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Aminopropylated PEG as a novel, eco-friendly and biodegradable basic catalyst for bis-Michael addition to α,β-unsaturated ketones under solvent-free conditions

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A solvent-free and highly efficient protocol has been developed for the synthesis of novel bis-Michael addition products (3a–o) using aminopropylated PEG-6000 (NH_2-PEG) as a biodegradable and recyclable catalyst in excellent yields under solvent-free conditions. Other remarkable features of this environmentally benign protocol are shorter reaction time, tolerance of a wide range of C—H-activated acids, high yield of products, and simple experimental and work-up procedure as compared to conventional methods. The NH_2-PEG catalyst is characterized by using FT-IR, powder XRD and scanning electron microscopy–energy dispersion X-ray spectrometric analyses. The catalyst can be recycled several times without significant loss of its catalytic activity. Copyright © 2014 John Wiley & Sons, Ltd.

Keywords: NH_2-PEG; bis-Michael addition products; solvent-free conditions

Introduction

The Michael addition reaction is a versatile method for the formation of carbon–carbon bonds in organic chemistry. Traditionally, the reaction is catalyzed by strong bases[1] and Lewis acids,[2] which often leads to undesirable side products and unsatisfactory product yield. However, now a considerable improvement in terms of yield and time has been observed in the Michael addition reaction. In this context, a number of reagents have been developed which include silica nanoparticles,[3] basic ionic liquid,[4] tributylphosphine,[5] poly(*N*-vinylimidazole),[6] st-DNA,[7] tetraethylammonium superoxide,[8] KF/CP,[9] [C_4dabco]OH ionic liquid,[10] Rasta resin,[11] immobilized lipase on Fe_3O_4/ZnO core/shell magnetic nanoparticles,[12] polyvinyl sulfonic acid,[13] silica sulfuric acid,[14] KG-60-NEt_2,[15] KF/NP,[16] $NaHSO_4.SiO_2$,[17] **1**-Gd$(OTf)_3$,[18] Kf/basic alumina,[19] Zn-HAP[20] and CSC-Star-SO_3AlCl_2.[21] Moreover, most of the reactions are referred to mono-Michael addition reaction, and very few reagents have been reported for the bis-Michael addition reaction to date.[3,5,22] Thus effective and high-yielding processes are still in demand for the development of a milder reagent for a general bis-Michael addition of a variety of C—H-activated acids to α, β-unsaturated ketones in a single step.

Catalytic applications of functional polymers in organic synthesis have attracted much attention from researchers all over the world.[23] To simplify the isolation of products and catalyst recycling, immobilization of catalyst over an inert solid support proved to be an efficient approach, leading towards green synthesis.[23] Among the wide range of polymeric matrices employed in solid-phase chemistry, polyethylene glycols have emerged as convenient supports for the synthesis of a variety of small organic molecules, ligands and catalysts.[24] Moreover, they are readily functionalized, environmentally benign and inexpensive.

To improve the efficiency of a catalytic process, an intense research activity has recently been devoted towards the development of solid supported catalysts involving easy catalyst recovery and recycling.[25] Herein, we have synthesized aminopropylated PEG-6000 (NH_2-PEG) as a polyamine basic catalyst which is novel, easily preparable, mild, biodegradable, recyclable and non-corrosive. Therefore, based on the above findings and in continuation of our interest in the synthesis of novel catalysts and development of efficient, economical methodologies,[26] we now wish to explore the catalytic activity of NH_2-PEG in bis-Michael addition of a variety of C—H-activated acids to bis-α,β-unsaturated ketones under solvent-free conditions (Scheme 2). The catalyst was recyclable up to several runs. The structure and morphology of the catalyst was established with the help of FT-IR, powder X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersion X-ray spectrometry (EDX).

Experimental

General Information

Melting points of all synthesized compounds were taken in a Riechert Thermover instrument and are uncorrected. The IR spectra (KBr) were recorded on PerkinElmer RXI spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-300 and Bruker Avance II 400 spectrometer using tetramethylsilane (TMS) as an internal standard and DMSO-d_6/$CDCl_3$ as solvent.

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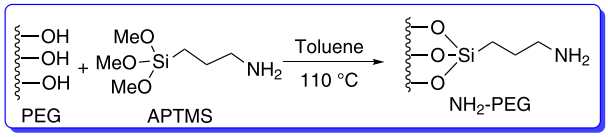


Scheme 1. Schematic illustration of preparation of the catalyst (NH_2-PEG).

Electrospray ionization (ESI) mass spectra were recorded on a Thermo Finnigan LCQ Advantage max ion trap mass spectrometer having an ESI source. Elemental analyses (C, H and N) were conducted using an Elemental Vario EL III elemental analyzer and the results were found to be in agreement with the calculated values. Chemicals were of commercial grade and used without further purification. Homogeneity of the compounds was checked by thin-layer chromatography (TLC) on glass plates coated with silica gel G254 (Merck) using a chloroform–methanol (3:1) mixture as mobile phase and visualized using iodine vapors. X-ray diffractograms of the catalyst were recorded in the 2θ range of 10–70° with a scan rate of 4° min^{-1} on a Rigaku Minifax X-ray diffractometer with Ni-filtered Cu-K_α radiation at a wavelength of 1.54060° A. SEM-EDX characterization of the catalyst was performed on a JEOL JSM-6510 scanning electron microscope equipped with energy-dispersive X-ray spectrometer operating at 20 kV.

Preparation of Catalyst

Aminopropylated PEG was prepared by refluxing PEG (10 g) with 3-aminopropyltrimethoxysilane (3.3 mmol) in dry toluene for 18 h. The solid material was then filtered off and washed with hot toluene and then dried in oven at 110°C overnight to give surface-bound amine.

General Procedure for the Bis-Michael Addition of Varieties of C—H-Activated Acids to Bis-α,β-Unsaturated Ketones under Solvent-Free Conditions

Bis-α, β-unsaturated ketones (**1a–b**) (10 mmol), acyclic and cyclic C—H-activated acids (**2a–m**) (20 mmol) and aminopropylated PEG (NH_2-PEG) catalyst (1.00 g) were mixed in a 100 ml round-bottom flask for the specified time (Table 3) at 70°C. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature and H_2O (50 ml) added and shaken for 3 min to dissolve the NH_2-PEG. The crude product (insoluble in water) was filtered and recrystallized from ethyl alcohol (30 ml) to afford the pure product (**3a–o**). In order to recover the catalyst, the filtrate was evaporated under reduced pressure and Et_2O (50 ml) added. The solid, as obtained, was filtered, washed with Et_2O (20 ml × 2) and reused after drying.

Spectral Data of Compounds

*3,3′-(1,4-Phenylene)bis(4-acetyl-1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl) hexane-1,5-dione) (**3a**)*

Yellow solid; m.p. 125–127°C; IR (KBr) cm^{-1}: 1627, 1654, 1686 (CO), 3428 (OH). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.86$ (12H, s, $4 \times CH_3$), 2.11 (6H, s, $2 \times CH_3$), 2.88–2.90 (4H, m, $2 \times CH_2$), 3.55–3.62 (2H, m, $2 \times CH3'$), 5.25 (2H, s, $2 \times H_5$), 5.74 (2H, d, $J = 5.9$ Hz, $2 \times CH3''$), 7.58 (4H, s, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 14.48$ ($2 \times CH_3$), 20.75 ($4 \times CH_3$), 44.8 ($2 \times CH3'$), 50.86 ($2 \times CH_2$), 52.69 ($2 \times CH3''$), 99.69 ($2 \times C3$), 102.40 ($2 \times C5$), 126.21, 137.49 (Ar—C), 161.29 ($2 \times C6$), 169.25 ($2 \times C2$), 182.95 ($2 \times C4$), 191.51 ($2 \times C1'$), 192.57 (2 x C4″), 192.76 ($2 \times C2''$). ESI-MS: (m/z) 634.2 ($M^+ + 1$). Anal. Calcd for $C_{33}H_{34}O_{12}$: C, 63.65; H, 5.50; found: C, 63.68; H, 5.52.

*3,3′-(1,3-Phenylene)bis(4-acetyl-1-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl) hexane-1,5-dione) (**3b**)*

White solid; m.p. 121–123°C; IR (KBr) cm^{-1}: 1630, 1658, 1696 (CO), 3431 (OH). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 1.98$ (12H, s, $4 \times CH_3$), 2.03 (6H, s, $2 \times CH_3$), 2.98–3.01 (4H, m, $2 \times CH_2$), 3.45–3.50 (2H, m, $2 \times CH3'$), 5.21 (2H, s, $2 \times H_5$), 5.71 (2H, d, $J = 5.4$ Hz, $2 \times CH3''$), 7.08–7.12 (3H, m, C_6H_4), 7.24 (1H, s, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 16.17$ ($2 \times CH_3$), 19.75 ($4 \times CH_3$), 43.7 ($2 \times CH3'$), 49.10

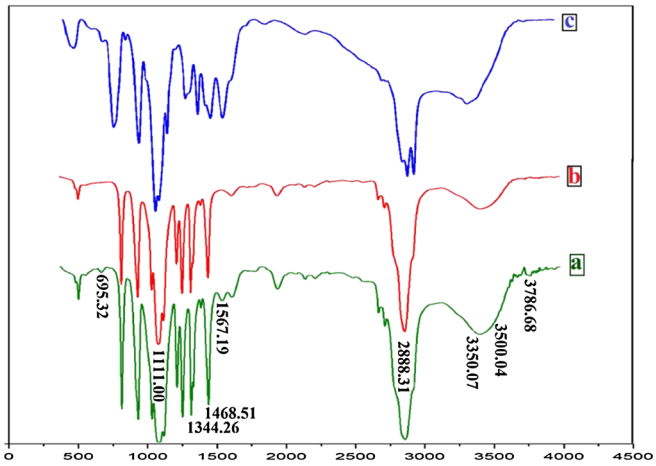


Figure 1. FT-IR spectra of (a) NH_2-PEG, (b) PEG and (c) APTMS.

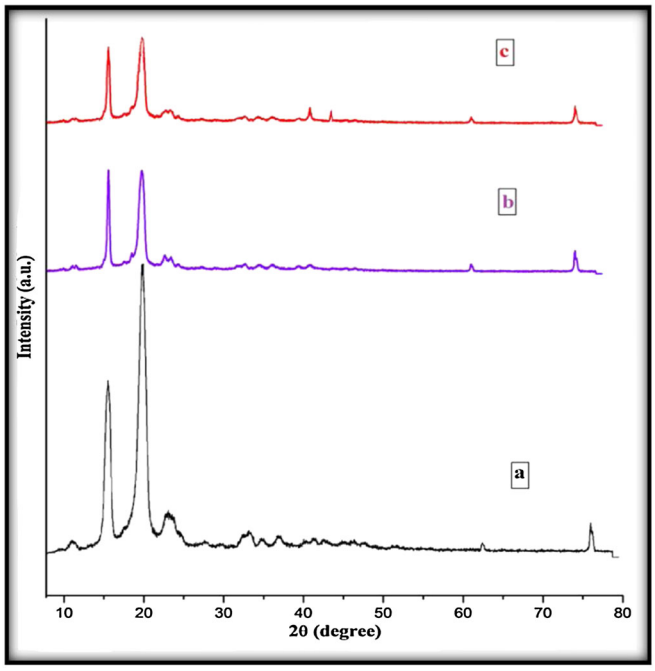


Figure 2. Powder XRD of (a) PEG, (b) fresh NH_2-PEG and (c) NH_2-PEG after eight runs.

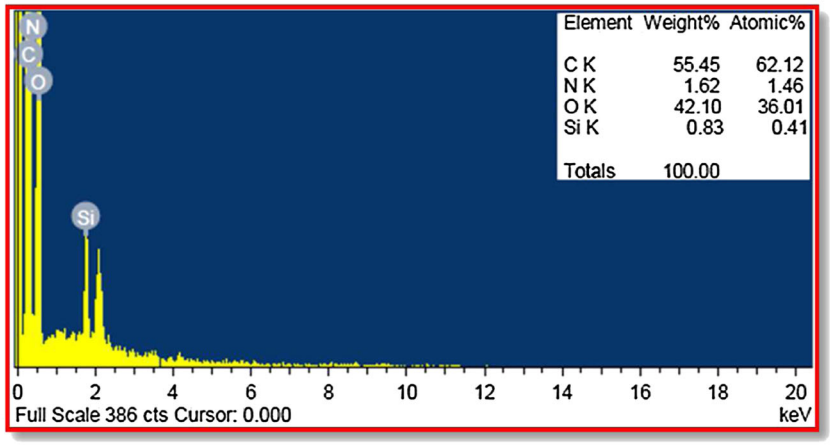


Figure 3. EDX analysis of the catalyst (NH_2-PEG).

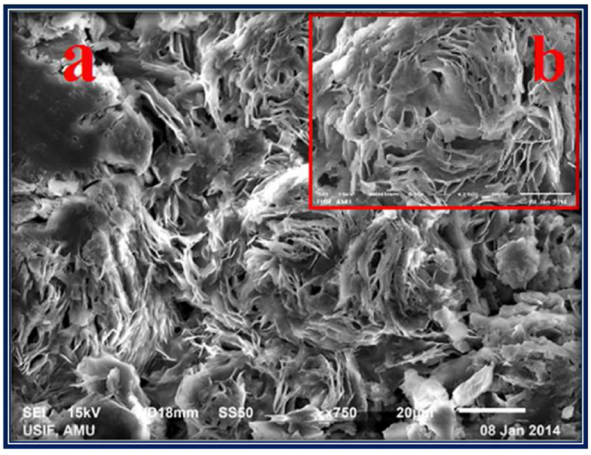


Figure 4. SEM images of fresh catalyst (NH_2-PEG) at different magnifications.

($2\times CH_2$), 53.10 ($2\times$CH3″), 99.71 ($2\times$C3), 101.81 ($2\times$C5), 123.30, 128.1, 135.72, 139.34 (Ar—C), 162.01 ($2\times$C6), 168.11 ($2\times$C2), 180.21 ($2\times$C4), 190.11 ($2\times$C1′), 191.31 ($2\times$C4″), 191.52 ($2\times$C2″). ESI-MS: (*m/z*) 634.1 (M^++1). Anal. Calcd for $C_{33}H_{34}O_{12}$: C, 63.65; H, 5.50; found: C, 63.62; H, 5.47.

*2,2′-(1,4-Phenylene)bis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl)dimalononitrile (**3c**)*

Shining red solid; m.p. 131–133°C; IR (KBr) cm^{-1}: 1642, 1722 (CO), 2214 (CN), 3416 (OH). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.04$ (6H, s, $2\times CH_3$), 2.93-2.95 (4H, m, $2\times CH_2$), 3.71–3.74 (2H, m, $2\times$CH3′), 5.31 (2H, s, $2\times H_5$), 5.71 (2H, d, $J = 5.0$ Hz, $2\times$CH2″), 7.56 (1H, s, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 20.90$ ($2\times CH_3$), 40.11 ($2\times$CH3′), 49.40 ($2\times CH_2$), 53.30 ($2\times$CH2″), 99.70 ($2\times$C3), 101.51 ($2\times$C5), 113.01 ($2\times$CN), 125.80, 138.61 (Ar—C), 161.20 ($2\times$C6), 168.21 ($2\times$C2), 181.20 ($2\times$C4), 190.20 ($2\times$C1′). ESI-MS: (*m/z*) 566.1 (M^++1). Anal. Calcd for $C_{30}H_{22}N_4O_8$: C, 63.60; H, 3.91; N, 9.89; found: C, 63.57; H, 3.89; N, 9.86.

*Tetraethyl-2,2′-(1,4-phenylene)bis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl)dimalonate (**3d**)*

Dark-red crystals; m.p. > 280°C; IR (KBr) cm^{-1}: 1623, 1654 (CO), 1710 (COO), 3374 (OH).^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.27$–1.29 (12H, m, $4\times CH_3$), 2.11 (6H, s, $2\times CH_3$), 2.86–2.90 (4H, m, $2\times CH_2$), 3.10–3.15 (2H, m, $2\times$CH3′), 4.11–4.15 (8H, m, $4\times OCH_2$), 5.71 (2H, d, $J = 5.4$ Hz, $2\times$CH3″), 6.01 (2H, s, $2\times H_5$), 7.58 (1H, s, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 13.59$ ($4\times CH_3$), 19.10 ($2\times CH_3$), 42.10 ($2\times$CH3′), 48.21 ($2\times CH_2$), 57.12 ($2\times$CH4″), 61.30 ($4\times OCH_2$), 99.19 ($2\times$C3), 101.01 ($2\times$C5), 128.80, 132.60 (Ar—C), 162.30 ($2\times$C6), 167.22 ($2\times$C2), 169.90 ($4\times$CO), 180.01 ($2\times$C4), 189.31 ($2\times$C1′). ESI-MS: (*m/z*) 754.2 (M^++1). Anal. Calcd for $C_{38}H_{42}O_{16}$: C, 60.47; H, 5.60; found: C, 60.50; H, 5.57.

*Diethyl-3,3′-(1,4-phenylene)bis(2-acetyl-5-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-5-oxopentanoate) (**3e**)*

White solid; m.p. 205–207°C; IR (KBr) cm^{-1}: 1629, 1657, 1699 (CO), 1711 (COO), 3413 (OH). ^{1}H NMR (400 MHz, $CDCl_3$): 1.27–1.30 (6H, m, $2\times CH_3$), 2311 (6H, s, $2\times CH_3$), 2.49 (6H, s, $2\times CH_3$), 3.09–3.11 (4H, m, $2\times CH_2$), 3.85–3.89 (2H, m, $2\times$CH3′), 4.19–4.21 (4H, m, $2\times OCH_2$), 5.80 (2H, d, $J = 5.2$ Hz, $2\times$CH3″), 6.18 (2H, s, $2\times H_5$), 7.11 (1H, s, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 15.03$ ($2\times CH_3$), 19.90 ($2\times CH_3$), 21.41 ($2\times CH_3$), 44.11 ($2\times$CH3′), 53.21 ($2\times CH_2$), 54.18 ($2\times$CH3″), 61.32 ($2\times OCH_2$), 98.23 ($2\times$C3), 101.25 ($2\times$C5), 129.23, 135.01 (Ar—C), 161.20 ($2\times$C6), 166.32 ($2\times$C2), 171.09 ($2\times$COO), 185.21 ($2\times$C4), 191.21 ($2\times$C1′), 194.11 ($2\times$C2″). ESI-MS: (*m/z*) 694.1 (M^++1). Anal. Calcd for $C_{36}H_{38}O_{14}$: C, 62.24; H, 5.51; found: C, 62.27; H, 5.48.

*Diethyl-3,3′-(1,4-phenylene)bis(2-cyano-5-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-5-oxopentanoate) (**3f**)*

Green solid; m.p. 257–259°C; IR (KBr) cm^{-1}: 1630, 1659 (CO), 1713 (COO), 2214 (CN), 3476 (OH). ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 1.29$–1.32 (6H, m, $2\times CH_3$), 2.51 (6H, s, $2\times CH_3$), 3.34–3.36 (4H, m, $2\times CH_2$), 3.62–3.65 (2H, m, $2\times$CH3′), 4.21–4.25 (4H, m, $2\times OCH_2$), 5.67 (2H, d, $J = 5.0$ Hz, $2\times$CH2″), 6.10 (2H, s, $2\times H_5$), 7.22 (1H, s, C_6H_4). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 14.10$ ($2\times CH_3$), 20.90 ($2\times CH_3$), 45.01 ($2\times$CH3′), 51.13 ($2\times CH_2$), 58.11 ($2\times$CH2″), 60.80 ($2\times OCH_2$), 101.31 ($2\times$C3), 105.10 ($2\times$C5), 116.21 ($2\times$CN), 126.80, 134.10 (Ar—C), 165.10 ($2\times$C6), 166.21 ($2\times$C2), 168.50 ($2\times$COO), 183.11 ($2\times$C4), 198.11 ($2\times$C1′). ESI-MS: (*m/z*) 658.2 (M^++1). Anal. Calcd for $C_{35}H_{34}N_2O_{11}$: C, 63.82; H, 5.20; N, 4.25; found: C, 63.80; H, 5.17; N, 4.22.

*Dimethyl-3,3′-(1,4-phenylene)bis(2-acetyl-5-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-5-oxopentanoate) (**3g**)*

White solid; m.p. 245°C; IR (KBr) cm^{-1}: 1627, 1659, 1691 (CO), 1714 (COO), 3484 (OH). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.01$ (6H, s, $2\times CH_3$), 2.21 (6H, s, $2\times CH_3$), 3.12–3.15 (4H, m, $2\times CH_2$), 3.31 (6H, s, $2\times OCH_3$), 3.46–3.48 (2H, m, $2\times$CH3′), 5.71 (2H, d, $J = 5.3$ Hz, $2\times$CH3″), 5.98 (2H, s, $2\times H_5$), 7.28 (4H, s, C_6H_4). ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 19.10$ ($2\times CH_3$), 22.02 ($2\times CH_3$), 43.27 ($2\times$CH3′), 47.01 ($2\times CH_2$), 50.19 ($2\times OCH_3$), 61.29 ($2\times$CH3″), 100.21 ($2\times$C3), 103.15 ($2\times$C5), 125.08, 131.11 (Ar—C), 162.01 ($2\times$C6), 166.23 ($2\times$C2), 171.01 ($2\times$C4″), 183.20 ($2\times$C4), 193.12 ($2\times$C1′), 198.11 ($2\times$C2″). ESI-MS: (*m/z*) 666.1 (M^++1). Anal. Calcd for $C_{34}H_{34}O_{14}$: C, 61.25; H, 5.14; found: C, 61.21; H, 5.11.

*3,3′-(1,4-Phenylene)bis(5-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-5-oxo-2-phenylpentanoic acid) (**3h**)*

Reddish-brown solid; m.p. > 300°C; IR (KBr) cm^{-1}: 1654, 1698 (CO), 1714 (COO), 3456 (OH). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 1.91$ (6H, s, $2\times CH_3$), 3.11–3.14 (4H, m, $2\times CH_2$), 3.70–3.72 (2H, m, $2\times$CH3′),

5.74 (2H, d, J = 5.6 Hz, 2 × CH3″), 6.94 (2H, s, 2 × H_5), 7.13–7.94 (14H, m, C_6H_4, Ar—H), 10.01 (2H, s, 2 × COOH). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 22.10 (2 × CH_3), 43.12 (2 × CH3′), 53.61 (2 × CH_2), 59.16 (2 × CH2″), 100.21 (2 × C3), 103.15 (2 × C5), 125.80, 128.19, 135.11, 139.31, 140.61 (Ar—C), 164.13 (2 × C6), 170.23 (2 × C2), 179.30 (2 × C1″), 181.21 (2 × C4), 198.11 (2 × C1′). ESI-MS: (*m/z*) 706.2 (M^++1). Anal. Calcd for $C_{40}H_{34}O_{12}$: C, 67.98; H, 4.84; found: C, 67.96; H, 4.86.

5,5′-(1,4-Phenylenebis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl))bis(1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione) (**3i**)

Light-yellow solid; m.p. > 300°C; IR (KBr) cm^{-1}: 1658, 1682, 1700 (CO), 3416 (OH). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.51 (6H, s, 2 × CH_3), 3.02 (12H, s, 4 × CH_3), 3.21–3.23 (4H, m, 2 × CH_2), 3.40–3.44 (2H, m, 2 × CH3′), 5.72 (2H, d, J = 5.8 Hz, 2 × CH5″), 6.12 (2H, s, 2 × H_5), 7.23 (4H, s, C_6H_4). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 23.01 (2 × CH_3), 27.41 (4 × CH_3), 37.13 (2 × CH3′), 45.16 (2 × CH_2), 50.21 (2 × CH5″), 98.91 (2 × C3), 100.01 (2 × C5), 129.11, 132.71, (Ar—C), 153.17 (2 × C2″), 163.11 (2 × C6), 165.21 (2 × C2), 170.13 (2 × C4″, C6″), 183.14 (2 × C4), 197.01 (2 × C1′). ESI-MS: (*m/z*) 746.2 (M^++1). Anal. Calcd for $C_{36}H_{34}N_4O_{14}$: C, 57.90; H, 4.59; N, 7.50; found: C, 57.87; H, 4.57; N, 7.47.

5,5′-(1,3-Phenylenebis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl))bis(1,3-dimethylpyrimidine-2,4,6(1H,3H,5H)-trione) (**3j**)

Yellow solid; m.p. > 300°C; IR (KBr) cm^{-1}: 1659, 1684, 1703 (CO), 3426 (OH). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.02 (6H, s, 2 × CH_3), 2.91 (12H, s, 4 × CH_3), 3.33–3.36 (4H, m, 2 × CH_2), 3.44–3.48 (2H, m, 2 × CH3′), 5.73 (2H, d, J = 5.6 Hz, 2 × CH5″), 6.09 (2H, s, 2 × H_5), 7.21–7.48 (3H, m, C_6H_4), 7.61 (1H, s, C_6H_4). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.23 (2 × CH_3), 29.40 (4 × CH_3), 38.32 (2 × CH3′), 48.16 (2 × CH_2), 50.23 (2 × CH5″), 98.11 (2 × C3), 101.51 (2 × C5), 123.31, 128.11, 133.21, 136.31, 139.01 (Ar—C), 150.71 (2 × C2″), 162.01 (2 × C6), 164.25 (2 × C2), 169.31 (2 × C4″, C6″), 181.21 (2 × C4), 195.25 (2 × C1′). ESI-MS: (*m/z*) 746.1 (M^++1). Anal. Calcd for $C_{36}H_{34}N_4O_{14}$: C, 57.90; H, 4.59; N, 7.50; found: C, 57.92; H, 4.56; N, 7.52.

2,2′-(1,4-Phenylenebis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl))bis(5,5-dimethylcyclohexane-1,3-dione)) (**3k**)

White powder; m.p. > 300°C; IR (KBr) cm^{-1}: 1625, 1658, 1698 (CO), 3377 (OH). ^{1}H NMR (400 MHz, DMSO-d_6): 1.01 (12H, s, 4 × CH_3), 2.09 (6H, s, 2 × CH_3), 2.62–2.65 (8H, m, 4 × CH_2), 3.03–3.06 (4H, m, 2 × CH_2), 3.35–3.38 (2H, m, 2 × CH3′), 5.42 (2H, d, J = 5.9 Hz, 2 × CH2″), 6.01 (2H, s, 2 × H_5), 7.31 (4H, s, C_6H_4). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 22.19 (4 × CH_3), 25.16 (2 × CH_3), 30.40 (2 × C5″), 40.11 (2 × CH3′), 46.61 (2 × CH_2), 52.11 (2 × C4″, C6″), 71.11 (2 × CH2″), 99.71 (2 × C3), 101.15 (2 × C5), 131.11, 138.25 (Ar—C), 164.23 (2 × C6), 169.10 (2 × C2), 182.01 (2 × C4), 193.15 (2 × C1′), 197.31 (2 × C1″, C3″). ESI-MS: (*m/z*) 714.1 (M^++1). Anal. Calcd for $C_{40}H_{42}O_{12}$: C, 67.21; H, 5.92; found: C, 67.17; H, 5.94.

2,2′-(1,4-Phenylenebis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl))bis(1H-indene-1,3(2H)-dione) (**3l**)

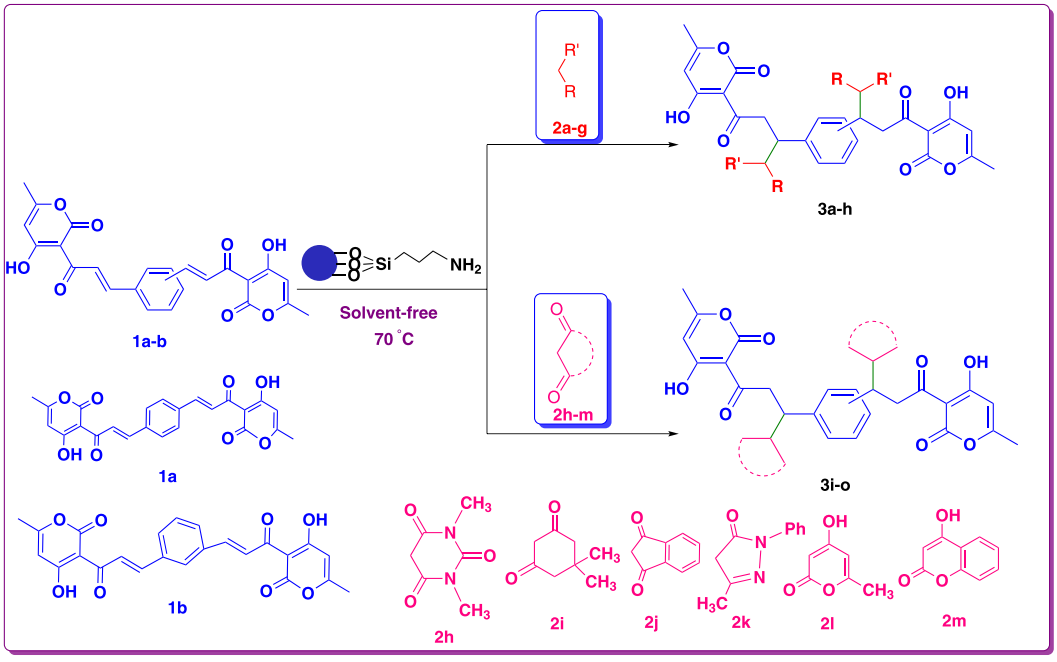
Red powder; m.p. 256°C; IR (KBr) cm^{-1}: 1658, 1702 (CO), 3420 (OH). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.11 (6H, s, 2 × CH_3), 3.28–3.31 (4H, m, 2 × CH_2), 4.06–4.08 (2H, m, 2 × CH3′), 5.87 (2H, d, J = 5.4 Hz, 2 × CH2″), 5.99 (2H, s, 2 × H_5), 7.27 (4H, s, C_6H_4), 7.98–8.05 (8H, m, Ar—H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 21.21 (2 × CH_3), 36.11 (2 × CH3′), 47.16 (2 × CH_2), 70.21 (2 × CH2″), 99.11 (2 × C3), 105.05 (2 × C5), 124.71, 127.93, 129.01, 133.14, 135.11 (Ar—C), 161.01 (2 × C6), 162.10 (2 × C2), 181.21 (2 × C4), 199.31 (2 × C1″, C3″), 200.11 (2 × C1′). ESI-MS: (*m/z*) 726.4 (M^++1). Anal. calcd for $C_{42}H_{30}O_{12}$: C, 67.98; H, 4.84; found: C, 67.95; H, 4.82.

3,3′-(1,4-Phenylenebis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl))bis(6-methyl-2H-pyran-2,4(3H)-dione) (**3m**)

Light-yellow powder; m.p. > 300°C; IR (KBr) cm^{-1}: 1653, 1685, 1698 (CO), 3429 (OH). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 1.94 (6H, s, 2 × CH_3), 2.43 (6H, s, 2 × CH_3), 3.03–3.05 (4H, m, 2 × CH_2), 3.23–3.26 (2H, m, 2 × CH3′), 5.40 (2H, d, J = 5.5 Hz, 2 × CH4″), 6.02 (2H, s, 2 × H_5), 7.27–7.81 (14H, m, C_6H_4, Ar—H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 15.21 (2 × CH_3), 19.19 (2 × CH_3), 39.01 (2 × CH3′), 44.70 (2 × CH_2), 51.01 (2 × CH4″), 100.10 (2 × C3), 103.02 (2 × C5), 125.81, 128.90, 130.16, 135.06, 138.90 (Ar—C), 153.13 (2 × C3″), 159.13 (2 × C6), 161.21 (2 × C5), 171.91 (2 × C5″), 183.01 (2 × C4), 192.21 (2 × C1′). ESI-MS: (*m/z*) 782.2 (M^++1). Anal. Calcd for $C_{44}H_{38}N_4O_{10}$: C, 67.51; H, 4.89; N, 7.15; found: C, 67.48; H, 4.85; N, 7.12.

3,3′-(1,4-Phenylenebis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl))bis(6-methyl-2H-pyran-2,4(3H)-dione) (**3n**)

White powder; m.p. > 300°C; IR (KBr) cm^{-1}: 1595, 1654, 1686 (CO), 3464 (OH). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 2.22 (6H, s, 2 × CH_3), 2.36 (6H, s, 2 × CH_3), 3.13–3.15 (4H,



Scheme 2. NH_2-PEG-catalyzed bis-Michael addition to bis-α,β-unsaturated ketones.

m, 2×CH_2), 3.85–3.89 (2H, m, 2×CH3′), 5.69 (2H, d, J=5.6 Hz, 2×CH3″), 6.09 (2H, s, 2×H_5″), 6.21 (2H, s, 2×H_5), 7.35 (4H, s, C_6H_4). ^{13}C NMR (100 MHz, DMSO-d_6): δ=18.01 (2×CH_3), 20.21 (2×CH_3), 40.01 (2×CH3′), 50.11 (2×CH_2), 63.12 (2×CH3″), 99.30 (2×C3), 103.01 (2×C5), 108.10 (2×C5″), 128.11, 136.02 (Ar—C), 159.01 (2×C6), 164.21 (2×C2), 169.11 (2×C2″), 170.01 (2×C6″), 182.12 (2×C4), 187.23 (2×C4″), 193.01 (2×C1′). ESI-MS: (*m/z*) 686.3 (M^++1). Anal. Calcd for $C_{36}H_{30}O_{14}$: C, 62.97; H, 4.40; found: C, 62.95; H, 4.37.

*3,3′-(1,4-Phenylenebis(3-(4-hydroxy-6-methyl-2-oxo-2H-pyran-3-yl)-3-oxopropane-1,1-diyl))bis(chroman-2,4-dione) (**3o**)*

Shining white powder; m.p. 265°C; IR (KBr) cm^{-1}: 1611, 1658, 1694 (CO), 3476 (OH). ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.13 (6H, s, 2×CH_3), 2.51–2.53 (4H, m, 2×CH_2), 4.21–4.25 (2H, m, 2×CH3′), 5.77 (2H, d, J=5.4 Hz, 2×CH3″), 6.32 (2H, s, 2×H_5), 7.15–7.81 (12H, m, C_6H_4, Ar—H). ^{13}C NMR (100 MHz, $CDCl_3$): δ=19.33 (2×CH_3), 39.01 (2×CH3′), 46.51 (2×CH_2), 61.20 (2×CH3″), 89.11 (2×C3), 103.18 (2×C5), 115.31 (2×C10″), 119.91, 125. 41, 128.11, 133.21, 136.02 (Ar—C), 152.53 (2×C9″), 160.01 (2×C6), 164.59 (2×C2), 167.80 (2×C2″), 180.65 (2×C4), 187.17 (2×C4″), 192.01 (2×C1′). ESI-MS: (*m/z*) 758.1 (M^++1). Anal. Calcd for $C_{42}H_{30}O_{14}$: C, 66.49; H, 3.98; found: C, 66.44; H, 4.94.

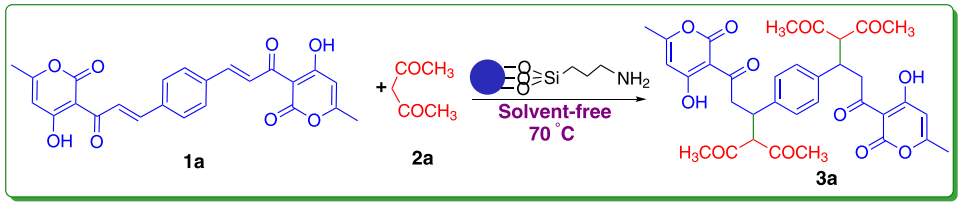
*4-Acetyl-1,3-diphenylhexane-1,5-dione (**3p**)*

White powder; m.p. 144–146°C (146–147°C); IR (KBr) cm^{-1}: 1657, 1676 (CO). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.80 (3H, s, CH_3), 2.18 (3H, s, CH_3), 3.10–3.19 (1H, dd), 3.25–3.30 (1H, dd), 4.18–4.26 (1H, m), 4.33–4.35 (1H, d, J=10.6 Hz), 7.10–7.15 (1H, m), 7.23–7.26 (4H, m), 7.36–7.40 (2H, m), 7.45–7.50 (1H,m), 7.77–7.80 (2H, m). ESI-MS: (*m/z*) 309.1 (M^++1). Anal. Calcd for $C_{20}H_{20}O_3$: C, 77.89; H, 6.53; found: C, 77.86; H, 6.55.

*Ethyl-(2-acetyl-5-oxo-3,5-diphenyl)pentanoate (**3q**)*

White solid; m.p. 115–117°C (lit. 116–118°C). IR (KBr) cm^{-1}: 1659, 1670 (CO), 1704 (COO). ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.01 (t, 3H), 2.05 (s, 3H), 3.35–3.54 (m, 2H), 3.93 (2H), 4.02–4.05 (m, 1H), 4.12–4.17 (m, 1H), 7.14–7.17 (m, 1H), 7.19–7.23 (m, 4H), 7.37–7.41 (m, 2H), 7.52–7.56 (m, 1H), 7.85–7.92 (m, 2H). ESI-MS: (*m/z*) 339.0 (M^++1). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.53; H, 6.55; found: C, 74.50; H, 6.52.

Table 1. Effect of various solvents versus the solvent-free on the model reaction[a]



Entry	Solvent	Temperature	Time[b]	Yield (%)[c]
1	Ethanol[d]	Reflux	15 h	Trace
2	Ethanol	Reflux	3.1 h	65
3	Acetic acid	Reflux	2.8 h	59
4	Methanol	Reflux	6 h	53
5	Isopropanol	Reflux	7.4 h	50
6	Water	Reflux	9.9 h	48
7	Dichloroethane	Reflux	13 h	34
8	Acetonitrile	Reflux	11 h	28
9	Dichloromethane	Reflux	15 h	23
10	THF	Reflux	16 h	22
11	DMF	Reflux	16 h	20
12	Dioxane	Reflux	24 h	—
13	Toluene	Reflux	24 h	—
14	Hexane	Reflux	24 h	—
15	PEG-200	Reflux	4.7 h	Trace
16	PEG-400	Reflux	4.3 h	29
17	PEG-600	Reflux	4.1 h	32
18	Ethylene glycol	Reflux	7 h	30
19	Glycerol	Reflux	5.3 h	32
20	Solvent-free (grinding)	Room Temperature	1.4 h	21
21	Solvent-free	50°C	16 min	76
22	Solvent-free	70°C	3 min	95
23	Solvent-free	80°C	3 min	95

[a]Reaction conditions: bis-α, β-unsaturated ketone, (**1a**, 1.00 mmol), acetyl acetone (**2a**, 2.00 mmol), catalyst (0.1 g).
[b]Reaction progress monitored by TLC.
[c]Isolated yields.
[d]No catalyst.

*3-Hydroxy-5,5-dimethyl-2-(3-oxo-1,3-diphenylpropyl)cyclohex-2-en-one (**3r**)*

White powder; m.p. 234°C; IR (KBr) cm^{-1}: 1680, 1595 (CO), 3430 (OH).^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 0.98$ (6H, s, CH_3), 2.00 (2H, s, CH_2), 2.25 (2H, s, CH_2), 3.55 (1H, dd, CH_2), 3.84 (1H, dd, CH_2), 4.75 (1H, t, CH), 7.06 (1H, t, Ar—H), 7.17 (2H, t, Ar—H), 7.28 (2H, d, $J = 7.5$ Hz, Ar—H), 7.53 (2H, t, Ar—H), 7.63 (1H, t, Ar—H), 7.93 (2H, d, $J = 7.4$ Hz, Ar—H), 10.44 (1H, br. s, OH). ^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 28.8$, 32.4, 35.6, 41.5, 115.7 (2 × C), 124.5, 127.3 (2 × C), 127.6 (2 × C), 127.8 (2 × C), 128.9 (2 × C), 133.5, 136.4, 145.9, 198.6 (2 × C). ESI-MS: (*m/z*) 349.0 (M^++1). Anal. Calcd for $C_{23}H_{24}O_3$: C, 79.28; H, 6.94; found: C, 79.30; H, 6.92.

Results and Discussion

Catalyst Preparation and Characterization

The strategy applied for the preparation of NH_2-PEG catalyst is outlined in Scheme 1.

FT-IR spectrum of catalyst

The FT-IR spectrum shows the characteristic bands belonging to the silanol groups at 3786 cm^{-1} (Fig. 1). A broad absorption band in the range 3350–3500 cm^{-1} was due to NH_2 stretching band overlapping with that of O—H stretching vibration.[27] The strong band at 2888 cm^{-1} was assigned to asymmetric stretching vibrations of CH_2 groups of *n*-propylamine and PEG moieties. The N—H bending vibrations and NH_2 symmetric bending vibrations were present at 695 and 1567 cm^{-1}.[28] Peaks in the range 1344–1468, 1111 cm^{-1} were due to (C—H) alkane scissoring, bending vibrations and C—O—C symmetric stretching of PEG moiety, respectively. Thus the FT-IR spectrum showed successful grafting of aminosilane species on the surface of PEG.

Powder XRD analysis of the catalyst

The structure of the catalyst (NH_2-PEG) was identified by powder XRD (Fig. 2). The XRD pattern showed characteristic diffraction peaks for the PEG moiety which indicated that the modification with aminopropyl groups did not result in changes to the structural properties of the PEG matrix.

EDX analysis of the catalyst

EDX analysis (Fig. 3) of the catalyst showed the presence of C, O, N and Si elements, indicating the formation of the NH_2-PEG catalytic system.

SEM analysis of the catalyst

SEM micrographs (Fig. 4) showed the smooth, compact and uniform surface of the catalyst.

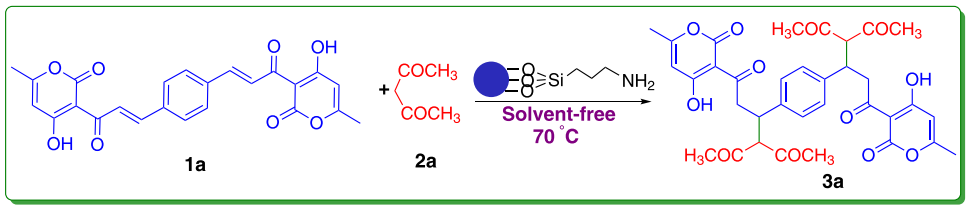
Optimization of Reaction Conditions and Catalytic Activity

The catalytic activity of aminopropylated PEG was explored for Michael addition of varieties of C—H-activated acids to bis-α,β-unsaturated ketones under solvent-free conditions (Scheme 2).

Effect of Different Solvents and Temperature

In order to optimize reaction conditions, the reaction was studied by employing both solvents and solvent-free conditions at altered temperature with the expectation to maximize product

Table 2. Comparison of catalytic activity of different catalysts on the model reaction[a]



Entry	Catalyst	Time[b]	Yield (%)[c]
1	NH_2-PEG	3 min	95
2	NaOH	45 min	32
3	KOH	60 min	43
4	K_2CO_3	1.4 h	55
5	Na_2CO_3	1.4 h	46
6	Et_3N	2.1 h	42
7	Pyridine	4.5 h	22
8	Piperidine	4.4 h	38
9	Urea	4.9 h	31
10	Thiourea	5.1 h	28
11	P_2O_5	3.5 h	33
12	L-proline	4.2 h	Trace
13	ZnO	5.3 h	Trace
14	MgO	5.7 h	Trace

[a]Reaction conditions: bis-α,β-unsaturated ketone (1a, 1.00 mmol), acetyl acetone (2a, 2.00 mmol), catalyst (0.1 g), solvent-free conditions, $T = 70$°C.
[b]Reaction progress monitored by TLC.
[c]Isolated yields.

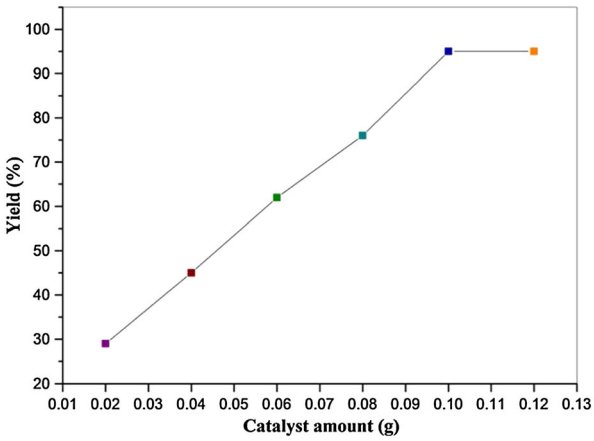


Figure 5. Effect of catalyst loading on the model reaction.

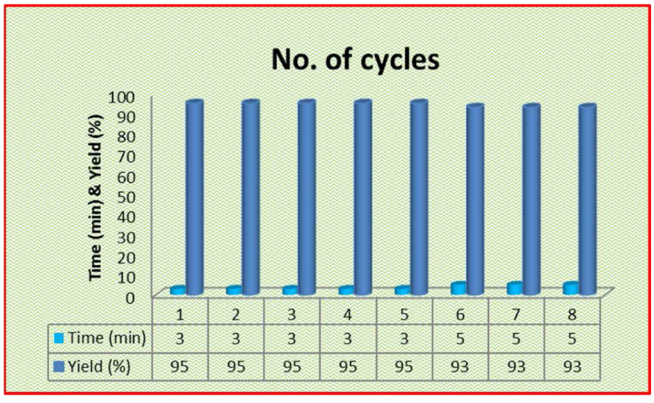


Figure 6. Recycling data of NH_2-PEG for model reaction.

yield in a minimum reaction time period (Table 1). For this purpose, reaction between bis-α,β-unsaturated ketone (**1a**) (1.00 mmol) and acetyl acetone (**2a**) (2.00 mmol) for the synthesis of adduct (**3a**) was selected as a model reaction in the presence of different protic, aprotic, non-polar solvents, and the results are summarized in Table 1. It was observed that when the model reaction was carried out in ethanol in the absence of any catalyst under reflux conditions, a trace amount of the product was obtained after 15 h (Table 1, entry 1) and indicated the need for a catalyst. Then, the reaction was conducted in the presence of NH_2-PEG under the same conditions as above and yielded product (65%) in 3.1 h. In other polar protic solvents such as acetic acid, methanol, isopropanol and water, a moderate yield of the desired product (**3a**) was obtained after a longer time period (Table 1, entries 3–6), whereas in polar aprotic solvents such as dichloroethane, acetonitrile, dichloromethane, THF and DMF, a lower yield of the product (**3a**) was obtained (Table 1, entries 7–11). In non-polar solvents such as dioxane, toluene and hexane, the reaction did not take place (entries 12–14), whereas in environmentally benign solvents such as PEG-200, PEG-400, PEG-600, ethylene glycol and glycerol the reaction gave unsatisfactory results in terms of time and yield of the product (entries 15–19). The reaction performance was drastically enhanced under solvent-free conditions at 70°C and gave **3a** in excellent yield (95%) within a few minutes (3 min) (Table 1, entries 20–23). Therefore, 70°C was chosen as the optimum temperature in further investigations. Further increase in temperature to 80°C did not show any significant enhancement in the yield of the desired product. Thus our study revealed that solvent-free conditions were best for NH_2-PEG-catalyzed bis-Michael addition to bis-α,β-unsaturated ketones in terms of reduced reaction time and enhanced yield of the products (Scheme 2). The highest catalytic activity under solvent-free conditions may be due to the good dispersion of active reagent sites, which facilitates better contact between reactant molecules and the catalyst.[29] Moreover, due to absence of any solvent (as medium), there is no dilution effect and the heat needed for energy of activation is directly available to the reactant molecules, leading to high conversions in a minimum time period.

Effect of Catalysts

A comparative study was also carried out using other catalysts for obtaining the best yield of **3a** under solvent-free conditions at 70°C. It afforded lower to moderate yields of the product with longer reaction time. When the model reaction was carried out in the presence of NH_2-PEG (0.1 g) under solvent-free conditions at 70°C, product **3a** was obtained in excellent yield (95%) in a short span of time (3 min) (Table 2, entry1).

Effect of Catalyst Loading

Variation of the catalyst loading also had a profound effect on the catalytic activity (Fig. 5). When the reaction was carried out using 0.02 g, 0.04 g, 0.06 g and 0.08 g of the catalysts, the rate of reaction progressed steadily with lower to moderate yields. However, the best performance was observed with 0.1 g NH_2-PEG under solvent-free conditions at 70°C. Further increase in the catalyst loading had no significant enhancement in the yield of the desired product and the rate of addition reaction.

Recycling Study of the Catalyst

The reusability of the catalyst was examined using the model reaction of bis-α,β-unsaturated ketone (**1a**) (1.00 mmol) and acetyl acetone (**2a**) (2.00 mmol) under solvent-free conditions (Fig. 6). After completion of the reaction, the reaction mixture was cooled to room temperature and H_2O (5 ml) added with shaking for 3 min to dissolve the NH_2-PEG. The crude product (insoluble in water) was filtered and recrystallized from ethyl alcohol (3 ml) to

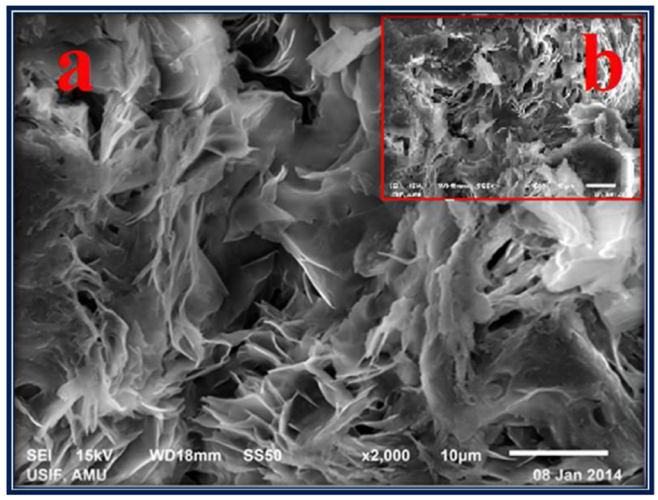


Figure 7. SEM images of recovered catalyst (NH_2-PEG) at different magnifications.

afford pure products (**3a–o**). In order to recover the catalyst, the filtrate was evaporated under reduced pressure and Et_2O (5 ml) added. The solid, as obtained, was filtered, washed with Et_2O (2 ml × 2) and dried in an oven at 50°C for 30 min. The recovered catalyst was employed for subsequent cycles (eight runs) adopting the identical protocol (Fig. 6). The yields obtained in nine, ten runs were 85% in 7 min and 77% in 9 min, respectively. Further, the yield decreased substantially after the tenth cycle (68% in 9 min) onwards.

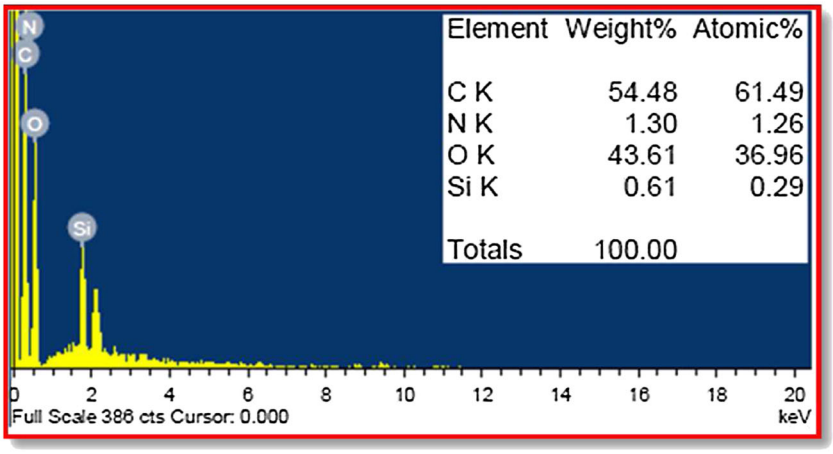


Figure 8. EDX analysis of the recovered catalyst (NH_2-PEG).

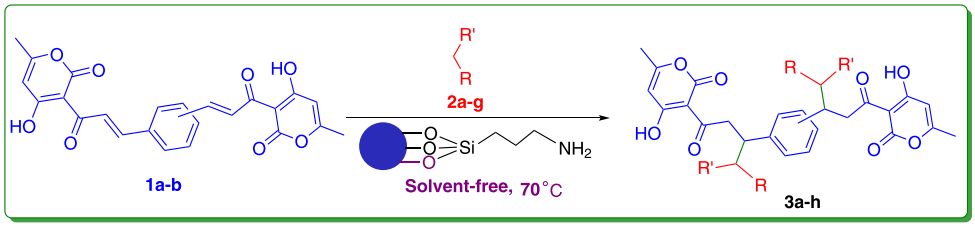
A similar pattern of powder XRD (Fig. 2c) and SEM-EDX analysis (Figs. 7a, b and Fig. 8) was observed for the recovered catalyst, with some low-intensity and extra peaks which may be due to the catalyst deactivation or some change in morphology of the catalyst after eight runs.

Encouraged by the remarkable results, we investigated the scope and generality of this protocol by the reaction of bis-α,β-unsaturated ketones (**1a–b**) with different acyclic (**2a–g**) and cyclic activated C—H acids (**2h–m**) under solvent-free conditions in the presence of NH_2-PEG as catalyst. All the reactions proceeded smoothly and were completed within 3–7 min to afford the products (**3a–o**) in excellent yield (95–90%) (Tables 3 and 4).

To further investigate scope of the reaction for construction of mono-Michael addition products, the reaction of α,β-unsaturated ketone (**1c**) was conducted with acetyl acetone (**2a**), ethyl acetoacetate (**2d**) and dimedone (**2i**) as C—H-activated acids by adopting an identical protocol. The reactions went on well, affording the products (**3p–r**) in very good yields (95–92%) in a short span of time (3–6 min) (Table 5).

The structure of compounds **3a–o** was deduced on the basis of their spectral analysis. The IR spectrum of the newly synthesized compound **3a** showed a broad band for OH groups at 3428 cm^{-1} and strong bands at 1686, 1654 and 1627cm^{-1} for carbonyl groups. ^1H NMR

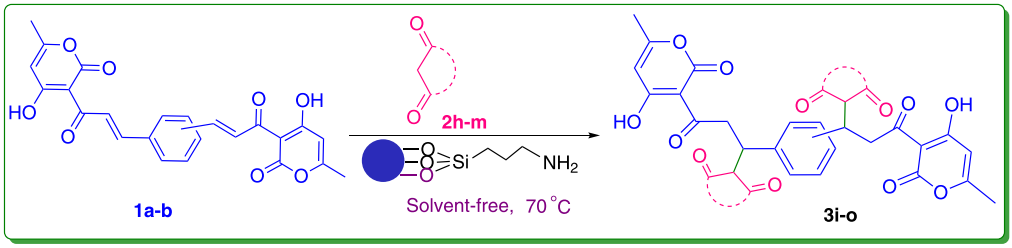
Table 3. Bis-Michael addition of acyclic activated C—H acids to bis-α,β-unsaturated ketones under solvent-free conditions[a]



Product	Dialdehyde	Activated C—H acids	Time[b] (min)	Yield[c] (%)
3a	**1a**	R = R′ = $COCH_3$	3	95
3b	**1b**	R = R′ = $COCH_3$	4	95
3c	**1a**	R = R′ = CN	3	95
3d	**1a**	R = R′ = COOEt	6	93
3e	**1a**	R = COOEt R′ = $COCH_3$	5	90
3f	**1a**	R = COOEt R′ = CN	4	94
3g	**1a**	R = $COOCH_3$ R′ = $COCH_3$	6	93
3h	**1a**	R = COOH R′ = CH_2Ph	7	92

[a]Reaction conditions: bis-α,β-unsaturated ketones (1a–b, 10 mmol), acyclic activated C—H acids (2a–g, 20 mmol), catalyst (1.00 g), solvent-free conditions, T = 70°C.
[b]Reaction progress monitored by TLC.
[c]Isolated yields.

Table 4. Bis-Michael addition of cyclic activated C—H acids to bis-α,β-unsaturated ketones under solvent-free conditions[a]



Product	Dialdehyde	Activated C—H acids	Time[b] (min)	Yield[c] (%)
3i	**1a**	2h	3	95
3j	**1b**	2h	3	95
3k	**1a**	2i	6	94
3l	**1a**	2j	7	90
3m	**1a**	2k	7	93
3n	**1a**	2l	4	94
3o	**1a**	2m	3	95

[a]Reaction conditions: bis-α,β-unsaturated ketones (1a–b, 10 mmol), cyclic activated C—H acids (2h–m, 20 mmol), catalyst (1.00 g), solvent-free conditions, $T = 70$°C.

[b]Reaction progress monitored by TLC.

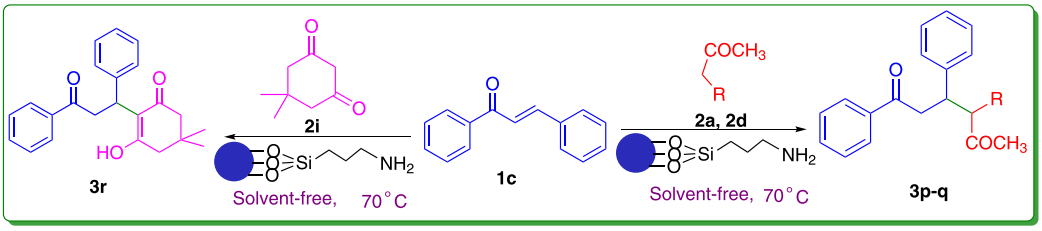
[c]Isolated yields.

spectroscopy exhibited sharp singlets at δ 1.86 and 2.11 for the methyl groups of acetyl acetone and lactone moieties, respectively. Two multiplets were displayed at δ 2.88–2.90 and 3.55–3.62 for $COCH_2$ and CH protons. Two more singlets integrating for two protons each at δ 5.25 and 5.74 were assigned to H_5 protons of lactone moieties and methine protons. Four aromatic protons appeared as a singlet at δ 7.58. The ^{13}C NMR spectrum showed aromatic carbons which appeared in the range δ 126.21–137.49, whereas signals at δ 169.25, 192.57 and 192.76 were due to carbonyl groups of lactone and acetyl acetone moieties, respectively. Another signal at δ 182.95 was assigned to the C-4 carbon of the lactone moiety. Further confirmation for **3a** was provided by the ESI mass spectrum, which showed the molecular ion peak as base peak at m/z 634.2 (M^++1). A plausible mechanism for the bis-Michael addition is depicted in Scheme 3.

Conclusion

In summary, we have synthesized NH_2-PEG as a biodegradable, highly cost-effective and environmentally benign polymer-based novel solid basic catalyst for the synthesis of bis-Michael addition products in excellent yields under solvent-free conditions. Mild reaction conditions, economic feasibility, environmental benignity, practicability, minimum reaction time period, easy work-up

Table 5. Mono-Michael addition of activated C—H acids to α,β-unsaturated ketone under solvent-free conditions[a]



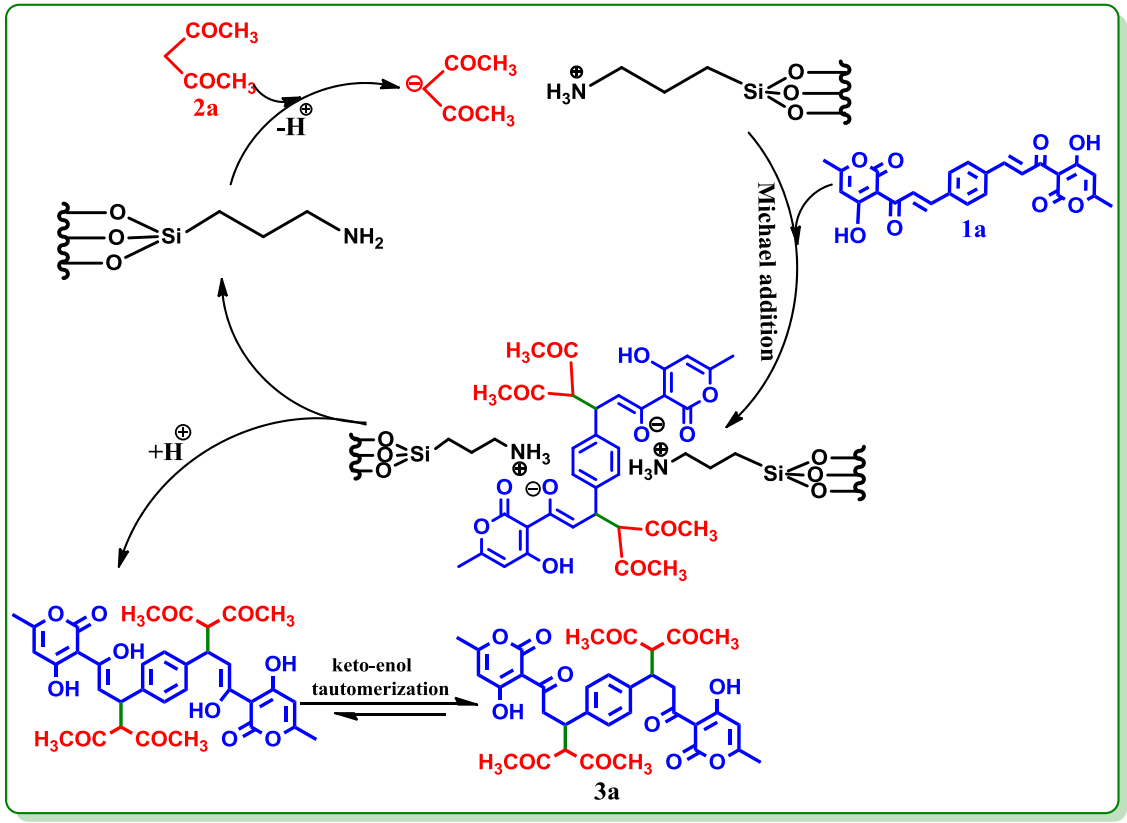
Product	Activated C—H acids	Time,[b] min (lit.)	Yield,[c] % (lit.)
3p[d]	R = $COCH_3$	3 (2 h)	95 (60)
3q[d]	R = COOEt	6 (2 h)	92 (53)
3r[d]	**2i**	6 (5 h)	94 (89)

[a]Reaction conditions: α,β-unsaturated ketone (1c, 10 mmol), activated C—H acids (2a, 2d, 2i, 10 mmol), catalyst (1.00 g), solvent-free conditions, $T = 70$°C.

[b]Reaction progress monitored by TLC.

[c]Isolated yields.

[d]The products were confirmed by melting points and compared with reported literature.[30,31]



Scheme 3. Plausible mechanism for the bis-Michael addition.

and reusability of the catalyst make this versatile protocol attractive. These features will enable this method to find extensive applications in the field of organic synthesis.

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