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Stereoselective Addition of Chiral Titanium Enolates to 5-Substituted Five-Membered Oxocarbenium Ions

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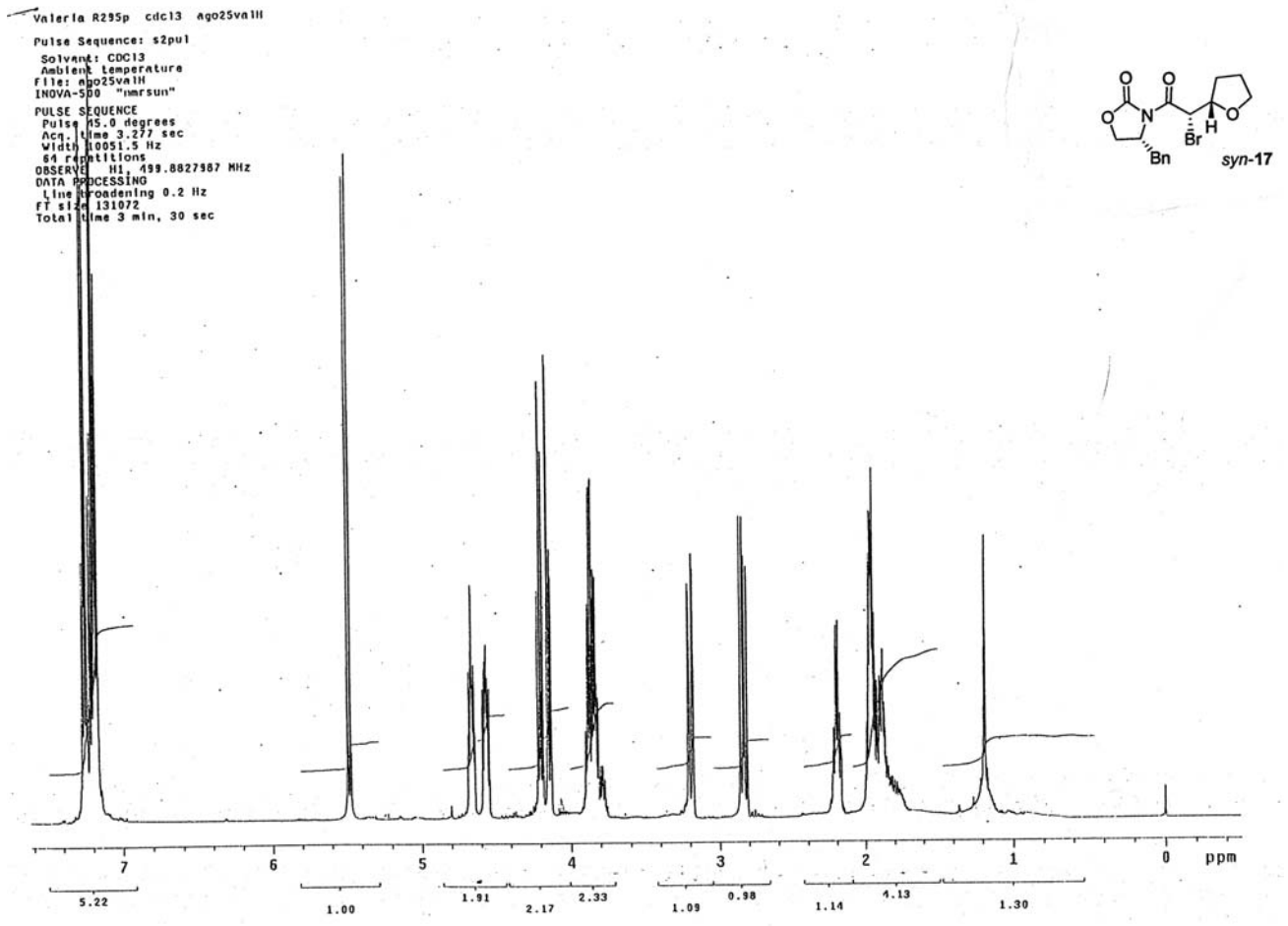

Figure S1. ^{1}H NMR spectrum of *syn*-**17** (500 MHz, $CDCl_3$)

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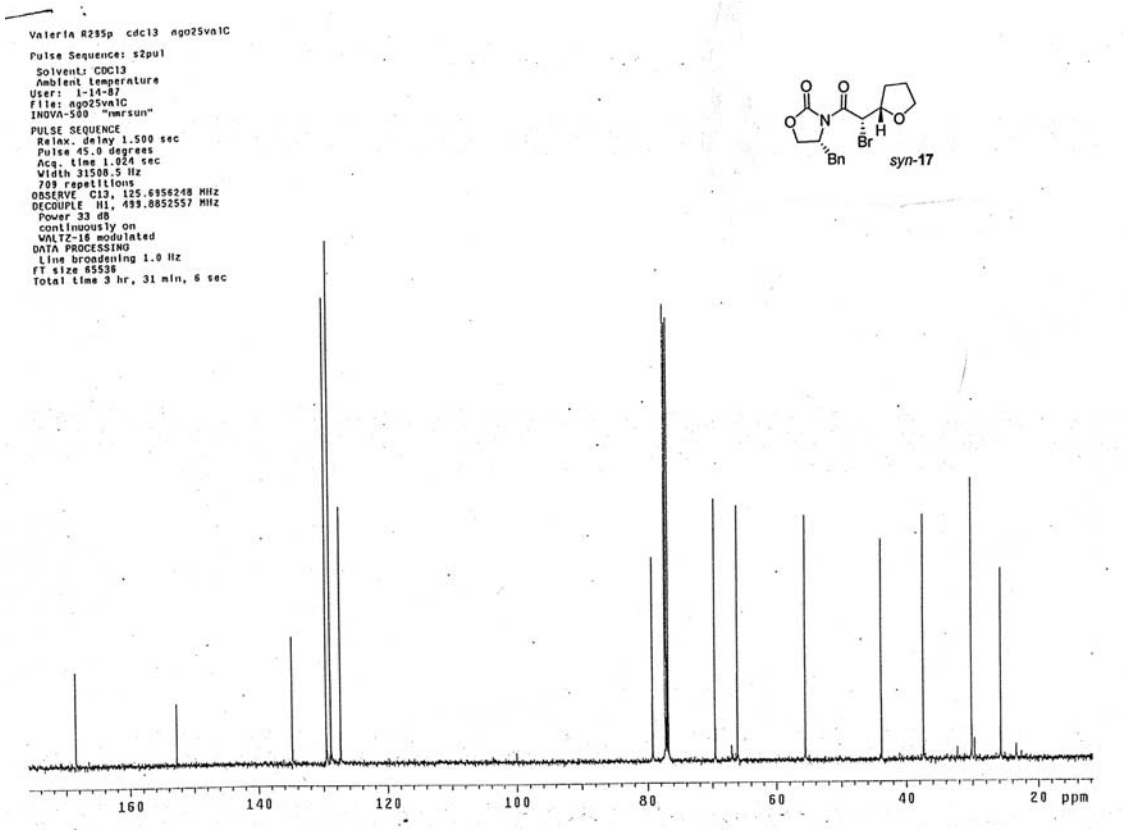

Figure S2. ^{13}C NMR spectrum of *syn*-**17** (125 MHz, $CDCl_3$)

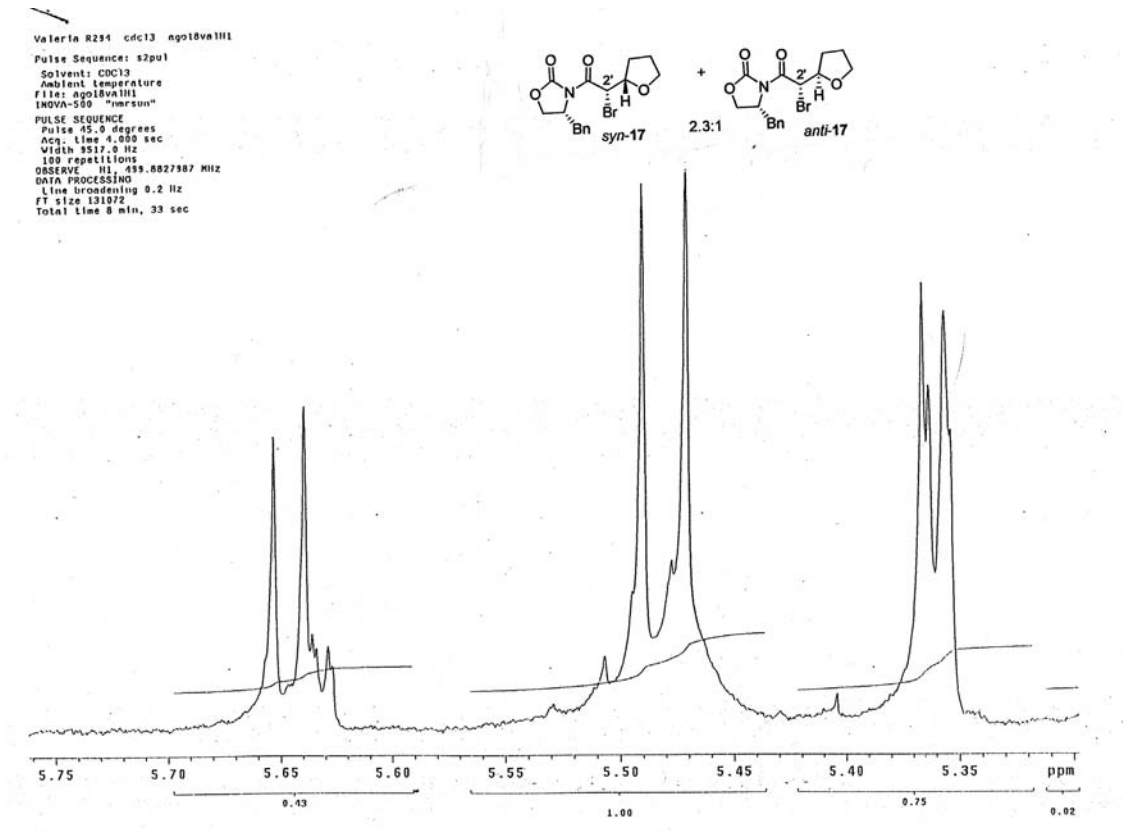

Figure S3. ^{1}H NMR spectrum of a crude mixture of *syn*-**17**/*anti*-**17** ($CDCl_3$, 500 MHz) *syn*-**17**: 5.48 (d, *J* 9.7 Hz, $H_{2'}$) and *anti*-**17**: 5.64 (d, *J* 7.0 Hz, $H_{2'}$)

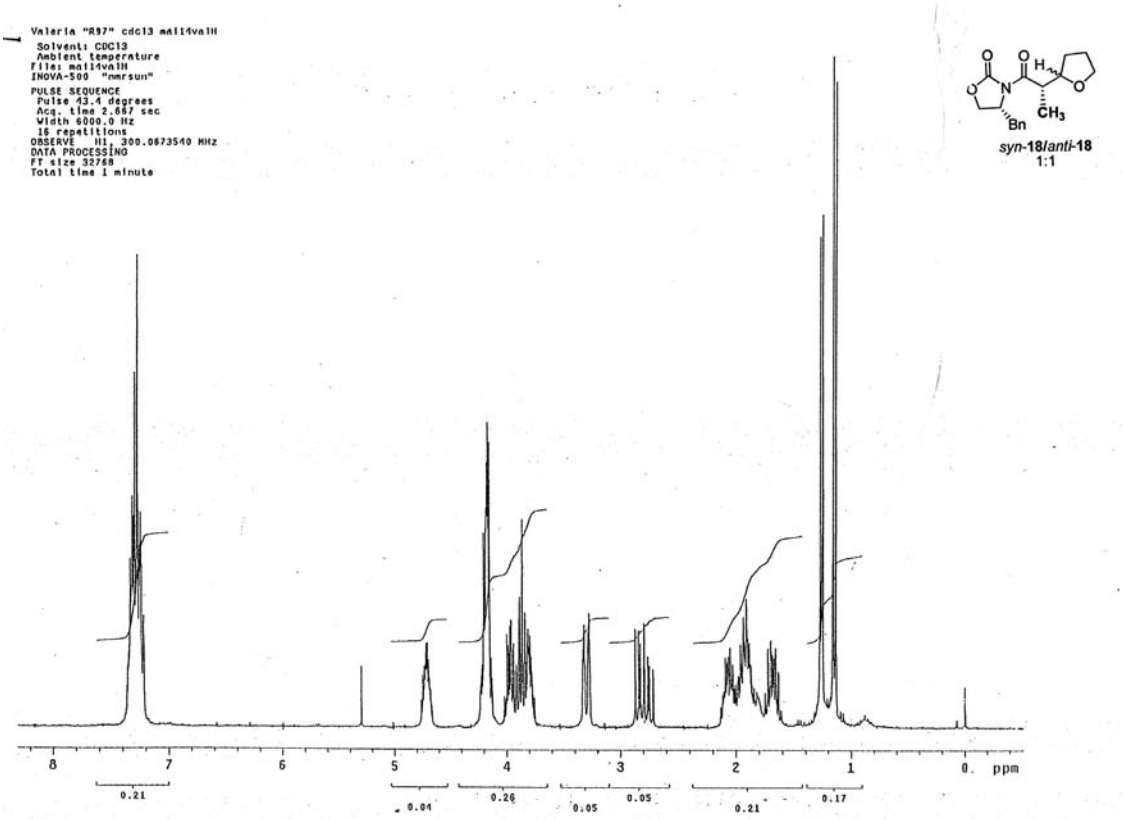

Figure S4. [1]H NMR spectrum of 1:1 *syn*-**18**/*anti*-**18** mixture (300 MHz, $CDCl_3$)

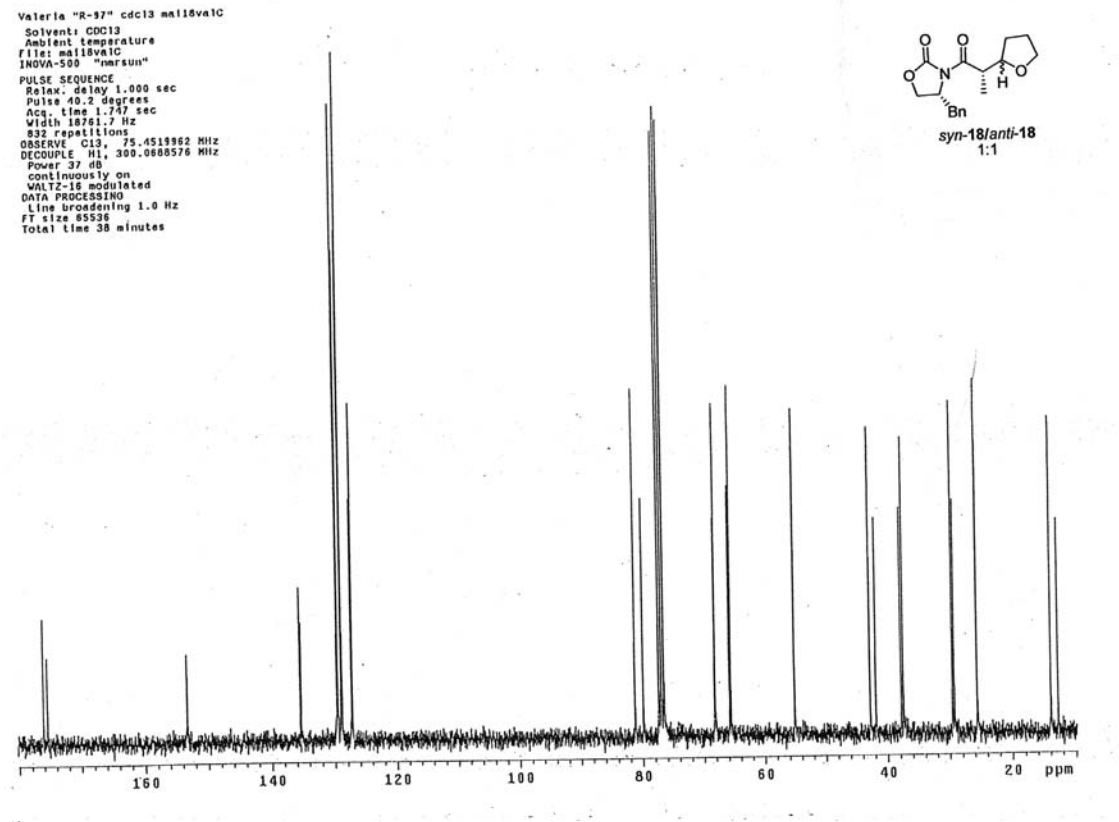

Figure S5. [13]C NMR spectrum of 1:1 *syn*-**18**/*anti*-**18** mixture (75 MHz, $CDCl_3$)

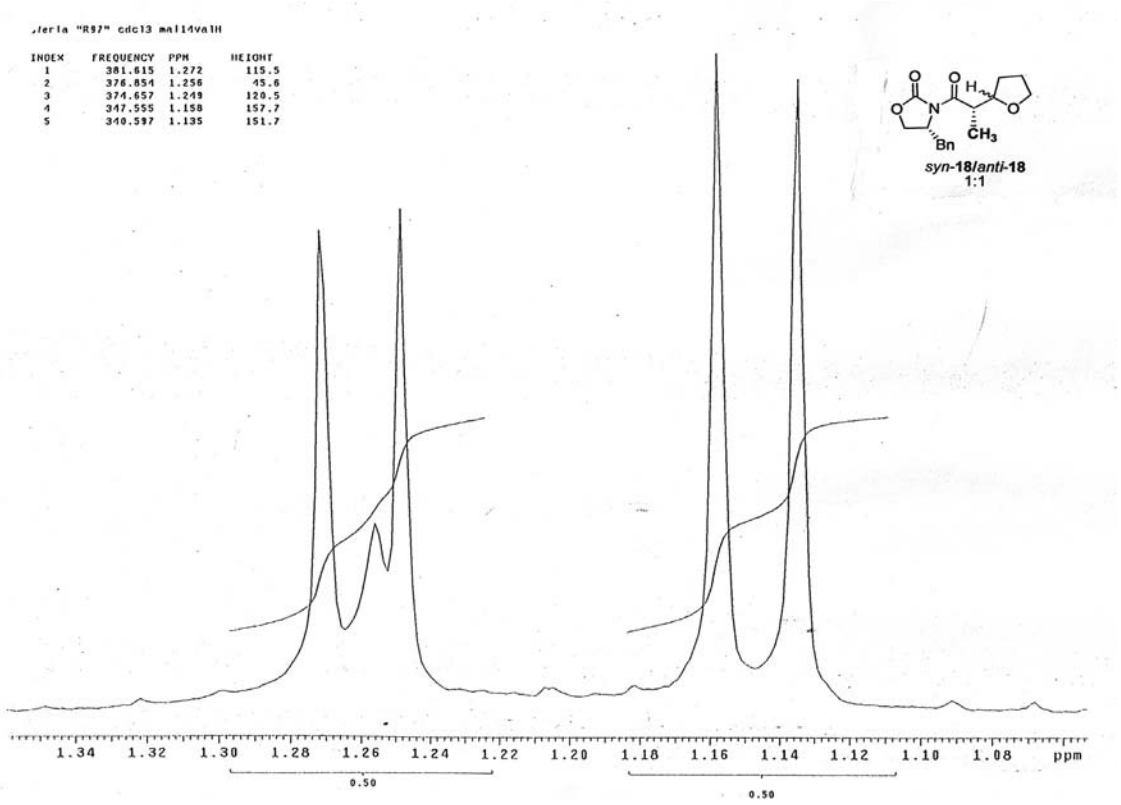

Figure S6. ^{1}H NMR spectrum of a crude mixture of *syn*-**18**/*anti*-**18** ($CDCl_3$, 300 MHz) 1.26 (d, *J* 7.0 Hz, CH_3) and 1.14 (d, *J* 7.0 Hz, CH_3)

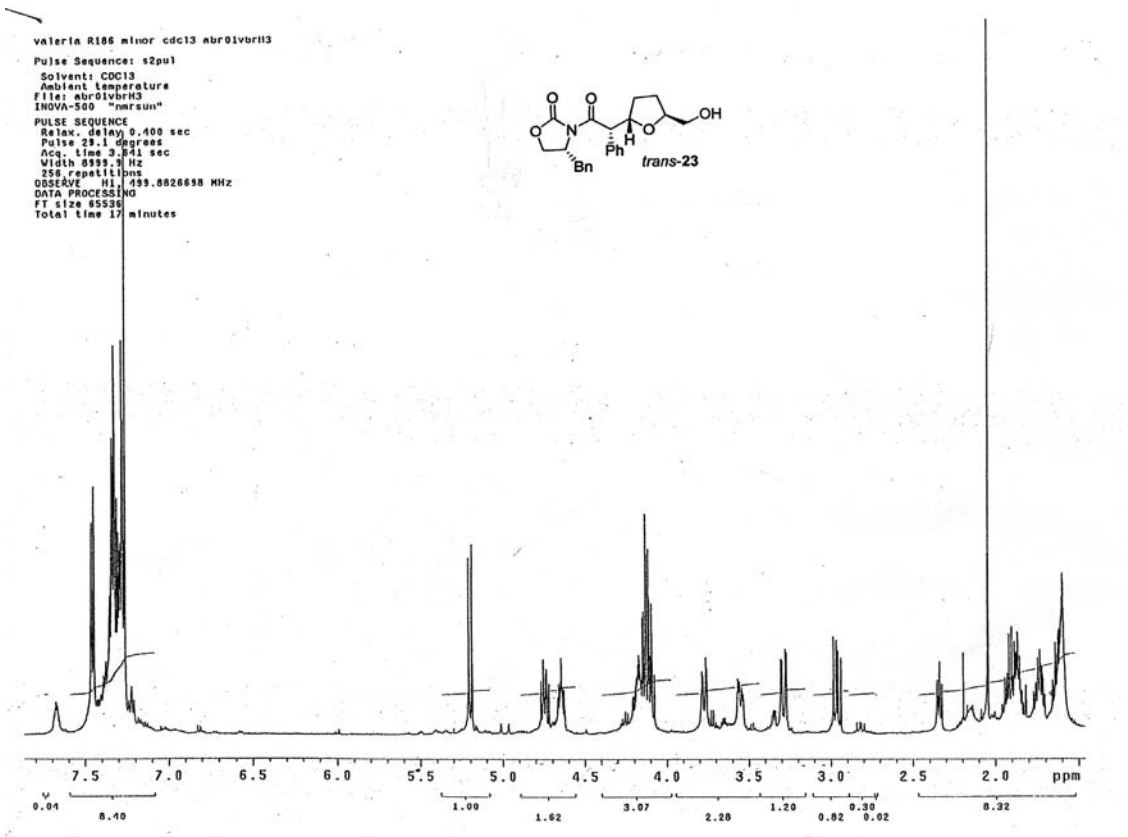

Figure S7. ^{1}H NMR spectrum of *trans*-**23** (500 MHz, $CDCl_3$)

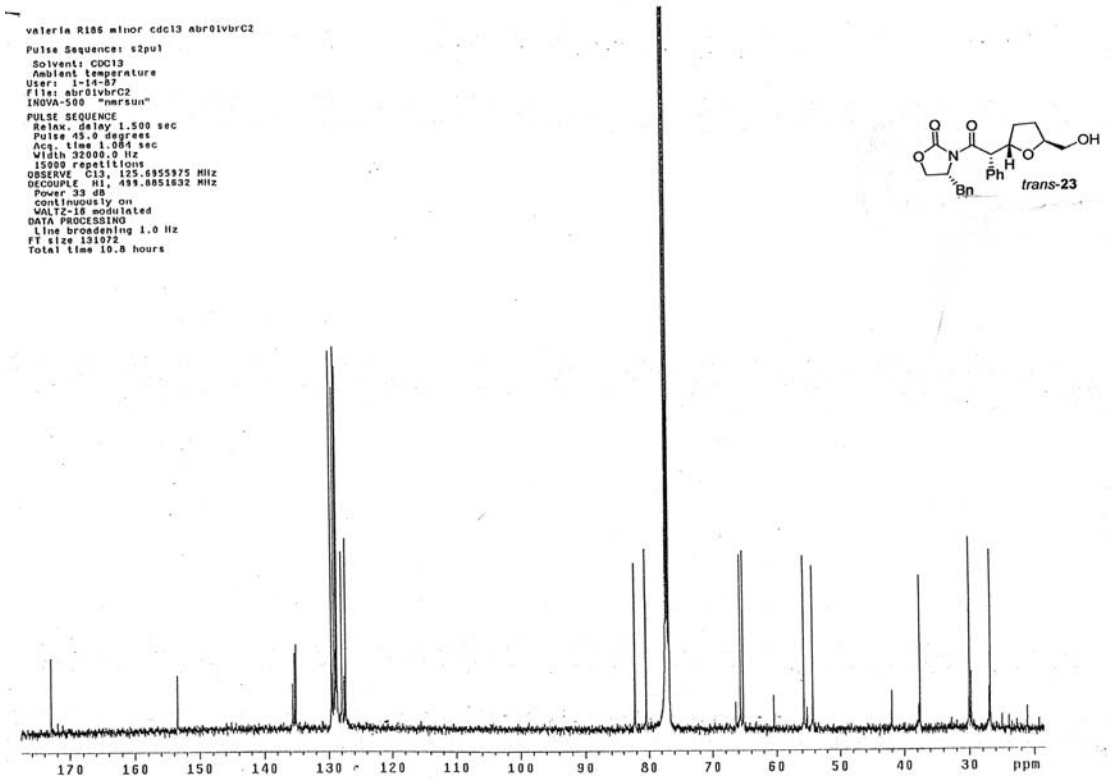

Figure S8. ^{13}C NMR spectrum of *trans*-**23** (125 MHz, $CDCl_3$)

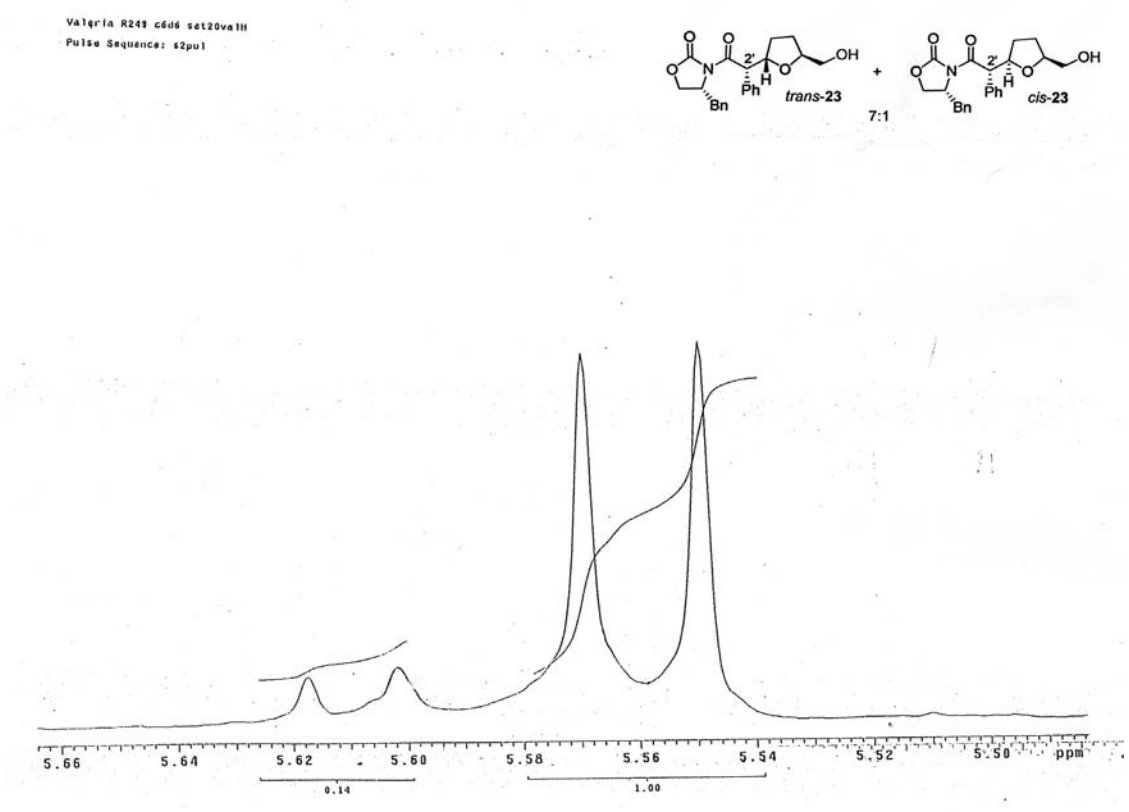

Figure S9. ^{1}H NMR spectrum of a crude mixture of *trans*-**23**/*cis*-**23** (C_6D_6, 500 MHz) *trans*-**23**: 5.56 (d, *J* 10.0 Hz, H_2) and *cis*-**23**: 5.61 (d, *J* 8.0 Hz, H_2)

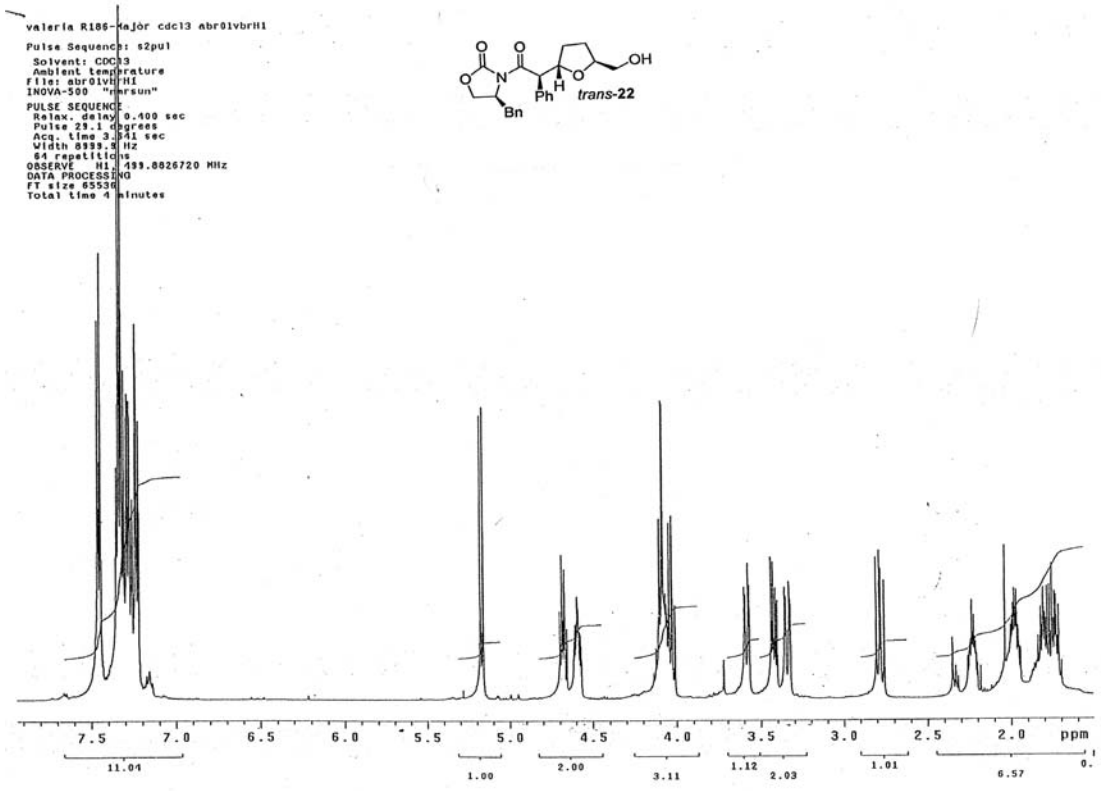

Figure S10. ^{1}H NMR spectrum of *trans*-**22** (500 MHz, $CDCl_3$)

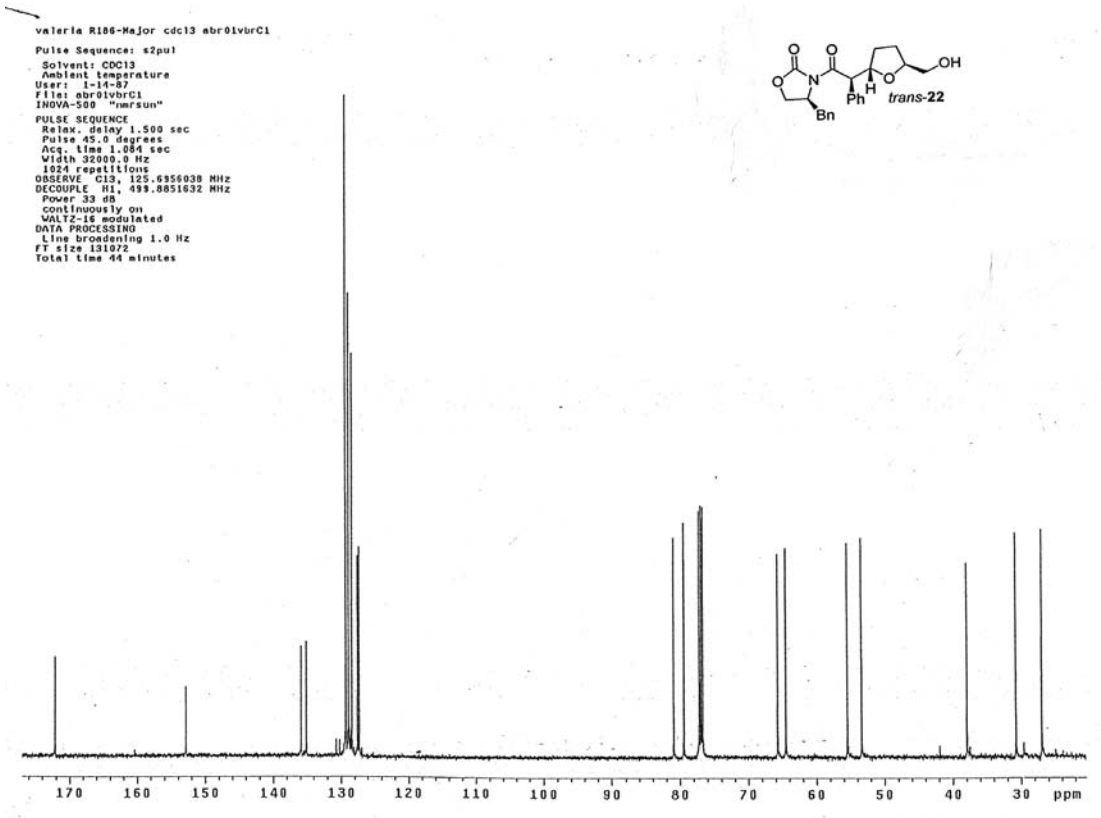

Figure S11. ^{13}C-NMR spectrum of *trans*-**22** (125 MHz, $CDCl_3$)

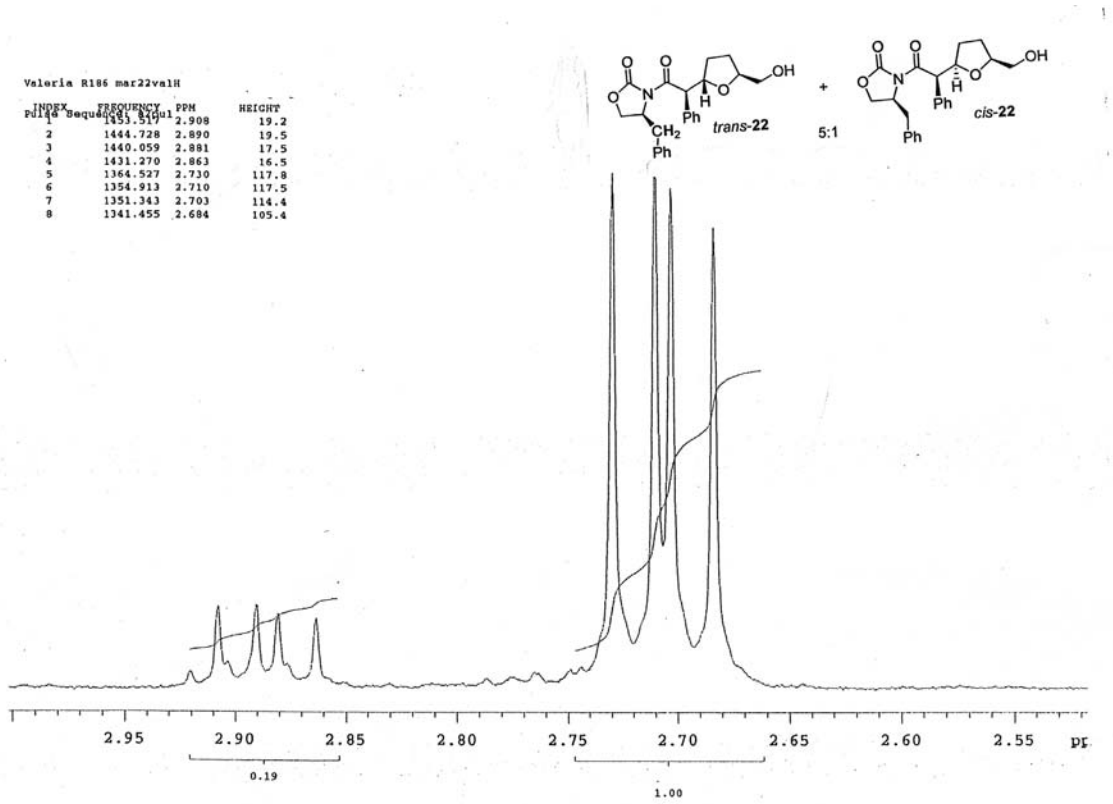

Figure S12. ^{1}H NMR spectrum of a crude mixture of *trans*-**22**/*cis*-**22** ($CDCl_3$, 500 MHz) *trans*-**22**: 2.70 (dd, *J* 9.6, 13.4 Hz, CH) and *cis*-**22**: 2.88 (dd, *J* 8.8, 13.4 Hz, CH)

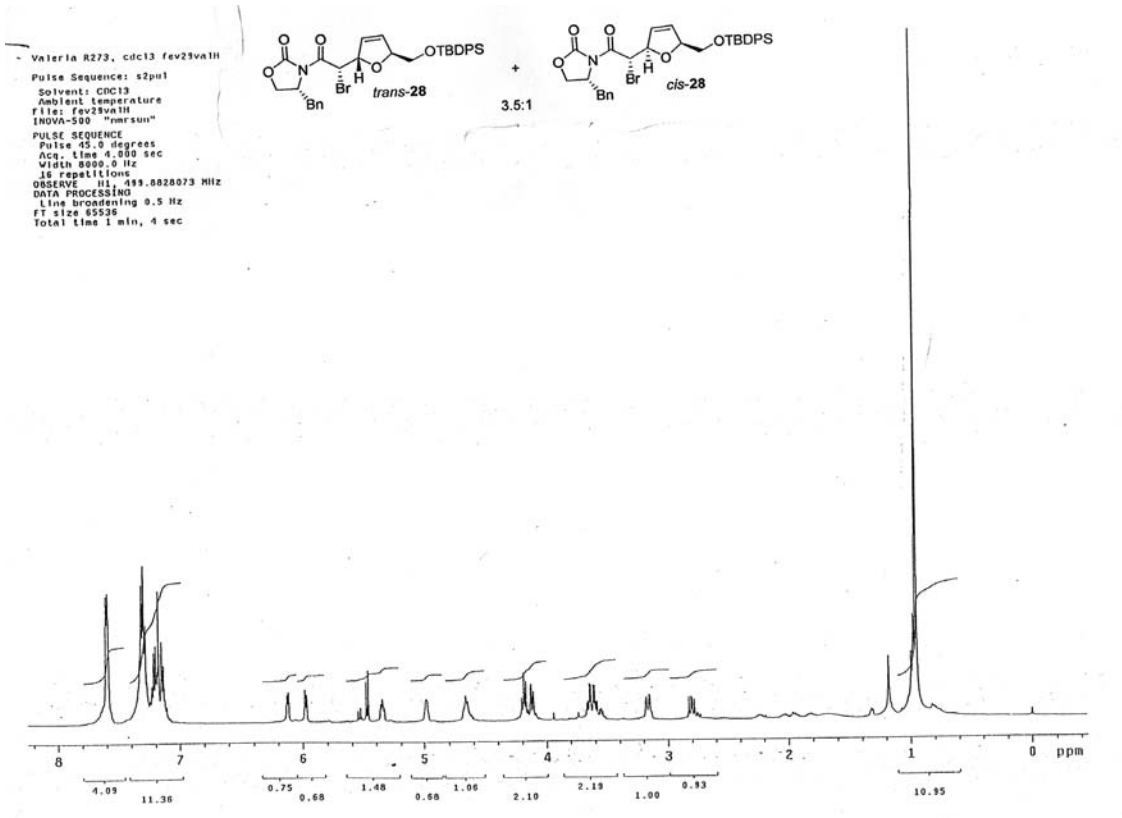

Figure S13. ^{1}H NMR spectrum of 3.5:1 *trans*-**28**/*cis*-**28** mixture (500 MHz, $CDCl_3$)

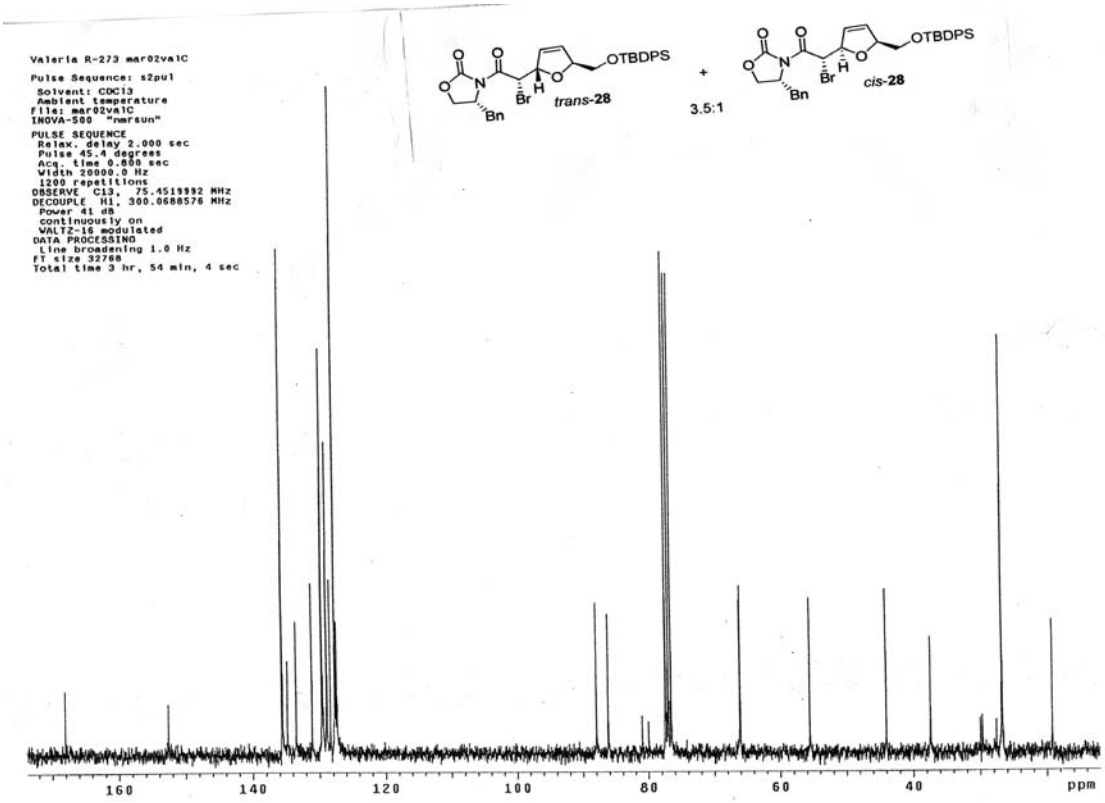

Figure S14. ^{13}C NMR spectrum of 3.5:1 *trans*-**28**/*cis*-**28** mixture (75 MHz, $CDCl_3$)

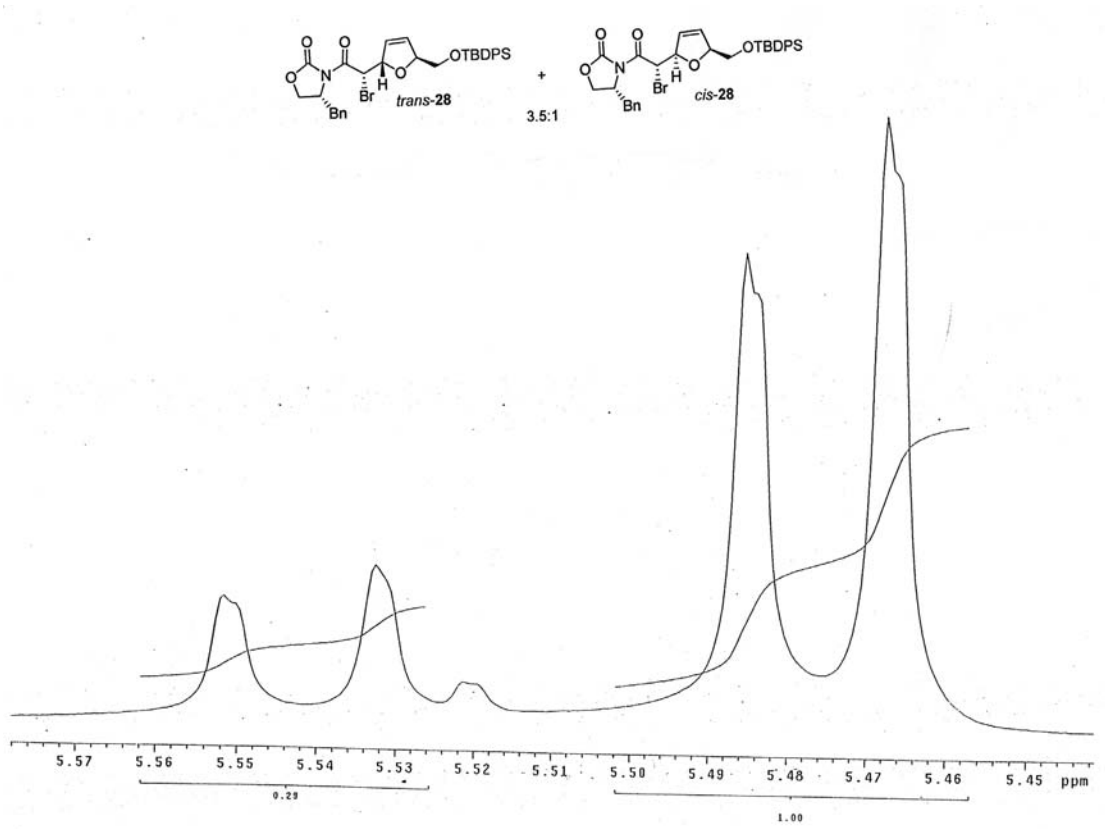

Figure S15. ^{1}H NMR spectrum of a crude mixture of *trans*-**28**/*cis*-**28** ($CDCl_3$, 500 MHz) *trans*-**28**: 5.47 (d, *J* 8.0 Hz, H_2) and *cis*-**28**: 5.54 (d, *J* 9.5 Hz, H_2)

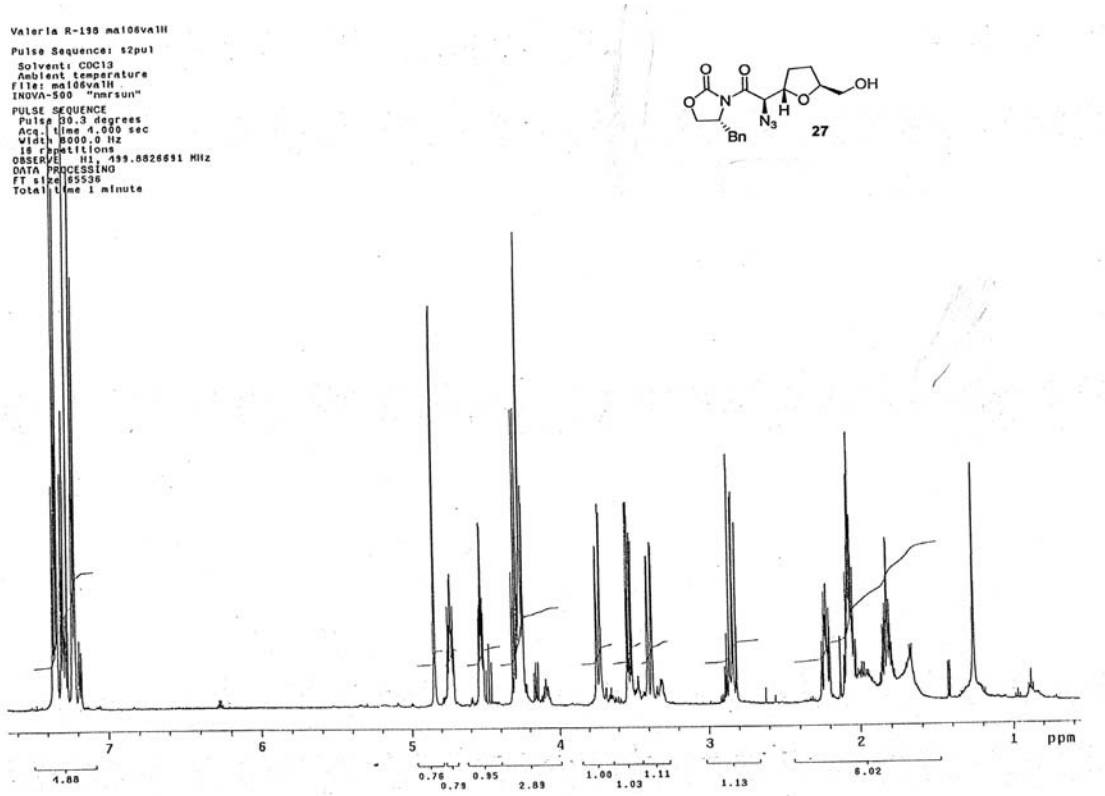

Figure S16. ^{1}H NMR spectrum of **27** (500 MHz, $CDCl_3$)

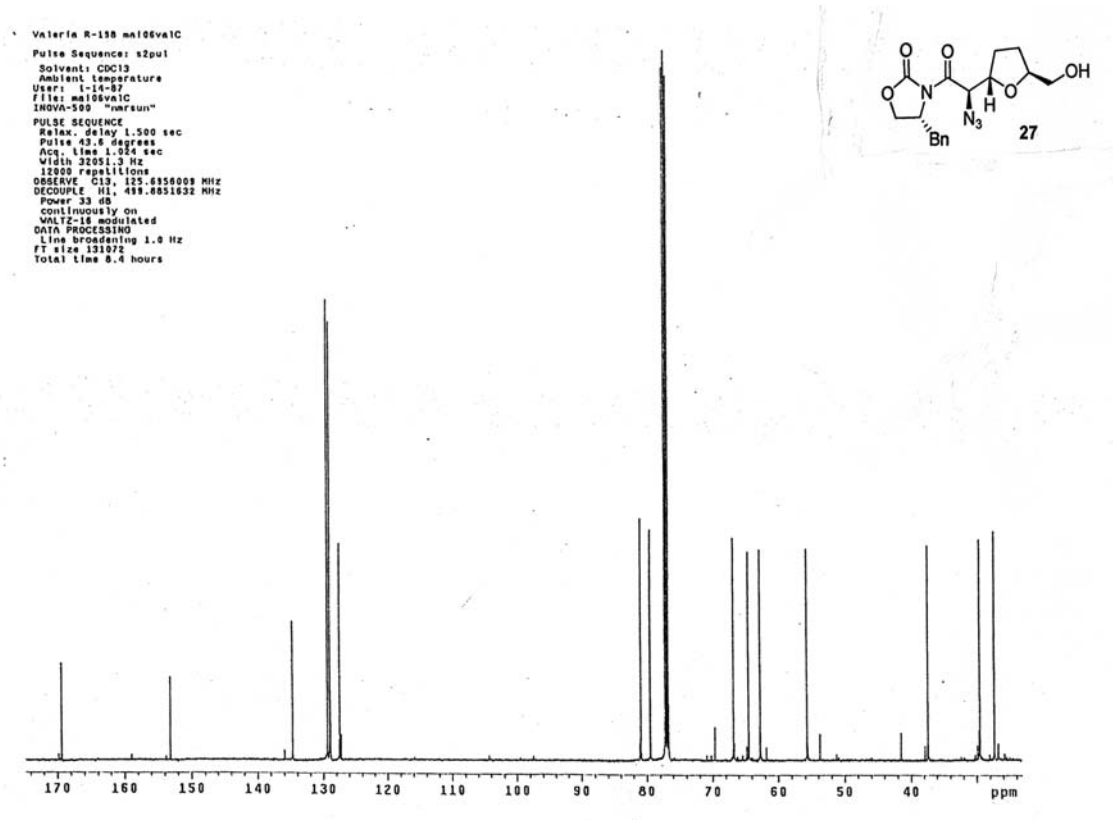

Figure S17. ^{13}C NMR spectrum of **27** (125 MHz, $CDCl_3$)