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Papers

VISIBLE LIGHT PROMOTED SYNTHESIS OF DISUBSTITUTED 1,2,3-THIADIAZOLES**

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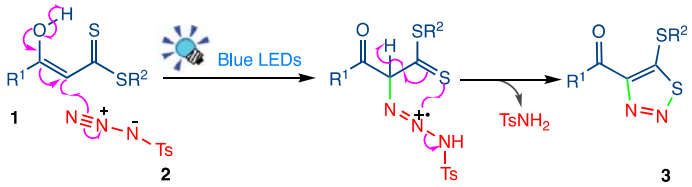
A novel one-pot visible light irradiated synthesis of disubstituted 1,2,3-thiadiazole from α-enolicdithioesters with tosyl azide have been reported. The reaction completed within 12-20 minutes, at room temperature, when a mixture of α-enolicdithioester and tosyl azide undergo photocatalysed reaction under solvent-free conditions. Furthermore, no co-catalyst or activator is necessary. This protocol includes eco-compatibility, mild conditions, excellent yields, easy purification, and avoidance of expensive/toxic reagents to synthesise organic compounds of medicinal importance, which fulfils the basic principle of green chemistry.



INTRODUCTION

Sunlight is a unique and renewable natural source.[1] The development of methods to efficiently harness the solar radiation energy has emerged as one of the central scientific challenges of the twenty first century.[2,3] The potential of developing new synthetic methodologies using visible light has recently received much attention from a number of research groups.[4,5] This is because solar energy (visible light) is clean, easy to handle and an unlimited energy source having great prospects for the development of sustainable and eco-friendly protocols for organic synthesis.[6] Visible light is increasingly appreciated as an abundant, renewable, and clean energy source for chemical reactions. Photoredox catalysis is an attractive approach to activating organic molecules by translating visible light energy via single-electron transfer (SET). Some pioneering researchers have dedicated to converting solar energy into chemical energy for chemical transformations,[7,8] which includes a promising strategy for the application of photoredox catalysts to initiate single electron transfer processes have been developed.[9,10] A surge of interest from the synthetic community has brought photoredox manifolds to the forefront of catalysis. In this sequence visible light photoredox catalysis has recently received much attention in organic synthesis owing to readily availability, sustainability, non-toxicity and ease of handling of visible light.[11–16]

The five-membered heterocyclic compounds have a great application and importance in heterocyclic chemistry. Among them thiadiazole is a versatile moiety that exhibits a wide variety of biological activities. Thiadiazole moiety acts as "hydrogen binding domain" and "two-electron donor system". It also acts as a constrained pharmacophore. Many drugs containing thiadiazole nucleus are available in the market such as acetazolamide, methazolamide, sulfa-methazole, etc.

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1,2,3-thiadiazoles are becoming a rapidly growing and independent branch of the chemistry of thiazoles. 1,2,3-thiadiazoles[17–19] are versatile bioactive moiety, found in many bioactive natural products and pharmaceuticals, which exhibit diverse medicinal[20–22] and agricultural[23–25] applications. Many 1,2,3-thiadiazoles have shown biological activities such as antiviral[26,27] systemic acquired resistance[28,29] fungicidal[30-32] and insecticidal activities.[33] The property of easy breakdown of the 1,2,3-thiadiazole ring into low molecular weight compounds favours the use of its derivatives as pesticides with low toxicity.[34] Tiadinil (TDL), a 4-methly-1,2,3-thiadiazole-5-carboxamide derivative containing a 3-chloro-4-methylphenyl moiety, has been recognized as a well- known commercialized fungicide as well as a plant elicitor.[35] 1,2,3-thiadiazoles and related compounds are of great interest in chemistry owing to their bioactivity of certain plant growth regulating effect as well as antimicrobial activity.[36,37]

The synthesis of 1,2,3-thiadiazole was previously reported by conventional method[38] but not by photocatalysed reaction so far. Meanwhile the catalyst free organic reactions have received a great importance in research during present time. Encouraged by our visible-light-mediated organic transformations[39–43] and in continuation of our work on development of novel environmentally benign synthesis[44–48] herein we report a simple, visible light irradiated, efficient and green protocol for the synthesis of 1,2,3- thiadiazoles, without catalyst, under solvent-free conditions with excellent yield as depicted in Table 2.

EXPERIMENTAL

Melting points were determined by an open glass capillary method and are uncorrected. All chemicals used were reagent grade and were used as received. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AVANCE DPX (400 MHz and 75 MHz) FT spectrometer in DMSO using TMS as an internal reference (chemical shift in δ, ppm). Mass spectra were recorded on JEOL SX-303 (FAB) mass spectrophotometer. Elemental analyses were carried out using a Coleman automatic C, H, N analyser. The commercially available starting materials were used as received without further purification. α-enolicdithioesters and tosyl azide were prepared by the reported procedures.

General procedure for the synthesis of disubstituted 1,2,3-thiadiazoles 3 (a-r)

A solution of α-enolicdithioesters **1** (1.0 mmol) and tosyl azide **2** (1.0 mmol) was taken and the mixture was irradiated with blue LEDs (2.4 W, 120 lm) with stirring at rt for 12−20 min. till the completion of the reaction (monitored by TLC). Methanol (1 mL) was added to the reaction mixture, followed by 1 mL of conc. HCl and 3 ml of water. The solid product obtained was filtered, washed with water, and finally recrystallized from MeOH–$CHCl_3$ mixture (1:1) to give the analytically pure sample. The products were purified by filtration through a short column filled with silica gel using EtOAc–hexane as eluent. The spectral and analytical data of all the compounds are given as follows.

4-Acetyl-5-methylsulfanyl-1,2,3-thiadiazole **(3a).** White solid; **mp** 118–119 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 2.84 (s, 3H, CH_3), 2.68 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 192.1, 167.0, 153.2, 28.5, 21.4. IR (KBr, cm^{-1}): 2974, 1638, 1386, 1211, 1017. **MS (ESI)**: m/z calcd. for $C_5H_6N_2OS_2$ $[M+H]^+$ = 173.99.

5-Methylsulfanyl-4-(2-thienoyl)-1,2,3-thiadiazole **(3b).** Yellow solid; **mp** 176–177 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.65 (d, J = 3.6 Hz, 1H, ArH), 7.78 (d, J = 4.8 Hz, 1H, ArH), 7.24 (dd, J = 5.7 Hz, J = 4.2 Hz, 1H, ArH), 2.72 (s, 3H, SCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 177.0, 169.6, 152.2, 142.2, 136.2, 135.6, 128.4, 21.8. IR (KBr, cm^{-1}): 3087, 2980, 1656, 1599, 1507, 1420, 1270, 1057, 838. **MS (ESI)**: m/z calcd. for $C_8H_6N_2OS_3$ $[M+H]^+$ = 241.96.

5-Benzylsulfanyl-4-(2-thienoyl)-1,2,3-thiadiazole **(3c).** Yellow solid; **mp** 111–112 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.61 (s, 1H, ArH), 7.76 (d, J = 4.5 Hz, 1H, ArH), 7.43–7.35 (m, 5H, ArH), 7.21 (s, 1H, ArH), 4.27 (s, 2H, CH_2). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.9, 166.3, 152.6, 142.1, 136.1, 135.6, 133.6, 129.1, 129.0, 128.5, 128.3, 42.7. IR (KBr, cm^{-1}): 3121, 2983, 1629, 1507, 1581, 1478, 1362, 1218, 1056. **MS (ESI)**: m/z calcd. for $C_{14}H_{10}N_2OS_3$ $[M+H]^+$ = 318.00.

5-Allylsulfanyl-4-(2-thienoyl)-1,2,3-thiadiazole **(3d)**. White solid; **mp** 119–120 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.64 (d, J = 3.6 Hz, 1H, ArH), 7.79 (d, J = 4.5 Hz, 1H, ArH), 7.28–7.22 (m, 1H, ArH), 6.00–5.87 (m, 1H, CH), 5.52 (d, J = 16.8 Hz, 1H, CH_2), 5.40 (d, J = 9.9 Hz, 1H, CH_2), 3.74 (d, J = 6.9 Hz, 2H, SCH_2). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 176.8, 166.2, 152.8, 142.1, 136.0, 135.5, 129.8, 128.2, 121.5, 40.9. IR (KBr, cm^{-1}): 3121, 3084, 3005, 2948, 2913, 1604, 1503, 1418, 1352, 1231, 1072, 1031. **MS (ESI)**: m/z calcd. for $C_{10}H_8N_2OS_3$ $[M+H]^+$ = 267.98.

5-Allylsulfanyl-4-(2-furoyl)-1,2,3-thiadiazole **(3e).** White solid; **mp** 101–102 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.10 (d, J = 3.6 Hz, 1H, ArH), 7.74 (s, 1H, ArH), 6.61 (d, J = 1.5 Hz, 1H, ArH), 5.95–5.82 (m, 1H, CH), 5.47 (d, J = 16.8 Hz, 1H, CH_2), 5.35 (d, J = 9.9 Hz, 1H, CH_2), 3.69 (d, J = 6.3 Hz, 2H, SCH_2). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 172.0, 166.0, 152.3, 151.0, 148.0, 129.8, 122.9, 121.5, 112.5, 40.9. IR (KBr, cm^{-1}): 3126, 3074, 3015, 2958, 2903, 1623, 1507, 1407, 1356, 1235, 1071, 1053. **MS (ESI)**: m/z calcd. for $C_{10}H_8N_2O_2S_2$ $[M+H]^+$ = 252.00.

4-(2-Furoyl)-5-methylsulfanyl-1,2,3-thiadiazole **(3f).** White solid; **mp** 198–199 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.07 (d, J = 3.3 Hz, 1H, ArH), 7.70 (s, 1H, ArH), 6.57 (d, J = 1.8 Hz, 1H, ArH), 2.63 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 172.0, 169.3, 151.6, 151.0, 148.0, 122.9, 112.5, 21.6. IR (KBr, cm^{-1}): 3089, 2979, 1666, 1587, 1516, 1418, 1268, 1049. **MS (ESI)**: m/z calcd. for $C_8H_6N_2O_2S_2$ $[M+H]^+$ = 225.99.

4-(N-Methylpyrrol-3-oyl)-5-methylsulfanyl-1,2,3-thiadiazole **(3g).** White crystalline solid; **mp** 148–149 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.06 (s, 1H, ArH), 6.92 (s, 1H, ArH), 6.56 (s, 1H, ArH), 3.66 (s, 3H, NCH_3), 2.59 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 178.8, 167.6, 153.5, 130.6, 123.8, 123.1, 111.1, 36.6, 21.6. IR (KBr, cm^{-1}): 3069, 2923, 2918, 1641, 1624, 1568, 1592, 1447, 1392, 1218, 1087. **MS (ESI)**: m/z calcd. for $C_9H_9N_3OS_2$ $[M+H]^+$ = 239.02.

4-Benzoyl-5-methylsulfanyl-1,2,3-thiadiazole **(3h).** White solid; **mp** 106–107 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.37 (d, J = 7.2 Hz, 2H, ArH), 7.61–7.50 (m, 3H, ArH), 2.71 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 185.7, 170.3, 153.0,

136.9, 133.1, 130.5, 128.2, 21.7. IR (KBr, cm^{-1}): 3072, 2916, 1624, 1568, 1592, 1447, 1392, 1218, 1087. **MS (ESI)**: m/z calcd. for $C_{10}H_8N_2OS_2$ $[M+H]^+$ = 236.01.

4-(2-Chlorobenzoyl)-5-methylsulfanyl-1,2,3-thiadiazole **(3i).** Yellow solid; **mp** 101–102 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.62–7.39 (m, 4H, ArH), 2.74 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 186.9, 169.5, 153.0, 138.2, 131.8, 131.7, 130.1, 129.6, 126.5, 21.7. IR (KBr, cm^{-1}): 3075, 2907, 1646, 1588, 1432, 1398, 1275, 1014, 878. **MS (ESI)**: m/z calcd. for $C_{10}H_7ClN_2OS_2$ $[M+H]^+$ = 269.97.

4-Benzoyl-5-ethylsulfanyl-1,2,3-thiadiazole **(3j).** White solid; **mp** 102–103 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.35 (d, J = 7.2 Hz, 2H, ArH), 7.61–7.51 (m, 3H, ArH), 3.09 (q, J = 7.4 Hz, 2H, CH_2), 1.52 (t, J = 6.9 Hz, 3H, CH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 185.7, 168.3, 153.3, 137.0, 133.0, 130.5, 128.2, 33.1, 13.1. IR (KBr, cm^{-1}): 3030, 2908, 2898, 1619, 1543, 1419, 1323, 1231, 1051, 853. **MS (ESI)**: m/z calcd. for $C_{11}H_{10}N_2OS_2$ $[M+H]^+$ = 250.02.

4-(4-Methylbenzoyl)-5-methylsulfanyl-1,2,3-thiadiazole **(3k).** White solid; **mp** 168–169 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.30 (d, J = 8.1 Hz, 2H, ArH), 7.32 (d, J = 8.1 Hz, 2H, ArH), 2.71 (s, 3H, SCH_3), 2.44 (s, 3H, $ArCH_3$). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 185.3, 170.0, 144.1, 134.4, 130.8, 129.0, 100.5, 21.8, 21.7. IR (KBr, cm^{-1}): 3070, 2950, 1620, 1602, 1563, 1414, 1394, 1183, 1076. **MS (ESI)**: m/z calcd. for $C_{11}H_{10}N_2OS_2$ $[M+H]^+$ = 252.02.

4-(4-Methoxybenzoyl)-5-methylsulfanyl-1,2,3-thiadiazole **(3l).** White solid; **mp** 169–170 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.47 (d, J = 8.7 Hz, 2H, ArH), 7.00 (d, J = 8.7 Hz, 2H, ArH), 3.90 (s, 3H, OCH_3), 2.70 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 183.9, 169.7, 163.7, 153.4, 133.1, 129.7, 113.6, 55.4, 21.7. IR (KBr, cm^{-1}): 3075, 2984, 2916, 1619, 1596, 1565, 1426, 1393, 1255, 1173, 1085. **MS (ESI)**: m/z calcd. for $C_{11}H_{10}N_2O_2S_2$ $[M+H]^+$ = 266.02.

5-Methylsulfanyl-4-(3-pyridoyl)-1,2,3-thiadiazole **(3m).** White solid; **mp** 100–101 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 9.51 (s, 1H, ArH), 8.80–8.66 (m, 2H, ArH), 7.49–7.45 (m, 1H, ArH), 2.71 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 183.9, 171.2, 152.7, 152.5, 151.1, 138.3, 132.7, 123.3, 21.8. IR (KBr, cm^{-1}): 3047, 2923, 2853, 1625, 1579, 1428, 1397, 1274, 1012, 879. **MS (ESI)**: m/z calcd. for $C_9H_7N_3OS_2$ $[M+H]^+$ = 237.00.

5-Methylsulfanyl-4(4-trifluoromethylbenzoyl)-1,2,3-thiadiazole **(3n).** White solid; **mp** 130–131 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.47 (d, J = 8.1 Hz, 2H, ArH), 7.78 (d, J = 8.1 Hz, 2H, ArH), 2.74 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 184.6, 171.2, 152.6, 139.8, 134.2 (q, J = 33.3 Hz, 1C), 130.8, 125.2, 121.8, 21.8. IR (KBr, cm^{-1}): 3063, 2948, 1631, 1609, 1544, 1424, 1386, 1165, 1079. **MS (ESI)**: m/z calcd. for $C_{11}H_7F_3N_2OS_2$ $[M+H]^+$ = 304.00.

5-Methylsulfanyl-4-(4-phenylbenzoyl)-1,2,3-thiadiazole **(3o).** White solid; **mp** 180–181 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.39 (d, J = 8.1 Hz, 2H, ArH), 7.66 (d, J = 8.4 Hz, 2H, ArH), 7.58 (d, J = 7.2 Hz, 2H, ArH), 7.42–7.29 (m, 3H, ArH), 2.63 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 185.1, 170.3, 153.2, 145.8, 139.8, 135.6, 131.2, 128.9, 128.1, 127.2, 126.9, 21.8. IR (KBr, cm^{-1}): 3071, 2921, 1638, 1559, 1583, 1439, 1386, 1223, 1076. **MS (ESI)**: m/z calcd. for $C_{16}H_{12}N_2OS_2$ $[M+H]^+$ = 312.04.

5-Methylsulfanyl-4-(1-naphthoyl)-1,2,3-thiadiazole **(3p).** White solid; **mp** 117–118 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.31 (d, J = 9.3 Hz, 1H, ArH), 8.04 (d, J = 3 Hz, 2H, ArH), 7.91 (d, J = 9.3 Hz, 1H, ArH), 7.58–7.52 (m, 3H, ArH), 2.73 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 188.6, 169.9, 154.1, 135.0, 133.6, 132.4, 130.7, 129.7, 128.4, 127.5, 126.3, 125.2, 124.2, 21.8. IR (KBr, cm^{-1}): 3049, 2909, 1629, 1505, 1436, 1409, 1274, 1058. **MS (ESI)**: m/z calcd. for $C_{14}H_{10}N_2OS_2$ $[M+H]^+$ = 286.02.

4-(3,4-Methylenedioxybenzoyl)-5-methylsulfanyl-1,2,3-thiadiazole **(3q).** White solid; **mp** 190–191 °C. **^{1}H NMR** (300 Hz, $CDCl_3$): δ 8.19 (dd, J = 8.1 Hz, J = 1.2 Hz, 1H, ArH), 7.89 (d, J = 1.5 Hz, 1H, ArH), 6.92 (d, J = 8.1 Hz, 1H, ArH), 6.07 (s, 2H, CH_2), 2.70 (s, 3H, SCH_3). **^{13}C NMR** (75 MHz, $CDCl_3$): δ 183.4, 169.8, 152.1, 147.9, 131.4, 127.8, 127.6, 110.4, 107.9, 101.8, 21.7. IR (KBr, cm^{-1}): 3054, 2924, 2890, 1641, 1608, 1499, 1439, 1398, 1266, 1075, 856. **MS (ESI)**: m/z calcd. for $C_{11}H_8N_2O_3S_2$ $[M+H]^+$ = 280.00.

4-Benzoyl-5-benzylsulfanyl-1,2,3-thiadiazole **(3r).** White solid; **mp** 135–136 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.34 (d, J = 7.2 Hz, 2H, ArH), 7.57 (d, J = 7.2 Hz, 1H, ArH), 7.51–7.41 (m, 4H, ArH), 7.33 (d, J = 6.6 Hz, 3H, ArH), 4.24 (s, 2H, CH_2). **^{13}CNMR** (75 MHz, $CDCl_3$): δ 185.5, 167.0, 153.4, 136.8, 133.6, 133.1, 130.5, 129.0, 128.9, 128.4, 128.2, 42.7. IR (KBr, cm^{-1}): 3148, 2903, 1629, 1521, 1548, 1427, 1359, 1218, 1061. **MS (ESI)**: m/z calcd. for $C_{16}H_{12}N_2OS_2$ $[M+H]^+$ = 312.04.

RESULTS AND DISCUSSION

β-oxo-dithioester is a thio-analogue of the normal β-ketoester, with different chemical reactivity from normal β-ketoester due to the unique array of three nucleophilic (O, C and S) and two electrophilic (CO and CS) centres. In the recent years, the presence of these active centres, enolic and dithioester moieties, the reactions of α-enolic-dithioesters with various electrophilic and nucleophilic reagents made them an important synthon, exploited to construct five-/six-membered and fused heterocycles, depending on the reaction conditions. In continuation of our ongoing program on the green synthesis of biologically important small heterocycles we became interested in the development of a new catalyst free photocatalysed organic synthesis of disubstituted 1,2,3-thiadiazoles, aimed at exploring visible light irradiated, efficient and green protocol under solvent-free conditions with excellent yield by applying synthetic utility of β-oxodithioesters.

Initially, to optimize the reaction conditions for the synthesis of disubstituted 1,2,3-thiadiazoles, α-enolicdithioesters[49] **1** and tosyl azide[50] **2** were taken as model substrates. We initially attempted a two-component condensation of α-enolicdithioesters **1** (1.0 mmol) and tosyl azide **2** (1.0 mmol) for synthesizing disubstituted 1,2,3-thiadiazoles using visible light as a promoter under catalyst free conditions in a variety of green as well as conventional organic solvents such as ethanol, glycerol, dicloromethane, ethyl acetate, tetrahydrofuran, acetonitrile etc. at room temperature (rt). No reaction was observed in any of the experiments, except in the case of ethanol (55%), Glycerol (48%) or methanol (53%) as a solvent.

Table 1

Initial optimization of the reaction conditions[a]

Entry	Solvent	Time (min)	1:1 (mmol)	Yield (%)[a,b]
1	EtOAc	20	1:1	Trace
2	DCM	20	1:1	Trace
3	THF	20	1:1	Trace
4	Acetonitrile	20	1:1	Trace
5	Methanol	20	1:1	53
6	Ethanol	20	1:1	55
7	Glycerol	20	1:1	48
8	Ethanol/water 1:1	20	1:1	60
9	None	12	1:1	96
10	None	16	0.5:1	68
11	None	16	1:0.5	68
12	None	14	1:2	86
13	None	14	1:2.5	86
14	None	17	2:1	68

[a] All reactions were carried out under visible light irradiation using a 8W CFL at room temperature.
[b] Isolated yields.

In our efforts to increase the yield of the products, we performed the reaction using ethanol/water 1:1, leading to a marginal increase in yield (60%) but no reduction in reaction time. At this juncture we thought of carrying out this reaction in solvent free conditions, which led to a drastic increase in yield (96%) with reduction in reaction time. If, we used a small excess of **2** (1 mmol) but with no success (Table 1, entry 10) as well as small excess of **1** (Table 1, entry 11). We now repeated the experiment using **1** mmol of tosyl azide **2**. To our surprise this led to a noticeable increase in yield and reduction in reaction time (Table 1, entry 12). A further increase in the amount of **2**, did not produce better results (Table 1, entry 13). However, a reduction in amount of 2 led to a lowering in yield and marginal increase in reaction time (Table 1, entry 14).

Experiments probing the scope and generality of this process under optimized conditions are summarized in Table 2. A broad spectrum of α-enolicdithioesters **1**, bearing R^1 as aryl, hetaryl, extended aromatics and alkyl groups, and R^2 as saturated and unsaturated alkyl groups, could be employed to afford disubstituted thiadiazoles **3** in good to excellent yields. As can be seen from Table 2, all reactions proceeded very fast and afforded the corresponding products **3** in high yields within 12–20 minutes at rt. It has been observed that α-enolicdithioesters bearing R^1 as aryl group with electron-donating substituents gave considerably higher yields.

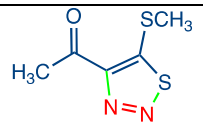
Taking into consideration the entire outcome, a plausible mechanistic path-way for the visible light promoted synthesis of disubstituted 1,2,3-thiadiazoles, is outlined in Scheme 1. The first step in the mechanism is believed to be the abstraction of enolic proton from α-enolicdithioesters **1** in presence of blue LED light, followed by nucleophilic attack of α-carbon on the sp-hybridized electrophilic nitrogen of tosylazide **2**, forming C–N bond to generate the radical cation which is further likely to to furnish disubstituted 1,2,3-thiadiazole **3** with elimination of tosylamine.

CONCLUSIONS

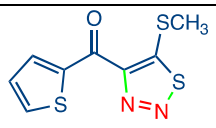
In summary, we have developed catalyst and solvent-free visible light irradiated synthesis of disubstituted 1,2,3-thiadiazole from α-enolicdithioesters with tosyl azide at room temperature for the first time. This transformation avoids the use of transition- metal catalyst as well as organic dyes and serves as a step-economical alternative to existing methods. The present methodology also offers many advantages of green chemistry such as reduced reaction time, one-pot consolidated procedure, high efficiency and consist of both synthetic and medicinal importance.

Table 2

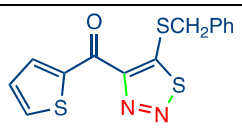
Scope of the reaction



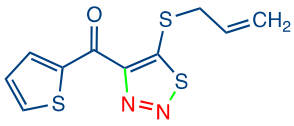
3a: 94%, 12 min



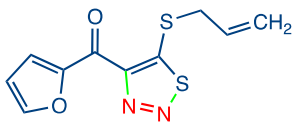
3b: 84%, 15 min



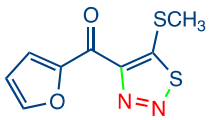
3c: 82%, 18 min



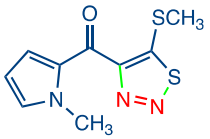
3d: 86%, 15 min



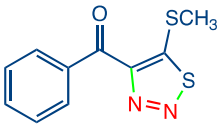
3e: 81%, 17 min



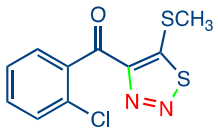
3f: 83%, 13 min



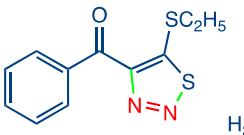
3g: 81%, 18 min



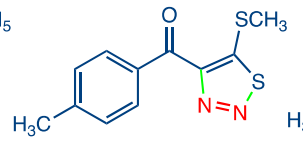
3h: 93%, 12 min



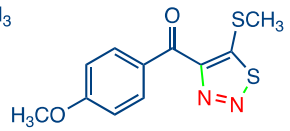
3i: 81%, 18 min



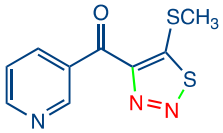
3j: 86%, 13 min



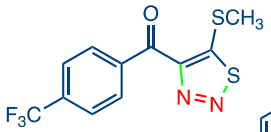
3k: 96%, 13 min



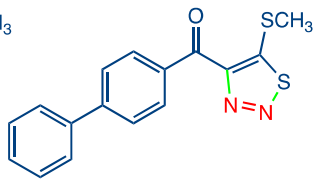
3l: 91%, 13 min



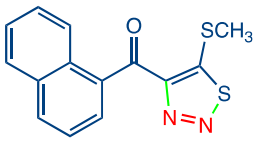
3m: 80%, 16 min



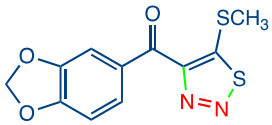
3n: 72%, 14 min



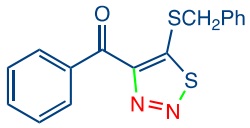
3o: 89%, 20 min



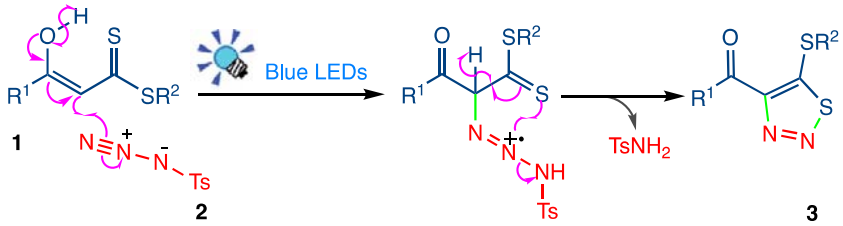
3p: 88%, 20 min



3q: 92%, 13 min



3r: 91%, 20 min



Scheme 1 – Plausible mechanism for the synthesis of disubstituted 1,2,3-thiadiazoles.

Supporting information

Supporting information including experimental procedures, spectroscopic data and $^{1}H/^{13}C$ NMR spectra is available.

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