

Table – 1 Some selected compounds of Coumarin with Pharmacological and Industrial properties

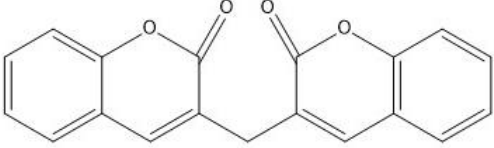
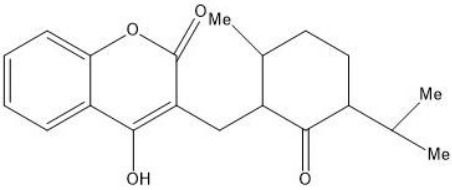
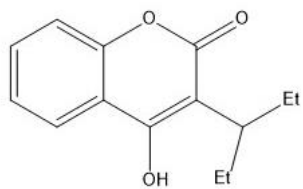
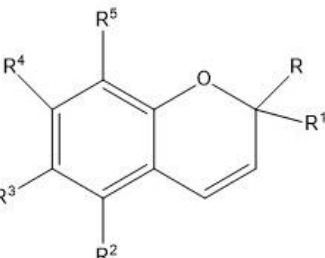
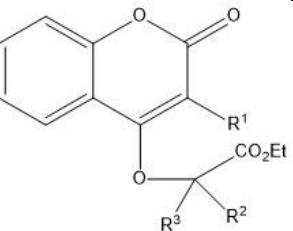
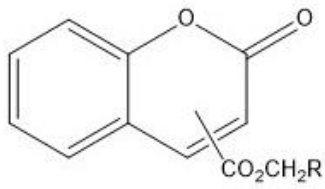
Substrates	Properties	Ref
	Anticoagulant	16,17
	Anticoagulant	16,17
	Hypo epidemic1	17
	Anti allergic	17a
	Anti inflammatory	18
	Anti hypertension	19

Table – 1 Some selected compounds of Coumarin with Pharmacological and Industrial properties

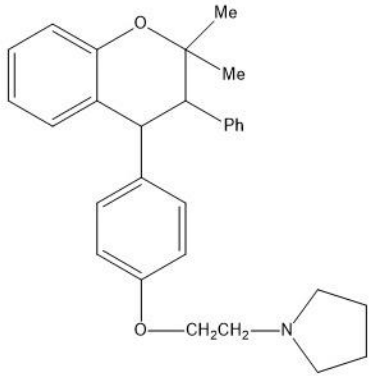
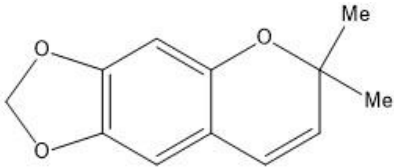
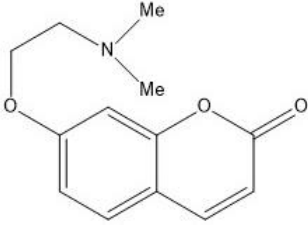
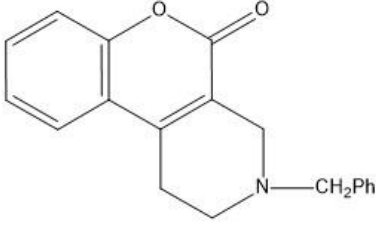
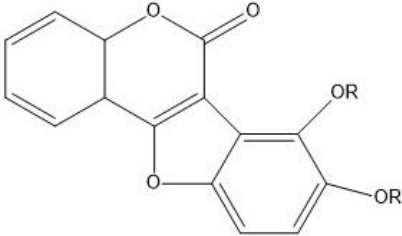
Substrates	Properties	Ref
	<p>Anti inflammatory</p> <p>Schistomiacide</p>	<p>20</p> <p>20</p>
	<p>Metamorphosis activity of insect</p>	<p>21</p>
	<p>Hypertensive</p>	<p>22</p>
	<p>Hypertensive</p>	<p>22</p>
	<p>Hypertensive</p>	<p>22</p>

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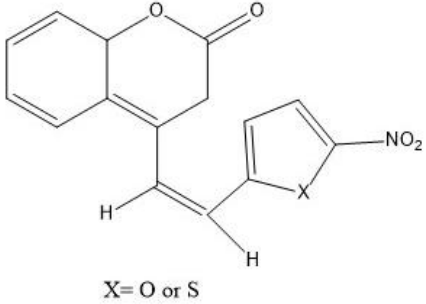
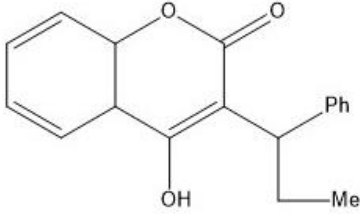
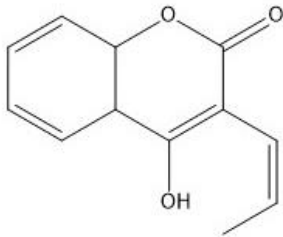
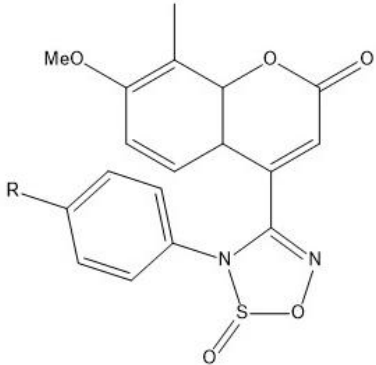
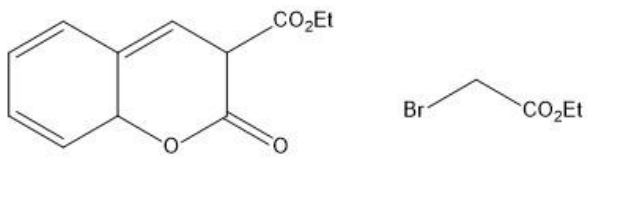
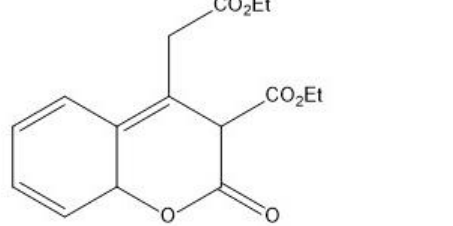
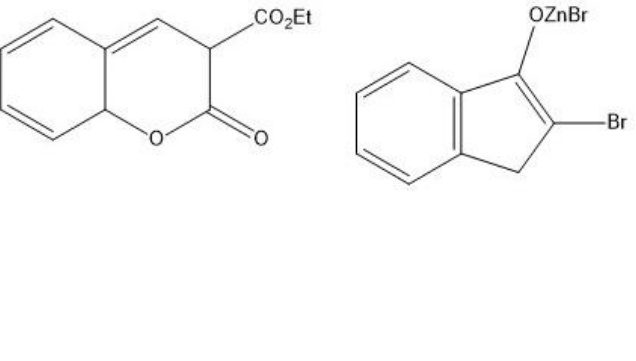
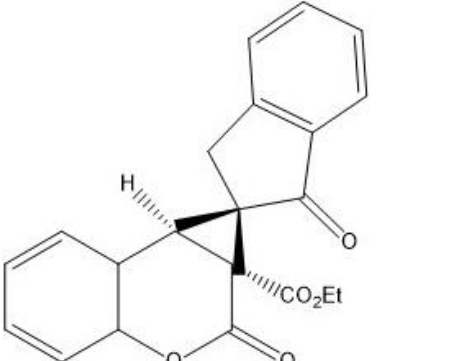
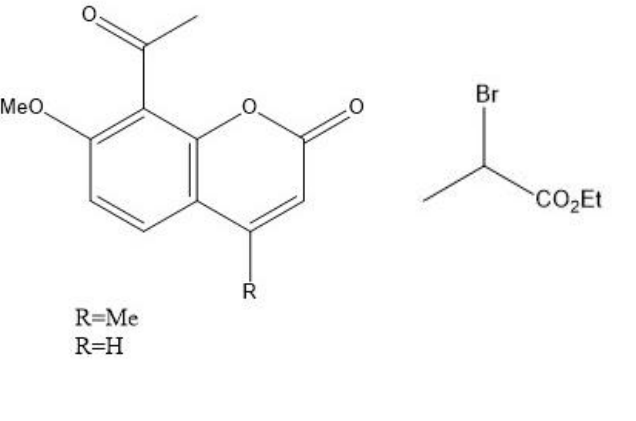
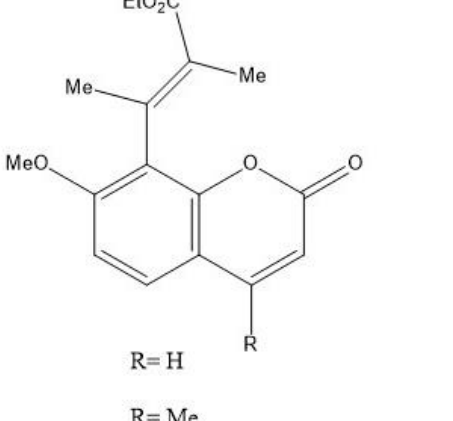
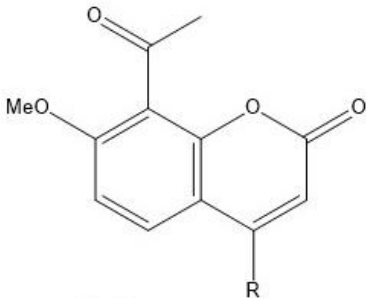

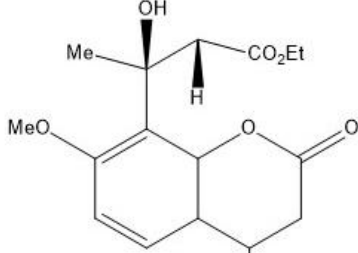
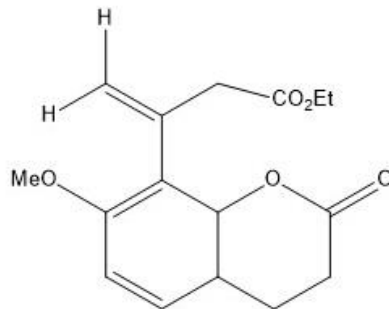
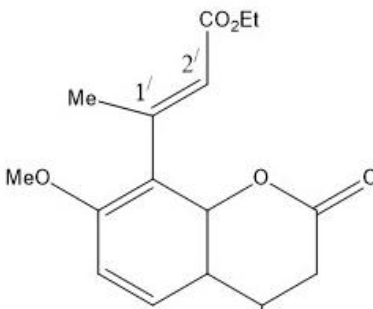
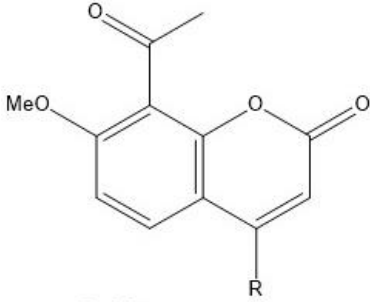
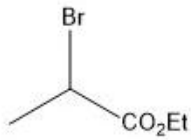
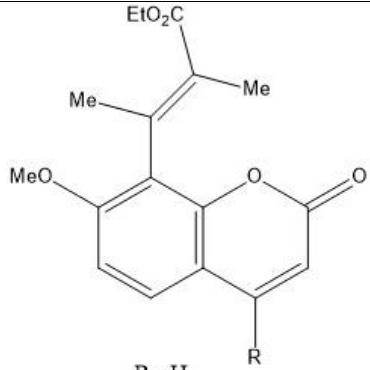
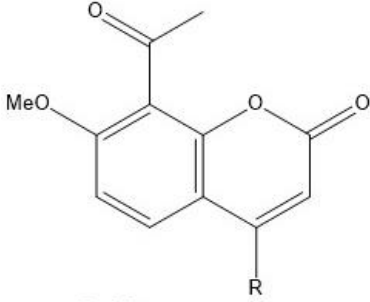
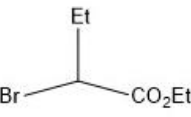
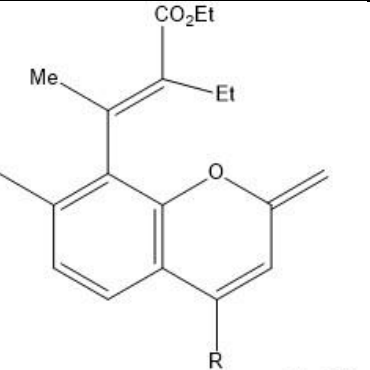
Substrates	Properties	Ref
 <p>X=O or S</p>	Anti tubercular	23
	Anti coagulant	23a
 	Anti inflammatory & Anti microbial	24,25

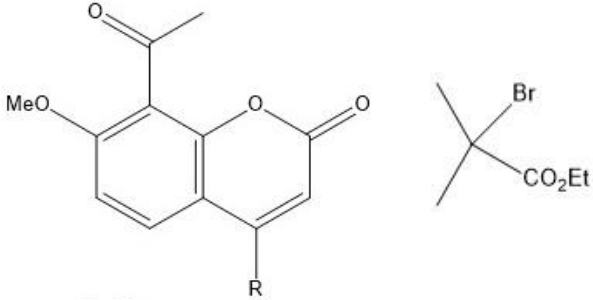
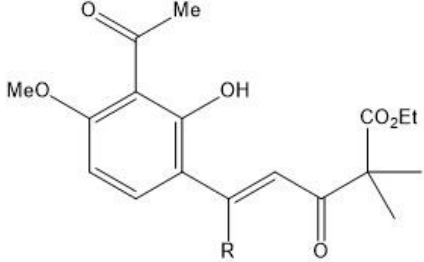
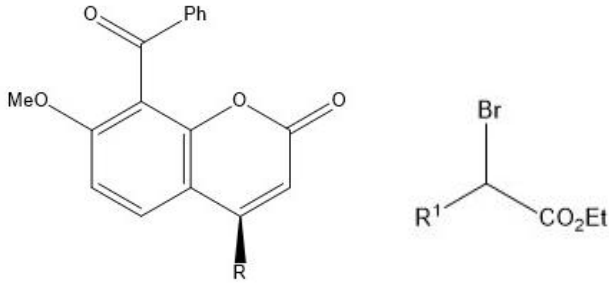
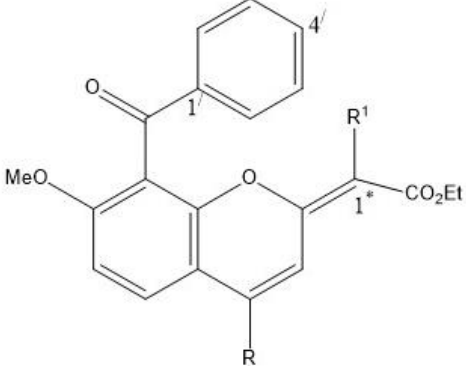
Table - 2 Selected Examples of Reformatsky Reaction with Coumarins/uncommon electrophiles

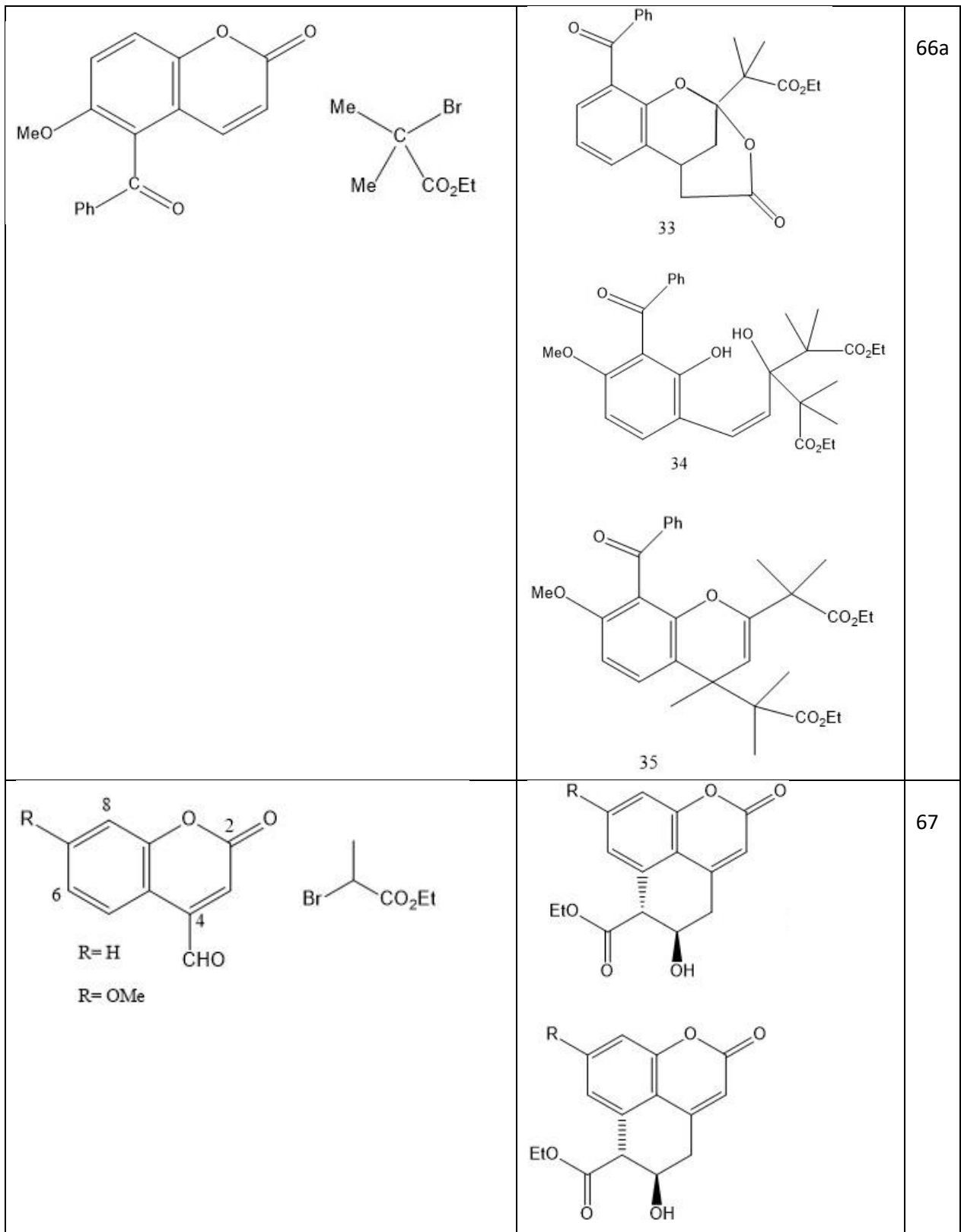
Substrates	Products	Ref
		63
		65
 <p data-bbox="263 1164 343 1232">R=Me R=H</p>	 <p data-bbox="1005 1209 1085 1299">R= H R= Me</p>	66

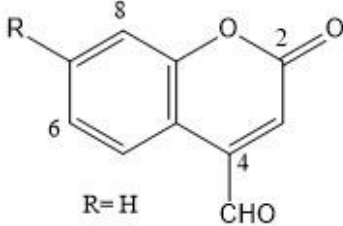
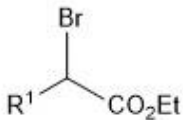
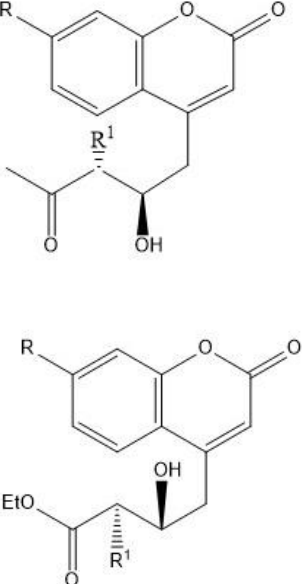
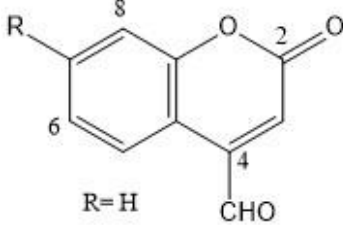
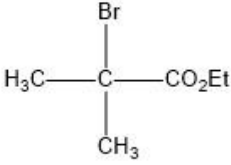
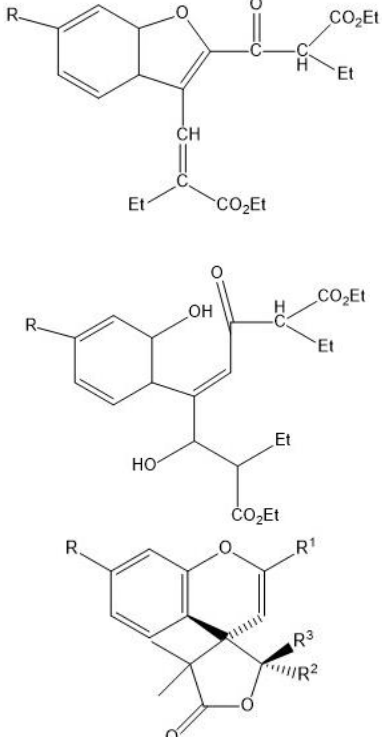
Table

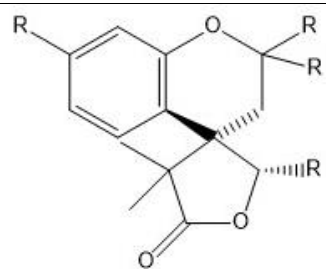
 <p>R=Me R=H</p>		<p>66</p>
	 <p>R=H R=Me</p>	
	 <p>R=H R=Me</p>	
	 <p>R=H R=Me</p>	

 <p>R=Me R=H</p>		 <p>R=H R=Me</p>	66
 <p>R=Me R=H</p>		 <p>R=H R=Me</p>	66

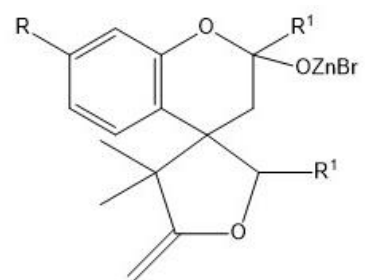
 <p>R=Me R=H</p>	 <p>R=H</p>	66
 <p>R= H, Me</p>	 <p>R= H R¹= H R= Me R¹=H R=H R¹= Me R=Me R¹=Me R=H R¹= Et R= Me R¹= Et</p>	66a



Substrates	Products	Ref
 <p>R=H R=OMe</p>	 <p>R^1-CH(Br)-CO₂Et</p>  <p>$R^1 = \text{Me, Et, CHMe}_2\text{CH}$ R=H, Me</p>	67
 <p>R=H R=OMe</p>	 <p>H₃C-C(Br)(CH₃)-CO₂Et</p>  <p>$R=R^2=H, R^3=\text{CMe}_2\text{CO}_2\text{Et}$ $R=R^3=H, R^2=\text{CMe}_2\text{CO}_2\text{Et}$ $R=\text{OMe}, R^1=R^3=\text{CMe}_2\text{CO}_2\text{Et}, R^2=H$</p>	67



$R = \text{CMe}_2\text{CO}_2\text{Et}$



$R = \text{H, OMe, R}^1 = \text{CMe}_2\text{CO}_2\text{Et}$

Table -3 Selected Examples of Reformatsky Reaction with Coumarins/uncommon electrophiles

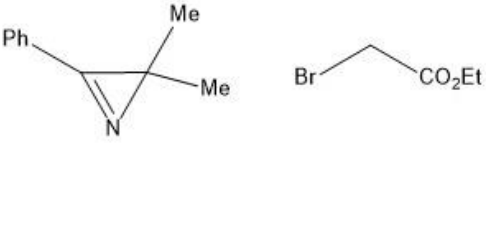
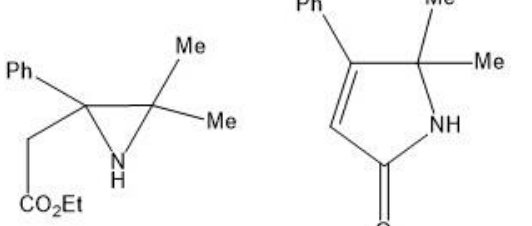
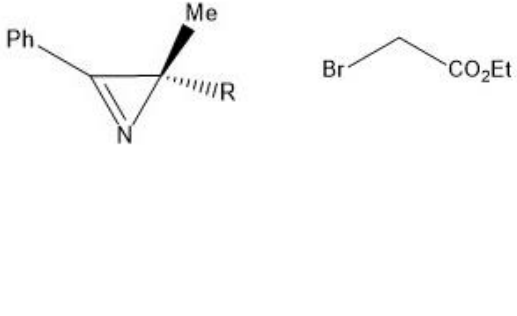
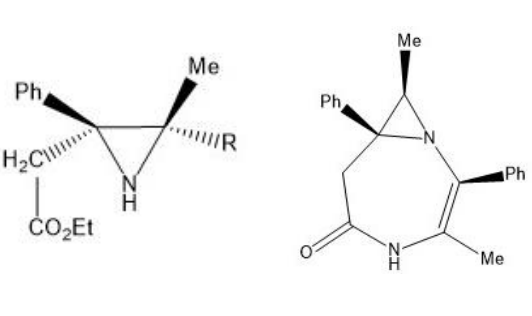
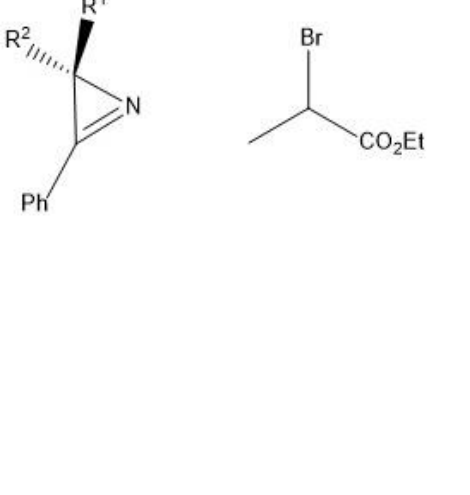
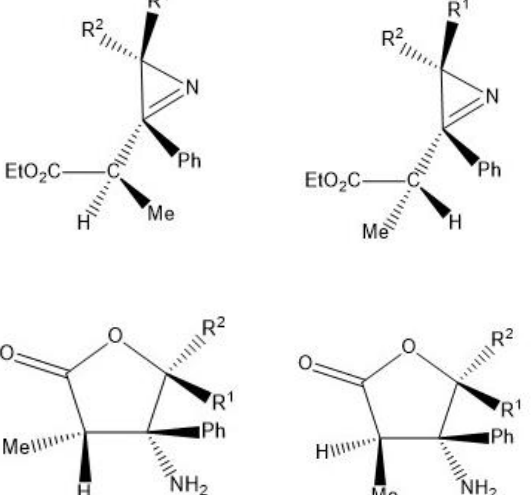
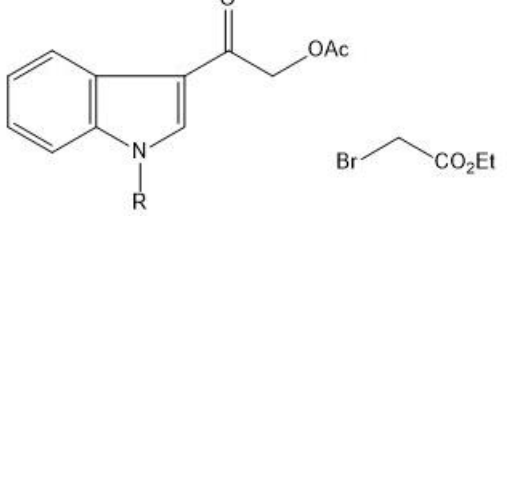
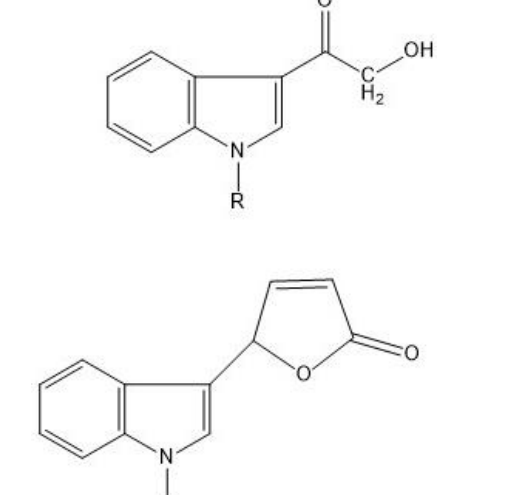
Substrates	Products	Ref
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		69
		70
		71

Table -3 Selected Examples of Reformatsky Reaction with Coumarins/uncommon electrophiles

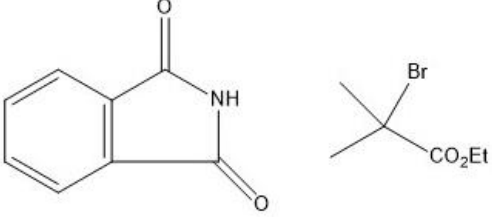
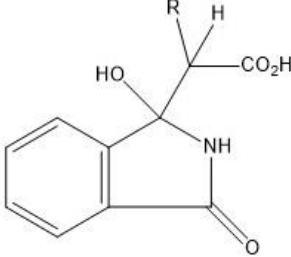
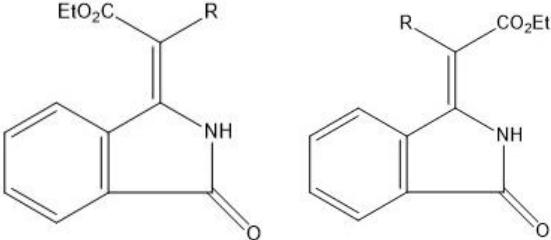
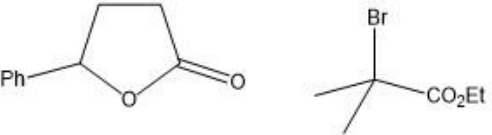
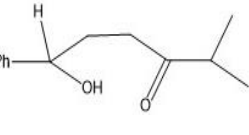
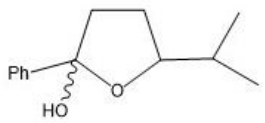
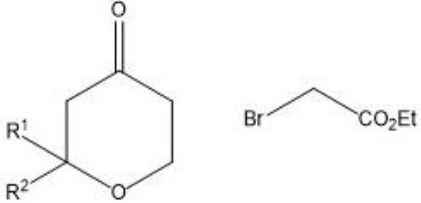
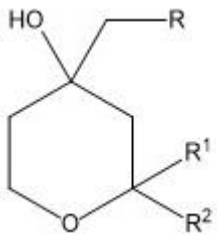
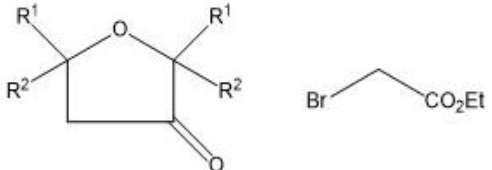
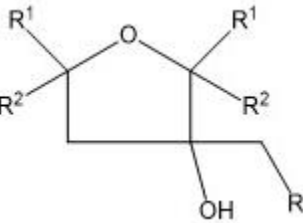
Substrates	Products	Ref
 <p>Indolin-3-one reacts with ethyl 2-bromo-2-methylpropanoate to form a 2-(2-hydroxy-2-methylpropanoate)-1H-indolin-3-one derivative.</p>	 	77
 <p>2-Phenyl-1,3-dioxolane-5-one reacts with ethyl 2-bromo-2-methylpropanoate to form 2-(2-hydroxy-2-methylpropanoate)-2-phenyl-1,3-dioxolane-5-one and its diastereomer.</p>	 	72
 <p>A substituted 2,6-dioxane-1-one (with R¹ and R² groups) reacts with ethyl bromoacetate to form a 2-(2-hydroxyethyl)-2,6-dioxane-1-one derivative.</p>		73
 <p>A substituted 2,5-dioxolane-2-one (with R¹ and R² groups) reacts with ethyl bromoacetate to form a 2-(2-hydroxyethyl)-2,5-dioxolane-2-one derivative.</p>		73

Table -3 Selected Examples of Reformatsky Reaction with Coumarins/uncommon electrophiles

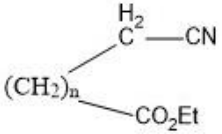
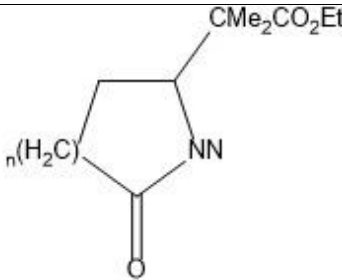
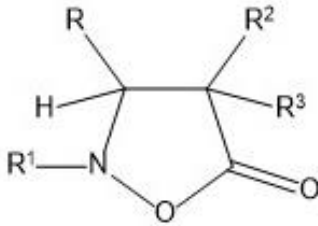
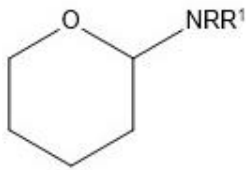
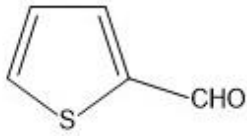
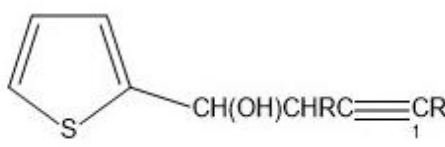
Substrates	Products	Ref
 <p style="text-align: center;">$RCH = N(O)R' \quad R^2CR^3BrCO_2R^4$</p>		74
	 <p style="text-align: center;"> $R = Me, R' = p-O\text{Me}-C_6H_4$ or, $R = Me, Et, CHMe_2, CHPh_2, R' = Ph$ $R^2 = R^3 = H, R^4 = Et, CMe$; $R^2 = R^3 = Me, R^4 = Et$ </p>	75
 <p style="text-align: center;">$BrCR^2R^3CN/Zn$</p>	<p style="text-align: center;">$OH-(CH_2)_4CH(NRR^1)CR^2R^3CN$</p> <p style="text-align: center;"> $R = Me, R' = p-O\text{Me}-C_6H_4$ or, $R = Me, Et, CHMe_2, CHPh_2, R' = Ph$ $R^2 = R^3 = H, R^4 = Et, CMe$; $R^2 = R^3 = Me, R^4 = Et$ </p>	75
 <p style="text-align: center;">$RCHBrC = CR^1$</p>	 <p style="text-align: center;"> $R = Me, R' = p-O\text{Me}-C_6H_4$ or, $R = Me, Et, CHMe_2, CHPh_2, R' = Ph$ </p>	75

Table -4 Selected Examples of Grignard Reaction with Coumarins

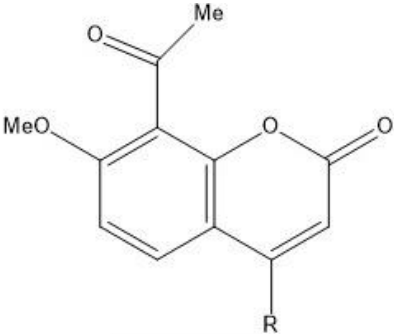
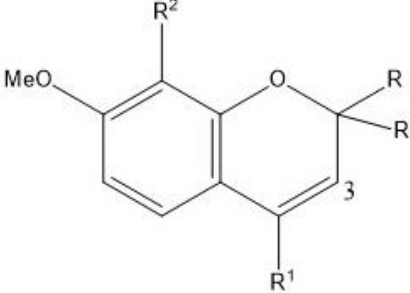
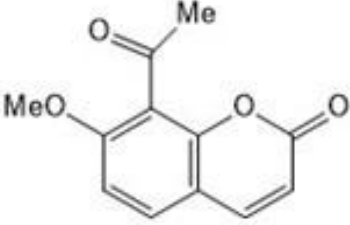
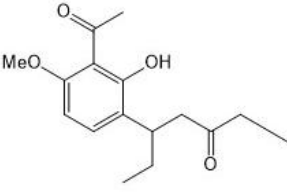
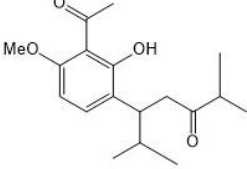
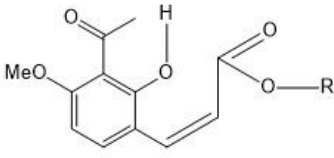
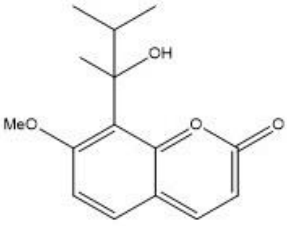
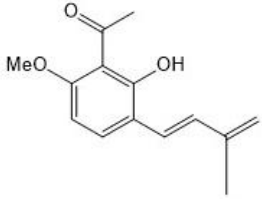
Substrates	Products	Ref
 <div style="border: 1px solid black; padding: 5px; margin-top: 10px;"> <p>RMgX R= Me, Et, Me₂CH₂, Ph, P-anisyl</p> </div>	 <div style="border: 1px solid black; padding: 10px; margin-top: 10px;"> <p>R= Ph, R¹= H₁ R₂= MeC¹/(OH)Ph R= P-Anisyl, R¹ H R₂=MeC(OH)Anisyl-P R,R₁= Me, R₂=MeC¹=C²/(H₂) R=Et, R¹=Me, R²=MeC¹/(OH)Et R=Prⁱ, R¹= Me, R²=MeC¹, C²/Me₂ R=(CH₂)₂Ph, R¹= Me R²= MeC¹/(OH)(CH₂)₂Ph R= Ph, R¹= Me, R²= MeC(OH)Ph R=P-Anisyl, R¹= Me R₂=P-AnisylC¹=C²/H₂</p> </div>	<p>101, 102</p>
	    	<p>101</p>

Table -4 Selected Examples of Grignard Reaction with Coumarins

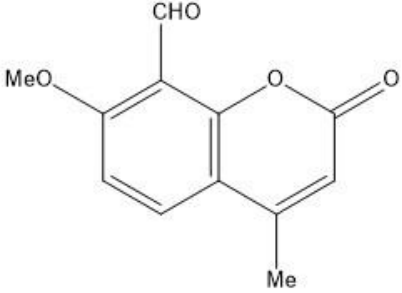
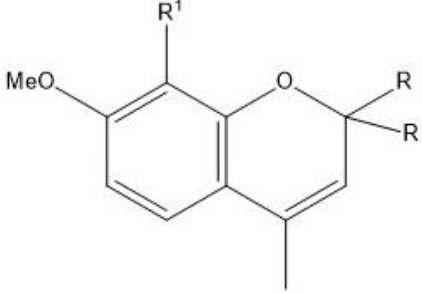
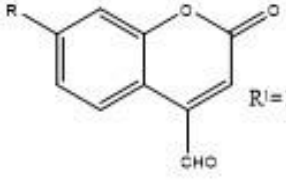
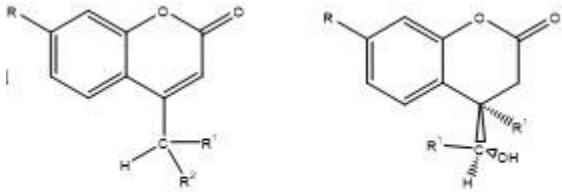
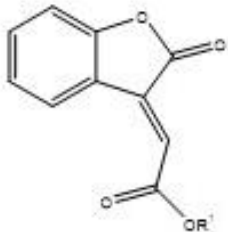
Substrates	Products	Ref
 <p> RMgX $\text{R} = \text{Me, Et, i-Pr, Ph, p-Anisyl}$ </p>	 <p> $\text{R} = \text{Me, R}^1 = \text{Me}=\text{CH}_2$ $\text{R} = \text{Et, R}^1 = \text{MeC}(\text{OH})\text{Et}$ $\text{R} = \text{CHMe}_2, \text{R}^1 = \text{Me}=\text{C}(\text{Me})_2$ $\text{R} = \text{Ph, R}^1 = \text{MeC}(\text{OH})\text{Ph}$ $\text{R} = \text{p-Anisyl, R}^1 = \text{p-Anisyl C}=\text{CH}_3$ $\text{R} = \text{Me, R}^1 = \text{CH}(\text{OH})\text{Me}$ $\text{R} = \text{Et, R}^1 = \text{CH}(\text{OH})\text{Et}$ $\text{R} = \text{CHMe}_2, \text{R}^1 = \text{CH}(\text{OH})\text{CMe}_2$ $\text{R} = \text{Ph, R}^1 = \text{CH}(\text{OH})\text{CPh}_2$ $\text{R} = \text{p-Anisyl, R}^1 = \text{CH}(\text{OH})\text{C p-Anisyl}$ </p>	102
 <p> $\text{R}^1\text{-MgX}$ $\text{R}^1 = \text{Ph, Et, Pr, Bu, p-Anisyl}$ </p> <p> $\text{R} = \text{H}$ $\text{R} = \text{OMe}$ </p>	 <p> $\text{R}, \text{R}^1 = \text{H, R}^2 = \text{OH}$ $\text{R} = \text{OMe, R}^1 = \text{H, R}^2 = \text{OH}$ $\text{R} = \text{H, R}^1 = \text{Ph, R}^2 = \text{OAc}$ $\text{R} = \text{OMe, R}^1 = \text{Ph, R}^2 = \text{OH}$ $\text{R} = \text{H, R}^1 = \text{p-Anisyl, R}^2 = \text{OAc}$ $\text{R} = \text{OMe, R}^1 = \text{p-Anisyl, R}^2 = \text{OH}$ $\text{R} = \text{H, R}^1 = \text{Et, R}^2 = \text{OH}$ $\text{R} = \text{OMe, R}^1 = \text{Et, R}^2 = \text{OH}$ $\text{R} = \text{OMe, R}^1 = \text{Pr, R}^2 = \text{OH}$ $\text{R} = \text{OMe, R}^1 = \text{Pr, R}^2 = \text{OAc}$ </p> <p> Z $\text{R} = \text{H, R}^1, \text{R}^2 = \text{CHCHMe}_2$ $\text{R} = \text{OMe, R}^1 = \text{Bu, R}^2 = \text{OH}$ </p>  <p> $\text{R} = \text{H, R}^1 = \text{Pr}$ $\text{R} = \text{OMe, R}^1 = \text{Pr}$ </p>	126

Table -4 Selected Examples of Grignard Reaction with Coumarins

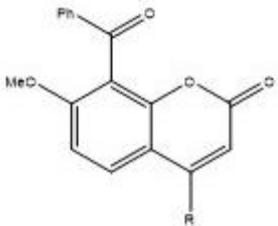
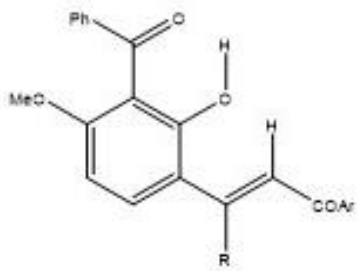
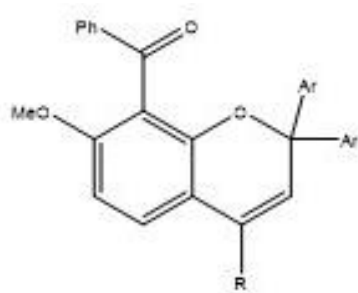
Substrates	Products	Ref
 <p style="text-align: center;">R=H R=Me</p> <p style="text-align: center;">ArMgBr</p>	 <p style="text-align: center;">Ar=Ph, R=H Ar= p-OMeC₆H₄, R=H</p>  <p style="text-align: center;">R=H, Ar= Ph R=Me, Ar=Ph R=Me, Ar= p-OMeC₆H₄</p>	<p>126</p>

Table -4 Selected Examples of Grignard Reaction with Coumarins

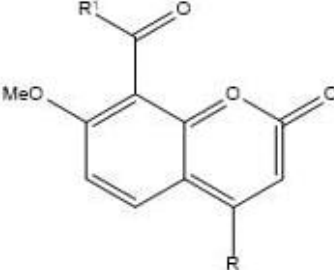
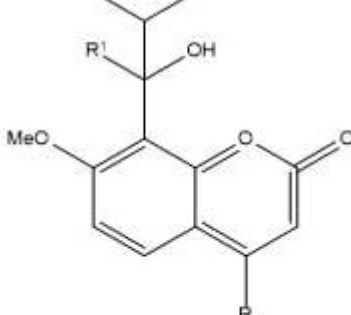
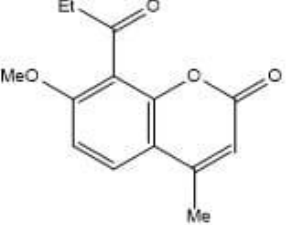
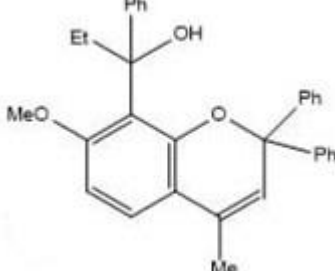
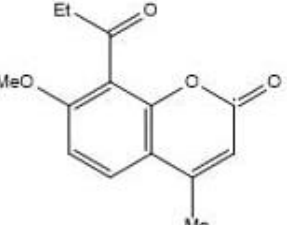
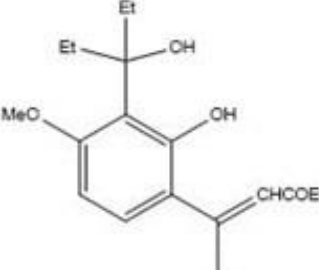
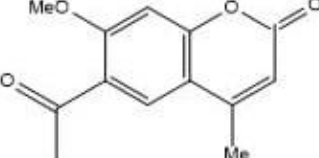
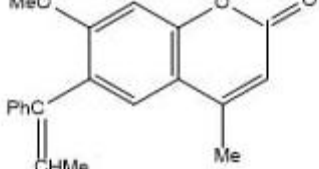
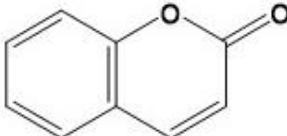
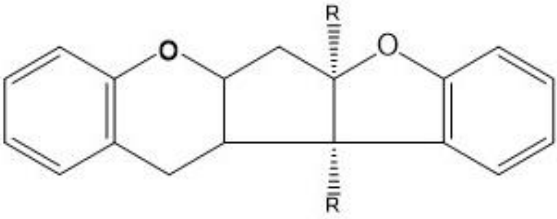
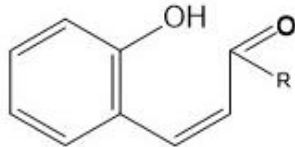
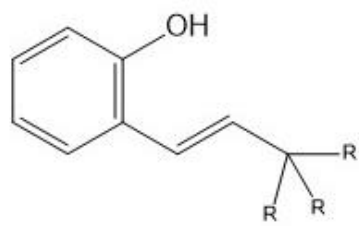
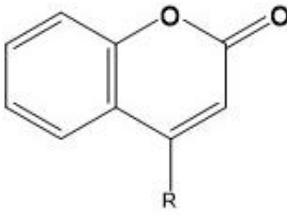
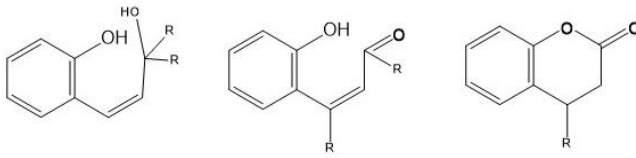
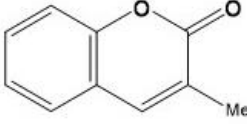
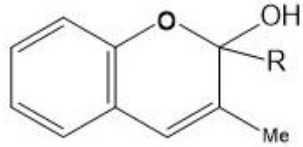
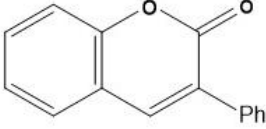
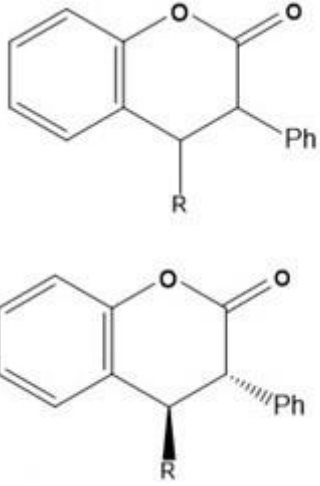
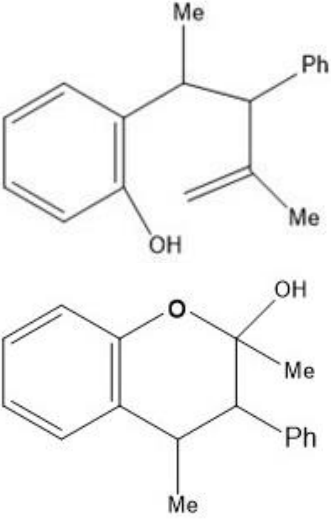
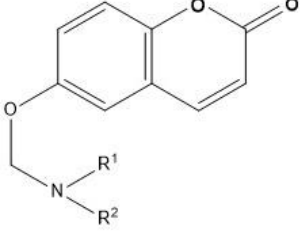
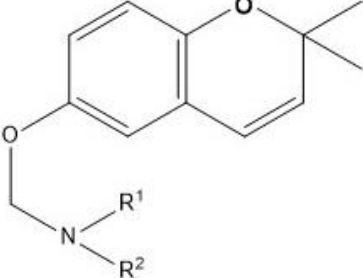
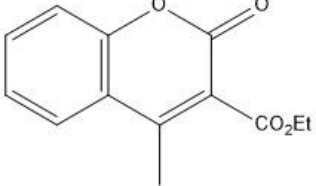
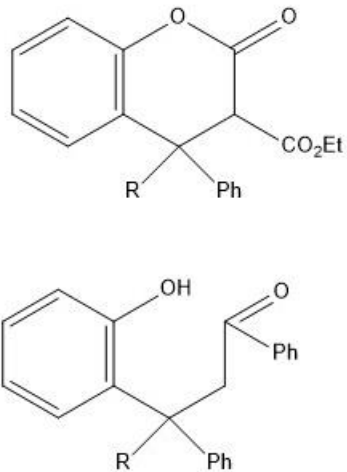
Substrates	Products	Ref
 <p style="text-align: center;"> $\text{R}^1-\text{C}(=\text{O})$ MeO R </p> <p> $\text{R}=\text{H}, \text{R}^1=\text{Me}$ $\text{R}=\text{Me}, \text{R}^1=\text{Me}$ $\text{R}=\text{H}, \text{R}^1=\text{Ph}$ $\text{R}=\text{Me}, \text{R}^1=\text{Ph}$ </p>	 <p style="text-align: center;"> R^1 OH MeO R </p> <p> $\text{R}=\text{H}, \text{R}^1=\text{Me}$ $\text{R}=\text{Me}, \text{R}^1=\text{Me}$ $\text{R}=\text{H}, \text{R}^1=\text{Ph}$ $\text{R}=\text{Me}, \text{R}^1=\text{Ph}$ </p>	127
 <p style="text-align: center;"> Et MeO Me </p> <p style="text-align: center;">PhMgBr</p>	 <p style="text-align: center;"> Ph Et OH MeO Ph Ph Me </p>	127
 <p style="text-align: center;"> Et MeO Me </p> <p style="text-align: center;">EtMgBr</p>	 <p style="text-align: center;"> Et Et OH MeO OH CHCOEt Me </p>	127
 <p style="text-align: center;"> MeO Me </p> <p style="text-align: center;">PhMgBr</p>	 <p style="text-align: center;"> MeO PhC CHMe Me </p>	127

Table-5 Selected Examples of Grignard Reaction with Coumarins

Substrates	Products	Ref
 <p>RMgX (R=Me, Ph)</p> <p>RMgX (R=Ph, CHMe₂)</p> <p>RMgX (R=Me, Pr, Ph, allyl)</p> <p>RMgX (R=PhCl₂CH₂, i-Pr)</p> <p>RMgX</p>	    	<p>103, 104</p> <p>105</p> <p>105</p> <p>105</p> <p>106, 107</p>
 <p>RMgX (R=Ph, p-Anisyl, naphthyl)</p>		<p>108, 109</p>

 <p>RMgX R=Et, Me₂CH, Me₃C</p>		109
<p>RMgX R=Me</p>		110
 <p>RMgX R=1-bromo naphthalene</p>		111
 <p>PhMgX</p>		112

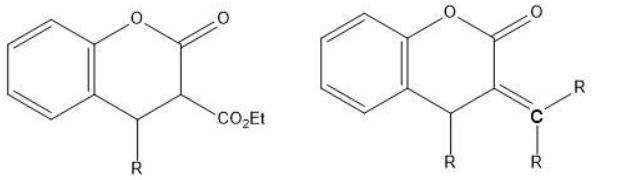
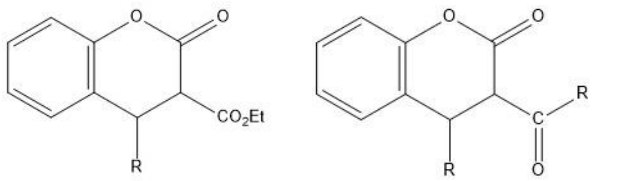
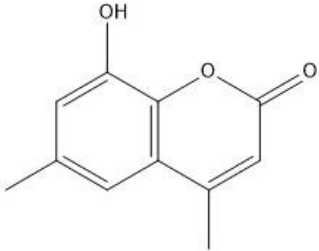
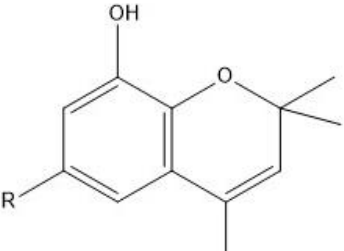
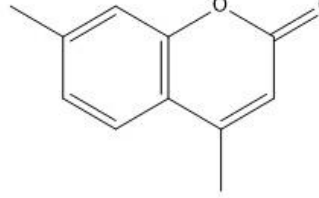
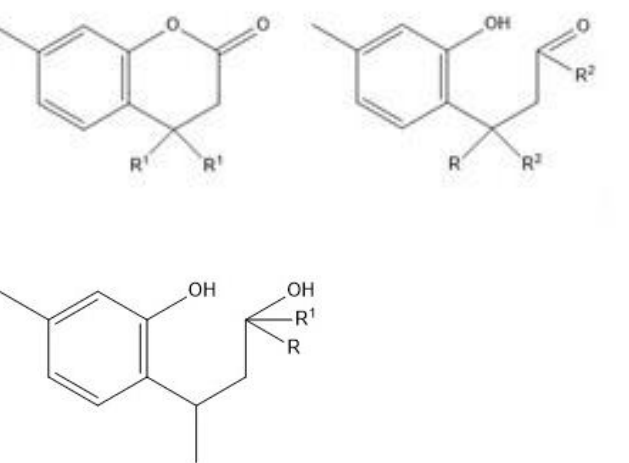
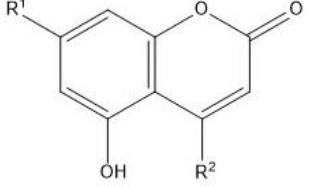
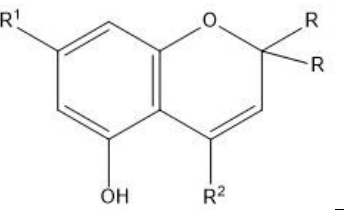
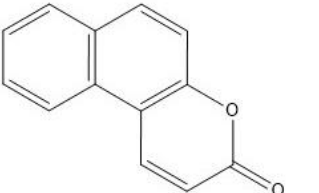
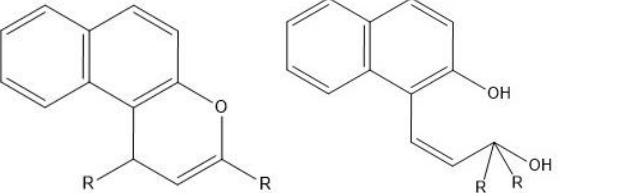
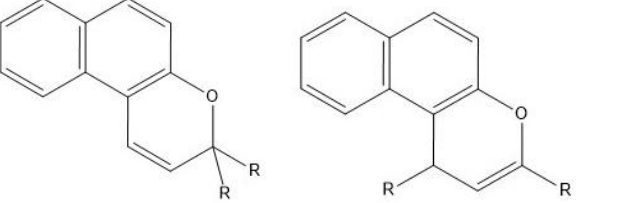
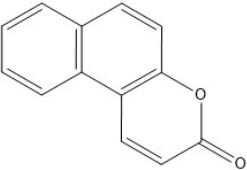
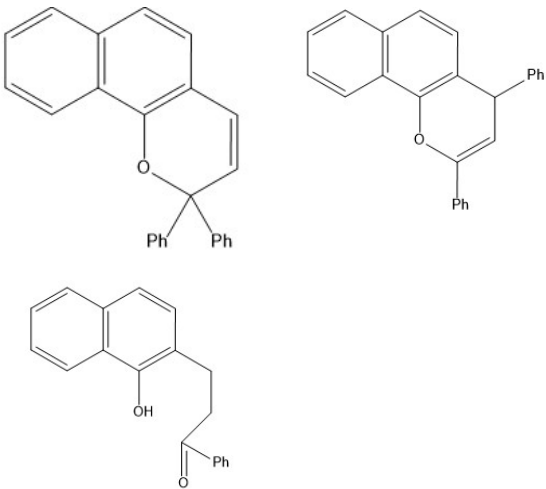
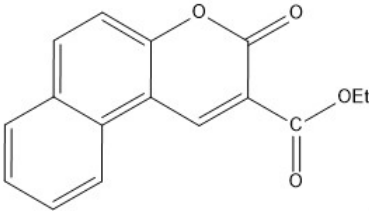
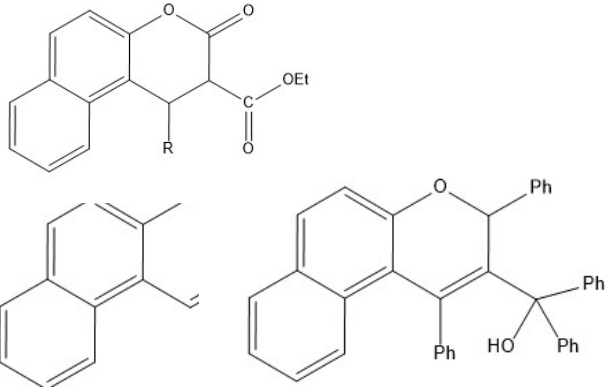
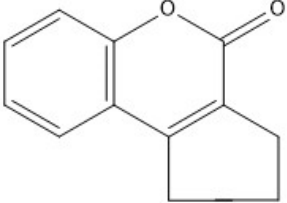
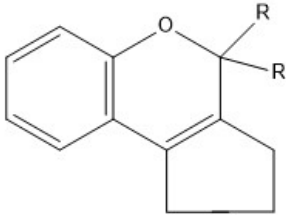
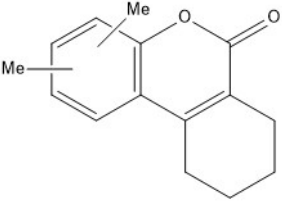
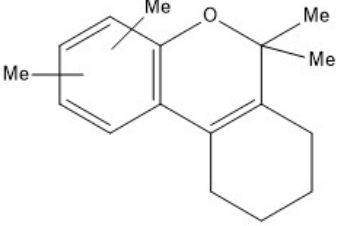
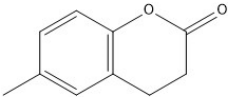
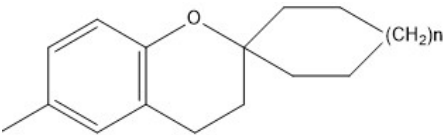
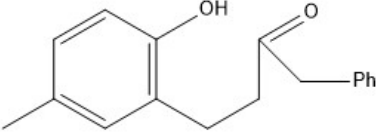
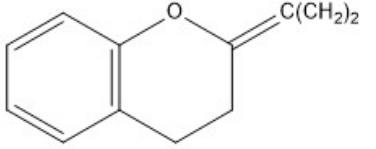
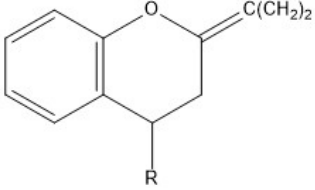
<p>RMgX R=p-anisyl</p>		113
<p>RMgX (R=Me,C)</p>		114
 <p>RMgX R=Me</p>		115
 <p>R¹MgX R¹= Et, Me2CH, Cyclohexyl</p>		115
 <p>RMgX R= Me,Ph</p>		115
 <p>RMgX R=o,m-anisyl</p>		116
<p>RMgX R=p-anisyl</p>		117

Table-5 Selected Examples of Grignard Reaction with Coumarins

Substrates	Products	Ref
 <p>PhMgX X=Br</p>		118, 119
 <p>RMgX RMgX R=Ph, i-pr R=Ph</p>		120
 <p>RMgX R=Me</p>		121
 <p>RMgX R=Me</p>		122

 <p> $\text{BrCH}_2(\text{CH}_2)_n\text{CH}_2\text{CH}_2\text{MgBr}$ $n=1,2$ PhCH_2MgBr </p>	 <p>123</p>  <p>124</p>	<p>123</p> <p>124</p>
 <p> RMgX $\text{R}=\text{Me,Et,Ph,Me}_2\text{CH}$ </p>		<p>125</p>