Available online at www.ilcpa.pl

International Letters of Chemistry, Physics and Astronomy

4 (2014) 66-81 ISSN 2299-3843

Insect antifeedant potent unsaturated 1,3-oxazine-2-amines

G. Thirunarayanan[1,]*, V. Renuka[2], K. G. Sekar[2], K. Lakshmanan[2], K. Anbarasu[3]

[1]Department of Chemistry, Annamalai University, Annamalainagar - 608002, India

[2]Department of Chemistry, National College, Tiruchirappalli - 620001, India

[3]Department of Chemistry, TRP Engineering College (SRM), Irungalur - 621105, India

E-mail address: drgtnarayanan@gmail.com

ABSTRACT

Insect antifeedant activities of some halo substituted aryl 1,3-oxazine-2-amines have been measured using 4th instar larvae *Achoea Janata L* by castor leaf discs-Dethler's method. The highly halo substituted oxazine amines have shown good insect antifeedant activities. The 1,3-oxazine amines have been synthesised by greener method by solvent-free cyclization of aryl enones with urea under microwave irradiation. The yields of the oxazines were more than 80 %. The synthesised oxazines were characterized by their physical constants, analytical and spectroscopic data.

***Keywords*:** Insect antifeedant activity; 4th instar larvae *Achoea Janata L*; Aryl 1,3-oxazine; Castor leaf discs; Green synthesis; IR and NMR spectra

1. INTRODUCTION

Numerous organic compounds used as agrochemicals such as halo ketones, unsaturated halo ketones [1], acyl halides [2], alkaloids [3], many naturally occurring compounds from plant extracts [4,5] and ω-substituted halo compounds [2]. This agrochemical possess many biological activities such as antimicrobial [6], antioxidant [7], fumigant activity [8], insecticides [9], weedicides [10], larvacidal [11] and insect antifeedants [12,13] due to the presence of alkenes, carbonyl, halogens and some polar groups in their structural moiety. The insect antifeedant activity is important in agricultural-agronomy fields. Due to feeding of leafs by the insects; the economic crises will occur in this field by low quality, recovery and finally the valuable plants will be lost. Therefore the insect antifeedant agents are important for protection of our plants. Many methods available for measuring this insect antifeedant activity such as, Boll Weevil antifeedant bioassay [14], castor leaf disc bioassay [15] and sweet potato leafs [16], Similarly many insects employed for evaluate the activity such as, 4th instar larvae *Achoe Janta L* [17], and common cut worms [18]. Recently Thirunarayanan et al., [19,23-27] have studied the insect antifeedant activities of some synthetic chalcones and acyl compounds. Nalwar, et al., [20] also studied the insect antifeedant activities with cotton leaf by in-vitro method. Dasharathi et al., [21] have studied the insect antifeedant activities of halogenated phenyl naphthyl chalcones. Within the above view, there is no report available for the synthesis and the study of insect antifeedant activities of halo oxazine derivatives. Therefore the author have taken efforts to synthesize of some halogenated oxazine derivatives and study the insect antifeedant activities using 4th instar larvae *Achoea Janata L* by castor leaf discs-Dethler's [22] method.

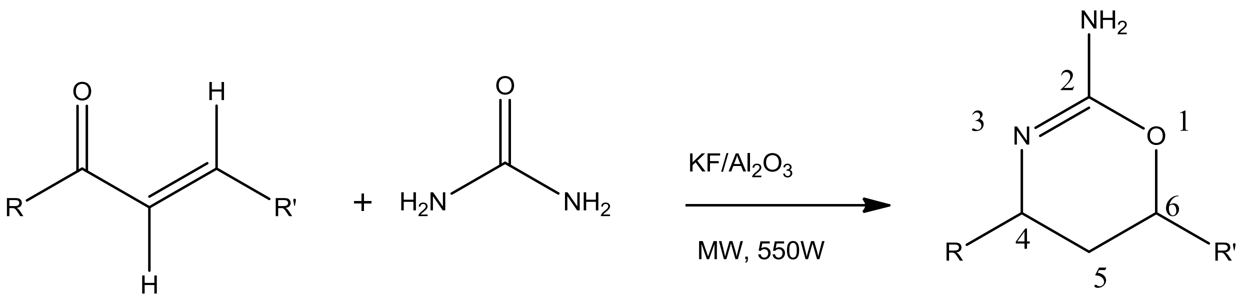
2. EXPERIMENTAL

2. 1. General

All chemicals used in this study were procure from Sigma-Aldrich Chemical company. Mettler FP51 melting point apparatus was used for determining the melting point of all synthesized oxazine-2-amines in open glass capillaries and are uncorrected. The AVATAR-300 Fourier transform spectrophotometer was used for recording infrared spectra (KBr, 4000-400 cm^{-1}) of all oxazines in KBr disc. The Bruker AV400 type NMR spectrometer was utilized for recording NMR spectra of all oxazines, operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard. Mass spectra of all synthesised oxazines were recorded on SHIMADZU mass spectrometer using chemical ionization technique.

2. 2. Synthesis of 4-(aryl)-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines.

An appropriate equi-molar quantities of chalcones (2 mmol), urea (2 mmol) and 0.2 g of KF/Al_2O_3 were taken in a 50 mL beaker, closed with the lid. This mixture was subjected to microwave irradiation for 2-4 minutes at 650W (Scheme 1) (Samsung, Microwave Oven, 100-700 W). After completion of the reaction, dichloromethane (20 mL) was added, followed by simple filtration. The solution was concentrated and purified by re-crystallization. The synthesized oxazines were characterized by their physical constants, IR, ^{1}H and ^{13}C NMR and Mass spectral data. The analytical, physical constants and mass fragments (m/z) data are presented in Table 1.



1-35

Scheme 1. Synthesis of 4-aryl-5,6-dihydro-6-(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines KF/Al_2O_3 catalyzed cyclization of aryl chalcones and urea under microwave irradiation.

The infrared and NMR spectral data of the synthesised oxazines are summarized below.

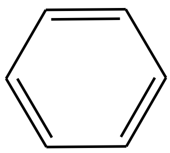
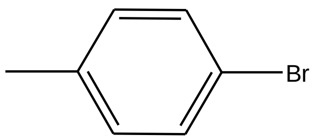
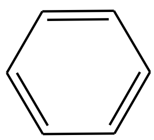
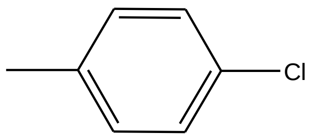
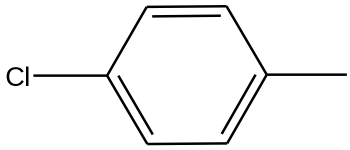
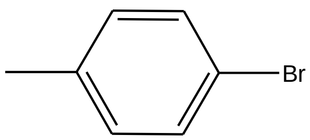
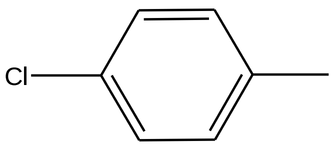
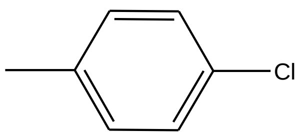
1. 4-Phenyl-5,6-dihydro-6-(4-bromophenyl)-^{4}*H*-1,3-oxazine-2-amines: FTIR (KBr): 3535 (NH), 1596(C=N), 1210(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.323(s, 1H, NH_2), 2.634(dd, 1H, H_4), 2.413(dd, 1H, H_5), 2.222(dd, 1H, $H_{5'}$), 4.252(dd, 1H, H_6), 6.543-7.367(m, 9H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.47(C_2), 52.65 (C_4), 47.78 (C_5), 65.78(C_6), 125.47-142.89(Ar-C)ppm.

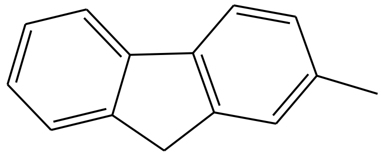
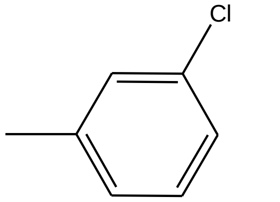
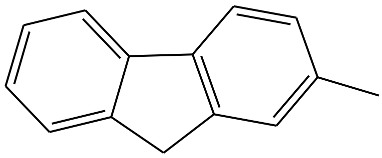
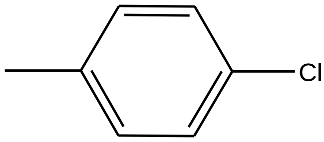
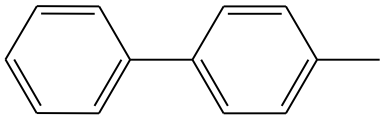
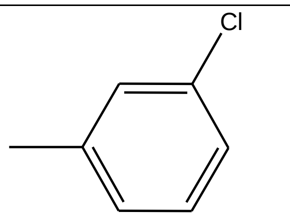
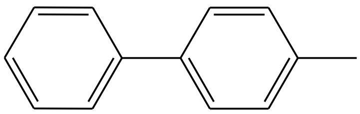
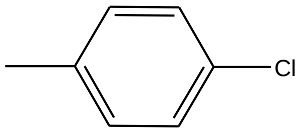
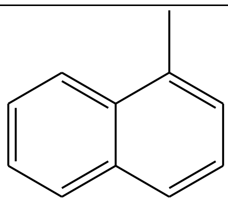
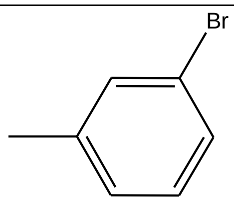
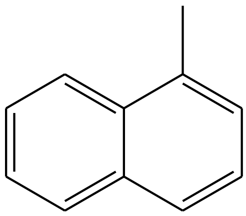
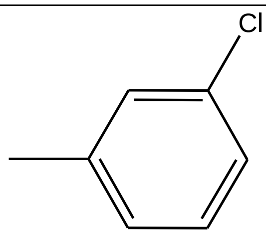
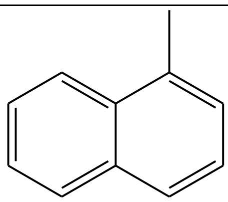
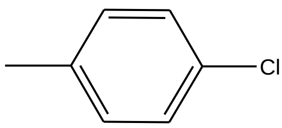
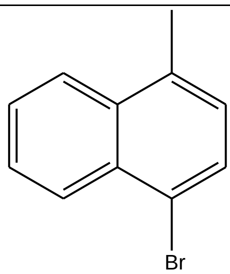
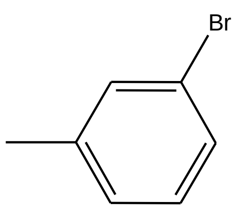
2. 4-Phenyl-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amines: FTIR (KBr): 3538 (NH), 1589(C=N), 1223(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.313(s, 1H, NH_2), 2.645(dd, 1H, H_4), 2.423(dd, 1H, H_5), 2.219(dd, 1H, $H_{5'}$), 4.265(dd, 1H, H_6), 6.534-7.387(m, 9H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.32(C_2), 52.87 (C_4), 47.98 (C_5), 65.47C_6), 125.54-142.67(Ar-C)ppm.

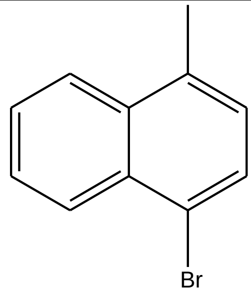
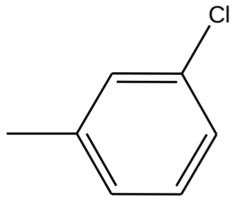
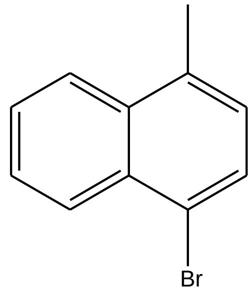
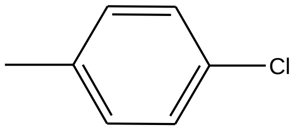
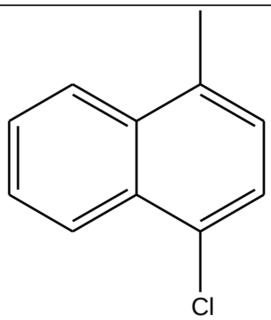
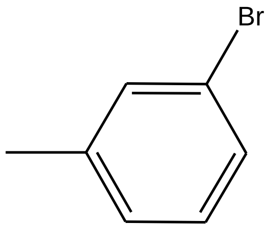
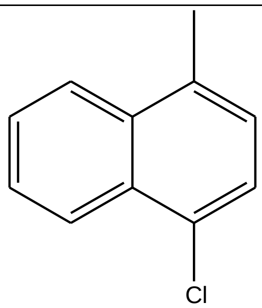
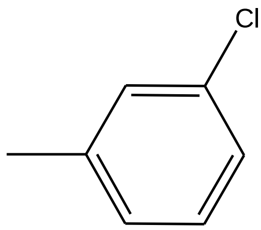
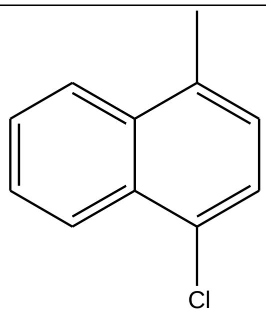
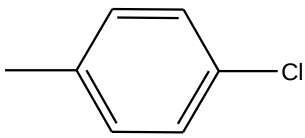
3. 4-Chlorohenyl-5,6-dihydro-6-(4-bromophenyl)-^{4}*H*-1,3-oxazine-2-amines: FTIR (KBr): 3547(NH), 1598(C=N), 1220(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.319(s, 1H, NH_2), 2.625(dd, 1H, H_4), 2.467(dd, 1H, H_5), 2.249(dd, 1H, $H_{5'}$), 4.267(dd, 1H, H_6), 6.545-7.398(m, 8H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.90(C_2), 52.78 (C_4), 47.57 (C_5), 65.78(C_6), 125.34-142.80(Ar-C)ppm.

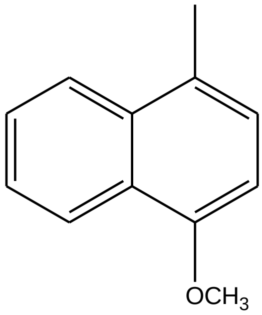
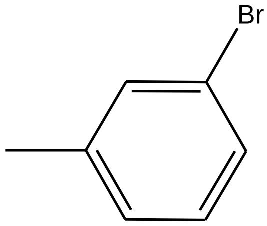
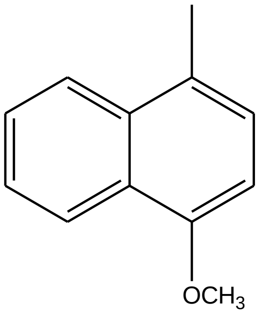
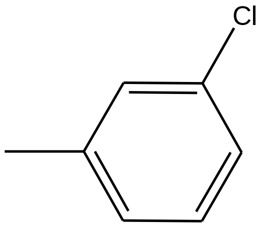
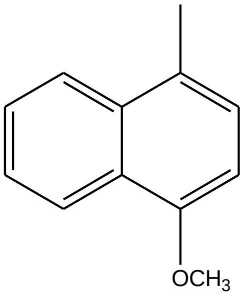
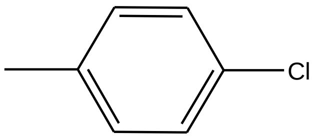
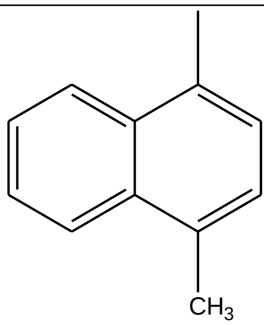
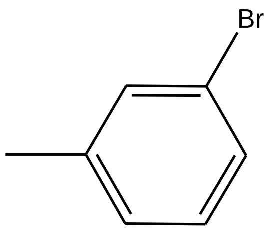
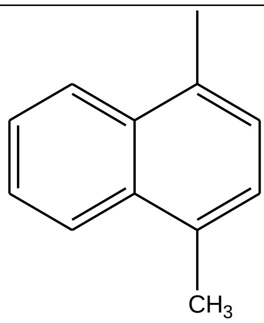
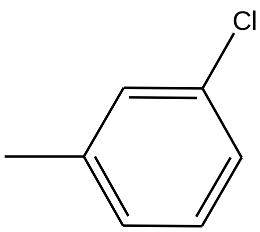
4. 4-Chlorohenyl-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3555(NH), 1593(C=N), 1216(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.324(s, 1H, NH_2), 2.365(dd, 1H, H_4), 2.476(dd, 1H, H_5), 2.246(dd, 1H, $H_{5'}$), 4.291(dd, 1H, H_6), 6.576-7.392(m, 8H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.56(C_2), 52.89 (C_4), 47.47 (C_5), 65.70(C_6), 125.34-142.78(Ar-C)ppm.

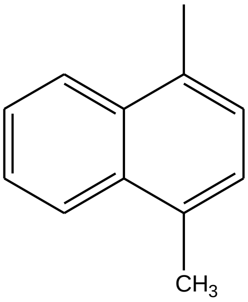
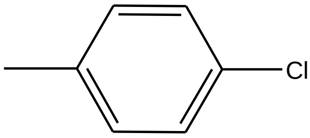
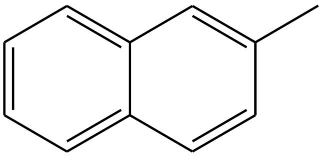
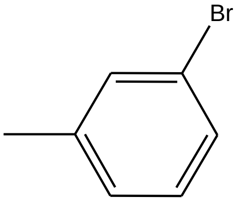
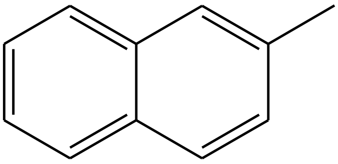
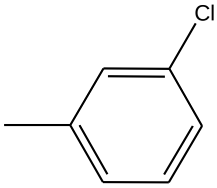
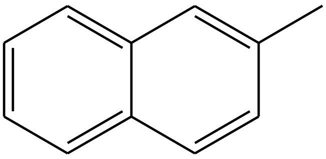
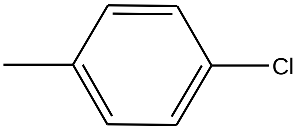
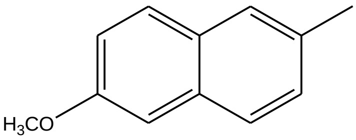
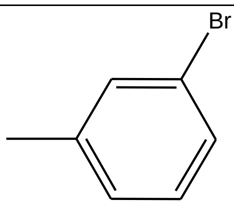
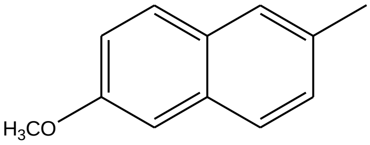
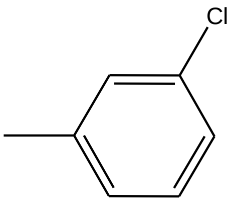
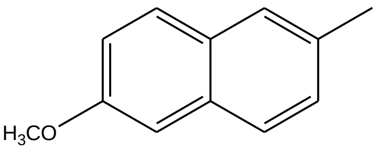
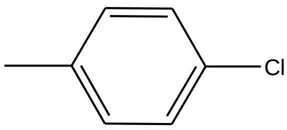
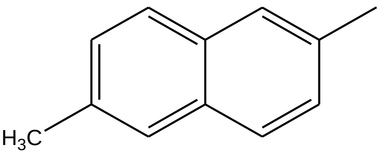
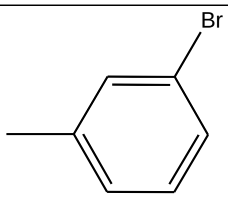
Table 1. Analytical, physical constants, yield and mass fragment of 4-aryl-5,6-dihydro-6(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines.

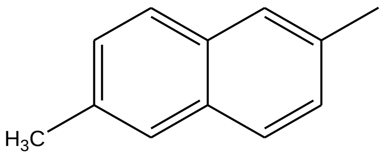
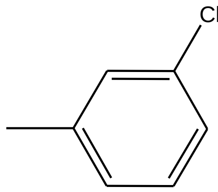
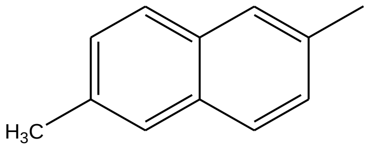
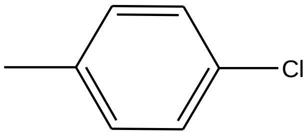
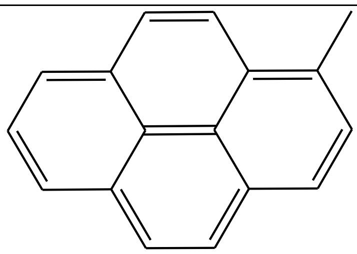
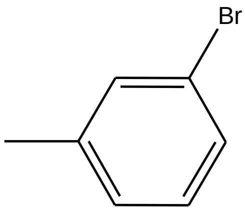
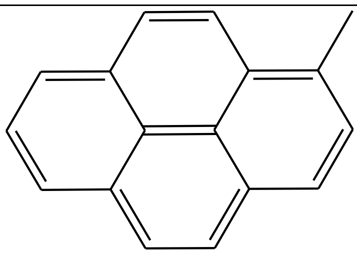
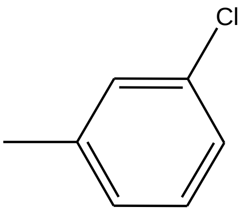
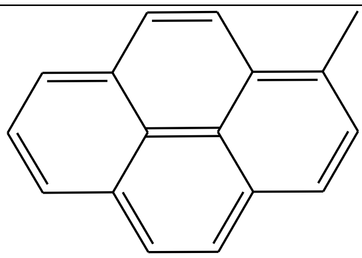
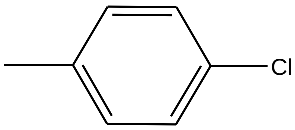
Entry	R	R′	M. W.	Yield (%)	m.p. (°C)	Mass (m/z)
1			332	87	132-133	332 [M^+], 334 [M^{2+}], 314, 272,237, 215, 175, 154, 79, 77, 58, 43, 42. 16
2			288	85	122-123	286 [M^+], 288 [M^{2+}], 270, 266, 251, 175, 160, 111, 107, 99, 84, 77, 43, 42, 35, 16
3			365	86	127-128	365 [M^+], 367 [M^{2+}], 369 [M^{4+}], 374, 285, 252, 209, 154, 99, 79, 54, 16,
4			322	85	113-114	322 [M^+], 324 [M^{2+}], 377 [M^{4+}], 304, 209, 111, 99. 77, 35, 16

5			375	86	77-78	375 [M^{+}], 377 [M^{2+}], 358, 339, 263, 248, 209, 175, 165, 118, 111, 84, 77, 58, 43, 35,16,
6			375	85	92-93	375 [M^{+}], 377 [M^{2+}], 358, 263, 248, 209, 175, 118, 84, 77, 58, 43, 42, 35,16,
7			362	85	121-122	362 [M^{+}], 364 [M^{2+}], 346, 327, 251, 236, 209, 153, 111, 84, 77, 58, 43, 35,16,
8			362	84	118-119	362 [M^{+}], 364 [M^{2+}], 346, 209, 175, 118, 99, 84, 77, 58, 43, 42, 35,16,
9			419	85	147-148	419 [M^{+}], 421 [M^{2+}], 403, 339, 248, 209, 175, 118, 111, 84, 77, 58, 43, 35,16,
10			375	85	121-122	375 [M^{+}], 377 [M^{2+}], 358, 339, 263, 248, 209, 175, 165, 118, 111, 84, 77, 58, 43, 35,16,
11			375	85	115-116	375 [M^{+}], 377 [M^{2+}], 358, 263, 248, 209, 175, 118, 84, 77, 58, 43, 42, 35,16,
12			460	85	117-118	460 [M^{+}], 462 [M^{2+}], 464 [M^{4+}], 441, 303, 339, 252, 209, 175, 127, 84, 79,77, 58, 43, 35,16

13			415	85	99-101	415 [M^+], 417 [M^{2+}], 419 [M^{4+}], 397, 379, 303, 335, 225, 209, 175, 127, 99, 77, 58, 43, 35,16,
14			415	86	131-132	415 [M^+], 417 [M^{2+}], 419 [M^{4+}], 397, 379, 303, 335, 209, 175, 127, 99, 77, 58, 43,41, 35,16,
15			416	85	123-124	416 [M^+], 418 [M^{2+}], 420 [M^{4+}], 397, 379, 364, 335, 286, 259, 253, 210, 161, 154, 127, 91, 84, 79,43, 42, 35, 16,
16			370	84	105-106	370 [M^+], 372 [M^{2+}], 374 [M^{4+}], 335,304, 259, 244, 232, 209, 202, 161, 111, 91, 77, 43, 42, 35,28, 16
17			370	86	116-117	370 [M^+], 372 [M^{2+}], 374 [M^{4+}], 335, 304, 259, 244, 232, 209, 202, 161, 111, 91, 77, 43, 42, 35,28, 16

18			411	55	98-99	411 [M^+], 413 [M^{2+}], 331, 316, 255, 240, 210, 157, 154, 91, 84, 77, 43, 42, 31, 16, 15
19			366	54	128-129	366 [M^+], 368 [M^{2+}], 335, 331, 278, 255, 209, 182, 168, 157, 154, 127, 111, 99, 91, 77, 58, 35, 31, 16, 15
20			366	55	113-114	366 [M^+], 368 [M^{2+}], 335, 331, 278, 255, 182,168, 157, 127, 111, 91, 77, 58, 43, 42, 35, 31, 16, 15
21			396	85	102-103	396 [M^+], 398 [M^{2+}], 378, 315, 252, 239, 154, 141, 91, 79, 77, 16, 15
22			350	85	117-118	350 [M^+], 452 [M^{2+}], 378, 315, 279, 255, 252, 239, 154, 141, 122, , 79, 77, 35,16, 15

23			350	86	124-125	350 [M$^+$], 452 [M^{2+}], 378, 315, 279, 255, 252, 239, 154, 141, 122, 91, 77, 36, 35, 16, 15
24			419	85	121-123	419 [M$^+$], 421 [M^{2+}], 403, 339, 248, 209, 175, 118, 111, 84, 77, 58, 43, 35,16,
25			375	85	119-120	375 [M$^+$], 377 [M^{2+}], 358, 263, 248, 209, 175, 118, 84, 77, 58, 43, 42, 35,16,
26			383	87	125-126	383 [M$^+$], 368, 353, 339, 263, 254, 165, 147, 106, 91, 77, 58, 44,43, 42, 16, 15
27			410	87	123-124	410 [M$^+$], 412 [M^{2+}], 331, 316, 301, 255, 175, 157, 91, 79,77, 45, 42, 31, 16,
28			366	86	130-131	366 [M$^+$], 368 [M^{2+}], 331, 350,335, 308, 272, 255, 209, 194, 157, 111,94, 91, 84, 77, 58, 43, 42, 35,31, 16,
29			366	86	114-115	366 [M$^+$], 368 [M^{2+}], 331, 335, 308, 272, 255, 111,94, 91, 84, 77, 42, 35,31, 16,
30			396	87	143-44	396 [M$^+$], 398 [M^{2+}], 378, 315, 252, 239, 154, 141, 91, 79, 77, 16, 15

31			350	88	116-117	350 [M+], 452 [M2+], 378, 315, 279, 255, 252, 239, 154, 141, 122, , 79, 77, 35,16, 15
32			350	87	123-124	350 [M+], 452 [M2+], 378, 315, 279, 255, 252, 239, 154, 141, 122, 91, 77, 36, 35, 16, 15
33			456	86	139-140	456 [M+], 458 [M2+], 394, 375, 299, 284, 209, 111, 77, 43, 42, 35, 16
34			410	85	119-120	410 [M+], 412 [M2+], 394, 375, 299, 284, 209, 111, 77, 43, 42, 35, 16
35			410	85	132-133	410 [M+], 412 [M2+], 394, 375, 299, 284, 209, 201, 111, 77, 44, 43, 42, 35, 16,

5. 4-(9H-Fluorene-2-yl)-5,6-dihydro-6-(3-phenylphenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3545(NH), 1593(C=N), 1216(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.254(s, 1H, NH_2), 2.215(dd, 1H, H_4), 2.264(dd, 1H, H_5), 2.031(dd, 1H, $H_{5'}$), 4.625(dd, 1H, H_6), 6.715-7.775(m, 11H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.89(C_2), 52.31 (C_4), 47.26 (C_5), 67.29 (C_6), 47.26(OCH_3), 121.25-138.32 (Ar-C)ppm.

6. 4-(9H-Fluorene-2-yl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3548 (NH), 1602(C=N), 1215(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.156(s, 1H, NH_2), 2.251(dd, 1H, H_4), 2.268(dd, 1H, H_5), 2.054(dd, 1H, $H_{5'}$), 4.698(dd, 1H, H_6), 6.853-7.895(m, 11H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.02(C_2), 52.16 (C_4), 47.29 (C_5), 67.28 (C_6), 121.35-139.35 (Ar-C)ppm.

7. 4-(4-Biphenyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3552(NH), 1593(C=N), 1221(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.242(s, 1H, NH_2), 2.217(dd, 1H, H_4), 2.254(dd, 1H, H_5), 2.024(dd, 1H, $H_{5'}$), 4.635(dd, 1H, H_6), 6.714-7.775(m, 11H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.89(C_2), 52.31 (C_4), 47.36 (C_5), 67.25 (C_6), 121.35-138.19 (Ar-C)ppm.

8. 4-(4-Biphenyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3555(NH), 1610(C=N), 1212(C-O-C) cm^{-1}. ^1H NMR ($CDCl_3$-d_6, TMS)δ: 2.125(s, 1H, NH_2), 2.274(dd, 1H, H_4), 2.277(dd, 1H, H_5), 2.055(dd, 1H, $H_{5'}$), 4.687(dd, 1H, H_6), 6.851-7.894(m, 11H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.22(C_2), 52.36 (C_4), 47.36 (C_5), 67.28(C_6), 121.35-139.35 (Ar-C)ppm.

9. 4-(1-Naphthyl)-5,6-dihydro-6-(3-bromophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3548(NH), 1586(C=N), 1226(C-O-C) cm^{-1}. ^1H NMR ($CDCl_3$-d_6, TMS)δ: 2.234(s, 1H, NH_2), 2.214(dd, 1H, H_4), 2.256(dd, 1H, H_5), 2.028(dd, 1H, $H_{5'}$), 4.643(dd, 1H, H_6), 6.723-7.767(m, 11H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.37(C_2), 52.36 (C_4), 47.34 (C_5), 66.25(C_6), 121.26-139.98 (Ar-C)ppm.

10. 4-(1-Naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3545(NH), 1612(C=N), 1223(C-O-C) cm^{-1}. ^1H NMR ($CDCl_3$-d_6, TMS)δ: 2.243(s, 1H, NH_2), 2.212(dd, 1H, H_4), 2.256(dd, 1H, H_5), 2.026(dd, 1H, $H_{5'}$), 4.634(dd, 1H, H_6), 6.722-7.789(m, 11H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.37(C_2), 52.80 (C_4), 47.22 (C_5), 66.44(C_6), 21.34-139.38(Ar-C)ppm.

11. 4-(1-Naphthyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3545(NH), 1608(C=N), 1212(C-O-C) cm^{-1}. ^1H NMR ($CDCl_3$-d_6, TMS)δ: 2.153(s, 1H, NH_2), 2.255(dd, 1H, H_4), 2.260(dd, 1H, H_5), 2.053(dd, 1H, $H_{5'}$), 4.697(dd, 1H, H_6), 6.851-7.894(m, 11H, Ar-H) ppm.; ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.18(C_2), 52.11 (C_4), 47.22 (C_5), 67.29(C_6), 121.25-138.32(Ar-C)ppm.

12. 4-(4-Bromo-1-naphthyl)-5,6-dihydro-6-(3-bromophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3552(NH), 1623(C=N), 1209(C-O-C) cm^{-1}. ^1H NMR ($CDCl_3$-d_6, TMS)δ: 2.221 (s, 1H, NH_2), 2.314 (dd, 1H, H_4), 2.22dd, 1H, H_5), 2.236 (dd, 1H, $H_{5'}$), 4.336(dd, 1H, H_6), 6.225-7.289 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.34 (C_2), 51.67 (C_4), 47.76(C_5), 66.43 (C_6), 124.26-139.39 (Ar-C)ppm.

13. 4-(4-Bromo-1-naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3548(NH), 1614(C=N), 1215(C-O-C) cm^{-1}. ^1H NMR ($CDCl_3$-d_6, TMS)δ: 2.215 (s, 1H, NH_2), 2.321 (dd, 1H, H_4), 2.421(dd, 1H, H_5), 2.265 (dd, 1H, $H_{5'}$), 4.323(dd, 1H, H_6), 6.232-7.278 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.33 (C_2), 51.23 (C_4), 47.87(C_5), 66.34 (C_6), 126.23-139.15 (Ar-C)ppm.

14. 4-(4-Bromo-1-naphthyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3552(NH), 1610(C=N), 1232(C-O-C) cm^{-1}. ^1H NMR ($CDCl_3$-d_6, TMS)δ: 2.217 (s, 1H, NH_2), 2.323 (dd, 1H, H_4), 2.420(dd, 1H, H_5), 2.238(dd, 1H, $H_{5'}$), 4.398(dd, 1H, H_6), 6.243-7.267 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.34 (C_2), 51.27 (C_4), 47.76(C_5), 66.98 (C_6), 126.37-139.87(Ar-C)ppm.

15. 4-(4-Chloro-1-naphthyl)-5,6-dihydro-6-(3-bromophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3552(NH), 1623(C=N), 1209(C-O-C) cm^{-1}. ^1H NMR ($CDCl_3$-d_6, TMS)δ: 2.221 (s, 1H, NH_2), 2.314 (dd, 1H, H_4), 2.22dd, 1H, H_5), 2.236 (dd, 1H, $H_{5'}$), 4.336(dd, 1H, H_6), 6.225-7.289 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.34 (C_2), 51.67 (C_4), 47.76(C_5), 66.43 (C_6), 124.26-139.39 (Ar-C)ppm.

16. 4-(4-Chloro-1-naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3548(NH), 1614(C=N), 1215(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.215 (s, 1H, NH_2), 2.321 (dd, 1H, H_4), 2.421(dd, 1H, H_5), 2.265 (dd, 1H, $H_{5'}$), 4.323(dd, 1H, H_6), 6.232-7.278 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.33 (C_2), 51.23 (C_4), 47.87(C_5), 66.34 (C_6), 126.23-139.15 (Ar-C)ppm.

17. 4-(4-Chloro-1-naphthyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3552(NH), 1610(C=N), 1232(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.217 (s, 1H, NH_2), 2.323 (dd, 1H, H_4), 2.420(dd, 1H, H_5), 2.238(dd, 1H, $H_{5'}$), 4.398(dd, 1H, H_6), 6.243-7.267 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.34 (C_2), 51.27 (C_4), 47.76(C_5), 66.98 (C_6), 126.37-139.87(Ar-C)ppm.

18. 4-(4-Methoxy-1-naphthyl)-5,6-dihydro-6-(3-bromophenyl)-^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3545(NH), 1605(C=N), 1215(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.225 (s, 1H, NH_2), 2.219 (dd, 1H, H_4), 2.265(dd, 1H, H_5), 2.025(dd, 1H, $H_{5'}$), 4.632(dd, 1H, H_6), 3.657(s, 3H, OCH_3), 6.725-7.787 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.25 (C_2), 51.65 (C_4), 47.20(C_5), 67.66 (C_6), (66.98, OCH_3), 121.24-141.39 (Ar-C)ppm.

19. 4-(4-Methoxy-1-naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3535(NH), 1589(C=N), 1212(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.125 (s, 1H, NH_2), 2.258 (dd, 1H, H_4), 2.264(dd, 1H, H_5), 2.038(dd, 1H, $H_{5'}$), 4.671(dd, 1H, H_6), 3.577(s, 3H, CH_3), 6.825-7.887 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.28(C_2), 52.87 (C_4), 47.35(C_5), 66.89 (C_6), (67.98, OCH_3), 118.46-139.67 (Ar-C)ppm.

20. 4-(4-Methoxy-1-naphthyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3555(NH), 1608(C=N), 1215(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.112 (s, 1H, NH_2), 2.232 (dd, 1H, H_4), 2.322(dd, 1H, H_5), 2.154(dd, 1H, $H_{5'}$), 4.776(dd, 1H, H_6), 3.087(s, 3H, CH_3), 6.667-7.946(m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.87(C_2), 52.32 (C_4), 47.443(C_5), 66.56 (C_6), (65.98, OCH_3), 118.57-139.79 (Ar-C)ppm.

21. 4-(4-Methyl-1-naphthyl)-5,6-dihydro-6-(3-bromophenyl) -^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3543(NH), 1597(C=N), 1213(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.219 (s, 1H, NH_2), 2.207 (dd, 1H, H_4), 2.257(dd, 1H, H_5), 2.019(dd, 1H, $H_{5'}$), 4.646(dd, 1H, H_6), 4.687(s, 3H, CH_3), 6.657-7.757 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.18 (C_2), 51.43 (C_4), 47.45(C_5), 67.67 (C_6), 25.98(CH_3), 121.24-141.39 (Ar-C)ppm.

22. 4-(4-Methyl-1-naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3538(NH), 1597(C=N), 1233(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.122 (s, 1H, NH_2), 2.256 (dd, 1H, H_4), 2.265(dd, 1H, H_5), 2.044(dd, 1H, $H_{5'}$), 4.664(dd, 1H, H_6), 4.534(s, 3H, CH_3), 6.823-7.877 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.68(C_2), 52.887 (C_4), 47.55(C_5), 66.86 (C_6), 26.48(CH_3), 118.67-139.48 (Ar-C)ppm.

23. 4-(4-Methyl-1-naphthyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3556(NH), 1618(C=N), 1217(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.121 (s, 1H, NH_2), 2.235 (dd, 1H, H_4), 2.329(dd, 1H, H_5), 2.134(dd, 1H, $H_{5'}$), 4.775(dd, 1H, H_6), 4.034(s, 3H, CH_3), 6.634-7.936(m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.56(C_2), 52.67 (C_4), 47.420(C_5), 66.57 (C_6), 25.92(CH_3), 118.59-139.92 (Ar-C)ppm.

24. 4-(2-Naphthyl)-5,6-dihydro-6-(3-bromophenyl)-^{4}H-1,3-oxazine-2-amine: FTIR (KBr): 3548(NH), 1603(C=N), 1218(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.225 (s, 1H, NH_2), 2.219 (dd, 1H, H_4), 2.262(dd, 1H, H_5), 2.034(dd, 1H, $H_{5'}$), 4.690(dd, 1H, H_6), 6.645-7.738 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.09 (C_2), 51.43 (C_4), 47.44(C_5), 67.90(C_6), 25.36(CH_3), 121.36-141.48 (Ar-C)ppm.

25. 4-(2-Naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3545(NH), 1605(C=N), 1215(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.225 (s, 1H, NH_2), 2.219 (dd, 1H, H_4), 2.265(dd, 1H, H_5), 2.025(dd, 1H, $H_{5'}$), 4.632(dd, 1H, H_6), 6.725-7.788 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.25 (C_2), 52.65 (C_4), 47.16(C_5), 67.32(C_6), 121.85-138.32 (Ar-C)ppm.

26. 4-(2-Naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3535(NH), 1589(C=N), 1222(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.125 (s, 1H, NH_2), 2.258 (dd, 1H, H_4), 2.264(dd, 1H, H_5), 2.038(dd, 1H, $H_{5'}$), 4.671(dd, 1H, H_6), 6.825-7.887 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.28(C_2), 52.87 (C_4), 47.21(C_5), 67.29(C_6), 121.90-139.38(Ar-C)ppm.

27. 4-(6-Methoxy-2-naphthyl)-5,6-dihydro-6-(3-bromophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3537(NH), 1617(C=N), 1223(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.217 (s, 1H, NH_2), 2.223 (dd, 1H, H_4), 2.234(dd, 1H, H_5), 2.024(dd, 1H, $H_{5'}$), 4.634(dd, 1H, H_6), 3.656(s, 3H, OCH_3), 6.711-7.723 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.56 (C_2), 51.75 (C_4), 47.27(C_5), 67.86 (C_6), (66.43, OCH_3), 121.26-141.87 (Ar-C)ppm.

28. 4-(6-Methoxy-1-naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3533(NH), 1592(C=N), 1218(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.123 (s, 1H, NH_2), 2.257 (dd, 1H, H_4), 2.278(dd, 1H, H_5), 2.029(dd, 1H, $H_{5'}$), 4.646(dd, 1H, H_6), 3.578(s, 3H, OCH_3), 6.833-7.867 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.22(C_2), 52.84 (C_4), 47.36(C_5), 66.80 (C_6), (67.66, OCH_3), 118.32-139.60 (Ar-C)ppm.

29. 4-(6-Methoxy-1-naphthyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3552(NH), 1623(C=N), 1246(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.120 (s, 1H, NH_2), 2.226 (dd, 1H, H_4), 2.334(dd, 1H, H_5), 2.165(dd, 1H, $H_{5'}$), 4.778(dd, 1H, H_6), 3.136(s, 3H, OCH_3), 6.636-7.989(m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.36(C_2), 52.89 (C_4), 47.490(C_5), 66.80 (C_6), (65.40, OCH_3), 118.22-139.69 (Ar-C)ppm.

30. 4-(6-Methyl-1-naphthyl)-5,6-dihydro-6-(3-bromophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3545(NH), 1583(C=N), 1223(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.223 (s, 1H, NH_2), 2.212 (dd, 1H, H_4), 2.246(dd, 1H, H_5), 2.023(dd, 1H, $H_{5'}$), 4.667(dd, 1H, H_6), 4.656(s, 3H, CH_3), 6.644-7.778 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.56 (C_2), 51.89 (C_4), 47.45(C_5), 67.89 (C_6), 25.67(CH_3), 121.33-141.56 (Ar-C)ppm.

31. 4-(6-Methyl-1-naphthyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3534(NH), 1593(C=N), 1213(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.123 (s, 1H, NH_2), 2.246 (dd, 1H, H_4), 2.236(dd, 1H, H_5), 2.034(dd, 1H, $H_{5'}$), 4.665(dd, 1H, H_6), 4.567(s, 3H, CH_3), 6.877-7.827 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.89(C_2), 52.865 (C_4), 47.80(C_5), 66.76 (C_6), 26.99(CH_3), 118.15-139.89 (Ar-C)ppm.

32. 4-(6-Methyl-1-naphthyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR (KBr): 3552(NH), 1612(C=N), 1213(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.115 (s, 1H, NH_2), 2.234 (dd, 1H, H_4), 2.336(dd, 1H, H_5), 2.136(dd, 1H, $H_{5'}$), 4.767(dd, 1H, H_6), 4.032(s, 3H, OCH_3), 6.636-7.947(m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.78(C_2), 52.89 (C_4), 47.490(C_5), 66.35 (C_6), 25.67(CH_3), 118.89-139.27(Ar-C)ppm.

33. 4-(1-Pyrenyl)-5,6-dihydro-6-(3-bromophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR(KBr): 3548(NH), 1598(C=N), 1223(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.217 (s, 1H, NH_2), 2.234 (dd, 1H, H_4), 2.267(dd, 1H, H_5), 2.022(dd, 1H, $H_{5'}$), 4.678(dd, 1H, H_6), 6.637-7.789 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.34 (C_2), 51.78 (C_4), 47.43(C_5), 67.36 (C_6), 121.57-141.90 (Ar-C)ppm.

34. 4-(1-Pyrenyl)-5,6-dihydro-6-(3-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine:FTIR(KBr): 3546(NH), 1594(C=N), 1245(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.118 (s, 1H, NH_2), 2.335 (dd, 1H, H_4), 2.232(dd, 1H, H_5), 2.045(dd, 1H, $H_{5'}$), 4.667(dd, 1H, H_6), 6.832-7.810 (m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 165.12(C_2), 52.848 (C_4), 47.32(C_5), 66.76 (C_6), 118.12-139.67 (Ar-C)ppm.

35. 4-(4-Methyl-1-naphthyl)-5,6-dihydro-6-(4-chlorophenyl)-^{4}*H*-1,3-oxazine-2-amine: FTIR(KBr): 3532(NH), 1623(C=N), 1256(C-O-C) cm^{-1}. ^{1}H NMR ($CDCl_3$-d_6, TMS)δ: 2.122 (s, 1H, NH_2), 2.234 (dd, 1H, H_4), 2.343(dd, 1H, H_5), 2.139(dd, 1H, $H_{5'}$), 4.736(dd, 1H, H_6), 6.634-7.909(m, 10H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$-d_6, TMS)δ: 164.34(C_2), 52.56 (C_4), 47.480(C_5), 66.48 (C_6), 118.34-139.78(ArC)ppm.

2. 3. Measurement of Insect antifeedant activities

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 ±1 °C and a relative humidity of 75-85 %. The leaf – disc bioassay method [28] 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. Castor leaf discs of a diameter of 1.85 cm were punched and intact with the petioles. All synthesized oxazine-2-amines 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 rest, 4th instar larvae of the test insect, which had been preserved on the leaf discs of all oxazine-2-amines and allowed to feed on them for 24 h. The areas of the leaf disc consumed were measured by Dethler's method [22]. The observed oxazine-2-amines were presented in Table 2

.

Table 2. The insect antifeedant activities of the 4-(aryl)-5,6-dihydro-6(substituted phenyl)-^{4}*H*-1,3-oxazine-2-amines.

Entry	4-6 pm	6-8 pm	8-10 pm	10-2 pm	12-6 am	6-8 am	8am-12Nn	12Nn-2pm	2-4 pm	Total leaf disc consumed in 24 h
1	1	1	1	0.5	0.5	1	1	1	1	8
2	2	10.5	1	1	1	1	1	0	0.5	9
3	1	2	2	1	0	0	1	1	1	9
4	0.5	1	1	0.25	0.5	0.5	0.5	1	1	6
5	1	1	1	1	0.5	0.5	0.5	1	0.5	7
6	1	1	1	1	0	0.5	0.5	1	0.5	6.5
7	1	0.5	1	1	1	1	0.5	0.5	0.5	7
8	1	1	1	0.25	0.25	1	0.5	1	0.5	7

9	1	0.5	1	1	1	0.5	1	0.5	0.5	7
10	1	1	0.5	1	0.5	0.5	0.5	0.5	0.5	6
11	1	0.5	1	0.5	0.5	1	1	1	1	8
12	0.5	0.25	0.5	0.25	0.5	0.5	0.5	1	1	5
13	0.25	0.25	0.25	0.25	0.5	0.5	0.5	1	0.5	4
14	0.25	0.25	0.25	0.25	0.25	0.5	0.25	1	0.5	3.5
15	0.25	0.25	0.25	0.25	0.5	0.5	0.5	1	0.5	4
16	0.25	0.25	0.25	0.25	0.25	0.5	0.25	1	0.5	3.5
17	0.25	0.25	0	0.25	0.5	0	0.25	1	0.5	3
18	0.25	0.25	0.25	0.25	0.5	0.5	0.5	1	0.5	4
19	0.25	0.25	0.25	0.25	0.25	0.5	0.25	1	0.5	3.5
20	1	0.5	1	1	1	1	0.5	0.5	0.5	7
21	1	1	1	0.25	0.25	1	0.5	1	0.5	7
22	1	0.5	1	1	1	0.5	1	0.5	0.5	7
23	1	1	0.5	1	0.5	0.5	0.5	0.5	0.5	6
24	1	0.5	1	0.5	0.5	1	1	1	1	8
15	2	1	1	0.5	0.5	1	1	1	1	9
26	1	0.5	1	0.5	0.5	1	1	1	1	8
27	2	2	1	0.5	0.5	1	1	1	1	10
28	2	2	1	0.5	1	1	1	1	0.5	11
29	1	2	2	1	0	0	1	1	1	9
30	1	1	1	1	0.5	0.5	0.5	1	1	8
31	1	0.5	1	1	0.5	0.5	0.5	1	0.5	7.5
32	2	1	1	0.5	1	0.5	0.5	1	0.5	8
33	1	0.5	1	1	1	1	0.5	0.5	0.5	7
34	1	1	1	0.25	0.25	1	0.5	1	0.5	7
35	1	0.5	1	1	1	0.5	1	0.5	0.5	7

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

3. RESULTS AND DISCUSSION

The results of the antifeedant activity of oxazine-2-amines are presented in Table 2 reveals that all halogenated compounds were found to reflect satisfactory insect antifeedant activities. This test was performed with the insects which ate only two-leaf disc soaked under the solution of this compound. All compounds were active for insect antifeedant activities. The oxazine derivatives **12-17** 4-(4-chloro-1-naphthyl) and 4(4-bromo-1-naphthyl)-5,6-dihydro-6(substituted phenyl)-^{4}H-1,3-oxazine-2-amines showed enough antifeedant activity. Further compounds **12-17** 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 3 and that the oxazine **12-17** showed an appreciable antifeedant activity at 150 ppm concentration.

Table 3. Antifeedant activity of compound **12-17** 4-(4-chloro-1-naphthyl) and 4(4-bromo-1-naphthyl)-5,6-dihydro-6(substituted phenyl)-4H-1,3-oxazine-2-amines showed an appreciable antifeedant activity at 3 different concentrations.

Entry	4-6 pm	6-8 pm	8-10 pm	10-2 pm	12-6 am	6-8 am	8am-12Nn	12Nn-2pm	2-4 pm	Total leaf disc consumed in 24 h
50	0.25	0	0.25	0.25	0	0	0	0	0	0. 75
100	0.25	0.25	0	0	0	0	0	0	0	0.5
150	0.25	0	0	0	0	0	0	0	0	0.25

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

4. CONCLUSIONS

Some unsaturated 1,3-oxazine derivatives have been synthesised and characterized by their physical constants and spectroscopic data. The insect antifeedant activities of these oxazine derivatives have been evaluated using the 4th instar larvae *Acheoa Janata L* by castor leaf disc method. The compounds **12-17** highly halogen substituted shows significant insect antifeedant activities.

ACKNOWLEDGMENT

The authors thank DST NMR facility, Department of Chemistry, Annamalai University, Annamalainagar-608002, India, for recording NMR spectra of all compounds.

Referenes

[1] Thirunarayanan G., Surya S., Srinivasan S., Vanangamudi G., Sathiyendiran V., *Spectrochim. Acta (A)* 75 (2010) 152-156.

[2] Thirunarayanan G., *Q-Science connect*. 2013. DOI: http://dx.doi.org/ 10.5339/ connect. 2013.6, 7.

[3] Howard Miles D., Maria Ly A., Randle S. A., Hedin P. A., Burks M. L., *J. Agric. Food Chem.* 35 (1987) 794-797.

[4] Omara S., et al., *J. Stored Prod. Res*. 43 (2007) 92.

[5] Ebadollahi A., *Biharean Biologist* 5 (1) (2011) 8-10.

[6] Wellsow J., Grayer R. J., Veitch N. C., Kokubun T., Lelli R., Kite, G. C., Simmonds M. S., *J. Phytochem.* 67 (2006) 1818-1825.

[7] Miranda C. L., Aponso G. L., Stevens J. F., Deinzer M. L., Buhler D. R., *J. Agric. Food Chem.* 48 (2000) 3876-3884

[8] Kim S. I., Park C., Ohh M. H., Cho H. C., Ahn, Y. J., *J. Stored Prod. Res.* 39 (2003) 11-19.

[9] Hiiesaar K., Švilponis E., Metspalu L., Jõgar K., Mänd M., Luik A., Karise R., *Agronomy Res.* 7 (2009) 251-256.

[10] Niemeyer H. M., *J. Agric. Food Chem.* 57(5) (2009) 1677-1696.

[11] Bhagat R. B., Kulkarni D. K., *Ann. Biol. Res.* 3(6) (2012) 2911-2916.

[12] Yasui H., *JARQ* 36(1) (2002) 25-30.

[13] Szczepanik M., Obara R., Szumny A., Gabryś B., Halarewicz-Pacan A., Nawrot J., Wawrzeńczyk C., *J. Agric. Food Chem.* 53(15) (2005) 5905-5910.

[14] Sunnerheim K, Nordqvist A, Nordlander G., Borg-Karlson A. K., Rickard Unelius C., Bohman B., Nordenhem H., Hellqvist C. and Karlén A., *J. Agric. Food Chem.* 55(23) (2007) 9365-9372.

[15] Sreelatha T., Hymavathi A., Suresh Babu K., Madhusudana Murthy J., Usha Rani P., Madhusudana Rao J., *J. Agric. Food Chem.* 57(14) (2009) 6090-6094.

[16] González-Coloma A., Gutiérrez C., Cabrera R., Reina M., *J. Agric. Food Chem.* 45(3) (1997) 946-950.

[17] Thirunarayanan G., *J. Indian Chem. Soc*. 85 (2008) 447-451.

[18] Morimoto M., Matsuda K., Ohta Y., Ihara T., Komai K., *J. Agric. Food Chem.* 52(15) (2004) 4737-4739.

[19] Thirunarayanan G., Mayavel P., Thirumurthy K., Vanangamudi G., Lakshmanan K., Sekar K. G., *Int. J. Chem.* 1(2) (2012) 166-172.

[20] Nalwar Y. S., Sayyed M. A., Mokle S. S., Zanwar P, R., Vibhute Y. B., *World J. Chem.* 4 (2009) 123.

[21] Dasharathi D., Netaji R., Basheer M. A., Vibhute Y. B., *Ultra Science* 17 (2005) 89.

[22] Dethler V. G., *Chemical insect attractants and Repellants*. Blackistan, Philadeciphia, pp. 210. (1947).

[23] Arulkumaran R., Vijayakumar S., Sundararajan R., Sakthinathan S. P., Kamalakkannan D., Suresh R., Ranganathan K., Vanangamudi G., Thirunarayanan G., *International Letters of Chemistry, Physics and Astronomy* 4 (2012) 17-38.

[24] K. Ranganathan, R. Suresh, D. Kamalakkannan, R. Arulkumaran, R. Sundararajan, S. P. Sakthinathan, S. Vijayakumar, G. Vanangamudi, K. Thirumurthy, P. Mayavel, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 4 (2012) 66-75.

[25] R. Arulkumaran, S. Vijayakumar, R. Sundararajan, S. P. Sakthinathan, D. Kamalakkannan, R. Suresh, K. Ranganathan, P. R. Rajakumar, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 5 (2013) 21-38.

[26] S. Vijayakumar, R. Arulkumaran, R. Sundararajan, S. P. Sakthinathan, R. Suresh, D. Kamalakkannan, K. Ranganathan, K. Sathiyamoorthy, V. Mala, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 9(1) (2013) 68-86.

[27] Thirunarayanan G., Sekar K. G., *International Letters of Chemistry, Physics and Astronomy* 10 (2013) 18-34.

[28] R. Sundararajan, R. Arulkumaran, S. Vijayakumar, D. Kamalakkannan, R. Suresh, S. John Joseph, K. Ranganathan, S. P. Sakthinathan, G. Vanangamudi, G. Thirunarayanan, *International Letters of Chemistry, Physics and Astronomy* 1 (2014) 67-73.

(Received 23 November 2013; accepted 29 November 2013)