Electronic Supplementary Information

Part I: Experimental studies

Stereochemistry and mechanistic insights in the [2^1 + 2^1 + 2^1]
annulations of thioketenes and imines

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1. $^1$H and $^{13}$C NMR Spectra of Unknown Compounds

4-(4-Iodophenyl)-1,2,3-thiadiazole (6d)
4-Pentyl-1,2,3-thiadiazole (6j)
4-Cyclohexyl-1,2,3-thiadiazole (6l)
rel(1S,9bR)-1-(tert-Butyl)-1,4,5,9b-tetrahydro-2H-azeto[2,1-a]isoquinoline-2-thione (3n)
rel(4b,SS,15b,5-[3-Methoxyphenyl]-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a]:4,9-diazoquinoline-6-thione (4a)
rel(4bR,5S,13bS)-5-(4-Methylphenyl)-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-α:4,3-α'] diisoquinoline-6-thione (4b)
rel(4bR,5S,13bS)-5-Phenyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4c)
rel(4b,5S,13bS,5'-4-Iodophenyl)-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a':4,3-a']diisoquinoline-6-thione (4d)
rel(4bR,5S,13bS)-5-(4-Chlorophenyl)-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4e)
rel(4bR,5S,13bS)-5-Methyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-α:4,3-α′]diisoquinoline-6-thione (4g)
rel(4R,5S,13bS)-5-Ethyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4h)
rel(4bR,5S13bS)-5-Isobutyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4i)
$\textit{rel}(4bR,5S,13bS)-5$-Pentyl-$4b,5,9,13b,15,16$-hexahydro-$6H,8H$-pyrimido[2,1-$a$:4,3-$a'$]diisoquinoline-$6$-thione (4j)
rel(4b,5S,13b)-5-Isopropyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']quinoline-6-thione (4b)
rel(4b,5S,13bS)-5-Cyclohexyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisouquinoline-6-thione (4l)
Ethyl

rel(4bR,5R,13bS)-6-thioxo-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-5-carboxylate (4m)
2. One-dimension NOE Spectra of $[2^i + 2^i + 2^i]$ Annuladducts

(600 MHz)

$rel(4bR,5S,13bS)-5$-(3-Methoxyphenyl)$-4b,5,9,13b,15,16$-hexahydro-$6H,8H$-pyrimido$[2,1-a,3-a']$diisoquinoline$-6$-thione (4a):
rel(4bR,5S,13bS)-5-(4-Methylphenyl)-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4b):
rel(4bR,5S,13bS)-5-Phenyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4c):
rel(4bR,5S,13bS)-5-(4-Iodophenyl)-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4d):
rel(4bR,5S,13bS)-5-(4-Chlorophenyl)-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4e):
rel(4bR,5S,13bS)-5-Methyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimidino[2,1-α:4,3-α′]diisoquinoline-6-thione (4g):
rel(4bR,5S,13bS)-5-Ethyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4h):
rel(4bR,5S,13bS)-5-Isobutyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4i):
*rel*(4bR,5S,13bS)-5-Pentyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a’]diisquinoline-6-thione (4j):
rel(4bR,5S,13bS)-5-Isopropyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a’]diisoquinoline-6-thione (4k):
rel(4bR,5S,13bS)-5-Cyclohexyl-4b,5,9,13b,15,16-hexahydro-6H,8H-pyrimido[2,1-a:4,3-a']diisoquinoline-6-thione (4l):
Ethyl \(\text{rel}(4bR,5R,13bS)-6\text{-thioxo-4b,5,9,13b,15,16-hexahydro-6}H,8H\text{-pyrimido}[2,1-a:4,3-a']\text{diisoquinoline-5-carboxylate (4m):}\)