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Enaminonitriles as building blocks in heterocyclic synthesis of some innovative *α*-naphthylamine derivatives of anticipated insecticidal activity against Egyptian cotton leafworm, *spodoptera littoralis* (Boisd.)

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Abstract
Enaminonitrile 2 was a valuable intermediate in organic synthesis, thus it reacted with various *N*-, *C*- and *O*-nucleophiles to furnish aminopyrido[2',3':3,4]pyrazolo[1,5-*a*]pyrimidine, triazolo[4,3-*a*]pyrimidinone, aminoisoxazole, benzo [4, 5] imidazo [1, 2-a]pyrimidine, aminopyridinone, hydroxylarylchromene, arylchromenes, pyrano [2,3-*d*]pyrimidinone and thiopyrano [2, 3-*d*] pyrimidinone incorporating *α*-naphthylamine moiety in a good yield. The chemical skeletons of the newly acquired compounds were interpreted by elemental analysis, FT-IR, MS and proton NMR spectroscopic techniques. Toxicological parameters showed a remarkable insecticidal action when the previously products were examined against the cotton leafworm, *Spodoptera littoralis*, under laboratory conditions. Regarding to LC_{50} and LC_{90} values, *α*-naphthylamine derivatives 7, 8, 9, 20 and 4 indicated a proper toxic effect with LC_{50} values of 19.551, 23.422, 28.181, 33.700 and 38.163 ppm, respectively, and toxicity index being 32.43, 27.07, 22.50, 18.81 and 16.61%, respectively, comparing with the already recommended insecticide, acetamiprid 20% SP (LC_{50} value, 6.340 ppm, toxicity index, 100%).

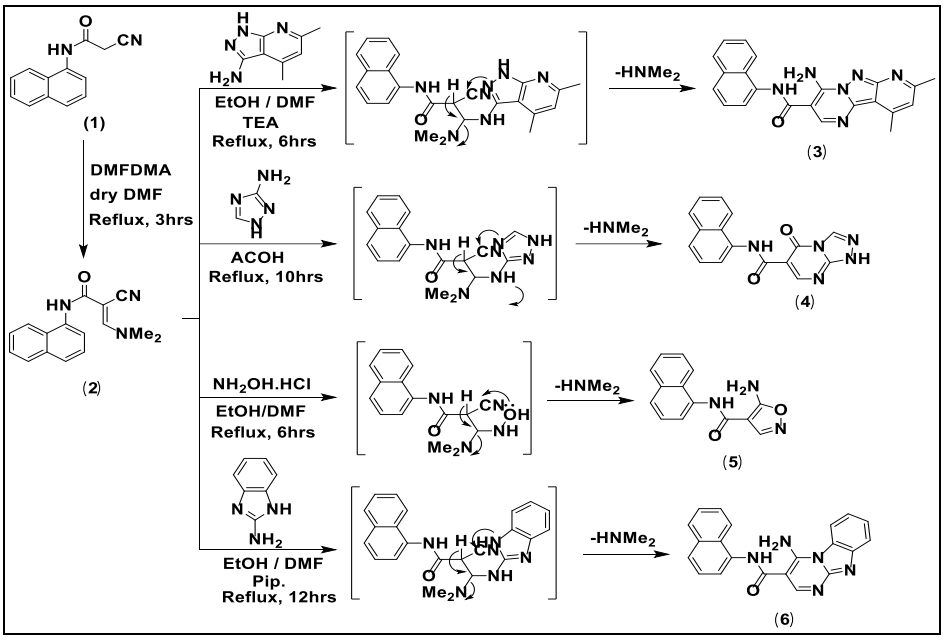
Keywords: cyanoacetanilide, enaminonitriles, *α*-naphthylamine, insecticidal activity, Egyptian cotton leafworm, *spodoptera littoralis*

Introduction
Functionally substituted enaminonitriles are excellent versatile, readily accessible building blocks for the synthesis of novel organic heterocyclic derivatives of promising anticipated biological activities, which will undoubtedly an important approach in the field of combinatorial chemistry **[1]**. The existence of numerous responsive centers in the molecules of these compounds increases its regioselective ability to design a great variety of novel biologically active polyfunctional heterocyclic compounds possessing various electrophilic and nucleophilic aspects [2]. The Egyptian cotton leafworm, *spodoptera littoralis* (Boisd.), is a highly polyphagous organism that is a pest of many cultivated plants and crops; they cause a lot of agricultural injuries by hasty reproduction, feeding on the leaves. As a result of feeding, plant yield is reduced. The goal of the entire work was the assessment of the insecticidal efficacy of the innovatively synthesized *α*-naphthylamine derivatives towards the cotton leafworm, *S. littoralis* [3].

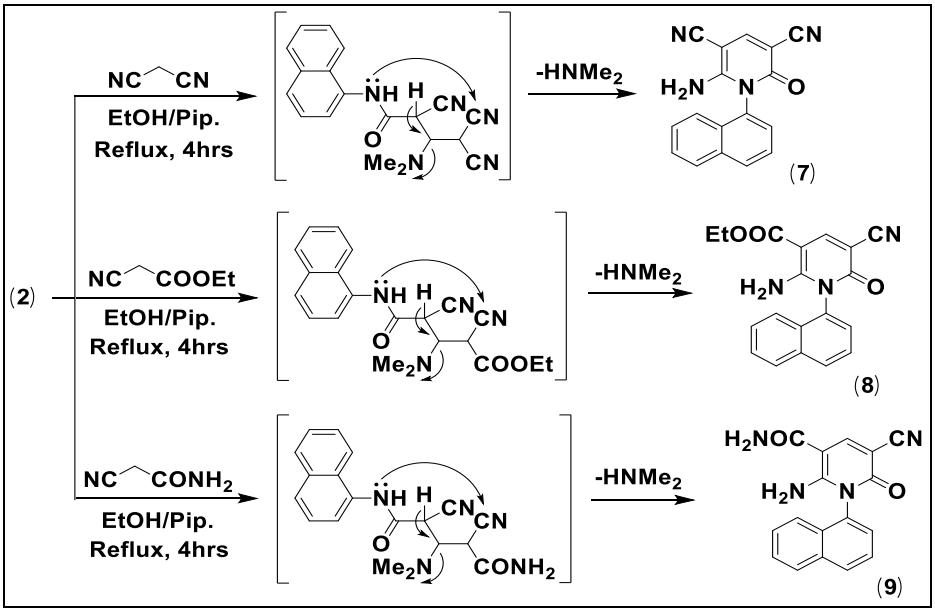
Results and Discussion
Chemistry
Target compounds were clarified by schemes (1-3). Thus, condensation of cyanoacetanilide 1 with (DMF-DMA) in refluxing dry DMF generated a brilliant reddish brown crystalline product formulated as (*E*)-2-cyano-3-(dimethylamino)-*N*-(naphthalen-1-yl)acrylamide 2 in adequate yield [4] (Scheme 1).
^{1}H NMR spectrum of enaminonitrile reagent 2 demonstrated four singlet signals at δ_H 3.22, 3.33, 7.90 and 9.26 ppm related to magnetically nonequivalent $N(CH_3)_2$ group, methine and *N*HCO protons, respectively, in addition to, a multiplet at δ_H 7.50- 7.97 ppm ascribed to seven aromatic protons. Also, its IR spectrum revealed absorption band at 3418 cm^{-1} due to (NH) groups, stretching absorption band at 2212 cm^{-1} ascribed to nitrile function (CN), beside a carbonyl group absorption band at 1680 cm^{-1}. Its MS spectrum indicated a parent ion peak at *m/z* 265 (M^+), which in compatibility with its molecular formula $C_{16}H_{15}N_3O$.
Enaminonitrile 2 was inspected as a key intermediate for designing of some complicated substituted polyfunctionally fused heterocyclic systems of anticipated broad spectrum bioresponses upon cyclocondensation with various *N*-, *C*- and *O*-nucleophiles [5]. These compounds could be Postulated to be synthesized *via* addition of *N*- or *C*- nucleophiles to the activated ethylenic double bond of enaminonitrile 2 followed by heterocyclization and elimination of a dimethylamine molecule as described in Scheme 1. Consequently, treatment of 2 with equimolar ratio of amino pyrazolo pyridine in hot ethanolic/DMF mixture using TEA as a catalyst generated pyrido pyrazolo pyrimidine derivative 3. The spectral data of 3 adopted the proposed structure. Hence, its IR

spectrum demonstrated no bands related to cyano function and displayed distinctive stretching absorption bands at 3465, 3380, 3296 and 1665 cm^{-1} certified to NH, NH_2, and amidic CO functions, respectively. Its MS spectrum revealed a parent ion peak (M^+), at *m/z* 382, equivalent to a molecular formula $C_{22}H_{18}N_6O$. Similarly, plausible yields of triazolo pyrimidinone 4, amino isoxazole 5 and benzo imidazo pyrimidine 6 derivatives were also acquired *via* regioselectively reaction of precursor 2 with 3-amino-1*H*-1,2,4-triazole in refluxing ACOH, hydroxylamine hydrochloride and 2-aminobenzimidazole in boiling ethanolic DMF piperidine solution, respectively. Spectra of compounds 4, 5 and 6 indicated no nitrile functions in the IR spectra and showed a molecular ion peaks (M^+), at *m/z* 305, 253 and 353 due to the molecular formulas $C_{16}H_{11}N_5O_2$, $C_{14}H_{11}N_3O_2$ and $C_{21}H_{15}N_5O$, respectively.

Otherwise, the applicability and synthetic potentiality of the enaminonitrile precursor 2 was also inspected upon cyclocondensation with different *C*- and *O*- nucleophiles to furnish some complicated polyfunctionally substituted fused 2-pyridone and chromenone derivatives incorporating *α*-naphthylamine moiety for which a wide variety of biological activity might be estimated [6-16].

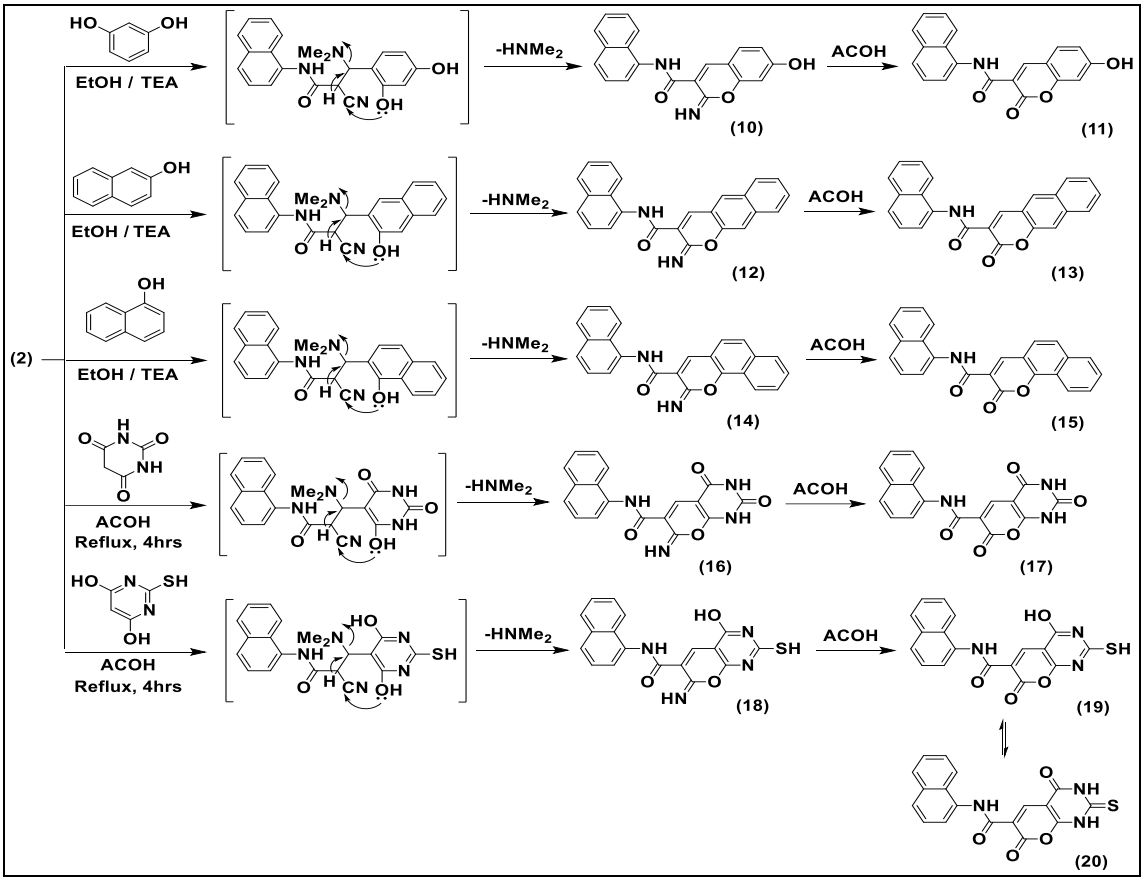


Scheme 1: Synthesis of enaminonitrile, pyrido pyrazolo pyrimidine, triazolo pyrimidinone, amino isoxazole and benzo imidazo pyrimidine derivatives



Scheme 2: Synthesis of 2-pyridone derivatives

Subsequently, treatment of enaminonitrile 2 with equimolar ratios of malononitrile, ethyl cyanoacetate and 2cyanoacetamide in ethanol under refluxing conditions and catalytic TEA, achieved the isolated polysubstituted 2-pyridones 7, 8 and 9 (Scheme 2).



Scheme 3: Synthesis of chromene derivatives

On the other hands, behavior of precursor 2 was also studied towards phenolic reagents such as resorcinol, *β*-naphthol and *α*-naphthol, furthermore, barbituric acid and thio barbituric acid, to afford anticipated bioactive coumarines 11, 13, 15, 17 and 20, respectively, (Scheme 3). The structures of the isolated products were in complete harmony with its elemental analysis and spectral data. Thus, The MS of compounds 7, 8, 9, 11, 13, 15, 17 and 20 showed a molecular ion peaks (M^+), at *m/z* 286, 333, 304, 331, 365, 365, 349 and 365 ascribed to the molecular formulas $C_{17}H_{10}N_4O$, $C_{19}H_{15}N_3O_3$, $C_{17}H_{12}N_4O_2$, $C_{20}H_{13}NO_4$, $C_{24}H_{15}NO_3$, $C_{24}H_{15}NO_3$, $C_{18}H_{11}N_3O_5$ and $C_{18}H_{11}N_3O_4S$, respectively.

Insecticidal activity

Toxicity test for Cotton leaf worm (S. littoralis, Family; Lepidoptera)

In continuous to our research, a laboratory insecticidal assessment was carried out to evaluate the toxic efficacy of the twelve innovatively synthesized tested compounds towards the freshly 2nd instar larval stage of the dangerous pest, cotton leafworm, *S. littoralis* (Boisd.) of laboratory strain, in Table 1. After 3 days of exposure, potent toxic effects were clearly observed owing to the examined insecticides, comparing with the already recommended, Acetamiprid insecticide 20% SP, that recorded the highest toxicity with LC_{50} value, 6.340 ppm, toxicity index, 100%. Also, *α*-naphthylamines 7, 8, 9, 20 and 4 displayed proper results with LC_{50}'s values 19.551, 23.422, 28.181, 33.700 and 38.163 ppm, respectively, and toxicity index being 32.43, 27.07, 22.50, 18.81 and 16.61%, respectively

Table 1: toxicological efficacy of the newly synthesized *α*-naphthylamine derivatives against 2nd instar larval stage of *S. littoralis* (Boisd.) comparing with, Acetamiprid insecticide 20% SP after 3 days of exposure.

Tested compounds	LC_{50} (ppm) and confidence limits at 95%	LC_{90} (ppm) and confidence limits at 95%	Slope	Toxicity index % at LC_{50} value
Acetamiprid 20% SP	6.340 3.439 8.527	27.800 19.674 60.688	1.996+/-0.458	100
7	19.551 15.320 23.370	55.570 44.457 79.525	2.825+/-0.427	32.43
8	23.422 18.770 27.873	69.990 54.249 107.988	2.696+/-0.421	27.07
9	28.181 23.230 33.429	83.597 63.331 136.340	2.714+/-0.432	22.50
20	33.700 28.508 39.932	93.399 70.341 155.254	2.895+/-0.463	18.81
4	38.163 32.570 43.741	92.382 73.128 143.289	3.338+/-0.575	16.61
17	43.810 38.152 50.520	103.776 80.802 167.263	3.422+/-0.591	14.47

3	50.592 44.498 59.373	115.538 88.566 193.903	3.575+/-0.625	12.53
6	55.822 50.129 62.730	110.618 90.215 163.623	4.315+/-0.748	11.36
5	62.910 57.967 68.617	107.938 93.778 135.609	5.466+/-0.744	10.08
11	71.258 65.786 78.591	118.559 101.064 159.618	5.769+/-0.959	8.90
13	78.351 73.571 83.299	116.070 103.742 141.034	7.509+/-1.138	8.09
15	85.647 80.911 91.966	119.086 106.667 147.622	8.953+/-1.586	7.40

Note: Toxicity index is defined as the ratio of the most effective compound's LC_{50} value to the other tested compound's LC_{50} value multiplying by 100.

Experimental

(E)-2-cyano-3-(dimethylamino)-N-(naphthalen-1-yl) acrylamide (2)

Condensation of cyanoacetanilide 1 (10.0 g, 0.048 mol) with *N*,*N*-dimethylformamide dimethylacetal (6.35 mL, 0.048 mol) in a 3 h, 25 ML refluxing dry DMF. The precipitate formed just the reaction content cooled to room temperature. The yielded enaminonitrile 2 was collected in pure form after washing with ethanol and recrystallization by EtOH/DMF mixture.

Brilliant reddish brown crystals; mp 145-147 ºC; yield 92%; IR (KBr) *ν*/cm^{-1}: 3418 (NH), 2212 (CN), 1680 (CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 3.22 (s, 3H, *N*CH$_3$), 3.33 (s, 3H, *N*CH$_3$), 7.50-7.97 (m, 7H, Ar-H), 7.90 (s, 1H, CH=), 9.26 (s, 1H, *N*HCO). MS *m/z* (%): 265 (M$^+$, 2.03), 247 (14.21), 217 (10.22), 182 (5.13), 146 (11.93), 114 (100), 95 (30.33), 73 (15.05), 69 (55.71), 55 (35.97). Anal. for $C_{16}H_{15}N_3O$ (265.32): calcd.: C, 72.43; H, 5.70; N, 15.84%; Found: C, 72.01; H, 5.35; N, 15.79%.

Reaction of enaminonitrile 2 with *N*-nucleophiles

Enaminonitrile 2 (0.4 g, 0.002 mol) was added to equimolar portions of 3-amino-4,6-dimethyl-1*H*-pyrazolo[3,4-*b*]pyridine (0.25 g), 3-amino-1*H*-1,2,4-triazole (0.13 g), hydroxylamine hydrochloride (0.1 g) and 2-aminobenzimidazole (0.2 g) in refluxing 6h 20 mL EtOH/DMF/drops TEA, 10h 20 mL ACOH, 6h 20 mL EtOH/DMF and 12h 20 mL EtOH/DMF/drops Pip., respectively. After cooling to r.t, the reaction contents added drop wise to a crushed ice/water blend acidified by few drops of HCl. The collected precipitates were purified by recrystallization from a mixture of EtOH/DMF (4:1) to acquire 3, 4, 5 and 6, respectively.

4-amino-8, 10-dimethyl-N-(naphthalen-1-yl) pyrido [2', 3':3, 4] pyrazolo[1,5-a]pyrimidine-3-carboxamide (3)

Dark red crystals; mp 160-162 ºC; yield 83%; IR (KBr) *ν*/cm^{-1}: 3465 (NH), 3380, 3296 (NH$_2$), 1665 (CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 2.48 (s, 3H, CH$_3$), 2.68 (s, 3H, CH$_3$), 6.87 (s, 1H, CH=), 7.08-8.12 (m, 7H, Ar-H), 8.20 (s, 1H, *N*CH=), 10.59 (s, 1H, *N*HCO). MS *m/z* (%): 382 (M$^+$, 10.93), 367 (25.04), 352 (33.12), 336 (22.50), 321 (9.03), 293 (7.66), 267 (15.73), 243 (35.25), 215 (44.35), 187 (14.25), 127 (100), 76 (85.32), 51 (87.45). Anal. for $C_{22}H_{18}N_6O$ (382.43): calcd.: C, 69.10; H, 4.74; N, 21.98%; Found: C, 69.01; H, 4.69; N, 21.44%.

N-(naphthalen-1-yl)-5-oxo-1,5-dihydro-[1,2,4]triazolo[4,3-a]pyrimidine-6-carboxamide (4)

Dark red crystals; mp 180-182 ºC; yield 84%; IR (KBr) *ν*/cm^{-1}: 3420, 3390 (2NH), 1688, 1675 (2CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 7.11-8.14 (m, 7H, Ar-H), 7.94 (s, 1H, triazole CH=), 9.46 (s, 1H, pyrimidinone CH=), 10.26 (s, 1H, *N*HCO). MS *m/z* (%): 305 (M$^+$, 20.18), 290 (33.04), 276 (15.35), 264 (9.65), 224 (8.15), 212 (35.16), 184 (45.14), 172 (43.98), 144 (56.12), 129 (100), 78 (79.17), 55 (93.04). Anal. for $C_{16}H_{11}N_5O_2$ (305.30): calcd.: C, 62.95; H, 3.63; N, 22.94%; Found: C, 62.03; H, 3.15; N, 22.02%.

5-amino-N-(naphthalen-1-yl) isoxazole-4-carboxamide (5)

Brown powder; mp 175-177 ºC; yield 63%; IR (KBr) *ν*/cm^{-1}: 3421 (NH), 3392, 3279 (NH$_2$), 1685 (CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 7.01-8.05 (m, 7H, Ar-H), 8.48 (s, 1H, oxazole CH=), 10.57 (s, 1H, *N*HCO). MS *m/z* (%): 253 (M$^+$, 26.81), 237 (53.08), 207 (23.15), 195 (14.18), 183 (9.23), 155 (100), 140 (73.65), 127 (84.15), 76 (77.81), 51 (93.03). Anal. for $C_{14}H_{11}N_3O_2$ (253.26): calcd.: C, 66.40; H, 4.38; N, 16.59%; Found: C, 66.13; H, 4.28; N, 16.33%.

4-amino-N-(naphthalen-1-yl) benzo [4,5]imidazo[1,2-a]pyrimidine-3-carboxamide (6)

Dark brown powder; mp 165-167 ºC; yield 86%; IR (KBr) *ν*/cm^{-1}: 3465 (NH), 3395, 3280 (NH$_2$), 1672 (CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 7.12-8.52 (m, 11H, Ar-H), 8.23 (s, 1H, pyrimidine CH=), 11.21 (s, 1H, *N*HCO). MS *m/z* (%): 353 (M$^+$, 33.72), 337 (10.91), 311 (12.19), 285 (40.12), 245 (53.87), 191 (70.57), 163 (100), 148 (62.04), 127 (25.81), 71 (93.14), 55 (97.48). Anal. for $C_{21}H_{15}N_5O$ (353.39): calcd.: C, 71.38; H, 4.28; N, 19.82%; Found: C, 71.12; H, 4.15; N, 19.38%.

Reaction of enaminonitrile 2 with *C*-nucleophiles

To a 25 mL EtOH, a mixture of enaminonitrile 2 (0.4 g, 0.002 mol) and an equimolar ratio of the appropriate *C*-nucleophiles namely malononitrile (0.1 g), ethyl cyanoacetate (0.16 mL) and 2-cyanoacetamide (0.13 g) including drops of catalytic piperidine was refluxed for 4 h to furnish pyridine derivatives 7, 8 and 9, respectively. Also, precursor 2 (0.4 g, 0.002 mol) was heated with resorcinol (0.17 g), *β*-naphthol (0.22 g) and *α*-naphthol (0.22 g) in EtOH/TEA for 4 h to get coumarines 11, 13 and 15, respectively. Likewise, enaminonitrile 2

(0.4 g, 0.002 mol) was refluxed with barbituric acid (0.19 g) and thiobarbituric acid (0.22 g)] in ACOH for 4 h to acquire coumarines 17 and 20, the reaction content was allowed to cool, and then added drop by drop to a crushed ice/water blend acidified by drops of HCl. The formed output was filtred, recrystallized from EtOH/DMF (4:1).

6-amino-1-(naphthalen-1-yl)-2-oxo-1,2-dihydropyridine-3,5-dicarbonitrile (7)
Dark brown crystals; mp 150-152 °C; yield 79%; IR (KBr) ν/cm^{-1}: 3362, 3254 (NH_2), 2226, 2212 (2CN), 1685 (CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 7.15-8.25 (m, 7H, Ar-H), 7.72 (s, 1H, pyridinone CH=). MS *m/z* (%): 286 (M^+, 100), 260 (43.05), 234 (40.37), 218 (35.13), 143 (82.51), 92 (93.67), 77 (94.17). Anal. for $C_{17}H_{10}N_4O$ (286.29): calcd.: C, 71.32; H, 3.52; N, 19.57%; Found: C, 71.02; H, 3.27; N, 19.18%.

Ethyl 2-amino-5-cyano-1-(naphthalen-1-yl)-6-oxo-1,6-dihydropyridine-3-carboxylate (8)
Deep red powder; mp 168-170 °C; yield 69%; IR (KBr) ν/cm^{-1}: 3365, 3298 (NH_2), 2225 (CN), 1745, 1672 (2CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 1.25 (t, 3H, CH_3), 4.21 (s, 2H, CH_2), 7.12-8.15 (m, 7H, Ar-H), 8.55 (s, 1H, pyridinone CH=). MS *m/z* (%): 333 (M^+, 5.35), 318 (10.12), 304 (11.15), 260 (24.85), 244 (33.15), 218 (15.17), 157 (48.43), 117 (100), 77 (79.61), 51 (83.26). Anal. for $C_{19}H_{15}N_3O_3$ (333.35): calcd.: C, 68.46; H, 4.54; N, 12.61%; Found: C, 68.26; H, 4.32; N, 12.18%.

2-amino-5-cyano-1-(naphthalen-1-yl)-6-oxo-1,6-dihydropyridine-3-carboxamide (9)
Brown powder; mp 140-142 °C; yield 78%; IR (KBr) ν/cm^{-1}: br 3425 ($2NH_2$), 2220 (CN), 1679, 1660 (2CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 7.08-8.25 (m, 7H, Ar-H), 8.56 (s, 1H, pyridinone CH=). MS *m/z* (%): 304 (M^+, 3.18), 262 (39.12), 246 (43.87), 220 (41.91), 143 (23.45), 129 (100), 79 (91.11), 55 (89.25). Anal. for $C_{17}H_{12}N_4O_2$ (304.31): calcd.: C, 67.10; H, 3.97; N, 18.41%; Found: C, 66.96; H, 3.88; N, 18.02%.

7-hydroxy-N-(naphthalen-1-yl)-2-oxo-2H-chromene-3-carboxamide (11)
Red crystals; mp 180-182 °C; yield 80%; IR (KBr) ν/cm^{-1}: 3512 (OH), 3345 (NH) 1735, 1675 (2CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 6.85-8.21 (m, 10H, Ar-H), 8.45 (s, 1H, coumarine CH=), 10.31 (s, 1H, *N*HCO), 10.64 (s, 1H, OH). MS *m/z* (%): 331 (M^+, 18.34), 314 (63.14), 263 (24.18), 171 (100), 143 (74.13), 128 (65.04), 77 (94.12), 55 (87.54). Anal. for $C_{20}H_{13}NO_4$ (331.33): calcd.: C, 72.50; H, 3.96; N, 4.23%; Found: C, 72.11; H, 3.35; N, 4.02%.

N-(naphthalen-1-yl)-2-oxo-2H-benzo[g]chromene-3-carboxamide (13)
Brown powder; mp 190-192 °C; yield 87%; IR (KBr) ν/cm^{-1}: 3365 (NH) 1730, 1672 (2CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 7.05-8.21 (m, 13H, Ar-H), 8.48 (s, 1H, coumarine CH=), 10.51 (s, 1H, *N*HCO). MS *m/z* (%): 365 (M^+, 10.51), 313 (13.51), 263 (25.35), 169 (16.85), 141 (100), 126 (63.01), 77 (92.51), 51 (63.45). Anal. for $C_{24}H_{15}NO_3$ (365.39): calcd.: C, 78.89; H, 4.14; N, 3.83%; Found: C, 78.23; H, 3.99; N, 3.49%.

N-(naphthalen-1-yl)-2-oxo-2H-benzo[h]chromene-3-carboxamide (15)
Brown powder; mp 188-190 °C; yield 85%; IR (KBr) ν/cm^{-1}: 3372 (NH) 1742, 1665 (2CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 7.08-8.15 (m, 13H, Ar-H), 8.48 (s, 1H, coumarine CH=), 10.55 (s, 1H, *N*HCO). MS *m/z* (%): 365 (M^+, 13.25), 313 (12.42), 263 (24.25), 169 (12.01), 141 (100), 126 (48.56), 77 (90.25), 51 (48.35). Anal. for $C_{24}H_{15}NO_3$ (365.39): calcd.: C, 78.89; H, 4.14; N, 3.83%; Found: C, 78.34; H, 3.95; N, 3.56%.

N-(naphthalen-1-yl)-2,4,7-trioxo-1,3,4,7-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carboxamide (17)
Dark brown powder; mp 170-172 °C; yield 63%; IR (KBr) ν/cm^{-1}: 3420, 3380, 3276 (3NH) 1741, 1673, 1660, 1638 (4CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 6.89-8.13 (m, 7H, Ar-H), 8.45 (s, 1H, coumarine CH=), 9.98 (s, 1H, *N*HCO), 10.58 (s, 1H, *N*HCO), 11.32 (s, 1H, *N*HCO). MS *m/z* (%): 349 (M^+, 2.43), 263 (31.77), 194 (100), 166 (41.95), 151 (61.71), 100 (11.18), 77 (52.41), 51 (53.12). Anal. for $C_{18}H_{11}N_3O_5$ (349.30): calcd.: C, 61.89; H, 3.17; N, 12.03%; Found: C, 61.73; H, 3.09; N, 11.93%.

N-(naphthalen-1-yl)-4,7-dioxo-2-thioxo-1,3,4,7-tetrahydro-2H-pyrano[2,3-d]pyrimidine-6-carboxamide (20)
Dark red powder; mp 180-182 °C; yield 58%; IR (KBr) ν/cm^{-1}: 3421, 3385, 3282 (3NH) 1735, 1681, 1652 (3CO); ^{1}H NMR (500 MHz, DMSO-d_6): δ_H ppm 6.95-8.10 (m, 7H, Ar-H), 8.55 (s, 1H, coumarine CH=), 10.15 (s, 1H, *N*HCO), 11.43 (s, 1H, *N*HCO), 13.25 (s, 1H, *N*HCO). MS *m/z* (%): 365 (M^+, 13.57), 321 (1.09), 291 (15.17), 263 (34.91), 182 (47.80), 154 (100), 139 (33.14), 88 (16.34), 77 (91.15), 55 (95.25). Anal. for $C_{18}H_{11}N_3O_4S$ (365.36): calcd.: C, 59.17; H, 3.03; N, 11.50%; Found: C, 58.97; H, 2.87; N, 11.17%.

Laboratory Bioassay
Cotton leaf worm (Spodoptera littoralis, Family; Lepidoptera)
A laboratory susceptible strain of cotton leafworm *S. littoralis* (Boisd.) was prepared as depicted by El-Defrawi *et al.* (1964) [17].

Pesticides
Acetamiprid 20% SP, (Figure 1).

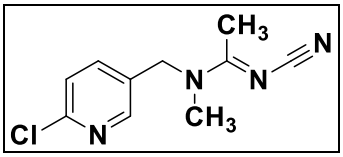


Fig 1

IUPAC name: *N*-[(6-chloro-3-pyridyl) methyl]-*N'*-cyano-*N*-methyl-acetamidine

Toxicological studies

Toxicological Studies were carried out according to the beforehand stated technique [3, 18-20].

Sadek (2003) [21] designed the examinations *via* the leaf dip technique. Statistical calculations were carried out according to Abbott's formula [22], and Finney's method [23]. Moreover, the efficacy of the tested insecticides was evaluated by:

Toxicity index = LC_{50} of the maximum toxic compound/LC_{50} of the examined compound x 100, as depicated by Sun [24].

Conclusions

In our research paper, enaminonitriles were valuable building blocks for the synthesis of newly anticipated insecticidal heterocyclic derivatives incorporating *α*-naphthylamine nucleus. These compounds indicated potent insecticidal effect against the 2nd instar larvae of cotton leafworm, *S. littoralis*. under laboratory conditions. *α*-naphthylamines 7, 8, 9, 20 and 4 demonstrated a proper toxic effect with LC_{50} values of 19.551, 23.422, 28.181, 33.700 and 38.163 ppm, respectively, and toxicity index being 32.43, 27.07, 22.50, 18.81 and 16.61%, respectively, comparing with the already recommended insecticide, acetamiprid 20% SP (LC_{50} value, 6.340 ppm, toxicity index, 100%).

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