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Green methodologies in organic synthesis: Microwave assisted solvent- and catalyst-free synthesis of enaminones and their conversion into 1,3,5-trisubstituted benzenes as well as 3-aroyl-6-substituted pyridines

Morsy Ahmed El-Apasery[a,b], Saleh Mohamed Al-Mousawi[a,*] and Mohamed Helmy Elnagdi[a]

[a] *Department of Chemistry, Faculty of Science, Kuwait University, Safat, 13060, Kuwait*
[b] *Dyeing, Printing and Textile Auxiliaries Department, Textile Research Division, National Research Centre, Dokki, Giza, 12622, Egypt*

**Corresponding author at: Department of Chemistry, Faculty of Science, Kuwait University, Safat, 13060, Kuwait. Tel.: +96599728120; fax: +96524816482.*
E-mail address: saleh.almousawi@yahoo.com (S.M. Al-Mousawi).

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ABSTRACT

Enaminones were obtained in good yields via condensing methyl ketones with (*N*,*N*-dimethylformamide dimethyl acetal) DMF-DMA under microwave irradiation in absence of solvent. These enaminones were readily converted into 1,3,5-trisubstituted benzenes. Reacting enaminones in presence of ammonium acetate has afforded pyridine derivatives.

Supplementary Materials

Crystal and molecular structure C14 H14 N2 O3

Experimental
Crystal data

$C_{14}H_{14}N_2O_3$
$C_{14}H_{14}N_2O_3$
M_r = 258.277
Triclinic
P1
a = 7.9478 (5)Å
b = 8.4931 (6)Å
c = 11.1333 (8)Å
α = 88.231 (2)°
β = 83.557 (2)°
γ = 62.615 (2)°
V = 662.90 (8)Å^3
Z = 2
D_x = 1.294 Mg m^{-3}
Density measured by: not measured
fine-focus sealed tube
Mo *K*α radiation
λ = 0.71073
Cell parameters from 2207
θ = 2.910—27.485 °
μ = 0.09 mm^{-1}
T = 298 K
Cube

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yellow
Crystal source:Local laboratory

Data collection

KappaCCD
CCD
Absorption correction: none
3228 measured reflections
2435 independent reflections
1252 observed reflections
Criterion: I> 3.00 sigma(I)
R_{int} = 0.036
θ_{max} = 27.58 °
h = -9 →9
k = -7 →10
l = -14 →14
h = 0 →9
k = -9 →10
l = -14 →14

Refinement

Refinement on F^2
fullmatrix least squares refinement
R(all) = 0.111
R(gt) = 0.064
wR(ref) = 0.119
wR(all) = 0.126
wR(gt)= 0.119
S(ref) = 1.537
S(all) = 1.320
S(gt) = 1.537
1251 reflections
172 parameters
0 restraints
Only coordinates of H atoms refined
Calculated weights sigma
Δ/σ_{max} = 0.009
$\Delta\rho_{max}$ = 0.40eÅ^3
$\Delta\rho_{min}$ = -0.32eÅ^3
Extinction correction: none
Atomic scattering factors from Waasmaier & Kirfel, 1995

Data collection: KappaCCD
Cell refinement: HKL Scalepack (Otwinowski & Minor 1997)
Data reduction: Denzo and Scalepak (Otwinowski & Minor, 1997)
Program(s) used to solve structure: *SIR*92 (Altomare et al., 1994)
Program(s) used to refine structure: maXus(Mackay et al., 1999)
Molecular graphics: *ORTEP* (Johnson, 1976)
Software used to prepare material for publication: maXus(Mackay et al., 1999)

Table 11. *Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2)U_{eq} = 1/3$\Sigma_i\Sigma_j$ U_{ij} a_i*a_j* a_i.a_j .*

	x	y	z	U_{eq}	Occ
O1	0.7613 (4)	0.3755 (5)	0.6495 (3)	0.082 (2)	1.00
N2	0.9786 (4)	0.3770 (4)	0.7704 (3)	0.0490 (17)	1.00
O3	1.2903 (5)	0.1002 (4)	0.6662 (3)	0.085 (2)	1.00
O4	1.1590 (4)	0.3255 (5)	0.9298 (3)	0.089 (2)	1.00
N5	0.9341 (5)	0.7328 (4)	0.6701 (3)	0.063 (2)	1.00
C6	0.8236 (6)	0.3521 (5)	0.7462 (4)	0.052 (2)	1.00
C7	1.0725 (5)	0.5687 (5)	0.6411 (3)	0.053 (2)	1.00
C8	0.7574 (6)	0.2936 (5)	0.8605 (3)	0.051 (2)	1.00
C9	1.2704 (6)	0.2467 (6)	0.6327 (4)	0.060 (2)	1.00
C10	0.8793 (5)	0.2783 (5)	0.9461 (3)	0.053 (2)	1.00
C11	0.5826 (7)	0.1994 (7)	1.0044 (5)	0.081 (3)	1.00
C12	0.6041 (6)	0.2587 (6)	0.8881 (4)	0.065 (3)	1.00
C13	1.0260 (6)	0.3257 (5)	0.8889 (4)	0.058 (2)	1.00
C14	1.4182 (6)	0.2619 (6)	0.5431 (4)	0.067 (2)	1.00
C15	1.1037 (5)	0.4064 (5)	0.6798 (3)	0.045 (2)	1.00
C16	0.7037 (7)	0.1812 (8)	1.0874 (4)	0.088 (3)	1.00

C17	0.9455 (8)	0.8850 (6)	0.6144 (5)	0.086 (3)	1.00
C18	0.7678 (6)	0.7750 (6)	0.7562 (4)	0.070 (3)	1.00
C19	0.8525 (7)	0.2234 (8)	1.0608 (4)	0.085 (3)	1.00
H11	0.482051	0.167387	1.025726	0.081096	1.00
H12	0.518497	0.277796	0.828552	0.066302	1.00
H14A	1.383831	0.383895	0.526388	0.063773	1.00
H14B	1.427963	0.200407	0.469725	0.063773	1.00
H14C	1.538704	0.207904	0.575622	0.063773	1.00
H16	0.687076	0.139490	1.166822	0.086355	1.00
H17A	0.835548	0.991715	0.644548	0.081590	1.00
H17B	0.949850	0.876513	0.528173	0.081590	1.00
H17C	1.058681	0.887690	0.634045	0.081590	1.00
H18A	0.688060	0.900971	0.762606	0.067498	1.00
H18B	0.807087	0.730590	0.833943	0.067498	1.00
H18C	0.697789	0.719042	0.728462	0.067498	1.00
H19	0.935789	0.215985	1.119249	0.084618	1.00
H7	1.177401	0.550751	0.581707	0.052555	1.00

Table 22. *Anisotropic displacement parameters (Å²)*

	U_{11}	U_{12}	U_{13}	U_{22}	U_{23}	U_{33}
O1	0.079 (2)	-0.0592 (19)	-0.0179 (16)	0.107 (2)	0.0184 (16)	0.0460 (18)
N2	0.0455 (19)	-0.0293 (15)	-0.0019 (15)	0.0541 (19)	0.0087 (14)	0.0367 (18)
O3	0.097 (3)	-0.0207 (17)	0.012 (2)	0.0428 (17)	0.0124 (15)	0.085 (2)
O4	0.066 (2)	-0.066 (2)	-0.0198 (17)	0.134 (3)	0.0245 (19)	0.0525 (19)
N5	0.066 (2)	-0.0226 (19)	0.0108 (19)	0.052 (2)	0.0065 (16)	0.048 (2)
C6	0.049 (2)	-0.0270 (19)	-0.0107 (19)	0.054 (2)	0.0081 (18)	0.040 (2)
C7	0.048 (2)	-0.024 (2)	0.0013 (18)	0.055 (2)	0.0030 (18)	0.040 (2)
C8	0.047 (2)	-0.0249 (18)	-0.0014 (19)	0.053 (2)	0.0081 (18)	0.040 (2)
C9	0.055 (3)	-0.025 (2)	-0.005 (2)	0.061 (3)	0.007 (2)	0.046 (2)
C10	0.049 (2)	-0.031 (2)	-0.0044 (19)	0.062 (2)	0.0074 (18)	0.035 (2)
C11	0.067 (3)	-0.055 (3)	0.010 (3)	0.095 (3)	0.009 (3)	0.066 (3)
C12	0.054 (2)	-0.045 (2)	-0.006 (2)	0.082 (3)	0.003 (2)	0.048 (2)
C13	0.048 (2)	-0.032 (2)	-0.004 (2)	0.066 (3)	0.007 (2)	0.047 (3)
C14	0.051 (2)	-0.014 (2)	0.009 (2)	0.062 (3)	-0.001 (2)	0.063 (3)
C15	0.042 (2)	-0.0224 (18)	0.0025 (18)	0.046 (2)	0.0050 (16)	0.0355 (19)
C16	0.074 (3)	-0.059 (3)	-0.003 (3)	0.118 (4)	0.023 (3)	0.053 (3)
C17	0.100 (4)	-0.030 (3)	0.007 (3)	0.056 (3)	0.015 (2)	0.074 (3)
C18	0.062 (3)	-0.023 (2)	0.005 (3)	0.061 (3)	-0.003 (2)	0.065 (3)
C19	0.065 (3)	-0.060 (3)	-0.013 (2)	0.123 (4)	0.030 (3)	0.051 (3)

Table 3.3 *Geometric parameters (Å, °)*

O1—C6	1.209 (5)
N2—C6	1.397 (6)
N2—C13	1.414 (6)
N2—C15	1.434 (5)
O3—C9	1.230 (5)
O4—C13	1.196 (5)
N5—C7	1.339 (6)
N5—C17	1.453 (6)
N5—C18	1.448 (6)
C6—C8	1.481 (6)
C7—C15	1.349 (5)
C8—C10	1.396 (6)
C8—C12	1.382 (7)
C9—C14	1.504 (6)
C9—C15	1.450 (6)
C10—C13	1.475 (6)
C10—C19	1.374 (6)
C11—C12	1.396 (7)
C11—C16	1.363 (8)
C16—C19	1.386 (7)
C7—H7	0.960 (4)
C11—H11	0.960 (5)
C12—H12	0.960 (5)
C14—H14A	0.960 (5)
C14—H14B	0.960 (6)
C14—H14C	0.960 (5)
C16—H16	0.960 (5)
C17—H17A	0.960 (5)

C17—H17B	0.960 (6)
C17—H17C	0.960 (7)
C18—H18A	0.960 (5)
C18—H18B	0.960 (5)
C18—H18C	0.960 (6)
C19—H19	0.960 (5)
C6—N2—C13	111.2 (4)
C6—N2—C15	124.4 (4)
C13—N2—C15	122.6 (4)
C7—N5—C17	120.0 (4)
C7—N5—C18	125.0 (4)
C17—N5—C18	115.0 (4)
O1—C6—N2	124.8 (4)
O1—C6—C8	129.0 (5)
N2—C6—C8	106.3 (4)
N5—C7—C15	133.3 (4)
C6—C8—C10	108.0 (4)
C6—C8—C12	130.2 (4)
C10—C8—C12	121.8 (4)
O3—C9—C14	120.5 (4)
O3—C9—C15	120.1 (4)
C14—C9—C15	119.4 (4)
C8—C10—C13	108.4 (4)
C8—C10—C19	120.5 (4)
C13—C10—C19	131.0 (4)
C12—C11—C16	121.7 (5)
C8—C12—C11	116.5 (5)
N2—C13—O4	124.4 (4)
N2—C13—C10	105.8 (4)
O4—C13—C10	129.7 (4)
N2—C15—C7	123.5 (3)
N2—C15—C9	114.7 (3)
C7—C15—C9	121.8 (4)
C11—C16—C19	121.5 (4)
C10—C19—C16	117.9 (5)
N5—C7—H7	120.3 (4)
C15—C7—H7	106.4 (4)
C12—C11—H11	119.1 (6)
C16—C11—H11	119.2 (5)
C8—C12—H12	119.5 (4)
C11—C12—H12	123.9 (5)
C9—C14—H14A	110.9 (4)
C9—C14—H14B	108.5 (5)
C9—C14—H14C	109.0 (4)
H14A—C14—H14B	109.5 (5)
H14A—C14—H14C	109.5 (6)
H14B—C14—H14C	109.5 (4)
C11—C16—H16	120.5 (5)
C19—C16—H16	118.0 (6)
N5—C17—H17A	109.4 (5)
N5—C17—H17B	109.8 (6)
N5—C17—H17C	109.2 (5)
H17A—C17—H17B	109.5 (6)
H17A—C17—H17C	109.5 (7)
H17B—C17—H17C	109.5 (5)
N5—C18—H18A	110.6 (4)
N5—C18—H18B	109.6 (4)
N5—C18—H18C	108.2 (5)
H18A—C18—H18B	109.5 (5)
H18A—C18—H18C	109.5 (5)
H18B—C18—H18C	109.5 (5)
C10—C19—H19	119.6 (5)
C16—C19—H19	122.5 (5)
C13—N2—C6—O1	-175.5 (5)
C6—N2—C13—O4	176.1 (6)
C13—N2—C6—C8	4.5 (3)
C6—N2—C13—C10	-4.7 (3)
C15—N2—C6—O1	-10.3 (4)
C6—N2—C15—C7	89.2 (5)
C15—N2—C6—C8	169.6 (5)
C6—N2—C15—C9	-91.5 (4)

C15—N2—C13—O4	10.7 (4)
C13—N2—C15—C7	-107.3 (5)
C13—N2—C15—C9	72.0 (4)
C15—N2—C13—C10	-170.1 (5)
C17—N5—C7—C15	177.4 (7)
C18—N5—C7—C15	-2.0 (4)
O1—C6—N2—C13	-175.5 (5)
O1—C6—N2—C15	-10.3 (4)
O1—C6—C8—C10	177.4 (6)
O1—C6—C8—C12	-3.4 (4)
N2—C6—C8—C10	-2.5 (3)
N2—C6—C8—C12	176.6 (6)
C8—C6—N2—C13	4.5 (3)
C8—C6—N2—C15	169.6 (5)
N5—C7—C15—N2	-0.1 (4)
N5—C7—C15—C9	-179.4 (7)
C15—C7—N5—C17	177.4 (7)
C15—C7—N5—C18	-2.0 (4)
C10—C8—C6—O1	177.4 (6)
C10—C8—C6—N2	-2.5 (3)
C6—C8—C10—C13	-0.2 (3)
C6—C8—C10—C19	-179.1 (5)
C12—C8—C6—O1	-3.4 (4)
C12—C8—C6—N2	176.6 (6)
C6—C8—C12—C11	178.0 (7)
C10—C8—C12—C11	-2.9 (4)
C12—C8—C10—C13	-179.5 (5)
C12—C8—C10—C19	1.6 (4)
O3—C9—C15—N2	3.8 (4)
O3—C9—C15—C7	-176.9 (6)
C14—C9—C15—N2	-176.1 (5)
C14—C9—C15—C7	3.3 (4)
C8—C10—C13—N2	2.9 (3)
C8—C10—C13—O4	-177.9 (6)
C13—C10—C8—C6	-0.2 (3)
C13—C10—C8—C12	-179.5 (5)
C19—C10—C8—C6	-179.1 (5)
C19—C10—C8—C12	1.6 (4)
C8—C10—C19—C16	1.1 (4)
C19—C10—C13—N2	-178.4 (6)
C19—C10—C13—O4	0.8 (5)
C13—C10—C19—C16	-177.5 (8)
C16—C11—C12—C8	1.7 (5)
C12—C11—C16—C19	1.0 (5)
C11—C12—C8—C6	178.0 (7)
C11—C12—C8—C10	-2.9 (4)
C8—C12—C11—C16	1.7 (5)
O4—C13—N2—C6	176.1 (6)
O4—C13—N2—C15	10.7 (4)
C10—C13—N2—C6	-4.7 (3)
N2—C13—C10—C8	2.9 (3)
C10—C13—N2—C15	-170.1 (5)
N2—C13—C10—C19	-178.4 (6)
O4—C13—C10—C8	-177.9 (6)
O4—C13—C10—C19	0.8 (5)
N2—C15—C7—N5	-0.1 (4)
C7—C15—N2—C6	89.2 (5)
C7—C15—N2—C13	-107.3 (5)
N2—C15—C9—O3	3.8 (4)
C9—C15—N2—C6	-91.5 (4)
C9—C15—N2—C13	72.0 (4)
N2—C15—C9—C14	-176.1 (5)
C7—C15—C9—O3	-176.9 (6)
C9—C15—C7—N5	-179.4 (7)
C7—C15—C9—C14	3.3 (4)
C11—C16—C19—C10	-2.4 (5)
C19—C16—C11—C12	1.0 (5)
C16—C19—C10—C8	1.1 (4)
C10—C19—C16—C11	-2.4 (5)

C16—C19—C10—C13	-177.5 (8)
C7—N5—C17—H17A	179.8 (6)
C7—N5—C17—H17B	59.6 (5)
C7—N5—C17—H17C	-60.5 (5)
C17—N5—C7—H7	-2.0 (4)
C7—N5—C18—H18A	179.9 (6)
C7—N5—C18—H18B	59.1 (4)
C7—N5—C18—H18C	-60.2 (4)
C18—N5—C7—H7	178.6 (6)
C18—N5—C17—H17A	-0.8 (4)
C18—N5—C17—H17B	-121.0 (6)
C18—N5—C17—H17C	119.0 (6)
C17—N5—C18—H18A	0.5 (4)
C17—N5—C18—H18B	-120.3 (5)
C17—N5—C18—H18C	120.4 (5)
H7—C7—N5—C17	-2.0 (4)
H7—C7—N5—C18	178.6 (6)
H7—C7—C15—N2	179.3 (5)
H7—C7—C15—C9	0.1 (3)
C6—C8—C12—H12	-3.0 (4)
C10—C8—C12—H12	176.1 (7)
O3—C9—C14—H14A	-179.4 (6)
O3—C9—C14—H14B	60.3 (5)
O3—C9—C14—H14C	-58.8 (5)
C15—C9—C14—H14A	0.4 (4)
C15—C9—C14—H14B	-119.9 (5)
C15—C9—C14—H14C	121.0 (5)
C8—C10—C19—H19	-178.7 (7)
C13—C10—C19—H19	2.8 (4)
C16—C11—C12—H12	-177.3 (8)
C12—C11—C16—H16	-179.6 (8)
H11—C11—C12—C8	-176.6 (7)
H11—C11—C12—H12	4.5 (5)
H11—C11—C16—C19	179.2 (8)
H11—C11—C16—H16	-1.4 (5)
C8—C12—C11—H11	-176.6 (7)
H12—C12—C8—C6	-3.0 (4)
H12—C12—C8—C10	176.1 (7)
H12—C12—C11—C16	-177.3 (8)
H12—C12—C11—H11	4.5 (5)
H14A—C14—C9—O3	-179.4 (6)
H14A—C14—C9—C15	0.4 (4)
H14B—C14—C9—O3	60.3 (5)
H14B—C14—C9—C15	-119.9 (5)
H14C—C14—C9—O3	-58.8 (5)
H14C—C14—C9—C15	121.0 (5)
N2—C15—C7—H7	179.3 (5)
C9—C15—C7—H7	0.1 (3)
C19—C16—C11—H11	179.2 (8)
C11—C16—C19—H19	177.4 (9)
H16—C16—C11—C12	-179.6 (8)
H16—C16—C11—H11	-1.4 (5)
H16—C16—C19—C10	178.2 (8)
H16—C16—C19—H19	-2.0 (5)
H17A—C17—N5—C7	179.8 (6)
H17A—C17—N5—C18	-0.8 (4)
H17B—C17—N5—C7	59.6 (5)
H17B—C17—N5—C18	-121.0 (6)
H17C—C17—N5—C7	-60.5 (5)
H17C—C17—N5—C18	119.0 (6)
H18A—C18—N5—C7	179.9 (6)
H18A—C18—N5—C17	0.5 (4)
H18B—C18—N5—C7	59.1 (4)
H18B—C18—N5—C17	-120.3 (5)
H18C—C18—N5—C7	-60.2 (4)
H18C—C18—N5—C17	120.4 (5)
C10—C19—C16—H16	178.2 (8)
H19—C19—C10—C8	-178.7 (7)
H19—C19—C10—C13	2.8 (4)
H19—C19—C16—C11	177.4 (9)
H19—C19—C16—H16	-2.0 (5)

O1—H14A^{i}	2.726 (3)
O1—H14C^{ii}	2.924 (4)
O1—H17A^{iii}	3.035 (4)
O1—H17B^{i}	2.913 (4)
O1—H7^{i}	2.674 (3)
O3—H14B^{iv}	2.836 (3)
O3—H16^{v}	2.672 (3)
O3—H17B^{i}	2.987 (5)
O4—H11^{vi}	2.625 (3)
O4—H12^{vi}	2.799 (3)
O4—H18B^{vii}	2.680 (3)
N5—H19^{vii}	2.790 (4)
C17—H17B^{viii}	2.893 (5)
C18—H11^{ix}	2.859 (5)
C18—H19^{vii}	2.896 (6)
H11—H11^{x}	2.7948
H11—H18A^{ix}	2.7642
H11—H18B^{ix}	2.4328
H11—H18C^{ix}	2.9119
H12—H14C^{ii}	2.8673
H12—H18A^{iii}	2.9245
H14B—H18C^{i}	2.4714
H14C—H17A^{xi}	2.4209
H16—H18C^{ix}	2.8399
H17A—H17B^{viii}	2.9574
H17B—H17B^{viii}	2.6026
H17B—H17C^{viii}	2.6374
H17C—H19^{vii}	2.8571
H18B—H19^{vii}	2.4001
O1—H14A^{i}	2.726 (3)
O1—H14C^{ii}	2.924 (4)
O1—H17A^{iii}	3.035 (4)
O1—H17B^{i}	2.913 (4)
O1—H7^{i}	2.674 (3)
O3—H14B^{iv}	2.836 (3)
O3—H16^{v}	2.672 (3)
O3—H17B^{i}	2.987 (5)
O4—H11^{vi}	2.625 (3)
O4—H12^{vi}	2.799 (3)
O4—H18B^{vii}	2.680 (3)
N5—H19^{vii}	2.790 (4)
C17—H17B^{viii}	2.893 (5)
C18—H11^{ix}	2.859 (5)
C18—H19^{vii}	2.896 (6)
H11—H11^{x}	2.7948
H11—H18A^{ix}	2.7642
H11—H18B^{ix}	2.4328
H11—H18C^{ix}	2.9119
H12—H14C^{ii}	2.8673
H12—H18A^{iii}	2.9245
H14B—H18C^{i}	2.4714
H14C—H17A^{xi}	2.4209
H16—H18C^{ix}	2.8399
H17A—H17B^{viii}	2.9574
H17B—H17B^{viii}	2.6026
H17B—H17C^{viii}	2.6374
H17C—H19^{vii}	2.8571
H18B—H19^{vii}	2.4001

Symmetry codes: (i) 2-x,1-y,1-z; (ii) x-1,y,z; (iii) x,y-1,z; (iv) 3-x,-y,1-z; (v) 2-x,-y,2-z; (vi) 1+x,y,z; (vii) 2-x,1-y,2-z; (viii) 2-x,2-y,1-z; (ix) 1-x,1-y,2-z; (x) 1-x,-y,2-z; (xi) 1+x,y-1,z.

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