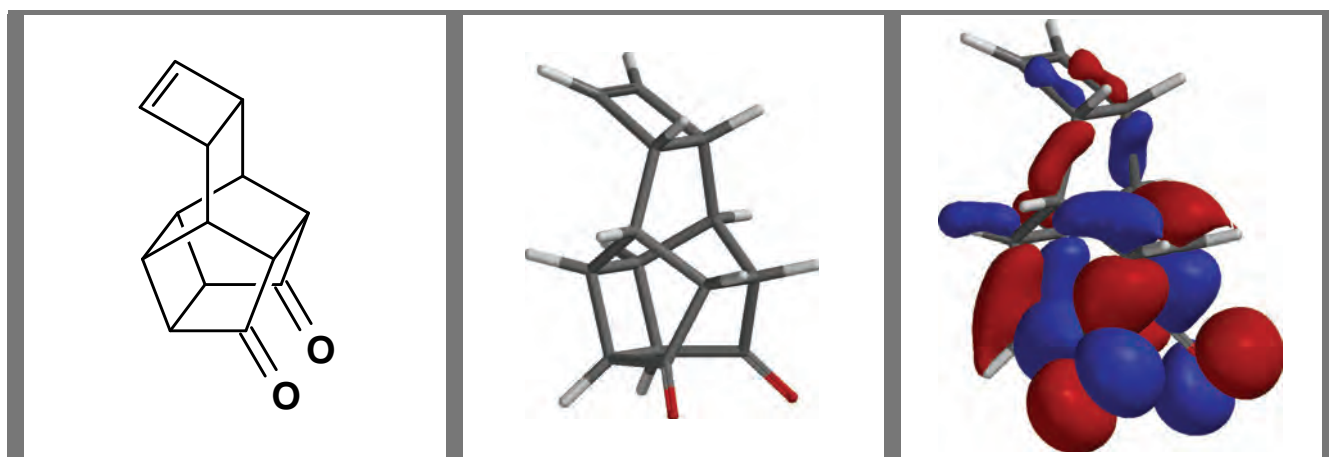


**Synthesis of selected cage alkenes and their attempted
ring-opening metathesis polymerisation with
well-defined ruthenium carbene catalysts**



Justus Röscher

Synthesis of selected cage alkenes and their attempted ring-opening metathesis polymerisation with well-defined ruthenium carbene catalysts

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M.Sc., H.E.D. (Potchefstroom University for Christian Higher Education)

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CHEMISTRY

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Promoter: Dr. A.M. Viljoen
Co-promoter: Prof. H.C.M. Vosloo

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of this study is acknowledged.**

Language usage

This thesis has been written in British English.

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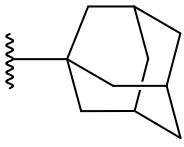
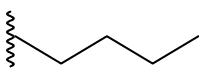
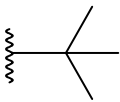
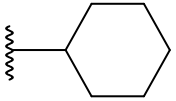
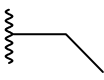
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Name	Compound number	Type	Page
Tetracyclo[6.3.0.0 ^{4,11} .0 ^{5,9}]undec-2-en-6-one	1	IR	127
		MS	133
		NMR	140
<i>Endo</i> -tetracyclo[6.3.0.0 ^{4,11} .0 ^{5,9}]undec-2-en-6-ol	118	IR	127
		MS	134
		NMR	142
<i>Endo</i> -tetracyclo[6.3.0.0 ^{4,11} .0 ^{5,9}]undec-2-en-6-yl acetate	121	IR	128
		MS	134
		NMR	145
4,5,6,7,16,16-Hexachlorohexacyclo[7.6.1.0 ^{3,8} .0 ^{2,13} .0 ^{10,14}]hexadec-5-en-11-one	126b	IR	128
		MS	135
		NMR	147
Hexacyclo[7.6.1.0 ^{3,8} .0 ^{2,13} .0 ^{10,14}]hexadec-5-ene	127	IR	129
		MS	135
		NMR	150
Tetracyclo[6.3.0.0 ^{4,11} .0 ^{5,9}]undec-2-ene	159	IR	129
		MS	236
		NMR	152
4-Isopropylidenepentacyclo[5.4.0.0 ^{2,6} .0 ^{3,10} .0 ^{5,9}]undecane-8,11-dione	23	IR	130
		MS	136
		NMR	155

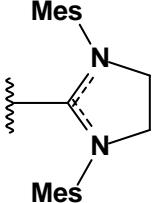
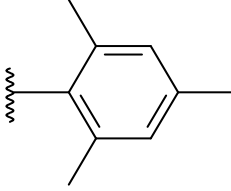
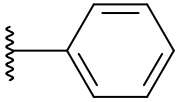
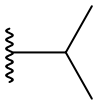
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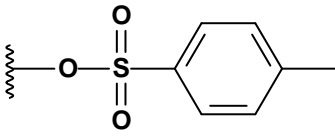
Name	Compound number	Type	Page
8-(Ethylene ketal)-4-isopropylidenepentacyclo[5.4.0.0 ^{2,6} .0 ^{3,10} .0 ^{5,9}]undecane-11-one	132	IR	130
		MS	137
		NMR	157
<i>Endo</i> -8-(ethylene ketal)-11-hydroxy-4-isopropylidenepentacyclo[5.4.0.0 ^{2,6} .0 ^{3,10} .0 ^{5,9}]-undecane-8-one	133	IR	131
		MS	137
		NMR	160
<i>Endo</i> -11-hydroxy-4-isopropylidenepentacyclo[5.4.0.0 ^{2,6} .0 ^{3,10} .0 ^{5,9}]undecane-8-one	134	IR	131
		MS	138
		NMR	163
<i>Exo</i> -4,11-dibromo-4-isopropylpentacyclo[5.4.0.0 ^{2,6} .0 ^{3,10} .0 ^{5,9}]undecane-8-one	151	IR	132
		MS	138
		NMR	165
Hexacyclo[8.4.0.0 ^{2,9} .0 ^{3,13} .0 ^{4,7} .0 ^{4,12}]tetradec-5-en-11,14-dione	3	IR	132
		MS	139
		NMR	168
Hexacyclo[8.4.0.0 ^{2,9} .0 ^{3,13} .0 ^{4,7} .0 ^{4,12}]tetradec-5-ene	175	IR	133
		MS	139
		NMR	170

Abbreviations

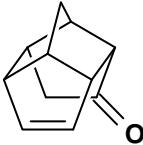
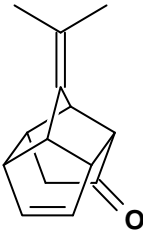
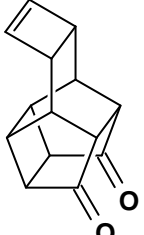
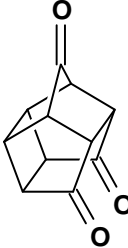
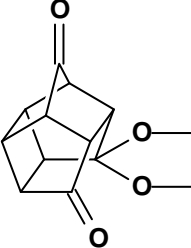
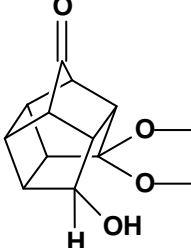
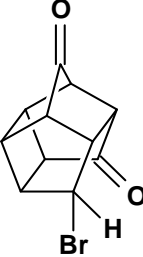
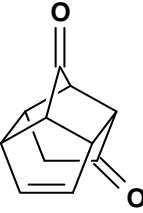
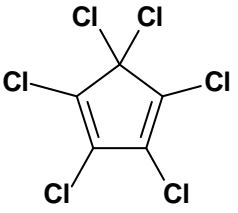
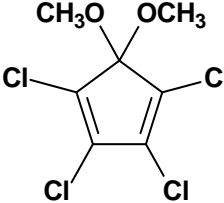
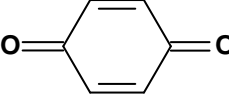
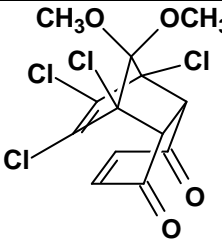
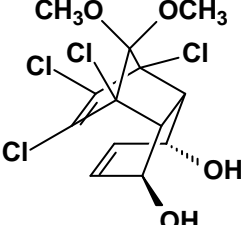
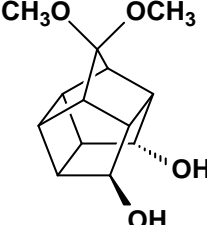
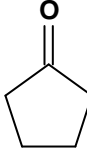
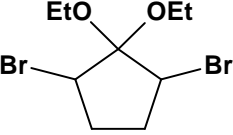

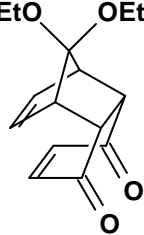
ΔG	Gibbs free energy change
ΔH	Enthalpy change
ΔS	Entropy change
$[M]_{eq}$	Equilibrium concentration
^a	<i>Anti</i>
Ac	Acetyl
Ad	
ADMET	Acyclic diene metathesis
Bu	
BuLi	
Bu ^t	
CM	Cross metathesis
COSY	Correlated spectroscopy
COT	1,3,5,7-Cyclooctatetraene
CPU	Central processing unit
Cy	
DCM	Dichloromethane
DEPT	Distortionless enhancement of polarisation transfer
DFT	Density functional theory
DMAP	4-(<i>N,N</i> -dimethylamino)pyridine
DMF	Dimethylformamide
DMSO	Dimethyl sulphoxide
DNP	Double numeric polarised basis set
DSC	Differential scanning calorimetry
Et	
FMO	Frontier molecular orbital
GC	Gas chromatography
GC-MS	Gas chromatography-mass spectrometry
GGA	Generalised gradient approximation
GPC	Gel permeation chromatography
HDD	Hard disk drive
HOMO	Highest occupied molecular orbital

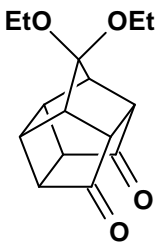
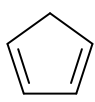
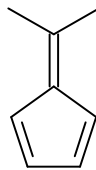
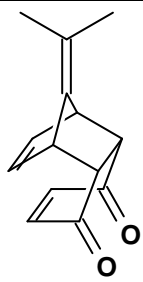
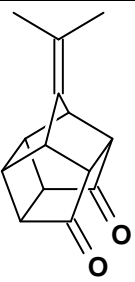
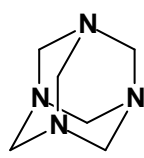
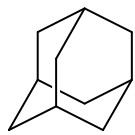
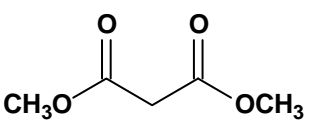
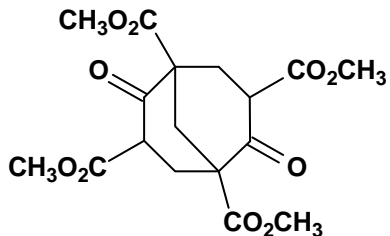
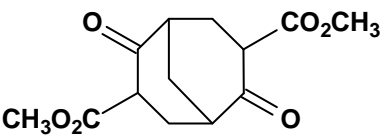
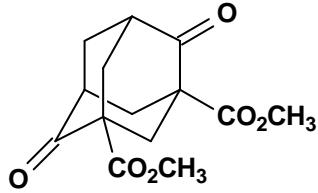
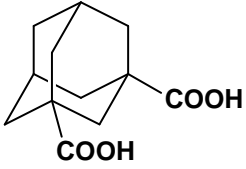
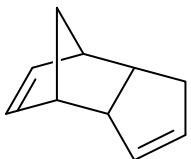
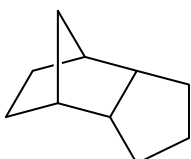
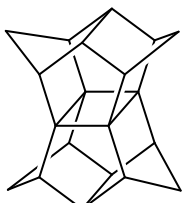
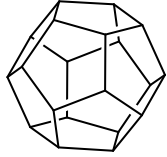
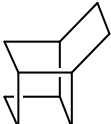


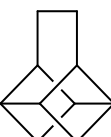
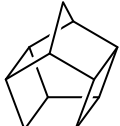
Abbreviations

HPC	High performance computing
HSQC	Heteronuclear multiple quantum coherence
IMes	
LUMO	Lowest unoccupied molecular orbital
Mes	
\bar{M}_n	Number average molecular mass
Ms	Mesyl (methanesulphonyl)
MSD	Mass selective detector
\bar{M}_w	Mass average molecular mass
NHOMO	Next-to-highest occupied molecular orbital. Also indicated as HOMO-1.
<i>NMP</i>	<i>N</i> -methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance spectroscopy
NOESY	Nuclear Overhauser effect spectroscopy
PCU	Pentacycloundecane
PDI	Polydispersion index
PES	Potential energy surface
Ph	
POP	Persistent organic pollutant
Pr ⁱ	
PTS	<i>p</i> -Toluenesulphonic acid
py	Pyridine
RCM	Ring-closing metathesis
ROESY	Rotating-frame Overhauser spectroscopy
ROMP	Ring-opening metathesis polymerisation
ROP	Ring-opening polymerisation
HSAB	Hard and soft acids and bases
SCF	Self consisted field
SLUMO	Second lowest unoccupied molecular orbital. Also indicated as LUMO+1.

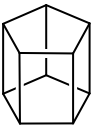
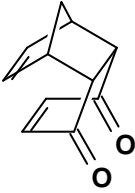
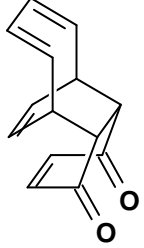
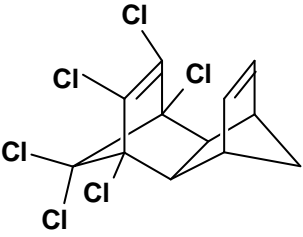
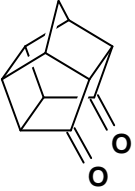
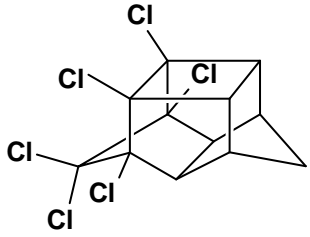
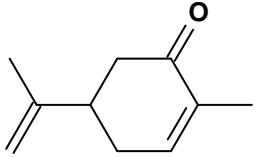
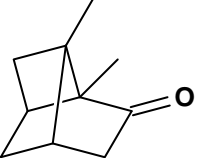
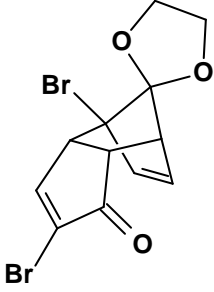
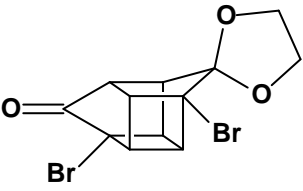
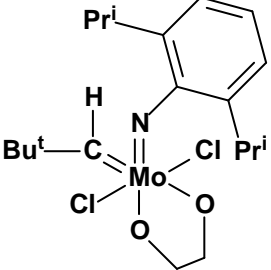
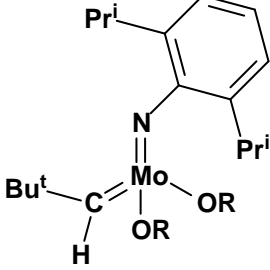
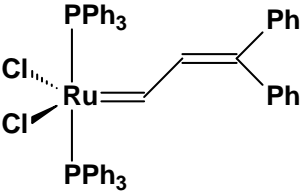
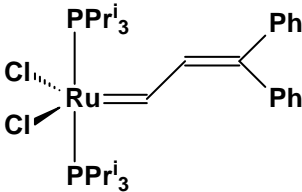
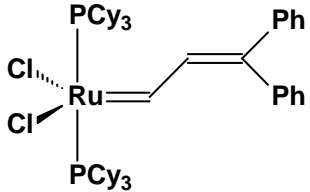
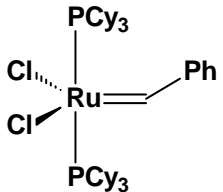
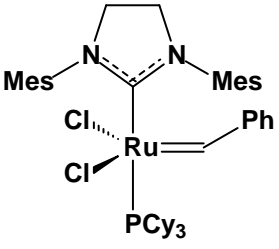
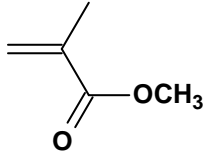
RSE	Ring strain energy
RSE ^f	Fractional ring strain energy
SI	Semi-empirical
s	<i>Syn</i>
TCU	Tetracycloundecane
TGA	Thermogravimetric analysis
THF	Tetrahydrofuran
TMSCl	Trimethylsilyl chloride
Ts	
TS	Transition state

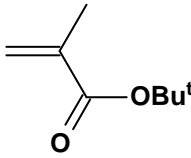
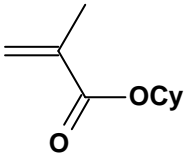
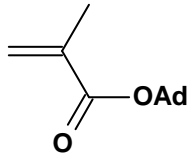
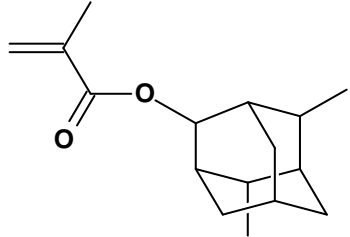
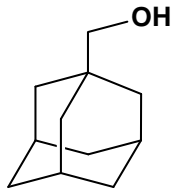
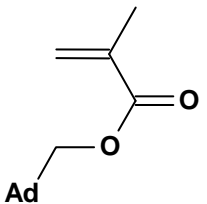
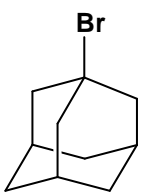
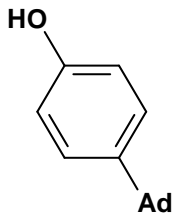
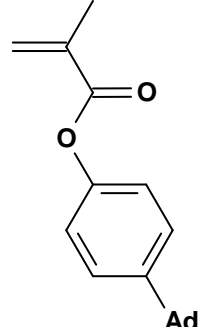
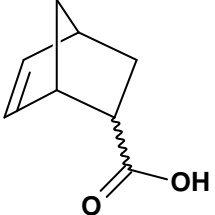
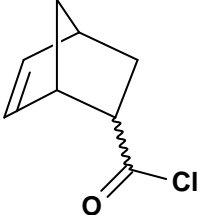
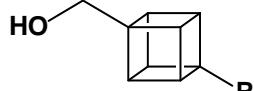
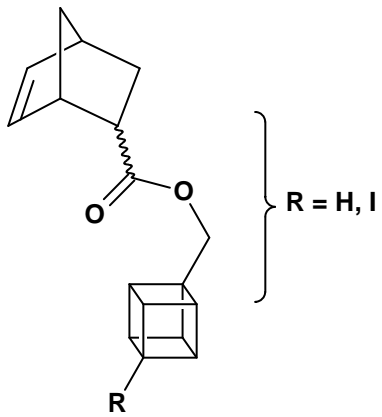
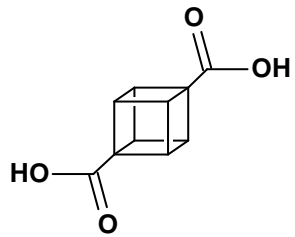
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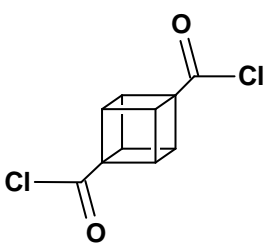
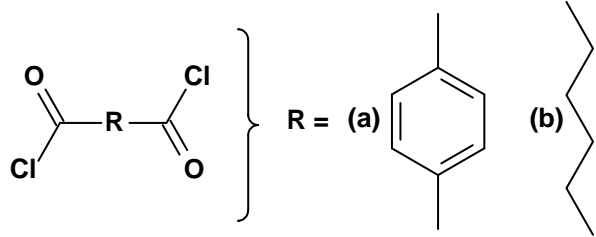
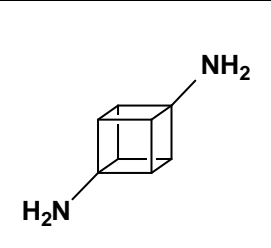
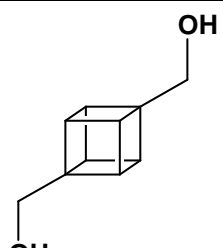
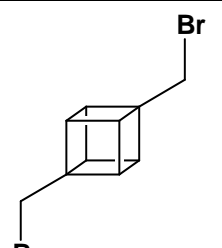
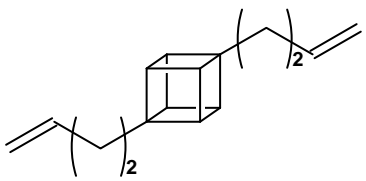
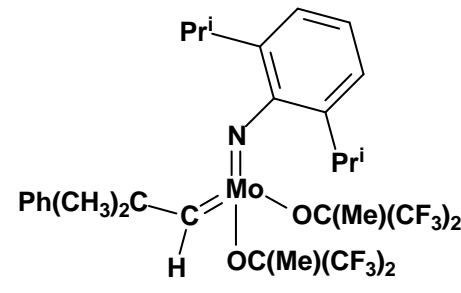

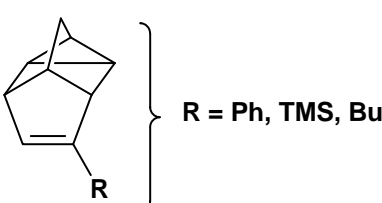
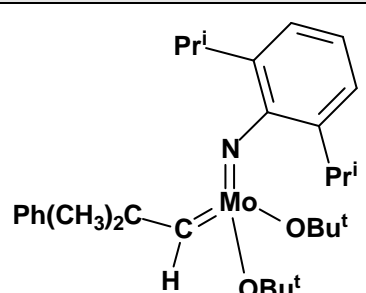
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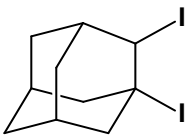
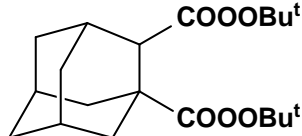
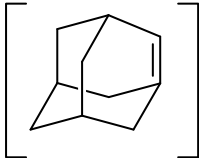
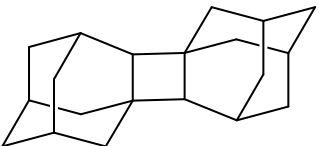
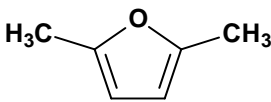
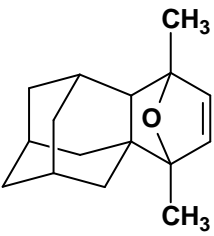
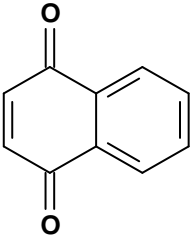
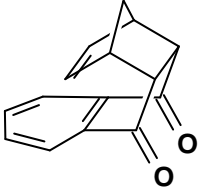
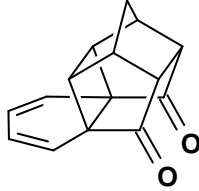
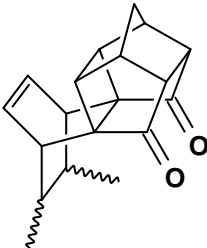
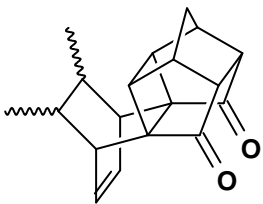
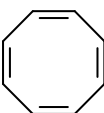
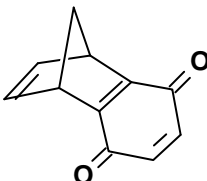
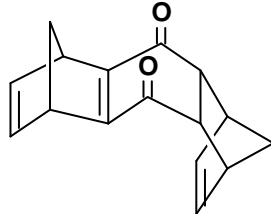
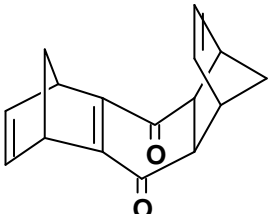
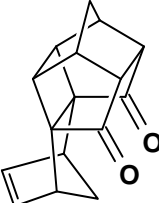
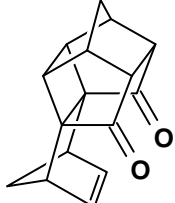
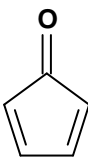
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55	56	58a

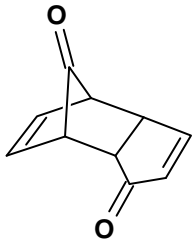
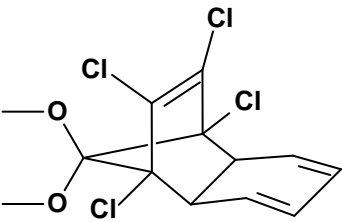
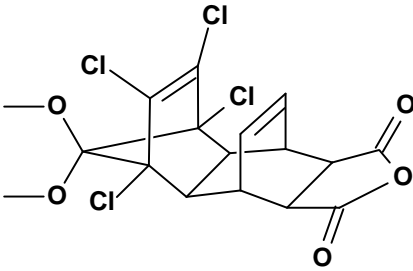
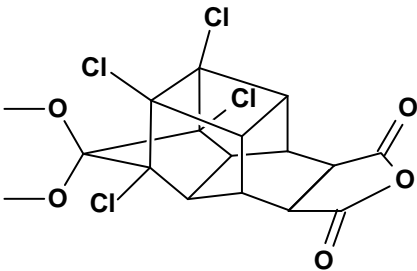
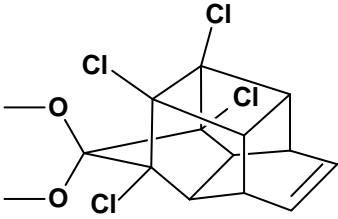
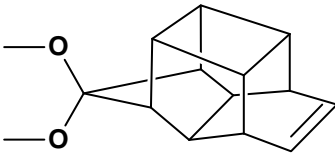
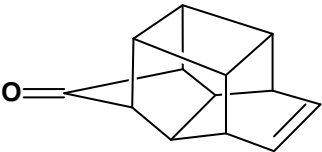
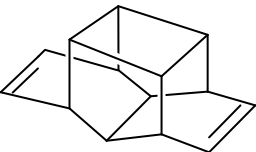
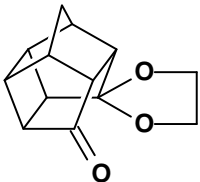
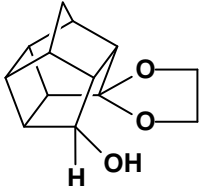
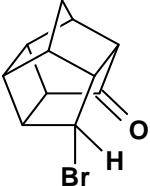
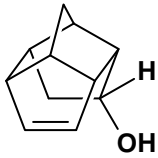
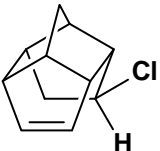

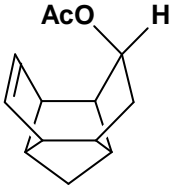
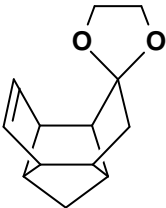
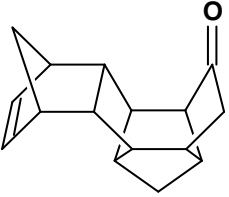
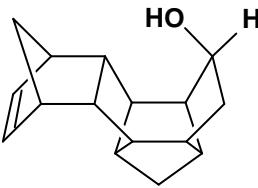
		
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68		70

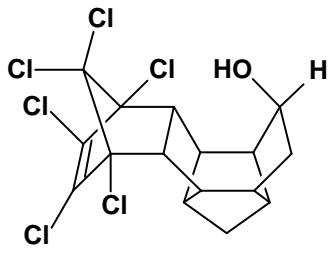
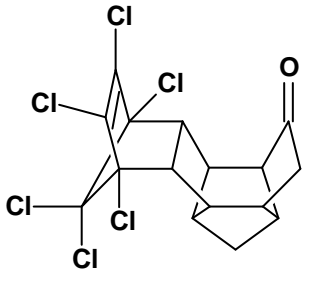
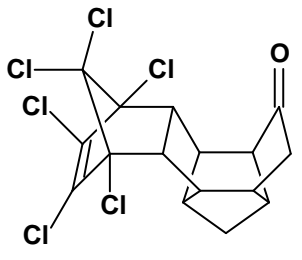
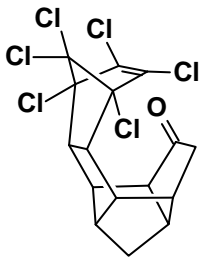
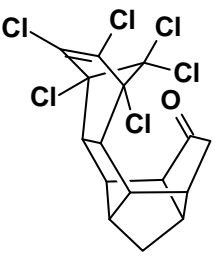
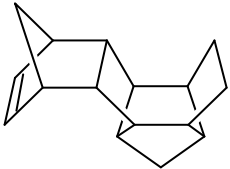
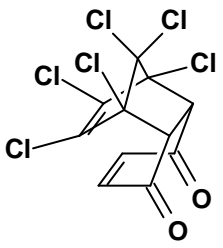
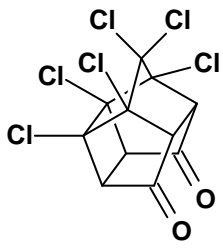
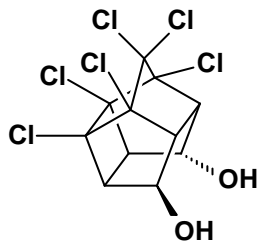
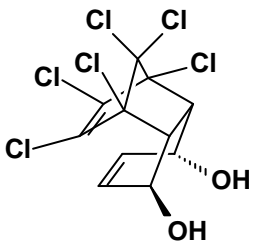
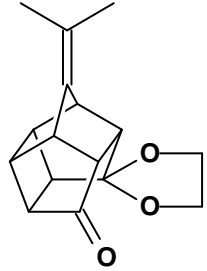
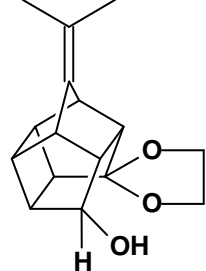
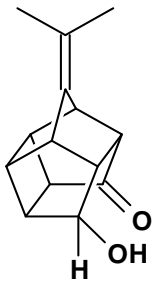
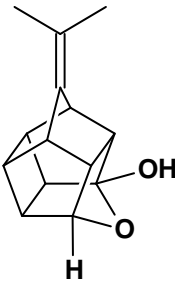
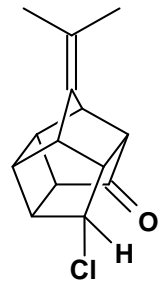
List of structures

$\left. \begin{array}{c} \text{H}_2\text{N}-\text{R}-\text{NH}_2 \\ \text{R} = \end{array} \right\} \begin{array}{l} \text{(a)} \text{ } \langle \text{---} \rangle \\ \text{(b)} \text{ } \langle \text{---} \rangle \text{O} \langle \text{---} \rangle \\ \text{(c)} \text{ } \text{O}=\text{S}=\text{O} \\ \text{(d)} \text{ } \langle \text{---} \rangle \langle \text{---} \rangle \langle \text{---} \rangle \\ \text{(e)} \text{ } \langle \text{---} \rangle \end{array}$		
71		
		
73	74	
		
75	78	79
		
80	82	
		
83	84	89

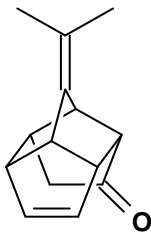
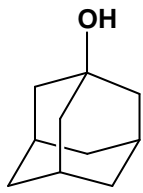
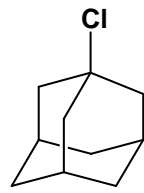
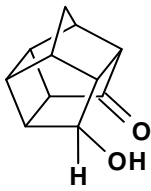
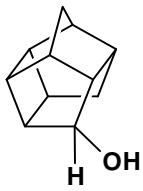
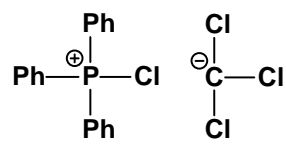
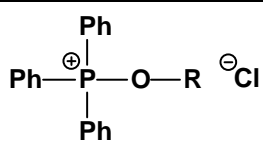
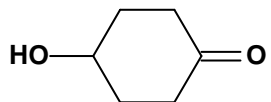
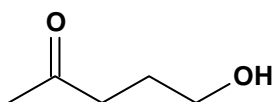
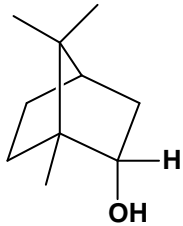
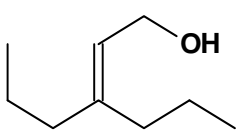
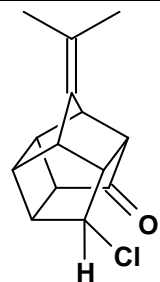
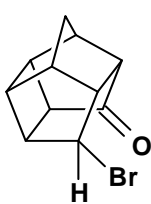
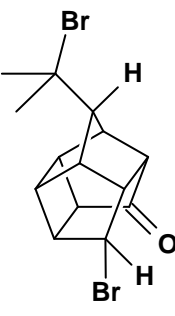
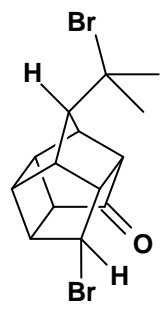
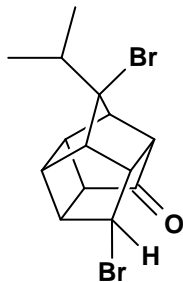
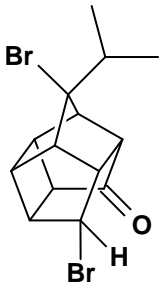
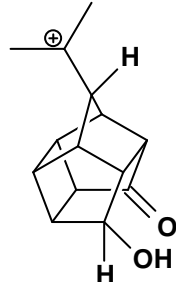
		
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93	94	95
		
96	97	98
		
99A	99B	100
		
101	102	103
		
104	105	106

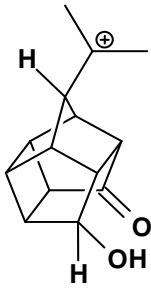
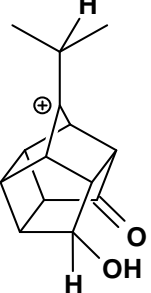
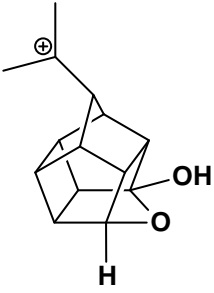
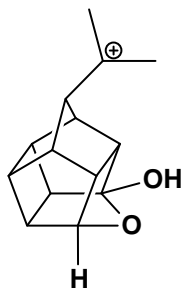
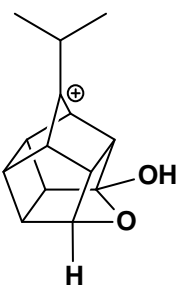
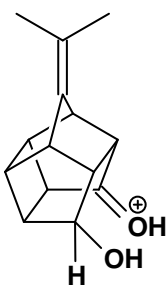
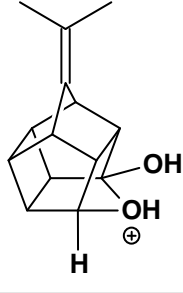
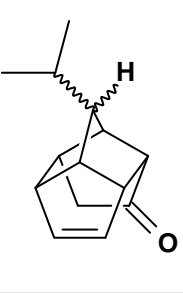
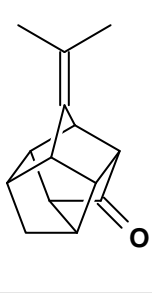
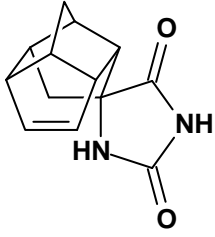
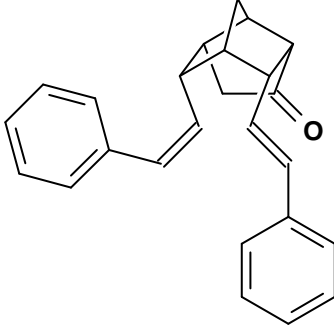
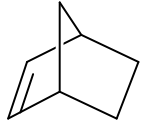

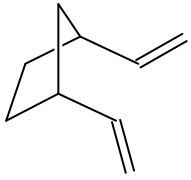
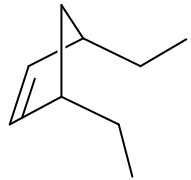
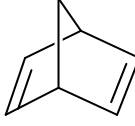
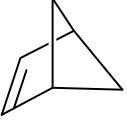
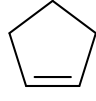
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110	111	112
		
113	114	115
		
116	117	118
		
119	120	121
		
122	123	124

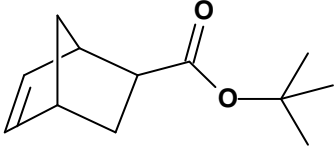
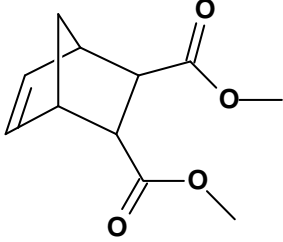
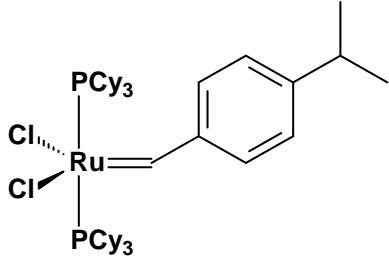
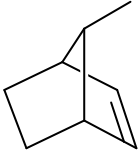
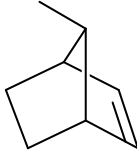
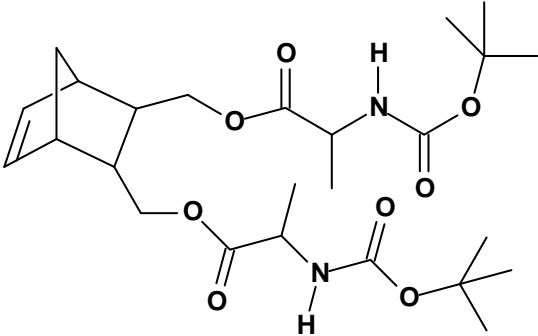
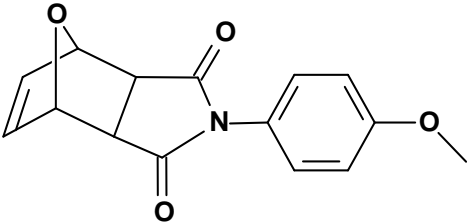
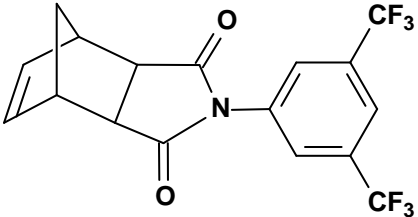
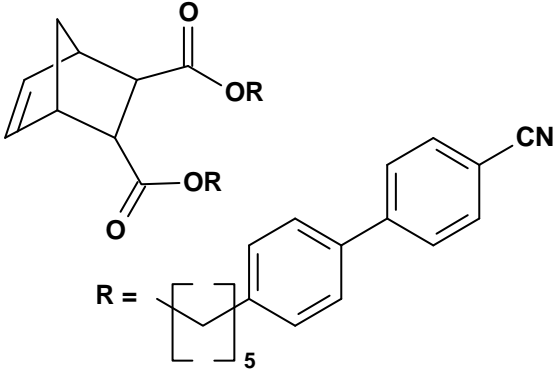
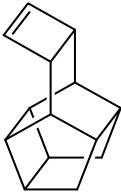
		
125	126a	126b
		
126c	126d	127
		
128	129	130
		
131	132	133
		
134a	134b	135

List of structures

		
136	137	138
		
139	140	141
		
143	144	145
		
146	147	148
		
149	150a	150b
		
151a	151b	152a

		
152b	152c	152d
		
152e	152f	153a
		
153b	154	155
		
156	157	158
		
159	160	161
		
162	163	164

List of structures

			
<p>165</p>	<p>166</p>	<p>167</p>	
			
<p>168a</p>		<p>168b</p>	
			
<p>170</p>	<p>171</p>		
			
<p>172</p>	<p>173</p>		
			
<p>175</p>			