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A facile Michael addition reaction of β-diketones to nitrostyrenes: Alkylamino substituted triazine as an efficient organocatalyst

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Various aminoalkyl substituted triazines have been synthesised and their activity as organocatalyst has been studied in Michael addition reactions of β-diketones to nitrostyrenes. All the catalysts are found to be effective towards the addition reaction and highest performance is achieved with the catalyst having long chain alkyl group. The effect of base and solvent has also been investigated, and the condition has been optimized with triethylamine as the base and chlorobenzene as the solvent for excellent yields. The reaction is highly remarkable since the catalyst under study is readily available and inexpensive compared to other organocatalyst known for the reaction.

Keywords Nitro styrene, β-diketone, Organocatalyst, Michael addition, Triazine

During the last decade, scientists are endeavoring to develop environmentally benign strategies in organic synthesis, and organocatalysis has gained tremendous impetus in the present day research due to its environmental advantages. Organocatalysis has been extensively studied and applied in many organic synthesis as an alternative to the conventional transition metal-catalyzed reactions[1-8]. In contrast to many transition metal catalysts, which are harmful to human health and the environment, organocatalysts are relatively nontoxic with no metallic wastes or by-products. They are easily handled and prepared from available, inexpensive crude materials leading to sustainable green synthesis. The idea of organocatalysis dates back to 1912 when Breding and Fiske reported the addition of hydrogen cyanide to aldehyde catalysed by cinchona alkaloids[9]. In the years since then, several organocatalysts have been reported, and amino acids are the most studied catalysts among them[10].

Michael addition reactions are well studied, and significant developments have been achieved with organocatalysts in recent years. There are several reports on the Michael addition reaction of ketones, aldehydes, and β-diketones to nitroolefins catalysed by various amino catalysts[11-15]. By virtue of the nitro functional groups that are easily transformable to different functional groups, Michael addition reaction to nitrostyrenes is a powerful tool towards functionalized organic molecules. Recently, Kumar et al. successfully achieved enantioselective Michael addition of ketones to nitrostyrenes using pyrrolidine-oxyimide organocatalyst[16]. L-prolinamides were also found to be effective in catalyzing the Michael addition of aldehydes to nitroolefines[17]. Impressive progress has been made by the application of bifunctional organocatalysts and has received much attention due to their wider applicability[18]. Takemoto et al. reveals that bifunctional organocatalysts containing thiourea and tertiary amino groups effectively activated nitro compounds for aza-Henry and Michael addition reactions[19-21]. The reaction was facilitated by the hydrogen bonding of thiourea with the nitro group. Several advancements have been made in this catalyst and furnished better enantioselectivity in the Michael addition of β-diketones to nitrostyrenes[22]. In view of the excellent activity of organocatalysts containing amino groups, and also due to our quest to develop readily available, inexpensive green organocatalysts, we synthesized various amino substituted triazine molecules and investigated their activity[23-24]. It was anticipated that the amino-functional groups of the catalyst could activate the Michael acceptor nitrostyrenes through hydrogen bonding to catalyze the reaction.

Experimental Details

Chemicals were used as purchased from commercial sources without further purification. Melting points were determined with JSGW melting point apparatus in open capillary tubes and were uncorrected. The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded in $CDCl_3$ and DMSO-d6 respectively with a Bruker Advance III FT-NMR. Chemical shifts are reported in ppm relative to TMS (δ = 0 ppm) internal standard. Infrared spectra were recorded with JASCO FTIR-4100 instrument. High-resolution mass spectra were recorded on using Waters Q-Tof mass spectrometer. Reactions were monitored by Agilent gas chromatography (GC-7890A) with an HP-5MS capillary column. Molecular mass was determined by electron spray ionization (ESI) method using LC-MS (Waters LC-e2695, Mass-3100).

General procedure for the synthesis of compounds 1-6

To a solution of cyanuric chloride (0.01 mol, 1 eqv.) in toluene (20 mL) at 10°C, a solution of corresponding amine (0.03 mol, 3 eqv.) in toluene (10 mL) was added dropwise. Then sodium hydroxide (0.03 mol, 3 eqv.) was added to the stirred solution and heated to reflux for 12 h. After completion of the reaction, the mixture was concentrated under reduced pressure, diluted with water and the products were extracted with dichloromethane. The organic layer was separated, dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure to afford the desired product.

N_2,N_4,N_6-tripropyl-1,3,5-triazine-2,4,6-triamine (1)[25]: White solid; yield 88%; m.p.: 55-57°C; IR (KBr): $\overline{V}$ = 3278, 2959, 2931, 1571, 1516, 1464, 1348, 812 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.12 (br s, 3H), 3.23 (br, 6H), 1.51-1.42 (m, 6H), 0.86-0.82 (t, J = 7.6 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.1, 41.4, 22.0,10.4; MS (ESI,+ve): m/z 253.18 $(M + H)^+$; HRMS (TOF MS ES^+) m/z $[M + H]^+$calcd for $C_{12}H_{25}N_6$ 253.2135,found 253.2184.

N_2,N_4,N_6-tributyl-1,3,5-triazine-2,4,6-triamine (2)[25]: Colorless oil; yield 89%; IR (KBr): $\overline{V}$ = 3283, 2956, 2866, 1585, 1517, 1421, 1356, 1115 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.21 (br s, 3H), 3.25 (br s, 6H), 1.46-1.39 (m, 6H), 1.31-1.22 (m, 6H), 0.84-0.81 (t, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.0, 39.3, 31.0, 19.0, 12.7; MS (ESI,+ve): m/z 296.26 $(M + 2H)^+$.

N_2,N_4,N_6-tripentyl-1,3,5-triazine-2,4,6-triamine (3)[25]: Colorless oil; yield 82%; IR (KBr): $\overline{V}$ = 3273, 2930, 2862, 1519, 1352, 1174, 812 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 4.75 (br s, 3H), 3.32 (br s, 6H), 1.55-1.52 (m, 6H), 1.34-1.32 (m,12H), 0.91-0.88 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.0, 39.6, 28.5, 28.1, 21.4, 12.9; MS (ESI,+ve): m/z 337.28 $(M + H)^+$.

N_2,N_4,N_6-trihexyl-1,3,5-triazine-2,4,6-triamine (4)[25]: Colorless oil; yield 90%; IR (KBr): $\overline{V}$ = 3272, 2927, 1516, 1353, 1170, 811 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.75 (br, 3H), 3.32 (br s, 6H), 1.55-1.49 (m, 6H), 1.36-1.27 (m, 18H), 0.90-0.86 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.13, 40.67, 31.57, 29.84, 26.62, 22.59, 14.01; MS (ESI,+ve): m/z 379.31 $(M + H)^+$.

N_2,N_4,N_6-trioctyl-1,3,5-triazine-2,4,6-triamine (5)[25]: White solid; yield 89%; m.p.: 55°C; IR (KBr): $\overline{V}$ = 3449, 3278, 2955, 2854, 1564, 1515, 1465, 1353, 1161 cm^{-1}; ^{1}H NMR (400MHz, $CDCl_3$): δ = 4.87 (br s, 3H), 3.34 (br s, 6H), 1.56-1.51 (m, 6H), 1.31-1.28 (m, 30H), 0.91-0.87 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 40.6, 31.8, 29.8, 29.3, 29.2, 26.9, 22.6, 14.0; HRMS (TOF MS ES+) m/z $[M + H]^+$calcd for $C_{27}H_{55}N_6$ 463.4483, found 463.4521.

N_2,N_4,N_6-tridodecyl-1,3,5-triazine-2,4,6-triamine (6)[25]: White solid; yield 82%; m.p.: 78°C; IR (KBr): $\overline{V}$ = 3409, 3264, 2968, 2933, 2872, 2810, 1566, 1514, 1382, 1068, 812 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.72 (br, 3H), 3.32 (br s, 6H), 1.54-1.49 (m, 6H), 1.30-1.25 (m, 54H), 0.84-0.81 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.2, 40.6, 31.9, 29.9, 29.6, 29.3, 26.9, 22.6, 14.0; HRMS (TOF MS ES^+) m/z $[M + H]^+$calcd for $C_{39}H_{78}N_6$ 631.6361, found 631.6353.

N_2,N_4,N_6-triphenyl-1,3,5-triazine-2,4,6-triamine (7)[26]: Cyanuric chloride (1.84 g, 0.01 mol) was added to a stirred solution of aniline (0.033 mol) in 75 mL of glacial acetic acid and was refluxed immediately after the addition of aniline. The product precipitated from the solution was recovered by filtration, washed with boiling water (approximately 20 mL x 3) to reach neutral pH and dried at 90°C in air to afford compound 7 as white solid. Yield 79%; m.p.: 230°C (lit.[26] 229–230 °C); IR (KBr): $\overline{V}$ = 3035, 1582, 1525, 1117, 840 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.22 (s, 1H), 7.80 (d, J = 7.6 Hz, 2H), 7.29 (t, J 7.2 Hz, 2H), 7.00 (t, J = 7.6 Hz, 1H); ^{13}C NMR

(100 MHz, DMSO-d_6): δ = 164.0, 139.8, 128.3, 122.0, 120.3; MS (ESI, +ve): m/z 355.14 $(M + H)^+$.

N_2,N_4,N_6-tricyclohexyl-1,3,5-triazine-2,4,6-triamine (8)[27]: Cyanuric chloride (0.01 mol) and Na_2CO_3 (0.03 mol) taken in a round-bottom-flask was added THF (50 mL) under nitrogen atmosphere. The mixture was stirred for 30 min at room temperature and then cyclohexylamine (0.033 mol) was added dropwise. The mixture was refluxed for 16 h and was then diluted with water. The product was extracted with chloroform, dried over anhydrous sodium sulfate, filtered and concentrated under reduced pressure to give the compound **8** as white solid. Yield 74 %; mp 190°C (lit.[27] 190°C); IR (KBr): $\overline{V}$ = 3424, 3245, 2925, 1524, 1364, 1166, 814 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.63 (s, 3H), 3.76-3.75. (m, 3H), 1.73-1.70 (m, 6H), 1.62-1.58 (m, 6H) 1.40-1.31 (m, 6H), 1.20-1.14(m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.5, 49.7, 33.4, 25.7, 24.9; MS (ESI, +ve): m/z 373.28 $(M + H)^+$.

N_2,N_4,N_6-tris(4-methoxyphenyl)-1,3,5-triazine-2,4,6-triamine (9)[26]: Cyanuric chloride (1.84 g, 0.01 mol) was added in one portion to a stirred solution of p-anisidine (0.033 mol) in 75 mL of glacial acetic acid, and the mixture was refluxed immediately after the addition of amine. The product precipitated from the solution was separated by filtration, washed with boiling water (approximately 20 mL x 3) to reach neutral pH and finally dried at 90°C in air to afford compounds **9** as white solid. Yield 73%; mp 216°C (lit.[26] 214–216°C); IR (KBr): $\overline{V}$ = 3230, 1580, 1510, 1240 cm^{-1}; ^{1}H NMR (400MHz, DMSO-d_6): δ = 8.96 (s, 3H), 7.64 (m, 6H), 6.87-6.85 (m, 6H), 3.73(s, 9H); ^{13}C NMR (100 MHz, DMSO-d6): δ = 164.0, 154.5, 132.9, 121.9, 113.5, 55.1; MS (ESI, +ve): m/z 445.17 $(M + H)^+$.

N_2,N_4,N_6-tris(4-nitrophenyl)-1,3,5-triazine-2,4,6-triamine (10)[28]: Cyanuric chloride (2.31 g, 12.5 mmol), p-nitroaniline (8.65 g, 62.5 mmol), and K_2CO_3 (10.4 g, 75 mmol) were mixed in 120 mL of 1,4-dioxane. The mixture was stirred well and refluxed for 24 h. The precipitated product was separated from the reaction mixture by filtration and purified by washing successively with water (100 mL × 3), methanol (50 mL × 3), and benzene (50 mL × 3). The solid was dried by keeping overnight under reduced pressure and was collected as a white solid. Yield 82%, m.p.> 300 °C (lit.[29]>300 °C); IR (KBr): $\overline{V}$ = 3340, 1630, 1590, 1510, 1340, 1240 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.31 (s, 3H), 8.22 (d, J = 8 Hz, 6H), 8.10 (d, J 8 Hz, 6H); MS (ESI, +ve): m/z 490.09 $(M + H)^+$.

General procedure for the synthesis of compounds 11 and 12

The reactions were carried out in a 100 mL autoclave under autogenous pressure. The reactor was charged with acetone (50 mL), cyanuric chloride (10 mmol, 1 eqv.), corresponding amine (30 mmol, 3 eqv.) and $NaHCO_3$ (30 mmol, 3 eqv.). The reaction mixture was heated at 100°C for 10 h. After cooling to room temperature, the precipitate was collected by filtration and washed with acetic acid to yield the desired products.

N_2,N_4,N_6-tri(naphthalen-1-yl)-1,3,5-triazine-2,4,6-triamine (11): Following the general reaction procedure, the reaction of cyanuric chloride (1.84 g, 0.01 mol) with 1-naphthylamine (0.03 mol) afforded the desired product 11 as white crystalline solid. Yield 80 %, m.p.: 210°C; IR (KBr): $\overline{V}$ = 3390, 1552, 1480, 1420, 1264 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.05 (s, 3H), 8.04-8.02 (m, 3H), 7.90-7.88 (m, 3H), 7.68-7.66 (m, 3H), 7.53-7.50 (m, 9H), 7.32-7.31 (m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 165.8, 134.1, 133.3, 128.5, 127.8, 126.0, 125.8, 125.5, 125.0, 121.5, 121.2; MS (ESI, +ve): m/z 505.19 $(M + H)^+$; HRMS (TOF MS ES^+) m/z $[M + H]^+$calcd for $C_{33}H_{25}N_6$ 505.2135, found 505.2160.

N_2,N_4,N_6-tri([1,1'-biphenyl]-4-yl)-1,3,5-triazine-2,4,6-triamine (12): Following the general reaction procedure, the reaction of cyanuric chloride (1.84 g, 0.01 mol) with biphenylamine (0.03 mol) afforded the desired product 12 as white solid. Yield 76 %, m.p.: 255°C; IR (KBr): $\overline{V}$ = 3401, 1594, 1523, 1232 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.44(s, 3H), 7.95 (d, J = 8 Hz, 6H), 7.68-7.62(m, 12H), 7.47-7.44(m, 6H), 7.35-7.31(m, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ = 164.0, 139.9, 139.4, 133.7, 128.8, 126.7, 126.5, 126.1, 120.6; MS (ESI, +ve): m/z 583.23 $(M + H)^+$; HRMS (TOF MS ES^+) m/z $[M + H]^+$calcd for $C_{39}H_{31}N_6$ 583.2605, found 583.2608.

General procedure for catalytic Michael addition of nitroolefins with various Michael donors

To a stirred solution of catalyst 6 (12.6 mg, 0.02 mmol, 10 mol%), nitroolefin (0.2 mmol) and Michael donor (0.4 mmol) in o-dichlorobenzene (1 mL), triethylamine was added. The reaction mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with water and was

extracted with ethyl acetate. The organic layer was separated, washed with water, followed by brine, dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (ethyl acetate and n-hexane as the eluent) to afford the corresponding Michael adducts (**15a-g**)

Diethyl 2-(2-nitro-1-phenylethyl)malonate (15a)[30]: According to the general procedure, **15a** was prepared from trans-β-nitrostyrene (29.8 mg, 0.2 mmol) and diethyl malonate (64 mg, 0.4 mmol) as white solid in 83% yield (51 mg). m.p.: 60°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33-7.22 (m, 5H), 4.94-4.83 (m, 2H), 4.23-4.22 (m, 3H), 4.01 (q, J = 7.2 Hz, 2H), 3.82 (d, J = 9.2 Hz, 1H), 1.27 (t, J = 7.4, 3H), 1.05 (t, J = 7.2 Hz, 3H) ppm; ^{13}C NMR (400 MHz, $CDCl_3$): δ = 167.4, 166.8, 136.2, 128.9, 128.3, 128.0, 77.6, 62.1, 61.8, 61.4, 55.0, 42.9, 13.9, 13.7 ppm.

Dimethyl 2-(2-nitro-1-phenylethyl)malonate (15b)[30]: According to general procedure, **15b** was prepared from trans-β-nitrostyrene (29.8 mg, 0.2 mmol) and dimethyl malonate (52 mg, 0.4 mmol) as white solid in 84% yield (47 mg). m.p.: 64°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34-7.27 (m, 3H), 7.23-7.21 (m, 2H), 4.95-4.84 (m, 2H), 4.27-4.21 (m, 1H), 3.86 (d, J = 9.2 Hz, 1H), 3.76 (s, 3H), 3.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8, 167.2, 136.1, 129.0, 128.4, 127.8, 54.7, 53.0, 52.8, 42.9 ppm.

Dimethyl 2-(1-(4-chlorophenyl)-2-nitroethyl) malonate (15c)[31]: According to general procedure, **15c** was prepared from 1-chloro-4-(2-nitroethyl) benzene (36.7 mg, 0.2 mmol) and dimethyl malonate (52 mg, 0.4 mmol) as pale yellow solid in 82% yield (52 mg). m.p.: 87°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31-7.29 (m, 2H), 7.18-7.17 (m, 2H), 4.89-4.84 (m, 2H), 4.23-4.21 (m, 1H), 3.82 (d, J = 8.8 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 167.0, 134.6, 134.4, 129.3, 129.2, 54.5, 53.0, 52.9, 42.3 ppm.

Dimethyl 2-(1-(4-bromophenyl)-2-nitroethyl) malonate (15d)[31]: According to general procedure, **15d** was prepared from 1-bromo-4-(2-nitroethyl) benzene (45.6 mg, 0.2 mmol) and dimethyl malonate (52 mg, 0.4 mmol) as white solid in 81% yield (58 mg). m.p.: 90°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46-7.44 (m, 2H), 7.12-7.11 (m, 2H), 4.92-4.81 (m, 2H), 4.24-4.18 (m, 1H), 3.82 (d, J = 8.8 Hz, 1H), 3.76 (s, 3H), 3.59 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 167.0, 135.2, 132.2, 129.6, 122.5, 54.4, 53.0, 52.9, 42.4 ppm.

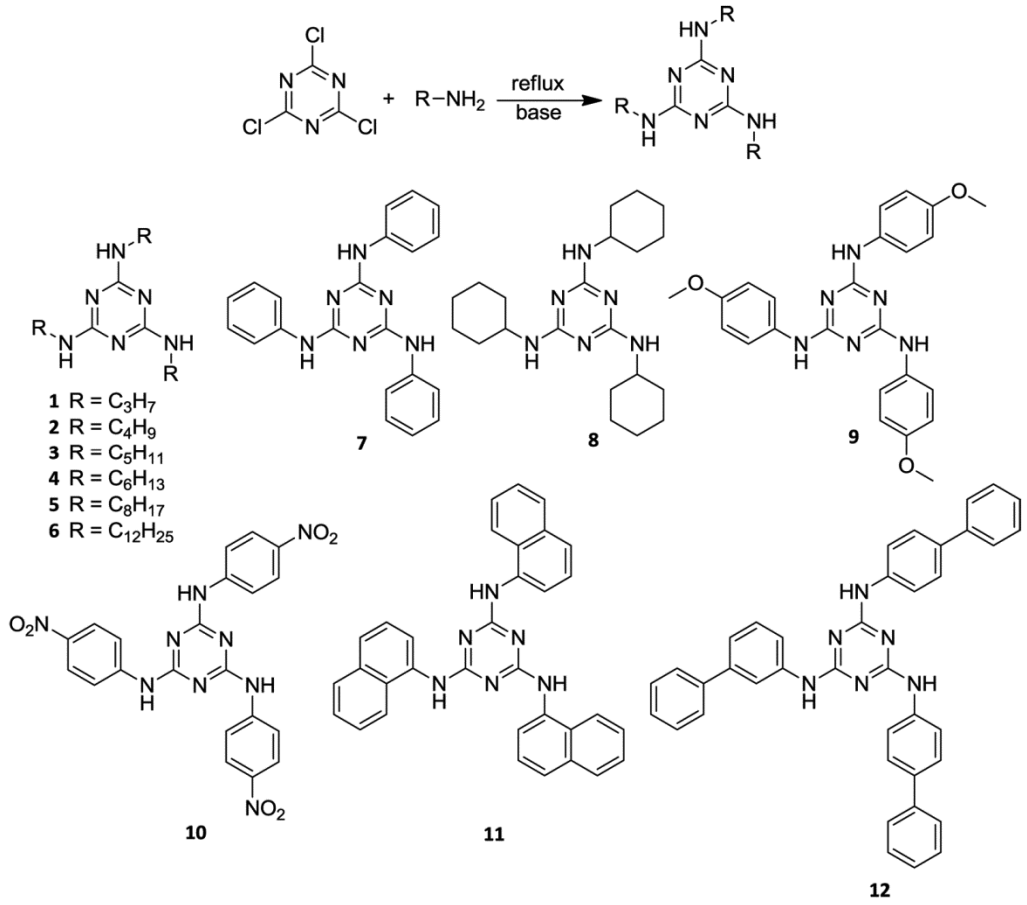
Dimethyl 2-(1-(4-methoxyphenyl)-2-nitroethyl) malonate (15e)[30]: According to general procedure, **15e** was prepared from 1-methoxy-4-(2-nitro-vinyl) benzene (35.8 mg, 0.2 mmol) and dimethyl malonate (52 mg, 0.4 mmol) as colorless oil in 78% yield (49 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.14 (d, J = 8.0 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 4.91-4.79 (m, 2H), 4.21-4.16 (m, 1H), 3.87 (d, J = 9.2 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 3.57 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9, 167.2, 159.4, 129.0, 127.9, 114.4, 55.2, 54.9, 52.9, 52.7, 42.3 ppm.

Dimethyl 2-(2-nitro-1-(4-nitrophenyl)ethyl) malonate (15f)[30]: According to general procedure, **15f** was prepared from 1-nitro-4-(2-nitrovinyl) benzene (38.8 mg, 0.2 mmol) and dimethyl malonate (52 mg, 0.4 mmol) as yellow color oil in 76% yield (50 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23 (d, J = 8.8 Hz, 2H), 7.47 (d, J = 8.8, 2H), 4.98-4.95 (m, 2H), 4.42-4.23 (m, 1H), 4.15 (d, 1H), 3.91-3.80 (s, 3H), 3.66-3.63 (s, 3H) ppm.

2-(2-nitro-1-phenylethyl)malononitrile (15g)[30]: According to general procedure **15g** was prepared from trans-β-nitrostyrene (29.8 mg, 0.2 mmol) and malononitrile (26 mg, 0.4 mmol) as white solid in 80% yield (34 mg). m.p.: 56°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.42 (m, 3H), 7.25-7.22 (m, 2H), 5.14 (m, 2H), 4.32 (d, J = 9.6 Hz 1H), 4.13 (m, 1H) ppm,

Results and Discussion

Our investigations on organocatalyzed Michael addition reaction of various nucleophiles to β-nitrostyrene commenced with the synthesis of a series of organocatalysts **1-12** (Scheme 1) from 2,4,6-tricholo-1,3,5-triazine, an easily available inexpensive crude material. We examined the catalytic activity of the prepared catalysts in the Michael addition of malonates to nitroolefins. The catalysts were screened by studying the reaction of dimethyl malonate and trans-β-nitrostyrene with various triazine derivatives in the presence of triethylamine in dichlorobenzene at room temperature for 12 h. The results showed that catalyst **4** exhibited high activity, and the product was formed in good yield (Table 1).



Scheme 1 — Synthesis of a series of organocatalysts (**1**-**12**)

Table 1 — Effect of catalyst[a]

Entry	Catalyst	Time(h)	Yield(%)[b]
1	none	12	45
2	4	12	76
3	7	12	68
4	8	12	63
5	9	12	45
6	10	12	49
7	11	12	48
8	12	12	47

[a]All reactions were carried out using trans-β-nitrostyrene (0.2 mmol) and dimethyl malonate (0.4 mmol) in the presence of different catalysts (0.02 mmol, 10 mol %) and 1 equiv. triethylamine in o-dichlorobenzene (1 mL) at rt. [b]Determined by GC analysis.

In the light of the above results, we assumed that catalyst having alkyl group directly attached to the amino groups gives good yield as compared to other catalysts. In order to evaluate the activity of catalysts with different alkyl chains, we investigated the activity of a range of catalysts. From Table 2, it is evident that catalyst **6** with long chain alkyl group gives the best result under similar condition.

Table 2 — Effect of alkyl chain on the rate of Michael addition reaction[a]

Entry	Catalyst	Time(h)	Yield(%)[b]
1	1	12	68
2	2	12	69
3	3	12	72
4	4	12	76
5	5	12	85
6	6	12	87

[a]All reactions were carried out using trans-β-nitrostyrene (0.2 mmol) and dimethyl malonate (0.4 mmol) in the presence of different catalyst (0.02 mmol, 10 mol%) and 1 equiv. triethylamine in o-dichlorobenzene (1 mL) at rt.. [b]Determined by GC analysis.

Further to the above studies, the Michael addition reaction was carried out in different solvents using catalyst **6**, keeping the other parameters constant. The results show that o-dichlorobenzene gives the best result for the reaction when carried out for 12 h. From Table 3, it is clear that the halogenated solvents and the aromatic halogenated solvents in particular furnished better results.

Table 3 — Effect of solvent[a]

Entry	Solvent	Time (h)	Yield (%)[b]
1	CH_2Cl_2	12	79
2	chloroform	12	79
3	THF	12	58
4	toluene	12	57
5	o-dichlorobenzene	12	87
6	dichloroethane	12	80
7	CH_3CN	12	51

[a]All reactions were carried out using trans-β-nitrostyrene (0.2 mmol) and dimethyl malonate (0.4 mmol) in the presence of catalyst 6 (0.02mmol, 10 mol%) and 1 equiv. triethylamine in o-dichlorobenzene (1 mL) at rt. [b]Determined by GC analysis

Table 4 — Effect of base[a]

Entry	Base	Time (h)	Yield (%)[b]
1	Na_2CO_3	12	43
2	DIPEA	12	76
3	triethylamine	12	87
4	DABCO	12	70
5	Pyridine	12	62

[a]All reactions were carried out using trans-β-nitrostyrene (0.2 mmol) and dimethyl malonate (0.4 mmol) in the presence of catalyst **6** (0.02mmol, 10 mol%) and 1 equiv. triethylamine in o-dichlorobenzene (1 mL) at rt. [b]Determined by GC analysis

Table 5 — The scope of catalyst 6 in Michael addition reaction with various substrates[a]

Entry[l]	R	R[1]	Time (h)	Yield (%)[b]
1	-H	$-CO_2Et$	12	83
2	-H	$-CO_2Me$	12	84
3	-Cl	$-CO_2Me$	12	82
4	-Br	$-CO_2Me$	12	81
5	-OMe	$-CO_2Me$	12	78
6	-NO2	$-CO_2Me$	12	76
7	-H	-CN	12	80

[a]All reactions were carried out using nitrostyrenes (0.2 mmol) and β-diketones (0.4 mmol) in the presence of catalyst **6** (0.02 mmol, 10 mol%) and 1 equiv. triethylamine in o-dichlorobenzene (1 mL) at rt. [b]Isolated yield

In the next phase of our studies, we tried to find out the best base suited for this reaction under an identical condition. As we expected, it is observed that triethylamine is more effective than other bases, such as DIPEA, Na_2CO_3, pyridine, and DABCO. The results are summarised in Table 4.

Having optimized the reaction conditions, we then studied the scope of this transformation with various nitroolefins and Michael donors using **6** as the organocatalyst. The catalyst was found to be effective with various substrates (Table 5). Addition of dimethyl malonate to nitrostyrene offered the highest yield and substituted β-nitrostyrenes bearing electron withdrawing or electron donating groups on the aromatic ring gave lower yields as compared to other substrates.

Conclusion

In summary, we have developed alkylamino substituted triazine based organocatalysts with a view to promote Michael addition reactions of β-diketones to nitrostyrenes. The catalyst 6 demonstrated excellent activity with long chain alkyl group in the triazine core. The reaction with triazine based catalysts is superior to the conventional base catalyzed Michael addition reactions in terms of mild conditions, good yields and less reaction time. Moreover, readily available low-cost, nontoxic crude materials of the catalysts make the reaction green.

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