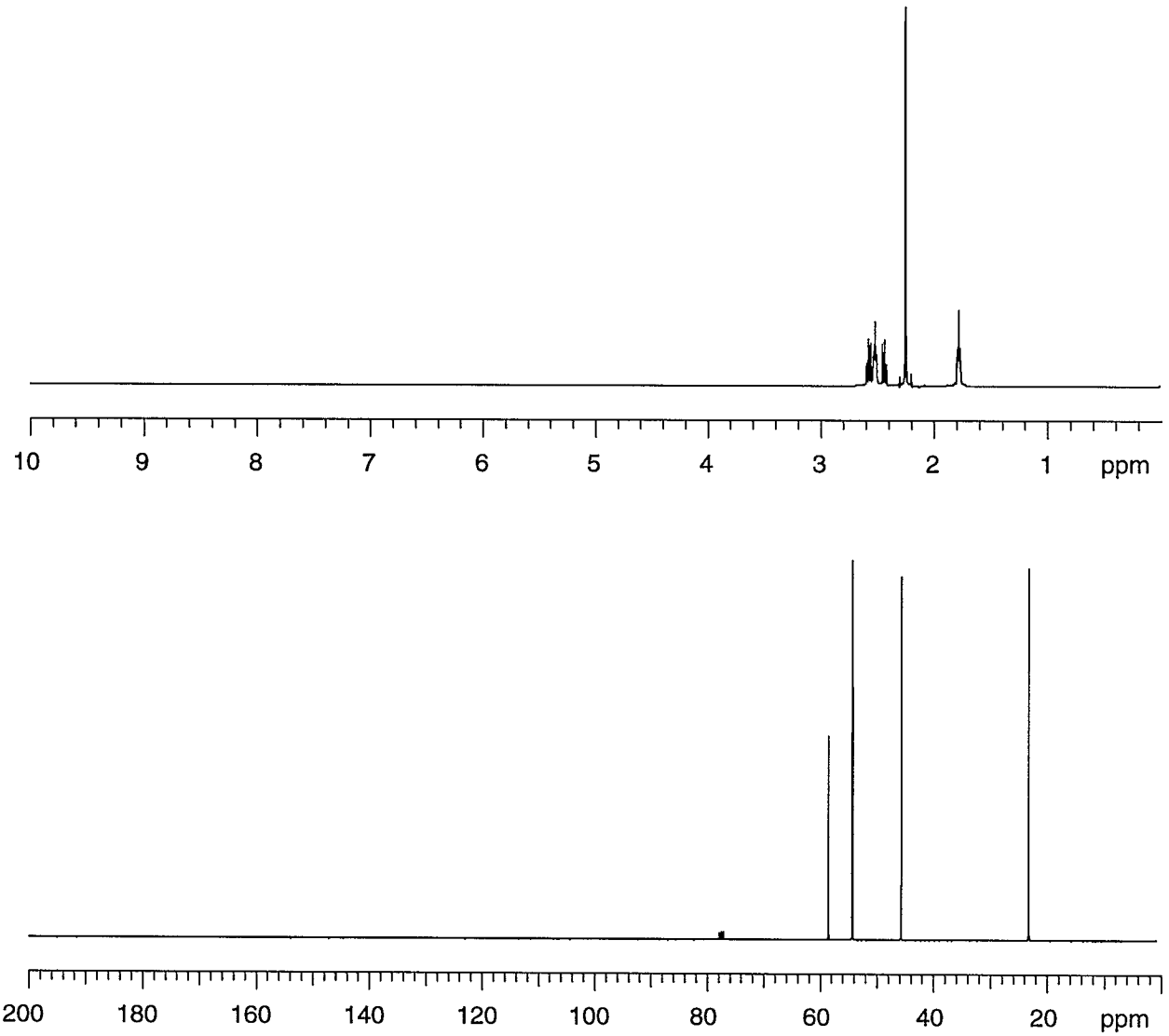


Figure XVIE. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for 2-(*N,N*-dimethylamino)pyrrolidinoethane (**G**) in $CDCl_3$. ^{1}H NMR ($CDCl_3$) δ1.77 (br m, 4H), 2.25 (s, 6H), 2.43 (t, J=7.0 Hz, 2H), 2.51 (br m, 4H), 2.57 (t, J=7.0 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ22.6, 45.1, 53.7, 58.0.

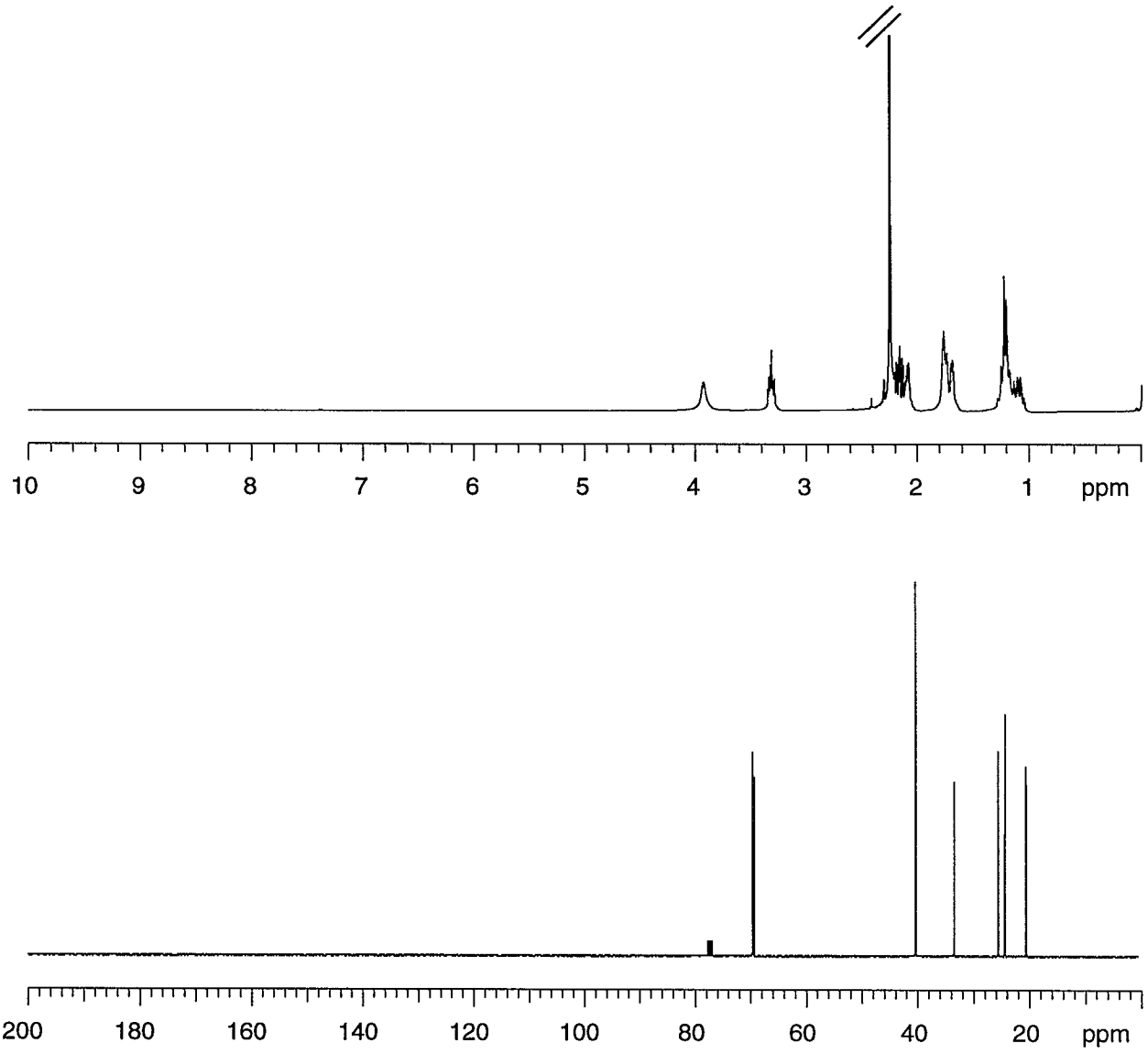


Figure XVIF. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for *trans*-2-(*N,N*-dimethylamino)cyclohexanol in $CDCl_3$. ^{1}H NMR ($CDCl_3$) δ1.10 (m, 1H), 1.23 (m, 3H), 1.71 (m, 1H), 1.78 (m, 2H), 2.10 (m, 1H), 2.17 (m,1H), 2.26 (s,6H), 3.32 (m, 1H), 3.94 (broad singlet, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ20.1, 23.9, 25.1, 33.0, 39.9, 69.1, 69.3.

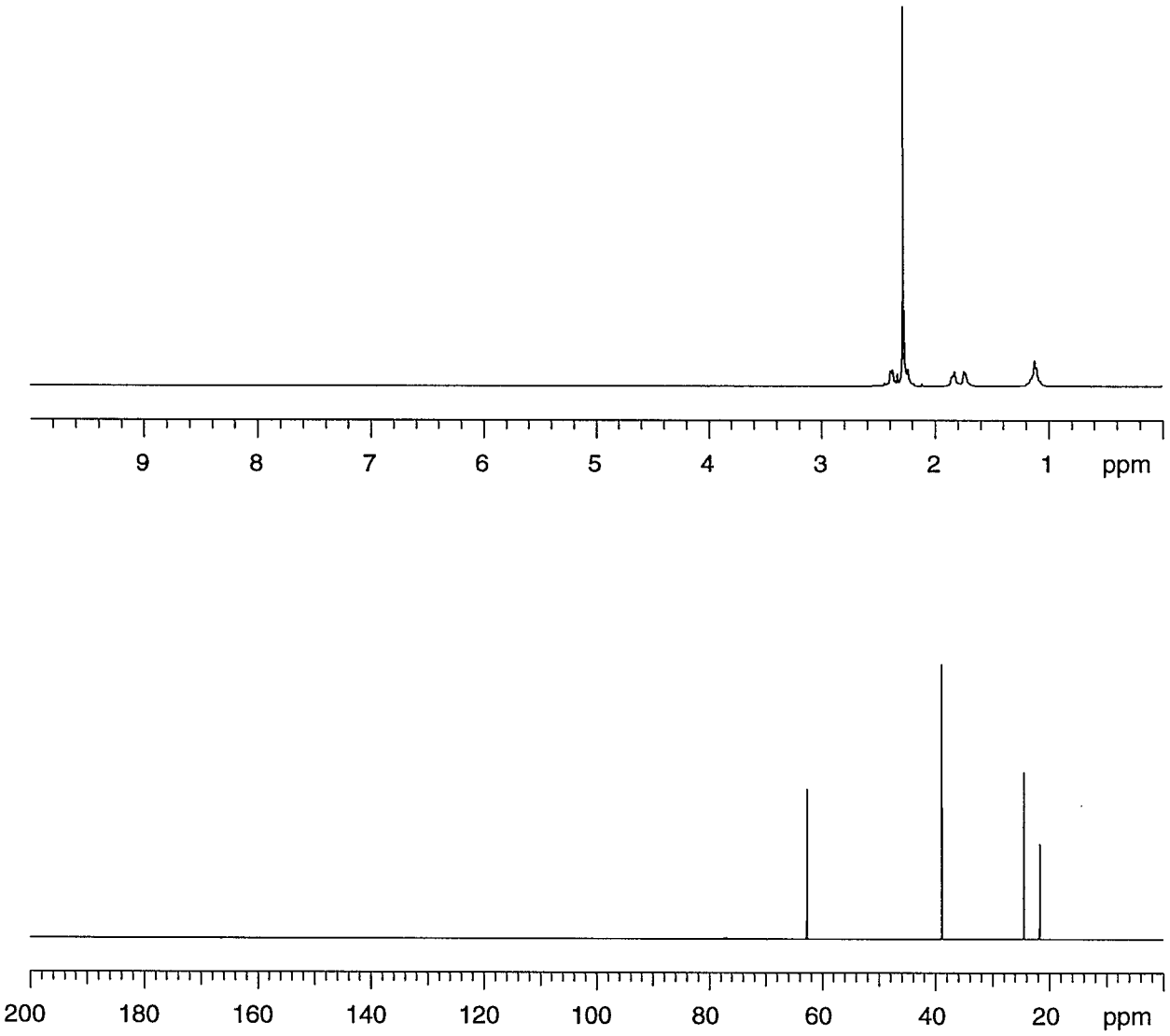


Figure XVIG. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for TMCDA (**B**) in $CDCl_3$. ^{1}H NMR ($CDCl_3$) δ1.11 (br m, 4H), 1.74 (br m, 2H), 1.84 (br m, 2H), 2.27 (s, 12H), 2.38 (br m, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ21.7, 24.5, 38.9, 62.7.

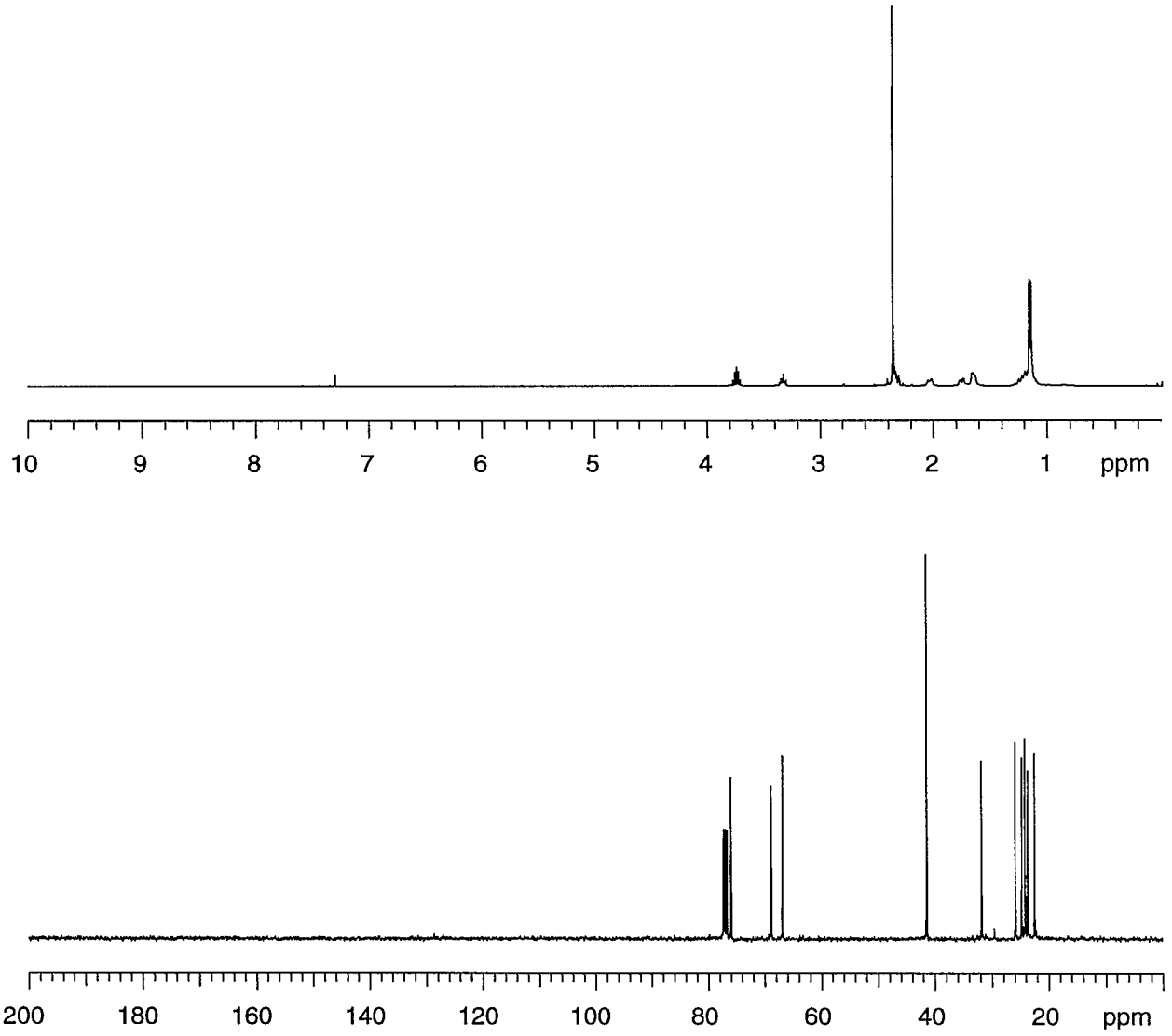


Figure XVIH. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for *trans*-2-isopropoxy-*N,N*-dimethyl-aminocyclohexane (**C**) in $CDCl_3$. ^{1}H NMR ($CDCl_3$) δ1.15 (d, J=6.2 Hz, 3H), 1.16 (d, J=6.2 Hz, 3H), 1.22 (m, 5H), 1.66 (m, 2H), 1.76 (m, 1H), 2.04 (m, 1H), 2.37 (s, 6H), 3.33 (m, 1H), 3.75 (septet, J=6.2 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$) δ22.5, 23.7, 24.2, 24.7, 25.9, 31.8, 41.4, 66.9, 68.9, 76.0.