Synthesis, spectral studies, pharmacological and insect antifeedant activities of some (*E*)-1-(2-(2-benzyloxy-3-methacrylate))-1-naphthyl enones

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ABSTRACT. Totally twelve title compounds have been synthesized by Claisen-Schmidt condensation of (*E*)-methyl 2-(2-(((1-acetylnaphthalen-2-yl)oxy)methyl)phenyl)-3-methoxy acrylate and substituted benzaldehydes in presence of catalytic quantity of LiOH.H₂O catalyst under stirring in room temperature. The yields of the compounds are more than 92%. The synthesized titled compounds were characterized by their physical constants, IR, NMR and Mass spectral data. The spectral data such as infrared ν CO_{*s-cis*}, *s-trans*, CO_{ester}, NMR chemical shifts (δ , ppm) of H _{α} , H _{β} , C _{α} , C _{β} , CO of enone moiety, H _{β'} and CO of acrylate moieties have been correlated with Hammett substituent constants, F and R parameters. The antimicrobial, antioxidant and insect antifeedant activities of all synthesized compounds have been evaluated using corresponding bacterial and fungal strains, DPPH radical scavenging and Disc diffusion bio-assay of 4th instar larvae *Achoea Janata L* with castor-leaf discs.

1. INTRODUCTION

Currently, chemists and organic synthetic researcher have paid much more attention for green solvent assisted and ground chemistry synthesis[1-6]. These synthetic methodology have merits over than conventional methods such as easy work-up procedure, handling technique, non-hazardousness, environmental pollution free from atmosphere, shorter reaction time and better yields[7]. Aryl enones and methacrylates possess many biological activities such as antimicrobial[8,9], acute toxicity[10], haemo toxicity[11], in-vivo toxicity[12], genotoxicity[13], antioxidant[14], anticancer[15], antiviral[16], site-specific peroral delivery[17] anti-inflammatory/analgesic[18], anti plasmodial[19], anti-tuberculosis[20] and insect antifeedant[21, 22] activities due to presence of carbonyl and vinyl segments present in their structural moieties. Various catalysts were used for synthesis of enones by conventional heating methods[4, 23, 24, 25]. Spectroscopic data have been utilized for prediction of ground state equilibration of organic molecules such as styrenes, *E s-cis* and *s-trans* styryl ketones, unsaturated acids and their derivatives, gauche- and anti- form of ω -halo acyl and its esters[26, 27]. Infrared spectroscopy is one of the tool for studying structural elucidation, qualitative and quantitative analysis. NMR spectroscopy is useful for prediction of spatial arrangement of protons such as *cis*- and *trans*- refer with coupling constants and their interactions[28]. Spectroscopic data is used for studying structure-activity relationships of organic substrates through Hammett equation. Recently John Joseph et. al., have synthesized and studied the spectral correlation and antimicrobial activities of some methoxy substituted phenyl chalcones^[29]. Thirunarayanan and his co-workers have studied the spectral correlation and pharmacological evaluation of chalcones, ¹H pyrazolines, N-acetyl-¹H-Pyrazolines, aryl acyl bromides and aryl ω -halo esters[27, 30, 31]. Sundararajan et al., have studied the solvent-free synthesis, spectral QSAR study antimicrobial and insect antifeedant activities of poly halo

substituted phenyl chalcones [32]. Within the above view, there is no report available for the synthesis, spectral studies and biological evaluation of (*E*)-2-benzyloxy-(3-methoxy acrylate)-1-naphthyl enones. Therefore the author have taken effort to synthesis and studied the spectral and biological evaluation such as antimicrobial, antioxidant and insect antifeedant activities of the title compound.

2.EXPERIMENTAL

2.1. General

All chemicals used in the present investigation were procured from Sigma-Aldrich and E-Merck chemical company. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400cm⁻¹) were recorded on Thermo Nicolet iS5 Fourier transform spectrophotometer. The NMR spectra of synthesized compounds were recorded in BRUKER AV 400 NMR spectrometer operating at 400MHz was used for ¹H spectra and 100MHz for ¹³C spectra in CDCl₃ solvent using TMS as internal standard. Mass spectra were recorded on a SIMADZU GC-MS2010 Spectrometer using Electron Impact (EI) techniques.

2.2.Synthesis of 2-Benzyloxy-(3-methacrylate)-1-acetyl naphthalene

Equimolar quantities of 2-hydroxy-1-acetylnaphthalene (1mmol), 2-(3-methacrylate)-benzyl bromide 0.5 g of sodium hydroxide and 20 mL were vigorously stirred in magnetic stirrer at room temperature for 6h. The completion of reaction was monitored by TLC. After completion of the reaction, the reaction mixtures was treated with 20 mL of 0.2 N HCl and thoroughly washed with water, the obtained solid was filtered. The crude compound was crystallized with ethanol.

2.3.General procedure for synthesis of (*E*)-1-(2-(2-benzyloxy-(3-methoxyacrylate))-1-naphthyl enones

An appropriate equi molar mixture of 2-benzyloxy-(3-methacrylate)-1-acetyl naphthalene (2 mmol) in 5 mL of ethanol and LiOH.H₂O (8 mg, 0.2 mmol) were stirred in magnetic stirrer at room temperature. To this substituted benzaldehydes (2 mmol) were added and the stirring was continued for 35-40 mins. The completion of the reaction was monitored by TLC. After completion of the reaction, the ethanol was removed by reduced pressure distillation. The residue obtained was treated with 10 mL of water, neutralized with diluted HCl (15 mL, 2%) and extracted with 20 mL of ethyl acetate. The collective extract was washed with 10 mL of brine solution and dried over on sodium sulphate. Evaporation of solvent gave the crude chalcones. It is further purified by column chromatogram using CH₂Cl₂:EtOAc (1:3) as eluents afforded more than 88% yield as pale yellow glittering solids. The physical constants and mass fragments (m/z) of the chalcones have been presented in Table 1.

Scheme 1. Synthesis of (*E*)-2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones

3. RESULTS AND DISCUSSION

3.1. Infrared spectral study

In the present investigation, the authors have studied the effect of substituents on the infrared carbonyl stretches (cm^{-1}) of keto- and ester- moiety of the synthesized (*E*)-2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones. The $\text{CO}_{s\text{-}cis}$ and $s\text{-}trans$ conformers are shown in Fig. 1. And the corresponding stretches of keto- and ester- moiety of the synthesized (*E*)-1-(2-(2-benzyloxy-(3-methoxyacrylate))-1-naphthyl enones were presented in Table 2. These stretches were correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis[2, 6,14,19, 24-32]. In the infrared spectral correlation, the Hammett equation is employed as in the form of

$$\nu = \rho\sigma + \nu_0 \quad (1)$$

where ν is the frequency for the members of the series; ρ is the reaction constant; σ is the substituent constant and ν_0 is the frequency for the parent member of the series.

Table 1. Physical constants, analytical and mass fragments of (*E*)-1-(2-(2-benzyloxy-(3-methoxyacrylate)))-1-naphthyl enones

Entry	X	M.F.	M.W.	Yield (%)	m.p. (°C)	Mass(m/z)
1	H	$\text{C}_{31}\text{H}_{26}\text{O}_5$	478	92	117-118	478 $[\text{M}^+]$, 347, 363, 279, 205, 131, 115, 77, 15
2	3-Br	$\text{C}_{31}\text{H}_{25}\text{BrO}_5$	557	90	102-103	557 $[\text{M}^+]$, 558 $[\text{M}^{2+}]$, 441, 351, 375, 205, 180, 115, 90, 79, 77, 15
3	4-Br	$\text{C}_{31}\text{H}_{25}\text{BrO}_5$	557	91	114-115	557 $[\text{M}^+]$, 558 $[\text{M}^{2+}]$, 388, 375, 335, 221, 180, 167, 79, 77
4	2-Cl	$\text{C}_{31}\text{H}_{25}\text{ClO}_5$	512	90	123-124	512 $[\text{M}^+]$, 514 $[\text{M}^{2+}]$, 453, 291, 375, 137, 77, 59, 35
5	3-Cl	$\text{C}_{31}\text{H}_{25}\text{ClO}_5$	512	90	136-137	512 $[\text{M}^+]$, 514 $[\text{M}^{2+}]$, 453, 321, 291, 221, 191, 126, 124, 77, 35
6	4-Cl	$\text{C}_{31}\text{H}_{25}\text{ClO}_5$	512	91	119-120	512 $[\text{M}^+]$, 514 $[\text{M}^{2+}]$, 401, 397, 307, 205, 115, 111, 77, 35
7	2-OH	$\text{C}_{31}\text{H}_{26}\text{O}_6$	494	92	98-99	494, 375, 347, 289, 205, 147, 119, 77, 17
8	4-OH	$\text{C}_{31}\text{H}_{26}\text{O}_6$	494	92	107-108	494, 388, 303, 273, 221, 191, 106, 77, 17
9	2-OCH ₃	$\text{C}_{32}\text{H}_{28}\text{O}_6$	508	93	124-125	508, 393, 375, 347, 287, 221, 161, 133, 115, 91, 77, 31, 15
10	4-CH ₃	$\text{C}_{32}\text{H}_{28}\text{O}_5$	492	93	115-116	492, 401, 347, 377, 145, 115, 91, 77, 15
11	2-NO ₂	$\text{C}_{31}\text{H}_{25}\text{NO}_7$	523	90	127-128	523, 388, 347, 302, 221, 176, 135, 77, 59
12	4-NO ₂	$\text{C}_{31}\text{H}_{25}\text{NO}_7$	523	90	134-135	523, 408, 375, 318, 205, 148, 115, 77, 59

Table 2. The infrared $\nu\text{CO}_{s\text{-}cis}$, $s\text{-}trans$, CO_{ester} , stretches (cm^{-1}), NMR chemical shifts (δ , ppm) of H_α , H_β , $\text{H}_{\beta'}$, C_α , C_β , CO_{ester} , $\text{C}_{\alpha'}$, $\text{C}_{\beta'}$, of (*E*)-1-(2-(2-benzyloxy-(3-methoxyacrylate))-1-naphthyl enones

Entry	X	IR			¹ H NMR			¹³ C NMR					
		$\text{CO}_{s\text{-}cis}$	$\text{CO}_{s\text{-}trans}$	CO_{ester}	H_α	H_β	$\text{H}_{\beta'}$	CO	C_α	C_β	CO_{ester}	$\text{C}_{\alpha'}$	$\text{C}_{\beta'}$
1	H	1673	1659	1603	7.386	7.916	8.314	189.13	123.57	139.62	164.81	114.74	149.38
2	3-Br	1676	1641	1610	7.324	7.924	8.004	189.97	123.56	139.74	164.25	117.46	149.72
3	4-Br	1674	1648	1605	7.431	7.859	8.101	190.32	124.16	141.36	162.35	115.45	151.63
4	2-Cl	1678	1634	1607	7.513	7.267	8.141	190.64	124.25	140.77	165.26	117.12	152.12
5	3-Cl	1680	1647	1603	7.501	7.358	8.091	189.71	124.23	138.74	164.59	112.81	153.72
6	4-Cl	1676	1643	1618	7.361	7.311	8.172	189.47	124.93	139.87	165.29	112.70	151.92
7	2-OH	1669	1635	1603	7.205	7.671	8.095	187.76	123.02	137.34	166.89	108.99	149.85
8	4-OH	1672	1640	1614	7.311	7.809	8.112	189.17	124.17	139.33	164.54	109.24	150.07
9	2-OCH ₃	1664	1638	1597	7.017	7.717	7.904	184.37	124.03	138.74	163.25	107.58	148.26
10	4-CH ₃	1666	1641	1604	7.321	7.964	8.119	183.46	124.01	139.66	163.58	108.36	148.58
11	2-NO ₂	1683	1658	1610	7.734	8.316	8.410	191.75	125.26	141.65	165.56	118.59	151.66
12	4-NO ₂	1686	1665	1621	7.774	8.567	8.560	191.96	125.69	142.01	165.95	118.85	151.92

Fig. 1. The *s-cis* and *s-trans* conformers of (*E*)-2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones

The results of statistical analysis are shown in Table 3. From the Table 3, The CO_{s-cis} stretches of enones correlated satisfactorily with Hammett substituent constants, F and R parameters. The $\text{CO}_{s-trans}$ stretches of enones correlated satisfactorily with Hammett σ , σ^+ , σ_L , constants and R parameters. The Hammett σ_R constant and F parameter were fail in correlation. The CO_{ester} stretches of enones correlated satisfactorily with Hammett substituent constants and F parameter. The R parameter was fail in correlation. All correlation gave positive ρ values. This implies that the normal substituent effect operates in all system. The degree of transmission of substituent effect on the νCO_{s-cis} conformer is higher than that of $\nu\text{CO}_{s-trans}$ conformers. The failure in correlation was due to the inability of predicting the effect of substituent on the carbonyl group and associated with the resonance-conjugative structure as shown in Fig. 2.

Fig. 2. The resonance-conjugative structure

Table 3. Results of statistical analysis of infrared $\nu\text{CO}_{s\text{-}cis}$, $s\text{-}trans$, CO_{ester} , stretches (cm^{-1}) of 1-(2-benzyloxy-(3-methoxyacrylate))-1-naphthyl enones with Hammett σ , σ^+ , σ_I , σ_R , constants, F and R parameters.

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
$\text{CO}_{s\text{-}cis}$	σ	0.924	1672.43	15.495	2.62	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.912	1673.72	10.260	3.82	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.907	1664.30	23.032	4.31	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.917	1678.47	18.834	4.02	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.905	1665.82	21.240	4.10	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.906	1678.69	16.146	4.22	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
$\text{CO}_{s\text{-}trans}$	σ	0.906	1643.21	17.015	7.84	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.905	1644.68	10.976	8.67	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.827	1641.11	12.637	9.07	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.918	1652.24	12.872	5.99	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.827	1640.38	13.339	9.10	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.907	1652.62	28.143	6.65	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
CO_{ester}	σ	0.953	1606.49	9.543	6.17	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.891	1607.49	4.233	6.92	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.915	1601.96	16.223	6.26	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.904	1610.48	13.005	6.46	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.925	1601.05	18.642	6.14	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.734	1609.99	8.525	6.86	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂

r=correlation coefficient; I= intercept; ρ =slope; s=number of correlated derivatives

The inability of some of the single parameter correlation to predict the substituent effects on the carbonyl stretches of the enones, they are worthful when seeking these in multi-correlation with σ_I and σ_R or F and R Swain-Lupton's[33] parameters. The generated multi-regression analysis equations are given in (2- 7).

$$\nu\text{CO}_{s\text{-}cis}(\text{cm}^{-1}) = 1670.83(\pm 2.031) + 17.993(\pm 4.085)\sigma_I + 13.606(\pm 3.626)\sigma_R \quad (2)$$

$(R = 0.992, n = 12, P > 95\%)$

$$\nu\text{CO}_{s\text{-}cis}(\text{cm}^{-1}) = 1670.57(\pm 2.286) + 19.672(\pm 4.699)F + 12.335(\pm 3.398)R \quad (3)$$

$(R = 0.990, n = 12, P > 95\%)$

$$\nu\text{CO}_{s\text{-}trans}(\text{cm}^{-1}) = 1652.01(\pm 4.521) + 5.530(\pm 0.091)\sigma_I + 32.718(\pm 8.066)\sigma_R \quad (4)$$

$(R = 0.982, n = 12, P > 95\%)$

$$\nu\text{CO}_{s\text{-trans}}(\text{cm}^{-1}) = 1651.30(\pm 5.076) + 3.144(\pm 1.014)F + 27.530(\pm 7.549)R \quad (5)$$

($R = 0.979$, $n = 12$, $P > 95\%$)

$$\nu\text{CO}_{ester}(\text{cm}^{-1}) = 1605.06(\pm 4.402) + 12.786(\pm 8.854) \sigma_I + 9.294(\pm 7.841) \sigma_R \quad (6)$$

($R = 0.960$, $n = 12$, $P > 95\%$)

$$\nu\text{CO}_{ester}(\text{cm}^{-1}) = 1603.06(\pm 4.7101) + 16.682(\pm 9.681) F + 5.294(\pm 2.701)R \quad (7)$$

($R = 0.958$, $n = 12$, $P > 95\%$)

3.2. NMR spectral study

3.2.1. ^1H NMR spectral study

In nuclear magnetic resonance spectra, the chemical shifts (δ)(ppm) of ^1H or the ^{13}C nuclei depend on the electronic environment of the nuclei concerned. These chemical shifts have been correlated with reactivity parameters. Thus the Hammett equation was used in the form as shown in (8).

$$\text{Log } \delta = \rho\sigma + \text{Log } \delta_0 \quad (8)$$

Where δ is the chemical shift of member of the series; ρ is the reaction constants; σ is the substituent constant and δ_0 is the chemical shift of the corresponding parent compound of the series. The assigned ^1H NMR chemical shifts (δ , ppm) of H_α , H_β of enone and $\text{H}_{\beta'}$ protons of enone and acrylate moieties of 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones are presented in Table 2. These chemical shifts (ppm) were correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis[2, 6,14,19, 24-32]. The results of statistical analyses are given in Table 4. From the Table 4, the correlation of δH_α chemical shifts (ppm) of the enones correlated satisfactorily with Hammett substituent constants, F and R parameters. The δH_β and $\delta\text{H}_{\beta'}$ chemical shifts (ppm) correlated satisfactorily with Hammett σ , σ^+ , σ_R constants and R parameters.

The Hammett σ_I constant and F parameters were fail in the correlations for δH_β and $\delta\text{H}_{\beta'}$ chemical shifts (ppm). The reflectance of substituent effect on the δH_α (ppm) is sensitive than δH_β and $\delta\text{H}_{\beta'}$ chemical shifts (ppm). All correlations gave positive ρ values. This shows that that normal substituent effect operates in all systems. The failure in correlation is due to the reason stated earlier and associated with the resonance-conjugative structure as shown in Fig. 2. Some of the single parameter correlations were fail for the δH_β and $\delta\text{H}_{\beta'}$ proton chemical shifts (ppm) with Hammett substituent constants, F and R

Table 4. Results of statistical analysis of ^1H NMR chemical shifts (δ , ppm) of H_α , H_β , $\text{H}_{\beta'}$ of 1-(2-benzyloxy-(3-methoxyacrylate))-1-naphthyl enones with Hammett σ , σ^+ , σ_I , σ_R , constants, F and R parameters.

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
H_α	σ	0.988	7.335	0.472	0.10	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.979	7.375	0.315	0.13	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.906	7.916	0.573	0.17	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.984	7.543	0.703	0.11	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.955	7.179	0.615	0.17	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.979	7.550	0.589	0.13	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
H_β	σ	0.900	7.745	0.407	0.37	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.902	7.786	0.199	0.39	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.816	7.703	0.286	0.40	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.905	7.975	0.855	0.33	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.824	7.635	0.464	0.39	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.904	7.960	0.630	0.36	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
$\text{H}_{\beta'}$	σ	0.967	8.122	0.309	0.13	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.954	8.150	0.180	0.15	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.833	8.770	0.275	0.17	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.977	8.278	0.558	0.11	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.803	8.054	0.317	0.17	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.907	8.281	0.464	0.12	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂

r=correlation coefficient; I= intercept; ρ =slope; s=number of correlated derivatives parameters.

While seeking they are worthful and produce satisfactory correlation in the multi-regression analysis with σ_I and σ_R or F and R parameters[33]. The generated multi-regression analysis equations are given in (9-14).

$$\delta\text{H}_\alpha(\text{ppm}) = 7.396(\pm 0.06) + 0.350(\pm 0.137)\sigma_I + 0.601(\pm 0.120)\sigma_R \quad (9)$$

($R = 0.991$, $n = 12$, $P > 95\%$)

$$\delta\text{H}_\alpha(\text{ppm}) = 7.372(\pm 0.428) + 0.428(\pm 0.194)F + 0.506(\pm 0.988)R \quad (10)$$

($R = 0.988$, $n = 12$, $P > 95\%$)

$$\delta\text{H}_\beta(\text{ppm}) = 7.992(\pm 0.256) - 0.038(\pm 0.005)\sigma_I + 0.867(\pm 0.245)\sigma_R \quad (11)$$

($R = 0.955$, $n = 12$, $P > 95\%$)

$$\delta\text{H}_\beta(\text{ppm}) = 7.857(\pm 0.283) + 0.024(\pm 0.052)F + 0.582(\pm 0.042)R \quad (12)$$

($R = 0.947$, $n = 12$, $P > 90\%$)

$$\delta\text{H}_{\beta'}(\text{ppm}) = 8.248(\pm 0.088) + 0.070(\pm 0.011)\sigma_I + 0.535(\pm 0.157)\sigma_R \quad (13)$$

($R = 0.978$, $n = 12$, $P > 95\%$)

$$\delta\text{H}_{\beta'}(\text{ppm}) = 8.216(\pm 0.095) + 0.157(\pm 0.202)F + 0.433(\pm 0.146)R \quad (14)$$

($R = 0.974$, $n = 12$, $P > 95\%$)

3.2.2. ^{13}C NMR spectral study

The assigned chemical shifts of δCO , C_α , C_β , CO_{ester} , $C_{\alpha'}$, $C_{\beta'}$ (ppm) of (*E*)-2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones have been assigned and tabulated in Table 2. These chemical shifts were correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis[2, 6, 14, 19, 24-32]. The results of statistical analyses are presented in Table 5. From the Table 5, the chemical shifts of δCO , C_α , C_β of enone moieties are satisfactorily correlated with Hammett substituent constants, F and R parameters. The chemical shifts (ppm) of $\delta\text{CO}_{\text{ester}}$ is correlated satisfactorily with Hammett σ and σ^+ constants. The correlation of the chemical shifts (ppm) of $\delta C_{\alpha'}$ is satisfactory with Hammett substituent constants, F and R parameters. The correlation of the chemical shifts (ppm) of $\delta C_{\beta'}$ is satisfactory with Hammett σ , σ^+ , σ_I constants and F parameters. The remaining Hammett sigma constants, F and R parameters were fail in correlation for the $\delta\text{CO}_{\text{ester}}$ and $\delta C_{\beta'}$ chemical shifts (ppm). All correlations gave positive ρ values. This implies that the normal substituent effect operates in all systems. The failure in the correlation is due to the reasons stated earlier and associated with the resonance-conjugative structure as shown in Fig. 2.

Some of the single parameter correlations were fail for the δC_β and $\delta C_{\beta'}$ carbon chemical shifts (ppm) with Hammett substituent constants, F and R parameters. While seeking they are worthful and produce satisfactory correlation in the multi-regression analysis[33] with σ_I and σ_R or F and R parameters. The generated multi-regression analysis equations for the $\delta\text{CO}_{\text{ester}}$, δC_β and $\delta C_{\beta'}$ carbons are given in (15-26).

$$\delta\text{CO}(\text{ppm}) = 186.86(\pm 1.228) + 7.608(\pm 2.471)\sigma_I + 3.417(\pm 2.198)\sigma_R \quad (15)$$

($R = 0.980$, $n = 12$, $P > 95\%$)

$$\delta\text{CO}(\text{ppm}) = 186.59(\pm 1.346) + 8.380(\pm 2.766)F + 2.884(\pm 0.200)R \quad (16)$$

($R = 0.978$, $n = 12$, $P > 95\%$)

$$\delta C_\alpha(\text{ppm}) = 123.88(\pm 0.368) + 1.171(\pm 0.721)\sigma_I + 1.388(\pm 0.064)\sigma_R \quad (17)$$

($R = 0.979$, $n = 12$, $P > 95\%$)

Table 5. Results of statistical analysis of ^{13}C NMR chemical shifts (δ , ppm) of CO, C_α , C_β of enone moiety, CO, $C_{\alpha'}$, $C_{\beta'}$ ester moiety of 1-(2-benzyloxy-(3-methoxyacrylate))-1-naphthyl enones with Hammett σ , σ^+ , σ_I , σ_R , constants, F and R parameters.

Freq.	Constt.	r	I	ρ	s	n	Correlated derivatives
CO	σ	0.977	188.20	5.194	1.75	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.969	188.63	3.469	1.98	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.974	185.72	8.873	1.83	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.905	190.08	5.623	2.33	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.971	185.45	9.443	1.88	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.843	190.07	4.508	2.41	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
C_α	σ	0.967	124.04	1.298	0.57	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.954	124.16	0.774	0.65	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.960	123.42	2.223	0.58	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.963	124.61	1.880	0.60	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.960	123.37	2.340	0.60	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.961	124.63	1.632	0.61	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂

C_β	σ	0.972	139.52	2.508	0.97	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.970	139.72	1.810	1.00	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.905	138.63	3.453	1.17	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.978	140.75	4.271	0.87	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.915	138.68	3.476	1.21	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.971	140.78	3.616	0.93	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
CO_{ester}	σ	0.903	164.56	0.856	1.25	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.900	164.65	0.365	1.28	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.812	164.24	1.222	2.26	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.705	164.74	0.269	2.29	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.729	164.03	0.800	1.20	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.803	164.76	0.280	1.29	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
$C_{\alpha'}$	σ	0.989	112.07	9.499	1.95	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.900	11.78	7.088	1.89	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.903	108.85	12.631	3.21	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.907	116.00	12.721	2.79	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.961	108.31	12.610	2.07	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.907	116.26	11.381	2.78	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
$C_{\beta'}$	σ	0.961	150.30	2.873	1.27	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ^+	0.965	150.53	2.063	1.30	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_I	0.617	148.81	5.741	1.23	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	σ_R	0.839	151.24	2.586	1.59	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	F	0.964	148.71	5.236	1.32	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂
	R	0.843	151.34	2.364	1.59	12	H, 3-Br, 4-Br, 2-Cl, 3-Cl, 4-Cl, 2-OH, 4-OH, 2-OCH ₃ , 4-CH ₃ , 2-NO ₂ , 3-NO ₂

r=correlation coefficient; I= intercept; ρ=slope; s=number of correlated derivatives

$$\delta C_\alpha(\text{ppm}) = 123.85(\pm 0.381) + 1.876(\pm 0.731)F + 1.278(\pm 0.563)R \quad (18)$$

$(R = 0.978, n = 12, P > 95\%)$

$$\delta C_\beta(\text{ppm}) = 139.85(\pm 0.559) + 2.099(\pm 1.124)\sigma_I + 3.660(\pm 0.992)\sigma_R \quad (19)$$

$(R = 0.985, n = 12, P > 95\%)$

$$\delta C_\beta(\text{ppm}) = 139.82(\pm 0.640) + 2.305(\pm 1.317)F + 3.169(\pm 0.952)R \quad (20)$$

$(R = 0.982, n = 12, P > 95\%)$

$$\delta CO_{ester}(\text{ppm}) = 164.21(\pm 0.957) + 1.206(\pm 0.192)\sigma_I + 0.097(\pm 0.001)\sigma_R \quad (21)$$

$(R = 0.921, n = 12, P > 90\%)$

$$\delta\text{CO}_{\text{ester}} (\text{ppm}) = 164.00(\pm 0.981) + 1.827(\pm 0.021)F + 0.073(\pm 0.001)R \quad (22)$$

$$(R = 0.988, n = 12, P > 95\%)$$

$$\delta\text{C}_{\alpha'} (\text{ppm}) = 112.240(\pm 1.150) + 8.876(\pm 3.058)\sigma_I + 110.149(\pm 2.705)\sigma_R \quad (23)$$

$$(R = 0.988, n = 12, P > 95\%)$$

$$\delta\text{C}_{\alpha} (\text{ppm}) = 112.507(\pm 1.640) + 9.508(\pm 3.371)F + 9.628(\pm 2.438)R \quad (24)$$

$$(R = 0.987, n = 12, P > 95\%)$$

$$\delta\text{C}_{\beta'} (\text{ppm}) = 149.20(\pm 0.906) + 4.807(\pm 1.823)\sigma_I + 1.190 (\pm 0.161)\sigma_R \quad (25)$$

$$(R = 0.972, n = 12, P > 95\%)$$

$$\delta\text{C}_{\beta} (\text{ppm}) = 149.33(\pm 0.994) + 4.751(\pm 2.042)F + 1.44 (\pm 0.147)R \quad (26)$$

$$(R = 0.968, n = 12, P > 95\%)$$

3.3. Antimicrobial activities

3.3.1. Antibacterial sensitivity assay

Antibacterial activity assay of prepared 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones were performed using Kirby-Bauer[34] disc diffusion technique. In every petri plate, about 0.5 mL of the test bacterial sample was spread over uniformly on the solidified Mueller Hinton agar using sterile glass spreader. Then the discs were made with 5mm of Whatmann No.1 filter paper, impregnated with the solution of the compounds placed on the medium using sterile forceps. Incubated the plates for 24 h at 37°C by keeping the plates upside down to prevent the collection of water droplets over the medium. After 24 h, the plates were visually examined and the diameter values of the zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure. The measured antibacterial activities of all oxazine are presented in Table 6.

The antibacterial activity assay of all prepared enones were studied against two gram positive pathogenic strains *Staphylococcus aureus*, *Enterococcus faecalis* and four gram negative strains *Escherichia coli*, *Klebsiella species*, *Pseudomonas* and *Proteus vulgaris*. The disc diffusion technique was followed using the Kirby-Bauer[]method, at a concentration of 250 µg/mL with Ampicillin and Streptomycin were used as standard drugs. Compounds **4**, **6** and **9** showed maximum zone of inhibition against *B. subtilis*, with greater than 20 mm compared to the ketones **1-3**, **5** and **10** are moderately active in 13-19 mm of zone of inhibition. Enone **9** was active with in 8-12 mm of zone of inhibition and the compounds **7** and **8** are inactive. The enones **1** and **6** were found to be effective against *S. aureus* within 20-24 mm of zone of inhibition.

Table 6. Antibacterial activities of 1-(2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones.

Entry	X	<i>B.subtilis</i>	<i>M.luteus</i>	<i>S.aures</i>	<i>E-coli</i>	<i>P.aeruginosa</i>	<i>K.pneumoniae</i>
1	H	+	+	++	+	++	+
2	3-Br	+	---	+	---	+	---
3	4-Br	+	+	---	+	+	+
4	2-Cl	++	+	+	+	---	+
5	3-Cl	+	---	+	++	++	++
6	4-Cl	++	±	++	±	+	+
7	2-OH	---	+	+	+	+	+
8	4-OH	---	++	+	±	+	±
9	2-OCH ₃	±	+	+	---	±	±
10	4-CH ₃	+	+	±	--	++	±
11	2-NO ₂	---	++	+	++	---	++
12	4-NO ₂	++	±	---	---	+	+

Compounds **1-4**, **7**, **9** and **10** were moderately active within 13-19 mm of zone of inhibition. The enones **8** and **12** were active within 8-12 mm of zone of inhibition. The chalcone derivatives **1**, **5** and **10** were more active against *Pseudomonas* a showing greater than 20 mm zone of inhibition and the other derivatives **2**, **3**, **6**, **7** and **12** showed the zone of inhibitions between 13-19 mm. Compound **9** was moderately active within 8-12 mm of zone of inhibition. The ketones **5** and **11** are

effective against *Klebsiella* with 20-24 mm zone of inhibition while the other compounds **1-4, 6, 7, 12** and 8-10 were showed a moderate activity within 13-19 and 8-12 mm of zone of inhibitions. The compounds **8** and **11** were active when it is screened against *M. luteus* at 20-24mm of zone of inhibition. Enones **1, 3, 4, 7, 8** and **10** were active at 13-19 mm of zone of inhibition. The ketones **8** and **12** have shown 8-12mm zone of inhibition. The enones **5** and **11** are active against *Escherichia coli* at 20-24mm of zone of inhibition. The other compounds **1-4, 7, 6** and **8** are moderately effective within 13-19 and 8-12 mm of zone of inhibitions.

3.3.2. Antifungal sensitivity assay

Antifungal sensitivity assay of synthesized enones were performed using Kirby-Bauer^[34] disc diffusion technique. The PDA medium was prepared and sterilized as above. This is poured (ear bearing heating condition) to the Petri-plate which was already filled with 1 mL of the fungal species. The plate was rotated clockwise and counter clock-wise for uniform spreading of the species. The discs were impregnated with the test solution. The test solution was prepared by dissolving 15 mg of the oxazine in 1 mL of DMSO solvent. The medium was allowed to solidify and kept for 24 h. Then the plates were visually examined and the diameter values of zone of inhibition were measured. Triplicate results were recorded by repeating the same procedure. The observed antifungal activities of all oxazine amines are presented in Table 7.

The study of antifungal activities of all 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones has been done with *Aspergillus niger*, *M.spp* and *T. viridi* fungal stains and the dilution method was adopted. The drug dilution was kept as 50 µg/mL. *Griseofulvin* has been taken as the standard drug.

Table 7. Antifungal activities 1-(2-benzyloxy-(3-methoxy acrylate)-1-naphthyl enones

Entry	X	<i>A.niger</i>	<i>M.spp</i>	<i>T. viridi</i>
1	H	±	+	---
2	3-Br	---	±	+
3	4-Br	±	+	+
4	2-Cl	+	±	+
5	3-Cl	---	+	++
6	4-Cl	+	++	+
7	2-OH	+	---	---
8	4-OH	++	---	++
9	4-OCH ₃	+	+	---
10	4-CH ₃	---	++	+
11	2-NO ₂	+	±	++
12	4-NO ₂	++	++	+

Standard: Griseofulvin and Gentamycin; Duration: 72 h; Control: Methanol; Medium: Potato dextrose agar; ++: No fungal colony; +: One fungal colony; ±: Two-three fungal colonies; ---: Heavy fungal colony.

The study of antifungal activities of all 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones against *A. niger* showed that the two compounds **8** and **12** are effective with 20 mm as the zone of inhibition in 250 µg/L disc while ketones **4, 6, 7, 9** and **11** are active with 13-19 mm zone of inhibition and the compound **1** and **3** was the least active with 8-12 mm zone of inhibitions. Compounds **6, 10** and **12** are visible against *M. spp.* species within 20mm zone of inhibitions and the development of the fungal colony (2-3 colonies) are recorded for the compounds **2, 4** and **11**. The inhibition of compounds **5, 8** and **11** against *T. viridi* were highly active and the enones **2-4, 6, 10** and **11** are active within 8-12 mm of zone of inhibition. Presence of halogens, methoxy, methyl and nitro substituents are responsible for antimicrobial activities of synthesized enones.

3.4. Antioxidant activity

The antioxidant activities of all synthesized enones have been evaluated by the DPPH radical scavenging effect[35]. The 0.1M acetate will be prepared by dissolving 1.64 g of sodium acetate in 15 mL of water and 150 μ L of acetic acid. The final volume will be adjusted to 20 mL by adding water. The 0.2 mmol of DPPH solution will be prepared by dissolving 3.9 g of DPPH in 50 mL of ethanol. α -Tocofereol (1mg in 10 mL of ethanol) solution was prepared. A series of test tubes will be arranged with 1.0 mL of buffer solution mixed with 0.5 mL of DPPH solution. A series of various concentrations of synthesized enones and α -Tocofereol (1 μ g in 1 mL of ethanol) will be added to each tube and mixed well. After 30 minutes in room temperature the absorbance of each solution will be measured by UV spectrophotometer at 517 nm. A mixture of buffer solution and ethanol used as the reference for the spectrophotometer. A graph was plotted with the weight of the compound Vs absorptions and IC₅₀ values will be determined. The antioxidant activity will be expressed in terms of IC₅₀ (μ g/mL, concentration required to inhibit DPPH radical formation by 50%). α -Tocofereol will be used as a positive control. The radical scavenging activity was calculated as,

$$\text{DPPH radical scavenging activity (\% of inhibition)} = \frac{\text{Control absorbance} - \text{Sample absorbance}}{\text{Control absorbance}} \times 100$$

From the experimental statistical results, the hydroxyl and methoxy substituted enones (**7-9**) were shown significant antioxidant activity.

3.5. Insect antifeedant activity

Generally organic compounds which are having carbonyl, unsaturation and halogen substitutions, they possess insect antifeedant activity. Therefore, the author wishes to examine the insect antifeedant activity of these enone derivatives and found to be active as insect antifeedant. This test was performed with a 4th instar larva *Achoea janata* L against castor *semilooper*, were reared as described on the leaves of castor, *Ricinus communis* in the laboratory at the temperature range of 26°C $\pm$ 1°C and a relative humidity of 75-85%. The leaf – disc bioassay method was used against the 4th instar larvae to measure the antifeedant activity. The 4th instar larvae were selected for testing because the larvae at this stage feed very voraciously.

3.5.1. Measurement of insect antifeedant activity of 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones

Castor leaf discs of a diameter of 1.85 cm were punched and intact with the petioles. The synthesized 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones were dissolved in acetone at a concentration of 200 ppm dipped for 5 minutes. The leaf discs were air-dried and placed in one litre beaker containing little water in order to facilitate translocation of water. Therefore, the leaf discs remain fresh throughout the duration of the test, 4th instar larvae of the test insect, which had been preserved on the leaf discs of all 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones and allowed to feed on them for 24 h. The area of the leaf disc consumed were measured by Dethler's method[36]. The observed antifeedant activity of 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones was presented in **Table 8**.

The results of the antifeedant activity of 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enones are presented in **Table 8** reveals that compound **6** 1-(2-benzyloxy-(3-methoxyacrylate)-1-naphthyl)-4-chloro phenyl chalcone was found to reflect satisfactory antifeedant. This test is performed with the insects which are only two-leaf disc soaked under the solution of this compound. Compound **5** showed enough antifeedant activity but lesser than **6**. Further compound **6** was subjected to measure the antifeedant activity at different 50, 100, 150 ppm concentrations and the observation reveals that as the concentrations decreased, the activity also decreased. It is observed from the results in **Table 9** and that the **6** 1-(2-benzyloxy-(3-methoxyacrylo)-1-naphthyl)-4-chlorophenyl chalcone showed an appreciable antifeedant activity at 150 ppm concentration.

Table 8. Insect antifeedant activities of 1-(2-benzyloxy-(3-methoxyacrylo)-1-naphthyl)-3-substitutedphenyl chalcone

Entry	X	4-6 pm	6-8 pm	8-10 pm	10-12 pm	12-6 am	6-8 am	8am-12Nn	12Nn-2pm	2-4 pm	Total leaf disc consumed in 24 h
1	H	1	1	0.5	0.5	0.5	1	1	1	1	8
2	3-Br	1	2	0.25	1	0.1	0	1	1	0.5	5
3	4-Br	0.5	0.25	0.25	0.5	0.5	0.5	1	1	0.5	5
4	2-Cl	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	4
5	3-Cl	0.5	0.5	0.25	1	0.5	0.5	0.25	0.25	0.25	4
6	4-Cl	0.5	0.5	0.25	1	0.5	0	0	0	0.25	3
7	2-OH	1	2	2	1	0	0	1	1	1	9
8	4-OH	1	1	1	0.5	0.5	1	2	1	1	10
9	4-OCH ₃	1	0.5	0.5	1	1	0	1	1	1	9
10	4-CH ₃	0.5	1	0.5	2	2	0.5	0.5	1	1	7
11	2-NO ₂	2	3	3	1	1	1	0.5	1	0	12
12	4-NO ₂	2	3	3	1	0	0	0.5	1	0	7

Number of leaf discs consumed by the insect (Values are mean + SE of five).

Table 9. Insect antifeedant activity of compound 6 1-(2-benzyloxy-(3-methoxyacrylo)-1-naphthyl)-4-chlorophenyl chalcone at the concentration of 50, 100 and 150 ppm.

ppm	4-6 pm	6-8 pm	8-10 pm	10-12 pm	12-6 am	6-8 am	8am-12Nn	12Nn-2pm	2-4 pm	Total leaf disc consumed in 24 h
50	0.5	0.5	0	0	0	0	0	0	0	0.1
100	0.1	0.5	0	0	0	0	0	0	0	0.15
150	0	0.25	0.25	0	0.0	0	0	0	0	0.05

Number of leaf discs consumed by the insect (Values are mean + SE of five).

4. CONCLUSIONS

A series of 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl enone derivatives have been synthesized by LiOH.H₂O catalyzed Claisen-Schmidt condensation of 2-benzyloxy-(3-methoxyacrylate)-1-naphthyl ketone and benzaldehydes. The yields of the enones are more than 90%. Synthesized enones were characterized by the physical constants and spectral data. The spectral group frequencies such as infrared ν CO_{*s-cis*, *s-trans*}, CO_{ester}, NMR chemical shifts (δ , ppm) of H _{α} , H _{β} , C _{α} , C _{β} , CO of enone moiety, H _{β'} and CO of acrylate moieties have been correlated with Hammett substituent constants, F and R parameters. From the results of statistical analysis almost all correlations gave satisfactory correlation in single and multiple linear-regression analysis. of The antimicrobial activities of synthesized enones have been evaluated using Bauer-Kirby methods. Enone derivatives containing halogens, methoxy, methyl and nitro substituents have shown good antimicrobial activities. The antioxidant activities of the enones were measured by DPPH radical scavenging method. The compounds containing hydroxyl and methoxy substituents shown antioxidant activity. The insect antifeedant activities of ketones have been evaluated using Dethler's leaf-disc bioassay method. The ketone 6 1-(2-benzyloxy-(3-methoxyacrylate)-1-naphthyl)-4-chloro phenyl chalcone showed an appreciable antifeedant activity.

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