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Microwave-induced one-pot synthesis of 4-[3-(aryl)-1,2,4-oxadiazol-5-yl]-butan-2-ones under solvent free conditions

Jucleiton José R. de Freitas,[b] Juliano Carlo R. de Freitas,[a] Ladjane P. da Silva,[a] João R. de Freitas Filho,[a,b,*] Gisele Y. V. Kimura[a] and Rajendra M. Srivastava[a,*]

[a]*Departamento de Química Fundamental, Universidade Federal de Pernambuco, 50.740-540 Recife, PE, Brazil*
[b]*Unidade Acadêmica de Garanhuns, Universidade Federal Rural de Pernambuco, Recife, PE, Brazil*

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Abstract—The synthesis of 4-[3-(aryl)-1,2,4-oxadiazol-5-yl]-butan-2-ones (**5a**–**l**) from methyl levulinate (**4**) and arylamidoximes (**1a**–**l**) is described. The reaction was carried out in a microwave oven without any solvent in much shorter time and in yields comparable with conventional heating.

1. Introduction

1,2,4-Oxadiazoles owe their significance primarily due to their wide range of biological activities, which have been well documented in four surveys.[1–4] During the last two decades, these heteroaryl compounds have been receiving considerable attention in the drug discovery programs with reported muscarinic agonist, benzodiazepine receptor agonist, 5HT agonist, and antirhinoviral activities.[5a–e] 1,2,4-Oxadiazoles are bioisosteres for esters and amides and the replacement of these groups with the heterocyclic ring makes them resistant to enzyme-catalyzed hydrolysis and improves their biological activities.[5c,6,7] The bioisosteres just mentioned above have also been utilized for planning the preparation of dipeptidomimetics.[8] Our own group has been involved in testing 1,2,4-oxadiazoles against inflammation and found several of them possessing antiinflammatory properties.[9a–d] Besides, *N*-methylpyridinium salts having a perfluoroalkylated 1,2,4-oxadiazoles have been prepared by Italian researchers and considered to be a new family of salts as prospective fluorous solvents.[10] Lately, Pibiri et al. synthesized and characterized a series of alkyl-1,2,4-oxadiazolylpyridinium salts and classified them as ionic liquids.[11]

In general, *O*-acylamidoximes are cyclodehydrated either by heat or by bases to generate 1,2,4-oxadiazoles.[12] In 2001, a publication appeared describing such cyclization by employing tetrabutylammonium fluoride (TBAF) as an activator.[13] 1,2,4-Oxadiazoles can also be obtained by the reaction of amidoximes and a carboxylic acid in the presence of a coupling reagent, like dicyclohexylcarbodiimide (DCC), diisopropylcarbodiimide (DIC), and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC).[14]

In the framework of our ongoing research, we needed 4-[3-(aryl)-1,2,4-oxadiazol-5-yl]-butan-2-ones, which we prepared by using an appropriate benzamidoxime or arylamidoxime and levulinic acid in the presence of DCC in methylene chloride to get *O*-acyl intermediates, which were cyclized to 1,2,4-oxadiazoles following the known procedure.[9a] This way, eight oxadiazoles **5a**–**e**,**g**,**i**,**l** were prepared although it took much longer reaction time and needed more work-up for acquiring the final products. While this work was in progress, we came across a recent report where carboxylic acid esters, amidoximes and potassium carbonate were refluxed in toluene for 6–12 h to obtain 1,2,4-oxadiazoles in moderate to excellent yields.[15] At this point, it occurred to us to try to discern a procedure, which could reduce the reaction time drastically. Apparently, microwave irradiation appeared to be the first option. We did attempt the microwave-accelerated preparation using methyl

* Corresponding authors. Tel.: +55 81 2126 8440x5015; fax: +55 81 2126 8442 (R.M.S.); tel.: +55 81 34530258 (J.R.F.F.); e-mail addresses: joaoveronice@yahoo.com.br; rms_indu@yahoo.com

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levulinate, amidoxime, and potassium carbonate under solventless conditions and indeed succeeded in synthesizing 12 1,2,4-oxadiazoles **5a**–**l** in 5–10 min.[16]

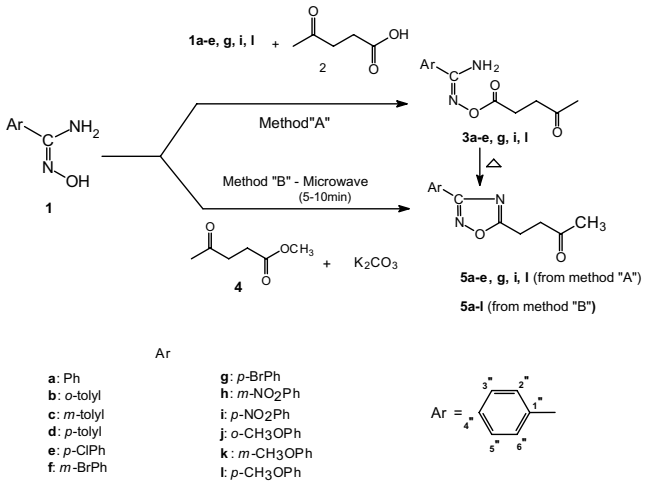
Table 1 shows the comparison of eight conventionally prepared oxadiazoles **5a**–**e**,**g**,**i**,**l** with the ones obtained by microwave procedure. The extensive diminution in reaction time in the latter method in conjunction with a very simple work-up and relatively high yields convinced us to communicate this environmentally benign synthesis of 1,2,4-oxadiazoles containing a carbonyl function in its C-5 side chain (Scheme 1).

The mechanism of formation of 1,2,4-oxadiazoles from amidoximes and an acid employing DCC as a carbonyl group activator is straight forward. The first step is the intermediate **3** production followed by thermal cyclodehydration to generate **5**.[9a] However, the formation of **5** by microwave-mediated process is quite different. In fact, there are two equally probable mechanisms: In path 'A' the base may abstract a proton from **1** to create an anion at the oxygen atom, which attacks the carbonyl carbon of **4** to furnish an unstable tetrahedral species **6** with subsequent loss of methanol to give **3**. This latter product ejects water to yield **5**. In path 'B', the alpha proton from **4** is extracted by the base to give **7**, which loses a methoxide anion to produce ketene **8**. This reactive ketene gets condensed with amidoxime to provide **3**, which expels a water molecule on heating to form the final heterocycle **5**. In both cases, methanol is produced and is quickly removed by evaporation, which drives the reaction to completion. Lately, acyl ketene formation from a β-keto ester under thermal condition has been reported.[17] Although, the esters in the present work are different, but we feel that ketene formation under basic condition should be favored. The reviewer suggested that the p*K*a value of a β-keto ester reported earlier[17] will be very different compared to the p*K*a value of the substrate described in this letter. This suggestion is genuine and we appreciate the referee's advice. Certainly, more work can be pursued to ascertain the mechanism of formation of these oxadiazoles involving the ketene formation. At this moment, it is not possible to confirm whether both mechanisms are operating or only one of them is responsible to give the desired products **5a**–**l**. Both mechanisms are depicted is Scheme 2.

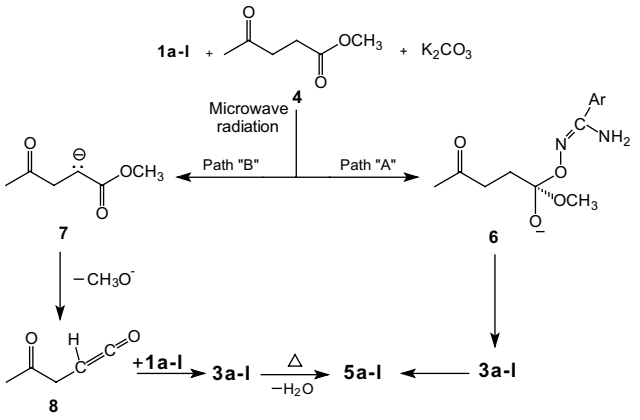
Table 1. Comparison of conventional heating and microwave irradiation on reaction of **1a–l** with **2** and **4**

Entry	Conventional method		Microwave method		
Compounds	Time (h)	Yield[a] (%)	Time (min)	Yield[a] (%)	R_f[b]
5a	18	87	10	93	0.70
5b	18	90	10	90	0.79
5c	18	89	10	90	0.78
5d	18	92	10	93	0.75
5e	18	85	8	89	0.81
5f	—	—	8	85	0.69
5g	18	89	8	91	0.83
5h	—	—	5	86	0.70
5i	18	75	5	88	0.67
5j	—	—	8	85	0.64
5k	—	—	8	85	0.64
5l	18	86	8	89	0.67

[a] Isolated yields.
[b] Determined in 9:1, CH_2Cl_2/EtOAc.



Scheme 1. Synthesis of 1,2,4-oxadiazoles employing conventional as well as microwave radiation techniques.



Scheme 2. Two possible paths for the formation of 5 from 4 and 1 in the presence of K_2CO_3.

The experimental procedures for the syntheses of both types are described,[18] while other properties are furnished in the reference section.[19]

In conclusion, we have discovered a practical and rapid procedure for the microwave-accelerated synthesis of 1,2,4-oxadiazoles from methyl levulinate and arylamidoximes in the presence of potassium carbonate without using any solvent. This method furnishes the products very quickly, simplifies the work-up and is environmentally benign. Besides, two possible mechanisms of formation of these heterocycles are suggested.

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16. Microwave reactions were performed in a domestic microwave oven, SANYO, model EM-300B (220 V; 650 W/2450 MHz). The precise heating area in the oven was located, and the experiments were repeated at least a couple of times. Therefore, we feel confident that these experiments can be repeated by any chemist.
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18. Synthesis of 4-[3-(aryl)-1,2,4-oxadiazol-5-yl]-butan-2-ones (**5a**–**e**,**g**,**i**,**l**).*Conventional method*: A mixture of levulinic acid **2** (28.0 mmol) and appropriate arylamidoxime **1a**, **g**, **i**, **l** (27.0 mmol) in dry dichloromethane (50 mL) was stirred in a 150 mL round-bottom flask under nitrogen atmosphere. Dicyclohexylcarbodiimide (DCC) (27.0 mmol) was added to it and the stirring continued for 3 h at rt to give *O*-levulinylarylamidoximes (**3a**–**e**,**g**,**i**,**l**). Filtration to remove DCU and solvent evaporation left an oil, which was heated in an oil bath at 78 °C for 18 h. After the reaction, the impure product was chromatographed over a silica gel column employing *n*-hexane–ethyl acetate (9:1) as an eluent. The fractions containg the right R_f values of the compound were combined and the solvent was evaporated to get chromatographically pure 4-[3-(aryl)-1,2,4-oxadiazol-5-yl]-butan-2-ones (**5a**–**e**,**g**,**i**,**l**). *Microwave method*: A mixture of methyl levulinate **4** (1.0 mmol), appropriate arylamidoximes **1a**–**l** (1.58 mmol) and K_2CO_3 (0.85 mmol) was well triturated and placed in a small glass test tube followed by irradiation in a domestic microwave oven (100% potency, 650 W) for 10 min and then cooled. After the reaction, the compound was chromatographed over a silica gel column and eluted with *n*-hexane–ethyl acetate (9:1). The fractions containing the desired compound were combined and the solvent evaporated to get chromatographically pure 4-[3-(aryl)-1,2,4-oxadiazol-5-yl]-butan-2-ones (**5a**–**l**).
19. *Compound 4-(3-phenyl-1,2,4-oxadiazol-5-yl)-butan-2-one* (**5a**): Pale yellow oil, yield 93%. IR (KBr): 1720; 1590; 1570; 1360; 1160; 720 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.07–8.02 (m, 2H, H-2′ and H-6′, Ph-H), 7.50–7.43 (m, 3H, H-3′, H-4′ and H-5′, Ph-H), 3.23–3.18 (ddd, 2H, $J = 1.5$ Hz, $J = 6.7$ Hz, $J = 14.3$ Hz, H-6 and H-6′), 3.09–3.04 (ddd, 2H, $J = 1.5$ Hz, $J = 6.6$ Hz, $J = 14.7$ Hz, H-7 and H-7′), 2.26 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6 (C-8); 179.2 (C-3); 170 (C-5); 131.5 (C-1″); 129.5 (C-3″ and C-5″); 129.1 (C-4″); 127.7 (C-2″ and C-6″); 39.6 (C-6); 30.25 (C-7); 21.1 (CH_3). Anal. Calcd for $C_{12}H_{12}O_2N_2$: C, 66.66; H, 5.55; N, 12.95. Found: C, 66.51; H, 5.62; N, 12.74.
Compound 4-(3-o-tolyl-1,2,4-oxadiazol-5-yl)-butan-2-one (**5b**): Pale yellow oil, yield 90%. IR (KBr): 1710; 1590; 1565; 1360; 1335; 1160; 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, $J = 7.2$ Hz, 1H, Ph-H), 7.38–7.25 (m, 3H, Ph-H), 3.20 (t, 2H, $J = 6.96$ Hz, H-6 and H-6′), 3.04 (t, 2H, $J = 6.78$ Hz, H-7 and H-7′),2.59 (s, 3H, Ph–CH_3), 2.22 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.7 (C-8); 178.1 (C-3); 169.1 (C-5); 138.5 (C-1″); 131.7 (C-3″); 126.4 (C-5″); 130.8 (C-2″); 130.3 (C-4″); 126.4 (C-6″); 39.5 (C-7); 30.25 (C-6); 20.9 (CH_3); 14.5 (Ph–CH_3). Anal. Calcd for $C_{13}H_{14}O_2N_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.83; H, 6.49; N, 12.06.
Compound 4-(3-m-tolyl-1,2,4-oxadiazol-5-yl)-butan-2-one (**5c**): Pale yellow oil, yield 89%. IR (KBr): 1720; 1595; 1575; 1350; 1150; 745 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.82–7.79 (m, 2H, Ph-H), 7.32–7.23 (m, 2H, Ph-H), 3.15 (dd, 2H, $J = 1.3$ Hz, $J = 7.5$ Hz, H-6 and H-6′), 3.00 (d, 2H, $J = 6.78$ Hz, H-7 and H-7′), 2.35 (s, 3H, Ph–CH_3), 2.18 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.7 (C-8); 179.2 (C-3); 1.68.6 (C-5); 138.9 (C-1″); 129 (C-2″); 129.3 (C-5″); 128.8 (C-4″); 132.2 (C-3″); 124.8 (C-6″); 39.5 (C-7); 30.0 (C-6); 21.6 (CH_3); 14.1 (Ph–CH_3). Anal. Calcd for $C_{13}H_{14}O_2N_2.1/2H_2O$: C, 65.24; H, 6.27; N, 11.71. Found: C, 65.83; H, 6.03; N, 11.61.
Compound 4-(3-p-tolyl-1,2,4-oxadiazol-5-yl)-butan-2-one (**5d**): Pale yellow oil, yield 92%. IR (KBr): 1720; 1590; 1565; 1350; 1120; 740 cm^1. ^1H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, $J = 8.1$ Hz, 2H, H-2″ and H-6″), 7.27 (d, $J = 7.8$ Hz, 2H, H-3″ and H-5″), 3.18 (dt, 2H, $J = 1.3$ Hz, J 8.1 Hz, H-6 and H-6′), 3.05 (dt, 2H, $J = 1.3$ Hz, $J = 8.1$ Hz, H-7 and H-7′), 2.39 (s, 3H, Ph–CH_3), 2.24 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.7 (C-8); 179.0 (C-3); 168.5 (C-5); 141.8 (C-1″); 129.8

(C-4″); 127.6 (C-3″ and C-5″); 124.3 (C-2″ and C-6″); 39.6 (C-6); 30.2 (C-7); 21.9 (CH_3); 21.0 (Ph–CH_3). Anal. Calcd for $C_{13}H_{14}O_2N_2$: C, 67.83; H, 6.13; N, 12.17. Found: C, 67.65; H, 6.16; N, 11.93.

*Compound 4-(3-p-chlorophenyl-1,2,4-oxadiazol-5-yl)-butan2-one (***5e***)*: Crystals from chloroform/cyclohexane, mp: 74–75 °C yield 89%. IR (KBr): 1740; 1580; 1540; 1360; 1160; 740 cm^1. ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, 2H, $J = 8.4$ Hz, H-2″ and H-6″), 7.44 (d, $J = 8.4$ Hz, 2H, H-3″ and H-5″), 3.20 (dt, 2H, $J = 1.3$ Hz, $J = 8.1$ Hz, H-6 and H-6′), 3.06 (dt, 2H, $J = 1.3$ Hz, $J = 6.8$ Hz, H-7 and H-7′), 2.25 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6 (C-8); 179.4 (C-3); 167.8 (C-5); 137.6 (C-1″); 129.5 (C-4″); 129.0 (C-3″ and C-5″); 125.7 (C-2″ and C-6″); 39.5 (C-7); 30.2 (C-6); 21.0(CH_3). Anal. Calcd for $C_{12}H_{11}O_2N_2Cl$: C, 57.49; H, 4.39; N, 11,17. Found: C, 57.45; H, 4.52; N, 11.05.

*Compound 4-(3-m-bromophenyl-1,2,4-oxadiazol-5-yl)-butan-2-one (***5f***)*: Semisolid, yield 85%. IR (KBr): 1718; 1589; 1558; 1350; 720 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.17 (t, $J = 1.5$ Hz, 1H, Ph), 7.94 (d, $J = 4.8$ Hz, 1H, Ph), 7.60 (d, $J = 6.3$ Hz, 1H, Ph), 3.17 (dt, $J = 1.5$ Hz, $J = 6.9$ Hz, H-6 and H-6′), 3.06 (dt, $J = 1.5$ Hz, $J = 6.3$ Hz, H-7 and H-7′), 2.26 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6 (C-8); 179.5 (C-3); 167.8 (C-5); 132.4 (C-1″); 129.2 (C-3″); 131.2 (C-5″); 126.2 (C-6′); 129.0 (C-2″); 125.7 (C-4″); 39.5 (C-7); 30.1 (C-6); 21.0 (Ph–CH_3). Anal. Calcd for $C_{12}H_{11}O_2N_2Br$: C, 48.84; H, 3.76; N, 9.49. Found: C, 49.20; H, 3.66; N, 9.24.

*Compound 4-(3-p-bromophenyl-1,2,4-oxadiazol-5-yl)-butan-2-one (***5g***)*: Crystals from chloroform/cyclohexane, mp: 84–84.5 °C, yield 91%. IR (KBr): 1700; 1585; 1540; 1360; 1180; 760 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.84 (d, $J = 8.6$ Hz, 2H, Ph–H), 7.53 (d, $J = 8.6$ Hz, 2H, Ph–H), 3.94 (dt, 2H, $J = 1.3$ Hz, $J = 6.96$ Hz, H-6 and H-6′), 3.02 (dt, 2H, $J = 1.3$ Hz, $J = 6.38$ Hz, H-7 and H-7′), 2.20 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6 (C-8); 179.5 (C-3); 167.8 (C-5); 132.4 (C-1″); 129.2 (C-3″ and C-5″); 129.0 (C-2″ and C-6″); 125.7 (C-4″); 39.5 (C-7); 30.1 (C-6); 21.0 (Ph–CH_3). Anal. Calcd for $C_{12}H_{11}O_2N_2Br$: C, 48.84; H, 3.76; N, 9.49. Found: C, 48.29; H, 3.65; N, 9.12.

*Compound 4-(3-m-nitrophenyl-1,2,4-oxadiazol-5-yl)-butan-2-one (***5h***)*: Semisolid, yield 86%. IR(KBr): 1707; 1572; 1352; 1167; 723 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 8.90 (t, 1H, $J = 1.5$ Hz, $J = 3.6$ Hz, Ph–H), 8.37 (t, 2H, $J = 1.8$ Hz, $J = 10.2$ Hz, Ph–H), 7.67 (t, 1H, $J = 0.6$ Hz, $J = 8.4$ Hz, Ph–H), 3.23 (dt, 2H, $J = 1.8$ Hz, $J = 12$ Hz, H-6 and H-6′), 3.06 (dt, 2H, $J = 1.5$ Hz, $J = 13.2$ Hz, H-7 and H-7′), 2.25 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6 (C-8); 179.4 (C-3); 167.8 (C-5); 137.6 (C-1″); 129.5 (C-4″); 132.2 (C-3″); 129.9 (C-5″); 125.7 (C-2″); 124.2 (C-6″); 39.5 (C-7); 30.2 (C-6); 21.0 (CH_3). Anal. Calcd for $C_{12}H_{11}O_4N_3$: C, 55.17; H, 4.24; N, 16.09. Found: C, 55.10; H, 4.13; N, 15.94.

*Compound 4-(3-p-nitrophenyl-1,2,4-oxadiazol-5-yl)-butan-2-one (***5i***)*: Crystals from chloroform/cyclohexane, mp: 73–74 °C, yield 88%. IR (KBr): 1700; 1580; 1540; 1360; 1160; 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.99 (d, 2H, $J = 8.4$ Hz, H-2″ and H-6″, Ph–H), 7.44 (d, $J = 8.4$ Hz, 2H, H-3″ and H-5″), 3.20 (dt, 2H, $J = 1.3$ Hz, $J = 8.1$ Hz, H-6 and H-6′), 3.06 (dt, 2H, $J = 1.3$ Hz, $J = 6.8$ Hz, H-7 and H-7′), 2.25 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.6 (C-8); 179.4 (C-3); 167.8 (C-5); 137.6 (C-1″); 129.5 (C-4″); 129.0 (C-3″ and C-5″); 125.7 (C-2″ and C-6″); 39.5 (C-7); 30.2 (C-6); 21.0 (Ph–CH_3). Anal. Calcd for $C_{12}H_{11}O_4N_3$: C, 55.17; H, 4.24; N, 16.09. Found: C, 55.22; H, 4.65; N, 15.93.

*Compound 4-(3-o-metoxyphenyl-1,2,4-oxadiazol-5-yl)-butan-2-one (***5j***)*: Pale yellow oil, yield 85%. IR (KBr): 1711; 1601; 1493; 1346; 1252; 757 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.94 (dd, 1H, $J = 2.1$ Hz, $J = 7.5$ Hz, Ph–H), 7.46 (dt, 1H, $J = 1.8$ Hz, $J = 14.1$ Hz, Ph–H), 7.05 (dt, 2H, $J = 1.8$ Hz, $J = 14.1$ Hz, Ph–H), 3.96 (s, 3H, OCH_3), 3.21 (dt, 2H, $J = 1.5$ Hz, $J = 8.7$ Hz, H-6 and H-6′), 3.07 (dt, 2H, $J = 1.5$ Hz, $J = 6.9$ Hz, H-7 and H-7′), 2.25 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.7 (C-8); 178.9 (C-3); 168.3 (C-5); 125.1 (C-1″); 162.2 (C-2″); 129.3 (C-4″); 119.6 (C-5″); 114.5 (C-3″); 128.2 (C-6″); 39.6 (C-7); 30.2 (C-6); 21.6 (CH_3O); 21.0 (CH_3). Anal. Calcd for $C_{13}H_{14}O_3N_2$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.31; H, 5.77; N, 11.12.

*Compound 4-(3-m-metoxyphenyl-1,2,4-oxadiazol-5-yl)-butan-2-one (***5k***)*: Semisolid, yield 85%. IR (KBr): 1717; 1572; 1468; 1348; 1045; 762 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (dt, 2H, $J = 1.5$ Hz, $J = 7.8$ Hz, Ph–H), 7.36 (dt, 1H, $J = 0.9$ Hz, $J = 8.4$ Hz, Ph–H), 3.85 (s, 3H, OCH_3), 3.20 (dt, 2H, $J = 1.5$ Hz, $J = 12.9$ Hz, H-6 and H-6′), 3.06 (dt, 2H, $J = 1.5$ Hz, $J = 13.2$ Hz, H-7 and H-7′), 2.24 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.7 (C-8); 178.9 (C-3); 168.3 (C-5); 162.2 (C-3″); 129.3 (C-1″); 119.6 (C-4″); 114.5 (C-2″); 130.2 (C-5′); 121.5 (C-6″); 39.6 (C-7); 30.2 (C-6); 21.6 (CH_3O); 21.0 (CH_3). Anal. Calcd for $C_{13}H_{14}O_3N_2$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.12; H, 5.81; N, 11.10.

*Compound 4-(3-p-metoxyphenyl-1,2,4-oxadiazol-5-yl)-butan-2-one (***5l***)*: Semisolid, yield 89%. IR (KBr): 1707; 1591; 1450; 1358; 1060; 750 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.98 (d, $J = 9.0$ Hz, 2H, H-2″ and H-6″, Ph–H), 6.96 (d, $J = 8.8$ Hz, 2H, H-3″ and H-5″, Ph–H), 3.84 (s, 3H, OCH_3), 3.19 (dt, 2H, $J = 1.5$ Hz, $J = 8.2$ Hz, H-6 and H-6′), 3.04 (dt, 2H, $J = 1.5$ Hz, $J = 8.1$ Hz, H-7 and H-7′), 2.24 (s, 3H, CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 205.7 (C-8); 178.9 (C-3); 168.3 (C-5); 162.2 (C-4″); 129.3 (C-1″); 119.6 (C-2″ and C-6″); 114.5 (C-3″ and C-5″); 39.6 (C-7); 30.2 (C-6); 21.6 (CH_3O); 21.0 (CH_3). Anal. Calcd for $C_{13}H_{14}O_3N_2$: C, 63.40; H, 5.73; N, 11.38. Found: C, 63.75; H, 5.68; N, 11.58.