Figure S22. ^{1}H NMR spectrum for **7** in $CDCl_3$ at 60 °C.

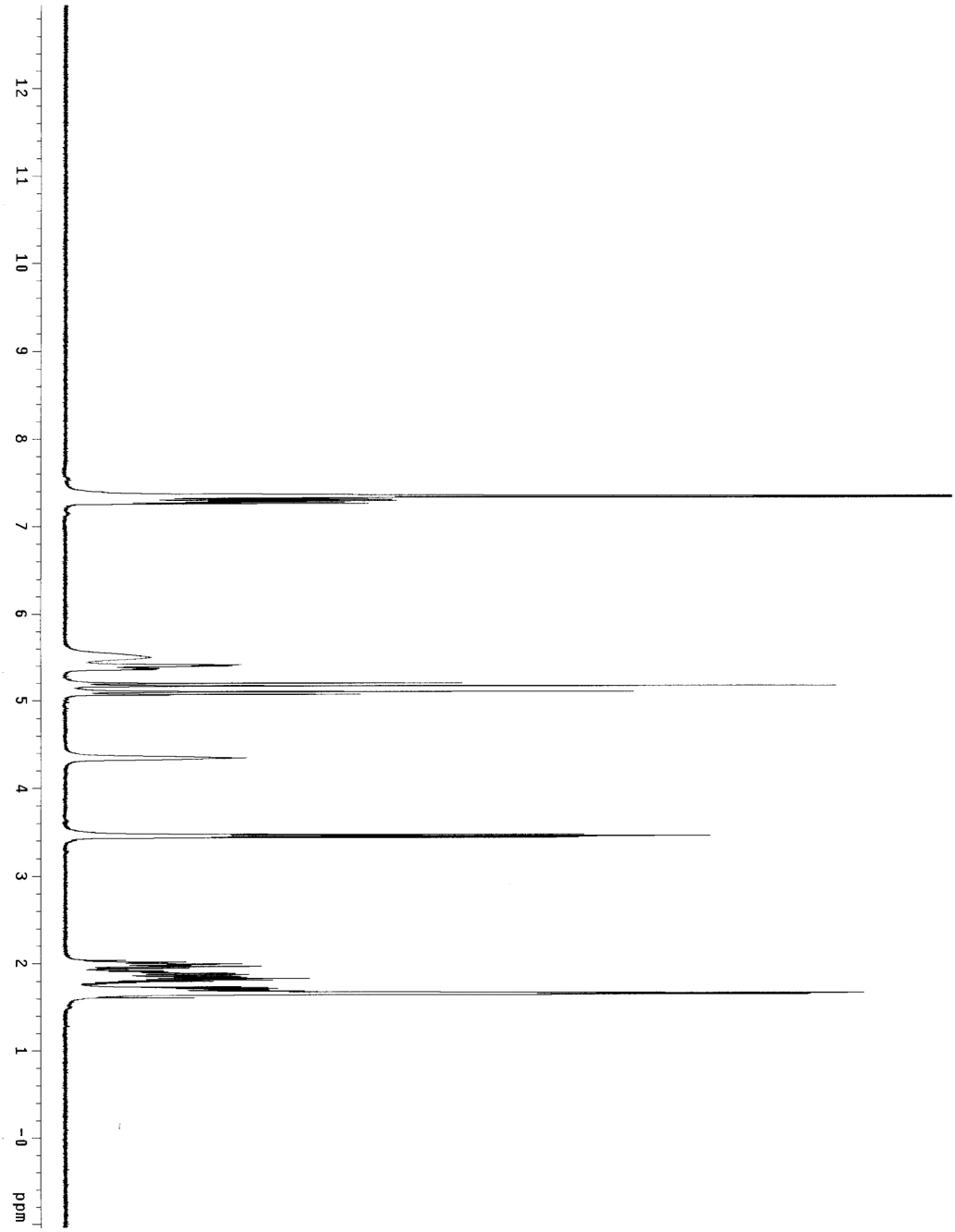


Figure S23. ^{13}C NMR spectrum for **7** in $CDCl_3$ at 60 ˚C.

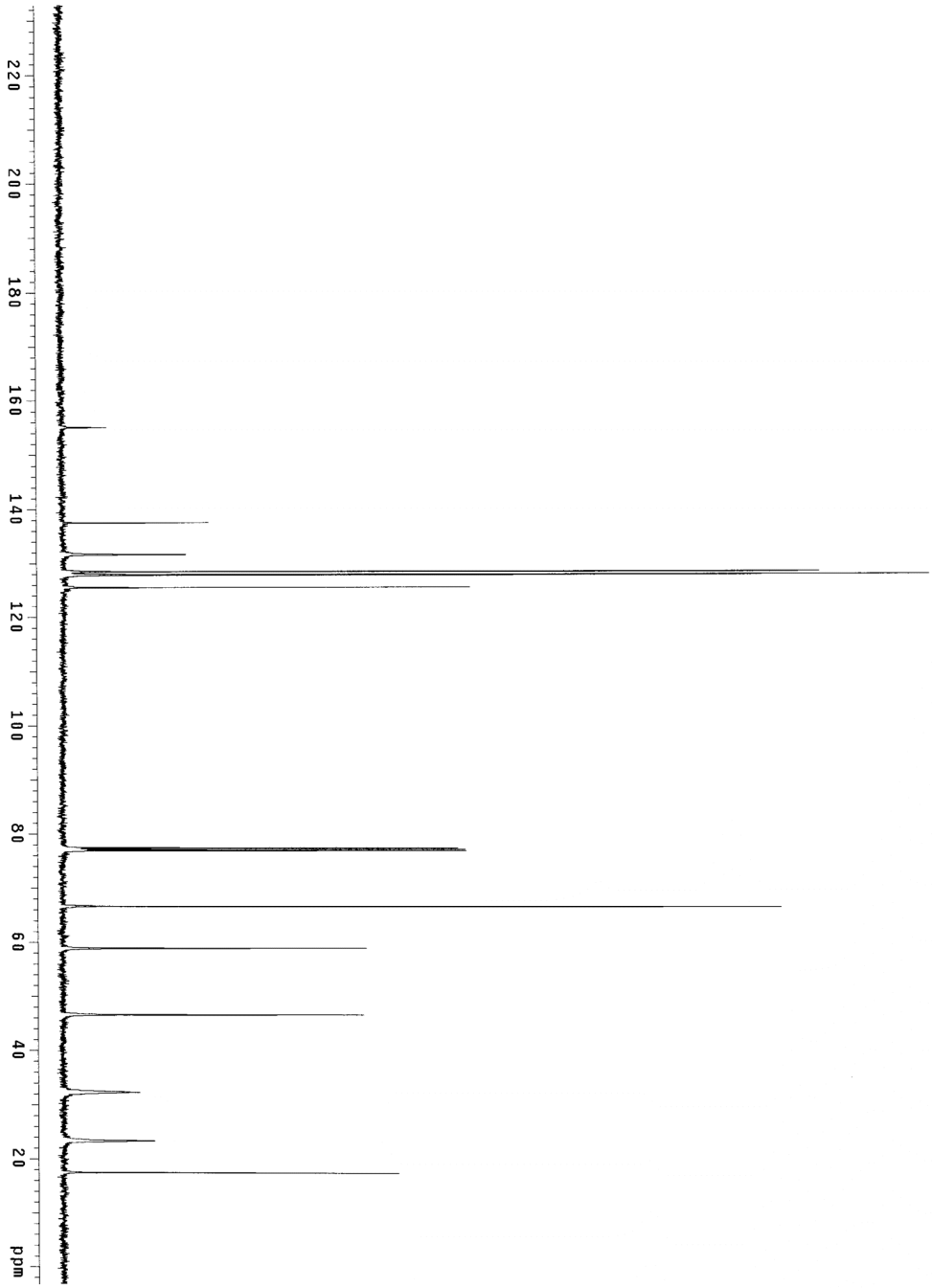


Figure S24. ^{1}H NMR spectrum of (*E*)-**9** in $CDCl_3$

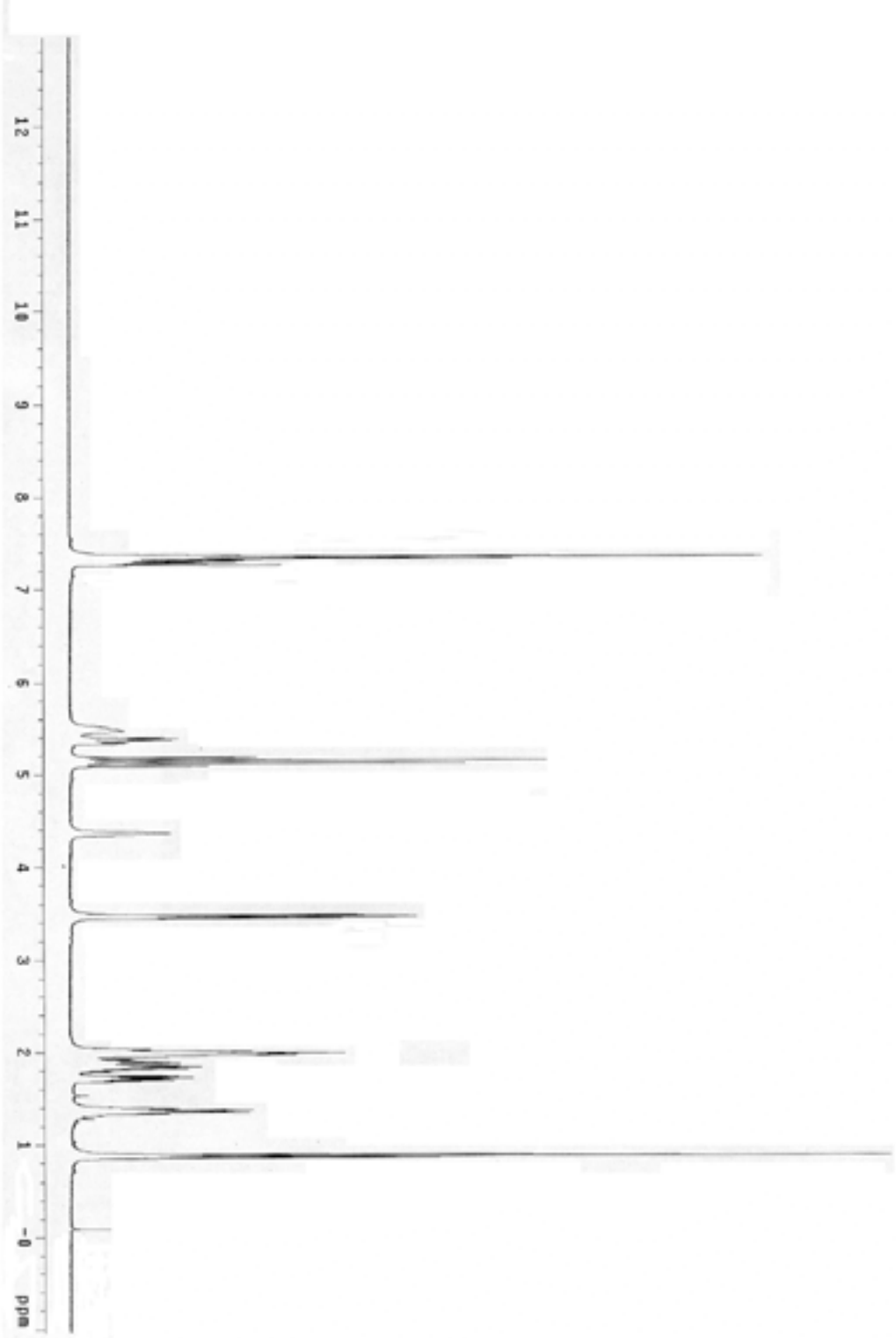


Figure S25. ^{13}C NMR spectrum of (*E*)-**9** in $CDCl_3$

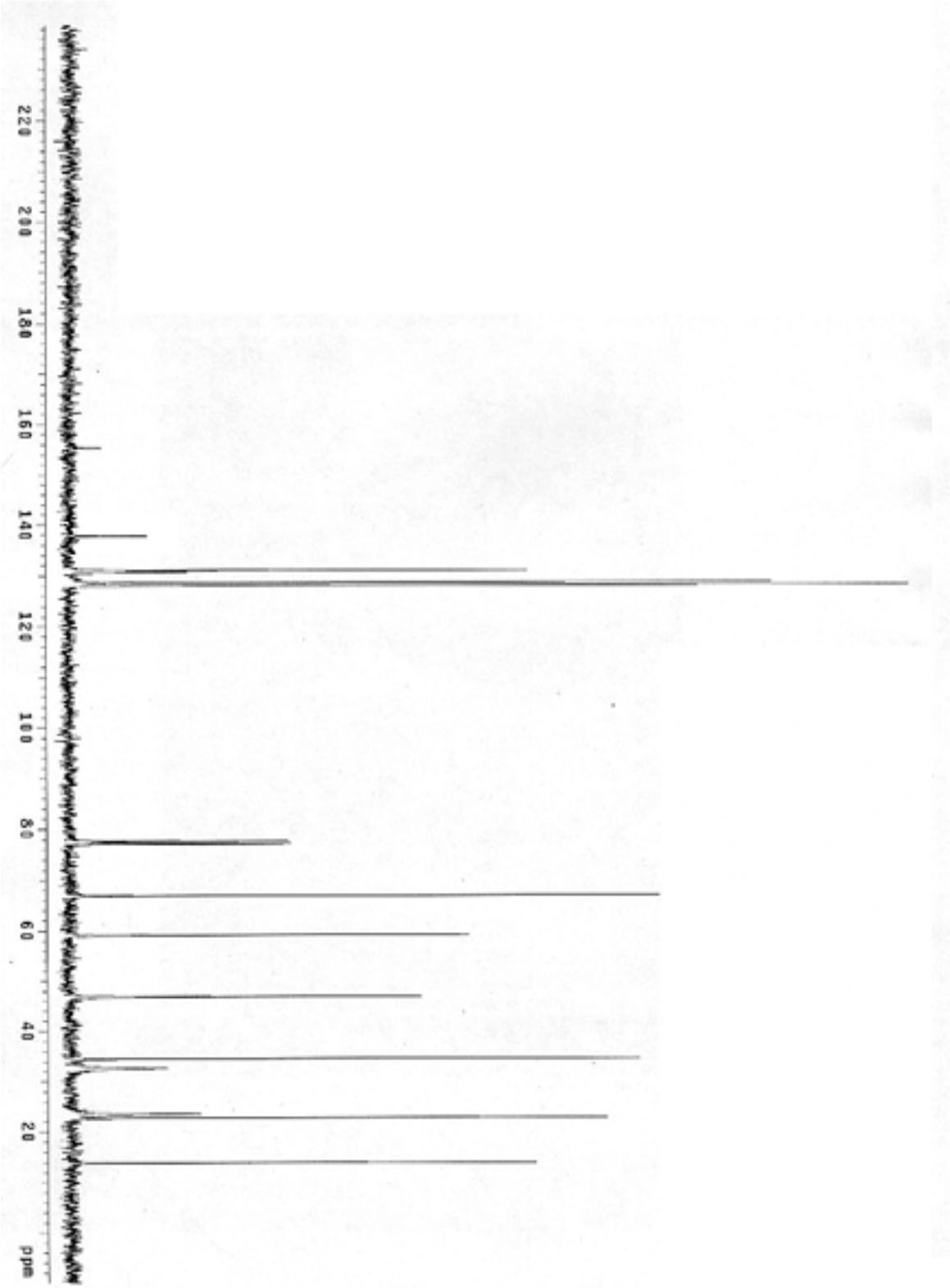


Figure S26. Chiral HPLC traces for *rac*-**9** (left trace) and (*R*)-**9** (right trace, 74% ee).

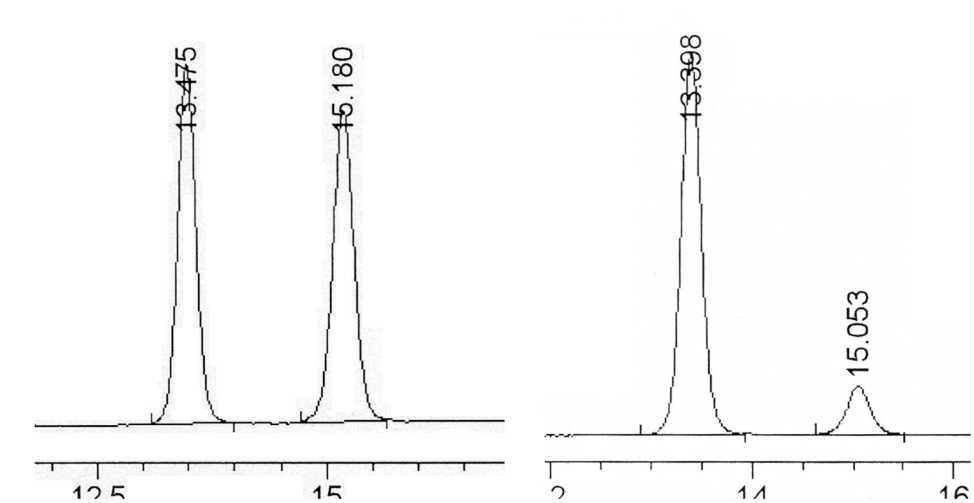


Figure S27. Chiral HPLC trace for (*R*),(*E*)-**9** (left trace) and for a 15:1 mixture of (*S*),(*Z*)-**9** and (*S*),(*E*)-**9** (right trace).

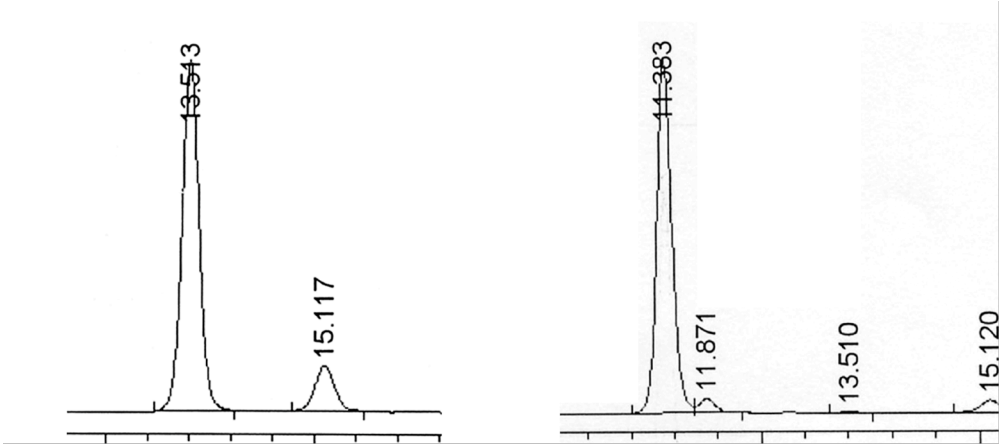


Figure S28. ^{1}H NMR spectrum of **S23**.

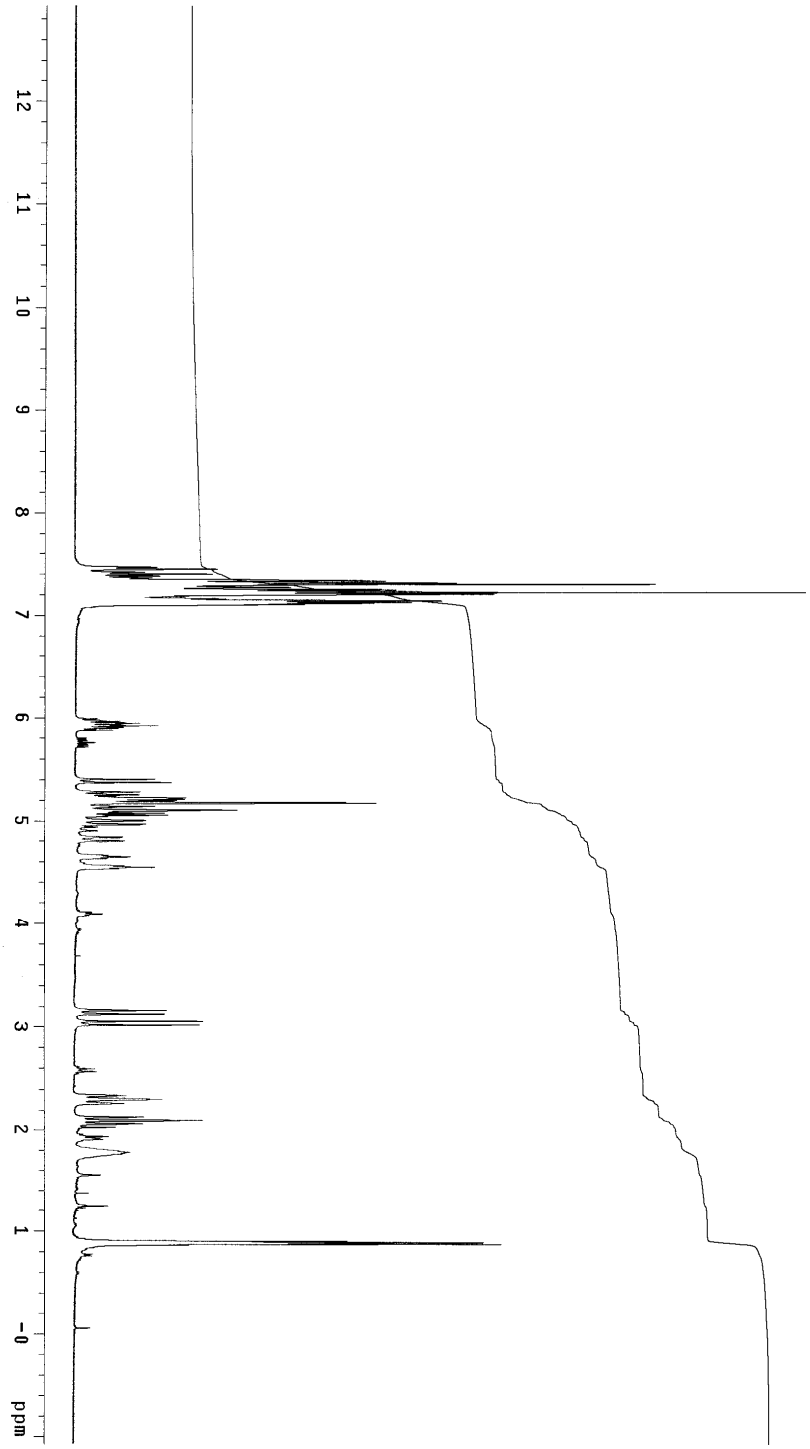


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of **S23**.

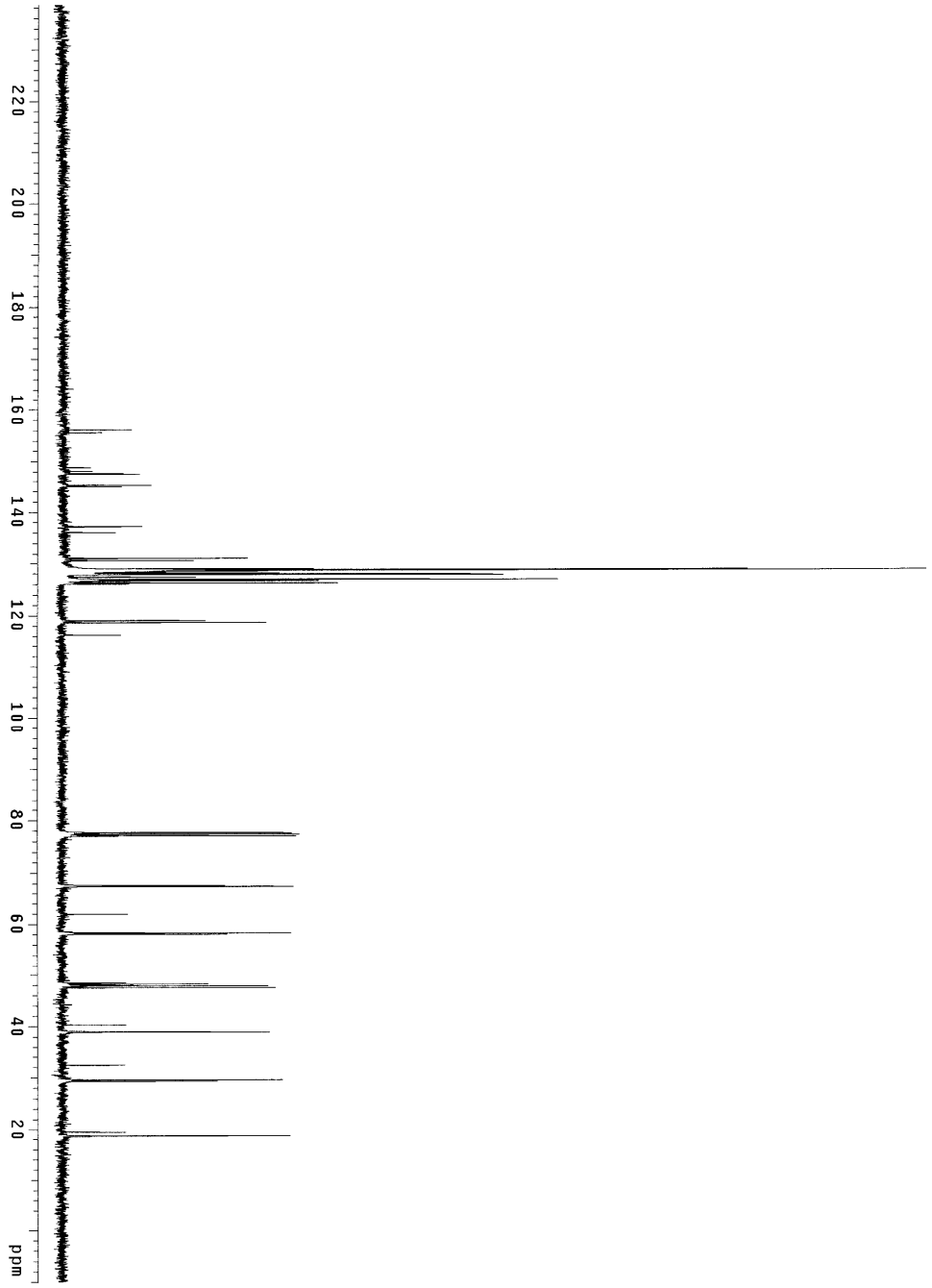


Figure S30. 800 MHz ^{1}H-^{1}H NOESY of **S23**.

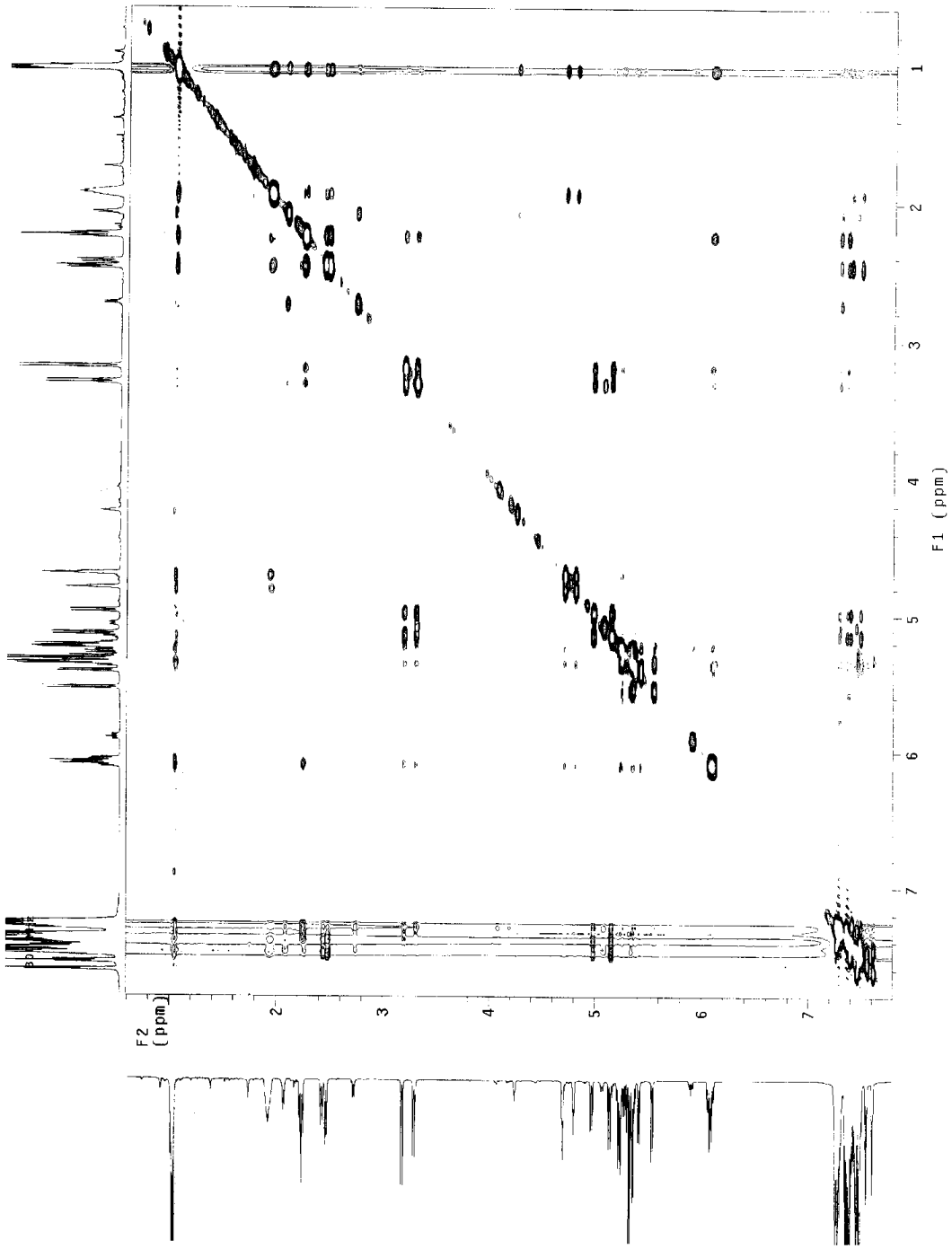


Figure S31. ^{1}H NMR spectrum of **S33**.

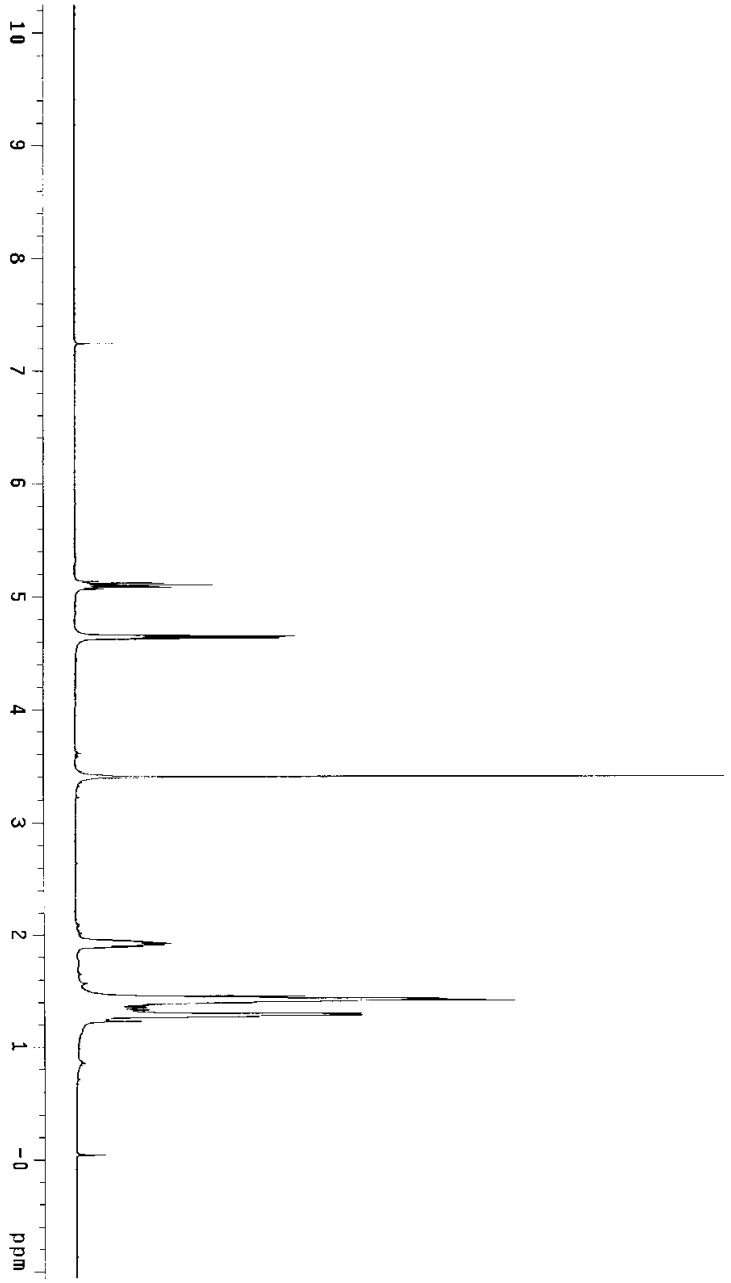


Figure S32. ^{13}C NMR spectrum of **S34**.

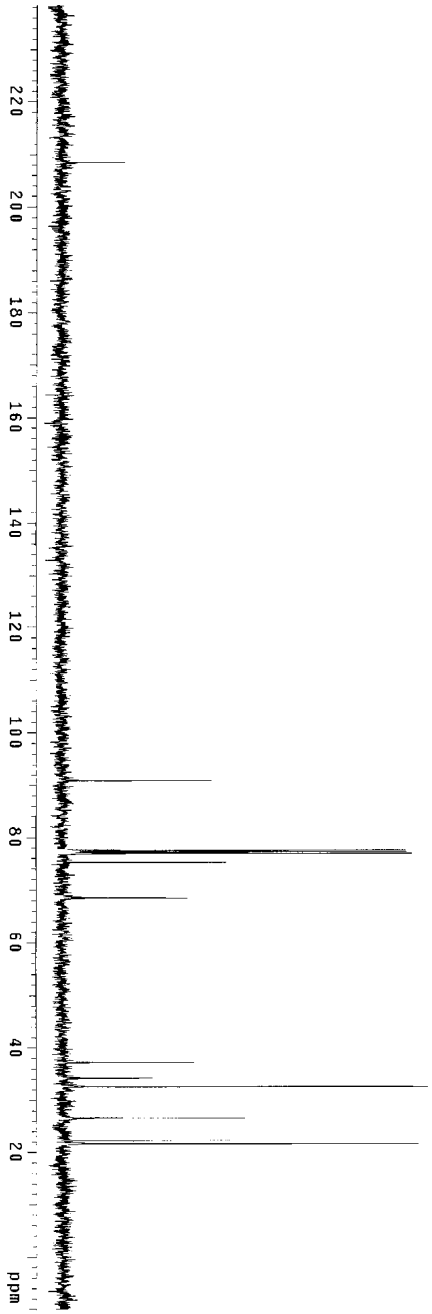


Figure S33. Chiral HPLC traces for *rac*-**17b** (left trace) and (*R*)-**17b** (right trace, 94 ± 3 % ee).

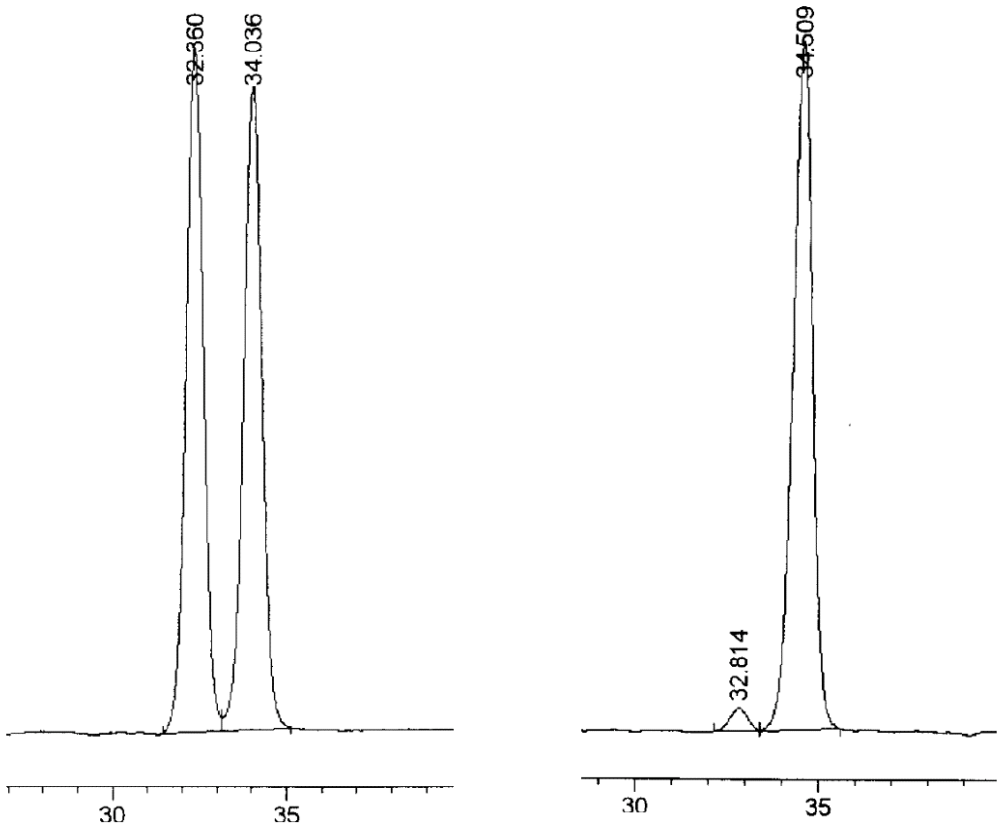


Figure S34. ^{1}H NMR spectrum of **S35**.

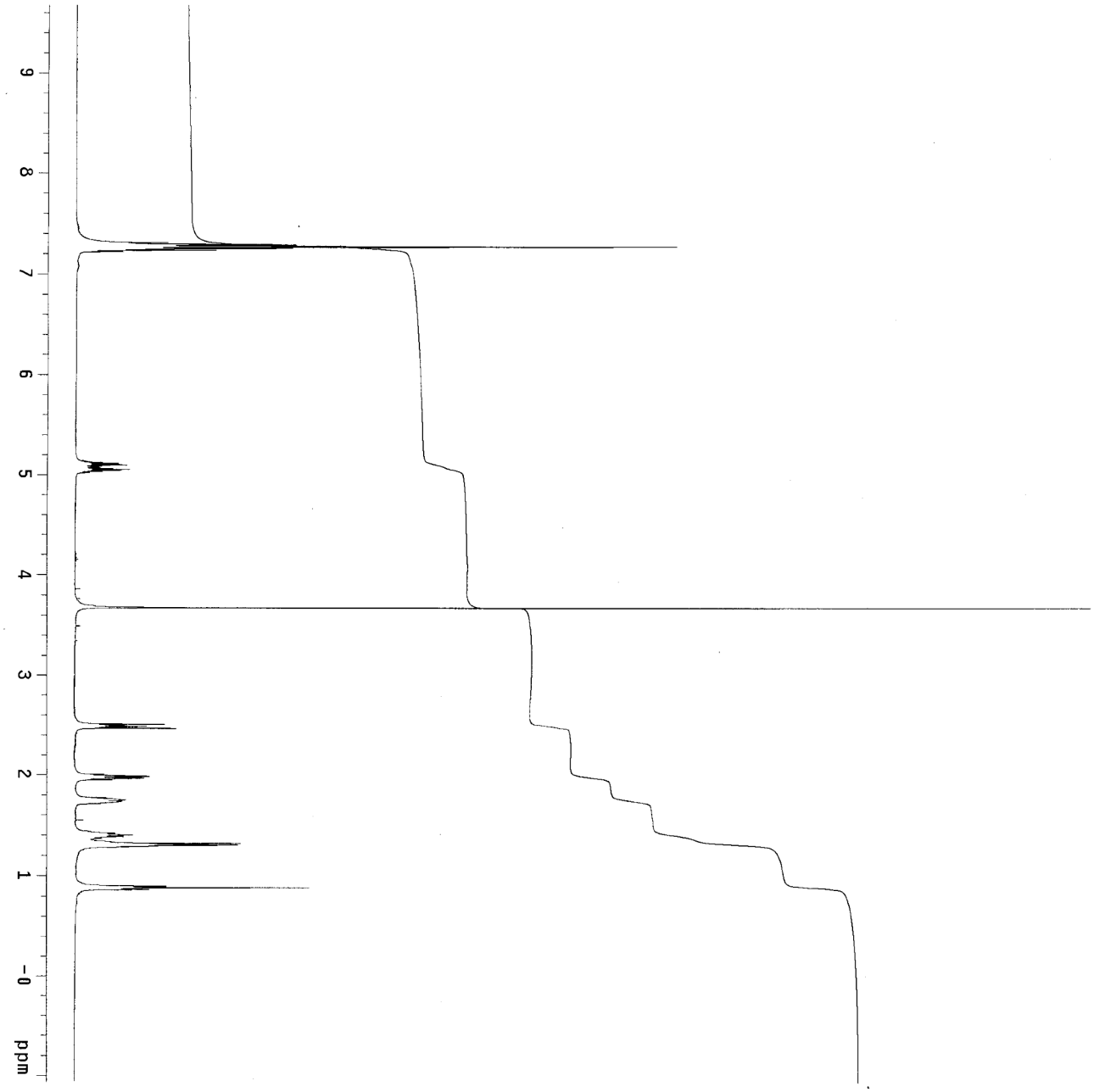


Figure S35. $^{13}C\ \{^{1}H\}$ NMR spectrum of **S35**.

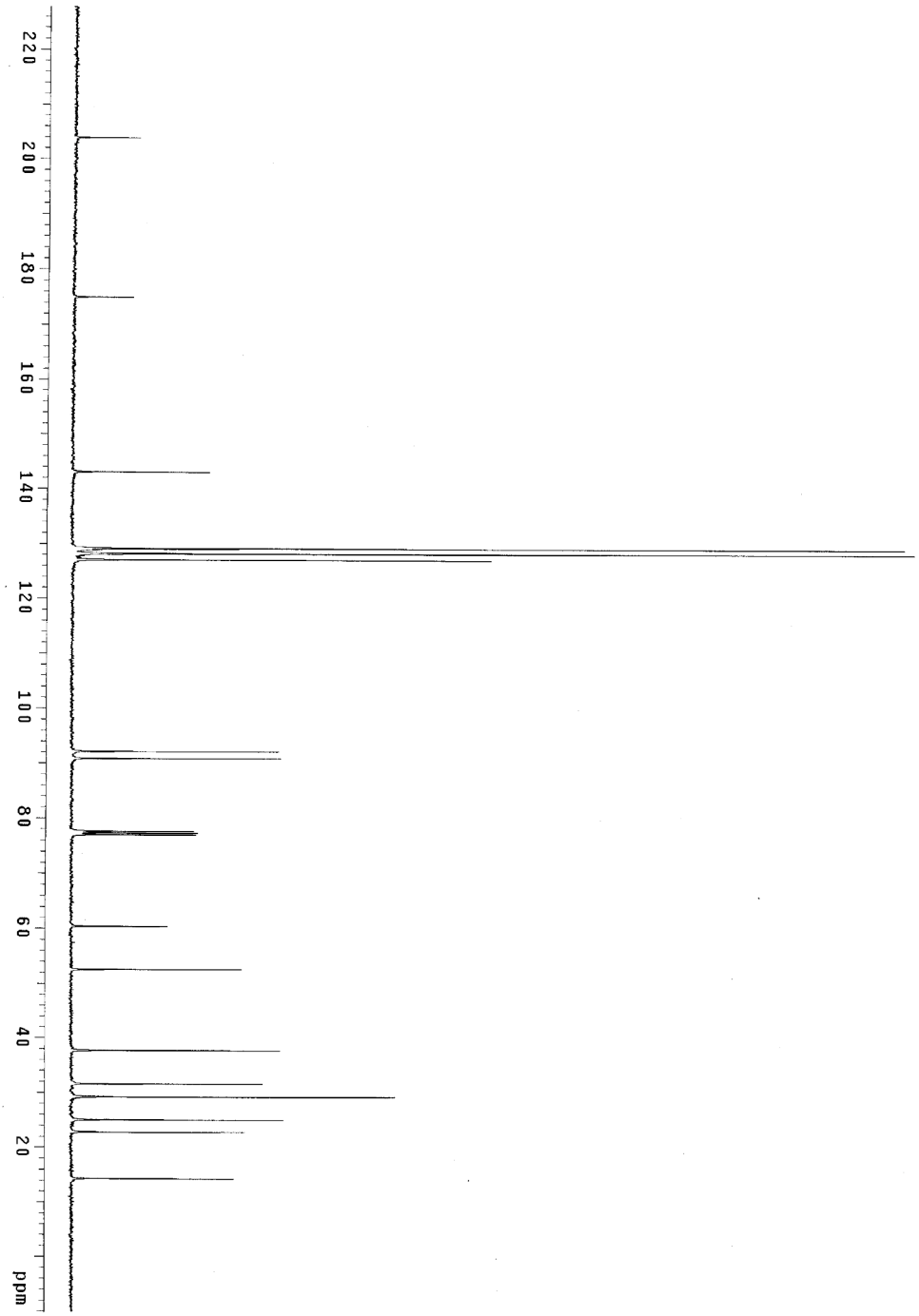


Figure S36. ^{1}H NMR spectrum of **19**

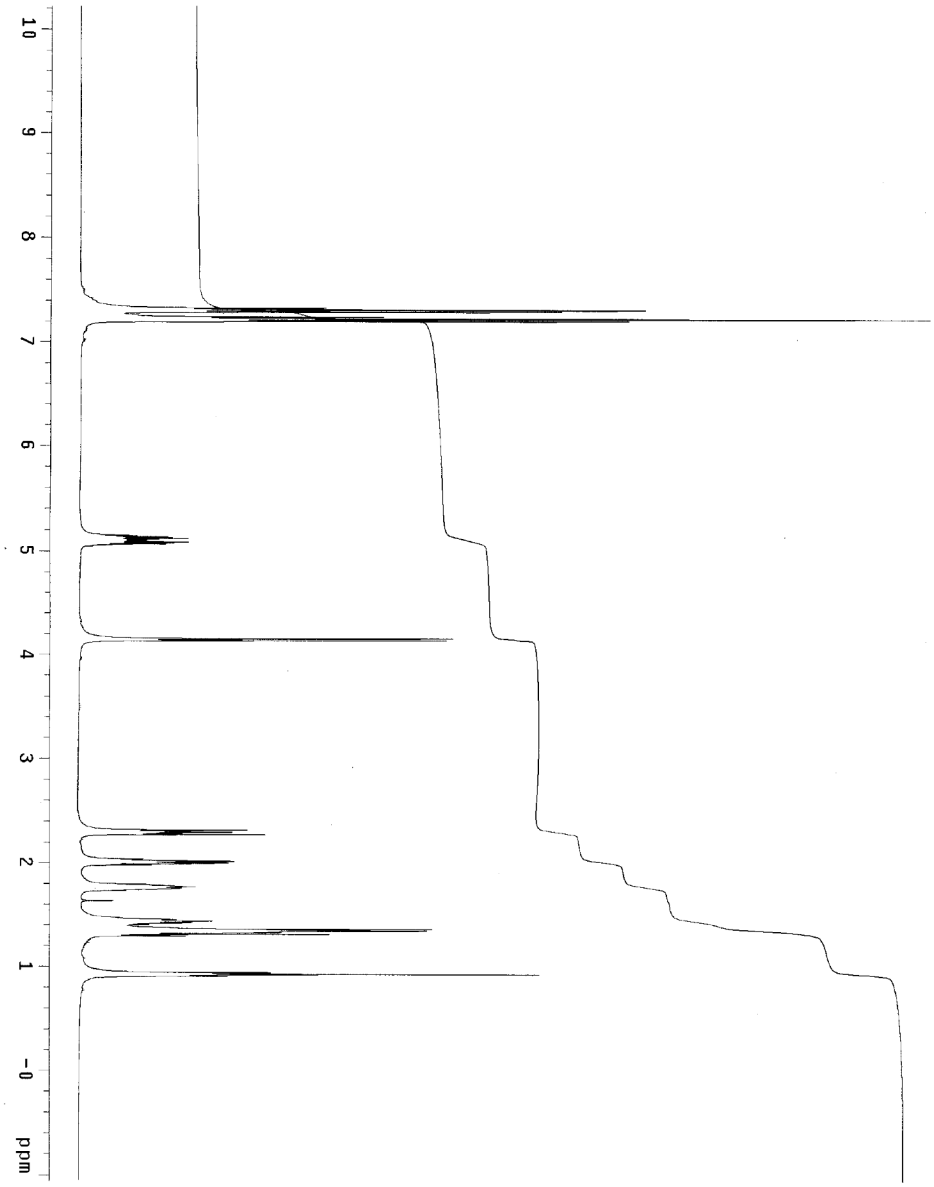


Figure S37. $^{13}C\ \{^{1}H\}$ NMR spectrum of **19**.

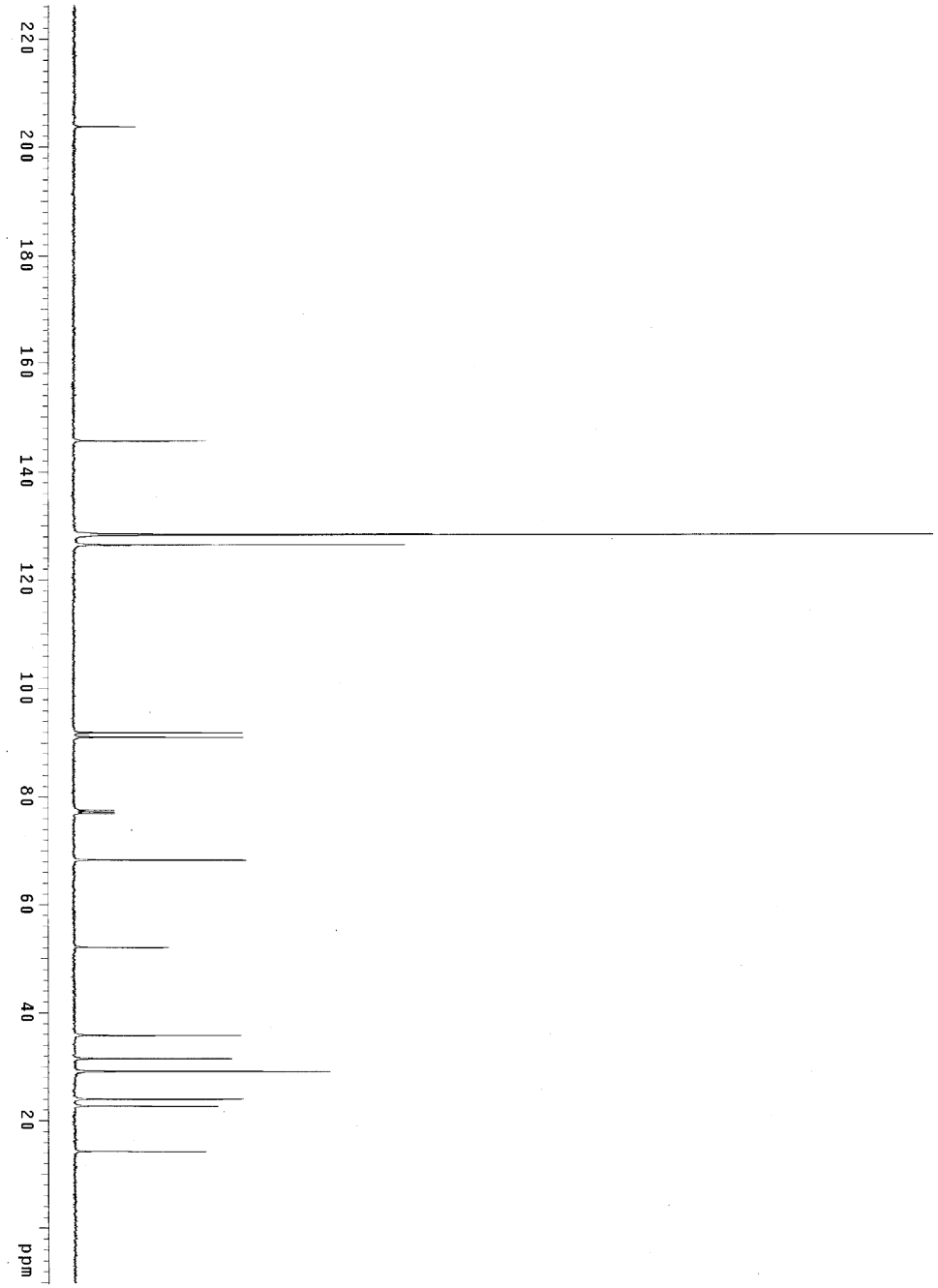


Figure S38. ^{1}H NMR spectrum of 3-methyl-5,5-diphenyl-2-vinyl-tetrahydropyran.

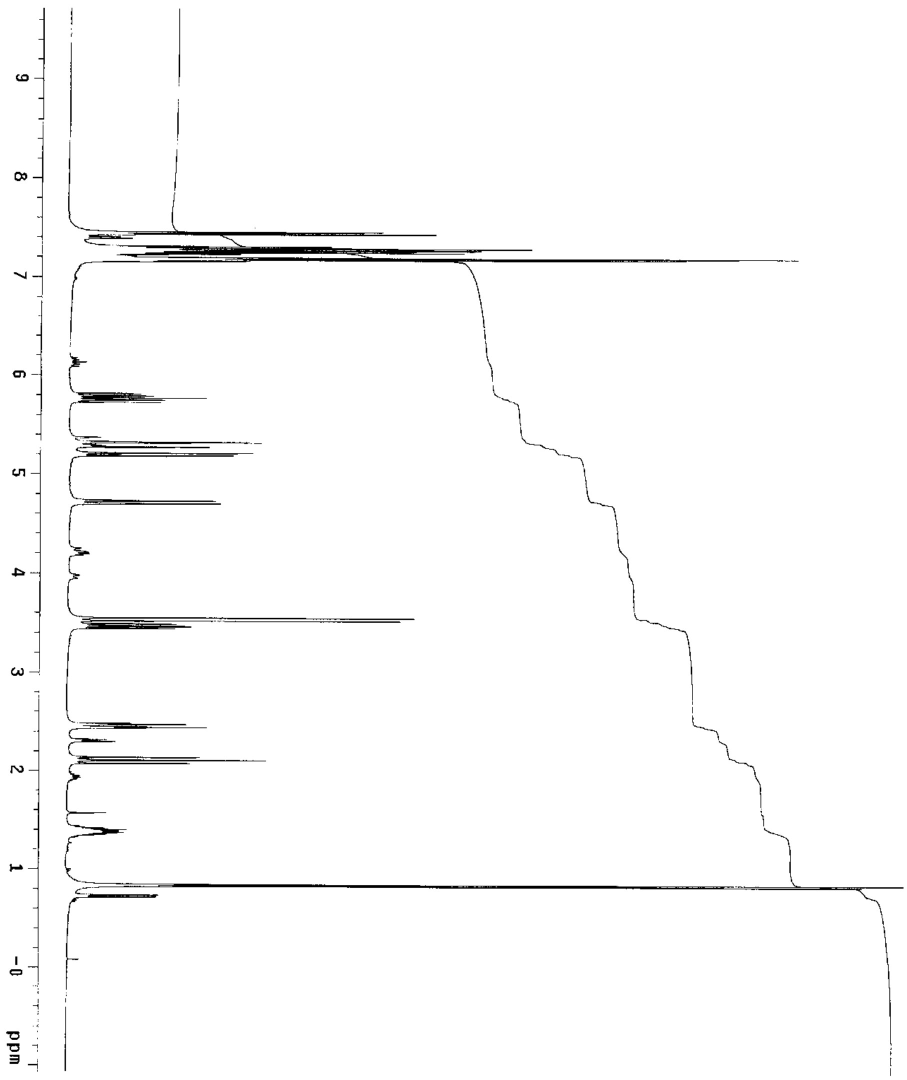


Figure S39. ^{13}C NMR spectrum of 3-methyl-5,5-diphenyl-2-vinyl-tetrahydropyran.

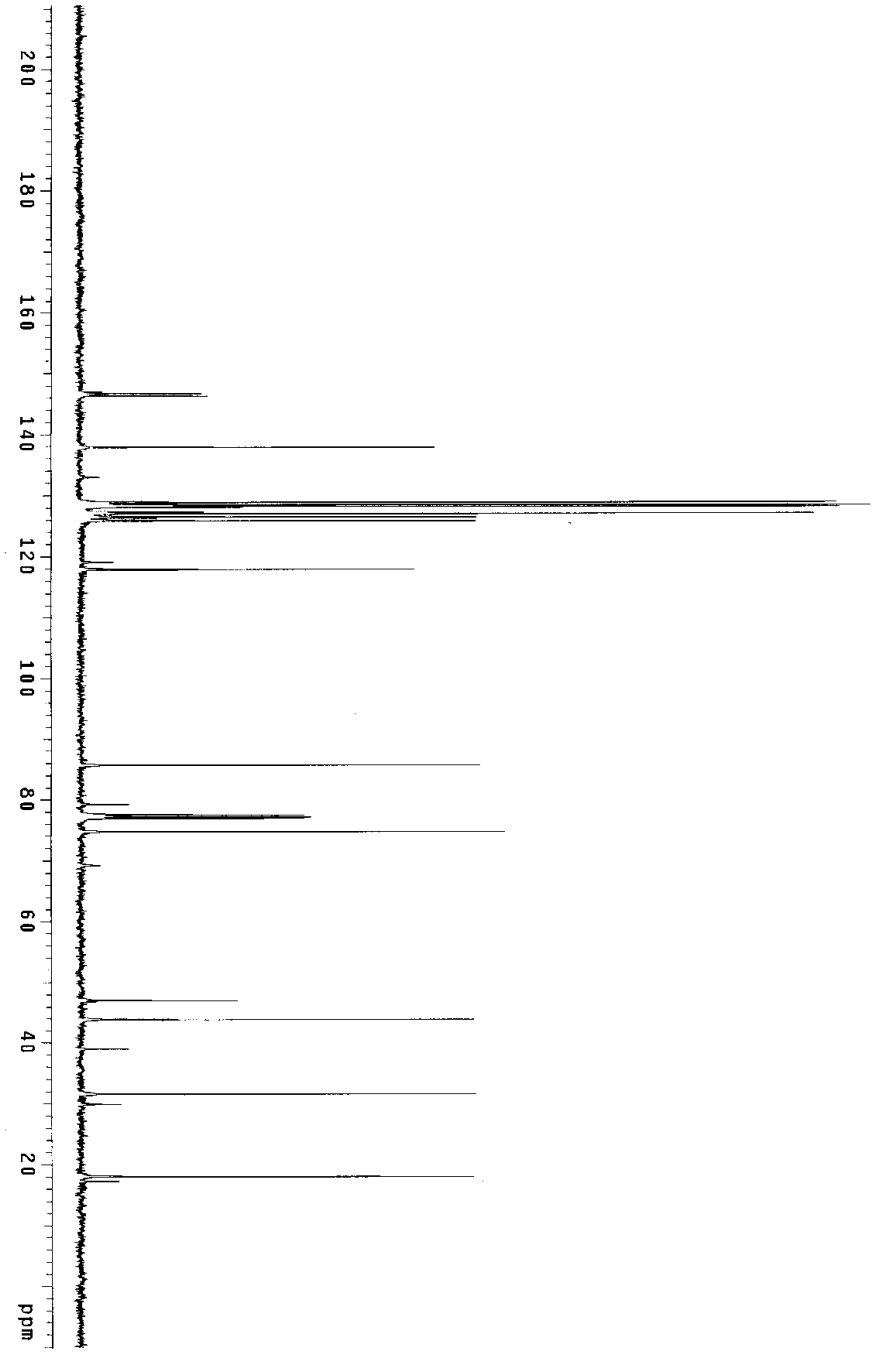


Figure S40. Chiral GC of a 5.3:1 mixture of enantiomerically enriched (*R*),(*E*)-**18a** and (*S*),(*Z*)-**18a** obtained from the Au-catalyzed cyclization of (*S*)-**17a** (84% ee).

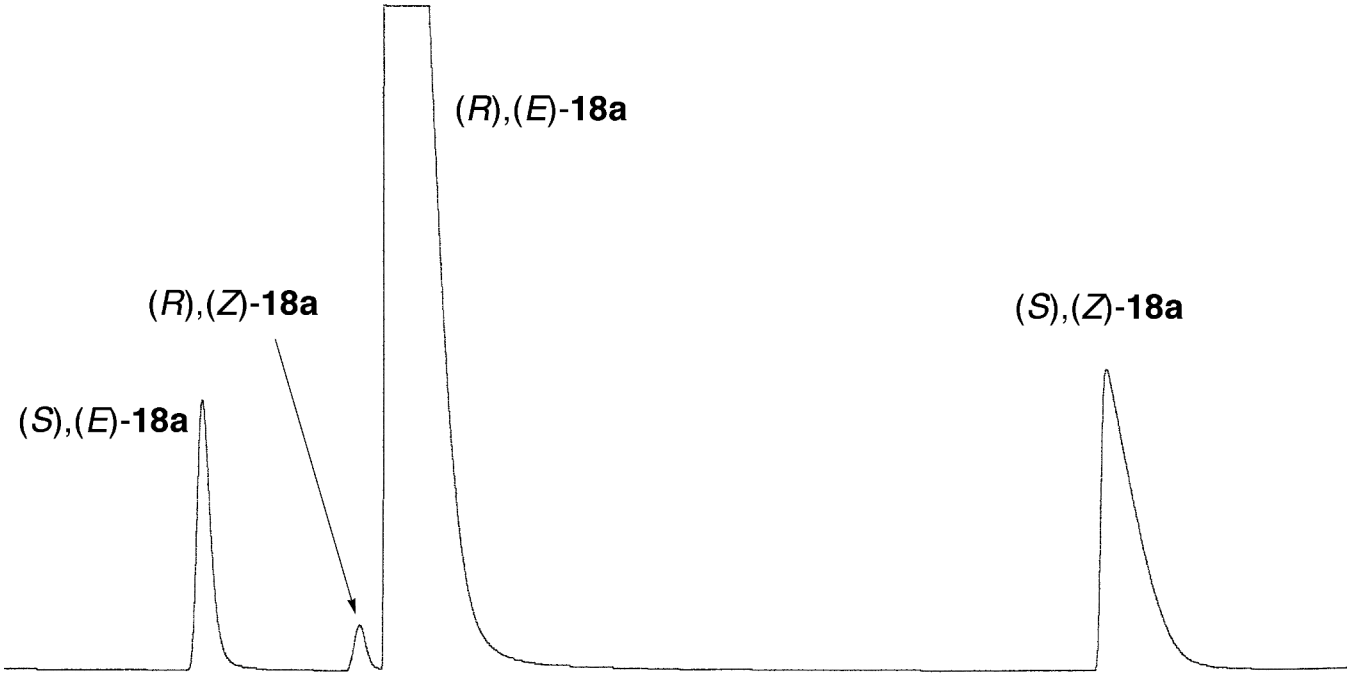


Figure S41. Chiral GC of a racemic 5.3:1 mixture of (*E*)-**18a** and (*Z*)-**18a** obtained from the Au-catalyzed cyclization of *rac*-**17a**.

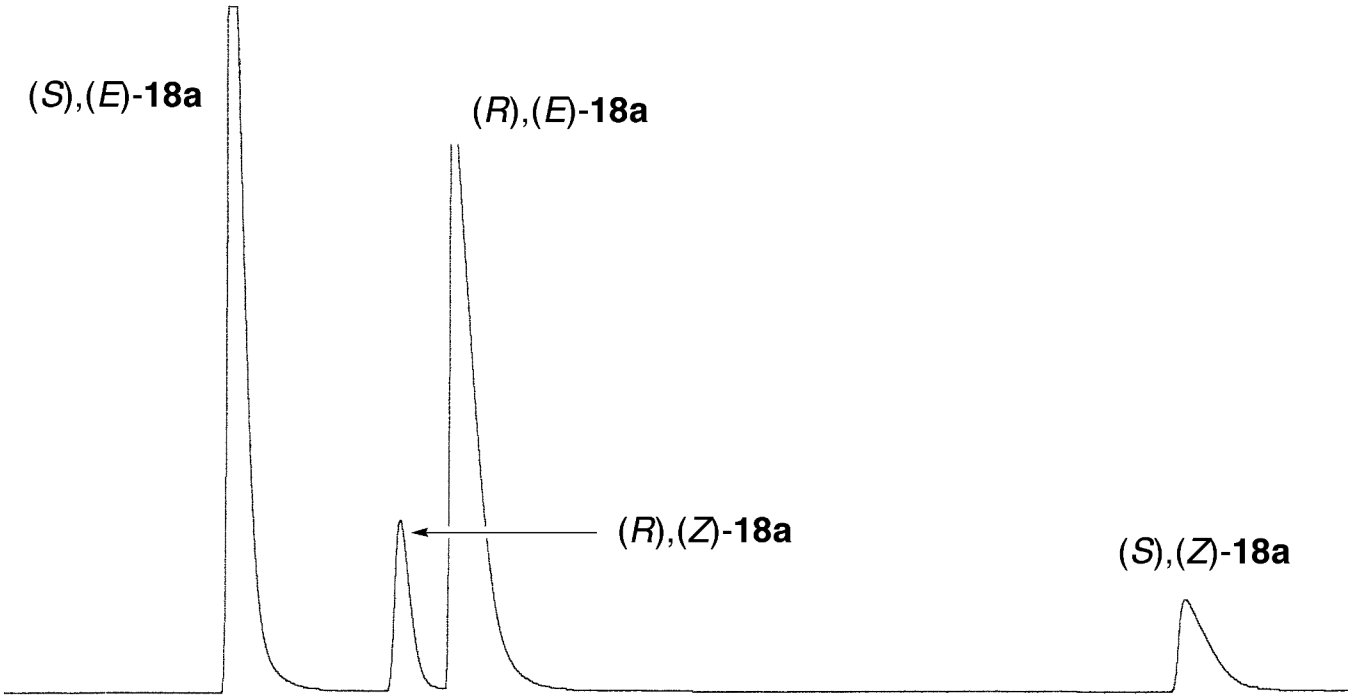


Figure S42. Chiral GC of an enantiomerically enriched 25:1 mixture of (*R*),(*Z*)-**18a** and (*R*),(*E*)-**18a** obtained from (*R*)-tetrahydrofurfuryl alcohol.

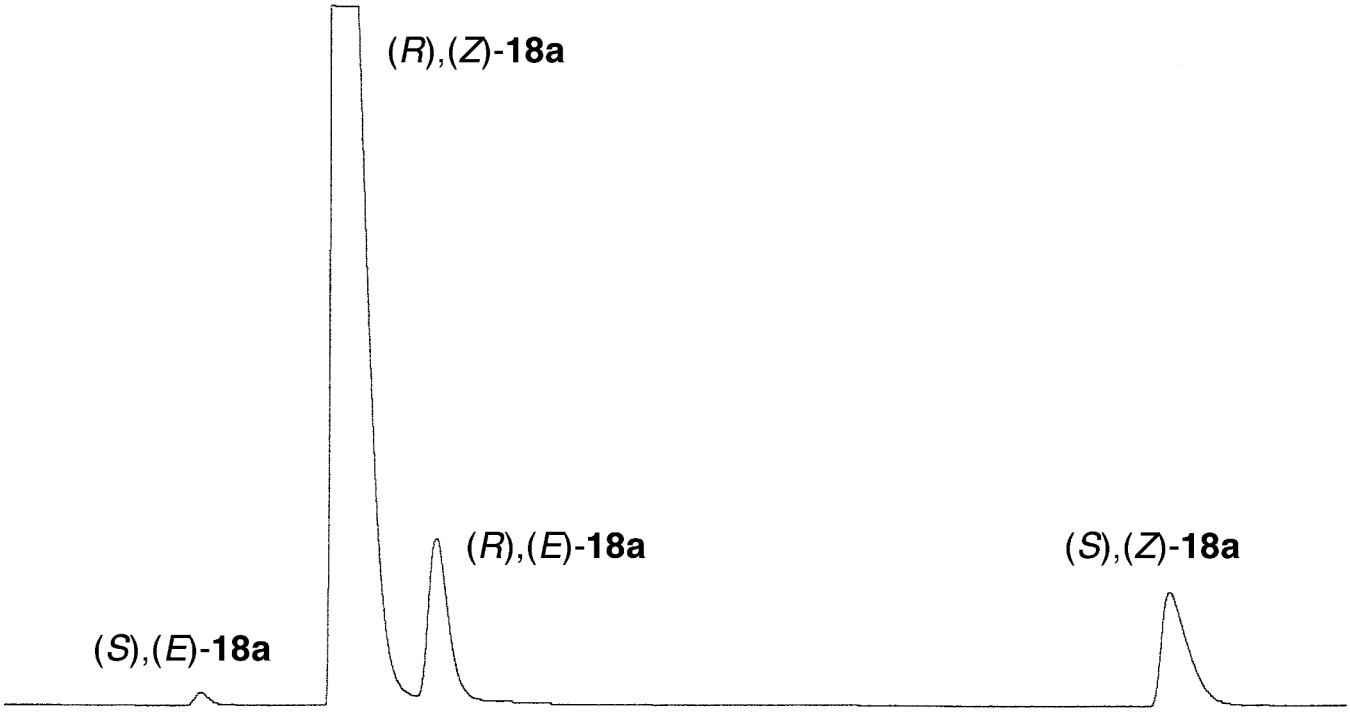


Figure S43. Chiral HPLC of *rac*-(*E*)-**18b** (top trace), a 1:1 mixture of *rac*-(*E*)-**18b** and *rac*-(*Z*)-**18b** (middle trace), and a 85.5:14:5 mixture of enantiomerically enriched (*E*)-**18b** and (*Z*)-**18b** (bottom trace).

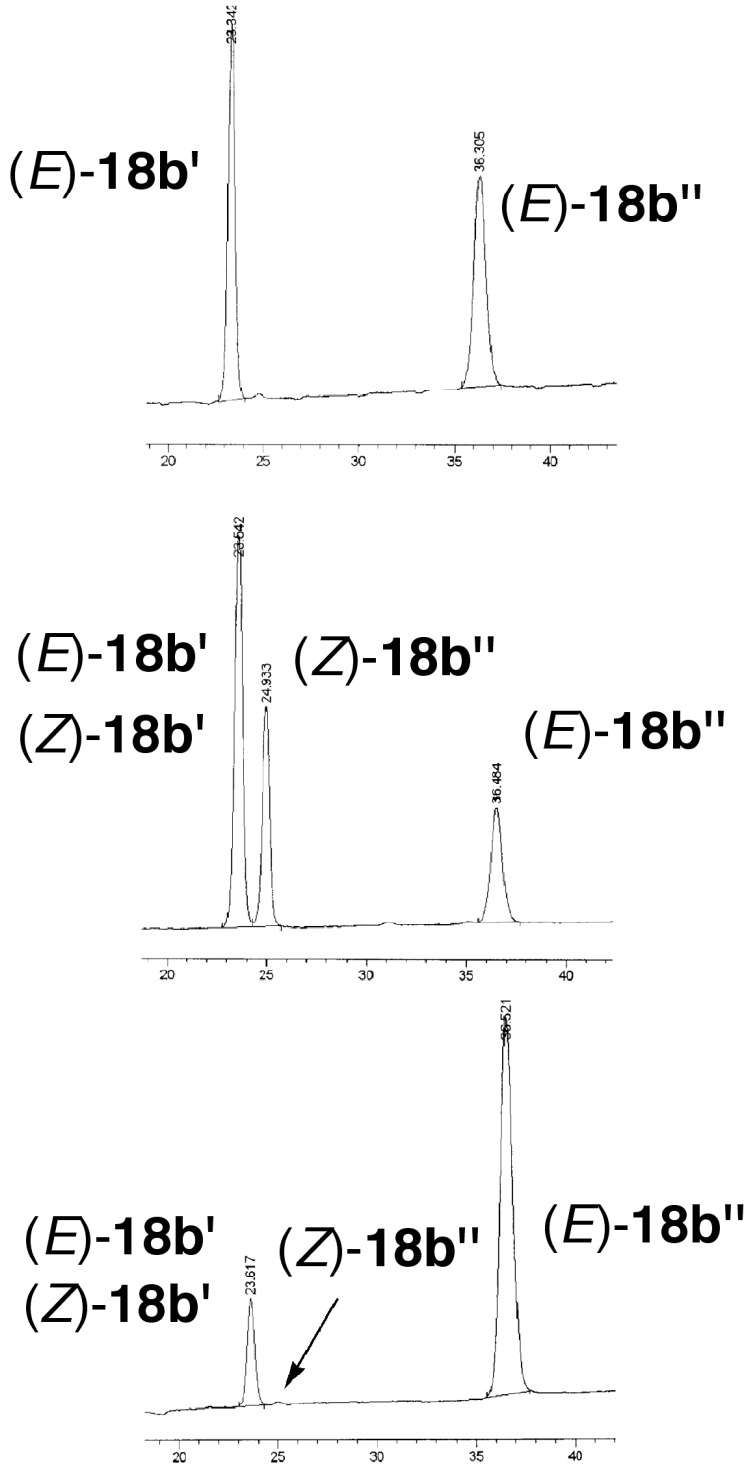


Figure S44. ^{1}H NMR spectrum of **20**.

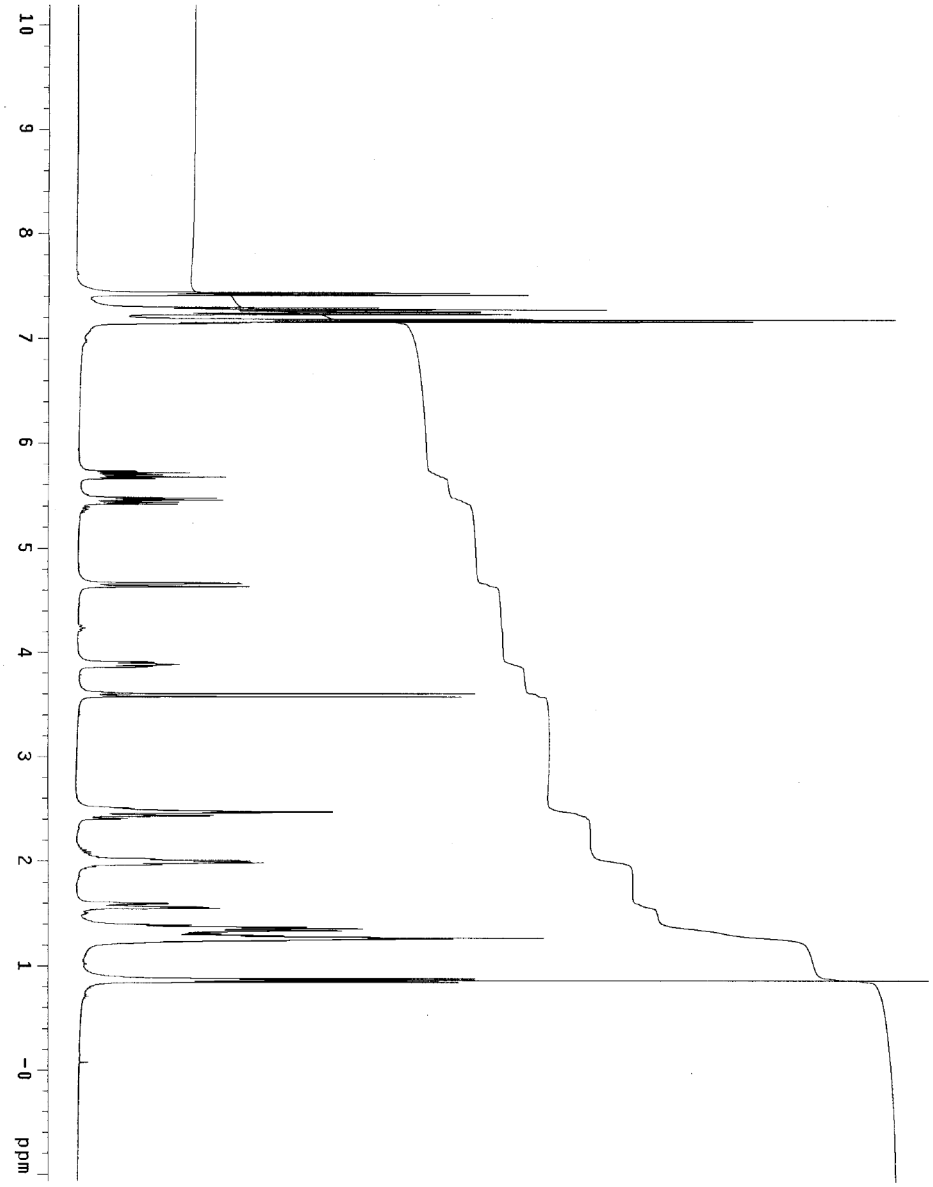


Figure S45. $^{13}C\ \{^{1}H\}$ NMR spectrum of **20**.

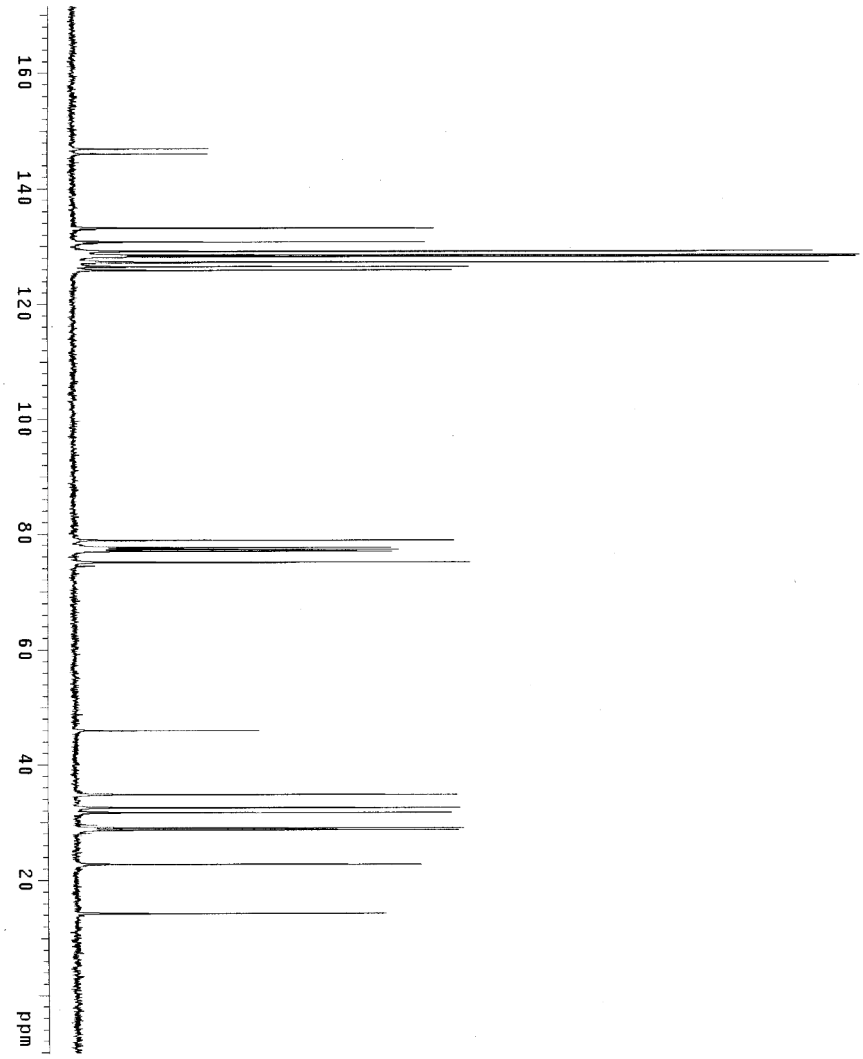


Figure S46. Chiral HPLC trace of *rac*-**35** (left trace) and enantiomerically enriched **35** (right trace; 67% ee).

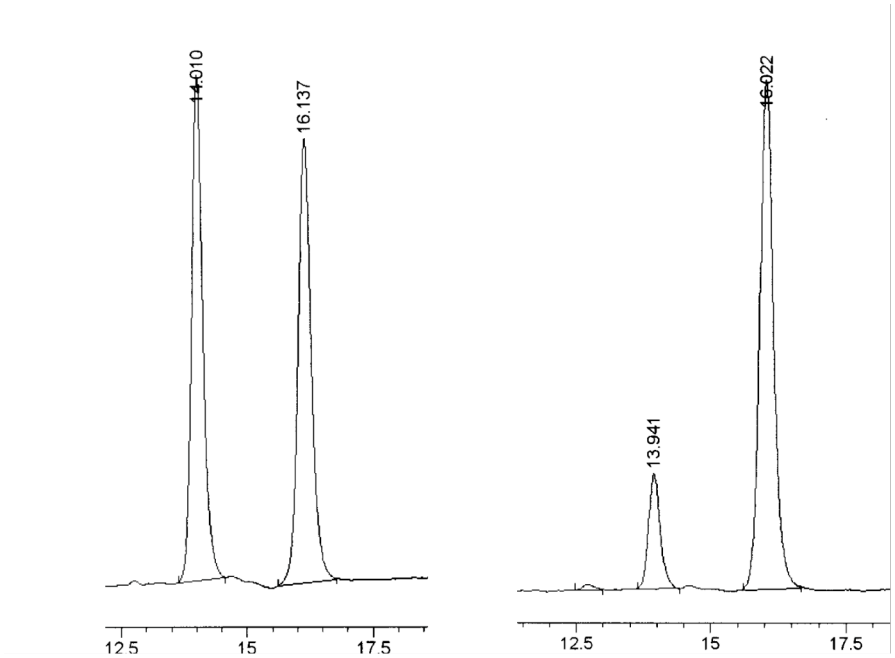


Figure S47. Chiral HPLC trace for racemic **24** (left trace) and (*R*)-**24** (right trace). Conditions: 245 nm, 97:3 hexanes:*i*-PrOH, 0.3 mL/min). An impurity in this particular sample of *rac*-**24** is indicated with an (×).

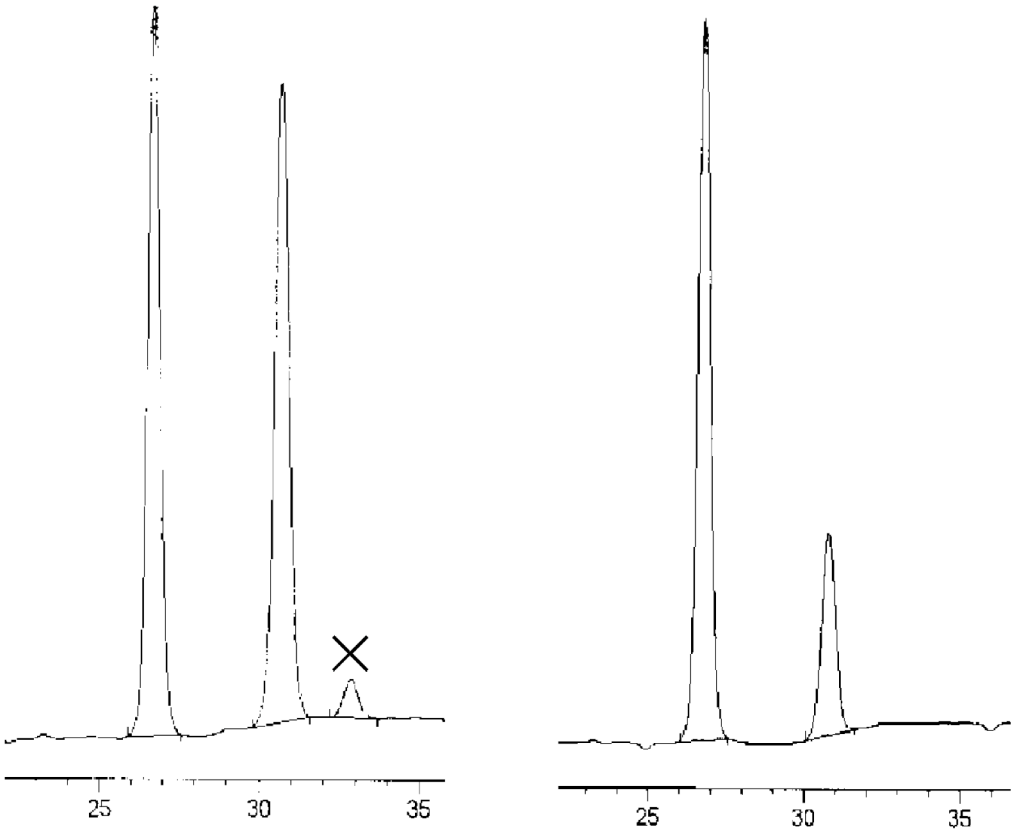
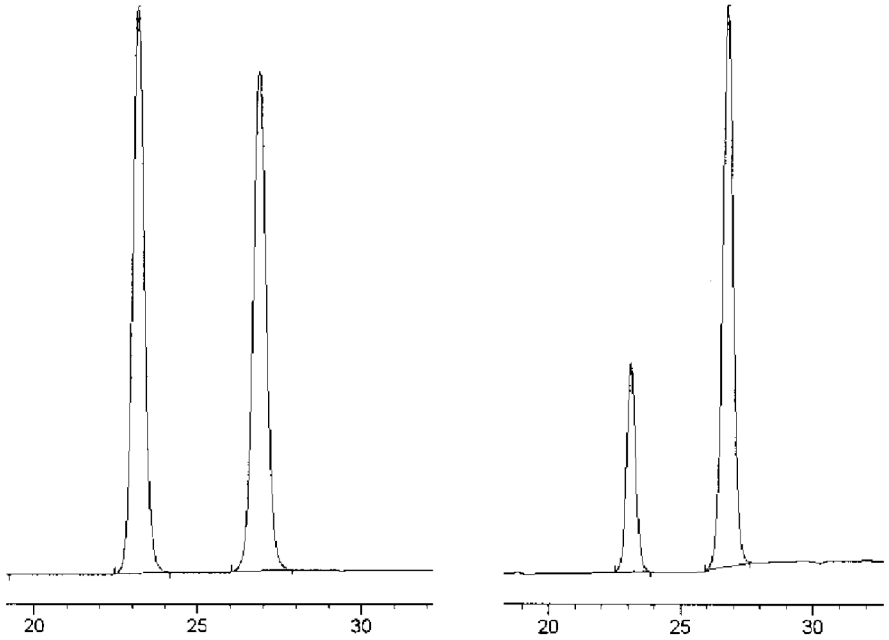


Figure S48. Chiral HPLC trace for racemic **25** (left trace) and enantiomerically enriched **25** (52% ee): Conditions: 245 nm, 97:3 hexanes:*i*-PrOH, 0.3 mL/min.



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