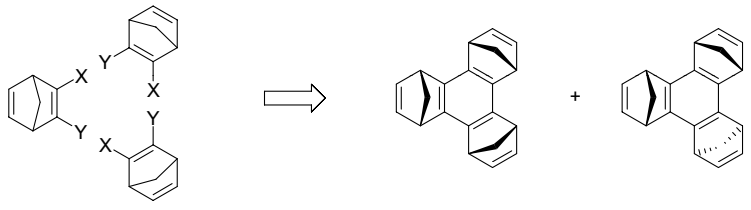
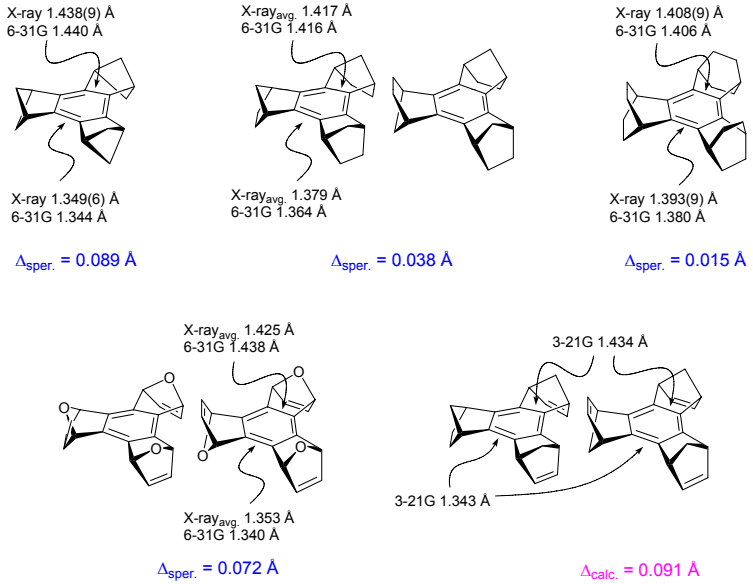
CYCLOTRIMERIZATION

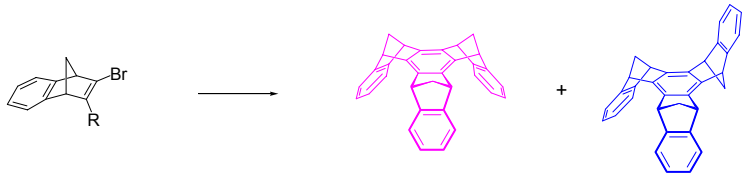


syn 1 *anti* 3

BOND ALTERNATION IN TRISANNELATED POLYCYCLIC BENZENES

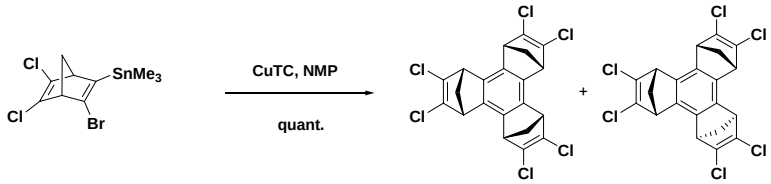


SUMMARY

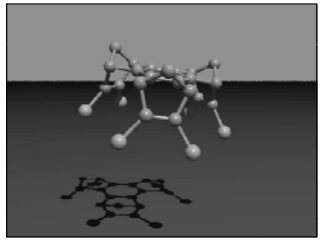


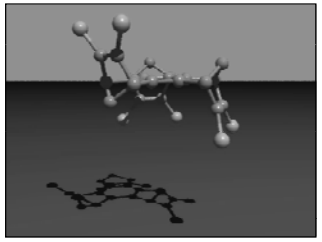
R	Reaction conditions	*Syn*	*Anti*	Yield
$SnMe_3$	CuI, LiCl, DMF, DME	4.5	1	83%
$SnMe_3$	CuTC, NMP	1	3	quant.
$SnBu_3$	$Pd(OAc)_2$ (Stille)	-	only	50%
Br	$Pd(OAc)_2$, $(R_3Sn)_2$ (Grigg)	-	only	quant.
H	$Pd(OAc)_2$ (Heck)	-	only	quant.

HEXACHLOROBENZOTRINORBORNADIENE

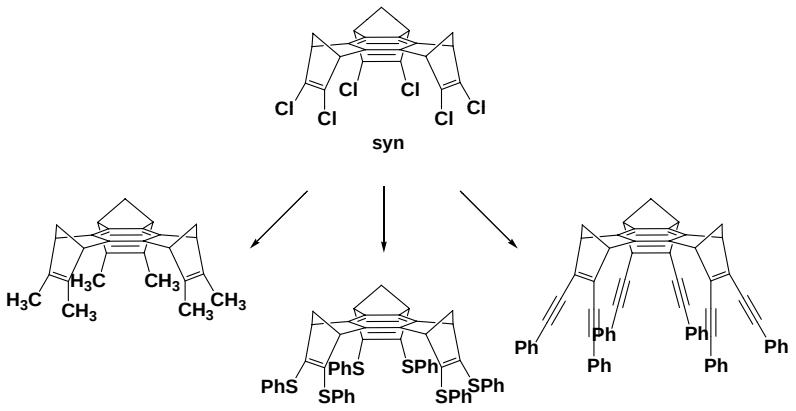


***syn/anti* 1 : 2**

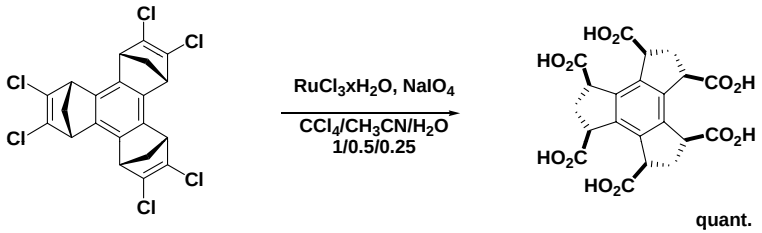


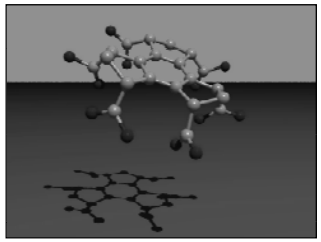


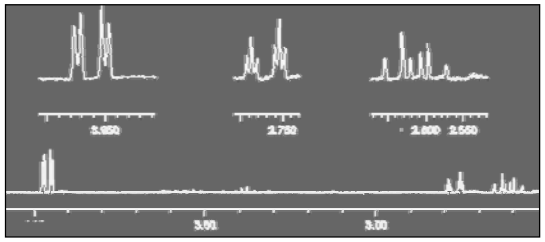
HEXACHLOROBENZOTRINORBORNADIENE DERIVATIVES



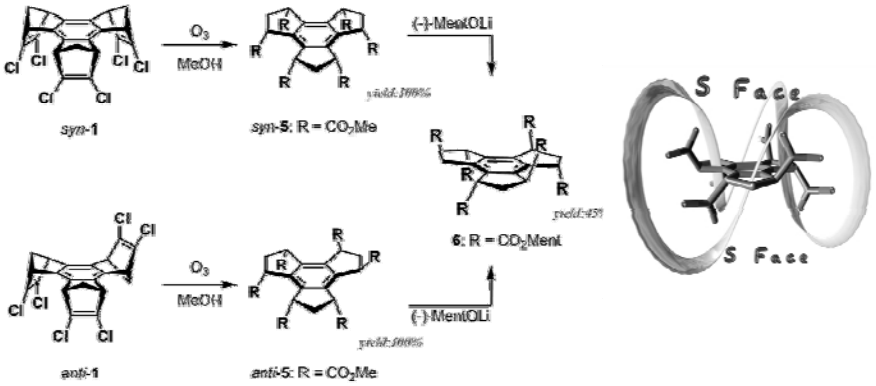
OXIDATION TO TRIINDANE



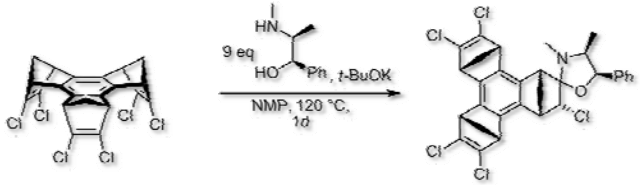


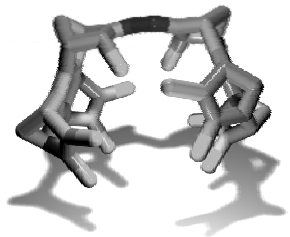


BASE EQUILIBRATION

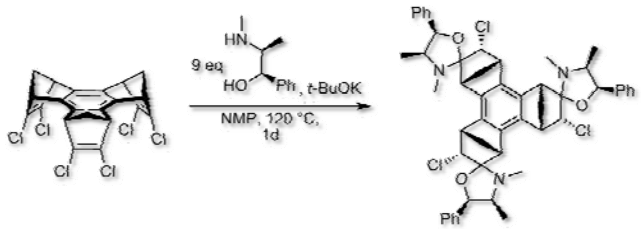


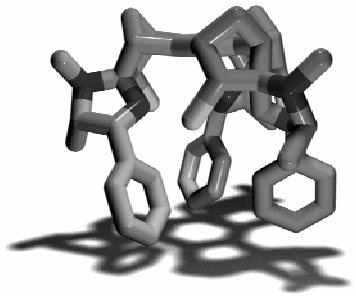
ENANTIOPURE MONOFUNCTIONALISATION



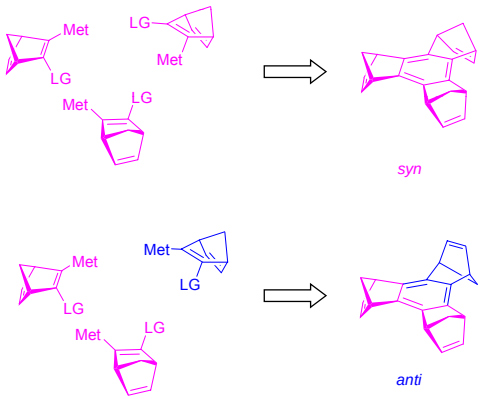


ENANTIOPURE C_3-SYMMETRIC BENZOCYCLOTRIMERS

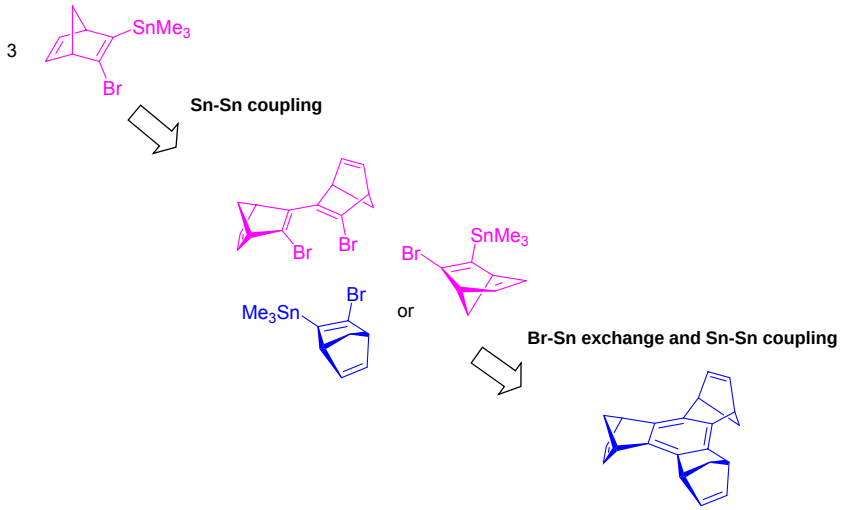




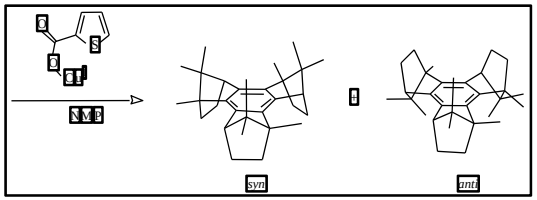
STEREOCHEMISTRY OF THE CYCLOTRIMERISATION REACTION



ANTI ONLY FROM ONE ENANTIOMER

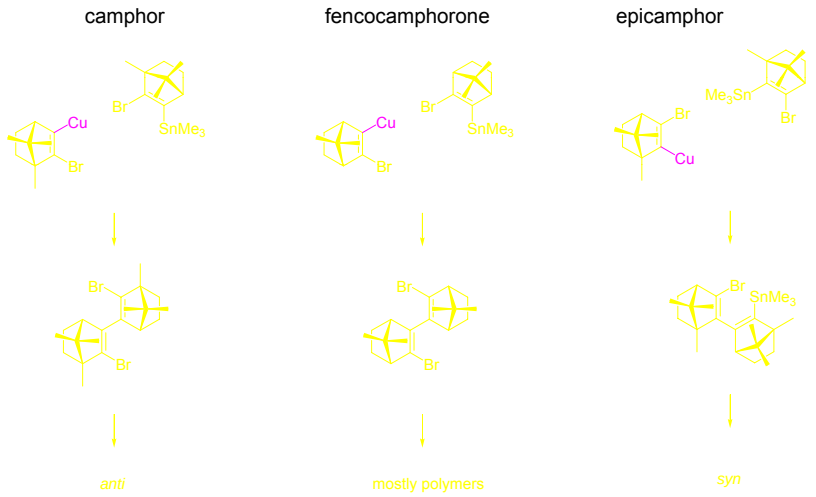


(+)-Benzotribornene

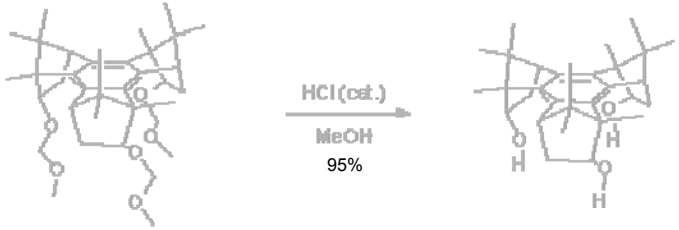


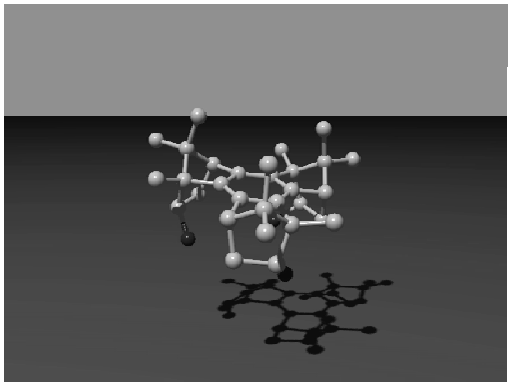
Syn/anti 1 : 6

Effect of the methyl group

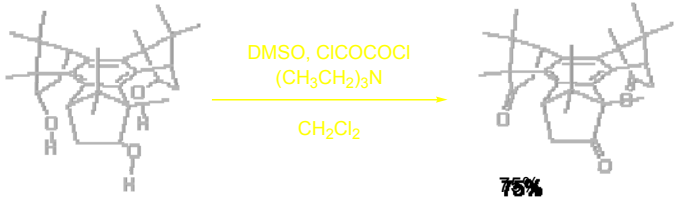


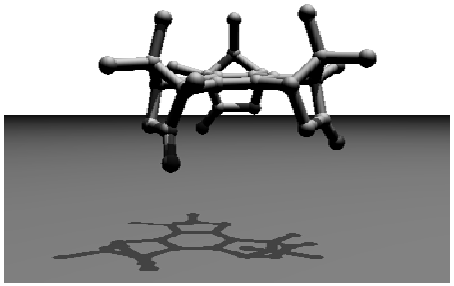
(+)-*Syn*-Benzotribornenol





Syn-Benzotricamphor





Syn-Benzotricamphor Modified Procedure

syn/*anti* 80 : 20

(overall yield 53%)

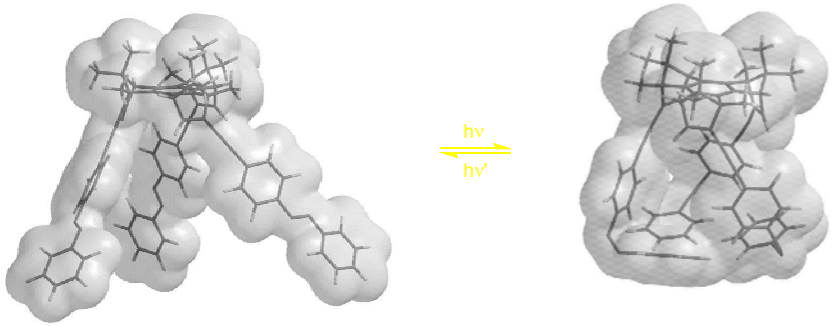
Syn-Benzotricamphor Triflate

Syn-Benzotricamphor triflate Sonogashira

Ar = Ph, C_6F_5, 3,5-Ph(OMe)$_2$

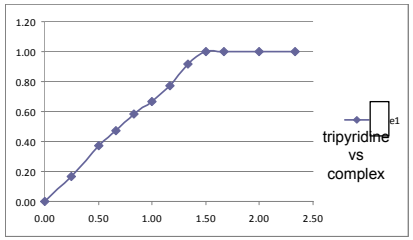
Syn-Benzotricamphor derived azo compound

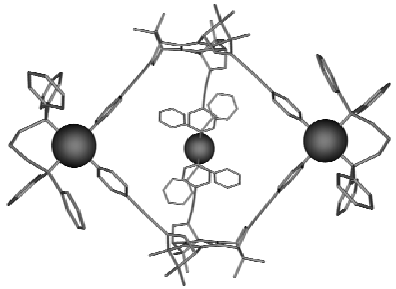
Syn-Benzotricamphor derived azo compound



Syn-Benzotricamphor derived metal framework

Syn-Benzotricamphor derived metal framework



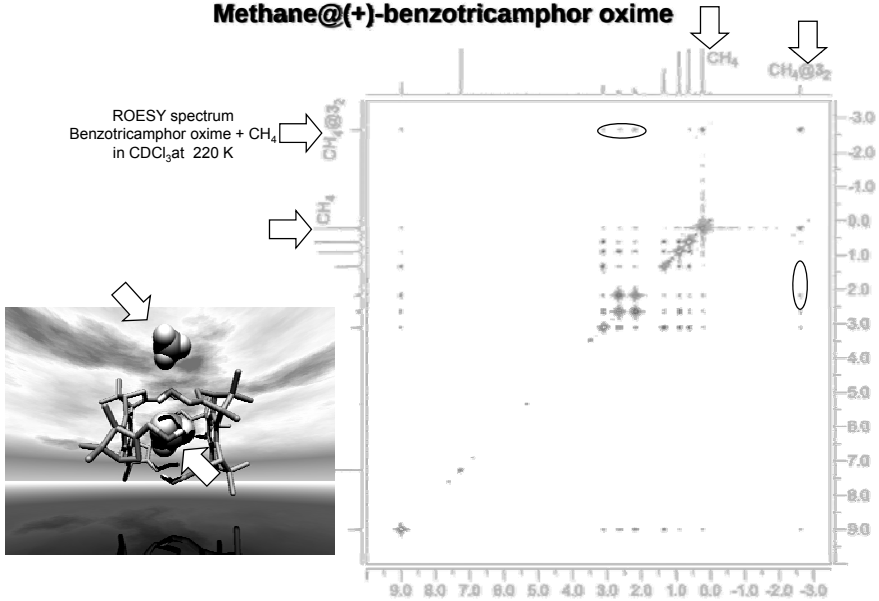


ESI-MS

1685.6 [tripyridine$_2$(dippp)Pt$_3$(OTf)$_4$]$^{2+}$
1073.1 [tripyridine$_2$(dippp)Pt$_3$(OTf)$_3$]$^{3+}$
768.5 [tripyridine$_2$(dippp)Pt$_3$(OTf)$_2$]$^{4+}$
584.1 [tripyridine$_2$(dippp)Pt$_3$(OTf)]$^{5+}$

(+)-Benzotricamphor oxime

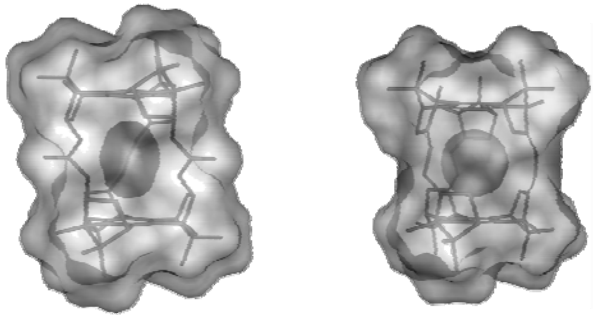
Methane@(+)-benzotricamphor oxime



Molecular cages

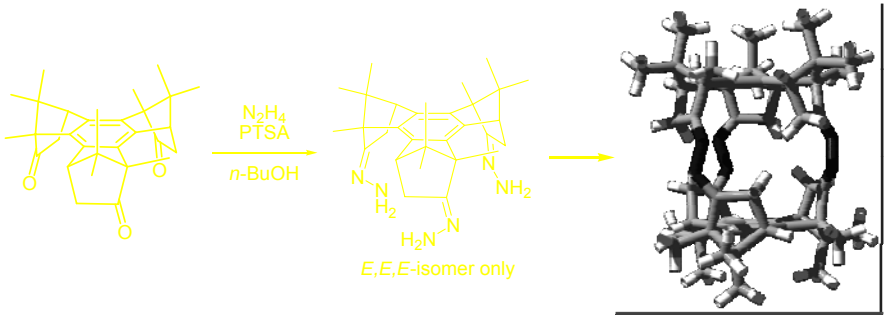
Molecular cages

Molecular cages

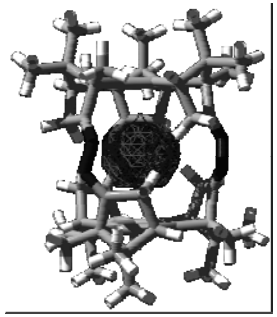


21 Å^3 16 Å^3

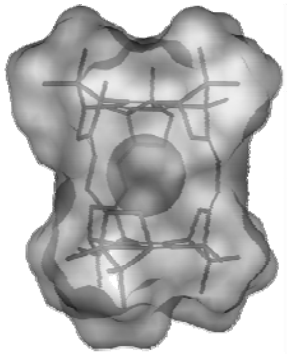
Molecular cages



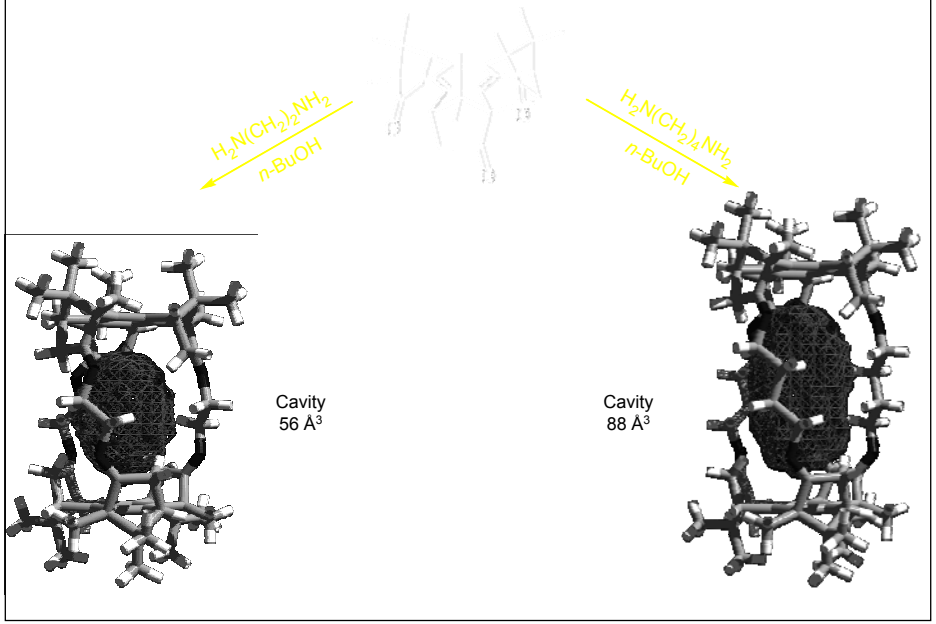
Molecular cages



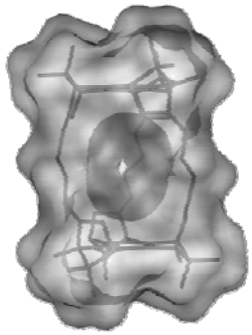
Cavity
16 Å^3



Molecular cages



Molecular cages



	Δδ (ppm)	K_{eq}	ΔH	ΔS
Methane	2.16	2.88	5.67	21.34
Acetylene	3.67	30.51	5.41	34.59
Ethylene	2.55	28.19	1.11	30.50
Ethane	2.19	1.23	2.88	9.65