Supporting Information for

Stereospecific chlorination of $\beta$-substituted cyclic alcohols using PPh$_3$/NCS: factors that control the stereospecificity

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Determination of Stereochemistry by $^1$H NMR

The stereochemistry of the product chlorides was determined by coupling pattern of methine protons in $^1$H NMR spectra. All the cis chlorides have doublet of triplet (dt) pattern due to one trans coupling and two cis couplings. Whereas the trans chlorides gave triplet of doublet (td) coupling pattern due to two trans coupling and one cis coupling. This is also confirmed by X-ray structure of selected compounds.

Representative $^1$H NMR spectrum for cis-chloride
Representative $^1$H NMR spectrum for trans-chloride
X-ray crystal structure of \textit{cis}-N-(2-chlorocyclohexyl)-4-methylbenzenesulfonamide. (30% Probability).

Crystallographic data for \textit{cis}-N-(2-chlorocyclohexyl)-4-methylbenzenesulfonamide:

C_{13} H_{18} Cl N O_2 S, M = 287.79, Triclinic, a = 6.7769(4), b = 9.7641(8), c = 11.4462(8) Å, α = 76.916(5), β = 80.416(4), γ = 74.897(4), V = 707.58(9), T = 273(2) K, space group \textit{P}-1, Z = 2, μ = 0.411 mm\(^{-1}\), \(R_{int} = 0.0280\) (for 4438 measured reflections), \(R_1 = 0.0626\) [for 1996 unique reflections with \(I > 2σ(I)\)], \(wR2 = 0.1733\) (for all 2382 unique reflections), CCDC 621755
X-ray crystal structures of \textit{trans}-2-hydroxycyclooctyl-4-nitrobenzoate. 30% Probability

Crystallographic data for \textit{trans}-2-hydroxycyclooctyl-4-nitrobenzoate. 30% Probability

C_{15}H_{19}NO_{5}, M = 293.31, Triclinic, \( a = 7.2564(6) \), \( b = 7.4017(5) \), \( c = 15.5988(13) \) Å, \( \alpha = 88.923(5) \), \( \beta = 85.403(5) \), \( \gamma = 62.334(4) \), \( V = 739.47(10) \) Å\(^3\), \( T = 293(2) \) K, space group P-1, \( Z = 2 \), \( \mu = 0.099 \) mm\(^{-1}\), \( R_{int} = 0.0237 \) (for 9003 measured reflections), \( R_1 = 0.0826 \) [for 2033 unique reflections with \( I > 2\sigma(I) \)], \( wR_2 = 0.2637 \) (for all 2530 unique reflections), CCDC 621756.
X-ray crystal structures of trans-2-(4-nitrophenylamino)cyclohexanol (30% Probability)

Crystallographic data for trans-2-(4-nitrophenylamino)cyclohexanol
C_{12} H_{16} N_{2} O_{3}, M = 236.27, Monoclinic, \( a = 18.6930(18), b = 9.9424(8), c = 14.9984(16) \, \text{Å} \), \( \beta = 122.342(10), V = 2355.1(4), T = 273(2) \, \text{K}, \) space group C2/c, \( Z = 8, \mu = 0.097 \, \text{mm}^{-1}, R_{\text{int}} = 0.0220 \) (for 16937 measured reflections), \( R_1 = 0.0526 \) [for 2723 unique reflections with I > 2\( \sigma(I) \)], \( wR_2 = 0.1973 \) (for all 4148 unique reflections), CCDC 622916.