

Supplementary data for the article entitled

Preparation of chiral 3-oxocycloalkanecarbonitrile and its derivatives by crystallization-induced diastereomer transformation of ketals with chiral 1,2-diphenylethane-1,2-diol

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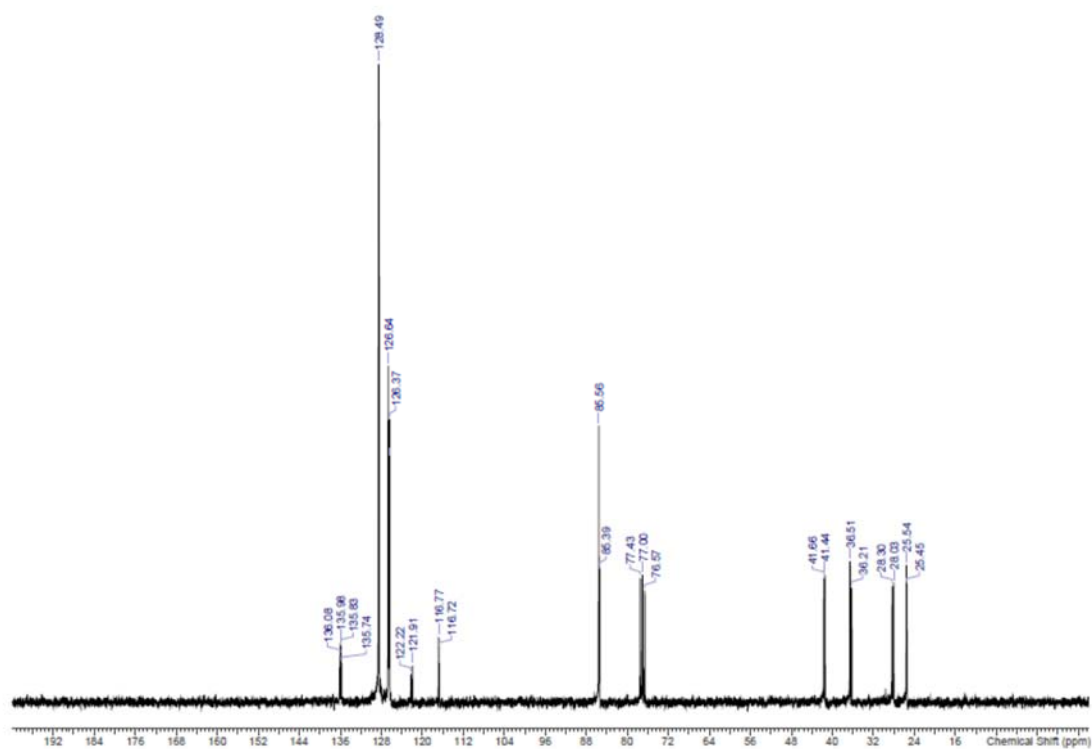
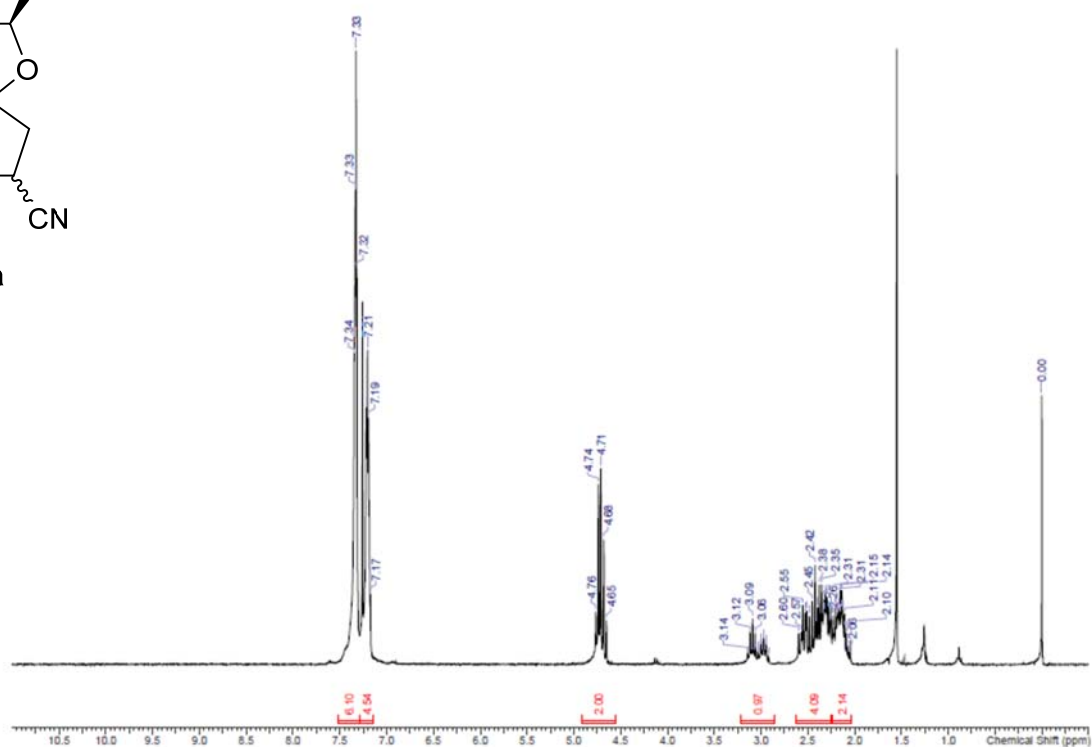
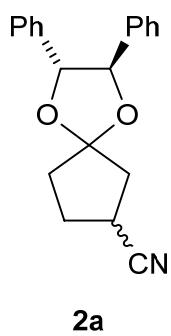
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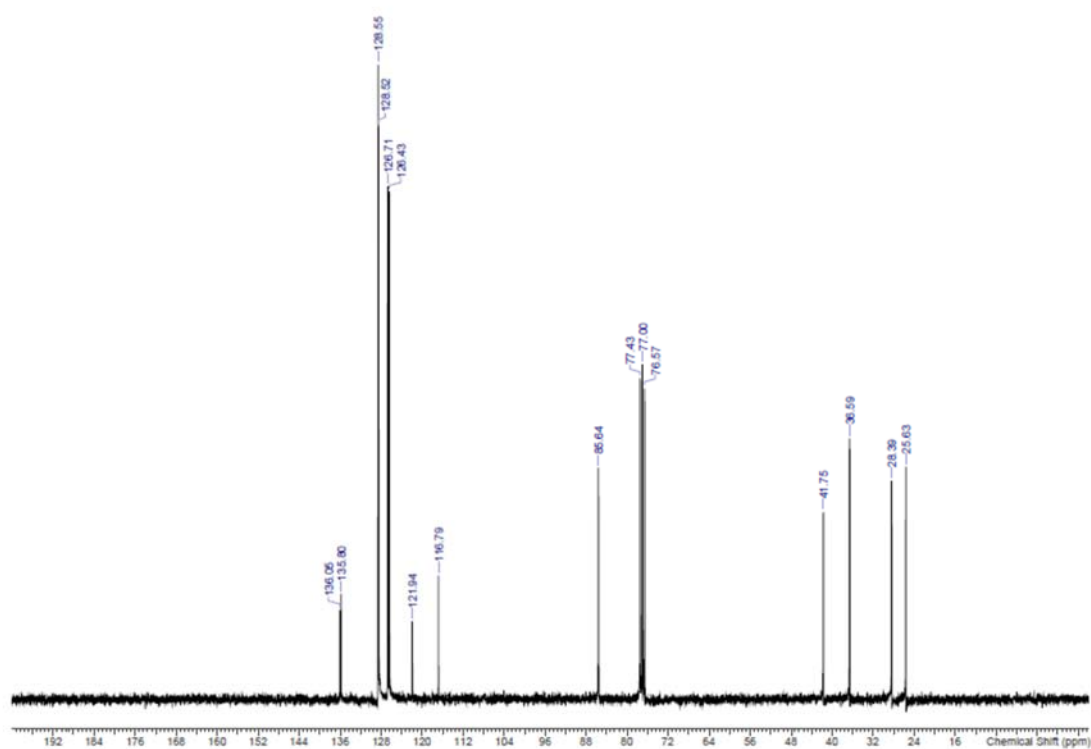
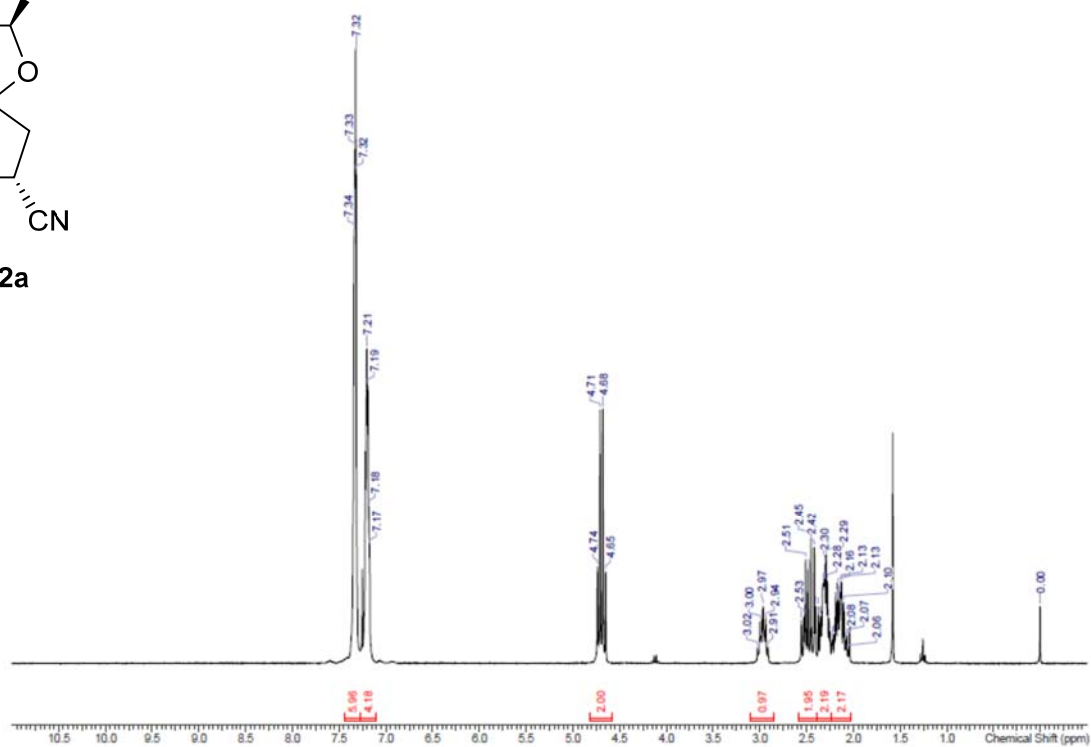
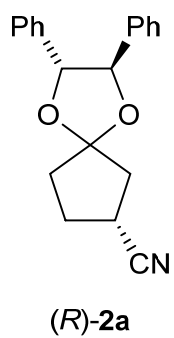
^c *Molecular Chirality Research Center, Chiba University, 1-33 Yayoicho, Inageku, Chiba, 263-8522, Japan.*

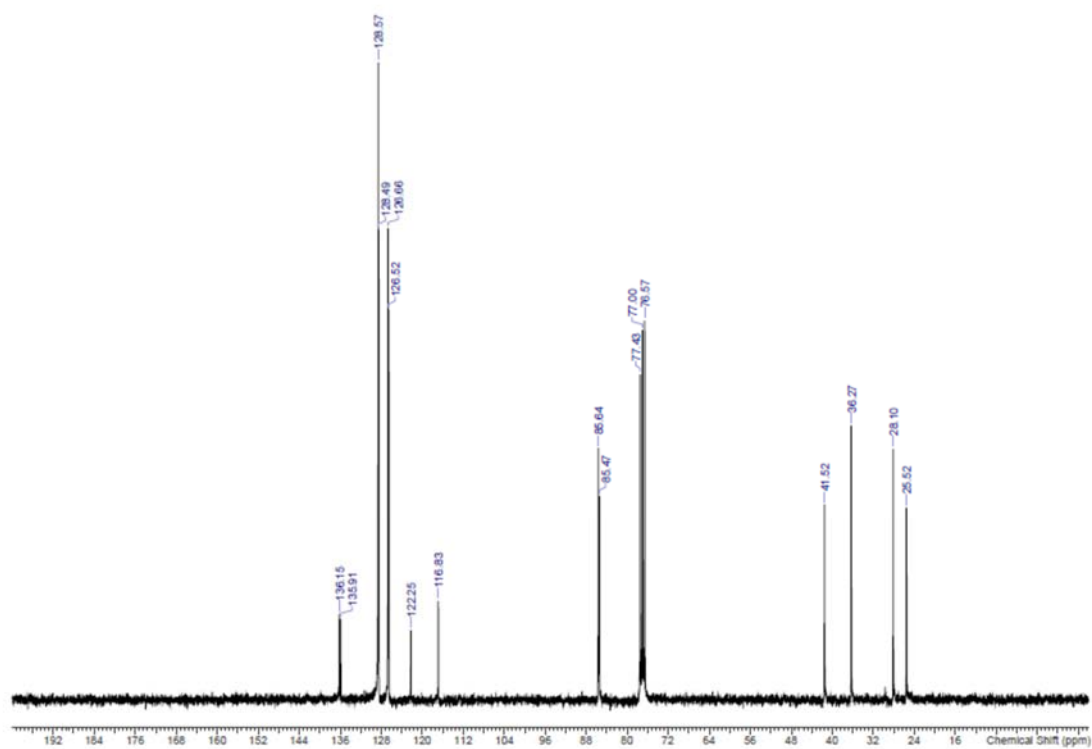
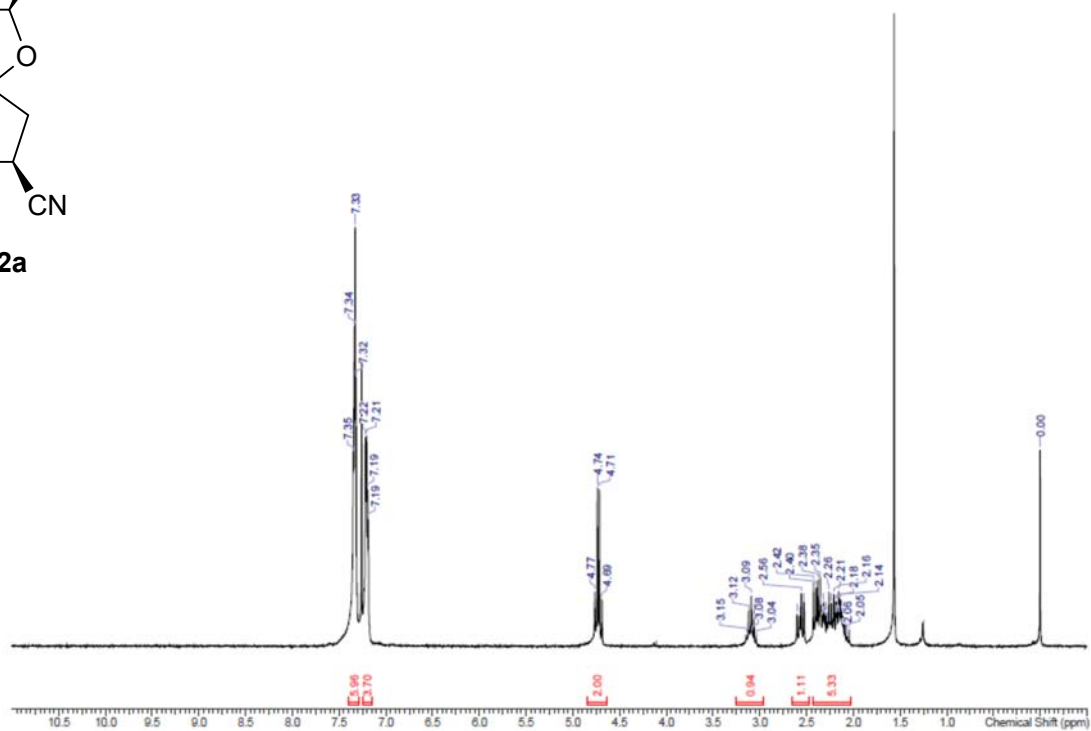
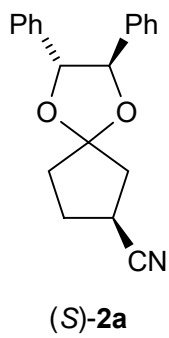
E-mail address: akazome@faculty.chiba-u.jp, yohei.yamashita@astellas.com

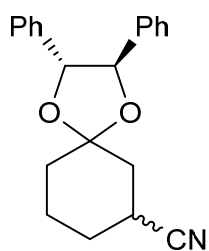
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2. Crystallographic data of (<i>R</i>)- 3a , (<i>S</i>)- 3a , (<i>R</i>)- 3b and (<i>S</i>)- 3bS16

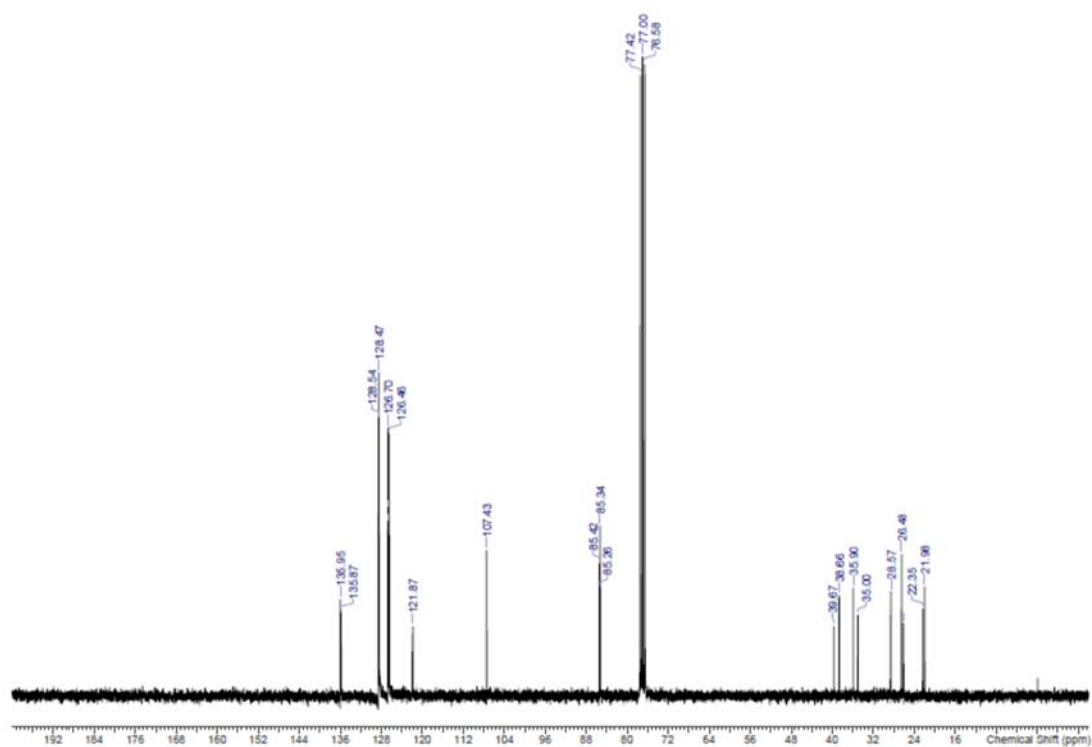
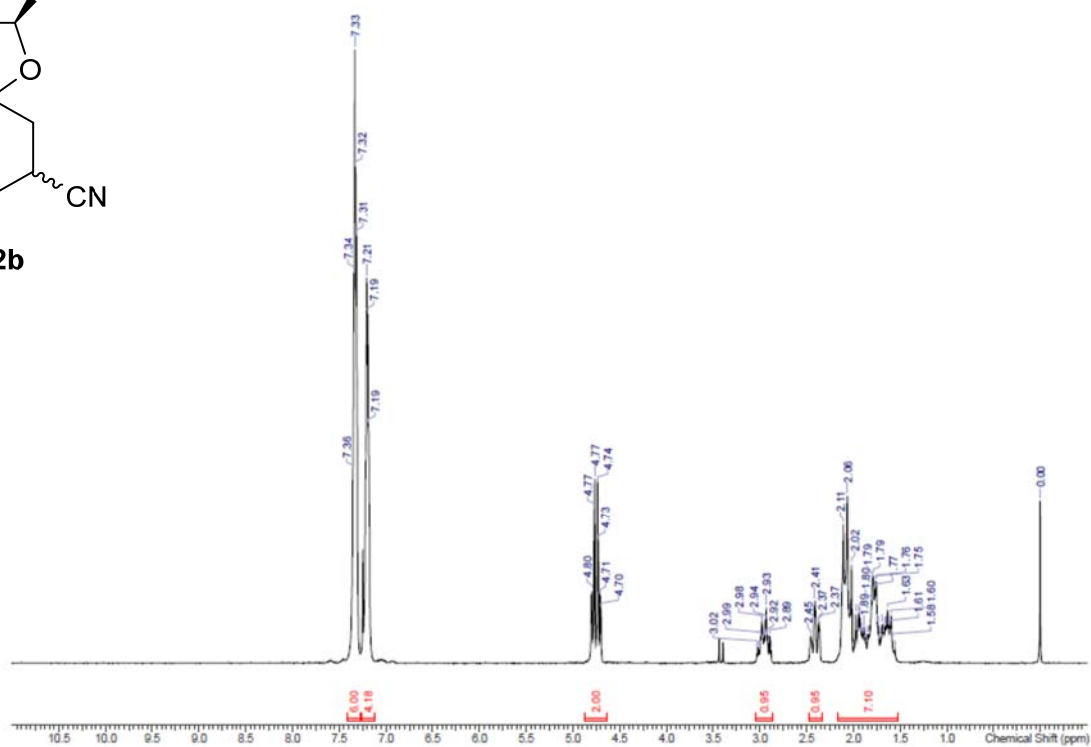


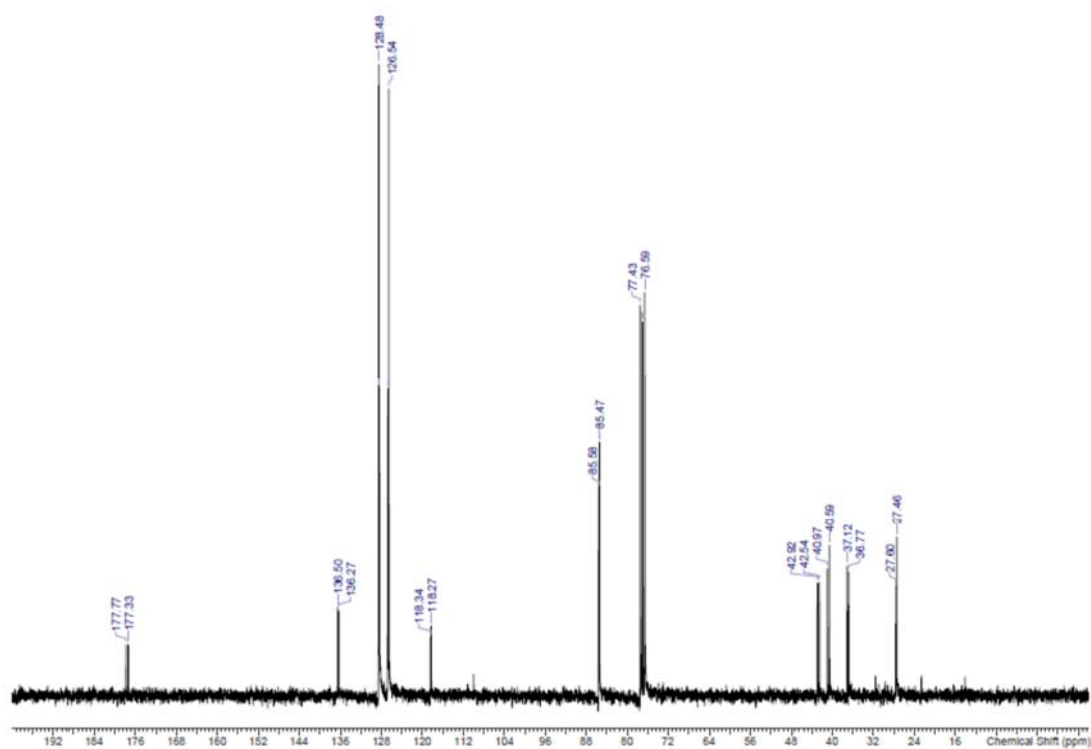
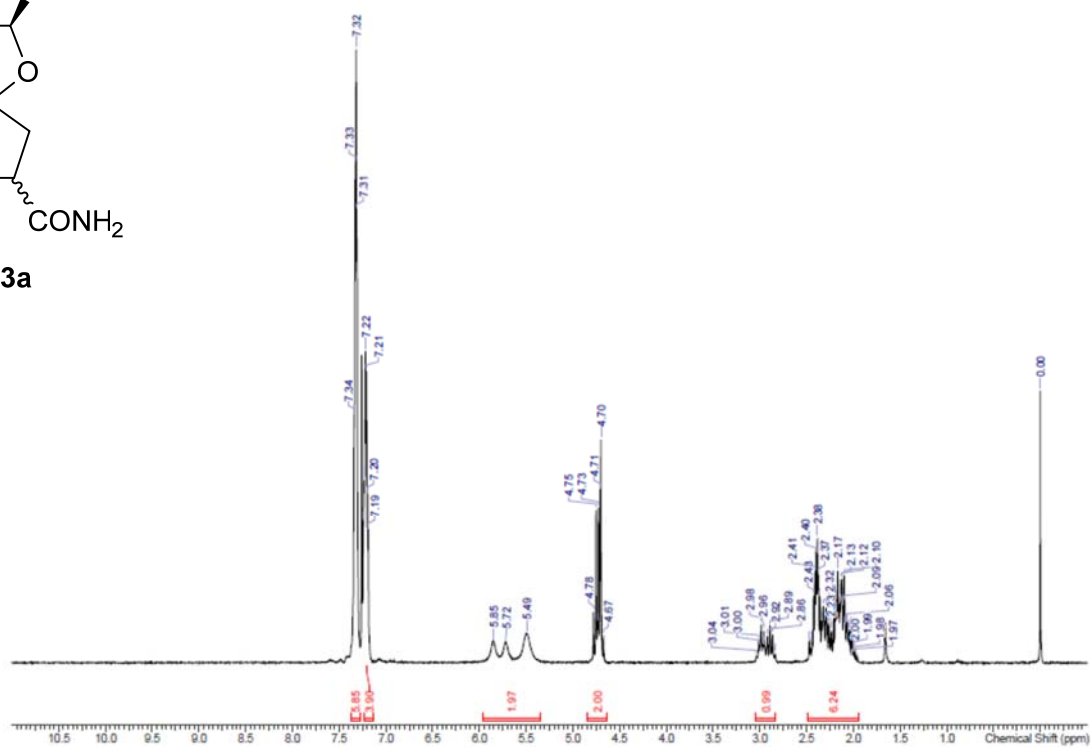
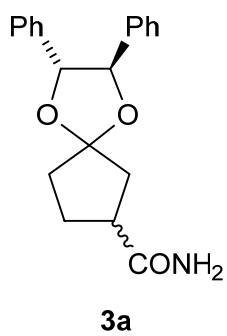


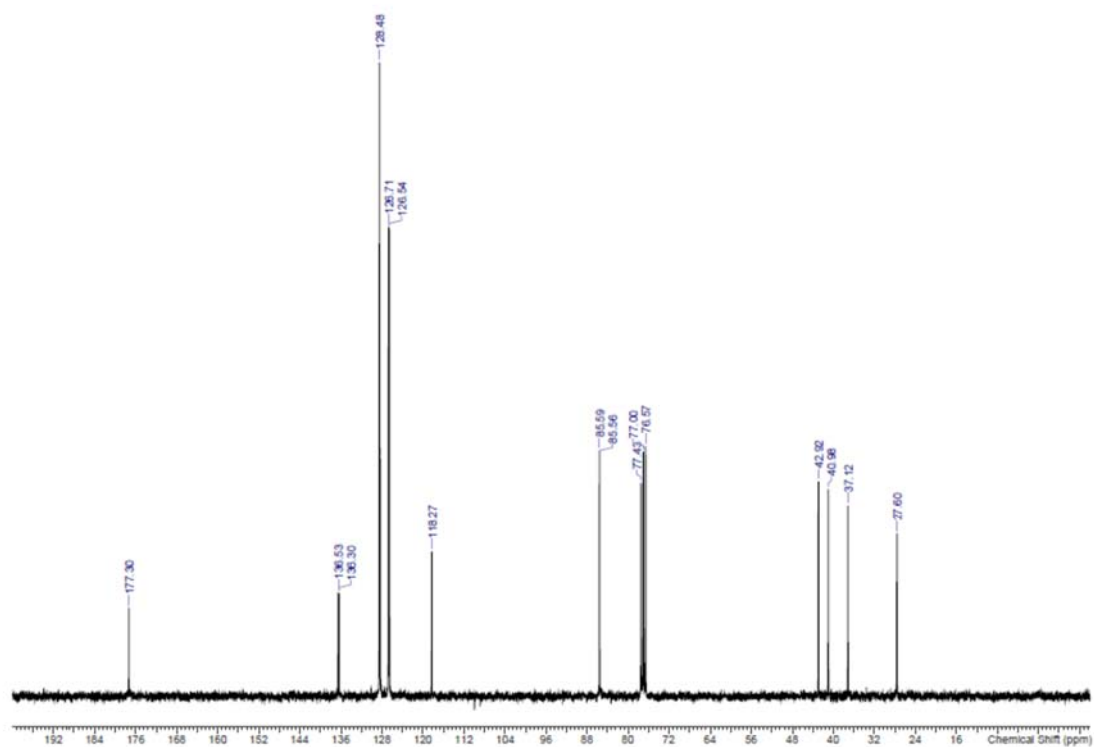
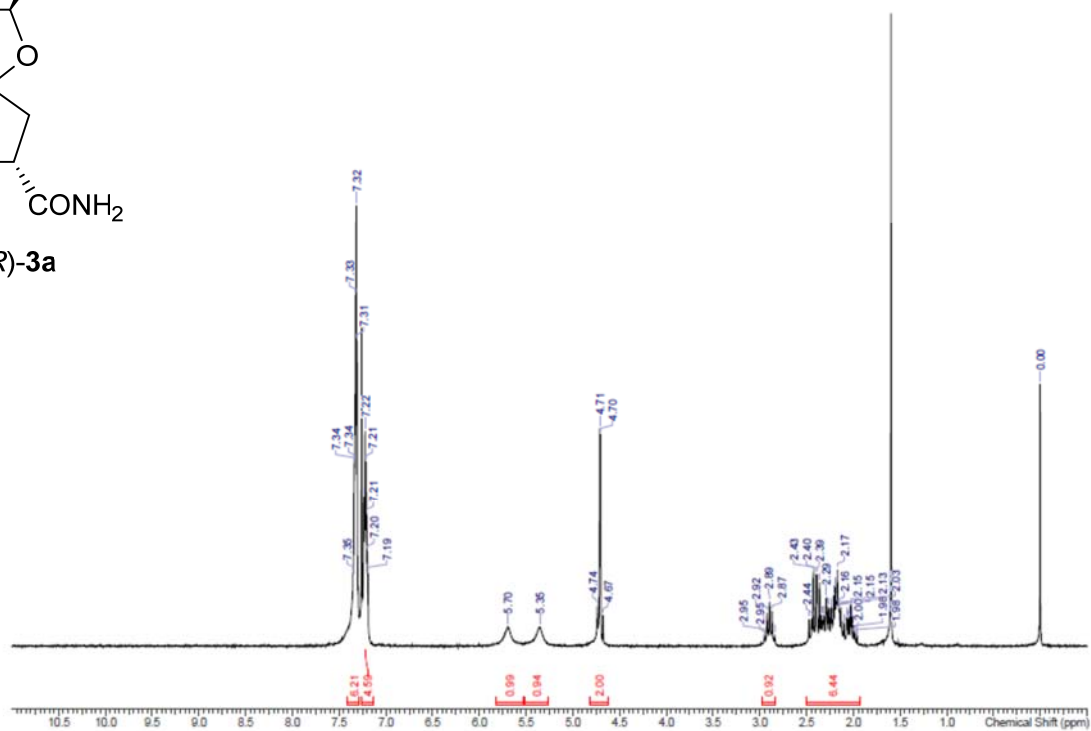
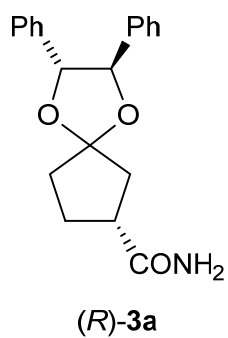


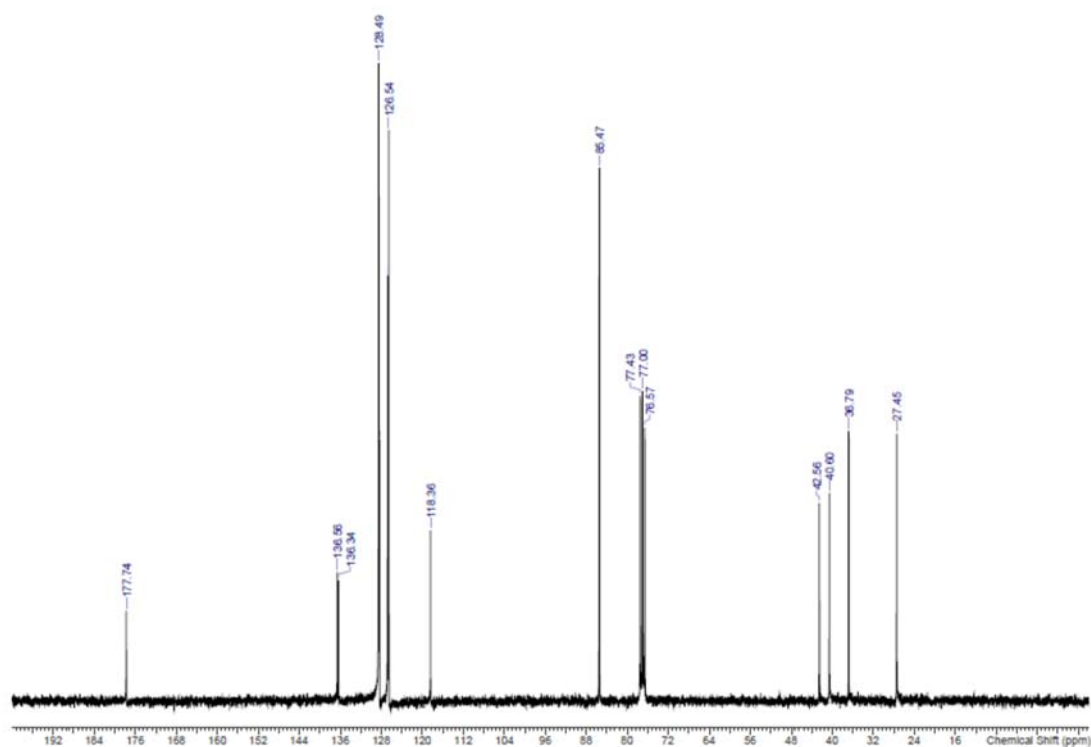
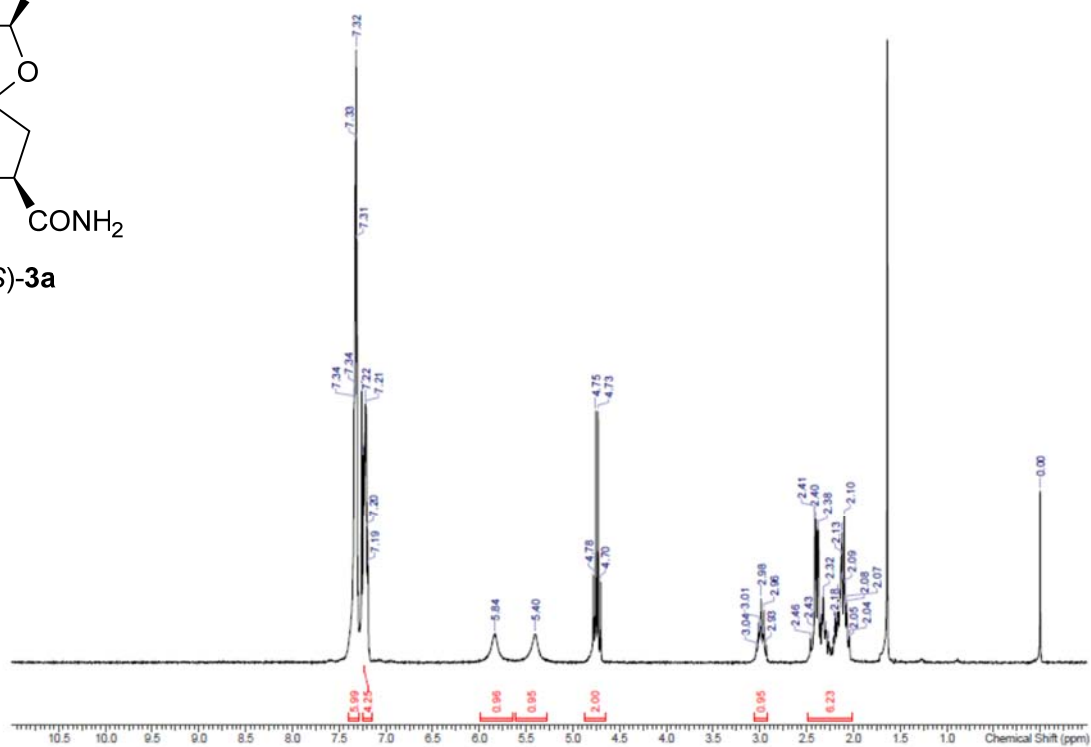
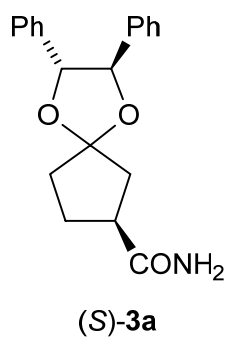


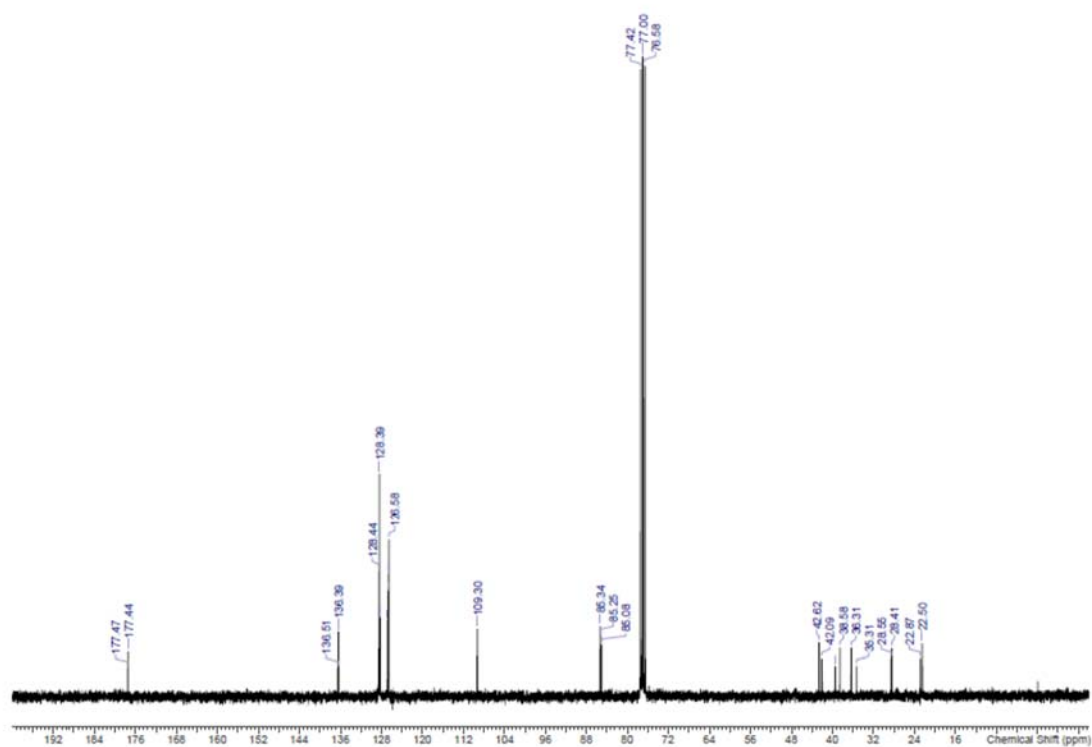
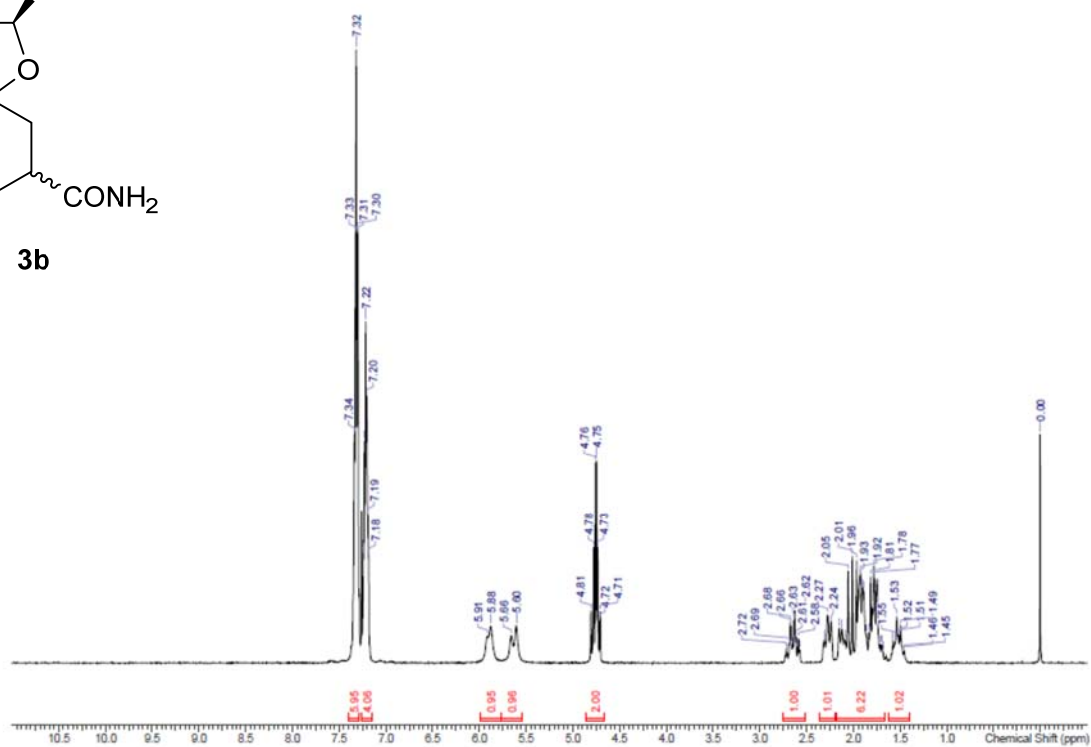
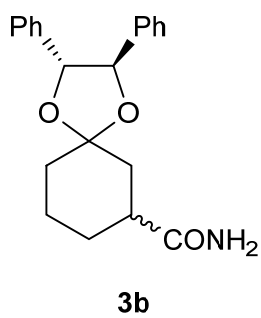
2b

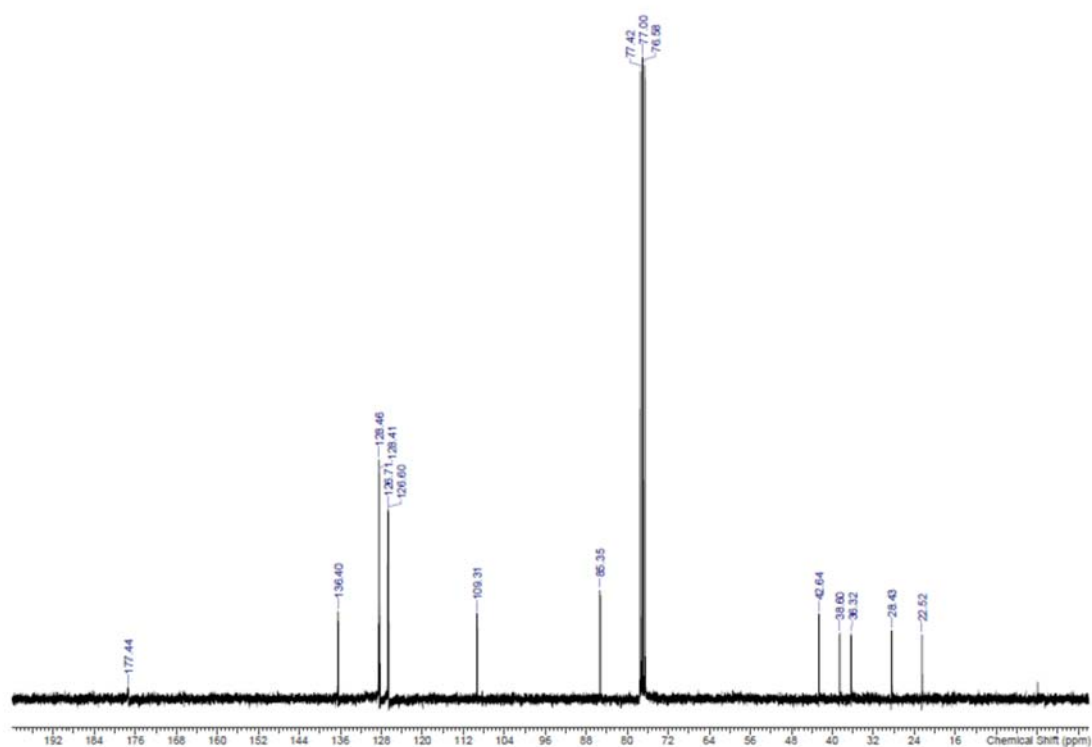
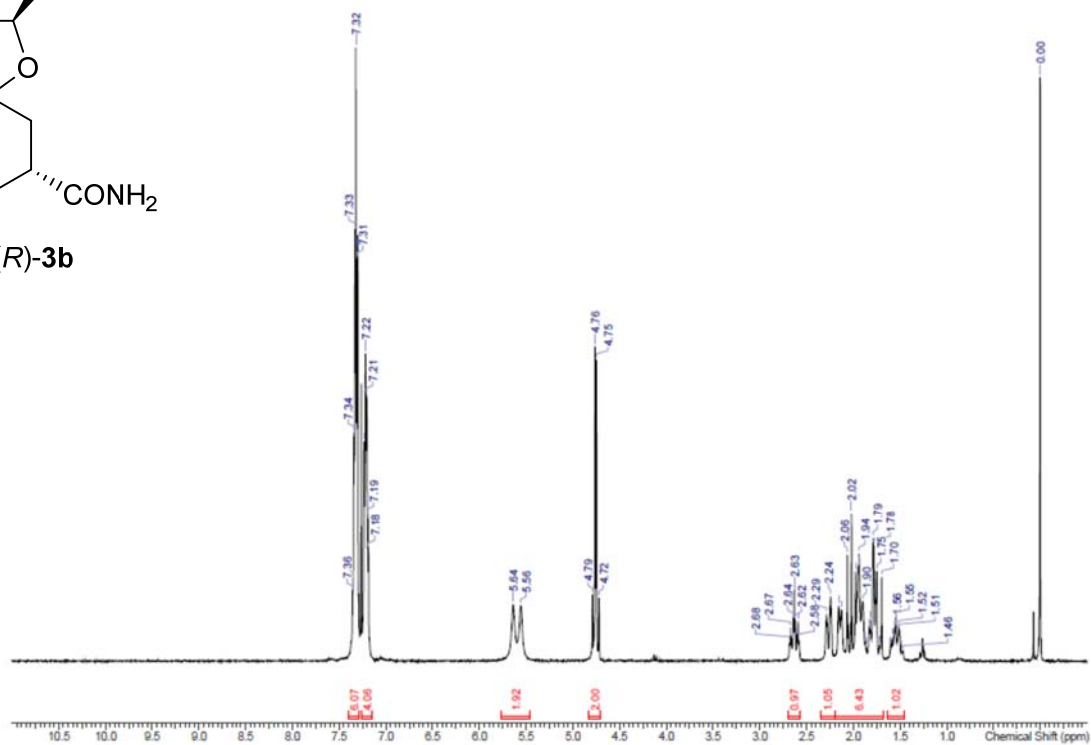
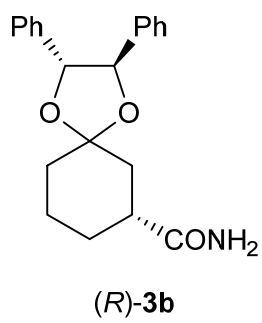


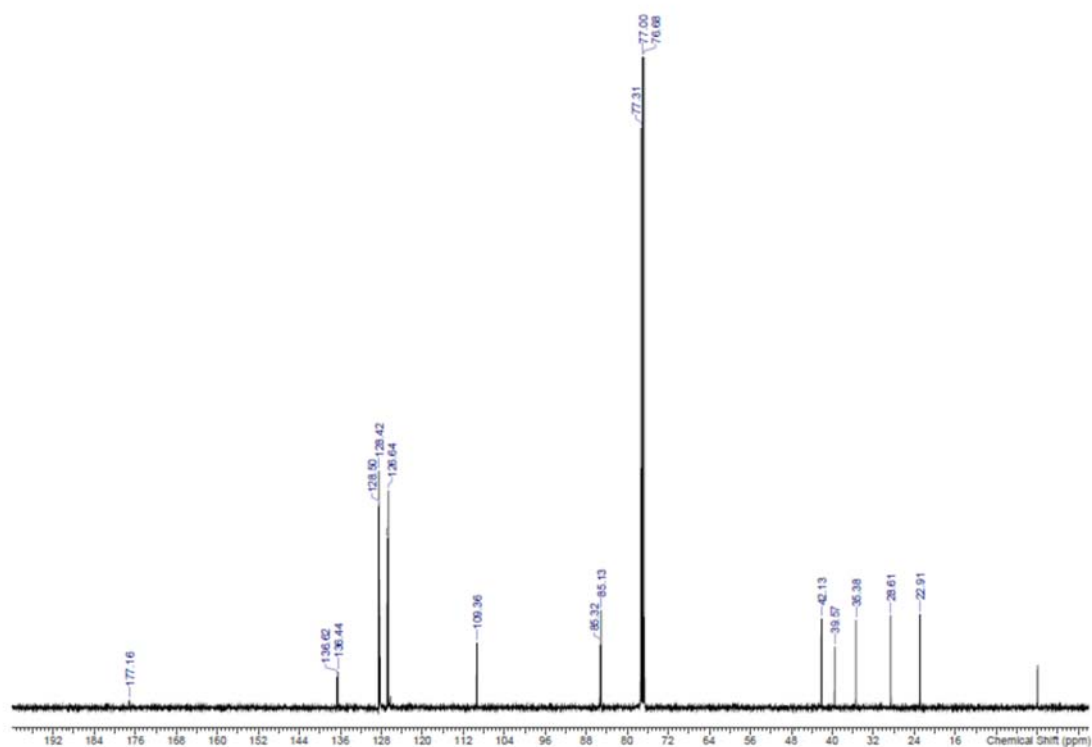
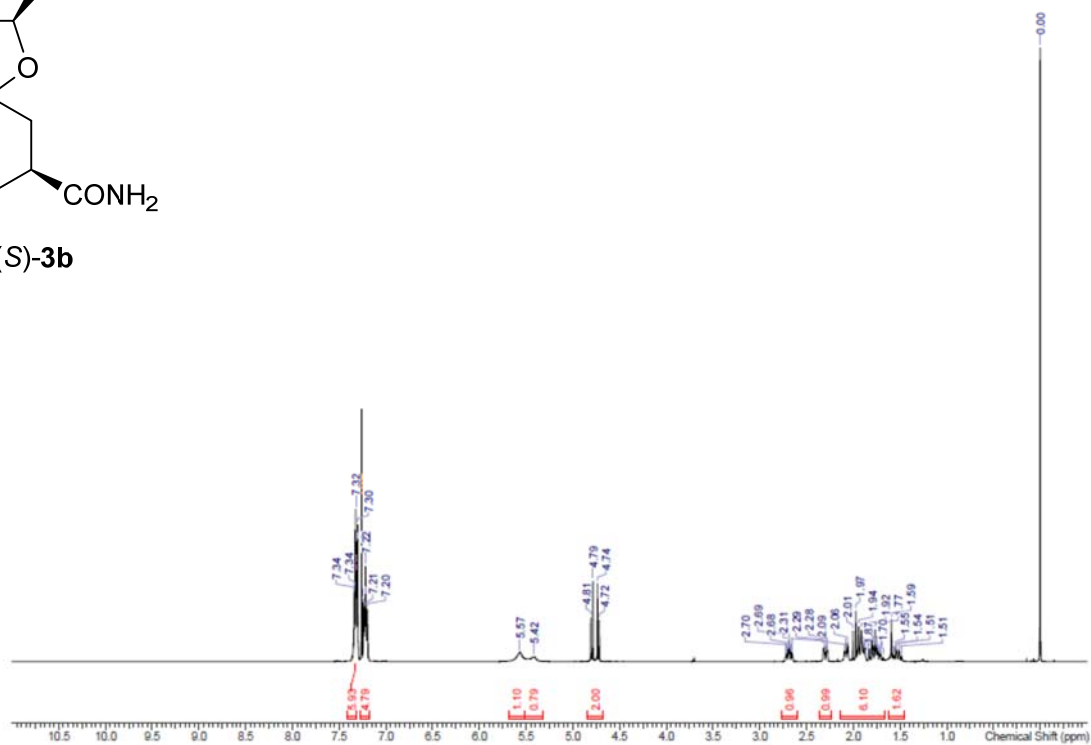
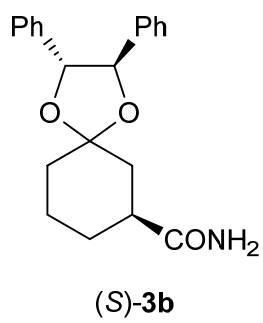


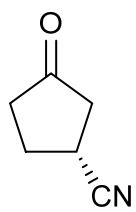




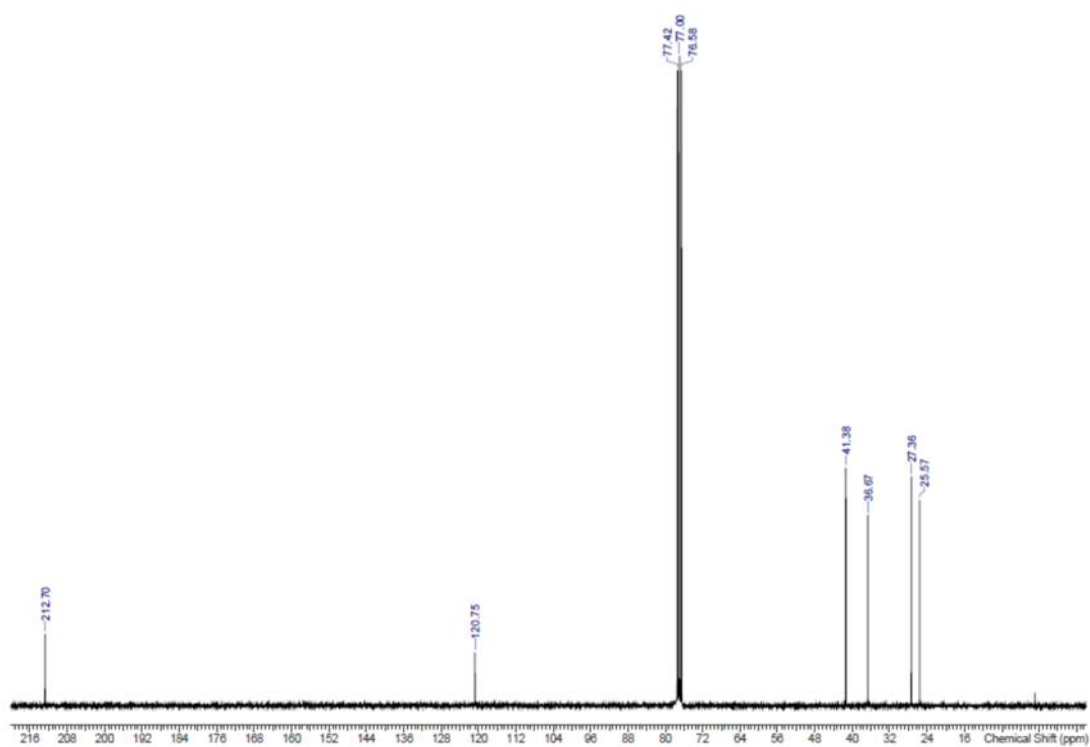
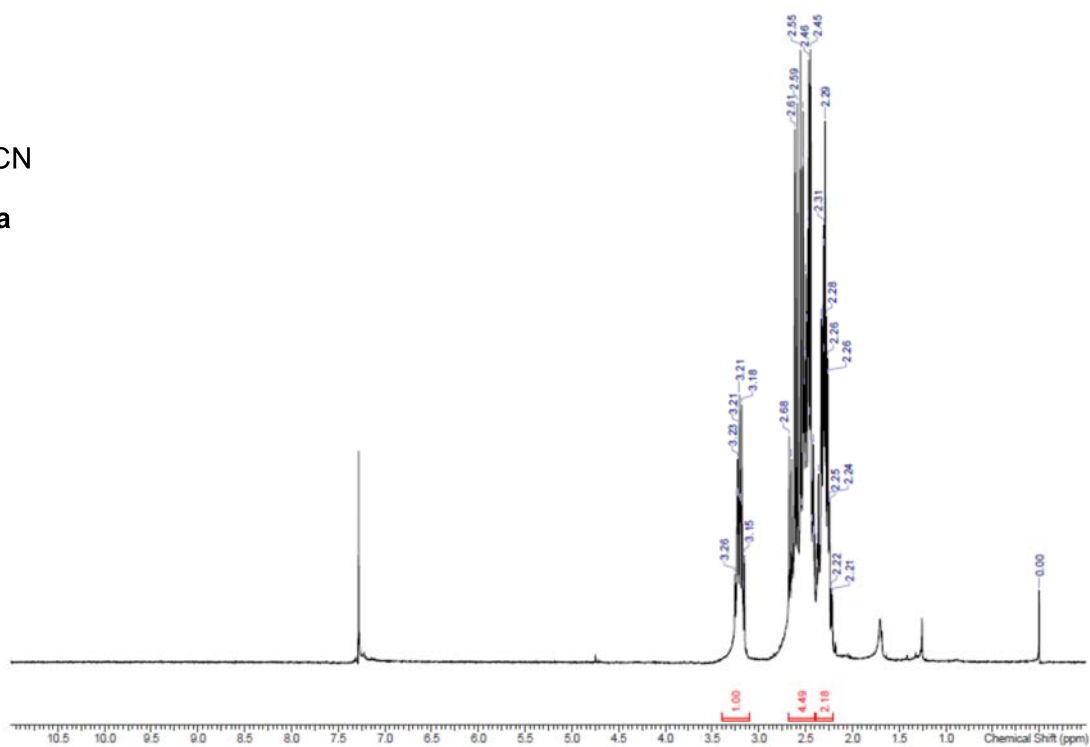


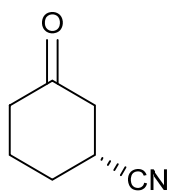




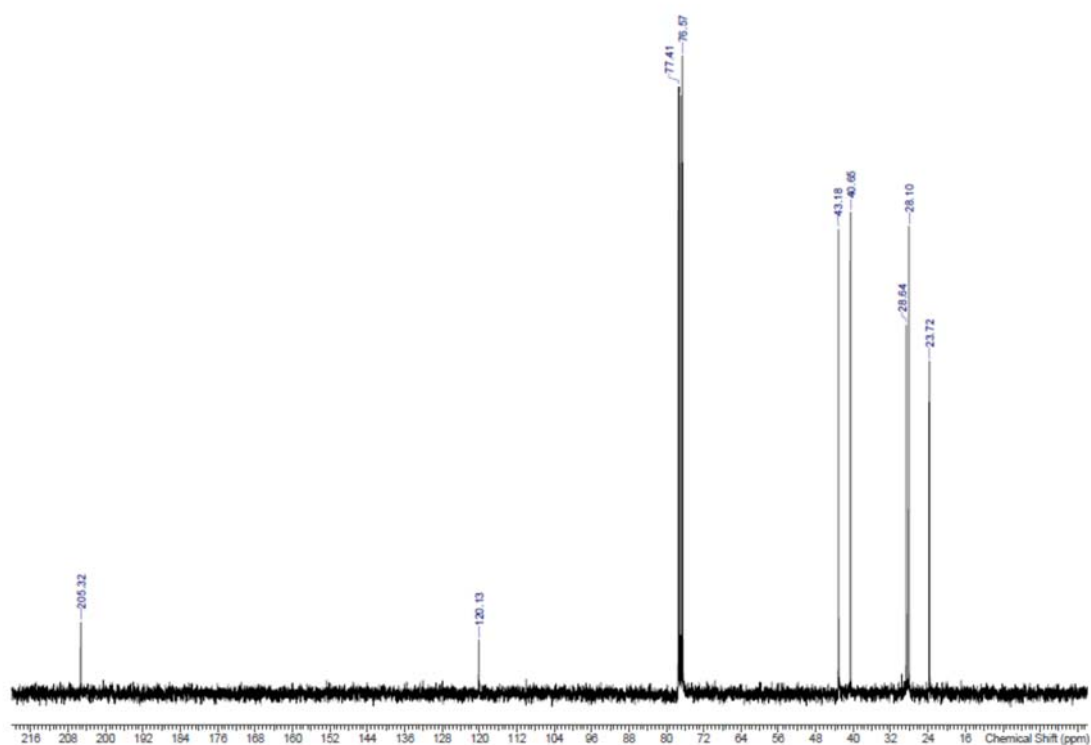
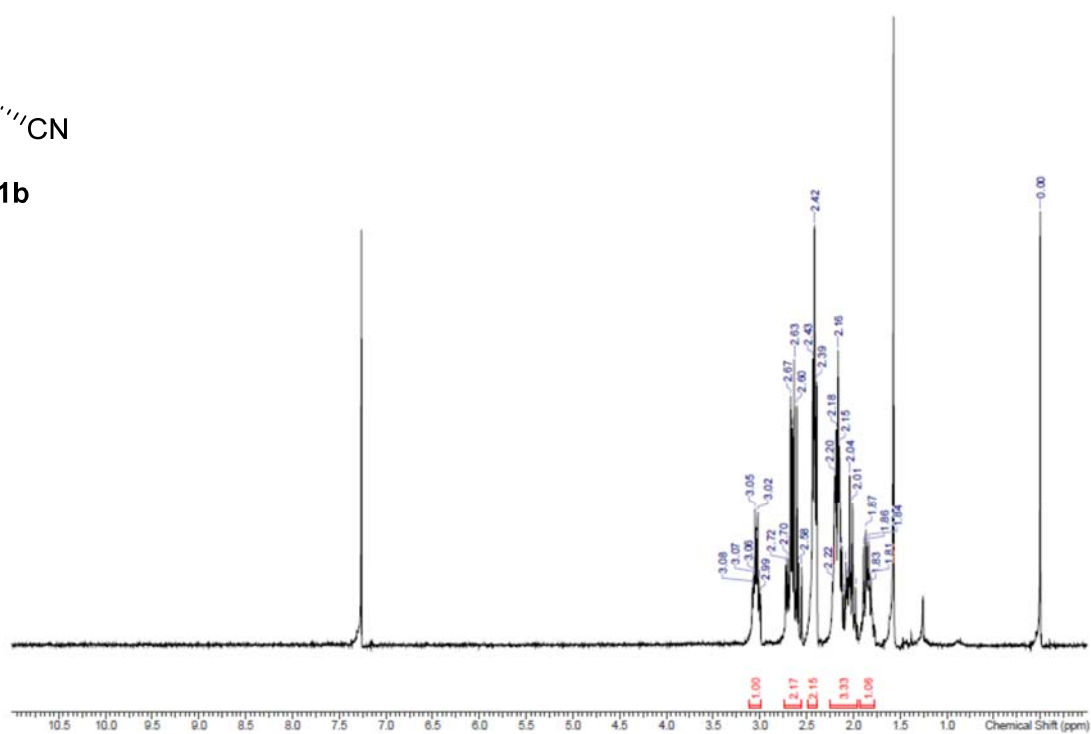


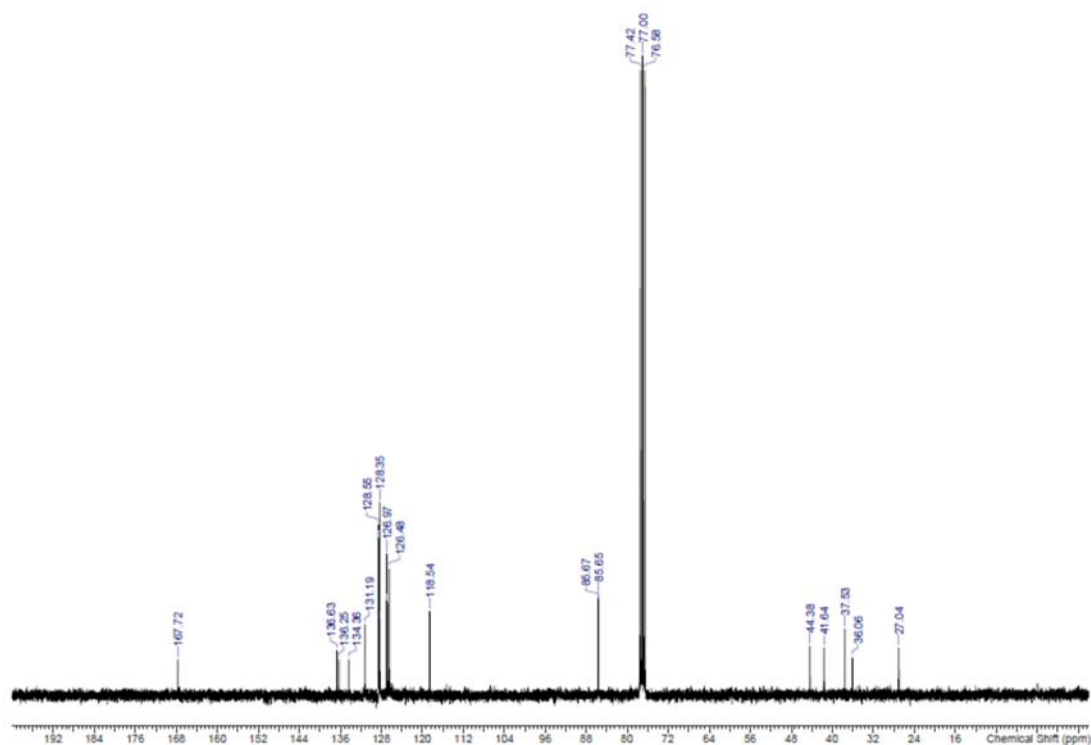
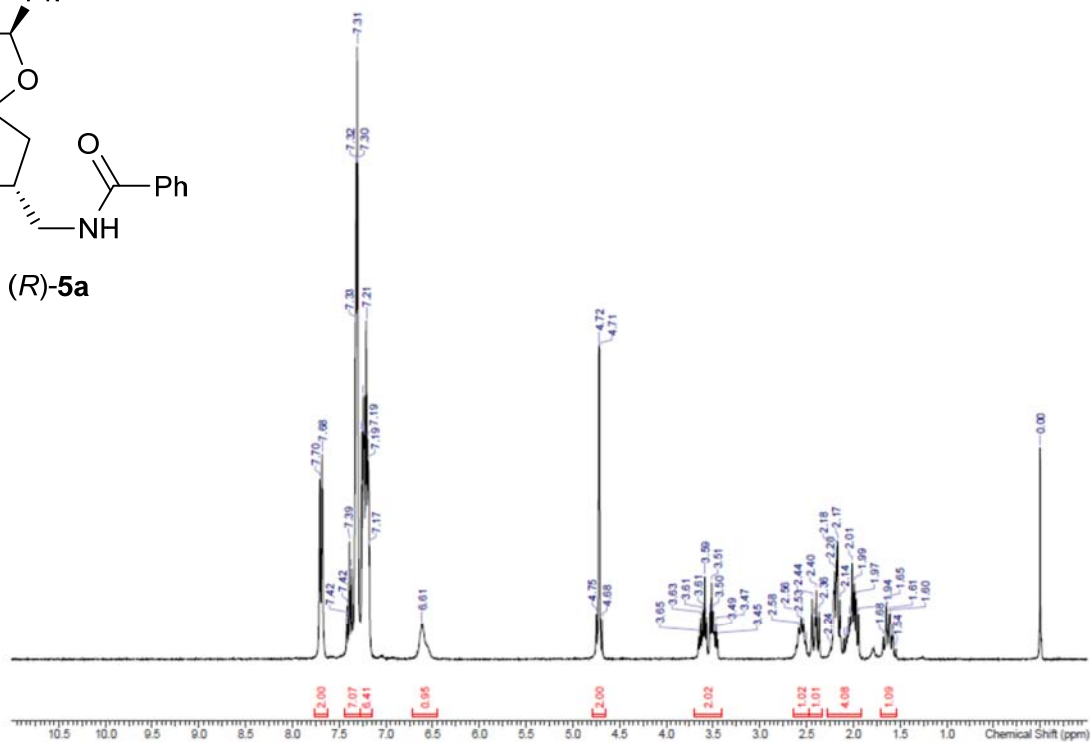
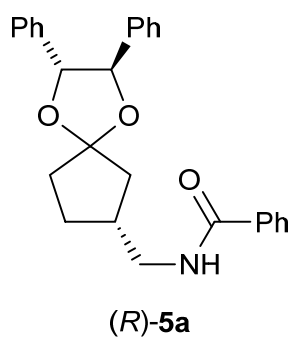
(R)-1a

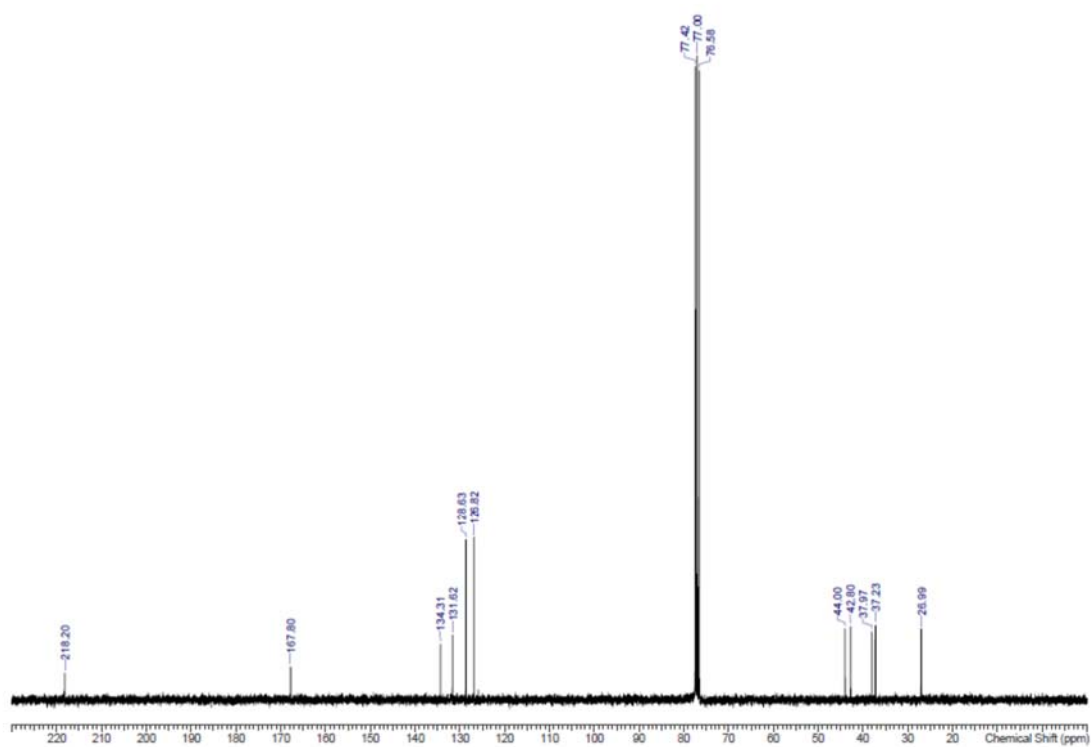
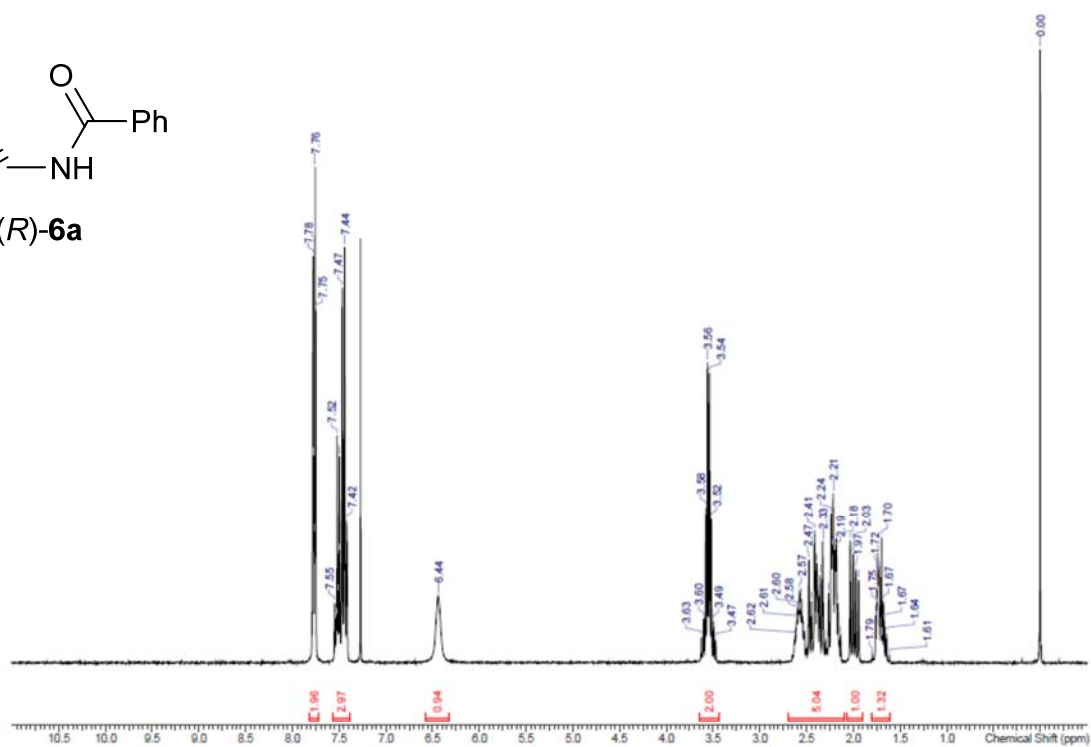
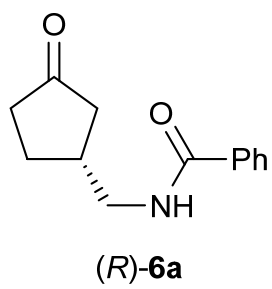




(R)-1b





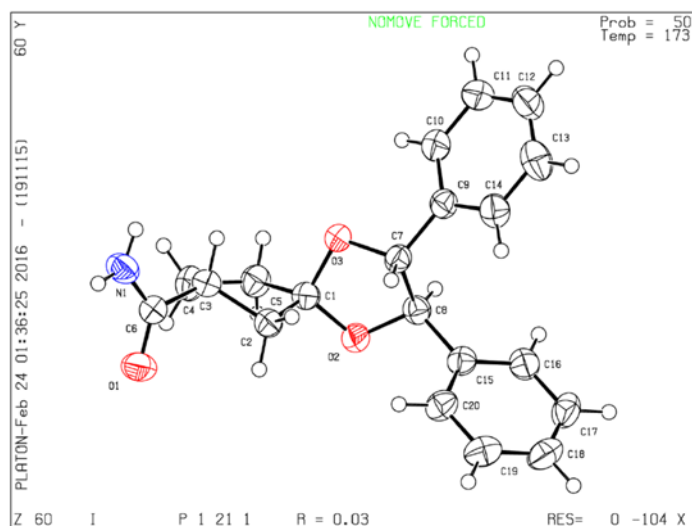
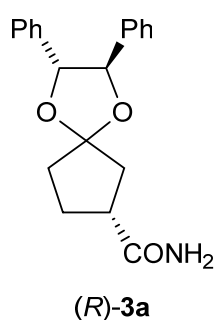


X-Ray crystal structure determination:

Crystals were grown by recrystallization in chloroform-toluene. Single crystals were mounted on a nylon loop with Paratone-N[®] oil and transferred to the cold gas stream (173 K) of these diffractometers. X-ray crystallographic data of (*R*)-**3a**, (*S*)-**3a**, and (*R*)-**3b** were measured on a Bruker APEXII Ultra CCD diffractometer. Regarding (*S*)-**3b**, the data were collected at a Bruker APEXII CCD diffractometer.

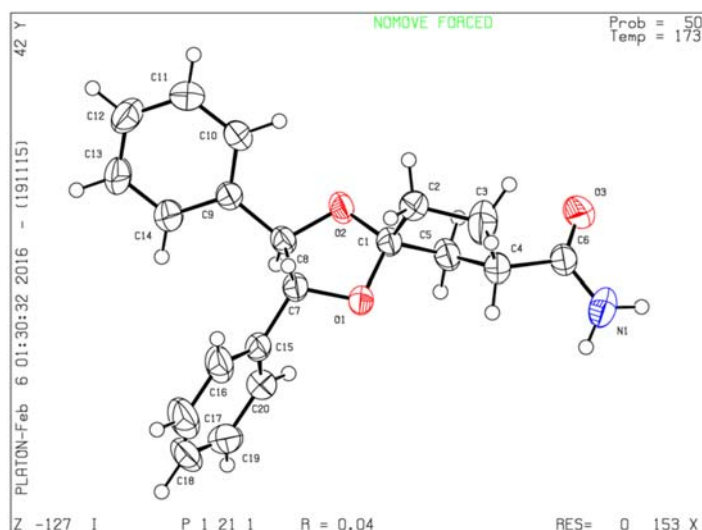
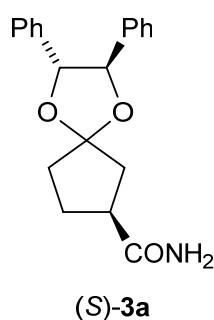
Crystallographic data of (*R*)-**3a** (recrystallized from chloroform-toluene):

C₂₀H₂₁NO₃, *M* = 323.38, monoclinic, space group *P*2₁ (no. 4), *a* = 6.2977(2), *b* = 7.4401(2), *c* = 18.2018(6) Å, β = 92.594(2)°, *V* = 851.98(5) Å³, *Z* = 2, *T* = 173 K, *D*_c = 1.261 gcm⁻³, μ (Cu-K α) = 0.680 mm⁻¹, *F*(000) = 344, 9149 measured reflections, 2815 independent, *R*(int) = 0.0192, 225 parameters were refined against 2815 reflections, *R*₁ = 0.0304 for 2709 [*I* > 2 σ (*I*)] and 0.0317 for all data, *wR*(*F*²) = 0.0805 (all data), GOF = 1.073, $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ = -0.158 and 0.216 e.Å⁻³. Flack parameter: 0.15(7) The *R* absolute configuration is assigned by reference to unchanging chiral centers of (1*R*,2*R*)-1,2-diphenylethane-1,2-diol used in the synthetic procedure (ketalization). CCDC 1849794 contains crystallographic data.



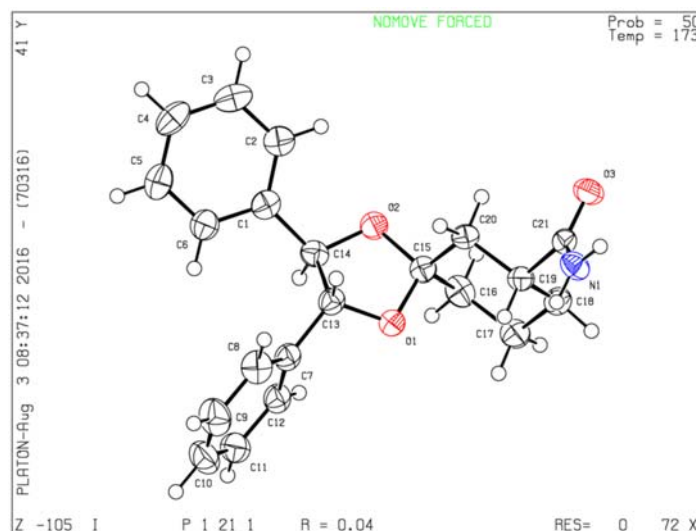
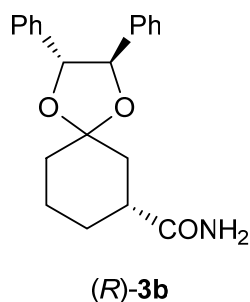
Crystallographic data of (*S*)-**3a** (recrystallized from chloroform-toluene):

C₂₀H₂₁NO₃, *M* = 323.38, monoclinic, space group *P*2₁ (no. 4), *a* = 6.2884(3), *b* = 9.3902(5), *c* = 14.9711(7) Å, β = 98.263(2)°, *V* = 874.86(7) Å³, *Z* = 2, *T* = 173 K, *D_c* = 1.228 gcm⁻³, μ (Cu-*K*α) = 0.662 mm⁻¹, *F*(000) = 344, 8323 measured reflections, 2857 independent, *R*(int) = 0.0218, 225 parameters were refined against 2857 reflections, *R*₁ = 0.0359 for 2790 [*I* > 2σ(*I*)] and 0.0367 for all data, *wR*(*F*²) = 0.1005 (all data), GOF = 1.035, Δρ_{min} and Δρ_{max} = −0.109 and 0.215 e.Å⁻³. Flack parameter: 0.11(7). The *S* absolute configuration is assigned by reference to unchanging chiral centers of (1*R*,2*R*)-1,2-diphenylethane-1,2-diol used in the synthetic procedure (ketalization). CCDC 1849795 contains crystallographic data.



Crystallographic data of (*R*)-**3b** (recrystallized from chloroform-toluene):

C₂₁H₂₃NO₃, *M* = 337.40, monoclinic, space group *P*2₁ (no. 4), *a* = 6.4767(4), *b* = 6.7235(5), *c* = 20.8609(14) Å, β = 93.851(4)°, *V* = 906.36(11) Å³, *Z* = 2, *T* = 173 K, *D*_c = 1.236 gcm⁻³, μ (Cu-K α) = 0.659 mm⁻¹, *F*(000) = 360, 6157 measured reflections, 2627 independent, *R*(int) = 0.0241, 226 parameters were refined against 2627 reflections, *R*₁ = 0.0386 for 2505 [*I* > 2 σ (*I*)] and 0.0408 for all data, *wR*(*F*²) = 0.0995 (all data), GOF = 1.073, $\Delta\rho_{\min}$ and $\Delta\rho_{\max}$ = -0.133 and 0.193 e.Å⁻³. Flack parameter: 0.26(12). The *R* absolute configuration is assigned by reference to unchanging chiral centers of (1*R*,2*R*)-1,2-diphenylethane-1,2-diol used in the synthetic procedure (ketalization). CCDC 1849796 contains crystallographic data.



Crystallographic data of (*S*)-**3b** (recrystallized from chloroform-toluene):

C₂₁H₂₃NO₃, *M* = 337.40, orthorhombic, space group *P*2₁2₁2₁ (no. 19), *a* = 9.5492(9), *b* = 9.6708(9), *c* = 19.5238(18) Å, *V* = 1803.0(3) Å³, *Z* = 4, *T* = 173 K, *D*_c = 1.243 g cm⁻³, $\mu(\text{Mo-K}\alpha) = 0.083 \text{ mm}^{-1}$, *F*(000) = 720, 10381 measured reflections, 4108 independent, *R*(int) = 0.0244, 226 parameters were refined against 4108 reflections, *R*₁ = 0.0348 for 3746 [*I* > 2σ(*I*)] and 0.0398 for all data, *wR*(*F*²) = 0.0815 (all data), GOF = 1.079, Δρ_{min} and Δρ_{max} = −0.133 and 0.193 e.Å⁻³. Flack parameter: −0.2(4). The *S* absolute configuration is assigned by reference to unchanging chiral centers of (1*R*,2*R*)-1,2-diphenylethane-1,2-diol used in the synthetic procedure (ketalization). CCDC 1849797 contains crystallographic data.

