

Abstract

Based on the fundamental aspects of green chemistry with considering the basic scientific challenges of protecting human health and environment, the sustainable development of more environmentally benign, efficient, clean and economically feasible organic syntheses under mild reaction condition using green reagents, eco-friendly catalysts and benign reaction mediums over traditional synthetic processes is a key driving force of the synthetic organic chemistry to achieve the ultimate goal of waste-free and energy-efficient syntheses in both industry and academic world. The investigations of sustainable and efficient alternative catalyst systems for chemical transformations using bio-based, renewable and natural feedstock as eco-catalyst are extensively acknowledged owing to their easy access, ease of biodegradability, cheapness, and environmental friendliness. Motivated by the search of the greener alternatives, versatile organic transformations such as the selective reduction of aromatic aldehydes to alcohols, decarboxylation of substituted aromatic acids to aromatic phenols, deacetylation, and debenzoylation of substituted aromatic compounds were performed in presence of cucumber (*Cucumis sativus* L.) juice abbreviated as CSJ.

In the new millennium, the diversity-oriented synthesis (DOS) for the library of “privileged medicinal structures or scaffolds” of heterocyclic architectures via one-pot multi-component reactions (MCRs) by using natural catalysts in presence of water acting as a greener reaction medium has been received significant importance from the standpoint of green chemistry. A greener, efficient, and economic approach for synthesis of several types of symmetric trisubstituted methane derivatives (TRSMs) such as bis(indolyl)methanes, bis-coumarins, bis-pyrones, bis(pyrazolyl)methanes, bis-lawsones and bis-dimedones via either electrophilic substitution or cascade Knoevenagel-Michael type reaction of one molecule aldehyde with two molecules of heterocyclics or 1,3-cyclic diketone systems was disclosed by using “water extract of sugarcane bagasse ash (WESBA)” as a renewable, and eco-catalyst from agro-industrial waste materials. Knoevenagel condensation is the most classical and versatile C-C bond forming reaction in organic chemistry. To develop an efficient and eco-friendly catalytic system for the Knoevenagel reaction, WESBA was also used for the fast and sustainable synthesis of substituted benzylidenemalononitriles, substituted 2-oxoindolin-3-ylidenes, substituted cinnamic acids, and substituted iminocoumarins from a broad range of aromatic aldehydes and substituted isatins with active methylene compounds like malononitrile or alkyl cyanoacetates or Meldrum's acid. Using the substituted benzylidenemalononitriles as the versatile intermediates, a large

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library of biologically potent 2-amino-4*H*-pyrans, 2-amino-4*H*-chromenes, 2-amino-spiro-oxindole-chromenes with either nitrile (cyano) or other functionality was successfully synthesized from a broad range of aromatic aldehydes or isatin derivatives, malononitrile or ethyl cyanoacetate and diverse electron-rich enolizable C-H activated acidic compounds such as 4-hydroxycoumarin, 4-hydroxy-6-methyl-2-oxo-pyran, dimedone, 3-methyl-1-phenyl-5-pyrazolone, uracil, lawsone, kojic acid and 4-hydroxy-1-methylquinolin-2(1*H*)-one via one pot 3-MCRs Knoevenagel condensation followed by Michael addition reaction in presence of WESBA as a natural catalyst. Furthermore, a sustainable, and efficient, protocol for the synthesis of 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives with a nitrile functionality was developed by the condensation of an aromatic aldehyde, malononitrile, and phthalhydrazide via one pot 3-MCRs Knoevenagel condensation followed by Michael addition reaction in presence of WESBA.

In the current industrial scenario, heterogeneous catalysis plays an important role in replacing hazardous homogeneous reagents for organic transformations. Searching for the efficient heterogeneous catalysts, a efficient and eco-friendly method for the formation of 3-hydroxy-1-alkyl-3-[(4-aryl-1*H*-1,2,3-triazol-1-yl)methyl]indolin-2-one derivatives was exploited through one-pot, 3-MCRs and “*Carbo-Click*” chemistry sequential approach for copper-catalyzed cycloaddition reaction of azide and alkyne and then the regio- and stereoselective ring-opening of spiro-epoxyoxindoles from the less hindered side by using sulfonated sugarcane bagasse ash (SBA-SO₃H) as an efficient solid acid heterogeneous catalyst in presence of water. Moreover, a simple, efficient method for the preparation of 3-substituted phthalides was employed from the reaction between phthalaldehydic acid with several types of nucleophilic species such as indole, β-keto acids, phenols via one-pot cascade nucleophilic addition followed by intramolecular cyclization approach using SBA-SO₃H in water as a greener solvent.

Key Words: natural feedstock; eco-catalyst; cucumber juice (CSJ); multi-component reactions (MCRs); symmetric trisubstituted methane derivatives (TRSMs); water extract of sugarcane bagasse ash (WESBA); Knoevenagel condensation; substituted benzylidenemalononitriles; substituted 2-oxindolin-3-ylidenes; substituted cinnamic acids; substituted iminocoumarins; 2-amino-4*H*-pyrans; 2-amino-4*H*-chromenes; 2-amino-spiro-oxindole-chromenes; Michael addition reaction; 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives; 3-hydroxy-1-alkyl-3-[(4-aryl-1*H*-1,2,3-triazol-1-yl)methyl]indolin-2-one derivatives; “*Carbo-Click*” chemistry; sulfonated sugarcane bagasse ash (SBA-SO₃H); copper-catalyzed cycloaddition reaction; 3-substituted phthalides.