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Indium chloride ($InCl_3$) catalysed domino protocol for the regioselective synthesis of highly functionalized pyranopyrazoles under mild conditions

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Abstract

Regioselective synthesis of highly functionalized pyranopyrazoles was achieved in excellent yield from phenyl pyrazolone, substituted aromatic aldehyde with nitroketene-N,S-acetal in the presence of indium trichloride as a versatile catalyst under reflux condition in ethanol-water mixture. All reactions proceeded within a short period of time with excellent purity. All of the synthesized compounds were identified by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopy. Quantitative yields, inexpensive and environmentally friendly solvent system and simple work-up procedure are the attractive features of the present method. It is thus enviro-economic method without producing hazardous wastes. The formed pyranopyrazoles might find to possess important biological and pharmaceutical applications.

Keywords: Pyranopyrazole; acetal chemistry; multicomponent; indium trichloride.

Introduction

Multicomponent reactions (MCRs) have steadily gained importance in synthetic organic chemistry. MCRs allow the creation of several bonds in a single operation and offer remarkable advantages like convergence, operational simplicity, facile automation, reduction in the number of work ups, extraction and purification processes and hence minimize waste generation [1]. One-pot, MCRs often shortens reaction time, giving higher overall chemical yields than multi-step syntheses, and therefore can reduce the use of energy and manpower. MCRs are useful for the expedient creation of chemical libraries of drug-like compounds with high levels of molecular complexity and diversity, thereby facilitating identification/optimization in drug discovery programmes [2]. Therefore, the design of new MCRs with green procedure has attracted huge attention, especially in the areas of drug discovery, organic synthesis, and material science [3]. Moreover,

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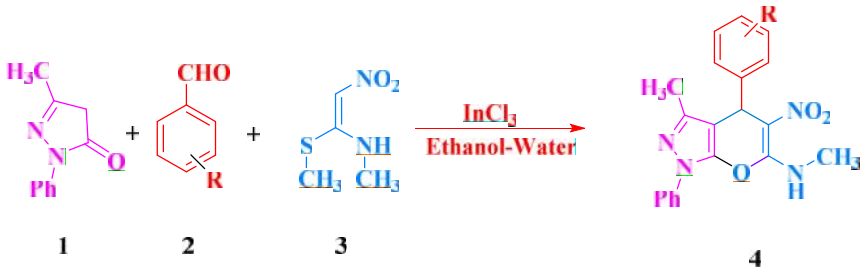
improving already known MCRs is also of a substantial interest in the field of current organic synthesis.

Pyrano[2,3-c]pyrazole derivatives are one of the biologically important scaffolds because of their wide applications in pharmaceuticals and in organic synthesis as essential intermediates [4]. These motifs have significant anti-cancer, anti-inflammatory, anti-microbial, fungicidal, insecticidal, molluscicidal, and analgesic properties [5]. In addition, they can also act as hypoglycaemics, biodegradable agrochemicals, vasodilators and hypotensives [6]. Pyrano[2,3-c]pyrazoles have been synthesized via multi-component reactions of aldehyde, ethyl acetoacetate, hydrazinehydrate and malononitrile [7]. However, most of the protocols used homogeneous and heterogeneous based toxic catalysts e.g. triethylamine, piperidine, per-6-amino-β-cyclodextrin, hexadecyl dimethyl benzyl ammoniumchloride, basic ionic liquids, disulfonic acid imidazoliumchloroaluminate meglumine, and sodium benzoate, while only a few methods involving heterogeneous catalysts, such as amberlyst-A21, γ-alumina, Fe3O4 nanoparticles and ZrO2 nanoparticles have also been reported [8]. The Use of hazardous solvents, low yields, high temperature conditions, lack of selectivity and long reaction time are the notable drawbacks of the reported methods. Thus, the development of general MCR protocols using a green solvent and heterogeneous catalyst leading to the pyrano[2,3-c]pyrazole derivatives is of considerable interest.

As a part of our efforts aimed at the discovery of selective and environmental friendly MCRs to synthesize bioactive heterocyclic compounds [9], herein we investigated a three component regioselective synthesis of pyrano[2,3-c]pyrazoles by the reaction of phenyl pyrazolone (**1**), aldehyde (**2**), and (E)-N-Methyl-1-(methylthio)-2-nitroethenamine (**3**) in ethanol-warer mixture catalyzed by indium trichloride (Scheme 1).



Scheme 1. A regioselective synthesis of pyrano[2,3-c]pyrazoles in ethanol-water mixture

Experimental

General

All chemicals were obtained from commercial suppliers and were used without further purification. Melting points were determined in open capillaries and were uncorrected. All reactions were monitored by thin layer chromatography (TLC) with 0.2 mm Merck silica gel F_{254} plates. NMR spectra were recorded on Bruker DRX FT NMR at 400 MHz spectrometer in DMSO-d_6 using TMS as internal standard (chemical shifts are expressed as δ values relative to TMS as internal standard). IR spectra were recorded on a Bruker VECTOR 22 FTIR spectrophotometer. ESI (positive) was

recorded on an Esquire-LC-00075 spectrometer.

General one-pot procedure for synthesis of pyrano[2,3-c]pyrazole derivatives

A mixture of phenyl pyrazolone (1mmol), Aldehyde (1 mmol) and (E)-N-Methyl-1-(methylthio)-2-nitroethenamine (1 mmol) was taken in a round bottom flask, to it 5 mL ethanol:water (4:1): solution and 10 mol% indium trichloride were added and refluxed for 2-3 h. The progress of reaction was monitored by TLC using hexane: ethyl acetate (6:4) as eluent. After completion of reaction, reaction mass was poured into ice water (50 mL), precipitate obtained was filtered, washed with cold water, dry and recrystallized from methanol to obtain pure product.

Spectral data of newly synthesized compounds

4-(3-methyl-6-(methylamino)-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-4-yl)benzonitrile (4b)

IR (KBr, cm^{-1}): 3838, 3769, 3185, 2228, 1653, 1616, 1492, 1447, 1386, 1348, 1265, 1231, 1128, 1048, 831, 754, 689, 662; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 1.90 (3H, s, -*CH*$_3$), 3.18 (3H, s, -*CH*$_3$), 5.35 (s, 1H, -*CH*-), 7.37-7.39 (t, 1H, Ar-*H*), 7.53-7.57 (t, 2H, Ar-*H*), 7.60-7.60 (d, 2H, *J* = 8Hz, Ar-*H*), 7.76 (m, 4H, Ar-*H*), 10.63 (s, 1H, -*NH*); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 12.99, 29.23, 38.59, 99.98, 108.69, 109.85, 119.33, 121.02, 127.24, 129.53, 129.97, 132.61, 137.54, 142.31, 145.82, 149.36, 159.12; MS (ESI): 388.1 (M+1).

N,3-dimethyl-5-nitro-1-phenyl-4-(3,4,5-trimethoxyphenyl)-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4h)

IR (KBr, cm^{-1}): 3841, 3741, 2931, 1649, 1592, 1509, 1451, 1451, 1353, 1386, 1229, 1323, 1188, 1124, 1046, 1002, 748, 823, 788, 687; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 2.03 (s, 3H, -CH_3), 3.19 (s, 3H, -CH_3), 3.63 (s, 3H, -CH_3), 3.74 (s, 6H, 2x-CH_3), 5.23 (s, 1H, -CH-), 6.62 (s, 2H, Ar-H), 7.35-7.38 (t, 1H, J = 8Hz, Ar-H), 7.53-7.57 (t, 1H, J = 8Hz, Ar-H), 7.75-7.77 (d, 2H, J = 8Hz, Ar-H), 10.60 (1H, s, -NH); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 13.00, 28.58, 38.69, 56.32, 60.82, 100.83, 105.64, 110.29, 120.70, 126.91, 129.47, 137.24, 137.48, 137.58, 141.93, 146.49, 153.09, 159.16; MS (ESI): 469 (M+NH_3).

4-(3,4-difluorophenyl)-3-methyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4i)

IR (KBr, cm^{-1}): 3178, 1654, 1614, 1516, 1434, 1386, 1359, 1270, 1229, 1124, 1045, 951, 901, 862, 862, 750, 687, 661; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 1.93 (s, 3H, -*CH*$_3$), 3.17 (s, 3H, -*CH*$_3$), 5.27 (s, 1H, -*CH*-), 7.26 (s, 1H, Ar-*H*), 7.31-7.38 (m, 2H, Ar-*H*), 7.47-7.57 (m, 3H, Ar-*H*), 7.75-7.77 (d, 2H, Ar-*H*), 10.61 (s, 1H, -*NH*); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 12.98, 29.20, 37.76, 100.27, 108.91, 117.20-117.27, 120.95, 125.27, 127.14, 129.94, 137.60, 141.49, 142.25, 145.84, 147.31-148.51, 149.74-150.95, 159.05; MS (ESI): 399 (M+1).

4-(3,4-dichlorophenyl)-N,3-dimethyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4j)

IR (KBr, cm^{-1}): 3735, 3182, 1648, 1515, 1462, 1428, 1362, 1261, 1229, 1122, 1049, 885, 823, 747, 678; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 1.93 (s, 3H, -*CH*$_3$), 3.17 (s, 3H, -*CH*$_3$), 5.29 (s, 1H, -*CH*-), 7.35-7.37 (d, 1H, *J* = 8Hz, Ar-*H*), 7.39-7.42 (m, 1H, Ar-*H*), 7.55-7.56 (3H, m, Ar-*H*), 7.69 (1H, s, Ar-*H*), 7.75-7.77 (d, 2H, *J* = 8Hz, Ar-*H*), 10.63 (s, 1H, -*NH*).; ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 13.04,

29.24, 37.77, 99.92, 108.68, 120.96, 127.18, 129.08, 129.57, 129.95, 130.35, 130.62, 131.21, 137.57, 142.28, 144.87, 145.85, 159.07; MS (ESI): 431 (M+1).

4-(2,4-dichlorophenyl)-N,3-dimethyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4l)

IR (KBr, cm^{-1}): 3738, 3173, 3065, 1660, 1620, 1589, 1516, 1459, 1391, 1359, 1269, 1232, 1129, 1055, 910, 837, 762, 690; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 1.92 (s, 3H, -*CH*$_3$), 3.18 (s, 3H, -*CH*$_3$), 5.60 (s, 1H, -*CH*-), 7.35-7.39 (m, 2H, Ar-*H*), 7.49-7.51(d, 1H, *J* = 8Hz, Ar-*H*), 7.54-7.56 (m, 3H, Ar-*H*), 7.75-7.77 (d, 2H, *J* = 8Hz, Ar-*H*), 10.64 (s, 1H, -*NH*); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 12.97, 29.22, 35.70, 99.29, 108.35, 120.96, 127.24, 128.00, 129.09, 129.99, 132.35, 132.53, 133.86, 137.51, 139.45, 142.59, 145.64, 159.23; MS (ESI): 431 (M+1).

4-(3,4-dimethoxyphenyl)-3-methyl-5-nitro-1-phenyl-1,4-dihydropyrano[2,3-c]pyrazol-6-amine (4m)

IR (KBr, cm^{-1}): 3856, 3737, 2938, 2833, 1651, 1587, 1517, 1479, 1429, 1388, 1354, 1283, 1255, 1222, 1123, 1170, 1050, 995, 795, 752, 685; ^{1}H NMR (DMSO-d_6, 400 MHz) δ = 1.92 (s, 3H, -*CH*$_3$), 3.18 (s, 3H, -*CH*$_3$), 3.56 (s, 3H, -*CH*$_3$), 3.75 (s, 3H, -*CH*$_3$), 5.35 (s, 1H, -*CH*-), 6.89-6.99 (m, 3H, Ar-*H*), 7.33-7.36 (t, 1H, *J* = 8Hz, Ar-*H*), 7.51-7.55 (t, 2H, *J* = 8Hz, Ar-*H*), 7.72-7.74 (d, 2H, Ar-*H*), 10.66 (s, 1H, -*NH*); ^{13}C NMR (DMSO-d_6, 100 MHz): δ = 12.75, 29.12, 35.59, 56.01, 59.99, 100.68, 109.20, 111.99, 120.75, 122.23, 123.74, 127.05, 130.00, 135.75, 137.64, 142.49, 145.72, 146.84, 152.89, 159.89; MS (ESI): 423 (M+1).

Results and discussion

In an initial endeavor condensation of phenyl pyrazolone **1**, anisaldehyde **2** and (*E*)-N-methyl-1-(methylthio)-2-nitroethenamine **3** were studied in the presence of different catalysts such as triethyl amine (TEA), 1,4-diazabicyclo-(2-2-2)-octane (DABCO), L-proline, piperidine and $InCl_3$ (10 mol%) using ethanol as a solvent under reflux condition. The results represented in Table 1 indicate that, $InCl_3$ played a crucial role in this reaction and no reaction occurred in the absence of catalyst under described reaction conditions even after 10 h (Table 1, Entry 1). When the reaction was carried out in the presence of TEA and DABCO, only 50-55% of product formation observed after 10 h (Table 1, Entry 2 and 3). In the presence of L-proline and piperidine, 62-67% product formation was observed after 5 h (Table 1, Entry 4 and 5). Significant increase in the yield of product (85%) was observed in the presence of $InCl_3$ within a short period of time; 2 h (Table 1, Entry 6). Further, we studied the effect of ethanol-water mixture on the yield of product. Surprisingly, increase in the yield of product was observed in ethanol-water solvent system. Excellent yield was obtained in ethanol-water (8:2) solvent system under reflux condition (Table 1, Entry 9).

Moreover, we found that the yields were obviously affected by the amount of loaded catalyst. When 5 mol%, 10 mol% and 15 mol% of $InCl_3$ were used, the yields were 64%, 85%, and 84%, respectively. Therefore, 10 mol% of the catalyst was sufficient to push the reaction forward, and further the increas in the amount of catalyst did not increase the yields. The above results showed that $InCl_3$ was essential in the reaction, and the best results were obtained when the reaction was carried out with 10 mol% of $InCl_3$ in ethanol-water mixture (8:2) under reflux conditions.

With the optimized procedure in hand, an investigation into the scope of the methodology, using a range of aromatic aldehydes, was conducted to prepare a series of functionalized pyranopyrazoles (Table 2, **4a-m**). In all cases, aromatic aldehydes bearing electron withdrawing and electron donating groups as well as heteroaromatic aldehydes, formation of corresponding pyrano[3,2-c]pyrazoles were obtained in good to excellent yields.

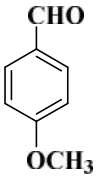
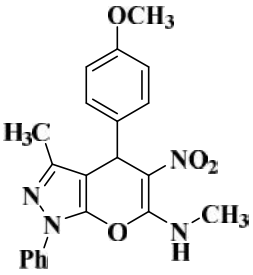
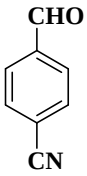
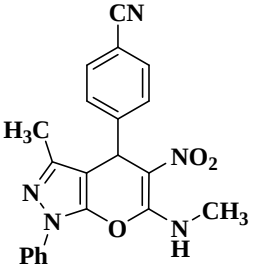
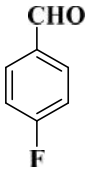
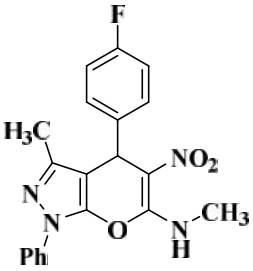
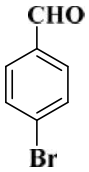
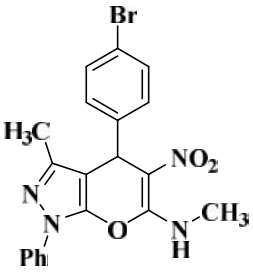
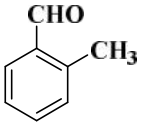
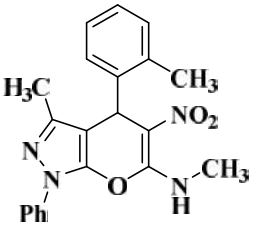
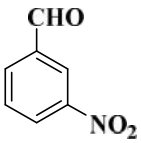
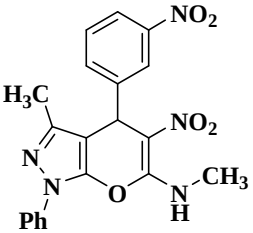
The structures of all the synthesized compounds were characterized by IR, ^{1}H NMR, ^{13}C NMR and mass spectroscopic data. Further studies on the extension of the scope of the use of the (*E*)-N-methyl-1-(methylthio)-2-nitroethenamine **3** in synthetic applications are currently under way in our laboratory.

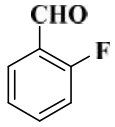
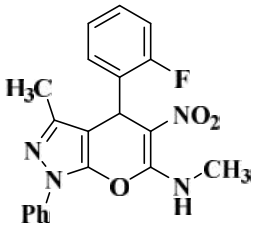
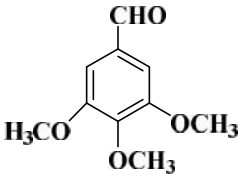
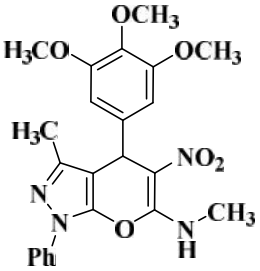
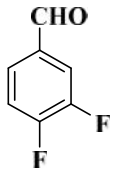
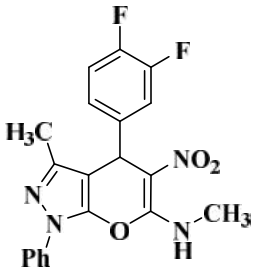
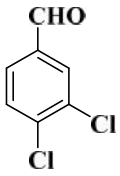
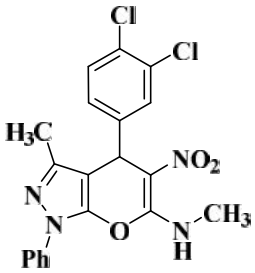
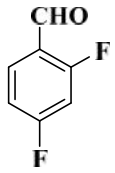
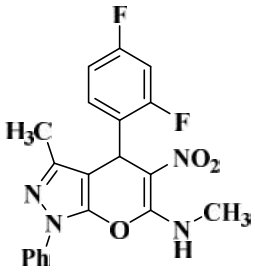
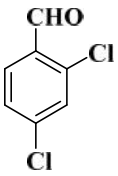
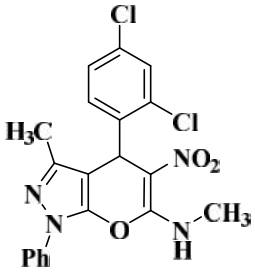
The plausible mechanism for the $InCl_3$ catalyzed regioselective synthesis of pyranopyrazoles is depicted in Scheme 2. Knoevenagel condensation of phenyl pyrazolone (**1**) with aldehyde (**2**) which gives α,β-unsaturated compound **5**, was attacked by the electron rich centre of the (*E*)-N-methyl-1-(methylthio)-2-nitroethenamine **3** to form intermediate **6**. Intermediate **6** on intramolecular cyclization with the loss of methanethiol afforded functionalized pyranopyrazoles (**4a-m**) (Scheme 2).

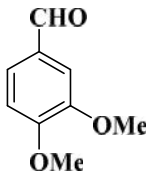
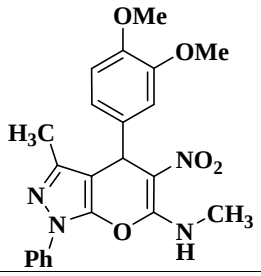
Table 1. Optimization of catalytic conditions for the synthesis of pyranopyrazoles

Entry	Solvent	Catalyst	Temp (^{o}C)	Time (h)	Yield (%)
1	Ethanol	No catalyst	reflux	10	No reaction
2	Ethanol	TEA	reflux	12	50
3	Ethanol	DABCO	reflux	10	55
4	Ethanol	L-Proline	reflux	7	62
5	Ethanol	Piperidine	reflux	5	67
6	Ethanol	$InCl_3$	reflux	2	85
7	Ethanol: Water (5:5)	$InCl_3$	reflux	2	76
8	Ethanol: Water (7:3)	$InCl_3$	reflux	2	90
9	Ethanol: Water (8:2)	$InCl_3$	reflux	2	94
10	Ethanol: Water (9:1)	$InCl_3$	reflux	2	92

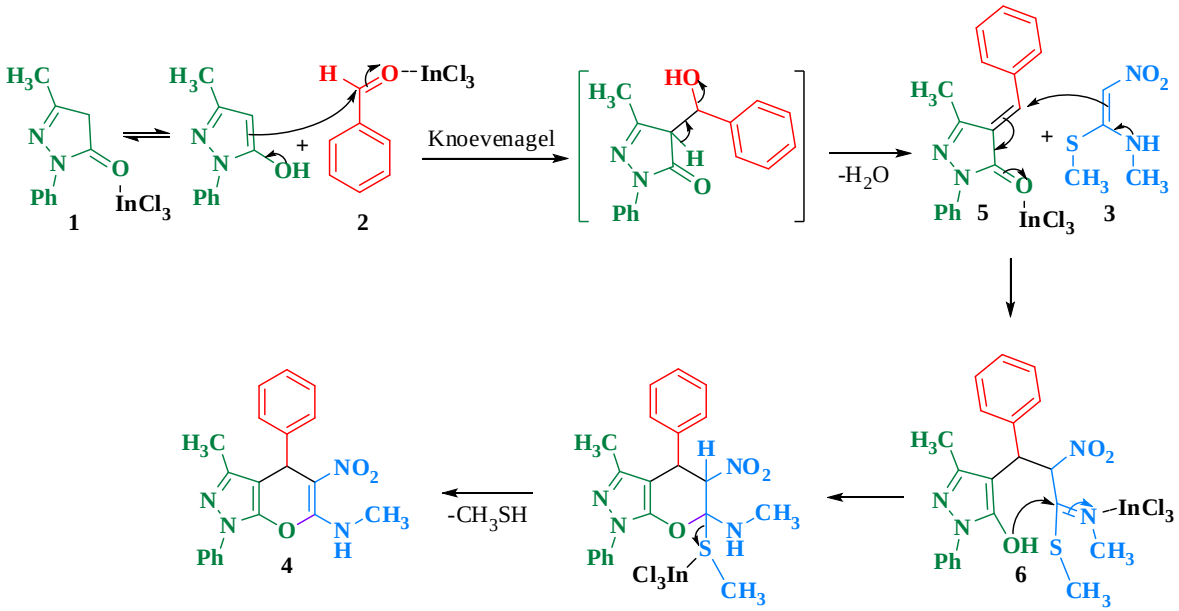
Table 2. Indium trichloride catalyzed synthesis of functionalizes pyranopyrazoles

Entry	Aldehyde	Product	Time (h)	Yield (%)[a]
4a			2.5	91
4b			2.5	92
4c			2.5	91
4d			2.5	90
4e			3	89
4f			3	92

4g			3	87
4h			3	91
4i			3	90
4j			3	91
4k			3	88
4l			3	86

4m			3	90

[a]Isolated Yields



Scheme 2. Plausible mechanism for the formation of pyranopyrazoles in the presence of $InCl_3$

Conclusion

In conclusion, we have developed a simple, efficient, and regioselective synthesis of highly functionalized pyranopyrazoles and by the reaction of pyrazolone, aromatic aldehydes and nitroketene-N,S-acetal in the presence of $InCl_3$ under mild condition. Excellent yield, short reaction time, simple workup procedure, enormous structural diversity, environment friendly solvent system and no chromatographic purification are the silent features of this protocol.

Acknowledgemens

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