Electronic Supplementary Information

Annuloselectivity and stereochemistry in the sulfa-Staudinger cycloadditions of cyclic imines

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1. Copies of $^1$H and $^{13}$C spectra of products

1-Chloro-2-(ethylsulfonyl)-1,2,3,4-tetrahydroisoquinoline (7)
rel(4bR,5R,13bR)-5-Phenyl-4b,5,9,13b,15,16-hexahydro-8H-[1,2,4]thiadiazino[3,2-a:5,4-a']dii soquinoline 6,6-dioxide (8)
rel(4bR,5S,13bR)-5-Phenyl-4b,5,9,13b,15,16-hexahydro-8H-[1,2,4]thiadiazino[3,2-a:5,4-a’]dii soquinoline 6,6-dioxide (9)
White solid (5% yield). ¹H NMR (600 MHz, CDCl₃) δ 5.69 (s, 1H in NC₉H₈N), 5.18 (d, J = 3.6 Hz, 1H in CHN), 4.84 (d, J = 3.6 Hz, 1H in CHS).

rel(1S,9bS)-1-Phenyl-1,4,5,9b-tetrahydro[1,2]thiazeto[3,2-a]isoquinoline 2,2-dioxide (11)
White solid (6.5% yield). ¹H NMR (600 MHz, CDCl₃) δ 5.31 (d, J = 4.5 Hz, 1H in CHN), 4.82 (d, J = 4.5 Hz, 1H in CHS). HRMS (ESI) calcd for C₁₆H₁₆NO₂S (M + H⁺) m/z 286.0896, found 286.0893.
rel(4bR,5R,13bS)-5-Phenyl-4b,5,9,13b,15,16-hexahydro-8H-[1,2,4]thiadiazino[3,2-a:5,4-a'] diisoquinoline 6,6-dioxide (10)
2-(Benzylsulfonyl)-1,2,3,4-tetrahydroisoquinolin-1-ol (12)
Ethyl rel(4bR,5R,13bS)-4b,5,9,13b,15,16-hexahydro-8H-[1,2,4]thiadiazino[3,2-a:5,4-a']diisoquinoline-5-carboxylate 6,6-dioxide (13)
Ethyl $rel(4bR,5R,13bR)-4b,5,9,13b,15,16$-hexahydro-$8H$-[1,2,4]thiadiazino[3,2-$a$:5,4-$a'$]diisoquinoline-5-carboxylate 6,6-dioxide (14)
rel\((4bR,5S,13bR)\)-5-(methylsulfonyl)-4b,5,9,13b,15,16-hexahydro-8\(H\)-[1,2,4]thiadiazino[3,2-\(a\):5,4-\(a'\)]diisoquinoline 6,6-dioxide (15)
rel(4\text{b}R,5\text{R},13\text{b}R)-5-(methylsulfonyl)-4\text{b},5,9,13\text{b},15,16-hexahydro-8\text{H}-[1,2,4]thiadiazino[3,2-a:5,4-a']diisoquinoline 6,6-dioxide (16)
5-Ethoxy-4-(ethylsulfonyl)-1-methyl-4,5-dihydro-1\textit{H}-benzo[\textit{f}]\textit{[1,4]}diazepin-2(3\textit{H})-one (18a)
4-(Benzylsulfonyl)-5-ethoxy-1-methyl-4,5-dihydro-$IH$-benzo[$f$][$1,4$]diazepin-2($3H$)-one (18b)
trans-6-Methyl-1-phenyl-1,10b-dihydro-6H-benzo[f][1,2]thiazeto[2,3-d][1,4]diaze pin-5(4H)-one 2,2-dioxide (19)
Ethyl \( \text{rel}(2S,10R,11S)-1,5,8,14\text{-tetraaza-9-thiadibenzo[}c,f\text{]tricyclo[9.5.0.0^{2,8}]hexadecane-6,15-dione-10-carboxylate 9,9\text{-dioxide}} \) (20)
Ethyl \( \text{rel}(2R,10S,11S)-1,5,8,14\text{-tetraaza-9-thiadibenzo}[c,f]tricyclo[9.5.0.0^{2,8}]\text{hexadecane-6,15-dione-10-carboxylate 9,9-dioxide} \) (21)
2. NOE spectra of $[2^s + 2^i + 2^i]$ annuladducts

$rel(4bR,5R,13bR)$- and $rel(4bR,5S,13bR)$-5-Phenyl-4b,5,9,13b,15,16-hexahydro-8H-[1,2,4]thiadiazino[3,2-$a$:5,4-$a'$]diisoquinoline 6,6-dioxide (8) and (9)
Ethyl \textit{rel}(4bR,5R,13bS)-4b,5,9b,13b,15,16-hexahydro-8\textit{H}+[1,2,4]thiadiazino[3,2-\textit{a}:5,4-\textit{a}'] diisoquinoline-5-carboxylate 6,6-dioxide (13)
Ethyl \textit{rel}(4bR,5R,13bR)-4b,5,9,13b,15,16-hexahydro-8H-[1,2,4]thiadiazino[3,2-\textit{a}:5,4-\textit{a}']diisoquinoline-5-carboxylate 6,6-dioxide (14)
rel(4bR,5S,13bR)-5-(Methylsulfonyl)-4b,5,9,13b,15,16-hexahydro-8H-[1,2,4]thiadiazino[3,2-a:5,4-a']diisoquinoline 6,6-dioxide (15)
rel(4bR,5R,13bR)-5-(Methylsulfonyl)-4b,5,9,13b,15,16-hexahydro-8H-[1,2,4]thiadiazino[3,2-a:5,4-a']diisoquinoline 6,6-dioxide (16)
Ethyl \( \text{rel}(2S,10R,11S)-1,5,8,14\)-tetraaza-9-thiadibenzo[\(c,f\)]tricyclo[9.5.0.0^{2,8}]\)hexadecane-6,15-dione-10-carboxylate 9,9-dioxide (20)
Ethyl $rel(2R,10S,11S)-1,5,8,14$-tetraza-$9$-$thiadibenzo[3,4]tricyclo[9.5.0.0$^{2,8}$]hexadecane-$6,15$-dione-10-carboxylate 9,9-dioxide (21)