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Supplementary Information

Novel Chiral Ionic Liquid (CIL) Assisted Selectivity Enhancement to (L)-Proline Catalyzed Asymmetric Aldol Reactions

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General remarks

^{1}H NMR spectra were recorded on a VARIAN Mercury 300 MHz spectrometer or VARIAN Mercury 600 MHz spectrometer. Chemical shifts are reported in ppm with the TMS as internal standard**.** The data are reported as (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, brs = broad singlet, coupling constant(s) in Hz, integration). ^{13}C NMR spectra were recorded on a VARIAN Mercury 75 MHz or VARIAN Mercury 125 MHz spectrometer. Chemical shifts are reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with silica gel-coated plates. Enantiomeric ratios were determined by HPLC, using a chiralpak AS-H column, a chiralpak AD-H column or a chiralcel OD-H column with hexane and *i*-PrOH as solvents. The configurations were assigned by comparison of the t_R with the reported data.[1,2]

Characterization of CILs

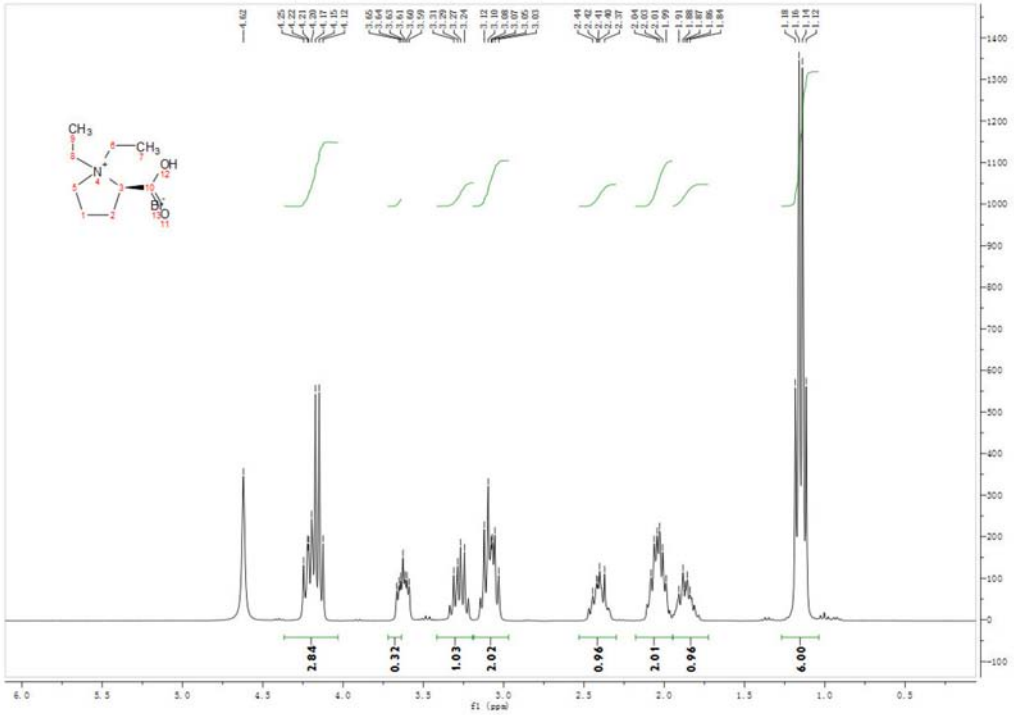


Figure S1. ^{1}H NMR (300 MHZ, D_2O) spectrum of **2a**.

*e-mail: zxh7954@hotmail.com

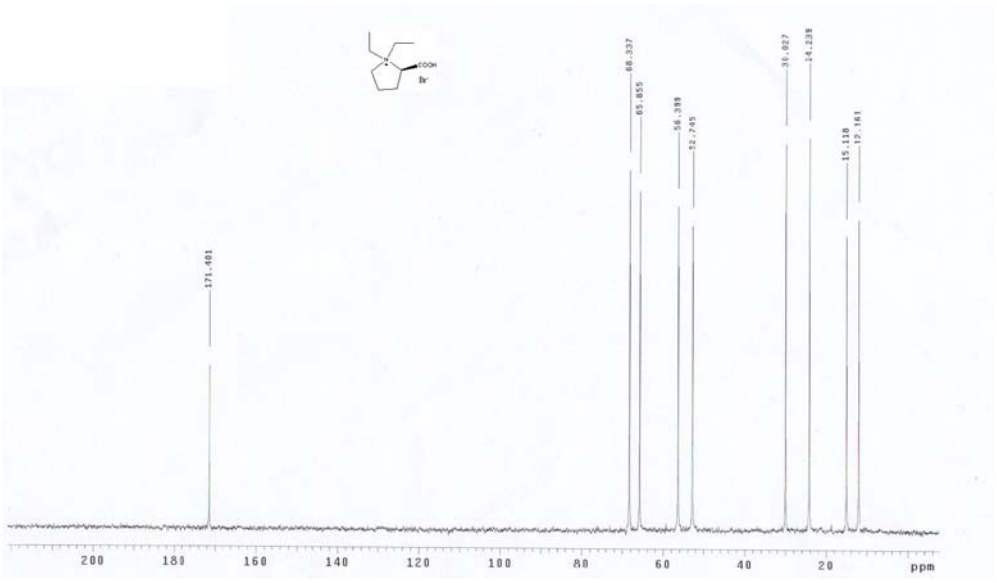


Figure S2. ^{13}C NMR (75 MHZ, D_2O) spectrum of **2a**.

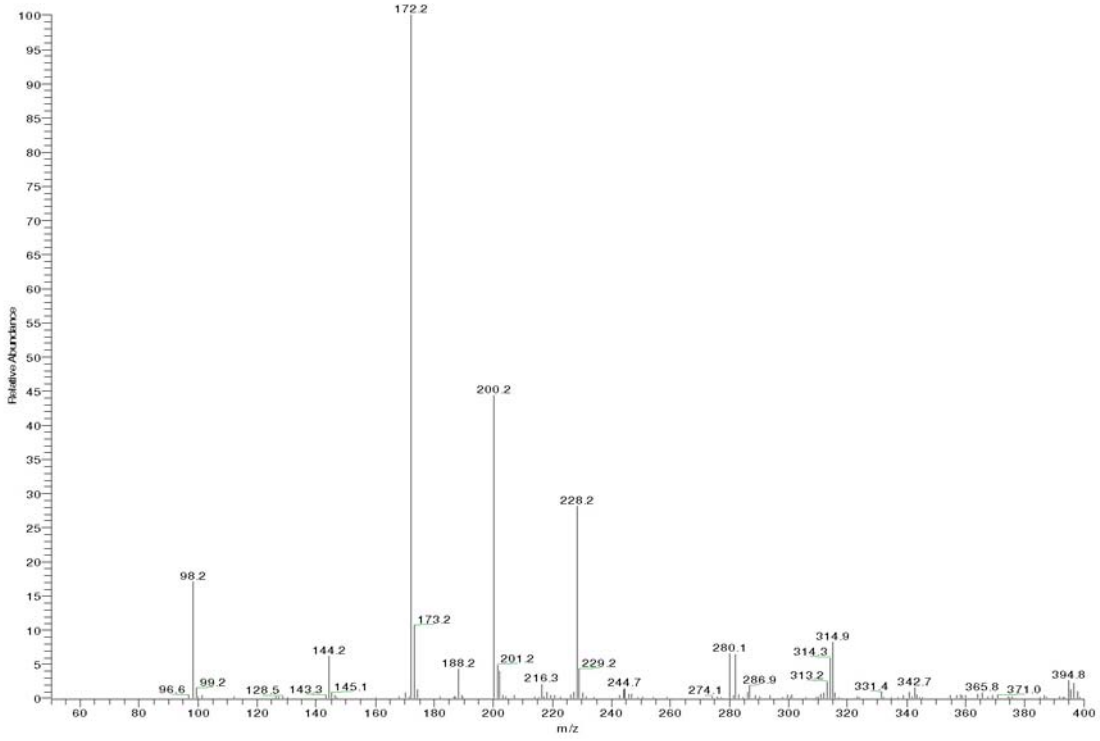


Figure S3. ESI-Mass spectrum of **2a**.

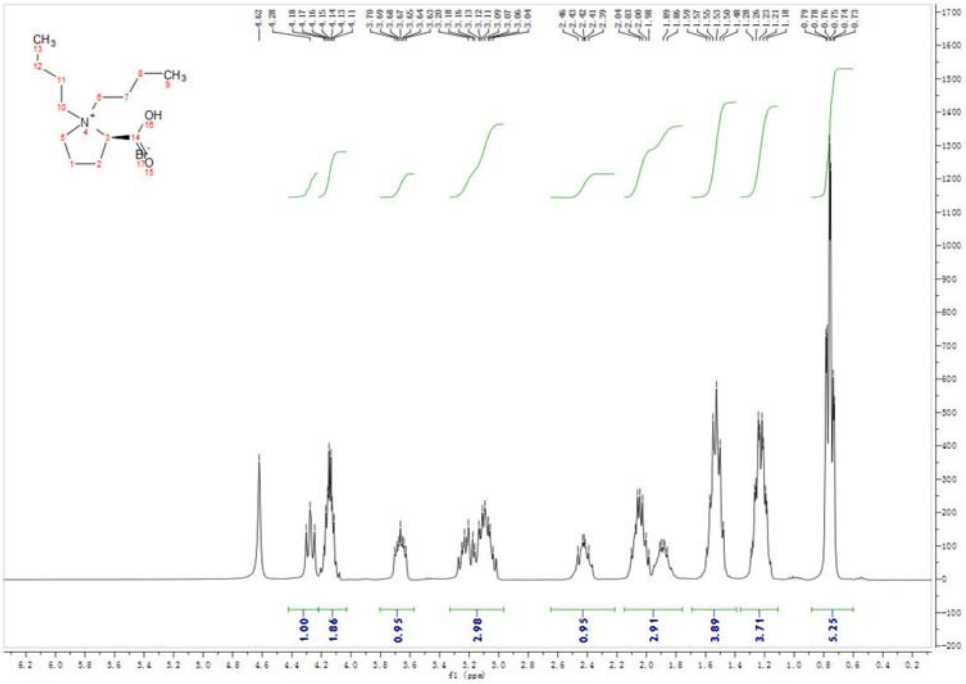


Figure S4. ^{1}H NMR (300 MHZ, D_2O) spectrum of **2b**.

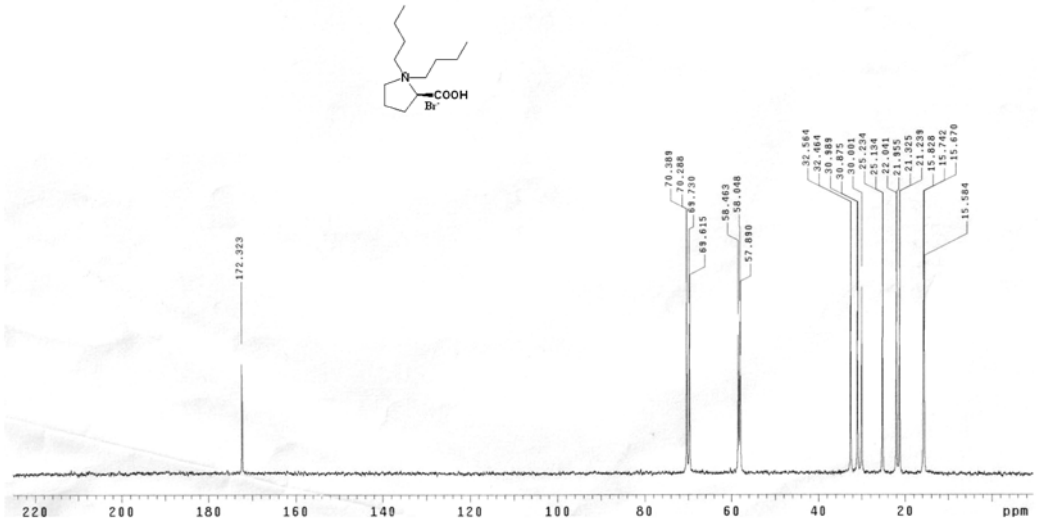


Figure S5. ^{13}C NMR (75 MHZ, D_2O) spectrum of **2b**.

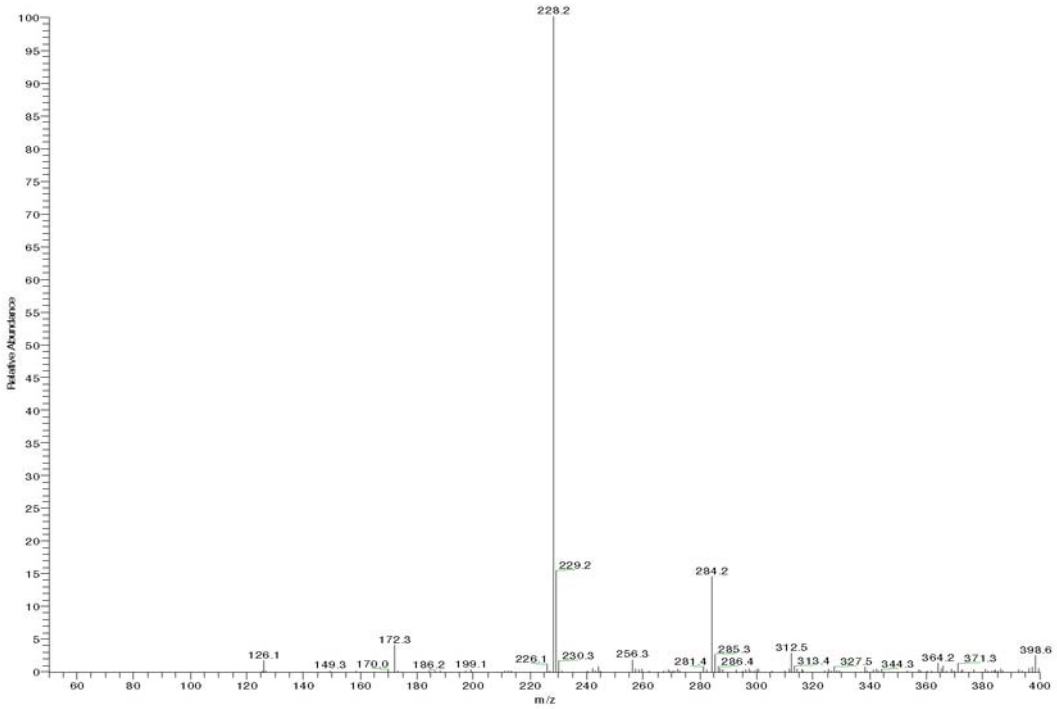


Figure S6. ESI-Mass spectrum of **2b**.

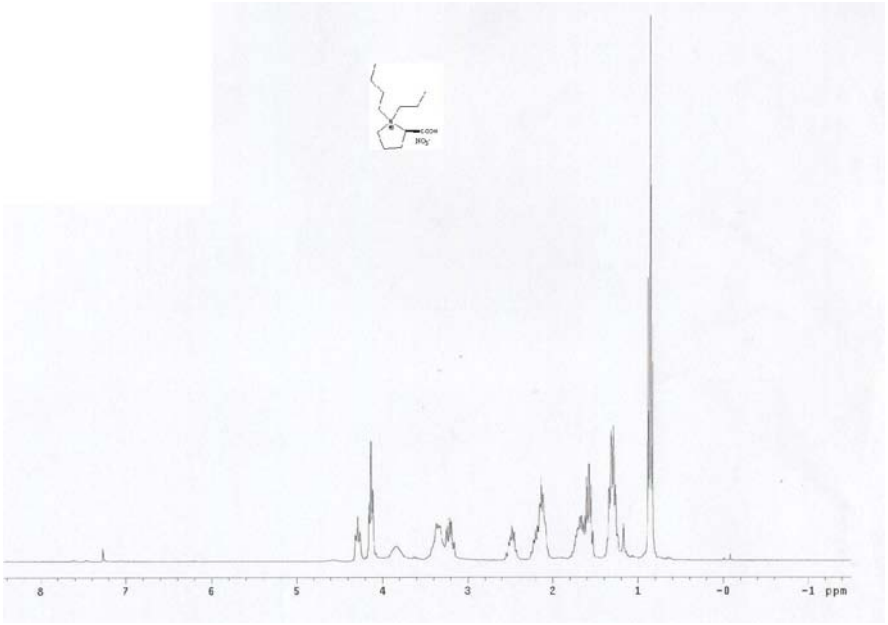


Figure S7. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **3a**.

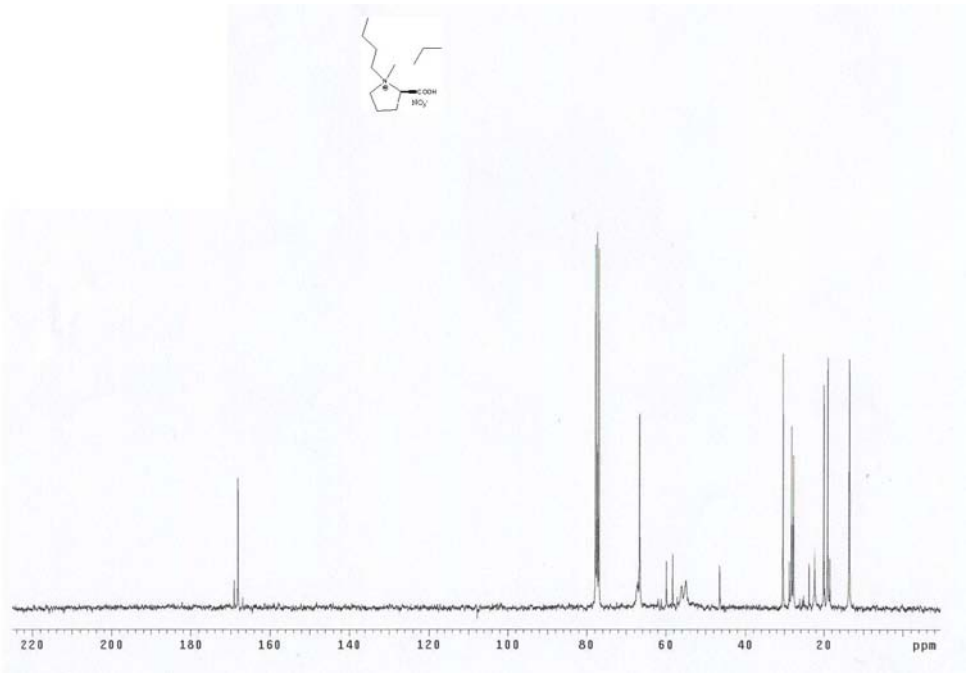


Figure S8. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **3a**.

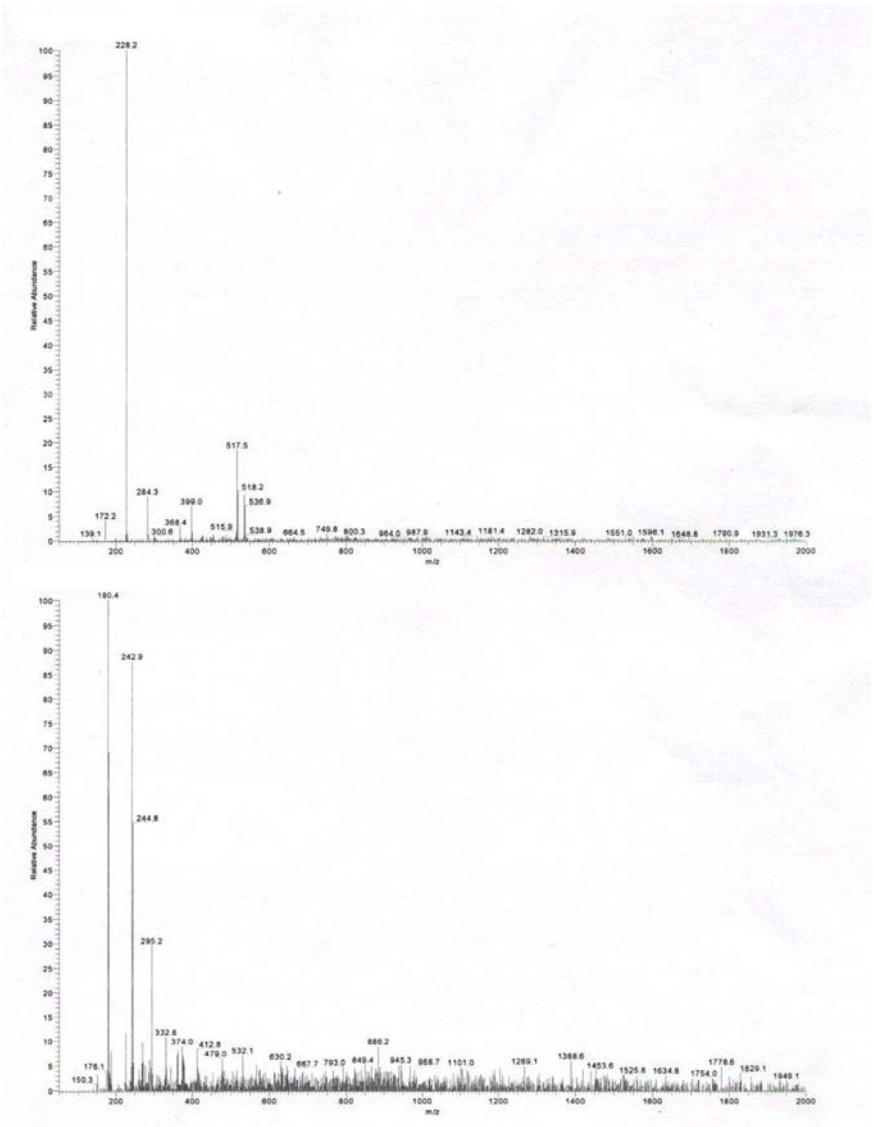


Figure S9. ESI-Mass spectrum of **3a**.

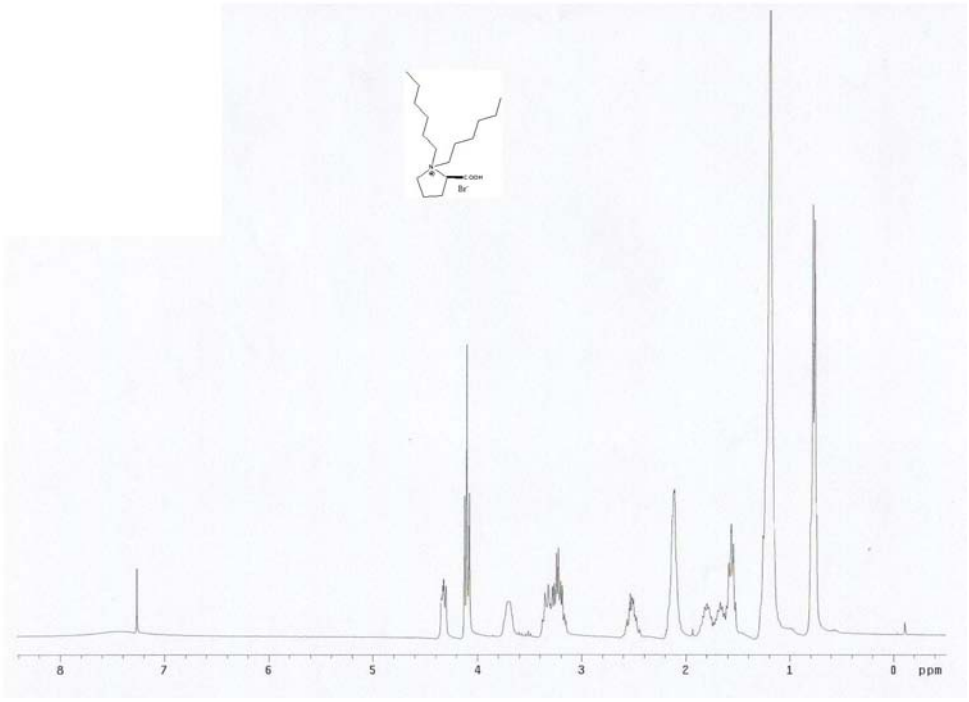


Figure S10. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **2c**.

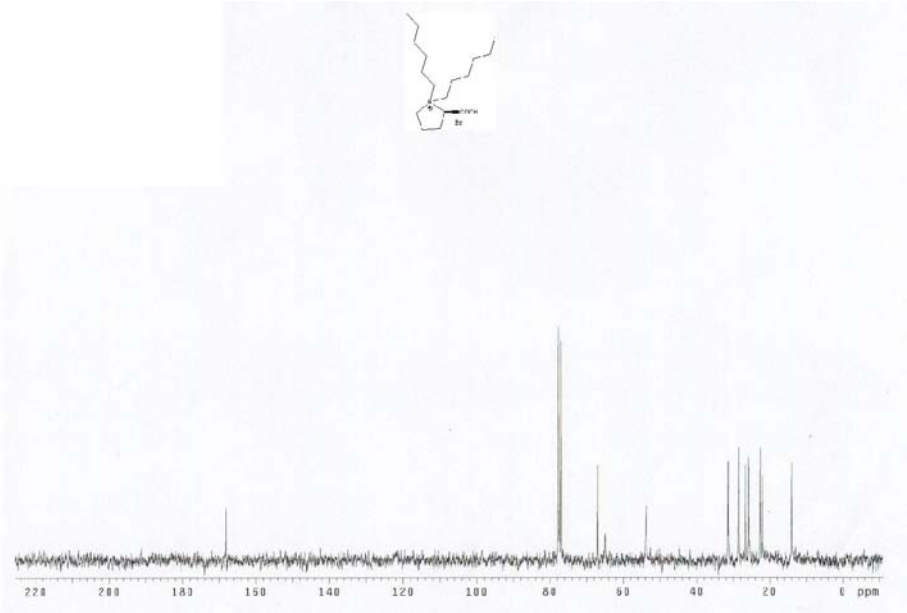


Figure S11. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **2c**.

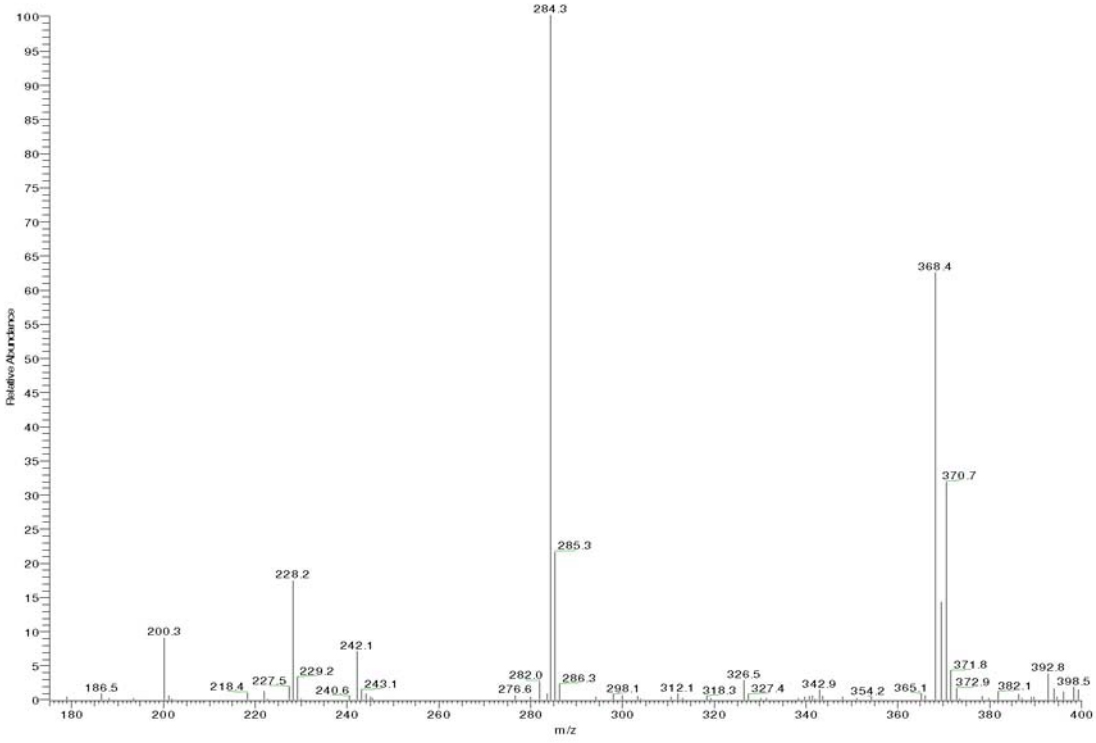


Figure S12. ESI-Mass spectrum of **2c**.

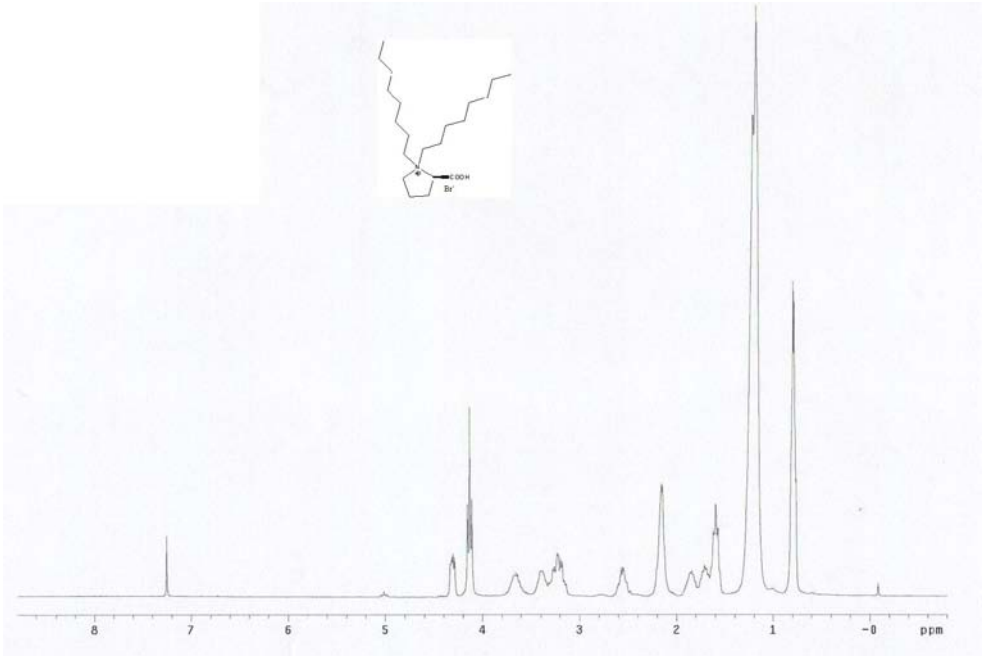


Figure S13. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **2d**.

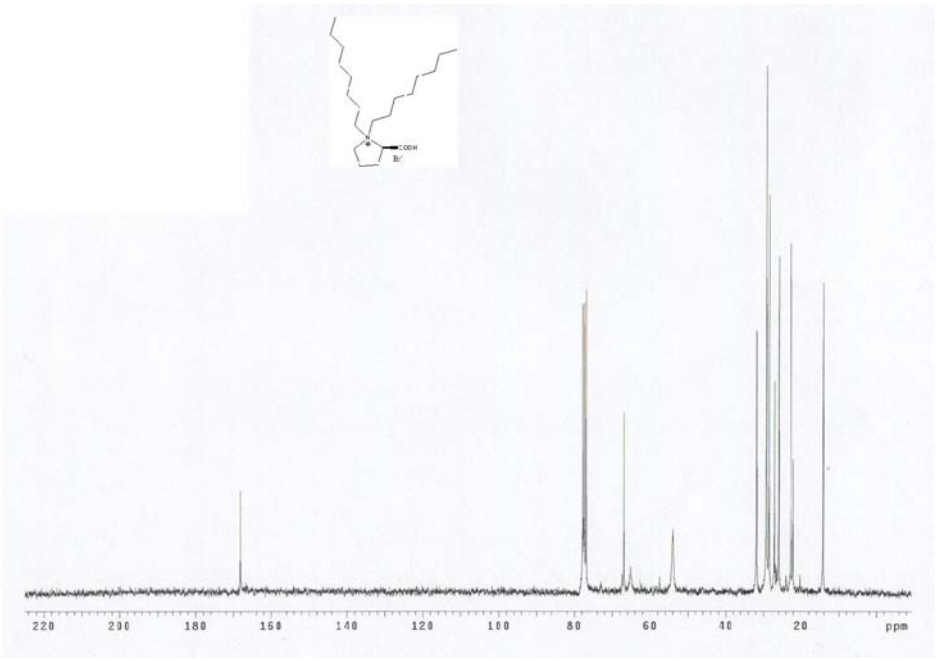


Figure S14. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **2d**.

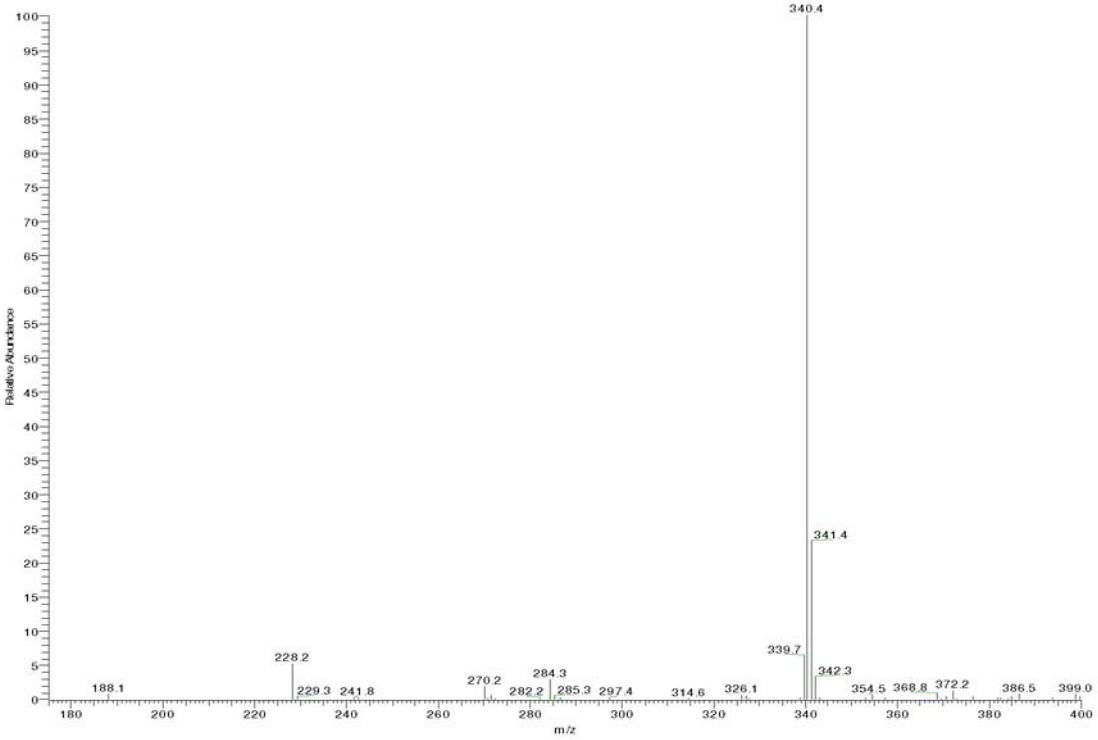


Figure S15. ESI-Mass spectrum of **2d**.

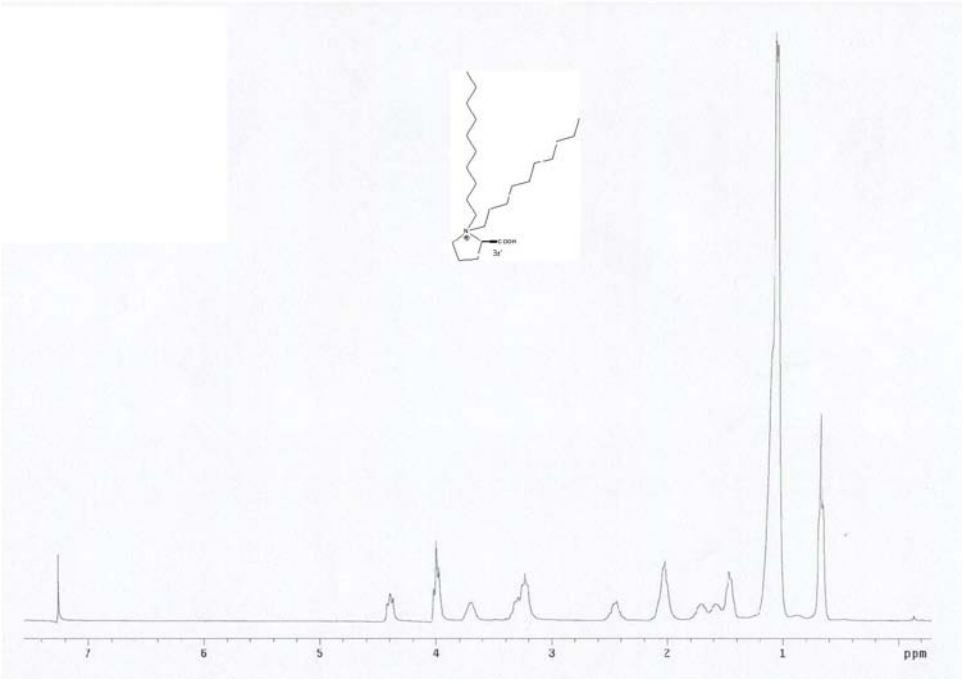


Figure S16. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **2e**.

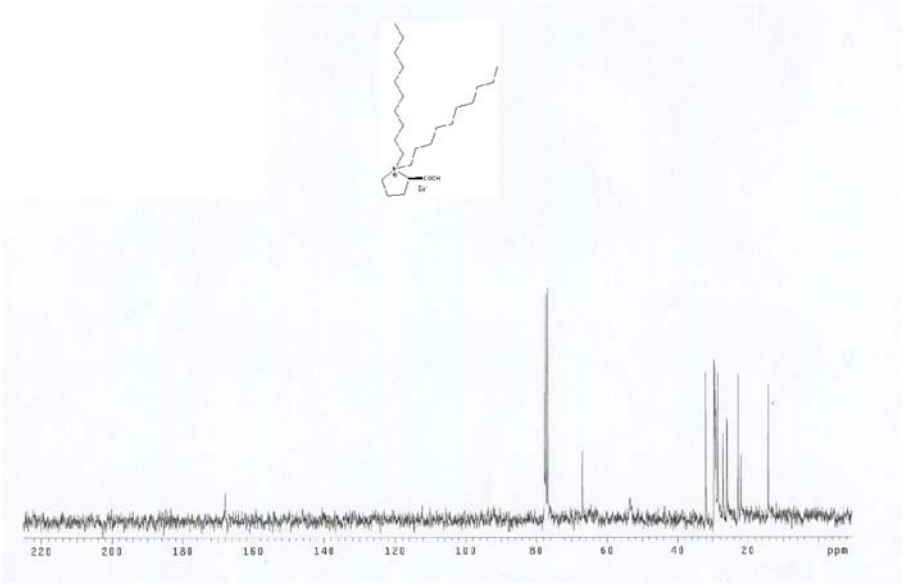


Figure S17. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **2e**.

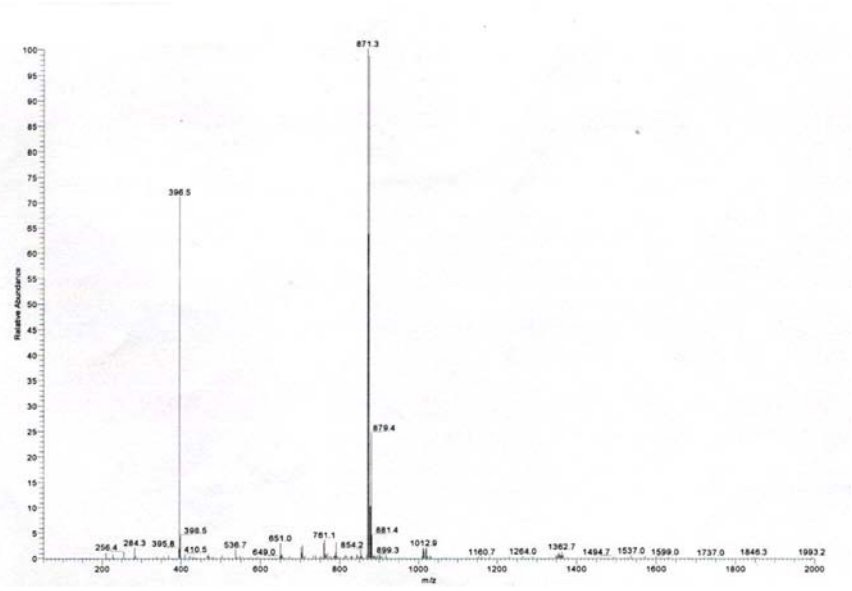


Figure S18. ESI-Mass spectrum of **2e**.

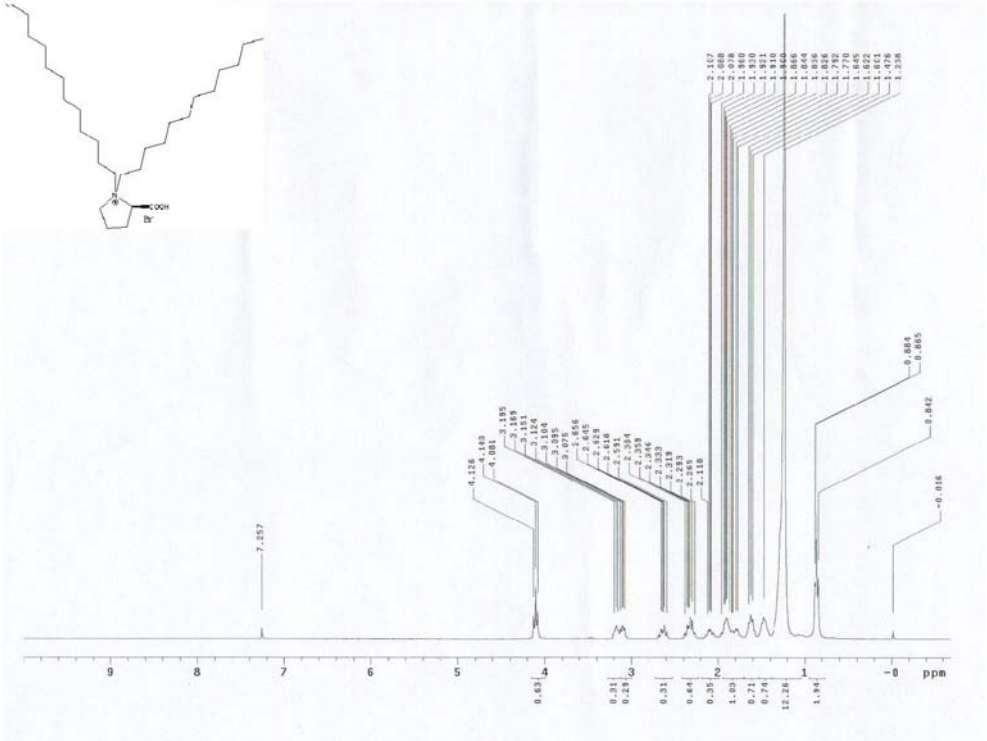


Figure S19. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **2f**.

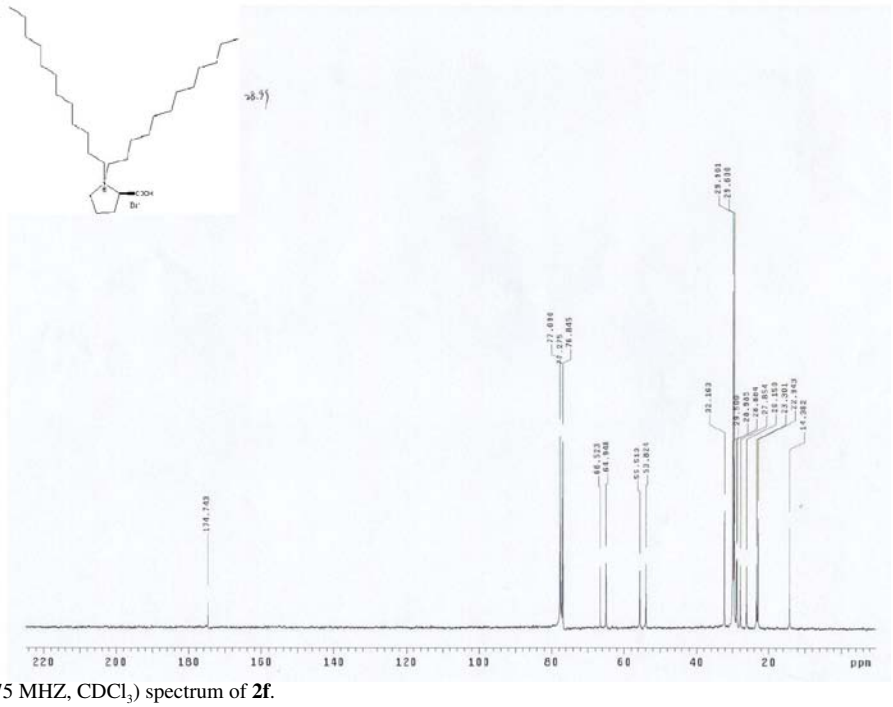


Figure S20. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **2f**.

Characterization of aldol products

NMR data

All available reagents and solvents were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were conducted on Mercury VX-300 (Varian 300 MHz) or Unity-Inova 600 (Varian 600 MHz) spectrometer. Chemical shifts are expressed in ppm use TMS as internal standard and coupling constants are reported in Hz.

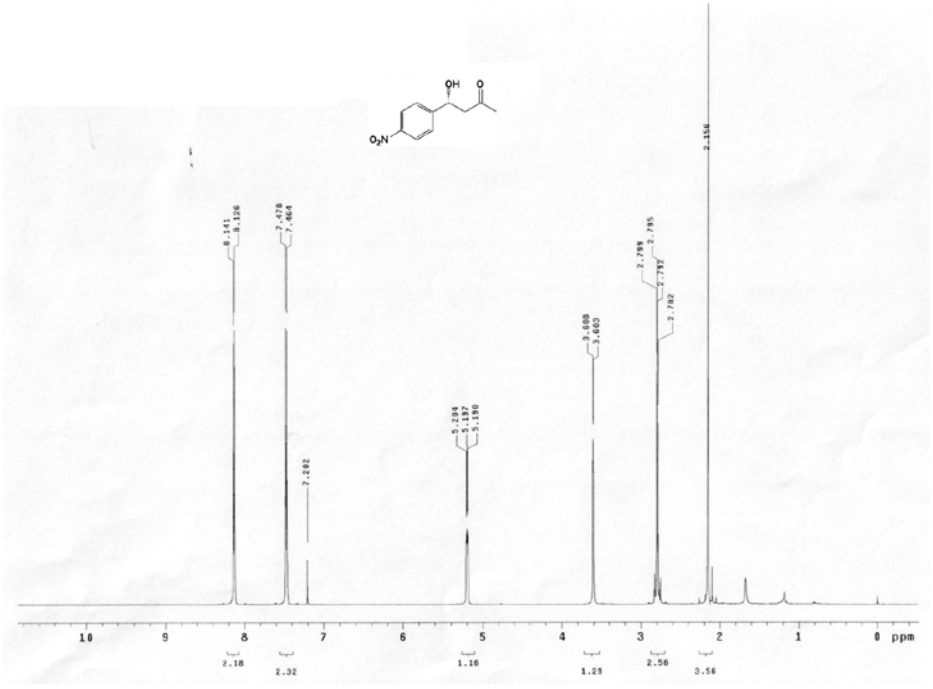


Figure S21. ^{1}H NMR (600 MHZ, $CDCl_3$) spectrum of **5a**.

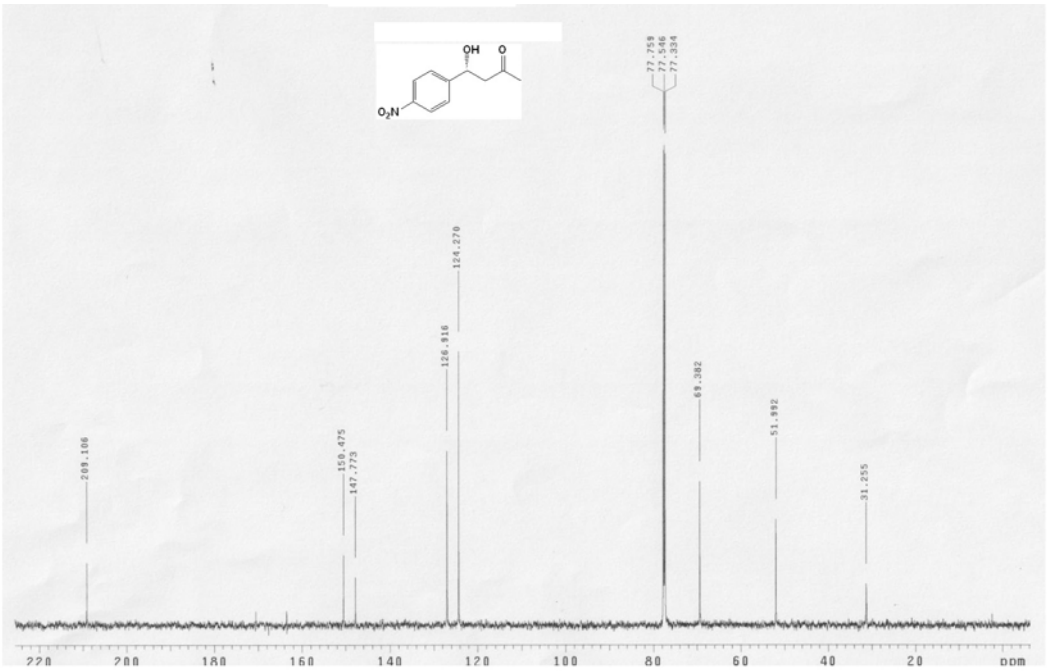


Figure S22. ^{13}C NMR (125 MHZ, $CDCl_3$) spectrum of **5a**.

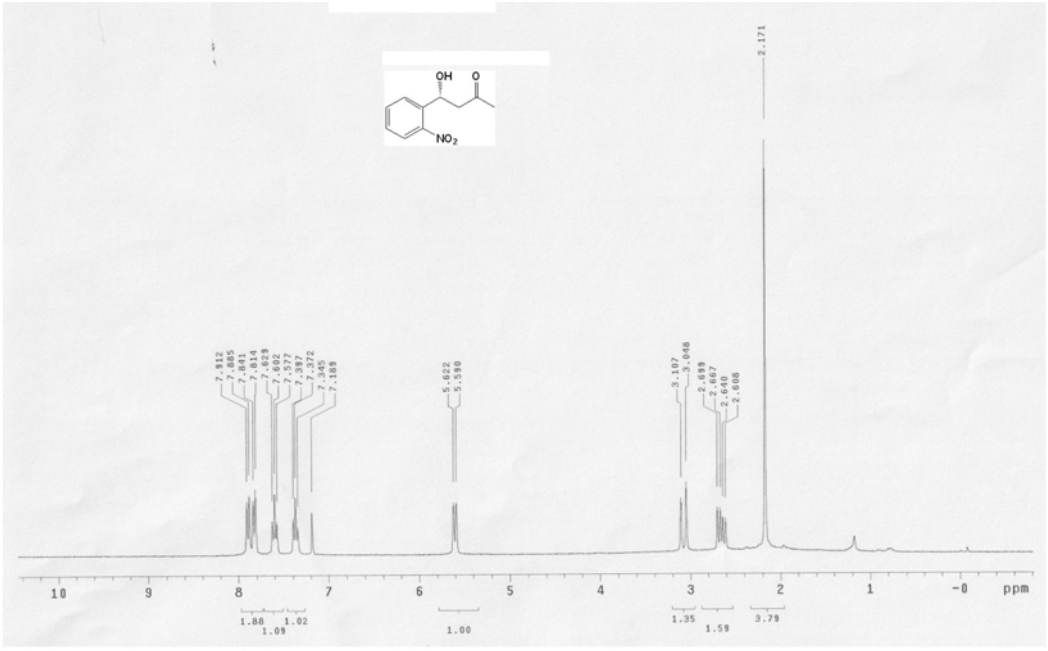


Figure S23. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **5b**.

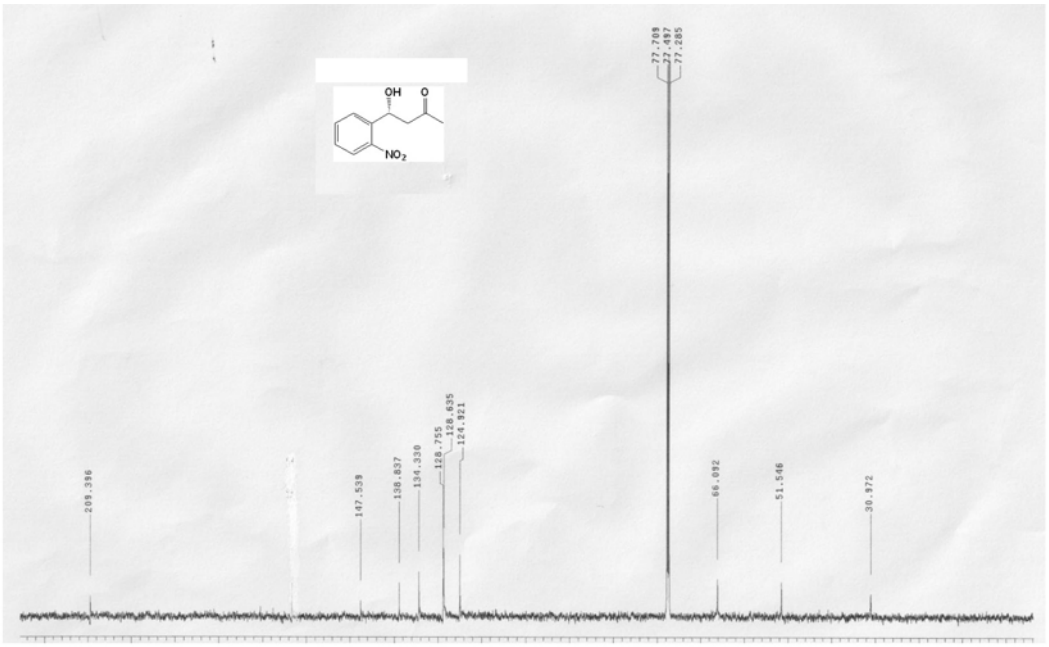


Figure S24. ^{13}C NMR (125 MHZ, $CDCl_3$) spectrum of **5b**.

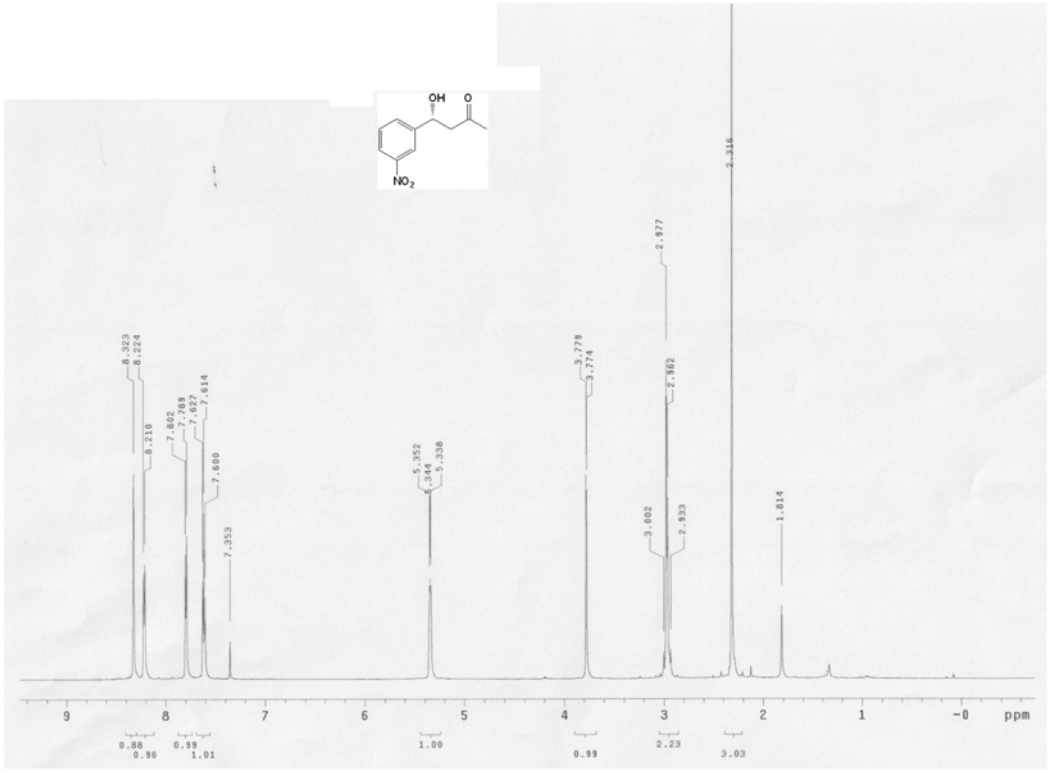


Figure S25. ^{1}H NMR (600 MHZ, $CDCl_3$) spectrum of **5c**.

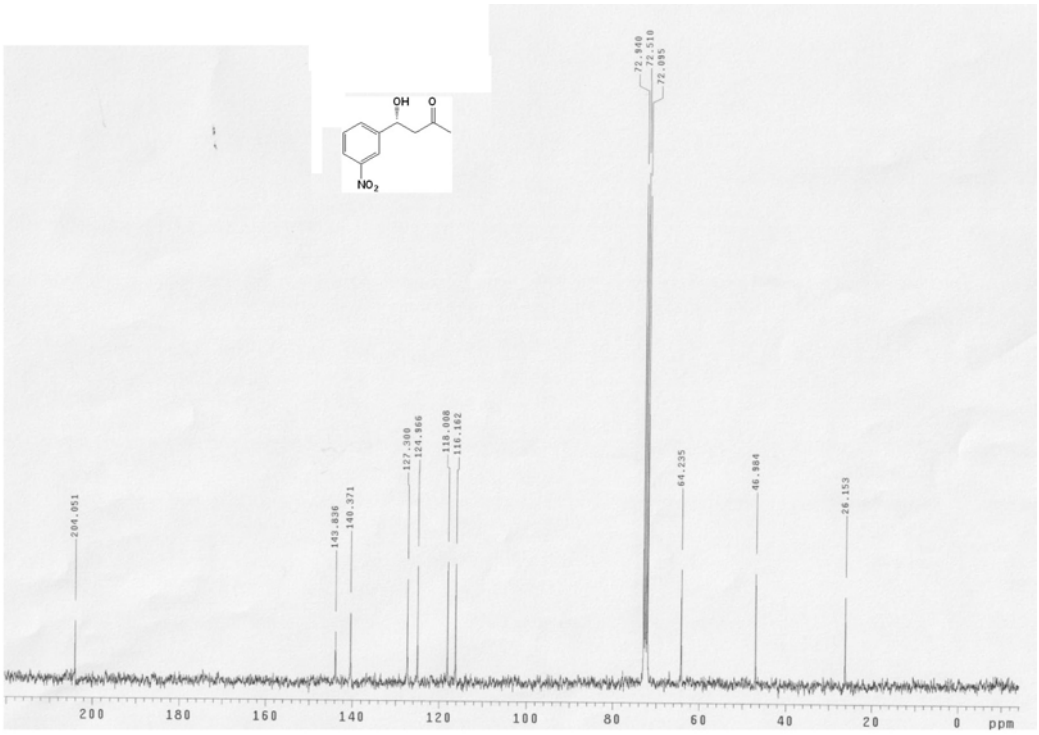


Figure S26. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **5c**.

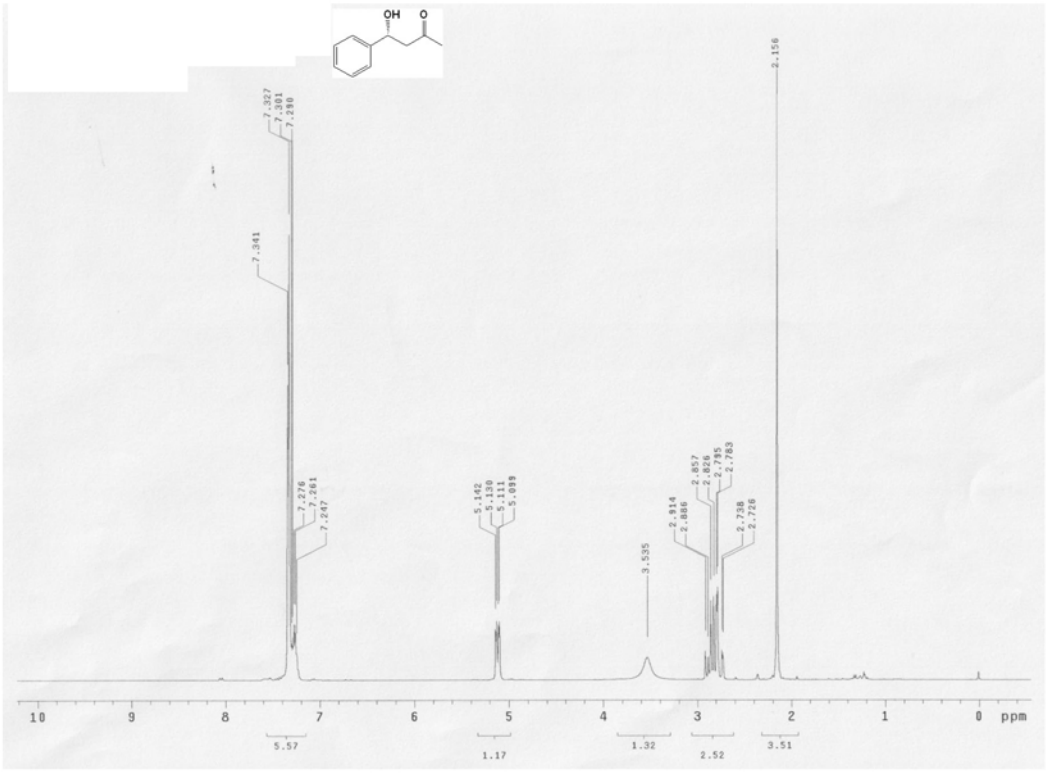


Figure S27. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **5d**.

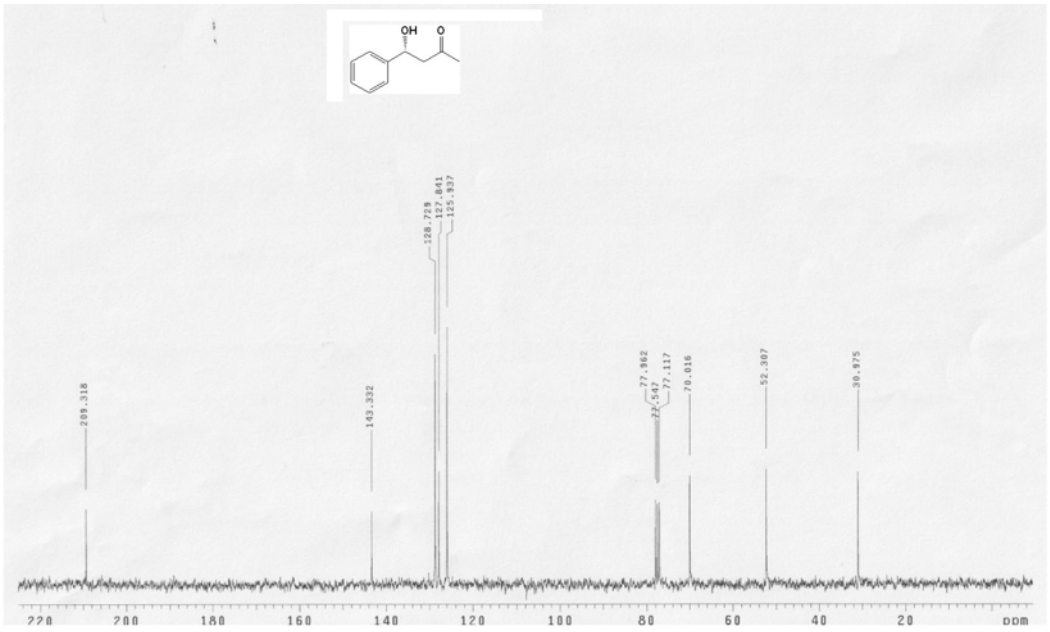


Figure S28. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **5d**.

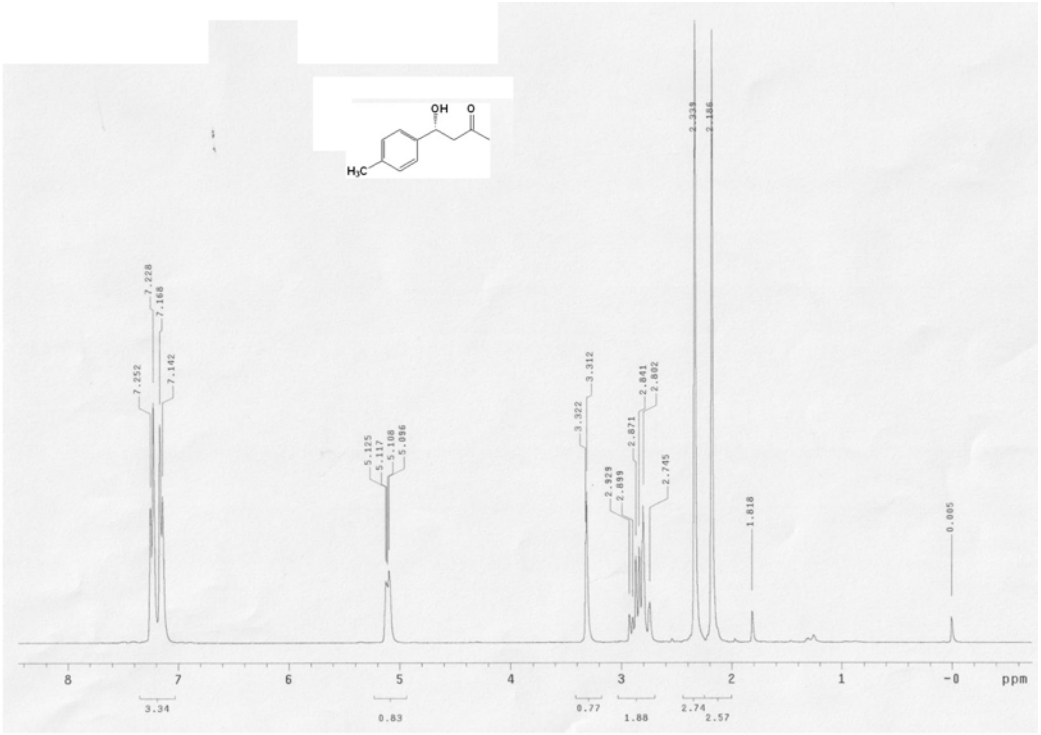


Figure S29. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **5e**.

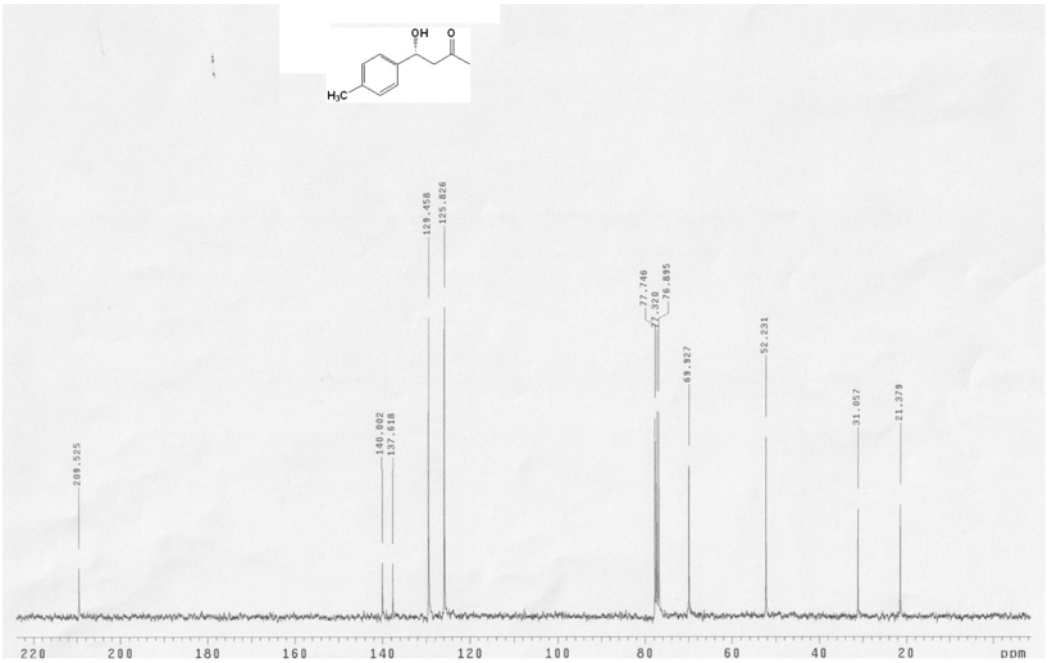


Figure S30. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **5e**.

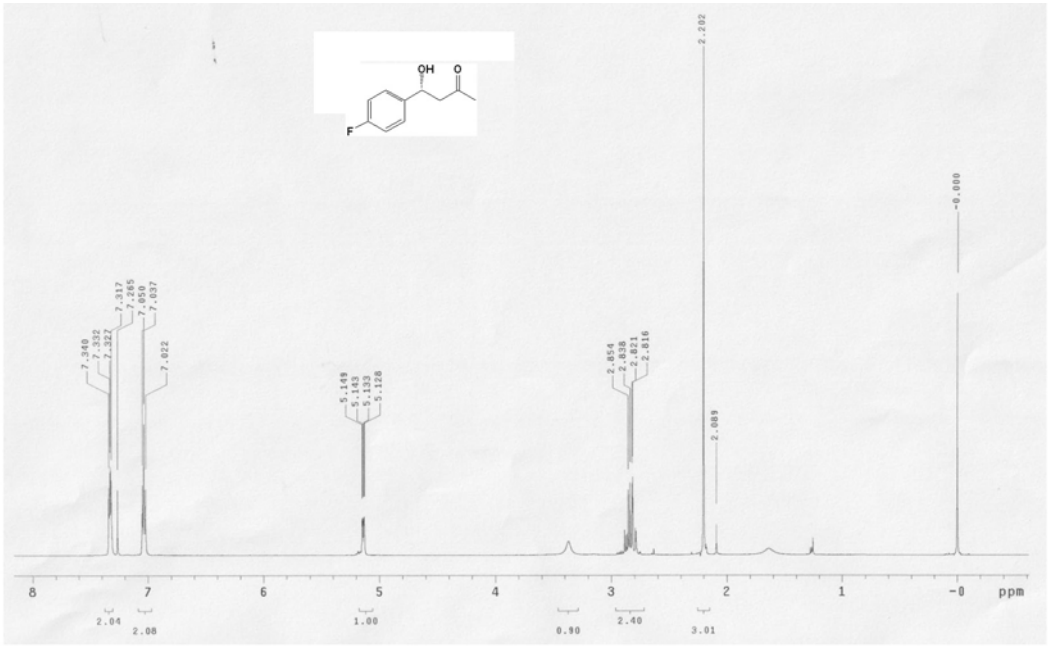


Figure S31. ^{1}H NMR (600 MHZ, $CDCl_3$) spectrum of **5f**.

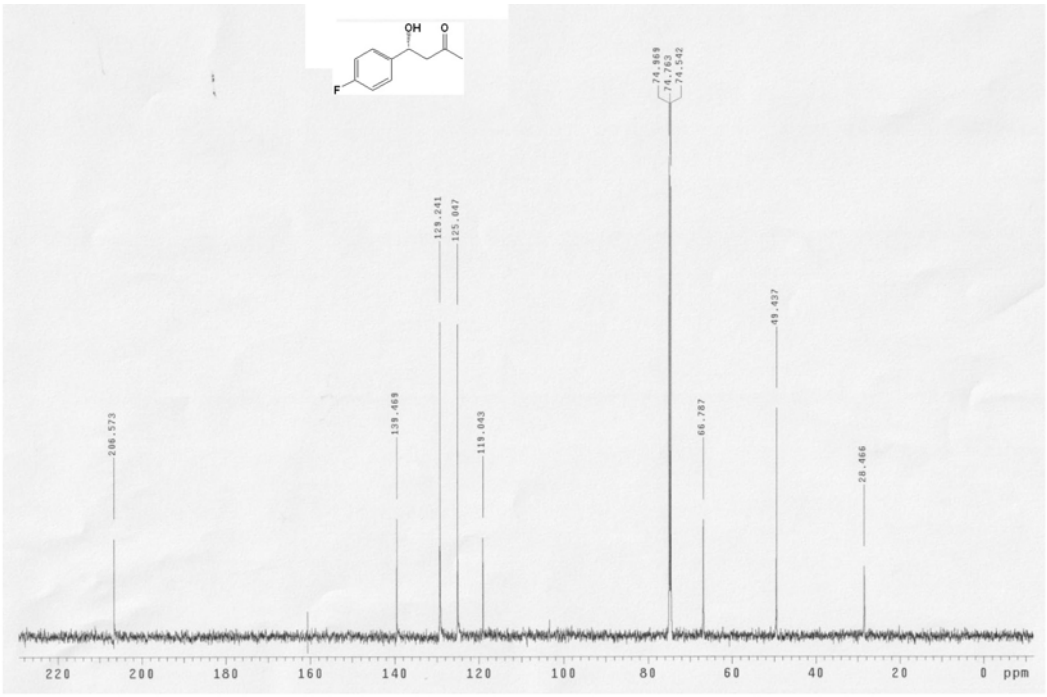


Figure S32. ^{13}C NMR (125 MHZ, $CDCl_3$) spectrum of **5f**.

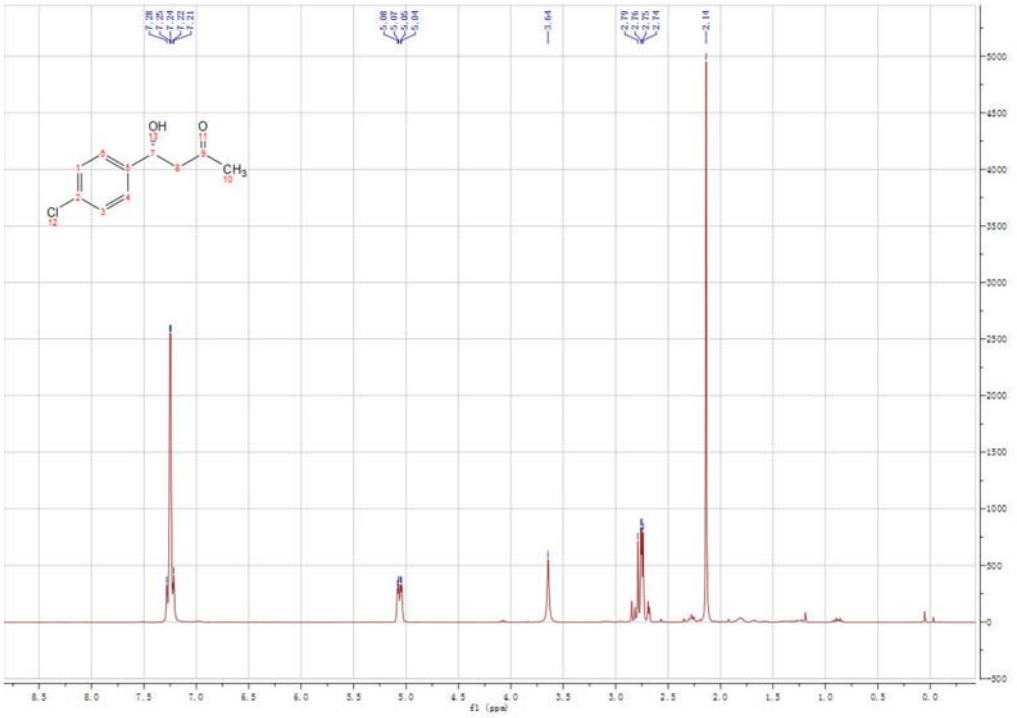


Figure S33. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **5g**.

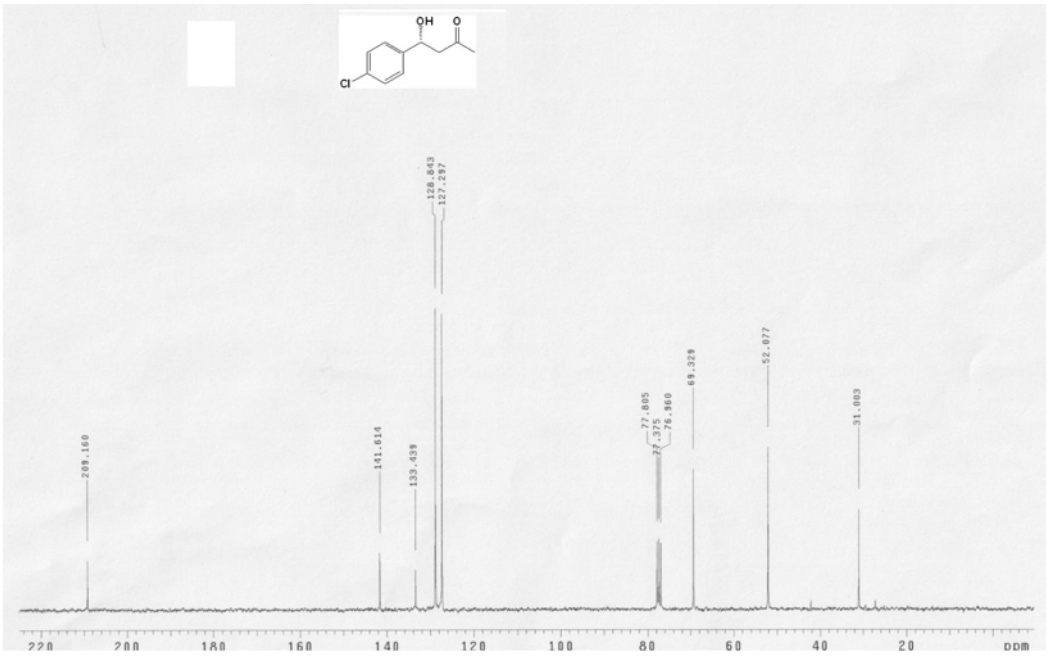


Figure S34. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **5g**.

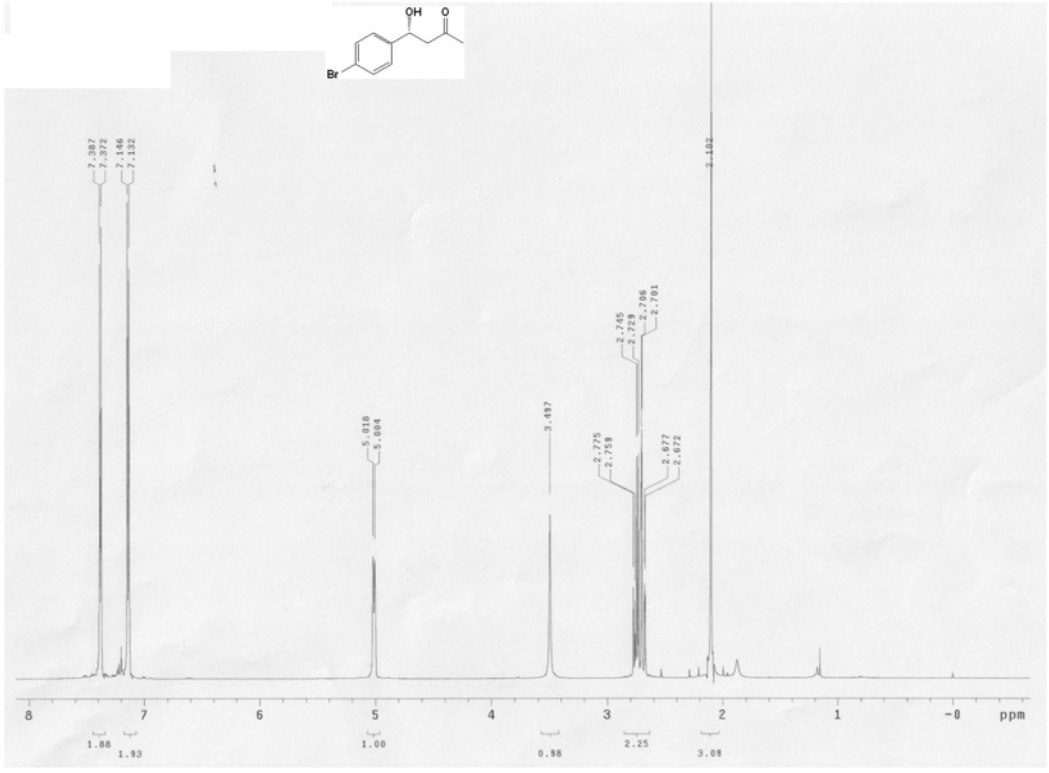


Figure S35. ^{1}H NMR (600 MHZ, $CDCl_3$) spectrum of **5h**.

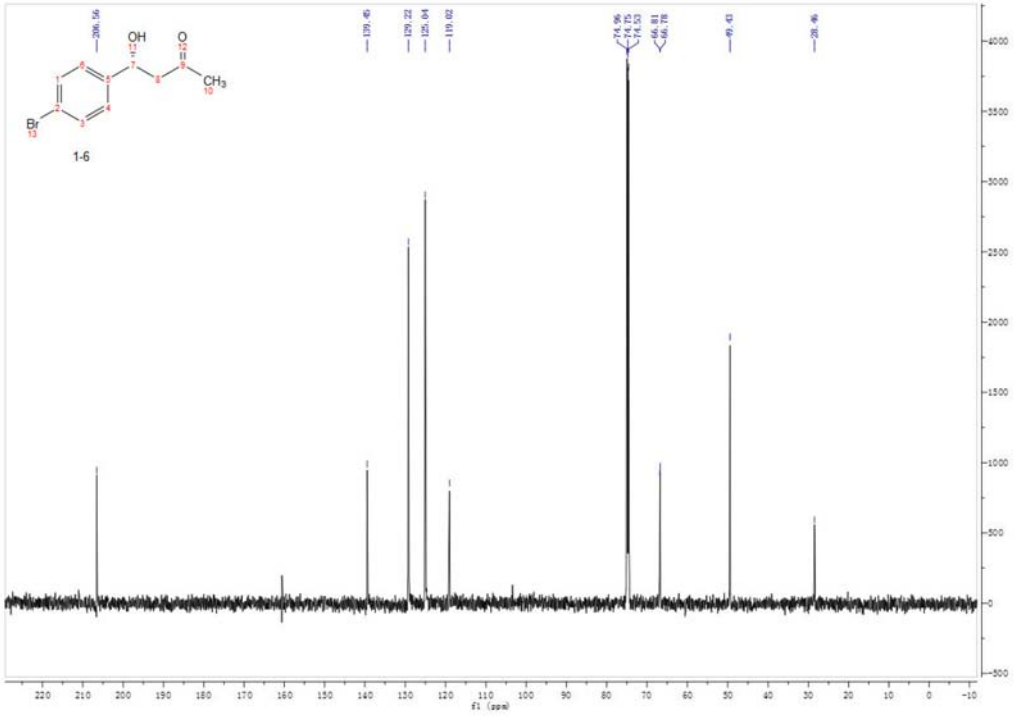


Figure S36. ^{13}C NMR (125 MHZ, $CDCl_3$) spectrum of **5h**.

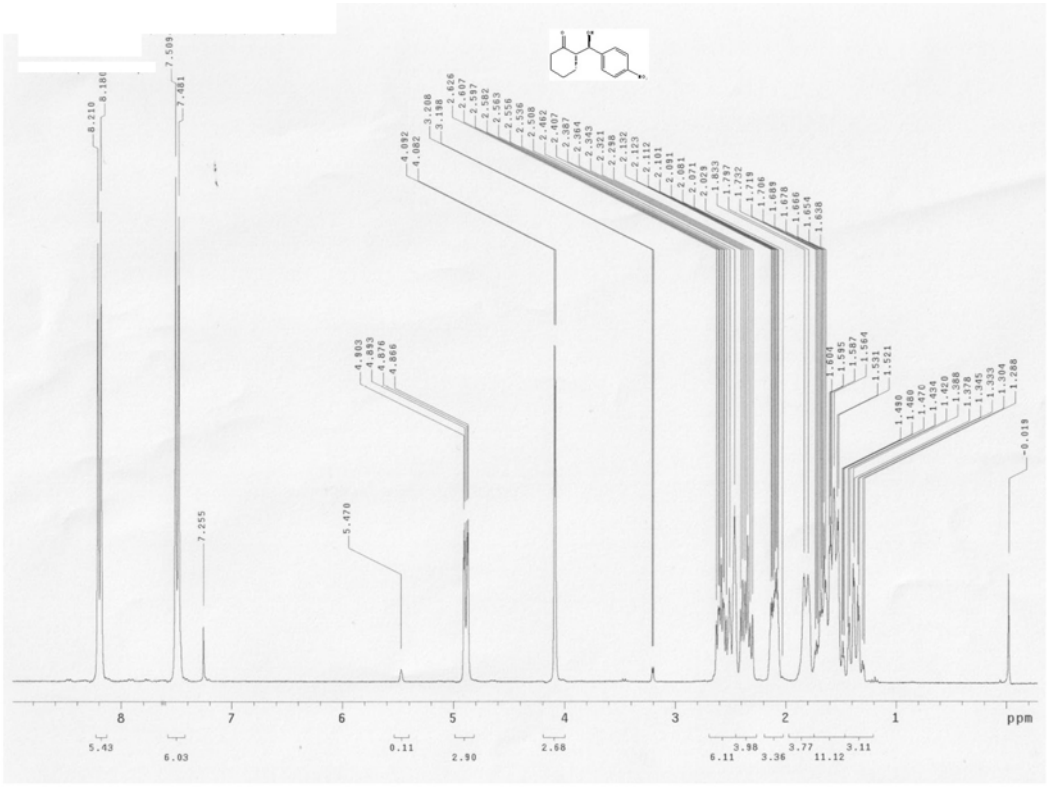


Figure S37. ^{1}H NMR (300 MHZ, $CDCl_3$) spectrum of **7**.

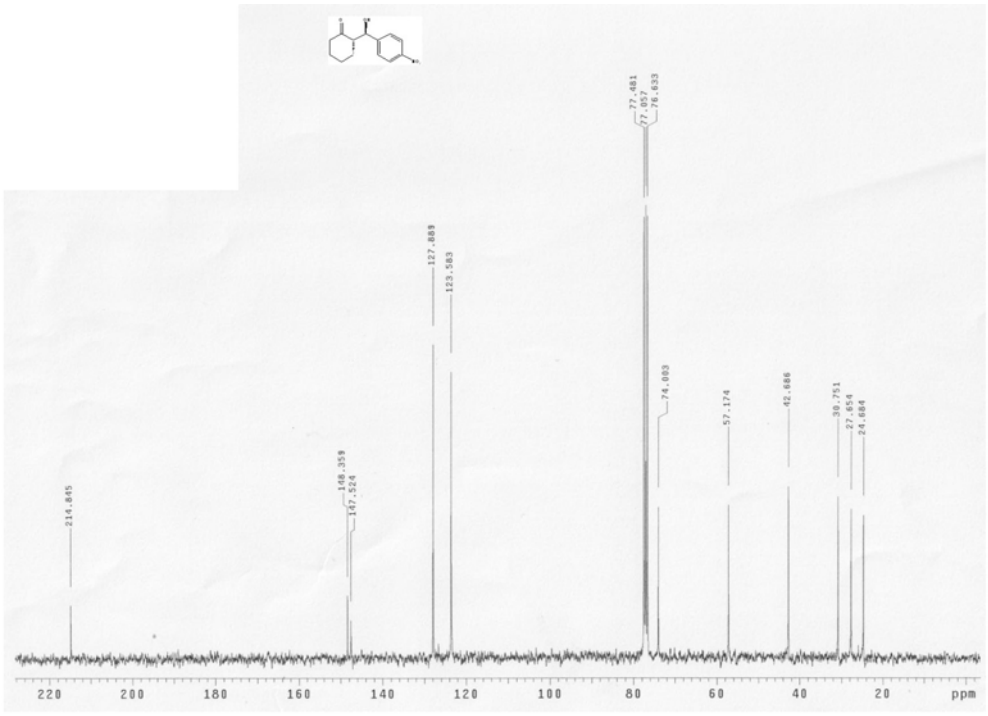
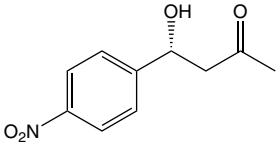


Figure S38. ^{13}C NMR (75 MHZ, $CDCl_3$) spectrum of **7**.

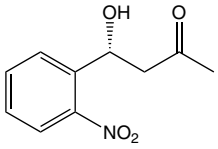
HPLC conditions for the aldol products

*4-Hydroxy-4-(4-nitrophenyl) butan-2-one (**5a**)*



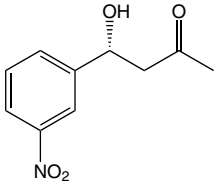
The optical purity was determined by HPLC on chiralpak AS-H column [hexane:2-propanol, 70:30]; flow rate 1.0 mL min^{-1}; λ = 210 nm; major: t_R = 12.8 min and minor: t_R =16.8 min.

*4-Hydroxy-4-(2-nitrophenyl) butan-2-one (**5b**)*



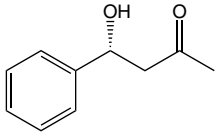
The optical purity was determined by HPLC on chiralpak AS-H column [hexane:2-propanol, 70:30]; flow rate 1.0 mL min^{-1}; λ = 220 nm; minor: t_R =8.3 min and major: t_R =11.2 min.

*4-Hydroxy-4-(3-nitrophenyl) butan-2-one (**5c**)*



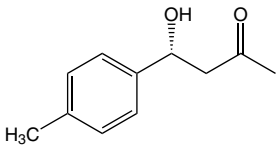
The optical purity was determined by HPLC on chiralpak OJ-H column [hexane:2-propanol, 70:30]; flow rate 1.0 mL min^{-1}; λ = 220 nm; major: t_R = 10.7 min and minor: t_R =12.4 min.

*4-Hydroxy-4-phenylbutan-2-one (**5d**)*



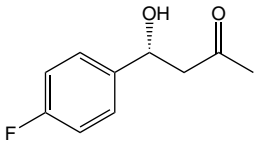
The optical purity was determined by HPLC on chiralpak AD-H column [hexane:2-propanol, 95:5]; flow rate 1.0 mL min^{-1}; λ = 210 nm; major: t_R =14.4 min and minor: t_R = 16.3 min.

*(R)-4-Hydroxy-4-p-tolylbutan-2-one (**5e**)*



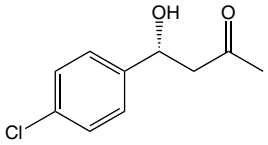
The optical purity was determined by HPLC on chiralpak AS-H column [hexane:2-propanol, 85:15]; flow rate 1.0 mL min^{-1}; λ = 220 nm; major: t_R =9.8 min and minor: t_R =12.2 min.

*4-(4-Fluorophenyl)-4-hydroxybutan-2-one (**5f**)*



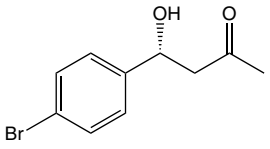
The optical purity was determined by HPLC on chiralpak AS-H column [hexane:2-propanol, 70:3]; flow rate 1.0 mL min^{-1}; λ = 220 nm , major: t_R =7.1 min and minor: 7.6 min.

*4-(4-Chlorophenyl)-4-hydroxybutan-2-one (**5g**)*



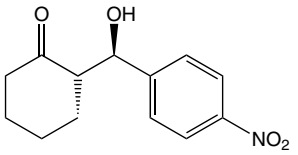
The optical purity was determined by HPLC on chiralpak AS-H column [hexane:2-propanol, 80:20]; flow rate 1.0 mL min^{-1}; λ = 220 nm; major: t_R = 9.0 min and minor: t_R =10.9 min.

*4-(4-Bromophenyl)-4-hydroxybutan-2-one (**5h**)*



The optical purity was determined by HPLC on chiralpak AS-H column [hexane:2-propanol, 70:30]; flow rate 1.0 mL min^{-1}; λ = 220 nm; major: t_R =7.0 min and minor: t_R =8.1 min.

*(S)-2-((R)-Hydroxy(4-nitrophenyl)methyl)cyclohexanone (**7**)*



The optical purity was determined by HPLC on chiralpak AD-H column [hexane:2-propanol, 80:20]; flow rate 0.5 mL min^{-1}; λ = 220 nm; mimor: t_R =21.6 min and 22.7, major: t_R =24.6 and 31.4 min.

HPLC spectra

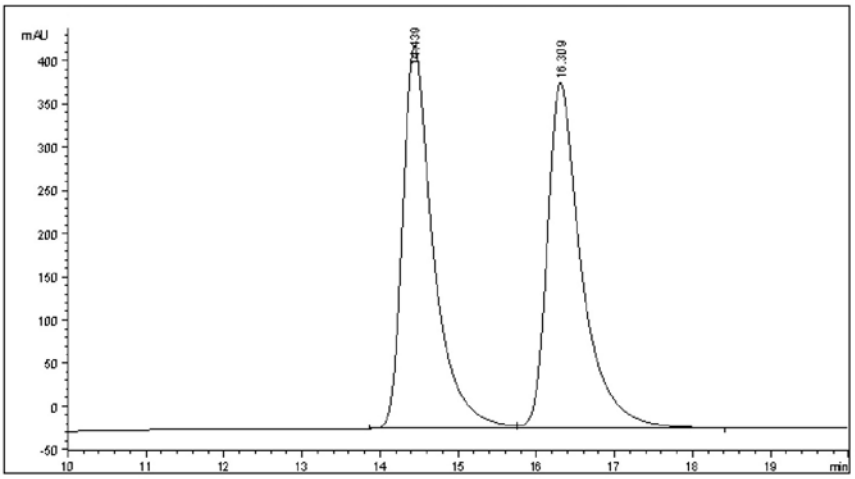


Figure S39. HPLC spectrum of **5a** (racemic).

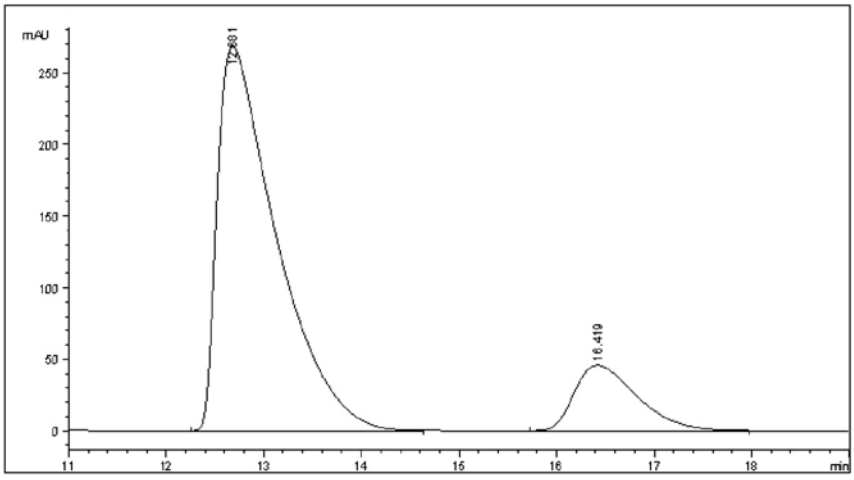


Figure S40. HPLC spectrum of **5a** (Table 1, entry 5).

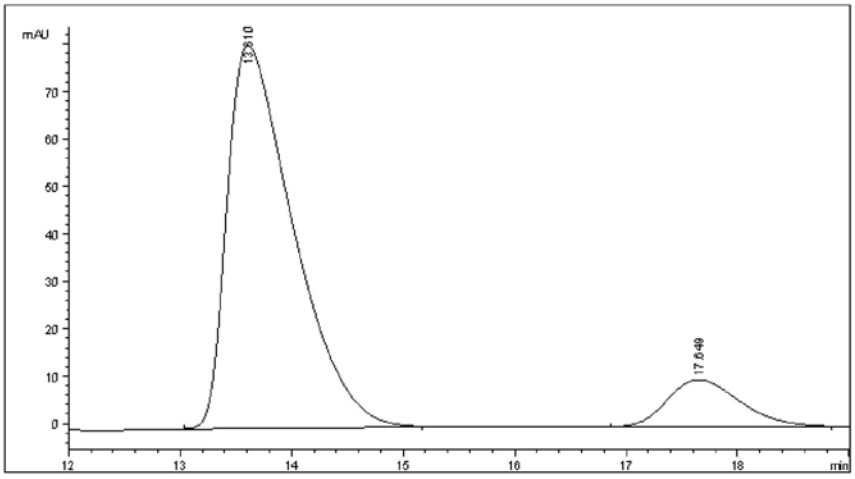


Figure S41. HPLC spectrum of **5a** (Table 1, entry 6).

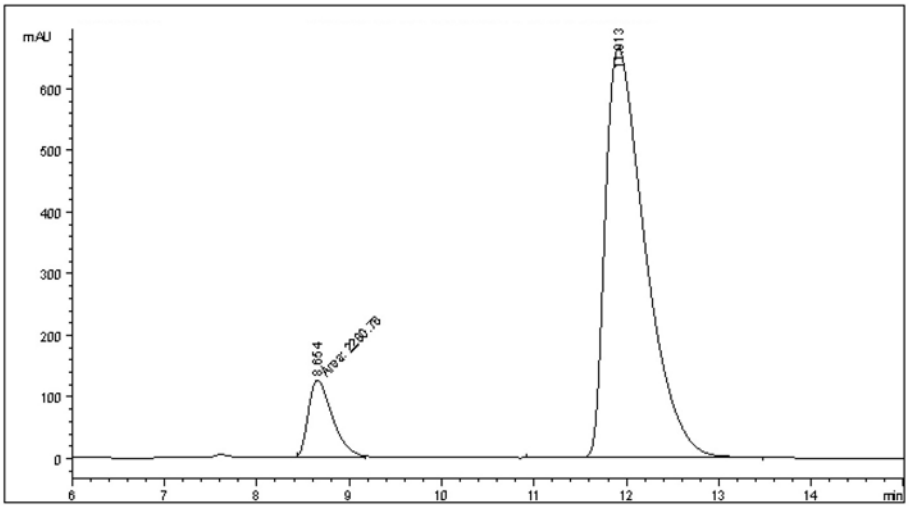


Figure S42. HPLC spectrum of **5b** (Table 1, entry 9).

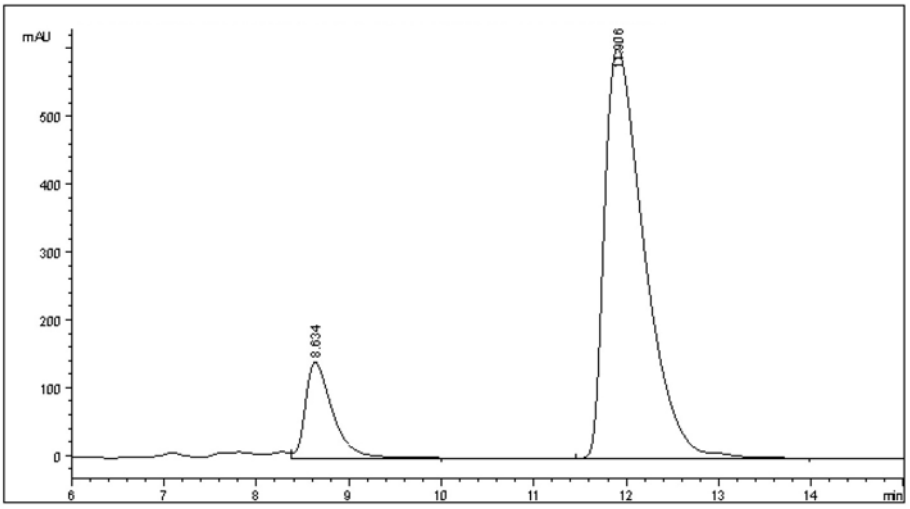


Figure S43. HPLC spectrum of **5b** (Table 1, entry 10).

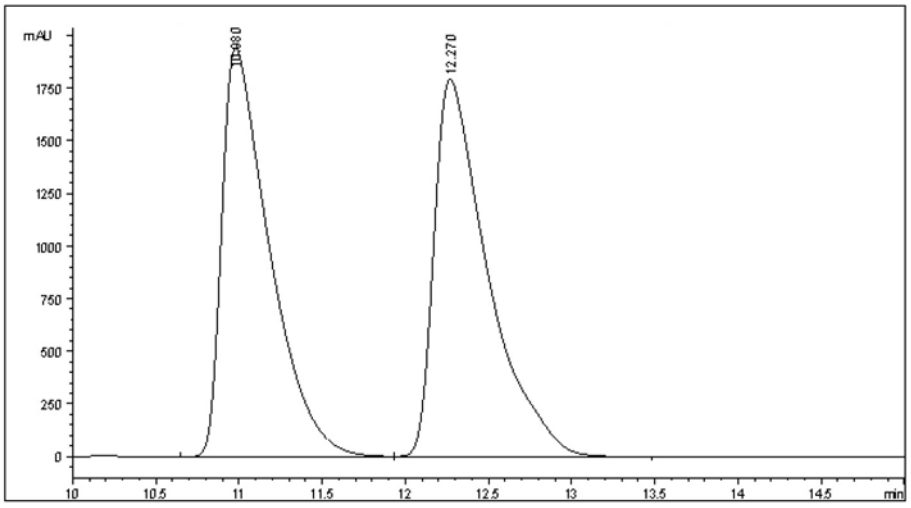


Figure S44. HPLC spectrum of **5c** (racemic).

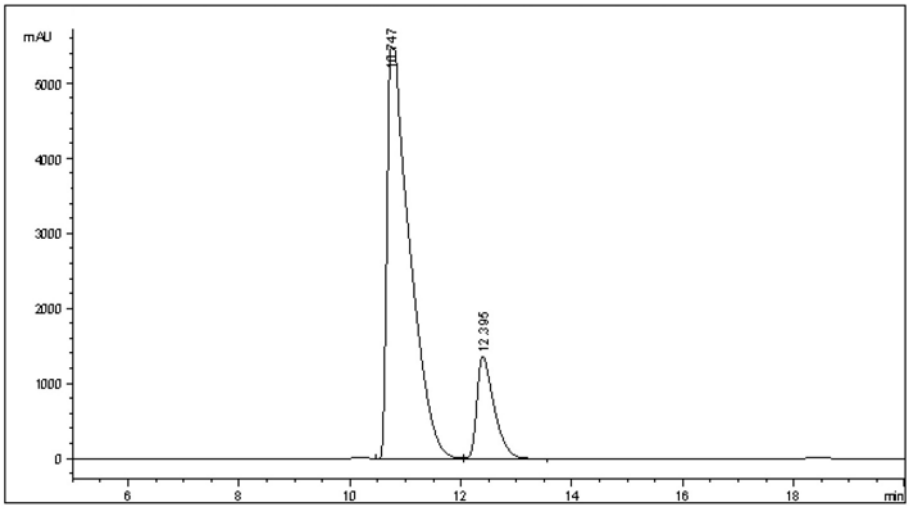


Figure S45. HPLC spectrum of **5c** (Table 1, entry 14).

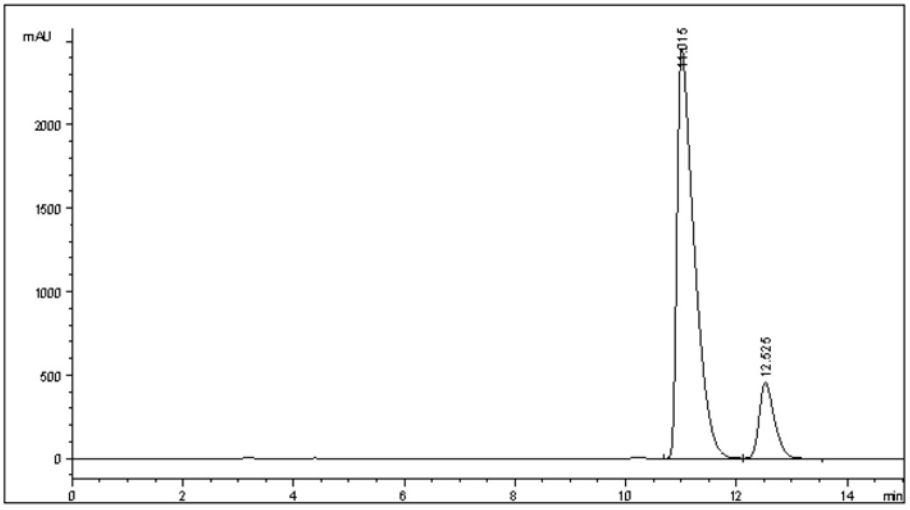


Figure S46. HPLC spectrum of **5c** (Table 1, entry 15).

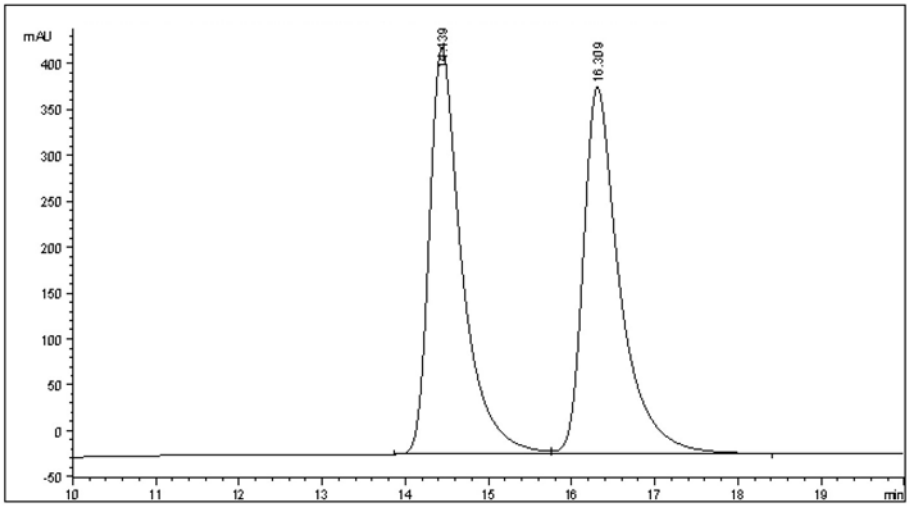


Figure S47. HPLC spectrum of **5d** (racemic).

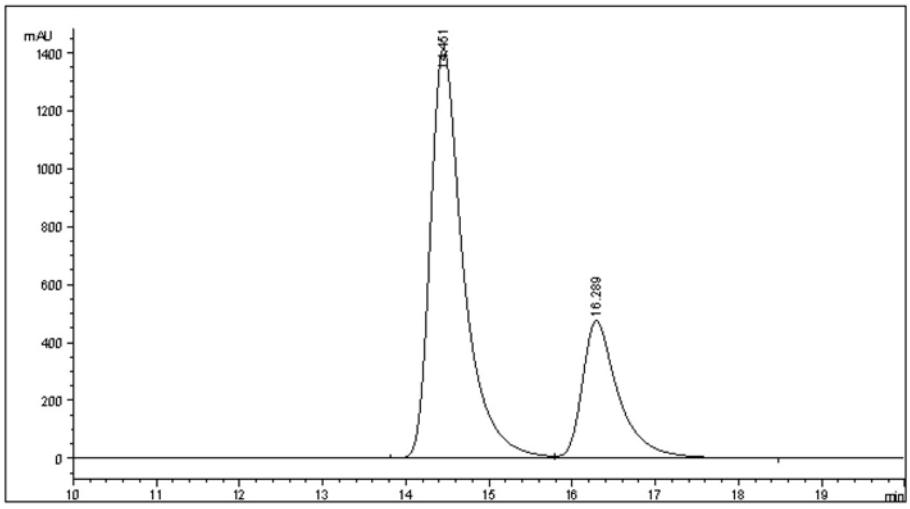


Figure S48. HPLC spectrum of **5d** (Table 1, entry 16).

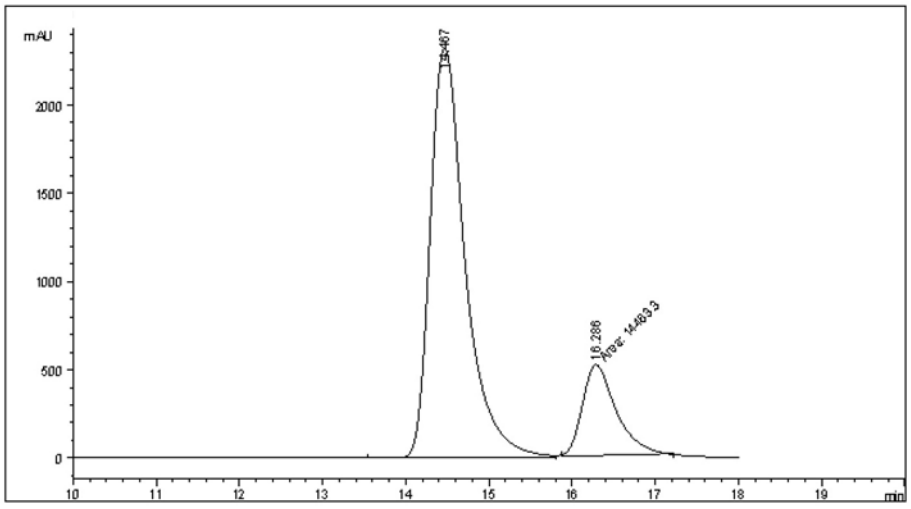


Figure S49. HPLC spectrum of **5d** (Table 1, entry 17).

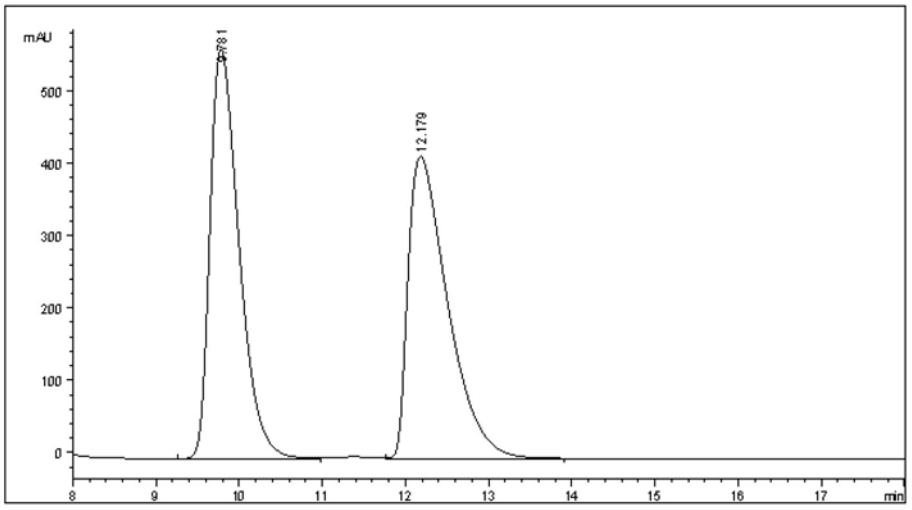


Figure S50. HPLC spectrum of **5e** (racemic).

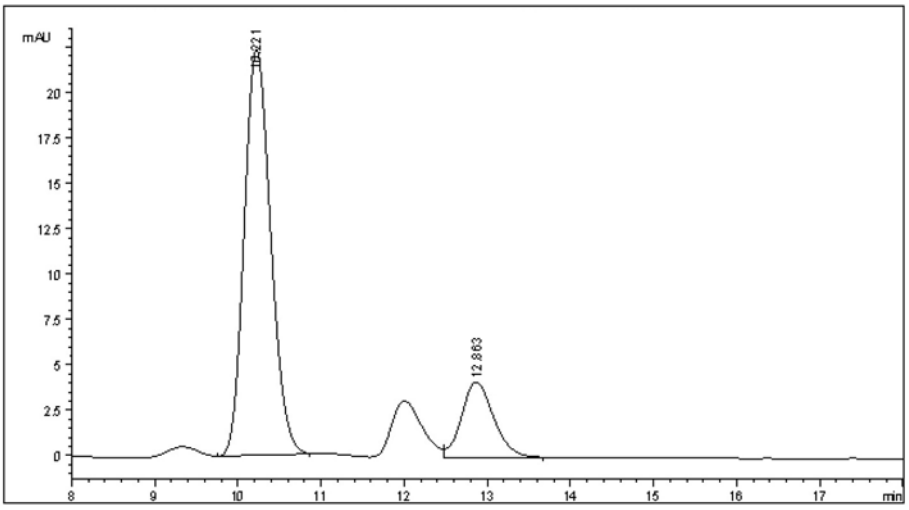


Figure S51. HPLC spectrum of **5e** (Table 1, entry 29).

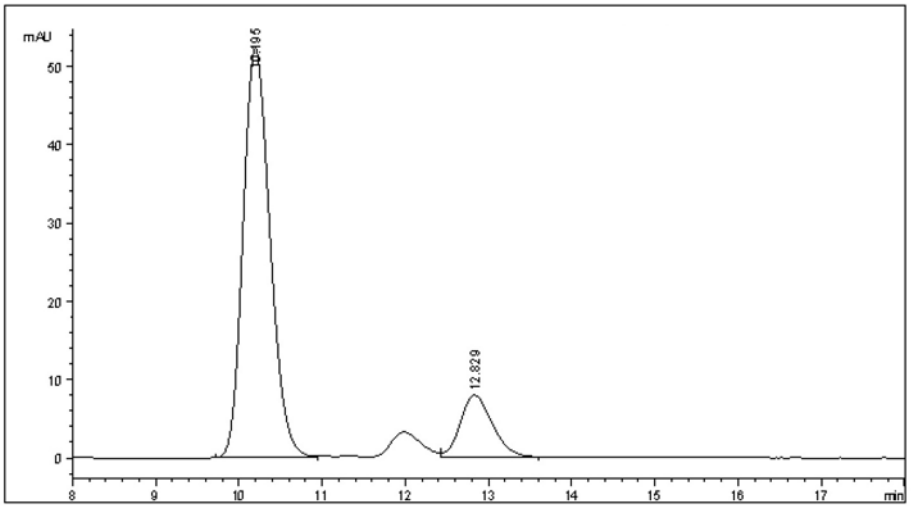


Figure S52. HPLC spectrum of **5e** (Table 1, entry 30).

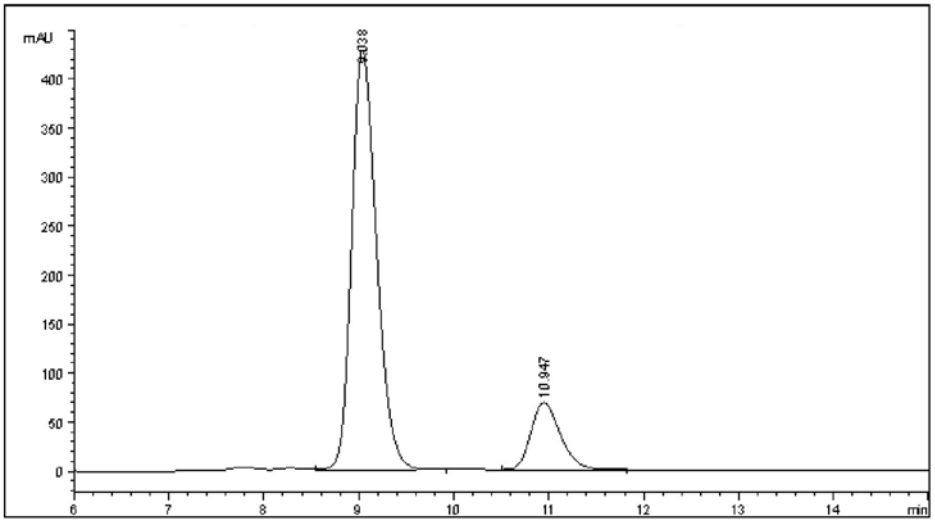


Figure S53. HPLC spectrum of **5f** (Table 1, entry 20).

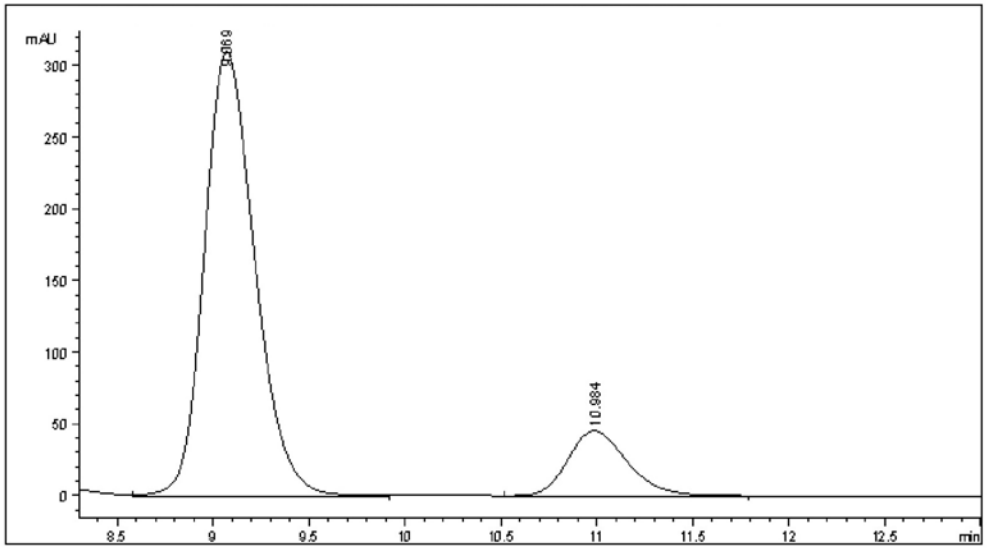


Figure S54. HPLC spectrum of **5f** (Table 1, entry 21).

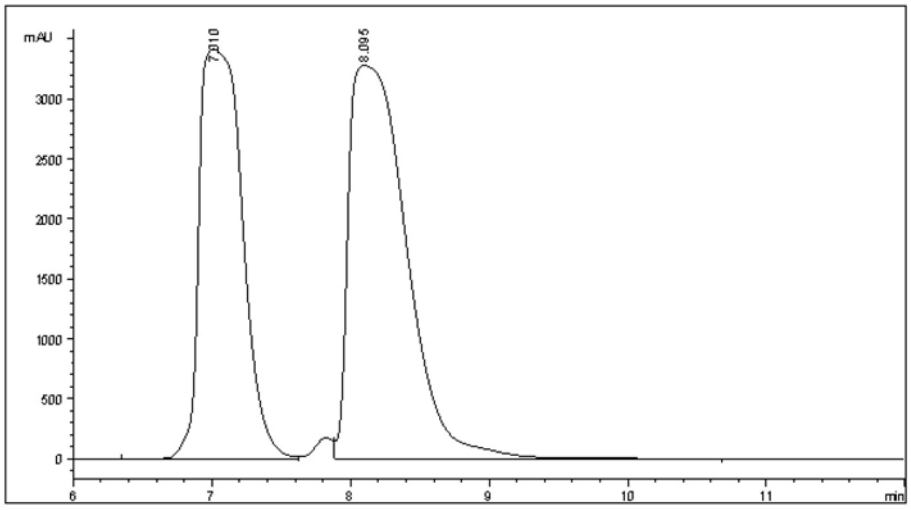


Figure S55. HPLC spectrum of **5g** (racemic).

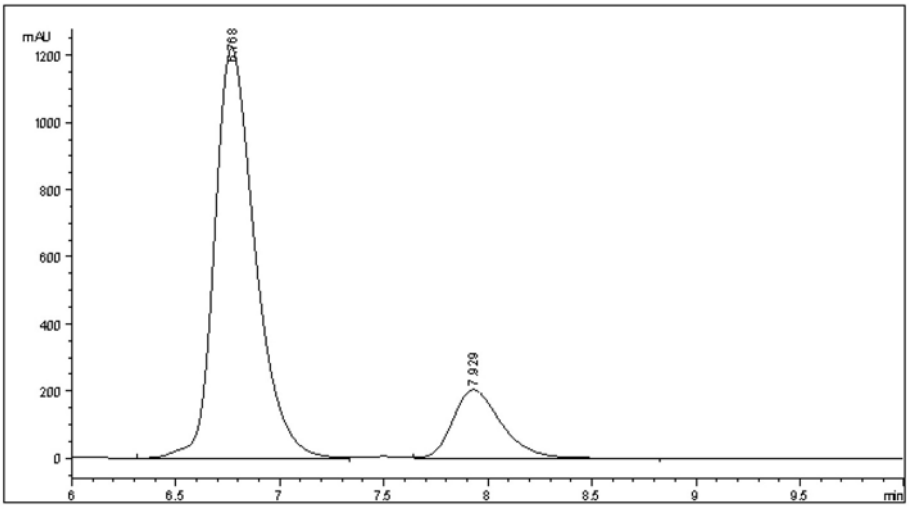


Figure S56. HPLC spectrum of **5g** (Table 1, entry 27).

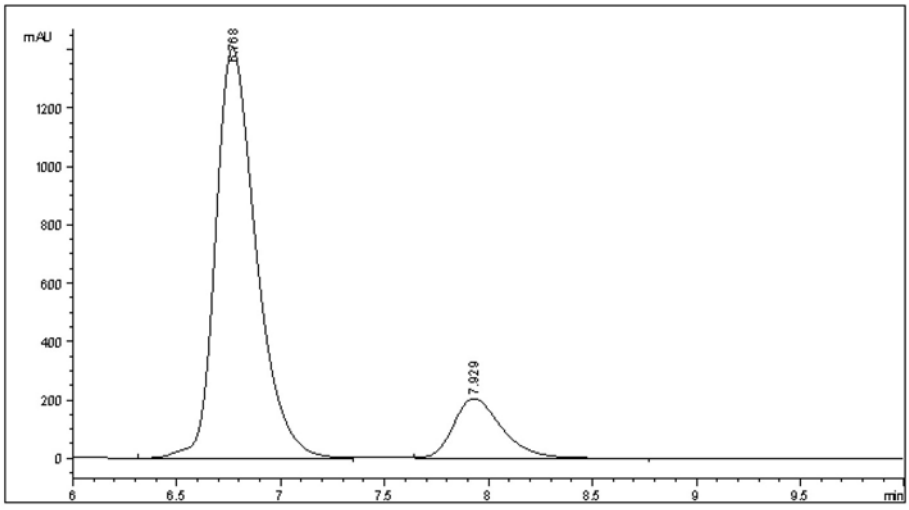


Figure S57. HPLC spectrum of **5g** (Table 1, entry 28).

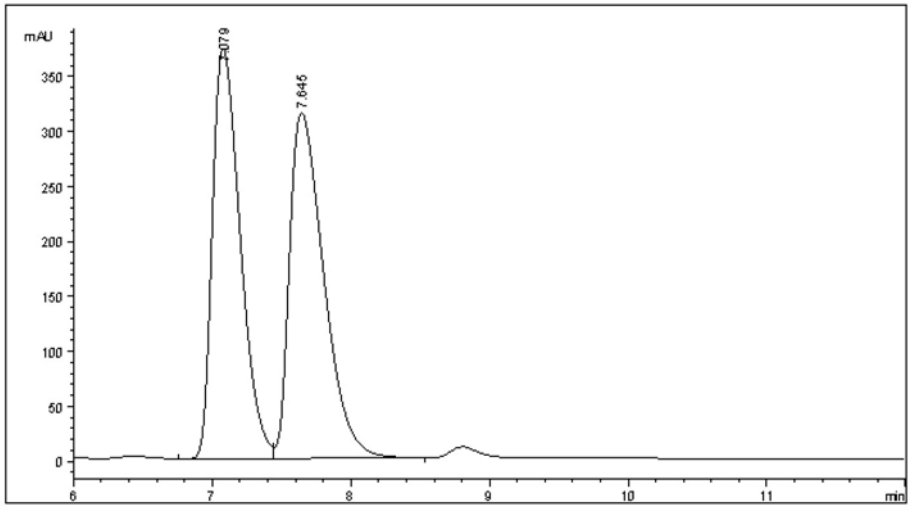


Figure S58. HPLC spectrum of **5h** (racemic).

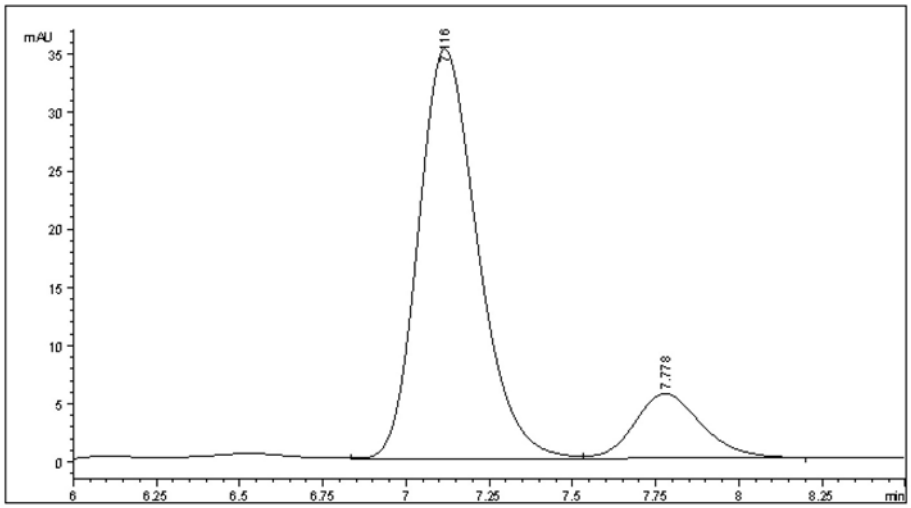


Figure S59. HPLC spectrum of **5h** (Table 1, entry 29).

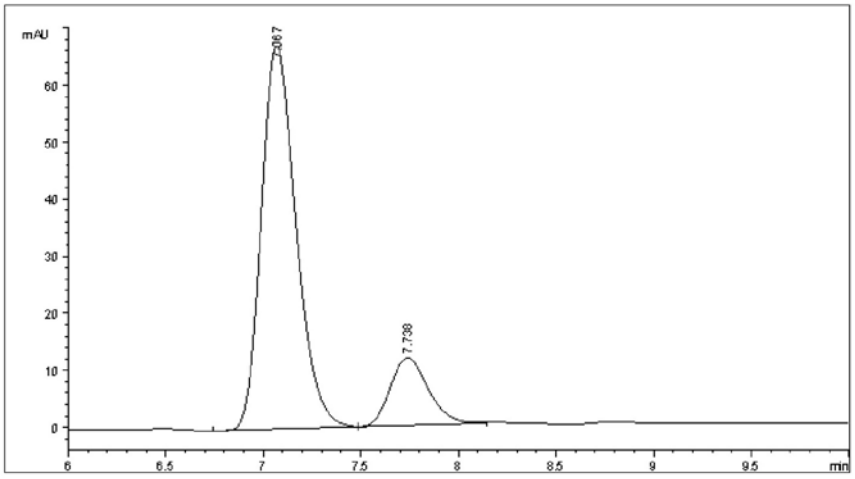


Figure S60. HPLC spectrum of **5h** (Table 1, entry 30).

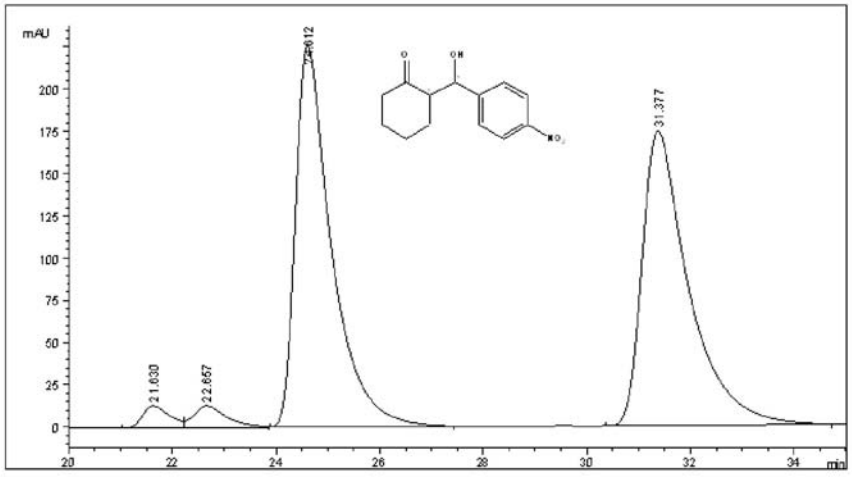


Figure S61. HPLC spectrum of **7** (racemic).

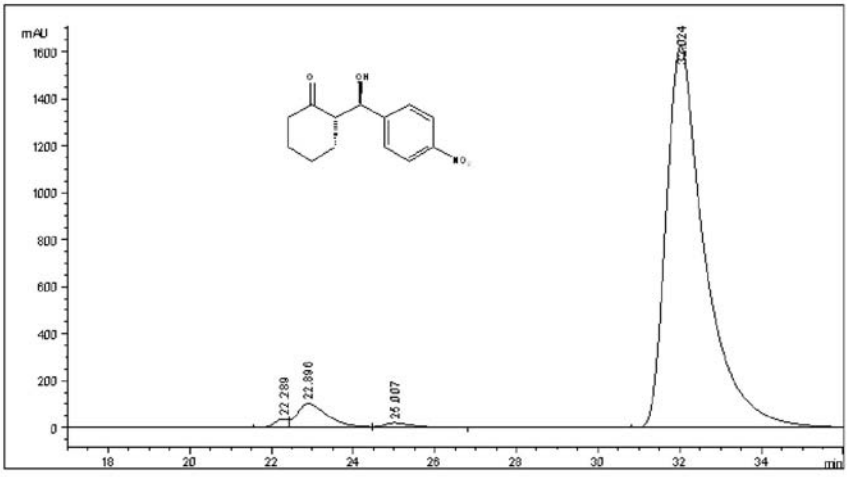


Figure S62. HPLC spectrum of **7** (Table 2, entry 5).

References

1. Zhou Y.; Shan Z.; *Tetrahedron: Asymmetry* **2006**, *17*, 1671.
2. Jia Y. N.; Wu, F. C.; Ma, X.; Zhu, G. J.; Da, C. S.; *Tetrahedron Lett.* **2009**, *50*, 3059.