Fabrication of High-Valent Manganese Nanoparticles: Easy Syntheses of Isoxazolines and Isoxazoles with Excellent Regio- and Stereoselectivity

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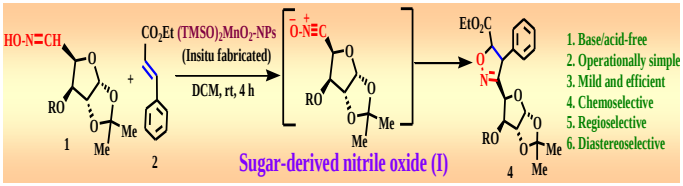
Abstract



It is the first report on synthesis of high-valent $(Me_3SiO)_2MnO_2$ species and fabrication of its low dimensional nanoparticles. Characterization of the small nanoparticles is studied by UV-vis, TEM, powder XRD, TG-DTA, FT-IR and ESI-MS measurements. The highly ordered manganese nanoparticles have shown a significantly improved magnetic property in the X-band ESR spectroscopy with the isotropic hyperfine splitting of six line spectrum. Their versatility and effectiveness as a mild oxidant are successfully examined towards generation of nitrile oxides from aldoximes and used for 1,3-dipolar cycloaddition reaction.

This synthetic protocol features fast reaction convergence under benign reaction conditions, simple operation, use of inexpensive precursors and lower amount of metal oxidant and also avoids use of base or acid. The strategy offers excellent chemo-, regio- and stereoselectivity in 1,3-DC of nitrile oxides by in situ trapping of alkenes and alkynes. Nitrile oxide bearing sugar-moiety is also generated by the mild reaction process to furnish optically pure isoxazoline and isoxazole possessing multiple chiral centers.

Keywords: High Valent Manganese Nanoparticles, Synthesis, Fabrication, Isoxazolines and Isoxazoles.

Introduction

Fabrication of new nanoparticles (NPs) and exploring their wide range of application have become the intensive areas of research in the chemical, biological, electronic science and technology.[1] Chemical reactivity of a bulk inorganic reagent can be significantly improved on transition to their low-dimensional NPs possessing highly active surface. Close packing of matter at nanoscale dimension has displayed exciting physical, chemical, electronic and magnetic properties as the consequence of their size, shape, nanoscale-strain, alteration of surface-interface energies, easy charge transfer and much diminished coordination number of the surface atoms.[2] Fabrication of low dimensional (LD) metal NPs with surfactant-assembled architecture is the key for development of new chemical properties, especially of high-valent transition metal nanomaterials which are not thoroughly investigated.

The surfactant molecules around the NPs not only play an important role toward fabrication of valuable nanomaterials of different size and shape, but also allow organic substrate to react with active surface charges.[2c] Recently, high-valent Mo^{VI}-nanowires are fabricated which have found valuable applications in the construction of lithium ion batteries, solar cells and lubricating materials.[3] Very small and high-valent manganese-NPs having highly active surface, incompletely filled d-orbital, strong electron affinity and unique redox capability would be an important candidate for redox reaction in a broad area of chemical transformations and construction of high-tech electronic devices.

However, controlling LD size and shape in higher oxidation state metal-NPs remains an extremely difficult job to the material scientists owing to their lack of stability and high reactivity especially under heating conditions. For example, fabrication of Mn^{III}-NPs requires thermal decomposition of manganese oxalate at 450 °C[4] and preparation of Mn^{IV}-NPs needs extra stabilization from co-metal ions (Zn^{+2}, Ni^{+2}, Cu^{+2} and Mg^{+2}).[5]

We are surprised to find that there are only few reports on applications of manganese-NPs in fundamental organic transformations.[6] Interestingly, despite synthetic difficulties, high-valent bulk Mn^{VI}-compounds have found outstanding applications in synthetic organic chemistry.[7]

$KMnO_4$ is an inexpensive oxidizing agent. Unfortunately, its strong oxidizing property prevents it from diverse utility in organic synthesis. Copper, ruthenium, barium, ammonium, phosphonium and crown ether stabilized permanganates have found only a limited success.[8] Even then, instances of explosions have been reported under certain reaction conditions.[8a] Transformation of a strong metal oxidant $KMnO_4$ into its mild high-valent analogue is possible by fabrication of small metal-NPs possessing appropriately polarized surface which can exchange electrons smoothly for oxidative organic transformation (Scheme 1).

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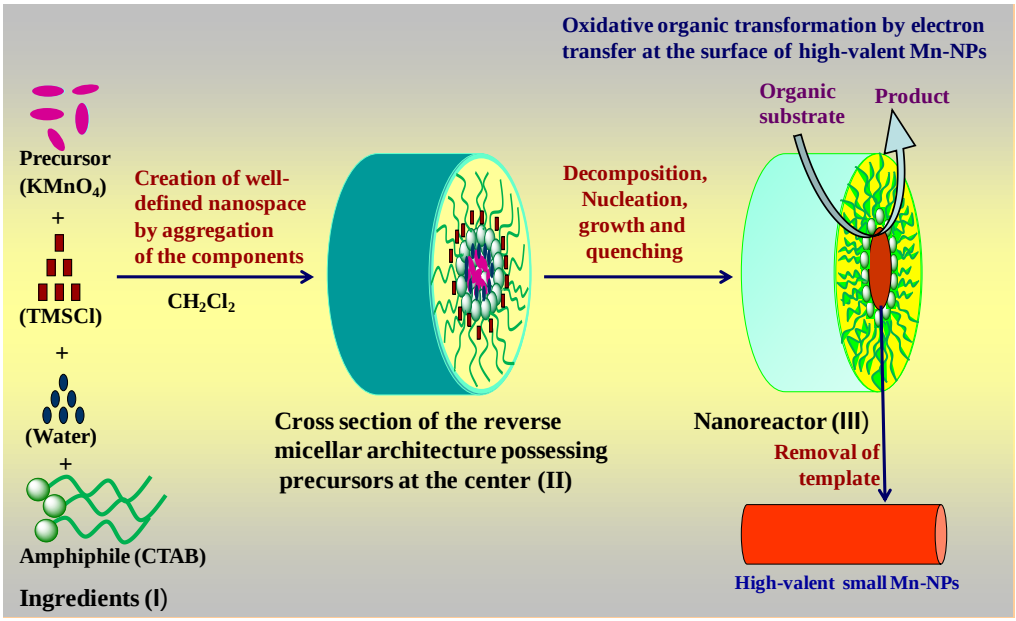


Scheme 1: Fabrication of High-Valent Mn-NPs and Their Application

1,3-Dipolar cycloaddition (DC) reaction is a powerful atom-economical tool which can construct bonds in a regio- and stereoselective way to furnish functional molecules.[9-14] Recently, a great effort has been devoted toward development of improved and new methods of Huisgen[9,10] reaction to afford valuable compounds. For instance, we[12] and others[13] have recently demonstrated 1,3-DC reaction as an outstanding tool for construction of useful *N*-heterocycles involving nitrillium betaines bearing highly functionalized substituents. Nitrile oxide has been identified as an important class of 1,3-dipole which undergoes 1,3-DC reaction with varied unsaturated bonds in an unique regio- and stereocontrolled fashion to afford valuable isoxazoline and isoxazole.[11a,d,12a,14]

The cycloadducts have found important application in medicinal chemistry to show antidepressant, antipsychotic, antianxiolytic and anticancer activities.[15] They are utilized for construction of valuable natural products, pharmaceuticals, agrochemicals and interesting new molecules.[16] Isoxazolines and isoxazoles offer high synthetic potential because several organic synthons can easily be synthesized involving reductive cleavage of N-O bond, hydrolysis of the intermediates, nucleophilic and electrophilic reactions to their responsive centers.[17] Thus, development of a nitrile oxide cycloaddition with excellent regio- and stereoselectivity would provide an important synthetic alternative to the stereoselective aldol and other related reactions.

However, generation of nitrile oxides and their 1,3-DC reaction is very tricky and challenging. Nitrile oxides are generally prepared by acid or base mediated dehydration of primary nitro compounds[18] or oxidation of aldoximes by a chlorinating agent in the presence of base.[19] The other methods involve use of oxidising agent hypervalent iodane ($PhICl_2$, DIB, HTIB, PhIO),[12a,20] KI/I_2,[21] *t*-BuOX,[22] and Chloramin T.[23] Preparation and 1,3-DC reaction of nitrile oxide under benign reaction conditions are extremely essential to avoid their dimerization and poor regio- and stereoselection in the cycloaddition step. In this context, use of metallic oxidant offers advantage over avoidance of base or acid which generates aldehyde and nitrile oxide dimerized byproduct,[24] racemization of sensitive chiral centers[25] and restriction in using diverse classes of aldoxime precursors. Mercuric(II) acetate[26a], MnO_2,[26b] cerric ammonium nitrate,[25c] and magtrieve,[26d] have been efficiently utilized for generation of nitrile oxides.

However, higher temperature (80 °C) and large excess quantity of the oxidant (six to ten equivalents) are generally employed. High-valent metallic nanomaterials possessing highly active surface offer an ideal reaction condition for generation of nitrile oxides from aldoxime under benign reaction condition to achieve excellent regio- and stereoselectivity in the product ratio. Herein, we report fabrication of high-valent manganese-NPs under benign reaction conditions, their characterization, development of novel magnetic and valuable mild oxidizing property toward smooth generation of nitrile oxides and their regio- and stereoselective 1,3-DC reaction.

Material and Methods

Procedure for the Preparation of Mn^{VI}-NPs and Their Characterization: In a 100 mL round bottomed flask, CTAB (364 mg, 1mmol), DCM (36.4 mL) and water (5µL) were taken together and stirred magnetically for 5 min. $KMnO_4$ (158 mg, 1 mmol) was added to the solution and stirring was continued. After 45 min., TMSCl (216 mg, 2 mmol) was added dropwise at 0°C and content of the reaction mixture was stirred for 10 mins. Finally, the reaction mixture was poured over 200 mL of DCM and centrifuged, washed with DCM (5 x 20 mL) and dried under vacuum to collect the Mn^{VI}-NPs (yield: 52%; 138 mg, 0.52 mmol).

FT-IR (KBr, cm^{-1}): 2922, 2858, 1718, 1621, 1534, 1469, 1393, 961, 907, 766.

General Procedure A for Generation of Nitrile Oxides and Their Intermolecular 1,3-DC Reaction with Alkenes: In a 100 mL round bottle flask, CTAB (364 mg, 1 mmol), water (5 μL) and DCM (36.4 mL) were taken and stirred magnetically for 5 min. $KMnO_4$ (158 mg,1mmol) was added to the solution and stirring was continued. After 45 mins, TMSCl (216 mg, 2 mmol) was added dropwise to the reaction mixture under ice-cold condition and stirred for another 10 mins. A mixture of oxime (1a-e; 1 mmol) and olefin (2a-d; 2.5 mmol) in minimum volume of DCM was added to it and stirred for 3.5-5.0 hours at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed in a rotary evaporator at room temperature under reduced pressure.

The reaction mixture was filtered through a sintered funnel and washed with a mixture of ethyl acetate and cold water. The filtrate was transferred to a separating funnel and extracted with EtOAc (3 x 30 mL). The combined EtOAc layer was washed with water (3 x 30 mL) and finally with brine solution (1 x 30 mL) and dried over anhydrous Na_2SO_4. Solvent was removed in a rotary evaporator at ambient temperature under reduced pressure. The residue was purified by column chromatography over silica gel (60-120 mesh) using ethyl acetate-petroleum ether as eluent to get the pure product 3a-h.

3-(4-Dichlorophenyl)-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester (3a):[38] Yield: 79% (199 mg, 0.79 mmol); yellow solid; m.p. 38-43 ºC [Lit.[38] 64-65.5 °C]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (3H, t, *J* = 7.2 Hz), 3.52-3.59 (2H, m), 4.21 (2H, q, *J* = 7.2 Hz), 5.10 (1H, dd, *J* = 7.8, 10.5 Hz), 7.31 (2H, d, *J* = 8.1 Hz), 7.60 (2H, d, *J* = 8.1 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 38.6, 62.1, 78.2, 126.8, 127.8, 128.9, 131.5, 136.5, 155.1, 172.5; FT-IR (KBr, cm^{-1}): 831, 1223, 1740, 2986.

3-(3,4-Dichlorophenyl)-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester (3b): Yield: 76 % (217 mg, 0.76 mmol); yellow solid; m.p. 70-73 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (3H, t, *J* = 7.2 Hz), 3.49-3.55 (2H, m), 4.21 (2H, q, *J* = 7.2 Hz), 5.09-5.16 (1H, m), 7.39-7.68 (2H, m), 7.78 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 38.4, 62.2, 78.6, 125.9, 126.1, 128.7, 130.9, 133.2, 134.7, 154.3, 169.7; FT-IR (KBr, cm^{-1}): 1030, 1397, 1734, 3140. HR-MS (*m*/*z*) for $C_{12}H_{11}Cl_2NO_3$ (M^+): Calculated 287.0116, found 287.0113 (One of the major peaks).

3-(3,4-Dichloro-phenyl)-4,5-dihydroisoxazole-5-carbonitrile (3c): Yield: 85% (204 mg, 0.85 mmol); colorless solid; m.p. 110º-112ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.62-3.69 (2H, m), 5.31-5.37 (1H, m), 7.45 (2H, s), 7.67 (1H, s). ^{13}C NMR (75 MHz, $CDCl_3$): δ 40.7, 66.9, 116.6, 126.0, 127.3, 128.8, 131.1, 133.5, 135.5, 154.5. FT-IR (KBr, cm^{-1}): 888, 1356, 2374. EI-MS (*m/z*): 241 (M^+), 207, 118, 105, 77, 51, 44. HR-MS (*m*/*z*) for $C_{10}H_6Cl_2N_2O$ (M^+): Calculated 239.9857, found 239.9851 (One of the major peaks).

3-(4-Fluoro-phenyl)-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester (3d): Yield: 81% (191 mg, 0.81 mmol); yellow solid; m.p. 38º- 43 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.24 (3H, t, *J* = 7.2 Hz), 3.50-3.56 (2H, m), 4.20 (2H, q, *J* = 7.2 Hz), 5.06-5.12 (1H, m), 6.98-7.11 (2H, m), 7.57-7.68 (2H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 38.8, 62.0, 78.1, 115.8, 116.1, 128.8, 128.9, 155.0, 162.3, 165.6, 170.0; FT-IR (KBr, cm^{-1}): 841, 1022, 1214, 1603, 1747; EI-MS (*m/z*): 237 (M^+), 164, 136, 95, 75. HR-MS (*m*/*z*) for $C_{12}H_{12}FNO_3$ (M^+): Calculated 237.0801, found 237.0807.

3-Naphthalen-2-yl-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester (3e): Yield: 80% (215 mg, 0.80 mmol); colorless solid; m.p. 68-73 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (3H, t, *J* = 7.2 Hz), 3.64- 3.71 (2H, m), 4.21 (2H, q, *J* = 7.2 Hz), 5.11-5.17 (1H, m), 7.44-7.51 (3H, m), 7.76-7.91 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.1, 38.8, 62.0, 78.3, 123.6, 126.2, 126.8, 127.3, 127.8, 128.4, 128.6, 132.9, 134.2, 156.1, 170.2; FT-IR (KBr, cm^{-1}): 475, 749, 1200, 1745, 2926; EI-MS (*m/z*): 269(M^+), 182, 104, 103, 102, 77, 51, 50, 44. HR-MS (*m*/*z*) for $C_{16}H_{15}NO_3$ (M^+): Calculated 269.1052, found 269.1050.

3-Naphthalen-2-yl-4,5-dihydroisoxazole-5-carbonitrile (3f): Yield: 83% (184 mg, 0.83 mmol); colorless solid; m.p. 101-105 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.75- 3.84 (2H, m), 5.34 (1H, m), 7.44-7.52 (3H, m), 7.77-7.85 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 41.1, 66.7, 117.1, 123.4, 124.9, 127.1, 127.7, 127.9, 128.5, 129.0, 132.8, 134.4, 156.4; FT-IR (KBr, cm^{-1}): 473, 756, 821, 887, 1345, 3043; EI-MS (*m/z*): 222 (M^+), 213, 179, 126, 118, 83, 44. HR-MS (*m*/*z*) for $C_{14}H_{10}N_2O$ (M^+): Calculated 222.0793, found 222.0798.

3-(4-Chlorophenyl)-5-ethenesulfonyl-4,5-dihydro-isoxazole (3g): Yield: 78% (185 mg, 0.78 mmol); colorless solid; m.p. 138-141 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.66-3.76 (1H, m), 3.92 (1H, dd, *J* = 4.8, 18.3 Hz), 5.46 (1H, dd, *J* = 4.8, 10.8 Hz), 6.27 (1H, d, *J* = 9.6 Hz), 6.52 (1H, d, *J* = 16.8 Hz), 6.72 (1H, dd, *J* = 9.6, 16.8 Hz), 7.35 (2H, dd, *J* = 1.8, 6.6 Hz), 7.55 (2H, dd, *J* = 1.8, 6.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 36.5, 92.5, 125.7, 128.4, 129.3, 132.7, 134.0, 156.2; FT-IR (KBr, cm^{-1}): 761, 1127, 1307, 1355, 2369; EI-MS (*m/z*): 271(M^+), 202, 182, 103, 77, 51, 44. HR-MS (*m*/*z*) for $C_{11}H_{10}ClNO_3S$ (M^+): Calculated 271.0070, found 271.0067 (One of the major peaks).

3-Furan-2-yl-4,5-dihydroisoxazole-5-carboxylic acid methyl ester (3h): Yield: 71% (138 mg, 0.71 mmol); colorless solid; m.p. 62-63 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.59- 3.63 (2H, dd, *J* = 5.4, 10.8 Hz), 3.81 (3H, s), 5.15 (1H, dd, *J* = 7.5, 10.8 Hz), 6.50 (1H, dd, *J* = 1.8, 3.6 Hz), 6.77 (1H, d, *J* = 3.6 Hz), 7.52 (1H, d, *J* = 1.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 38.7, 52.8, 111.8, 112.5, 143.9, 144.6,

148.2, 170.3; FT-IR (KBr, cm^{-1}): 755, 884, 1014, 1219,1747; EI-MS (*m/z*): 196(M^+), 136, 108, 81, 44, 32, 28. HR-MS (*m/z*) for $C_9H_9NO_4$ (M^+): Calculated 195.0532, found 195.0537.

General Procedure B for Generation of Sugar-Derived Nitrile Oxides and Their Intermolecular Cycloaddition with Alkenes: In a 100 mL round bottle flask, CTAB (364 mg, 1mmol), water (5µL) and DCM (36.4 mL) were taken and stirred magnetically for 5 min. $KMnO_4$ (158 mg,1mmol) was added to the solution and stirring was continued. After 45 min., TMSCl (216 mg, 2 mmol) was added dropwise to the reaction mixture under ice-cold condition and stirred for another 10 min. A mixture of chiral oxime (1f, g; 1 mmol) and olefin **(**2b, c, e; 2.5 mmol) in minimum volume of DCM was added to it and stirred for 4.5-5.0 hours at room temperature. The progress of the reaction was monitored by TLC and developed by charring on a hot plate after spraying with aqueous H_2SO_4 (30%). After completion of the reaction the solvent was removed in a rotary evaporator at room temperature under reduced pressure.

The whole reaction mixture was filtered through a sintered funnel and washed with a mixture of ethyl acetate and cold water. The filtrate was transferred to a separating funnel and extracted with EtOAc (3 x 30 mL). The combined EtOAc layer was washed with water (3 x 30 mL) and finally with brine solution (1 x 30 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent in a rotary evaporator left the crude product which was purified by column chromatography over silica gel (60-120 mesh) using ethyl acetate-petroleum ether as eluent to afford the optically pure diastereomer or mixture of diastereomers 5a-d/6a-d.

3-(6-Methoxy-2,2-dimethyltetrahyrofuro[2,3-*d*][1,3] dioxol-5-yl)-4-phenyl-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester (5a/6a): One diastereomer was obtained; yield: 70% (273 mg, 0.70 mmol); yellow viscous liquid; $[\alpha]_D^{20}$: –106.7° (*c* 0.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.22-1.29 (6H, m), 1.47 (3H, s), 3.19 (3H, s), 3.90 (1H, d, *J* = 3.6 Hz), 4.17-4.26 (3H, m), 4.53 (1H, d, *J* = 3.6 Hz), 5.21 (1H, d, *J* = 3.6 Hz), 5.68 (1H, d, *J* = 6.6 Hz), 5.85 (1H, d, *J* = 3.6 Hz), 7.30-7.33 (5H, m)^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 26.3, 26.9, 57.9, 61.7, 63.1, 76.2, 81.6, 86.4, 87.3, 105.4, 112.3, 125.7, 128.6, 139.5, 154.0, 169.3 FT-IR (neat, cm^{-1}): 768, 903, 1033, 1405, 1739, 2201, 2345 HR-MS (*m/z*) for $C_{20}H_{26}NO_7$ (M+H): Calculated 392.1665, found 392.1668.

3-(6-Benzyloxy-2,2-dimethyltetrahyro-furo[2,3-*d*][1,3] dioxol-5-yl)-4-phenyl-4,5-dihydroisoxazole-5-carboxylic acid ethyl ester (5b/6b): One diastereomer was obtained; yield: 68% (308 mg, 0.68 mmol); yellow viscous liquid; $[\alpha]_D^{20}$: –108.9° (*c* 2.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.28-1.33 (6H, m), 1.50 (3H, s), 4.20-4.31 (3H, m), 4.39-4.43 (1H, m), 4.51-4.61 (2H, m), 5.28 (1H, d, *J* = 3.6 Hz), 5.75 (1H, d, *J* = 7.8 Hz), 5.92 (1H, d, *J* = 3.6 Hz), 7.08-7.38 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 14.0, 26.3, 26.9, 61.8, 63.1, 72.4, 76.5, 82.1, 84.8, 86.6, 105.3, 112.3, 125.7, 127.5, 127.9, 128.4, 128.5, 128.7, 136.7, 139.0, 154.0, 170.0; FT-IR (neat, cm^{-1}): 1031, 1163, 1219, 1259, 1402, 1455, 1738; HR-MS (*m/z*) for $C_{26}H_{30}NO_7$ (M+H): Calculated 468.1944, found 468.1938.

3-(6-Methoxy-2,2-dimethyltetrahyrofuro[2,3-*d*] [1,3] dioxol-5-yl)-5-phenyl-4,5-dihydroisoxazole (5c and 6c): Diastereomeric ratio (dr): 60:40 (separated in silica-gel column chromatography; yield: 72% (228 mg, 0.72 mmol). Major diastereomer (faster moving in column chromatography). Yield: 137 mg; yellow viscous liquid. $[\alpha]_D^{20}$: -75.08° (*c* 1.2, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (3H, s), 1.44 (3H, s), 3.09(1H,m), 3.18 (3H, s), 3.40-3.49 (1H, m), 3.84 (1H, d, *J* = 3.6 Hz), 4.51 (1H, d, *J* = 3.6 Hz), 5.08 (1H, d, *J* = 3.6 Hz), 5.50 (1H, dd, J = 7.8, 11.1 Hz), 5.89 (1H, d, *J* = 3.6 Hz), 7.19-7.30 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.3, 26.8, 43.6, 57.9, 76.2, 81.6, 87.2, 105.2, 112.2, 125.9, 128.0, 128.5, 141.0, 156.8 FT-IR (neat, cm^1): 542, 642, 699, 759, 857, 889, 1026, 1080, 1218, 1377, 1457, 1719 ,2374, 2933, 2983; HR-MS (*m/z*) for $C_{17}H_{22}NO_5$ (M+H): Calculated 320.1520, found 320.1515.

Minor diastereoisomer (slower moving in column chromatography): Yield: 91 mg; yellow viscous liquid; $[\alpha]_D^{20}$: +45.33° (*c* 0.9, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.26 (3H, s), 1.44 (3H, s), 3.05 (1H, dd, *J* = 8.1, 17.4 Hz), 3.34 (3H, s), 3.45 (1H, dd, *J* = 11.1, 17.4 Hz), 3.85 (1H, d, *J* = 3.6 Hz), 4.55 (1H, d, *J* = 3.6 Hz), 5.06 (1H, d, *J* = 3.6 Hz), 5.51 (1H, dd, *J* = 8.1, 11.1 Hz), 5.88 (1H, d, *J* = 3.6 Hz), 7.21-7.30 (5H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.8, 43.6, 58.0, 76.1, 81.5, 82.0, 86.9, 105.2, 112.2, 125.9, 128.6,140.8,156.5; FT-IR (neat, cm^1): 700, 878, 1026, 1079, 1213, 1377, 1451, 1614, 2929; HR-MS (*m/z*) for $C_{17}H_{22}NO_5$ (M+H): Calculated 320.1520, found 320.1516.

3-(6-Benzyloxy-2,2-dimethyltetrahyrofuro[2,3-*d*] [1,3] dioxol-5-yl)-4,5-dihydroisoxazole-5-carboxylic acid methyl ester (5d and 6d): Diastereomeric ratio (dr): 57:43**;** yield: 75% (278 mg, 0.75 mmol); Yellow viscous liquid**;** data for mixture of two diastereomers: ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25 (3H, s), 1.41 (6H, s), 3.33 (4H, t, *J* = 9 Hz), 3.54 (3H, s), 3.69 (3H, s), 4.08 (2H, dd, *J* = 6, 6 Hz), 4.40-4.59 (6H, m), 4.89-4.96 (2H, m), 5.08 (2H, d, *J* = 3 Hz), 5.92 (2H, d, *J* = 1.8 Hz), 7.15-7.30 (10H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.8, 40.1, 40.2, 52.4, 52.6, 72.3, 72.5, 75.8, 75.9, 77.0, 77.1, 82.1, 82.2, 84.5, 84.9, 105.3, 112.3, 127.5, 128.0, 128.1,128.5, 128.6, 136.8, 136.9, 156.4, 157.0, 170.6, 170.7; FT-IR (neat, cm^{-1}): 696, 760, 809, 1148, 1230, 1392, 1452, 1589, 1674, 2366, 2923, 3438. HR-MS (*m/z*) for $C_{19}H_{24}NO_7$ (M+H): Calculated 378.1553, found 378.1556.

4-(6-Benzyloxy-2,2-dimethyltetrahydrofuro[2,3-*d*] [1,3] dioxol-5-yl)-3-(4-chlorophenyl)-4,5-dihydroisoxazole (5e and 6e): The chiral isoxazolines were prepared according to the general procedure B using achiral aldoxime (1a) and sugar-derived chiral olefin (2f). The chiral disoxazolines

(61:39) were separated by silica-gel column chromatography. yield: 65% (278 mg, 0.65 mmol).

Major diastereomer: Yield: 170 mg (61%); yellow viscous liquid; $[\alpha]_D^{20}$ -83.09° (*c* 0.85, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.31 (3H, s) , 1.46 (3H, s) 3.46 (2H, t, *J* = 9.9 Hz), 4.13 (1H, d, *J* = 3 Hz), 4.23 (1H, dd, *J* = 3.0 Hz, *J* = 8.1 Hz), 4.67 (3H, dd, *J* = 3.6 Hz, 16.2 Hz), 5.08 (1H, m), 5.93 (1H, d, *J* = 3.6 Hz), 7.31-7.39 (7H, m), 7.61(2H, d, *J* = 8.4 Hz); ^{13}C NMR (75MHz,$CDCl_3$): δ 26.3, 26.8, 38.0, 72.6, 76.6, 80.6, 81.5, 82.9, 105.2, 112.0, 118.2, 127.8, 128.0, 128.5, 130.0, 136.2, 137.5, 156.1; FT-IR (neat, cm^{-1}): 1020, 1089, 1218, 1379, 1595, 2875, 2933; HR-MS (*m*/*z*) for $C_{23}H_{25}ClNO_5$ (M+H): Calculated 429.1343, found 429.1347 (One of the major peaks).

Minor diastereomer: Yield: 108 mg; yellow viscous liquid; $[\alpha]_D^{20}$: +2.20° (*c* 0.85, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.34 (3H, s), 1.48 (3H, s), 2.82-2.90 (1H, m), 3.10-3.19 (1H, m), 4.04 (1H, d, *J* = 3.6Hz), 4.32 (1H, dd, *J* = 3.9, 7.5 Hz), 4.40 (1H, d, *J* = 12 Hz), 4.68-4.7 (2H, m), 4.98-5.01(1H, m), 6.03(1H, d, *J* = 3.6 Hz), 7.26-7.33 (7H, m), 7.45(2H, d, *J* = 8.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.5, 27.0, 29.6, 37.0, 53.4, 71.9, 79.9, 81.4, 82.1, 82.2, 105.7, 112.3, 127.8, 127.9, 128.1, 128.2, 128.5, 128.9, 135.9, 136.9, 155.4; FT-IR (neat, cm^{-1}): 1078, 1377, 1459, 1603, 1736, 2857, 2923, 3451; HR-MS (*m*/*z*) for $C_{23}H_{25}ClNO_5$ (M+H): Calculated 429.1343, found 429.1345 (One of the major peaks).

3-(4-bromophenyl)-4-[5-(2,2-dimethyl-[1,3]dioxolan-4-yl)-2,2-dimethyltetrahydrofuro[2,3-*d*][1,3]dioxol-6-yloxy methyl]-4,5-dihydroisoxazole (5f and 6f): These isoxazolines were prepared according to the general procedure B using achiral aldoxime (1h) and sugar-derived chiral olefin (2g). Diastereomeric ratio: 55:45; yield: 64% (235 mg, 0.55 mmol). yellow viscous liquid. Spectroscopic data for mixture of two diastereomers: ^{1}H NMR (300MHz, $CDCl_3$): δ 1.24-1.29 (12H, m), 3.33 (2H ,d, *J* = 9.3Hz), 3.71-3.82 (3H, m), 3.97 (3H, d, *J* = 6.3 Hz), 4.02-4.07 (2H, m), 4.57 (1H, d, *J* = 6.3 Hz), 5.85 (1H, d, *J* = 15 Hz), 7.52 (4H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.2, 26.7, 29.3, 29.6, 31.4, 64.4, 68.8, 69.1, 79.6, 80.1, 81.9, 82.2, 84.2, 84.5, 105.3, 111.9, 128.0, 128.2, 131.9, 132.0, 132.1, 162.8; FT-IR (neat, cm^{-1}): 825, 908, 1256, 1401, 1726, 2362, 2927. HR-MS (*m*/*z*) for $C_{22}H_{29}BrNO_7$ (M+H): Calculated 498.1127, found 498.1131 (One of the major peaks).

General Procedure C for Synthesis of Fused-Isoxazolines by Intramolecular Nitrile Oxide Cycloaddition: In a 100 mL round bottle flask, CTAB (364 mg, 1mmol), water (5μL) and DCM (36.4 mL) were taken and stirred magnetically for 5 min. $KMnO_4$ (158 mg,1 mmol) was added to the solution and stirring was continued. After 45 mins TMSCl (216 mg, 2 mmol) was added dropwise to the reaction mixture under ice-cold condition and stirred for another 10 mins. Oxime (9a-f: 1 mmol) dissolved in minimum volume of DCM was added to it and stirred for 3.5-5.0 hours at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the solvent was removed in a rotary evaporator at room temperature under reduced pressure.

The reaction mixture was filtered through a sintered funnel and washed with a mixture of ethyl acetate and cold water. The filtrate was transferred to a separating funnel and extracted with EtOAc (3 x 30 mL). The combined EtOAc layer was washed with water (2 x 30 mL) and finally with brine solution (1 x 30 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent in a rotary evaporator left the crude product which was purified by column chromatography over silica gel (60-120 mesh) using ethyl acetate-petroleum ether as eluent to afford the pure fused-isoxazolines 10a-f.

3-Phenyl-3a,4-dihydro-3*H*-chromeno[4,3-*c*]isoxazole (10a):[20e,39] Yield: 73% (182 mg, 0.73 mmol); light yellow solid; m.p. 158-159 ºC [Lit.[20e] 156-158 ºC]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84-3.94 (1H, m), 4.22 (1H, dd, *J* = 10.2, 12.3 Hz), 4.63 (1H, dd, *J* = 5.7, 10.2 Hz), 5.25(1H, d, *J* = 12.3 Hz), 6.93-7.04 (2H, m), 7.30-7.57 (6H, m), 7.82-7.87 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 52.9, 69.0, 85.7, 113.1, 117.4, 121.9, 125.5, 126.6, 128.9, 132.5, 137.2, 153.3, 155.5; FT-IR (KBr, cm^{-1}): 696, 757, 854, 995, 1222, 1460, 1601; EI-MS (*m*/*z*): 253 (M+2), 195, 160, 77, 44.

6-Methoxy-3-phenyl-3a,4-dihydro-3*H*-chromeno[4,3-*c*] isoxazole (10b):[20e] Yield: 71% (199 mg, 0.71 mmol); cream colored solid; m.p. 130-131 ºC [Lit. 130-132 ºC]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81-3.90 (4H, m), 4.20 (1H, dd, *J* = 10.5, 12.1 Hz), 4.69 (1H, dd, *J* = 5.7, 10.5 Hz), 5.19 (1H, d, *J* = 12.6 Hz), 6.84-6.89 (2H, m), 7.28-7.39 (6H, m);^{13}C NMR (75 MHz, $CDCl_3$): δ 52.6, 56.0, 69.5, 85.8, 113.7, 117.0, 121.6, 126.6, 128.9, 137.1, 145.2, 148.6, 153.2; IR (KBr, cm^{-1}): 696, 757, 854, 1220, 1460, 1601.

8-Methoxy-3-phenyl-3a,4-dihydro-3*H*-chromeno[4,3-*c*] isoxazole (10c): Yield: 76% (212 mg, 0.76 mmol); yellow solid; m.p.76-78 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.81 (3H, s), 3.83-3.91(1H, m), 4.19 (1H, t, *J* = 9 Hz), 4.60 (1H, dd, *J* = 4.8, 10.5 Hz), 5.25 (1H, d, J = 12.6 Hz), 6.87- 6.94 (2H, m), 7.27–7.30 (2H, m), 7.37-7.45 (4H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 30.8, 52.9, 55.8, 69.0, 85.9, 107.1, 118.6, 121.1, 126.6, 127.9, 128.9, 137.1, 150.0, 153.8, 154.3; FT-IR (KBr, cm^{-1}): 694, 749, 850, 1023, 1206, 1484; EI-MS (*m*/*z*): 281 (M+), 207, 104, 44, 32, 28. HR-MS (*m*/*z*) for $C_{17}H_{15}NO_3$ (M^+): Calculated 281.1052, found 281.1059.

7-Allyloxy-3*a*,4-dihydro-3*H*-chromeno[4,3-*c*]isoxazole (10d): Yield: 74% (195 mg, 0.74 mmol); colorless solid; m.p. 138-140 ºC; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.84-3.92 (2H, m), 4.03-4.10 (1H, m), 4.51-4.54(2H, m), 4.63-4.68 (2H, m), 5.28-5.44 (2H, m), 5.98-6.07 (1H, m), 6.45 (1H, d, *J* = 2.7 Hz), 6.60 (1H, dd, *J* = 2.7, 8.7 Hz), 7.69 (1H, d, *J* = 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 46.1, 68.9, 69.3, 70.1, 102.3, 105.9, 110.3, 118.0, 126.8, 132.5, 152.5, 157.0,

162.1; FT-IR (KBr, cm^{-1}): 21, 1017, 1170, 1270, 1436, 1615, 2925; EI-MS (*m/z*): 231 (M^+), 164, 44, 32, 28. HR-MS (*m/z*) for $C_{13}H_{13}NO_3$ (M^+): Calculated 231.0895, found 231.0892.

6,8-di-*tert*-butyl-3a,4-dihydro-3*H*-chromeno[4,3-*c*] isoxazole (10e):[20e] Yield: 68% (195 mg, 0.68 mmol); White solid; m.p. 185-186 ºC [Lit. 185-187 ºC]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.27 (9H, s), 3.78-4.01 (3H, m), 4.60-4.68 (2H, m), 7.32 (1H, d, *J* = 2.4 Hz), 7.62 (1H, d, *J* = 2.4 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 29.6, 31.3, 34.5, 35.1, 45.9, 68.7, 70.6, 112.7, 119.8, 127.3, 137.9, 143.8, 152.3, 154.1; FT-IR (KBr, cm^{-1}): 835 106, 1219, 1474, 2872, 2957; EI-MS (*m/z*): 287 (M^+), 273, 272, 129, 57.

6-Methoxy-3a,4-dihydro-3*H*-chromeno[4,3-*c*]isoxazole (10f):[20e] Yield: 70% (143 mg, 0.70 mmol); colorless solid; m.p. 94-96 ºC [Lit. 95-96 ºC]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.88 (3H, s), 3.89-3.99 (2H, m), 4.06-4.15 (1H, m), 4.63-4.64 (1H, m), 4.72-4.84 (1H, m), 6.90-6.97 (2H, m), 7.37-7.40 (1H, m); ^{13}C NMR (75 MHz, $CDCl_3$): δ 45.7, 55.9, 69.6, 70.6, 113.5, 113.6, 117.1, 121.5, 145.2, 148.6 152.5; FT-IR (KBr, cm^{-1}): 734, 784, 834, 1056, 1229, 1267, 1452, 1578.

Synthesis of Achiral and Chiral Fused-Isoxazoles by Intramolecular Nitrile Oxide Cycloaddition Reaction: Fused-isoxazole (11a, b) and chiral fused-isoxazole (11c-f) were synthesized according to the general procedure C by preparation of corresponding nitrile oxides from aldoxime (10g-l) bearing triple bond and their INOC.

4*H*-Chromeno[4,3-*c*]isoxazole (11a):[20e] Yield: 74% (128 mg, 0.74 mmol); colorless viscous liquid;[20e] ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.78 (1H, s), 6.54-6.64 (2H, m), 6.86-6.92 (1H,m), 7.41 (1H, dd, *J* = 4.8 Hz), 7.75 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 61.3, 111.2, 117.8, 122.4, 124.6, 132.1, 150.6; FT-IR (KBr, cm^{-1}): 755, 1095, 1400,1602, 2357, 2918.

8-Methoxy-4*H*-chromeno[4,3-*c*]isoxazole (11b):[40] Yield: 73% (148 mg, 0.73 mmol); colorless solid; m.p.: 52-53 ºC [Lit.[40] 57-58 ºC]; ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.82 (3H, s), 5.18 (2H, s), 6.94-6.98 (2H, m), 7.36 (1H, s), 8.20 (1H, s); ^{13}C NMR (75 MHz, $CDCl_3$): δ 55.8, 61.2, 107.4, 111.5, 114.2, 118.96, 119.6, 149.0, 150.6, 154.1, 154.8; FT-IR (KBr, cm^{-1}): 785, 1032, 1193, 1623, 2375, 2862, 3258.

(+)-(5aR,6S,7R)-6-Prop-2-ynyloxy-7-prop-2-ynyloxy-methyl-6,7-dihydro-4*H*,5a*H*-2,5,8-trioxa-1-aza-cyclo-penta[*a*]naphthalene (11c): Yield: 66 % (197 mg, 0.66 mmol); white solid; m.p. 120°- 122°; $[\alpha]_D^{20}$: +18.8° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.47 (2H, s), 3.89 (2H, t, *J* = 5.7Hz), 4.24 (2H, d, *J* = 2.4 Hz), 4.26 (1H, d, *J* = 5.4 Hz), 4.30 (2H, d, *J* = 3.3 Hz), 4.5 (1H, dd, *J* = 2.4, 10.5 Hz), 4.63 (1H, d, *J* = 1.2Hz), 4.96 (1H, d, *J* = 14.1 Hz), 7.80 (1H, s), 8.09 (1H, s); ^{13}CNMR (75MHz, $CDCl_3$): δ 58.7, 59.6, 61.1, 68.2, 68.7, 72.1, 74.9, 79.1, 80.0, 99.5, 111.9, 142.7, 150.4, 153.6; FT-IR (KBr, cm^{-1}): 944, 1064, 1106, 1146, 1197, 1366, 1412, 1610, 1655, 2111, 2369, 2860, 2929, 3259; HR-MS (*m/z*) for $C_{16}H_{16}NO_5$ (M+H): Calculated 302.0950, found 302.0955.

(-)-(5aR,6R,7R)-6-Prop-2-ynyloxy-7-prop-2-ynyloxy-methyl-6,7-dihydro-4*H*,5a*H*-2,5,8-trioxa-1-aza-cyclo-penta[*a*]naphthalene (11d): Yield: 62% (185 mg, 0.62 mmol); yellow viscous liquid; $[\alpha]_D^{20}$: -6.25° (*c* 0.5, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 2.31 (2H, s), 3.59-3.64 (1H, m), 3.74-3.77(2H, m), 4.05 (1H, d, *J* = 4.5 Hz), 4.21 (2H, t, *J* = 9.9 Hz), 4.27-4.40 (3H, m), 5.86 (1H, s), 6.07 (1H, s), 6.63 (1H, d, *J* = 17.4 Hz); ^{13}CNMR (75 MHz, $CDCl_3$): δ 58.0, 58.2, 58.6, 67.3, 69.5, 71.5, 73.6, 74.9, 75.6, 75.8, 83.3, 107.8, 115.0, 142.4, 144.1 ; FT-IR (neat, cm^{-1}): 1097, 1384, 1596, 2363, 2924, 3442; HR-MS (*m/z*) for $C_{16}H_{16}NO_5$ (M+H): Calculated 302.0950, found 302.0952.

(+)-(5aS,5bR,8aR,9aR)-7,7-Dimethyl-5a,5b,8a,9a-tetra-hydro-4*H*-2,5,6,8,9-pentaoxa-1-azacyclopenta[*b*]-as-inda cene (11e): Yield: 72 % (172 mg, 0.72 mmol); cololess solid; m.p. 151-152 °C; $[\alpha]_D^{20}$: +41.50° (*c* 0.7, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.37 (3H, s), 1.57 (3H, s), 4.13 (1H, d, *J* = 2.1 Hz), 4.55 (1H, dd, *J* = 0.9, 14.4 Hz), 4.71 (1H, d, *J* = 3.6 Hz), 4.92 (1H, d, *J* = 14.4 Hz), 5.21 (1H, d, *J* = 2.1 Hz), 6.00 (1H, d, *J* = 3.6 Hz), 8.25 (1H, s); ^{13}C NMR (75MHz, $CDCl_3$): δ 26.2, 26.8, 60.5, 68.4, 80.4, 83.4, 106.4, 112.4, 112.5, 151.4, 154.6; FT-IR (KBr, cm^{-1}): 799, 859, 1013, 1092, 1228, 1381, 1428, 1616, 1721, 2859, 2991, 3117. HR-MS (*m/z*) for $C_{11}H_{14}NO_5$ (M+H): Calculated 240.0872, found 240.0870.

(+)-(5aS,5bR,8aR,9aR)-3,7,7-Trimethyl-5a,5b,8a,9a-tetrahydro-4*H*-2,5,6,8,9-pentaoxa-1-azacyclopenta[*b*]-as -indacene (11f): Yield: 70% (177 mg, 0.72 mmol); white solid; m.p. 134-135 °C; $[\alpha]_D^{20}$: +30.94° (*c* 0.7, $CHCl_3$); ^{1}H NMR (300MHz, $CDCl_3$): δ 1.32 (3H, s), 1.52 (3H, s), 2.31 (3H, s), 4.04 (1H, d, *J* = 1 Hz), 4.42(1H, d, *J* = 13.8 Hz), 4.64 (1H, d, *J* = 3.3 Hz), 4.72 (1H, d, *J* = 14 Hz), 5.10 (1H, d, *J* = 2 Hz), 5.94 (1H, d, *J* = 3.6Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 11.2, 26.2, 26.8, 60.7, 68.8, 80.2, 83.4, 105.9, 108.4, 112. 3, 155.4, 162.0; FT-IR (KBr, cm^{-1}): 852, 1017, 1094,1360, 1458, 1652, 2864, 2929, 2991. HR-MS (*m/z*) for $C_{12}H_{16}NO_5$ (M+H): Calculated 254.1028, found 254.1024.

Results and Discussion

The surfactant-assembled supramolecular architecture (Scheme 1) could play dual role: (i) absorbs precursors and their subsequent chemical transformation inside its core to fabricate high-valent LD-NPs and (ii) performs as an ideal system for fundamental oxidative transformation of organic substrate by controlled electron transfer to the surface of the high valent metal-NPs. We have envisioned that development of such a process can be utilized as an ideal protocol for chemo-, regio- and stereoselective transformation of aldoximes to nitrile oxides and their inter- and intramolecular 1,3-DC reaction to valuable heterocycles. In our experiment, treatment of easily available cationic surfactant cetyltrimethyl ammonium

bromide (CTAB), $KMnO_4$, trimethylsilyl chloride (TMSCl) and water (I, Scheme 1) in CH_2Cl_2 (DCM) builds up the reverse micellar architecture possessing hollow tube-like nanospace at the center (II).

Herein, in presence of water and TMSCl, $KMnO_4$ generates Mn^{VI}-complex at the core of the supramolecular assembly. On nucleation, growth and quenching inside the created-nanospace[2a,b] at ambient temperature lead to fabrication of Mn^{VI}-NPs (III). For characterization purpose, the organic template is removed by centrifugation and subsequent washing (several times) with DCM to afford reddish brown nanomaterials. Morphology of the NPs is determined by TEM imaging (panel a). It reveals construction of needle-like very small nanomaterials. It exhibits a broad and unsymmetrical UV-vis absorption (panel b). The overall crystallinity of the product is examined by powder XRD (panel c).

Before X-ray diffraction measurement, small nanofibrils are heated in a Muffle furnace at 150 °C for 5 h to get the crystalline state. The X-ray diffraction peaks (2θ) of the material appear at 28.1^0, 40.2^0, 49.8^0, 58.1^0, 66.1^0 and 73.1^0. To investigate thermal stabilities of the novel nanomaterials, thermogravimetric (TG) and differential thermal analysis (DTA) are recorded (supporting information).

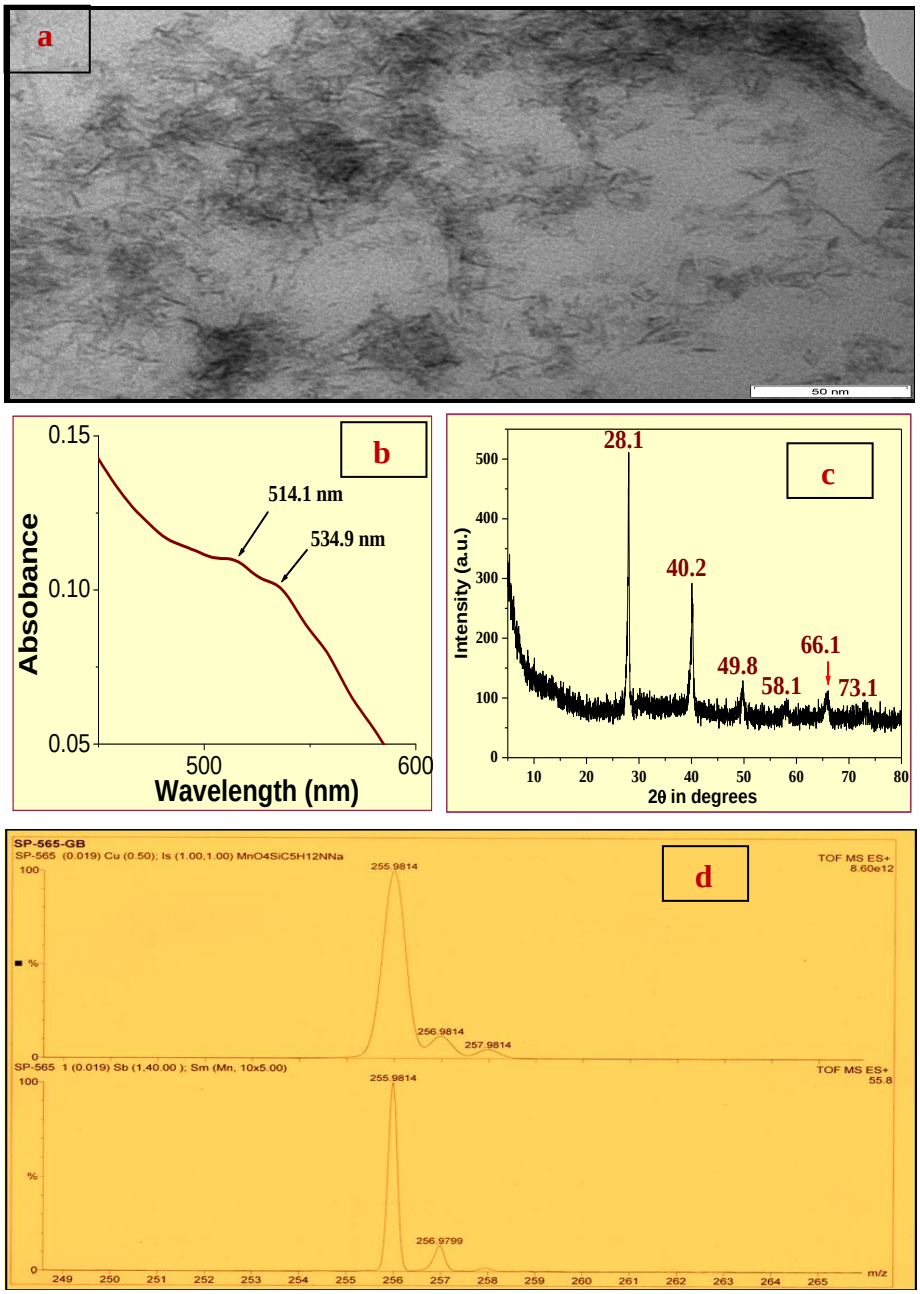


Figure 1: Characterization of High-Valent Manganese NPs: (a) TEM, (b) UV-vis, (c) XRD and (d) ESI-MS Spectra of High-Valent Manganese-NPs

The major weight loss (32%) occurs from 101^0 - 414^0C which may be due to loss of organic component attached to it. It is expected that six CH_3 groups are lost at this temperature region which is comparable to the calculated weight loss of 33% of the expected compound $(Me_3SiO)_2MnO_2$. Presence of TMS group is confirmed by the stretching frequency bands of C-H (2922 and 2858 cm^{-1}) and Si-O (1393 cm^{-1}) obtained in the FT-IR spectrum.

Expected mass for $(Me_3SiO)_2MnO_2$ is 265.0124. Electrospray ionization-mass spectrometry (ESI-MS) of the Mn-NPs $[(Me_3SiO)_2MnO_2]$ is performed in CH_3CN medium and a new ESI-MS-generated ionized species $MnO_4SiC_5H_{12}NNa[(Me_3SiO_2)MnO_2.CH_3CN+Na]$ of mass 255.9814 (329.0287-73.0474; panel e) is generated from $[(Me_3SiO)_2MnO_2.CH_3CN+Na]$ of mass 329.0287 with the loss of Me_3Si (73.0474). Calculated (255.9814; panel d) and experimental (ESI-MS; panel e) mass pattern of the ionized species are completely matched.

Next, we turned our attention for determination of magnetic parameter of the small manganese NPs which has currently attracted scientists for their applications.[27] We have measured X-band ESR spectrum of the powdered nanomaterial at liquid nitrogen temperature. Gratifyingly, a significantly improved isotropic hyperfine splitting (^{55}Mn; *I* = 5/2) of six-line spectrum (g=1.99836) is found. Earlier, Meyer et al[28] has reported a six-line EPR spectrum (g ~2.0) of $[(cyclam)Mn^{VI}(N)(NCCH_3)]^{3+}$-complex with d^1 electronic configuration.

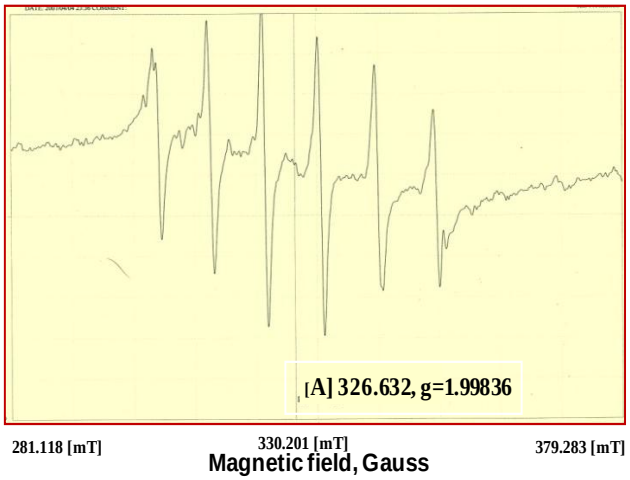
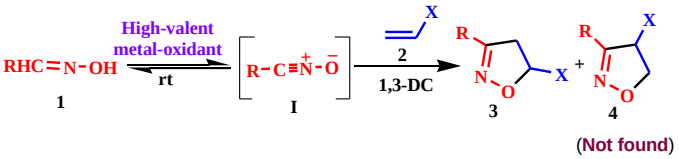


Figure 2: ESR Spectrum of $(TMSO)_2MnO_2$

To develop an operationally simple method, several reaction conditions have been examined for simultaneous fabrication of high-valent Mn^{VI}-NPs and *in situ* transformation of 4-chlorophenyl aldoxime (1a) to corresponding nitrile oxide (I, Scheme 2). Formation of nitrile oxide (I) is confirmed by trapping it with ethyl acrylate (2a, entry 1, table 1) to afford the known Δ^2-isoxazoline (3a, entry 1, table 2).[12a] Gratifyingly, other regioisomer 4 is not found in the benign synthetic process utilizing high-valent Mn^{VI}-NPs. The poor yield (65%, entry 1) may result due to presence of insufficient quantity (one mole) of TMSCl.

To our delight, use of $KMnO_4$ and TMSCl in 1:2 molar ratio reveals that 3a could be obtained in excellent yield (81%) after purification of the isoxazoline by SiO_2 gel column chromatography (entry 2).

The reaction is rapid (4 h) and requirement of oxidizing agent is just one equivalent. However, comparable yield (82%) is found on enhancement of TMSCl to three equivalents (entry 3). Combination of TMSOTf-$KMnO_4$ is also found as the alternative reagent for the reaction (entry 4). However, yield is reduced on use of more lipophilic TBDMSCl to generate $(TBDMSO)_2MnO_2$ (entry 5). Template-free $(Me_3SiO)_2MnO_2$ NPs are recovered and used successfully (entry 6) for the 1,3-DC reaction with comparable yield (83%). However, satisfactory results are not found by direct use of $KMnO_4$, cetyltrimethylammonium permanganate ($CTA.MnO_4$) or Me_3SiMnO_4 as an oxidant (entries 7-9).



Scheme 2: Generation of Nitrile Oxides and Their Regioselective Cyclization to Δ^2-Isoxazolines

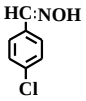
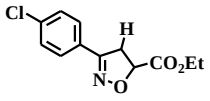
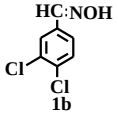
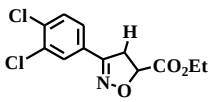
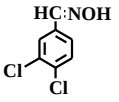
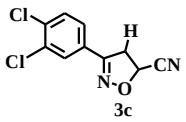
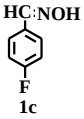
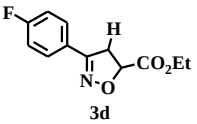
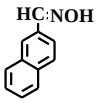
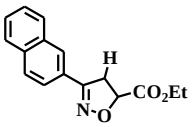
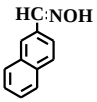
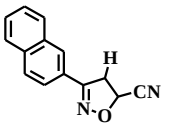
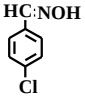
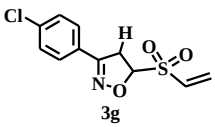
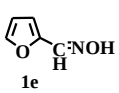
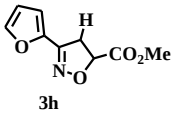
With this set of conditions in hand, the versatility of the intermolecular 1,3-DC approach by $(Me_3SiO)_2MnO_2$-NPs is demonstrated with several aldoximes (1) and alkenes to afford corresponding functionalized Δ^2-isoxazolines (3, table 2). This extraordinary reaction rate and regioselectivity can be explained in terms of *in situ* fabrication of highly active small Mn^{VI}-NPs and coordination of the metal during the cycloaddition step. Both the electron-rich and electron-deficient aromatic substituents and a number of functional groups (ester, CN and vinyl sulfone) are tolerated in the benign approach. The results in table 2 also demonstrate that the reaction rate (3.5-5.0 h) and yield (71-85%) are almost independent of nature of the substrates used. Formation of byproducts is not found from the post reaction mixture.

Carbohydrates are inexpensive, abundant, biocompatible and valuable precursors for installation of multiple chiral centers in the target molecules.[29] Synthesis of sugar-derived chiral compounds is gaining greater importance in catalysis, asymmetric synthesis, construction of chiral natural products, new molecules for drug design and organic nanostructured materials.[30,31] Sugar-derived nitrile oxides are used for construction of pseudodisaccharides and higher carbon-chain monosaccharides,[32c] cyclization to chiral benzimidazole, benzoxazole and benzthiazole,[32b] multistep synthesis of bioactive natural products[32a] and bioactive isoxazolines.[33]

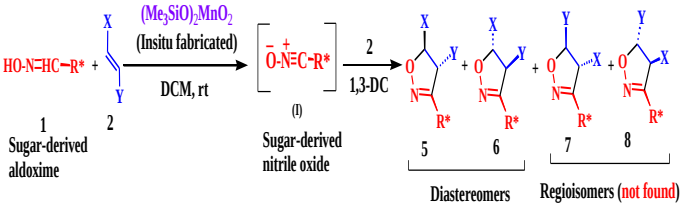
Table 1
Development and Optimization of the Reaction

Entry	reagents	reaction conditions	conversion (%)	3a, yield (%)
1	$KMnO_4$, TMSCl (1 mol)	CTAB, CH_2Cl_2, rt, H_2O, 4 h	100	65
2	$KMnO_4$, TMSCl (2 mol)	CTAB, CH_2Cl_2, rt, H_2O, 4 h	100	81
3	$KMnO_4$, TMSCl (3 mol)	CTAB, CH_2Cl_2, rt, H_2O, 5 h	100	82
4	$KMnO_4$, TMSOTf (2 mol)	CTAB, CH_2Cl_2, rt, H_2O, 3 h	100	80
5	$KMnO_4$, TBDMSCl (2 mol)	CTAB, CH_2Cl_2, rt, H_2O, 7 h	50	63
6	$(TMSO)_2MnO_2$ (1 mol)	CH_2Cl_2, rt, 5 h	100	83
7	$KMnO_4$ (2 mol)	CH_2Cl_2, rt, 24 h	80	40
8	CTA.MnO_4 (1.5 mol)	CH_2Cl_2, rt, 24h	Decomposition	-
9	Me_3SiMnO_4 (1 mol)	CH_2Cl_2, rt, 8 h	100	62

Table 2
Experimental Data of Intermolecular 1,3-DC Reaction

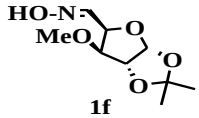
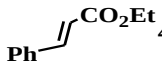
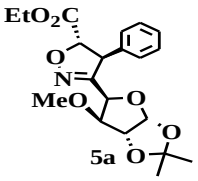
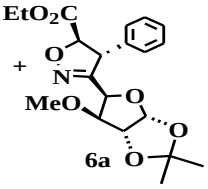
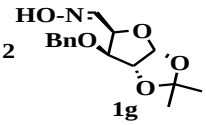
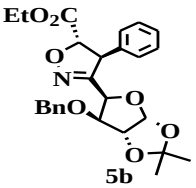
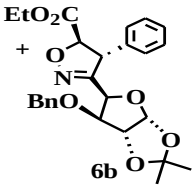
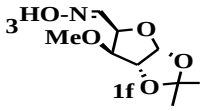
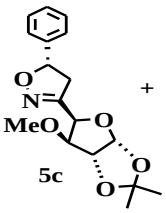
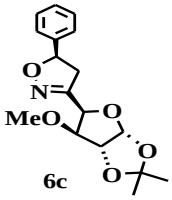
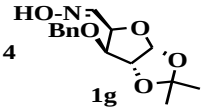
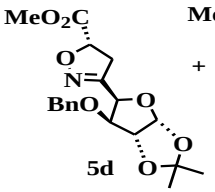
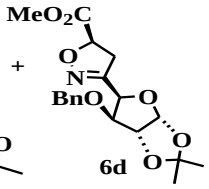
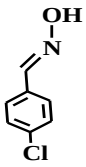
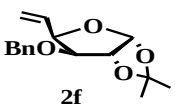
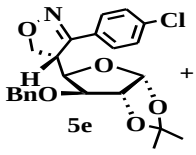
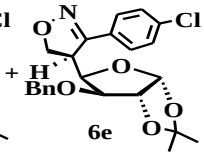
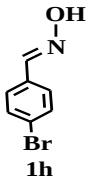
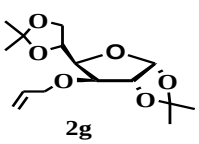
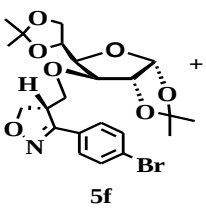
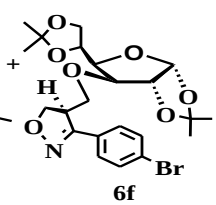
entry	aldoxime	alkene	time (h)	product	yield (%)
1.	 1a	 2a	4.5	 3a	79
2.	 1b	 2a	4.0	 3b	76
3.	 1b	 2b	4.5	 3c	85
4.	 1c	 2a	3.5	 3d	81
5.	 1d	 2a	5.0	 3e	80
6.	 1d	 2b	4.0	 3f	83
7.	 1a	 2c	4.5	 3g	78
8.	 1e	 2d	5.0	 3h	71

Recently, Jäger et al[34] have reported efficient routes to antibiotic L-(+)-Furanomycin and L-Carbafuranomycin from sugar-derived nitrile oxide utilizing commonly used *N*-chlorosuccinimide-HCl method. However, use of HCl is harmful for sugar moieties possessing ether linkages. So, easy access to sensitive sugar-derived nitrile oxides under neutral and benign reaction conditions is highly desirable. Pursuing our interest for construction of sugar-derived heterocycles,[12a,c,d,31,35] we have successfully utilized $(Me_3SiO)_2MnO_2$-NPs for generation of chiral nitrile oxides bearing sugar-moieties and their intermolecular 1,3-DC reaction with achiral olefins (2).



Scheme 3: Generation of Sugar-Derived Nitrile Oxides and Their Intermolecular 1,3-DC Reaction

Table 3
Diastereoselective Intermolecular 1,3-DC Reaction to Sugar-Derived Isoxazolines

entry	aldoxime	dienophile	time(h)	diastereomers	yield(%)	Selectivity
1	 1f	 2e	4.5	 5a +  6a	70	100:0
2	 1g	2e	4.0	 5b +  6b	68	100:0
3	 1f	 2b	5.0	 5c +  6c	72	60:40
4	 1g	 2c	4.5	 5d +  6d	75	57:43
5	 1a	 2f	10	 5e +  6e	65	61:39
6	 1h	 2g	16	 5f +  6f	64	55:45

Herein, regio- and diastereoselective intermolecular 1,3-DC reactions with olefin (2) were investigated under neutral reaction conditions at ambient temperature to achieve corresponding four possible isomeric isoxazolines (5-8, Scheme 3). The regio-isomers 7 and 8 are not found in the high-valent metal-NPs mediated synthesis. Gratifyingly, excellent chemo-, regio- and stereoselectivity are found using sugar-derived aldoxime 1f and 1g and *trans*-ethyl cinnamate (2e: X = CO_2Et and Y = Ph) where only one chiral isoxazoline (5a/6a and 5b/6b) is found from the post reaction mixture (entries 1,2, Table 3). In general, sugar-based chiral nitrile oxide is known to produce less diastereomeric excess (de) during intermolecular 1,3-DC with achiral dipolarophile.[11a]

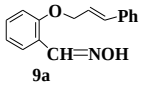
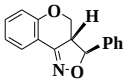
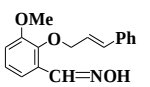
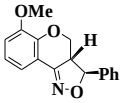
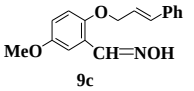
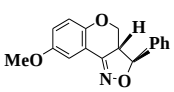
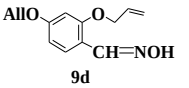
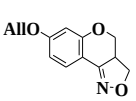
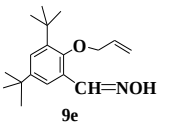
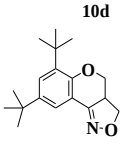
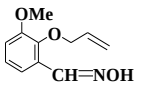
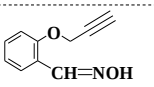
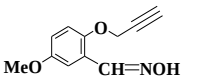
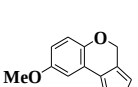
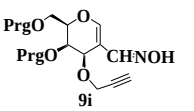
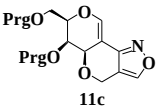
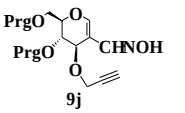
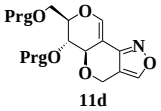
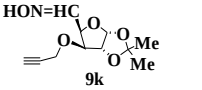
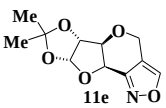
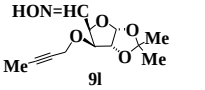
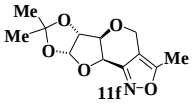
Herein, $(Me_3SiO)_2MnO_2$-NPs have played important role for controlling the stereoselection during cycloaddition step to furnish 100% de (entries 1,2). Earlier, Bode and Carreira[36] have synthesized optically pure isoxazolines using non-sugar chiral nitrile oxides. Even though the newly generated chiral center is far away (three bond distance) from the chiral center, good diastereomeric excesses are noted (entries 3, 4). Total reaction time is only 4-5 h and the optically pure cycloadducts are separated by SiO_2 gel column chromatography to obtain in good yield (68-70%). A moderate diastereoselectivity is observed for 1,3-DC reaction of sugar-based chiral olefin with the *in situ* generated achiral nitrile oxides (entries 5,6).

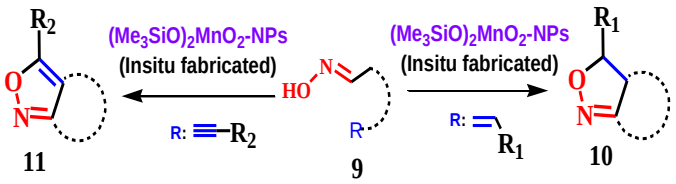
Intramolecular nitrile oxide cycloaddition (INOC) is a fascinating approach to afford difficultly accessible natural products, carbocycle, macrocycles and optically active compounds involving C-C coupling reaction.[37] Due to the favorable entropy and conformational restriction in the transition state, outstanding regio- and stereoselectivity are achieved in the final product mixture. The scope of the Mn^{VI}-NPs mediated benign synthetic protocol is extended toward INOC with alkene and alkyne to furnish fused isoxazolines (10) and isoxazoles (11, Scheme 4).

As shown in table 4, the INOC reaction provides the desired benzopyranoisoxazolines regardless of the presence of aromatic moieties and their substituents. Complete *cis*-stereoselectivity is observed in the intramolecular cycloaddition processes using phenyl as terminal substituent to the *trans*- - olefin (entries 1-3). The desired heterocycles are obtained possessing *anti*-stetreochemisty at the newly generated stereogenic centers.

The reaction rate is fast (3.5-5.0 h) and yield is also high (78-86%). Synthesis of isoxazoles (11a, b) is achieved by the INOC reaction of aldoxime (9g, h) bearing acetylene moiety (entries 7, 8). We have successfully extended this robust cycloaddition approach toward oxidative transformation of functionalized sugar-derived aldoximes (9i-l, entries 9-12) to corresponding nitrile oxides and their *in situ* intramolecular 1,3-DC reaction with alkynes to afford optically pure fused-Δ^2-isoxazoles (11c-f) with fast reaction convergence (2.5-4.5 h) and good yield (62-72%).

Table 4
Synthesis of Fused-Isoxazolines and Isoxazoles by INOC Reaction

entry	aldoxime	time (h)	isoxazoline/isoxazole	yield (%)
1	 9a	3.5	 (±)-10a	73
2	 9b	4.0	 (±)-10b	71
3	 9c	4.5	 (±)-10c	76
4	 9d	3.5	 10d	74
5	 9e	5.0	 10e	68
6	 9f	5.0	 10f	70
7	 9g	4.0	 11a	74
8	 9h	5.0	 11b	73
9	 9i	4.0	 11c	66
10	 9j	4.5	 11d	62
11	 9k	2.5	 11e	72
12	 9l	3.0	 11f	70



Scheme 4: INOC Reaction to Fused-Isoxazolines and Isoxazoles

Conclusion

In conclusion, fabrication of high-valent Mn^{VI}-NPs is demonstrated utilizing inexpensive $KMnO_4$ under benign reaction conditions. Characterization, determination of morphology and novel properties of the LD-NPs are investigated by means of TEM, powder XRD, TG-DTA, DLS, UV-vis and ESR spectral analyses. A significantly improved isotropic hyperfine splitting of six-line spectrum is found in the X-band ESR spectrum of the powdered nanomaterial. Mn^{VI}-NPs are developed as the mild oxidant toward generation of nitrile oxides from aldoximes and used for 1,3-DC reaction.

A robust synthetic protocol is established which features fast reaction convergence under benign reaction conditions, simple operation, use of inexpensive precursors and lower amount of metal oxidant and also avoids use of base or acid. Chemo-, regio- and stereoselectivities in both the inter- and intramolecular 1,3-DC reactions with olefin and alkyne are successfully examined to afford isoxazolines and isoxazoles. Synthesis of optically pure sugar-derived isoxazolines and isoxazoles is also demonstrated. We believe this approach will find widespread applications in chemical, medical, material and electronic sciences.

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Supporting Information

Materials and methods, ESI-MS and TG-DTA spectra, synthesis of sugar-based chiral aldoximes and olefin and copies of ^1H and ^{13}C NMR spectra for all new compounds are available.

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