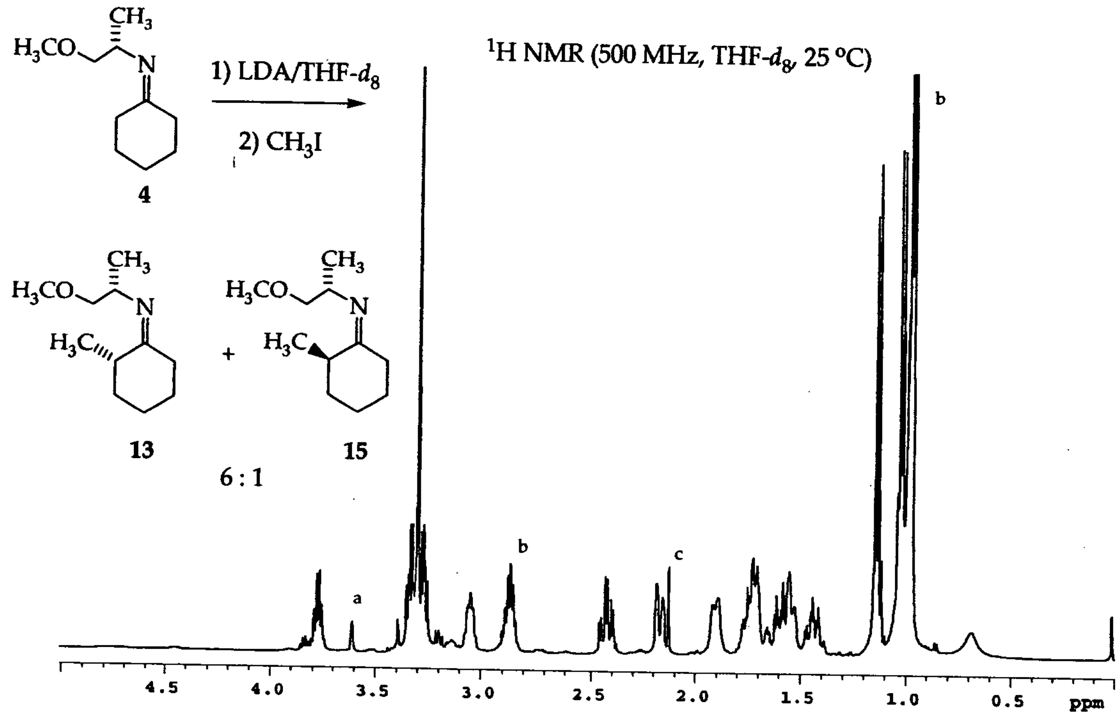
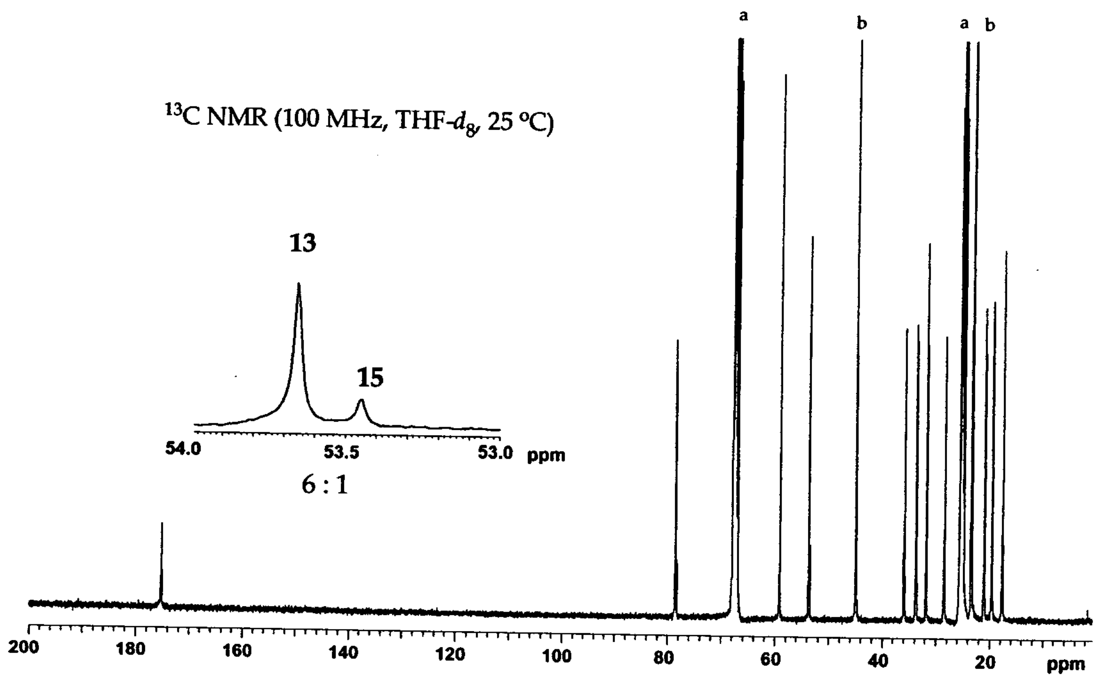
XI. Conformational assignments of a 6:1 mixture of imines **13** and **15** in THF-d_8.

XI-A. ^{1}H and ^{13}C NMR spectra of a 6:1 mixture of imines **13** and **15**[a] in THF-d_8.



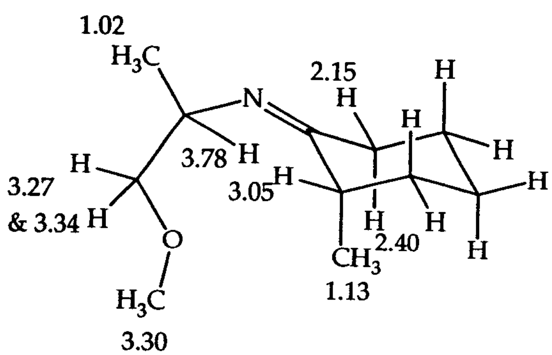


a = THF, b = HN(i-Pr)$_2$, c = CH_3I

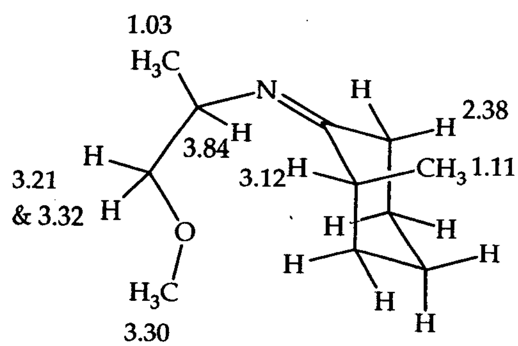
[a]A 6:1 mixture of **13** and **15** was prepared in situ by lithiation (LDA, 1.1 equiv, -65 °C) and alkylation (CH_3I, 1.1 equiv, -78 °C) of **4** (0.26 M).

XI-B. [1]H NMR (**13**): δ 1.02 (d, *J* = 6.5 Hz, 3H), 1.13 (d, *J* = 7.0 Hz, 3H), 1.41 (qt, *J* = 13.5, 4.3 Hz, 1H), 1.52 (dm, *J* = 13.5 Hz, 1H), 1.55 (tt, *J* = 13.0, 4.8 Hz, 1H), 1.69 (dm, *J* = 13.0 Hz, 1H), 1.72 (qt, *J* = 13.0, 4.0 Hz, 1H), 1.88 (dm, *J* = 13.0 Hz, 1H), 2.15 (dm, *J* = 14.0 Hz, 1H), 2.40 (td, *J* = 14.0, 5.5 Hz, 1H), 3.05 (quint, *J* = 7.0 Hz, 1H), 3.27 (t, *J* = 9.0 Hz, 1H), 3.30 (s, 3H), 3.34 (t, *J* = 9.0 Hz, 1H), 3.78 (sext, *J* = 6.0 Hz, 1H); (**15**): δ 1.03 (d, *J* = 6.5 Hz, 3H), 1.11 (d, *J* = 7.0 Hz, 3H), 1.46 (qt, *J* = 13.5, 4.3 Hz, 1H), 1.60 (tt, *J* = 13.0, 4.8 Hz, 1H), 1.63 (m, 1H), 1.66 (m, 1H), 1.87 (dm, *J* = 13.0 Hz, 1H), 2.38 (td, *J* = 14.0, 5.5 Hz, 1H), 3.12 (m, 1H), 3.21 (t, *J* = 9.0 Hz, 1H), 3.30 (s, 3H), 3.32 (t, *J* = 9.0 Hz, 1H), 3.84 (sext, *J* = 6.0 Hz, 1H). [13]C NMR (**13**): δ 17.5, 19.6, 20.9, 28.4, 31.8, 33.7, 35.9, 53.6, 59.0, 78.6, 175.1; (**15**): δ 17.7, 19.5, 21.0, 28.6, 31.9, 33.6, 36.0, 53.4, 59.1, 78.3, 175.1.

The structures of **13** and **15** are shown below. See 2D NMR spectra (section **XI**: **C-E**) for detailed assignments.

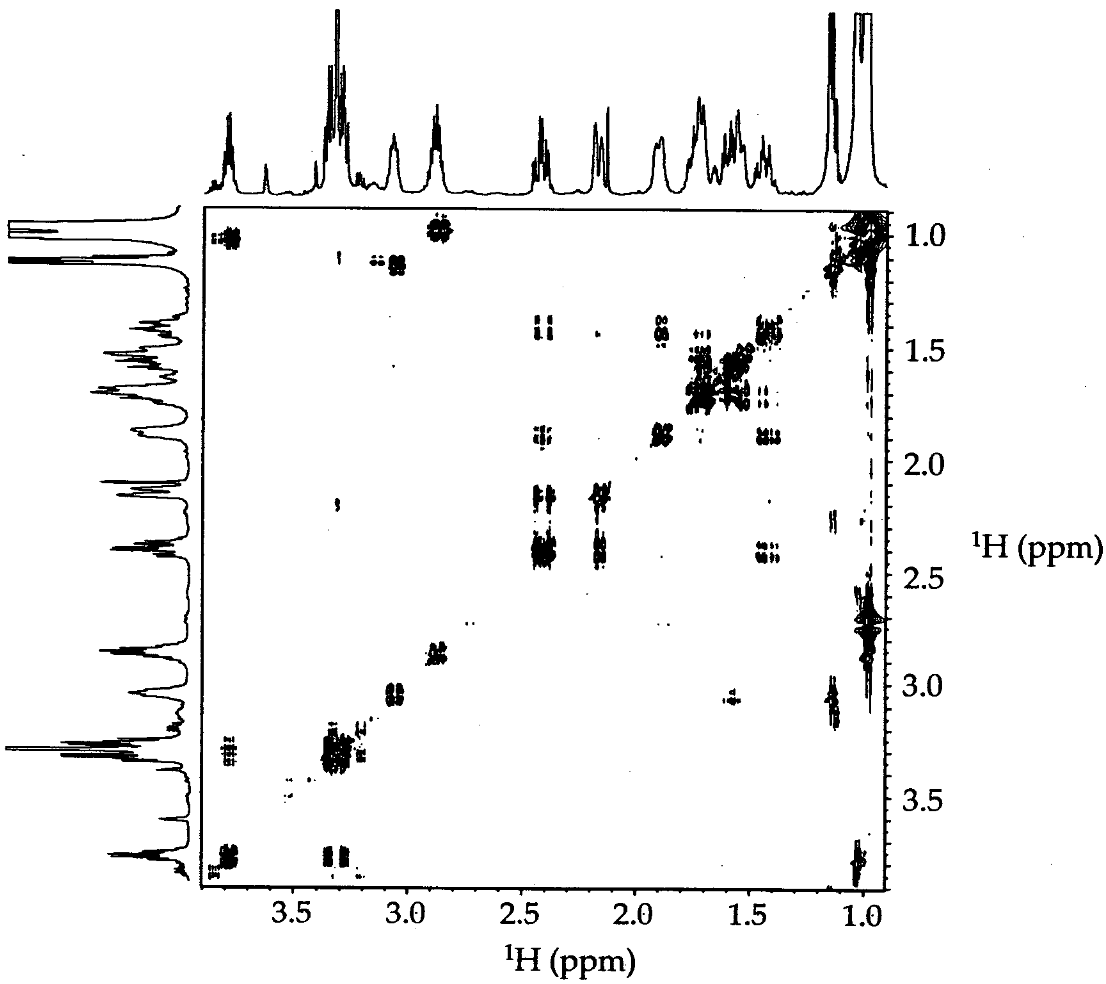


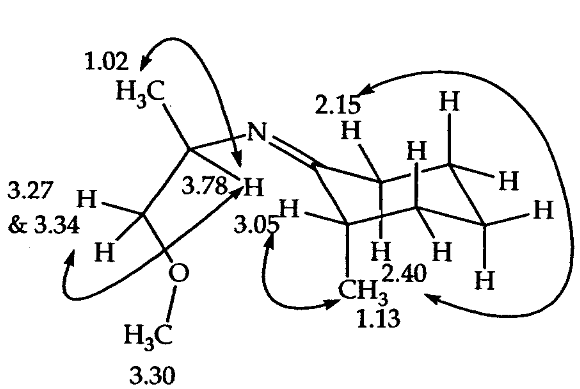
13



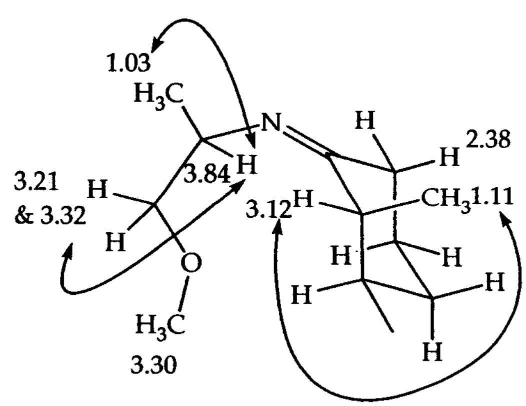
15

XI-C. ^{1}H,^{1}H-COSY spectrum of a 6:1 mixture of imines **13** (major) and **15** (minor) (500 MHz, THF-d_8, 25 °C).



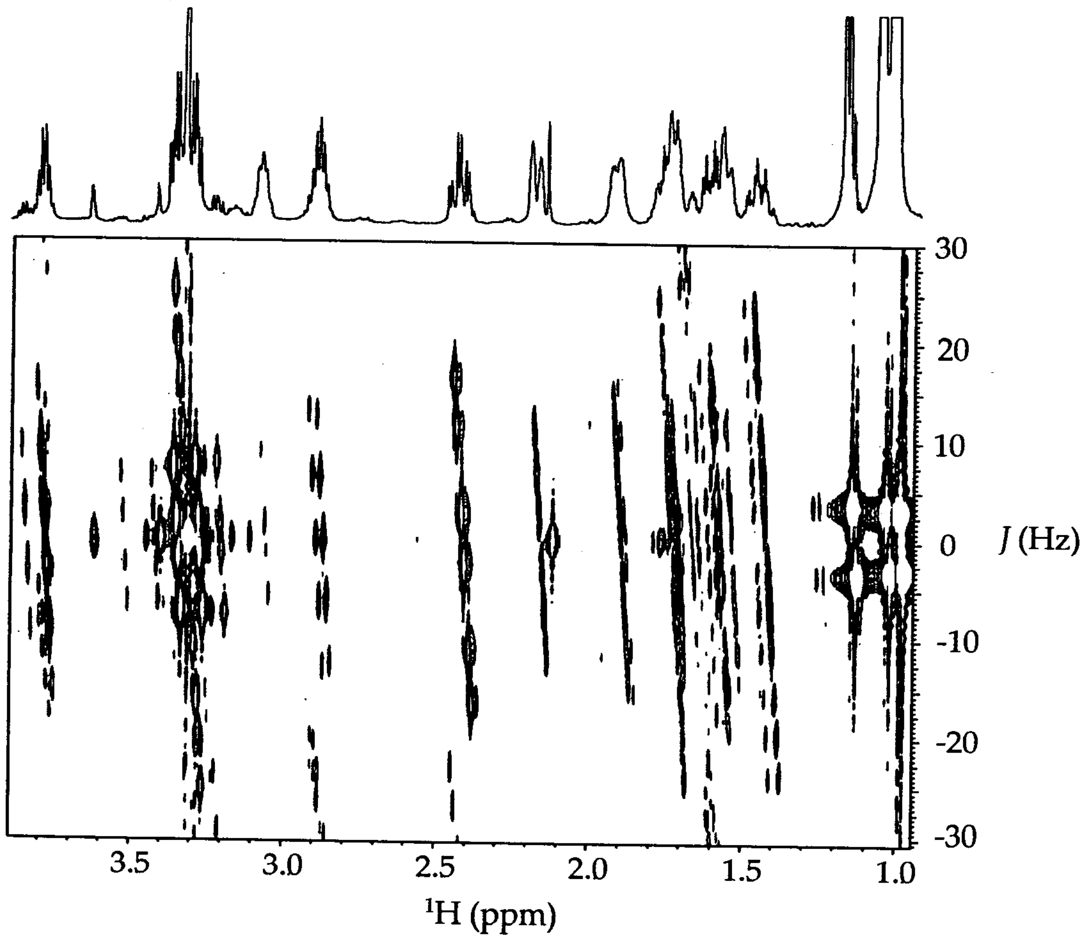


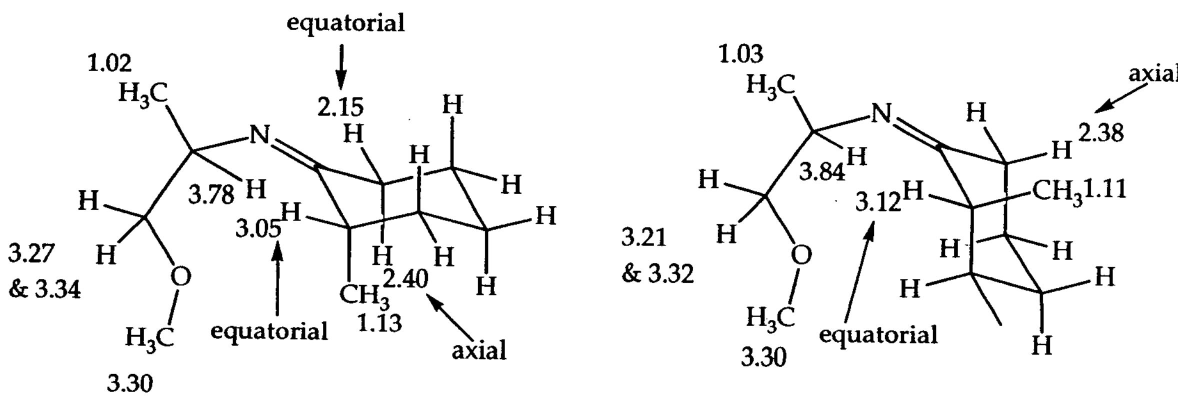
13



15

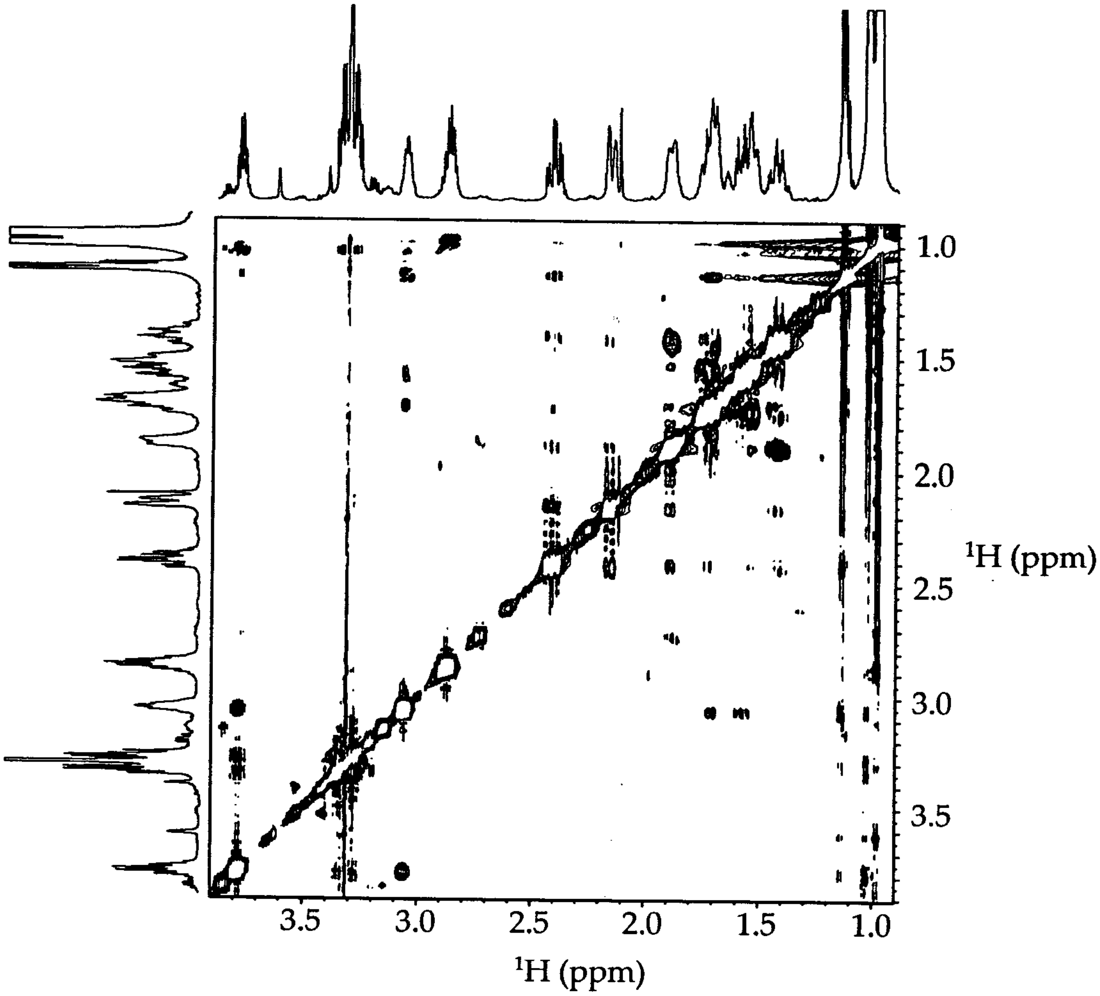
XI-D. $J(^1H,^1H)$-resolved spectrum of a 6:1 mixture of imines **13** (major) and **15** (minor) (500 MHz, THF-d_8, 25 °C).

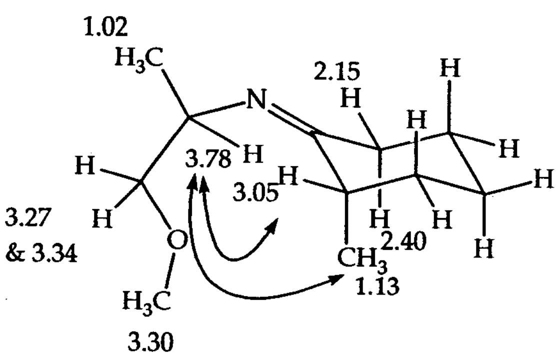




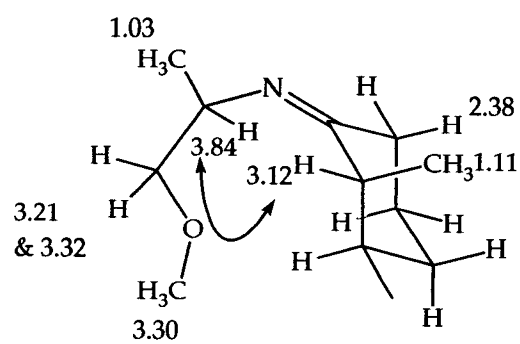
13 **15**

XI-E. ^{1}H,^{1}H-NOESY spectrum of a 6:1 mixture of imines **13** (major) and **15** (minor) (500 MHz, THF-d_8, 25 °C).





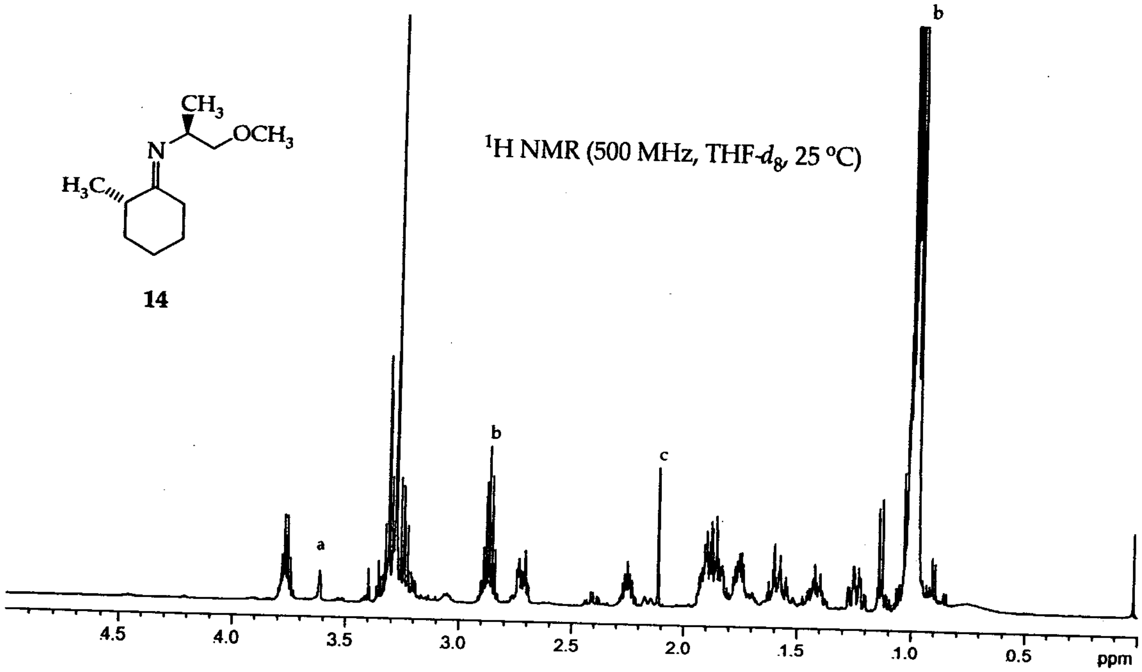
13

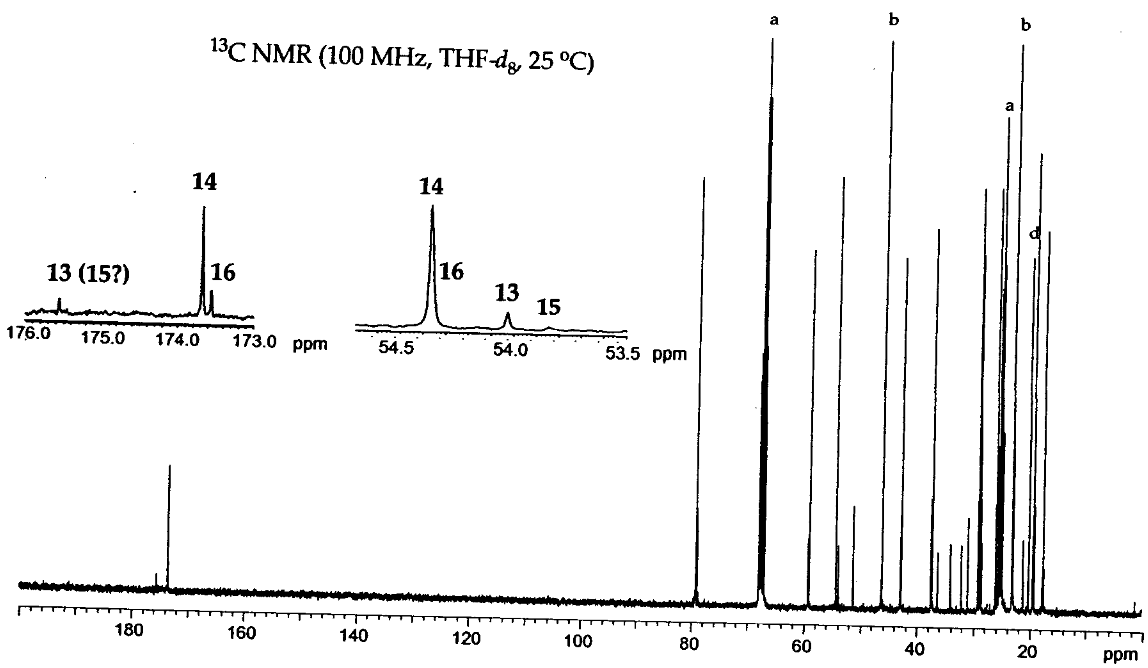


15

XII. Conformational assignments of imine 14 in THF-d_8.

XII-A. ^1H and ^{13}C NMR spectra of imine 14[a] in THF-d_8.



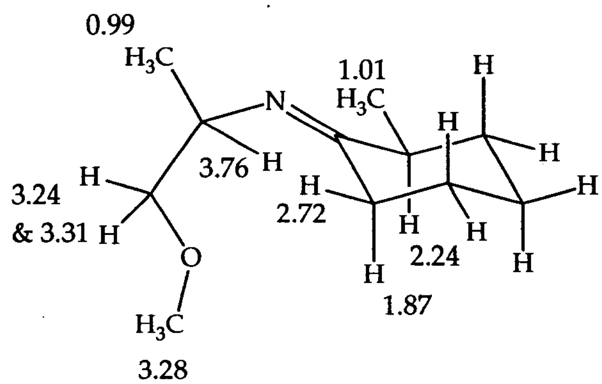


a = THF, b = HN(i-Pr)$_2$, c = CH_3I, d = CH_3N(i-Pr)$_2$ (?)

[a]From isomerization/epimerization of a 6:1 mixture of imines **13** and **15** prepared by lithiation and alkylation of imine **4** (section **XI-A**). The equilibrated ratio is **13**: 8%, **14**: 71%, **15**: 2%, **16**: 19% (also available in section **XVI**). **13**, **15** and **16** are characterized in sections **XI** and **XIII**.

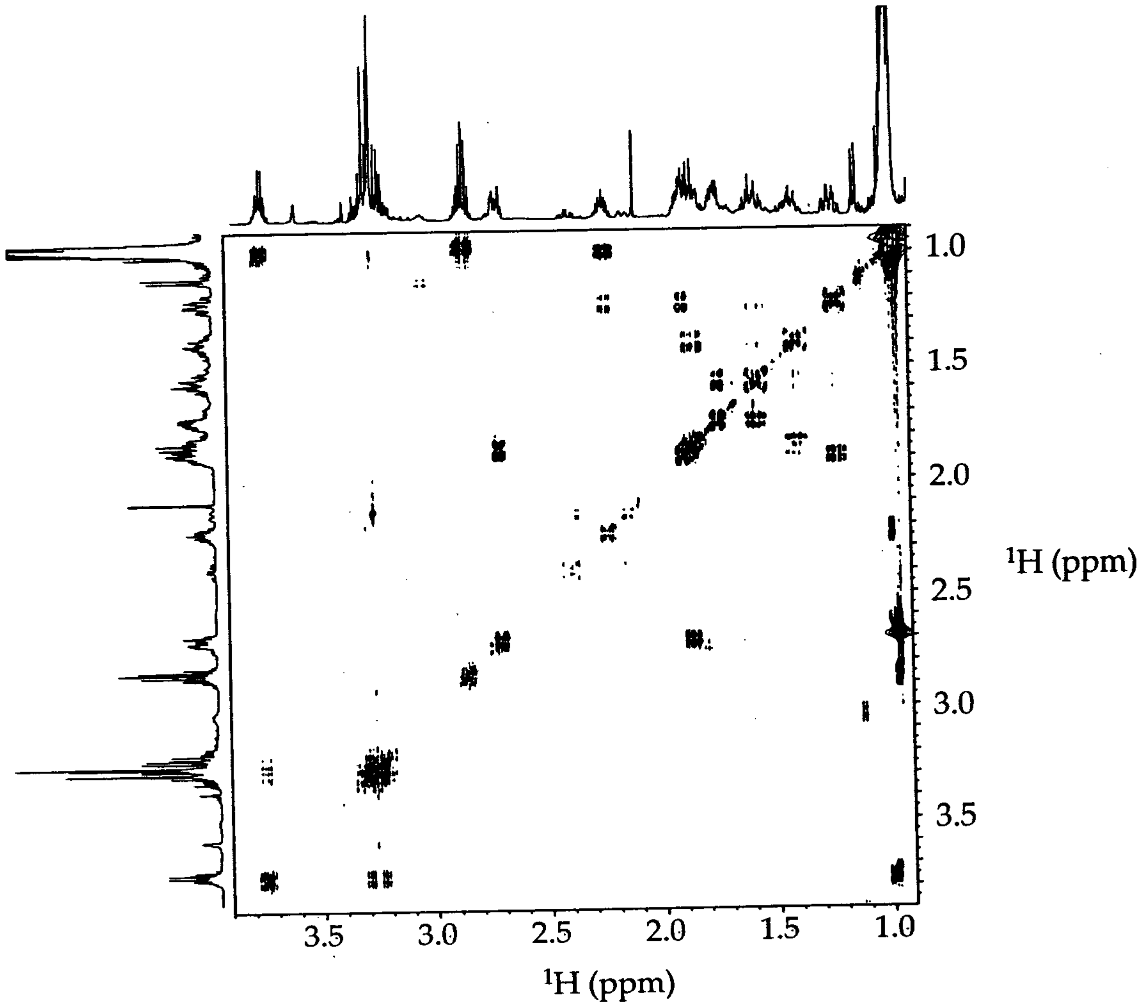
XII-B. ^{1}H NMR: δ 0.99 (d, *J* = 6.0 Hz, 3H), 1.01 (d, *J* = 6.5 Hz, 3H), 1.24 (dtd, *J* = 13.0, 11.0, 3.9 Hz, 1H), 1.41 (qt, *J* = 10.0, 4.0 Hz, 1H), 1.60 (qt, *J* = 12.0, 4.2 Hz, 1H), 1.75 (dt, *J* = 13.0, 4.5 Hz, 1H), 1.85 (dm, *J* = 14.0 Hz, 1H), 1.87 (td, *J* = 13.0, 5.0 Hz, 1H), 1.90 (m, 1H), 2.24 (dqd, *J* = 13.5, 6.5, 4.9 Hz, 1H), 2.72 (dt, *J* = 14.0, 4.6 Hz, 1H), 3.24 (t, *J* = 9.0 Hz, 1H), 3.28 (s, 3H), 3.31 (t, *J* = 9.0 Hz, 1H), 3.76 (sext, *J* = 6.5 Hz, 1H). ^{13}C NMR: δ 17.7, 19.6, 26.1, 28.9, 29.2, 37.4, 42.9, 54.4, 59.2, 79.3, 173.7.

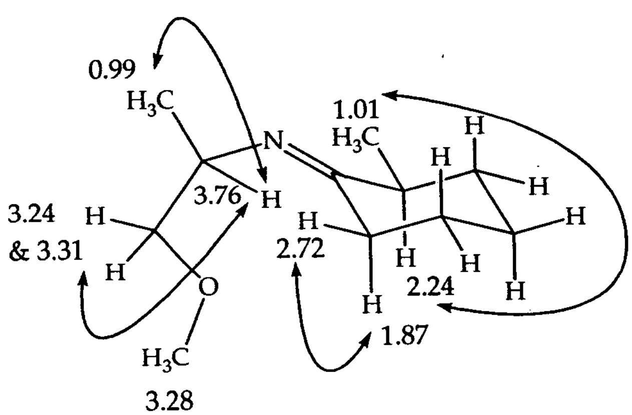
The structure of **14** is shown below. See 2D NMR spectra (section **XII: C-E**) for detailed assignments.



14

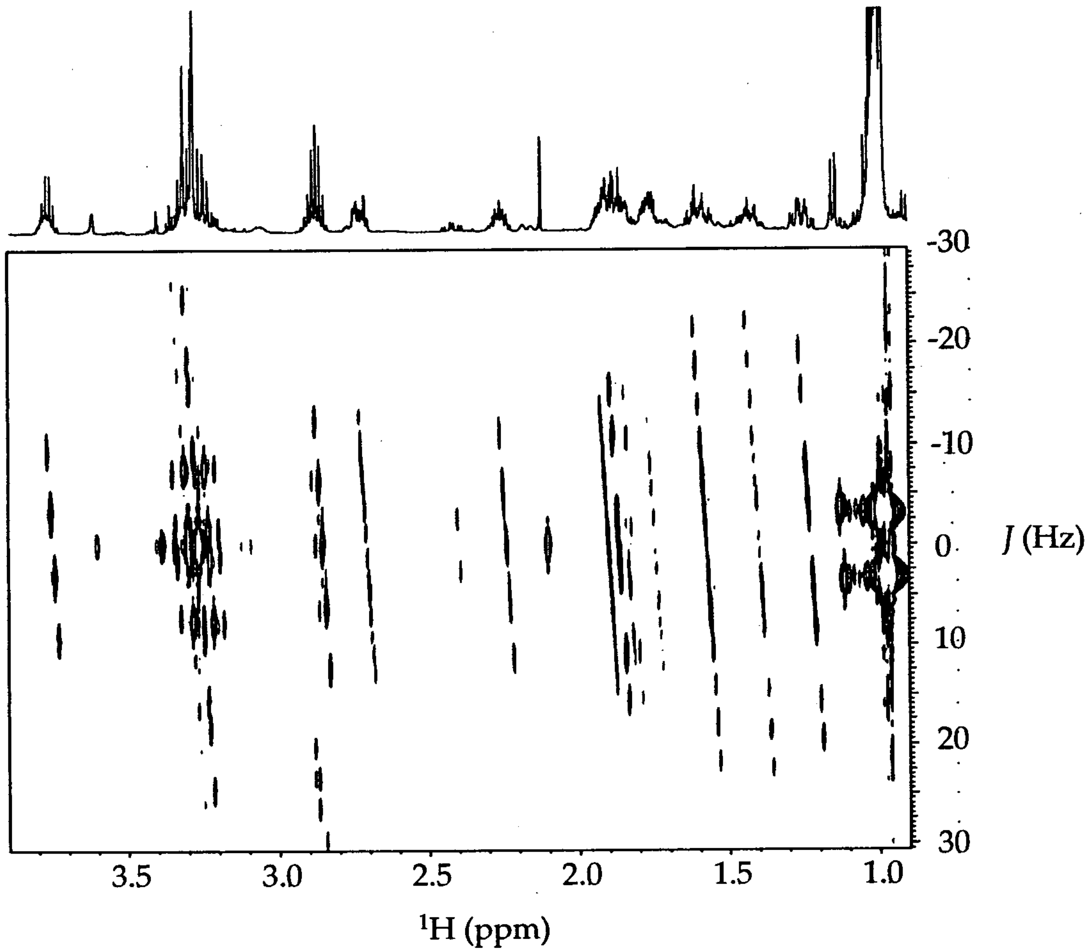
XII-C. $^{1}H,^{1}H$-COSY spectrum of **14** (500 MHz, THF-d_8, 25 °C).

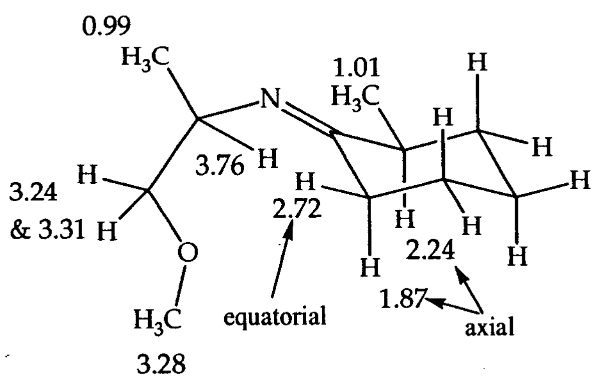




14

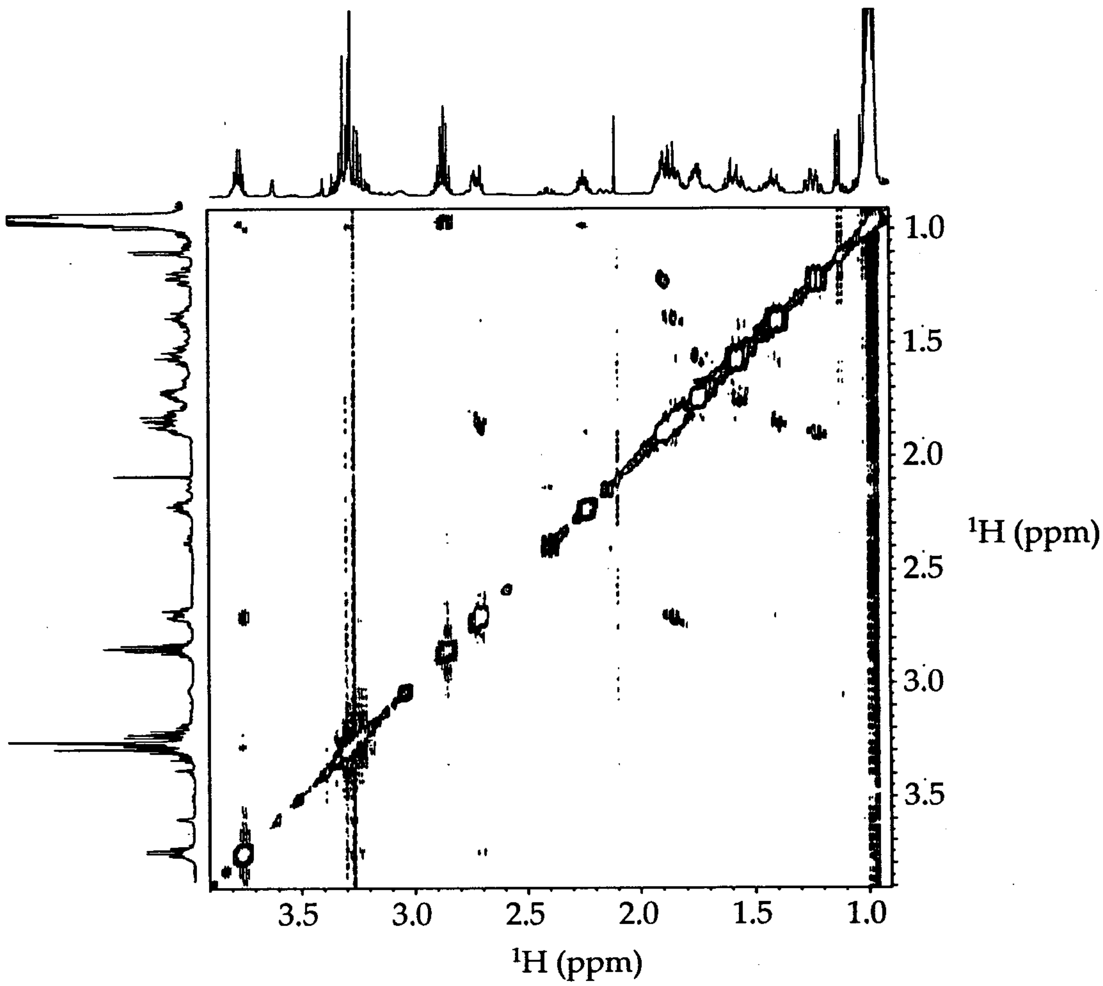
XII-D. $J(^1H,^1H)$-resolved spectrum of **14** (500 MHz, THF-d_8, 25 °C).

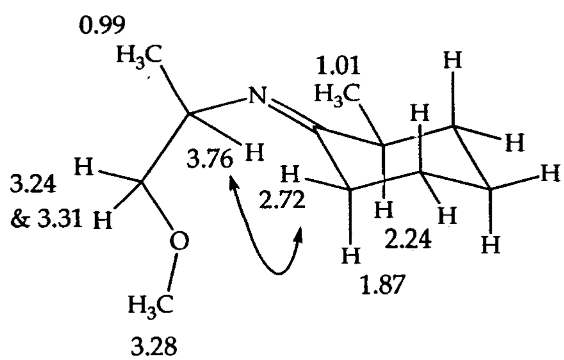




14

XII-E. $^1H,^1H$-NOESY spectrum of **14** (500 MHz, THF-d_8, 25 °C).

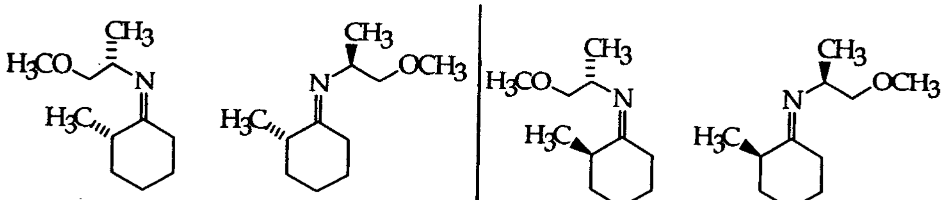




14

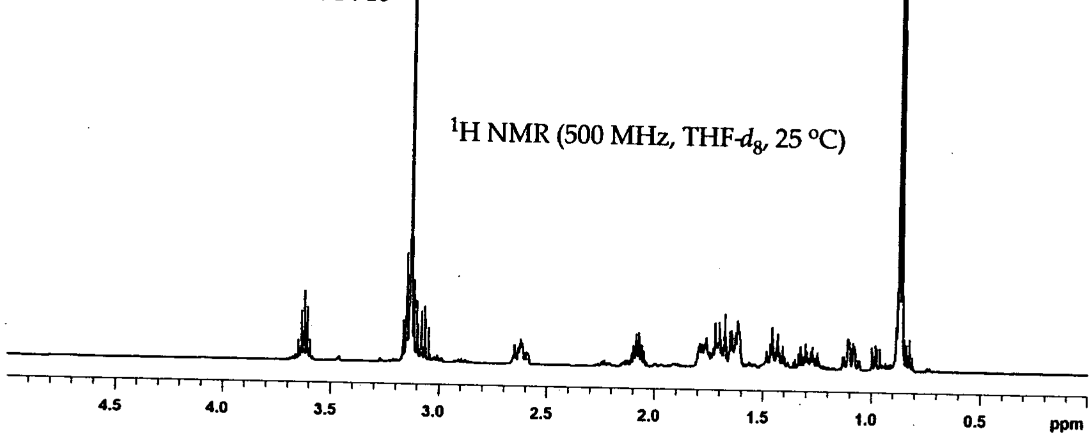
XIII. Conformational assignments of imines **14** and **16** in THF-d_8.

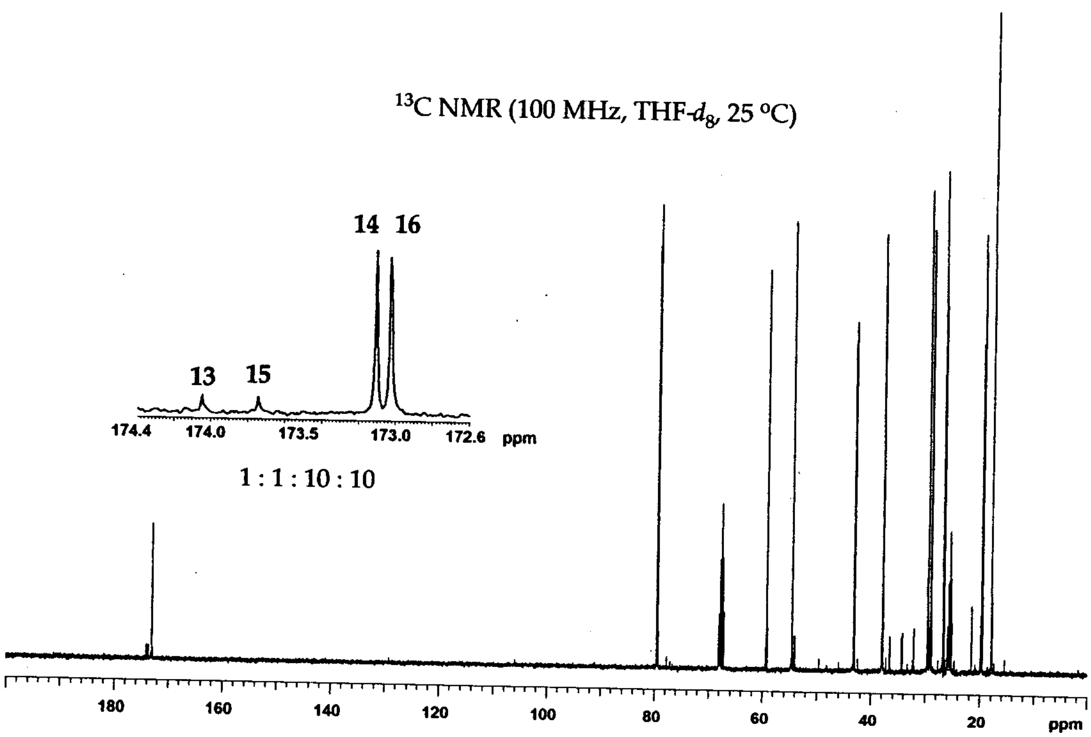
XIII-A. ^1H and ^{13}C NMR spectra of a 1:10:1:10 mixture of imines **13** (minor), **14** (major), **15** (minor), and **16** (major) in THF-d_8.



13 **14** **15** **16**

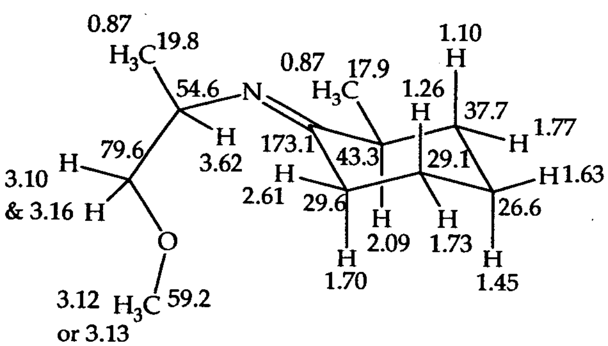
1 : 10 : 1 : 10



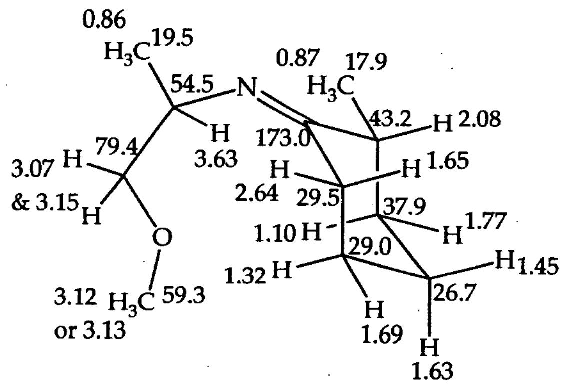


XIII-B. ^{1}H NMR (**14**): δ 0.87 (d, J = 6.5 Hz, 6H), 1.10 (qd, J = 11.0, 3.9 Hz, 1H), 1.26 (qt, J = 12.0, 4.0 Hz, 1H), 1.45 (qt, J = 12.0, 3.9 Hz, 1H), 1.63 (dm, J = 15.0 Hz, 1H), 1.70 (td, J = 14.0, 4.5 Hz, 1H), 1.73 (m, 1H), 1.78 (dm, J =13.0 Hz, 1H), 2.09 (dqd, J = 13.0, 6.5, 4.0 Hz, 1H), 2.61 (dm, J = 13.0 Hz, 1H), 3.10 (dd, J = 9.0, 6.5 Hz, 1H), 3.12 or 3.13 (s, 3H), 3.15 (dd, J = 9.0, 7.0 Hz, 1H), 3.62 (sext, J = 6.5 Hz, 1H); (**16**): δ 0.86 (d, J = 6.5 Hz, 6H), 0.87 (d, J = 6.5 Hz, 3H), 1.10 (qd, J = 11.0, 3.9 Hz, 1H), 1.32 (qt, J = 12.0, 4.0 Hz, 1H), 1.45 (qt, J = 12.0, 3.9 Hz, 1H), 1.63 (dm, J = 15.0 Hz, 1H), 1.65 (td, J = 14.0, 4.5 Hz, 1H), 1.69 (m, 1H), 1.78 (dm, J =13.0 Hz, 1H), 2.08 (dqd, J = 13.0, 6.5, 4.0 Hz, 1H), 2.64 (dm, J = 13.0 Hz, 1H), 3.07 (dd, J = 9.0, 6.5 Hz, 1H), 3.12 or 3.13 (s, 3H), 3.15 (dd, J = 9.0, 7.0 Hz, 1H), 3.63 (sext, J = 6.5 Hz, 1H). ^{13}C NMR (**14**): δ 17.9, 19.8, 26.6, 29.1, 29.6, 37.7, 43.3, 54.6, 59.2, 79.6, 173.1; (**16**): δ 17.9, 19.5, 26.7, 29.0, 29.5, 37.9, 43.2, 54.5, 59.3, 79.4, 173.0.

The structures of **14** and **16** are shown below. See 2D NMR spectra (section **XIII**: **C-G**) for detailed assignments.

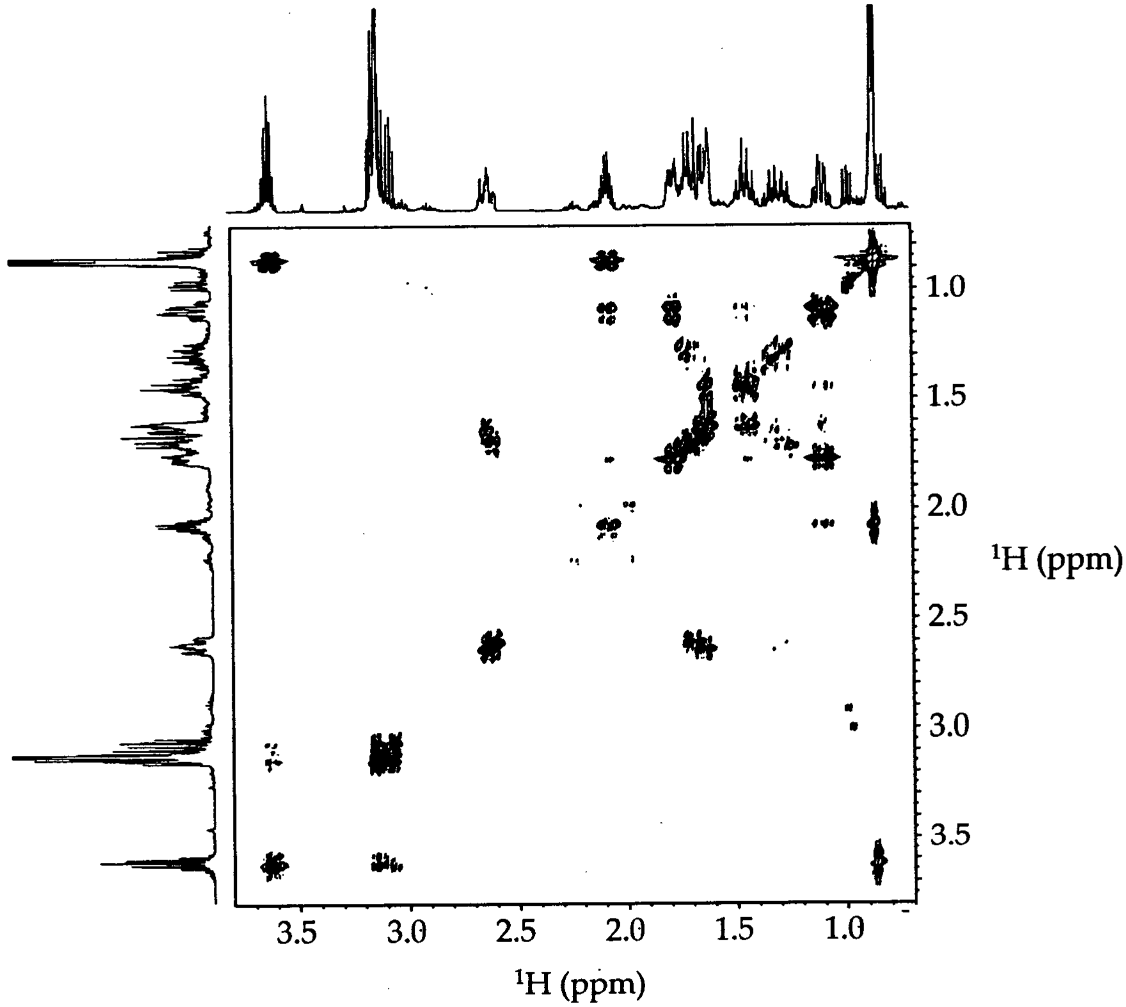


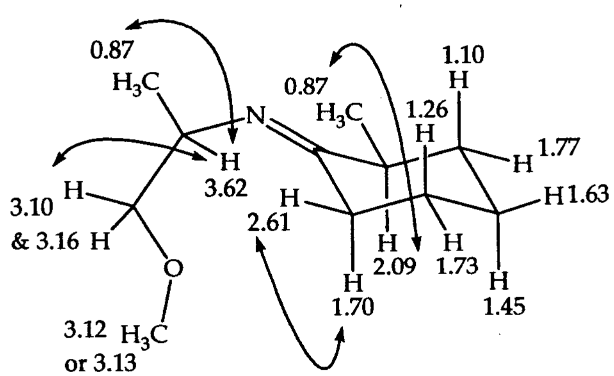
14



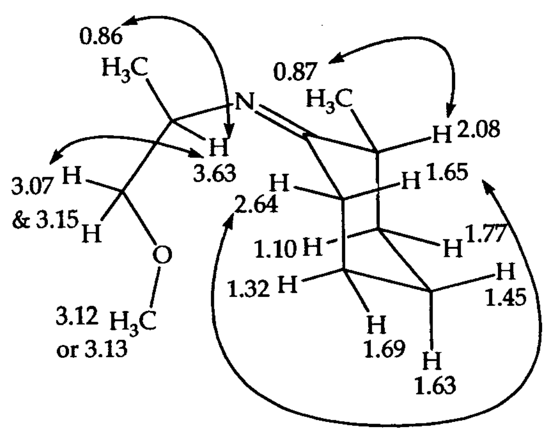
16

XIII-C. ^{1}H,^{1}H-COSY spectrum of a 1:10:1:10 mixture of imines **13** (minor), **14** (major), **15** (minor), and **16** (major) (500 MHz, THF-d_8, 25 °C).



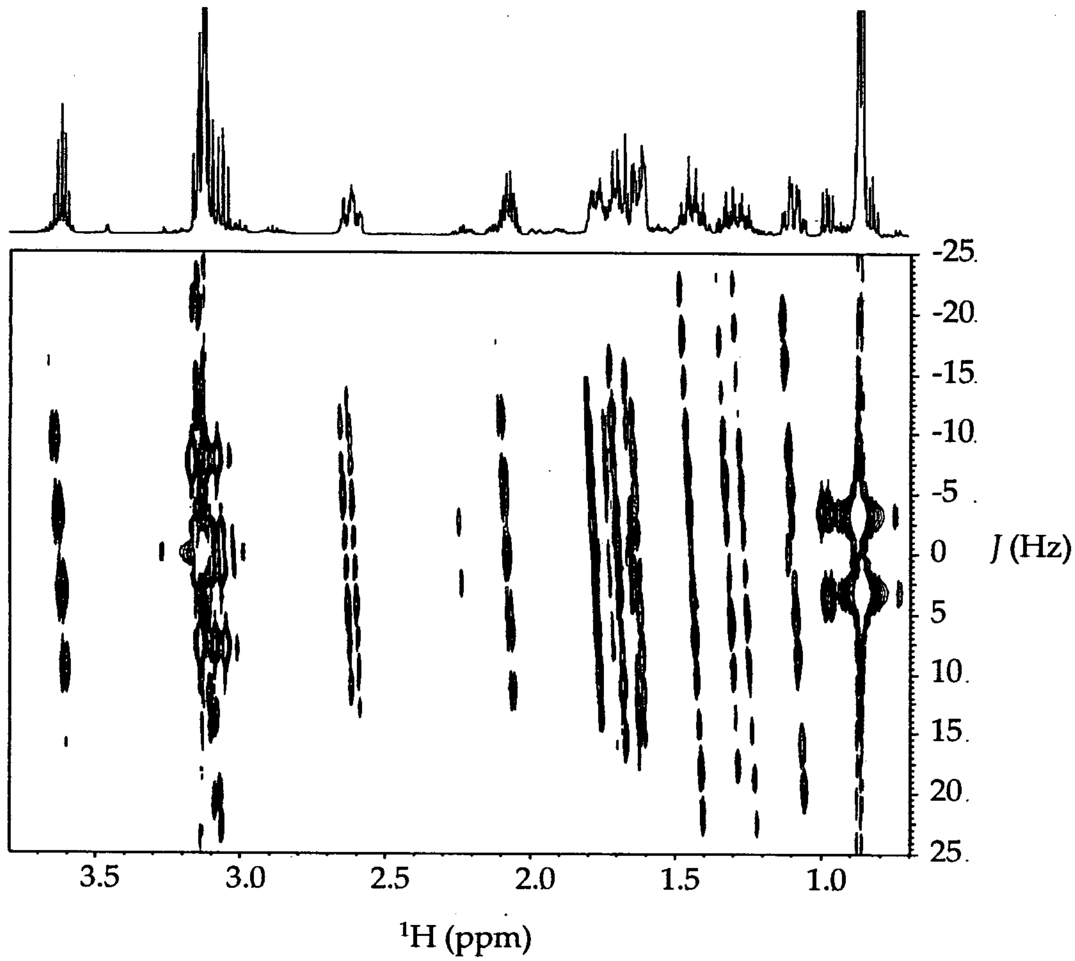


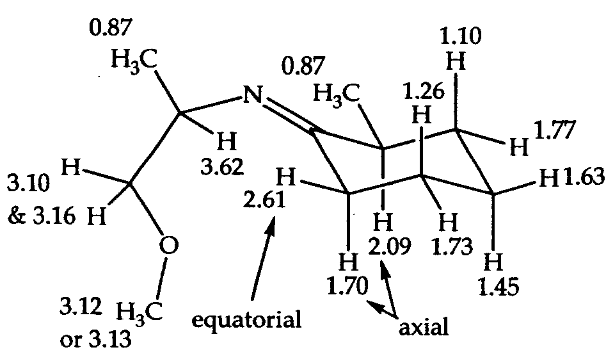
14



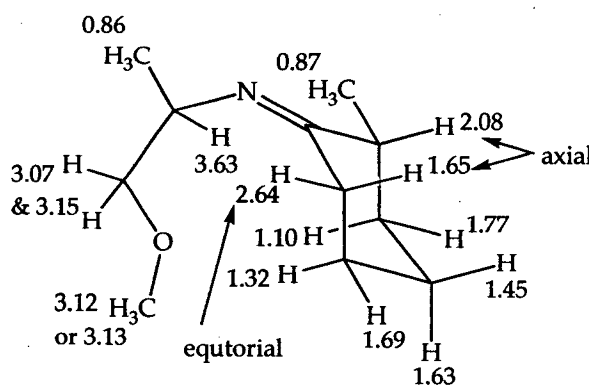
16

XIII-D. $J(^1H,^1H)$-resolved spectrum of a 1:10:1:10 mixture of imines **13**(minor), **14** major), **15** (minor), and **16** (major) (500 MHz, THF-d_8, 25 °C).



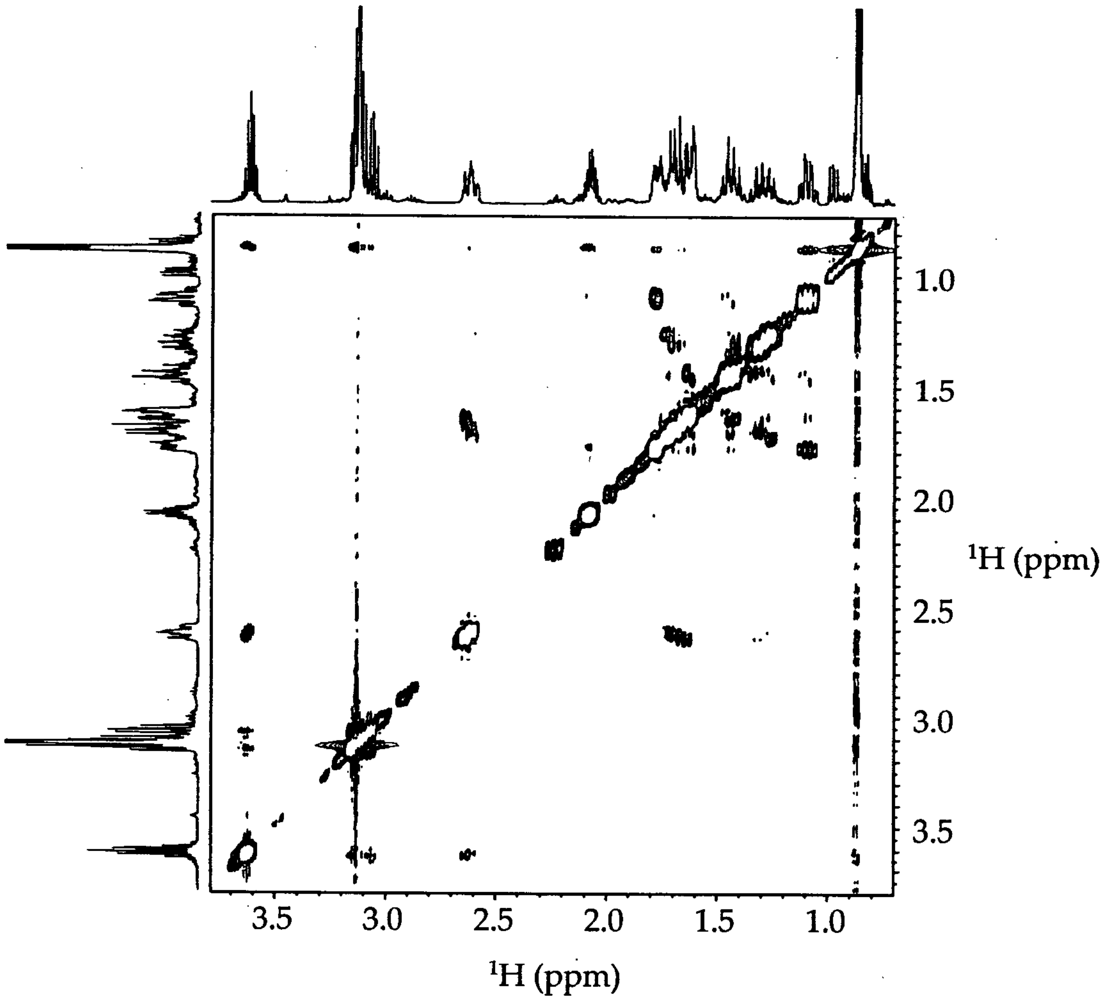


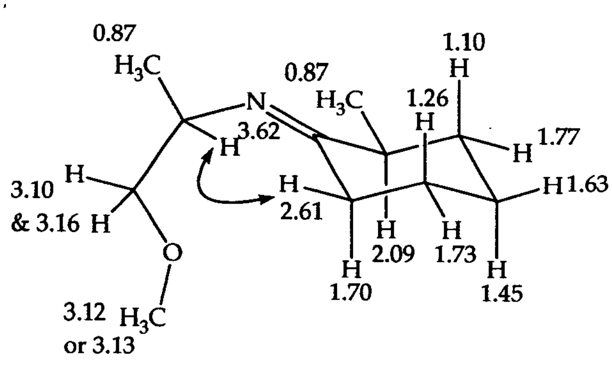
14



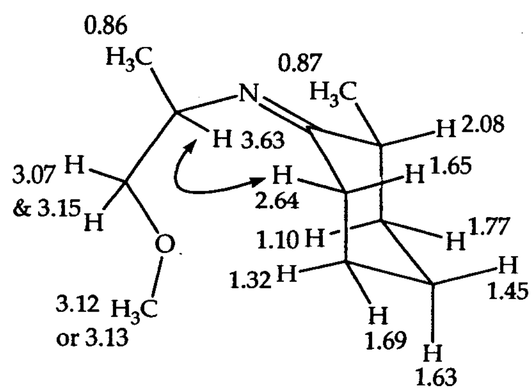
16

XIII-E. ^{1}H,^{1}H-NOESY spectrum of a 1:10:1:10 mixture of imines **13** (minor), **14** (major), **15** (minor), and **16** (major) (500 MHz, THF-d_8, 25 °C).



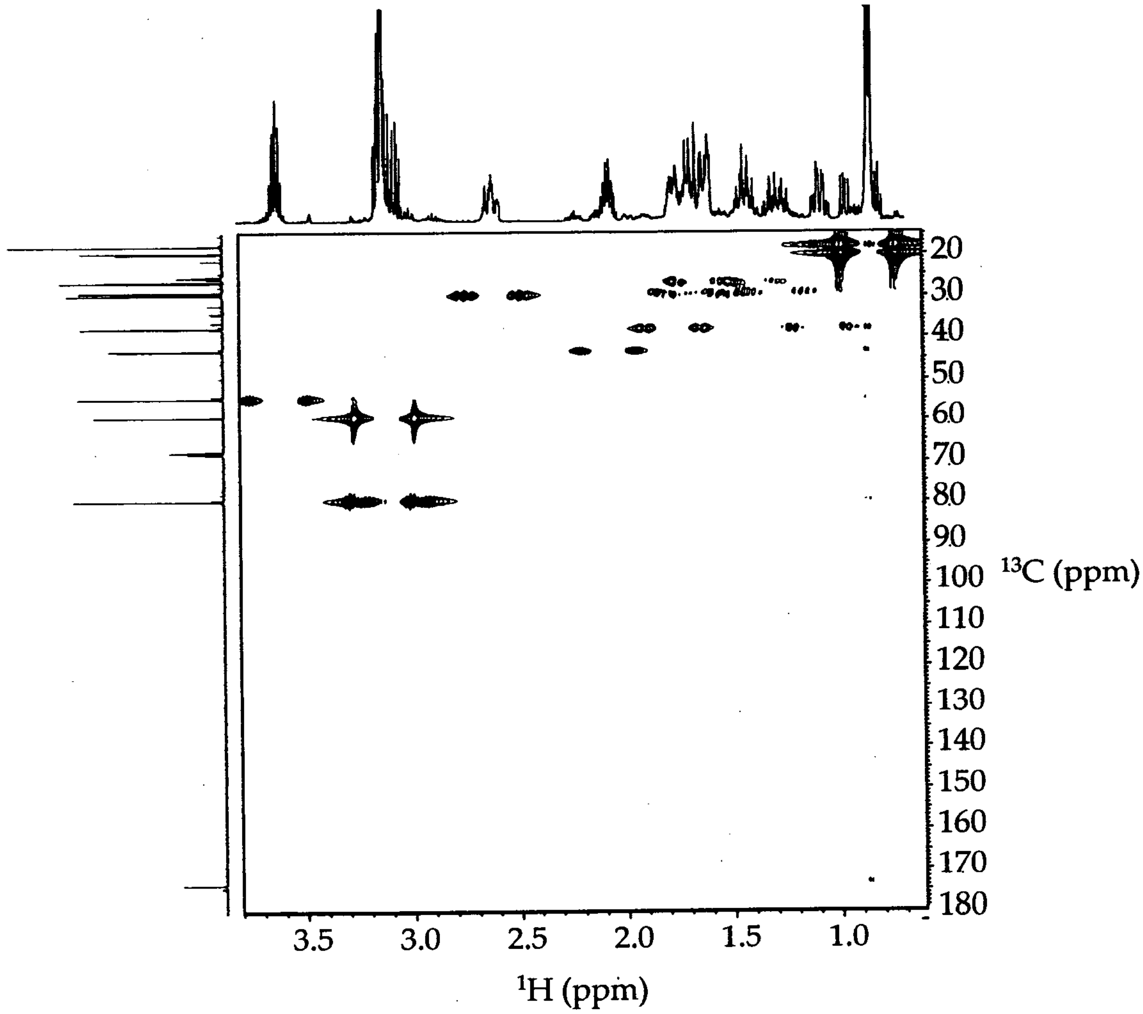


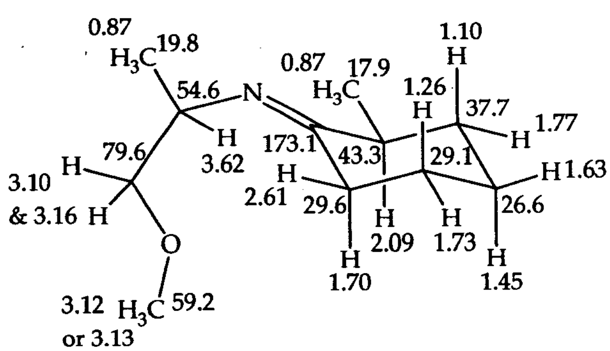
14



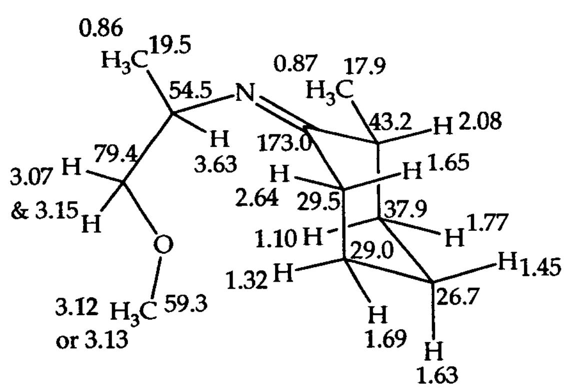
16

XIII-F. ¹H,¹³C-HMQC spectrum of a 1:10:1:10 mixture of imines **13** (minor), **14** (major), **15** (minor), and **16** (major) (500 MHz, THF-d_8, 25 °C).



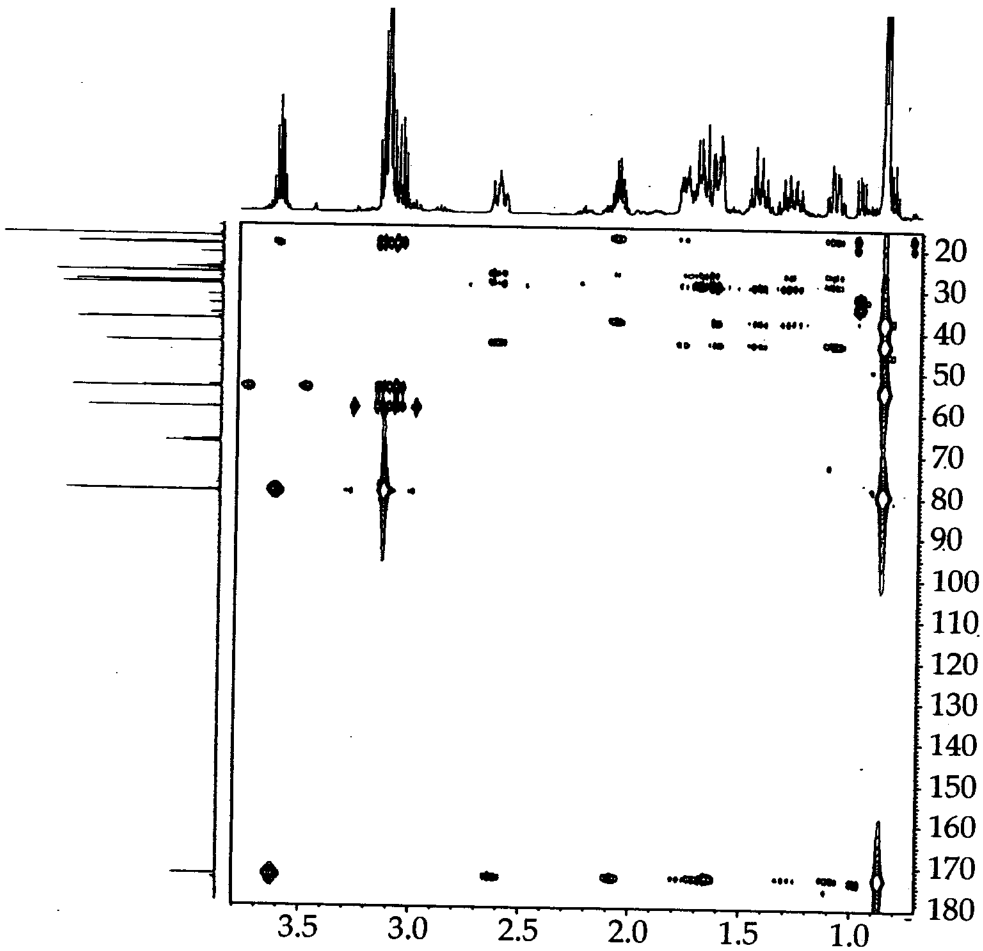


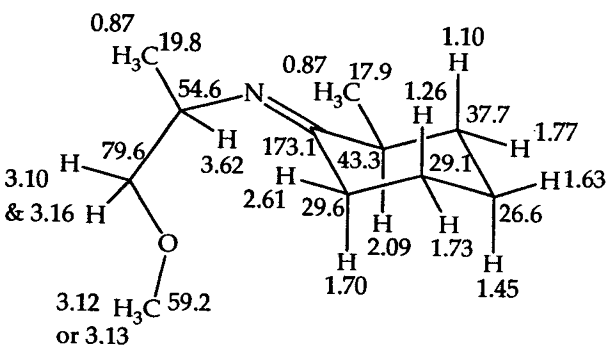
14



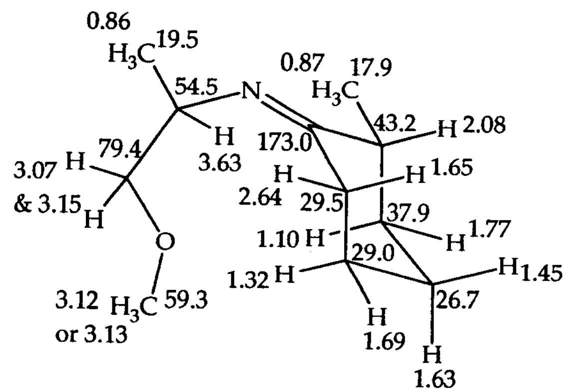
16

XIII-G. $^{1}H,^{13}C$-HMBC spectrum of a 1:10:1:10 mixture of imines **13** (minor), **14** (major), **15** (minor) and **16** (major) (500 MHz, THF-d_8, 25 °C).



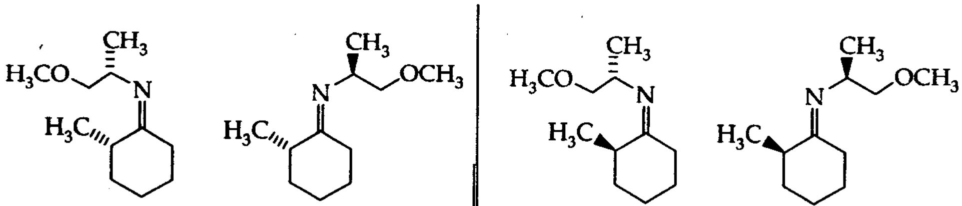


14



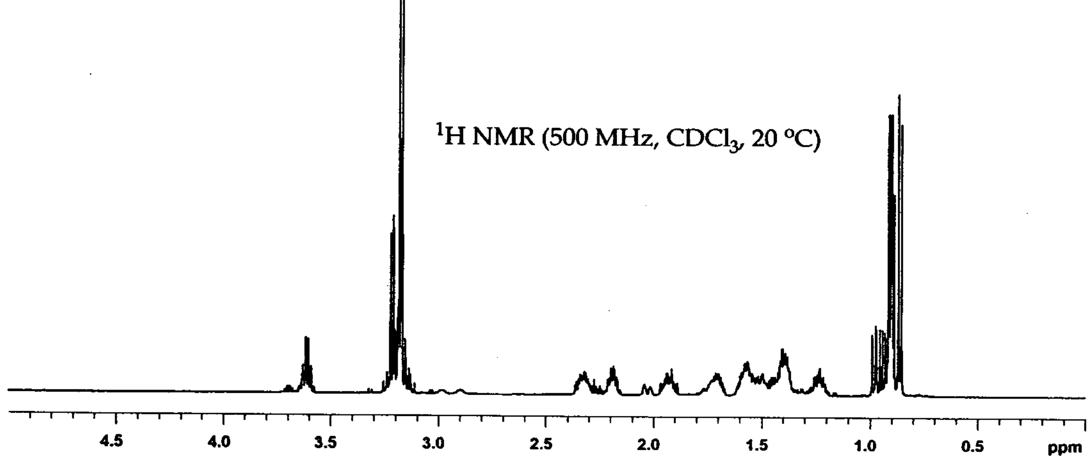
16

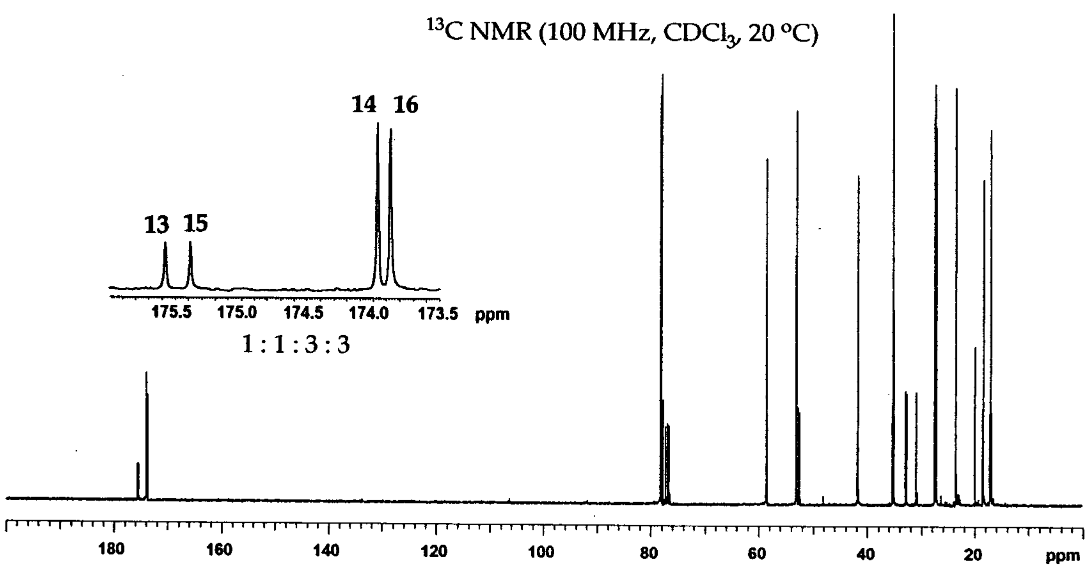
XIII-H. ^{1}H and ^{13}C NMR spectra of a 1:3:1:3 mixture of imines **13** (minor), **14** (major), **15** (minor) and **16** (major) in $CDCl_3$.[a]



13 **14** **15** **16**

1 : 3 : 1 : 3

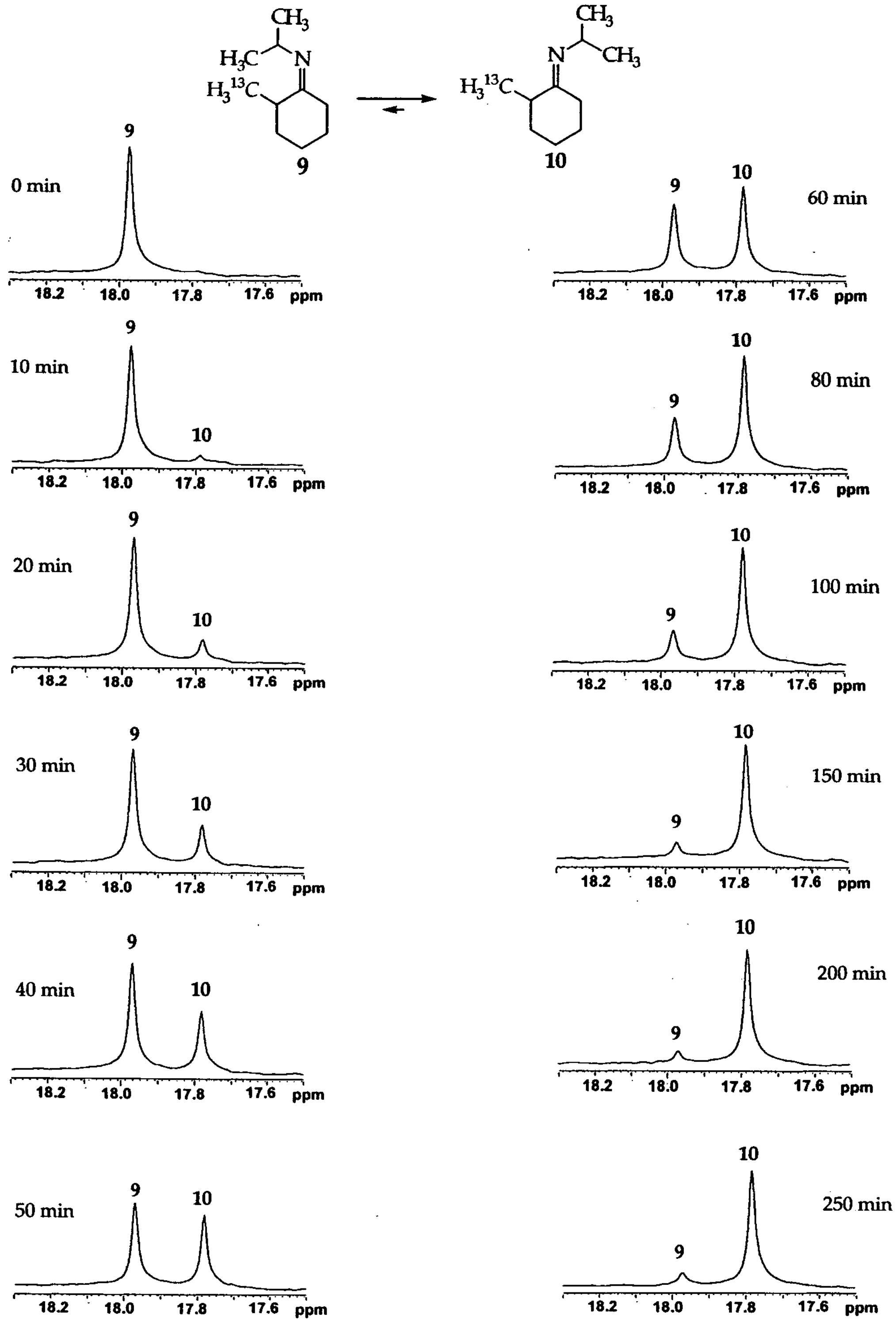




XIII-H. (Continued)
^{1}H NMR: δ 0.86 (d, *J* = 6.5 Hz, 3H, major[b]), 0.90 (d, *J* = 7.0 Hz, 3H, major), 0.90 (d, *J* = 6.5 Hz, 3H, minor[c]), 0.91 (d, *J* = 6.5 Hz, 3H, major), 0.91 (d, *J* = 7.0 Hz, 3H, major), 0.94 (d, *J* = 6.5 Hz, 3H, minor), 0.96 (d, *J* = 7.0 Hz, 3H, minor), 0.98 (d, *J* = 7.0 Hz, 3H, minor), 1.18-1.27 (m, 1H, **14** + **16**), 1.31 (m, 1H, **13** + **15**), 1.35-1.63 (m, 4H, **13-16**), 1.60-1.75 (m, 1H, **14** + **16**), 1.77 (m, 1H, **13** + **15**), 1.88-1.97 (m, 1H, **14** + **16**), 2.03 (dm, *J* = 14.0 Hz, 1H, **13** + **15**), 2.15-2.23 (m, 1H, **14** + **16**), 2.25 (tt, *J* = 14.0, 5.5 Hz, 1H, **13** + **15**), 2.28-2.38 (m, 1H, **14** + **16**), 2.90 (quint, *J* = 6.5 Hz, minor), 2.98 (quint, *J* = 6.5 Hz, minor), 3.11-3.26 (m, 2H, **13-16**), 3.17 (s, 3H, major), 3.18 (s, 3H, major), 3.21 (s, 3H, minor), 3.22 (s, 3H, minor), 3.61 (sext, *J* = 6.5 Hz, 1H, minor + **14** + **16**), 3.70 (sext, *J* = 6.5 Hz, 1H, minor). ^{13}C NMR[a]: δ (**13**) 16.9, 18.6, 20.0, 27.5, 31.0, 33.0, 35.3, 52.7, 58.5, 78.1, 175.6; (**14**) 17.1, 18.4, 23.5, 27.3, 27.5, 35.2, 41.8, 53.0, 58.6, 78.2, 174.0; (**15**) 17.0, 18.5, 20.0, 27.5, 31.0, 32.8, 35.4, 52.5, 58.7, 77.7, 175.4; (**16**) 17.1, 18.3, 13.6, 17.2, 27.4, 35.2, 41.7, 53.1, 58.6, 78.0, 173.9.

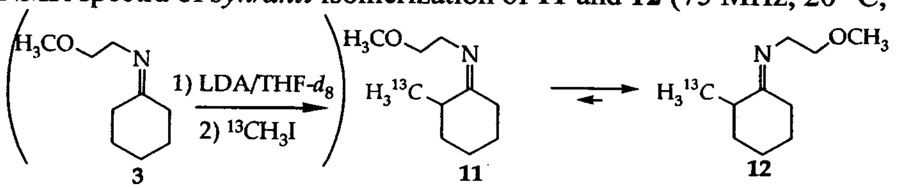
[a]Chemical shifts were assigned to four isomers by comparing the above spectrum with the spectra recorded in THF-d_8 (**13-16** were characterized individually, **XI-XIII**) and the spectrum recorded in 1:1 mixture of $CDCl_3$ and THF-d_8 (**XIX**). Some peaks are overlapped. [b]**14** or **16**. [c]**13** or **15**.

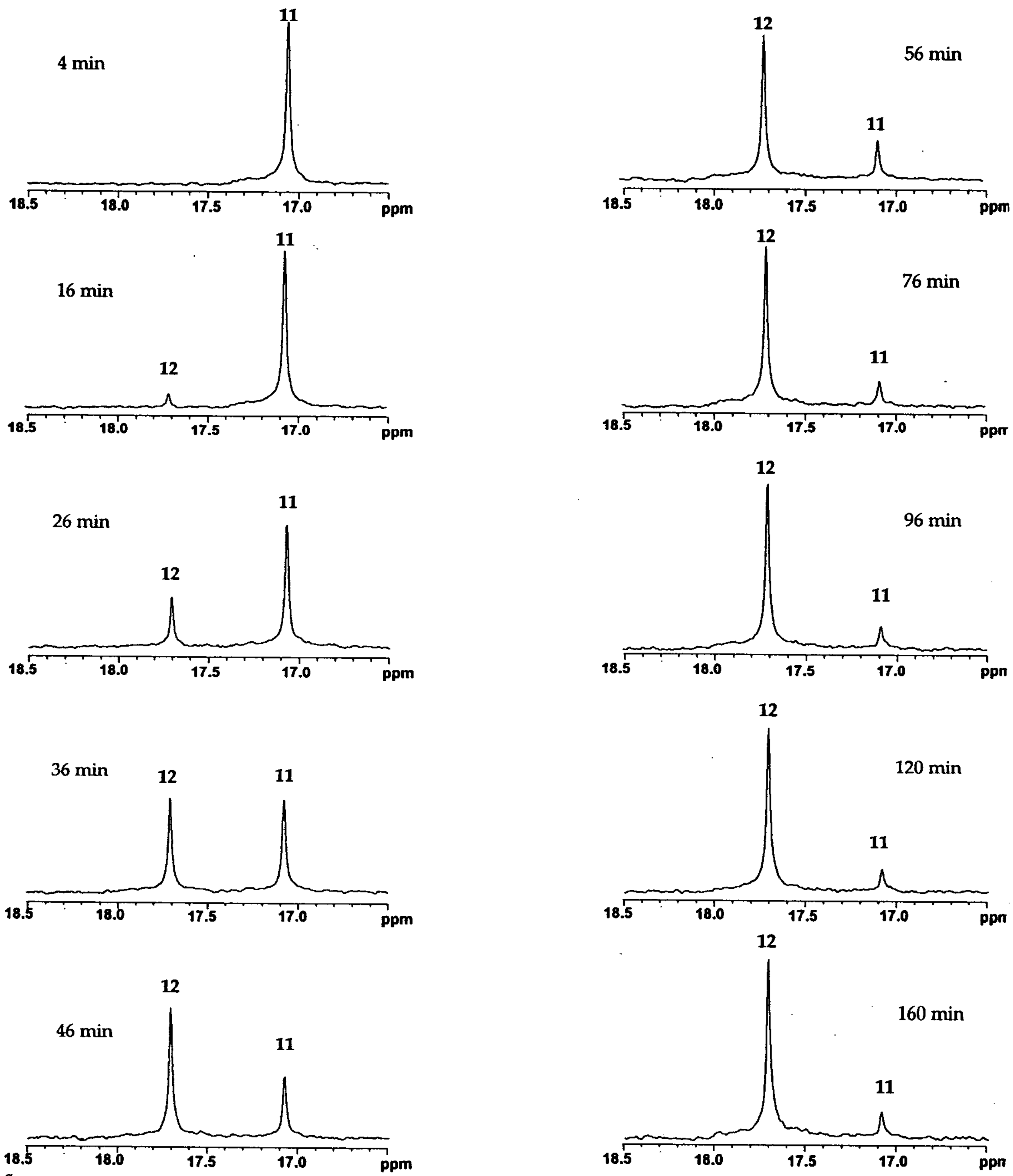
XIV. ^{13}C NMR spectra of *syn/anti* isomerization of **9** and **10** (75 MHz, 35 °C, THF-d_8).[a]



[a]Imine **9** was prepared in situ by lithiation (LDA, 1.1 equiv, 0 °C) and alkylation ($^{13}CH_3I$, 1.1 equiv, -78 °C) of imine **2** (0.26 M) (section **VIII-A**). The sample was sealed in an NMR tube under Ar and kept at -78 °C until the spectra were recorded. One scan was taken for each spectrum. The equilibrated ratio of **9** and **10** is 1:10.

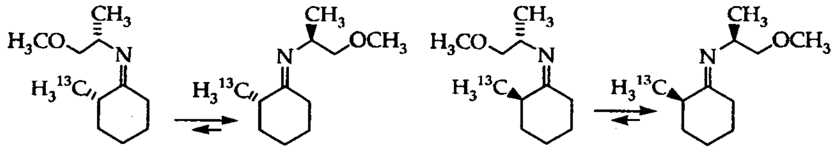
XV. ^{13}C NMR spectra of *syn/anti* isomerization of **11** and **12** (75 MHz, 20 °C, THF-d_8).[a]



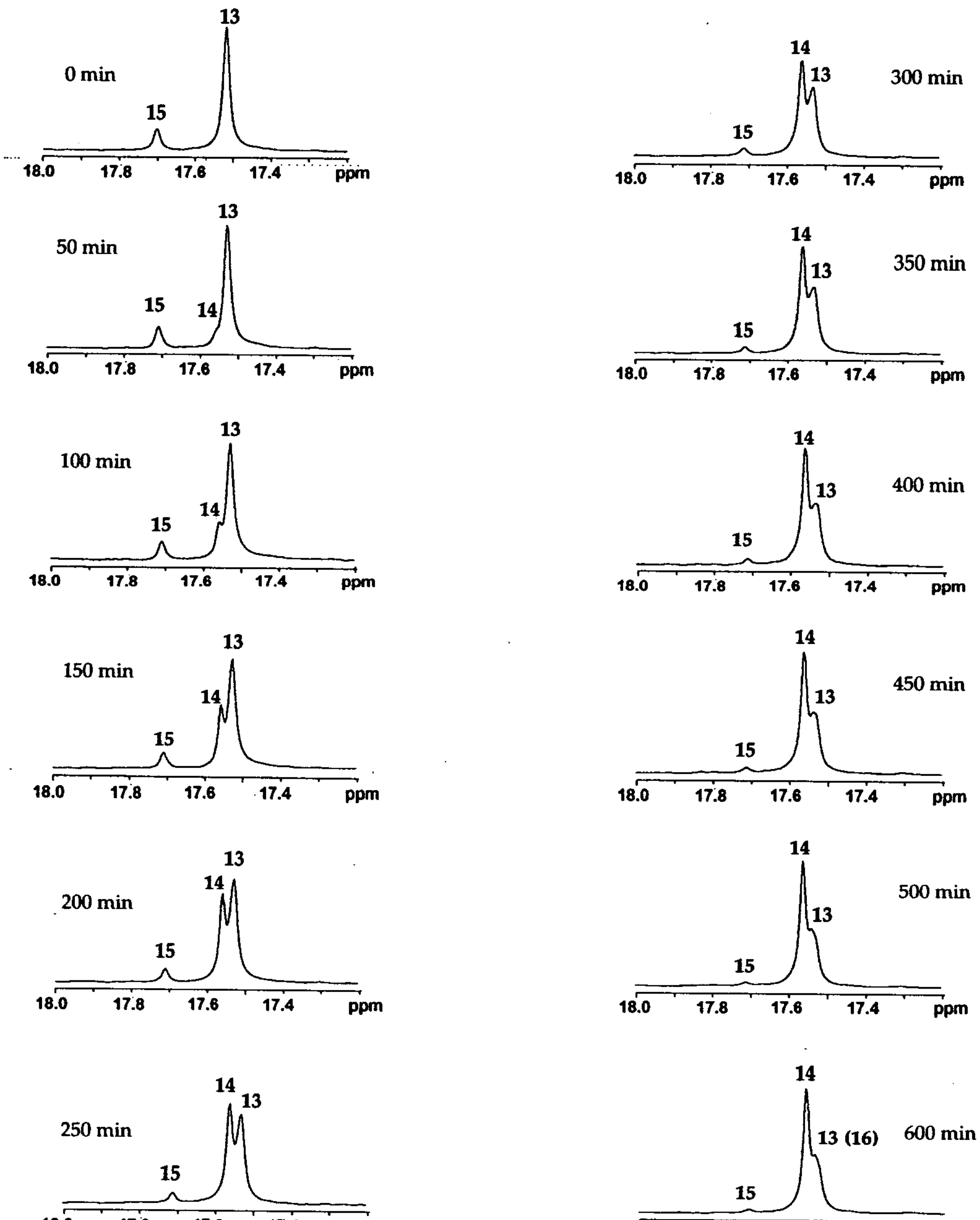


[a]Imine **11** was prepared in situ by lithiation (LDA, 1.1 equiv, -78 °C) and alkylation ($^{13}CH_3I$, 1.1 equiv, -78 °C) of imine **3** (0.20 M). The sample was sealed in an NMR tube under Ar and kept at -78 °C until the spectra were recorded. One scan was taken for each spectrum. The equilibrated ratio of **11** and **12** is 1:10 (section **X-H**).

XVI. ^{13}C NMR spectra of *syn/anti* isomerization of **13**, **14**, **15** and **16** (75 MHz, 35 °C, THF-d_8).[a]

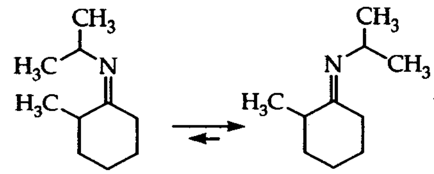


13 **14** **15** **16**

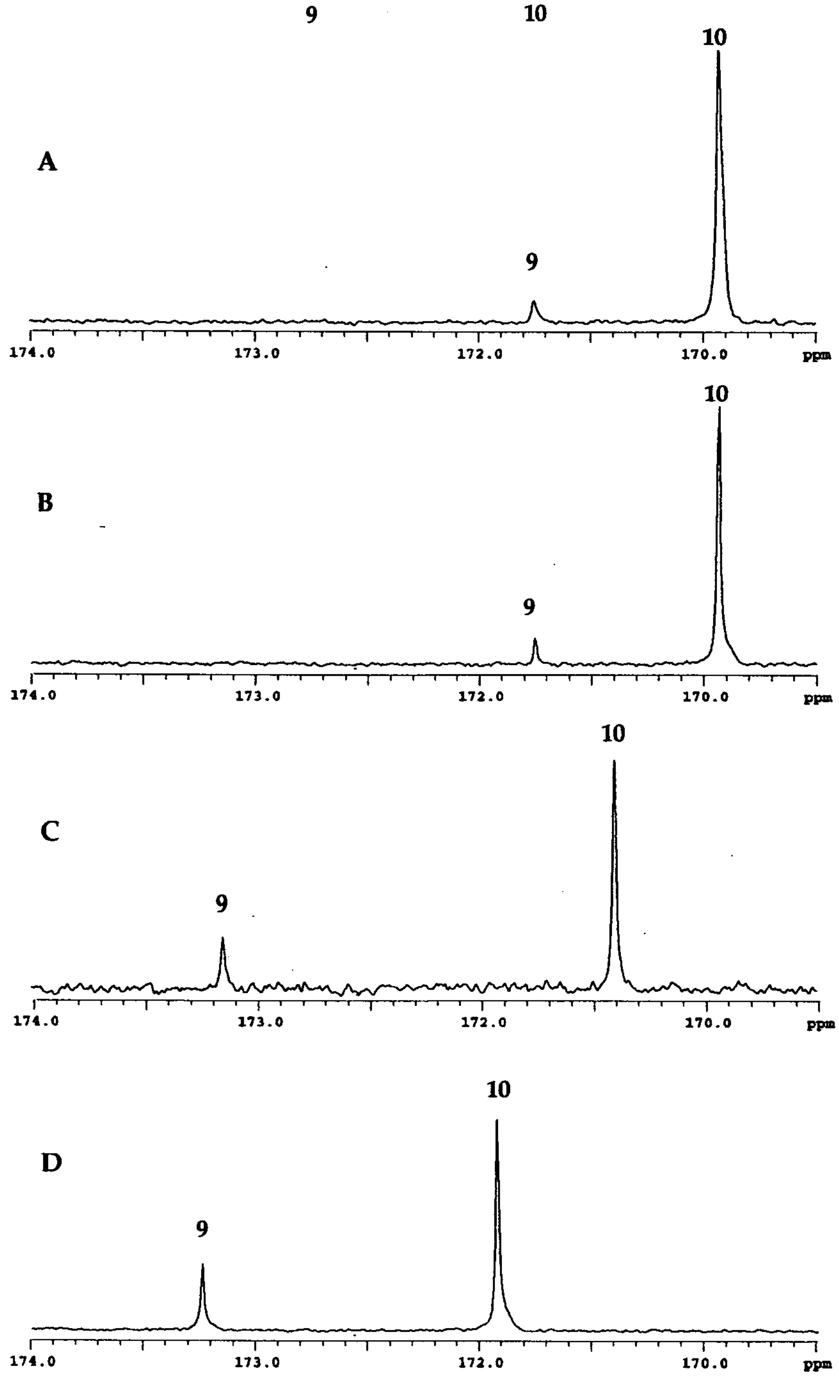


[a]A 6:1 mixture of **13** and **15** was prepared in situ by lithiation (LDA, 1.1 equiv, -65 °C) and alkylation ($^{13}CH_3I$, 1.1 equiv, -78 °C) of **4** (0.26 M) (section **XI-A**). The sample was sealed in an NMR tube under Ar and kept at -78 °C until the spectra were recorded. One scan was taken for each spectrum. The peak of **16** is hidden under those of **13** and **14**. Equilibrated ratio: **13**: 8%, **14**: 71%, **15**: 2%, **16**: 19% (also available in **XII-A**).

XVII. ^{13}C NMR spectra (100 MHz) of **9** and **10** in THF-d_8/$CDCl_3$ at 25 °C to measure the solvent effect on the *syn*/*anti* ratio.

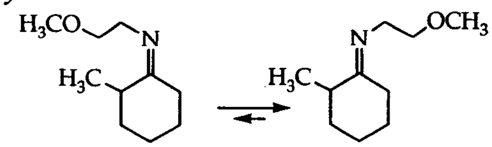


9 **10**

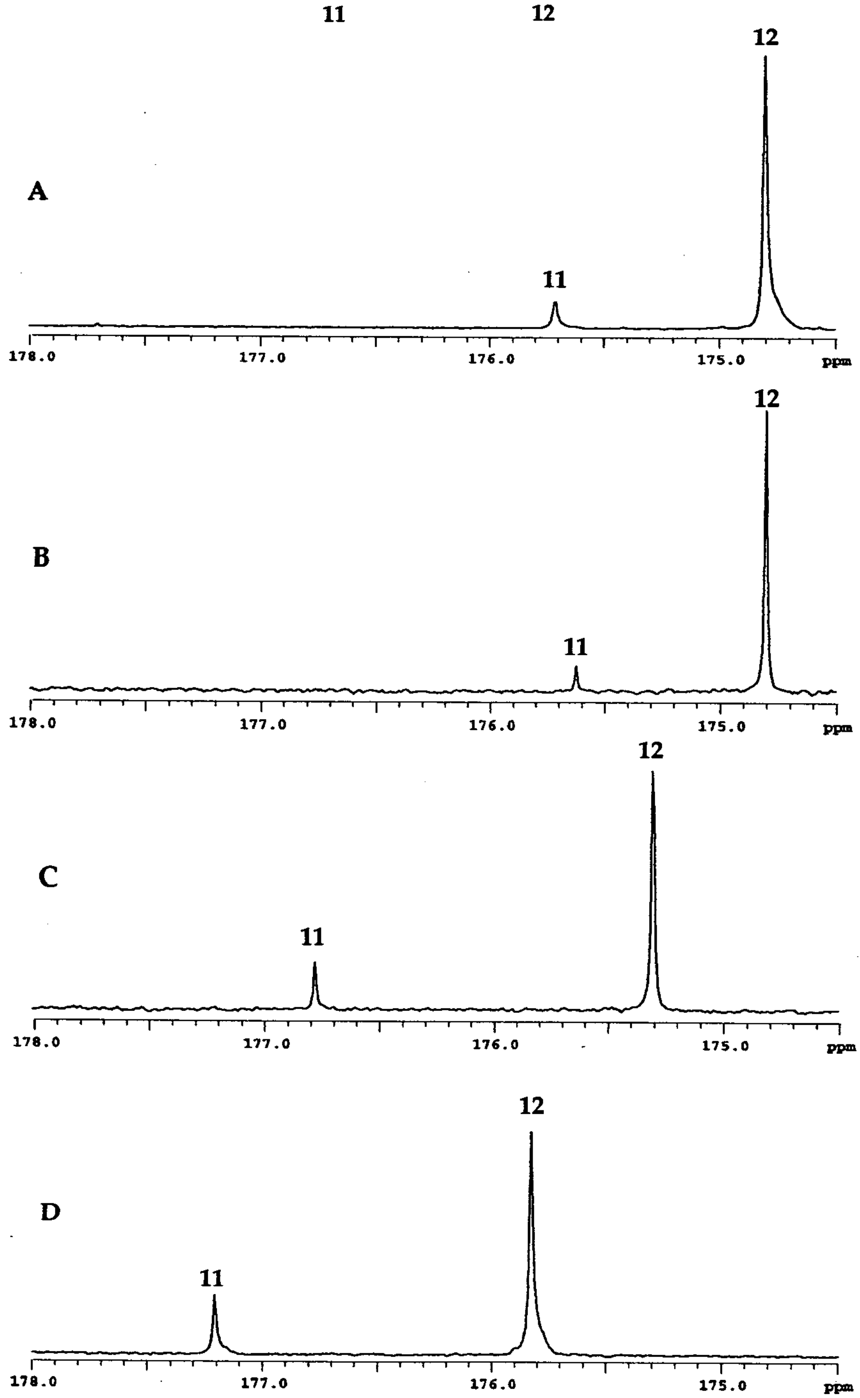


(A) neat imine, **9**:**10** = 1:17; **(B)** in THF-d_8, **9**:**10** = 1:10; **(C)** in 1:1 mixture of THF-d_8 and $CDCl_3$, **9**:**10** = 1:7; **(D)** in $CDCl_3$, **9**:**10** = 1:3.

XVIII. ^{13}C NMR spectra (100 MHz) of **11** and **12** in THF-d_8/$CDCl_3$ at 20 °C to measure the solvent effect on the *syn/anti* ratio.

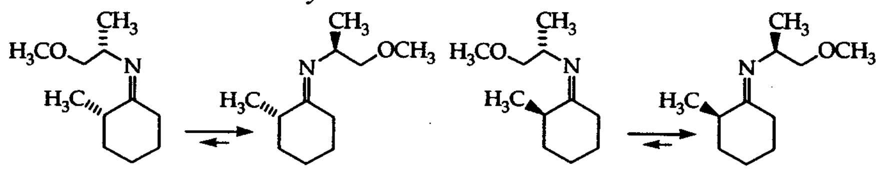


11 **12**

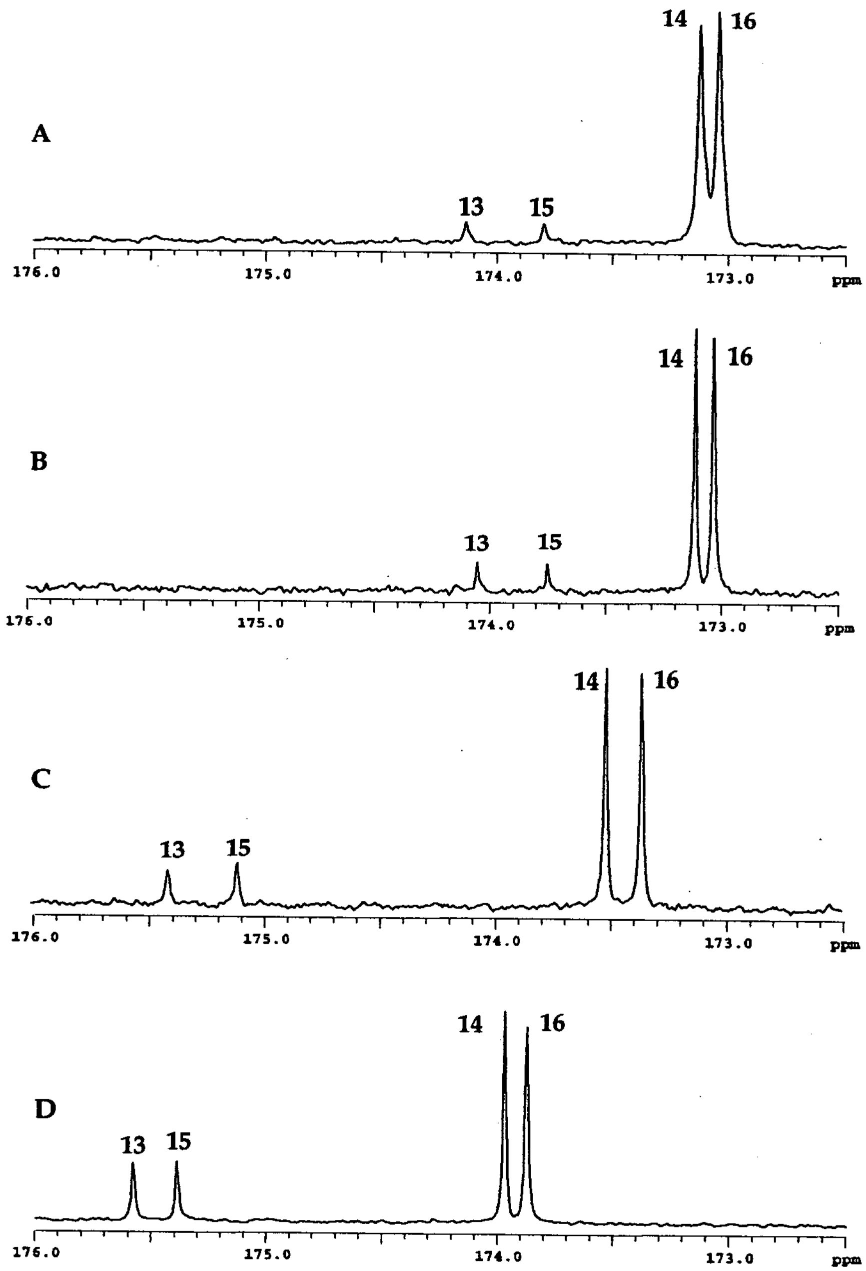


(A) neat imine, **11**:**12** = 1:11; **(B)** in THF-d_8, **11**:**12** = 1:10; **(C)** in 1:1 mixture of THF-d_8 and $CDCl_3$, **11**:**12** = 1:6; **(D)** in $CDCl_3$, **11**:**12** = 1:4.

XIX. ^{13}C NMR spectra (100 MHz) of **13**, **14**, **15** and **16** in THF-d_8/$CDCl_3$ at 25 °C to measure the solvent effect on the *syn/anti* ratio.

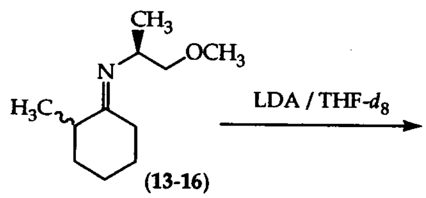


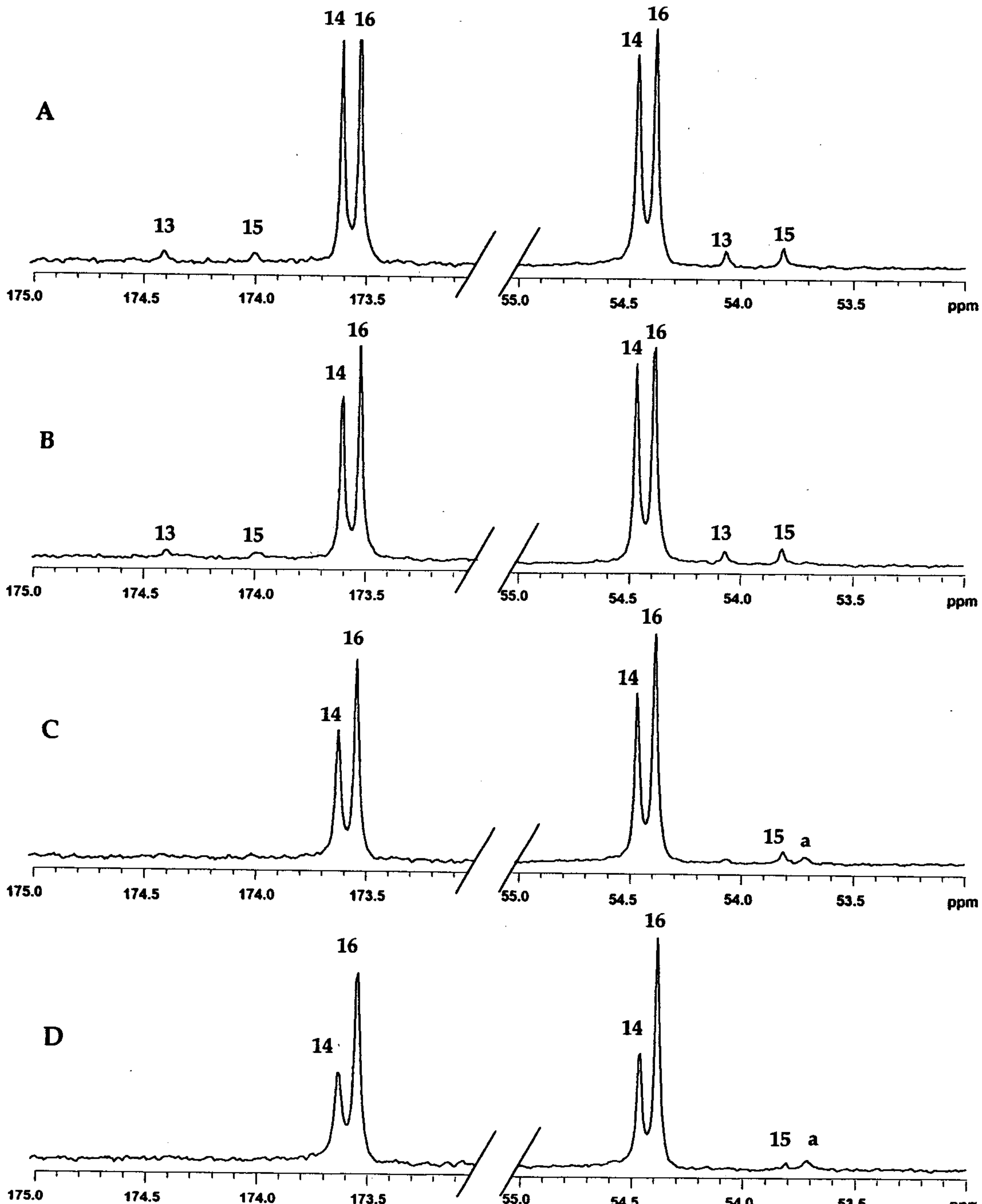
13 **14** **15** **16**



(A) neat imine, **13**:**14**:**15**:**16** = 1:15:1:15; **(B)** in THF-d_8, **13**:**14**:**15**:**16** = 1:10:1:10; **(C)** in 1:1 mixture of THF-d_8 and $CDCl_3$, **13**:**14**:**15**:**16** = 1:6:1:6; **(D)** in $CDCl_3$, **13**:**14**:**15**:**16** = 1:3:1:3.

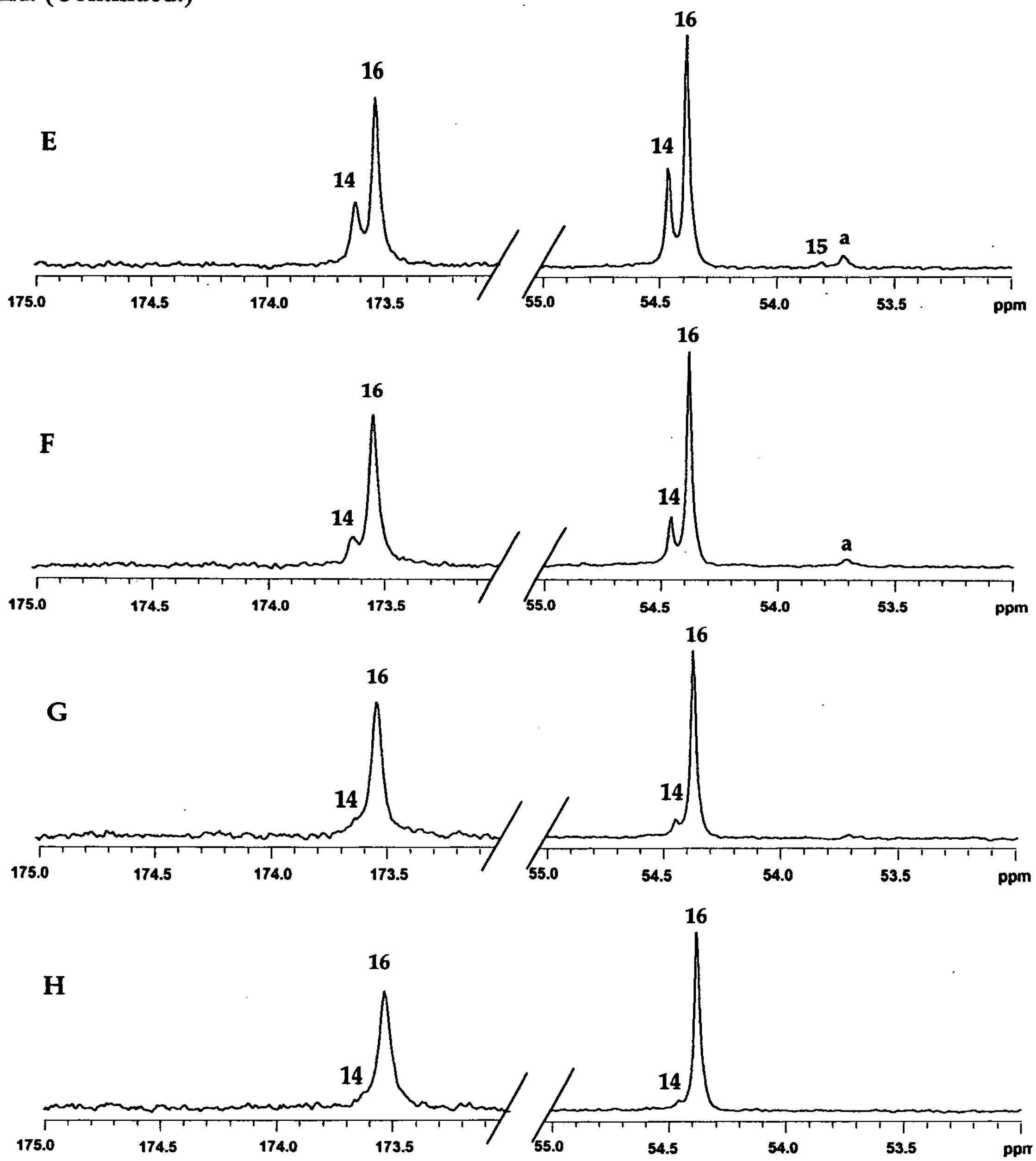
XX. ^{13}C NMR spectra of the lithiation of **13**, **14**, **15** and **16** by LDA (100 MHz, THF-d_8, -90 °C,).





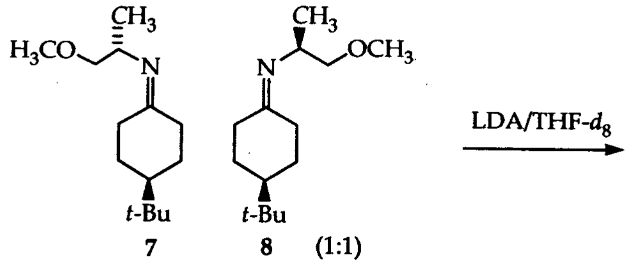
a = product

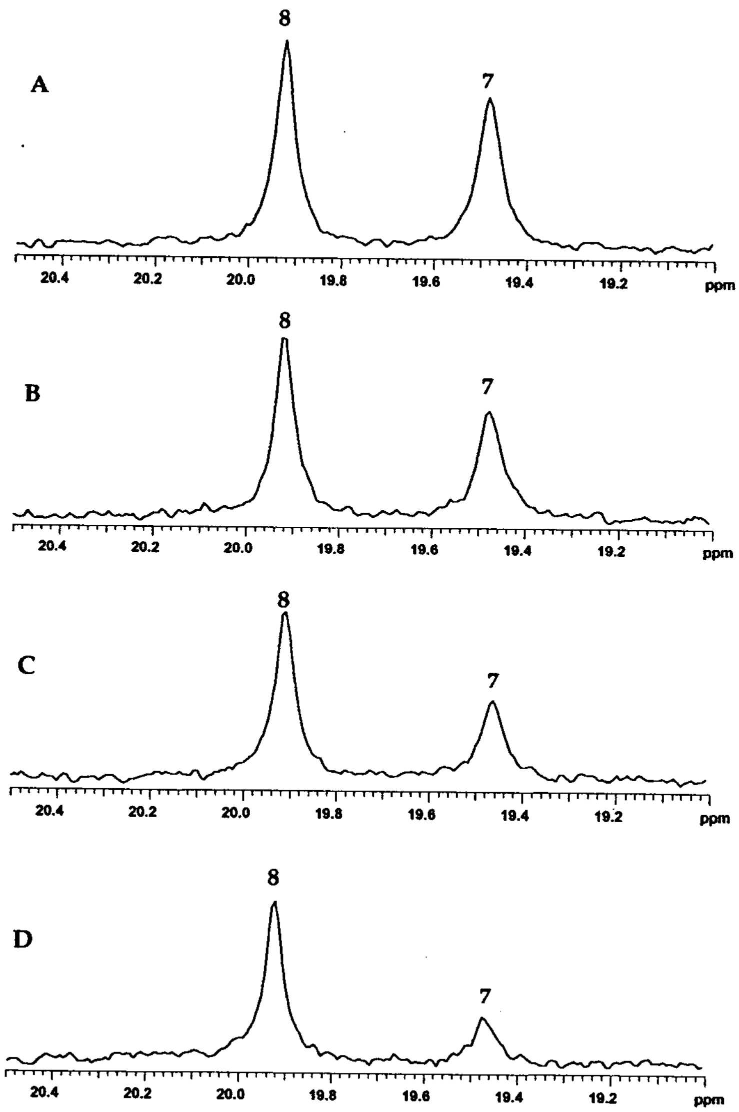
XX. (Continued.)



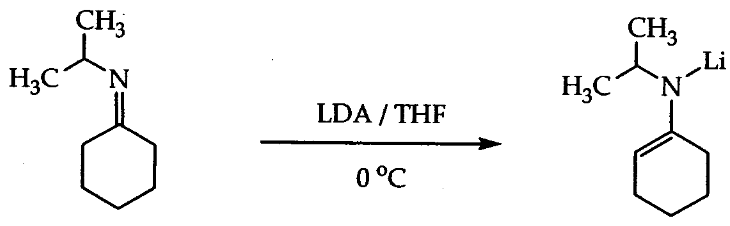
The preparation of the NMR sample is described in section **LXXII-E** (concentrations: imine 0.3 M, LDA 0.33 M). ^{13}C peaks of imines **13-16** (See section **XI** - **XIII** for the assignments.) were followed as the lithiation proceeded. The NMR probe was pre-cooled to -90 °C. The NMR tube was inserted and sequentially warmed up to different temperatures to prompt lithiation and cooled back to -90 °C for spectra taken: **(A)** no warm-up, no reaction compared with a control tube; **(B)** -60 °C x 15 min; **(C)** -30 °C x 5 min; **(D)** -10 °C x 4 min; **(E)** -10 °C x 4 min; **(F)** 0 °C x 5 min; **(G)** 10 °C x 4 min; **(H)** 30 °C x 5 min. Integrations of different peaks were scaled to the THF-d_8 quintet at 67.6 ppm as the internal standard. Qualitatively, the reaction rates of imines are **13** > **14** $\approx$ **15** >> **16**. From **A** to **D**, both **14** and **15** reached half-life while **16** reacted <5%. k_{rel} of **15** was therefore crudely estimated as equal to that of **14**. From **E** to **H**, **16** reacted 15%.

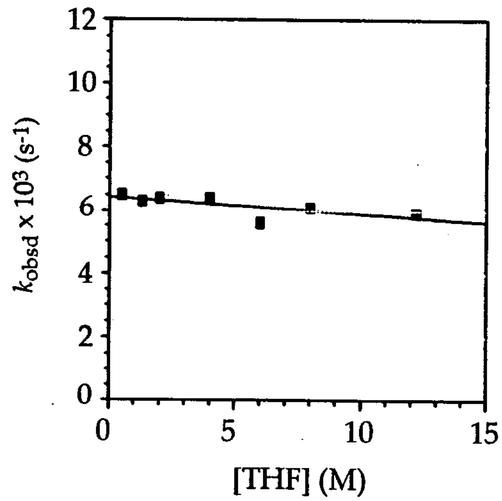
XXI. ^{13}C NMR spectra of the lithiation of **7** and **8** by LDA (100 MHz, THF-d_8, -90 °C,).





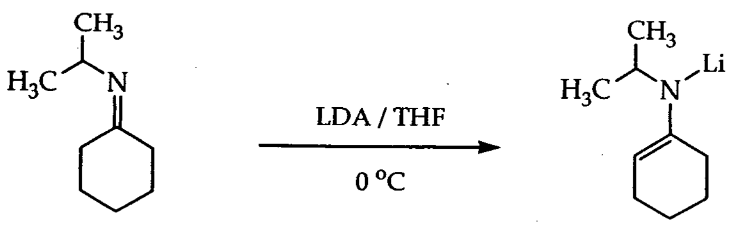
The lithiation of 1:1 mixture of **7** and **8** (0.3 M) by LDA (1.1 equiv) in THF-d_8 was carried out in the same manner as described in section **XX**. There is no strong evidence in the 2D NMR experiments (section **VII**) to distinguish between the two diastereomers. The isomer which reacts faster was assigned to the one which facilitates a chelation-assisted axial deprotonation, **7**. The other isomer was then assigned to **8**. By IR kinetics, the relative rate of **7** to **8** at -40 °C is 5.4:1.



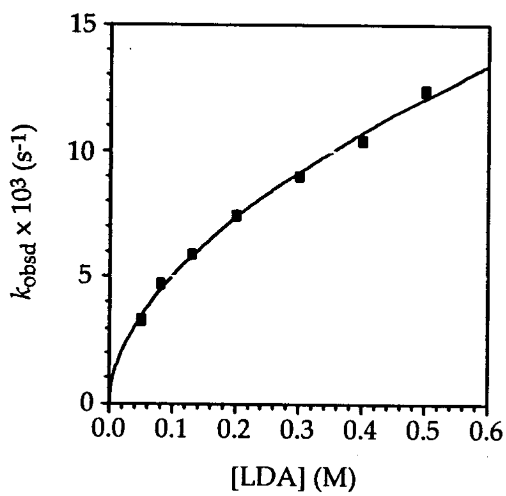


XXII. Plot of k_{obsd} vs free [THF] in hexane cosolvent for the deprotonation of **2** (0.005 M) by LDA (0.13 M) at 0 °C. The curve depicts an unweighted least-squares fit to k_{obsd} = k[THF] + k' (k = -5 ± 3 x 10^{-5}, k' =6.4 ± 0.2 x 10^{-3}).

[THF] (M)	k_{obsd} x 10^3 (s^{-1})
0.50	6.5(1)
1.30	6.3(3)
2.00	6.4(1)
4.00	6.4(1)
6.00	5.6(1)
8.00	6.1(1)
12.2	5.9(2)

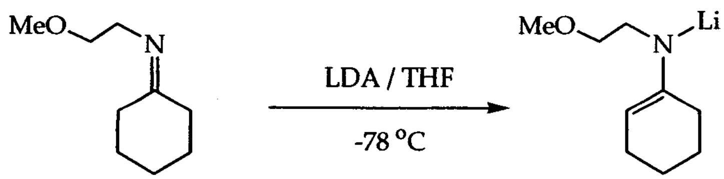


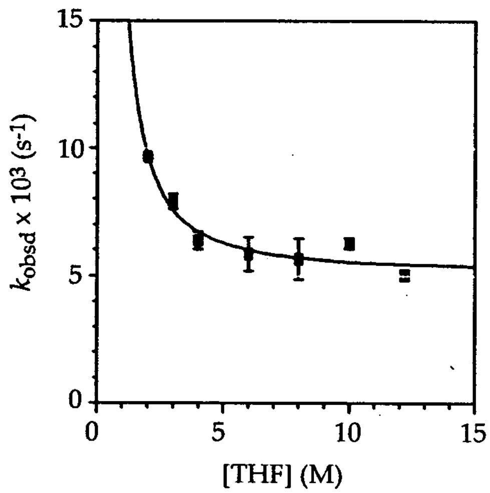
2 Li - 2



XXIII. Plot of k_{obsd} vs [LDA] in neat THF (12.3 M) for the lithiation of **2** (0.005 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[LDA]^n$ ($k = 1.76 \pm 0.05 \times 10^{-2}$, $n = 0.54 \pm 0.02$).

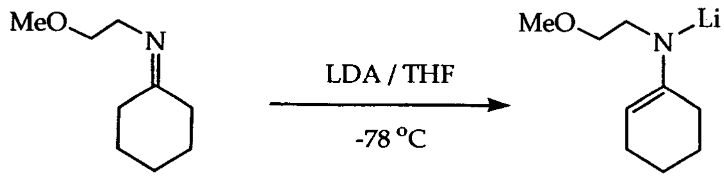
[LDA] (M)	$k_{obsd} \times 10^3$ (s^{-1})
0.050	3.3(1)
0.080	4.7(2)
0.130	5.9(2)
0.200	7.4(4)
0.300	9.0(4)
0.400	10.4(9)
0.500	12.4(7)



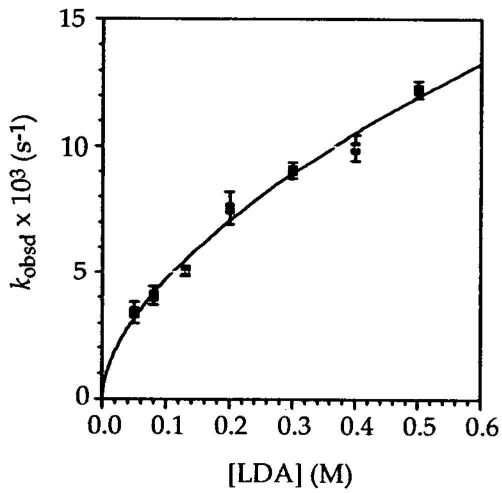


XXIV. Plot of k_{obsd} vs free [THF] in hexane cosolvent for the lithiation of **3** (0.005 M) by LDA (0.13 M) at -78 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[THF]^n + k'$ ($k = 1.4 \pm 0.5 \times 10^{-2}$, $k' = 5.2 \pm 0.6 \times 10^{-3}$, $n = -1.6 \pm 0.6$).

[THF] (M)	k_{obsd} x 10^3 (s^{-1})		Average k_{obsd} x 10^3 (s^{-1})
2.00	9.6(8)	9.7(5)	9.7
3.00	7.7(9)	8.1(3)	7.9
4.00	6.6(2)	6.1(3)	6.3
6.00	6.3(3)	5.4(2)	5.9
8.00	5.1(1)	6.2(2)	5.7
10.0	6.1(4)	6.4(2)	6.2
12.2	4.9(2)	5.2(1)	5.1

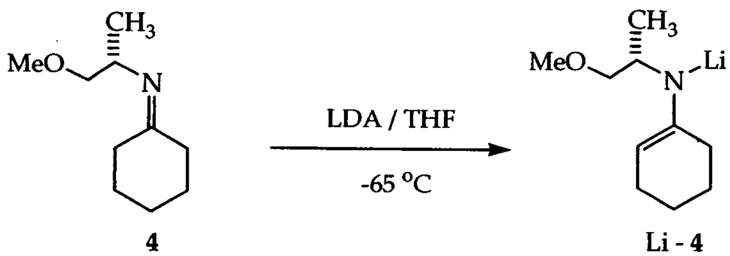


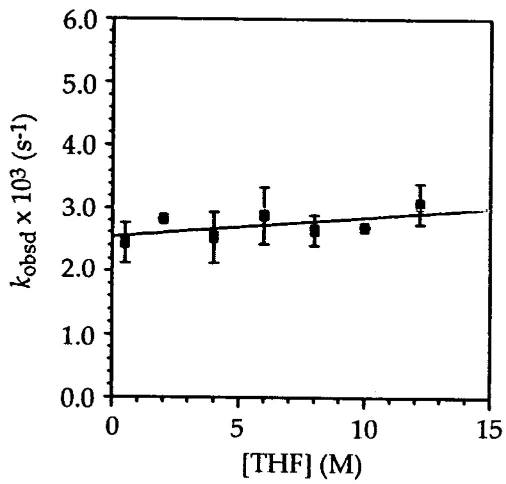
3 Li - 3



XXV. Plot of k_{obsd} vs [LDA] in neat THF (12.3 M) for the lithiation of **3** (0.005 M) at -78 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[\text{LDA}]^n$ ($k = 1.78 \pm 0.08 \times 10^{-2}$, $n = 0.58 \pm 0.04$).

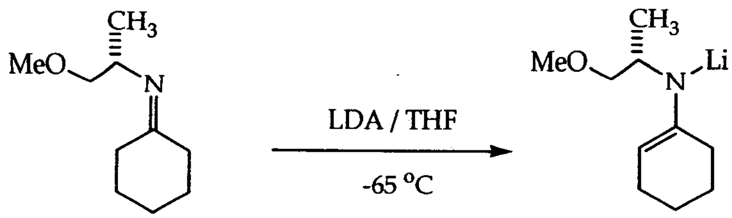
[LDA] (M)	$k_{obsd} \times 10^3$ (s^{-1})		Average $k_{obsd} \times 10^3$ (s^{-1})
0.050	3.7(3)	3.10(8)	3.4
0.080	4.31(8)	3.8(2)	4.1
0.130	4.9(2)	5.2(1)	5.1
0.200	7.1(3)	8.0(5)	7.6
0.300	8.8(4)	9.3(2)	9.1
0.400	9.6(9)	10.3(9)	10.0
0.500	12.5(8)	12.0 (5)	12.3



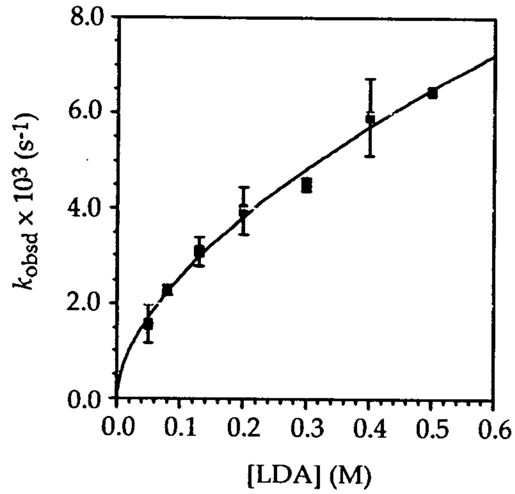


XXVI. Plot of k_{obsd} vs free [THF] in hexane cosolvent for the lithiation of **4** (0.005 M) by LDA (0.13 M) at -65 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[THF] + k'$ ($k = 3 \pm 2 \times 10^{-5}$, $k' = 2.5 \pm 0.1 \times 10^{-3}$).

[THF] (M)	k_{obsd} x 10^3 (s^{-1})		Average k_{obsd} x 10^3 (s^{-1})
0.50	2.66(6)	2.22(7)	2.44
2.00	2.82(8)	2.81(9)	2.82
4.00	2.82(6)	2.24(6)	2.53
6.00	2.55(6)	3.20(7)	2.88
8.00	2.81(5)	2.47(7)	2.64
10.0	2.67(5)	2.69(7)	2.68
12.2	3.1(1)	2.83(7)	3.0

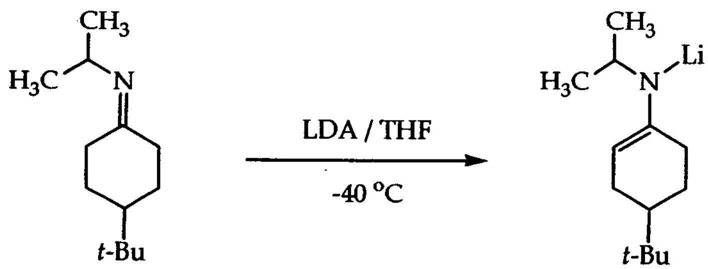


4 Li - 4

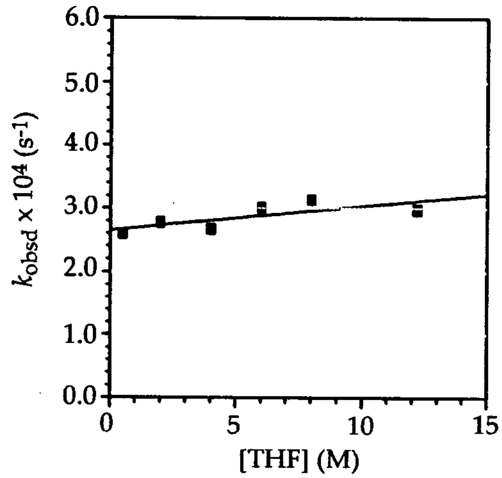


XXVII. Plot of k_{obsd} vs [LDA] in neat THF (12.3 M) for the lithiation of 4 (0.005 M) at -65 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[\mathrm{LDA}]^n$ ($k = 9.8 \pm 0.4 \times 10^{-3}$, $n = 0.59 \pm 0.03$).

[LDA] (M)	$k_{obsd} \times 10^3$ (s^{-1})		Average $k_{obsd} \times 10^3$ (s^{-1})
0.050	1.27(2)	1.87(2)	1.57
0.080	2.22(4)	2.36(5)	2.29
0.130	3.1(1)	2.83(7)	3.0
0.200	3.6(1)	4.3(1)	4.0
0.300	4.6(2)	4.4(1)	4.5
0.400	6.3(3)	5.4(2)	5.9
0.500	6.4(3)	6.5(3)	6.5



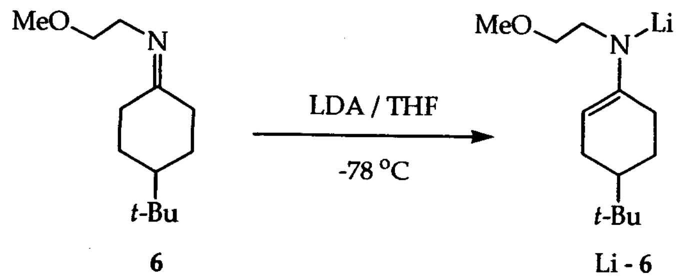
5 → **Li - 5**

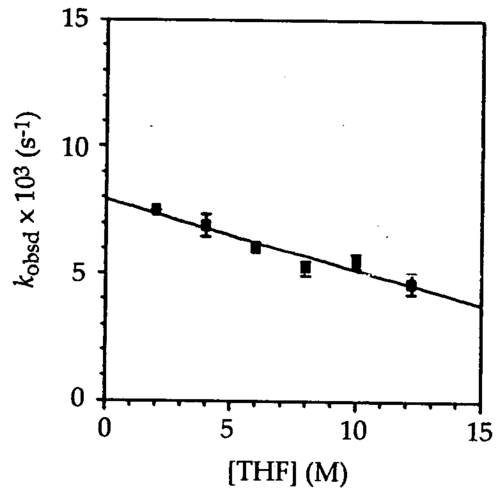


XXVIII. Plot of k_{obsd} vs free [THF] in hexane cosolvent for the lithiation of **5** (0.005 M) by LDA (0.13 M) at -40 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[\mathrm{THF}] + k'$ ($k = 4 \pm 2 \times 10^{-6}$, $k' = 2.7 \pm 0.2 \times 10^{-4}$).

[THF] (M)	$k_{obsd} \times 10^4$ (s^{-1})
0.50	2.59(3)
2.00	2.77(2)
4.00	2.67(3)
6.00	3.01(2)
8.00	3.13(2)
12.2	2.97[a]

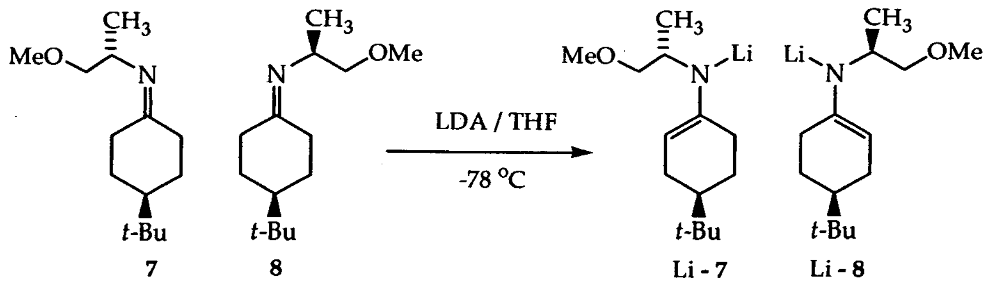
[a]Average of two runs.

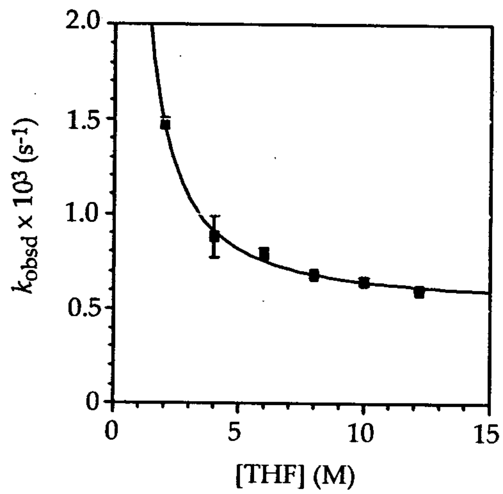




XXIX. Plot of k_{obsd} vs free [THF] in hexane cosolvent for the lithiation of **6** (0.005 M) by LDA (0.13 M) at -78 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[THF] + k'$ ($k = -2.8 \pm 0.4 \times 10^{-4}$, $k' = 7.9 \pm 0.3 \times 10^{-3}$).

[THF] (M)	$k_{obsd} \times 10^3$ (s^{-1})		Average $k_{obsd} \times 10^3$ (s^{-1})
2.00	7.5(9)	7.5(4)	7.5
4.00	7.2(1)	6.6(3)	6.9
6.00	6.2(1)	5.9(3)	6.1
8.00	5.0(2)	5.4(2)	5.2
10.0	5.3(5)	5.7(2)	5.5
12.2	4.9(1)	4.3(2)	4.6

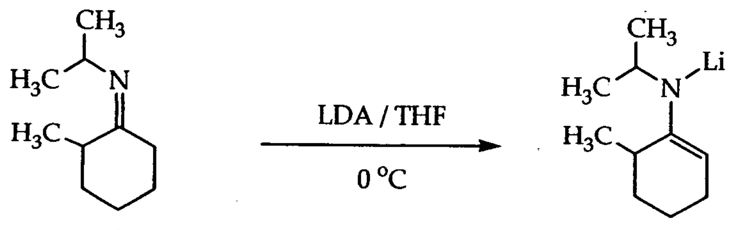


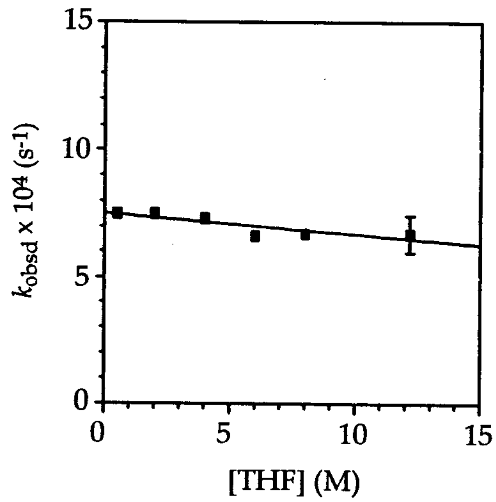


XXX. Plot of k_{obsd}[a] vs free [THF] in hexane cosolvent for the lithiation of **7** and **8** (0.005 M)[b] by LDA (0.13 M) at -78 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[\mathrm{THF}]^n + k'$ ($k = 2.4 \pm 0.3 \times 10^{-3}$, $k' = 5.3 \pm 0.5 \times 10^{-4}$, $n = -1.3 \pm 0.2$).

[THF] (M)	$k_{obsd} \times 10^3$ (s^{-1})		Average $k_{obsd} \times 10^3$ (s^{-1})
2.00	1.50(1)	1.46(3)	1.48
4.00	0.80(2)	0.96(2)	0.88
6.00	0.81(2)	0.77(1)	0.79
8.00	0.68(2)	0.685(9)	0.68
10.0	0.63(1)	0.66(1)	0.64
12.2	0.603(9)	0.597(7)	0.60

[a]Each k_{obsd} is the average rate constant of two isomers. [b]Total concentration of **7** and **8**.

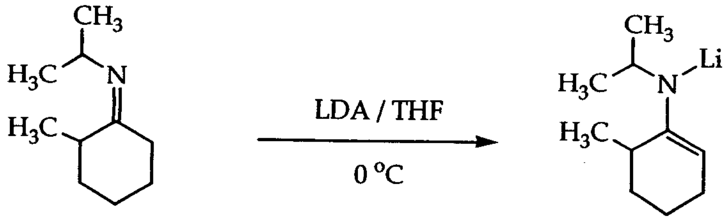




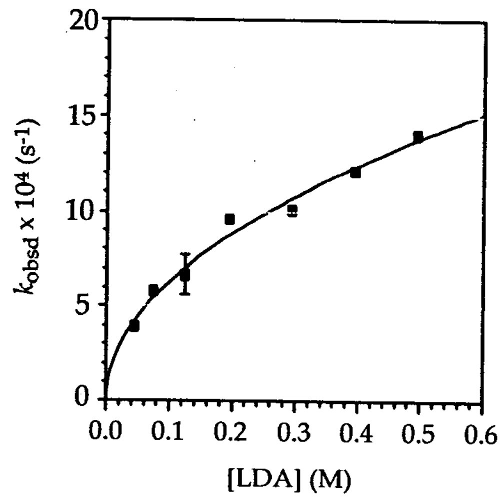
XXXI. Plot of k_{obsd} vs free [THF] in hexane cosolvent for the lithiation of **9** (0.005 M)[a] by LDA (0.124 M) at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[THF] + k'$ ($k = -8 \pm 3 \times 10^{-6}$, $k' = 7.5 \pm 0.2 \times 10^{-4}$).

[THF] (M)	$k_{obsd} \times 10^4$ (s^{-1})
0.50	7.5(2)
2.00	7.5(1)
4.00	7.3(5)
6.00	6.6(2)
8.00	6.7(1)
12.2	6.7[b]

[a]Imine **9** is generated in situ by alkylating lithiated **2** (Li-**2** 0.006 M) with CH_3I (0.005 M) at 0 °C. [b]Average of two runs.



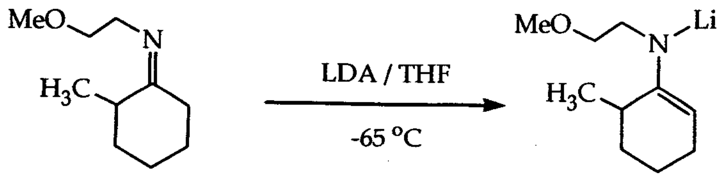
9 **Li - 9**

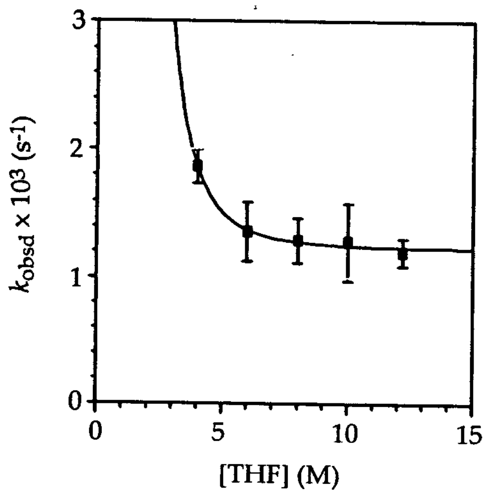


XXXII. Plot of k_{obsd} vs [LDA] in neat THF (12.3 M) for the lithiation of **9** (0.005 M)[a] at 0 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[\mathrm{LDA}]^n$ ($k = 1.9 \pm 0.1 \times 10^{-3}$, $n = 0.49 \pm 0.04$).

[LDA] (M)	k_{obsd} x 10^4 (s^{-1})
0.044	3.9(1)
0.074	5.8(1)
0.124	6.7[b]
0.194	9.6(3)
0.294	10.1(6)
0.394	12.1(5)
0.494	14(2)

[a]Imine **9** is generated in situ by alkylating lithiated **2** (Li-**2** 0.006 M) with CH_3I (0.005 M) at 0 °C. [b]Average of two runs.





XXXIII. Plot of k_{obsd} vs free [THF] in hexane cosolvent for the lithiation of **11** (0.005 M)[a] by LDA (0.124M) at -65 °C. The curve depicts an unweighted least-squares fit to $k_{obsd} = k[THF]^n + k'$ ($k = 1 \pm 1 \times 10^{-1}$, $k' = 1.22 \pm 0.04 \times 10^{-3}$, $n = -3.6 \pm 0.9$).

[THF] (M)	k_{obsd} x 10^3 (s^{-1})		Average k_{obsd} x 10^3 (s^{-1})
4.00[b]	1.96(4)	1.77(4)	1.87
6.00	1.52(3)	1.19(2)	1.36
8.00	1.16(2)	1.41(5)	1.29
10.0	1.06(3)	1.49(7)	1.28
12.2	1.12(2)	1.27(2)	1.20

[a]Imine **11** is generated in situ by alkylating lithiated **3** (Li-**3** 0.006 M) with CH_3I (0.005 M) at -65 °C. [b]Reactions at lower [THF] (< 4M) are heterogeneous (data not shown).